

*Supplementary Information for*

## **Halogencarbene-Free Ciamician-Dennstedt Single-Atom Skeletal**

### **Editing**

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## 1. General Information

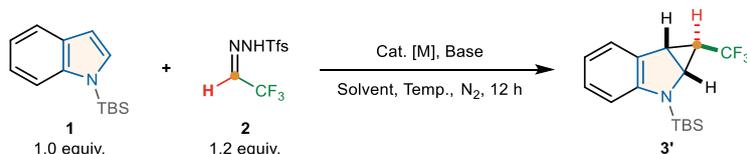
The products were purified by column chromatography over silica gel (200-300 mesh). NMR spectra were recorded on a Bruker Advance 600 ( $^1\text{H}$ : 600 MHz,  $^{13}\text{C}$ : 150 MHz,  $^{19}\text{F}$ : 564 MHz) and Bruker Advance 500 ( $^1\text{H}$ : 500 MHz,  $^{13}\text{C}$ : 125 MHz,  $^{19}\text{F}$ : 470 MHz) at ambient temperature.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were reported as chemical shifts in parts per million (ppm) downfield from tetramethylsilane, using the residual undeuterated solvent ( $\text{CHCl}_3$  at 7.26 ppm  $^1\text{H}$  NMR, 77.00 ppm  $^{13}\text{C}$  NMR) or tetramethylsilane as reference.  $^{19}\text{F}$  NMR spectra were reported as chemical shifts in parts per million (ppm) using  $\text{CFCl}_3$  (0 ppm) in  $\text{CDCl}_3$  as reference. Coupling constants were reported in hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High-resolution mass spectra (HRMS) were recorded on Bruker microTof by using ESI method. Melting points were determined with XRC-1 and are uncorrected.

All chemicals were purchased from Adamas-Beta, Energy Chemical Company, ALDRICH, and J&K Scientific Ltd, and were used as received from the commercial suppliers without further purification unless mentioned otherwise. All solvents were purified and dried according to standard methods prior to use. Unless otherwise stated, all reactions were carried out in flame-dried glassware under a dry argon atmosphere.

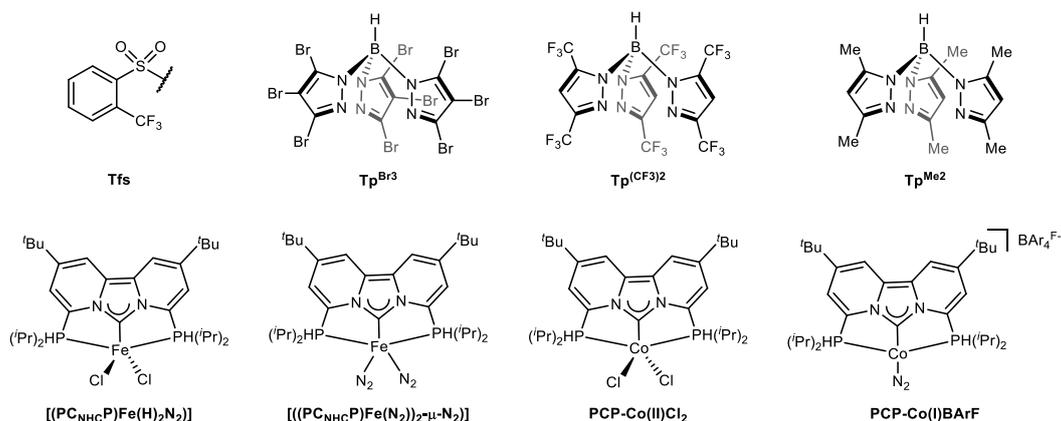
**Caution:** *The differential scanning calorimetry (DSC) shows that N-trifosylhydrazones do not exhibit impact sensitivity (IS) and/or explosive propagation (EP). Although we found no energetic decomposition in our work with N-trifosylhydrazones, caution should be taken in handling large quantities of N-trifosylhydrazones, because the diazo compounds generated from N-trifosylhydrazones are high-energy compounds.*

## 2. Detailed Optimization of Conditions

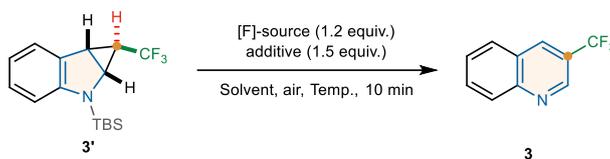
**Supplementary Table 1.** Optimization of cyclopropanation of *N*-TBS indole and TFHZ-Tfs



Entry	Cat. [M] (mol%)	Base	Solvent	Temp. (°C)	Yield of <b>3'</b>
1	Tp <sup>Br3</sup> Ag(thf) (10)	NaH	PhCF <sub>3</sub>	60	12%
2	Tp <sup>CF3</sup> Ag(thf) (10)	NaH	PhCF <sub>3</sub>	60	trace
<b>3</b>	<b>Tp<sup>Br3</sup>Cu(CH<sub>3</sub>CN) (10)</b>	<b>NaH</b>	<b>PhCF<sub>3</sub></b>	<b>60</b>	<b>94%</b>
4	Tp <sup>Me2</sup> Cu(CH <sub>3</sub> CN) (10)	NaH	PhCF <sub>3</sub>	60	27%
5	[(PC <sub>NHC</sub> P)Fe(H) <sub>2</sub> N <sub>2</sub> ] (5)	NaH	PhCF <sub>3</sub>	60	N.D.
6	[((PC <sub>NHC</sub> P)Fe(N <sub>2</sub> ) <sub>2</sub> -μ-N <sub>2</sub> )] (5)	NaH	PhCF <sub>3</sub>	60	N.D.
7	PCP-Co(II)Cl <sub>2</sub> (5)	NaH	PhCF <sub>3</sub>	60	N.D.
8	PCP-Co(I)-BARF (5)	NaH	PhCF <sub>3</sub>	60	N.D.
9	Rh <sub>2</sub> (OAc) <sub>4</sub> (1)	NaH	PhCF <sub>3</sub>	60	13%
10	Rh <sub>2</sub> (Oct) <sub>4</sub> (1)	NaH	PhCF <sub>3</sub>	60	45%
11	Tp <sup>Br3</sup> Cu(CH <sub>3</sub> CN) (10)	Cs <sub>2</sub> CO <sub>3</sub>	PhCF <sub>3</sub>	60	61%
12	Tp <sup>Br3</sup> Cu(CH <sub>3</sub> CN) (10)	DIPEA	PhCF <sub>3</sub>	60	trace
13	Tp <sup>Br3</sup> Cu(CH <sub>3</sub> CN) (10)	NaH	DCM	60	79%
14	Tp <sup>Br3</sup> Cu(CH <sub>3</sub> CN) (10)	NaH	DCE	60	73%
15	Tp <sup>Br3</sup> Cu(CH <sub>3</sub> CN) (10)	NaH	PhMe	60	62%
16	Tp <sup>Br3</sup> Cu(CH <sub>3</sub> CN) (10)	NaH	PhCF <sub>3</sub>	40	63%
17	Tp <sup>Br3</sup> Cu(CH <sub>3</sub> CN) (10)	NaH	PhCF <sub>3</sub>	80	84%



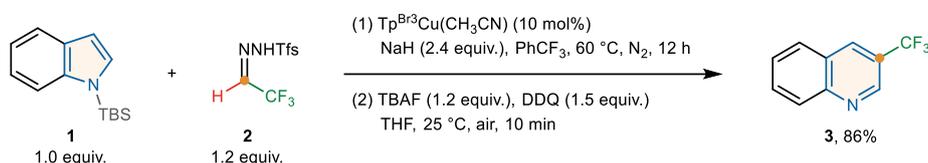
Reaction conditions: indole **1** (0.3 mmol, 1.0 equiv.), TFHZ-Tfs **2** (0.36 mmol, 1.2 equiv.), Cat. [M] (1-10 mol%), base (0.72 mmol, 2.4 equiv.), solvent (10 mL), under N<sub>2</sub> for 12 hours. The yield of cyclopropane **3'** was determined by <sup>1</sup>H NMR analysis of the crude reaction mixture using dibromomethane as an internal standard. N.D. means that no product was detected.

**Supplementary Table 2.** Optimization of ring-opening **3'** to afford 3-(trifluoromethyl)quinoline

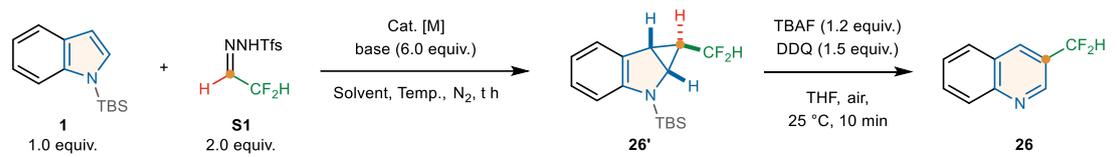
Entry	[F]-source	Solvent	Additive	Temp. (°C)	Yield of <b>3</b>
1	TBAF	THF	-	25	44%
2	TMAF	THF	-	25	N.D.
3	TEAF	THF	-	25	N.D.
4	TBAF	1,4-dioxane	-	25	28%
5	TBAF	MeCN	-	25	15%
6	TBAF	THF	-	0	52%
7	TBAF	THF	-	-20	66%
8	TBAF	THF	-	-60	71%
9	TBAF	THF	DDQ	25	92%

Reaction conditions: crude product **3**, [F]-source (1.2 equiv.), additive (1.5 equiv.), was carried out in 10 mL of solvent for 10 min. Isolated yield. N.D. means that no product was detected.

### The optimal reaction conditions for one-carbon insertion of indole with TFHZ-Tfs



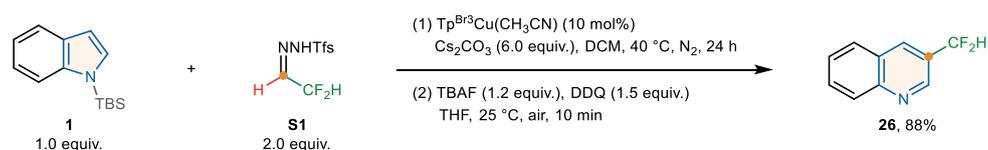
**Procedure:** To an oven-dried screw-cap reaction tube was charged with *N*-TBS indole **1** (69.3 mg, 0.3 mmol, 1.0 equiv.), TFHZ-Tfs **2** (115.3 mg, 0.36 mmol, 1.2 equiv.), NaH (28.8 mg, 0.72 mmol, 2.4 equiv., 60 wt% dispersion in mineral oil),  $\text{Tp}^{\text{Br}^3}\text{Cu}(\text{CH}_3\text{CN})$  (30.0 mg, 10.0 mol%) and  $\text{PhCF}_3$  (10 mL) inside a glove box with nitrogen atmosphere. After transfer out of the glove box, the reaction was stirred at 60 °C for 12 h. The reaction mixture was filtered through a short pad of silica gel with DCM as an eluent. After removal of the solvent *in vacuo*, the residue was added TBAF (0.36 mL, 0.36 mmol, 1.0 mol/L in THF, 1.2 equiv.), DDQ (102.2 mg, 0.45 mmol, 1.5 equiv.) and THF (10 mL). The resulting mixture was stirred at 25 °C for 10 min and filtered through a short pad of silica gel (pre-treated with triethylamine) with DCM as an eluent. After removal of the solvent *in vacuo*, the residue was purified by flash column chromatography on silica gel (pre-treated with trimethylamine, using petroleum ether-EtOAc (50/1), as eluent) to give the product **3**.

**Supplementary Table 3.** Optimization for one-carbon insertion of indole with DFHZ-Tfs


Entry	Cat. [M] (mol%)	Base	Solvent	Temp. ( °C )	t (h)	Yield of 26
1	Tp <sup>Br3</sup> Cu(CH <sub>3</sub> CN) (10)	NaH	PhCF <sub>3</sub>	60	12	40%
2	Tp <sup>Br3</sup> Ag(thf) (10)	NaH	PhCF <sub>3</sub>	60	12	N.D.
3	[(PC <sub>NHC</sub> P)Fe(H) <sub>2</sub> N <sub>2</sub> ] (5)	NaH	PhCF <sub>3</sub>	60	12	N.D.
4	[((PC <sub>NHC</sub> P)Fe(N <sub>2</sub> ) <sub>2</sub> -μ-N <sub>2</sub> )] (5)	NaH	PhCF <sub>3</sub>	60	12	N.D.
5	PCP-Co(II)Cl <sub>2</sub> (5)	NaH	PhCF <sub>3</sub>	60	12	N.D.
6	PCP-Co(I)-BARF (5)	NaH	PhCF <sub>3</sub>	60	12	N.D.
7	Rh <sub>2</sub> (OAc) <sub>4</sub> (1)	NaH	PhCF <sub>3</sub>	60	12	36%
8	Tp <sup>Br3</sup> Cu(CH <sub>3</sub> CN) (10)	NaH	PhCF <sub>3</sub>	60	12	trace
9	Tp <sup>Br3</sup> Cu(CH <sub>3</sub> CN) (10)	DIPEA	PhCF <sub>3</sub>	60	12	22%
10	Tp <sup>Br3</sup> Cu(CH <sub>3</sub> CN) (10)	K <sub>2</sub> CO <sub>3</sub>	PhCF <sub>3</sub>	60	12	37%
11	Tp <sup>Br3</sup> Cu(CH <sub>3</sub> CN) (10)	Cs <sub>2</sub> CO <sub>3</sub>	PhCF <sub>3</sub>	60	12	54%
12	Tp <sup>Br3</sup> Cu(CH <sub>3</sub> CN) (10)	Cs <sub>2</sub> CO <sub>3</sub>	DCM	60	12	68%
13	Tp <sup>Br3</sup> Cu(CH <sub>3</sub> CN) (10)	Cs <sub>2</sub> CO <sub>3</sub>	1,4-dioxane	60	12	44%
14	Tp <sup>Br3</sup> Cu(CH <sub>3</sub> CN) (10)	Cs <sub>2</sub> CO <sub>3</sub>	DCM	40	12	70%
15	Tp <sup>Br3</sup> Cu(CH <sub>3</sub> CN) (10)	Cs <sub>2</sub> CO <sub>3</sub>	DCM	40	24	88%

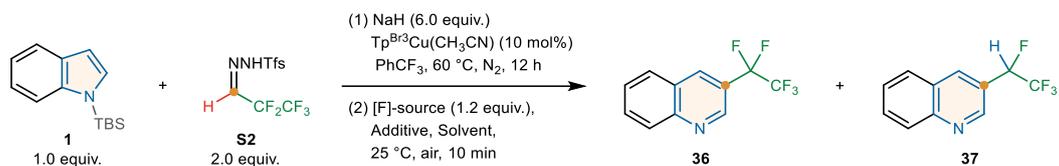
Reaction conditions: indole **1** (0.3 mmol, 1.0 equiv.), DFHZ-Tfs **S1** (0.6 mmol, 2.0 equiv.), Cat. [M] (1-10 mol%), base (1.8 mmol, 6.0 equiv.), solvent (10 mL), under N<sub>2</sub> for 12 or 24 hours. Isolated yield. N.D. means that no product was detected.

### The optimal reaction conditions for one-carbon insertion of indole with DFHZ-Tfs



**Procedure:** To an oven-dried screw-cap reaction tube was charged with DFHZ-Tfs **S1** (181.3 mg, 0.6 mmol, 2.0 equiv.), Cs<sub>2</sub>CO<sub>3</sub> (586.5 mg, 1.8 mmol, 6.0 equiv.), *N*-TBS indole **1** (69.3 mg, 0.3 mmol, 1.0 equiv.), Tp<sup>Br3</sup>Cu(CH<sub>3</sub>CN) (30.0 mg, 10.0 mol%) and DCM (10 mL) inside a glove box with nitrogen atmosphere. After transfer out of the glove box, the reaction was stirred at 40 °C for 24 h. The reaction mixture was filtered through a short pad of silica gel with DCM as an eluent. After removal of the solvent *in vacuo*, the residue was added TBAF (0.36 mL, 0.36 mmol, 1.0 mol/L in THF, 1.2 equiv.), DDQ (102.2 mg, 0.45 mmol, 1.5 equiv.) and THF (10 mL). The resulting mixture was stirred at 25 °C for 10 min and filtered through a short pad of silica gel (pre-treated with triethylamine) with DCM as an eluent. After removal of the solvent *in vacuo*, the residue was purified by flash column chromatography on silica gel (pre-treated with trimethylamine, using petroleum ether-EtOAc (50/1) as eluent) to give the product **26**.

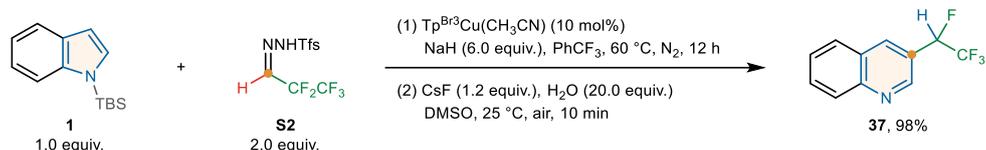
**Supplementary Table 4.** Optimization for hydrodefluorinative one-carbon insertion of indole with fluoroalkyl *N*-triflylhydrazones



Entry	[F]-source	Solvent	Additive	Temp. (°C)	Yield of 36	Yield of 37
1	TBAF	THF	DDQ (1.5 equiv.)	25	60%	20%
2	TBAF	THF	-	25	44%	23%
3	CsF	DMSO	-	25	37%	48%
4	CsF	DMF	-	25	36%	46%
5	CsF	DME	-	25	40%	47%
7	CsF	DMSO	H <sub>2</sub> O (20 equiv.)	25	N.D.	98%

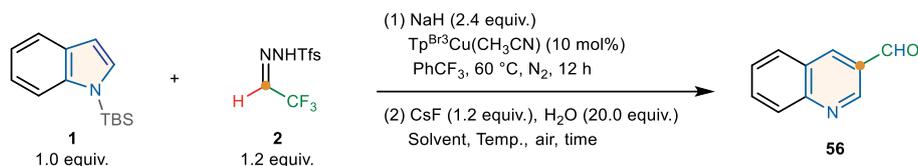
Reaction conditions: (1) indole **1** (0.3 mmol, 1.0 equiv.), *N*-triflylhydrazone **S2** (0.6 mmol, 2.0 equiv.), Tp<sup>Br3</sup>Cu(CH<sub>3</sub>CN) (10 mol%), NaH (1.8 mmol, 6.0 equiv.), PhCF<sub>3</sub> (10 mL), under N<sub>2</sub> for 12 hours. (2) [F]-source (1.2 equiv.), additive, solvent (10 mL), 25 °C, under air for 10 min. Isolated yield.

**The optimal reaction conditions for hydrodefluorinative one-carbon insertion reaction:**



**Procedure:** To an oven-dried screw-cap reaction tube was charged with *N*-TBS indole **1** (69.3 mg, 0.3 mmol, 1.0 equiv.), *N*-triflylhydrazone **S2** (222.0 mg, 0.6 mmol, 2.0 equiv.), NaH (72.0 mg, 1.8 mmol, 6.0 equiv., 60 wt% dispersion in mineral oil), Tp<sup>Br3</sup>Cu(CH<sub>3</sub>CN) (30.0 mg, 10.0 mol%) and PhCF<sub>3</sub> (10 mL) inside a glove box with nitrogen atmosphere. After transfer out of the glove box, the reaction was stirred at 60 °C for 12 h. The reaction mixture was filtered through a short pad of silica gel with DCM as an eluent. After removal of the solvent *in vacuo*, the residue was added CsF (54.7 mg, 0.36 mmol, 1.2 equiv.), H<sub>2</sub>O (20.0 equiv.) and DMSO (10 mL). The resulting mixture was stirred at 25 °C for 10 min and then was diluted with DCM, washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was evaporated under reduced pressure to leave a crude product, which was purified by flash column chromatography on silica gel (pre-treated with trimethylamine, using petroleum ether-EtOAc (50/1) as eluent) to give the product **37**.

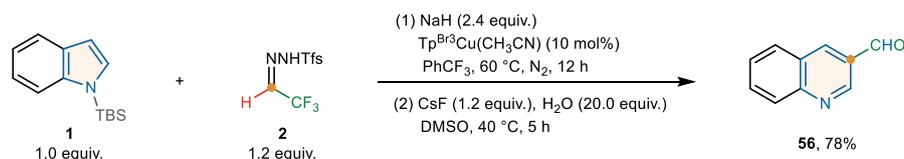
**Supplementary Table 5.** Optimization for defluorinative formylation insertion of indole with TFHZ-Tfs leading to quinoline-3-carboxaldehyde



Entry	Solvent	Temp. ( °C)	time	Yield of <b>56</b>
1	DMSO	25	10 min	15%
2	DMSO	0	1.0 h	9%
3	DMSO	25	5.0 h	54%
4	DMSO	40	5.0 h	78%
5	DMSO	60	5.0 h	77%

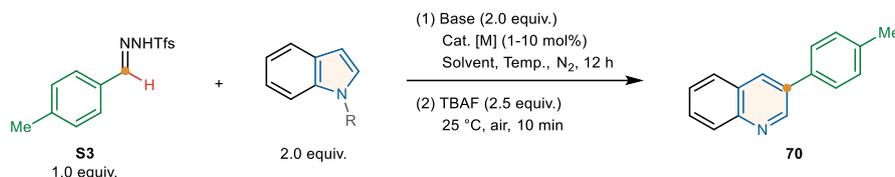
Reaction conditions: (1) indole **1** (0.3 mmol, 1.0 equiv.), *N*-trifosylhydrazone **2** (0.36 mmol, 1.2 equiv.),  $\text{Tp}^{\text{Br}^3}\text{Cu}(\text{CH}_3\text{CN})$  (10 mol%), NaH (0.72 mmol, 2.4 equiv.),  $\text{PhCF}_3$  (10 mL), under  $\text{N}_2$  for 12 hours. (2) CsF (0.36 mmol, 1.2 equiv.),  $\text{H}_2\text{O}$  (20.0 equiv.), DMSO (10 mL), 0-60 °C, under air for 10 min-5 h. Isolated yield.

**The optimal reaction conditions for defluorinative formylation one-carbon insertion reaction:**



**Procedure:** To an oven-dried screw-cap reaction tube was charged with *N*-TBS indole **1** (69.3 mg, 0.3 mmol, 1.0 equiv.), *N*-trifosylhydrazone **2** (115.3 mg, 0.36 mmol, 1.2 equiv.), NaH (28.8 mg, 0.72 mmol, 2.4 equiv., 60 wt% dispersion in mineral oil),  $\text{Tp}^{\text{Br}^3}\text{Cu}(\text{CH}_3\text{CN})$  (30.0 mg, 10.0 mol%) and  $\text{PhCF}_3$  (10 mL) inside a glove box with nitrogen atmosphere. After transfer out of the glove box, the reaction was stirred at 60 °C for 12 h. After cooling to room temperature, the reaction mixture was filtered through a short pad of silica gel with DCM as an eluent. After removal of the solvent *in vacuo*, the residue was added CsF (54.7 mg, 0.36 mmol, 1.2 equiv.),  $\text{H}_2\text{O}$  (20.0 equiv.) and DMSO (10 mL). The resulting mixture was stirred at 40 °C for 5 h. After completion of the reaction, the mixture was diluted with DCM, washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and the solvent was evaporated under reduced pressure to leave a crude product, which was purified by flash column chromatography on silica gel (pre-treated with trimethylamine, using petroleum ether-EtOAc (50/1) as eluent) to give product **56**.

**Supplementary Table 6.** Optimization for one-carbon insertion of indole with aryl-substituted *N*-triflylhydrazone

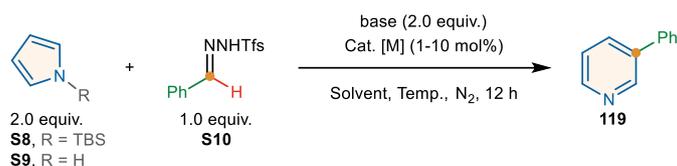


Entry	Cat. [M] (mol%)	Base	Solvent	Temp. ( °C)	R	Yield (%) of <b>70</b>
1	Tp <sup>Br3</sup> Cu(CH <sub>3</sub> CN) (10)	NaH	PhCF <sub>3</sub>	60	TBS	20
2	Tp <sup>Me2</sup> Cu(CH <sub>3</sub> CN) (10)	NaH	PhCF <sub>3</sub>	60	TBS	13
3	Tp <sup>Br3</sup> Ag(thf) (10)	NaH	PhCF <sub>3</sub>	60	TBS	97
4	Tp <sup>(CF3)2</sup> Ag(thf) (10)	NaH	PhCF <sub>3</sub>	60	TBS	92
5	AgOTf (10)	NaH	PhCF <sub>3</sub>	60	TBS	48
6	Rh <sub>2</sub> (esp) <sub>2</sub> (1)	NaH	PhCF <sub>3</sub>	60	TBS	83
7	Pd(OAc) <sub>2</sub> (5)	NaH	PhCF <sub>3</sub>	60	TBS	trace
8	Tp <sup>Br3</sup> Ag(thf) (10)	Cs <sub>2</sub> CO <sub>3</sub>	PhCF <sub>3</sub>	60	TBS	77
9	Tp <sup>Br3</sup> Ag(thf) (10)	K <sub>2</sub> CO <sub>3</sub>	PhCF <sub>3</sub>	60	TBS	64
10	Tp <sup>Br3</sup> Ag(thf) (10)	LiO <sup>t</sup> Bu	PhCF <sub>3</sub>	60	TBS	72
11	Tp <sup>Br3</sup> Ag(thf) (10)	DIPEA	PhCF <sub>3</sub>	60	TBS	trace
12	Tp <sup>Br3</sup> Ag(thf) (10)	NaH	DCM	60	TBS	34(32)
13	Tp <sup>Br3</sup> Ag(thf) (10)	NaH	DCE	60	TBS	36(35)
14	Tp <sup>Br3</sup> Ag(thf) (10)	NaH	CHCl <sub>3</sub>	60	TBS	trace
15	Tp <sup>Br3</sup> Ag(thf) (10)	NaH	PhCF <sub>3</sub>	40	TBS	57
16	Tp <sup>Br3</sup> Ag(thf) (10)	NaH	PhCF <sub>3</sub>	80	TBS	94
17	Tp <sup>Br3</sup> Ag(thf) (10)	NaH	PhCF <sub>3</sub>	60	H( <b>S4</b> )	43
18	Tp <sup>Br3</sup> Ag(thf) (10)	NaH	PhCF <sub>3</sub>	60	TMS( <b>S5</b> )	82
19	Tp <sup>Br3</sup> Ag(thf) (10)	NaH	PhCF <sub>3</sub>	60	TIPS( <b>S6</b> )	95
20	Tp <sup>Br3</sup> Ag(thf) (10)	NaH	PhCF <sub>3</sub>	60	Boc( <b>S7</b> )	0(90)

Reaction conditions: (1) *N*-triflylhydrazone (0.3 mmol, 1.0 equiv.), indole (0.6 mmol, 2.0 equiv.), Cat. [M] (1-10 mol%), base (0.6mmol, 2.0 equiv.) and solvent (5 mL), under N<sub>2</sub> for 12 hours. (2) TBAF (0.75 mmol, 2.5 equiv.), 25 °C, under air for 10 min. Isolated yield. Isolated yield. Yield in parentheses is unconverted cyclopropane.

**Procedure:** To an oven-dried screw-cap reaction tube was charged with *N*-triflylhydrazone **S3** (102.6 mg, 0.3 mmol, 1.0 equiv.), base (0.6 mmol, 2.0 equiv.), *N*-protected indole (0.6 mmol, 2.0 equiv.), catalyst and solvent (5 mL) inside a glove box with nitrogen atmosphere. After transfer out of the glove box, the reaction was stirred at indicated temperature for 12 h. The reaction mixture was cooled to room temperature. Then, TBAF (0.75 mL, 0.75 mmol, 1.0 mol/L in THF, 2.5 equiv.) was added and stirred at 25 °C under air for 10 min. After completion of the reaction, the mixture was filtered through a short pad of silica gel (pre-treated with triethylamine) with DCM as an eluent. After removal of the solvent *in vacuo*, the residue was purified by flash chromatography on silica gel (pre-treated with trimethylamine, using petroleum ether-EtOAc (50/1) as eluent) to give product **70**.

**Supplementary Table 7.** Optimization for one-carbon insertion of pyrrole with *N*-triflylhydrazone



Entry	R	Cat. [M] (mol%)	Base	Solvent	Temp. ( °C)	Yield of <b>119</b>
1*	TBS	Tp <sup>Br3</sup> Ag(thf) (10)	NaH	PhCF <sub>3</sub>	60	trace
2*	TBS	Tp <sup>Br3</sup> Cu(CH <sub>3</sub> CN) (10)	NaH	PhCF <sub>3</sub>	60	N.D.
3*	TBS	Rh <sub>2</sub> (esp) <sub>2</sub> (1)	NaH	PhCF <sub>3</sub>	60	N.D.
4	H	Tp <sup>Br3</sup> Ag(thf) (10)	NaH	PhCF <sub>3</sub>	60	11%
5	H	Tp <sup>Br3</sup> Cu(CH <sub>3</sub> CN) (10)	NaH	PhCF <sub>3</sub>	60	N.D.
6	H	Rh <sub>2</sub> (esp) <sub>2</sub> (1)	NaH	PhCF <sub>3</sub>	60	48%
7	H	Tp <sup>CF3</sup> Ag(thf) (10)	NaH	PhCF <sub>3</sub>	60	10%
8	H	Tp <sup>Me2</sup> Cu(CH <sub>3</sub> CN) (10)	NaH	PhCF <sub>3</sub>	60	N.D.
10	H	[(PC <sub>NHC</sub> P)Fe(H) <sub>2</sub> N <sub>2</sub> ] (5)	NaH	PhCF <sub>3</sub>	60	N.D.
11	H	PCP-Co(II)Cl <sub>2</sub> (5)	NaH	PhCF <sub>3</sub>	60	N.D.
12	H	Rh <sub>2</sub> (OAc) <sub>4</sub> (1)	NaH	PhCF <sub>3</sub>	60	41%
13	H	Rh <sub>2</sub> (esp) <sub>2</sub> (1)	Cs <sub>2</sub> CO <sub>3</sub>	PhCF <sub>3</sub>	60	18%
14	H	Rh <sub>2</sub> (esp) <sub>2</sub> (1)	K <sub>2</sub> CO <sub>3</sub>	PhCF <sub>3</sub>	60	15%
15	H	Rh <sub>2</sub> (esp) <sub>2</sub> (1)	LiO <sup>t</sup> Bu	PhCF <sub>3</sub>	60	22%
16	H	Rh <sub>2</sub> (esp) <sub>2</sub> (1)	NaH	DCM	60	40%
17	H	Rh <sub>2</sub> (esp) <sub>2</sub> (1)	NaH	DCE	60	23%
18	H	Rh <sub>2</sub> (esp) <sub>2</sub> (1)	NaH	PhCF <sub>3</sub>	40	32%
19	H	Rh <sub>2</sub> (esp) <sub>2</sub> (1)	NaH	PhCF <sub>3</sub>	80	46%

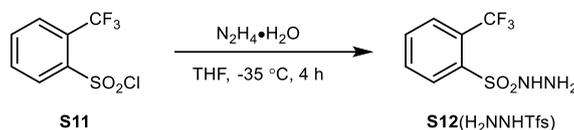
Reaction conditions: *N*-triflylhydrazone **S10** (0.3 mmol, 1.0 equiv.), pyrrole (0.6 mmol, 2.0 equiv.), Cat. [M] (1-10 mol%), base (0.6mmol, 2.0 equiv.) and solvent (5 mL), under N<sub>2</sub> for 12 hours. Isolated yield. N.D. means that no product was detected. \*TBAF was added into reaction mixture after the reaction is completed.

**Procedure:** To an oven-dried screw-cap reaction tube was charged with *N*-triflylhydrazone **S10** (98.4 mg, 0.3 mmol, 1.0 equiv.), base (0.6 mmol, 2.0 equiv.), pyrrole (0.6 mmol, 2.0 equiv.) catalyst and 5 mL solvent inside a glove box with nitrogen atmosphere. After transfer out of the glove box, the reaction was stirred at the required temperature for 12 h. The mixture was filtered through a short pad of silica gel (pre-treated with triethylamine) with DCM as an eluent. After removal of the solvent *in vacuo*, the residue was purified by flash chromatography on silica gel (pre-treated with trimethylamine, using petroleum ether-EtOAc (50/1) as eluent) to give the product **119**.

## 3. Preparation of Starting Materials

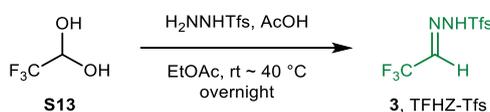
### 3.1 The Preparation of *N*-Triftosylhydrazones

#### 3.1.1 The Preparation of H<sub>2</sub>NNHTfs

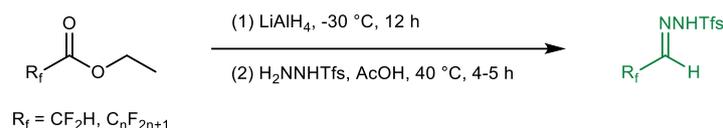


**Procedure:** A 500 mL bottom flask was charged with 2-(trifluoromethyl)benzenesulfonyl chloride **S11** (24.4 g, 100 mmol) and THF (200 mL). Then N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O (24.3 mL, 250 mmol, 80 % in H<sub>2</sub>O) was added dropwise and stirred at -35 °C. The mixture was then stirred for 4 h at -35 °C. After removal of the most solvent *in vacuo*, the mixture was extracted with EtOAc (50 mL × 3). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and removed the most solvent under reduced pressure. The residues was recrystallized in Pe/EtOAc to give H<sub>2</sub>NNHTfs (**S12**), as a white solid, 89% yield, m.p: 120-121 °C; **<sup>1</sup>H NMR** (600 MHz, DMSO-*d*<sub>6</sub>) δ 8.79 (s, 1H), 8.07 (d, *J* = 7.8 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.88 (t, *J* = 7.5 Hz, 1H), 7.83 (t, *J* = 7.5 Hz, 1H), 4.29 (s, 2H). **<sup>13</sup>C NMR** (150 MHz, DMSO-*d*<sub>6</sub>) δ 137.5, 133.0, 132.8, 131.1, 128.2 (q, *J* = 6.0 Hz), 126.8 (q, *J* = 33.0 Hz), 122.9 (q, *J* = 273.0 Hz). **<sup>19</sup>F NMR** (564 MHz, DMSO-*d*<sub>6</sub>) δ -56.19. **HRMS** (ESI) *m/z* calculated for C<sub>7</sub>H<sub>6</sub>F<sub>3</sub>N<sub>2</sub>O<sub>2</sub>S<sup>-</sup> [M-H]<sup>-</sup> 239.0108, found 239.0060.

#### 3.1.2 The Preparation of Fluoroalkyl Substituted *N*-Triftosylhydrazones

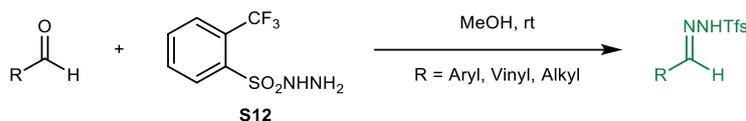


**Procedure:** TFHZ-Tfs was prepared according to literature procedure<sup>[1]</sup>. A 500 mL bottom flask was charged with trifluoroacetaldehyde monohydrate **S13** (14.9 g, 127.5 mmol), H<sub>2</sub>NNHTfs **S12** (20.4 g, 85.0 mmol) and EtOAc (310.0 mL). Then AcOH (4.3 mL, 7.7 mmol) was added dropwise and stirred at ice water bath for 10 min under nitrogen. Then the mixture was transferred to room temperature and stirred for 80 min. After that, the mixture was transferred to 40 °C and stirred overnight. After the reaction was completion, the mixture was concentrated under reduced pressure and washed by PE/EtOAc to afford TFHZ-Tfs **3** as a white solid, 90% yield, m.p: 124-125 °C; **<sup>1</sup>H NMR** (500 MHz, DMSO-*d*<sub>6</sub>) δ 13.01 (s, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.88 (t, *J* = 8.0 Hz, 1H), 7.81 (t, *J* = 8.0 Hz, 1H), 7.52 (q, *J* = 8.0 Hz, 1H). **<sup>13</sup>C NMR** (150 MHz, DMSO-*d*<sub>6</sub>) δ 137.5, 134.6, 133.5 (q, *J* = 37.6 Hz), 133.5 (q, *J* = 37.9 Hz), 132.1, 129.1 (q, *J* = 6.3 Hz), 127.0 (q, *J* = 33.0 Hz), 123.1 (q, *J* = 272.4 Hz), 120.4 (q, *J* = 271.5 Hz). **<sup>19</sup>F NMR** (564 MHz, DMSO-*d*<sub>6</sub>) δ -51.95, -61.95 (d, *J* = 3.8 Hz). **HRMS** (ESI) *m/z* calculated for C<sub>9</sub>H<sub>6</sub>F<sub>3</sub>N<sub>2</sub>NaO<sub>2</sub>S<sup>+</sup> [M+Na]<sup>+</sup> 342.9946, found 342.9955. The spectrum was consistent with the previous literature<sup>[1]</sup>.

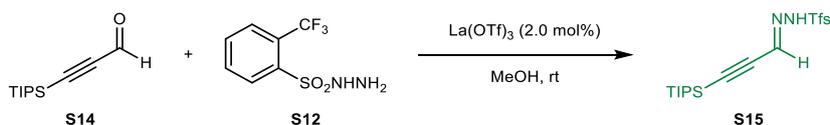


**Procedure:** Fluoroalkyl *N*-triftosylhydrazones were prepared according to literature procedure<sup>[2]</sup>. A 250 mL bottom flask was charged with ethyl perfluorate (75.0 mmol) and EtOAc (200.0 mL). The LiAlH<sub>4</sub> (1.1 equiv.) was added into the reaction mixture dropwise at -30 °C under N<sub>2</sub> atmosphere. The reaction mixture were continued stired for 12 h at -30 °C. Then H<sub>2</sub>NNHTfs (50.0 mmol) and AcOH (5.5 mmol) was added dropwise under N<sub>2</sub> atmosphere. The mixture was transferred to 40 °C and stirred for 4-5 h, and monitored by TLC. After the reaction was complete, the mixture was concentrated under reduced pressure and washed by Pe/PE/EtOAc to afford the desired *N*-triftosylhydrazones DFHZ-Tfs **S2**, as a white solid. m.p: 86-87 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.07 (s, 1H), 8.35-8.30 (m, 1H), 7.93-7.90 (m, 1H), 7.82-7.77 (m, 2H), 7.22-7.19 (m, 1H), 5.99 (td, *J* = 54.5, 6.0 Hz, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 139.7 (t, *J* = 33.5 Hz), 136.1, 134.1, 133.1, 132.8, 128.6 (q, *J* = 6.5 Hz), 127.8 (q, *J* = 33.0 Hz), 122.6 (q, *J* = 272.5 Hz), 112.2 (t, *J* = 234.5 Hz). <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -58.30, -117.13 (d, *J* = 54.5 Hz). HRMS (ESI) *m/z* calcd. for C<sub>9</sub>H<sub>7</sub>F<sub>5</sub>N<sub>2</sub>NaO<sub>2</sub>S<sup>+</sup> [M+Na]<sup>+</sup> 325.0041, found 325.0047.

### 3.1.3 The Preparation of *N*-Triftosylhydrazone-Derived from Aldehyde



**General Procedure:** The *N*-triftosylhydrazone-derived from aldehyde was prepared according to the literature procedure<sup>[3]</sup>. To a stirred solution of H<sub>2</sub>NNHTfs (2.0 mmol) of methanol (2 mL), aldehyde (2.2 mmol, 1.1 equiv.) was added dropwise. The resulting the mixture was stirred at room temperature for 1-5 h. The mixture was filtered and the resulting solid was washed with ice cold diethyl ether and dried under reduced pressure to give the corresponding pure *N*-triftosylhydrazones.



**Procedure:** The alkyne *N*-triftosylhydrazone was prepared according to literature procedure<sup>[4]</sup>. To a rapidly stirred suspension of H<sub>2</sub>NNHTfs **S12** (2.0 mmol, 1.0 equiv.) and La(OTf)<sub>3</sub> (2.0 mol %) in MeOH (10 mL), 3-(triisopropylsilyl)propionaldehyde **S14** (2.2 mmol, 1.1 equiv.) was added dropwise. The resulting the mixture was stirred at 0 °C for 2 h (monitored by TLC) and the crude products are obtained as solid precipitates. Then the crude products were purified by flash chromatography on silica gel (using petroleum ether-EtOAc (5/1) as eluent) to afford the desired alkyne *N*-triftosylhydrazones **S15**, as a pale yellow solid. m.p: 48-49 °C. <sup>1</sup>H NMR (600 MHz, DMSO) δ 10.88 (s, 1H), 8.10 (d, *J* = 7.8 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.94 (t, *J* = 7.8 Hz, 1H), 7.90 (t, *J* = 7.8 Hz, 1H), 7.05 (s, 1H), 1.19-1.11 (m, 4H), 1.08 (d, *J* = 7.2 Hz, 18H). <sup>13</sup>C NMR (125 MHz, DMSO) δ 137.1, 133.9, 133.3, 131.4, 128.6 (q, *J* = 6.3 Hz), 127.8, 126.4 (q, *J* = 32.5 Hz), 122.7 (q, *J* = 272.5 Hz), 106.3, 95.3, 18.3, 10.4. <sup>19</sup>F NMR (470 MHz, DMSO) δ -56.51. HRMS (ESI) *m/z* calcd. for C<sub>19</sub>H<sub>28</sub>F<sub>3</sub>N<sub>2</sub>O<sub>2</sub>SSi<sup>+</sup> [M+H]<sup>+</sup> 433.1587, found 433.1598.



<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 6.89 (d, *J* = 1.2 Hz, 2H), 6.42 (d, *J* = 1.2 Hz, 2H), 0.99 (s, 9H), 0.53 (s, 6H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 123.8, 110.4, 25.8, 18.2, -5.5.

The spectrum was consistent with the previous literature.<sup>[6]</sup>



**(135) 1-(*tert*-Butyldimethylsilyl)-2-methyl-1*H*-indole**

Prepared according to the general procedure, 70% yield, as a colorless oil.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.63-7.54 (m, 2H), 7.19-7.11 (m, 2H), 6.43 (s, 1H), 2.58 (s, 3H), 1.07 (s, 9H), 0.76 (s, 6H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 142.7, 142.0, 131.3, 120.3, 119.6, 119.1, 114.1, 106.1, 26.8, 20.6, 17.5, -0.5.

The spectrum was consistent with the previous literature.<sup>[5]</sup>



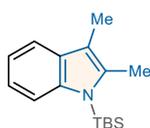
**(S16) 1-(*tert*-Butyldimethylsilyl)-3-methyl-1*H*-indole**

Prepared according to the general procedure, 91% yield, as a colorless oil.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.59 (d, *J* = 7.2 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.22-7.13 (m, 2H), 6.97 (s, 1H), 2.36 (s, 3H), 0.97 (s, 9H), 0.61 (s, 6H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 141.4, 131.7, 128.2, 121.3, 119.2, 118.7, 113.8, 113.5, 26.3, 19.5, 9.7, -3.9.

The spectrum was consistent with the previous literature.<sup>[5]</sup>



**(S17) 1-(*tert*-Butyldimethylsilyl)-2,3-dimethyl-1*H*-indole**

Prepared according to the general procedure, 64% yield, as a colorless oil.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.49 (d, *J* = 7.2 Hz, 1H), 7.45 (d, *J* = 7.2 Hz, 1H), 7.08 (m, 2H), 2.42 (s, 3H), 2.23 (s, 3H), 0.99 (s, 9H), 0.66 (s, 6H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 141.5, 137.2, 132.1, 120.3, 119.1, 117.6, 113.9, 111.3, 26.8, 20.5, 14.4, 8.9, -0.3.

The spectrum was consistent with the previous literature.<sup>[5]</sup>



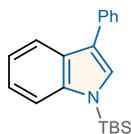
**(S18) 1-(*tert*-Butyldimethylsilyl)-2-phenyl-1*H*-indole**

Prepared according to the general procedure, 57% yield, as a white solid; mp: 68-69 °C.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.23-8.11 (m, 2H), 8.04-7.97 (m, 2H), 7.97-7.87 (m, 3H), 7.76-7.65 (m, 2H), 7.09 (s, 1H), 1.53 (s, 9H), 0.71 (s, 6H).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  146.4, 142.5, 136.7, 131.2, 130.7, 128.0, 127.4, 121.0, 120.2, 120.0, 115.2, 108.1, 27.7, 20.6, -1.3.

The spectrum was consistent with the previous literature.<sup>[5]</sup>



**(S19) 1-(*tert*-Butyldimethylsilyl)-3-phenyl-1*H*-indole**

Prepared according to the general procedure, 87% yield, as a pale yellow solid; mp: 70-71 °C.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 (d,  $J = 7.8$  Hz, 1H), 7.66 (d,  $J = 7.8$  Hz, 2H), 7.55 (d,  $J = 8.0$  Hz, 1H), 7.43 (t,  $J = 7.8$  Hz, 2H), 7.31 (s, 1H), 7.27 (t,  $J = 7.2$  Hz, 1H), 7.23-7.15 (m, 2H), 0.96 (s, 9H), 0.63 (s, 6H).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  141.9, 135.6, 129.2, 128.7, 127.6, 125.9, 121.8, 120.2, 120.2, 119.7, 114.2, 26.3, 19.5, -3.9.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{20}\text{H}_{26}\text{NSi}^+$   $[\text{M} + \text{H}]^+$  308.1829, found 308.1783.



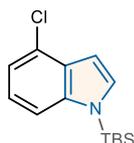
**(S20) 1-(*tert*-Butyldimethylsilyl)-4-methyl-1*H*-indole**

Prepared according to the general procedure, 90% yield, as a colorless oil.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 (d,  $J = 8.4$  Hz, 1H), 7.36-7.32 (m, 1H), 7.24 (t,  $J = 7.8$  Hz, 1H), 7.09 (d,  $J = 7.2$  Hz, 1H), 6.81 (s, 1H), 2.73 (s, 3H), 1.10 (s, 9H), 0.76 (s, 6H).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  140.7, 131.1, 130.3, 130.0, 121.4, 120.0, 111.5, 103.2, 26.3, 19.5, 19.0, -4.0.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{15}\text{H}_{24}\text{NSi}^+$   $[\text{M} + \text{H}]^+$  246.1673, found 246.1628.



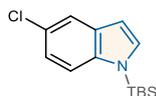
**(S21) 1-(*tert*-Butyldimethylsilyl)-4-chloro-1*H*-indole**

Prepared according to the general procedure, 92% yield, as a colorless oil.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 (d,  $J = 8.0$  Hz, 1H), 7.28 (d,  $J = 3.0$  Hz, 1H), 7.20 (d,  $J = 7.8$  Hz, 1H), 7.14 (t,  $J = 8.0$  Hz, 1H), 6.81 (d,  $J = 3.0$  Hz, 1H), 0.99 (s, 9H), 0.67 (s, 6H).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  141.7, 131.5, 130.2, 125.7, 121.9, 119.5, 112.4, 103.4, 26.2, 19.4, -4.0.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{14}\text{H}_{19}\text{ClNSi}^-$   $[\text{M} - \text{H}]^-$  264.0981, found 264.0955.



**(S22) 1-(*tert*-Butyldimethylsilyl)-5-chloro-1*H*-indole**

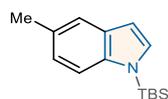
Prepared according to the general procedure, 96% yield, as a white solid; mp: 43-44 °C.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 (s, 1H), 7.39 (d,  $J = 9.0$  Hz, 1H), 7.17 (d,  $J = 3.0$  Hz, 1H), 7.08 (d,  $J =$

9.0 Hz, 1H), 6.53 (s, 1H), 0.89 (s, 9H), 0.56 (s, 6H).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  139.3, 132.5, 132.4, 125.4, 121.6, 120.0, 114.6, 104.4, 26.2, 19.4, -4.1.

The spectrum was consistent with the previous literature.<sup>[7]</sup>



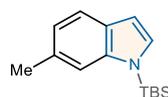
### (S23) 1-(*tert*-Butyldimethylsilyl)-5-methyl-1*H*-indole

Prepared according to the general procedure, 98% yield, as a white solid; mp: 42-43 °C.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51-7.44 (m, 2H), 7.21 (d,  $J$  = 3.0 Hz, 1H), 7.05 (d,  $J$  = 7.8 Hz, 1H), 6.60 (d,  $J$  = 3.0 Hz, 1H), 2.51 (s, 3H), 0.99 (s, 9H), 0.65 (s, 6H).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  139.2, 131.6, 131.0, 128.9, 122.9, 120.3, 113.5, 104.3, 26.3, 21.3, 19.5, -4.0.

The spectrum was consistent with the previous literature.<sup>[7]</sup>



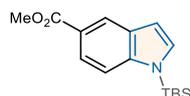
### (S24) 1-(*tert*-Butyldimethylsilyl)-6-methyl-1*H*-indole

Prepared according to the general procedure, 97% yield, as a colorless oil.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 (d,  $J$  = 7.8 Hz, 1H), 7.39 (s, 1H), 7.17 (d,  $J$  = 3.0 Hz, 1H), 7.03 (d,  $J$  = 7.8 Hz, 1H), 6.64 (d,  $J$  = 3.0 Hz, 1H), 2.55 (s, 3H), 1.01 (s, 9H), 0.66 (s, 6H).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  141.5, 130.8, 130.3, 129.1, 121.5, 120.2, 113.9, 104.6, 26.3, 22.0, 19.5, -3.9.

The spectrum was consistent with the previous literature.<sup>[7]</sup>



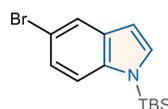
### (S25) Methyl 1-(*tert*-butyldimethylsilyl)-1*H*-indole-5-carboxylate

Prepared according to the general procedure, 91% yield, as a white solid; mp: 90-91 °C.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.39 (s, 1H), 7.86 (d,  $J$  = 8.7 Hz, 1H), 7.51 (d,  $J$  = 8.7 Hz, 1H), 7.24 (d,  $J$  = 3.0 Hz, 1H), 6.70 (d,  $J$  = 3.1 Hz, 1H), 3.93 (s, 3H), 0.93 (s, 9H), 0.62 (s, 6H).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  168.1, 143.8, 132.3, 131.0, 123.4, 122.7, 121.8, 113.3, 106.0, 51.8, 26.2, 19.4, -4.0.

The spectrum was consistent with the previous literature.<sup>[5]</sup>



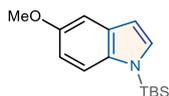
### (S26) 5-Bromo-1-(*tert*-butyldimethylsilyl)-1*H*-indole

Prepared according to the general procedure, 98% yield, as a colorless oil.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (s, 1H), 7.45 (d,  $J$  = 9.0 Hz, 1H), 7.30 (d,  $J$  = 9.0 Hz, 1H), 7.25 (d,  $J$  = 3.0 Hz, 1H), 6.62 (s, 1H), 0.99 (s, 9H), 0.67 (s, 6H).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  139.6, 133.2, 132.2, 124.1, 123.1, 115.1, 113.1, 104.3, 26.2, 19.4, -4.1.

The spectrum was consistent with the previous literature.<sup>[5]</sup>



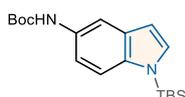
**(S27) 1-(*tert*-Butyldimethylsilyl)-5-methoxy-1*H*-indole**

Prepared according to the general procedure, 97% yield, as a colorless oil.

$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 (d,  $J = 9.0$  Hz, 1H), 7.22 (s, 1H), 7.16 (d,  $J = 6.0$  Hz, 1H), 6.90 (d,  $J = 9.0$  Hz, 1H), 6.62 (d,  $J = 3.0$  Hz, 1H), 3.91 (s, 3H), 0.99 (s, 9H), 0.65 (s, 6H).

$^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ )  $\delta$  154.1, 136.0, 131.9, 131.7, 114.4, 111.3, 104.6, 102.3, 55.6, 26.3, 19.4, -4.1.

The spectrum was consistent with the previous literature.<sup>[5]</sup>



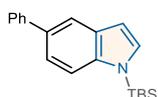
**(S28) *tert*-Butyl (1-(*tert*-butyldimethylsilyl)-1*H*-indol-5-yl)carbamate**

Prepared according to the general procedure, 67% yield, as a pale yellow solid; mp: 92-93 °C.

$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67 (s, 1H), 7.41 (d,  $J = 9.0$  Hz, 1H), 7.16 (d,  $J = 3.0$  Hz, 1H), 7.08 (d,  $J = 8.5$  Hz, 1H), 6.55 (d,  $J = 3.0$  Hz, 1H), 6.49 (s, 1H), 1.54 (s, 9H), 0.92 (s, 9H), 0.59 (s, 6H).

$^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ )  $\delta$  153.4, 137.7, 131.7, 131.7, 130.8, 114.7, 113.8, 111.0, 104.8, 28.4, 26.9, 26.2, 19.4, -4.1.

**HRMS** (ESI)  $m/z$  calcd. for  $\text{C}_{19}\text{H}_{31}\text{N}_2\text{O}_2\text{Si}^+$   $[\text{M} + \text{H}]^+$  347.2149, found 347.2086.



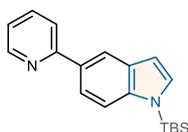
**(S29) 1-(*tert*-Butyldimethylsilyl)-5-phenyl-1*H*-indole**

Prepared according to the general procedure, 89% yield, as a colorless oil.

$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (s, 1H), 7.68 (d,  $J = 7.8$  Hz, 2H), 7.60 (d,  $J = 8.4$  Hz, 1H), 7.45 (dd,  $J = 15.0, 7.8$  Hz, 3H), 7.33 (t,  $J = 7.2$  Hz, 1H), 7.24 (d,  $J = 3.0$  Hz, 1H), 6.69 (d,  $J = 3.0$  Hz, 1H), 0.99 (s, 9H), 0.65 (s, 6H).

$^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ )  $\delta$  142.4, 140.5, 133.2, 131.9, 131.7, 128.6, 127.3, 126.2, 121.2, 119.1, 114.0, 105.1, 26.3, 19.5, -4.0.

The spectrum was consistent with the previous literature.<sup>[8]</sup>



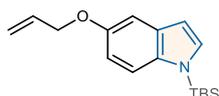
**(S30) 1-(*tert*-Butyldimethylsilyl)-5-(pyridin-2-yl)-1*H*-indole**

Prepared according to the general procedure, 82% yield, as a pale yellow solid; mp: 128-129 °C.

$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.70 (d,  $J = 4.2$  Hz, 1H), 8.29 (s, 1H), 7.87 (d,  $J = 8.4$  Hz, 1H), 7.79 (d,  $J = 7.8$  Hz, 1H), 7.71 (t,  $J = 7.8$  Hz, 1H), 7.61 (d,  $J = 9.0$  Hz, 1H), 7.23 (d,  $J = 3.0$  Hz, 1H), 7.18-7.14 (m, 1H), 6.71 (d,  $J = 2.4$  Hz, 1H), 0.96 (s, 9H), 0.64 (s, 6H).

$^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ )  $\delta$  158.6, 149.4, 141.6, 136.5, 131.8, 131.7, 131.4, 121.0, 120.7, 120.2, 119.3, 114.0, 105.5, 26., 19.45, -4.1.

The spectrum was consistent with the previous literature.<sup>[5]</sup>



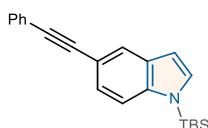
**(S31) 5-(Allyloxy)-1-(*tert*-butyldimethylsilyl)-1*H*-indole**

Prepared according to the general procedure, 90% yield, as a colorless oil.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.38 (d, *J* = 9.0 Hz, 1H), 7.13 (d, *J* = 3.0 Hz, 1H), 7.09 (d, *J* = 1.8 Hz, 1H), 6.83 (dd, *J* = 9.0, 2.4 Hz, 1H), 6.52 (d, *J* = 3.0 Hz, 1H), 6.13-6.04 (m, 1H), 5.42 (d, *J* = 17.4 Hz, 1H), 5.25 (d, *J* = 10.8 Hz, 1H), 4.55 (d, *J* = 5.4 Hz, 2H), 0.90 (s, 9H), 0.56 (s, 6H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 153.0, 136.1, 134.1, 131.8, 131.7, 117.1, 114.3, 112.0, 104.6, 103.7, 69.5, 26.3, 19.4, -4.1.

The spectrum was consistent with the previous literature.<sup>[5]</sup>



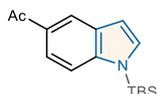
**(S32) 1-(*tert*-Butyldimethylsilyl)-5-(phenylethynyl)-1*H*-indole**

Prepared according to the general procedure, 89% yield, as a white solid; mp: 98-99 °C.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.91 (s, 1H), 7.61 (d, *J* = 6.6 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.38 (t, *J* = 7.2 Hz, 3H), 7.35 (d, *J* = 7.2 Hz, 1H), 7.24 (d, *J* = 3.0 Hz, 1H), 6.66 (s, 1H), 0.97 (s, 9H), 0.65 (s, 6H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 140.8, 131.9, 131.44, 131.3, 128.2, 127.6, 125.0, 124.4, 124.0, 114.3, 113.8, 104.9, 91.0, 87.1, 26.2, 19.4, -4.0.

HRMS (ESI) *m/z* calcd. for C<sub>22</sub>H<sub>26</sub>NSi<sup>+</sup> [M + H]<sup>+</sup> 332.1829, found 332.1768.



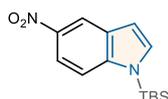
**(S33) 1-(1-(*tert*-Butyldimethylsilyl)-1*H*-indol-5-yl)ethan-1-one**

Prepared according to the general procedure, 92% yield, as a colorless oil.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.29 (s, 1H), 7.83 (d, *J* = 9.0 Hz, 1H), 7.53 (d, *J* = 9.0 Hz, 1H), 7.24 (d, *J* = 3.0 Hz, 1H), 6.72 (d, *J* = 3.0 Hz, 1H), 2.66 (s, 3H), 0.93 (s, 9H), 0.62 (s, 6H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 198.2, 143.8, 132.5, 130.9, 129.8, 122.6, 121.6, 113.5, 106.2, 26.5, 26.2, 19.4, -4.0.

HRMS (ESI) *m/z* calcd. for C<sub>16</sub>H<sub>24</sub>NOSi<sup>+</sup> [M + H]<sup>+</sup> 274.1622, found 274.1561.



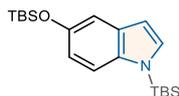
**(S34) 1-(*tert*-Butyldimethylsilyl)-5-nitro-1*H*-indole**

Prepared according to the general procedure, 84% yield, as a yellow oil.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.55 (s, 1H), 8.05 (dd, *J* = 9.0, 1.8 Hz, 1H), 7.51 (d, *J* = 9.0 Hz, 1H), 7.32 (d, *J* = 3.0 Hz, 1H), 6.76 (d, *J* = 3.0 Hz, 1H), 0.92 (s, 9H), 0.64 (s, 6H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 144.2, 141.6, 134.1, 130.8, 117.4, 116.8, 113.4, 106.8, 26.0, 19.3, -4.1.

The spectrum was consistent with the previous literature.<sup>[9]</sup>



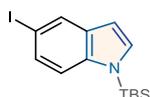
**(S35) 1-(*tert*-Butyldimethylsilyl)-5-((*tert*-butyldimethylsilyloxy)-1*H*-indole**

Prepared according to the general procedure, 95% yield, as a white solid; mp: 53-54 °C.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.37 (d, *J* = 9.0 Hz, 1H), 7.17 (d, *J* = 2.4 Hz, 1H), 7.09 (s, 1H), 6.75 (d, *J* = 9.0 Hz, 1H), 6.54 (d, *J* = 1.8 Hz, 1H), 1.06 (s, 9H), 0.96 (s, 9H), 0.62 (s, 6H), 0.25 (s, 6H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 149.3, 136.5, 132.1, 131.6, 115.4, 114.0, 109.9, 104.4, 26.3, 25.8, 19.5, 18.2, -4.0, -4.4.

HRMS (ESI) *m/z* calcd. for C<sub>20</sub>H<sub>36</sub>NOSi<sub>2</sub><sup>+</sup> [M + H]<sup>+</sup> 362.2330, found 362.2262.



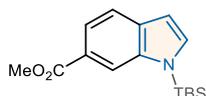
**(S36) 1-(*tert*-Butyldimethylsilyl)-5-iodo-1*H*-indole**

Prepared according to the general procedure, 96% yield, as a white solid; mp: 98-99 °C.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.98 (d, *J* = 7.2 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 3.0 Hz, 1H), 6.56 (d, *J* = 3.0 Hz, 1H), 0.94 (s, 9H), 0.61 (s, 6H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 140.1, 134.0, 131.8, 129.6, 129.4, 115.7, 104.0, 83.5, 26.2, 19.4, -4.1.

The spectrum was consistent with the previous literature.<sup>[5]</sup>



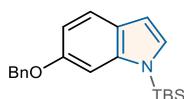
**(S37) Methyl 1-(*tert*-butyldimethylsilyl)-1*H*-indole-6-carboxylate**

P Prepared according to the general procedure, 95% yield, as a colorless oil.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.34 (s, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.35 (d, *J* = 3.0 Hz, 1H), 6.67 (d, *J* = 3.0 Hz, 1H), 3.96 (s, 3H), 0.96 (s, 9H), 0.67 (s, 6H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 168.1, 140.2, 135.1, 134.3, 123.0, 120.8, 120.0, 116.0, 105.0, 51.7, 26.1, 19.2, -4.1.

The spectrum was consistent with the previous literature<sup>[7]</sup>



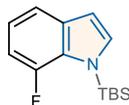
**(S38) 6-(Benzyloxy)-1-(*tert*-butyldimethylsilyl)-1*H*-indole**

Prepared according to the general procedure, 94% yield, as a colorless oil.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.54 (d, *J* = 8.4 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 2H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.10 (d, *J* = 3.0 Hz, 1H), 7.08 (s, 1H), 6.94 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.58 (d, *J* = 3.0 Hz, 1H), 5.17 (s, 2H), 0.93 (s, 9H), 0.57 (s, 6H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 154.8, 141.6, 137.7, 129.9, 128.5, 127.7, 127.2, 125.8, 120.8, 110.3, 104.5, 99.8, 70.8, 26.3, 19.5, -4.1.

The spectrum was consistent with the previous literature.<sup>[5]</sup>



**(S39) 1-(*tert*-Butyldimethylsilyl)-7-fluoro-1*H*-indole**

Prepared according to the general procedure, 86% yield, as a colorless oil.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.47-7.41 (m, 1H), 7.29 (d, *J* = 3.0 Hz, 1H), 7.11-7.04 (m, 1H), 6.96-6.89 (m, 1H), 6.68 (d, *J* = 3.0 Hz, 1H), 0.98 (s, 9H), 0.63 (s, 6H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 150.3 (d, *J* = 243.0 Hz), 135.6 (d, *J* = 6.0 Hz), 132.6, 128.4 (d, *J* = 12.0 Hz), 120.4 (d, *J* = 7.5 Hz), 116.3, 107.3 (d, *J* = 19.5 Hz), 105.2, 26.3, 19.4, -3.1 (d, *J* = 9.0 Hz).

<sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -121.52 (d, *J* = 9.6 Hz).

HRMS (ESI) *m/z* calcd. for C<sub>14</sub>H<sub>21</sub>FNSi<sup>+</sup> [M + H]<sup>+</sup> 250.1422, found 250.1375.



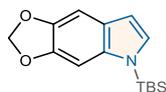
**(S40) 1-(*tert*-Butyldimethylsilyl)-1*H*-pyrrolo[2,3-*b*]pyridine**

Prepared according to the general procedure, 93% yield, as a colorless oil.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.32 (d, *J* = 4.8 Hz, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 3.6 Hz, 1H), 7.06 (dd, *J* = 7.6, 4.8 Hz, 1H), 6.57 (d, *J* = 3.6 Hz, 1H), 0.99 (s, 9H), 0.69 (s, 6H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 154.1, 142.4, 130.7, 127.8, 122.4, 115.9, 102.8, 26.5, 19.0, -4.3.

The spectrum was consistent with the previous literature.<sup>[5]</sup>



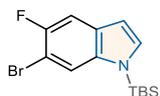
**(S41) 5-(*tert*-Butyldimethylsilyl)-5*H*-[1,3]dioxolo[4,5-*f*]indole**

Prepared according to the general procedure, 92% yield, as a white solid; mp: 75-76 °C.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.08 (d, *J* = 2.7 Hz, 1H), 7.03 (s, 2H), 6.52 (s, 1H), 5.95 (s, 2H), 0.96 (s, 9H), 0.60 (s, 6H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 144.4, 142.7, 135.7, 129.7, 125.1, 104.9, 100.5, 99.0, 94.8, 26.3, 19.4, -4.0.

HRMS (ESI) *m/z* calcd. for C<sub>15</sub>H<sub>22</sub>NO<sub>2</sub>Si<sup>+</sup> [M + H]<sup>+</sup> 276.1414, found 276.1368.



**(S42) 6-Bromo-1-(*tert*-Butyldimethylsilyl)-5-fluoro-1*H*-indole**

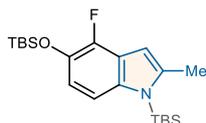
Prepared according to the general procedure, 95% yield, as a colorless oil.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.66 (s, 1H), 7.35 (d, *J* = 9.0 Hz, 1H), 7.22 (s, 1H), 6.57 (s, 1H), 0.94 (s, 9H), 0.62 (s, 6H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 153.7 (d, *J* = 235.5 Hz), 137.9, 133.2, 131.1 (d, *J* = 9.0 Hz), 117.5, 106.1 (d, *J* = 24.0 Hz), 104.9 (d, *J* = 4.5 Hz), 102.4 (d, *J* = 25.5 Hz), 26.2, 19.3, -4.1.

<sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>) δ (-119.22)-(-119.33) (m).

HRMS (ESI) *m/z* calcd. for C<sub>14</sub>H<sub>18</sub>BrFNSi<sup>-</sup> [M - H]<sup>-</sup> 326.0381, found 326.0322.



**(S43) 1-(*tert*-Butyldimethylsilyl)-5-((*tert*-butyldimethylsilyl)oxy)-4-fluoro-2-methyl-1*H*-indole**

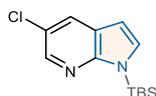
Prepared according to the general procedure, 71% yield, as a colorless oil.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.06 (d, *J* = 9.0 Hz, 1H), 6.63 (t, *J* = 9.0 Hz, 1H), 6.35 (s, 1H), 2.46 (s, 3H), 1.02 (s, 9H), 0.94 (s, 9H), 0.64 (s, 6H), 0.19 (s, 6H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 145.3 (d, *J* = 240.0 Hz), 142.6, 139.6 (d, *J* = 8.8 Hz), 134.9 (d, *J* = 10.0 Hz), 121.3 (d, *J* = 18.8 Hz), 115.4, 109.4 (d, *J* = 3.8 Hz), 101.6, 26.7, 25.7, 20.6, 18.3, 17.5, -0.6, -4.7.

<sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -142.79 (d, *J* = 7.99 Hz).

HRMS (ESI) *m/z* calcd. for C<sub>21</sub>H<sub>37</sub>FNOSi<sub>2</sub><sup>+</sup> [M + H]<sup>+</sup> 394.2392, found 394.2318



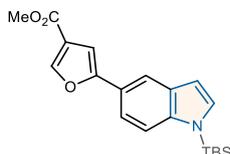
**(S44) 1-(*tert*-Butyldimethylsilyl)-5-chloro-1*H*-pyrrolo[2,3-*b*]pyridine**

Prepared according to the general procedure, 88% yield, as a white solid; mp: 105-106 °C.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.24 (s, 1H), 7.84 (s, 1H), 7.29 (d, *J* = 3.0 Hz, 1H), 6.49 (d, *J* = 3.0 Hz, 1H), 0.95 (s, 9H), 0.65 (s, 6H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 152.1, 141.0, 132.5, 127.0, 123.9, 123.3, 102.5, 26.4, 19.0, -4.4.

HRMS (ESI) *m/z* calcd. for C<sub>13</sub>H<sub>20</sub>ClN<sub>2</sub>Si<sup>+</sup> [M + H]<sup>+</sup> 267.1079, found 267.1025.



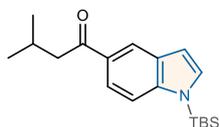
**(S45) Methyl 5-(1-(*tert*-Butyldimethylsilyl)-1*H*-indol-5-yl)furan-3-carboxylate**

Prepared according to the general procedure, 89% yield, as a colorless oil.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.01 (s, 1H), 7.95 (s, 1H), 7.52 (d, *J* = 9.0 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.20 (d, *J* = 3.0 Hz, 1H), 6.89 (s, 1H), 6.64 (d, *J* = 3.0 Hz, 1H), 3.87 (s, 3H), 0.93 (s, 9H), 0.62 (s, 6H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 163.9, 156.8, 146.1, 140.9, 132.0, 131.6, 122.1, 120.8, 118.2, 116.5, 114.1, 105.3, 102.6, 51.6, 26.3, 19.5, -4.0.

HRMS (ESI) *m/z* calcd. for C<sub>20</sub>H<sub>26</sub>NO<sub>3</sub>Si<sup>+</sup> [M + H]<sup>+</sup> 356.1676, found 356.1609.



**(S46) 1-(1-(*tert*-Butyldimethylsilyl)-1*H*-indol-5-yl)-3-methylbutan-1-one**

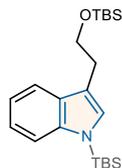
Prepared according to the general procedure, 93% yield, as a colorless oil.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.28 (s, 1H), 7.82 (d, *J* = 9.0 Hz, 1H), 7.52 (d, *J* = 9.0 Hz, 1H), 7.24 (d, *J* = 3.0 Hz, 1H), 6.71 (d, *J* = 3.0 Hz, 1H), 2.89 (d, *J* = 7.2 Hz, 2H), 2.34 (dp, *J* = 13.8, 6.6 Hz, 1H), 1.01 (d, *J* = 6.6 Hz, 6H), 0.93 (s, 9H), 0.62 (s, 6H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 200.4, 143.7, 132.4, 130.9, 130.0, 122.3, 121.7, 113.6, 106.2, 47.5, 26.20,

25.61, 22.86, 19.44, -3.99.

**HRMS** (ESI)  $m/z$  calcd. for  $C_{19}H_{30}NOSi^+$   $[M + H]^+$  316.2091, found 316.2032.



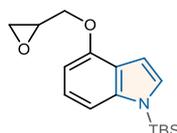
**(S47) 1-(*tert*-Butyldimethylsilyl)-3-(2-((*tert*-butyldimethylsilyloxy)ethyl)-1*H*-indole**

Prepared according to the general procedure, 71% yield, as a white solid; mp: 52-53 °C.

**$^1H$  NMR** (600 MHz,  $CDCl_3$ )  $\delta$  7.62 (d,  $J = 7.2$  Hz, 1H), 7.52 (d,  $J = 7.8$  Hz, 1H), 7.20-7.12 (m, 2H), 7.06 (s, 1H), 3.93 (t,  $J = 7.2$  Hz, 2H), 3.02 (t,  $J = 7.2$  Hz, 2H), 0.97 (s, 9H), 0.95 (s, 9H), 0.62 (s, 6H), 0.08 (s, 6H).

**$^{13}C$  NMR** (150 MHz,  $CDCl_3$ )  $\delta$  141.3, 131.2, 128.8, 121.2, 119.2, 118.8, 115.1, 113.9, 63.7, 29.0, 26.4, 26.0, 19.5, 18.6, -3.9, -5.3.

The spectrum was consistent with the previous literature.<sup>[5]</sup>



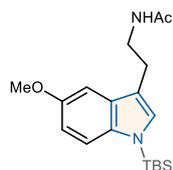
**(S48) 1-(*tert*-Butyldimethylsilyl)-4-(oxiran-2-ylmethoxy)-1*H*-indole**

Prepared according to the general procedure, 90% yield, as a white solid; mp: 70-71 °C.

**$^1H$  NMR** (600 MHz,  $CDCl_3$ )  $\delta$  7.21 (d,  $J = 8.4$  Hz, 1H), 7.14 (d,  $J = 3.0$  Hz, 1H), 7.10 (t,  $J = 7.8$  Hz, 1H), 6.82 (d,  $J = 3.0$  Hz, 1H), 6.57 (d,  $J = 7.8$  Hz, 1H), 4.37 (dd,  $J = 11.0, 3.0$  Hz, 1H), 4.17 (dd,  $J = 11.0, 5.4$  Hz, 1H), 3.47 (s, 1H), 2.95 (t,  $J = 4.2$  Hz, 1H), 2.83 (d,  $J = 4.2$  Hz, 1H), 0.96 (d,  $J = 6.0$  Hz, 9H), 0.64 (s, 6H).

**$^{13}C$  NMR** (150 MHz,  $CDCl_3$ )  $\delta$  152.0, 142.5, 129.5, 122.1, 121.8, 107.8, 101.9, 100.9, 68.7, 50.3, 44.8, 26.2, 19.4, -4.0.

**HRMS** (ESI)  $m/z$  calcd. for  $C_{17}H_{26}NO_2Si^+$   $[M + H]^+$  304.1727, found 304.1671.



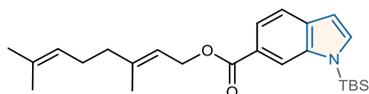
**(S49) *N*-(2-(1-(*tert*-Butyldimethylsilyl)-5-methoxy-1*H*-indol-3-yl)ethyl)acetamide**

Prepared according to the general procedure, 65% yield, as a colorless oil.

**$^1H$  NMR** (600 MHz,  $CDCl_3$ )  $\delta$  7.37 (d,  $J = 9.0$  Hz, 1H), 7.01 (d,  $J = 1.8$  Hz, 1H), 6.97 (s, 1H), 6.82 (dd,  $J = 9.0, 1.8$  Hz, 1H), 5.60 (s, 1H), 3.85 (s, 3H), 3.58 (q,  $J = 6.6$  Hz, 2H), 2.92 (t,  $J = 6.6$  Hz, 2H), 1.92 (s, 3H), 0.91 (s, 1H), 0.57 (s, 1H).

**$^{13}C$  NMR** (150 MHz,  $CDCl_3$ )  $\delta$  170.0, 154.0, 136.5, 131.2, 129.5, 114.6, 114.5, 111.5, 100.5, 55.8, 39.51, 26.2, 25.2, 23.3, 19.4, -4.0.

The spectrum was consistent with the previous literature.<sup>[5]</sup>



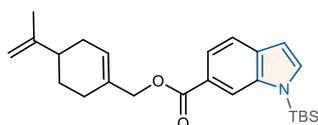
**(S50)**

Prepared according to the general procedure, 87% yield, as a colorless oil.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 8.31 (s, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.33 (d, *J* = 3.0 Hz, 1H), 6.65 (d, *J* = 3.0 Hz, 1H), 5.52 (t, *J* = 7.2 Hz, 1H), 5.12 (t, *J* = 6.6 Hz, 1H), 4.87 (d, *J* = 7.2 Hz, 2H), 2.15 (dd, *J* = 14.4, 7.2 Hz, 2H), 2.12-2.07 (m, 2H), 1.79 (s, 3H), 1.69 (s, 3H), 1.62 (s, 3H), 0.94 (s, 9H), 0.65 (s, 6H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 167.8, 141.9, 140.3, 135.0, 134.3, 131.7, 123.8, 123.5, 120.9, 120.0, 118.9, 116.1, 105.1, 61.5, 39.6, 26.4, 26.2, 25.7, 19.3, 17.7, 16.6, -4.0.

**HRMS** (ESI) *m/z* calcd. for C<sub>25</sub>H<sub>38</sub>NO<sub>2</sub>Si<sup>+</sup> [M + H]<sup>+</sup> 412.2666, found 412.2590.



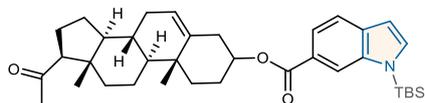
**(S51)**

Prepared according to the general procedure, 90% yield, as a colorless oil.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 8.31 (s, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.34 (d, *J* = 3.0 Hz, 1H), 6.65 (d, *J* = 3.0 Hz, 1H), 5.86 (s, 1H), 4.76-4.69 (m, 4H), 2.25-2.14 (m, 4H), 2.06-1.97 (m, 1H), 1.91-1.85 (m, 1H), 1.76 (s, 3H), 1.28-1.22 (m, 1H), 0.94 (s, 9H), 0.64 (s, 6H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 167.6, 149.7, 140.3, 135.1, 134.4, 133.0, 124.9, 123.3, 120.9, 120.1, 116.2, 108.8, 105.1, 68.4, 41.0, 30.5, 27.4, 26.4, 26.3, 20.8, 19.3, -4.0.

**HRMS** (ESI) *m/z* calcd. for C<sub>25</sub>H<sub>36</sub>NO<sub>2</sub>Si<sup>+</sup> [M + H]<sup>+</sup> 410.2510, found 410.2430.



**(S52)**

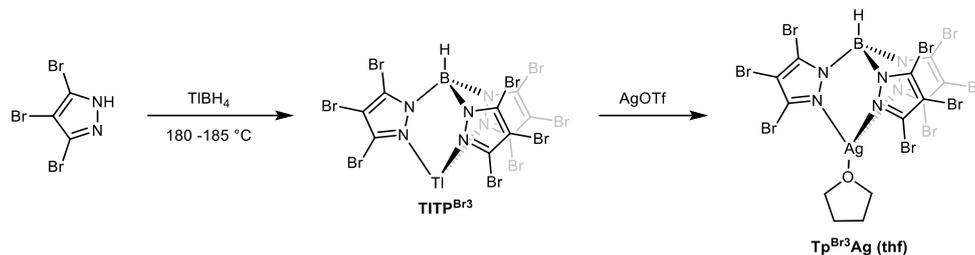
Prepared according to the general procedure, 81% yield, as a white solid; mp: 170-171 °C.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 8.29 (s, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.33 (d, *J* = 3.0 Hz, 1H), 6.64 (s, 1H), 5.43 (s, 1H), 4.90-4.80 (m, 1H), 2.59-2.41 (m, 3H), 2.23-2.15 (m, 1H), 2.13 (s, 3H), 2.09-1.99 (m, 3H), 1.97-1.85 (m, 2H), 1.85-1.63 (m, 6H), 1.56-1.43 (m, 3H), 1.09 (s, 3H), 0.93 (s, 9H), 0.90-0.81 (m, 2H), 0.65 (s, 3H), 0.64 (s, 6H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 212.6, 209.6, 167.2, 140.3, 135.0, 134.3, 123.7, 122.3, 120.8, 120.0, 116.1, 105.1, 74.1, 63.7, 56.9, 49.9, 44.0, 38.8, 38.3, 37.1, 36.7, 31.9, 31.8, 31.5, 28.0, 26.3, 24.5, 22.9, 21.1, 19.4, 19.3, 13.2, -4.0.

**HRMS** (ESI) *m/z* calcd. for C<sub>36</sub>H<sub>52</sub>NO<sub>3</sub>Si<sup>+</sup> [M + H]<sup>+</sup> 574.3711, found 574.3650.

### 3.3 The Preparation of Ligands and Catalysts



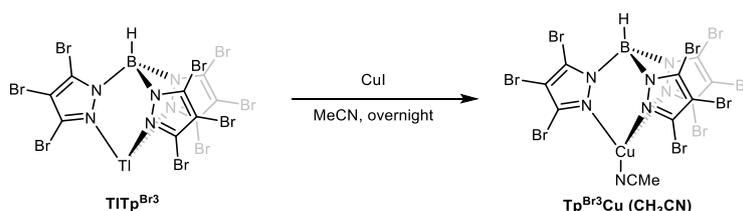
**Procedure:** Previously sublimed 1H-3,4,5-tribromopyrazole (12.19 g, 40.0 mmol) and thallium(I) borohydride (2.19 g, 10.0 mmol) were added to a 500 mL Schlenk tube. The tube was closed with a rubber septum and three vacuum/nitrogen cycles were made. The septum was replaced with a reflux condenser fitted with a bubbler on top. The nitrogen flow was stopped and the stirred solid mixture was slowly warmed to 180-185 °C for 2 h before the temperature was increased to 200 °C and the reaction mixture stirred for an additional 2 h. After cooling to room temperature, the obtained white solid was directly purified by sublimation to remove the unreacted pyrazole (150 °C, 2 mbar).  $\text{TITp}^{\text{Br}3}$  was obtained as a white solid in 89% yield (13.4 g).

Silver triflate (1.29 g, 5.0 mmol) was added to a solution of  $\text{TITp}^{\text{Br}3}$  (5.64 g, 5.0 mmol) in acetone. After 20 h of stirring in the dark, a white solid precipitated from the initially colorless solution. The solid was filtered off and dried under vacuum to give complex  $[\text{Tp}^{\text{Br}3}\text{Ag}]_2 \cdot \text{CH}_3\text{COCH}_3$ .  $[\text{Tp}^{\text{Br}3}\text{Ag}]_2 \cdot \text{CH}_3\text{COCH}_3$  (5.0 mmol) was stirred in fresh distilled THF (100 mL) for 30 min in the dark. After the removal of the volatiles under reduced pressure, a white solid was obtained in quantitative yield.

Data for  $\text{TITp}^{\text{Br}3}$ :  $^1\text{H NMR}$  (600 MHz,  $\text{DMSO}-d_6$ )  $\delta$  4.79 (s, br, 1H);  $^{13}\text{C NMR}$  (150 MHz,  $\text{DMSO}-d_6$ )  $\delta$  127.5, 120.5, 97.9;  $^{11}\text{B NMR}$  (193 MHz,  $\text{CDCl}_3$ )  $\delta$  2.22 (s, br).

Data for  $\text{Tp}^{\text{Br}3}\text{Ag}(\text{thf})$ :  $^1\text{H NMR}$  (600 MHz,  $\text{DMSO}-d_6$ )  $\delta$  5.18 (s, br, 1H), 3.60-3.57 (m, 4H), 1.77-1.72 (m, 4H);  $^{13}\text{C NMR}$  (150 MHz,  $\text{DMSO}-d_6$ )  $\delta$  134.1, 126.4, 103.6, 71.5, 29.6;  $^{11}\text{B NMR}$  (193 MHz,  $\text{DMSO}-d_6$ )  $\delta$  -4.70 (s, br).

Spectroscopic data in agreement with those reported in literature.<sup>[10]</sup>

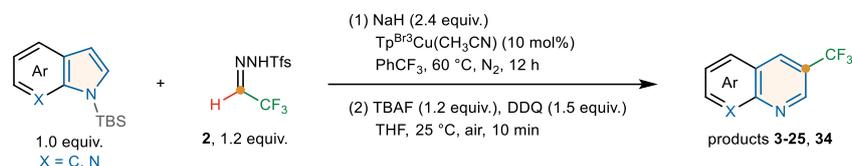


**Procedure:**  $\text{CuI}$  (952.3 mg, 5.0 mmol) and 1.127 g of  $\text{TITp}^{\text{Br}3}$  (5.64 g, 5.0 mmol) were solved in acetonitrile (200 mL). The reaction mixture was stirred overnight at room temperature. Solvent was removed in vacuo,  $\text{CH}_2\text{Cl}_2$  (100 mL) was added and the resulting solution was filtered. After addition of petroleum (~10 mL), white crystals (3.90 g, 76% yield) were grown from the concentrated solutions at -20 °C. Data for  $\text{Tp}^{\text{Br}3}\text{Cu}(\text{CH}_3\text{CN})$ :  $^1\text{H NMR}$  (600 MHz,  $\text{DMSO}-d_6$ )  $\delta$  5.3 (s, br, 1H), 2.17 (s, 3H);  $^{13}\text{C NMR}$  (150 MHz,  $\text{DMSO}-d_6$ )  $\delta$  134.81, 127.80, 122.45, 104.62, 5.65;  $^{11}\text{B NMR}$  (193 MHz,  $\text{DMSO}-d_6$ )  $\delta$  -6.61 (s, br).

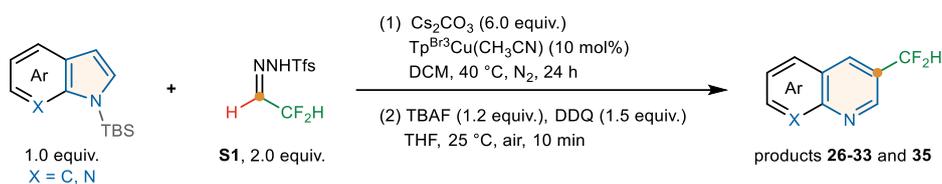
Spectroscopic data in agreement with those reported in literature.<sup>[10]</sup>

## 4. Experimental Procedures

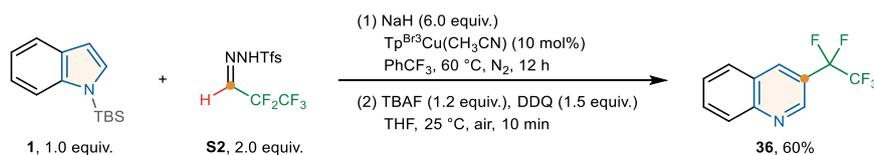
### 4.1 General Procedures for One-Carbon Insertion of Indoles with Fluoroalkyl *N*-Triftosylhydrazones



**General Procedure A:** In a glove box, an oven-dried screw-cap reaction tube was charged with fluoroalkyl *N*-triftosylhydrazone **2** (0.36 mmol, 1.2 equiv.), NaH (0.72 mmol, 2.4 equiv., 60 wt% dispersion in mineral oil), *N*-TBS indole (0.3 mmol, 1.0 equiv.), Tp<sup>Br3</sup>Cu(CH<sub>3</sub>CN) (30.0 mg, 10 mol%) and PhCF<sub>3</sub> (10 mL). Next, the sealed vial was removed from glovebox and stirred at 60 °C for 12 h. After cooling to room temperature, the reaction mixture was filtered through a short pad of silica gel with DCM as an eluent. After removal of the solvent *in vacuo*, the residue was added TBAF (0.36 mL, 0.36 mmol, 1.0 mol/L in THF, 1.2 equiv.) and DDQ (0.45 mmol, 1.5 equiv.) and THF (10 mL). The resulting mixture was stirred at 25 °C for 10 min and filtered through a short pad of silica gel (pre-treated with triethylamine) with DCM as an eluent. After removal of the solvent *in vacuo*, the residue was purified by flash column chromatography on silica gel (pre-treated with trimethylamine, using petroleum ether-EtOAc (50/1) as eluent) to afford the products **3–25** and **34**.



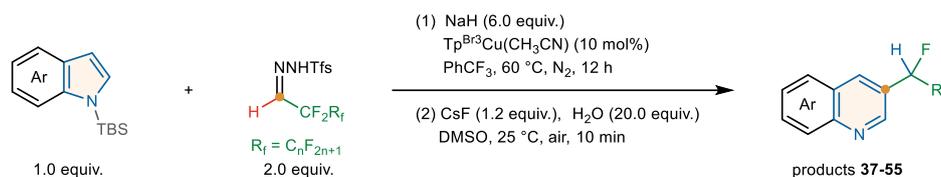
**General Procedure B:** In a glove box, an oven-dried screw-cap reaction tube was charged with *N*-triftosylhydrazones **S1** (0.6 mmol, 2.0 equiv.), Cs<sub>2</sub>CO<sub>3</sub> (1.8 mmol, 6.0 equiv.), *N*-TBS indole (0.3 mmol, 1.0 equiv.), Tp<sup>Br3</sup>Cu(CH<sub>3</sub>CN) (30.0 mg, 10 mol%) and DCM (10 mL). Next, the sealed vial was removed from glovebox and stirred at 60 °C for 24 h. After cooling to room temperature, the reaction mixture was filtered through a short pad of silica gel with DCM as an eluent. After removal of the solvent *in vacuo*, the residue was added TBAF (0.36 mL, 0.36 mmol, 1.0 mol/L in THF, 1.2 equiv.), DDQ (0.45 mmol, 1.5 equiv.) and THF (10 mL). The resulting mixture was stirred at 25 °C for 10 min and filtered through a short pad of silica gel (pre-treated with triethylamine) with DCM as an eluent. After removal of the solvent *in vacuo*, the residue was purified by flash column chromatography on silica gel (pre-treated with trimethylamine, using petroleum ether-EtOAc (50/1) as eluent) to give the products **26–33** and **35**.



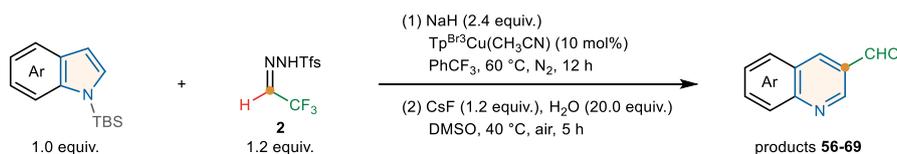
**General Procedure C:** In a glove box, an oven-dried screw-cap reaction tube was charged with *N*-triftosylhydrazone **S2** (0.6 mmol, 2.0 equiv.), NaH (1.8 mmol, 6.0 equiv., 60 wt% dispersion in mineral oil), *N*-TBS indole (0.3 mmol, 1.0 equiv.), Tp<sup>Br3</sup>Cu(CH<sub>3</sub>CN) (30.0 mg, 10 mol%) and PhCF<sub>3</sub> (10 mL).

Next, the sealed vial was removed from glovebox and stirred at 60 °C for 12 h. After cooling to room temperature, the reaction mixture was filtered through a short pad of silica gel with DCM as an eluent. After removal of the solvent *in vacuo*, the residue was added TBAF (0.36 mL, 0.36 mmol, 1.0 mol/L in THF, 1.2 equiv.), DDQ (0.45 mmol, 1.5 equiv.) and THF (10 mL). The resulting mixture was stirred at 25 °C for 10 min and filtered through a short pad of silica gel (pre-treated with triethylamine) with DCM as an eluent. After removal of the solvent *in vacuo*, the residue was purified by flash column chromatography on silica gel (pre-treated with trimethylamine, using petroleum ether-EtOAc (50/1) as eluent) to give the product **36** (44.5 mg, 60% yield).

#### 4.2 General Procedures for Defluorinative One-Carbon Insertion of Indoles with Fluoroalkyl *N*-triflylhydrazones

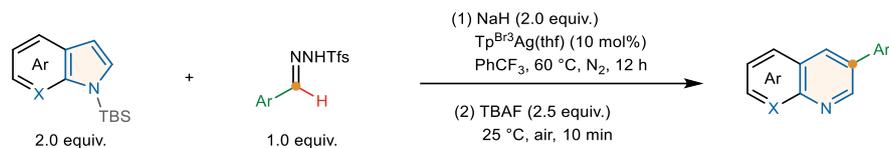


**General Procedure D:** In a glove box, an oven-dried screw-cap reaction tube was charged with *N*-triflylhydrazone (0.6 mmol, 2.0 equiv.), NaH (1.8 mmol, 6.0 equiv., 60 wt% dispersion in mineral oil), *N*-TBS indole (0.3 mmol, 1.0 equiv.),  $Tp^{Br^3}Cu(CH_3CN)$  (30.0 mg, 10.0 mol%) and  $PhCF_3$  (10 mL). Next, the sealed vial was removed from glovebox and stirred at 60 °C for 12 h. After cooling to room temperature, the reaction mixture was filtered through a short pad of silica gel with DCM as an eluent. After removal of the solvent *in vacuo*, the residue was added CsF (0.36 mmol, 1.2 equiv.),  $H_2O$  (20.0 equiv.) and DMSO (10 mL). The resulting mixture was stirred at 25 °C for 10 min and diluted with DCM, washed with brine, dried over anhydrous  $Na_2SO_4$ , filtered and the solvent was evaporated under reduced pressure to leave a crude product, which was purified by flash column chromatography on silica gel (pre-treated with trimethylamine, using petroleum ether-EtOAc (50/1) as eluent) to give the products **37–55**.

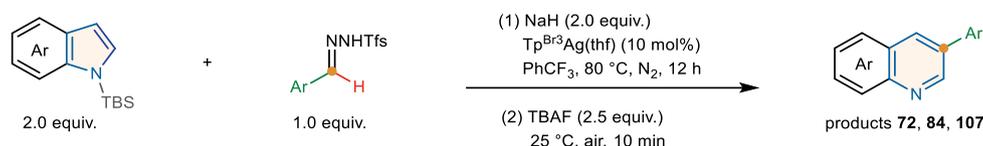


**General Procedure E:** In a glove box, an oven-dried screw-cap reaction tube was charged with *N*-triflylhydrazone **3** (0.36 mmol, 1.2 equiv.), NaH (0.72 mmol, 2.4 equiv., 60 wt% dispersion in mineral oil), *N*-TBS indoles (0.3 mmol, 1.0 equiv.),  $Tp^{Br^3}Cu(CH_3CN)$  (30.0 mg, 10 mol%) and  $PhCF_3$  (10 mL). Next, the sealed vial was removed from glovebox and stirred at 60 °C for 12 h. After cooling to room temperature, the reaction mixture was filtered through a short pad of silica gel with DCM as an eluent. After removal of the solvent *in vacuo*, the residue was added CsF (0.36 mmol, 1.2 equiv.),  $H_2O$  (20.0 equiv.) and DMSO (10 mL). The resulting mixture was stirred at 25 °C for 10 min and diluted with DCM, washed with brine, dried over anhydrous  $Na_2SO_4$ , filtered and the solvent was evaporated under reduced pressure to leave a crude product, which was purified by flash column chromatography on silica gel (pre-treated with trimethylamine, using petroleum ether-EtOAc (30/1) as eluent) to give the 3-formylquinoline products **56–69**.

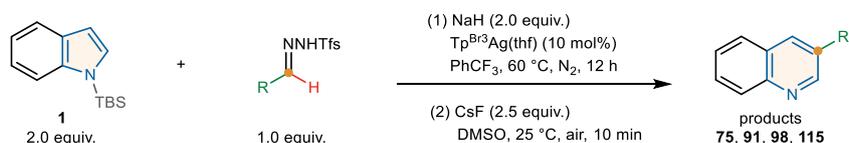
### 4.3 General Procedures for One-Carbon Insertion of Indoles with Functionalized *N*-triftosylhydrazones



**General Procedure F:** In a glove box, an oven-dried screw-cap reaction tube was charged with *N*-triftosylhydrazone (0.3 mmol, 1.0 equiv.), NaH (0.6 mmol, 2.0 equiv., 60 wt% dispersion in mineral oil), *N*-TBS indole (0.6 mmol, 2.0 equiv.),  $\text{Tp}^{\text{Br}_3}\text{Ag}(\text{thf})$  (36.0 mg, 10 mol%) and  $\text{PhCF}_3$  (5.0 mL). Next, the sealed vial was removed from glovebox and stirred at 60 °C for 12 h. After cooling to room temperature, the reaction mixture was added TBAF (0.75 mL, 0.75 mmol, 1.0 mol/L in THF, 2.5 equiv.) and stirred at 25 °C for 10 min. After completion of the reaction, the mixture was filtered through a short pad of silica gel (pre-treated with triethylamine) with DCM as an eluent. After removal of the solvent *in vacuo*, the residue was purified by flash chromatography on silica gel (pre-treated with trimethylamine, using petroleum ether-EtOAc (40/1) as eluent) to give the corresponding 3-arylquinoline products.

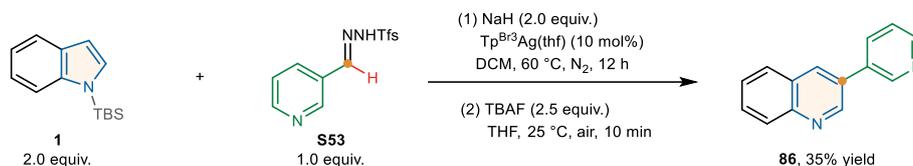


**General Procedure G:** In a glove box, an oven-dried screw-cap reaction tube was charged with *N*-triftosylhydrazone (0.3 mmol, 1.0 equiv.), NaH (0.6 mmol, 2.0 equiv., 60 wt% dispersion in mineral oil), *N*-TBS indole (0.6 mmol, 2.0 equiv.),  $\text{Tp}^{\text{Br}_3}\text{Ag}(\text{thf})$  (36.0 mg, 10 mol%) and  $\text{PhCF}_3$  (5.0 mL). Next, the sealed vial was removed from glovebox and stirred at 60 °C for 12 h. After cooling to room temperature, the reaction mixture was added TBAF (0.75 mL, 0.75 mmol, 1.0 mol/L in THF, 2.5 equiv.) and stirred at 25 °C for 10 min. After completion of the reaction, the mixture was filtered through a short pad of silica gel (pre-treated with triethylamine) with DCM as an eluent. After removal of the solvent *in vacuo*, the residue was purified by flash chromatography on silica gel (pre-treated with trimethylamine, using petroleum ether-EtOAc (40/1) as eluent) to give products **72**, **84** and **107**.

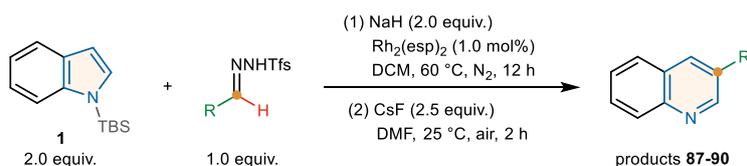


**General Procedure H:** In a glove box, an oven-dried screw-cap reaction tube was charged with *N*-triftosylhydrazones (0.3 mmol, 1.0 equiv.), NaH (0.6 mmol, 2.0 equiv., 60 wt% dispersion in mineral oil), *N*-TBS indole **1** (0.6 mmol, 2.0 equiv.),  $\text{Tp}^{\text{Br}_3}\text{Ag}(\text{thf})$  (36.0 mg, 10 mol%) and  $\text{PhCF}_3$  (5.0 mL). Next, the sealed vial was removed from glovebox and stirred at 60 °C for 12 h. After cooling to room temperature, the reaction mixture was filtered through a short pad of silica gel (pre-treated with triethylamine) with DCM as an eluent. After removal of the solvent *in vacuo*, the residue was added CsF (0.36 mmol, 2.5 equiv.) and DMSO (3.0 mL). The resulting mixture was stirred at 25 °C for 10 min and diluted with DCM, washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and the solvent was evaporated under reduced pressure to leave

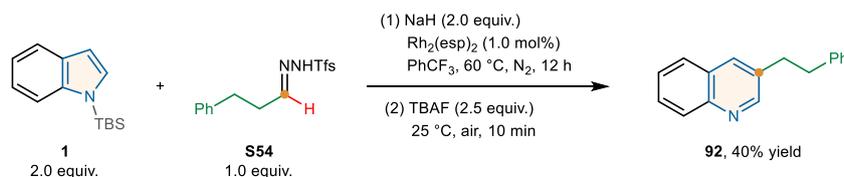
a crude product, which was purified by flash column chromatography on silica gel (pre-treated with trimethylamine, using petroleum ether-EtOAc (30/1) as eluent) to give the products **75**, **91**, **98** and **115**.



**General Procedure I:** In a glove box, an oven-dried screw-cap reaction tube was charged with *N*-triflylhydrazone **S56** (0.3 mmol, 1.0 equiv.), NaH (0.6 mmol, 2.0 equiv., 60 wt% dispersion in mineral oil), *N*-TBS indole **1** (0.6 mmol, 2.0 equiv.),  $\text{TpBr}^3\text{Ag}(\text{thf})$  (36.0 mg, 10 mol%) and DCM (5.0 mL). Next, the sealed vial was removed from glovebox and stirred at 60 °C for 12 h. After cooling to room temperature, the reaction mixture was filtered through a short pad of silica gel (pre-treated with triethylamine) with DCM as an eluent. After removal of the solvent *in vacuo*, the residue was added TBAF (0.75 mL, 0.75 mmol, 1.0 mol/L in THF, 2.5 equiv.) and THF (5.0 mL). The resulting mixture was stirred at 25 °C for 10 min and filtered through a short pad of silica gel (pre-treated with triethylamine) with DCM as an eluent. After removal of the solvent *in vacuo*, the residue was purified by flash chromatography on silica gel (pre-treated with trimethylamine, using petroleum ether-EtOAc (20/1) as eluent) to give product **86** (21.6 mg, 35% yield).



**General Procedure J:** In a glove box, an oven-dried screw-cap reaction tube was charged with *N*-triflylhydrazone (0.3 mmol, 1.0 equiv.), NaH (0.6 mmol, 2.0 equiv., 60 wt% dispersion in mineral oil), *N*-TBS indole **1** (0.6 mmol, 2.0 equiv.),  $\text{Rh}_2(\text{esp})_2$  (1.0 mol%) and DCM (5.0 mL). Next, the sealed vial was removed from glovebox and stirred at 60 °C for 12 h. After cooling to room temperature, the reaction mixture was filtered through a short pad of silica gel with DCM as an eluent. After removal of the solvent *in vacuo*, the residue was added CsF (0.36 mmol, 2.5 equiv.) and DMF (3.0 mL). The resulting mixture was stirred at 25 °C for 2 h and diluted with DCM, washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and the solvent was evaporated under reduced pressure to leave a crude product, which was purified by flash column chromatography on silica gel (pre-treated with trimethylamine, using petroleum ether-EtOAc (40/1) as eluent) to give the products **87-90**.



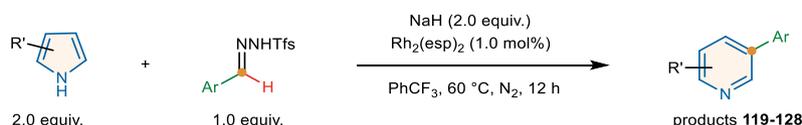
**General Procedure K:** In a glove box, an oven-dried screw-cap reaction tube was charged with *N*-triflylhydrazone **S57** (0.3 mmol, 1.0 equiv.), NaH (0.6 mmol, 2.0 equiv., 60 wt% dispersion in mineral oil), *N*-TBS indole **1** (0.6 mmol, 2.0 equiv.),  $\text{Rh}_2(\text{esp})_2$  (1.0 mol%) and  $\text{PhCF}_3$  (5.0 mL). Next, the sealed vial

was removed from glovebox and stirred at 60 °C for 12 h. After cooling to room temperature, the reaction mixture was added TBAF (0.75 mL, 0.75 mmol, 1.0 mol/L in THF, 2.5 equiv.) and stirred at 25 °C for 10 min. After completion of the reaction, the mixture was filtered through a short pad of silica gel (pre-treated with triethylamine) with DCM as an eluent. After removal of the solvent *in vacuo*, the residue was purified by flash chromatography on silica gel (pre-treated with trimethylamine, using petroleum ether-EtOAc (50/1) as eluent) to give the product **92** (28.0 mg, 40% yield).



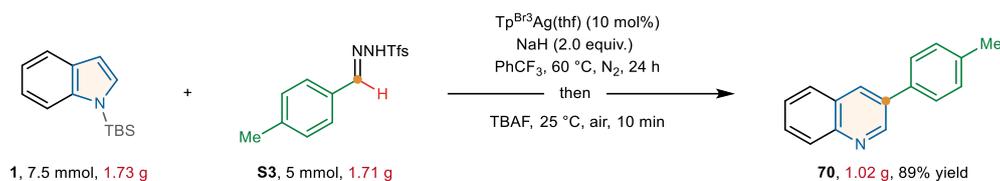
**Procedure L:** In a glove box, an oven-dried screw-cap reaction tube was charged with *N*-triflylhydrazone (0.3 mmol, 1.0 equiv.), NaH (0.6 mmol, 2.0 equiv., 60 wt% dispersion in mineral oil), *N*-TBS indole **S44** (0.6 mmol, 2.0 equiv.),  $\text{Tp}^{\text{Br}_3}\text{Ag}(\text{thf})$  (36.0 mg, 10 mol%) and  $\text{PhCF}_3$  (5.0 mL). Next, the sealed vial was removed from glovebox and stirred at 80 °C for 12 h. After cooling to room temperature, the reaction mixture was filtered through a short pad of silica gel with DCM as an eluent. After removal of the solvent *in vacuo*, the residue was added CsF (0.36 mmol, 2.5 equiv.) and DMSO (3.0 mL). The resulting mixture was stirred at 25 °C for 10 min. After completion of the reaction, the mixture was diluted with DCM, washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and the solvent was evaporated under reduced pressure to leave a crude product, which was purified by flash column chromatography on silica gel (pre-treated with trimethylamine, using petroleum ether-EtOAc (20/1) as eluent) to give the product **108** (74.5 mg, 93%).

#### 4.4 General Procedure for One-Carbon Insertion of Pyrroles with *N*-Triflylhydrazones



**General Procedure M:** In a glove box, an oven-dried screw-cap reaction tube was charged with *N*-triflylhydrazones (0.3 mmol, 1.0 equiv.), NaH (0.6 mmol, 2.0 equiv., 60 wt% dispersion in mineral oil), pyrroles (0.6 mmol, 2.0 equiv.),  $\text{Rh}_2(\text{esp})_2$  (1.0 mol%) and  $\text{PhCF}_3$  (5.0 mL). Next, the sealed vial was removed from glovebox and stirred at 60 °C for 12 h. After cooling to room temperature, the reaction mixture was filtered through a short pad of silica gel (pre-treated with triethylamine) with DCM as an eluent. After removal of the solvent *in vacuo*, the residue was purified by flash chromatography on silica gel (pre-treated with trimethylamine, using petroleum ether-EtOAc (40/1) as eluent) to give the pyridine products **119–128**.

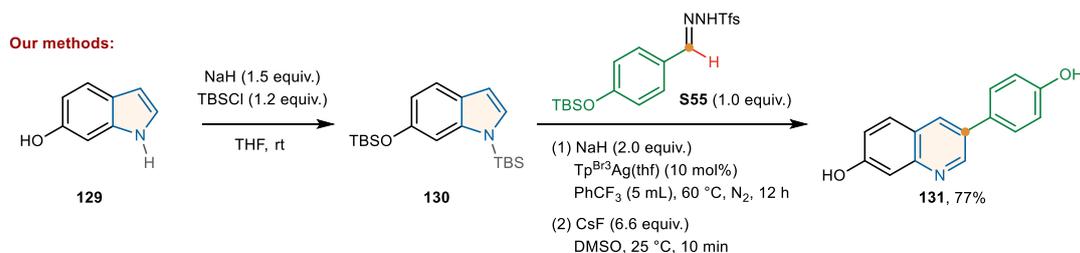
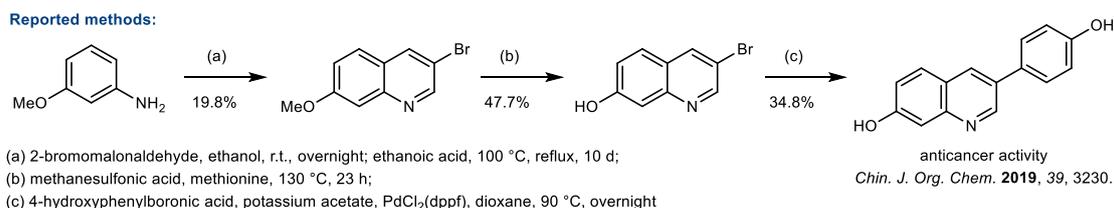
## 4.5 Gram-scale Experiment



**Procedure:** In a glove box, an oven-dried 250 mL Schlenk tube containing a stir bar was charged with *N*-trifosylhydrazone **S3** (1.71 g, 5.0 mmol, 1.0 equiv.), NaH (0.4 g, 2.0 equiv., 60 wt% dispersion in mineral oil), and  $\text{PhCF}_3$  (50.0 mL). The reaction mixture was stirred at ambient temperature for 30 min, and then *N*-TBS indole **1** (1.73 g, 7.5 mmol, 1.5 equiv.) and  $\text{Tp}^{\text{Br}_3}\text{Ag}(\text{thf})$  (0.6 g, 10.0 mol%) were added into the reaction mixture. Next, the sealed vial was removed from glovebox and stirred at 60 °C for 24 h. After cooling to room temperature, the reaction mixture was added TBAF (15.0 mL, 15.0 mmol, 1.0 mol/L in THF, 2.0 equiv.) and stirred at 25 °C for 10 min. The reaction mixture was filtered through a short pad of silica gel (pre-treated with triethylamine) with DCM as an eluent. After removal of the solvent *in vacuo*, the residue was purified by flash chromatography on silica gel (pre-treated with trimethylamine, using petroleum ether-EtOAc (40/1) as eluent) to give the product **70** (1.02 g, 89% yield).

## 4.6 Total Synthesis of Bioactive Molecules using the One-Carbon Insertion as Key Step

### Synthesis of compound 131

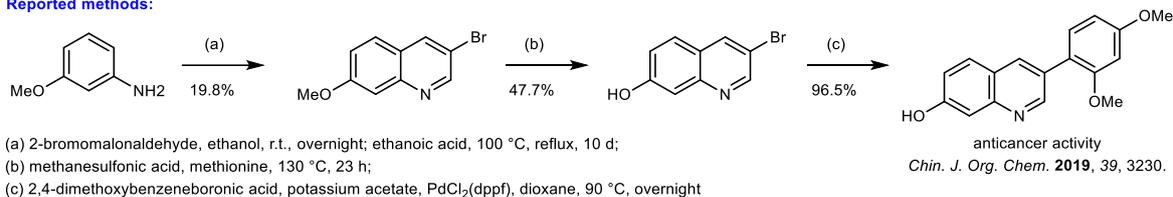


**Step1:** In a 50 mL round bottom flask equipped with a stirring bar, NaH (120 mg, 1.5 equiv., 60 wt% dispersion in mineral oil) was added to anhydrous THF (5 mL) in one portion. The resulting suspension was stirred until the gas evolution stopped. In a separate vial, the 6-hydroxyindole **129** (266 mg, 2.0 mmol, 1.0 equiv.) was dissolved in anhydrous THF (5 mL) and added to the suspension in one portion. The mixture was stirred for approximately 30 minutes at room temperature. In another separate vial, TBSCl (360 mg, 2.4 mmol, 1.2 equiv) was dissolved in anhydrous THF (5 mL) and added to the reaction mixture. Upon completion of the reaction, which was monitored by TLC, brine (20 mL) was added and the reaction mixture was extracted with EtOAc (3 × 20 mL). The combined organic phases were dried over  $\text{Na}_2\text{SO}_4$ , filtered, and all volatiles were evaporated under reduced pressure to leave a crude product, which was purified by flash column chromatography on silica gel (using petroleum as eluent) to give the product **130** (672 mg, 93% yield).

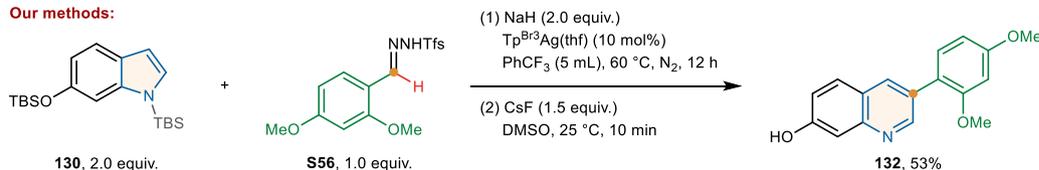
**Step 2:** In a glove box, an oven-dried tube was charged with *N*-triflylhydrazone **S55** (137.4 mg, 0.3 mmol, 1.0 equiv.), NaH (24 mg, 0.6 mmol, 2.0 equiv., 60 wt% dispersion in mineral oil), 6-OTBS-*N*-TBS indole **130** (216.6 mg, 0.6 mmol, 2.0 equiv.),  $\text{Tp}^{\text{Br}^3}\text{Ag}(\text{thf})$  (36.0 mg, 10.0 mol%) and  $\text{PhCF}_3$  (5.0 mL). Next, the sealed vial was removed from glovebox and stirred at 60 °C for 24 h. After cooling to room temperature, the reaction mixture was filtered through a short pad of silica gel with DCM as an eluent. After removal of the solvent *in vacuo*, the residue was added CsF (304 mg, 2.0 mmol, 6.6 equiv.) and DMSO (10.0 mL). The resulting mixture was stirred at 25 °C for 10 min. After completion of the reaction, the mixture was diluted with DCM, washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and the solvent was evaporated under reduced pressure to leave a crude product, which was purified by flash column chromatography on silica gel (pre-treated with trimethylamine, using petroleum ether-EtOAc (20/1) as eluent) to give the product **131** (54.7 mg, 77% yield), as a pale yellow solid solid; mp: 214-215 °C.  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO}-d_6$ )  $\delta$  10.12 (s, 1H), 9.62 (s, 1H), 9.02 (d,  $J = 2.0$  Hz, 1H), 8.35 (d,  $J = 2.0$  Hz, 1H), 7.84 (d,  $J = 9.0$  Hz, 1H), 7.64 (d,  $J = 8.5$  Hz, 2H), 7.25 (d,  $J = 2.0$  Hz, 1H), 7.17 (dd,  $J = 9.0, 2.5$  Hz, 1H), 6.91 (d,  $J = 8.5$  Hz, 2H).  $^{13}\text{C NMR}$  (150 MHz,  $\text{DMSO}-d_6$ )  $\delta$  157.8, 149.0, 148.6, 147.7, 130.6, 130.2, 129.2, 127.3, 124.4, 122.2, 119.4, 114.4, 109.8. **HRMS** (ESI)  $m/z$  calcd. for  $\text{C}_{15}\text{H}_{12}\text{NO}_2^+$   $[\text{M} + \text{H}]^+$  238.0863, found 238.0875. The spectrum was consistent with the previous literature<sup>[11]</sup>.

## Synthesis of compound 132

### Reported methods:



### Our methods:

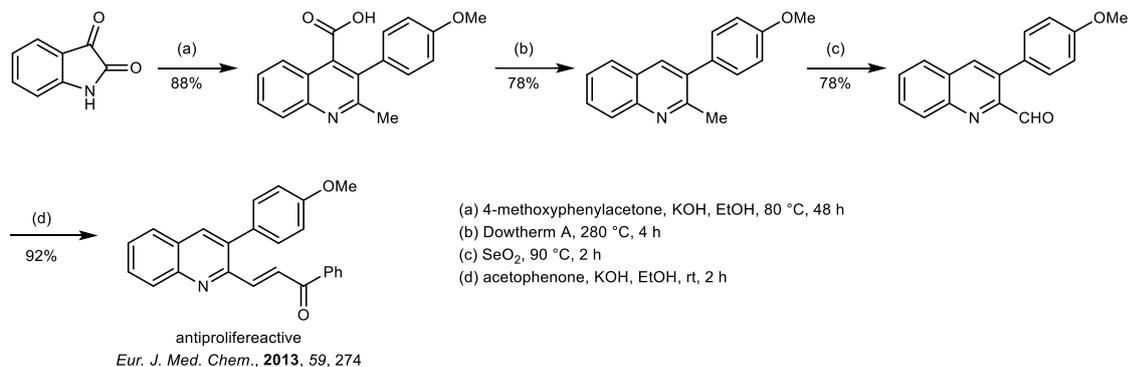


**Procedure:** In a glove box, an oven-dried tube was charged with *N*-triflylhydrazone **S56** (116.4 mg, 0.3 mmol, 1.0 equiv.), NaH (24 mg, 0.6 mmol, 2.0 equiv., 60 wt% dispersion in mineral oil), 6-OTBS-*N*-TBS indole **130** (216.6 mg, 0.6 mmol, 2.0 equiv.),  $\text{Tp}^{\text{Br}^3}\text{Ag}(\text{thf})$  (36.0 mg, 10 mol%) and  $\text{PhCF}_3$  (5.0 mL). Next, the sealed vial was removed from glovebox and stirred at 60 °C for 12 h. After cooling to room temperature, the reaction mixture was filtered through a short pad of silica gel with DCM as an eluent. After removal of the solvent *in vacuo*, the residue was added CsF (228 mg, 1.5 mmol, 5.0 equiv.) and DMSO (10.0 mL). The resulting mixture was stirred at 25 °C for 10 min. After completion of the reaction, the mixture was diluted with DCM, washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and the solvent was evaporated under reduced pressure to leave a crude product, which was purified by flash column chromatography on silica gel (pre-treated with trimethylamine, using petroleum ether-EtOAc (20/1) as eluent) to give the product **132** (44.7 mg, 53% yield), as a pale solid solid; mp: 210-211 °C.  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO}-d_6$ )  $\delta$  10.13 (s, 1H), 8.82 (d,  $J = 2.0$  Hz, 1H), 8.19 (d,  $J = 1.6$  Hz, 1H), 7.82 (d,  $J = 9.0$  Hz, 1H), 7.36 (d,  $J = 8.5$  Hz, 1H), 7.24 (d,  $J = 2.0$  Hz, 1H), 7.16 (dd,  $J = 9.0, 2.0$  Hz, 1H), 6.72 (d,  $J = 2.5$  Hz, 1H), 6.67 (dd,  $J = 8.5, 2.0$  Hz, 1H), 3.83

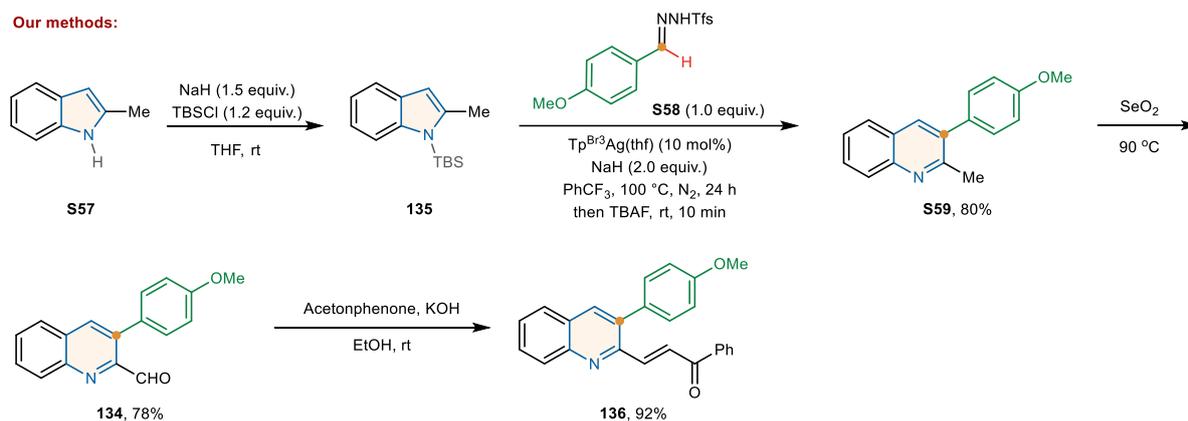
(s, 3H), 3.80 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz, DMSO- $d_6$ )  $\delta$  160.6, 158.3, 157.5, 151.6, 147.9, 134.5, 131.2, 129.5, 128.4, 122.0, 119.5, 119.3, 109.8, 105.7, 99.1, 55.8, 55.5. HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{17}\text{H}_{16}\text{NO}_3^+$   $[\text{M} + \text{H}]^+$  282.1125, found 282.1117. The spectrum was consistent with the previous literature<sup>[11]</sup>.

## Synthesis of compound 136

### Reported methods:



### Our methods:



**Step 1:** In a 50 mL round bottom flask equipped with a stirring bar, NaH (180 mg, 1.5 equiv., 60 wt% dispersion in mineral oil) was added to anhydrous THF (5 mL) in one portion. The resulting suspension was stirred until the gas evolution stopped. In a separate vial, the 2-Me-1H-indole **S57** (393 mg, 3.0 mmol, 1.0 equiv.) was dissolved in anhydrous THF (5 mL) and added to the suspension in one portion. The mixture was stirred for approximately 30 minutes at room temperature. In another separate vial, TBSCl (540 mg, 3.6 mmol, 1.2 equiv.) was dissolved in anhydrous THF (5 mL) and added to the reaction mixture. Upon completion of the reaction, which was monitored by TLC, brine (20 mL) was added and the reaction mixture was extracted with EtOAc (3  $\times$  20 mL). The combined organic phases were dried over  $\text{Na}_2\text{SO}_4$ , filtered, and all volatiles were evaporated under reduced pressure to leave a crude product, which was purified by flash column chromatography on silica gel (using petroleum ether as eluent) to give the product **135** (515 mg, 70% yield).

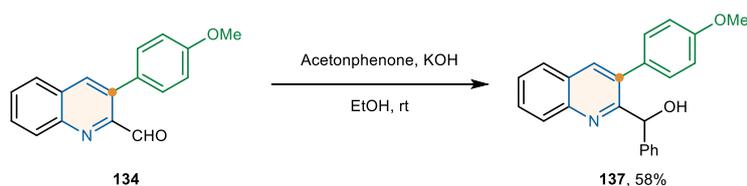
**Step 2:** In a glove box, an oven-dried tube was charged with *N*-triflylhydrazone **S58** (358.0 mg, 1.0 mmol, 1.0 equiv.), NaH (80 mg, 2.0 mmol, 2.0 equiv., 60 wt% dispersion in mineral oil), 1-(*tert*-butyldimethylsilyl)-2-methyl-1H-indole **135** (490.0 mg, 2.0 mmol, 2.0 equiv.),  $\text{Tp}^{\text{Br}_3}\text{Ag}(\text{thf})$  (120.0 mg, 10.0 mol%) and  $\text{PhCF}_3$  (10.0 mL). Next, the sealed vial was removed from glovebox and stirred at 100 °C for 24 h. After cooling to room temperature, the reaction mixture was added TBAF (2.5 mL, 2.5

mmol, 1.0 mol/L in THF, 2.5 equiv.) and stirred at 25 °C for 10 min. After completion of the reaction, the mixture was filtered through a short pad of silica gel (pre-treated with triethylamine) with DCM as an eluent. After removal of the solvent *in vacuo*, the residue was purified by flash chromatography on silica gel (pre-treated with trimethylamine, using petroleum ether-EtOAc (40/1) as eluent) to give the product **S59** (199.2 mg, 80% yield), as a white solid; mp: 69-70 °C. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.06 (d, *J* = 8.5 Hz, 1H), 7.89 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.68-7.63 (m, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.32-7.27 (m, 2H), 7.00-6.95 (m, 2H), 3.84 (s, 3H), 2.67 (s, 3H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 159.0, 157.5, 146.8, 135.8, 135.2, 132.0, 130.2, 129.0, 128.3, 127.2, 126.8, 125.8, 113.7, 55.2, 24.5. **HRMS** (ESI) *m/z* calcd. for C<sub>17</sub>H<sub>6</sub>NO<sup>+</sup> [M + H]<sup>+</sup> 250.1226, found 250.1225.

**Step 3:** [<sup>12</sup>A mixture **S59** (124.5 mg, 0.5 mmol, 1.0 equiv.) and selenium dioxide (111.0 mg, 1.0 mmol, 2.0 equiv.) in 1,4-dioxane (5.0 mL) was heated to 100 °C for 2 h. The mixture was diluted with saturated aqueous NaHCO<sub>3</sub> (50 mL) and extracted with DCM (10 mL × 3). The combined organic layers were washed with H<sub>2</sub>O followed by brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated. The crude mixture was purified by column chromatography on silica gel (using petroleum ether-EtOAc (30/1) as eluent) to give the product **134** (102.6 mg, 78% yield), as a white solid; mp: 105-106 °C. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 10.27 (s, 1H), 8.30 (d, *J* = 8.5 Hz, 1H), 8.18 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.82-7.77 (m, 1H), 7.70-7.65 (m, 1H), 7.38-7.33 (m, 2H), 7.05-6.99 (m, 2H), 3.88 (s, 3H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 192.5, 159.7, 149.9, 146.9, 138.4, 135.5, 130.7, 130.5, 130.3, 129.3, 129.1, 128.9, 127.5, 114.0, 55.3. **HRMS** (ESI) *m/z* calcd. for C<sub>17</sub>H<sub>14</sub>NO<sub>2</sub><sup>+</sup> [M + H]<sup>+</sup> 264.1019, found 264.1022.

**Step 4:** [<sup>13</sup>Compound **134** (78.9 mg, 0.3 mmol, 1.0 equiv.) and acetophenone (39.6 mg, 0.33 mmol, 1.1 equiv.) in EtOH (5.0 mL) were stirred at 0 °C for 15 min. Aqueous solution of KOH (6.0 equiv.) was added and the mixture was stirred at room temperature for 12 h. After the reaction reached completion, the resulting mixture was added 1 M HCl until pH 3 resulted and extracted with ethyl acetate (10 mL × 3). The organic layer was collected, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated. The crude mixture was purified by column chromatography on silica gel (using petroleum ether-EtOAc (30/1) as eluent) to give the product **136** (100.7 mg, 92% yield), as a white solid; mp: 140-142 °C. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.40 (d, *J* = 15.0 Hz, 1H), 8.19 (d, *J* = 8.5 Hz, 1H), 8.15-8.09 (m, 3H), 8.02 (d, *J* = 15.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.75 (t, *J* = 7.5 Hz, 1H), 7.62-7.55 (m, 2H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.40-7.35 (m, 2H), 7.06-7.02 (m, 2H), 3.90 (s, 3H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 190.3, 159.6, 151.5, 147.2, 141.3, 138.0, 136.9, 136.3, 133.0, 131.1, 130.5, 129.8, 129.7, 128.8, 128.6, 128.3, 127.46, 127.45, 127.4, 114.2, 55.4. **HRMS** (ESI) *m/z* calcd. for C<sub>25</sub>H<sub>20</sub>NO<sub>2</sub><sup>+</sup> [M + H]<sup>+</sup> 366.1489, found 366.1492. The spectrum was consistent with the previous literature<sup>[13]</sup>.

### Synthesis of compound 137

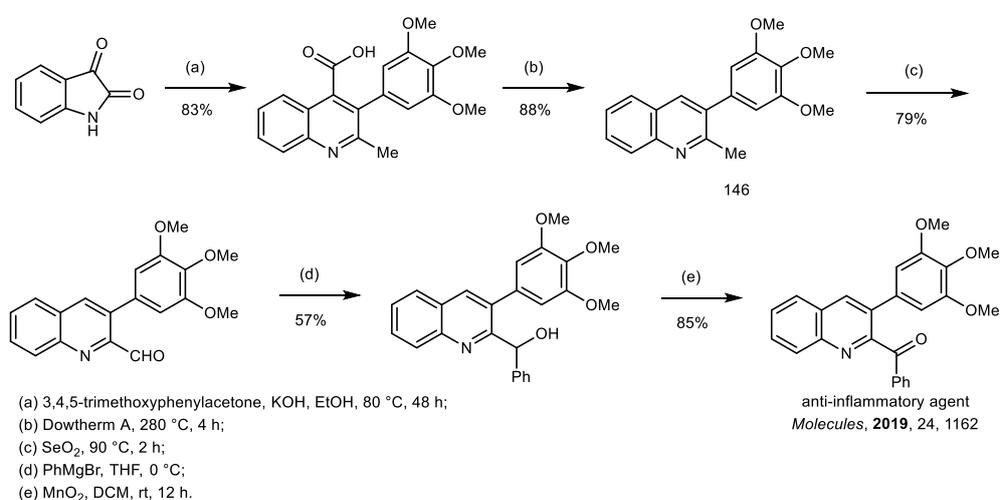


**Procedure A:** [<sup>14</sup>A mixture of **134** (78.9 mg, 0.3 mmol), phenyl magnesium bromide (0.9 mL, 0.9 mmol, 1 M solution in THF), and THF (10 mL) was stirred at 0 °C for 12 h. The reaction was quenched by addition of water (5.0 mL) and partitioned between H<sub>2</sub>O (10 mL) and DCM (15 mL). The organic layer was washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated. The crude mixture was purified by

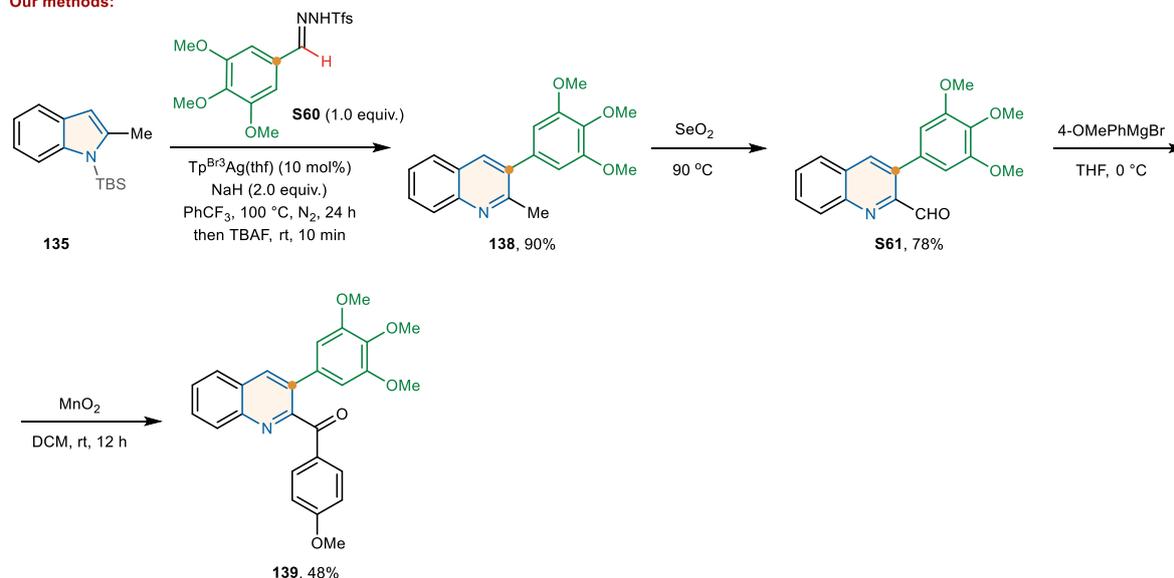
column chromatography on silica gel (using petroleum ether-EtOAc (15/1) as eluent) to give the product **137** (59.3 mg, 58% yield), as a white solid; mp: 115-117 °C.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.24 (d,  $J = 8.5$  Hz, 1H), 7.93 (s, 1H), 7.82 (d,  $J = 8.0$  Hz, 1H), 7.78 (t,  $J = 7.5$  Hz, 1H), 7.58 (t,  $J = 7.5$  Hz, 1H), 7.15-7.06 (m, 3H), 7.00-6.94 (m, 2H), 6.91-6.86 (m, 2H), 6.86-6.82 (m, 2H), 6.37 (d,  $J = 6.5$  Hz, 1H), 6.05 (d,  $J = 6.5$  Hz, 1H), 3.87 (s, 3H).  $^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ )  $\delta$  159.2, 159.0, 145.0, 142.3, 137.4, 133.8, 130.4, 130.0, 129.6, 128.5, 127.8, 127.5, 127.4, 127.3, 127.1, 126.7, 113.6, 72.7, 55.2. **HRMS** (ESI)  $m/z$  calcd. for  $\text{C}_{23}\text{H}_{20}\text{NO}_2^+$   $[\text{M} + \text{H}]^+$  342.1489, found 342.1488. The spectrum was consistent with the previous literature<sup>[14]</sup>.

## Synthesis of compound 139

### Reported methods:



### Our methods:



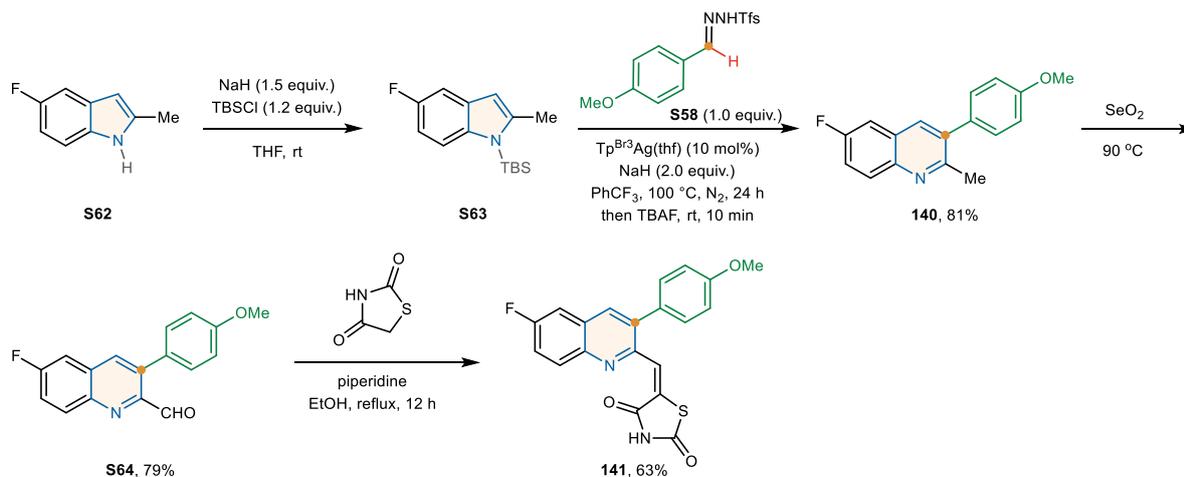
**Step 1:** In a glove box, an oven-dried tube was charged with *N*-triflylhydrazone **S60** (418.0 mg, 1.0 mmol, 1.0 equiv.), NaH (80 mg, 2.0 mmol, 2.0 equiv., 60 wt% dispersion in mineral oil), 1-(*tert*-butyldimethylsilyl)-2-methyl-1*H*-indole **135** (490.0 mg, 2.0 mmol, 2.0 equiv.),  $\text{TpBr}^3\text{Ag}(\text{thf})$  (120.0 mg, 10.0 mol%) and  $\text{PhCF}_3$  (10.0 mL). Next, the sealed vial was removed from glovebox and stirred at

100 °C for 24 h. After cooling to room temperature, the reaction mixture was added TBAF (2.5 mL, 2.5 mmol, 1.0 mol/L in THF, 2.5 equiv.) and stirred at 25 °C for 10 min. After completion of the reaction, the mixture was filtered through a short pad of silica gel (pre-treated with triethylamine) with DCM as an eluent. After removal of the solvent *in vacuo*, the residue was purified by flash chromatography on silica gel (pre-treated with trimethylamine, using petroleum ether-EtOAc (30/1) as eluent) to give the product **138** (278.1 mg, 90% yield), as a pale yellow oil. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.05 (d, *J* = 8.5 Hz, 1H), 7.96 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 6.59 (s, 2H), 3.94 (s, 3H), 3.88 (s, 6H), 2.69 (s, 3H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 157.2, 152.9, 147.0, 137.3, 135.8, 135.6, 135.5, 129.3, 128.4, 127.3, 126.6, 126.1, 106.4, 61.0, 56.2, 24.5. **HRMS** (ESI) *m/z* calcd. for C<sub>19</sub>H<sub>20</sub>NO<sub>3</sub><sup>+</sup> [*M* + *H*]<sup>+</sup> 310.1438, found 310.1449.

**Step 2:** [<sup>12</sup>I]A mixture **138** (1.0 mmol, 1.0 equiv.) and selenium dioxide (2.0 mmol, 2.0 equiv.) in 1,4-dioxane (5.0 mL) was heated to 100 °C for 2 h. The mixture was diluted with saturated aqueous NaHCO<sub>3</sub> (50 mL) and extracted with DCM (10 mL × 3). The combined organic layers were washed with H<sub>2</sub>O followed by brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated. The crude mixture was purified by column chromatography on silica gel (using petroleum ether-EtOAc (30/1) as eluent) to give the product **S61** (126.0 mg, 78% yield), as a white solid. mp: 140-142 °C. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 10.28 (s, 1H), 8.34 (d, *J* = 8.5 Hz, 1H), 8.24 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.86-7.81 (m, 1H), 7.74-7.69 (m, 1H), 6.63 (s, 2H), 3.94 (s, 3H), 3.89 (s, 6H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 192.3, 153.2, 149.9, 147.1, 138.3, 138.1, 135.9, 132.4, 130.61, 130.57, 129.5, 128.8, 127.5, 107.0, 61.0, 56.2. **HRMS** (ESI) *m/z* calcd. for C<sub>19</sub>H<sub>18</sub>NO<sub>4</sub><sup>+</sup> [*M* + *H*]<sup>+</sup> 324.1230, found 324.1218.

**Step 3:** [<sup>12</sup>I]A mixture of **S61** (0.3 mmol), phenyl magnesium bromide (0.9 mmol, 0.9 mL of a 1 M solution in THF), and THF (10 mL) was stirred at 0 °C for 12 h. The reaction was quenched by addition of water (5.0 mL) and partitioned between H<sub>2</sub>O (10 mL) and DCM (15 mL). The organic layer was washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated. The crude product was used in the following step without further purification. [<sup>12</sup>I]A mixture of the crude product and MnO<sub>2</sub> (10.0 mmol, 10 equiv.) in DCM (20 mL) was stirred at room temperature for 12 h. The reaction mixture was partitioned between H<sub>2</sub>O (10 mL) and DCM (15 mL). The organic layer was washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated. The crude mixture was purified by column chromatography on silica gel (using petroleum ether-EtOAc (25/1) as eluent) to give the product **139** (61.8 mg, 48% yield), as a white solid; mp: 152-153 °C. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.28 (s, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.90-7.85 (m, 2H), 7.80-7.75 (m, 1H), 7.65 (t, *J* = 7.5 Hz, 1H), 6.91-6.86 (m, 2H), 6.61 (s, 2H), 3.85 (s, 3H), 3.83 (s, 3H), 3.69 (s, 6H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 194.0, 164.0, 156.9, 153.2, 146.1, 137.8, 136.5, 133.6, 133.1, 132.7, 130.1, 129.6, 129.4, 127.9, 127.8, 127.7, 113.8, 106.4, 60.8, 56.0, 55.5. **HRMS** (ESI) *m/z* calcd. for C<sub>26</sub>H<sub>24</sub>NO<sub>5</sub><sup>+</sup> [*M* + *H*]<sup>+</sup> 430.1649, found 430.1650. The spectrum was consistent with the previous literature<sup>[12]</sup>.

## Synthesis of compound 141



**Step 1:** In a 50 mL round bottom flask equipped with a stirring bar, NaH (180 mg, 1.5 equiv., 60 wt% dispersion in mineral oil) was added to anhydrous THF (5 mL) in one portion. The resulting suspension was stirred until the gas evolution stopped. In a separate vial, the 2-Me-5-F-1*H*-indole **S62** (447 mg, 3.0 mmol, 1.0 equiv.) was dissolved in anhydrous THF (5 mL) and added to the suspension in one portion. The mixture was stirred for approximately 30 minutes at room temperature. In another separate vial, TBSCl (540 mg, 3.6 mmol, 1.2 equiv.) was dissolved in anhydrous THF (5 mL) and added to the reaction mixture. Upon completion of the reaction, which was monitored by TLC, brine (20 mL) was added and the reaction mixture was extracted with EtOAc (3 × 20 mL). The combined organic phases were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and all volatiles were evaporated under reduced pressure to leave a crude product, which was purified by flash column chromatography on silica gel (using petroleum ether as eluent) to give the product **S63** (608 mg, 77% yield).

**Step 2:** In a glove box, an oven-dried tube was charged with *N*-triflylhydrazone **S58** (358.0 mg, 1.0 mmol, 1.0 equiv.), NaH (80 mg, 2.0 mmol, 2.0 equiv., 60 wt% dispersion in mineral oil), 1-(*tert*-butyldimethylsilyl)-5-fluoro-2-methyl-1*H*-indole **S63** (526.0 mg, 2.0 mmol, 2.0 equiv.), Tp<sup>Br3</sup>Ag(thf) (120.0 mg, 10.0 mol%) and PhCF<sub>3</sub> (10.0 mL). Next, the sealed vial was removed from glovebox and stirred at 100 °C for 24 h. After cooling to room temperature, the reaction mixture was added TBAF (2.5 mL, 2.5 mmol, 1.0 mol/L in THF, 2.5 equiv.) and stirred at 25 °C for 10 min. After completion of the reaction, the mixture was filtered through a short pad of silica gel (pre-treated with triethylamine) with DCM as an eluent. After removal of the solvent *in vacuo*, the residue was purified by flash chromatography on silica gel (pre-treated with trimethylamine, using petroleum ether-EtOAc (40/1) as eluent) to give the product **140** (216.3 mg, 81% yield), as a white solid; mp: 86-88 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.03 (dd, *J* = 9.0, 5.5 Hz, 1H), 7.87 (s, 1H), 7.43 (td, *J* = 9.0, 3.0 Hz, 1H), 7.37 (dd, *J* = 9.0, 3.0 Hz, 1H), 7.34-7.29 (m, 2H), 7.03-6.98 (m, 2H), 3.88 (s, 3H), 2.65 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 160.2 (d, *J* = 246.0 Hz), 159.3, 157.0 (d, *J* = 1.5 Hz), 144.0, 136.2, 135.3 (d, *J* = 4.5 Hz), 131.8, 130.8 (d, *J* = 7.5 Hz), 130.3, 127.4 (d, *J* = 10.5 Hz), 119.2 (d, *J* = 25.5 Hz), 113.9, 110.3 (d, *J* = 21.0 Hz), 55.3, 24.5. <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ (-114.47)-(-114.59) (m). HRMS (ESI) *m/z* calcd. for C<sub>17</sub>H<sub>15</sub>FNO<sup>+</sup> [M + H]<sup>+</sup> 268.1132, found 268.1135.

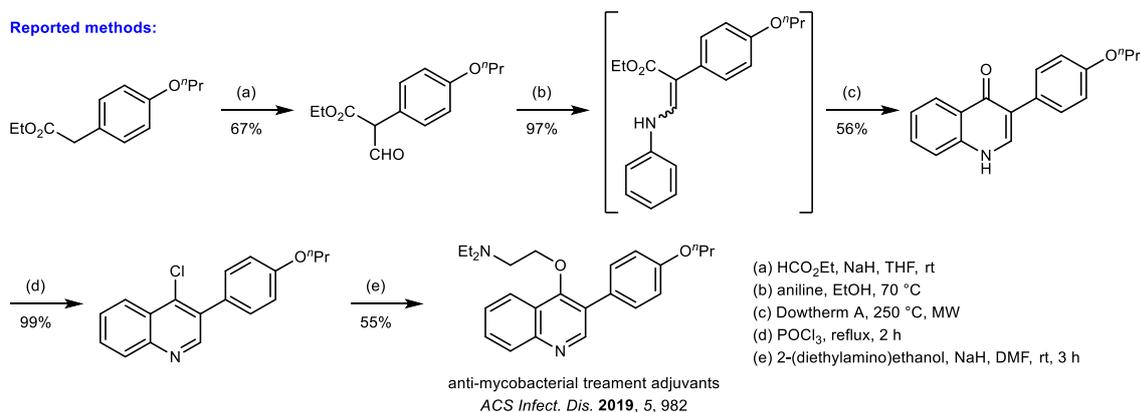
**Step 3:** <sup>[12]</sup>A mixture **140** (133.5 mg, 0.5 mmol, 1.0 equiv.) and selenium dioxide (112.0 mg, 1.0 mmol, 2.0 equiv.) in 1,4-dioxane (5.0 mL) was heated to 100 °C for 2 h. The mixture was diluted with saturated aqueous NaHCO<sub>3</sub> (50 mL) and extracted with DCM (10 mL × 3). The combined organic layers were

washed with H<sub>2</sub>O followed by brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated. The crude mixture was purified by column chromatography on silica gel (using petroleum ether-EtOAc (30/1) as eluent) to give the product **S64** (111.0 mg, 79% yield), as a white solid; mp: 122-123 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 10.24 (s, 1H), 8.32 (dd, *J* = 9.5, 5.5 Hz, 1H), 8.13 (s, 1H), 7.61-7.55 (m, 1H), 7.49 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.39-7.33 (m, 2H), 7.06-7.00 (m, 2H), 3.89 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 192.2, 162.2 (d, *J* = 252.0 Hz), 159.9, 149.4 (d, *J* = 4.5 Hz), 144.1, 137.7 (d, *J* = 6.0 Hz), 136.3, 133.3 (d, *J* = 9.0 Hz), 130.8, 129.9 (d, *J* = 10.5 Hz), 128.7, 121.0 (d, *J* = 25.5 Hz), 114.1, 110.4 (d, *J* = 22.5 Hz), 55.4. <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ (-115.37)-(-115.26) (m). HRMS (ESI) *m/z* calcd. for C<sub>17</sub>H<sub>13</sub>FNO<sub>2</sub><sup>+</sup> [M + H]<sup>+</sup> 282.0925, found 282.0927.

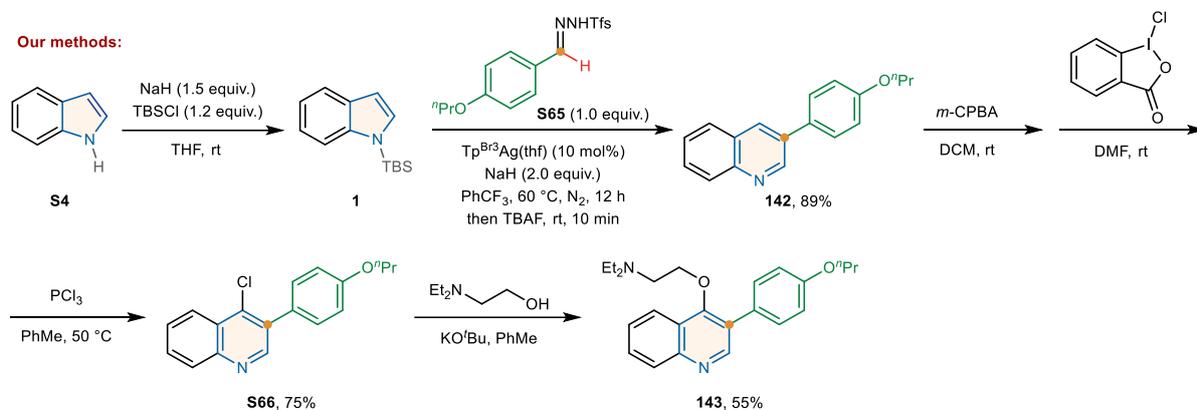
**Step 4:** <sup>[15]</sup>The compound **S64** (84.3 mg, 0.3 mmol, 1.0 equiv.) and 2,4-thiazolidinedione (52.7 mg, 0.45 mmol, 1.5 equiv.) were dissolved in anhydrous EtOH (10 mL) at room temperature and piperidine (0.1 mmol) was added to the reaction flask. The reaction mixture was stirred at 75 °C for 24 h and then allowed to cool down to room temperature until the reaction was completed. After removal of the solvent *in vacuo*, the residue was purified by flash chromatography on silica gel (pre-treated with trimethylamine, using petroleum ether-EtOAc (20/1) as eluent) to give the product **141** (71.8 mg, 63% yield), as a red solid, mp: 297-298 °C. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 12.48 (s, 1H), 8.33 (s, 1H), 8.18 (dd, *J* = 9.0, 5.5 Hz, 1H), 7.80 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.72 (td, *J* = 9.0, 3.0 Hz, 1H), 7.67 (s, 1H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.14 (d, *J* = 8.5 Hz, 2H), 3.86 (s, 3H). <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>) δ 172.9, 167.9, 161.1 (d, *J* = 247.5 Hz), 159.9, 149.5, 143.5, 137.3, 137.1, 131.5, 131.4, 131.2, 129.5, 128.2 (d, *J* = 10.5 Hz), 124.9, 121.3 (d, *J* = 25.5 Hz), 114.8, 111.5 (d, *J* = 21.0 Hz), 55.8. <sup>19</sup>F NMR (564 MHz, DMSO-*d*<sub>6</sub>) δ (-110.85)-(-110.95) (m). HRMS (ESI) *m/z* calcd. for C<sub>20</sub>H<sub>14</sub>FN<sub>2</sub>O<sub>3</sub>S<sup>+</sup> [M + H]<sup>+</sup> 381.0704, found 381.0709.

## Synthesis of compound 143

### Reported methods:



### Our methods:



**Step 1:** In a 50 mL round bottom flask equipped with a stirring bar, NaH (180 mg, 1.5 equiv., 60 wt% dispersion in mineral oil) was added to anhydrous THF (5 mL) in one portion. The resulting suspension was stirred until the gas evolution stopped. In a separate vial, the 1*H*-indole **S4** (351 mg, 3.0 mmol, 1.0 equiv.) was dissolved in anhydrous THF (5 mL) and added to the suspension in one portion. The mixture was stirred for approximately 30 minutes at room temperature. In another separate vial, TBSCl (540 mg, 3.6 mmol, 1.2 equiv) was dissolved in anhydrous THF (5 mL) and added to the reaction mixture. Upon completion of the reaction, which was monitored by TLC, brine (20 mL) was added and the reaction mixture was extracted with EtOAc (3 × 20 mL). The combined organic phases were dried over  $\text{Na}_2\text{SO}_4$ , filtered, and all volatiles were evaporated under reduced pressure to leave a crude product, which was purified by flash column chromatography on silica gel (using petroleum ether as eluent) to give the product **1** (665 mg, 96% yield).

**Step 2:** In a glove box, an oven-dried tube was charged with *N*-triflylhydrazone **S65** (386.0 mg, 1.0 mmol, 1.0 equiv.), NaH (80 mg, 2.0 mmol, 2.0 equiv., 60 wt% dispersion in mineral oil), *N*-TBS indole **1** (462.0 mg, 2.0 mmol, 2.0 equiv.),  $\text{Tp}^{\text{Br}_3}\text{Ag}(\text{thf})$  (120.0 mg, 10.0 mol%) and  $\text{PhCF}_3$  (10.0 mL). Next, the sealed vial was removed from glovebox and stirred at 60 °C for 12 h. After cooling to room temperature, the reaction mixture was added TBAF (2.5 mL, 2.5 mmol, 1.0 mol/L in THF, 2.5 equiv.) and stirred at 25 °C for 10 min. After completion of the reaction, the mixture was filtered through a short pad of silica gel (pre-treated with triethylamine) with DCM as an eluent. After removal of the solvent *in vacuo*, the residue was purified by flash chromatography on silica gel (pre-treated with trimethylamine, using petroleum ether-EtOAc (40/1) as eluent) to give the product **142** (234.1 mg, 88% yield), as a white solid; mp: 72–74 °C.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.16 (d,  $J = 2.0$  Hz, 1H), 8.22 (d,  $J = 2.0$  Hz, 1H), 8.12 (d,  $J = 8.0$  Hz, 1H), 7.84 (d,  $J = 8.0$  Hz, 1H),

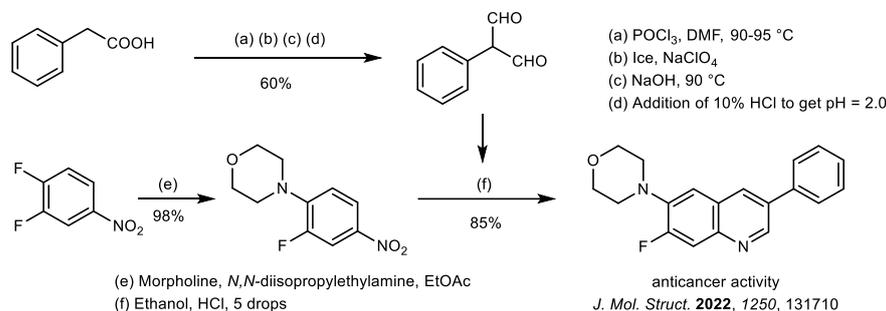
7.71-7.65 (m, 1H), 7.65-7.60 (m, 2H), 7.54 (t,  $J = 7.5$  Hz, 1H), 7.06-7.01 (m, 2H), 3.98 (t,  $J = 6.6$  Hz, 2H), 1.89-1.80 (m, 2H), 1.07 (t,  $J = 7.5$  Hz, 3H).  $^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ )  $\delta$  159.3, 149.8, 147.0, 133.5, 132.2, 130.0, 129.1, 128.9, 128.4, 128.1, 127.8, 126.8, 115.2, 69.6, 22.5, 10.5. **HRMS** (ESI)  $m/z$  calcd. for  $\text{C}_{18}\text{H}_{18}\text{NO}^+$  [ $\text{M} + \text{H}$ ] $^+$  264.1383, found 264.1394.

**Step 3:**  $^{[16]}$ To a 100 mL round bottom flask equipped with a magnetic stirbar, compound **142** (131.6 mg, 0.5 mmol, 1.0 equiv.), *m*-chloroperbenzoic acid (172.6 mg, 2.0 mmol, 2.0 equiv.) and DCM (10.0 mL) were added. The mixture was stirred for 12 h at room temperature and then the organic phase was washed with a saturated aqueous  $\text{NaHCO}_3$  solution (20 mL) and brine (20 mL). The aqueous layer was extracted with DCM (25 mL  $\times$  3). The combined organic layers were dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and concentrated under reduced pressure. The crude mixture was used in the following step without further purification.  $^{[17]}$ To a stirred solution of crude mixture in anhydrous DMF (10.0 mL) at room temperature was added chlorinating reagent 1-Chloro-1,2-benziodoxol-3-(1*H*)-one (282.46 mg, 1.0 mmol), and the mixture was stirred for 12 h under air condition. After completion of reaction monitored by TLC, the resulting mixture quenched with saturated aqueous  $\text{NaHCO}_3$ , then extracted with ethyl acetate (15 mL  $\times$  3). The combined organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and filtered. The solution was removed by evaporation under reduced pressure to afford the crude product. The crude product was used in the following step without further purification.  $^{[18]}$ Then the crude product was dissolved in toluene in round bottom flask with stirring at room temperature. And then  $\text{PCl}_3$  (103.0 mg, 0.75 mmol) was added, and stirred at 50  $^\circ\text{C}$  for 3 h. Saturated  $\text{NaHCO}_3$  was added to the reaction mixture, and extracted with ethyl acetate (15 mL  $\times$  3), washed with brine (15.0 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and evaporated. The crude mixture was purified by column chromatography on silica gel (pre-treated with trimethylamine, using petroleum ether-EtOAc (40/1) as eluent) to give the product **S66** (111.4 mg, 75% yield), as a white solid; mp: 76-77  $^\circ\text{C}$ .  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.86 (s, 1H), 8.37-8.31 (m, 1H), 8.15 (d,  $J = 8.5$  Hz, 1H), 7.80-7.73 (m, 1H), 7.70-7.65 (m, 1H), 7.51-7.46 (m, 2H), 7.08-7.01 (m, 2H), 4.00 (t,  $J = 6.5$  Hz, 2H), 1.92-1.81 (m, 2H), 1.08 (t,  $J = 7.5$  Hz, 3H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  159.3, 151.7, 147.7, 139.6, 132.9, 131.1, 129.8, 129.6, 128.3, 127.9, 126.5, 124.6, 114.5, 69.6, 22.6, 10.5. **HRMS** (ESI)  $m/z$  calcd. for  $\text{C}_{18}\text{H}_{17}\text{ClNO}^+$  [ $\text{M} + \text{H}$ ] $^+$  298.0993, found 298.0980.

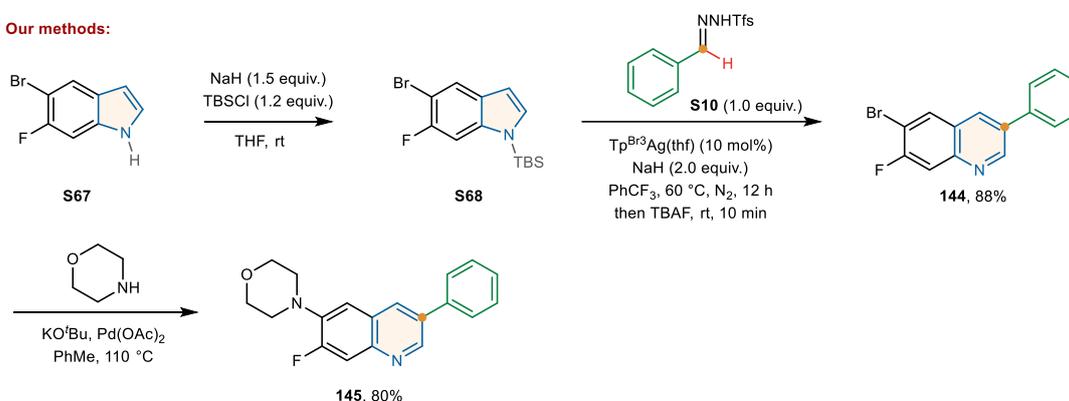
**Step 4:**  $^{[19]}$ Under a  $\text{N}_2$  atmosphere, a solution of 2-(diethylamino)ethanol (105.5 mg, 0.9 mmol, 3.0 equiv.) in dry DMF (1.00 mL) was added to a suspension of NaH (48 mg, 1.2 mmol, 60 wt% dispersion in mineral oil, 4.0 equiv.) in dry DMF (1.0 mL). After 10 min of stirring, a solution of compound **S66** (89.13 mg, 0.3 mmol, 1.0 equiv.) in dry DMF (1.0 mL) was added, and the reaction mixture was stirred at room temperature for 3 h. Then, the mixture was poured in ice/water and extracted with EtOAc (10 mL  $\times$  3). The organic layer was washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and evaporated. The crude mixture was purified by column chromatography on silica gel (pre-treated with trimethylamine, using petroleum ether-EtOAc (20/1) as eluent) to give the product **143** (62.4 mg, 55% yield), as a yellow oil.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.84 (s, 1H), 8.31 (d,  $J = 8.5$  Hz, 1H), 8.08 (d,  $J = 8.5$  Hz, 1H), 7.72-7.67 (m, 1H), 7.59-7.52 (m, 3H), 7.04-6.99 (m, 2H), 3.98 (t,  $J = 6.5$  Hz, 2H), 3.79 (t,  $J = 6.5$  Hz, 2H), 2.71 (t,  $J = 6.5$  Hz, 2H), 2.47 (q,  $J = 7.0$  Hz, 4H), 1.89-1.80 (m, 2H), 1.07 (t,  $J = 7.5$  Hz, 3H), 0.94 (t,  $J = 7.5$  Hz, 6H).  $^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ )  $\delta$  159.4, 158.9, 153.4, 148.9, 130.4, 129.3, 129.1, 127.7, 126.3, 124.17, 124.15, 122.6, 114.8, 71.7, 69.6, 52.6, 47.3, 22.6, 11.7, 10.5. **HRMS** (ESI)  $m/z$  calcd. for  $\text{C}_{24}\text{H}_{31}\text{N}_2\text{O}_2^+$  [ $\text{M} + \text{H}$ ] $^+$  397.2380, found 397.2397. The spectrum was consistent with the previous literature $^{[19]}$ .

## Synthesis of compound 145

### Reported methods:



### Our methods:



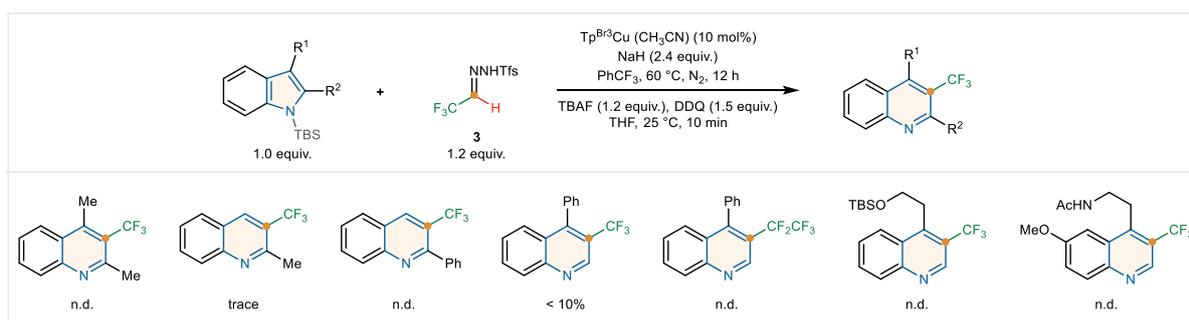
**Step 1:** In a 50 mL round bottom flask equipped with a stirring bar,  $\text{NaH}$  (180 mg, 1.5 equiv., 60 wt% dispersion in mineral oil) was added to anhydrous THF (5 mL) in one portion. The resulting suspension was stirred until the gas evolution stopped. In a separate vial, the 5-bromo-6-fluoro-1*H*-indole **S67** (639 mg, 3.0 mmol, 1.0 equiv.) was dissolved in anhydrous THF (5 mL) and added to the suspension in one portion. The mixture was stirred for approximately 30 minutes at room temperature. In another separate vial, TBSCl (540 mg, 3.6 mmol, 1.2 equiv) was dissolved in anhydrous THF (5 mL) and added to the reaction mixture. Upon completion of the reaction, which was monitored by TLC, brine (20 mL) was added and the reaction mixture was extracted with EtOAc ( $3 \times 20$  mL). The combined organic phases were dried over  $\text{Na}_2\text{SO}_4$ , filtered, and all volatiles were evaporated under reduced pressure to leave a crude product, which was purified by flash column chromatography on silica gel (using petroleum ether as eluent) to give the product **S68** (932 mg, 95% yield).

**Step 2:** In a glove box, an oven-dried tube was charged with *N*-trifosylhydrazone **S10** (328 mg, 1.0 mmol, 1.0 equiv.),  $\text{NaH}$  (80.0 mg, 2.0 mmol, 2.0 equiv., 60 wt% dispersion in mineral oil), 5-bromo-1-(*tert*-butyldimethylsilyl)-6-fluoro-1*H*-indole **S68** (654.0 mg, 2.0 mmol, 2.0 equiv.),  $\text{Tp}^{\text{Br}_3}\text{Ag}(\text{thf})$  (120.0 mg, 10.0 mol%) and  $\text{PhCF}_3$  (10.0 mL). Next, the sealed vial was removed from glovebox and stirred at 60 °C for 12 h. After cooling to room temperature, the reaction mixture was added TBAF (2.5 mL, 2.5 mmol, 1.0 mol/L in THF, 2.5 equiv.) and stirred at 25 °C for 10 min. After completion of the reaction, the mixture was filtered through a short pad of silica gel (pre-treated with triethylamine) with DCM as an eluent. After removal of the solvent *in vacuo*, the residue was purified by flash chromatography on silica gel (pre-treated with trimethylamine, using petroleum ether-EtOAc (40/1) as eluent) to give the product **144** (264.9 mg, 88% yield), as a white solid; mp: 164-166 °C.  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.19 (d,  $J = 2.4$  Hz, 1H),

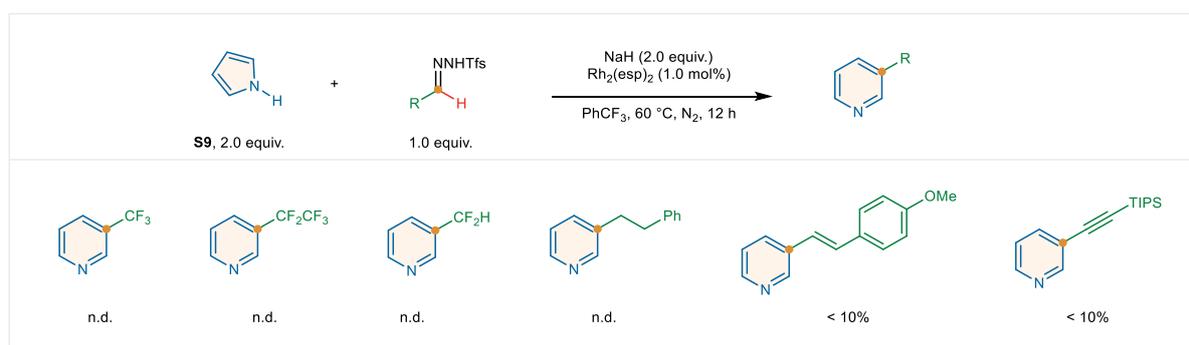
8.22 (d,  $J = 2.4$  Hz, 1H), 8.14 (d,  $J = 7.2$  Hz, 1H), 7.84 (d,  $J = 9.6$  Hz, 1H), 7.71-7.67 (m, 2H), 7.54 (t,  $J = 7.8$  Hz, 2H), 7.48-7.44 (m, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  158.7 (d,  $J = 250.0$  Hz), 151.2, 147.0 (d,  $J = 11.2$  Hz), 137.1, 134.1 (d,  $J = 2.5$  Hz), 132.3, 131.9, 129.3, 128.4, 127.3, 125.9, 114.1 (d,  $J = 21.3$  Hz), 110.9 (d,  $J = 25.0$  Hz).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -104.30 (t,  $J = 8.5$  Hz). HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{15}\text{H}_{10}\text{BrFN}^+$   $[\text{M} + \text{H}]^+$  301.9975, found 301.9962.

**Step 3:**  $^{[20]}$ Compound **144** (90.3 mg, 0.3 mmol, 1.0 equiv.) and morpholine (31.4 mg, 0.36 mmol, 1.2 equiv.) were added to a mixture of  $\text{Pd}(\text{OAc})_2$  (3.4 mg, 5 mol%), BINAP (18.7 mg, 10 mol%), and  $\text{KO}^t\text{Bu}$  (40.4 mg, 0.36 mmol, 1.2 equiv.) in toluene (3 mL). The reaction mixture was reflux for 24 h. After completion of the reaction, the mixture was diluted with DCM, washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and the solvent was evaporated under reduced pressure to leave a crude product, which was purified by flash column chromatography on silica gel (pre-treated with trimethylamine, using petroleum ether-EtOAc (20/1) as eluent) to give the product **145** (73.9 mg, 80% yield), as a pale yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.02 (d,  $J = 2.0$  Hz, 1H), 8.17 (d,  $J = 1.5$  Hz, 1H), 7.72 (d,  $J = 13.5$  Hz, 1H), 7.67 (d,  $J = 7.5$  Hz, 2H), 7.51 (t,  $J = 7.5$  Hz, 2H), 7.43 (t,  $J = 7.5$  Hz, 1H), 7.21 (d,  $J = 9.0$  Hz, 1H), 3.97-3.91 (m, 4H), 3.24-3.19 (m, 4H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  157.6 (d,  $J = 252.0$  Hz), 148.5, 144.1 (d,  $J = 13.5$  Hz), 141.3 (d,  $J = 10.0$  Hz), 137.8, 133.5 (d,  $J = 1.5$  Hz), 131.9, 129.1, 128.0, 127.3, 125.7, 114.2 (d,  $J = 4.5$  Hz), 114.0 (d,  $J = 21.0$  Hz), 66.8, 51.0 (d,  $J = 4.5$  Hz).  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -117.46 (dd,  $J = 13.5, 9.0$  Hz). HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{19}\text{H}_{18}\text{FN}_2\text{O}^+$   $[\text{M} + \text{H}]^+$  309.1398, found 309.1409. The spectrum was consistent with the previous literature $^{[21]}$ .

## 5. Unsuccessful Reactions



**Supplementary Fig. 1.** The unsuccessful reaction for ring expansion of indoles with fluoroalkyl *N*-triflylhydrazones.



**Supplementary Fig. 2.** The unsuccessful reaction for one-carbon insertion of 1*H*-pyrrole.

## 6. DSC Analysis

As shown in Supplementary Fig. 3, the initiation temperature ( $T_{\text{init}}$ , the temperature at which exothermic) of trifluoroacetaldehyde *N*-triftosylhydrazone was approximately 172.9 °C, and onset temperature ( $T_{\text{onset}}$ ) was approximately 173.1 °C. For phenyl *N*-triftosylhydrazone, the initiation temperature was approximately 151.8 °C, and onset temperature ( $T_{\text{onset}}$ ) was approximately 181.7 °C. At least, the  $\Delta H_d$  values obtained from the temperature are 4.2 J/g and 463.2 J/g respectively, both lower than the  $\Delta H_d$  values of the commonly used as carbene precursors. Furthermore, using the formula corrected by Yoshida and Pfizer, the impact sensitivity (IS) and explosive propagation (EP) potential are obtained, both of which are less than zero.

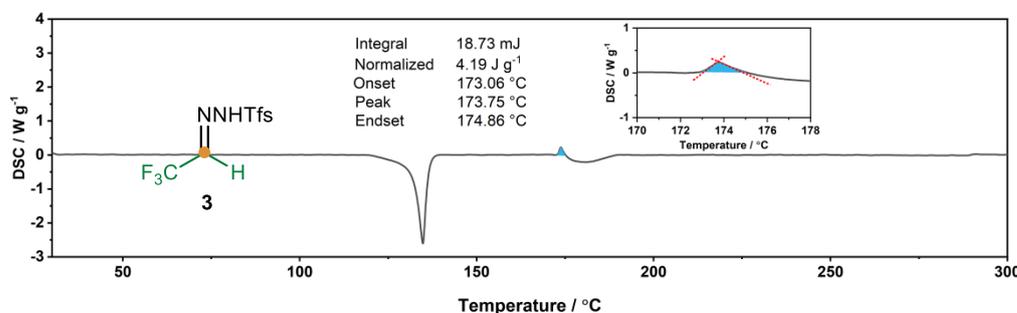
**Supplementary Table 8.** Thermal properties of arylchlorodiazirines measured by Differential Scanning Calorimetry (DSC).<sup>[a]</sup>

Entry	<i>N</i> -triftosylhydrazones	$T_{\text{init}}$ (°C)	$T_{\text{onset}}$ (°C)	$-\Delta H_d$ (J/g)	$-\Delta H_d$ (kJ/mol)	Yoshiada		Pfizer	
						IS	EP	IS	EP
1	-CF <sub>3</sub>	172.9	173.1	4.2	1.3	-2.54	-2.49	-2.15	-2.29
2	-Ph	151.8	181.7	463.2	152.0	-0.52	-0.47	-0.12	-0.25

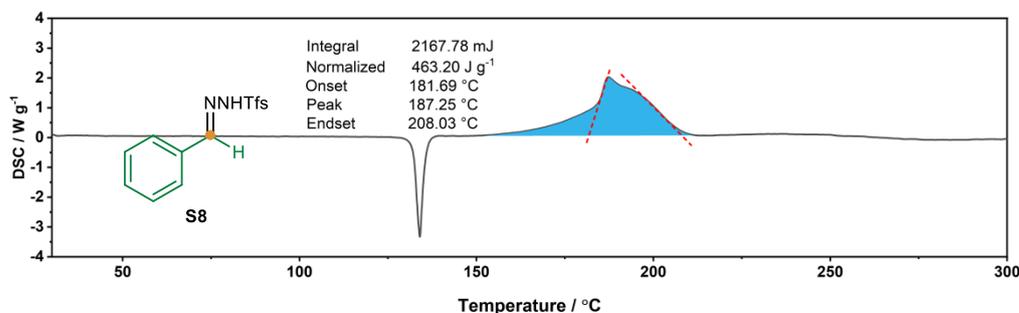
<sup>[a]</sup> $T_{\text{init}}$  is the temperature at which the normalized heatflow exceeds 0.01 W/g above the baseline;  $T_{\text{onset}}$  is the intersection of the maximum peak gradient and the baseline;  $\Delta H_d$  is the integral area of the exotherm peak; IS (impact sensitivity) and EP (explosive propagation) calculated according to Equations (Yoshida, Pfizer).

### DSC Method:

Approximately 5 mg of material was weighed into an aluminum oxide crucible using a 7-place balance. After equilibrating the sample at 25 °C, the sample was heated at 5 °C/min. The measurements were made to 300 °C. Exothermic events are positive in the  $y$ -axis.



**Supplementary Fig. 3.** DSC measurement curve for trifluoroacetaldehyde *N*-triftosylhydrazone. (4.47 mg)

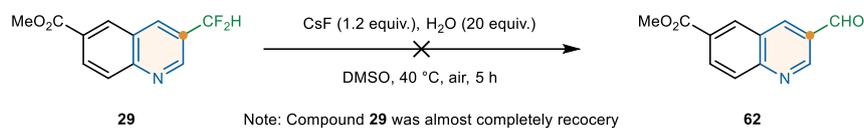


**Supplementary Fig. 4.** DSC measurement curve for phenyl *N*-triftosylhydrazone. (4.68 mg)

## 7. Mechanistic Considerations

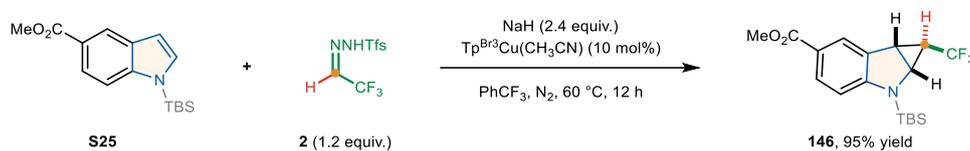
### 7.1 Controlled Experiment

#### 7.1.1 Identification of the Reaction Intermediate



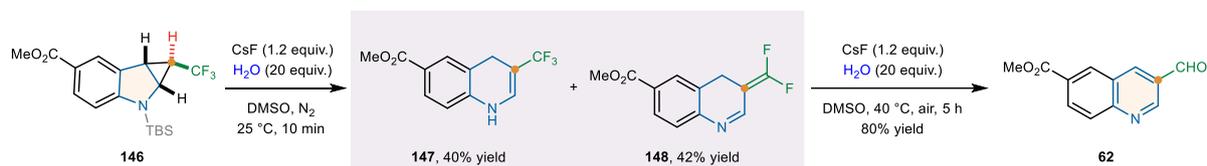
**Supplementary Fig. 5.** The conversion attempt of the compound **29** to the compound **62**

The compound **29** (71.1 mg, 0.3 mmol, 1.0 equiv.) was dissolved in DMSO (5.0 mL). Then H<sub>2</sub>O (20 equiv.) and CsF (54.7 mg, 0.36 mmol, 1.2 equiv.) were added into the reaction mixture. The reaction was continued for an additional 5 h at 40 °C. The experimental results showed that no product **62** was generated, while compound **29** was almost completely recovered.



**Supplementary Fig. 6.** Preparation of cyclopropane intermediate **146**

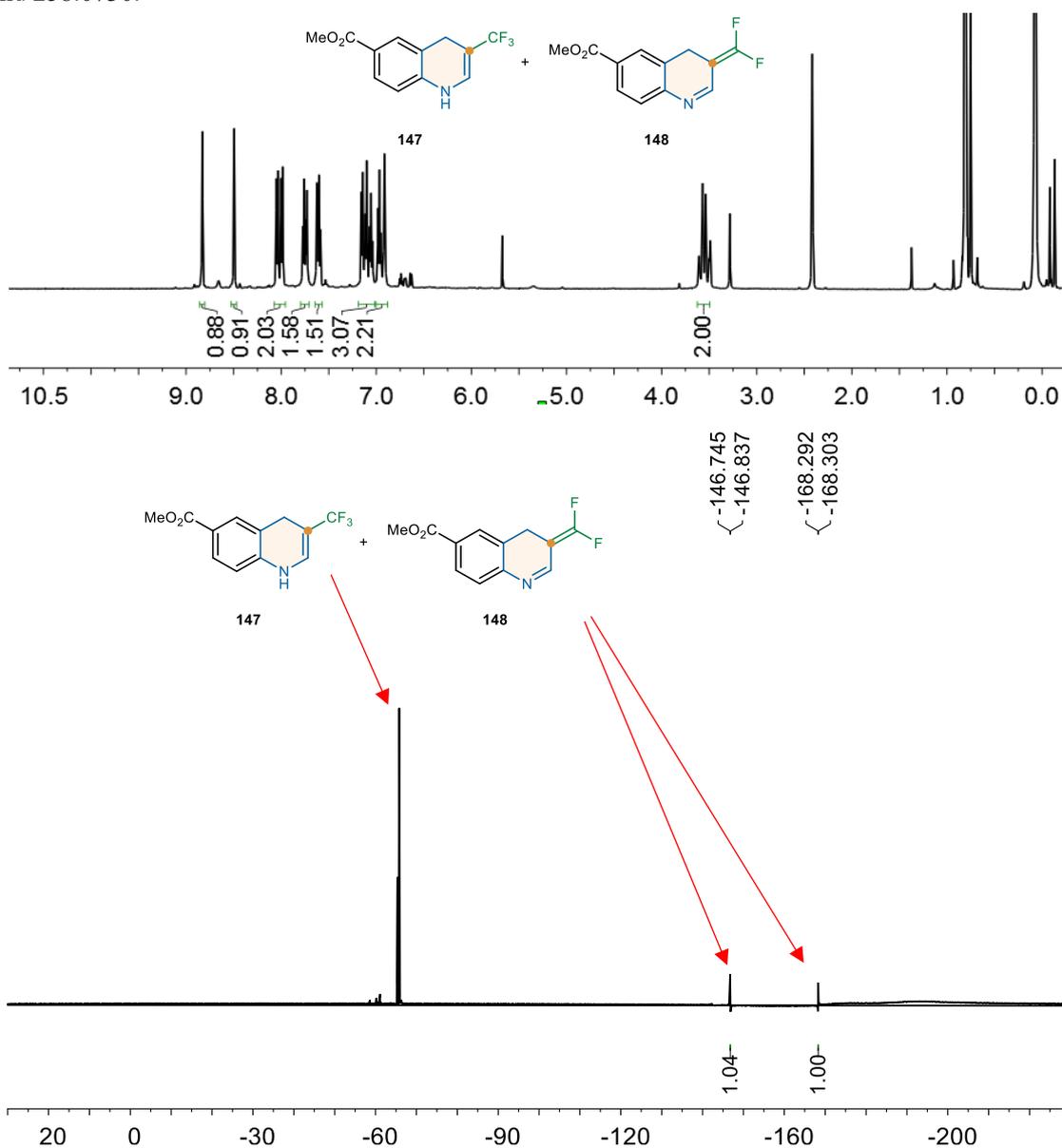
To an oven-dried screw-cap reaction tube were added TFHZ-Tfs **2** (115.3 mg, 0.36 mmol, 1.2 equiv.), NaH (28.8 mg, 0.72 mmol, 60 wt% dispersion in mineral oil, 2.4 equiv.), methyl 1-(*tert*-butyldimethylsilyl)-1*H*-indole-5-carboxylate **S25** (86.7 mg, 0.3 mmol, 1.0 equiv.), Tp<sup>Br<sub>3</sub></sup>Cu(CH<sub>3</sub>CN) (30.0 mg, 10.0 mol%) and PhCF<sub>3</sub> (10 mL) inside a glove box with nitrogen atmosphere. After transfer out of the glove box, the reaction was continued for an additional 12 h at 60 °C. The reaction mixture was filtered through a short pad of silica gel with DCM as an eluent. After removal of the solvent, the residue was purified by flash column chromatography on silica gel (using petroleum ether-EtOAc (100/1) as eluent) to give the product **146** (105.7mg, 95% yield), as a white solide, mp: 110-112 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.99 (s, 1H), 7.78 (d, *J* = 8.5 Hz, 1H), 6.73 (d, *J* = 8.5 Hz, 1H), 3.92 (s, 1H), 3.86 (s, 3H), 3.10 (d, *J* = 4.0 Hz, 1H), 0.99 (s, 9H), 0.80-0.73 (m, 1H), 0.43 (d, *J* = 17.0 Hz, 6H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 167.1, 154.7, 130.1, 129.8, 126.3, 126.2 (q, *J* = 270.0 Hz), 119.8, 110.6, 51.7, 44.2 (q, *J* = 4.5 Hz), 26.4, 24.9 (q, *J* = 4.5 Hz), 21.3 (q, *J* = 36.0 Hz), 20.2, -4.6. <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -64.25 (d, *J* = 7.3 Hz). HRMS (ESI) *m/z* calcd. for C<sub>18</sub>H<sub>25</sub>F<sub>3</sub>NO<sub>2</sub>Si<sup>+</sup> [M + H]<sup>+</sup> 372.1601, found 372.1594.



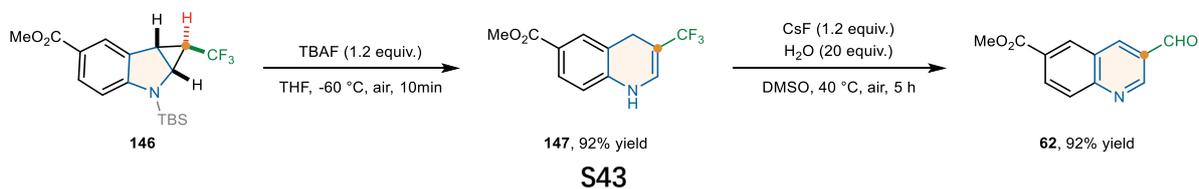
Compound **146** (0.1 mmol, 1.0 equiv.), CsF (0.12 mmol, 1.2 equiv.), and H<sub>2</sub>O (20 equiv.) in DMSO-*d*<sub>6</sub> (1.0 mL) were stirred at 25 °C for 10 min under N<sub>2</sub> atmosphere. The mixture was directly analyzed by <sup>1</sup>H NMR spectroscopy. The results showed that approximately 40% of the products **147** and 42% of the products **148** were produced in the reaction system. Product **147** can be separated by column chromatography, and the spectrum is shown below, while product **148** can not be separated by column chromatography.

Treating these mixtures of **147** and **148** to oxidative conditions in water furnished the quinoline-3-carboxaldehyde product **62** in 80% yield, indicating **147** or **148** could be the critical intermediate of the process.

**(147)**  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75-7.71 (m, 1H), 7.70 (s, 1H), 6.63 (d,  $J = 4.0$  Hz, 1H), 6.57 (d,  $J = 8.0$  Hz, 1H), 5.89 (s, 1H), 3.87 (s, 3H), 3.68 (s, 2H).  $^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ )  $\delta$  166.6, 141.4, 131.5, 129.4, 128.0 (q,  $J = 6.0$  Hz), 124.8 (q,  $J = 267.0$  Hz), 124.2, 98.5 (q,  $J = 33.0$  Hz) 118.5, 114.2, 51.9, 24.1.  $^{19}\text{F NMR}$  (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -68.22. **HRMS** (ESI)  $m/z$  calcd. for  $\text{C}_{12}\text{H}_{11}\text{F}_3\text{NO}_2^+$   $[\text{M} + \text{H}]^+$  258.0736, found 258.0730.

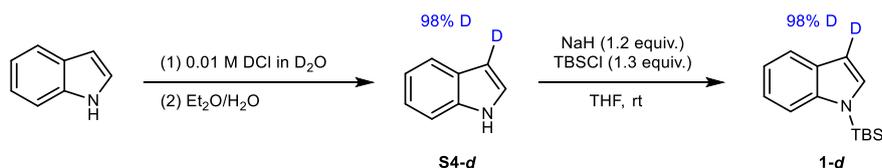


**Supplementary Fig. 7.** The  $^1\text{H NMR}$  spectrum and  $^{19}\text{F NMR}$  spectrum of of the mixture of **147** and **148**



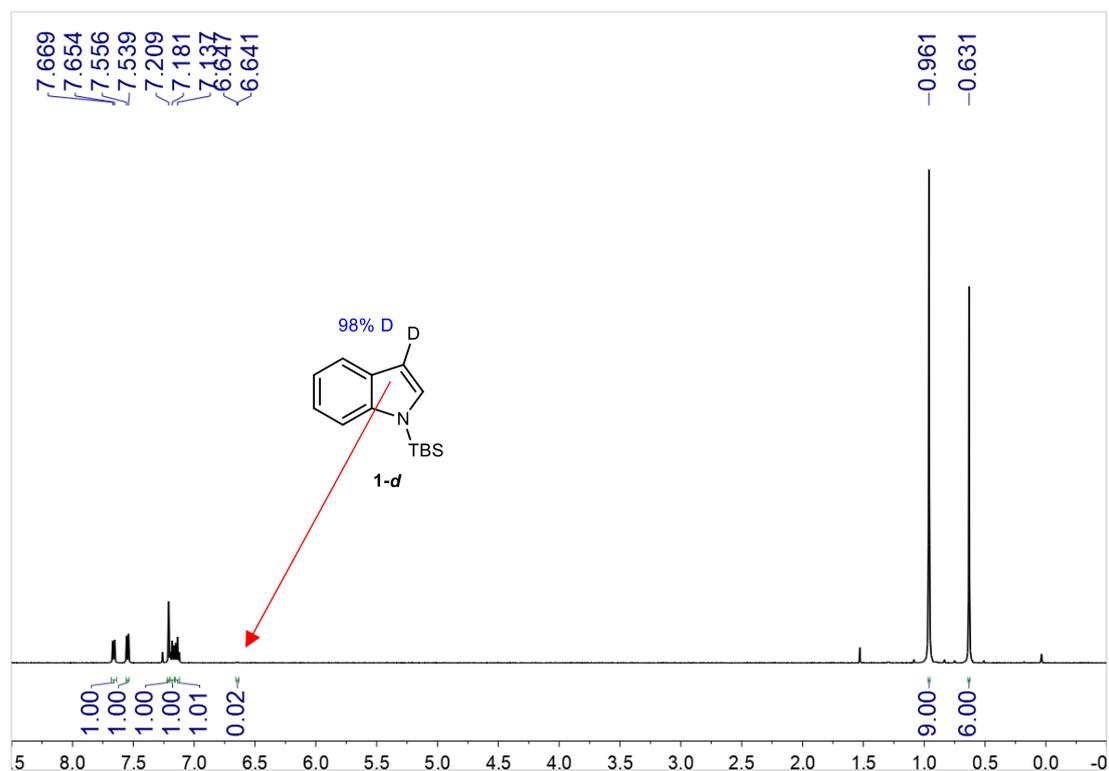
The TBAF (0.12 mL, 0.12 mmol, 1.0 mol/L in THF, 1.2 equiv.) was added into compound **146** (37.1 mg, 0.1 mmol, 1.0 equiv.) in THF (5.0 mL) at -60 °C, and continued stirring for 10 min. After completion of the reaction, the mixture was filtered through a short pad of silica gel (pre-treated with triethylamine) with DCM as an eluent. After removal of the solvent *in vacuo*, the residue was purified by flash chromatography on silica gel (pre-treated with trimethylamine, using petroleum ether-EtOAc (40/1) as eluent) to give the product **147** in 95% yield. Treating the compound **147** to oxidative conditions in water furnished the quinoline-3-carboxaldehyde product **62** in 90% yield.

### 7.1.2 Deuterium-Labeling Experiments

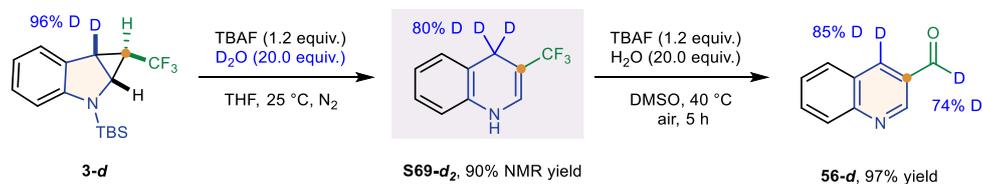


**Procedure:** The **S4-d** was prepared according to literature procedure. <sup>[22]</sup>Indole (585 mg, 5.0 mmol, 1.0 equiv.) was stirred in a 0.01 M solution of DCl in D<sub>2</sub>O (20 mL) at 60 °C for 4 h under N<sub>2</sub>. The reaction was cooled and extracted three times with dry Et<sub>2</sub>O. The organic layers were combined, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered and reduced under vacuum. The resulting oil was triturated in pentane to afford a colorless solid. The solid ([1,3-D]indole) was dissolved in a mixture of Et<sub>2</sub>O (20 mL) and H<sub>2</sub>O (10 mL) and stirred for 2 h at room temperature. The layers were separated and the aqueous layer extracted twice with Et<sub>2</sub>O (20 mL). The organic layers were combined, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered and reduced under vacuum to give the **S4-d** as a white solid.

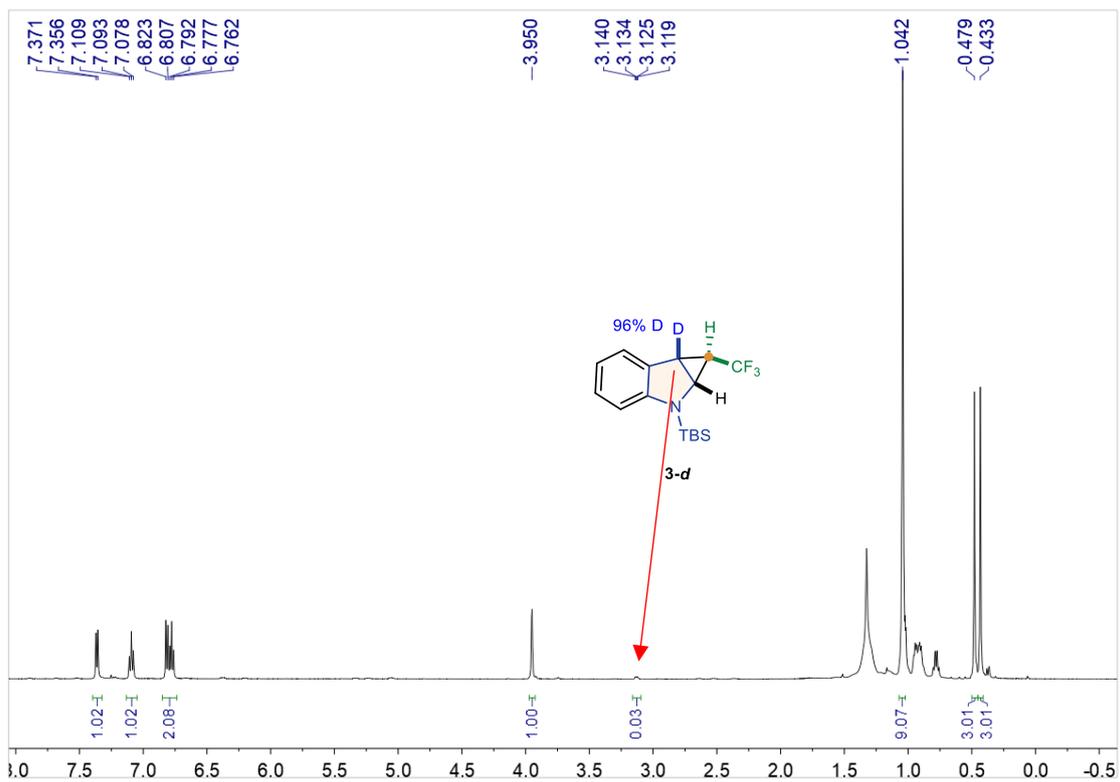
The **S4-d** in anhydrous THF (20 mL) was added dropwise to a stirred suspension of NaH (2.4 g, 6.0 mmol, 1.2 equiv., 60% dispersion in mineral oil) in THF (40 mL) at 0 °C. The mixture was allowed to slowly warm to room temperature over 30 min, cooled to 0 °C, and TBSCl (979.6 mg, 6.5 mmol, 1.3 equiv.) was added portionwise. The resulting mixture was slowly warmed to room temperature and stirred until full consumption of starting material as monitored by TLC. On completion, the reaction was quenched at 0 °C with sat. aqueous NH<sub>4</sub>Cl solution (10 mL) and extracted with EtOAc (20 mL). The combined organic phases were washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The crude mixture was concentrated under reduced pressure and purified by flash column chromatography (using petroleum ether as eluent) to afford product **1-d** as white solid (1.1 g, 95% yield). Compound **1-d**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.66 (d, *J* = 7.5 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.21 (s, 1H), 7.20-7.16 (m, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 6.64 (d, *J* = 3.0 Hz, 1H), 0.96 (s, 1H), 0.63 (s, 1H).



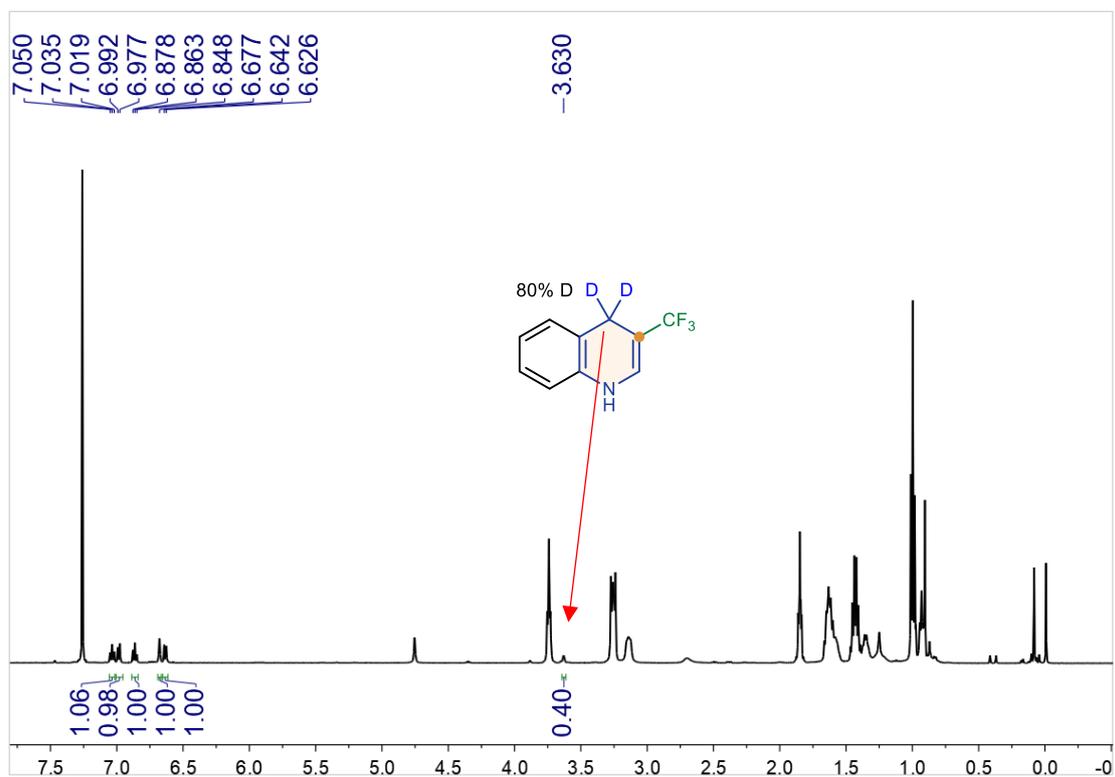
The  $^1\text{H}$  NMR spectrum of **1-d**



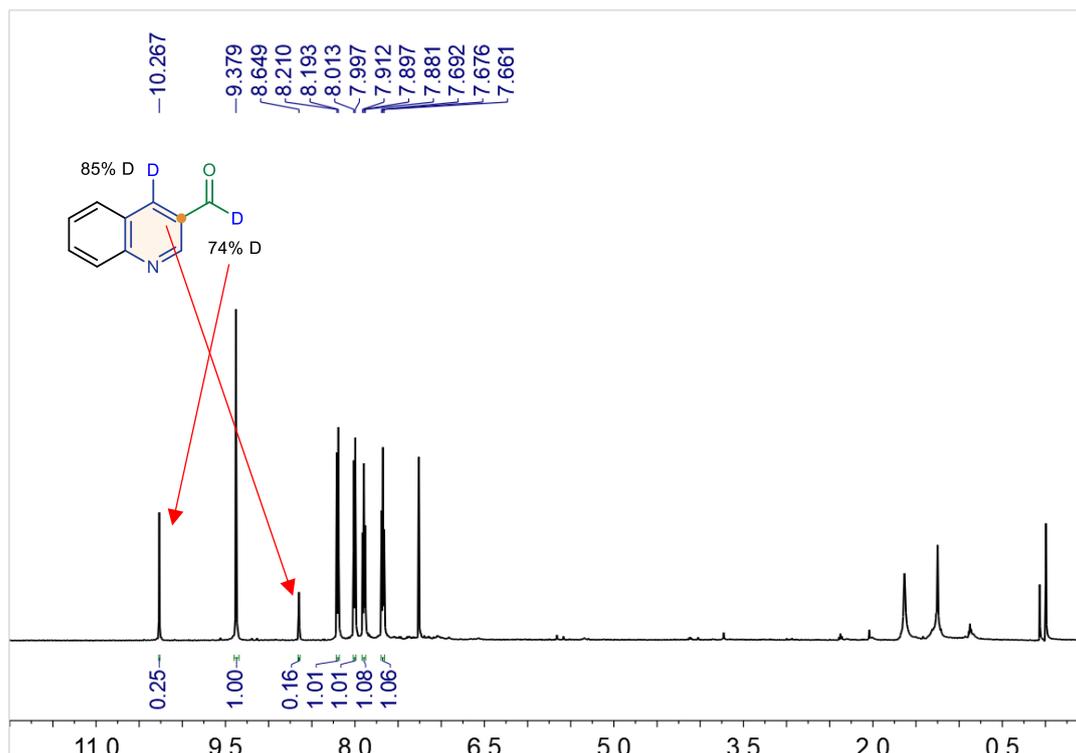
The compound **3-d** can be obtained under standard conditions. To an oven-dried screw-cap reaction tube were added **3-d** (31.4 mg, 0.1 mmol, 1.0 equiv.), TBAF (0.12 mL, 0.12 mmol, 1.0 mol/L in THF, 1.2 equiv.),  $\text{D}_2\text{O}$  (20 equiv.) were stirred at 25 °C for 10 min under  $\text{N}_2$  atmosphere. The mixture was directly analyzed by  $^1\text{H}$  NMR spectroscopy and HRMS. The intermediate **S69-d<sub>2</sub>** can be observed in the  $^1\text{H}$  NMR spectrum of the reaction mixture. And then  $\text{CsF}$ ,  $\text{H}_2\text{O}$  and DMSO were added into the reaction mixture, and stirred at 40 °C for 5 h under air atmosphere. The deuterated product **56-d** can be obtained. The deuterium ratio is shown below.



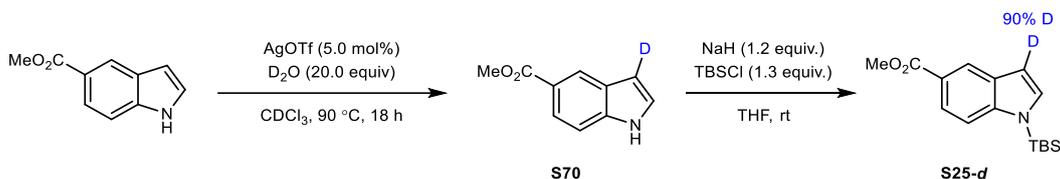
The <sup>1</sup>H NMR spectrum of **3-d<sub>2</sub>**



The <sup>1</sup>H NMR spectrum of **S69-d<sub>2</sub>**



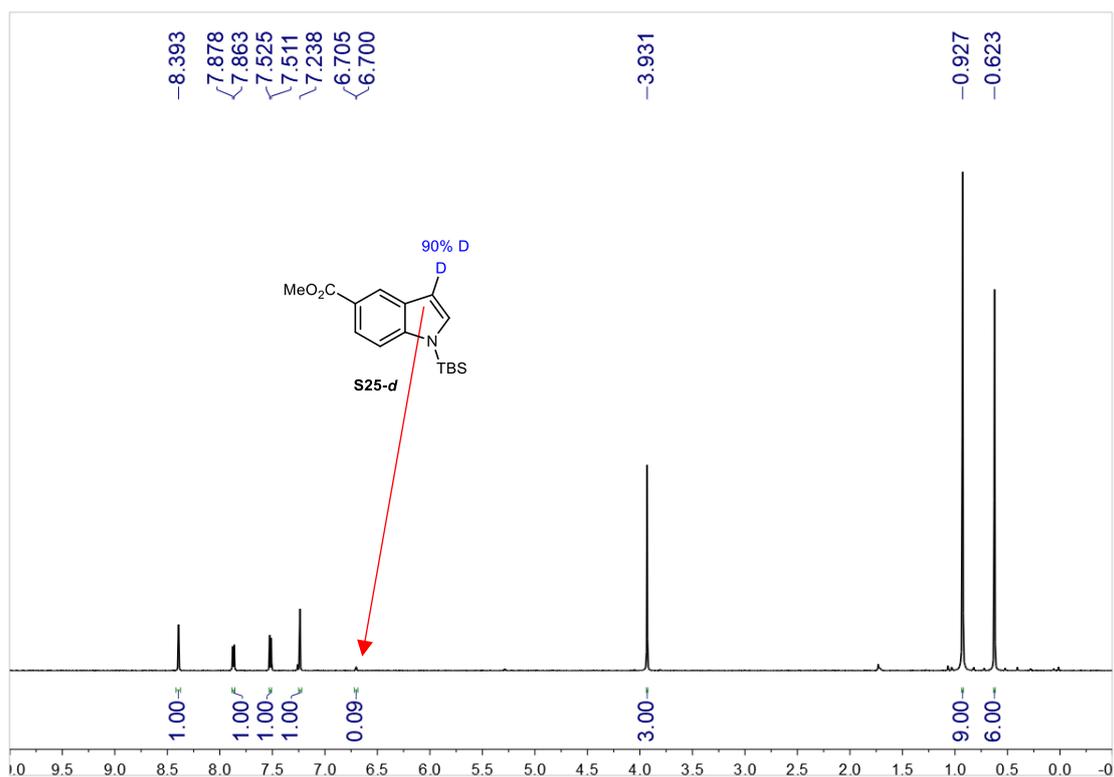
Supplementary Fig. 8. The  $^1\text{H}$  NMR spectrum of **56-d**



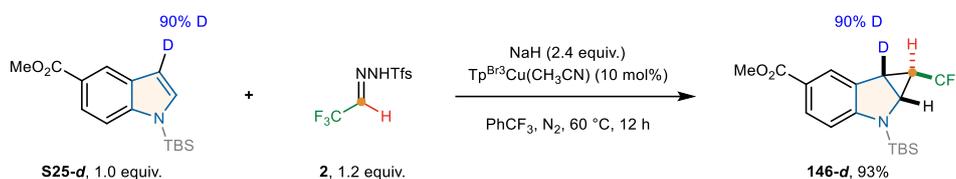
**Procedure:** The **S70** was prepared according to literature procedure. <sup>[23]</sup>A dried Schlenk tube were placed aromatic compounds methyl indole-5-carboxylate (875 mg, 5.0 mmol, 1.0 equiv.), AgOTf (30 mg, 0.25 mmol, 10 mol%), D<sub>2</sub>O (20 equiv) and CDCl<sub>3</sub> (15 mL). The reaction mixture was heated at 90 °C for 18 h. The mixture was then cooled to room temperature, diluted with 5 mL of ethyl acetate, filtered through a celite pad, and washed with EtOAc. The combined organic extracts were concentrated under vacuum to give deuterated products. The deuterium incorporation was determined by  $^1\text{H}$  NMR.

The **S70** in anhydrous THF (20 mL) was added dropwise to a stirred suspension of NaH (2.4 g, 6.0 mmol, 1.2 equiv., 60% dispersion in mineral oil) in THF (40 mL) at 0 °C. The mixture was allowed to slowly warm to room temperature over 30 min, cooled to 0 °C, and TBSCl (979.6 mg, 6.5 mmol, 1.3 equiv.) was added portionwise. The resulting mixture was slowly warmed to room temperature and stirred until full consumption of starting material as monitored by TLC. On completion, the reaction was quenched at 0 °C with sat. aqueous NH<sub>4</sub>Cl solution (10 mL) and extracted with EtOAc (20 mL). The combined organic phases were washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The crude mixture was concentrated under reduced pressure and purified by flash column chromatography (using petroleum ether-EtOAc (100/1) as eluent) to afford product **S25-d** as white solid (1.2 g, 87% yield).

**Compound S26-d:**  $^1\text{H}$  NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.39 (s, 1H), 7.87 (d,  $J$  = 9.0 Hz, 1H), 7.52 (d,  $J$  = 9.0 Hz, 1H), 7.24 (s, 1H), 6.70 (d,  $J$  = 3.0 Hz, 1H), 3.93 (s, 3H), 0.93 (s, 9H), 0.62 (s, 3H).

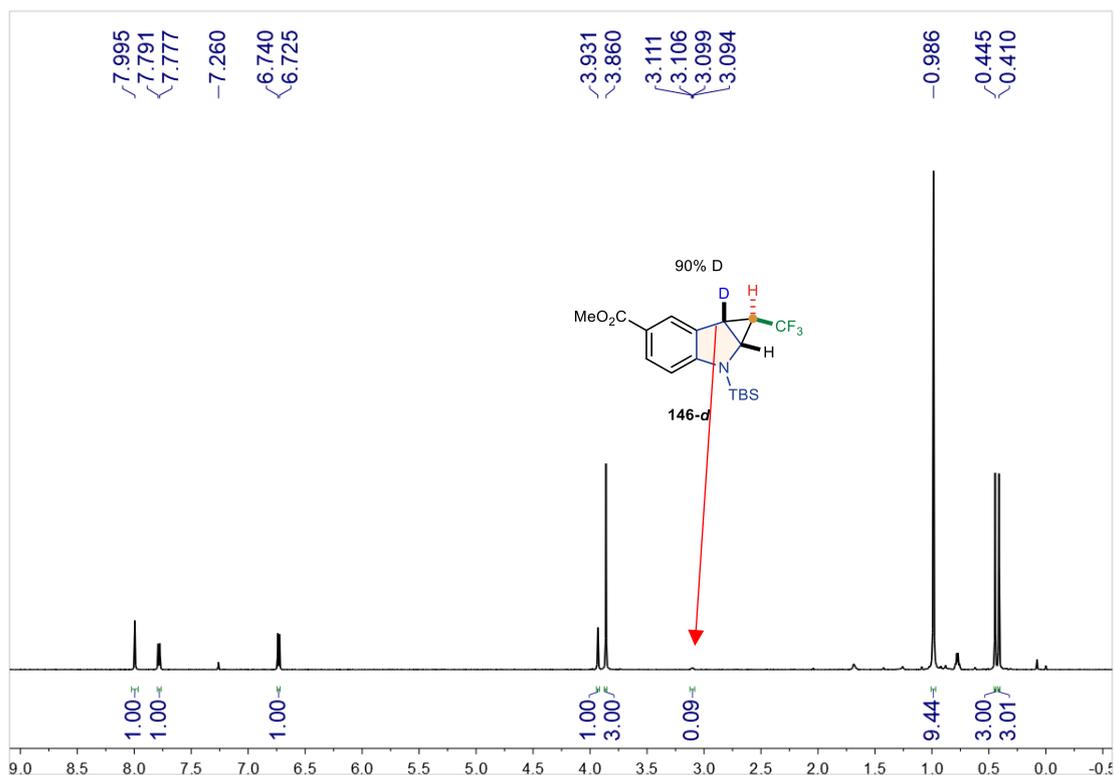


Supplementary Fig. 9. The  $^1\text{H}$  NMR spectrum of **S25-d**

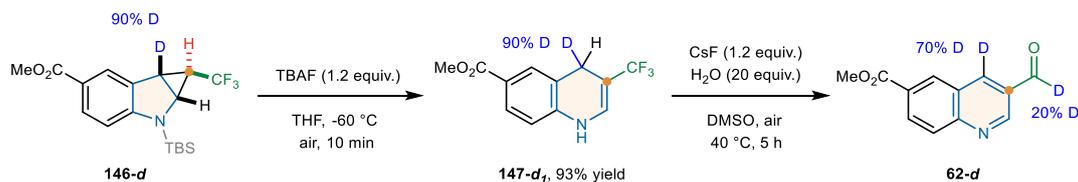


To an oven-dried screw-cap reaction tube were added TFHZ-Tfs **2** (115.3 mg, 0.36 mmol, 1.2 equiv.), NaH (28.8 mg, 0.72 mmol, 60 wt% dispersion in mineral oil, 2.4 equiv.), **S25-d** (87 mg, 0.3 mmol, 1.0 equiv.),  $\text{Tp}^{\text{Br}_3}\text{Cu}(\text{CH}_3\text{CN})$  (30.0 mg, 10.0 mol%) and  $\text{PhCF}_3$  inside a glove box with nitrogen atmosphere. After transfer out of the glove box, the reaction was continued for an additional 12 h at 60 °C. The reaction mixture was filtered through a short pad of silica gel with DCM as an eluent. After removal of the solvent *in vacuo*, the residue was purified by flash column chromatography on silica gel (using petroleum ether-EtOAc (100/1) as eluent) to give the product **146-d** (103.8 mg, 93% yield). The deuterium ratio is shown below.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 (s, 1H), 7.78 (d,  $J = 8.5$  Hz, 1H), 6.73 (d,  $J = 8.5$  Hz, 1H), 3.93 (s, 1H), 3.86 (s, 3H), 3.10 (d,  $J = 4.0$  Hz, 1H), 0.99 (s, 9H), 0.80-0.73 (m, 1H), 0.44 (s, 3H), 0.41 (s, 3H).

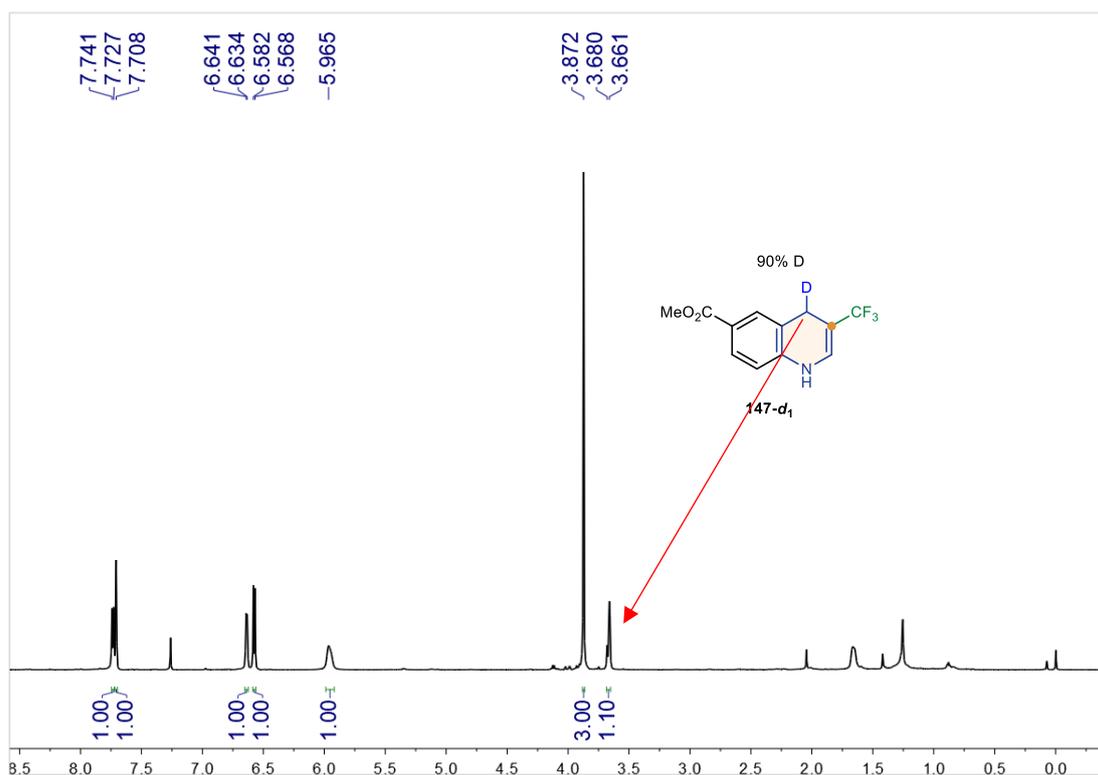


Supplementary Fig. 10. The  $^1\text{H}$  NMR spectrum of **146-d**

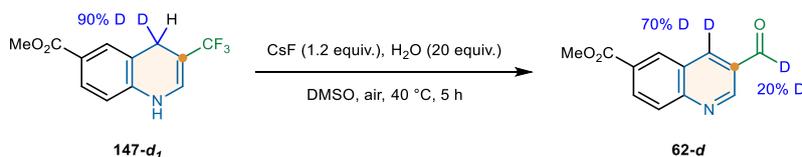


The TBAF (0.12 mL, 0.12 mmol, 1.0 mol/L in THF, 1.2 equiv.) was added into compound **146-d** (37.2 mg, 0.1 mmol) in THF (2.0 mL) at  $-60\text{ }^\circ\text{C}$ , and continued stirring for 10 min. After completion of the reaction, the mixture was filtered through a short pad of silica gel (pre-treated with triethylamine) with DCM as an eluent. After removal of the solvent *in vacuo*, the residue was purified by flash chromatography on silica gel (pre-treated with trimethylamine, using petroleum ether-EtOAc (40/1) as eluent) to give the product **147-d<sub>1</sub>**. The deuterium ratio is shown below.

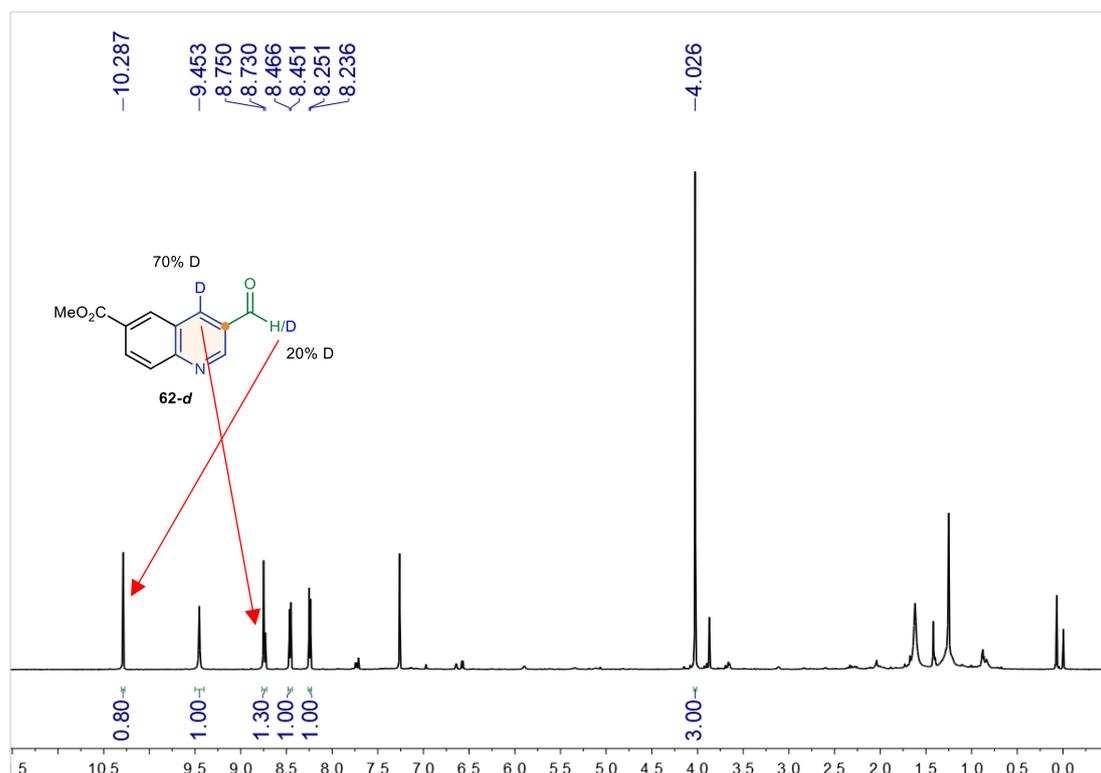
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75-7.71 (m, 1H), 7.71 (s, 1H), 6.64 (d,  $J = 4.0$  Hz, 1H), 6.58 (d,  $J = 8.0$  Hz, 1H), 5.89 (s, 1H), 3.87 (s, 3H), 3.68 (s, 2H).



**Supplementary Fig. 11.** The  $^1\text{H}$  NMR spectrum of **147-d<sub>1</sub>**

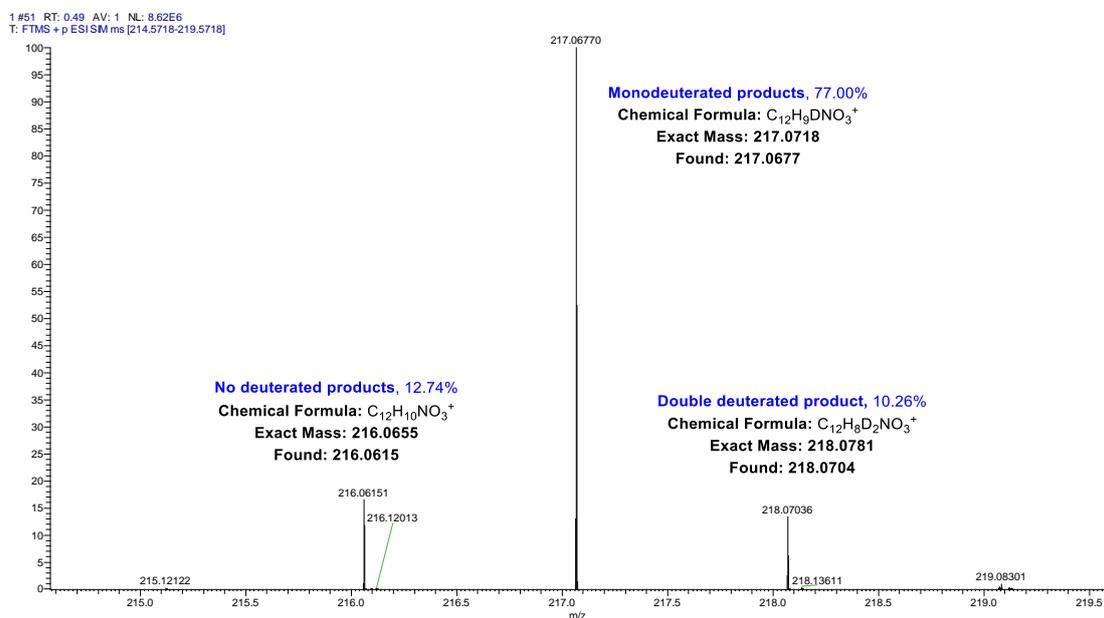


Treating the compound **147-d<sub>1</sub>** to oxidative conditions in water furnished the quinoline-3-carboxaldehyde product **62-d** in 90% yield. We can see from this that almost all of the deuterium elements in molecule **147-d<sub>1</sub>** are retained inside molecule **62-d**. Therefore, this indirectly proves that 1,3-H shift is not an intermolecular process. The deuterium ratio is shown below:



Supplementary Fig. 12. The  $^1\text{H}$  NMR spectrum of **62-d**

We can see from this that almost all of the deuterium elements in molecule **148-d** are retained inside molecule **62-d**. Meanwhile, according to the isotope distribution in the the HRMS data, we found that the mono-deuterated product **62-d** accounts for the majority of the proportion.



Supplementary Fig. 13. The  $^1\text{H}$  NMR spectrum of **62-d**

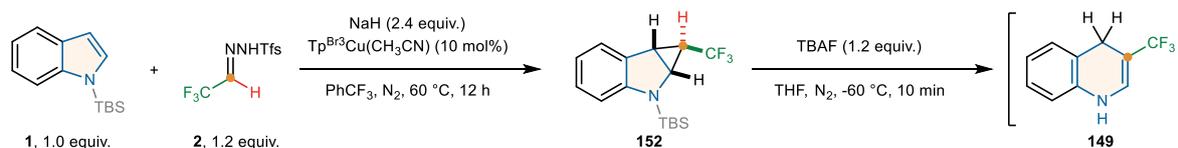
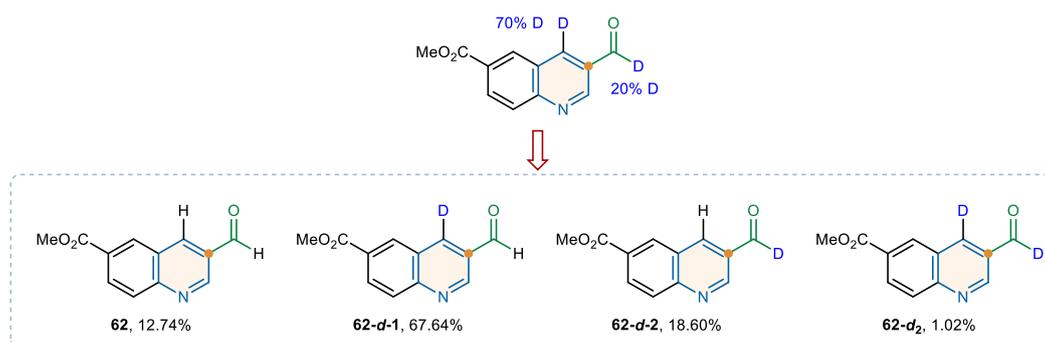
The contribution of natural abundance for no deuterated product **62** to monodeuterated product **62-d** can be ignored due to the the percentage of no deuterated product is relatively low. However, the contribution of natural abundance for monodeuterated product **62-d** to double deuterated product

**62-d<sub>2</sub>** needs to be calculated. According to the formula  $(a+b)^n$  (a, light isotope abundance; b, heavy isotope abundance; n, the number of atoms in this element; considering only the isotopic distribution of carbon element), the contribution of monodeuterated product **62-d** to double deuterated product **62-d<sub>2</sub>** is about 12% of its own. Therefore, it can be calculated that the actual percentage content of monodeuterated product **62-d** is 86.24%, and the actual percentage content of double deuterated product **62-d<sub>2</sub>** is 1.02%.

**Supplementary Table 9.** The actual percentage content of three types of products.

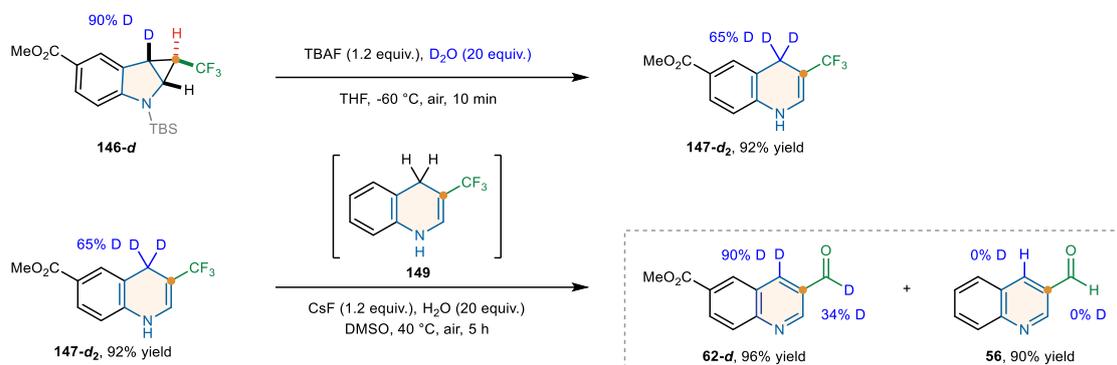
Compound	Calcd. for	[M+H] <sup>+</sup>	Found	Ratio (%)
<b>62</b>	C <sub>12</sub> H <sub>10</sub> NO <sub>3</sub> <sup>+</sup>	216.06552	216.0615	12.74%
<b>62-d</b>	C <sub>12</sub> H <sub>9</sub> DNO <sub>3</sub> <sup>+</sup>	217.07180	217.0677	86.24%
<b>62-d<sub>2</sub></b>	C <sub>12</sub> H <sub>8</sub> D <sub>2</sub> NO <sub>3</sub> <sup>+</sup>	218.07807	218.0704	1.02%

In addition, the percentage content of **62-d-1** and **62-d-2** can be calculated by the deuterium ratio between carbonyl carbon position and C4-position. We can see from this that the hydrogen at the carbonyl carbon come from the C4-position.

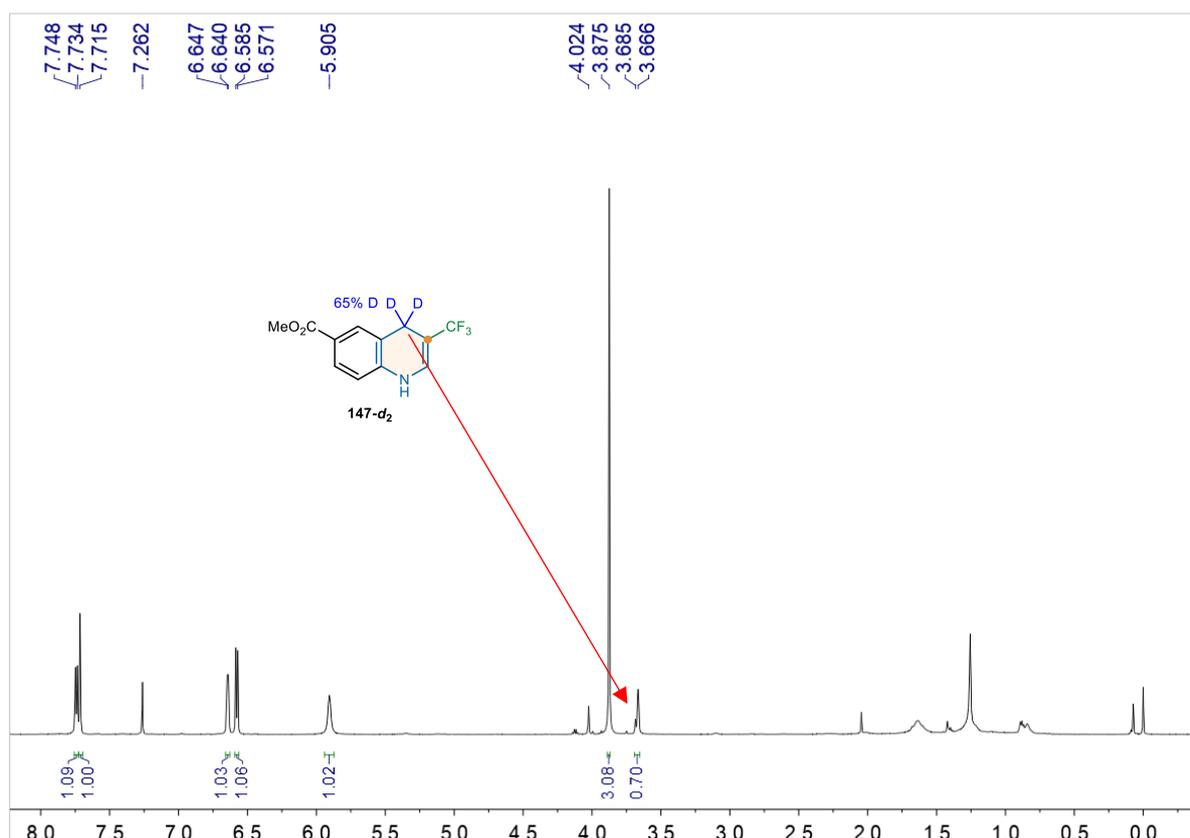


To an oven-dried screw-cap reaction tube were added TFHZ-Tfs **2** (115.3 mg, 0.36 mmol, 1.2 equiv.), NaH (28.8 mg, 0.72 mmol, 60 wt% dispersion in mineral oil, 2.4 equiv.), *N*-TBS indole **1** (69.4 mg, 0.3 mmol, 1.0 equiv.), TpBr<sub>3</sub>Cu(CH<sub>3</sub>CN) (30.0 mg, 10.0 mol%) and PhCF<sub>3</sub> inside a glove box with nitrogen atmosphere. After transfer out of the glove box, the reaction was continued for an additional 12 h at 60 °C. The reaction mixture was filtered through a short pad of silica gel with DCM as an eluent. After removal of the solvent *in vacuo*, the residue was purified by flash column chromatography on silica gel (using petroleum ether as eluent) to give the product **152** (85.4 mg, 91% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.34 (d, *J* = 7.5 Hz, 1H), 7.06 (dd, *J* = 11.5, 4.0 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.75 (dd, *J* = 11.5, 4.0 Hz, 1H), 3.92 (dd, *J* = 7.0, 2.0 Hz, 1H), 3.10 (dd, *J* = 7.0, 3.0 Hz, 1H), 1.00 (s, 9H), 0.44 (s, 3H), 0.40 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 150.3, 129.7, 127.2, 126.6 (q, *J* = 270.0 Hz), 124.6, 117.8, 111.4, 43.5

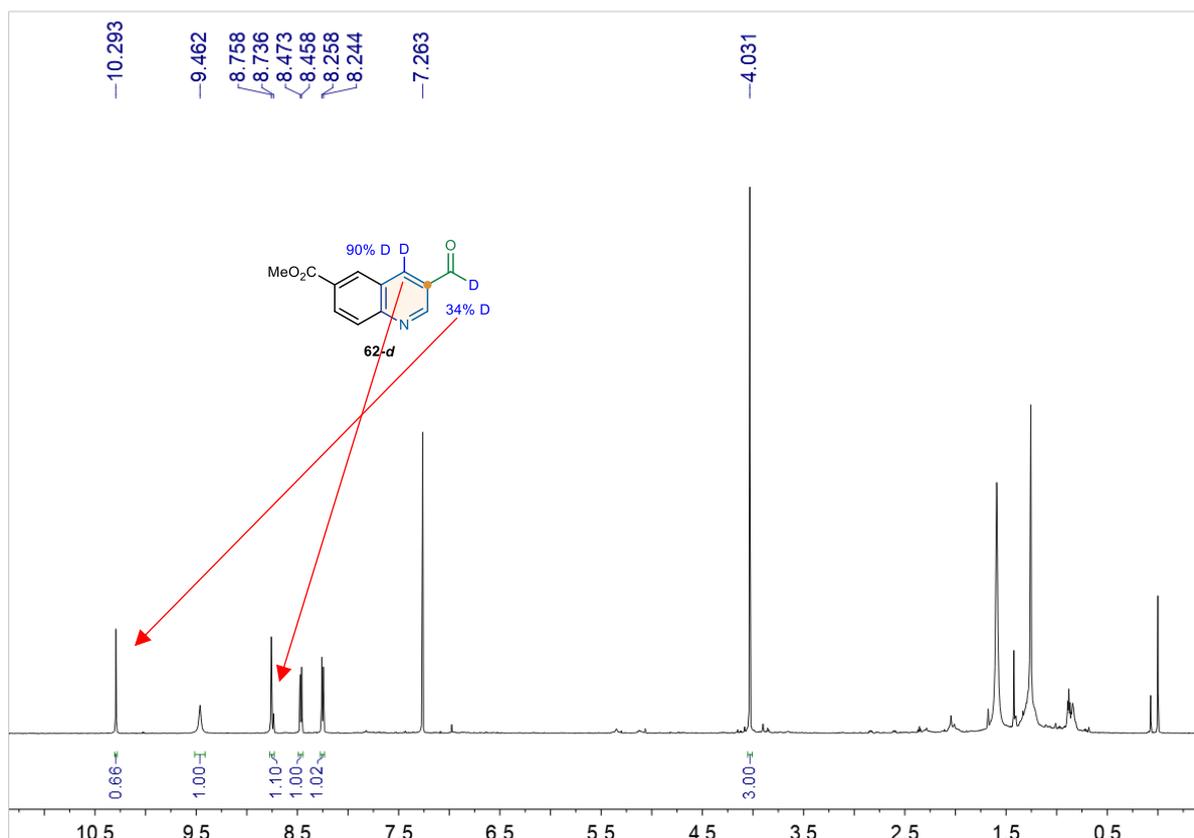
(q,  $J = 3.0$  Hz), 26.5, 25.4 (q,  $J = 3.0$  Hz), 21.1 (q,  $J = 36.0$  Hz), 20.2, -4.65, -4.68.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -64.04 (d,  $J = 7.3$  Hz). HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{16}\text{H}_2\text{F}_3\text{NSi}^+$   $[\text{M} + \text{H}]^+$  314.1546, found 314.1544.



The **147-d<sub>2</sub>** can be obtained in the presence of  $\text{D}_2\text{O}$  by treating compound **146-d** with TBAF. Mix **147-d<sub>2</sub>** and **149** in equal amounts and stir in the presence of CsF,  $\text{H}_2\text{O}$ , DMSO at  $40\text{ }^\circ\text{C}$  for 5 h. The results showed that the deuterium element in product **62-d** did not run towards product **56**. Therefore, this indirectly proves that 1,3-H shift is not an intermolecular process.

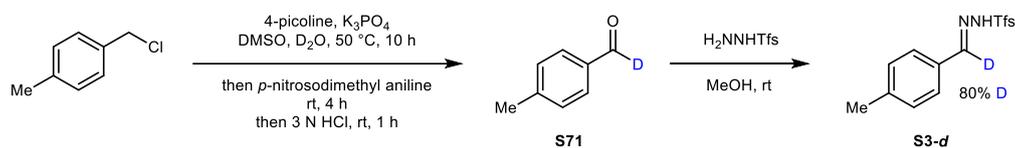


Supplementary Fig. 14. The  $^1\text{H}$  NMR spectrum of **147-d<sub>2</sub>**

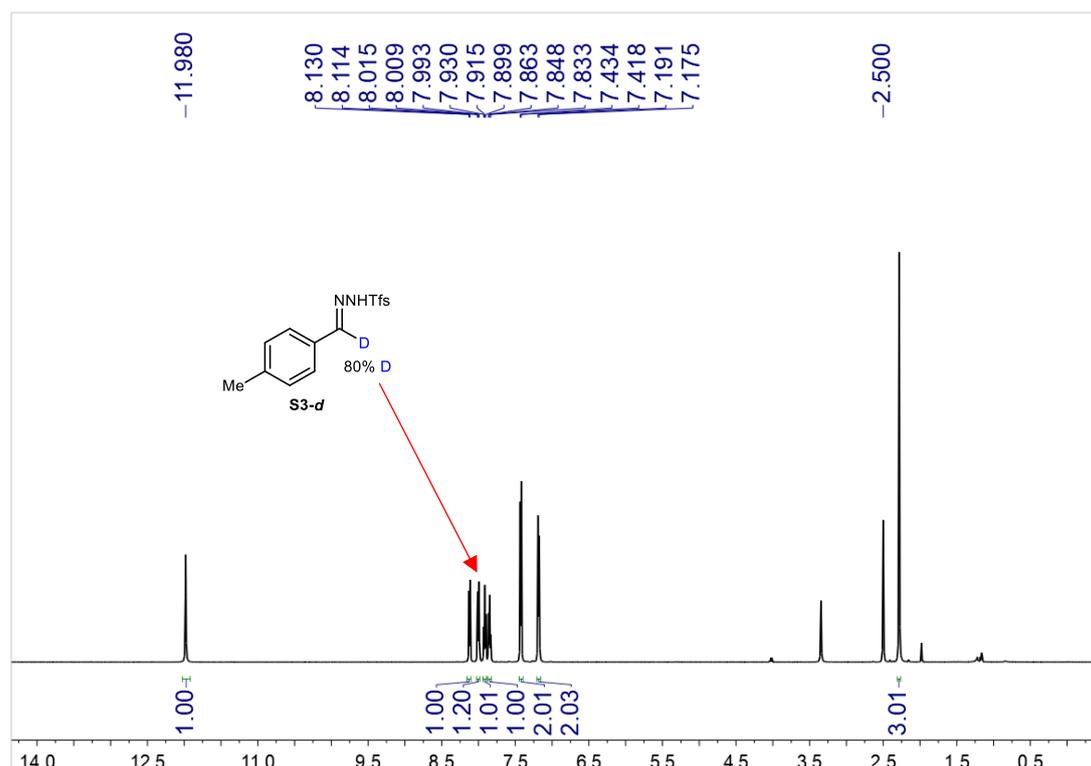


Supplementary Fig. 15. The  $^1\text{H}$  NMR spectrum of **62-d**

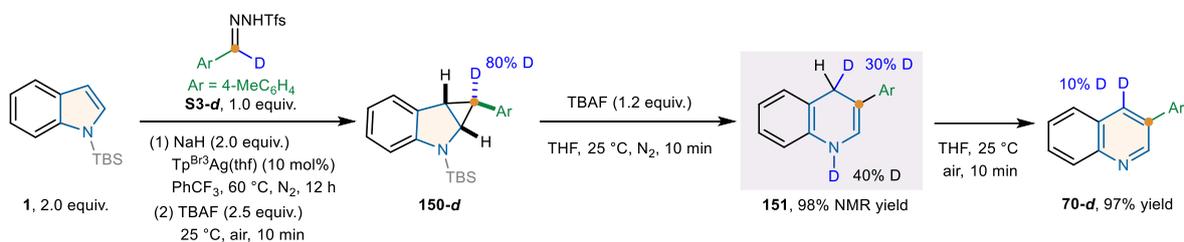
#### For Aryl-substituted *N*-trifosylhydrazone



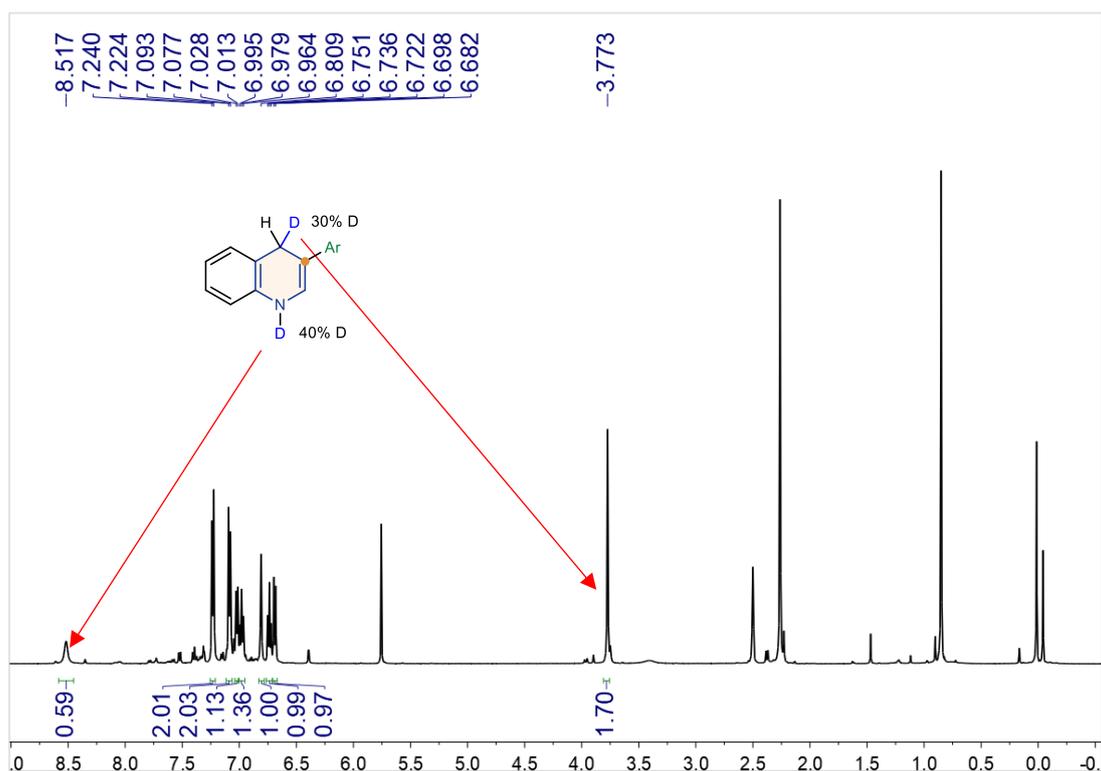
[24]To a pre-mixed solution of DMSO (3 mL) and  $\text{D}_2\text{O}$  (1 mL), 1-(chloromethyl)-4-methylbenzene (281.2 mg, 2.0 mmol), 4-picoline (745.0 mg, 8.0 mmol),  $\text{K}_3\text{PO}_4$  (169.6 mg, 8.0 mmol) was added. The resulting mixture was stirred at 50 °C for 10 h. *p*-Nitrosodimethyl aniline (600.7 mg, 4.0 mmol) was then added at room temperature. The mixture was continuously stirred for 4 h at room temperature before slowly poured to stirred HCl (3 N, 12 mL) at 0 °C. The resulting mixture was stirred vigorously for 1 h before extracted with ethyl acetate (10 mL) for 3 times. The combined organic phase was washed with brine and dried with anhydrous  $\text{Na}_2\text{SO}_4$ . The crude product was vacuo evaporated and purified by flash column chromatography on a silica gel (using petroleum ether-EtOAc (100/1) as eluent) to give corresponding deuterated 4-methylbenzaldehyde **S71** (179.1 mg, 74% yield). And then preparing the deuterated *N*-trifosylhydrazone **S3-d** according to the literature.<sup>[3]</sup>



**Supplementary Fig. 16.** The  $^1\text{H}$  NMR spectrum of deuterated *N*-sulfonylhydrazone **S3-d**  
 $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  11.98 (s, 1H), 8.12 (d,  $J = 8.0$  Hz, 1H), 8.03-7.96 (m, 2H), 7.91 (t,  $J = 7.5$  Hz, 1H), 7.85 (t,  $J = 7.5$  Hz, 1H), 7.43 (d,  $J = 8.0$  Hz, 2H), 7.18 (d,  $J = 8.0$  Hz, 2H), 2.28 (s, 3H).

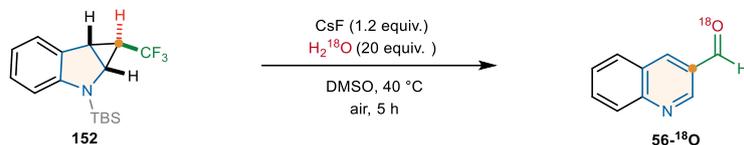


The compound **150-d** can be obtained under the standard conditions. Then compound **150-d** (28.5 mg, 0.1 mmol, 1.0 equiv.), TBAF (0.12 mL, 0.12 mmol, 1.2 equiv., 1.0 mol/L in THF) and THF (3.0 mL) were stirred at 25 °C for 10 min under  $\text{N}_2$  atmosphere. The mixture was directly analyzed by  $^1\text{H}$  NMR spectroscopy and HRMS. The deuterium ratio of **151** can be observed in the  $^1\text{H}$  NMR spectrum of the reaction mixture. Then the reaction was continued for an additional 10 min at 25 °C under air atmosphere. The product **70-d** (97% yield). The deuterium ratio is shown below.



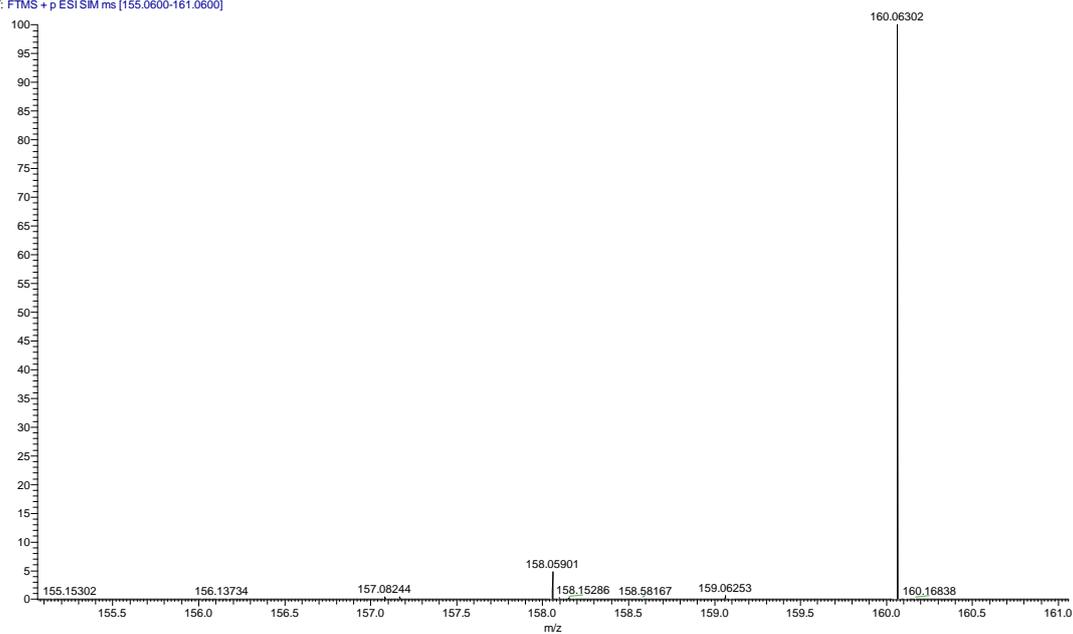
Supplementary Fig. 17.  $^1\text{H}$  NMR spectrum of **151**.

### 7.1.3 $^{18}\text{O}$ -Labeling Experiments



Compound **152** (93.9 mg, 0.3 mmol, 1.0 equiv.), CsF (54.7 mg, 0.36 mmol, 1.2 equiv.), and  $\text{H}_2^{18}\text{O}$  (20 equiv.) in DMSO (5.0 mL) were stirred at 25 °C for 10 min. After completion of the reaction, the mixture was diluted with DCM, washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and the solvent was evaporated under reduced pressure to leave a crude product, which was purified by flash column chromatography on silica gel (pre-treated with trimethylamine, using petroleum ether-EtOAc (40/1) as eluent) to give the product **56- $^{18}\text{O}$** . The product was analyzed by HRMS.

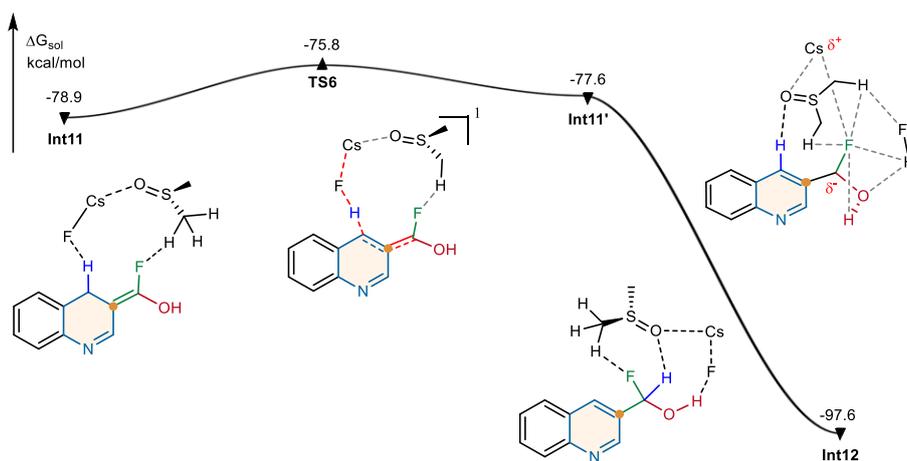
2\_20231025105135 #11 RT: 0.12 AV: 1 NL: 2.43E6  
T: FTMS + p ESI SIM ms [155.0600-161.0600]



**Supplementary Fig. 18.** HRMS of  $56\text{-}^{18}\text{O}$ , HRMS (ESI) m/z, found 160.0630.

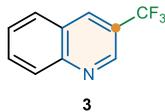
## 7.2 Computational Details

All DFT calculations described in this work were carried out with Gaussian16 suite of programs<sup>[25]</sup>. All geometry optimizations were presented by using the M06 functional<sup>[26]</sup> by using the SMD solvent (DMSO) model<sup>[27]</sup>. The Cs atom was represented with the effective core potential SDD basis set<sup>[28,29]</sup>, all the other atoms were described with 6-31G(d,p) basis set.<sup>[30-32]</sup> Intrinsic Reaction Paths (IRPs)<sup>[33,34]</sup> were traced from the various transition structures to obtain the connected intermediates. The nature of the local minima was established with analytical frequencies calculations and geometry optimizations were computed without any symmetry constraints. 3D structures of optimized geometries were generated using CYLview visualization software.<sup>[35]</sup>



**Supplementary Fig. 19.** A CsF/DMSO-assisted formal 1,3-H transfer of enol intermediate **Int11** with CF<sub>3</sub>-substituted carbenes. Allyl carbon anion intermediate **Int11'** was firstly formed with an energy barrier of 3.1 kcal/mol, the HF-DMSO-Cs adduct then give the H atom to the allyl carbon anion instantly to form **Int12**.

## 8. Characterization Data of Products



### (3) 3-(Trifluoromethyl)quinolone

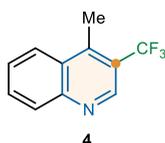
Prepared according to **General Procedure A** using TFHZ-Tfs **2** (115.3 mg, 0.36 mmol) and *N*-TBS indole (69.4 mg, 0.3 mmol) afforded **3** (50.9 mg, 86% yield) as a white solid; mp: 38-40 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.10 (d, *J* = 2.0 Hz, 1H), 8.44 (s, 1H), 8.19 (d, *J* = 8.5 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.88-7.82 (m, 1H), 7.66 (t, *J* = 7.5 Hz, 1H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 149.3, 146.0 (q, *J* = 3.5 Hz), 133.9 (q, *J* = 4.5 Hz), 131.7, 129.6, 128.6, 128.0, 126.2, 123.7 (q, *J* = 271.5 Hz), 123.6 (q, *J* = 33.0 Hz).

<sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -61.81.

HRMS (ESI) *m/z* calcd. for C<sub>10</sub>H<sub>7</sub>F<sub>3</sub>N<sup>+</sup> [M + H]<sup>+</sup> 198.0525, found 198.0528.



### (4) 4-Methyl-3-(trifluoromethyl)quinolone

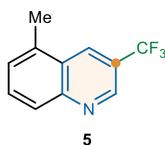
Prepared according to **General Procedure A** using TFHZ-Tfs **2** (115.3 mg, 0.36 mmol) and 1-(*tert*-butyldimethylsilyl)-3-methyl-1*H*-indole (73.6 mg, 0.3 mmol) afforded **4** (12.7 mg, 20% yield) as a white solid; mp: 58-60 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.07 (s, 1H), 8.17 (t, *J* = 7.5 Hz, 2H), 7.83 (t, *J* = 7.5 Hz, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 2.87 (s, 3H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 149.0, 145.9 (q, *J* = 6.0 Hz), 145.1 (q, *J* = 1.5 Hz), 131.2, 130.3, 127.6, 127.3, 124.32, 124.30 (q, *J* = 273.0 Hz), 121.9 (q, *J* = 30.0 Hz), 14.7 (q, *J* = 1.5 Hz).

<sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -58.67.

HRMS (ESI) *m/z* calcd. for C<sub>11</sub>H<sub>9</sub>F<sub>3</sub>N<sup>+</sup> [M + H]<sup>+</sup> 212.0682, found 212.0684.



### (5) 5-Methyl-3-(trifluoromethyl)quinoline

Prepared according to **General Procedure A** using TFHZ-Tfs **2** (115.3 mg, 0.36 mmol) and 1-(*tert*-butyldimethylsilyl)-4-methyl-1*H*-indole (73.6 mg, 0.3 mmol) afforded **5** (46.9 mg, 74% yield) as a white solid; mp: 40-42 °C.

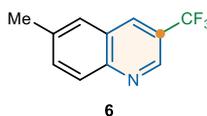
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.10 (d, *J* = 2.0 Hz, 1H), 8.60 (s, 1H), 8.04 (d, *J* = 8.5 Hz, 1H), 7.77-7.71 (m, 1H), 7.49 (d, *J* = 7.0 Hz, 1H), 2.75 (s, 3H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 149.8, 145.6 (q, *J* = 3.0 Hz), 135.7, 131.5, 130.4 (q, *J* = 4.5 Hz), 128.4, 127.8, 125.8, 123.8 (q, *J* = 270.0 Hz), 123.1 (q, *J* = 31.5 Hz), 18.5.

<sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -61.58.

**HRMS** (ESI)  $m/z$  calcd. for  $C_{11}H_9F_3N^+$   $[M + H]^+$  212.0682, found 212.0684.

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**(6) 6-Methyl-3-(trifluoromethyl)quinoline**

Prepared according to **General Procedure A** using TFHZ-Tfs **2** (115.3 mg, 0.36 mmol) and 1-(*tert*-butyldimethylsilyl)-5-methyl-1*H*-indole (73.6 mg, 0.3 mmol) afforded **6** (53.2 mg, 84% yield) as a white solid; mp: 68-70 °C.

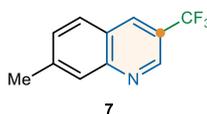
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.03 (d,  $J = 2.0$  Hz, 1H), 8.35 (s, 1H), 8.07 (d,  $J = 9.0$  Hz, 1H), 7.71-7.65 (m, 2H), 2.58 (s, 3H).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 148.0, 145.1 (q,  $J = 4.5$  Hz), 138.2, 134.1, 133.2 (q,  $J = 4.5$  Hz), 129.2, 127.3, 126.3, 123.8 (q,  $J = 270.0$  Hz), 123.5 (q,  $J = 32.5$  Hz), 21.6.

**<sup>19</sup>F NMR** (470 MHz, CDCl<sub>3</sub>) δ -61.76.

**HRMS** (ESI)  $m/z$  calcd. for  $C_{11}H_9F_3N^+$   $[M + H]^+$  212.0682, found 212.0683.

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**(7) 7-Methyl-3-(trifluoromethyl)quinoline**

Prepared according to **General Procedure A** using TFHZ-Tfs **2** (115.3 mg, 0.36 mmol) and 1-(*tert*-butyldimethylsilyl)-6-methyl-1*H*-indole (73.6 mg, 0.3 mmol) afforded **7** (55.1 mg, 87% yield) as a white solid; mp: 51-53 °C.

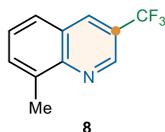
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.05 (s, 1H), 8.40 (s, 1H), 7.96 (s, 1H), 7.82 (d,  $J = 8.5$  Hz, 1H), 7.50 (d,  $J = 8.5$  Hz, 1H), 2.62 (s, 3H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 149.6, 146.0 (q,  $J = 3.5$  Hz), 142.6, 133.5 (q,  $J = 4.5$  Hz), 130.3, 128.6, 128.2, 124.3, 123.8 (q,  $J = 271.5$  Hz), 122.7 (q,  $J = 33.0$  Hz), 22.0.

**<sup>19</sup>F NMR** (564 MHz, CDCl<sub>3</sub>) δ -61.65.

**HRMS** (ESI)  $m/z$  calcd. for  $C_{11}H_9F_3N^+$   $[M + H]^+$  212.0682, found 212.0684.

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**(8) 8-Methyl-3-(trifluoromethyl)quinoline**

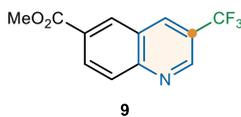
Prepared according to **General Procedure A** using TFHZ-Tfs **2** (115.3 mg, 0.36 mmol) and 1-(*tert*-butyldimethylsilyl)-7-methyl-1*H*-indole (73.6 mg, 0.3 mmol) afforded **8** (51.3 mg, 81% yield) as a white solid; mp: 39-41 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.12 (d,  $J = 2.0$  Hz, 1H), 8.42 (s, 1H), 7.77 (d,  $J = 8.0$  Hz, 1H), 7.70 (d,  $J = 7.0$  Hz, 1H), 7.55 (t,  $J = 7.5$  Hz, 1H), 2.84 (s, 3H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 148.4, 144.8 (q,  $J = 3.0$  Hz), 137.6, 134.1 (q,  $J = 4.5$  Hz), 131.8, 127.8, 126.6, 126.3, 123.8 (q,  $J = 270.0$  Hz), 123.3 (q,  $J = 31.5$  Hz), 18.0.

**<sup>19</sup>F NMR** (564 MHz, CDCl<sub>3</sub>) δ -61.77.

**HRMS** (ESI)  $m/z$  calcd. for  $C_{11}H_9F_3N^+$   $[M + H]^+$  212.0682, found 212.0684.



**(9) Methyl 3-(trifluoromethyl)quinoline-6-carboxylate**

Prepared according to **General Procedure A** using TFHZ-Tfs **2** (115.3 mg, 0.36 mmol) and methyl 1-(*tert*-butyldimethylsilyl)-1*H*-indole-5-carboxylate (86.8 mg, 0.3 mmol) afforded **9** (69.8 mg, 91% yield) as a white solid; mp: 102-104 °C.

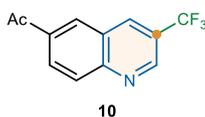
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.17 (d, *J* = 2.0 Hz, 1H), 8.68 (d, *J* = 1.5 Hz, 1H), 8.54 (s, 1H), 8.42 (dd, *J* = 9.0, 2.0 Hz, 1H), 8.22 (d, *J* = 9.0 Hz, 1H), 4.01 (s, 3H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 166.0, 151.0, 148.1 (q, *J* = 3.0 Hz), 135.1 (q, *J* = 4.5 Hz), 131.5, 131.2, 130.0, 129.6, 125.5, 124.4 (q, *J* = 33.0 Hz), 123.4 (q, *J* = 271.5 Hz), 52.6.

**<sup>19</sup>F NMR** (564 MHz, CDCl<sub>3</sub>) δ -62.00.

**HRMS** (ESI) *m/z* calcd. for C<sub>12</sub>H<sub>9</sub>F<sub>3</sub>NO<sub>2</sub><sup>+</sup> [M + H]<sup>+</sup> 256.0580, found 256.0578.

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**(10) 1-(3-(Trifluoromethyl)quinolin-6-yl)ethan-1-one**

Prepared according to **General Procedure A** using TFHZ-Tfs **2** (115.3 mg, 0.36 mmol) and 1-(1-(*tert*-butyldimethylsilyl)-1*H*-indol-5-yl)ethan-1-one (82.0 mg, 0.3 mmol) afforded **10** (45.9 mg, 64% yield) as a white solid; mp: 87-89 °C.

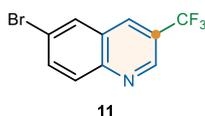
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.20 (d, *J* = 2.0 Hz, 1H), 8.60-8.54 (m, 2H), 8.41 (dd, *J* = 9.0, 2.0 Hz, 1H), 8.26 (d, *J* = 9.0 Hz, 1H), 2.77 (s, 3H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 196.8, 151.1, 148.2 (q, *J* = 3.0 Hz), 136.1, 135.3 (q, *J* = 3.0 Hz), 130.3, 130.0, 125.6, 124.6 (q, *J* = 33.0 Hz), 123.4 (q, *J* = 270.0 Hz), 26.8.

**<sup>19</sup>F NMR** (564 MHz, CDCl<sub>3</sub>) δ -61.97.

**HRMS** (ESI) *m/z* calcd. for C<sub>12</sub>H<sub>9</sub>F<sub>3</sub>NO<sup>+</sup> [M + H]<sup>+</sup> 240.0631, found 240.0632.

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**(11) 6-Bromo-3-(trifluoromethyl)quinoline**

Prepared according to **General Procedure A** using TFHZ-Tfs **2** (115.3 mg, 0.36 mmol) and 5-bromo-1-(*tert*-butyldimethylsilyl)-1*H*-indole (93.1 mg, 0.3 mmol) afforded **11** (161.8 mg, 92% yield) as a white solid; mp: 89-91 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.10 (d, *J* = 1.5 Hz, 1H), 8.36 (s, 1H), 8.10 (d, *J* = 1.5 Hz, 1H), 8.06 (d, *J* = 9.0 Hz, 1H), 7.93 (dd, *J* = 9.0, 2.0 Hz, 1H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 148.0, 146.4 (q, *J* = 3.0 Hz), 135.3, 132.9 (q, *J* = 4.5 Hz), 131.3, 130.5, 127.4, 124.7 (q, *J* = 33.0 Hz), 123.4 (q, *J* = 270.0 Hz), 122.1.

**<sup>19</sup>F NMR** (564 MHz, CDCl<sub>3</sub>) δ -62.00.

**HRMS** (ESI) *m/z* calcd. for C<sub>10</sub>H<sub>6</sub>BrF<sub>3</sub>N<sup>+</sup> [M + H]<sup>+</sup> 275.9630, found 275.9631.

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**(12) 6-Methoxy-3-(trifluoromethyl)quinoline**

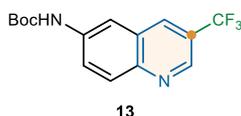
Prepared according to **General Procedure A** using TFHZ-Tfs **2** (115.3 mg, 0.36 mmol) and 1-(*tert*-butyldimethylsilyl)-5-methoxy-1*H*-indole (78.4 mg, 0.3 mmol) afforded **12** (49.1 mg, 72% yield) as a white solid; mp: 38-40 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.93 (d, *J* = 1.0 Hz, 1H), 8.31 (s, 1H), 8.05 (d, *J* = 9.5 Hz, 1H), 7.48 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.13 (d, *J* = 2.5 Hz, 1H), 3.94 (s, 3H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 158.8, 145.6, 143.5 (q, *J* = 3.0 Hz), 132.4 (q, *J* = 4.5 Hz), 131.0, 127.5, 124.7, 123.9 (q, *J* = 33.0 Hz), 123.8 (q, *J* = 271.5 Hz), 105.6, 55.6.

<sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -61.81.

HRMS (ESI) *m/z* calcd. for C<sub>11</sub>H<sub>9</sub>F<sub>3</sub>NO<sup>+</sup> [M + H]<sup>+</sup> 228.0631, found 228.0630.



**(13) *tert*-Butyl (3-(trifluoromethyl)quinolin-6-yl)carbamate**

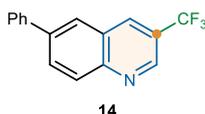
Prepared according to **General Procedure A** using TFHZ-Tfs **2** (115.3 mg, 0.36 mmol) and *tert*-butyl (1-(*tert*-butyldimethylsilyl)-1*H*-indol-5-yl)carbamate (104.0 mg, 0.3 mmol) afforded **13** (54.3 mg, 58% yield) as a white solid; mp: 145-147 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.96 (d, *J* = 1.5 Hz, 1H), 8.34 (s, 1H), 8.21 (s, 1H), 8.07 (d, *J* = 9.0 Hz, 1H), 7.61 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.97 (s, 1H), 1.55 (s, 9H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 152.5, 146.0, 144.4 (q, *J* = 3.0 Hz), 137.7, 133.2 (q, *J* = 4.5 Hz), 130.3, 127.2, 124.6, 124.1 (q, *J* = 33.0 Hz), 123.7 (q, *J* = 271.5 Hz), 114.1, 81.4, 28.3.

<sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -61.93.

HRMS (ESI) *m/z* calcd. for C<sub>15</sub>H<sub>16</sub>F<sub>3</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> [M + H]<sup>+</sup> 313.1158, found 313.1155.



**(14) 6-Phenyl-3-(trifluoromethyl)quinoline**

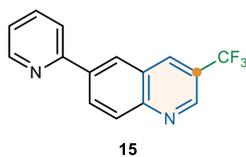
Prepared according to **General Procedure A** using TFHZ-Tfs **2** (115.3 mg, 0.36 mmol) and 1-(*tert*-butyldimethylsilyl)-5-phenyl-1*H*-indole (92.3 mg, 0.3 mmol) afforded **14** (71.3 mg, 87% yield) as a white solid; mp: 72-74 °C.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 9.10 (d, *J* = 1.8 Hz, 1H), 8.49 (s, 1H), 8.25 (d, *J* = 8.4 Hz, 1H), 8.11 (dd, *J* = 8.4, 1.8 Hz, 1H), 8.08 (d, *J* = 1.8 Hz, 1H), 7.74-7.69 (m, 2H), 7.55-7.49 (m, 2H), 7.47-7.42 (m, 1H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 148.7, 145.9 (q, *J* = 3.0 Hz), 140.8, 139.5, 134.0 (q, *J* = 4.5 Hz), 131.5, 130.0, 129.1, 128.2, 127.4, 126.5, 126.0, 123.9 (q, *J* = 33.0 Hz), 123.7 (q, *J* = 270.0 Hz).

<sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -61.80.

HRMS (ESI) *m/z* calcd. for C<sub>16</sub>H<sub>11</sub>F<sub>3</sub>N<sup>+</sup> [M + H]<sup>+</sup> 274.0838, found 274.0840.



**(15) 6-(Pyridin-2-yl)-3-(trifluoromethyl)quinoline**

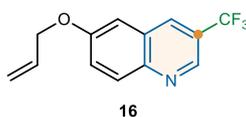
Prepared according to **General Procedure A** using TFHZ-Tfs **2** (115.3 mg, 0.36 mmol) and 1-(*tert*-butyldimethylsilyl)-5-(pyridin-2-yl)-1*H*-indole (92.6 mg, 0.3 mmol) afforded **15** (25.5 mg, 31% yield) as a white solid; mp: 118-120 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.10 (d, *J* = 1.0 Hz, 1H), 8.76 (d, *J* = 4.5 Hz, 1H), 8.56 (s, 1H), 8.54-8.47 (m, 2H), 8.26 (d, *J* = 9.0 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.85-7.79 (m, 1H), 7.34-7.28 (m, 1H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 155.6, 150.0, 149.5, 146.4 (q, *J* = 3.8 Hz), 138.8, 137.1, 134.5 (q, *J* = 3.8 Hz), 130.5, 130.0, 126.6, 126.4, 124.0 (q, *J* = 32.5 Hz), 123.6 (q, *J* = 270.0 Hz), 122.9, 120.9.

<sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -61.86.

**HRMS** (ESI) *m/z* calcd. for C<sub>15</sub>H<sub>10</sub>F<sub>3</sub>N<sub>2</sub><sup>+</sup> [M + H]<sup>+</sup> 275.0791, found 275.0792.



**(16) 6-(Allyloxy)-3-(trifluoromethyl)quinoline**

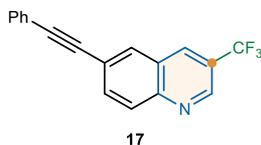
Prepared according to **General Procedure A** using TFHZ-Tfs **2** (115.3 mg, 0.36 mmol) and 5-(allyloxy)-1-(*tert*-butyldimethylsilyl)-1*H*-indole (86.2 mg, 0.3 mmol) afforded **16** (63.7 mg, 84% yield) as a white solid; mp: 43-45 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.94 (d, *J* = 1.5 Hz, 1H), 8.31 (s, 1H), 8.08 (d, *J* = 9.0 Hz, 1H), 7.53 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.16 (d, *J* = 2.5 Hz, 1H), 6.17-6.05 (m, 1H), 5.52-5.46 (m, 1H), 5.38-5.34 (m, 1H), 4.70-4.65 (m, 2H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 157.7, 145.6, 143.6 (q, *J* = 3.0 Hz), 132.5 (q, *J* = 4.5 Hz), 132.4, 131.0, 127.5, 125.0, 123.9 (q, *J* = 33.0 Hz), 123.8 (q, *J* = 271.5 Hz), 118.3, 106.8, 69.2.

<sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -61.79.

**HRMS** (ESI) *m/z* calcd. for C<sub>13</sub>H<sub>11</sub>F<sub>3</sub>NO<sup>+</sup> [M + H]<sup>+</sup> 254.0787, found 254.0789.



**(17) 6-(Phenylethynyl)-3-(trifluoromethyl)quinoline**

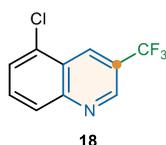
Prepared according to **General Procedure A** using TFHZ-Tfs **2** (115.3 mg, 0.36 mmol) and 1-(*tert*-butyldimethylsilyl)-5-(phenylethynyl)-1*H*-indole (99.5 mg, 0.3 mmol) afforded **17** (79.3 mg, 89% yield) as a white solid; mp: 110-112 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.08 (s, 1H), 8.39 (s, 1H), 8.15 (d, *J* = 9.0 Hz, 1H), 8.09 (s, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.63-7.55 (m, 2H), 7.44-7.34 (m, 3H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 148.6, 146.4 (q, *J* = 3.8 Hz), 134.4, 133.5 (q, *J* = 3.8 Hz), 131.8, 131.5, 129.7, 128.9, 128.5, 126.1, 124.3 (q, *J* = 32.5 Hz), 123.5 (q, *J* = 270.0 Hz), 123.3, 122.5, 91.9, 88.2.

<sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -61.92.

**HRMS** (ESI) *m/z* calcd. for C<sub>18</sub>H<sub>11</sub>F<sub>3</sub>N<sup>+</sup> [M + H]<sup>+</sup> 298.0838, found 298.0840.



**(18) 5-Chloro-3-(trifluoromethyl)quinoline**

Prepared according to **General Procedure A** using TFHZ-Tfs **2** (115.3 mg, 0.36 mmol) and 1-(*tert*-butyldimethylsilyl)-4-chloro-1*H*-indole (79.8 mg, 0.3 mmol) afforded **18** (43.6 mg, 63% yield) as a white solid; mp: 33-35 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.14 (d, *J* = 2.0 Hz, 1H), 8.86 (s, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.78 (t, *J* = 8.0 Hz, 1H), 7.76-7.72 (m, 1H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 150.0, 146.7 (q, *J* = 3.0 Hz), 132.2, 131.5, 131.1 (q, *J* = 4.5 Hz), 128.8, 128.0, 124.7, 124.5 (q, *J* = 34.5 Hz), 123.5 (q, *J* = 271.5 Hz).

**<sup>19</sup>F NMR** (564 MHz, CDCl<sub>3</sub>) δ -61.82.

**HRMS** (ESI) *m/z* calcd. for C<sub>10</sub>H<sub>6</sub>ClF<sub>3</sub>N<sup>+</sup> [M + H]<sup>+</sup> 232.0135, found 232.0130.

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**(19) 7-Iodo-3-(trifluoromethyl)quinoline**

Prepared according to **General Procedure A** using TFHZ-Tfs **2** (115.3 mg, 0.36 mmol) and 1-(*tert*-butyldimethylsilyl)-6-iodo-1*H*-indole (107.2 mg, 0.3 mmol) afforded **19** (82.4 mg, 85% yield) as a white solid; mp: 74-76 °C.

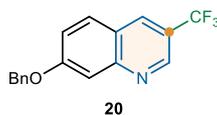
**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 9.10 (d, *J* = 1.8 Hz, 1H), 8.333 (s, 1H), 8.331 (s, 1H), 8.09 (dd, *J* = 9.0, 1.8 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 148.3, 146.5 (q, *J* = 3.0 Hz), 140.5, 137.2, 132.7 (q, *J* = 4.5 Hz), 131.2, 127.9, 124.3 (q, *J* = 33.0 Hz), 123.4 (q, *J* = 270.0 Hz), 93.8.

**<sup>19</sup>F NMR** (564 MHz, CDCl<sub>3</sub>) δ -61.97.

**HRMS** (ESI) *m/z* calcd. for C<sub>10</sub>H<sub>6</sub>I<sub>3</sub>N<sup>+</sup> [M + H]<sup>+</sup> 323.9492, found 323.9495.

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**(20) 7-(Benzyloxy)-3-(trifluoromethyl)quinoline**

Prepared according to **General Procedure A** using TFHZ-Tfs **2** (115.3 mg, 0.36 mmol) and 6-(benzyloxy)-1-(*tert*-butyldimethylsilyl)-1*H*-indole (101.3 mg, 0.3 mmol) afforded **20** (76.4 mg, 84% yield) as a white solid; mp: 93-95 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.02 (s, 1H), 8.34 (s, 1H), 7.80 (d, *J* = 9.0 Hz, 1H), 7.56 (s, 1H), 7.50 (d, *J* = 7.5 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.40-7.32 (m, 2H), 5.24 (s, 2H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 161.5, 151.3, 146.3 (q, *J* = 3.0 Hz), 135.9, 133.4 (q, *J* = 4.5 Hz), 129.6, 128.7, 128.3, 127.7, 123.9 (q, *J* = 270.0 Hz), 121.7, 121.6 (q, *J* = 33.0 Hz), 121.5, 108.6, 70.4.

**<sup>19</sup>F NMR** (564 MHz, CDCl<sub>3</sub>) δ -61.39.

**HRMS** (ESI) *m/z* calcd. for C<sub>17</sub>H<sub>13</sub>F<sub>3</sub>NO<sup>+</sup> [M + H]<sup>+</sup> 304.0944, found 304.0946.

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**(21) 8-Fluoro-3-(trifluoromethyl)quinoline**

Prepared according to **General Procedure A** using TFHZ-Tfs **2** (115.3 mg, 0.36 mmol) and 1-(*tert*-butyldimethylsilyl)-7-fluoro-1*H*-indole (74.8 mg, 0.3 mmol) afforded **21** (52.2 mg, 81% yield) as a white solid; mp: 42-44 °C.

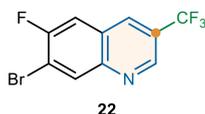
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.06 (s, 1H), 8.40 (s, 1H), 8.20 (dd, *J* = 9.0, 5.0 Hz, 1H), 7.63 (td, *J* = 9.0, 2.5 Hz, 1H), 7.55 (dd, *J* = 8.5, 2.5 Hz, 1H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 161.1 (d, *J* = 249.0 Hz), 146.5, 145.5-145.2 (m), 133.4-133.1 (m), 132.3 (d, *J* = 9.0 Hz), 127.1 (d, *J* = 10.5 Hz), 124.4 (q, *J* = 31.5 Hz), 123.5 (q, *J* = 271.5 Hz), 122.2 (d, *J* = 25.5 Hz), 111.6 (d, *J* = 22.5 Hz).

<sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -61.97, (-110.50)-(-110.57) (m).

HRMS (ESI) *m/z* calcd. for C<sub>10</sub>H<sub>6</sub>F<sub>4</sub>N<sup>+</sup> [M + H]<sup>+</sup> 216.0431, found 216.0433.

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**(22) 7-Bromo-6-fluoro-3-(trifluoromethyl)quinoline**

Prepared according to **General Procedure A** using TFHZ-Tfs **2** (115.3 mg, 0.36 mmol) and 6-bromo-1-(*tert*-butyldimethylsilyl)-5-fluoro-1*H*-indole (98.5 mg, 0.3 mmol) afforded **22** (72.7 mg, 83% yield) as a white solid; mp: 92-94 °C.

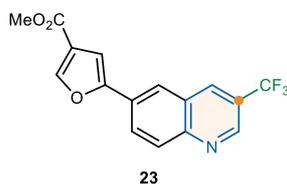
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.06 (s, 1H), 8.46 (d, *J* = 6.5 Hz, 1H), 8.38 (s, 1H), 7.61 (d, *J* = 8.0 Hz, 1H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 157.4 (d, *J* = 251.3 Hz), 146.5, 146.4-146.2 (m), 135.0, 133.2-133.0 (m), 126.1 (d, *J* = 8.8 Hz), 124.6 (q, *J* = 33.8 Hz), 123.3 (q, *J* = 271.3 Hz), 116.3 (d, *J* = 23.8 Hz), 112.3 (d, *J* = 23.8 Hz).

<sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -62.07, -105.37 (t, *J* = 7.5 Hz).

HRMS (ESI) *m/z* calcd. for C<sub>10</sub>H<sub>5</sub>BrF<sub>4</sub>N<sup>+</sup> [M + H]<sup>+</sup> 293.9536, found 293.9539.

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**(23) Methyl 5-(3-(trifluoromethyl)quinolin-6-yl)furan-3-carboxylate**

Prepared according to **General Procedure A** using TFHZ-Tfs **2** (115.3 mg, 0.36 mmol) and methyl 5-(1-(*tert*-butyldimethylsilyl)-1*H*-indol-5-yl)furan-3-carboxylate (106.7 mg, 0.3 mmol) afforded **23** (81.0 mg, 84% yield) as a white solid; mp: 152-154 °C.

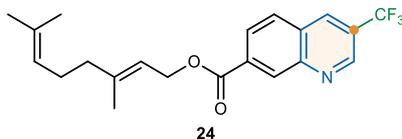
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.05 (d, *J* = 1.5 Hz, 1H), 8.43 (s, 1H), 8.20-8.15 (m, 2H), 8.12-8.06 (m, 2H), 7.16 (s, 1H), 3.89 (s, 3H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 163.1, 153.6, 148.9, 147.7, 146.1 (q, *J* = 3.0 Hz), 133.9 (q, *J* = 4.5 Hz), 130.3, 129.1, 127.9, 126.5, 124.4 (q, *J* = 33.0 Hz), 123.5 (q, *J* = 271.5 Hz), 122.8, 121.4, 106.7, 51.9.

$^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -61.98.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{16}\text{H}_{11}\text{F}_3\text{NO}_3^+$   $[\text{M} + \text{H}]^+$  322.0686, found 322.0690.

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**(24) 3,7-Dimethylocta-2,6-dien-1-yl 3-(trifluoromethyl)quinoline-7-carboxylate**

Prepared according to **General Procedure A** using TFHZ-Tfs **2** (115.3 mg, 0.36 mmol) and 3,7-dimethylocta-2,6-dien-1-yl 1-(*tert*-butyldimethylsilyl)-1*H*-indole-6-carboxylate (123.5 mg, 0.3 mmol) afforded **24** (84.9 mg, 75% yield) as a white solid; mp: 38-40 °C.

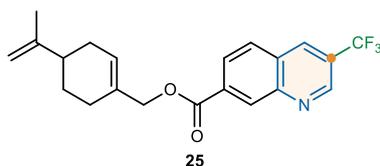
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.14 (s, 1H), 8.87 (s, 1H), 8.45 (s, 1H), 8.24 (d,  $J = 8.5$  Hz, 1H), 7.96 (d,  $J = 8.5$  Hz, 1H), 5.51 (t,  $J = 6.5$  Hz, 1H), 5.08 (t,  $J = 6.0$  Hz, 1H), 4.92 (d,  $J = 7.0$  Hz, 2H), 2.18-2.03 (m, 4H), 1.79 (s, 3H), 1.65 (s, 3H), 1.59 (s, 3H).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  165.6, 148.8, 146.8 (q,  $J = 3.0$  Hz), 143.1, 133.6 (q,  $J = 4.5$  Hz), 133.5, 131.9, 131.8, 128.7, 128.4, 127.5, 125.0 (q,  $J = 33.0$  Hz), 123.6, 123.3 (q,  $J = 271.5$  Hz), 117.9, 62.5, 39.5, 26.2, 25.6, 17.6, 16.5.

$^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.10.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{21}\text{H}_{23}\text{F}_3\text{NO}_2^+$   $[\text{M} + \text{H}]^+$  378.1675, found 378.1677.

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**(25) (4-(Prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl 3-(trifluoromethyl)quinoline-7-carboxylate**

Prepared according to **General Procedure A** using TFHZ-Tfs **2** (115.3 mg, 0.36 mmol) and (4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl 1-(*tert*-butyldimethylsilyl)-1*H*-indole-6-carboxylate (122.9 mg, 0.3 mmol) afforded **25** (75.5 mg, 67% yield) as a white solid; mp: 57-59 °C.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.17 (d,  $J = 2.0$  Hz, 1H), 8.90 (s, 1H), 8.49 (s, 1H), 8.27 (dd,  $J = 8.5, 1.5$  Hz, 1H), 8.00 (d,  $J = 8.5$  Hz, 1H), 5.91 (s, 1H), 4.85-4.76 (m, 2H), 4.76-4.71 (m, 2H), 2.27-2.16 (m, 4H), 2.07-1.97 (m, 1H), 1.93-1.86 (m, 1H), 1.75 (s, 3H), 1.60-1.49 (m, 1H).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  165.5, 149.5, 148.8, 146.9 (q,  $J = 3.0$  Hz), 133.7 (q,  $J = 4.5$  Hz), 133.4, 132.3, 131.9, 128.9, 128.6, 127.6, 126.5, 125.1 (q,  $J = 33.0$  Hz), 123.4 (q,  $J = 271.5$  Hz), 108.9, 69.7, 40.8, 30.5, 27.3, 26.5, 20.7.

$^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.07.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{21}\text{H}_{21}\text{F}_3\text{NO}_2^+$   $[\text{M} + \text{H}]^+$  376.1519, found 376.1520.

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**(26) 3-(Difluoromethyl)quinoline**

Prepared according to **General Procedure B** using DFHZ-Tfs (181.3 mg, 0.6 mmol) and *N*-TBS indole (69.4 mg, 0.3 mmol) afforded **26** (47.3 mg, 88% yield) as a white solid; mp: 28-30 °C.

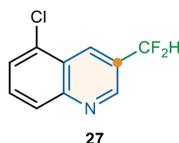
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.03 (s, 1H), 8.29 (s, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.81 (t, *J* = 7.5 Hz, 1H), 7.62 (t, *J* = 8.0 Hz, 1H), 6.88 (t, *J* = 56.0 Hz, 1H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 149.1, 147.1 (t, *J* = 6.0 Hz), 133.8 (t, *J* = 7.5 Hz), 131.0, 129.5, 128.3, 127.6, 127.1 (t, *J* = 22.5 Hz), 126.8, 113.7 (t, *J* = 238.5 Hz).

**<sup>19</sup>F NMR** (564 MHz, CDCl<sub>3</sub>) δ -111.53 (d, *J* = 56.0 Hz).

**HRMS** (ESI) *m/z* calcd. for C<sub>10</sub>H<sub>8</sub>F<sub>2</sub>N<sup>+</sup> [M + H]<sup>+</sup> 180.0619, found 180.0621.

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### (27) 5-Chloro-3-(difluoromethyl)quinoline

Prepared according to **General Procedure A** using DFHZ-Tfs (181.3 mg, 0.6 mmol) and 1-(*tert*-butyldimethylsilyl)-4-chloro-1*H*-indole (79.8 mg, 0.3 mmol) afforded **27** (45.5 mg, 71% yield) as a white solid; mp: 44-46 °C.

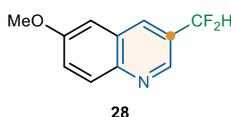
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.08 (s, 1H), 8.71 (s, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.77-7.66 (m, 2H), 6.93 (t, *J* = 55.5 Hz, 1H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 149.7, 147.8 (t, *J* = 4.5 Hz), 132.0, 131.0 (t, *J* = 7.5 Hz), 130.7, 128.8, 128.0 (t, *J* = 22.5 Hz), 127.6, 125.2, 113.5 (t, *J* = 238.5 Hz).

**<sup>19</sup>F NMR** (564 MHz, CDCl<sub>3</sub>) δ -111.63 (d, *J* = 55.5 Hz).

**HRMS** (ESI) *m/z* calcd. for C<sub>10</sub>H<sub>7</sub>ClF<sub>2</sub>N<sup>+</sup> [M + H]<sup>+</sup> 214.0230, found 214.0233.

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### (28) 3-(Difluoromethyl)-6-methoxyquinoline

Prepared according to **General Procedure B** using DFHZ-Tfs (181.3 mg, 0.6 mmol) and 1-(*tert*-butyldimethylsilyl)-5-methoxy-1*H*-indole (78.4 mg, 0.3 mmol) afforded **28** (50.8 mg, 81% yield) as a white solid; mp: 48-50 °C.

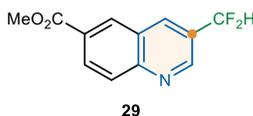
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.86 (s, 1H), 8.17 (s, 1H), 8.03 (d, *J* = 9.2 Hz, 1H), 7.44 (dd, *J* = 9.2, 2.5 Hz, 1H), 7.10 (d, *J* = 2.5 Hz, 1H), 6.85 (t, *J* = 56.0 Hz, 1H), 3.93 (s, 3H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 158.4, 145.3, 144.5 (t, *J* = 6.0 Hz), 132.4 (t, *J* = 7.5 Hz), 130.8, 128.0, 127.4 (t, *J* = 22.5 Hz), 123.9, 113.8 (t, *J* = 238.5 Hz), 105.4, 55.6.

**<sup>19</sup>F NMR** (564 MHz, CDCl<sub>3</sub>) δ -111.56 (d, *J* = 56.0 Hz).

**HRMS** (ESI) *m/z* calcd. for C<sub>11</sub>H<sub>10</sub>F<sub>2</sub>NO<sup>+</sup> [M + H]<sup>+</sup> 210.0725, found 210.0728.

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### (29) Methyl 3-(difluoromethyl)quinoline-6-carboxylate

Prepared according to **General Procedure B** using DFHZ-Tfs (181.3 mg, 0.6 mmol) and methyl 1-(*tert*-butyldimethylsilyl)-1*H*-indole-5-carboxylate (86.8 mg, 0.3 mmol) afforded **29** (69.0 mg, 97% yield) as a white solid; mp: 105-107 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.11 (s, 1H), 8.65 (s, 1H), 8.41-8.36 (m, 2H), 8.20 (d, *J* = 9.0 Hz, 1H), 6.91

(t,  $J = 56.0$  Hz, 1H), 4.01 (s, 3H).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  166.2, 150.8, 149.2 (t,  $J = 4.5$  Hz), 135.0 (t,  $J = 7.5$  Hz), 131.4, 130.5, 129.9, 129.2, 128.0 (t,  $J = 24.0$  Hz), 126.0, 113.3 (t,  $J = 238.5$  Hz), 52.6.

$^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -112.10 (d,  $J = 56.0$  Hz).

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{12}\text{H}_{10}\text{F}_2\text{NO}_2^+$   $[\text{M} + \text{H}]^+$  238.0674, found 238.0677.

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### (30) 7-(Benzyloxy)-3-(difluoromethyl)quinoline

Prepared according to **General Procedure B** using DFHZ-Tfs (181.3 mg, 0.6 mmol) and 6-(benzyloxy)-1-(*tert*-butyldimethylsilyl)-1*H*-indole (101.3 mg, 0.3 mmol) afforded **30** (71.0 mg, 83% yield) as a white solid; mp: 61-63 °C.

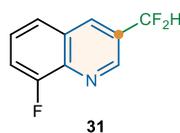
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.95 (s, 1H), 8.22 (s, 1H), 7.79 (d,  $J = 9.0$  Hz, 1H), 7.55 (d,  $J = 2.0$  Hz, 1H), 7.50 (d,  $J = 7.5$  Hz, 2H), 7.42 (t,  $J = 7.5$  Hz, 2H), 7.38-7.33 (m, 2H), 6.86 (t,  $J = 56.0$  Hz, 1H), 5.24 (s, 2H).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  161.0, 151.0, 147.4 (t,  $J = 6.0$  Hz), 136.0, 133.5 (t,  $J = 6.0$  Hz), 129.4, 128.7, 128.3, 127.7, 125.2 (t,  $J = 22.5$  Hz), 122.2, 121.3, 113.9 (t,  $J = 237.0$  Hz), 108.6, 70.4.

$^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -110.71 (d,  $J = 56.0$  Hz).

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{17}\text{H}_{14}\text{F}_2\text{NO}^+$   $[\text{M} + \text{H}]^+$  286.1038, found 286.1041.

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### (31) 3-(Difluoromethyl)-8-fluoroquinoline

Prepared according to **General Procedure B** using DFHZ-Tfs (181.3 mg, 0.6 mmol) and 1-(*tert*-butyldimethylsilyl)-7-fluoro-1*H*-indole (74.8 mg, 0.3 mmol) afforded **31** (47.3 mg, 80% yield) as a white solid; mp: 71-73 °C.

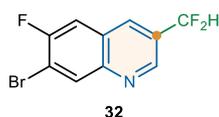
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.08 (s, 1H), 8.35 (s, 1H), 7.71 (d,  $J = 8.0$  Hz, 1H), 7.61-7.55 (m, 1H), 7.54-7.47 (m, 1H), 6.91 (t,  $J = 56.0$  Hz, 1H).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  158.0 (d,  $J = 256.5$  Hz), 147.4 (t,  $J = 4.5$  Hz), 139.3 (d,  $J = 12.0$  Hz), 133.6 (td,  $J = 7.5, 3.0$  Hz), 128.4 (d,  $J = 1.5$  Hz), 128.2 (t,  $J = 24.0$  Hz), 127.6 (d,  $J = 7.5$  Hz), 124.0 (d,  $J = 4.5$  Hz), 115.1 (d,  $J = 19.5$  Hz), 113.3 (t,  $J = 238.5$  Hz).

$^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -112.24 (d,  $J = 56.0$  Hz), (-124.41)-(-124.47) (m).

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{10}\text{H}_7\text{F}_3\text{N}^+$   $[\text{M} + \text{H}]^+$  198.0525, found 198.0528.

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### (32) 7-Bromo-3-(difluoromethyl)-6-fluoroquinoline

Prepared according to **General Procedure B** using DFHZ-Tfs (181.3 mg, 0.6 mmol) and 6-bromo-1-(*tert*-butyldimethylsilyl)-5-fluoro-1*H*-indole (98.5 mg, 0.3 mmol) afforded **32** (73.7 mg, 89% yield) as a white solid; mp: 107-109 °C.

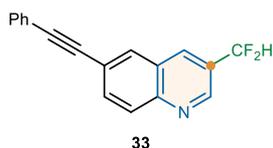
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.99 (s, 1H), 8.44 (d, *J* = 6.5 Hz, 1H), 8.24 (s, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 6.87 (t, *J* = 55.5 Hz, 1H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 157.2 (d, *J* = 249.0 Hz), 147.5-147.3 (m), 146.3, 134.9, 133.0 (q, *J* = 6.0 Hz), 128.1 (t, *J* = 22.5 Hz), 126.6 (d, *J* = 9.0 Hz), 115.3 (d, *J* = 24.0 Hz), 113.2 (t, *J* = 237.0 Hz), 112.1 (d, *J* = 22.5 Hz).

**<sup>19</sup>F NMR** (564 MHz, CDCl<sub>3</sub>) δ -106.28, (t, *J* = 6.6 Hz), -112.41 (d, *J* = 55.5 Hz).

**HRMS** (ESI) *m/z* calcd. for C<sub>10</sub>H<sub>6</sub>BrF<sub>3</sub>N<sup>+</sup> [M + H]<sup>+</sup> 275.9630, found 275.9632.

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### (33) 3-(Difluoromethyl)-6-(phenylethynyl)quinoline

Prepared according to **General Procedure B** using DFHZ-Tfs (181.3 mg, 0.6 mmol) and 1-(*tert*-butyldimethylsilyl)-5-(phenylethynyl)-1*H*-indole (99.5 mg, 0.3 mmol) afforded **33** (78.8 mg, 94% yield) as a white solid; mp: 108-110 °C.

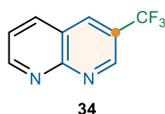
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.02 (s, 1H), 8.26 (s, 1H), 8.13 (d, *J* = 8.5 Hz, 1H), 8.07 (d, *J* = 1.5 Hz, 1H), 7.90 (dd, *J* = 9.0, 1.5 Hz, 1H), 7.62-7.55 (m, 2H), 7.41-7.33 (m, 3H), 6.89 (t, *J* = 56.0 Hz, 1H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 148.4, 147.6 (t, *J* = 6.0 Hz), 133.7, 133.5 (t, *J* = 6.0 Hz), 131.7, 131.4, 129.6, 128.8, 128.5, 127.8 (t, *J* = 22.5 Hz), 126.7, 122.9, 122.7, 113.5 (d, *J* = 238.5 Hz), 91.5, 88.4.

**<sup>19</sup>F NMR** (564 MHz, CDCl<sub>3</sub>) δ -111.92 (d, *J* = 56.0 Hz).

**HRMS** (ESI) *m/z* calcd. for C<sub>18</sub>H<sub>12</sub>F<sub>2</sub>N<sup>+</sup> [M + H]<sup>+</sup> 280.0932, found 280.0937.

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### (34) 3-(Trifluoromethyl)-1,8-naphthyridine

Prepared according to **General Procedure A** using TFHZ-Tfs **2** (115.3 mg, 0.36 mmol) and 1-(*tert*-butyldimethylsilyl)-1*H*-pyrrolo[2,3-*b*]pyridine (69.7 mg, 0.3 mmol) afforded **34** (30.9 mg, 52% yield) as a white solid; mp: 174-176 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.34 (d, *J* = 2.0 Hz, 1H), 9.29-9.24 (m, 1H), 8.52 (s, 1H), 8.33 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.64 (dd, *J* = 8.0, 4.0 Hz, 1H).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 157.0, 155.9, 149.4 (q, *J* = 2.5 Hz), 137.9, 135.3 (q, *J* = 3.8 Hz), 124.7 (q, *J* = 33.8 Hz), 123.5, 123.2 (q, *J* = 270.0 Hz), 121.1.

**<sup>19</sup>F NMR** (564 MHz, CDCl<sub>3</sub>) δ -61.84.

**HRMS** (ESI) *m/z* calcd. for C<sub>9</sub>H<sub>6</sub>F<sub>3</sub>N<sub>2</sub><sup>+</sup> [M + H]<sup>+</sup> 199.0478, found 199.0480.

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### (35) 3-(Difluoromethyl)-1,8-naphthyridine

Prepared according to **General Procedure B** using DFHZ-Tfs (181.3 mg, 0.6 mmol) and 1-(*tert*-butyldimethylsilyl)-1*H*-pyrrolo[2,3-*b*]pyridine (69.7 mg, 0.3 mmol) afforded **35** (37.3 mg, 69% yield) as a white solid; mp: 165-167 °C

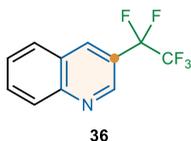
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.25 (d, *J* = 1.0 Hz, 1H), 9.24-9.20 (m, 1H), 8.37 (s, 1H), 8.29 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.59 (dd, *J* = 8.5, 4.5 Hz, 1H), 6.93 (t, *J* = 56.0 Hz, 1H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 156.8, 155.1, 150.4 (t, *J* = 6.0 Hz), 137.6, 135.1 (t, *J* = 6.0 Hz), 128.3 (t, *J* = 24.0 Hz), 123.1, 121.6, 113.1 (t, *J* = 238.5 Hz).

**<sup>19</sup>F NMR** (564 MHz, CDCl<sub>3</sub>) δ -112.18 (d, *J* = 56.0 Hz).

**HRMS** (ESI) *m/z* calcd. for C<sub>9</sub>H<sub>7</sub>F<sub>2</sub>N<sub>2</sub><sup>+</sup> [M + H]<sup>+</sup> 181.0572, found 181.0576.

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### (36) 3-(1,2,2,2-tetrafluoroethyl)quinoline

Prepared according to **General Procedure B** using *N*-trifosylhydrazone (222.0 mg, 0.6 mmol) derived from ethyl 2,2,3,3,3-pentafluoropropanoate and *N*-TBS indole (69.3 mg, 0.3 mmol) afforded **36** (44.5 mg, 60% yield) as a pale yellow oil.

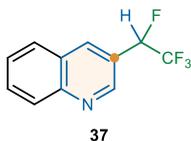
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.06 (s, 1H), 8.45 (s, 1H), 8.21 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.91-7.86 (m, 1H), 7.72-7.66 (m, 1H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 149.4, 146.4 (t, *J* = 5.0 Hz), 135.6 (t, *J* = 6.8 Hz), 131.9, 129.6, 128.5, 128.0, 126.3, 121.8 (t, *J* = 24.0 Hz), 119.1 (qt, *J* = 286.0, 39.0 Hz), 113.2 (tq, *J* = 254.7, 39.0 Hz).

**<sup>19</sup>F NMR** (564 MHz, CDCl<sub>3</sub>) δ -84.7 (t, *J* = 2.0 Hz), -114.7 (q, *J* = 2.1 Hz).

**HRMS** (ESI) *m/z* calcd. for C<sub>11</sub>H<sub>7</sub>F<sub>5</sub>N<sup>+</sup> [M + H]<sup>+</sup> 248.0493, found 248.0498.

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### (37) 3-(1,2,2,2-tetrafluoroethyl)quinoline

Prepared according to **General Procedure D** using *N*-trifosylhydrazone (222.0 mg, 0.6 mmol) derived from ethyl 2,2,3,3,3-pentafluoropropanoate and *N*-TBS indole (69.3 mg, 0.3 mmol) afforded **37** (67.3 mg, 98% yield) as a pale yellow solid; mp: 38-40 °C.

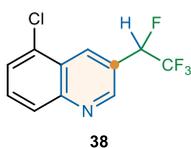
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.95 (s, 1H), 8.29 (s, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.83-7.77 (m, 1H), 7.64-7.59 (m, 1H), 5.83 (qd, *J* = 44.0, 6.0 Hz, 1H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 148.9, 148.0 (d, *J* = 6.0 Hz), 135.5 (d, *J* = 7.5 Hz), 131.0, 129.5, 128.2, 127.6, 127.0, 123.3 (d, *J* = 19.5 Hz), 122.0 (dq, *J* = 280.5, 28.5 Hz), 87.5 (dq, *J* = 186.0, 36.0 Hz).

**<sup>19</sup>F NMR** (564 MHz, CDCl<sub>3</sub>) δ -78.56 (dd, *J* = 13.0, 6.8 Hz), -196.21 (dq, *J* = 44.0, 13.0 Hz).

**HRMS** (ESI) *m/z* calcd. for C<sub>11</sub>H<sub>8</sub>F<sub>4</sub>N<sup>+</sup> [M + H]<sup>+</sup> 230.0587, found 230.0590.

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### (38) 5-Chloro-3-(1,2,2,2-tetrafluoroethyl)quinoline

Prepared according to **General Procedure D** using *N*-trifosylhydrazone (222.0 mg, 0.6 mmol) derived from ethyl 2,2,3,3,3-pentafluoropropanoate and 1-(*tert*-butyldimethylsilyl)-4-chloro-1*H*-indole (39.5 mg,

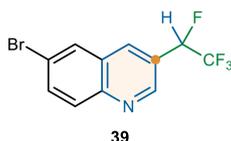
0.3 mmol) afforded **38** (47.5 mg, 50% yield) as a white solid; mp: 47-49 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.01 (s, 1H), 8.69 (s, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.77-7.68 (m, 2H), 5.90 (dq, *J* = 44.0, 6.0 Hz, 1H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 149.5, 148.6 (d, *J* = 5.5 Hz), 132.5 (d, *J* = 7.5 Hz), 131.8, 130.7, 128.7, 127.7, 125.3, 124.3 (d, *J* = 19.5 Hz), 121.9 (qd, *J* = 279.0, 30.0 Hz), 87.5 (dq, *J* = 187.5, 36.0 Hz).

<sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -78.42 (dd, *J* = 13.0, 6.0 Hz), -196.65 (dq, *J* = 43.0, 13.0 Hz).

HRMS (ESI) *m/z* calcd. for C<sub>11</sub>H<sub>7</sub>ClF<sub>4</sub>N<sup>+</sup> [M + H]<sup>+</sup> 264.0198, found 264.0201.



### (39) 6-Bromo-3-(1,2,2,2-tetrafluoroethyl)quinoline

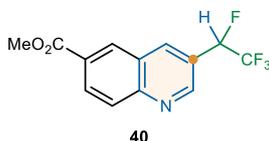
Prepared according to **General Procedure D** using *N*-trifosylhydrazone (222.0 mg, 0.6 mmol) derived from ethyl 2,2,3,3,3-pentafluoropropanoate and 5-bromo-1-(*tert*-butyldimethylsilyl)-1*H*-indole (92.7 mg, 0.3 mmol) afforded **39** (82.0 mg, 89% yield) as a white solid; mp: 79-81 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.94 (s, 1H), 8.20 (s, 1H), 8.04 (d, *J* = 2.0 Hz, 1H), 8.02 (d, *J* = 9.0 Hz, 1H), 7.86 (dd, *J* = 9.0, 2.0 Hz, 1H), 5.84 (dq, *J* = 44.0, 6.0 Hz, 1H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 148.3 (d, *J* = 6.0 Hz), 147.5, 134.5, 134.3 (d, *J* = 7.5 Hz), 131.2, 130.2, 128.1, 124.2 (d, *J* = 19.5 Hz), 121.9 (qd, *J* = 280.5, 28.5 Hz), 121.7, 87.3 (dq, *J* = 186.0, 36.0 Hz).

<sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -78.52 (dd, *J* = 13.0, 6.0 Hz), -197.05 (dq, *J* = 43.4, 13.0 Hz).

HRMS (ESI) *m/z* calcd. for C<sub>11</sub>H<sub>7</sub>BrF<sub>4</sub>N<sup>+</sup> [M + H]<sup>+</sup> 307.9693, found 307.9696.



### (40) Methyl 3-(1,2,2,2-tetrafluoroethyl)quinoline-6-carboxylate

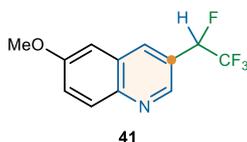
Prepared according to **General Procedure D** using *N*-trifosylhydrazone (222.0 mg, 0.6 mmol) derived from ethyl 2,2,3,3,3-pentafluoropropanoate and methyl 1-(*tert*-butyldimethylsilyl)-1*H*-indole-5-carboxylate (86.7 mg, 0.3 mmol) afforded **40** (80.1 mg, 93% yield) as a pale yellow solid; mp: 140-142 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.04 (s, 1H), 8.66 (s, 1H), 8.42-8.36 (m, 2H), 8.20 (d, *J* = 9.0 Hz, 1H), 5.87 (dq, *J* = 44.0, 6.0 Hz, 1H), 4.01 (s, 3H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 166.1, 150.6, 150.0 (d, *J* = 6.0 Hz), 136.6 (d, *J* = 7.5 Hz), 131.3, 130.5, 129.9, 129.2, 126.2, 124.2 (d, *J* = 19.5 Hz), 121.9 (qd, *J* = 280.5, 28.5 Hz), 87.3 (dq, *J* = 187.5, 36.0 Hz), 52.6.

<sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -78.51 (dd, *J* = 13.0, 6.0 Hz), -196.95 (dq, *J* = 44.0, 13.0 Hz).

HRMS (ESI) *m/z* calcd. for C<sub>13</sub>H<sub>10</sub>F<sub>4</sub>NO<sub>2</sub><sup>+</sup> [M + H]<sup>+</sup> 288.0642, found 288.0645.



#### (41) 6-Methoxy-3-(1,2,2,2-tetrafluoroethyl)quinoline

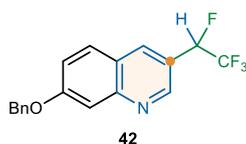
Prepared according to **General Procedure D** using *N*-trifosylhydrazone (222.0 mg, 0.6 mmol) derived from ethyl 2,2,3,3,3-pentafluoropropanoate and 1-(*tert*-butyldimethylsilyl)-5-methoxy-1*H*-indole (138.6 mg, 0.3 mmol) afforded **41** (63.7 mg, 82% yield) as a white solid; mp: 70-72 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.78 (s, 1H), 8.17 (s, 1H), 8.03 (d, *J* = 9.0 Hz, 1H), 7.44 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.10 (d, *J* = 2.5 Hz, 1H), 5.80 (dq, *J* = 44.0, 6.0 Hz, 1H), 3.92 (s, 3H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 158.5, 145.5 (d, *J* = 6.0 Hz), 145.2, 134.0 (d, *J* = 7.5 Hz), 130.8, 128.2, 124.0, 123.5 (d, *J* = 19.5 Hz), 122.0 (dq, *J* = 280.5, 30.0 Hz), 105.3, 87.5 (dq, *J* = 186.0, 36.0 Hz), 55.6.

<sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -78.56 (dd, *J* = 13.0, 6.0 Hz), -196.20 (dq, *J* = 44.0, 13.0 Hz).

HRMS (ESI) *m/z* calcd. for C<sub>12</sub>H<sub>10</sub>F<sub>4</sub>NO<sup>+</sup> [M + H]<sup>+</sup> 260.0693, found 260.0690.



#### (42) 7-(Benzyloxy)-3-(1,2,2,2-tetrafluoroethyl)quinoline

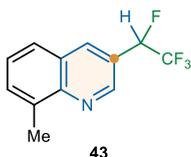
Prepared according to **General Procedure D** using *N*-trifosylhydrazone (222.0 mg, 0.6 mmol) derived from ethyl 2,2,3,3,3-pentafluoropropanoate and 6-(benzyloxy)-1-(*tert*-butyldimethylsilyl)-1*H*-indole (101.1 mg, 0.3 mmol) afforded **42** (68.3 mg, 68% yield) as a white solid; mp: 105-107 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.87 (s, 1H), 8.21 (s, 1H), 7.78 (d, *J* = 9.0 Hz, 1H), 7.54 (s, 1H), 7.50 (d, *J* = 7.5 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.39-7.32 (m, 2H), 5.79 (dq, *J* = 44.0, 6.0 Hz, 1H), 5.24 (s, 2H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 161.0, 150.8, 148.5 (d, *J* = 7.5 Hz), 136.0, 135.1 (d, *J* = 7.5 Hz), 129.3, 128.7, 128.3, 127.7, 122.4, 122.1 (qd, *J* = 280.0, 28.8 Hz), 121.3, 121.1 (d, *J* = 21.3 Hz), 108.5, 87.6 (dq, *J* = 186.3, 36.3 Hz), 70.3.

<sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -78.57 (dd, *J* = 13.0, 6.0 Hz), -194.72 (dq, *J* = 44.0, 13.0 Hz).

HRMS (ESI) *m/z* calcd. for C<sub>18</sub>H<sub>14</sub>F<sub>4</sub>NO<sup>+</sup> [M + H]<sup>+</sup> 336.1006, found 336.1008.



#### (43) 8-Methyl-3-(1,2,2,2-tetrafluoroethyl)quinoline

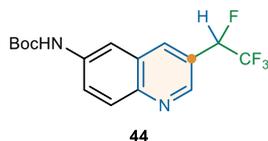
Prepared according to **General Procedure D** using *N*-trifosylhydrazone (222.0 mg, 0.6 mmol) derived from ethyl 2,2,3,3,3-pentafluoropropanoate and 1-(*tert*-butyldimethylsilyl)-7-methyl-1*H*-indole (73.5 mg, 0.3 mmol) afforded **43** (59.0 mg, 81% yield) as a white solid; mp: 49-50 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.98 (s, 1H), 8.27 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 7.0 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 5.84 (dq, *J* = 44.0, 6.0 Hz, 1H), 2.83 (s, 3H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 148.1, 146.9 (d, *J* = 5.5 Hz), 137.5, 135.7 (d, *J* = 6.3 Hz), 131.1, 127.4, 127.0, 126.2, 123.0 (d, *J* = 20.0 Hz), 122.1 (qd, *J* = 280.0, 28.8 Hz), 87.6 (dq, *J* = 186.3, 36.3 Hz), 18.0.

<sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -78.54 (dd, *J* = 13.0, 6.0 Hz), 196.09 (dq, *J* = 44.0, 13.0 Hz).

HRMS (ESI) *m/z* calcd. for C<sub>12</sub>H<sub>10</sub>F<sub>4</sub>N<sup>+</sup> [M + H]<sup>+</sup> 244.0744, found 244.0746.



**(44) tert-Butyl (3-(1,2,2,2-tetrafluoroethyl)quinolin-6-yl)carbamate**

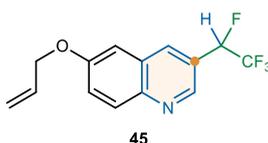
Prepared according to **General Procedure C** using *N*-trifosylhydrazone (222.0 mg, 0.6 mmol) derived from ethyl 2,2,3,3,3-pentafluoropropanoate and *tert*-butyl (1-(*tert*-butyldimethylsilyl)-1*H*-indol-5-yl)carbamate (103.8 mg, 0.3 mmol) afforded **44** (76.4 mg, 74% yield) as a pale yellow solid; mp: 125-127 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.82 (s, 1H), 8.23-8.17 (m, 2H), 8.06 (d, *J* = 9.0 Hz, 1H), 7.55 (dd, *J* = 9.0, 2.0 Hz, 1H), 6.84 (s, 1H), 5.80 (dq, *J* = 44.0, 6.0 Hz, 1H), 1.56 (s, 9H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 152.5, 146.4 (d, *J* = 6.0 Hz), 145.7, 137.3, 134.9 (d, *J* = 7.5 Hz), 130.2, 127.8, 124.0, 123.8 (d, *J* = 19.5 Hz), 122.0 (qd, *J* = 279.0, 28.5 Hz), 113.9, 87.6 (dq, *J* = 186.0, 36.0 Hz), 81.4, 28.3.

<sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -78.53 (dd, *J* = 13.0, 6.0 Hz), -196.35 (dq, *J* = 44.0, 13.0 Hz).

**HRMS** (ESI) *m/z* calcd. for C<sub>16</sub>H<sub>17</sub>F<sub>4</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> [M + H]<sup>+</sup> 345.1121, found 345.1123.



**(45) 6-(Allyloxy)-3-(1,2,2,2-tetrafluoroethyl)quinoline**

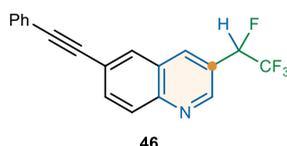
Prepared according to **General Procedure D** using *N*-trifosylhydrazone (222.0 mg, 0.6 mmol) derived from ethyl 2,2,3,3,3-pentafluoropropanoate and 5-(Allyloxy)-1-(*tert*-butyldimethylsilyl)-1*H*-indole (86.1 mg, 0.3 mmol) afforded **45** (61.6 mg, 72% yield) as a white solid; mp: 55-57 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.79 (s, 1H), 8.17 (s, 1H), 8.05 (d, *J* = 9.2 Hz, 1H), 7.48 (dd, *J* = 9.2, 2.5 Hz, 1H), 7.13 (d, *J* = 2.5 Hz, 1H), 6.18-6.05 (m, 1H), 5.80 (dq, *J* = 44.0, 6.0 Hz, 1H), 5.51-5.45 (m, 1H), 5.37-5.33 (m, 1H), 4.70-4.64 (m, 2H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 157.4, 145.6 (d, *J* = 5.0 Hz), 145.2, 134.0 (d, *J* = 6.3 Hz), 132.5, 130.9, 128.2, 124.3, 123.6 (d, *J* = 20.0 Hz), 122.0 (qd, *J* = 280.0, 28.9 Hz), 118.2, 106.5, 88.6 (dq, *J* = 186.3, 35.0 Hz), 69.1.

<sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -78.52 (dd, *J* = 13.0, 6.0 Hz), -196.18 (dq, *J* = 44.0, 13.0 Hz).

**HRMS** (ESI) *m/z* calcd. for C<sub>14</sub>H<sub>12</sub>F<sub>4</sub>NO<sup>+</sup> [M + H]<sup>+</sup> 286.0580, found 286.0583.



**(46) 6-(Phenylethynyl)-3-(1,2,2,2-tetrafluoroethyl)quinoline**

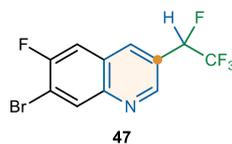
Prepared according to **General Procedure D** using *N*-trifosylhydrazone (222.0 mg, 0.6 mmol) derived from ethyl 2,2,3,3,3-pentafluoropropanoate and 1-(*tert*-butyldimethylsilyl)-5-(phenylethynyl)-1*H*-indole (99.3 mg, 0.3 mmol) afforded **46** (80.0 mg, 81% yield) as a white solid; mp: 103-105 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.94 (s, 1H), 8.24 (s, 1H), 8.12 (d, *J* = 9.0 Hz, 1H), 8.06 (d, *J* = 1.0 Hz, 1H), 7.90 (dd, *J* = 9.0, 1.5 Hz, 1H), 7.62-7.55 (m, 2H), 7.42-7.35 (m, 3H), 5.83 (dq, *J* = 44.0, 6.0 Hz, 1H).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  148.4 (d,  $J = 6.0$  Hz), 148.2, 135.0 (d,  $J = 7.5$  Hz), 133.7, 131.7, 131.2, 129.6, 128.8, 128.5, 126.8, 124.0 (d,  $J = 21.0$  Hz), 122.9, 122.6, 121.9 (qd,  $J = 279.0, 28.5$  Hz), 91.5, 88.4, 87.4 (dq,  $J = 186.0, 36.0$  Hz).

$^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -78.48 (dd,  $J = 13.0, 6.8$  Hz), -196.65 (dq,  $J = 44.0, 13.0$  Hz).

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{19}\text{H}_{12}\text{F}_4\text{N}^+$   $[\text{M} + \text{H}]^+$  330.0900, found 330.0905.



**(47) 7-Bromo-6-fluoro-3-(1,2,2,2-tetrafluoroethyl)quinoline**

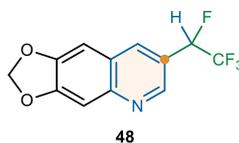
Prepared according to **General Procedure D** using *N*-trifosylhydrazone (222.0 mg, 0.6 mmol) derived from ethyl 2,2,3,3,3-pentafluoropropanoate and 6-bromo-1-(*tert*-butyldimethylsilyl)-5-fluoro-1*H*-indole (98.1 mg, 0.3 mmol) afforded **47** (79.0 mg, 81% yield) as a white solid; mp: 95-97 °C.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.91 (s, 1H), 8.44 (d,  $J = 7.0$  Hz, 1H), 8.23 (s, 1H), 7.57 (d,  $J = 8.0$  Hz, 1H), 5.83 (dq,  $J = 44.0, 6.0$  Hz, 1H).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  157.2 (d,  $J = 250.5$  Hz), 148.2 (d,  $J = 3.0$  Hz), 146.1, 134.8, 134.5 (t,  $J = 6.0$  Hz), 126.8 (d,  $J = 9.0$  Hz), 124.4 (d,  $J = 19.5$  Hz), 121.8 (qd,  $J = 279.0, 28.5$  Hz), 115.3 (d,  $J = 24.0$  Hz), 111.9 (d,  $J = 24.0$  Hz), 87.2 (dq,  $J = 187.5, 36.0$  Hz).

$^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -78.49 (dd,  $J = 13.0, 6.0$  Hz), -106.15 (t,  $J = 7.3$  Hz), -197.40 (dq,  $J = 44.0, 13.0$  Hz).

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{11}\text{H}_6\text{BrF}_5\text{N}^+$   $[\text{M} + \text{H}]^+$  325.9598, found 325.9595.



**(48) 7-(1,2,2,2-Tetrafluoroethyl)-[1,3]dioxolo[4,5-g]quinoline**

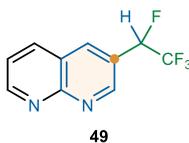
Prepared according to **General Procedure D** using *N*-trifosylhydrazone (222.0 mg, 0.6 mmol) derived from ethyl 2,2,3,3,3-pentafluoropropanoate and 5-(*tert*-butyldimethylsilyl)-5*H*-[1,3]dioxolo[4,5-*f*]indole (82.5 mg, 0.3 mmol) afforded **48** (42.6 mg, 52% yield) as a white solid; mp: 80-82 °C.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.71 (s, 1H), 8.07 (s, 1H), 7.40 (s, 1H), 7.08 (s, 1H), 6.14 (s, 2H), 5.75 (dq,  $J = 44.0, 6.0$  Hz, 1H).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  152.0, 148.2, 147.7, 146.0 (d,  $J = 6.0$  Hz), 133.9 (d,  $J = 6.0$  Hz), 124.4, 122.1 (qd,  $J = 279.0, 28.5$  Hz), 121.6 (d,  $J = 19.5$  Hz), 105.8, 102.9, 102.1, 87.5 (dq,  $J = 186.0, 34.5$  Hz).

$^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -78.61 (dd,  $J = 13.5, 6.8$  Hz), -195.14 (dq,  $J = 44.0, 13.5$  Hz).

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{12}\text{H}_8\text{F}_4\text{NO}_2^+$   $[\text{M} + \text{H}]^+$  274.0486, found 274.0488.



**(49) 3-(1,2,2,2-Tetrafluoroethyl)-1,8-naphthyridine**

Prepared according to **General Procedure D** using *N*-trifosylhydrazone (222.0 mg, 0.6 mmol) derived

from ethyl 2,2,3,3,3-pentafluoropropanoate and 1-(*tert*-butyldimethylsilyl)-1*H*-pyrrolo[2,3-*b*]pyridine (69.6 mg, 0.3 mmol) afforded **49** (30.4 mg, 44% yield) as a white solid; mp: 148-150 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.23 (d, *J* = 3.0 Hz, 1H), 9.18 (s, 1H), 8.38 (s, 1H), 8.29 (d, *J* = 8.0 Hz, 1H), 7.60 (dd, *J* = 8.0, 4.5 Hz, 1H), 5.91 (dq, *J* = 44.0, 6.0 Hz, 1H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 156.6, 155.2, 151.3 (d, *J* = 6.0 Hz), 137.5, 136.6 (d, *J* = 6.0 Hz), 124.6 (d, *J* = 19.5 Hz), 123.1, 121.84 (qd, *J* = 280.5, 28.5 Hz), 121.78, 87.1 (dq, *J* = 187.5, 36.0 Hz).

**<sup>19</sup>F NMR** (564 MHz, CDCl<sub>3</sub>) δ -78.52 (dd, *J* = 11.8, 5.1 Hz), -196.97 (dq, *J* = 44.0, 13.5 Hz).

**HRMS** (ESI) *m/z* calcd. for C<sub>10</sub>H<sub>7</sub>F<sub>4</sub>N<sub>2</sub><sup>+</sup> [M + H]<sup>+</sup> 231.0540, found 231.0545.

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**50**

### (**50**) 3-(1,2,2,3,3,3-Hexafluoropropyl)quinoline

Prepared according to **General Procedure D** using *N*-trifosylhydrazone (252.0 mg, 0.6 mmol) derived from ethyl 2,2,3,3,4,4,4-heptafluorobutanoate and *N*-TBS indole (69.3 mg, 0.3 mmol) afforded **50** (67.8 mg, 81% yield) as a white solid; mp: 44-46 °C.

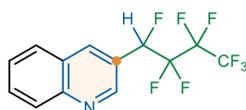
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.05 (s, 1H), 8.41 (d, *J* = 1.5 Hz, 1H), 8.15 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.83 (t, *J* = 7.5 Hz, 1H), 7.65 (t, *J* = 7.5 Hz, 1H), 5.92 (dq, *J* = 33.5, 7.5 Hz, 1H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 148.9, 148.2 (q, *J* = 6.0 Hz), 136.0 (q, *J* = 7.5 Hz), 131.1, 129.5, 128.3, 127.7, 127.0, 122.7 (q, *J* = 21.0 Hz), 118.5 (qt, *J* = 285.0, 34.5 Hz), 110.9 (tqd, *J* = 260.0, 37.5, 29.0 Hz), 87.9 (ddd, *J* = 186.0, 34.5, 24.0 Hz).

**<sup>19</sup>F NMR** (564 MHz, CDCl<sub>3</sub>) δ -81.97 (d, *J* = 11.0 Hz), -122.35 (dd, *J* = 284.3, 11.8 Hz), -131.35 (dt, *J* = 284.3, 16.4 Hz), (-197.31)-(-197.53) (m).

**HRMS** (ESI) *m/z* calcd. for C<sub>12</sub>H<sub>8</sub>F<sub>6</sub>N<sup>+</sup> [M + H]<sup>+</sup> 280.0555, found 280.0557.

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**51**

### (**51**) 3-(1,2,2,3,3,4,4,4-Octafluorobutyl)quinoline

Prepared according to **General Procedure D** using *N*-trifosylhydrazone (282 mg, 0.6 mmol) derived from ethyl 2,2,3,3,4,4,5,5,5-nonafluoropentanoate and *N*-TBS indole (69.3 mg, 0.3 mmol) afforded **51** (81.9 mg, 83% yield) as a colorless oil.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.94 (s, 1H), 8.30 (s, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.84-7.78 (m, 1H), 7.66-7.59 (m, 1H), 6.04 (ddd, *J* = 43.5, 19.0, 2.5 Hz, 1H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 148.9, 148.3 (d, *J* = 6.0 Hz), 136.1 (d, *J* = 7.5 Hz), 131.1, 129.5, 128.2, 127.6, 127.0, 122.7 (d, *J* = 21.0 Hz), 117.5 (qt, *J* = 288.0, 32.5 Hz), 114.8-106.3 (m, 2C), 86.8 (ddd, *J* = 187.5, 33.0, 22.5 Hz).

**<sup>19</sup>F NMR** (564 MHz, CDCl<sub>3</sub>) δ (-80.76)-(-80.89) (m), (-119.35)-(-120.05) (m), (-126.26)-(-126.40) (m), (-126.47)-(-126.55) (m), (-127.71)-(-128.43) (m), (-196.55)-(-196.79) (m).

**HRMS** (ESI) *m/z* calcd. for C<sub>13</sub>H<sub>8</sub>F<sub>8</sub>N<sup>+</sup> [M + H]<sup>+</sup> 330.0524, found 330.0526.

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52

**(52) 3-(1,2,2,3,3,4,4,5,5,5-Decafluoropentyl)quinoline**

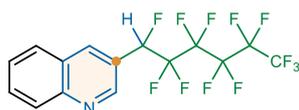
Prepared according to **General Procedure D** using *N*-trifosylhydrazone (312.0 mg, 0.6 mmol) derived from ethyl 2,2,3,3,4,4,5,5,6,6,6-undecafluorohexanoate and *N*-TBS indole (69.3 mg, 0.3 mmol) afforded **52** (89.8 mg, 79% yield) as a pale yellow oil.

$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.94 (s, 1H), 8.28 (s, 1H), 8.16 (d,  $J = 8.5$  Hz, 1H), 7.86 (d,  $J = 8.5$  Hz, 1H), 7.79 (t,  $J = 7.5$  Hz, 1H), 7.60 (t,  $J = 7.5$  Hz, 1H), 6.04 (ddd,  $J = 43.5, 18.5, 2.0$  Hz, 1H).

$^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ )  $\delta$  149.0, 148.3 (d,  $J = 6.0$  Hz), 136.1 (d,  $J = 6.0$  Hz), 131.1, 129.5, 128.2, 127.6, 127.0, 122.7 (d,  $J = 19.5$  Hz), 117.3 (qt,  $J = 288.0, 33.0$  Hz), 115.4-106.0 (m, 3C), 87.0 (ddd,  $J = 187.5, 33.0, 24.0$  Hz).

$^{19}\text{F NMR}$  (564 MHz,  $\text{CDCl}_3$ )  $\delta$  (-81.02)-(-81.11) (m), (-118.92)-(-119.67) (m), (-123.02)-(-123.21) (m), (-125.34)-(-127.54) (m), (-196.57)-(-196.82) (m).

**HRMS** (ESI)  $m/z$  calcd. for  $\text{C}_{14}\text{H}_8\text{F}_{10}\text{N}^+$   $[\text{M} + \text{H}]^+$  380.0492, found 380.0495.



53

**(53) 3-(1,2,2,3,3,4,4,5,5,6,6,6-Dodecafluorohexyl)quinoline**

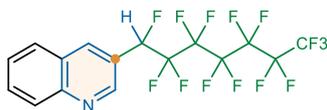
Prepared according to **General Procedure D** using *N*-trifosylhydrazone (342.0 mg, 0.6 mmol) derived from ethyl 2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptanoate and *N*-TBS indole (69.3 mg, 0.3 mmol) afforded **53** (100.4 mg, 78% yield) as a pale yellow oil.

$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.95 (s, 1H), 8.31 (s, 1H), 8.17 (d,  $J = 8.5$  Hz, 1H), 7.90 (d,  $J = 8.0$  Hz, 1H), 7.82 (t,  $J = 7.5$  Hz, 1H), 7.64 (t,  $J = 7.5$  Hz, 1H), 6.06 (ddd,  $J = 43.5, 18.5, 2.5$  Hz, 1H).

$^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ )  $\delta$  149.0, 148.4 (d,  $J = 6.0$  Hz), 136.2 (d,  $J = 6.0$  Hz), 131.1, 129.6, 128.3, 127.7, 127.0, 122.7 (d,  $J = 21.0$  Hz), 117.2 (qt,  $J = 288.0, 32.5$  Hz), 115.5-80.85 (m, 4C), 87.0 (ddd,  $J = 187.5, 33.0, 22.5$  Hz).

$^{19}\text{F NMR}$  (564 MHz,  $\text{CDCl}_3$ )  $\delta$  (-80.74)-(-) (m), (-118.69)-(-119.49) (m), (-121.43)-(-123.82) (m), (-125.31)-(-127.31) (m), (-196.40)-(-196.70) (m).

**HRMS** (ESI)  $m/z$  calcd. for  $\text{C}_{15}\text{H}_8\text{F}_{12}\text{N}^+$   $[\text{M} + \text{H}]^+$  430.0460, found 430.0462.



54

**(54) 3-(1,2,2,3,3,4,4,5,5,6,6,7,7,7-Tetradecafluoroheptyl)quinoline**

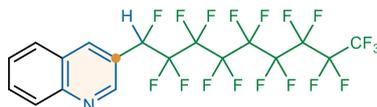
Prepared according to **General Procedure D** using *N*-trifosylhydrazone (394.8 mg, 0.6 mmol) derived from ethyl 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanoate and *N*-TBS indole (69.3 mg, 0.3 mmol) afforded **54** (110.6 mg, 77% yield) as a pale yellow solid; mp: 58-59 °C.

$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.95 (s, 1H), 8.30 (s, 1H), 8.17 (d,  $J = 8.5$  Hz, 1H), 7.88 (d,  $J = 8.0$  Hz, 1H), 7.81 (t,  $J = 7.5$  Hz, 1H), 7.62 (t,  $J = 7.5$  Hz, 1H), 6.05 (ddd,  $J = 43.5, 18.5, 2.5$  Hz, 1H).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  149.0, 148.3 (d,  $J = 6.0$  Hz), 136.2 (d,  $J = 6.0$  Hz), 131.1, 129.5, 128.2, 127.6, 127.0, 122.8 (d,  $J = 21.0$  Hz), 117.1 (qt,  $J = 288.0, 33.0$  Hz), 115.6-107.7 (m, 5C), 87.1 (ddd,  $J = 187.5, 34.5, 24.0$  Hz).

$^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  (-80.83)-(-80.95) (m), (-118.68)-(-119.47) (m), (-121.25)-(-123.65) (m), (-125.36)-(-127.26) (m), (-196.43)-(-196.68) (m).

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{16}\text{H}_8\text{F}_{14}\text{N}^+$   $[\text{M} + \text{H}]^+$  480.0428, found 480.0430.



55

### (55) 3-(1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Octadecafluorononyl)quinoline

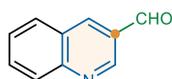
Prepared according to **General Procedure D** using *N*-triftosylhydrazone (454.8 mg, 0.6 mmol) derived from ethyl 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-nonadecafluorodecanoate and *N*-TBS indole (69.3 mg, 0.3 mmol) afforded **55** (110.6 mg, 65% yield) as a pale yellow solid; mp: 76-78 °C.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.95 (s, 1H), 8.32 (s, 1H), 8.18 (d,  $J = 8.4$  Hz, 1H), 7.91 (d,  $J = 8.4$  Hz, 1H), 7.86-7.81 (m, 1H), 7.67-7.62 (m, 1H), 6.07 (ddd,  $J = 43.5, 18.5, 2.5$  Hz, 1H).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  149.0, 148.4 (d,  $J = 6.0$  Hz), 136.2 (d,  $J = 6.0$  Hz), 131.1, 129.6, 128.3, 127.7, 127.0, 122.7 (d,  $J = 21.0$  Hz), 117.1 (qt,  $J = 288.0, 32.5$  Hz), 115.4-107.7 (m, 7C), 87.1 (ddd,  $J = 187.5, 33.0, 24.0$  Hz).

$^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  (-80.68)-(-80.78) (m), (-118.58)-(-119.40) (m), (-120.99)-(-123.48) (m), (-125.30)-(-127.18) (m), (-196.34)-(-196.63) (m).

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{18}\text{H}_8\text{F}_{18}\text{N}^+$   $[\text{M} + \text{H}]^+$  580.0364, found 580.0366.



56

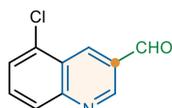
### (56) Quinoline-3-carbaldehyde

Prepared according to **General Procedure E** using TFHZ-Tfs **2** (115.3 mg, 0.36 mmol) and *N*-TBS indole (69.4 mg, 0.3 mmol) afforded **56** (36.8 mg, 78% yield) as a white solid; mp: 68-71 °C.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  10.26 (s, 1H), 9.37 (d,  $J = 2.0$  Hz, 1H), 8.64 (d,  $J = 1.5$  Hz, 1H), 8.19 (d,  $J = 8.5$  Hz, 1H), 8.00 (d,  $J = 8.0$  Hz, 1H), 7.89 (t,  $J = 8.0$  Hz, 1H), 7.67 (t,  $J = 7.5$  Hz, 1H).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  190.7, 150.6, 149.1, 140.1, 132.7, 129.7, 129.4, 128.6, 127.9, 127.0.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{10}\text{H}_8\text{NO}^+$   $[\text{M} + \text{H}]^+$  158.0600, found 158.0604.



57

### (57) 5-Chloroquinoline-3-carbaldehyde

Prepared according to **General Procedure E** using TFHZ-Tfs **2** (115.3 mg, 0.36 mmol) and 1-(tert-butyldimethylsilyl)-4-chloro-1H-indole (79.8 mg, 0.3 mmol) afforded **57** (34.5 mg, 60% yield) as a white solid; mp: 132-134 °C.

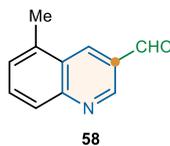
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  10.31 (s, 1H), 9.40 (d,  $J = 1.5$  Hz, 1H), 9.03 (d,  $J = 1.5$  Hz, 1H), 8.12 (d,  $J$

= 8.5 Hz, 1H), 7.80 (t,  $J = 7.5$  Hz, 1H), 7.74 (d,  $J = 7.5$  Hz, 1H).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  190.5, 151.2, 149.5, 137.3, 133.0, 132.3, 129.1, 128.9, 127.9, 125.5.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{10}\text{H}_7\text{ClNO}^+$   $[\text{M} + \text{H}]^+$  192.0211, found 192.0213.

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### (58) 5-Methylquinoline-3-carbaldehyde

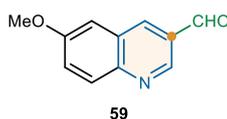
Prepared according to **General Procedure E** using TFHZ-Tfs **2** (115.3 mg, 0.36 mmol) and 1-(*tert*-butyldimethylsilyl)-4-methyl-1*H*-indole (73.6 mg, 0.3 mmol) afforded **58** (35.4 mg, 69% yield) as a white solid; mp: 73-75 °C.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  10.27 (s, 1H), 9.34 (d,  $J = 1.5$  Hz, 1H), 8.80 (d,  $J = 1.5$  Hz, 1H), 8.02 (d,  $J = 8.5$  Hz, 1H), 7.76 (t,  $J = 7.5$  Hz, 1H), 7.48 (d,  $J = 7.0$  Hz, 1H), 2.78 (s, 3H).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  190.9, 151.1, 148.9, 136.7, 136.4, 132.4, 128.3, 128.1, 127.9, 126.5, 18.6.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{11}\text{H}_{10}\text{NO}^+$   $[\text{M} + \text{H}]^+$  172.0757, found 172.0755.

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### (59) 6-Methoxyquinoline-3-carbaldehyde

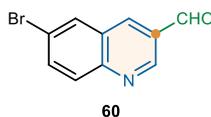
Prepared according to **General Procedure E** using TFHZ-Tfs **2** (115.3 mg, 0.36 mmol) and 1-(*tert*-butyldimethylsilyl)-5-methoxy-1*H*-indole (78.4 mg, 0.3 mmol) afforded **59** (42.1 mg, 75% yield) as a white solid; mp: 83-85 °C.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  10.24 (s, 1H), 9.21 (d,  $J = 1.5$  Hz, 1H), 8.53 (d,  $J = 1.5$  Hz, 1H), 8.08 (d,  $J = 9.0$  Hz, 1H), 7.53 (dd,  $J = 9.0, 2.5$  Hz, 1H), 7.21 (d,  $J = 2.5$  Hz, 1H), 3.97 (s, 3H).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  191.0, 158.6, 146.98, 146.91, 138.3, 131.0, 128.8, 128.3, 125.6, 106.3, 55.7.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{11}\text{H}_{10}\text{NO}_2^+$   $[\text{M} + \text{H}]^+$  188.0706, found 188.0704.

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### (60) 6-Bromoquinoline-3-carbaldehyde

Prepared according to **General Procedure E** using TFHZ-Tfs **2** (115.3 mg, 0.36 mmol) and 5-bromo-1-(*tert*-butyldimethylsilyl)-1*H*-indole (93.1 mg, 0.3 mmol) afforded **60** (62.3 mg, 88% yield) as a white solid; mp: 163-164 °C.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  10.25 (s, 1H), 9.36 (s, 1H), 8.53 (s, 1H), 8.14 (d,  $J = 2.0$  Hz, 1H), 8.05 (d,  $J = 9.0$  Hz, 1H), 7.93 (dd,  $J = 9.0, 2.0$  Hz, 1H).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  190.3, 149.4, 149.1, 138.7, 136.0, 131.4, 131.2, 129.1, 128.2, 121.9.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{10}\text{H}_7\text{BrNO}^+$   $[\text{M} + \text{H}]^+$  235.9706, found 235.9703.

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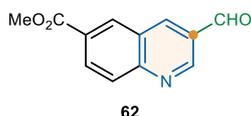
**(61) 6-Phenylquinoline-3-carbaldehyde**

Prepared according to **General Procedure E** using TFHZ-Tfs **2** (115.3 mg, 0.36 mmol) and 1-(*tert*-butyldimethylsilyl)-5-phenyl-1*H*-indole (92.3 mg, 0.3 mmol) afforded **61** (54.6 mg, 78% yield) as a white solid; mp: 70-72 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 10.27 (s, 1H), 9.35 (d, *J* = 1.5 Hz, 1H), 8.68 (d, *J* = 1.5 Hz, 1H), 8.25 (d, *J* = 9.0 Hz, 1H), 8.17-8.12 (m, 2H), 7.72 (d, *J* = 7.5 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.45 (t, *J* = 7.0 Hz, 1H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 190.7, 149.9, 149.0, 140.8, 140.2, 139.5, 132.4, 130.1, 129.1, 129.0, 128.2, 127.5, 127.3, 126.8.

HRMS (ESI) *m/z* calcd. for C<sub>16</sub>H<sub>12</sub>NO<sup>+</sup> [M + H]<sup>+</sup> 234.0913, found 234.0911.



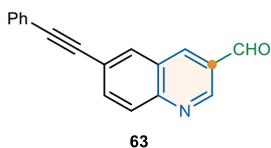
**(62) Methyl 3-formylquinoline-6-carboxylate**

Prepared according to **General Procedure E** using TFHZ-Tfs **2** (115.3 mg, 0.36 mmol) and 1-(*tert*-butyldimethylsilyl)-1*H*-indole-5-carboxylate (86.8 mg, 0.3 mmol) afforded **62** (57.4 mg, 89% yield) as a white solid; mp: 146-148 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 10.28 (s, 1H), 9.45 (d, *J* = 2.0 Hz, 1H), 8.75 (d, *J* = 2.0 Hz, 1H), 8.73 (d, *J* = 2.0 Hz, 1H), 8.46 (dd, *J* = 9.0, 2.0 Hz, 1H), 8.24 (d, *J* = 9.0 Hz, 1H), 4.03 (s, 3H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 190.2, 166.0, 152.2, 151.1, 141.1, 132.3, 132.0, 130.1, 129.5, 129.1, 126.3, 52.7.

HRMS (ESI) *m/z* calcd. for C<sub>12</sub>H<sub>10</sub>NO<sub>3</sub><sup>+</sup> [M + H]<sup>+</sup> 216.0655, found 216.0656.



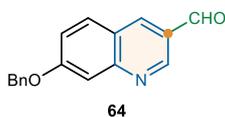
**(63) 6-(Phenylethynyl)quinoline-3-carbaldehyde**

Prepared according to **General Procedure E** using TFHZ-Tfs **2** (115.3 mg, 0.36 mmol) and 1-(*tert*-butyldimethylsilyl)-5-(phenylethynyl)-1*H*-indole (99.5 mg, 0.3 mmol) afforded **63** (62.5 mg, 81% yield) as a white solid; mp: 105-107 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 10.26 (s, 1H), 9.35 (s, 1H), 8.59 (s, 1H), 8.17-8.13 (m, 2H), 7.97 (d, *J* = 9.0 Hz, 1H), 7.62-7.55 (m, 2H), 7.42-7.35 (m, 3H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 190.5, 149.9, 149.6, 139.5, 135.2, 132.2, 131.8, 129.9, 129.1, 128.9, 128.5, 126.9, 123.2, 122.5, 91.9, 88.2.

HRMS (ESI) *m/z* calcd. for C<sub>18</sub>H<sub>12</sub>NO<sup>+</sup> [M + H]<sup>+</sup> 258.0913, found 258.0912.



**(64) 7-(Benzyloxy)quinoline-3-carbaldehyde**

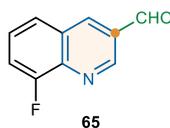
Prepared according to **General Procedure E** using TFHZ-Tfs **2** (115.3 mg, 0.36 mmol) and 6-(benzyloxy)-1-(*tert*-butyldimethylsilyl)-1*H*-indole (101.3 mg, 0.3 mmol) afforded **64** (62.4 mg, 79% yield) as a white solid; mp: 125-127 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 10.19 (s, 1H), 9.27 (d, *J* = 1.5 Hz, 1H), 8.54 (d, *J* = 1.5 Hz, 1H), 7.88 (d, *J* = 9.0 Hz, 1H), 7.57 (d, *J* = 2.0 Hz, 1H), 7.49 (d, *J* = 7.5 Hz, 2H), 7.42 (t, *J* = 7.0 Hz, 2H), 7.39-7.34 (m, 2H), 5.25 (s, 2H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 190.5, 162.4, 152.7, 150.0, 139.1, 135.7, 130.6, 128.7, 128.4, 127.7, 127.1, 122.3, 121.6, 108.9, 70.5.

HRMS (ESI) *m/z* calcd. for C<sub>17</sub>H<sub>14</sub>NO<sub>2</sub><sup>+</sup> [M + H]<sup>+</sup> 264.1019, found 264.1015.

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**(65) 8-Fluoroquinoline-3-carbaldehyde**

Prepared according to **General Procedure E** using TFHZ-Tfs **2** (115.3 mg, 0.36 mmol) and 1-(*tert*-butyldimethylsilyl)-7-fluoro-1*H*-indole (74.8 mg, 0.3 mmol) afforded **65** (39.4 mg, 75% yield) as a white solid; mp: 91-93 °C.

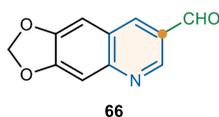
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 10.27 (s, 1H), 9.39 (d, *J* = 2.0 Hz, 1H), 8.66 (t, *J* = 1.5 Hz, 1H), 7.80 (d, *J* = 6.5 Hz, 1H), 7.63-7.59 (m, 1H), 7.59-7.54 (m, 1H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 190.4, 157.9 (d, *J* = 256.5 Hz), 149.2, 140.4 (d, *J* = 10.5 Hz), 139.6 (d, *J* = 3.0 Hz), 129.2, 128.6 (d, *J* = 1.5 Hz), 127.9 (d, *J* = 7.5 Hz), 125.0 (d, *J* = 4.5 Hz), 116.8 (d, *J* = 19.5 Hz).

<sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ (-123.61)-(-123.70) (m).

HRMS (ESI) *m/z* calcd. for C<sub>10</sub>H<sub>7</sub>FNO<sup>+</sup> [M + H]<sup>+</sup> 176.0506, found 176.0508.

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**(66) [1,3]Dioxolo[4,5-g]quinoline-7-carbaldehyde**

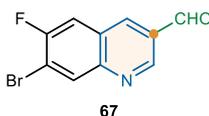
Prepared according to **General Procedure E** using TFHZ-Tfs **2** (115.3 mg, 0.36 mmol) and 5-(*tert*-butyldimethylsilyl)-5*H*-[1,3]dioxolo[4,5-*f*]indole (82.6 mg, 0.3 mmol) afforded **66** (47.1 mg, 78% yield) as a white solid; mp: 138-140 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 10.17 (s, 1H), 9.13 (d, *J* = 2.0 Hz, 1H), 8.42 (d, *J* = 1.5 Hz, 1H), 7.44 (s, 1H), 7.18 (s, 1H), 6.18 (s, 2H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 190.7, 153.4, 149.8, 148.9, 148.0, 137.3, 127.4, 124.4, 106.2, 103.9, 102.4.

HRMS (ESI) *m/z* calcd. for C<sub>11</sub>H<sub>8</sub>NO<sub>3</sub><sup>+</sup> [M + H]<sup>+</sup> 202.0499, found 202.0497.

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**(67) 7-Bromo-6-fluoroquinoline-3-carbaldehyde**

Prepared according to **General Procedure E** using TFHZ-Tfs **2** (115.3 mg, 0.36 mmol) and 6-bromo-1-(*tert*-butyldimethylsilyl)-5-fluoro-1*H*-indole (98.5 mg, 0.3 mmol) afforded **67** (57.2 mg, 75%

yield) as a white solid; mp: 163-165 °C.

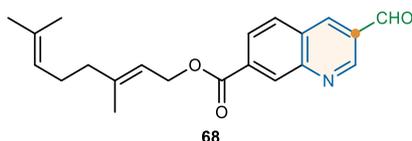
$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  10.26 (s, 1H), 9.33 (d,  $J = 1.5$  Hz, 1H), 8.57 (d,  $J = 1.5$  Hz, 1H), 8.48 (d,  $J = 6.6$  Hz, 1H), 7.67 (d,  $J = 8.4$  Hz, 1H).

$^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ )  $\delta$  190.1, 157.3 (d,  $J = 250.5$  Hz), 149.5 (d,  $J = 3.0$  Hz), 147.7, 138.9 (d,  $J = 6.0$  Hz), 135.1, 129.1, 126.9 (d,  $J = 9.0$  Hz), 117.1 (d,  $J = 24.0$  Hz), 112.9 (d,  $J = 22.5$  Hz).

$^{19}\text{F NMR}$  (564 MHz,  $\text{CDCl}_3$ )  $\delta$  (-105.64)-(-105.71) (m).

**HRMS** (ESI)  $m/z$  calcd. for  $\text{C}_{10}\text{H}_6\text{BrFNO}^+$   $[\text{M} + \text{H}]^+$  253.9611, found 253.9612.

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**(68) (*E*)-3,7-Dimethylocta-2,6-dien-1-yl 3-formylquinoline-7-carboxylate**

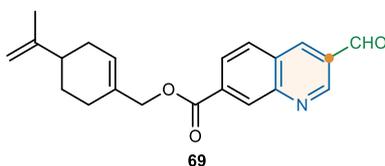
Prepared according to **General Procedure E** using TFHZ-Tfs **2** (115.3 mg, 0.36 mmol) and (*E*)-3,7-dimethylocta-2,6-dien-1-yl 1-(*tert*-butyldimethylsilyl)-1*H*-indole-6-carboxylate (123.5 mg, 0.3 mmol) afforded **68** (76.9 mg, 76% yield) as a white solid; mp: 88-90 °C.

$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  10.29 (s, 1H), 9.43 (d,  $J = 1.5$  Hz, 1H), 8.89 (s, 1H), 8.66 (d,  $J = 1.5$  Hz, 1H), 8.26 (dd,  $J = 8.5, 1.5$  Hz, 1H), 8.05 (d,  $J = 8.5$  Hz, 1H), 5.52 (t,  $J = 7.0$  Hz, 1H), 5.13-5.06 (m, 1H), 4.93 (d,  $J = 7.0$  Hz, 2H), 2.19-2.04 (m, 4H), 1.80 (s, 3H), 1.67 (s, 3H), 1.61 (s, 3H).

$^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ )  $\delta$  190.5, 165.7, 150.0, 149.8, 143.2, 139.7, 134.1, 132.0, 131.9, 129.5, 129.3, 127.4, 123.6, 117.8, 62.6, 39.5, 26.3, 25.7, 17.7, 16.6.

**HRMS** (ESI)  $m/z$  calcd. for  $\text{C}_{21}\text{H}_{24}\text{NO}_3^+$   $[\text{M} + \text{H}]^+$  338.1751, found 338.1751.

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**(69) (4-(Prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl 3-formylquinoline-7-carboxylate**

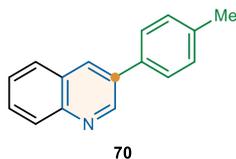
Prepared according to **General Procedure E** using TFHZ-Tfs **2** (115.3 mg, 0.36 mmol) and (4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl 1-(*tert*-butyldimethylsilyl)-1*H*-indole-6-carboxylate (122.9 mg, 0.3 mmol) afforded **69** (68.4 mg, 68% yield) as a white solid; mp: 97-99 °C.

$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  10.30 (s, 1H), 9.44 (d,  $J = 1.5$  Hz, 1H), 8.90 (s, 1H), 8.68 (d,  $J = 1.5$  Hz, 1H), 8.27 (dd,  $J = 8.5, 1.5$  Hz, 1H), 8.07 (d,  $J = 8.5$  Hz, 1H), 5.91 (s, 1H), 4.86-4.77 (m, 2H), 4.76-4.72 (m, 2H), 2.28-2.14 (m, 4H), 2.08-1.96 (m, 1H), 1.94-1.85 (m, 1H), 1.76 (s, 3H), 1.61-1.49 (m, 1H).

$^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  190.4, 165.6, 150.0, 149.9, 149.5, 139.7, 134.0, 132.3, 132.0, 129.62, 129.59, 129.4, 127.4, 126.5, 108.9, 69.7, 40.8, 30.5, 27.3, 26.5, 20.8.

**HRMS** (ESI)  $m/z$  calcd. for  $\text{C}_{21}\text{H}_{22}\text{NO}_3^+$   $[\text{M} + \text{H}]^+$  336.1594, found 336.1596.

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### (70) 3-(*p*-Tolyl)quinoline

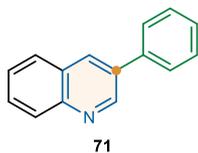
Prepared according to **General Procedure F** using *N*-trifosylhydrazone (102.6 mg, 0.3 mmol) derived from 4-methylbenzaldehyde and *N*-TBS indole (138.6 mg, 0.6 mmol) afforded **70** (63.7 mg, 97% yield) as a white solid; mp: 79-80 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.18 (s, 1H), 8.26 (s, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.61 (d, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 7.5 Hz, 2H), 2.43 (s, 3H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 149.9, 147.2, 138.0, 134.9, 133.7, 132.7, 129.8, 129.2, 129.1, 128.0, 127.9, 127.2, 126.9, 21.1.

HRMS (ESI) *m/z* calcd. for C<sub>16</sub>H<sub>14</sub>N<sup>+</sup> [M + H]<sup>+</sup> 220.1121, found 220.1124.

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### (71) 3-Phenylquinoline

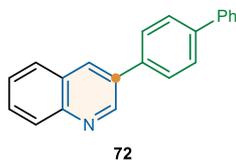
Prepared according to **General Procedure F** using *N*-trifosylhydrazone (98.4 mg, 0.3 mmol) derived from benzaldehyde and *N*-TBS indole (138.6 mg, 0.6 mmol) afforded **71** (54.1 mg, 88% yield) as a white solid; mp: 52-54 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.19 (d, *J* = 2.5 Hz, 1H), 8.29 (d, *J* = 1.5 Hz, 1H), 8.15 (d, *J* = 8.5 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.75-7.68 (m, 3H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 1H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 149.9, 147.3, 137.8, 133.8, 133.2, 129.3, 129.2, 129.1, 128.1, 128.0, 127.9, 127.4, 127.0.

HRMS (ESI) *m/z* calcd. for C<sub>15</sub>H<sub>12</sub>N<sup>+</sup> [M + H]<sup>+</sup> 206.0964, found 206.0966.

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### (72) 3-([1,1'-Biphenyl]-4-yl)quinoline

Prepared according to **General Procedure G** using *N*-trifosylhydrazone (121.2 mg, 0.3 mmol) derived from [1,1'-biphenyl]-4-carbaldehyde and *N*-TBS indole (138.6 mg, 0.6 mmol) afforded **72** (66.6 mg, 79% yield) as a white solid; mp: 145-147 °C.

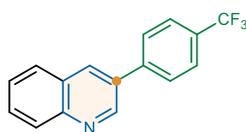
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.25 (d, *J* = 2.5 Hz, 1H), 8.35 (d, *J* = 2.0 Hz, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.5 Hz, 2H), 7.76 (d, *J* = 8.5 Hz, 2H), 7.75-7.71 (m, 1H), 7.67 (d, *J* = 7.5 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 1H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 149.8, 147.4, 141.0, 140.4, 136.7, 133.3, 133.0, 129.4, 129.3, 128.9,

128.04, 127.99, 127.9, 127.7, 127.6, 127.1, 127.0.

**HRMS** (ESI)  $m/z$  calcd. for  $C_{21}H_{16}N^+$   $[M + H]^+$  282.1277, found 282.1279.

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73

### (73) 3-(4-(Trifluoromethyl)phenyl)quinoline

Prepared according to **General Procedure F** using *N*-trifosylhydrazone (118.8 mg, 0.3 mmol) derived from 4-(trifluoromethyl)benzaldehyde and *N*-TBS indole (138.6 mg, 0.6 mmol) afforded **73** (47.5 mg, 58% yield) as a white solid; mp: 136-137 °C.

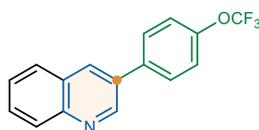
**<sup>1</sup>H NMR** (500 MHz,  $CDCl_3$ )  $\delta$  9.18 (d,  $J = 2.0$  Hz, 1H), 8.35 (d,  $J = 2.0$  Hz, 1H), 8.18 (d,  $J = 8.5$  Hz, 1H), 7.92 (d,  $J = 8.0$  Hz, 1H), 7.83 (d,  $J = 8.0$  Hz, 2H), 7.81-7.75 (m, 3H), 7.62 (t,  $J = 7.5$  Hz, 1H).

**<sup>13</sup>C NMR** (125 MHz,  $CDCl_3$ )  $\delta$  149.3, 147.6, 141.4, 134.0, 132.5, 130.3 (q,  $J = 32.5$  Hz), 130.1, 129.2, 128.1, 127.83, 127.75, 127.4, 126.1 (q,  $J = 3.8$  Hz), 124.1 (q,  $J = 271.3$  Hz).

**<sup>19</sup>F NMR** (564 MHz,  $CDCl_3$ )  $\delta$  -62.55.

**HRMS** (ESI)  $m/z$  calcd. for  $C_{16}H_{11}F_3N^+$   $[M + H]^+$  274.0838, found 274.0840.

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74

### (74) 3-(4-(Trifluoromethoxy)phenyl)quinoline

Prepared according to **General Procedure F** using *N*-trifosylhydrazone (123.6 mg, 0.3 mmol) derived from 4-(trifluoromethoxy)benzaldehyde and *N*-TBS indole (138.6 mg, 0.6 mmol) afforded **74** (70.2 mg, 81% yield) as a white solid; mp: 86-88 °C.

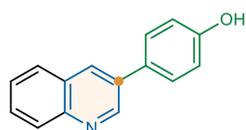
**<sup>1</sup>H NMR** (500 MHz,  $CDCl_3$ )  $\delta$  9.14 (s, 1H), 8.27 (d,  $J = 1.0$  Hz, 1H), 8.15 (d,  $J = 8.5$  Hz, 1H), 7.87 (d,  $J = 8.0$  Hz, 1H), 7.76-7.70 (m, 3H), 7.59 (t,  $J = 7.5$  Hz, 1H), 7.37 (d,  $J = 8.5$  Hz, 2H).

**<sup>13</sup>C NMR** (125 MHz,  $CDCl_3$ )  $\delta$  149.4, 149.2 (q,  $J = 1.3$  Hz), 147.4, 136.5, 133.4, 132.5, 129.7, 129.2, 128.8, 128.0, 127.8, 127.2, 121.6, 120.5 (q,  $J = 256.3$  Hz)

**<sup>19</sup>F NMR** (470 MHz,  $CDCl_3$ )  $\delta$  -57.78.

**HRMS** (ESI)  $m/z$  calcd. for  $C_{16}H_{11}F_3NO^+$   $[M + H]^+$  290.0787, found 290.0782.

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75

### (75) 4-(Quinolin-3-yl)phenol

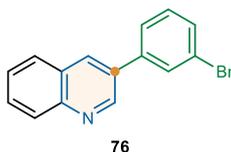
Prepared according to **General Procedure H** using *N*-trifosylhydrazone (137.4 mg, 0.3 mmol) derived from 4-((*tert*-butyldimethylsilyloxy)benzaldehyde and *N*-TBS indole (138.6 mg, 0.6 mmol) afforded **75** (42.4 mg, 64% yield) as a pale yellow solid; mp: 225-227 °C.

**<sup>1</sup>H NMR** (500 MHz, DMSO-*d*<sub>6</sub>) δ 9.76 (s, 1H), 9.20 (s, 1H), 8.51 (s, 1H), 8.01 (t, *J* = 8.0 Hz, 2H), 7.79-7.66 (m, 3H), 7.61 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 8.5 Hz, 2H).

**<sup>13</sup>C NMR** (150 MHz, DMSO-*d*<sub>6</sub>) δ 157.9, 149.4, 146.4, 132.9, 131.4, 129.1, 128.7, 128.5, 128.3, 127.9, 127.8, 127.0, 116.2.

**HRMS** (ESI) *m/z* calcd. for C<sub>15</sub>H<sub>12</sub>NO<sup>+</sup> [M + H]<sup>+</sup> 222.0913, found 222.0912.

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### (76) 3-(3-Bromophenyl)quinoline

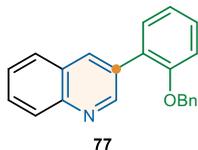
Prepared according to **General Procedure F** using *N*-trifosylhydrazone (122.1 mg, 0.3 mmol) derived from 3-bromobenzaldehyde and *N*-TBS indole (138.6 mg, 0.6 mmol) afforded **76** (45.0 mg, 53% yield) as a white solid; mp: 88-90 °C.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 9.13 (d, *J* = 2.4 Hz, 1H), 8.27 (d, *J* = 1.8 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.86-7.83 (m, 1H), 7.76-7.72 (m, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.57-7.54 (m, 1H), 7.39 (t, *J* = 7.8 Hz, 1H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 149.4, 147.5, 140.0, 133.5, 132.4, 131.1, 130.6, 130.4, 129.8, 129.2, 128.0, 127.8, 127.2, 126.0, 123.3.

**HRMS** (ESI) *m/z* calcd. for C<sub>15</sub>H<sub>11</sub>BrN<sup>+</sup> [M + H]<sup>+</sup> 284.0069, found 284.0062.

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### (77) 3-(2-(Benzyloxy)phenyl)quinoline

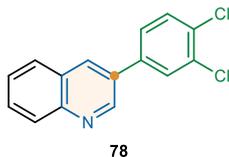
Prepared according to **General Procedure F** using *N*-trifosylhydrazone (130.2 mg, 0.3 mmol) derived from 2-(benzyloxy)benzaldehyde and *N*-TBS indole (138.6 mg, 0.6 mmol) afforded **77** (81.2 mg, 87% yield) as a white solid; mp: 110-112 °C.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 9.17 (s, 1H), 8.28 (d, *J* = 1.8 Hz, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.70-7.66 (m, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.44 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.37-7.33 (m, 1H), 7.32-7.26 (m, 4H), 7.25-7.21 (m, 1H), 7.11-7.06 (m, 2H), 5.10 (s, 2H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 155.8, 151.9, 146.8, 136.6, 135.6, 131.6, 131.0, 129.5, 129.10, 129.05, 128.5, 127.9, 127.8, 127.7, 127.6, 126.9, 126.5, 121.5, 113.1, 70.5.

**HRMS** (ESI) *m/z* calcd. for C<sub>22</sub>H<sub>18</sub>NO<sup>+</sup> [M + H]<sup>+</sup> 312.1383, found 312.1380.

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### (78) 3-(3,4-Dichlorophenyl)quinoline

Prepared according to **General Procedure F** using *N*-trifosylhydrazone (119.1 mg, 0.3 mmol) derived from 3,4-dichlorobenzaldehyde and *N*-TBS indole (138.6 mg, 0.6 mmol) afforded **78** (41.9 mg, 51% yield)

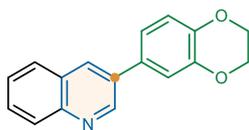
as a white solid; mp: 159-160 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.11 (d, *J* = 2.0 Hz, 1H), 8.28 (d, *J* = 1.5 Hz, 1H), 8.15 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 2.0 Hz, 1H), 7.78-7.30 (m, 1H), 7.64-7.57 (m, 2H), 7.56-7.51 (m, 1H).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 149.1, 147.6, 137.9, 133.44, 133.40, 132.5, 131.5, 131.1, 130.0, 129.3, 129.2, 128.0, 127.7, 127.4, 126.6.

**HRMS** (ESI) *m/z* calcd. for C<sub>15</sub>H<sub>10</sub>Cl<sub>2</sub>N<sup>+</sup> [M + H]<sup>+</sup> 274.0185, found 274.0186.

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79

### (79) 3-(2,3-Dihydrobenzo[*b*][1,4]dioxin-6-yl)quinoline

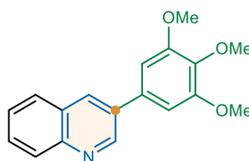
Prepared according to **General Procedure F** using *N*-trifosylhydrazone (115.8 mg, 0.3 mmol) derived from 2,3-dihydrobenzo[*b*][1,4]dioxine-6-carbaldehyde and *N*-TBS indole (138.6 mg, 0.6 mmol) afforded **79** (77.3 mg, 98% yield) as a white solid; mp: 98-100 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.12 (d, *J* = 2.5 Hz, 1H), 8.19 (d, *J* = 2.0 Hz, 1H), 8.11 (d, *J* = 8.5 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.70-7.63 (m, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 2.0 Hz, 1H), 7.18 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.99 (d, *J* = 8.5 Hz, 1H), 4.29 (s, 4H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 149.7, 147.0, 144.0, 143.8, 133.1, 132.4, 131.2, 129.1, 129.0, 128.0, 127.8, 126.8, 120.3, 118.0, 116.0, 64.4, 64.3.

**HRMS** (ESI) *m/z* calcd. for C<sub>17</sub>H<sub>14</sub>NO<sub>2</sub><sup>+</sup> [M + H]<sup>+</sup> 264.1019, found 264.1022.

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80

### (80) 3-(3,4,5-Trimethoxyphenyl)quinoline

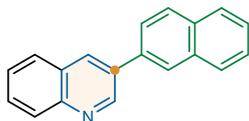
Prepared according to **General Procedure F** using *N*-trifosylhydrazone (125.4 mg, 0.3 mmol) derived from 3,4,5-trimethoxybenzaldehyde and *N*-TBS indole (138.6 mg, 0.6 mmol) afforded **80** (67.2 mg, 76% yield) as a white solid; mp: 99-100 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.14 (d, *J* = 2.0 Hz, 1H), 8.25 (d, *J* = 2.0 Hz, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.75-7.68 (m, 1H), 7.61-7.55 (m, 1H), 6.88 (s, 2H), 3.97 (s, 6H), 3.94 (s, 3H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 153.7, 149.8, 147.3, 138.2, 133.9, 133.7, 133.0, 129.4, 129.2, 127.89, 127.87, 127.1, 104.8, 61.1, 56.3.

**HRMS** (ESI) *m/z* calcd. for C<sub>18</sub>H<sub>18</sub>NO<sub>3</sub><sup>+</sup> [M + H]<sup>+</sup> 296.1281, found 296.1283.

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81

### (81) 3-(Naphthalen-2-yl)quinoline

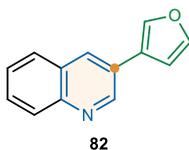
Prepared according to **General Procedure F** using *N*-trifosylhydrazone (113.4 mg, 0.3 mmol) derived from 2-naphthaldehyde and *N*-TBS indole (138.6 mg, 0.6 mmol) afforded **81** (62.7 mg, 82% yield) as a white solid; mp: 111-113 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.32 (d, *J* = 2.5 Hz, 1H), 8.41 (d, *J* = 1.0 Hz, 1H), 8.21-8.15 (m, 2H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.97-7.93 (m, 1H), 7.93-7.88 (m, 2H), 7.84 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.77-7.71 (m, 1H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.58-7.51 (m, 2H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 150.1, 147.4, 135.1, 133.73, 133.65, 133.4, 132.9, 129.4, 129.3, 129.0, 128.3, 128.1, 128.0, 127.7, 127.0, 126.6, 126.5, 126.4, 125.2.

**HRMS** (ESI) *m/z* calcd. for C<sub>19</sub>H<sub>14</sub>N<sup>+</sup> [M + H]<sup>+</sup> 256.1121, found 256.1123.

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### (82) 3-(Furan-3-yl)quinoline

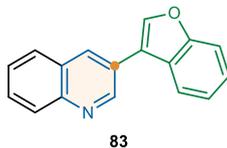
Prepared according to **General Procedure F** using *N*-trifosylhydrazone (95.4 mg, 0.3 mmol) derived from furan-3-carbaldehyde and *N*-TBS indole (138.6 mg, 0.6 mmol) afforded **82** (30.4 mg, 52% yield) as a white solid; mp: 75-78 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.22 (d, *J* = 2.0 Hz, 1H), 8.36 (d, *J* = 1.5 Hz, 1H), 8.09 (d, *J* = 8.5 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.70-7.64 (m, 1H), 7.59-7.51 (m, 2H), 6.87 (d, *J* = 3.5 Hz, 1H), 6.57-6.52 (m, 1H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 151.4, 147.10, 147.08, 143.1, 129.3, 129.2, 129.1, 127.94, 127.87, 127.2, 124.1, 112.0, 106.7.

**HRMS** (ESI) *m/z* calcd. for C<sub>13</sub>H<sub>10</sub>NO<sup>+</sup> [M + H]<sup>+</sup> 196.0757, found 196.0762.

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### (83) 3-(Benzofuran-3-yl)quinoline

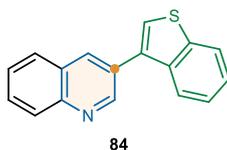
Prepared according to **General Procedure F** using *N*-trifosylhydrazone (110.4 mg, 0.3 mmol) derived from benzofuran-3-carbaldehyde and *N*-TBS indole (138.6 mg, 0.6 mmol) afforded **83** (52.9 mg, 72% yield) as a white solid; mp: 108-109 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.21 (d, *J* = 2.0 Hz, 1H), 8.40 (d, *J* = 2.0 Hz, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 7.97 (s, 1H), 7.92-7.87 (m, 2H), 7.77-7.72 (m, 1H), 7.63-7.57 (m, 2H), 7.45-7.35 (m, 2H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 155.8, 149.8, 147.4, 142.0, 133.2, 129.41, 129.36, 128.1, 127.8, 127.2, 126.1, 125.4, 125.1, 123.4, 120.0, 119.1, 112.0.

**HRMS** (ESI) *m/z* calcd. for C<sub>17</sub>H<sub>12</sub>NO<sup>+</sup> [M + H]<sup>+</sup> 246.0913, found 246.0917.

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### (84) 3-(Benzo[*b*]thiophen-3-yl)quinoline

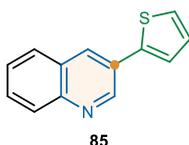
Prepared according to **General Procedure G** using *N*-trifosylhydrazone (115.2 mg, 0.3 mmol) derived from benzo[*b*]thiophene-3-carbaldehyde and *N*-TBS indole (138.6 mg, 0.6 mmol) afforded **84** (67.3 mg, 86% yield) as a white solid; mp: 108-110 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.16 (d, *J* = 2.0 Hz, 1H), 8.33 (d, *J* = 2.0 Hz, 1H), 8.19 (d, *J* = 8.5 Hz, 1H), 7.99-7.90 (m, 2H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.79-7.73 (m, 1H), 7.63-7.57 (m, 1H), 7.56 (s, 1H), 7.47-7.40 (m, 2H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 150.8, 147.4, 140.7, 137.6, 134.7, 134.4, 129.5, 129.3, 129.0, 127.9, 127.8, 127.1, 125.0, 124.8, 124.7, 123.1, 122.4.

**HRMS** (ESI) *m/z* calcd. for C<sub>17</sub>H<sub>12</sub>NS<sup>+</sup> [M + H]<sup>+</sup> 262.0685, found 262.0693.

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### (85) 3-(Thiophen-2-yl)quinoline

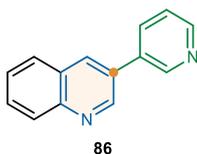
Prepared according to **General Procedure I** using *N*-trifosylhydrazone (100.2 mg, 0.3 mmol) derived from thiophene-2-carbaldehyde and *N*-TBS indole (138.6 mg, 0.6 mmol) afforded **85** (53.2 mg, 84% yield) as a white solid; mp: 67-68 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.20 (d, *J* = 2.0 Hz, 1H), 8.24 (d, *J* = 2.0 Hz, 1H), 8.09 (d, *J* = 8.5 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.70-7.65 (m, 1H), 7.57-7.51 (m, 1H), 7.48 (d, *J* = 3.5 Hz, 1H), 7.38 (dd, *J* = 3.5, 1.0 Hz, 1H), 7.15 (d, *J* = 5.0, 4.0 Hz, 1H).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 148.6, 147.2, 140.7, 131.3, 129.3, 128.4, 127.9, 127.8, 127.5, 127.2, 126.0, 124.4.

**HRMS** (ESI) *m/z* calcd. for C<sub>13</sub>H<sub>10</sub>NS<sup>+</sup> [M + H]<sup>+</sup> 212.0528, found 212.0529.

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### (86) 3-(Pyridin-3-yl)quinoline

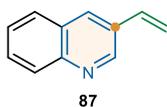
Prepared according to **General Procedure J** using *N*-trifosylhydrazone (98.7 mg, 0.3 mmol) derived from nicotinaldehyde and *N*-TBS indole (138.6 mg, 0.6 mmol) afforded **86** (21.6 mg, 35% yield) as a white solid; mp: 118-120 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.15 (d, *J* = 2.0 Hz, 1H), 8.97 (d, *J* = 1.5 Hz, 1H), 8.71-8.65 (m, 1H), 8.32 (d, *J* = 1.0 Hz, 1H), 8.15 (d, *J* = 8.5 Hz, 1H), 8.03-7.97 (m, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.79-7.72 (m, 1H), 7.64-7.57 (m, 1H), 7.45 (dd, *J* = 7.5, 5.0 Hz, 1H).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 149.3, 149.2, 148.5, 147.7, 134.6, 133.62, 133.58, 130.6, 129.9, 129.3, 128.0, 127.8, 127.3, 123.8.

**HRMS** (ESI) *m/z* calcd. for C<sub>14</sub>H<sub>11</sub>N<sub>2</sub><sup>+</sup> [M + H]<sup>+</sup> 207.0917, found 207.0917.

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S87

### (87) 3-Vinylquinoline

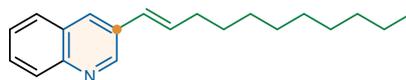
Prepared according to **General Procedure J** using *N*-trifosylhydrazone (166.8 mg, 0.6 mmol) derived from acrylaldehyde and *N*-TBS indole (69.3 mg, 0.3 mmol) afforded **87** (35.3 mg, 76% yield) as a pale yellow oil.

$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.03 (d,  $J = 1.5$  Hz, 1H), 8.11-8.05 (m, 2H), 7.80 (d,  $J = 8.0$  Hz, 1H), 7.71-7.65 (m, 1H), 7.56-7.51 (m, 1H), 6.87 (dd,  $J = 18.0, 11.0$  Hz, 1H), 5.99 (d,  $J = 18.0$  Hz, 1H), 5.47 (d,  $J = 11.0$  Hz, 1H).

$^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  149.1, 147.6, 133.8, 132.5, 130.3, 129.3, 129.2, 128.0, 127.9, 126.9, 116.4.

**HRMS** (ESI)  $m/z$  calcd. for  $\text{C}_{11}\text{H}_9\text{N}^+$   $[\text{M} + \text{H}]^+$  156.0808, found 156.0808.

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88

### (88) 3-(Undec-1-en-1-yl)quinoline

Prepared according to **General Procedure J** using *N*-trifosylhydrazone (121.2 mg, 0.3 mmol) derived from dodec-2-enal and *N*-TBS indole (138.6 mg, 0.6 mmol) afforded **88** (74.2 mg, 88% yield) as a pale yellow oil.

$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.97 (d,  $J = 2.0$  Hz, 1H), 8.05 (d,  $J = 8.5$  Hz, 1H), 7.97 (d,  $J = 1.5$  Hz, 1H), 7.76 (d,  $J = 8.0$  Hz, 1H), 7.66-7.61 (m, 1H), 7.53-7.47 (m, 1H), 6.52 (d,  $J = 16.0$  Hz, 1H), 6.47 (dt,  $J = 16.0, 6.5$  Hz, 1H), 2.28 (q,  $J = 7.0$  Hz, 2H), 1.56-1.47 (m, 2H), 1.42-1.20 (m, 14H), 0.88 (t,  $J = 6.8$  Hz, 3H).

$^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ )  $\delta$  149.4, 147.2, 134.0, 131.4, 130.8, 129.2, 128.7, 128.2, 127.6, 126.7, 126.5, 33.3, 31.9, 29.6, 29.5, 29.31, 29.25, 29.2, 22.7, 14.1.

**HRMS** (ESI)  $m/z$  calcd. for  $\text{C}_{20}\text{H}_{28}\text{N}^+$   $[\text{M} + \text{H}]^+$  282.2216, found 282.2218.

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89

### (89) 3-(Undec-1-en-1-yl)quinoline

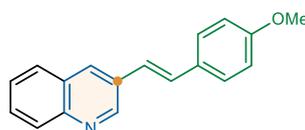
Prepared according to **General Procedure J** using *N*-trifosylhydrazone (91.8 mg, 0.3 mmol) derived from 3-methylbut-2-enal and *N*-TBS indole (138.6 mg, 0.6 mmol) afforded **89** (47.8 mg, 87% yield) as a pale yellow oil.

$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.80 (s, 1H), 8.06 (d,  $J = 8.5$  Hz, 1H), 7.95 (s, 1H), 7.78 (d,  $J = 8.0$  Hz, 1H), 7.66 (t,  $J = 7.5$  Hz, 1H), 7.52 (t,  $J = 7.5$  Hz, 1H), 6.38 (s, 1H), 1.99 (s, 3H), 1.95 (s, 3H).

$^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ )  $\delta$  152.0, 146.3, 138.8, 134.1, 131.6, 129.1, 128.7, 127.9, 127.6, 126.6, 121.6, 27.0, 19.6.

**HRMS** (ESI)  $m/z$  calcd. for  $\text{C}_{13}\text{H}_{14}\text{N}^+$   $[\text{M} + \text{H}]^+$  184.1121, found 184.1122.

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90

### (90) 3-(4-Methoxystyryl)quinoline

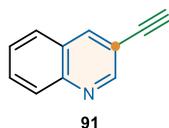
Prepared according to **General Procedure K** using *N*-trifosylhydrazone (115.2 mg, 0.3 mmol) derived from 3-(4-methoxyphenyl)acrylaldehyde and *N*-TBS indole (138.6 mg, 0.6 mmol) afforded **90** (64.2 mg, 82% yield) as a white solid; mp: 98-100 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.11 (d, *J* = 2.0 Hz, 1H), 8.14 (d, *J* = 1.5 Hz, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.69-7.63 (m, 1H), 7.57-7.50 (m, 3H), 7.29 (d, *J* = 16.5 Hz, 1H), 7.11 (d, *J* = 16.5 Hz, 1H), 6.96-6.91 (m, 2H), 3.85 (s, 3H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 159.8, 149.4, 147.2, 131.7, 130.7, 130.4, 129.5, 129.2, 129.0, 128.2, 128.0, 127.7, 126.9, 123.0, 114.3, 55.3.

HRMS (ESI) *m/z* calcd. for C<sub>18</sub>H<sub>16</sub>NO<sup>+</sup> [M + H]<sup>+</sup> 262.1226, found 262.1225.

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### (91) 3-Ethynylquinoline

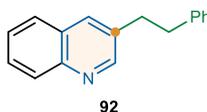
Prepared according to **General Procedure H** using *N*-trifosylhydrazone (129.6 mg, 0.3 mmol) derived from 3-(triisopropylsilyl)propionaldehyde and *N*-TBS indole (138.6 mg, 0.6 mmol) afforded **91** (21.6 mg, 47% yield) as a white solid; mp: 69-70 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.95 (d, *J* = 1.5 Hz, 1H), 8.29 (d, *J* = 1.0 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.76-7.71 (m, 1H), 7.60-7.55 (m, 1H), 3.28 (s, 1H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 152.3, 147.1, 139.3, 130.4, 129.5, 127.6, 127.4, 127.0, 116.2, 80.9, 80.5.

HRMS (ESI) *m/z* calcd. for C<sub>11</sub>H<sub>8</sub>N<sup>+</sup> [M + H]<sup>+</sup> 154.0651, found 154.0657.

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### (92) 3-Phenethylquinoline

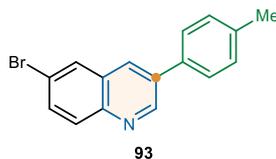
Prepared according to **General Procedure H** using *N*-trifosylhydrazone (106.8 mg, 0.3 mmol) derived from 3-phenylpropanal and *N*-TBS indole (138.6 mg, 0.6 mmol) afforded **92** (28.0 mg, 40% yield) as a pale yellow oil.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.75 (s, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 7.87 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.24-7.20 (m, 1H), 7.19 (d, *J* = 7.5 Hz, 2H), 3.16-3.10 (m, 2H), 3.07-3.00 (m, 2H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 152.0, 146.9, 140.8, 134.4, 134.2, 129.2, 128.7, 128.5, 128.1, 127.3, 126.6, 126.2, 37.4, 35.1.

HRMS (ESI) *m/z* calcd. for C<sub>17</sub>H<sub>16</sub>N<sup>+</sup> [M + H]<sup>+</sup> 234.1277, found 234.1281.

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### (93) 6-Bromo-3-(*p*-tolyl)quinoline

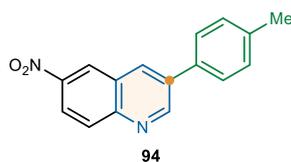
Prepared according to **General Procedure F** using *N*-trifosylhydrazone (102.6 mg, 0.3 mmol) derived from 4-methylbenzaldehyde and 5-bromo-1-(*tert*-butyldimethylsilyl)-1*H*-indole (186.0 mg, 0.6 mmol) afforded **93** (82.2 mg, 92% yield) as a white solid; mp: 143-145 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.16 (d, *J* = 2.0 Hz, 1H), 8.15 (d, *J* = 2.0 Hz, 1H), 8.01 (d, *J* = 2.0 Hz, 1H), 7.98 (d, *J* = 9.0 Hz, 1H), 7.75 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 150.3, 145.7, 138.4, 134.6, 134.4, 132.6, 131.6, 130.9, 130.0, 129.9, 129.2, 127.2, 120.8, 21.2.

**HRMS** (ESI) *m/z* calcd. for C<sub>16</sub>H<sub>13</sub>BrN<sup>+</sup> [M + H]<sup>+</sup> 298.0226, found 298.0231.

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#### (94) 6-Nitro-3-(*p*-tolyl)quinoline

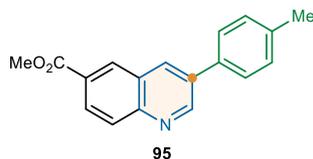
Prepared according to **General Procedure F** *N*-trifosylhydrazone (102.6 mg, 0.3 mmol) derived from 4-methylbenzaldehyde and 1-(*tert*-butyldimethylsilyl)-5-nitro-1*H*-indole (165.6 mg, 0.6 mmol) afforded **94** (34.1 mg, 43% yield) as a yellow solid; mp: 183-185 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.33 (d, *J* = 2.0 Hz, 1H), 8.83 (d, *J* = 2.0 Hz, 1H), 8.48-8.41 (m, 2H), 8.25 (d, *J* = 9.0 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 2.45 (s, 3H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 153.5, 149.0, 145.9, 139.0, 135.7, 134.0, 133.6, 131.1, 130.2, 127.3, 127.0, 124.6, 122.5, 21.2.

**HRMS** (ESI) *m/z* calcd. for C<sub>16</sub>H<sub>13</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> [M + H]<sup>+</sup> 265.0972, found 265.0974.

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#### (95) Methyl 3-(*p*-tolyl)quinoline-6-carboxylate

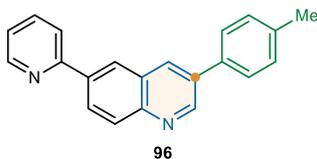
Prepared according to **General Procedure F** *N*-trifosylhydrazone (102.6 mg, 0.3 mmol) derived from 4-methylbenzaldehyde and methyl 1-(*tert*-butyldimethylsilyl)-1*H*-indole-5-carboxylate (173.4 mg, 0.6 mmol) afforded **95** (77.3 mg, 93% yield) as a white solid; mp: 123-125 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.23 (s, 1H), 8.61 (s, 1H), 8.33 (s, 1H), 8.26 (d, *J* = 9.0 Hz, 1H), 8.14 (d, *J* = 9.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 3.99 (s, 3H), 2.43 (s, 3H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 166.6, 152.0, 148.9, 138.4, 134.5, 134.3, 133.7, 131.1, 130.0, 129.5, 128.6, 128.4, 127.22, 127.17, 52.4, 21.1.

**HRMS** (ESI) *m/z* calcd. for C<sub>18</sub>H<sub>16</sub>NO<sub>2</sub><sup>+</sup> [M + H]<sup>+</sup> 278.1176, found 278.1177.

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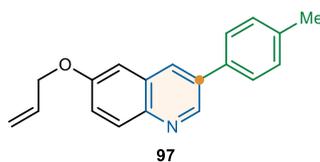
**(96) 6-(Pyridin-2-yl)-3-(*p*-tolyl)quinoline**

Prepared according to **General Procedure F** using *N*-trifosylhydrazone (102.6 mg, 0.3 mmol) derived from 4-methylbenzaldehyde and 1-(*tert*-butyldimethylsilyl)-5-(pyridin-2-yl)-1*H*-indole (184.8 mg, 0.6 mmol) afforded **96** (38.2 mg, 43% yield) as a yellow oil.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.19 (d, *J* = 2.0 Hz, 1H), 8.77 (d, *J* = 5.0 Hz, 1H), 8.54 (d, *J* = 1.5 Hz, 1H), 8.37 (d, *J* = 2.0 Hz, 1H), 8.35 (dd, *J* = 8.5, 2.0 Hz, 1H), 8.22 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.82 (td, *J* = 7.5, 1.5 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.30 (dd, *J* = 7.5, 5.0 Hz, 1H), 2.45 (s, 3H).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 156.5, 150.5, 149.9, 147.5, 138.2, 137.7, 136.9, 134.9, 134.2, 133.4, 129.9, 129.7, 128.2, 127.9, 127.2, 126.3, 122.5, 120.9, 21.2.

**HRMS** (ESI) *m/z* calcd. for C<sub>21</sub>H<sub>17</sub>N<sub>2</sub><sup>+</sup> [M + H]<sup>+</sup> 297.1386, found 297.1387.



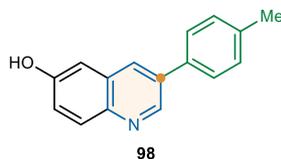
**(97) 6-(Allyloxy)-3-(*p*-tolyl)quinoline**

Prepared according to **General Procedure F** using *N*-trifosylhydrazone (102.6 mg, 0.3 mmol) derived from 4-methylbenzaldehyde and 5-(allyloxy)-1-(*tert*-butyldimethylsilyl)-1*H*-indole (172.2 mg, 0.6 mmol) afforded **97** (58.6 mg, 71% yield) as a white solid; mp: 75-77 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.02 (d, *J* = 1.5 Hz, 1H), 8.15 (s, 1H), 8.03 (d, *J* = 9.0 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.39 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 2.5 Hz, 1H), 6.18-6.08 (m, 1H), 5.49 (d, *J* = 17.5 Hz, 1H), 5.35 (d, *J* = 10.5 Hz, 1H), 4.68 (d, *J* = 5.0 Hz, 2H), 2.43 (s, 3H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 157.0, 147.5, 143.4, 138.0, 135.1, 134.1, 132.8, 131.7, 130.6, 129.8, 129.1, 127.2, 122.2, 118.0, 106.5, 69.1, 21.2.

**HRMS** (ESI) *m/z* calcd. for C<sub>19</sub>H<sub>18</sub>NO<sup>+</sup> [M + H]<sup>+</sup> 276.1383, found 276.1385.



**(98) 3-(*p*-Tolyl)quinolin-6-ol**

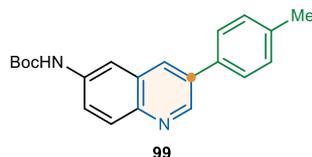
Prepared according to **General Procedure H** using *N*-trifosylhydrazone (102.6 mg, 0.3 mmol) derived from 4-methylbenzaldehyde and 1-(*tert*-butyldimethylsilyl)-5-((*tert*-butyldimethylsilyl)oxy)-1*H*-indole (216.6 mg, 0.6 mmol) afforded **98** (57.1 mg, 81% yield) as a white solid; mp: 246-248 °C.

**<sup>1</sup>H NMR** (500 MHz, DMSO-*d*<sub>6</sub>) δ 10.07 (s, 1H), 8.98 (d, *J* = 2.0 Hz, 1H), 8.37 (d, *J* = 1.5 Hz, 1H), 7.89 (d, *J* = 9.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.37-7.28 (m, 3H), 7.23 (d, *J* = 2.5 Hz, 1H), 2.36 (s, 3H).

$^{13}\text{C}$  NMR (150 MHz, DMSO- $d_6$ )  $\delta$  156.0, 146.1, 142.2, 137.6, 134.6, 132.8, 130.7, 130.2, 129.9, 129.3, 127.0, 122.0, 108.7, 20.8.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{16}\text{H}_{14}\text{NO}^+$   $[\text{M} + \text{H}]^+$  236.1070, found 236.1075.

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**(99) *tert*-Butyl (3-(*p*-tolyl)quinolin-6-yl)carbamate**

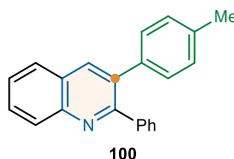
Prepared according to **General Procedure F** using *N*-trifosylhydrazone (102.6 mg, 0.3 mmol) derived from 4-methylbenzaldehyde and *tert*-butyl (1-(*tert*-butyldimethylsilyl)-1*H*-indol-5-yl)carbamate (207.6 mg, 0.6 mmol) afforded **99** (53.1 mg, 53% yield) as a white solid; mp: 158-160 °C.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.04 (d,  $J = 2.0$  Hz, 1H), 8.18 (d,  $J = 1.5$  Hz, 1H), 8.15 (s, 1H), 8.02 (d,  $J = 9.0$  Hz, 1H), 7.58 (d,  $J = 8.0$  Hz, 2H), 7.45 (dd,  $J = 9.0, 2.5$  Hz, 1H), 7.32 (d,  $J = 8.0$  Hz, 2H), 6.88 (s, 1H), 2.43 (s, 3H), 1.56 (s, 9H).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  152.7, 148.5, 144.0, 138.0, 136.6, 135.0, 134.2, 132.3, 129.9, 128.8, 127.2, 122.2, 114.0, 81.1, 28.3, 21.2.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{21}\text{H}_{23}\text{N}_2\text{O}_2^+$   $[\text{M} + \text{H}]^+$  335.1754, found 335.1754.

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**(100) 2-Phenyl-3-(*p*-tolyl)quinoline**

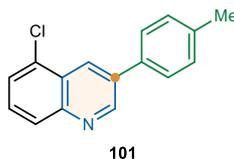
Prepared according to **General Procedure F** *N*-trifosylhydrazone (102.6 mg, 0.3 mmol) derived from 4-methylbenzaldehyde and 1-(*tert*-butyldimethylsilyl)-2-phenyl-1*H*-indole (184.2 mg, 0.6 mmol) afforded **100** (47.8 mg, 54% yield) as a pale yellow oil.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.20 (d,  $J = 8.5$  Hz, 1H), 8.16 (s, 1H), 7.86 (d,  $J = 8.0$  Hz, 1H), 7.73 (t,  $J = 7.5$  Hz, 1H), 7.56 (t,  $J = 7.5$  Hz, 1H), 7.50-7.44 (m, 2H), 7.34-7.26 (m, 3H), 7.14 (d,  $J = 8.0$  Hz, 2H), 7.11 (d,  $J = 8.0$  Hz, 2H), 2.36 (s, 3H).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  158.5, 147.2, 140.6, 137.4, 137.0, 136.9, 134.5, 130.0, 129.6, 129.43, 129.40, 128.9, 127.9, 127.4, 127.3, 126.6, 21.1.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{22}\text{H}_{18}\text{N}^+$   $[\text{M} + \text{H}]^+$  296.1434, found 296.1433.

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**(101) 5-Chloro-3-(*p*-tolyl)quinoline**

Prepared according to **General Procedure F** using *N*-trifosylhydrazone (102.6 mg, 0.3 mmol) derived from 4-methylbenzaldehyde and 1-(*tert*-butyldimethylsilyl)-4-chloro-1*H*-indole (159.0 mg, 0.6 mmol)

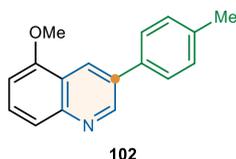
afforded **101** (63.0 mg, 83% yield) as a white solid; mp: 75-77 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.20 (d, *J* = 2.0 Hz, 1H), 8.66 (d, *J* = 1.0 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.67-7.56 (m, 4H), 7.34 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 150.5, 147.7, 138.4, 134.6, 134.5, 131.4, 129.9, 129.4, 128.7, 128.4, 127.3, 126.9, 126.2, 21.2.

HRMS (ESI) *m/z* calcd. for C<sub>16</sub>H<sub>13</sub>ClN<sup>+</sup> [M + H]<sup>+</sup> 254.0731, found 254.0733.

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### (102) 5-Methoxy-3-(*p*-tolyl)quinoline

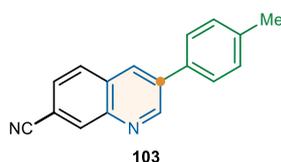
Prepared according to **General Procedure F** using *N*-trifosylhydrazone (102.6 mg, 0.3 mmol) derived from 4-methylbenzaldehyde and 1-(*tert*-butyldimethylsilyl)-4-methoxy-1*H*-indole (156.6 mg, 0.6 mmol) afforded **102** (70.2 mg, 94% yield) as a white solid; mp: 101-102 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.17 (d, *J* = 2.0 Hz, 1H), 8.72 (d, *J* = 1.5 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.60 (t, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.88 (d, *J* = 8.0 Hz, 1H), 4.03 (s, 3H), 2.43 (s, 3H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 155.3, 150.0, 147.9, 137.8, 135.2, 132.9, 129.8, 129.1, 127.7, 127.2, 121.3, 120.6, 104.5, 55.8, 21.1.

HRMS (ESI) *m/z* calcd. for C<sub>17</sub>H<sub>16</sub>NO<sup>+</sup> [M + H]<sup>+</sup> 250.1226, found 250.1222.

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### (103) 3-(*p*-Tolyl)quinoline-7-carbonitrile

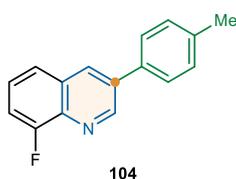
Prepared according to **General Procedure F** using *N*-trifosylhydrazone (102.6 mg, 0.3 mmol) derived from 4-methylbenzaldehyde and 1-(*tert*-butyldimethylsilyl)-1*H*-indole-6-carbonitrile (153.6 mg, 0.6 mmol) afforded **103** (37.3 mg, 51% yield) as a white solid; mp: 155-158 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.28 (d, *J* = 2.0 Hz, 1H), 8.49 (s, 1H), 8.31 (d, *J* = 2.0 Hz, 1H), 7.96 (d, *J* = 8.5 Hz, 1H), 7.71 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.65-7.60 (m, 2H), 7.39-7.33 (m, 2H), 2.45 (s, 3H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 151.9, 145.9, 139.1, 136.3, 135.2, 133.9, 132.3, 130.2, 130.1, 129.3, 127.7, 127.3, 118.6, 112.4, 21.2.

HRMS (ESI) *m/z* calcd. for C<sub>17</sub>H<sub>13</sub>N<sub>2</sub><sup>+</sup> [M + H]<sup>+</sup> 245.1073, found 245.1080.

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#### (104) 8-Fluoro-3-(*p*-tolyl)quinoline

Prepared according to **General Procedure F** using *N*-trifosylhydrazone (102.6 mg, 0.3 mmol) derived from 4-methylbenzaldehyde and 1-(*tert*-butyldimethylsilyl)-7-fluoro-1*H*-indole (149.4 mg, 0.6 mmol) afforded **104** (69.7 mg, 98% yield) as a white solid; mp: 81-82 °C.

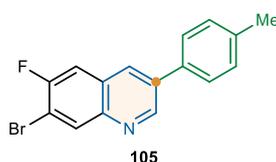
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.19 (d, *J* = 2.0 Hz, 1H), 8.25-8.22 (m, 1H), 7.61 (d, *J* = 8.5 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.49-7.42 (m, 1H), 7.38-7.32 (m, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.41 (s, 3H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 158.0 (d, *J* = 255.0 Hz), 150.0, 138.3, 137.2 (d, *J* = 12.0 Hz), 134.7, 134.3, 132.3 (d, *J* = 3.0 Hz), 129.9, 129.7 (d, *J* = 1.5 Hz), 127.1, 126.6 (d, *J* = 7.5 Hz), 123.4 (d, *J* = 4.5 Hz), 113.1 (d, *J* = 18.0 Hz), 21.1.

<sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ (-125.69)- (-125.82) (m).

HRMS (ESI) *m/z* calcd. for C<sub>16</sub>H<sub>13</sub>FN<sup>+</sup> [M + H]<sup>+</sup> 238.1027, found 238.1034.

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#### (105) 7-Bromo-6-fluoro-3-(*p*-tolyl)quinoline

Prepared according to **General Procedure F** using *N*-trifosylhydrazone (102.6 mg, 0.3 mmol) derived from 4-methylbenzaldehyde and 6-bromo-1-(*tert*-butyldimethylsilyl)-5-fluoro-1*H*-indole (196.8 mg, 0.6 mmol) afforded **105** (88.2 mg, 93% yield) as a white solid; mp: 164-166 °C.

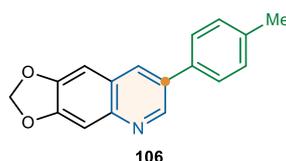
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.12 (d, *J* = 2.0 Hz, 1H), 8.37 (d, *J* = 6.5 Hz, 1H), 8.17 (d, *J* = 2.0 Hz, 1H), 7.60-7.56 (m, 2H), 7.52 (d, *J* = 8.5 Hz, 1H), 7.35-7.31 (m, 2H), 2.43 (s, 3H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 156.8 (d, *J* = 247.5 Hz), 150.2 (d, *J* = 3.0 Hz), 144.4, 138.6, 134.7, 134.4, 134.2, 131.7 (d, *J* = 6.0 Hz), 130.0, 127.9 (d, *J* = 7.5 Hz), 127.2, 112.7 (d, *J* = 25.5 Hz), 111.6 (d, *J* = 22.5 Hz), 21.2.

<sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -108.13 (t, *J* = 7.9 Hz).

HRMS (ESI) *m/z* calcd. for C<sub>16</sub>H<sub>12</sub>BrFN<sup>+</sup> [M + H]<sup>+</sup> 316.0132, found 316.0128.

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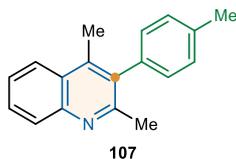
#### (106) 7-(*p*-Tolyl)-[1,3]dioxolo[4,5-*g*]quinoline

Prepared according to **General Procedure F** using *N*-trifosylhydrazone (102.6 mg, 0.3 mmol) derived from 4-methylbenzaldehyde and 5-(*tert*-butyldimethylsilyl)-5*H*-[1,3]dioxolo[4,5-*f*]indole (165.0 mg, 0.6 mmol) afforded **106** (66.3 mg, 84% yield) as a white solid; mp: 166-168 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.92 (d, *J* = 1.5 Hz, 1H), 8.02 (s, 1H), 7.53 (d, *J* = 7.5 Hz, 2H), 7.37 (s, 1H), 7.27 (d, *J* = 7.5 Hz, 2H), 7.02 (s, 1H), 6.05 (s, 2H), 2.40 (s, 3H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 150.4, 148.0, 147.2, 145.3, 137.6, 135.0, 132.1, 131.8, 129.7, 126.9, 125.0, 105.5, 102.7, 101.6, 21.0.

HRMS (ESI) *m/z* calcd. for C<sub>17</sub>H<sub>14</sub>NO<sub>2</sub><sup>+</sup> [M + H]<sup>+</sup> 264.1019, found 264.1021.



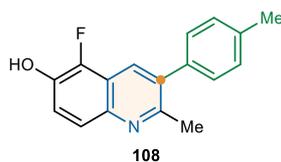
**(107) 2,4-Dimethyl-3-(*p*-tolyl)quinoline**

Prepared according to **General Procedure G** using *N*-trifosylhydrazone (102.6 mg, 0.3 mmol) derived from 4-methylbenzaldehyde and 1-(*tert*-butyldimethylsilyl)-2,3-dimethyl-1*H*-indole (155.4 mg, 0.6 mmol) afforded **107** (41.5 mg, 56% yield) as a white solid; mp: 66-68 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.06 (d, *J* = 8.5 Hz, 1H), 8.00-7.97 (m, 1H), 7.71-7.66 (m, 1H), 7.55-7.49 (m, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 2.45 (s, 3H), 2.44 (s, 3H), 2.39 (s, 3H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 157.8, 146.5, 141.3, 137.0, 136.5, 134.9, 129.3, 129.2, 129.1, 128.7, 126.8, 125.6, 124.1, 25.4, 21.2, 15.9.

**HRMS** (ESI) *m/z* calcd. for C<sub>18</sub>H<sub>18</sub>N<sup>+</sup> [M + H]<sup>+</sup> 248.1434, found 248.1432.



**(108) 5-Fluoro-2-methyl-3-(*p*-tolyl)quinolin-6-ol**

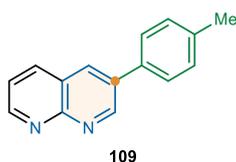
Prepared according to **General Procedure L** using *N*-trifosylhydrazone (102.6 mg, 0.3 mmol) derived from 4-methylbenzaldehyde and 1-(*tert*-butyldimethylsilyl)-5-((*tert*-butyldimethylsilyl)oxy)-4-fluoro-2-methyl-1*H*-indole (235.8 mg, 0.6 mmol) afforded **108** (66.5 mg, 83% yield) as a pale yellow solid; mp: 221-222 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.16 (s, 1H), 7.85 (d, *J* = 9.5 Hz, 1H), 7.72 (t, *J* = 9.0 Hz, 1H), 7.32-7.27 (m, 4H), 5.98 (s, 1H), 2.66 (s, 3H), 2.44 (s, 3H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 157.4, 146.8 (d, *J* = 254.0 Hz), 143.6, 139.6 (d, *J* = 8.5 Hz), 137.7, 136.5, 136.3 (d, *J* = 1.5 Hz), 129.2, 129.0, 128.6 (d, *J* = 4.5 Hz), 124.7 (d, *J* = 4.5 Hz), 121.8, 118.4 (d, *J* = 12.0 Hz), 24.6, 21.2.

<sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -143.23 (d, *J* = 8.46 Hz).

**HRMS** (ESI) *m/z* calcd. for C<sub>17</sub>H<sub>15</sub>FNO<sup>+</sup> [M + H]<sup>+</sup> 268.1132, found 268.1135.



**(109) 3-(*p*-Tolyl)-1,8-naphthyridine**

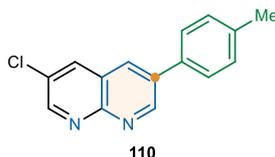
Prepared according to **General Procedure F** using *N*-trifosylhydrazone (102.6 mg, 0.3 mmol) derived from 4-methylbenzaldehyde and 1-(*tert*-butyldimethylsilyl)-1*H*-pyrrolo[2,3-*b*]pyridine (139.2 mg, 0.6 mmol) afforded **109** (60.1 mg, 91% yield) as a white solid; mp: 163-165 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.35 (s, 1H), 9.07 (s, 1H), 8.24 (s, 1H), 8.19 (d, *J* = 7.5 Hz, 1H), 7.57 (d, *J* = 7.5 Hz, 2H), 7.50-7.43 (m, 1H), 7.30 (d, *J* = 7.5 Hz, 2H), 2.40 (s, 3H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 155.3, 153.02, 152.96, 138.4, 137.1, 134.7, 133.9, 133.3, 129.9, 127.1, 122.5, 122.3, 21.1.

**HRMS** (ESI) *m/z* calcd. for C<sub>15</sub>H<sub>13</sub>N<sub>2</sub><sup>+</sup> [M + H]<sup>+</sup> 221.1073, found 221.1076.

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### (110) 3-Chloro-6-(*p*-tolyl)-1,8-naphthyridine

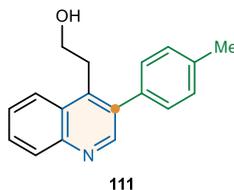
Prepared according to **General Procedure F** using *N*-trifosylhydrazone (102.6 mg, 0.3 mmol) derived from 4-methylbenzaldehyde and 1-(*tert*-butyldimethylsilyl)-5-chloro-1*H*-pyrrolo[2,3-*b*]pyridine (159.6 mg, 0.6 mmol) afforded **110** (67.8 mg, 89% yield) as a white solid; mp: 238-239 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.37 (d, *J* = 2.5 Hz, 1H), 9.01 (d, *J* = 2.5 Hz, 1H), 8.24 (d, *J* = 2.5 Hz, 1H), 8.23 (d, *J* = 2.5 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 2.45 (s, 3H).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 153.4, 153.3, 152.4, 139.0, 135.9, 134.9, 133.5, 132.5, 130.1, 129.9, 127.3, 122.9, 21.2.

**HRMS** (ESI) *m/z* calcd. for C<sub>15</sub>H<sub>12</sub>ClN<sub>2</sub><sup>+</sup> [M + H]<sup>+</sup> 255.0684, found 255.0680.

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### (111) 2-(3-(*p*-Tolyl)quinolin-4-yl)ethan-1-ol

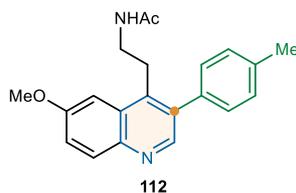
Prepared according to **General Procedure F** using *N*-trifosylhydrazone (102.6 mg, 0.3 mmol) derived from 4-methylbenzaldehyde and 1-(*tert*-butyldimethylsilyl)-3-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-1*H*-indole (233.4 mg, 0.6 mmol) afforded **111** (56.8 mg, 72% yield) as a white solid; mp: 108-110 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.71 (s, 1H), 8.15 (d, *J* = 8.5 Hz, 1H), 8.09 (d, *J* = 8.5 Hz, 1H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.31-7.26 (m, 4H), 3.87 (t, *J* = 7.5 Hz, 2H), 3.38 (t, *J* = 7.5 Hz, 2H), 2.43 (s, 3H), 1.99 (s, 1H).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 151.7, 147.3, 141.0, 137.6, 135.43, 135.41, 130.1, 129.6, 129.3, 128.9, 127.3, 126.9, 124.1, 62.7, 32.1, 21.2.

**HRMS** (ESI) *m/z* calcd. for C<sub>18</sub>H<sub>18</sub>NO<sup>+</sup> [M + H]<sup>+</sup> 264.1383, found 264.1385.

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### (112) *N*-(2-(6-Methoxy-3-(*p*-tolyl)quinolin-4-yl)ethyl)acetamide

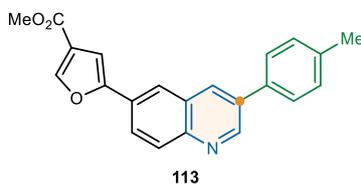
Prepared according to **General Procedure F** using *N*-trifosylhydrazone (102.6 mg, 0.3 mmol) derived from 4-methylbenzaldehyde and *tert*-butyl (2-(1-(*tert*-butyldimethylsilyl)-5-methoxy-1*H*-indol-3-yl)ethyl)carbamate (242.4 mg, 0.6 mmol) afforded **112** (32.9 mg, 28% yield) as a white solid; mp: 186-188 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.58 (s, 1H), 8.01 (d, *J* = 9.0 Hz, 1H), 7.75 (d, *J* = 2.5 Hz, 1H), 7.37 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 5.62 (s, 1H), 4.06 (s, 3H), 3.45-3.38 (m, 2H), 3.29-3.22 (m, 2H), 2.44 (s, 3H), 1.90 (s, 3H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 170.3, 158.5, 148.9, 143.4, 139.8, 137.6, 135.7, 135.1, 131.3, 129.4, 129.3, 128.4, 121.9, 102.4, 56.0, 39.8, 29.1, 23.2, 21.2.

HRMS (ESI) *m/z* calcd. for C<sub>24</sub>H<sub>29</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup> [M + H]<sup>+</sup> 393.2173, found 393.2175.

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#### (113) Methyl 5-(3-(*p*-tolyl)quinolin-6-yl)furan-3-carboxylate

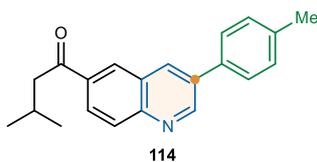
Prepared according to **General Procedure F** using *N*-trifosylhydrazone (102.6 mg, 0.3 mmol) derived from 4-methylbenzaldehyde and methyl 5-(1-(*tert*-butyldimethylsilyl)-1*H*-indol-5-yl)furan-3-carboxylate (213.0 mg, 0.6 mmol) afforded **113** (38.1 mg, 37% yield) as a white solid; mp: 188-189 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.15 (d, *J* = 2.0 Hz, 1H), 8.28 (d, *J* = 1.5 Hz, 1H), 8.16 (d, *J* = 1.5 Hz, 1H), 8.14 (d, *J* = 9.0 Hz, 1H), 8.11 (s, 1H), 7.97 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.14 (s, 1H), 3.89 (s, 3H), 2.45 (s, 3H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 163.4, 154.5, 150.2, 147.4, 146.8, 138.3, 134.7, 134.6, 132.9, 130.0, 129.9, 128.21, 128.15, 127.2, 125.5, 122.5, 121.2, 105.8, 51.8, 21.2.

HRMS (ESI) *m/z* calcd. for C<sub>22</sub>H<sub>18</sub>NO<sub>3</sub><sup>+</sup> [M + H]<sup>+</sup> 344.1281, found 344.1284.

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#### (114) 3-Methyl-1-(3-(*p*-tolyl)quinolin-6-yl)butan-1-one

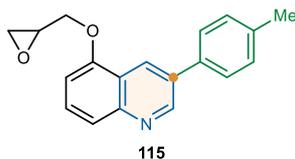
Prepared according to **General Procedure F** using *N*-trifosylhydrazone (102.6 mg, 0.3 mmol) derived from 4-methylbenzaldehyde and 1-(1-(*tert*-butyldimethylsilyl)-1*H*-indol-5-yl)-3-methylbutan-1-one (189.0 mg, 0.6 mmol) afforded **114** (41.8 mg, 46% yield) as a white solid; mp: 94-96 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.25 (d, *J* = 2.0 Hz, 1H), 8.49 (d, *J* = 1.5 Hz, 1H), 8.39 (d, *J* = 2.0 Hz, 1H), 8.25 (dd, *J* = 9.0, 2.0 Hz, 1H), 8.17 (d, *J* = 9.0 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 2.99 (d, *J* = 7.0 Hz, 2H), 2.45 (s, 3H), 2.43-2.33 (m, 1H), 1.05 (d, *J* = 7.0 Hz, 6H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 199.6, 152.1, 148.9, 138.5, 135.5, 134.7, 134.4, 134.0, 130.0, 129.8, 129.5, 127.5, 127.4, 127.2, 47.7, 25.3, 22.8, 21.2.

HRMS (ESI) *m/z* calcd. for C<sub>21</sub>H<sub>22</sub>NO<sup>+</sup> [M + H]<sup>+</sup> 304.1696, found 304.1701.

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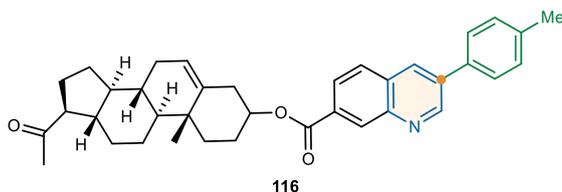
**(115) 5-(Oxiran-2-ylmethoxy)-3-(*p*-tolyl)quinoline**

Prepared according to **General Procedure H** using *N*-trifosylhydrazone (102.6 mg, 0.3 mmol) derived from 4-methylbenzaldehyde and 1-(*tert*-butyldimethylsilyl)-4-(oxiran-2-ylmethoxy)-1*H*-indole (181.1 mg, 0.6 mmol) afforded **115** (35.8 mg, 41% yield) as a white solid; mp: 96-98 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.17 (d, *J* = 2.0 Hz, 1H), 8.74 (d, *J* = 1.5 Hz, 1H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 7.5 Hz, 1H), 4.47 (dd, *J* = 11.0, 3.0 Hz, 1H), 4.14 (dd, *J* = 11.0, 6.0 Hz, 1H), 3.55-3.49 (m, 1H), 2.99 (t, *J* = 4.5 Hz, 1H), 2.87-2.83 (m, 1H), 2.44 (s, 3H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 154.1, 150.2, 148.0, 137.9, 135.2, 133.1, 129.8, 128.9, 127.6, 127.3, 122.0, 120.6, 105.7, 69.5, 50.1, 44.7, 21.2.

**HRMS** (ESI) *m/z* calcd. for C<sub>19</sub>H<sub>18</sub>NO<sub>2</sub><sup>+</sup> [M + H]<sup>+</sup> 292.1332, found 292.1331.



**(116)**

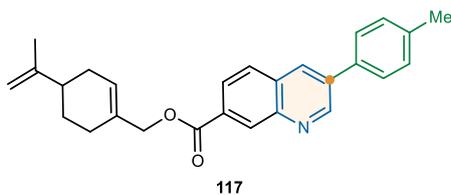
**17-acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 3-(*p*-tolyl)quinoline-7-carboxylate**

Prepared according to **General Procedure F** using *N*-trifosylhydrazone (102.6 mg, 0.3 mmol) derived from 4-methylbenzaldehyde and corresponding *N*-TBS indole (343.8 mg, 0.6 mmol) afforded **116** (70.7 mg, 42% yield) as a white solid; mp: >300 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.25 (d, *J* = 2.0 Hz, 1H), 8.85 (s, 1H), 8.30 (s, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 5.45 (d, *J* = 4.0 Hz, 1H), 4.99-4.87 (m, 1H), 2.58-2.50 (m, 3H), 2.44 (s, 3H), 2.23-2.15 (m, 1H), 2.13 (s, 3H), 2.09-2.04 (m, 2H), 1.99-1.91 (m, 1H), 1.86-1.75 (m, 1H), 1.75-1.57 (m, 5H), 1.57-1.42 (m, 3H), 1.33-1.14 (m, 4H), 1.09 (s, 3H), 0.65 (s, 3H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 209.6, 165.7, 150.9, 146.4, 139.6, 138.6, 135.4, 134.4, 132.3, 131.8, 131.2, 130.5, 130.0, 128.1, 127.3, 126.5, 122.5, 74.9, 63.7, 56.9, 49.9, 44.0, 38.8, 38.2, 37.0, 36.7, 31.82, 31.79, 31.5, 27.9, 24.5, 22.8, 21.2, 21.1, 19.4, 13.2.

**HRMS** (ESI) *m/z* calcd. for C<sub>38</sub>H<sub>44</sub>NO<sub>3</sub><sup>+</sup> [M + H]<sup>+</sup> 562.3316, found 562.3314.



**(117) (4-(Prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl 3-(*p*-tolyl)quinoline-7-carboxylate**

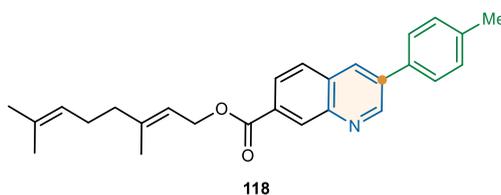
Prepared according to **General Procedure F** using *N*-trifosylhydrazone (102.6 mg, 0.3 mmol) derived from 4-methylbenzaldehyde and corresponding *N*-TBS indole (245.4 mg, 0.6 mmol) afforded **117** (104.8 mg, 88% yield) as a pale yellow oil.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.25 (d, *J* = 2.0 Hz, 1H), 8.86 (s, 1H), 8.30 (d, *J* = 1.5 Hz, 1H), 8.18 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 5.93-5.88 (m, 1H), 4.83-4.77 (m, 2H), 4.77-4.72 (m, 2H), 2.44 (s, 3H), 2.28-2.16 (m, 4H), 2.08-1.98 (m, 1H), 1.95-1.84 (m, 1H), 1.76 (s, 3H), 1.62-1.48 (m, 1H).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 166.1, 150.9, 149.6, 146.4, 138.6, 135.4, 134.4, 132.5, 132.3, 131.8, 130.8, 130.6, 130.0, 128.1, 127.3, 126.5, 126.0, 108.8, 69.3, 40.8, 30.5, 27.4, 26.5, 21.2, 20.8.

**HRMS** (ESI) *m/z* calcd. for C<sub>27</sub>H<sub>28</sub>NO<sub>2</sub><sup>+</sup> [*M* + *H*]<sup>+</sup> 398.2115, found 398.2117.

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**(118) 3,7-Dimethylocta-2,6-dien-1-yl 3-(*p*-tolyl)quinoline-7-carboxylate**

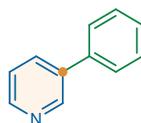
Prepared according to **General Procedure F** using *N*-trifosylhydrazone (102.6 mg, 0.3 mmol) derived from 4-methylbenzaldehyde and corresponding *N*-TBS indole (246.6 mg, 0.6 mmol) afforded **118** (93.4 mg, 78% yield) as a pale yellow oil.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.25 (s, 1H), 8.86 (s, 1H), 8.30 (s, 1H), 8.18 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 5.53 (t, *J* = 7.0 Hz, 1H), 5.11 (t, *J* = 6.5 Hz, 1H), 4.93 (d, *J* = 7.0 Hz, 2H), 2.45 (s, 3H), 2.19-2.07 (m, 4H), 1.80 (s, 3H), 1.68 (s, 3H), 1.62 (s, 3H).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 166.3, 150.9, 146.5, 142.8, 138.6, 135.4, 134.4, 132.3, 131.9, 131.8, 131.0, 130.5, 130.0, 128.1, 127.3, 126.5, 123.7, 118.2, 62.3, 58.5, 39.6, 26.3, 25.7, 21.2, 16.6.

**HRMS** (ESI) *m/z* calcd. for C<sub>27</sub>H<sub>30</sub>NO<sub>2</sub><sup>+</sup> [*M* + *H*]<sup>+</sup> 400.2271, found 400.2270.

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**(119) 3-Phenylpyridine**

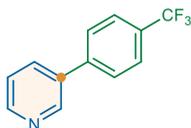
Prepared according to **General Procedure M** using *N*-trifosylhydrazone (98.4 mg, 0.3 mmol) derived from benzaldehyde and pyrrole (40.2 mg, 0.6 mmol) afforded **119** (22.3 mg, 48% yield) as a colorless oil.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.86 (s, 1H), 8.59 (d, *J* = 4.0 Hz, 1H), 7.91-7.83 (m, 1H), 7.61-7.55 (m, 2H), 7.52-7.44 (m, 2H), 7.43-7.38 (m, 1H), 7.36 (dd, *J* = 8.0, 5.0 Hz, 1H).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 148.4, 148.3, 137.8, 136.6, 134.3, 129.0, 128.0, 127.1, 123.5.

**HRMS** (ESI) *m/z* calcd. for C<sub>11</sub>H<sub>10</sub>N<sup>+</sup> [*M* + *H*]<sup>+</sup> 156.0808, found 156.0810.

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120

### (120) 3-(4-(Trifluoromethyl)phenyl)pyridine

Prepared according to **General Procedure M** using *N*-trifosylhydrazone (118.8 mg, 0.3 mmol) derived from 4-(trifluoromethyl)benzaldehyde and pyrrole (40.2 mg, 0.6 mmol) afforded **120** (54.2 mg, 81% yield) as a white solid; mp: 57-58 °C.

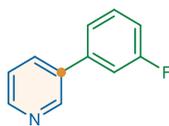
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.86 (s, 1H), 8.68-8.62 (m, 1H), 7.91-7.86 (m, 1H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.40 (dd, *J* = 7.5, 5.0 Hz, 1H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 149.4, 148.3, 141.4, 135.2, 134.5, 130.2 (q, *J* = 31.5 Hz), 127.5, 126.0 (q, *J* = 4.5 Hz), 124.0 (q, *J* = 270.0 Hz), 123.7.

**<sup>19</sup>F NMR** (564 MHz, CDCl<sub>3</sub>) δ -62.55.

**HRMS** (ESI) *m/z* calcd. for C<sub>12</sub>H<sub>9</sub>F<sub>3</sub>N<sup>+</sup> [M + H]<sup>+</sup> 224.0682, found 224.0684.

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121

### (121) 3-(3-Fluorophenyl)pyridine

Prepared according to **General Procedure M** using *N*-trifosylhydrazone (103.8 mg, 0.3 mmol) derived from 4-fluorobenzaldehyde and pyrrole (40.2 mg, 0.6 mmol) afforded **121** (32.7 mg, 63% yield) as a white oil.

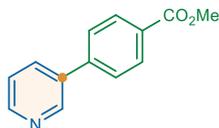
**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 8.83 (d, *J* = 1.8 Hz, 1H), 8.64-8.58 (m, 1H), 7.88-7.82 (m, 1H), 7.47-7.41 (m, 1H), 7.40-7.33 (m, 2H), 7.30-7.25 (m, 1H), 7.10 (td, *J* = 8.4, 1.8 Hz, 1H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 163.2 (d, *J* = 246.0 Hz), 149.0, 148.2, 140.0 (d, *J* = 7.5 Hz), 135.4 (d, *J* = 1.5 Hz), 134.3, 130.6 (d, *J* = 9.0 Hz), 123.6, 122.8 (d, *J* = 3.0 Hz), 114.9 (d, *J* = 21.0 Hz), 114.1 (d, *J* = 22.0 Hz).

**<sup>19</sup>F NMR** (564 MHz, CDCl<sub>3</sub>) δ (-112.19)-(112.29) (m).

**HRMS** (ESI) *m/z* calcd. for C<sub>11</sub>H<sub>9</sub>FN<sup>+</sup> [M + H]<sup>+</sup> 174.0714, found 174.0715.

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122

### (122) Methyl 4-(pyridin-3-yl)benzoate

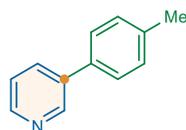
Prepared according to **General Procedure M** using *N*-trifosylhydrazone (115.8 mg, 0.3 mmol) derived from methyl 4-formylbenzoate and pyrrole (40.2 mg, 0.6 mmol) afforded **122** (36.4 mg, 57% yield) as a white solid; mp: 100-103 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.87 (d, *J* = 1.5 Hz, 1H), 8.66-8.60 (m, 1H), 8.14 (d, *J* = 8.5 Hz, 2H), 7.92-7.87 (m, 1H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.41-7.36 (m, 1H), 3.94 (s, 3H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 166.7, 149.2, 148.3, 142.2, 135.5, 134.4, 130.3, 129.7, 127.0, 123.6, 52.2.

HRMS (ESI)  $m/z$  calcd. for  $C_{13}H_{12}NO_2^+$   $[M + H]^+$  214.0863, found 214.0862.

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### (123) 3-(*p*-Tolyl)pyridine

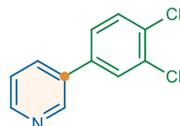
Prepared according to **General Procedure M** using *N*-trifosylhydrazone (102.6 mg, 0.3 mmol) derived from 4-methylbenzaldehyde and pyrrole (40.2 mg, 0.6 mmol) afforded **123** (20.3 mg, 40% yield) as a white solid; mp: 45-46 °C.

$^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  8.84 (d,  $J = 1.5$  Hz, 1H), 8.60-8.54 (m, 1H), 7.87-7.81 (m, 1H), 7.48 (d,  $J = 8.0$  Hz, 2H), 7.33 (dd,  $J = 8.0, 5.0$  Hz, 1H), 7.28 (d,  $J = 8.0$  Hz, 2H), 2.40 (s, 3H).

$^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  148.14, 148.12, 137.9, 136.5, 134.9, 134.0, 129.7, 126.9, 123.4, 21.1.

HRMS (ESI)  $m/z$  calcd. for  $C_{12}H_{12}N^+$   $[M + H]^+$  170.0964, found 170.0961.

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### (124) 3-(3,4-Dichlorophenyl)pyridine

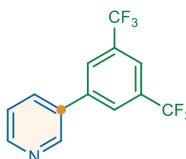
Prepared according to **General Procedure M** using *N*-trifosylhydrazone (119.1 mg, 0.3 mmol) derived from 3,4-dichlorobenzaldehyde and pyrrole (40.2 mg, 0.6 mmol) afforded **124** (41.7 mg, 62% yield) as a white solid; mp: 86-88 °C.

$^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  8.80 (d,  $J = 1.8$  Hz, 1H), 8.66-8.60 (m, 1H), 7.83 (dt,  $J = 8.4, 1.8$  Hz, 1H), 7.66 (d,  $J = 1.8$  Hz, 1H), 7.55 (d,  $J = 8.4$  Hz, 1H), 7.41 (dd,  $J = 8.4, 2.4$  Hz, 1H), 7.38 (dd,  $J = 7.8, 4.8$  Hz, 1H).

$^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  149.3, 148.0, 137.8, 134.4, 134.2, 133.3, 132.5, 131.0, 129.0, 126.3, 123.7

HRMS (ESI)  $m/z$  calcd. for  $C_{11}H_8Cl_2N^+$   $[M + H]^+$  224.0028, found 224.0033.

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### (125) 3-(3,5-Bis(trifluoromethyl)phenyl)pyridine

Prepared according to **General Procedure M** using *N*-trifosylhydrazone (139.2 mg, 0.3 mmol) derived from 3,5-bis(trifluoromethyl)benzaldehyde and pyrrole (40.2 mg, 0.6 mmol) afforded **125** (57.6 mg, 66% yield) as a white solid; mp: 53-55 °C.

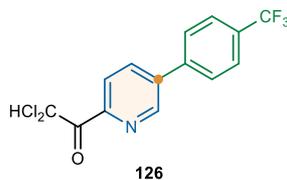
$^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  8.87 (s, 1H), 8.70 (d,  $J = 4.5$  Hz, 1H), 8.01 (s, 2H), 7.94-7.89 (m, 2H), 7.44 (dd,  $J = 8.0, 5.0$  Hz, 1H).

$^{13}C$  NMR (150 MHz,  $CDCl_3$ )  $\delta$  150.1, 148.2, 140.1, 134.5, 133.9, 132.5 (q,  $J = 33.0$  Hz), 127.3 (q,  $J = 3.0$  Hz), 123.8, 123.0 (q,  $J = 271.5$  Hz), 121.9-121.6 (m).

$^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.94.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{13}\text{H}_8\text{F}_6\text{N}^+$   $[\text{M} + \text{H}]^+$  292.0555, found 292.0554.

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**(126) 2,2,2-Trichloro-1-(5-(4-(trifluoromethyl)phenyl)pyridin-2-yl)ethan-1-one**

Prepared according to **General Procedure M** using *N*-trifosylhydrazone (118.8 mg, 0.3 mmol) derived from 4-(trifluoromethyl)benzaldehyde and 2,2,2-trichloro-1-(1*H*-pyrrol-2-yl)ethan-1-one (127.2 mg, 0.9 mmol) afforded **126** (58.9 mg, 59% yield) as a white solid; mp: 97-98 °C.

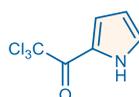
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.95 (d,  $J$  = 1.5 Hz, 1H), 8.29 (d,  $J$  = 8.0 Hz, 1H), 8.12 (dd,  $J$  = 8.0, 2.0 Hz, 1H), 7.80 (d,  $J$  = 8.5 Hz, 2H), 7.76 (d,  $J$  = 8.5 Hz, 2H), 7.65 (s, 1H).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  186.3, 148.7, 147.8, 139.9, 139.8, 135.9, 131.3 (q,  $J$  = 33.0 Hz), 127.8, 126.3 (q,  $J$  = 3.0 Hz), 124.5, 123.8 (q,  $J$  = 270.0 Hz), 66.1.

$^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.72.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{14}\text{H}_9\text{Cl}_2\text{F}_3\text{NO}^+$   $[\text{M} + \text{H}]^+$  334.0008, found 334.0003.

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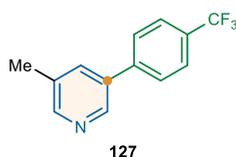


$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.78 (s, 1H), 7.40 (s, 1H), 7.19 (s, 1H), 6.43-6.33 (m, 1H).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  173.3, 127.4, 122.9, 121.3, 111.8, 94.9.

The spectrum was consistent with the previous literature.<sup>[36]</sup>

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**(127) 3-Methyl-5-(4-(trifluoromethyl)phenyl)pyridine**

Prepared according to **General Procedure M** using *N*-trifosylhydrazone (118.8 mg, 0.3 mmol) derived from 4-(trifluoromethyl)benzaldehyde and 3-methyl-1*H*-pyrrole (48.6 mg, 0.6 mmol) afforded **127** (22.7 mg, 32% yield) as a white solid; mp: 55-56 °C.

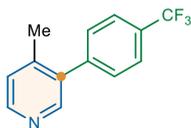
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.66 (d,  $J$  = 1.5 Hz, 1H), 8.48 (s, 1H), 7.73 (d,  $J$  = 8.5 Hz, 2H), 7.70-7.66 (m, 3H), 2.42 (s, 3H).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  149.9, 145.5, 141.5, 135.1, 134.8, 133.3, 130.1 (q,  $J$  = 33.0 Hz), 127.5, 125.9 (q,  $J$  = 3.0 Hz), 124.1 (q,  $J$  = 270.0 Hz), 18.4.

$^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.54.

HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{13}\text{H}_{11}\text{F}_3\text{N}^+$   $[\text{M} + \text{H}]^+$  238.0838, found 238.0844.

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**(128) 4-Methyl-3-(4-(trifluoromethyl)phenyl)pyridine**

Prepared according to **General Procedure M** using *N*-triftosylhydrazone (118.8 mg, 0.3 mmol) derived from 4-(trifluoromethyl)benzaldehyde and 3-methyl-1*H*-pyrrole (48.6 mg, 0.6 mmol) afforded **128** (17.1 mg, 24% yield) as a white solid; mp: 58-60 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.49 (d, *J* = 5.0 Hz, 1H), 8.43 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 5.0 Hz, 1H), 2.29 (s, 3H).

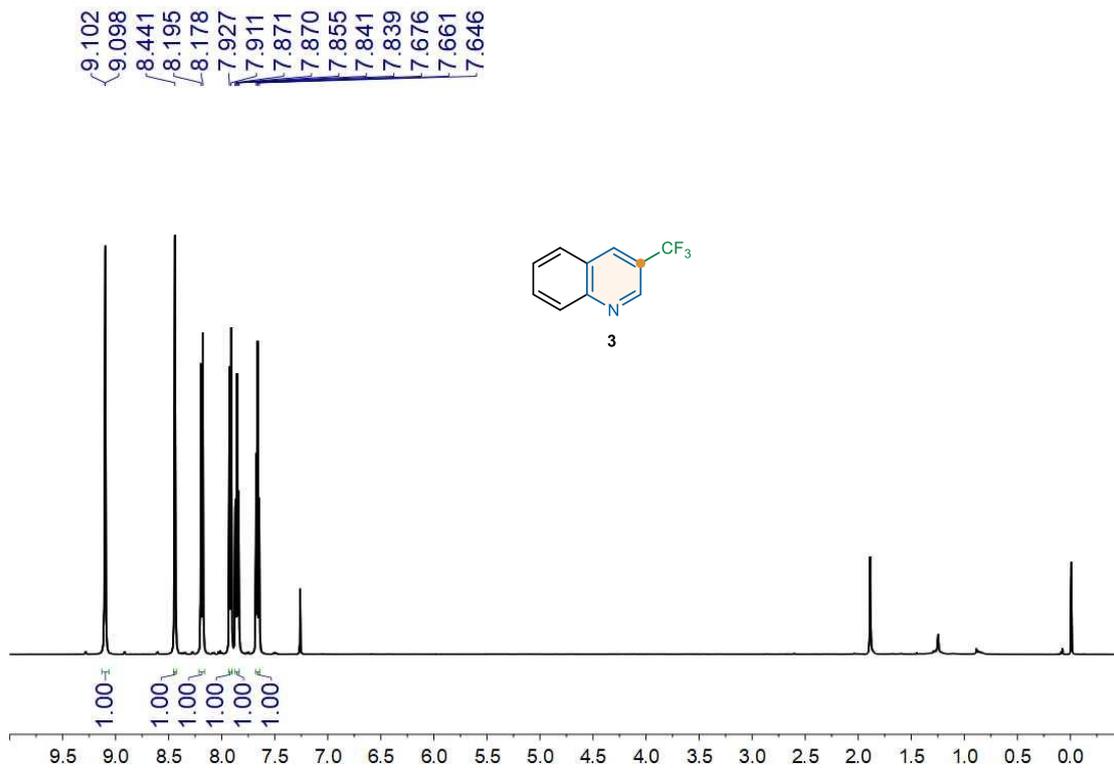
<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 149.7, 149.0, 144.4, 141.6, 136.4, 129.9 (q, *J* = 31.5 Hz), 129.7, 125.4 (q, *J* = 3.0 Hz), 125.3, 124.1 (q, *J* = 270.0 Hz), 19.7.

<sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -62.54.

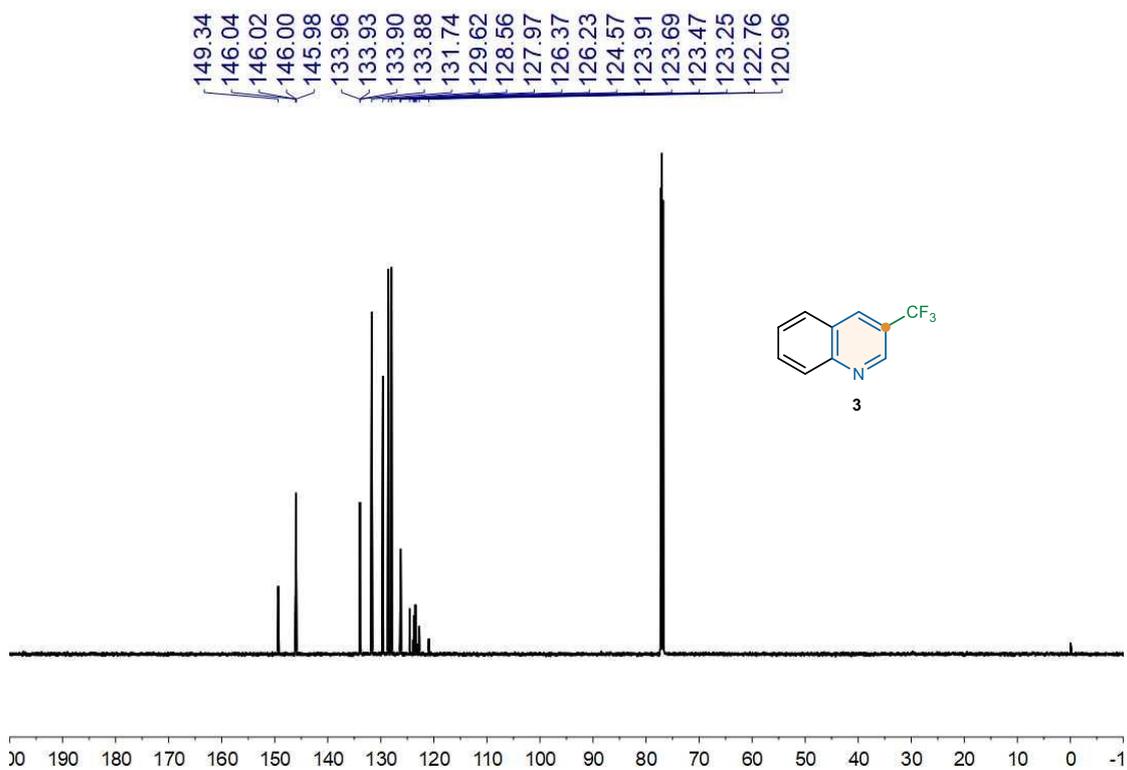
**HRMS** (ESI) *m/z* calcd. for C<sub>13</sub>H<sub>11</sub>F<sub>3</sub>N<sup>+</sup> [M + H]<sup>+</sup> 238.0838, found 238.0842.

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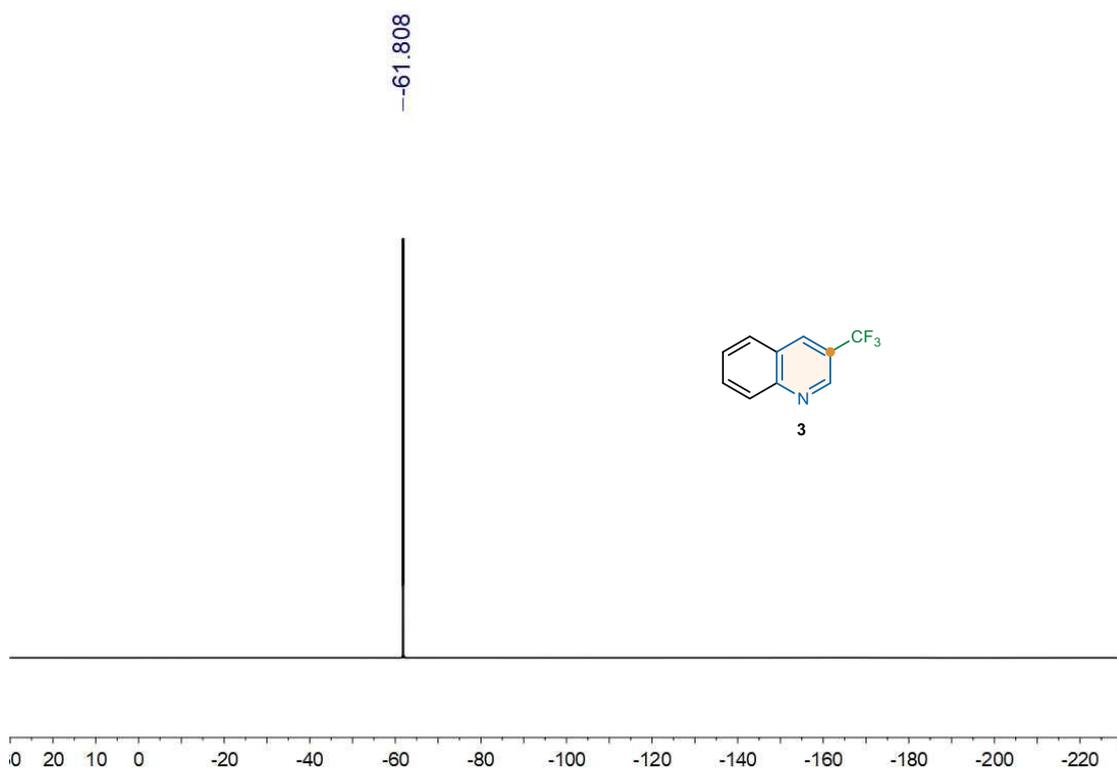
## 9. NMR Spectra of Products



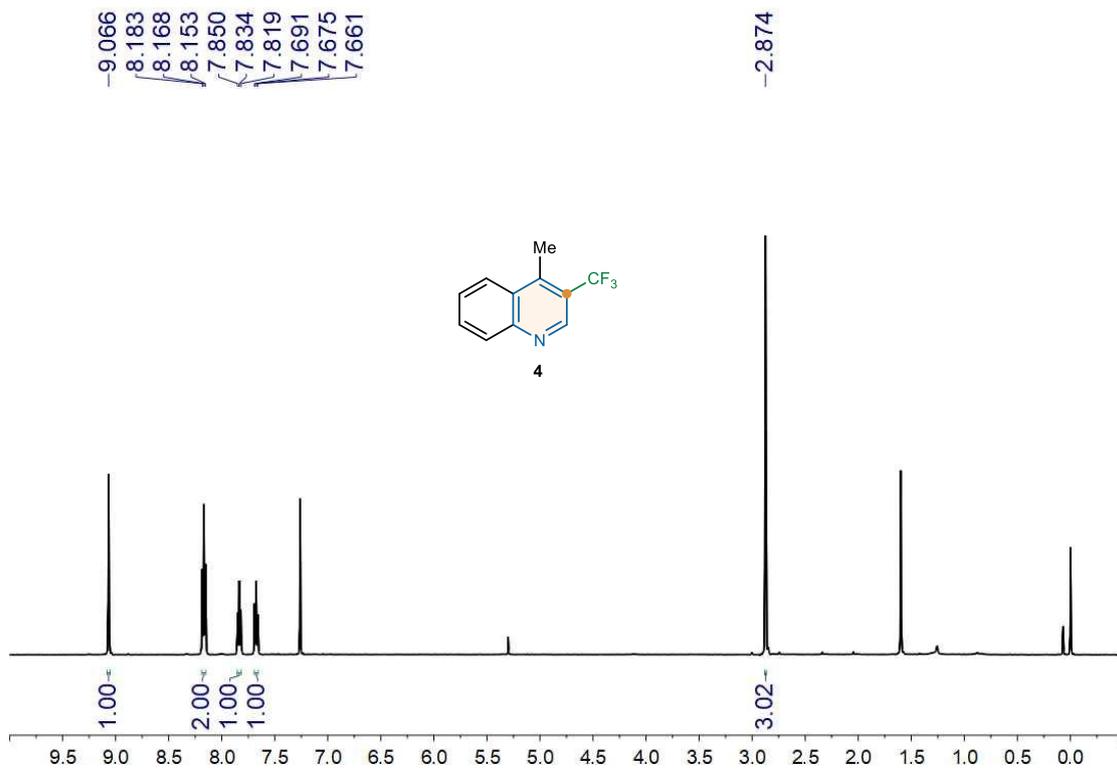
Supplementary Fig. 21. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **3**



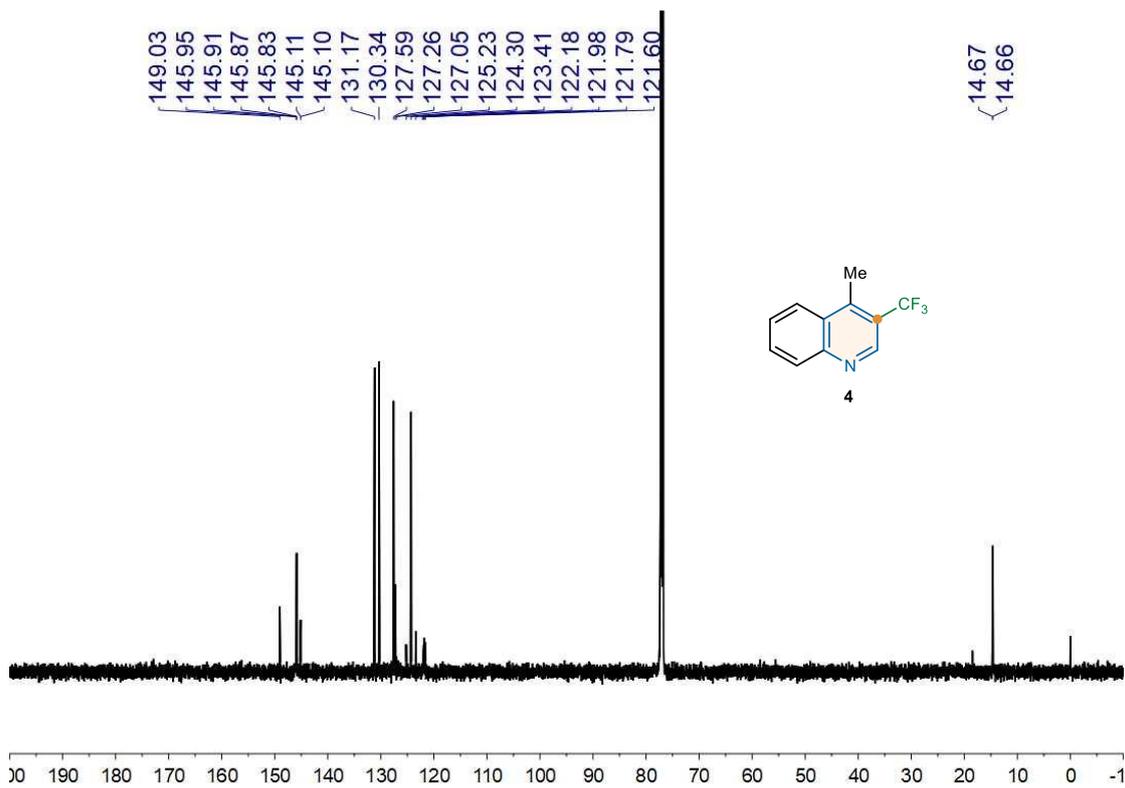
Supplementary Fig. 22. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of **3**



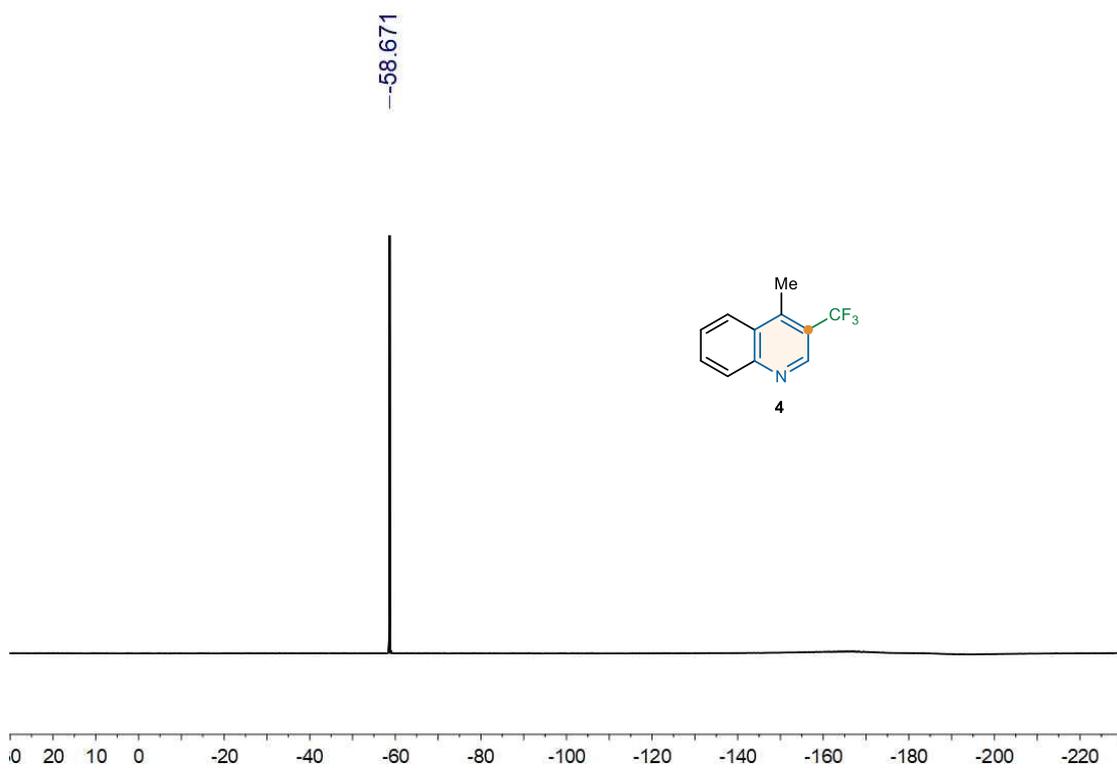
Supplementary Fig. 23.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ) spectrum of 3



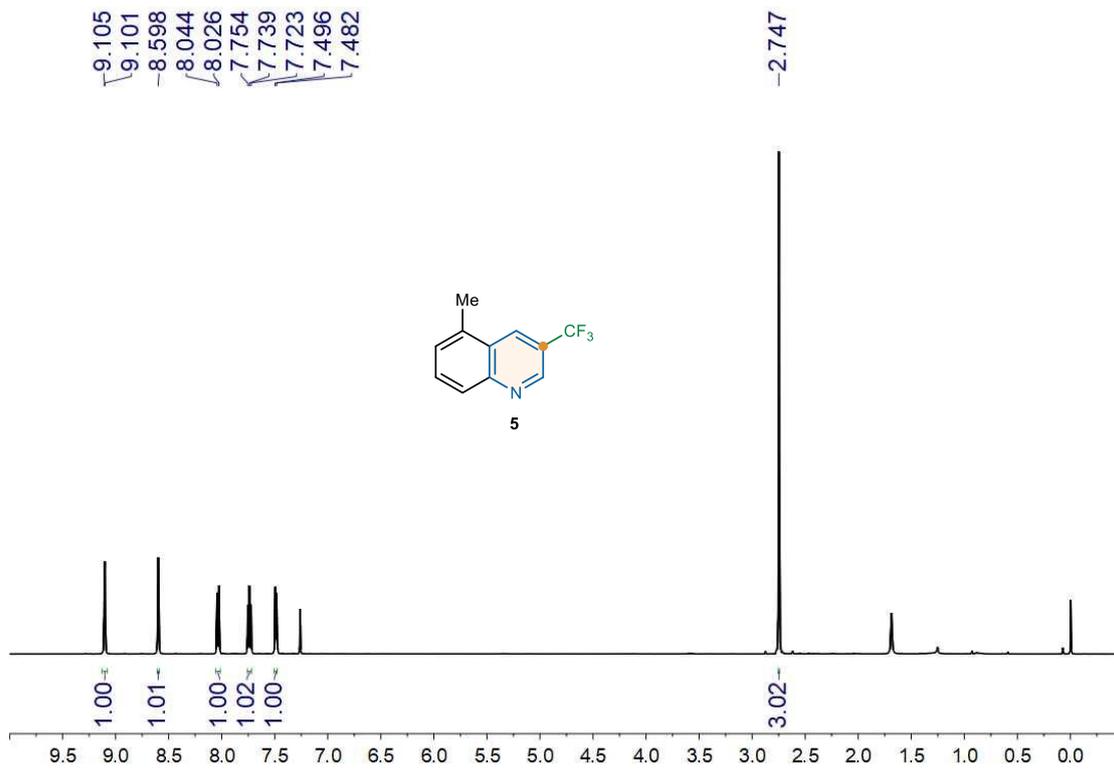
Supplementary Fig. 24.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of 4



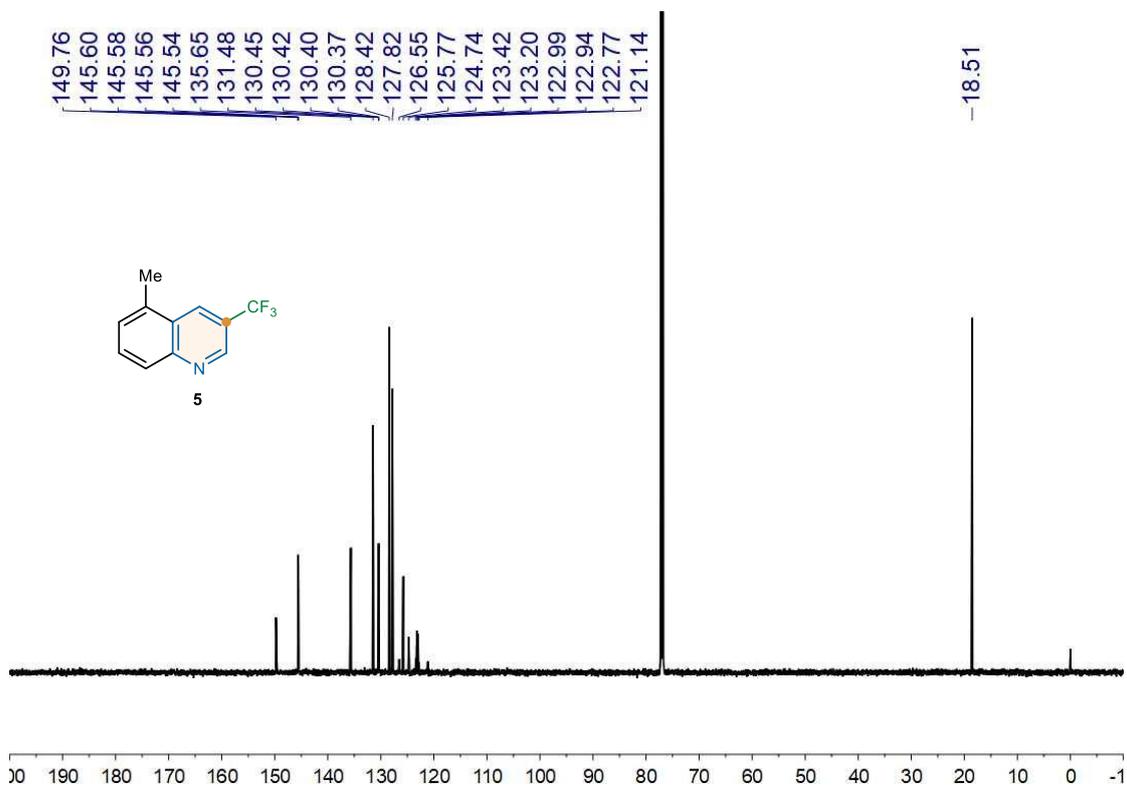
Supplementary Fig. 25.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of 4



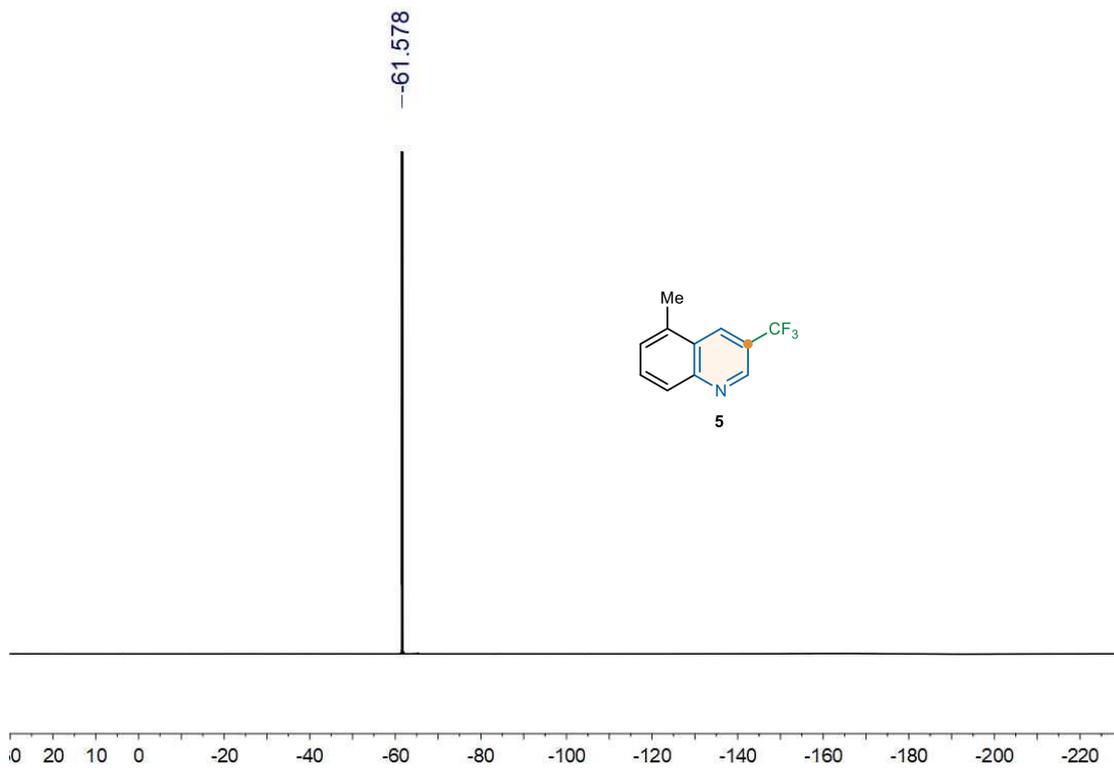
Supplementary Fig. 26.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ) spectrum of 4



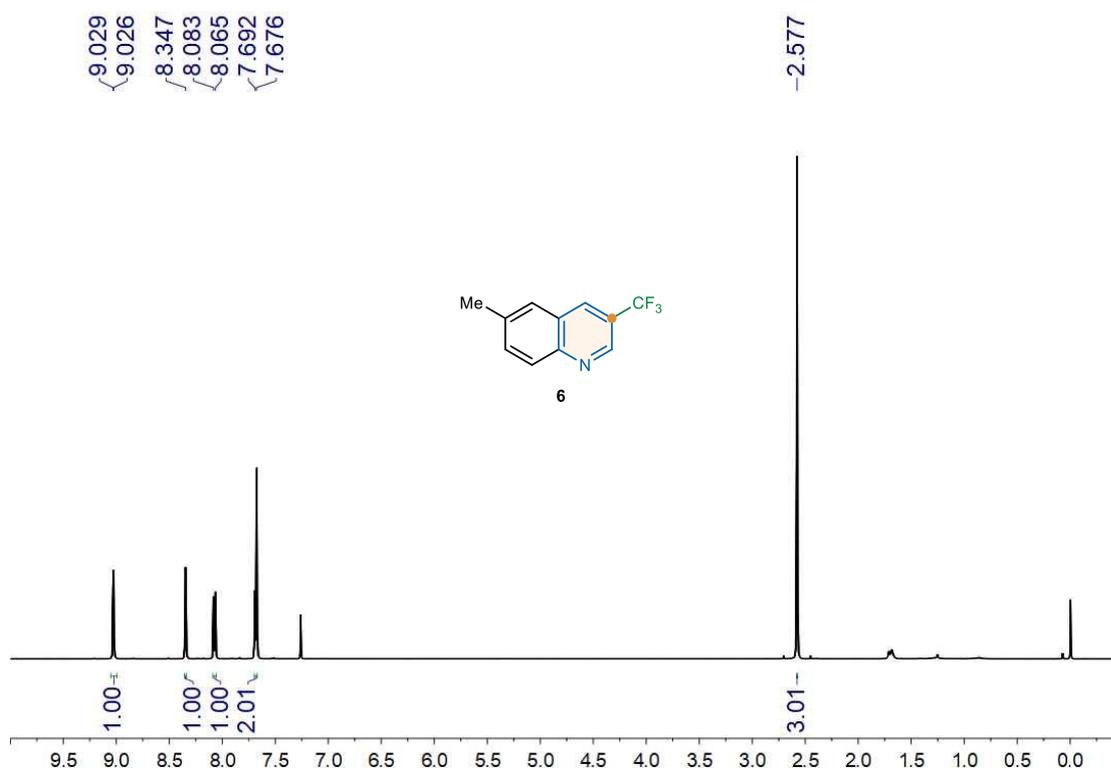
Supplementary Fig. 27.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of 5



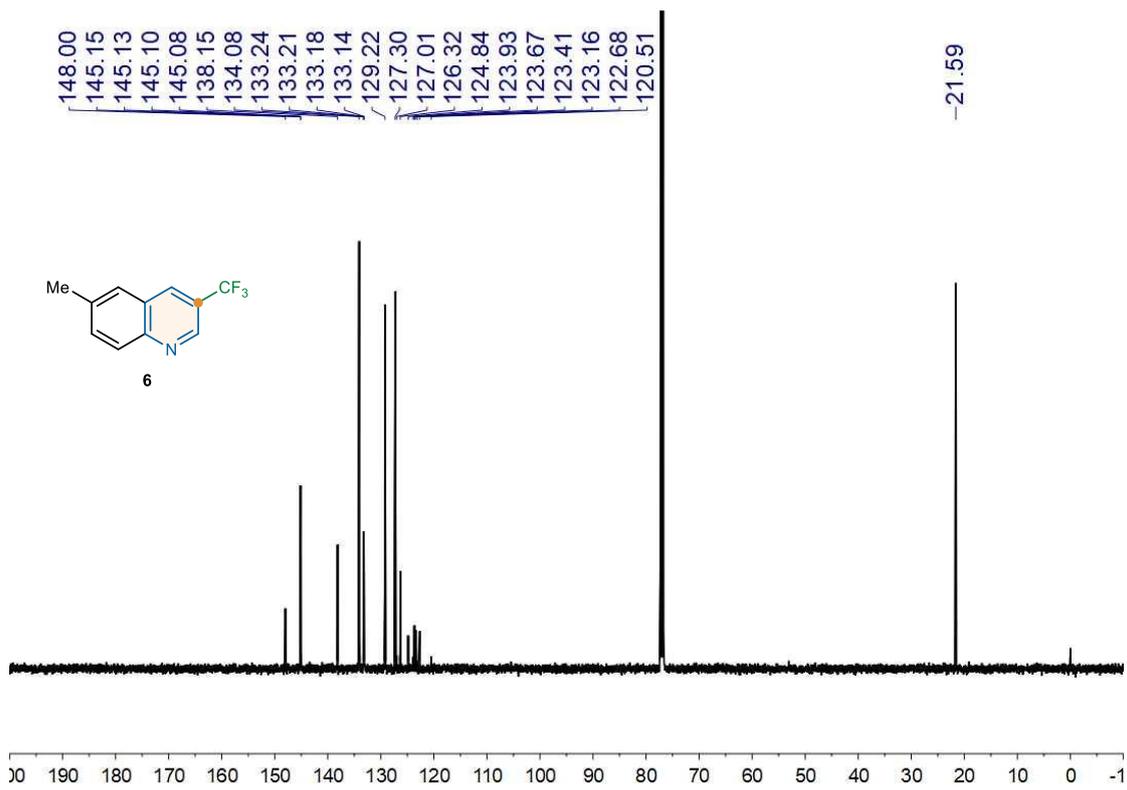
Supplementary Fig. 28.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of 5



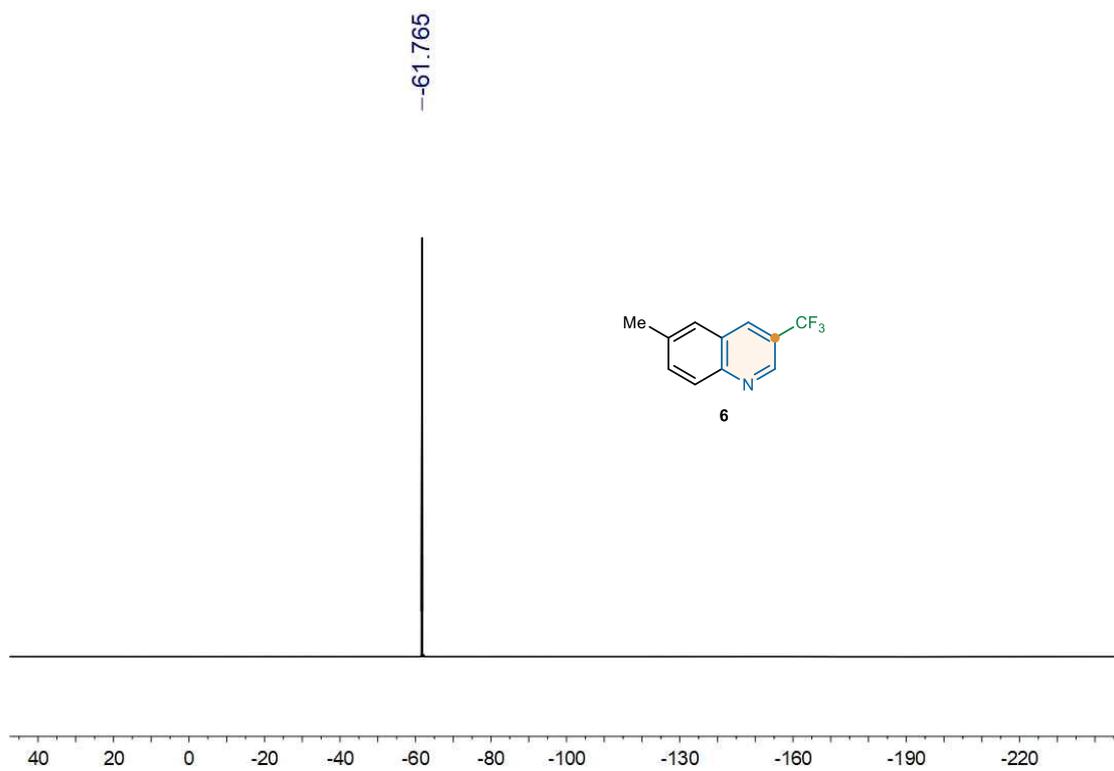
Supplementary Fig. 29.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ) spectrum of 5



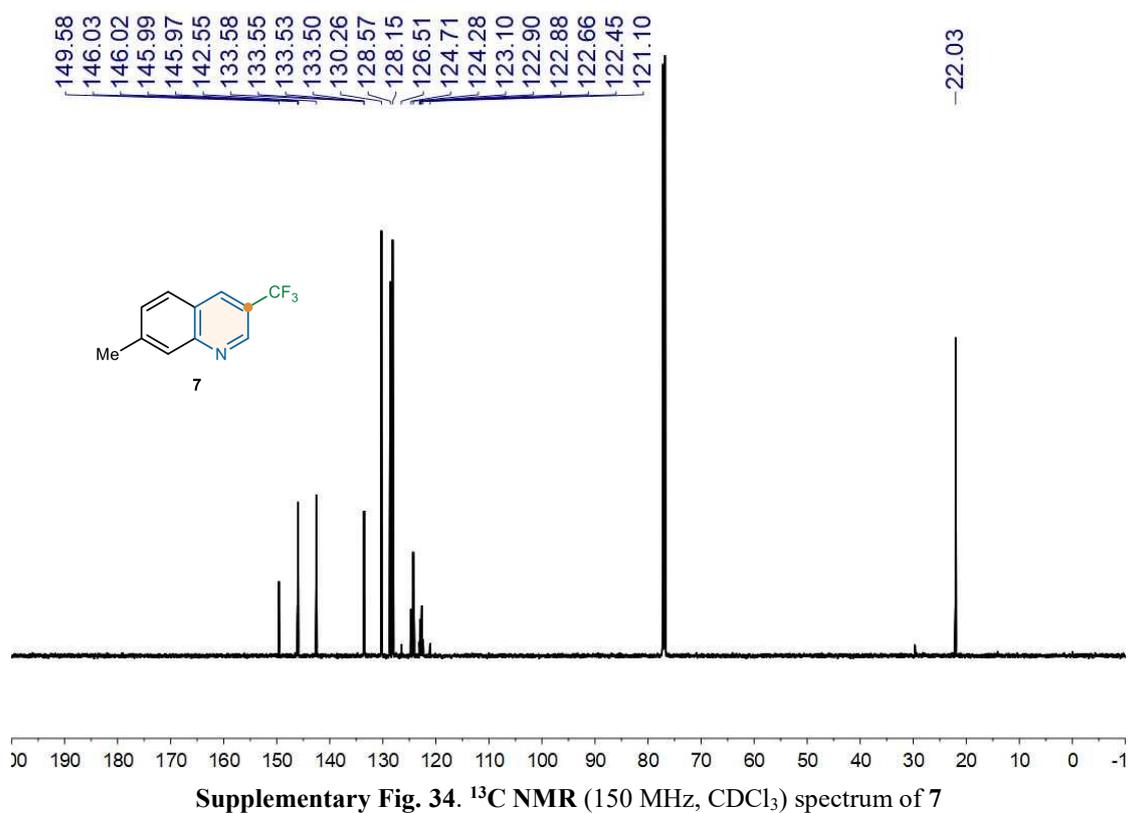
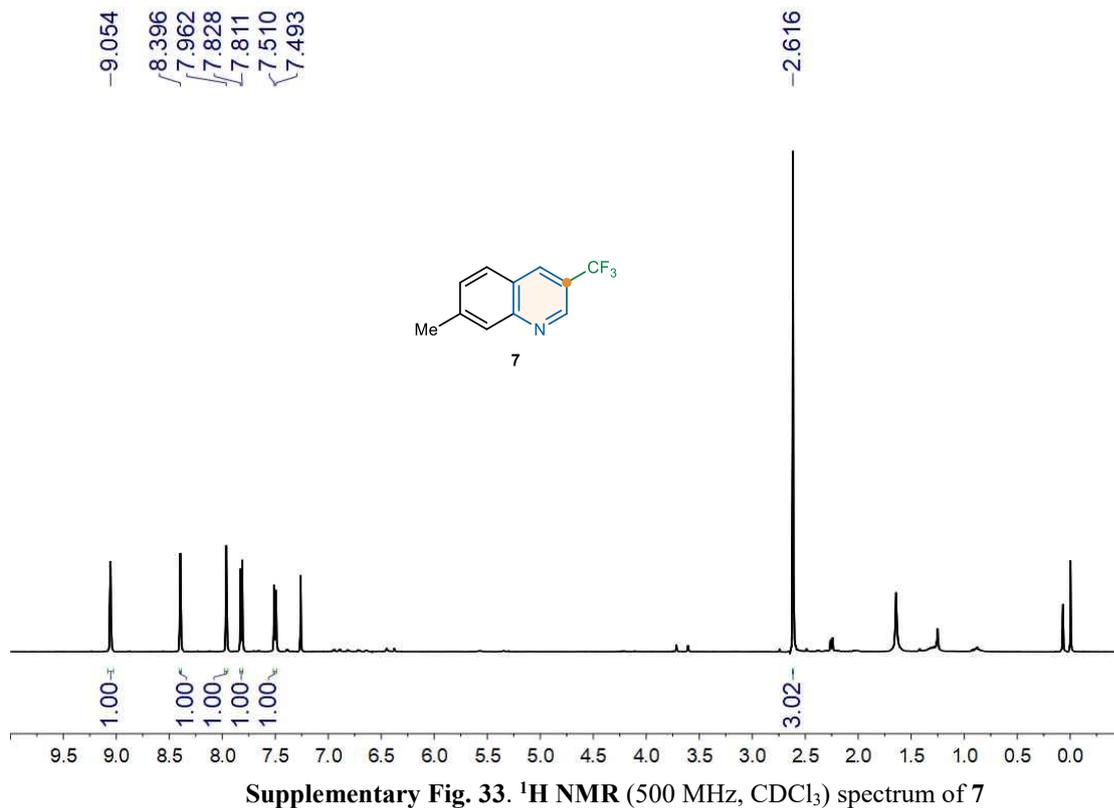
Supplementary Fig. 30.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of 6

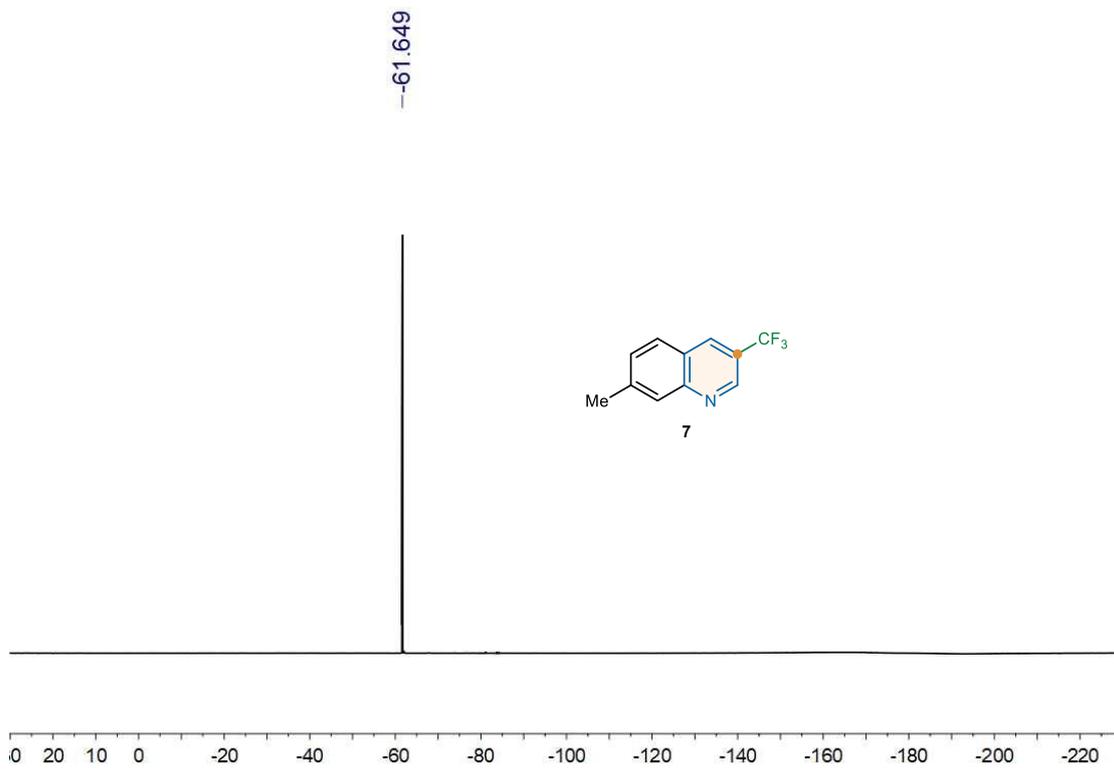


Supplementary Fig. 31. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of 6

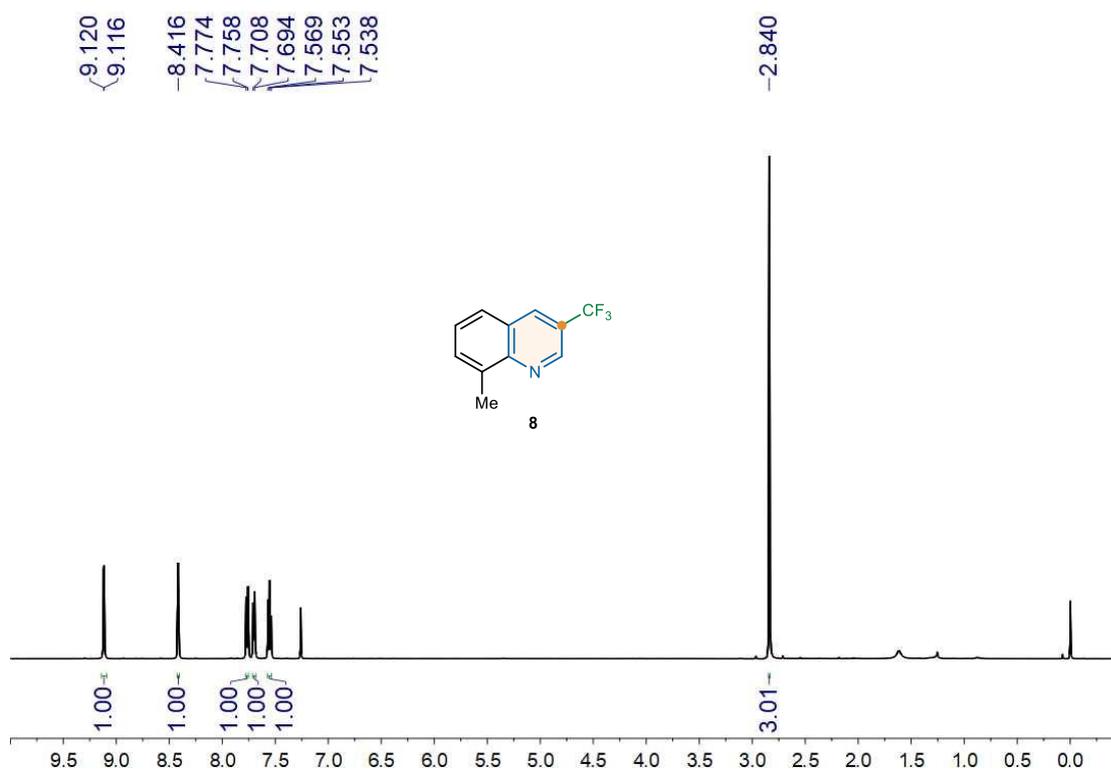


Supplementary Fig. 32. <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) spectrum of 6

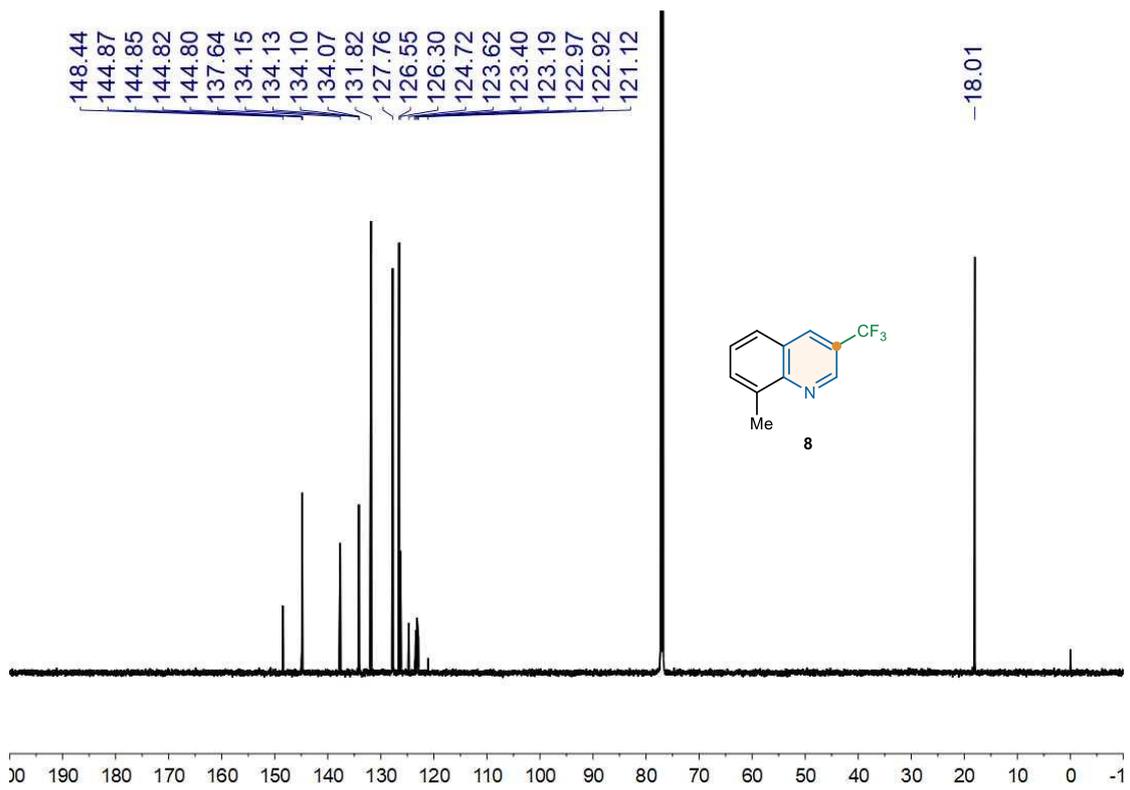




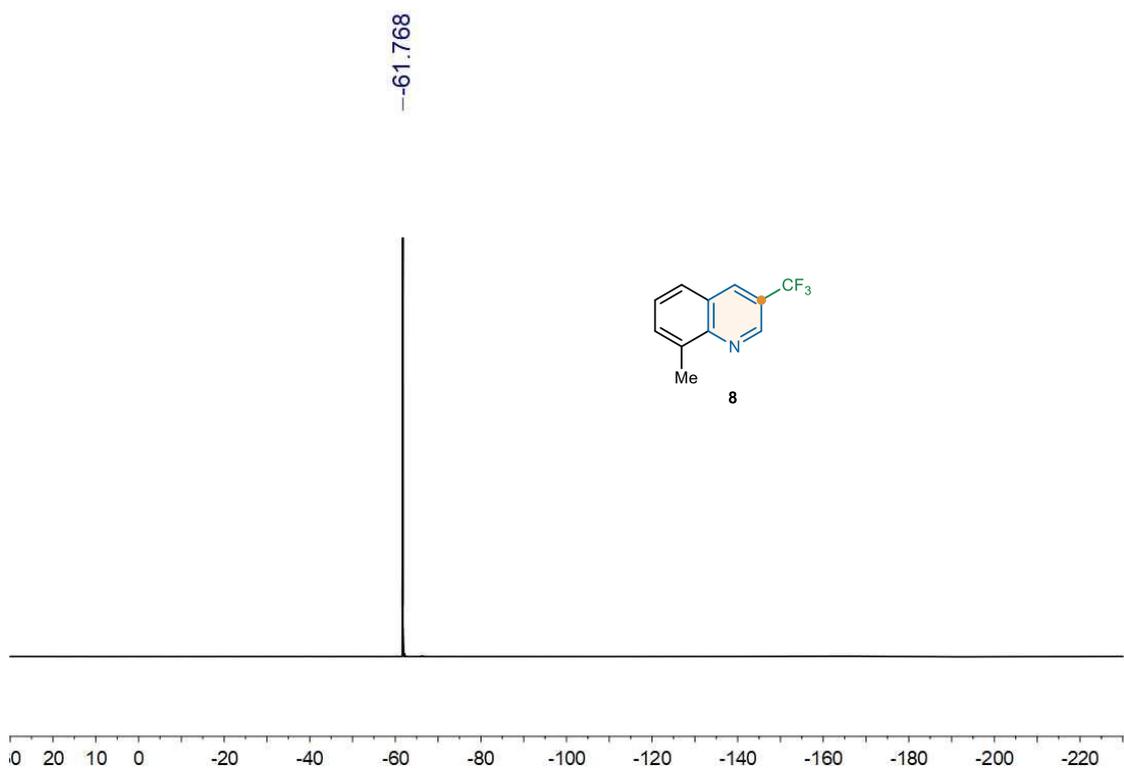
Supplementary Fig. 35.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ) spectrum of **7**



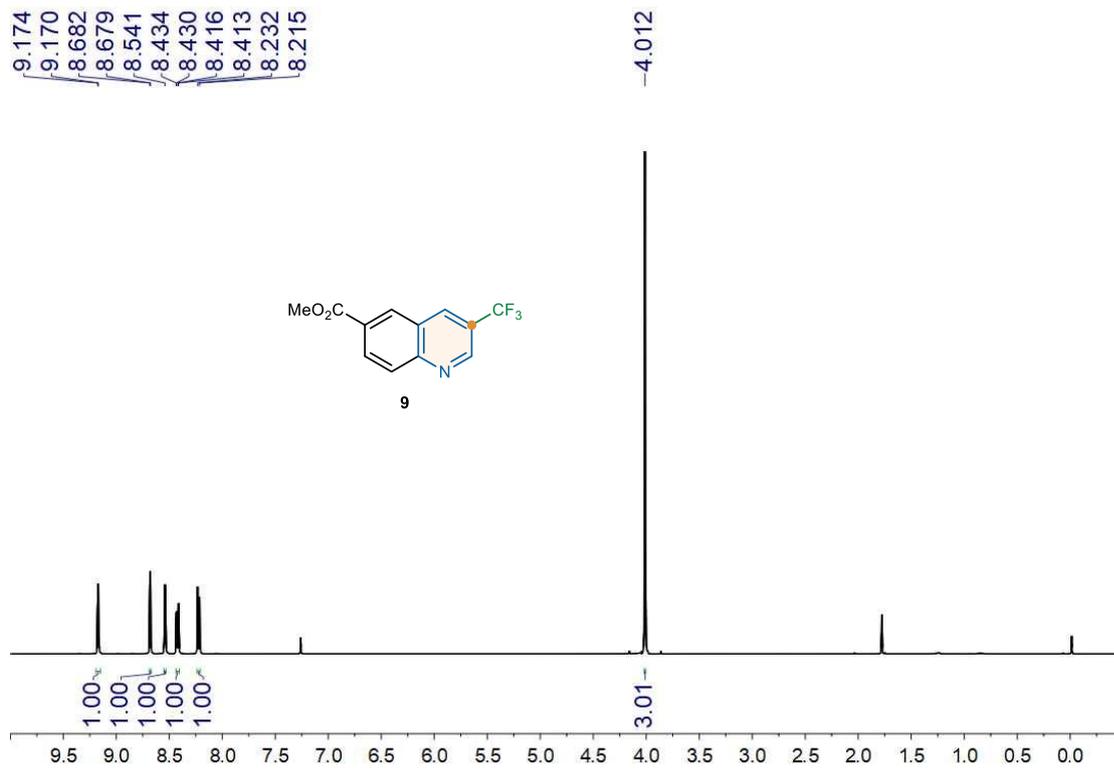
Supplementary Fig. 36.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **8**



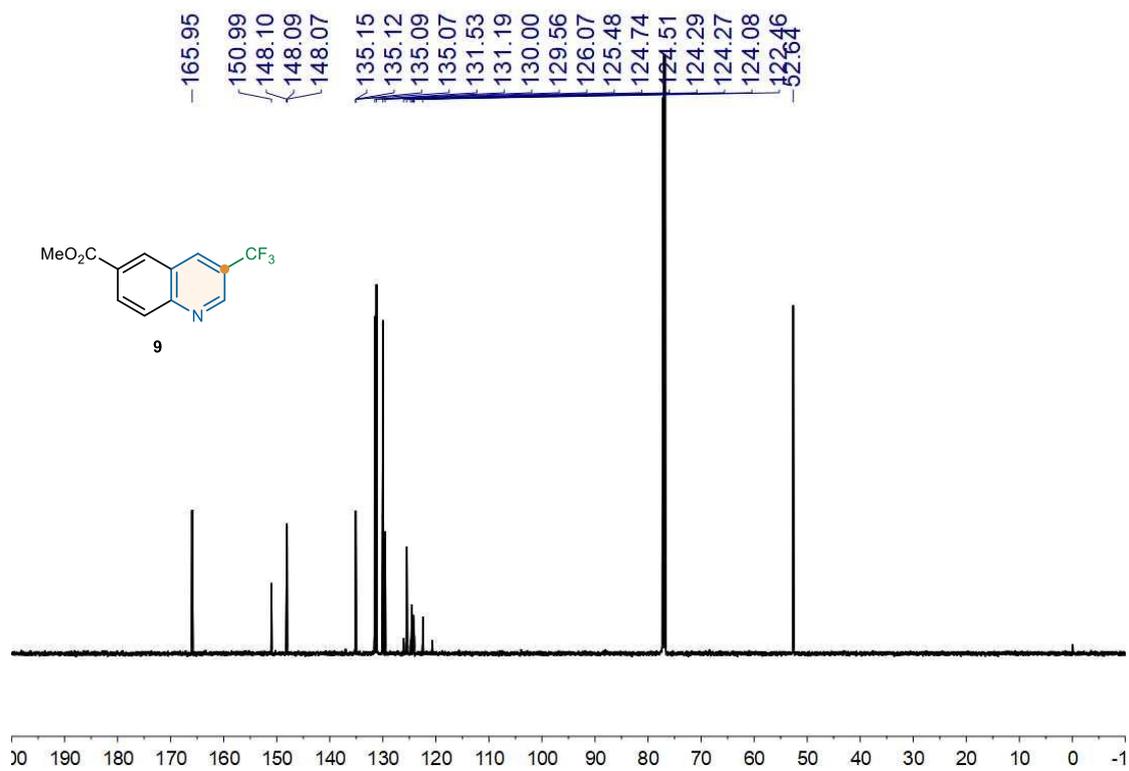
Supplementary Fig. 37. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of **8**



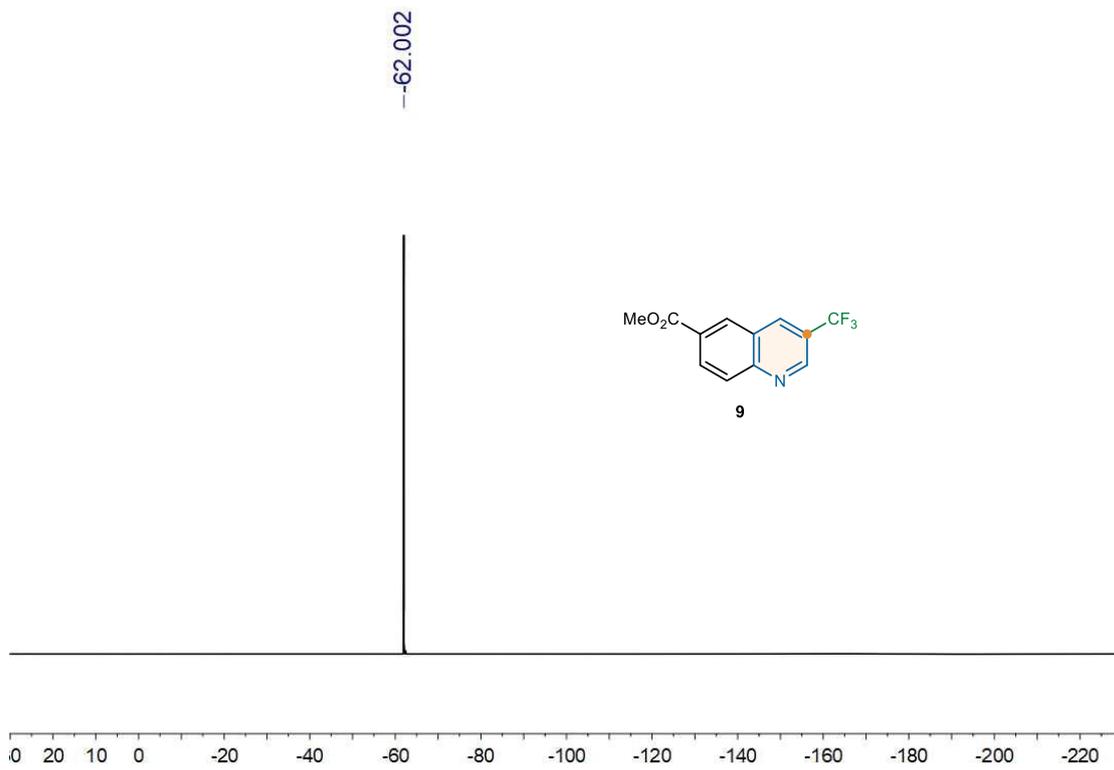
Supplementary Fig. 38. <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) spectrum of **8**



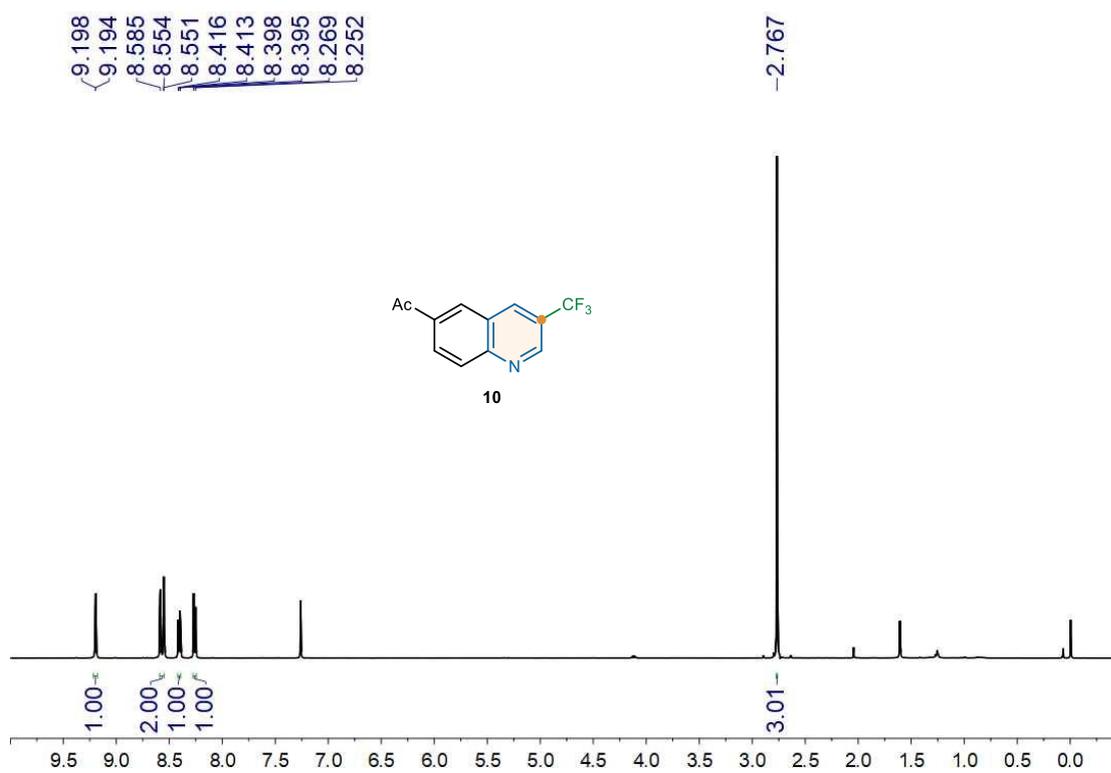
Supplementary Fig. 39. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **9**



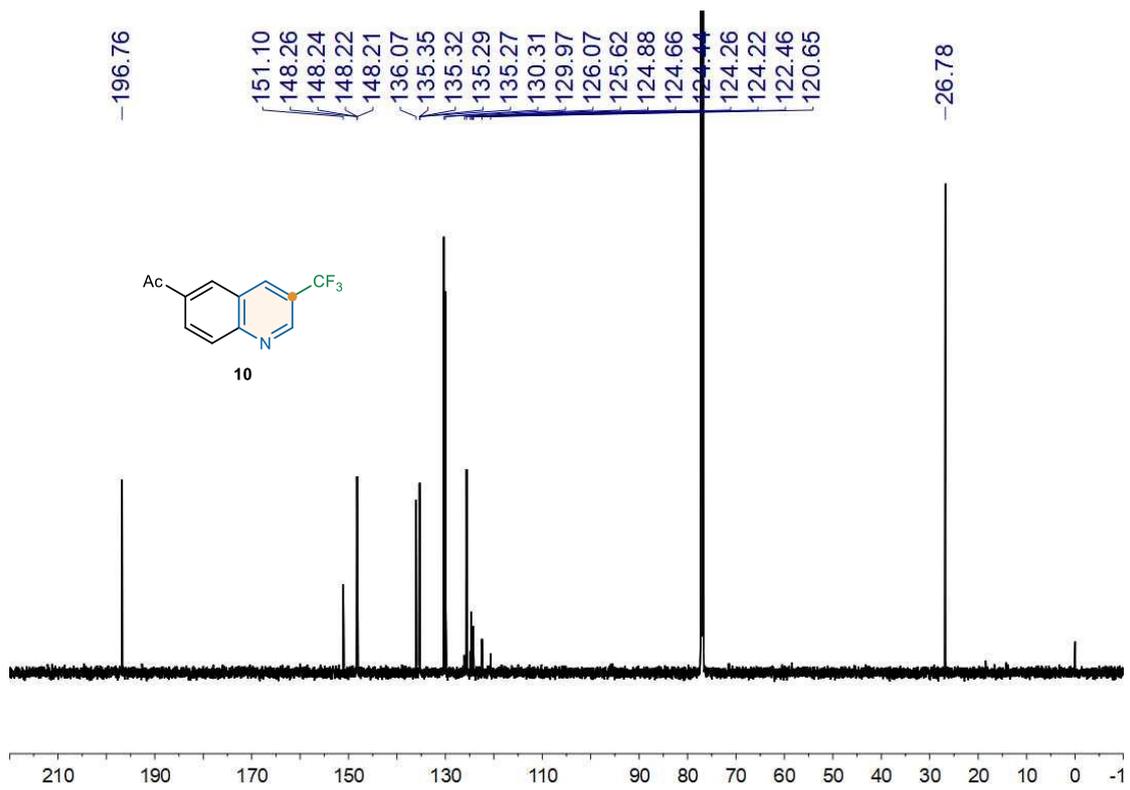
Supplementary Fig. 40. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of **9**



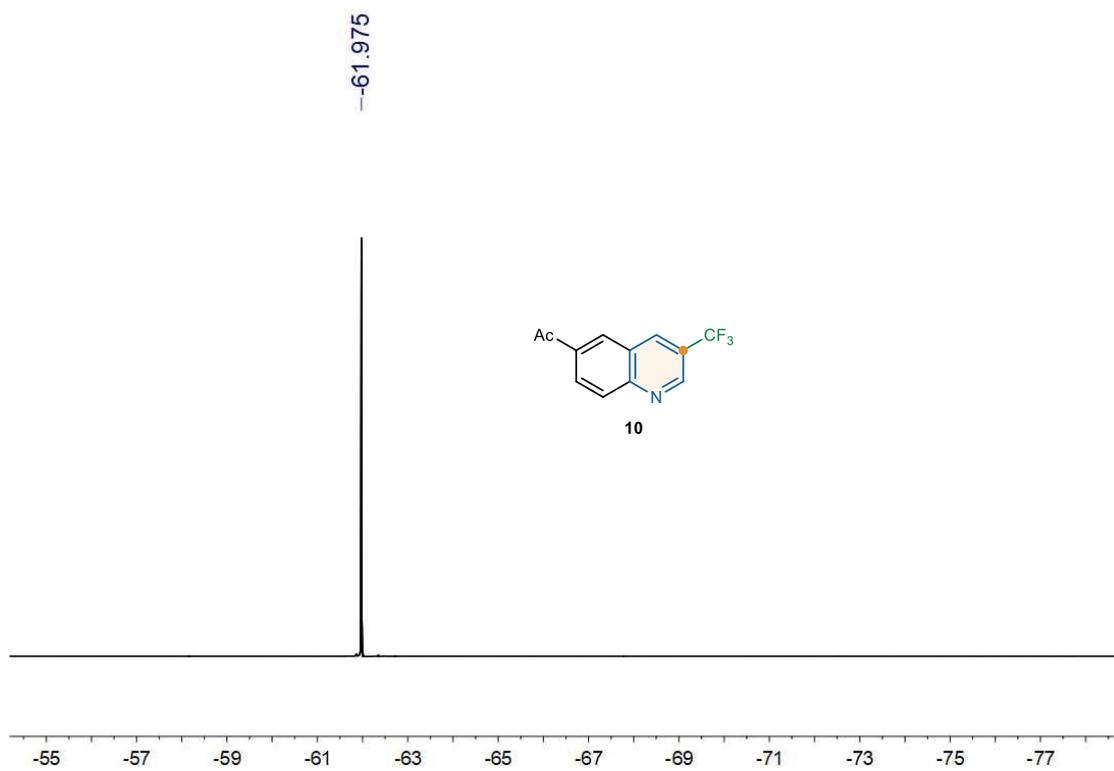
Supplementary Fig. 41.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ) spectrum of **9**



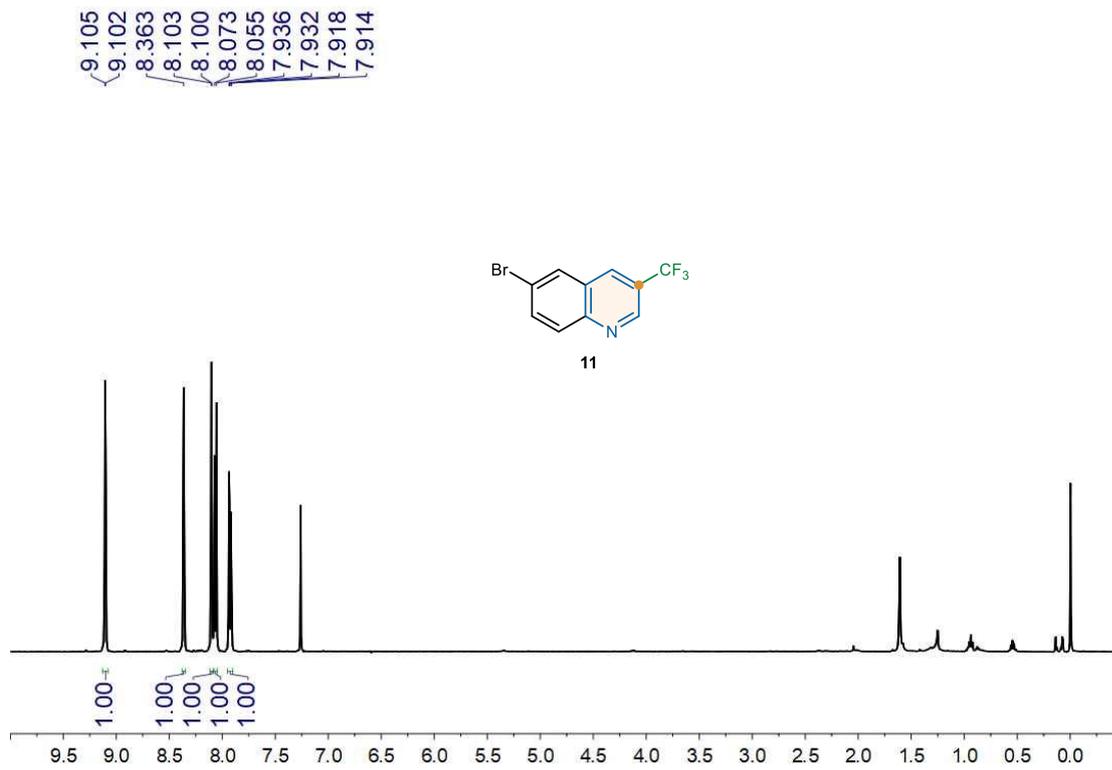
Supplementary Fig. 42.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **10**



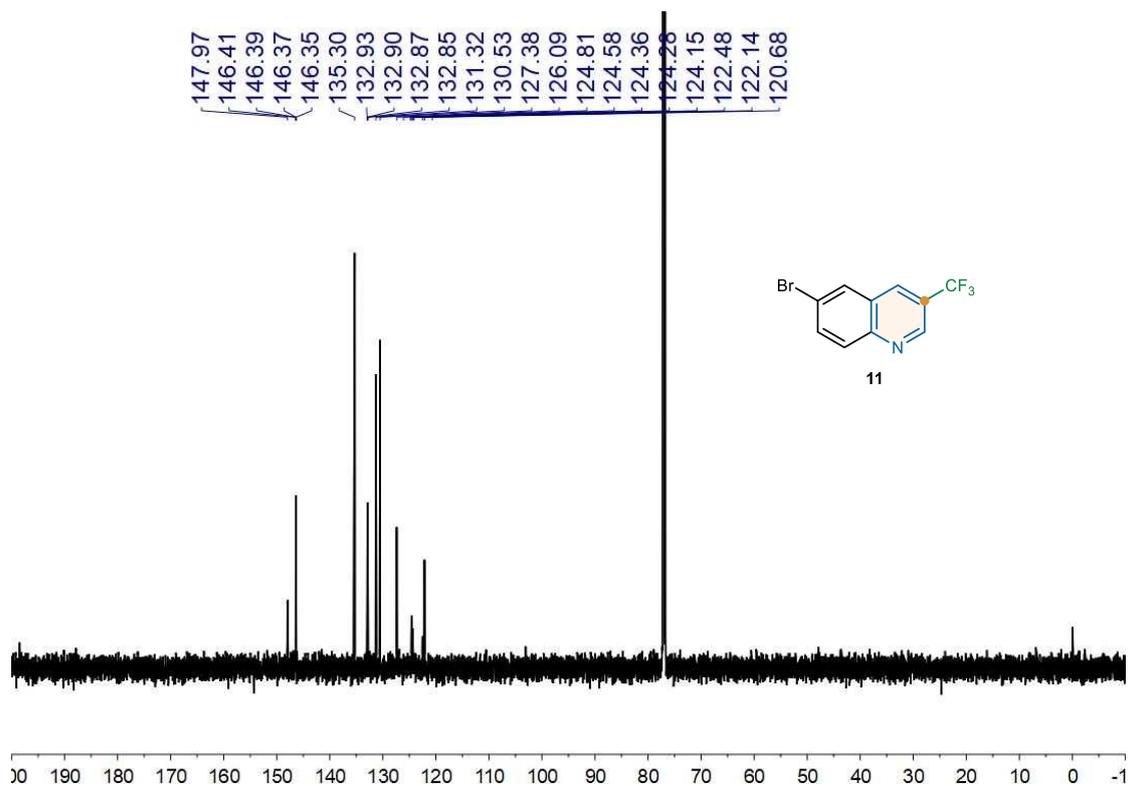
Supplementary Fig. 43.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **10**



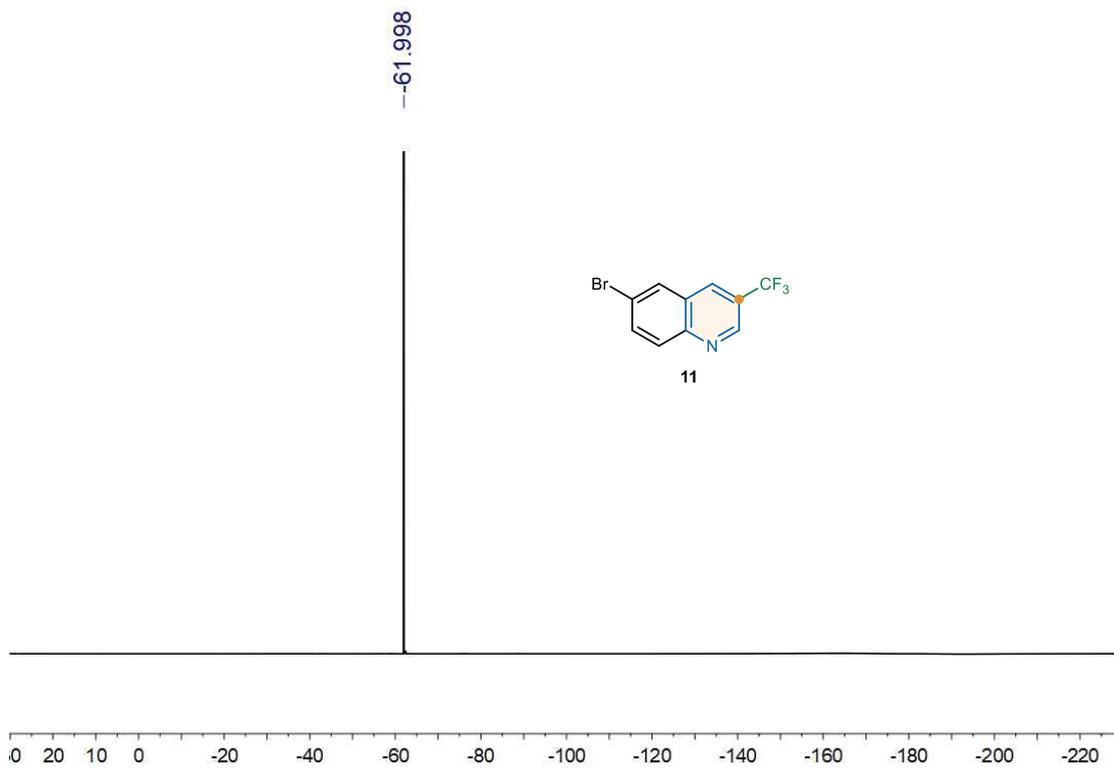
Supplementary Fig. 44.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ) spectrum of **10**



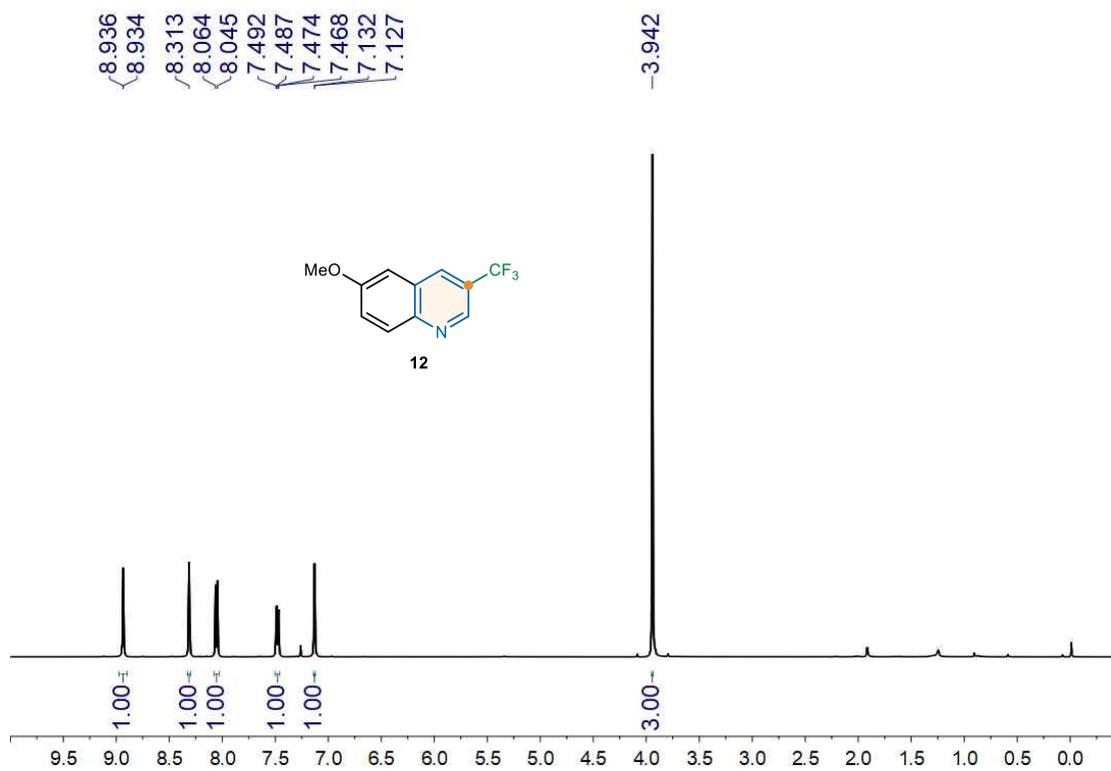
Supplementary Fig. 45.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **11**



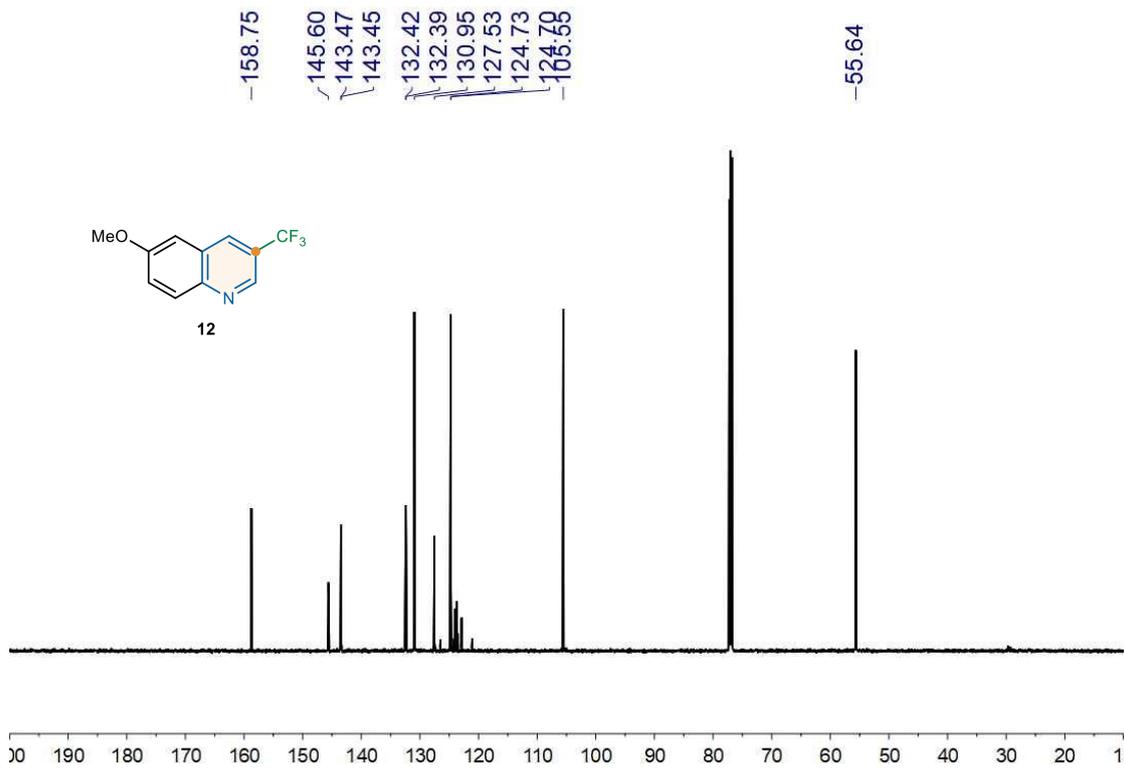
Supplementary Fig. 46.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **11**



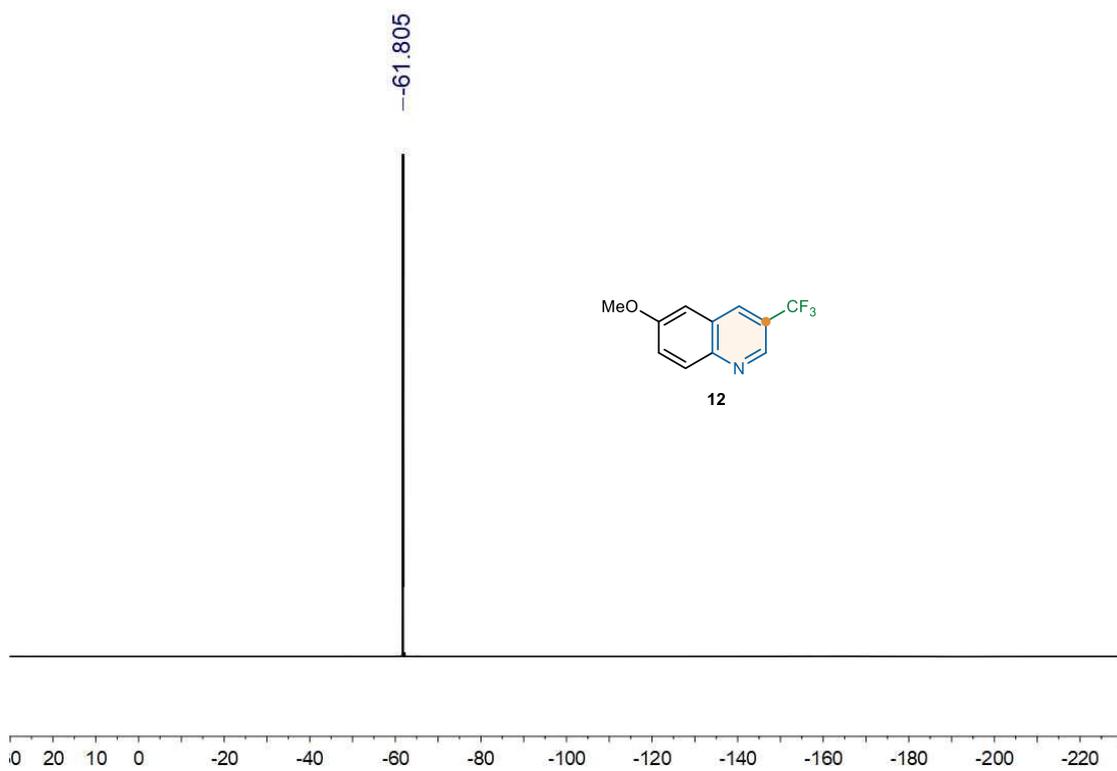
Supplementary Fig. 47.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ) spectrum of **11**



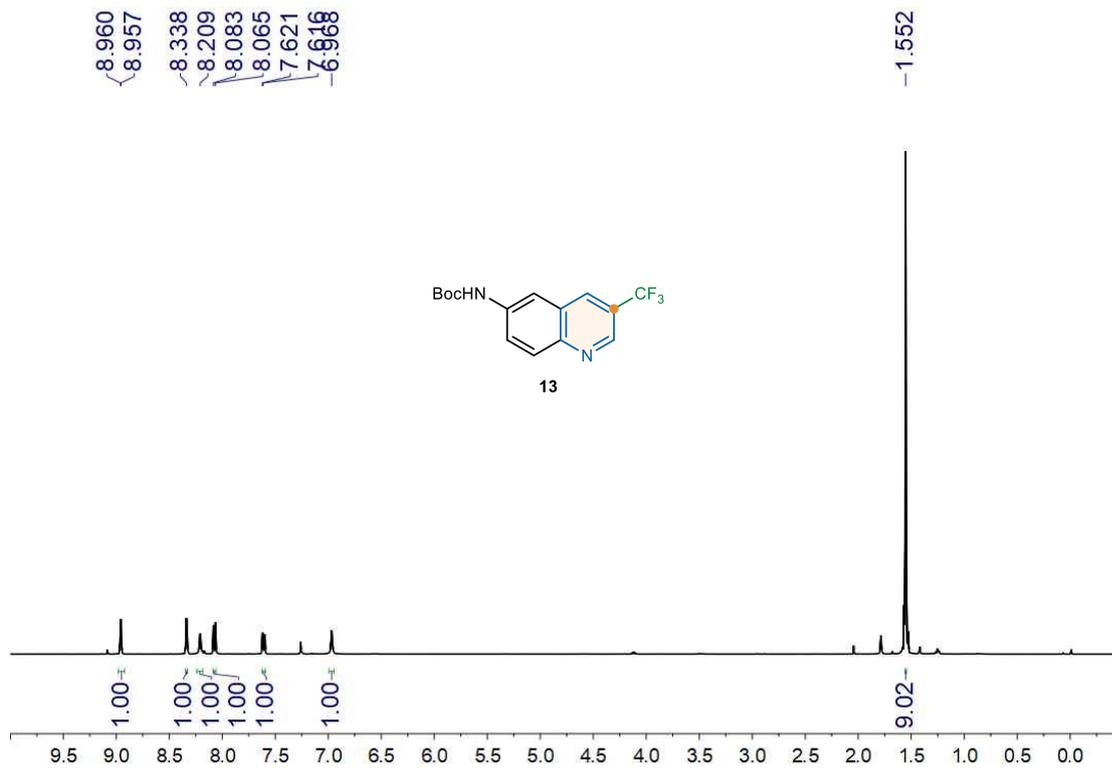
Supplementary Fig. 48.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **12**



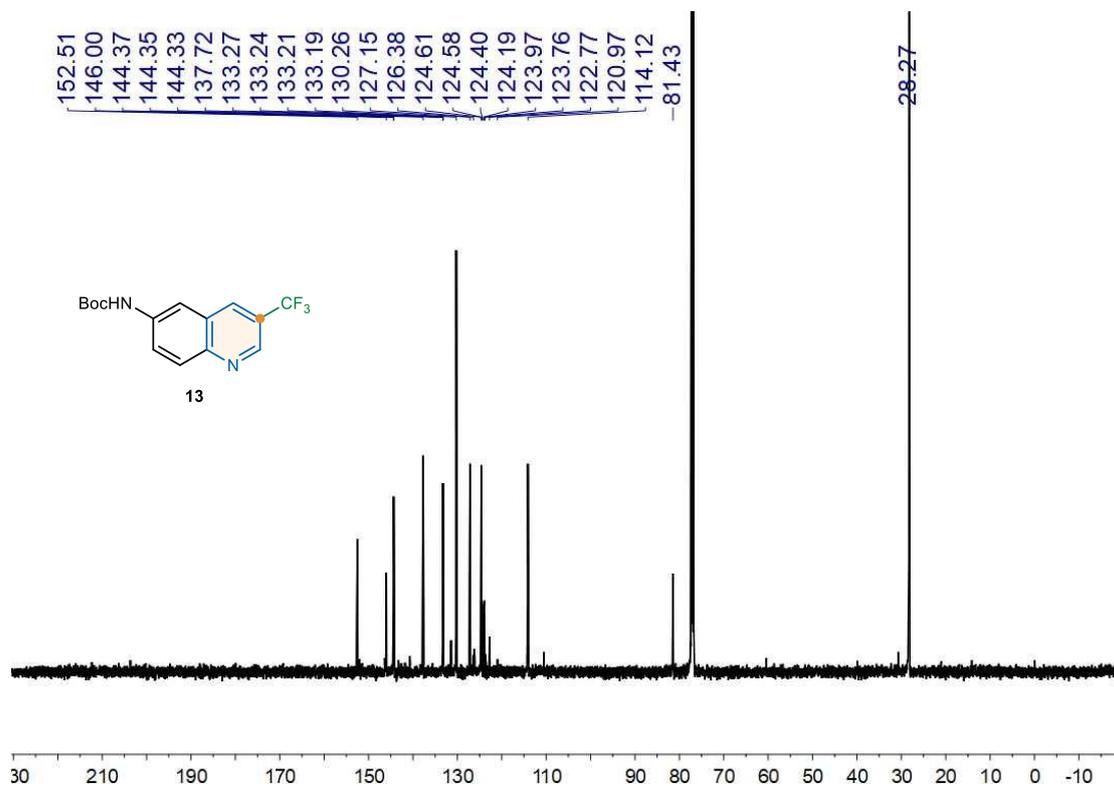
Supplementary Fig. 49. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of 12



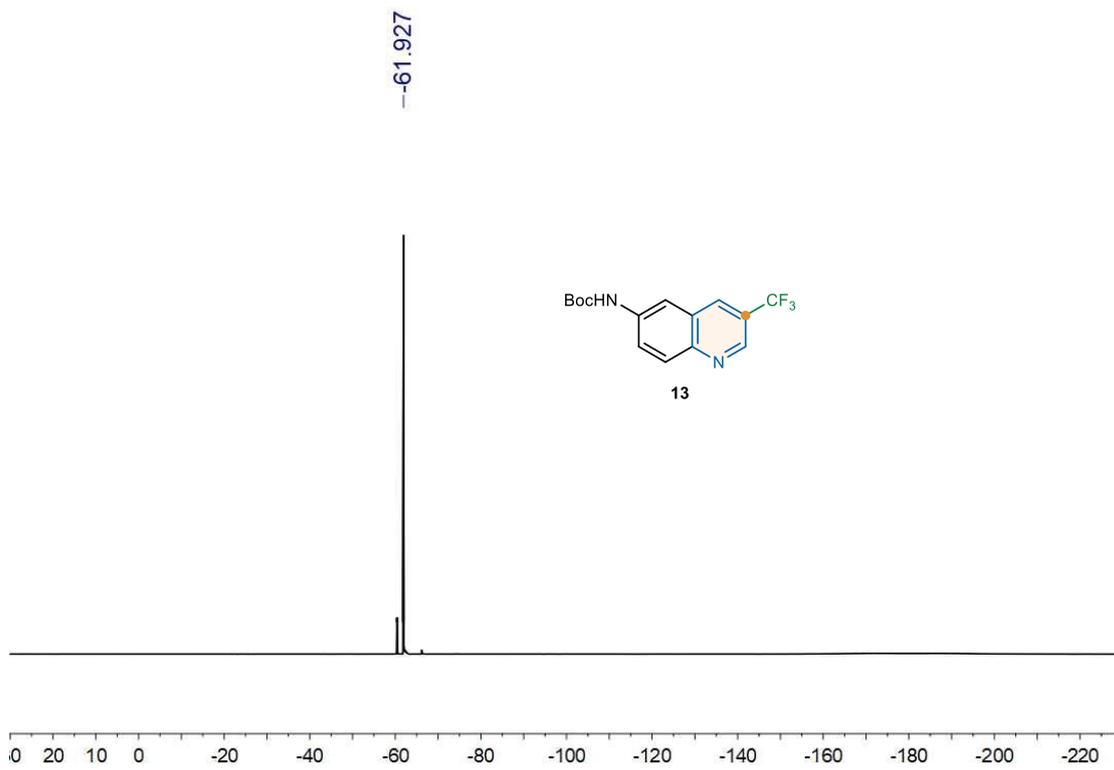
Supplementary Fig. 50. <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) spectrum of 12



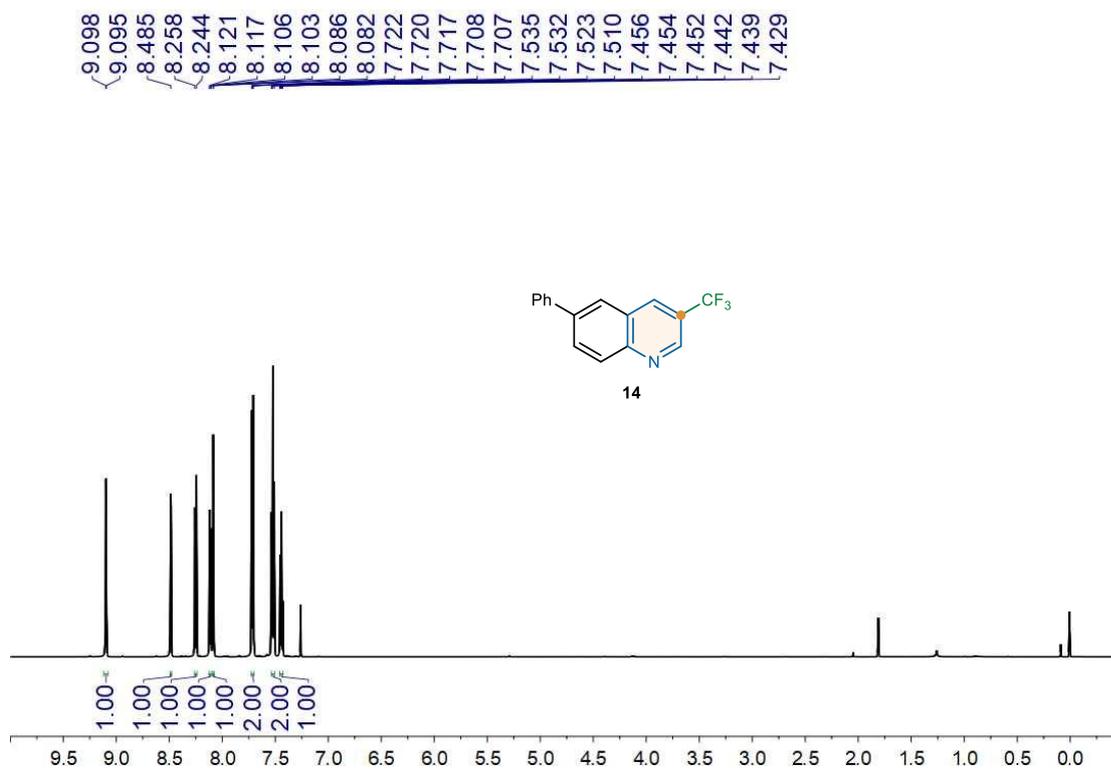
Supplementary Fig. 51. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **13**



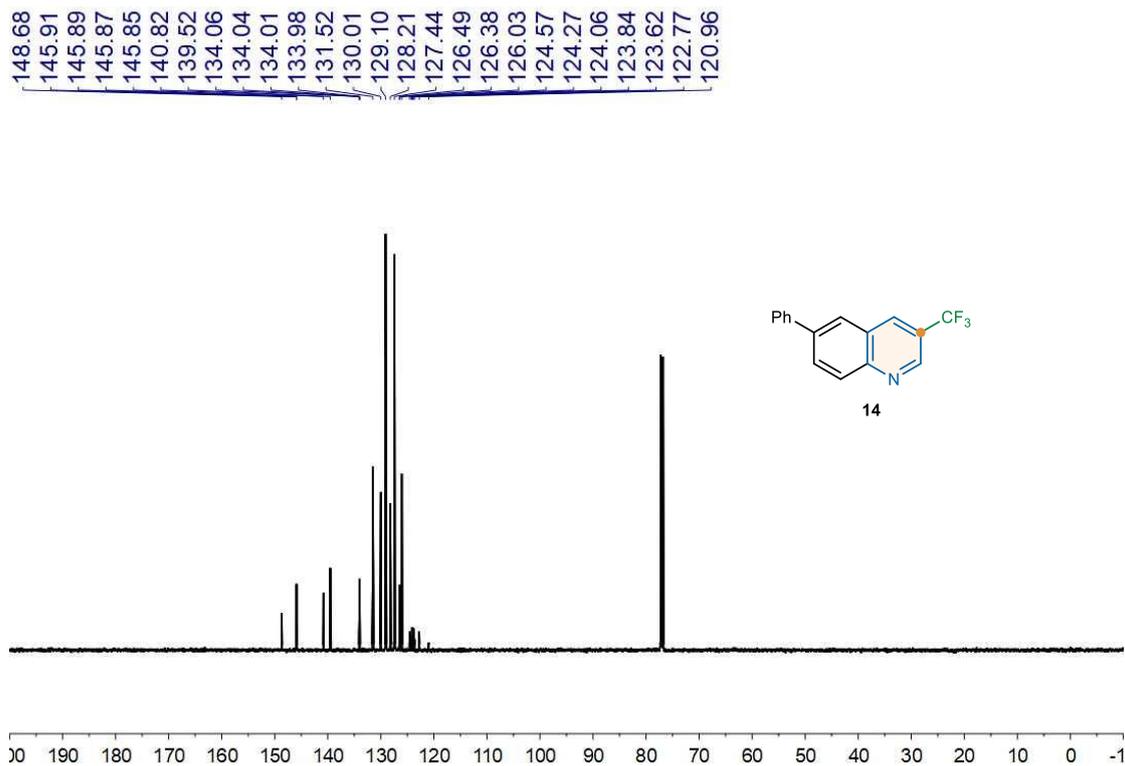
Supplementary Fig. 52. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of **13**



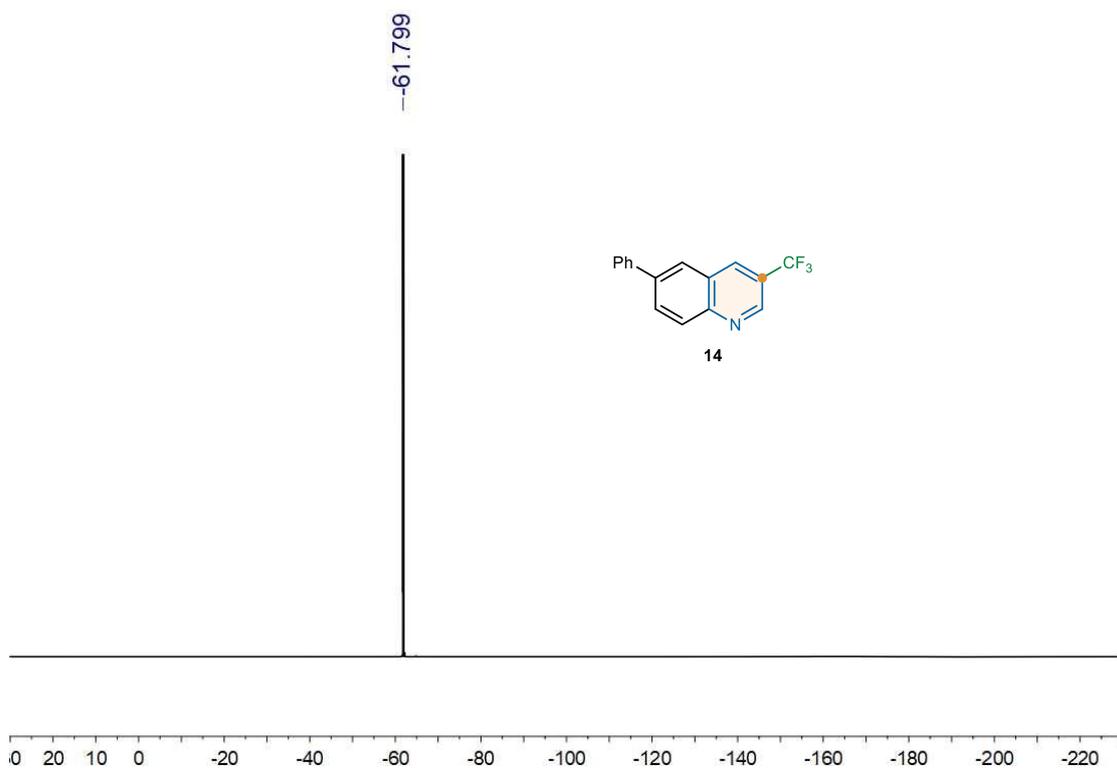
Supplementary Fig. 53.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ) spectrum of **13**



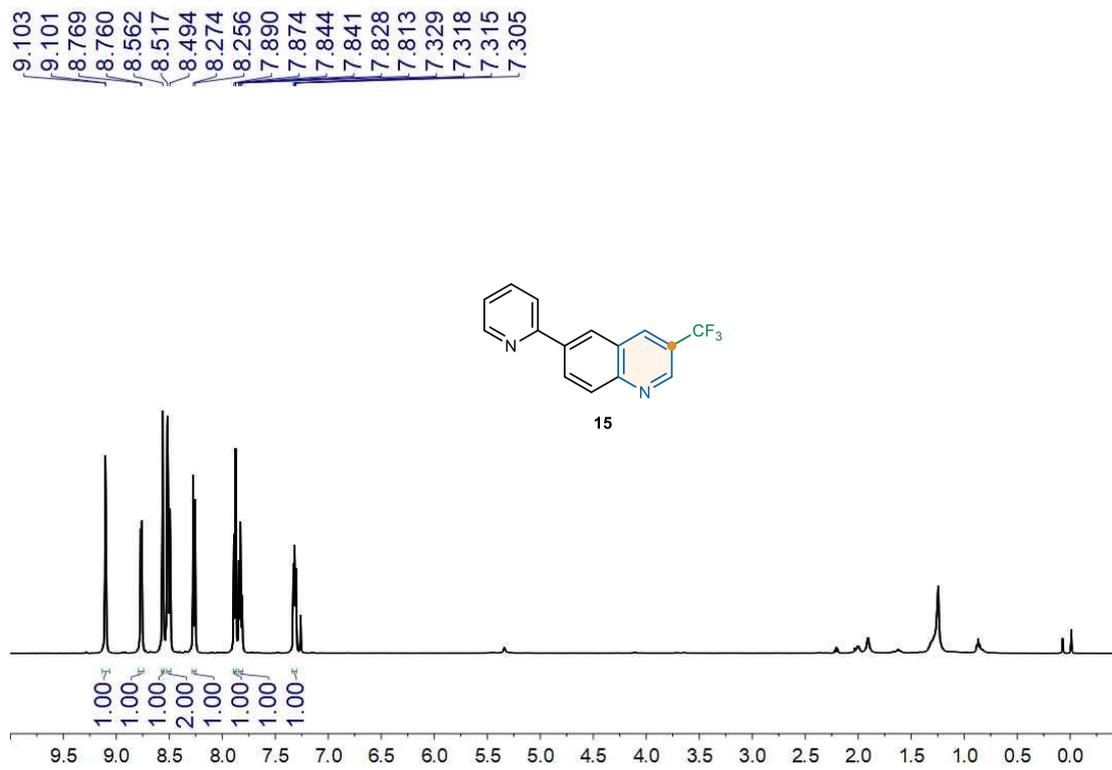
Supplementary Fig. 54.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) spectrum of **14**



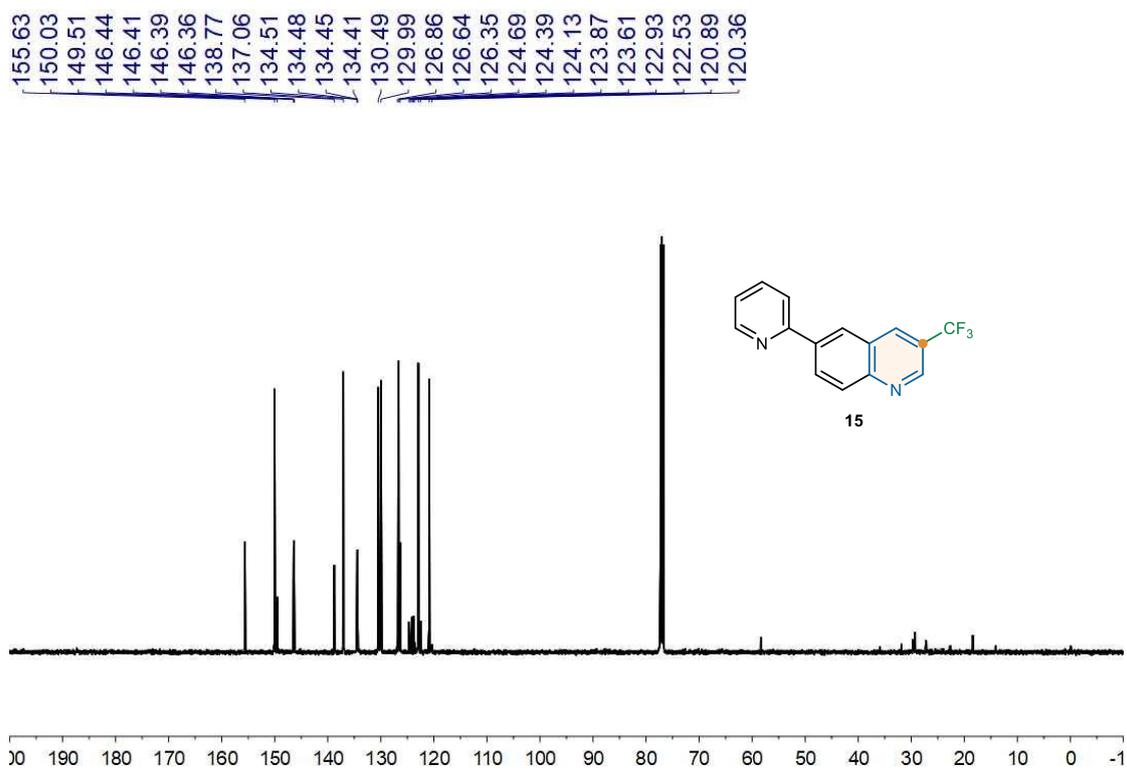
Supplementary Fig. 55. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of 14



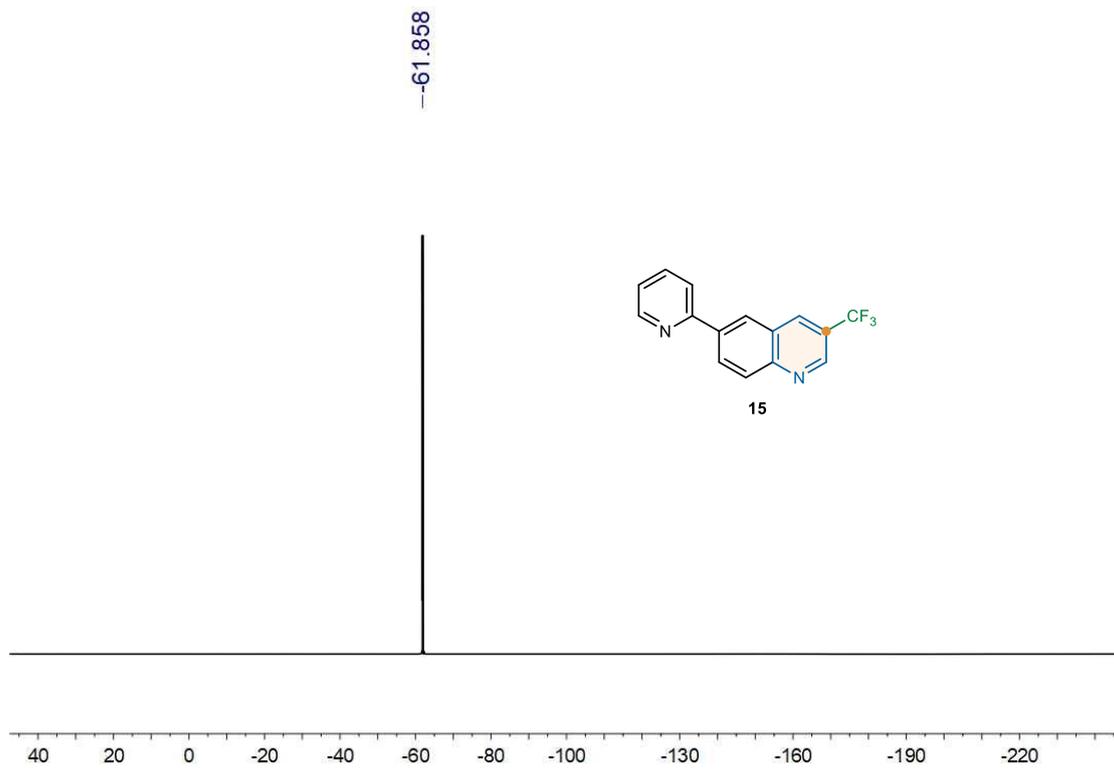
Supplementary Fig. 56. <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) spectrum of 14



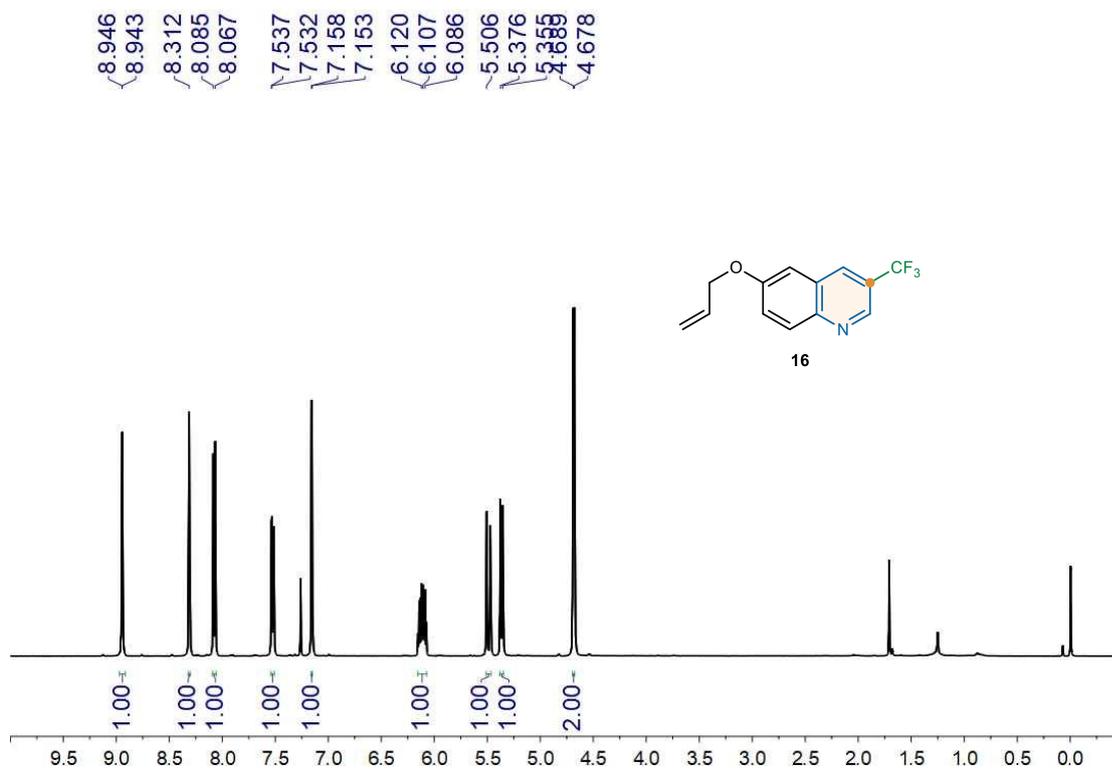
Supplementary Fig. 57.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **15**



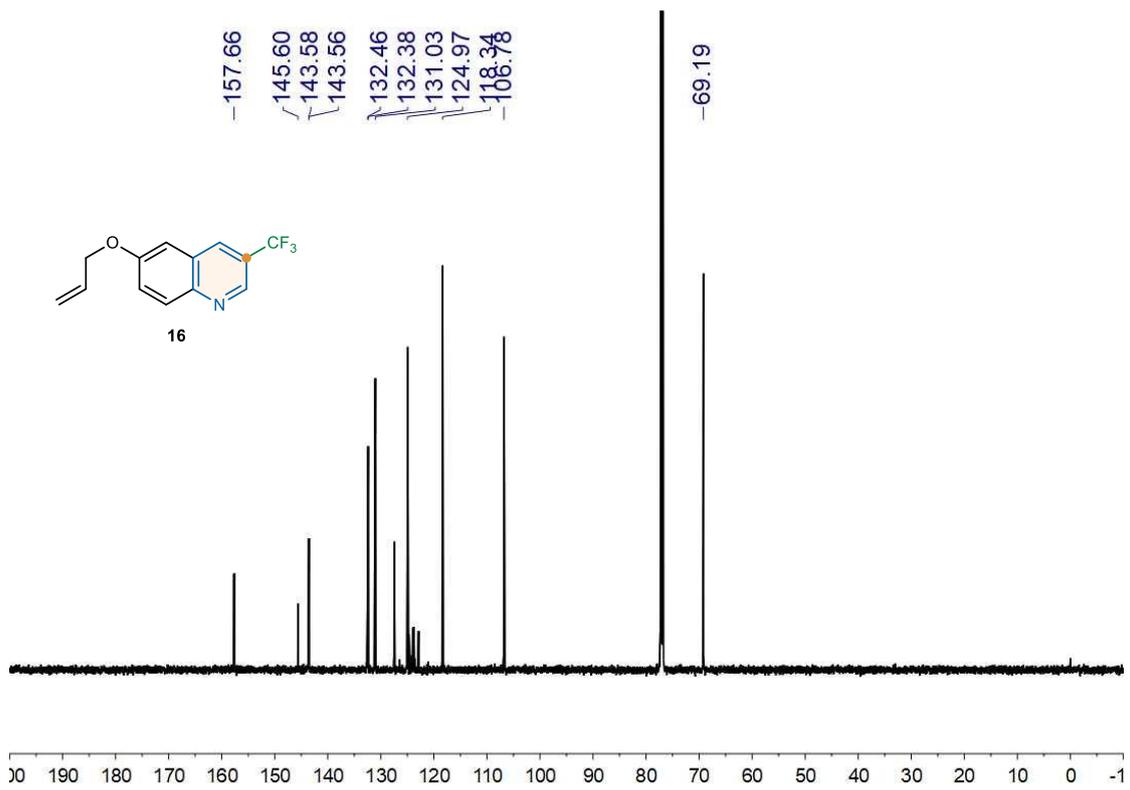
Supplementary Fig. 58.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of **15**



Supplementary Fig. 59.  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ) spectrum of 15



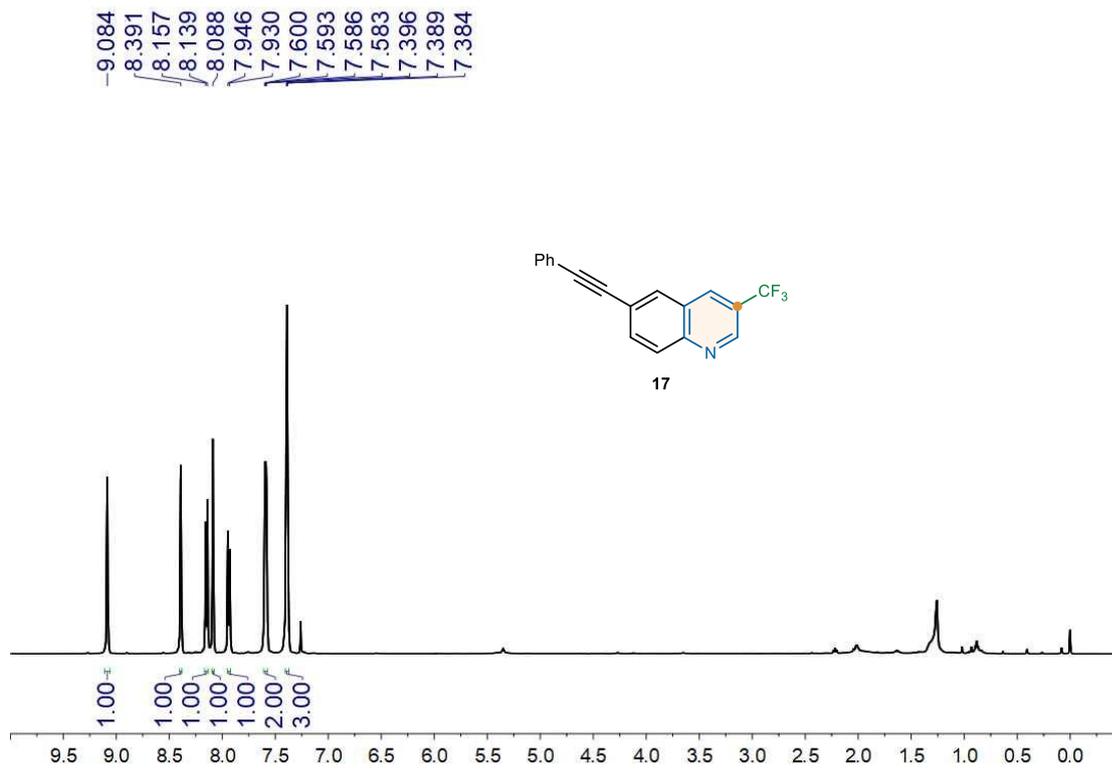
Supplementary Fig. 60.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of 16



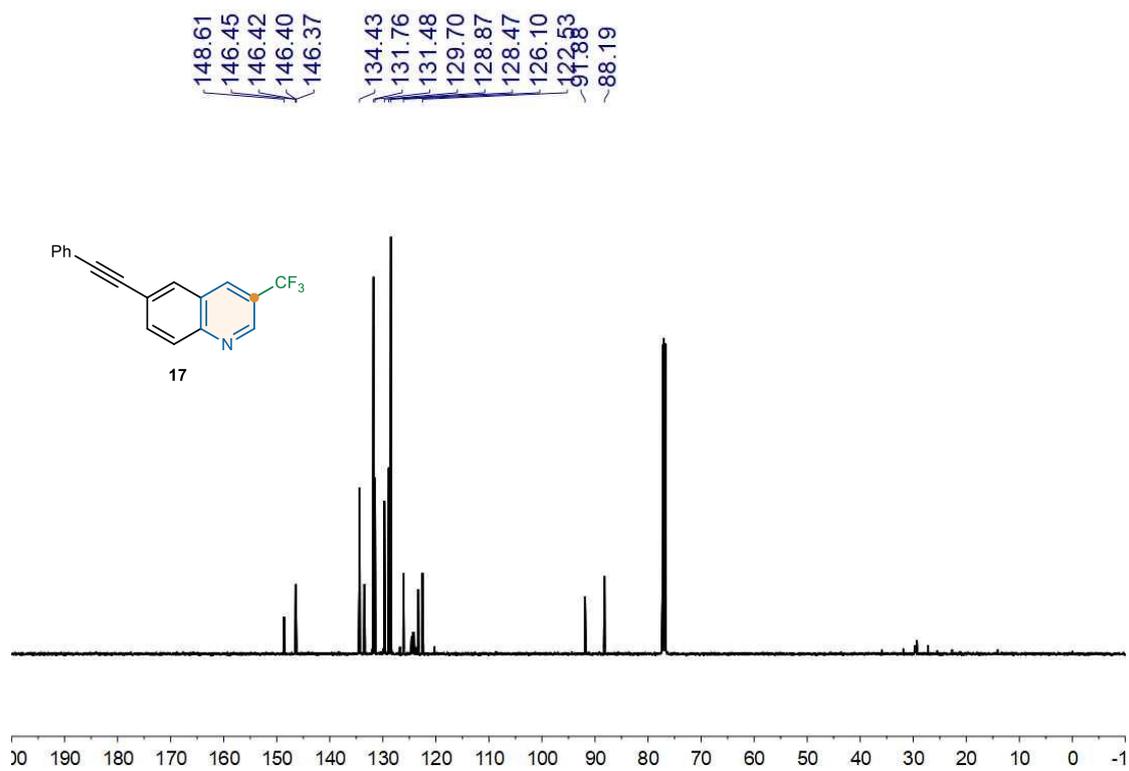
Supplementary Fig. 61. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of 16



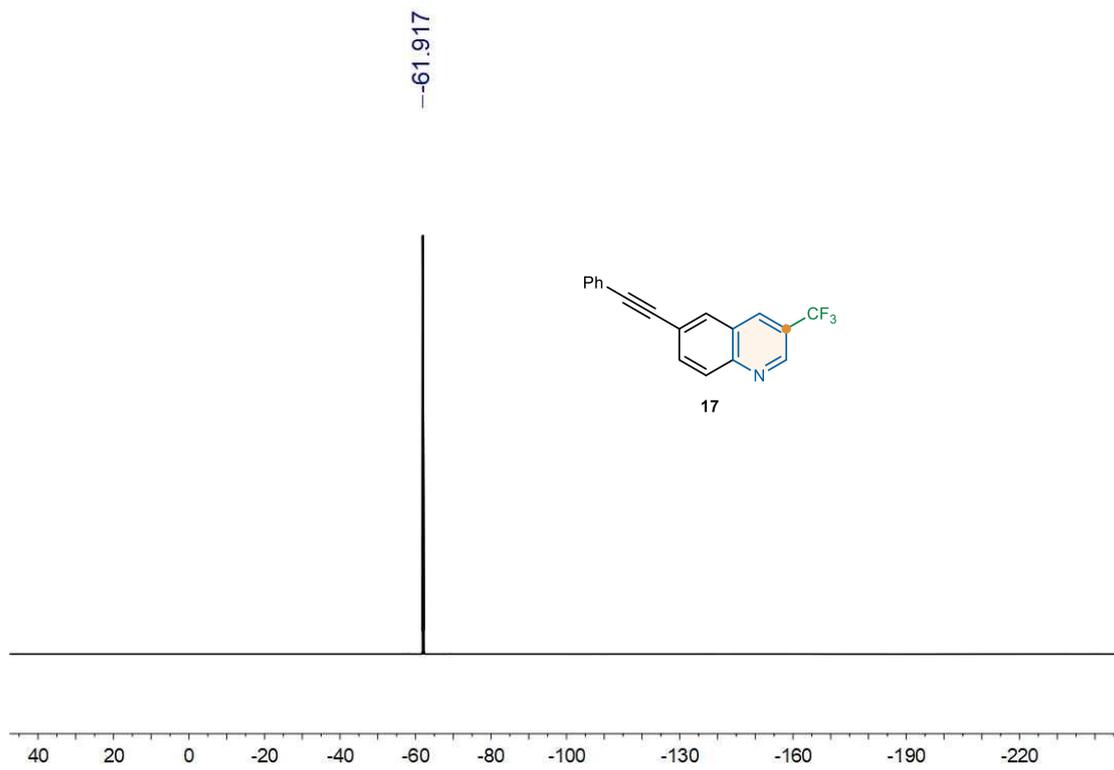
Supplementary Fig. 62. <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) spectrum of 16



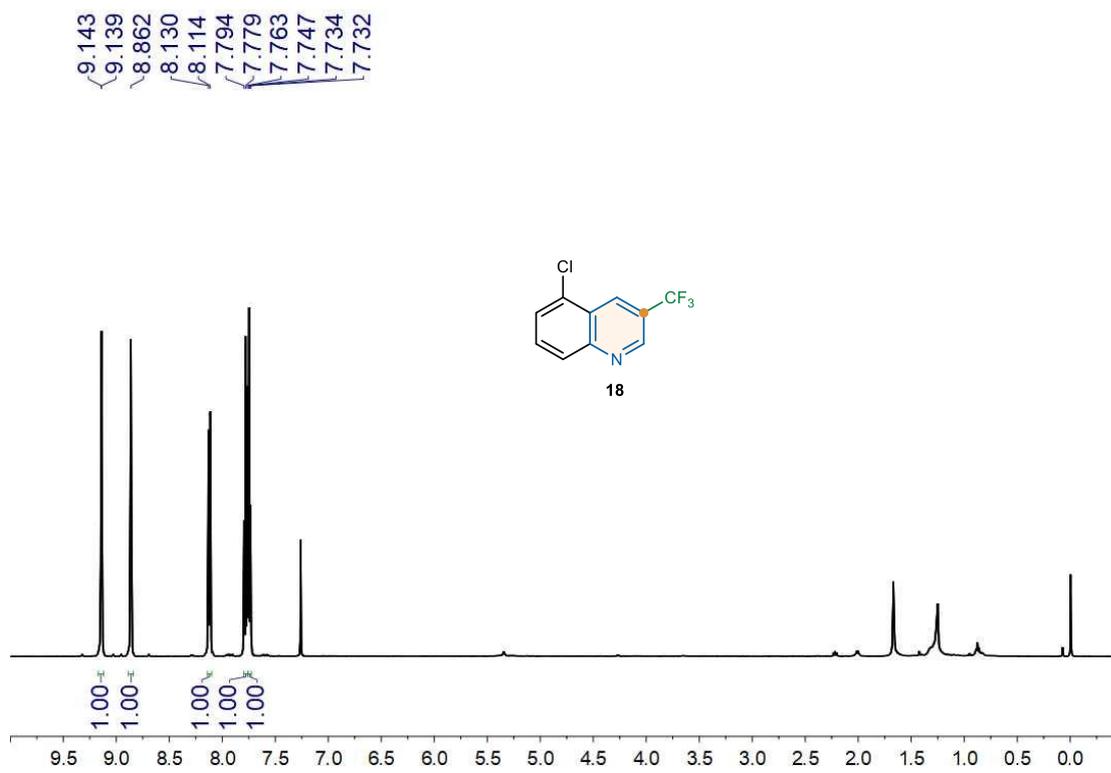
Supplementary Fig. 63. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of 17



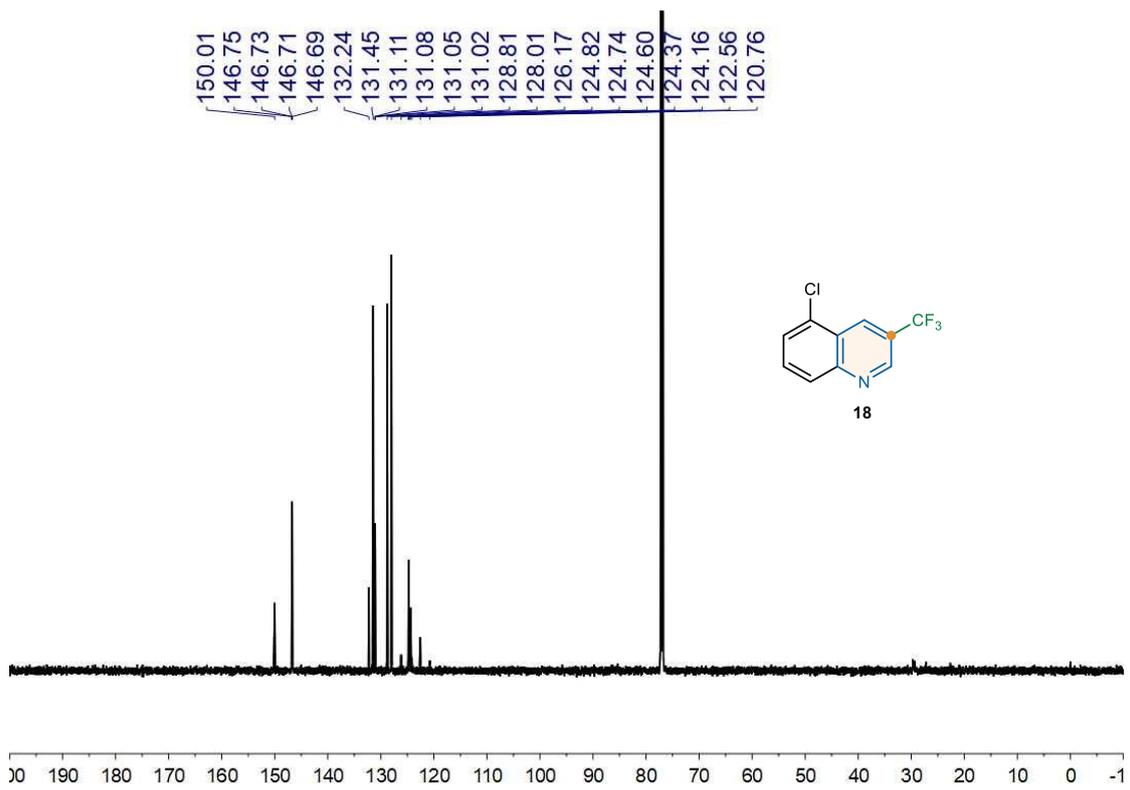
Supplementary Fig. 64. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of 17



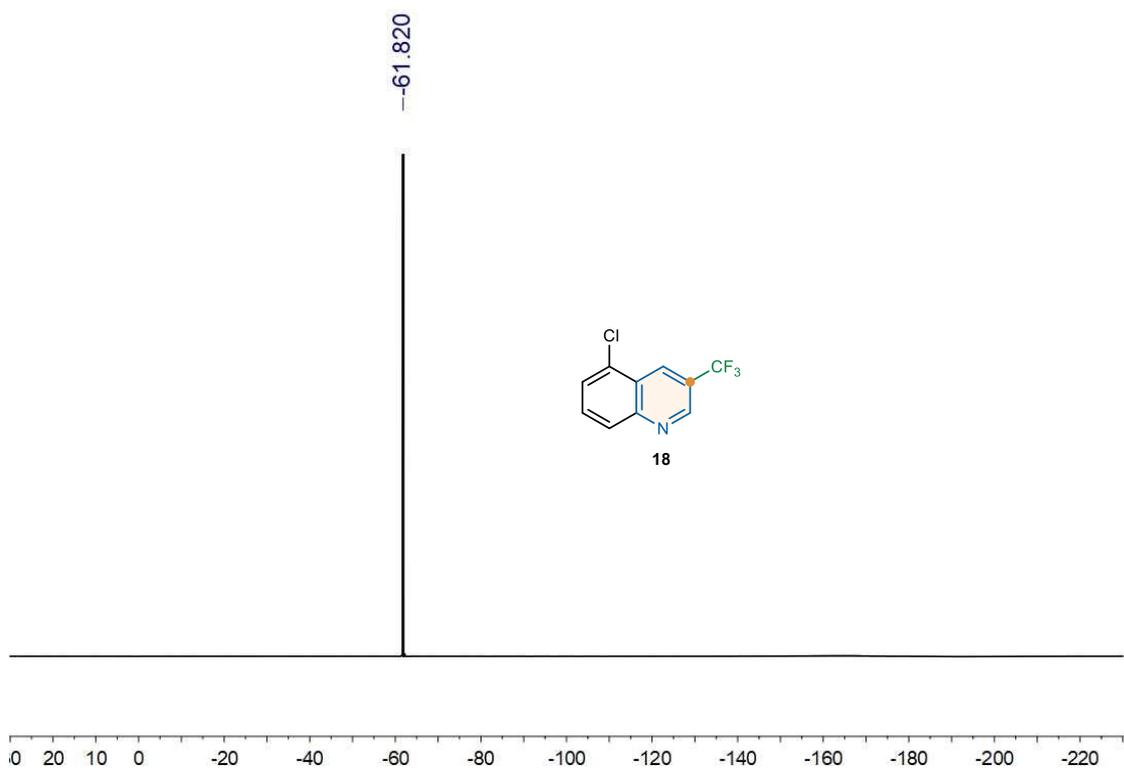
Supplementary Fig. 65.  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ) spectrum of **17**



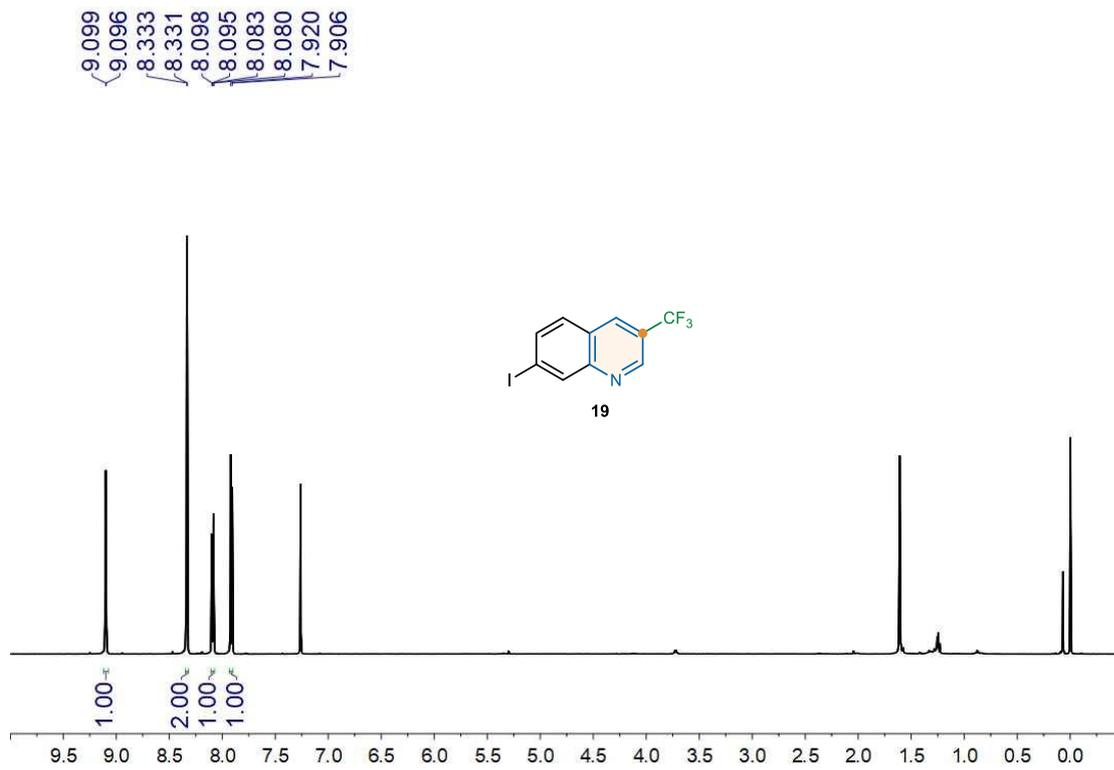
Supplementary Fig. 66.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **18**



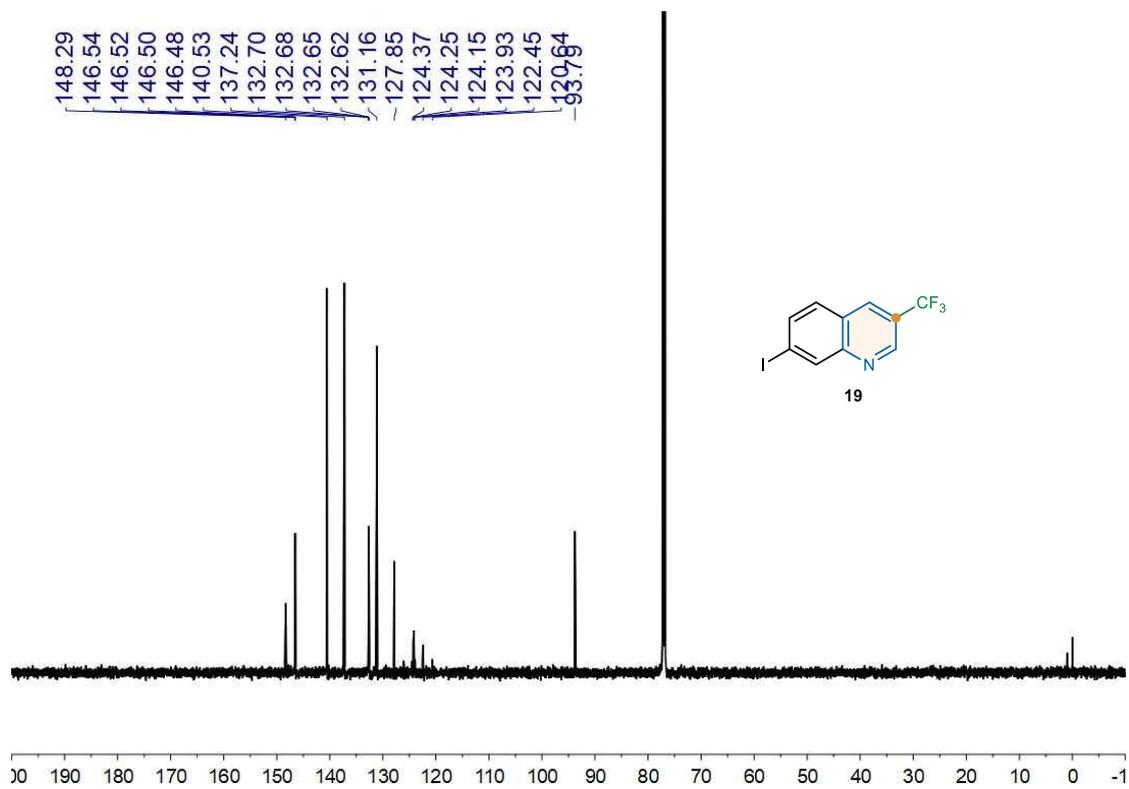
Supplementary Fig. 67. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of **18**



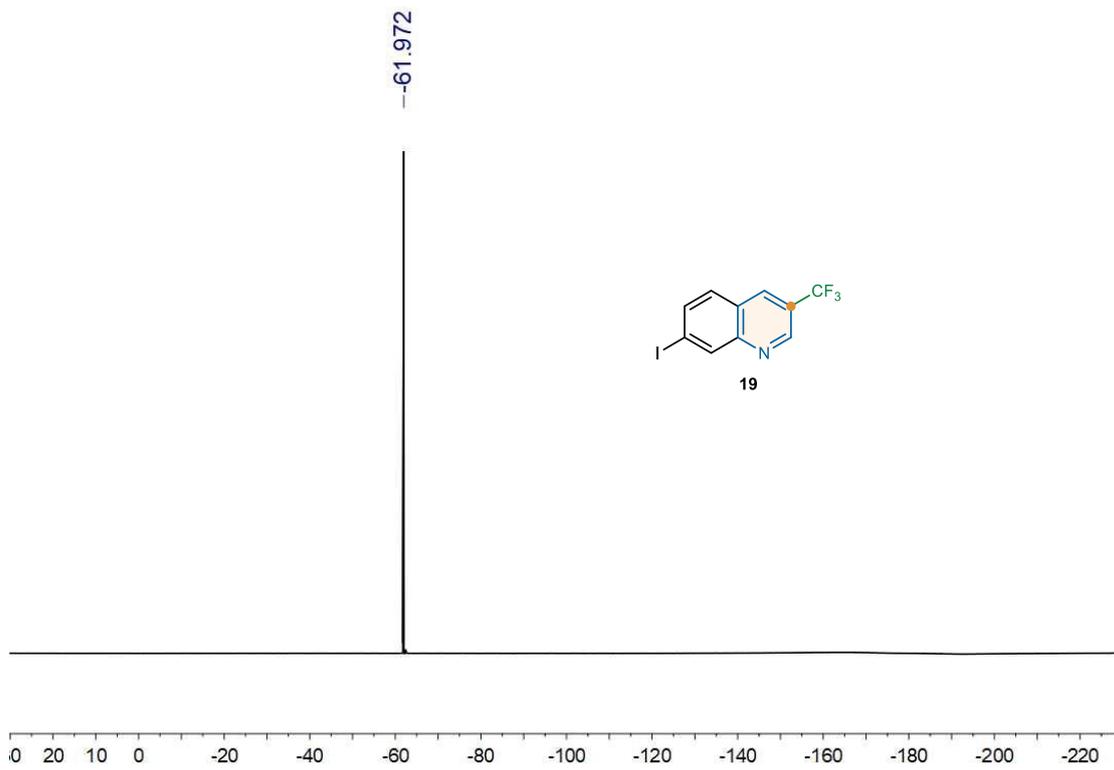
Supplementary Fig. 68. <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) spectrum of **18**



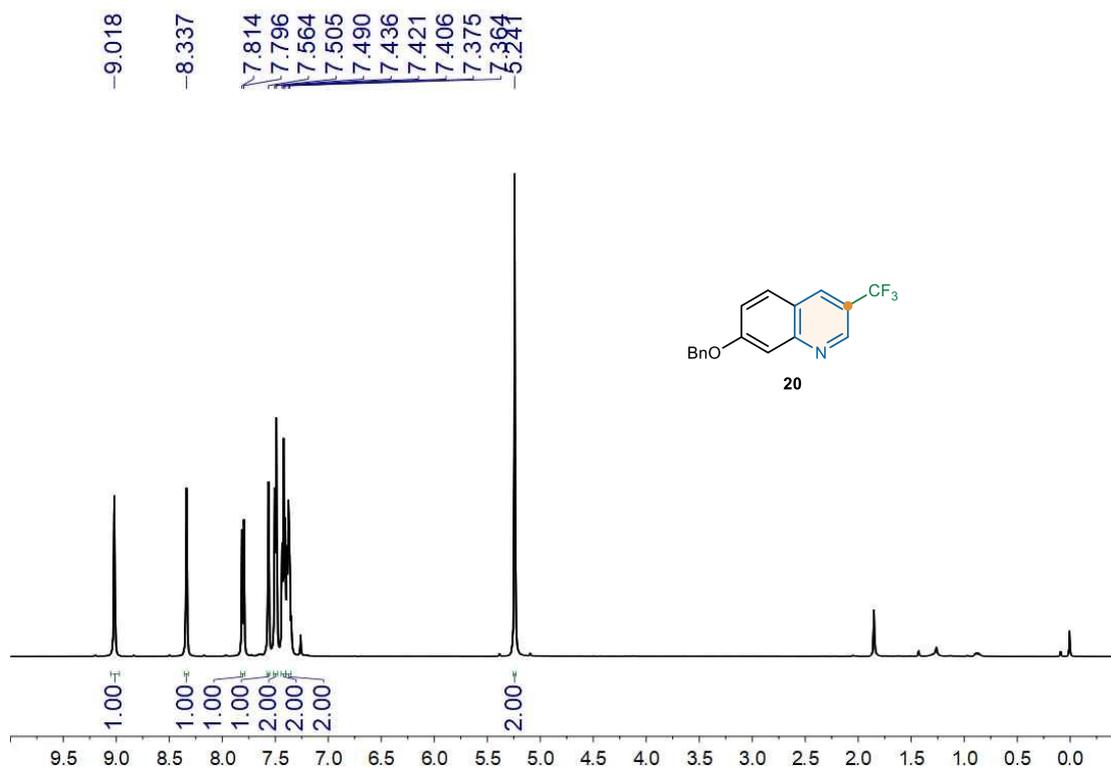
Supplementary Fig. 69.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of 19



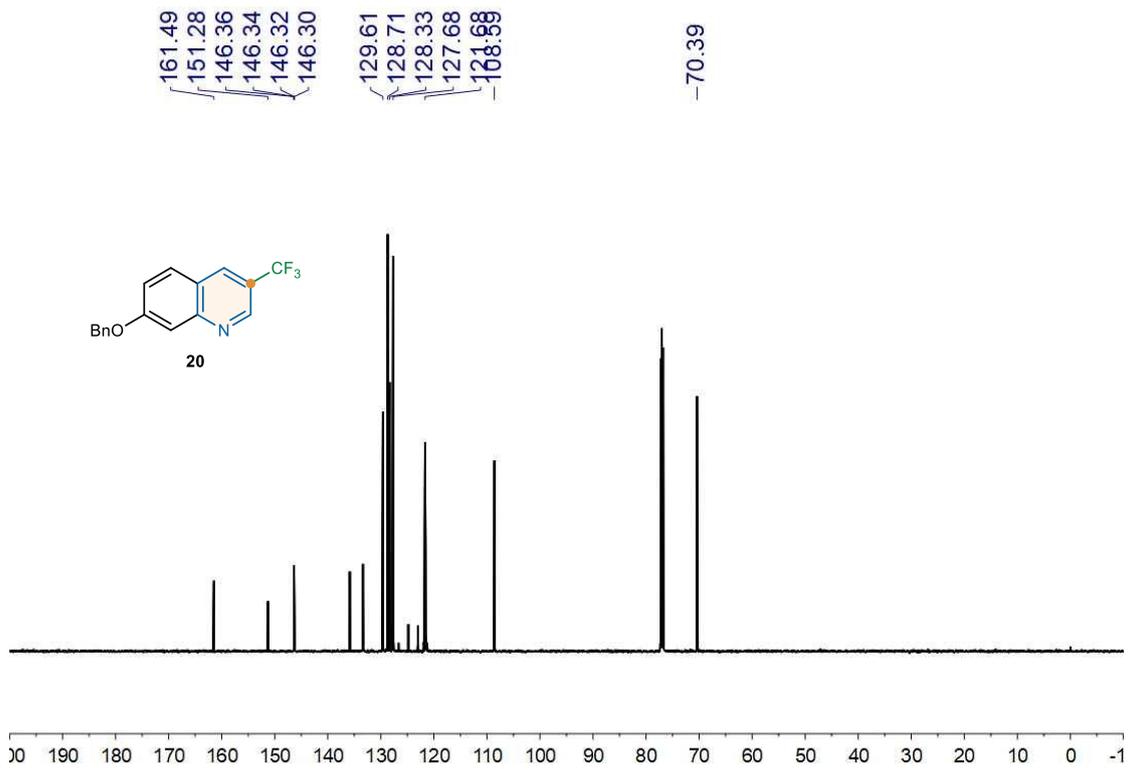
Supplementary Fig. 70.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of 19



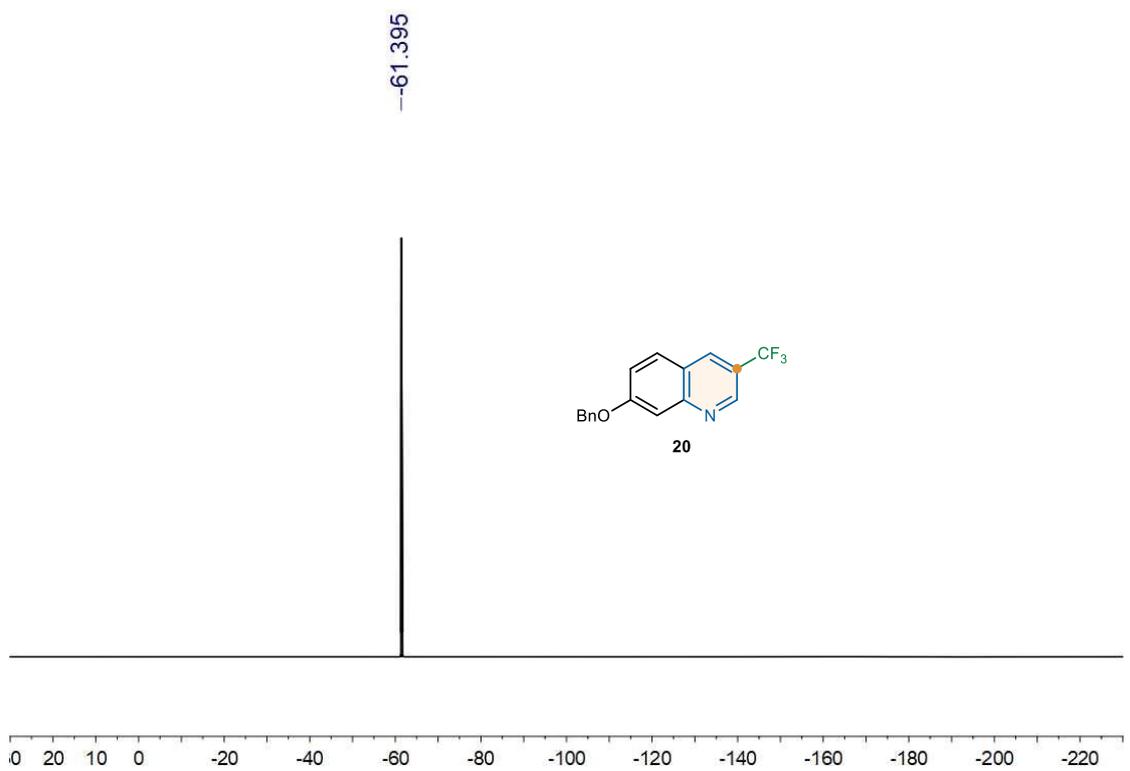
Supplementary Fig. 71.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ) spectrum of **19**



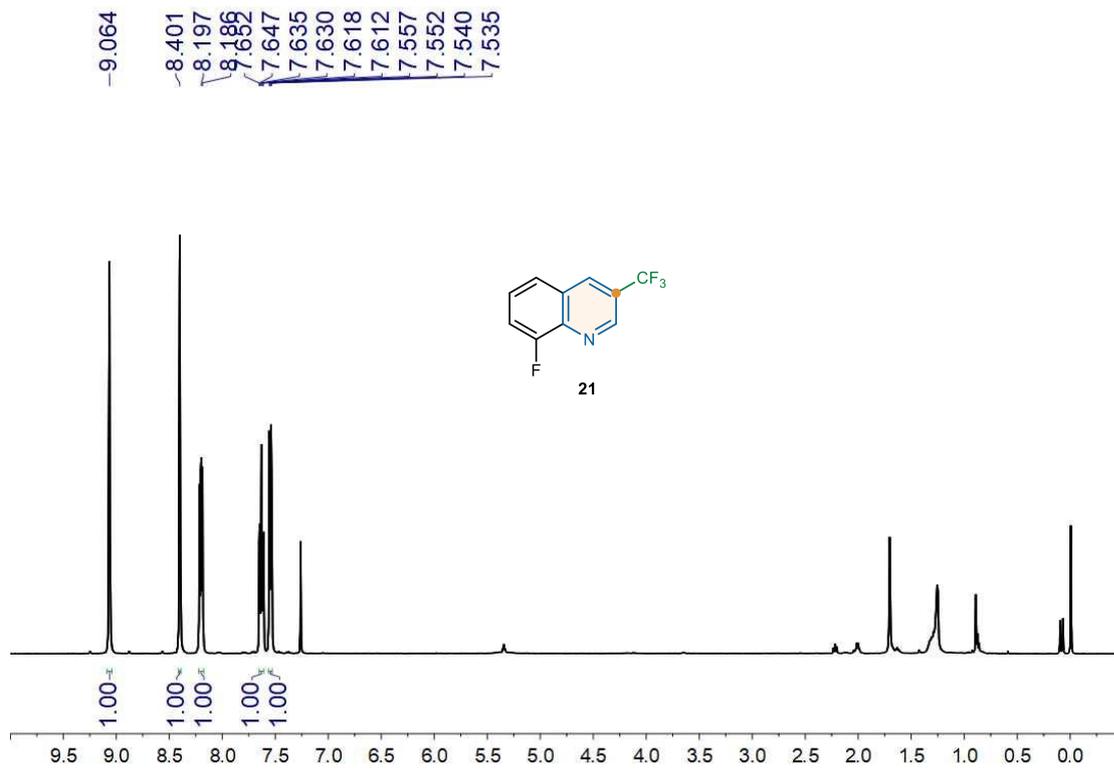
Supplementary Fig. 72.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **20**



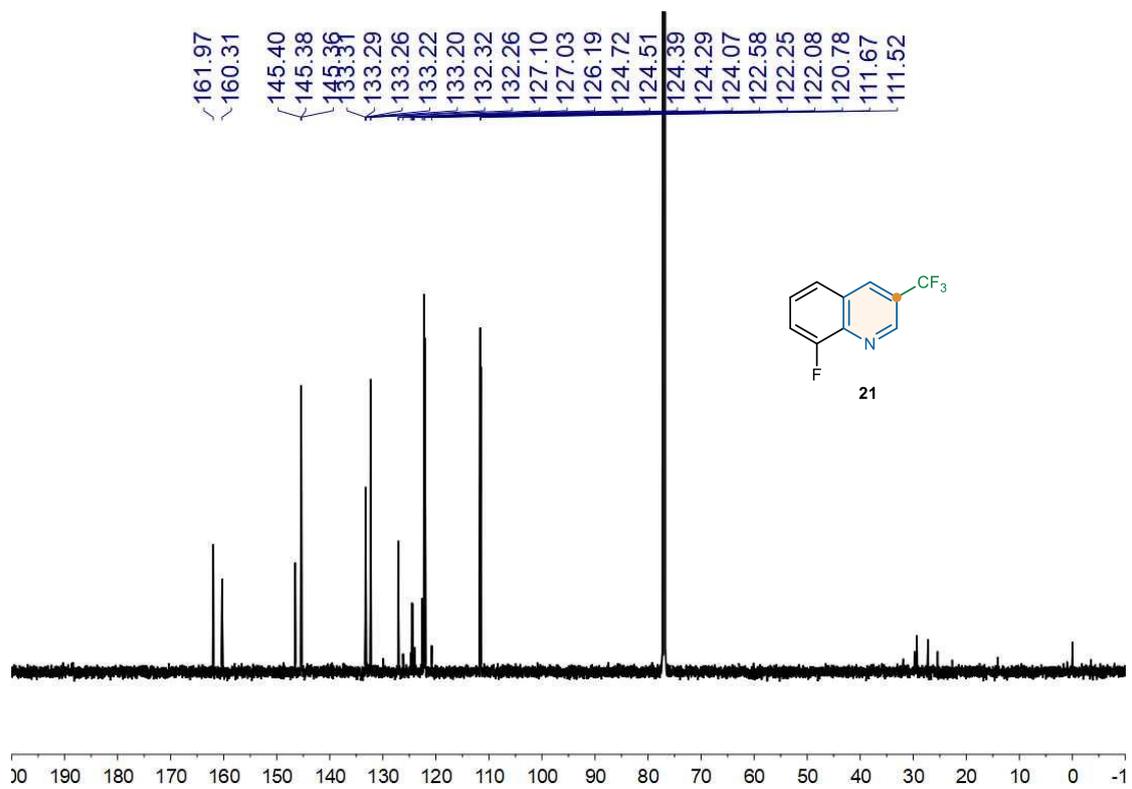
Supplementary Fig. 73. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of **20**



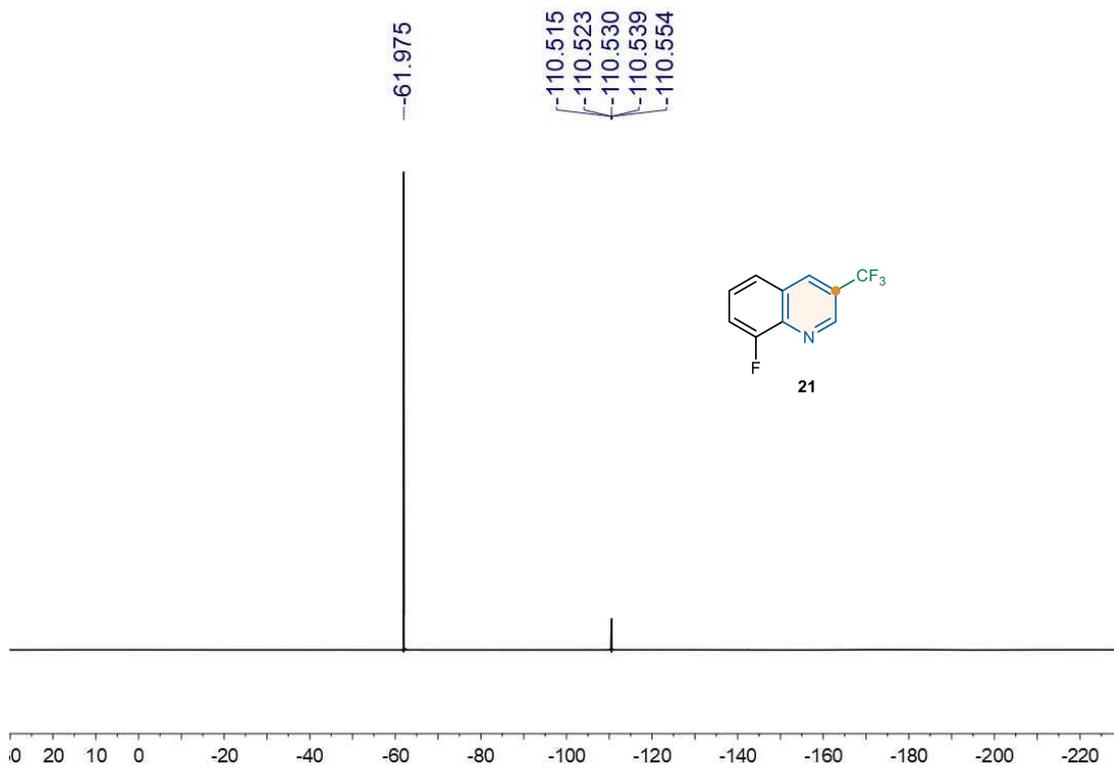
Supplementary Fig. 74. <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) spectrum of **20**



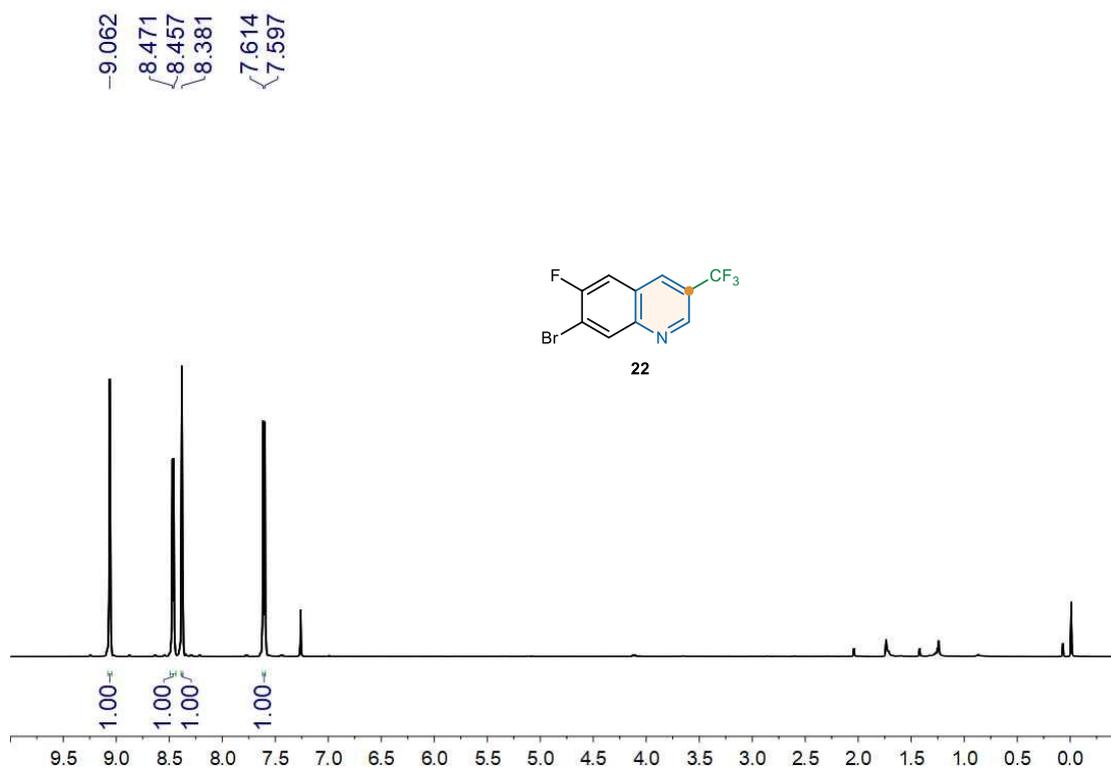
Supplementary Fig. 75.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **21**



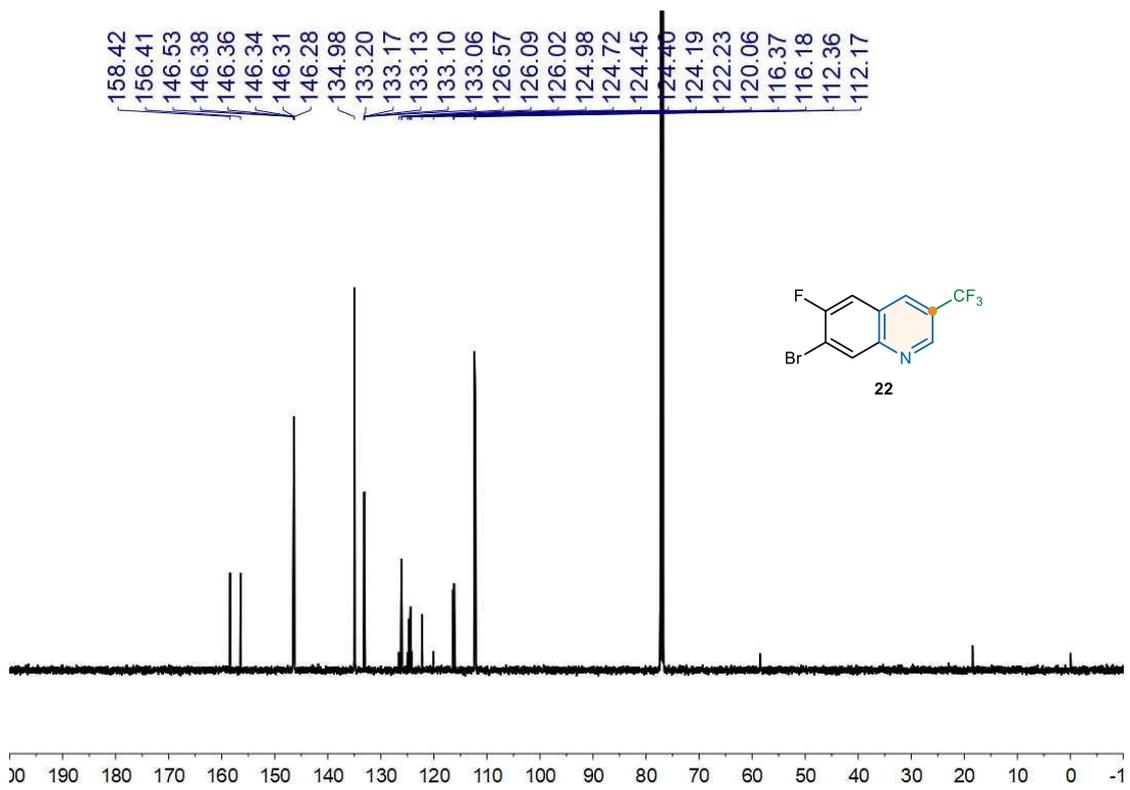
Supplementary Fig. 76.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **21**



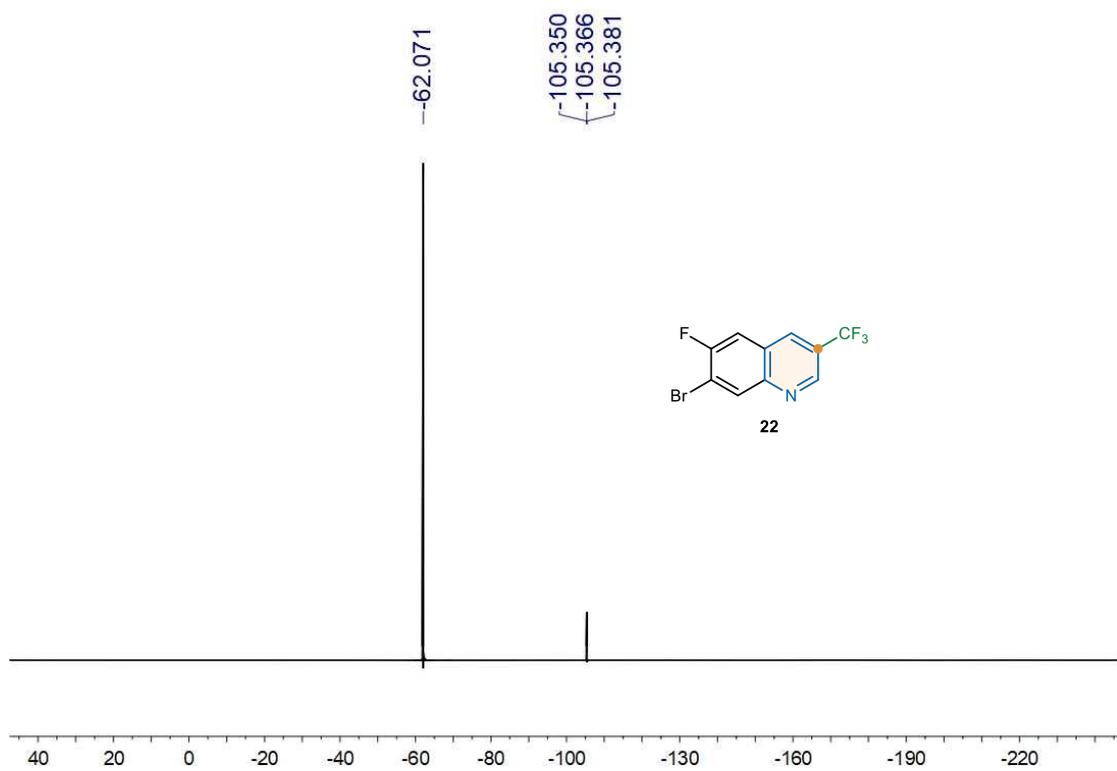
Supplementary Fig. 77.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ) spectrum of **21**



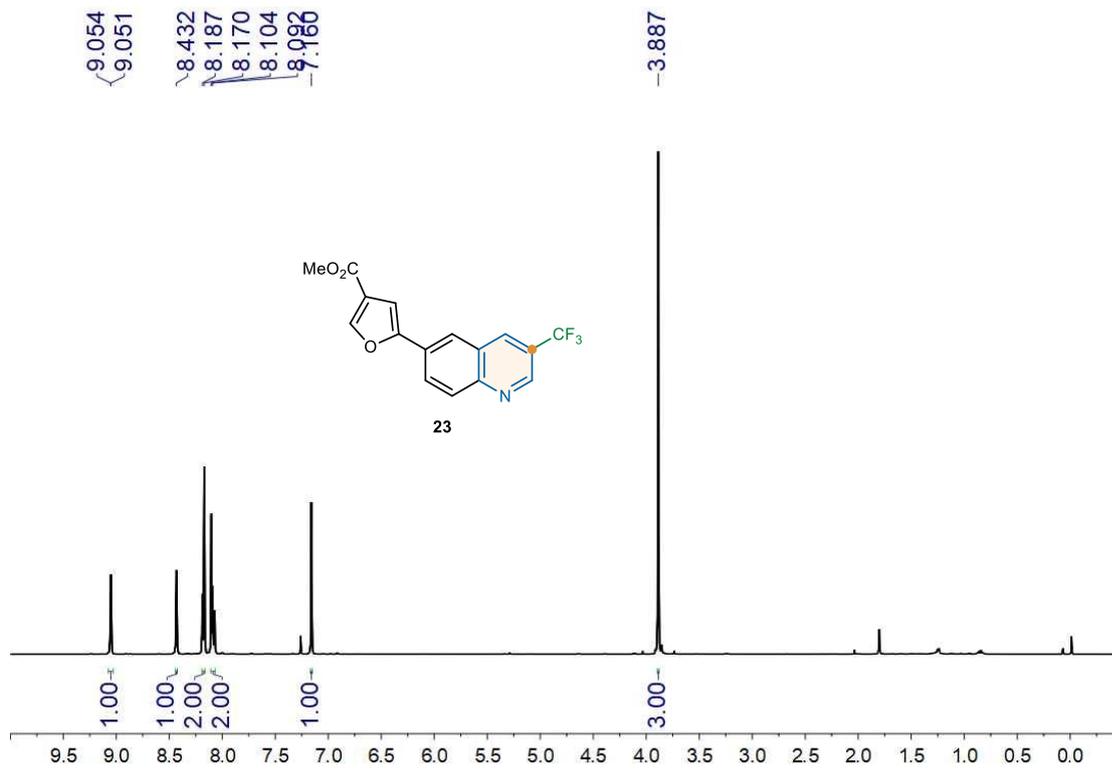
Supplementary Fig. 78.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **22**



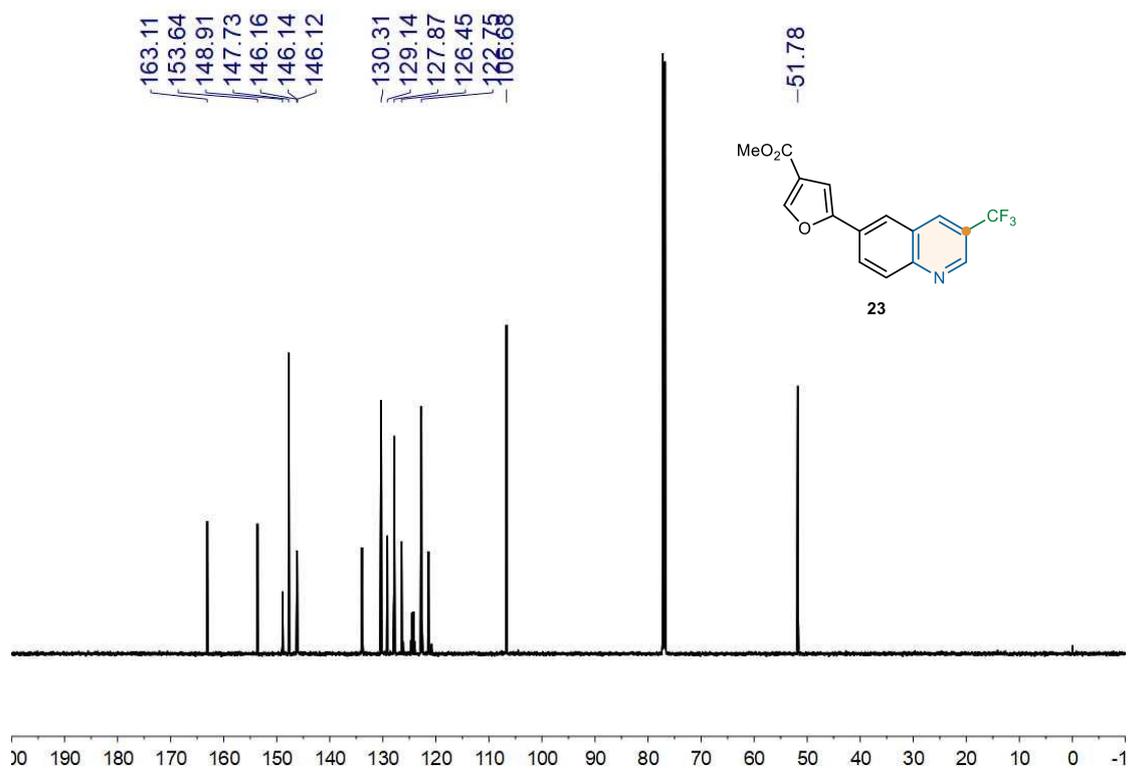
Supplementary Fig. 79.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of **22**



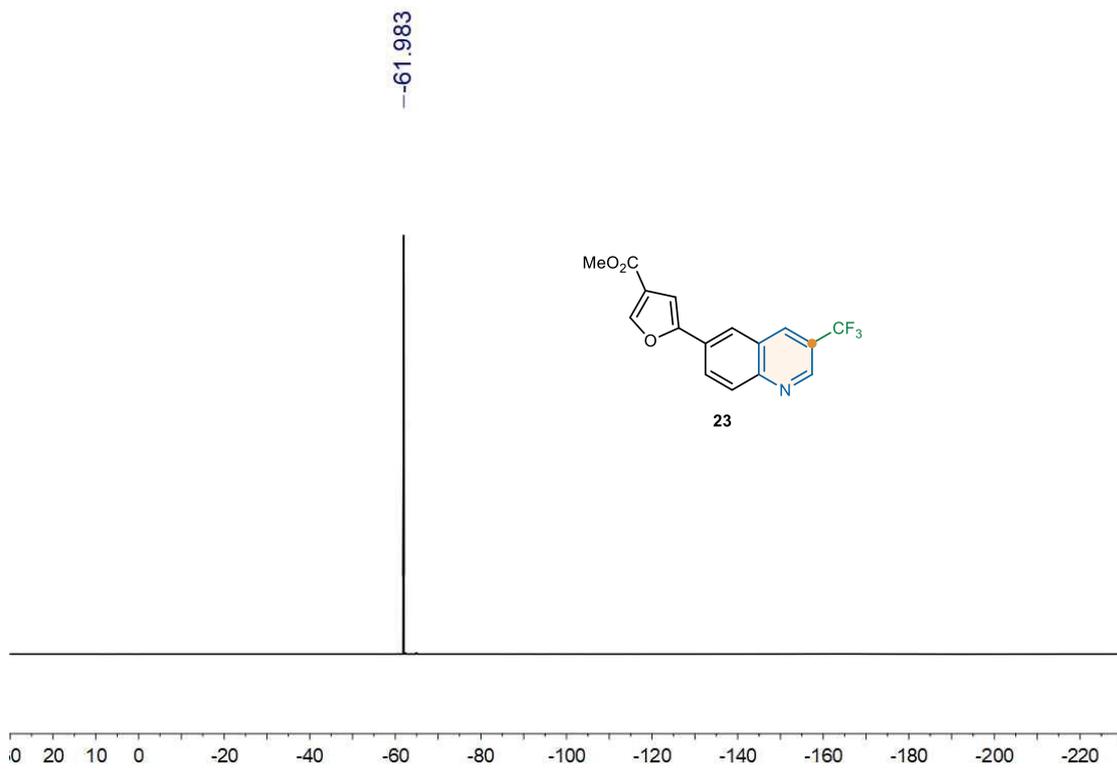
Supplementary Fig. 80.  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ) spectrum of **22**



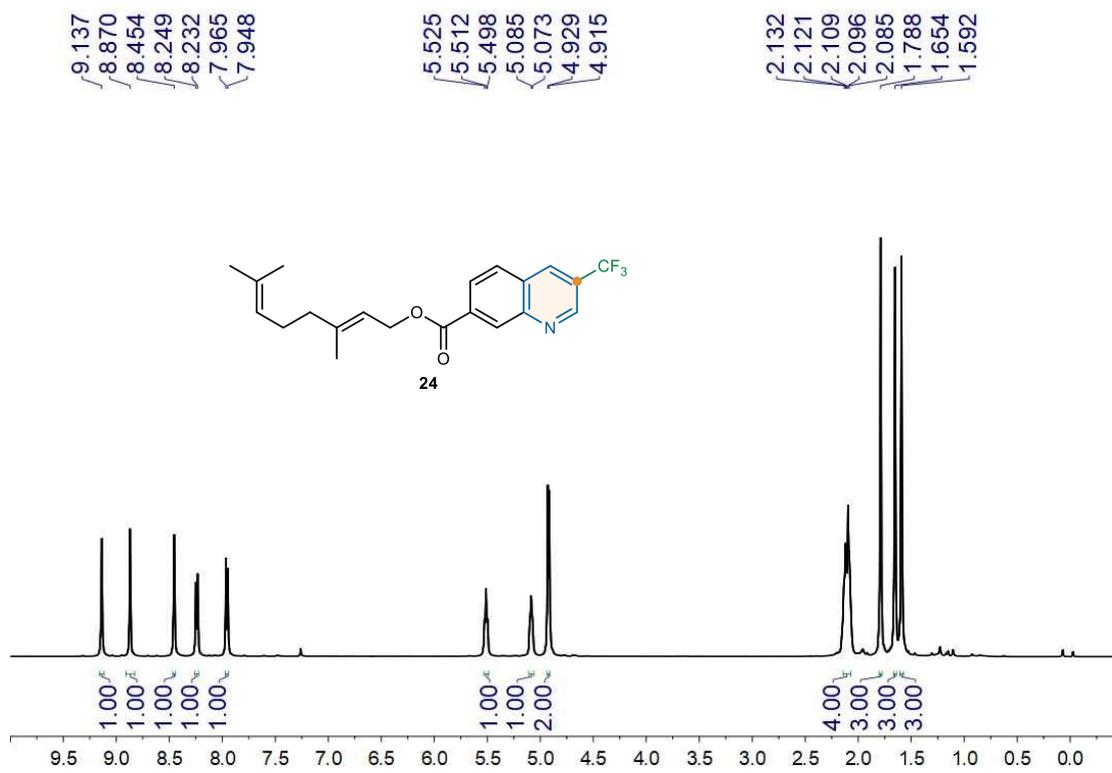
Supplementary Fig. 81. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **23**



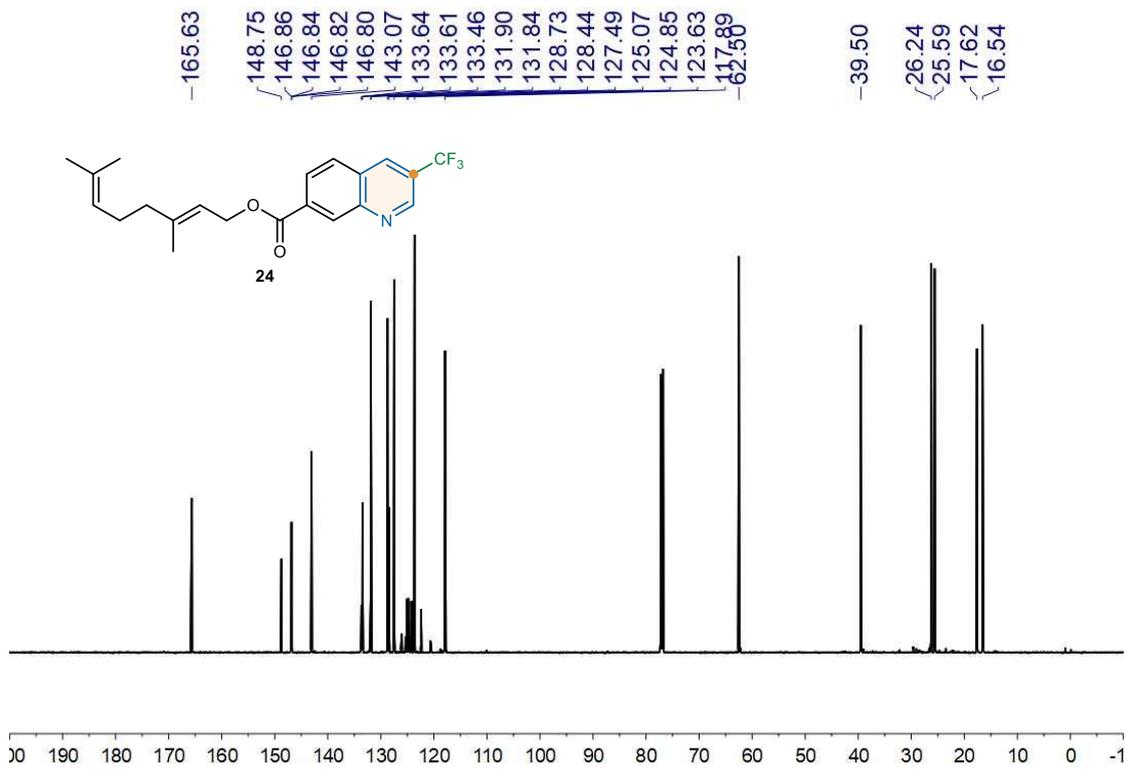
Supplementary Fig. 82. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of **23**



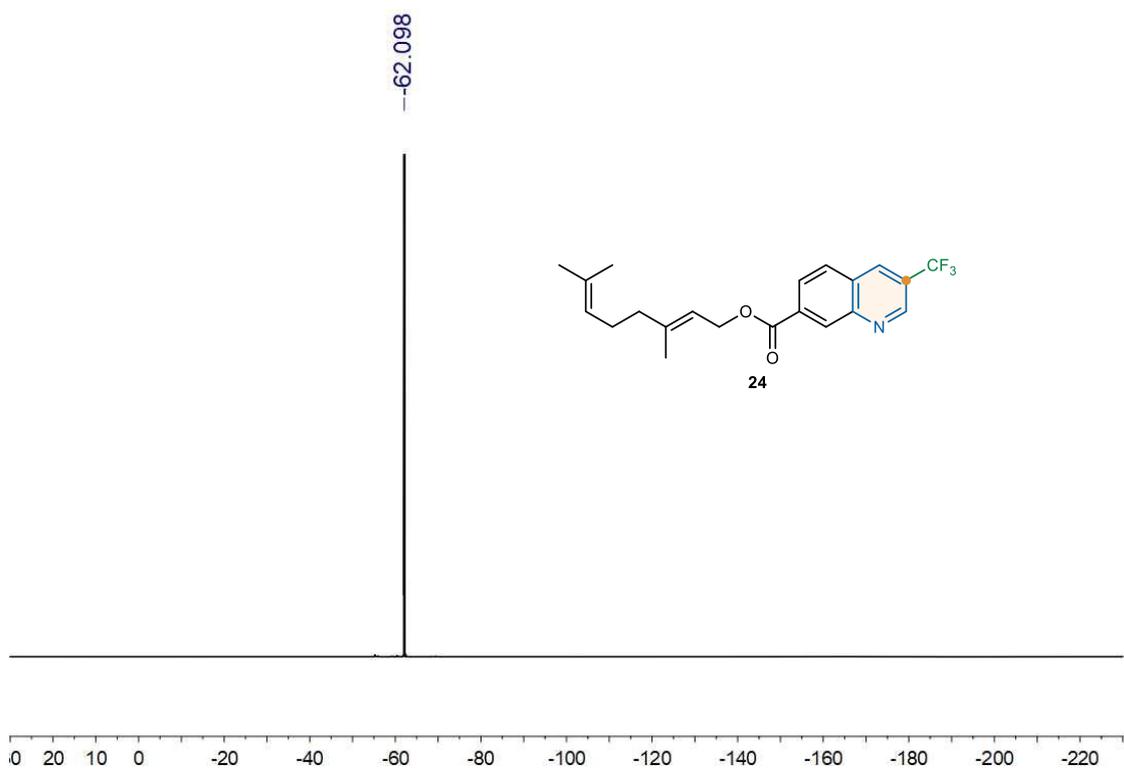
Supplementary Fig. 83.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ) spectrum of **23**



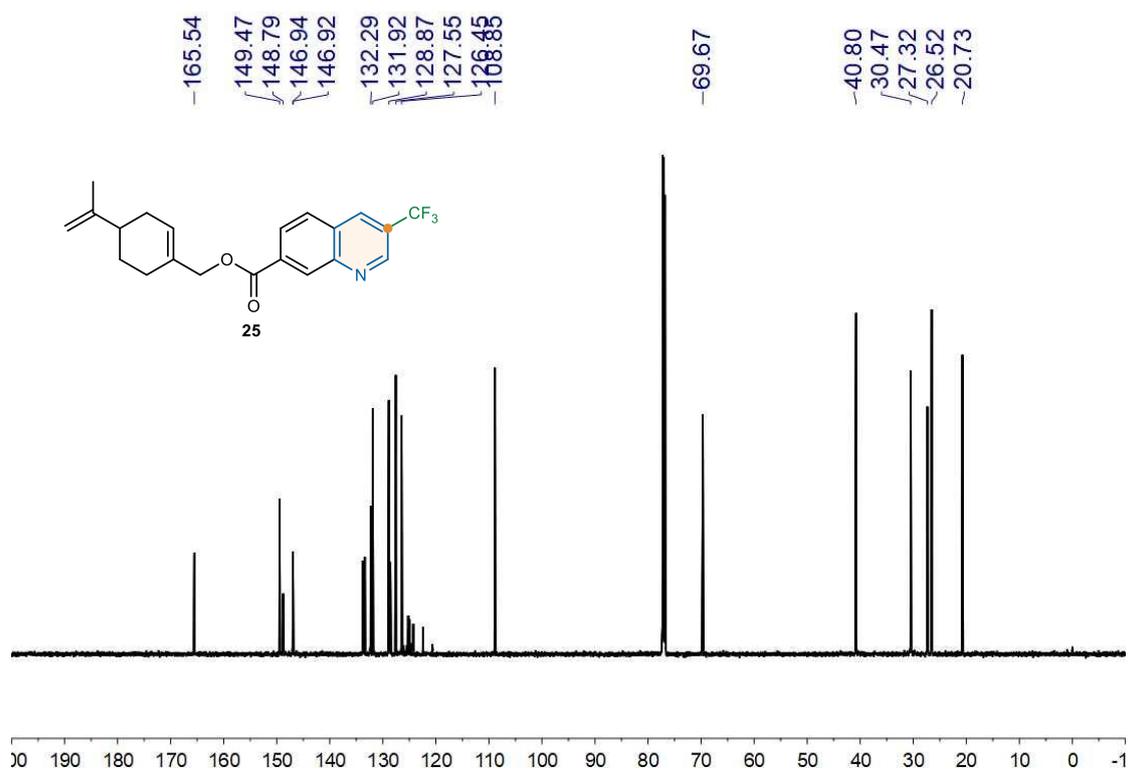
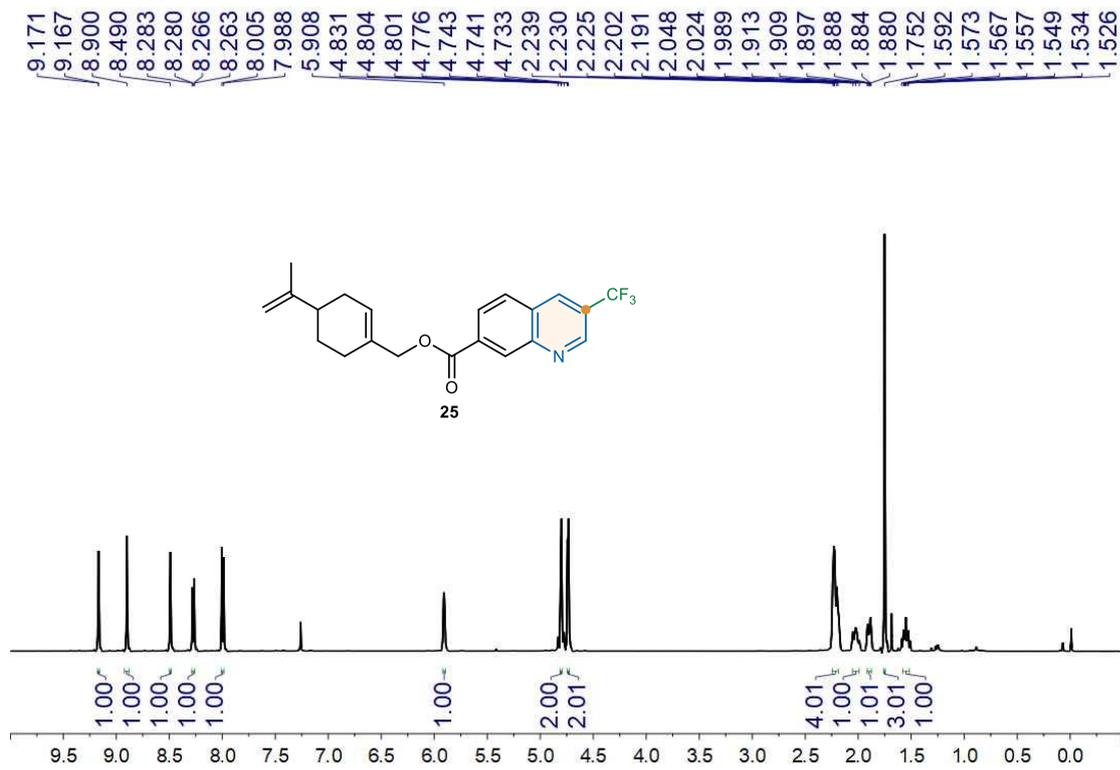
Supplementary Fig. 84.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **24**

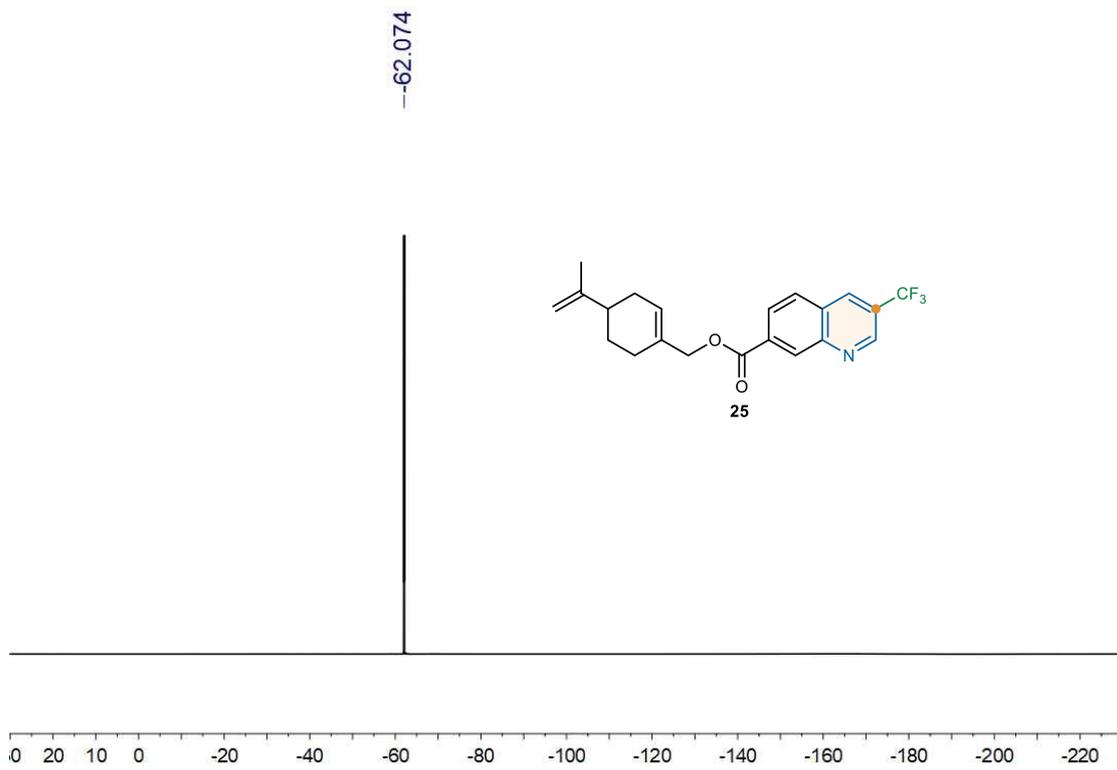


Supplementary Fig. 85. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of 24

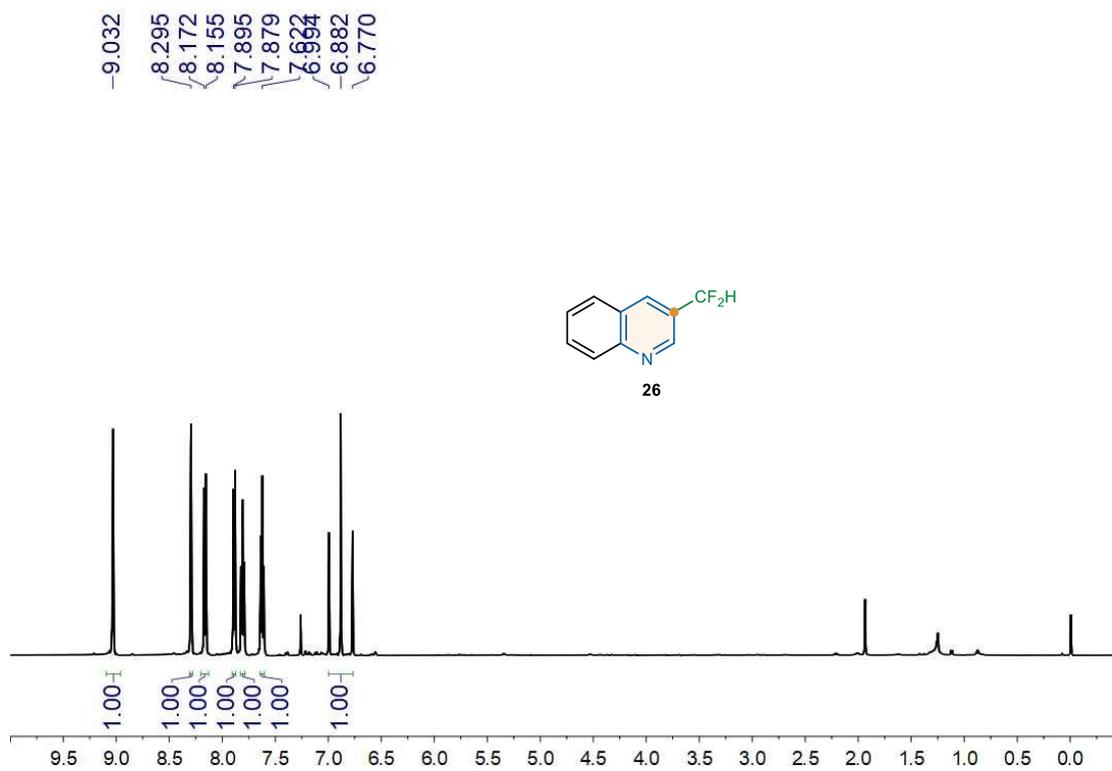


Supplementary Fig. 86. <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) spectrum of 24

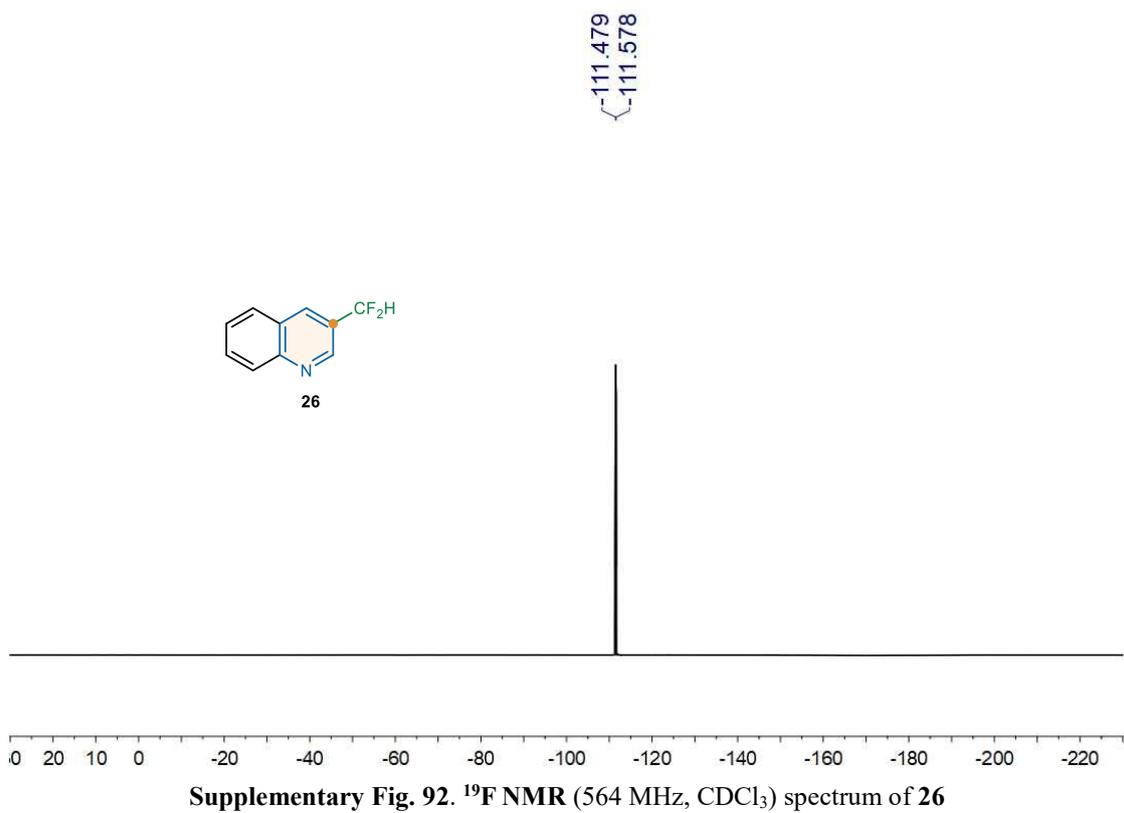
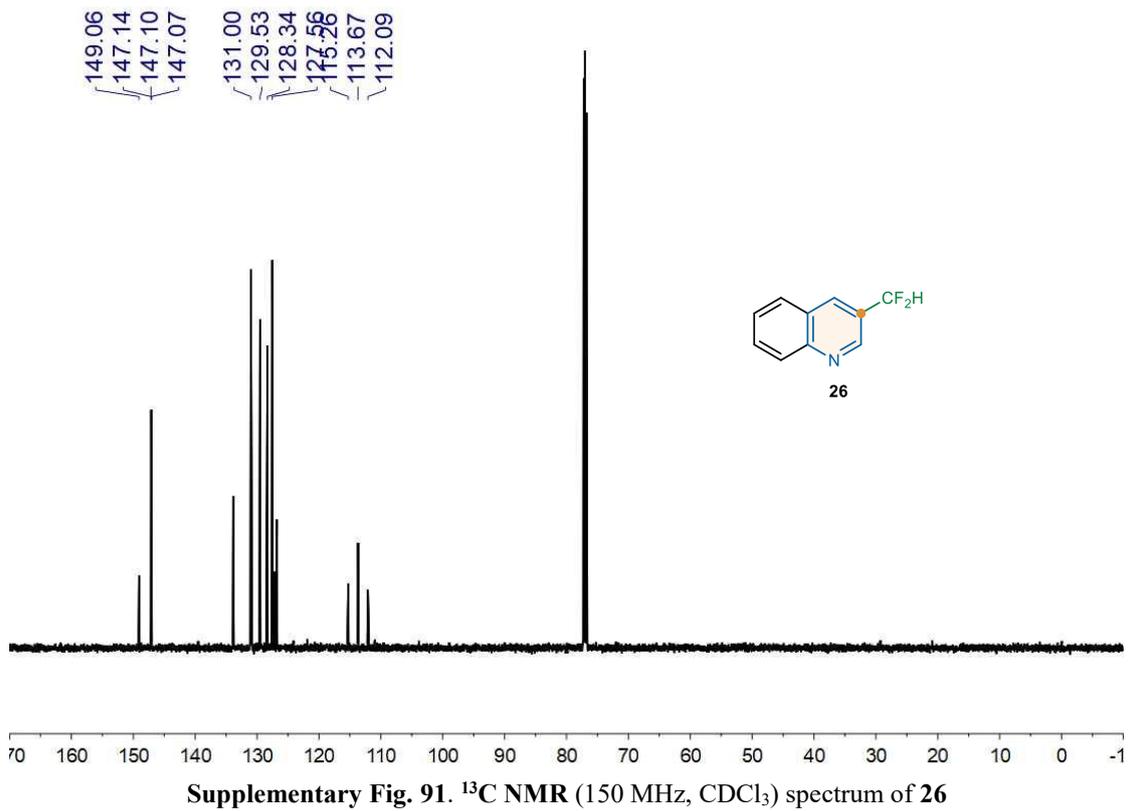


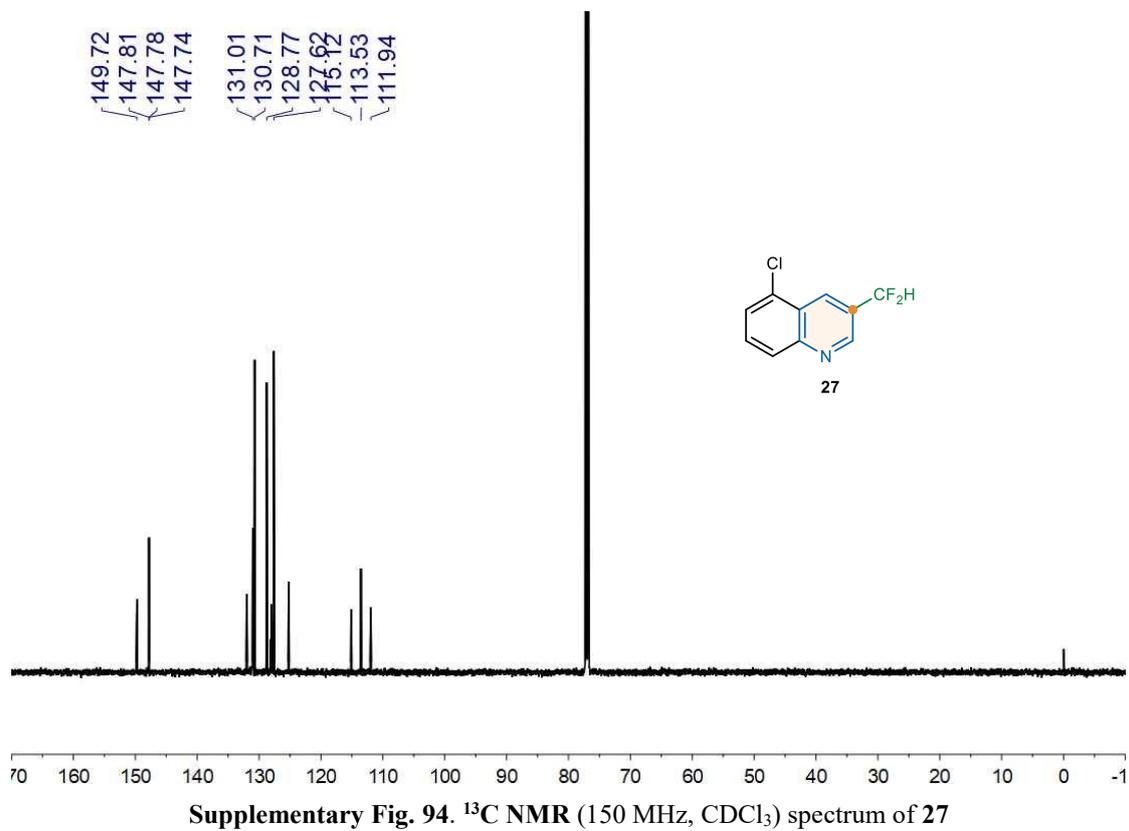
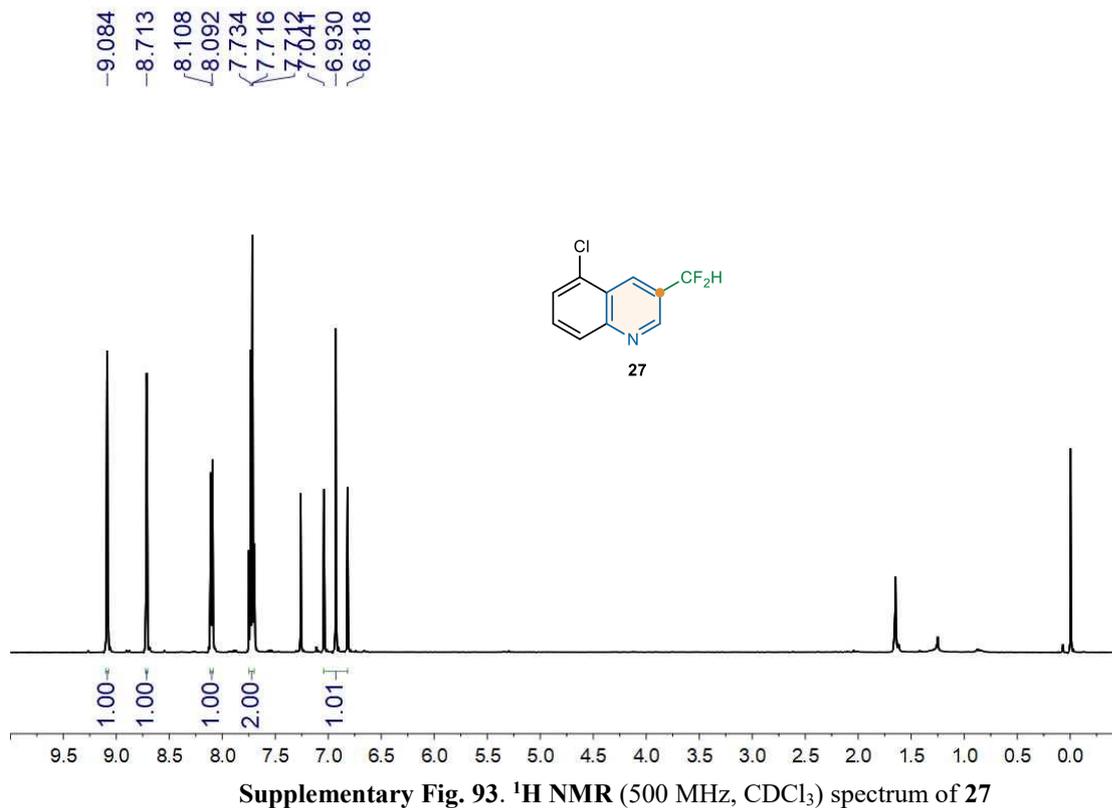


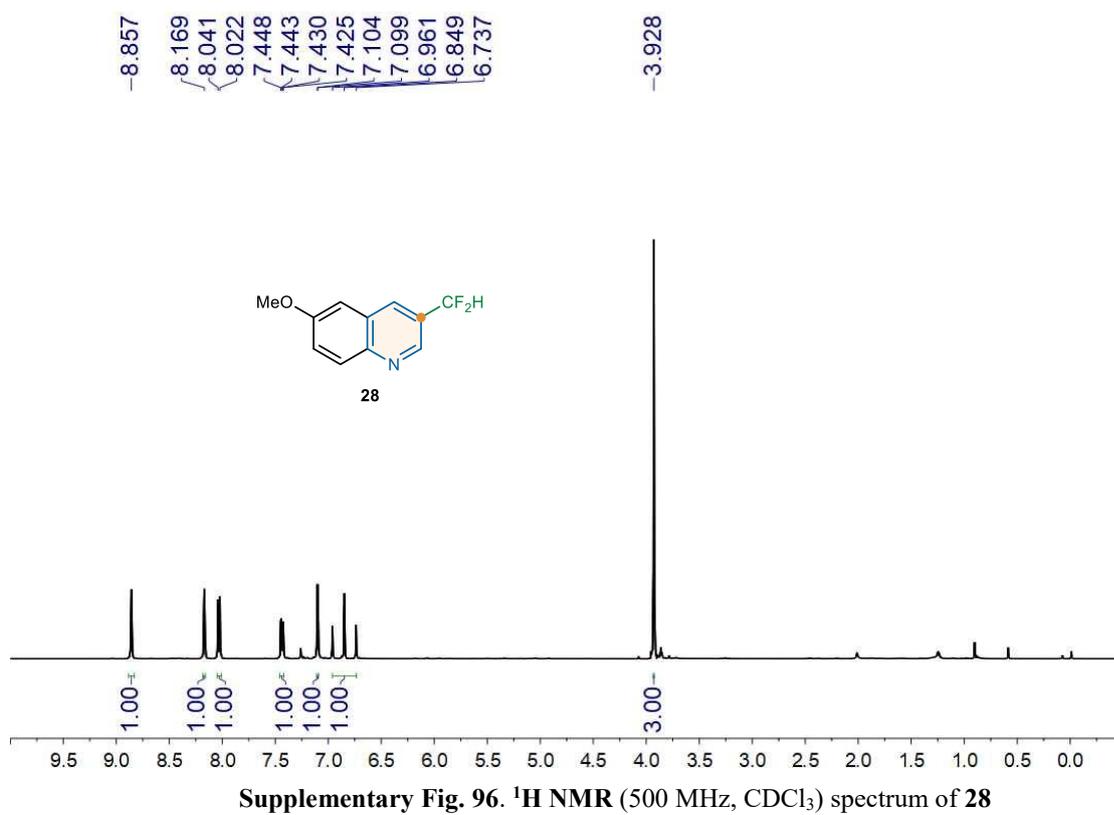
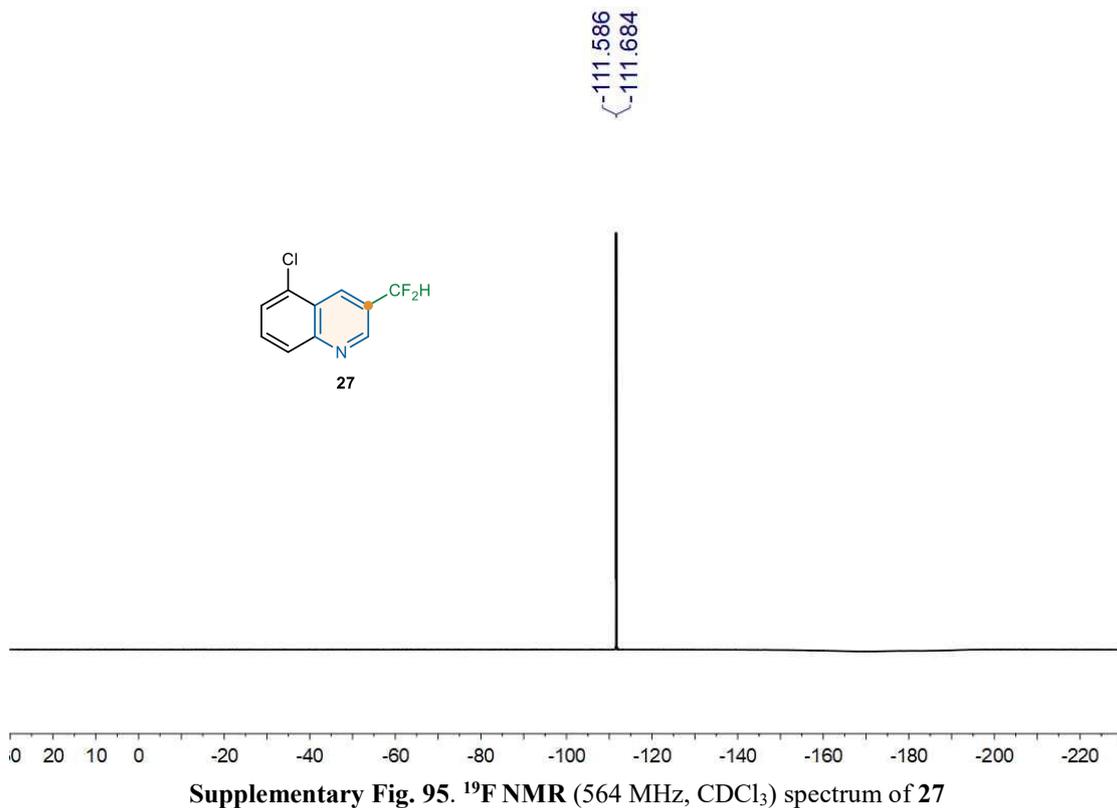
Supplementary Fig. 89.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ) spectrum of 25

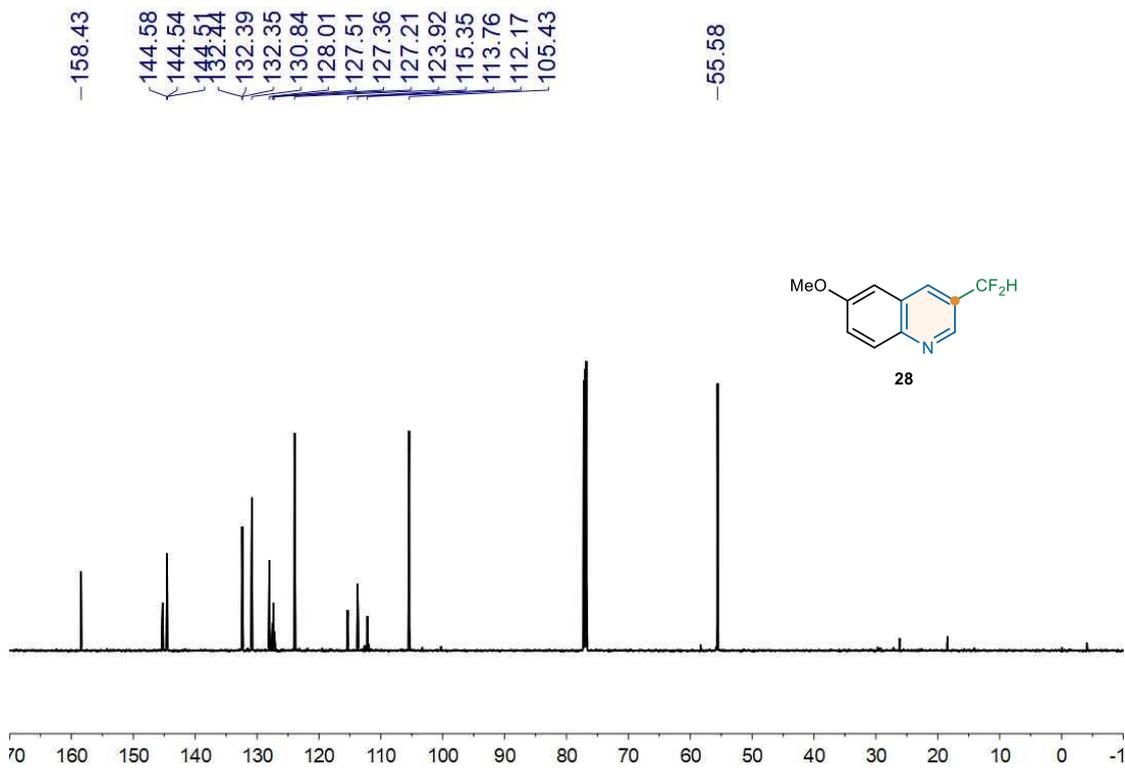


Supplementary Fig. 90.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of 26

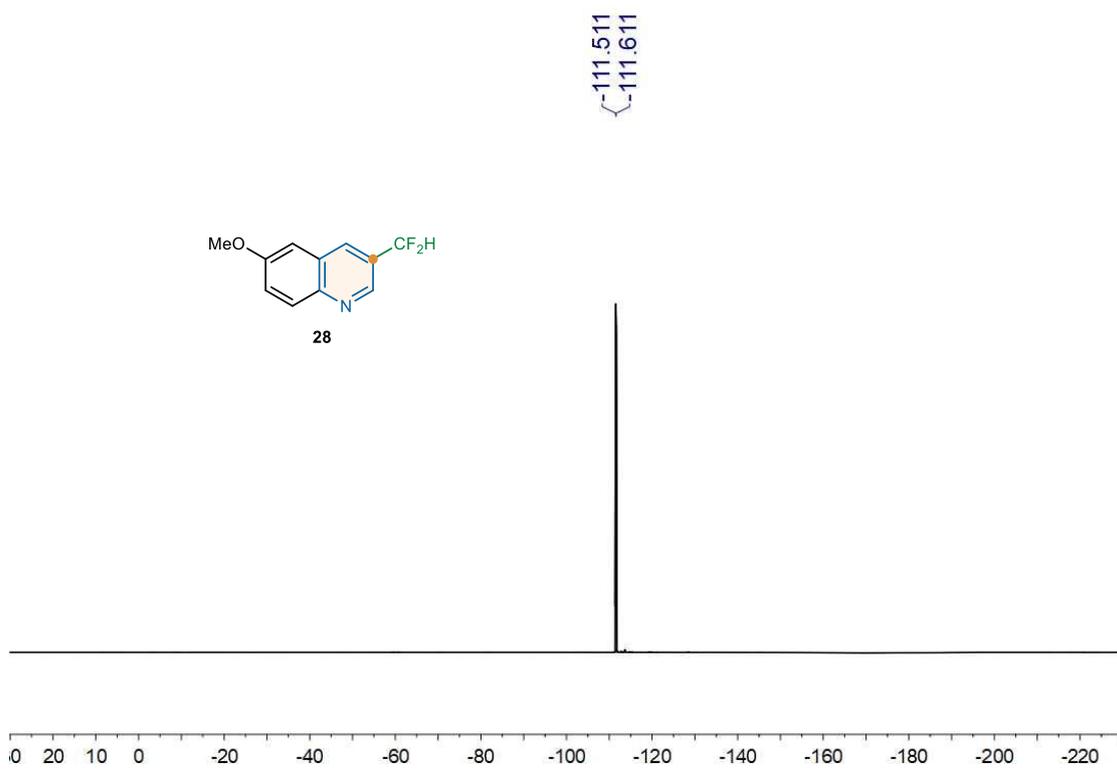




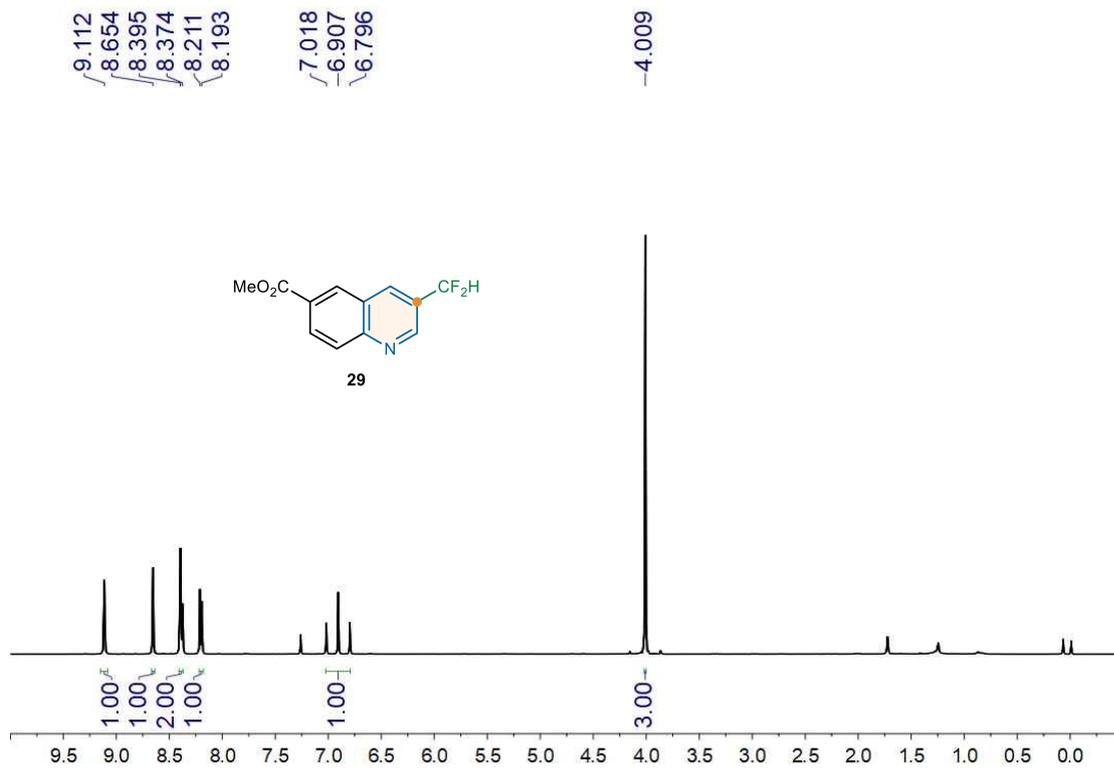




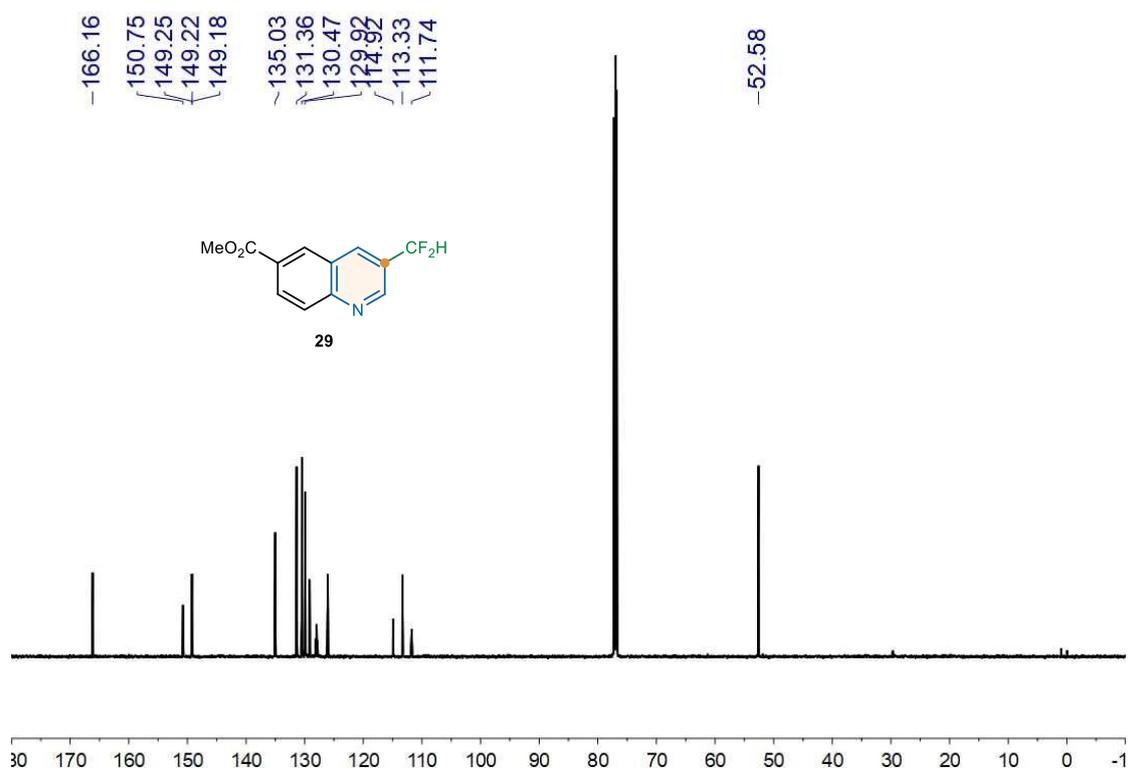
Supplementary Fig. 97.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **28**



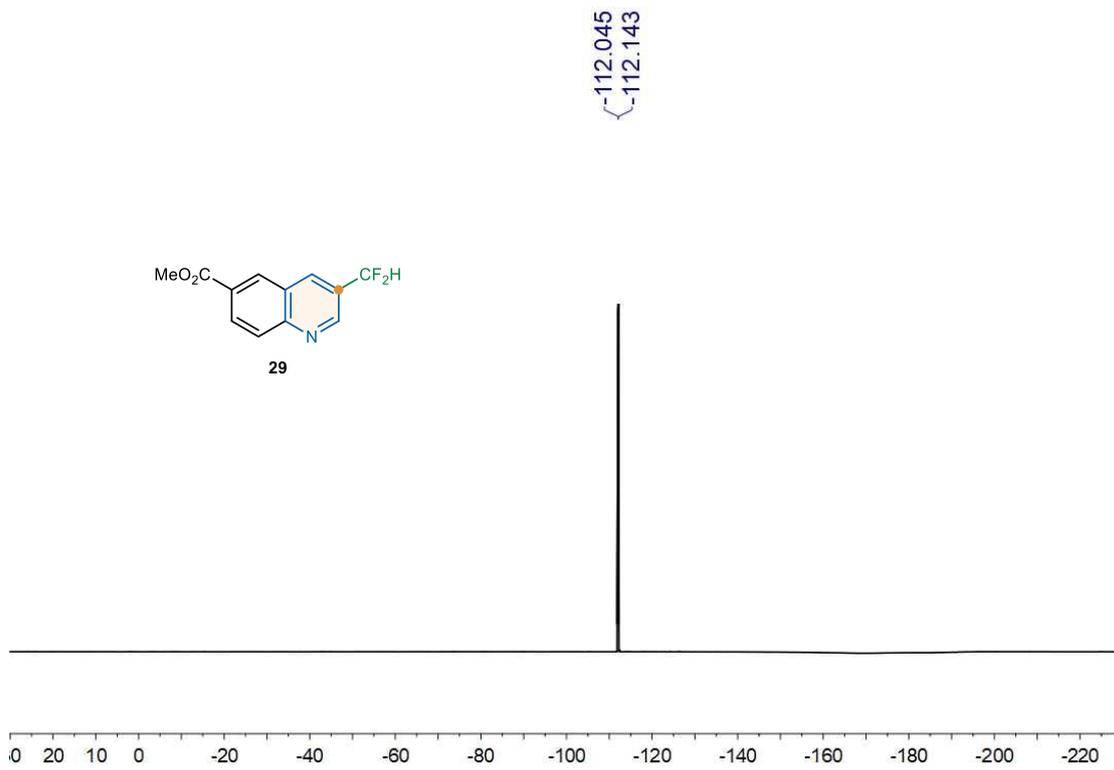
Supplementary Fig. 98.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ) spectrum of **28**



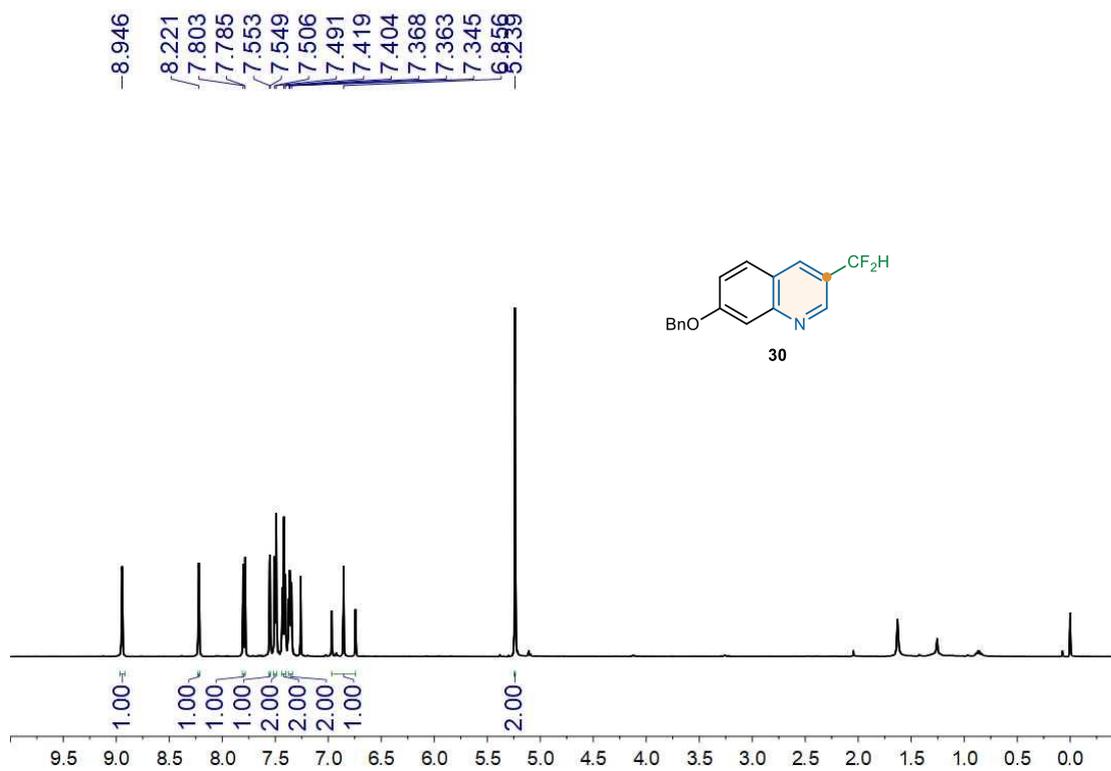
Supplementary Fig. 99. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **29**



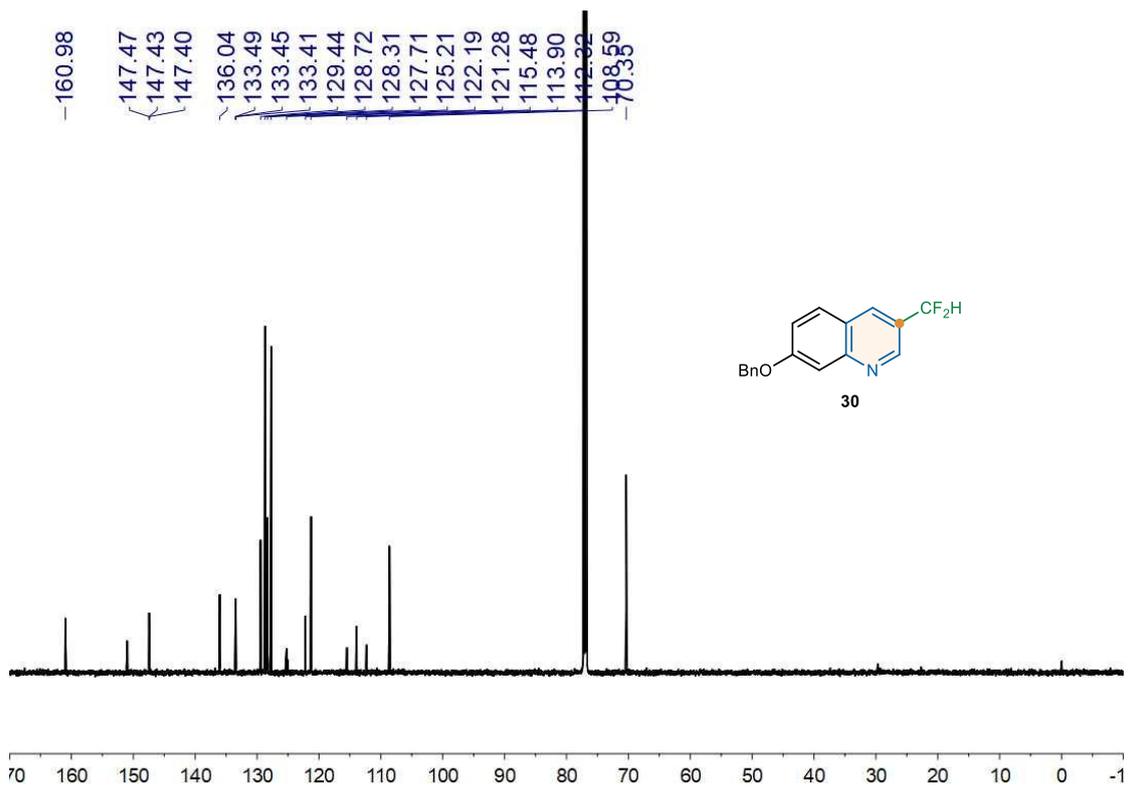
Supplementary Fig. 100. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of **29**



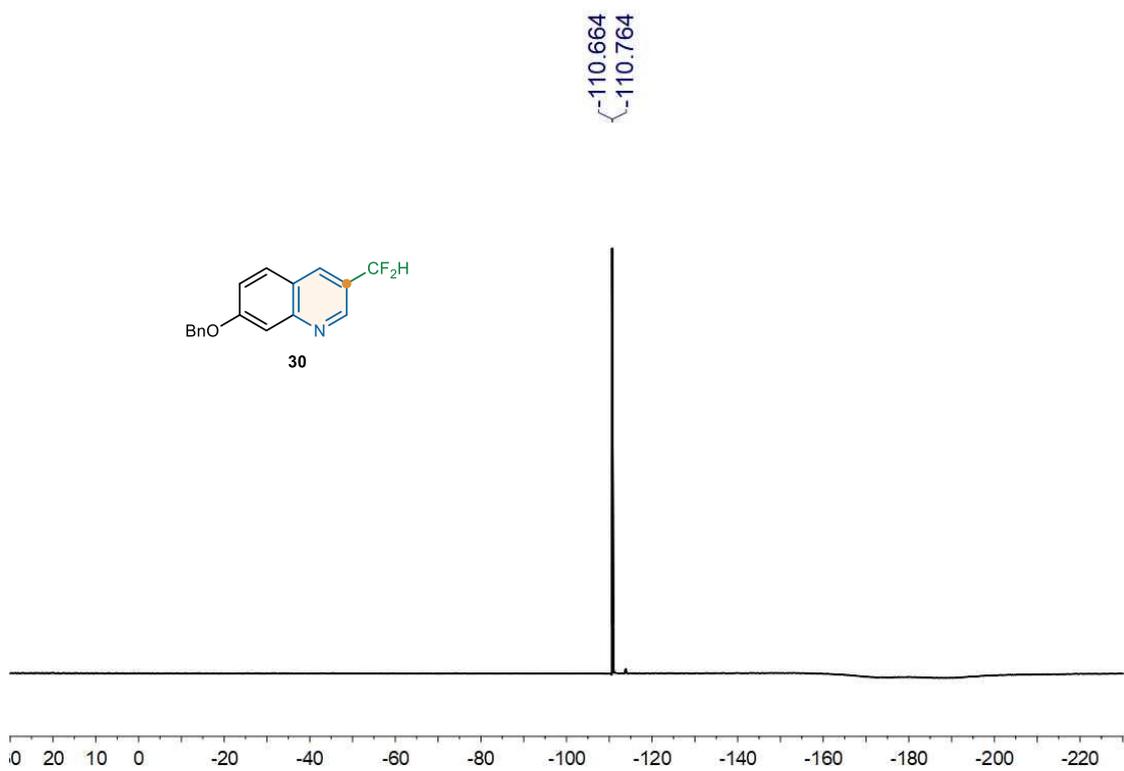
Supplementary Fig. 101.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ) spectrum of **29**



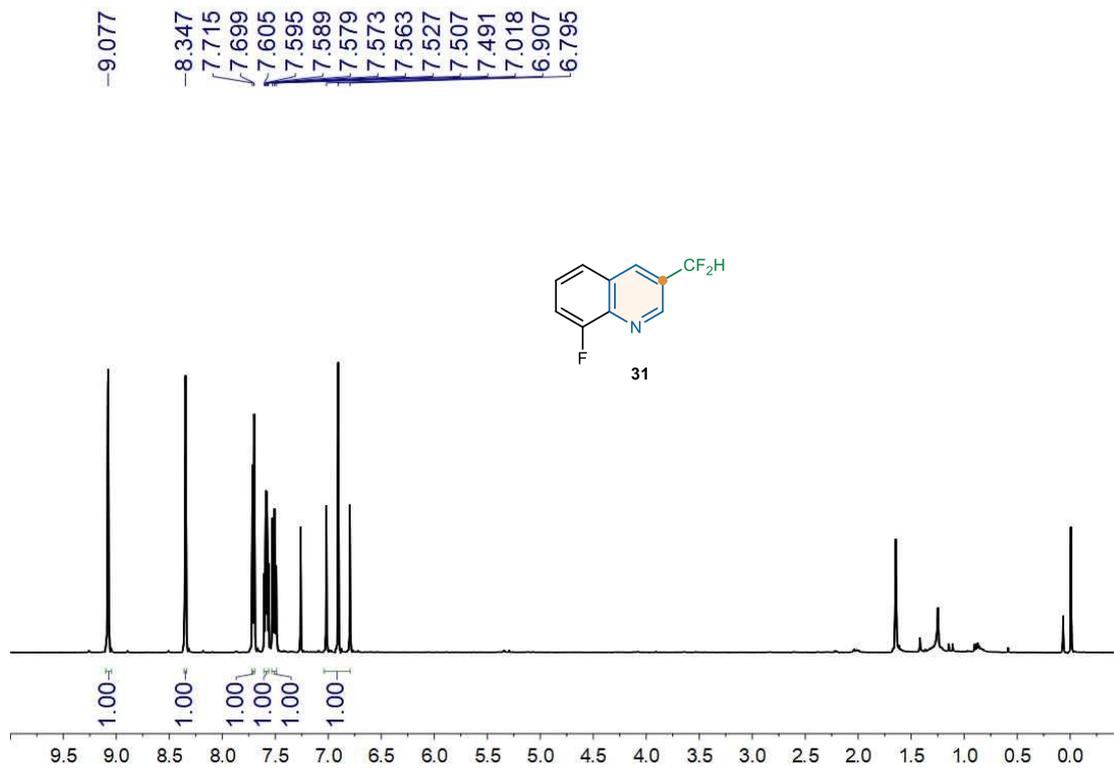
Supplementary Fig. 102.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **30**



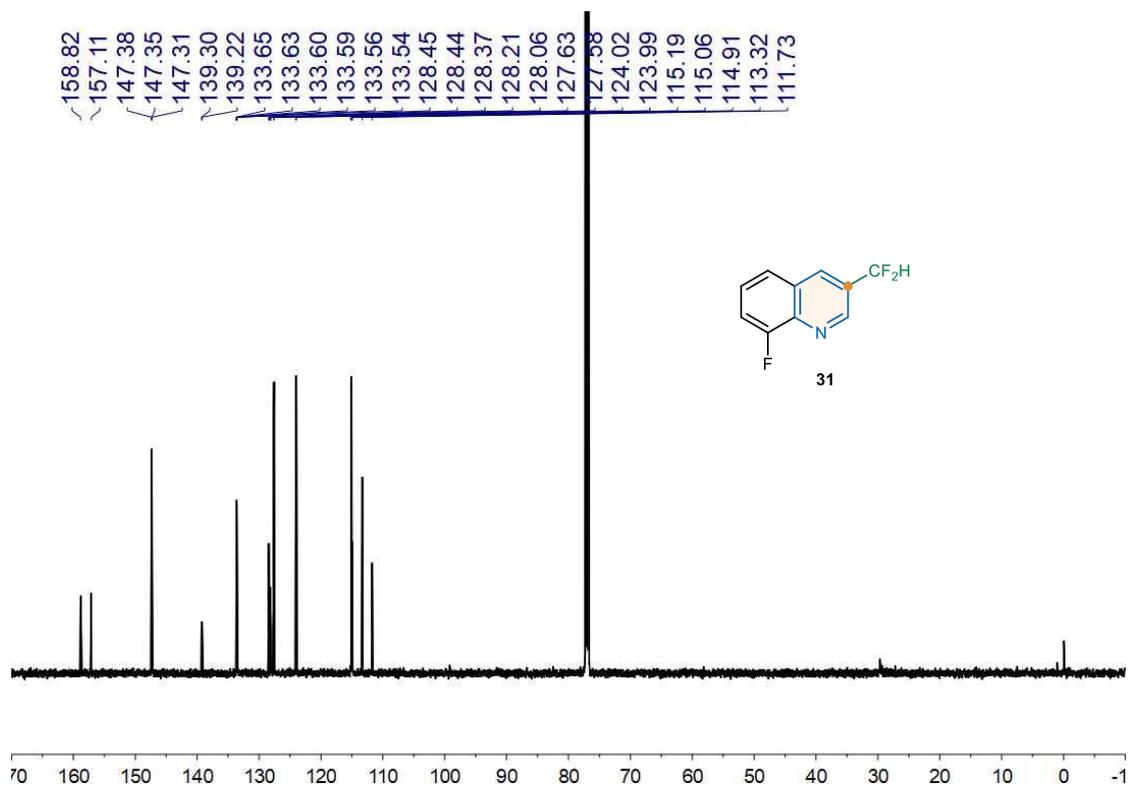
Supplementary Fig. 103.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of 30



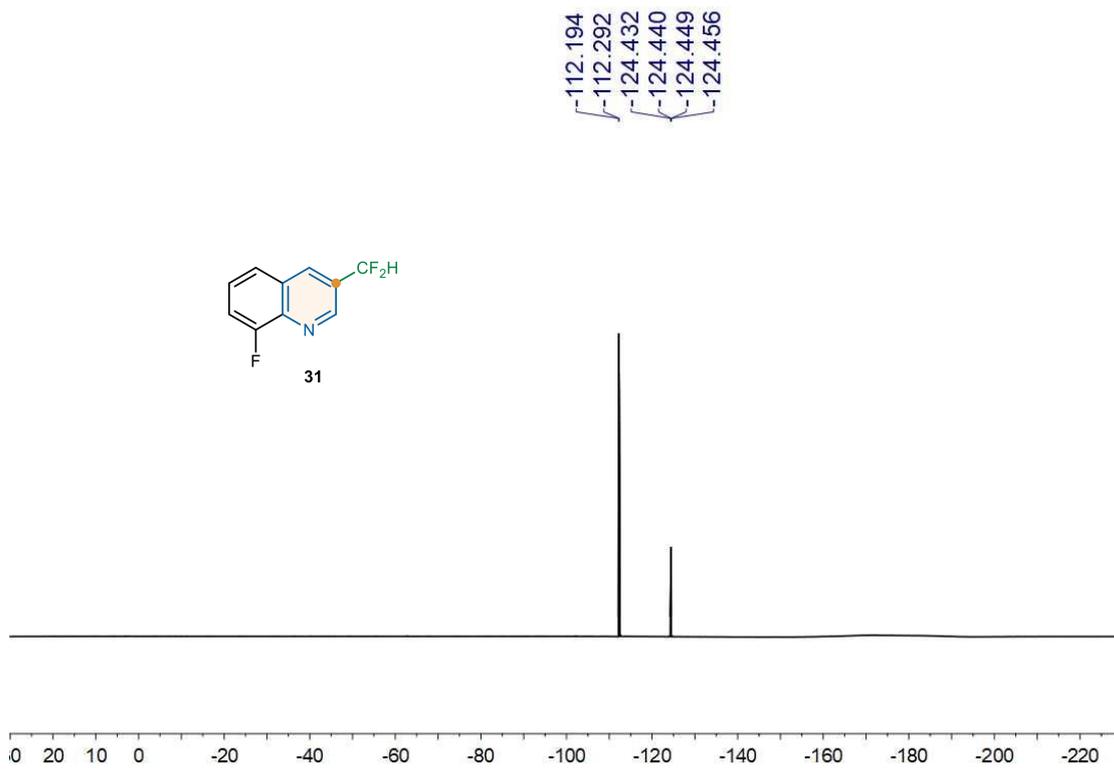
Supplementary Fig. 104.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ) spectrum of 30



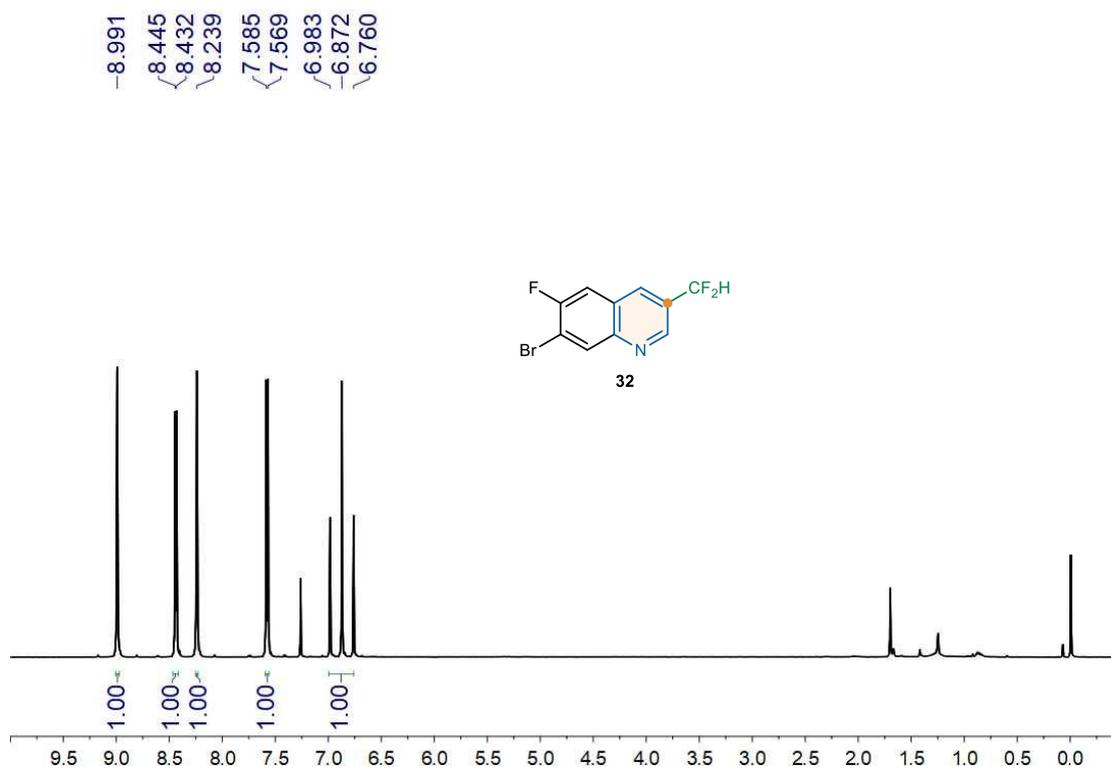
Supplementary Fig. 105. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of 31



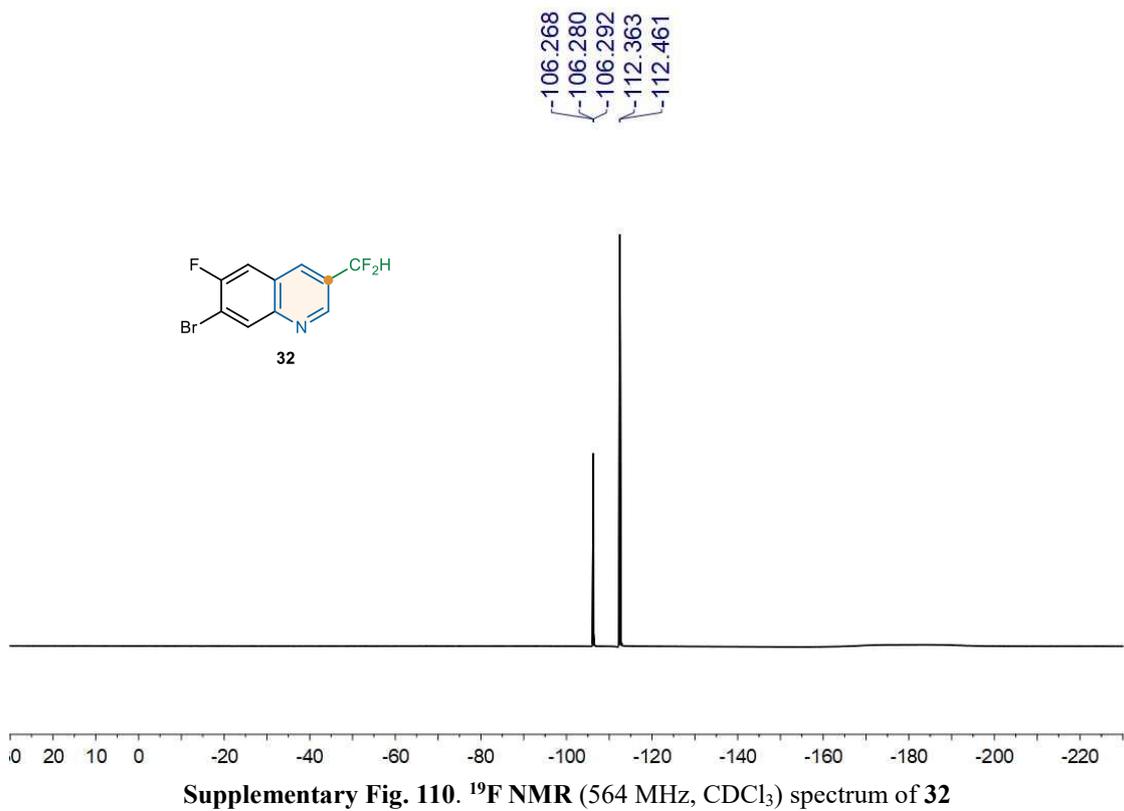
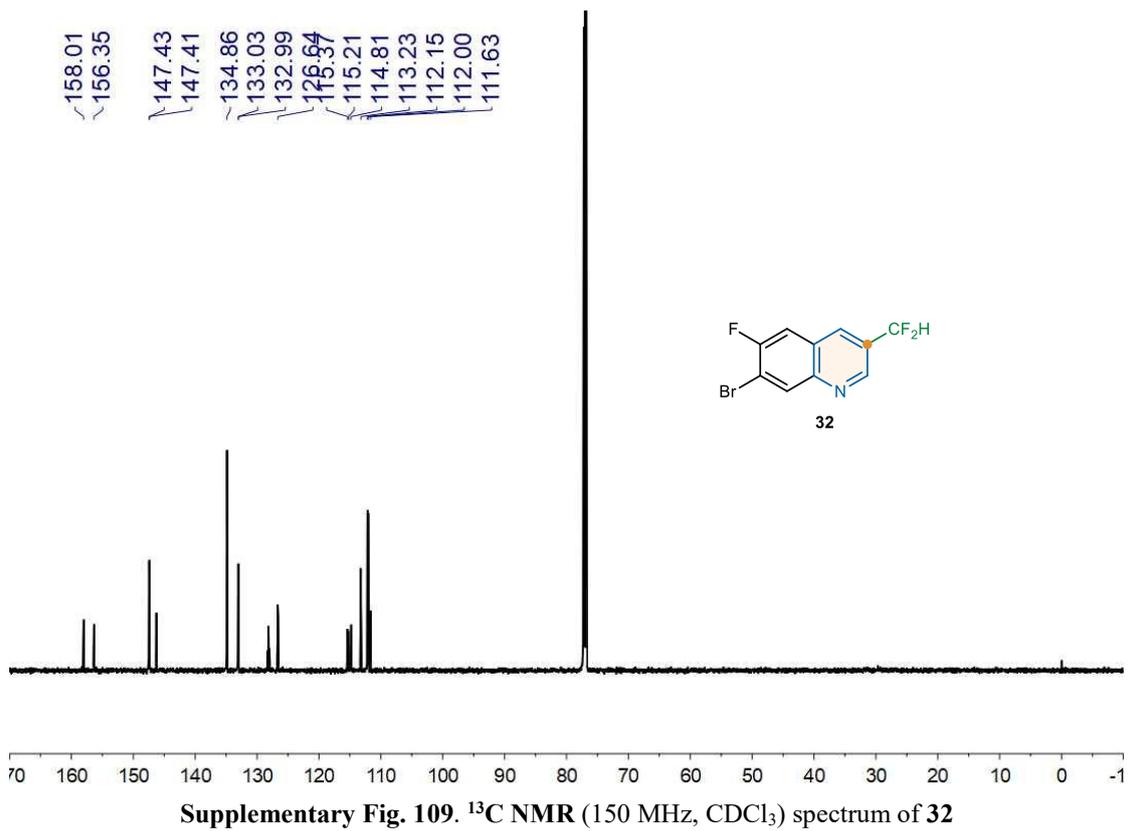
Supplementary Fig. 106. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of 31

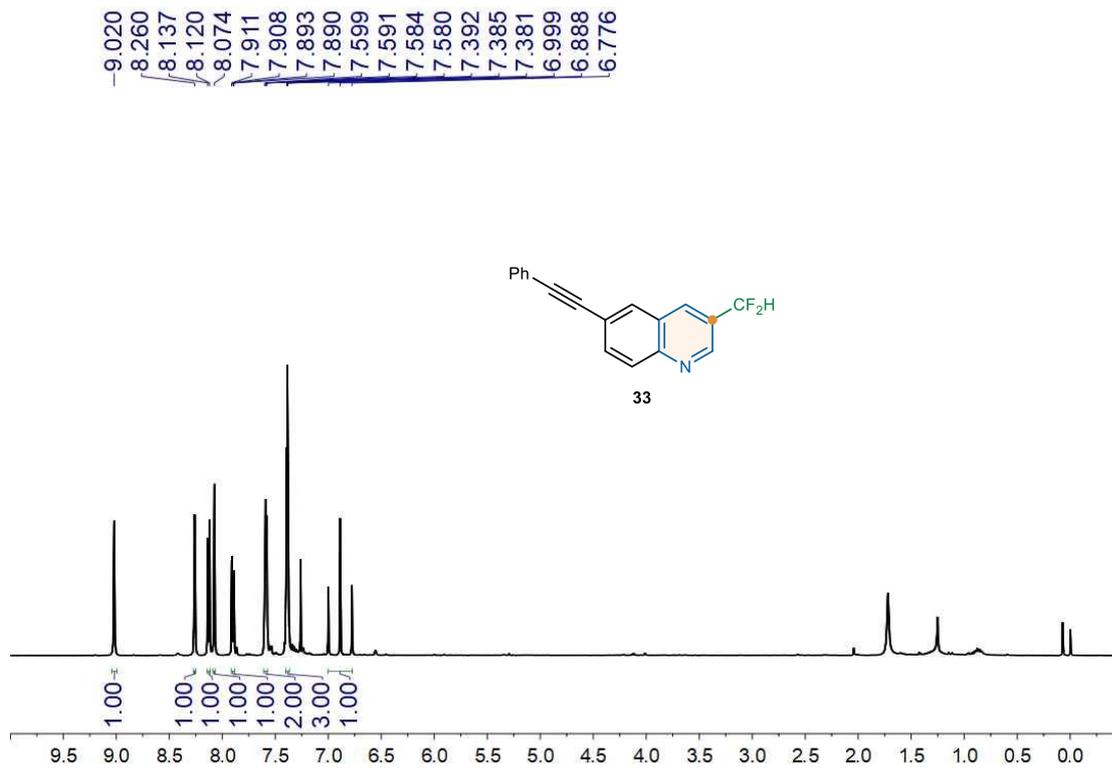


Supplementary Fig. 107.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ) spectrum of **31**

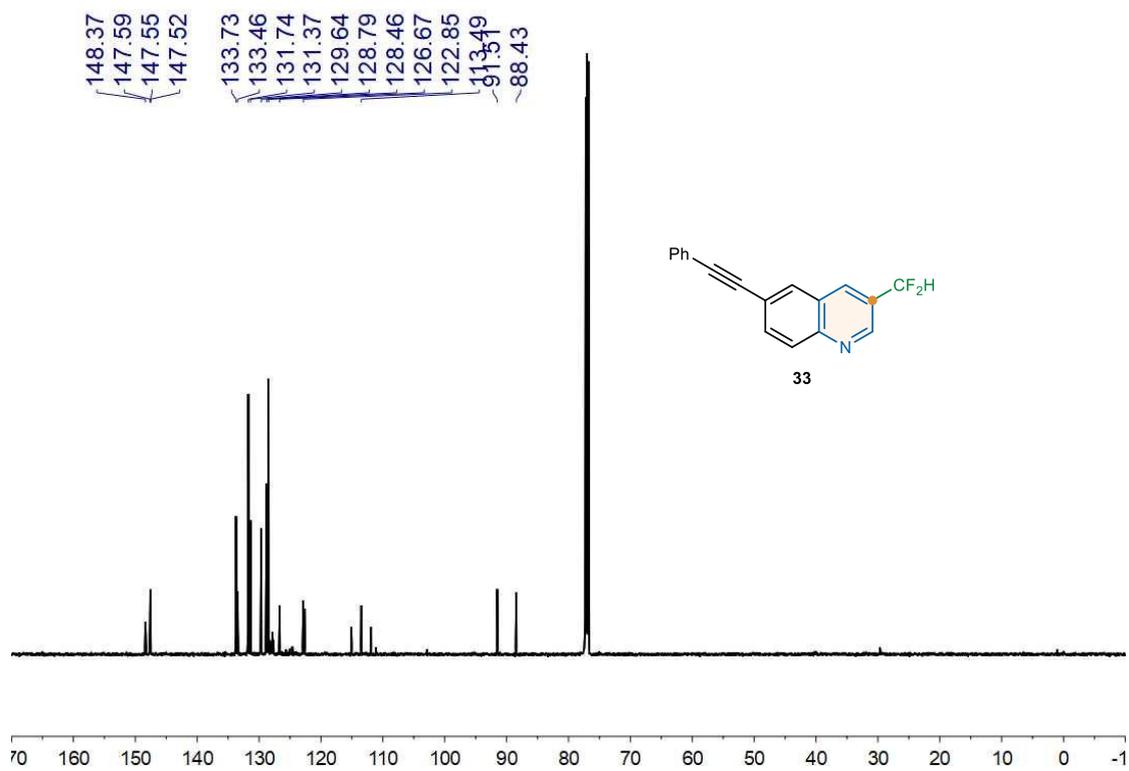


Supplementary Fig. 108.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **32**

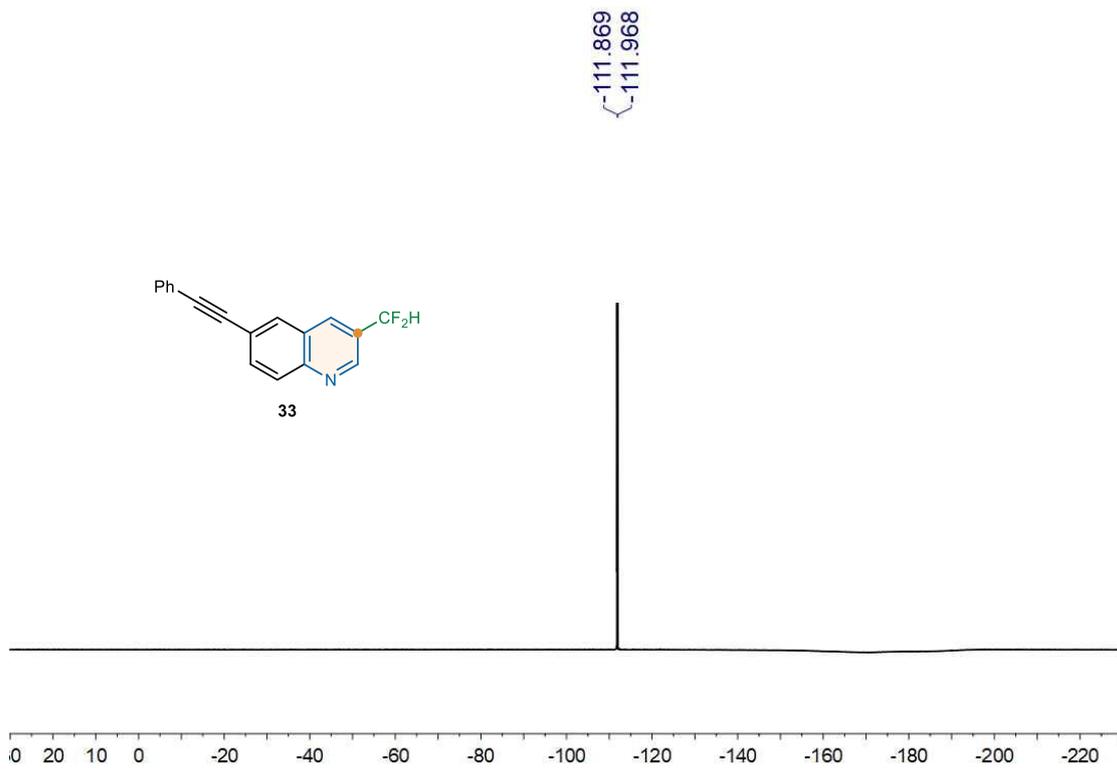




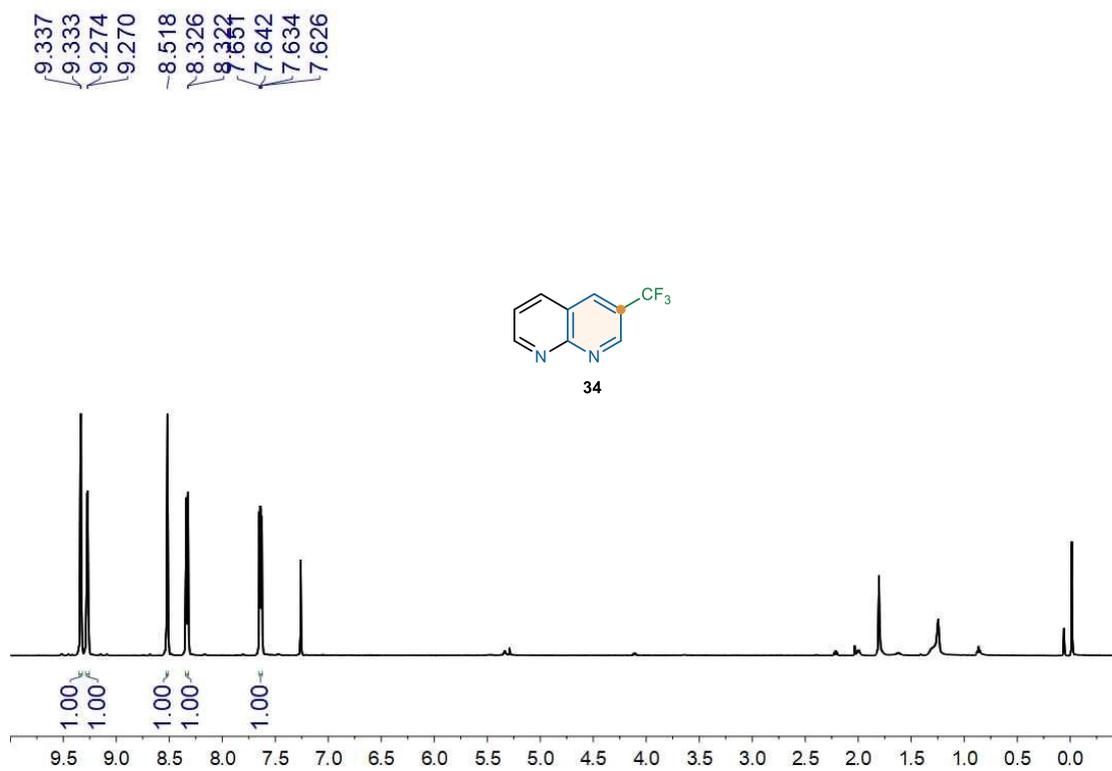
Supplementary Fig. 111. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of 33



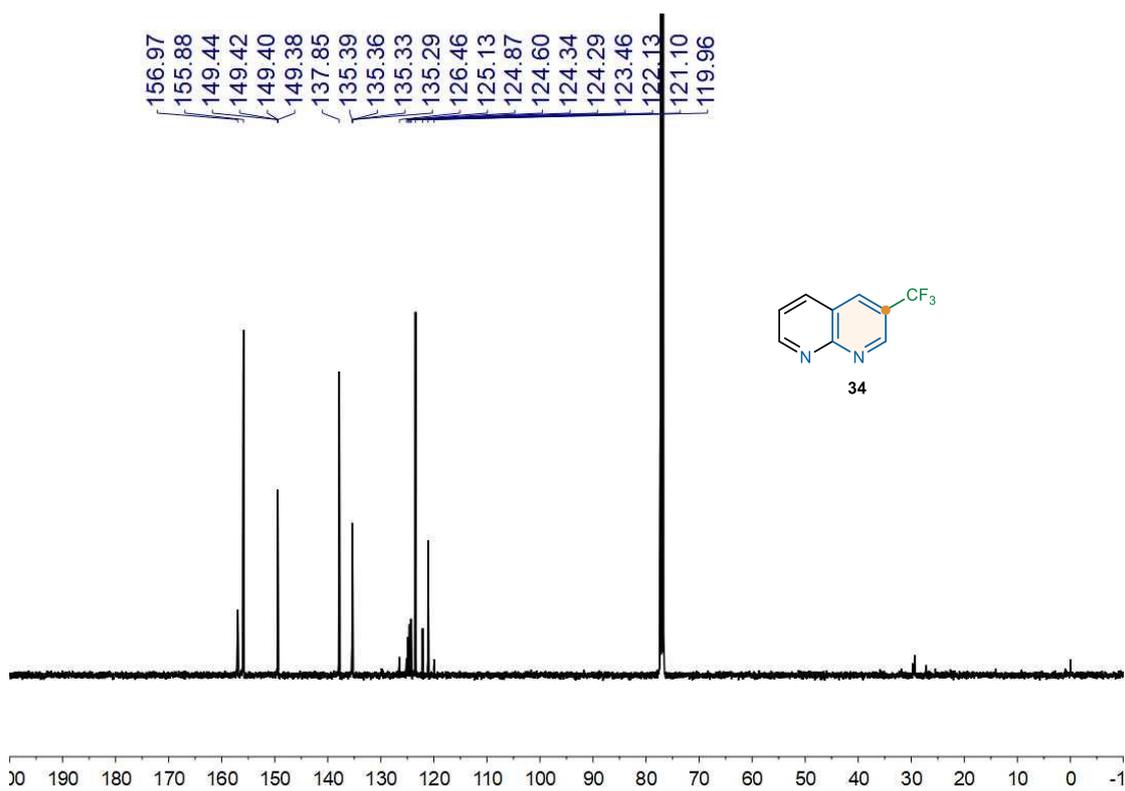
Supplementary Fig. 112. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of 33



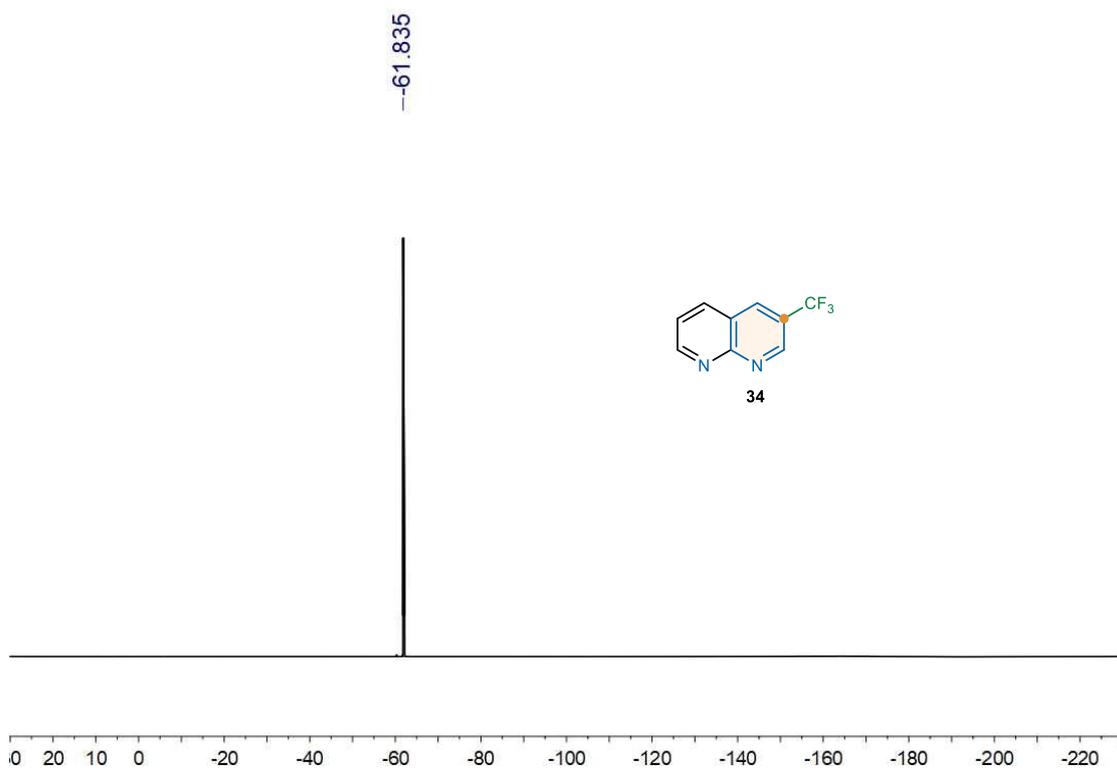
Supplementary Fig. 113.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ) spectrum of **33**



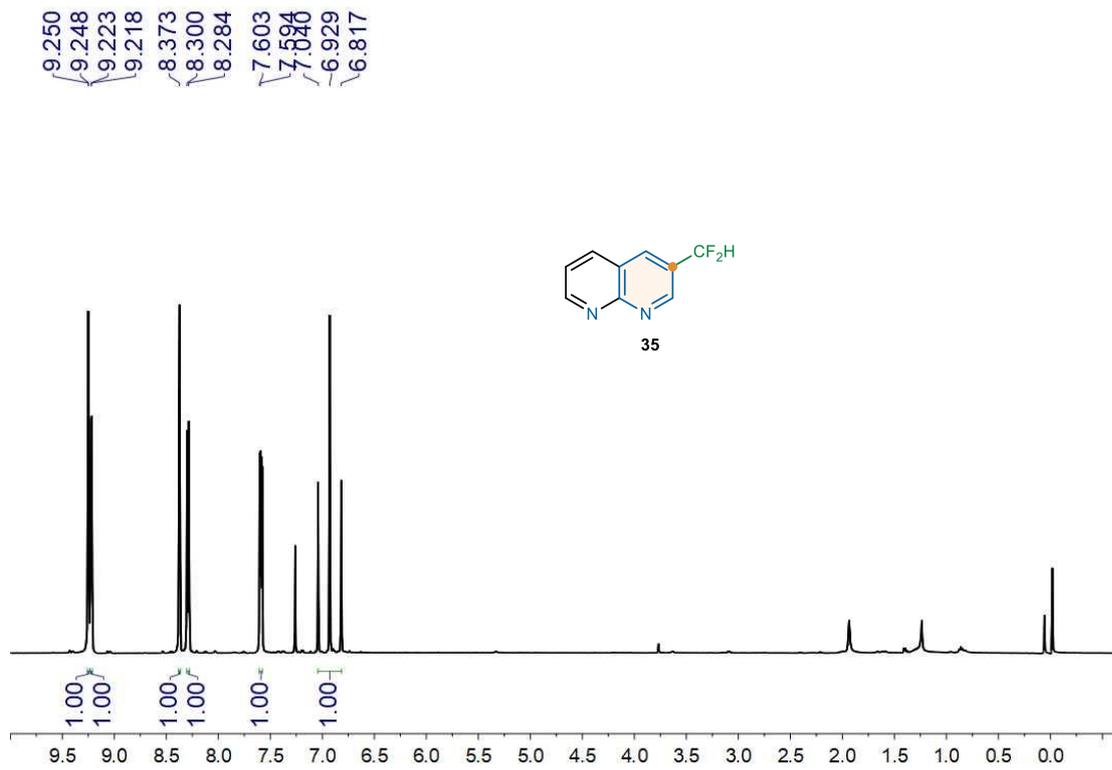
Supplementary Fig. 114.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **34**



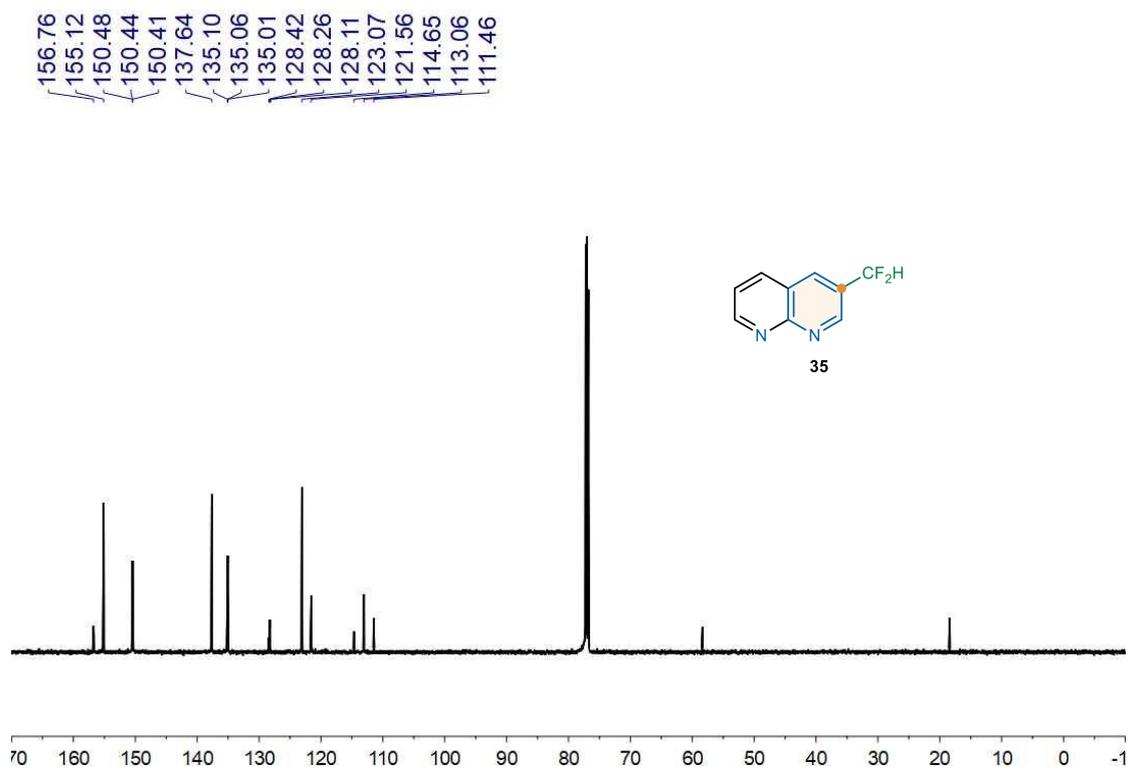
Supplementary Fig. 115.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of 34



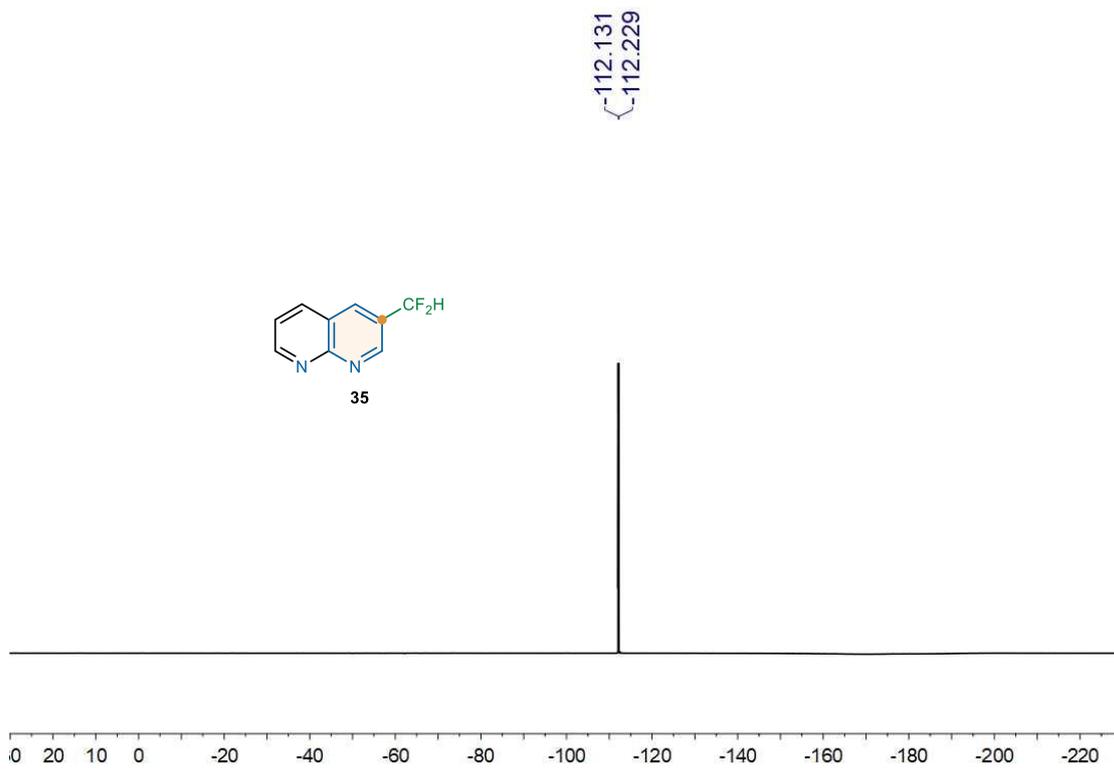
Supplementary Fig. 116.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ) spectrum of 34



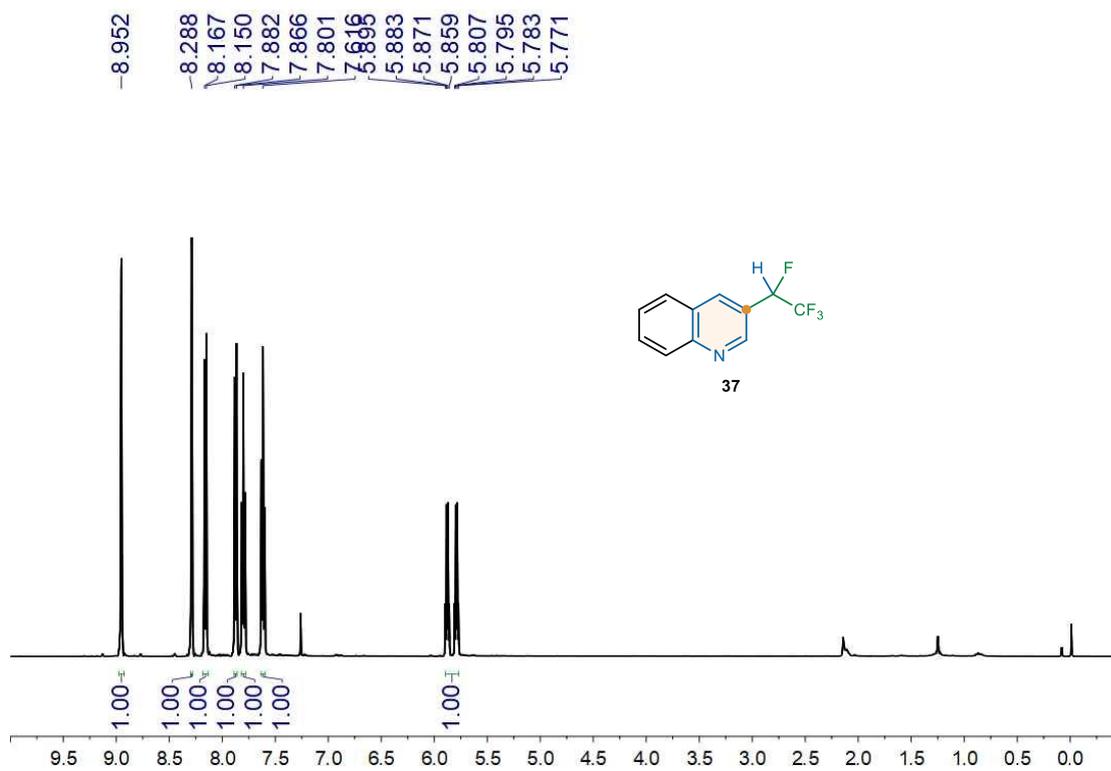
Supplementary Fig. 117.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **35**



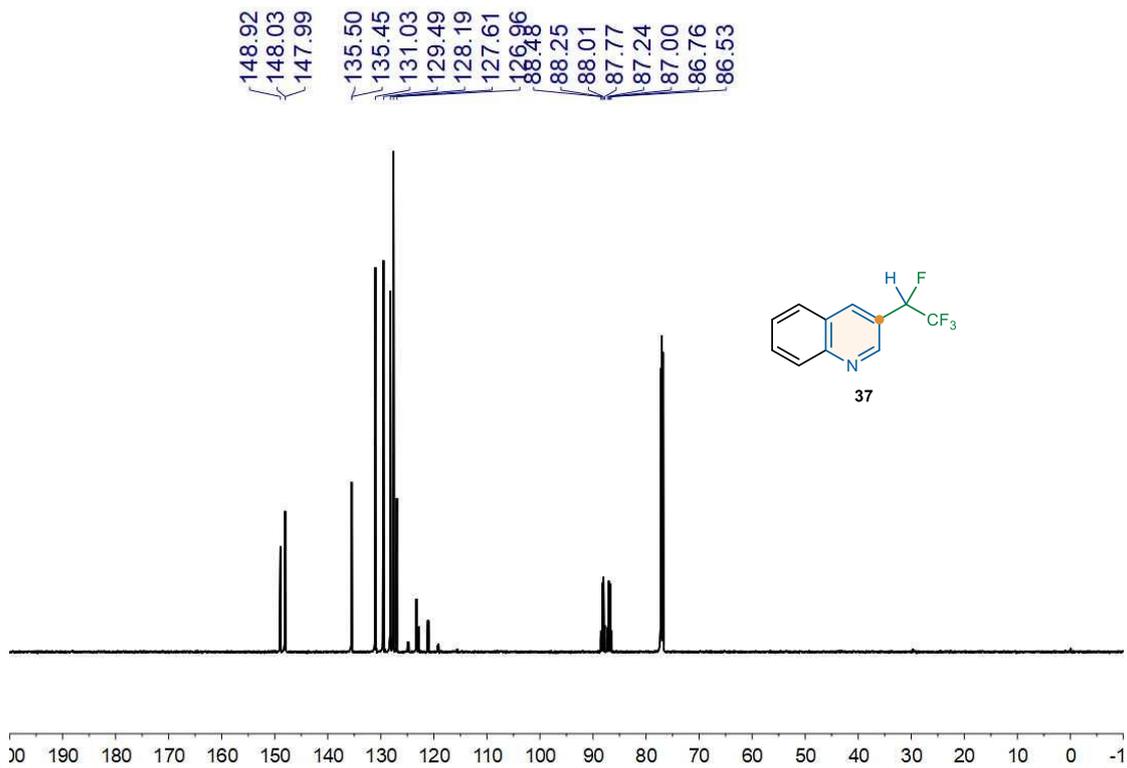
Supplementary Fig. 118.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **35**



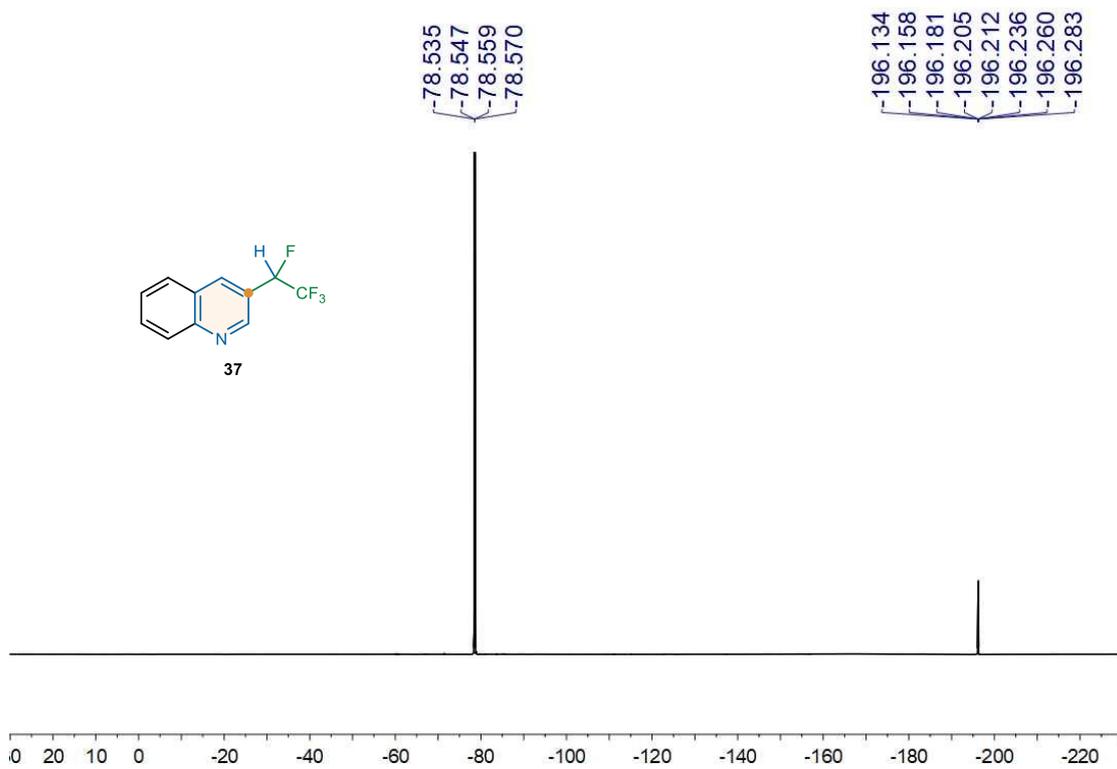
Supplementary Fig. 119.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ) spectrum of **35**



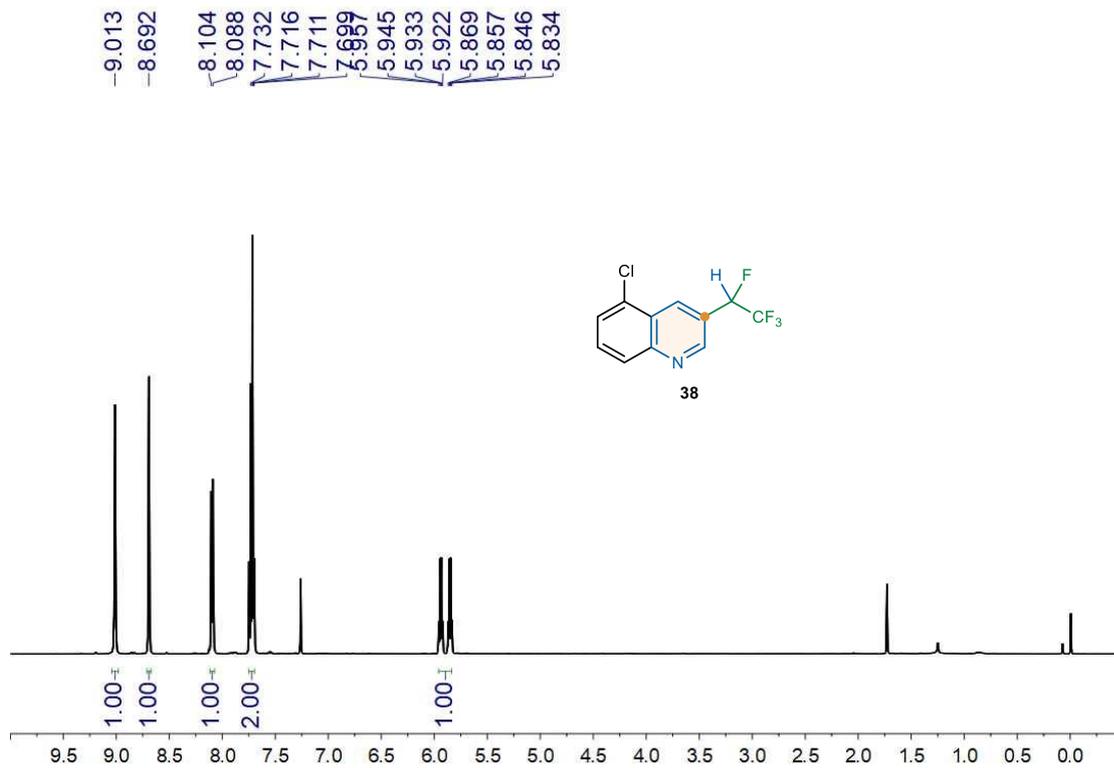
Supplementary Fig. 120.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **37**



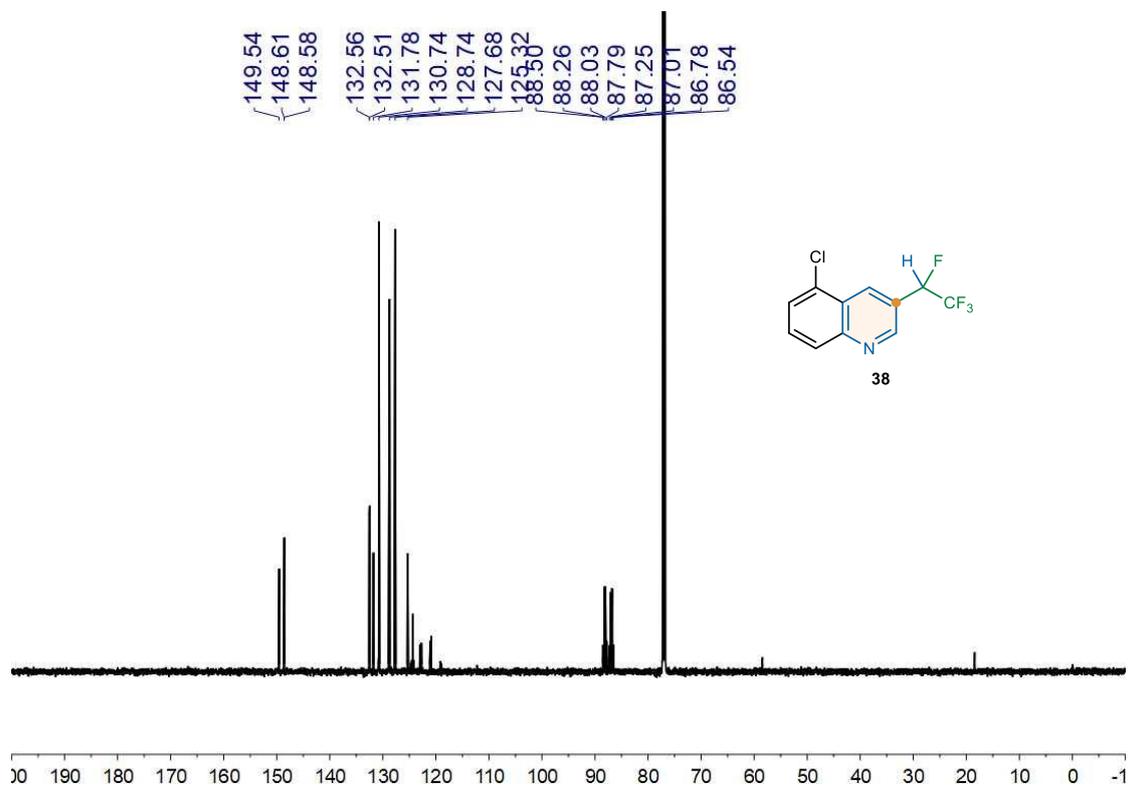
Supplementary Fig. 121. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of 37



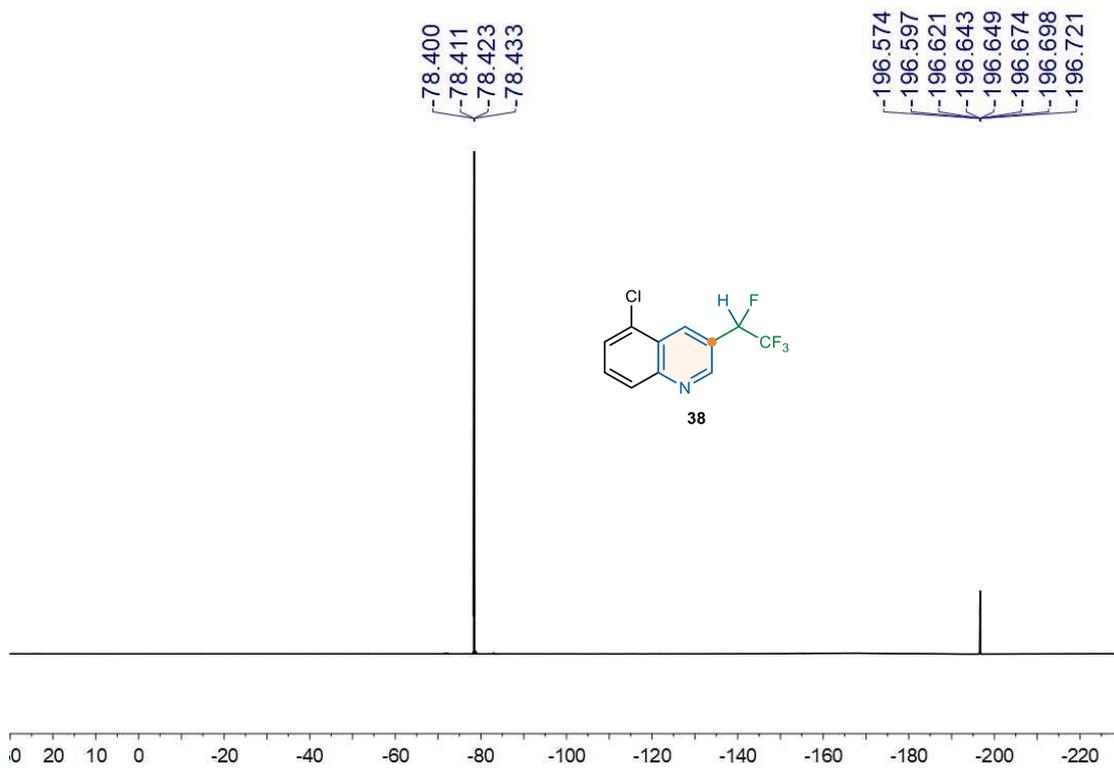
Supplementary Fig. 122. <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) spectrum of 37



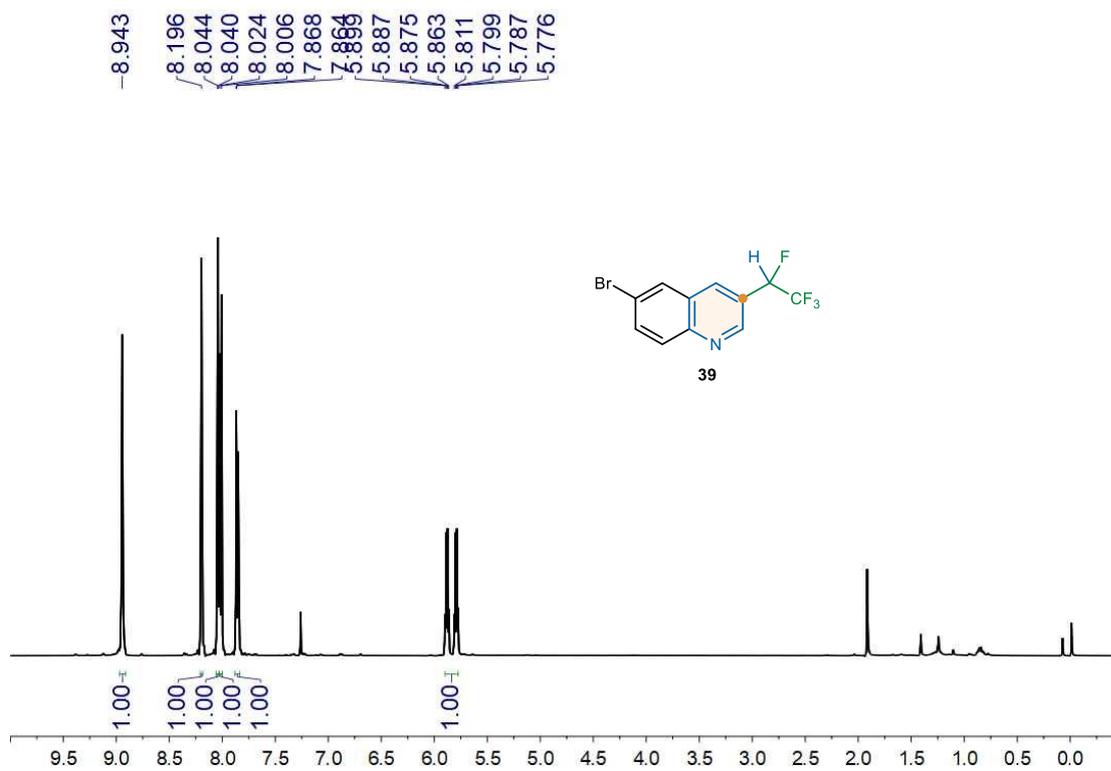
Supplementary Fig. 123.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **38**



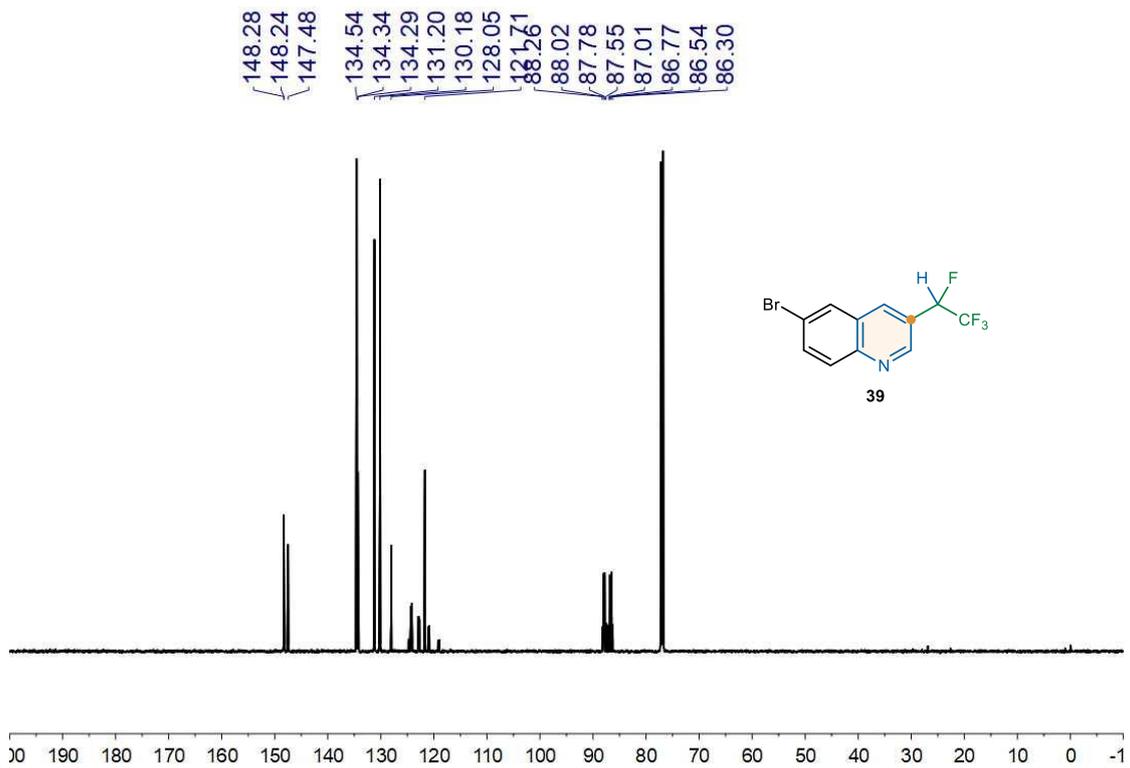
Supplementary Fig. 124.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **38**



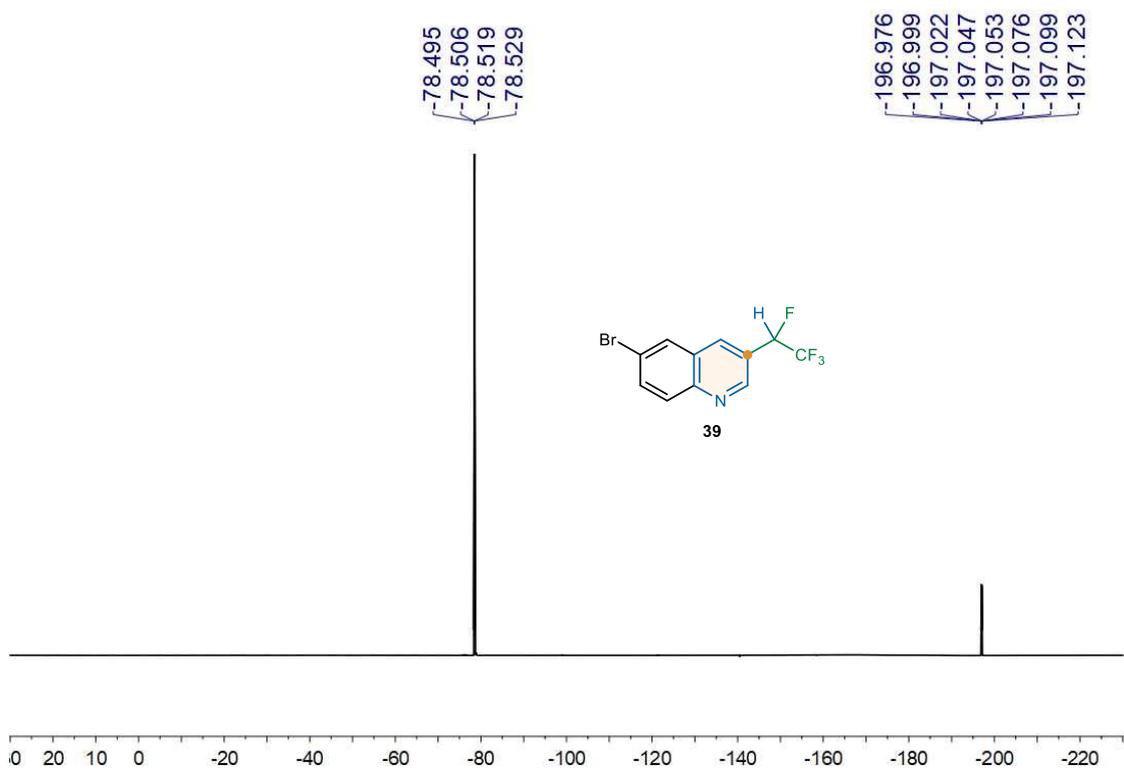
Supplementary Fig. 125.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ) spectrum of **38**



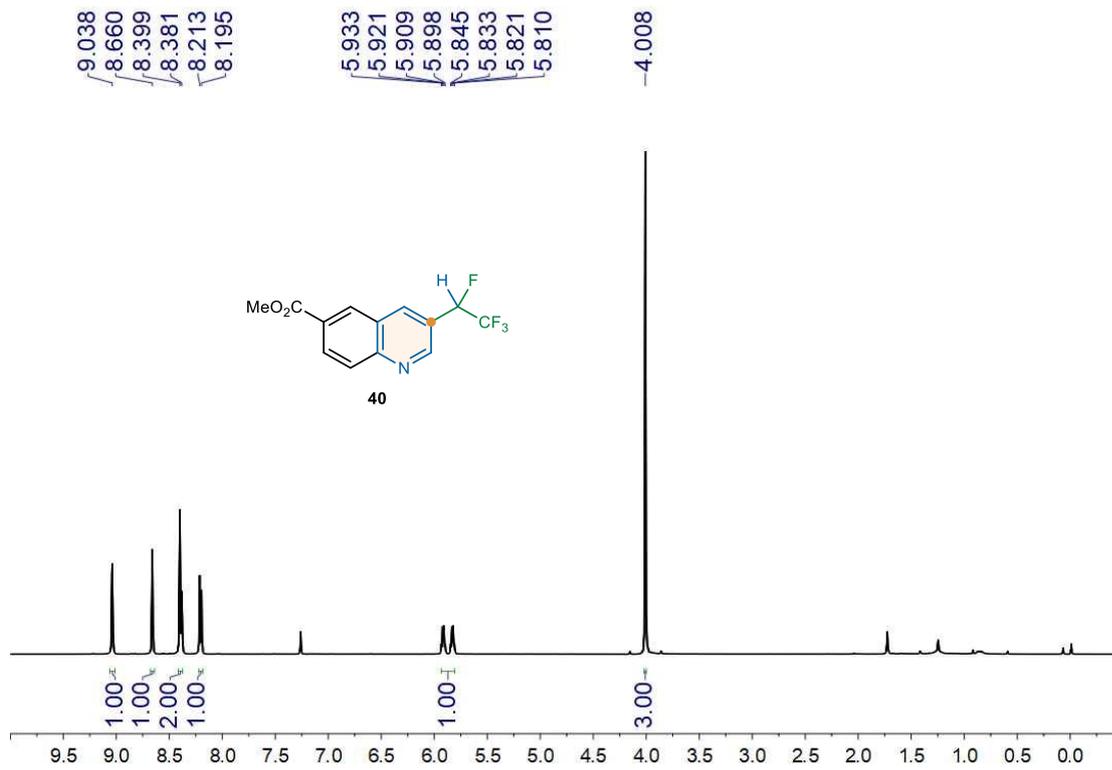
Supplementary Fig. 126.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **39**



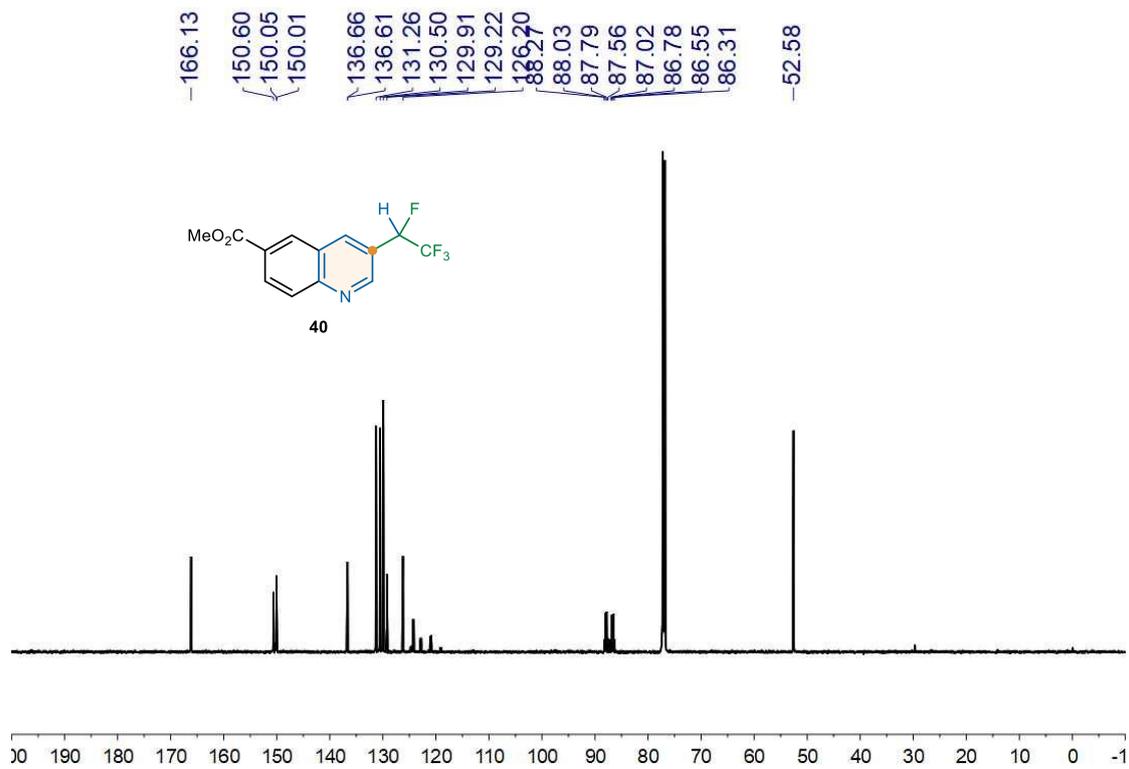
Supplementary Fig. 127. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of 39



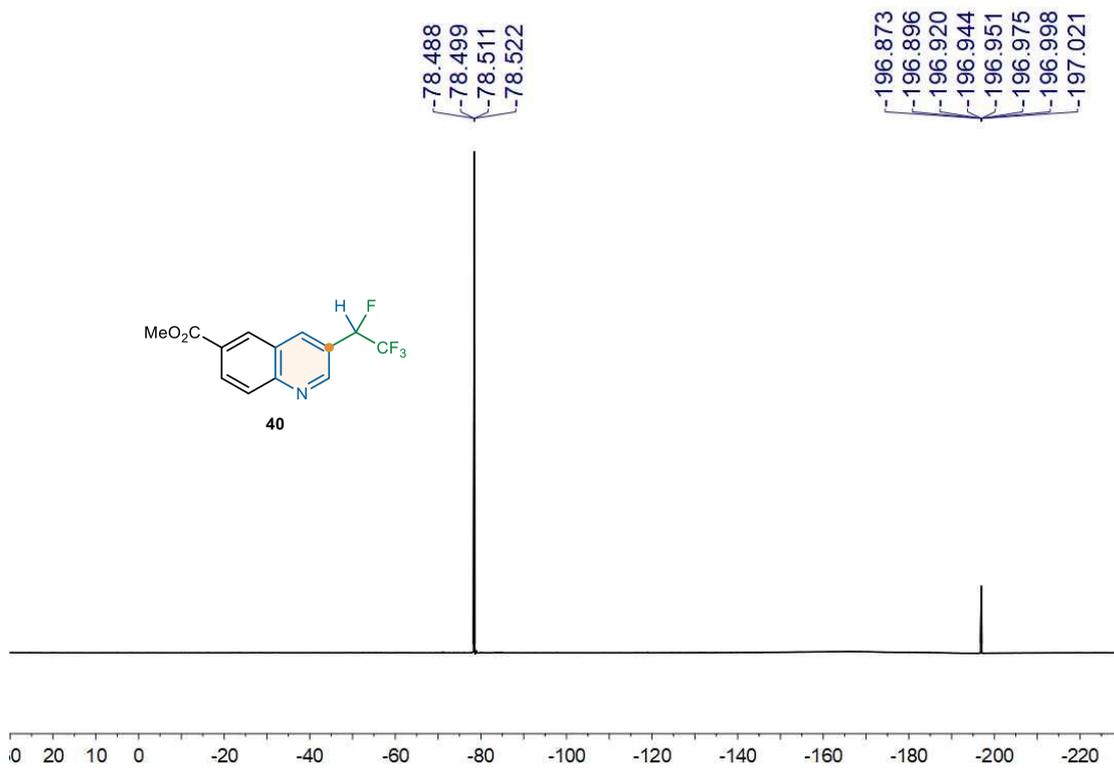
Supplementary Fig. 128. <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) spectrum of 39



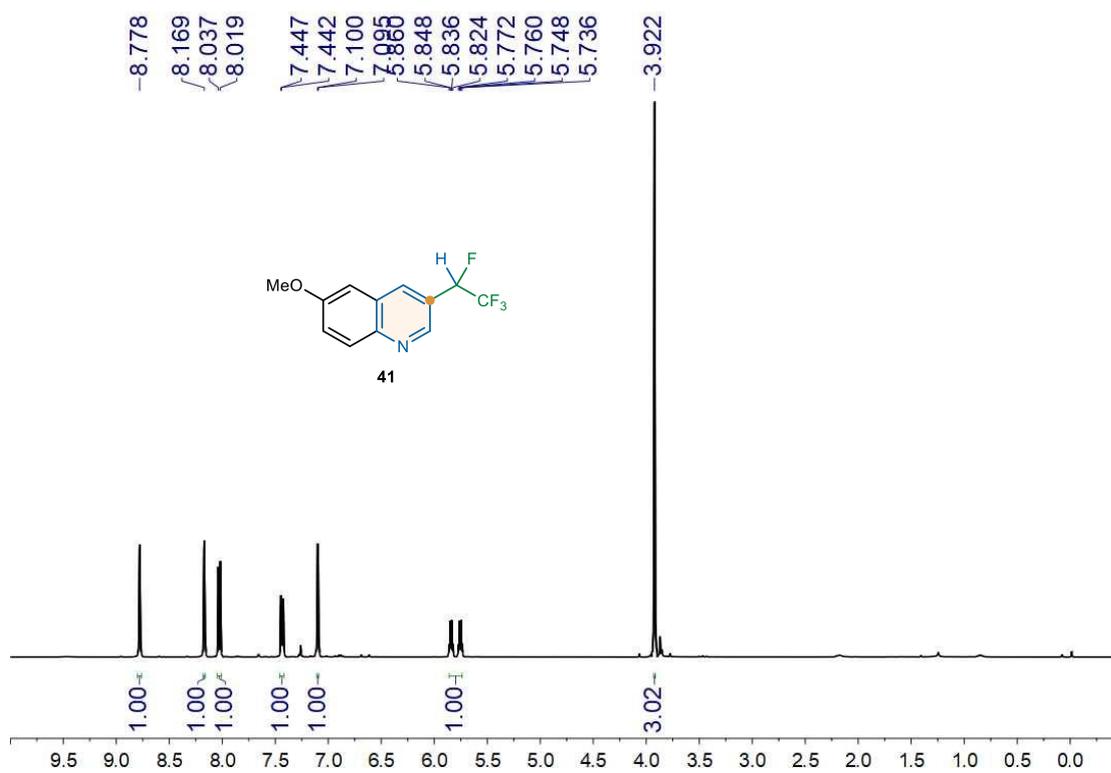
Supplementary Fig. 129.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **40**



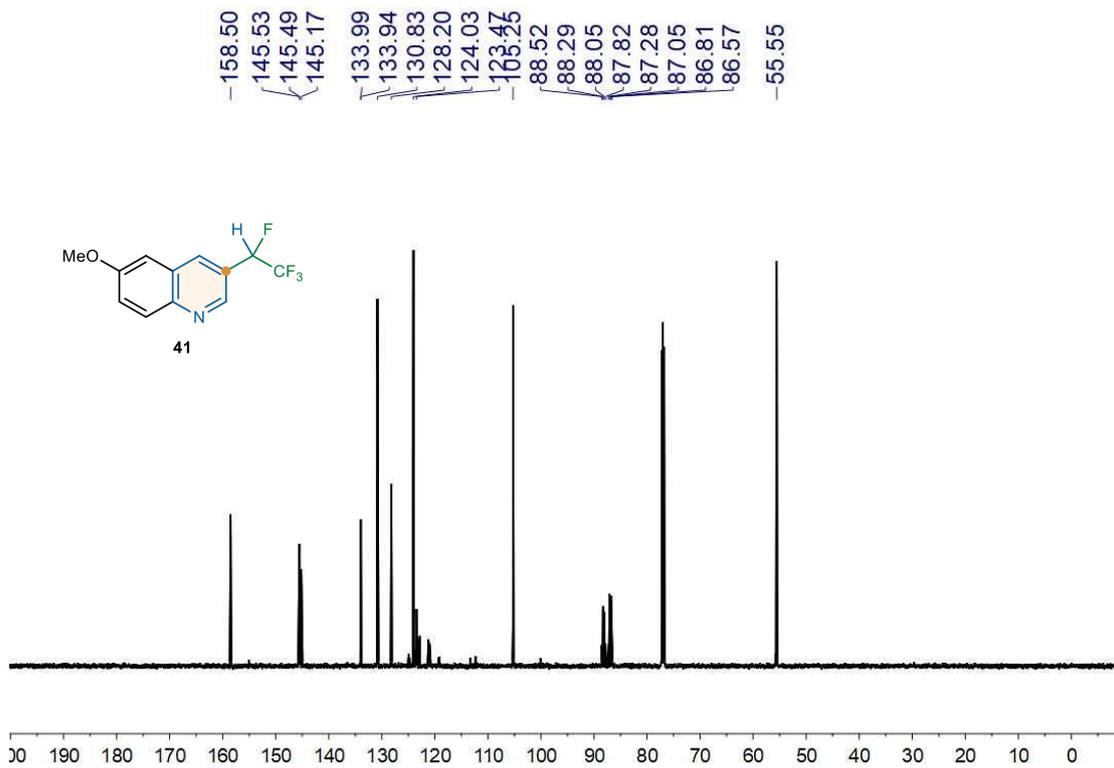
Supplementary Fig. 130.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **40**



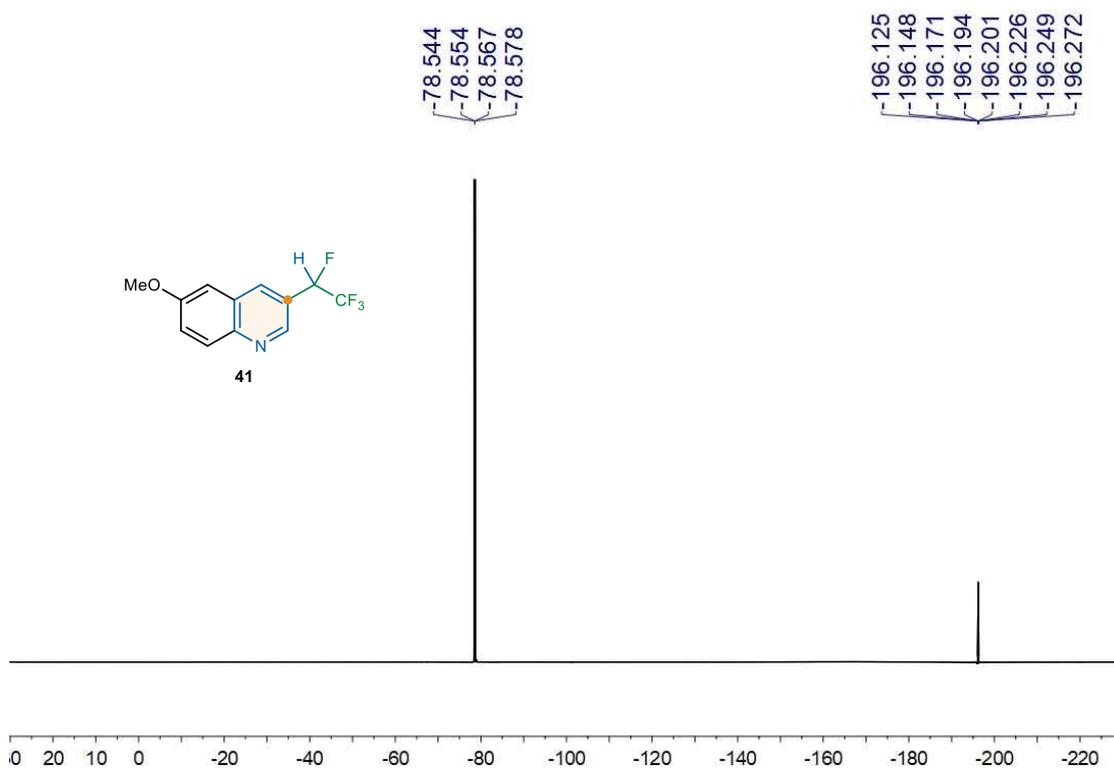
Supplementary Fig. 131.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ) spectrum of 40



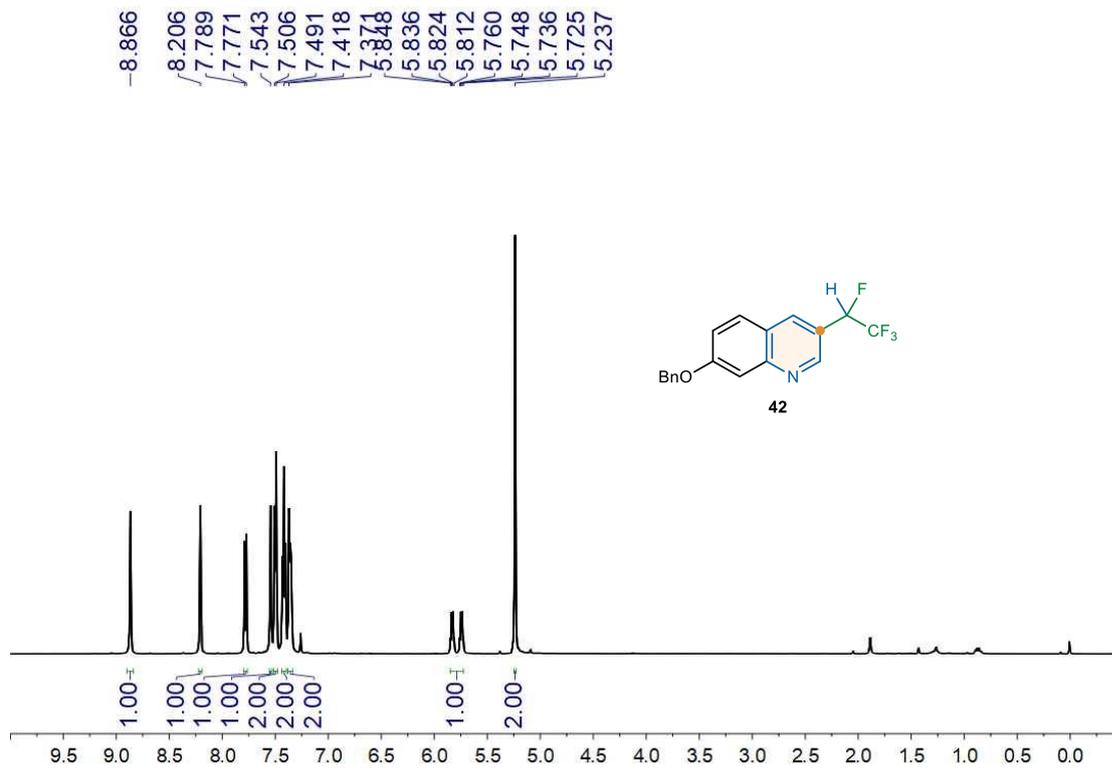
Supplementary Fig. 132.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of 41



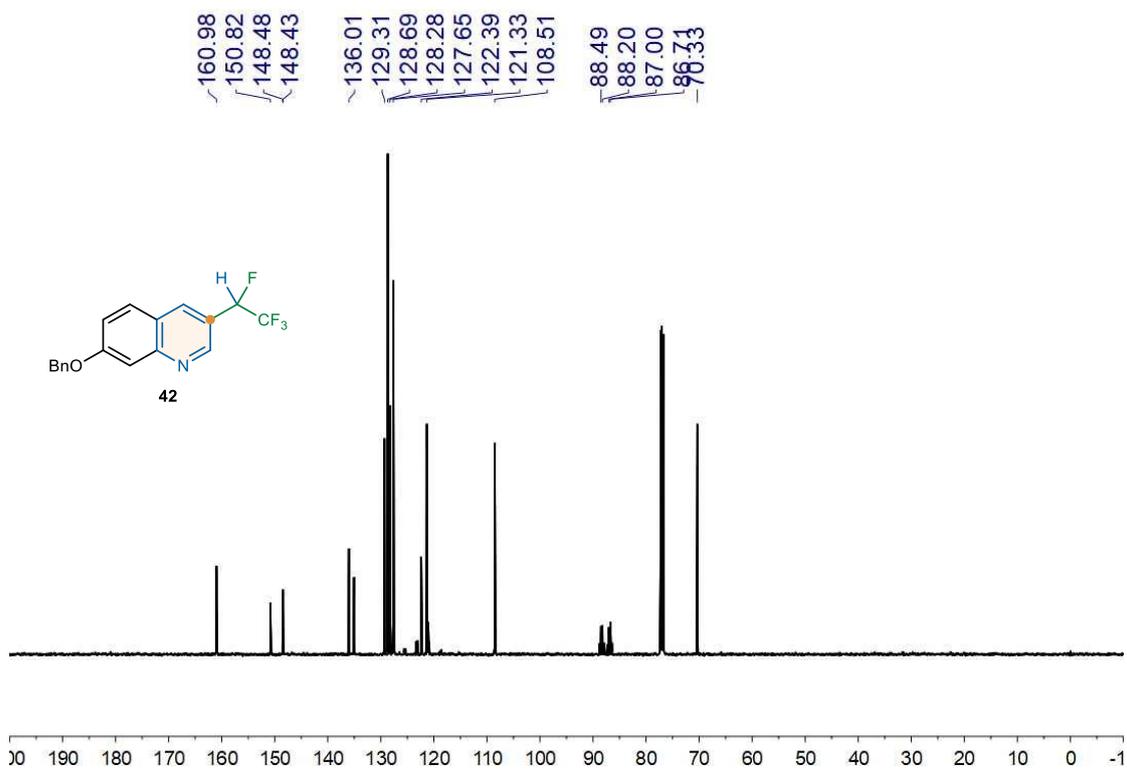
Supplementary Fig. 133. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of 41



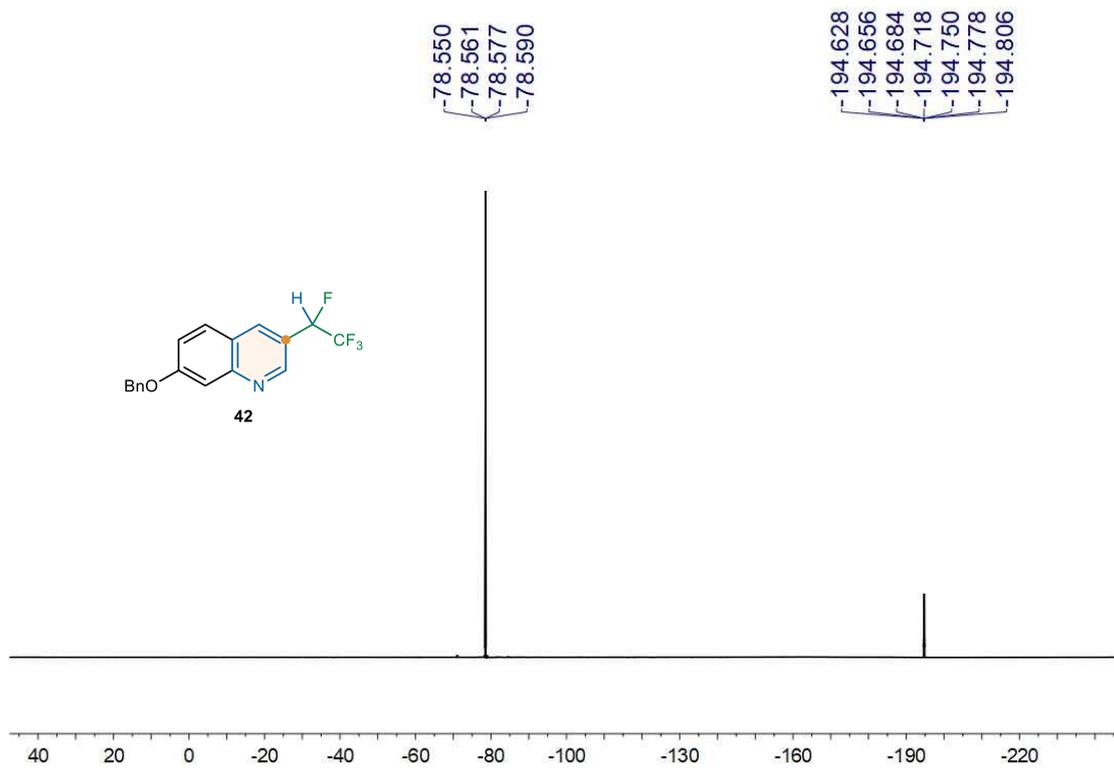
Supplementary Fig. 134. <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) spectrum of 41



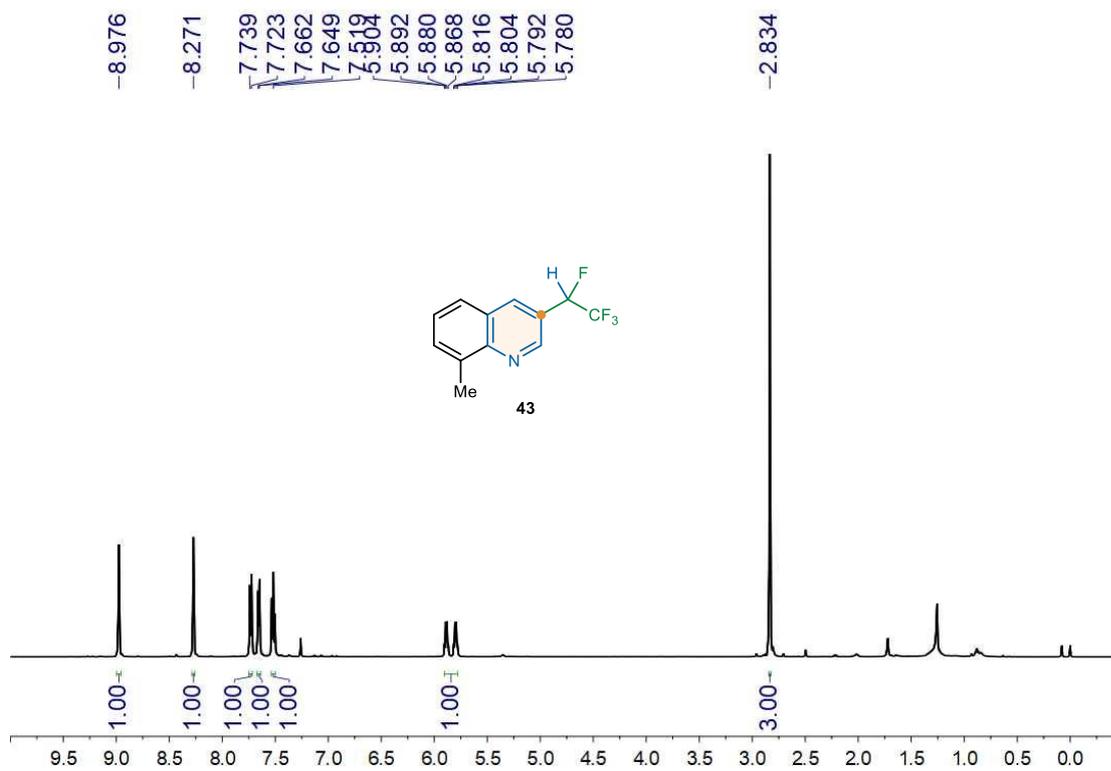
Supplementary Fig. 135. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **42**



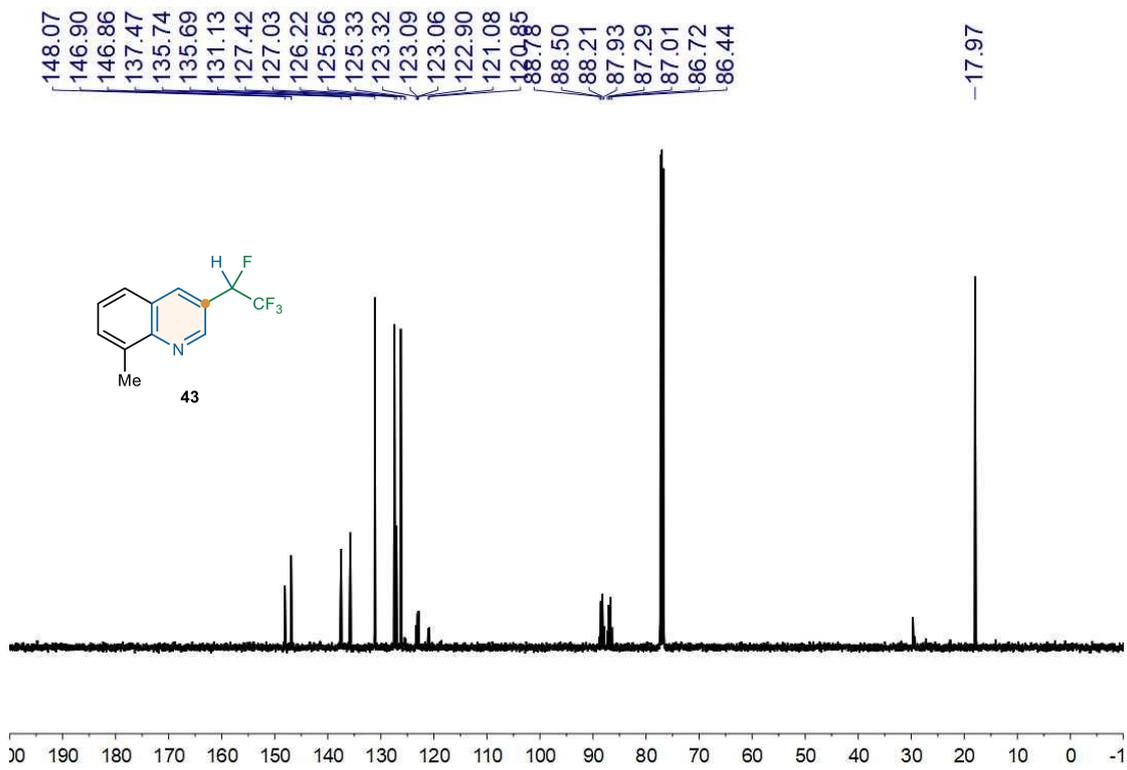
Supplementary Fig. 136. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of **42**



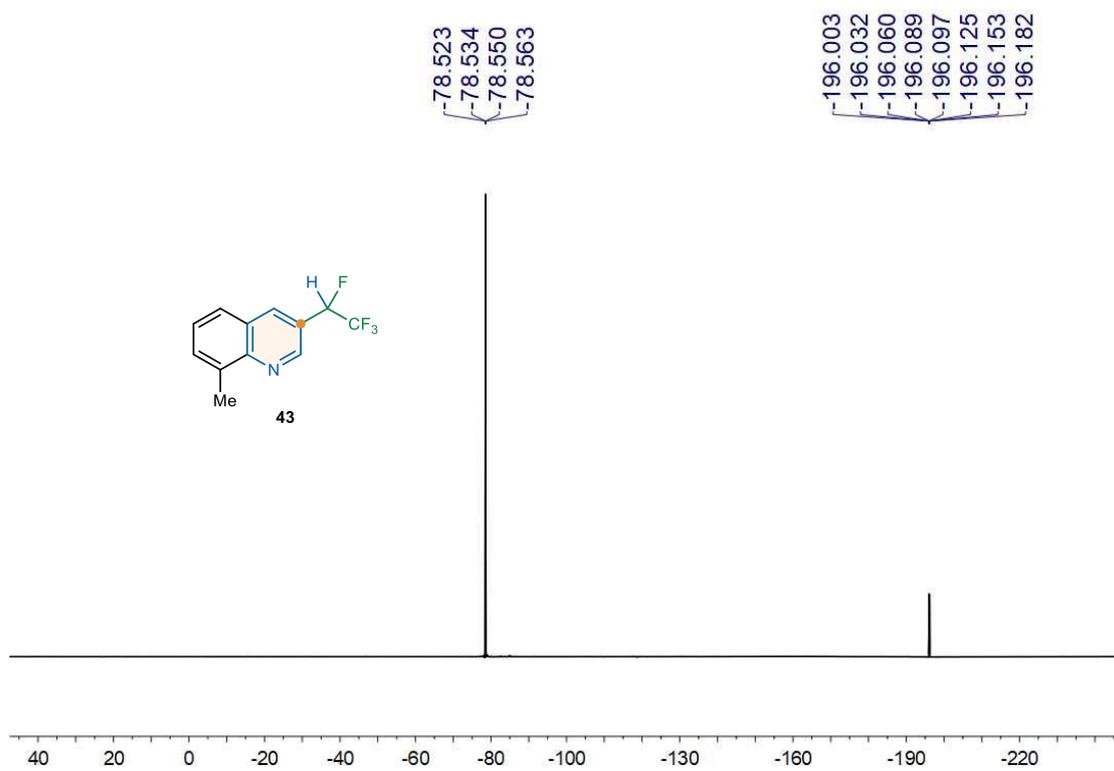
Supplementary Fig. 137.  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ) spectrum of **42**



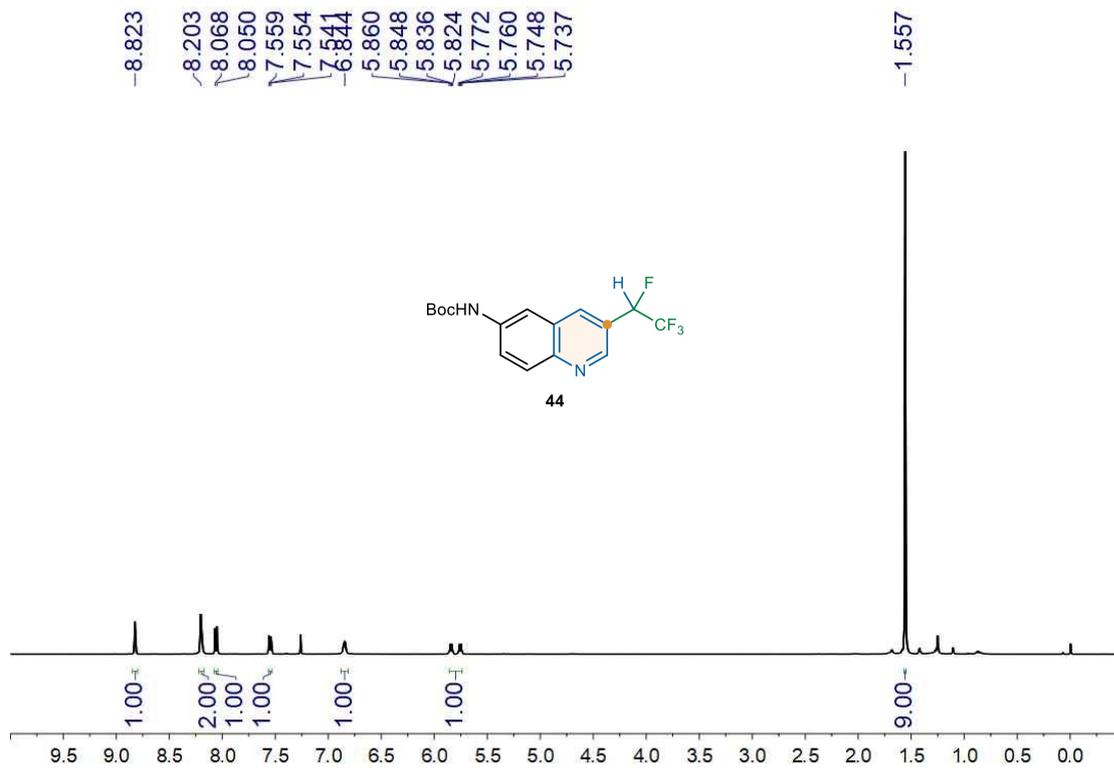
Supplementary Fig. 138.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **43**



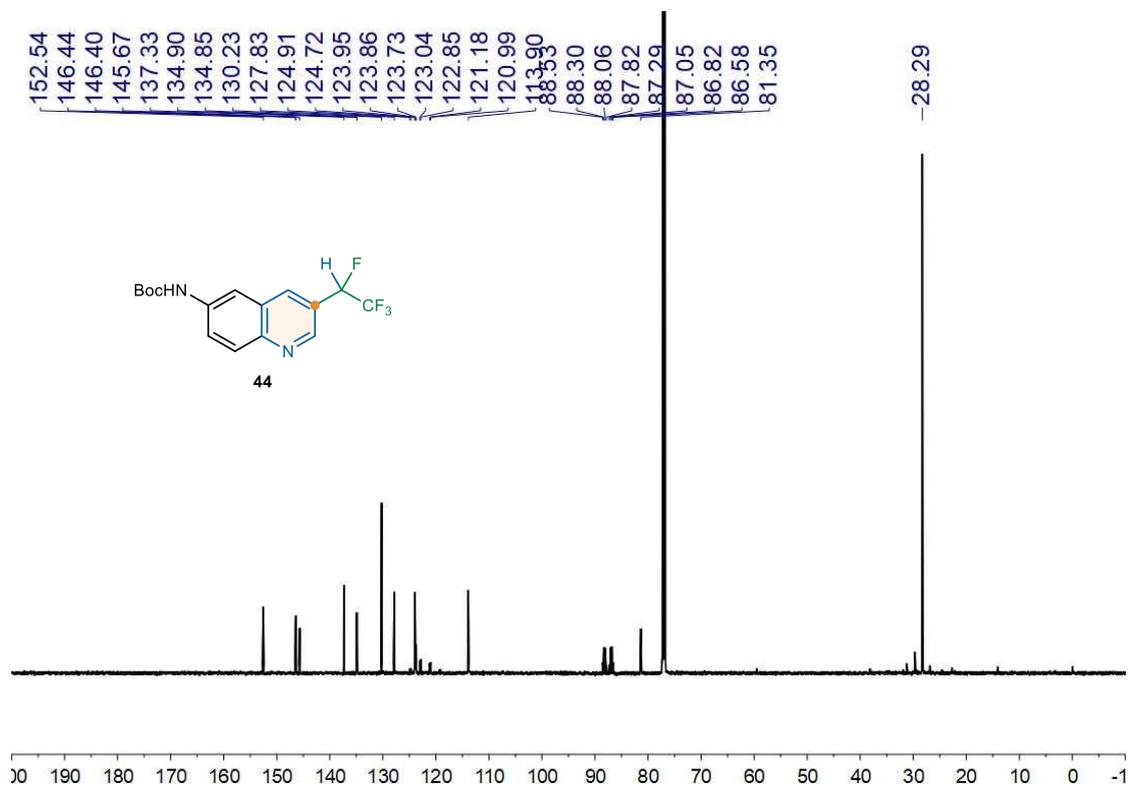
Supplementary Fig. 139. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of 43



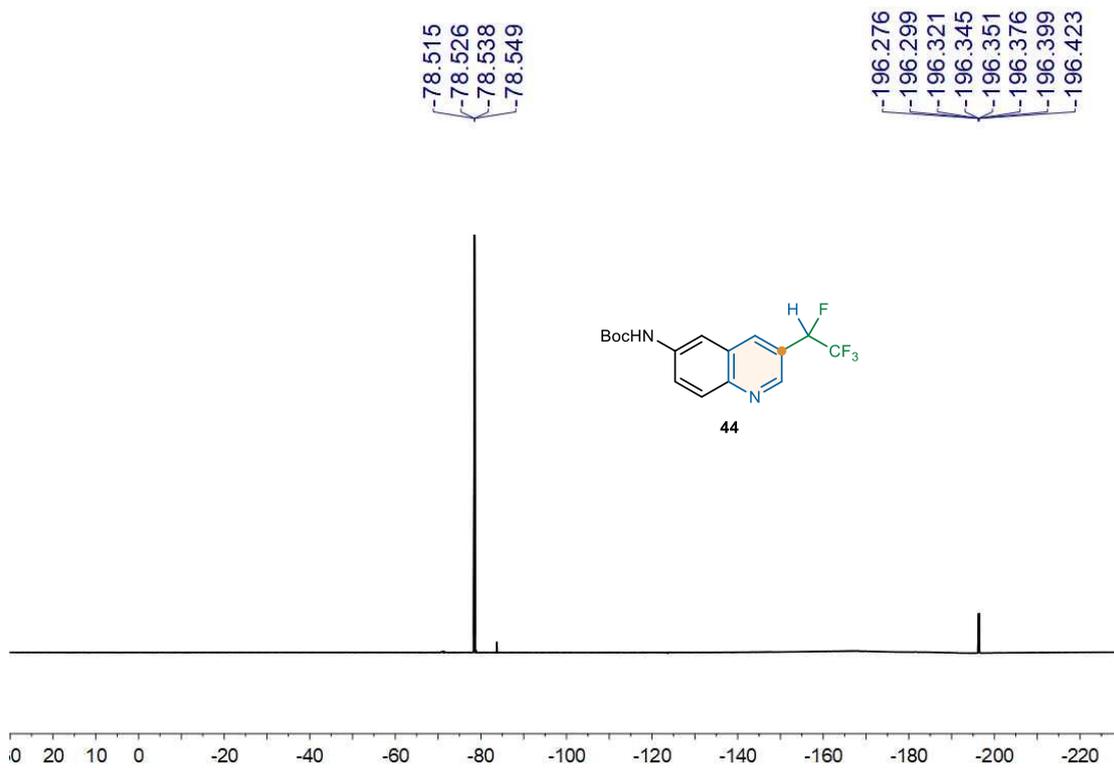
Supplementary Fig. 140. <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) spectrum of 43



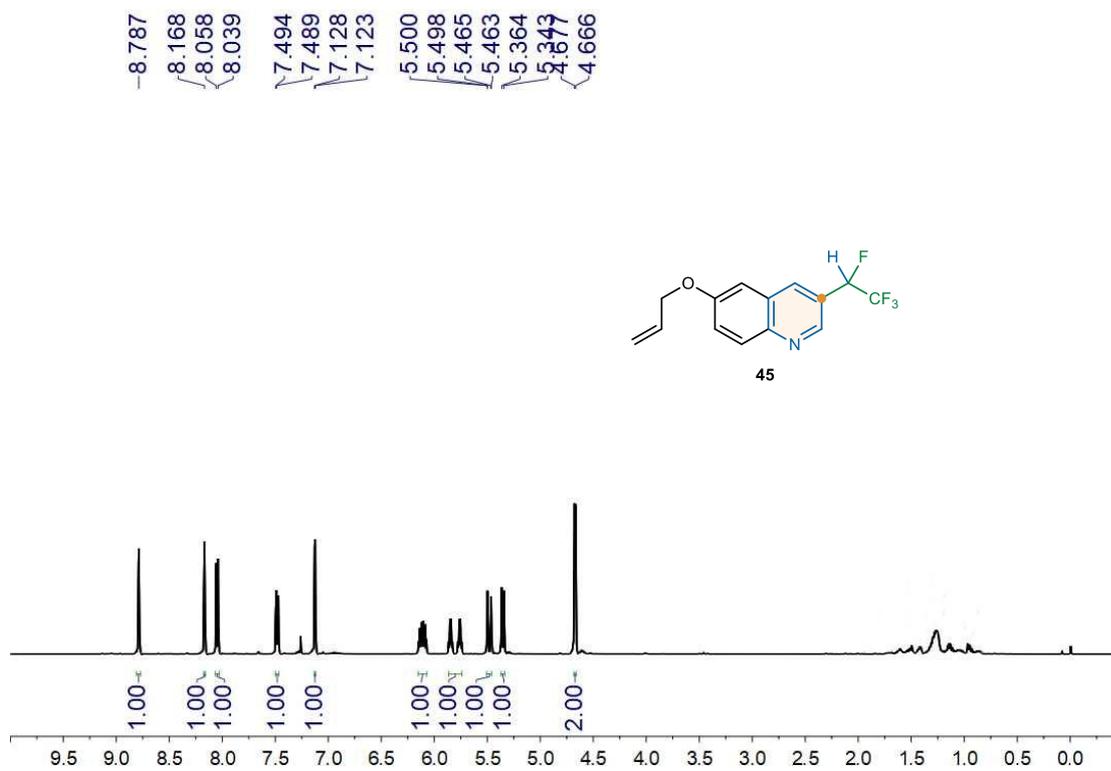
Supplementary Fig. 141. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of 44



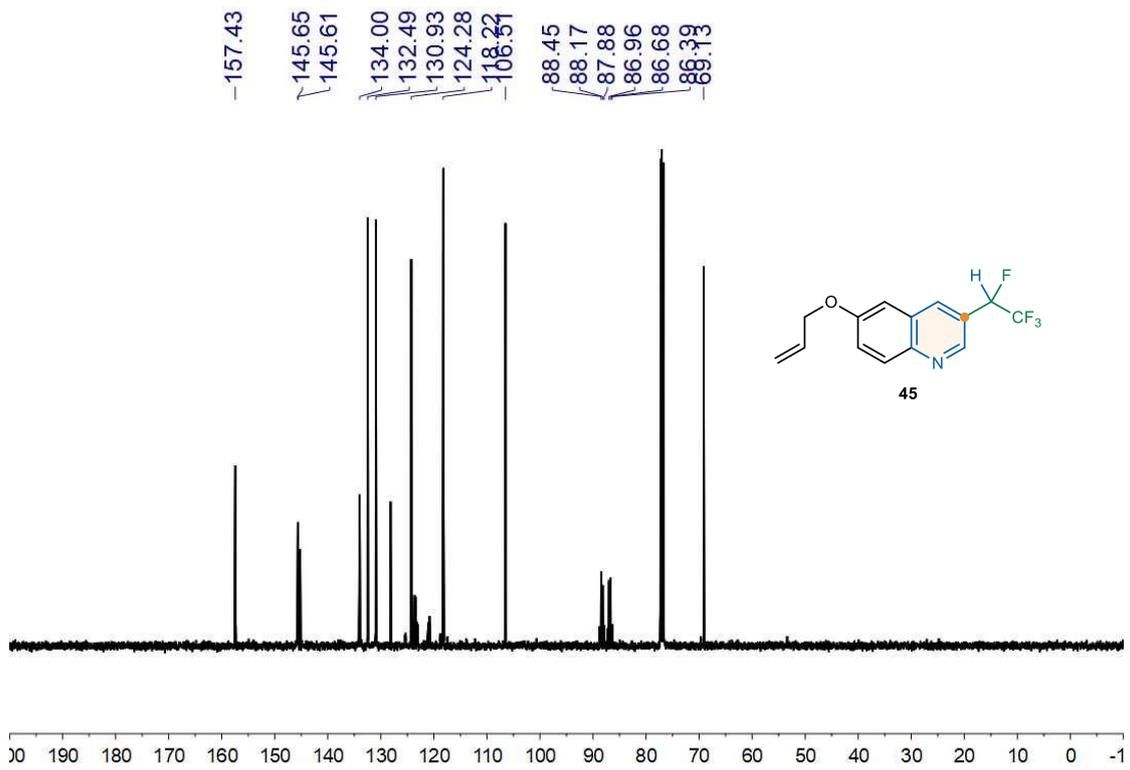
Supplementary Fig. 142. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of 44



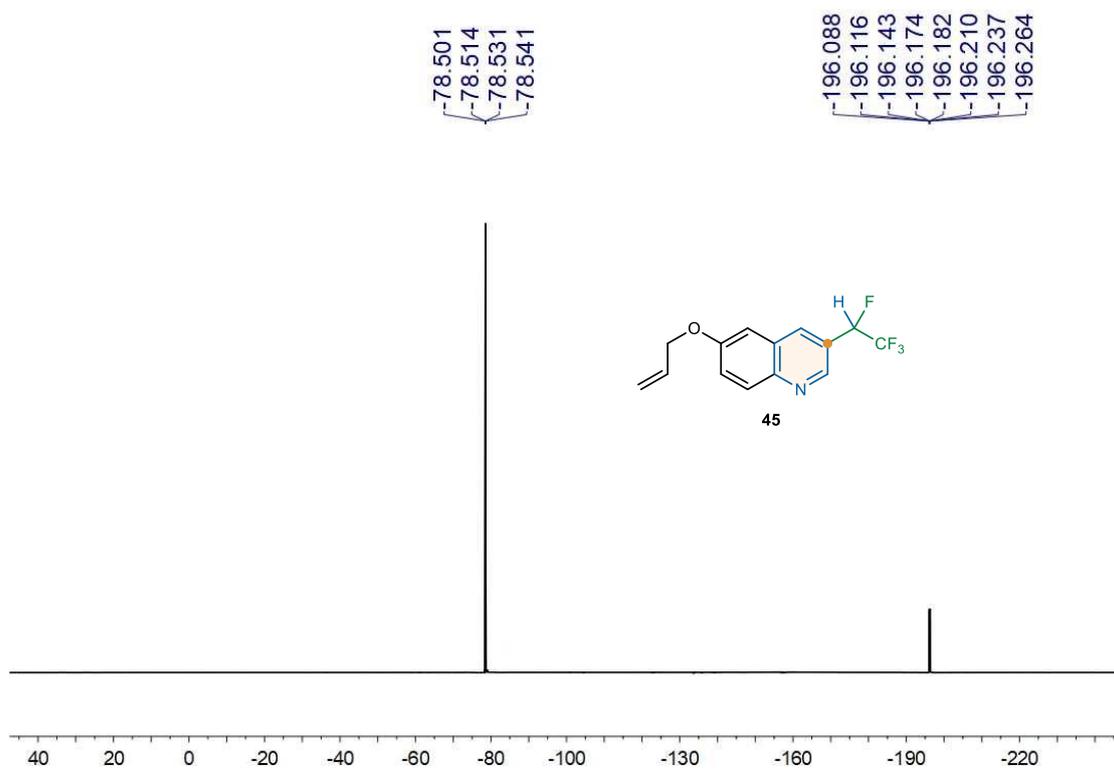
Supplementary Fig. 143. <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) spectrum of 44



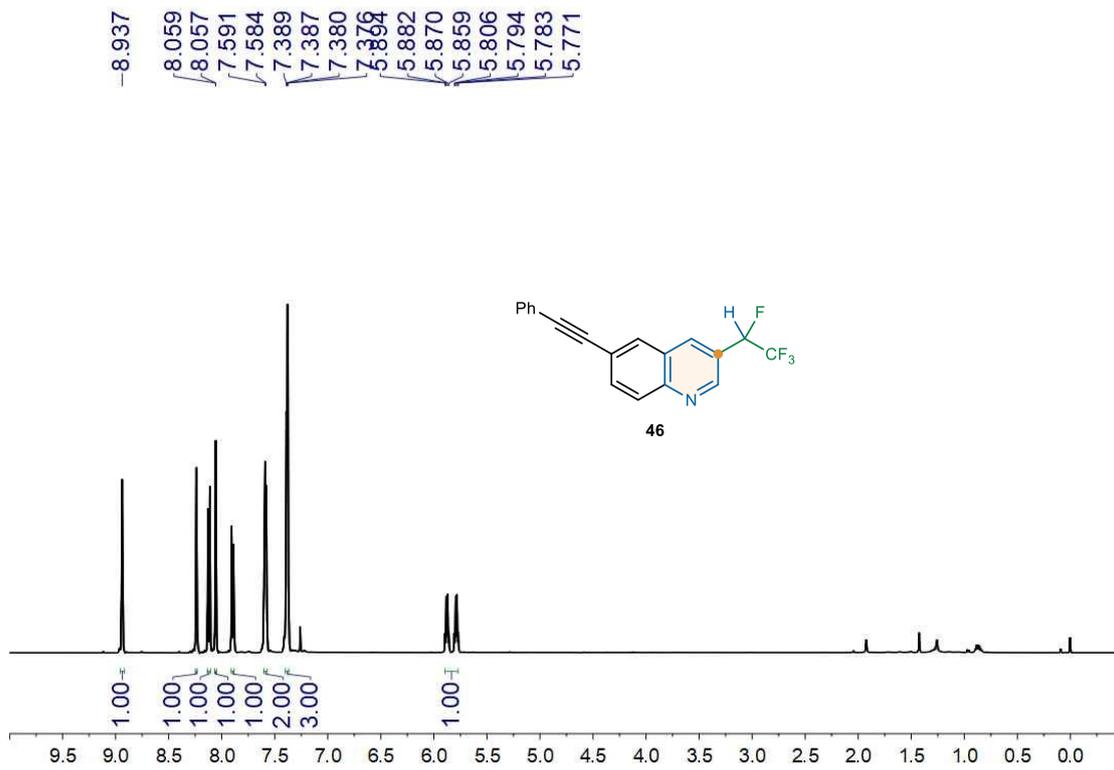
Supplementary Fig. 144. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of 45



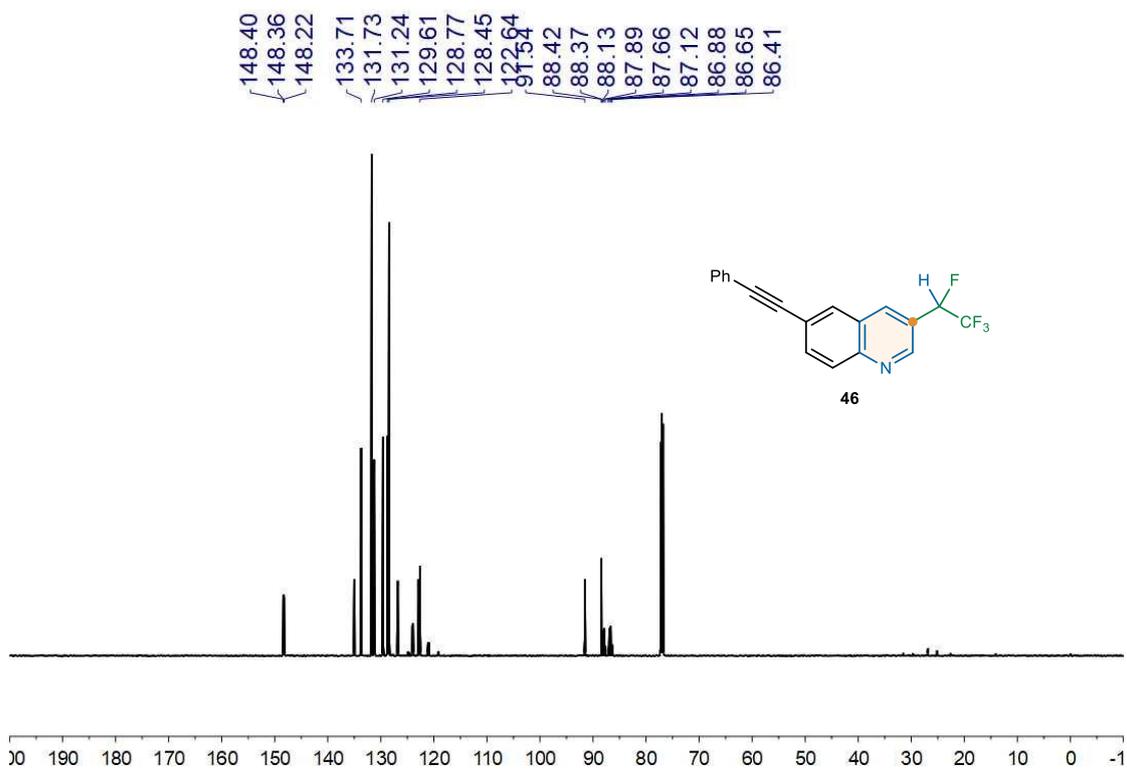
Supplementary Fig. 145. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of 45



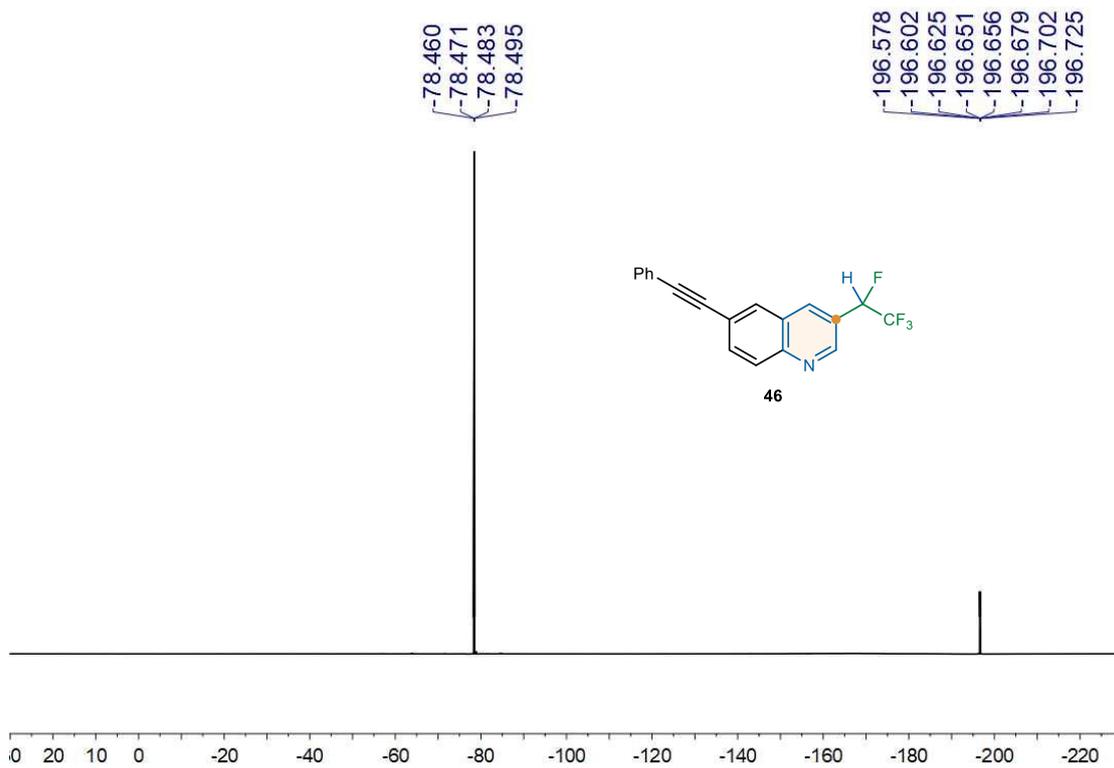
Supplementary Fig. 146. <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) spectrum of 45



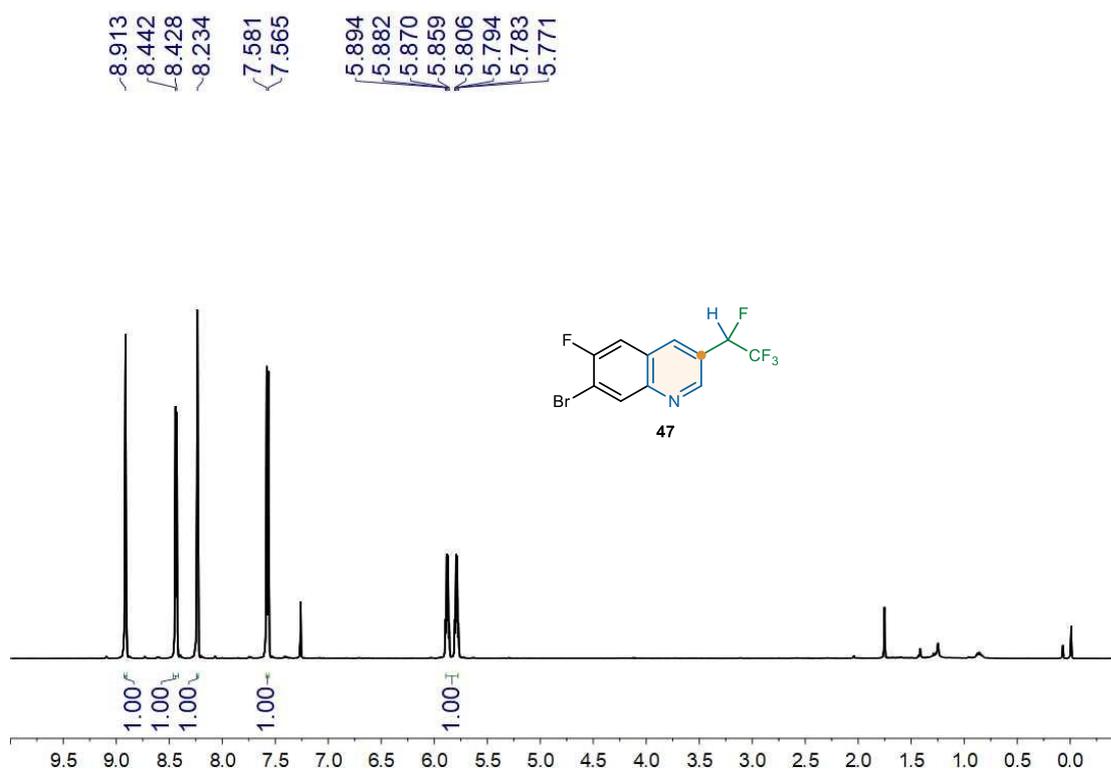
Supplementary Fig. 147. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **46**



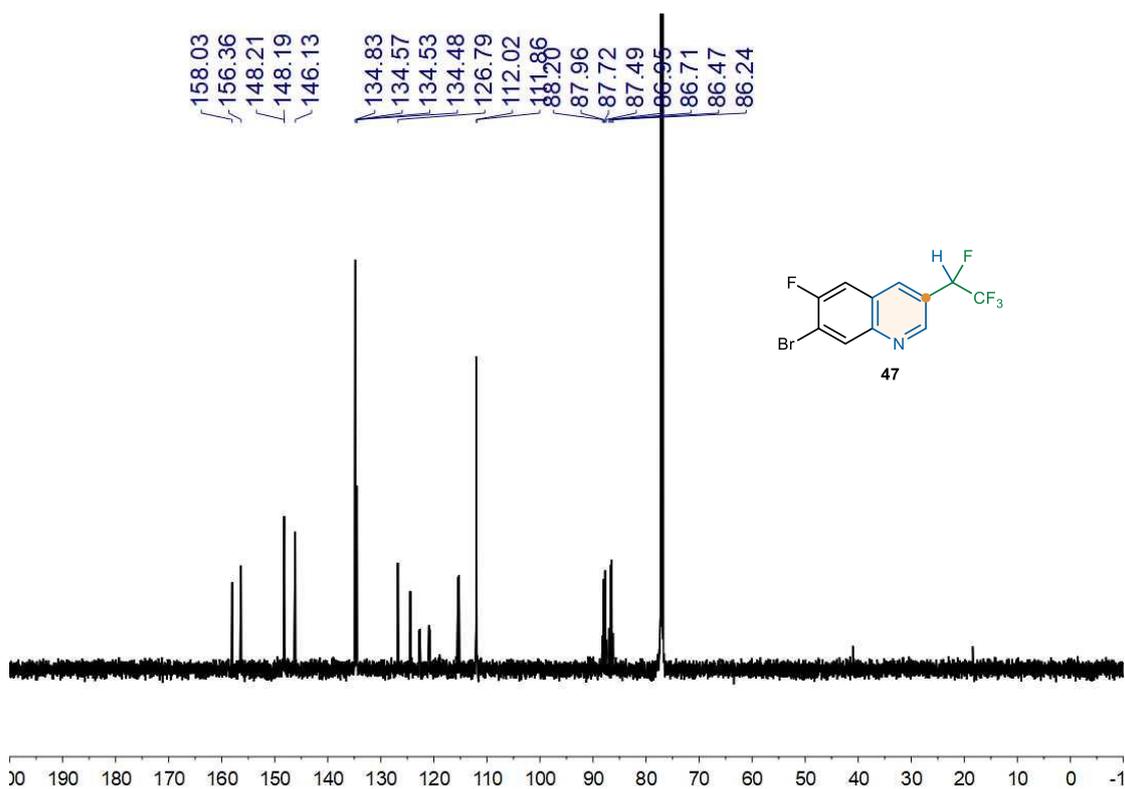
Supplementary Fig. 148. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of **46**



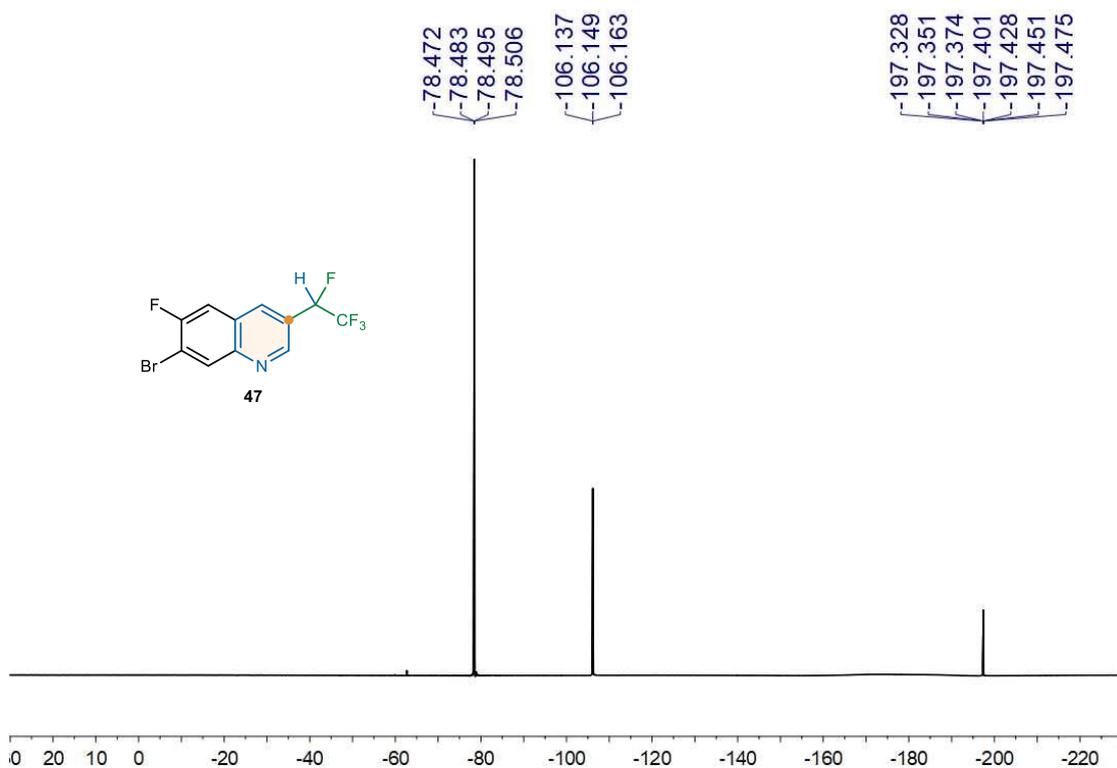
Supplementary Fig. 149. <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) spectrum of 46



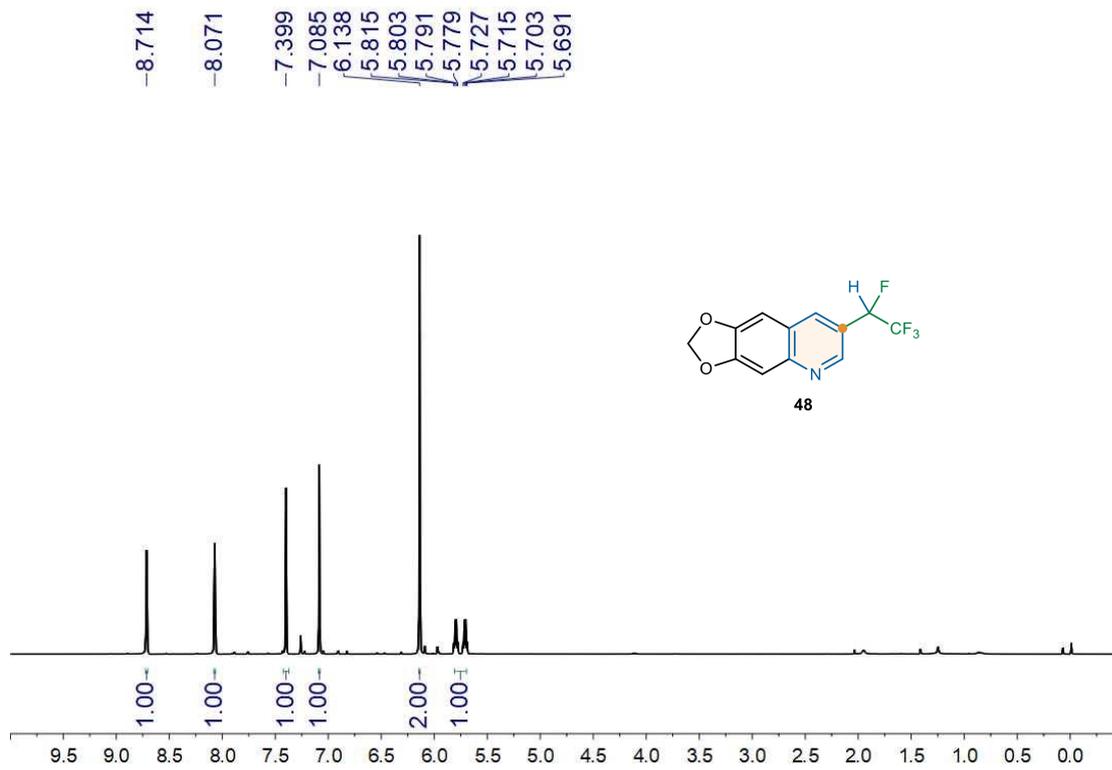
Supplementary Fig. 150. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of 47



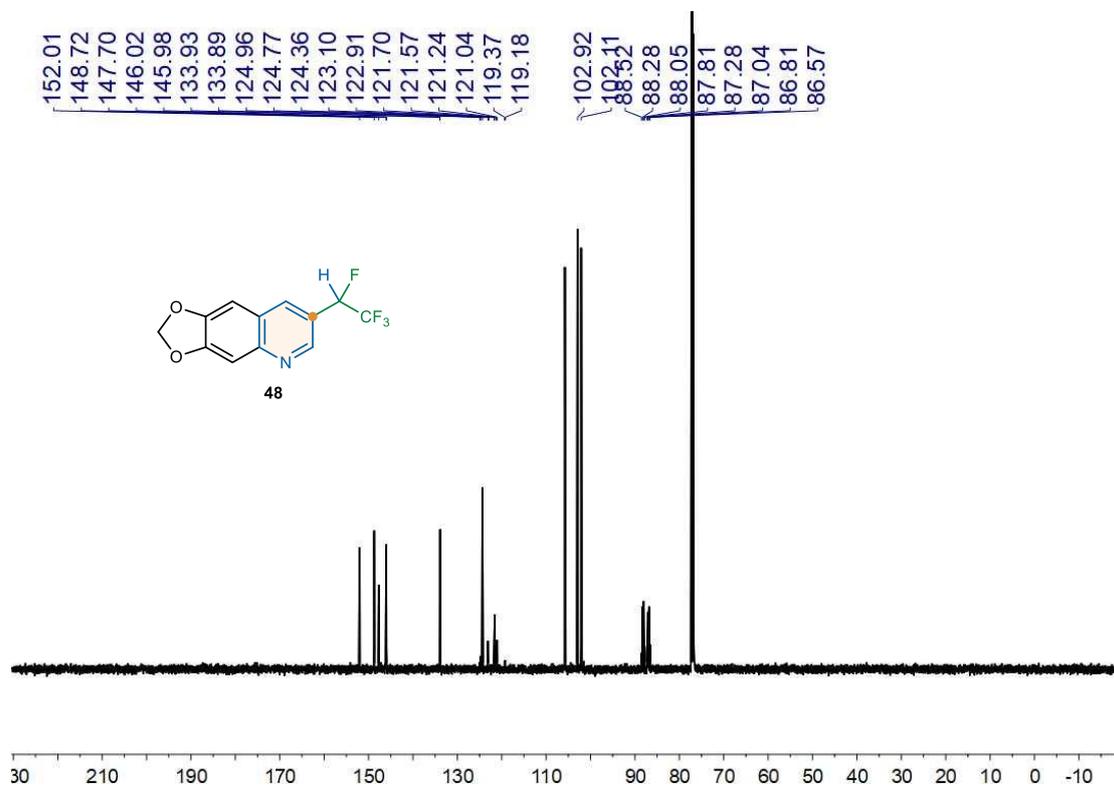
Supplementary Fig. 151. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of 47



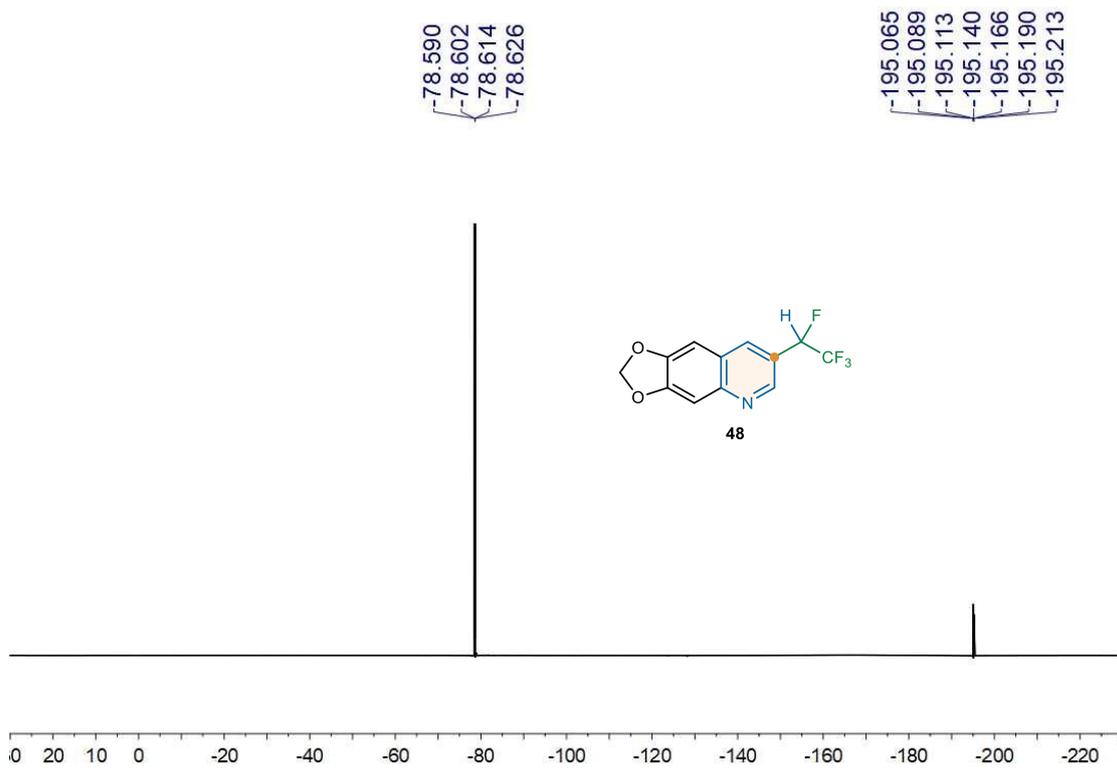
Supplementary Fig. 152. <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) spectrum of 47



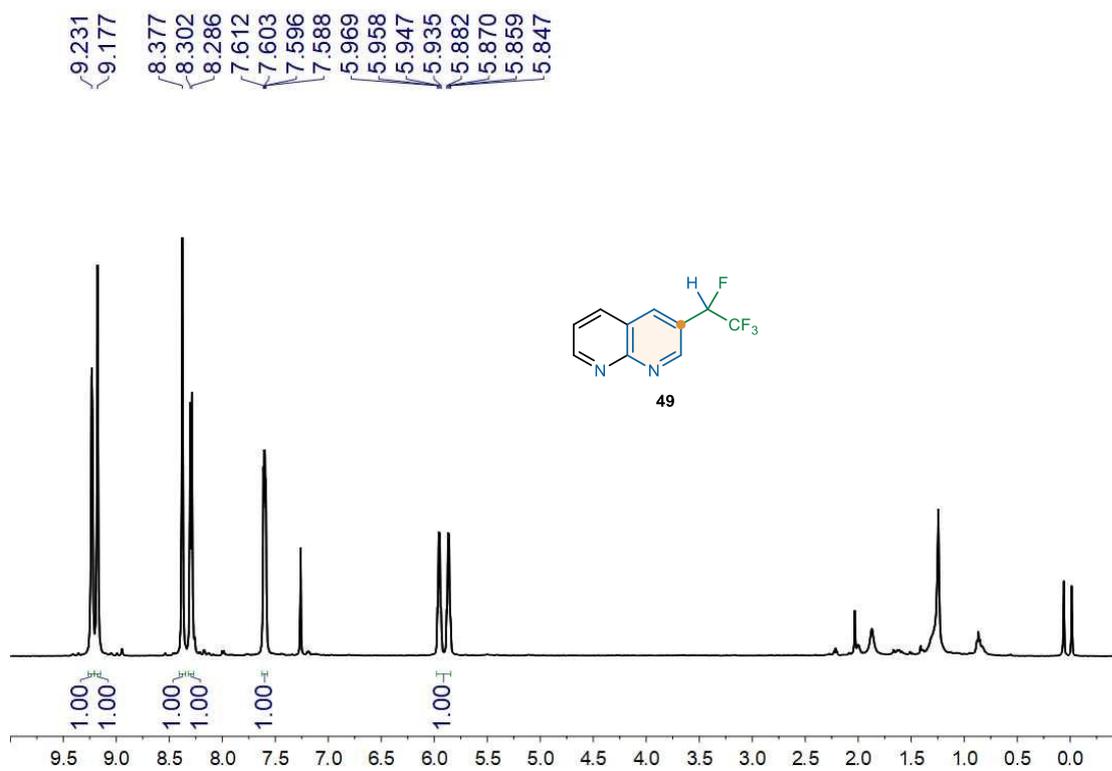
Supplementary Fig. 153.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **48**



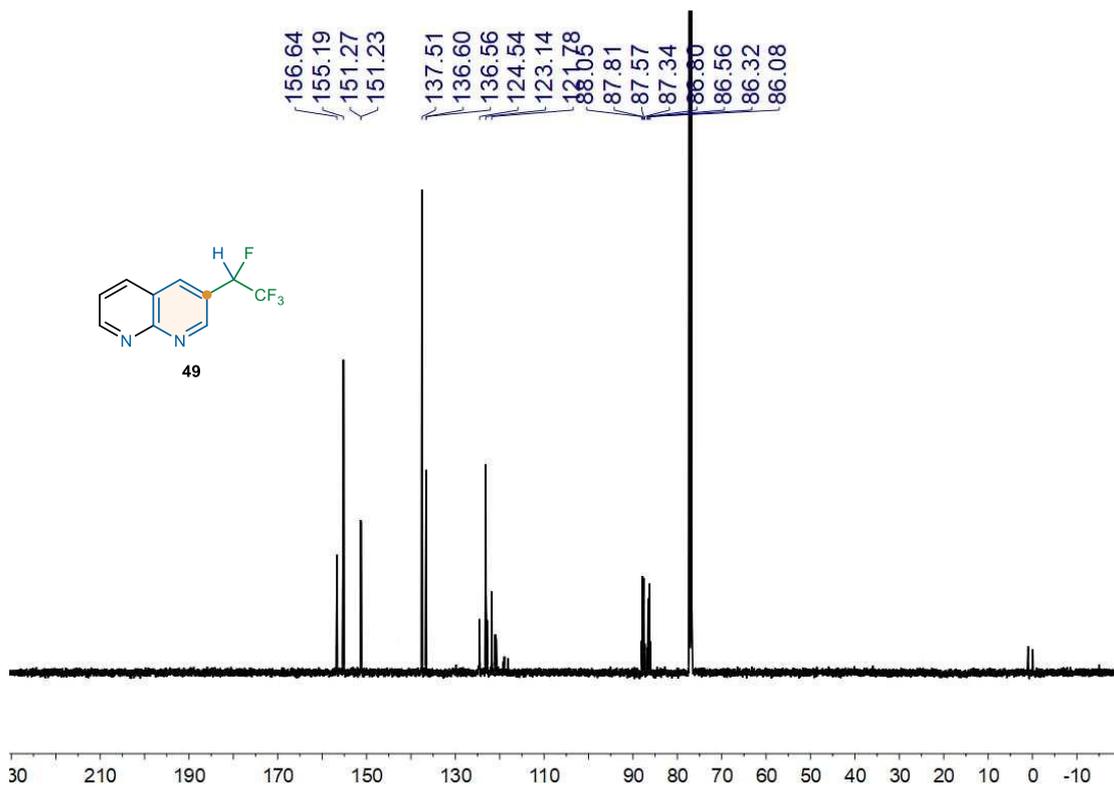
Supplementary Fig. 154.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **48**



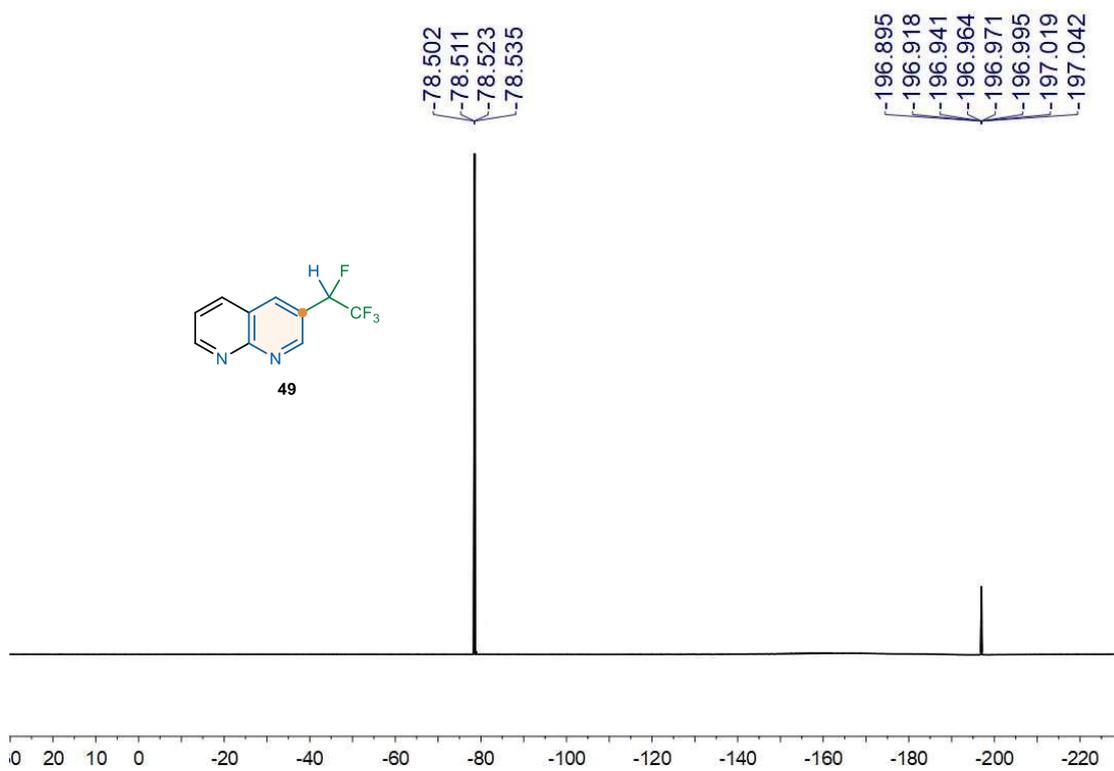
Supplementary Fig. 155.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ) spectrum of **48**



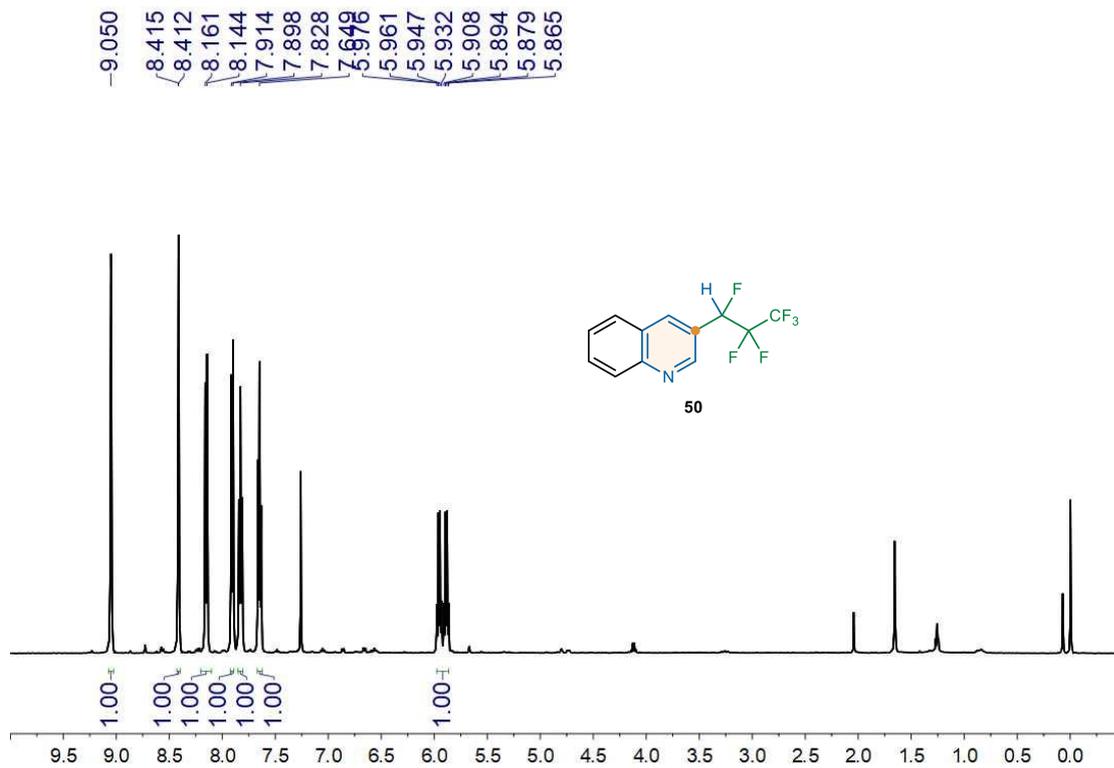
Supplementary Fig. 156.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **49**



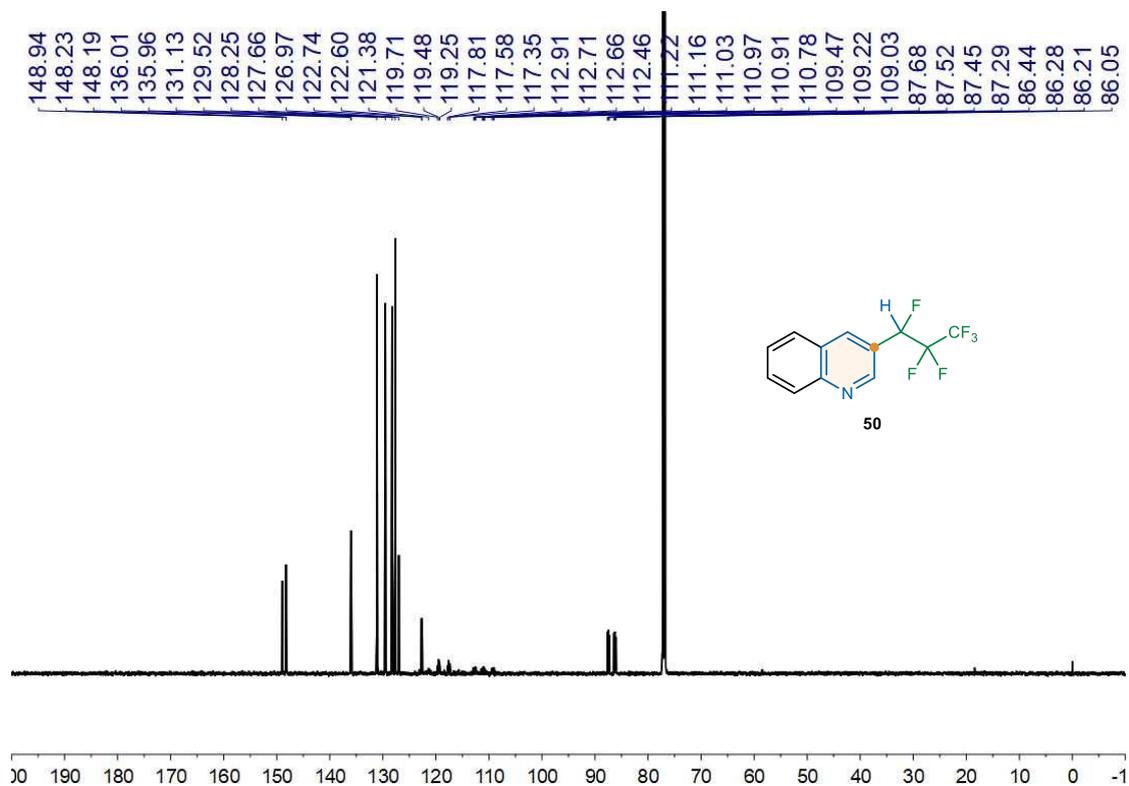
Supplementary Fig. 157. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of 49



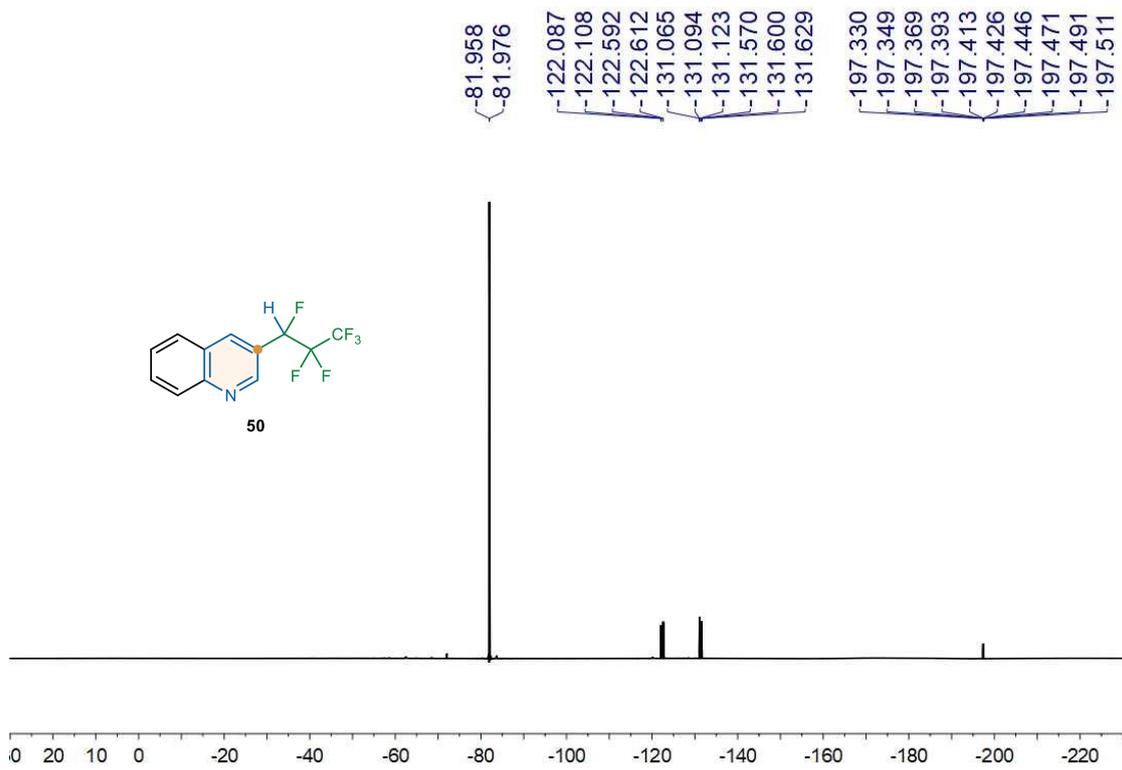
Supplementary Fig. 158. <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) spectrum of 49



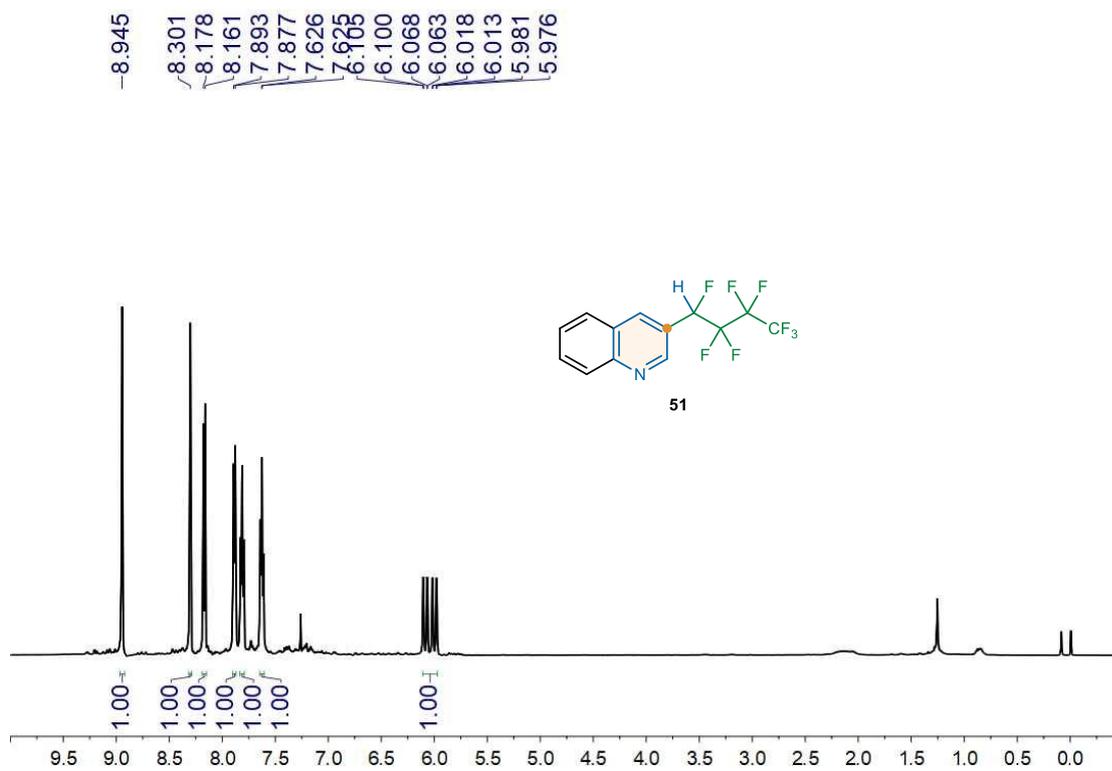
Supplementary Fig. 159.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **50**



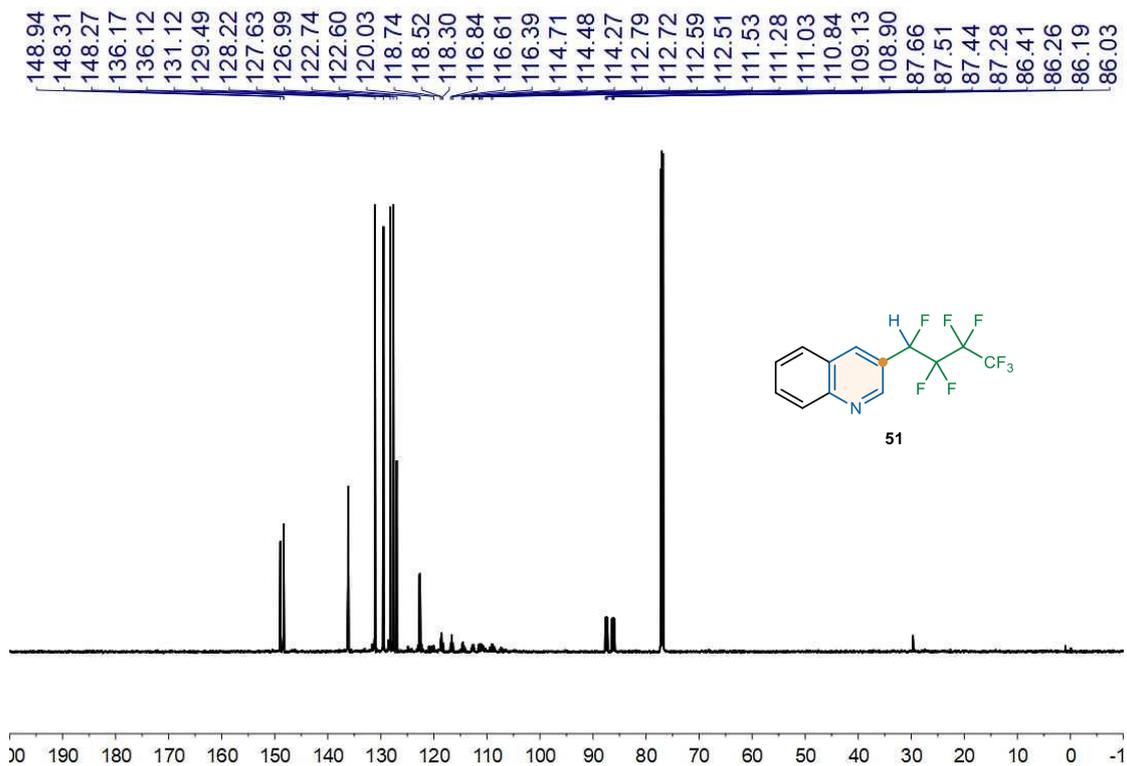
Supplementary Fig. 160.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **50**



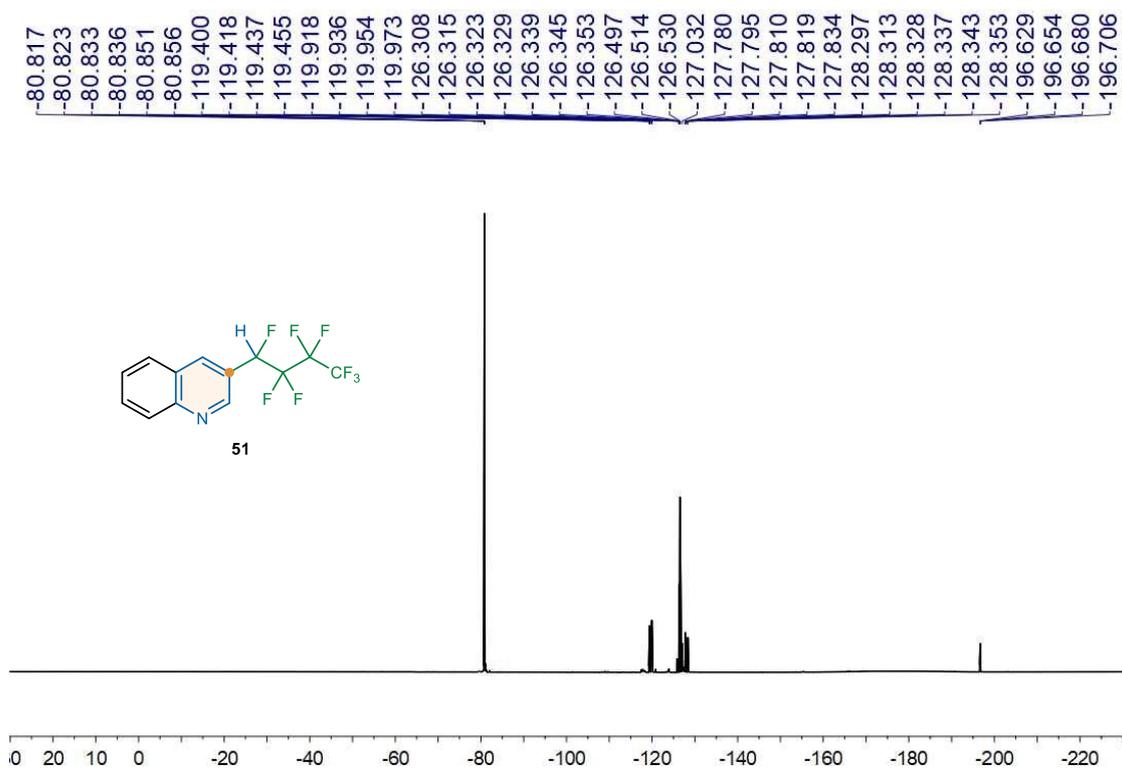
Supplementary Fig. 161.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ) spectrum of **50**



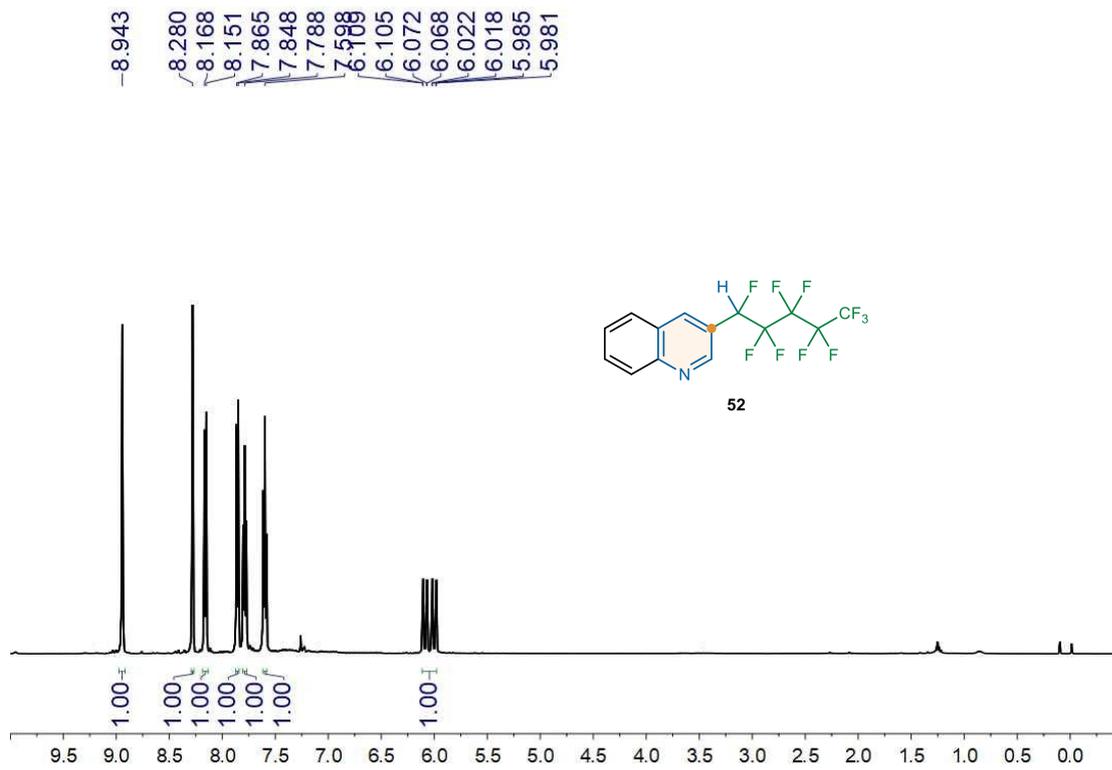
Supplementary Fig. 162.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **51**



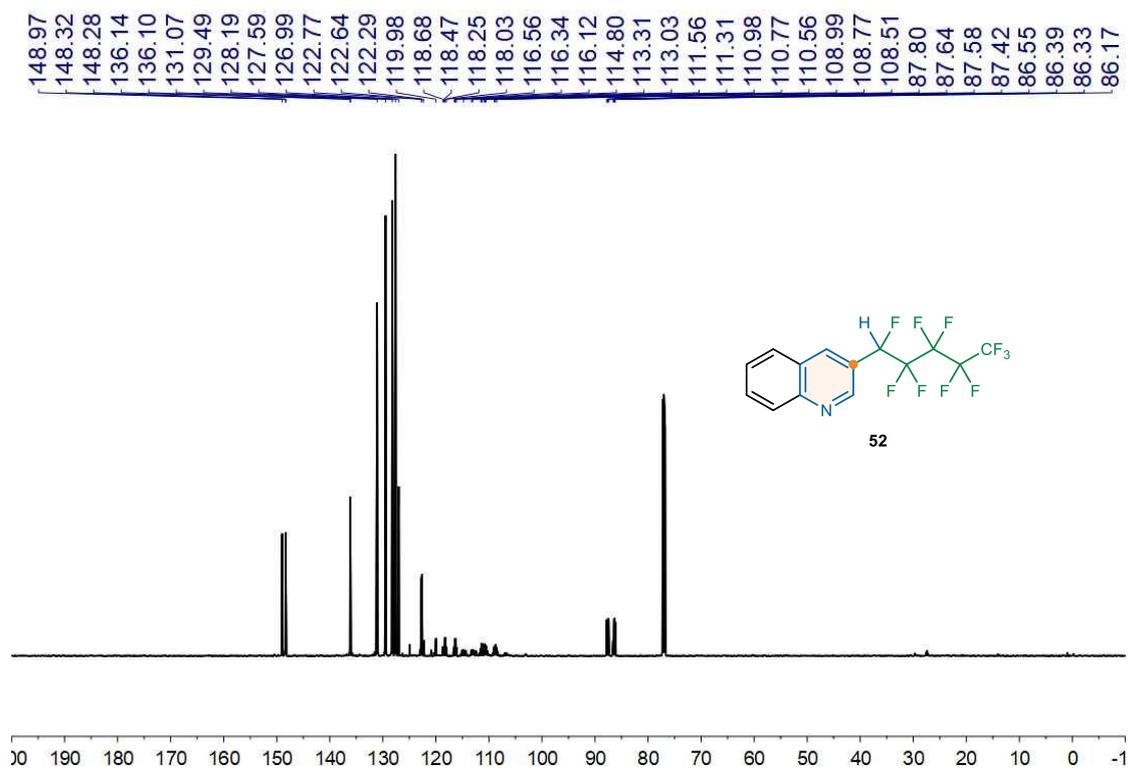
Supplementary Fig. 163. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of 51



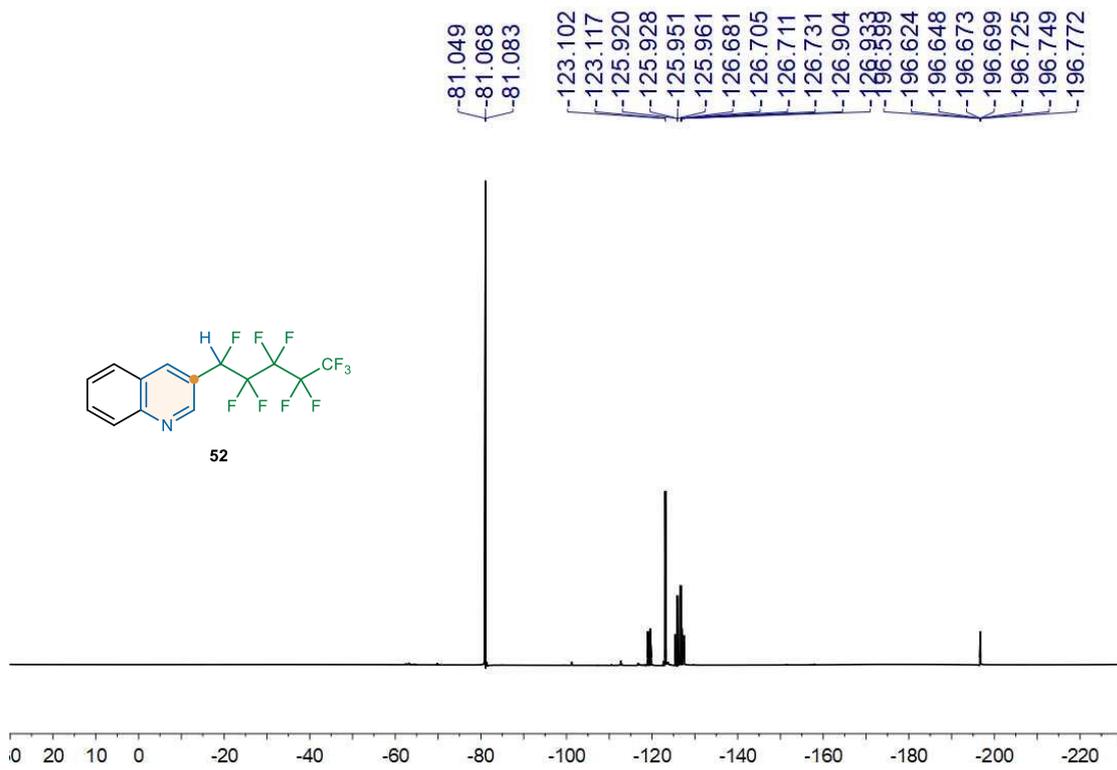
Supplementary Fig. 164. <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) spectrum of 51



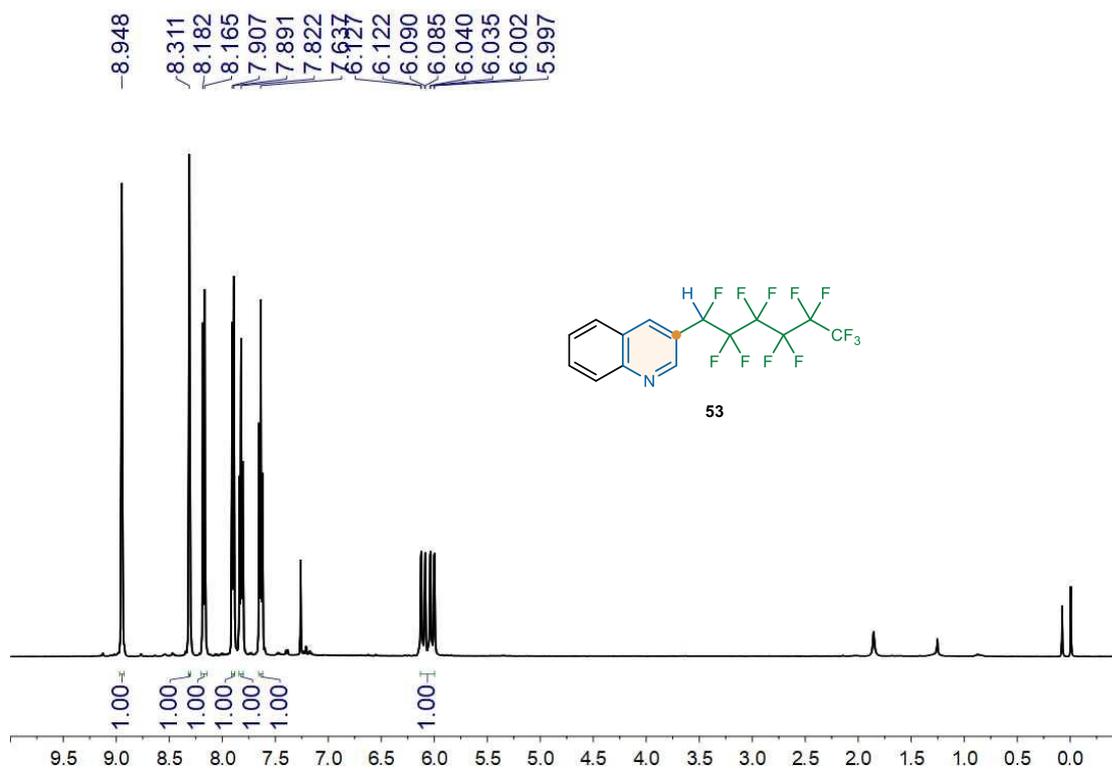
Supplementary Fig. 165.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **52**



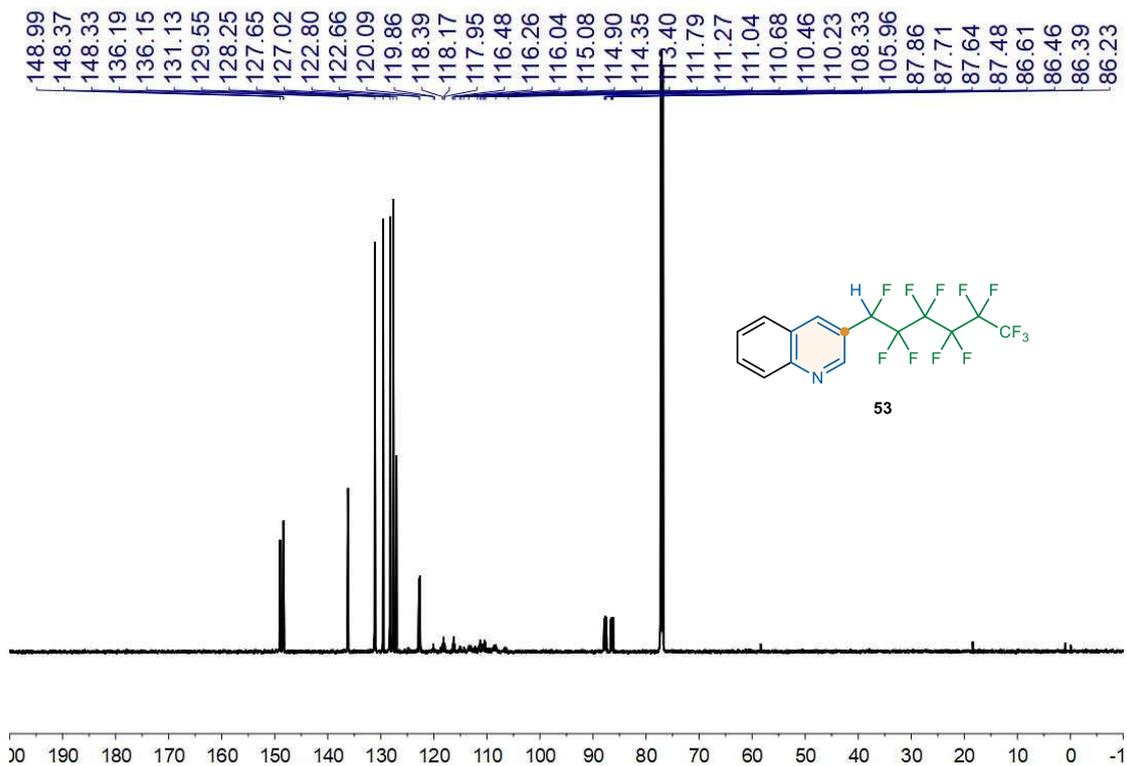
Supplementary Fig. 166.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **52**



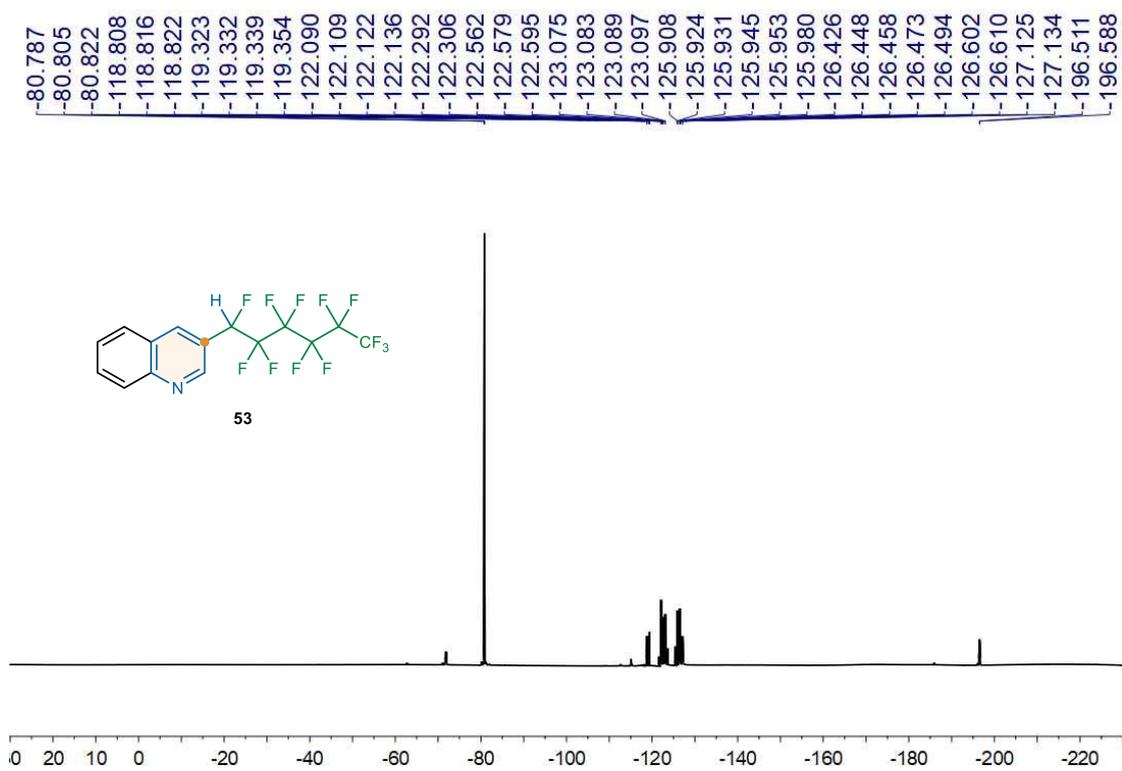
Supplementary Fig. 167. <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) spectrum of 52



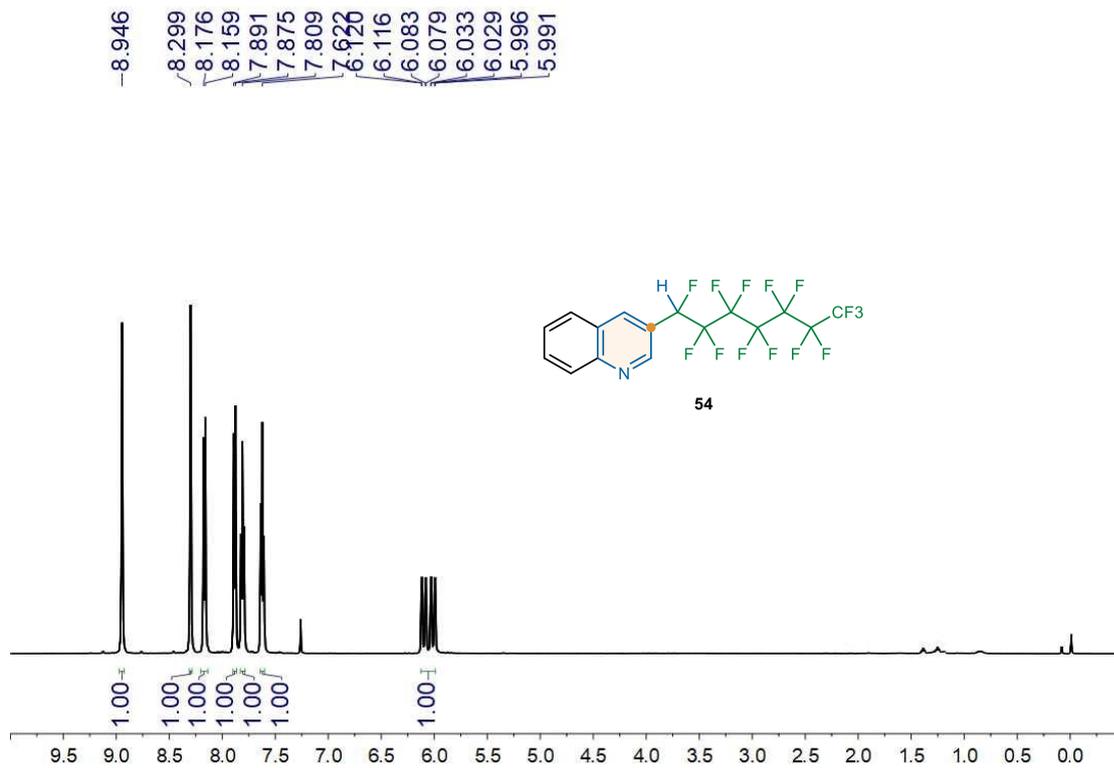
Supplementary Fig. 168. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of 53



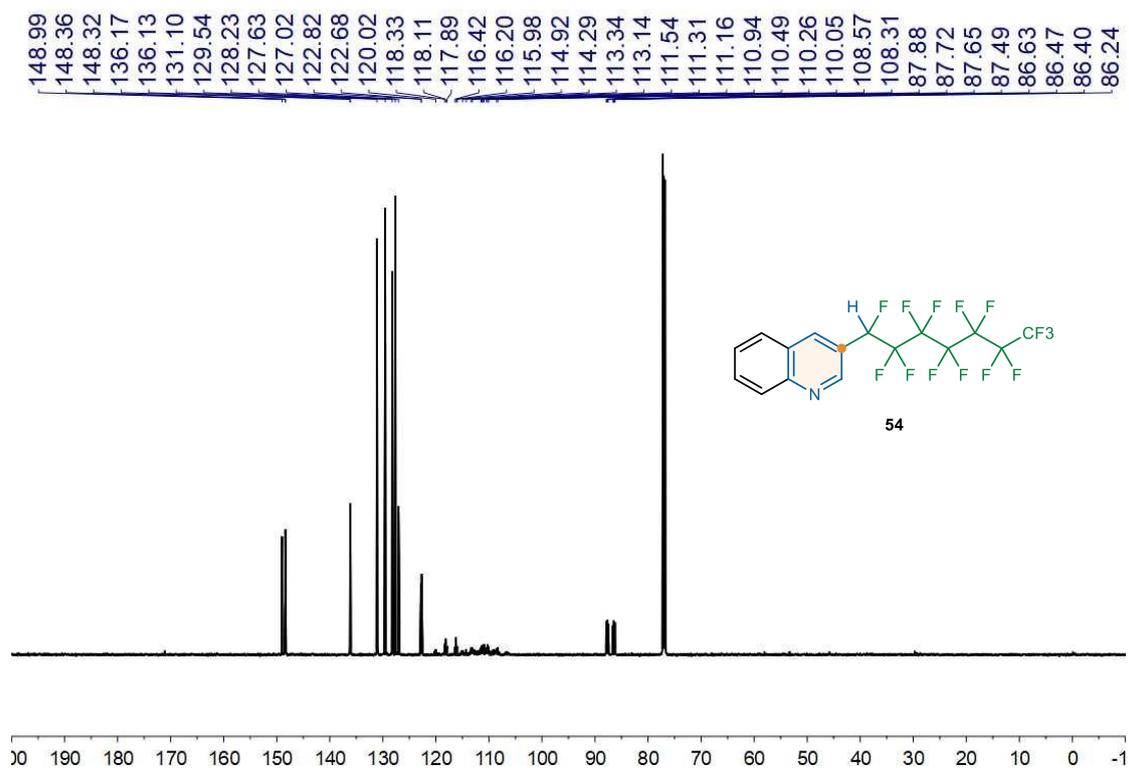
Supplementary Fig. 169. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of 53



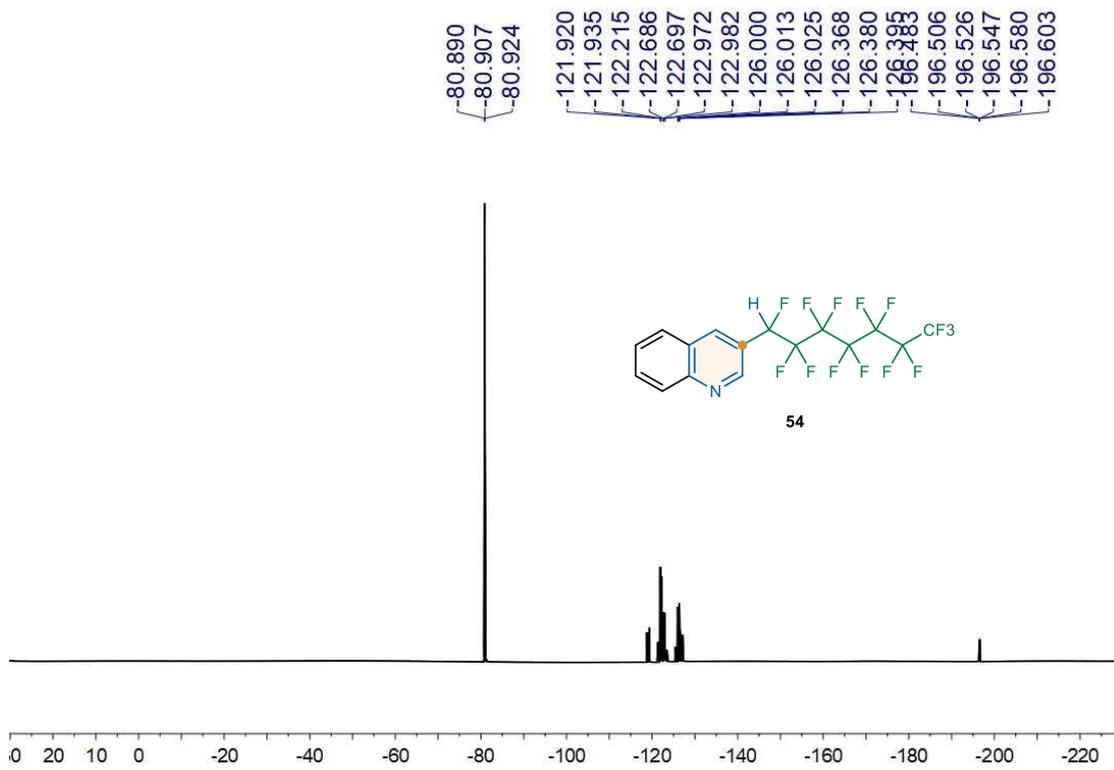
Supplementary Fig. 170. <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) spectrum of 53



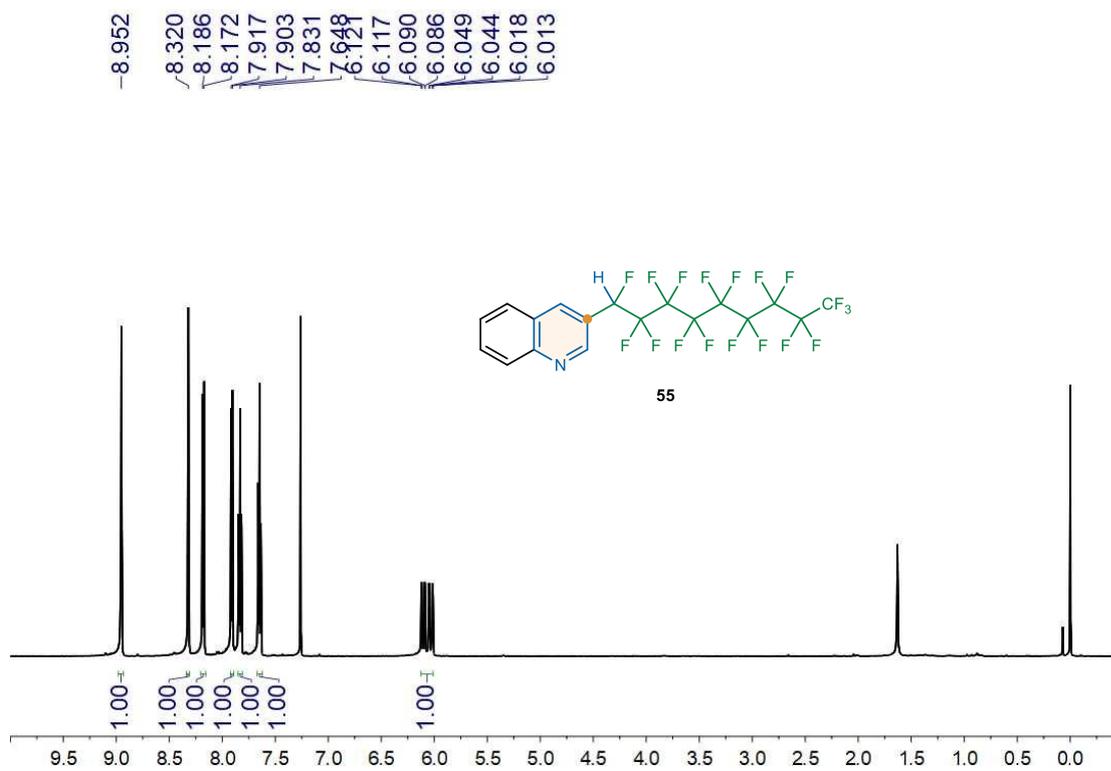
Supplementary Fig. 171.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **54**



Supplementary Fig. 172.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **54**

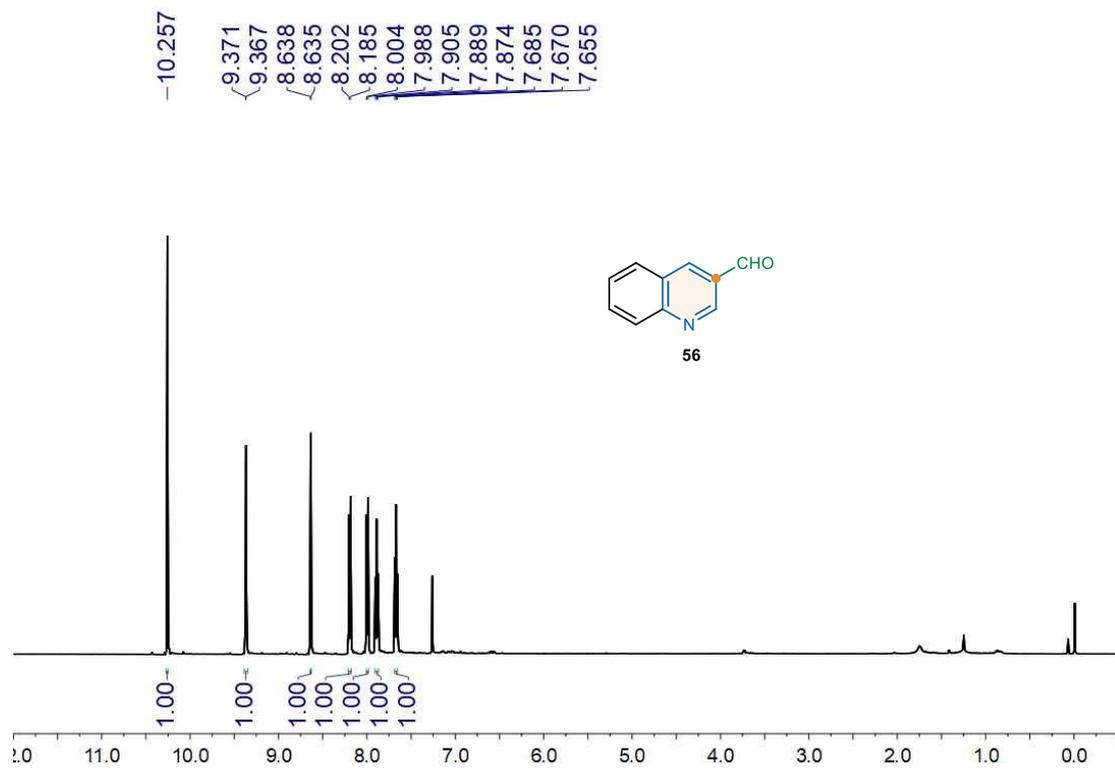


Supplementary Fig. 173. <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) spectrum of 54

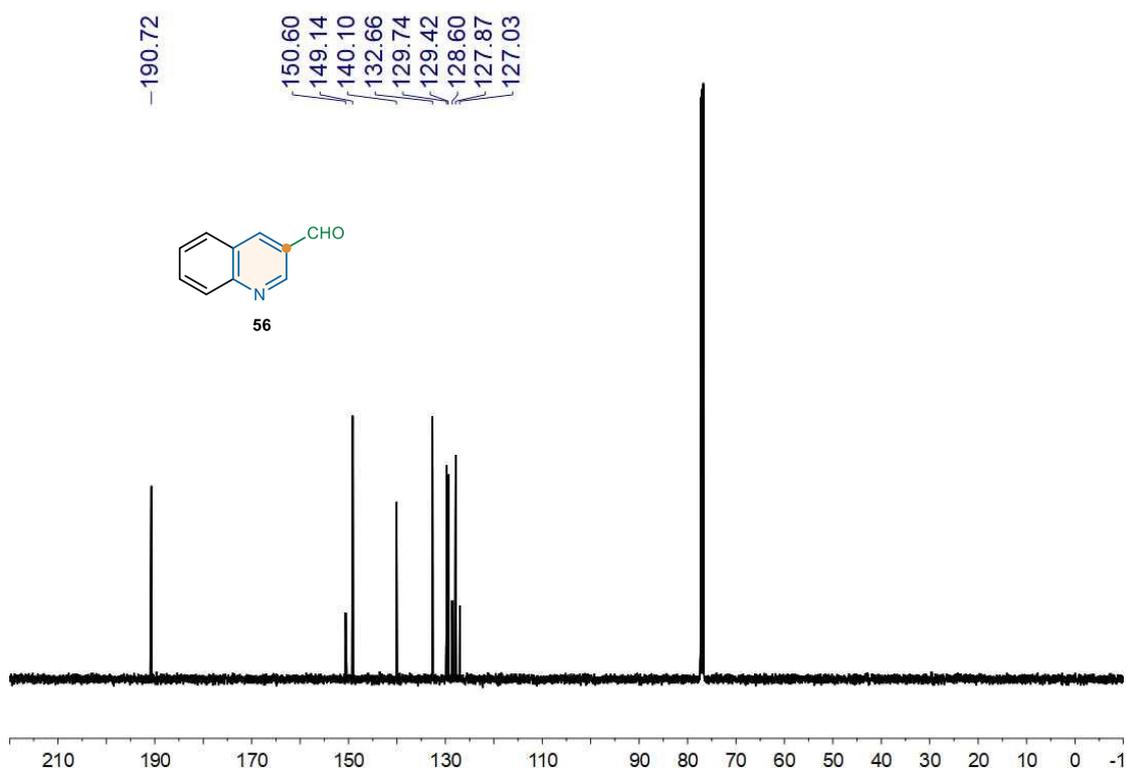


Supplementary Fig. 174. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of 55

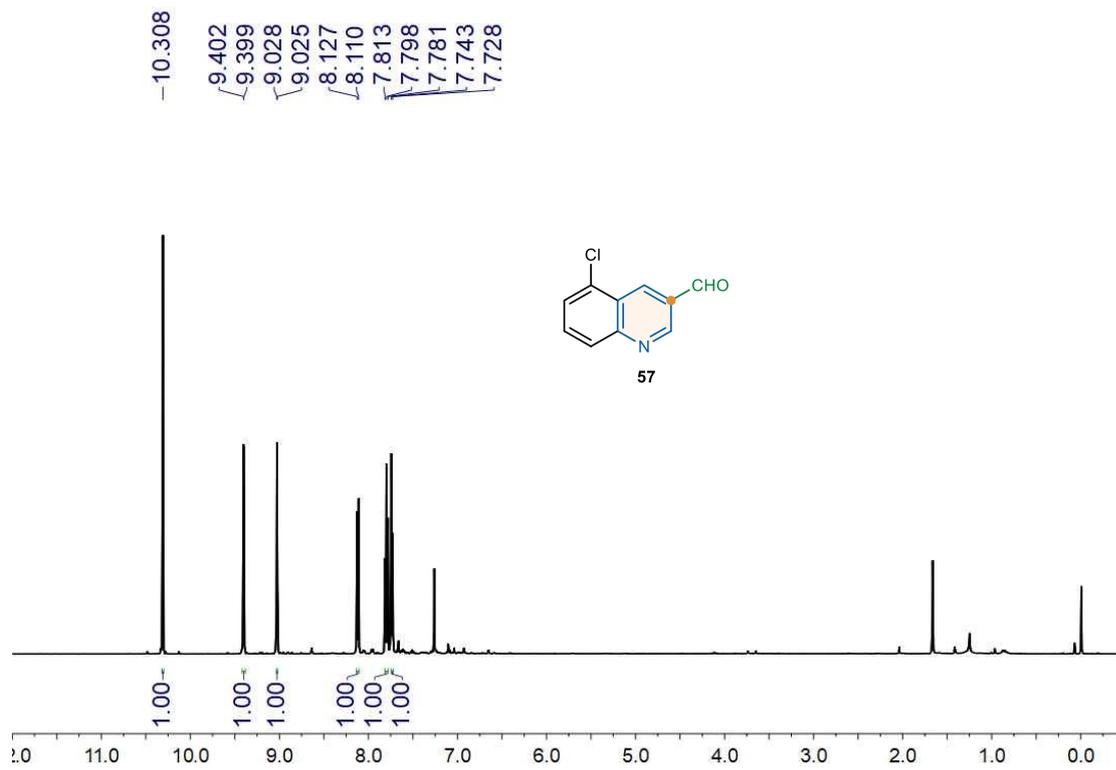




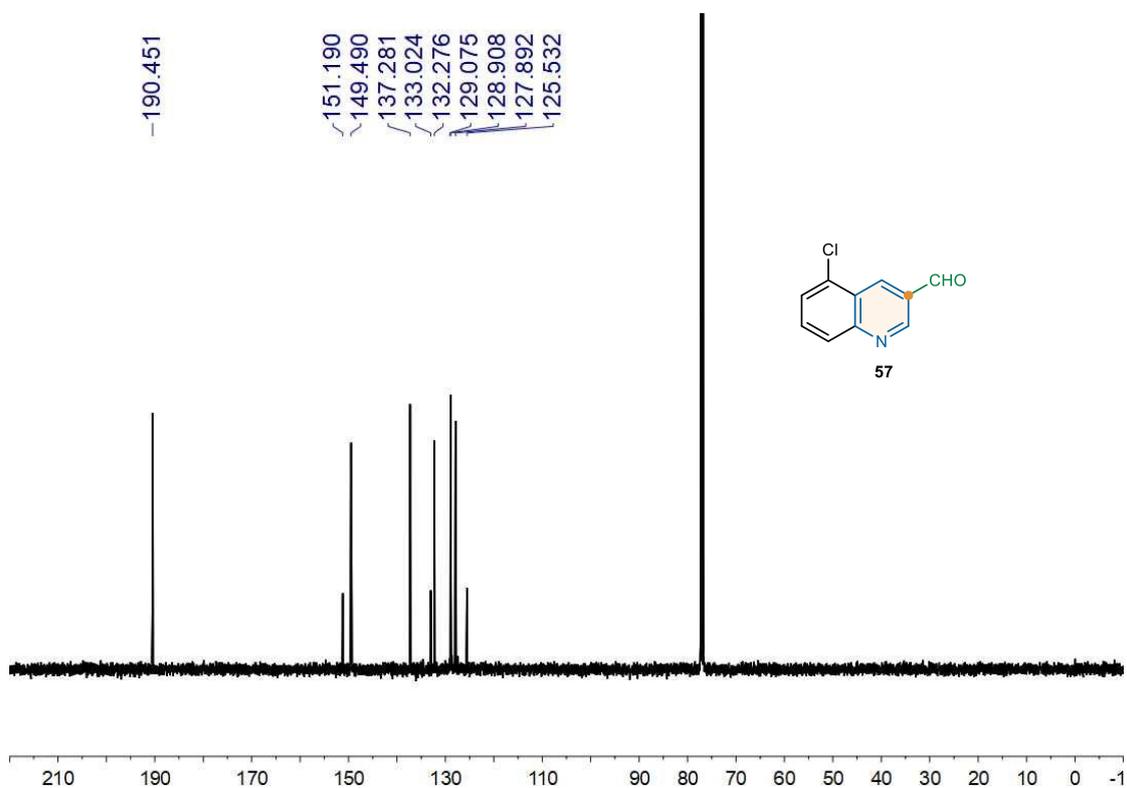
Supplementary Fig. 177.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **56**



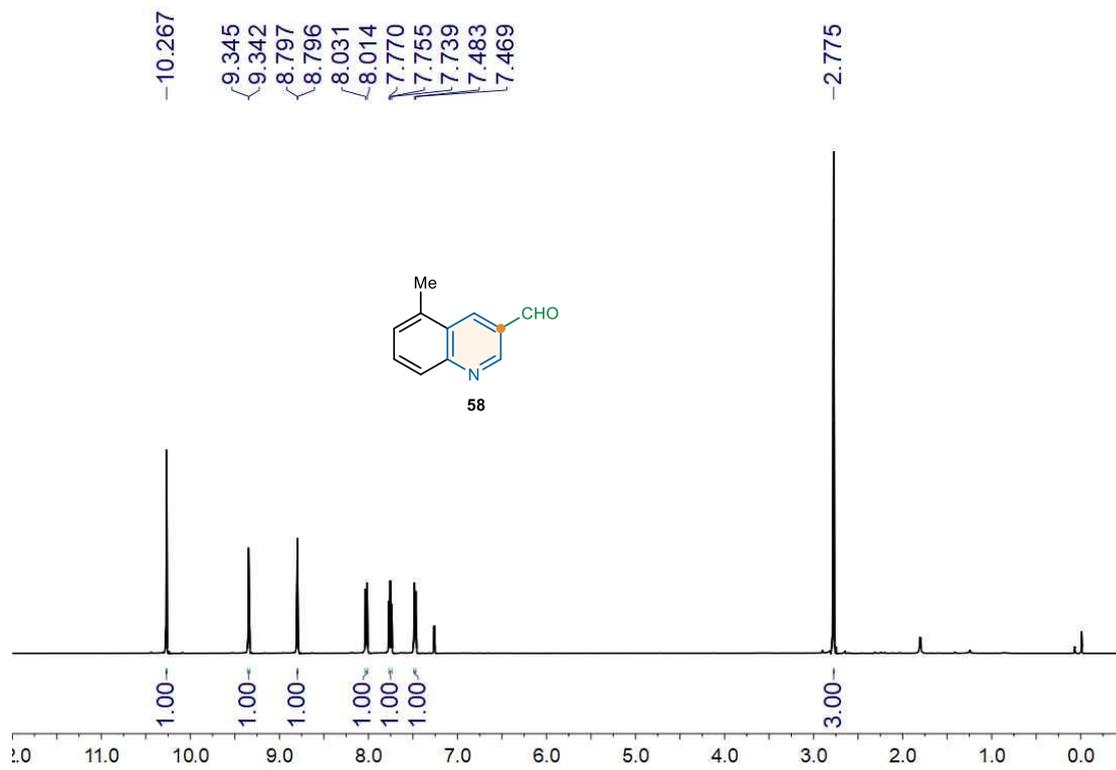
Supplementary Fig. 178.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of **56**



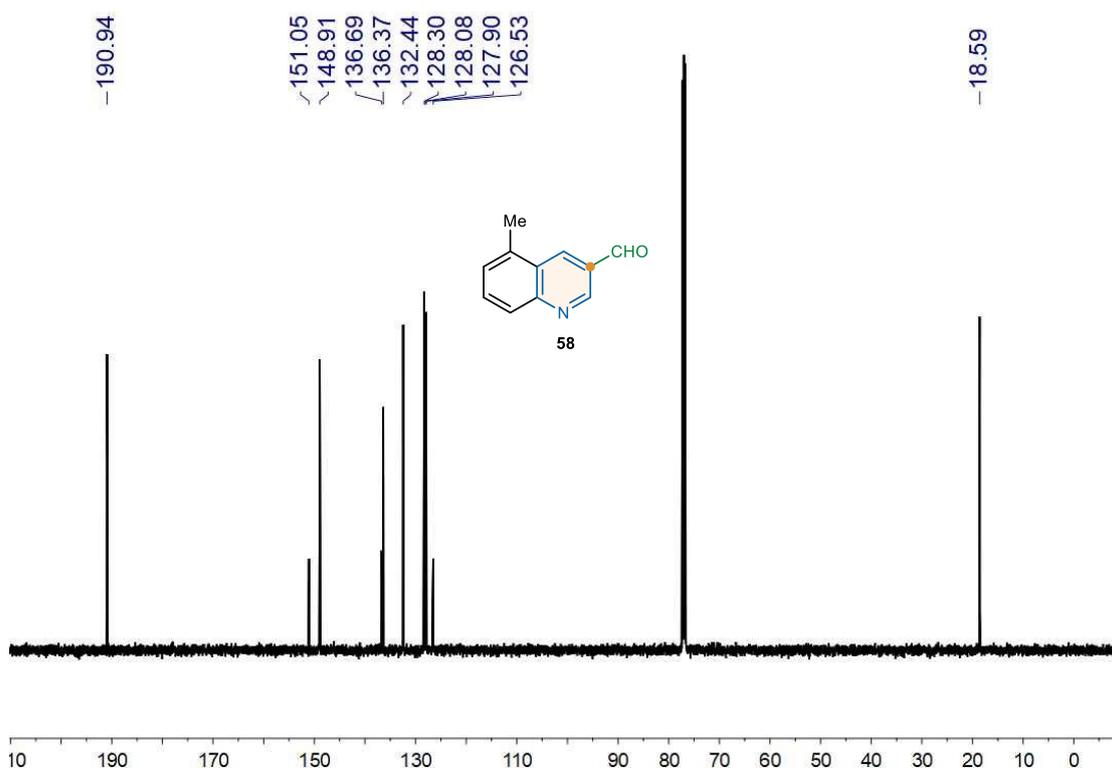
Supplementary Fig. 179.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of 57



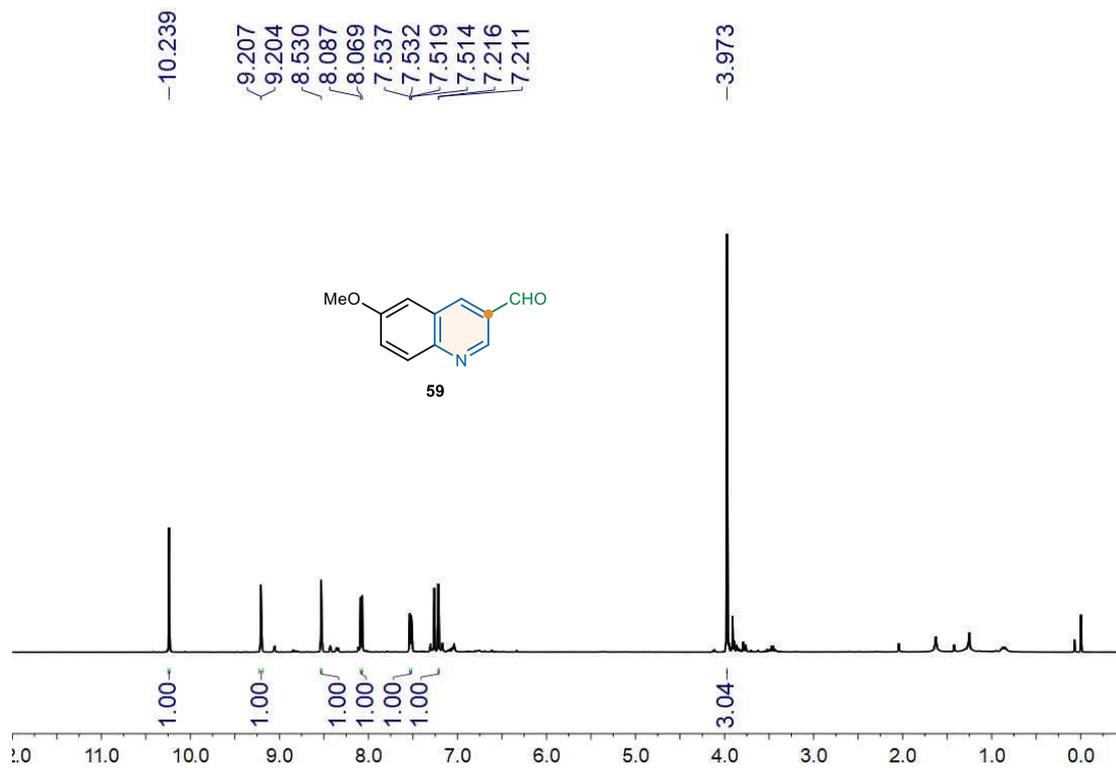
Supplementary Fig. 180.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of 57



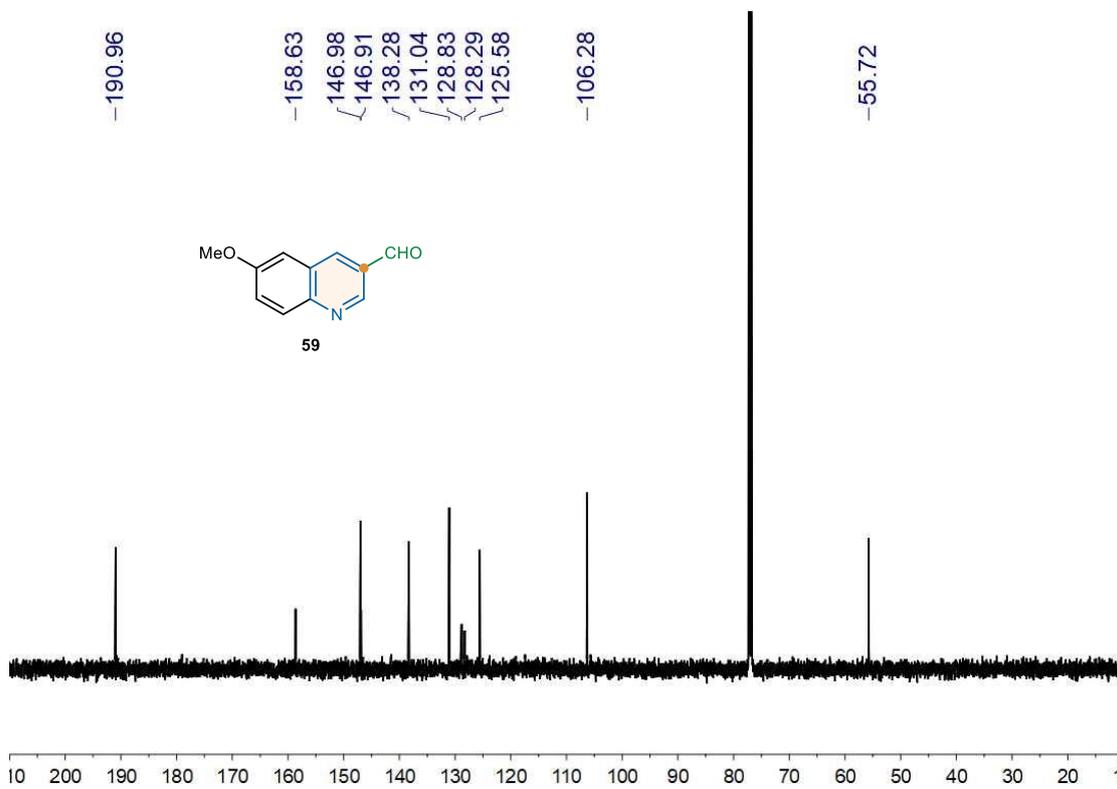
Supplementary Fig. 181. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **58**



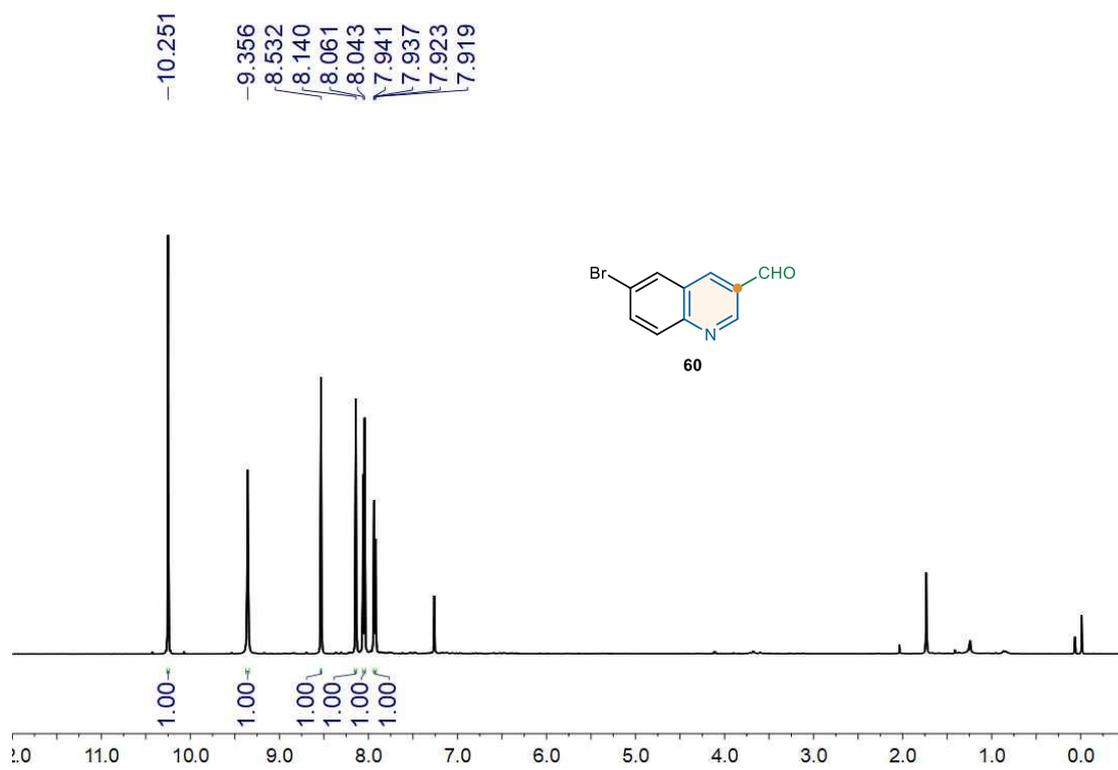
Supplementary Fig. 182. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of **58**



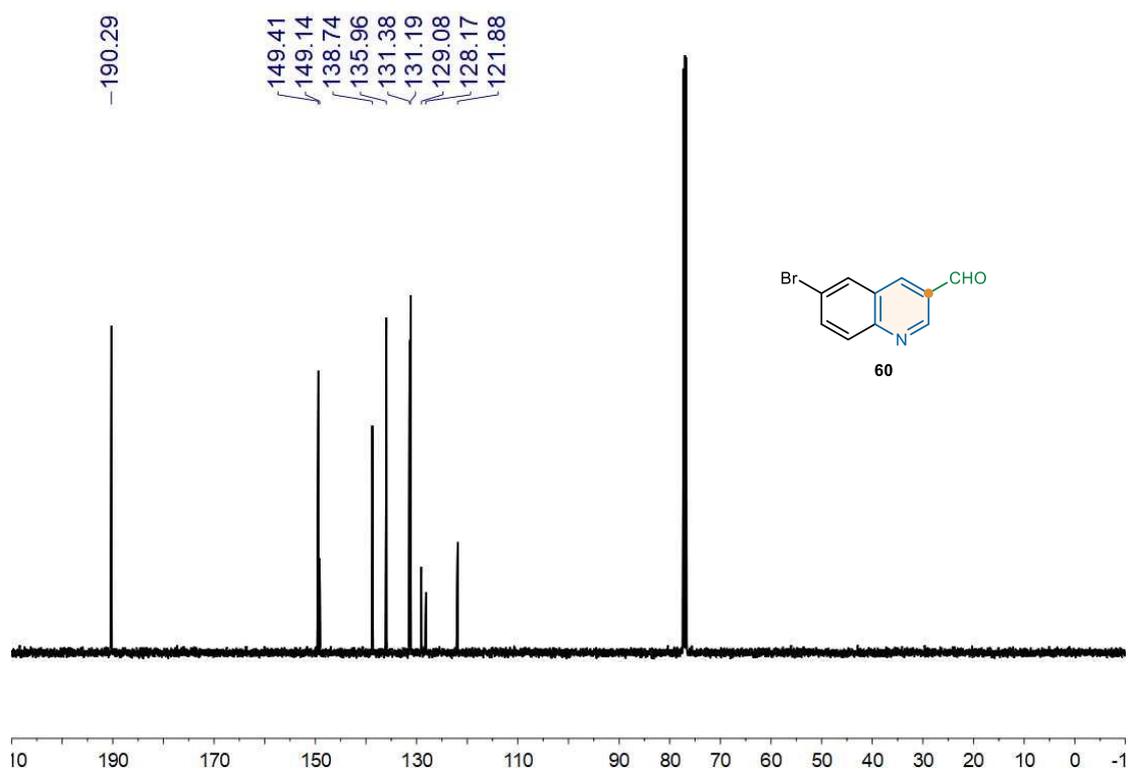
Supplementary Fig. 183. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **59**



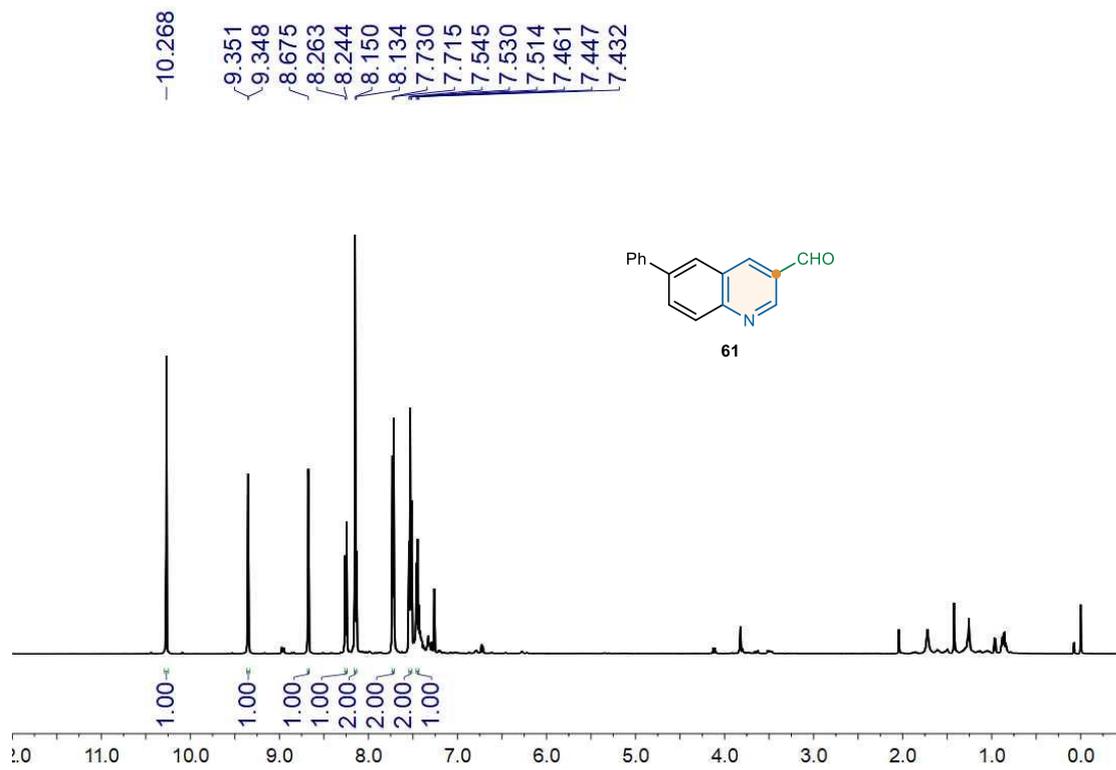
Supplementary Fig. 184. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of **59**



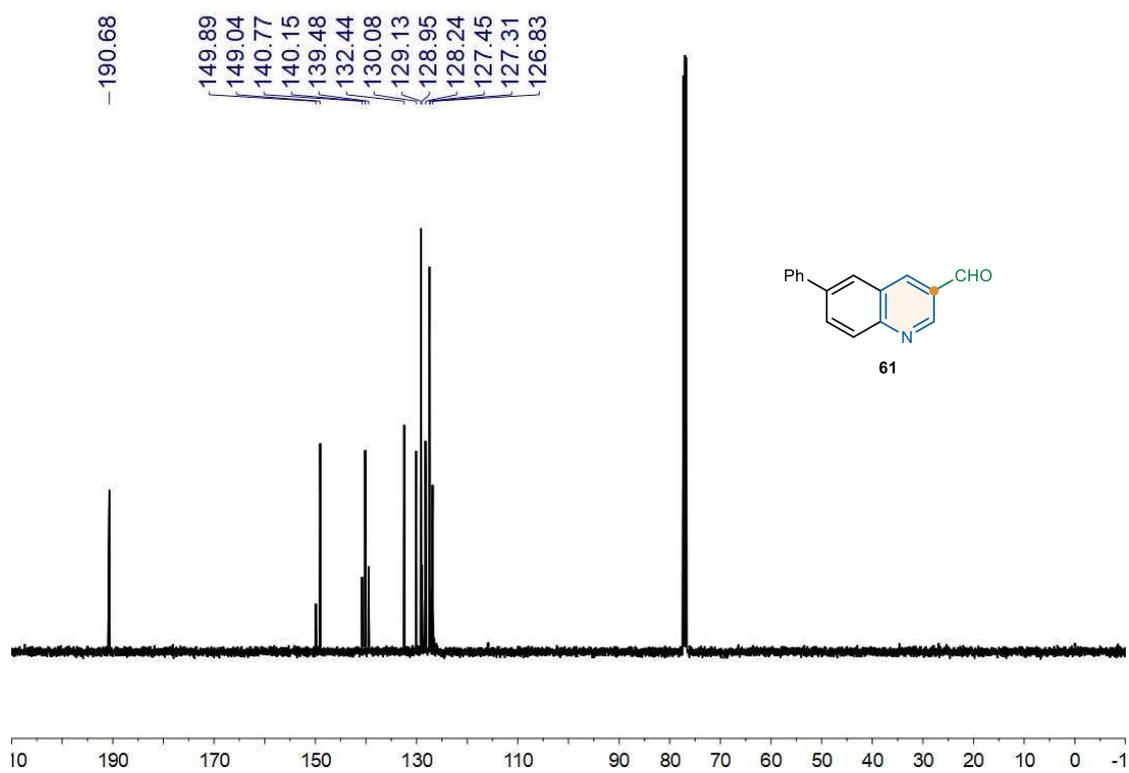
Supplementary Fig. 185.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **60**



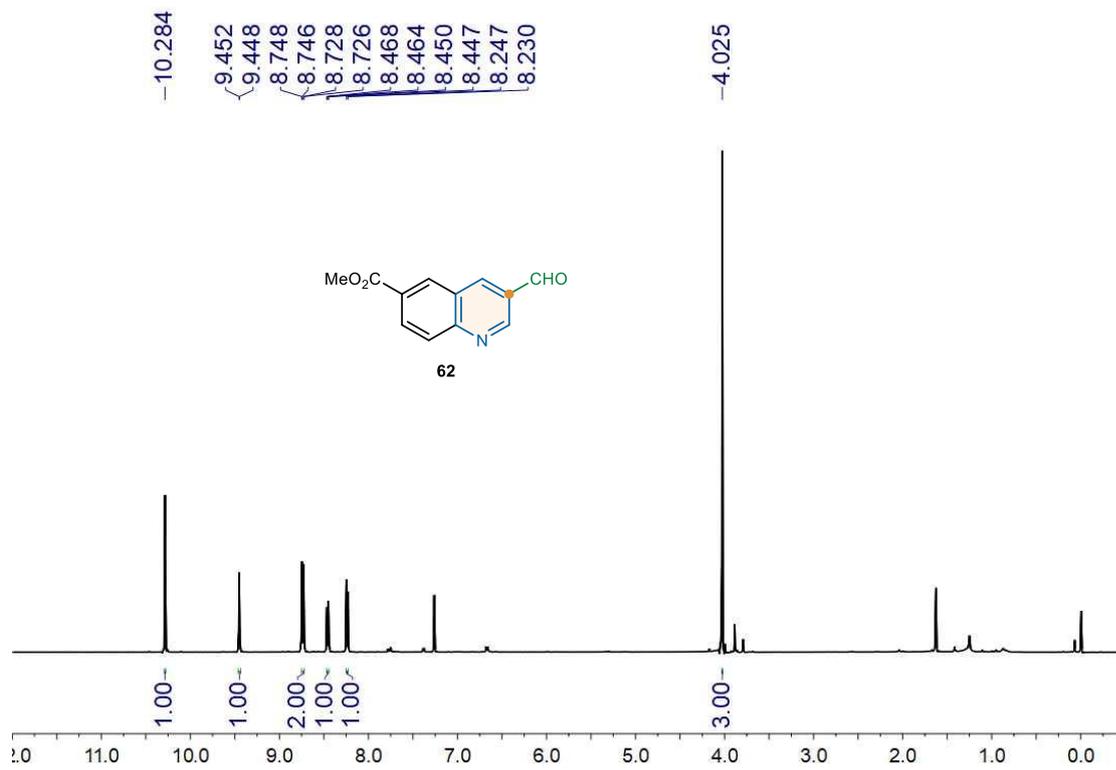
Supplementary Fig. 186.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of **60**



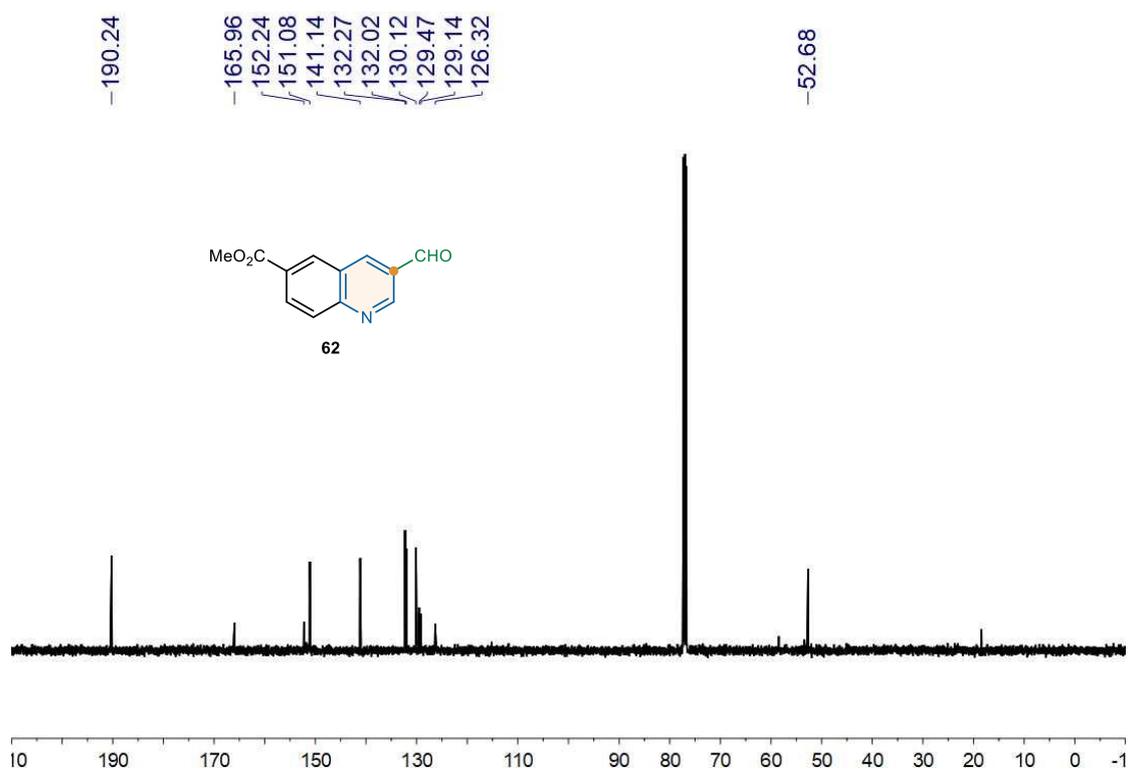
Supplementary Fig. 187.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **61**



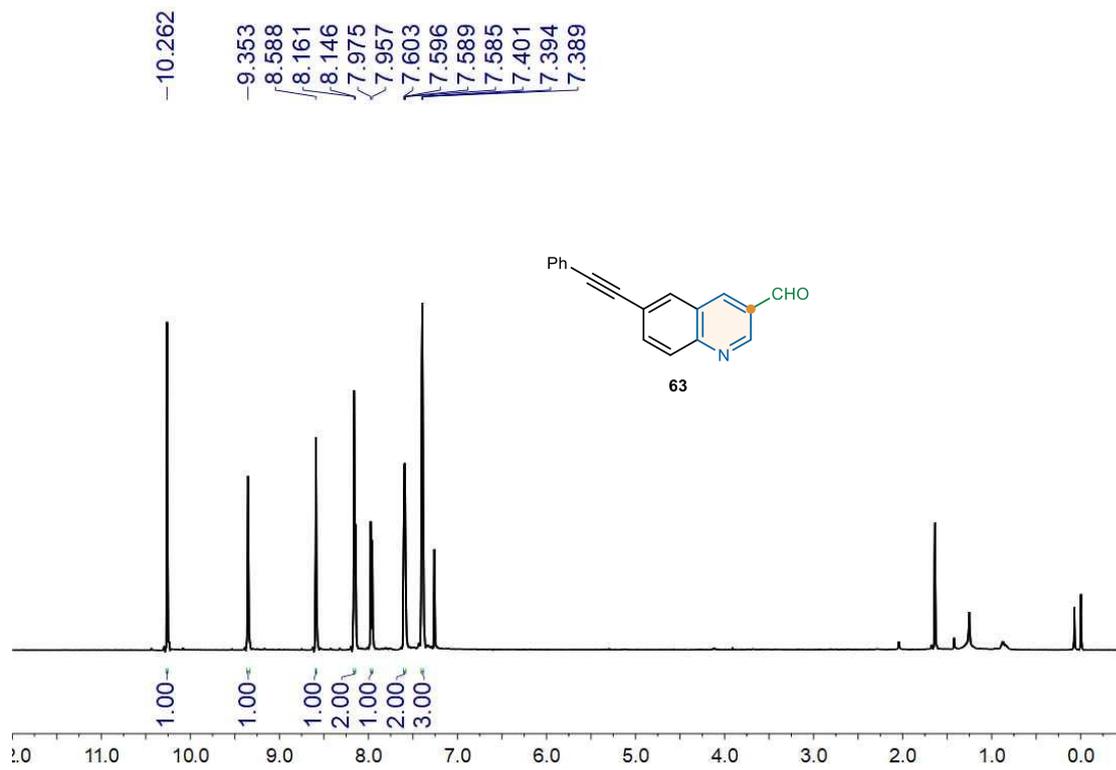
Supplementary Fig. 188.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of **61**



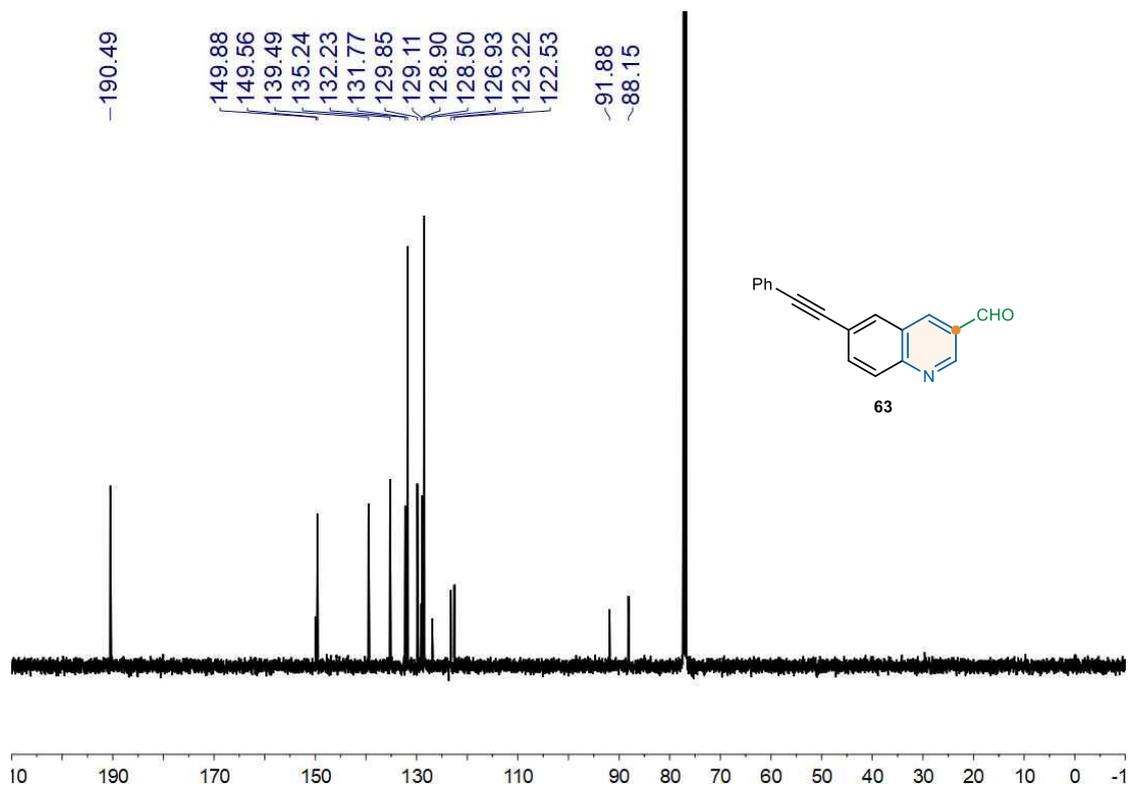
Supplementary Fig. 189.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **62**



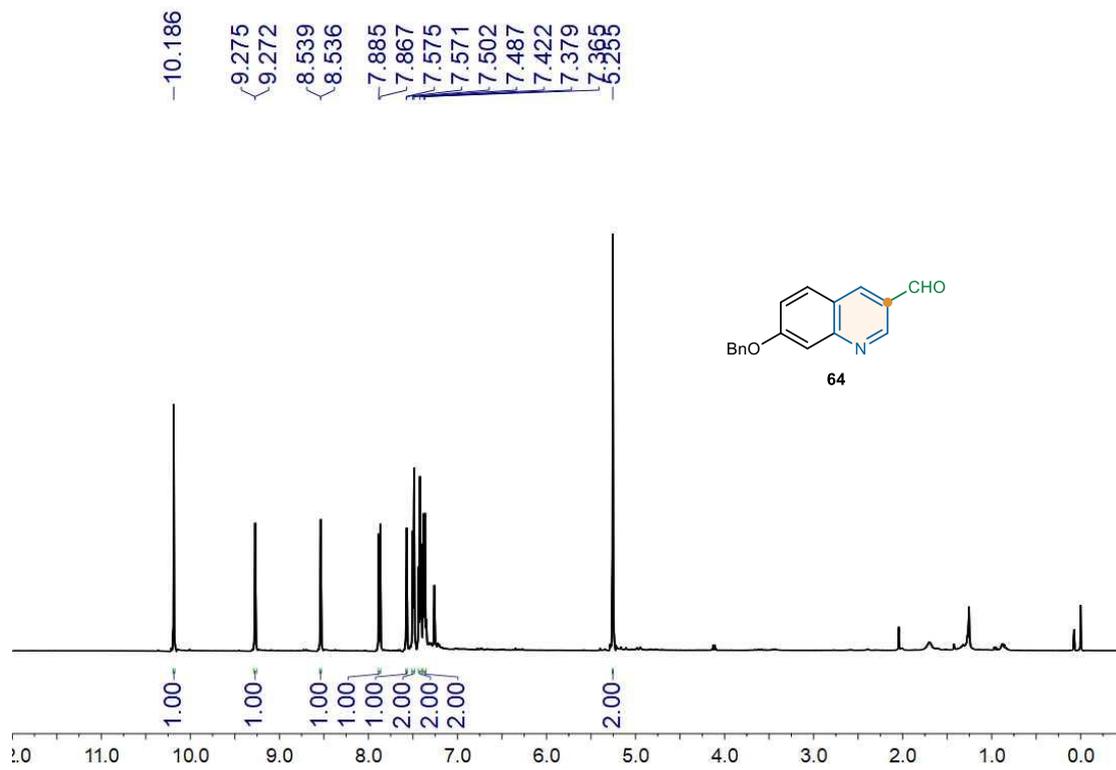
Supplementary Fig. 190.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of **62**



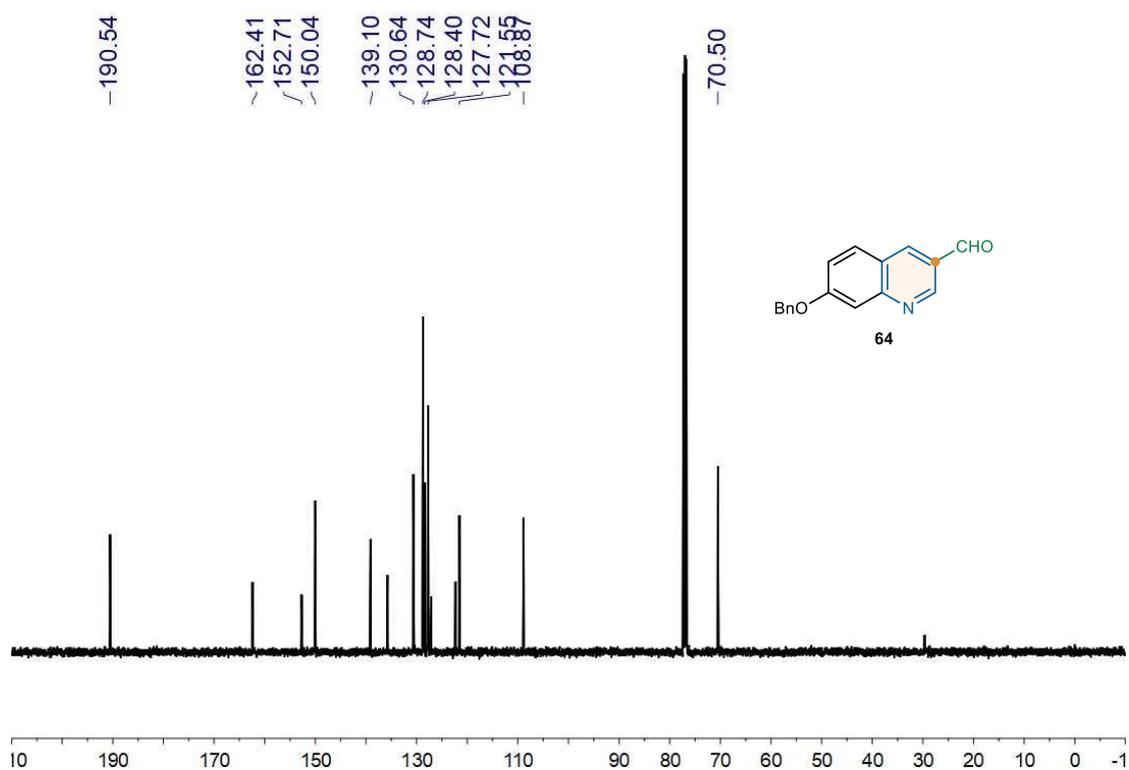
Supplementary Fig. 191.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **63**



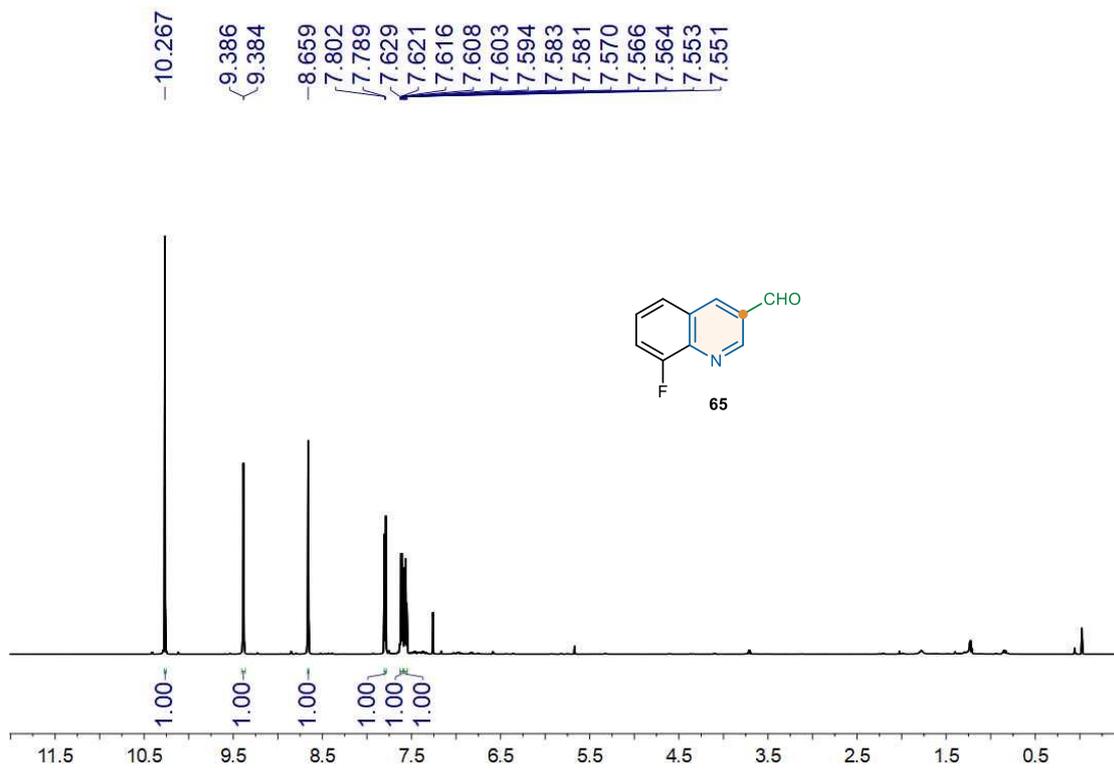
Supplementary Fig. 192.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of **63**



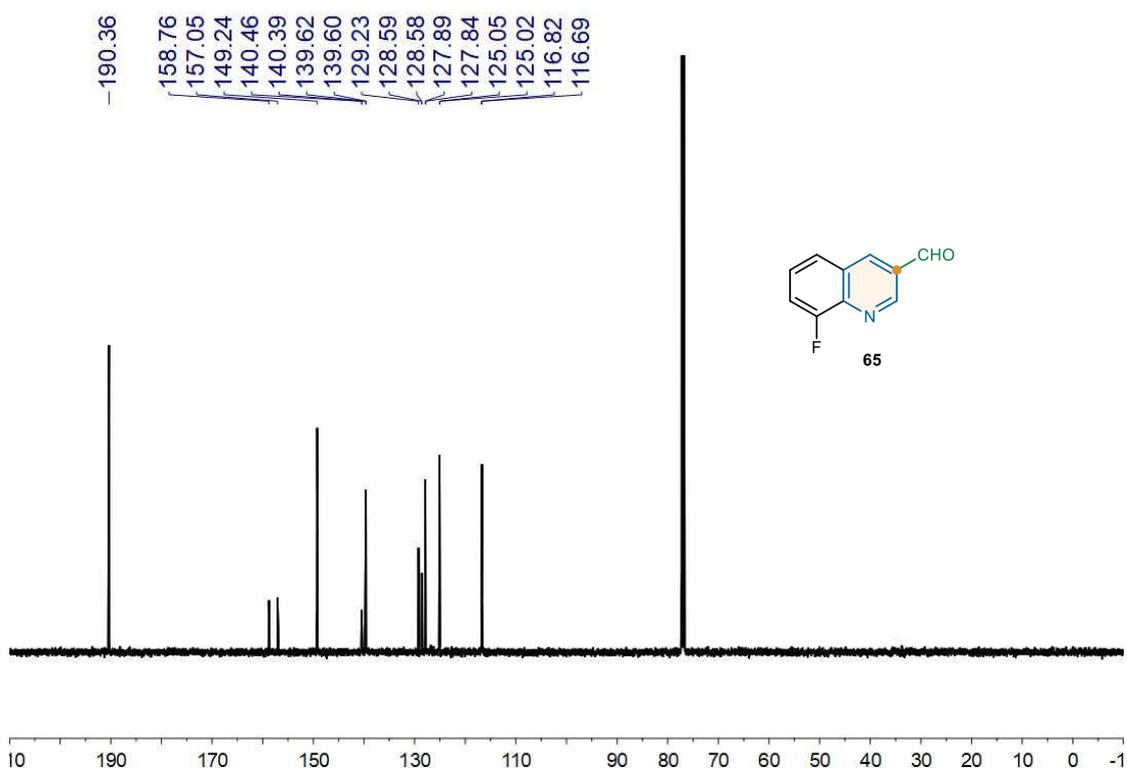
Supplementary Fig. 193.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **64**



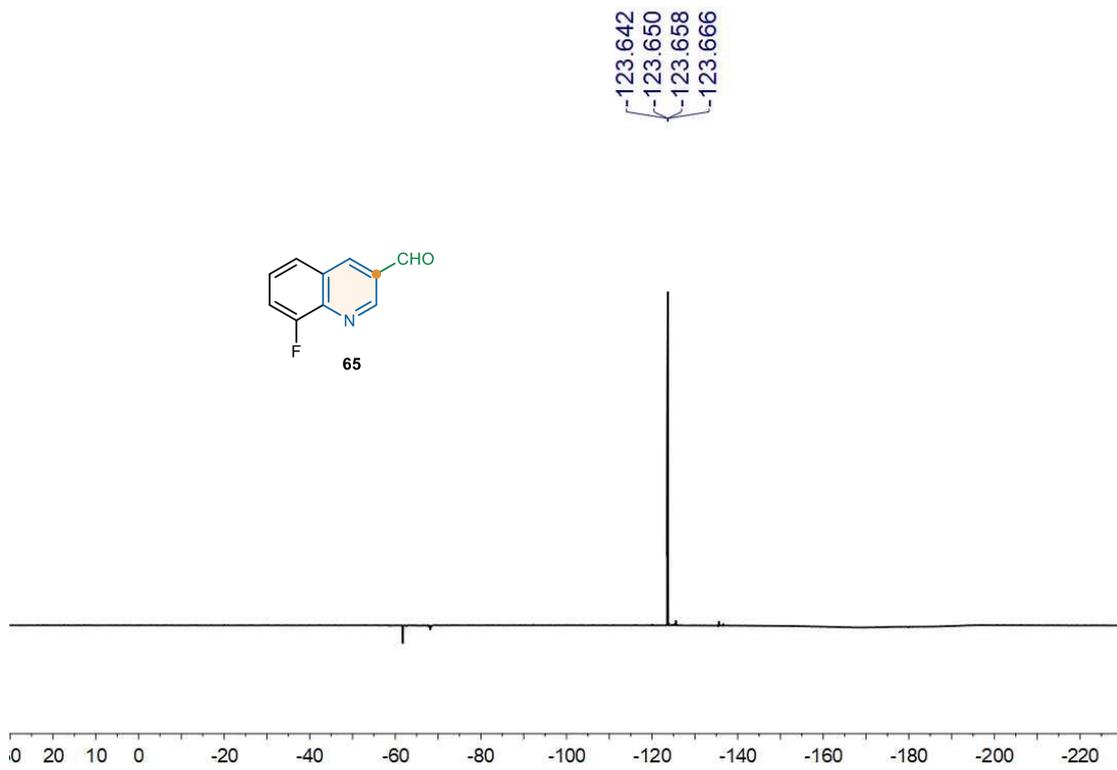
Supplementary Fig. 194.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of **64**



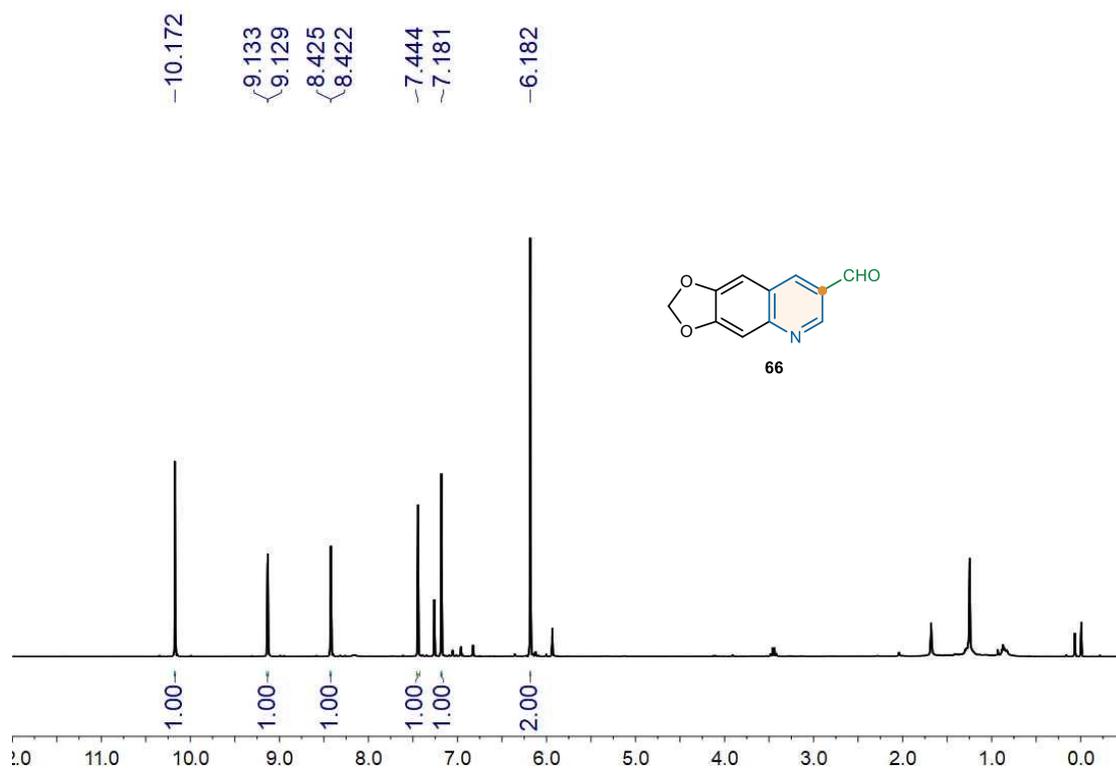
Supplementary Fig. 195.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) spectrum of **65**



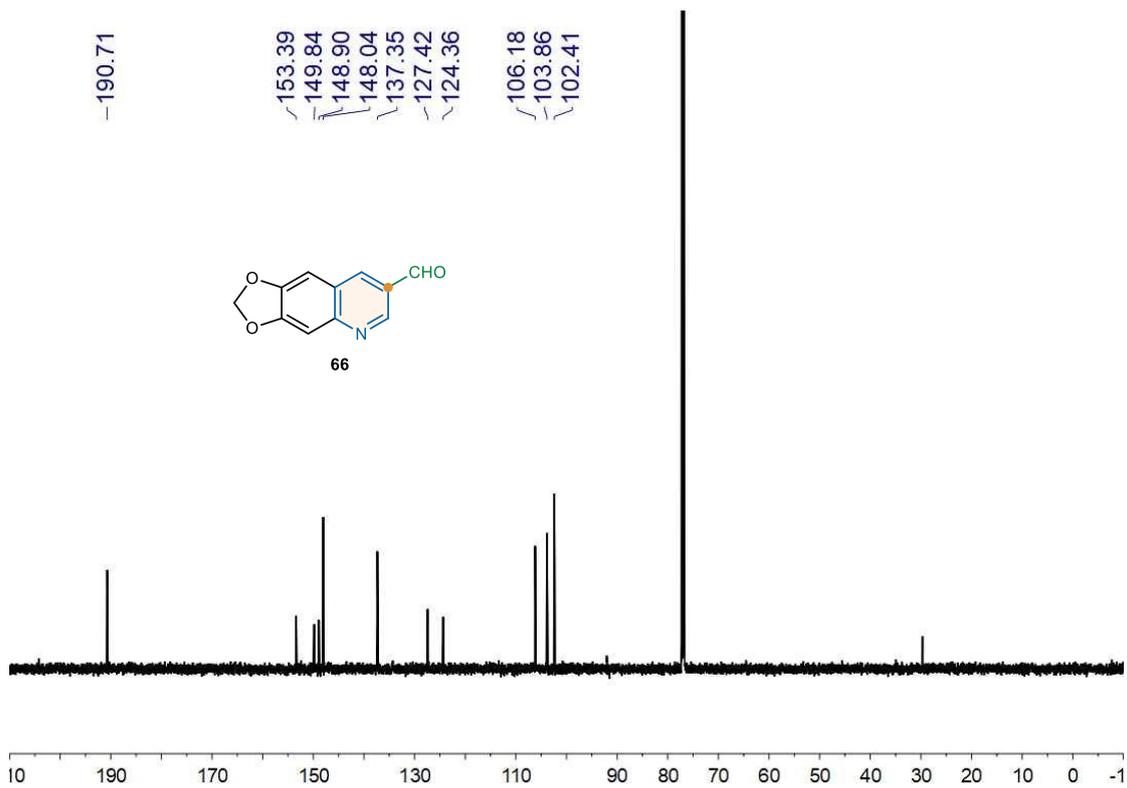
Supplementary Fig. 196.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **65**



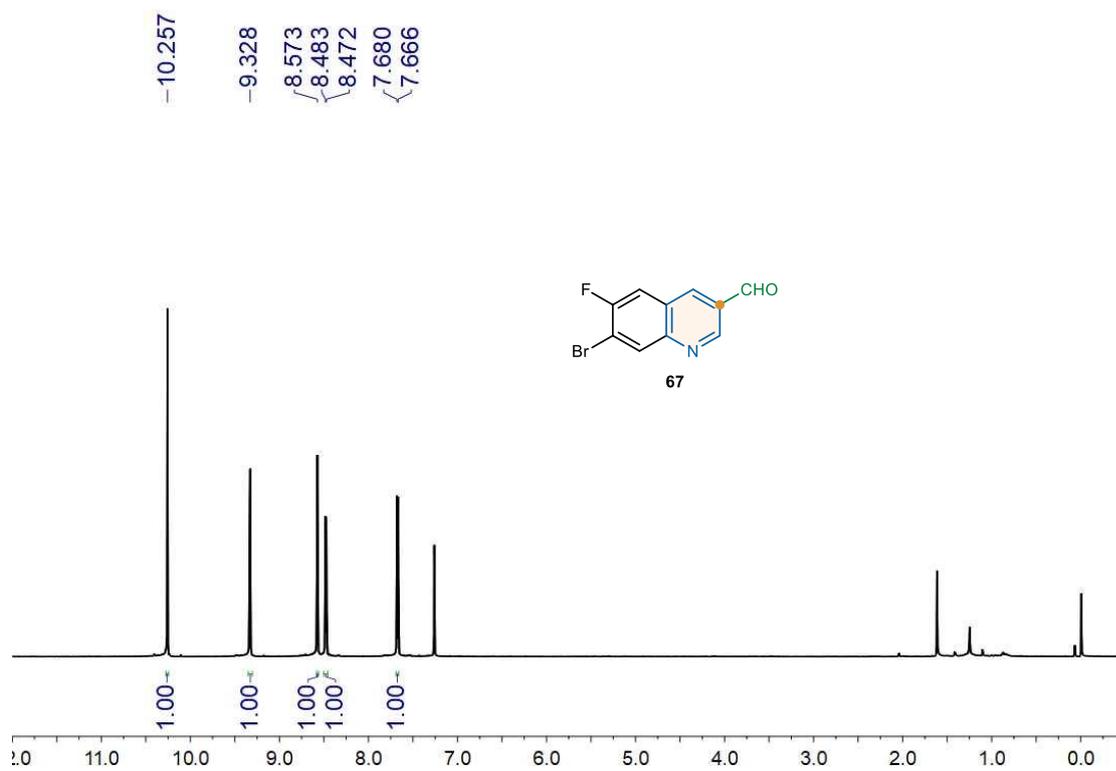
Supplementary Fig. 197.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ) spectrum of **65**



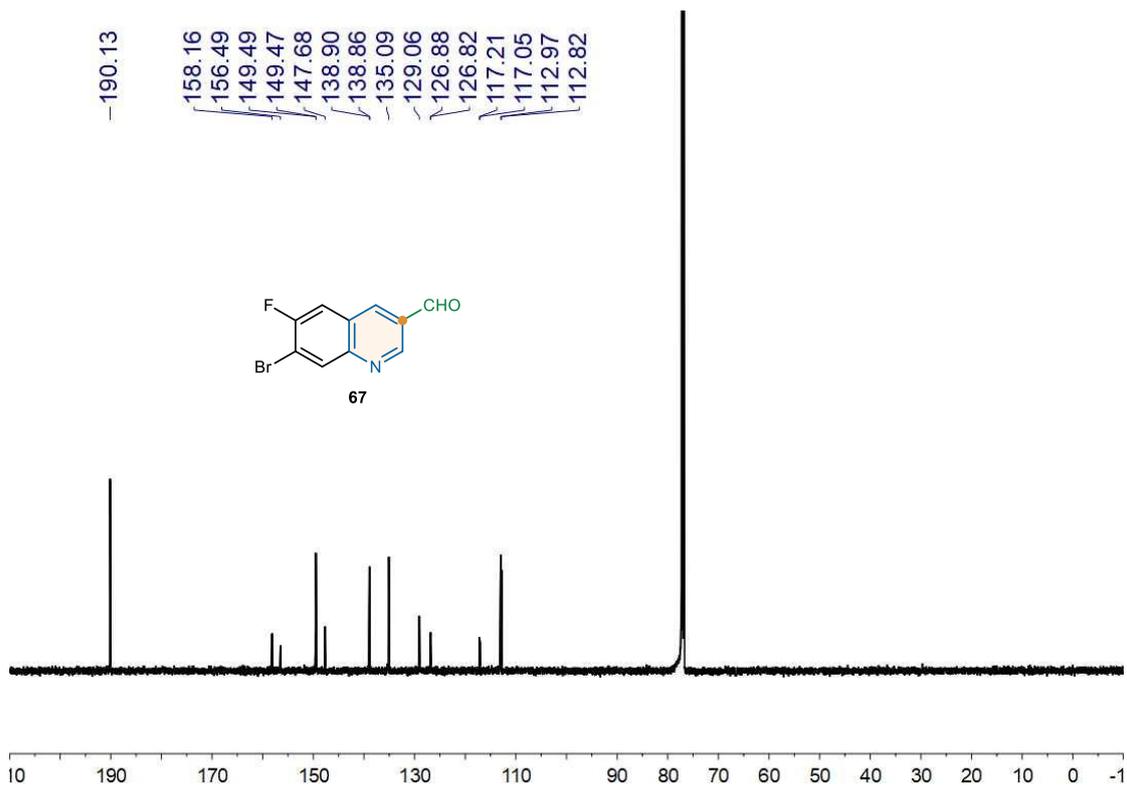
Supplementary Fig. 198.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **66**



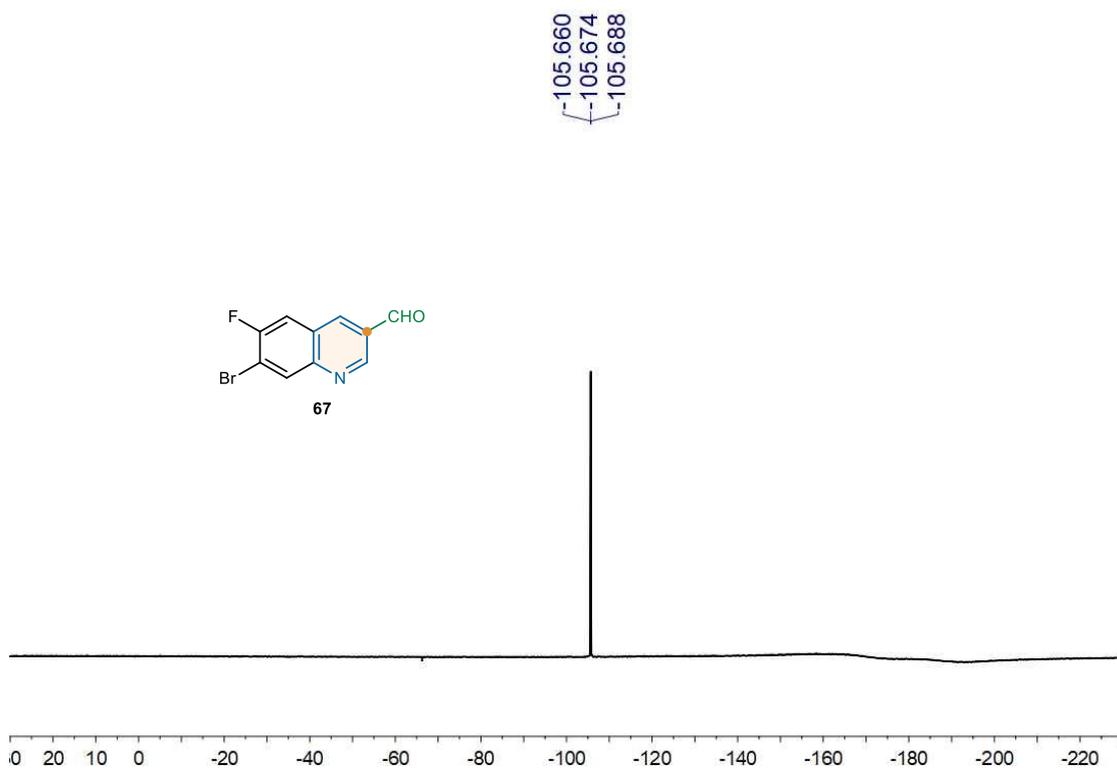
Supplementary Fig. 199. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of **66**



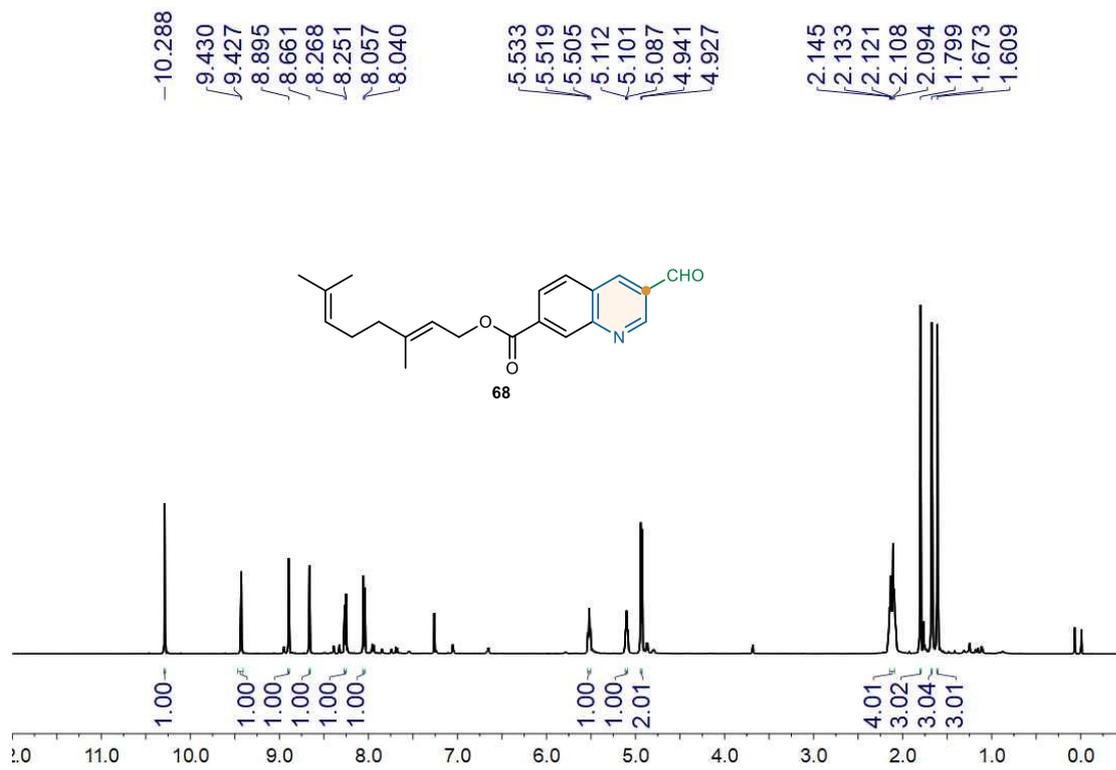
Supplementary Fig. 200. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of **67**



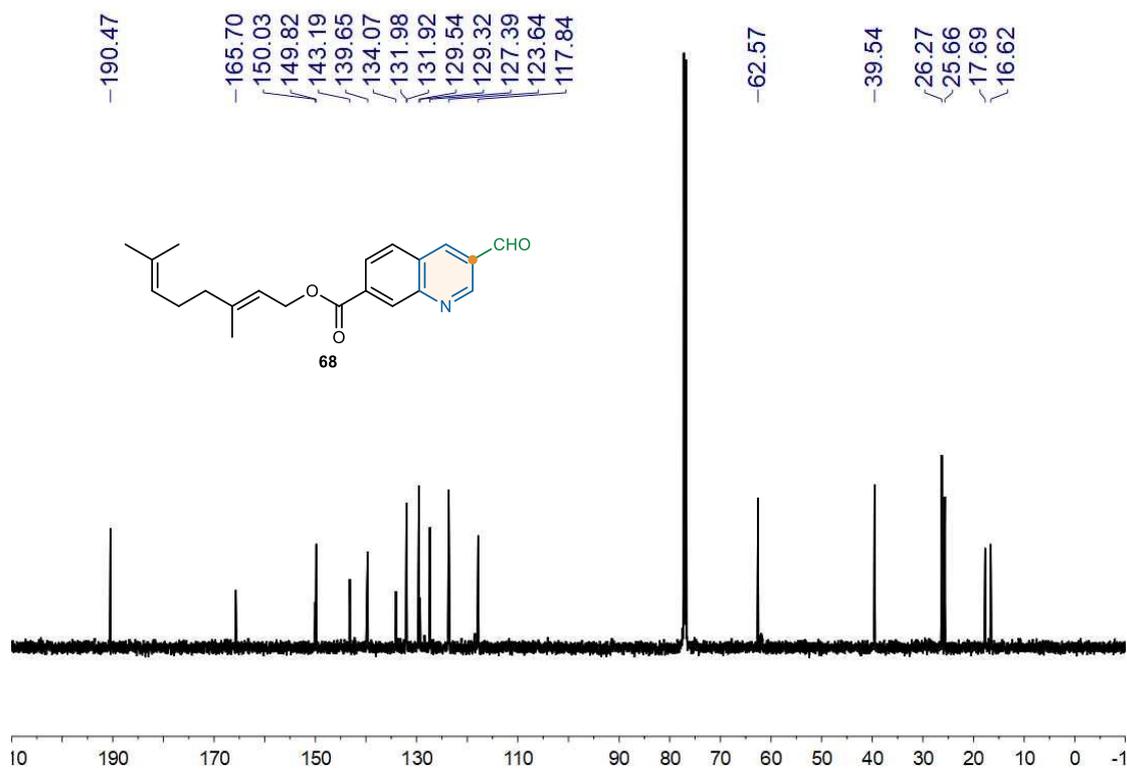
Supplementary Fig. 201. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of 67



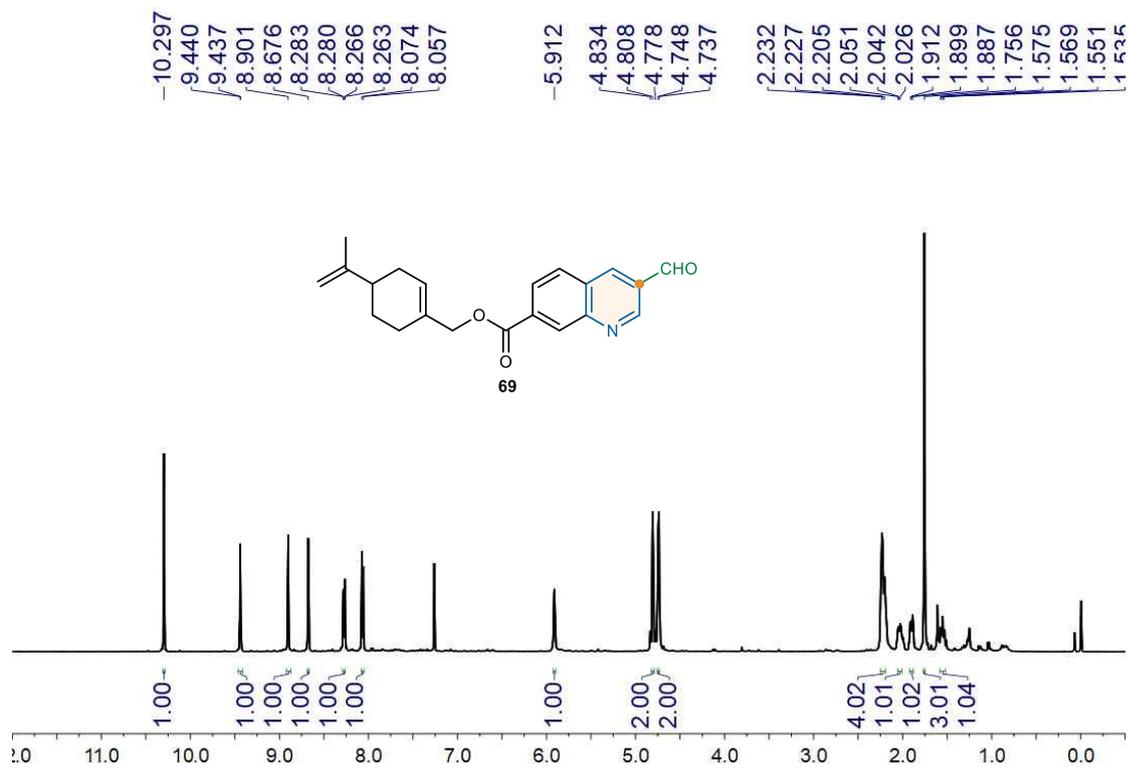
Supplementary Fig. 202. <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) spectrum of 67



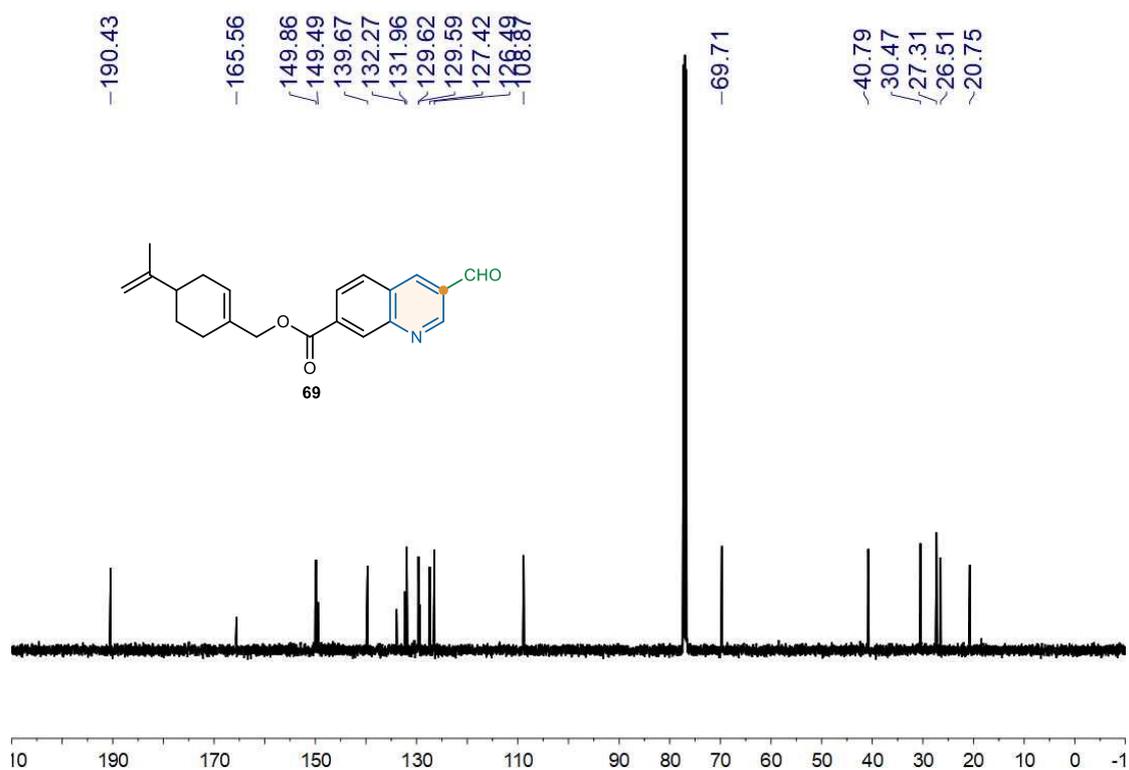
Supplementary Fig. 203. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **68**



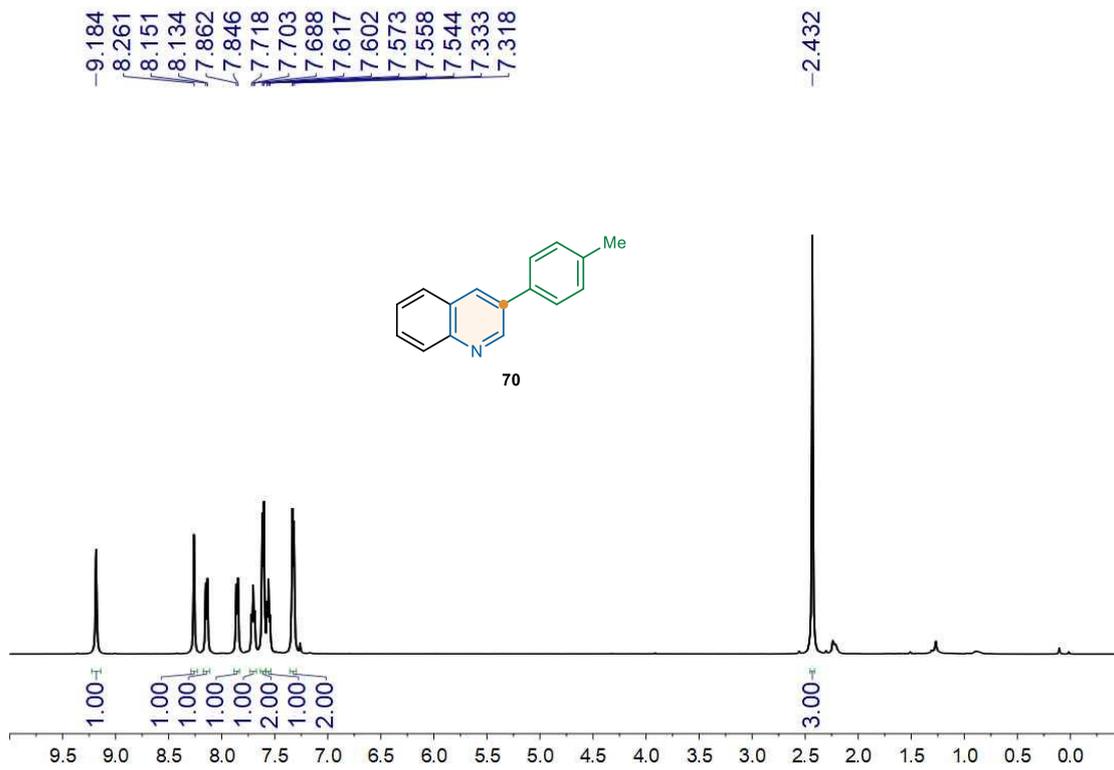
Supplementary Fig. 204. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of **68**



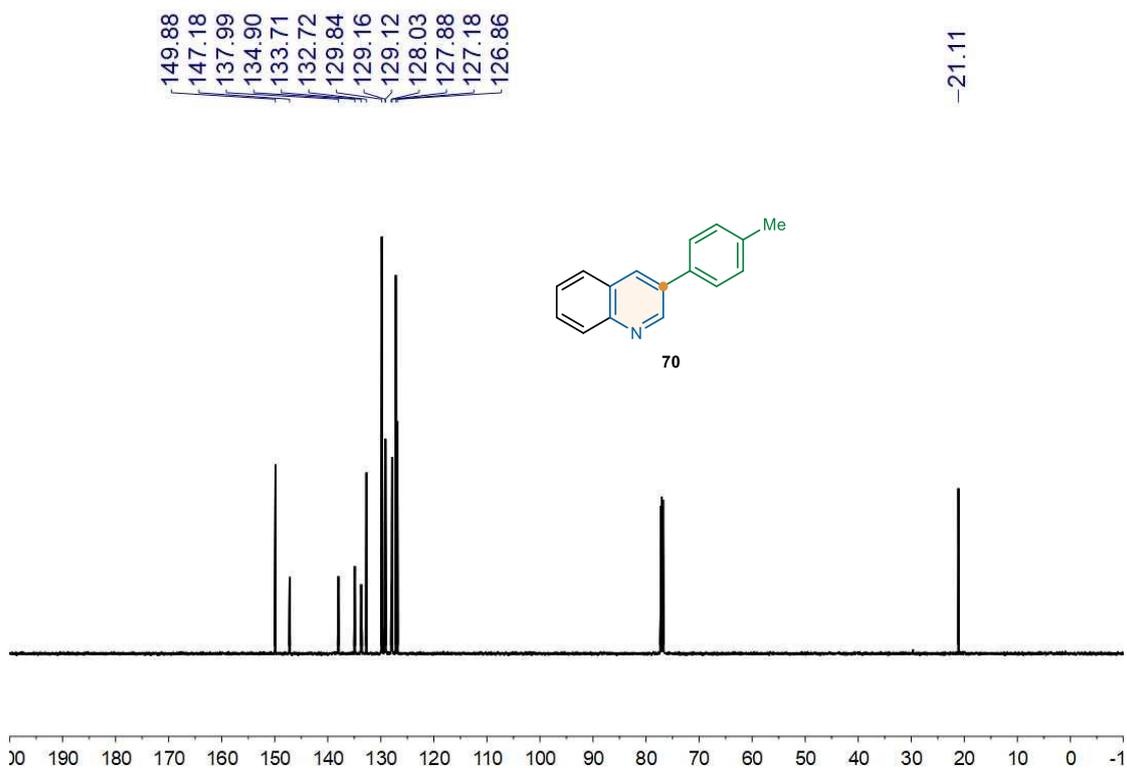
Supplementary Fig. 205. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of 69



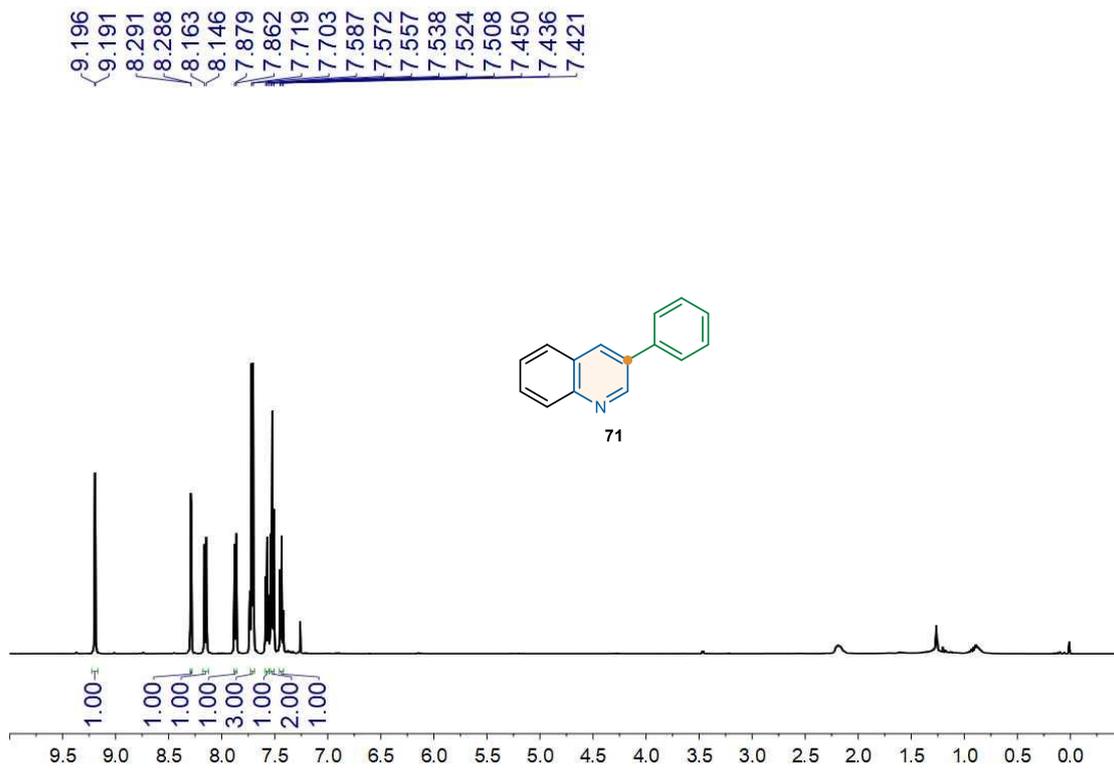
Supplementary Fig. 206. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of 69



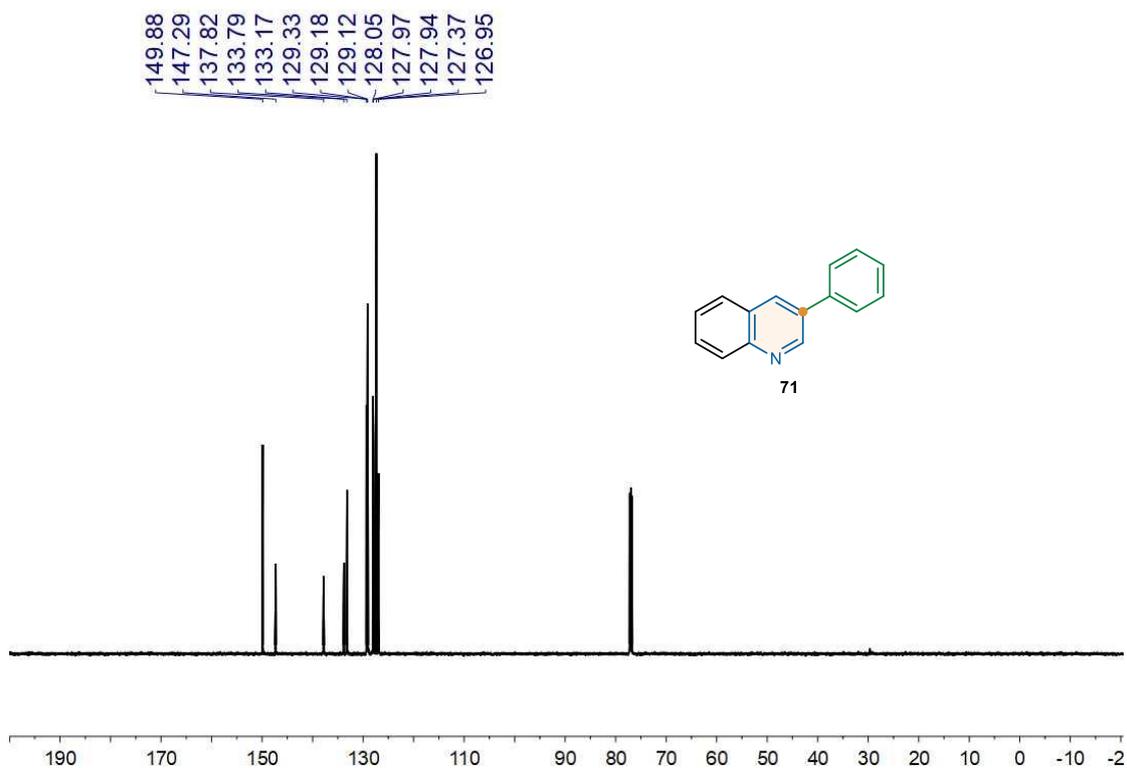
Supplementary Fig. 207. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of 70



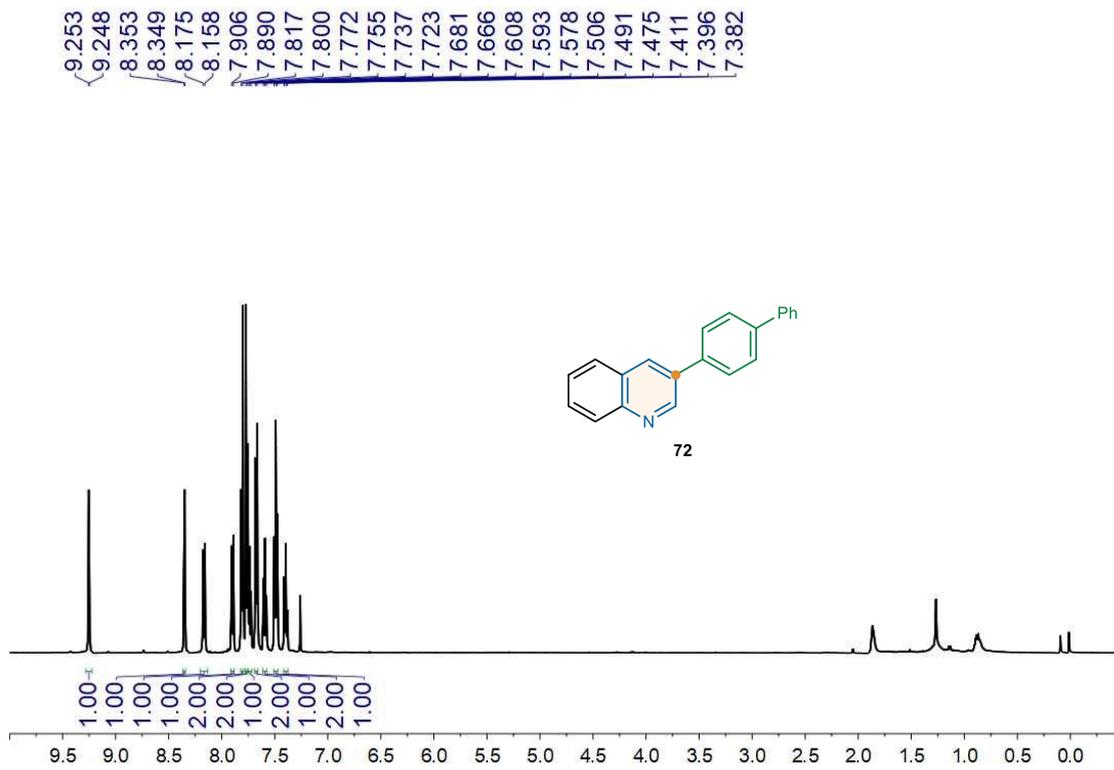
Supplementary Fig. 208. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of 70



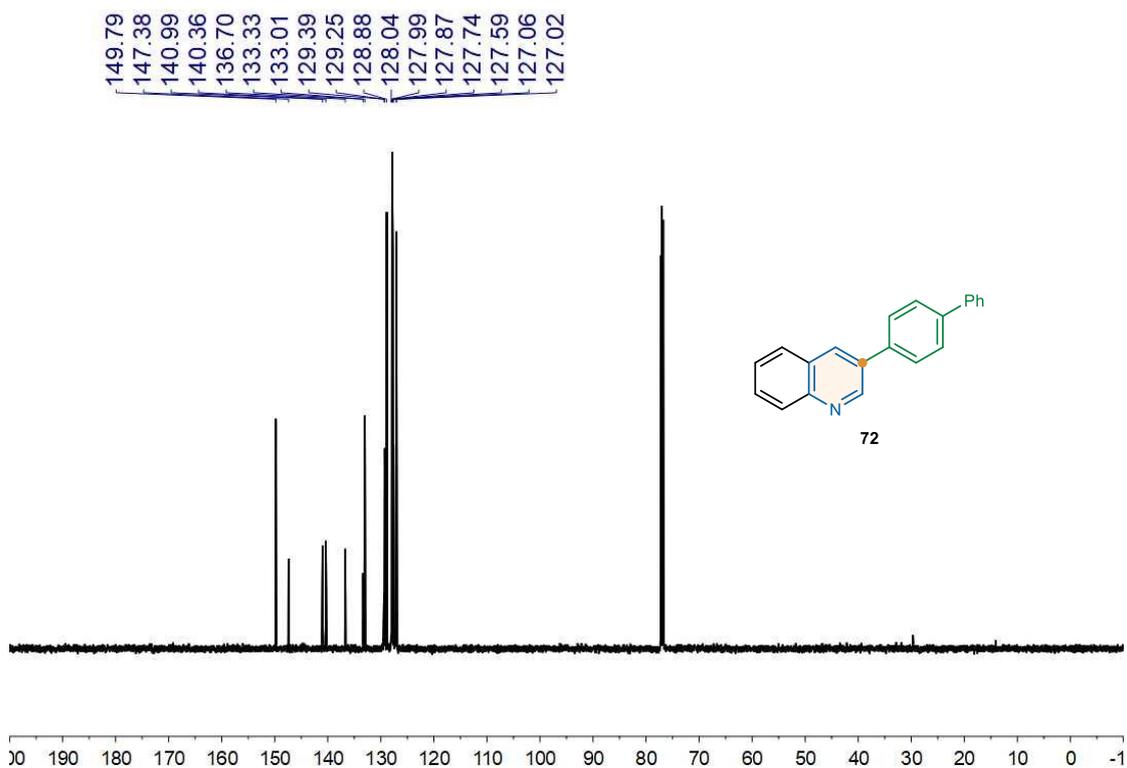
Supplementary Fig. 209.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of 71



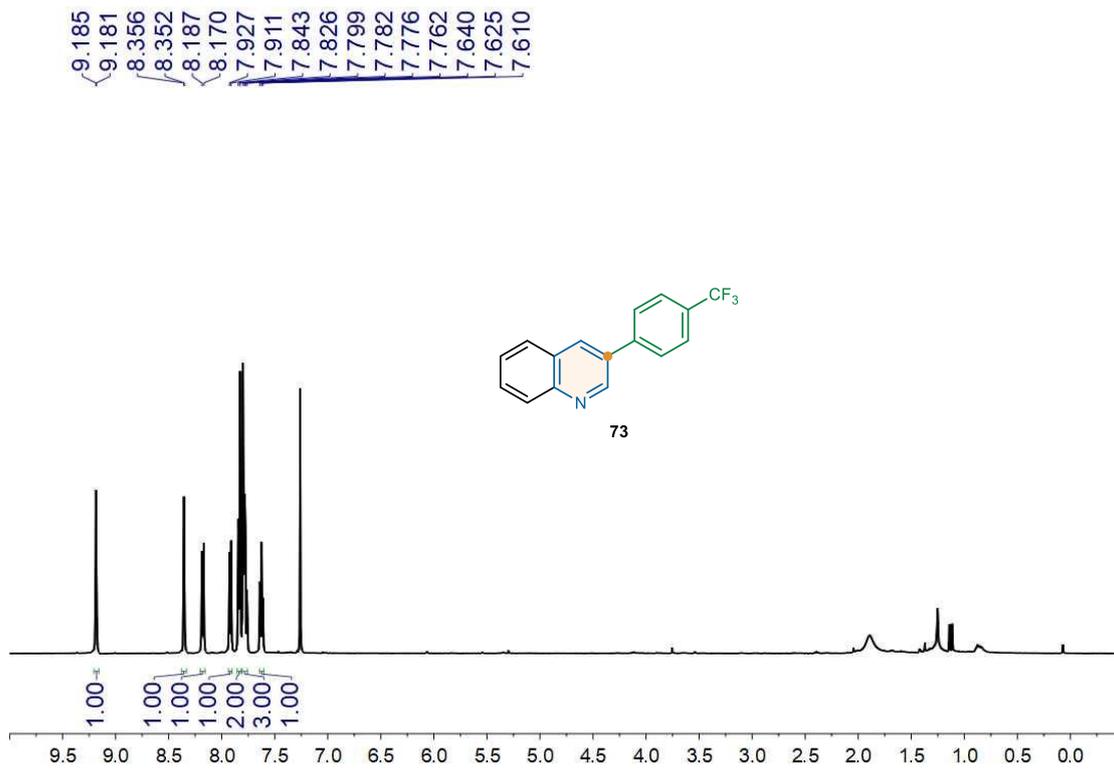
Supplementary Fig. 210.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of 71



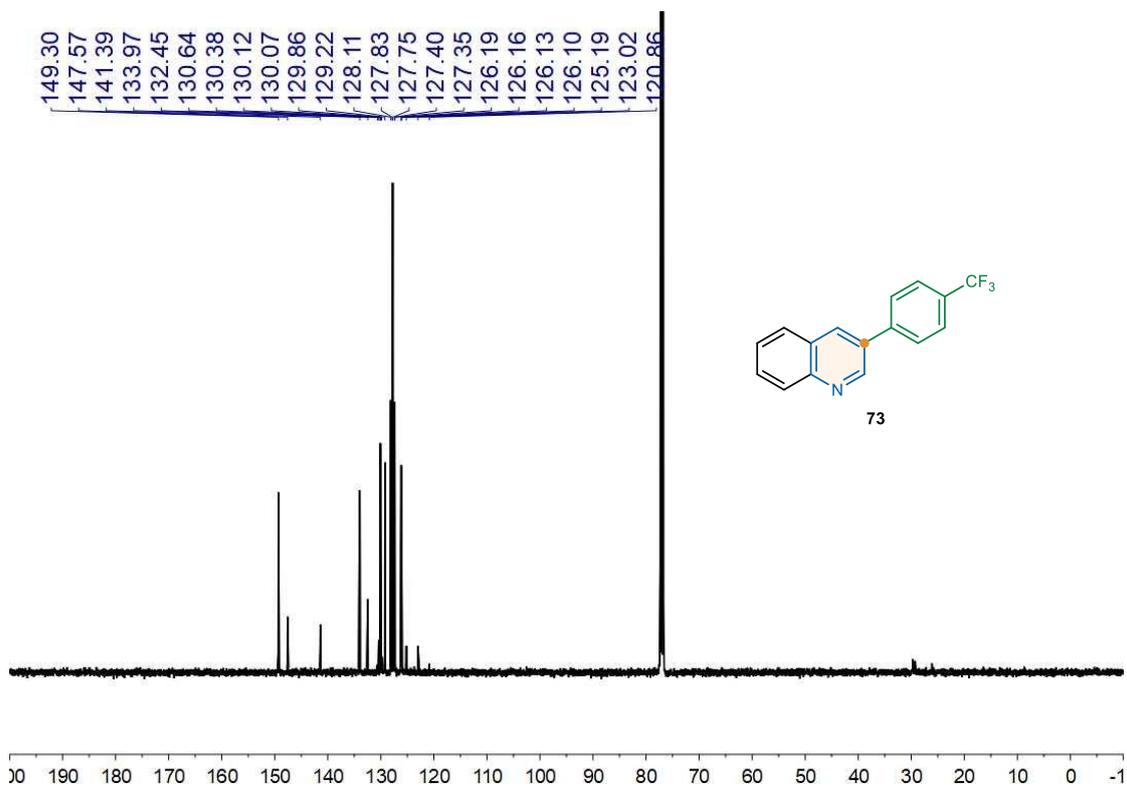
Supplementary Fig. 211.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **72**



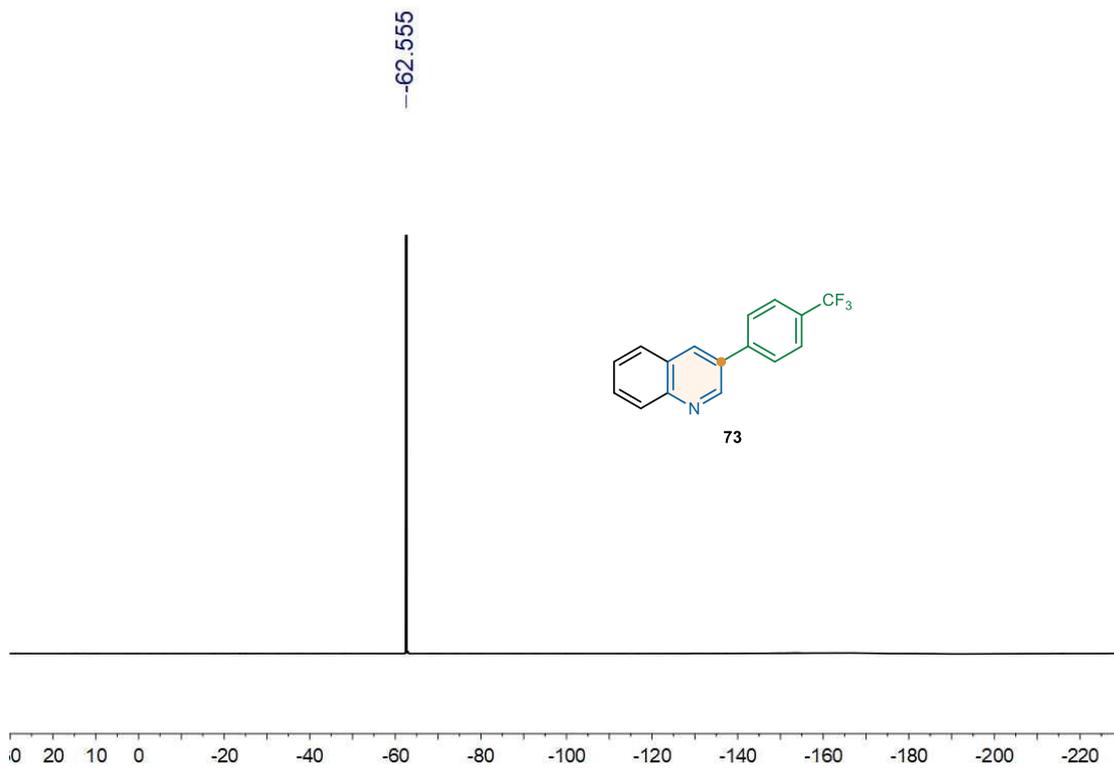
Supplementary Fig. 212.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **72**



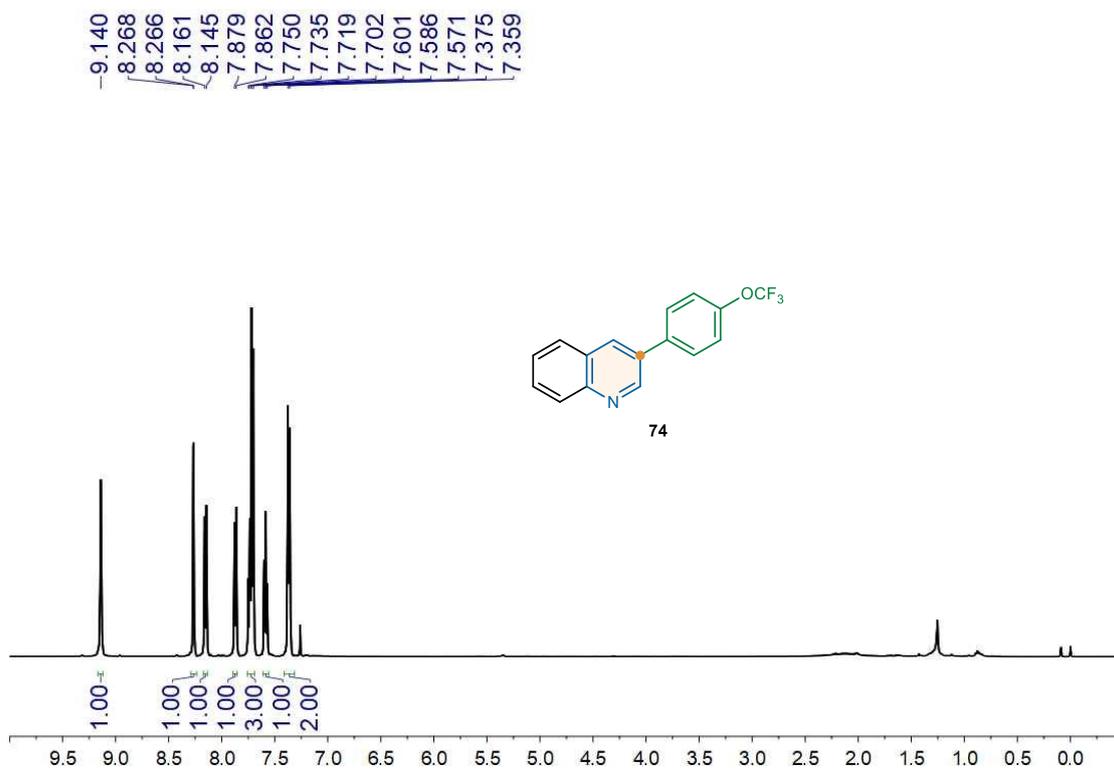
Supplementary Fig. 213.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of 73



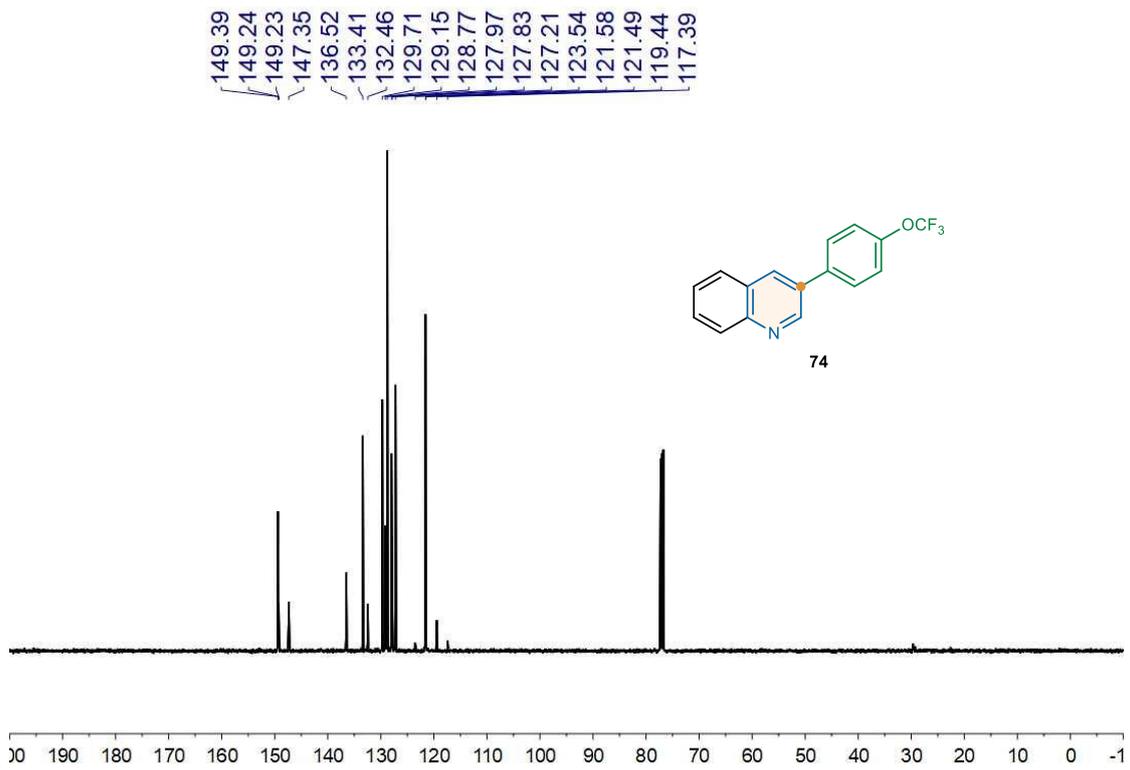
Supplementary Fig. 214.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of 73



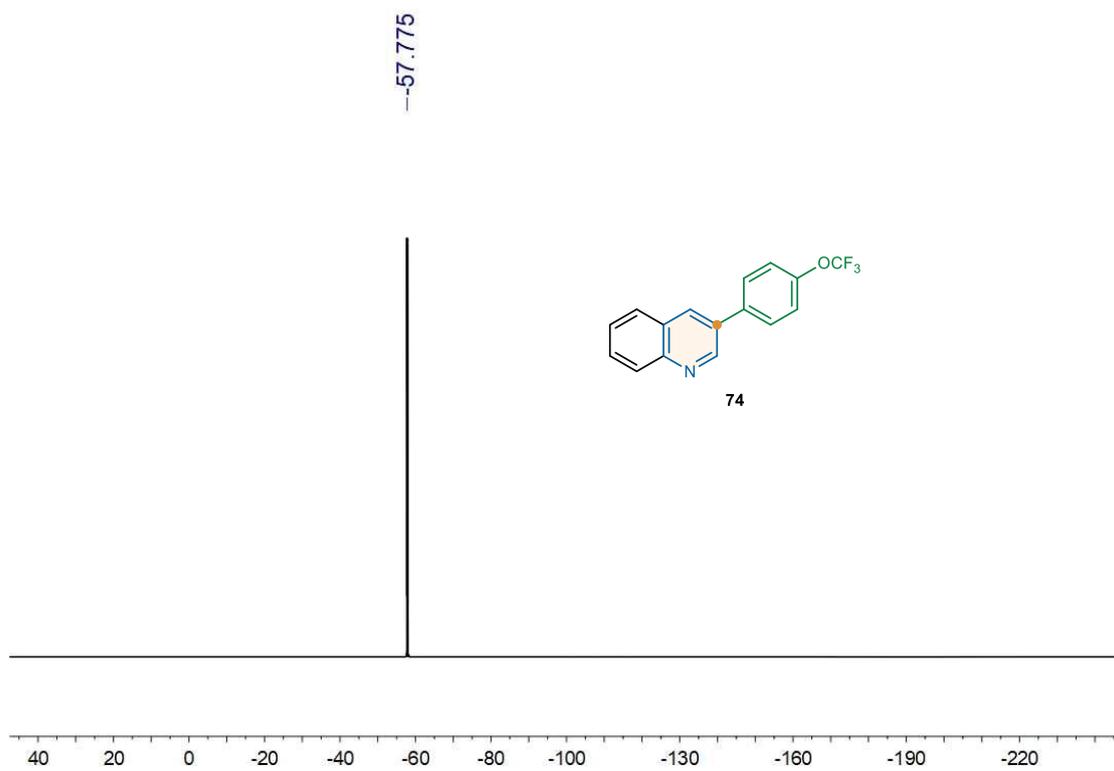
Supplementary Fig. 215.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ) spectrum of 72



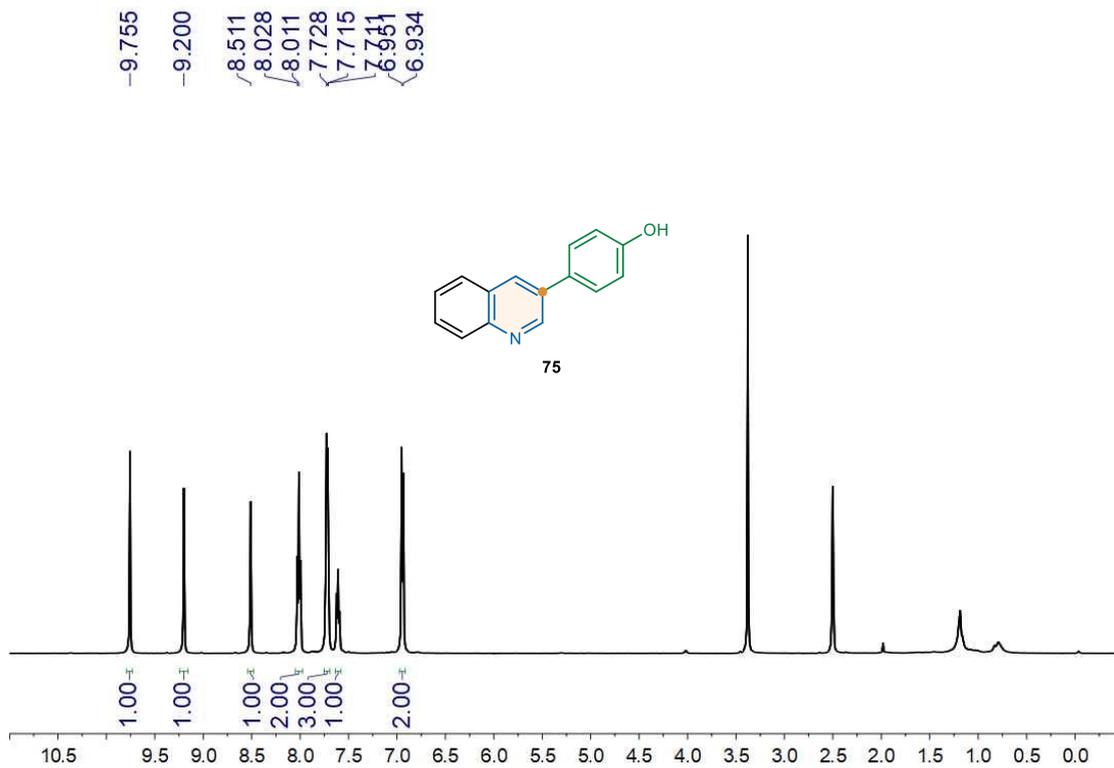
Supplementary Fig. 216.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of 74



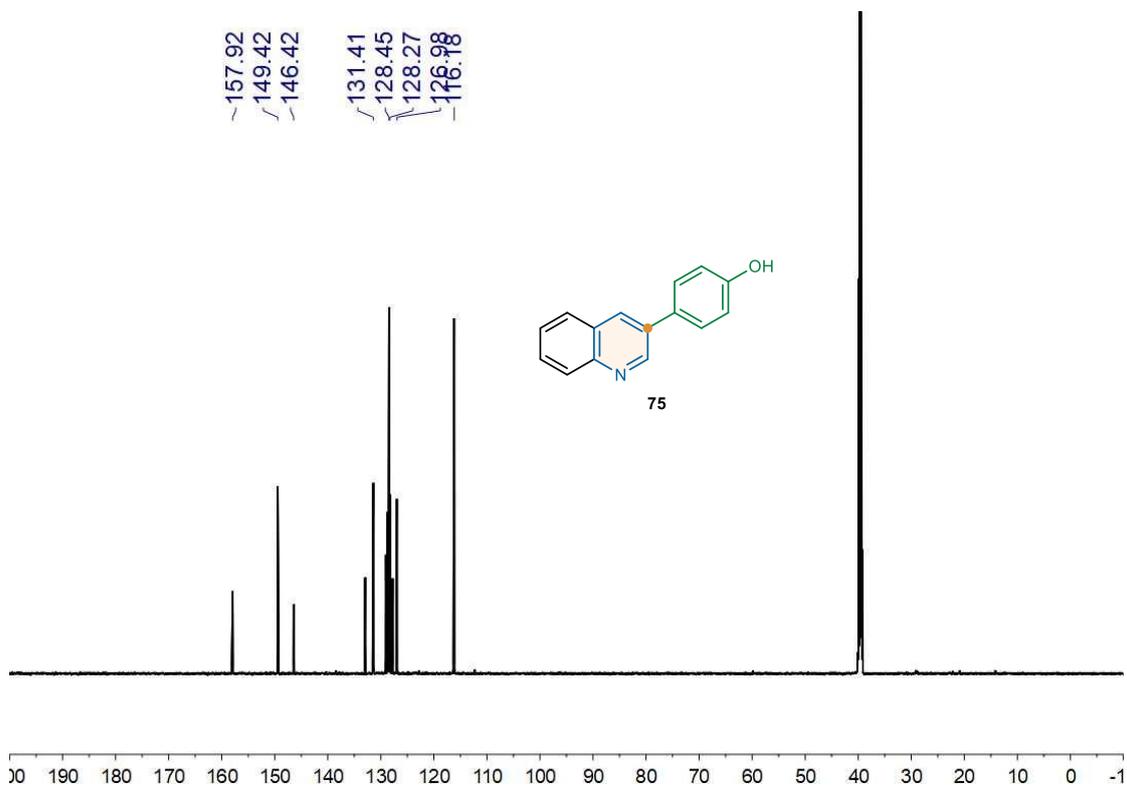
Supplementary Fig. 217. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of 74



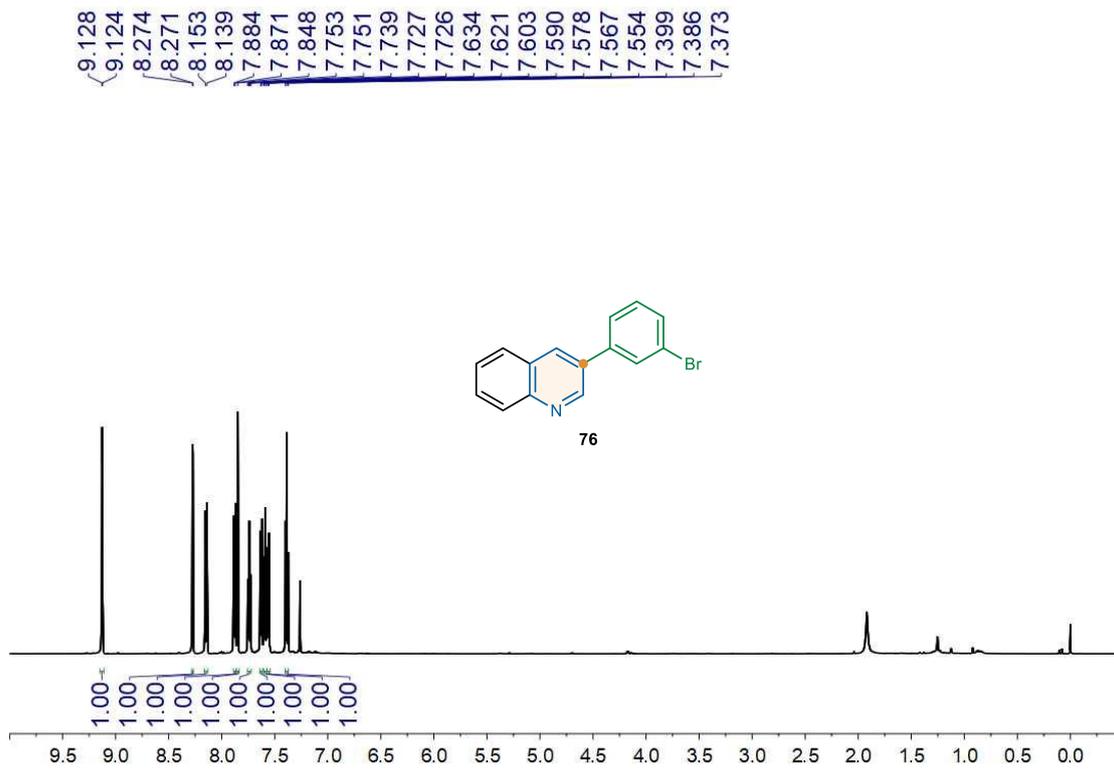
Supplementary Fig. 218. <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) spectrum of 74



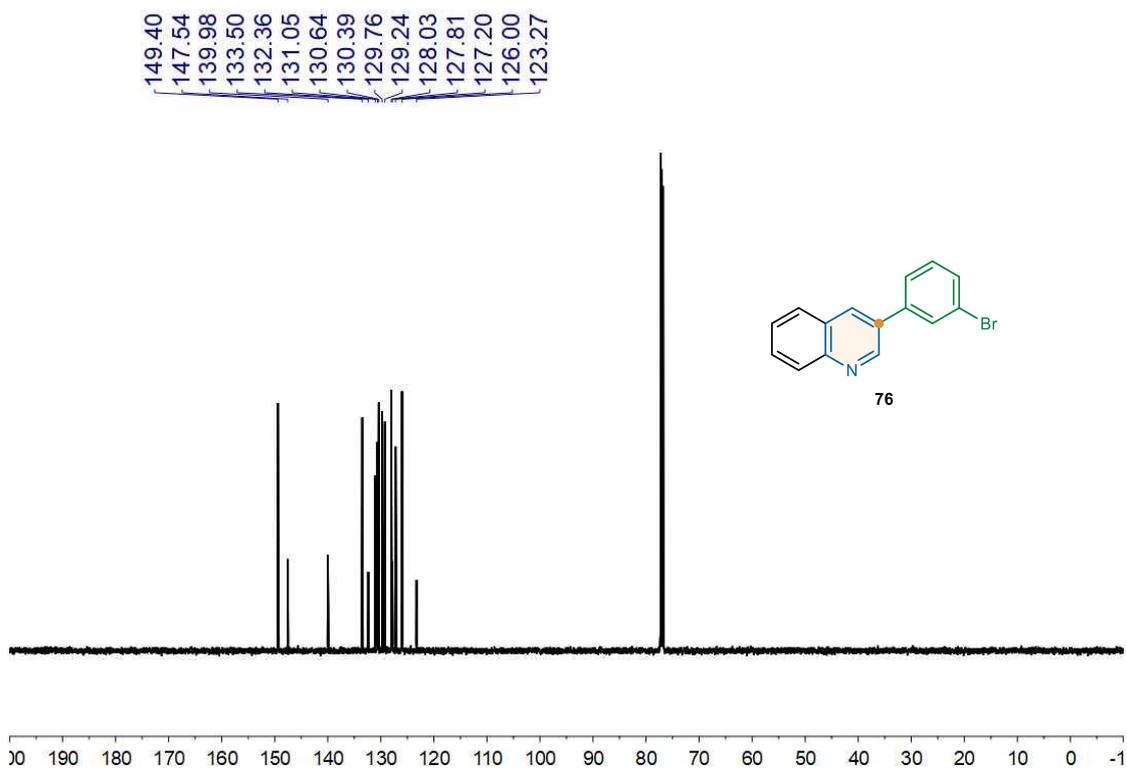
Supplementary Fig. 219.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ ) spectrum of **75**



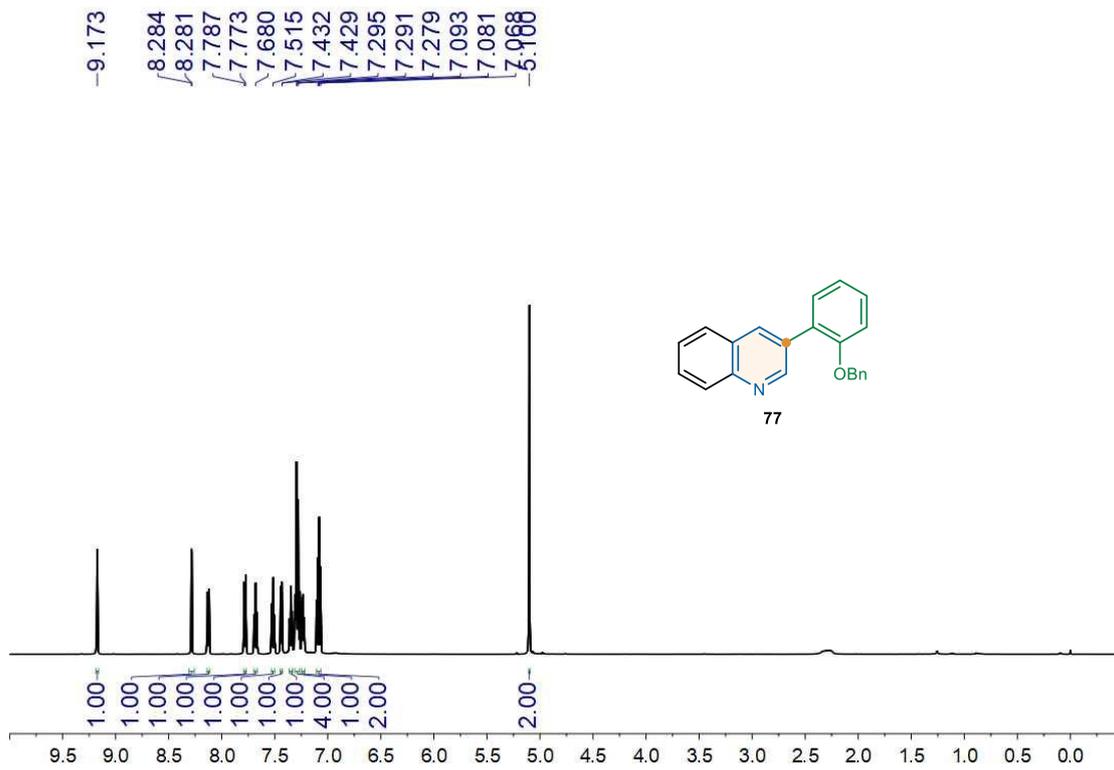
Supplementary Fig. 220.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6$ ) spectrum of **75**



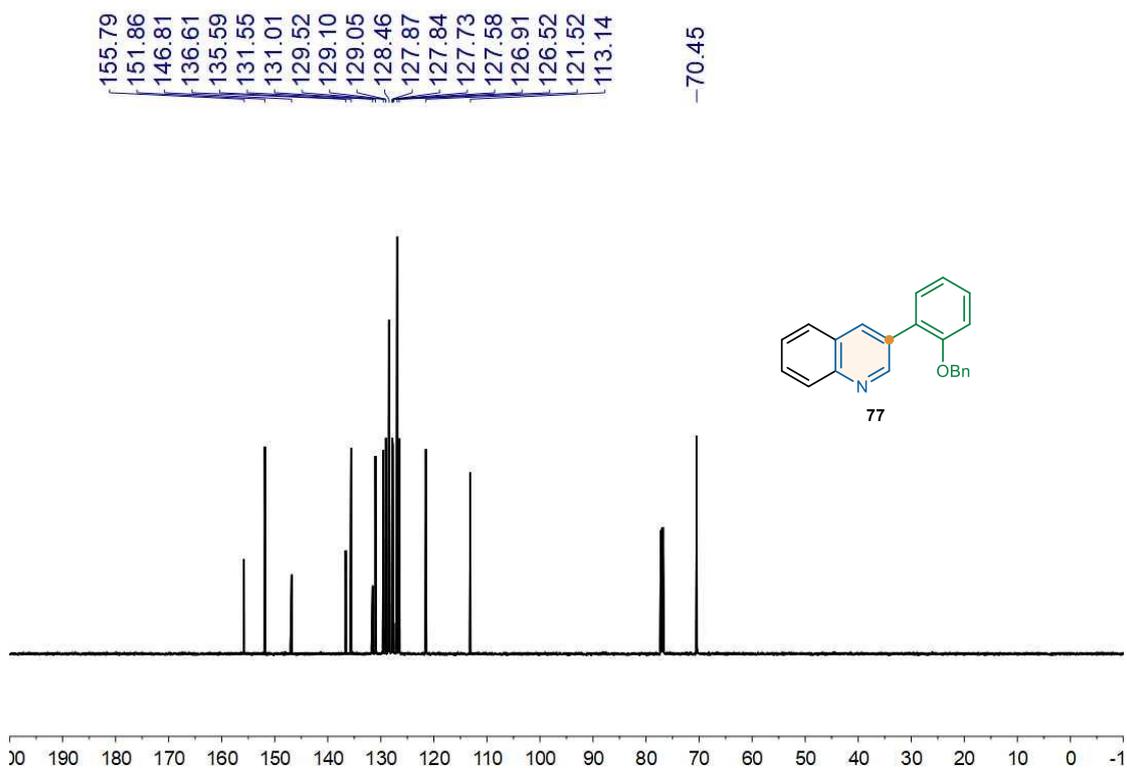
Supplementary Fig. 221.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) spectrum of 76



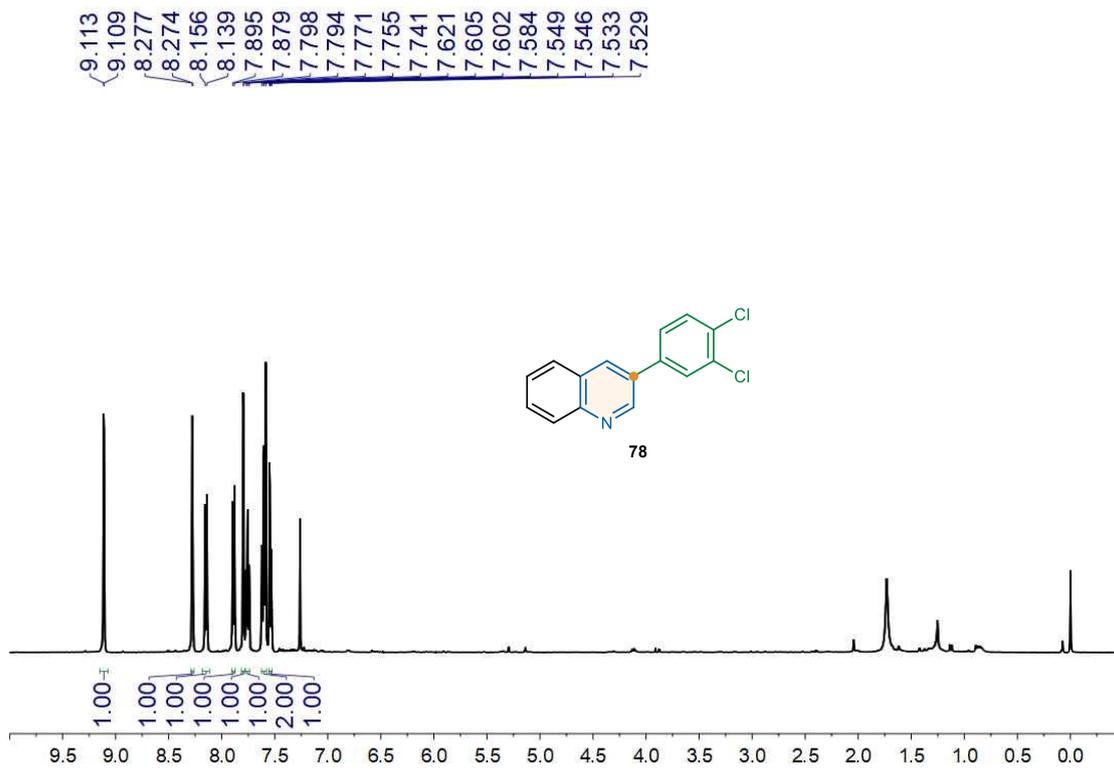
Supplementary Fig. 222.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of 76



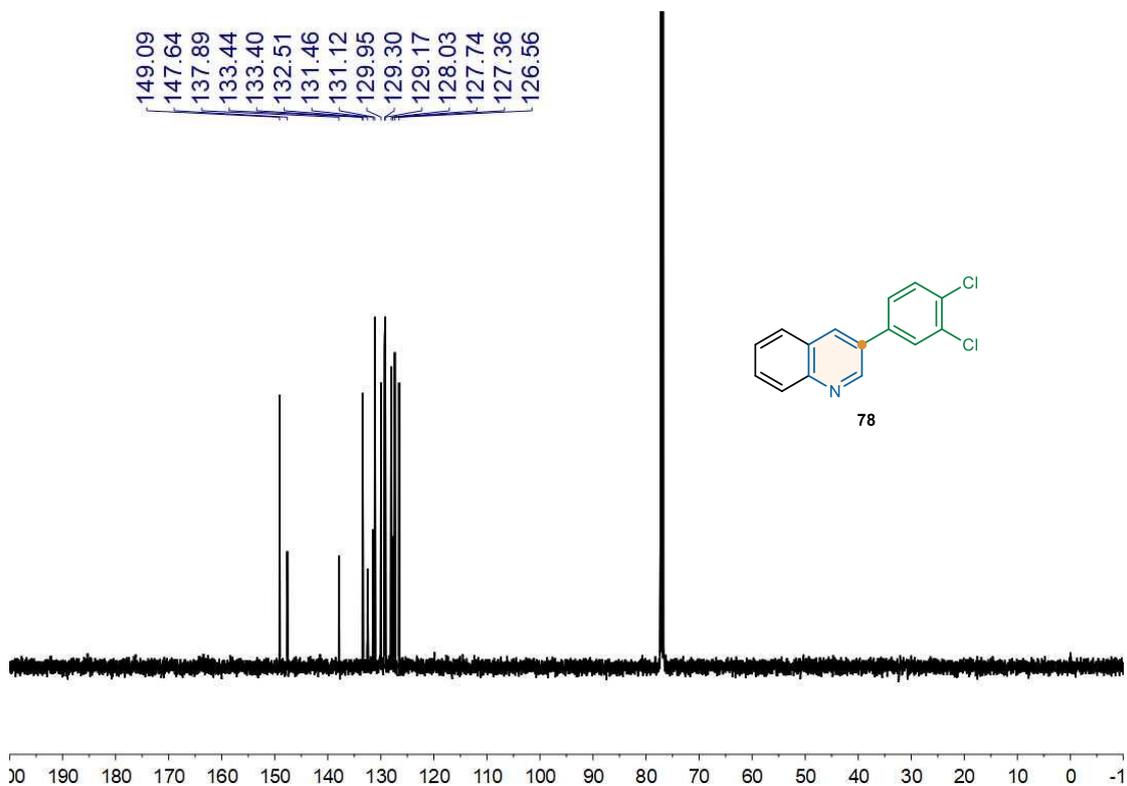
Supplementary Fig. 223.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) spectrum of 77



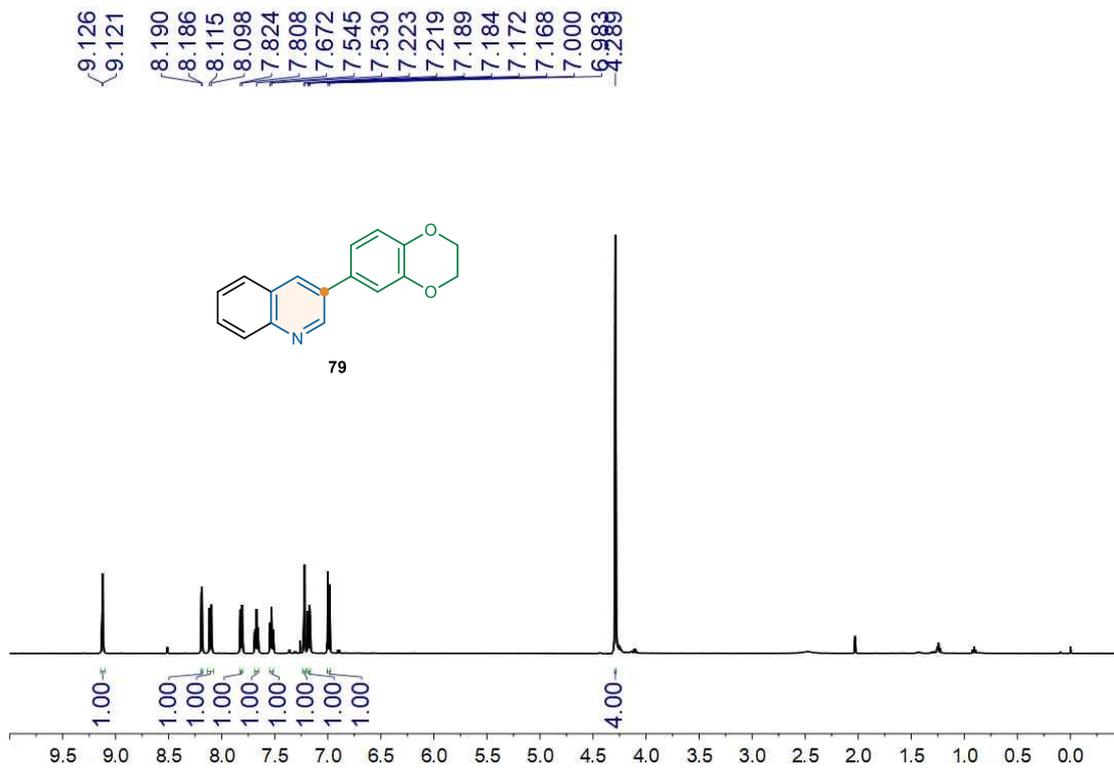
Supplementary Fig. 224.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of 77



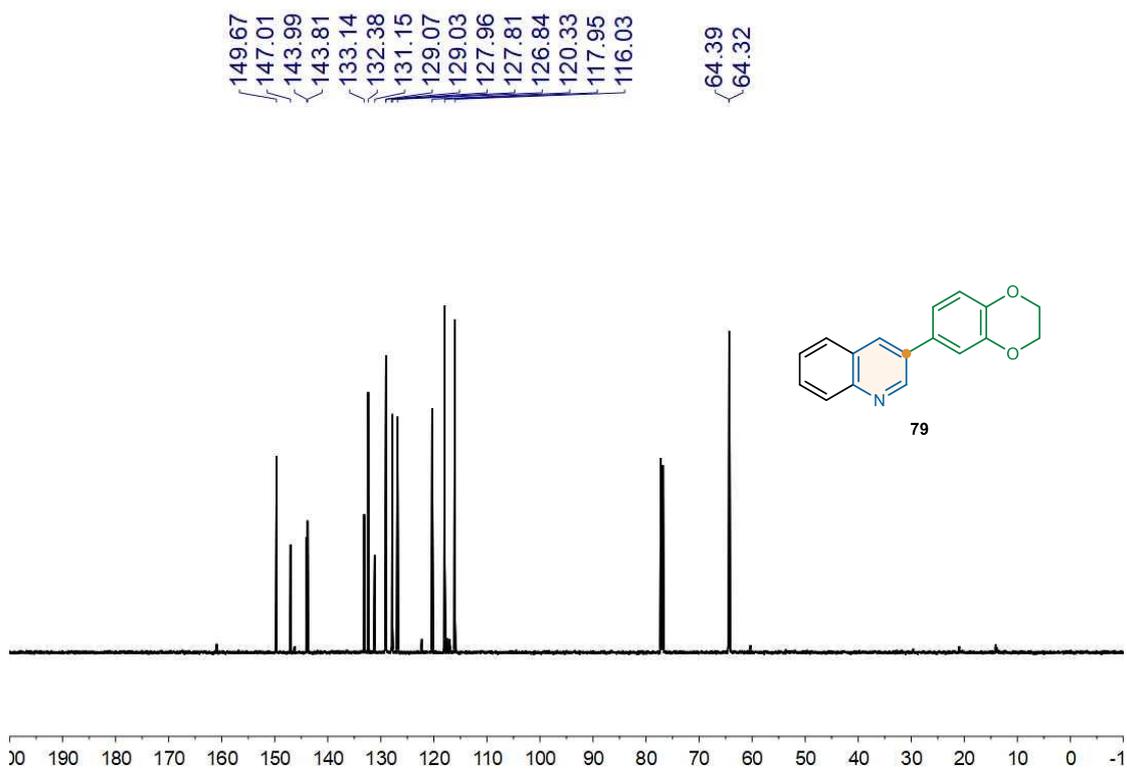
Supplementary Fig. 225.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of 78



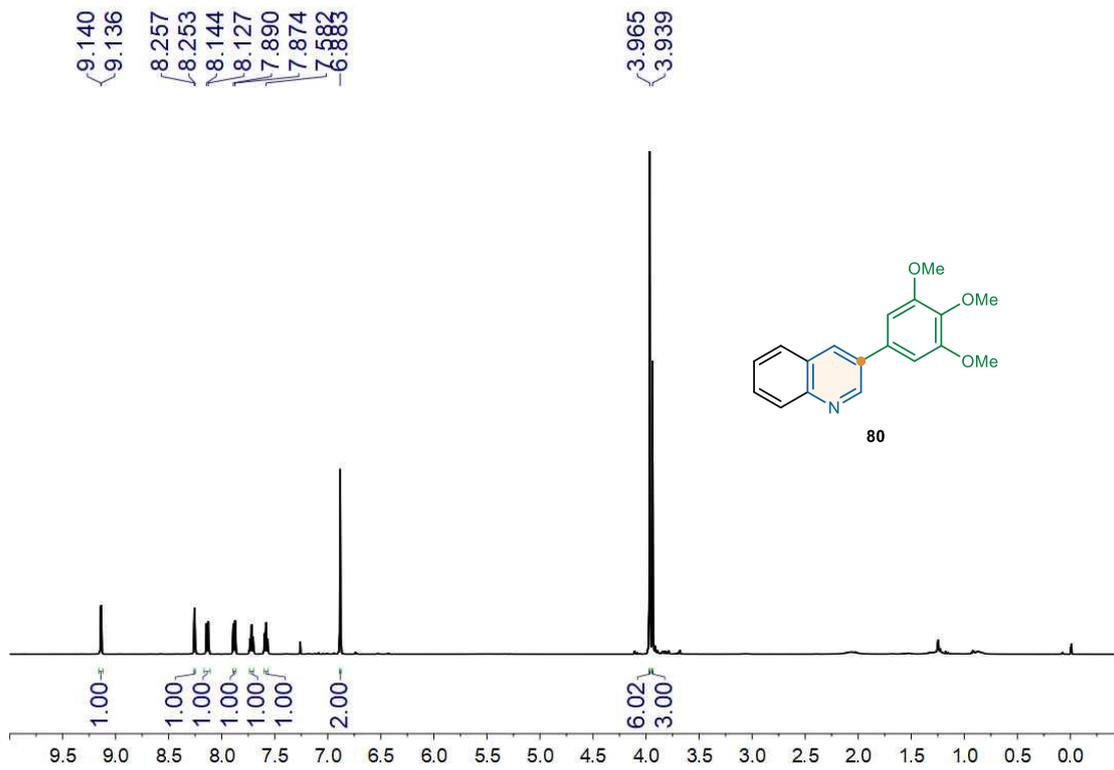
Supplementary Fig. 226.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of 78



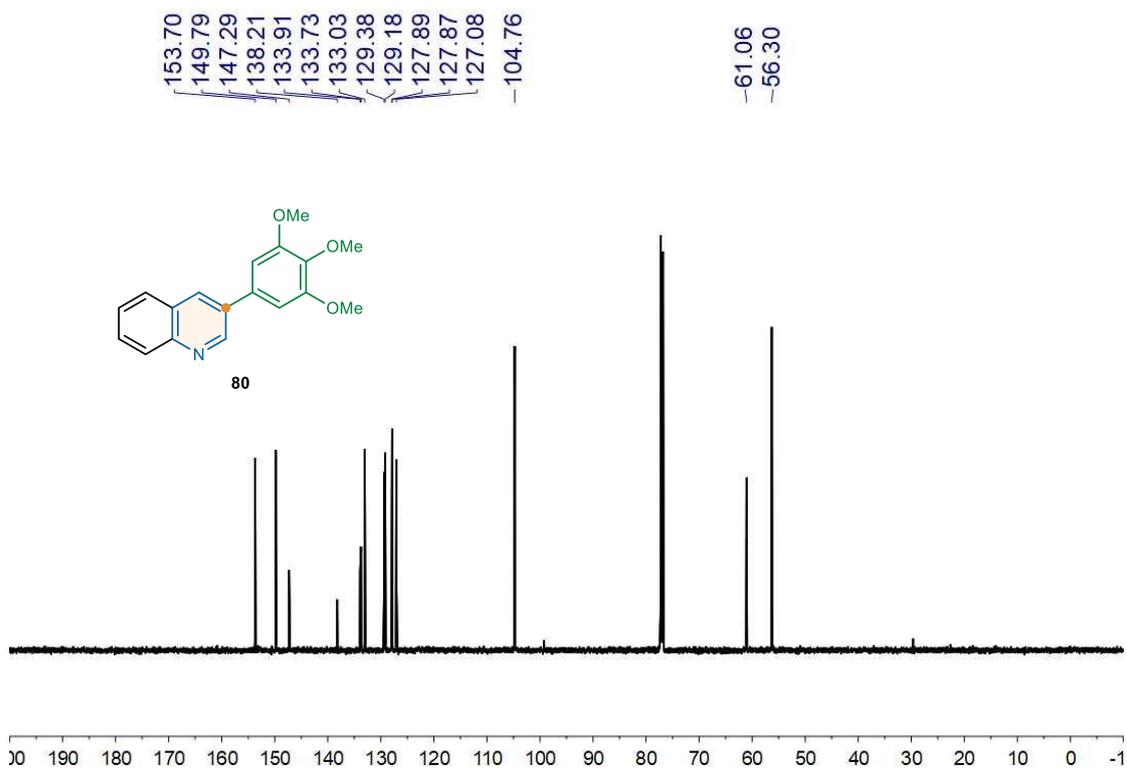
Supplementary Fig. 227.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of 79



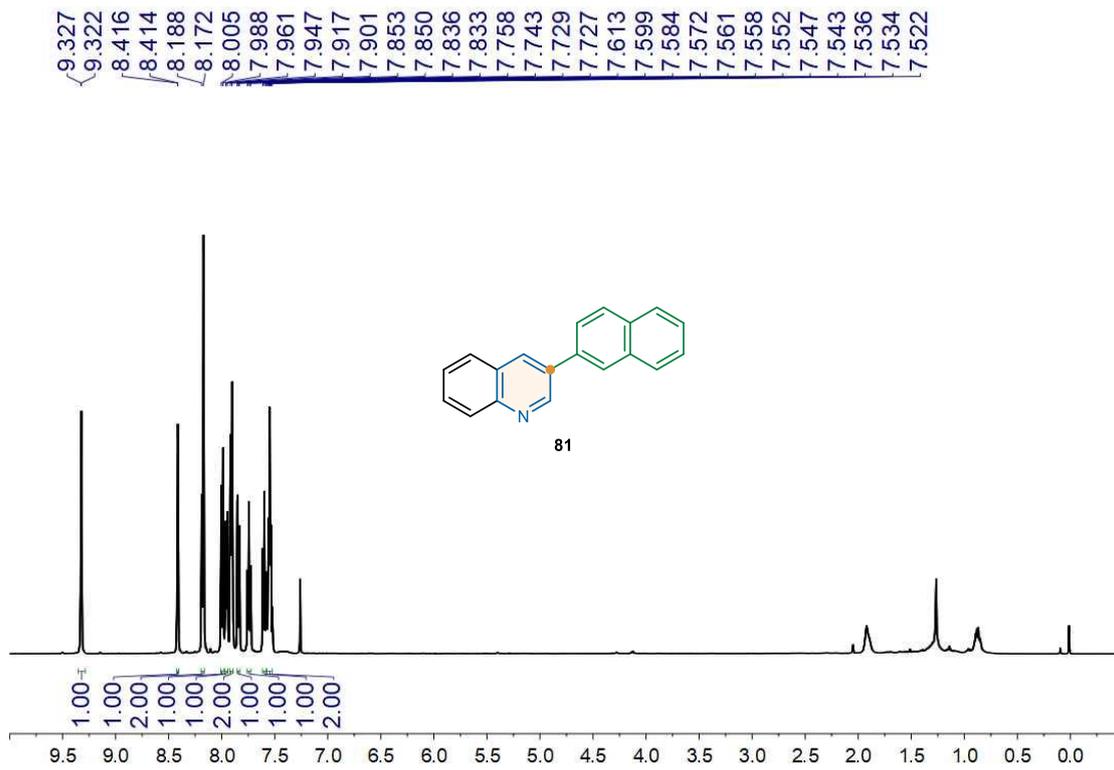
Supplementary Fig. 228.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of 79



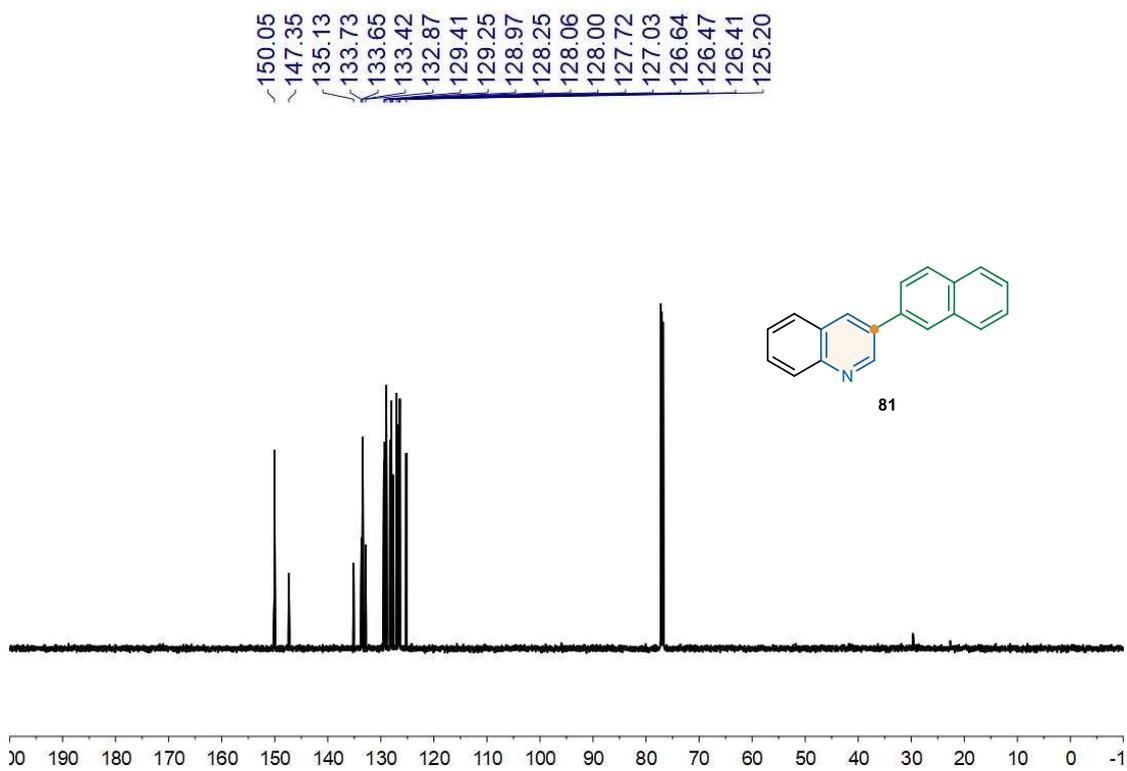
Supplementary Fig. 229.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **80**



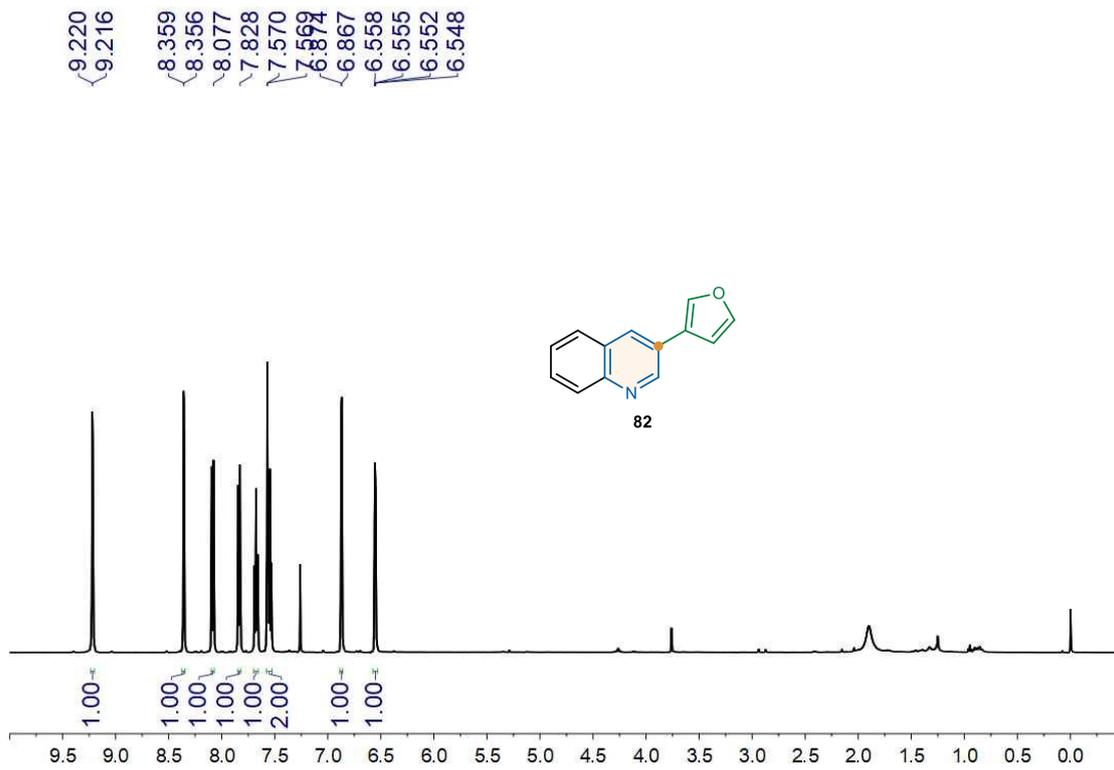
Supplementary Fig. 330.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **80**



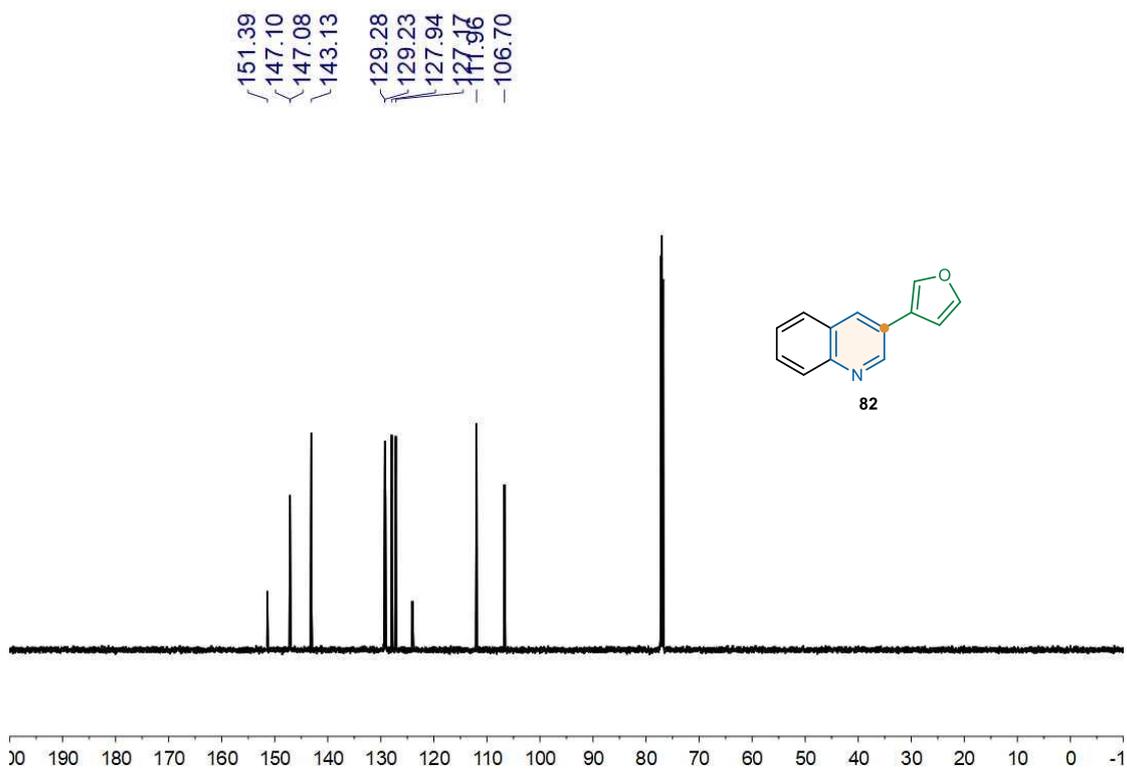
Supplementary Fig. 231.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **81**



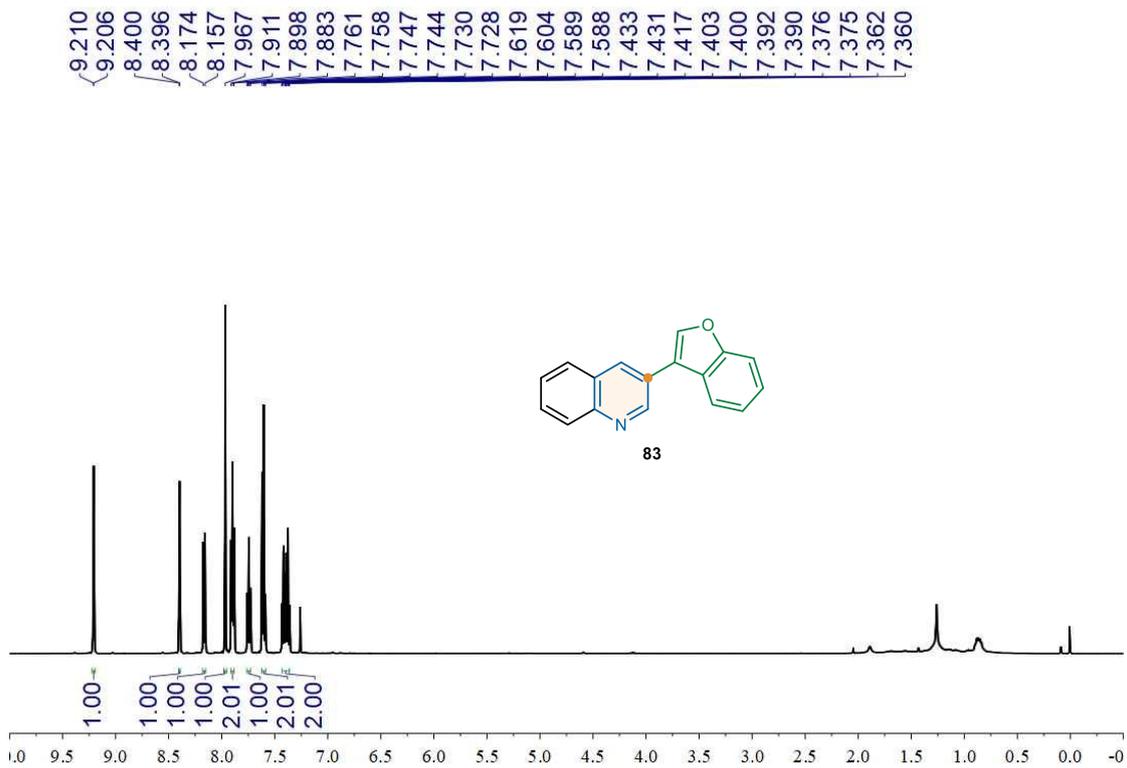
Supplementary Fig. 232.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **81**



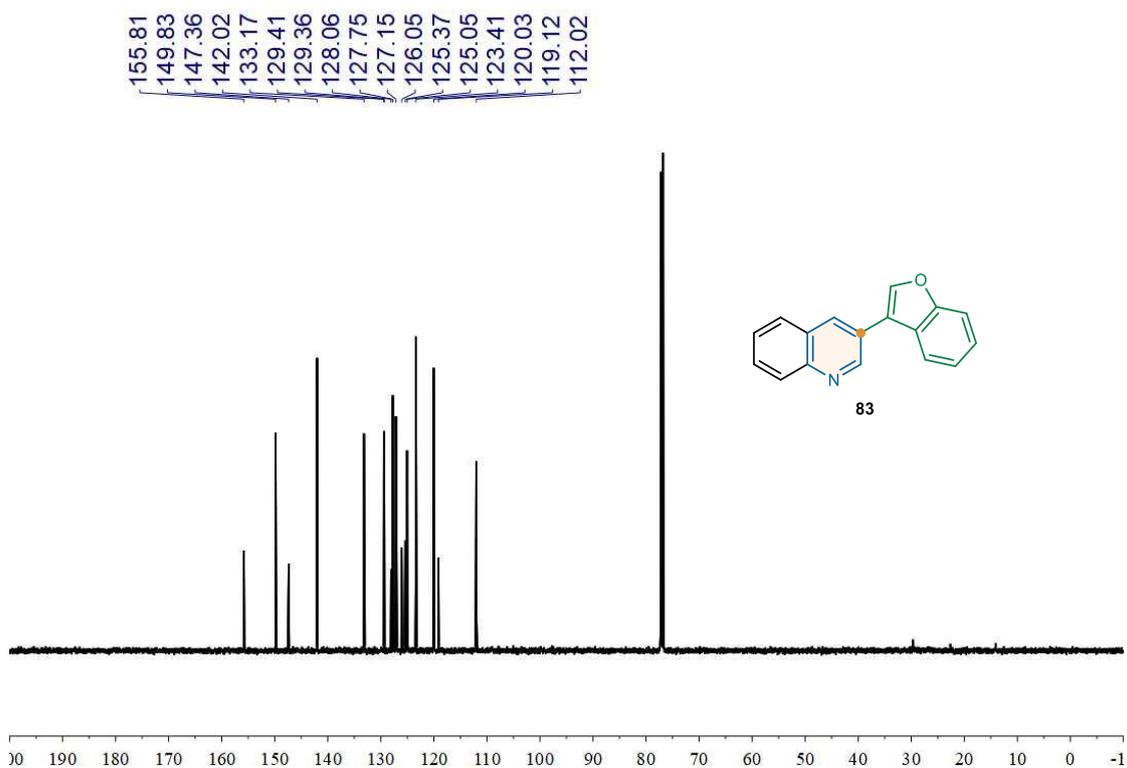
Supplementary Fig. 233.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **82**



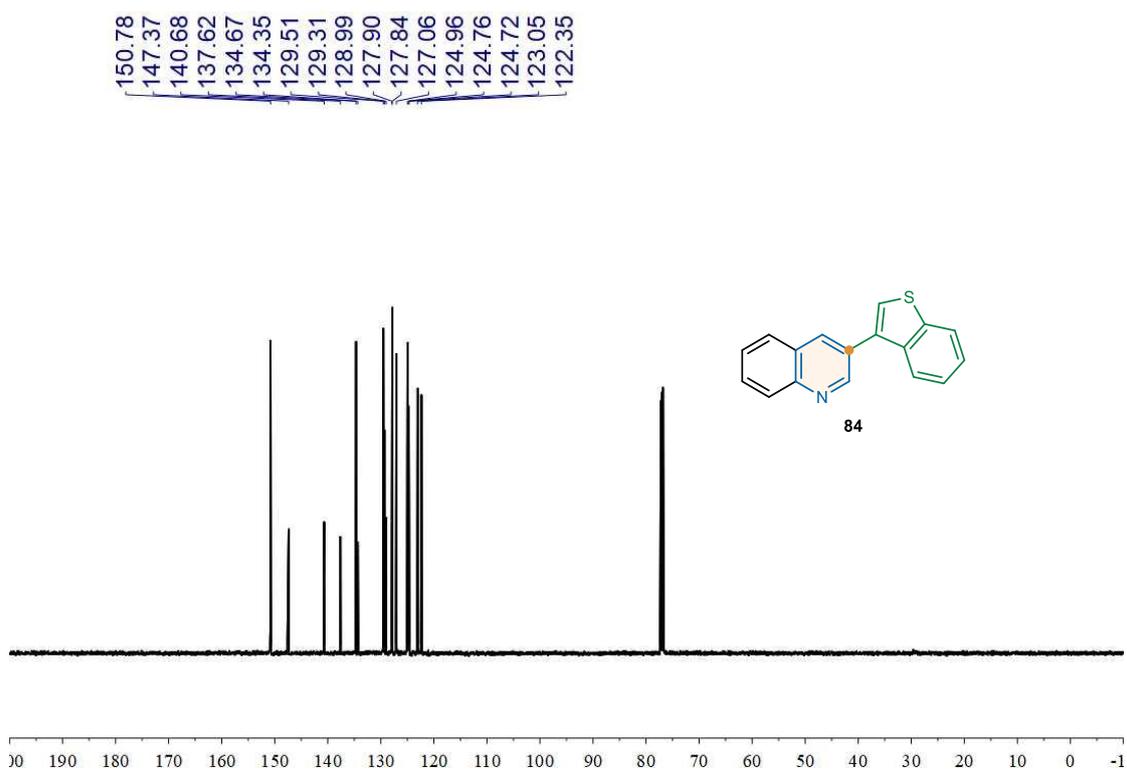
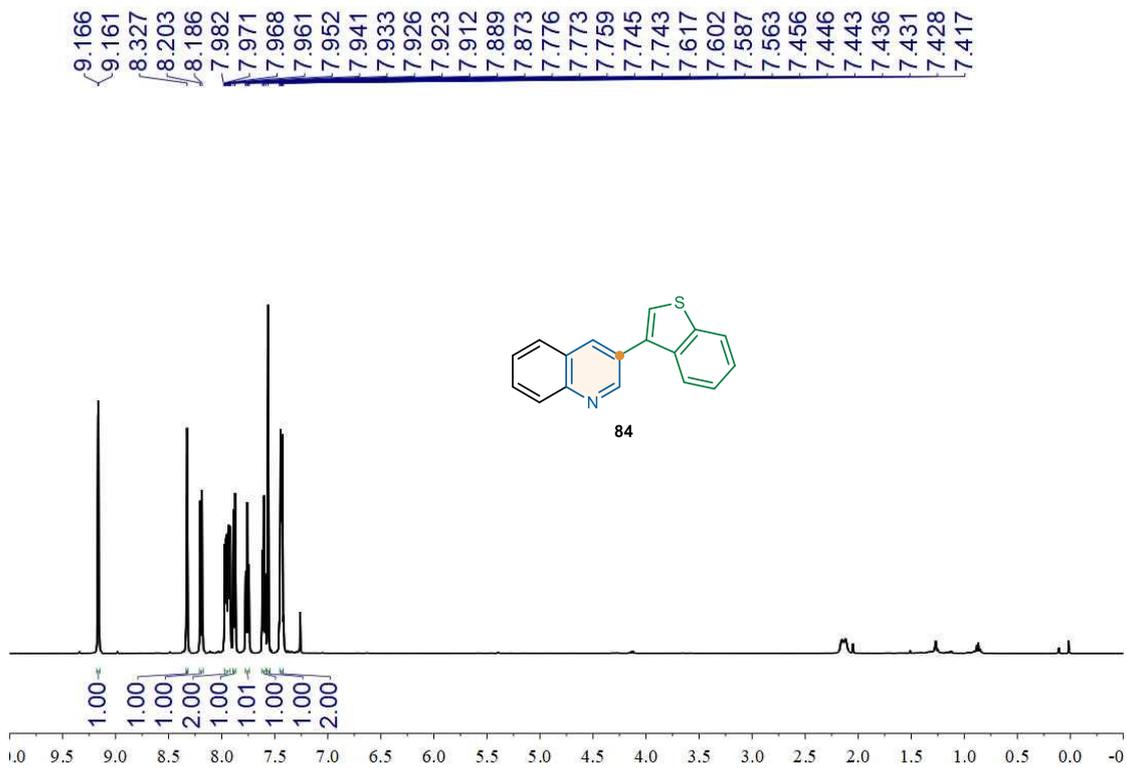
Supplementary Fig. 234.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **82**

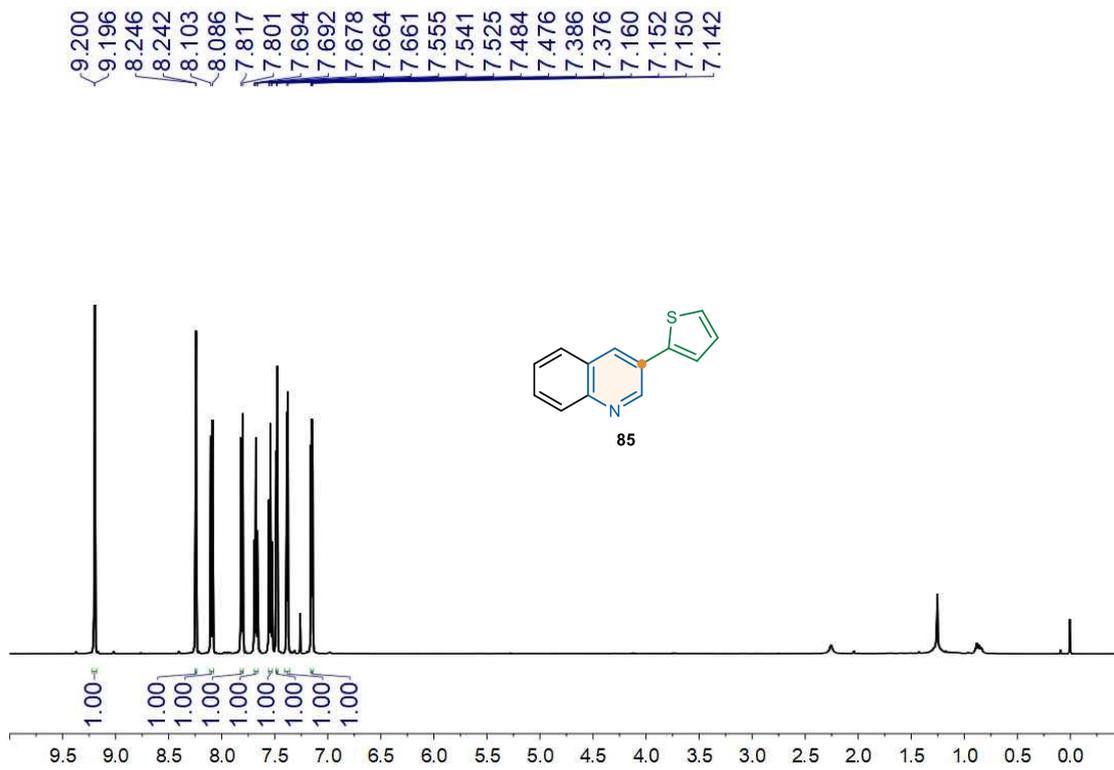


Supplementary Fig. 235.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **83**

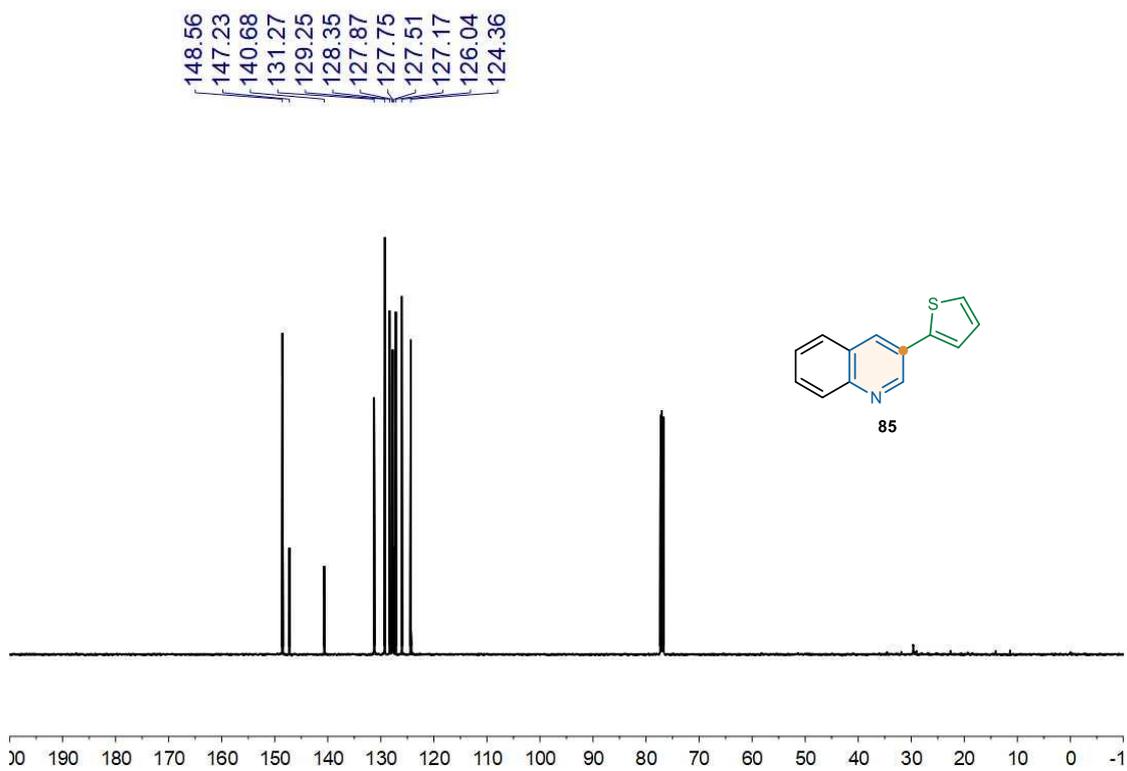


Supplementary Fig. 236.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **83**

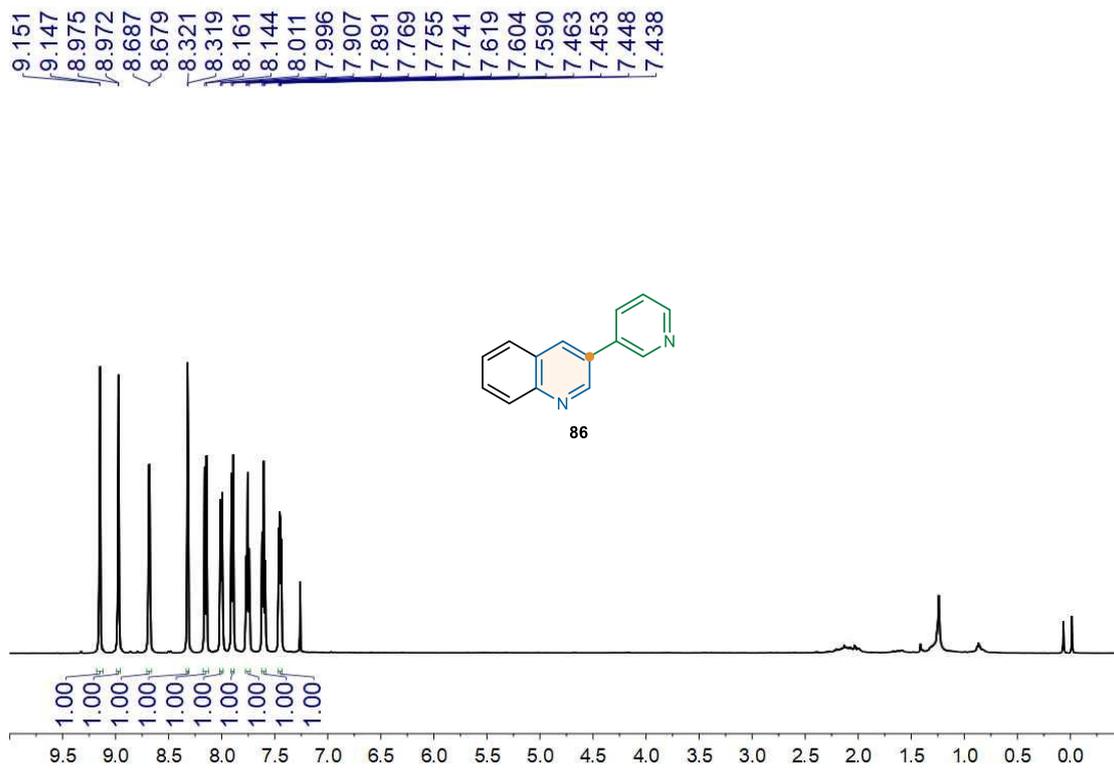




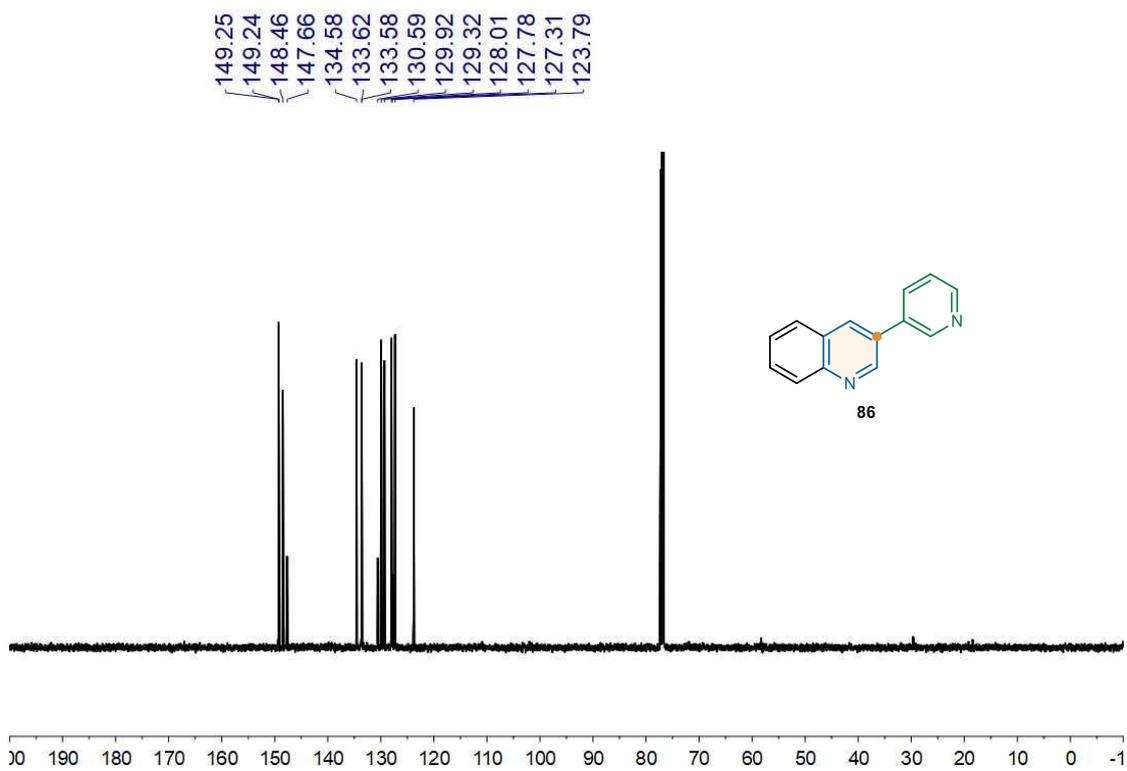
Supplementary Fig. 239.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **85**



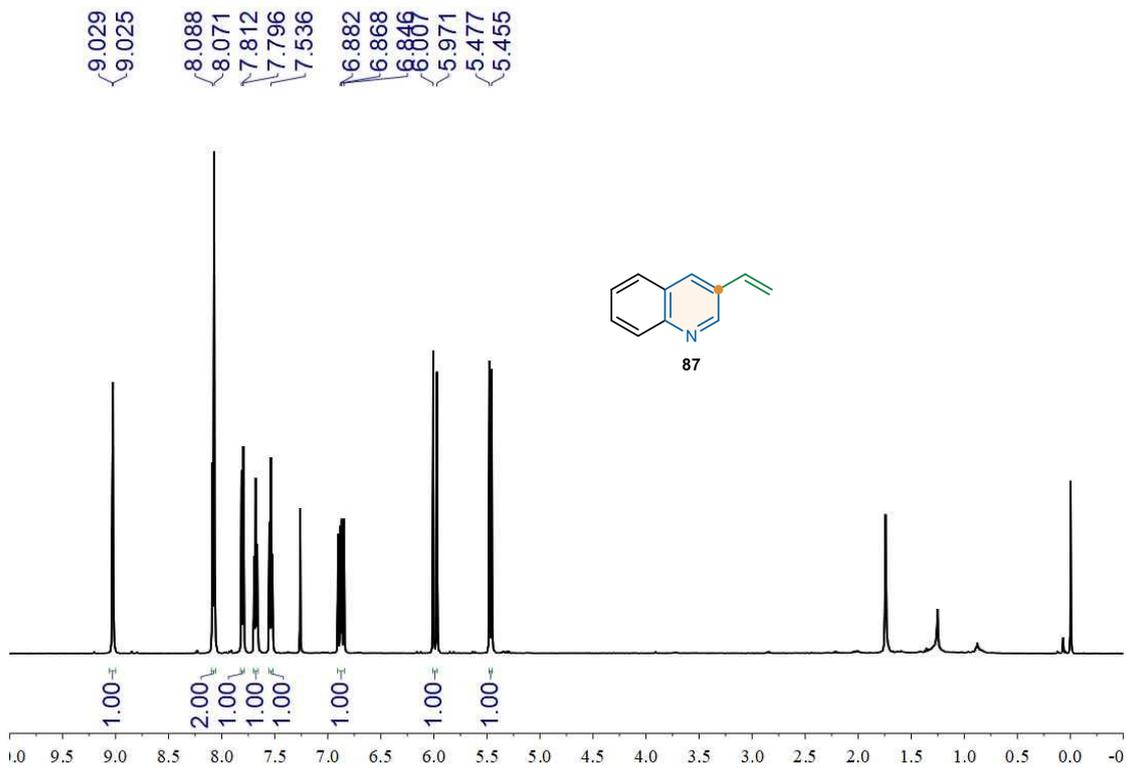
Supplementary Fig. 240.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of **85**



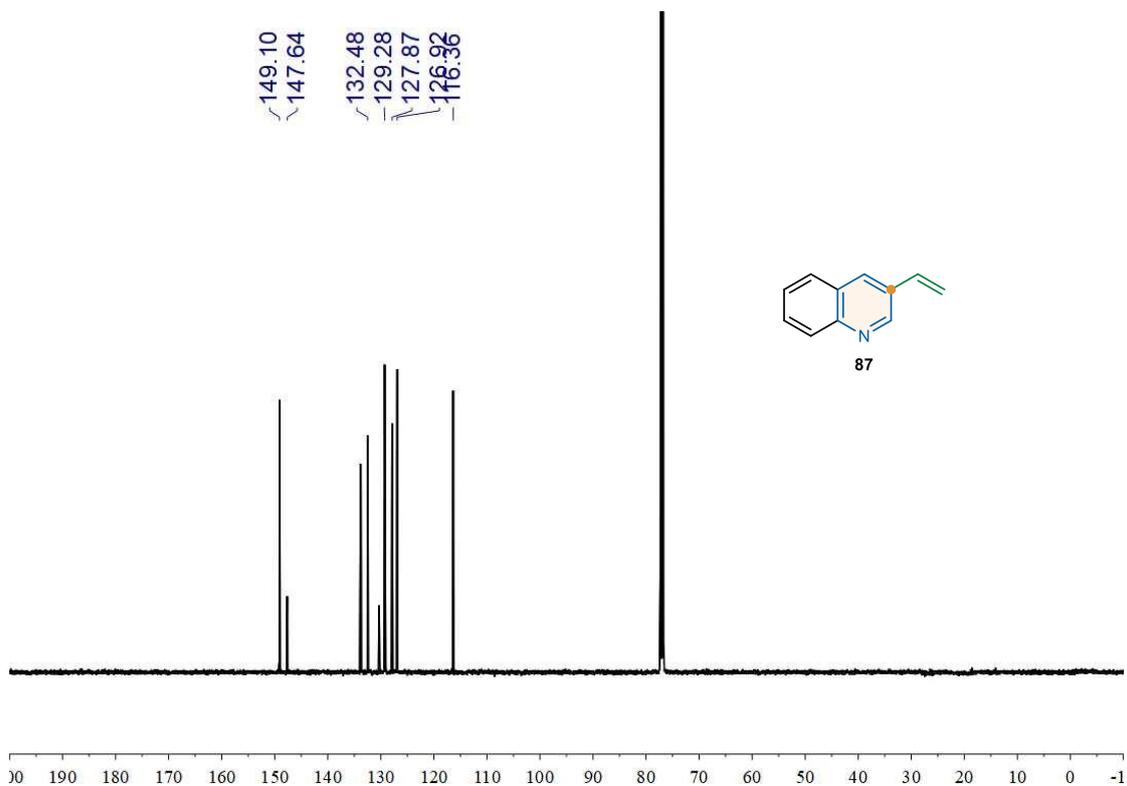
Supplementary Fig. 241.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **86**



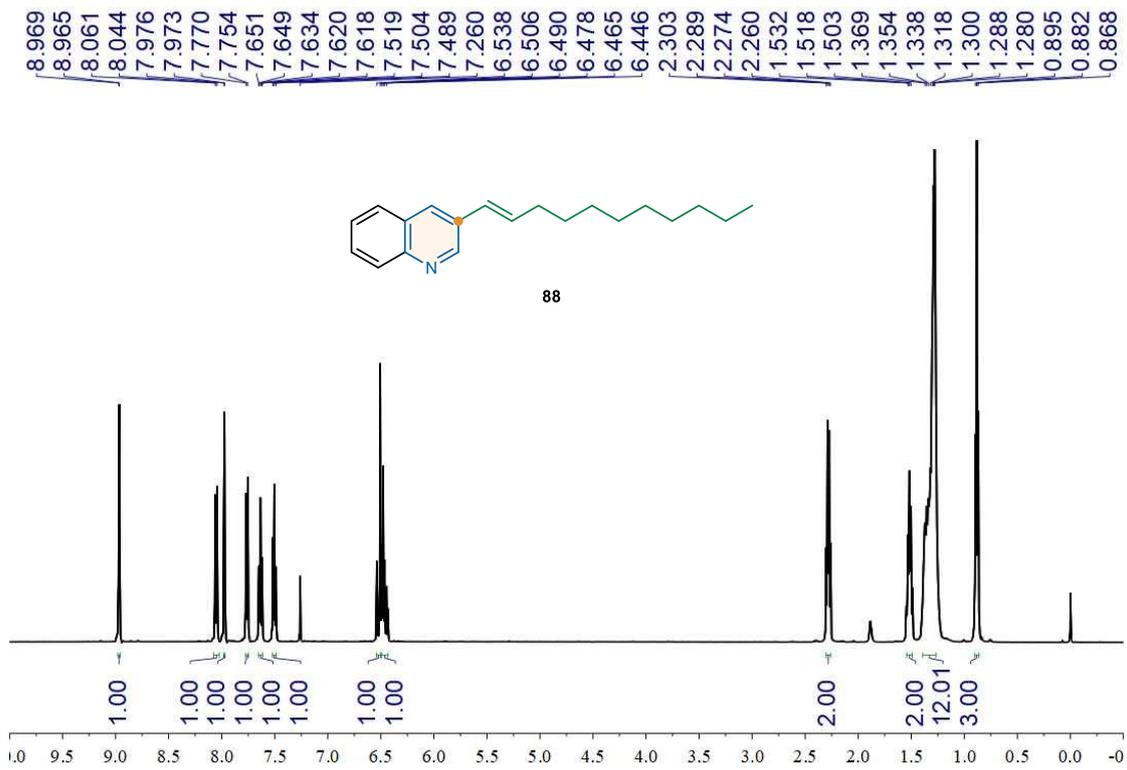
Supplementary Fig. 242.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of **86**



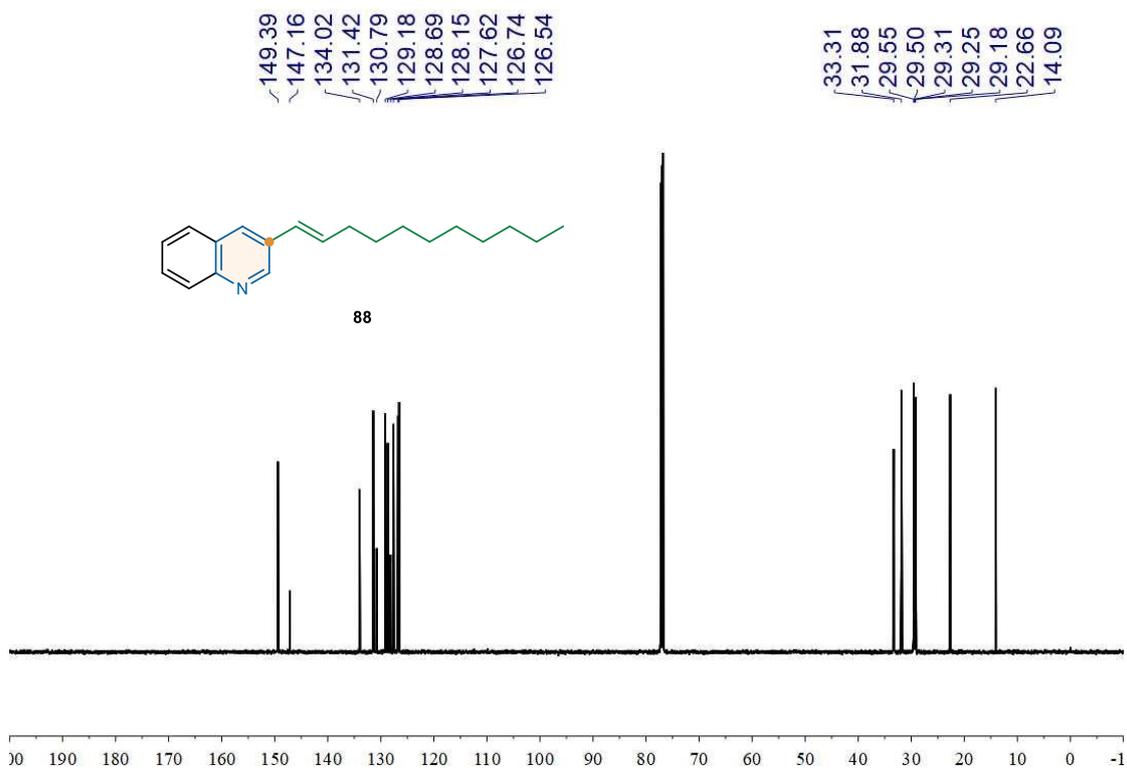
Supplementary Fig. 243.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **87**



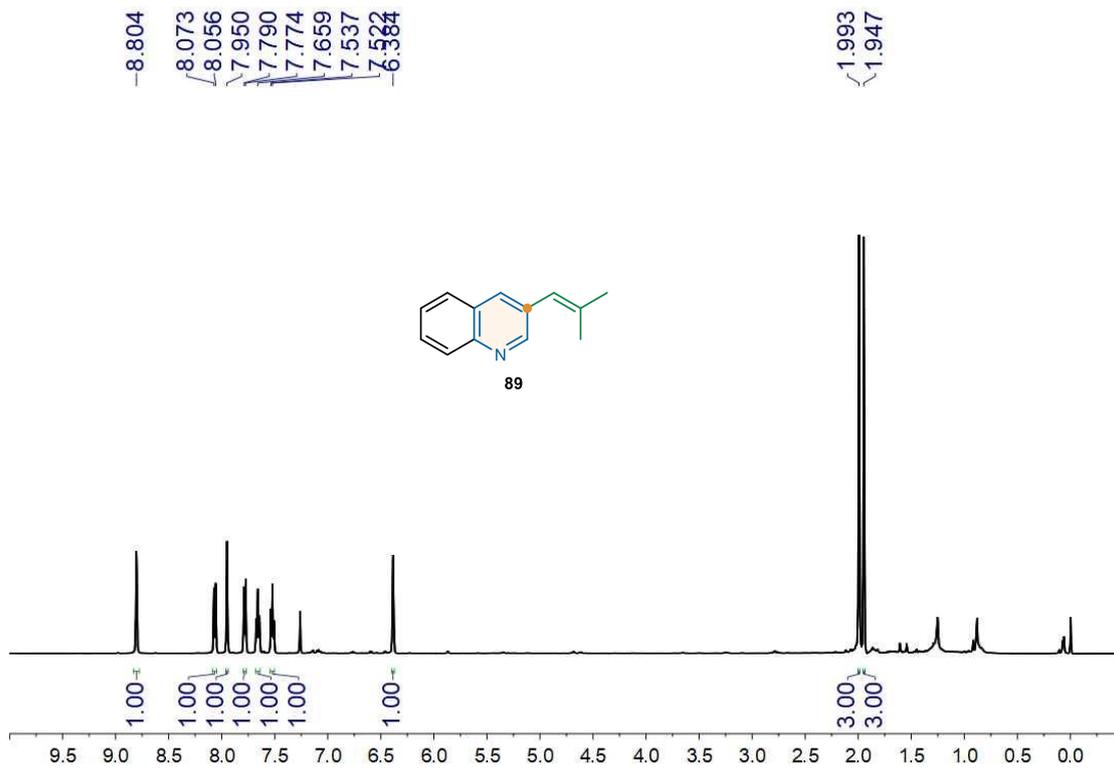
Supplementary Fig. 244.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of **87**



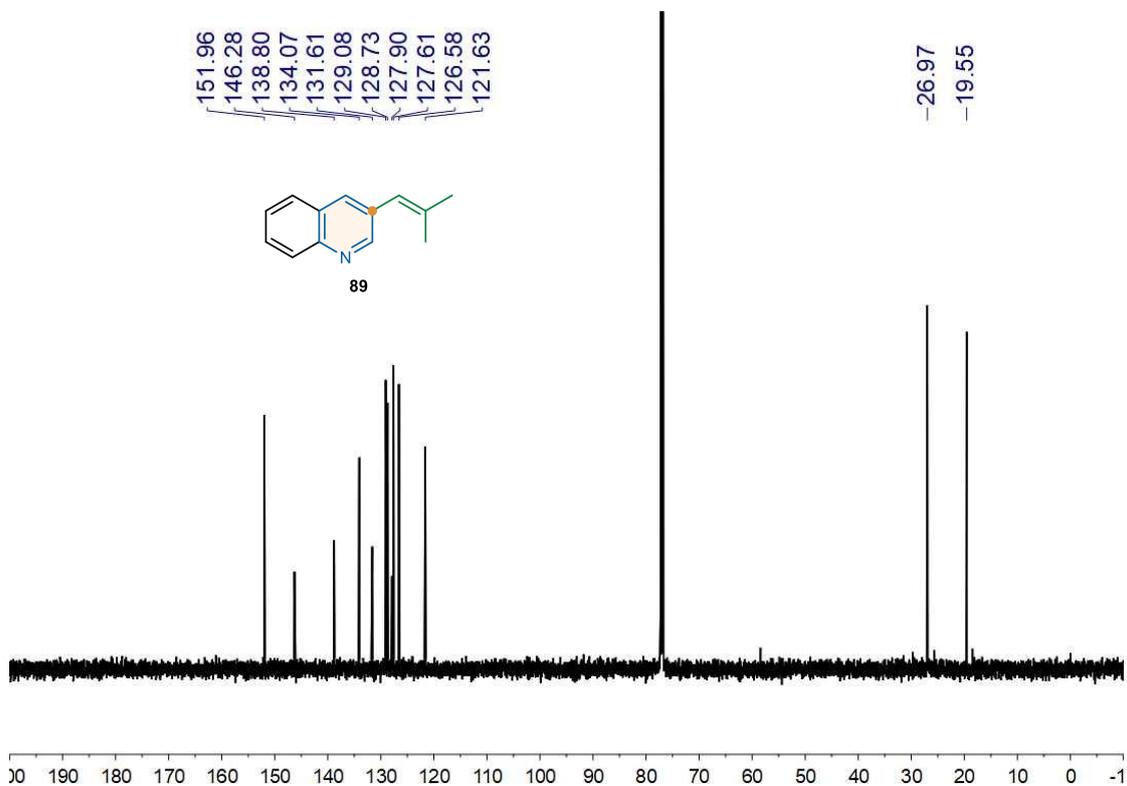
Supplementary Fig. 245. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **88**



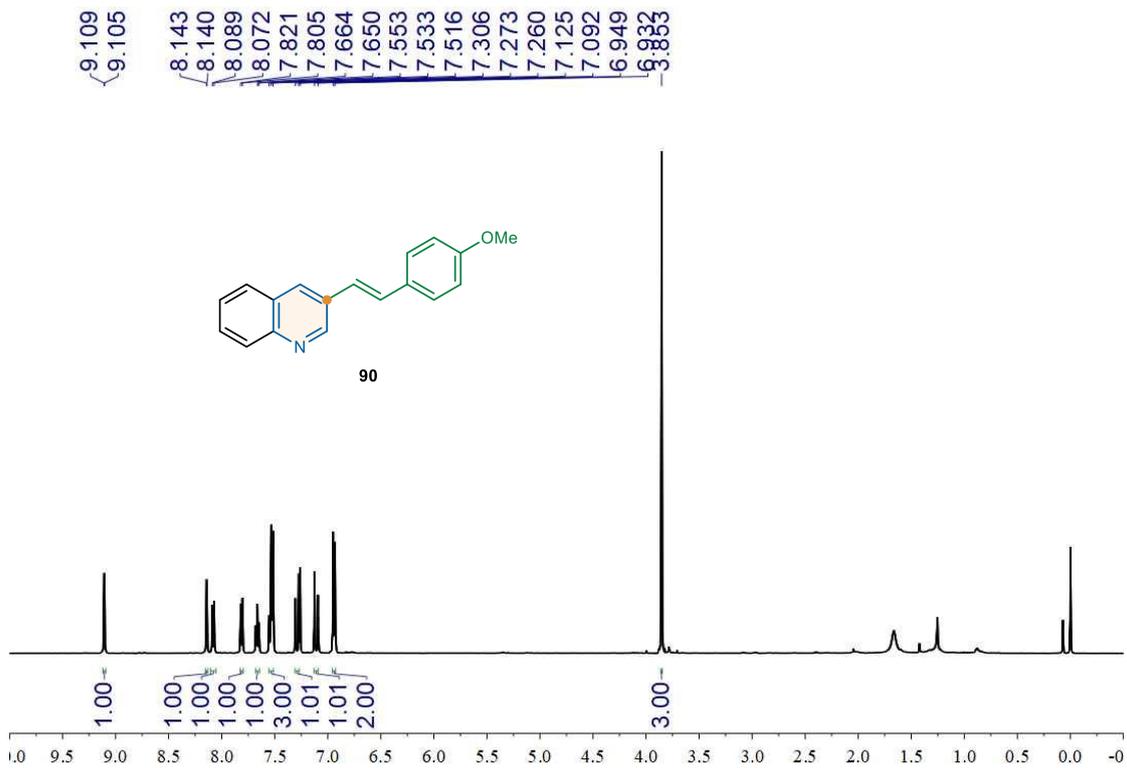
Supplementary Fig. 246. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of **88**



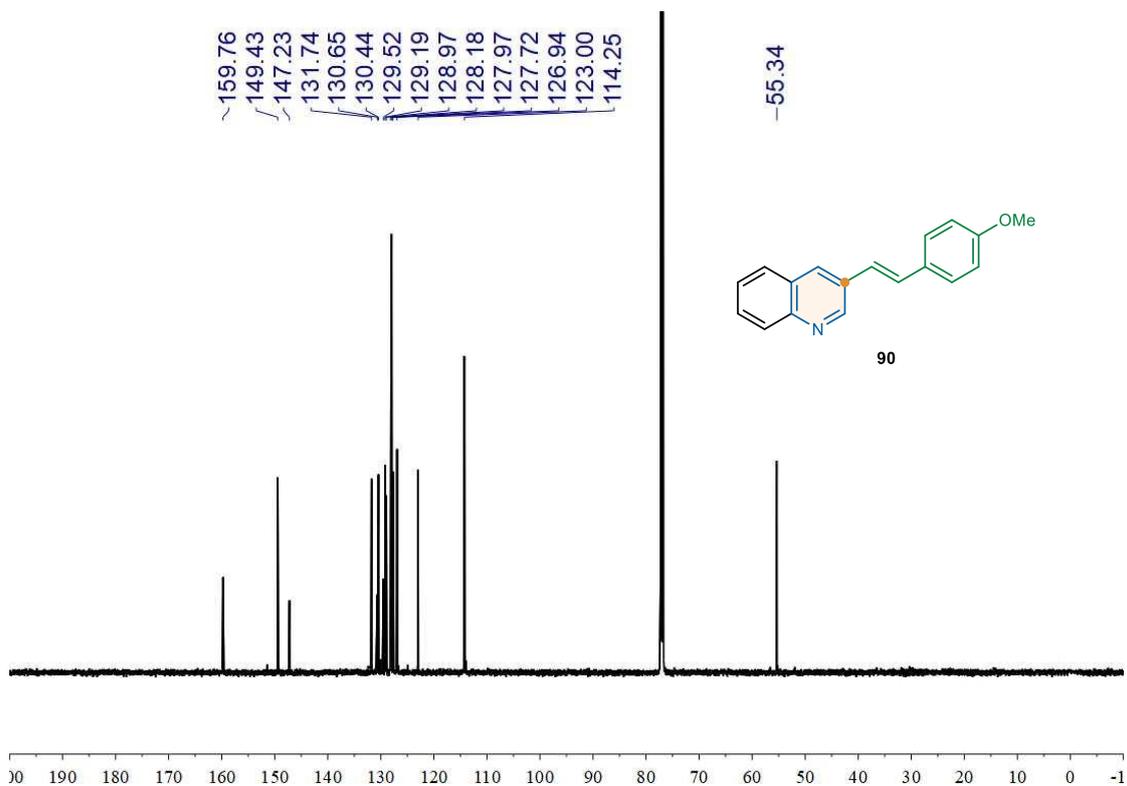
Supplementary Fig. 247. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **89**



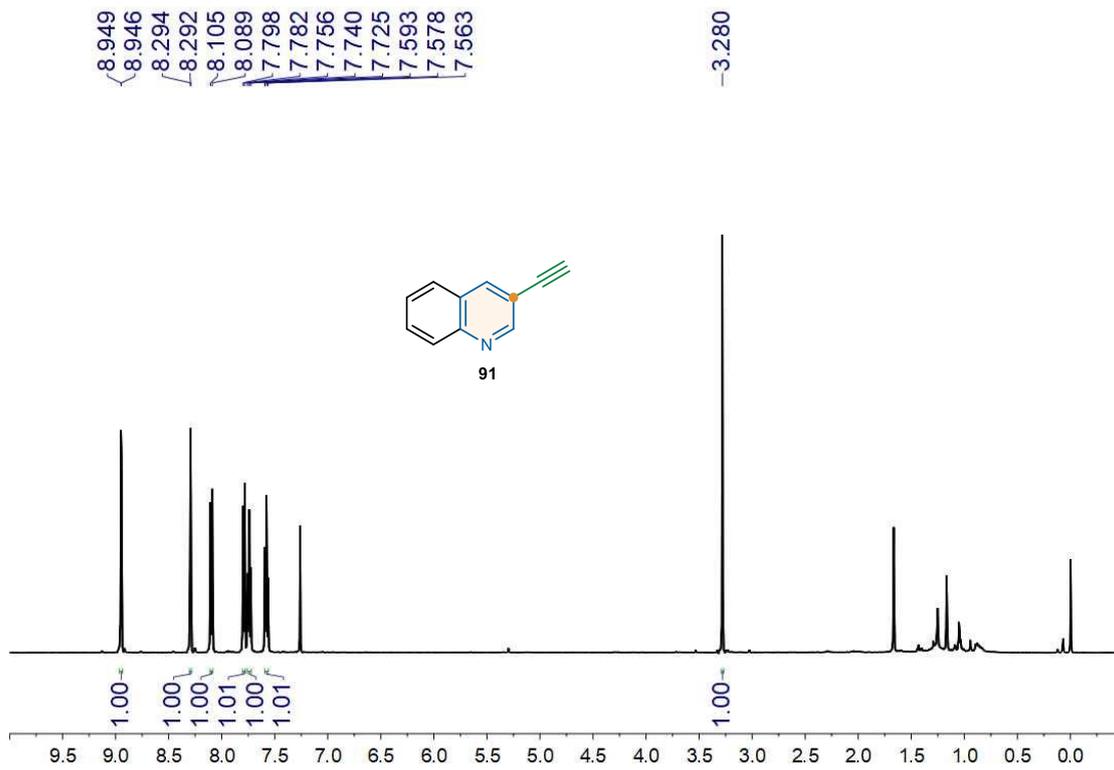
Supplementary Fig. 248. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of **89**



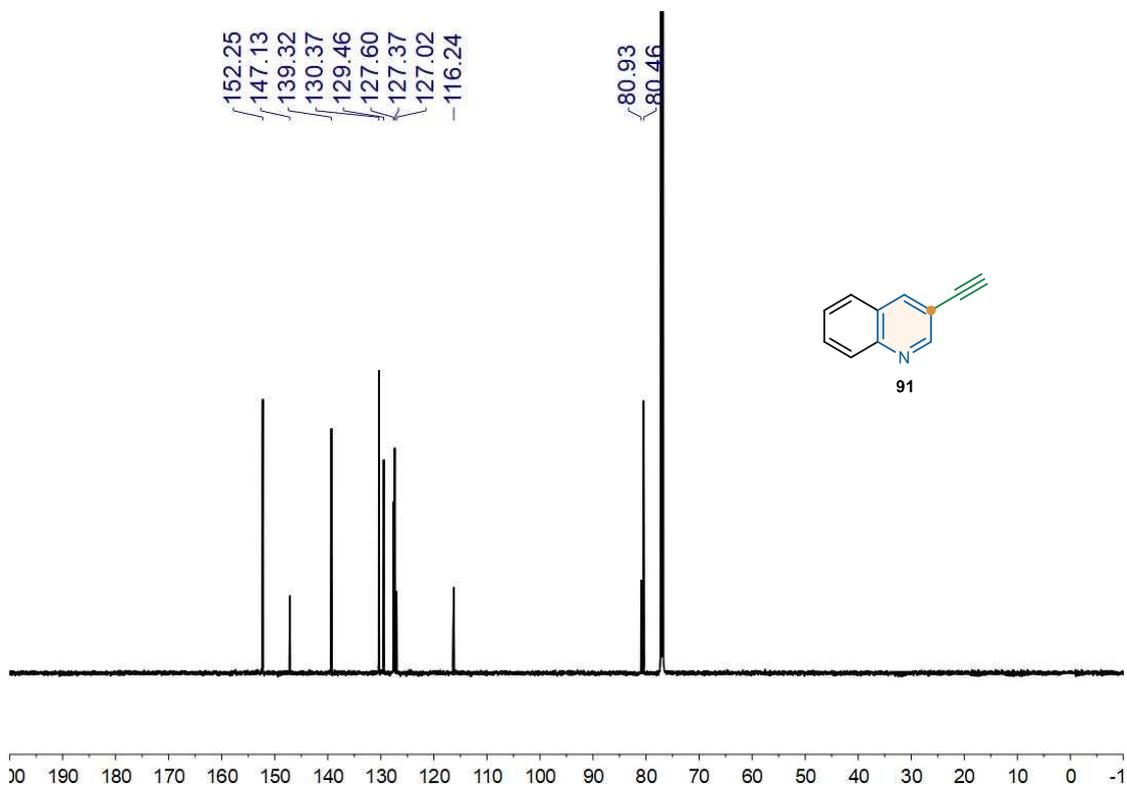
Supplementary Fig. 249. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of 90



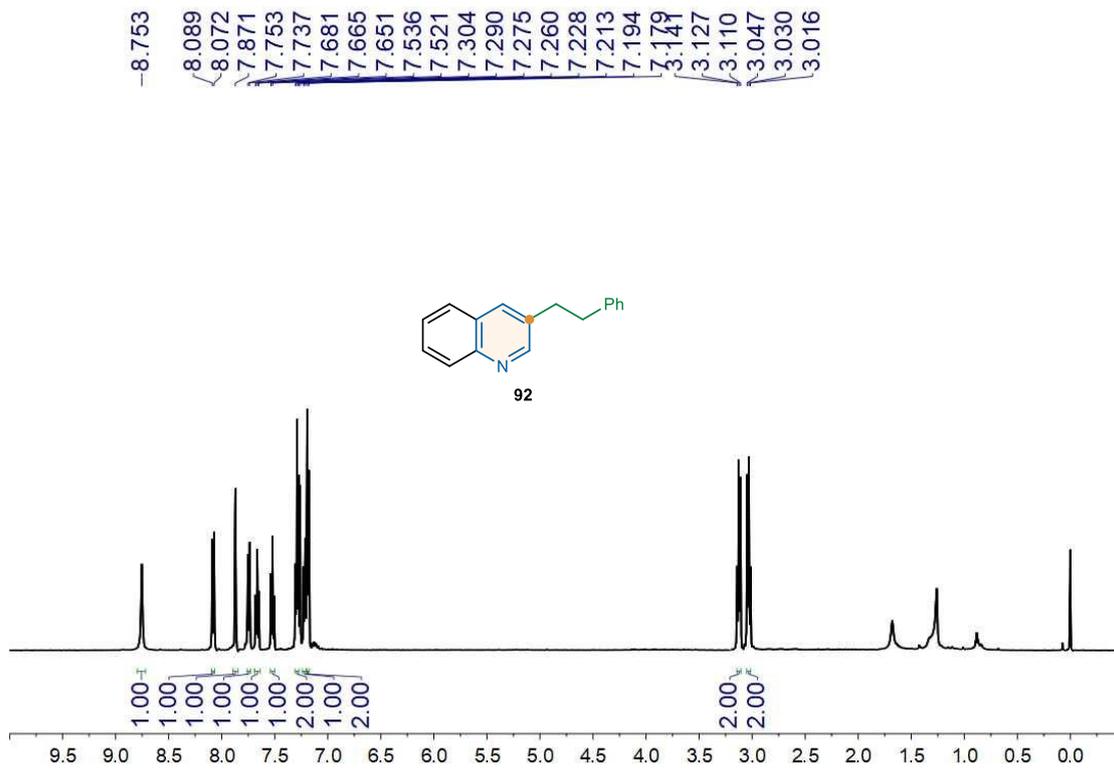
Supplementary Fig. 250. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of 90



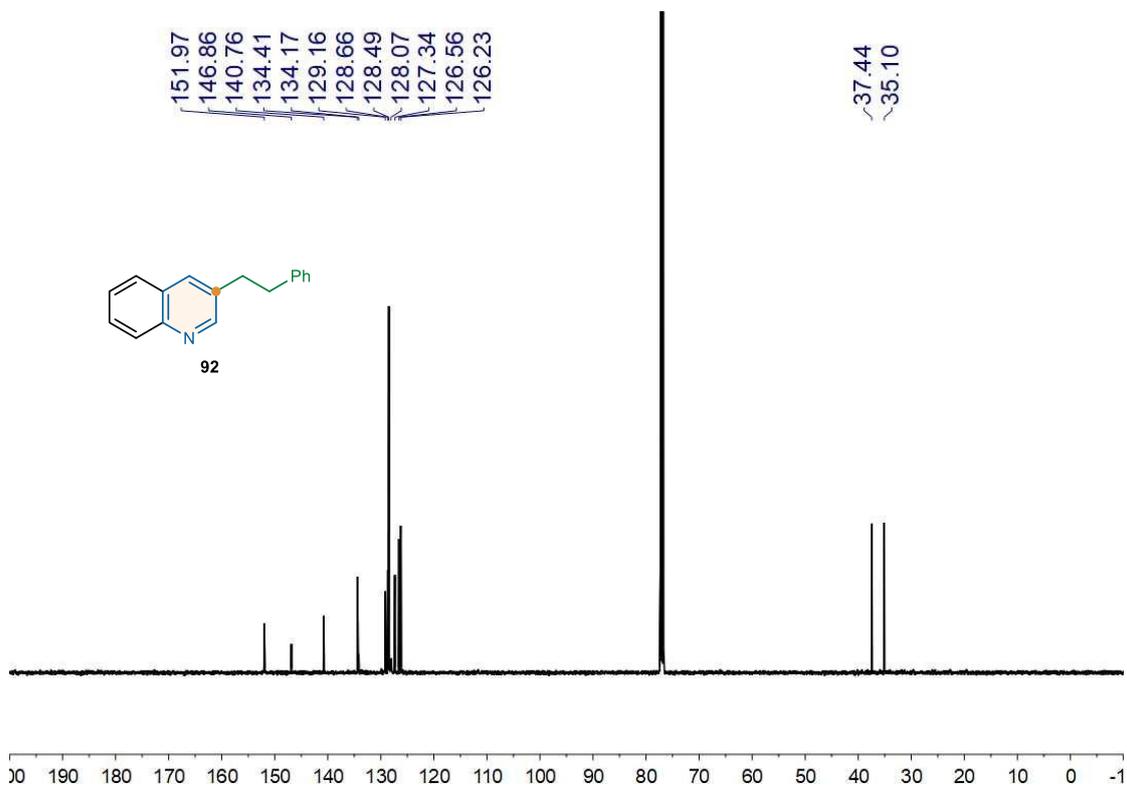
Supplementary Fig. 251. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of 91



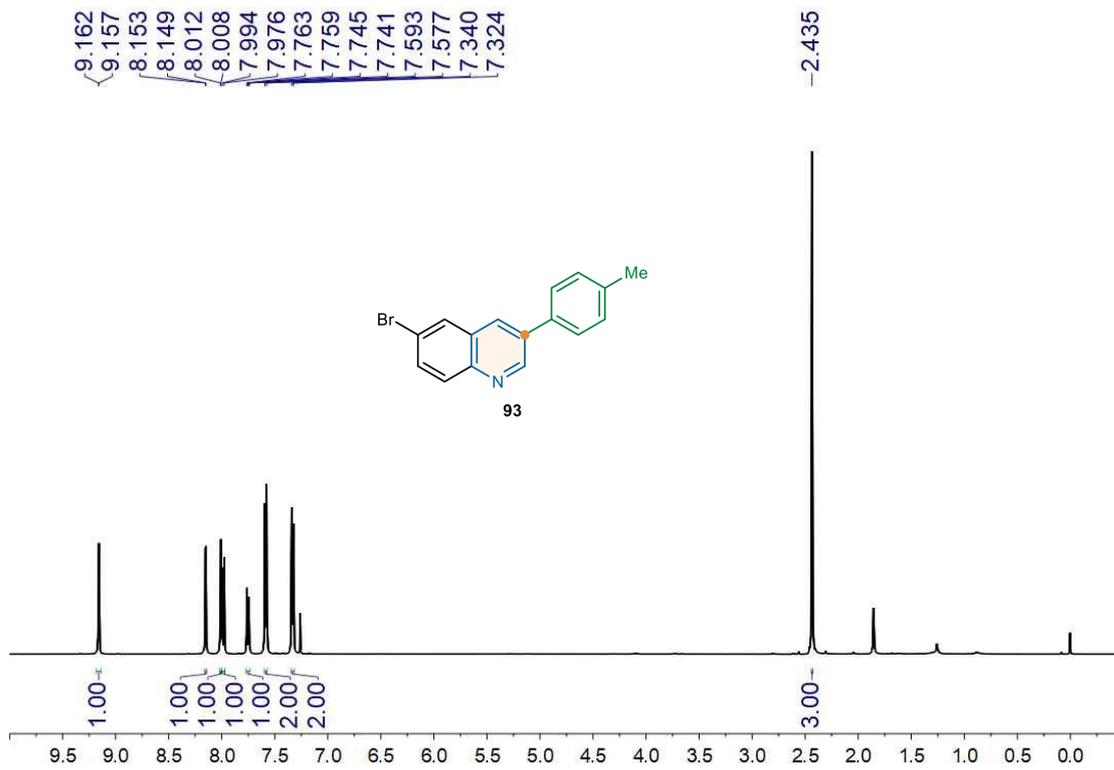
Supplementary Fig. 252. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of 91



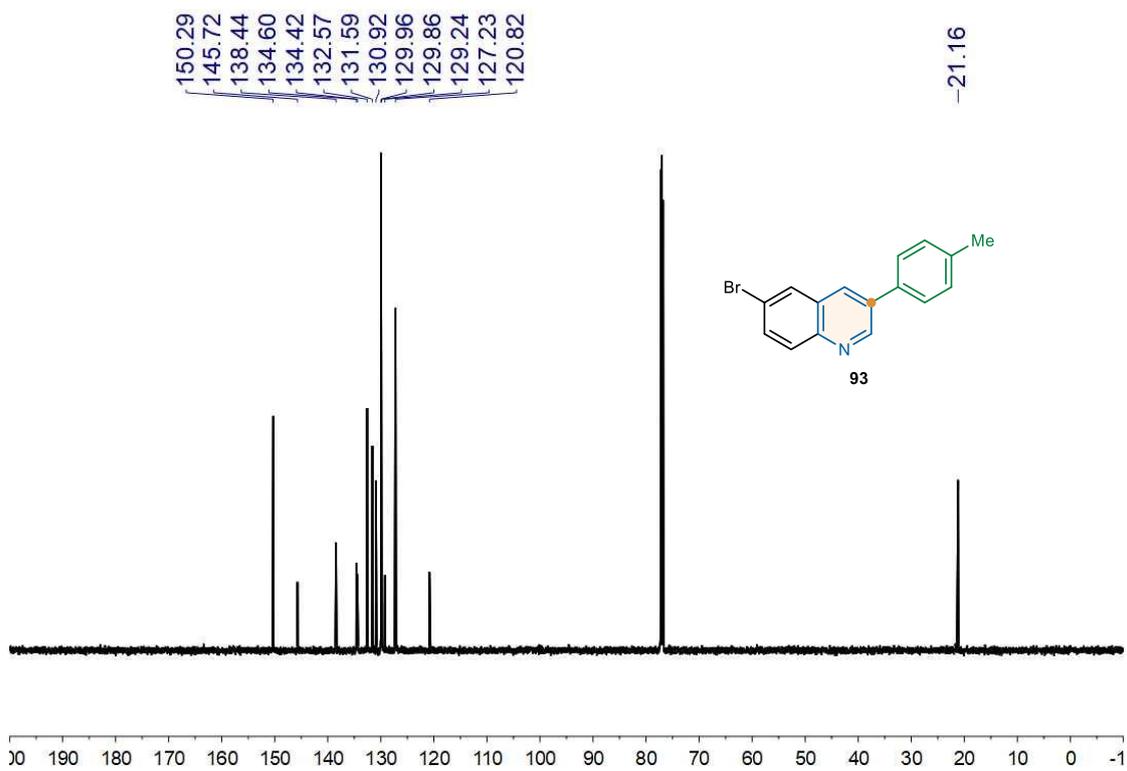
Supplementary Fig. 253.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **92**



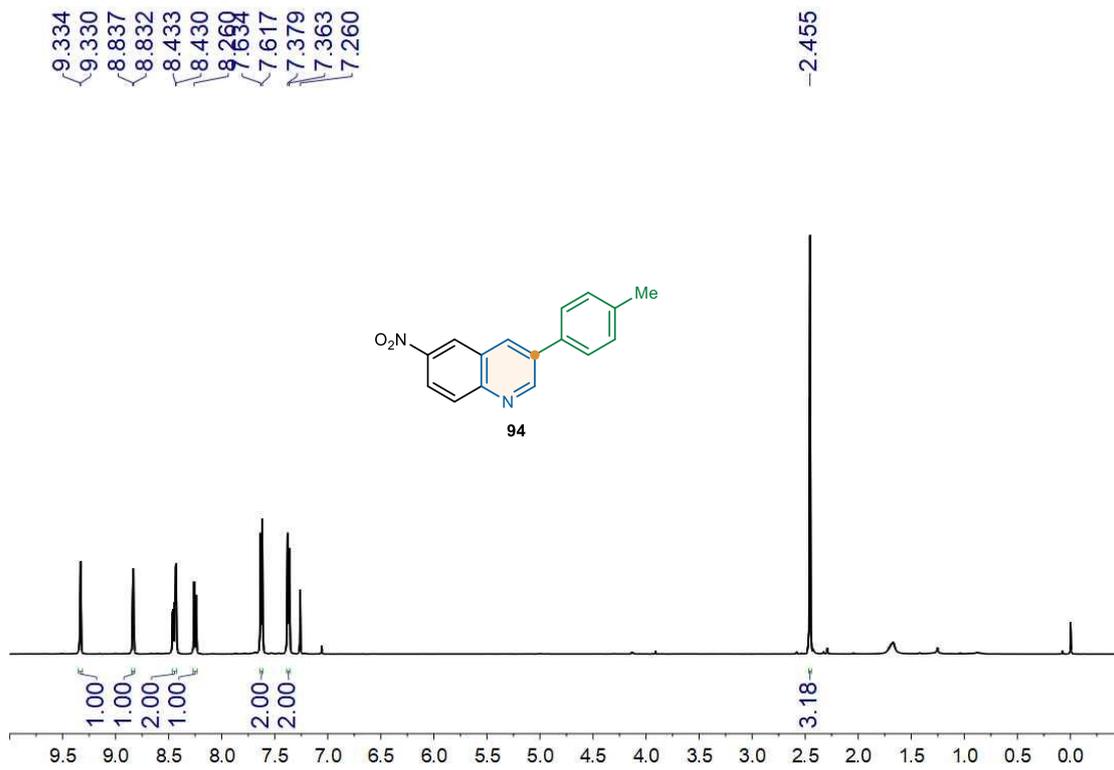
Supplementary Fig. 254.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of **92**



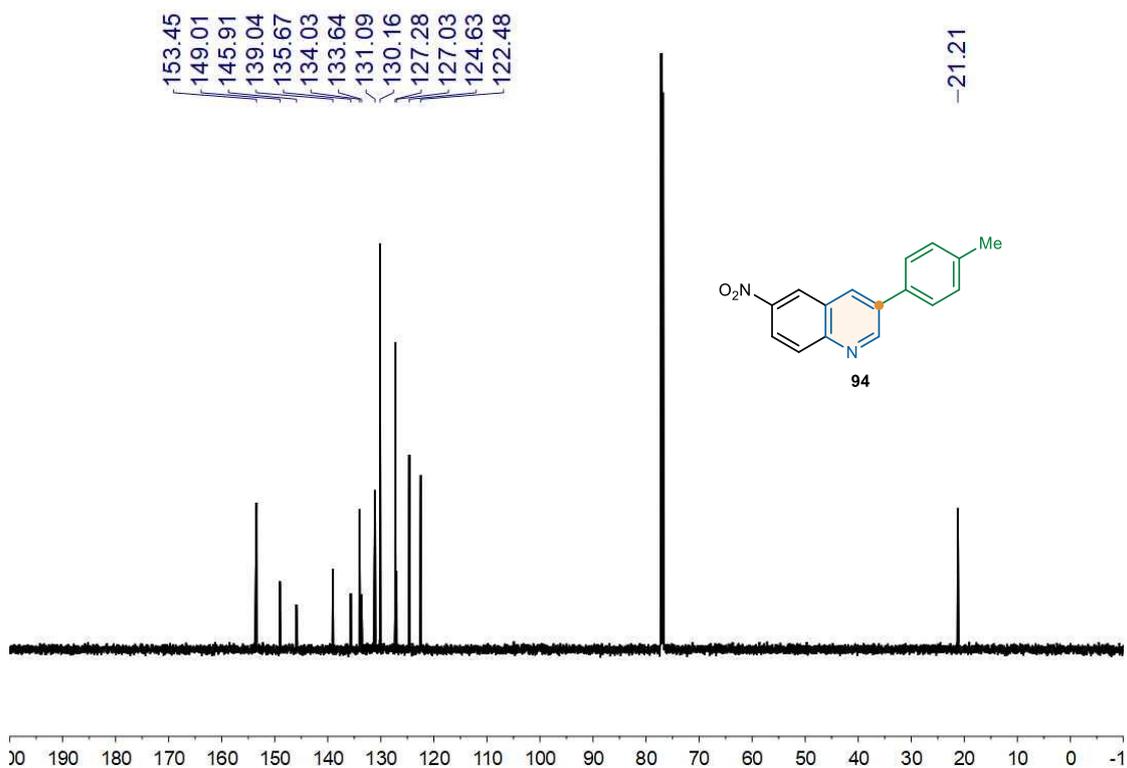
Supplementary Fig. 255.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of 93



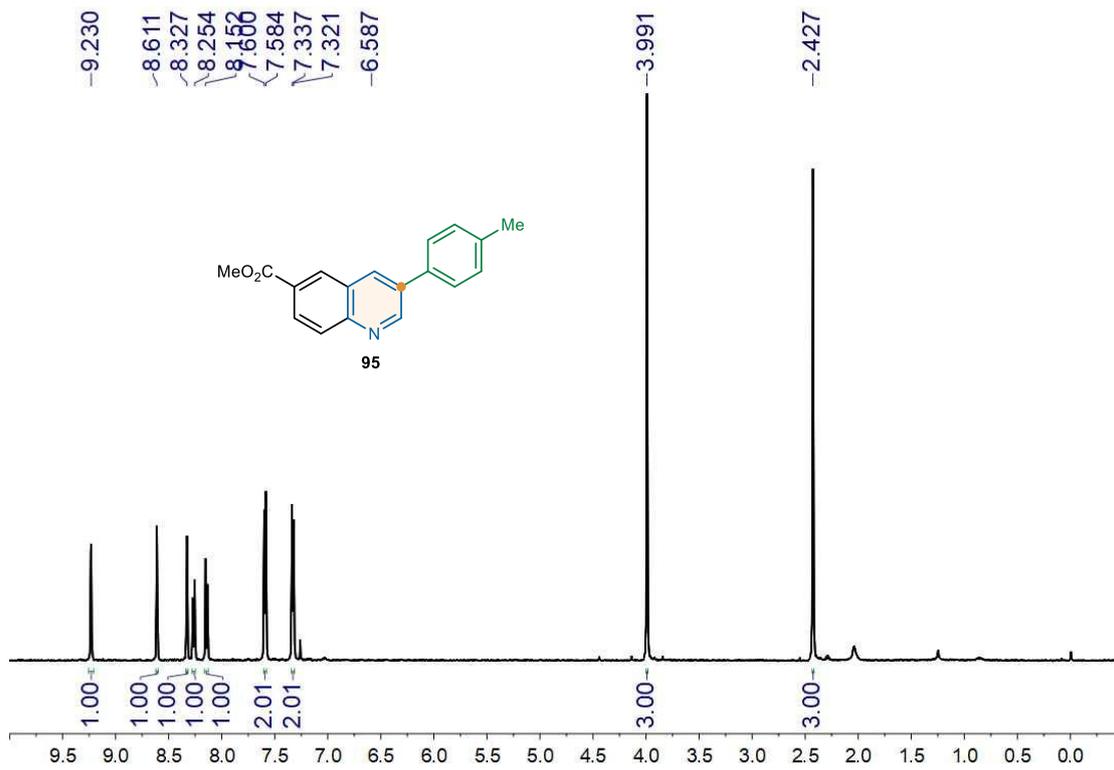
Supplementary Fig. 256.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of 93



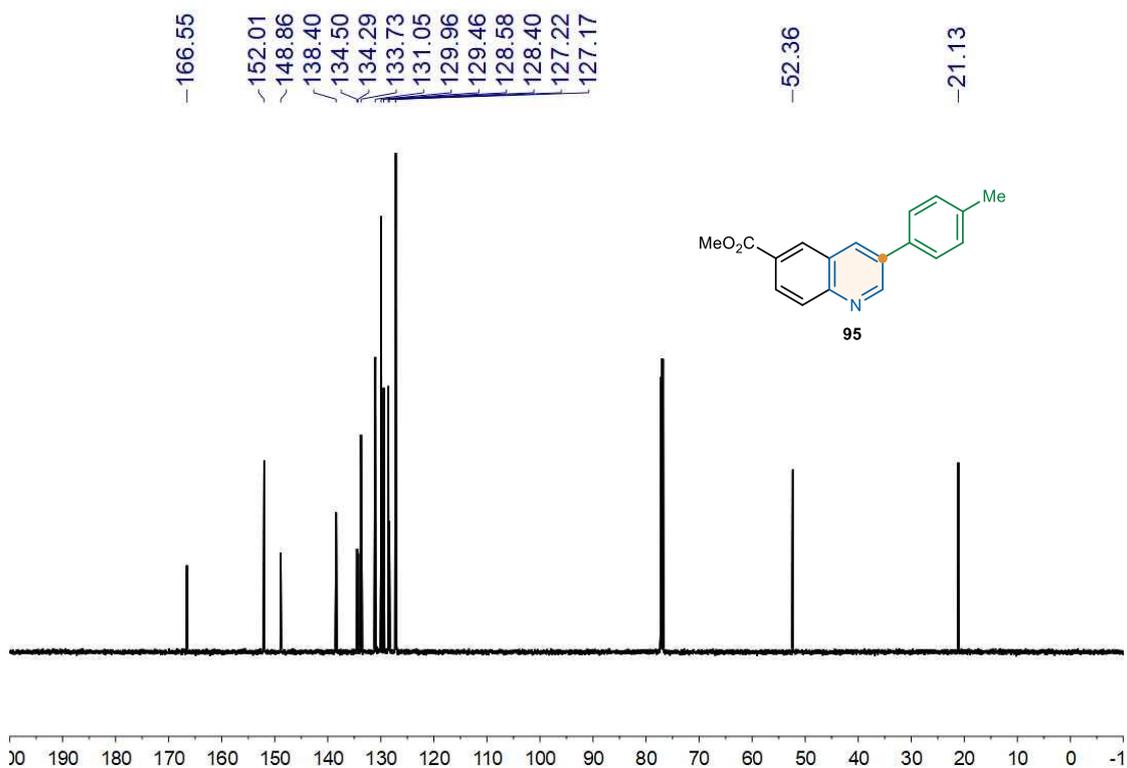
Supplementary Fig. 257. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of 94



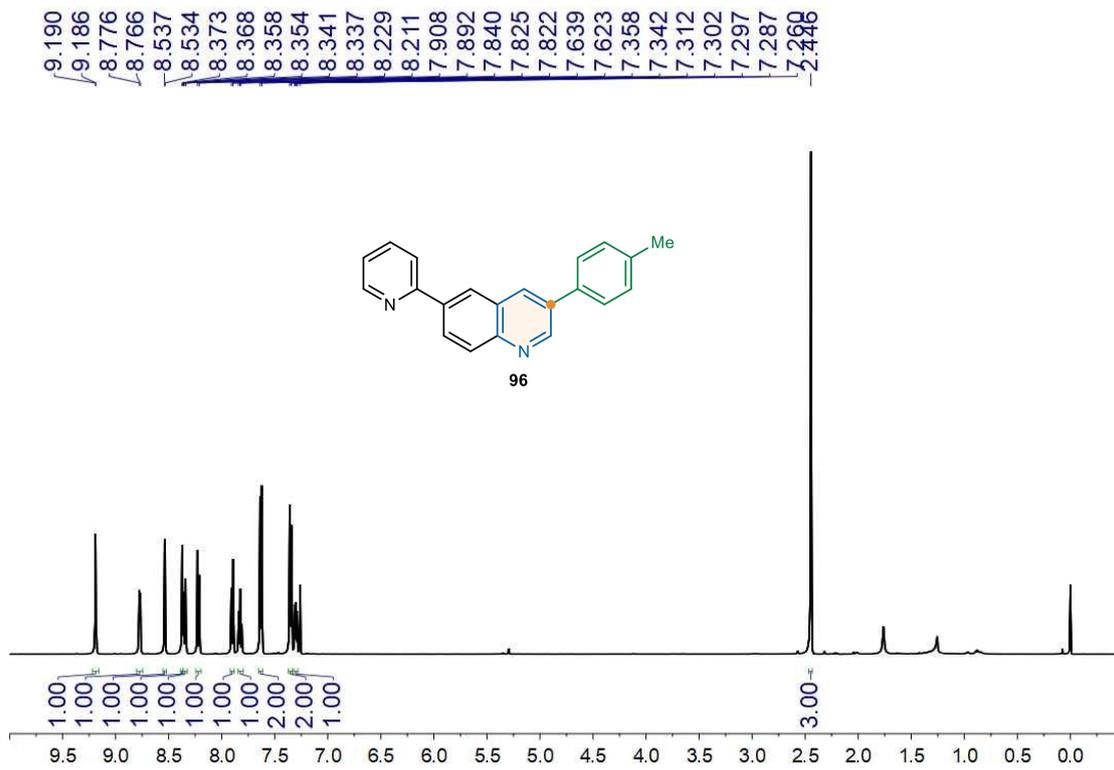
Supplementary Fig. 258. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of 94



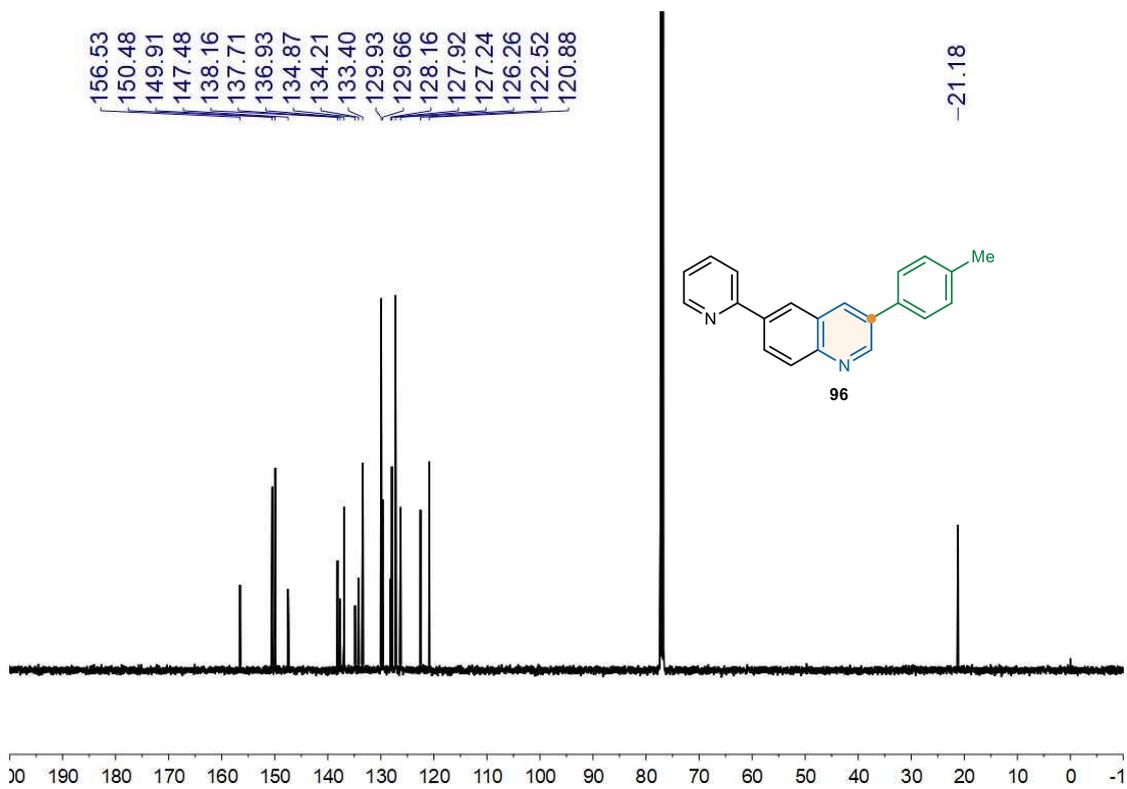
Supplementary Fig. 259.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of 95



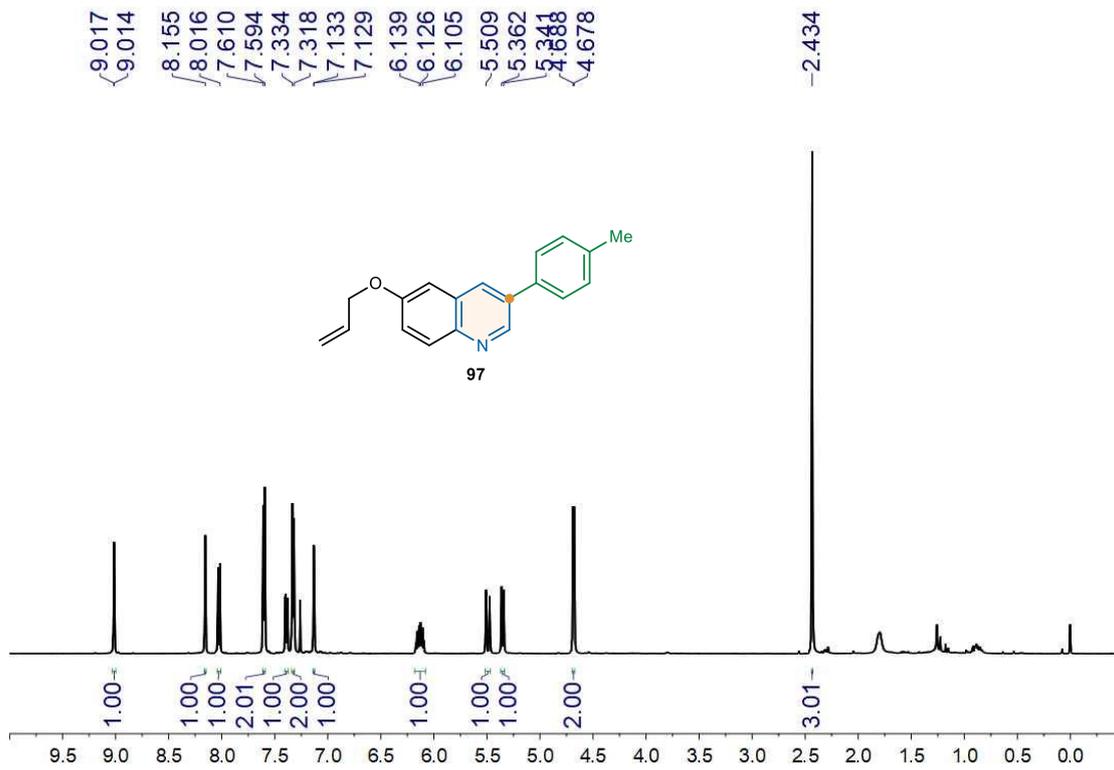
Supplementary Fig. 260.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of 95



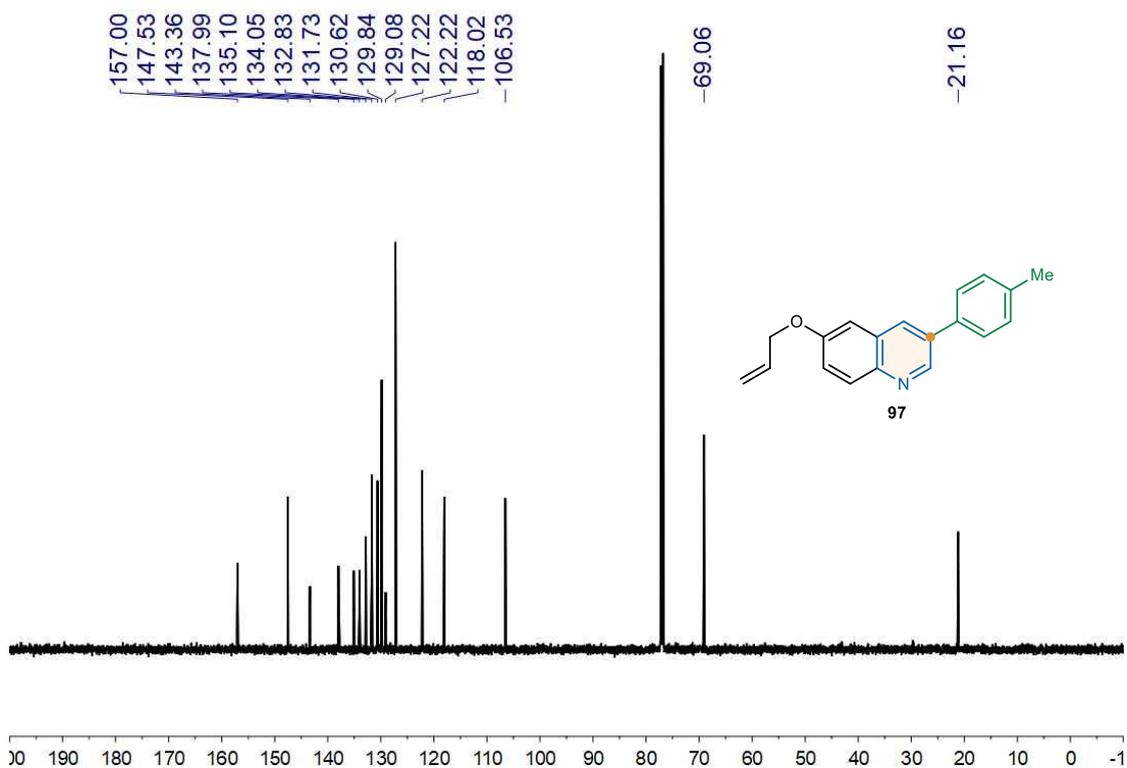
Supplementary Fig. 261. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of 96



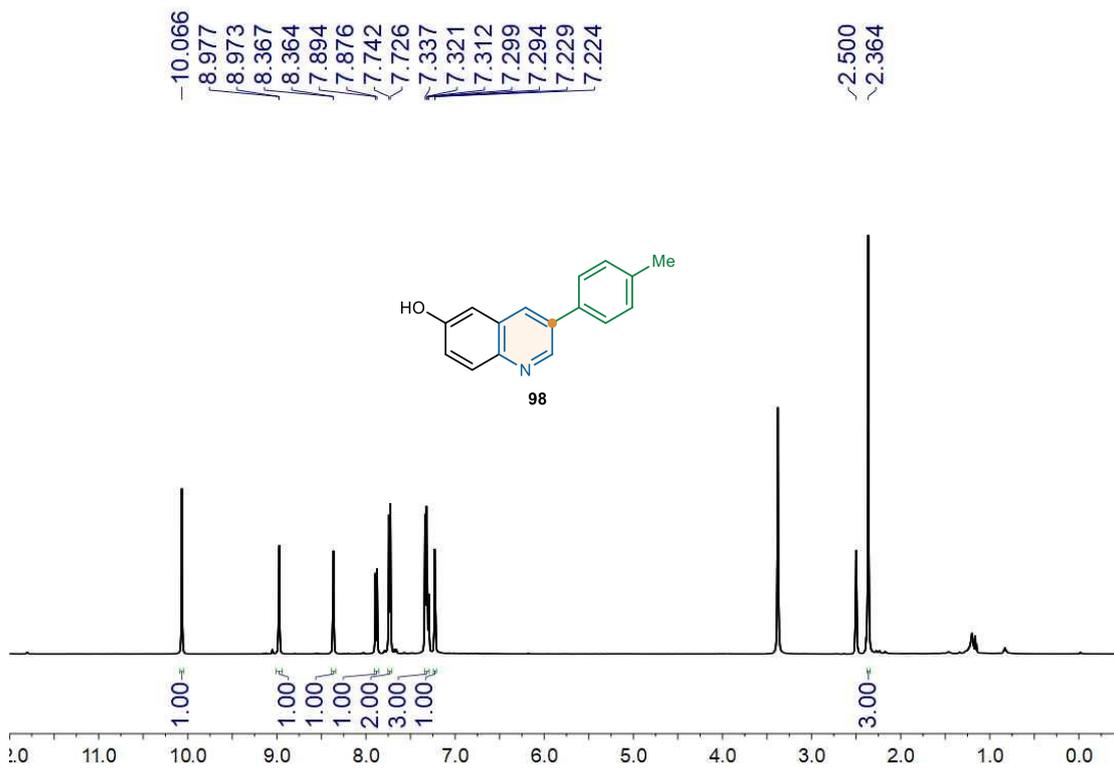
Supplementary Fig. 262. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of 96



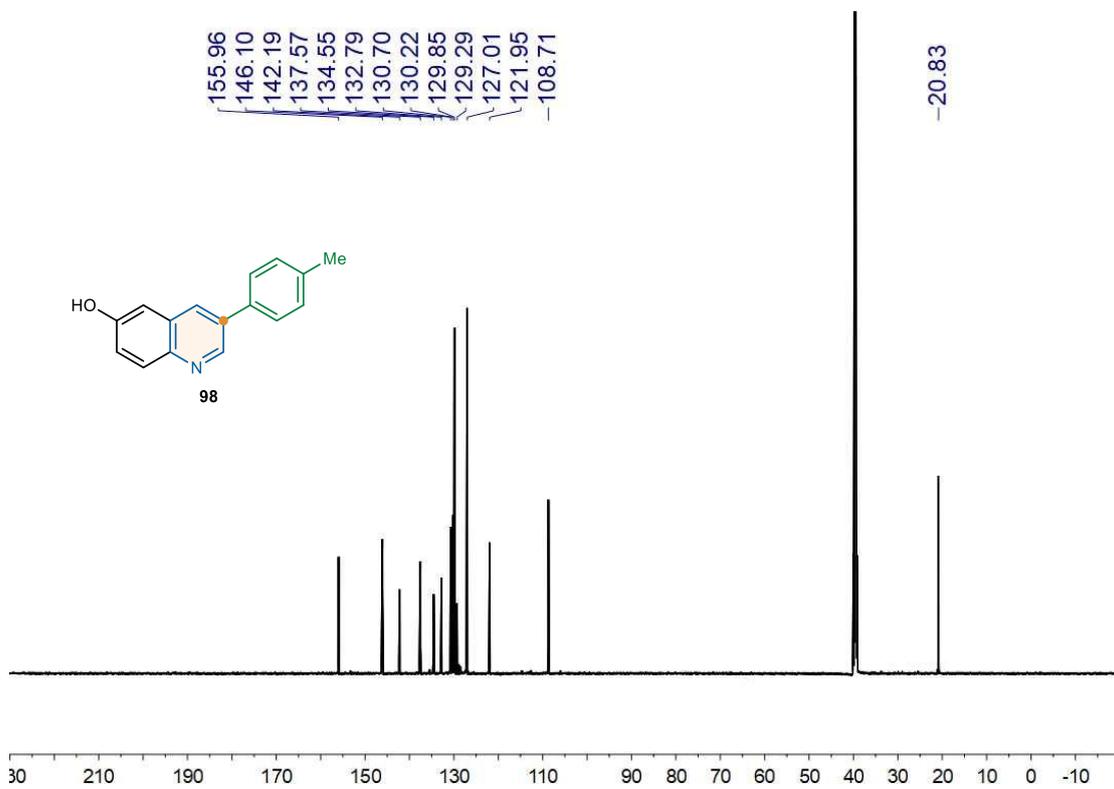
Supplementary Fig. 263. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of 97



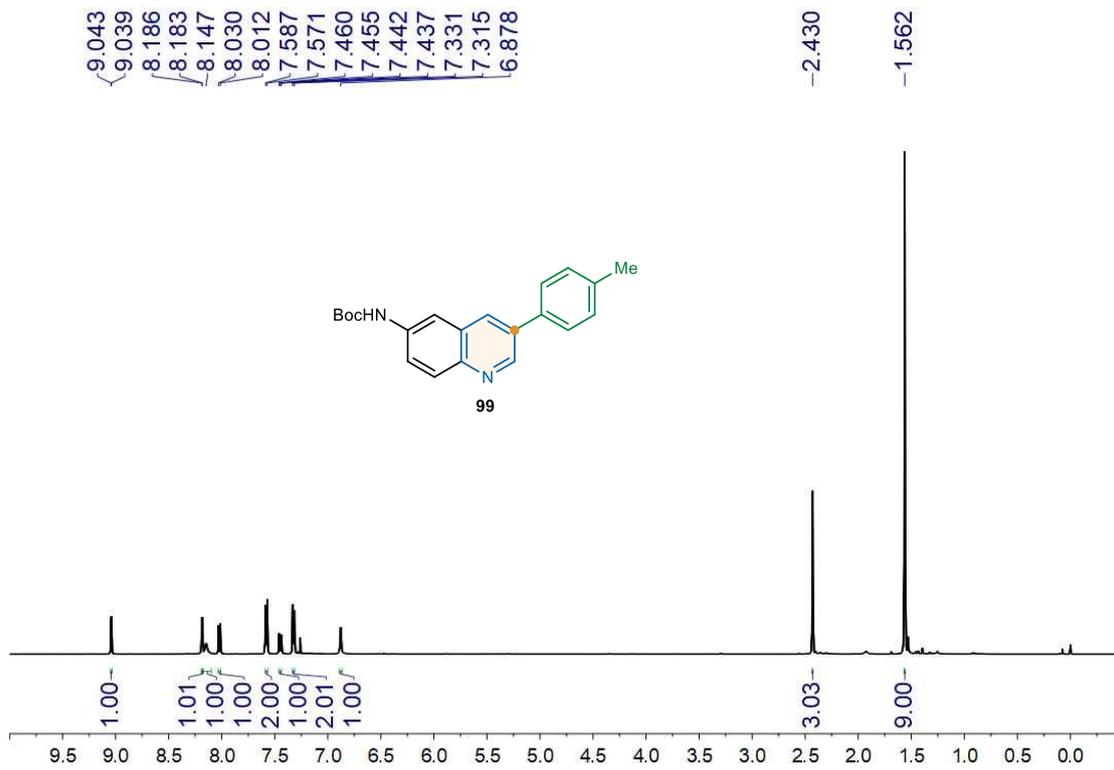
Supplementary Fig. 264. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of 97



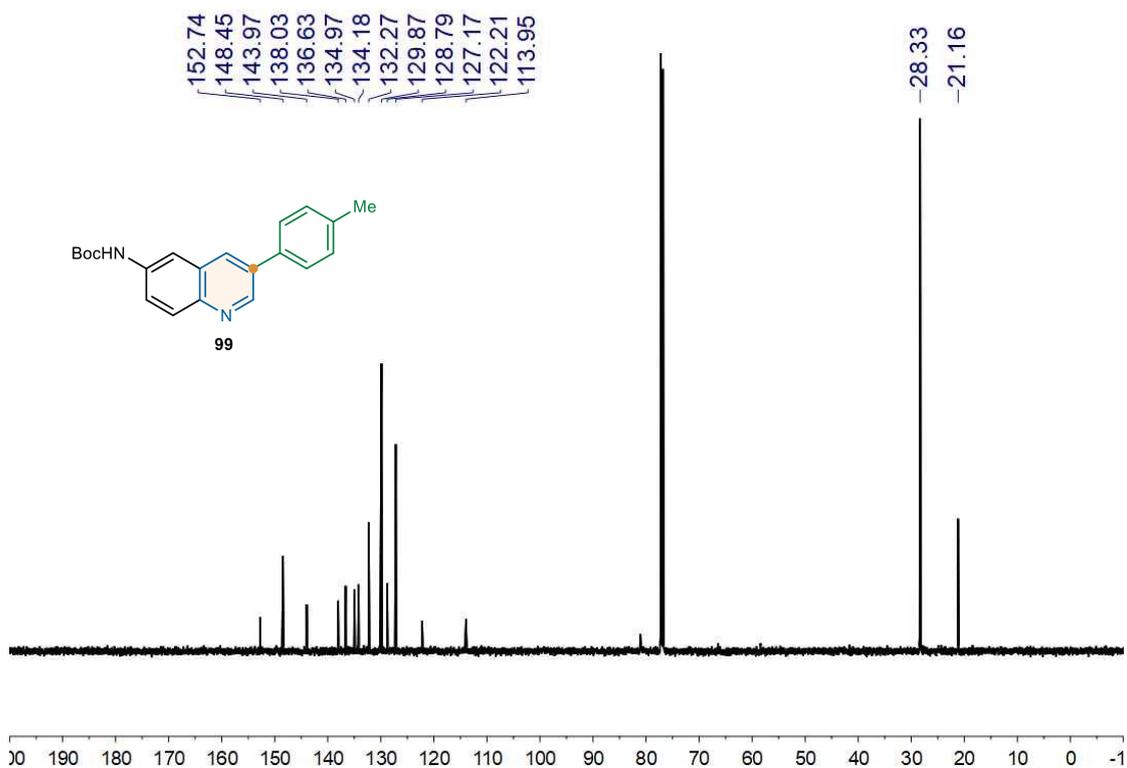
Supplementary Fig. 265. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) spectrum of 98



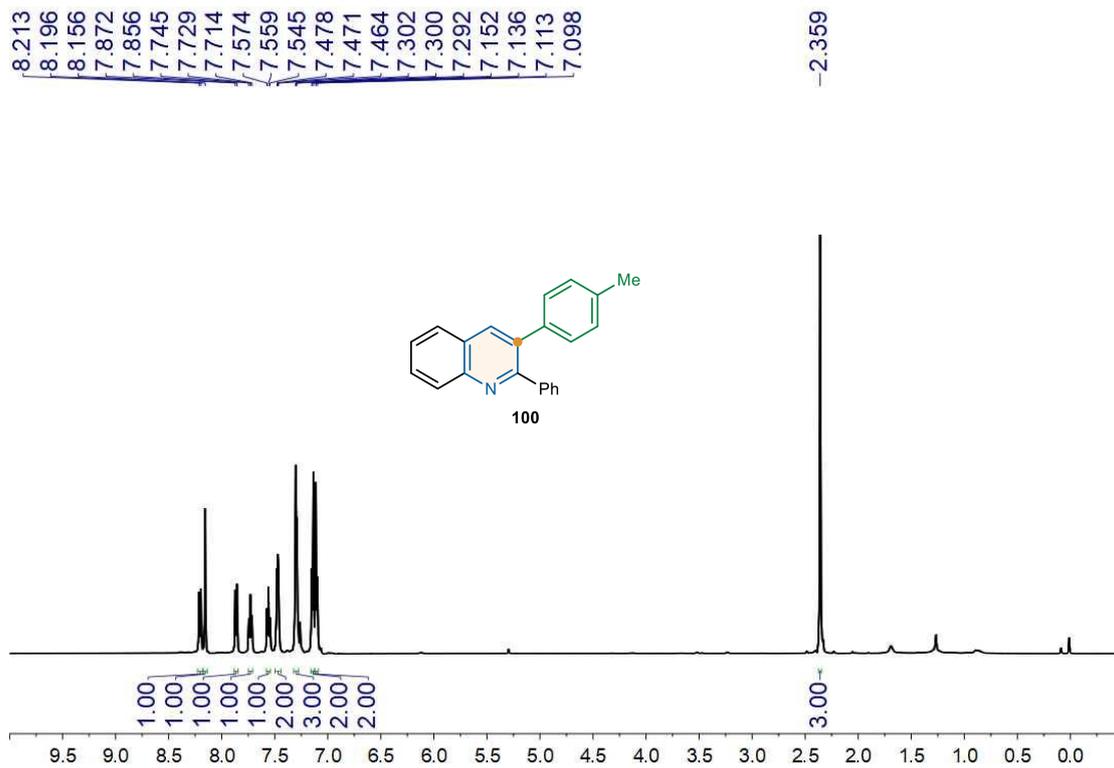
Supplementary Fig. 266. <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>) spectrum of 98



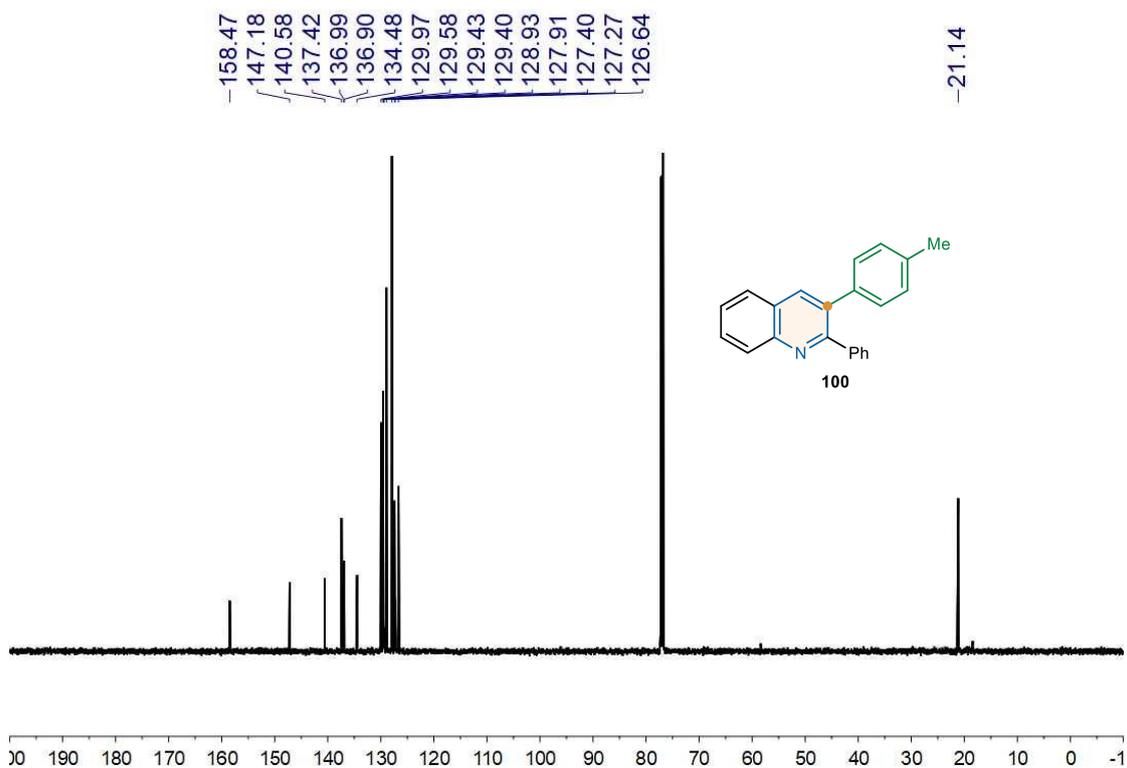
Supplementary Fig. 267. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **99**



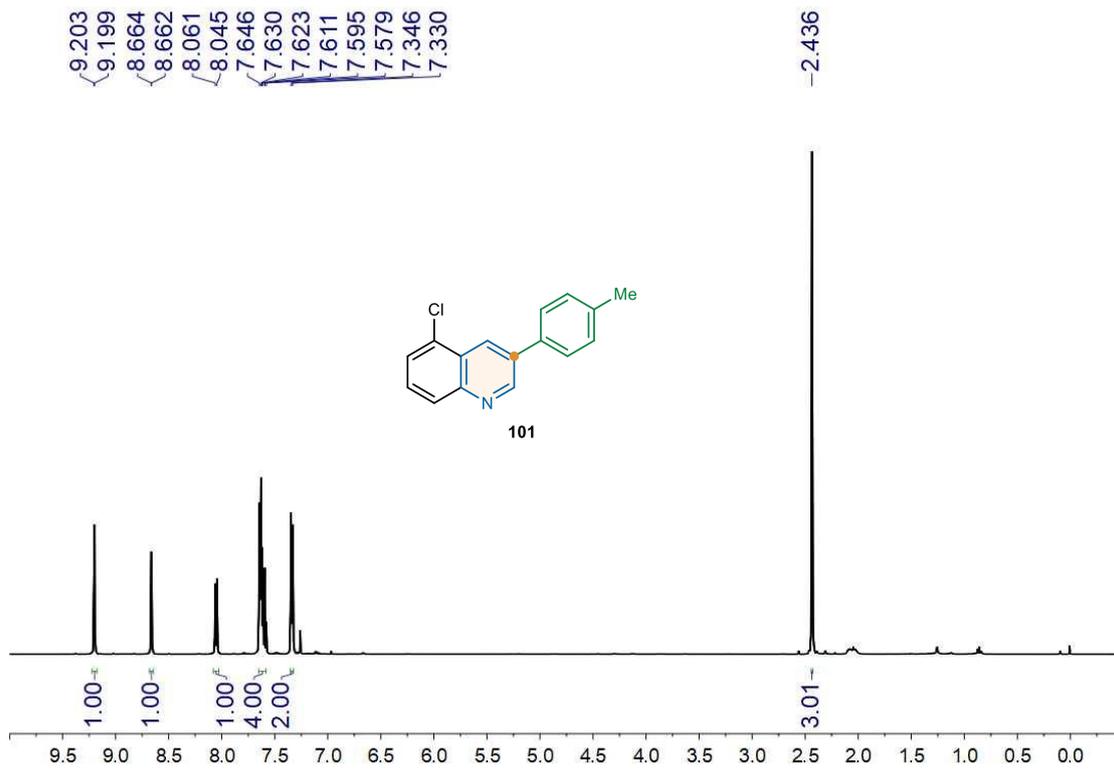
Supplementary Fig. 268. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of **99**



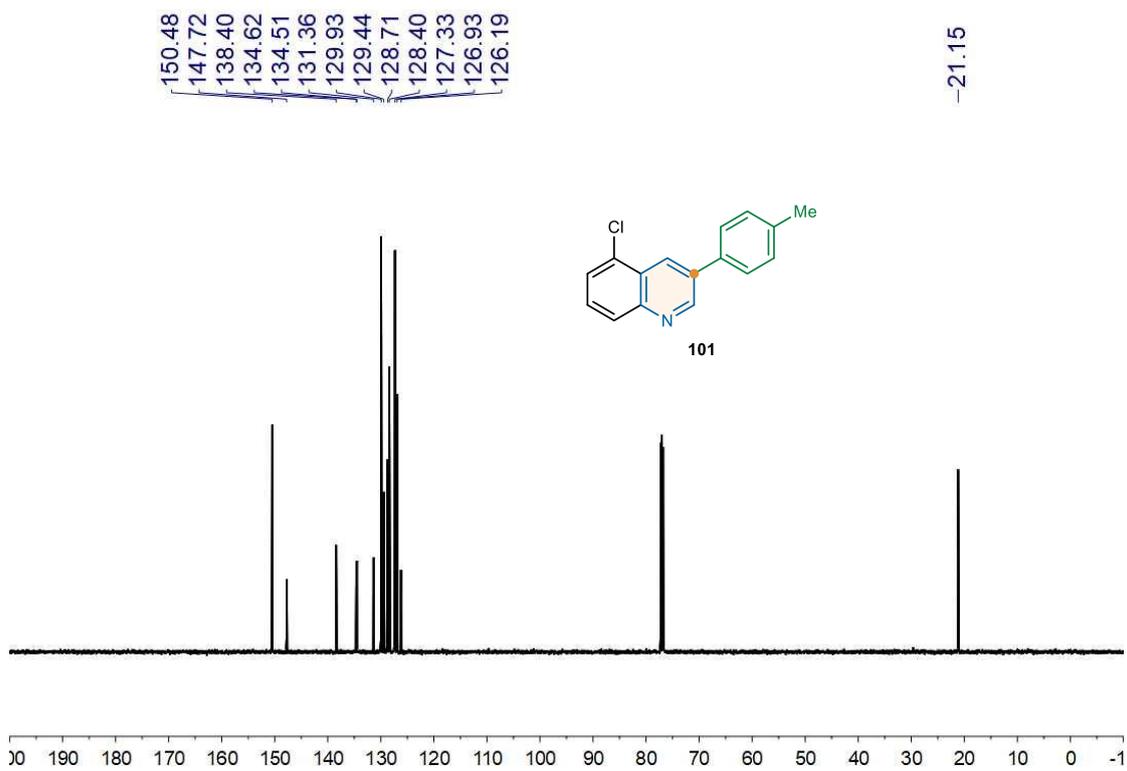
Supplementary Fig. 269.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **100**



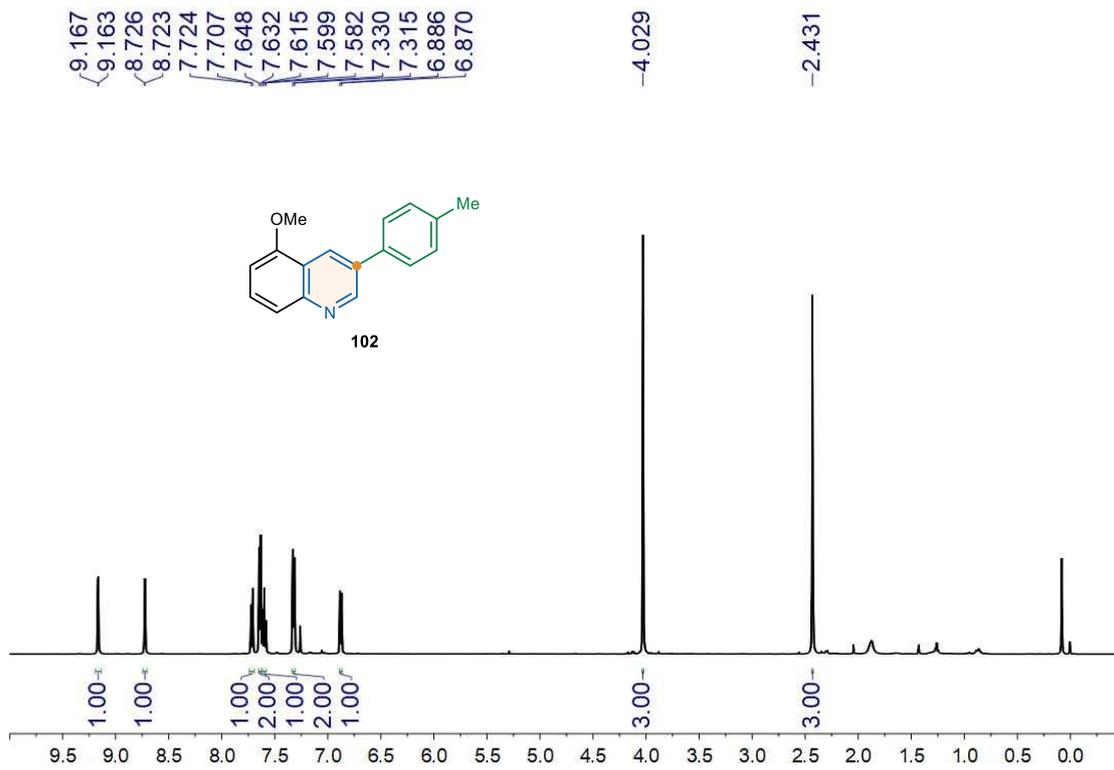
Supplementary Fig. 270.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **100**



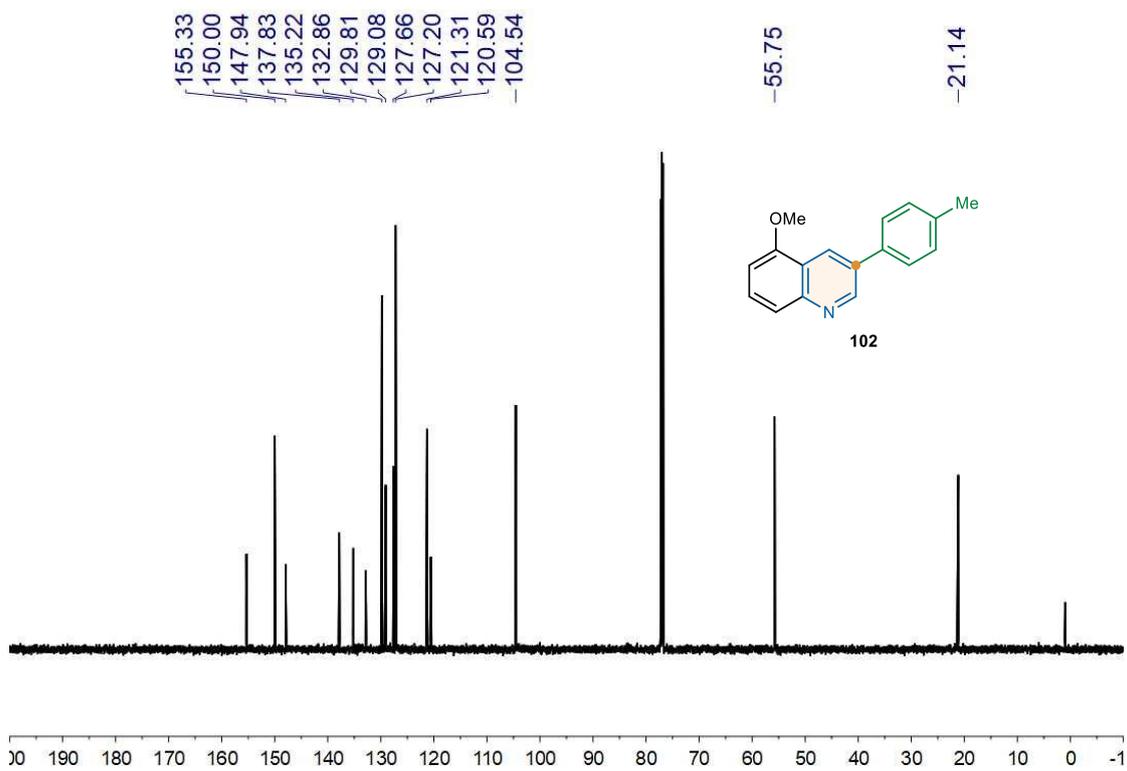
Supplementary Fig. 271.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **101**



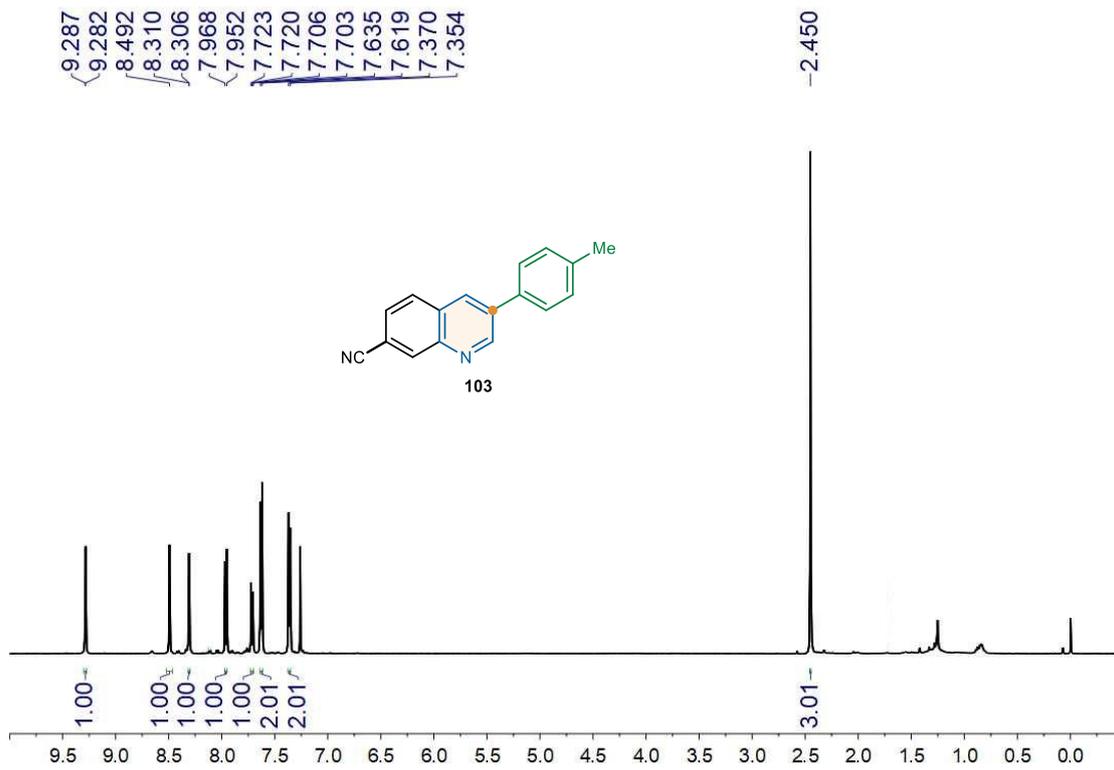
Supplementary Fig. 272.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **101**



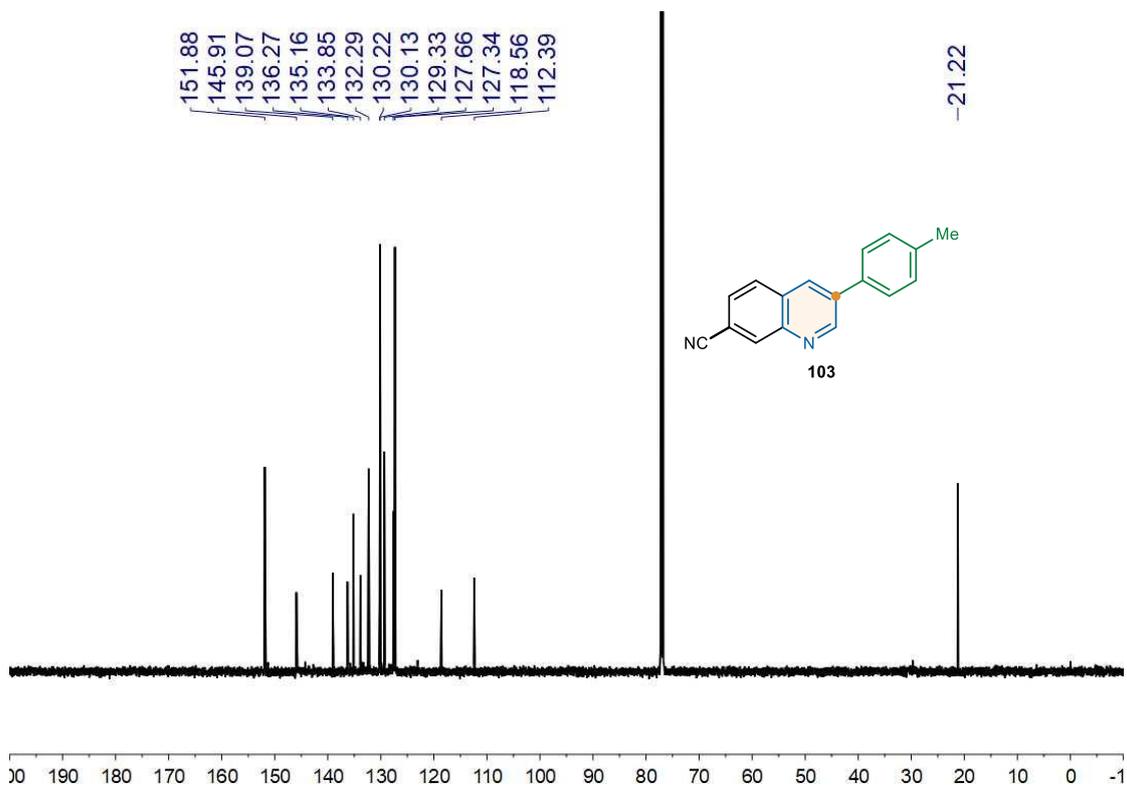
Supplementary Fig. 273. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **102**



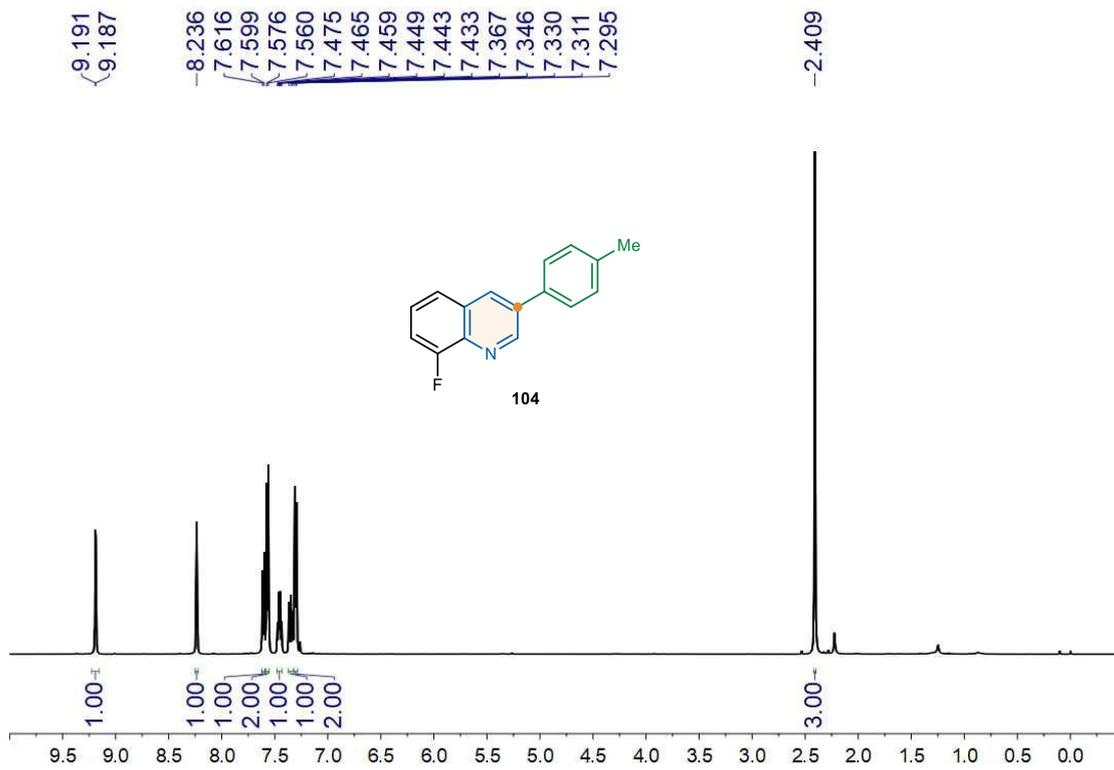
Supplementary Fig. 274. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of **102**



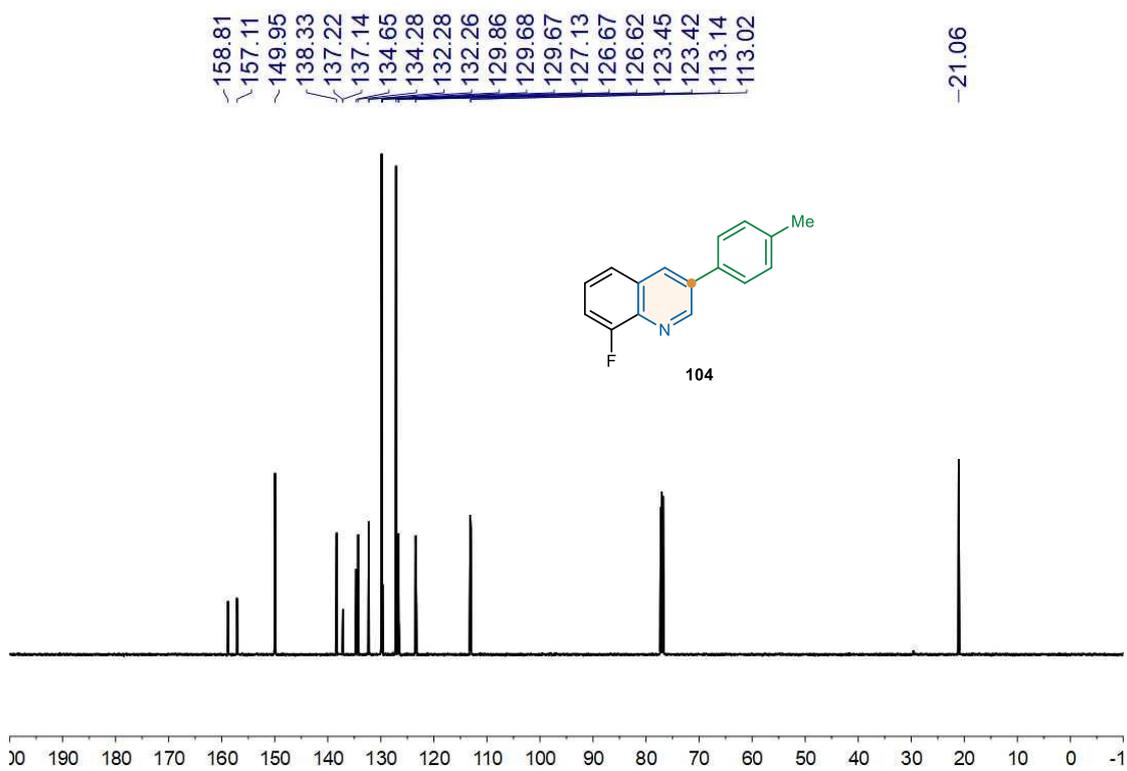
Supplementary Fig. 275.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **103**



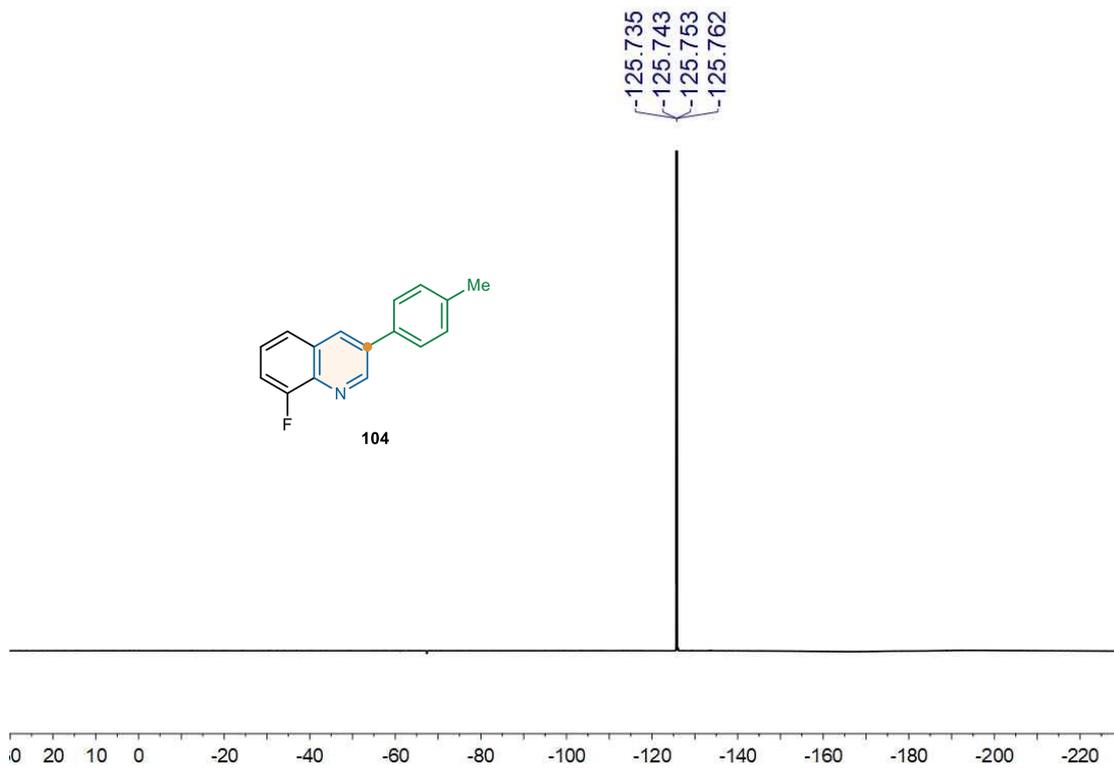
Supplementary Fig. 276.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **103**



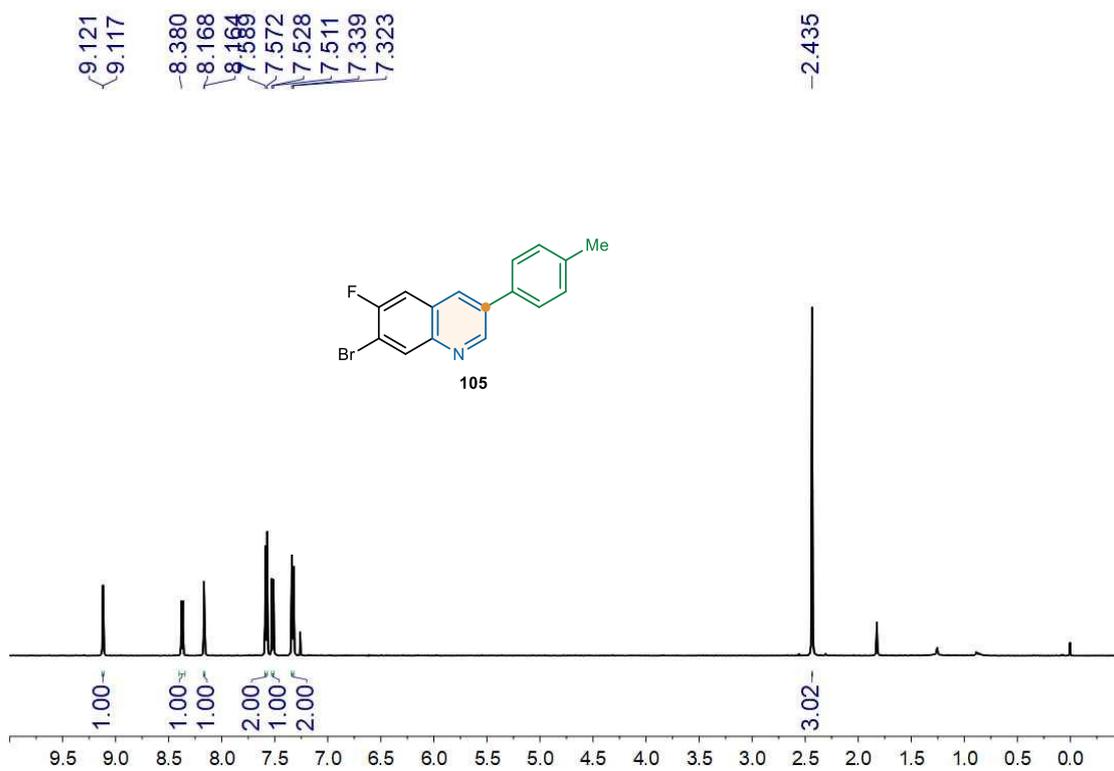
Supplementary Fig. 277.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **104**



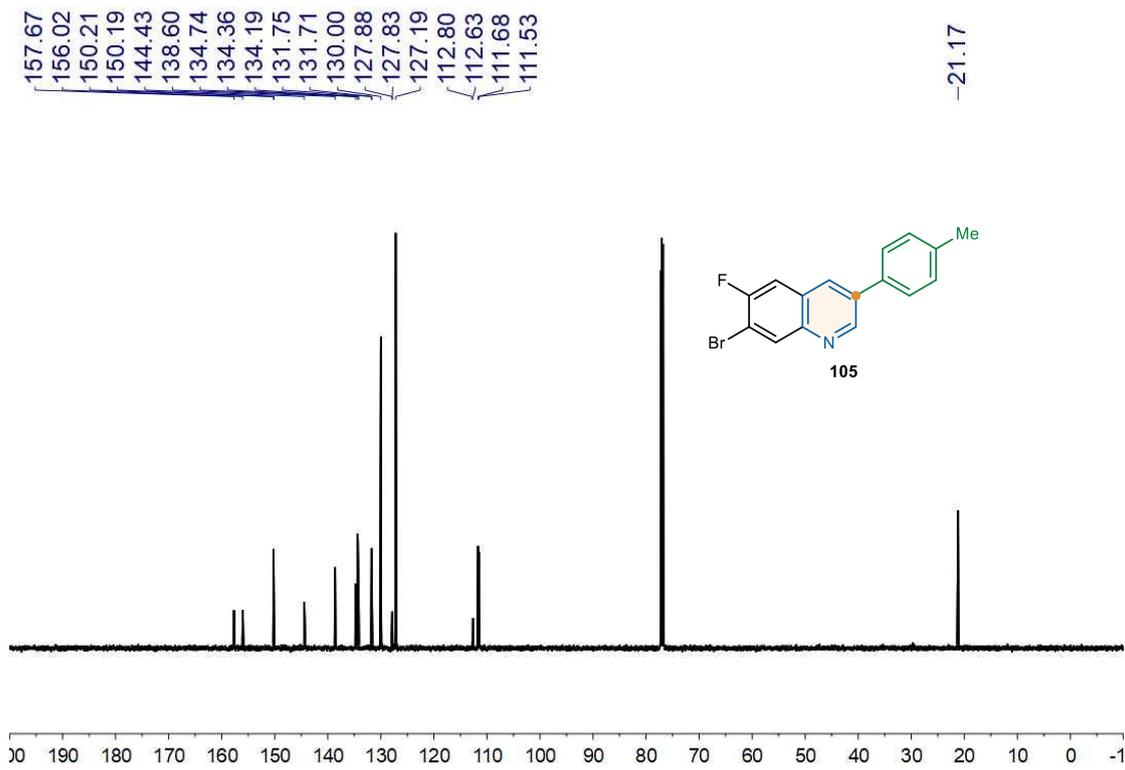
Supplementary Fig. 278.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **104**



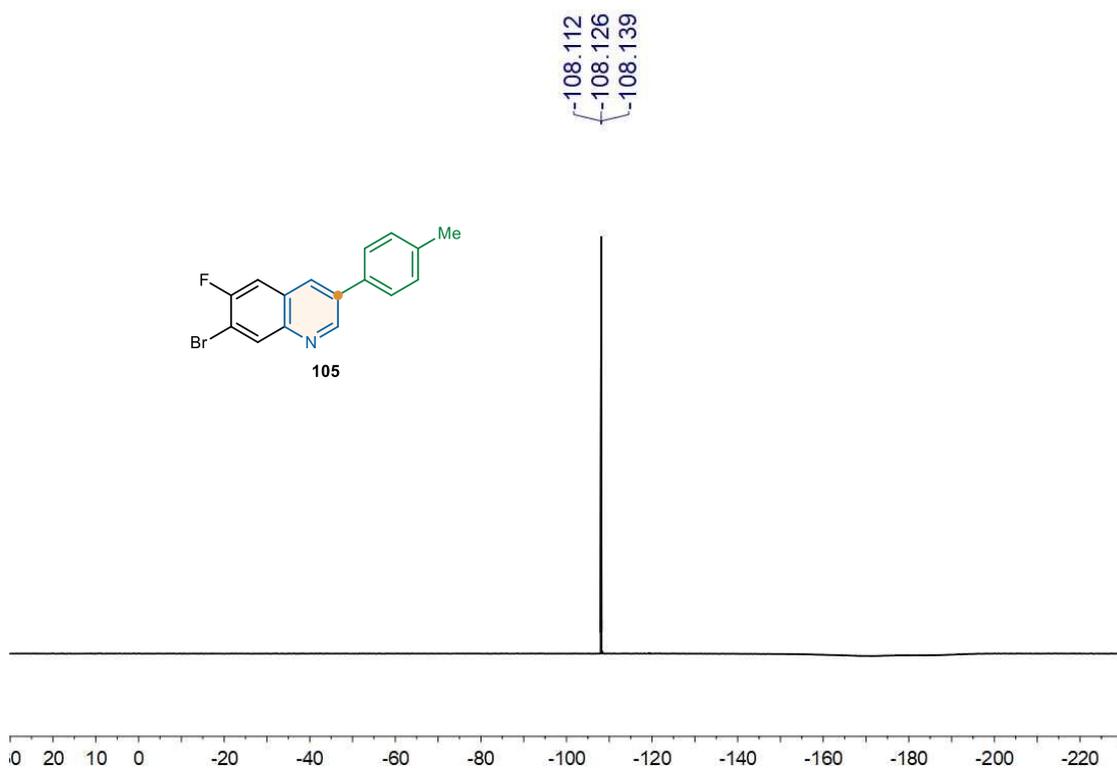
Supplementary Fig. 279.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ) spectrum of **104**



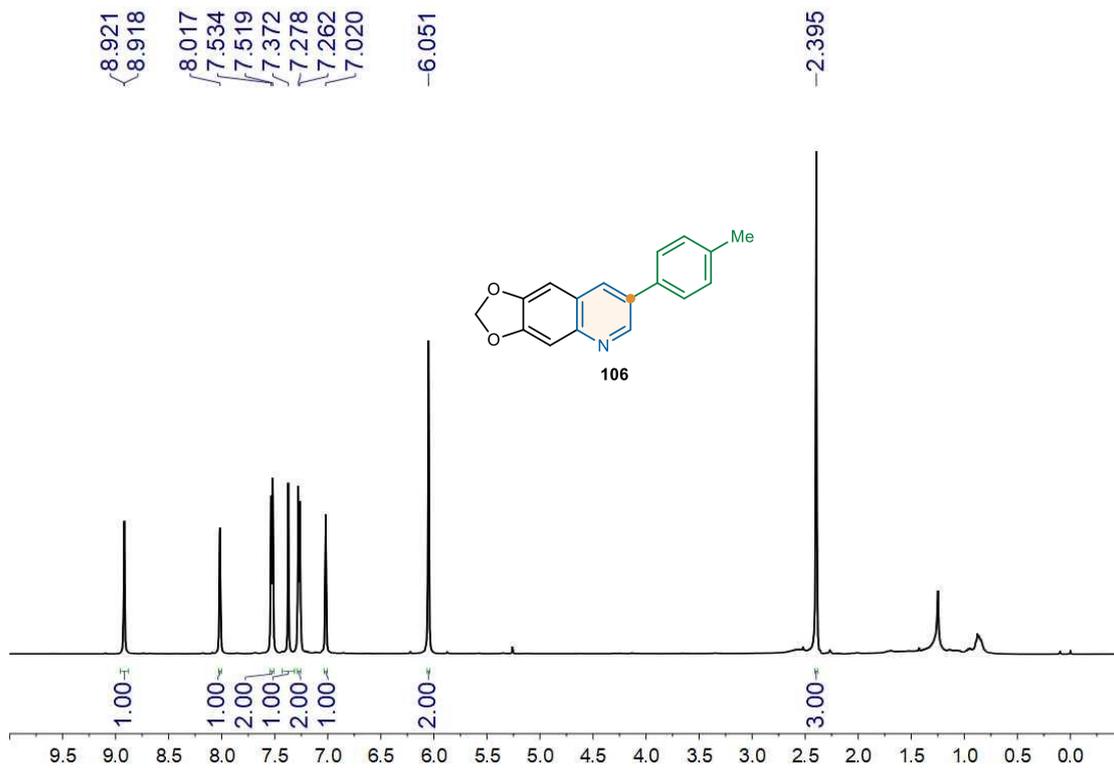
Supplementary Fig. 280.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **105**



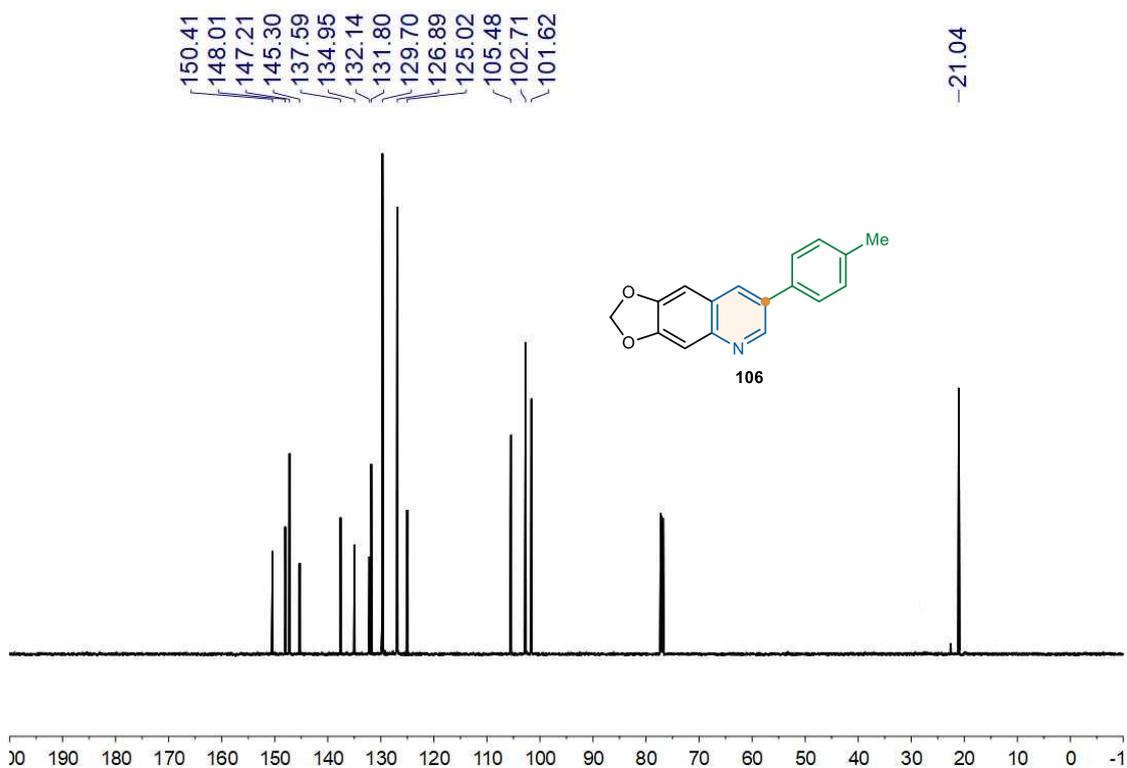
Supplementary Fig. 281.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **105**



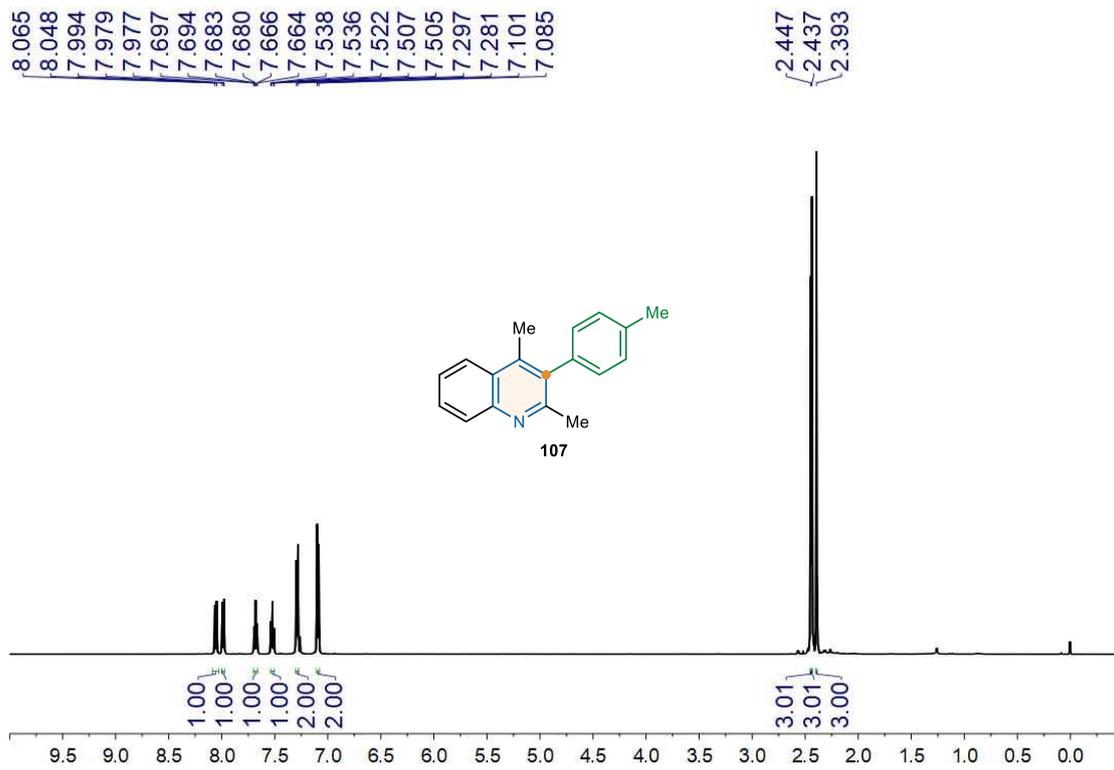
Supplementary Fig. 282.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ) spectrum of **105**



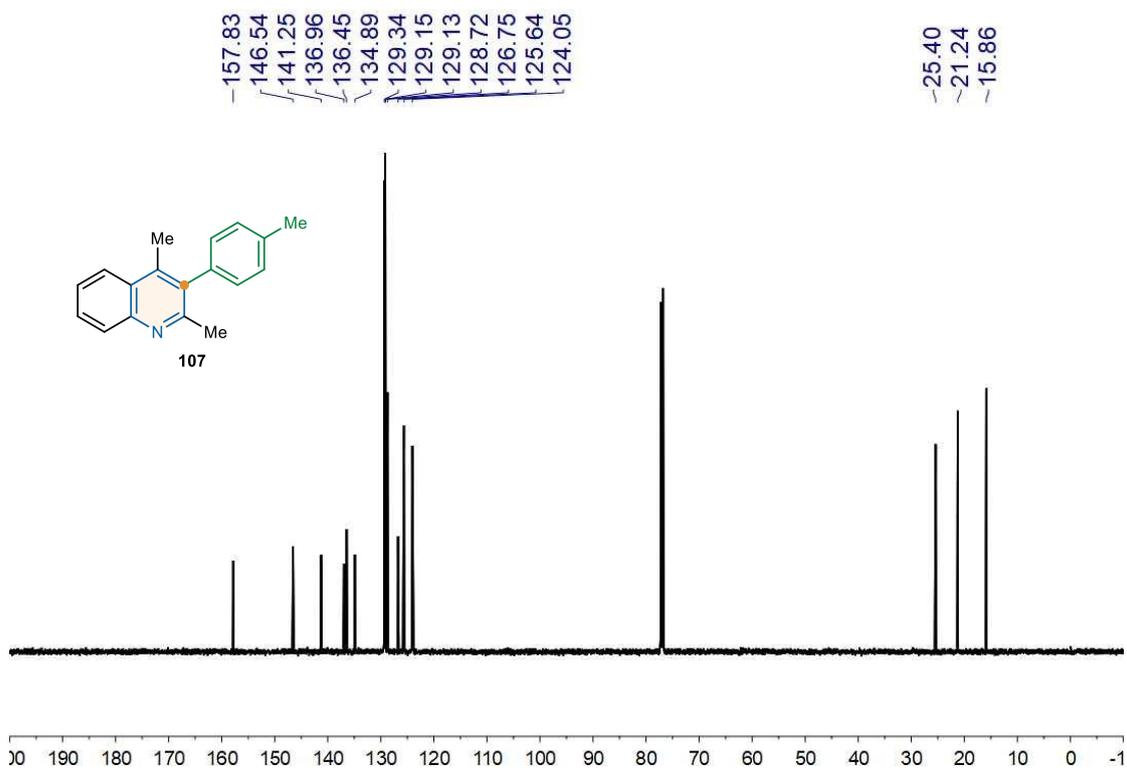
Supplementary Fig. 283.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **106**



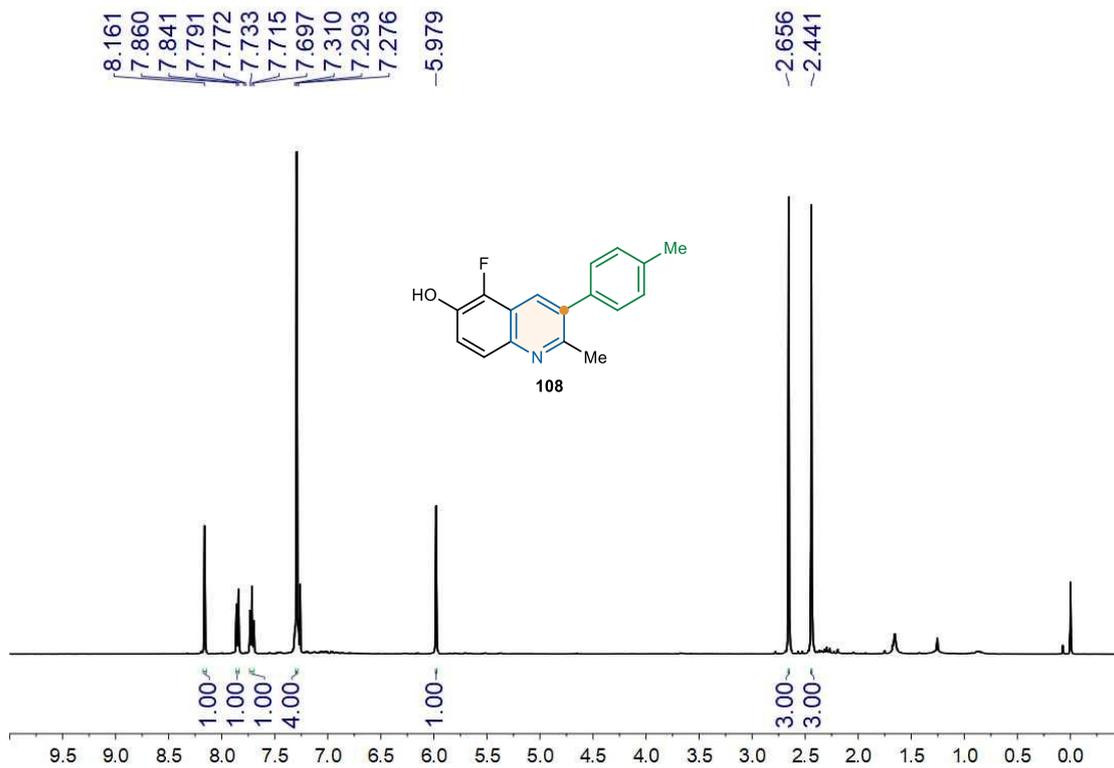
Supplementary Fig. 284.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **106**



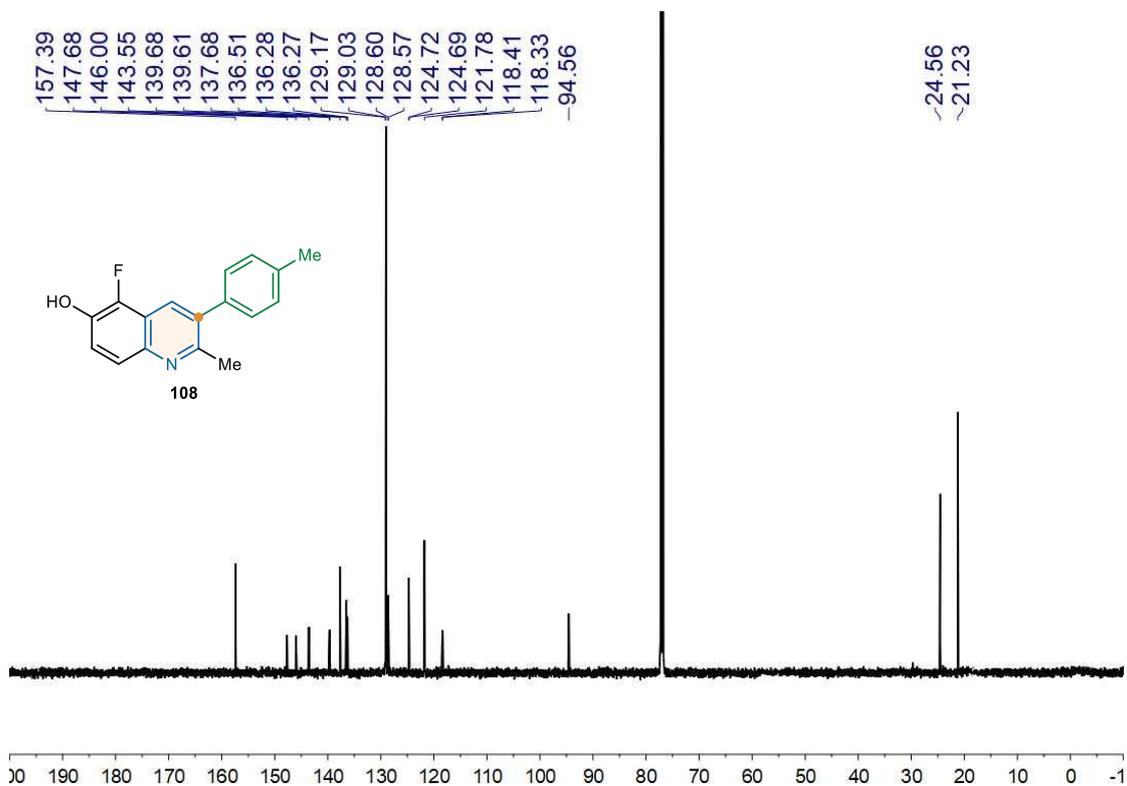
Supplementary Fig. 285. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **107**



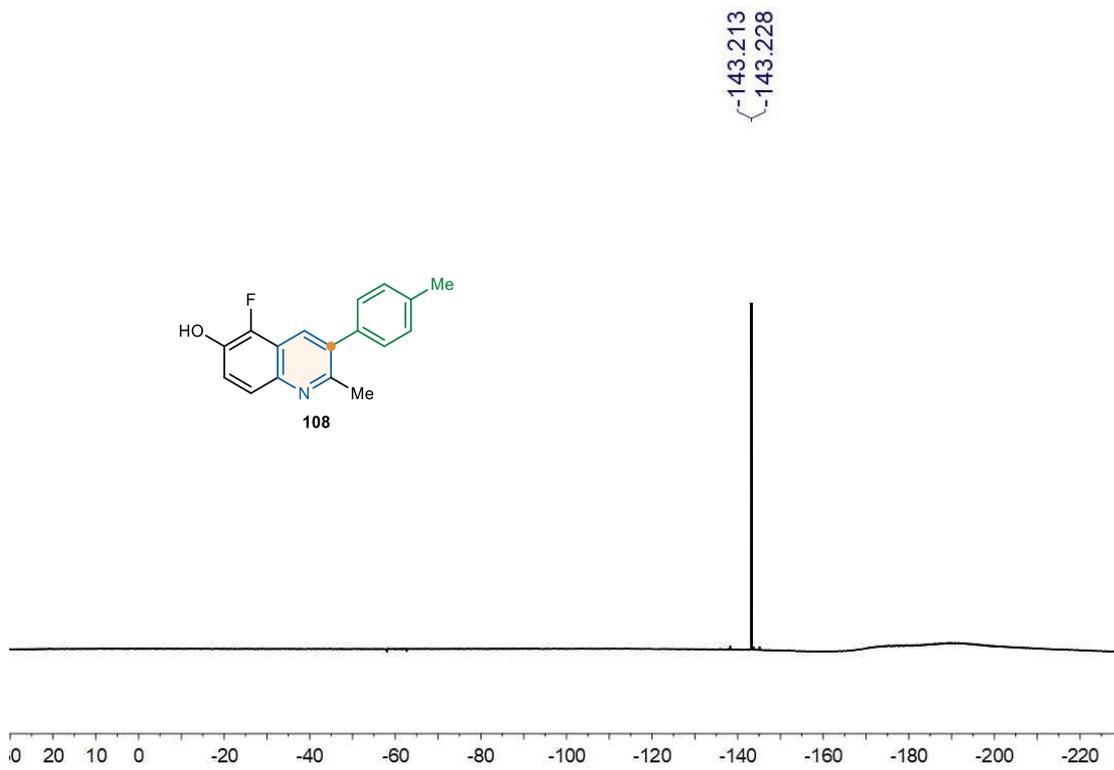
Supplementary Fig. 286. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of **107**



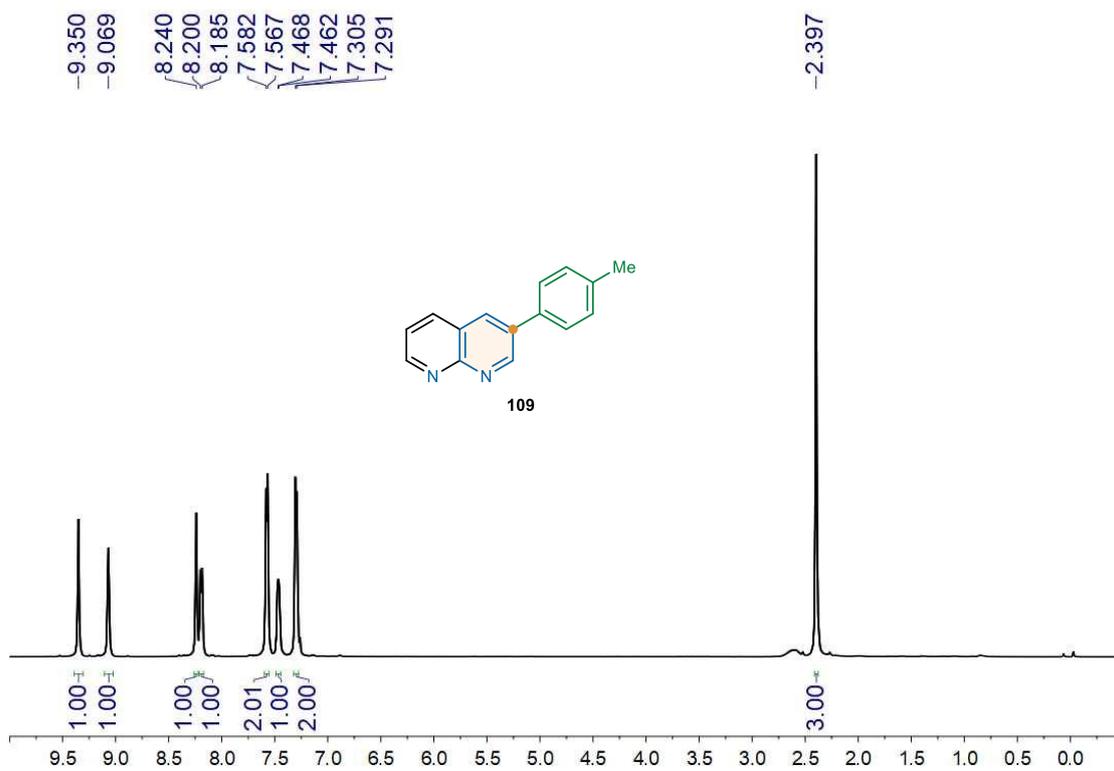
Supplementary Fig. 287.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **108**



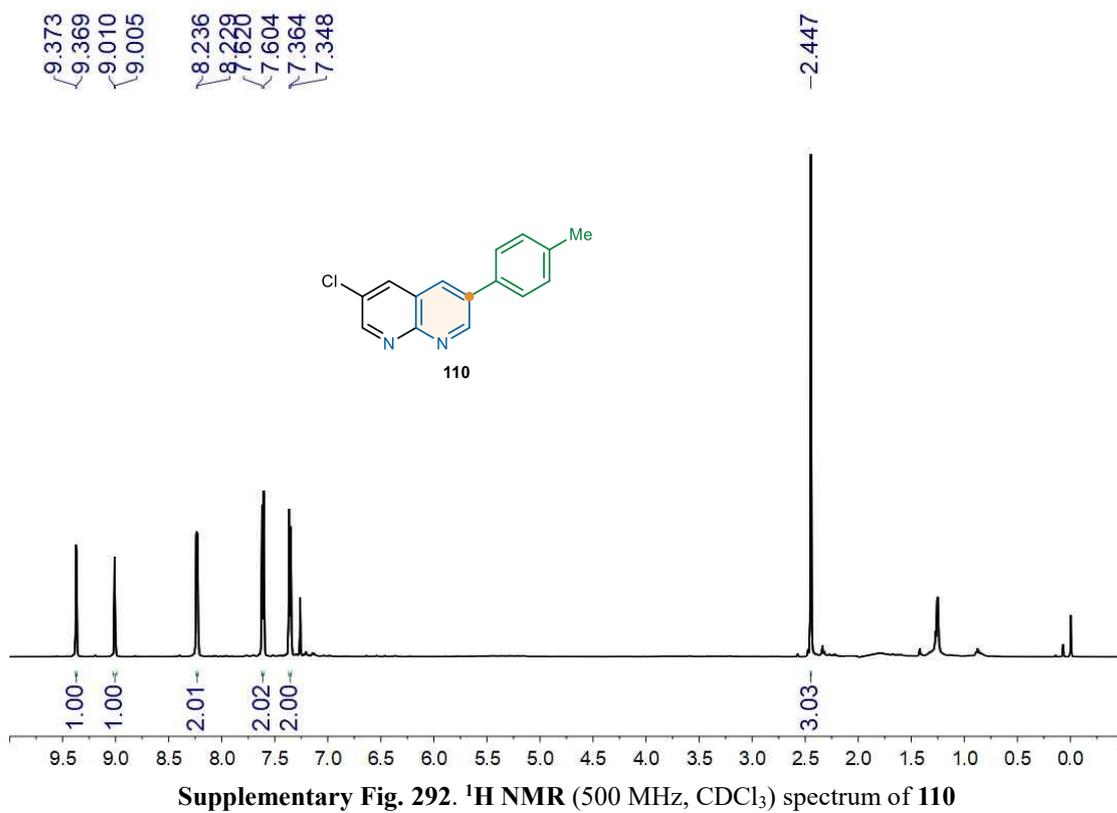
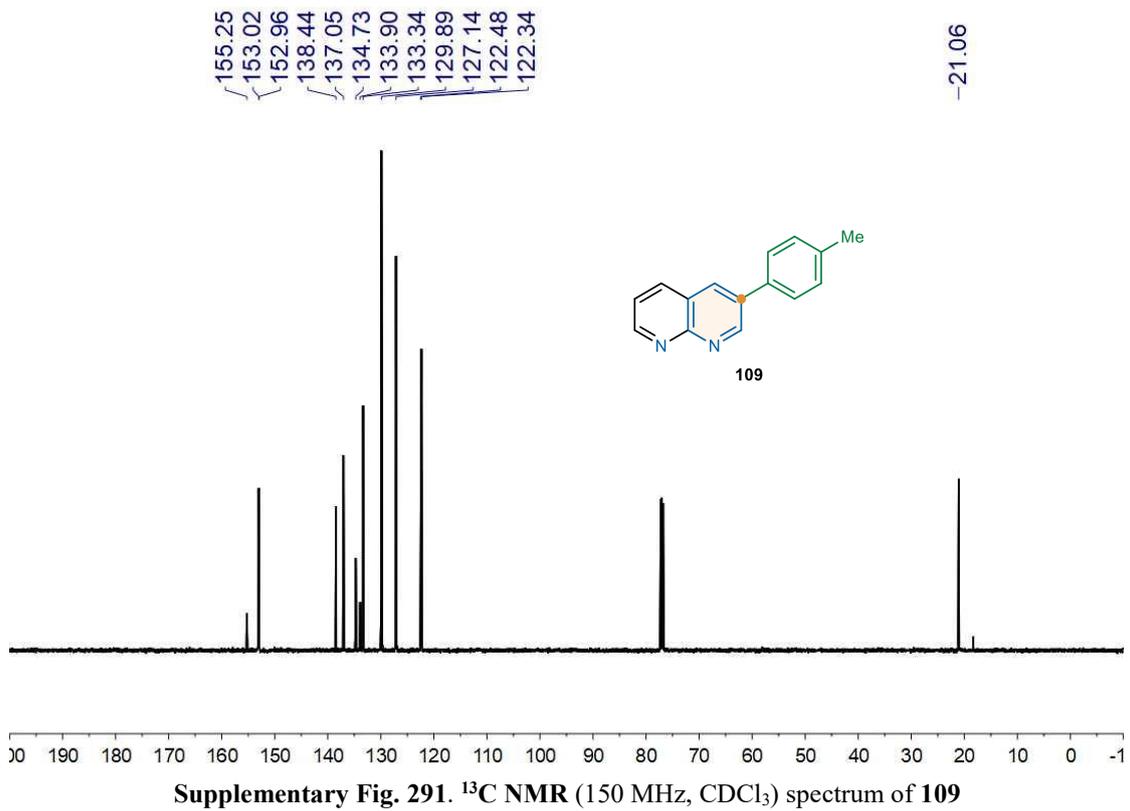
Supplementary Fig. 288.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **108**

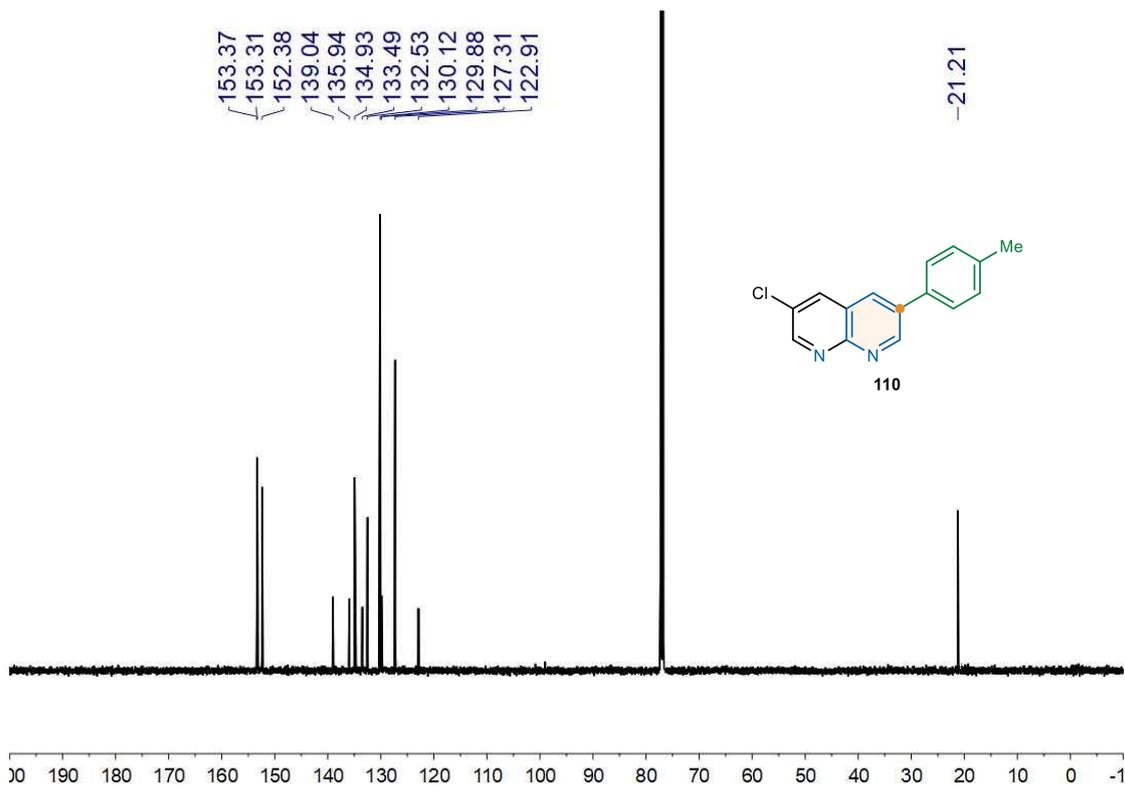


Supplementary Fig. 289.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ) spectrum of **108**

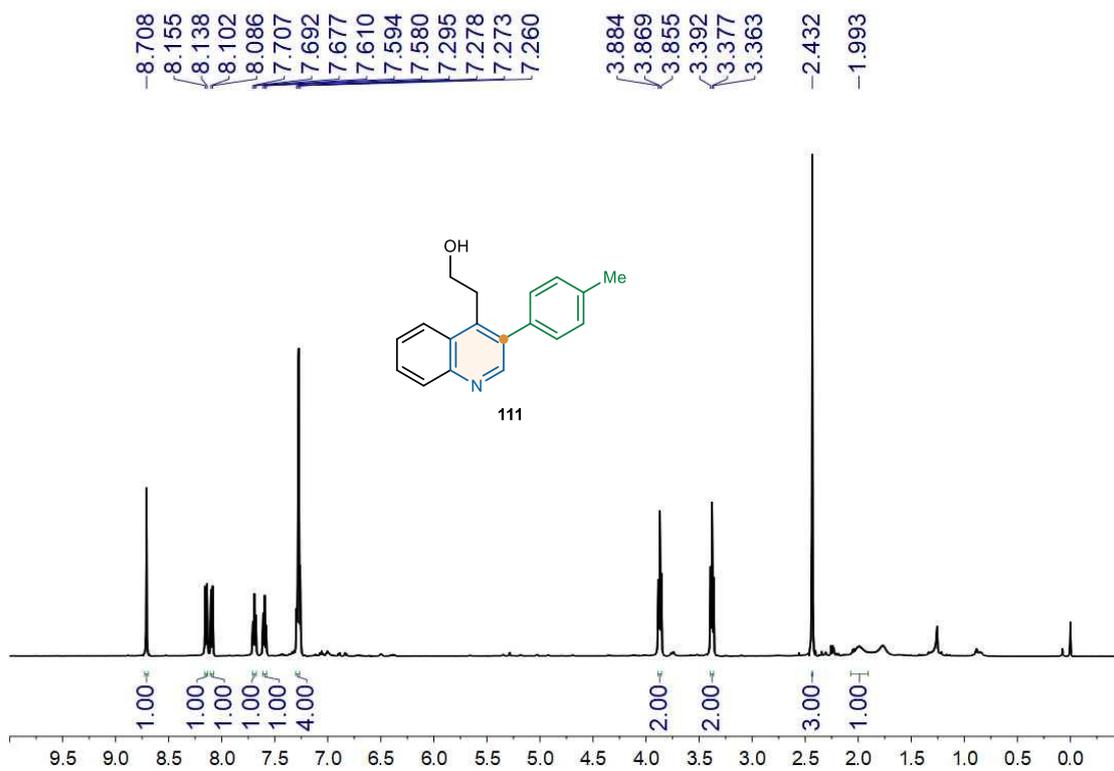


Supplementary Fig. 290.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **109**

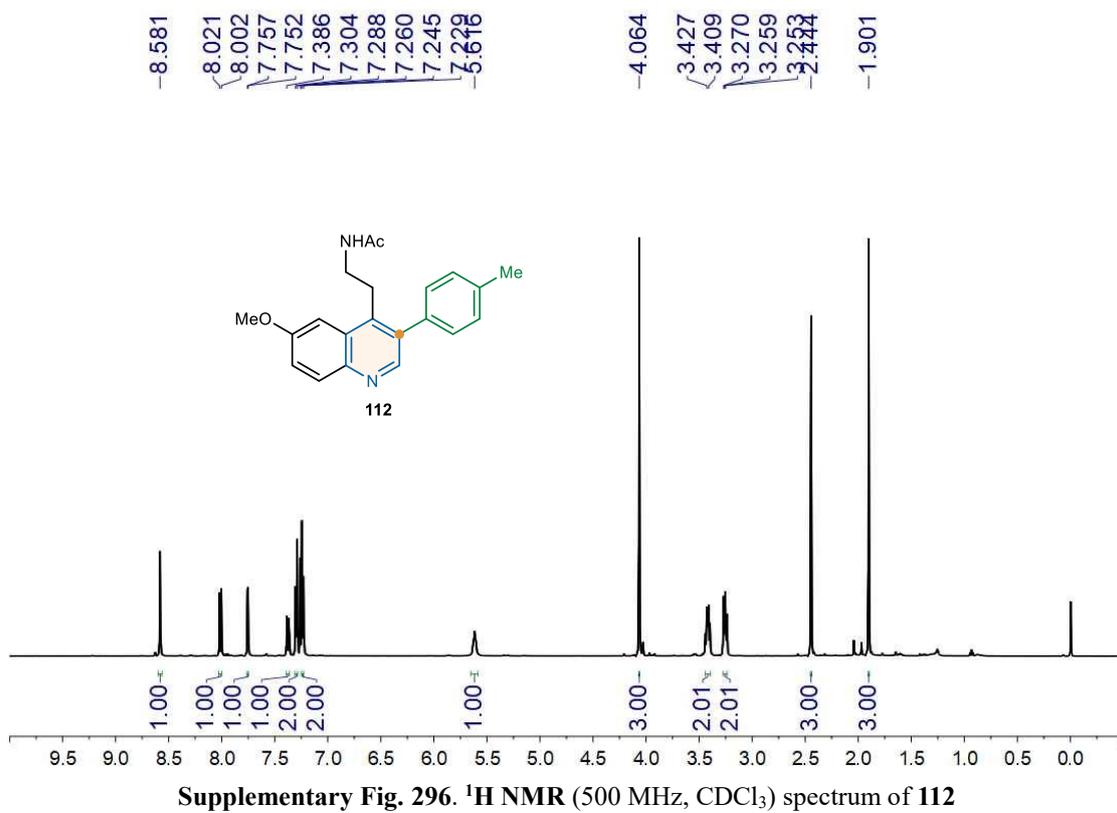
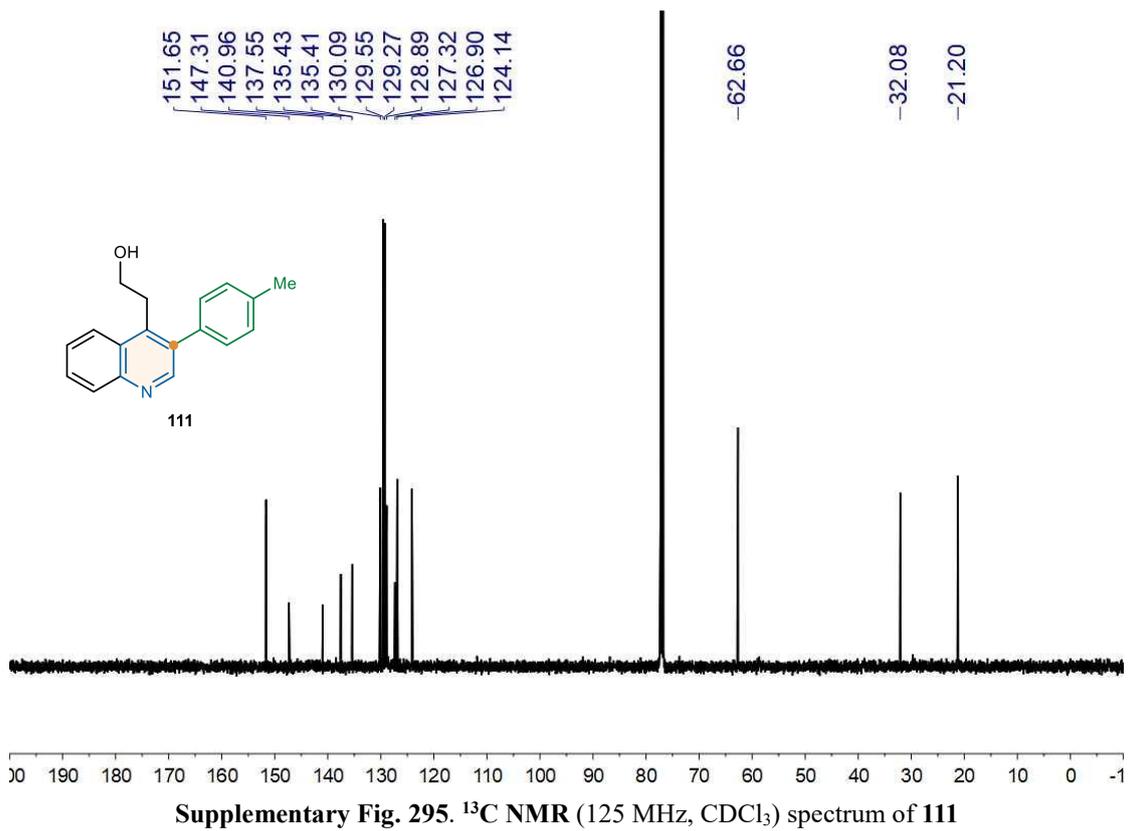


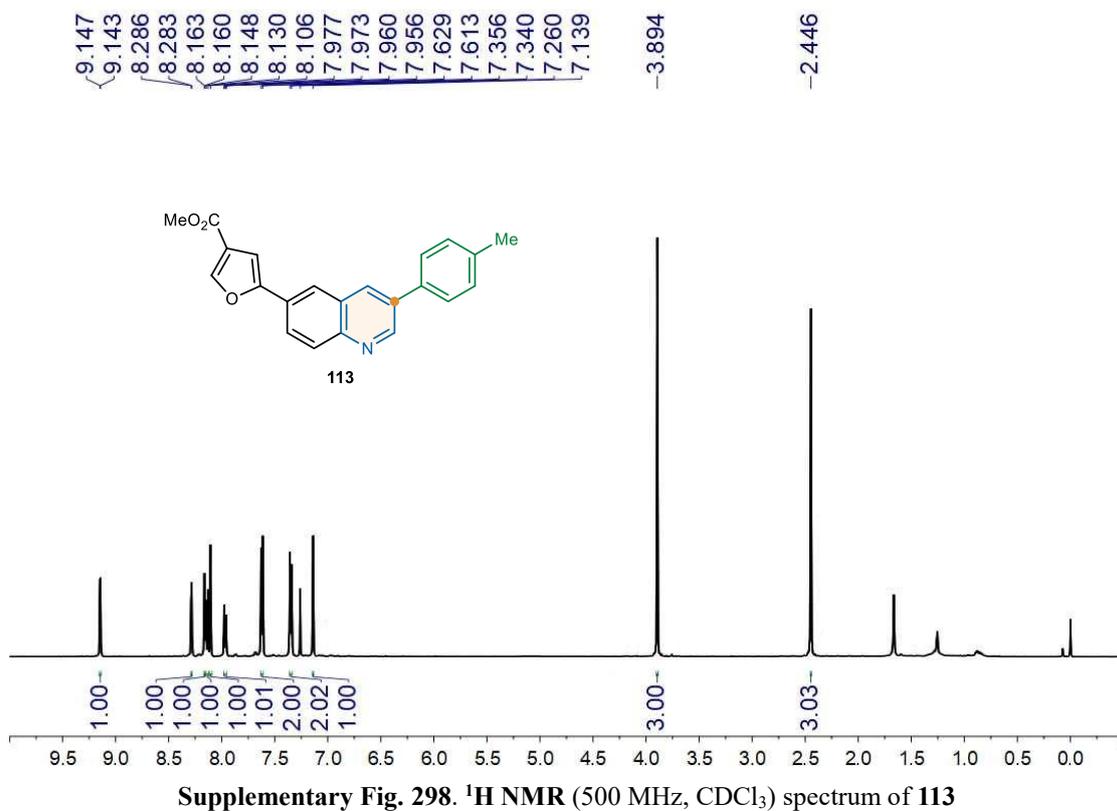
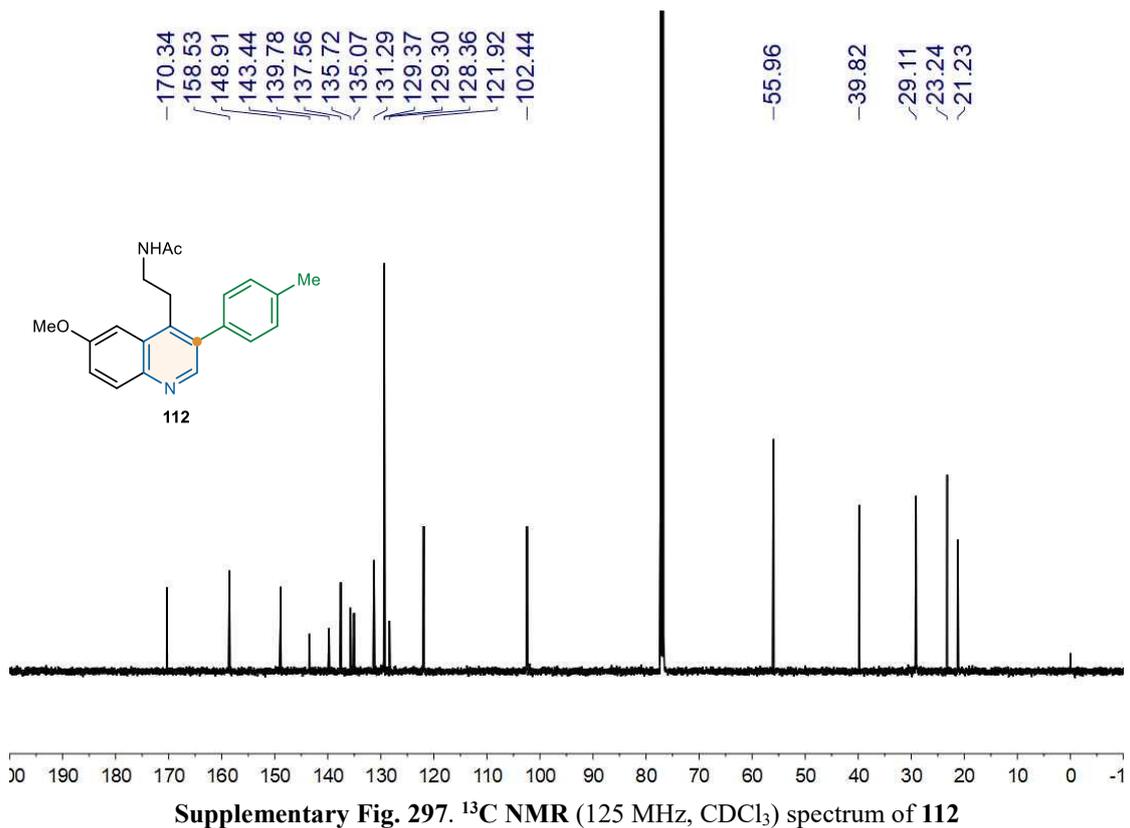


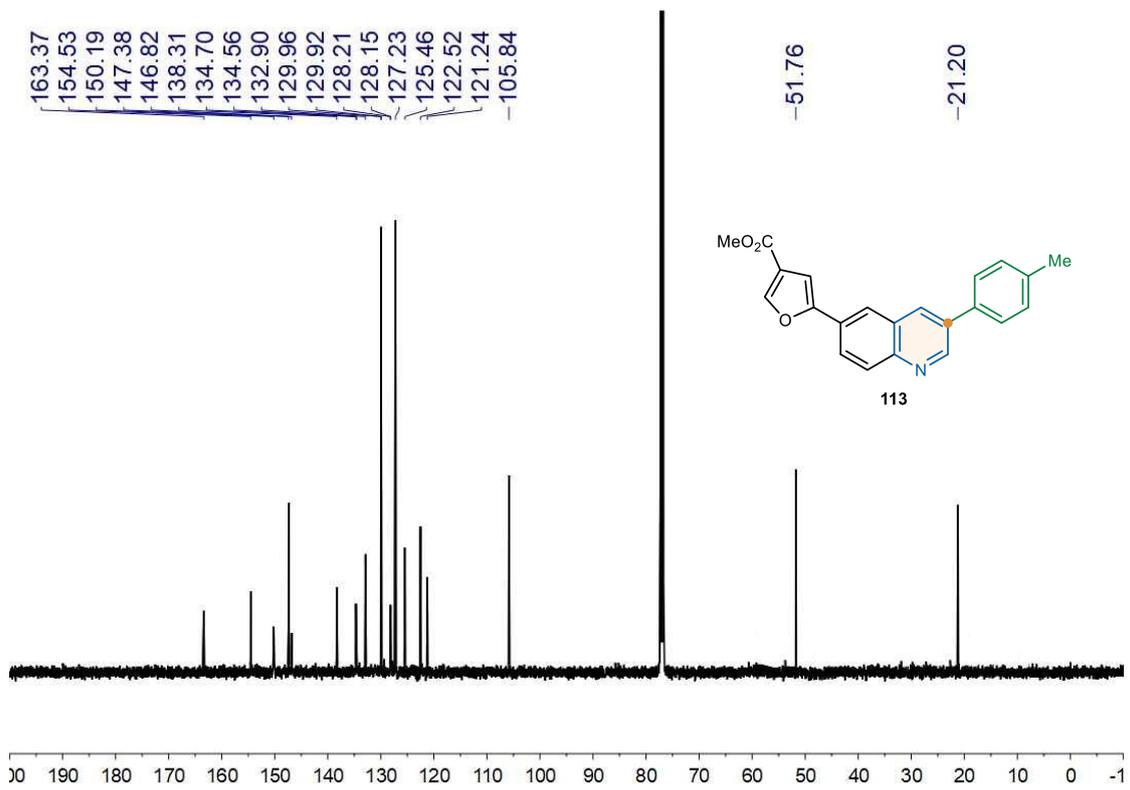
Supplementary Fig. 293. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of **110**



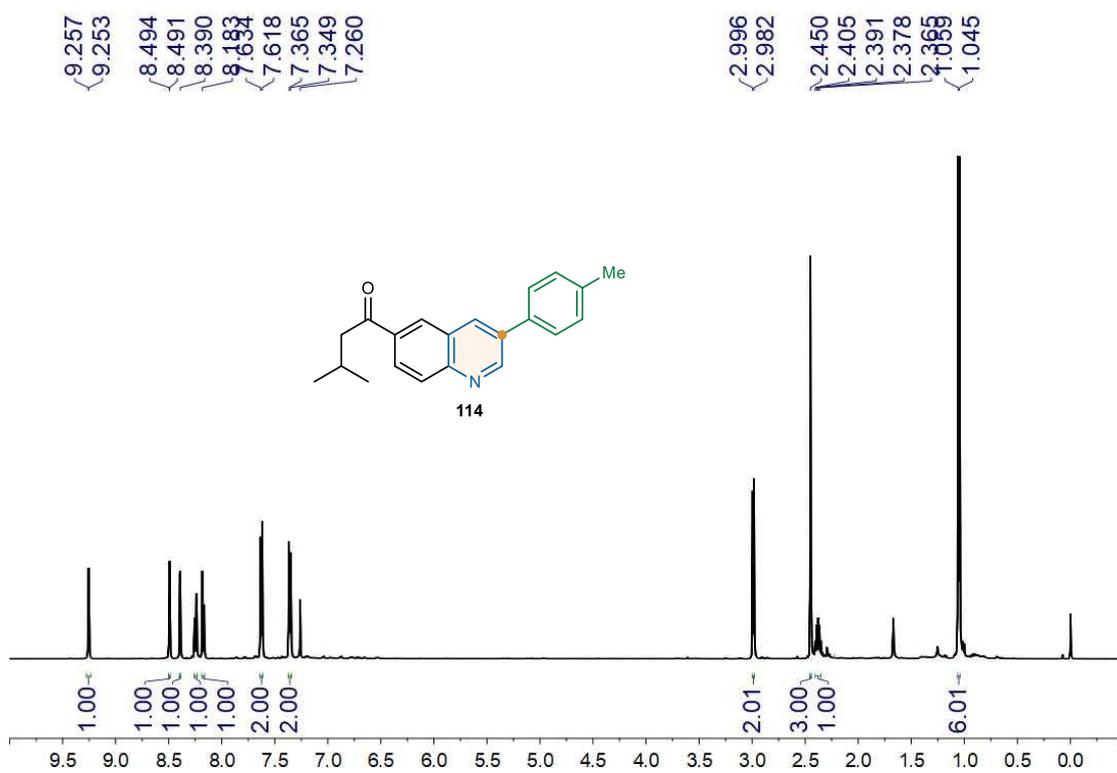
Supplementary Fig. 294. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **111**



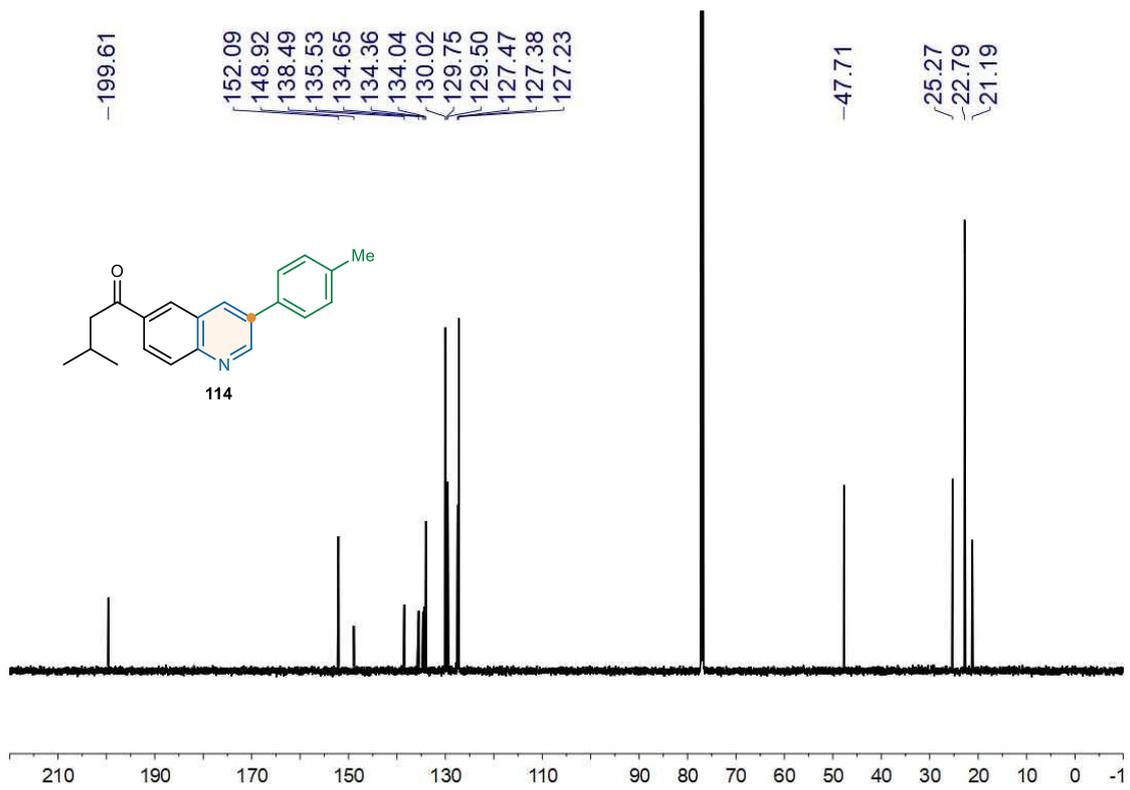




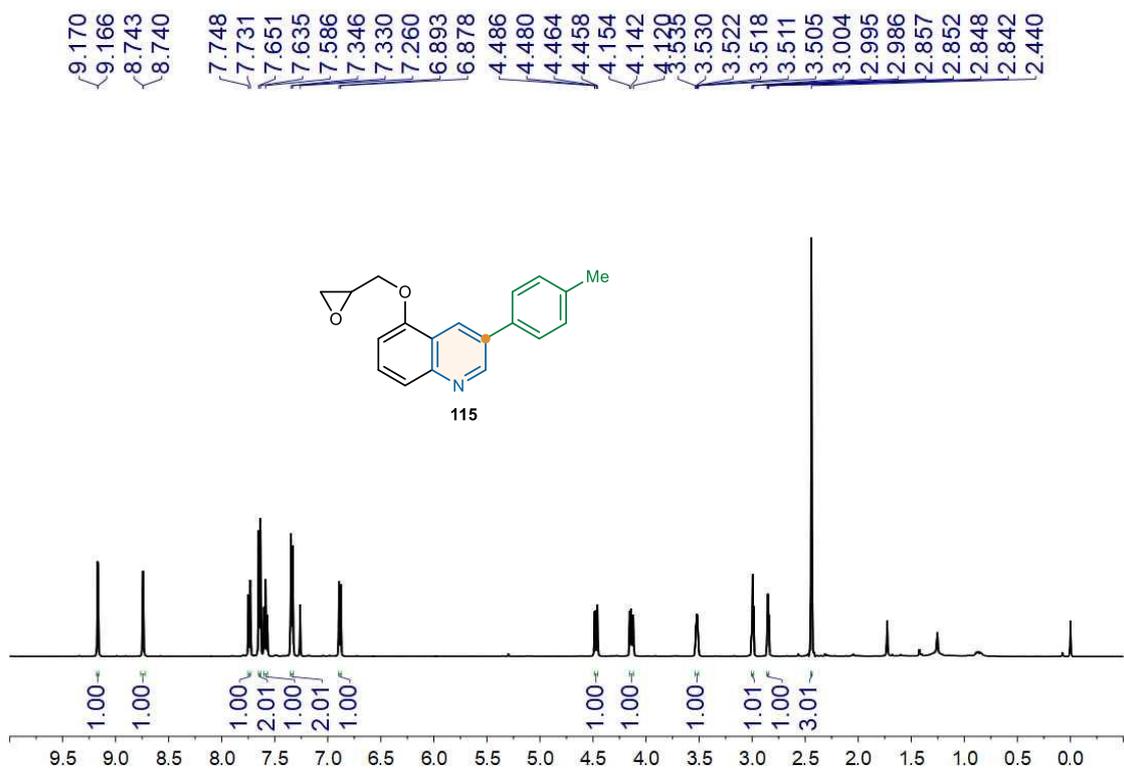
Supplementary Fig. 299.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of 113



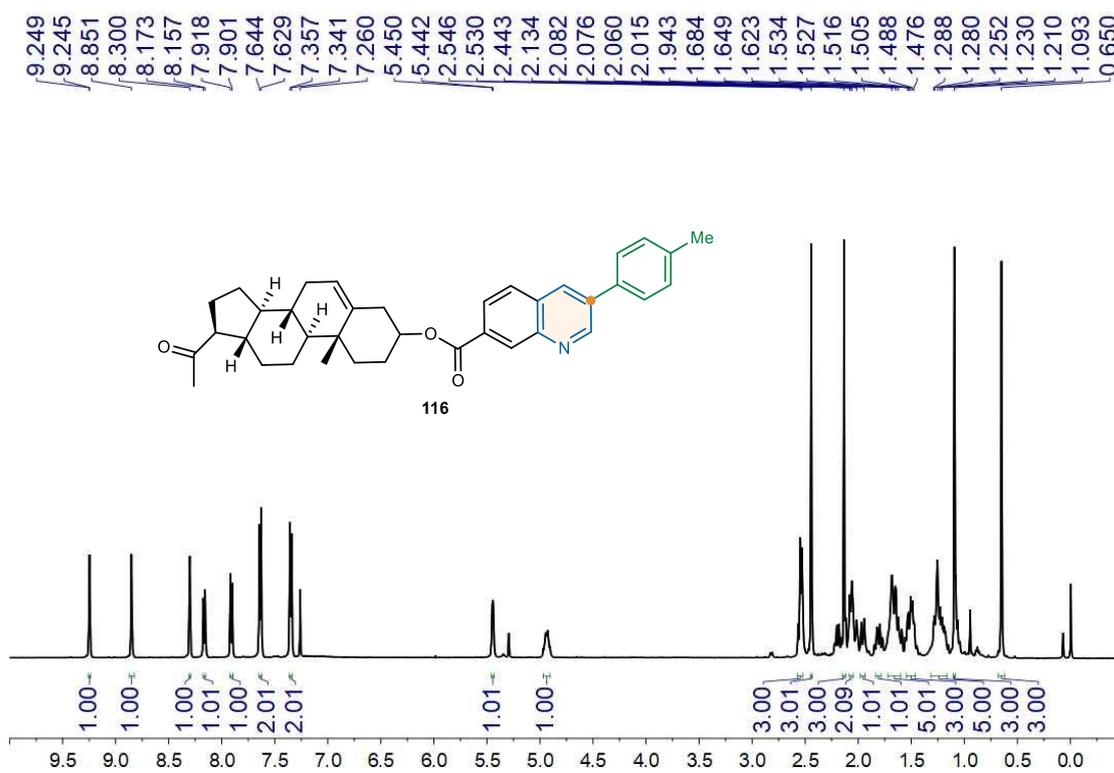
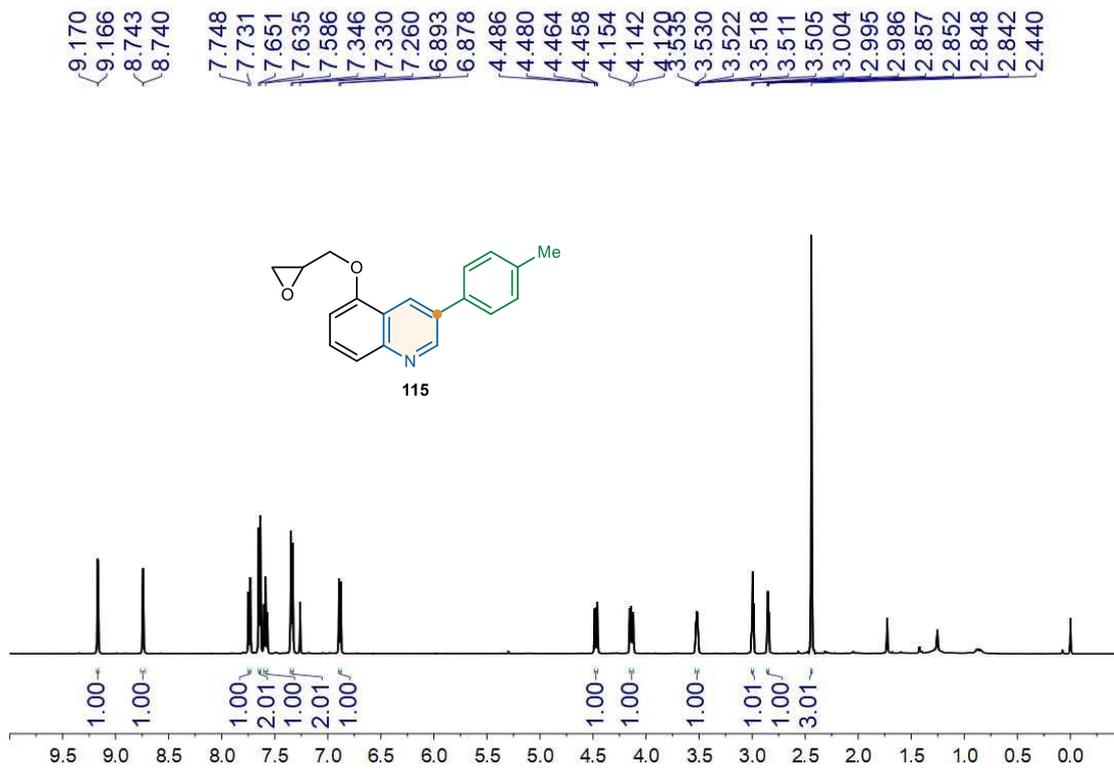
Supplementary Fig. 300.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of 114

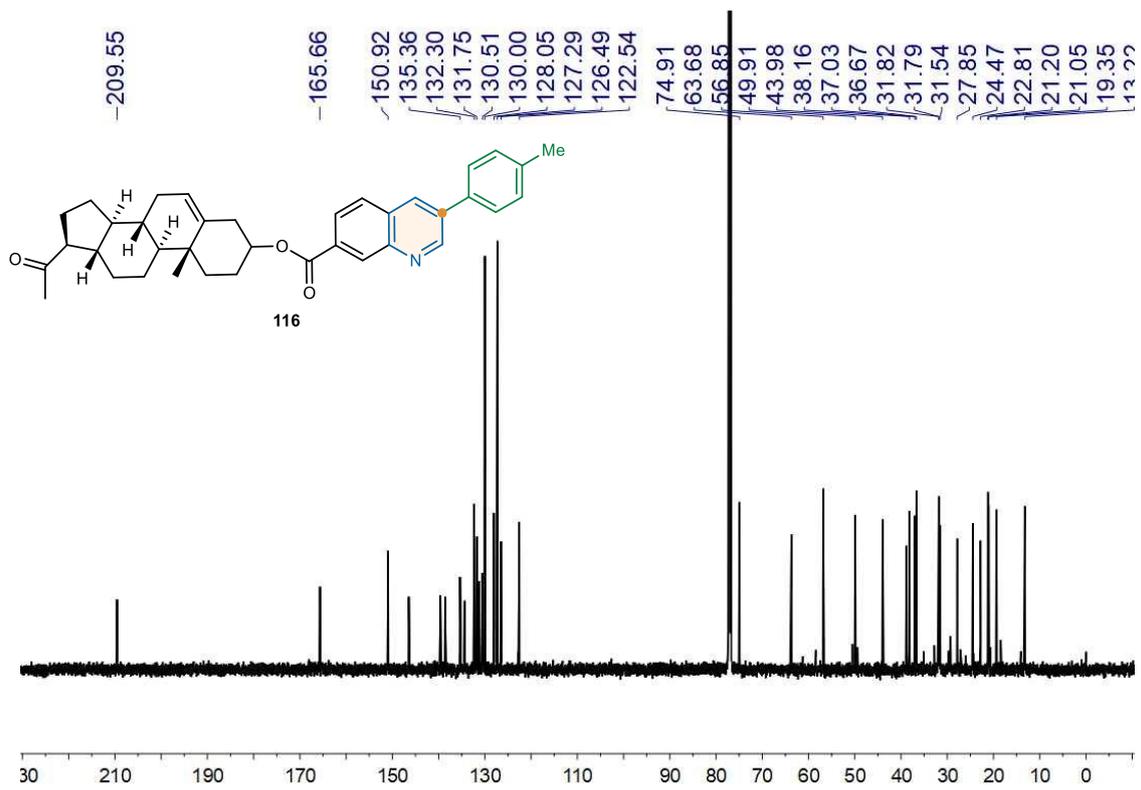


Supplementary Fig. 301. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of 114

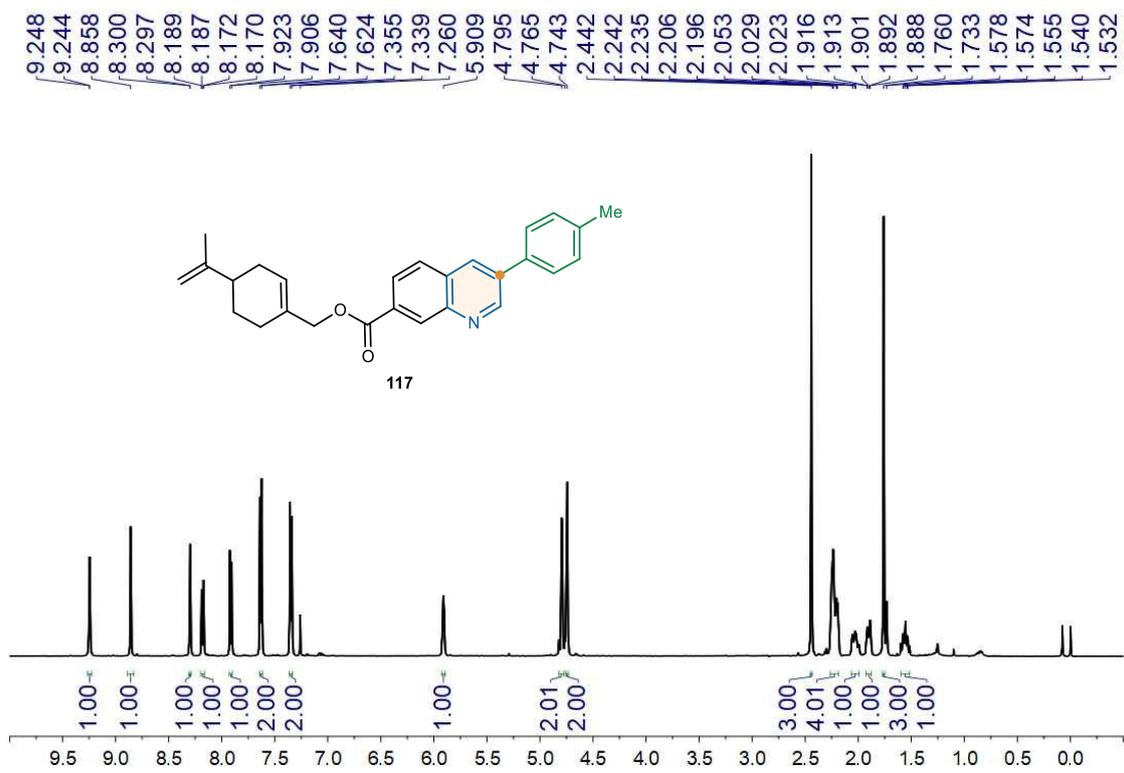


Supplementary Fig. 302. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of 115

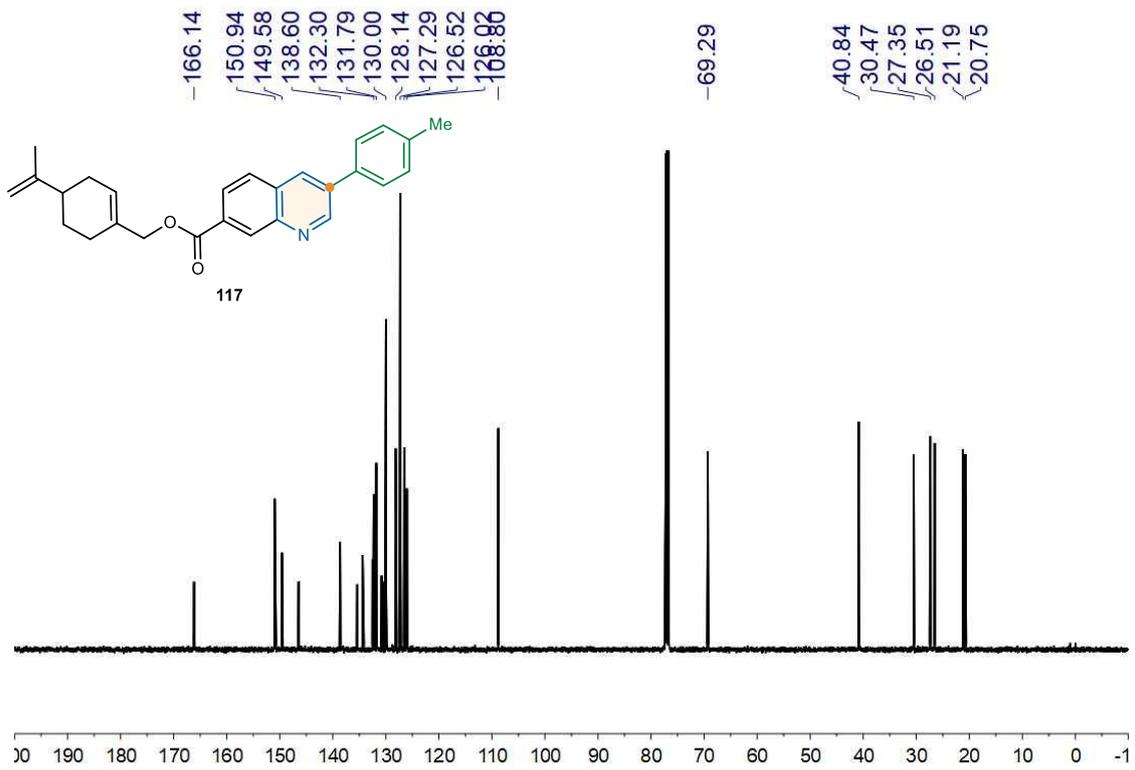




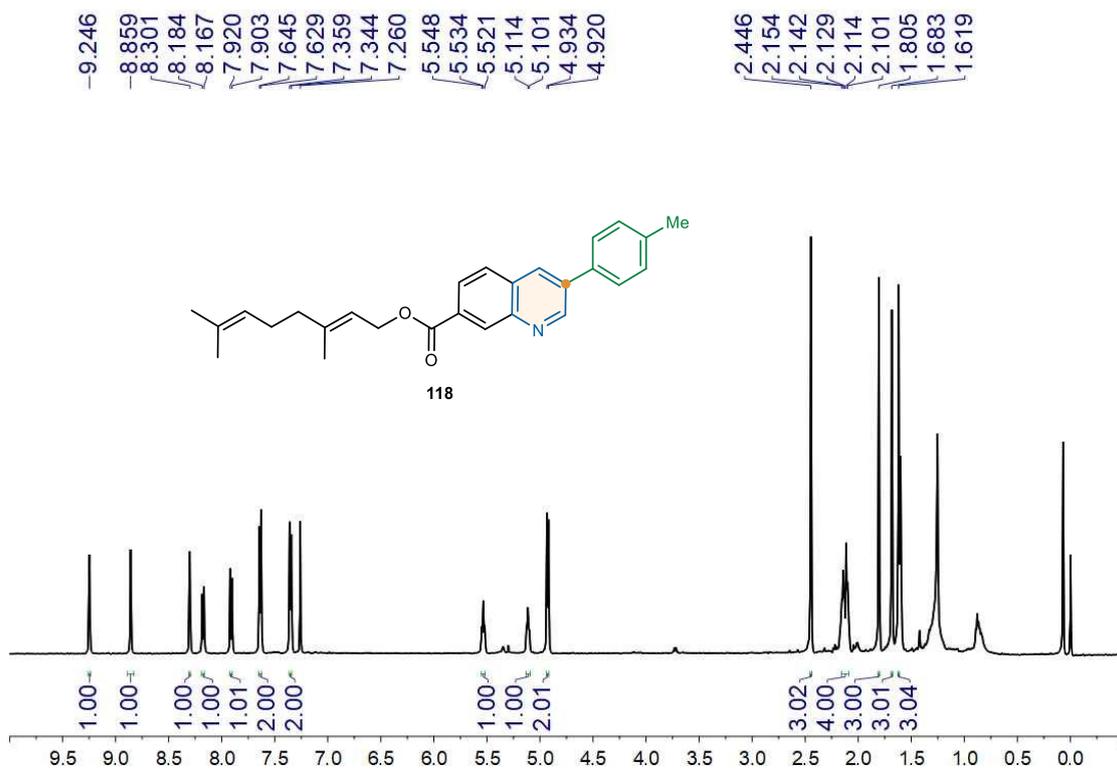
Supplementary Fig. 305.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **116**



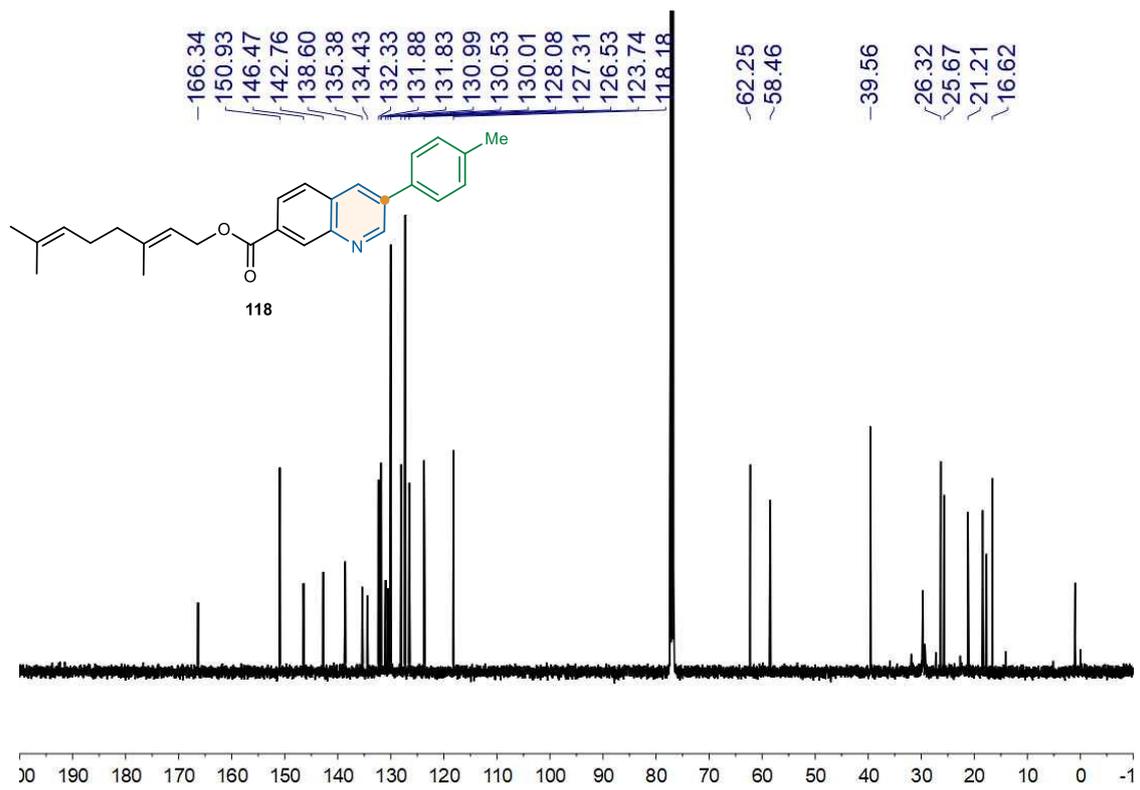
Supplementary Fig. 306.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **117**



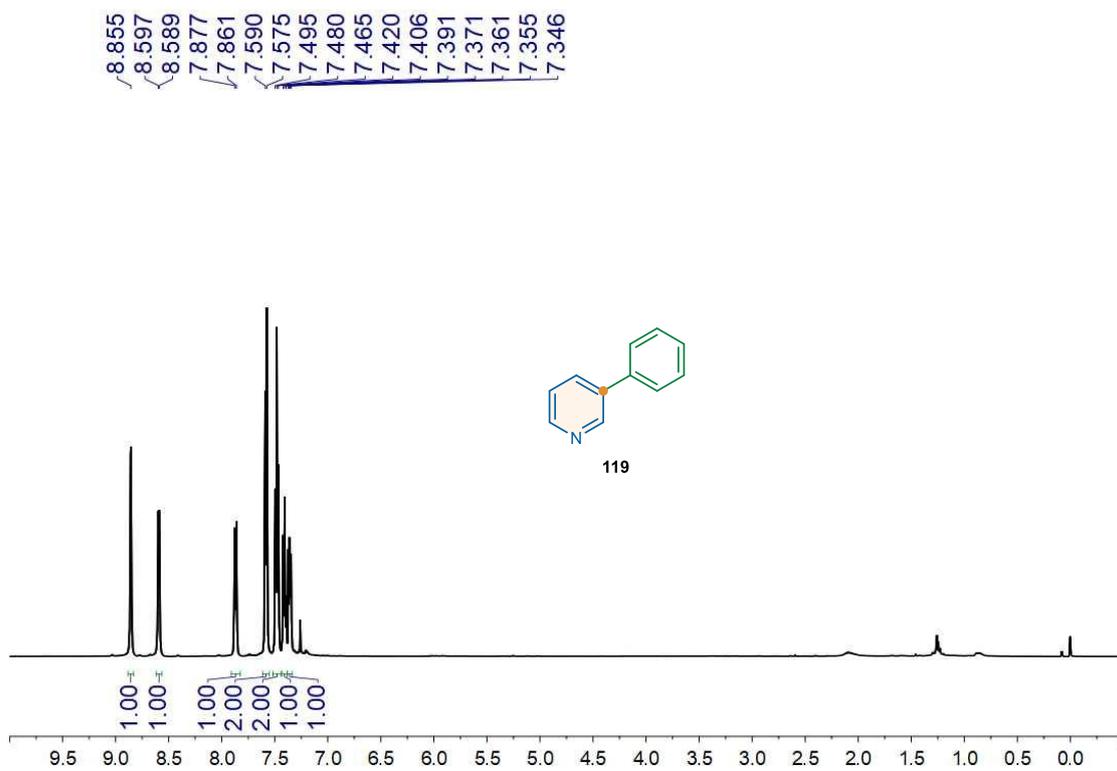
Supplementary Fig. 307. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of 117



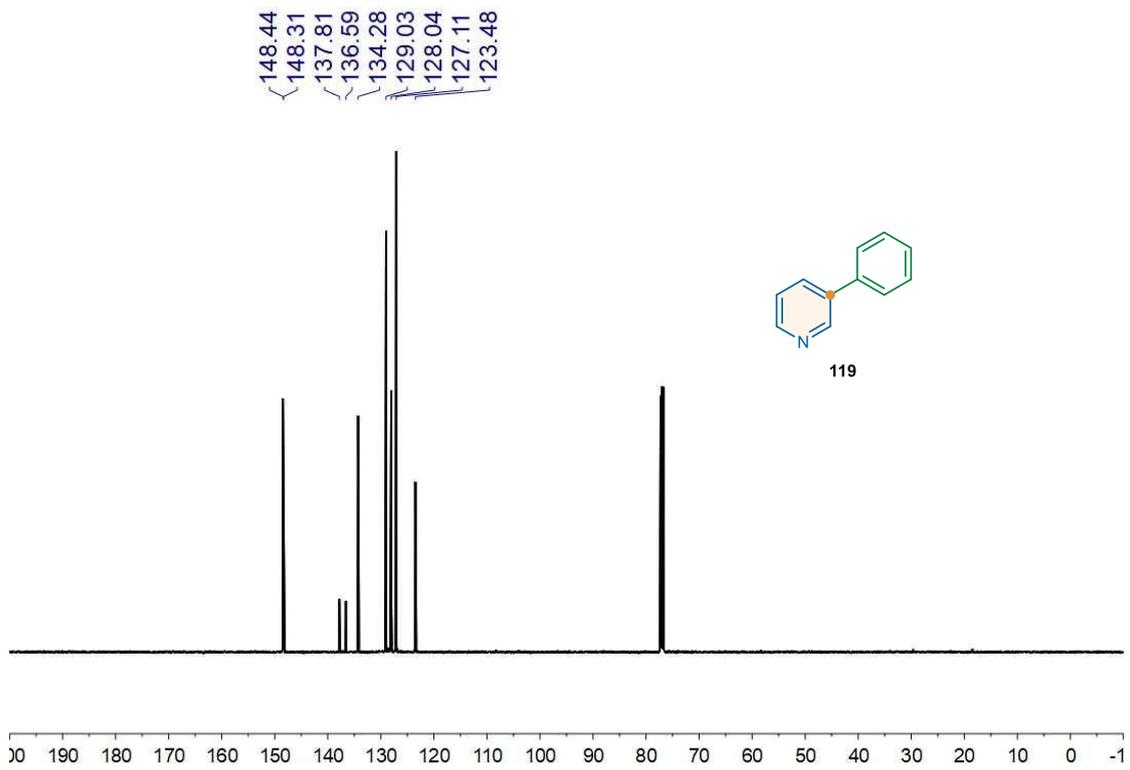
Supplementary Fig. 308. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of 118



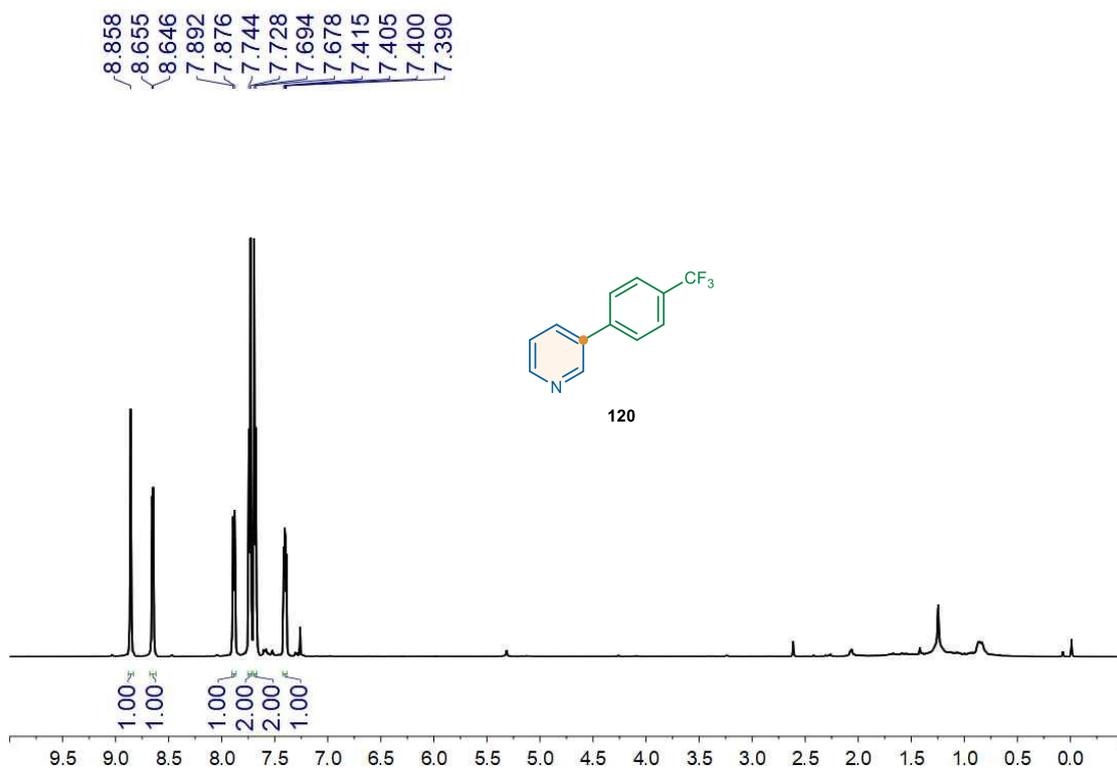
Supplementary Fig. 309. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of 118



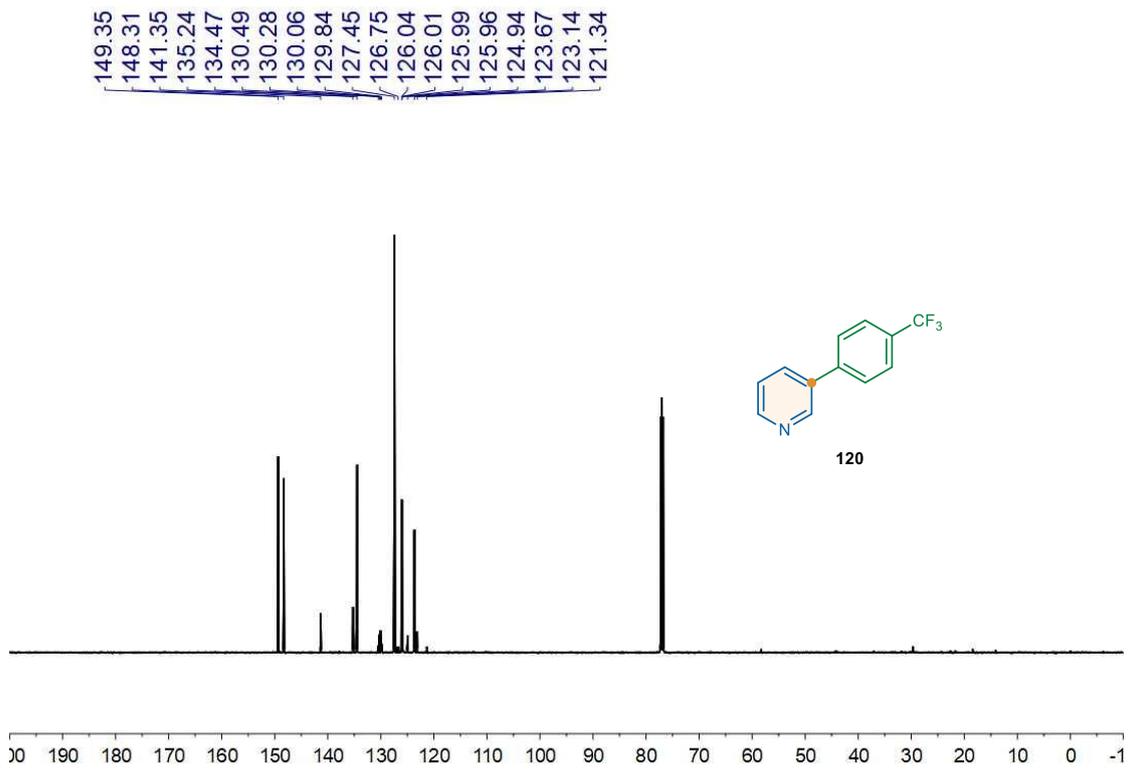
Supplementary Fig. 310. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of 119



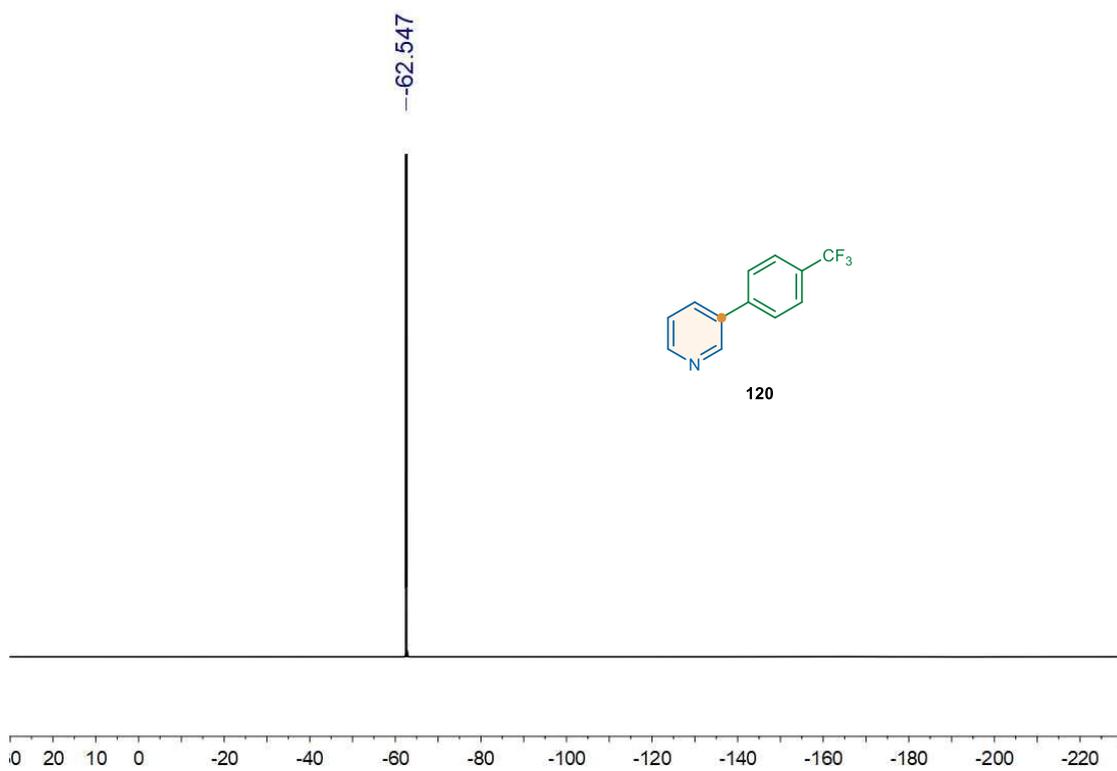
Supplementary Fig. 311. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of **119**



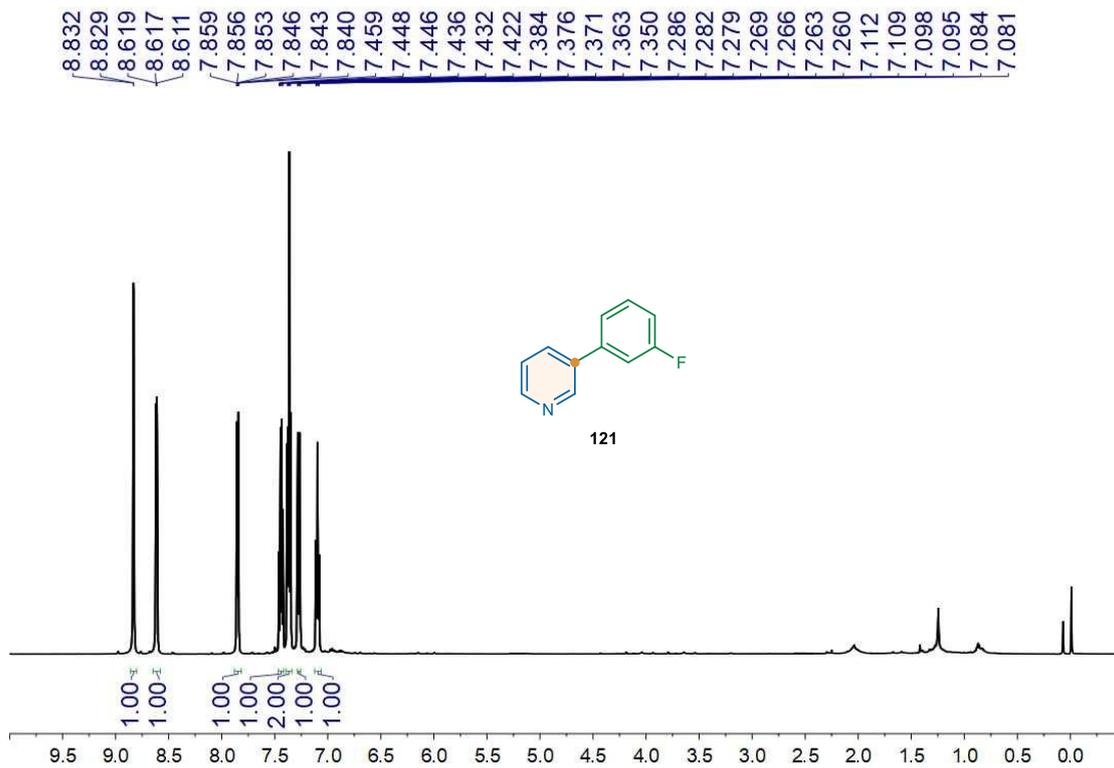
Supplementary Fig. 312. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **120**



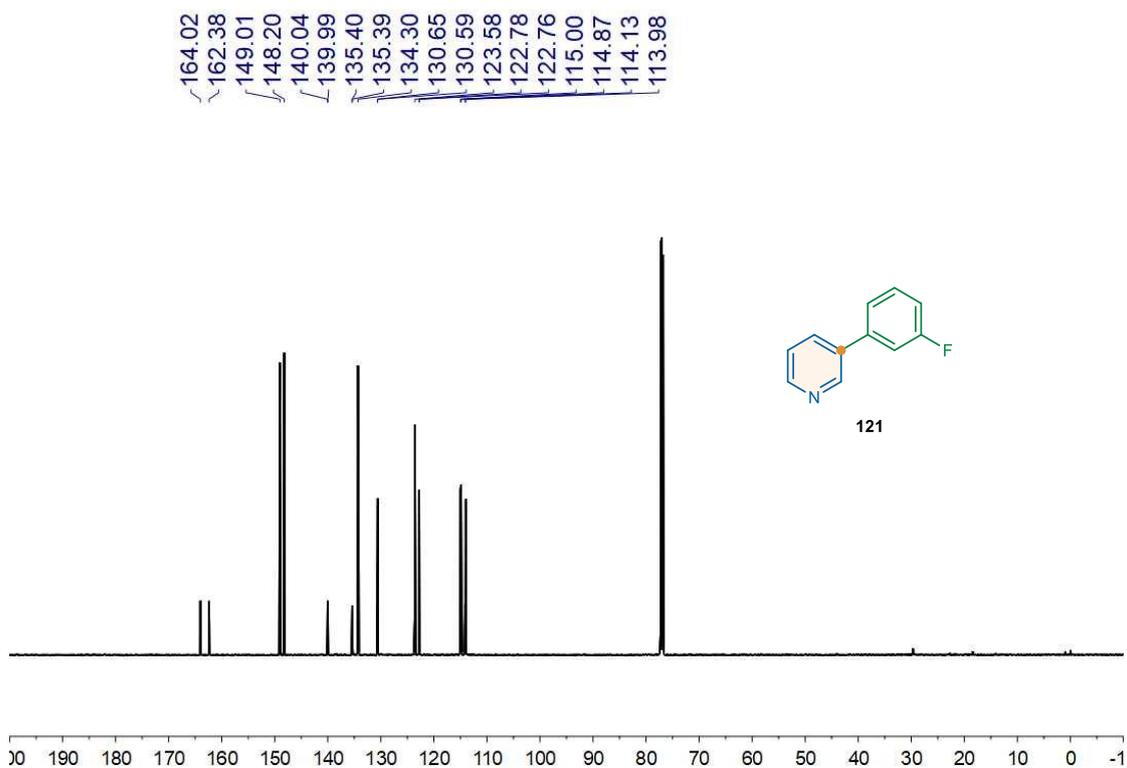
Supplementary Fig. 313.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **120**



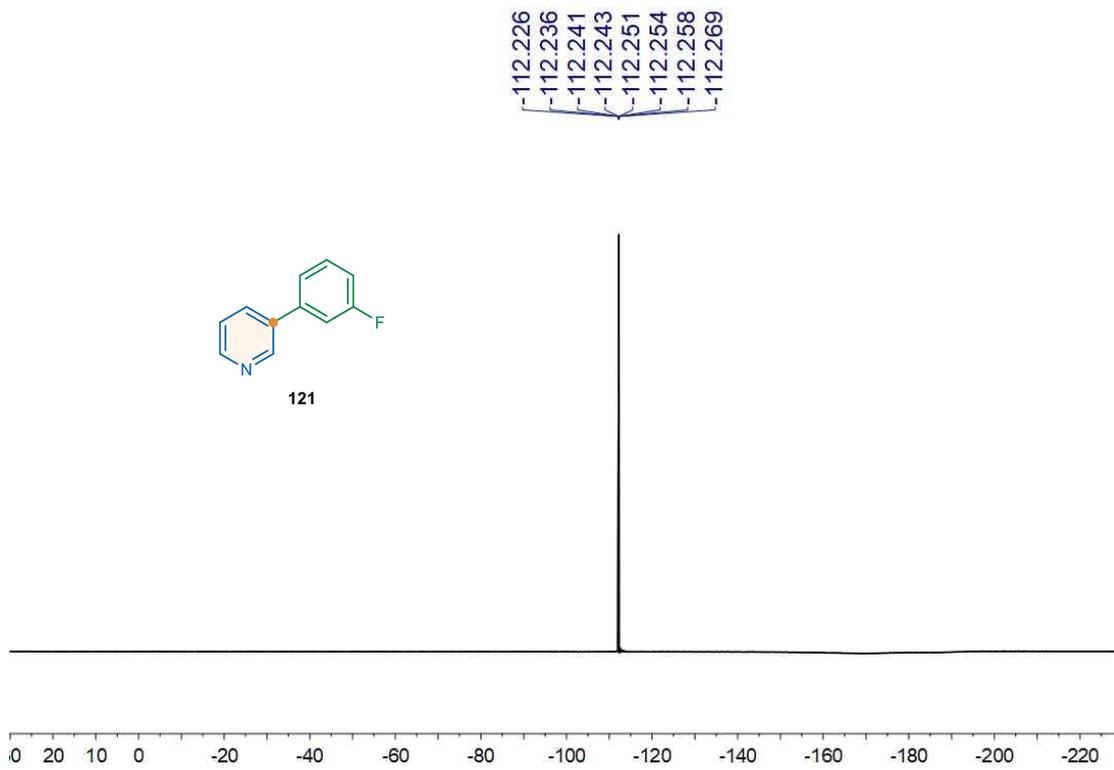
Supplementary Fig. 314.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ) spectrum of **120**



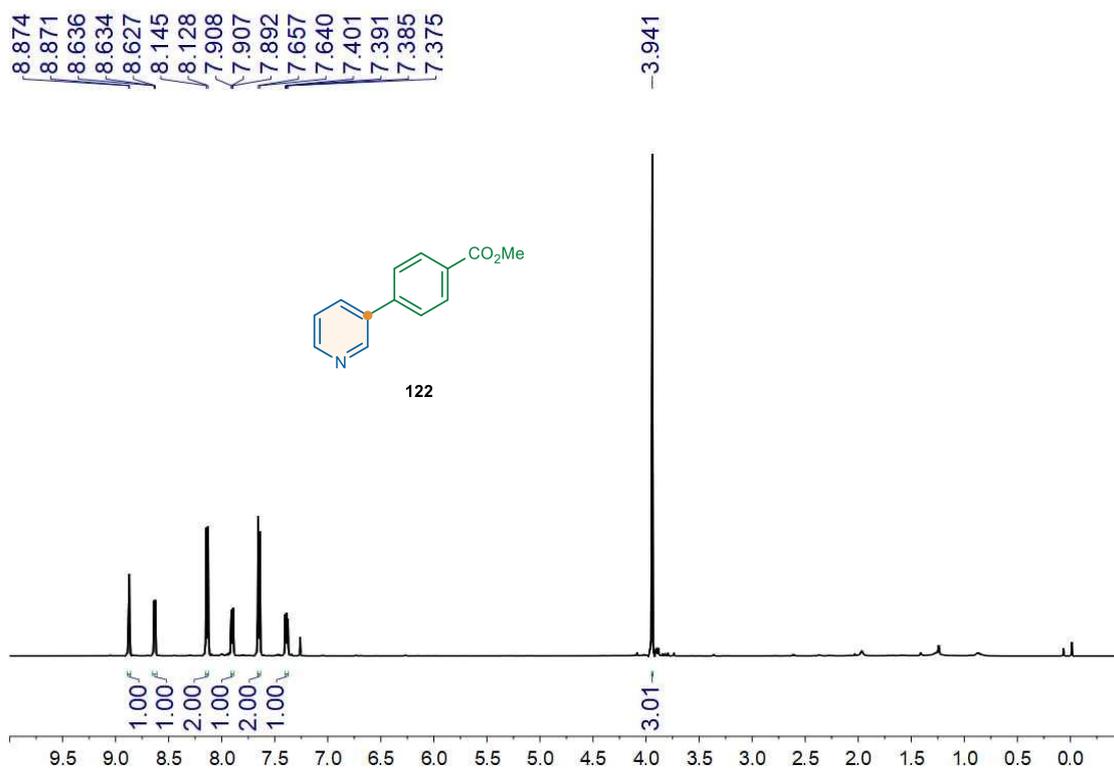
Supplementary Fig. 315. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of 121



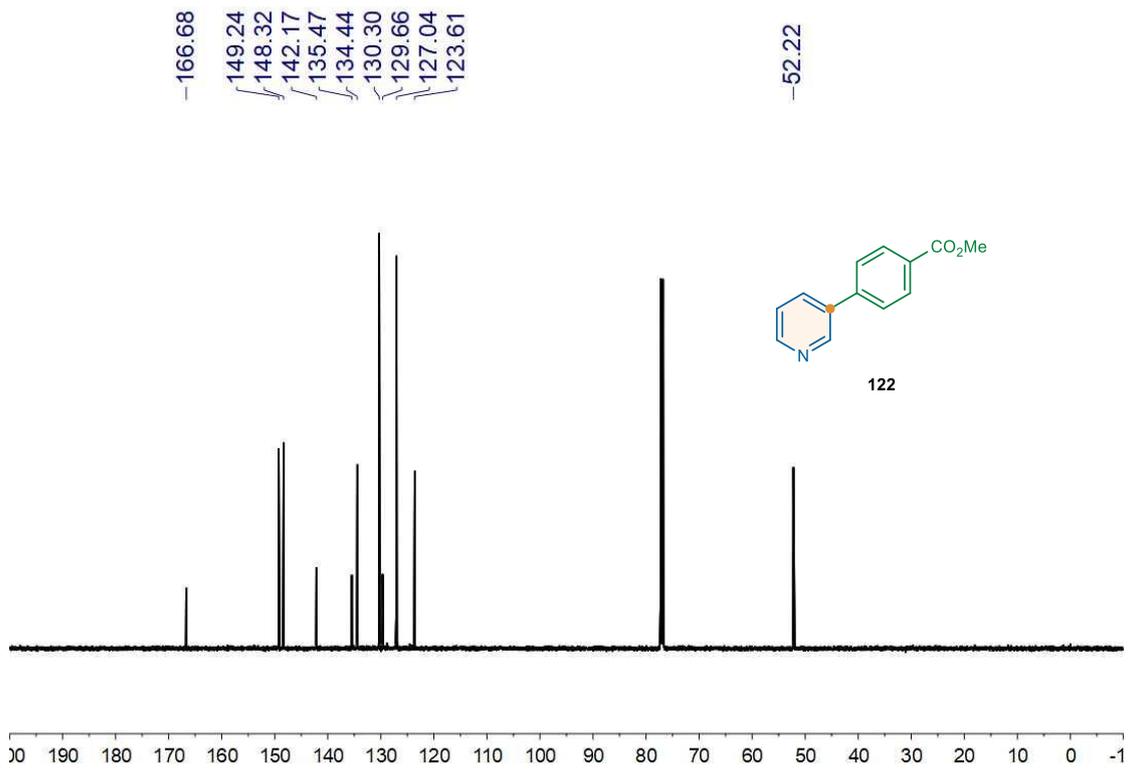
Supplementary Fig. 316. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of 121



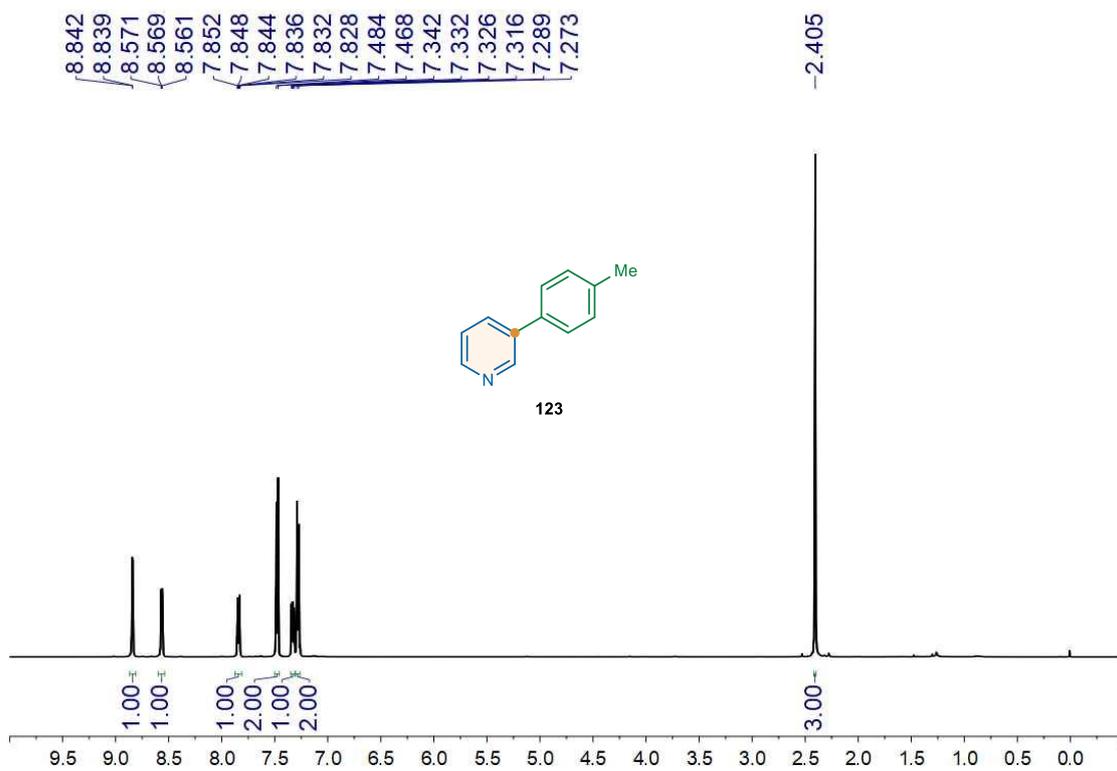
Supplementary Fig. 317. <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) spectrum of **121**



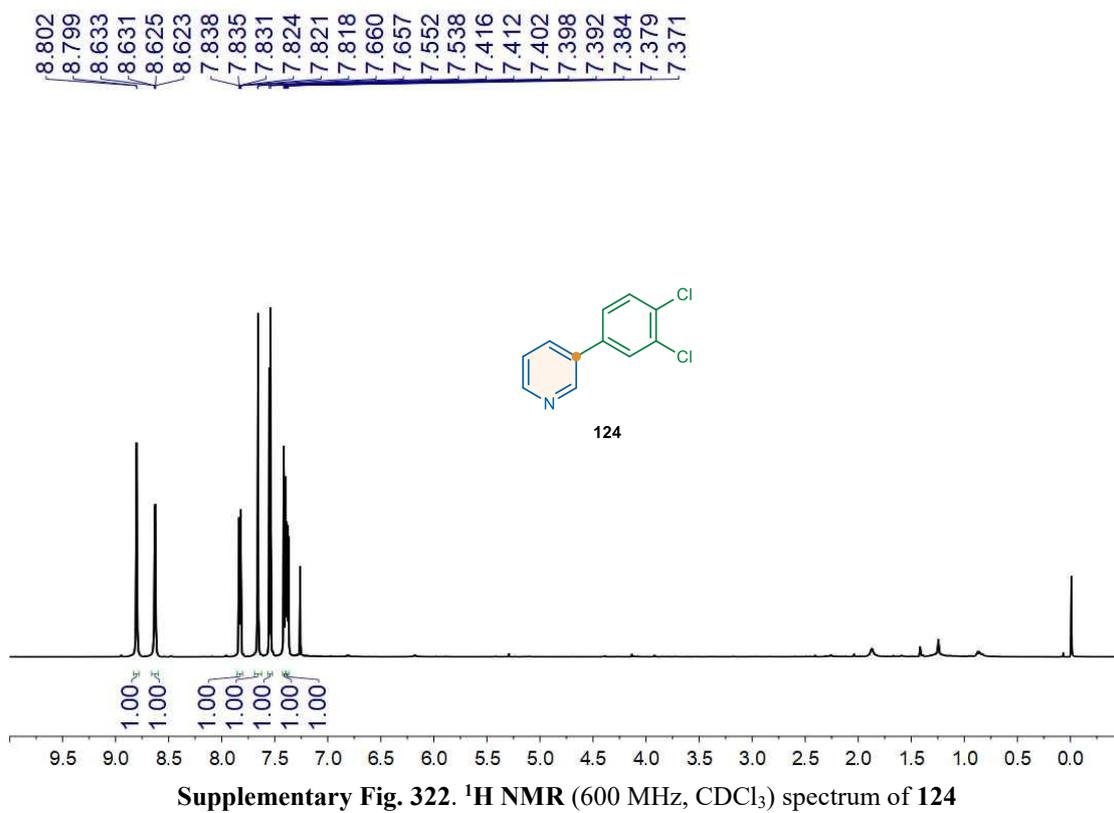
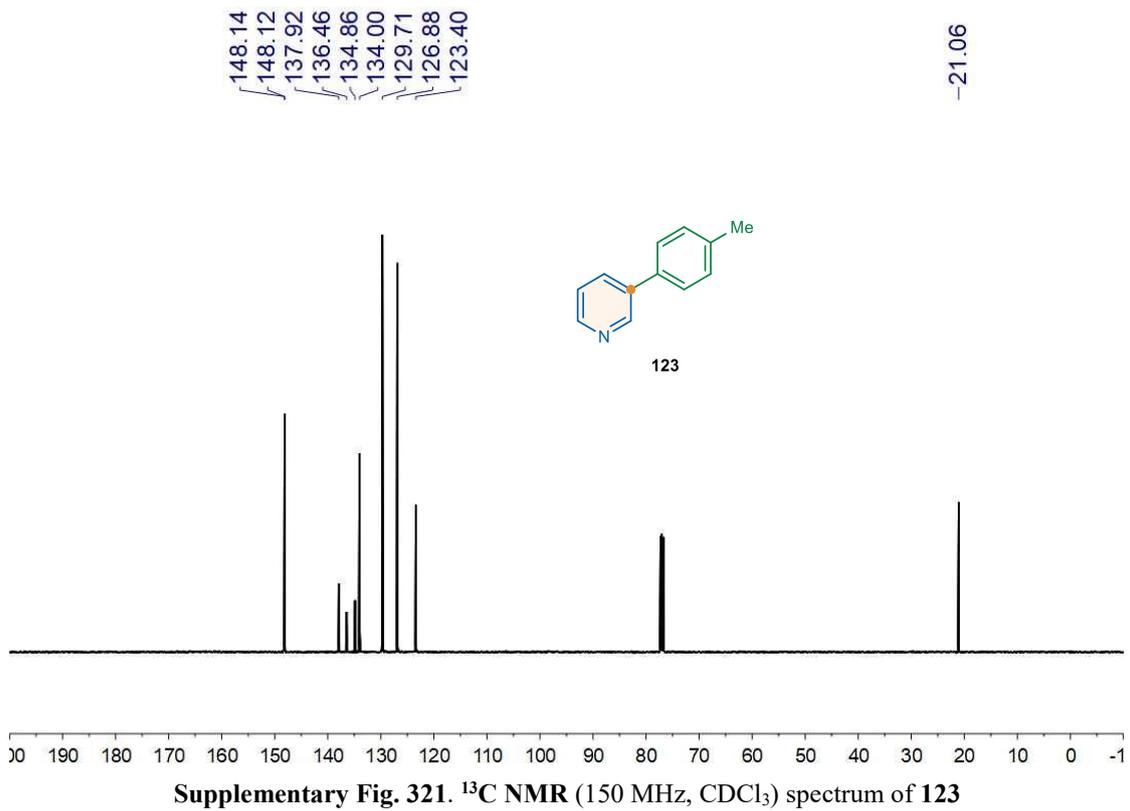
Supplementary Fig. 318. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **122**

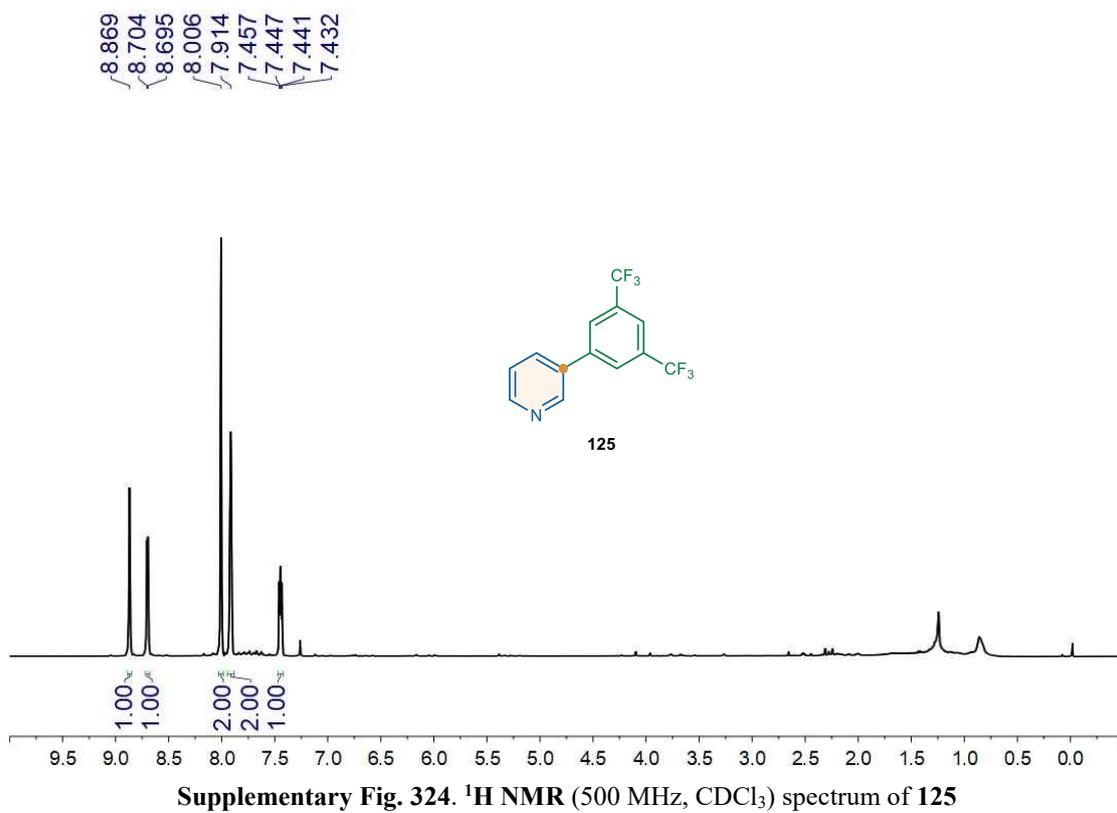
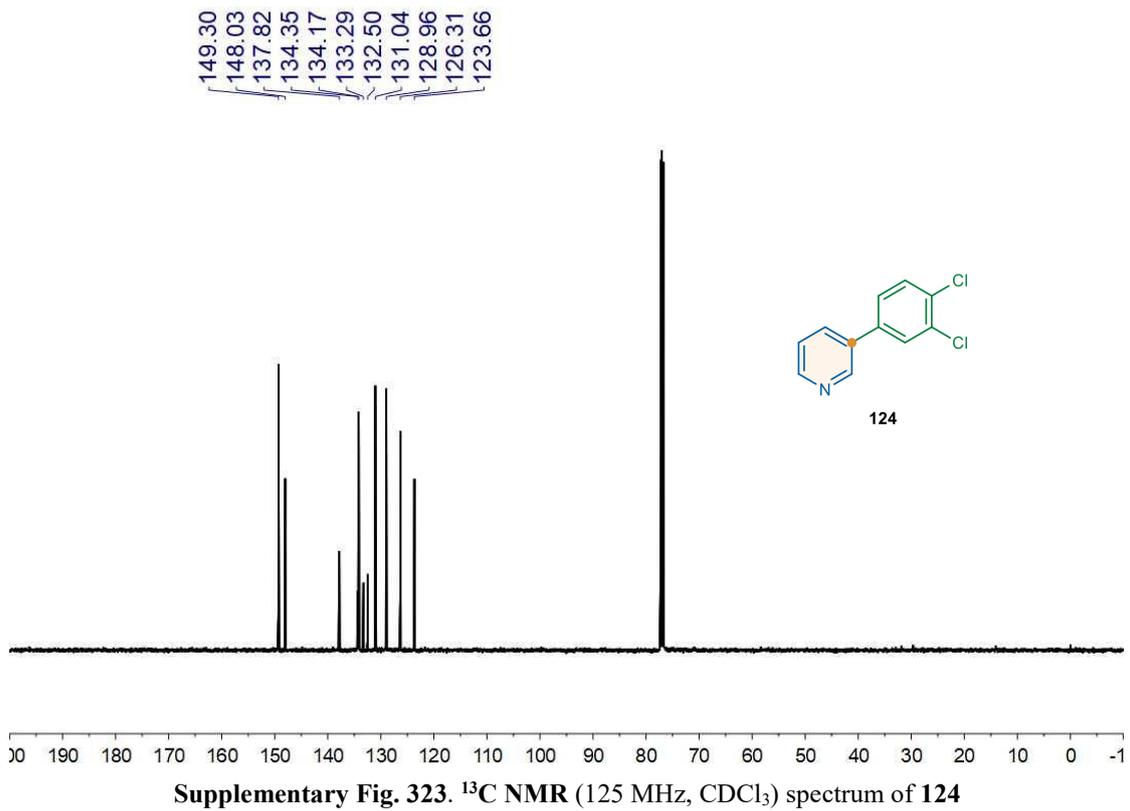


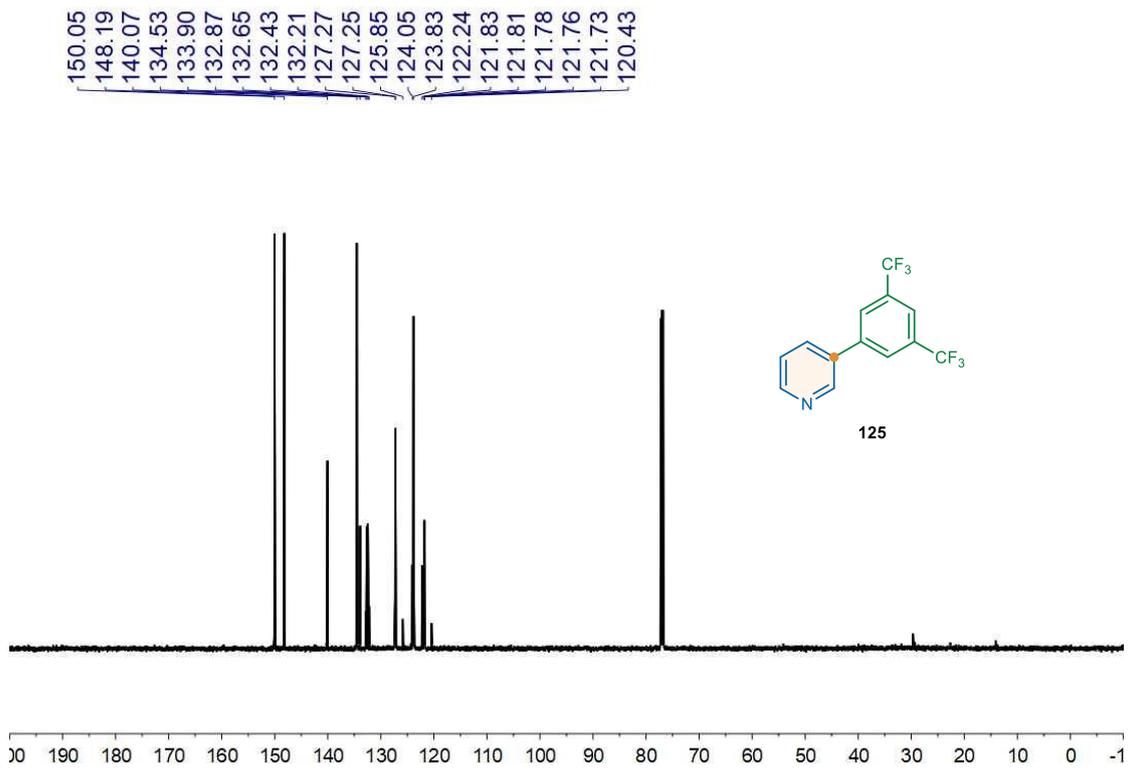
Supplementary Fig. 319. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of **122**



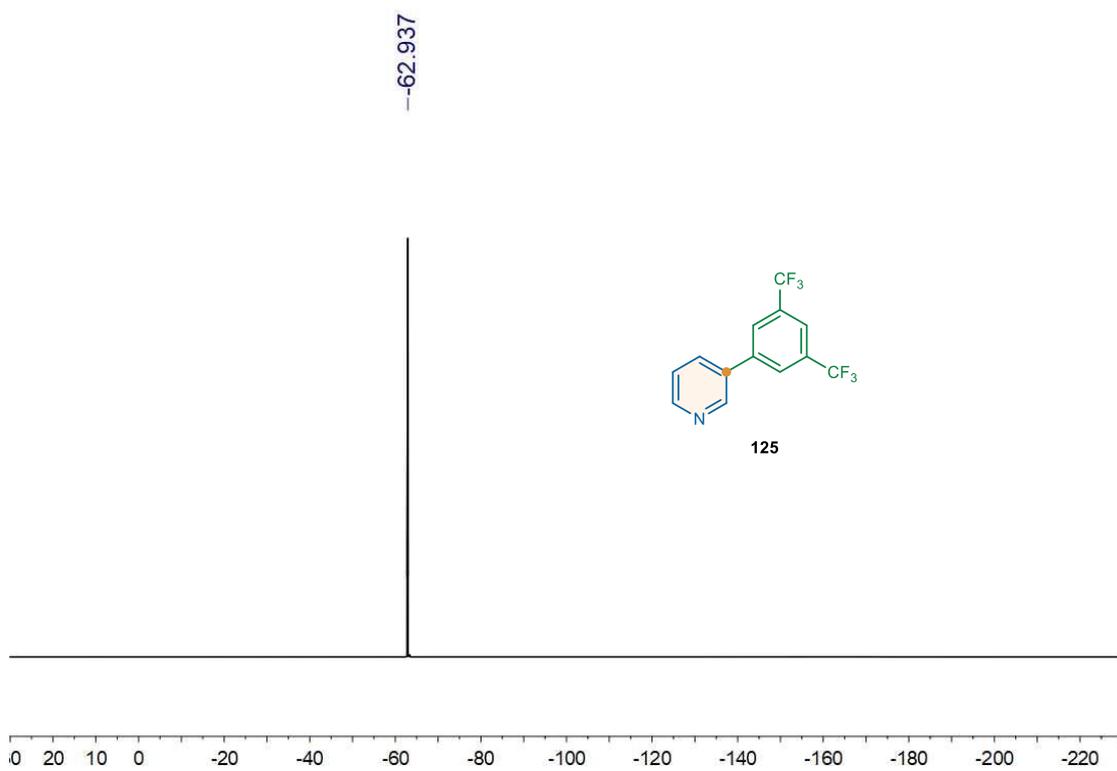
Supplementary Fig. 320. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **123**



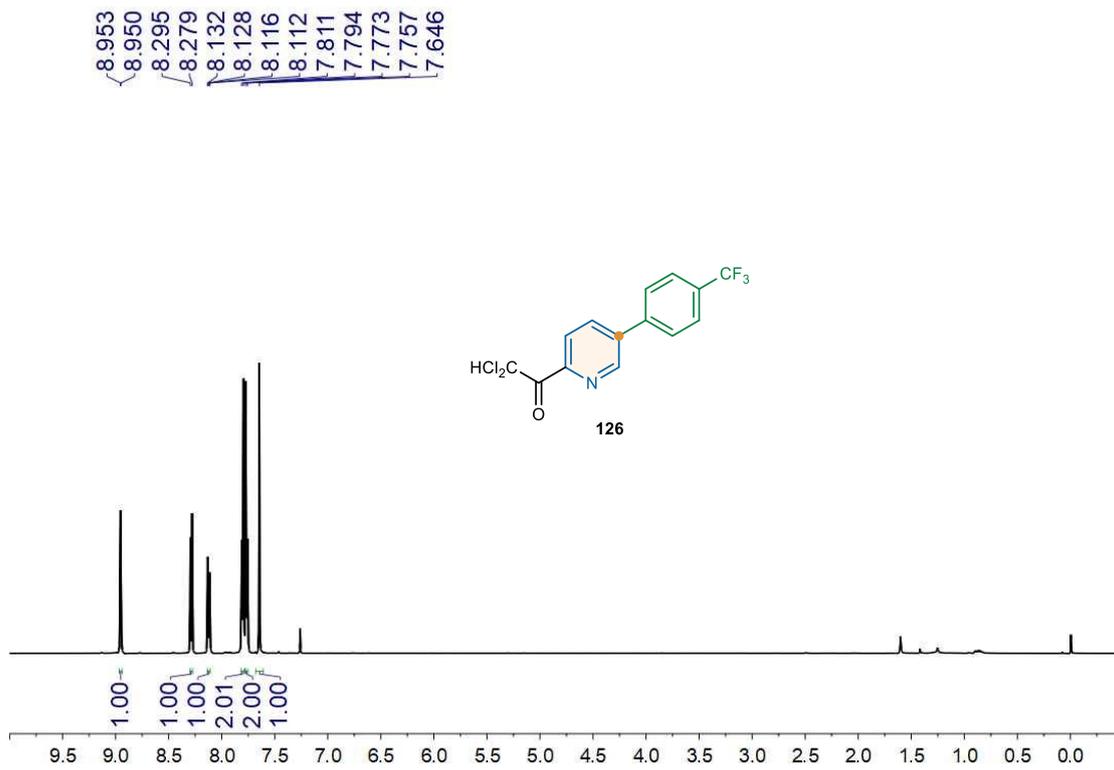




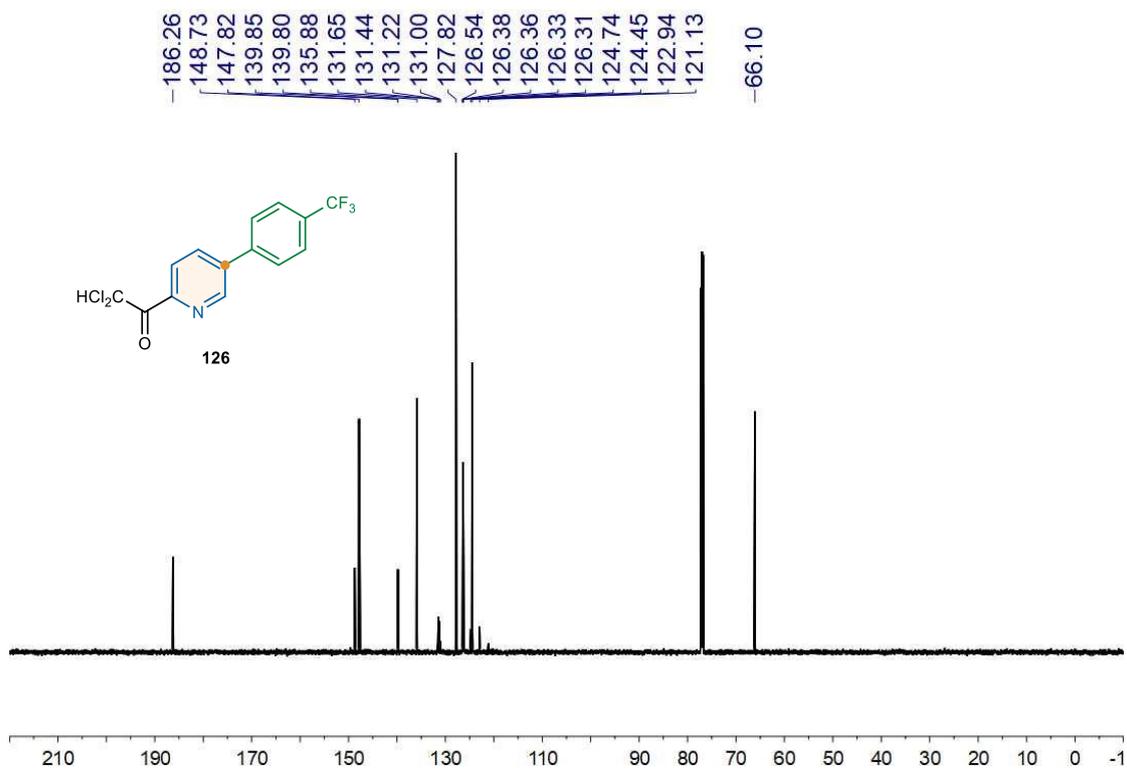
Supplementary Fig. 325.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **125**



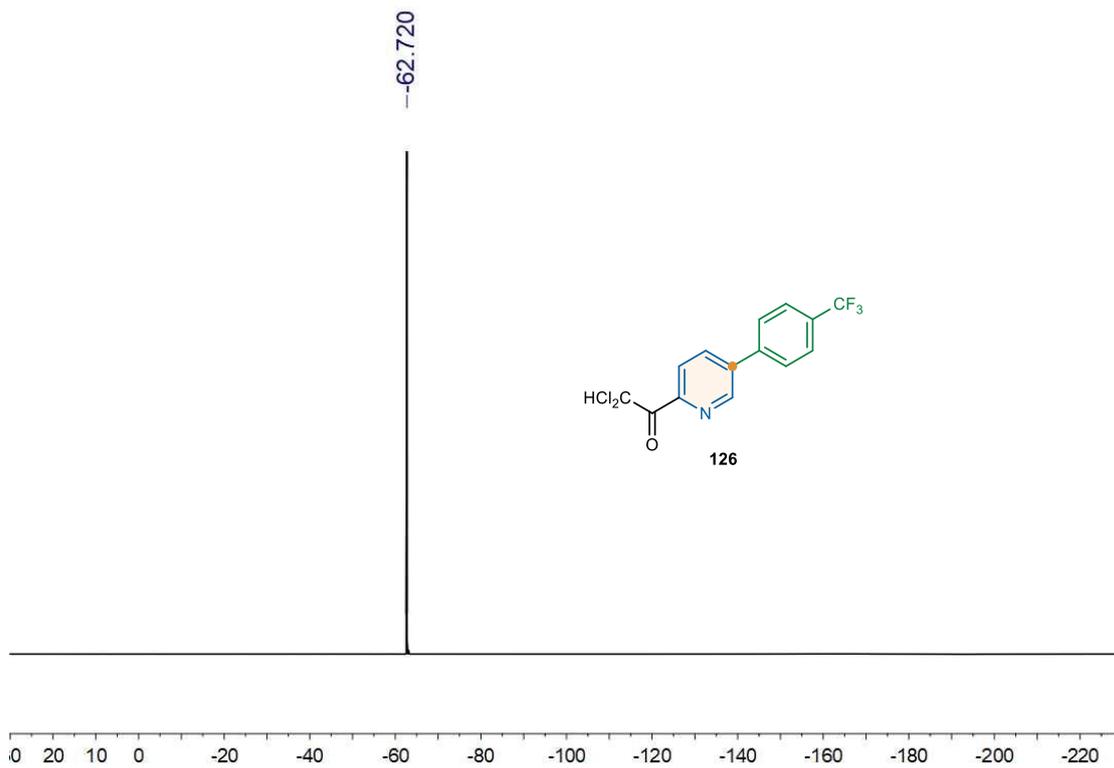
Supplementary Fig. 326.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ) spectrum of **125**



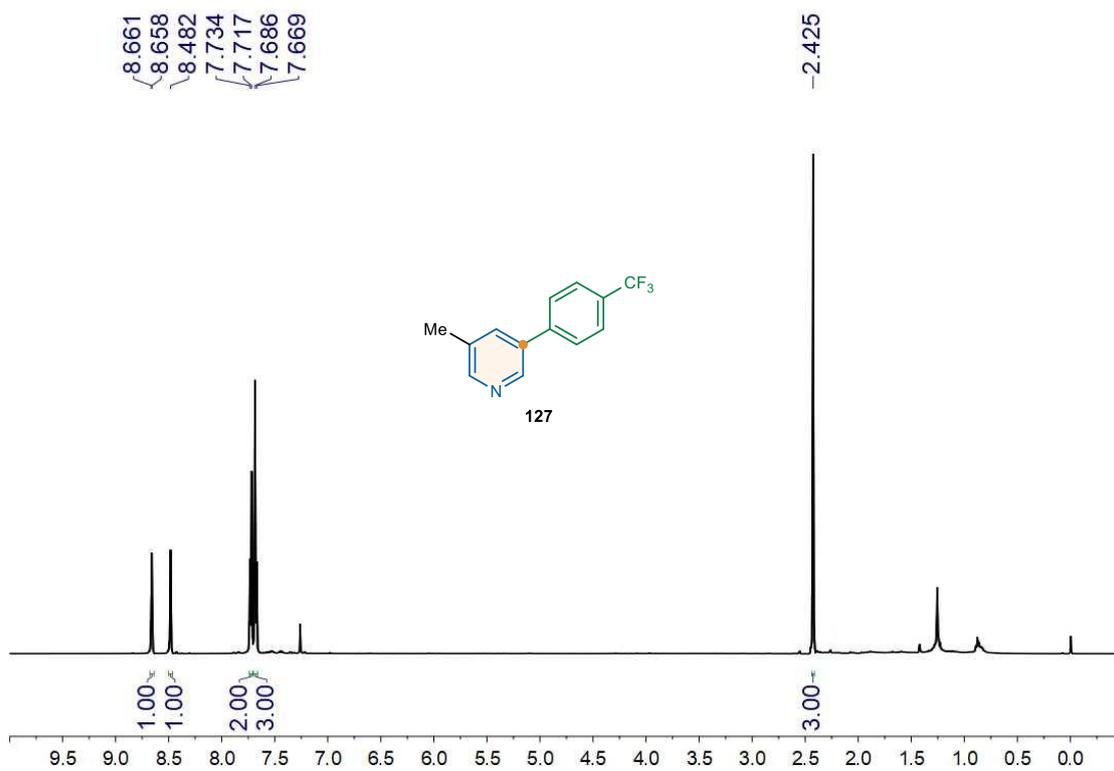
Supplementary Fig. 327.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of 126



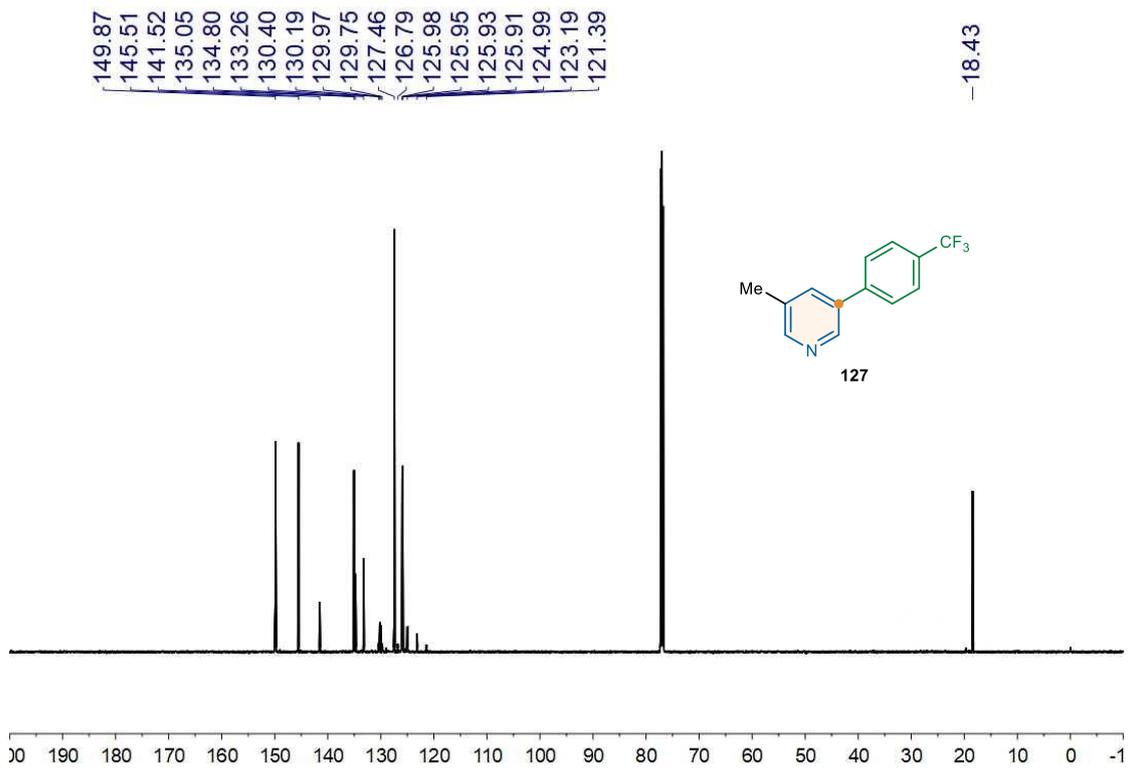
Supplementary Fig. 328.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of 126



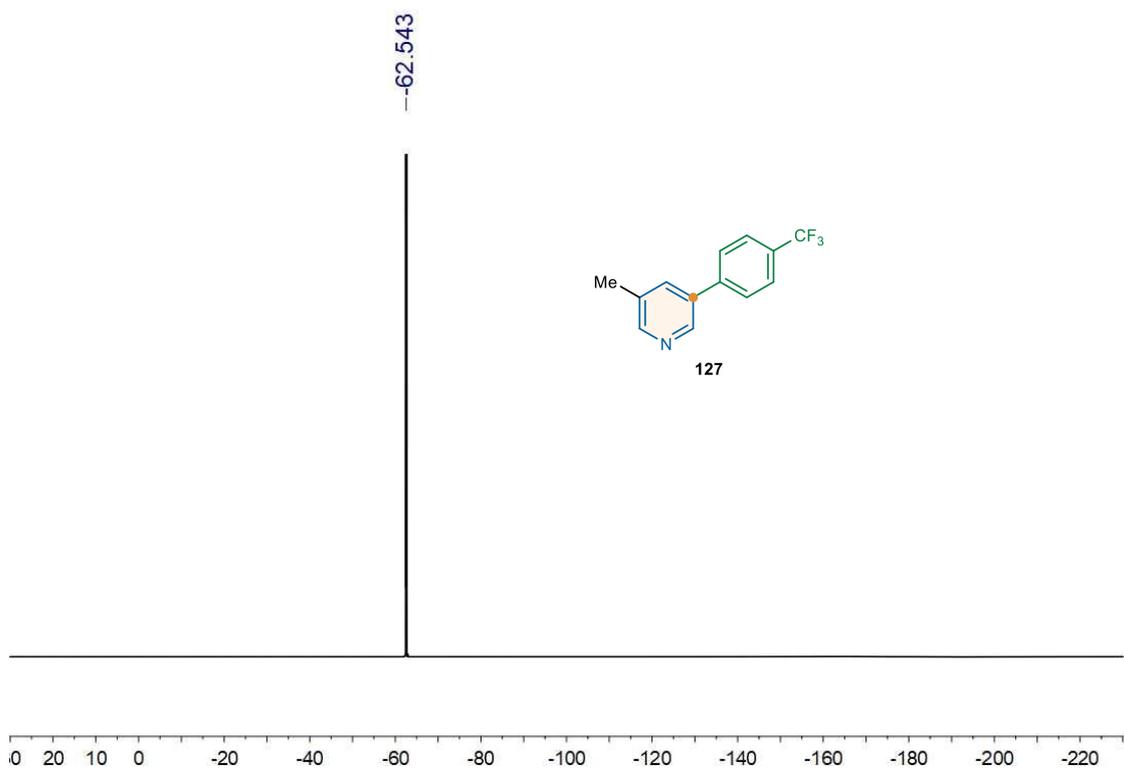
Supplementary Fig. 329.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ) spectrum of 126



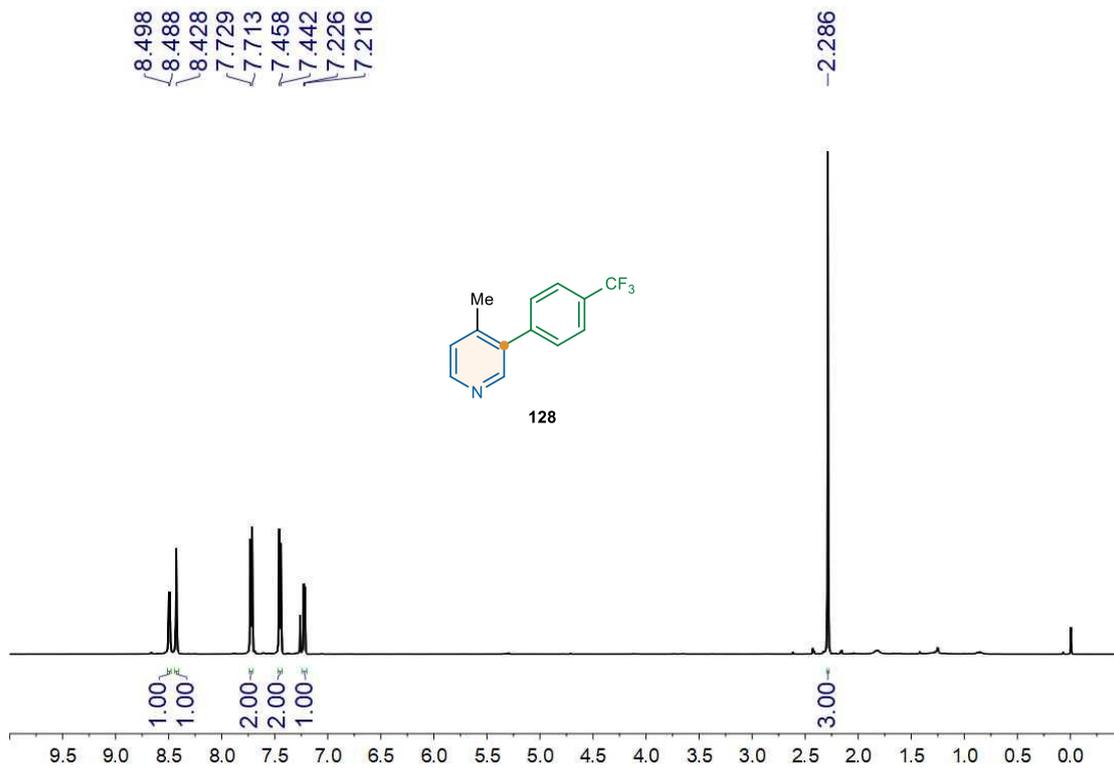
Supplementary Fig. 330.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of 127



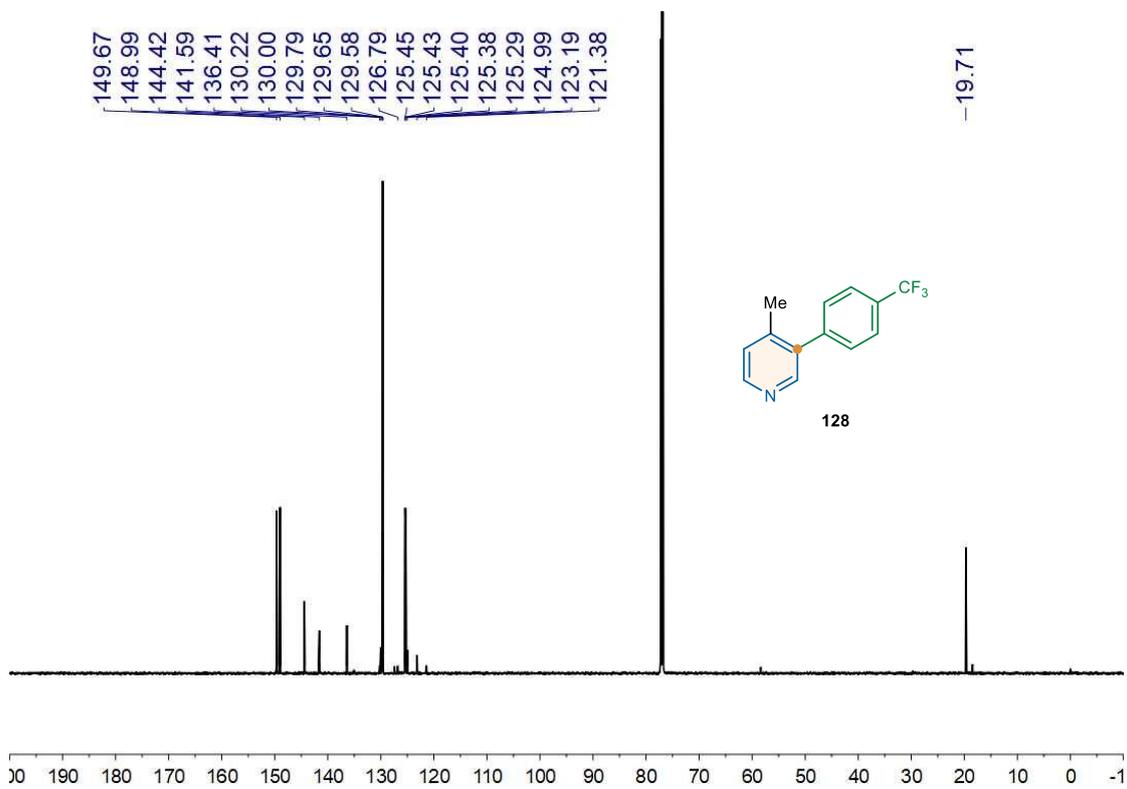
Supplementary Fig. 331. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of 127



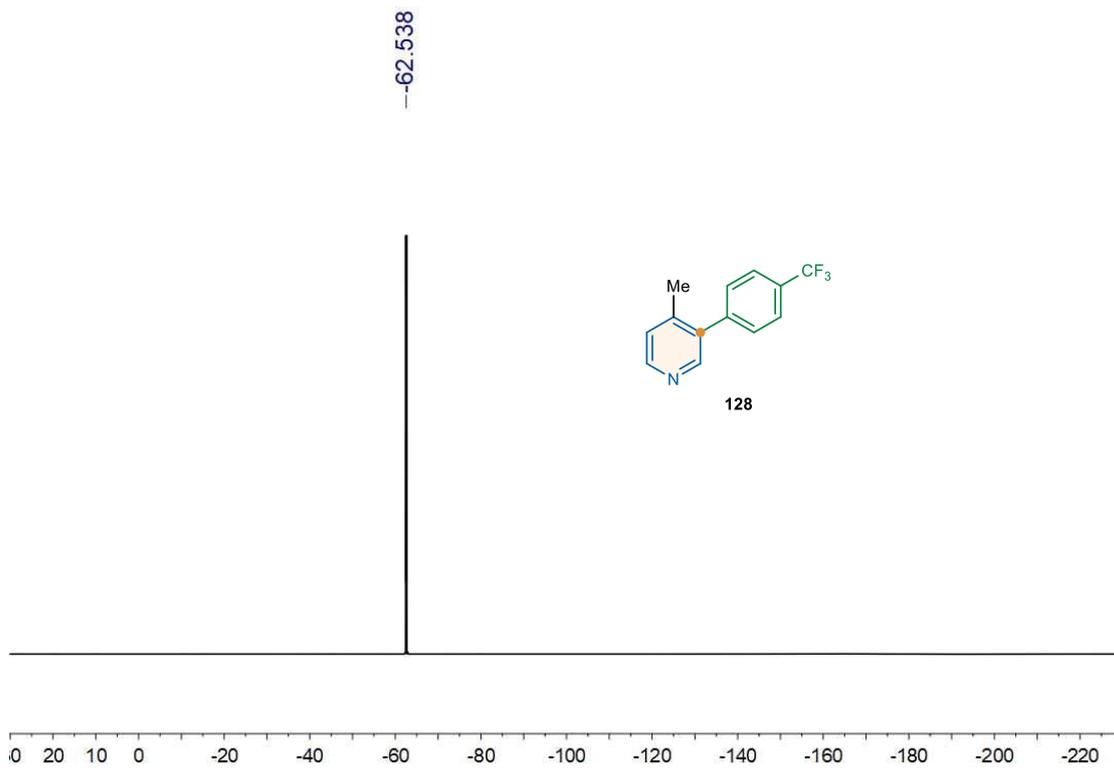
Supplementary Fig. 332. <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) spectrum of 127



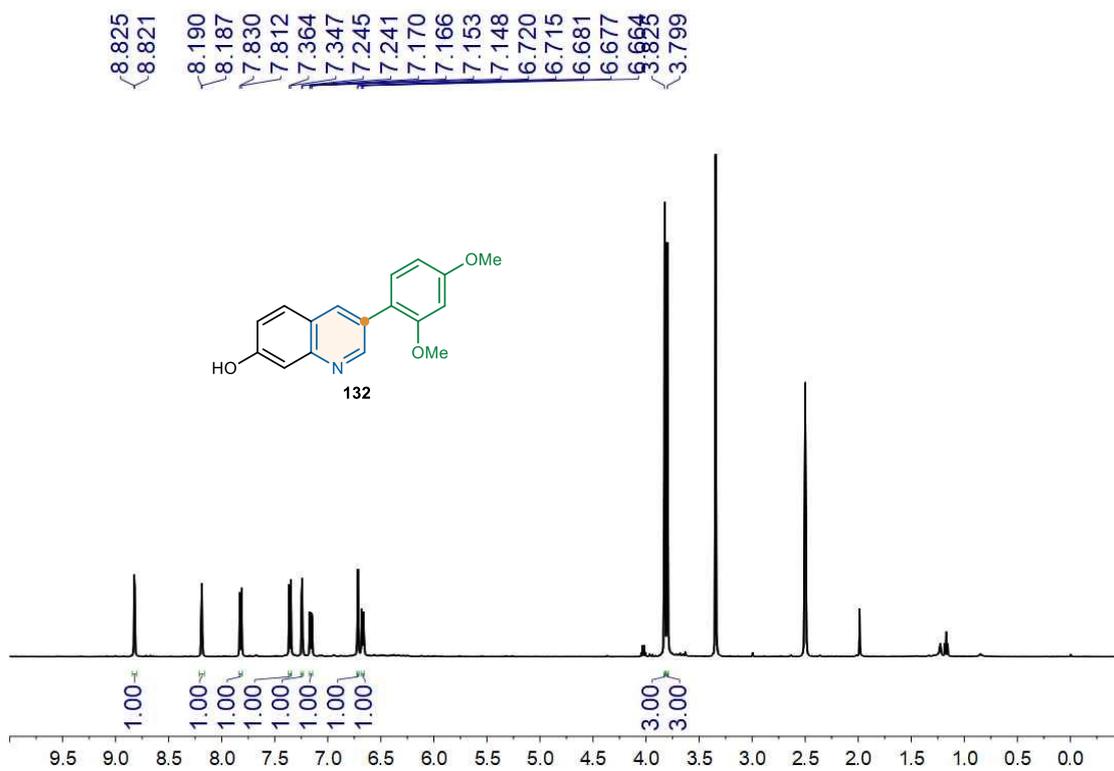
Supplementary Fig. 333.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **128**



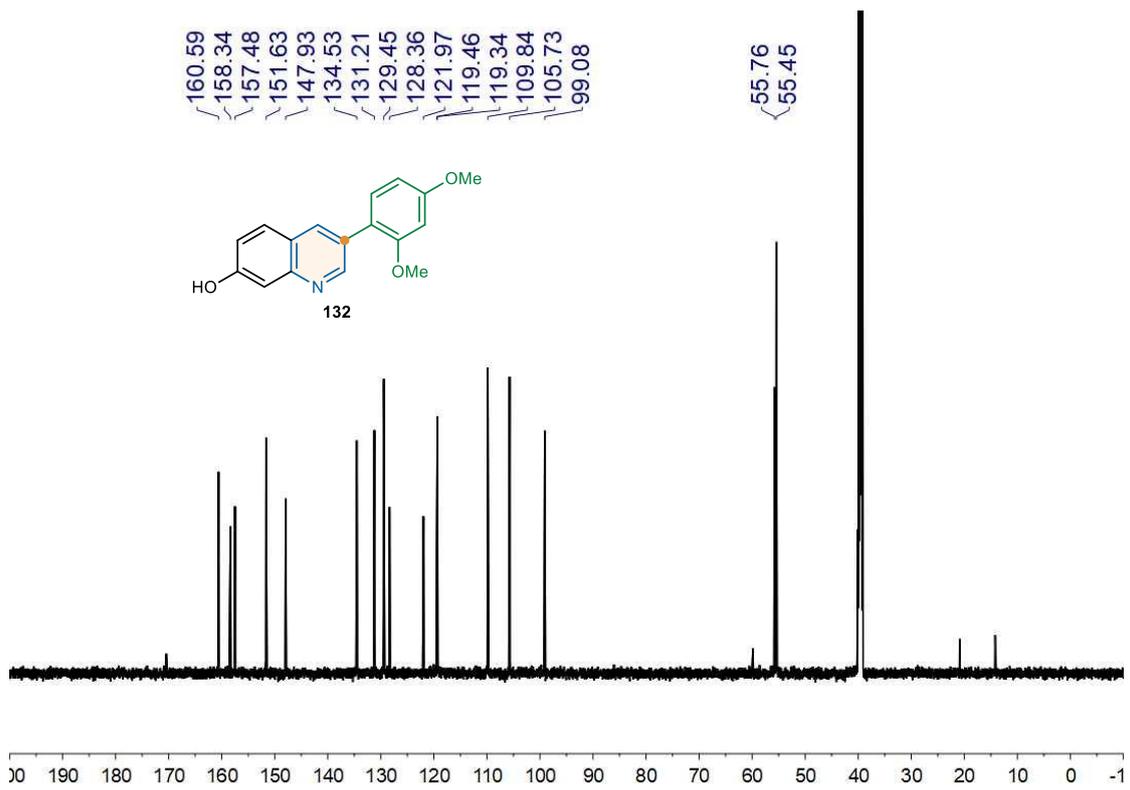
Supplementary Fig. 334.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **128**



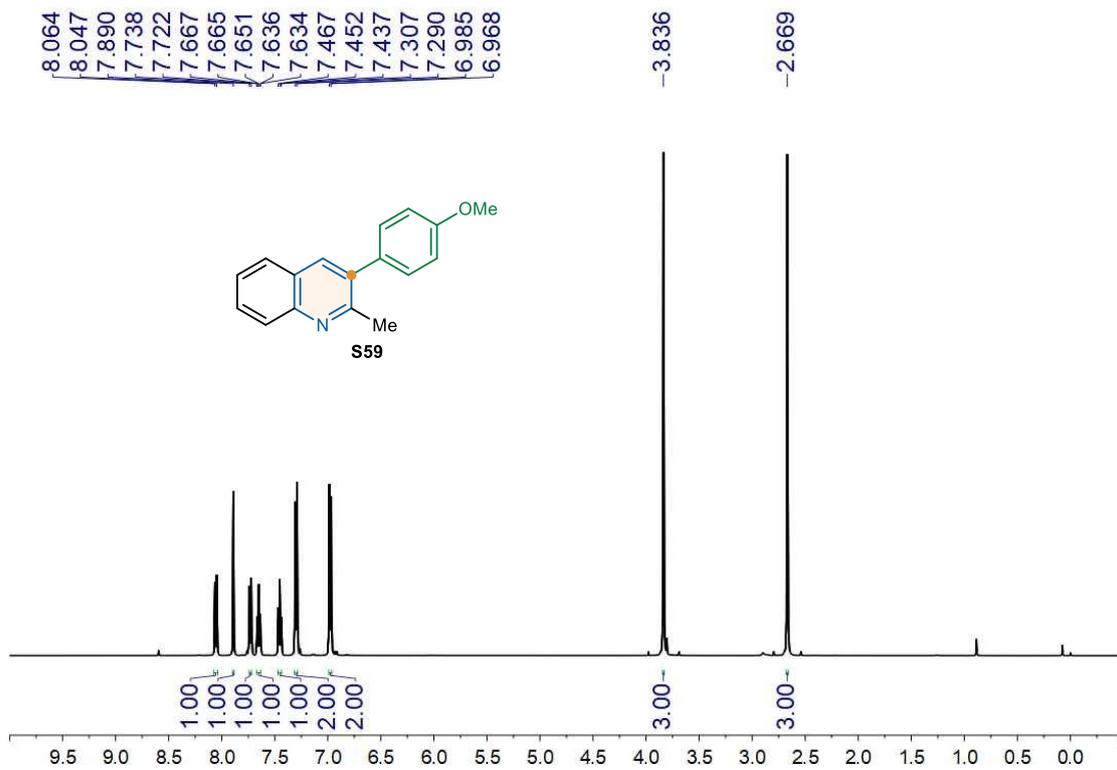
Supplementary Fig. 335.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ) spectrum of **128**



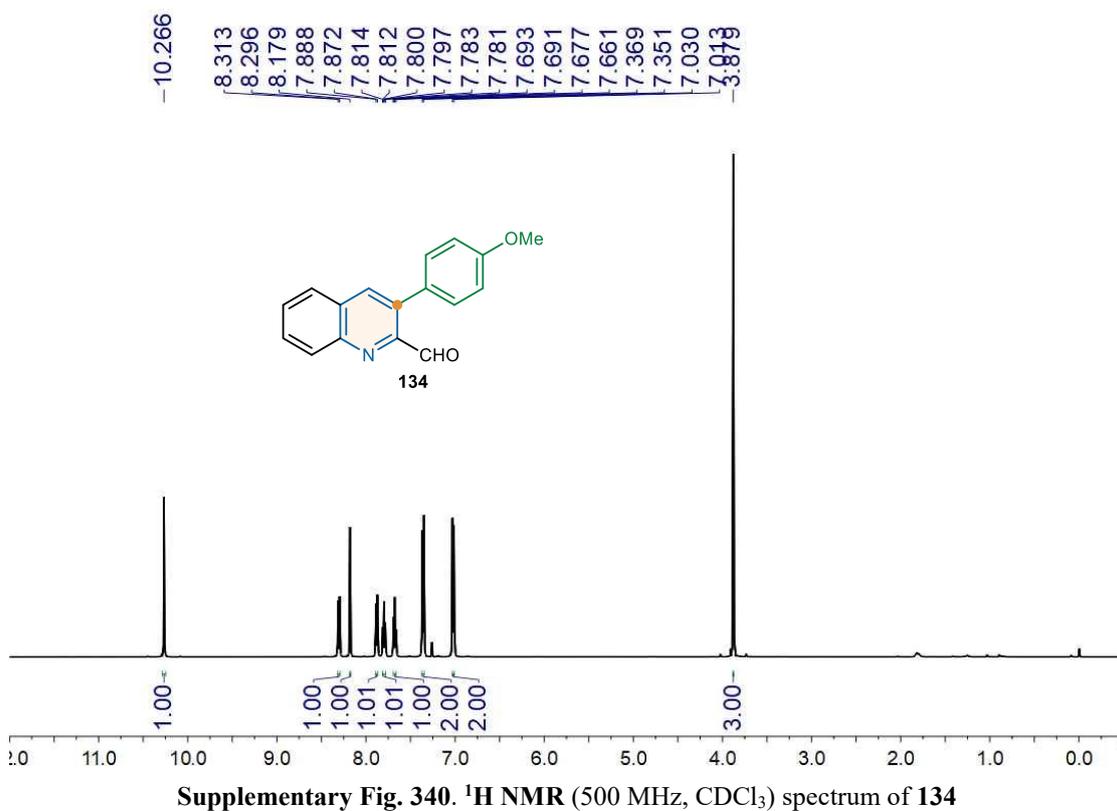
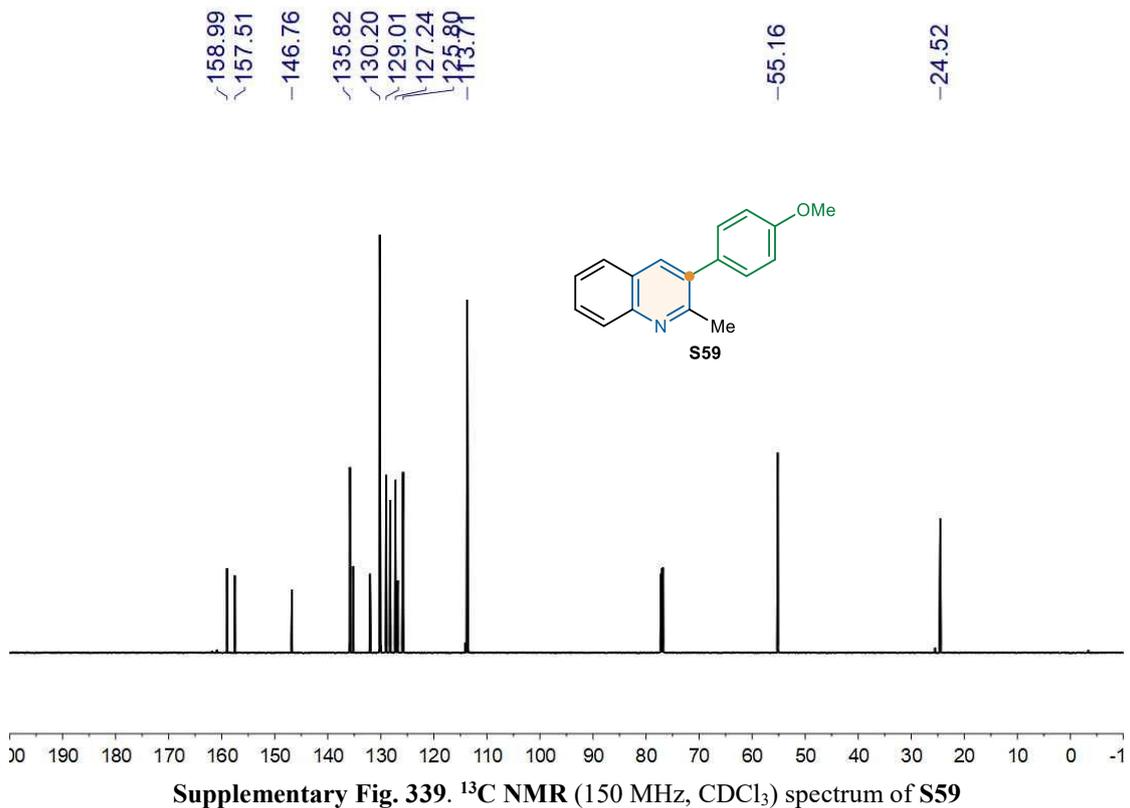
Supplementary Fig. 336.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ ) spectrum of **132**

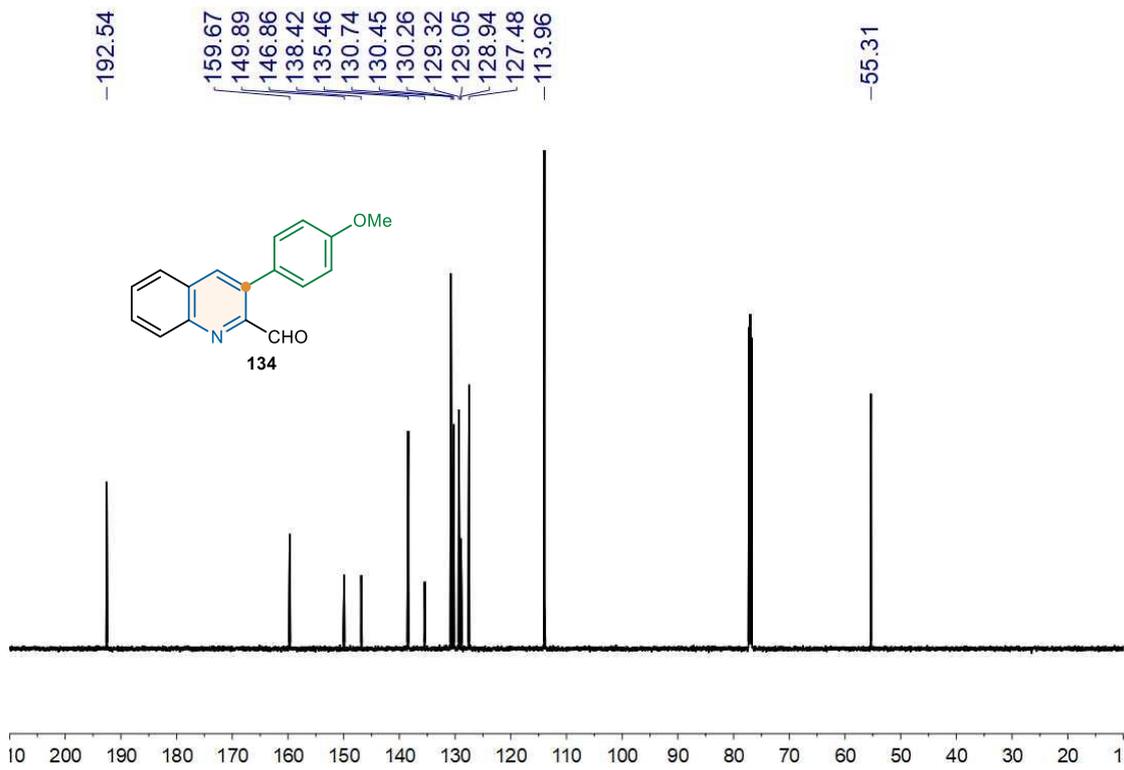


Supplementary Fig. 337. <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>) spectrum of **132**

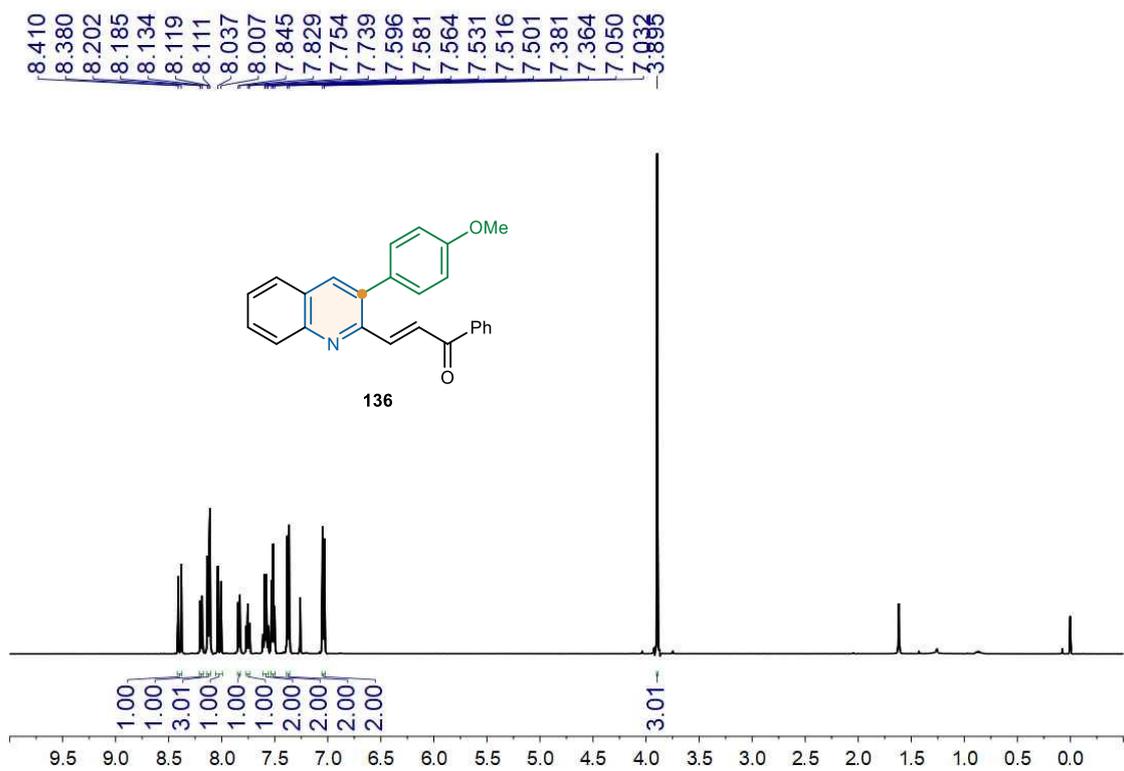


Supplementary Fig. 338. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **S59**

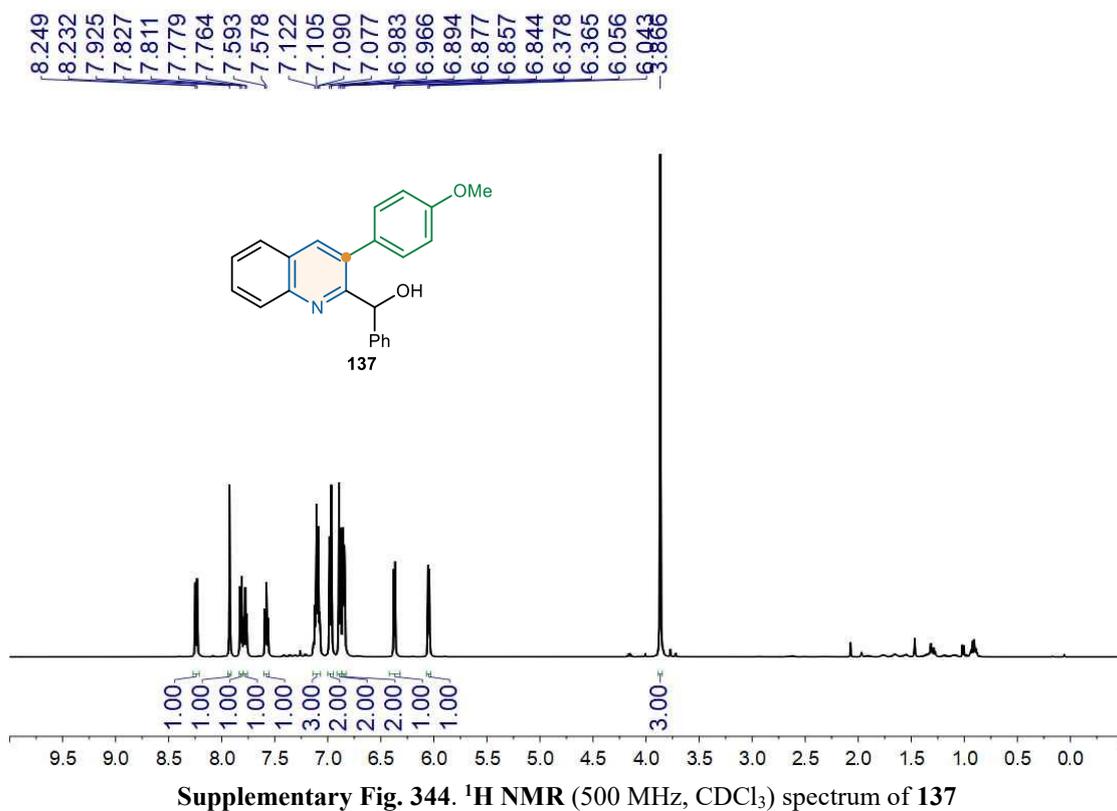
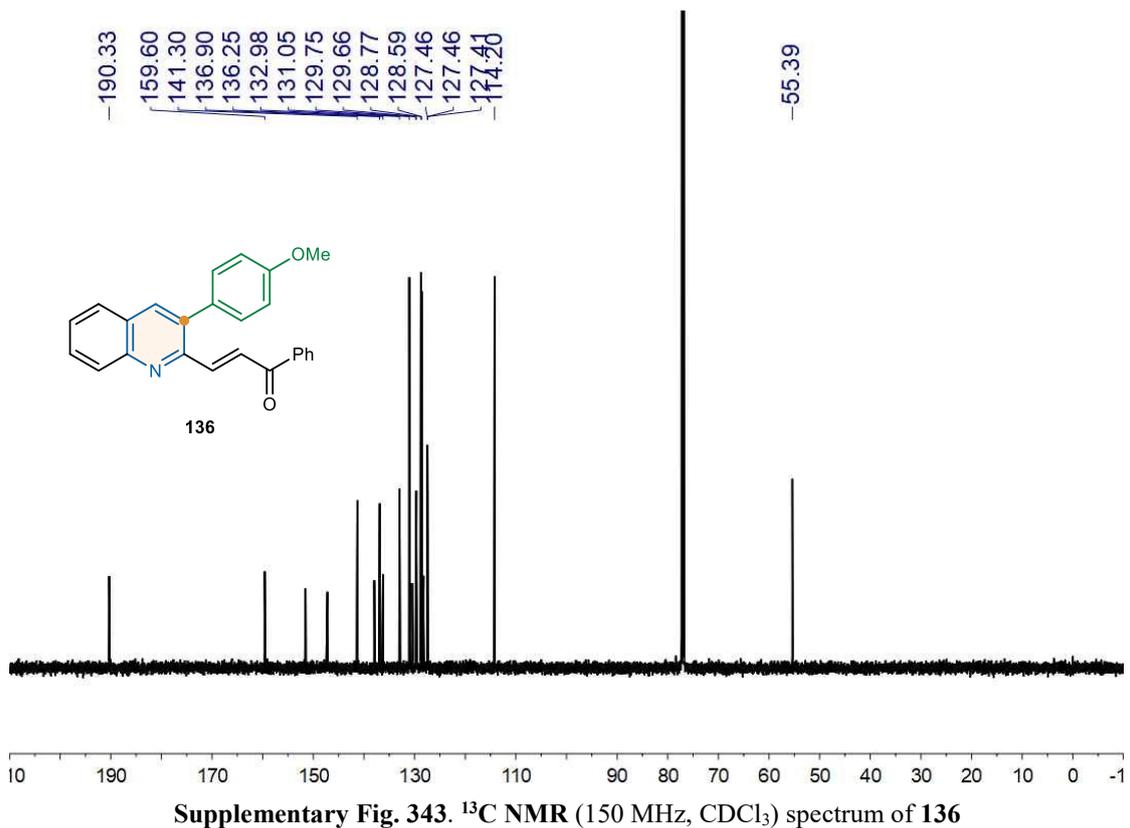


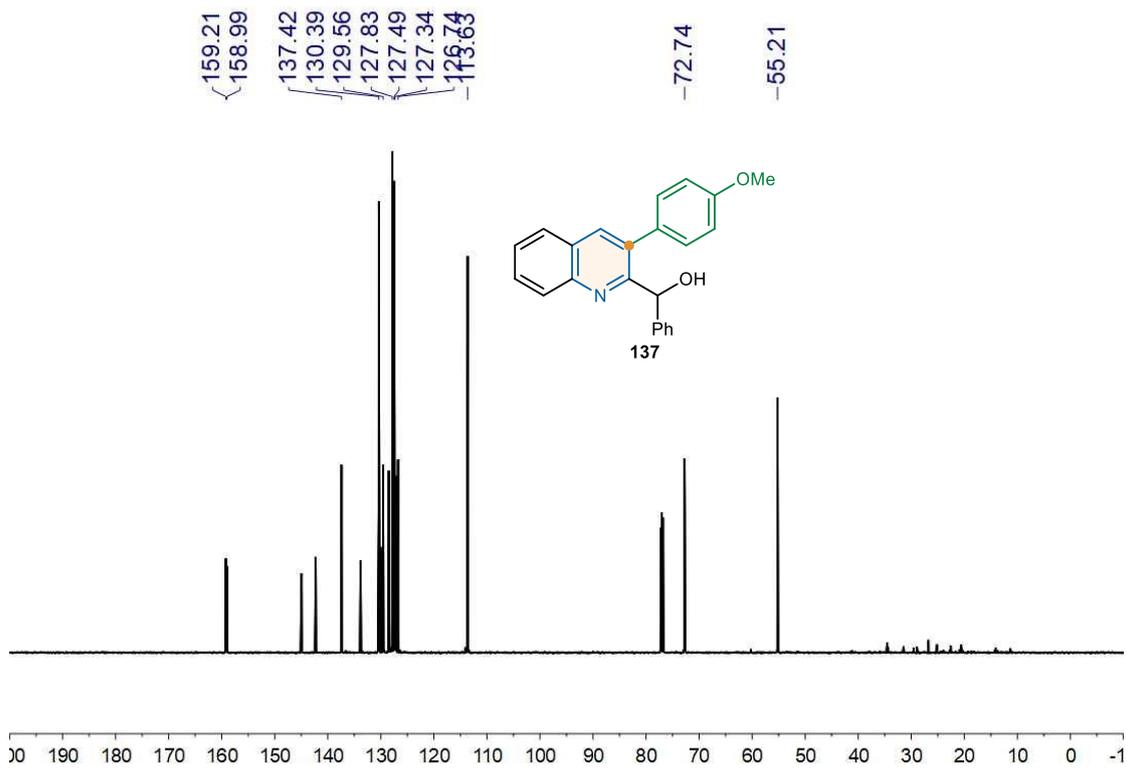


Supplementary Fig. 341.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **134**

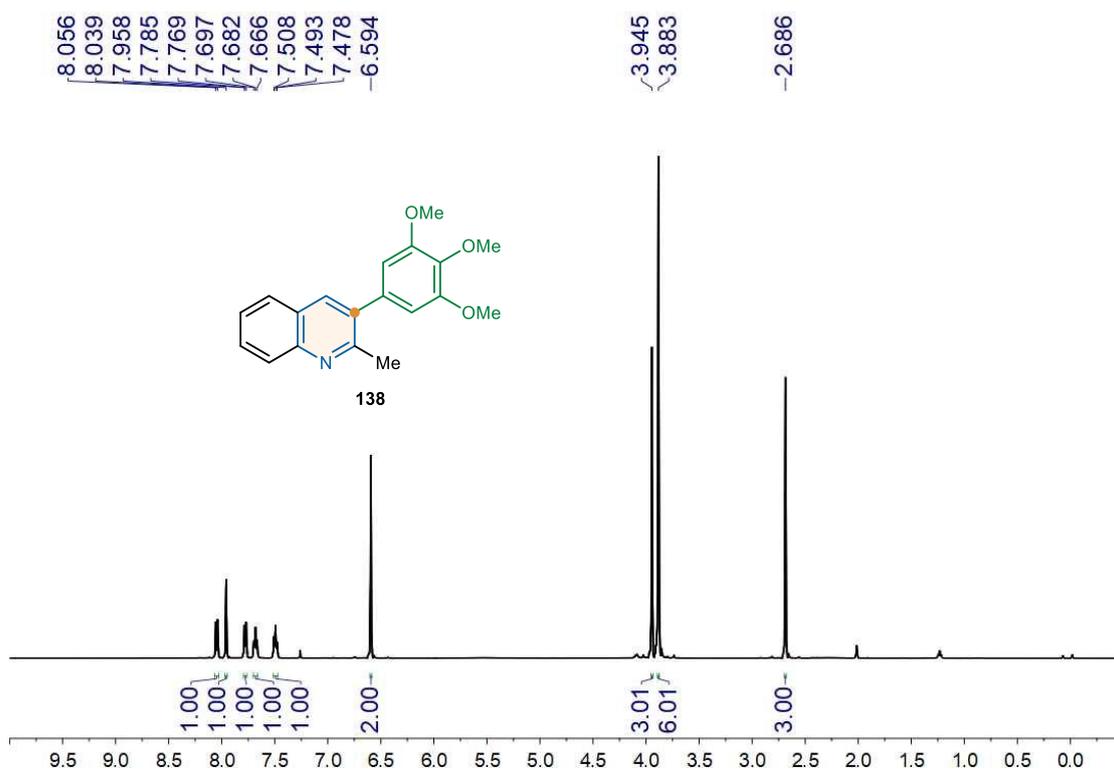


Supplementary Fig. 342.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **136**

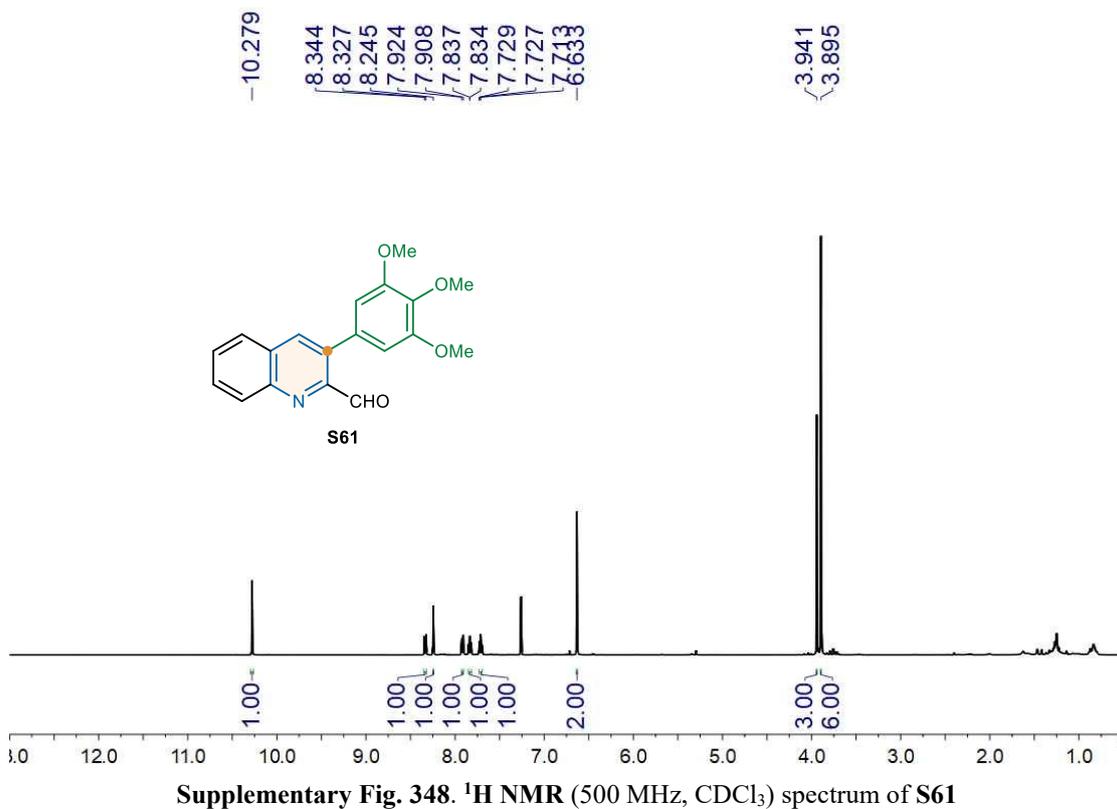
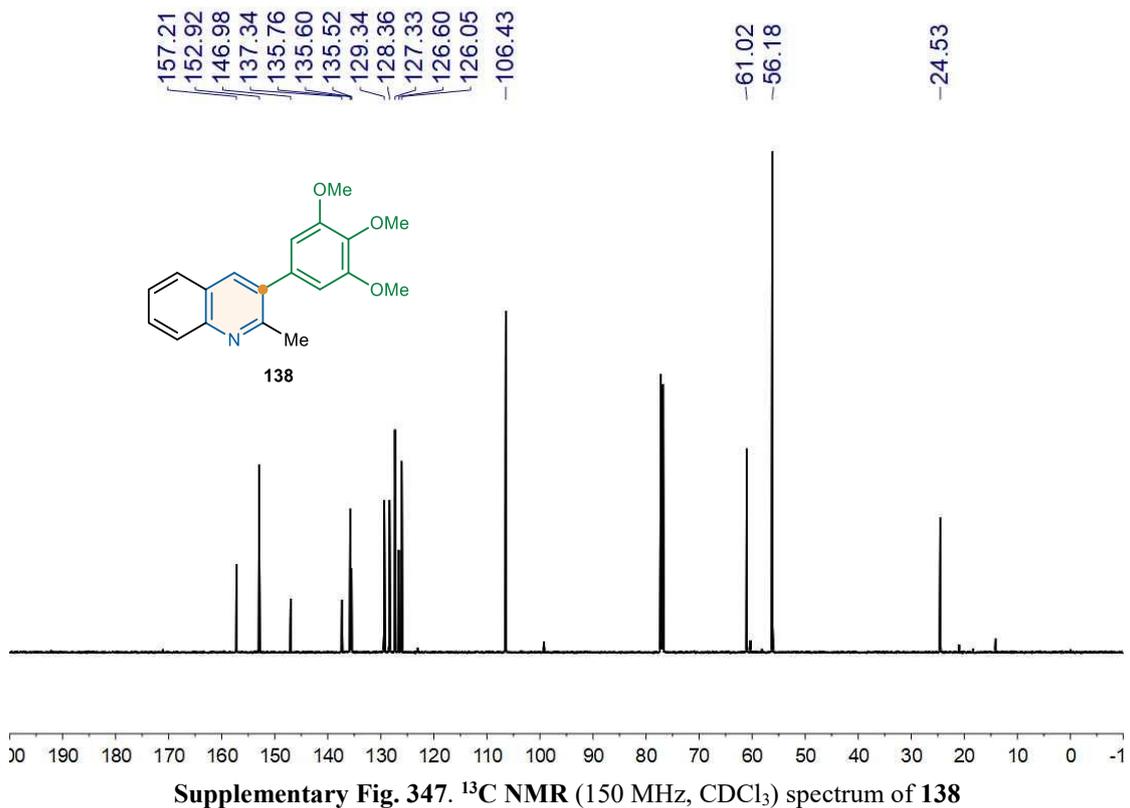


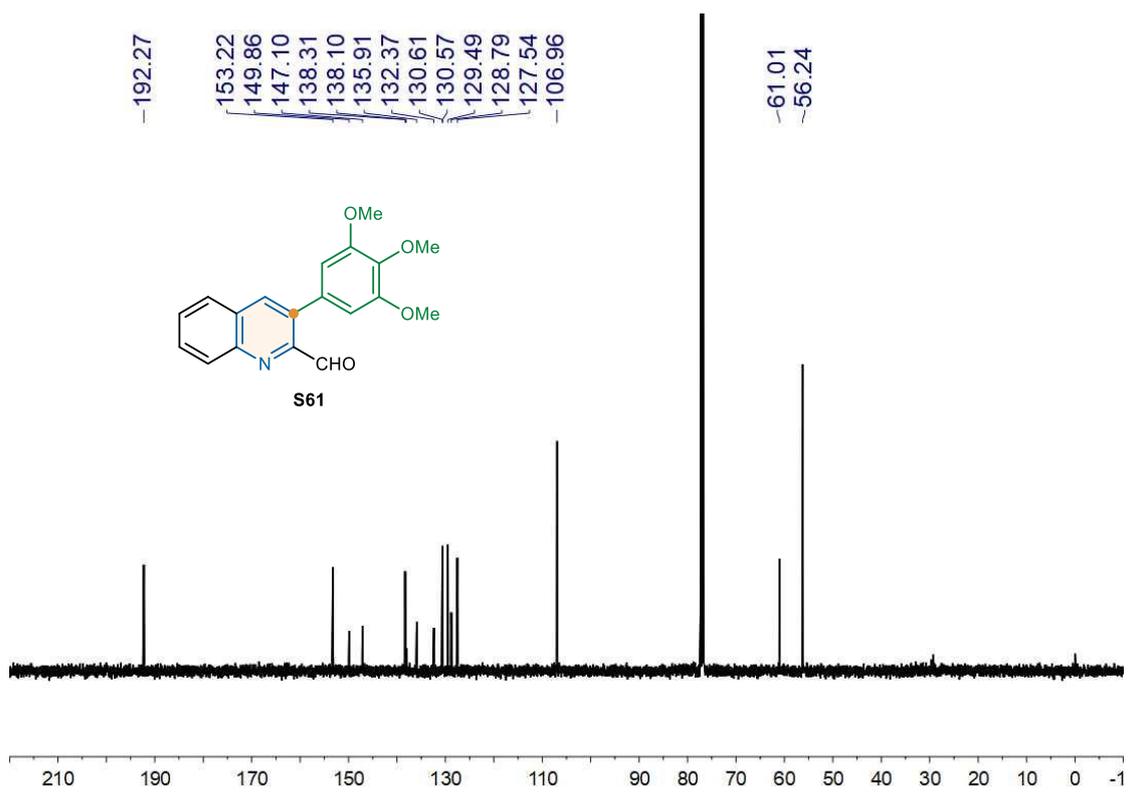


Supplementary Fig. 345. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of **137**

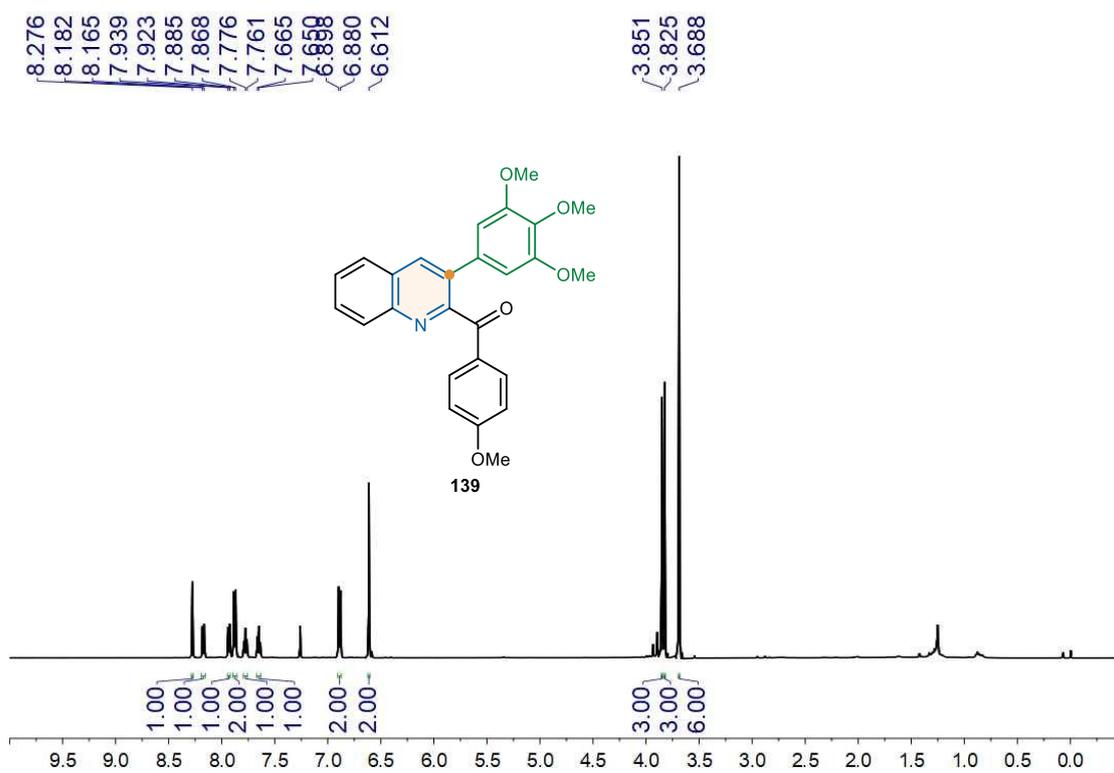


Supplementary Fig. 346. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **138**

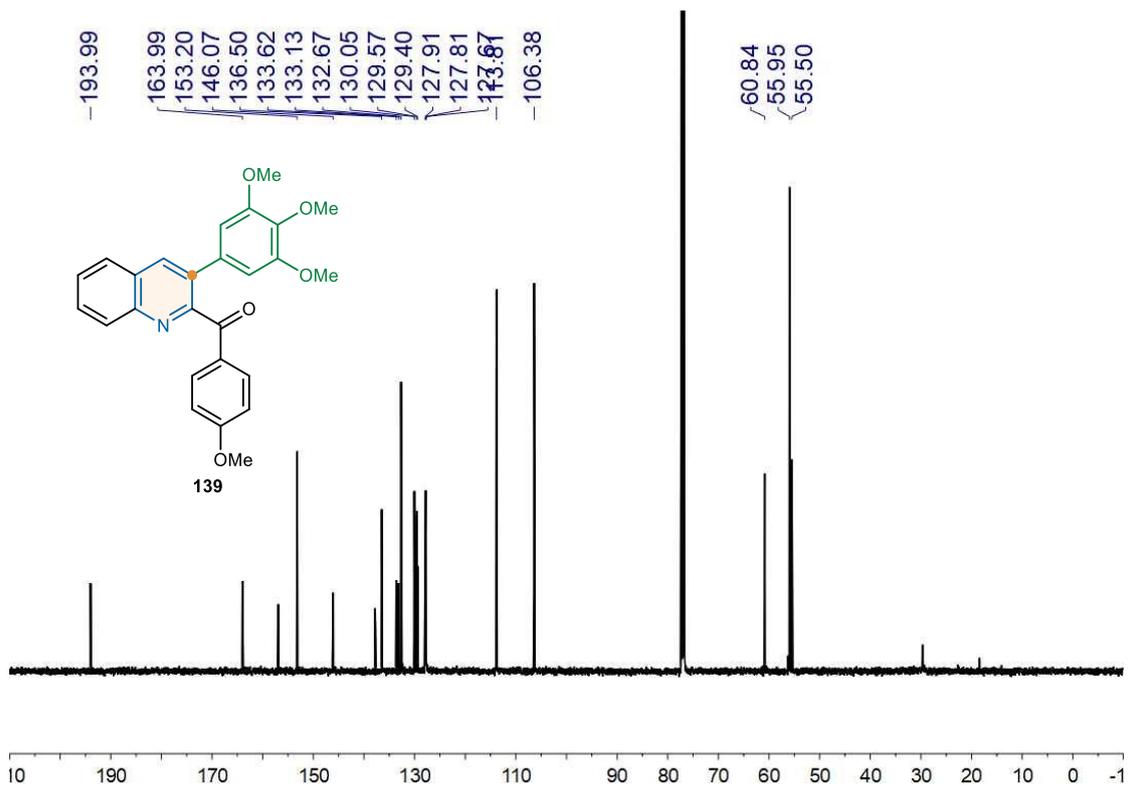




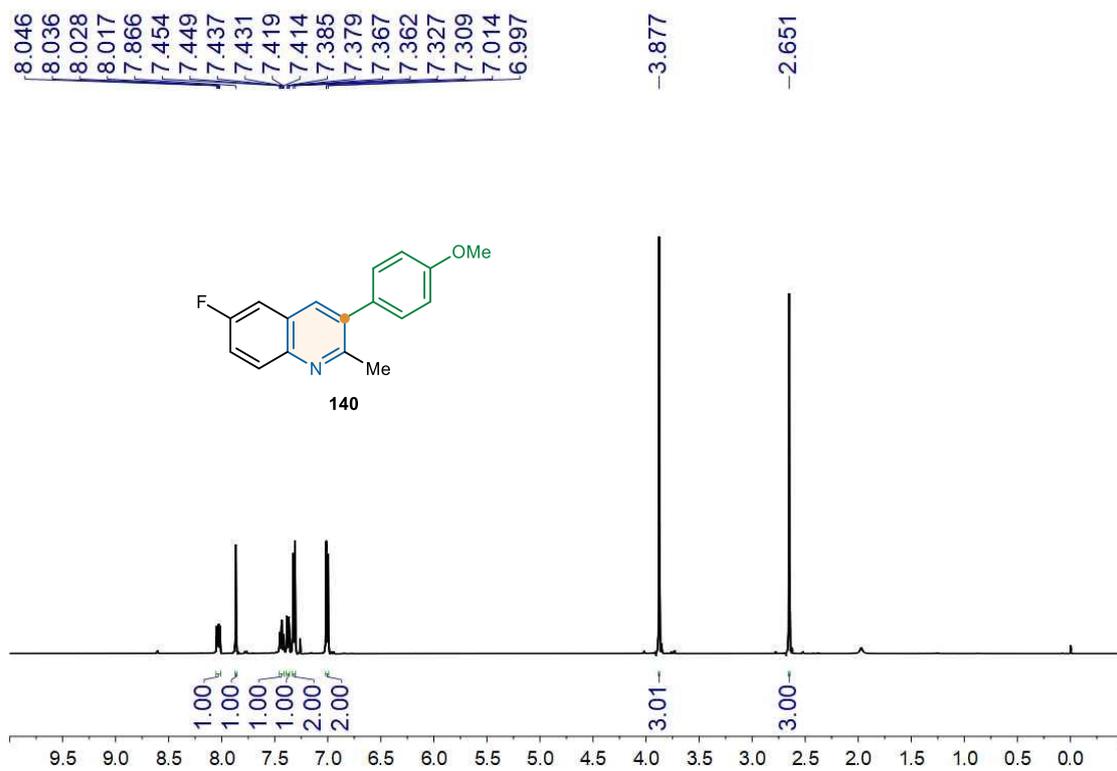
Supplementary Fig. 349. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of S61



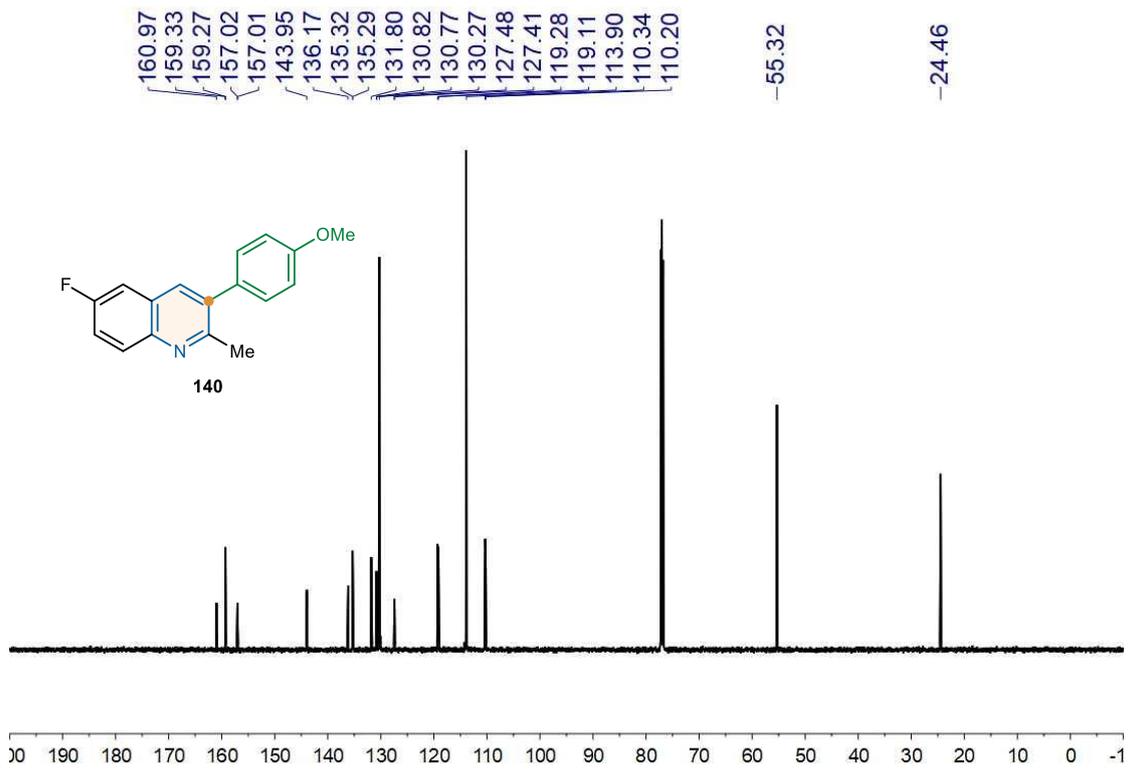
Supplementary Fig. 350. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of 139



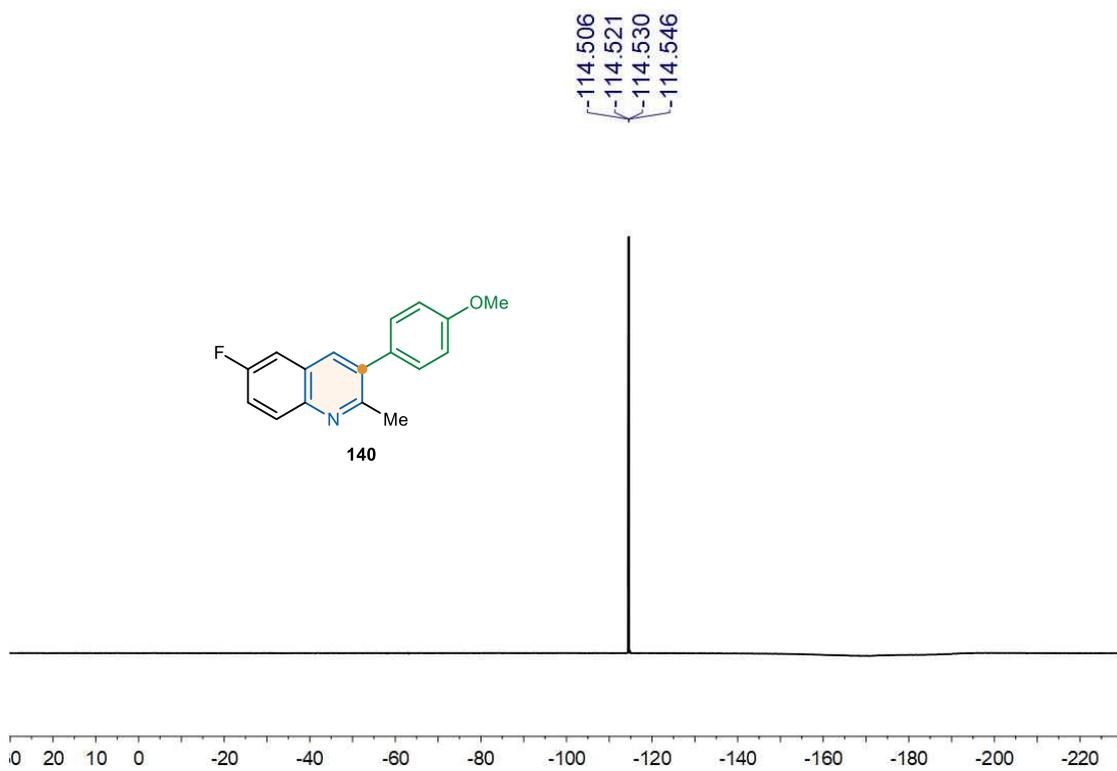
Supplementary Fig. 351.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of **139**



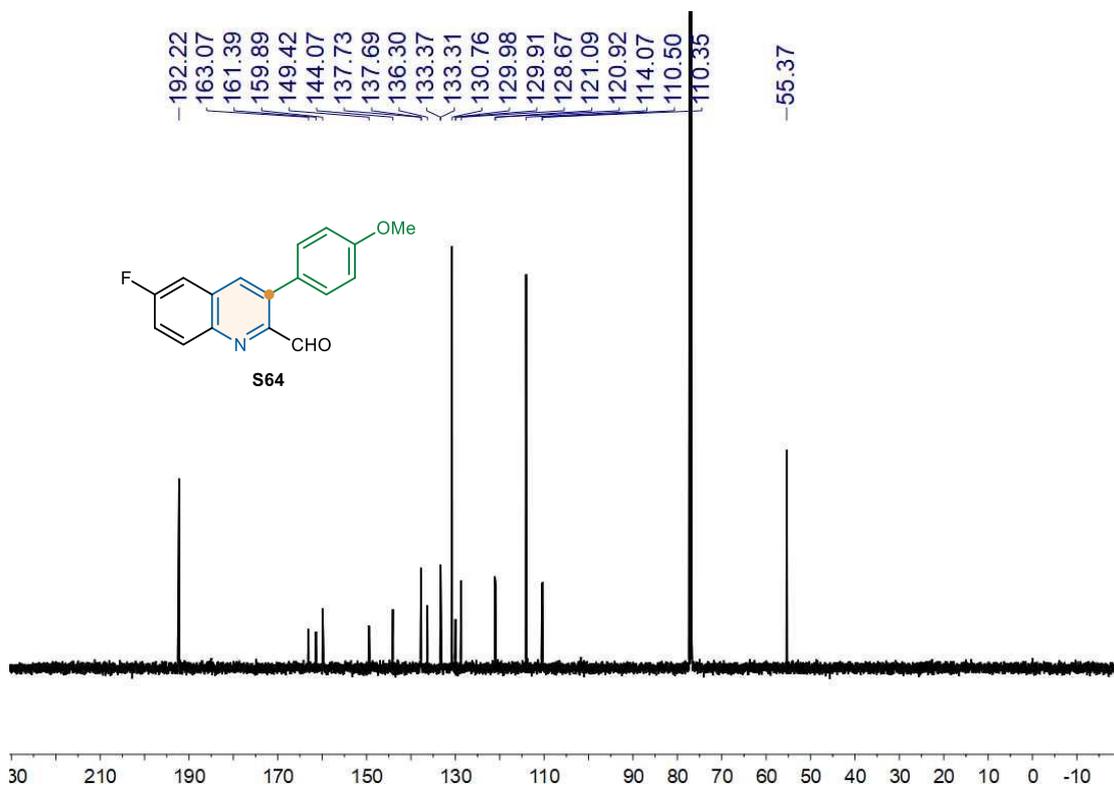
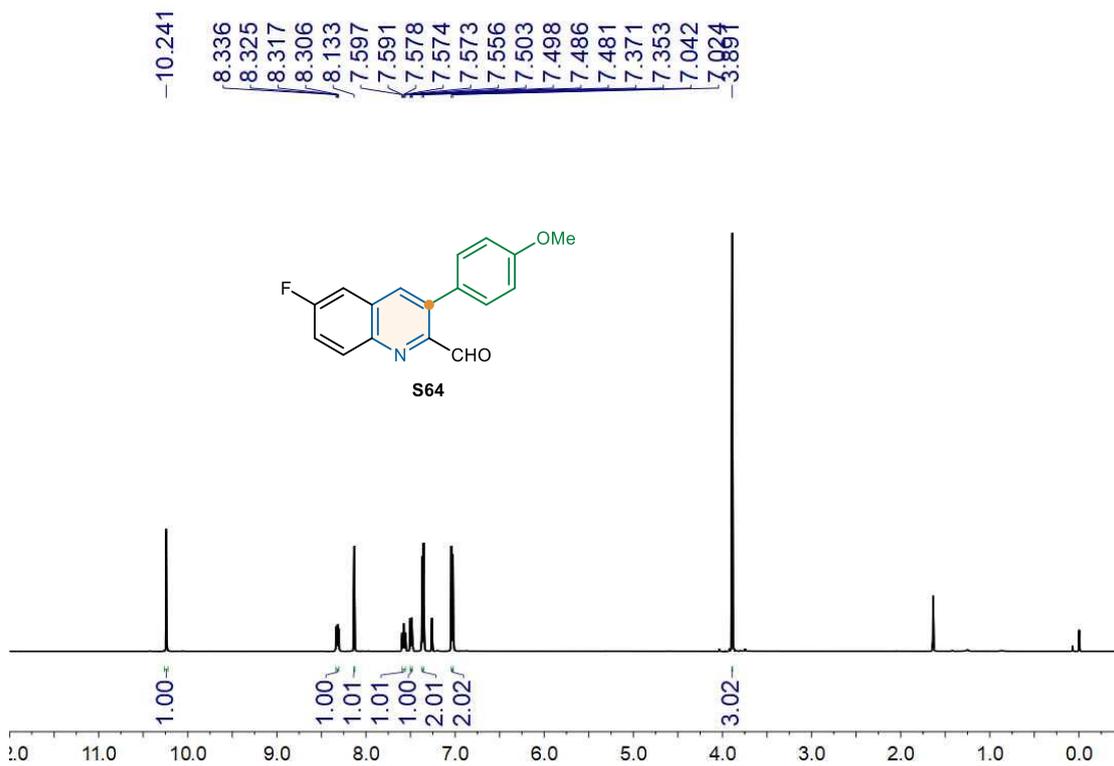
Supplementary Fig. 352.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **140**

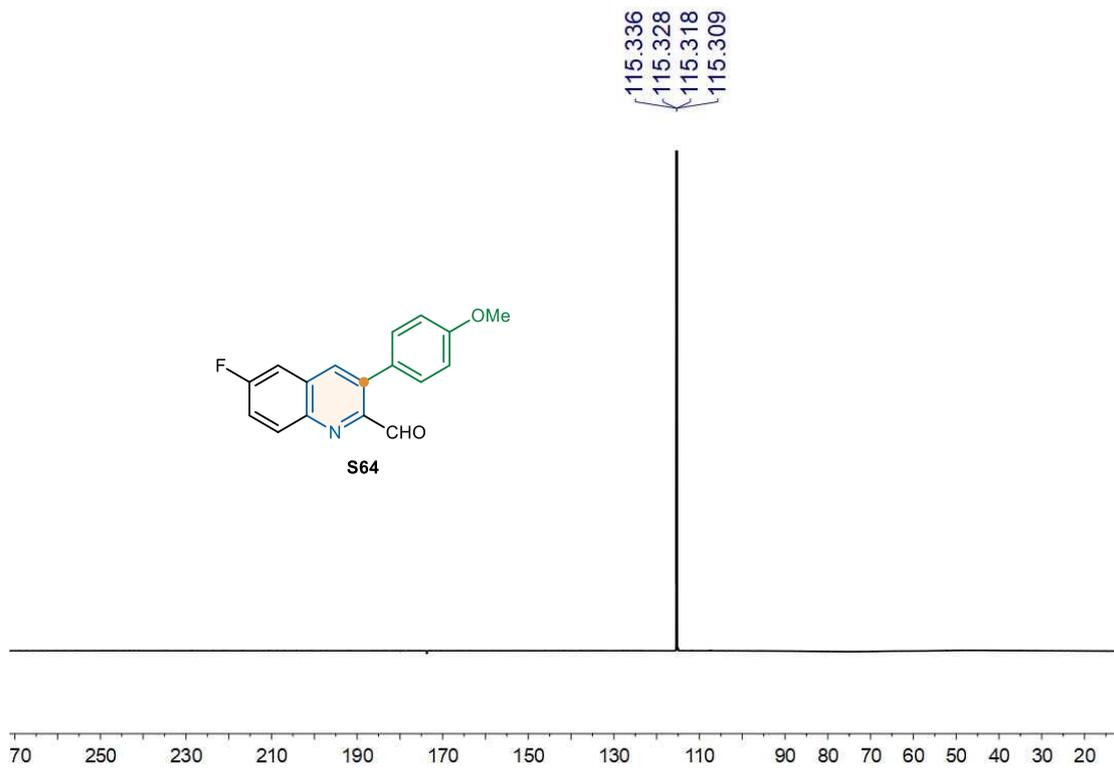


Supplementary Fig. 353. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of **140**

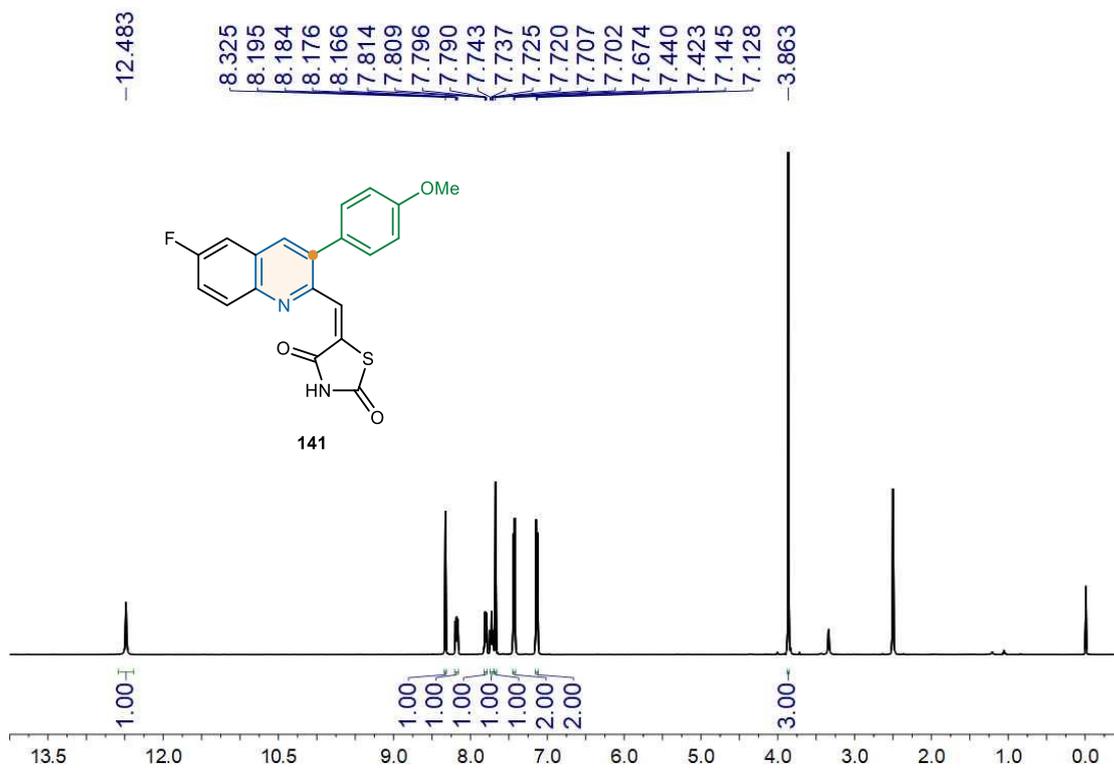


Supplementary Fig. 354. <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) spectrum of **140**

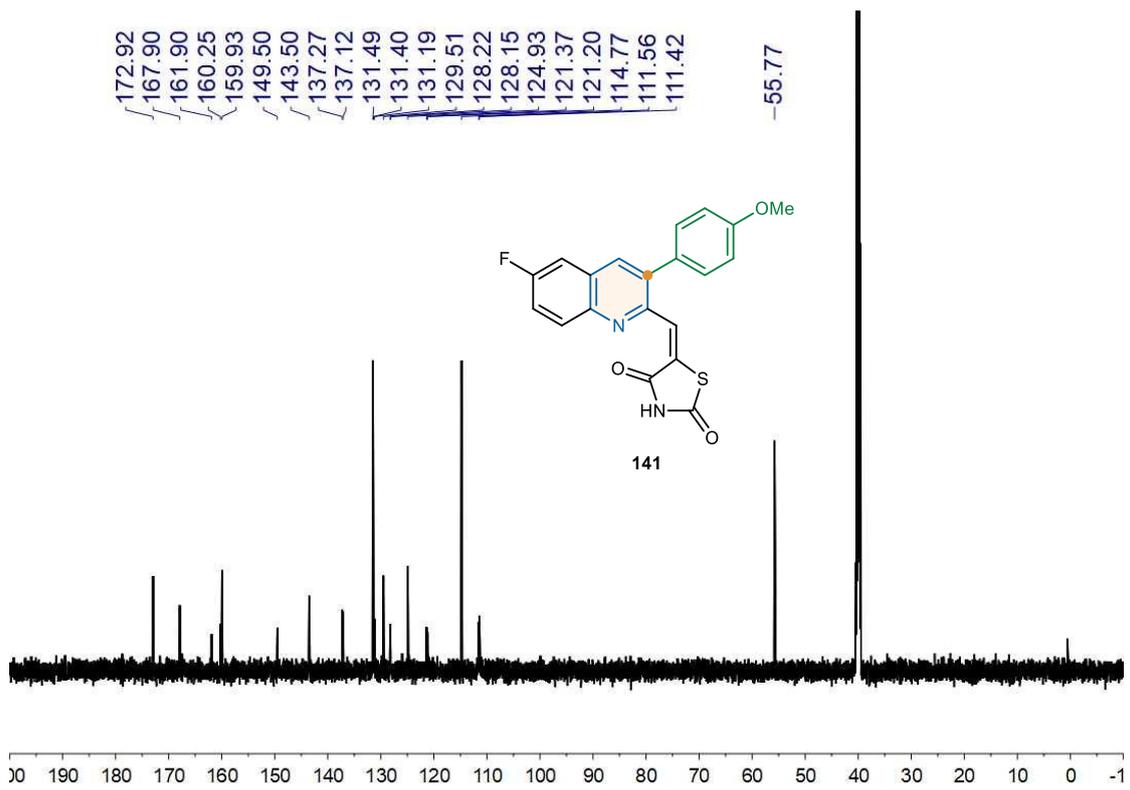




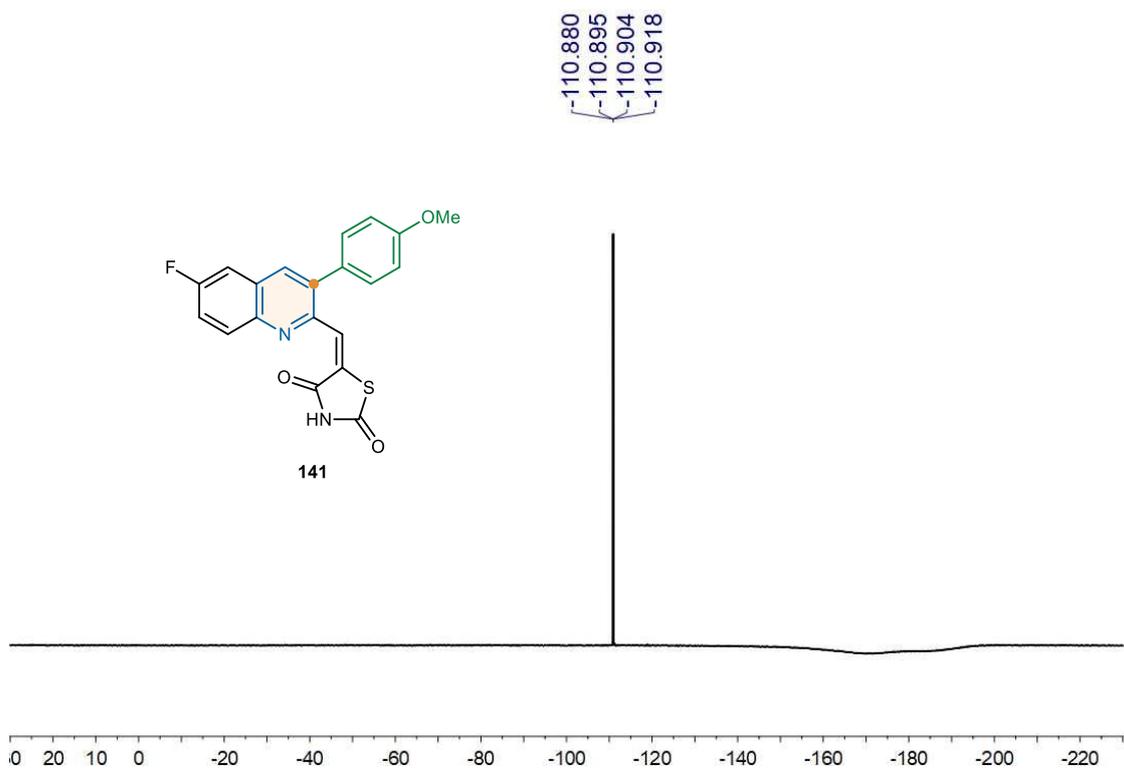
Supplementary Fig. 357.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ) spectrum of **S64**



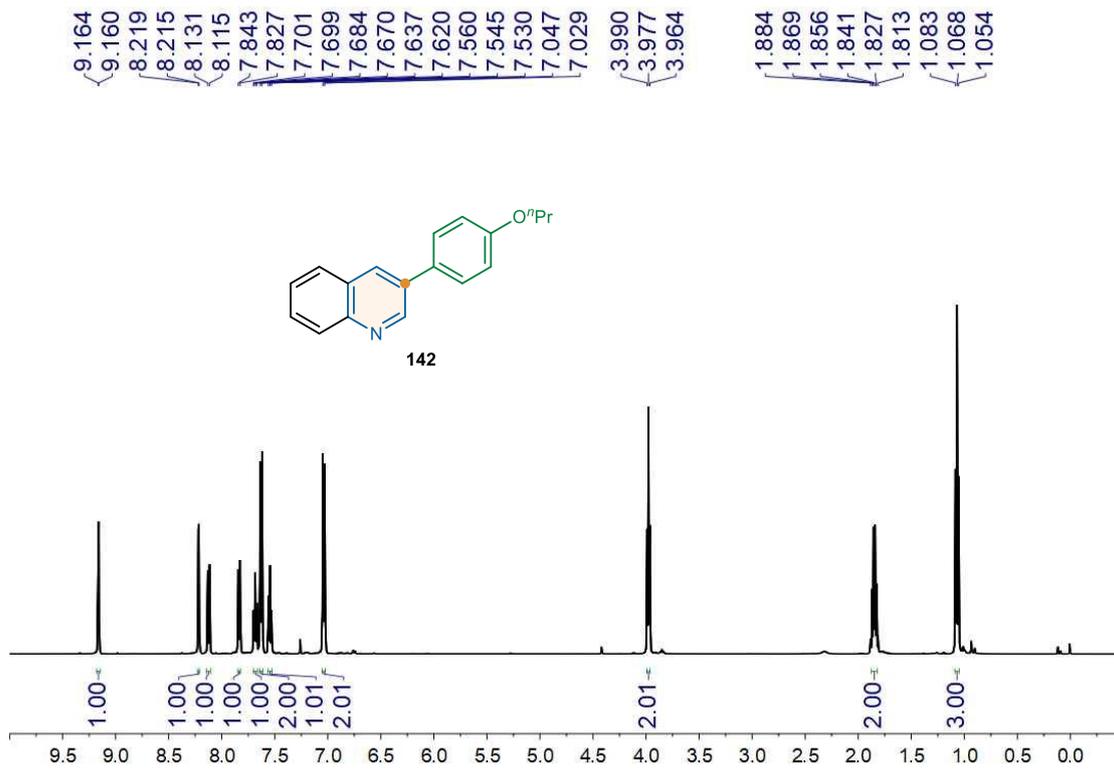
Supplementary Fig. 358.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ ) spectrum of **141**



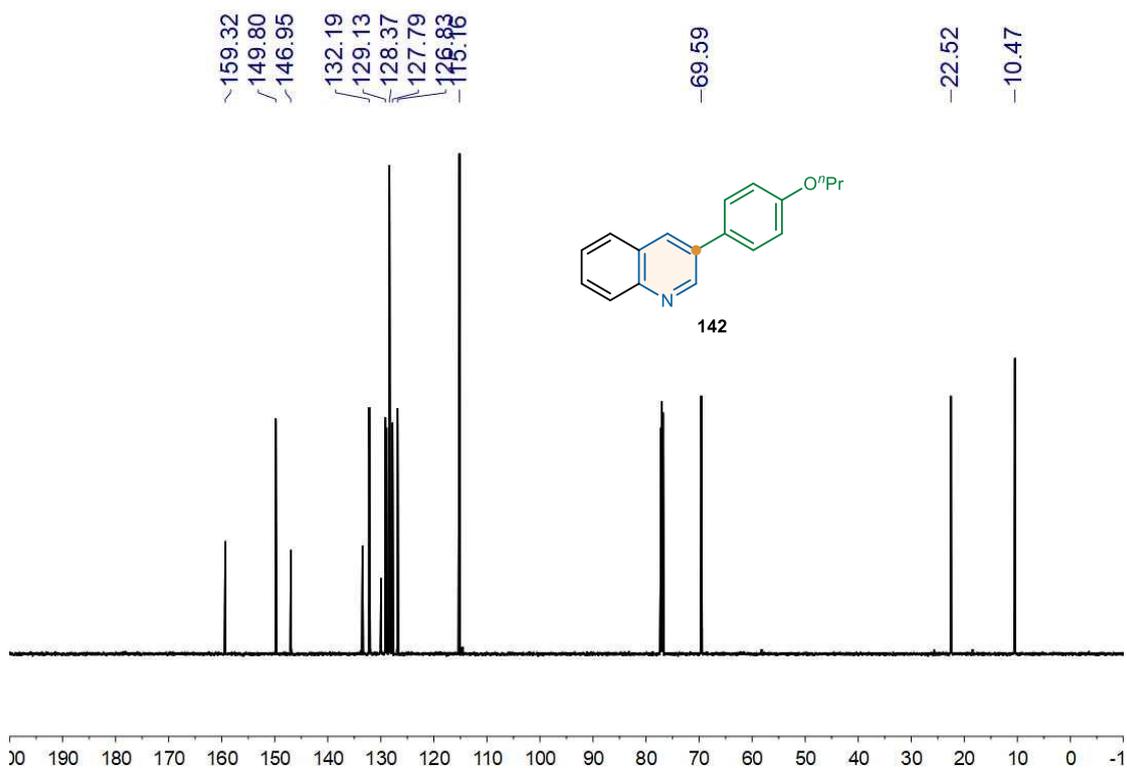
Supplementary Fig. 359. <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>) spectrum of 141



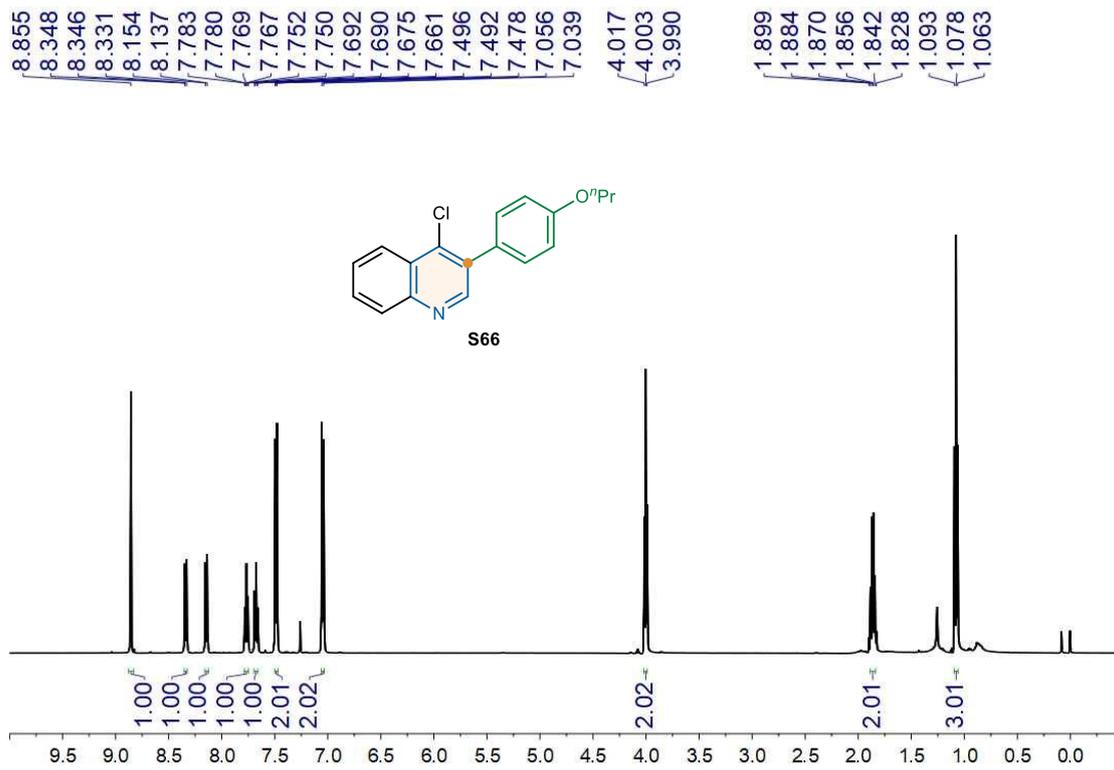
Supplementary Fig. 360. <sup>19</sup>F NMR (564 MHz, DMSO-*d*<sub>6</sub>) spectrum of 141



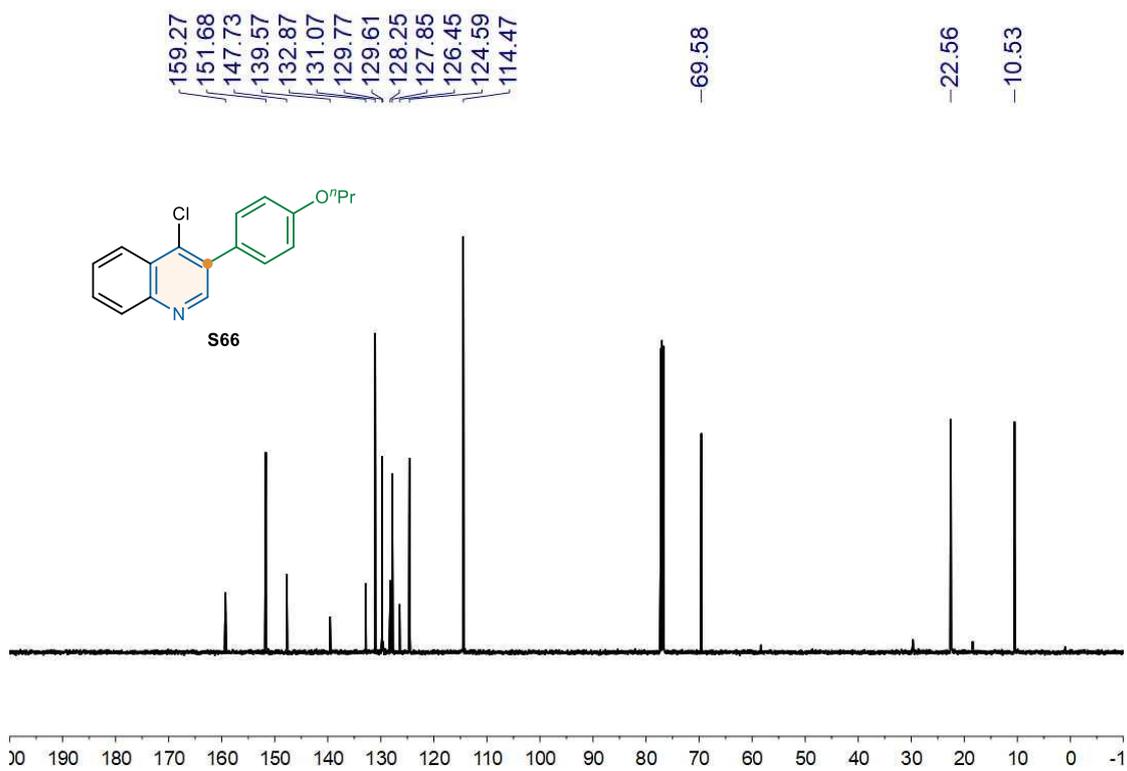
Supplementary Fig. 361.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **142**



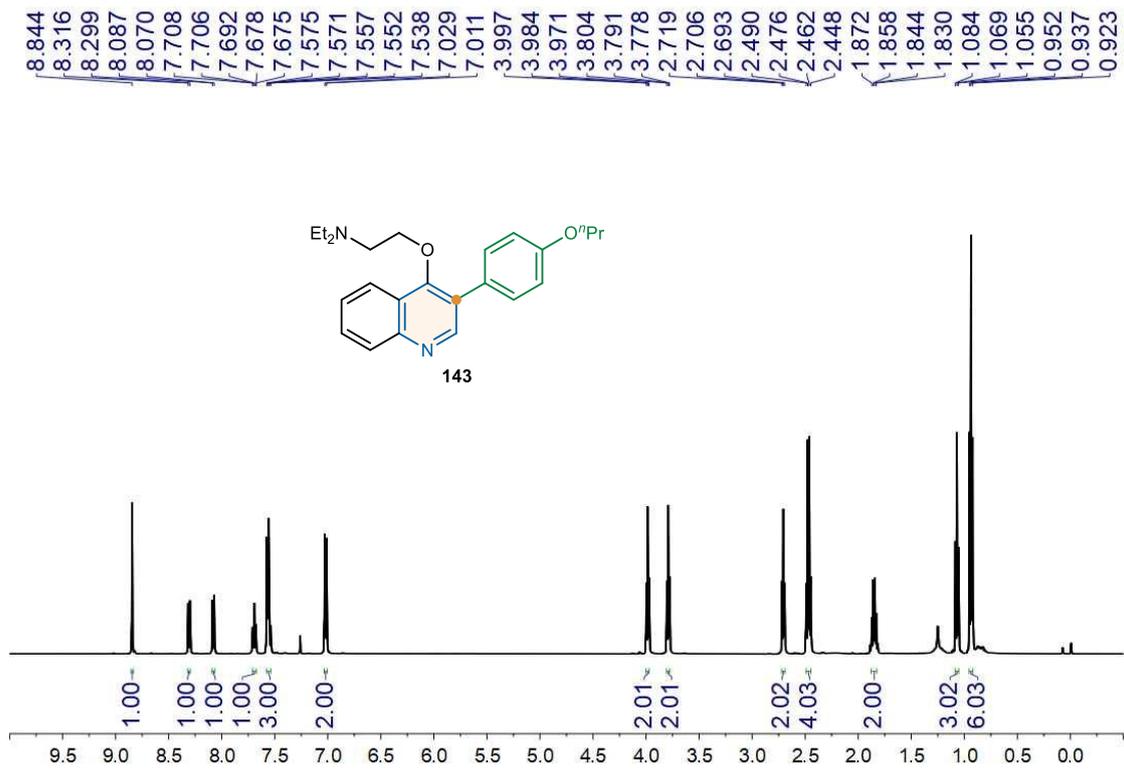
Supplementary Fig. 362.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **142**



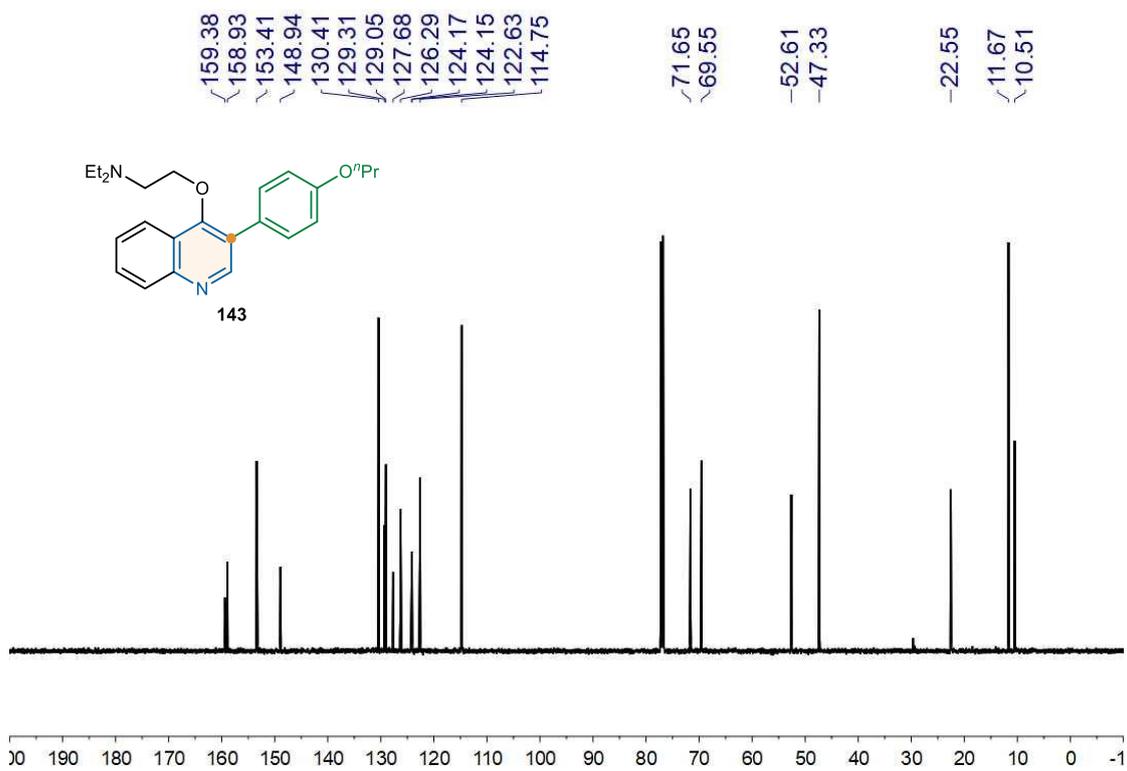
Supplementary Fig. 363.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of S66



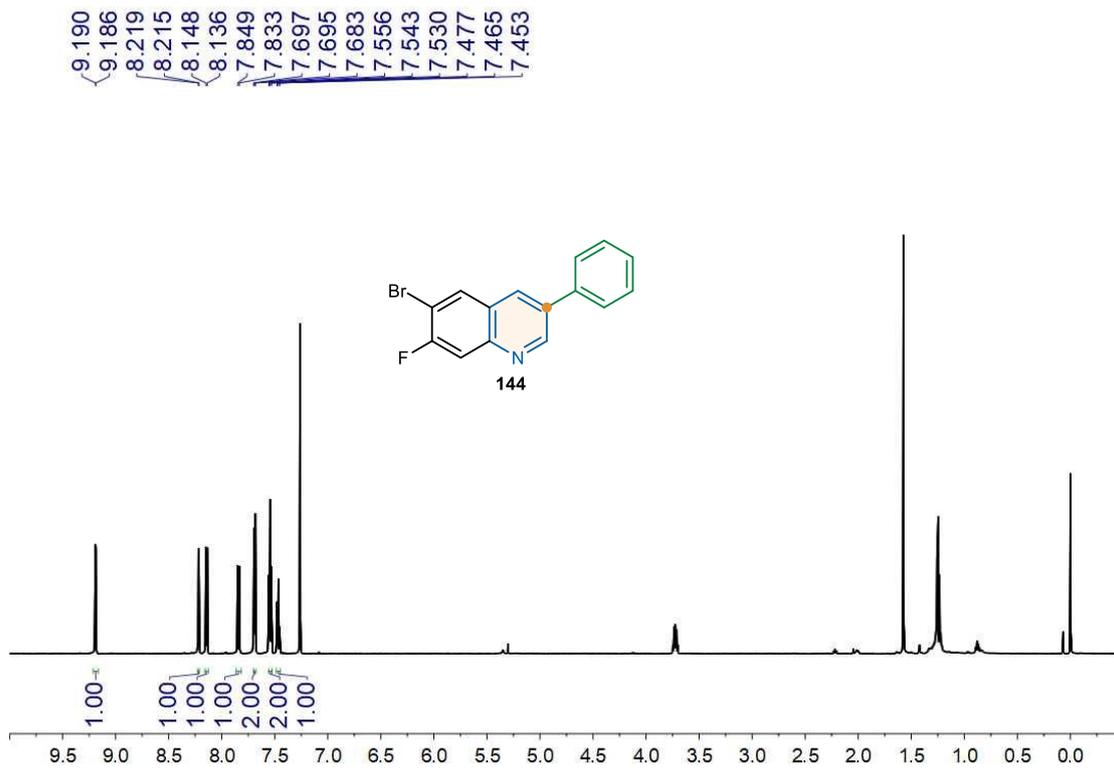
Supplementary Fig. 364.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of S66



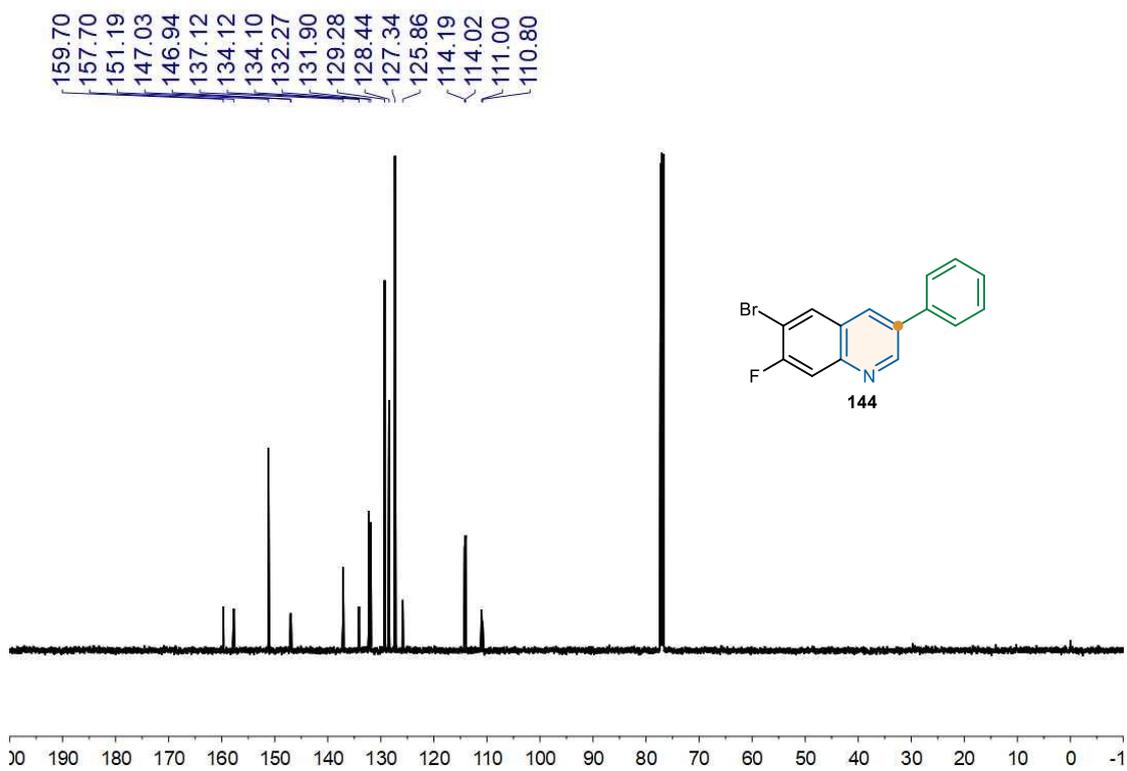
Supplementary Fig. 365. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **143**



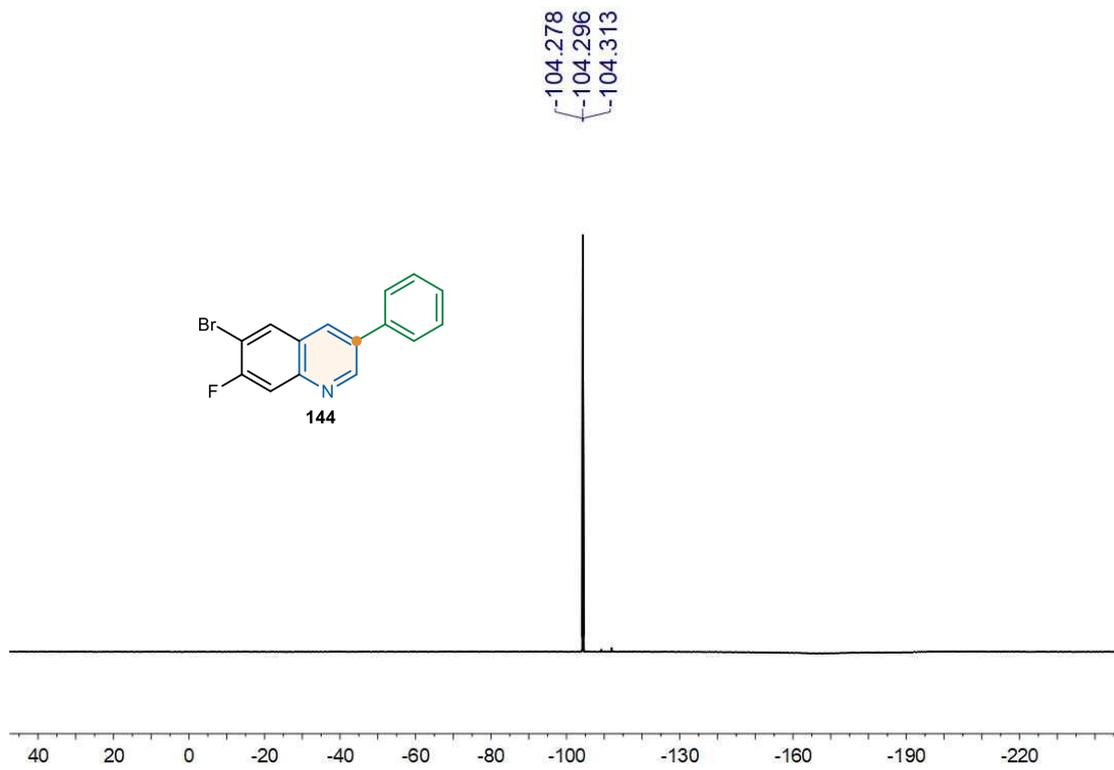
Supplementary Fig. 366. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of **143**



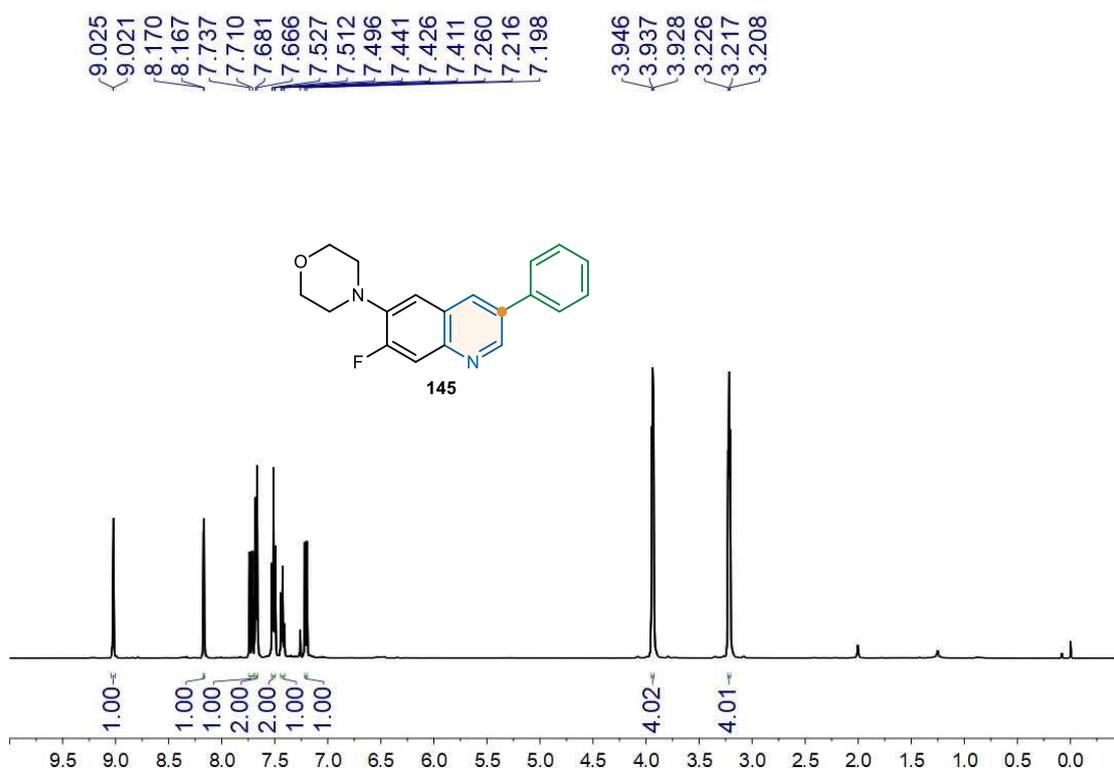
Supplementary Fig. 367.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) spectrum of 144



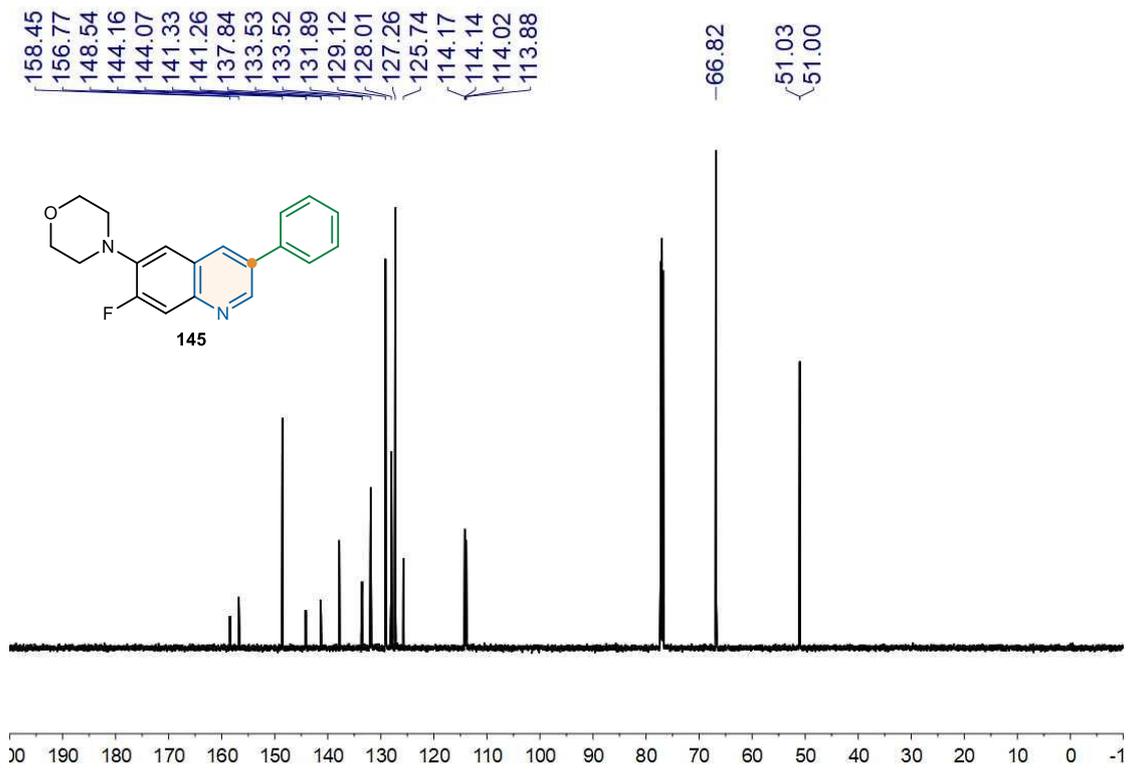
Supplementary Fig. 368.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of 144



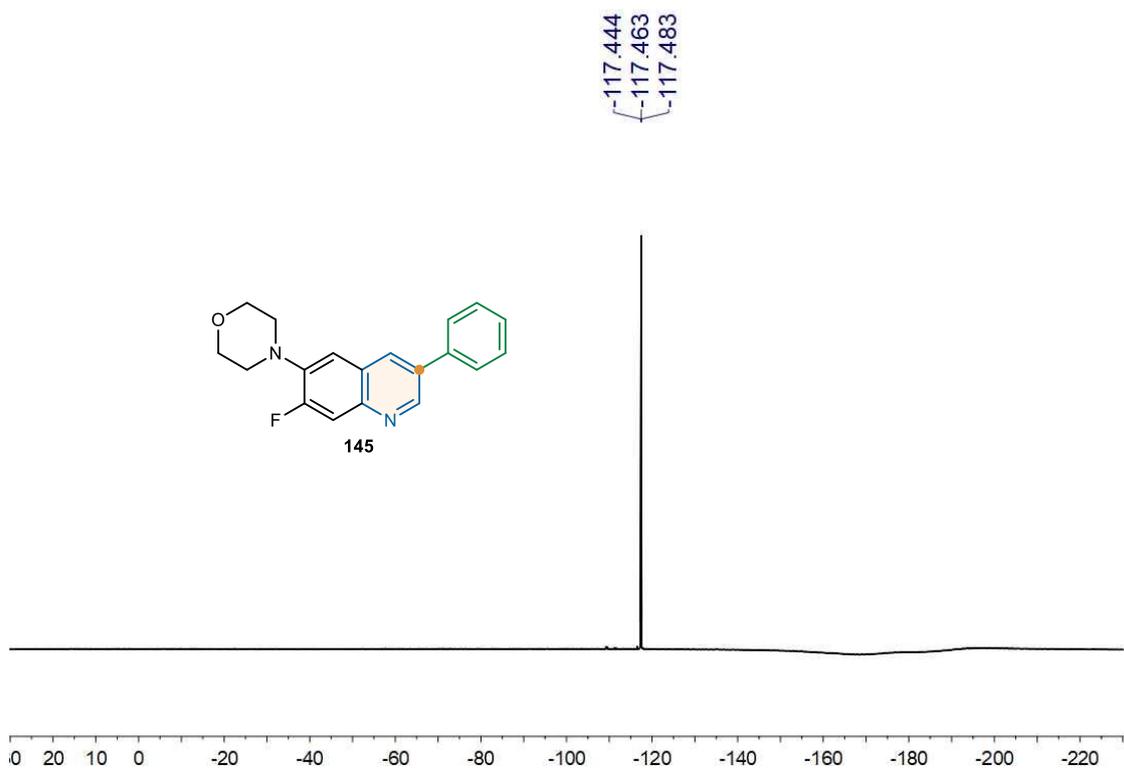
Supplementary Fig. 369.  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ) spectrum of **144**



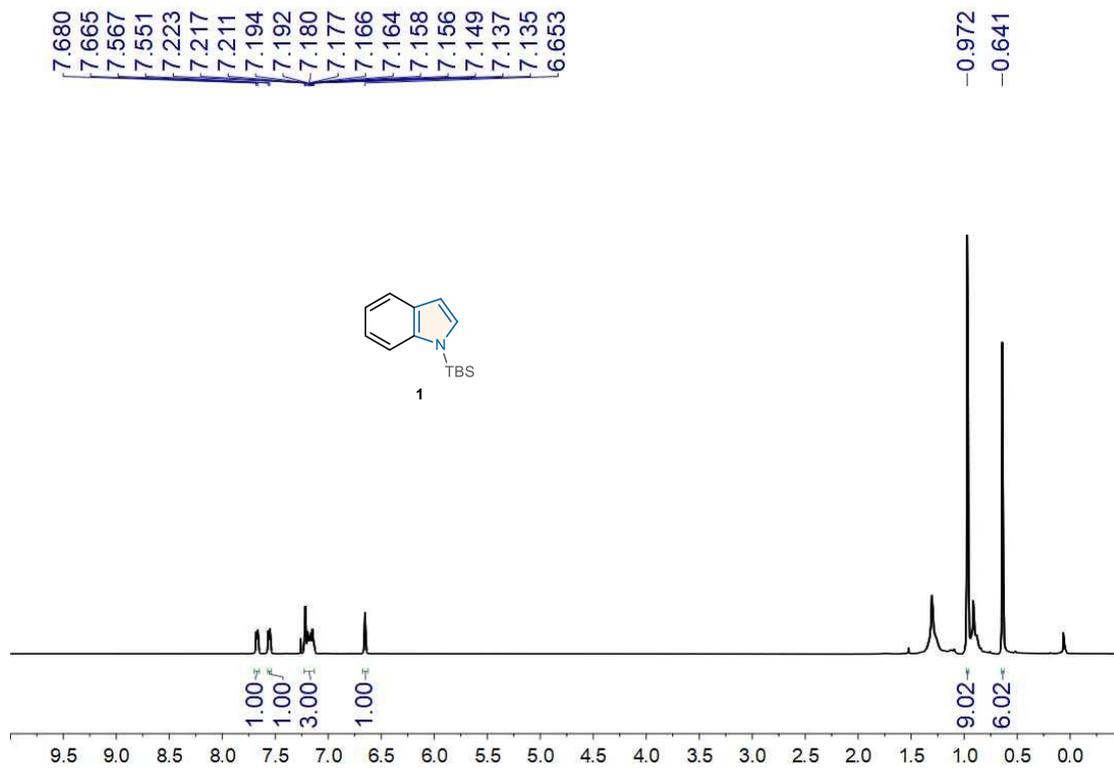
Supplementary Fig. 370.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **145**



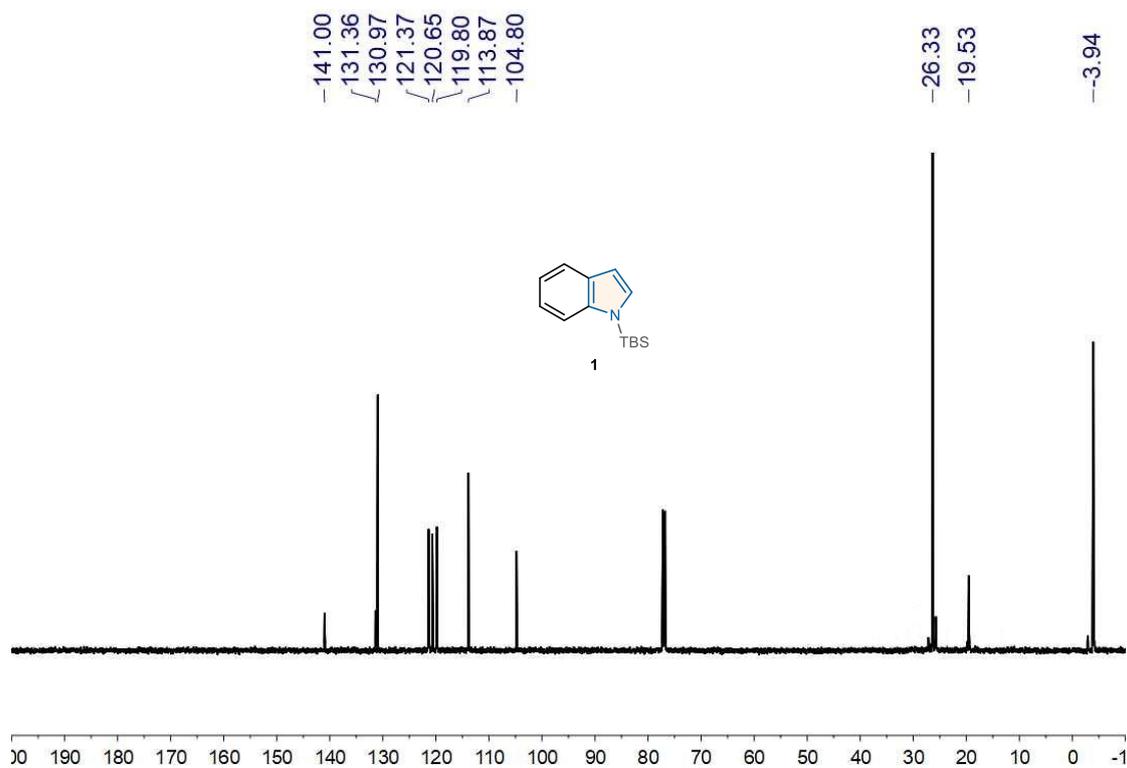
Supplementary Fig. 371. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of 145



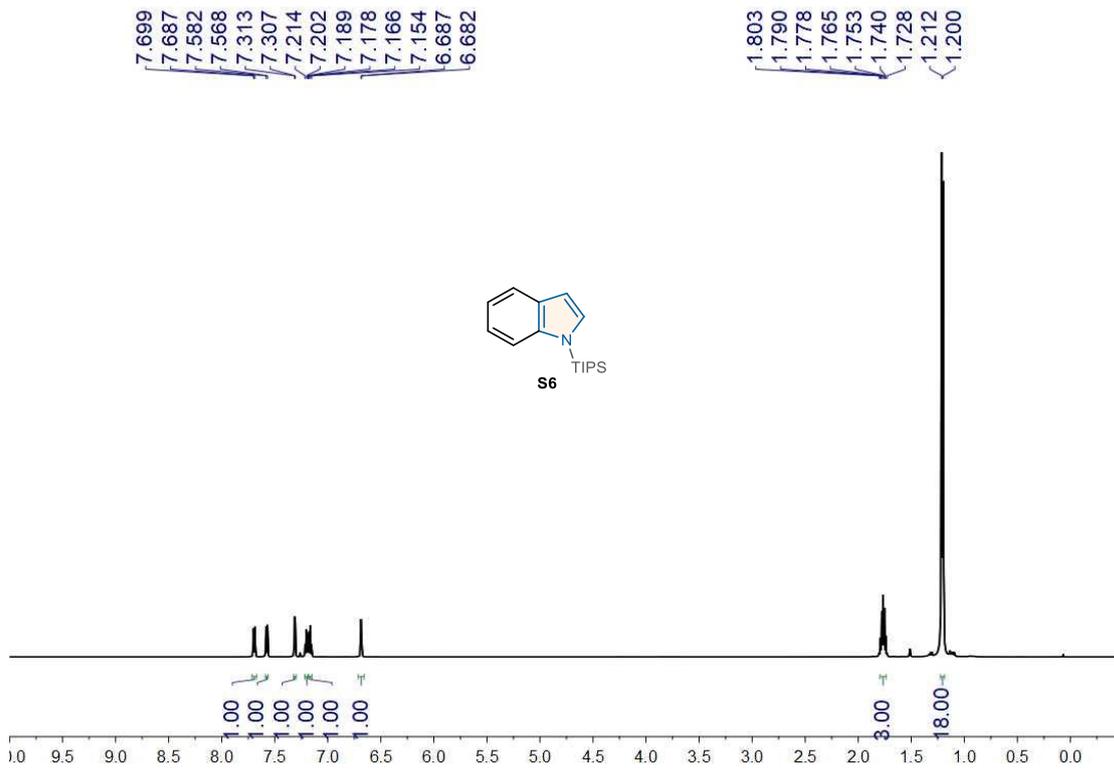
Supplementary Fig. 372. <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) spectrum of 145



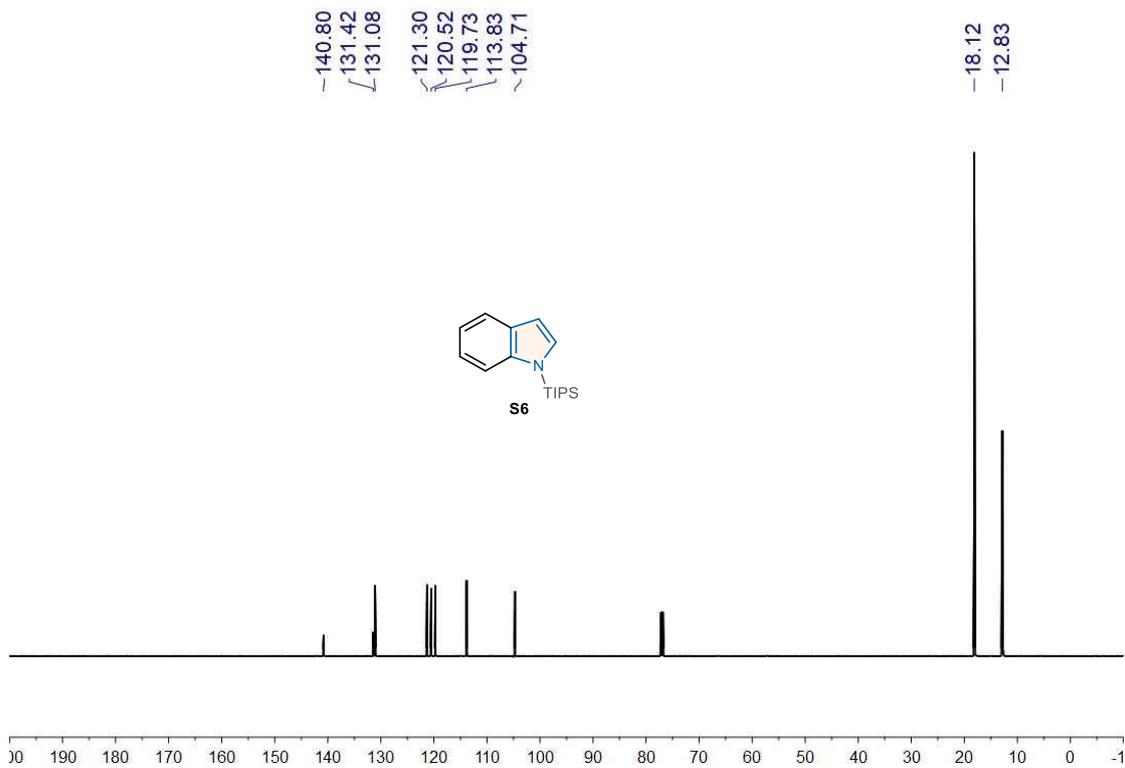
Supplementary Fig. 373. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of 1



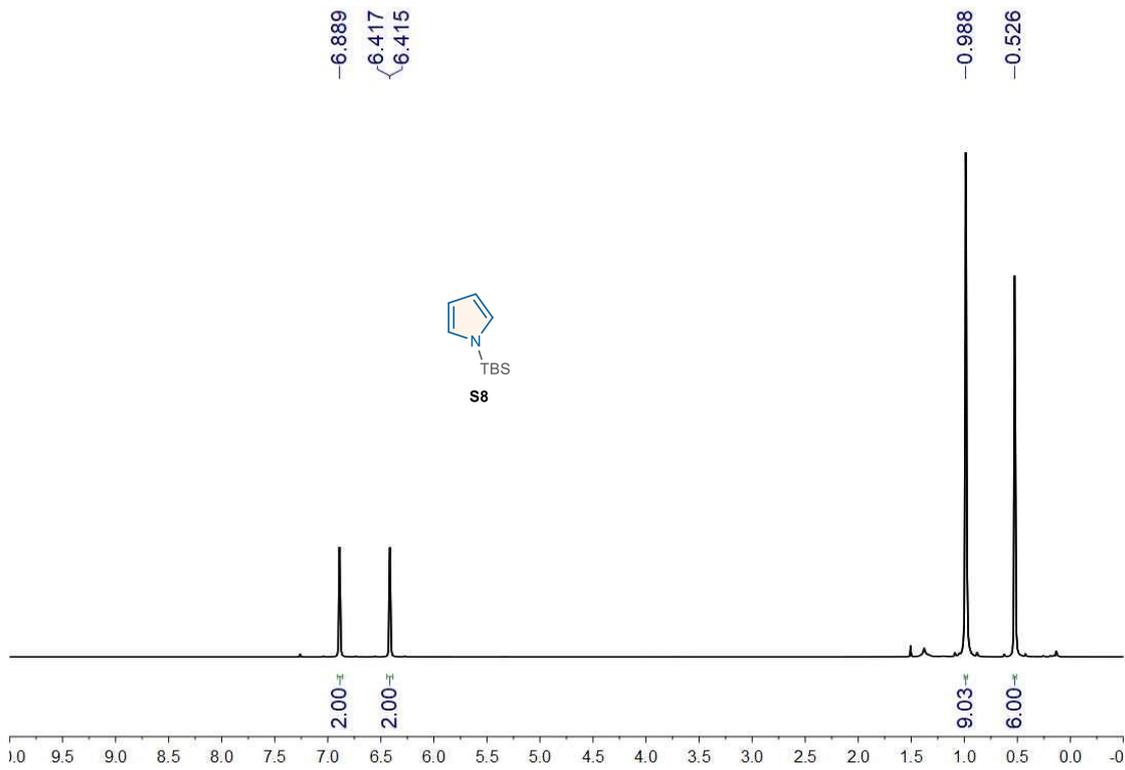
Supplementary Fig. 374. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of 1



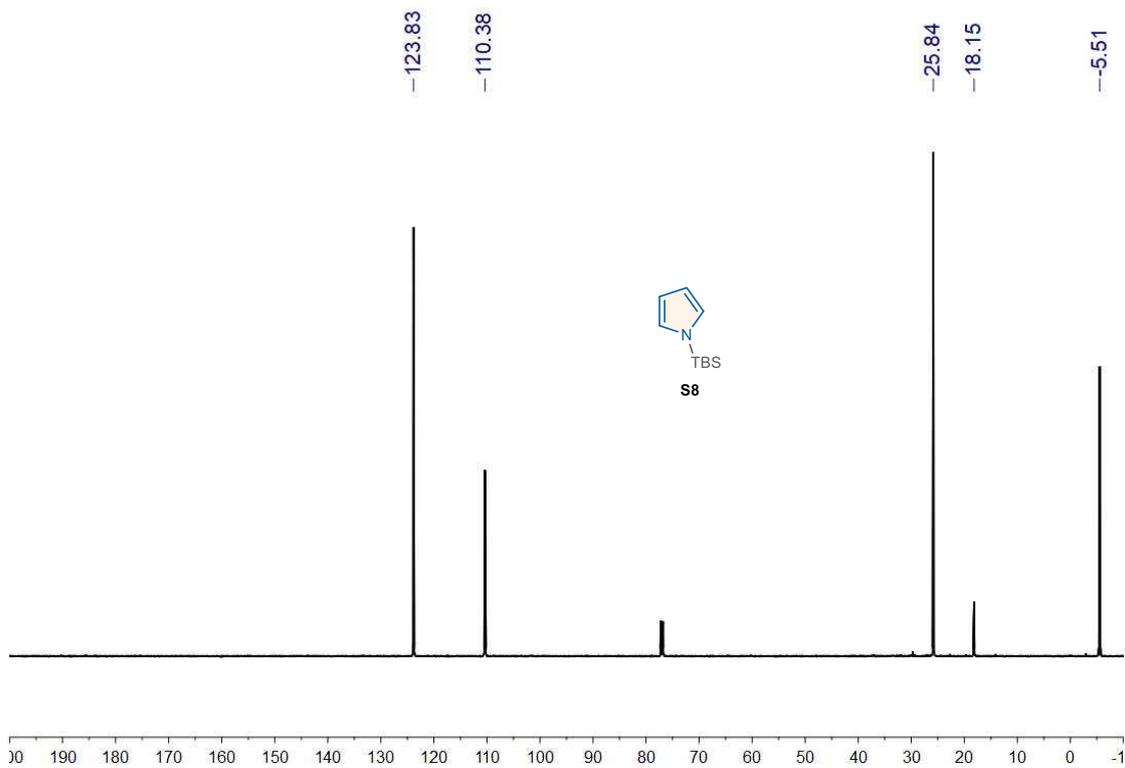
Supplementary Fig. 375. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of S6



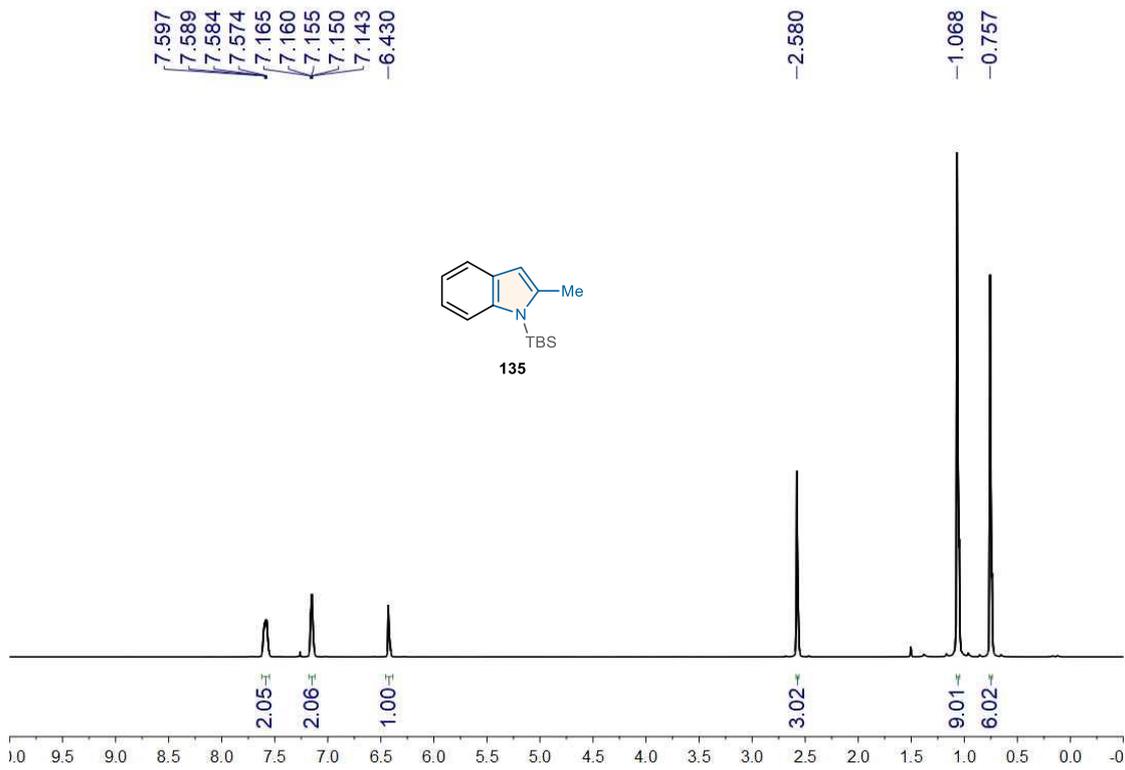
Supplementary Fig. 376. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of S6



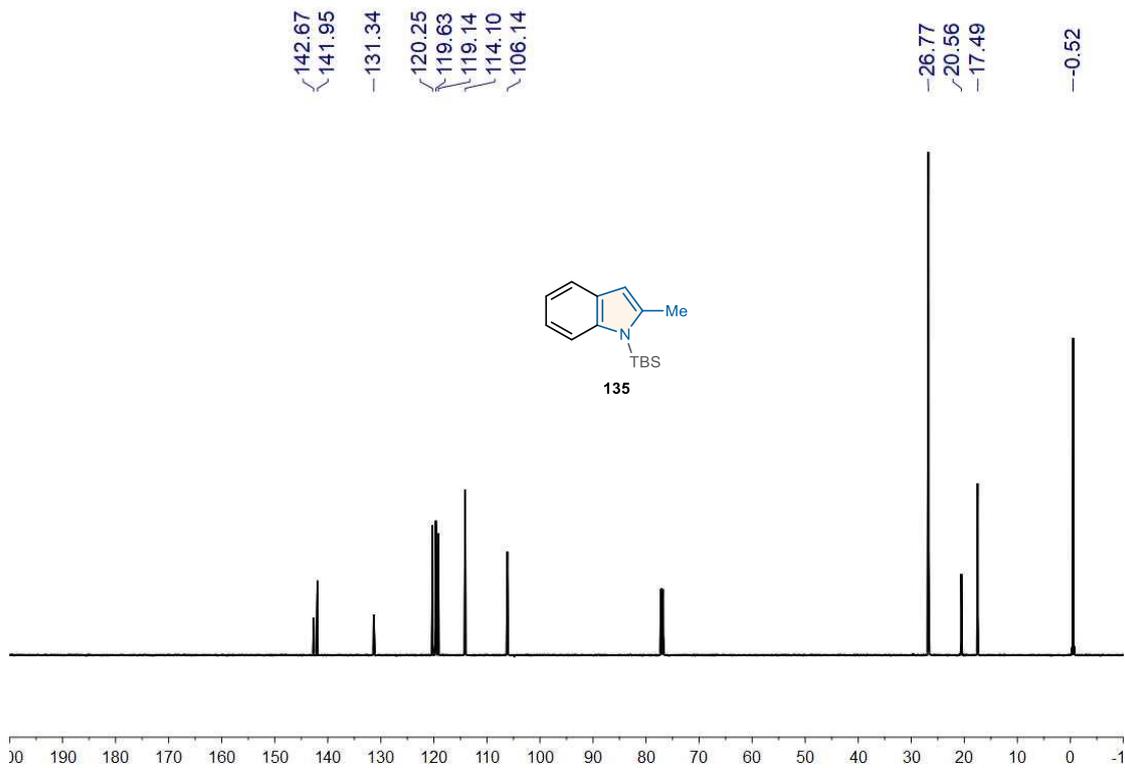
Supplementary Fig. 377.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) spectrum of S8



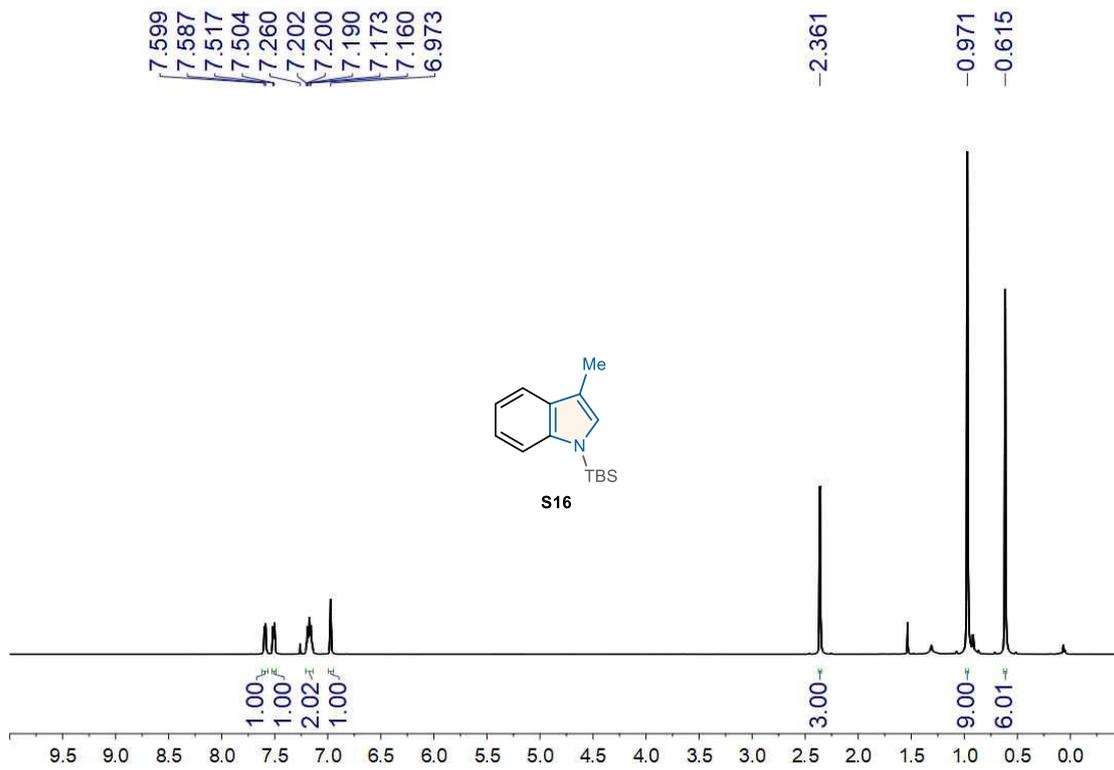
Supplementary Fig. 378.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of S8



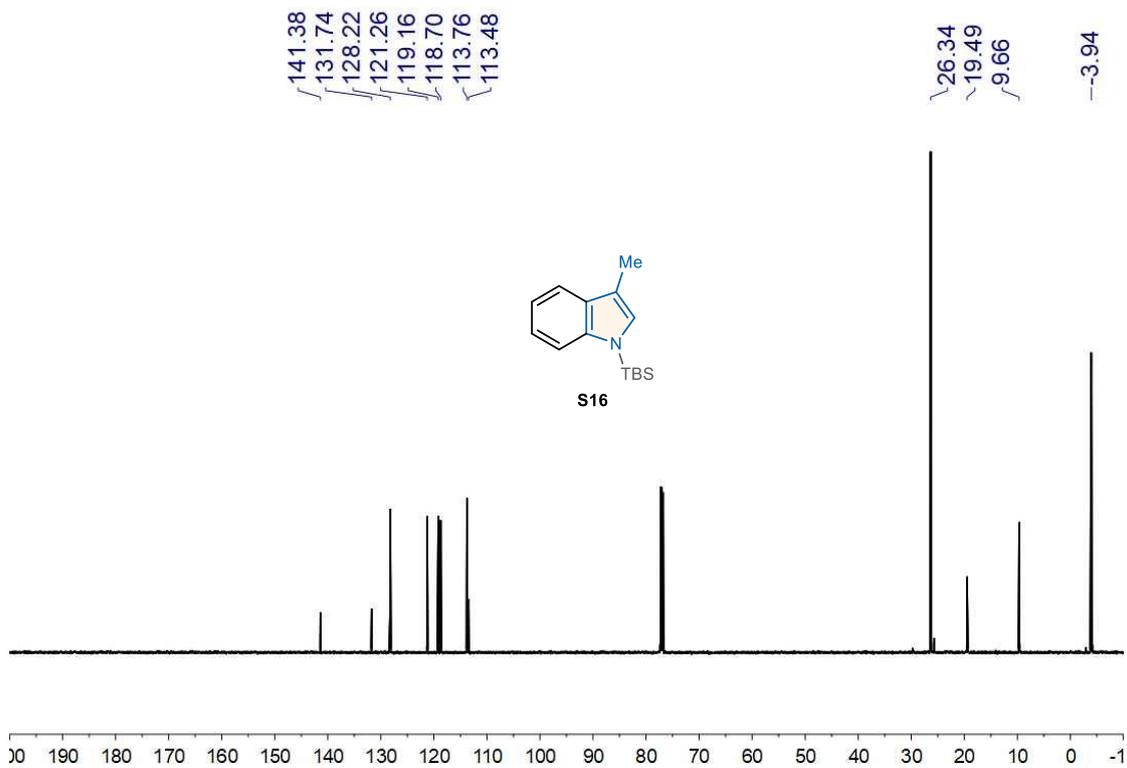
Supplementary Fig. 379.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) spectrum of **135**



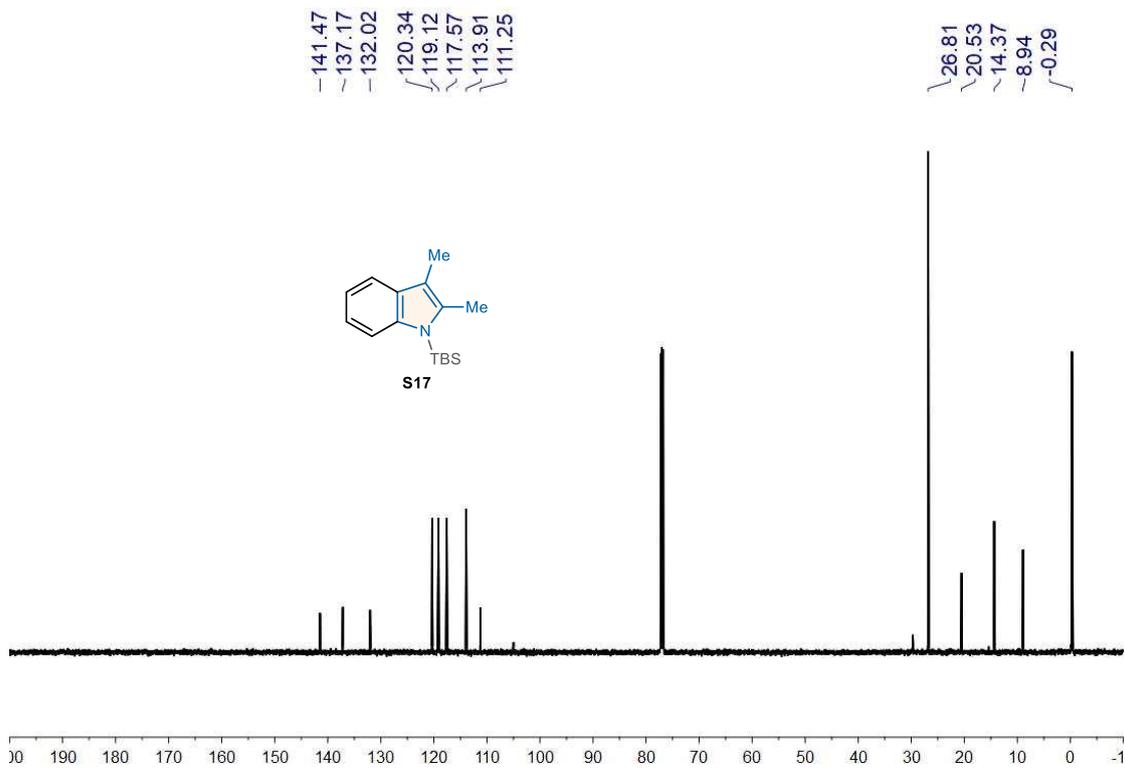
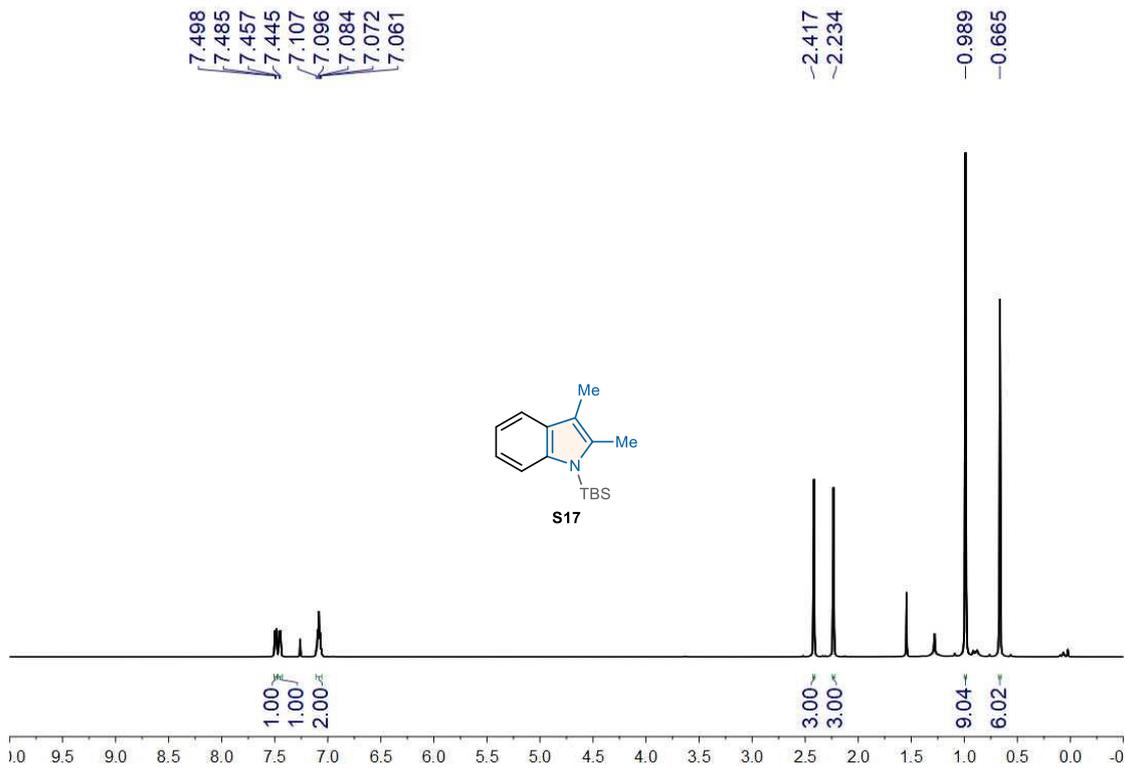
Supplementary Fig. 380.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of **135**

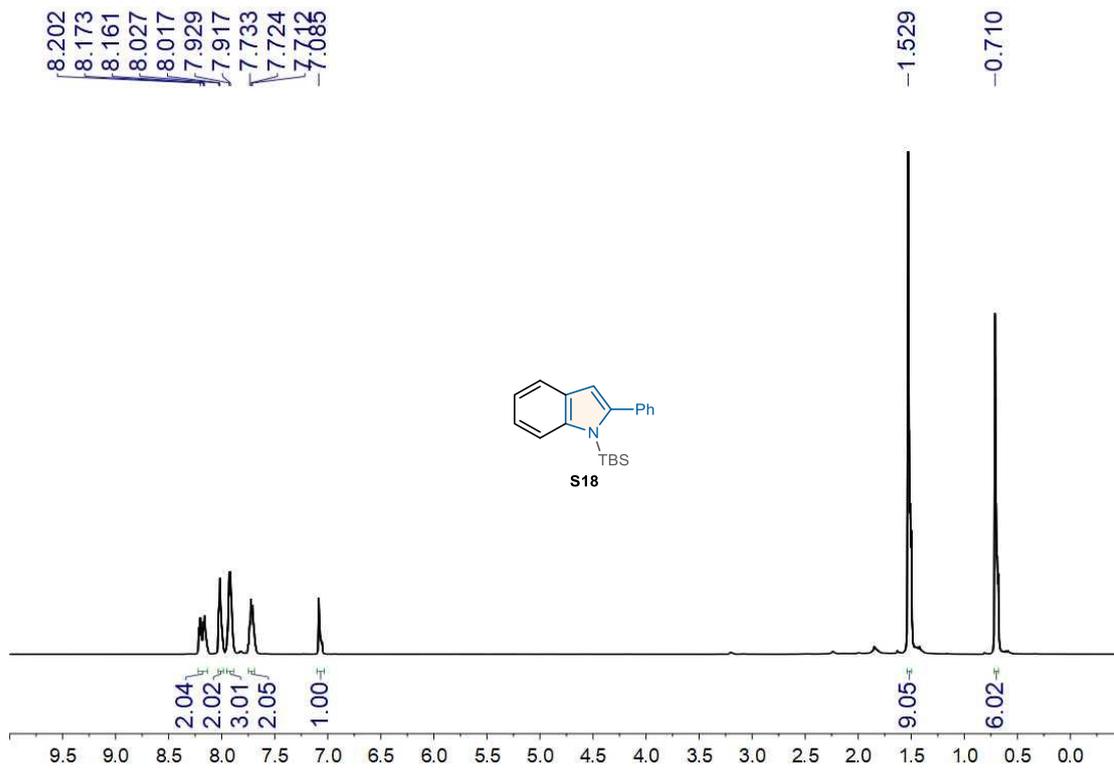


Supplementary Fig. 381. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of S16

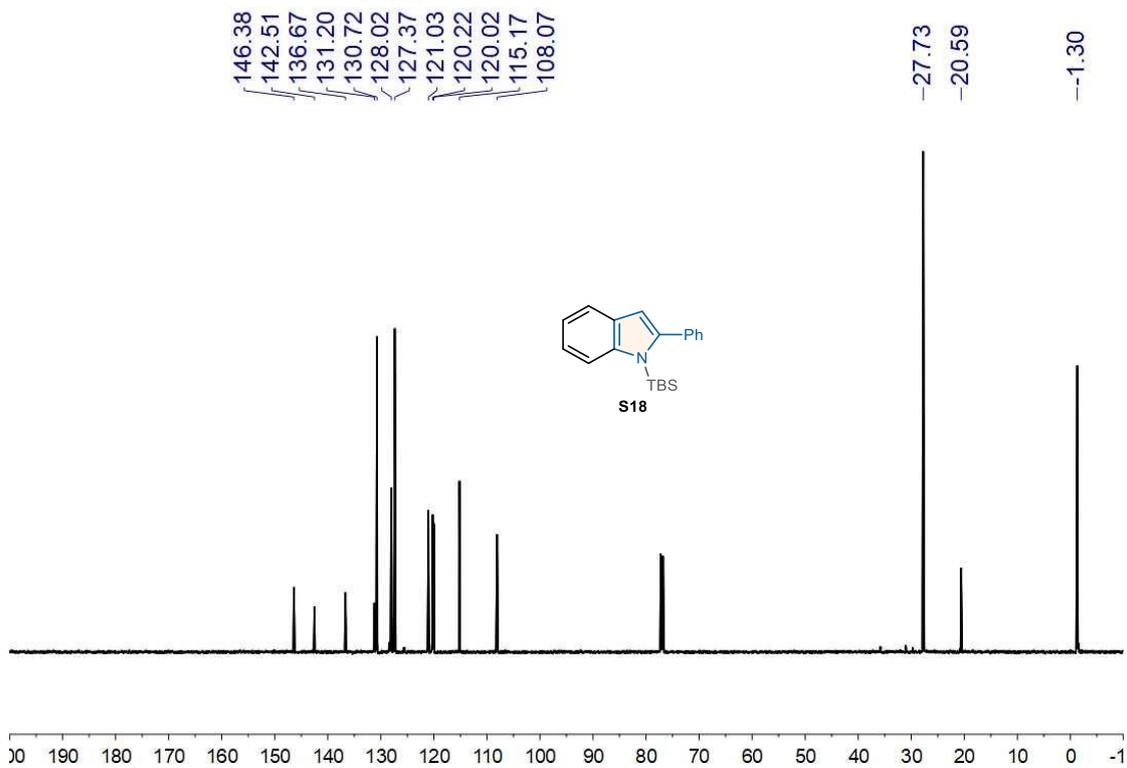


Supplementary Fig. 382. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of S16

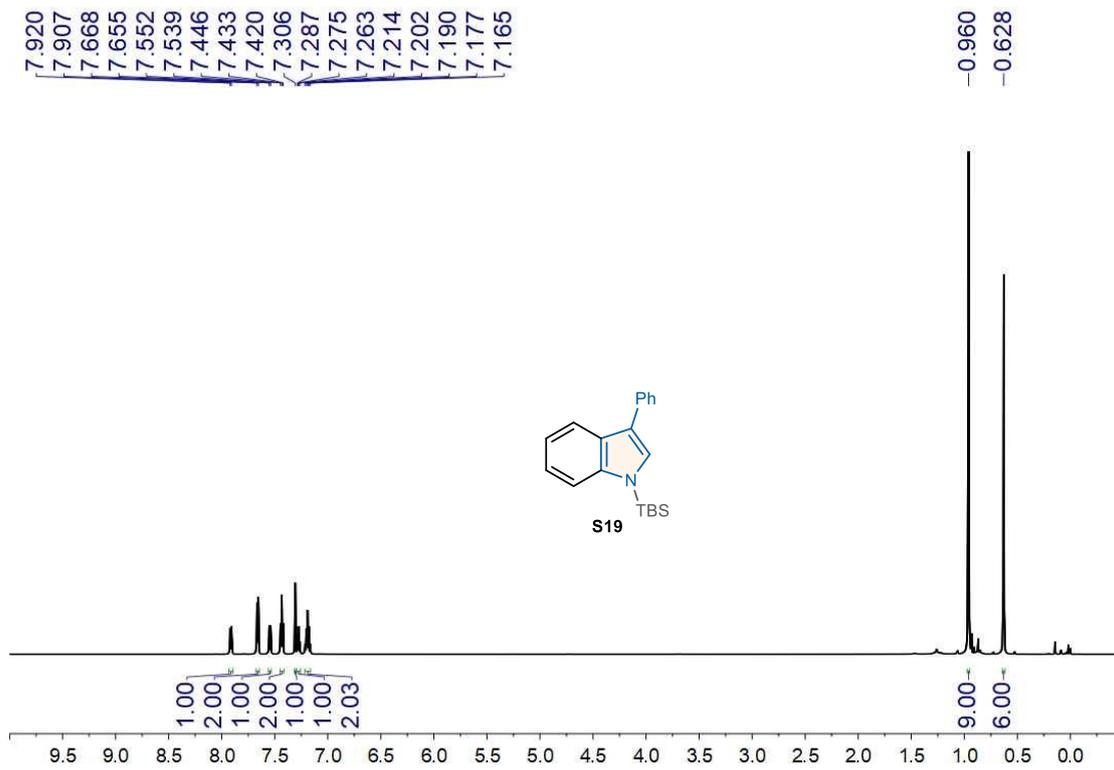




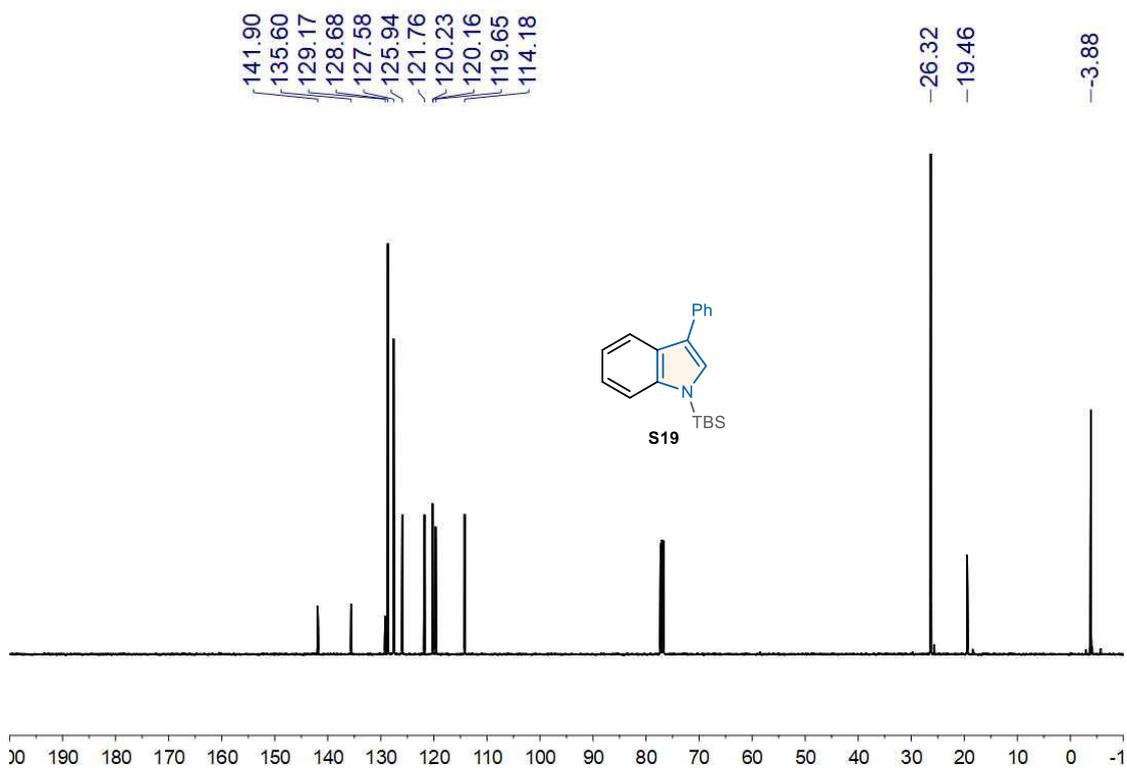
Supplementary Fig. 385.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) spectrum of S18



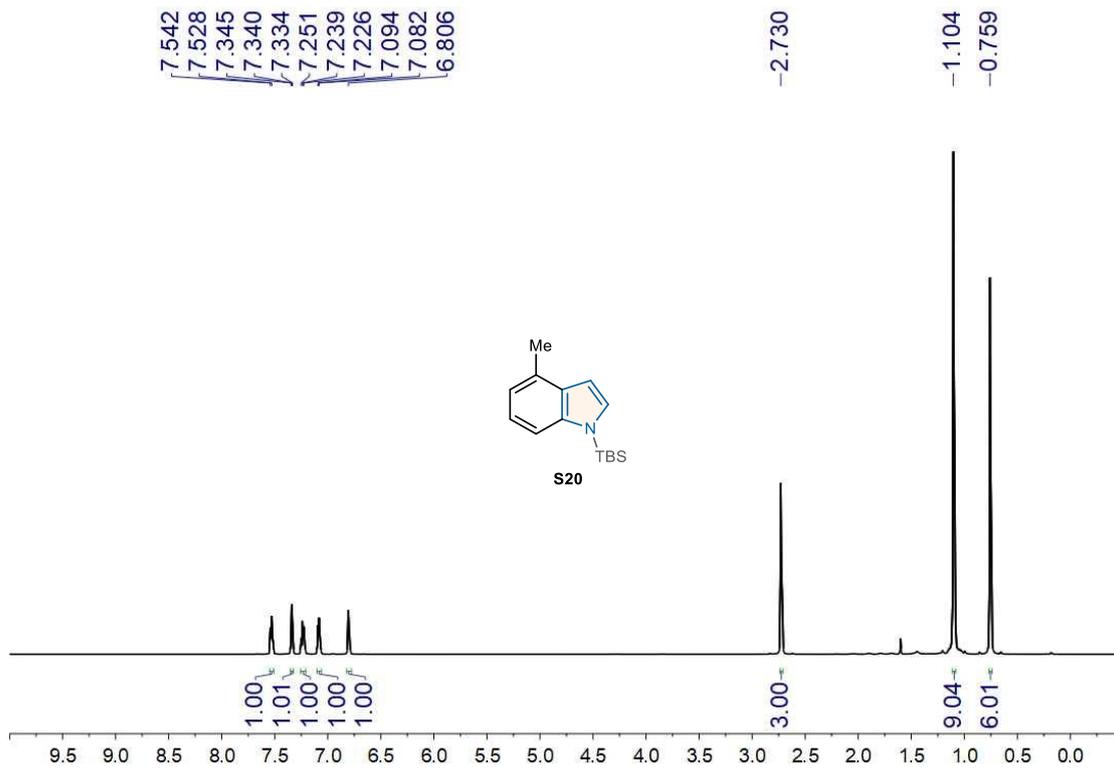
Supplementary Fig. 386.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of S18



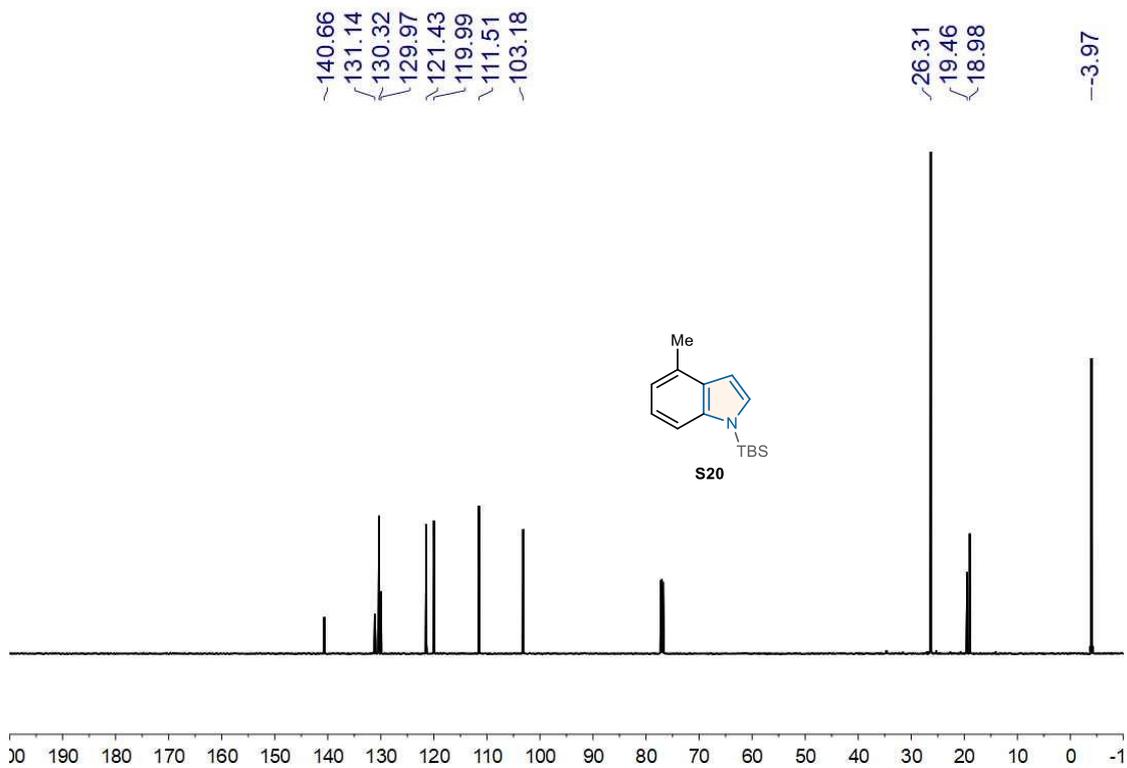
Supplementary Fig. 387. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of S19



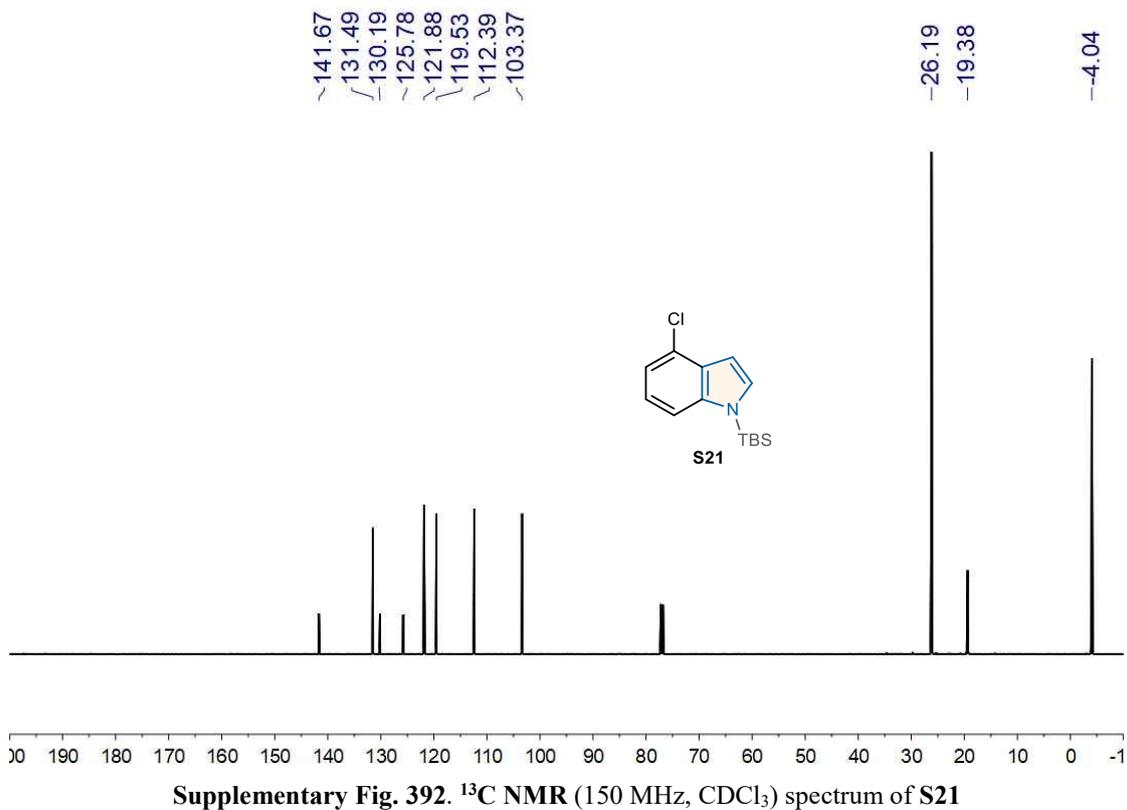
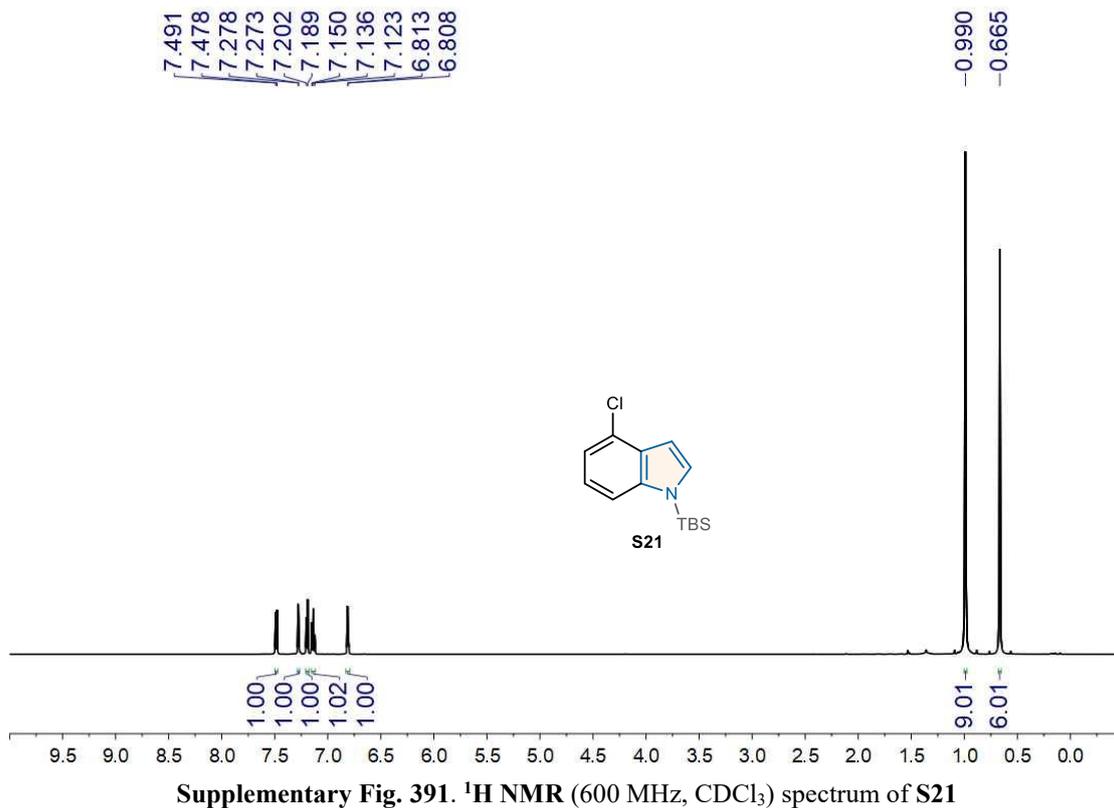
Supplementary Fig. 388. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of S19

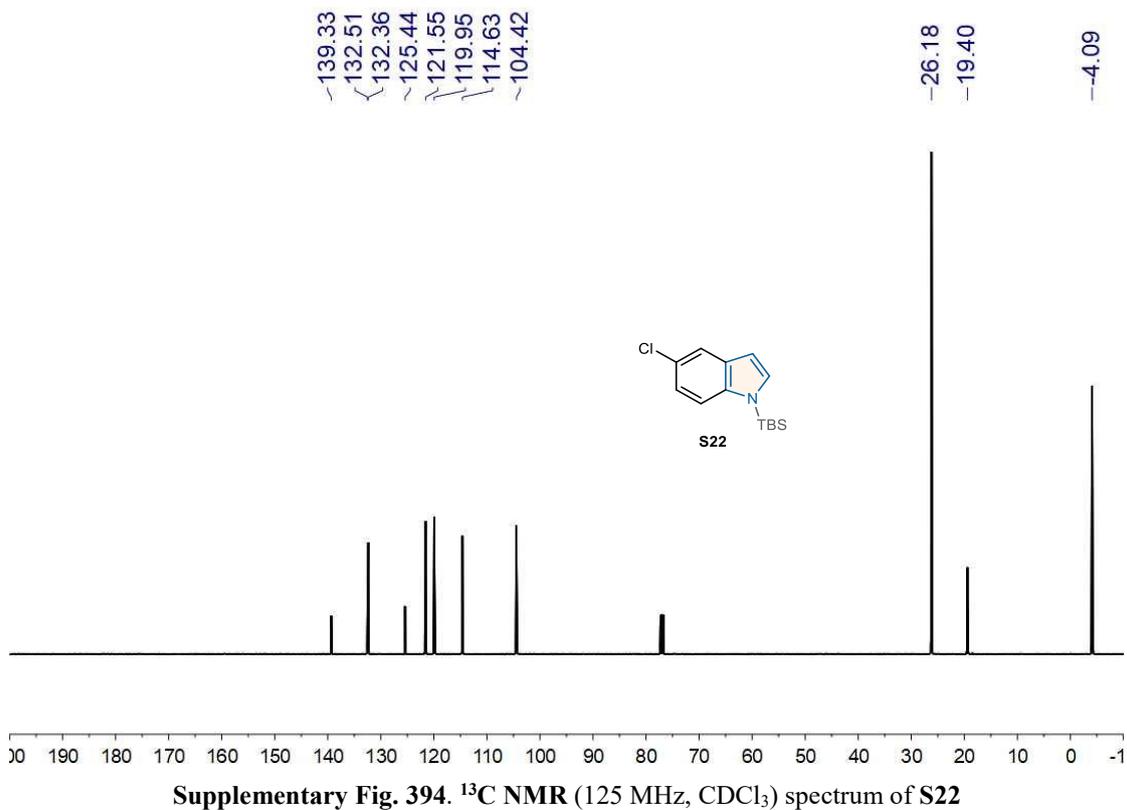
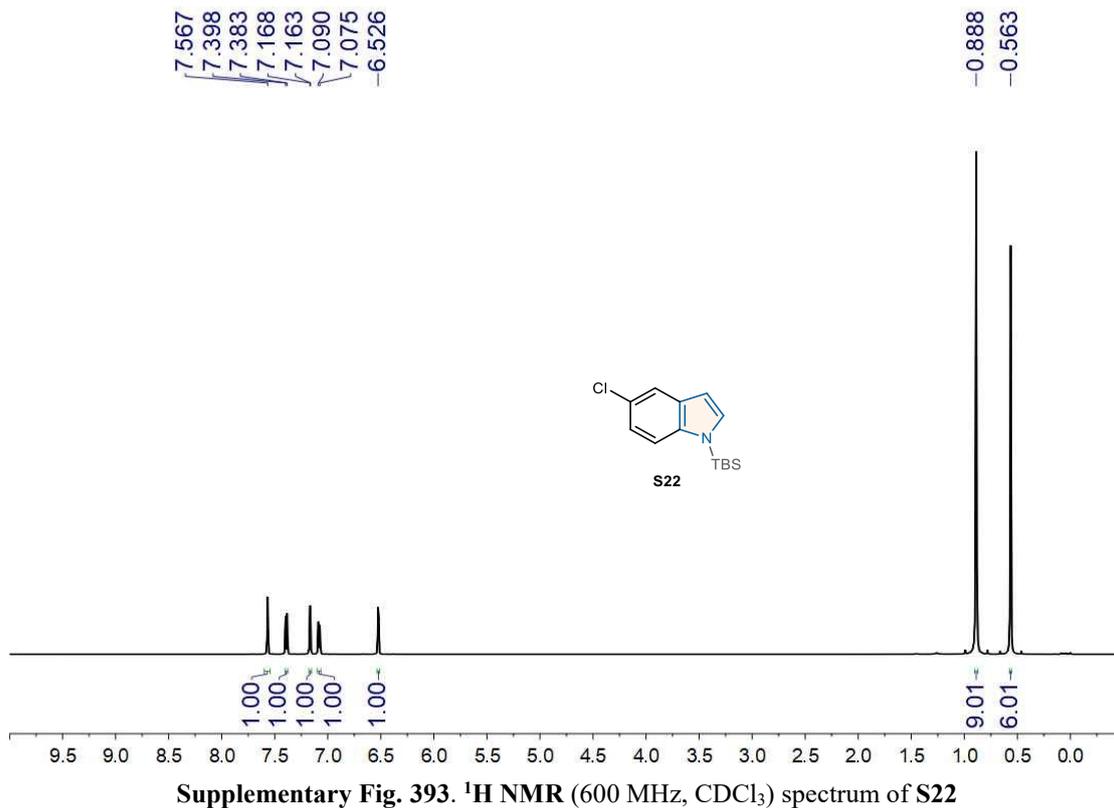


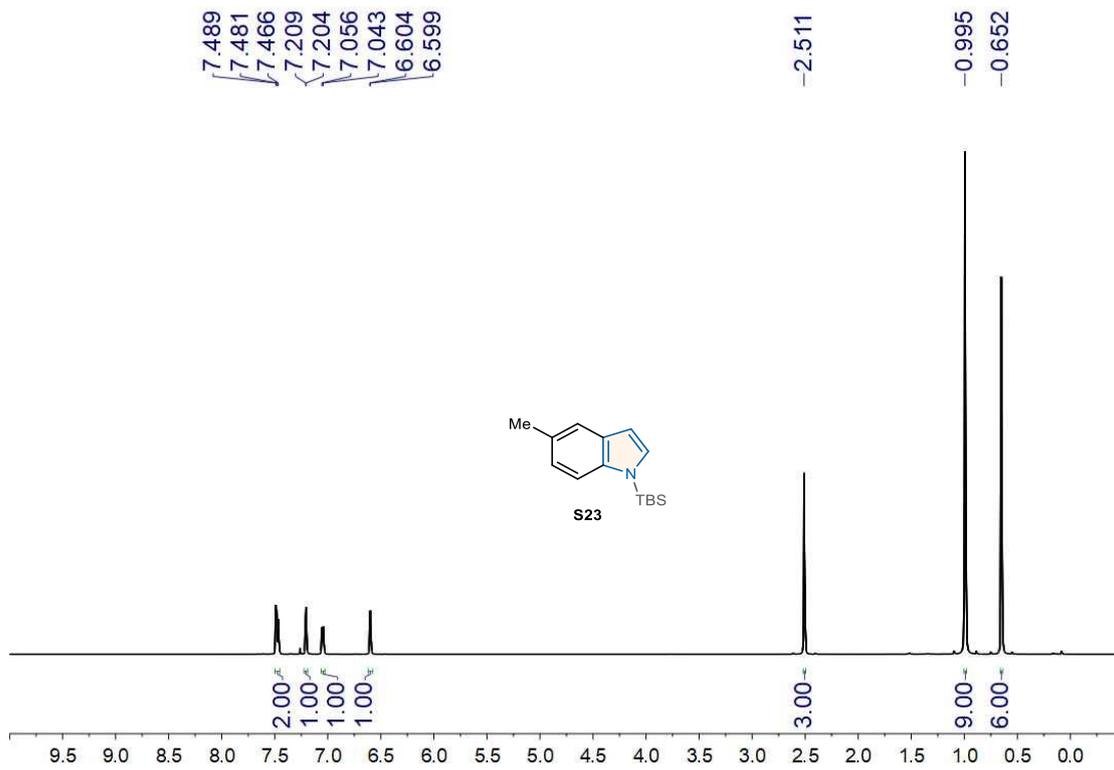
Supplementary Fig. 389.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) spectrum of S20



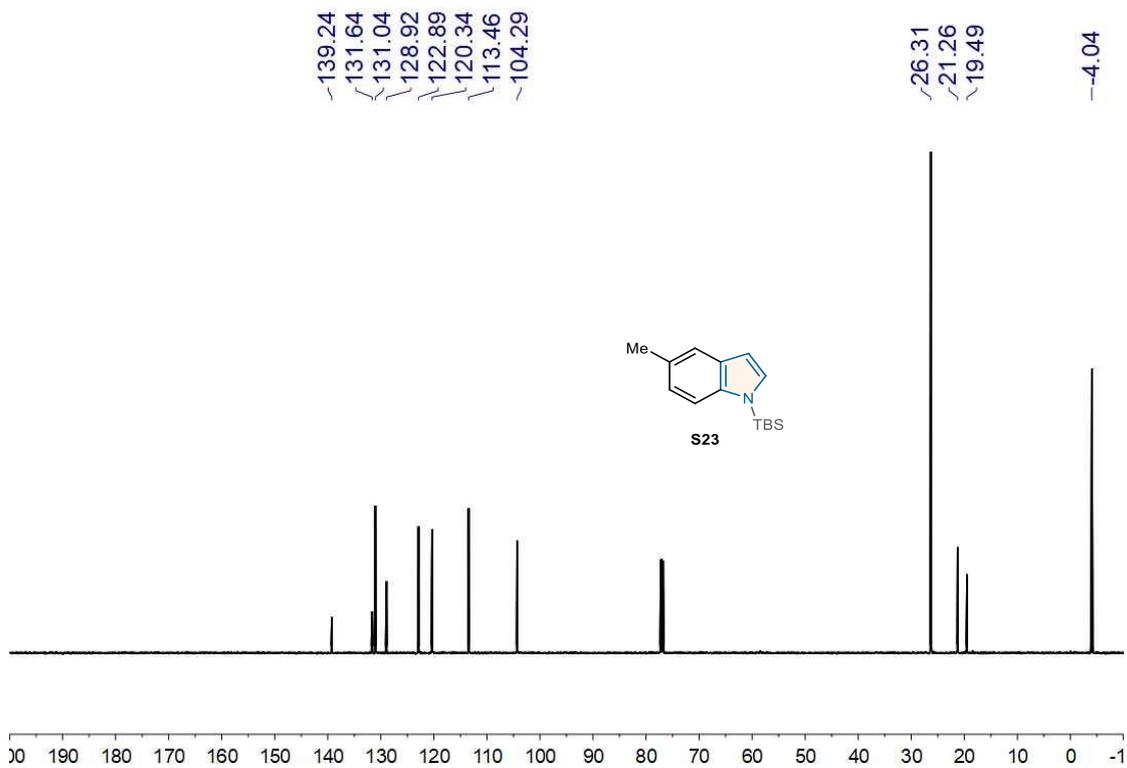
Supplementary Fig. 390.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of S20



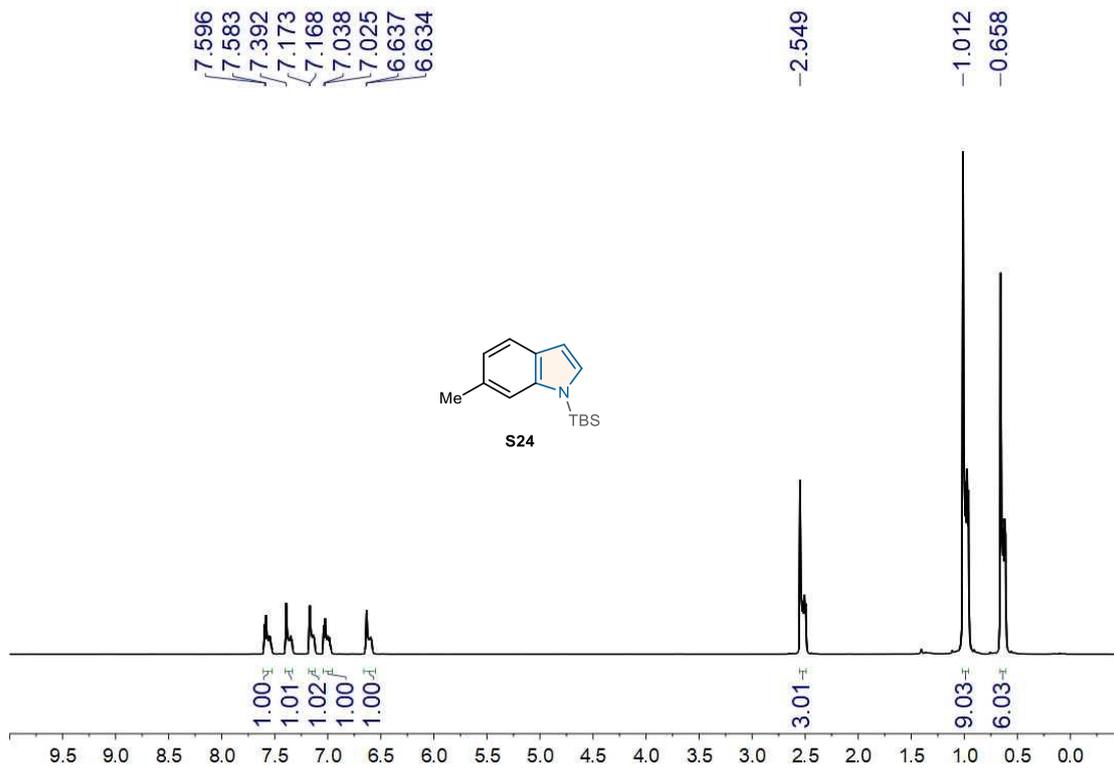




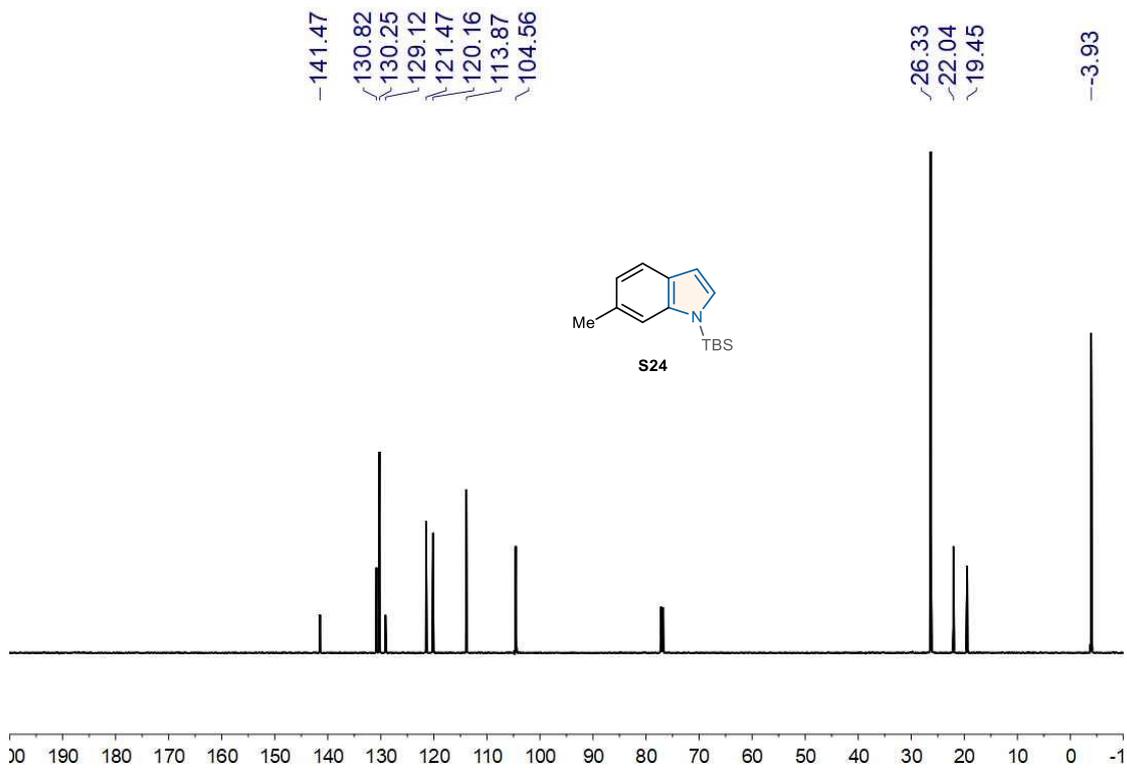
Supplementary Fig. 395. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of S23



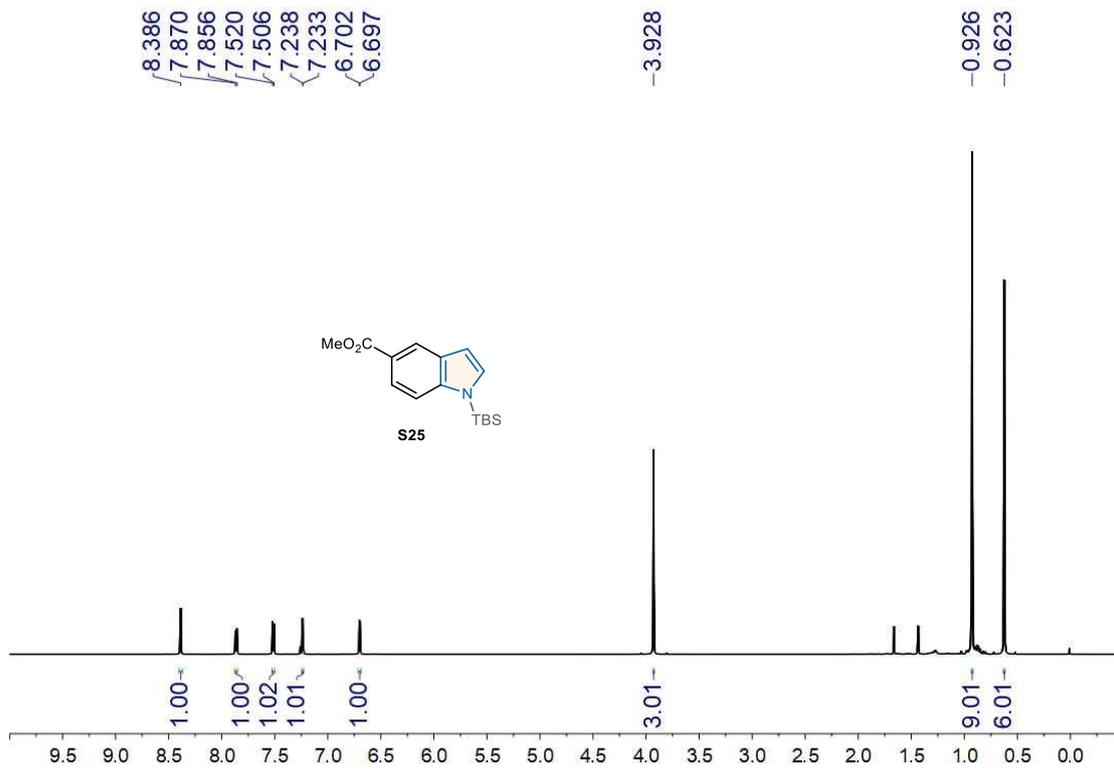
Supplementary Fig. 396. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of S23



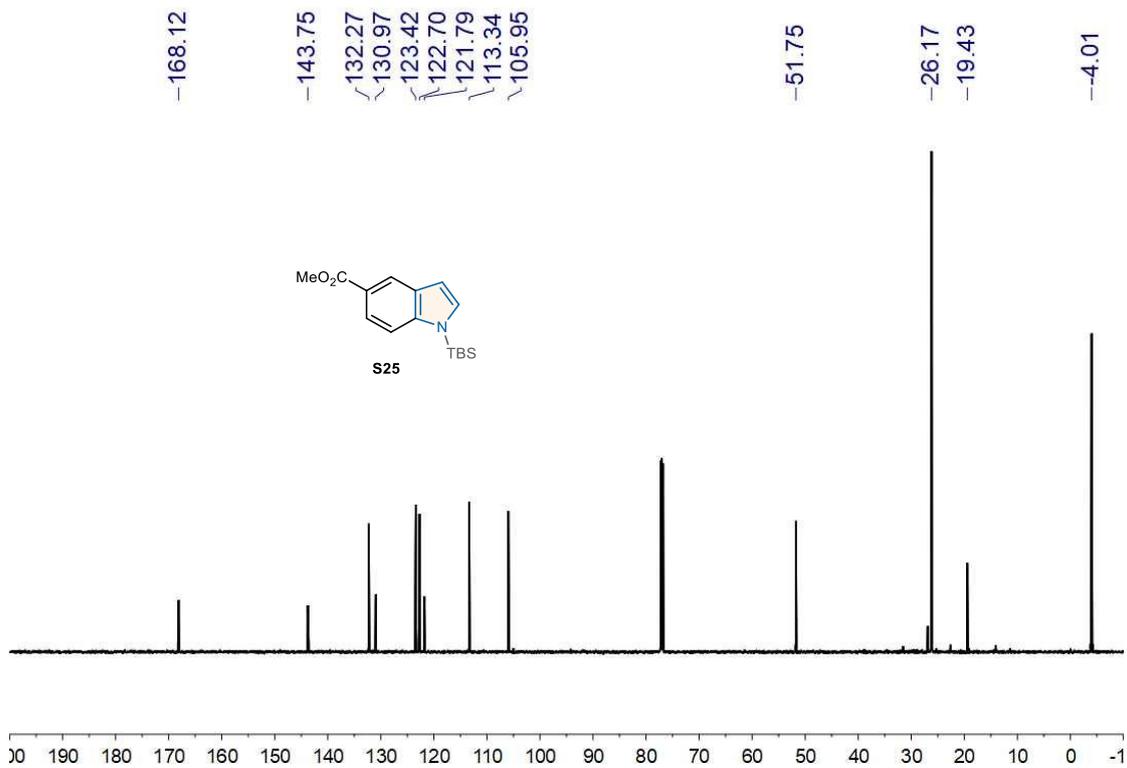
Supplementary Fig. 397.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) spectrum of S24



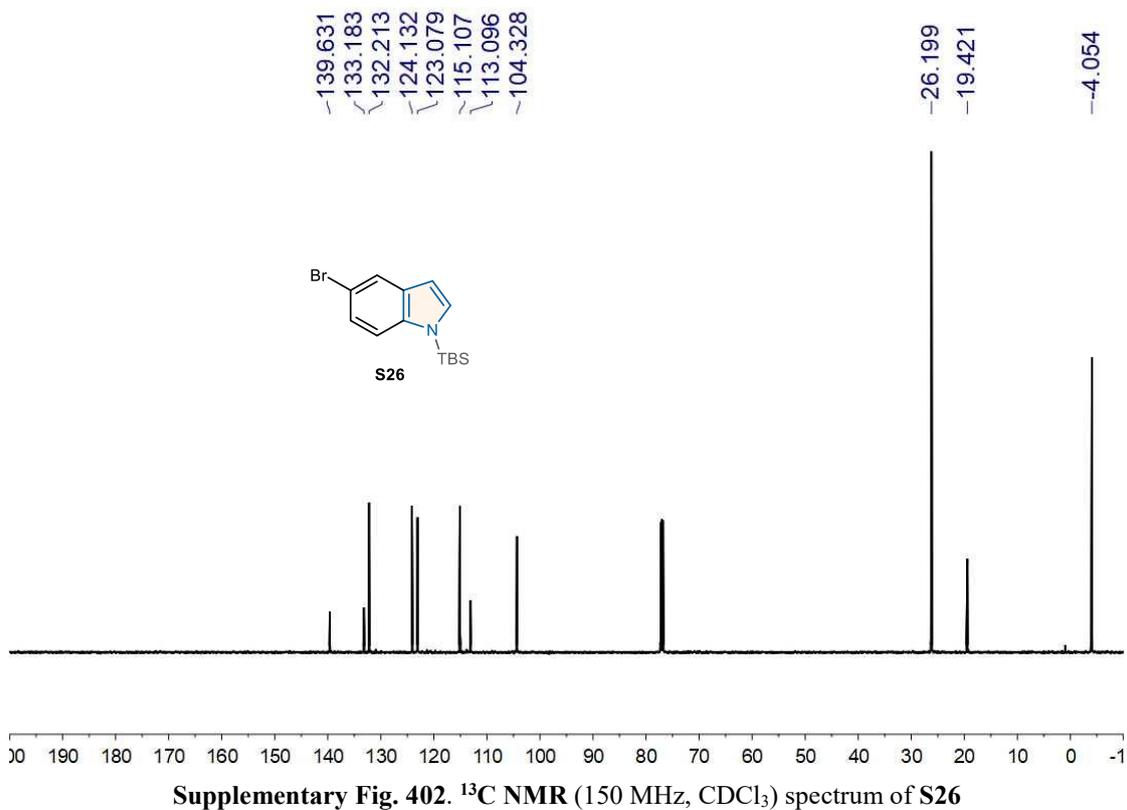
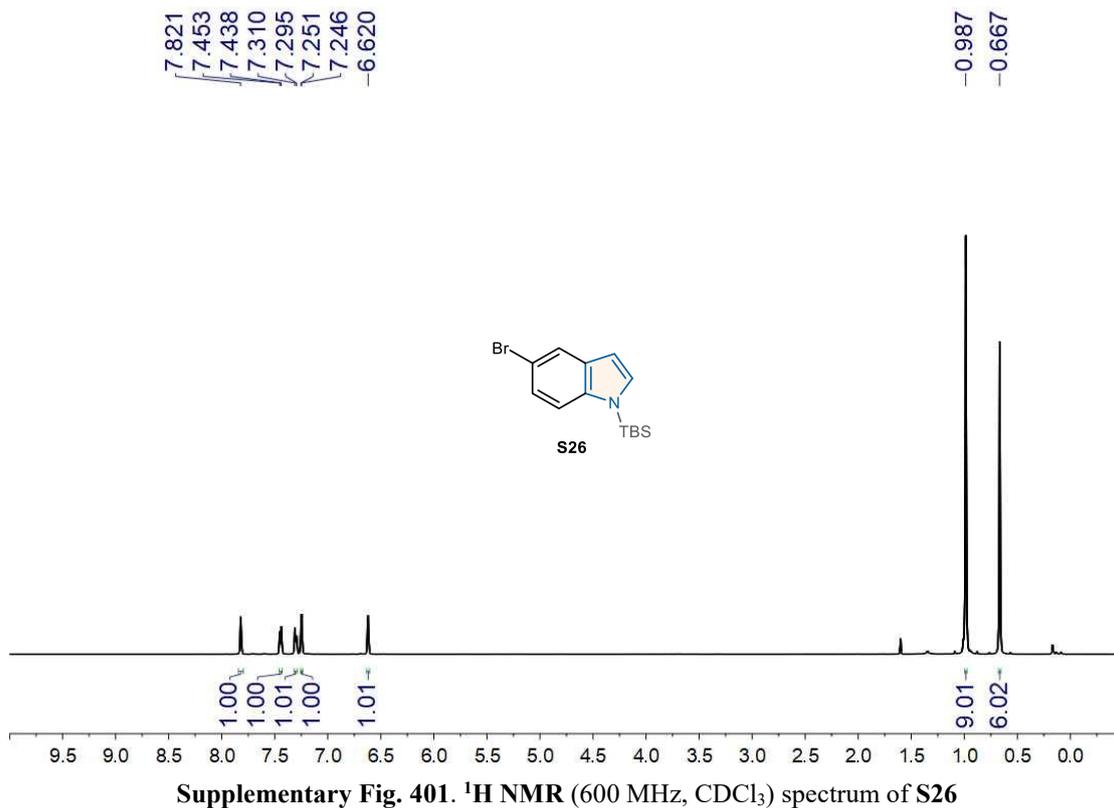
Supplementary Fig. 398.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of S24

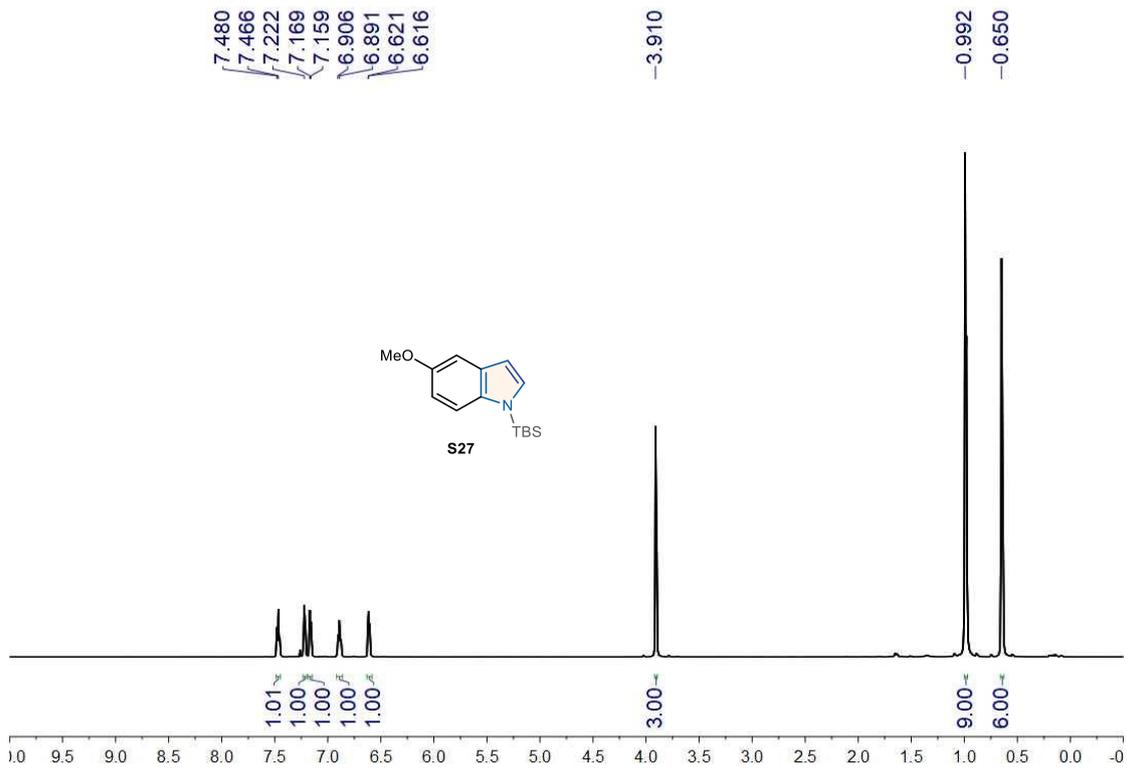


Supplementary Fig. 399. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of S25

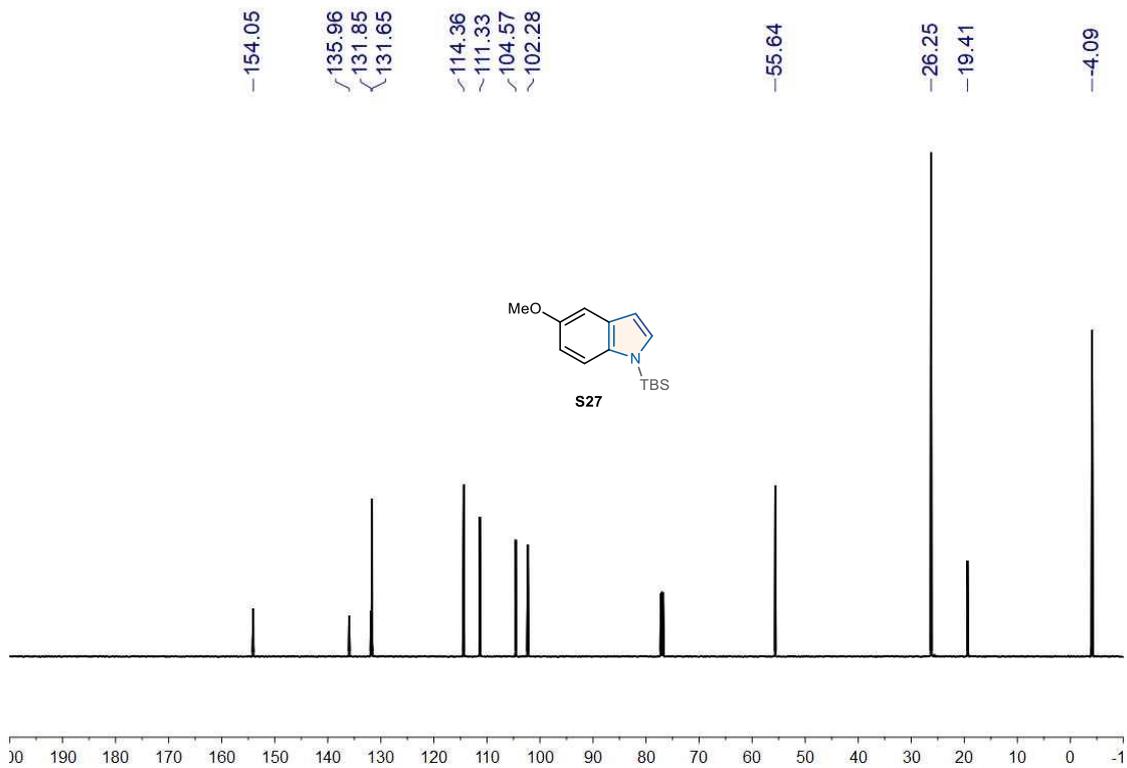


Supplementary Fig. 400. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of S25

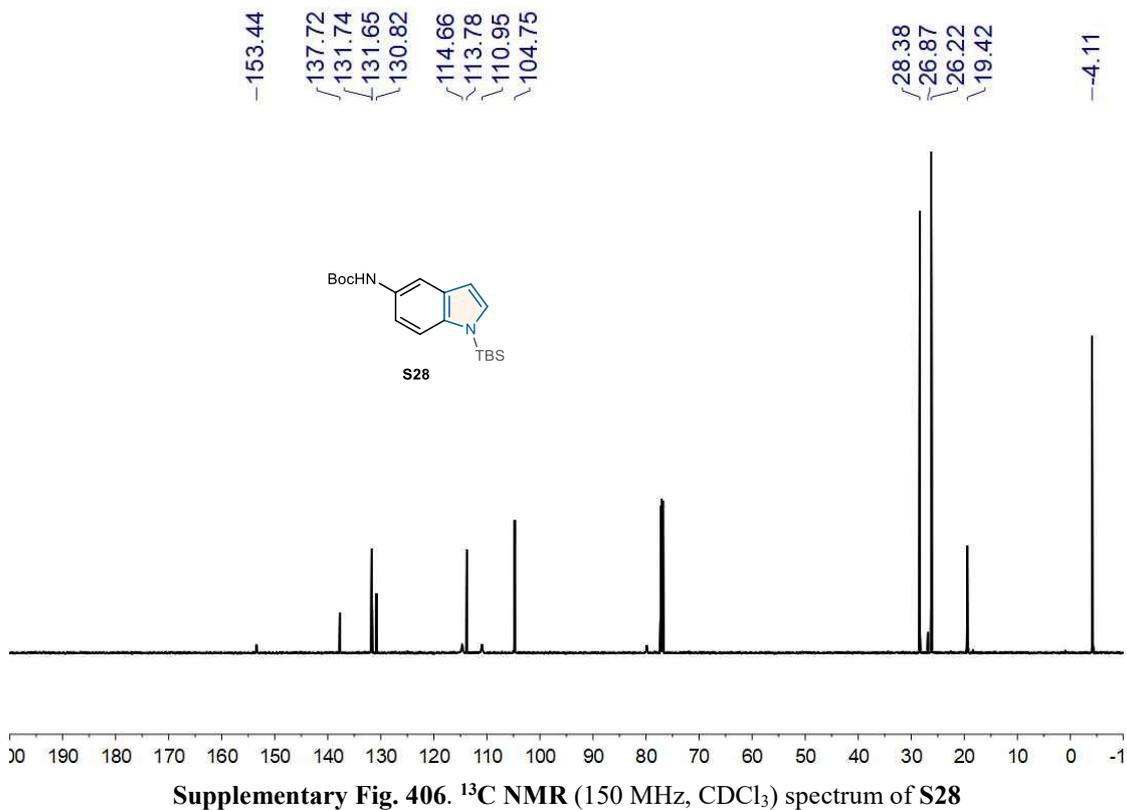
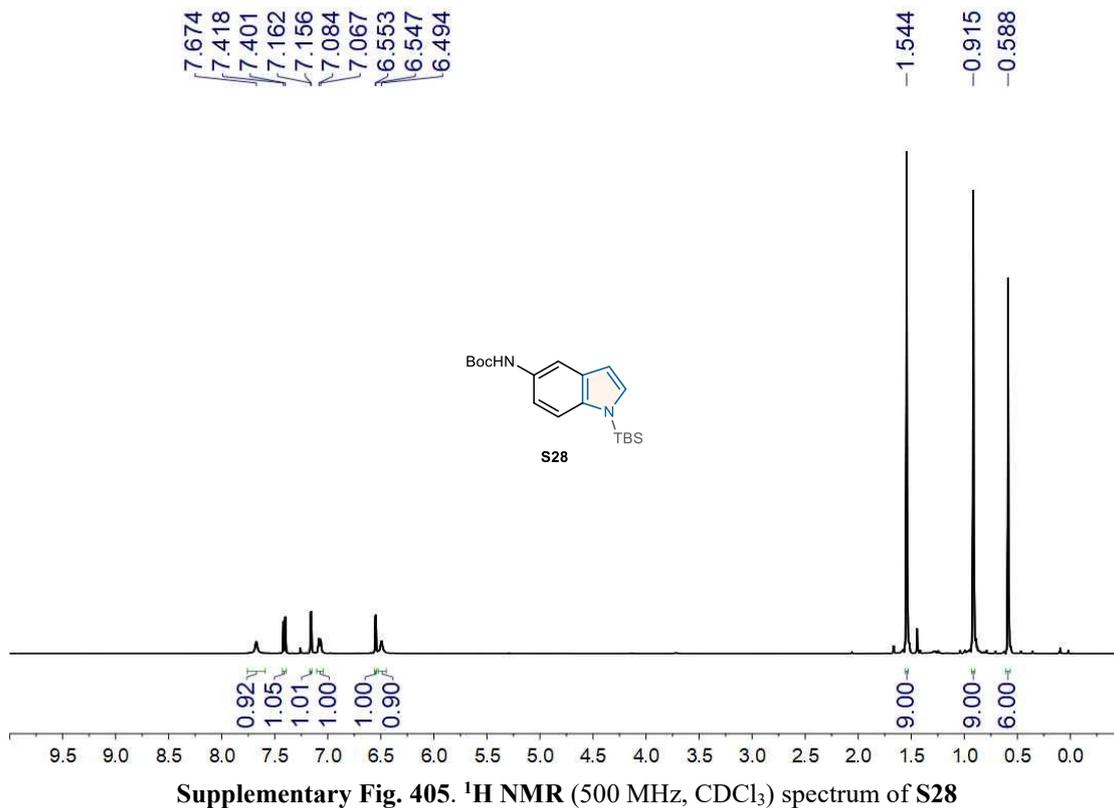


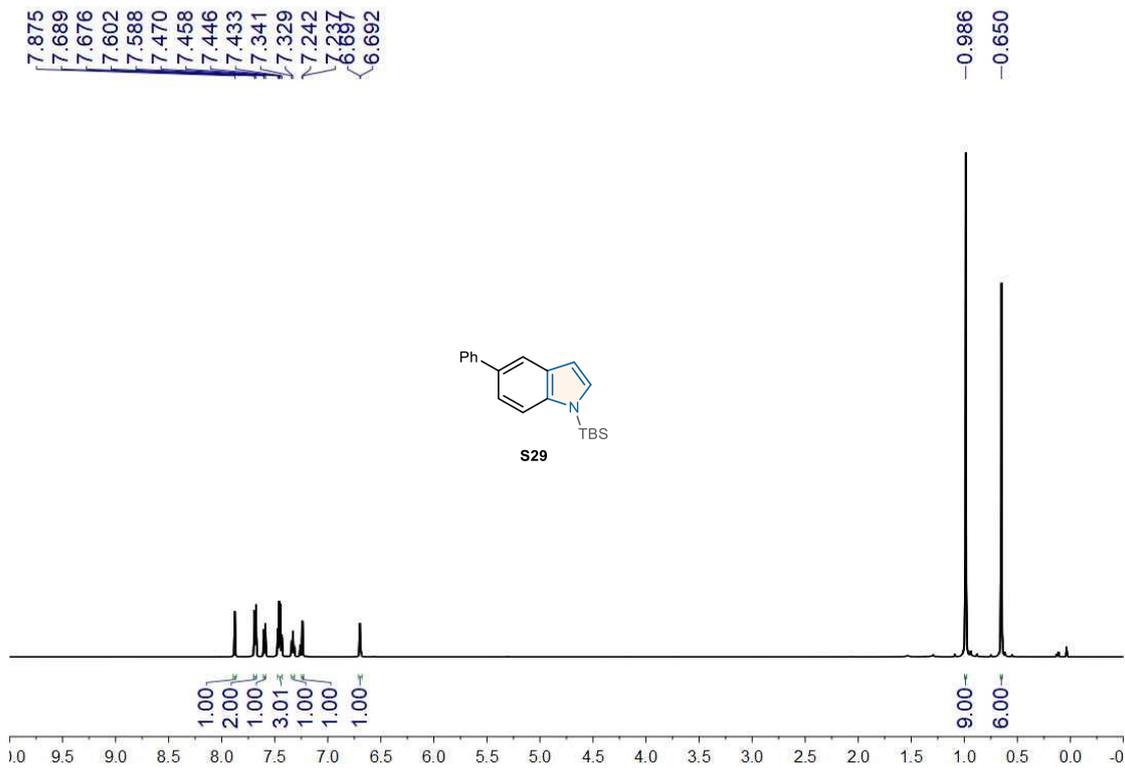


Supplementary Fig. 403. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of S27

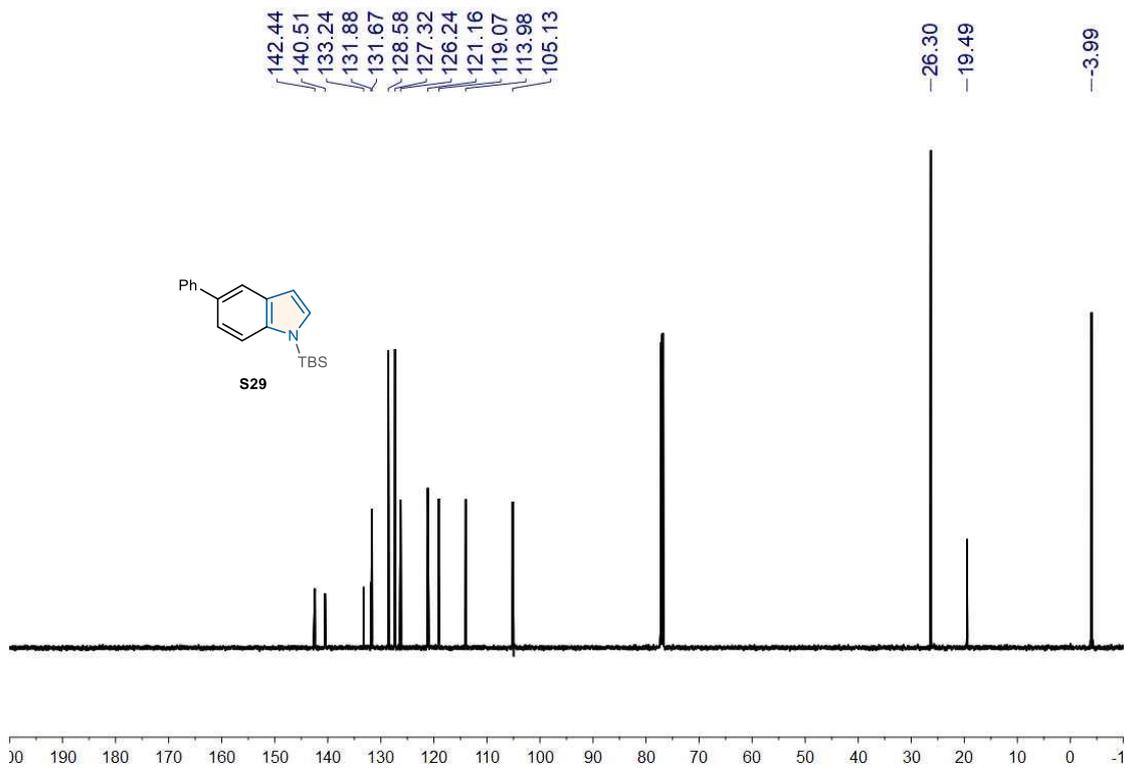


Supplementary Fig. 404. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of S27

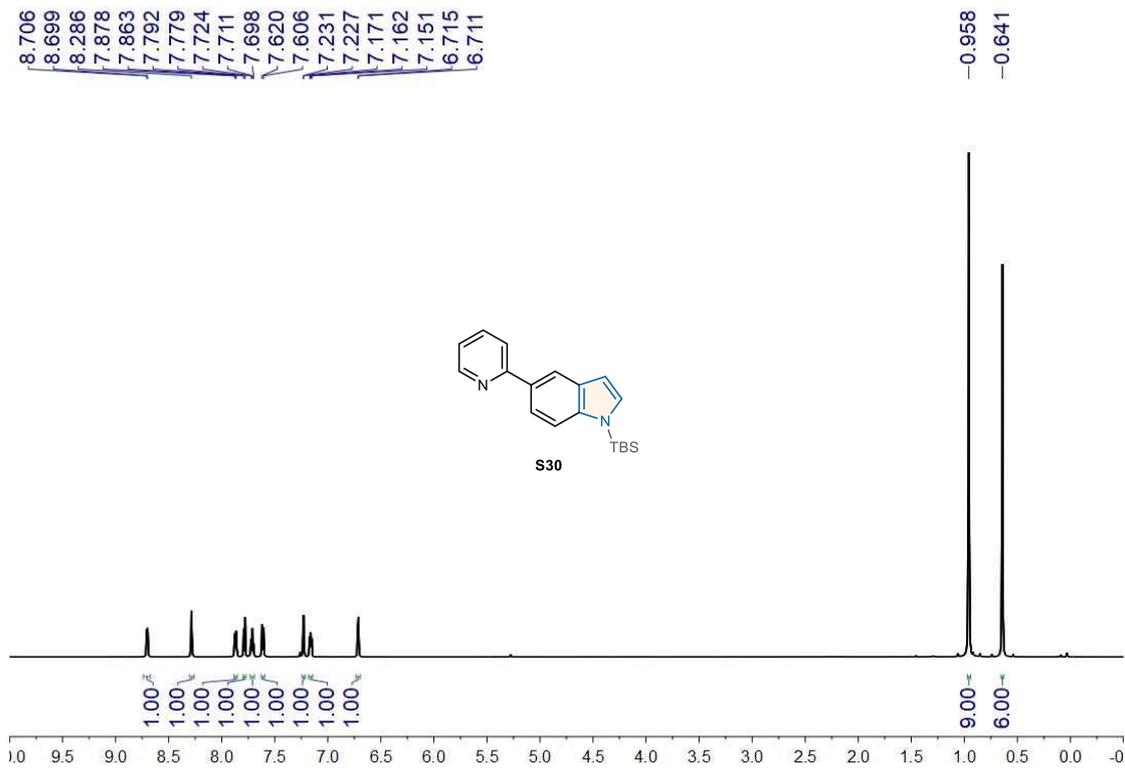




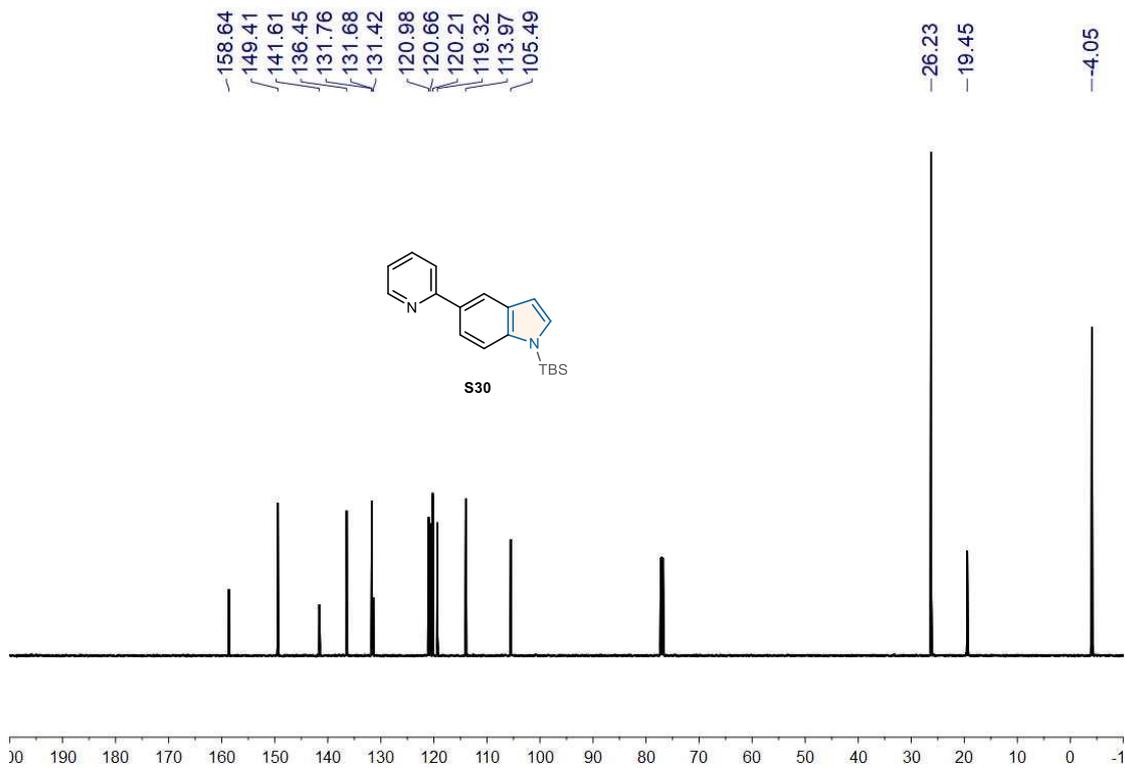
Supplementary Fig. 407. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of S29



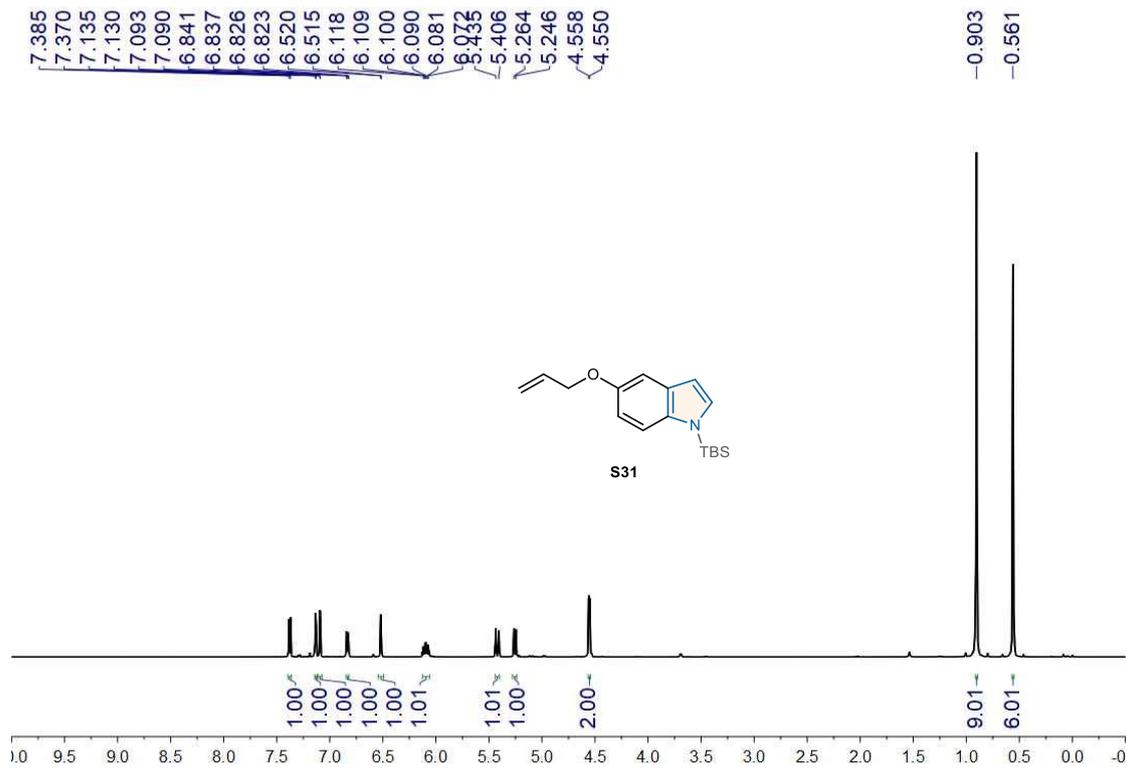
Supplementary Fig. 408. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of S29



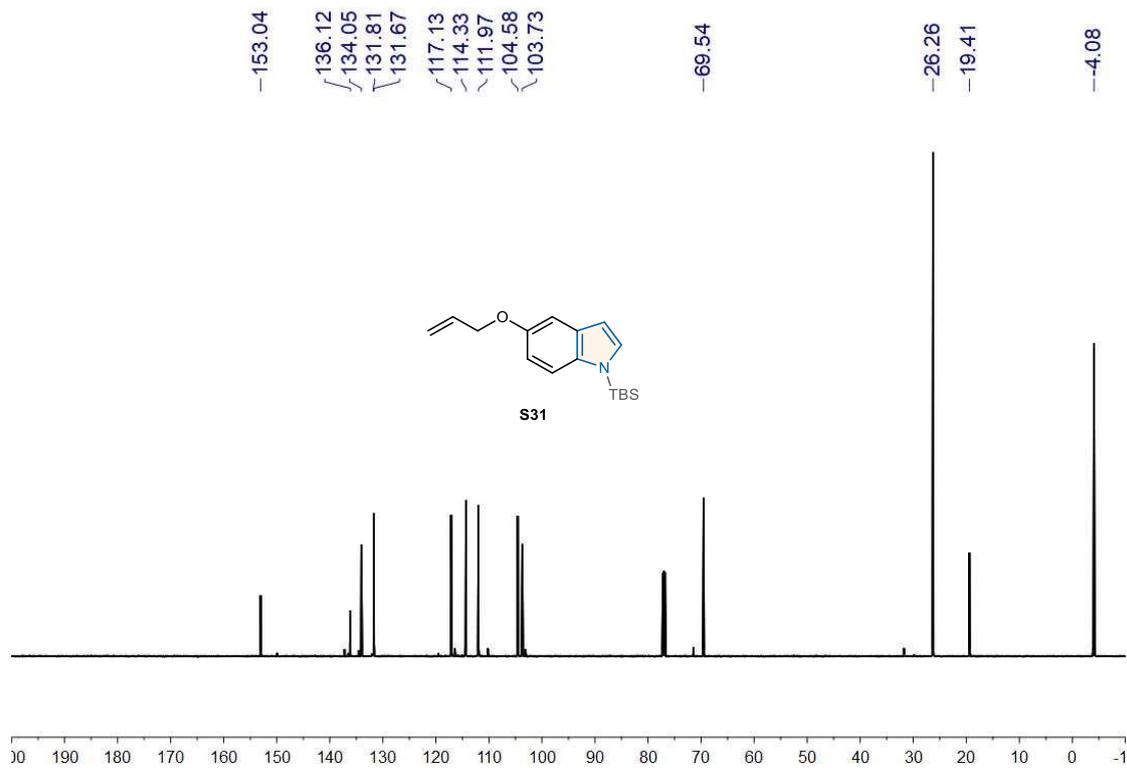
Supplementary Fig. 409.  $^{13}\text{C}$  NMR (600 MHz,  $\text{CDCl}_3$ ) spectrum of S30



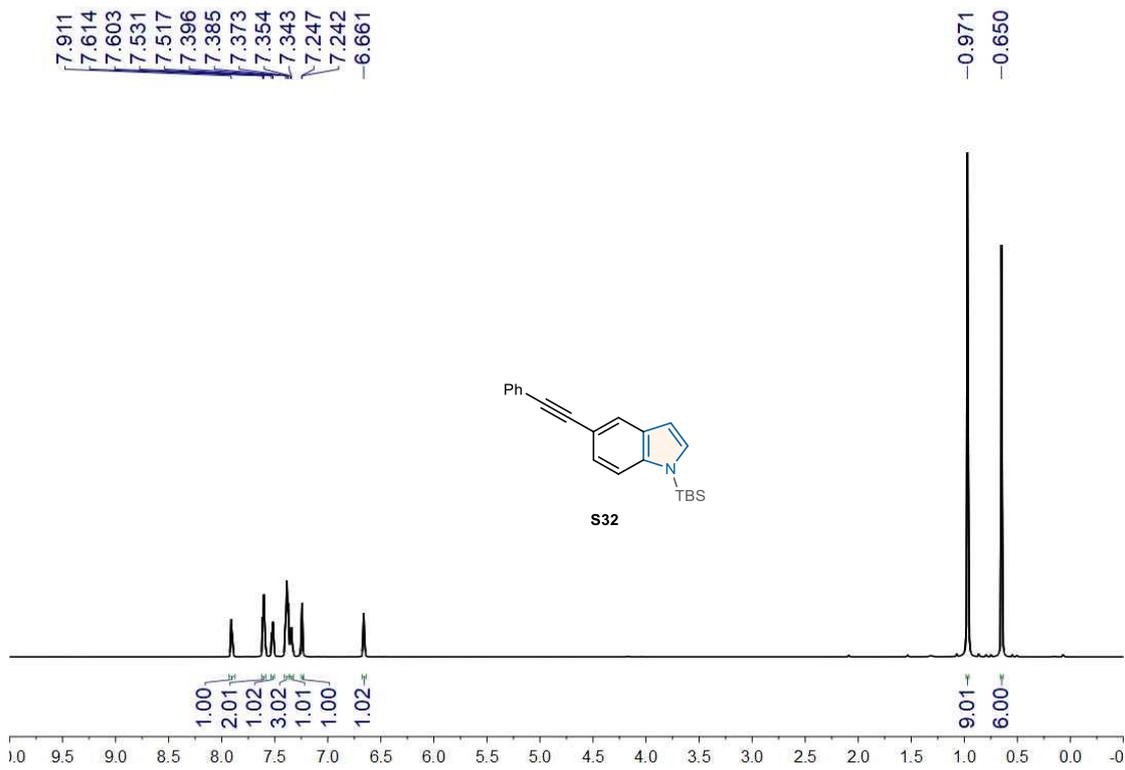
Supplementary Fig. 410.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of S30



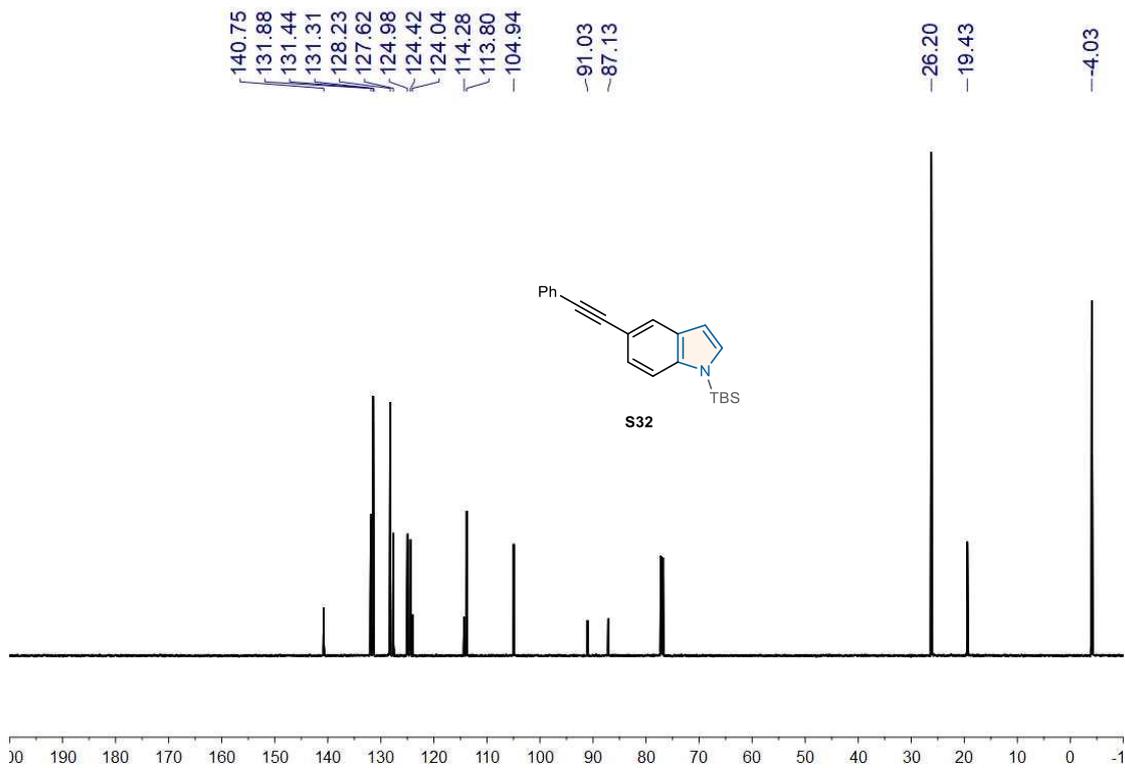
Supplementary Fig. 411. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of S31



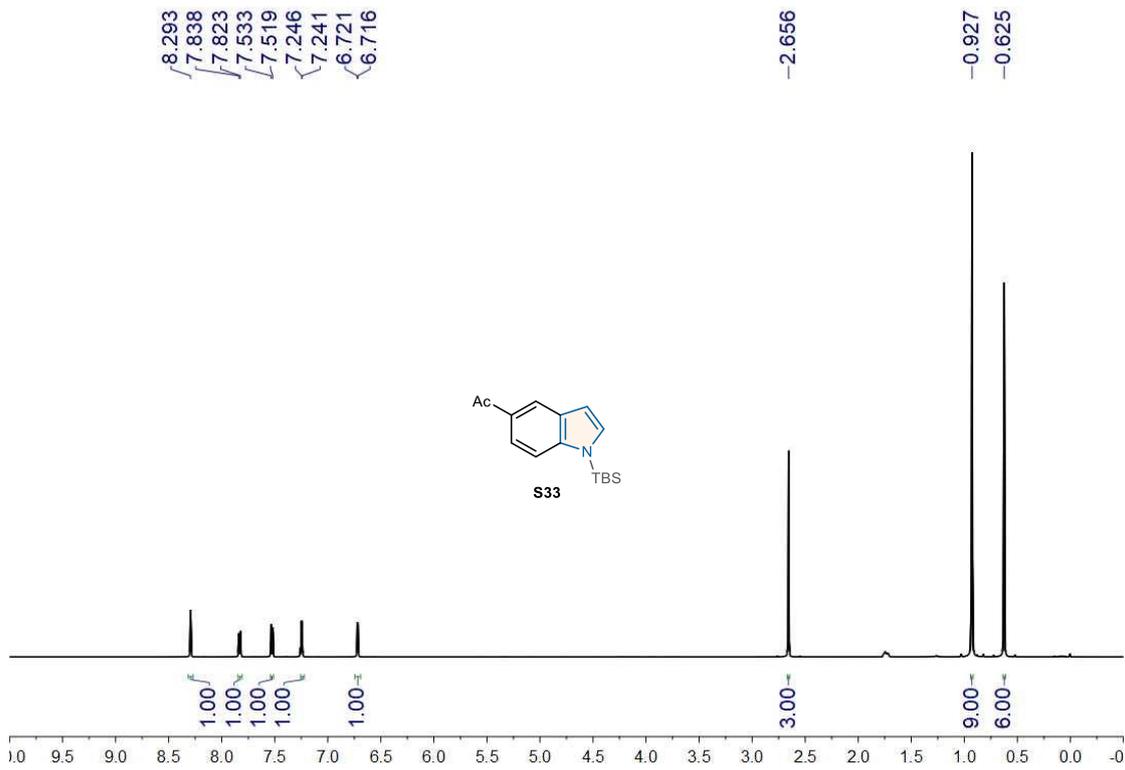
Supplementary Fig. 412. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of S31



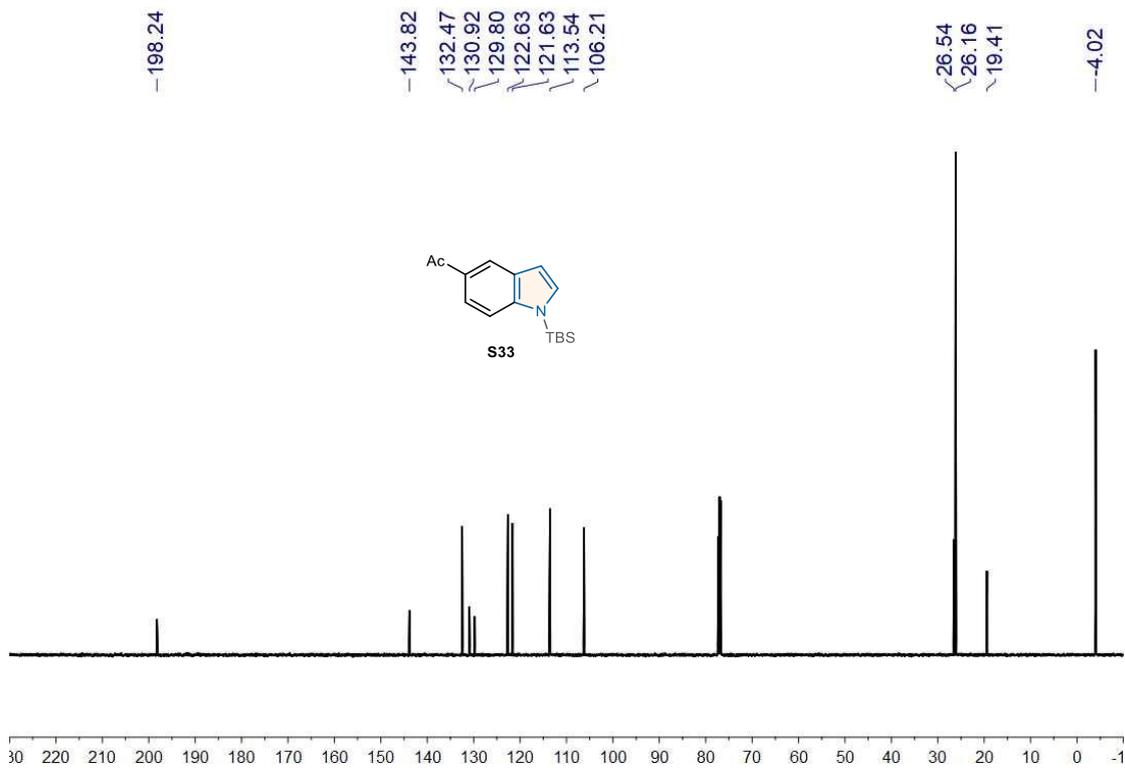
Supplementary Fig. 413.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) spectrum of S32



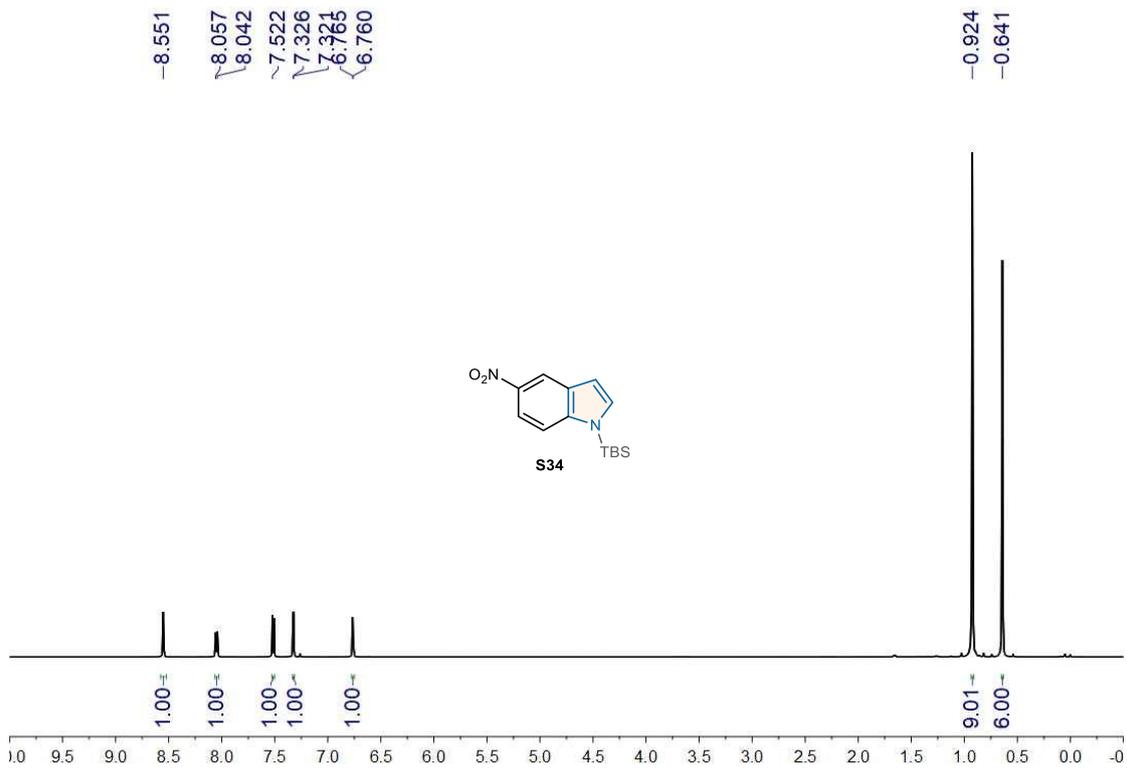
Supplementary Fig. 414.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of S32



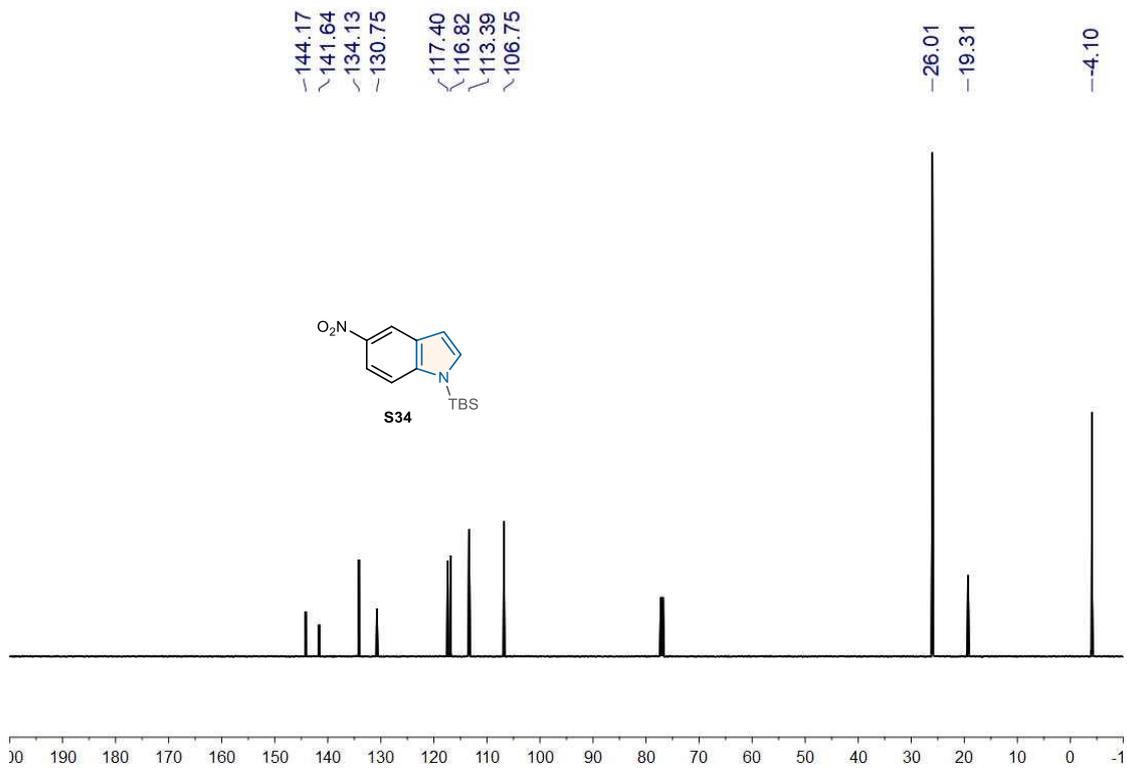
Supplementary Fig. 415.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) spectrum of S33



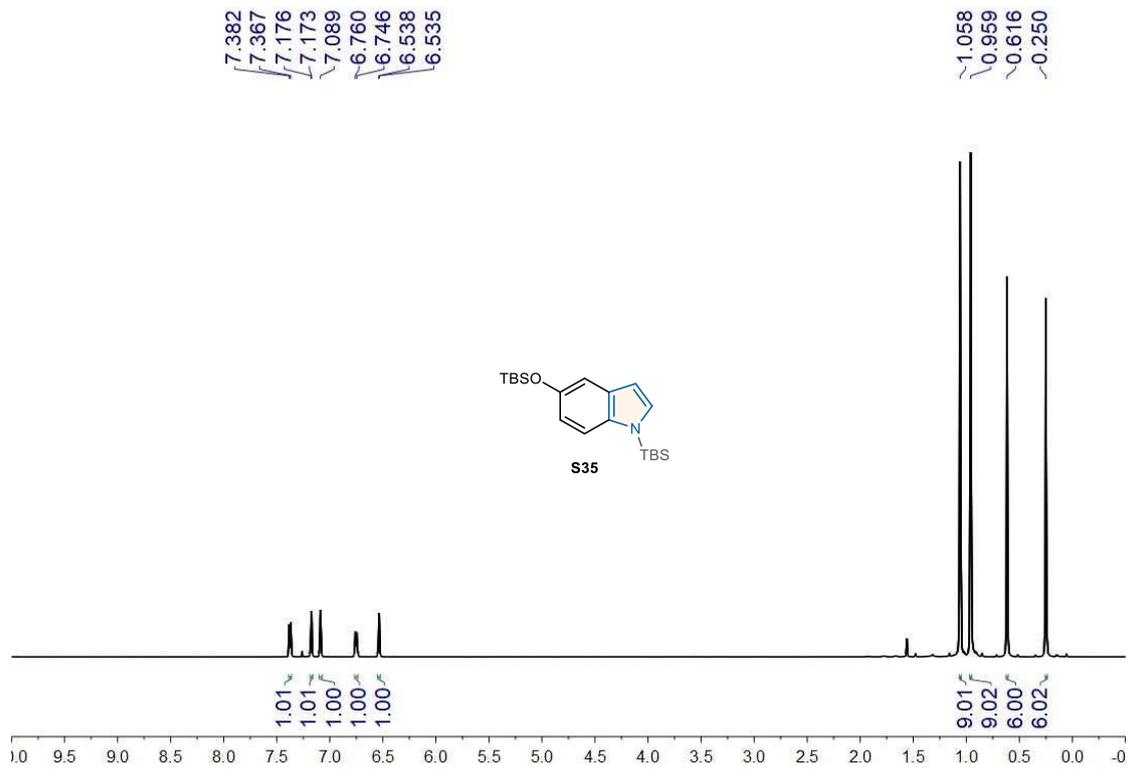
Supplementary Fig. 416.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of S33



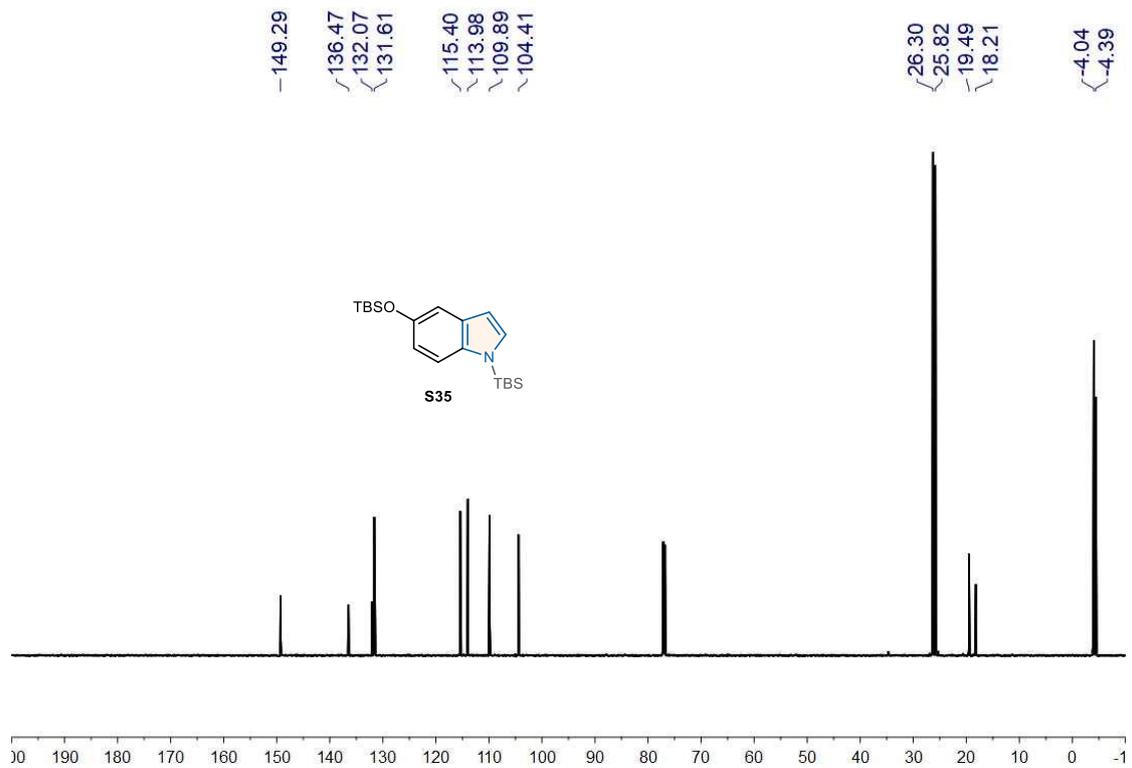
Supplementary Fig. 417. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of S34



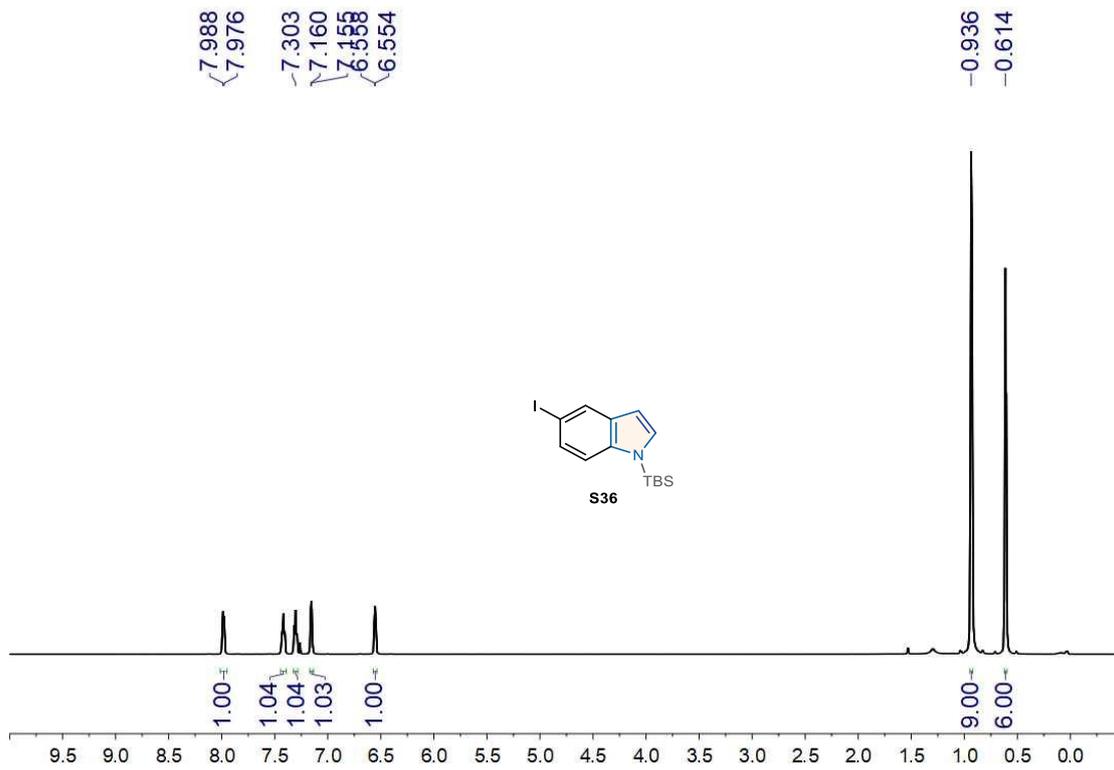
Supplementary Fig. 418. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of S34



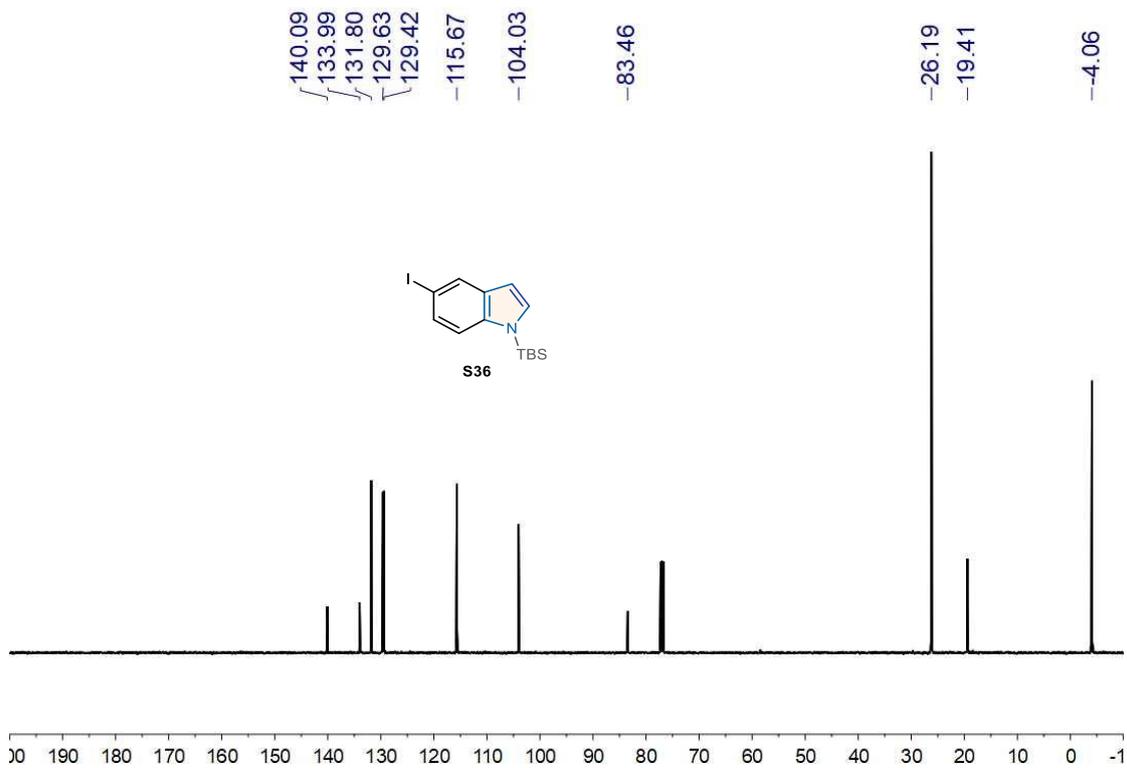
Supplementary Fig. 419. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of S35



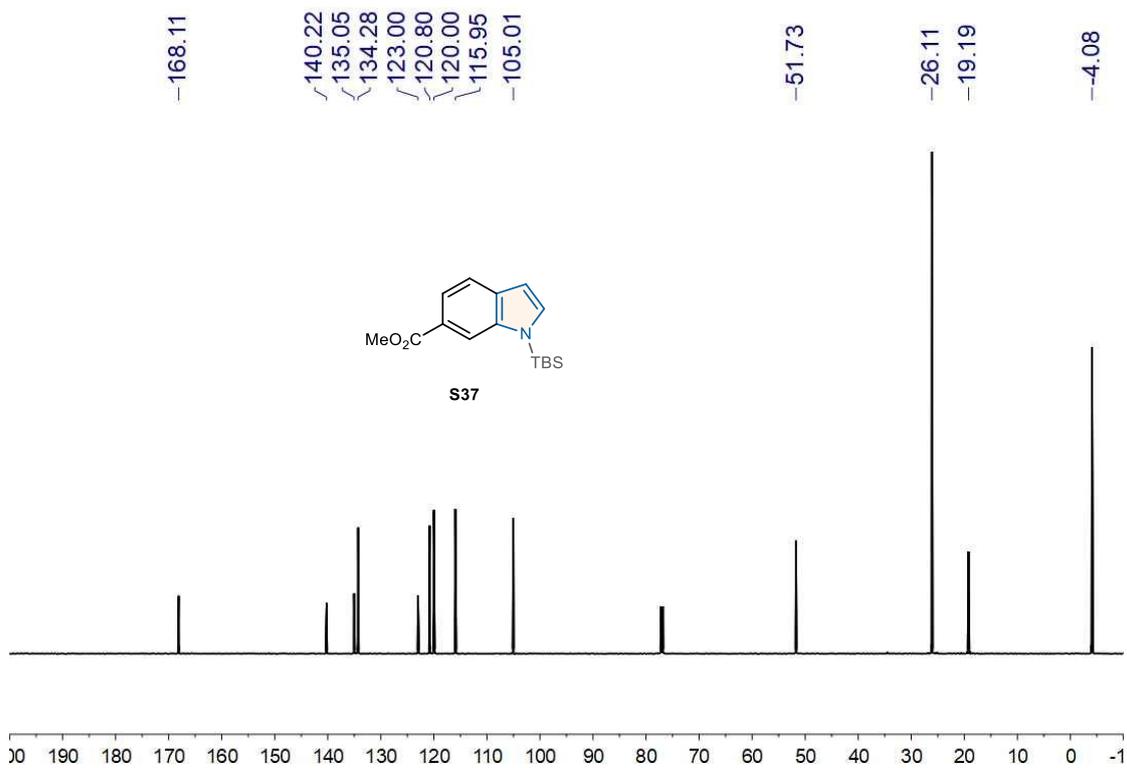
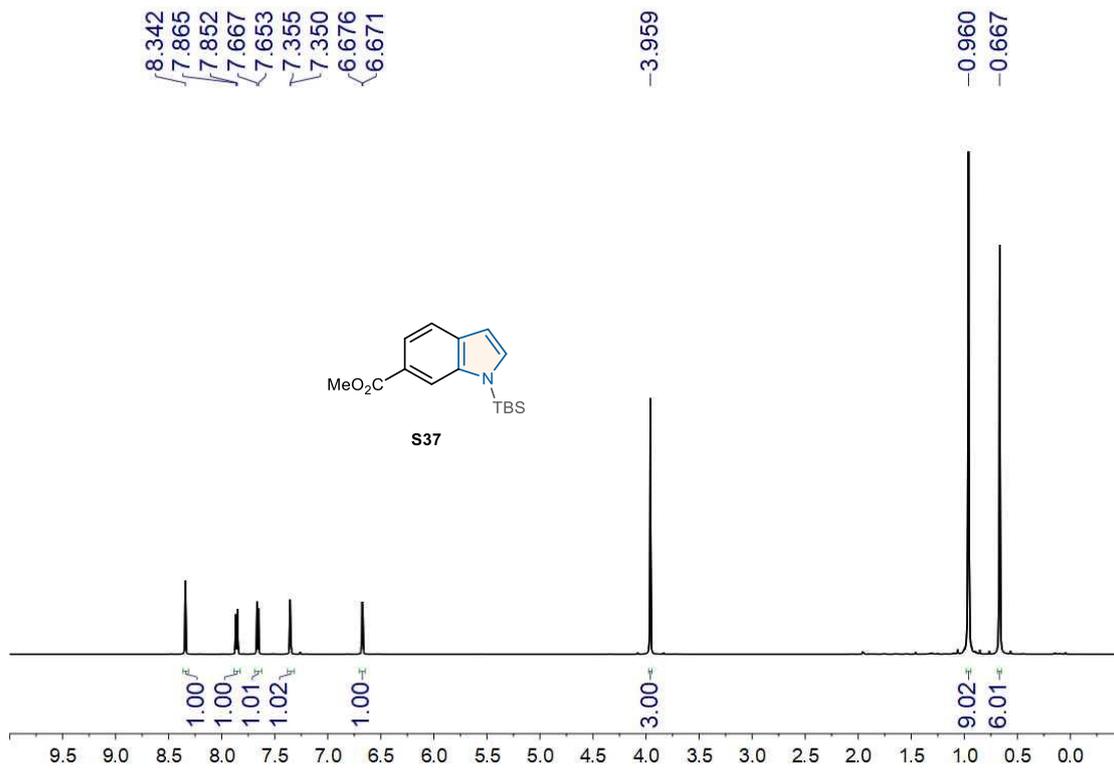
Supplementary Fig. 420. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of S35

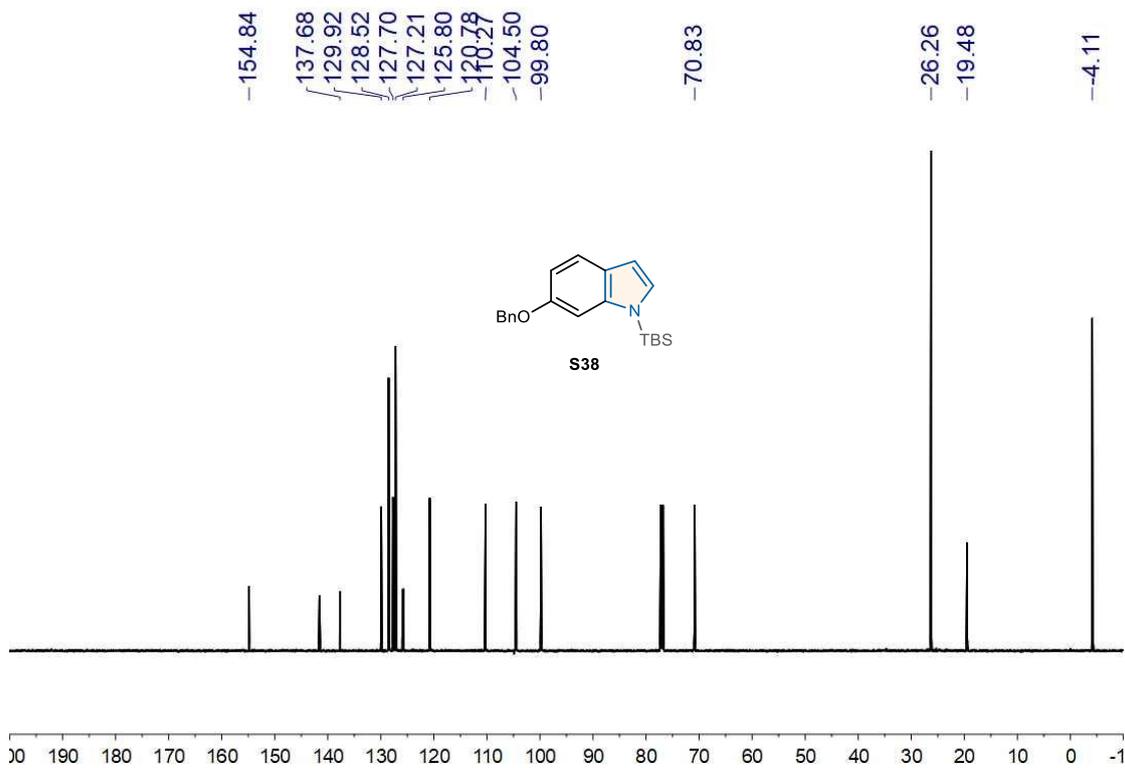
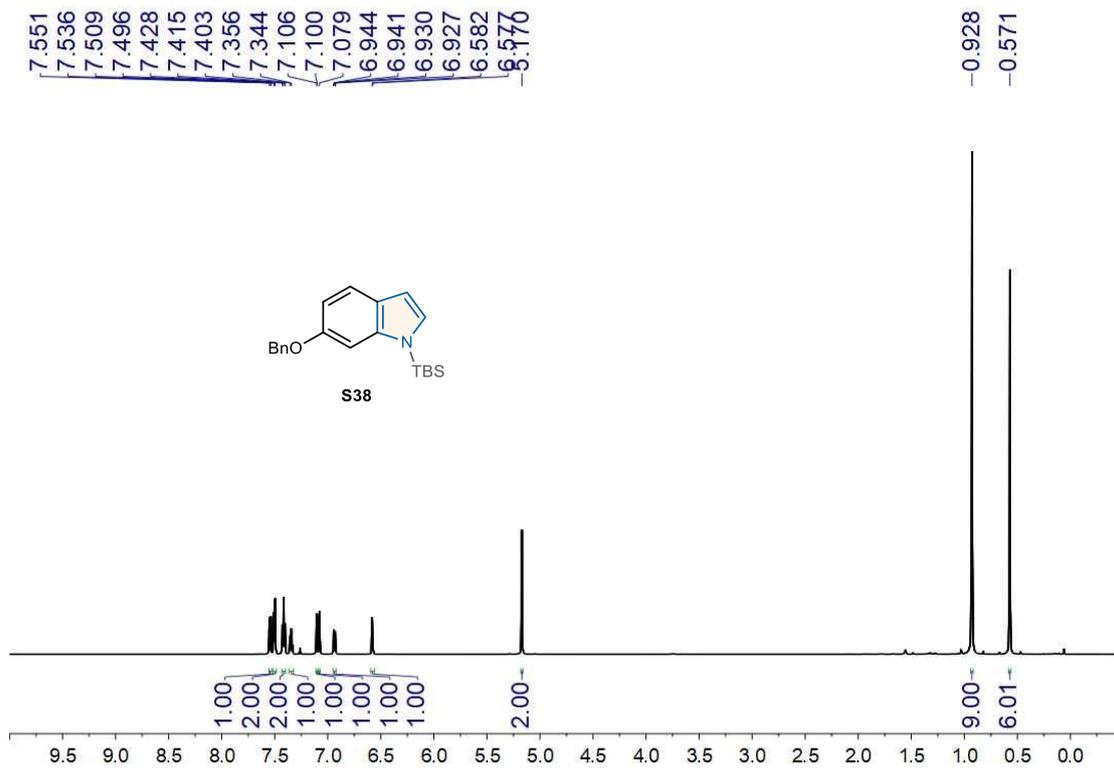


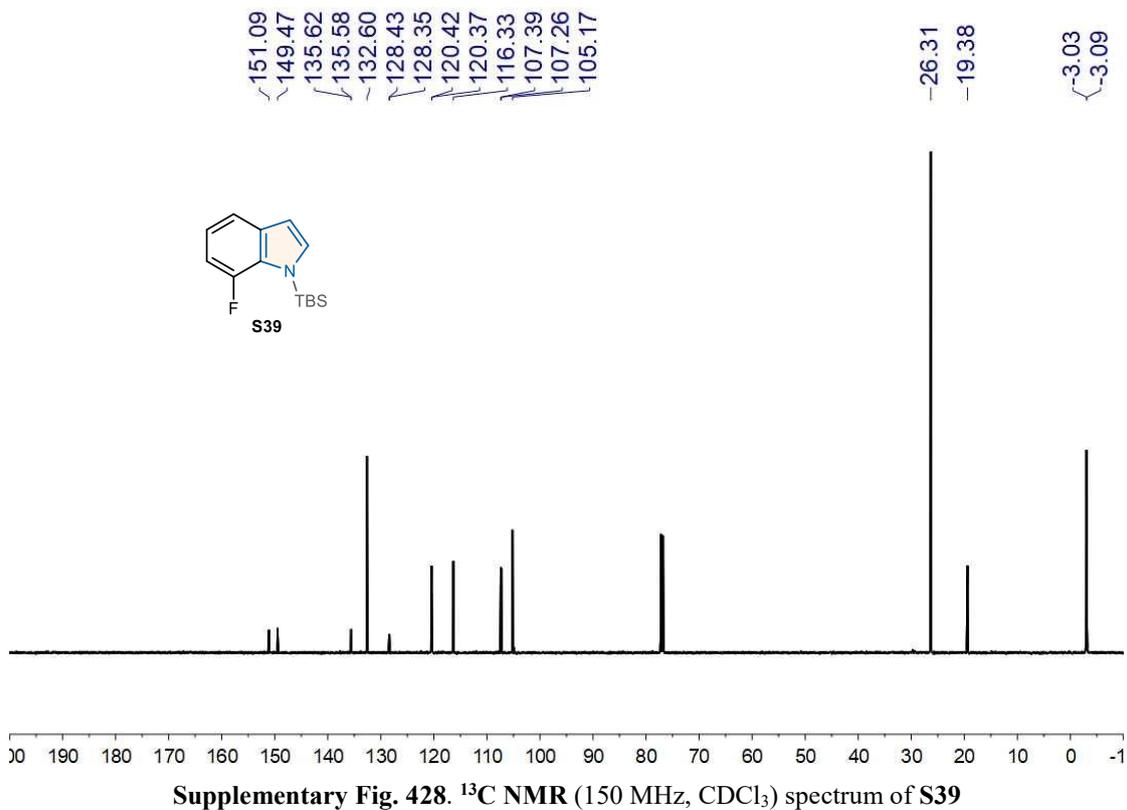
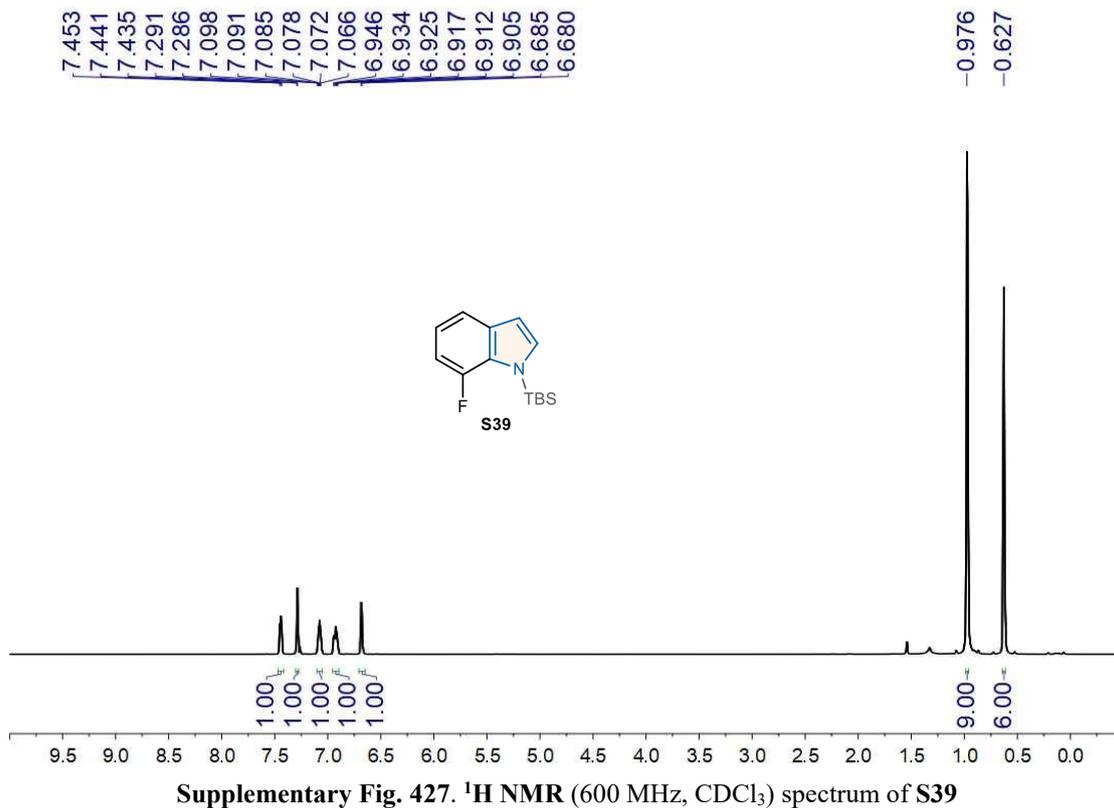
Supplementary Fig. 421. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of S36

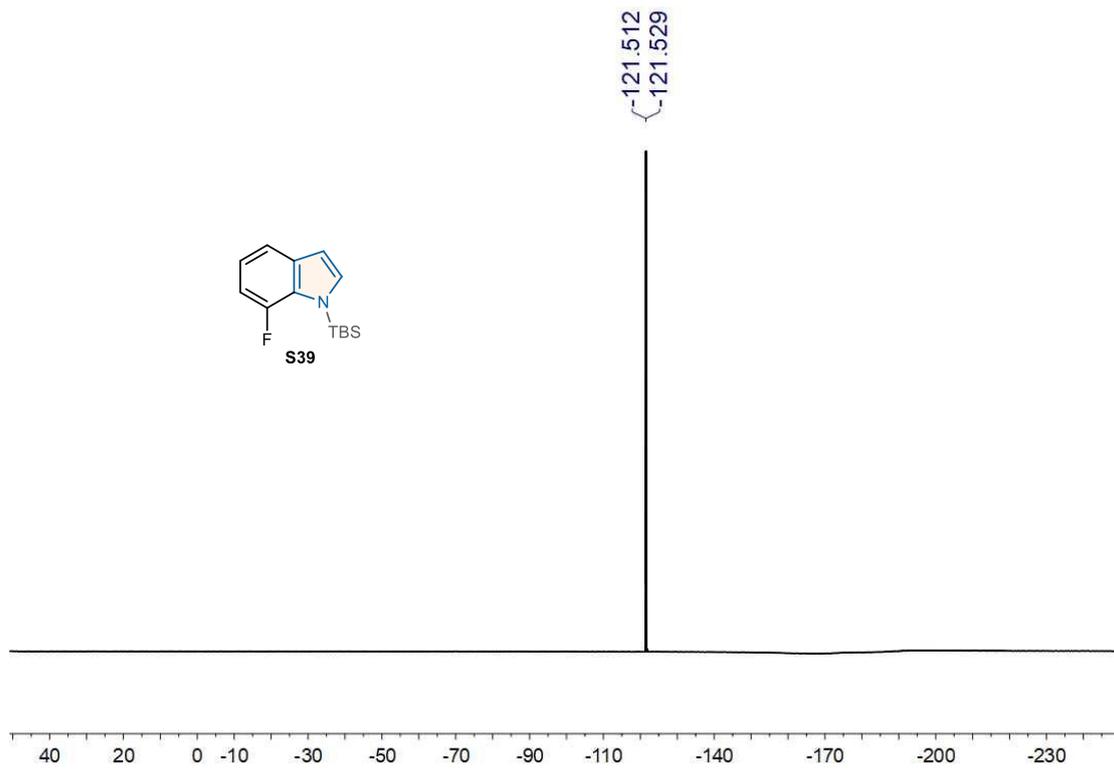


Supplementary Fig. 422. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of S36

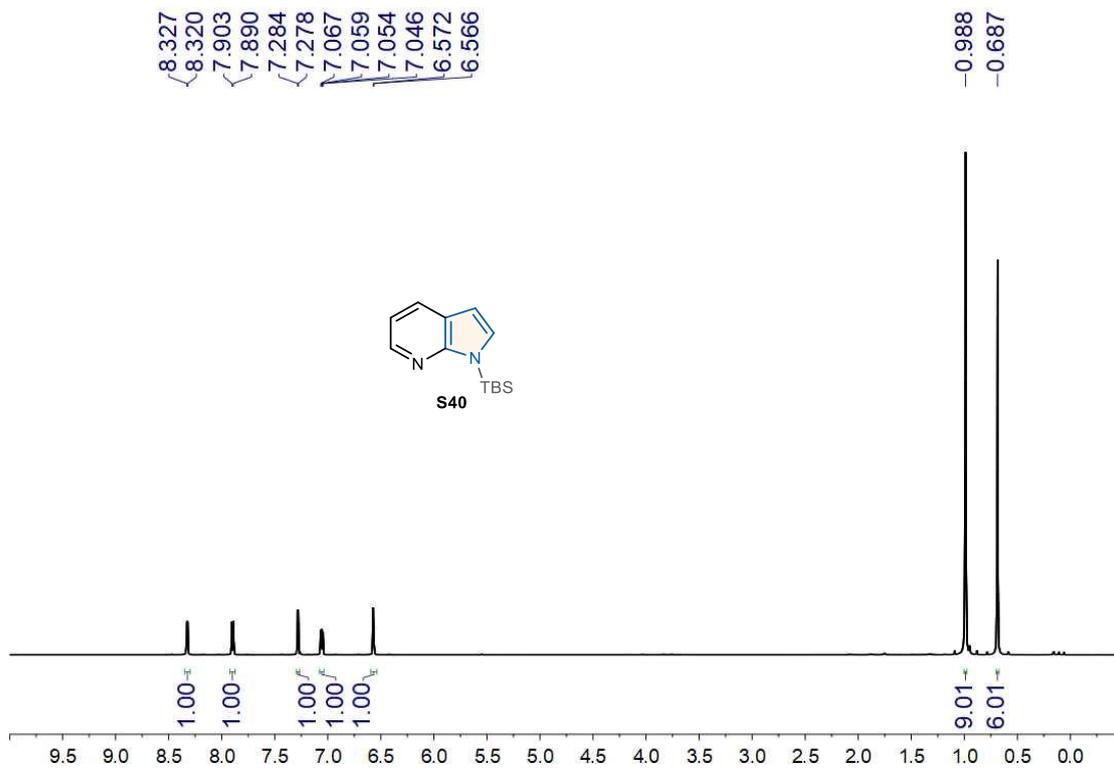




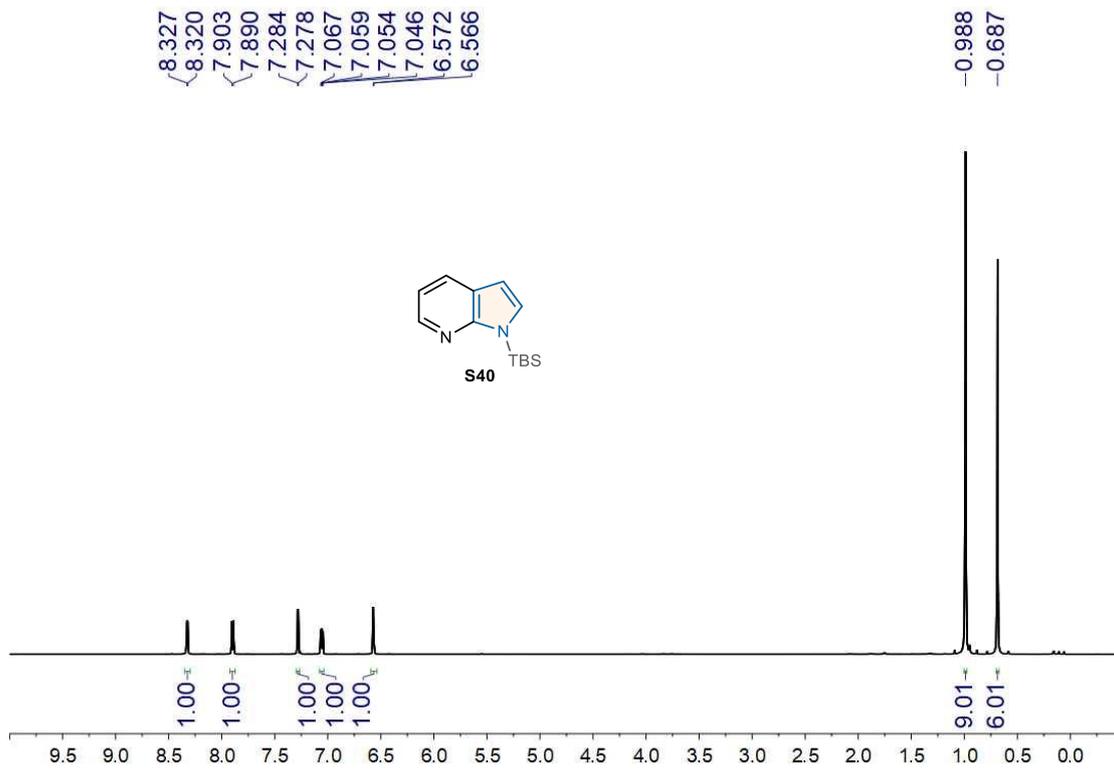




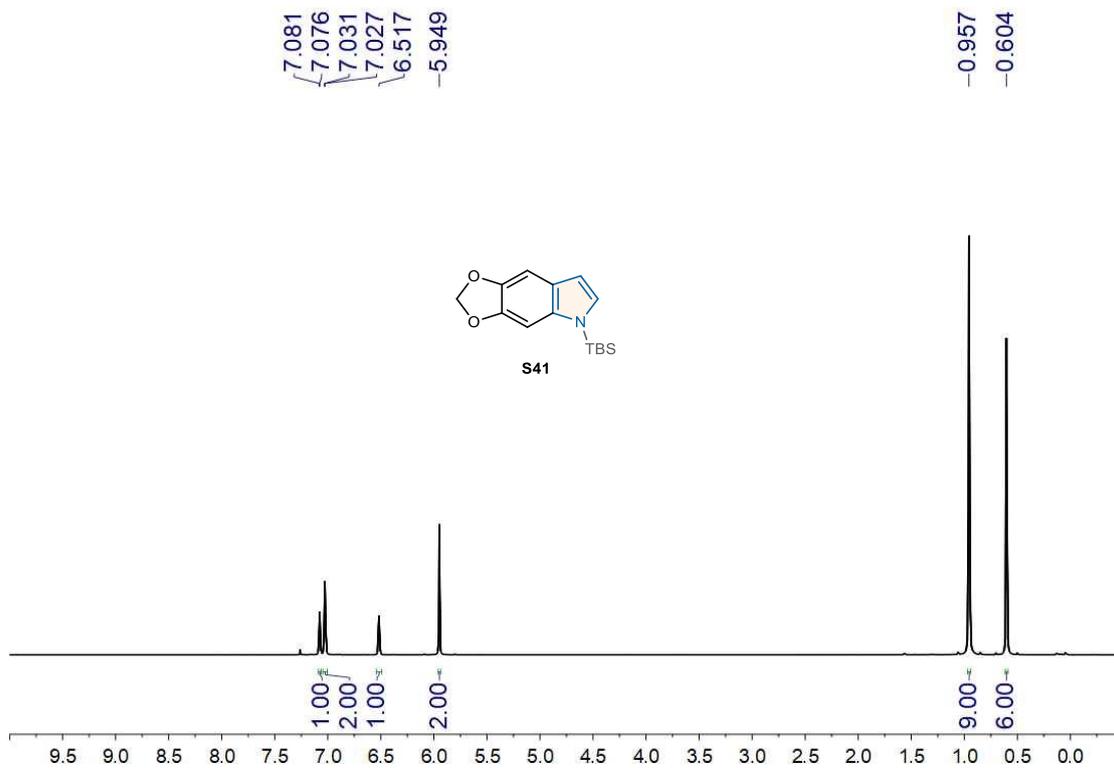
Supplementary Fig. 429. <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) spectrum of S39



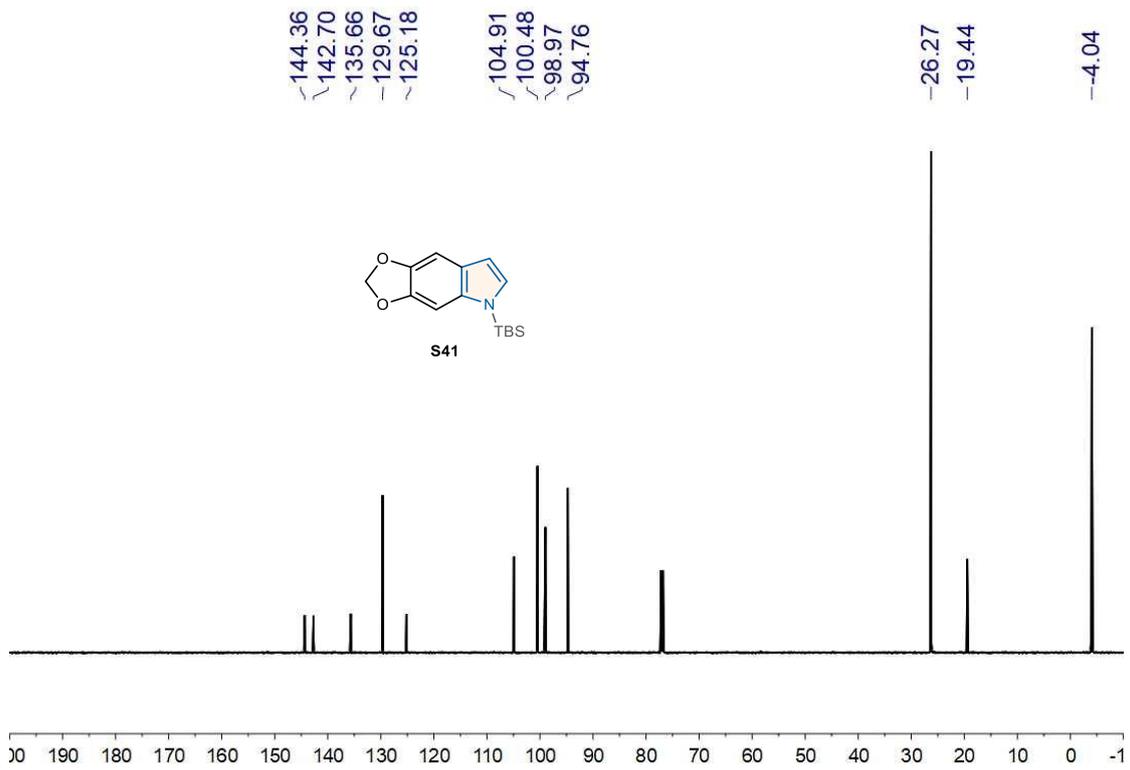
Supplementary Fig. 430. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of S40



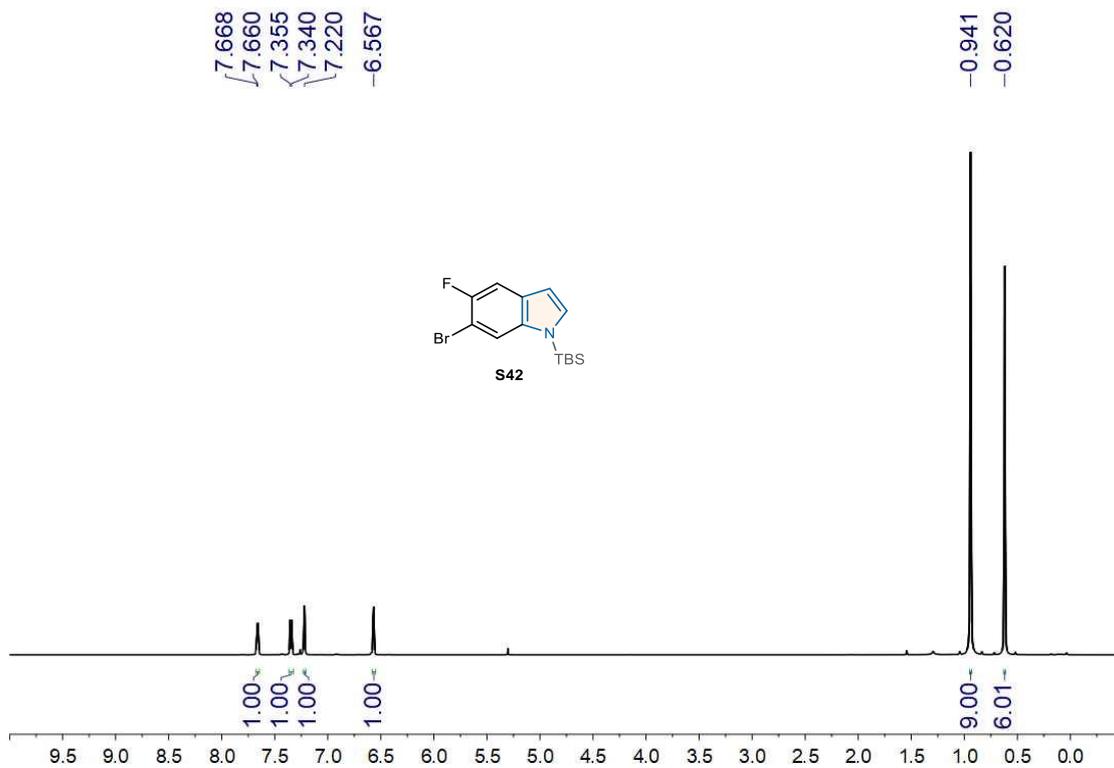
Supplementary Fig. 431.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of S40



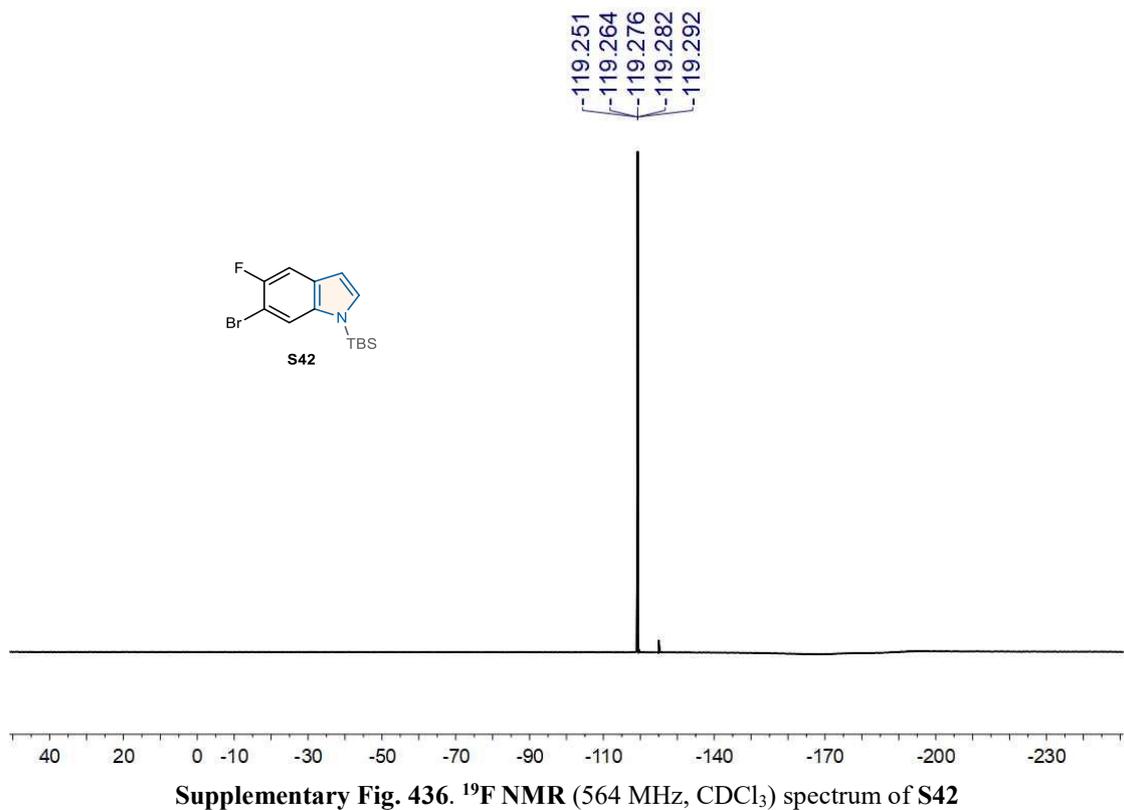
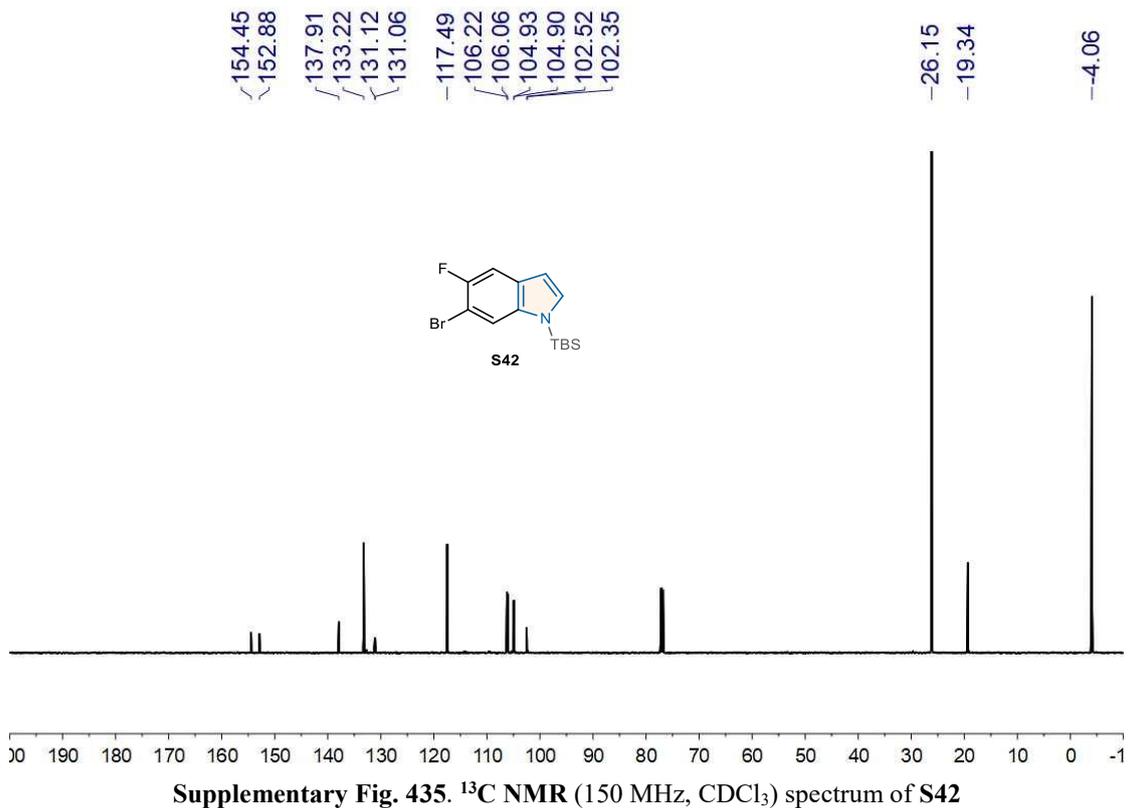
Supplementary Fig. 432.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) spectrum of S41

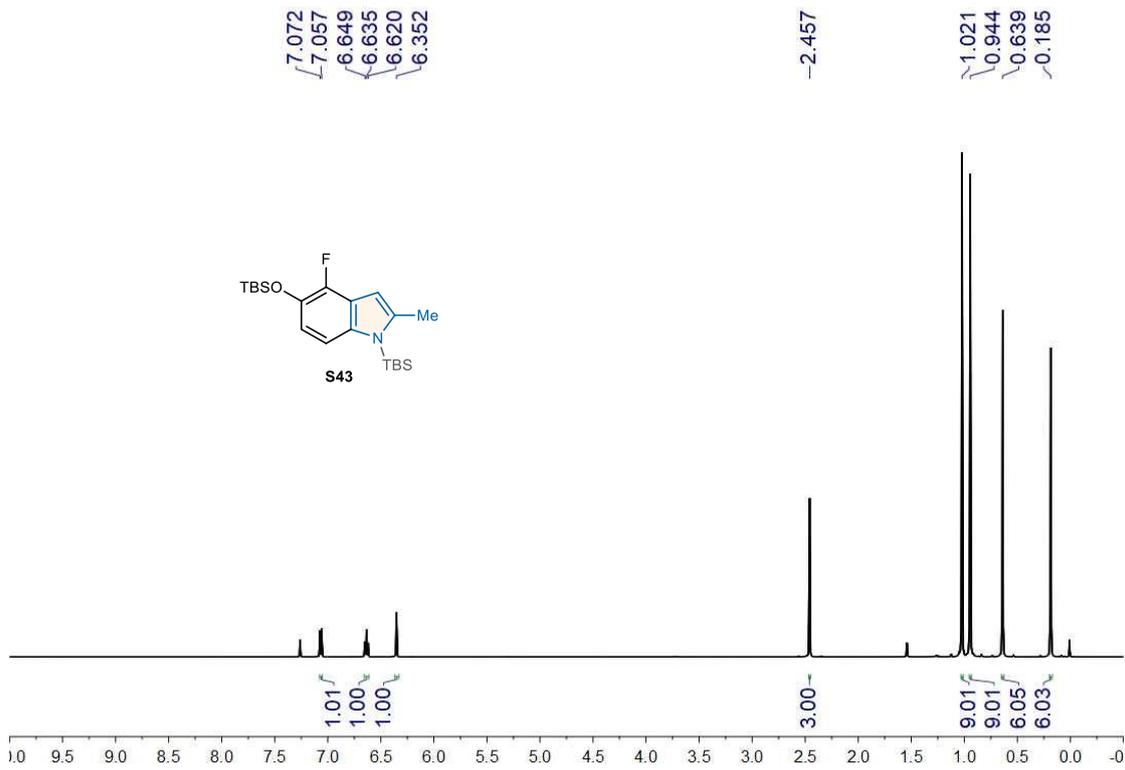


Supplementary Fig. 433.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of S41

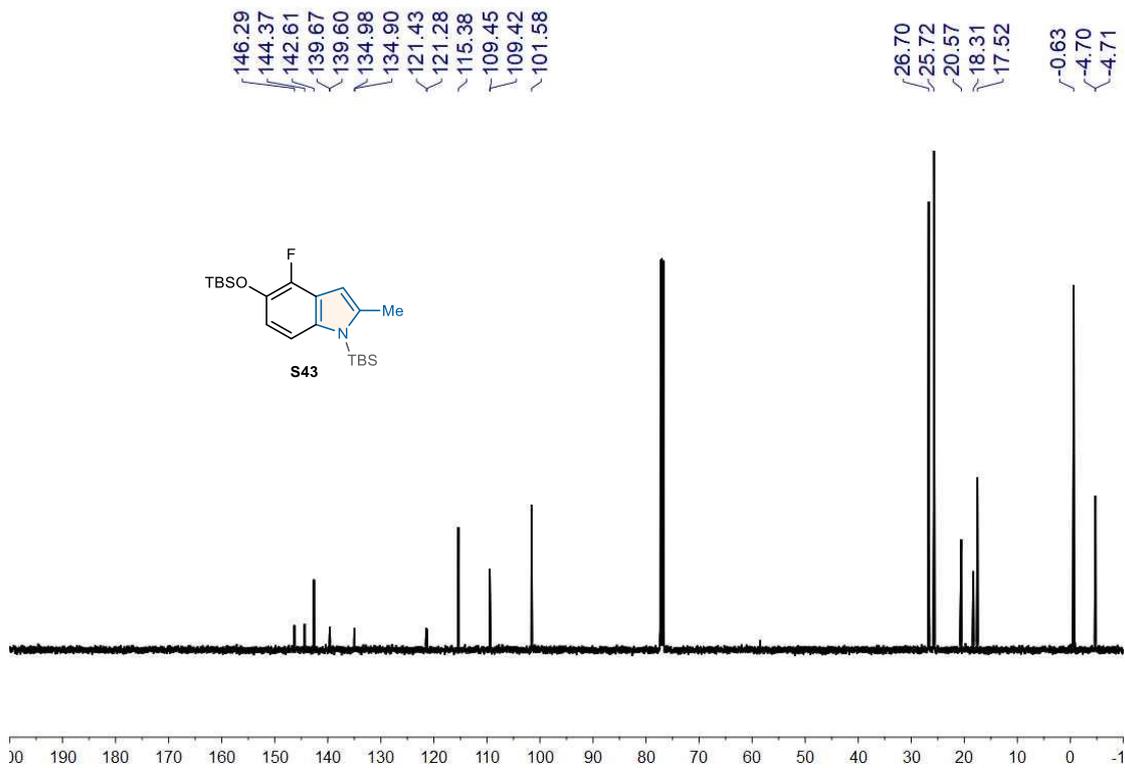


Supplementary Fig. 434.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) spectrum of S42

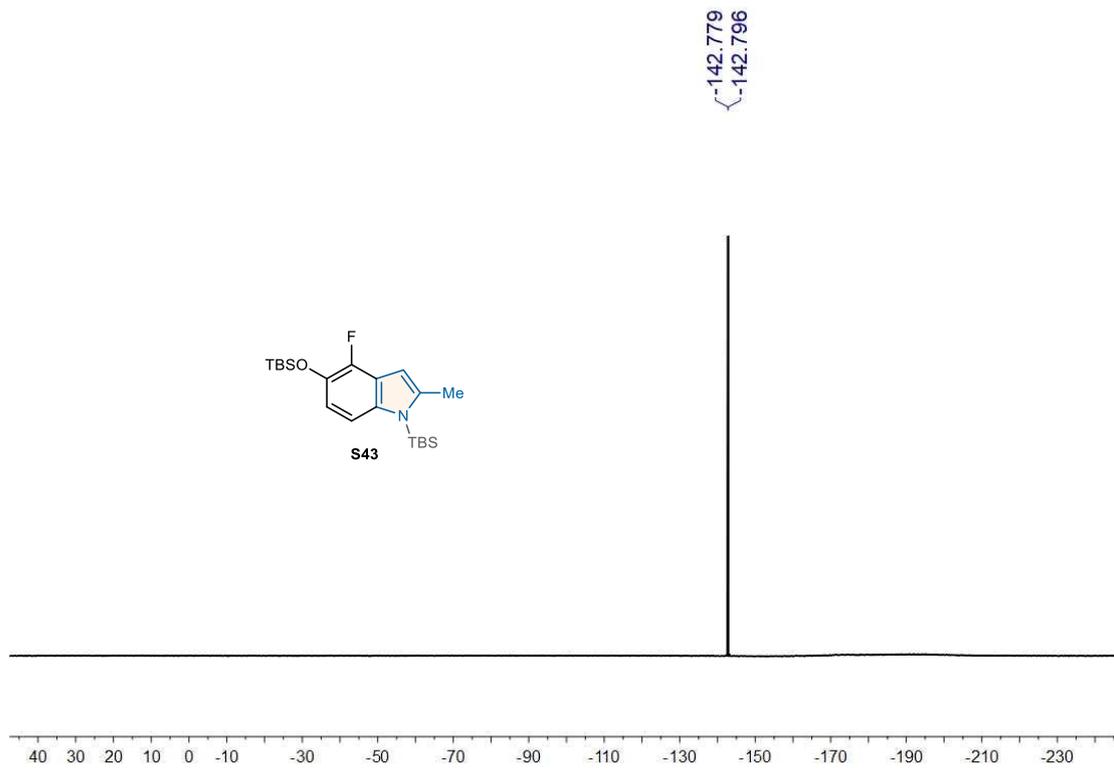




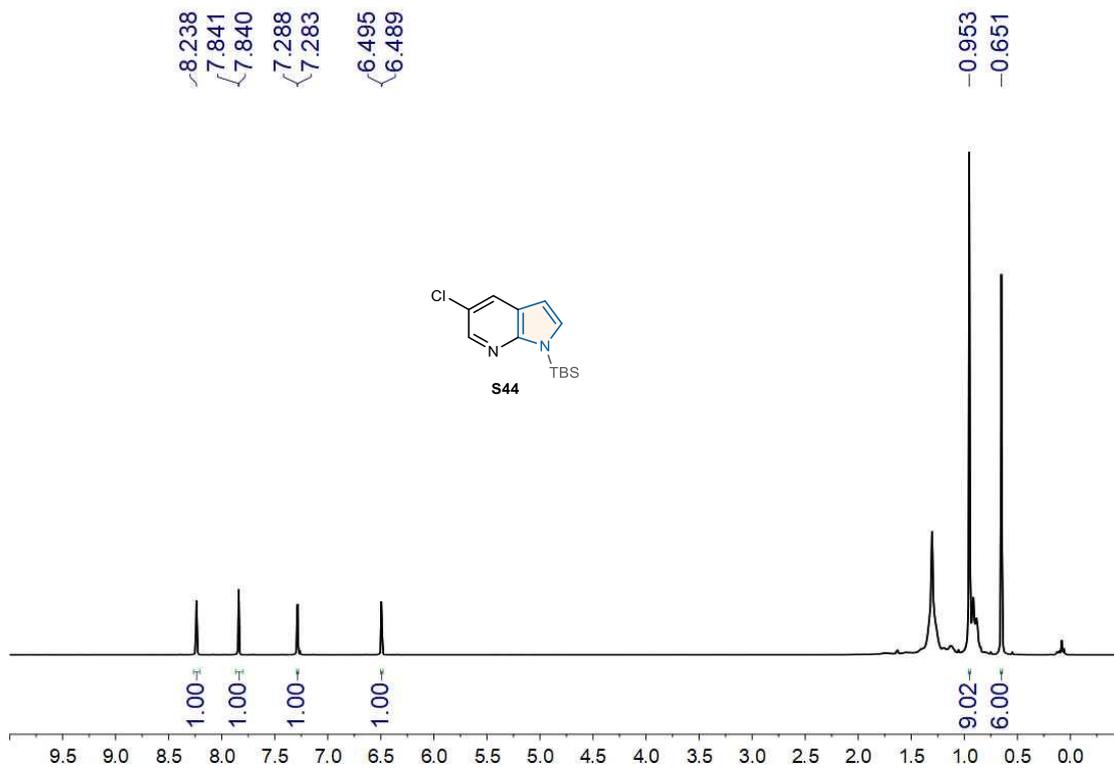
Supplementary Fig. 437. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of S43



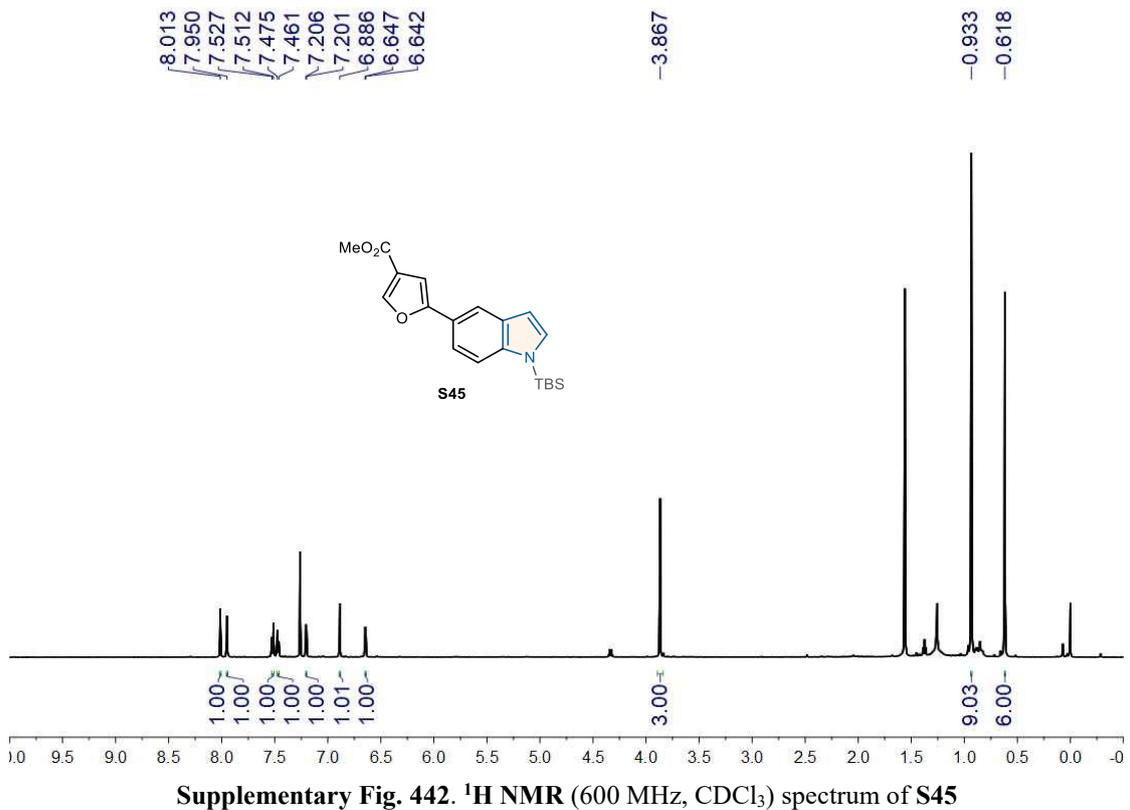
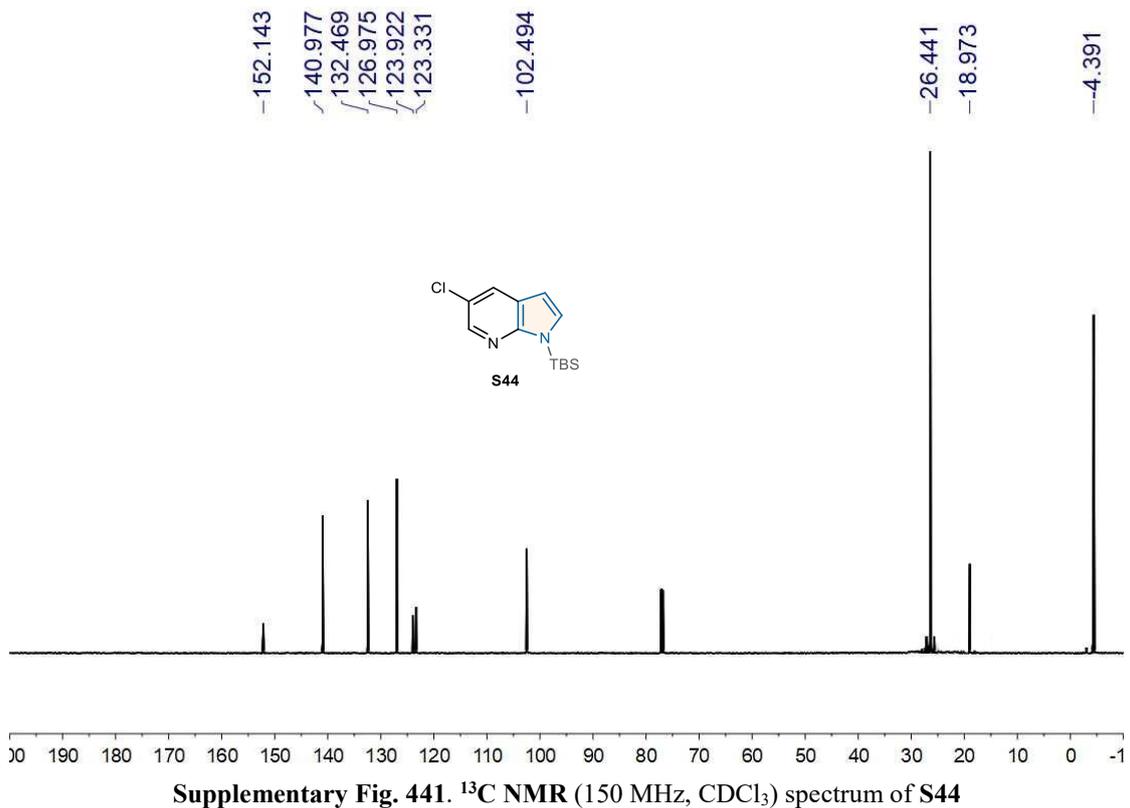
Supplementary Fig. 438. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of S43

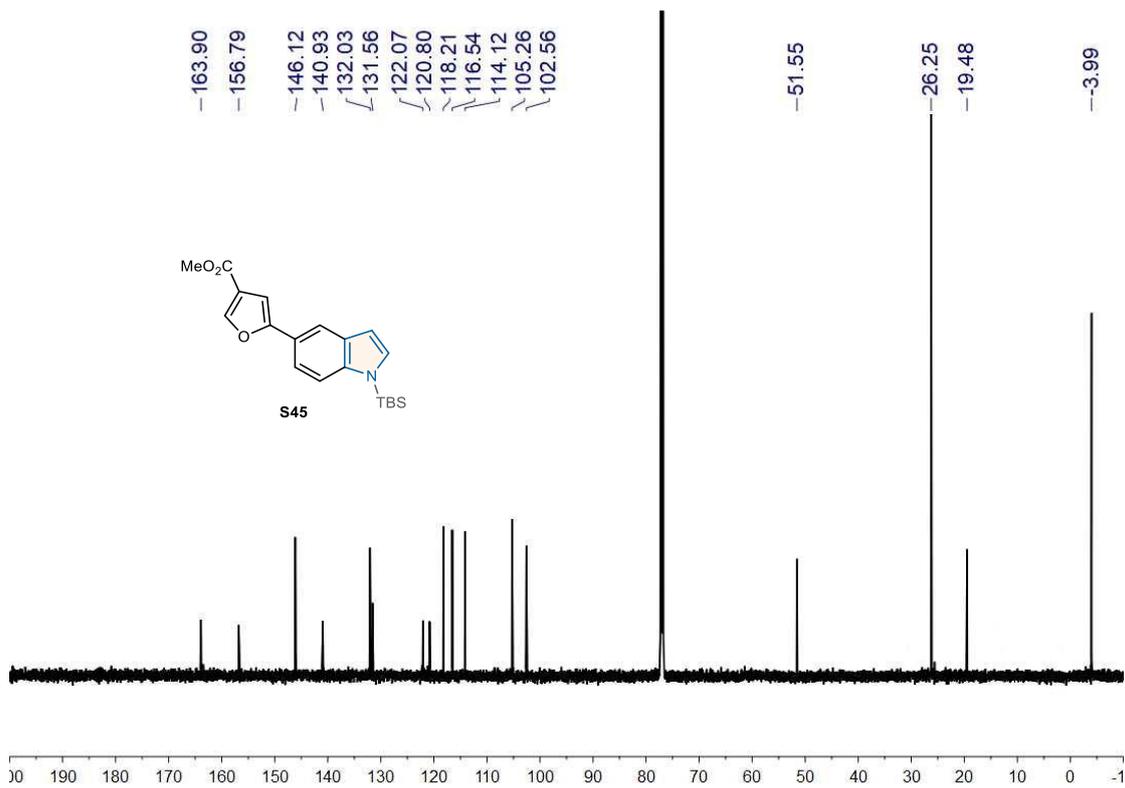


Supplementary Fig. 439.  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ) spectrum of S43

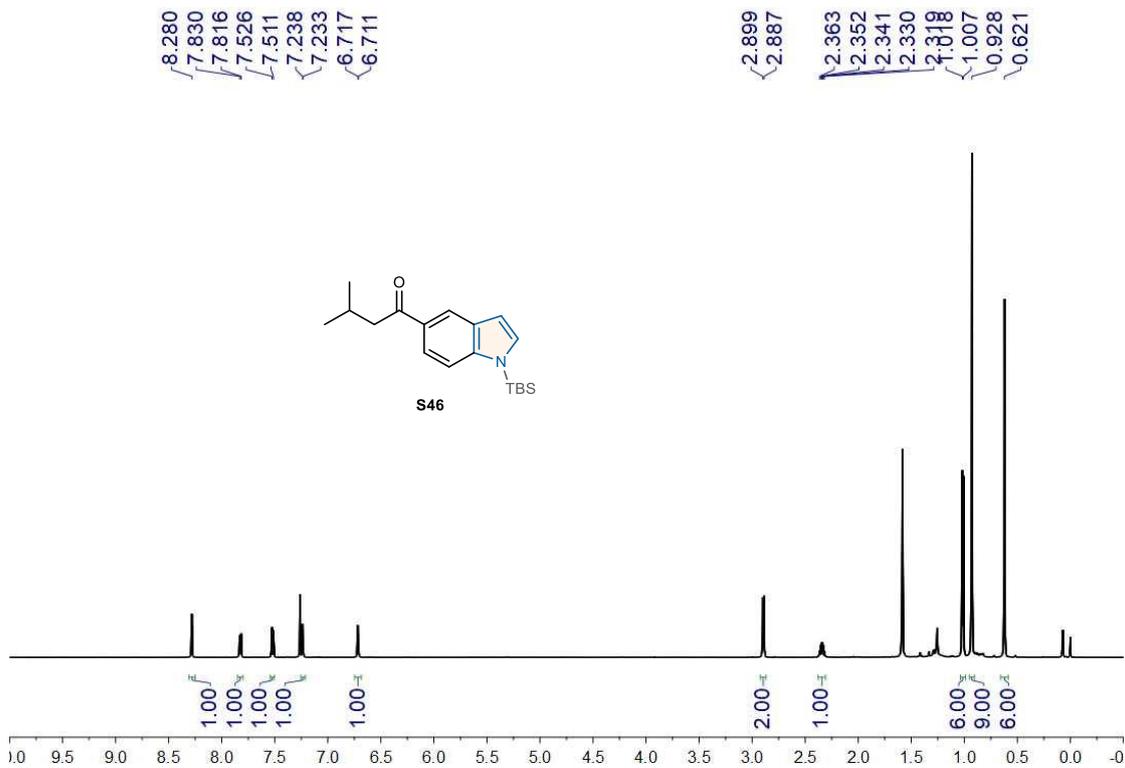


Supplementary Fig. 440.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) spectrum of S44

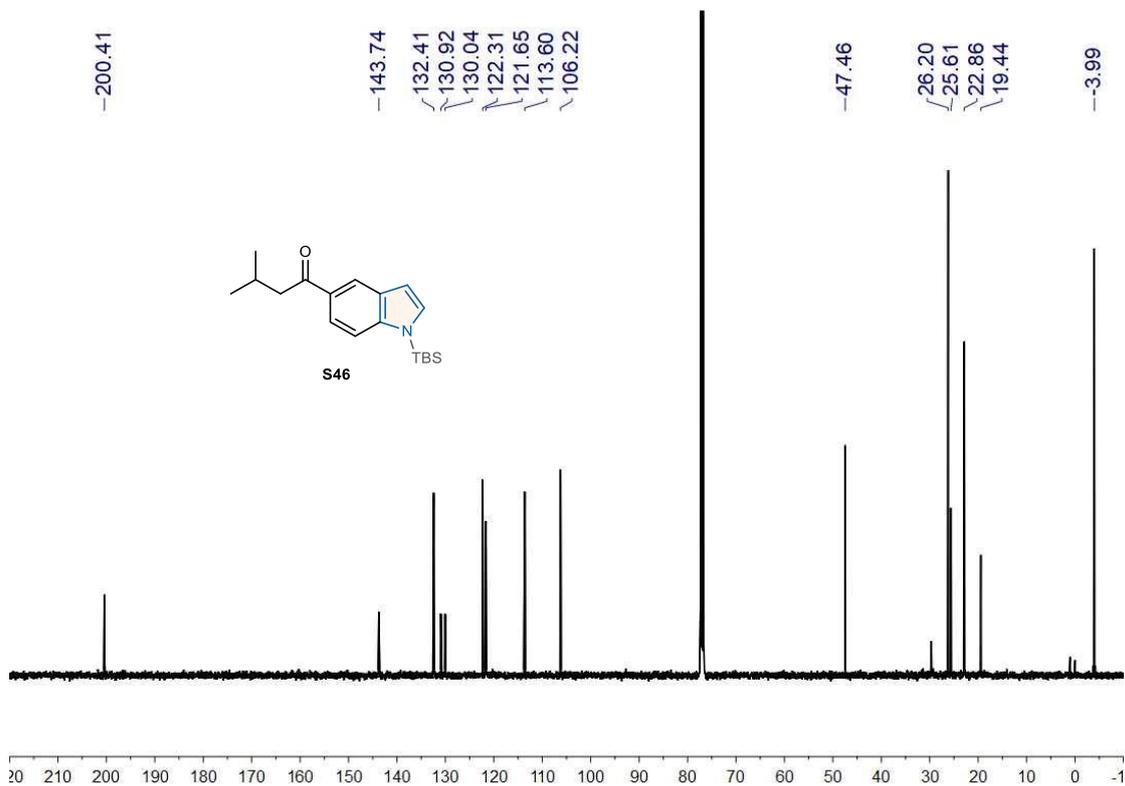




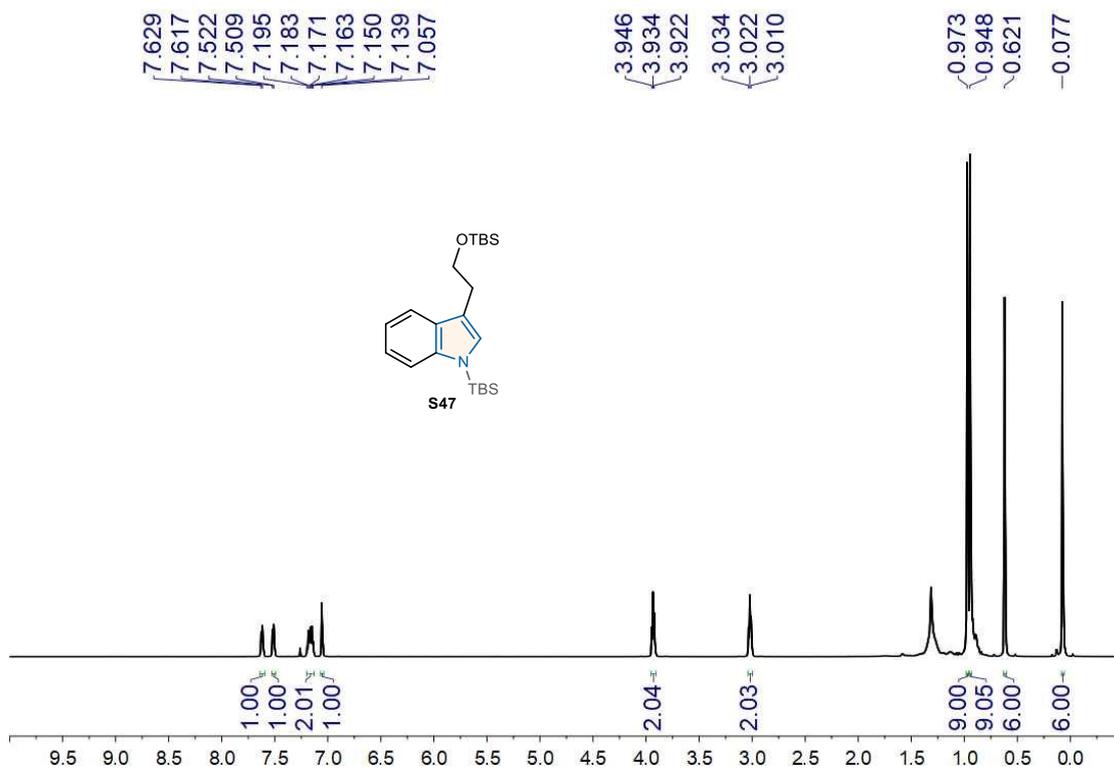
Supplementary Fig. 443. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of S45



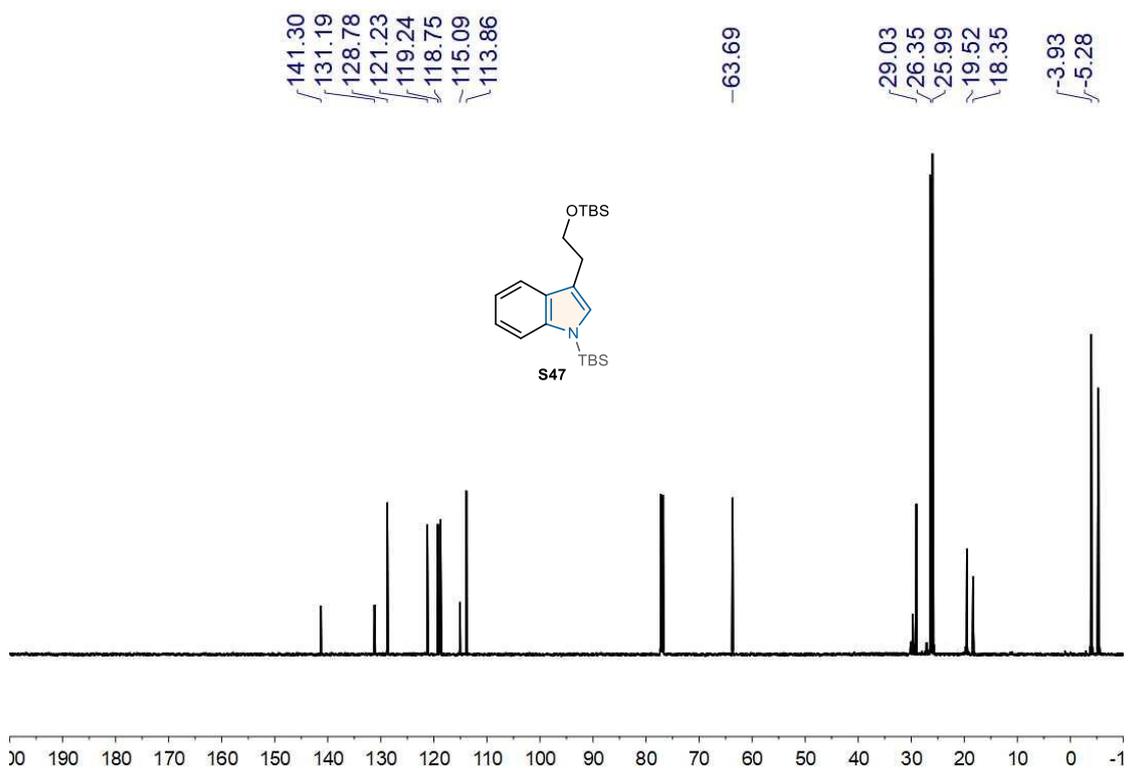
Supplementary Fig. 444. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of S46



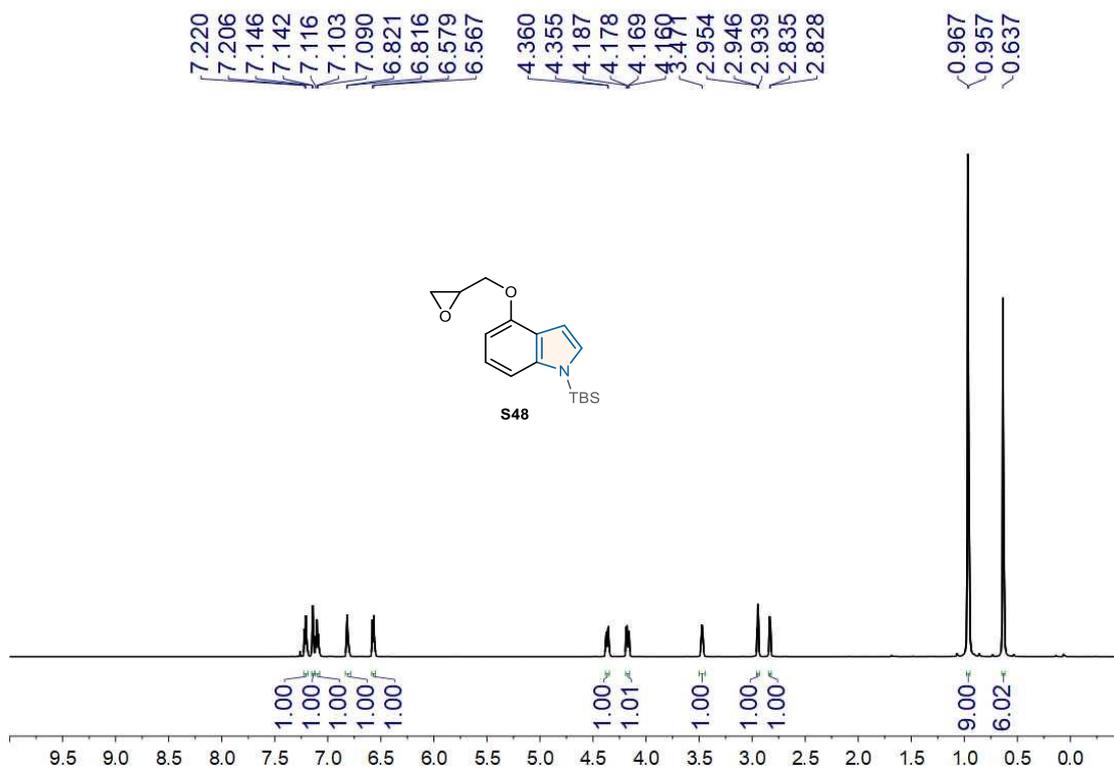
Supplementary Fig. 445. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of S46



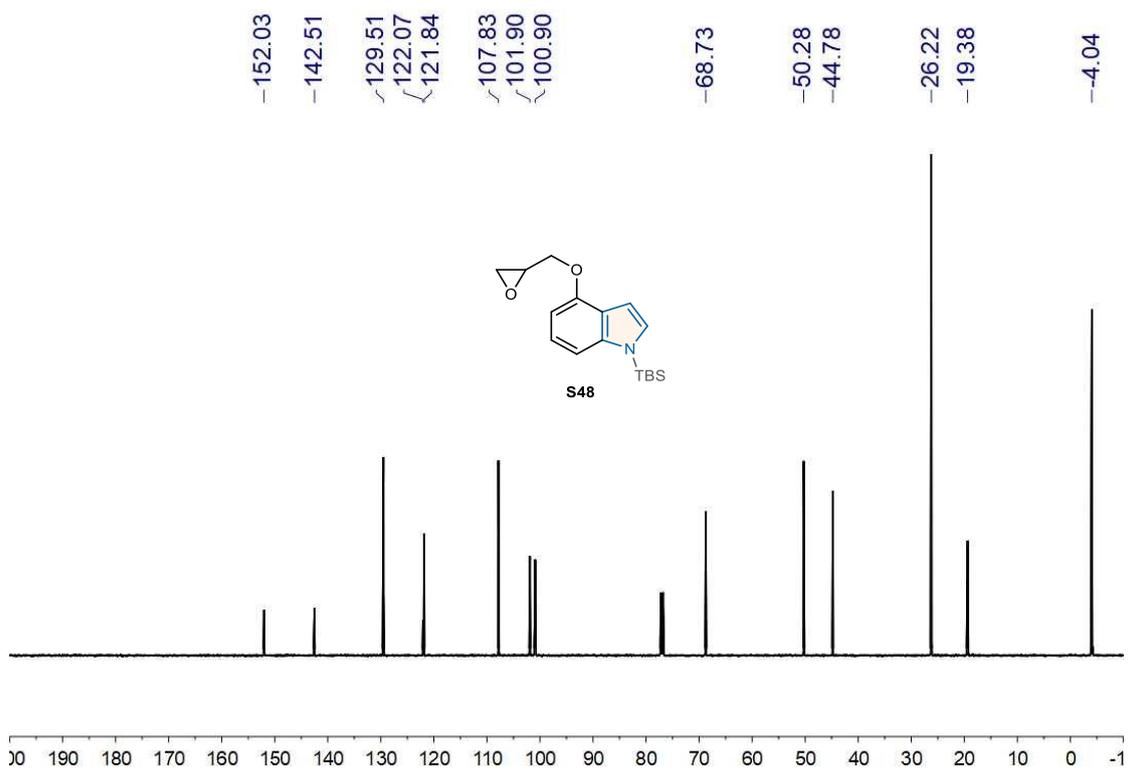
Supplementary Fig. 446. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of S47



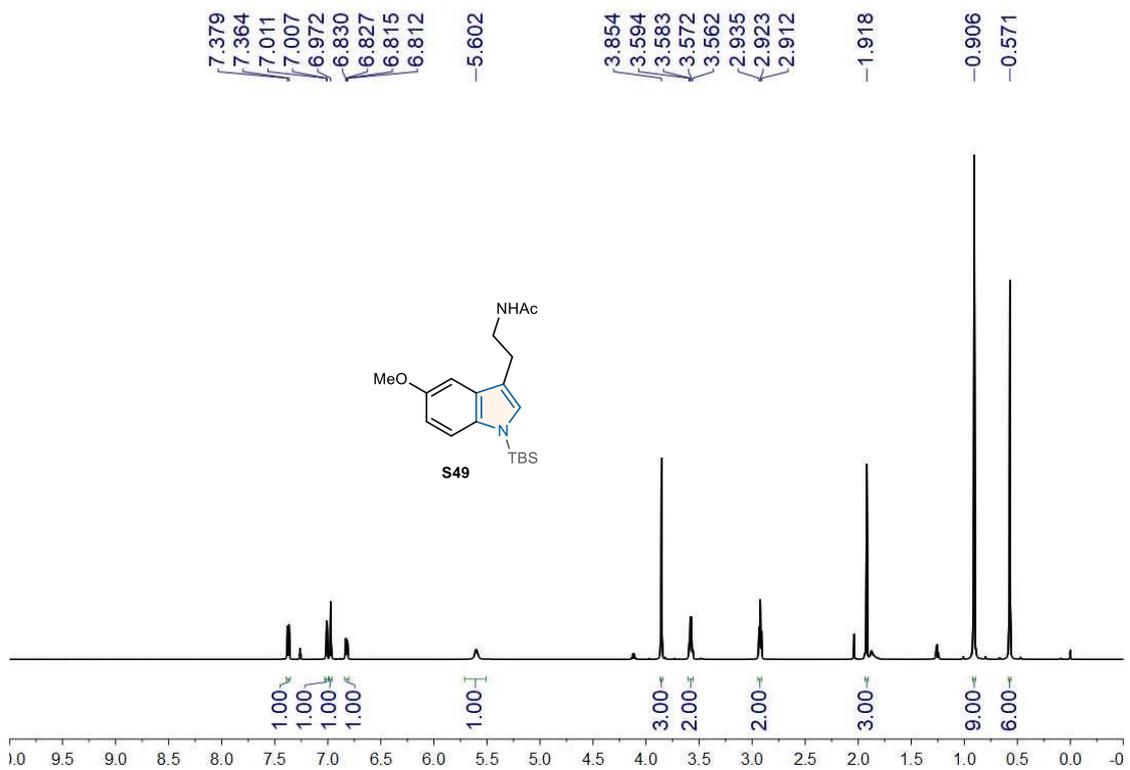
Supplementary Fig. 447. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of S47



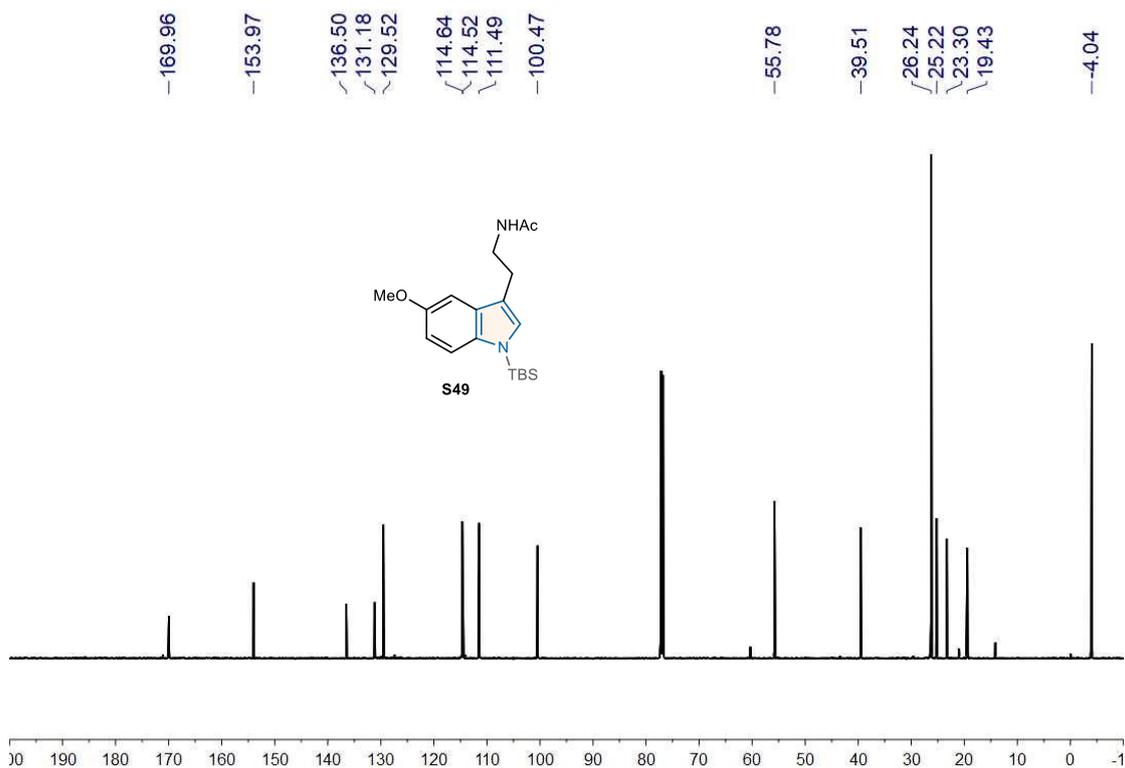
Supplementary Fig. 448. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of S48



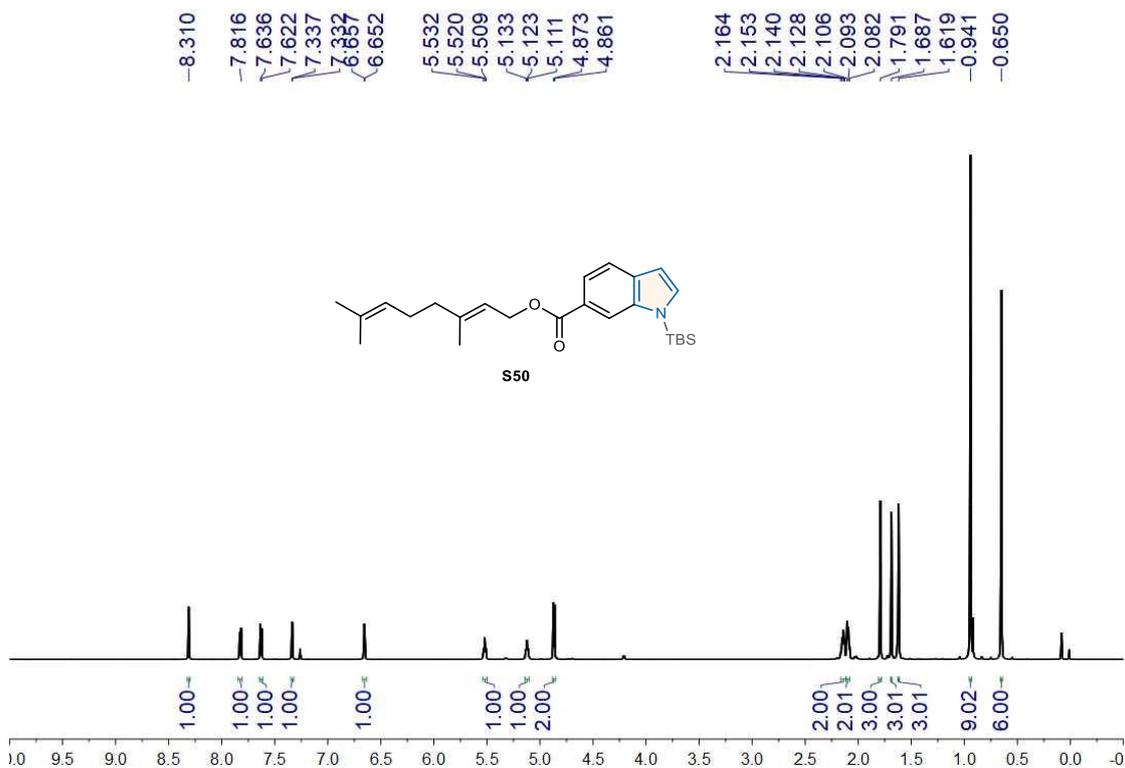
Supplementary Fig. 449. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of S48



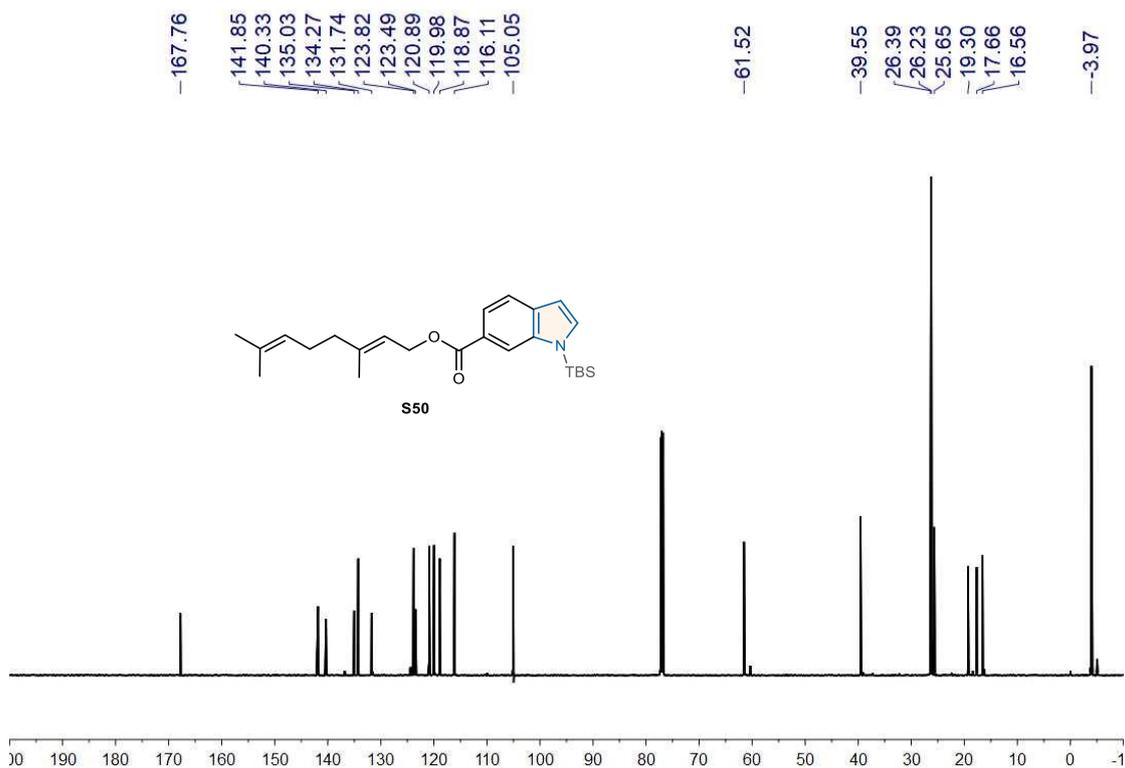
Supplementary Fig. 450. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of S49



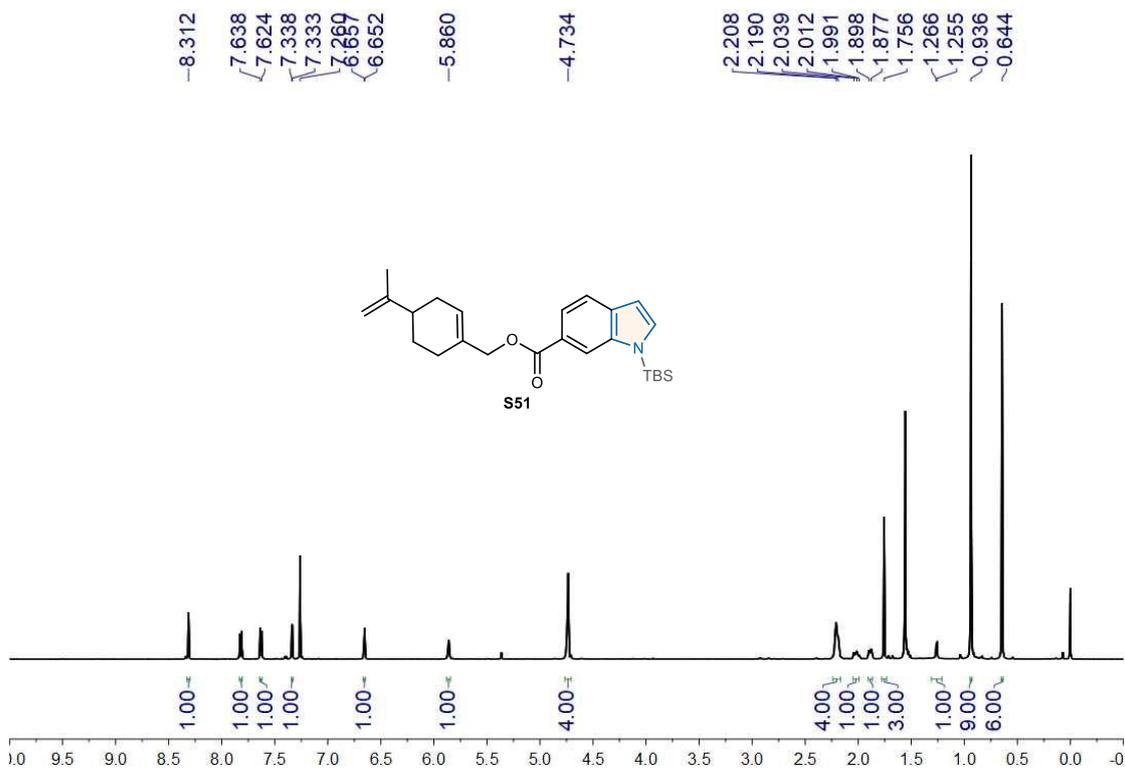
Supplementary Fig. 451. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of S49



Supplementary Fig. 452. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of S50

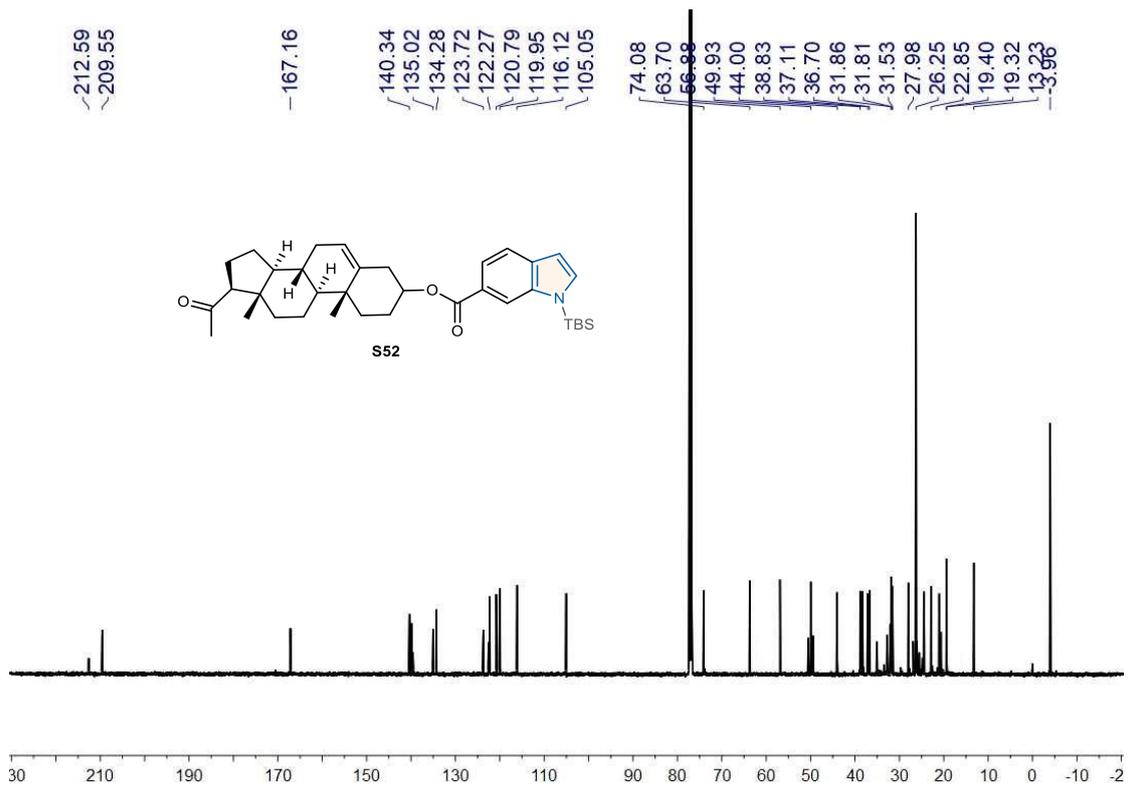


Supplementary Fig. 453. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of S50

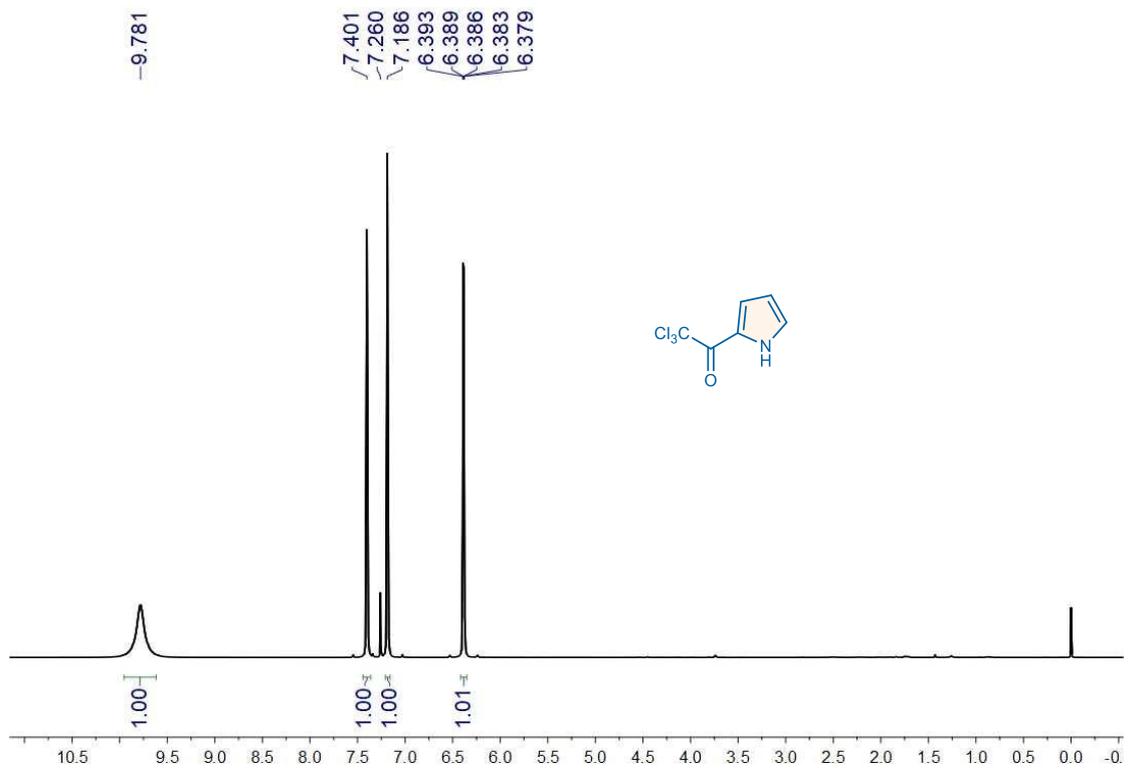


Supplementary Fig. 454. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of S51

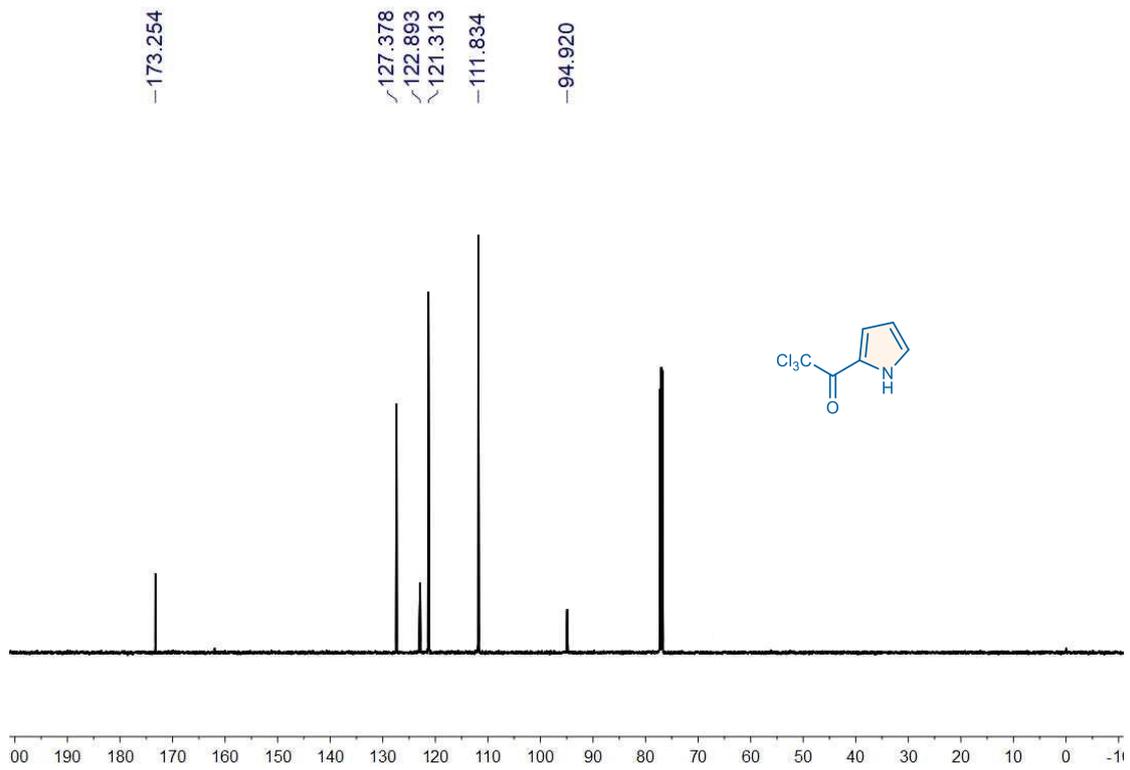




Supplementary Fig. 457.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of S52



Supplementary Fig. 458.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) spectrum of 2-(trichloroacetyl)-1H-pyrrole



Supplementary Fig. 459.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) spectrum of 2-(trichloroacetyl)-1H-pyrrole

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