Contents

1. General

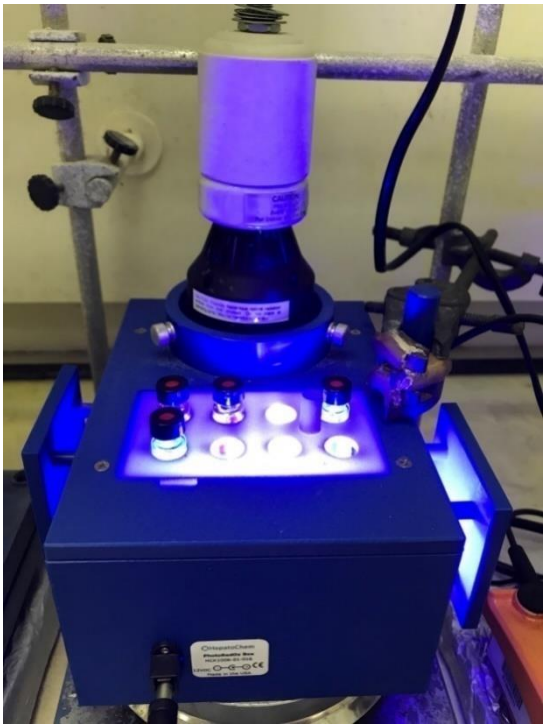
Proton, carbon and fluorine NMR spectra were recorded on Bruker 400 MHz (^{1}H NMR at 400 MHz, ^{13}C NMR at 101 MHz, and ^{19}F NMR at 377 MHz) or Bruker 500 MHz (^{1}H NMR at 500 MHz, ^{13}C NMR at 126 MHz). Chemical shifts for protons are reported in parts per million downfield from $Si(CH_3)_4$ and are referenced to residual protium in the deuterated solvent ($CHCl_3$ at 7.26 ppm, DMSO at 3.31 (H_2O), 2.50 depending on solvent used). Chemical shifts for fluorines are reported in parts per million downfield from $CFCl_3$. NMR data are presented in the following format: chemical shift (multiplicity [app = apparent, br = broad, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, ddd = doublet of doublet of doublets, m = multiplet], coupling constant [in Hz], number of equivalent nuclei by integration).

High-resolution mass spectra (ESI) were recorded on Bruker μTOF mass spectrometer. Infrared spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer as a thin film. Only selected maximum absorbances are reported (in ν_{max} (cm^{-1})). Melting points were obtained on a Leica Galen III Hot-stage melting point apparatus and microscope and on a Kofler hot block and are reported uncorrected. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel 60 F254 plates and visualised with UV light (254 or 365 nm), and/or $KMnO_4$ and/or Vanillin. Silica gel column chromatography was performed using 60 Å silica gel 40-63 μm purchased from Sigma-Aldrich. Samples were dried onto silica gel prior to addition to column.

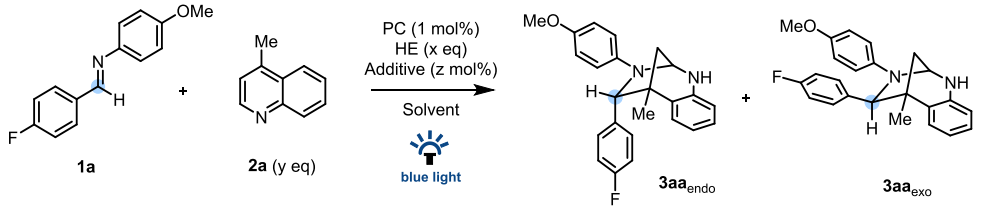
All reactions were performed using reagents obtained from Sigma-Aldrich, Acros Organics, Alfa Aesar, STREM or Fluorochem without further purification unless stated. Zinc (II) Triflimide was purchased from TCI Chemicals. Iridium photocatalysts were synthesized in house (see procedures). All water used was purified through a Merck Millipore reverse osmosis purification system prior to use. Dimethyl sulfoxide (anhydrous), tetrahydrofuran (anhydrous), 1,4-dioxane (anhydrous), and dimethylformamide (anhydrous) were used as supplied. Deuterated solvents were used as supplied. Reactions were performed in under an atmosphere of N_2 if not stated. Temperatures quoted are external. Solvents were removed under reduced pressure using Büchi Rotavapor apparatus.

2. Photoreactor Set-Up

Hepatochem PhotoRedOx Box, equipped with an EvoluChem LED 18 W light source supplied by Hepatochem. A cardboard cover was also placed over the reactor during reactions.



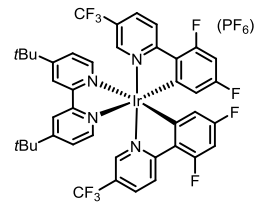
3. Full Optimization Details



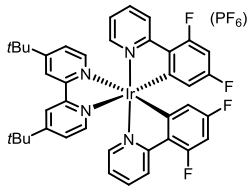
Entry	PC	HE	x eq	Solvent	y eq	[M]	Additive (z mol%)	3aa	dr
1	Ir1	HE1	1.5	DMSO	3	0.1	-	81	1.5:1
2	Ir1	HE2	1.5	DMSO	3	0.1	-	77	2.1:1
3	Ir1	HE3	1.5	DMSO	3	0.1	-	88	1.5:1
4	Ir1	HE4	1.5	DMSO	3	0.1	-	90	1.9:1
5	Ir1	HE5	1.5	DMSO	3	0.1	-	76	1.9:1
6	Ir1	HE6	1.5	DMSO	3	0.1	-	88	1.8:1
7	Ir1	HE7	1.5	DMSO	3	0.1	-	83	1.8:1
8	Ir1	HE8	1.5	DMSO	3	0.1	-	*	-
9	Ir1	HE9	1.5	DMSO	3	0.1	-	*	-
10	Ir1	HE10	1.5	DMSO	3	0.1	-	*	-
11	Ir1	HE11	1.5	DMSO	3	0.1	-	*	-
12	Ir1	HE12	1.5	DMSO	3	0.1	-	76	1.9:1
13	Ir1	HE13	1.5	DMSO	3	0.1	-	88	1.7:1
14	Ir1	HE14	1.5	DMSO	3	0.1	-	89	1.6:1
15	Ir2	HE4	1.5	DMSO	3	0.1	-	28	1.3:1
16	Ir3	HE4	1.5	DMSO	3	0.1	-	20	1.5:1
17	Ir4	HE4	1.5	DMSO	3	0.1	-	88	1.7:1
18	*fac*-Ir(ppy)$_3$	HE4	1.5	DMSO	3	0.1	-	-	-
19	[Ru(bpy)$_3$](PF$_6$)$_2$	HE4	1.5	DMSO	3	0.1	-	-	-
20	[Ru(dtbbpy)$_3$](PF$_6$)$_2$	HE4	1.5	DMSO	3	0.1	-	-	-
21	4-CzIPN	HE4	1.5	DMSO	3	0.1	-	77	1.8:1
22	Ir1	HE4	2	DMSO	3	0.1	-	89	1.9:1
23	Ir1	HE4	1.3	DMSO	3	0.1	-	86	2.0:1
24	Ir1	HE4	1.1	DMSO	3	0.1	-	67	2.0:1
25	Ir1	HE4	1	DMSO	3	0.1	-	63	1.3:1
26	Ir1	HE4	1.5	DMSO	1.5	0.1	-	67	1.8:1
27	Ir1	HE4	1.5	DMSO	2	0.1	-	84	2.4:1
28	Ir1	HE4	1.5	DMSO	4	0.1	-	81	1.8:1
29	Ir1	HE4	1.5	DMSO	5	0.1	-	81	2.0:1
30	Ir1	HE4	1.5	DMSO	3:1	0.1	-	2	-
31	Ir1	HE4	1.5	DMF	3	0.1	-	28	1.3:1
32	Ir1	HE4	1.5	DCM	3	0.1	-	61	1.9:1
33	Ir1	HE4	1.5	DMA	3	0.1	-	3	-
34	Ir1	HE4	1.5	1,4-dioxane	3	0.1	-	c.m.	-
35	Ir1	HE4	1.5	MeOH	3	0.1	-	-	-
36	Ir1	HE4	1.5	DMSO:MeOH (10:1)	3	0.1	-	84	1.7:1
37	Ir1	HE4	1.5	DMSO:H$_2$O (10:1)	3	0.1	-	84	1.9:1
38	Ir1	HE4	1.5	DMSO:DCM (10:1)	3	0.1	-	82	2.0:1
39	Ir1	HE4	1.5	DMSO:H$_2$O (1:1)	3	0.1	-	-	-
40	Ir1	HE4	1.5	DMSO	3	0.25	-	84	1.9:1
41	Ir1	HE4	1.5	DMSO	3	0.5	-	77	2.1:1
43	Ir1	HE4	1.5	DMSO	3	0.067	-	91	2.4:1
43	Ir1	HE4	1.5	DMSO	3	0.1	Sc(OTf)$_3$ (30)	100	1.1:1
44	Ir1	HE4	1.5	DMSO	3	0.1	TFA (30)	100	1.0:1
45	Ir1	HE4	1.5	DMSO	3	0.1	AgSbF$_6$ (30)	92	1.2:1
46	Ir1	HE4	1.5	DMSO	3	0.1	Quinuclidine (30)	-	-
47	Ir1	HE4	1.5	DMSO	3	0.1	NiCl$_2$(DME) (30)	36	1:1
48	Ir1	HE4	1.5	DMSO	3	0.1	Zn(OTf)$_2$ (30)	94	2.8:1
49	Ir1	HE4	1.5	DMSO	3	0.1	In(OTf)$_3$ (30)	100	1.4:1
50	Ir1	HE4	1.5	DMSO	3	0.1	Al(O*i*Pr)$_3$ (30)	45	2.8:1
51	Ir1	HE4	1.5	DMSO	3	0.1	Zn(OAc)$_2$ (30)	12	1:1
52	Ir1	HE4	1.5	DMSO	3	0.1	Zn (30)	54	1.8:1
53	***Ir1***	***HE4***	***1.5***	***DMSO***	***3***	***0.1***	***Zn(NTf$_2$)$_2$ (30)***	***94***	***3.2:1***
54	Ir1	HE4	1.5	DMSO	3	0.1	ZnBr$_2$ (30)	74	2.4:1
55	Ir1	HE4	1.5	DMSO	3	0.1	MAD (30)	c.m.	-
55	Ir1	HE4	1.5	DMSO	3	0.1	Zn(NTf$_2$)$_2$ (10)	94	2.9:1
56	Ir1	HE4	1.5	DMSO	3	0.1	Zn(NTf$_2$)$_2$ (20)	93	3.0:1
57	Ir1	HE4	1.5	DMSO	3	0.1	Zn(NTf$_2$)$_2$ (50)	94	3.1:1
58	Ir1	HE4	1.5	DMSO	3	0.1	Zn(NTf$_2$)$_2$ (100)	94	2.2:1
59	Ir1 (3 mol%)	HE4	1.5	DMSO	3	0.1	Zn(NTf$_2$)$_2$ (50)	100	2.2:1
60**	Ir1	HE4	1.5	DMSO	3	0.1	Zn(NTf$_2$)$_2$ (50)	95	3.0:1

c.m. = complex mixture * Hantzsch addition products formed. ** *in situ* formation of imine . MAD = methylaluminium bis(2,6-di-tert-butyl-4-methylphenoxide)

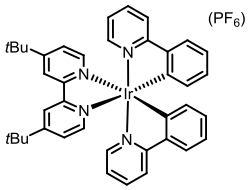
KEY



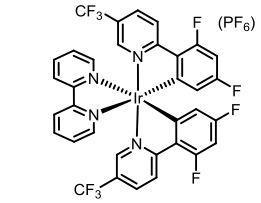
[Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (Ir1)



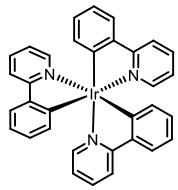
[Ir(dFppy)$_2$(dtbbpy)]PF$_6$ (Ir2)



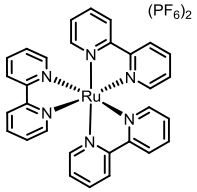
[Ir(ppy)$_2$(dtbbpy)]PF$_6$ (Ir3)



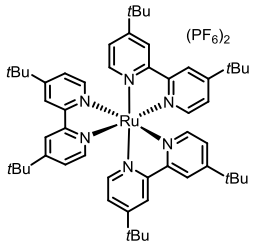
[Ir(dF(CF$_3$)ppy)$_2$(bpy)]PF$_6$ (Ir4)



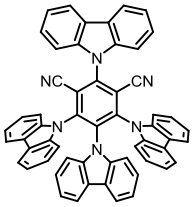
fac-Ir(ppy)$_3$



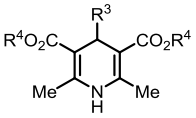
[Ru(bpy)$_3$](PF$_6$)$_2$



[Ru(dtbbpy)$_3$](PF$_6$)$_2$



4-CzIPN

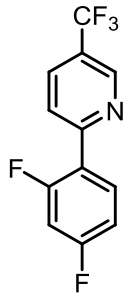


R^3	R^4	HE
H	Et	HE1
Me	Et	HE2
Ph	Et	HE3
4-CO_2MePh	Et	HE4
Et	Et	HE5
4-OMe-Ph	Et	HE6
4-CF_3-Ph	Et	HE7
Cy	Et	HE8
*i*Pr	Et	HE9
Cy	Me	HE10
Bn	Et	HE11
H	Me	HE12
4-F-Ph	Et	HE13
4-Br-Ph	Et	HE14

4. Synthesis of Starting Materials

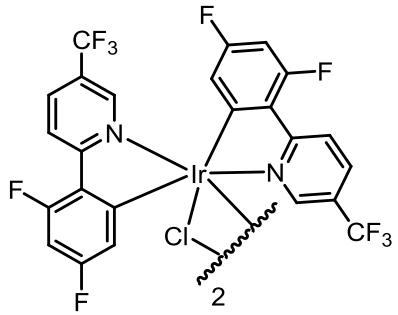
4.1: Synthesis of Photocatalyst

Synthesis of 2-(2,4-difluorophenyl)-5-(trifluoromethyl)pyridine



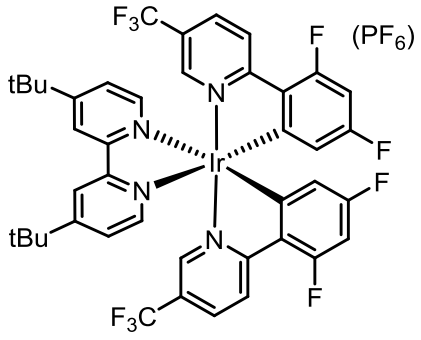
To a three-necked 250 mL round bottomed flask was charged with 2,4-difluorophenylboronic acid (5.68 g, 36.0 mmol), 2-bromo-5-trifluoromethylpyridine (6.78 g, 30.0 mmol), potassium carbonate (12.4 g, 90.0 mmol), palladium acetate (202 mg, 0.90 mmol) and triphenylphosphine (472 mg, 1.80 mmol). The flask was equipped with a condenser then evacuated and refilled with N_2 three times. Following this, toluene (40 mL), water (40 mL) and ethanol (8 mL) were added *via* septum. The flask was heated to reflux for 16 h. After this time, the flask was cooled to room temperature and was added water (100 mL). The organic phase was separated and then the aqueous phase re-extracted with Et_2O (3 x 200 mL). The combined organics were washed with brine (3 x 200 mL) and then dried over $MgSO_4$ and concentrated *in vacuo*. The crude residue was the then purified *via* silica gel column chromatography (EtOAc:Pentane 1:99 – 4:96 v:v) to give the title compound as a white solid (6.62 g, 25.5 mmol, 85%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.85 (dd, *J* = 2.4, 1.2 Hz, 1 H), 7.99 (td, *J* = 8.9, 6.6 Hz, 1 H), 7.87 (dd, *J* = 8.3, 2.4 Hz, 1 H), 7.82 – 7.76 (m, 1 H), 6.98 – 6.88 (m, 1 H), 6.82 (ddd, *J* = 11.3, 8.7, 2.5 Hz, 1 H). **^{19}F NMR** (377 MHz, $CDCl_3$): δ -62.49, -107.28 (t, *J* = 8.0 Hz), -112.04 (d, *J* = 10.0 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 164.0 (dd, *J* = 252.8, 12.5 Hz), 161.1 (dd, *J* = 253.6, 12.0 Hz), 155.9, 146.7 (q, *J* = 4.2 Hz), 133.8 (q, *J* = 3.5 Hz), 132.6 (dd, *J* = 10.0, 4.2 Hz), 125.3 (q, *J* = 33.2 Hz), 123.7 (q, *J* = 272.3 Hz), 123.7 (d, *J* = 11.1 Hz), 122.5 (dd, *J* = 11.3, 3.8 Hz), 112.4 (dd, *J* = 21.1, 3.6 Hz), 106.5 – 101.0 (app t). Data was consistent with literature precedent.[1]

Synthesis of $[Ir(dF(CF_3)ppy)_2Cl]_2$



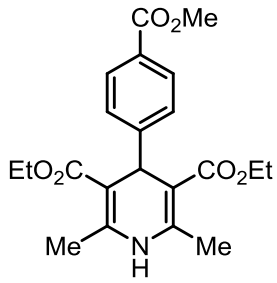
To a three-necked 100 mL round bottomed flask was charged iridium(III) chloride hydrate (448 mg, 1.50 mmol) and 2-(2,4-difluorophenyl)-5-(trifluoromethyl)pyridine (856 mg, 3.30 mmol). The flask was equipped with a condenser, then evacuated and refilled with nitrogen three times. Rigorously degassed 2-ethoxyethanol (18 mL) and water (6 mL) were added *via* syringe. The reaction mixture was heated 150 °C for 16 h. After this time the reaction mixture was allowed to return to room temperature and the bright yellow precipitate formed was filtered under a blanket of N_2, washing with water (150 mL) and then hexane (60 mL), to give title compound after further removal of water *via* high vacuum (960 mg, 0.65 mmol, 86%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.51 (d, *J* = 2.1 Hz, 1 H), 8.46 (dd, *J* = 8.7, 3.0 Hz, 1 H), 8.05 (dd, *J* = 8.7, 2.3 Hz, 1 H), 6.43 (ddd, *J* = 12.5, 8.8, 2.3 Hz, 1 H), 5.07 (dd, *J* = 8.8, 2.3 Hz, 1 H). **^{19}F NMR** (377 MHz, $CDCl_3$): δ -62.36 (12 F), -103.41 – -103.72 (m, 4 F), -106.97 – -107.91 (m, 4 F). Data was consistent with literature precedent.[1]

Synthesis of (Ir[dF(CF_3)ppy)$_2$](dtbpy))PF_6 – **[Ir]**



To a three-necked 250 mL round bottomed flask was charged [Ir(dF(CF_3)ppy)$_2$Cl]$_2$ (960 mg, 0.65 mmol) and 4,4'-di-*tert*-butyl-2,2'-dipyridyl (429 mg, 1.60 mmol). The flask was equipped with a reflux condenser, then evacuated and refilled three times with nitrogen. Rigorously degassed ethylene glycol (44 mL) was then added *via* syringe. The reaction mixture was then heated to 150 °C for 16 h. After this time the flask was allowed to return to room temperature. The mixture was diluted in water (300 mL) and hexane (300 mL). The aqueous phase was then separated and then re-extracted with hexane (2 x 300 mL). The aqueous phase was then decanted into a 2 L conical flask and equipped with a stirrer bar. The flask was heated at 80 °C for 1 hour to remove residual hexane. The flask was allowed to return to room temperature, and an aqueous solution of potassium hexafluorophosphate (7 g in 70 mL water) was added with stirring, and a vibrant yellow precipitate was formed. The mixture was then allowed to stand at 5 °C for 1 hour, before the precipitate was collected *via* vacuum filtration washing with water (150 mL) and hexane (100 mL), The collected powdery solid was then subjected to further water removal *via* high vacuum, to give the title compound, (915 mg, 0.82 mmol, 63%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.88 (d, *J* = 2.1 Hz, 2 H), 8.47 (dd, *J* = 8.7, 3.1 Hz, 2 H), 8.04 (dd, *J* = 8.8, 2.1 Hz, 2 H), 7.86 (d, *J* = 5.9 Hz, 2 H), 7.59 (dd, *J* = 5.9, 1.9 Hz, 2 H), 7.41 (s, 2 H), 6.64 (ddd, *J* = 11.6, 8.9, 2.3 Hz, 2 H), 5.63 (dd, *J* = 8.0, 2.4 Hz, 2 H), 1.50 (s, 18 H). **^{19}F NMR** (377 MHz, $CDCl_3$): δ -62.99 (6 F), -72.24 (3 F), -74.13 (3 F), -101.81 (dt, *J* = 12.4, 8.4 Hz, 2 F), -105.92 (td, *J* = 12.4, 3.4 Hz, 2 F). NMR Spectra matched those from commercial sources.

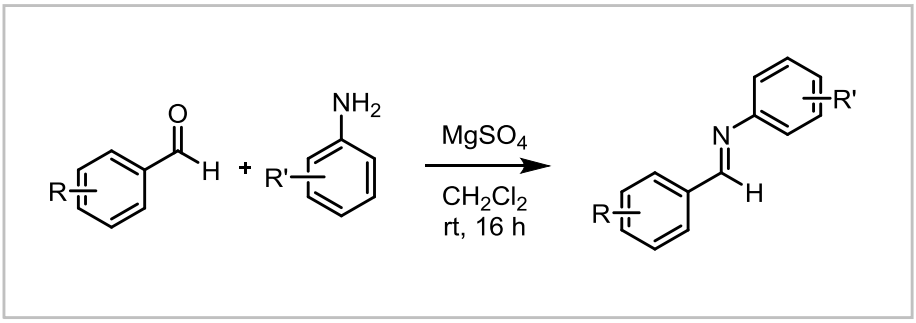
4.2: Synthesis of Hantzsch Ester



To a 1 L rbf was added methyl 4-formylbenzoate (8.2 g, 50 mmol), ethyl acetoacetate (12.7 mL, 100 mmol), ammonium acetate (3.85 g, 50 mmol), and EtOH (200 mL). The reaction mixture was heated to 80 °C for 16 h. After this time the reaction mixture was cooled to rt and concentrated *in vacuo*. The crude residue was dispersed in CH_2Cl_2 (300 mL) and brine (300 mL). The organic phase was extracted and the aqueous phase re-extracted with CH_2Cl_2 (2 x 300 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The crude powder was purified *via* recrystallization from EtOH to give the Hantzsch ester as a vibrant yellow crystalline solid, **HE4**, 74% (14.3 g). **mp** (from EtOH): 178-180 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3340, 2981, 1722, 1698, 1653, 1608. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.3 Hz, 2H), 7.48 – 7.26 (m, 2H), 6.09 (s, 1H), 5.03 (s, 1H), 4.07 (qd, *J* = 7.1, 4.7 Hz, 4H), 3.87 (s, 3H), 2.32 (s, 6H), 1.20 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.50, 167.45, 153.2, 144.6, 129.4, 128.2, 128.0, 103.6, 59.9, 52.1, 40.1, 19.6, 14.4. **HRMS** (ESI): m/z calculated for $C_{21}H_{26}O_6N_1$ requires 388.17546 for $[M+H]^+$, found 388.17496.

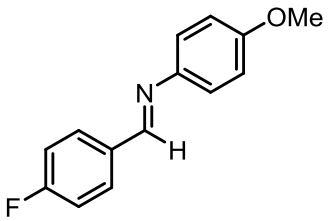
4.3: Synthesis of Imines

General Procedure **A** for the Synthesis of *N*-Arylaldimines.



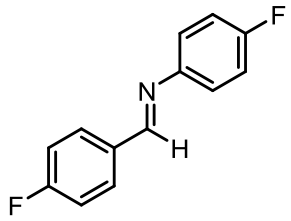
A 25 mL round bottomed flask or carousel tube was charged with CH_2Cl_2 (10 mL) and $MgSO_4$ (~1 g) and allowed to stir for 5 minutes at rt. To the flask was added relevant aldehyde (10 mmol) and aniline (10 mmol). The flask was sealed and purged with nitrogen for 10 minutes. The needle was removed and the reaction mixture was allowed to stir under a balloon of nitrogen for 16 hours. After this time the mixture was diluted further with CH_2Cl_2 and filtered through a pad of cotton wool. The filtrate was concentrated *in vacuo* to give crude aldimine. The compounds were either used crude as ^{1}H NMR showed >95% purity, or purified *via* trituration with pentane, or recrystallization from EtOH or CH_2Cl_2/pentane where stated.

Synthesis of **1a**



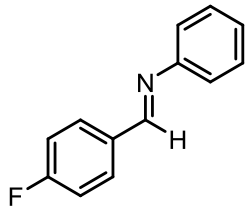
The above compound was prepared according to General Procedure **A** using 4-fluorobenzaldehyde (1.07 mL, 1.24 g, 10 mmol) and *p*-anisidine (1.23 g, 10 mmol). Recrystallization from EtOH gave a pale brown solid, 50% (1.15 g). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.89 (dd, *J* = 8.6, 5.6 Hz, 2H), 7.25 – 7.20 (m, 2H), 7.19 – 7.11 (m, 2H), 6.97 – 6.89 (m, 2H), 3.83 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -108.60 – -108.77 (m). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.5 (d, *J* = 251.2 Hz), 158.4, 156.8, 144.7, 132.8, 130.5 (d, *J* = 8.6 Hz), 122.2, 115.9 (d, *J* = 22.0 Hz), 114.4, 55.5. Data was consistent with literature precedent.[2]

Synthesis of **1c**



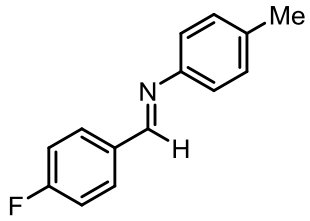
The above compound was prepared according to General Procedure **A** using 4-fluorobenzaldehyde (1.07 mL, 1.24 g, 10 mmol) and 4-fluoroaniline (0.95 mL, 1.11 g, 10 mmol). The compound was used crude as >95% purity was confirmed *via* ^{1}H NMR, off-white solid, 89% (1.93 g). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.95 – 7.81 (m, 2H), 7.24 – 7.12 (m, 4H), 7.12 – 7.00 (m, 2H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -107.88 (tt, *J* = 8.1, 5.1 Hz), -116.76 – -117.46 (m). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.7 (d, *J* = 252.1 Hz), 161.3 (d, *J* = 244.7 Hz), 158.6, 147.8, 132.4 (d, *J* = 2.6 Hz), 130.8 (d, *J* = 8.8 Hz), 122.3 (d, *J* = 8.6 Hz), 116.1 (d, *J* = 6.9 Hz), 115.8 (d, *J* = 7.2 Hz). Data was consistent with literature precedent.[2]

Synthesis of **1b**



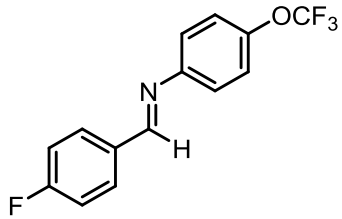
The above compound was prepared according to General Procedure **A** using 4-fluorobenzaldehyde (1.07 mL, 1.24 g, 10 mmol) and aniline (0.91 mL, 0.93 g, 10 mmol). The compound was used crude as >95% purity was confirmed *via* ^{1}H NMR, off-white solid, 95% (1.89 g). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.85 – 7.76 (m, 2H), 7.30 (dd, *J* = 8.3, 7.4 Hz, 2H), 7.18 – 7.09 (m, 3H), 7.06 (t, *J* = 8.6 Hz, 2H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -108.02 (ddd, *J* = 13.9, 8.7, 5.5 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.8 (d, *J* = 252.5 Hz), 158.9, 152.0, 132.7 (d, *J* = 3.2 Hz), 130.9 (d, *J* = 8.9 Hz), 129.3, 126.1, 121.0, 116.0 (d, *J* = 22.1 Hz). Data was consistent with literature precedent.[2]

Synthesis of **1d**



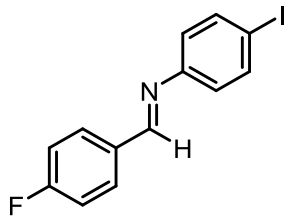
The above compound was prepared according to General Procedure **A** using 4-fluorobenzaldehyde (1.07 mL, 1.24 g, 10 mmol) and *p*-toluidine (1.24 g, 10 mmol). The compound was used crude as >95% purity was confirmed *via* ^{1}H NMR, off-white solid, 84% (1.79 g). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.98 (dd, *J* = 8.8, 5.6 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.27 – 7.20 (m, 4H), 2.47 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -108.34 (tt, *J* = 8.9, 5.6 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.7 (d, *J* = 251.8 Hz), 158.1, 149.3, 136.0, 132.8 (d, *J* = 3.1 Hz), 130.8 (d, *J* = 8.3 Hz), 129.9, 120.9, 115.6 (d, *J* = 22.3 Hz), 21.1. Data was consistent with literature precedent.[3]

Synthesis of **1e**



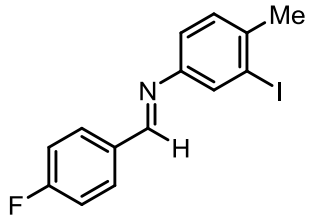
The above compound was prepared according to General Procedure **A** using 4-fluorobenzaldehyde (0.54 mL, 5 mmol) and 4-(trifluoromethoxy)aniline (0.67 mL, 5 mmol). After concentration the compound was crystallized at -78 °C, to give a powdery white solid, 82% (1.15 g). **mp** (from CH_2Cl_2): 32-34 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 1633, 1603, 1591, 1509. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.99 – 7.85 (m, 2H), 7.29 – 7.16 (m, 6H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -58.01 (s, C*F*$_3$), -106.86 – -107.92 (m, Ar*F*). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.0 (d, *J* = 252.8 Hz), 159.6, 150.6, 147.4, 132.4 (d, *J* = 3.1 Hz), 131.1 (d, *J* = 8.8 Hz), 122.1, 122.0, 119.4, 116.2 (d, *J* = 22.2 Hz). **HRMS** (ESI): m/z calculated for $C_{14}H_9O_1N_1F_4$ requires 284.06930 for $[M+H]^+$, found 284.06921.

Synthesis of **1f**



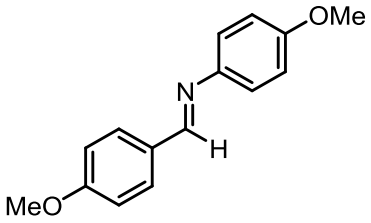
The above compound was prepared according to General Procedure **A** using 4-fluorobenzaldehyde (0.54 mL, 5 mmol) and 4-iodoaniline (1.10 g, 5 mmol). The compound was used crude as >95% purity was confirmed *via* ^{1}H NMR, light purple solid, 85% (1.37 g). **mp** (from CH_2Cl_2): 76-78 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3073, 2981, 2881, 1623, 1601, 1590, 1570, 1507. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.94 – 7.86 (m, 2H), 7.78 – 7.68 (m, 2H), 7.16 (t, *J* = 8.6 Hz, 2H), 7.00 – 6.89 (m, 2H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -106.86 – -107.90 (m). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.9 (d, *J* = 252.7 Hz), 159.2, 151.5, 138.2, 132.3 (d, *J* = 2.7 Hz), 130.9 (d, *J* = 9.0 Hz), 122.9, 116.0 (d, *J* = 21.7 Hz), 90.4. **HRMS** (ESI): m/z calculated for $C_{13}H_9N_1F_1I_1$ requires 325.98365 for $[M+H]^+$, found 325.98370.

Synthesis of **1g**



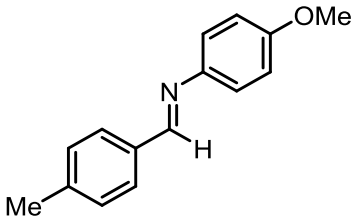
The above compound was prepared according to General Procedure **A** using 4-fluorobenzaldehyde (0.54 mL, 5 mmol) and 3-iodo-4-methylaniline (1.16 g, 5 mmol). After concentration Et_2O (2 mL) and pentane (30 mL) were added. The solution was then cooled to -78 °C, and allowed to crystallized for 1 hour. The white precipitate was then filtered washing with pentane (cooled to -78 °C) to give white solid, 69% (1.17 g). **mp** (from Et_2O): 34-36 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3052, 2980, 2915, 2882, 1629, 1601, 1584, 1551. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.83 – 7.76 (m, 2H), 7.60 (d, *J* = 2.2 Hz, 1H), 7.20 – 7.14 (m, 1H), 7.12 – 7.00 (m, 3H), 2.37 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -107.65 (tt, *J* = 9.0, 5.5 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.0 (d, *J* = 252.4 Hz), 159.1, 150.6, 139.1, 132.5 (d, *J* = 3.2 Hz), 131.0, 130.9 (d, *J* = 7.1 Hz), 130.0, 121.3, 116.1 (d, *J* = 21.6 Hz), 101.2, 27.6. **HRMS** (ESI): m/z calculated for $C_{14}H_{11}N_1F_1I_1$ requires 339.99930 for $[M+H]^+$, found 339.99960.

Synthesis of **1h**



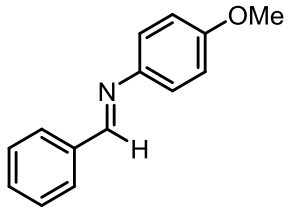
The above compound was prepared according to General Procedure **A** using *p*-anisaldehyde (1.21 mL, 1.36 g, 10 mmol) and *p*-anisidine (1.23 g, 10 mmol). The compound was used crude as >95% purity was confirmed *via* ^{1}H NMR, white solid, 78% (1.89 g). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.86 (d, *J* = 8.8 Hz, 2H), 7.23 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 3.89 (s, 3H), 3.85 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.1, 158.1, 158.0, 145.4, 130.4, 129.6, 122.2, 114.46, 114.3, 55.6, 55.5. Data was consistent with literature precedent.[2]

Synthesis of **1i**



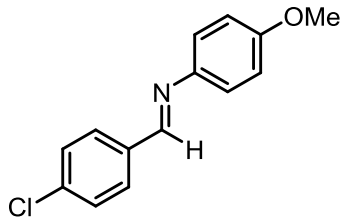
The above compound was prepared according to General Procedure **A** using 4-tolualdehyde (1.18 mL, 1.20 g, 10 mmol) and *p*-anisidine (1.23 g, 10 mmol). The compound was used crude as >95% purity was confirmed *via* ^{1}H NMR, grey solid, 72% (1.62 g). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.18 – 7.09 (m, 2H), 6.91 – 6.75 (m, 2H), 3.73 (s, 3H), 2.32 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.6, 158.2, 145.2, 141.6, 134.0, 129.6, 128.7, 122.3, 114.5, 55.6, 21.7. Data was consistent with literature precedent.[2]

Synthesis of **1j**



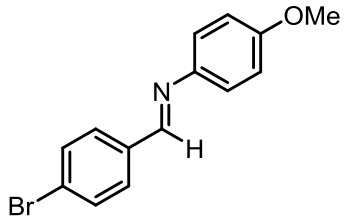
The above compound was prepared according to General Procedure **A** using benzaldehyde (1.02 mL, 1.06 g, 10 mmol) and *p*-anisidine (1.23 g, 10 mmol). The compound was used crude as >95% purity was confirmed *via* ^{1}H NMR, grey solid, 78% (1.65 g). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.08 – 7.87 (m, 2H), 7.57 – 7.42 (m, 3H), 7.28 (d, *J* = 8.9 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.5, 158.4, 145.0, 136.5, 131.1, 128.8, 128.7, 122.3, 114.5, 55.6. Data was consistent with literature precedent.[2]

Synthesis of **1k**



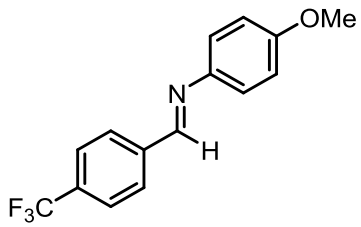
The above compound was prepared according to General Procedure **A** using 4-chlorobenzaldehyde (1.40 g, 10 mmol) and *p*-anisidine (1.23 g, 10 mmol). The compound was purified *via* recrystallization from EtOH (200 mg, 8%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.83 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.26 – 7.19 (m, 2H), 7.00 – 6.81 (m, 2H), 3.84 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.6, 156.8, 144.6, 137.1, 135.1, 129.8, 129.2, 122.4, 114.6, 55.7. Data was consistent with literature precedent.[2]

Synthesis of **1l**



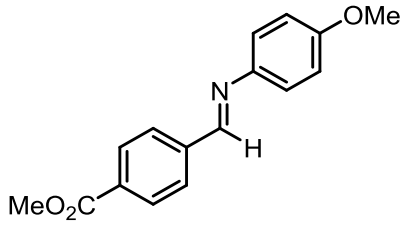
The above compound was prepared according to General Procedure **A** using 4-bromobenzaldehyde (925 mg, 5 mmol) and *p*-anisidine (615 mg, 5 mmol). The compound was used crude as >95% purity was confirmed *via* ^{1}H NMR, off-white solid, 65% (936 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.83 – 7.75 (m, 2H), 7.70 – 7.56 (m, 2H), 7.30 – 7.23 (m, 2H), 7.01 – 6.90 (m, 2H), 3.86 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.7, 156.9, 144.6, 135.5, 132.1, 132.1, 130.0, 125.6, 122.4, 114.6, 55.6. Data was consistent with literature precedent.[3]

Synthesis of **1m**



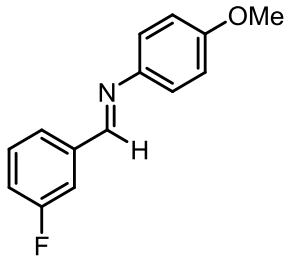
The above compound was prepared according to General Procedure **A** using 4-trifluoromethylbenzaldehyde (1.36 mL, 1.74 g, 10 mmol) and *p*-anisidine (1.23 g, 10 mmol). The compound was used crude as >95% purity was confirmed *via* ^{1}H NMR, off-white solid, 79% (2.21 g). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.92 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 8.1 Hz, 2H), 7.20 (dd, J = 9.2, 2.5 Hz, 2H), 7.00 – 6.79 (m, 2H), 3.77 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.74. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.0, 156.3, 144.2, 139.7, 132.4 (q, J = 32.4 Hz), 128.8, 125.8 (q, J = 3.8 Hz), 122.5, 114.6, 55.6. Data was consistent with literature precedent.[2]

Synthesis of **1n**



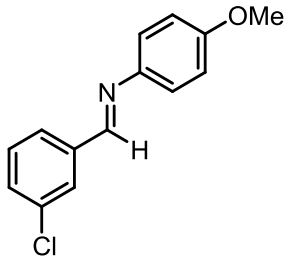
The above compound was prepared according to General Procedure **A** using methyl 4-formylbenzoate (821 mg, 5 mmol) and *p*-anisidine (623 g, 5 mmol). The compound was used crude as >95% purity was confirmed *via* ^{1}H NMR, yellow solid, 90% (1.21 g). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.11 – 7.99 (m, 2H), 7.90 – 7.83 (m, 2H), 7.27 – 7.11 (m, 2H), 6.96 – 6.72 (m, 2H), 3.87 (s, 3H), 3.76 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.8, 158.9, 156.9, 144.4, 140.5, 132.1, 130.1, 128.5, 128.5, 122.5, 114.6, 114.6, 55.6, 52.4. Data was consistent with literature precedent.[4]

Synthesis of **1o**



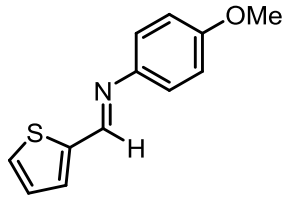
The above compound was prepared according to General Procedure **A** using 3-fluorobenzaldehyde (1.06 mL, 1.24 g, 10 mmol) and *p*-anisidine (1.23 g, 10 mmol). The compound was used crude as >95% purity was confirmed *via* ^{1}H NMR, deep grey solid, 90% (2.07 g). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36 (d, J = 1.3 Hz, 1H), 7.56 (ddd, J = 9.6, 2.7, 1.5 Hz, 1H), 7.52 (dt, J = 7.6, 1.2 Hz, 1H), 7.33 (td, J = 7.9, 5.6 Hz, 1H), 7.20 – 7.11 (m, 2H), 7.06 (tdd, J = 8.3, 2.7, 1.0 Hz, 1H), 6.89 – 6.79 (m, 2H), 3.74 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -112.66 (td, J = 8.9, 5.6 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.2 (d, J = 246.4 Hz), 158.7, 156.8 (d, J = 3.1 Hz), 144.4, 138.9 (d, J = 7.2 Hz), 130.4 (d, J = 8.5 Hz), 124.9 (d, J = 3.0 Hz), 122.4, 118.0 (d, J = 21.5 Hz), 114.6 (d, J = 22.4 Hz), 114.6, 55.6. Data was consistent with literature precedent.[2]

Synthesis of **1p**



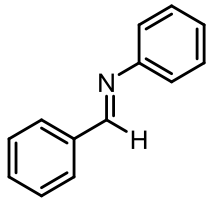
The above compound was prepared according to General Procedure **A** using 3-chlorobenzaldehyde (1.14 mL, 1.41 g, 10 mmol) and *p*-anisidine (1.23 g, 10 mmol). The compound was used crude as >95% purity was confirmed *via* ^{1}H NMR, pale off-white solid, 96% (2.36 g). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.83 (t, *J* = 1.8 Hz, 1H), 7.63 (dt, *J* = 7.3, 1.5 Hz, 1H), 7.42 – 7.24 (m, 2H), 7.21 – 7.03 (m, 2H), 6.85 (d, *J* = 8.9 Hz, 2H), 3.74 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.7, 156.5, 144.3, 138.4, 135.0, 131.0, 130.1, 128.2, 127.0, 122.4, 114.6, 55.6. Data was consistent with literature precedent.[2]

Synthesis of **1q**



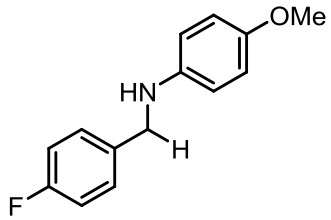
The above compound was prepared according to General Procedure **A** using 2-thiophene carboxaldehyde (0.93 mL, 1.12 g, 10 mmol) and *p*-anisidine (1.23 g, 10 mmol). The compound was used crude as >95% purity was confirmed *via* ^{1}H NMR, pale off-white solid, 95% (1.95 g). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 0.9 Hz, 1H), 7.52 – 7.36 (m, 2H), 7.28 – 7.18 (m, 2H), 7.12 (dd, *J* = 4.9, 3.7 Hz, 1H), 6.93 (d, *J* = 2.2 Hz, 1H), 3.82 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.4, 151.2, 144.4, 143.3, 131.7, 129.8, 127.8, 122.4, 114.5, 114.4, 55.6. Data was consistent with literature precedent.[5]

Synthesis of **1r**



The above compound was prepared according to General Procedure **A** using benzaldehyde (1.02 mL, 1.06 g, 10 mmol) and aniline (0.91 mL, 0.93 g, 10 mmol). The compound was used crude as >95% purity was confirmed *via* ^{1}H NMR, pale canary yellow solid, 89% (1.61 g). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.86 – 7.76 (m, 2H), 7.44 – 7.34 (m, 3H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.21 – 6.96 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.5, 152.2, 136.3, 131.5, 129.3, 128.9, 128.9, 126.0, 121.0. Data was consistent with literature precedent.[2]

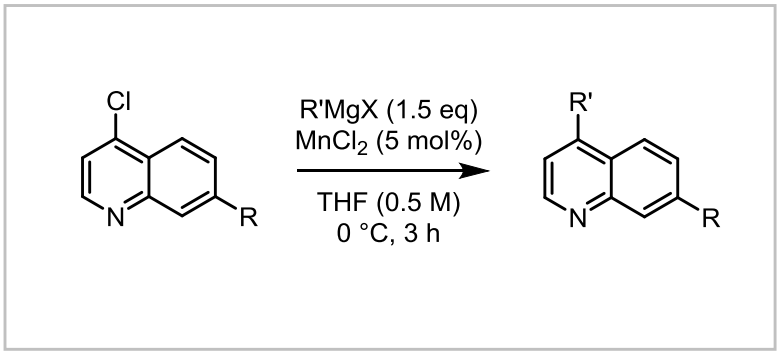
Synthesis of **S1a**



To a vial equipped with a stirrer bar was added **1a** (228 mg, 1 mmol) and MeOH (4 mL). The vial was cooled to 0 °C and sodium borohydride (42 mg, 1.1 mmol) was added portionwise. The vial was allowed to return to room temperature and stir for 2 hours. The reaction mixture was diluted in EtOAc (50 mL) and brine (50 mL) and the organic phase separated. The aqueous phase was re-extracted with EtOAc (2 x 50 mL) and the combined organics were dried over $MgSO_4$ and concentrated *in vacuo* to give pure title compound, 85% (196 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 2H), 7.03 (t, *J* = 8.7 Hz, 2H), 6.86 – 6.62 (m, 2H), 6.67 – 6.50 (m, 2H), 4.26 (s, 2H), 3.75 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -115.71 (tt, *J* = 9.1, 5.1 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.1 (d, *J* = 245.2 Hz), 152.4, 142.3, 135.5 (d, *J* = 3.2 Hz), 129.2 (d, *J* = 8.0 Hz), 115.5 (d, *J* = 21.4 Hz), 115.0, 114.3, 55.9, 48.6. Data was consistent with literature precedent.[2]

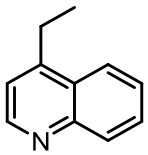
4.4: Synthesis of Quinolines

General procedure **B** for the synthesis of 4-substituted quinolines.



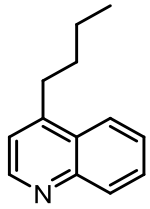
Adapted from a literature procedure.[6] To an oven dried carousel tube or rbf was added 4-chloroquinoline (1 eq), and manganese(II) chloride (5 mol%). The flask was sealed then evacuated and refilled with argon three times, and cooled to 0 °C. To the flask was added THF (anhydrous, 0.5M), followed by relevant magnesium halide solution (1.5 eq) dropwise. The temperature was maintained at 0 °C and the flask allowed to stir for 3 hours (or overnight if TLC analysis showed presence of 4-chloroquinoline). The reaction mixture was quenched with sat. NH_4Cl solution, then diluted with EtOAc and H_2O. The organic phase was extracted and the aqueous phase re-extracted with EtOAc (2x). The combined organics were dried over $MgSO_4$ and concentrated *in vacuo*. The crude residue was then purified *via* silica gel column chromatography (EtOAc:Pentane 5:95 – 30:70 v:v) to give pure quinoline substrate. (Note: quinolines generally stain white under Vanillin).

Synthesis of 4-ethylquinoline (**2b**)



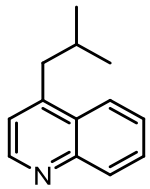
General Procedure **B** was followed using 4-chloroquinoline (491 mg, 3 mmol) and ethyl magnesium bromide solution (3 M in Et_2O, 1.5 mL). Silica gel column chromatography gave a colourless oil, 79% (370 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.81 (d, *J* = 4.5 Hz, 1H), 8.15 – 8.08 (m, 1H), 8.04 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.69 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H), 7.55 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.24 (dd, *J* = 4.4, 0.9 Hz, 1H), 3.11 (qd, *J* = 7.6, 0.9 Hz, 2H), 1.39 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.5, 150.0, 148.4, 130.4, 129.1, 127.6, 126.4, 123.5, 119.9, 25.1, 14.1. Data is in line with literature precedent.[7]

Synthesis of 4-butylquinoline (**2c**)



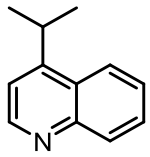
General Procedure **B** was followed using 4-chloroquinoline (491 mg, 3 mmol) and *n*-butyl magnesium bromide solution (2 M in THF, 2.25 mL). Silica gel column chromatography gave a colourless oil, 57% (317 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.79 (d, *J* = 4.4 Hz, 1H), 8.11 (dd, *J* = 8.4, 1.4 Hz, 1H), 8.03 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.68 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.53 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.21 (d, *J* = 4.4 Hz, 1H), 3.12 – 2.97 (m, 2H), 1.81 – 1.60 (m, 2H), 1.45 (dq, *J* = 14.6, 7.3 Hz, 2H), 0.97 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.3, 148.8, 148.5, 130.3, 129.0, 127.7, 126.3, 123.7, 120.8, 32.3, 31.9, 22.9, 14.0. Data is in line with literature precedent.[8]

Synthesis of 4-isobutylquinoline (**2d**)



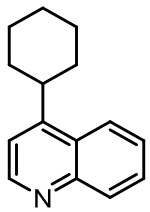
General Procedure **B** was followed using 4-chloroquinoline (491 mg, 3 mmol) and *i*-butyl magnesium chloride solution (2 M in Et_2O, 2.25 mL).Work-up (no purification by column chromatography required) gave a colourless oil, 86% (480 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 4.5 Hz, 1H), 8.21 – 8.08 (m, 1H), 8.02 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.69 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 7.54 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.19 (d, *J* = 4.4 Hz, 1H), 2.92 (d, *J* = 7.3 Hz, 3H), 2.09 (dp, *J* = 13.5, 6.7 Hz, 1H), 0.98 (d, *J* = 6.6 Hz, 7H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.1, 148.6, 147.7, 130.3, 129.0, 128.0, 126.2, 124.0, 122.0, 41.7, 29.5, 22.9. Data is in line with literature precedent.[9]

Synthesis of 4-isopropylquinoline (**2e**)



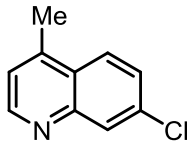
General Procedure **B** was followed using 4-chloroquinoline (1.64 g, 10 mmol) and isopropyl magnesium bromide solution (3 M in 2-MeTHF, 5 mL). Silica gel column chromatography gave a colourless oil, 34% (580 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.85 (d, *J* = 4.6 Hz, 1H), 8.16 – 8.06 (m, 2H), 7.69 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.56 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 7.30 (d, *J* = 4.6 Hz, 1H), 3.75 (hept, *J* = 6.8 Hz, 1H), 1.40 (d, *J* = 6.8 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.4, 150.5, 148.4, 130.4, 128.8, 126.9, 126.2, 123.1, 116.9, 28.3, 22.9. Data is in line with literature precedent.[10]

Synthesis of 4-cyclohexylquinoline (**2f**)



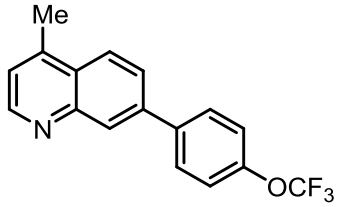
General Procedure **B** was followed using 4-chloroquinoline (491 mg, 3 mmol) and cyclohexyl magnesium chloride solution (2 M in Et_2O, 2.25 mL). Silica gel column chromatography gave a colourless oil, 88% (560 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.84 (d, *J* = 4.6 Hz, 1H), 8.10 (td, *J* = 8.5, 1.3 Hz, 2H), 7.68 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 7.55 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 7.35 – 7.15 (m, 1H), 3.33 (ddt, *J* = 8.3, 5.0, 3.1 Hz, 1H), 2.08 – 1.78 (m, 5H), 1.55 (ddt, *J* = 9.8, 7.6, 2.5 Hz, 4H), 1.43 – 1.24 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.5, 150.6, 148.6, 130.6, 128.9, 127.1, 126.2, 123.2, 117.6, 39.0, 33.7, 27.0, 26.4. Data is in line with literature precedent.[8]

Synthesis of 7-chloro-4-methylquinoline (**2g**)



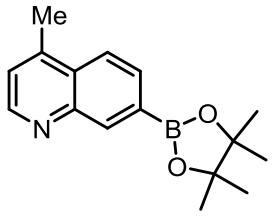
General Procedure **B** was followed using 4,7-dichloroquinoline (7.98 g, 40 mmol) and methyl magnesium bromide solution (3 M in Et_2O, 20 mL). Silica gel column chromatography gave a white powdery solid, 62% (4.43 g). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 4.4 Hz, 1H), 8.04 (d, *J* = 2.2 Hz, 1H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.43 (dd, *J* = 8.9, 2.2 Hz, 1H), 7.16 (dd, *J* = 4.4, 1.0 Hz, 1H), 2.62 (app d, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.3, 148.5, 144.4, 135.0, 128.9, 127.3, 126.7, 125.3, 122.1, 18.7. Data is in line with literature precedent.[11]

Synthesis of 4-methyl-7-(4-(trifluoromethoxy)phenyl)quinoline (**2h**)



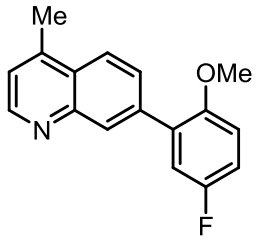
To an oven-dried carousel tube was charged 7-chloro-4-methylquinoline (**2g**, 200 mg, 1.12 mmol), palladium(II) acetate (3.6 mg, 0.016 mmol, 3 mol%), 2'-(dicyclohexylphosphaneyl)-N,N-dimethyl-[1,1'-biphenyl]-2-amine (DavePhos, 9.4 mg, 0.024 mmol, 4.5 mol%), potassium phosphate tribasic (713 mg, 3.36 mmol), and (4-(trifluoromethoxy)phenyl)boronic acid (254 mg, 1.23 mmol). The flask was sealed with a Teflon cap, then evacuated and refilled three times with argon. To the mixture was added 1,4-dioxane (anhydrous, 4 mL) and the vessel was lowered into a preheated oil bath (110 °C) and heated at this temperature for 16 h. After this time the reaction mixture was allowed to cool to room temperature and was filtered through a pad of silica, eluting with EtOAc. The filtrate was concentrated *in vacuo* to give the above compound as an off-white powder, 80% (271 mg). **mp** (from EtOAc): 82-84 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3042, 2981, 1617, 1595, 1570, 1522, 1503. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 4.4 Hz, 1H), 8.29 (d, *J* = 2.0 Hz, 1H), 8.06 (d, *J* = 8.7 Hz, 1H), 7.82 – 7.67 (m, 3H), 7.45 – 7.33 (m, 2H), 7.24 (dd, *J* = 4.4, 1.0 Hz, 1H), 2.72 (d, *J* = 1.0 Hz, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -57.75 (s). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.9, 149.1, 148.3, 144.2, 140.3, 139.0, 128.8, 127.8, 127.6, 125.5, 124.7, 122.1, 121.4, 120.6 (q, *J* = 257.2 Hz), 18.6. **HRMS** (ESI): m/z calculated for $C_{17}H_{12}O_1N_1F_3$ requires 304.09438 for $[M+H]^+$, found 304.09424.

Synthesis of **2i**



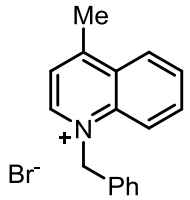
To an oven dried carousel tube was charged 7-chloro-4-methylquinoline (**2g**, 200 mg, 1.12 mmol), bis(pinacolato)diboron (B_2Pin_2, 853 mg, 3.36 mmol), Pd_2dba_3 (2.1 mg, 0.0224 mmol, 2 mol%), XPhos (2.2 mg, 0.045 mmol, 4 mol%), and potassium acetate (330 mg, 3.36 mmol). The tube was sealed with a Teflon cap, then evacuated and refilled three times with argon. To the tube was charged anhydrous 1,4-dioxane (3.5 mL). The cap was then sealed and the reaction mixture heated to 110 °C for 16 hours. After this time the reaction mixture was allowed to cool and filtered through a short plug of silica, eluting with EtOAc. The filtrate was concentrated *in vacuo*. The residue was then purified *via* silica gel column chromatography (EtOAc:Pentane 30:70 v:v) to give **2i** as a white solid, 99% (300 mg). **mp** (from EtOAc:Pentane): 84-88 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 2901, 2889, 1619, 1596, 1564, 1508. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 4.4 Hz, 1H), 8.67 – 8.52 (m, 1H), 7.95 (d, *J* = 8.3 Hz, 1H), 7.90 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.23 (dd, *J* = 4.3, 1.1 Hz, 1H), 2.69 (d, *J* = 0.9 Hz, 3H), 1.38 (s, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.2, 147.4, 144.2, 138.0, 131.0, 130.0, 123.0, 122.6, 84.2, 25.0, 18.7. (*C*-B not observed) **HRMS** (ESI): m/z calculated for $C_{16}H_{20}O_2N_1B_1$ requires 269.16962 for $[M+H]^+$, found 269.16979.

Synthesis of 7-(5-fluoro-2-methoxyphenyl)-4-methylquinoline (**2j**)



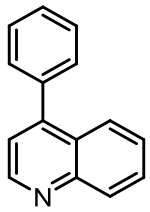
To an oven-dried carousel tube was charged 7-chloro-4-methylquinoline (**2g**, 600 mg, 3.36 mmol), palladium(II) acetate (10.8 mg, 0.048 mmol, 3 mol%), 2'-(dicyclohexylphosphaneyl)-N,N-dimethyl-[1,1'-biphenyl]-2-amine (DavePhos, 28.2 mg, 0.072 mmol, 4.5 mol%), potassium phosphate tribasic (2.13 g, 10.08 mmol), and (5-fluoro-2-methoxyphenyl)boronic acid (827 mg, 3.70 mmol). The flask was sealed with a Teflon cap, then evacuated and refilled three times with argon. To the mixture was added 1,4-dioxane (anhydrous, 9 mL) and the vessel was lowered into a preheated oil bath (110 °C) and heated at this temperature for 16 h. After this time the reaction mixture was allowed to cool to room temperature and was filtered through a pad of silica, eluting with EtOAc. The filtrate was concentrated *in vacuo* and purified via silica gel column chromatography (EtOAc:Pentane 20:80 - 30:70 v:v) to give the above compound as an off-white powder, 98% (880 mg). **mp** (from EtOAc:Pentane): 62-66 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 2981, 2903, 1614, 1593, 1566. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.79 (d, *J* = 4.4 Hz, 1H), 8.25 (d, *J* = 1.8 Hz, 1H), 8.01 (d, *J* = 8.6 Hz, 1H), 7.75 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.24 – 7.16 (m, 2H), 7.05 (ddd, *J* = 9.0, 7.8, 3.1 Hz, 1H), 6.94 (dd, *J* = 9.0, 4.5 Hz, 1H), 3.80 (s, 3H), 2.71 (d, *J* = 0.9 Hz, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -123.67 (td, *J* = 9.0, 8.6, 4.6 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.3 (d, *J* = 239.2 Hz), 153.0 (d, *J* = 2.3 Hz), 150.6, 148.1, 144.2, 138.6, 131.2 (d, *J* = 7.2 Hz), 128.2, 127.5, 123.5, 122.0, 117.7 (d, *J* = 23.6 Hz), 115.0 (d, *J* = 23.0 Hz), 112.6 (d, *J* = 8.1 Hz), 56.3, 18.7. **HRMS** (ESI): m/z calculated $C_{17}H_{14}O_1N_1F_1$ requires 268.11322 for $[M+H]^+$, found 268.11298.

Synthesis of 1-benzyl-4-methylquinolin-1-ium bromide (**2l**)



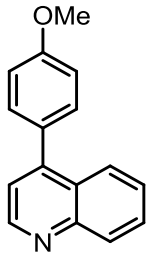
To a 100 mL rbf containing lepidine (1.31 mL, 10 mmol) and anhydrous MeOH (15 mL) was charged benzyl bromide (1.31 mL, 11 mmol). The reaction mixture was then heated to reflux for 4 days. After this time the reaction mixture was allowed to cool and concentrated *in vacuo*. The crude residue was then purified *via* trituration with CH_2Cl_2 to leave pure quinolinium salt. Concentration of CH_2Cl_2 triturate and repeated trituration with CH_2Cl_2 (2x whole process) led to second and third crops of quinolinium salt **2l**, 47% (1.48 g). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.77 (d, J = 6.1 Hz, 1H), 8.67 – 8.42 (m, 2H), 8.24 – 8.13 (m, 2H), 7.99 (t, J = 7.7 Hz, 1H), 7.46 – 7.20 (m, 5H), 6.40 (s, 2H), 3.04 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 159.5, 149.2, 136.8, 135.1, 134.1, 129.6, 129.0, 128.6, 127.2, 127.1, 122.9, 119.7, 119.2, 59.4, 19.9. Data is in line with literature precedent.[12]

Synthesis of 4-phenylquinoline (**2m**)



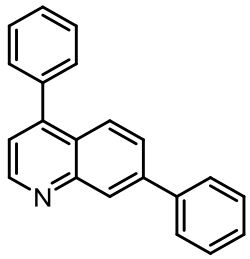
General Procedure **B** was followed using 4-chloroquinoline (491 mg, 3 mmol) and phenyl magnesium bromide solution (3 M in Et_2O, 1.5 mL). Silica gel column chromatography gave a colourless oil, 76% (468 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.95 (d, J = 4.4 Hz, 1H), 8.21 – 8.14 (m, 1H), 7.93 (dd, J = 8.5, 1.4 Hz, 1H), 7.73 (ddd, J = 8.5, 6.8, 1.4 Hz, 1H), 7.58 – 7.45 (m, 6H), 7.34 (d, J = 4.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.1, 148.9, 148.6, 138.2, 130.0, 129.7, 129.4, 128.7, 128.6, 126.9, 126.7, 126.0, 121.5. Data is in line with literature precedent.[13]

Synthesis of 4-(4-methoxyphenyl)quinoline (**2n**)



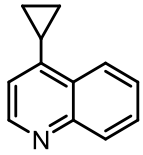
General Procedure **B** was followed using 4-chloroquinoline (491 mg, 3 mmol) and 4-methoxphenyl magnesium bromide solution (0.5 M in THF, 9 mL). Silica gel column chromatography gave a white solid, 82% (575 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.91 (d, *J* = 4.5 Hz, 1H), 8.27 – 8.11 (m, 1H), 7.96 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.71 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H), 7.49 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.30 (d, *J* = 4.4 Hz, 1H), 7.10 – 7.01 (m, 2H), 3.89 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.0, 150.1, 148.9, 148.3, 130.9, 130.4, 130.0, 129.3, 127.1, 126.6, 126.6, 126.0, 121.4, 114.2, 55.5. Data is in line with literature precedent.[14]

Synthesis of 4-7-diphenylquinoline (**2o**)



General Procedure **B** was followed using 4,7-dichloroquinoline (594 mg, 3 mmol) and phenyl magnesium bromide solution (3 M in Et_2O, 1.5 mL). Silica gel column chromatography gave a white solid, 52% (438 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.97 (d, *J* = 4.4 Hz, 1H), 8.41 (d, *J* = 1.9 Hz, 1H), 8.00 (d, *J* = 8.8 Hz, 1H), 7.78 (dt, *J* = 8.1, 1.5 Hz, 3H), 7.60 – 7.49 (m, 7H), 7.46 – 7.37 (m, 1H), 7.34 (d, *J* = 4.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.6, 149.2, 148.5, 142.1, 140.3, 138.1, 129.7, 129.2, 128.8, 128.6, 128.1, 127.6, 127.6, 126.5, 126.4, 126.0, 121.4. Data is in line with literature precedent.[15]

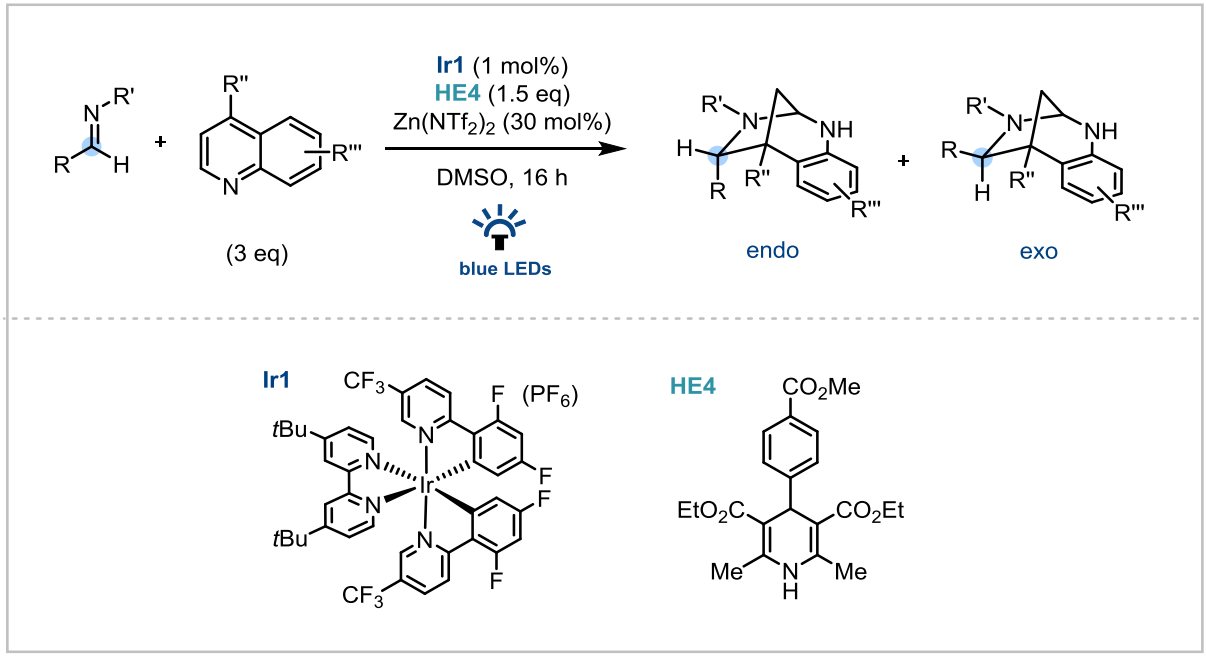
Synthesis of 4-cyclopropylquinoline (**2p**)



To an oven dried carousel tube was charged 4-chloroquinoline (491 mg, 3 mmol), cyclopropyl boronic acid (1.03 g, 12 mmol), palladium acetate (67 mg, 0.3 mmol, 10 mol%), tricyclohexylphosphine (168 mg, 0.6 mmol, 20 mol%), and potassium phosphate tribasic (2.22 g, 10.5 mmol). The tube was sealed with a Teflon cap and subsequently evacuated and refilled with argon three times. To the reaction vessel was charged anhydrous toluene (12 mL), and water (0.6 mL) *via* septum, and the tube was then heated to 100 °C overnight. After this time the reaction mixture was diluted with sat. $NaHCO_3$ solution (50 mL) and EtOAc (50 mL). The organic phase was extracted and the aqueous phase re-extracted with EtOAc (2x). The combined organics were dried over $MgSO_4$ and concentrated *in vacuo*. The crude residue was then purified *via* silica gel column chromatography (EtOAc:Pentane 10:90 – 20:80 v:v) to give **2n** as a pale yellow oil, 78% (396 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.79 (d, *J* = 4.6 Hz, 1H), 8.34 (dd, *J* = 8.5, 1.5 Hz, 1H), 8.26 – 8.01 (m, 1H), 7.72 (ddd, *J* = 8.5, 6.8, 1.4 Hz, 1H), 7.59 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.04 (dd, *J* = 4.5, 0.9 Hz, 1H), 2.44 (ttd, *J* = 8.5, 5.3, 0.8 Hz, 1H), 1.30 – 1.13 (m, 2H), 0.92 – 0.76 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.4, 149.8, 148.1, 130.1, 129.2, 128.9, 126.4, 124.1, 117.2, 12.2, 8.0. Data is in line with literature precent.[16]

5. Synthesis of Bridged 1,3-Diazepanes

General Procedure **C** for the dearomative synthesis of bridged 1,3-diazepanes



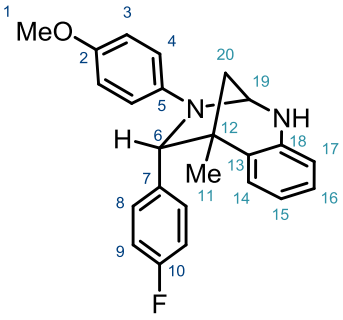
To an oven dried 1.7 mL glass vial was charged relevant imine (0.1 mmol), diethyl 4-(4-(methoxycarbonyl)phenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (HE4, 58 mg, 0.15 mmol, 1.5 eq), zinc di[bis(trifluoromethylsulfonyl)imide] (18.3 mg, 0.03 mmol, 30 mol%), and $[Ir([dFCF_3]ppy)_2(dtbbpy)]PF_6$ (1.1 mg, 0.001 mmol, 1 mol%) and relevant quinoline derivative (0.3 mmol, 3 eq). To the vial was added DMSO (anhydrous, 1 mL), and under stirring, the reaction mixture was sparged with a N_2 stream for ~5 minutes. After this time the vial was sealed with a screw cap and irradiated with blue light for 16 hours. After this time the diastereomeric ratio was determined *via* analysis of a 0.1 mL aliquot of the reaction mixture by ^1H NMR or $\{^1H\}^{19}F$ NMR. The NMR sample was recombined and the reaction mixture diluted in EtOAc (10 mL) and was added water (5 mL) and brine (5 mL). The organic phase was extracted and the aqueous phased re-extracted with EtOAc (2 x 10 mL). The combined organics were dried over $MgSO_4$ and concentrated *in vacuo*. The crude residue was purified *via* silica gel column chromatography (CH_2Cl_2:Pentane) to give either a fully or partially separable mixture of endo and exo diastereomers. Unless otherwise stated the endo diastereomer dominates.

Note: when discussed below 'full separable' and 'partially separable' relate to one pass of chromatography. All compounds except **3al** have different polarities in CH_2Cl_2:Pentane eluents and can be fully separated if required.

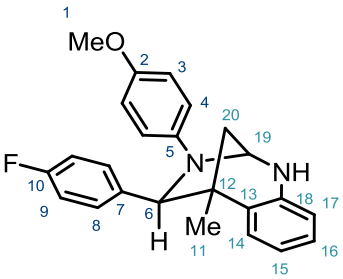
Synthesis of **3aa**

The compound was synthesized according to General Procedure **C** using **1a** (23 mg, 0.1 mmol), and lepidine (40 µL, 0.3 mmol). Crude dr: 3.2:1 (endo:exo). Silica gel column chromatography (CH_2Cl_2:Pentane 30:70 – 70:30 v:v) gave a separable mixture of diastereomers, combined yield 82% (30.6 mg).

Note: Both diastereomers of **3aa** are fully assigned and further examples analysed by analogy.



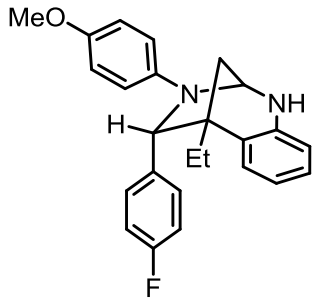
Data for **3aa$_{(endo)}$**. White solid. **mp** (from $CHCl_3$): 144-146 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3391, 2965, 1605, 1510, 1474. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.96 (td, *J* = 7.6, 1.5 Hz, 1H, **15**), 6.81 (t, *J* = 6.4 Hz, 2H, **9**), 6.73 (d, *J* = 8.6 Hz, 2H, **8**), 6.71 – 6.66 (m, 2H, **4**), 6.60 (dd, *J* = 8.0, 1.2 Hz, 1H, **14**), 6.45 – 6.38 (m, 3H, **16** & **3**), 6.25 (dd, *J* = 7.7, 1.5 Hz, 1H, **17**), 5.30 (s, 1H, N*H*), 5.11 (d, *J* = 5.0 Hz, 1H, **19**), 4.48 (s, 1H, **6**), 3.68 (s, 3H, **1**), 2.45 (d, *J* = 10.7 Hz, 1H, **20a**), 2.26 (dd, *J* = 10.7, 5.0 Hz, 1H, **20b**), 1.51 (s, 3H, **11**). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -115.95 (tt, *J* = 8.4, 5.6 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.0 (d, *J* = 244.3 Hz, **10**), 151.7 (**2**), 143.0 (**13**), 140.3 (**5**), 133.8 (d, *J* = 3.6 Hz, **7**), 128.9 (**18**), 128.5 (d, *J* = 7.9 Hz, **8**), 127.9 (**16**), 126.5 (**14**), 118.6 (**15**), 115.5 (**17**), 114.8 (**4**), 114.6 (d, *J* = 21.1 Hz, **9**), 113.7 (**3**), 78.6 (**6**), 72.1 (**19**), 55.9 (**1**), 46.4 (**12**), 41.3 (**20**), 19.9 (**11**). **HRMS** (ESI): m/z calculated for $C_{24}H_{23}O_2N_2F_1$ requires 375.18672 for $[M+H]^+$, found 375.18610.



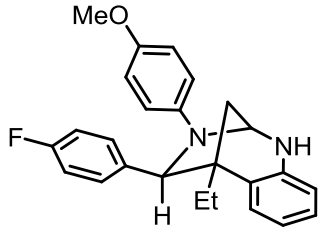
Data for **3aa$_{(exo)}$**. White solid. **mp** (from $CHCl_3$): 226-230 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3401, 2981, 2886, 1604, 1509, 1474. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25 – 7.17 (m, 3H, **14** & **9**), 7.07 – 6.97 (m, 3H, **16** & **8**), 6.74 (td, *J* = 7.5, 1.3 Hz, 1H, **15**), 6.70 (d, *J* = 9.1 Hz, 2H, **4**), 6.52 (dd, *J* = 7.9, 1.3 Hz, 1H, **17**), 6.45 – 6.38 (m, 2H, **3**), 5.46 (d, *J* = 4.5 Hz, 1H, **19**), 5.15 (s, 1H, N*H*), 4.58 (s, 1H, **6**), 3.67 (s, 3H, **1**), 2.31 (dd, *J* = 11.2, 4.7 Hz, 1H, **20a**), 2.14 (d, *J* = 11.2 Hz, 1H, **20b**), 1.05 (s, 3H, **11**). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -115.93 (td, *J* = 8.4, 4.3 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.2 (d, *J* = 245.1 Hz, **10**), 151.4 (**2**), 141.9 (**18**), 138.8 (**5**), 136.7 (d, *J* = 3.6 Hz, **7**), 134.2 (**13**), 128.5 (app s, **8**), 127.6 (**16**), 123.8 (**14**), 118.6 (**15**), 115.9 (**17**), 115.4 (d, *J* = 21.6 Hz, **9**), 115.0 (**4**), 113.8 (**3**), 76.8 (**6**), 66.6 (**19**), 55.7 (**1**), 44.6 (**12**), 36.9 (**20**), 19.9 (**11**). **HRMS** (ESI): m/z calculated for $C_{24}H_{24}O_1N_2F_1$ requires 375.18672 for $[M+H]^+$, found 375.18640.

Synthesis of **3ab**

The compound was synthesized according to General Procedure **C** using **1a** (23 mg, 0.1 mmol), and 4-ethylquinoline (**2b**, 51 mg, 0.3 mmol). Crude dr: 4.4:1 (endo:exo). Silica gel column chromatography (CH_2Cl_2:Pentane 30:70 – 70:30 v:v) gave a fully separable mixture of diastereomers, combined yield 73% (28.3 mg).



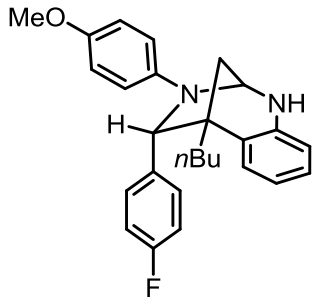
Data for **3ab$_{(endo)}$**. Amorphous solid. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3386, 2968, 1605, 1509, 1472. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.95 (td, *J* = 7.7, 1.4 Hz, 1H), 6.85 – 6.66 (m, 6H), 6.61 (dd, *J* = 7.9, 1.2 Hz, 1H), 6.47 – 6.33 (m, 3H), 6.18 (dd, *J* = 7.8, 1.5 Hz, 1H), 5.12 (d, *J* = 5.0 Hz, 1H), 4.73 (s, 1H), 4.51 (s, 1H), 3.68 (s, 3H), 2.48 (d, *J* = 10.6 Hz, 1H), 2.19 (dd, *J* = 10.7, 5.1 Hz, 1H), 2.09 (dt, *J* = 14.6, 7.3 Hz, 1H), 1.84 (dd, *J* = 14.2, 7.3 Hz, 1H), 1.00 (t, *J* = 7.4 Hz, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -116.02 (ddd, *J* = 14.1, 8.9, 5.9 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.0 (d, *J* = 244.7 Hz), 151.7, 143.9, 140.4, 134.0 (d, *J* = 2.6 Hz), 128.5 (d, *J* = 7.9 Hz), 127.7, 126.9, 126.6, 118.5, 115.9, 114.8, 114.5 (d, *J* = 21.0 Hz), 113.7, 78.4, 72.0, 55.9, 50.6, 37.4, 25.1, 9.3. **HRMS** (ESI): m/z calculated for $C_{25}H_{25}O_1N_2F_1$ requires 389.20237 for $[M+H]^+$, found 389.20193.



Data for **3ab$_{(exo)}$**. Off-white solid. **mp** (from $CHCl_3$): 202-208 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3395, 2980, 1604, 1509, 1474. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.20 (dd, *J* = 8.4, 5.5 Hz, 2H), 7.13 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.07 – 6.92 (m, 3H), 6.75 (td, *J* = 7.5, 1.3 Hz, 1H), 6.72 – 6.64 (m, 2H), 6.53 (dd, *J* = 7.9, 1.3 Hz, 1H), 6.44 – 6.34 (m, 2H), 5.47 (d, *J* = 4.6 Hz, 1H), 5.11 (s, 1H), 4.62 (s, 1H), 3.66 (s, 3H), 2.29 (d, *J* = 11.1 Hz, 1H), 2.17 (dd, *J* = 11.2, 4.8 Hz, 1H), 2.00 – 1.86 (m, 1H), 0.83 – 0.72 (m, 4H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -115.45 (ddd, *J* = 14.0, 8.9, 5.1 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.3 (d, *J* = 245.7 Hz), 151.5, 143.2, 138.9, 136.4 (d, *J* = 2.9 Hz), 131.5, 128.9 (app s), 127.5, 124.7, 118.8, 116.6, 115.5 (d, *J* = 21.1 Hz), 115.1, 113.9, 78.0, 66.7, 55.8, 49.3, 33.8, 25.1, 9.4. **HRMS** (ESI): m/z calculated for $C_{25}H_{25}O_1N_2F_1$ requires 389.20237 for $[M+H]^+$, found 389.20270.

Synthesis of **3ac**

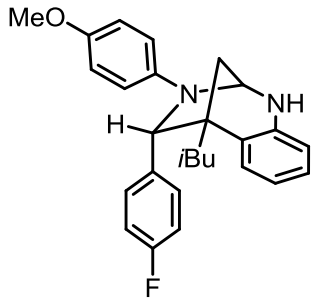
The compound was synthesized according to General Procedure **C** using **1a** (23 mg, 0.1 mmol), and 4-butylquinoline (**2c**, 56 mg, 0.3 mmol). Crude dr: 4.2:1 (endo:exo). Silica gel column chromatography (CH_2Cl_2:Pentane 30:70 – 70:30 v:v) gave a partially separable mixture of diastereomers, combined yield 72% (27.2 mg).



Data for **3ac$_{(endo)}$**. Off-white solid. **mp** (from $CHCl_3$): 134-138 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3392, 2930, 1605, 1509, 1470. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.95 (td, *J* = 7.6, 1.4 Hz, 1H), 6.85 – 6.65 (m, 6H), 6.60 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.48 – 6.35 (m, 3H), 6.17 (dd, *J* = 7.8, 1.5 Hz, 1H), 5.10 (d, *J* = 5.1 Hz, 1H), 4.70 (s, 1H), 4.50 (s, 1H), 3.67 (s, 2H), 2.48 (d, *J* = 10.7 Hz, 1H), 2.19 (dd, *J* = 10.7, 5.2 Hz, 1H), 2.01 (ddt, *J* = 13.7, 10.4, 4.6 Hz, 1H), 1.76 (ddd, *J* = 13.8, 10.8, 5.5 Hz, 1H), 1.47 – 1.31 (m, 4H), 0.93 (t, *J* = 6.9 Hz, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -116.05 (ddd, *J* = 14.0, 8.7, 5.7 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.0 (d, *J* = 244.0 Hz), 151.7, 143.8, 140.4, 134.0 (d, *J* = 3.1 Hz), 128.5 (d, *J* = 8.0 Hz), 127.7, 127.0, 126.9, 118.5, 115.9, 114.8, 114.5 (d, *J* = 21.3 Hz), 113.7, 78.7, 72.1, 55.9, 50.2, 38.0, 32.3, 27.1, 23.6, 14.2. **HRMS** (ESI): m/z calculated for $C_{27}H_{29}O_1N_2F_1$ requires 417.23367 for $[M+H]^+$, found 417.23306.

Synthesis of **3ad**

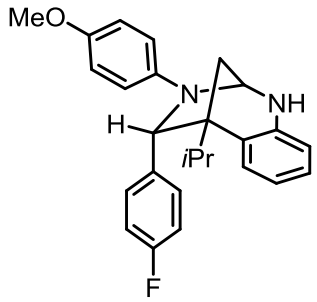
The compound was synthesized according to General Procedure **C** using **1a** (23 mg, 0.1 mmol), and 4-butylquinoline (**2d**, 56 mg, 0.3 mmol). Crude dr: 6.2:1 (endo:exo). Silica gel column chromatography (CH_2Cl_2:Pentane 30:70 – 50:50 v:v) gave a partially separable mixture of diastereomers, combined yield 64% (26.6 mg).



Data for **3ac$_{(endo)}$**. Off-white solid. **mp** (from $CHCl_3$): 84-88 °C. **FT-IR** (thin film): ν_{max}(cm^{-1}) = 3383, 2954, 1605, 1510. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.95 (td, *J* = 7.6, 1.4 Hz, 1H), 6.82 – 6.69 (m, 4H), 6.68 (d, *J* = 9.1 Hz, 2H), 6.61 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.48 – 6.32 (m, 3H), 6.17 (dd, *J* = 7.8, 1.4 Hz, 1H), 5.10 (d, *J* = 5.1 Hz, 1H), 4.74 (s, 1H), 4.47 (s, 1H), 3.67 (s, 3H), 2.59 (d, *J* = 10.6 Hz, 1H), 2.28 (dd, *J* = 10.7, 5.2 Hz, 1H), 2.02 (dd, *J* = 14.2, 3.7 Hz, 1H), 1.74 (ddp, *J* = 10.2, 6.6, 3.6 Hz, 1H), 1.62 (dd, *J* = 14.2, 7.1 Hz, 1H), 1.03 (d, *J* = 6.5 Hz, 3H), 0.94 (d, *J* = 6.7 Hz, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -115.96 (ddd, *J* = 14.1, 8.6, 5.9 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.0 (d, *J* = 244.5 Hz), 151.7, 143.8, 140.3, 133.9 (d, *J* = 2.8 Hz), 128.7 (d, *J* = 7.8 Hz), 127.7, 127.4, 127.1, 118.4, 115.9, 114.7, 114.5 (d, *J* = 21.6 Hz), 113.7, 79.6, 72.3, 55.8, 50.5, 41.1, 38.6, 25.5, 24.9, 24.8. **HRMS** (ESI): m/z calculated for $C_{27}H_{29}O_1N_2F_1$ requires 417.23367 for $[M+H]^+$, found 417.23315.

Synthesis of **3ae**

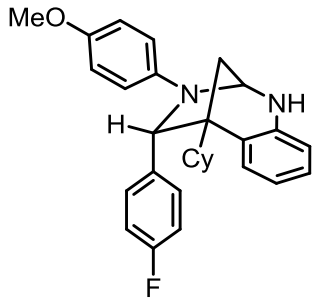
The compound was synthesized according to General Procedure **C** using **1a** (23 mg, 0.1 mmol), and 4-isopropylquinoline (**2e**, 51 mg, 0.3 mmol). Crude dr: 7.4:1 (endo:exo). Silica gel column chromatography (CH_2Cl_2:Pentane 30:70 – 60:40 v:v) gave a partially separable mixture of diastereomers, combined yield 94% (38.0 mg).



Data for **3ae$_{(endo)}$**. Off-white solid. **mp** (from $CHCl_3$): 154-158 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3381, 2964, 1604, 1510, 1472. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.92 (td, *J* = 7.5, 1.5 Hz, 1H), 6.70 (dq, *J* = 10.5, 3.8, 3.2 Hz, 6H), 6.60 (dd, *J* = 7.9, 1.3 Hz, 1H), 6.44 – 6.39 (m, 2H), 6.37 (td, *J* = 7.6, 1.3 Hz, 1H), 6.19 (dd, *J* = 8.0, 1.4 Hz, 1H), 5.12 (d, *J* = 5.3 Hz, 1H), 4.90 (s, 1H), 4.67 (s, 1H), 3.68 (s, 3H), 2.45 – 2.36 (m, 1H), 2.34 (dd, *J* = 10.7, 5.3 Hz, 1H), 2.25 (d, *J* = 10.7 Hz, 1H), 1.36 (d, *J* = 6.7 Hz, 3H), 0.93 (d, *J* = 6.6 Hz, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -116.25 (p, *J* = 8.0, 7.5 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.9 (d, *J* = 244.5 Hz), 151.6, 144.2, 140.5, 134.5 (d, *J* = 3.2 Hz), 128.2 (d, *J* = 8.0 Hz), 127.44, 127.38, 127.36, 118.4, 116.2, 114.8, 114.5 (d, *J* = 21.0 Hz), 113.6, 73.2, 71.6, 55.9, 53.8, 32.0, 25.8, 19.4, 18.0. **HRMS** (ESI): m/z calculated for $C_{26}H_{27}O_1N_2F_1$ requires 403.21802 for $[M+H]^+$, found 403.21768.

Synthesis of **3af**

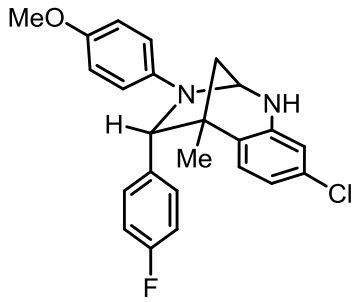
The compound was synthesized according to General Procedure **C** using **1a** (23 mg, 0.1 mmol), and 4-cyclohexylquinoline (**2f**, 63 mg, 0.3 mmol). Crude dr: 8.0:1 (endo:exo). Silica gel column chromatography (CH_2Cl_2:Pentane 30:70 – 60:40 v:v) gave a partially separable mixture of diastereomers, combined yield 86% (38.1 mg).



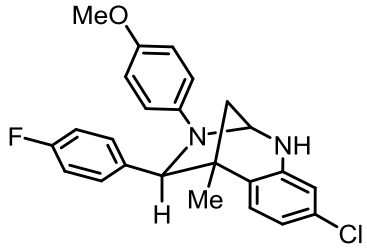
Data for **3af$_{(endo)}$**. White solid. **mp** (from $CHCl_3$): 182-186 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3372, 2981, 1604, 1510, 1472.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.91 (td, *J* = 7.6, 1.4 Hz, 1H), 6.69 (dq, *J* = 10.5, 3.8 Hz, 6H), 6.59 (dd, *J* = 7.9, 1.3 Hz, 1H), 6.46 – 6.39 (m, 2H), 6.38 – 6.31 (m, 1H), 6.15 (dd, *J* = 7.9, 1.4 Hz, 1H), 5.08 (d, *J* = 4.6 Hz, 1H), 4.98 (s, 1H), 4.65 (s, 1H), 3.67 (s, 3H), 2.45 – 2.24 (m, 3H), 2.06 – 1.88 (m, 2H), 1.84 – 1.65 (m, 3H), 1.57 – 1.37 (m, 2H), 1.35 – 1.13 (m, 2H), 0.99 – 0.82 (m, 1H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -116.32 (p, *J* = 7.0 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.8 (d, *J* = 244.3 Hz), 151.6, 144.3, 140.5, 134.5 (d, *J* = 2.9 Hz), 128.2 (d, *J* = 7.8 Hz), 127.3 (d, *J* = 9.4 Hz), 118.4, 116.3, 114.8, 114.5 (d, *J* = 21.2 Hz), 113.6, 72.0, 71.7, 55.9, 53.6, 36.5, 33.4, 29.3, 28.2, 27.1, 27.0, 26.9. **HRMS** (ESI): m/z calculated for $C_{29}H_{31}O_1N_2F_1$ requires 443.24932 for $[M+H]^+$, found 443.24905.

Synthesis of **3ag**

The compound was synthesized according to General Procedure **C** using **1a** (23 mg, 0.1 mmol), and 7-chloro-4-methylquinoline (**2g**, 53 mg, 0.3 mmol). Crude dr: 2.3:1 (endo:exo). Silica gel column chromatography (CH_2Cl_2:Pentane 30:70 – 70:30 v:v) gave a fully separable mixture of diastereomers, combined yield 68% (28.0 mg).



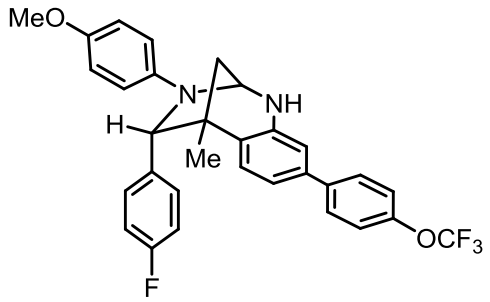
Data for **3ag$_{(endo)}$.** White solid. **mp** (from $CHCl_3$): 200-204 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3396, 2934, 1602, 1509, 1464. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.90 – 6.72 (m, 4H), 6.71 – 6.65 (m, 2H), 6.58 (d, *J* = 2.1 Hz, 1H), 6.44 – 6.35 (m, 3H), 6.15 (d, *J* = 8.3 Hz, 1H), 5.08 (d, *J* = 4.8 Hz, 1H), 4.83 (s, 1H), 4.47 (s, 1H), 3.68 (s, 3H), 2.38 (d, *J* = 10.7 Hz, 1H), 2.25 (dd, *J* = 10.7, 5.0 Hz, 1H), 1.48 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -115.60 (tt, *J* = 8.2, 5.4 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.0 (d, *J* = 244.4 Hz), 151.8, 144.1, 139.9, 133.3 (d, *J* = 3.2 Hz), 133.1, 128.3 (d, *J* = 7.9 Hz), 127.6, 127.2, 118.2, 114.8 (d, *J* = 13.4 Hz), 114.7, 114.5, 113.4, 78.9, 71.7, 55.71, 46.1, 41.0, 19.7. **HRMS** (ESI): m/z calculated for $C_{24}H_{22}O_1N_2Cl_1F_1$ requires 409.14775 for $[M+H]^+$, found 409.14749



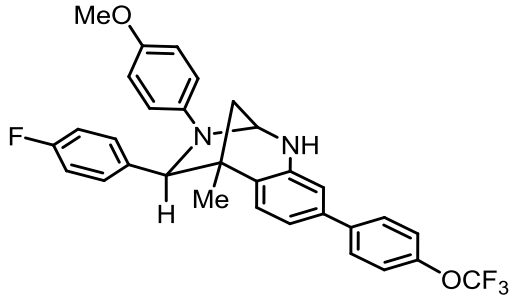
Data for **3ag$_{(exo)}$.** White solid. **mp** (from $CHCl_3$): 94-100 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3402, 2956, 1602, 1509, 1463. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 (dd, *J* = 8.5, 5.4 Hz, 2H), 7.10 (d, *J* = 8.3 Hz, 1H), 7.03 (t, *J* = 8.7 Hz, 2H), 6.74 – 6.65 (m, 3H), 6.49 (d, *J* = 2.1 Hz, 1H), 6.44 – 6.35 (m, 2H), 5.44 (d, *J* = 3.0 Hz, 1H), 5.21 (s, 0H), 4.53 (s, 1H), 3.68 (s, 3H), 2.31 (dd, *J* = 11.2, 4.6 Hz, 1H), 2.08 (d, *J* = 11.2 Hz, 1H), 1.02 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -115.14 – -115.35 (m). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.4 (d, *J* = 245.6 Hz), 151.8, 143.3, 138.6, 136.5 (d, *J* = 2.7 Hz), 133.0, 132.6, 128.6 (app s), 125.2, 118.4, 115.5 (d, *J* = 21.8 Hz), 115.4, 115.2, 114.0, 76.8, 66.6, 55.8, 44.5, 36.8, 19.9. **HRMS** (ESI): m/z calculated for $C_{24}H_{22}O_1N_2Cl_1F_1$ requires 409.14775 for $[M+H]^+$, found 409.14780.

Synthesis of **3ah**

The compound was synthesized according to General Procedure **C** using **1a** (23 mg, 0.1 mmol), and 4-methyl-7-(4-(trifluoromethoxy)phenyl)quinoline (**2h**, 91 mg, 0.3 mmol). Crude dr: 2.2:1 (endo:exo). Silica gel column chromatography (CH_2Cl_2:Pentane 20:80 – 40:60 v:v) gave a partially separable mixture of diastereomers, combined yield 57% (31.0 mg).



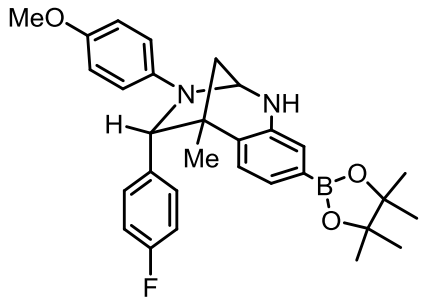
Data for **3ah$_{(endo)}$**. Off-white solid. **mp** (from $CHCl_3$): 82-84 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3396, 2980, 2361, 1606, 1510, 1463.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 – 7.46 (m, 2H), 7.25 – 7.18 (m, 2H), 6.85 (t, *J* = 6.7 Hz, 2H), 6.80 (d, *J* = 1.9 Hz, 1H), 6.74 (d, *J* = 8.6 Hz, 2H), 6.72 – 6.67 (m, 2H), 6.62 (dd, *J* = 8.0, 1.9 Hz, 1H), 6.47 – 6.41 (m, 2H), 6.32 (d, *J* = 8.0 Hz, 1H), 5.14 (d, *J* = 4.9 Hz, 1H), 4.87 (s, 1H), 4.51 (s, 1H), 3.68 (s, 3H), 2.47 (d, *J* = 10.7 Hz, 1H), 2.30 (dd, *J* = 10.7, 5.1 Hz, 1H), 1.54 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -57.82 (s), -115.76 (ddd, *J* = 14.1, 9.0, 5.5 Hz). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 162.1 (d, *J* = 245.0 Hz), 151.8, 148.6, 143.5, 140.2, 139.9, 139.5, 133.6 (d, *J* = 2.9 Hz), 128.5, 128.5 (d, *J* = 6.9 Hz), 128.3, 127.1, 123.3, 121.3, 120.7 (q, *J* = 256.7 Hz), 117.3, 114.6 (d, *J* = 21.6 Hz), 113.9, 113.7, 78.6, 72.0, 55.9, 46.4, 41.3, 19.9. **HRMS** (ESI): m/z calculated for $C_{31}H_{26}O_2N_2F_4$ requires 535.20032 for $[M+H]^+$, found 535.19983.



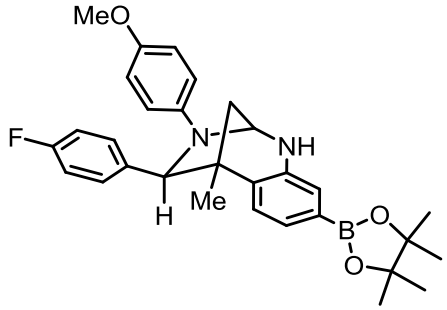
Data for **3ah$_{(exo)}$**. Off-white solid. **mp** (from $CHCl_3$): >260 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3401, 2970, 1605, 1510, 1463. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.45 (m, 2H), 7.32 – 7.16 (m, 5H), 7.04 (t, *J* = 8.4 Hz, 2H), 6.92 (dd, *J* = 7.9, 1.9 Hz, 1H), 6.75 – 6.65 (m, 3H), 6.48 – 6.38 (m, 2H), 5.50 (d, *J* = 4.5 Hz, 1H), 5.26 (s, 1H), 4.61 (s, 1H), 3.67 (s, 3H), 2.35 (dd, *J* = 11.2, 4.6 Hz, 1H), 2.16 (d, *J* = 11.1 Hz, 1H), 1.08 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -57.80, -115.32 (ddd, *J* = 13.5, 8.3, 5.2 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.4 (d, *J* = 245.9 Hz), 151.7, 148.6, 142.5, 139.9, 139.4, 138.8, 136.6 (d, *J* = 2.9 Hz), 133.8, 128.6 (app s), 128.4, 124.6, 121.2, 119.6 (app m), 117.5, 115.6 (d, *J* = 21.2 Hz), 115.2, 114.5, 114.0, 76.9, 66.7, 55.8, 44.7, 37.1, 20.0. **HRMS** (ESI): m/z calculated for $C_{31}H_{26}O_2N_2F_4$ requires 535.20032 for $[M+H]^+$, found 535.20032

Synthesis of **3ai**

The compound was synthesized according to General Procedure **C** using **1a** (23 mg, 0.1 mmol), and **2i** (81 mg, 0.3 mmol). Crude dr: 2.1:1 (endo:exo). Silica gel column chromatography (CH_2Cl_2:Acetone 100:0 – 99:1 v:v) gave a partially separable mixture of diastereomers, combined yield 58% (28.8 mg).



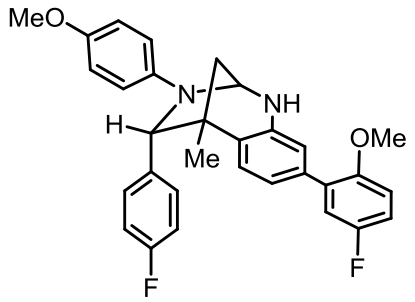
Data for **3ai$_{(endo)}$**. White solid. **mp** (from $CHCl_3$): 120-124 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3369, 2978, 2931, 2832, 1606, 1558, 1510. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.04 (d, *J* = 1.2 Hz, 1H), 6.85 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.83 – 6.76 (m, 2H), 6.71 (d, *J* = 8.5 Hz, 2H), 6.69 – 6.64 (m, 2H), 6.43 – 6.36 (m, 2H), 6.27 (d, *J* = 7.7 Hz, 1H), 5.08 (d, *J* = 4.9 Hz, 1H), 4.48 (s, 1H), 3.67 (s, 3H), 2.42 (d, *J* = 10.7 Hz, 1H), 2.25 (dd, *J* = 10.7, 5.1 Hz, 1H), 1.50 (s, 3H), 1.32 (d, *J* = 1.6 Hz, 12H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -115.95 (tt, *J* = 8.3, 5.2 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.0 (d, *J* = 244.4 Hz), 151.7, 142.5, 140.3, 133.5 (d, *J* = 2.9 Hz), 132.2, 128.6 (d, *J* = 8.1 Hz), 126.0, 125.0, 121.6, 114.7, 114.55 (app s), 113.8, 83.8, 77.4, 72.1, 55.8, 46.6, 41.2, 25.0, 25.0, 19.8. **HRMS**(ESI): m/z calculated for $C_{30}H_{34}O_3N_2B_1F_1$ requires 500.27556 for $[M+H]^+$, found 500.27563.



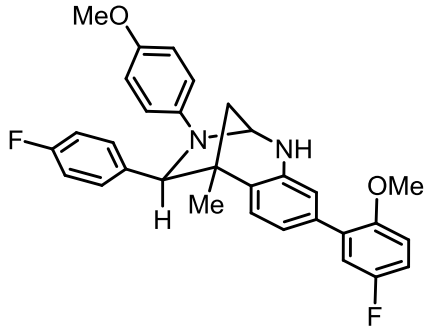
Data for **3ai$_{(exo)}$**. White solid. **mp** (from $CHCl_3$): 236-239 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3395, 3045, 2975, 2927, 1604, 1558, 1510. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.24 – 7.14 (m, 4H), 7.02 (t, *J* = 8.5 Hz, 2H), 6.96 (d, *J* = 1.1 Hz, 1H), 6.72 – 6.66 (m, 2H), 6.43 – 6.31 (m, 2H), 5.45 (d, *J* = 4.5 Hz, 1H), 5.19 (s, 1H), 4.56 (s, 1H), 3.67 (s, 3H), 2.31 (dd, *J* = 11.2, 4.7 Hz, 1H), 2.14 (d, *J* = 11.2 Hz, 1H), 1.29 (s, 12H), 1.05 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -115.35 – -115.56 (m). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.3 (d, *J* = 245.3 Hz), 151.6, 141.6, 138.9, 137.4, 136.8 (d, *J* = 3.0 Hz), 128.6 (app s), 125.2, 123.4, 122.2, 115.5 (d, *J* = 21.4 Hz), 115.2, 114.0, 83.8, 76.9, 66.8, 55.9, 44.9, 36.9, 25.0, 24.9, 19.9. **HRMS** (ESI): m/z calculated for $C_{30}H_{34}O_3N_2B_1F_1$ requires 500.27556 for $[M+H]^+$, found 500.27600.

Synthesis of **3aj**

The compound was synthesized according to General Procedure **C** using **1a** (23 mg, 0.1 mmol), and 7-(5-fluoro-2-methoxyphenyl)-4-methylquinoline (**2j**, 80 mg, 0.3 mmol). Crude dr: 2.0:1 (endo:exo). Silica gel column chromatography (CH_2Cl_2:Pentane 20:80 – 40:60 v:v) gave a fully separable mixture of diastereomers, combined yield 85% (42.5 mg).



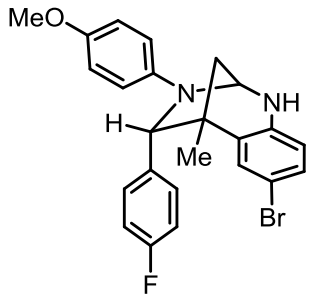
Data for **3aj$_{(endo)}$**. Pale orange amorphous solid. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3389, 2936, 1608, 1562, 1509, 1492, 1462, 1419. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.00 – 6.91 (m, 2H), 6.87 (dd, *J* = 8.4, 4.5 Hz, 3H), 6.80 – 6.64 (m, 5H), 6.56 (dd, *J* = 8.0, 1.8 Hz, 1H), 6.47 – 6.39 (m, 2H), 6.29 (d, *J* = 8.0 Hz, 1H), 5.14 (d, *J* = 4.9 Hz, 1H), 4.78 (s, 1H), 4.51 (s, 1H), 3.73 (s, 3H), 3.69 (s, 3H), 2.50 (d, *J* = 10.7 Hz, 1H), 2.28 (dd, *J* = 10.7, 5.1 Hz, 1H), 1.54 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -115.88 (ddd, *J* = 14.1, 8.9, 5.8 Hz), -123.96 (td, *J* = 8.6, 4.9 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.0 (d, *J* = 244.7 Hz), 157.2 (d, *J* = 238.5 Hz), 152.8, 151.6, 142.6, 140.2, 137.1, 133.7 (d, *J* = 2.9 Hz), 132.3 (d, *J* = 7.4 Hz), 128.4 (d, *J* = 8.0 Hz), 128.0, 126.1, 119.6, 117.2 (d, *J* = 23.2 Hz), 116.3, 114.7, 114.4 (d, *J* = 21.4 Hz), 114.1 (d, *J* = 22.4 Hz), 113.6, 112.8 (d, *J* = 8.1 Hz), 78.5, 72.0, 56.5, 55.7, 46.3, 41.1, 19.7. **HRMS** (ESI): m/z calculated for $C_{31}H_{28}O_2N_2F_2$ requires 499.21916 for $[M+H]^+$, found 499.21887.



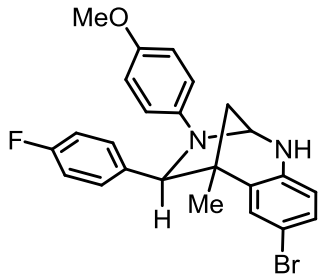
Data for **3aj$_{(exo)}$**. Pale orange solid. **mp** (from $CHCl_3$): 88-92 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3401, 2935, 1607, 1562, 1509, 1492, 1462, 1418. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.24 (dt, *J* = 8.5, 3.4 Hz, 3H), 7.04 (t, *J* = 8.4 Hz, 2H), 6.99 (dd, *J* = 9.2, 3.2 Hz, 1H), 6.97 – 6.89 (m, 2H), 6.85 (dd, *J* = 9.0, 4.6 Hz, 1H), 6.73 – 6.69 (m, 2H), 6.68 (d, *J* = 1.8 Hz, 1H), 6.46 – 6.39 (m, 2H), 5.48 (d, *J* = 4.5 Hz, 1H), 5.16 (s, 1H), 4.65 (s, 1H), 3.76 (s, 3H), 3.67 (s, 3H), 2.33 (dd, *J* = 11.2, 4.7 Hz, 1H), 2.16 (d, *J* = 11.2 Hz, 1H), 1.08 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -115.46 (ddd, *J* = 13.8, 8.6, 5.4 Hz), -124.12 – -124.60 (m). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 162.4 (d, *J* = 245.3 Hz), 157.2 (d, *J* = 238.4 Hz), 152.7, 151.6, 141.9, 138.9, 136.9, 136.8 (d, *J* = 2.4 Hz), 133.5, 131.9 (d, *J* = 7.6 Hz), 128.6 (d, *J* = 13.0 Hz), 123.8, 119.9, 117.5, 117.3, 116.9, 115.5 (d, *J* = 21.1 Hz), 115.1, 114.1 (d, *J* = 22.8 Hz), 114.0, 112.1 (d, *J* = 8.3 Hz), 76.7, 66.8, 56.3, 55.9, 44.6, 37.1, 19.9.. **HRMS** (ESI): m/z calculated for $C_{31}H_{28}O_2N_2F_2$ requires 499.21916 for $[M+H]^+$, found 499.21893.

Synthesis of **3ak**

The compound was synthesized according to General Procedure **C** using **1a** (23 mg, 0.1 mmol), and 6-bromo-4-methylquinoline (**2k**, 67 mg, 0.3 mmol). Crude dr: 1.5:1 (endo:exo). Silica gel column chromatography (CH_2Cl_2:Pentane 20:80 – 40:60 v:v) gave a fully separable mixture of diastereomers, combined yield 54% (24.6 mg).



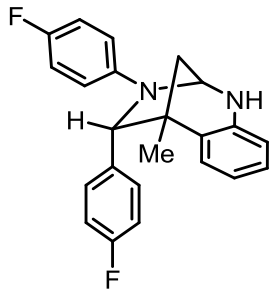
Data for **3ak$_{(endo)}$**. Off-white amorphous solid. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3392, 2980, 1607, 1510. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.05 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.78 (t, *J* = 8.3 Hz, 4H), 6.72 – 6.65 (m, 2H), 6.47 (d, *J* = 8.4 Hz, 1H), 6.44 – 6.36 (m, 2H), 6.34 (d, *J* = 2.2 Hz, 1H), 5.09 (d, *J* = 4.9 Hz, 1H), 4.76 (s, 1H), 4.47 (s, 1H), 3.67 (s, 3H), 2.39 (d, *J* = 10.7 Hz, 1H), 2.25 (dd, *J* = 10.8, 5.0 Hz, 1H), 1.48 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -115.39 – -115.52 (m). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.2 (d, *J* = 245.2 Hz), 151.9, 142.1, 140.0, 133.2 (d, *J* = 2.9 Hz), 131.1, 130.6, 129.3, 128.4 (d, *J* = 7.9 Hz), 116.9, 114.79 (d, *J* = 21.6 Hz), 114.79, 113.8, 110.6, 78.6, 71.8, 55.8, 46.6, 40.8, 19.8. **HRMS** (ESI): m/z calculated for $C_{24}H_{22}O_1N_2Br_1F_1$ requires 453.09723 for $[M+H]^+$, found 453.09705.



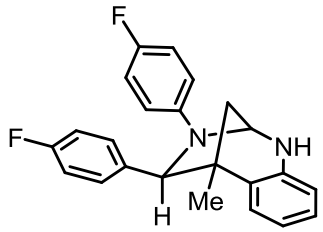
Data for **3ak$_{(exo)}$**. White solid. **mp** (from $CHCl_3$): 58-60 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3403.1, 2917, 2849, 1602, 1509. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 2.2 Hz, 1H), 7.22 (dd, *J* = 8.4, 5.4 Hz, 2H), 7.08 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.06 – 7.00 (m, 2H), 6.71 (d, *J* = 9.1 Hz, 2H), 6.40 (t, *J* = 8.5 Hz, 3H), 5.45 (d, *J* = 4.6 Hz, 1H), 5.16 (s, 1H), 4.57 (s, 1H), 3.67 (s, 3H), 2.31 (dd, *J* = 11.3, 4.7 Hz, 1H), 2.09 (d, *J* = 11.2 Hz, 1H), 1.02 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -115.16 (tt, *J* = 8.9, 5.5 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.4 (d, *J* = 246.0 Hz), 151.8, 141.2, 138.6, 136.4 (d, *J* = 2.9 Hz), 136.2, 130.4, 128.6 (app s), 127.0, 117.5, 115.6 (d, *J* = 21.2 Hz), 115.1, 114.1, 110.6, 76.7, 66.5, 55.8, 44.8, 36.7, 19.9. **HRMS** (ESI): m/z calculated for $C_{24}H_{22}O_1N_2Br_1F_1$ requires 453.09723 for $[M+H]^+$, found 453.09720.

Synthesis of **3b**

The compound was synthesized according to General Procedure **C** using **1b** (21.7 mg, 0.1 mmol), and lepidine (40 μL, 0.3 mmol). Crude dr: 2.4:1 (endo:exo). Silica gel column chromatography (CH_2Cl_2:Pentane 10:90 – 30:70 v:v) gave a fully separable mixture of diastereomers, combined yield 71% (25.7 mg).



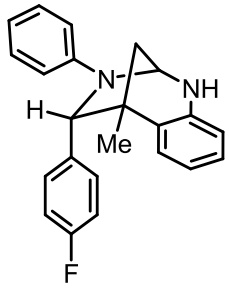
Data for **3b$_{(endo)}$**. White solid. **mp** (from $CHCl_3$): 170-172 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3391, 3052, 2987, 1606, 1508, 1474. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.97 (td, *J* = 7.6, 1.5 Hz, 1H), 6.89 – 6.68 (m, 6H), 6.60 (dd, *J* = 7.9, 1.2 Hz, 1H), 6.48 – 6.33 (m, 3H), 6.26 (dd, *J* = 7.8, 1.5 Hz, 1H), 5.12 (d, *J* = 5.0 Hz, 1H), 4.74 (s, 1H), 4.48 (s, 1H), 2.46 (d, *J* = 10.7 Hz, 1H), 2.27 (dd, *J* = 10.7, 5.1 Hz, 1H), 1.52 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -115.67 (p, *J* = 6.9 Hz), -128.48 (tt, *J* = 8.6, 4.3 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 162.1 (d, *J* = 244.9 Hz), 155.6 (d, *J* = 235.8 Hz), 142.8, 142.3 (d, *J* = 1.4 Hz), 133.3 (d, *J* = 3.0 Hz), 128.7, 128.5 (d, *J* = 8.0 Hz), 128.0, 126.5, 118.7, 115.6, 115.4 (d, *J* = 4.7 Hz), 114.6 (d, *J* = 21.4 Hz), 113.5 (d, *J* = 7.2 Hz), 78.5, 71.9, 46.4, 41.3, 19.9. **HRMS** (ESI): m/z calculated for $C_{23}H_{20}N_2F_2$ requires 363.16673 for $[M+H]^+$, found 363.16779.



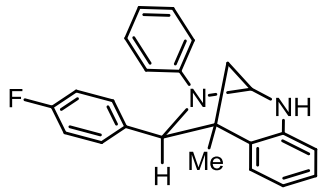
Data for **3b$_{(exo)}$**. White solid. **mp** (from $CHCl_3$): 179-182 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3404, 2917, 1605, 1507. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.13 (m, 3H), 7.10 – 6.94 (m, 3H), 6.88 – 6.68 (m, 3H), 6.53 (dd, *J* = 7.9, 1.3 Hz, 1H), 6.38 (dd, *J* = 9.2, 4.3 Hz, 2H), 5.46 (d, *J* = 4.6 Hz, 1H), 5.21 – 5.03 (m, 1H), 4.59 (s, 1H), 2.32 (dd, *J* = 11.2, 4.7 Hz, 1H), 2.14 (d, *J* = 11.2 Hz, 1H), 1.05 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -114.90 – -115.39 (m), -128.83 (tt, *J* = 8.8, 4.4 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.3 (d, *J* = 245.7 Hz), 155.4 (d, *J* = 235.9 Hz), 141.7, 140.8 (d, *J* = 1.4 Hz), 136.2 (d, *J* = 2.8 Hz), 133.9, 128.3 (d, *J* = 17.7 Hz), 127.7, 123.9, 118.8, 115.8 (d, *J* = 3.8 Hz), 115.6 (d, *J* = 4.0 Hz), 115.4, 113.6 (d, *J* = 7.2 Hz), 76.9, 66.7, 44.6, 36.9, 19.8. **HRMS** (ESI): m/z calculated for $C_{23}H_{20}N_2F_2$ requires 363.16673 for $[M+H]^+$, found 363.16666.

Synthesis of **3c**

The compound was synthesized according to General Procedure **C** using **1c** (19.9 mg, 0.1 mmol), and lepidine (40 μL, 0.3 mmol). Crude dr: 2.3:1 (endo:exo). Silica gel column chromatography (CH_2Cl_2:Pentane 30:70 – 50:50 v:v) gave an almost fully separable mixture of diastereomers, combined yield 68% (23.3 mg).



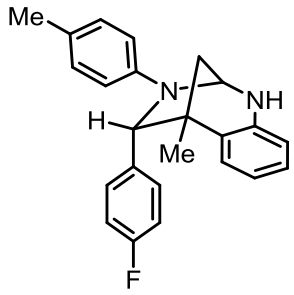
Data for **3b$_{(endo)}$**. Off-white amorphous solid. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3394, 2971, 1598, 1502, 1474. **^{1}H NMR** (400 MHz, $CDCl_3$, note: some exo diastereomer in NMR) δ 7.09 (dd, *J* = 8.7, 7.3 Hz, 2H), 6.97 (td, *J* = 7.6, 1.5 Hz, 1H), 6.89 – 6.69 (m, 4H), 6.65 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.60 (dd, *J* = 7.9, 1.2 Hz, 1H), 6.49 – 6.44 (m, 2H), 6.42 (td, *J* = 7.5, 1.3 Hz, 1H), 6.26 (dd, *J* = 7.8, 1.5 Hz, 1H), 5.20 (d, *J* = 4.9 Hz, 1H), 4.78 (s, 1H), 4.53 (s, 1H), 2.47 (d, *J* = 10.7 Hz, 1H), 2.27 (dd, *J* = 10.7, 5.1 Hz, 1H), 1.52 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -115.92 (tt, *J* = 8.0, 5.5 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.1 (d, *J* = 244.2 Hz), 145.7, 142.8, 133.6 (d, *J* = 2.8 Hz), 129.1, 128.8, 128.4 (d, *J* = 8.0 Hz), 127.9, 126.5, 118.7, 117.2, 115.4, 114.6 (d, *J* = 21.4 Hz), 112.9, 78.2, 71.4, 46.4, 41.2, 19.9. **HRMS** (ESI): m/z calculated for $C_{25}H_{21}F_1N_2$ requires 345.17620 for $[M+H]^+$, found 345.17563.



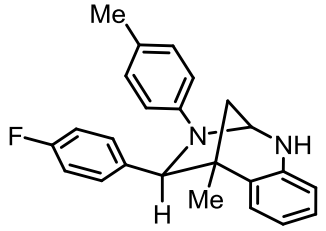
Data for **3b$_{(exo)}$**. Off-white solid. **mp** (from $CHCl_3$): 154-156 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3403, 2971, 1598, 1503, 1475. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.17 (m, 3H), 7.13 – 7.07 (m, 2H), 7.06 – 6.96 (m, 3H), 6.75 (td, *J* = 7.6, 1.3 Hz, 1H), 6.63 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.53 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.50 – 6.44 (m, 2H), 5.52 (d, *J* = 4.6 Hz, 1H), 5.19 (s, 1H), 4.64 (s, 1H), 2.32 (dd, *J* = 11.3, 4.8 Hz, 1H), 2.15 (d, *J* = 11.2 Hz, 1H), 1.06 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -115.39 (ddd, *J* = 13.7, 8.5, 5.4 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.2 (d, *J* = 245.6 Hz), 144.3, 141.9, 136.2 (d, *J* = 3.0 Hz), 134.0, 129.3, 128.5 (app s), 127.7, 123.9, 118.8, 116.9, 116.1, 115.4 (d, *J* = 21.3 Hz), 113.1, 76.7, 66.4, 44.5, 36.8, 19.8. **HRMS** (ESI): m/z calculated for $C_{25}H_{21}F_1N_2$ requires 345.17620 for $[M+H]^+$, found 345.17610.

Synthesis of **3d**

The compound was synthesized according to General Procedure **C** using **1d** (29.7 mg, 0.1 mmol), and lepidine (40 μL, 0.3 mmol). Crude dr: 2.6:1 (endo:exo). Silica gel column chromatography (CH_2Cl_2:Pentane 20:80 – 50:50 v:v) gave a partially separable mixture of diastereomers, combined yield 83% (29.7 mg).



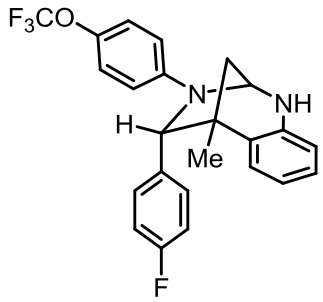
Data for **3d$_{(endo)}$**. Off-white amorphous solid. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3394, 2980, 1606, 1517, 1473. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.96 (td, *J* = 7.6, 1.5 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.85 – 6.67 (m, 4H), 6.60 (dd, *J* = 7.9, 1.2 Hz, 1H), 6.47 – 6.36 (m, 3H), 6.25 (dd, *J* = 7.7, 1.5 Hz, 1H), 5.15 (d, *J* = 5.0 Hz, 1H), 4.71 (d, *J* = 31.2 Hz, 1H), 4.50 (s, 1H), 2.46 (d, *J* = 10.6 Hz, 1H), 2.29 – 2.21 (m, 1H), 2.17 (s, 3H), 1.51 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -116.01 (ddd, *J* = 14.1, 8.9, 5.9 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.0 (d, *J* = 244.0 Hz), 143.6, 143.0, 133.8 (d, *J* = 3.1 Hz), 129.6, 128.9, 128.4 (d, *J* = 8.0 Hz), 127.9, 126.5, 126.3, 118.6, 115.4, 114.6 (d, *J* = 21.4 Hz), 112.8, 78.4, 71.7, 46.4, 41.2, 20.4, 19.9. **HRMS** (ESI): m/z calculated for $C_{24}H_{23}N_2F_1$ requires 359.19180 for $[M+H]^+$, found 359.19144.



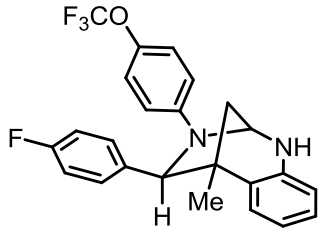
Data for **3d$_{(exo)}$**. Off-white solid. **mp** (from $CHCl_3$): 178-182 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3403, 2980, 1605, 1518, 1507, 1474. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.15 (m, 3H), 7.09 – 6.95 (m, 3H), 6.95 – 6.87 (m, 2H), 6.75 (td, *J* = 7.5, 1.2 Hz, 1H), 6.52 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.45 – 6.35 (m, 2H), 5.50 (d, *J* = 4.6 Hz, 1H), 5.19 (s, 1H), 4.62 (s, 1H), 2.31 (dd, *J* = 11.2, 4.7 Hz, 1H), 2.17 (s, 3H), 2.14 (d, *J* = 11.3 Hz, 1H), 1.06 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -115.39 – -115.64 (m). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.2 (d, *J* = 245.2 Hz), 142.0 (d, *J* = 13.5 Hz), 136.5 (d, *J* = 3.2 Hz), 134.1, 129.8, 128.54, 128.46 (app s), 127.6, 126.0, 123.8, 118.7, 116.1, 115.4 (d, *J* = 21.4 Hz), 113.0, 76.6, 66.4, 44.5, 36.9, 20.2, 19.8. **HRMS** (ESI): m/z calculated for $C_{24}H_{23}N_2F_1$ requires 359.19180 for $[M+H]^+$, found 359.19116.

Synthesis of **3e**

The compound was synthesized according to General Procedure **C** using **1e** (28.3 mg, 0.1 mmol), and lepidine (40 μL, 0.3 mmol). Crude dr: 2.0:1 (endo:exo). Silica gel column chromatography (CH_2Cl_2:Pentane 30:70 – 60:40 v:v) gave a fully separable mixture of diastereomers, combined yield 65% (27.7 mg).



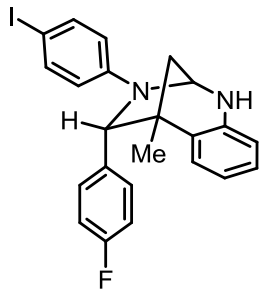
Data for **3e(endo)**. White solid. **mp** (from $CHCl_3$): 142-144 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3400, 2980, 1607, 1509, 1474. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.05 – 6.86 (m, 3H), 6.74 (s, 4H), 6.60 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.48 – 6.32 (m, 3H), 6.25 (dd, *J* = 7.8, 1.5 Hz, 1H), 5.17 (d, *J* = 4.8 Hz, 1H), 4.76 (s, 1H), 4.49 (s, 1H), 2.47 (d, *J* = 10.7 Hz, 1H), 2.27 (dd, *J* = 10.8, 5.0 Hz, 1H), 1.52 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -58.45, -115.48 (ddd, *J* = 14.0, 8.2, 5.8 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.2 (d, *J* = 245.1 Hz), 144.5, 142.6, 140.3, 133.0 (d, *J* = 2.9 Hz), 128.5, 128.4 (d, *J* = 8.1 Hz), 128.0, 126.5, 122.2, 120.4 (q, *J* = 255.5 Hz), 118.8, 115.4, 114.7 (d, *J* = 21.3 Hz), 113.2, 78.4, 71.5, 46.5, 41.2, 19.9. **HRMS** (ESI): m/z calculated for $C_{24}H_{20}O_1N_2F_4$ requires 429.15845 for $[M+H]^+$, found 429.15835.



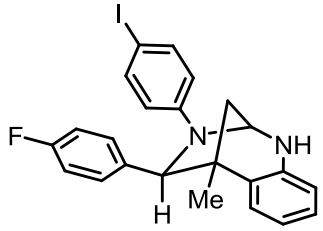
Data for **3e(exo)**. White solid. **mp** (from $CHCl_3$): 204-208 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3406, 2980, 1606, 1509, 1475. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.16 (m, 3H), 7.10 – 6.99 (m, 3H), 6.98 – 6.90 (m, 2H), 6.77 (td, *J* = 7.5, 1.2 Hz, 1H), 6.55 (dd, *J* = 7.9, 1.2 Hz, 1H), 6.46 – 6.33 (m, 2H), 5.48 (d, *J* = 4.6 Hz, 1H), 5.12 (s, 1H), 4.61 (s, 1H), 2.33 (dd, *J* = 11.3, 4.8 Hz, 1H), 2.15 (d, *J* = 11.2 Hz, 1H), 1.06 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -58.44, -114.84 – -115.04 (m). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.4 (d, *J* = 246.0 Hz), 143.3, 141.7, 140.3 (d, *J* = 2.0 Hz), 135.9 (d, *J* = 2.9 Hz), 133.8, 128.6 (app s), 127.9, 124.1, 122.5, 121.8 (app m), 119.0, 116.1, 115.7 (d, *J* = 21.5 Hz), 113.5, 77.1, 66.8, 44.7, 37.0, 19.9. **HRMS** (ESI): m/z calculated for $C_{24}H_{20}O_1N_2F_4$ requires 429.15845 for $[M+H]^+$, found 429.15829.

Synthesis of **3f**

The compound was synthesized according to General Procedure **C** using **1f** (32.5 mg, 0.1 mmol), and lepidine (40 μL, 0.3 mmol). Crude dr: 2.0:1 (endo:exo). Silica gel column chromatography (CH_2Cl_2:Pentane 30:70 – 60:40 v:v) gave a partially separable mixture of diastereomers, combined yield 64% (30.0 mg).



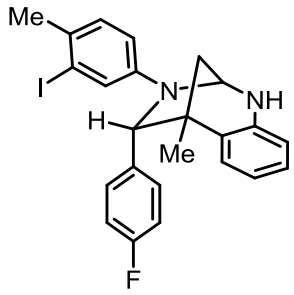
Data for **3f$_{(endo)}$**. White solid. **mp** (from $CHCl_3$): 176-178 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3397, 2980, 1604, 1584, 1507, 1490. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 2H), 6.96 (td, *J* = 7.6, 1.5 Hz, 1H), 6.73 (s, 4H), 6.59 (dd, *J* = 7.9, 1.2 Hz, 1H), 6.42 (td, *J* = 7.5, 1.3 Hz, 1H), 6.29 – 6.20 (m, 3H), 5.13 (d, *J* = 4.9 Hz, 1H), 4.75 (s, 1H), 4.48 (s, 1H), 2.45 (d, *J* = 10.8 Hz, 1H), 2.26 (dd, *J* = 10.8, 5.1 Hz, 1H), 1.51 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -115.50 (p, *J* = 7.2 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.1 (d, *J* = 245.1 Hz), 145.2, 142.5, 137.6, 132.9 (d, *J* = 2.9 Hz), 128.5, 128.4 (d, *J* = 6.8 Hz), 128.0, 126.5, 118.8, 115.4, 115.2, 114.7 (d, *J* = 21.6 Hz), 78.3, 78.1, 71.2, 46.4, 41.1, 19.9. **HRMS** (ESI): m/z calculated for $C_{23}H_{20}N_2F_1I_1$ requires 471.07280 for $[M+H]^+$, found 471.07245.



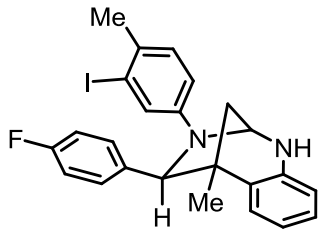
Data for **3f$_{(exo)}$**. White solid. **mp** (from $CHCl_3$): 200-208 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3401, 2980, 1603, 1585, 1506, 1489. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 2H), 7.20 (ddd, *J* = 13.6, 8.0, 3.4 Hz, 3H), 7.12 – 6.96 (m, 3H), 6.77 (td, *J* = 7.5, 1.3 Hz, 1H), 6.53 (dd, *J* = 7.9, 1.3 Hz, 1H), 6.30 – 6.20 (m, 2H), 5.46 (d, *J* = 4.7 Hz, 1H), 5.10 (s, 1H), 4.59 (s, 1H), 2.31 (dd, *J* = 11.3, 4.8 Hz, 1H), 2.14 (d, *J* = 11.3 Hz, 1H), 1.06 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -114.94 (tt, *J* = 8.9, 5.5 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.4 (d, *J* = 246.3 Hz), 144.0, 141.7, 138.1, 137.9, 135.7 (d, *J* = 2.9 Hz), 133.8, 128.5 (app s), 128.0, 124.1, 119.1, 116.1, 115.8, 115.6, 78.2, 66.6, 44.7, 36.9, 19.8. **HRMS** (ESI): m/z calculated for $C_{23}H_{20}N_2F_1I_1$ requires 471.07280 for $[M+H]^+$, found 471.07254.

Synthesis of **3g**

The compound was synthesized according to General Procedure **C** using **1g** (33.9 mg, 0.1 mmol), and lepidine (40 μL, 0.3 mmol). Crude dr: 1.9:1 (endo:exo). Silica gel column chromatography (CH_2Cl_2:Pentane 50:50 – 70:30 v:v) gave a fully separable mixture of diastereomers, combined yield 61% (29.7 mg).



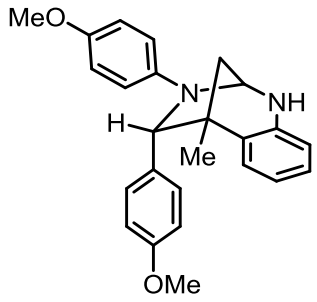
Data for **3g$_{(endo)}$**. Off-white amorphous solid. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3394, 2980, 1599, 1542, 1493. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.04 (d, *J* = 2.6 Hz, 1H), 6.97 (td, *J* = 7.6, 1.5 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.77 – 6.70 (m, 4H), 6.60 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.42 (td, *J* = 7.6, 1.3 Hz, 1H), 6.32 – 6.16 (m, 2H), 5.12 (d, *J* = 4.9 Hz, 1H), 4.77 (s, 1H), 4.47 (s, 1H), 2.45 (d, *J* = 10.7 Hz, 1H), 2.30 (d, *J* = 16.2 Hz, 1H), 2.24 (s, 3H), 1.51 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -115.63 (td, *J* = 8.8, 4.5 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.1 (d, *J* = 244.4 Hz), 144.7, 142.6, 133.1 (d, *J* = 3.4 Hz), 129.5, 129.47, 128.5, 128.4 (d, *J* = 8.3 Hz), 128.0, 126.4, 123.1, 118.7, 115.4, 114.7 (d, *J* = 21.4 Hz), 112.9, 101.8, 78.2, 71.5, 46.3, 41.1, 26.8, 19.9. **HRMS** (ESI): m/z calculated for $C_{24}H_{22}N_2F_1I_1$ requires 485.08845 for $[M+H]^+$, found 485.08810.



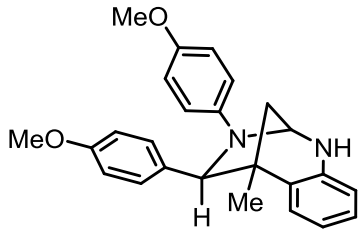
Data for **3g$_{(exo)}$**. Off-white solid. **mp** (from $CHCl_3$): 80-84 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3400m 2980, 1600, 1542, 1493.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.19 (dd, *J* = 8.2, 5.4 Hz, 2H), 7.09 – 6.96 (m, 4H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.79 (td, *J* = 7.6, 1.2 Hz, 1H), 6.61 (dd, *J* = 7.8, 1.2 Hz, 1H), 6.33 (dd, *J* = 8.4, 2.6 Hz, 1H), 5.49 (d, *J* = 4.6 Hz, 1H), 4.58 (s, 1H), 2.31 (dd, *J* = 11.3, 4.7 Hz, 1H), 2.23 (s, 3H), 2.16 (d, *J* = 11.3 Hz, 1H), 1.06 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -115.04 (td, *J* = 8.7, 4.4 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.4 (d, *J* = 246.0 Hz), 143.4, 141.7, 135.9 (d, *J* = 2.9 Hz), 133.9, 129.88, 129.4, 128.6 (app s), 127.9, 124.0, 123.0, 119.0, 116.1, 115.6 (d, *J* = 21.7 Hz), 113.5, 102.2, 76.7, 66.6, 44.6, 36.8, 26.8, 19.9. **HRMS** (ESI): m/z calculated for $C_{24}H_{22}N_2F_1I_1$ requires 485.08845 for $[M+H]^+$, found 485.08823.

Synthesis of **3h**

The compound was synthesized according to General Procedure **C** using **1h** (24.1 mg, 0.1 mmol), and lepidine (40 μL, 0.3 mmol). Crude dr: 2.7:1 (endo:exo). Silica gel column chromatography (CH_2Cl_2:Pentane 50:50 – 90:10 v:v) gave a partially separable mixture of diastereomers, combined yield 79% (30.5 mg).



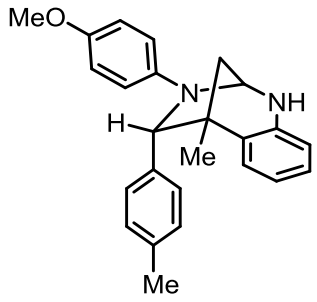
Data for **3h$_{(endo)}$**. White solid. **mp** (from $CHCl_3$): 58-64 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3375, 2930, 1609, 1510, 1464. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.96 (td, *J* = 7.5, 1.4 Hz, 1H), 6.81 – 6.72 (m, 2H), 6.71 – 6.63 (m, 2H), 6.63 – 6.52 (m, 3H), 6.48 – 6.38 (m, 3H), 6.28 (dd, *J* = 7.8, 1.5 Hz, 1H), 5.09 (d, *J* = 5.0 Hz, 1H), 4.72 (s, 1H), 4.44 (s, 1H), 3.69 (s, 3H), 3.67 (s, 3H), 2.44 (d, *J* = 10.6 Hz, 1H), 2.24 (dd, *J* = 10.6, 5.1 Hz, 1H), 1.50 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.7, 151.5, 143.1, 140.7, 130.0, 129.3, 128.2, 127.7, 126.7, 118.6, 115.5, 114.7, 113.7, 113.1, 79.0, 72.1, 55.9, 55.2, 46.3, 41.3, 20.0. **HRMS** (ESI): m/z calculated for $C_{25}H_{26}O_2N_2$ requires 387.20670 for $[M+H]^+$, found 387.20638.



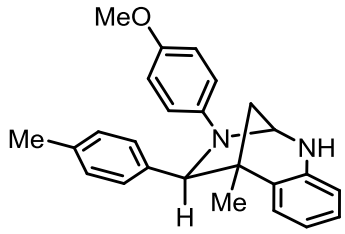
Data for **3h$_{(exo)}$**. White solid. **mp** (from $CHCl_3$): 174-178 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3403, 2931, 1608, 1510. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.17 (d, *J* = 8.3 Hz, 2H), 6.99 (td, *J* = 7.5, 1.4 Hz, 1H), 6.91 – 6.83 (m, 2H), 6.78 – 6.66 (m, 3H), 6.52 (dd, *J* = 7.9, 1.3 Hz, 1H), 6.46 – 6.37 (m, 2H), 5.45 (d, *J* = 4.6 Hz, 1H), 5.13 (s, 1H), 4.55 (s, 1H), 3.80 (s, 3H), 3.67 (s, 3H), 2.33 (dd, *J* = 11.0, 4.7 Hz, 1H), 2.11 (d, *J* = 11.1 Hz, 1H), 1.05 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.0, 151.4, 142.2, 139.1, 134.7, 133.2, 128.2, 127.6, 124.0, 118.7, 116.1, 115.1, 113.9, 113.9, 66.7, 55.9, 55.4, 44.8, 37.1, 20.0. **HRMS** (ESI): m/z calculated for $C_{25}H_{26}O_2N_2$ requires 387.20670 for $[M+H]^+$, found 387.20690.

Synthesis of **3i**

The compound was synthesized according to General Procedure **C** using **1i** (22.5 mg, 0.1 mmol), and lepidine (40 μL, 0.3 mmol). Crude dr: 2.8:1 (endo:exo). Silica gel column chromatography (CH_2Cl_2:Pentane 30:70 – 60:40 v:v) gave a partially separable mixture of diastereomers, combined yield 95% (35.2 mg).



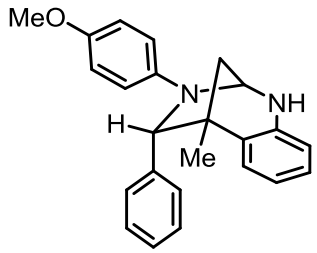
Data for **3i$_{(endo)}$**. White solid. **mp** (from $CHCl_3$): 68-74 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3389, 2933, 1607, 1510, 1472. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.97 (td, *J* = 7.6, 1.5 Hz, 1H), 6.85 (d, *J* = 7.7 Hz, 2H), 6.81 – 6.65 (m, 4H), 6.61 (dd, *J* = 7.9, 1.3 Hz, 1H), 6.51 – 6.39 (m, 3H), 6.28 (dd, *J* = 7.7, 1.5 Hz, 1H), 5.10 (d, *J* = 5.0 Hz, 1H), 4.74 (s, 1H), 4.46 (s, 1H), 3.67 (s, 3H), 2.45 (d, *J* = 10.6 Hz, 1H), 2.25 (dd, *J* = 10.7, 5.2 Hz, 1H), 2.22 (s, 3H), 1.52 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.5, 143.1, 140.7, 136.4, 134.9, 129.4, 128.3, 127.7, 127.0, 126.6, 118.5, 115.5, 114.8, 113.6, 79.3, 72.1, 55.9, 46.3, 41.4, 21.2, 20.0. **HRMS** (ESI): m/z calculated for $C_{25}H_{26}O_1N_2$ requires 371.21179 for $[M+H]^+$, found 371.21149.



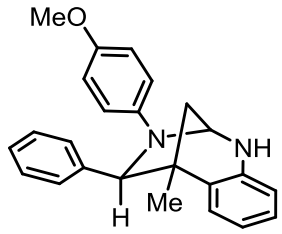
Data for **3i$_{(exo)}$**. Off-white solid. **mp** (from $CHCl_3$): 192-196 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3403, 2932, 1606, 1510, 1476. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.14 (app s, 4H), 6.99 (td, *J* = 7.6, 1.4 Hz, 1H), 6.81 – 6.64 (m, 3H), 6.52 (dd, *J* = 7.9, 1.3 Hz, 1H), 6.43 (d, *J* = 9.1 Hz, 2H), 5.45 (d, *J* = 4.6 Hz, 1H), 5.15 (s, 1H), 4.57 (s, 1H), 3.66 (s, 3H), 2.34 (s, 4H), 2.12 (d, *J* = 11.1 Hz, 1H), 1.05 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.4, 142.2, 139.2, 138.0, 137.0, 134.7, 129.3, 127.6, 127.6, 124.0, 118.7, 116.1, 115.1, 113.8, 77.5, 66.7, 55.9, 44.7, 37.2, 21.3, 20.0. **HRMS** (ESI): m/z calculated for $C_{25}H_{26}O_1N_2$ requires 371.21179 for $[M+H]^+$, found 371.21149.

Synthesis of **3j**

The compound was synthesized according to General Procedure **C** using **1j** (21.1 mg, 0.1 mmol), and lepidine (40 μL, 0.3 mmol). Crude dr: 3.2:1 (endo:exo). Silica gel column chromatography (CH_2Cl_2:Pentane 30:70 – 70:30 v:v) gave a fully separable mixture of diastereomers, combined yield 81% (29.0 mg).



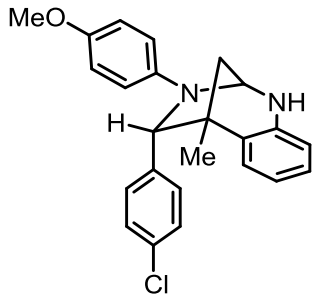
Data for **3j$_{(endo)}$**. White solid. **mp** (from $CHCl_3$): 144-148 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3386, 3026, 2933, 1606, 1510, 1466. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.13 – 7.00 (m, 3H), 6.96 (td, *J* = 7.6, 1.5 Hz, 1H), 6.86 (d, *J* = 7.2 Hz, 2H), 6.74 – 6.66 (m, 2H), 6.61 (dd, *J* = 7.9, 1.2 Hz, 1H), 6.48 – 6.42 (m, 2H), 6.44 – 6.36 (m, 1H), 6.25 (dd, *J* = 7.8, 1.5 Hz, 1H), 5.13 (d, *J* = 5.0 Hz, 1H), 4.76 (s, 1H), 4.50 (s, 1H), 3.68 (s, 3H), 2.46 (d, *J* = 10.6 Hz, 1H), 2.27 (dd, *J* = 10.7, 5.1 Hz, 1H), 1.54 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.6, 143.1, 140.5, 138.1, 129.2, 127.7, 127.6, 127.1, 127.0, 126.4, 118.5, 115.5, 114.8, 113.6, 79.4, 72.0, 55.9, 46.5, 41.4, 20.0. **HRMS** (ESI): m/z calculated for $C_{24}H_{24}O_1N_2$ requires 357.19614 for $[M+H]^+$, found 357.19489.



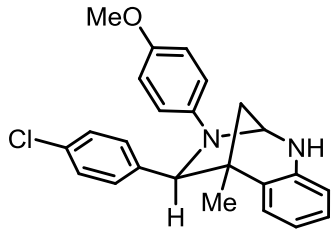
Data for **3j$_{(exo)}$**. White solid. **mp** (from $CHCl_3$): 200-202 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3404, 2970, 1605, 1510. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (dt, *J* = 8.0, 1.6 Hz, 2H), 7.30 – 7.18 (m, 4H), 7.00 (td, *J* = 7.6, 1.5 Hz, 1H), 6.75 (td, *J* = 7.5, 1.3 Hz, 1H), 6.72 – 6.66 (m, 2H), 6.53 (dd, *J* = 7.8, 1.3 Hz, 1H), 6.46 – 6.38 (m, 2H), 5.47 (d, *J* = 4.6 Hz, 1H), 5.16 (s, 1H), 4.60 (s, 1H), 3.66 (s, 3H), 2.37 (dd, *J* = 11.1, 4.7 Hz, 1H), 2.13 (d, *J* = 11.1 Hz, 1H), 1.05 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.4, 142.2, 141.1, 134.6, 128.6, 127.6, 127.5, 127.2, 124.0, 118.7, 116.1, 115.1, 113.9, 77.7, 66.8, 55.9, 44.7, 37.2, 20.0. **HRMS** (ESI): m/z calculated for $C_{24}H_{24}O_1N_2$ requires 357.19614 for $[M+H]^+$, found 357.19623.

Synthesis of **3k**

The compound was synthesized according to General Procedure **C** using **1k** (24.6 mg, 0.1 mmol), and lepidine (40 μL, 0.3 mmol). Crude dr: 1.3:1 (endo:exo). Silica gel column chromatography (CH_2Cl_2:Pentane 30:70 – 60:40 v:v) gave a fully separable mixture of diastereomers, combined yield 78% (30.3 mg).



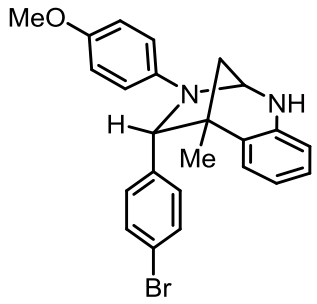
Data for **3k$_{(endo)}$**. White solid. **mp** (from $CHCl_3$): 102-104 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3393, 2981, 2889, 1607, 1510, 1473. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.07 – 6.91 (m, 3H), 6.88 – 6.74 (m, 2H), 6.73 – 6.64 (m, 2H), 6.60 (dd, *J* = 7.9, 1.2 Hz, 1H), 6.46 – 6.37 (m, 3H), 6.26 (dd, *J* = 7.8, 1.5 Hz, 1H), 5.10 (d, *J* = 4.9 Hz, 1H), 4.74 (s, 1H), 4.47 (s, 1H), 3.68 (s, 3H), 2.45 (d, *J* = 10.7 Hz, 1H), 2.26 (dd, *J* = 10.7, 5.1 Hz, 1H), 1.51 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.8, 143.0, 140.2, 136.9, 132.7, 128.7, 128.4, 127.9, 127.9, 126.5, 118.7, 115.5, 114.8, 113.7, 78.7, 72.1, 55.9, 46.4, 41.3, 19.9. **HRMS** (ESI): m/z calculated for $C_{24}H_{23}O_1N_2Cl_1$ requires 391.15717 for $[M+H]^+$, found 391.15671.



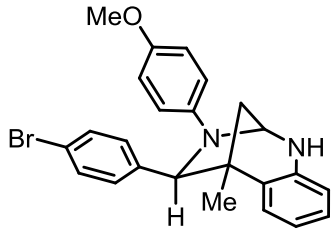
Data for **3k$_{(exo)}$**. White solid. **mp** (from $CHCl_3$): 220-222 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3400, 2981, 2888, 1510, 1474. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 2H), 7.23 – 7.18 (m, 3H), 7.00 (td, *J* = 7.6, 1.5 Hz, 1H), 6.74 (td, *J* = 7.6, 1.3 Hz, 1H), 6.72 – 6.68 (m, 2H), 6.52 (dd, *J* = 7.8, 1.2 Hz, 1H), 6.43 – 6.36 (m, 2H), 5.46 (d, *J* = 4.5 Hz, 1H), 5.15 (s, 1H), 4.58 (s, 1H), 3.67 (s, 3H), 2.30 (dd, *J* = 11.2, 4.7 Hz, 1H), 2.14 (d, *J* = 11.2 Hz, 1H), 1.06 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.6, 142.0, 139.7, 138.8, 134.2, 133.2, 128.8, 128.5, 127.8, 123.9, 118.8, 116.1, 115.1, 114.0, 76.9, 66.8, 55.9, 44.7, 37.2, 20.0. **HRMS** (ESI): m/z calculated for $C_{24}H_{23}O_1N_2Cl_1$ requires 391.15717 for $[M+H]^+$, found 391.15717.

Synthesis of **3l**

The compound was synthesized according to General Procedure **C** using **1l** (29.0 mg, 0.1 mmol), and lepidine (40 μL, 0.3 mmol). Crude dr: 1.2:1 (endo:exo). Silica gel column chromatography (CH_2Cl_2:Pentane 30:70 – 60:40 v:v) gave a fully separable mixture of diastereomers, combined yield 71% (31.1 mg).



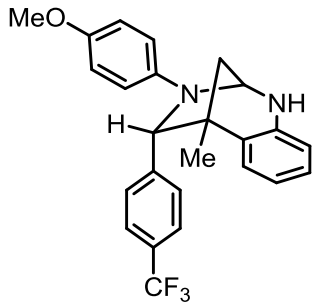
Data for **3l$_{(endo)}$**. White solid. **mp** (from $CHCl_3$): 74-78 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3992, 2980, 1607, 1510, 1486. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.3 Hz, 2H), 6.97 (td, *J* = 7.6, 1.5 Hz, 1H), 6.78 – 6.65 (m, 4H), 6.60 (dd, *J* = 7.9, 1.2 Hz, 1H), 6.47 – 6.35 (m, 3H), 6.27 (dd, *J* = 7.8, 1.4 Hz, 1H), 5.10 (d, *J* = 4.9 Hz, 1H), 4.75 (s, 1H), 4.45 (s, 1H), 3.68 (s, 3H), 2.45 (d, *J* = 10.7 Hz, 1H), 2.26 (dd, *J* = 10.7, 5.0 Hz, 1H), 1.51 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.8, 142.9, 140.2, 137.4, 130.8, 128.8, 128.7, 127.9, 126.5, 120.9, 118.7, 115.5, 114.8, 113.7, 78.8, 72.1, 55.9, 46.4, 41.4, 19.9. **HRMS** (ESI): m/z calculated for $C_{24}H_{23}O_1N_2Br_1$ requires 435.10665 for $[M+H]^+$, found 435.10669.



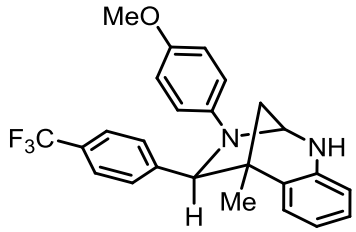
Data for **3l$_{(exo)}$**. White solid. **mp** (from $CHCl_3$): 208-210 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3405, 2980, 1606, 1510, 1485. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.1 Hz, 2H), 7.21 – 7.18 (m, 1H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.00 (td, *J* = 7.6, 1.5 Hz, 1H), 6.79 – 6.67 (m, 3H), 6.52 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.44 – 6.34 (m, 2H), 5.46 (d, *J* = 4.5 Hz, 1H), 5.15 (s, 1H), 4.56 (s, 1H), 3.67 (s, 3H), 2.30 (dd, *J* = 11.2, 4.7 Hz, 1H), 2.14 (d, *J* = 11.2 Hz, 1H), 1.06 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.7, 142.0, 140.2, 138.8, 134.2, 131.8, 128.9, 127.8, 123.9, 121.3, 118.8, 116.0, 115.1, 114.0, 77.0, 66.8, 55.9, 44.6, 37.1, 20.0. **HRMS** (ESI): m/z calculated for $C_{24}H_{23}O_1N_2Br_1$ requires 435.10665 for $[M+H]^+$, found 435.10654.

Synthesis of **3m**

The compound was synthesized according to General Procedure **C** using **1m** (27.9 mg, 0.1 mmol), and lepidine (40 μL, 0.3 mmol). Crude dr: 1.6:1 (endo:exo). Silica gel column chromatography (CH_2Cl_2:Pentane 40:60 – 50:50 v:v) gave a fully separable mixture of diastereomers, combined yield 89% (37.2 mg)



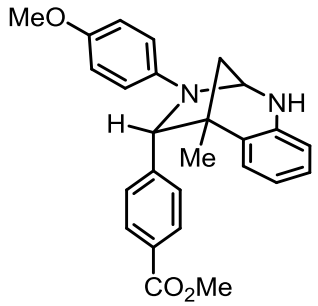
Data for **3m$_{(endo)}$**. White solid. **mp** (from $CHCl_3$): 65-70 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3392, 3045, 2966, 2935, 2833, 1618, 1608, 1579, 1511.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.1 Hz, 2H), 7.02 – 6.91 (m, 3H), 6.75 – 6.66 (m, 2H), 6.62 (dd, *J* = 7.9, 1.2 Hz, 1H), 6.48 – 6.33 (m, 3H), 6.21 (dd, *J* = 7.8, 1.4 Hz, 1H), 5.14 (d, *J* = 4.9 Hz, 1H), 4.77 (s, 1H), 4.56 (s, 1H), 3.68 (s, 3H), 2.48 (d, *J* = 10.7 Hz, 1H), 2.30 (dd, *J* = 10.8, 5.1 Hz, 1H), 1.54 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.28. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.9, 142.9, 142.7, 140.0, 129.2 (q, *J* = 32.3 Hz), 128.4, 128.1, 127.3, 126.3, 124.6 (q, *J* = 3.8 Hz), 123.3, 118.7, 115.5, 114.8, 113.7, 78.9, 72.1, 55.8, 46.6, 41.4, 19.9. **HRMS** (ESI): m/z calculated for $C_{25}H_{23}O_1N_2F_3$ requires 425.18352 for $[M+H]^+$, found 425.18289.



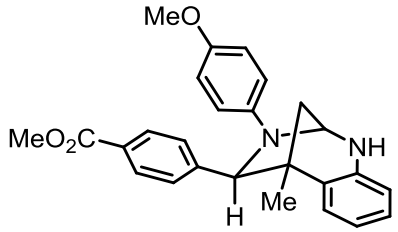
Data for **3m$_{(exo)}$**. White solid. **mp** (from $CHCl_3$): 200-204 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3403, 3044, 2968, 1617, 1607, 1579, 1511. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 7.9 Hz, 2H), 7.22 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.01 (td, *J* = 7.6, 1.4 Hz, 1H), 6.75 (td, *J* = 7.6, 1.2 Hz, 1H), 6.73 – 6.63 (m, 2H), 6.53 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.44 – 6.33 (m, 2H), 5.49 (d, *J* = 4.5 Hz, 1H), 5.16 (s, 1H), 4.67 (s, 1H), 3.67 (s, 3H), 2.32 (dd, *J* = 11.2, 4.7 Hz, 1H), 2.17 (d, *J* = 11.2 Hz, 1H), 1.06 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.29. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.8, 145.3, 142.0, 138.7, 134.0, 129.8 (q, *J* = 32.4 Hz), 127.9, 127.5 (app s), 125.7 (app d, *J* = 3.8 Hz), 123.9, 118.8, 116.1, 115.2, 114.1, 77.1, 66.9, 55.8, 44.8, 37.2, 20.0. **HRMS** (ESI): m/z calculated for $C_{25}H_{23}O_1N_2F_3$ requires 425.18352 for $[M+H]^+$, found 425.18329.

Synthesis of **3n**

The compound was synthesized according to General Procedure **C** using **1n** (26.9 mg, 0.1 mmol), and lepidine (40 μL, 0.3 mmol). Crude dr: 2.1:1 (endo:exo). Silica gel column chromatography (CH_2Cl_2:Pentane 60:40 – 80:20 v:v) gave a primarily separable mixture of diastereomers, combined yield 92% (38.1 mg)



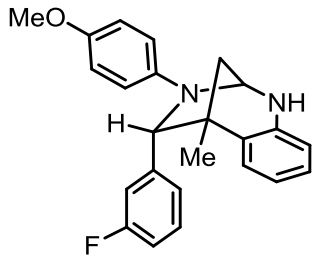
Data for **3n$_{(endo)}$**. White solid. **mp** (from $CHCl_3$): 64-68 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3379, 2951, 1715, 1609, 1510, 1475. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.9 Hz, 2H), 6.95 (td, *J* = 7.6, 1.5 Hz, 2H), 6.71 – 6.66 (m, 2H), 6.61 (dd, *J* = 7.9, 1.2 Hz, 1H), 6.46 – 6.29 (m, 3H), 6.21 (dd, *J* = 7.8, 1.5 Hz, 1H), 5.13 (d, *J* = 4.9 Hz, 1H), 4.76 (s, 1H), 4.55 (s, 1H), 3.84 (s, 3H), 3.67 (s, 3H), 2.47 (d, *J* = 10.7 Hz, 1H), 2.29 (dd, *J* = 10.7, 5.1 Hz, 1H), 1.54 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.3, 151.8, 144.1, 143.0, 140.1, 129.0, 129.0, 128.5, 128.0, 127.1, 126.3, 118.7, 115.5, 114.8, 113.6, 79.0, 72.0, 55.9, 52.1, 46.7, 41.5, 20.0. **HRMS** (ESI): m/z calculated for $C_{26}H_{26}O_3N_2$ requires 415.20162 for $[M+H]^+$, found 415.20150.



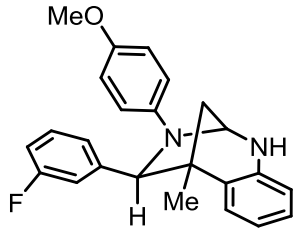
Data for **3n$_{(exo)}$**. White solid. **mp** (from $CHCl_3$): 56-60 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3402, 2950, 1718, 1612, 1513, 1435. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.9 Hz, 2H), 7.07 – 6.82 (m, 3H), 6.67 (d, *J* = 9.1 Hz, 1H), 6.61 (dd, *J* = 7.9, 1.2 Hz, 1H), 6.47 – 6.30 (m, 3H), 6.21 (dd, *J* = 7.8, 1.5 Hz, 1H), 5.13 (d, *J* = 4.9 Hz, 1H), 4.55 (s, 1H), 3.84 (s, 3H), 3.67 (s, 3H), 2.47 (d, *J* = 10.7 Hz, 1H), 2.29 (dd, *J* = 10.7, 5.1 Hz, 1H), 1.54 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.3, 151.8, 144.1, 143.0, 140.1, 129.0, 129.0, 128.5, 128.0, 127.1, 126.3, 118.7, 115.5, 114.8, 113.6, 79.0, 72.0, 55.9, 52.1, 46.7, 41.5, 20.0. **HRMS** (ESI): m/z calculated for $C_{26}H_{26}O_3N_2$ requires 415.20162 for $[M+H]^+$, found 415.20175.

Synthesis of **3o**

The compound was synthesized according to General Procedure **C** using **1o** (22.9 mg, 0.1 mmol), and lepidine (40 μL, 0.3 mmol). Crude dr: 1.8:1 (endo:exo). Silica gel column chromatography (CH_2Cl_2:Pentane 30:70 – 60:40 v:v) gave a fully separable mixture of diastereomers, combined yield 82% (30.7 mg).



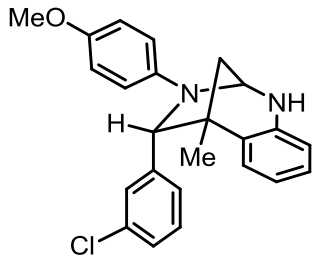
Data for **3o$_{(endo)}$**. Off-white solid. **mp** (from $CHCl_3$): 166-163 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3387, 3041, 1589, 1510. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.05 – 6.99 (m, 1H), 6.97 (td, *J* = 7.6, 1.5 Hz, 1H), 6.77 (tdd, *J* = 8.4, 2.7, 1.0 Hz, 1H), 6.73 – 6.65 (m, 3H), 6.61 (dd, *J* = 7.9, 1.3 Hz, 1H), 6.52 (d, *J* = 10.2 Hz, 1H), 6.47 – 6.37 (m, 3H), 6.27 (dd, *J* = 7.7, 1.5 Hz, 1H), 5.11 (d, *J* = 5.0 Hz, 1H), 4.76 (s, 1H), 4.48 (s, 1H), 3.68 (s, 3H), 2.46 (d, *J* = 10.7 Hz, 1H), 2.26 (dd, *J* = 10.7, 5.1 Hz, 1H), 1.53 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -114.40 (q, *J* = 8.8 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.7 (d, *J* = 244.7 Hz), 151.8, 142.9, 141.3 (d, *J* = 6.8 Hz), 140.3, 129.0 (d, *J* = 7.8 Hz), 128.7, 128.0, 126.3, 122.7 (d, *J* = 2.8 Hz), 118.6, 115.6, 114.8, 114.0 (d, *J* = 21.5 Hz), 113.9 (d, *J* = 22.0 Hz), 113.6, 78.8, 72.1, 55.9, 46.5, 41.4, 20.0. **HRMS** (ESI): m/z calculated for $C_{24}H_{23}O_1N_2F_1$ requires 375.18672 for $[M+H]^+$, found 375.18643.



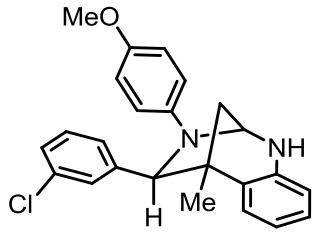
Data for **3o$_{(exo)}$**. Off-white solid. **mp** (from $CHCl_3$): 202-206 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3403, 2968, 1589, 1510, 1482. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 1H), 7.21 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.06 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.03 – 6.94 (m, 3H), 6.82 – 6.66 (m, 3H), 6.52 (dd, *J* = 7.9, 1.3 Hz, 1H), 6.48 – 6.37 (m, 2H), 5.47 (d, *J* = 4.5 Hz, 1H), 5.16 (s, 1H), 4.59 (s, 1H), 3.68 (s, 3H), 2.34 (dd, *J* = 11.2, 4.7 Hz, 1H), 2.15 (d, *J* = 11.2 Hz, 1H), 1.07 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -112.94 (br s). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.3 (d, *J* = 245.5 Hz), 151.7, 144.2 (d, *J* = 5.9 Hz, & s, 2C), 142.0, 138.8, 134.2, 130.1 (d, *J* = 8.1 Hz), 127.8, 123.9, 122.9 (app s), 118.8, 116.0, 115.1, 114.5 (d, *J* = 21.4 Hz), 114.0, 77.1, 66.8, 55.9, 44.8, 37.2, 19.9. **HRMS** (ESI): m/z calculated for $C_{24}H_{23}O_1N_2F_1$ requires 375.18672 for $[M+H]^+$, found 375.18622.

Synthesis of **3p**

The compound was synthesized according to General Procedure **C** using **1m** (24.5 mg, 0.1 mmol), and lepidine (40 μL, 0.3 mmol). Crude dr: 1.5:1 (endo:exo). Silica gel column chromatography (CH_2Cl_2:Pentane 30:70 – 60:40 v:v) gave a fully separable mixture of diastereomers, combined yield 82% (32.1 mg).



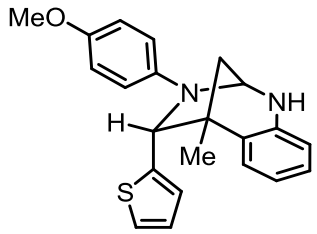
Data for **3p$_{(endo)}$**. White solid. **mp** (from $CHCl_3$): 140-144 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3378, 2917, 2849, 1597, 15010, 1473. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.06 (ddd, *J* = 7.8, 2.1, 1.0 Hz, 1H), 7.01 – 6.92 (m, 2H), 6.87 (s, 1H), 6.74 – 6.66 (m, 3H), 6.62 (dd, *J* = 7.9, 1.2 Hz, 1H), 6.49 – 6.37 (m, 3H), 6.27 (dd, *J* = 7.8, 1.5 Hz, 1H), 5.11 (d, *J* = 5.0 Hz, 1H), 4.81 (s, 1H), 4.45 (s, 1H), 3.68 (s, 3H), 2.46 (d, *J* = 10.7 Hz, 1H), 2.26 (dd, *J* = 10.7, 5.1 Hz, 1H), 1.52 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.8, 143.0, 140.7, 140.2, 133.6, 128.9, 128.7, 128.0, 127.3, 127.2, 126.4, 125.2, 118.6, 115.6, 114.9, 113.7, 78.9, 72.2, 55.9, 46.6, 41.4, 19.9. **HRMS** (ESI): m/z calculated for $C_{24}H_{23}O_1N_2Cl_1$ requires 391.15717 for $[M+H]^+$, found 391.15735.



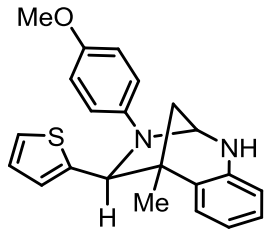
Data for **3p$_{(exo)}$**. White solid. **mp** (from $CHCl_3$): 212-220 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3403, 2933, 1604, 1510, 1475. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 3H), 7.21 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.18 – 7.11 (m, 1H), 7.00 (td, *J* = 7.6, 1.5 Hz, 1H), 6.77 – 6.66 (m, 3H), 6.52 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.46 – 6.38 (m, 2H), 5.47 (d, *J* = 4.5 Hz, 1H), 5.16 (s, 1H), 4.56 (s, 1H), 3.68 (s, 3H), 2.33 (dd, *J* = 11.2, 4.7 Hz, 1H), 2.15 (d, *J* = 11.2 Hz, 1H), 1.07 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.7, 143.5, 142.0, 138.8, 134.7, 134.1, 129.9, 128.8, 127.8, 127.2, 125.5, 123.9, 118.8, 116.0, 115.1, 114.1, 77.1, 66.8, 55.9, 44.8, 37.2, 20.0. **HRMS** (ESI): m/z calculated for $C_{24}H_{23}O_1N_2Cl_1$ requires 391.15717 for $[M+H]^+$, found 391.15699.

Synthesis of **3q**

The compound was synthesized according to General Procedure **C** using **1q** (24.5 mg, 0.1 mmol), and lepidine (40 μL, 0.3 mmol). Crude dr: 1.7:1 (endo:exo). Silica gel column chromatography (CH_2Cl_2:Pentane 30:70 – 80:20 v:v) gave a fully separable mixture of diastereomers, combined yield 40% (14.4 mg).



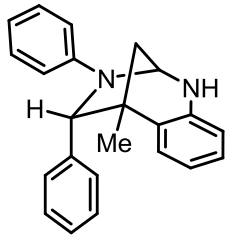
Data for **3q$_{(endo)}$**. Brown solid. **mp** (from $CHCl_3$): 120-122 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3363, 2980, 1607, 1510, 1464. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.01 (ddd, *J* = 7.9, 6.8, 1.9 Hz, 1H), 6.94 (dd, *J* = 5.0, 1.3 Hz, 1H), 6.80 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.79 – 6.75 (m, 1H), 6.75 – 6.70 (m, 2H), 6.63 (dd, *J* = 7.8, 1.2 Hz, 1H), 6.59 – 6.53 (m, 2H), 6.52 – 6.45 (m, 2H), 5.06 (d, *J* = 5.0 Hz, 1H), 4.76 (s, 1H), 3.69 (s, 3H), 2.48 (d, *J* = 10.8 Hz, 1H), 2.21 (dd, *J* = 10.8, 5.1 Hz, 1H), 1.57 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 152.0, 143.5, 142.9, 140.8, 129.3, 128.0, 126.4, 125.8, 124.3, 118.8, 116.0, 114.7, 113.9, 75.7, 72.9, 55.8, 46.4, 40.9, 29.9, 19.9. **HRMS** (ESI): m/z calculated for $C_{22}H_{22}O_1N_2S_1$ requires 363.15256 for $[M+H]^+$, found 363.15237.



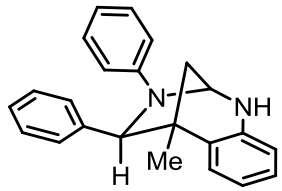
Data for **3q$_{(exo)}$**. Brown solid. **mp** (from $CHCl_3$): 120-122 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3400, 2980, 1605, 1510. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 – 7.15 (m, 2H), 7.05 – 6.91 (m, 3H), 6.77 – 6.69 (m, 3H), 6.60 – 6.52 (m, 2H), 6.50 (dd, *J* = 8.0, 1.2 Hz, 1H), 5.40 (d, *J* = 4.5 Hz, 1H), 5.12 (s, 1H), 4.83 (s, 1H), 3.68 (s, 3H), 2.53 (dd, *J* = 11.2, 4.6 Hz, 1H), 2.17 (d, *J* = 11.2 Hz, 1H), 1.18 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.8, 147.1, 142.0, 138.9, 133.7, 127.8, 127.1, 124.3, 124.2, 124.1, 118.7, 116.0, 115.1, 114.2, 73.5, 66.8, 55.8, 44.7, 36.9, 19.4. **HRMS** (ESI): m/z calculated for $C_{22}H_{22}O_1N_2S_1$ requires 363.15256 for $[M+H]^+$, found 363.15237.

Synthesis of **3r**

The compound was synthesized according to General Procedure **C** using **1n** (18.1 mg, 0.1 mmol), and lepidine (40 μL, 0.3 mmol). Crude dr: 3.1:1 (endo:exo). Silica gel column chromatography (CH_2Cl_2:Pentane 30:70 – 60:40 v:v) gave a fully separable mixture of diastereomers, combined yield 91% (19.6 mg).



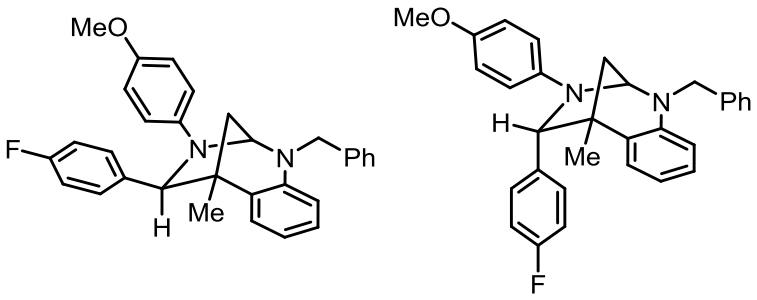
Data for **3r$_{(endo)}$**. White solid. **mp** (from $CHCl_3$): 146-150 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3394, 2966, 1598, 1501, 1473. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 – 7.00 (m, 5H), 6.96 (td, *J* = 7.6, 1.5 Hz, 1H), 6.85 (s, 1H), 6.66 – 6.56 (m, 2H), 6.51 – 6.46 (m, 2H), 6.40 (td, *J* = 7.5, 1.3 Hz, 1H), 6.25 (dd, *J* = 7.7, 1.5 Hz, 1H), 5.22 (d, *J* = 5.0 Hz, 1H), 4.79 (s, 1H), 4.55 (s, 1H), 2.48 (d, *J* = 10.6 Hz, 1H), 2.28 (dd, *J* = 10.7, 5.1 Hz, 1H), 1.55 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.9, 142.9, 137.8, 129.1, 129.1, 127.8, 127.6, 127.0, 127.0, 126.4, 118.5, 117.0, 115.4, 112.8, 78.9, 71.4, 46.4, 41.3, 20.0. **HRMS** (ESI): m/z calculated for $C_{23}H_{22}N_2$ requires 327.18558 for $[M+H]^+$, found 327.18561.



Data for **3r$_{(exo)}$**. White solid. **mp** (from $CHCl_3$): 178-180 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3401, 2969, 1598, 1501, 1475, 1454. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 2H), 7.28 – 7.19 (m, 4H), 7.13 – 7.04 (m, 2H), 7.00 (td, *J* = 7.6, 1.5 Hz, 1H), 6.76 (td, *J* = 7.5, 1.3 Hz, 1H), 6.66 – 6.57 (m, 1H), 6.53 (dd, *J* = 7.9, 1.2 Hz, 1H), 6.51 – 6.46 (m, 2H), 5.53 (d, *J* = 4.7 Hz, 1H), 5.20 (s, 1H), 4.66 (s, 1H), 2.38 (dd, *J* = 11.2, 4.9 Hz, 1H), 2.14 (d, *J* = 11.2 Hz, 1H), 1.07 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.6, 142.1, 140.6, 134.4, 129.3, 128.6, 127.7, 127.6, 127.5, 124.1, 118.9, 116.8, 116.2, 113.1, 77.6, 66.5, 44.7, 37.0, 20.0. **HRMS** (ESI): m/z calculated for $C_{23}H_{22}N_2$ requires 327.18558 for $[M+H]^+$, found 327.18524.

Synthesis of **3al**

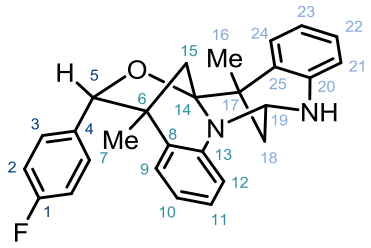
The compound was synthesized according to General Procedure **C** using **1a** (22.9 mg, 0.1 mmol), and **3m** (94, 0.3 mmol). Crude dr: 1.0:1. Silica gel column chromatography (CH_2Cl_2:Pentane 40:60 – 70:30 v:v) gave an inseparable mixture of diastereomers, combined yield 51% (23.7 mg).



Combined data for **3al$_{(exo)}$** & **3al$_{(endo)}$**. Light brown solid. **mp** (from $CHCl_3$): 56-60 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) =2918, 1602, 1509, 1493, 1451. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 – 7.46 (m, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 4.5 Hz, 5H), 7.31 – 7.27 (m, 2H), 7.19 (dd, *J* = 8.1, 5.5 Hz, 2H), 7.07 – 6.95 (m, 4H), 6.94 – 6.86 (m, 2H), 6.82 – 6.72 (m, 3H), 6.70 – 6.60 (m, 4H), 6.59 – 6.52 (m, 2H), 6.45 – 6.36 (m, 3H), 6.36 – 6.26 (m, 3H), 5.38 (d, *J* = 4.1 Hz, 1H), 5.02 (d, *J* = 4.6 Hz, 1H), 4.74 (d, *J* = 2.8 Hz, 2H), 4.66 – 4.60 (m, 3H), 4.41 (s, 1H), 3.66 (s, 3H), 3.65 (s, 3H), 2.45 (d, *J* = 10.6 Hz, 1H), 2.20 (dd, *J* = 11.0, 4.2 Hz, 1H), 2.15 (dd, *J* = 10.6, 4.8 Hz, 1H), 1.99 (d, *J* = 11.0 Hz, 1H), 1.56 (s, 3H), 1.09 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -115.48 – -115.63 (m), -115.91 (tt, *J* = 8.4, 5.2 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.3 (d, *J* = 245.1 Hz), 162.1 (d, *J* = 244.3 Hz), 151.9, 151.6, 145.2, 144.4, 141.4, 139.5, 139.1, 138.6, 136.4 (d, *J* = 2.4 Hz), 134.8, 134.5 (d, *J* = 3.2 Hz), 129.0, 128.92, 128.77 (app s), 128.7, 128.6, 128.4 (d, *J* = 7.7 Hz), 128.0, 127.80, 127.76, 127.4, 127.2, 126.0, 123.9, 118.0, 117.6, 115.5, 115.4 (d, *J* = 18.7 Hz), 115.3, 114.68 (d, *J* = 21.4 Hz), 114.66, 114.5, 113.9, 113.5, 78.6, 77.6, 75.3, 73.9, 57.1, 55.9, 55.81, 55.77, 46.6, 45.0, 40.3, 35.2, 20.6, 20.3. **HRMS** (ESI): m/z calculated for $C_{31}H_{29}O_1N_2F_1$ requires 465.23367 for $[M+H]^+$, found 465.23337.

Synthesis of **5a**

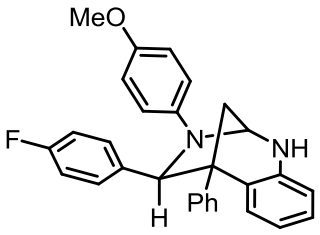
The compound was synthesized according to a modification of General Procedure **C** using 4-fluorobenzaldehyde (**4a**, 10.7 μL, 0.1 mmol), Hantzsch ester (66 mg, 0.2 mmol) and lepidine **2a** (53 μL, 0.4 mmol). Crude dr: unknown. Silica gel column chromatography (CH_2Cl_2:Pentane 40:60 – 50:50 v:v) gave one single isolable diastereomer (multiple products formed), single diastereomer yield 25% (10.2 mg).



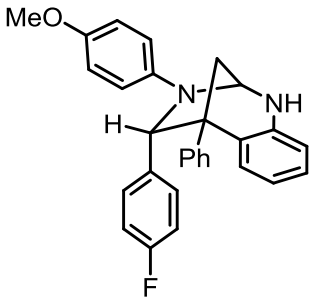
mp (from $CHCl_3$): 226-228 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3400, 2962, 2926, 2854, 1603, 1575, 1509, 1490, 1474, 1461. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 1.5 Hz, 1H, 24), 7.09 – 7.02 (m, 2H, 22 & **11**), 7.01 – 6.97 (m, 2H, **2**), 6.84 – 6.77 (m, 3H, **3** & 23), 6.60 – 6.56 (m, 1H, **12**), 6.51 (dd, *J* = 8.0, 1.2 Hz, 1H, 21), 6.43 – 6.35 (m, 2H, **9** & **10**), 5.39 (d, *J* = 4.6 Hz, 1H, 19), 4.98 (s, 1H, **5**), 4.86 (s, 1H, N*H*), 2.53 (dd, *J* = 10.8, 4.7 Hz, 1H, 18a), 2.20 (d, *J* = 10.7 Hz, 1H, **15a**), 2.19 (d, *J* = 11.1 Hz, 1H, 18b), 1.62 (s, 3H, 16), 1.42 (s, 3H, **7**), 1.40 (d, *J* = 11.0 Hz, 1H, **15b**). Diastereomer confirmed *via* NOESY correlation between **5** and **15**, and then **3** and 18. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -115.66 (ddd, *J* = 14.2, 8.7, 5.1 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.2 (d, *J* = 245.0 Hz, **1**), 142.2 (20), 140.6 (**13**), 134.6 (d, *J* = 2.9 Hz, **4**), 130.3 (25), 127.9 (app d, **2** & **11** & 22), 127.6 (**8**), 126.2 (**9**), 125.5 (24), 118.9 (23), 116.8 (**10**), 116.3 (21), 114.5 (d, *J* = 21.7 Hz, **2**), 108.9 (23), 102.8 (**14**), 95.7 (**5**), 64.2 (**19**), 47.7 (**6**), 44.5 (17), 40.6 (**15**), 37.6 (18), 19.6 (**7**), 16.9 (16). **HRMS** (ESI): m/z calculated for $C_{27}H_{25}O_1N_2F_1$ requires 413.20237 for $[M+H]^+$, found 413.20239.

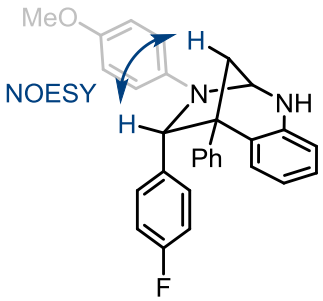
Synthesis of **3am**

The compound was synthesized according to General Procedure **C** using **1a** (22.9 mg, 0.1 mmol), and 4-phenylquinoline **3m** (62 mg, 0.3 mmol). Crude dr: 4.5:1 (exo:endo). Silica gel column chromatography (CH_2Cl_2:Pentane 40:60 – 70:30 v:v) gave a fully separable mixture of diastereomers, combined yield 78% (34.0 mg).



Data for **3am$_{(exo)}$**. White solid. **mp** (from $CHCl_3$): 100-104 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3403, 2981, 1602, 1509, 1474. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 7.25 – 7.19 (m, 4H), 7.17 – 7.09 (m, 1H), 7.01 – 6.89 (m, 2H), 6.84 – 6.71 (m, 4H), 6.64 – 6.52 (m, 4H), 5.66 (d, *J* = 4.8 Hz, 1H), 5.29 (s, 1H), 5.25 (s, 1H), 3.69 (s, 3H), 3.14 (dd, *J* = 11.1, 4.9 Hz, 1H), 2.85 (d, *J* = 11.2 Hz, 1H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -115.23 (tt, *J* = 8.9, 5.5 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.8 (d, *J* = 245.7 Hz), 151.8, 142.0, 138.6, 138.6, 137.4 (d, *J* = 3.2 Hz), 132.6, 130.5 (d, *J* = 8.0 Hz), 130.1, 127.9, 127.6, 126.7, 126.6, 118.4, 116.5, 115.1, 114.9 (d, *J* = 21.4 Hz), 114.3, 77.4, 66.8, 55.8, 55.3, 34.9. **HRMS** (ESI): m/z calculated for $C_{29}H_{25}O_1N_2F_1$ requires 437.20237 for $[M+H]^+$, found 437.20242.

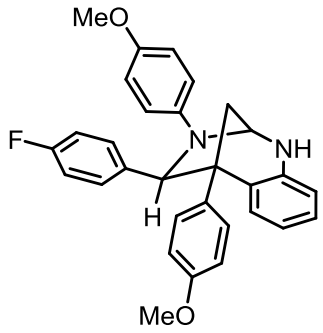




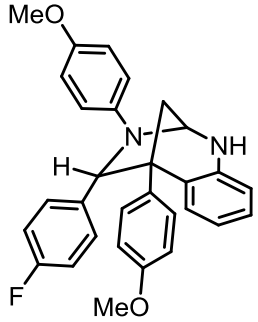
Data for **3am$_{(endo)}$**. White solid. **mp** (from $CHCl_3$): 174-176 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3393, 2981, 1603, 1509, 1473. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 – 7.53 (m, 2H), 7.43 – 7.34 (m, 2H), 7.33 – 7.27 (m, 1H), 7.04 – 6.90 (m, 3H), 6.74 – 6.63 (m, 5H), 6.53 (d, *J* = 9.1 Hz, 2H), 6.35 (td, *J* = 7.5, 1.3 Hz, 1H), 6.06 (dd, *J* = 7.6, 1.4 Hz, 1H), 5.45 (s, 1H), 5.12 (d, *J* = 5.0 Hz, 1H), 4.86 (s, 1H), 3.68 (s, 3H), 2.88 (d, *J* = 10.8 Hz, 1H), 2.54 (dd, *J* = 10.8, 5.1 Hz, 1H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -115.56 (tt, *J* = 8.4, 5.6 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.0 (d, *J* = 245.4 Hz), 151.9, 143.7, 142.4, 140.1, 134.6 (d, *J* = 3.2 Hz), 130.5, 130.3 (d, *J* = 7.9 Hz), 128.6, 128.4, 128.2, 128.1, 127.0, 118.4, 115.8, 114.7, 114.5 (d, *J* = 21.1 Hz), 114.1, 74.5, 71.6, 55.8, 55.7, 43.1. **HRMS** (ESI): m/z calculated for $C_{29}H_{25}O_1N_2F_1$ requires 437.20237 for $[M+H]^+$, found 437.20230.

Synthesis of **3an**

The compound was synthesized according to General Procedure **C** using **1a** (22.9 mg, 0.1 mmol), and **3n** (71 mg, 0.3 mmol). Crude dr: 3.8:1 (exo:endo). Silica gel column chromatography (CH_2Cl_2:Pentane 40:60 – 70:30 v:v, then EtOAc:Pentane 5:95 to 10:90) gave a fully separable mixture of diastereomers, combined yield 55% (25.6 mg).



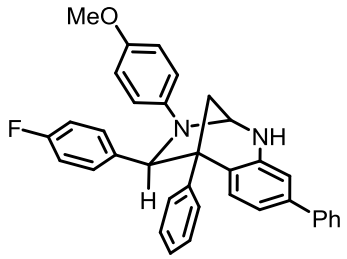
Data for **3an$_{(exo)}$**. Off-white solid. **mp** (from $CHCl_3$): 196-200 °C **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3402, 2981, 1603, 1510, 1474. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 (ddd, *J* = 8.8, 6.4, 2.3 Hz, 4H), 7.02 – 6.88 (m, 2H), 6.83 – 6.69 (m, 6H), 6.61 – 6.51 (m, 4H), 5.64 (d, *J* = 4.7 Hz, 1H), 5.27 (s, 1H), 5.20 (s, 1H), 3.75 (s, 3H), 3.68 (s, 3H), 3.09 (dd, *J* = 11.1, 4.9 Hz, 1H), 2.81 (d, *J* = 11.1 Hz, 1H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -115.32 (tt, *J* = 9.0, 5.1 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.8 (d, *J* = 245.6 Hz), 158.0, 151.8, 142.0, 138.7, 137.5 (d, *J* = 3.3 Hz), 133.1, 131.0, 130.8, 130.5 (d, *J* = 8.0 Hz), 127.9, 126.6, 118.5, 116.5, 115.1, 114.9 (d, *J* = 21.4 Hz), 114.3, 112.9, 77.5, 66.8, 55.8, 55.2, 54.6, 35.1. **HRMS** (ESI): m/z calculated for $C_{30}H_{27}O_1N_2F_1$ requires 467.21293 for $[M+H]^+$, found 467.21286.



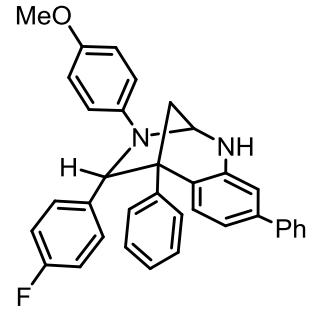
Data for **3an$_{(endo)}$**. Amorphous off-white solid. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3377, 2928, 1605, 1510. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 – 7.45 (m, 2H), 7.02 – 6.94 (m, 3H), 6.93 – 6.85 (m, 2H), 6.74 – 6.65 (m, 5H), 6.57 – 6.47 (m, 2H), 6.35 (td, *J* = 7.5, 1.3 Hz, 1H), 6.09 (dd, *J* = 7.7, 1.5 Hz, 1H), 5.37 (s, 1H), 4.83 (s, 1H), 3.83 (s, 3H), 3.68 (s, 3H), 2.86 (d, *J* = 10.7 Hz, 1H), 2.52 (dd, *J* = 10.8, 5.1 Hz, 1H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -115.57 (ddd, *J* = 14.0, 8.9, 5.1 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.0 (d, *J* = 245.5 Hz), 158.4, 151.9, 143.7, 140.2, 134.7 (d, *J* = 3.2 Hz), 134.2, 130.4, 130.3 (d, *J* = 7.9 Hz), 129.3, 128.8, 128.1, 118.4, 116.6, 115.8, 115.0, 114.7, 114.5 (d, *J* = 21.2 Hz), 114.1, 113.6, 75.0, 71.7, 55.8, 55.4, 55.0, 43.0. **HRMS** (ESI): m/z calculated for $C_{30}H_{27}O_1N_2F_1$ requires 467.21293 for $[M+H]^+$, found 467.21320.

Synthesis of **3ao**

The compound was synthesized according to General Procedure **C** using **1a** (22.9 mg, 0.1 mmol), and **3n** (84 mg, 0.3 mmol). Crude dr: 3.3:1 (exo:endo). Silica gel column chromatography (CH_2Cl_2:Pentane 40:60 – 70:30 v:v, then EtOAc:Pentane 5:95 to 10:90) gave a fully separable mixture of diastereomers, combined yield 60% (30.8 mg).



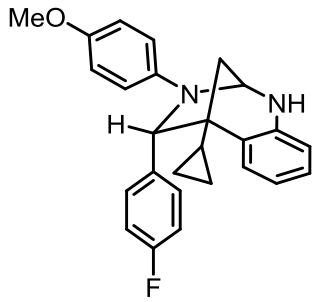
Data for **3an$_{(exo)}$**. White solid. **mp** (from $CHCl_3$): 172-176 °C**. FT-IR** (thin film): ν_{max} (cm^{-1}) = 3397, 2981, 2889, 1603, 1558, 1509. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 2H), 7.31 – 7.19 (m, 5H), 7.19 – 7.12 (m, 4H), 7.10 – 7.01 (m, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.75 – 6.63 (m, 6H), 6.58 – 6.48 (m, 2H), 5.60 (d, *J* = 4.7 Hz, 1H), 5.29 (s, 1H), 5.20 (s, 1H), 3.60 (s, 3H), 3.08 (dd, *J* = 11.2, 4.9 Hz, 1H), 2.79 (d, *J* = 11.2 Hz, 1H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -115.17 (ddd, *J* = 14.2, 8.7, 5.3 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.8 (d, *J* = 245.7 Hz), 151.9, 142.3, 140.9 (d, *J* = 3.6 Hz), 138.6, 138.5, 137.3 (d, *J* = 3.0 Hz), 131.7, 130.5 (d, *J* = 8.1 Hz), 130.1, 128.7, 127.6, 127.3, 127.1, 127.0, 126.8, 117.3, 115.2, 115.1, 114.9 (d, *J* = 21.4 Hz), 114.3, 77.2, 66.8, 55.8, 55.2, 35.0. **HRMS** (ESI): m/z calculated for $C_{35}H_{29}F_1N_2O_1$ requires 513.23367 for $[M+H]^+$, found 513.23322.



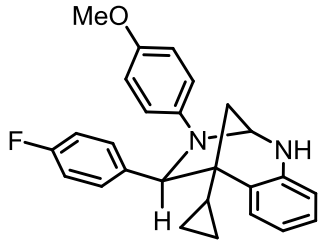
Data for **3an$_{(endo)}$**. White solid. **mp** (from $CHCl_3$): 94-98 °C**. FT-IR** (thin film): ν_{max} (cm^{-1}) = 3394, 2927, 1603, 1510. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 – 7.58 (m, 2H), 7.58 – 7.49 (m, 2H), 7.44 – 7.35 (m, 4H), 7.38 – 7.27 (m, 2H), 7.08 – 6.98 (m, 2H), 6.93 (d, *J* = 1.9 Hz, 1H), 6.78 – 6.63 (m, 4H), 6.63 – 6.56 (m, 1H), 6.59 – 6.49 (m, 2H), 6.14 (d, *J* = 8.1 Hz, 1H), 5.47 (s, 1H), 5.16 (d, *J* = 4.9 Hz, 1H), 4.96 (s, 1H), 3.68 (s, 3H), 2.91 (d, *J* = 10.8 Hz, 1H), 2.57 (dd, *J* = 10.9, 5.1 Hz, 1H).**^{19}F NMR** (377 MHz, $CDCl_3$) δ -115.31 – -115.53 (m). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.0 (d, *J* = 245.5 Hz), 151.9, 144.0, 142.2, 141.1, 141.0, 140.1, 134.6 (d, *J* = 3.1 Hz), 130.9, 130.3 (d, *J* = 7.9 Hz), 128.8, 128.4, 128.2, 127.8, 127.4, 127.1, 127.0, 117.3, 114.7, 114.6 (d, *J* = 21.3 Hz), 114.3, 114.2, 74.6, 71.6, 55.8, 55.6, 43.2. **HRMS** (ESI): m/z calculated for $C_{35}H_{29}F_1N_2O_1$ requires 513.23367 for $[M+H]^+$, found 513.23364.

Synthesis of **3ap**

The compound was synthesized according to General Procedure **C** using **1a** (22.9 mg, 0.1 mmol), and 4-cyclopropylquinoline **3p** (51 mg, 0.3 mmol). Crude dr: 4.3:1 (endo:exo). Silica gel column chromatography (CH_2Cl_2:Pentane 40:60 – 50:50 v:v) gave a partially separable mixture of diastereomers, combined yield 59% (23.8 mg).



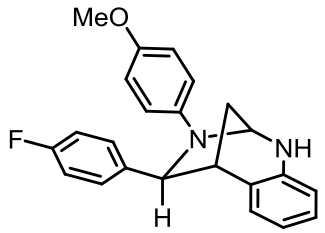
Data for **3ap$_{(endo)}$**. Amorphous colourless solid. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3391, 2981, 2889, 1605, 1510, 1473. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.97 (td, *J* = 7.6, 1.5 Hz, 1H), 6.94 – 6.81 (m, 2H), 6.73 (t, *J* = 9.1 Hz, 2H), 6.71 – 6.65 (m, 2H), 6.60 (dt, *J* = 8.0, 1.2 Hz, 2H), 6.49 – 6.39 (m, 3H), 5.18 – 5.00 (m, 1H), 4.74 (s, 1H), 4.67 (s, 1H), 3.68 (s, 3H), 1.98 – 1.83 (m, 2H), 1.39 (tt, *J* = 8.0, 6.1 Hz, 1H), 0.75 – 0.53 (m, 3H), 0.32 – 0.15 (m, 1H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -115.91 (tt, *J* = 8.8, 5.4 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.1 (d, *J* = 244.2 Hz), 151.7, 143.1, 140.2, 134.0 (d, *J* = 2.9 Hz), 129.0, 128.7 (d, *J* = 7.8 Hz), 127.8, 127.0, 118.7, 115.4, 114.8, 114.6 (d, *J* = 21.1 Hz), 113.7, 78.4, 71.7, 55.9, 49.9, 32.8, 12.7, 3.2, 2.0. **HRMS** (ESI): m/z calculated for $C_{26}H_{25}F_1N_2O_1$ requires 401.2024 for $[M+H]^+$, found 401.2021.



Data for **3ap$_{(exo)}$**. White solid. **mp** (from $CHCl_3$): 221-224 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3394, 2980, 2926, 1604, 1510, 1473. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.27 – 7.21 (m, 2H), 7.05 – 6.95 (m, 3H), 6.77 (td, *J* = 7.5, 1.3 Hz, 1H), 6.73 – 6.66 (m, 2H), 6.51 (dd, *J* = 7.9, 1.2 Hz, 1H), 6.47 – 6.38 (m, 2H), 5.47 (d, *J* = 4.7 Hz, 1H), 5.13 (s, 1H), 4.73 (s, 1H), 3.67 (s, 3H), 2.05 (dd, *J* = 10.8, 4.9 Hz, 1H), 1.67 (d, *J* = 10.7 Hz, 1H), 0.93 – 0.85 (m, 1H), 0.62 – 0.39 (m, 1H), 0.04 – -0.07 (m, 1H), -0.07 – -0.21 (m, 2H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -115.82 – -116.05 (m). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.3 (d, *J* = 245.0 Hz), 151.6, 142.2, 138.7, 136.7 (d, *J* = 2.9 Hz), 134.4, 128.8 (d, *J* = 8.0 Hz), 127.6, 124.8, 118.8, 115.9, 115.2 (d, *J* = 21.6 Hz), 115.1, 114.1, 77.5, 66.6, 55.9, 48.8, 29.1, 14.3, 3.3, 2.0, 1.2. **HRMS** (ESI): m/z calculated for $C_{26}H_{25}F_1N_2O_1$ requires 401.2024 for $[M+H]^+$, found 401.2023.

Synthesis of **S3a**

The compound was synthesized according to General Procedure **C** using **1a** (23 mg, 0.1 mmol), and quinoline (35 μL, 0.3 mmol). Crude dr: 1.3:1 (exo:endo). Silica gel column chromatography (CH_2Cl_2:Pentane 30:70 – 70:30 v:v) gave a separable mixture of diastereomers. Multiple other products co-elute with proposed endo isomer therefore detailed analysis was problematic, yield of exo alone, 40% (14.0 mg).

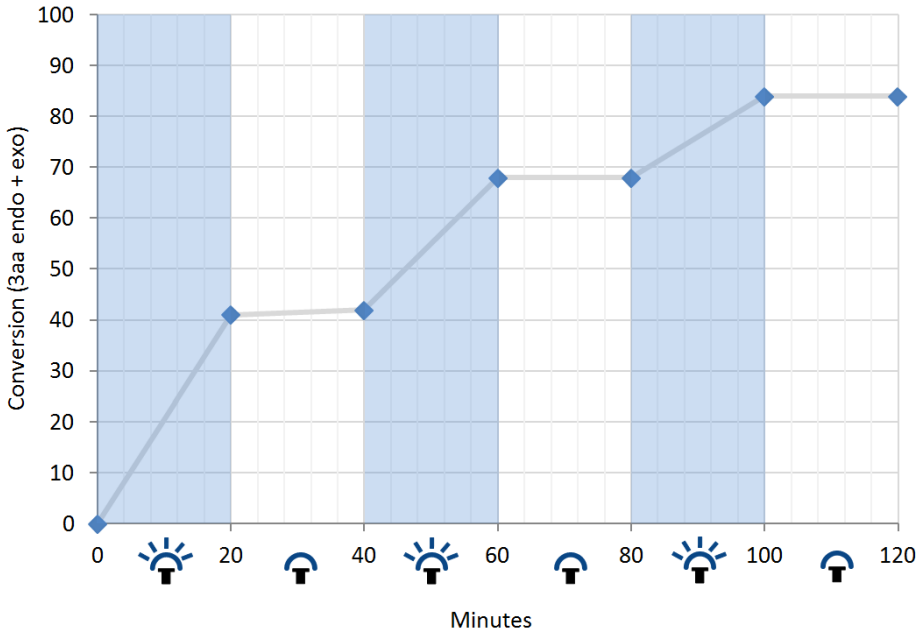


Data for **S3a$_{(exo)}$**. **mp** (from $CHCl_3$): 200-204 °C. **FT-IR** (thin film): ν_{max} (cm^{-1}) = 3405, 2957, 1605, 1509, 1476. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 8.7, 5.6 Hz, 2H), 7.09 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.06 – 6.95 (m, 3H), 6.78 – 6.71 (m, 2H), 6.69 (dd, *J* = 7.3, 1.2 Hz, 1H), 6.51 (dd, *J* = 7.9, 1.2 Hz, 1H), 6.47 – 6.40 (m, 2H), 5.42 (d, *J* = 4.4 Hz, 1H), 5.07 (s, 1H), 4.80 (s, 1H), 3.70 (s, 3H), 3.04 (d, *J* = 3.6 Hz, 1H), 2.40 (dt, *J* = 11.0, 4.2 Hz, 1H), 2.09 (d, *J* = 10.9 Hz, 1H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -116.01 (ddd, *J* = 14.0, 8.9, 5.1 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.1 (d, *J* = 245.0 Hz), 151.7, 141.9, 138.9, 137.7 (d, *J* = 2.7 Hz), 129.6, 128.0, 127.7 (d, *J* = 7.8 Hz), 127.1, 118.5, 115.8, 115.5 (d, *J* = 21.7 Hz), 115.1, 114.1, 73.9, 67.2, 55.9, 48.4, 29.0. **HRMS** (ESI): m/z calculated for $C_{25}H_{21}O_1N_2F_1$ requires 361.17107 for $[M+H]^+$, found 361.17059.

6. Further Experiments

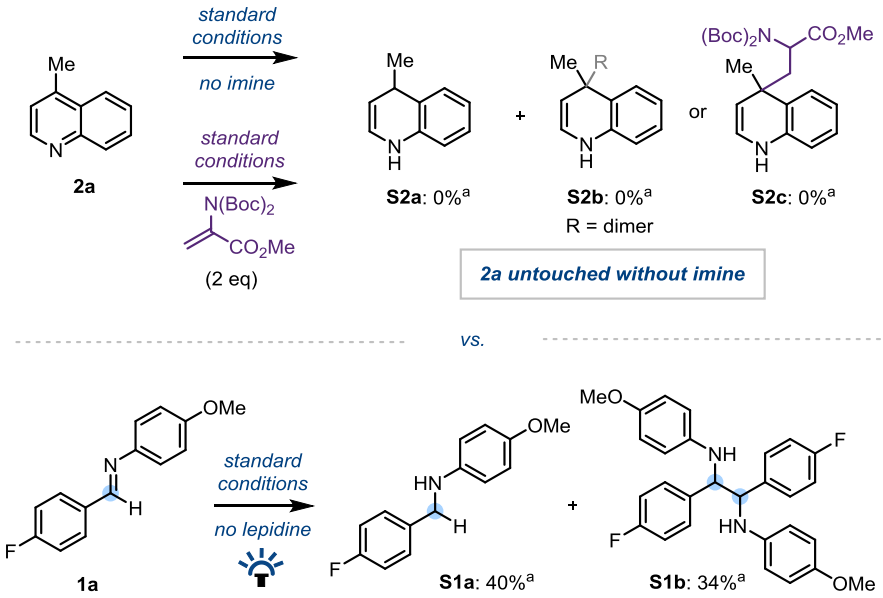
6.1: Control Experiments

Figure S1: On-off experiments



On-off experiments demonstrated that product was only observed in the presence of light. Exclusion studies (see optimization above) also demonstrated light and photocatalyst dependent reactivity.

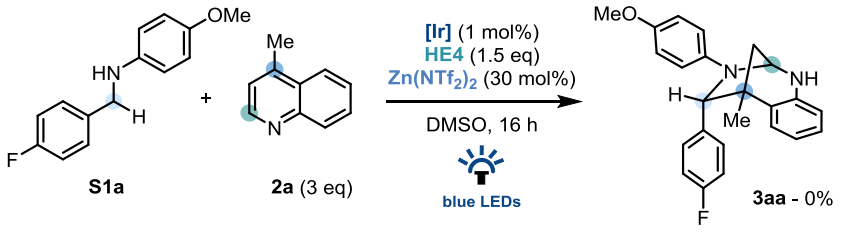
Scheme S1: Control experiments for lepidine and imine radical formation



[a] Conversion as denoted via ^{1}H or $^{19}F\{1H\}$ analysis of the crude reaction mixture

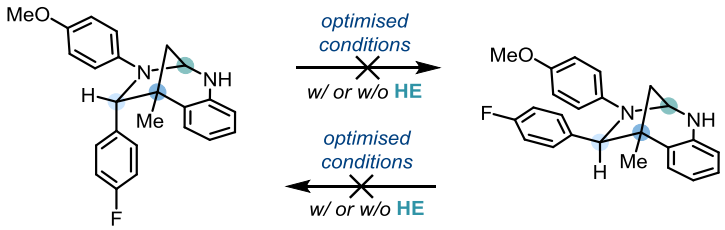
Using the standard reaction conditions either with or without a radical trap led to no conversion of lepidine (100% SM observed). Whereas with the imine under a similar reaction time-frame almost full conversion was observed to over-reduced amine product (formed *via* over-reduction and subsequent protonation of an α-amino radical intermediate) and aza-pinacol dimer (formed *via* dimerization of the α-amino radical intermediate) suggest formation of an α-amino radical under the conditions from the imine and no formation of a lepidine-based radical.

Scheme S2: Control experiments for using amine as a starting material



We also looked to elucidate – as over-reduced product **S1a** is often a by-product – whether this amine could partake in the mechanism, as is already at the correct oxidation state. Pleasingly, no conversion from amine was observed under the reaction conditions, demonstrating that the reductive imine pathway is operative to produce the α-amino radical.

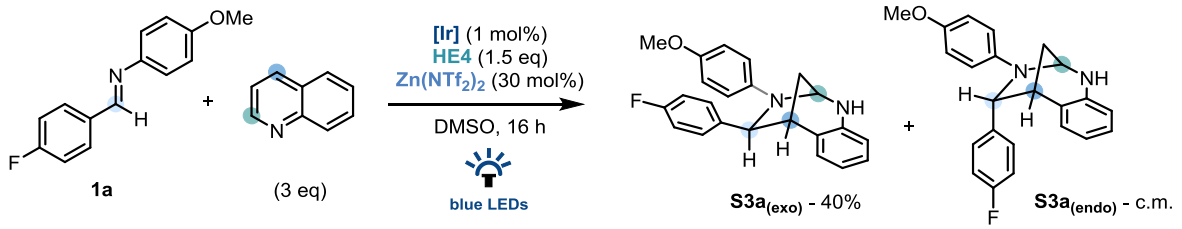
Scheme S3: Control experiments for interconversion of the diastereomers



Our previous studies have demonstrated that cyclic structures formed from α-amino radicals can epimerise towards the major diastereomer, enhancing diastereoselectivity of the reaction.[2] This was proposed to take place *via* single electron oxidation of the product and subsequent α-deprotonation of this amine radical cation leads to a planar α-amino radical. Re-donation of the proton and electron would then lead to enhancement of the thermodynamically favoured diastereomer.

In this case we observed that under the reaction conditions, with and without the stoichiometric Hantzsch ester reductant, no interconversion of diastereomers was observed.

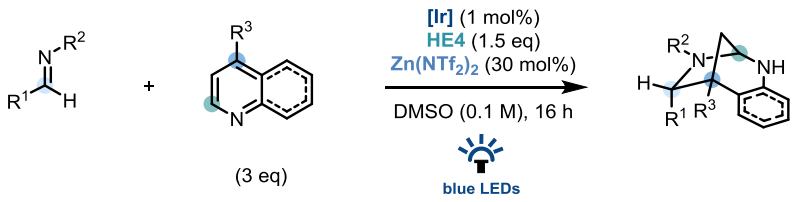
Scheme S4: Reaction with quinoline



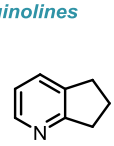
When performing the reaction using quinoline as coupling partner the C4 selective product was still formed, with **S3a$_{(exo)}$** isolated in modest yield cleanly (data included above in the synthetic section).

Analysis of the crude $^{19}F\{^{1}H\}$ NMR analysis, suggested a dr of ~1.3:1 in favour of exo. Despite numerous attempts to isolate a pure fraction of the endo isomer this was unsuccessful. We believe that the co-eluting by-product is a C4-Minisci product, based on M/S analysis and NMR analysis of the product mixture. Despite this, the spectra are not of publishable quality to include in the manuscript.

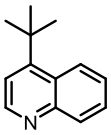
Scheme S5 – Unsuccessful/low yielding substrates



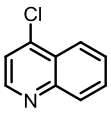
Quinolines



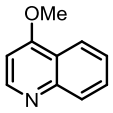
complex mixture



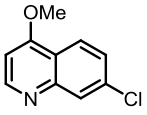
~40% NMR yield complex mixture on isolation



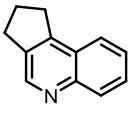
complex mixture



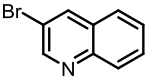
complex mixture



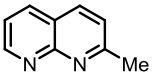
complex mixture



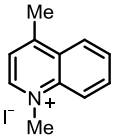
complex mixture



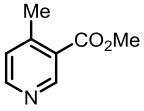
multiple products <15% diazpeane



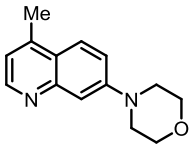
complex mixture



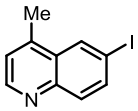
dealkylation major



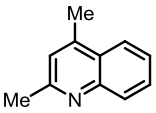
complex mixture



no reaction

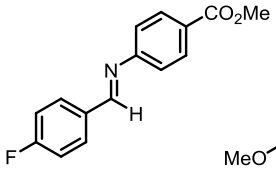


20% isolated

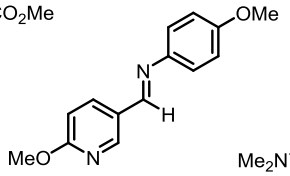


multiple products complex mixture on isolation

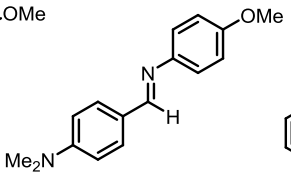
Imines



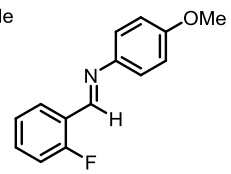
primarily imine hydrolysis



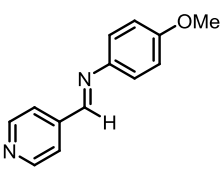
complex mixture



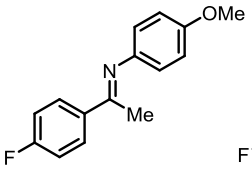
no reaction



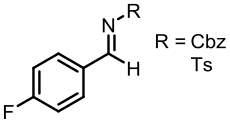
~50% NMR yield complex mixture on isolation



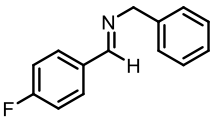
complex mixture



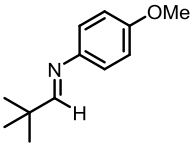
hydrolysis to ketimine major



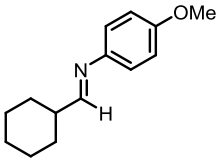
complex mixture



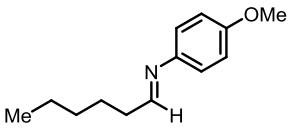
complex mixture



low conversion



low conversion

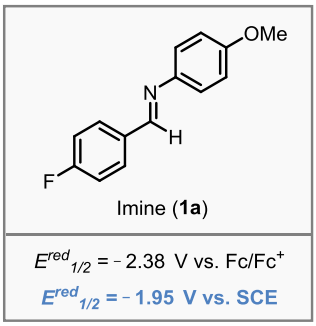


complex mixture

6.2: Electrochemical Measurements

Experimental redox potentials were calculated *via* Square Wave Voltammetry using an Autolab Potentiostat and Nova 2.0 Software. Polished glassy carbon, platinum wire and $Ag/AgNO_3$ were used as the working, counter, and reference electrodes, respectively. Measurements were made using a frequency of 2 Hz, and a modulation amplitude of 0.05 V.

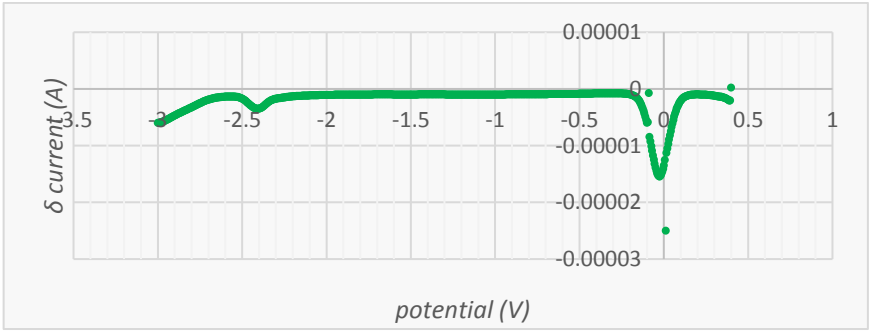
To an oven-dried electrochemical cell was added degassed tetrabutylammonium hexafluorophosphate (0.2 M in DMSO, 2 mL). The cell was sealed and sparged with a nitrogen needle for 5 minutes. A background measurement was then taken. Following this 20-80 μL of the appropriate compounds (0.02 M in DMSO) were added to the cell, and the solution sparged again with nitrogen for 1 minute. A second measurement was then taken. Finally, a ferrocene standard was added, the solution again sparged for 1 minute and a third measurement taken. The final measurement with ferrocene standard is shown below. The redox potential was calculated vs. Fc/Fc^+ and then converted to vs. SCE using Astruc's conversion.[17]

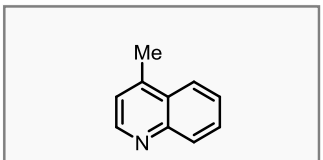


Imine (**1a**)

$E^{red}_{1/2}$ = - 2.38 V vs. Fc/Fc^+

$E^{red}_{1/2}$ = - 1.95 V vs. SCE

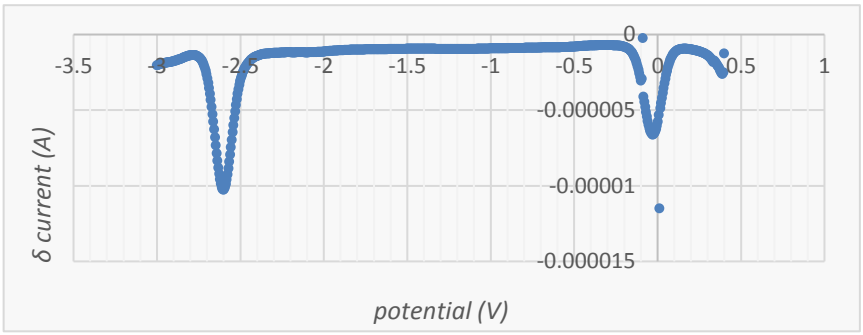




Lepidine (**2a**)

$E^{red}_{1/2}$ = - 2.57 V vs. Fc/Fc^+

$E^{red}_{1/2}$ = - 2.14 V vs. SCE

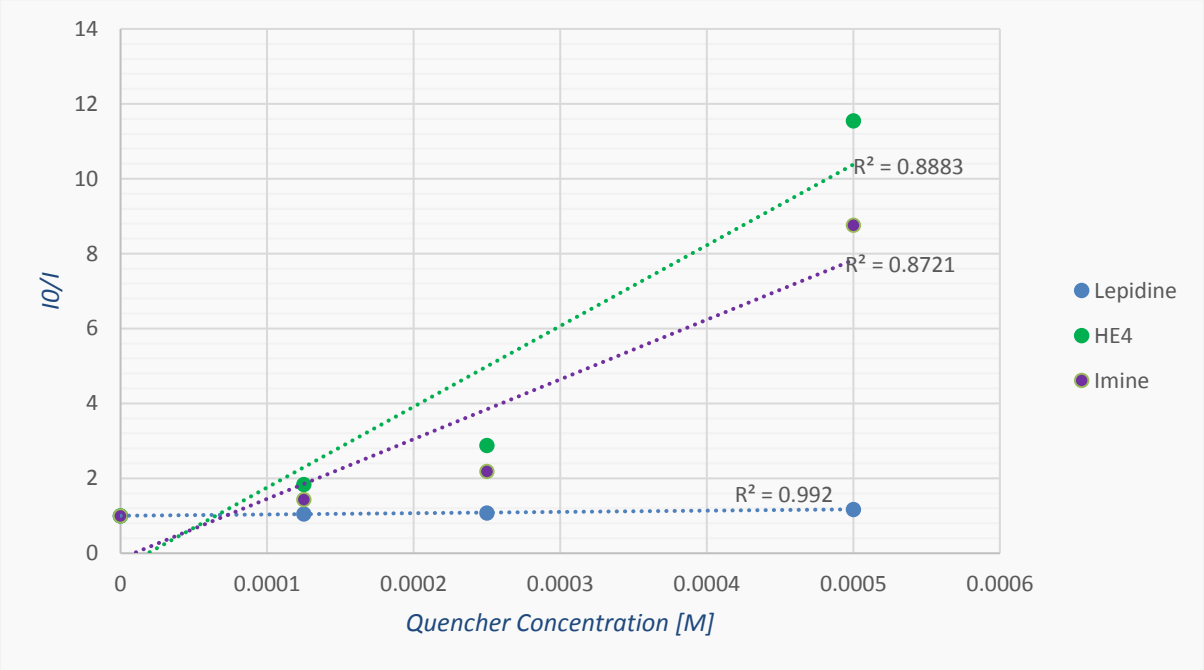


6.3: Stern-Volmer Luminescence Quenching Studies

A 4 x 10^{-8} M solution of (Ir[dF(CF_3)ppy]$_2$(dtbbpy))PF_6 (**Ir1**) in 25 mL DMSO, and 0.02 M solutions of quenchers (Imine **1a**, Lepidine, **2a**, Hantzsch Ester **HE4**) in 10 mL DMSO were prepared. The solutions were then thoroughly degassed with Argon.

A 1 mL aliquot of the iridium solution made up to 2 mL with DMSO was irradiated at 380.00 nm and the emission intensity was measured between 400-700 nm. (Ir[dF(CF3)ppy]2(dtbbpy))PF6 gives an emission peak ~481 nm.

Following this quenching measurements were made using 1 mL iridium solution, appropriate quantity of the quencher solution, which was then made up to 2 mL with DMSO. Concentrations of 1.25 x10^{-4}, 2.5 x10^{-4}, and 5 x10^{-3} were chosen as competing Hantzsch ester emission complicates analysis at higher concentrations. The quenching was calculated through calculating I0/I with the appropriate quencher.



This data demonstrates that both the Hantzsch ester and the imine substrate are capable of quenching the photoexcited iridium species. Using our values from the cyclic voltammetry and computationally calculated redox potentials (see 7.4: Redox Potentials and pKa's Calculations), the imine lies firmly outside the redox potential to quench the photoexcited photocatalyst ($E^0_{1/2}$ = –0.89 V in MeCN). For this reason we suggest that the quenching of the photocatalyst by the imine substrate (**1a**) takes place through either one of two mechanisms: 1. Energy transfer from the photoexcited iridium species to the imine, or 2. Trace hydrolysis and anisidine formed is capable of readily quenching the iridium species. From these investigations, we have deduced that the Hantzsch ester quenches the iridium species through single electron oxidation.

7. Computational Studies

7.1: Computational Methods

Calculations were performed using *Gaussian 16* A.03.[18] Geometry optimizations of all structures were carried out with the hybrid meta-generalized gradient (GGA) ωB97X-D functional in combination with the 6-31G(d) basis set.[19] The effect of dimethyl sulfoxide (DMSO) solvation was evaluated using the SMD implicit solvent model.[20] Harmonic vibrational frequencies at the same level of theory were calculated to characterize stationary points as either minima or transition state (TS) structures and to calculate the zero-point vibrational energy and thermal corrections. Free energies were evaluated at 25 °C and have been corrected to a standard liquid state of 1 mol/L. In all cases, vibrational entropies were obtained using a quasi-harmonic approximation, treating vibrational modes below 100 cm^{-1} as free rotors and as rigid rotors above this cut-off, as first proposed by Grimme[21] and implemented in Python.[22] Single point energies were evaluated with at the SMD(DMSO)-ωB97X-D/6-311++G(d,p) level of theory. Molecular graphics were generated with *PyMol 4.50.5*.

7.2: Regioselectivity 3aa

Conformational Search. Due to the presence of several rotatable bonds, various possible conformations for the first step. Those conformations were explored by carrying out a scan of the dihedral bond involving the bond being formed at TS1, with the bond being formed kept constant at a distance of 2.06 Å. As observed in Figure S3, three different minima exist for both C2 and C4 TS1. Those structures were further optimized with no restrain and the lowest energy TS was used for further calculations.

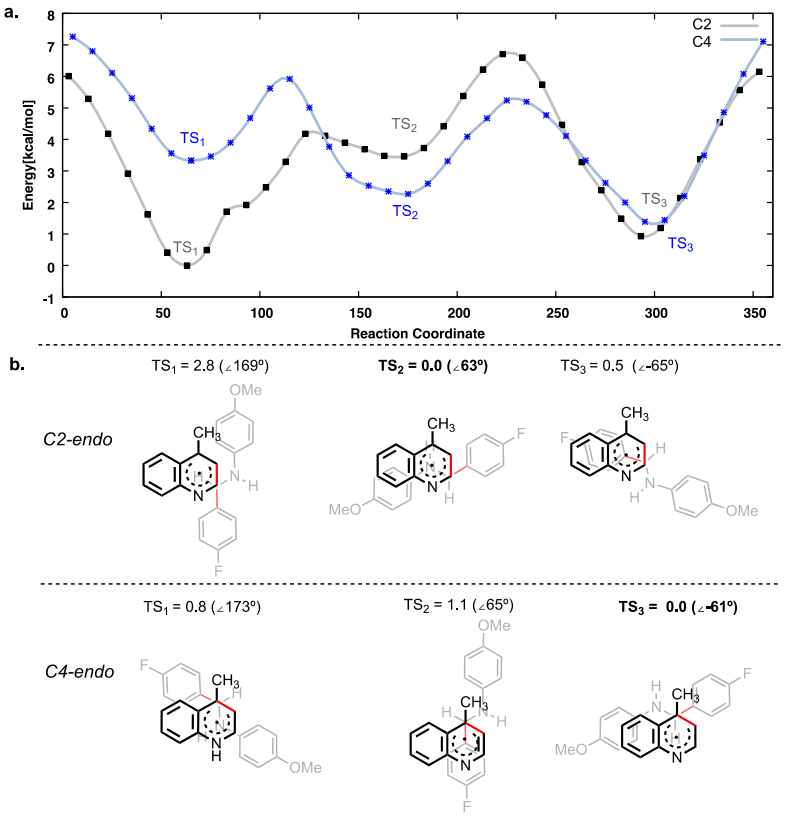
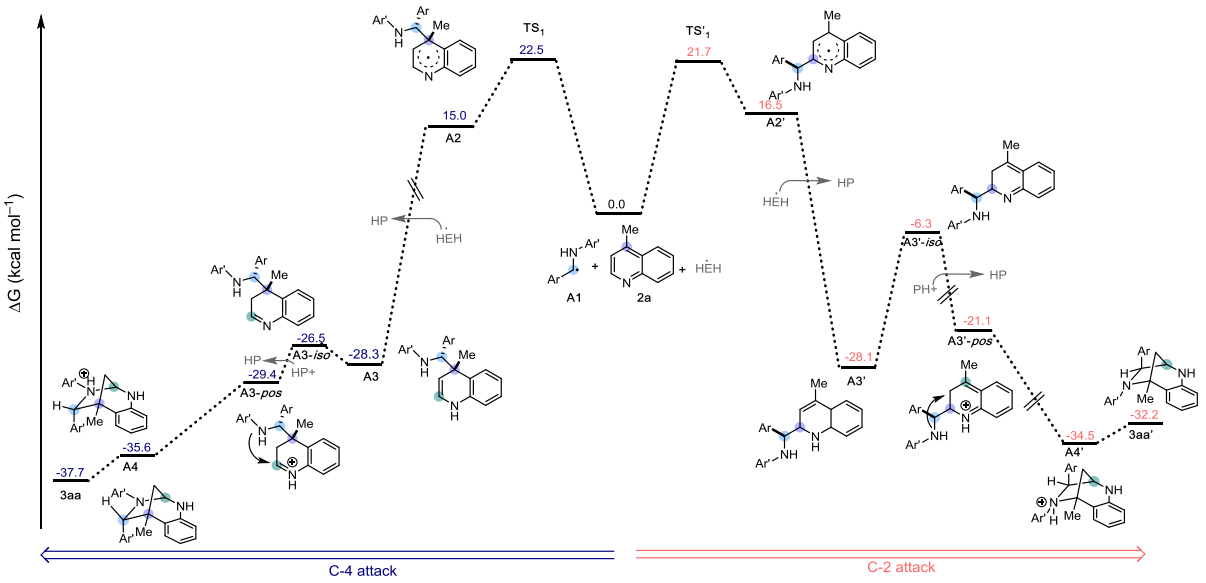


Figure S2: a) Potential energy profile for the C_1-C_2-C_3-N_4 dihedral angle (red) rotation, with the C_2-C_3 bond distance fixed at 2.06 Å, for the *endo* radical addition at the C2 and C4 position. Energies were computed at the SMD(DMSO)-ωB97X-D/6-31G(d) level of theory. **b**) Relative energies obtained at the same level of theory. All energies are in kcal mol^{-1}.



Scheme S4. Proposed reaction pathways for the formation of substrate **3aa** via C2 (right) and C4 (left). All values are reported in kcal mol^{-1} and are relative to the starting materials **A1** and **2a** at the SMD(DMSO)-ωB97X-D/6-311++G(d,p)//SMD(DMSO)-ωB97X-D/6-31G(d) level of theory.

As can be seen in **Scheme S4**, the transition state for the final ring closure step of the reaction is not included. Considerable difficulty was encountered in finding this TS. Scan calculations along the bond being formed at **A3-*pos*** suggested that ring closure occurs spontaneously, without significant energy cost (**Figure S3**). This result suggests that a concerted mechanism for the formation of **A4-*pos*,** wherein the intramolecular attack occurs simultaneously with the protonation event, possibly facilitated by a partially oxidized Hantzsch ester species. This is also confirmed by the fact that an energy barrier only appears when the lepidine nitrogen is deprotonated. Similar results were obtained for **3am**.

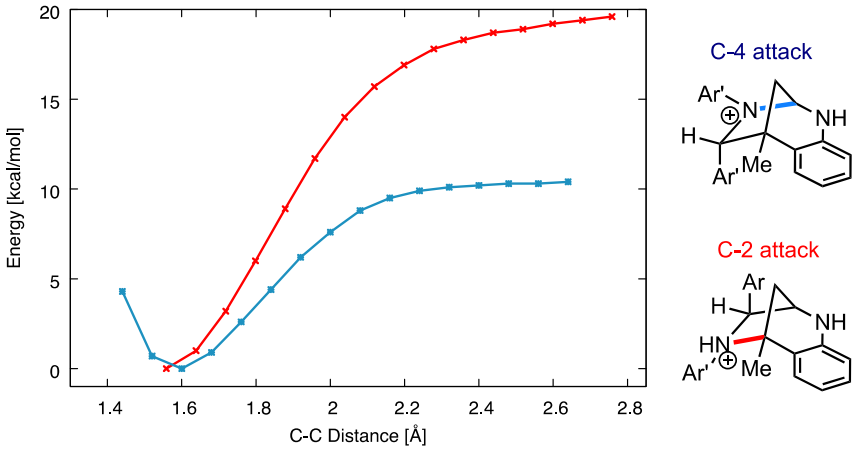


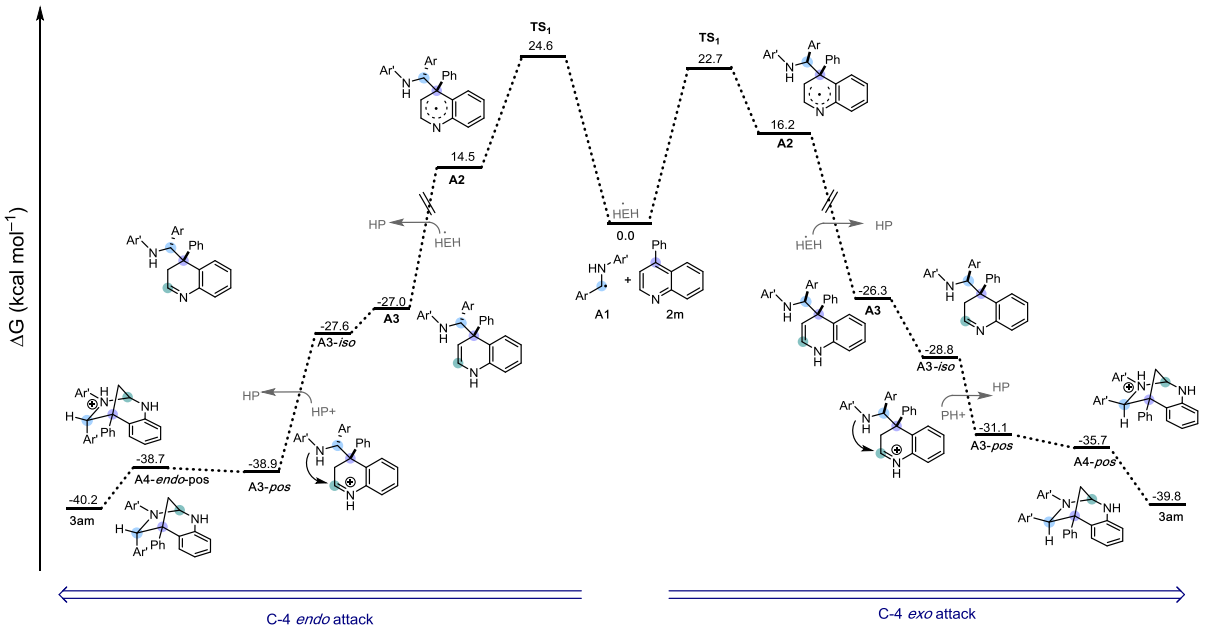
Figure S3: a) Potential energy profile along the forming the C-C bond for the *endo* ring closing reaction at the C2 and C4 position (shown on the right). Energies were computed at the SMD(DMSO)-ωB97X-D/6-31G(d) level of theory.

Table S1. Relative energies for species in the proposed formation of **3aa**-*exo* and **3aa**-*endo* at the SMD(DMSO)-ωB97X-D/6-311++G(d,p)//SMD(DMSO)-ωB97X-D/6-31G(d) level of theory. Values are given in kcal mol^{-1}. Absolute energies in **Table S5**

	C4					**C2**			
	endo		*exo*			*endo*		*exo*	
Species	E_{rel}	G_{rel}	E_{rel}	G_{rel}		E_{rel}	G_{rel}	E_{rel}	G_{rel}
A1+2a	0.0	**0.0**	0.0	**0.0**	*A1+2a*	0.0	**0.0**	0.0	**0.0**
TS1	8.6	**22.5**	8.4	**22.4**	*TS1*	6.9	**21.7**	7.4	**21.5**
A2	1.7	**15.0**	1.4	**15.3**	*A2*	1.0	**16.5**	2.2	**17.2**
A3	-43.2	**-28.3**	-43.9	**-28.9**	*A3*	-46.3	**-28.1**		
A3-iso	-41.9	**-26.5**	-42.7	**-27.3**	*A3-iso*	-23.7	**-6.3**		
A3-pos	-44.6	**-29.4**	-45.5	**-30.3**	*A3-pos*	-39.7	**-22.5**		
A4-pos	-52.4	**-35.6**	-47.8	**-31.0**	*A4-pos*	-56.1	**-34.5**		
3aa	-54.3	**-37.7**	-52.4	**-35.9**	*3aa*	-52.7	**-32.2**		

7.3: Diastereoselectivity for 3am

The energy profile for 3am is shown in Scheme S5. In contrast to other systems, a preference for the *exo* product is observed under kinetic control (ΔG^{o} =1.9 kcal mol^{-1} d.r: = 19:1 *exo:endo*); in qualitative agreement with the experimental result (d.r = 4:1 *exo:endo*). A similar result is observed when comparing the products, with the **3am-*exo*** product being thermodynamically more stable than the **3am-*endo*** one (ΔG^{o} =1.9 kcal mol^{-1}). Thus, providing additional driving force for the formation of this stereoisomer (Scheme **S5**).



Scheme S5. Proposed reaction pathways for the formation of the *endo* and *exo* diastereomers of substrate **3am**. All values are reported in kcal mol^{-1} and are relative to the starting materials **A1** and **2m** at the SMD(DMSO)-ωB97X-D/6-311++G(d,p)//SMD(DMSO)-ωB97X-D/6-31G(d) level of theory.

Table S2. Relative energies for species in the proposed formation of **3am**-*exo* and **3am**-*endo* at the SMD(DMSO-ωB97X-D/6-311++G(d,p)//SMD(DMSO)-ωB97X-D/6-31G(d) level of theory. Values are given in kcal mol^{-1}.

3am-*exo*			**3am**-*endo*		
Species	E_{rel}	G_{rel}		E_{rel}	G_{rel}
A1+2m	0.0	**0.0**	*A1+2m*	0.0	**0.0**
TS1-exo	8.3	**22.7**	*TS1-endo*	9.6	**24.6**
A2-exo	2.0	**16.2**	*A2-endo*	0.7	**14.5**
A3-exo-iso	-43.8	**-28.8**	*A3-endo-iso*	-42.9	**-27.6**
A3-pos-exo	-45.8	**-31.1**	*A3-endo*	-55.0	**-38.9**
A4-pos-exo	-51.3	**-35.7**	*A4-pos-endo*	-55.4	**-38.7**
3am-exo	-55.9	**-39.8**	*3am-endo*	-56.3	**-40.3**

7.4: Redox Potentials and pK_a's Calculations

7.4.1: Methodology

Calculations were performed using *Gaussian 16* A.03.[18] Geometries were optimized at the SMD (DMSO)PBE-D3BJ/6-31+G(d,p) level of theory.[23,24] This functional was chosen based on benchmark studies carried out within the group which demonstrated that the PBE functional leads to values within 0.05 V of those obtained using M06-2X functional (previously suggested by Neese and Pantazis)[25] at a much lower computational cost. Furthermore, Hansen and co-workers have also recently reported the good performance of the PBE functional for reduction potential calculations of small molecules and organometallic species.[26]

Ho has previously reported the use of the M06-2X functional for the pK_a calculation of small organic molecules in DMSO, acetonitrile and water.[27] Similarly, Schlegel and co-workers have found that the PBE functional gives results with comparable accuracy to the M062X functional.[28] Hence, for consistency and comparability of values, all redox and pK_a calculations were performed using the same methodology. Entropy corrections were incorporated as described above.

The reduction and oxidation potentials (eq. **1** and **2,** respectively) were calculated using the Nernst equation (eq. **3**), following the protocol reported by Nicewicz and coworkers.[29] The values for the Faraday's constant (**F**) and the reference electrode ($\mathbf{E_{1/2}}$, **SCE**) in DMSO are given as 23.061 kcal/V and 4.360 V respectively.

$$\mathbf{A_{(solv)}} + \mathbf{e^-} \xrightarrow[reduction]{\Delta G^o_{1/2}} \mathbf{A^{-\bullet}_{(solv)}} \quad \textbf{(1)}$$

$$\mathbf{A^{-\bullet}_{(solv)}} \xrightarrow[oxidation]{\Delta G^o_{1/2}} \mathbf{A_{(solv)}} + \mathbf{e^-} \quad \textbf{(2)}$$

$$E^0_{1/2} = -\frac{(\Delta G_{reduced} - \Delta G_{oxidised})}{n_e F} - E^{0,SCE(MeCN)}_{1/2} = -\frac{\Delta G^0_{1/2}}{n_e F} \quad \textbf{(3)}$$

The pK_a was calculated using eq. **4** - **6** (where *R* is the gas constant (1.987 × 10^{-3} kcal mol^{-1} K^{-1} and T is the temperature, taken as 298 K).[27] $\mathbf{G_{solv}(A^-)}$ and $\mathbf{G_{solv}(HA)}$ are obtained of computationally from the thermodynamic data of the conjugate base and acid in solution. From literature, $\mathbf{G_{solv}(H^+)}$ = –273.3 kcal mol^{-1} in DMSO. and $\mathbf{G_{gas}(H^+)}$ = -6.3 kcal mol^{-1}.[27] A correction of $\mathbf{X_{corr}}$ = 1.4 kcal mol^{-1} is included as a standard state correction for the model.[27]

$$\mathbf{HA_{(solv)}} \xrightarrow[dissociation]{\Delta G_{solv}} \mathbf{A^-_{(solv)}} + \mathbf{H^+_{(solv)}} \quad \textbf{(4)}$$

$$pKa = \frac{\Delta G_{solv}}{RTln(10)} \quad \textbf{(5)}$$

$$\Delta G_{solv} = G_{solv}(A^-) - G_{solv}(HA) + G_{solv}(H^+) - G_{gas}(H^+) + X_{corr} \quad \textbf{(6)}$$

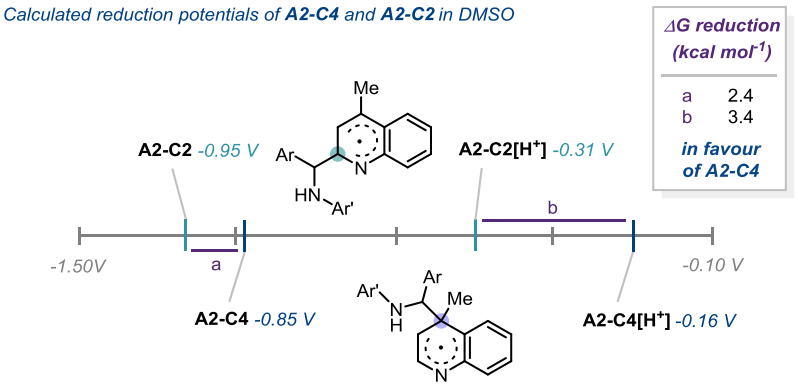
Although the reduction potentials for starting materials **1a** and **2a** can be determined experimentally using cyclic voltammetry experiments, the same techniques are not applicable towards the reactive intermediates in the transformation (due to issues with stability and isolation). As a result, redox values were obtained for all relevant species computationally, in order to allow direct comparison of all values and consistency in the method. Furthermore, the computationally-generated values were found to be within 0.06 V of those reported in literature and our own electrochemical measurements for biaryl imines,[29] thereby validating the accuracy of the chosen approach.

Table S3. Free energies of reduction ($\mathbf{\Delta G^0_{1/}}$, in kcal mol^{-1}) and reduction potentials ($\mathbf{\Delta E^0_{1/2}}$, volts (V)) for the starting materials **1a** and **2a** in their neutral and protonated forms, as well as the iridium catalyst (**[Ir]**). $\mathbf{\Delta E^0_{1/2}}$ values were derived from corresponding $\mathbf{\Delta G^0_{1/2}}$ using Eq. **1**. Absolute energies are presented in Table **S9**.

Species	$\mathbf{\Delta G^0_{1/2}}$	$\mathbf{\Delta E^0_{1/2}}$
1a	-59.8	-1.97
1a[H⁺]	-82.7	-0.97
2a	-54.0	-2.22
2a [H+]	-75.5	-1.29
$Ir^{III/II}$	-70.4	-1.51

7.4.2: Reduction Potentials of Intermediates

To rationalize the regioselectivity of diazepane formation (for **3aa**), a comparison was drawn between the reduction potentials of the proposed intermediate species **A2-C4** and **A2-C2** (Scheme **S4**). These two regioisomers are formed following the addition of the α-amino radical **A1** into **2a** at either the **C4** or the **C2** position on the ring respectively. Similarly to the reduction potentials of the starting materials, both the protonated and deprotonated versions of the radical species were considered in order to account for a possible PCET event, assisted by an acidic Hantzsch ester intermediate (Scheme **S6**). It was found that **A2-C4** had a lower reduction potential than its **A2-C2** counterpart in both the protonated and neutral form (Scheme **S4**). As a result, this species is more likely to be reduced by the partially oxidised Hantzsch Ester (HEH•) to give the following **A3-C4** intermediate. Given that the initial radical addition step is believed to be reversible (see Scheme 5 in main text), and that the formation of the Minisci-type product requires more reducing conditions, the theoretical data presents a plausible explanation as to why products of **C2** addition are not observed under experimental conditions.

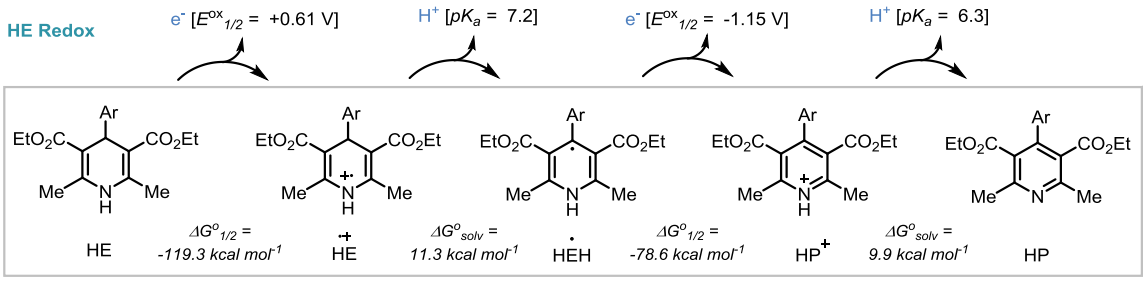


Scheme **S6.** Reduction potentials of regioisomers **A2-C4** and **A2-C2** in both their protonated and neutral forms. Values are reported in volts (V) and kcal mol^{-1} and were obtained at the SMD(DMSO)-PBE-D3BJ/6-311++G(d,p)//SMD(DMSO)-PBE-D3BJ/6-31+G(d,p) level of theory.

Table S4. Free energies of reduction ($\mathbf{\Delta G^0_{1/2}}$, in kcal mol^{-1}) and reduction potentials ($\mathbf{\Delta E^0_{1/2}}$, in volts (V)) for two possible regioisomeric intermediates in the initial radical addition. $\mathbf{\Delta E^0_{1/2}}$ values were derived from corresponding $\mathbf{\Delta G^0_{1/2}}$ using Eq. **1** described previously. Absolute energies presented in Table **S10.**

Species	$\mathbf{\Delta G^0_{1/2}}$	$\mathbf{\Delta E^0_{1/2}}$
A2-C4	-85.7	-0.84
A2-C4[H+]	-101.5	-0.16
A2C2	-83.3	-0.95
A2-C2[H+]	-98.0	-0.31

7.4.3: Oxidation Potentials and pK_a's of Hantzsch Ester Intermediates



Scheme **S5**. Oxidation potentials and pK_a's of Hantzsch ester (HE) and its intermediates. Free energies of reduction ($\mathbf{\Delta G^0_{1/2}}$) and free energies of proton dissociation ($\mathbf{\Delta G_{solv}}$), reported in kcal mol^{-1} and reduction potentials ($\mathbf{\Delta E^0_{1/2}}$), reported in volts (V). $\mathbf{\Delta E^0_{1/2}}$ values were derived from corresponding $\mathbf{\Delta G^0_{1/2}}$ using Eq. **1**. Absolute energies are presented in Table **S11**. Values were obtained at the SMD(DMSO)-PBE-D3BJ/6-311++G(d,p)//SMD(DMSO)-PBE-D3BJ/6-31+G(d,p) level of theory.

7.5 Absolute Energies

Table S5. Absolute energies for species in the proposed formation of the **3aa**-endo and **3aa**-*exo* diastereomers. Units are given in Hartrees. $\mathbf{E_{el}}$: absolute electronic energies, **ZPE**: zero-point energy correction, **H**: enthalpy and **qh-G(T)**: quasi-harmonic Gibbs energy (calculated at the SMD(DMSO)-ω**B97X-D/6-31G(d)** level of theory). $\mathbf{E_{el}}^{high}$ corresponds to the single point energies, which were calculated at the SMD(DMSO)/ω**B97X-D/6-311+G(d,p)** level of theory. Thermochemistry was evaluated at 298.15 K and 1M.

	Species	***E***	***ZPE***	***H***	***qh-G(T)***	$\mathbf{E_{el}}^{high}$	***TS Freq***
Hantzsch Ester	*HE*	-1093.239263	0.396743	-1092.817686	-1092.889395	-1093.521816	
	HE$^+$	-1093.049963	0.395300	-1092.629440	-1092.702789	-1093.325535	
	HEH·	-1092.603386	0.381864	-1092.196038	-1092.270041	-1092.886149	
	HP$^+$	-1092.499432	0.386158	-1092.088466	-1092.160386	-1092.774735	
	HP	-1092.039007	0.371642	-1091.642561	-1091.714591	-1092.316768	
	A1	-770.846981	0.241151	-770.59012	-770.64418	-771.04844	
	2a	-441.107809	0.165913	-440.93281	-440.97172	-441.21002	
3aa-C2-endo	*TS1-endo*	-1211.945332	0.409142	-1211.511920	-1211.582919	-1212.247435	-493.9
	A2-endo	-1211.956017	0.410451	-1211.521243	-1211.592502	-1212.256803	
	A3-endo	-1212.595998	0.424335	-1212.146890	-1212.219138	-1212.901606	
	A3-endo-iso	-1212.562290	0.423048	-1212.114300	-1212.186789	-1212.865583	
	A3-pos-endo	-1213.050185	0.436897	-1212.588312	-1212.660289		
	A4-pos-endo	-1213.078686	0.441781	-1212.613610	-1212.681878	-1213.375132	
	3aa-endo	-1212.612267	0.425558	-1212.163170	-1212.231855	-1212.911770	
3aa-C2-exo	*TS1-exo*	-1211.944353	0.408698	-1211.511196	-1211.582994	-1212.246732	-469.3
	A2-exo	-1211.953579	0.410608	-1211.518455	-1211.590651	-1212.255028	
3aa-C4-endo	*TS1-endo*	-1211.943193	0.408767	-1211.510185	-1211.581001	-1212.245943	-460.1
	A2-endo	-1211.956890	0.410271	-1211.522164	-1211.593906	-1212.258656	
	A3-endo-iso	-1212.595249	0.423675	-1212.146943	-1212.218156	-1212.902151	
	A3-endo	-1212.598163	0.424366	-1212.149577	-1212.219992	-1212.900444	
	A3-pos-endo	-1213.063999	0.438986	-1212.600708	-1212.671324	-1213.362833	
	A4-pos-endo	-1213.080674	0.442056	-1212.615364	-1212.683457	-1213.377353	
	3aa-endo	-1212.621118	0.426110	-1212.171635	-1212.240014	-1212.921148	
3aa-C4-exo	*TS1-exo*	-1211.943767	0.409116	-1211.510478	-1211.581130	-1212.246499	-470.4
	A2-exo	-1211.957967	0.410681	-1211.523109	-1211.593899	-1212.259226	
	A3-exo-iso	-1212.599042	0.424353	-1212.150483	-1212.220806	-1212.901750	
	A3-exo	-1212.596624	0.424061	-1212.148010	-1212.219023	-1212.903670	
	A3-pos-exo	-1213.064248	0.438246	-1212.601622	-1212.672262	-1213.363692	
	A4-pos-exo	-1213.073096	0.441915	-1212.607888	-1212.676038	-1213.369844	
	3aa-exo	-1212.618217	0.425833	-1212.168870	-1212.237634	-1212.917880	

Table S6. Absolute energies for species in the proposed formation of the **3am**-endo and **3am**-*exo* diastereomers. Units are given in Hartrees. $\mathbf{E_{el}}$: absolute electronic energies, **ZPE**:zero point energy correction, **H**: enthalpy and **qh-G(T)**: quasi-harmonic Gibbs energy (calculated at the SMD(DMSO)-ω**B97X-D/6-31G(d)** level of theory). $\mathbf{E_{el}}^{high}$ corresponds to the single point energies, which were calculated at the SMD(DMSO)/ω**B97X-D/6-311+G(d,p)** level of theory. Thermochemistry was evaluated at 298.15 K and 1M.

	Species	***E***	***ZPE***	***H***	***qh-G(T)***	$\mathbf{E_{el}}^{high}$	***TS Freq***
	A1	-770.846981	0.241151	-770.59012	-770.64418	-771.04844	
	2n	-632.781546	0.21975	-632.549645	-632.59566	-632.92482	
	2n-H	-633.246264	0.234024	-633.000005	-633.04612	-633.38613	
3am-C4-endo	*TS1-endo*	-1403.614098	0.46283	-1403.124056	-1403.2007	-1403.958	*-472.9*
	A2-endo	-1403.629572	0.463514	-1403.138318	-1403.2167	-1403.9722	
	A2-pos-endo	-1404.103178	0.478718	-1403.596548	-1403.675	-1404.4434	
	A3-endo-iso	-1404.266367	0.477237	-1403.761247	-1403.8392	-1404.611	
	A3-endo	-1404.270609	0.477533	-1403.765197	-1403.8429	-1404.6188	
	A3-pos-endo	-1404.750079	0.495431	-1404.227983	-1404.3032	-1405.0883	
	A4-pos-endo	-1404.750799	0.496109	-1404.228246	-1404.3028	-1405.0888	
	3am-endo	-1404.290866	0.479734	-1403.784492	-1403.8595	-1404.6323	
3am-C4-exo	*TS1-exo*	-1403.61677	0.462586	-1403.126964	-1403.2036	-1403.9601	-451.8
	A2-exo	-1403.627867	0.464094	-1403.136226	-1403.2141	-1403.97	
	A2-pos-exo	-1404.101164	0.478768	-1403.594573	-1403.6728	-1404.441	
	A3-exo-iso	-1404.269072	0.477398	-1403.764142	-1403.8412	-1404.6125	
	A3-exo	-1404.26883	0.477018	-1403.763833	-1403.8419	-1404.6162	
	A3-pos-exo	-1404.733469	0.492162	-1404.213817	-1404.2906	-1405.0735	
	A4-pos-exo	-1404.744374	0.494993	-1404.222682	-1404.2979	-1405.0823	
	3am-exo	-1404.290587	0.48025	-1403.783722	-1403.8588	-1404.6317	

Redox Potentials and pK_a's Calculations

Table S7. Absolute energies for the starting materials **1a** and **2a**, their corresponding radical species, the different Hantzsch Ester species. $\mathbf{E_{el}}$: absolute electronic energies, **ZPE**:zero point energy correction, **H**:enthalpy and **qh-G(T)**: quasi-harmonic Gibbs energy (calculated at the SMD(DMSO)/**PBE-D3/6-31+G(d,p)** level of theory). **SP** $\mathbf{E_{el}}$ corresponds to the single point energies, which were calculated at the SMD(DMSO)/**PBE-D3/6-311++G(d,p)** level of theory. Thermochemistry was evaluated at 298.15 K and 1M.

Species	E_{el}	***ZPE***	***H***	***qh-G(T)***	***SP E(el)***
1a	-670.523072	0.228866	-670.279291	-670.330998	-670.648444
A1	-670.611588	0.225197	-670.371129	-670.424115	-670.73914
1a[H+]	-670.980801	0.244065	-670.721864	-670.773333	-671.105527
A1[H+]	-671.10562	0.240069	-670.850228	-670.903096	-671.232455
2a	-440.747422	0.158919	-440.578987	-440.618668	-440.825113
2a radical	-440.82584	0.154569	-440.661331	-440.702372	-440.905903
2a[H+]	-441.207214	0.172699	-441.024886	-441.064743	-441.284325
2a[H+] radical	-441.320214	0.168578	-441.141494	-441.182866	-441.39948
[Ir^{III}]	-2939.735479	0.667196	-2939.015041	-2939.14186	-2940.88658
[Ir^{II}]	-2939.833629	0.662257	-2939.118445	-2939.245949	-2940.800624
HE	-1320.030436	0.419774	-1319.579668	-1319.664538	-1320.307373
HE^+	-1319.840457	0.419408	-1319.390006	-1319.475826	-1320.116018
HEH·	-1319.410723	0.40694	-1318.972723	-1319.058292	-1319.687678
HP^+	-1319.291424	0.41044	-1318.85037	-1318.934496	-1319.566948
HP	-1318.773249	0.395792	-1318.346674	-1318.43142	-1319.112744

Table S8. Absolute and single point energies for the intermediates **A2-C4** and **A2-C2,** as well as their corresponding reduced and protonated species. $\mathbf{E_{el}}$: absolute electronic energies, **ZPE**: zero-point energy correction, **H**: enthalpy and **qh-G(T)**: quasi-harmonic Gibbs energy (calculated at the SMD(DMSO)-**PBE-D3/6-31+G(d,p)** level of theory). $\mathbf{E_{el}^{high}}$ corresponds to the single point energies, which were calculated at the SMD(DMSO)-**PBE-D3/6-311++G(d,p)** level of theory. Thermochemistry was evaluated at 298.15 K and 1M.

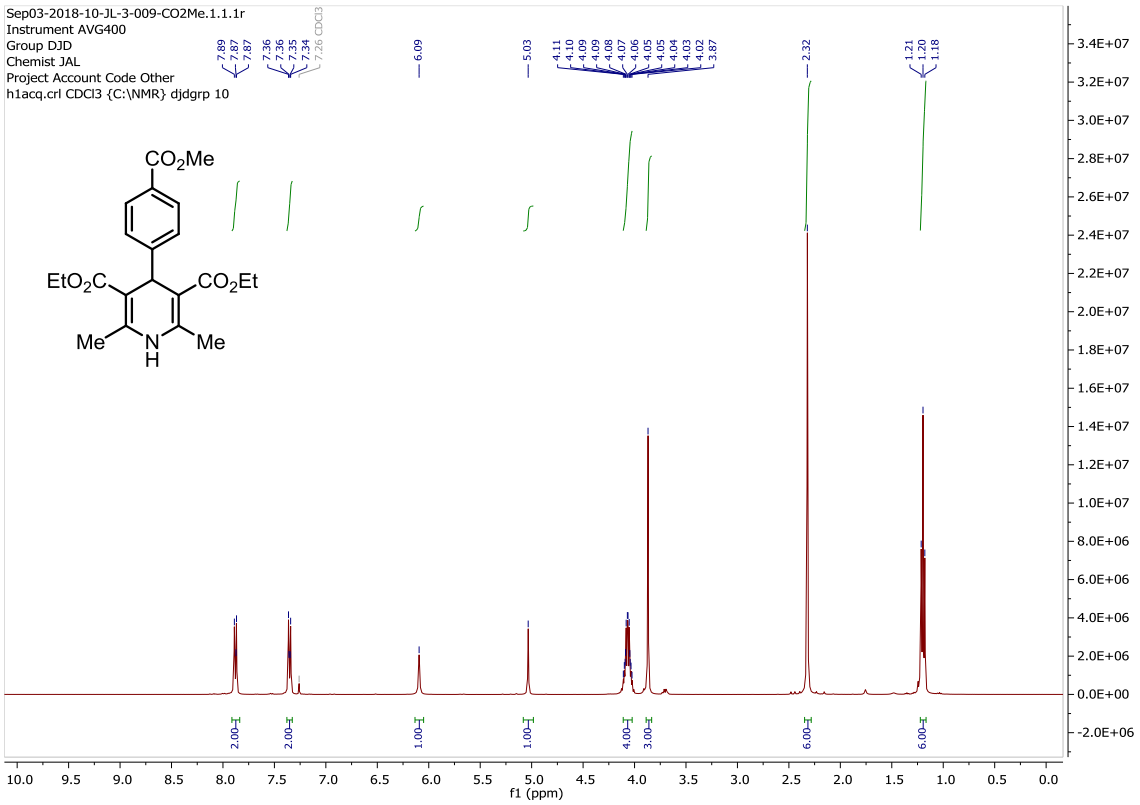
Species	E_{el}	***ZPE***	***H***	***qh-G(T)***	$\mathbf{E_{el}^{high}}$
A2-C4	-1211.000599	0.393123	-1210.58189	-1210.655596	-1211.232722
A3-C4 neg	-1211.133914	0.391304	-1210.71708	-1210.789905	-1211.368263
A2-C4[H+]	-1211.47506	0.407116	-1211.042158	-1211.116122	-1211.706688
A3-C4	-1211.633894	0.405604	-1211.202482	-1211.275711	-1211.867641
A2-C2	-1211.001642	0.392245	-1210.58361	-1210.658172	-1211.23365
A3-C2 neg	-1211.132009	0.39108	-1210.71522	-1210.788658	-1211.366303
A2-C2[H+]	-1211.48183	0.407208	-1211.048832	-1211.122819	-1211.713336
A3-C2	-1211.63502	0.406038	-1211.203023	-1211.2773	-1211.868274

8. References

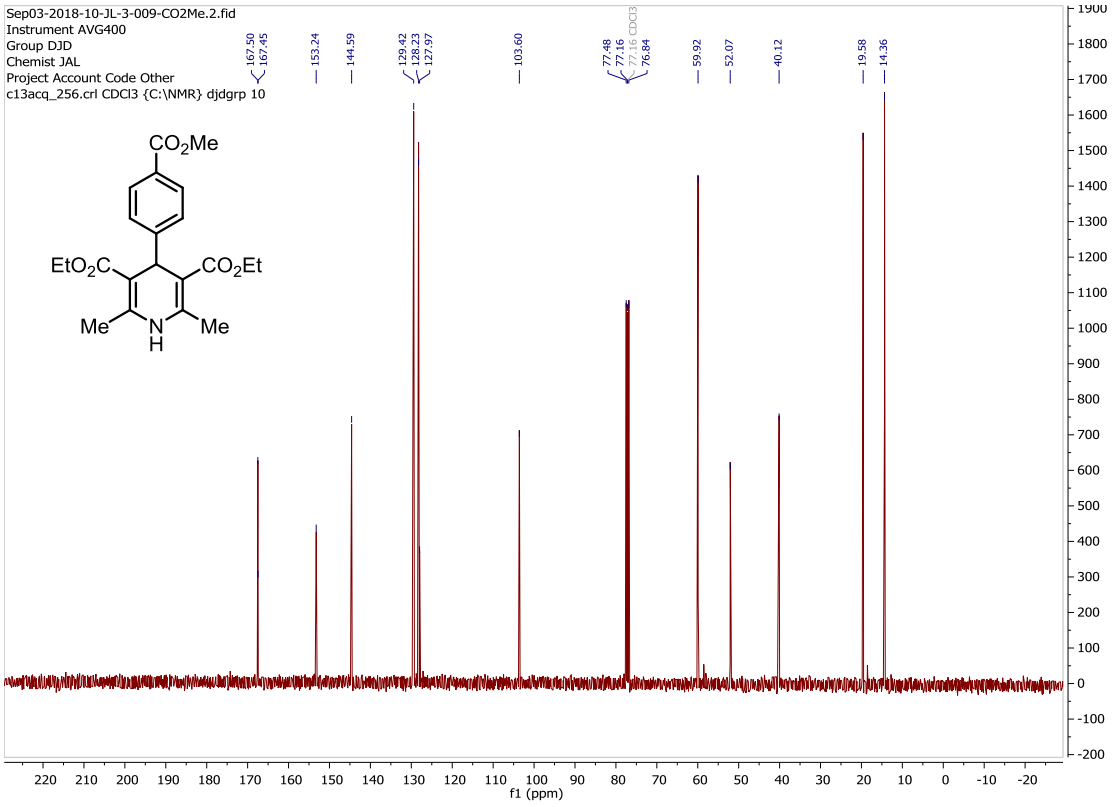
1. Choi, G. B.; Zhu, Q.; Miller, D. C.; Gu, C. J.; Knowles, R. R. *Nature*, **2016**, *539*, 268.
2. Leitch, J. A.; Fuentes de Arriba, A. L.; Tan, J.; Hoff, O. Matinez, C. M.; Dixon, D. J. *Chem. Sci.* **2018**, *9*, 6653-6658.
3. Kallitsakis, M. G.; Tancini, P. D.; Dixit, M.; Mpourmpakis, G.; Lykakis, I. N. *J. Org. Chem.* **2018**, *83*, 1176-1184.
4. Grote, R. E.; Jarvo, E. R. *Org. Lett.* **2009**, *11*, 485-488.
5. Bao, W.; Kossen, H.; Schneider, U. *J. Am. Chem. Soc.* **2017**, *139*, 4362-4365.
6. Rueping, M.; Ieawsuwan, W. *Synlett*, **2007**, 0247-0250.
7. Danahy, K. E.; Cooper, J. C.; Van Humbeck, J. F. *Angew. Chem. Int. Ed.* **2018**, *57*, 5134-5138.
8. Panda, S.; Coffin, A.; Nguyen, Q. N.; Tantillo, D. J.; Ready, J. M. *Angew. Chem. Int. Ed.* **2016**, *55*, 2205-2209.
9. Rueping, M.; Ieawsuwan, W. *Synlett*, **2007**, 0247-0250
10. Chen, Q.; Mollat du Jourdain, X.; Knochel, P. *J. Am. Chem. Soc.* **2013**, *135*, 4958-4961.
11. Malhotra, S.; Seng, P. S.; Koenig, S. G.; Deese, A. J.; Ford, K. A. *Org. Lett.* **2013**, *15*, 3698-3701.
12. Jean-Gérard, L.; Pauvert, M.; Collet, S.; Guingant, A.; Evin, M. *Tetrahedron* **2007**, *63*, 11250-11259.
13. Kuriyama, M.; Matsuo, S.; Shinozawa, M.; Onomura, O. *Org. Lett.* **2013**, *15*, 2716-2719.
14. Wang, Z.-Y.; Ma, Q.-N.; Li, R.-H.; Shao, L.-X. Org. Biomol. Chem. 2013, 11, 7899-7906
15. Deng, Q.; Shen, Y.; Zhu, H.; Tu, T. Chem. Commun. 2017, 53, 13063-13066.
16. Garza-Sanchez, R. A.; Patra, T.; Tlahuext-Aca, A.; Strieth-Kalthoff, F.; Glorius, F. *Chem. Eur. J.* **2018**, *24*, 10064-10068.
17. Aranzaes, J. R.; Daniel, M.-C.; Astruc, D. *Can. J. Chem.* **2006**, *84*, 288-299.
18. Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
19. Chai, J.D.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615-6620.
20. Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2009**, *113*, 6378–6396.
21. Grimme, S. *Chem. Eur. J.* **2012**, *18*, 9955–9964.
22. Funes-Ardoiz, I.; Paton, R. S. GoodVibes v2.0.2 DOI: 10.5281/zenodo.595246.
23. Perdew, J. P; Burke, K; Ernzerhof, M; *Phys. Rev. Lett.* **1996**, *77*, 3865-68.
24. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104-154119.
25. Isegawa, M.; Neese, F.; Pantazis, D. A. *J. Chem. Theory Comput* **2016**, *12*, 2272–2284.
26. Demissie, T. B.; Ruud, K.; Hansen, J. H. *Organometallics* **2015**, *34*, 4218–4228.
27. Ho, J. *Phys. Chem. Chem. Phys.* **2015**, *17*, 2859–2868.
28. Thapa, B.; Schlegel, H. B. *J. Phys. Chem. A* **2016**, *120*, 5726–5735.
29. Roth, H. G.; Romero, N. A.; Nicewicz, D. A. *Synlett* **2016**, *27*, 714–723.

9. NMR Spectra

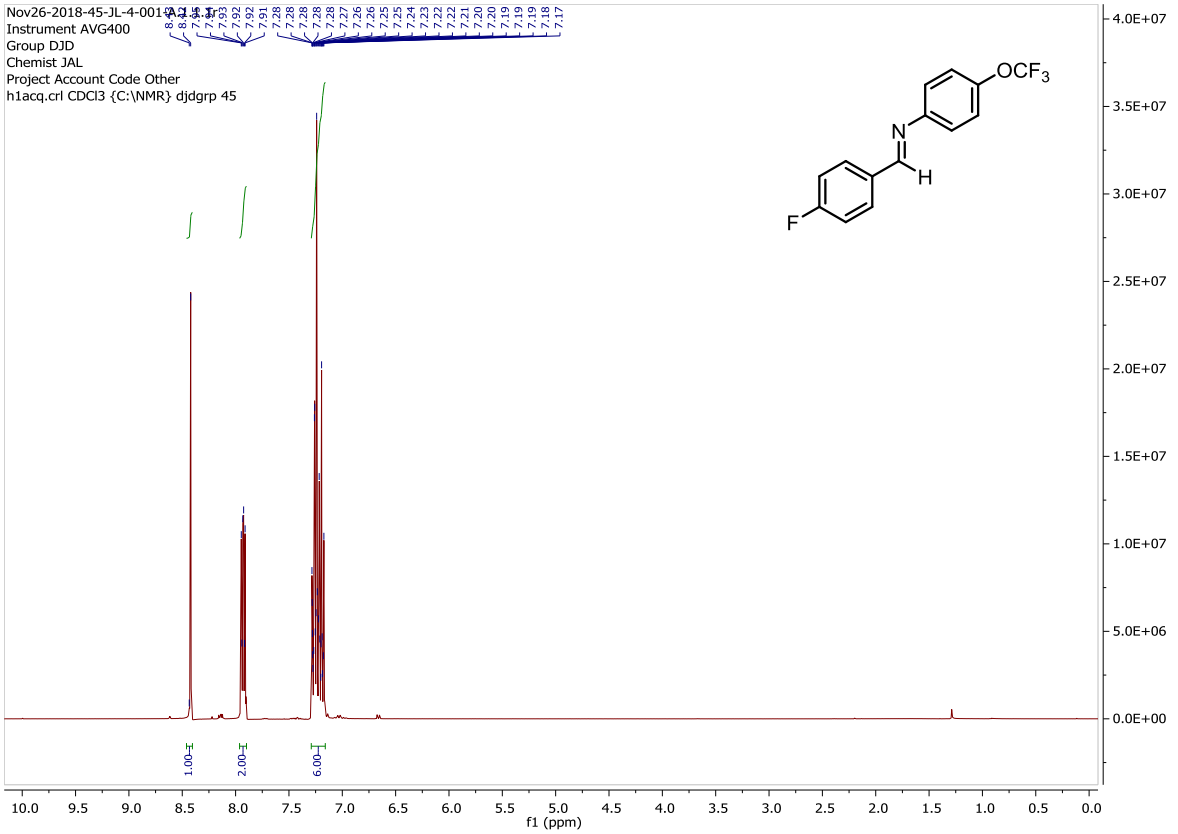
HE4 – ^{1}H NMR (400 MHz, $CDCl_3$)



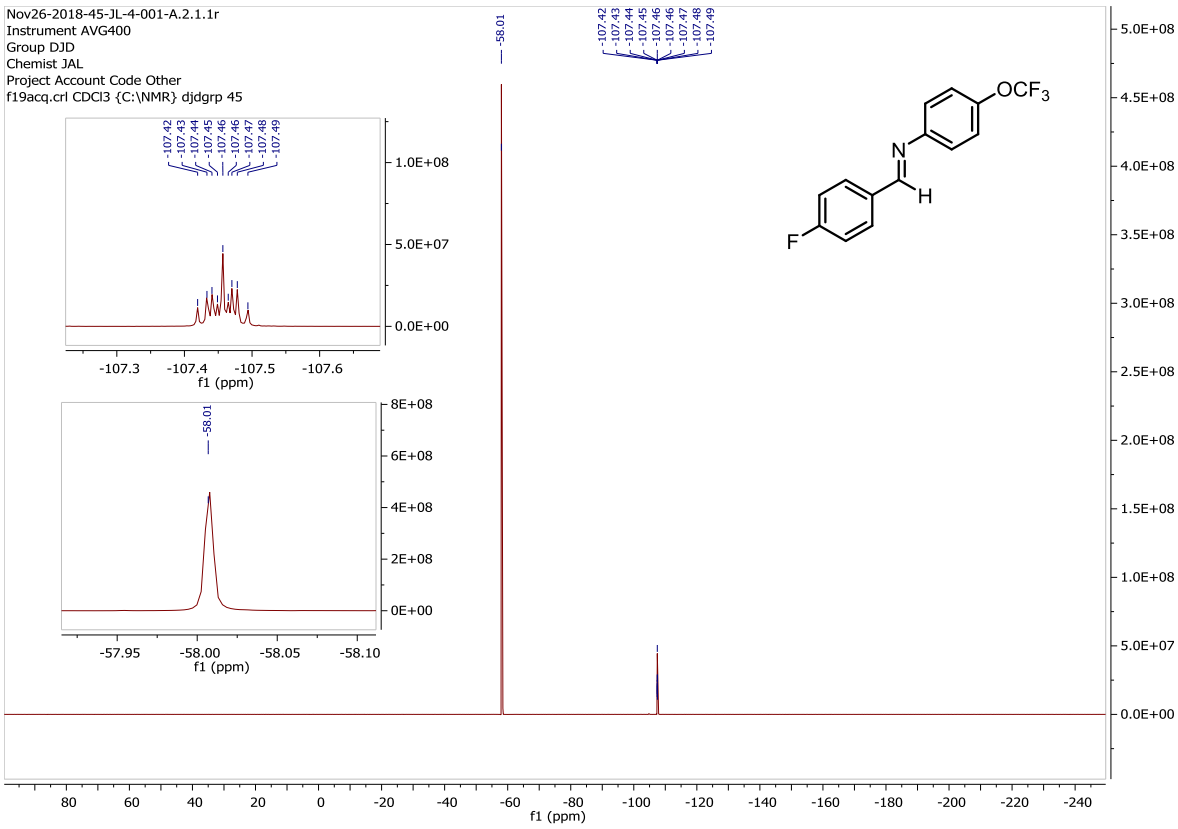
HE4 – ^{13}C NMR (101 MHz, $CDCl_3$)



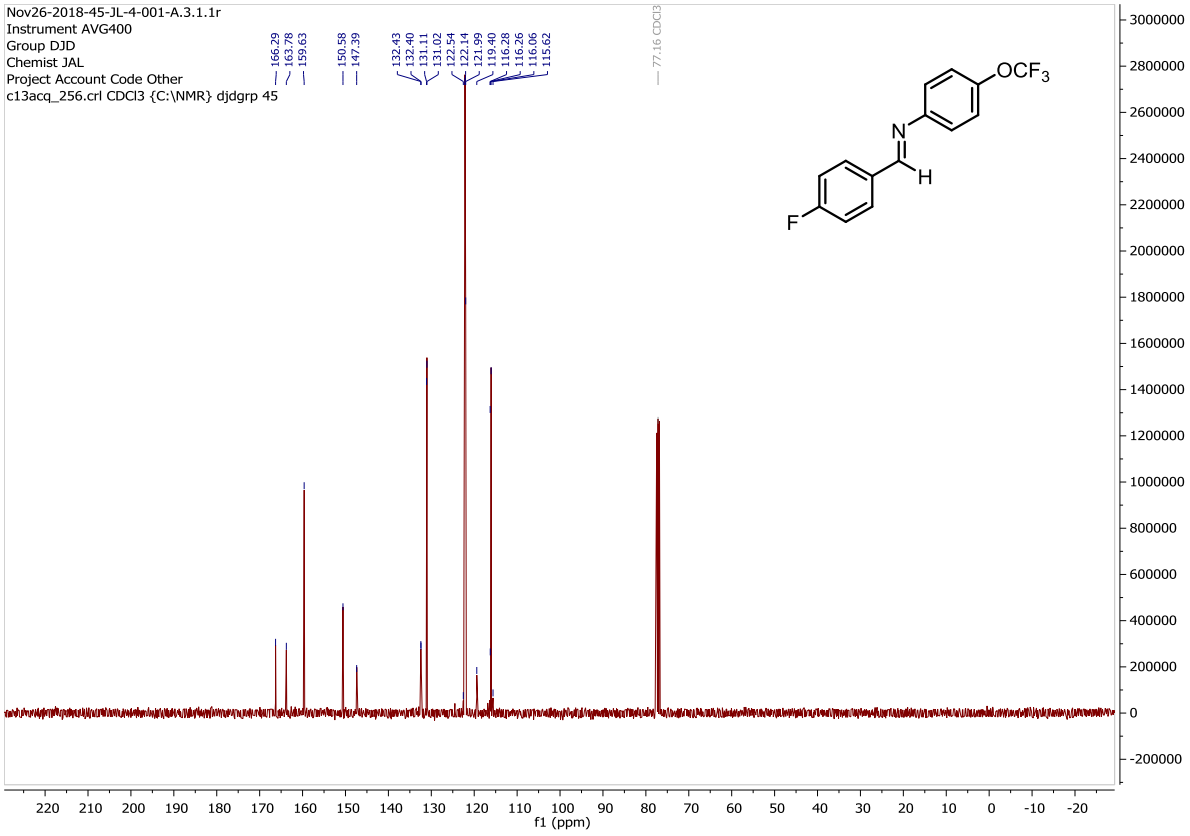
1e – ^{1}H NMR (400 MHz, $CDCl_3$)



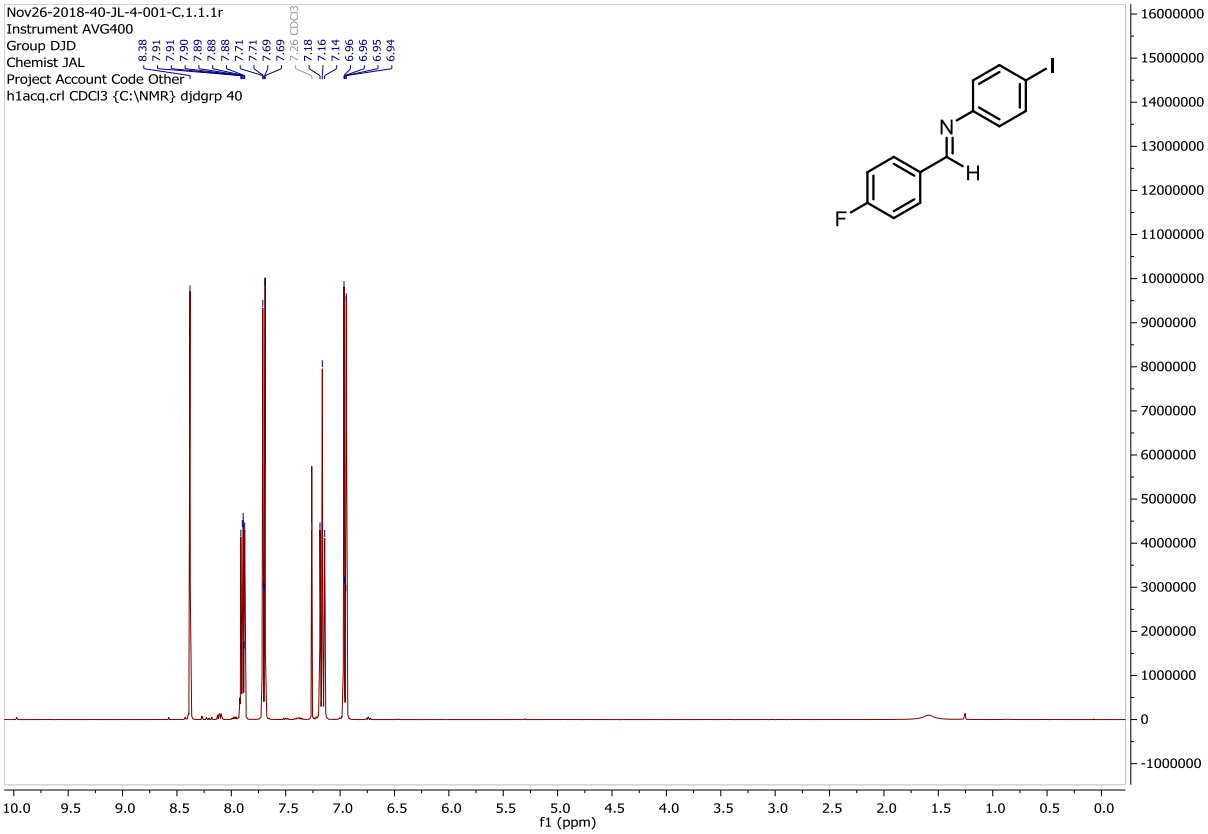
1e – ^{19}F NMR (377 MHz, $CDCl_3$)



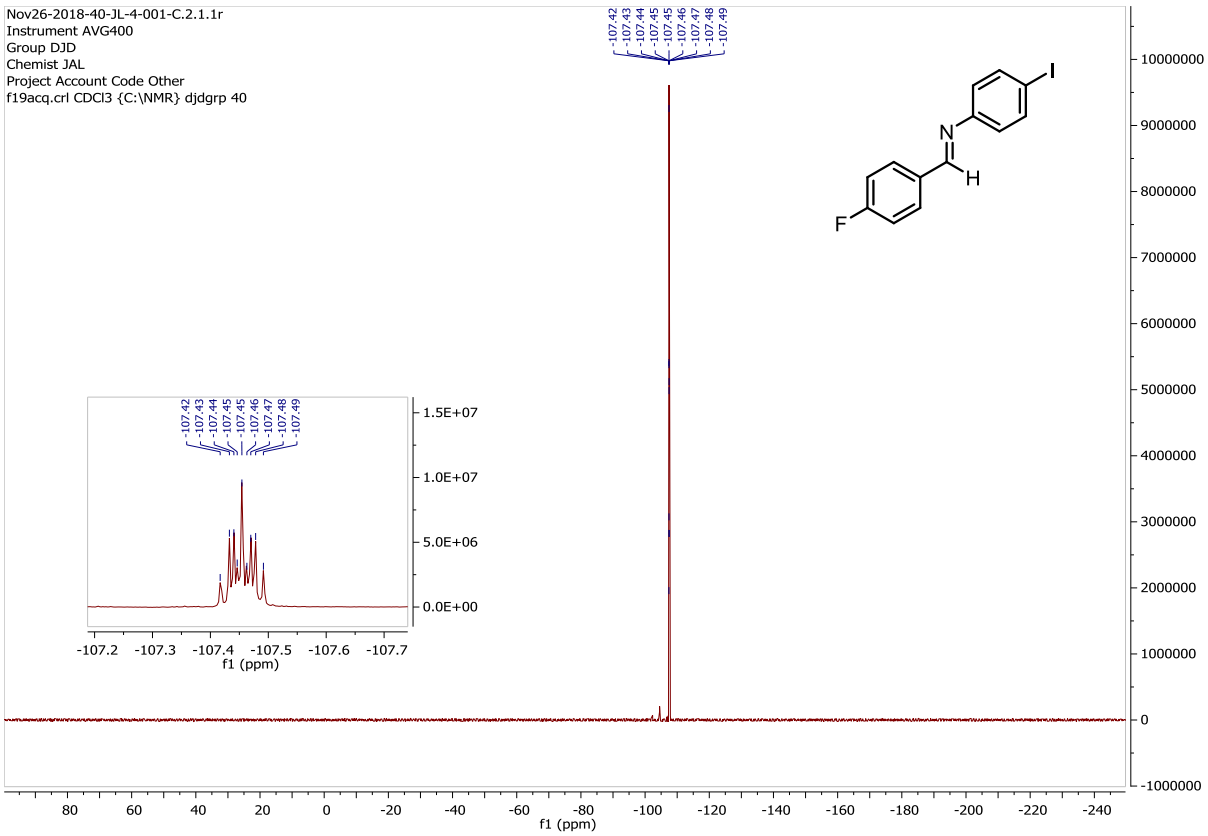
1e – ^{13}C NMR (101 MHz, $CDCl_3$)



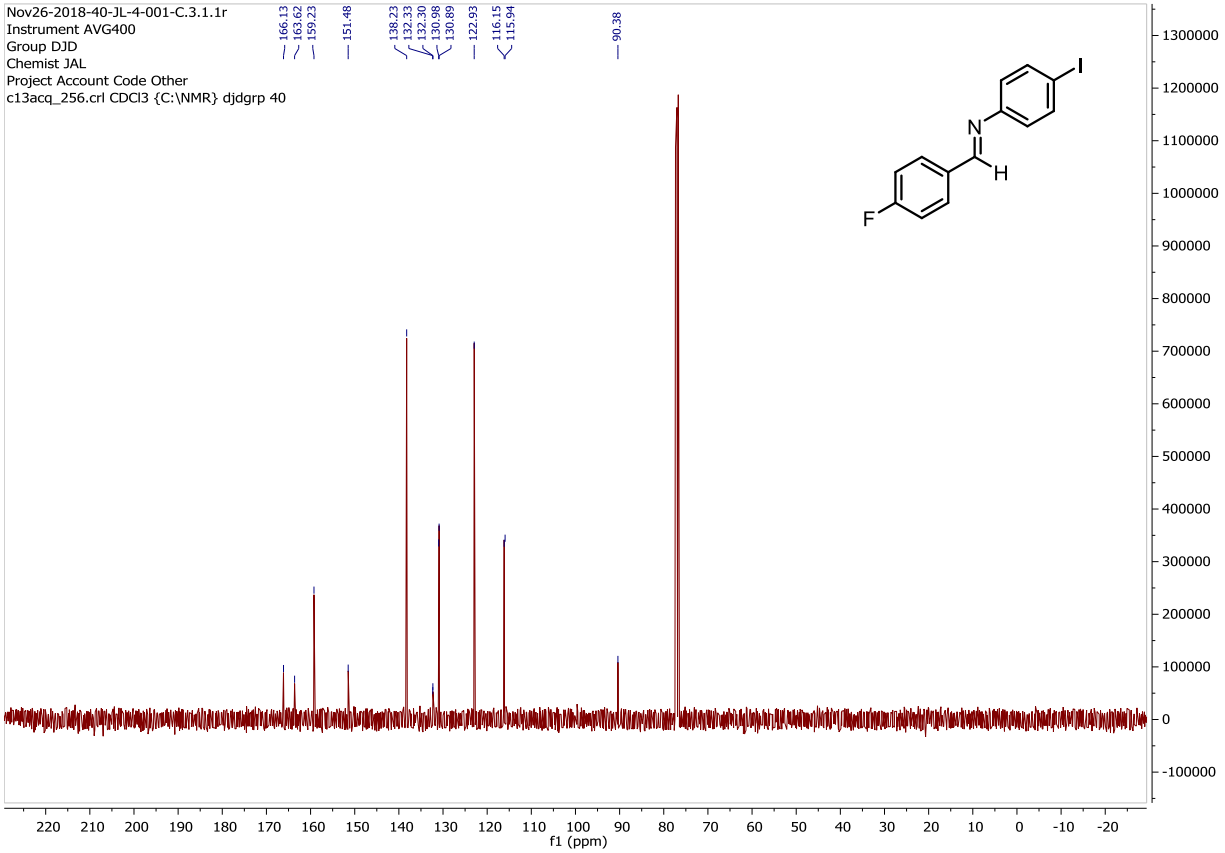
1f – ^{1}H NMR (400 MHz, $CDCl_3$)



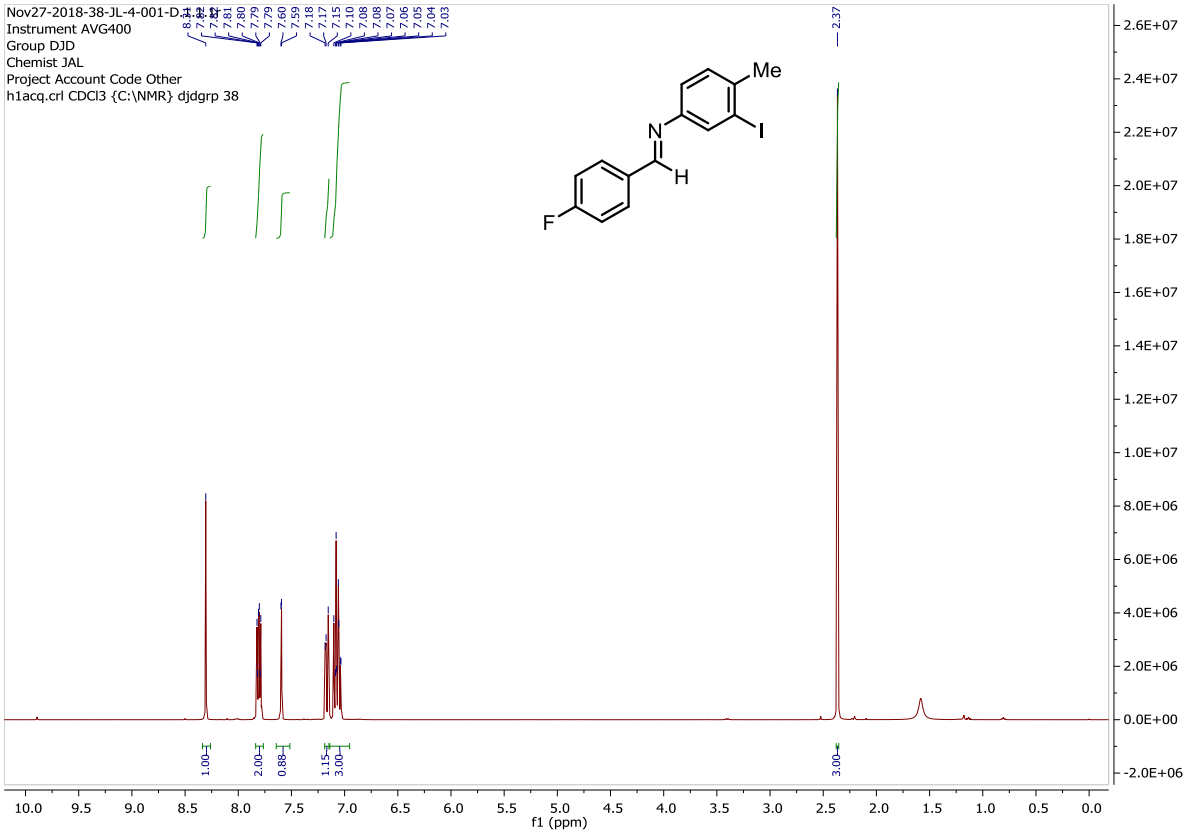
1f – ^{19}F NMR (377 MHz, $CDCl_3$)



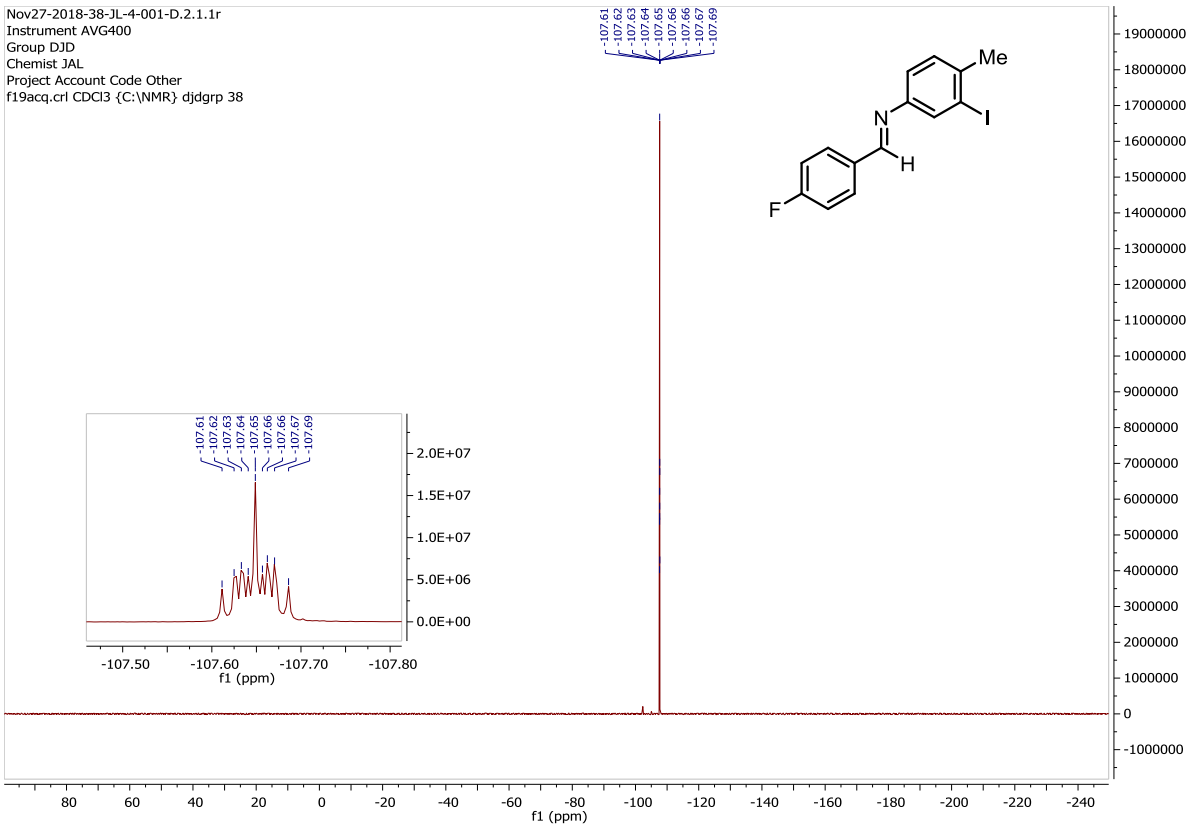
1f – ^{13}C NMR (101 MHz, $CDCl_3$)



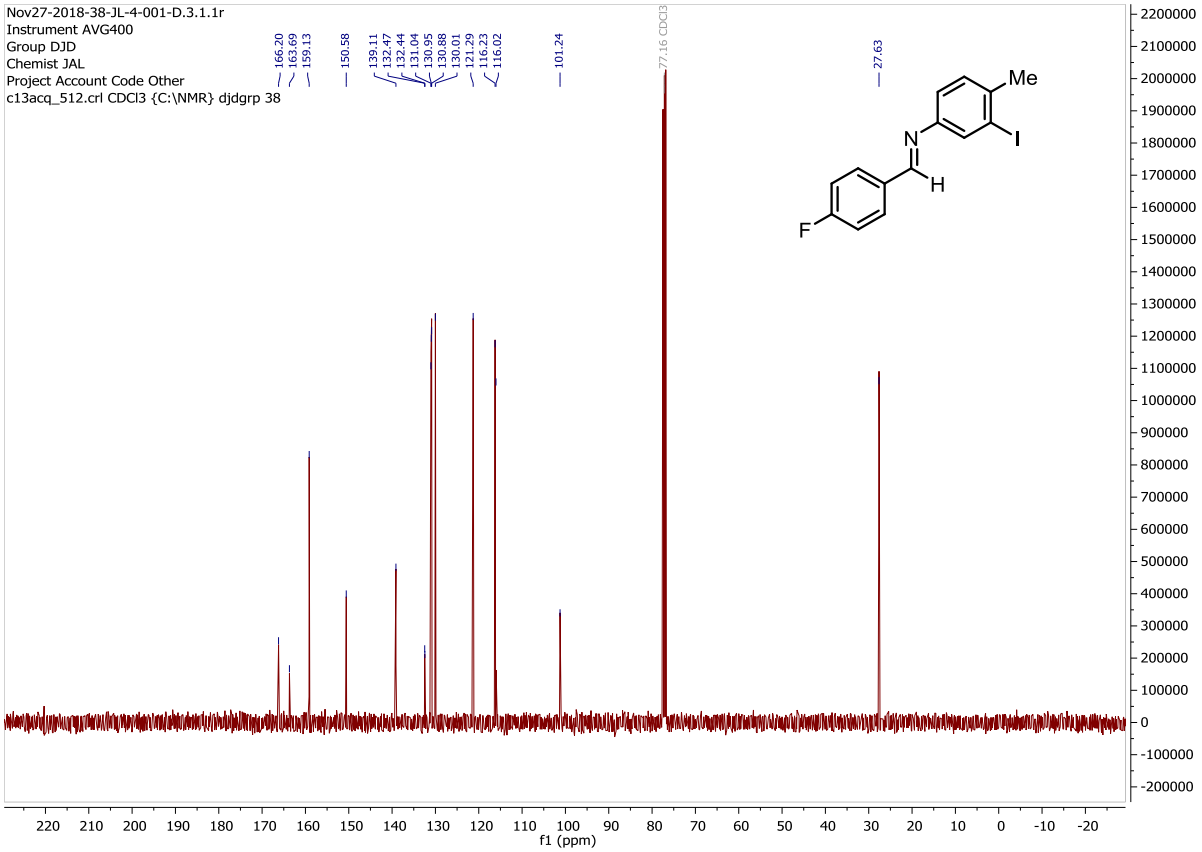
1g – ^{1}H NMR (400 MHz, $CDCl_3$)



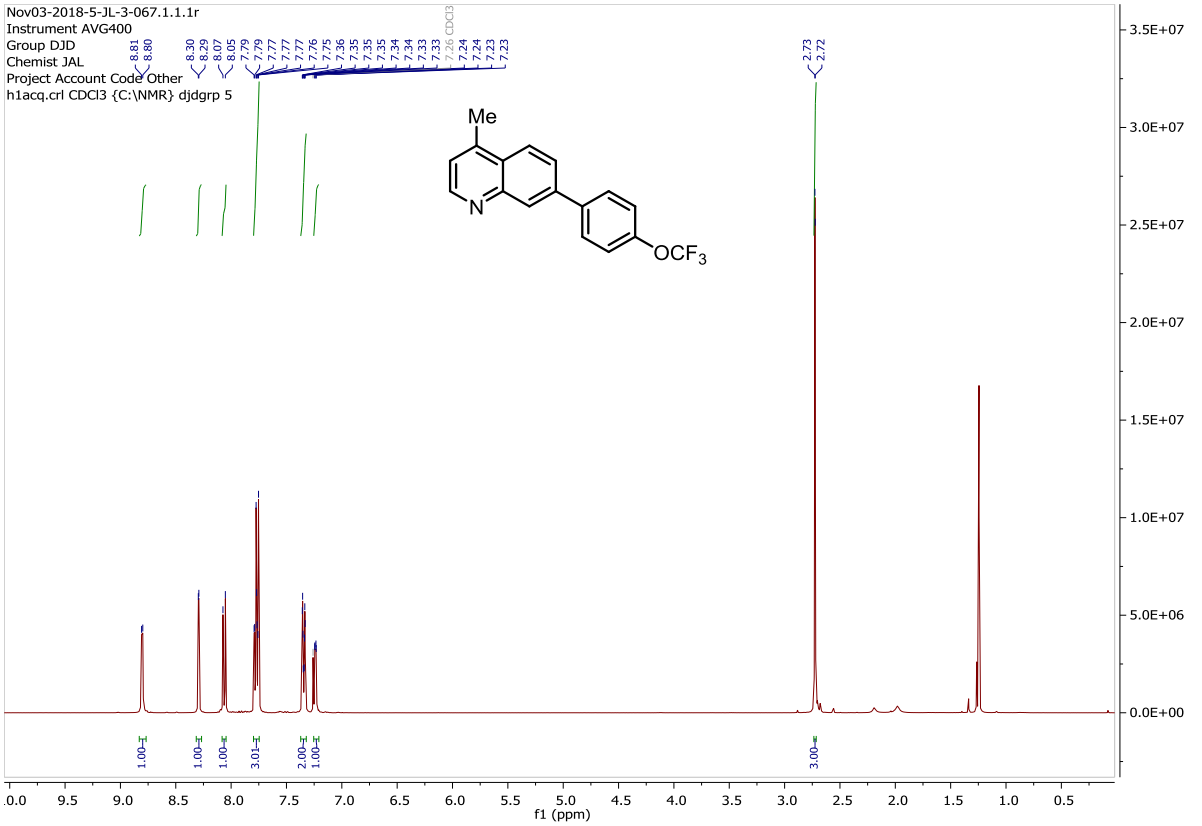
1g – ^{19}F NMR (377 MHz, $CDCl_3$)



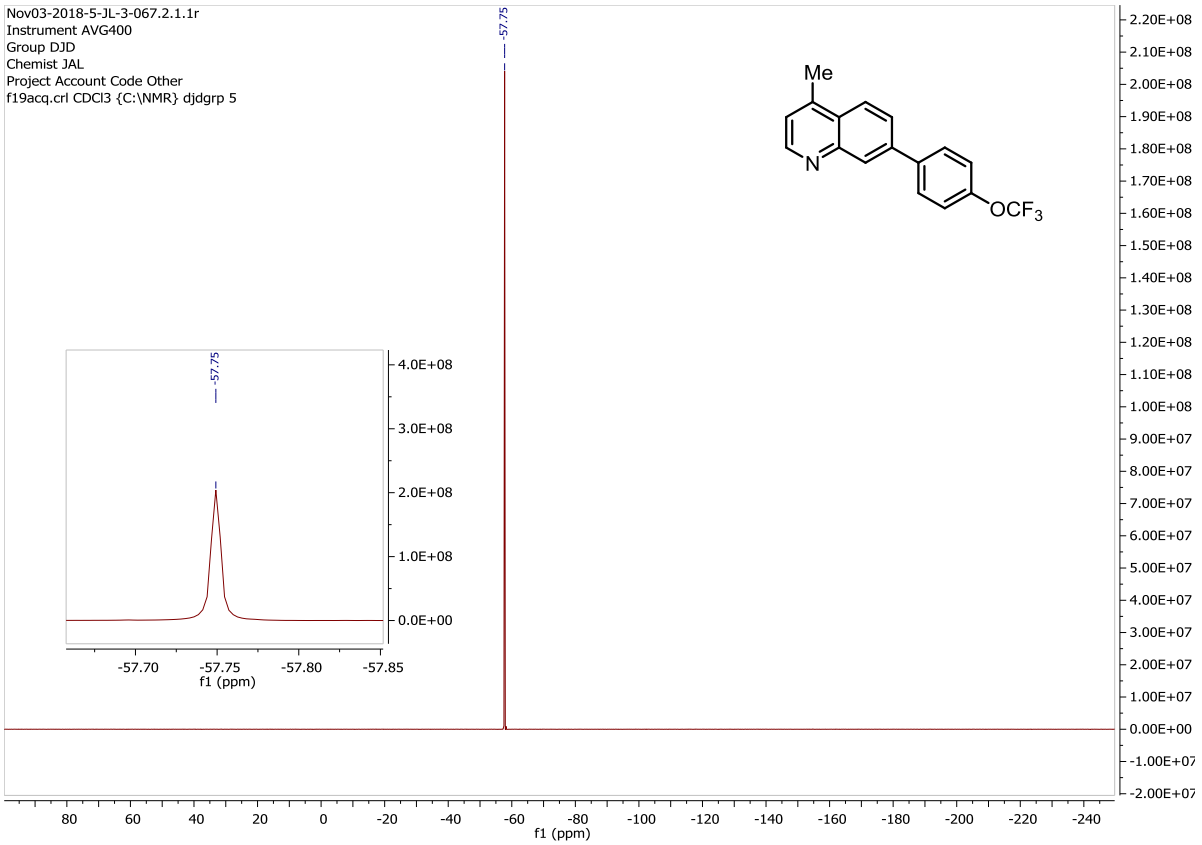
1g – ^{13}C NMR (101 MHz, $CDCl_3$)



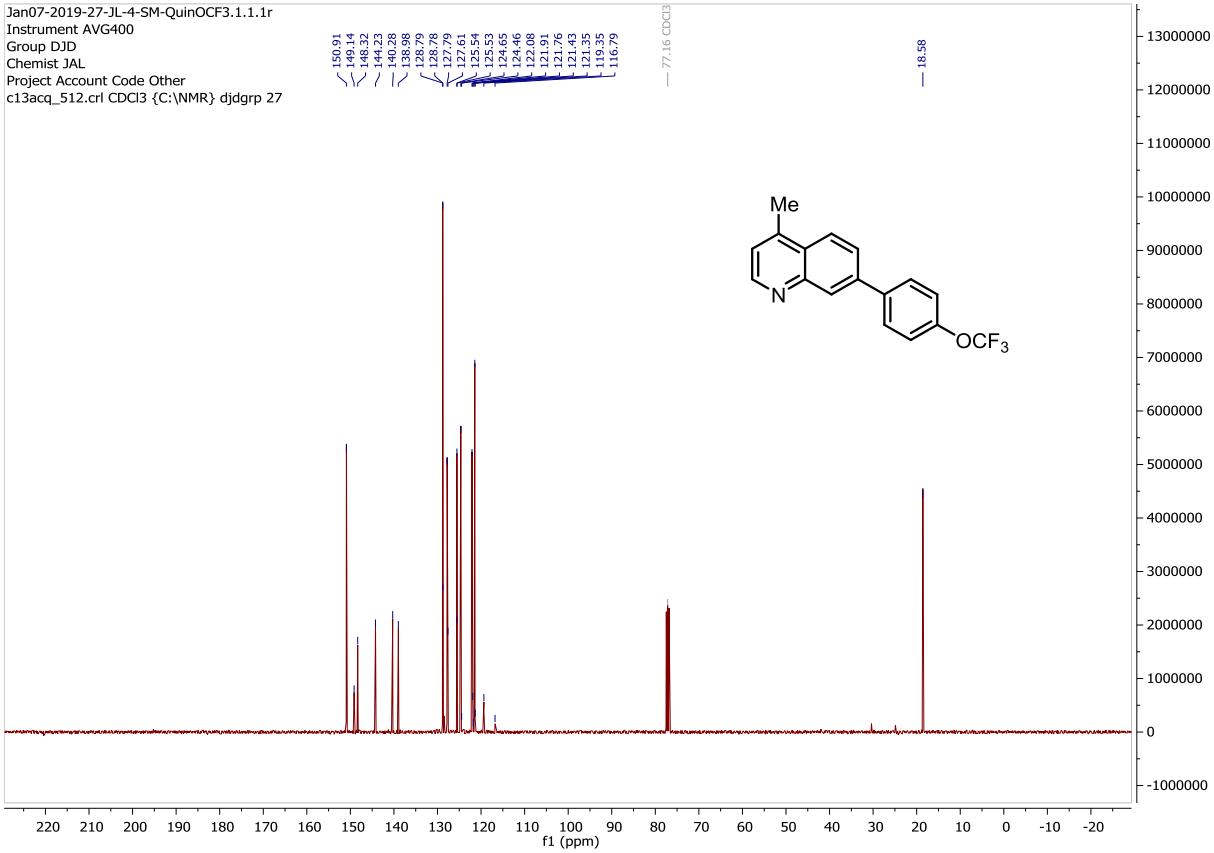
2h – ^{1}H NMR (400 MHz, $CDCl_3$)



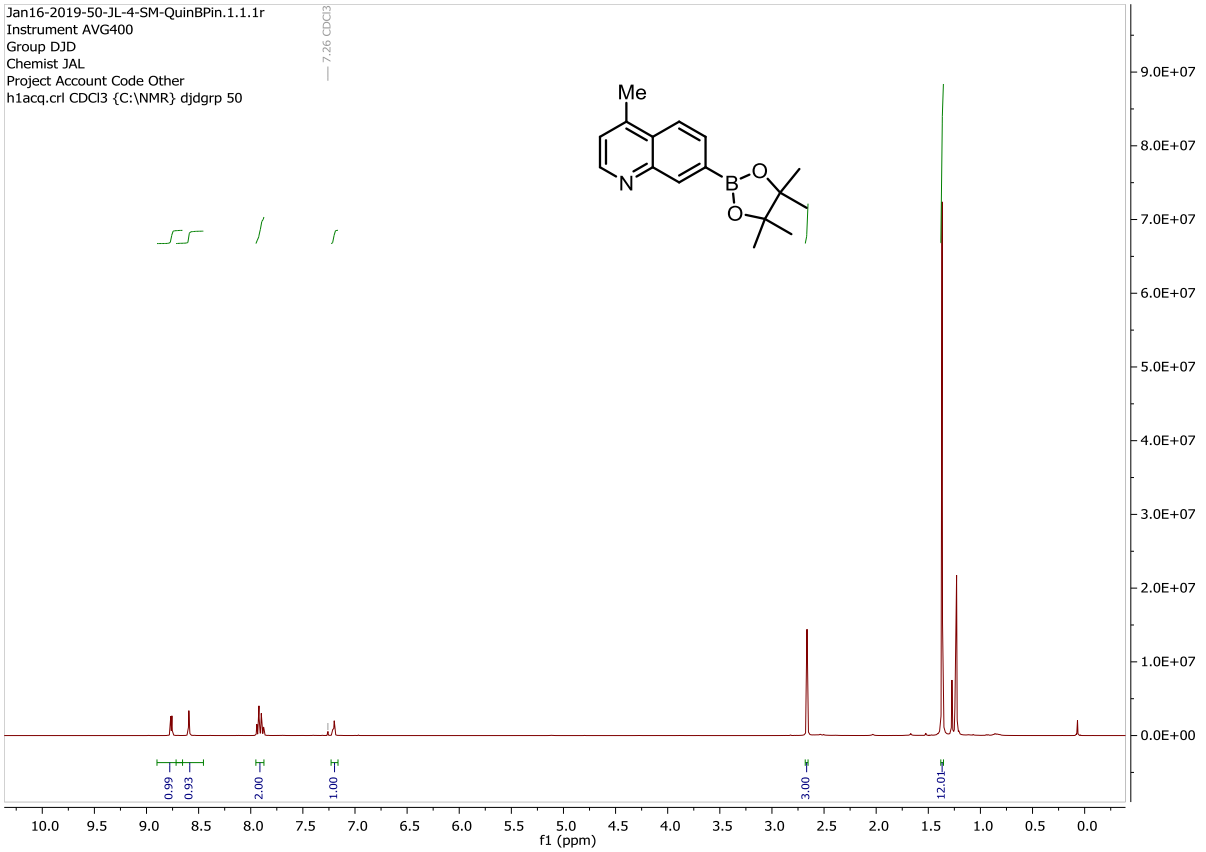
2h – ^{19}F NMR (377 MHz, $CDCl_3$)



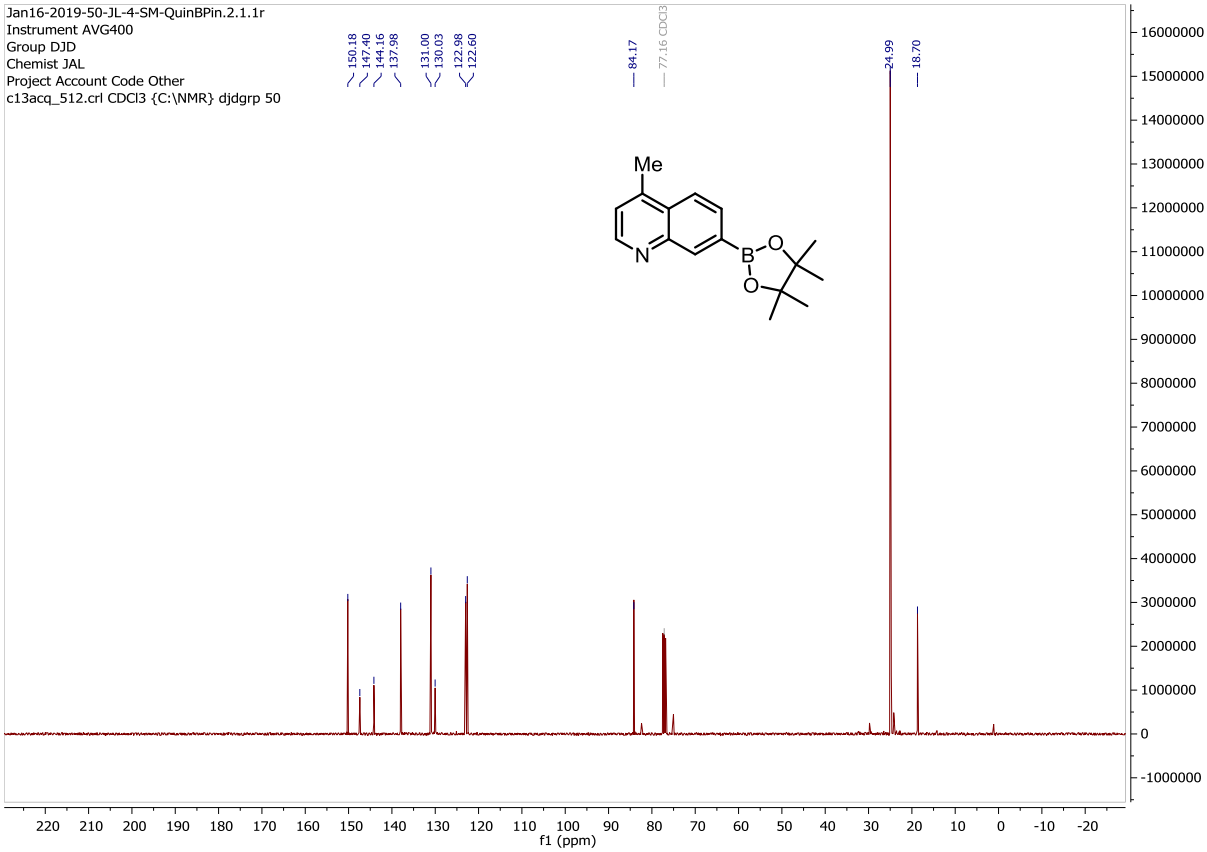
2h – ^{13}C NMR (101 MHz, $CDCl_3$)



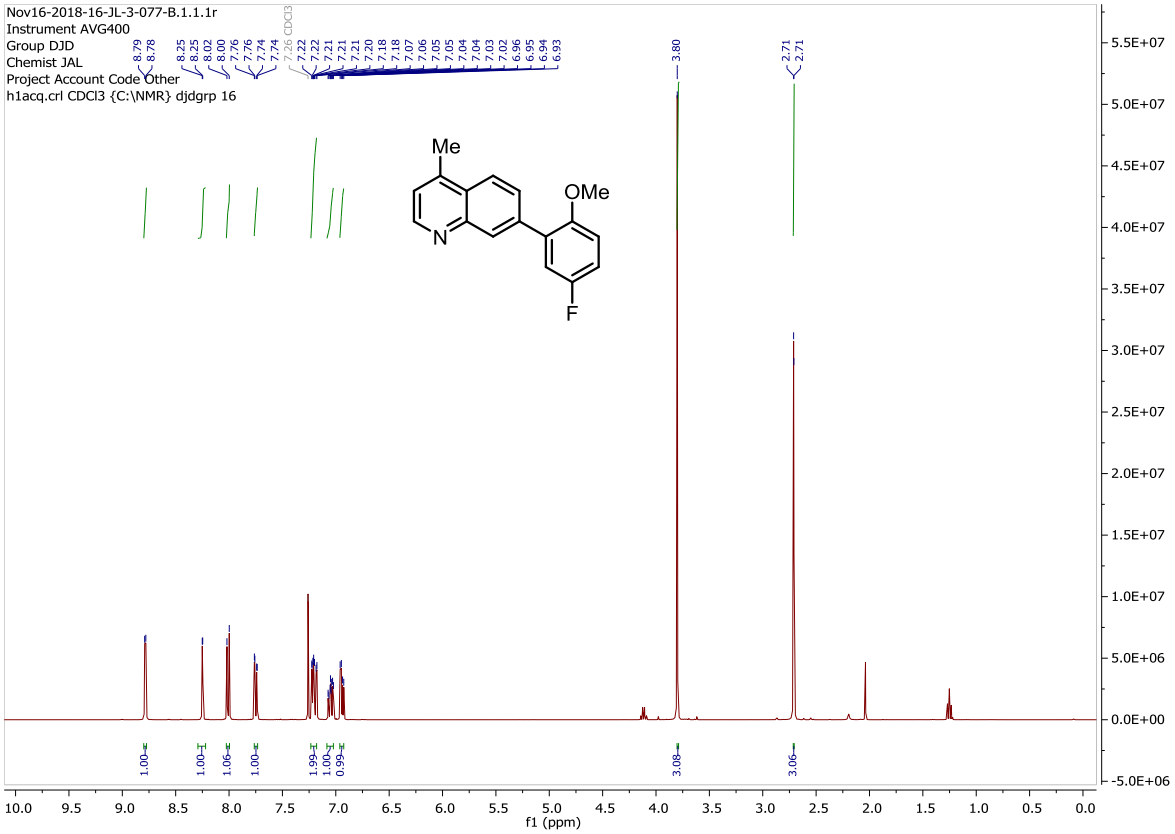
2i – ^{1}H NMR (400 MHz, $CDCl_3$)



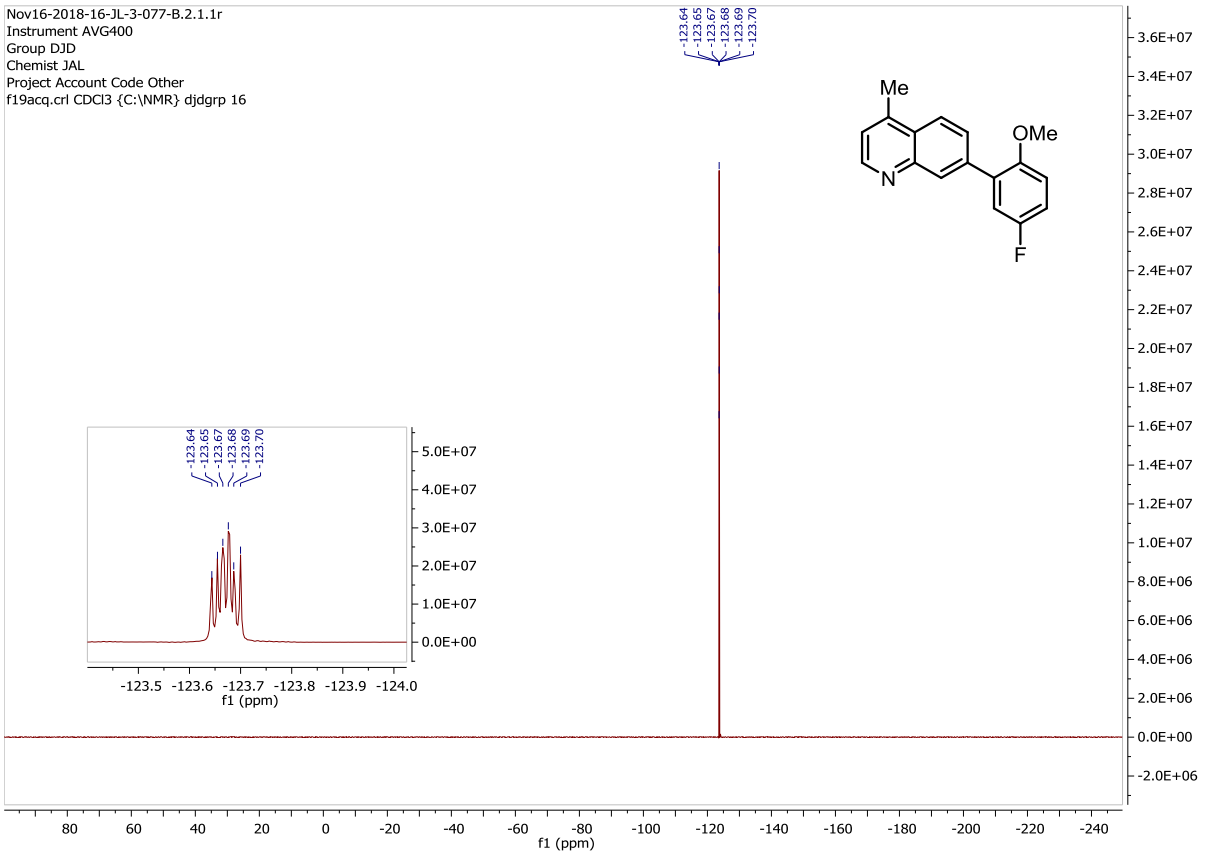
2i – ^{13}C NMR (101 MHz, $CDCl_3$)



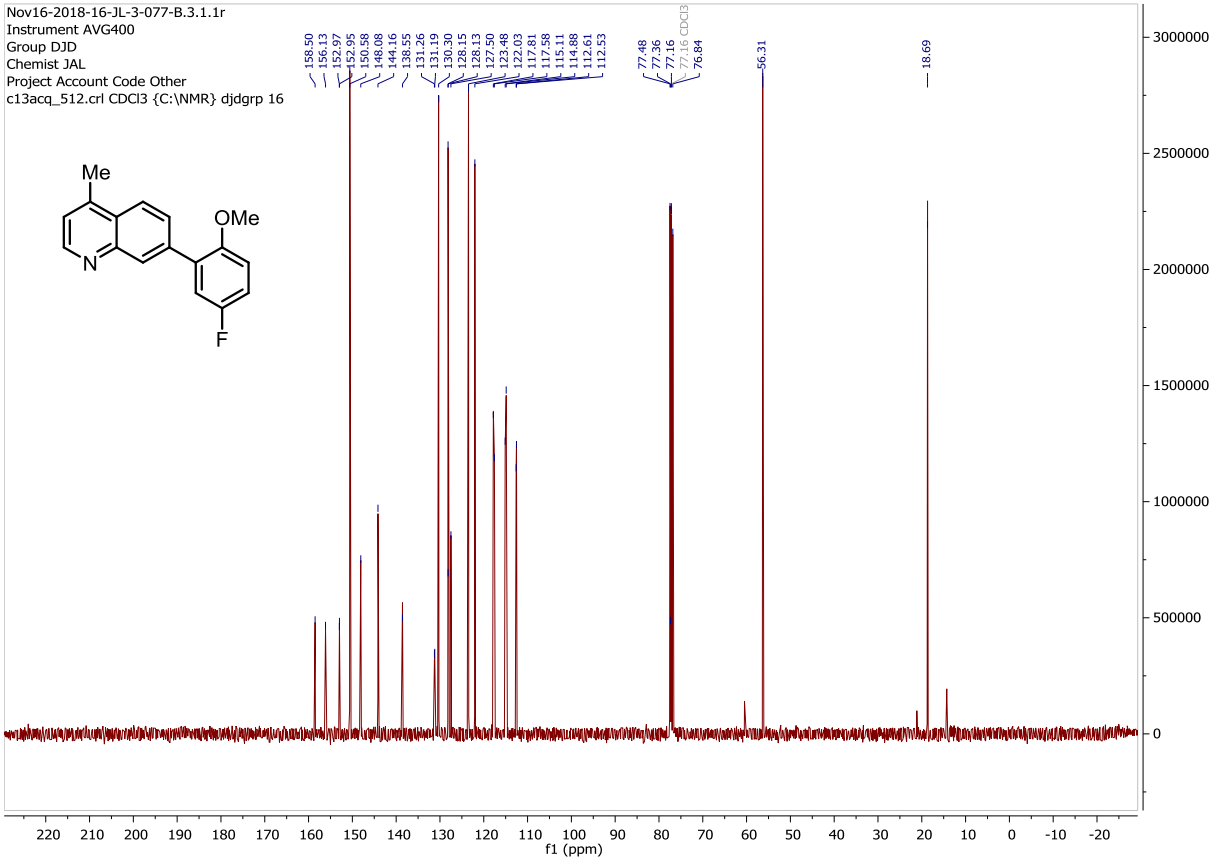
2j – ^{1}H NMR (400 MHz, $CDCl_3$)



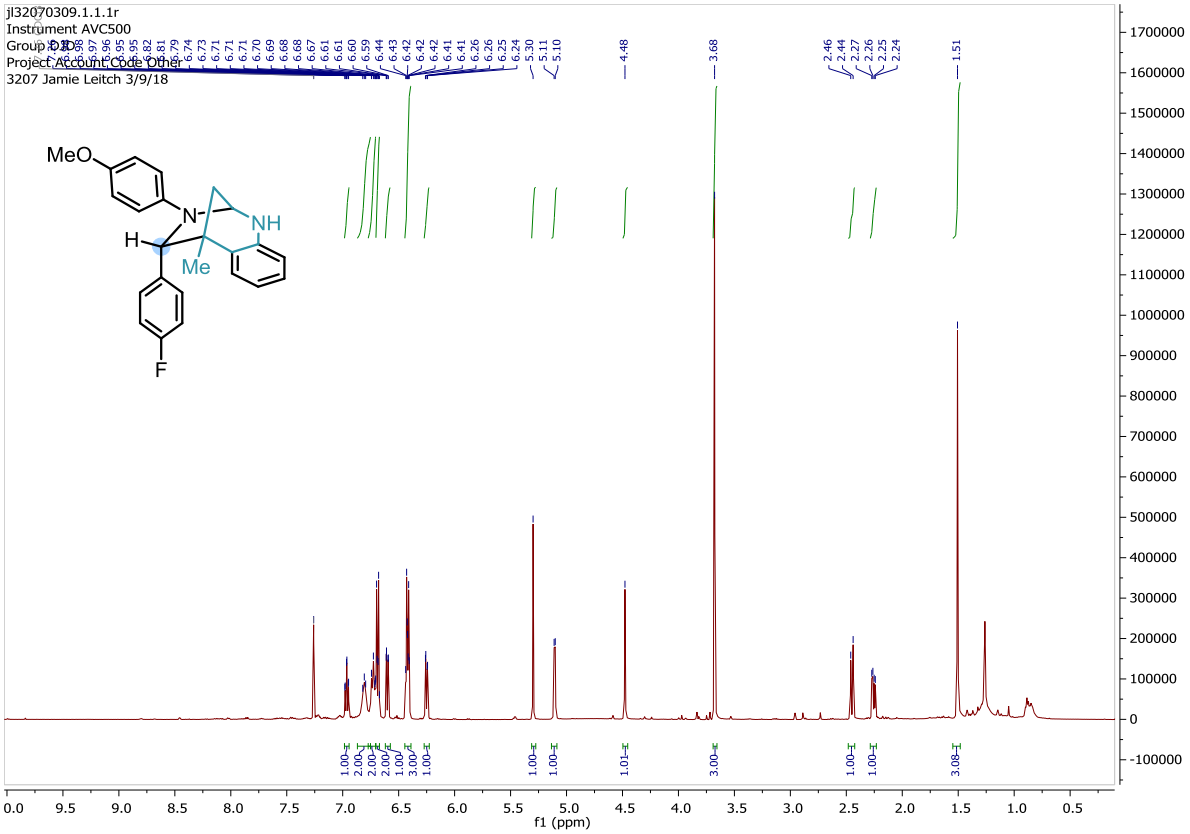
2j – ^{19}F NMR (377 MHz, $CDCl_3$)



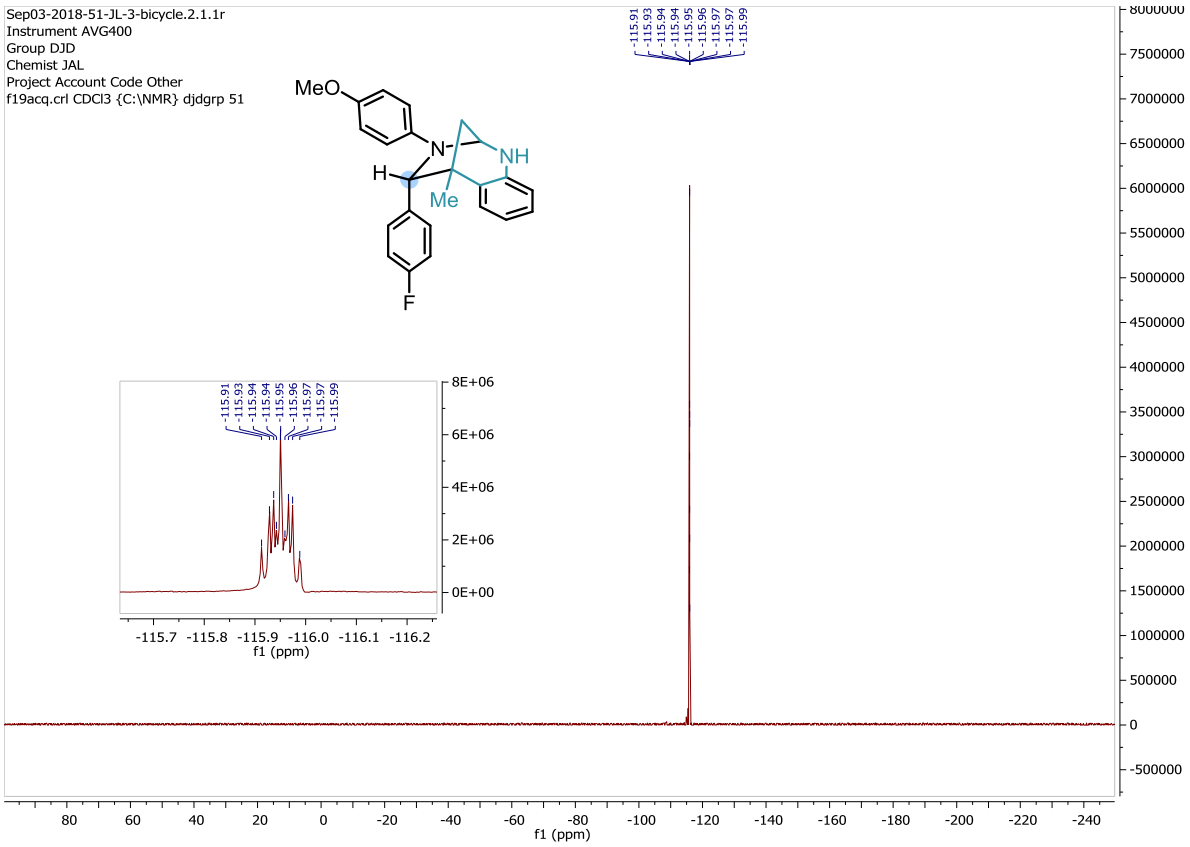
2j – ^{13}C NMR (101 MHz, $CDCl_3$)



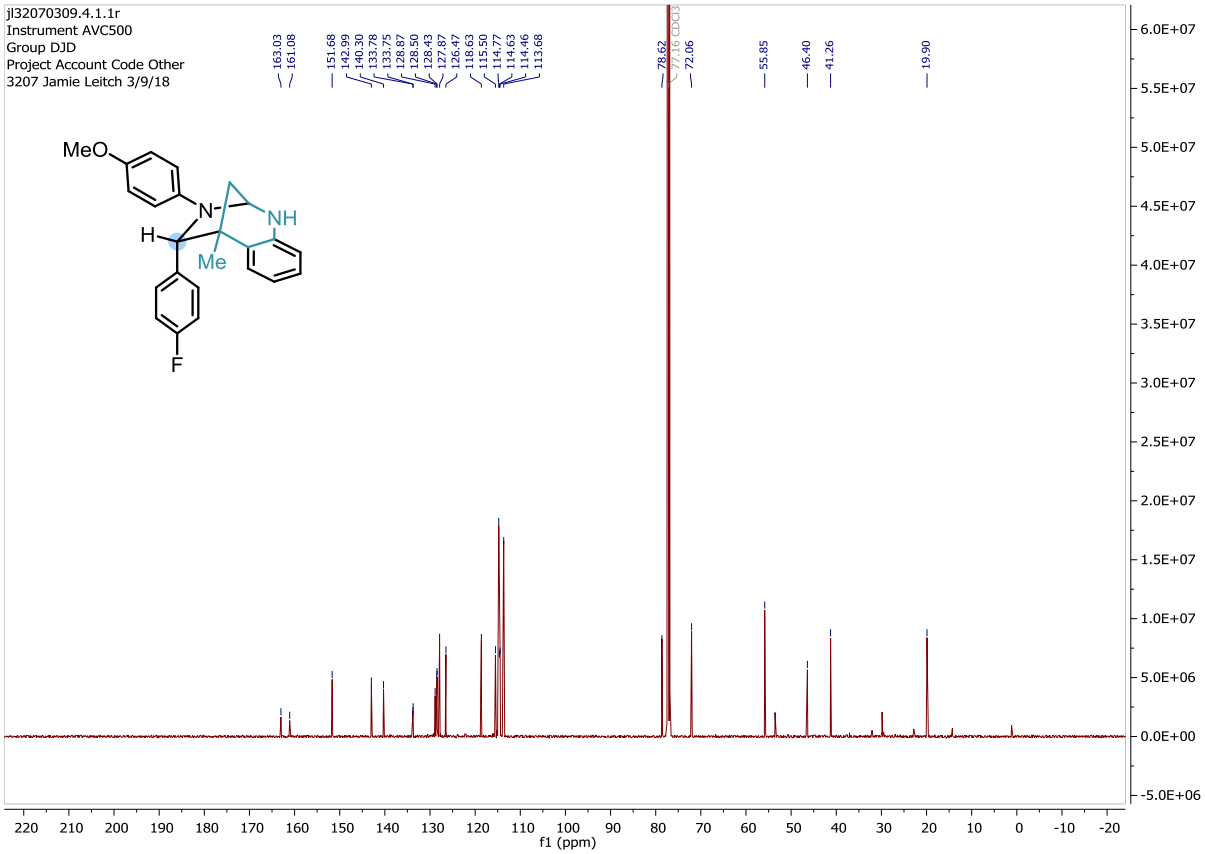
3aa$_{(endo)}$ – ^{1}H NMR (500 MHz, $CDCl_3$)



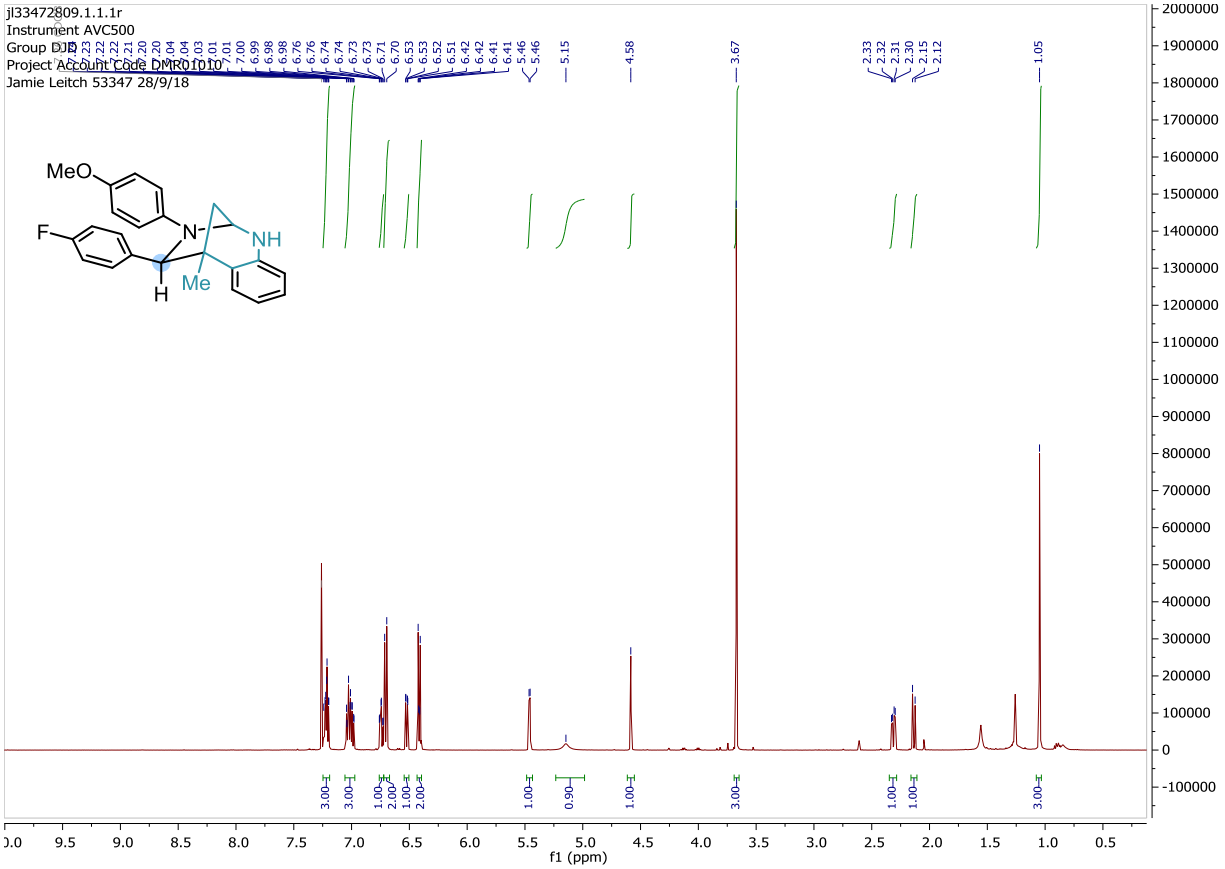
3aa$_{(exo)}$ – ^{19}F NMR (377 MHz, $CDCl_3$)



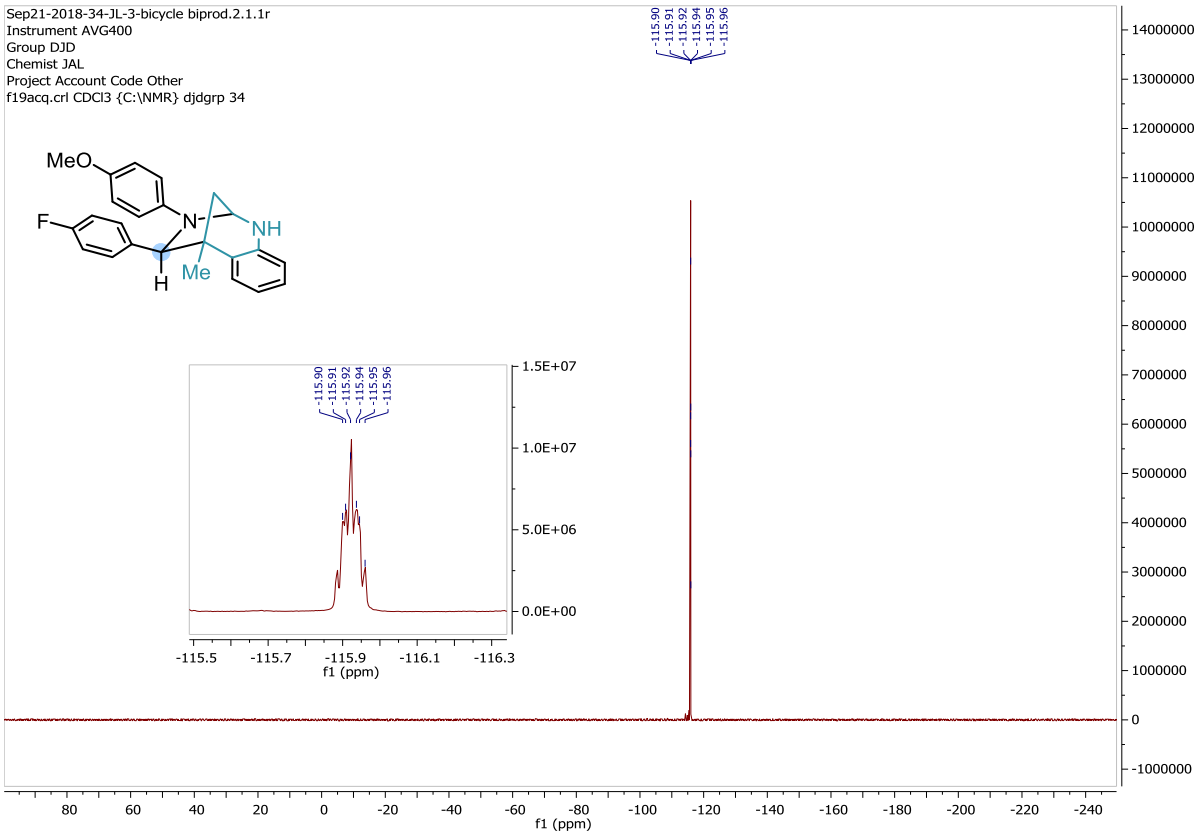
3aa$_{(endo)}$ – ^{13}C NMR (126 MHz, $CDCl_3$)



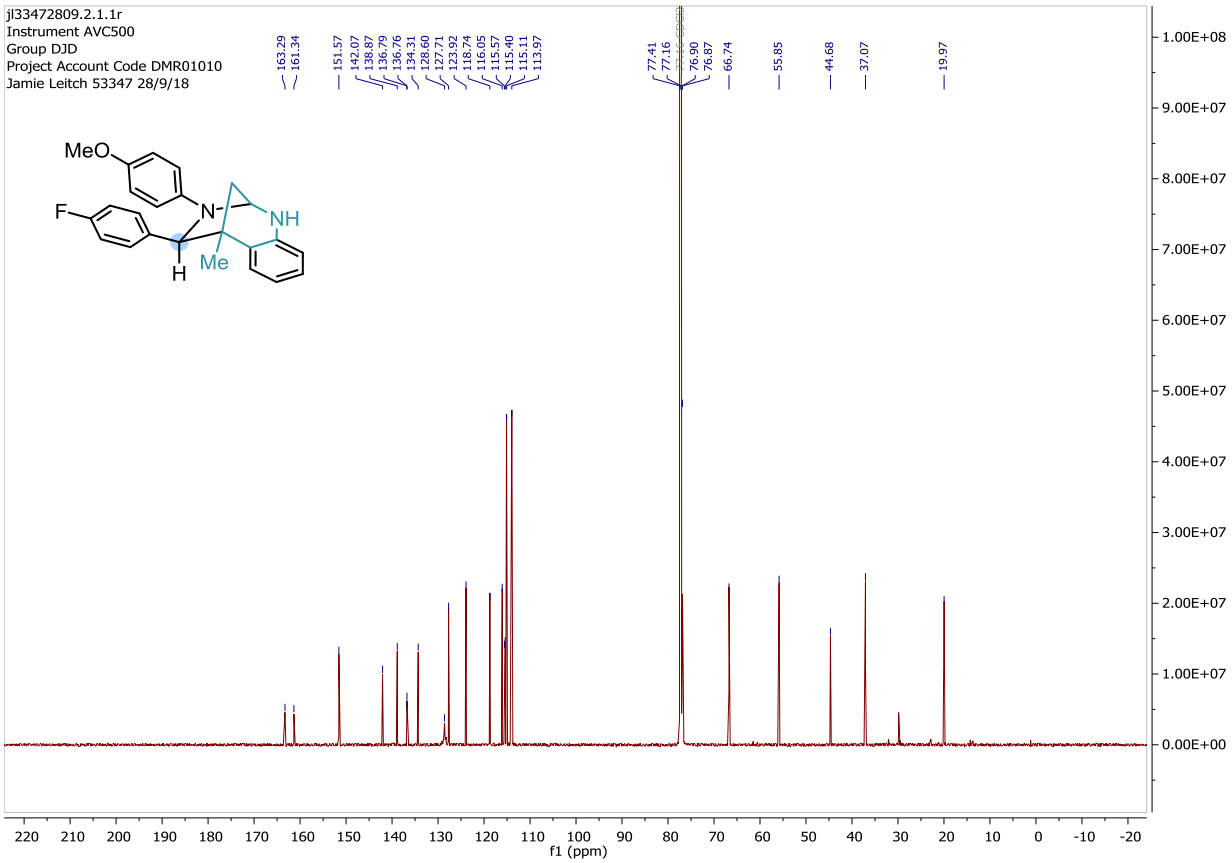
3aa$_{(exo)}$ – ^{1}H NMR (500 MHz, $CDCl_3$)



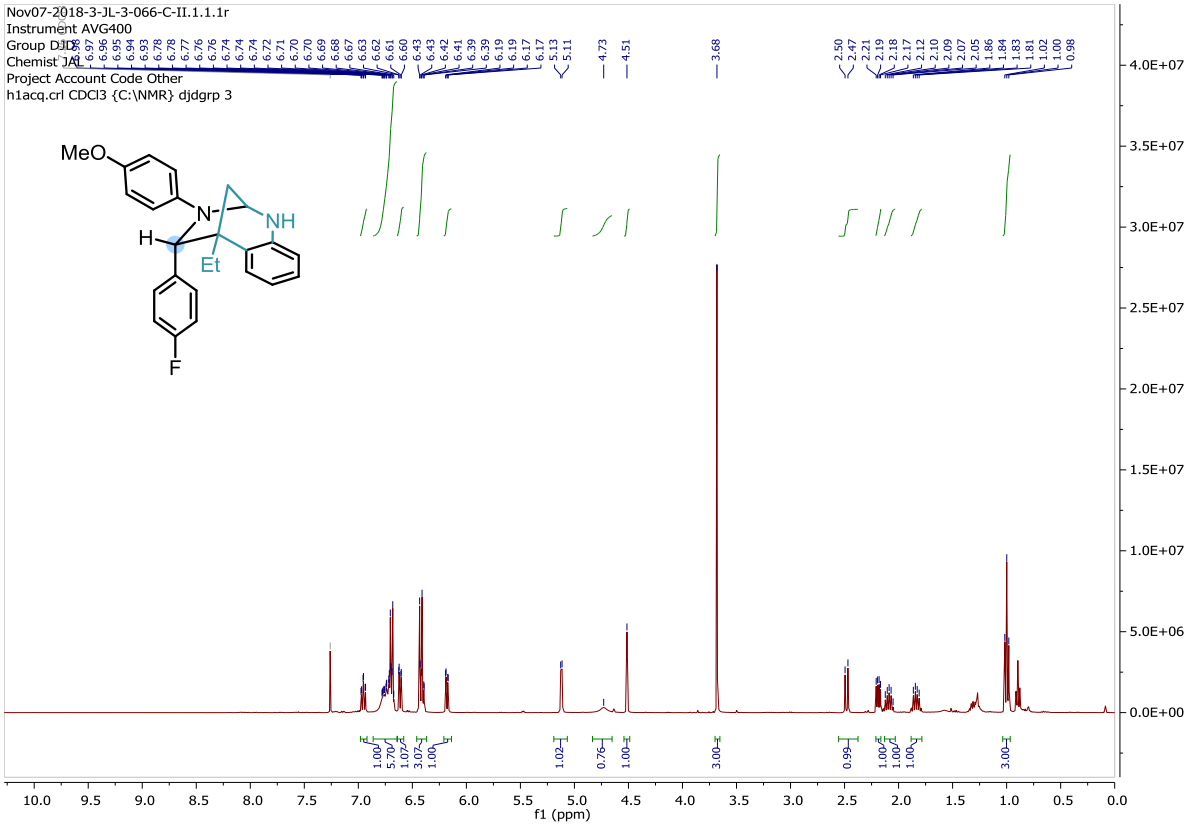
3aa$_{(exo)}$ – ^{19}F NMR (377 MHz, $CDCl_3$)



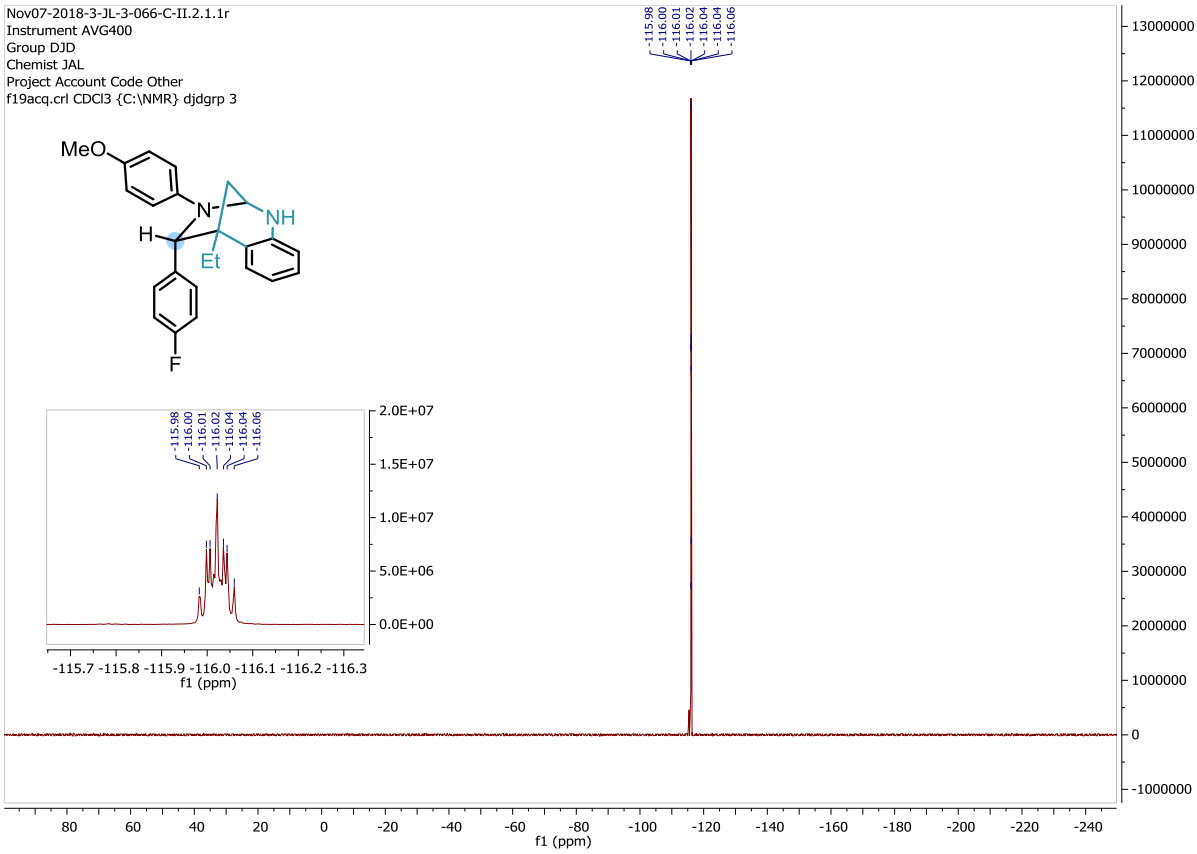
3aa$_{(exo)}$ – ^{13}C NMR (126 MHz, $CDCl_3$)



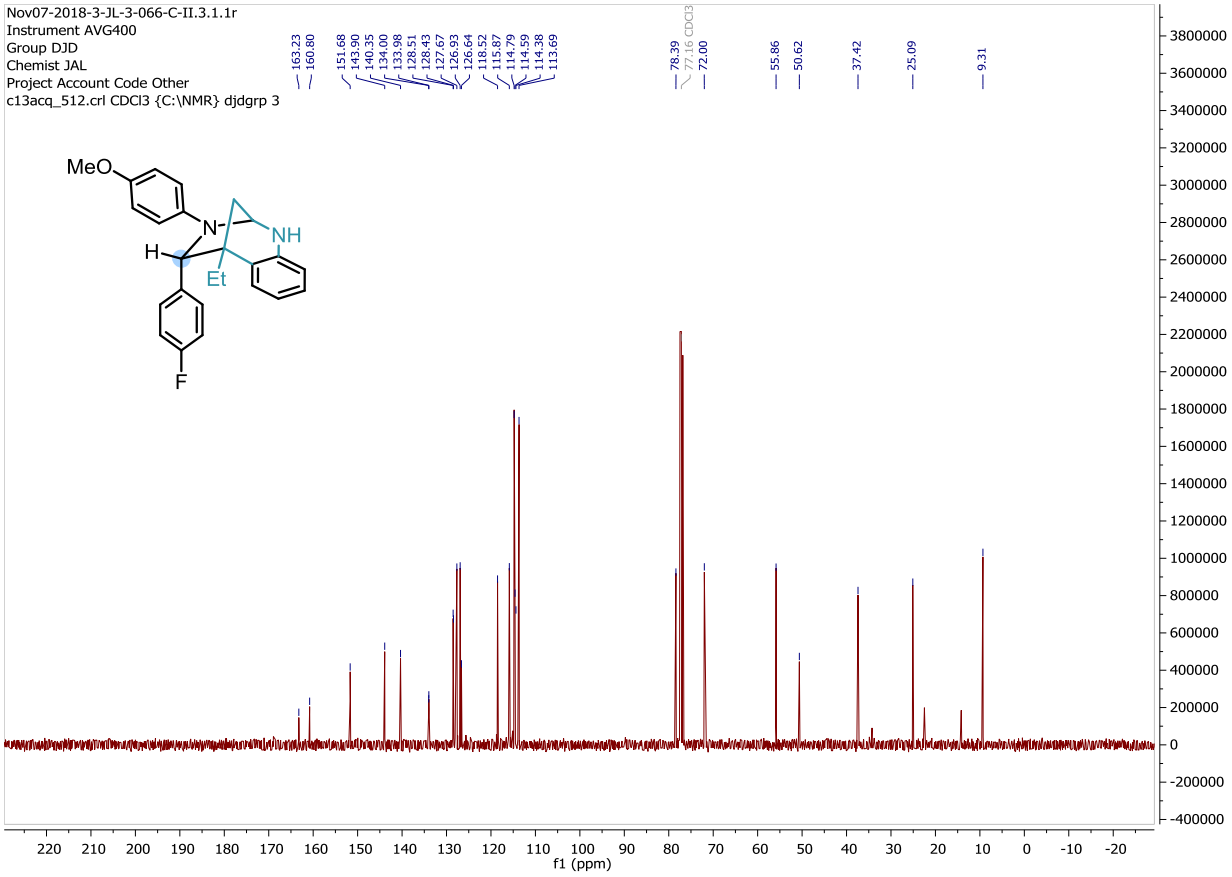
3ab$_{(endo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



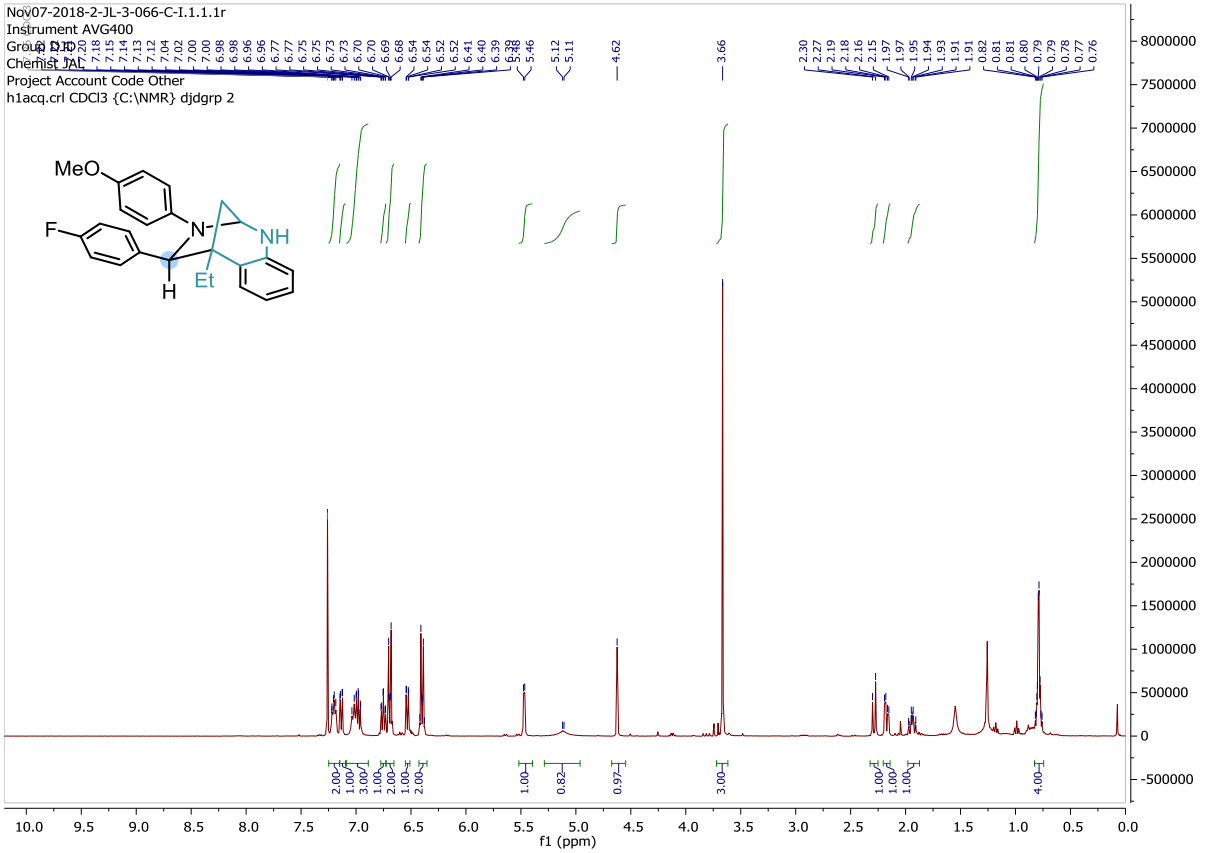
3ab$_{(endo)}$ – ^{19}F NMR (377 MHz, $CDCl_3$)



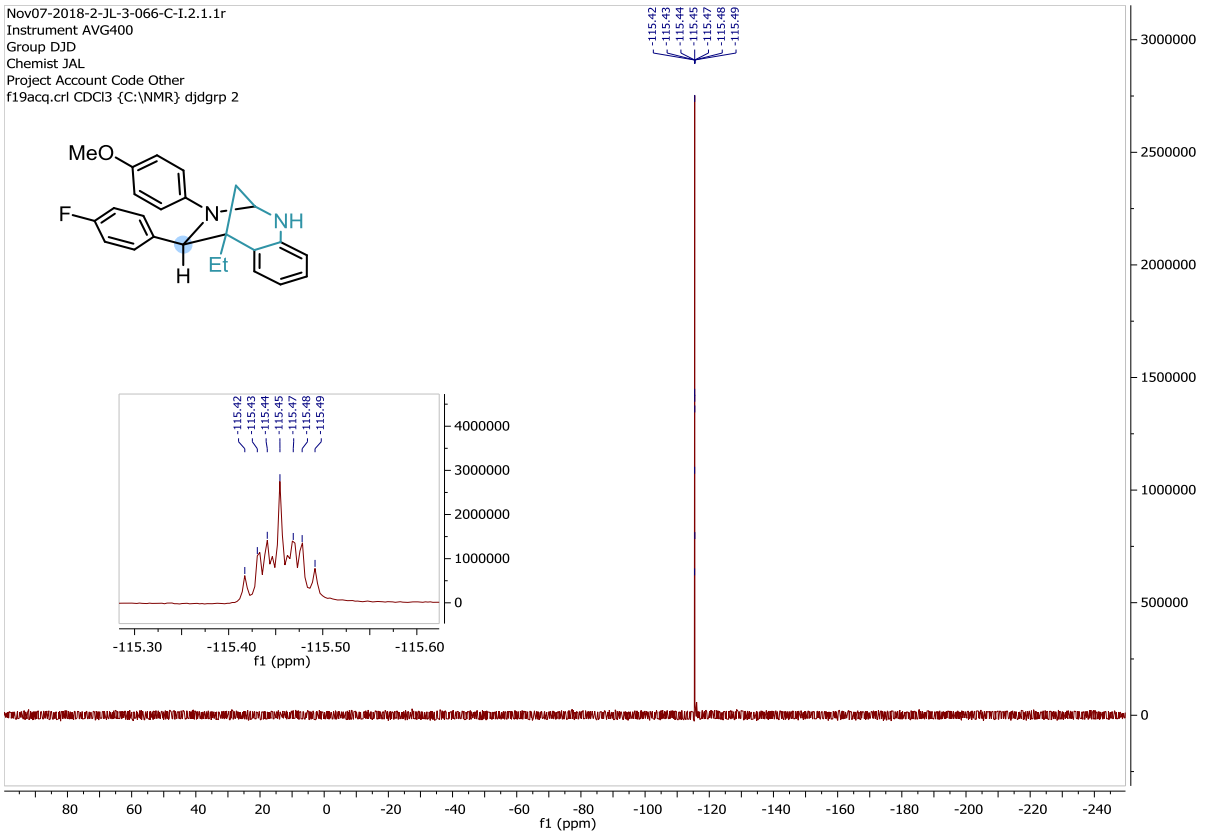
3ab$_{(endo)}$ – ^{13}C NMR (101 MHz, $CDCl_3$)



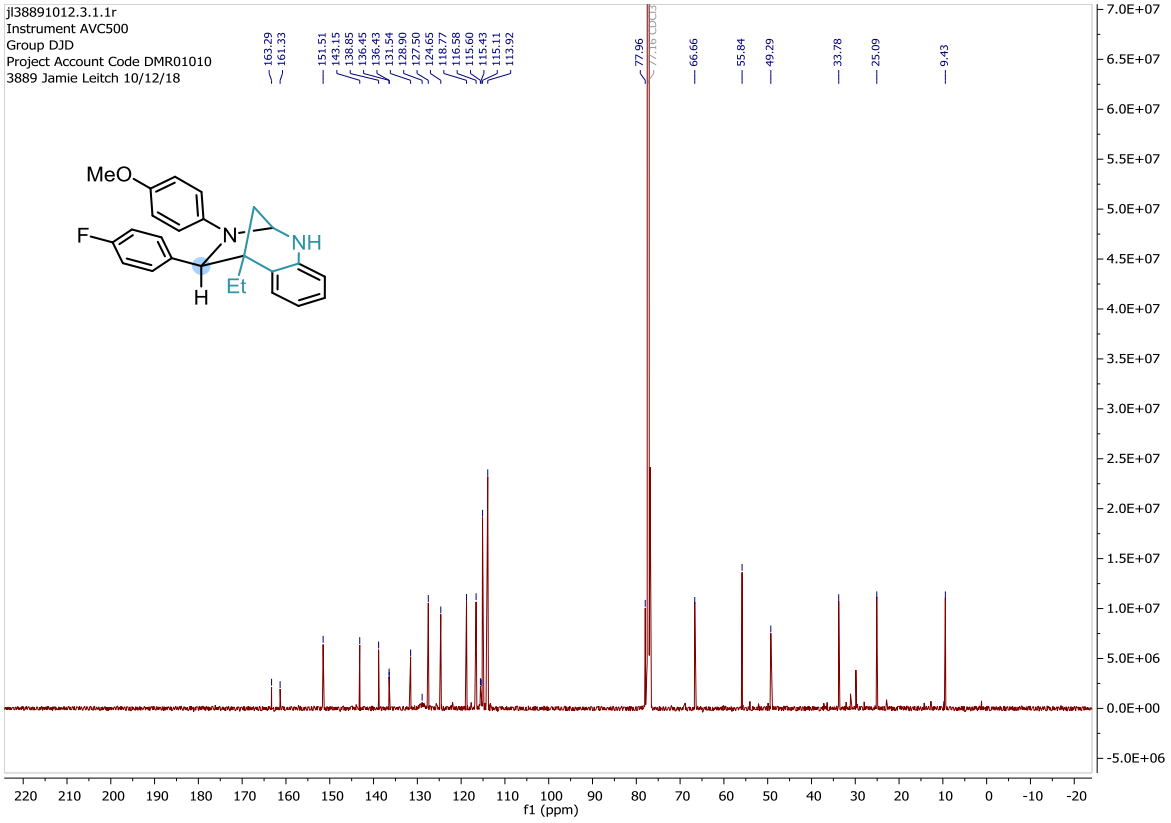
3ab$_{(exo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



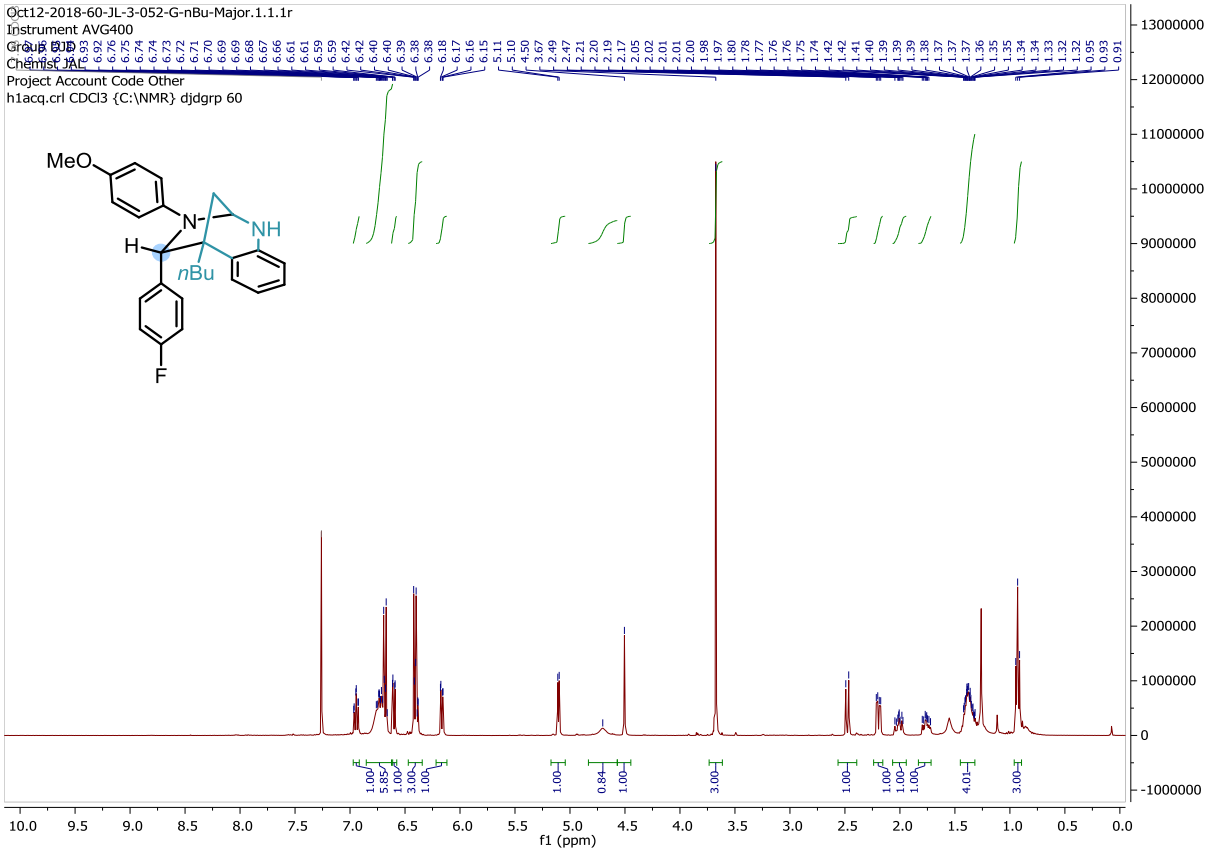
3ab$_{(exo)}$ – ^{19}F NMR (377 MHz, $CDCl_3$)



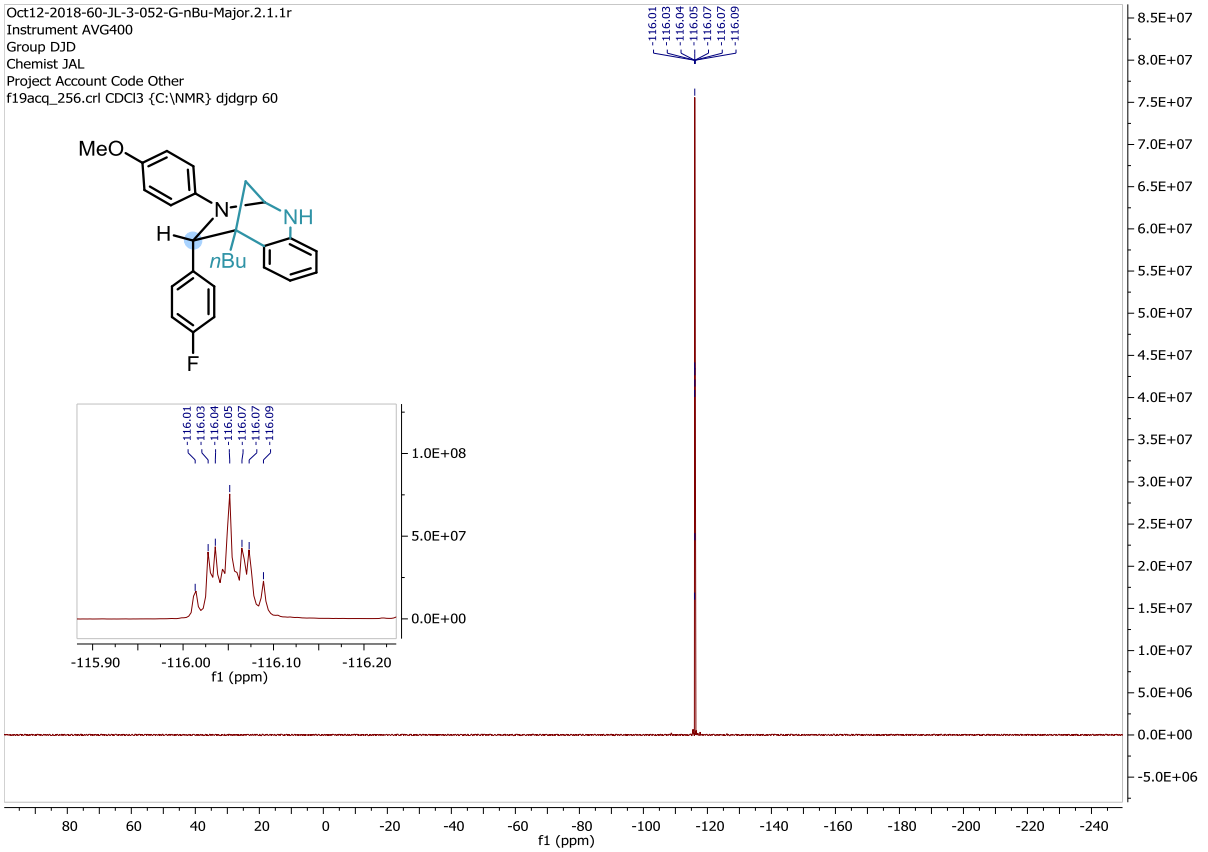
3ab$_{(exo)}$ – ^{13}C NMR (126 MHz, $CDCl_3$)



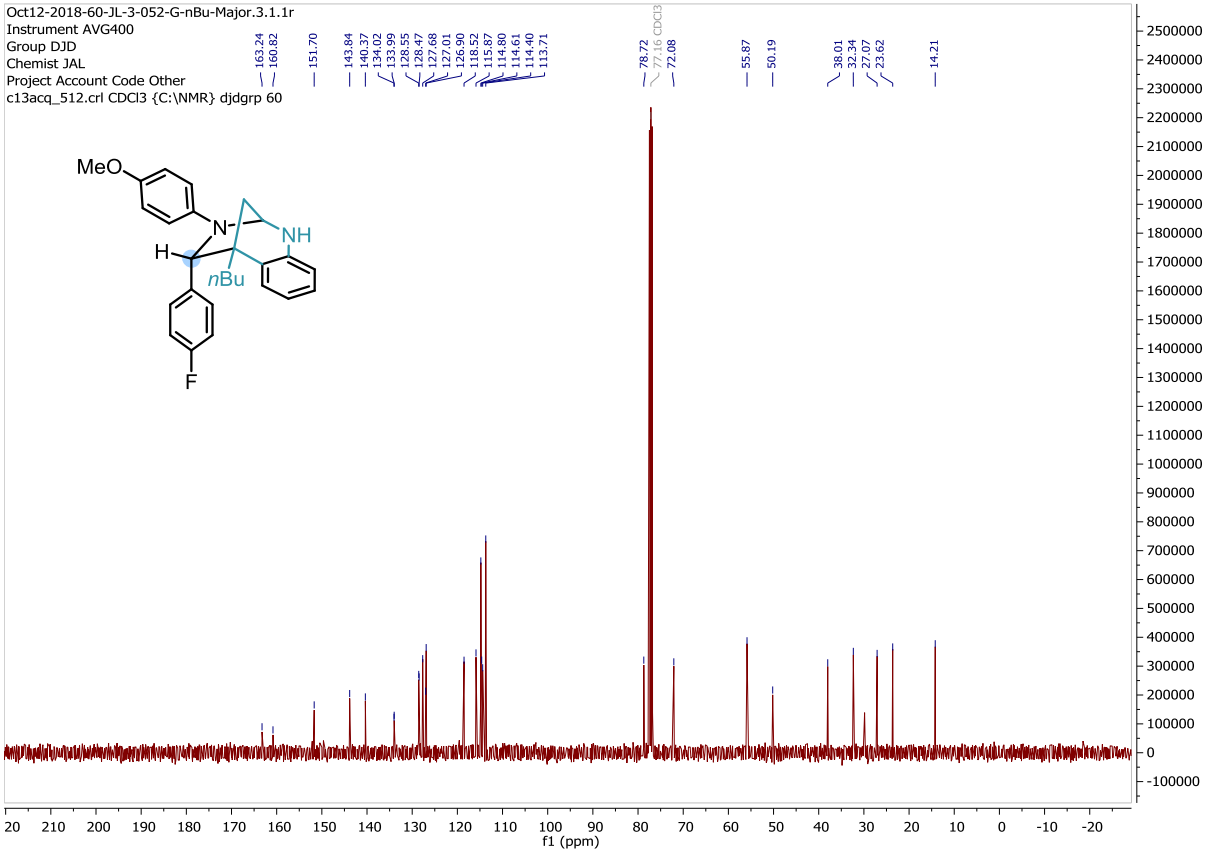
3ac$_{(endo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



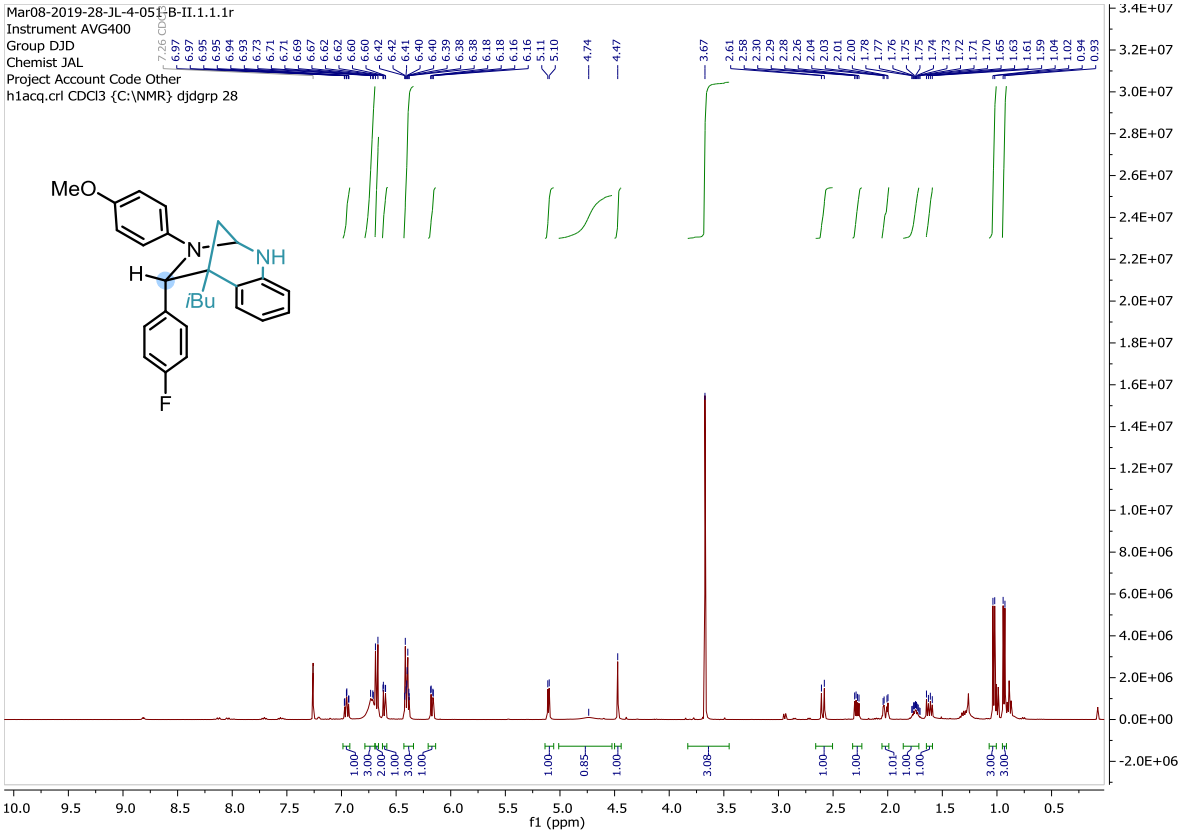
3ac$_{(endo)}$ – ^{19}F NMR (377 MHz, $CDCl_3$)



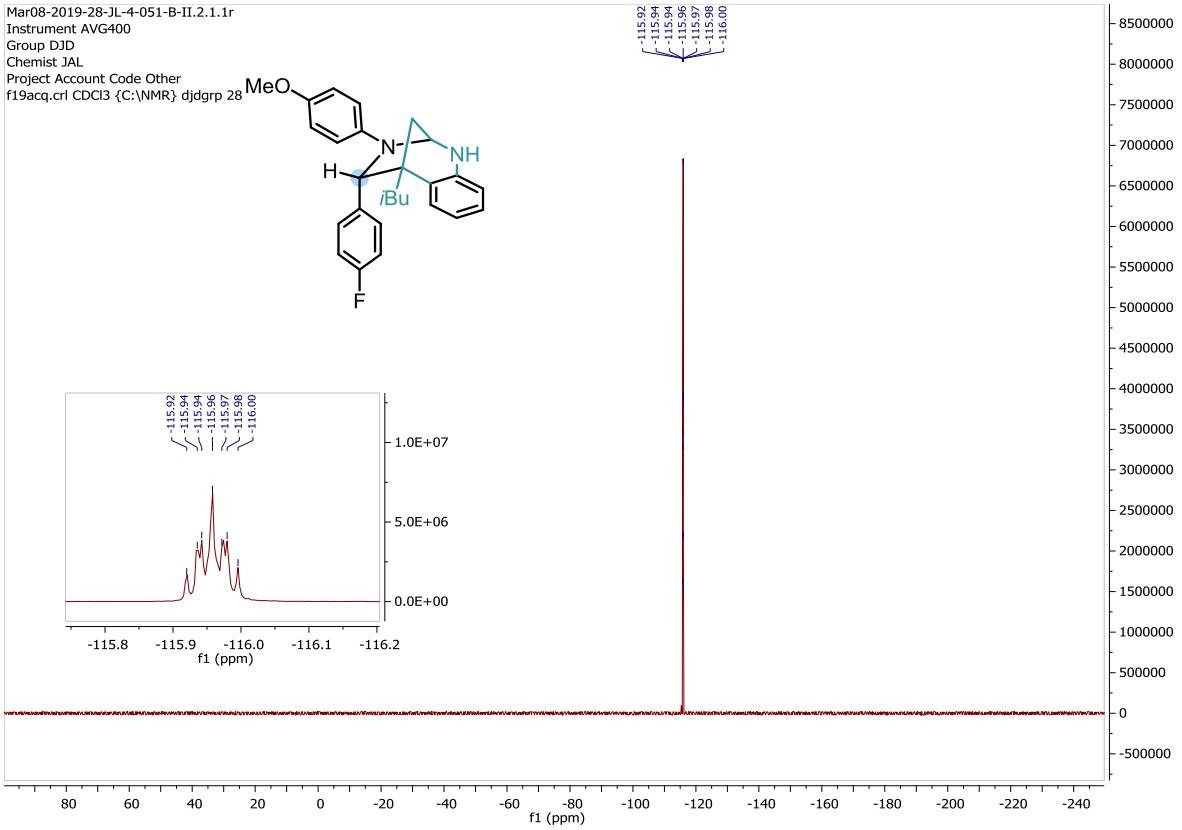
3ac$_{(endo)}$ – ^{13}C NMR (101 MHz, $CDCl_3$)



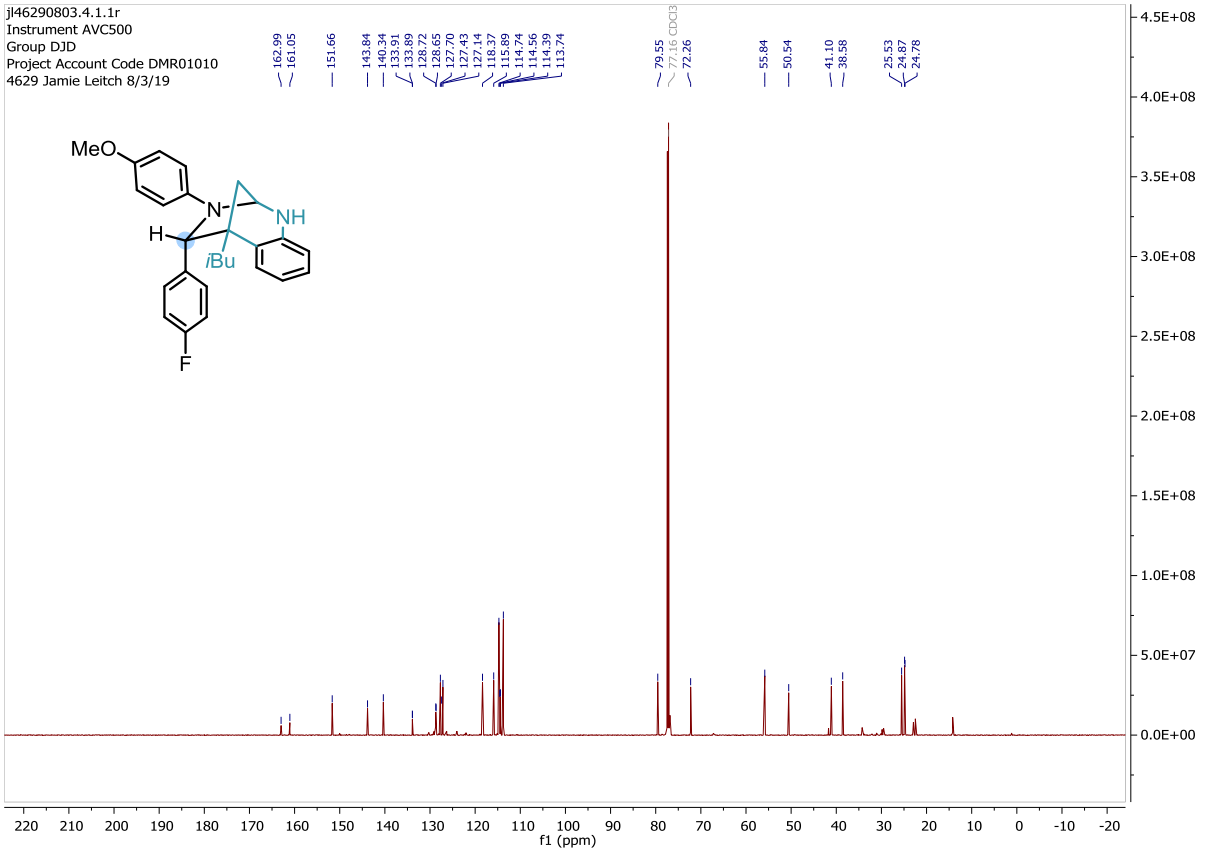
3ad$_{(endo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



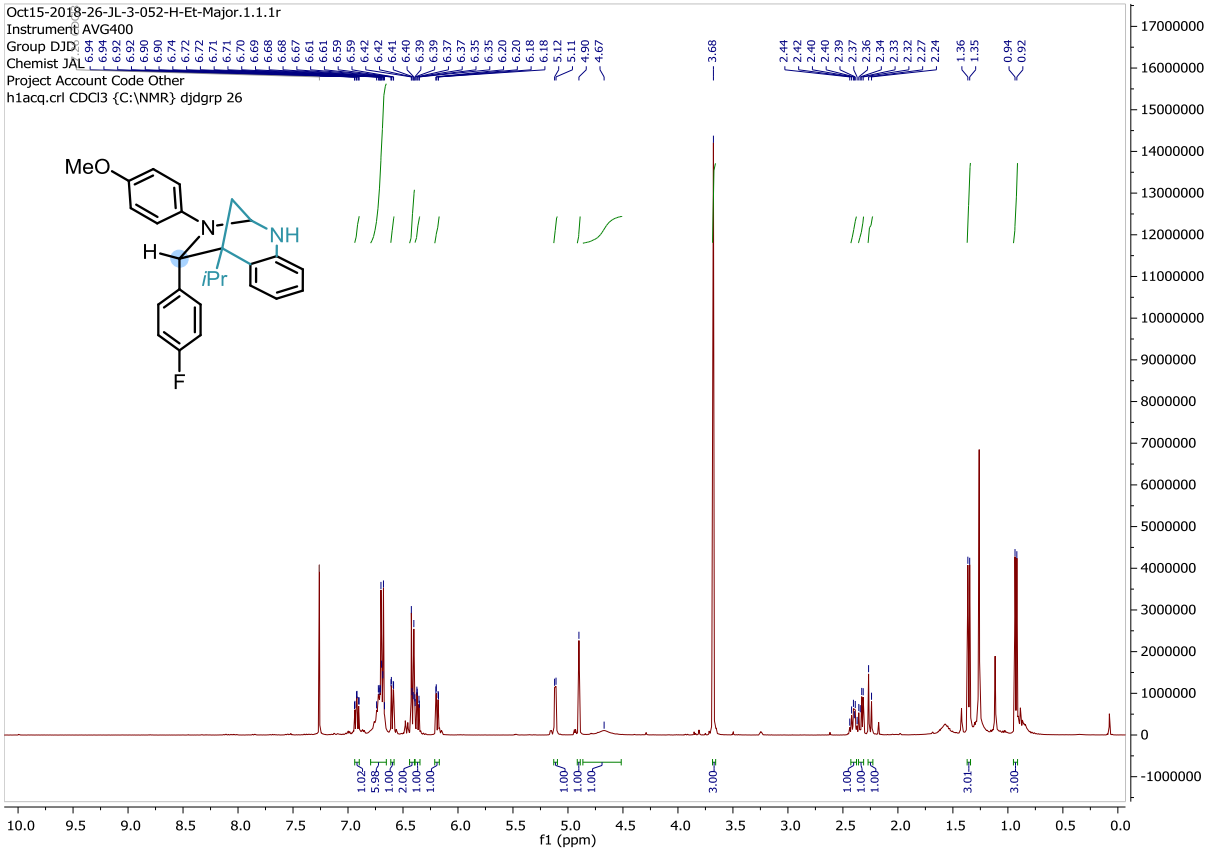
3ad$_{(endo)}$ – ^{19}F NMR (377 MHz, $CDCl_3$)



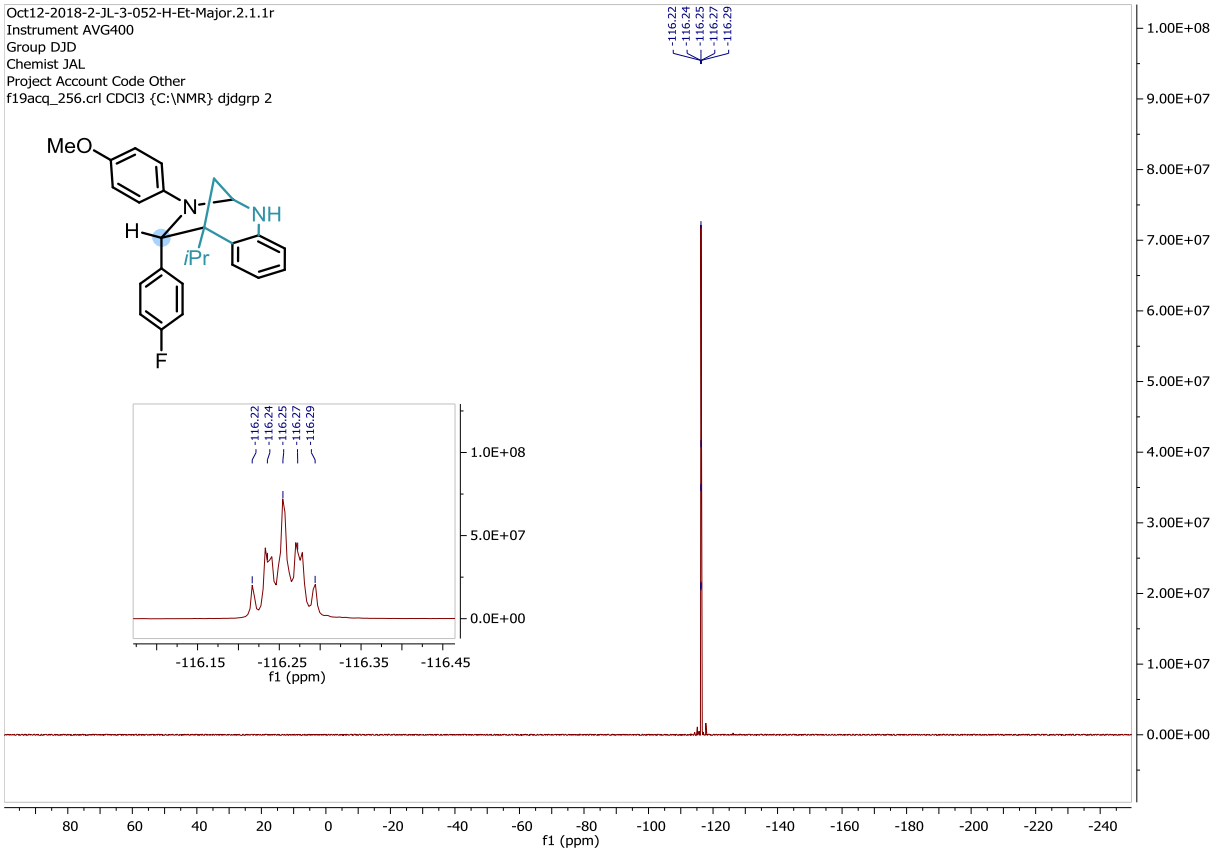
3ad$_{(endo)}$ – ^{13}C NMR (126 MHz, $CDCl_3$)



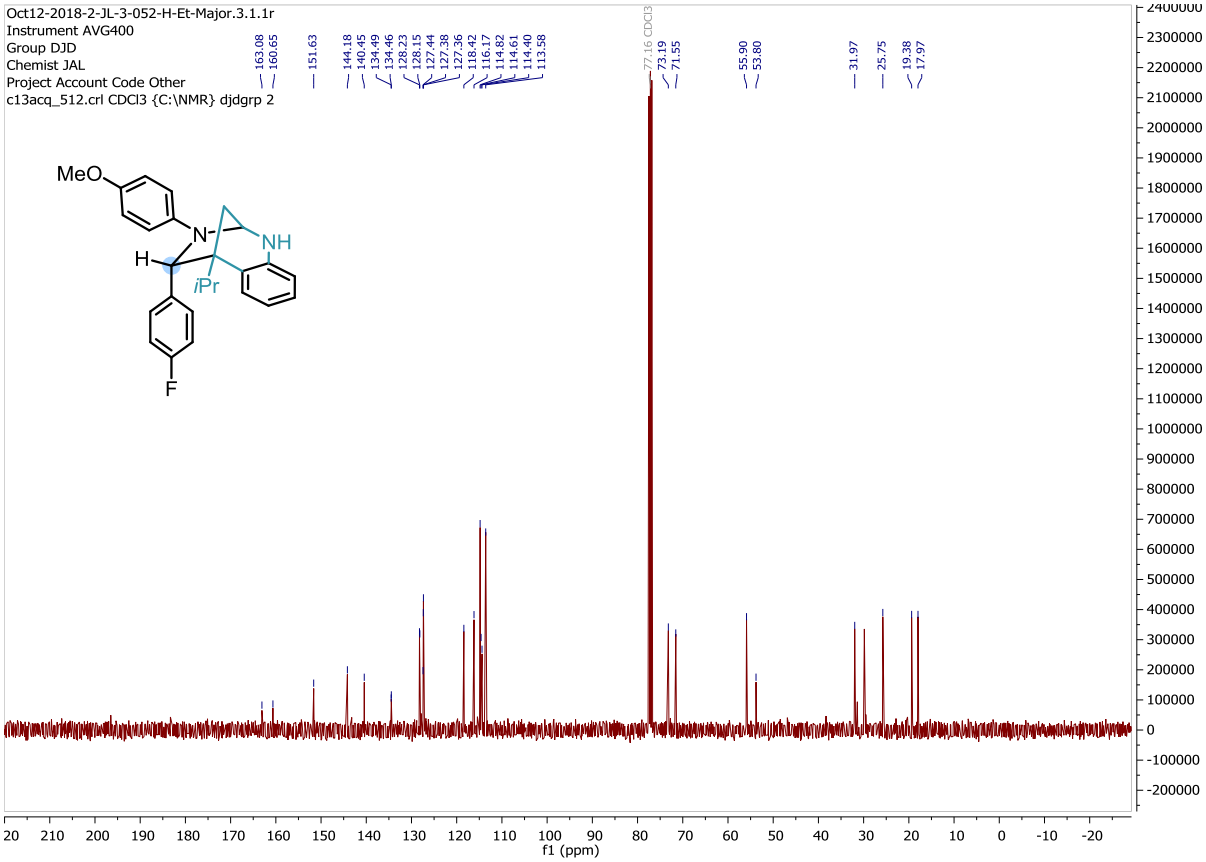
3ae$_{(endo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



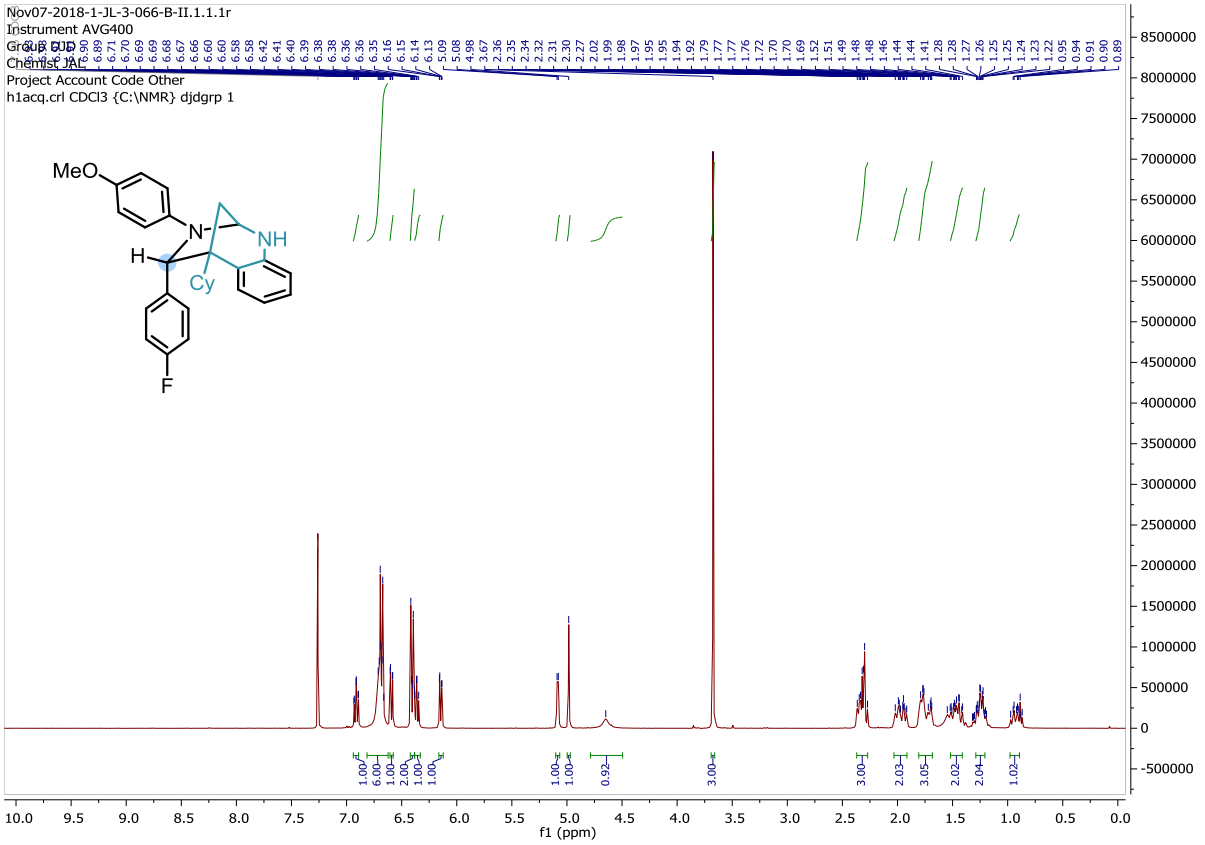
3ae$_{(endo)}$ – ^{19}F NMR (377 MHz, $CDCl_3$)



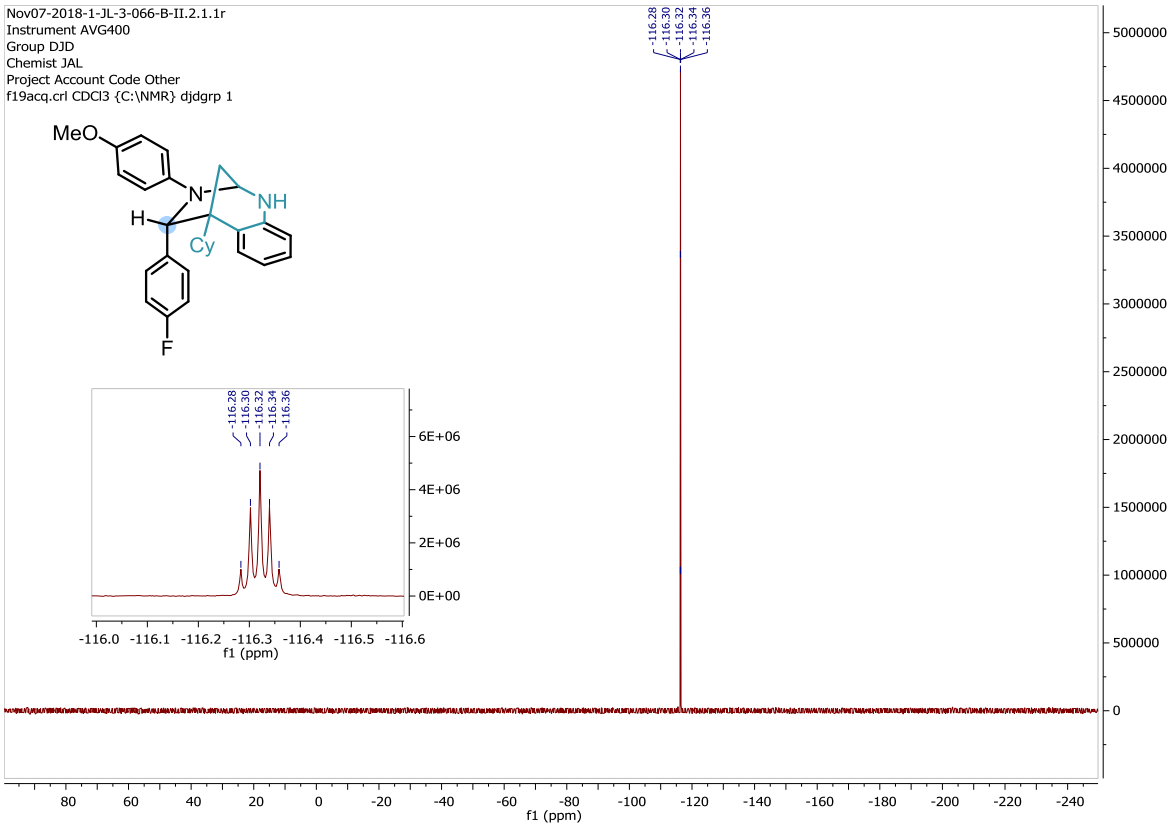
3ae$_{(endo)}$ – ^{13}C NMR (101 MHz, $CDCl_3$)



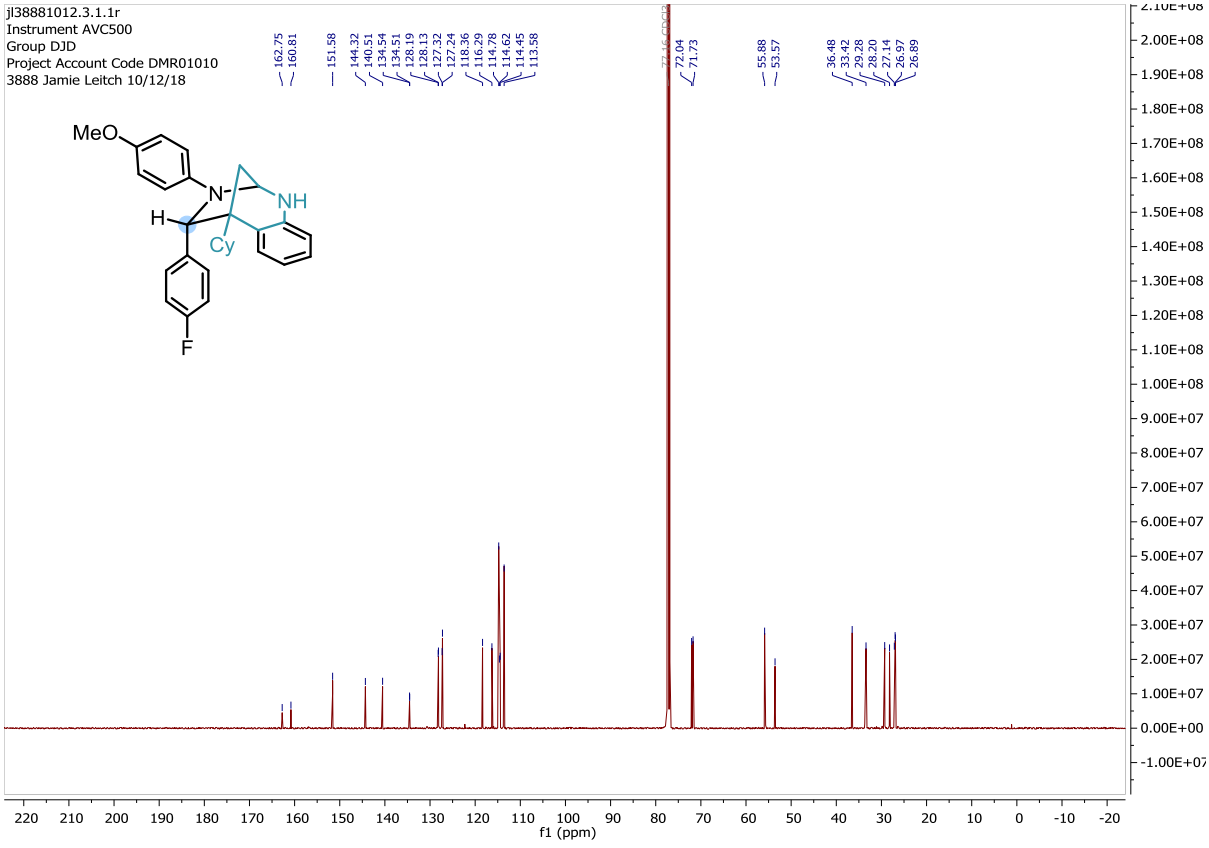
3af$_{(endo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



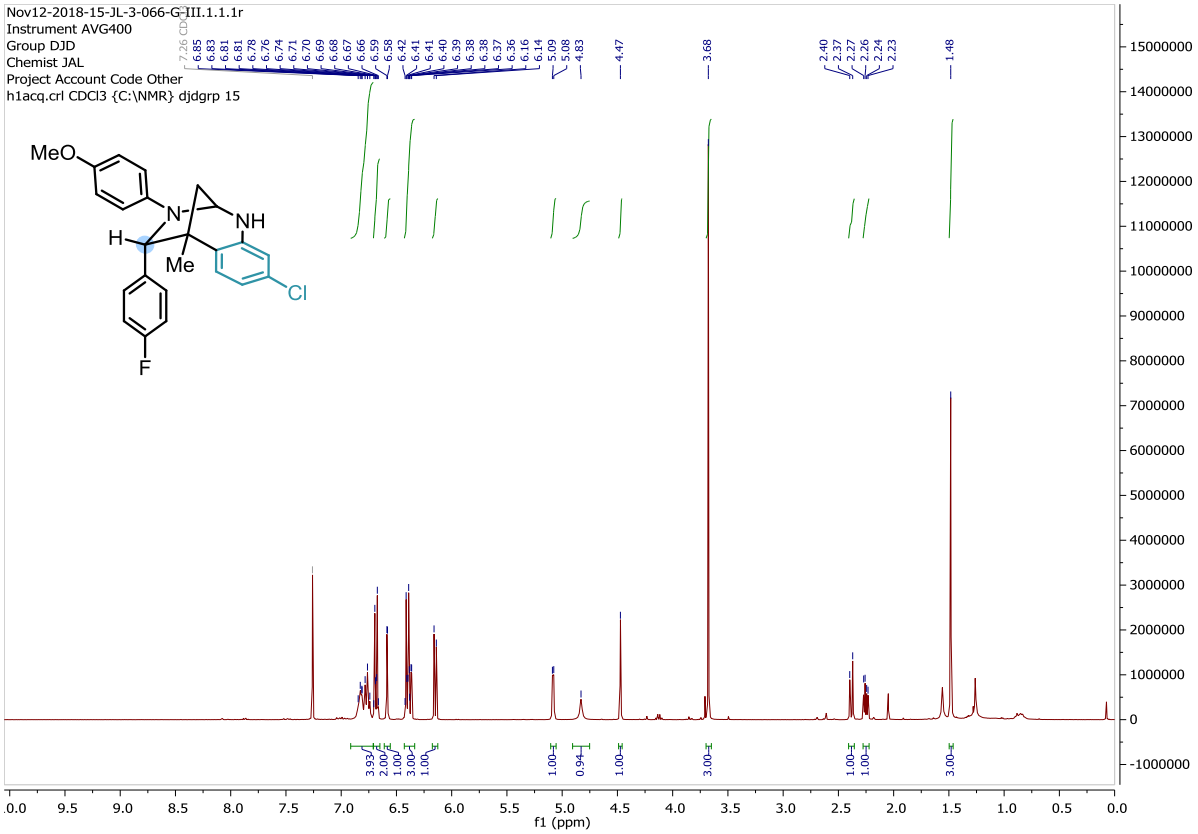
3af$_{(endo)}$ – ^{19}F NMR (377 MHz, $CDCl_3$)



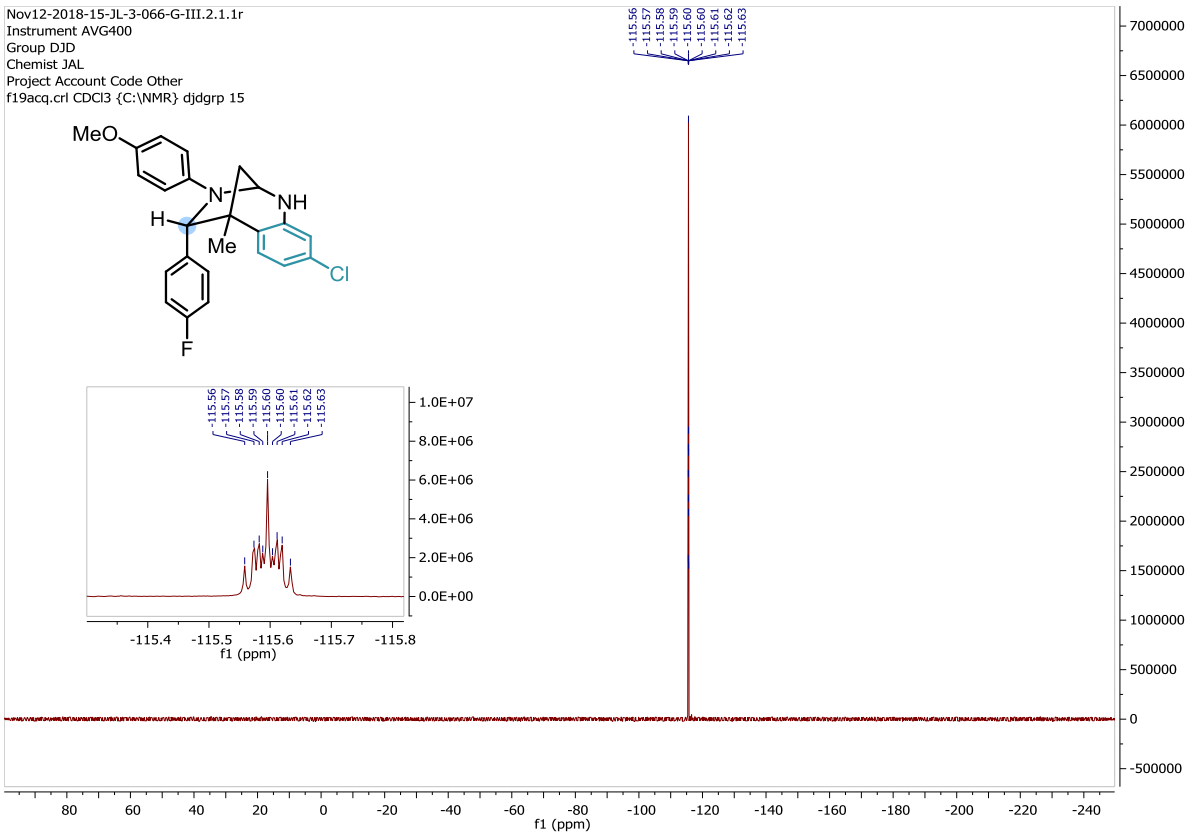
3af$_{(endo)}$ – ^{13}C NMR (126 MHz, $CDCl_3$)



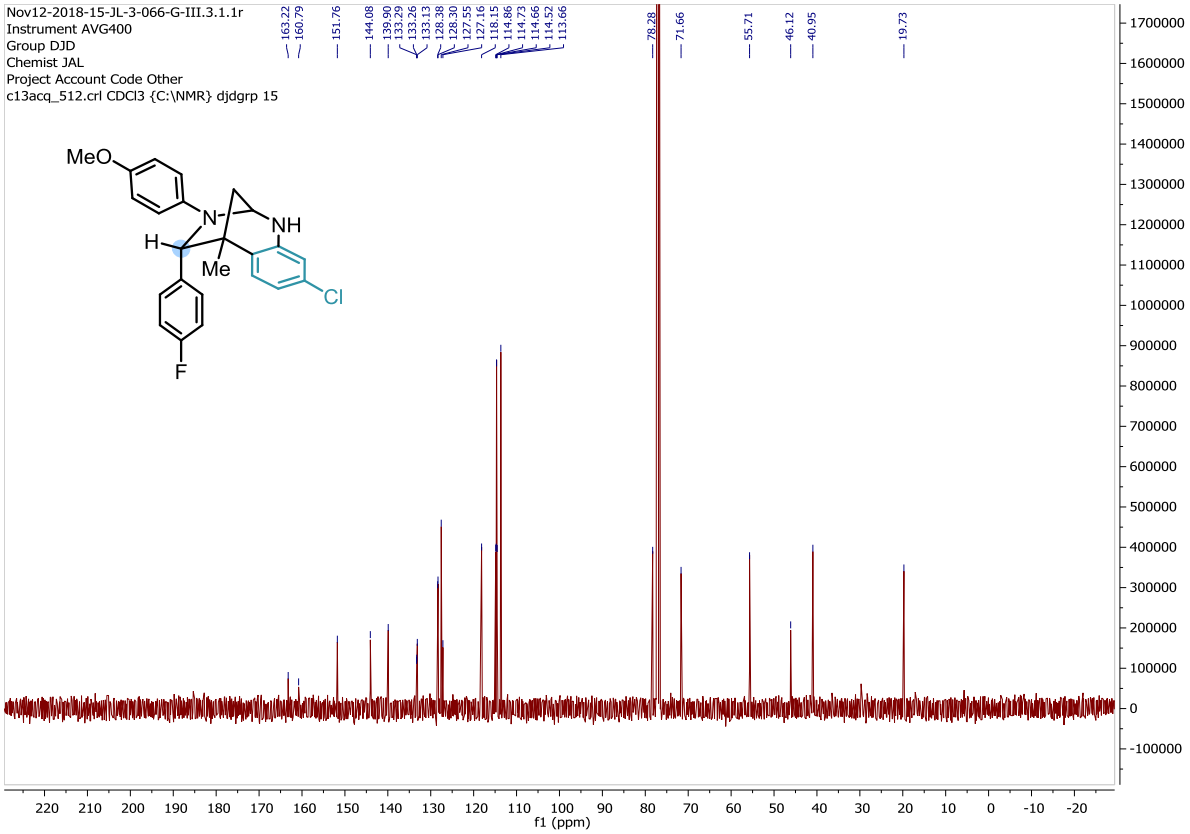
3ag$_{(endo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



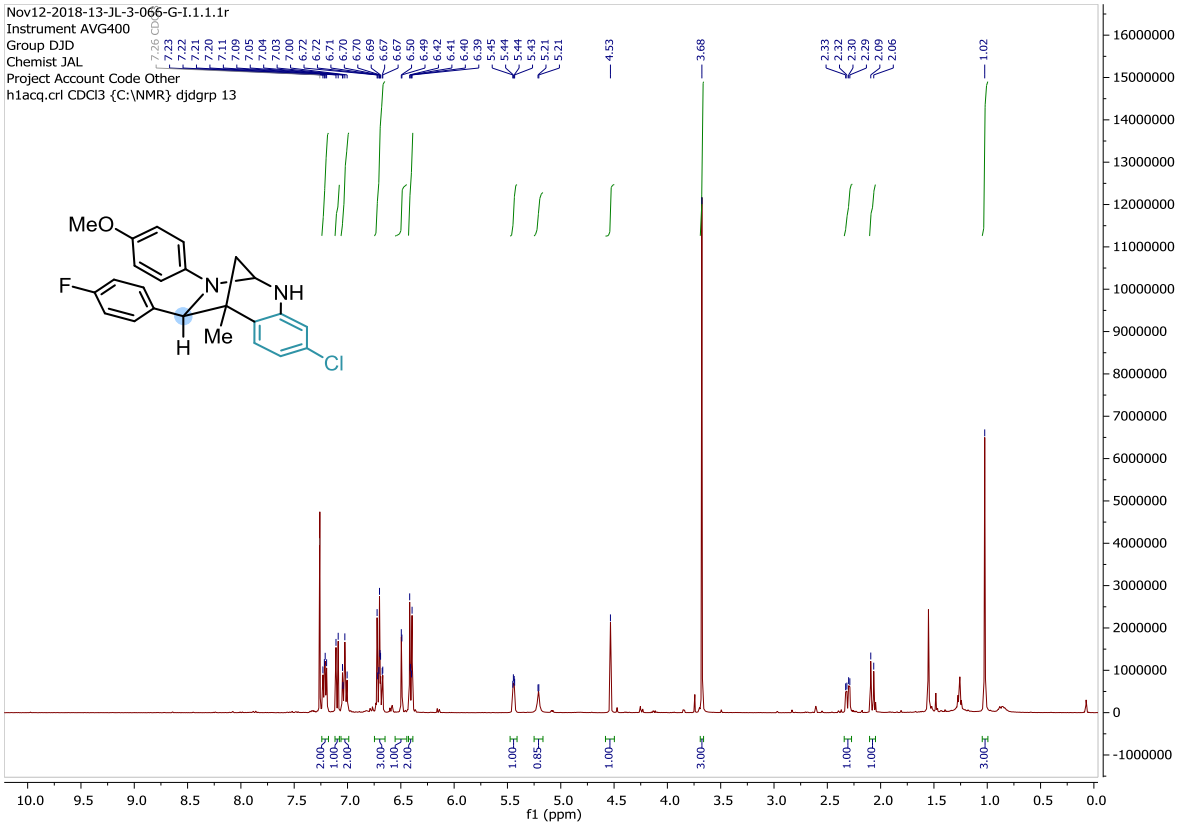
3ag$_{(endo)}$ – ^{19}F NMR (377 MHz, $CDCl_3$)



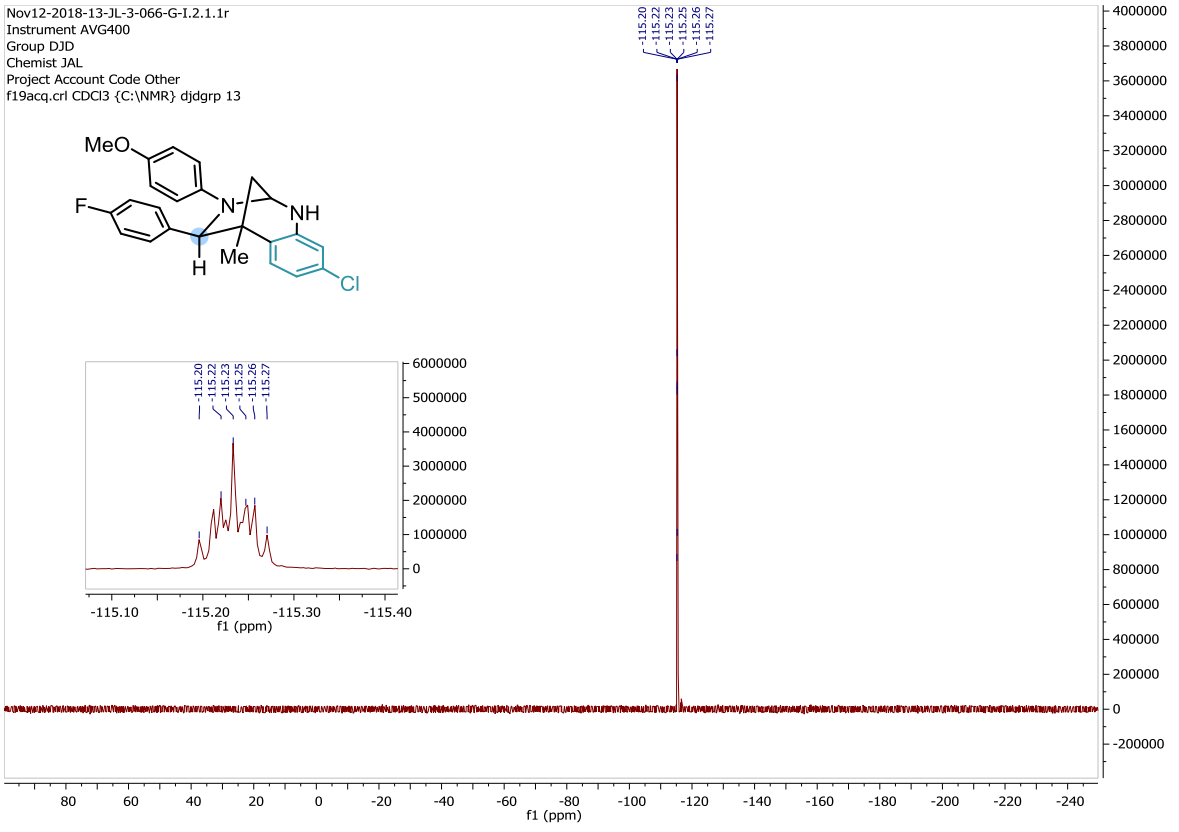
3ag$_{(endo)}$ – ^{13}C NMR (101 MHz, $CDCl_3$)



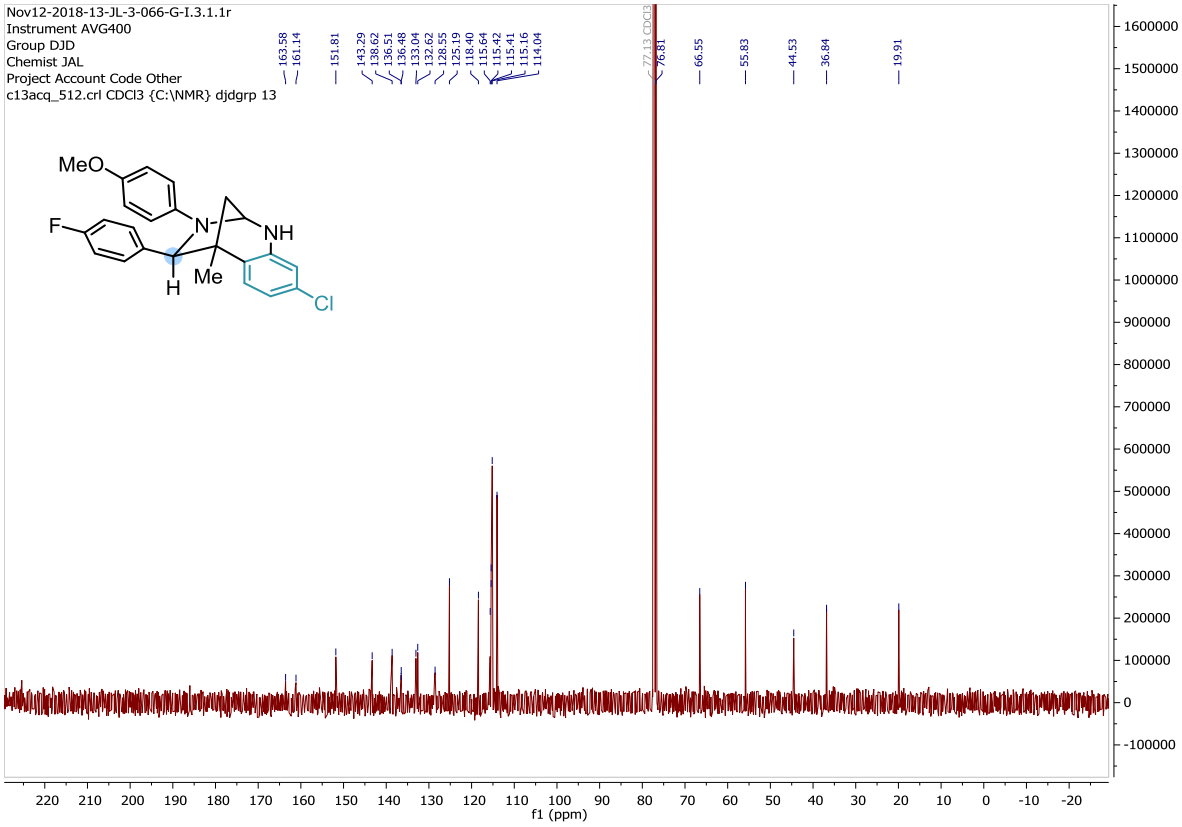
3ag$_{(exo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



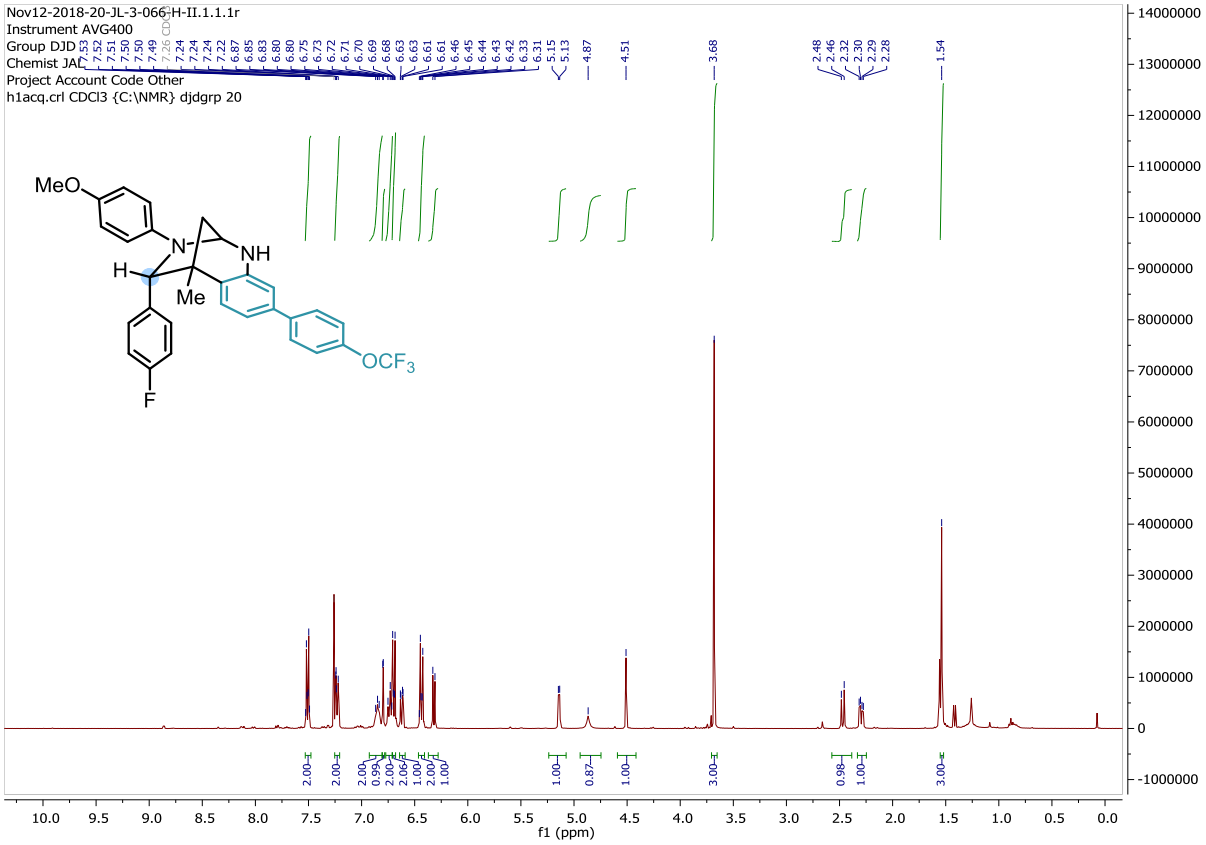
3ag$_{(exo)}$ – ^{19}F NMR (377 MHz, $CDCl_3$)



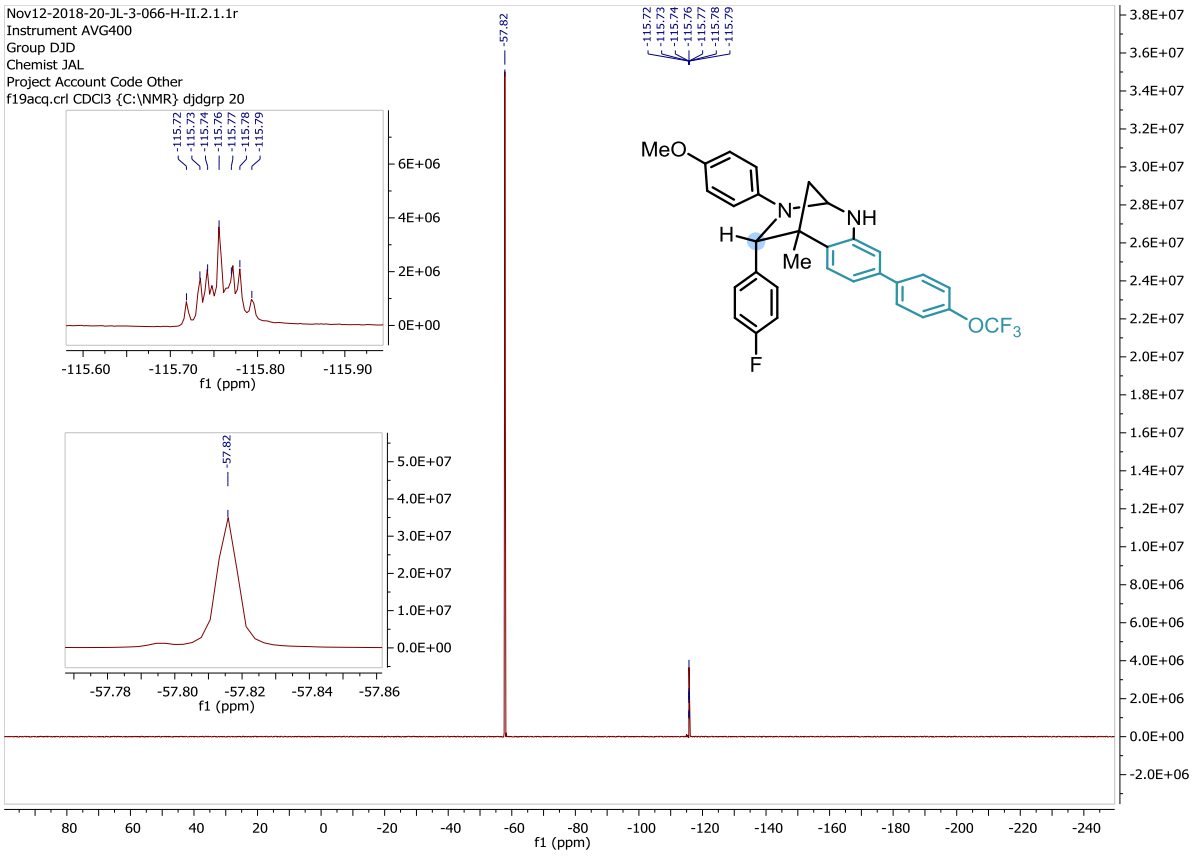
3ag$_{(exo)}$ – ^{13}C NMR (101 MHz, $CDCl_3$)



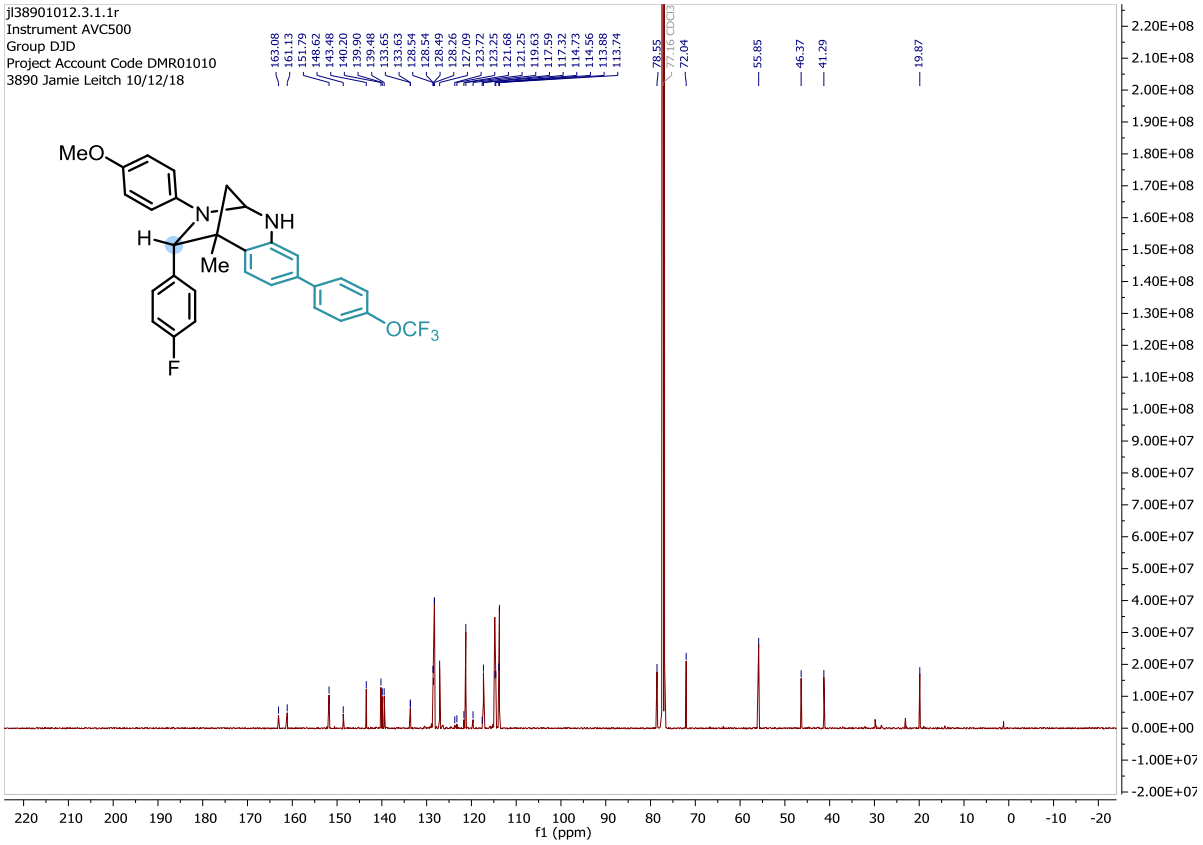
3ah$_{(endo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



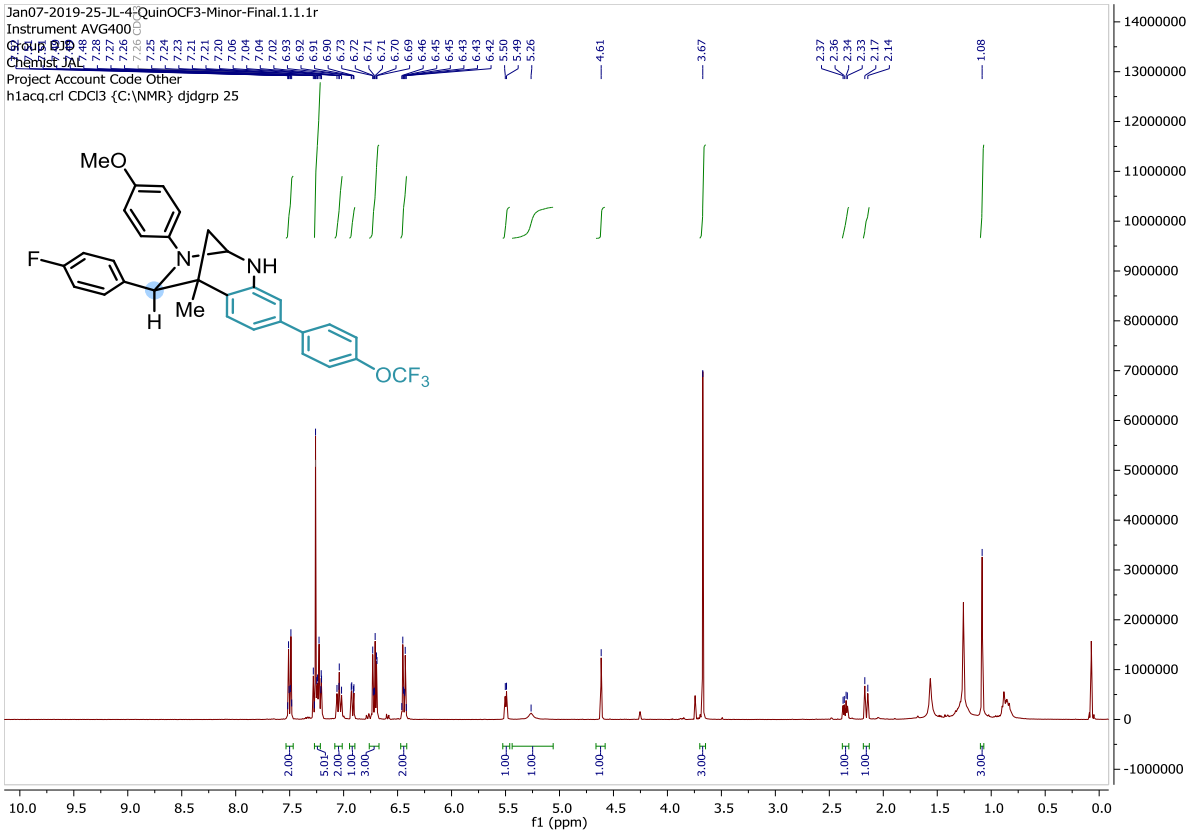
3ah$_{(endo)}$ – ^{19}F NMR (377 MHz, $CDCl_3$)



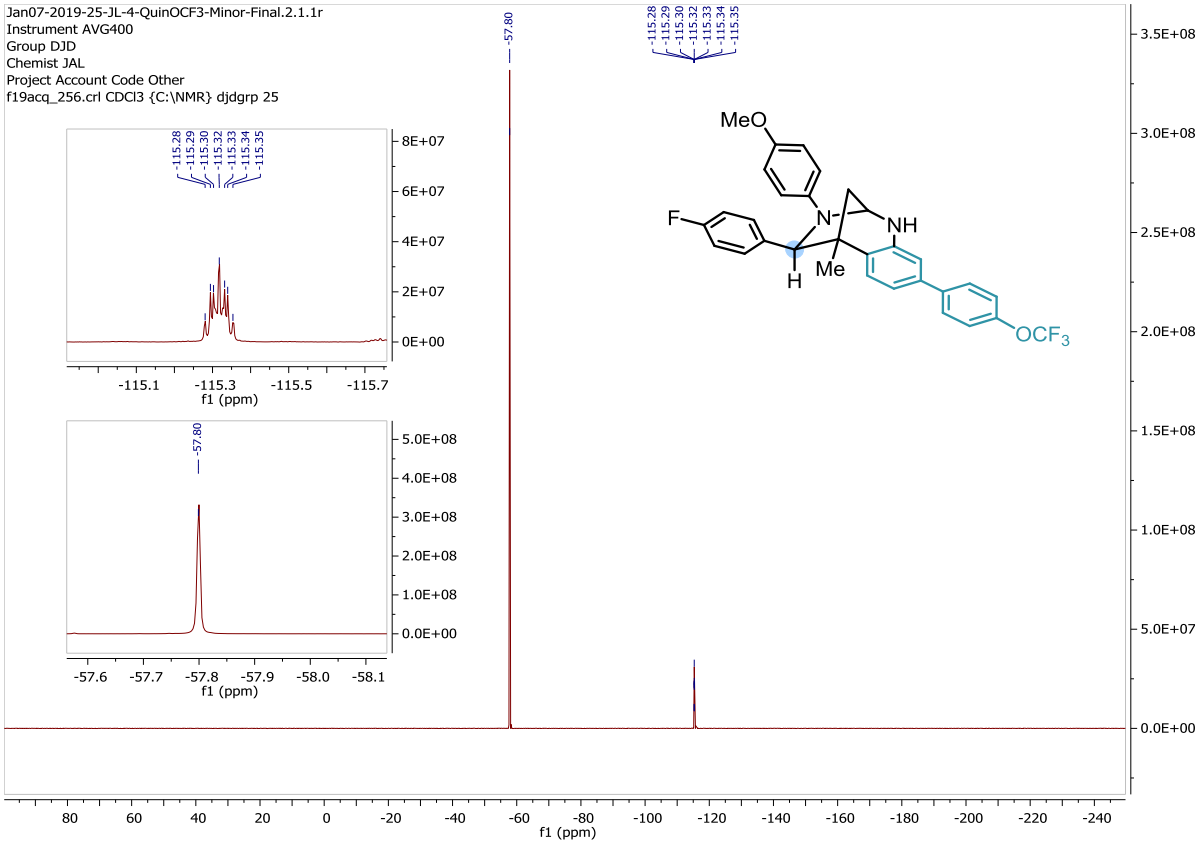
3ah$_{(endo)}$ – ^{13}C NMR (126 MHz, $CDCl_3$)



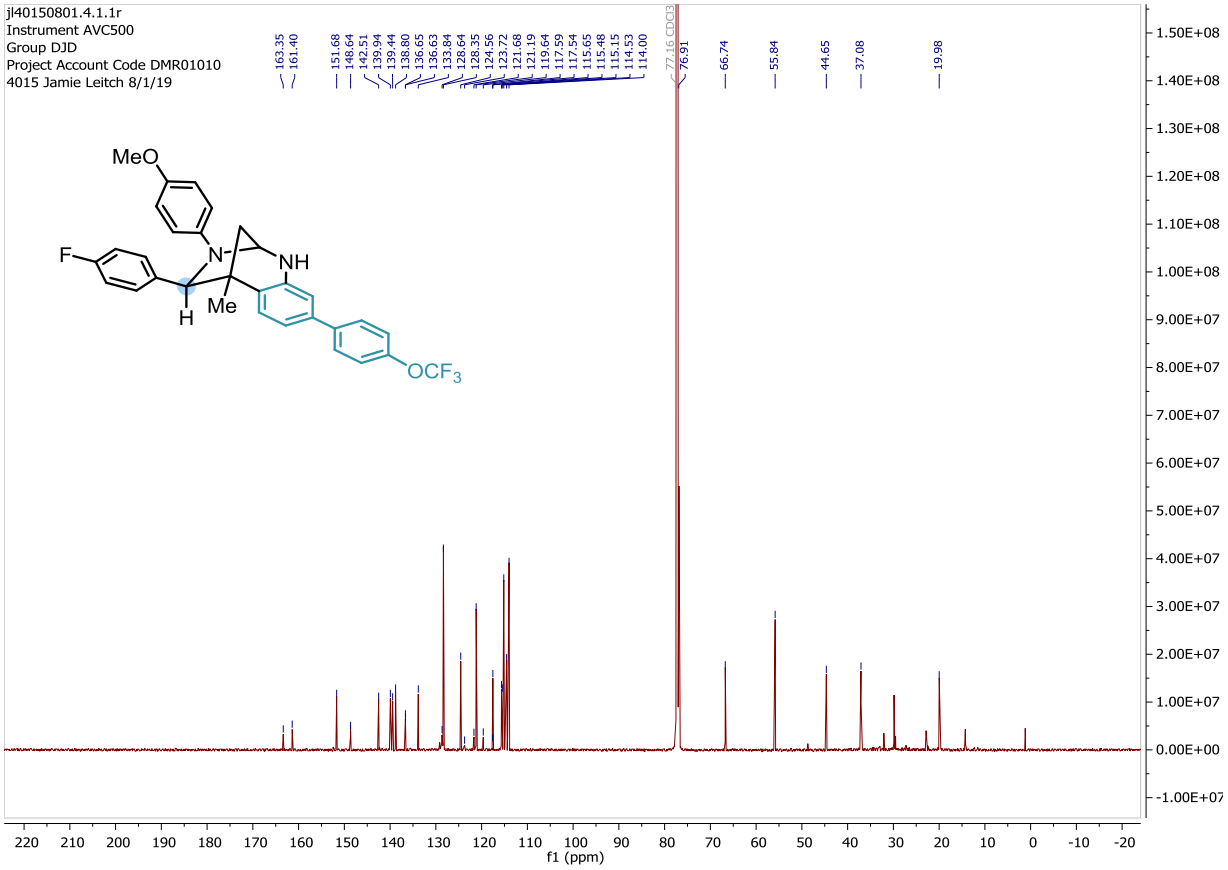
3ah$_{(exo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



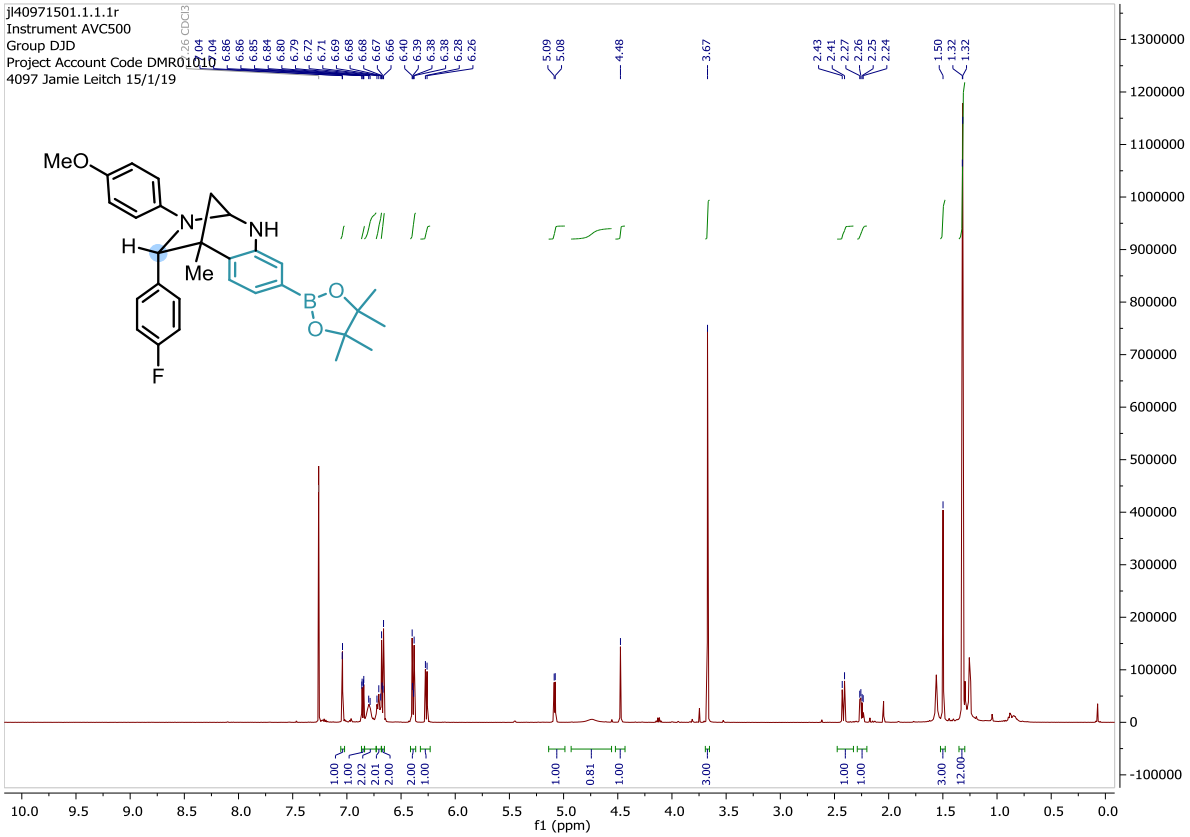
3ah$_{(exo)}$ – ^{19}F NMR (377 MHz, $CDCl_3$)



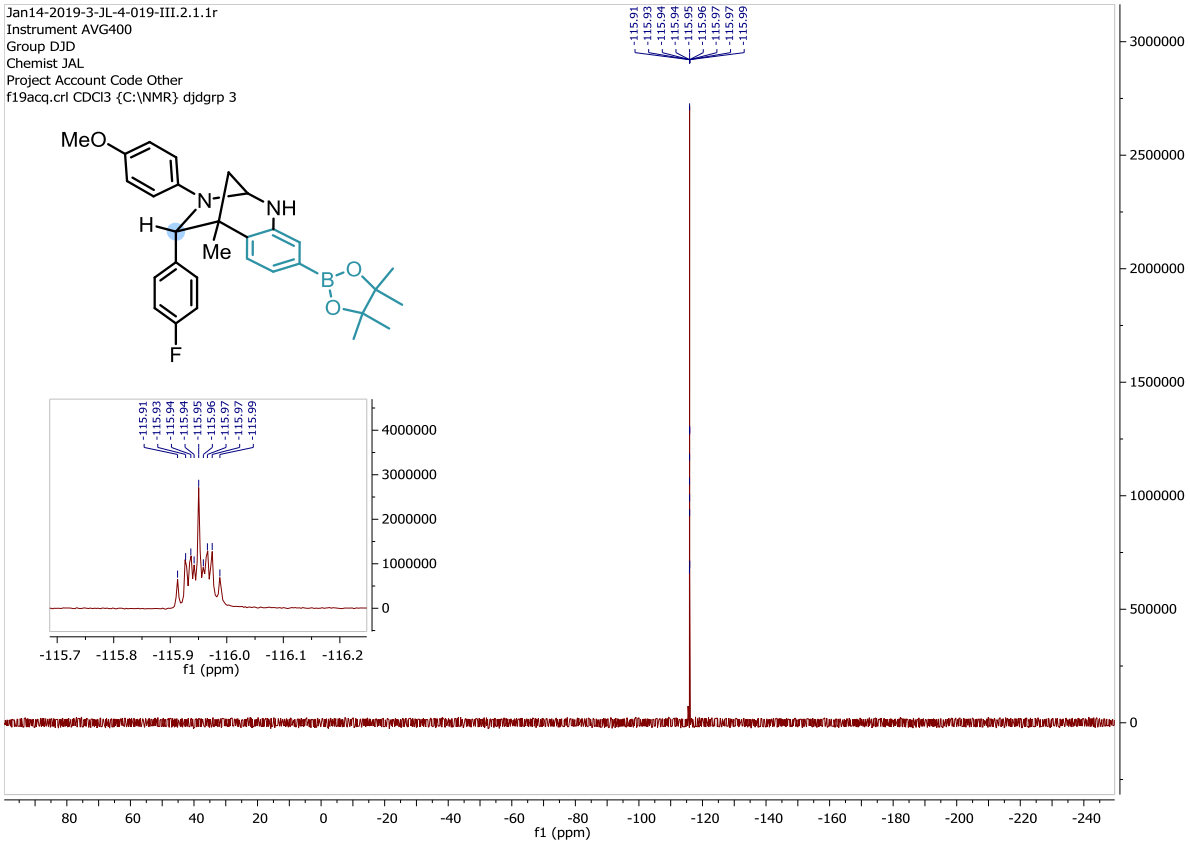
3ah$_{(exo)}$ – ^{13}C NMR (126 MHz, $CDCl_3$)



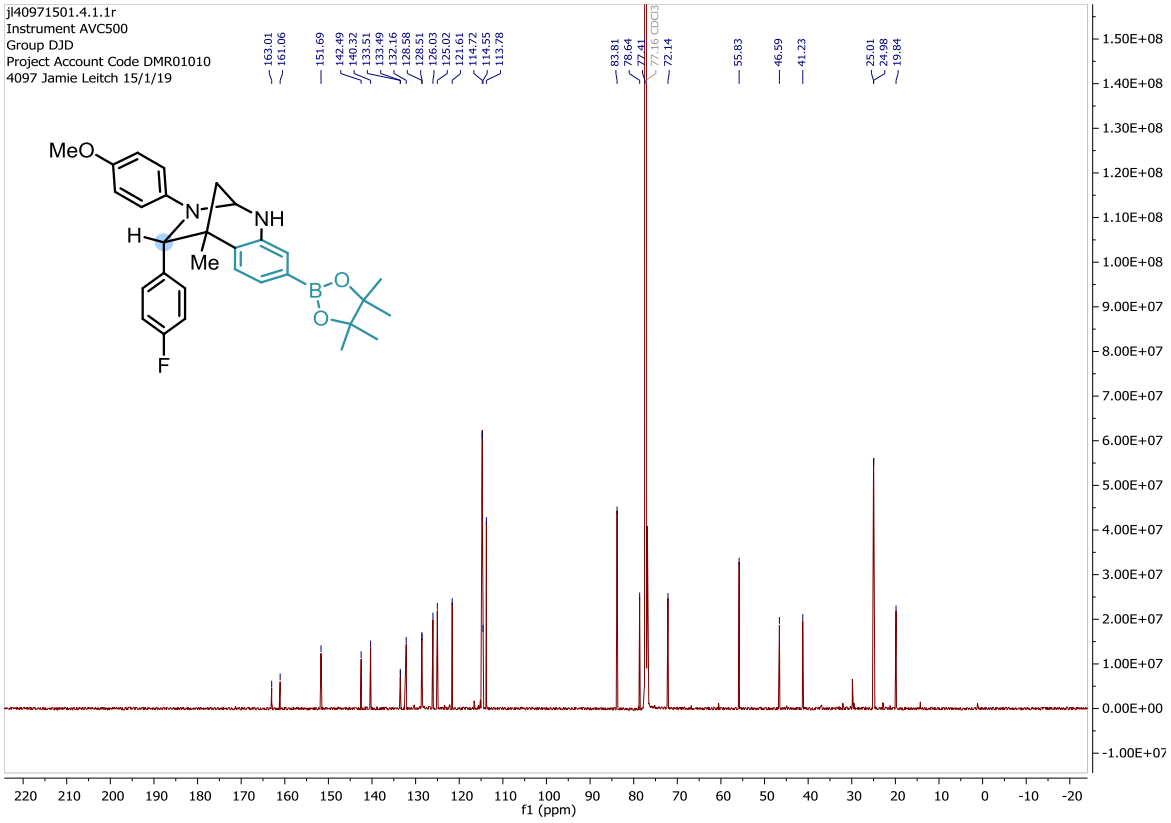
3ai$_{(endo)}$ – ^{1}H NMR (500 MHz, $CDCl_3$)



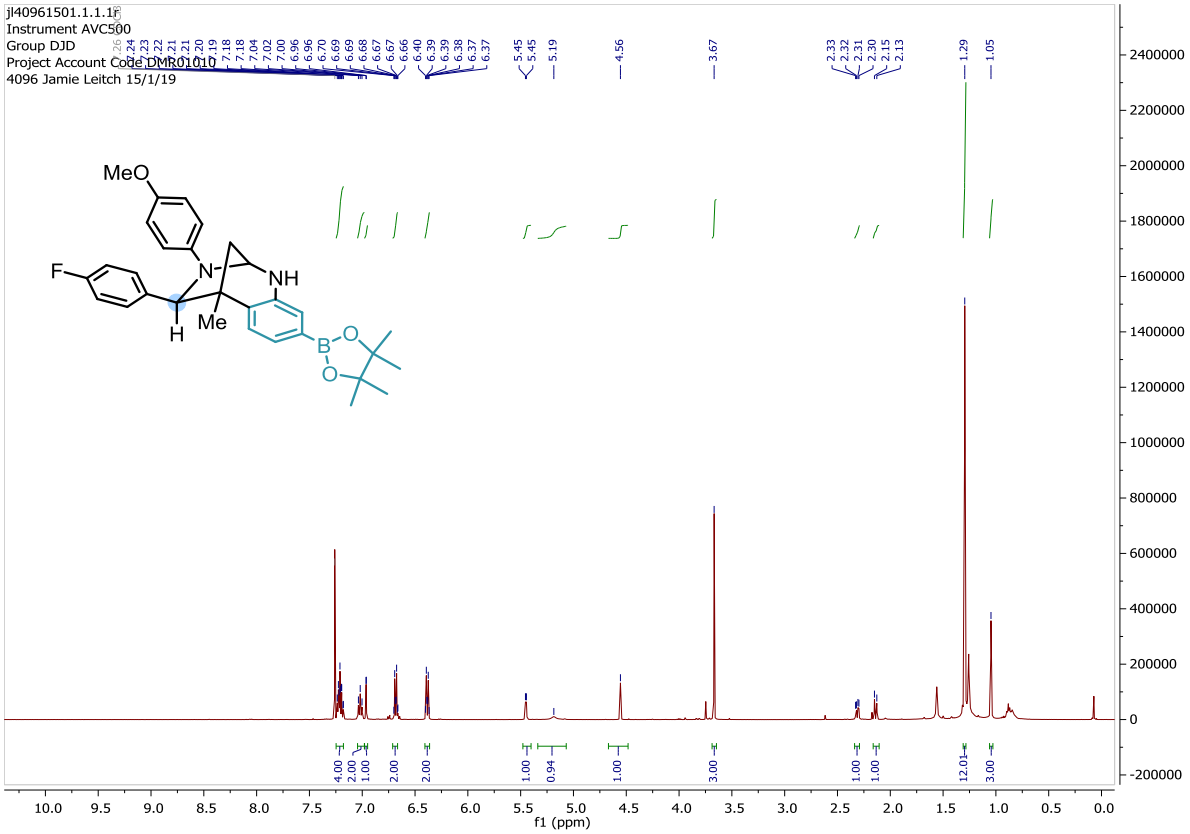
3ai$_{(endo)}$ – ^{19}F NMR (337 MHz, $CDCl_3$)



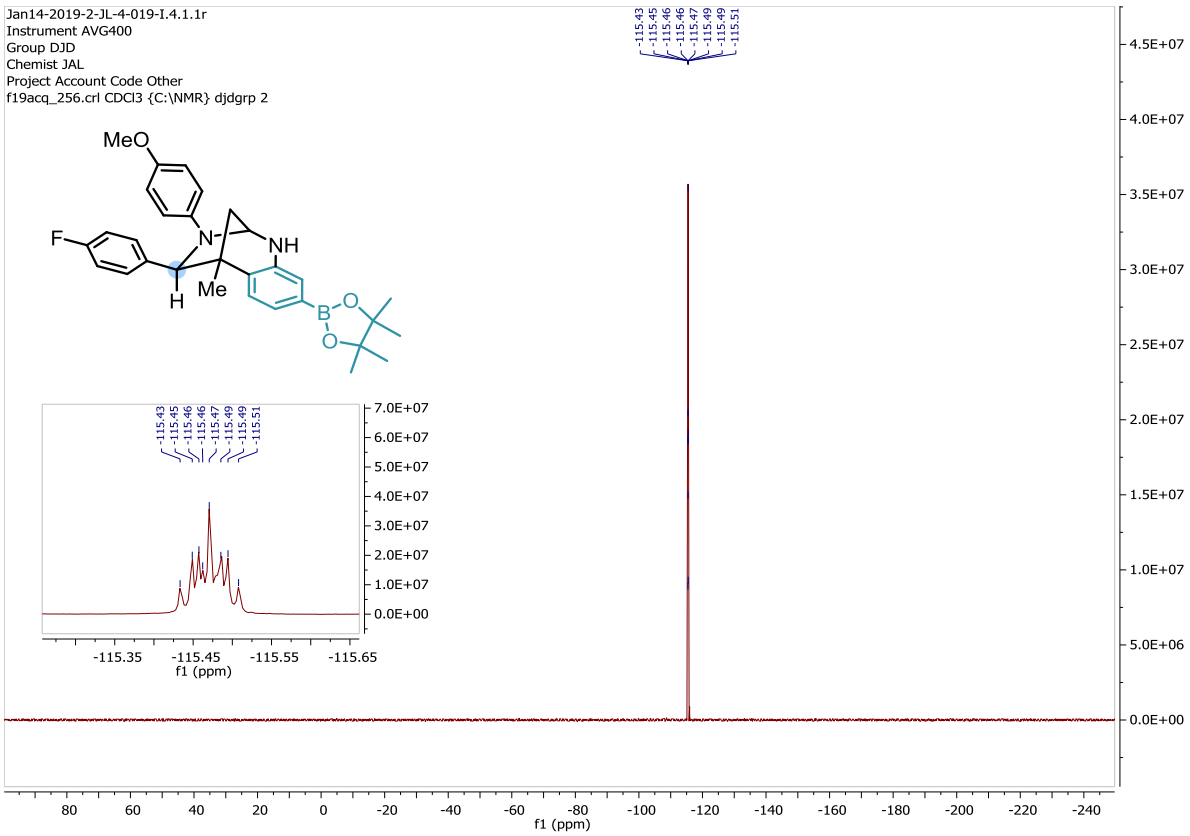
3ai$_{(endo)}$ – ^{13}C NMR (126 MHz, $CDCl_3$)



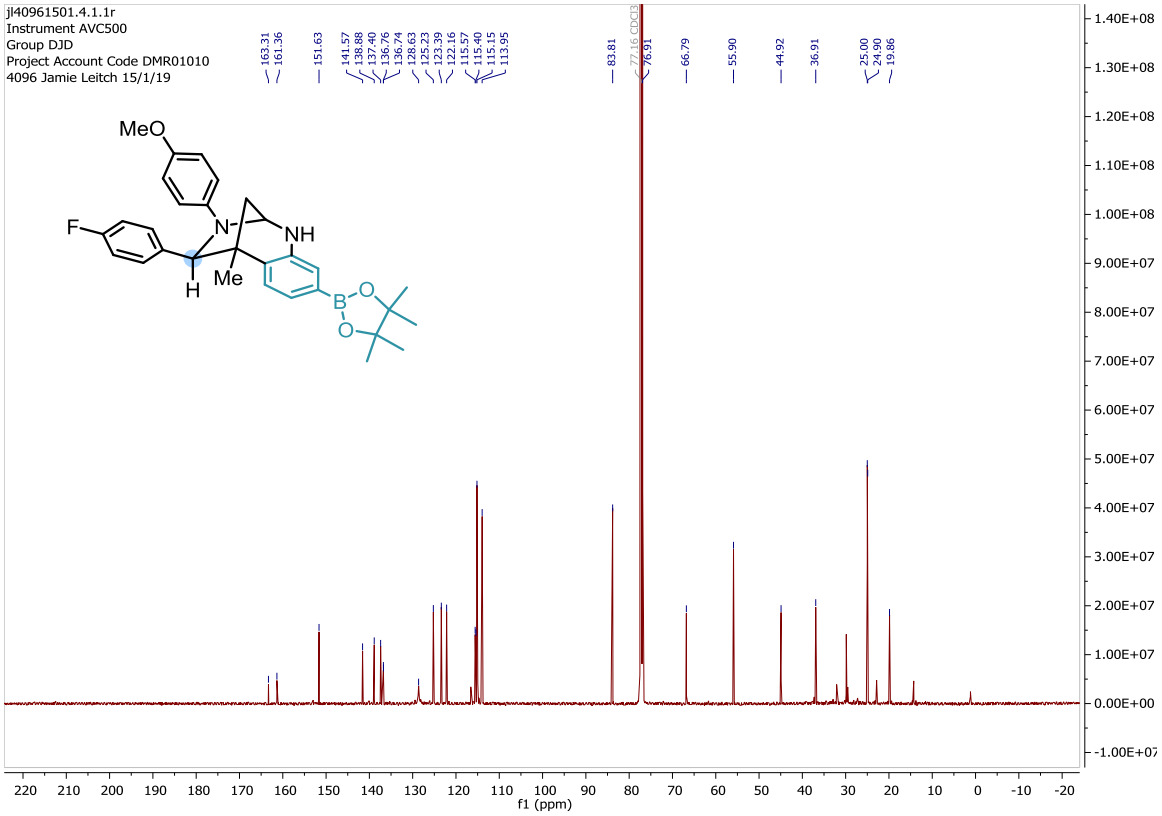
3ai$_{(exo)}$ – ^{1}H NMR (500 MHz, $CDCl_3$)



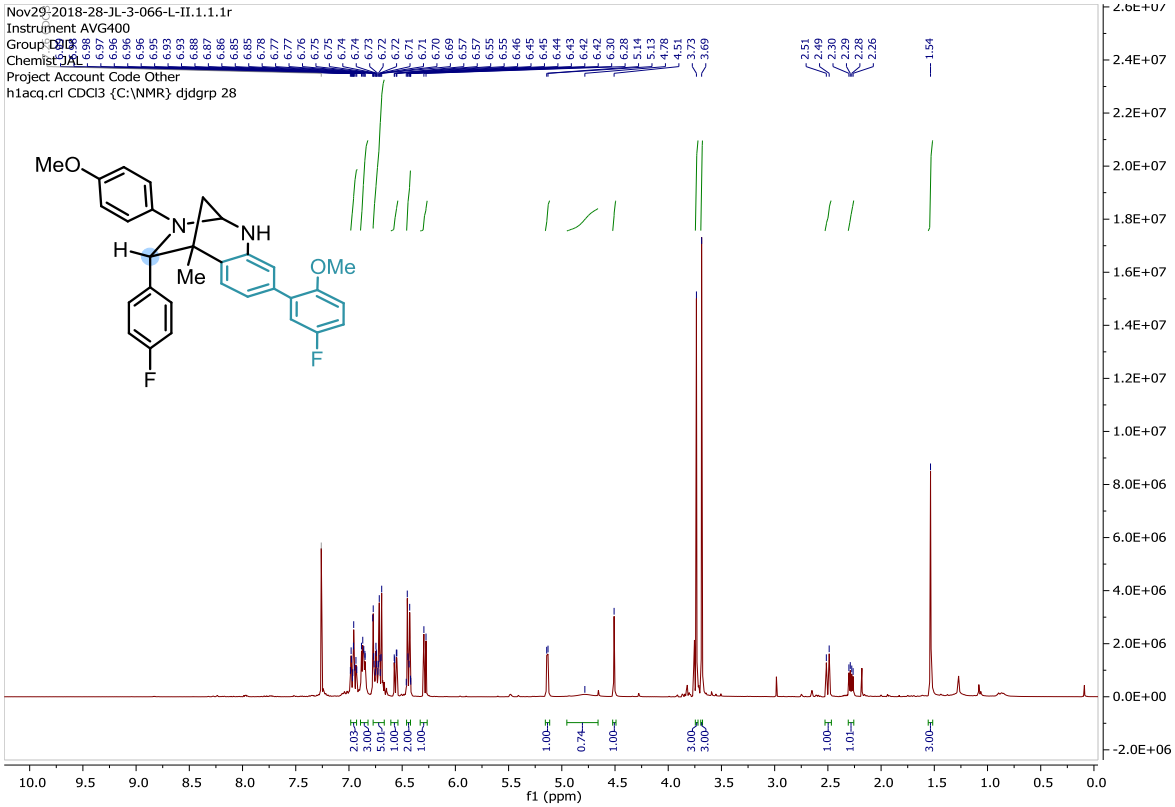
3ai$_{(exo)}$ – ^{19}F NMR (377 MHz, $CDCl_3$)



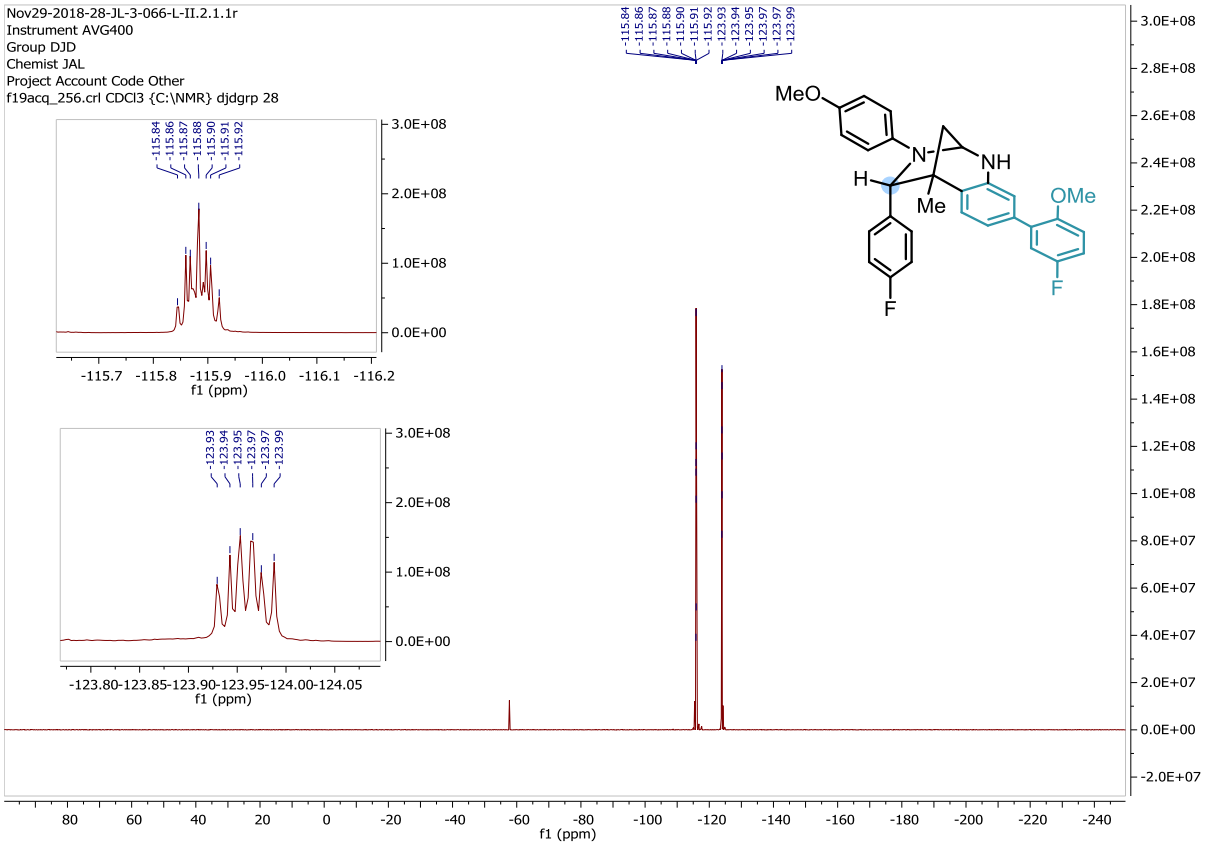
3ai$_{(exo)}$ – ^{13}C NMR (126 MHz, $CDCl_3$)



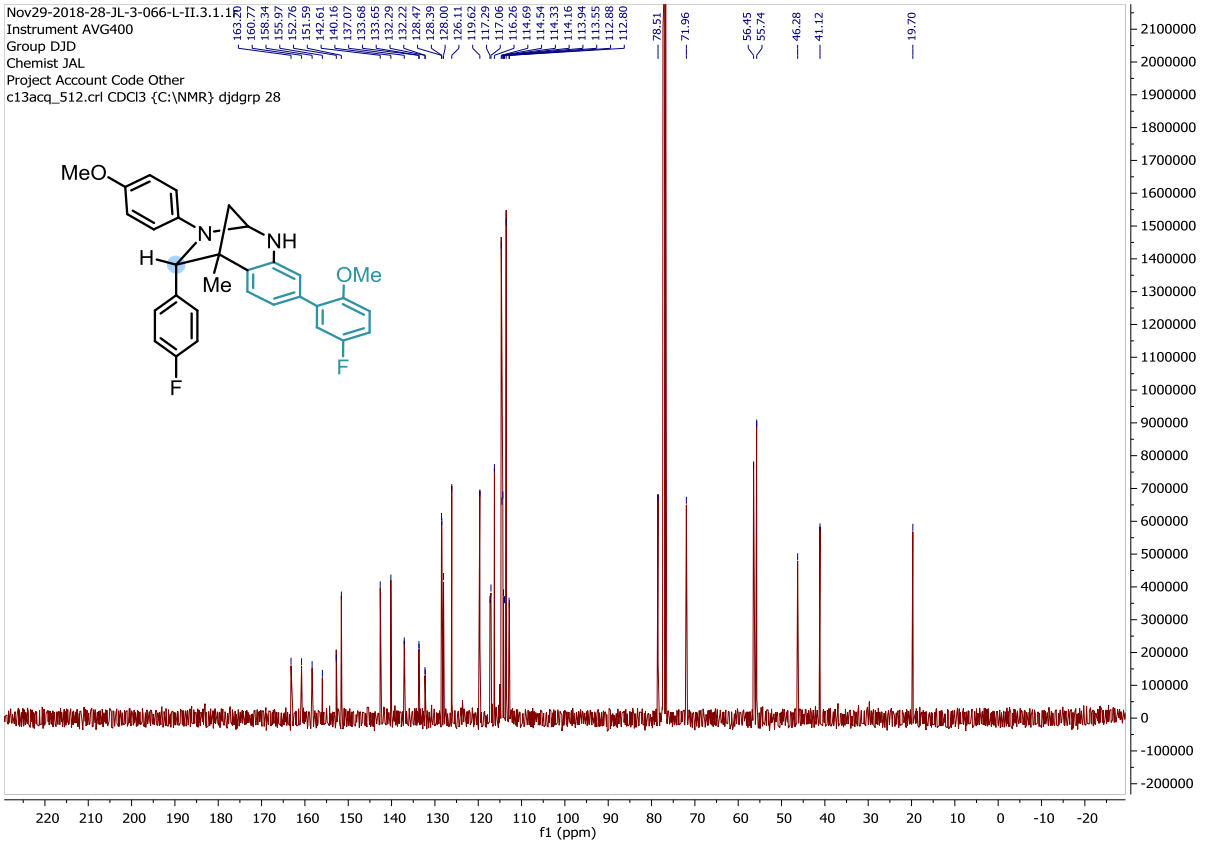
3aj(endo) – ^{1}H NMR (400 MHz, $CDCl_3$)



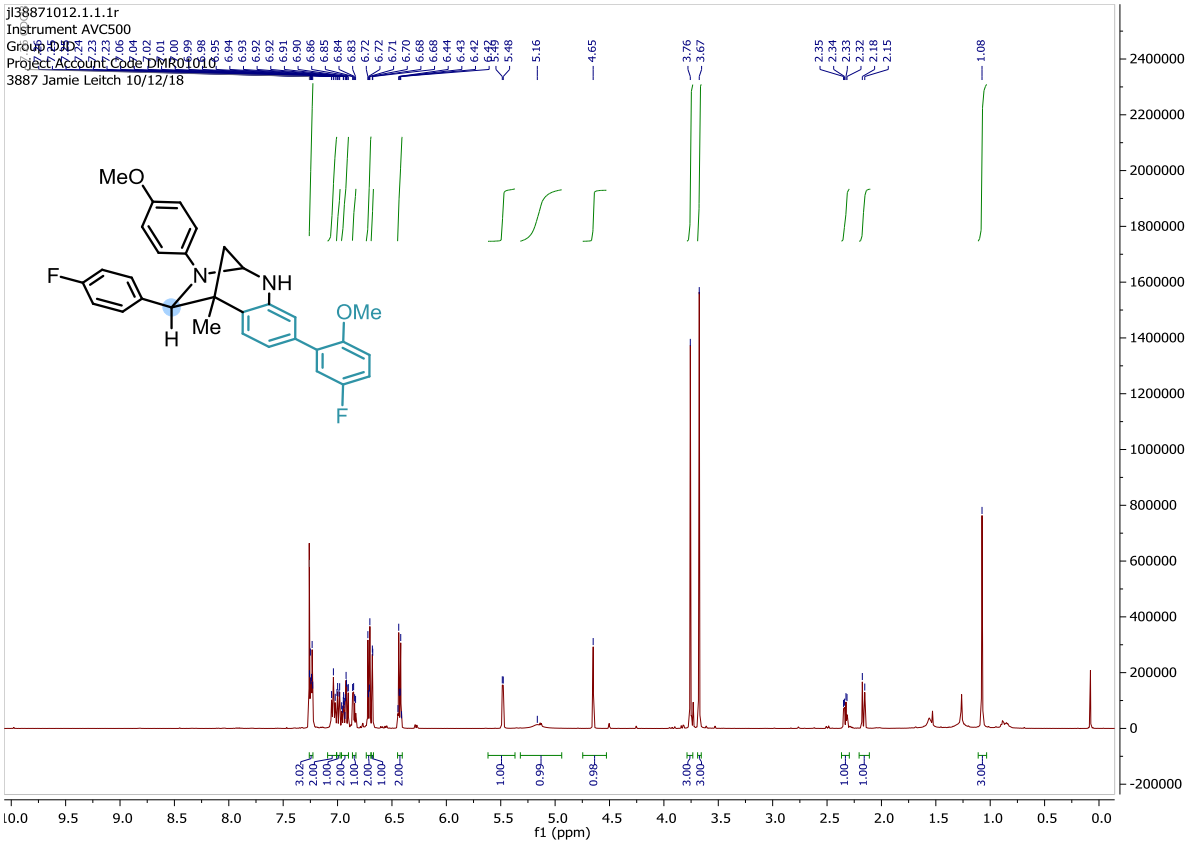
3aj(endo) – ^{19}F NMR (377 MHz, $CDCl_3$)



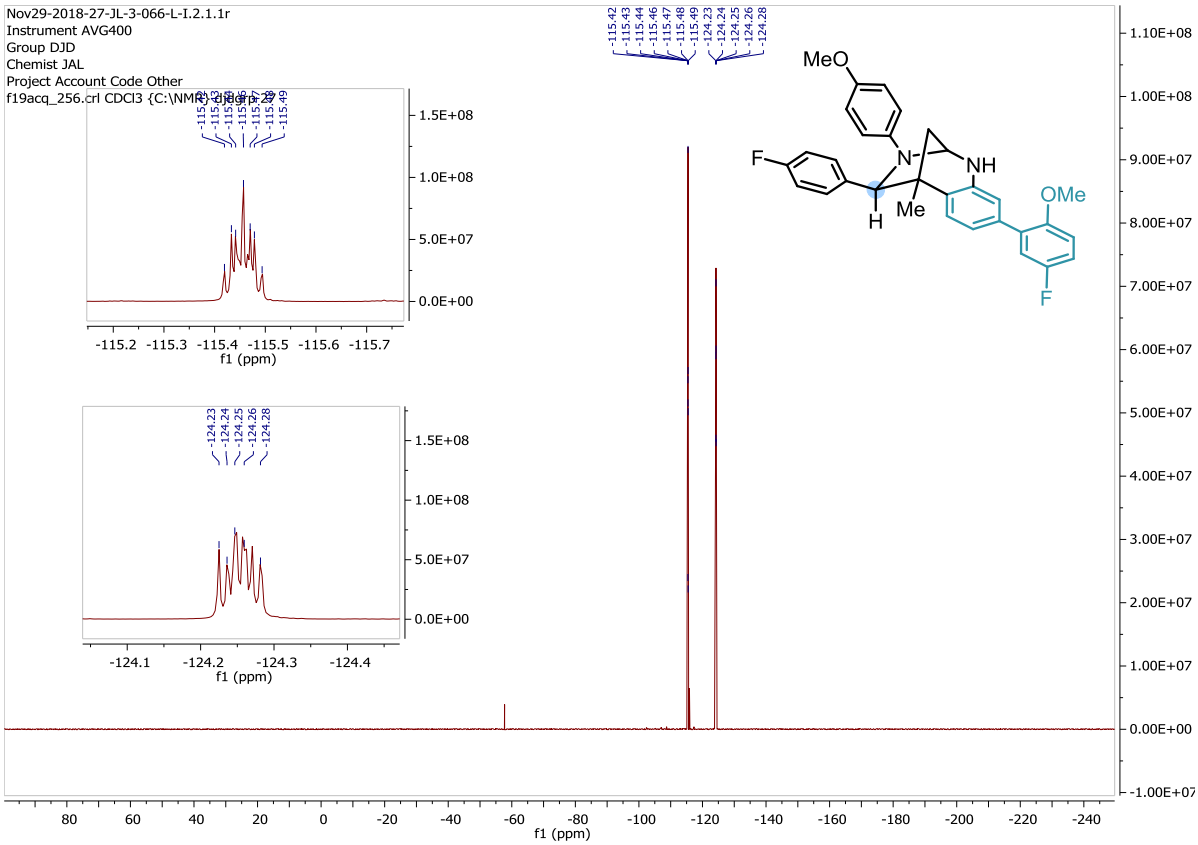
3aj$_{(endo)}$ – ^{13}C NMR (101 MHz, $CDCl_3$)



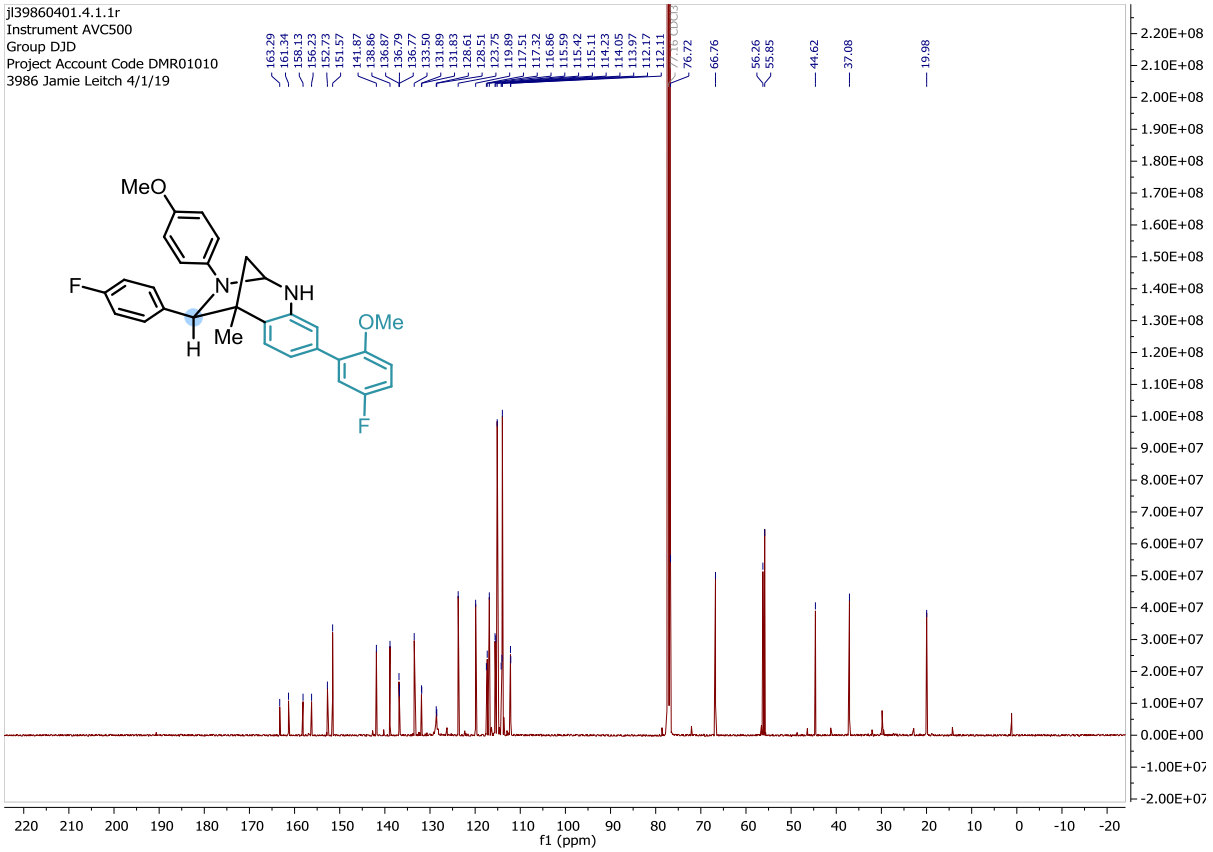
3aj$_{(exo)}$ – ^{1}H NMR (500 MHz, $CDCl_3$)



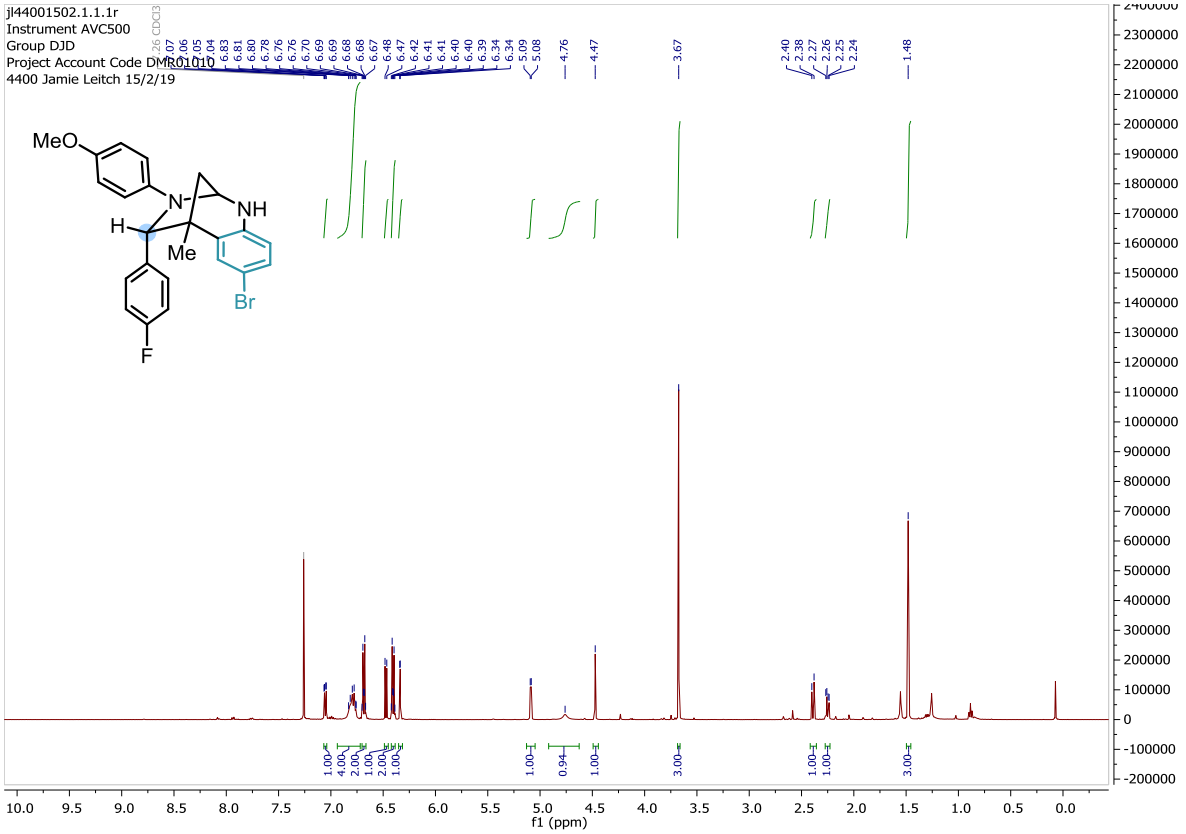
3aj$_{(exo)}$ – ^{19}F NMR (377 MHz, $CDCl_3$)



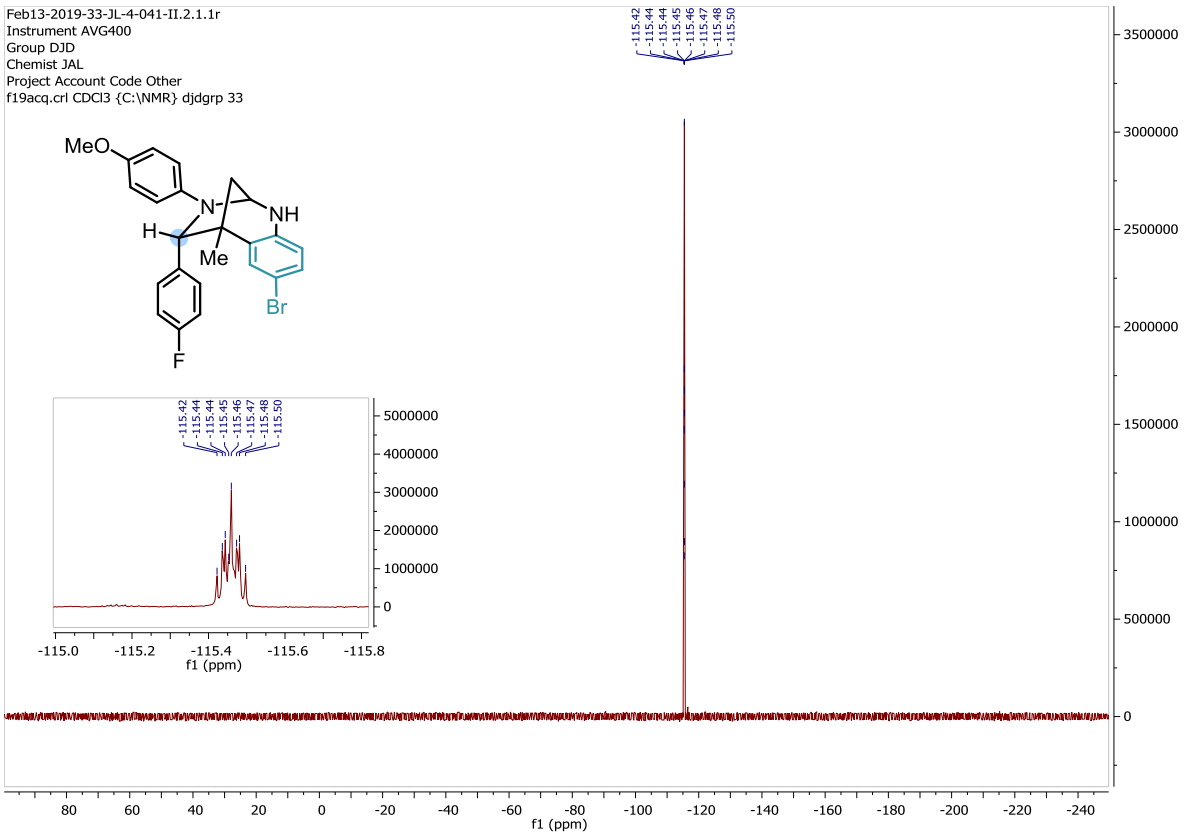
3aj$_{(exo)}$ – ^{13}C NMR (126 MHz, $CDCl_3$)



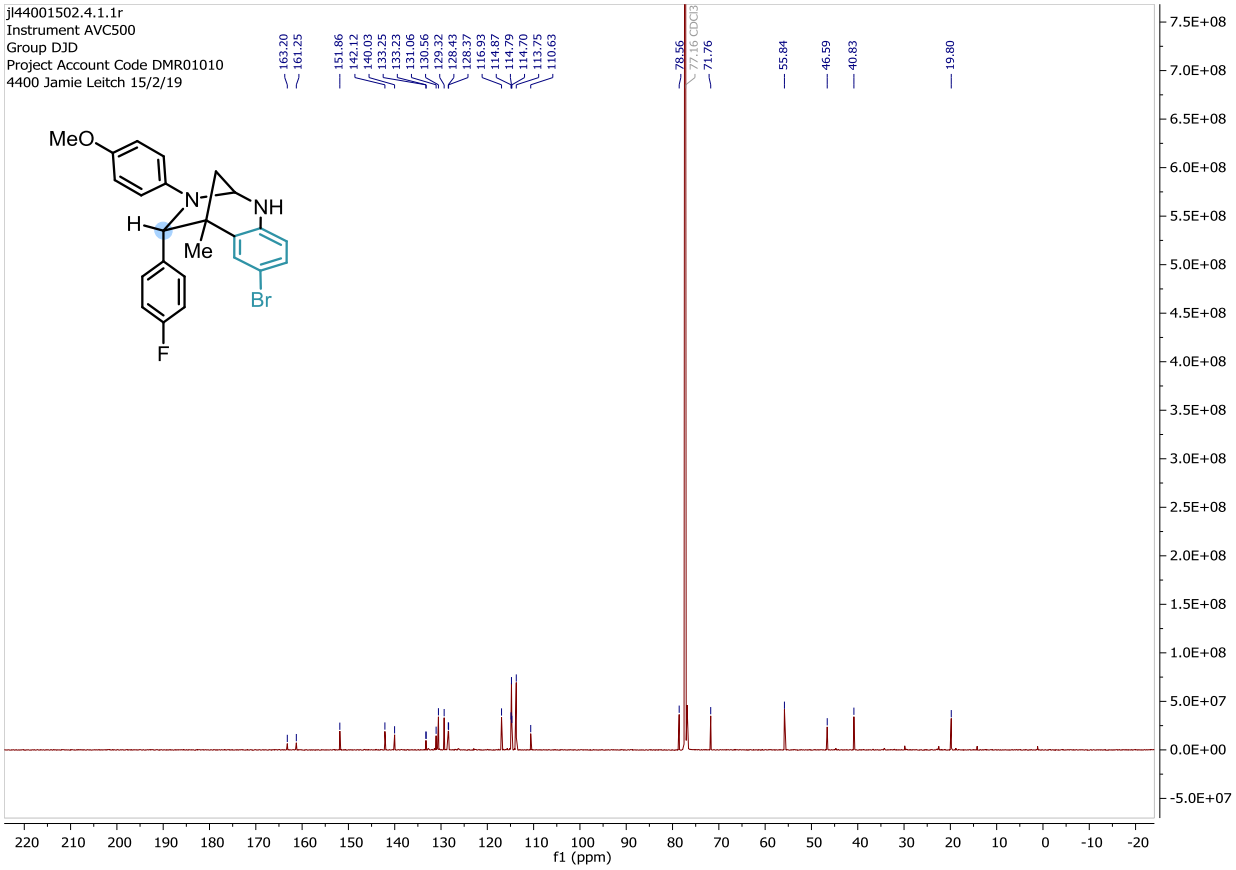
3ak$_{(endo)}$ – ^{1}H NMR (500 MHz, $CDCl_3$)



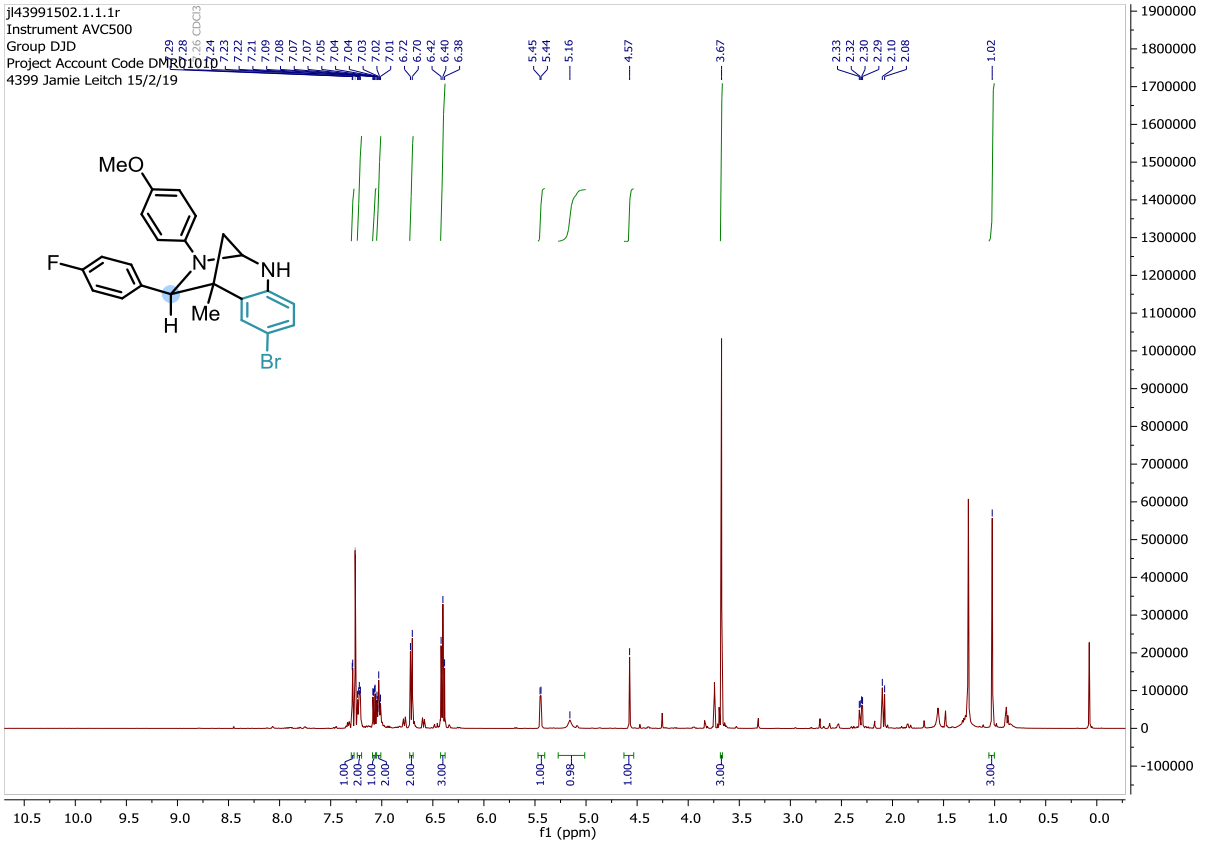
3ak$_{(endo)}$ – ^{19}F NMR (377 MHz, $CDCl_3$)



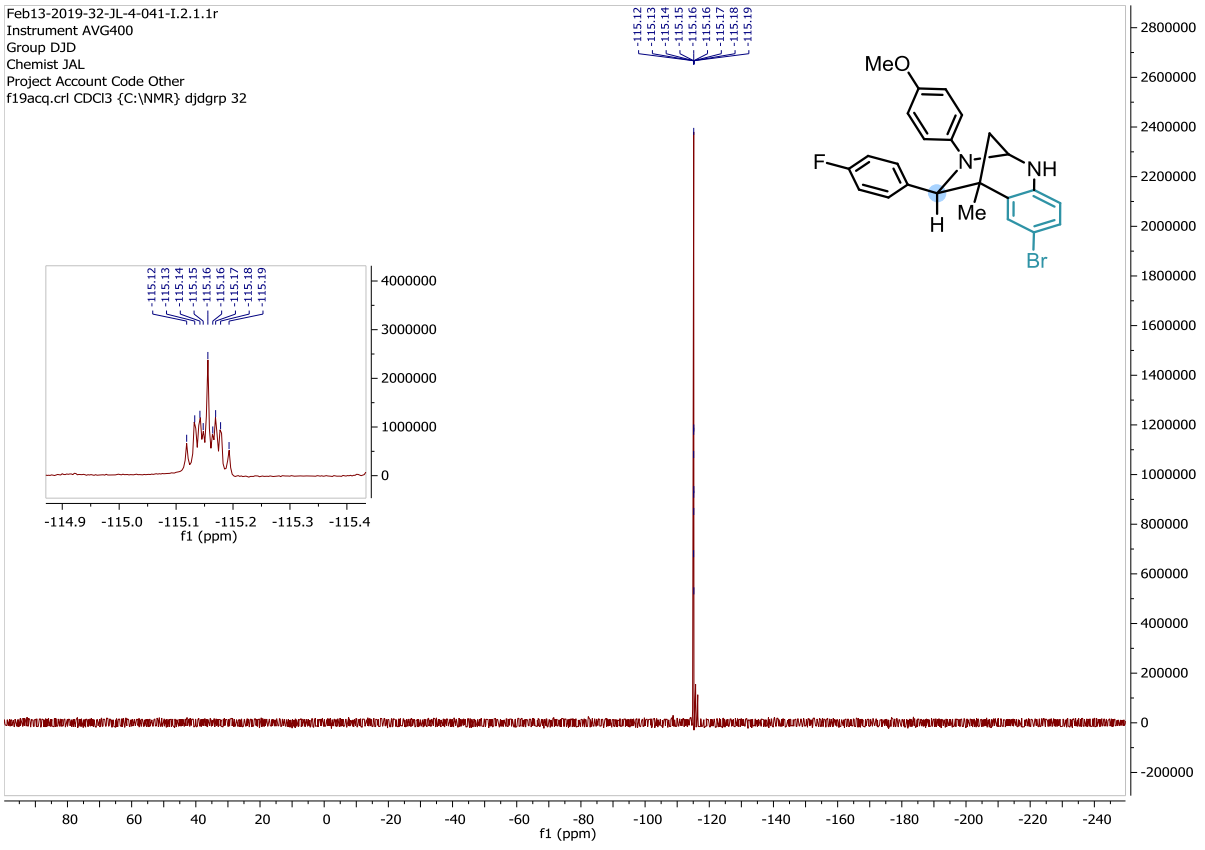
3ak$_{(endo)}$ – ^{13}C NMR (126 MHz, $CDCl_3$)



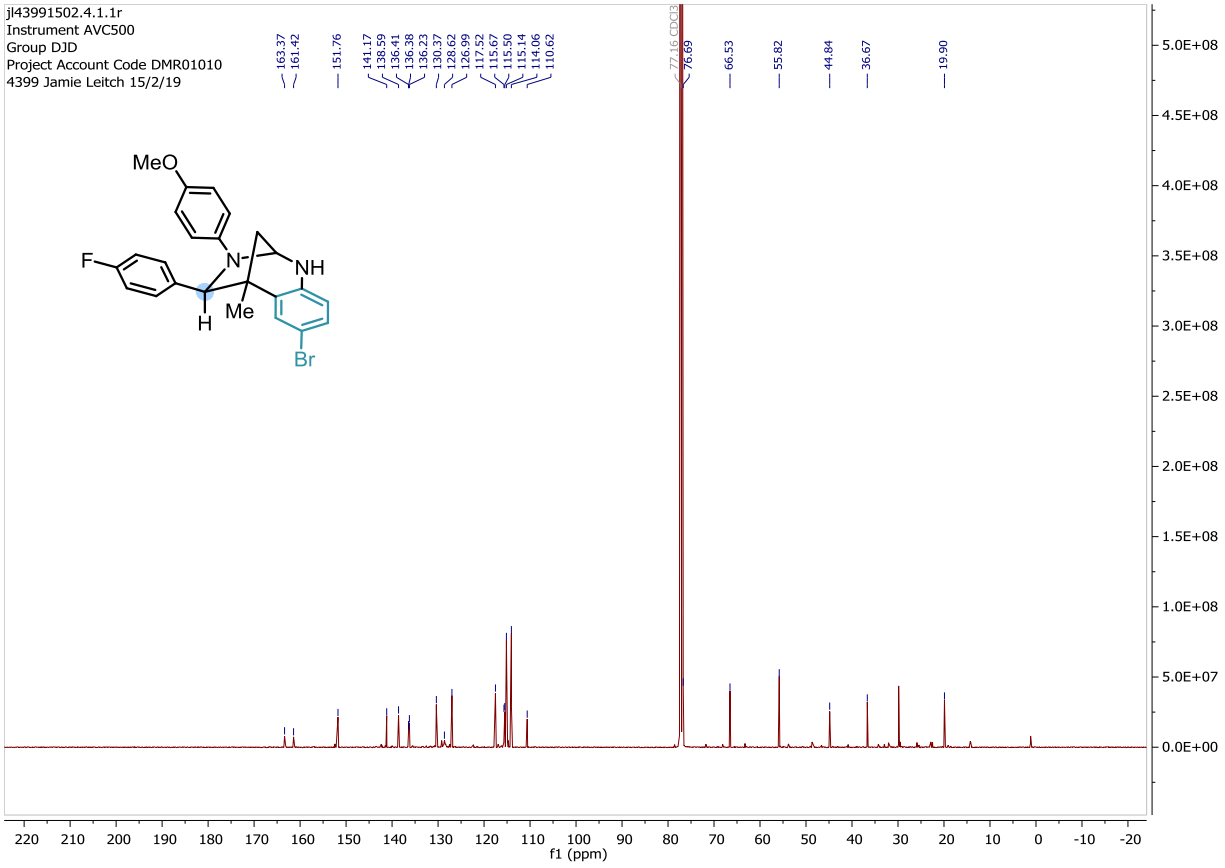
3ak$_{(exo)}$ – ^{1}H NMR (500 MHz, $CDCl_3$)



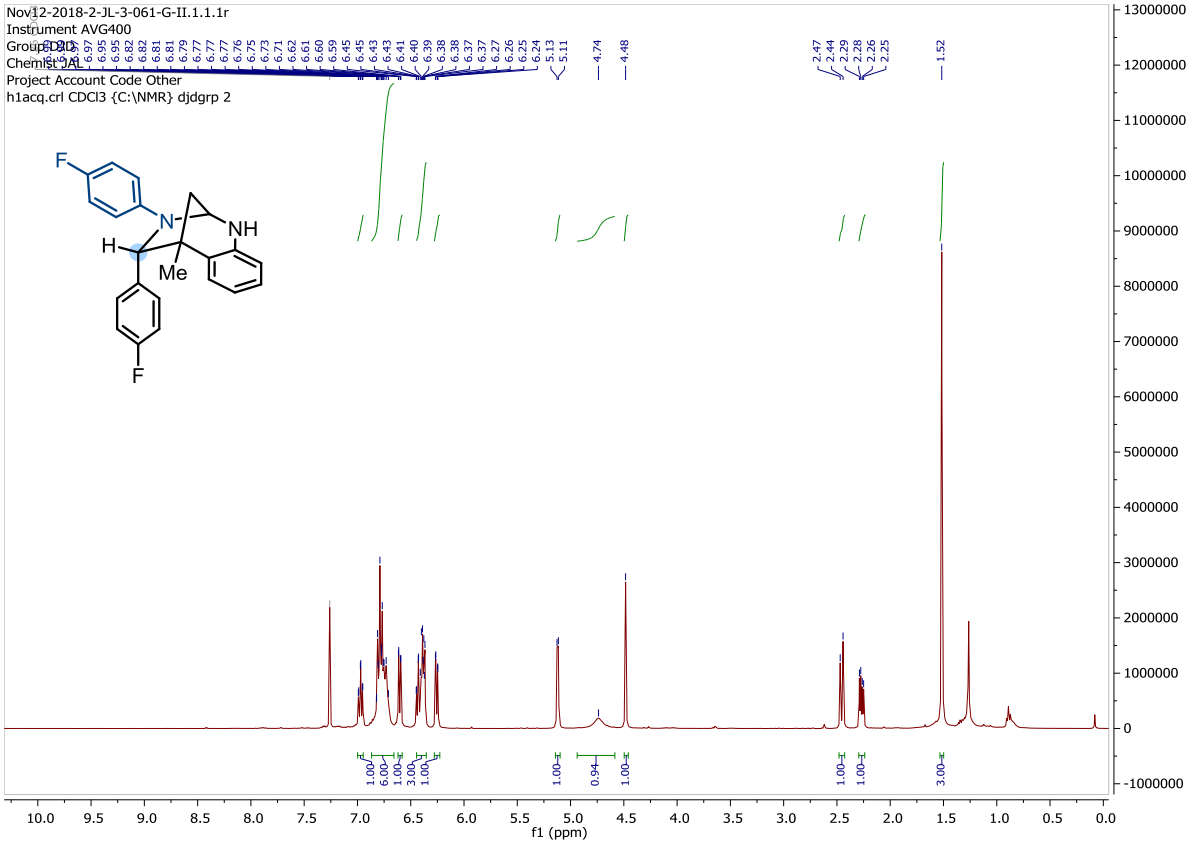
3ak$_{(exo)}$ – ^{19}F NMR (377 MHz, $CDCl_3$)



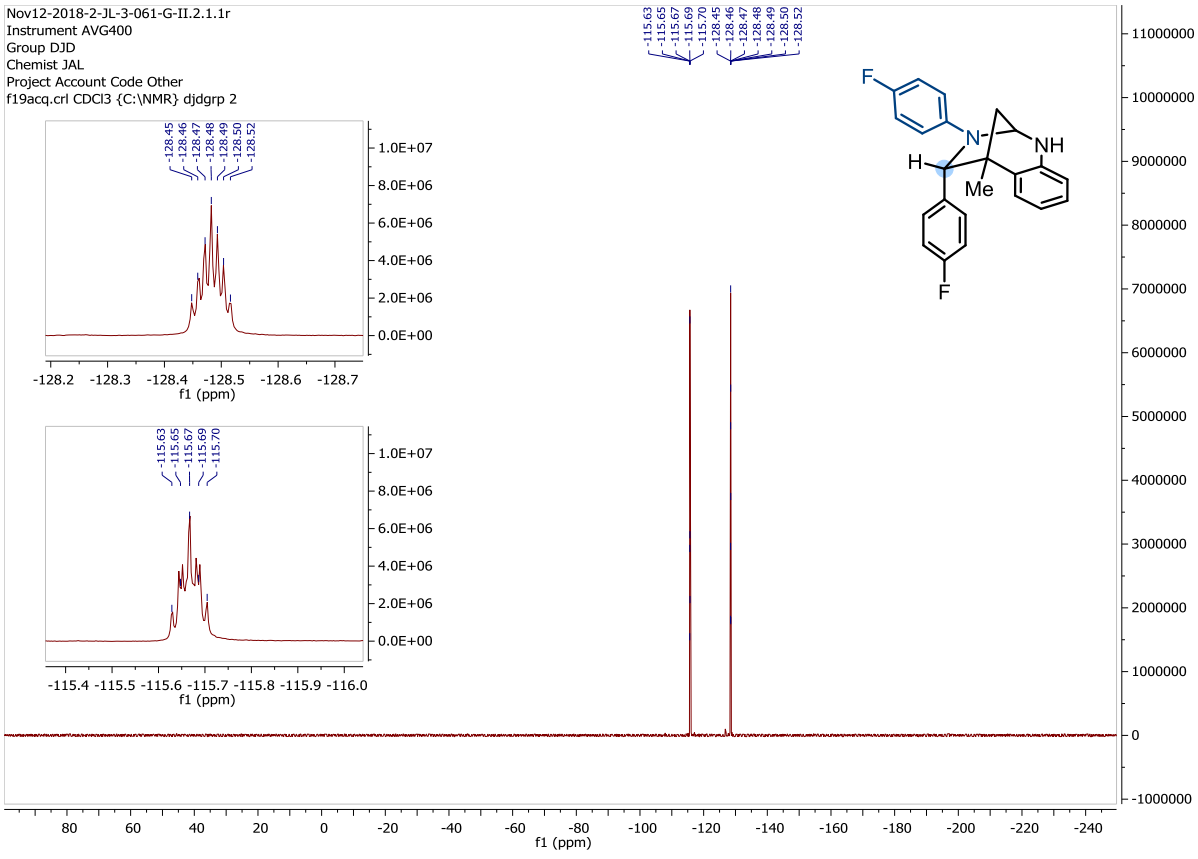
3ak$_{(exo)}$ – ^{13}C NMR (126 MHz, $CDCl_3$)



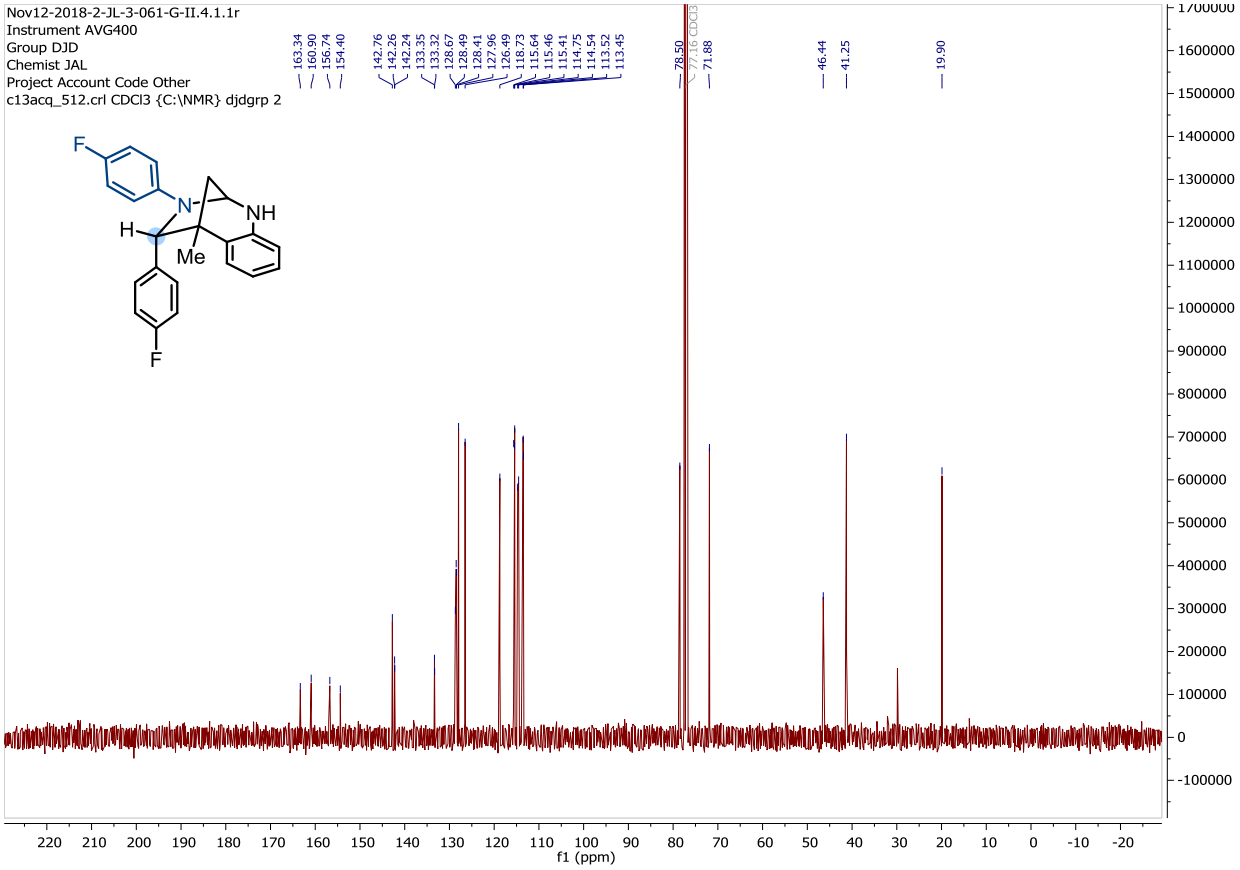
3b(endo) – ^{1}H NMR (400 MHz, $CDCl_3$)



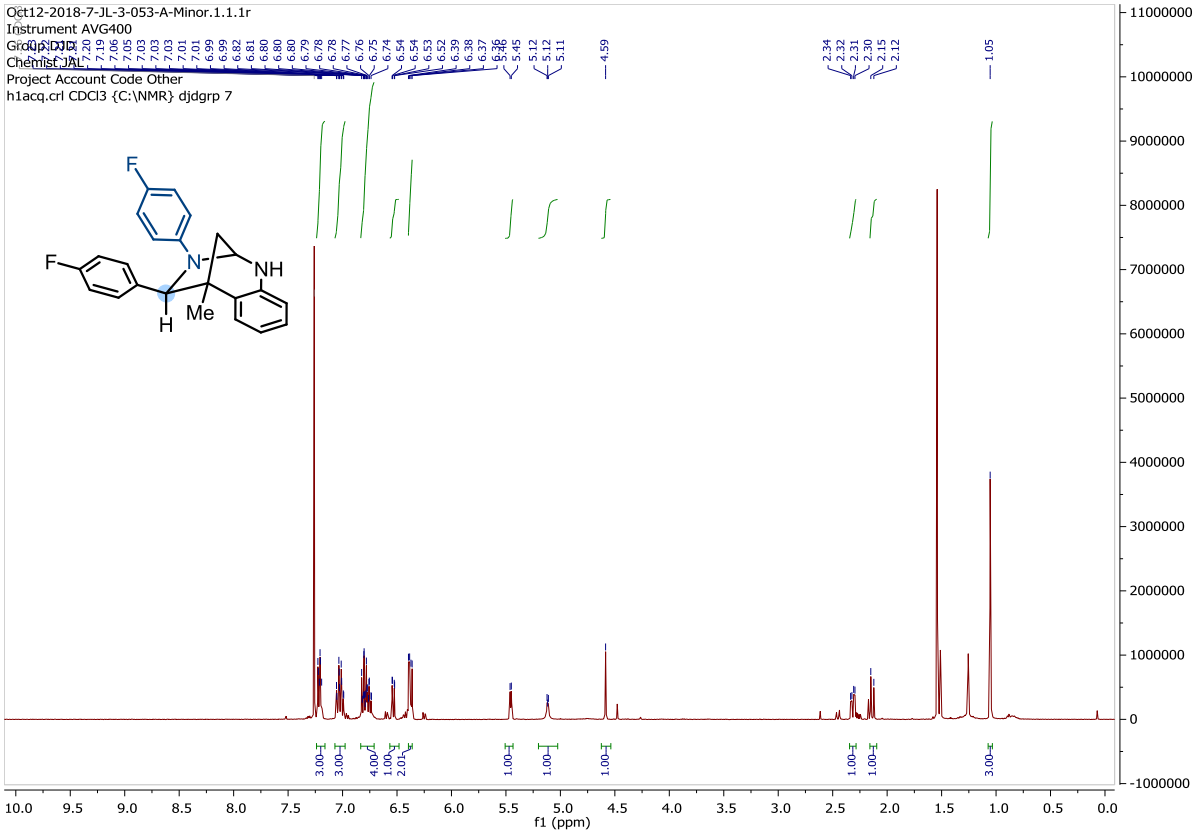
3b(endo) – ^{19}F NMR (377 MHz, $CDCl_3$)



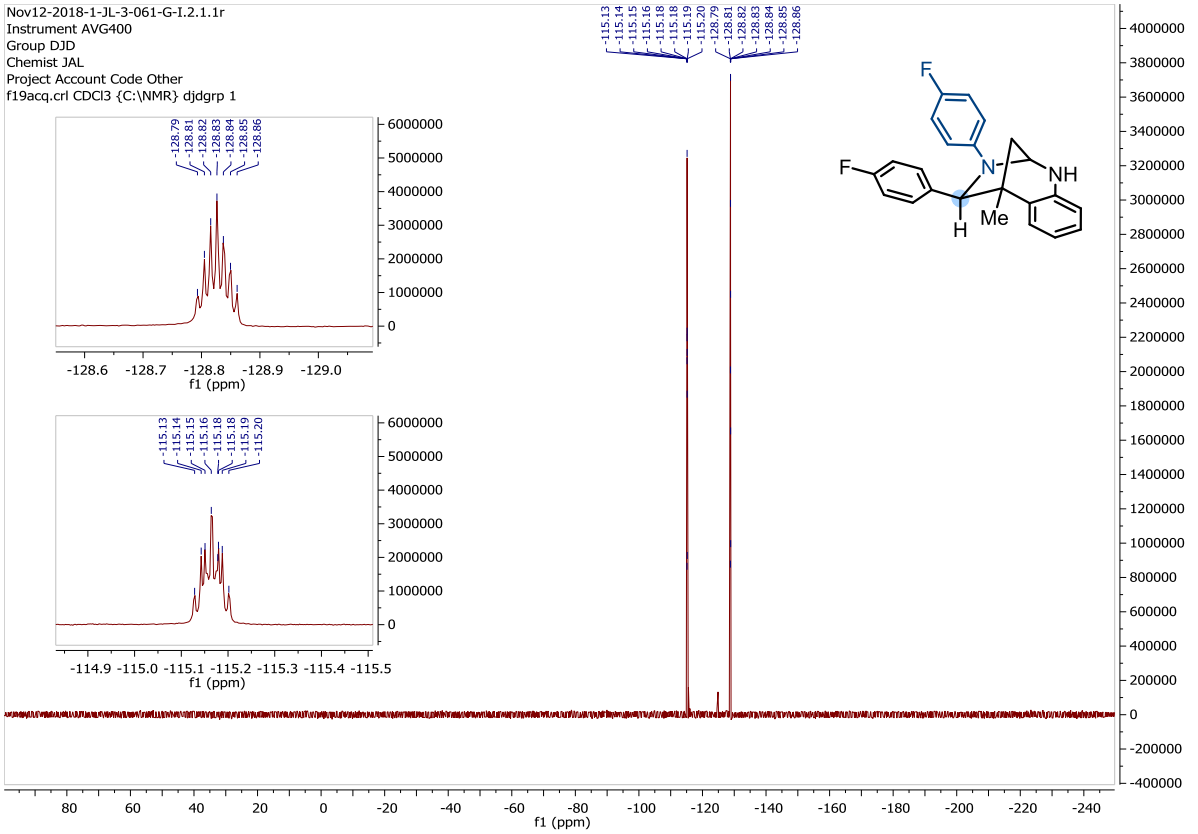
3b$_{(endo)}$ – ^{13}C NMR (101 MHz, $CDCl_3$)



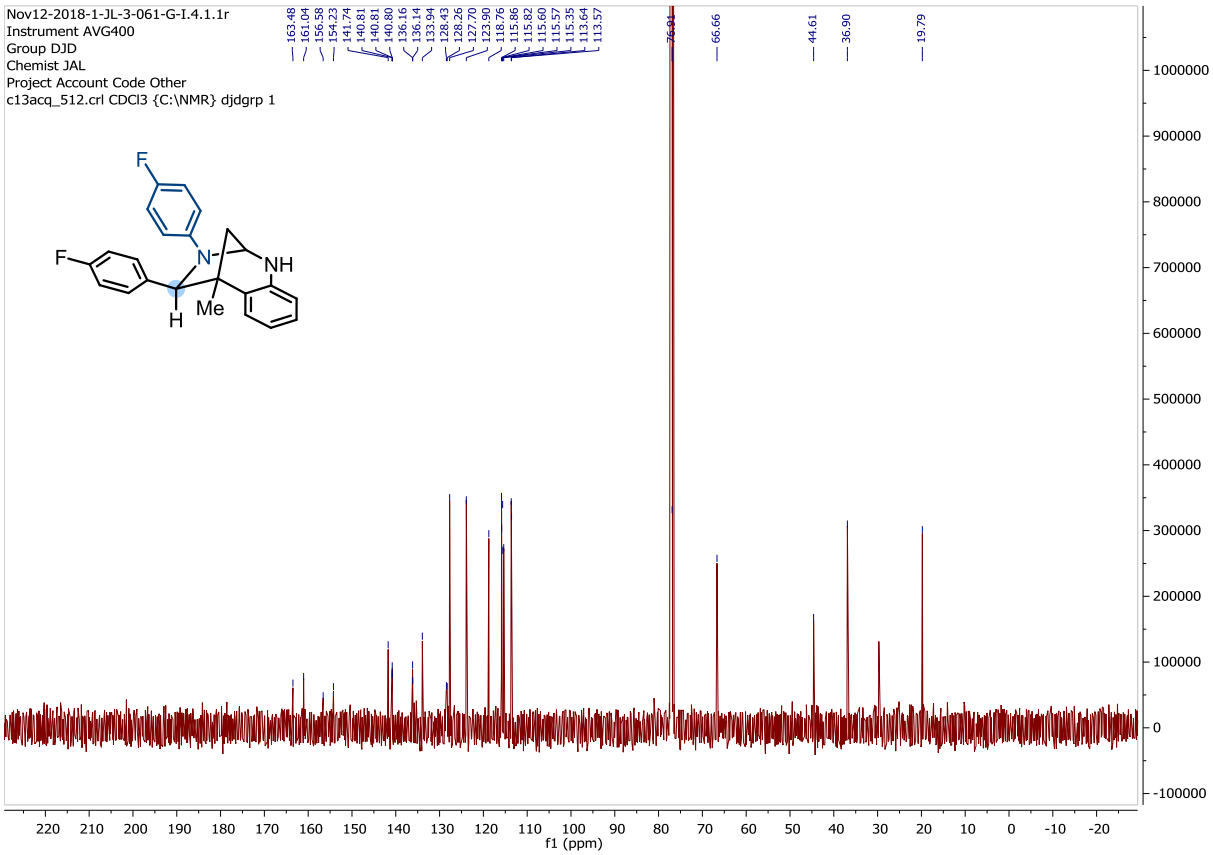
3b(exo) – ^{1}H NMR (400 MHz, $CDCl_3$)



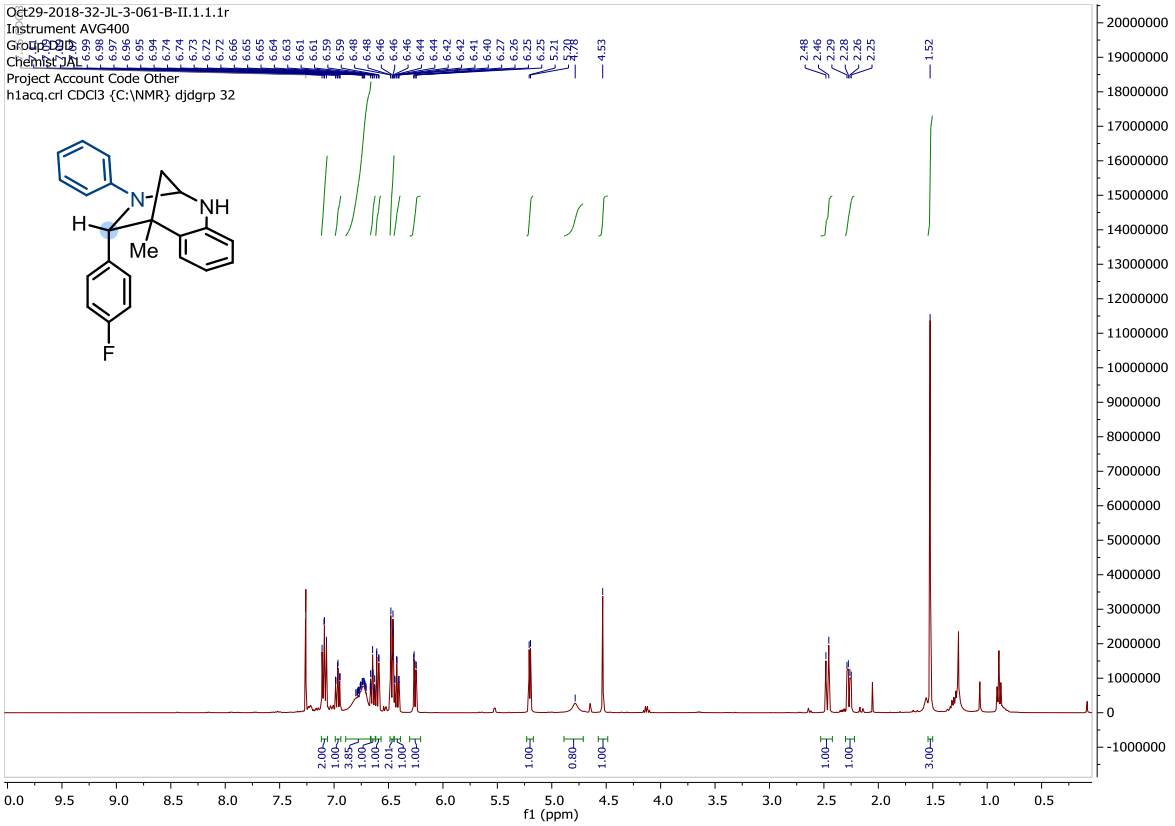
3b(exo) – ^{19}F NMR (377 MHz, $CDCl_3$)



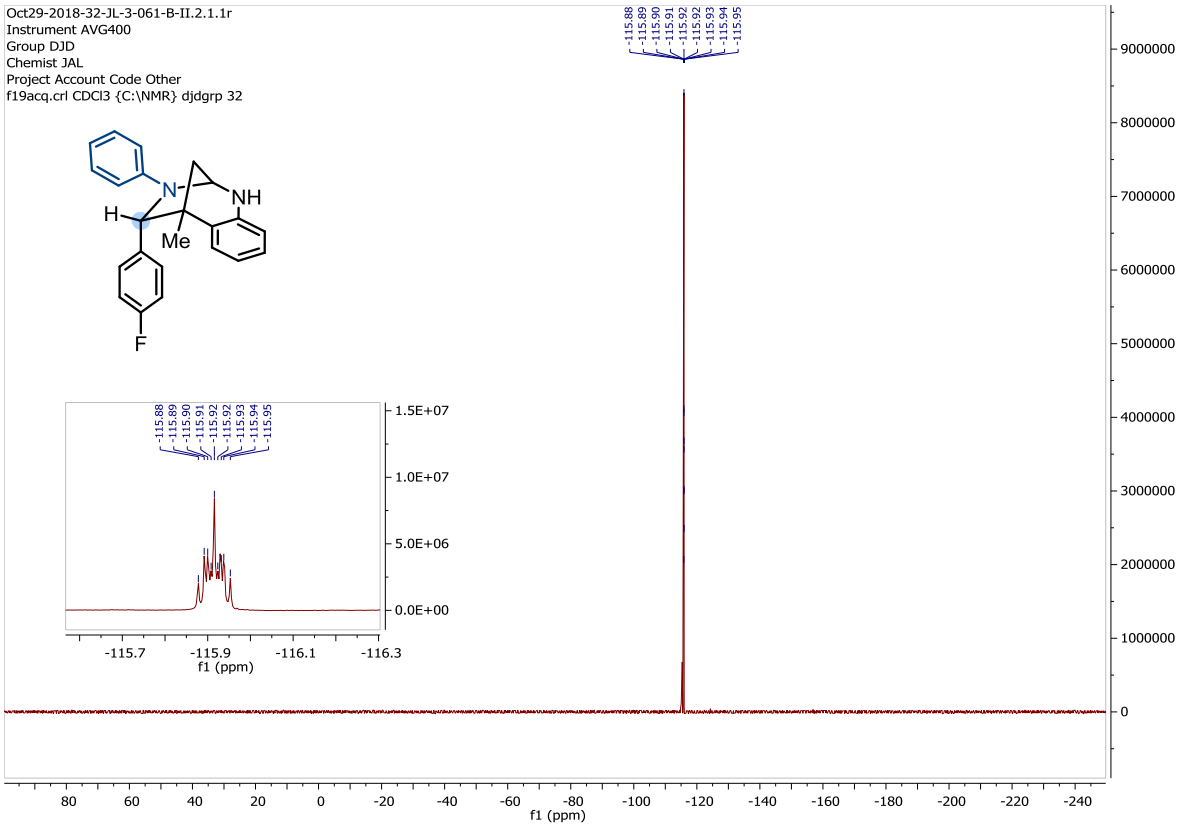
3b$_{(exo)}$ – ^{13}C NMR (101 MHz, $CDCl_3$)



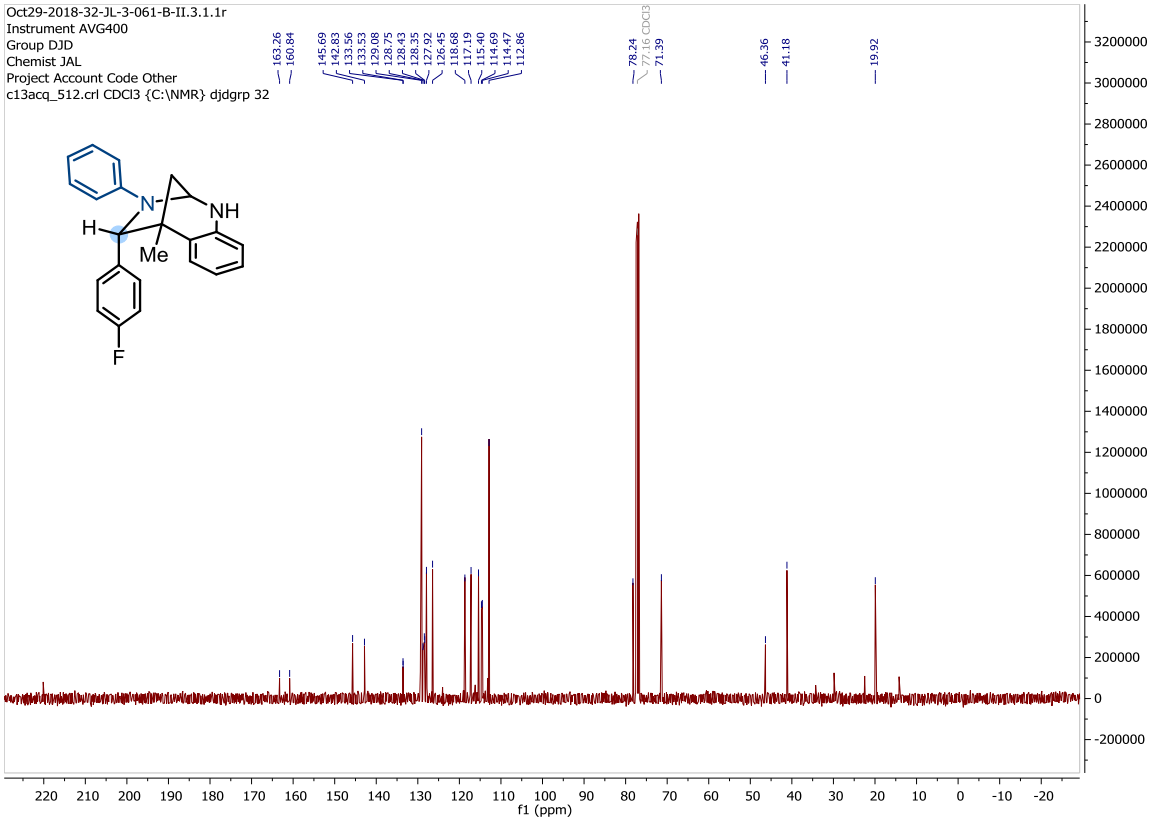
3c$_{(endo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



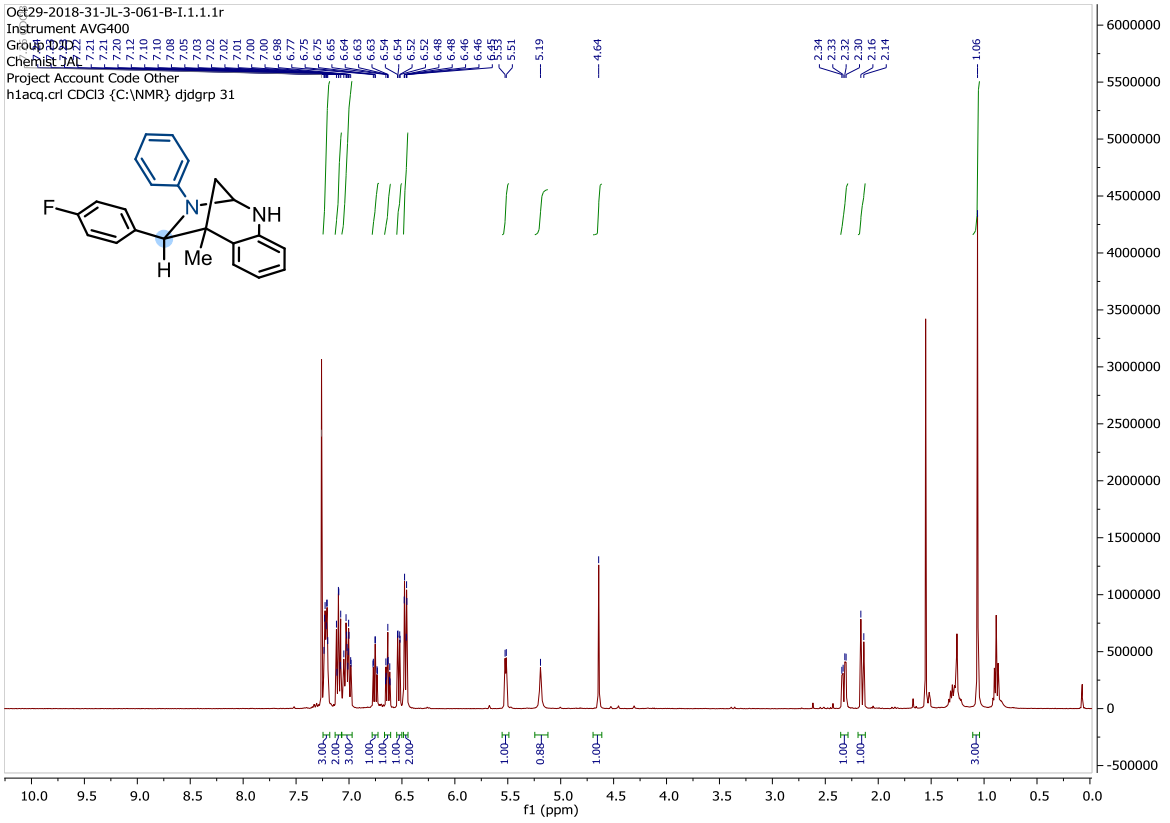
3c$_{(endo)}$ – ^{19}F NMR (377 MHz, $CDCl_3$)



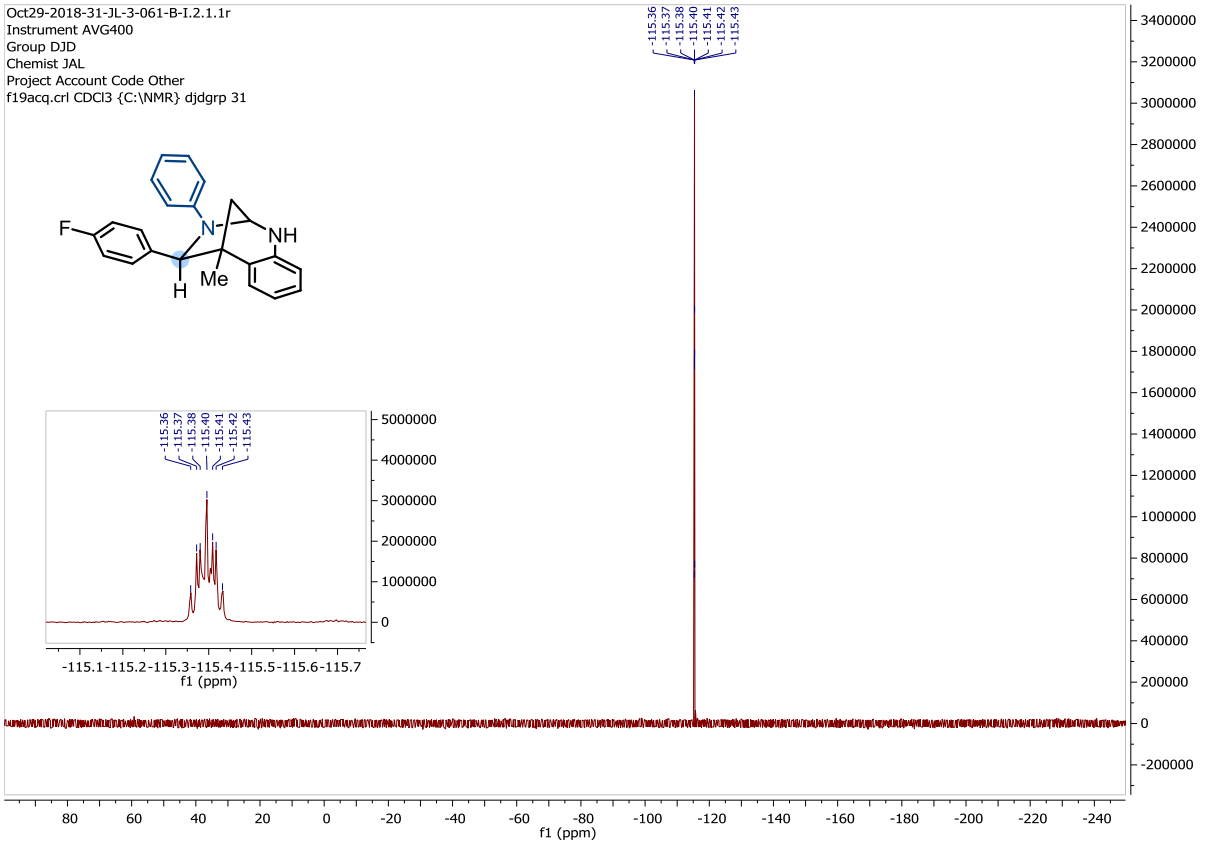
3c$_{(endo)}$ – ^{13}C NMR (101 MHz, $CDCl_3$)



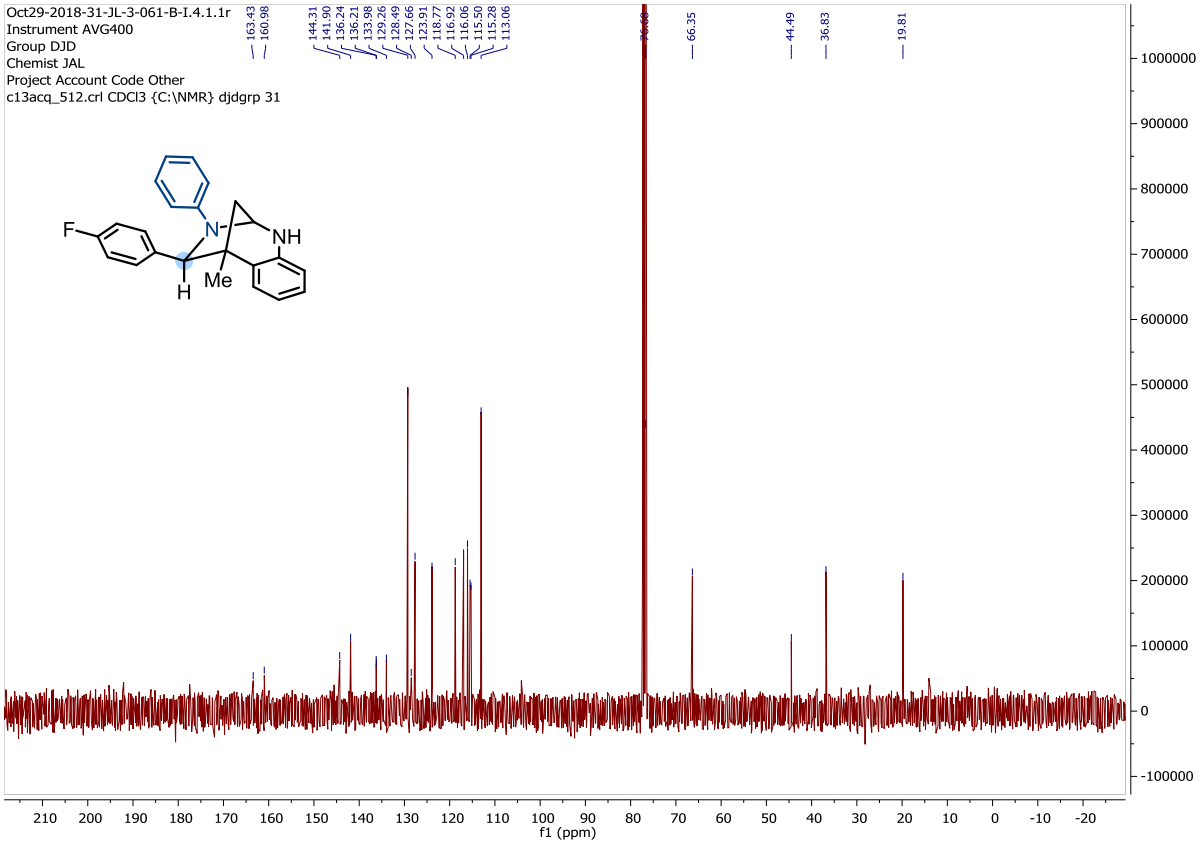
3c$_{(exo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



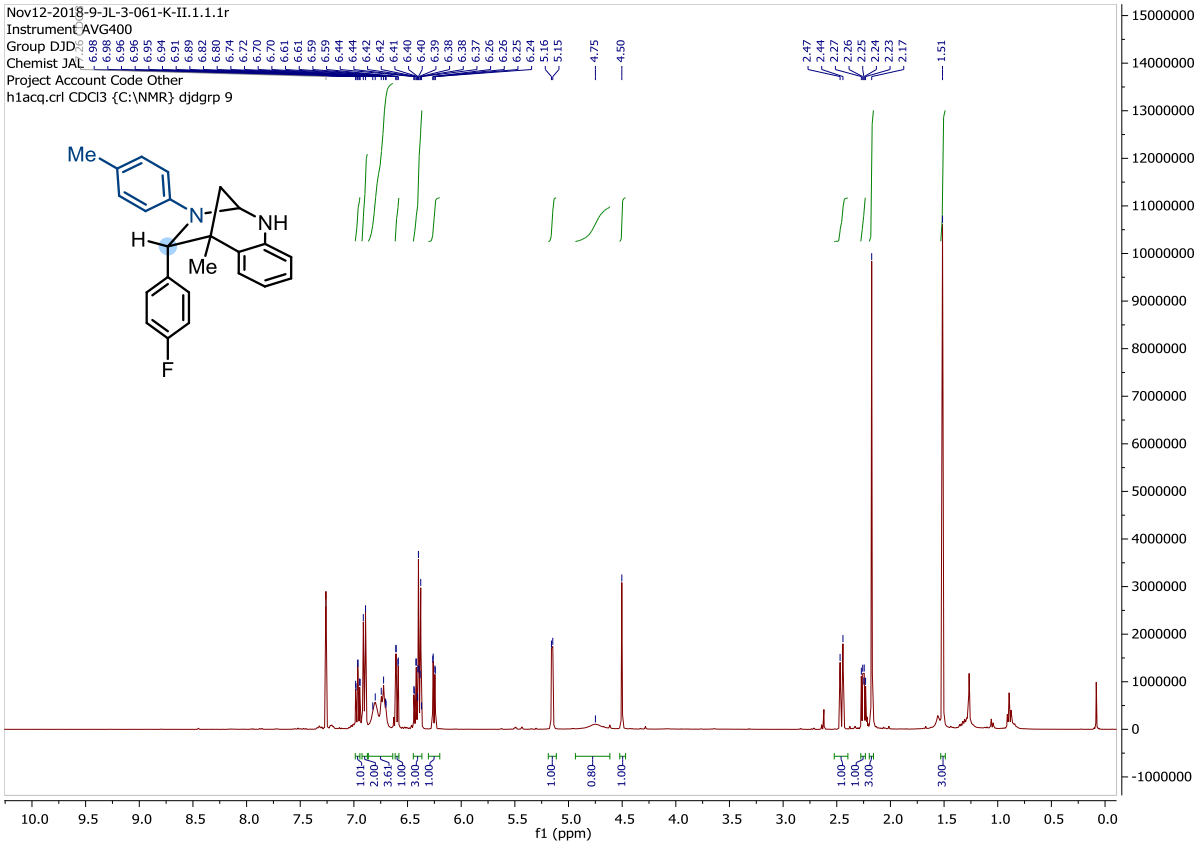
3c$_{(exo)}$ – ^{19}F NMR (377 MHz, $CDCl_3$)



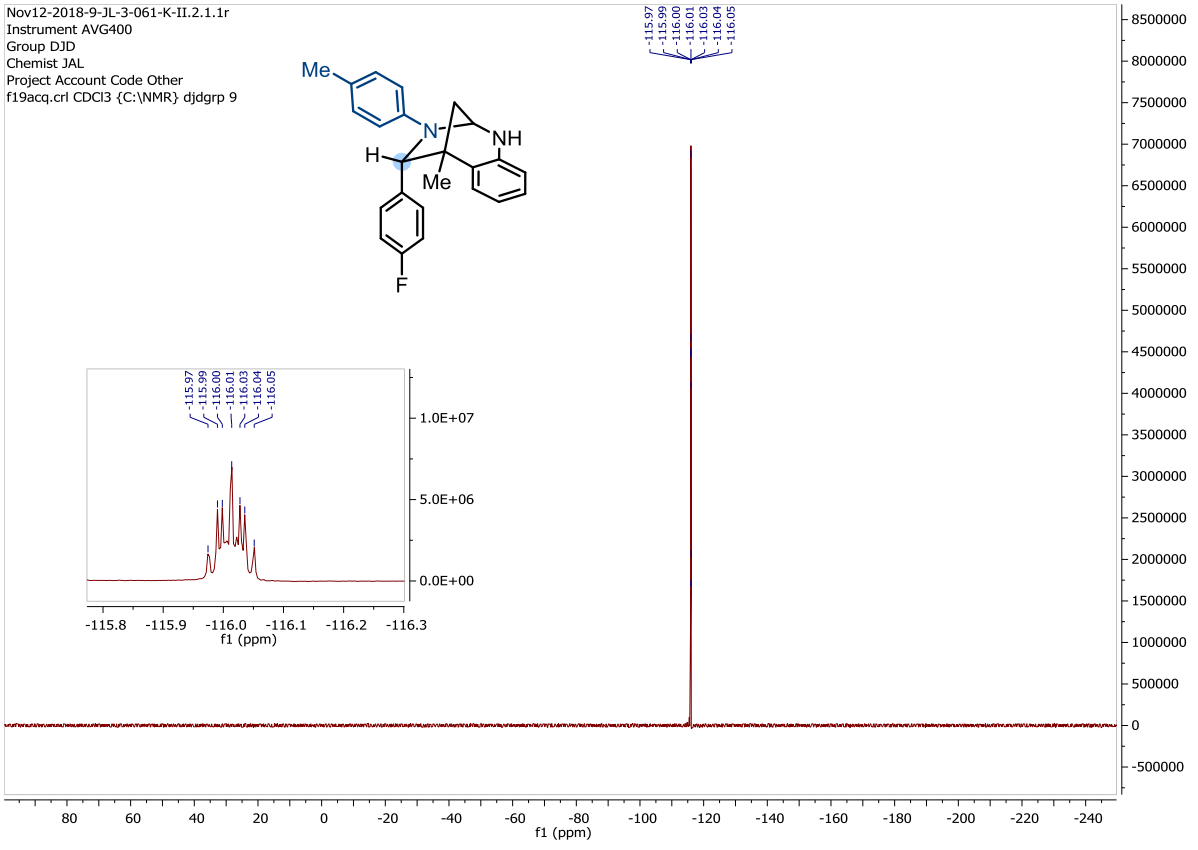
3c$_{(exo)}$ – ^{13}C NMR (101 MHz, $CDCl_3$)



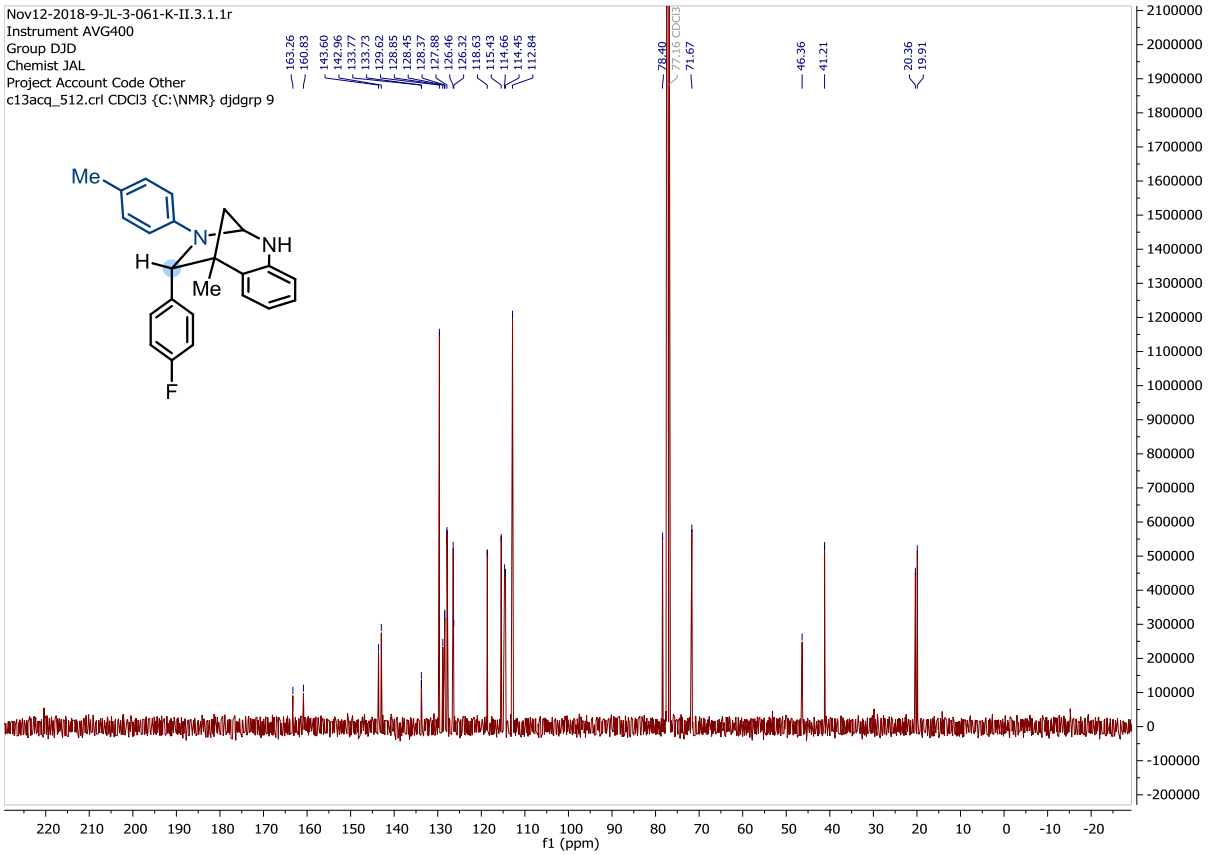
3d$_{(endo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



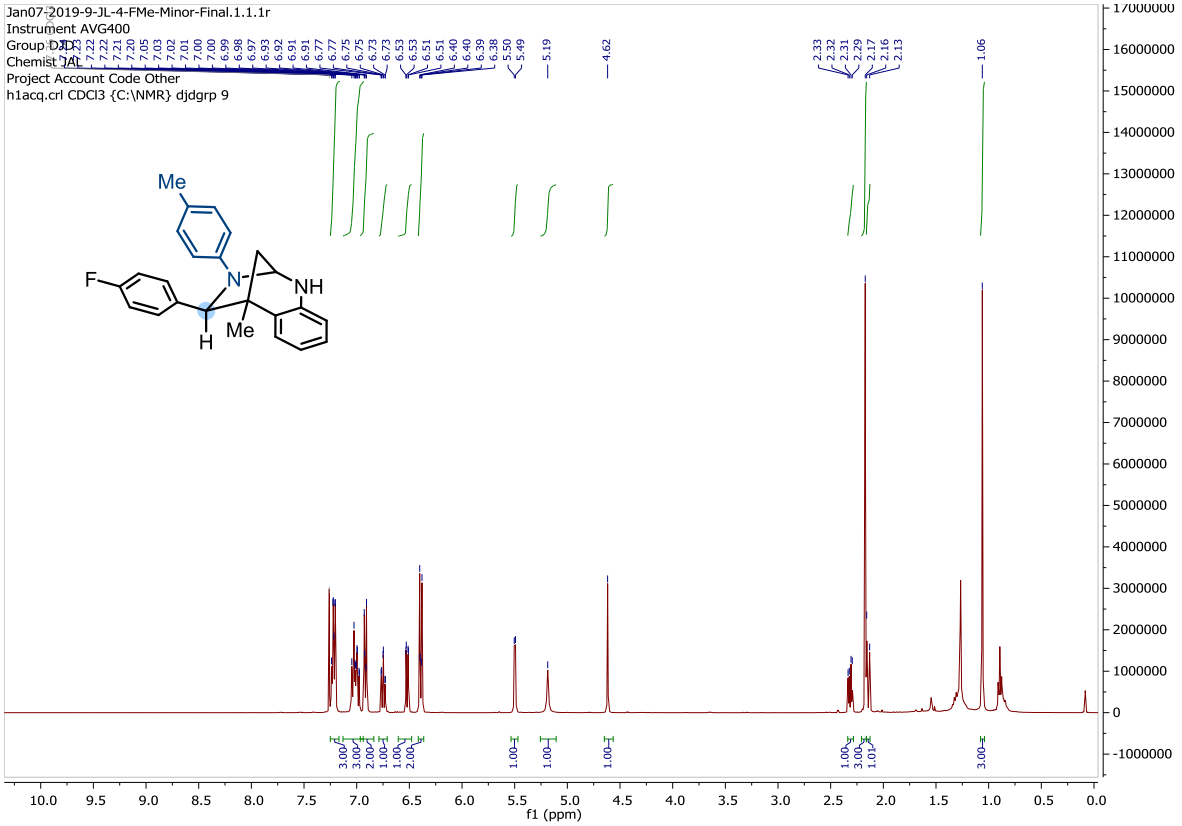
3d$_{(endo)}$ – ^{19}F NMR (377 MHz, $CDCl_3$)



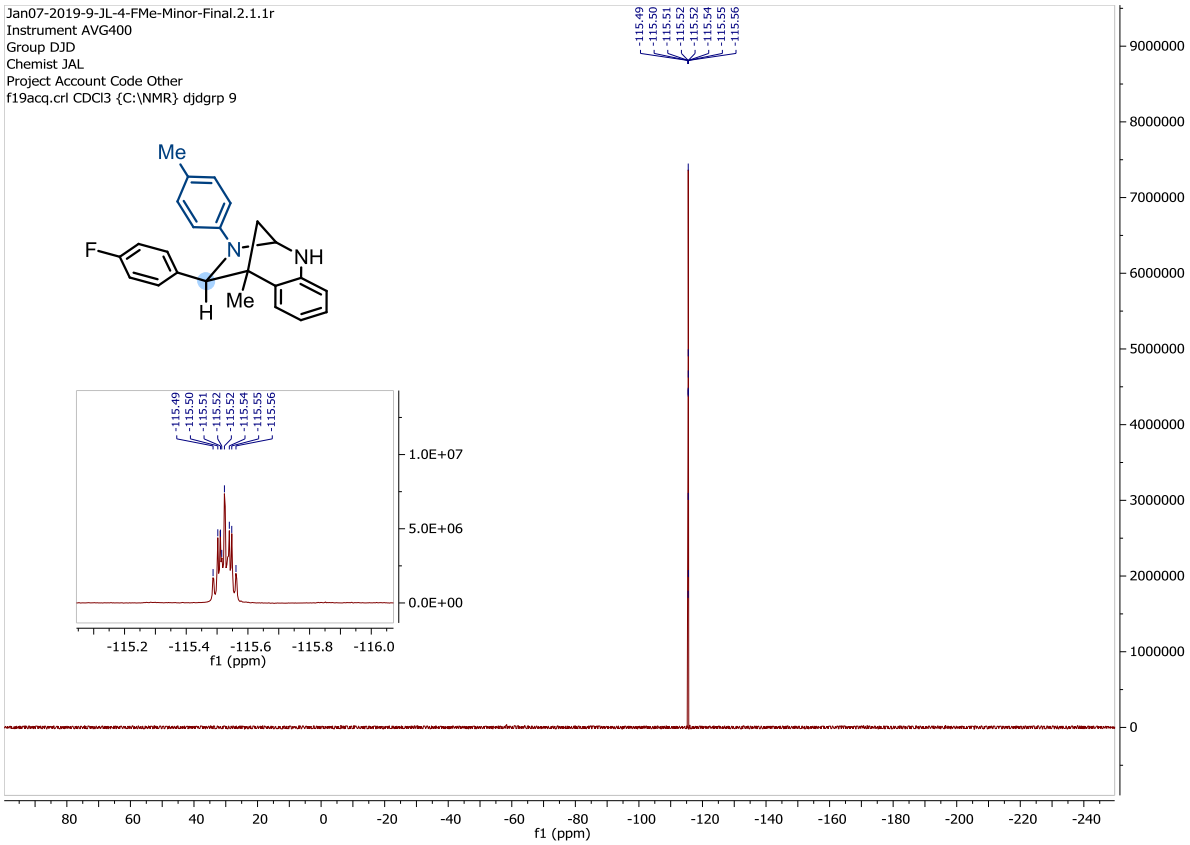
3d$_{(endo)}$ – ^{13}C NMR (101 MHz, $CDCl_3$)



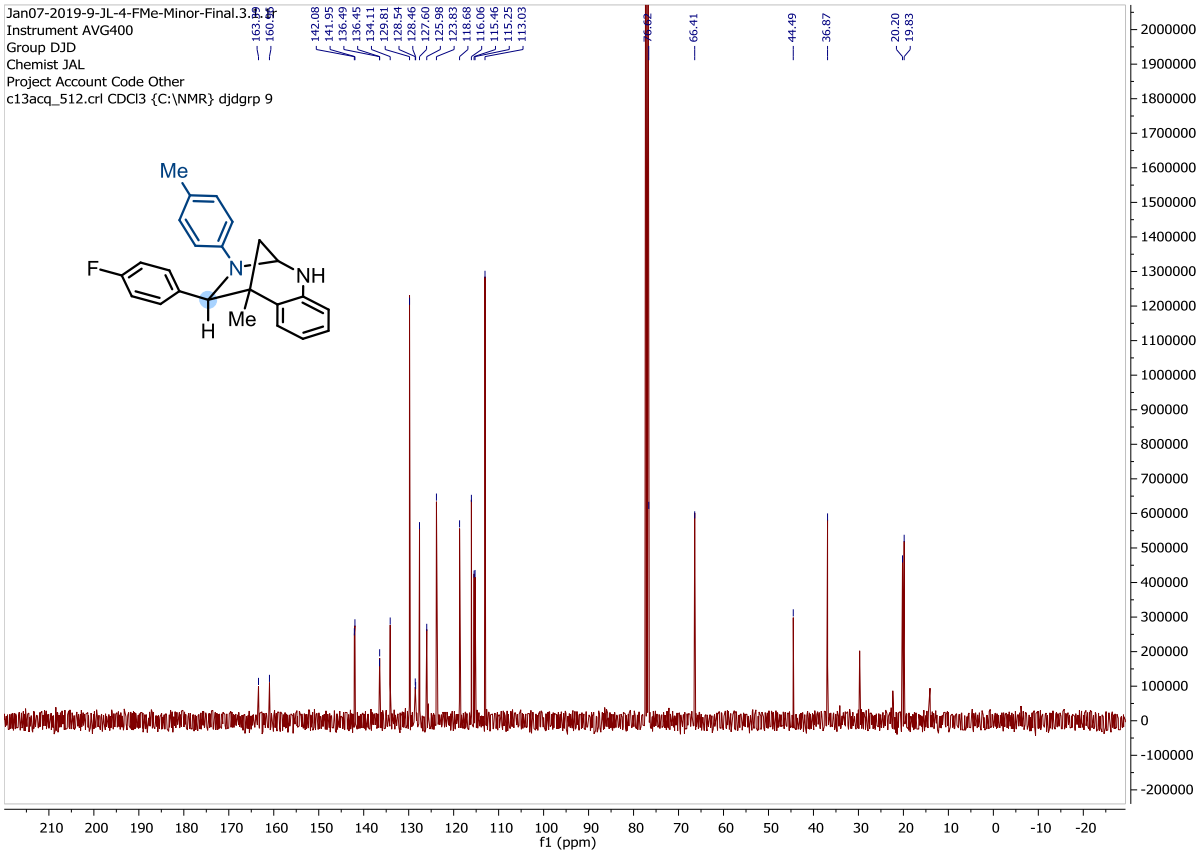
3d$_{(exo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



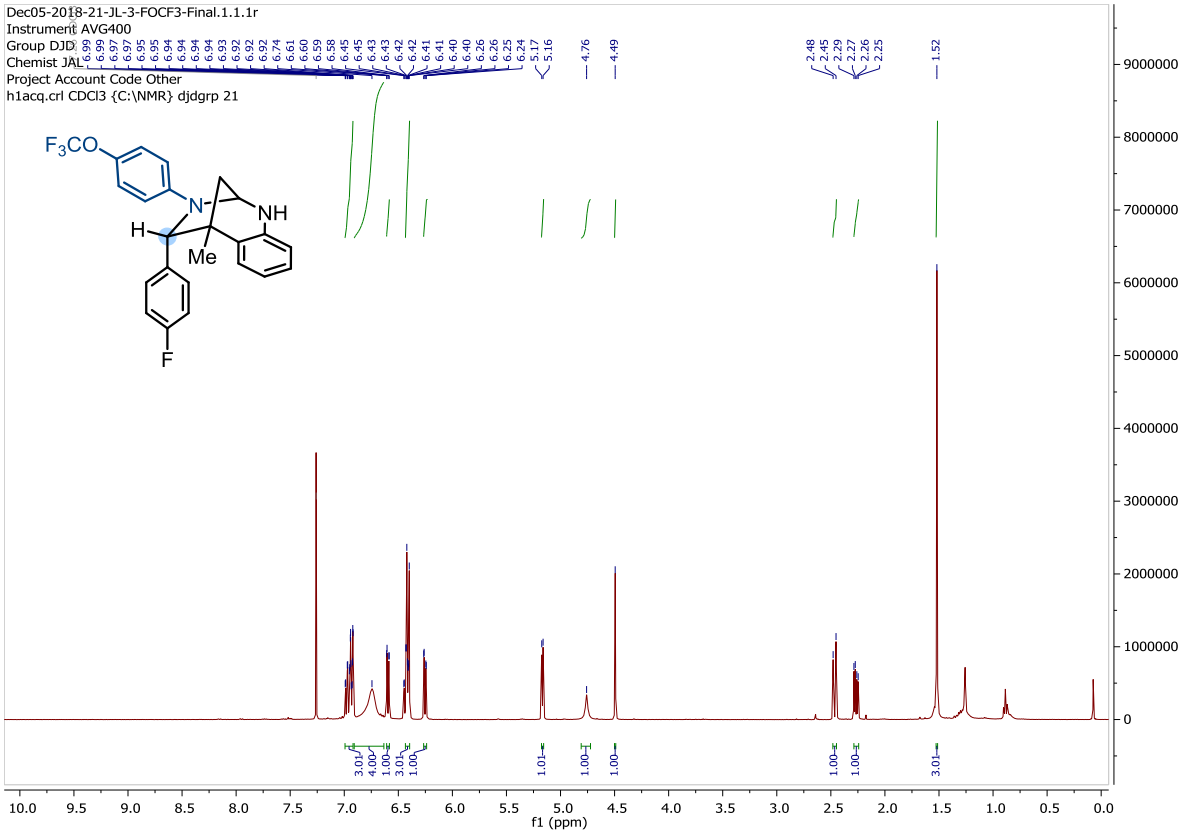
3d$_{(exo)}$ – ^{19}F NMR (377 MHz, $CDCl_3$)



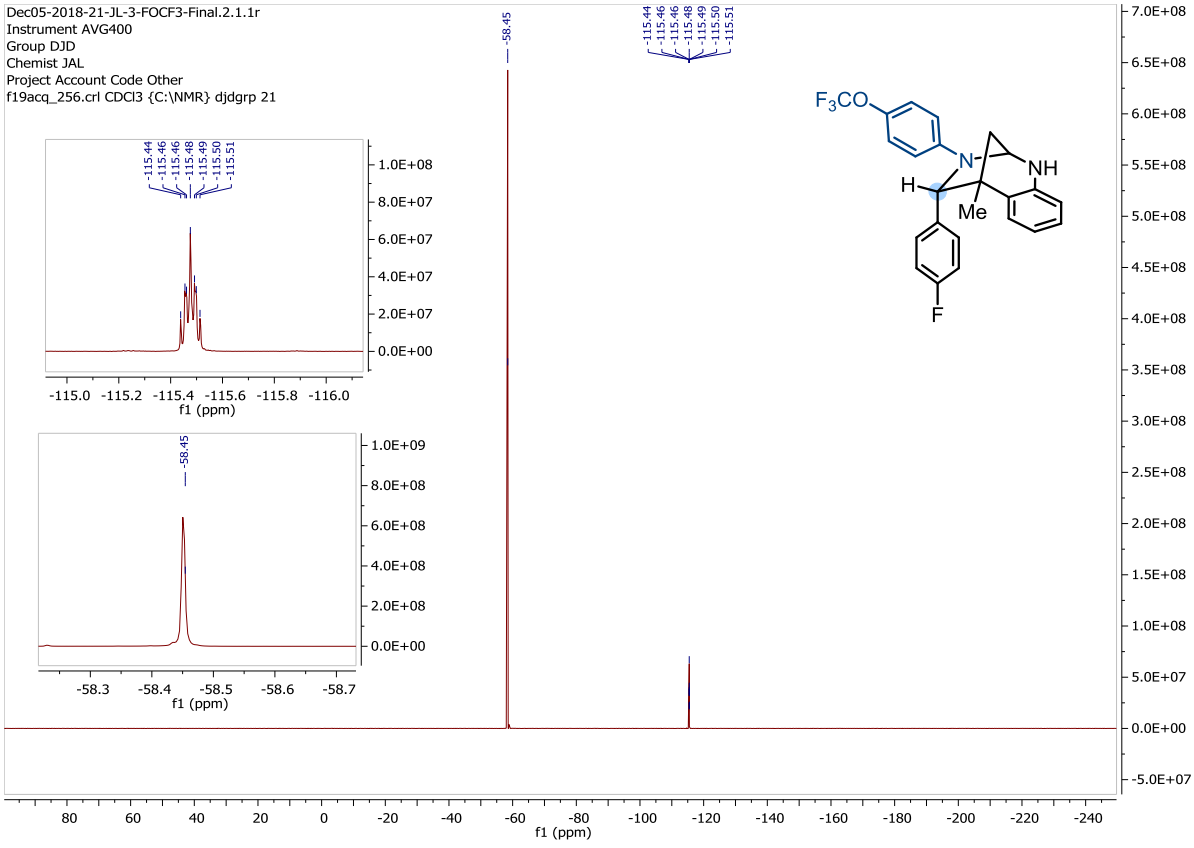
3d$_{(exo)}$ – ^{13}C NMR (101 MHz, $CDCl_3$)



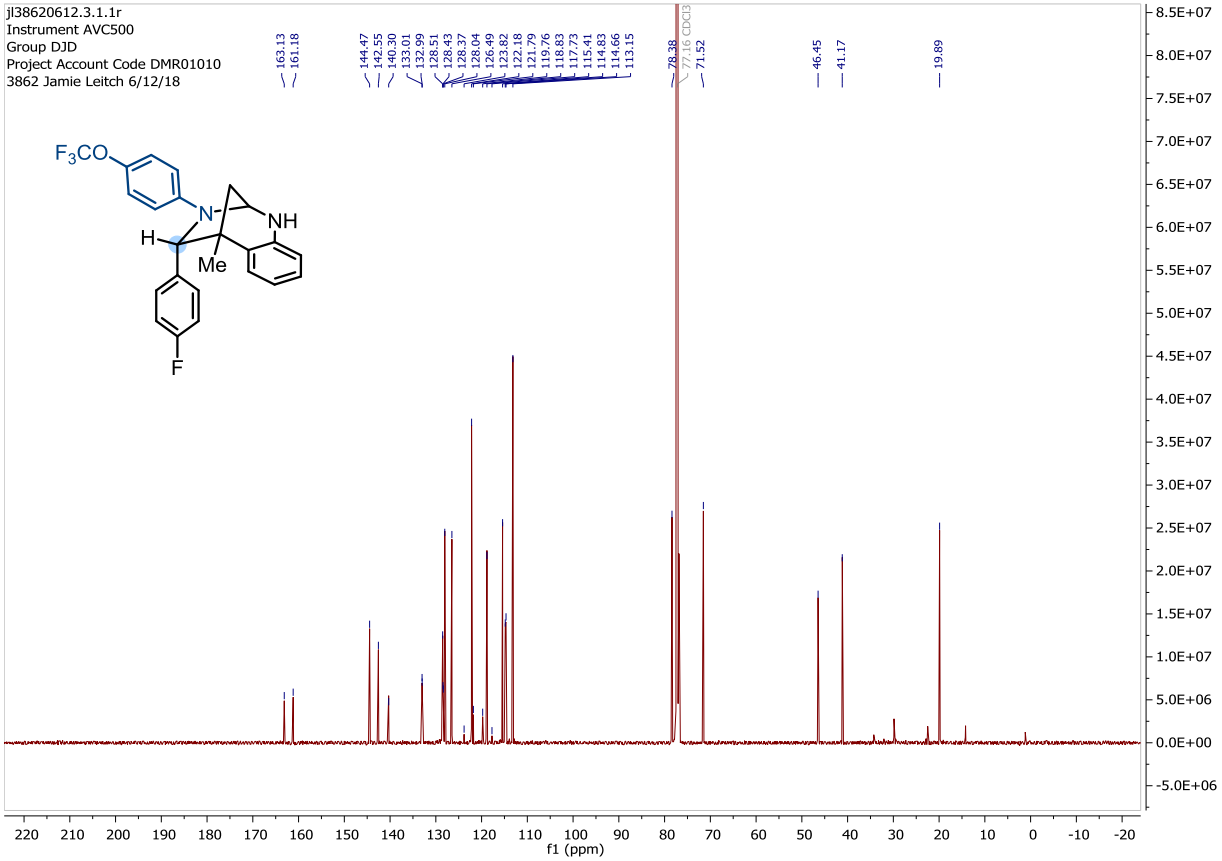
3e$_{(endo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



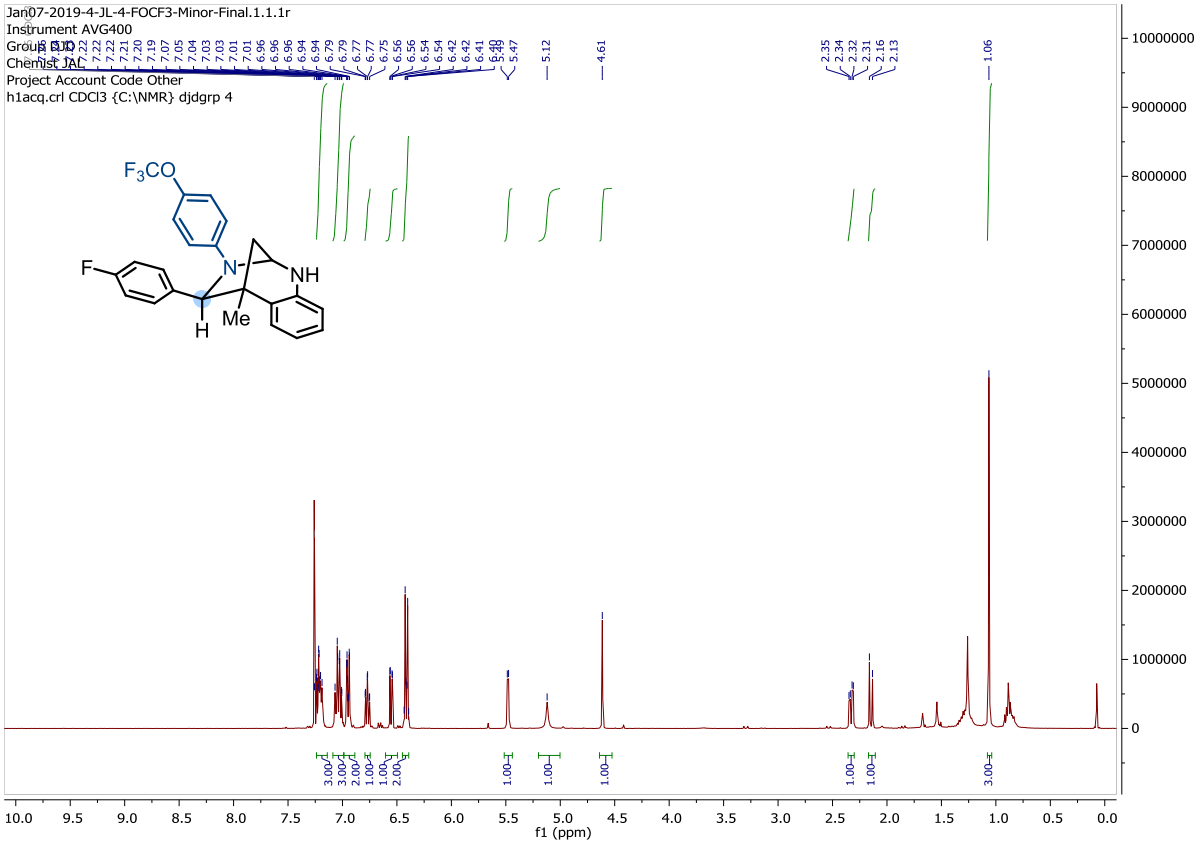
3e$_{(endo)}$ – ^{19}F NMR (377 MHz, $CDCl_3$)



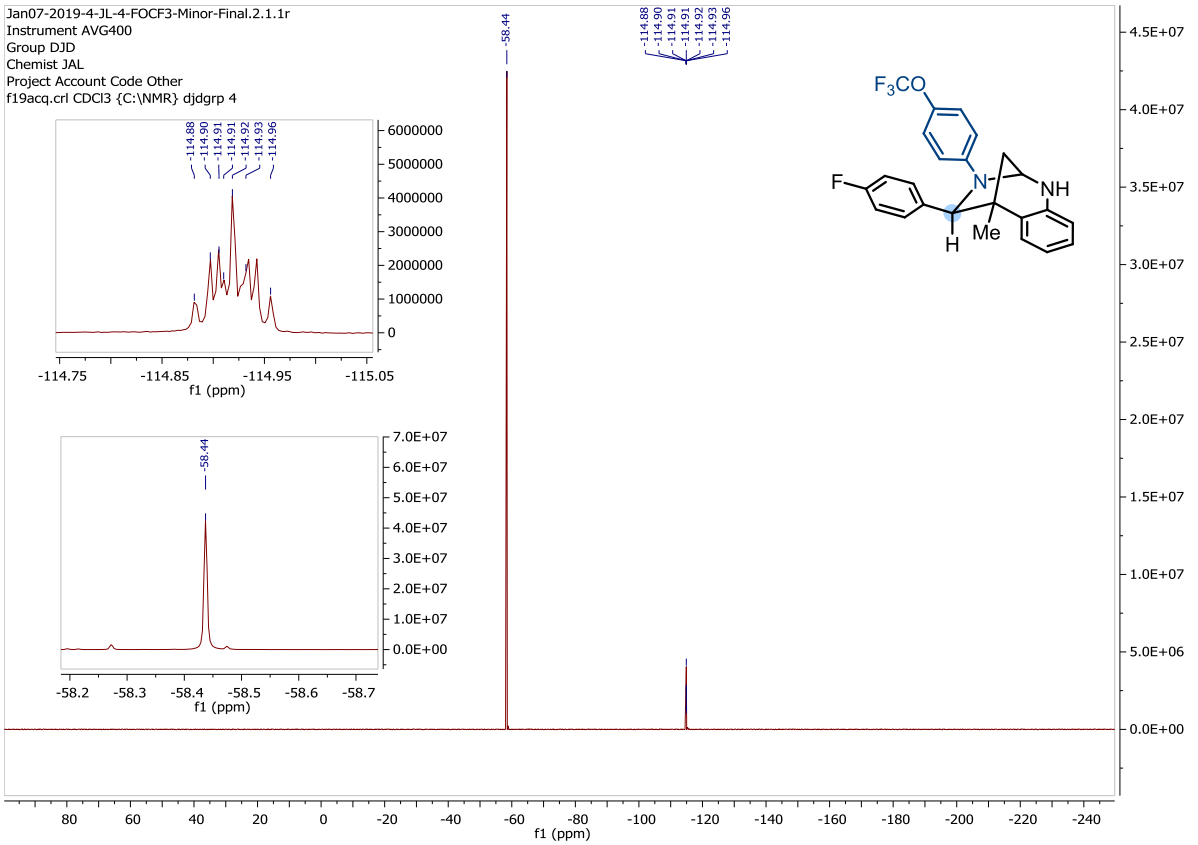
3e$_{(endo)}$ – ^{13}C NMR (126 MHz, $CDCl_3$)



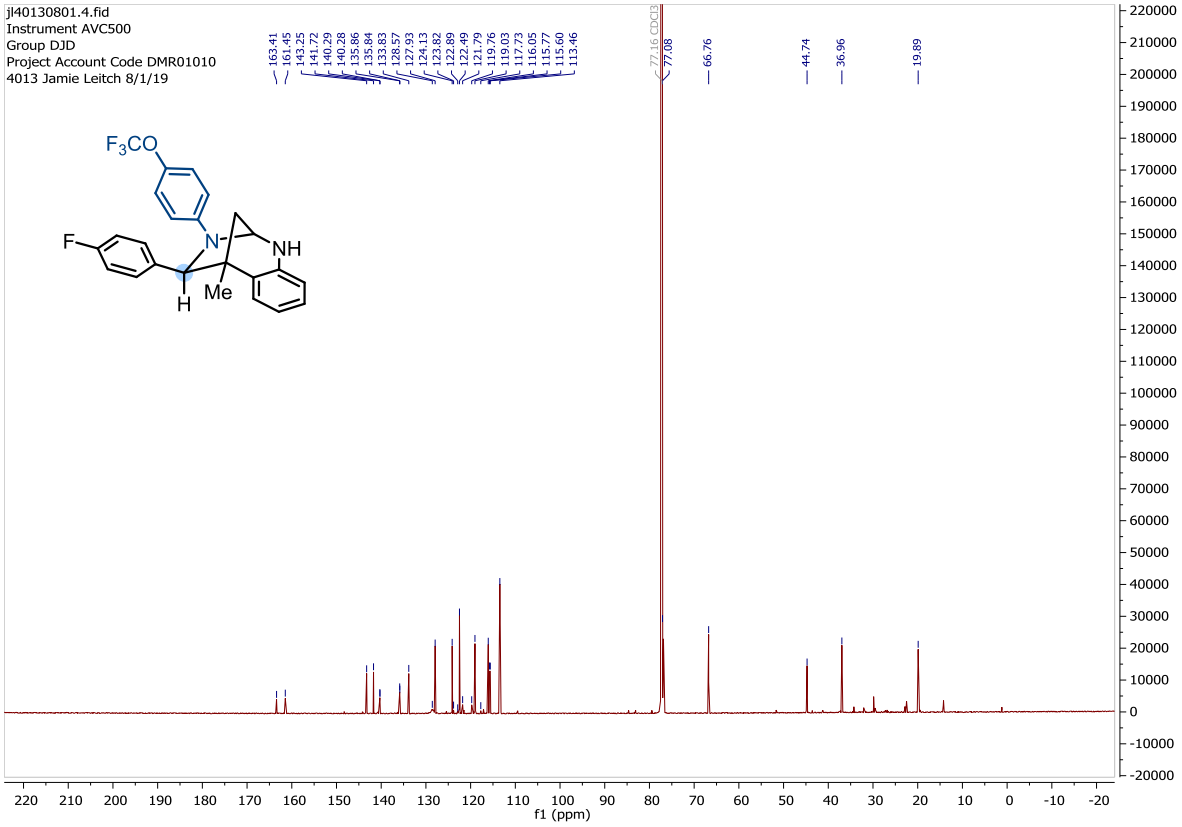
3e(exo) – ^{1}H NMR (400 MHz, $CDCl_3$)



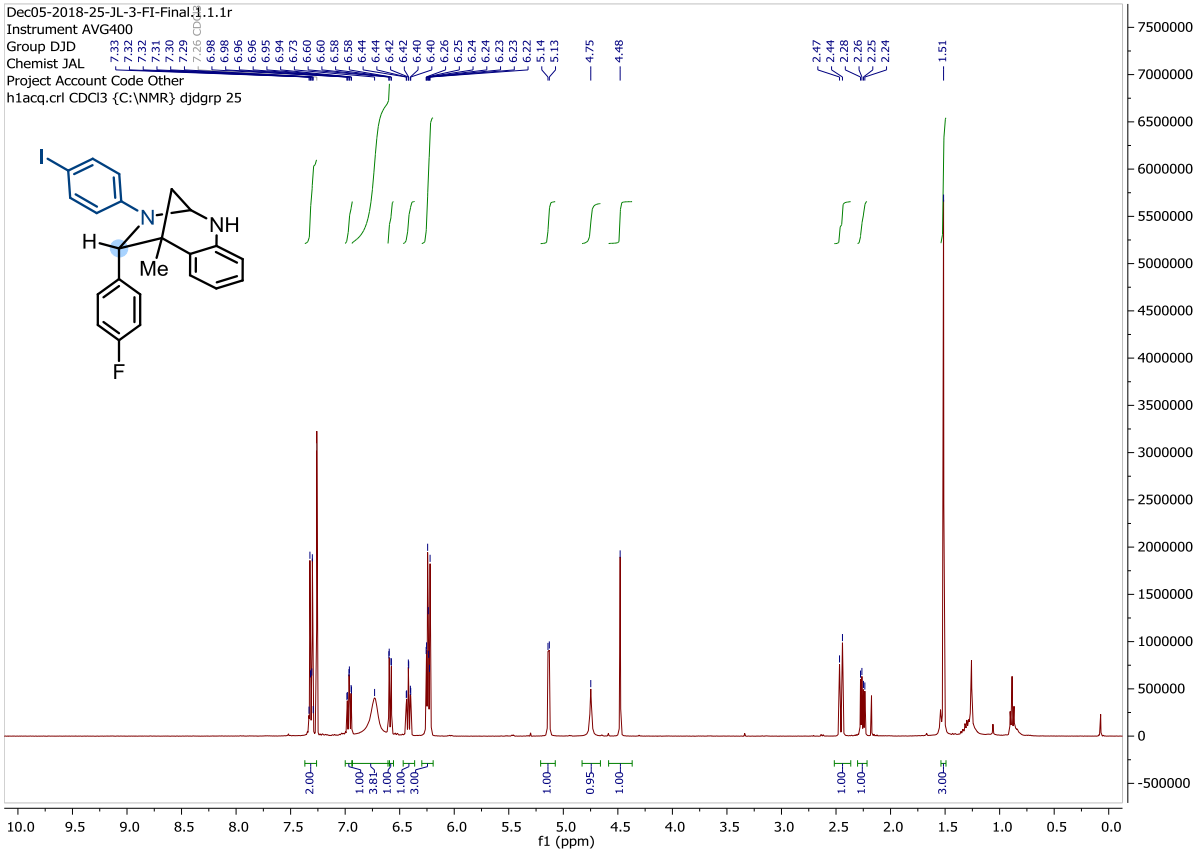
3e(exo) – ^{19}F NMR (377 MHz, $CDCl_3$)



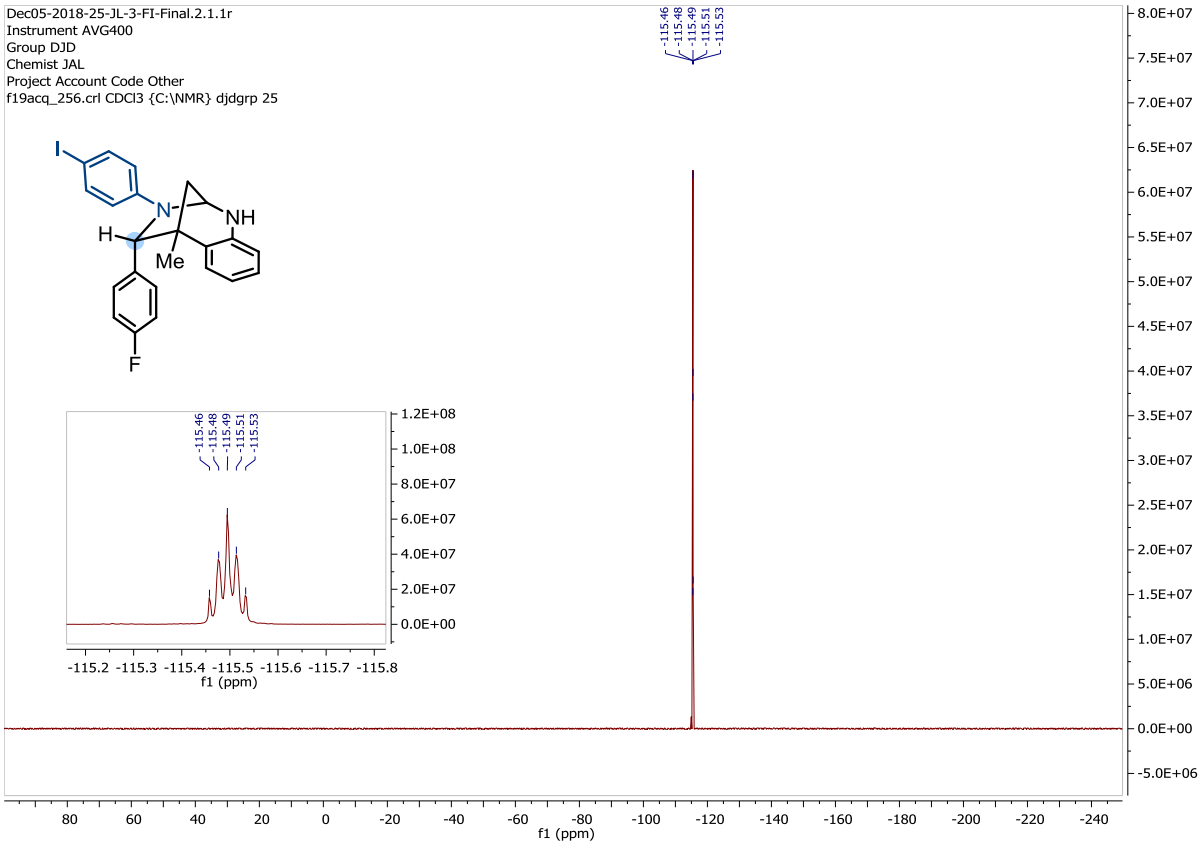
3e$_{(exo)}$ – ^{13}C NMR (126 MHz, $CDCl_3$)



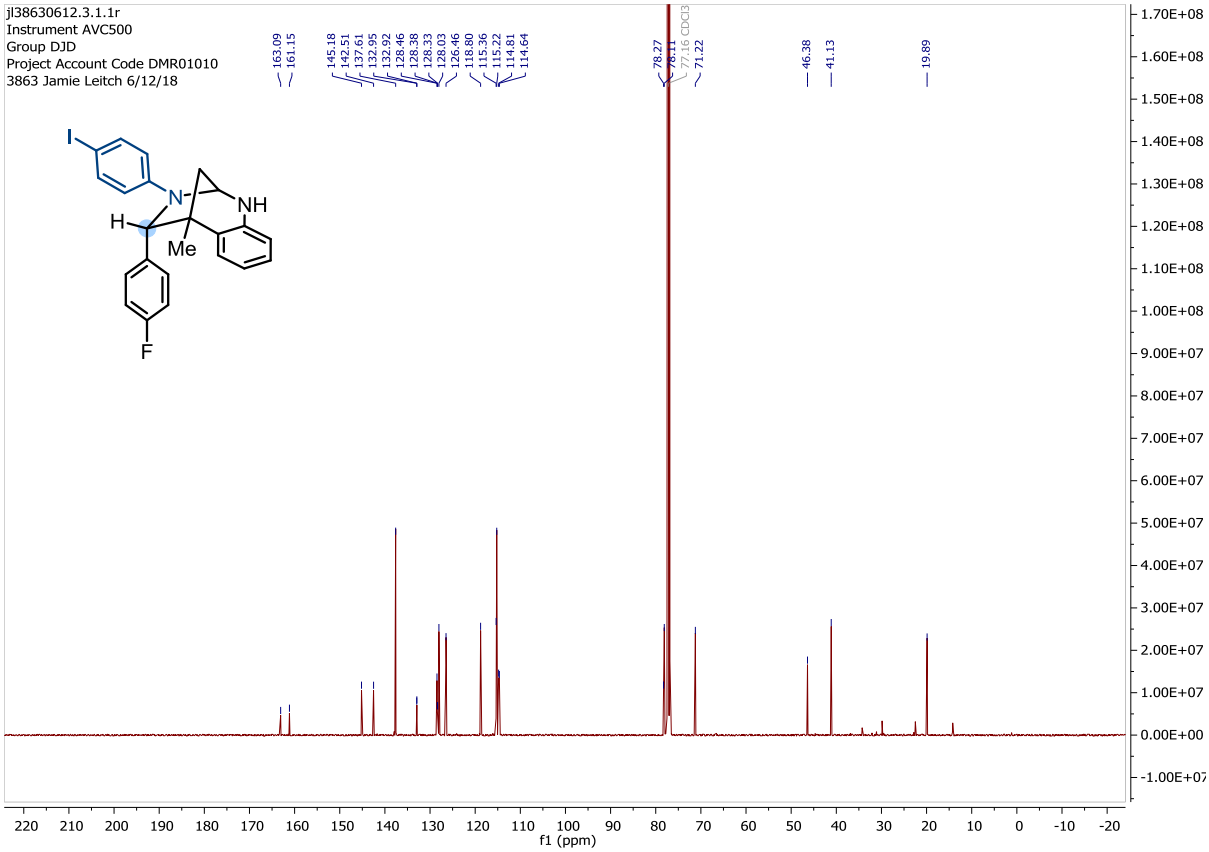
3f$_{(endo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



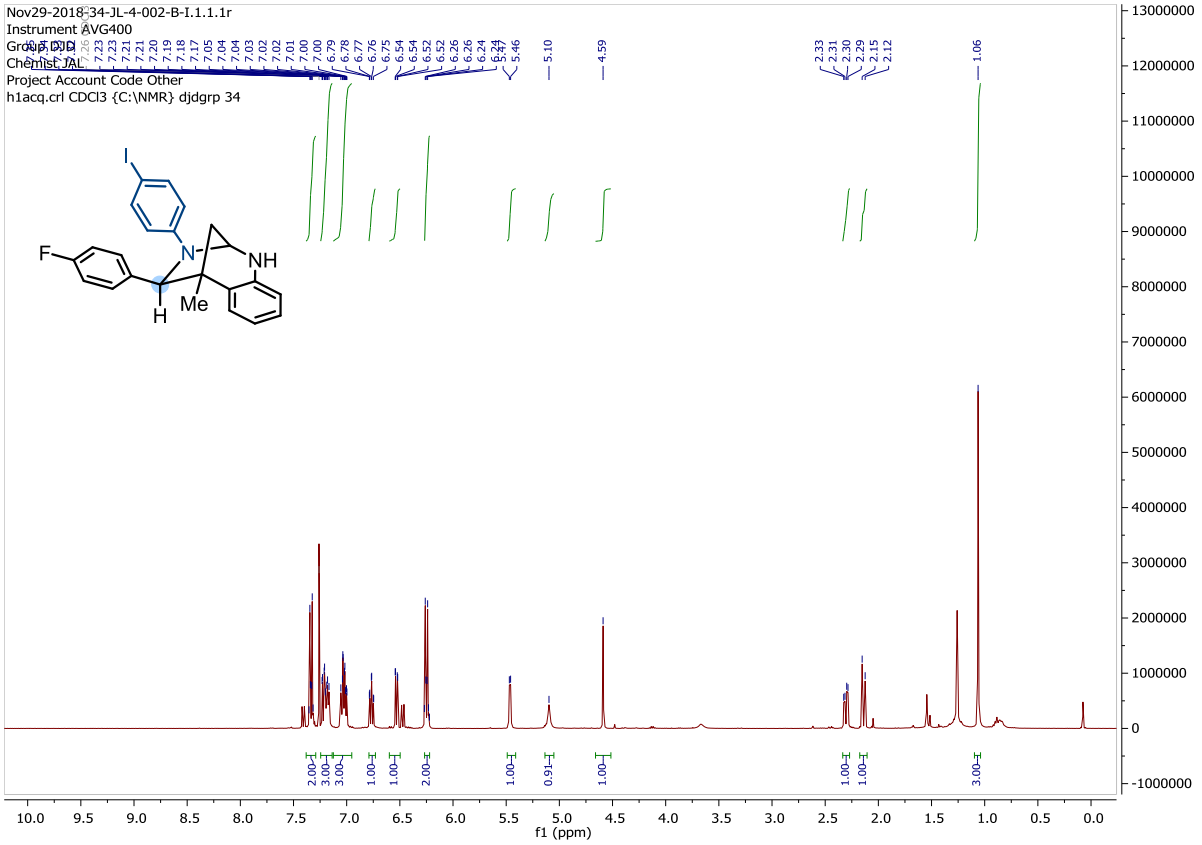
3f$_{(endo)}$ – ^{19}F NMR (377 MHz, $CDCl_3$)



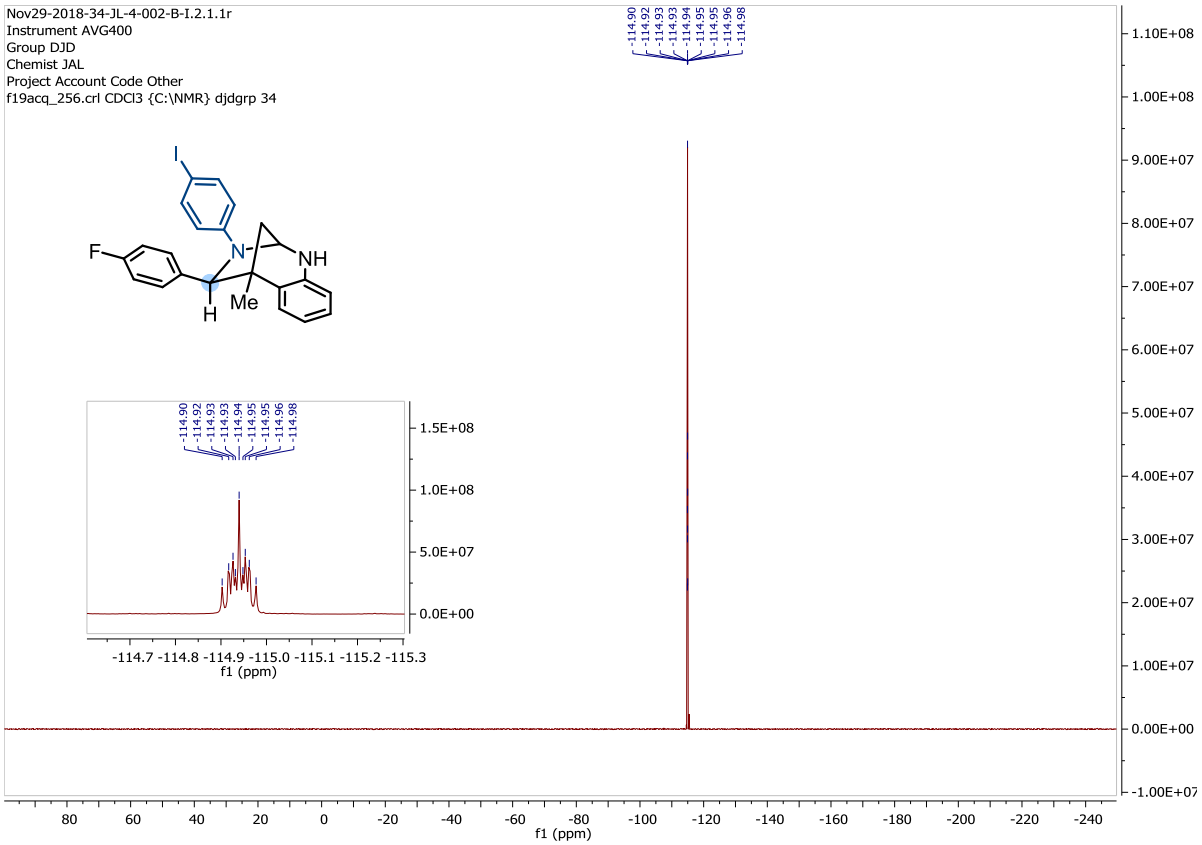
3f$_{(endo)}$ – ^{13}C NMR (126 MHz, $CDCl_3$)



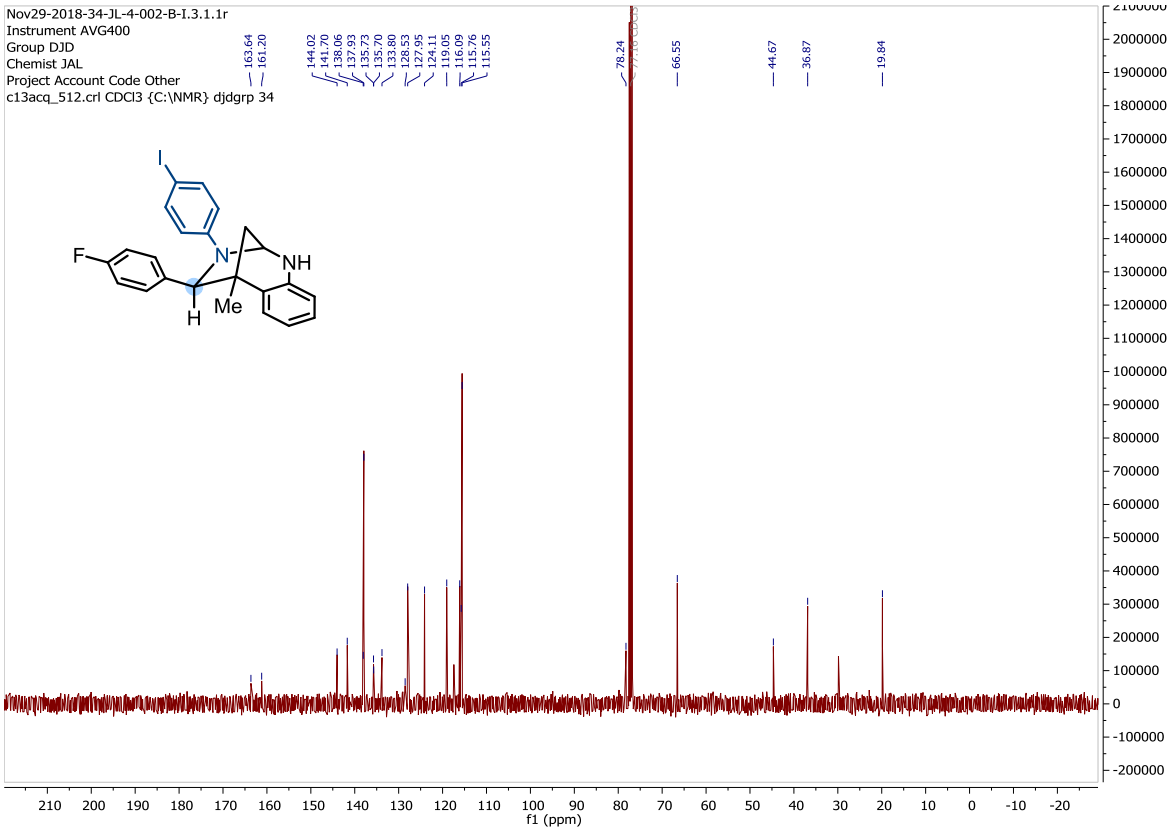
3f$_{(exo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



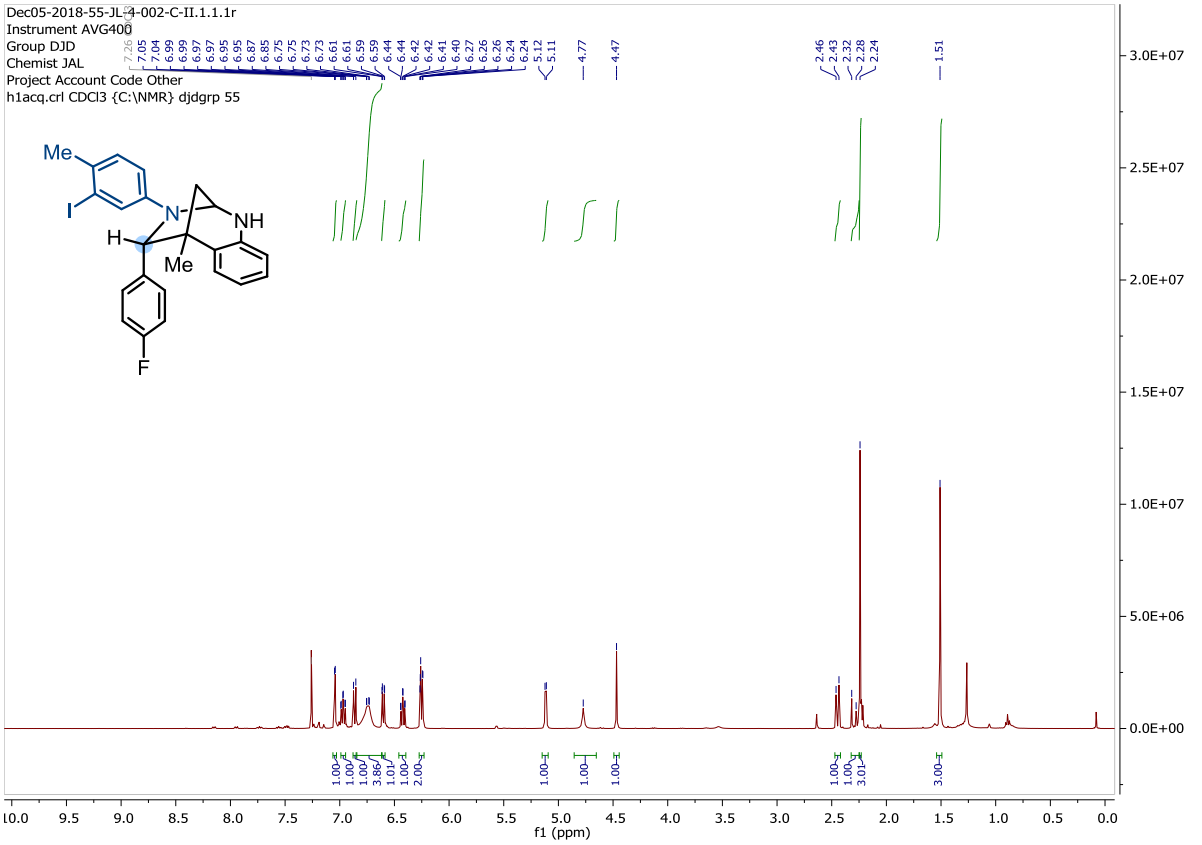
3f$_{(exo)}$ – ^{19}F NMR (377 MHz, $CDCl_3$)



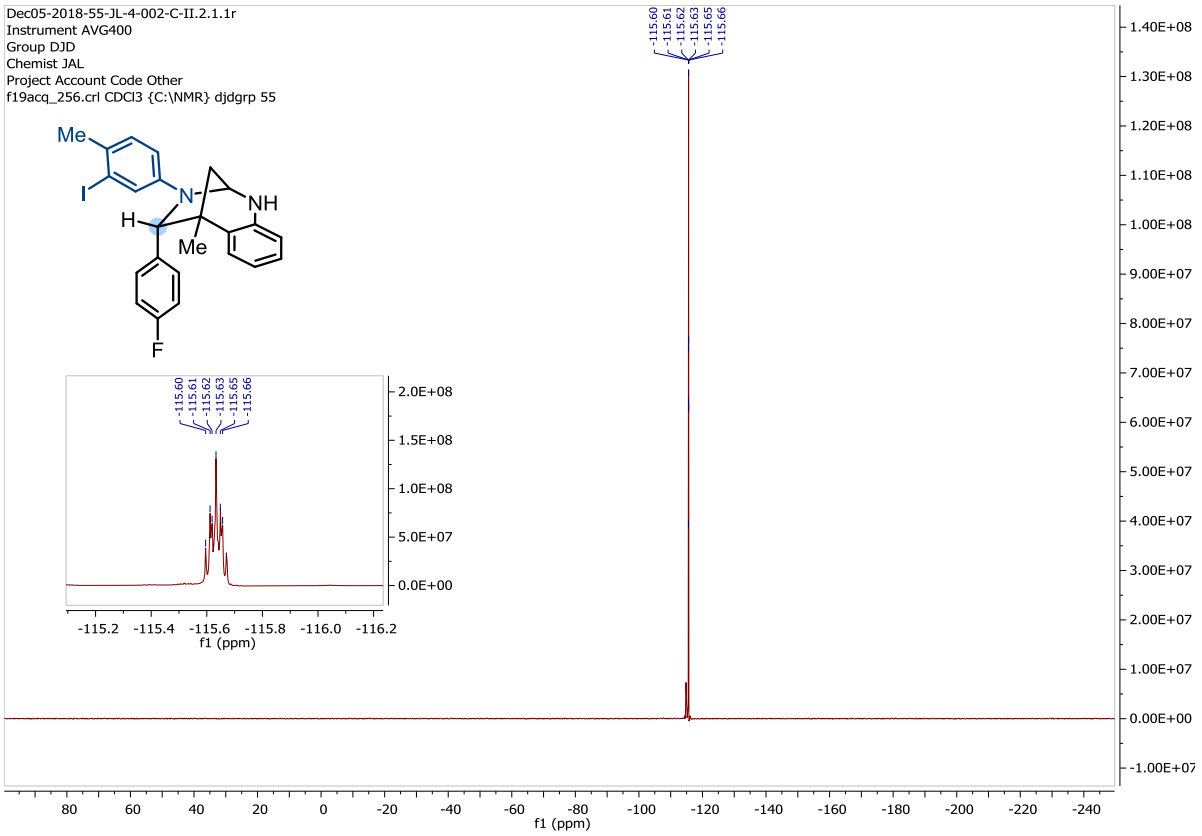
3f$_{(exo)}$ – ^{13}C NMR (101 MHz, $CDCl_3$)



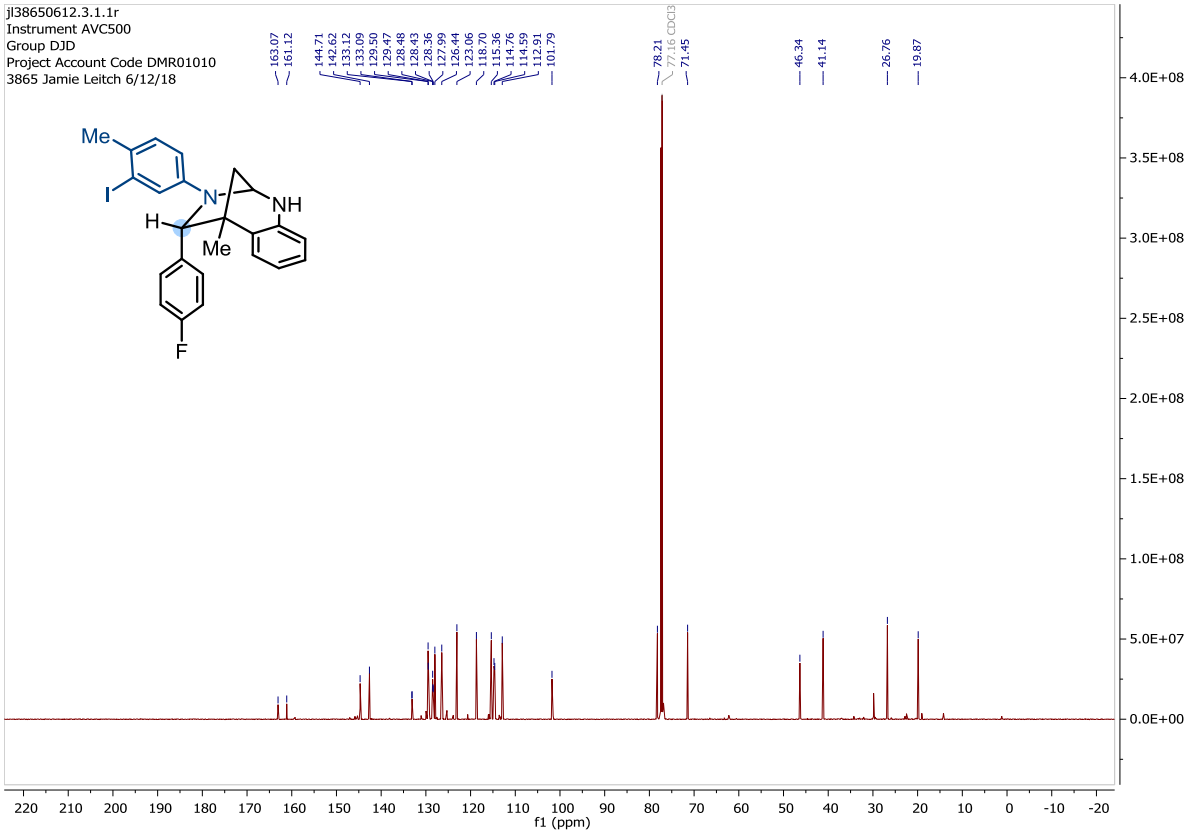
3g(endo) – ^{1}H NMR (400 MHz, $CDCl_3$)



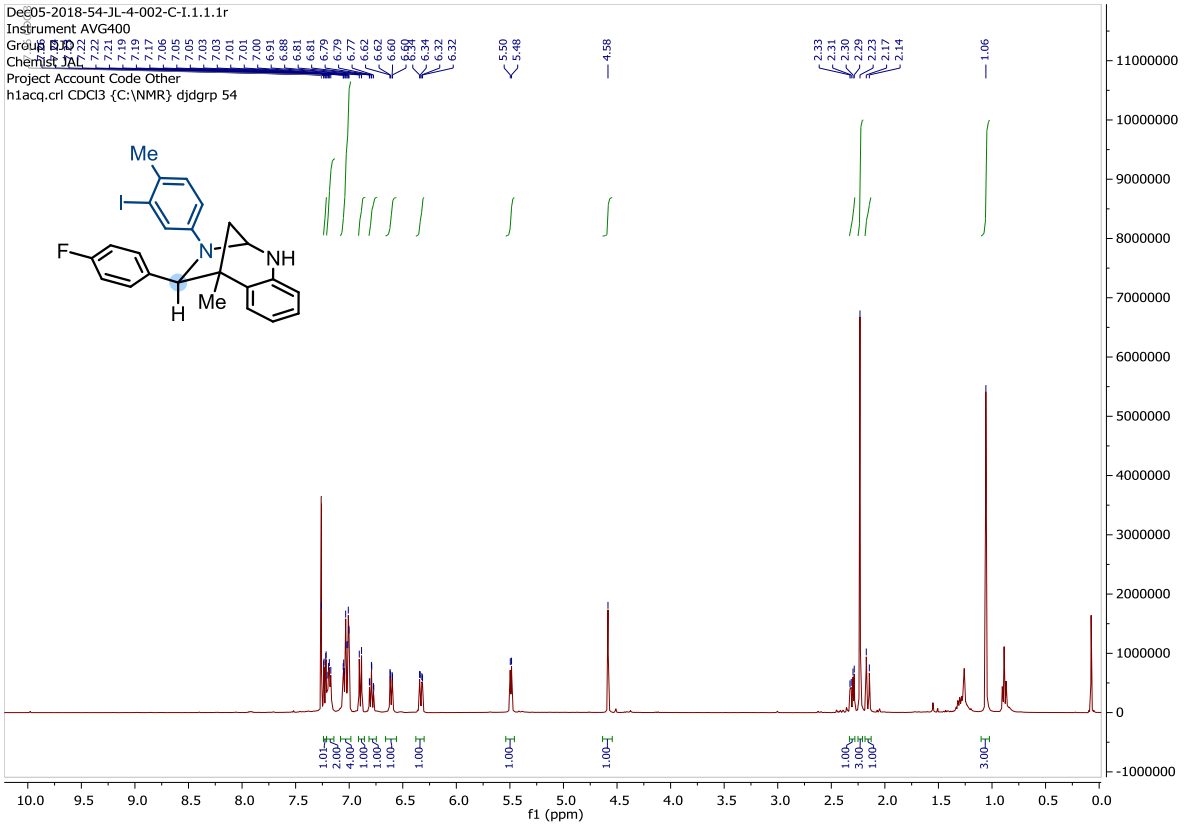
3g(endo) – ^{19}F NMR (377 MHz, $CDCl_3$)



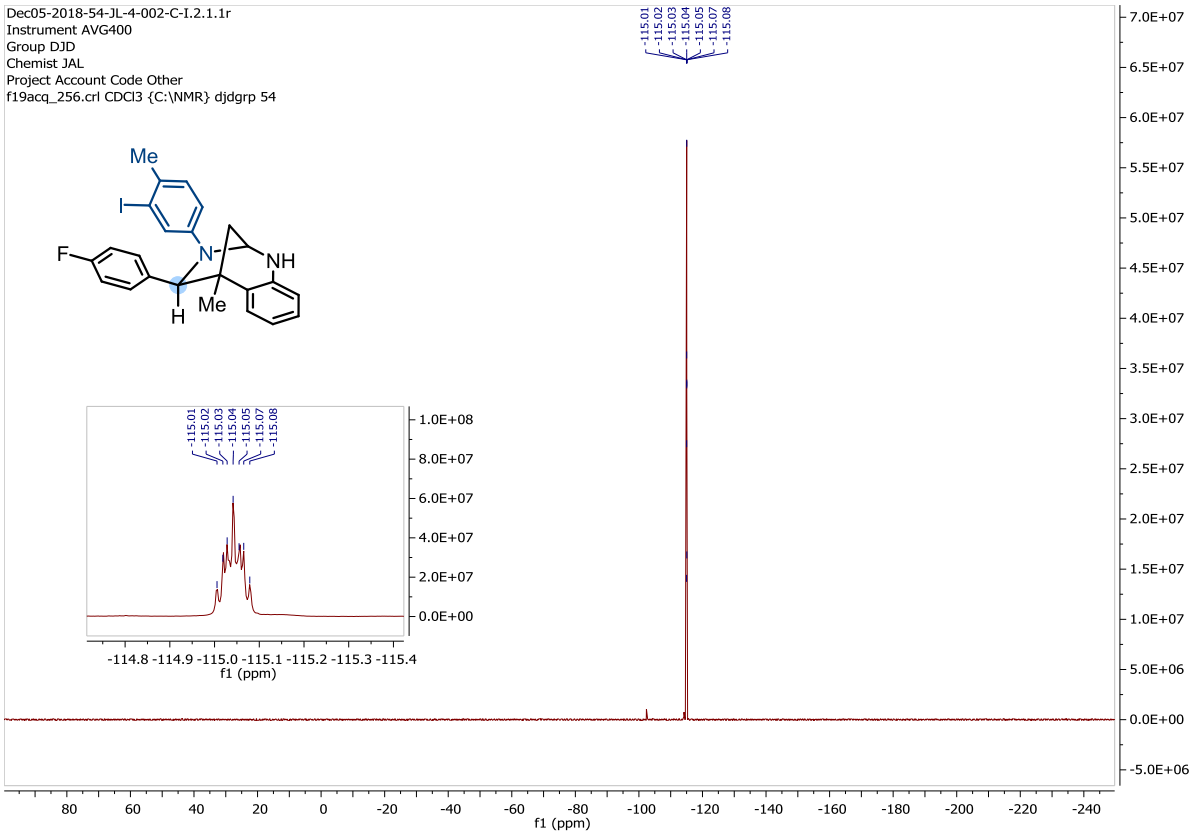
3g$_{(exo)}$ – ^{13}C NMR (126 MHz, $CDCl_3$)



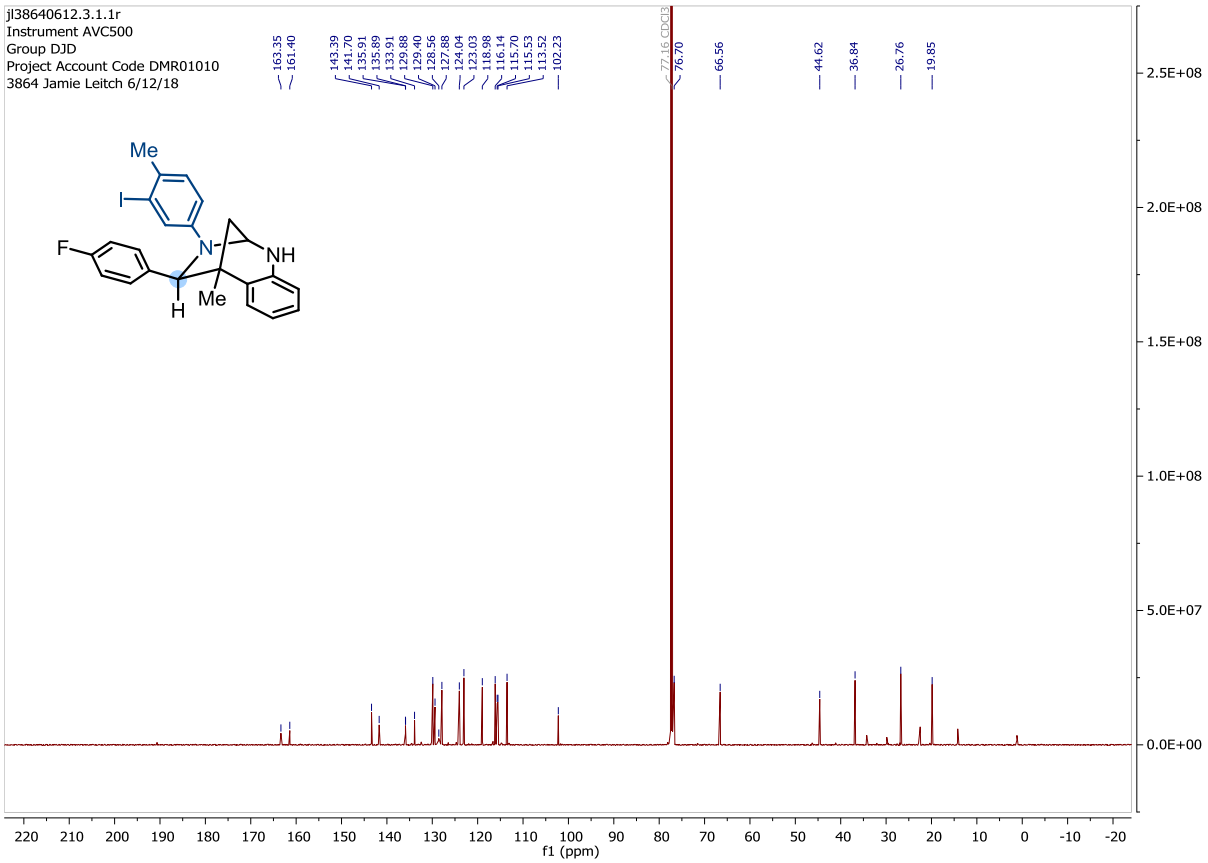
3g(exo) – ^{1}H NMR (400 MHz, $CDCl_3$)



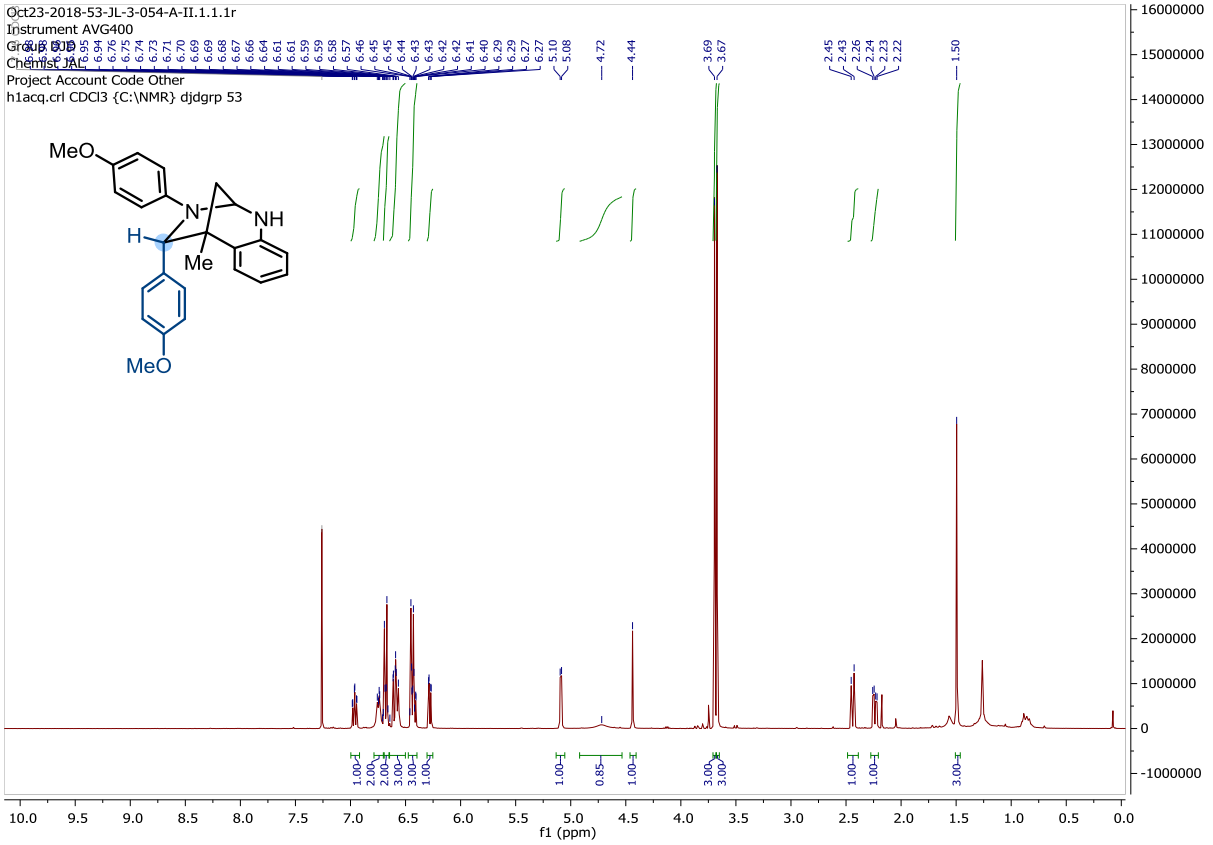
3g(exo) – ^{19}F NMR (377 MHz, $CDCl_3$)



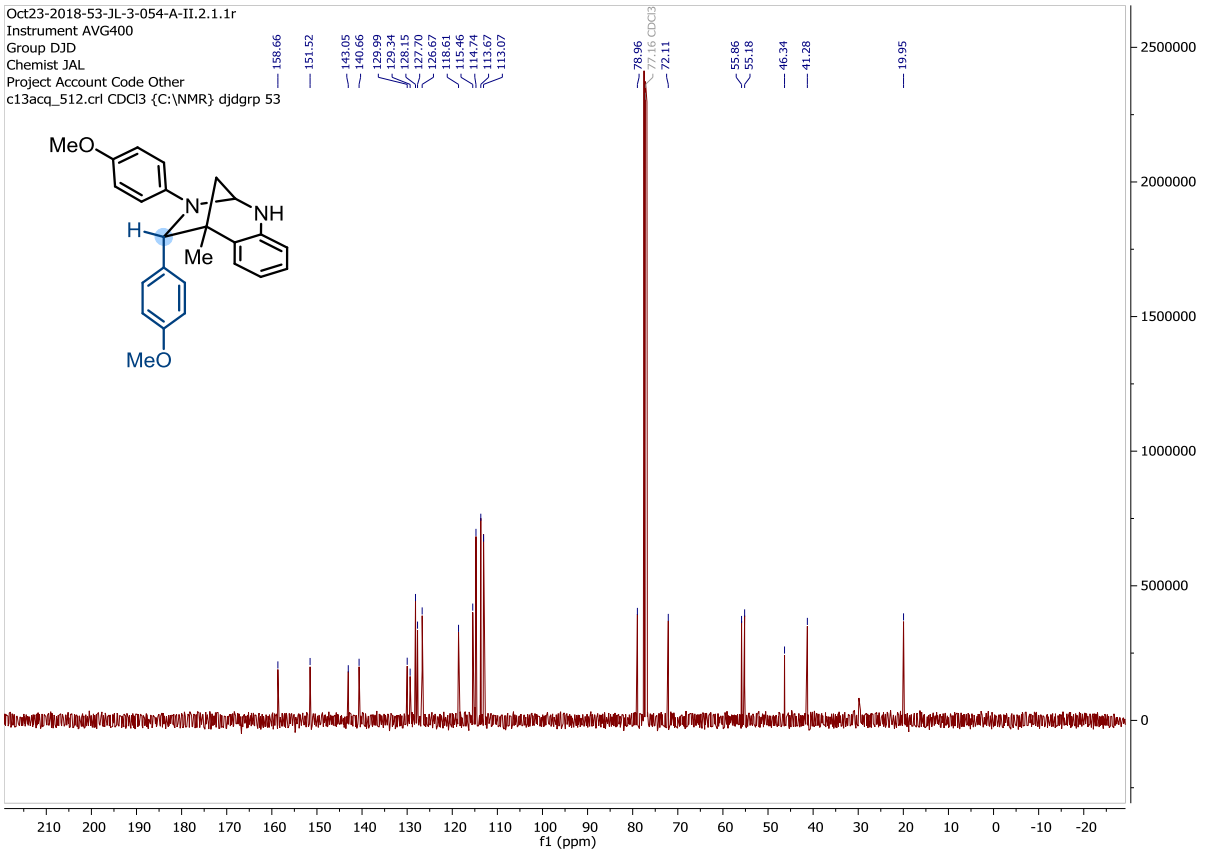
3g$_{(exo)}$ – ^{13}C NMR (126 MHz, $CDCl_3$)



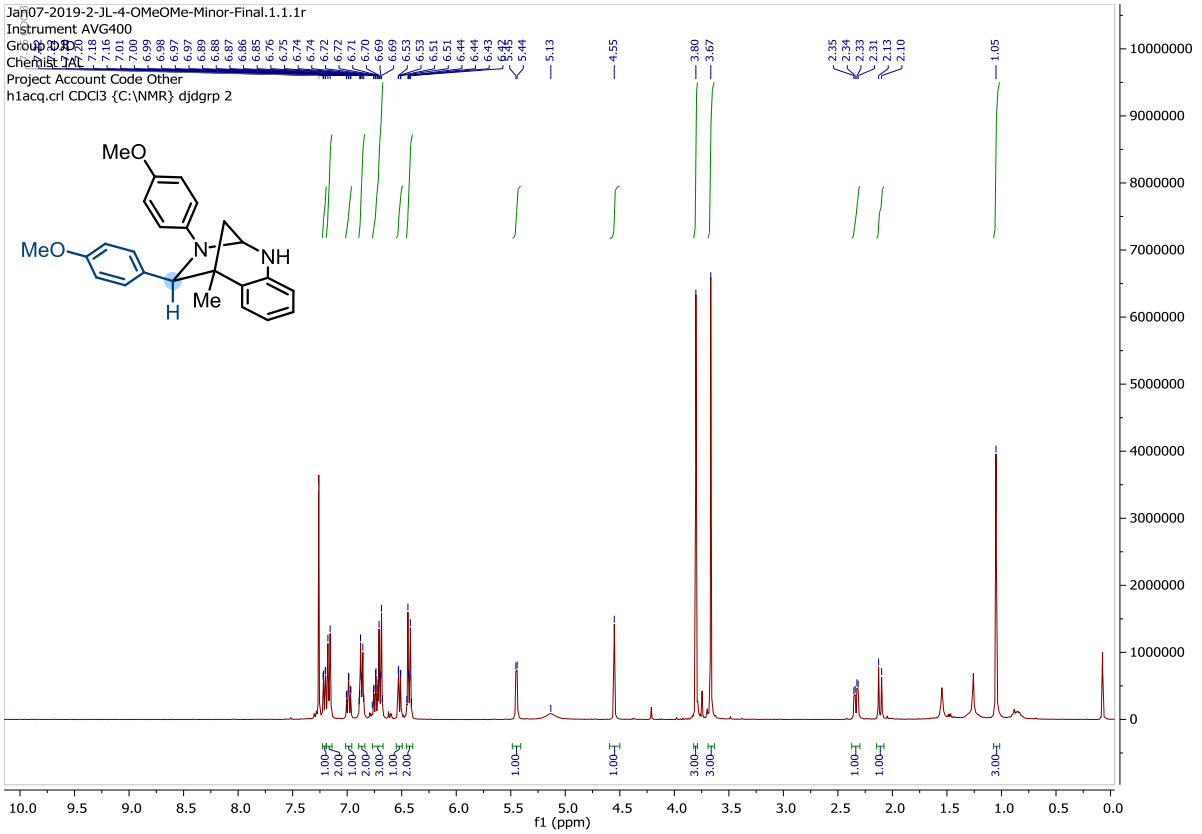
3h$_{(endo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



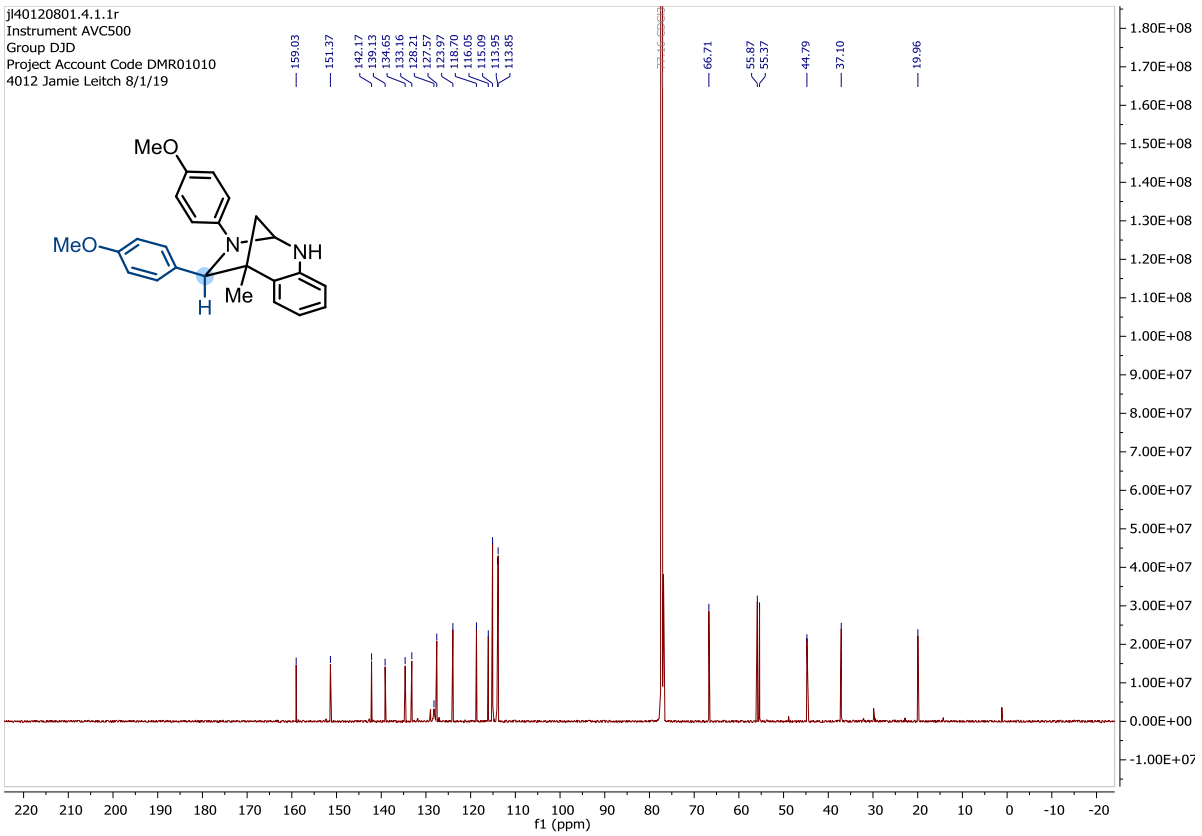
3h$_{(endo)}$ – ^{13}C NMR (101 MHz, $CDCl_3$)



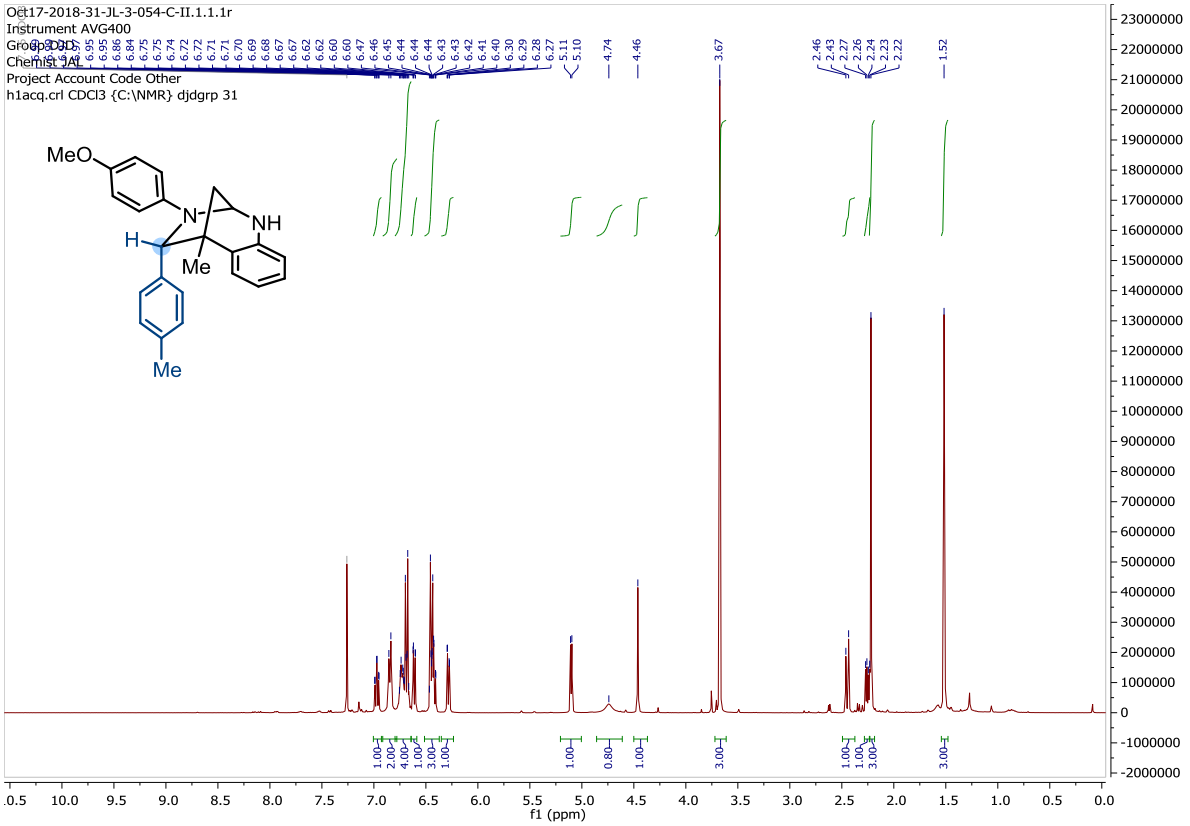
3h$_{(exo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



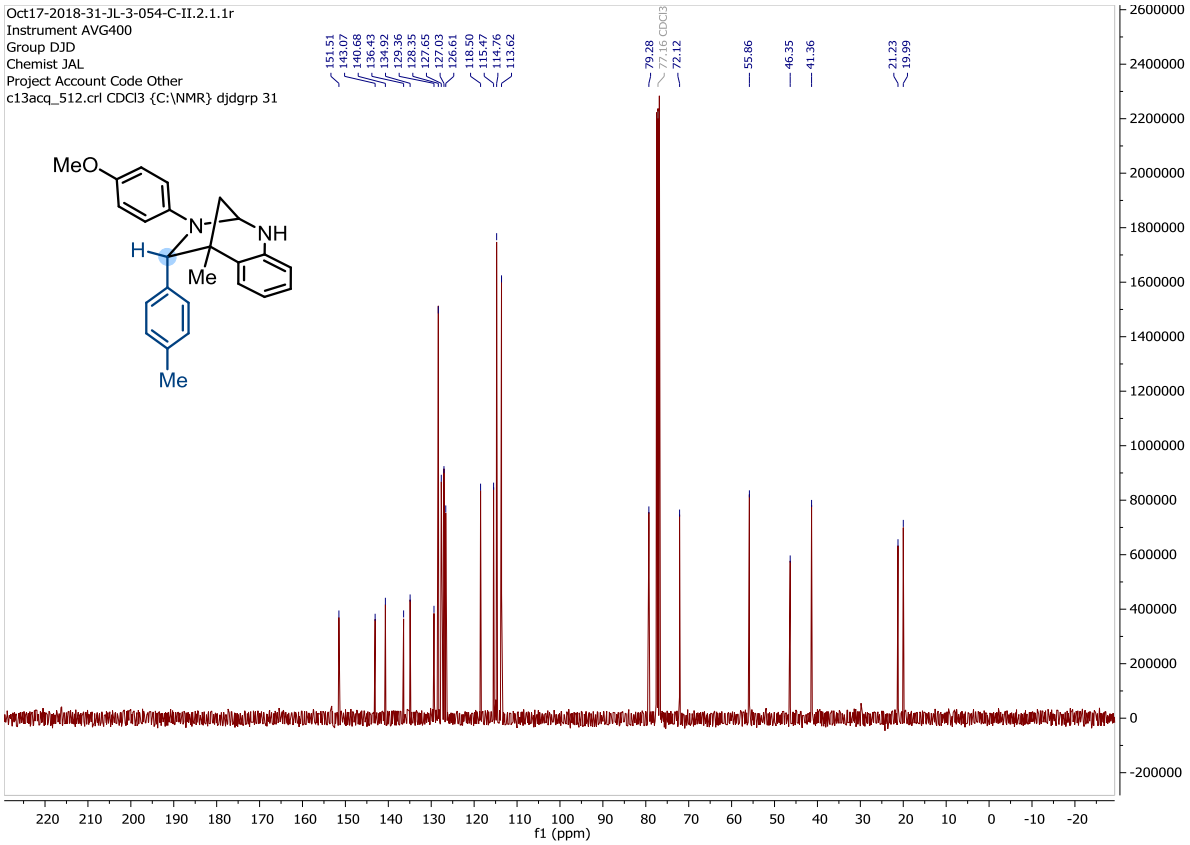
3h$_{(exo)}$ – ^{13}C NMR (126 MHz, $CDCl_3$)



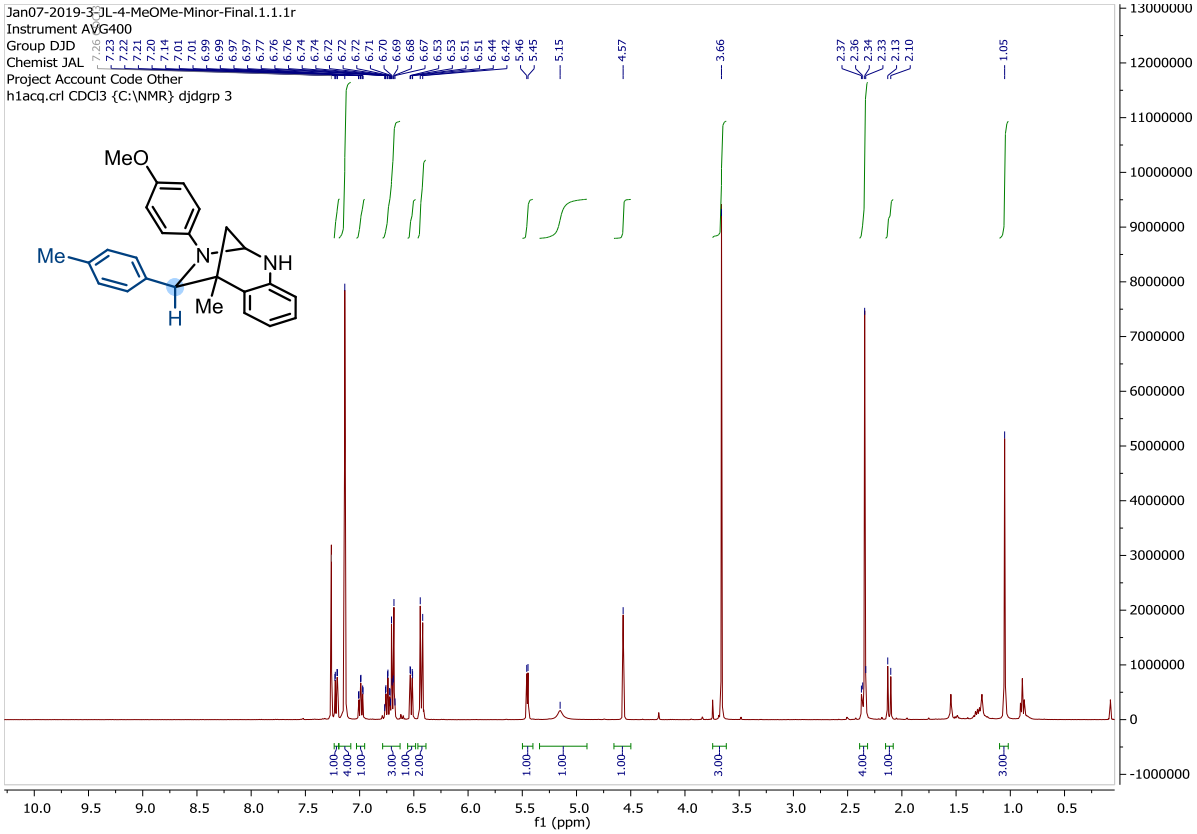
3i$_{(endo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



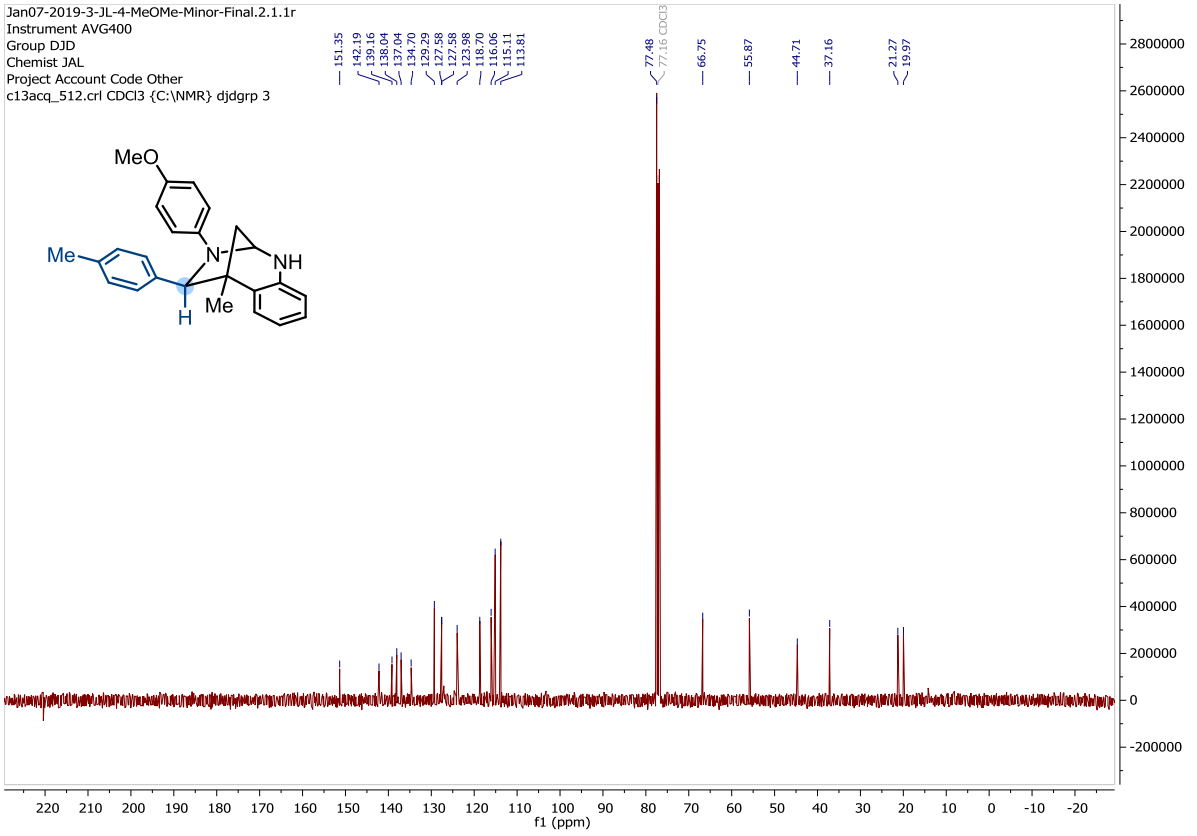
3i$_{(endo)}$ – ^{13}C NMR (101 MHz, $CDCl_3$)



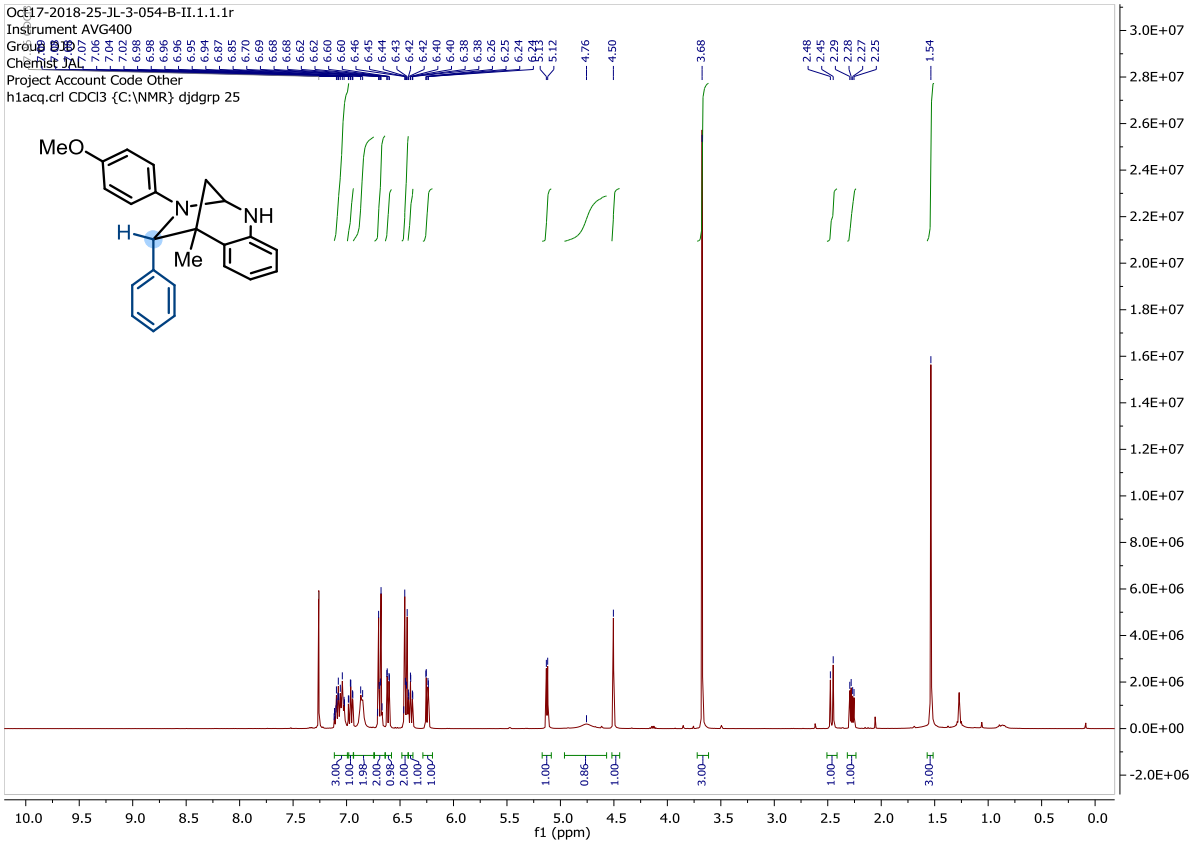
3i$_{(exo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



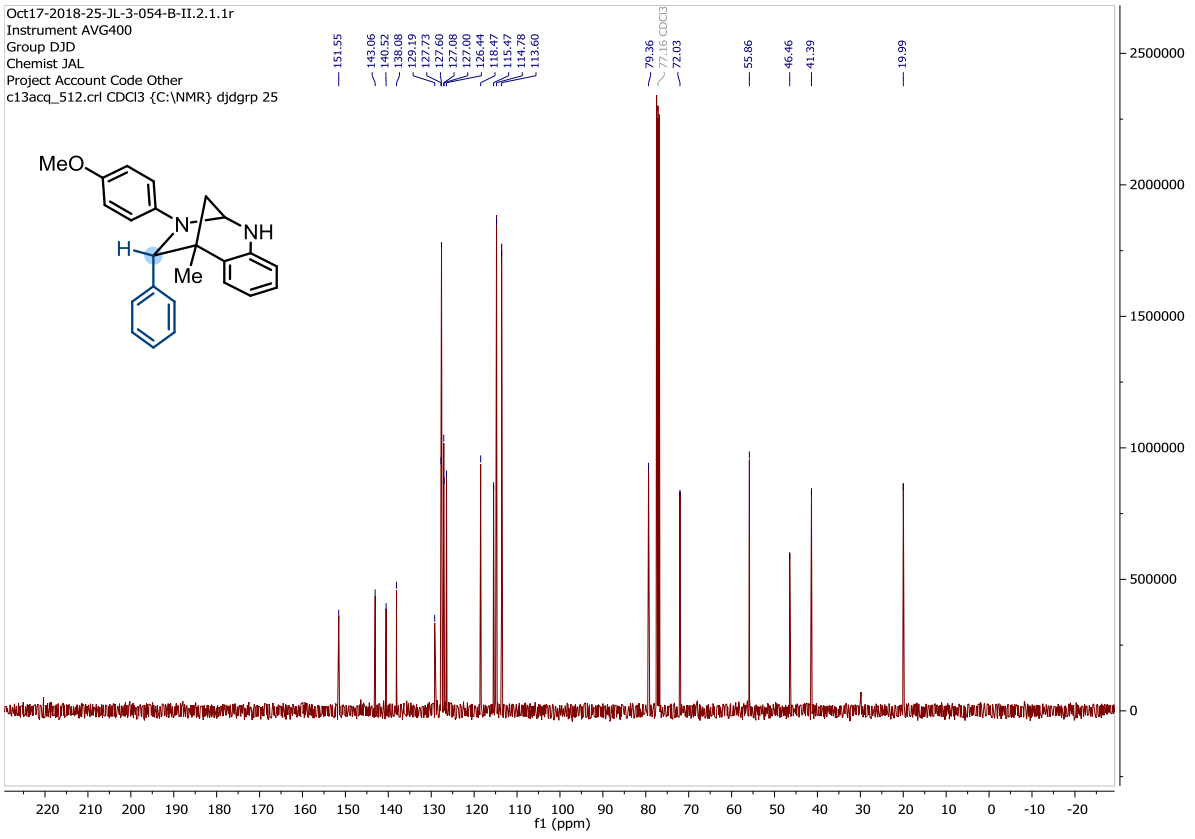
3i$_{(exo)}$ – ^{13}C NMR (101 MHz, $CDCl_3$)



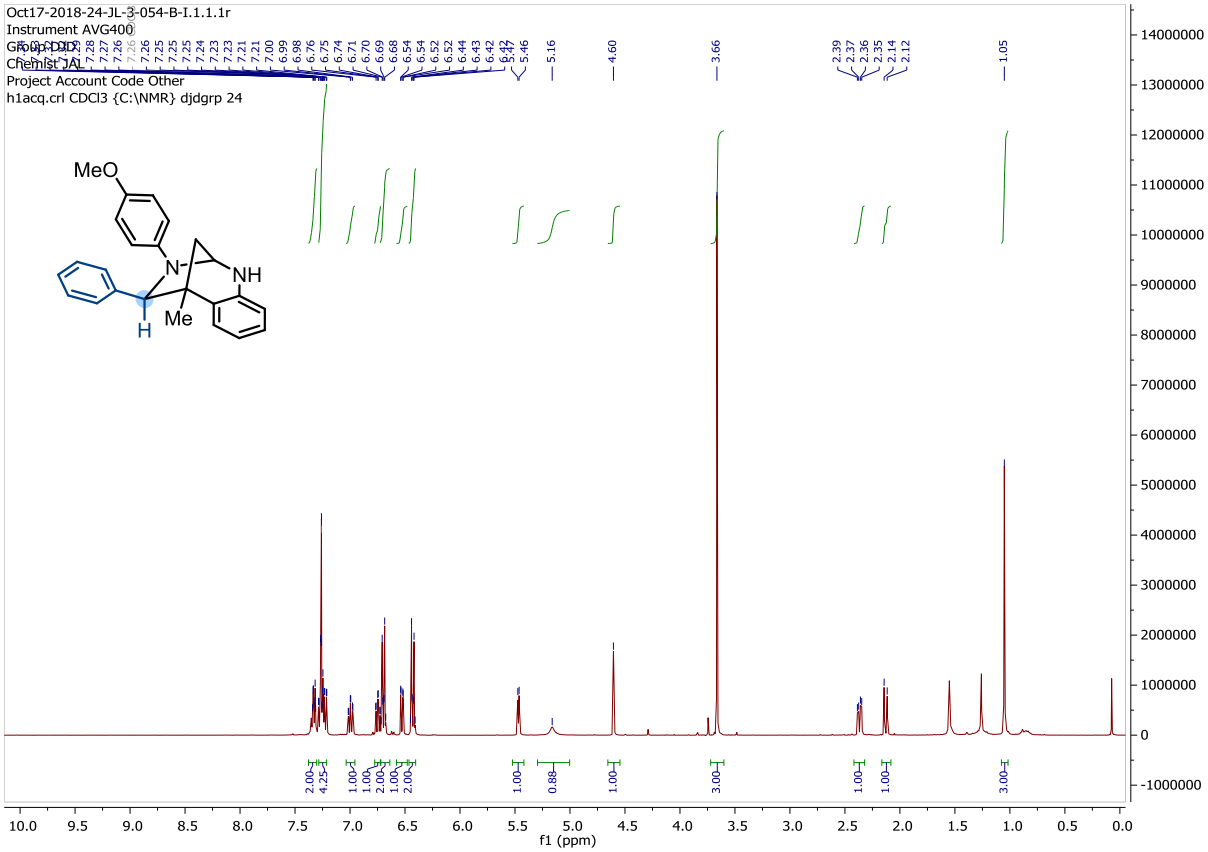
3j(endo) – ^{1}H NMR (400 MHz, $CDCl_3$)



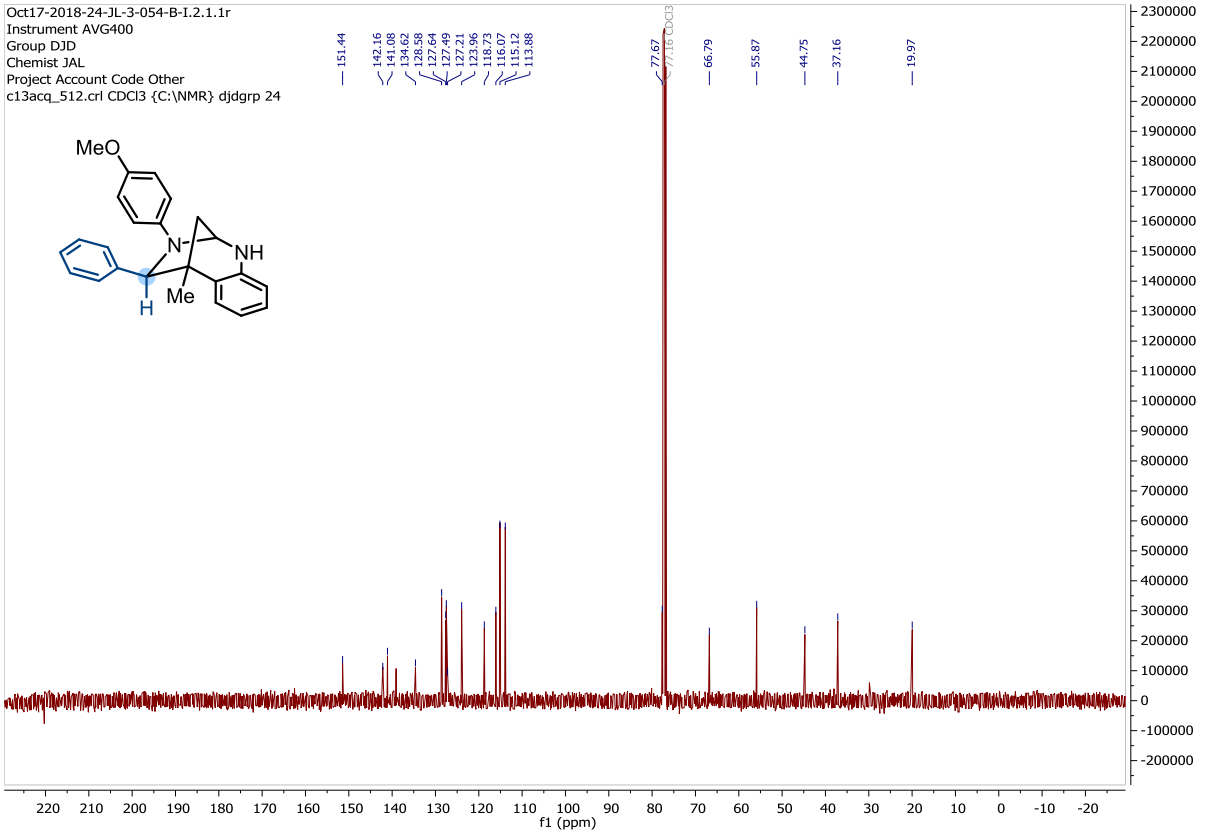
3j(endo) – ^{13}C NMR (101 MHz, $CDCl_3$)



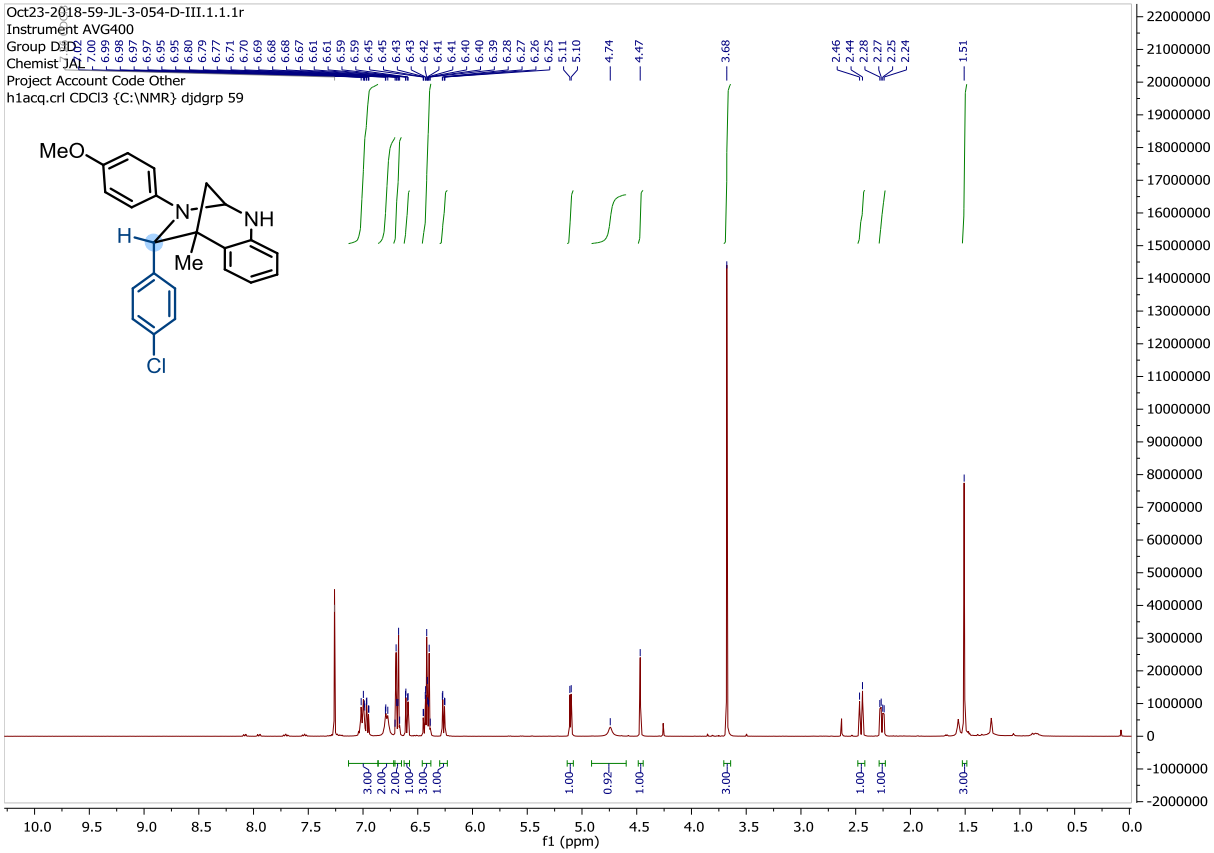
3j$_{(exo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



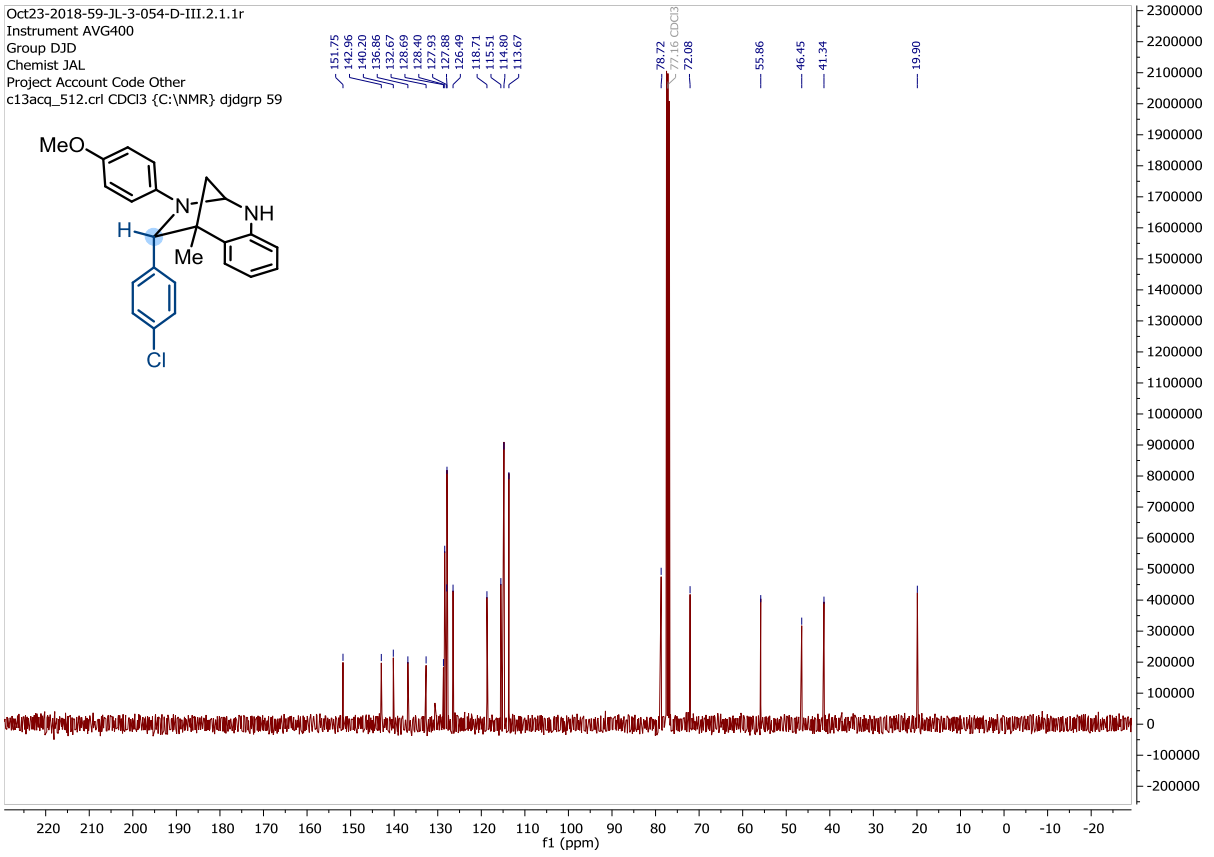
3j$_{(exo)}$ – ^{13}C NMR (101 MHz, $CDCl_3$)



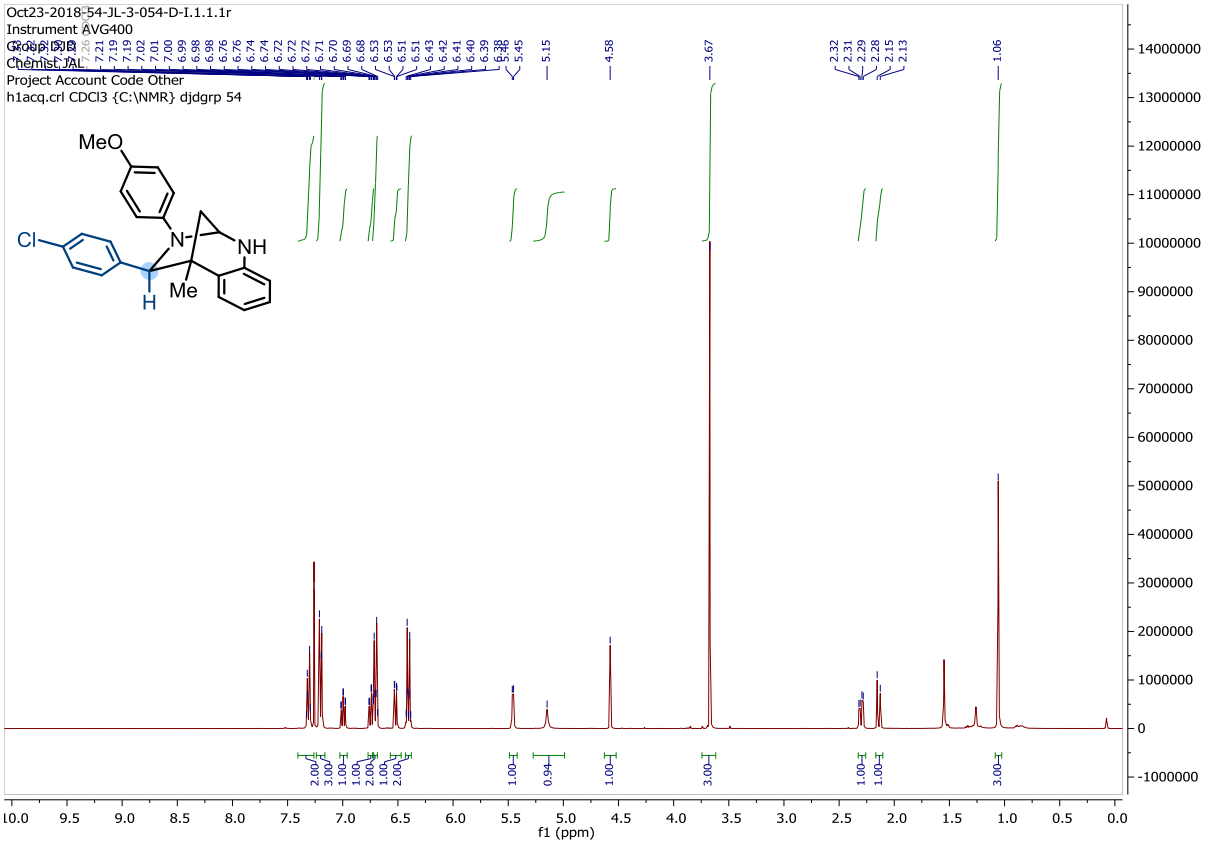
3k$_{(endo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



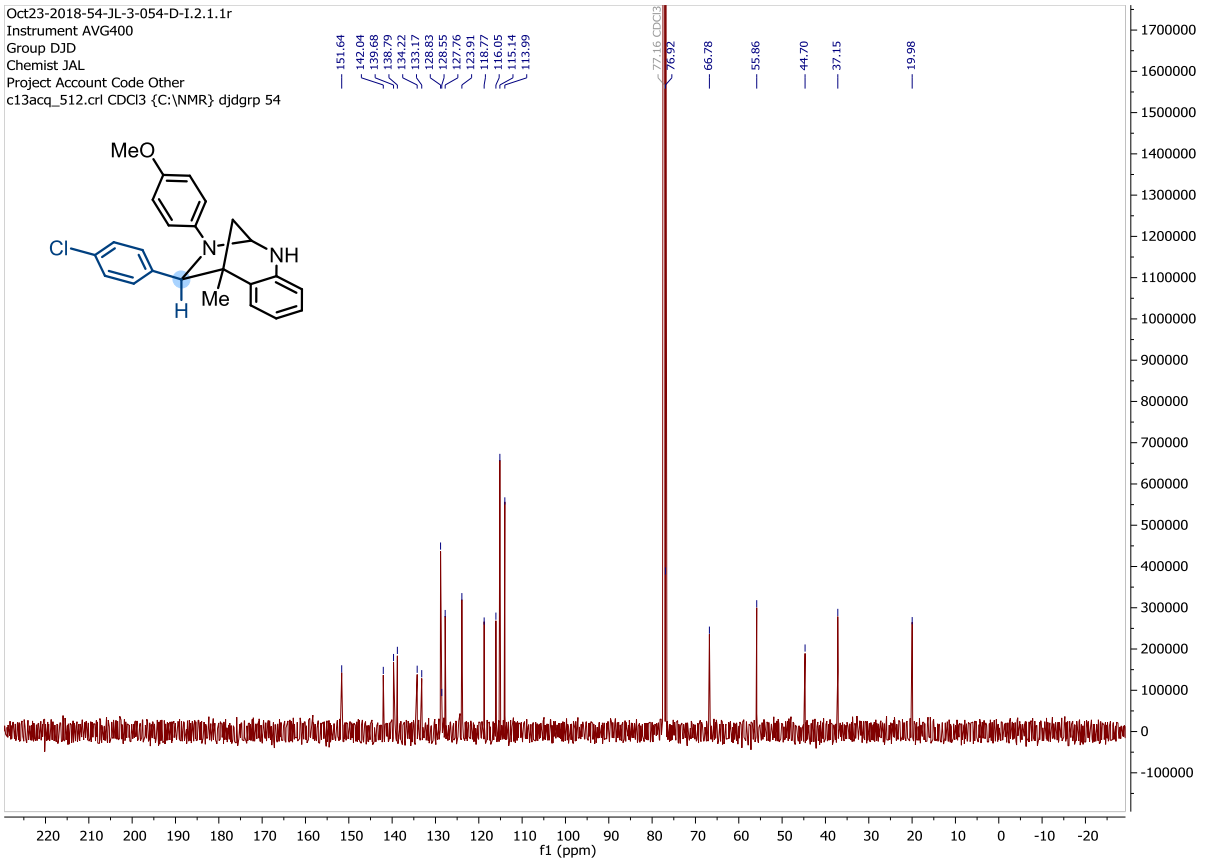
3k$_{(endo)}$ – (101 MHz, $CDCl_3$)



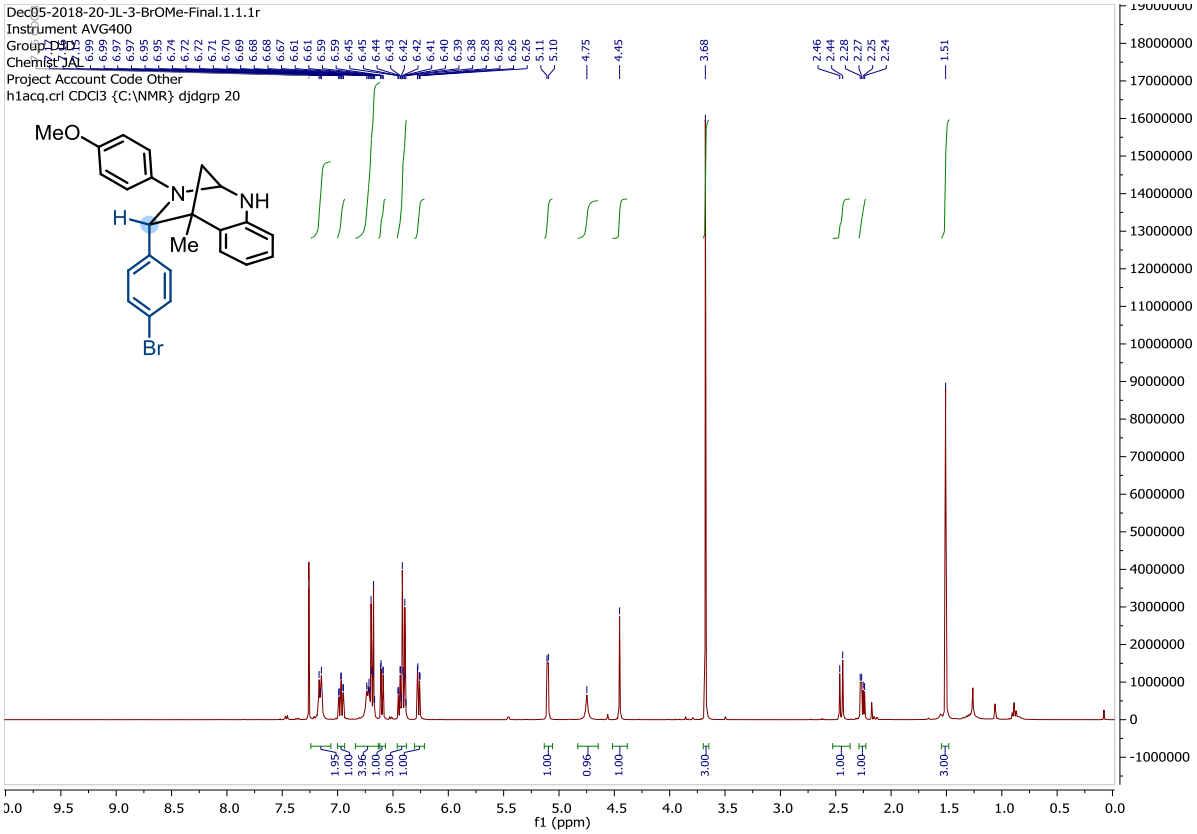
3k$_{(exo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



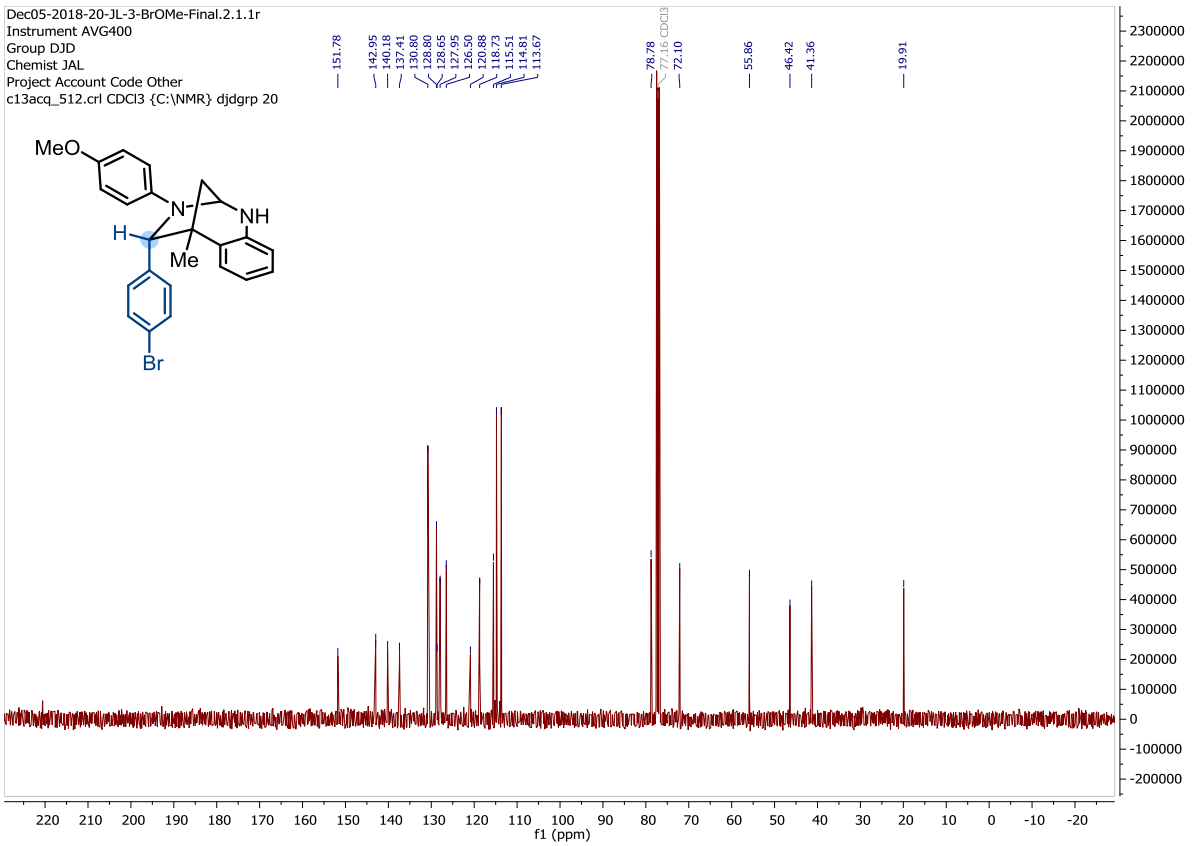
3k$_{(exo)}$ – ^{13}C NMR (101 MHz, $CDCl_3$)



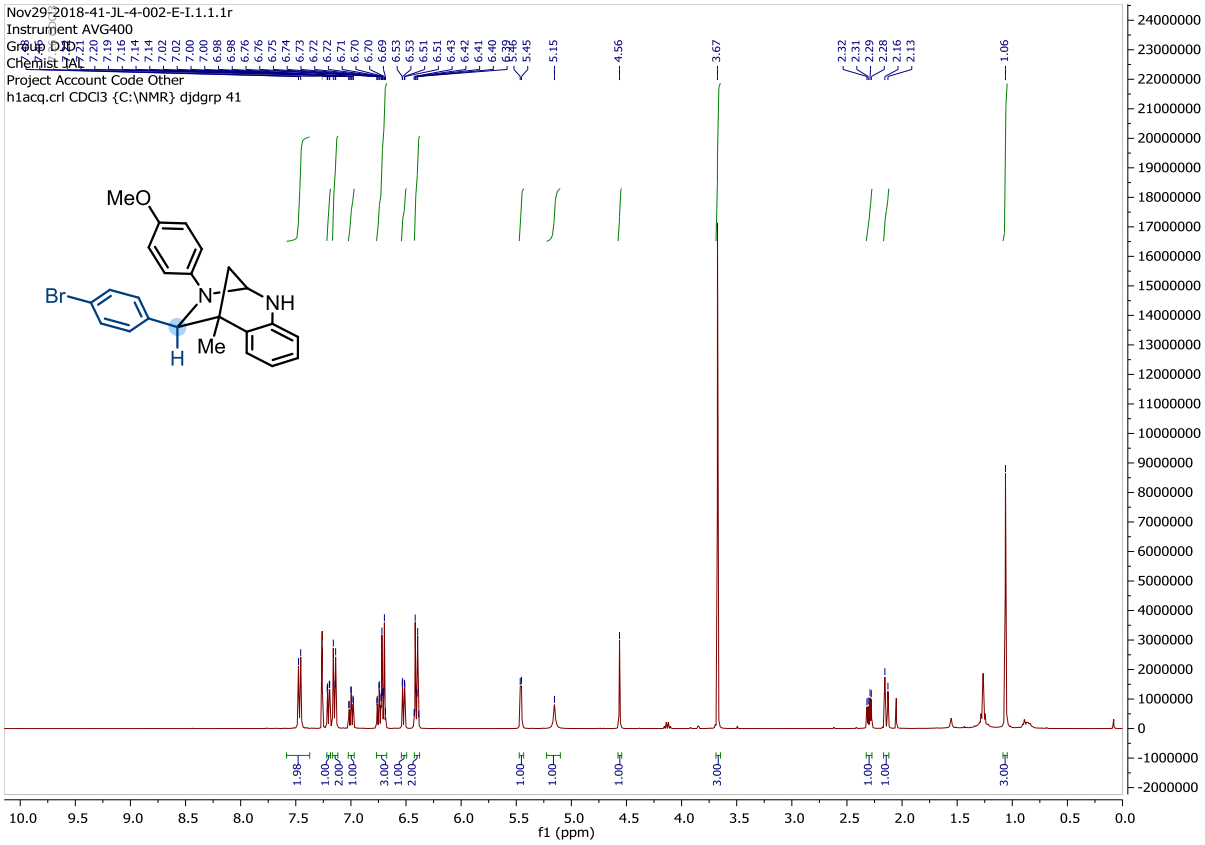
3l(endo) – ^{1}H NMR (400 MHz, $CDCl_3$)



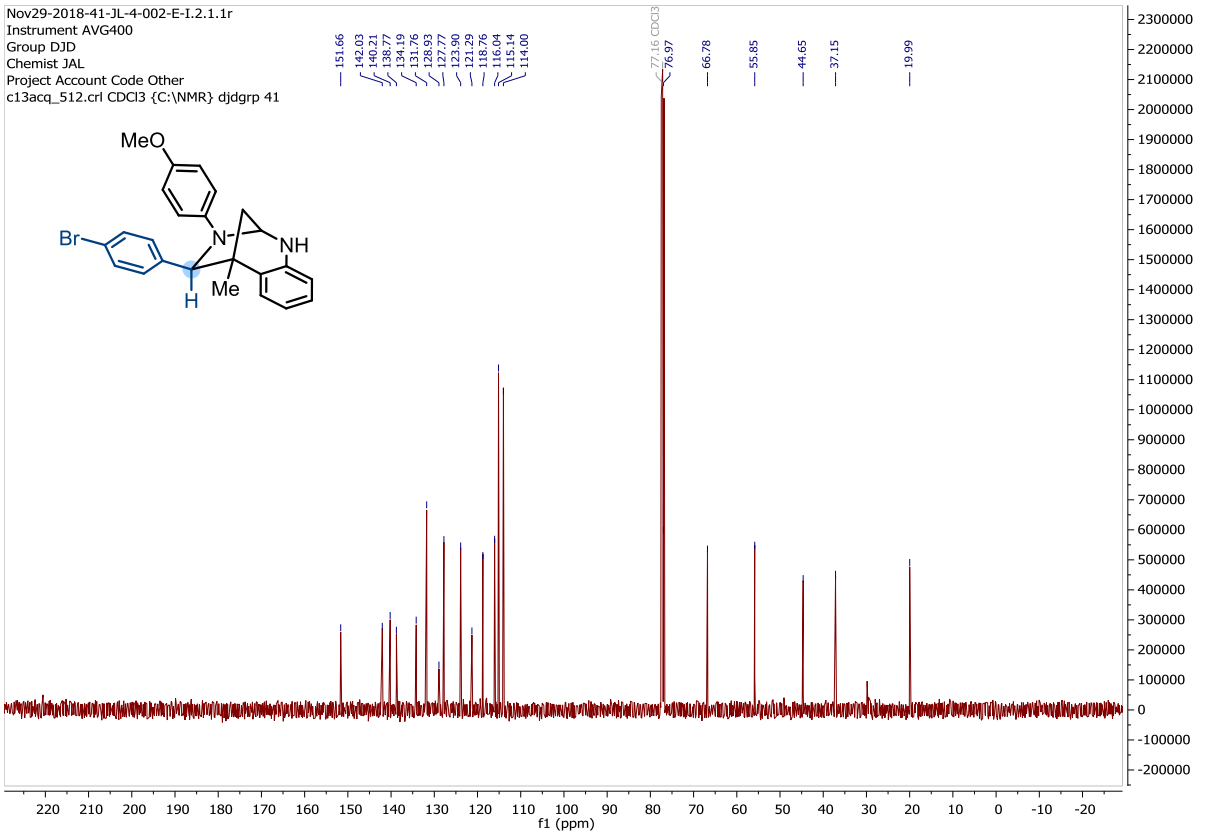
3l(endo) – ^{13}C NMR (101 MHz, $CDCl_3$)



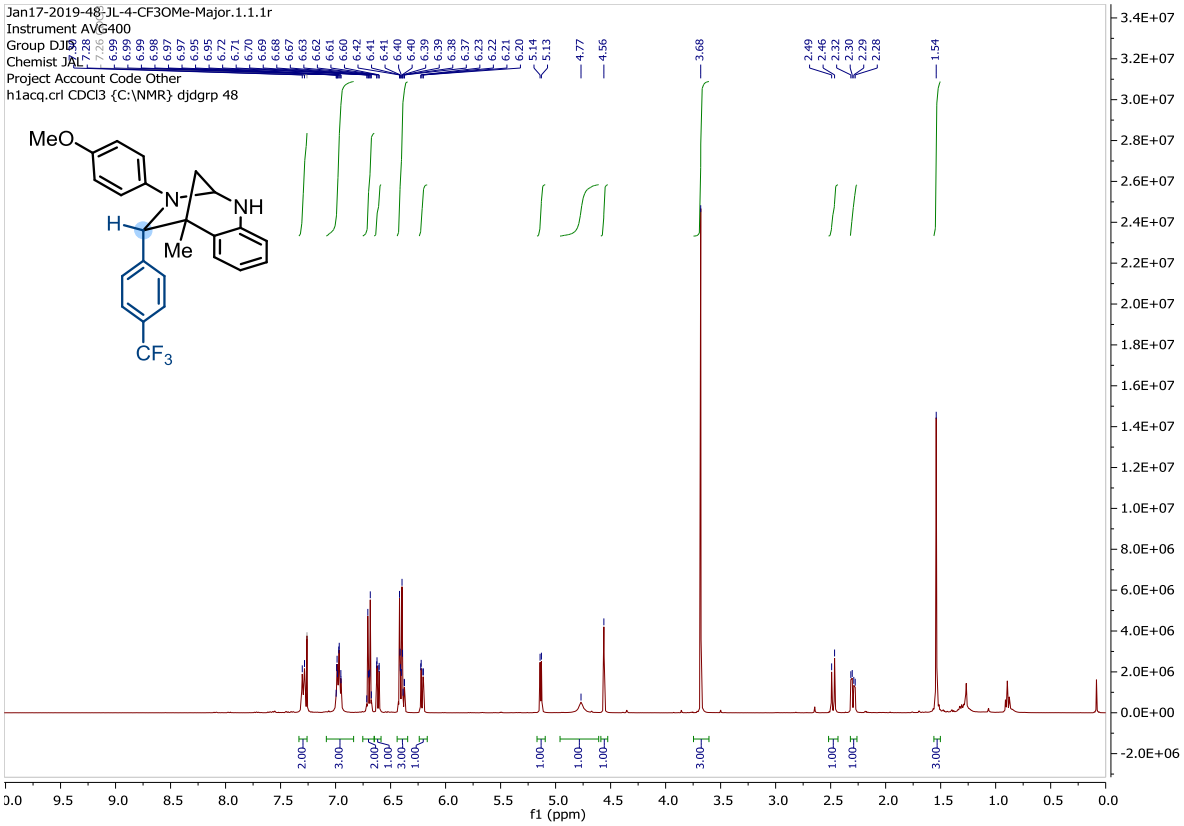
3l$_{(exo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



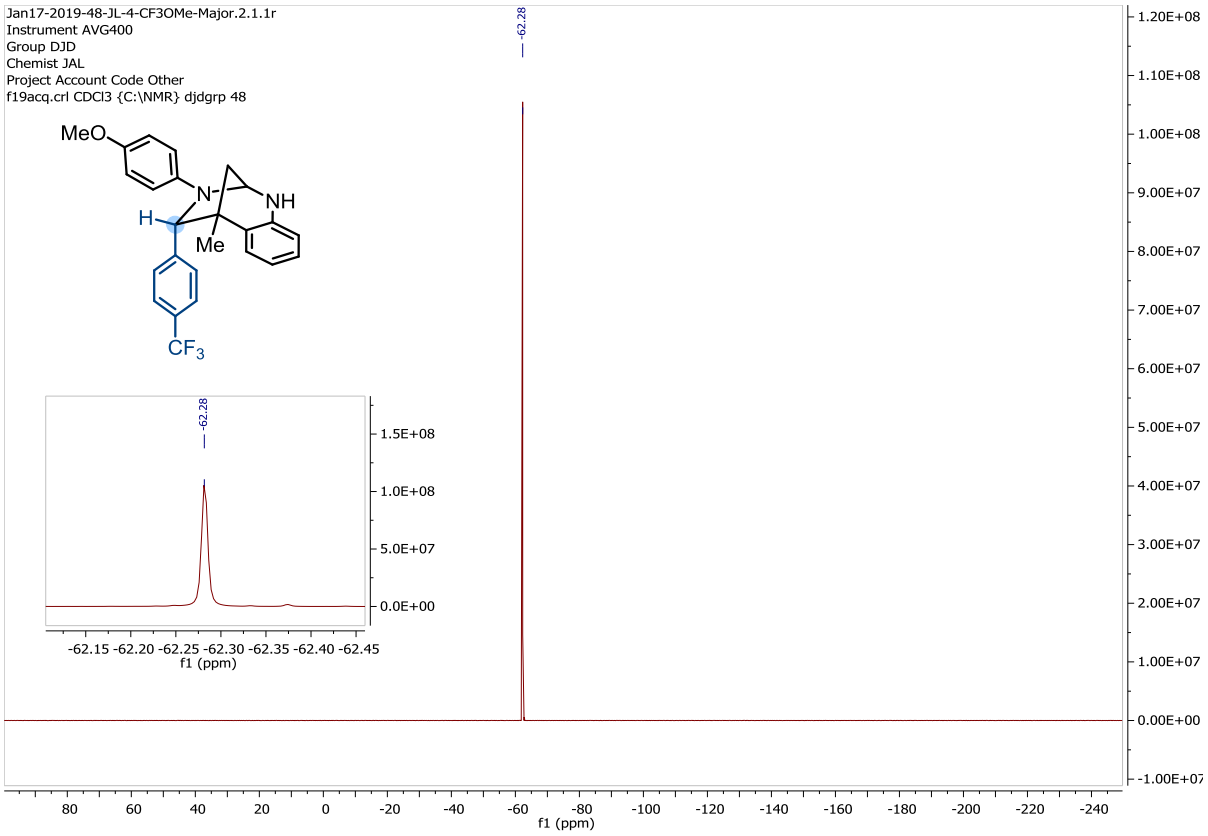
3l$_{(exo)}$ – ^{13}C NMR (101 MHz, $CDCl_3$)



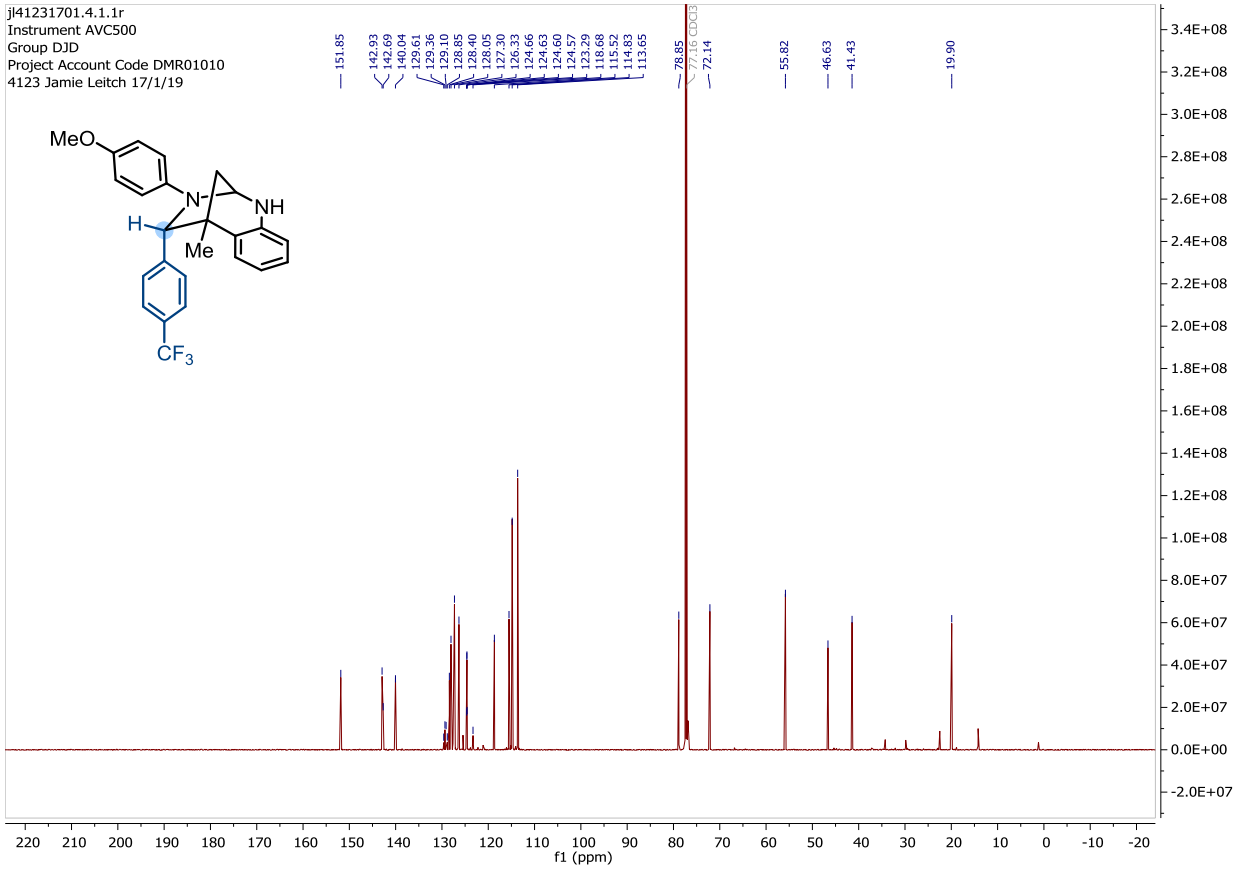
3m$_{(endo)}$ - ^{1}H NMR (400 MHz, $CDCl_3$)



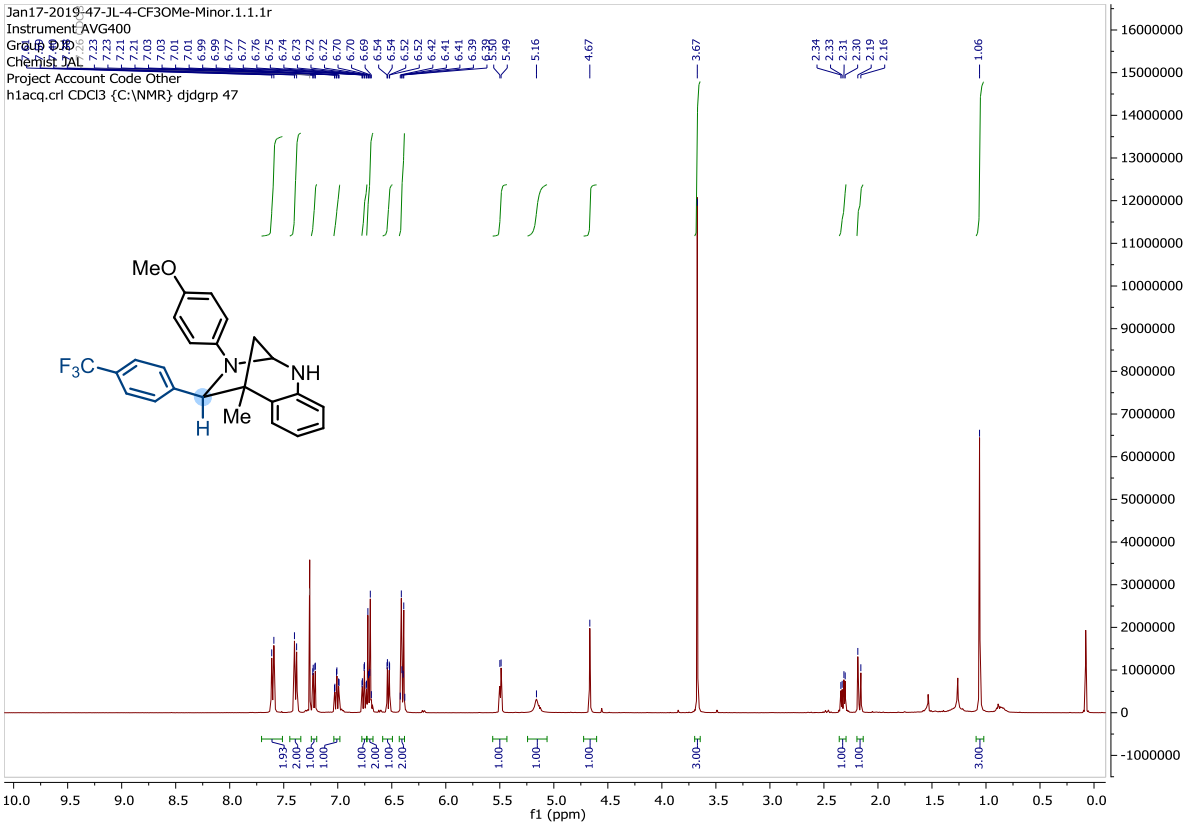
3m$_{(endo)}$ – ^{19}F NMR (377 MHz, $CDCl_3$)



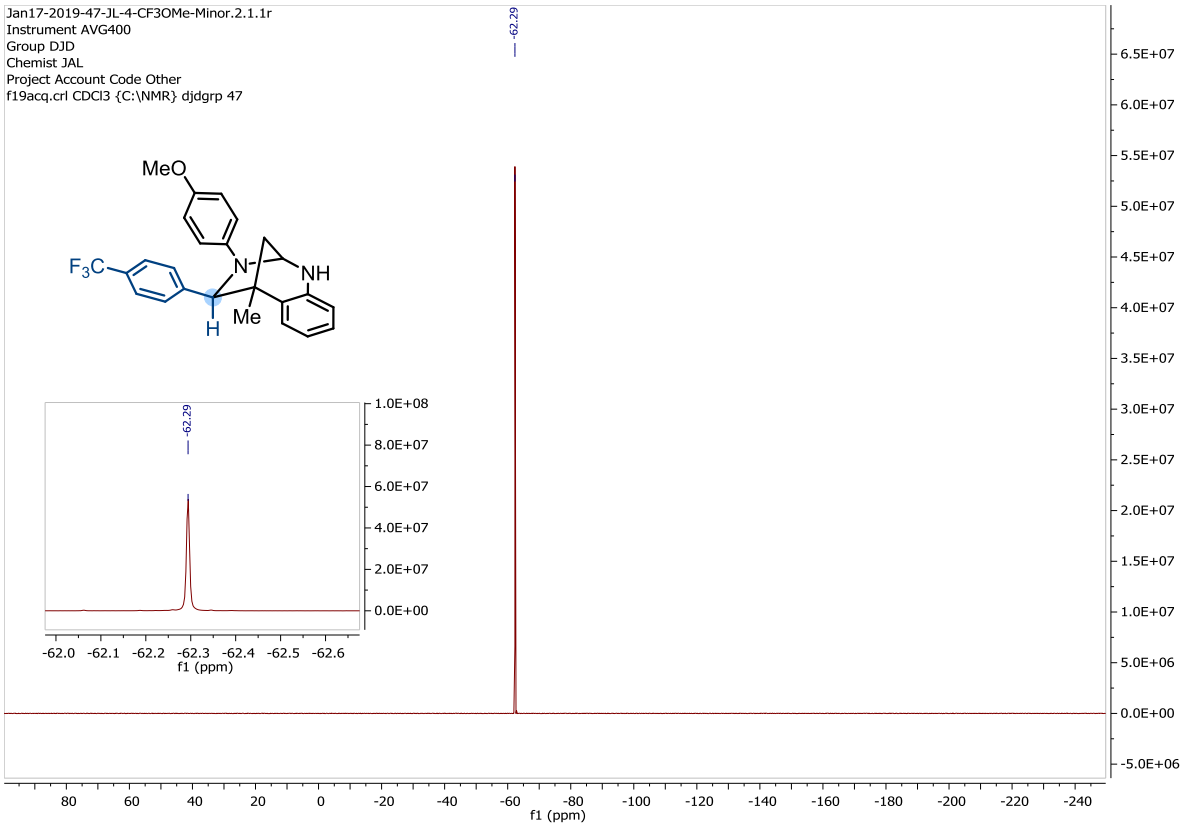
3m$_{(endo)}$ – ^{13}C NMR (126 MHz, $CDCl_3$)



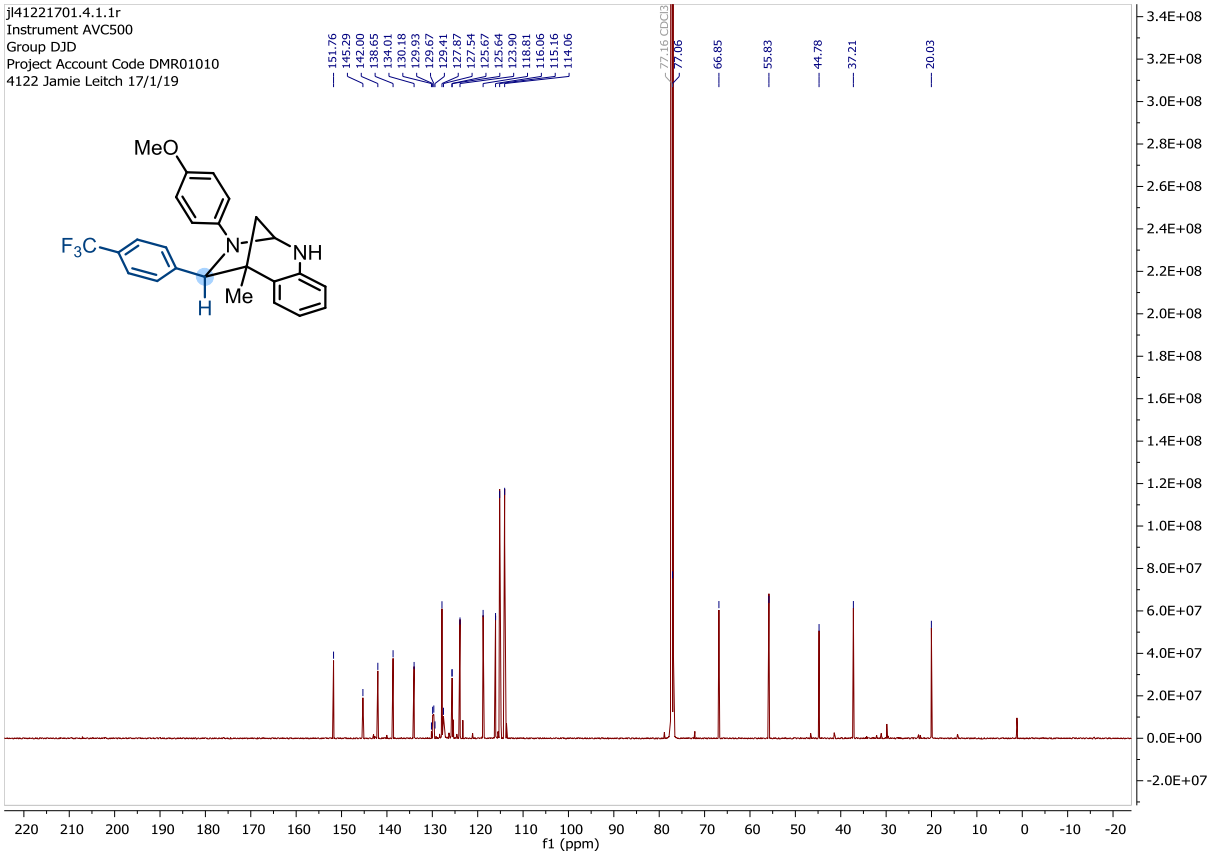
3m$_{(exo)}$ - ^{1}H NMR (400 MHz, $CDCl_3$)



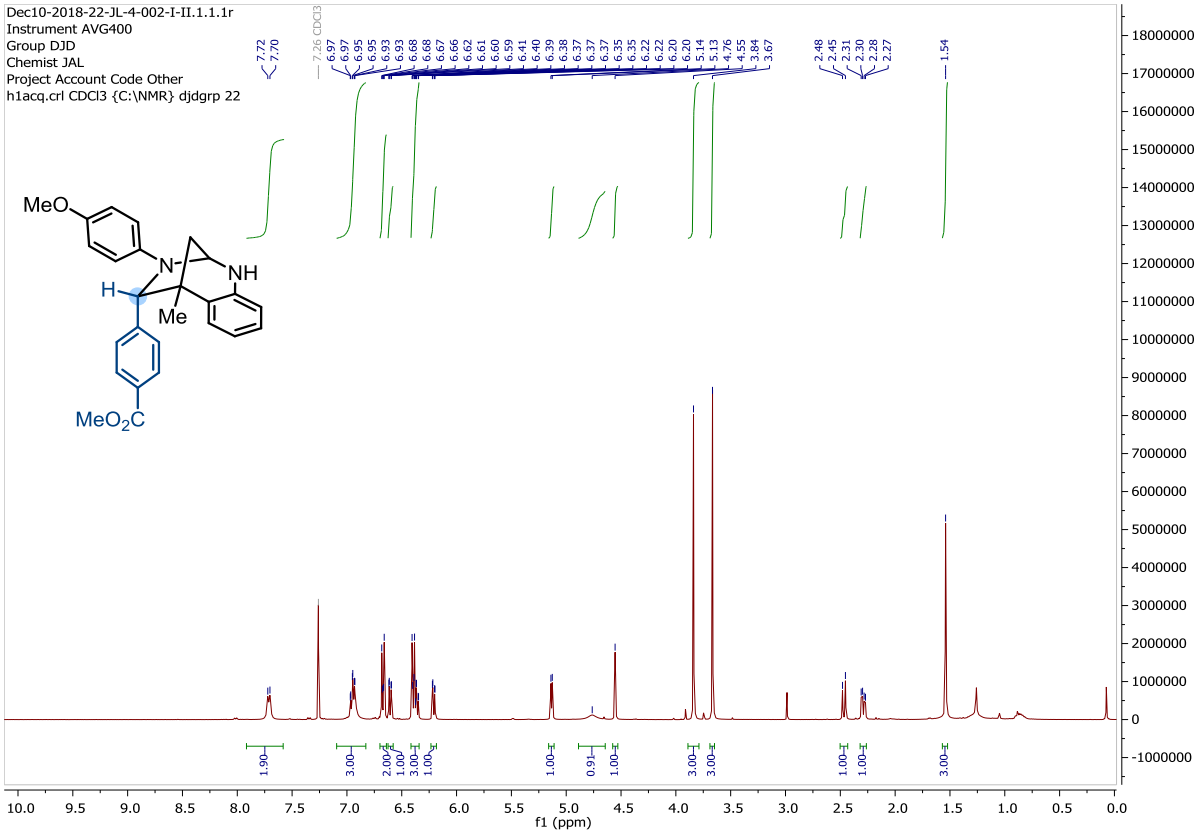
3m$_{(exo)}$ – ^{19}F NMR (377 MHz, $CDCl_3$)



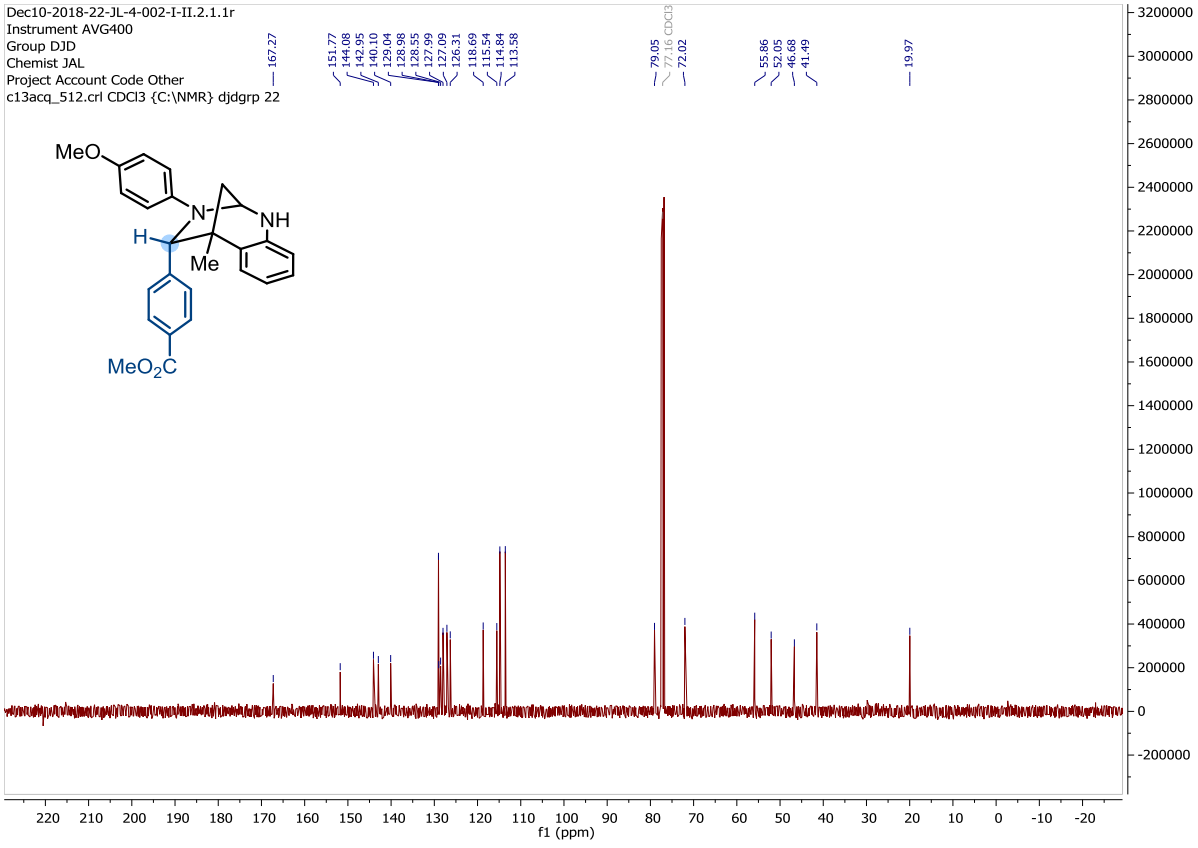
3m$_{(exo)}$ – ^{13}C NMR (126 MHz, $CDCl_3$)



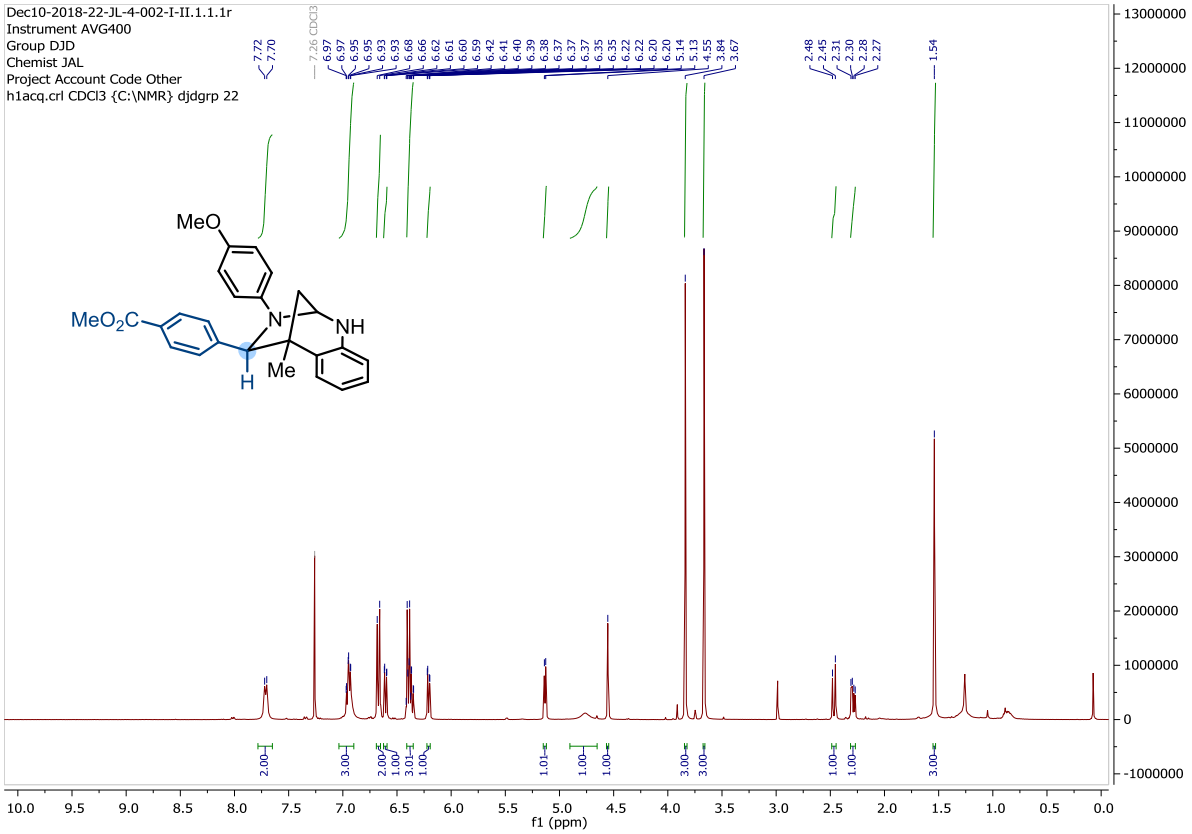
3n$_{(endo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



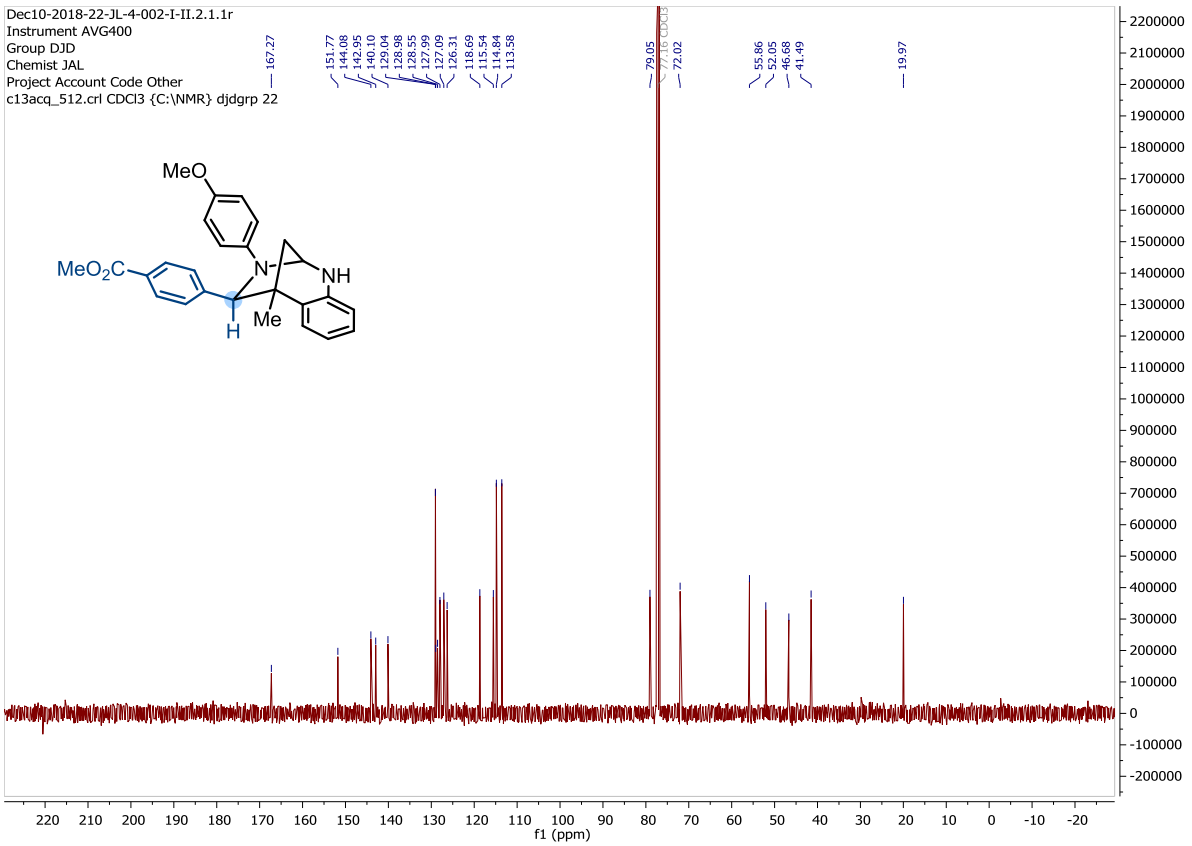
3n$_{(endo)}$ – ^{13}C NMR (101 MHz, $CDCl_3$)



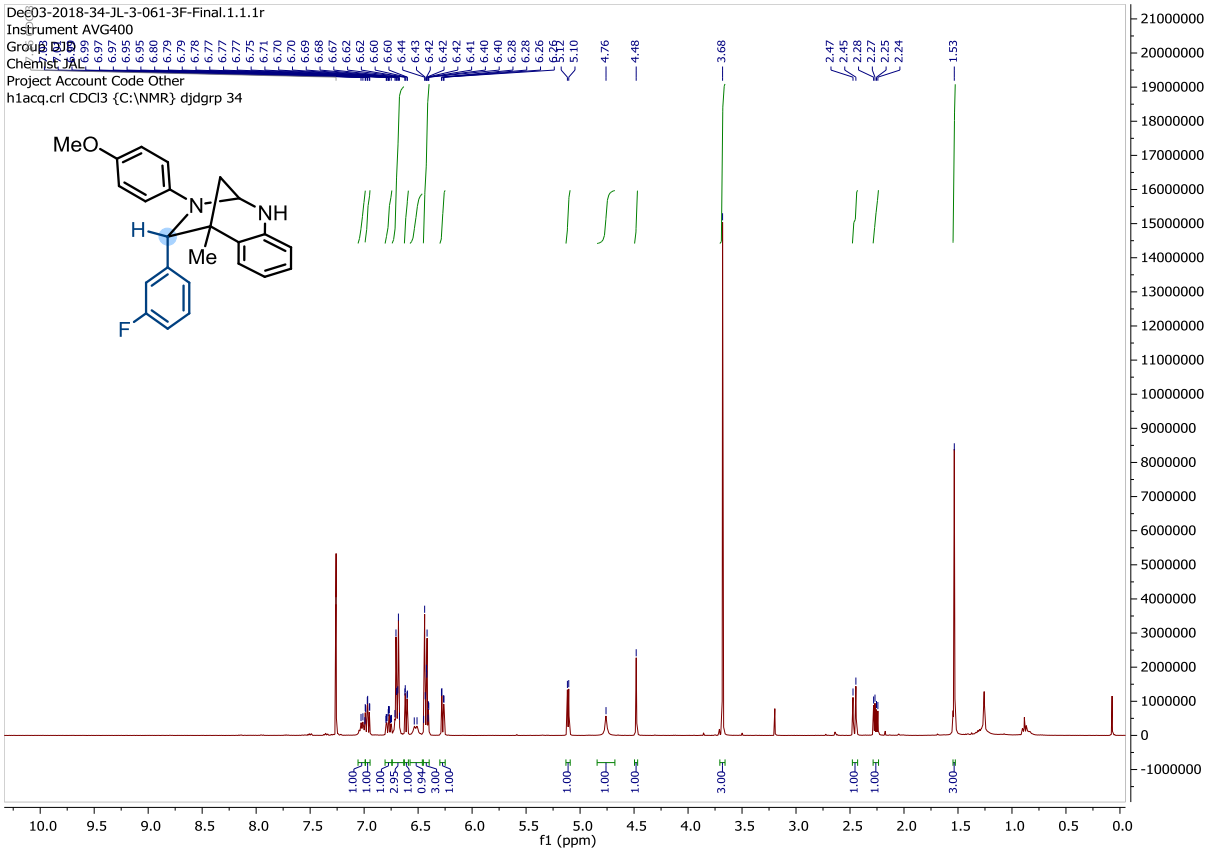
3n$_{(exo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



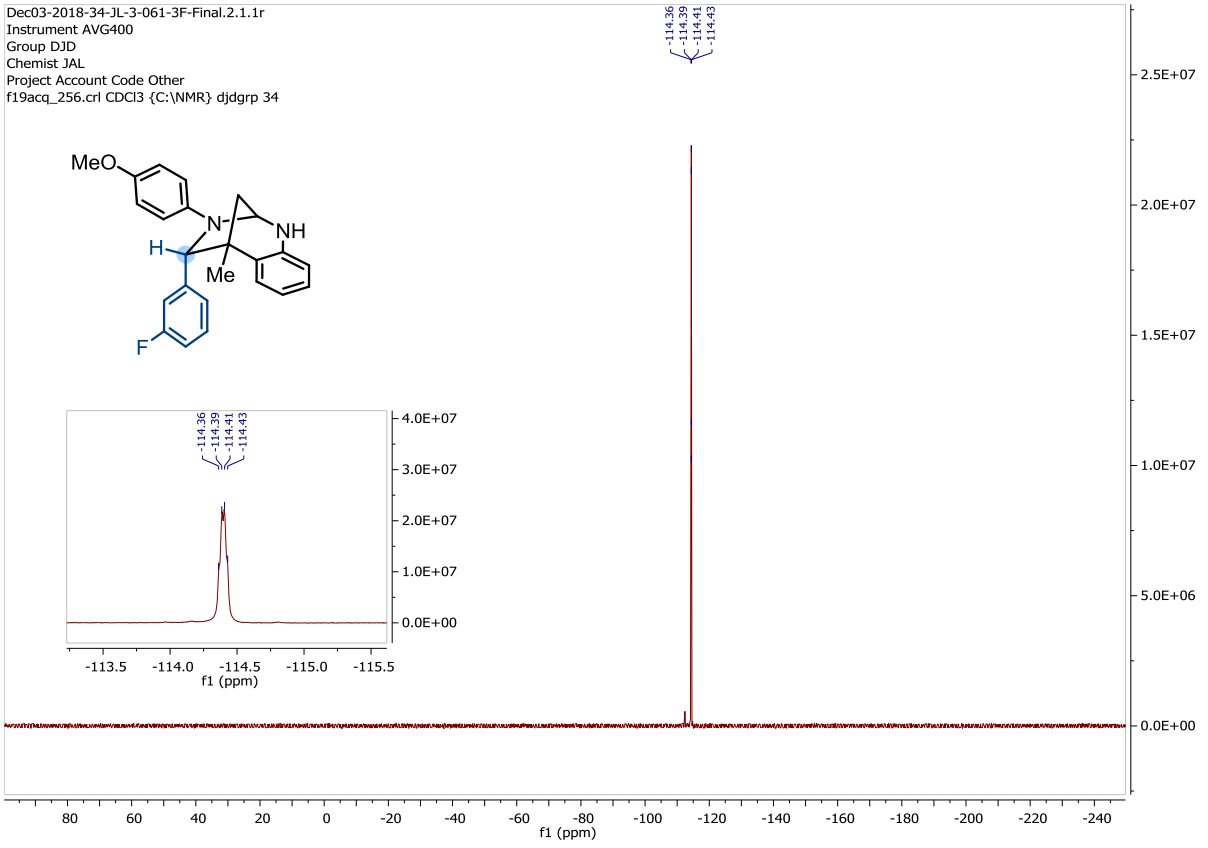
3n$_{(exo)}$ – ^{13}C NMR (101 MHz, $CDCl_3$)



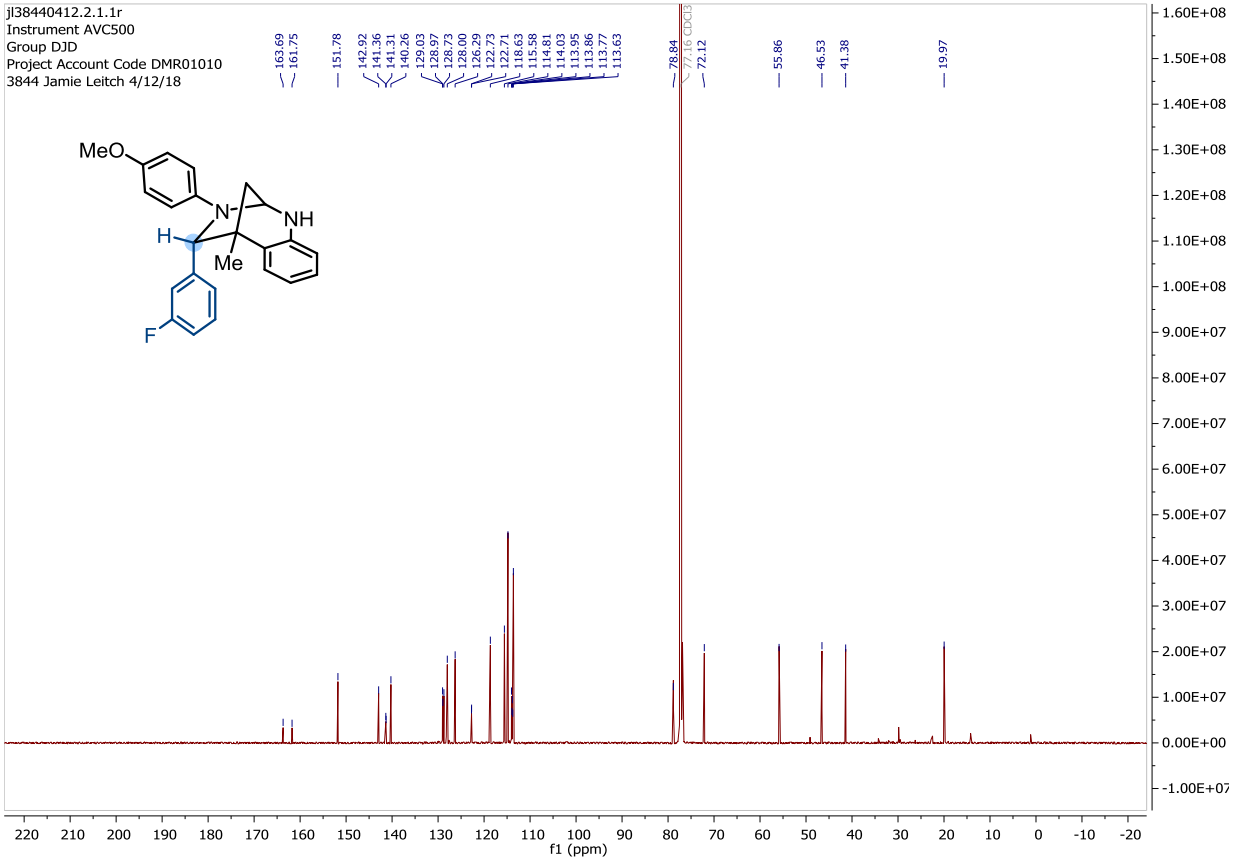
3o$_{(endo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



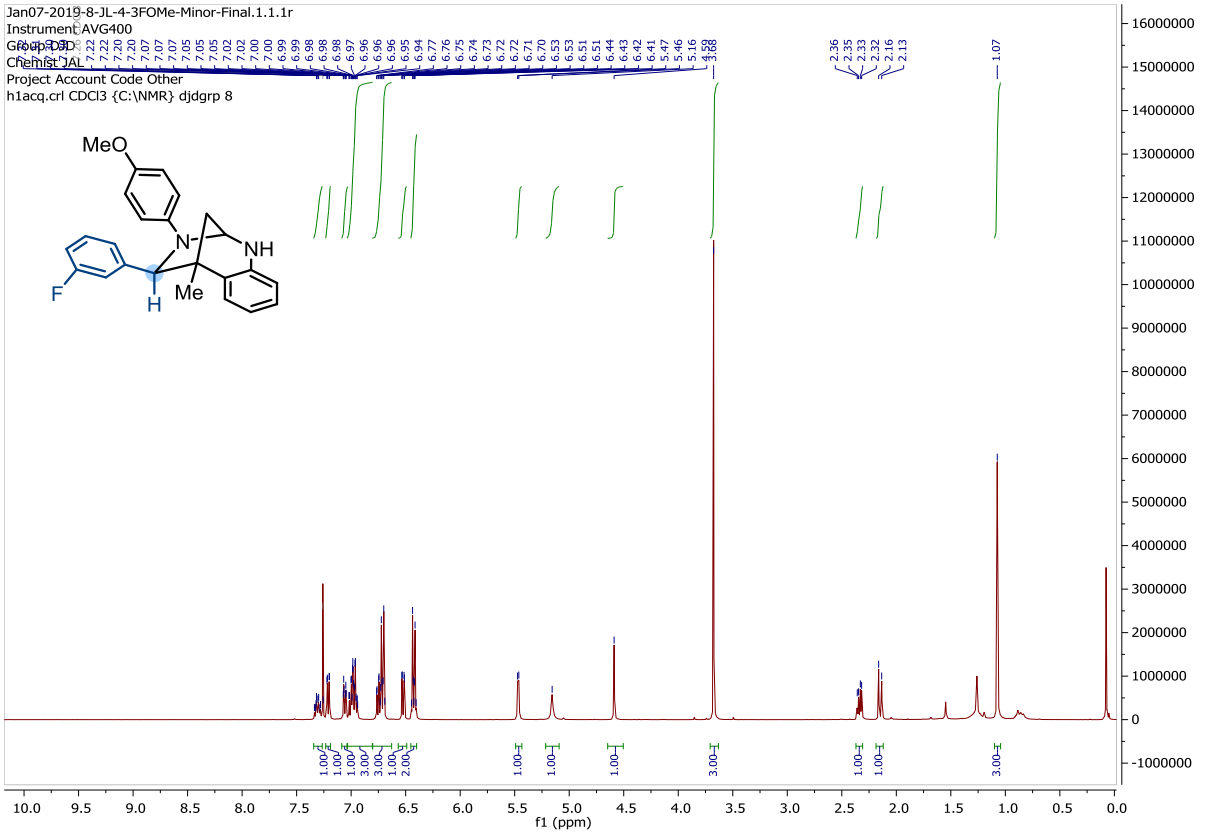
3o$_{(endo)}$ – ^{19}F NMR (377 MHz, $CDCl_3$)



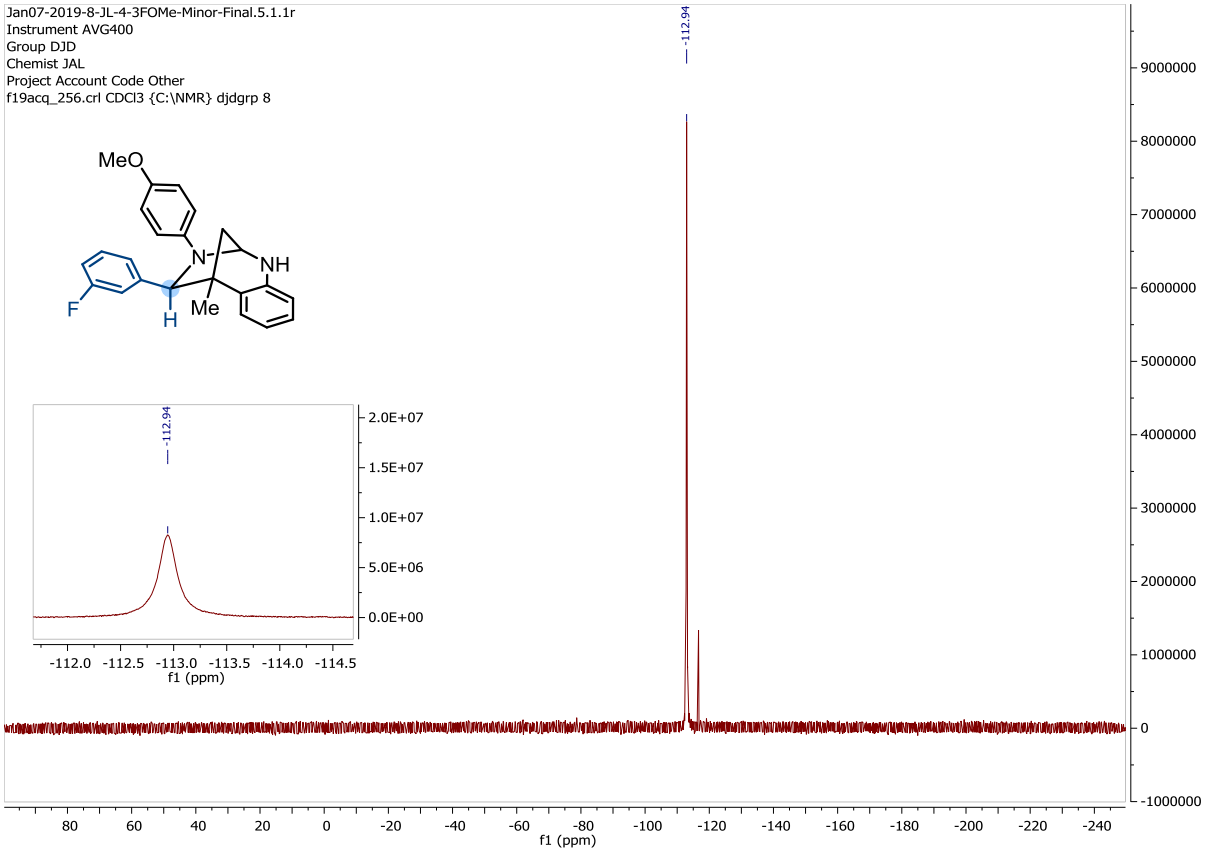
3o$_{(endo)}$ – ^{13}C NMR (126 MHz, $CDCl_3$)



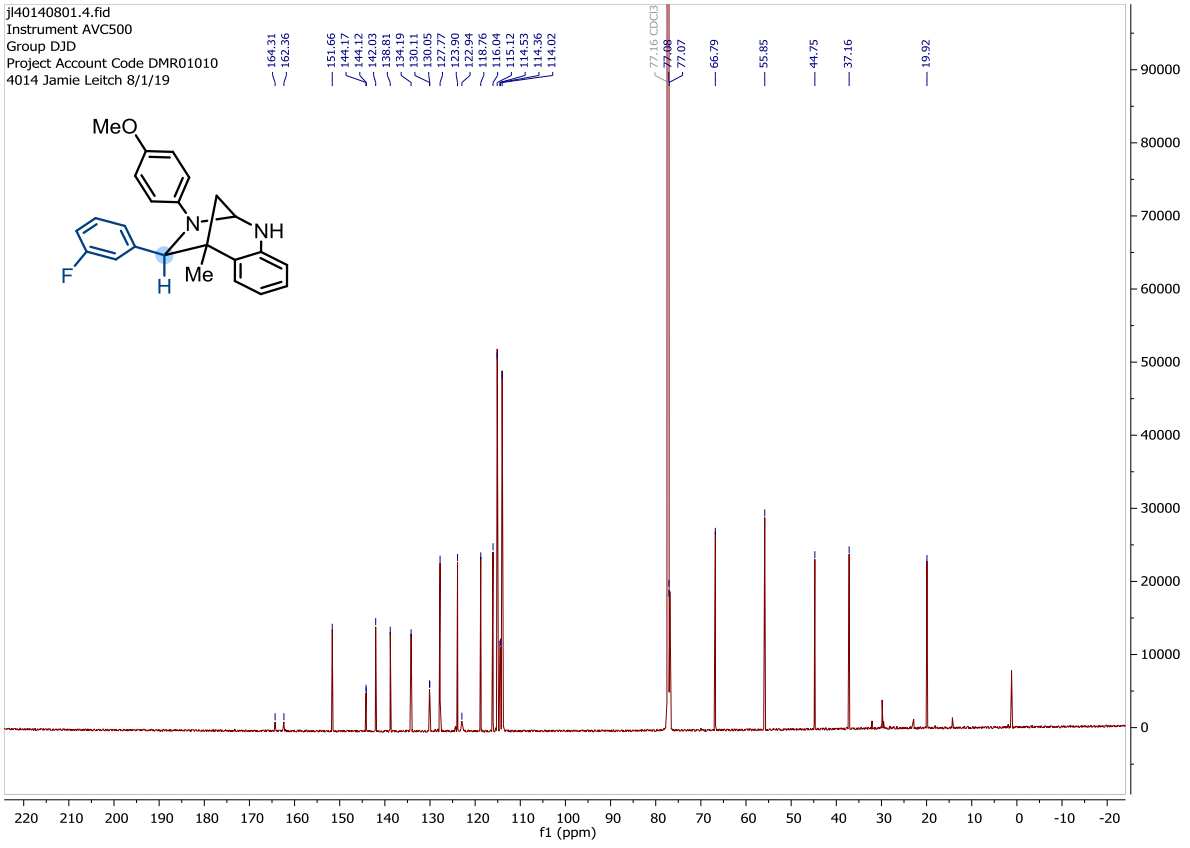
3o(exo) – ^{1}H NMR (400 MHz, $CDCl_3$)



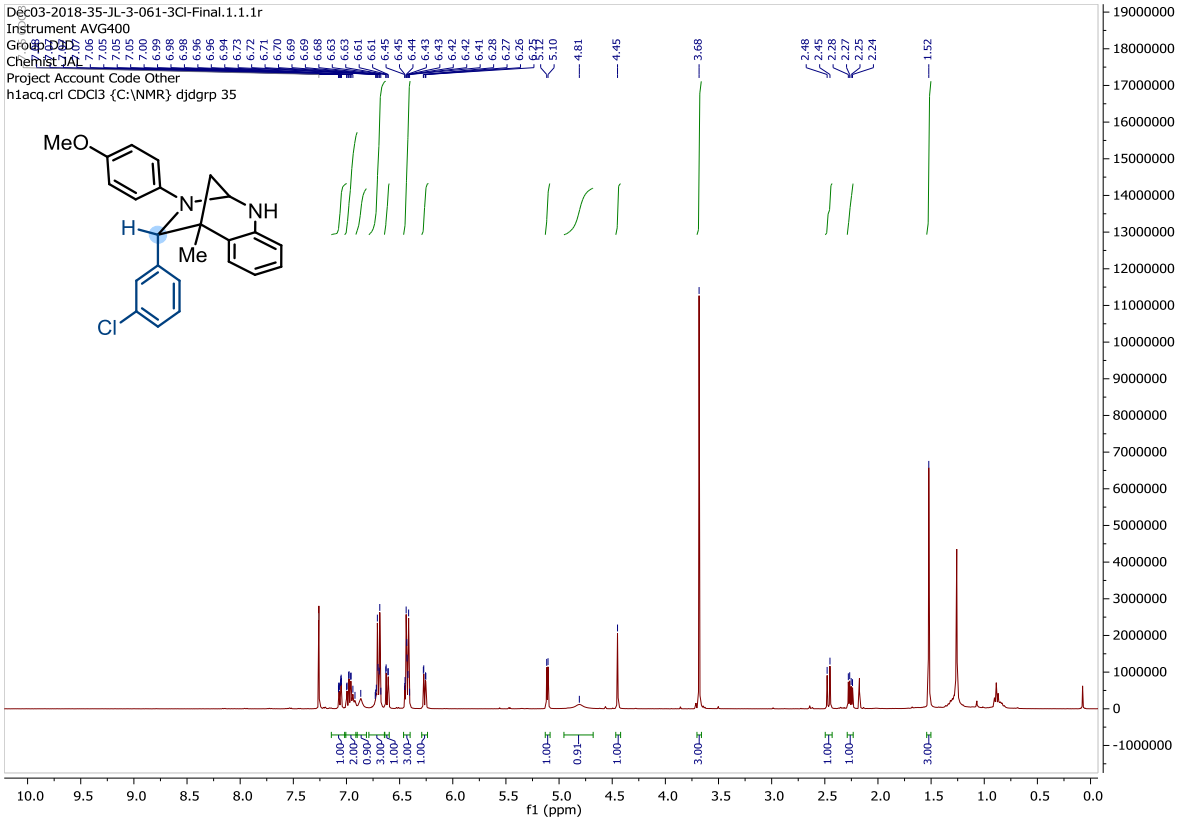
3o(exo) – ^{19}F NMR (377 MHz, $CDCl_3$)



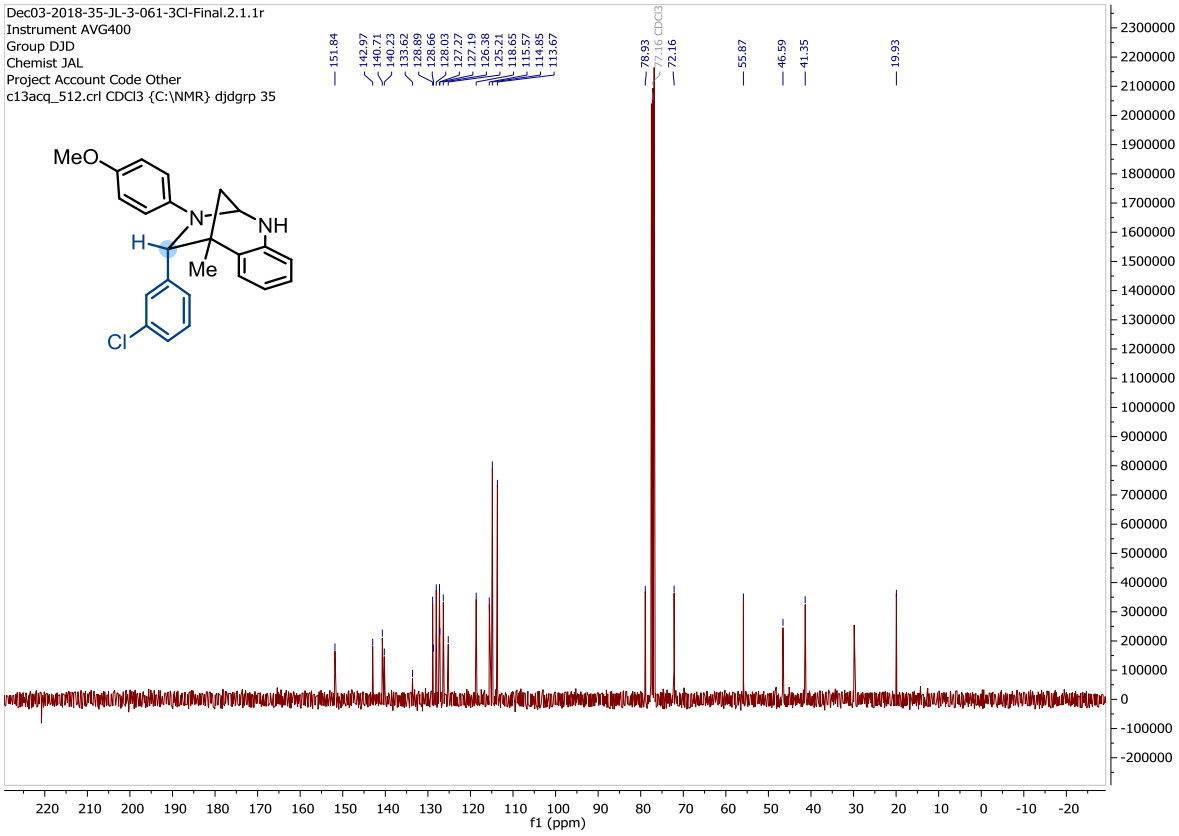
3o$_{(exo)}$ – ^{13}C NMR (126 MHz, $CDCl_3$)



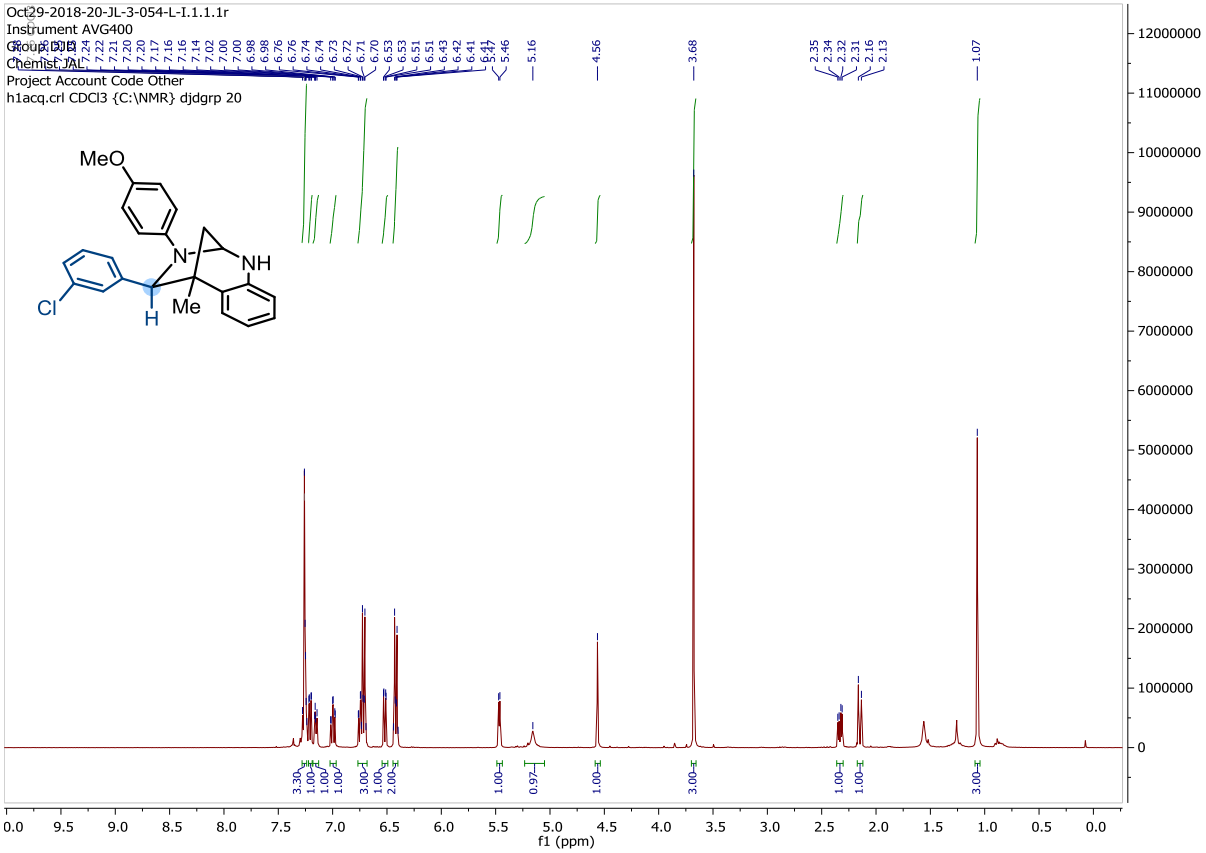
3p(endo) – ^{1}H NMR (400 MHz, $CDCl_3$)



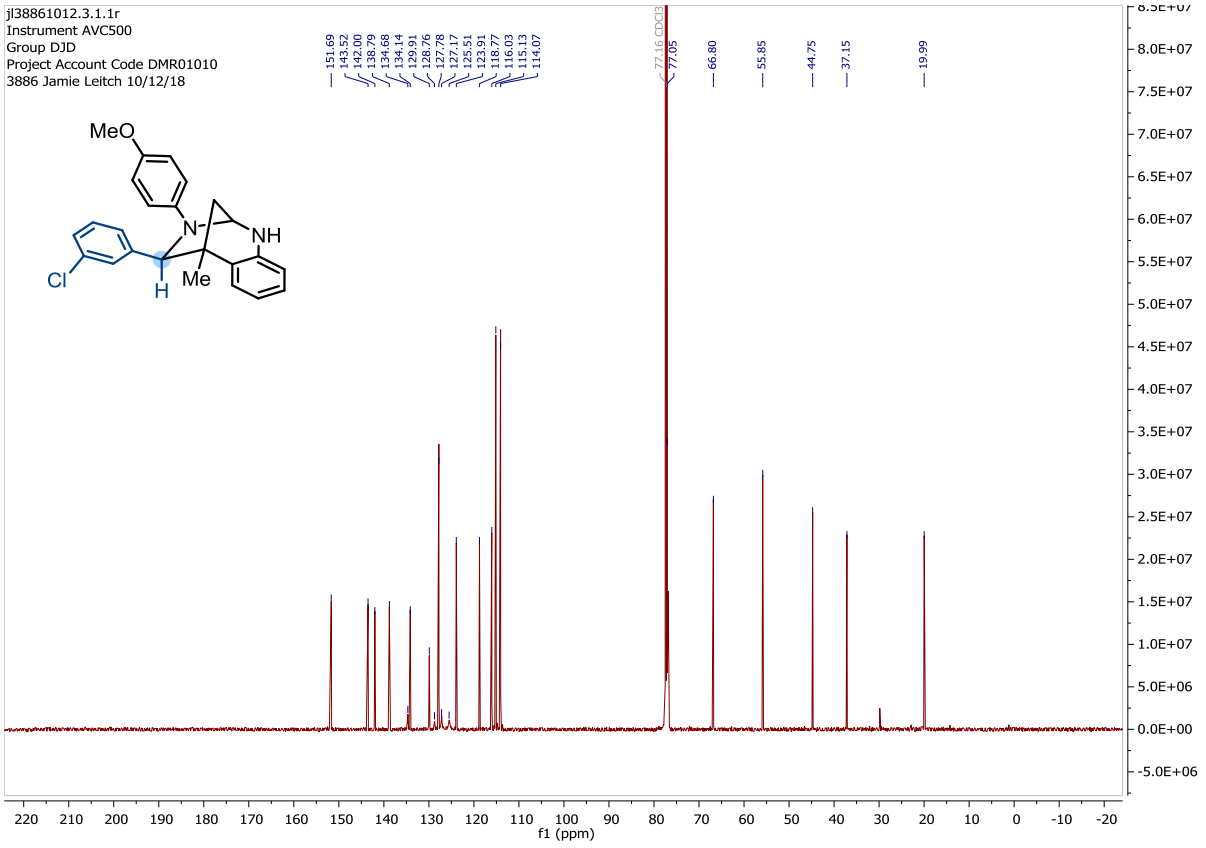
3p(exo) – ^{13}C NMR (101 MHz, $CDCl_3$)



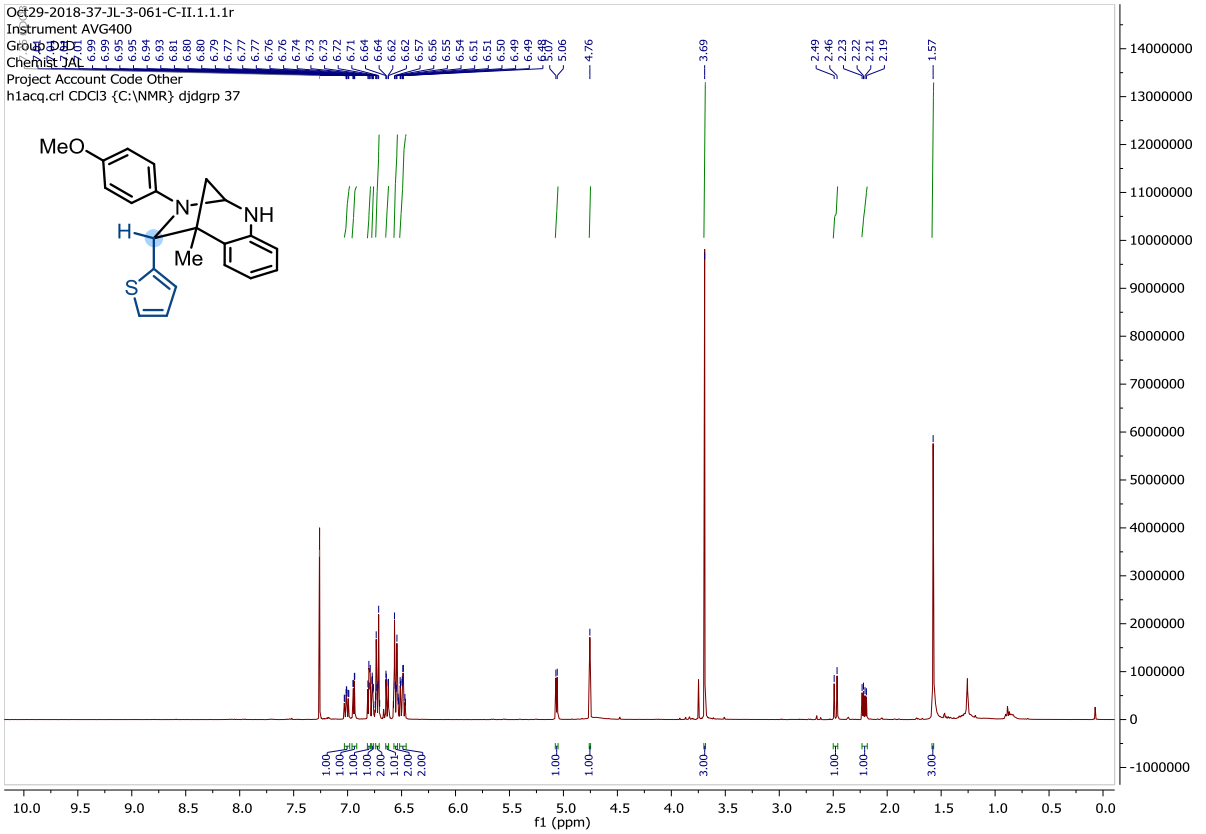
3p(exo) – ^{1}H NMR (400 MHz, $CDCl_3$)



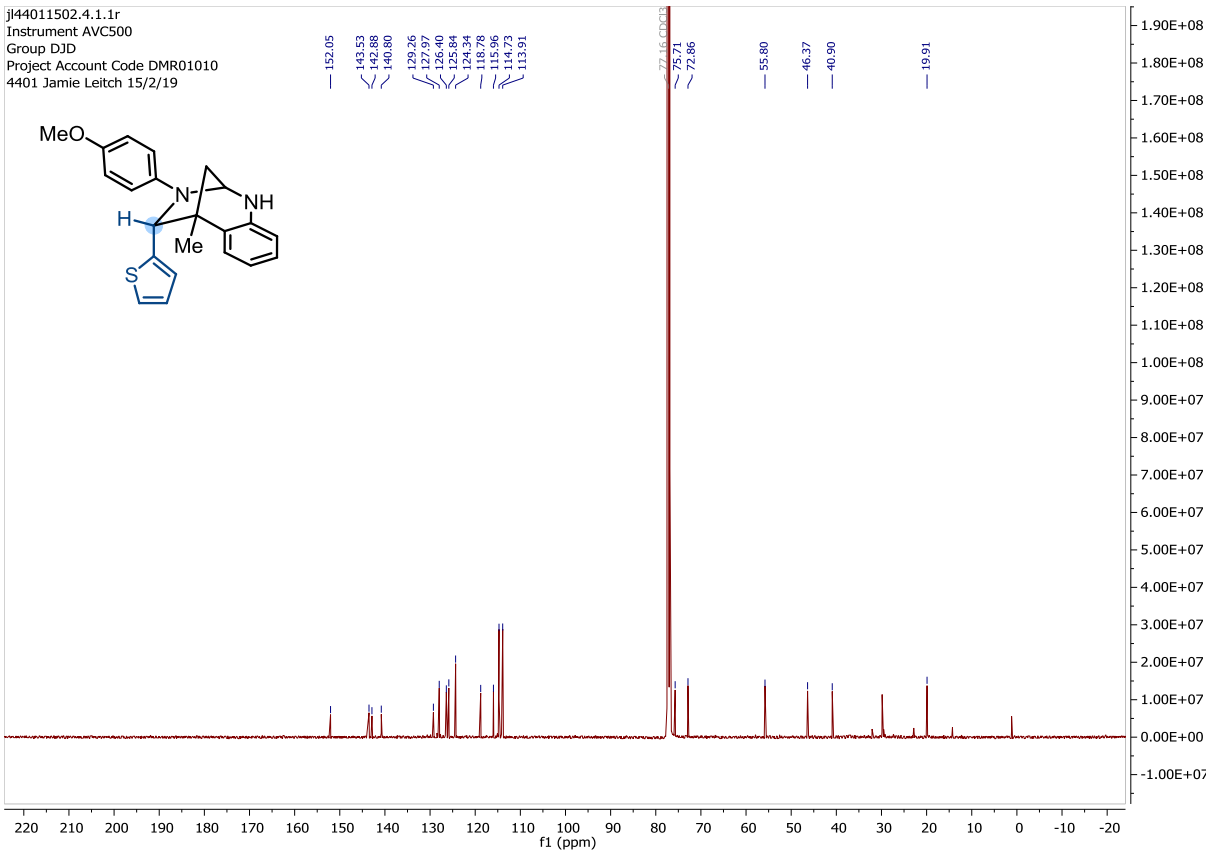
3p(exo) – ^{13}C NMR (126 MHz, $CDCl_3$)



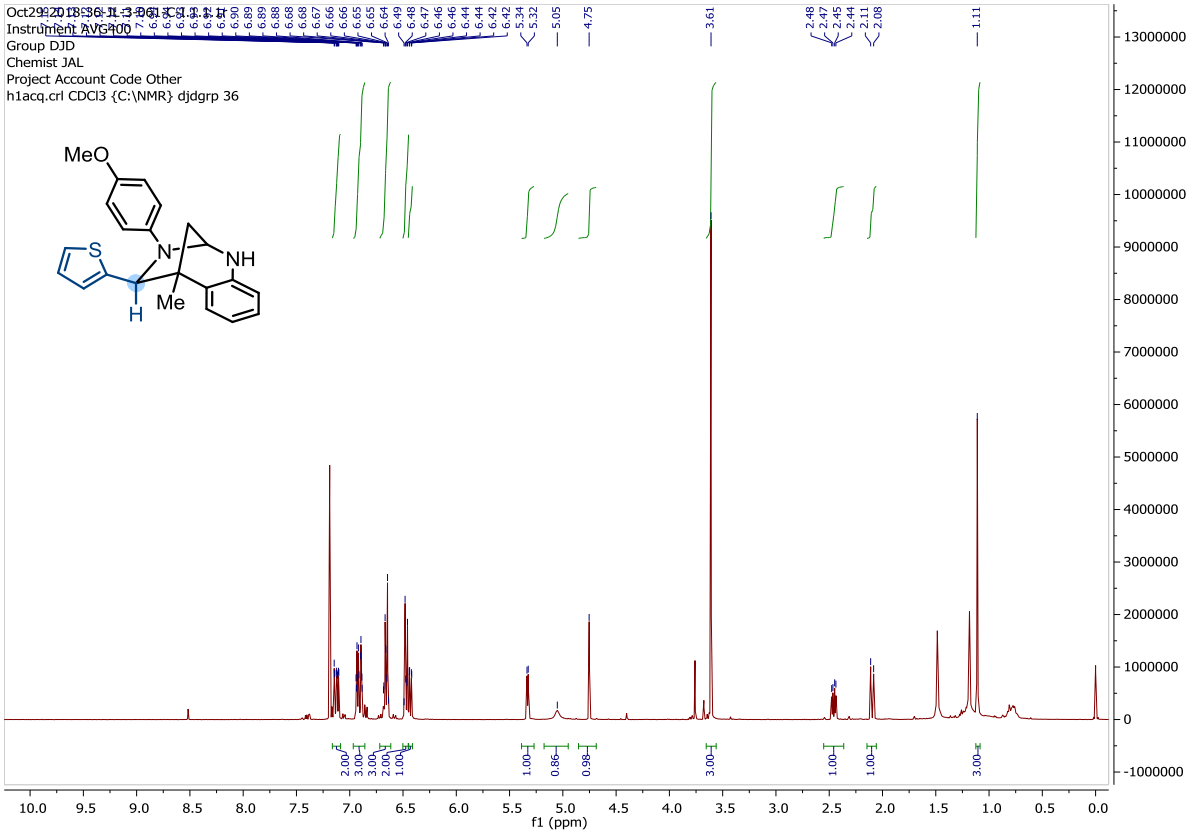
3q(endo) – ^{1}H NMR (400 MHz, $CDCl_3$)



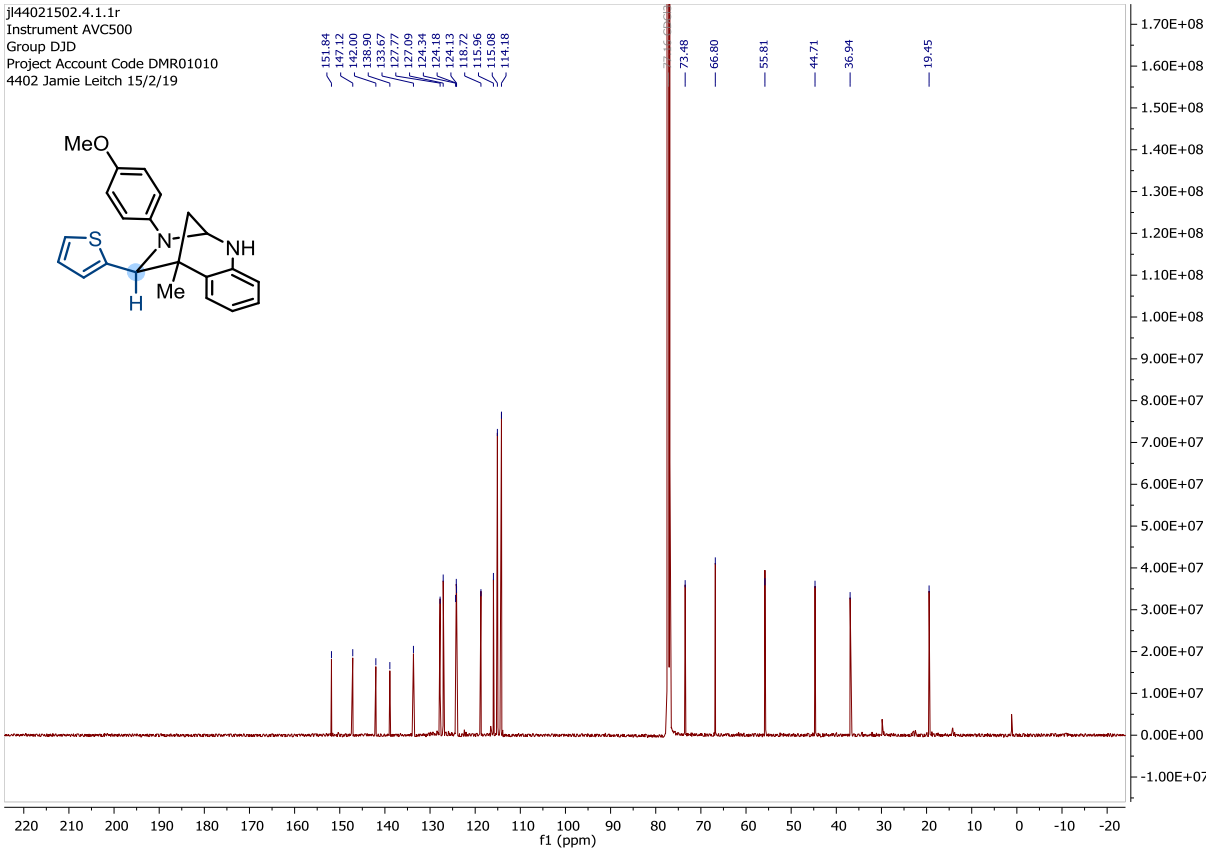
3q(endo) – ^{13}C NMR (126 MHz, $CDCl_3$)



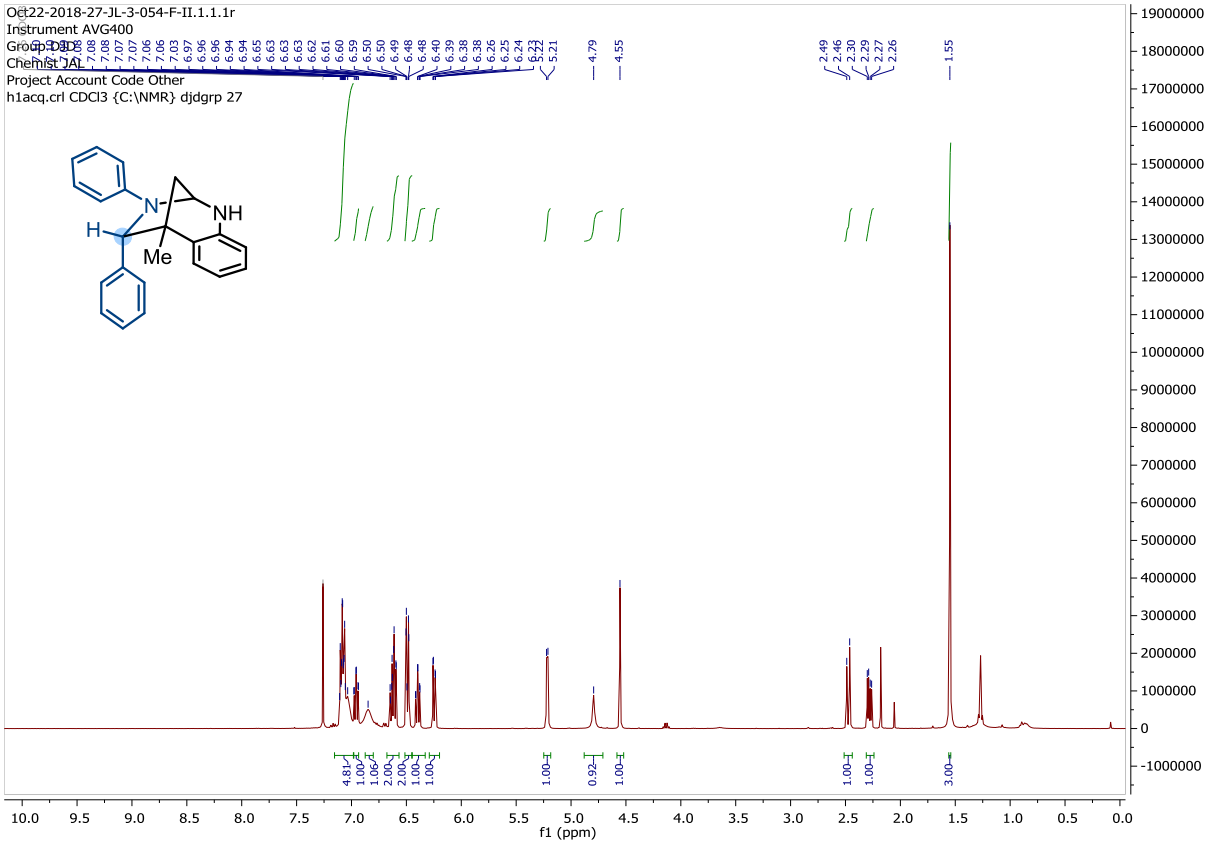
3q(exo) – ^{1}H NMR (400 MHz, $CDCl_3$)



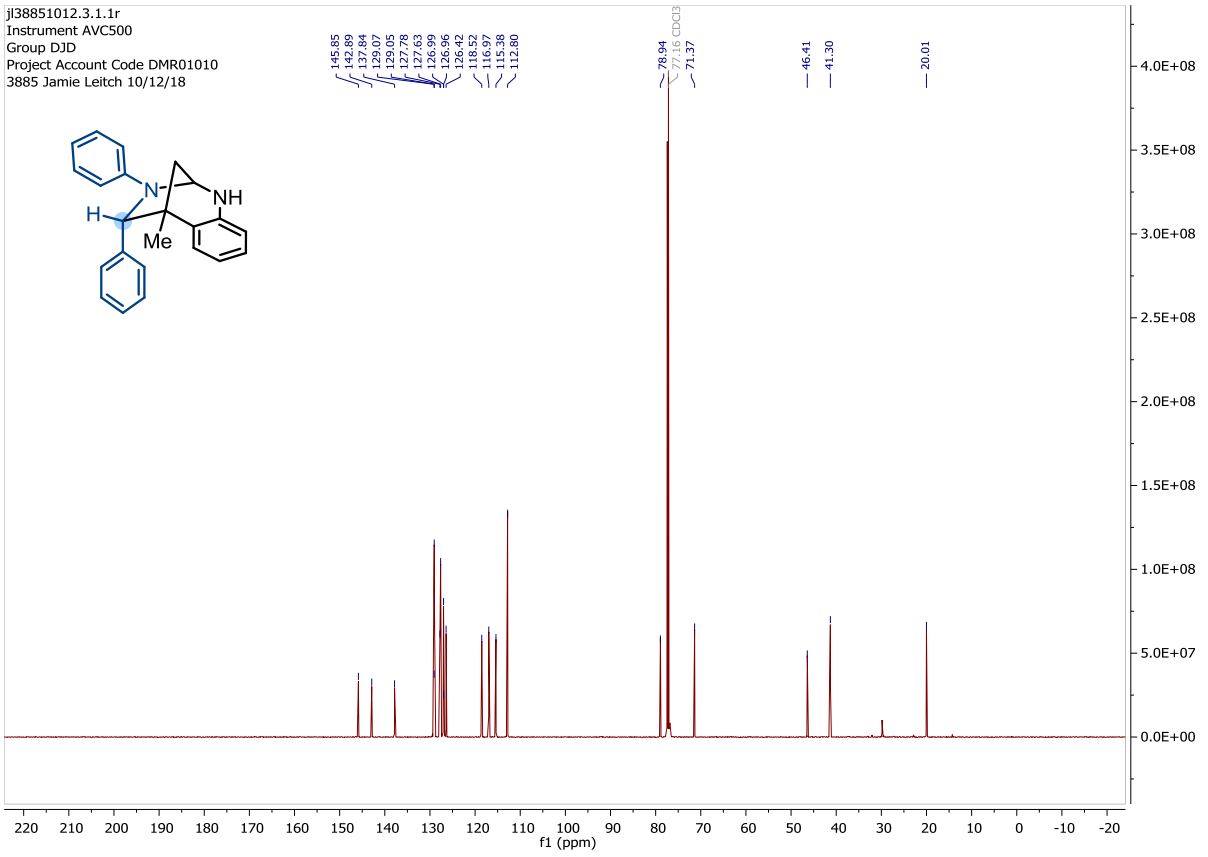
3q(exo) – ^{13}C NMR (125 MHz, $CDCl_3$)



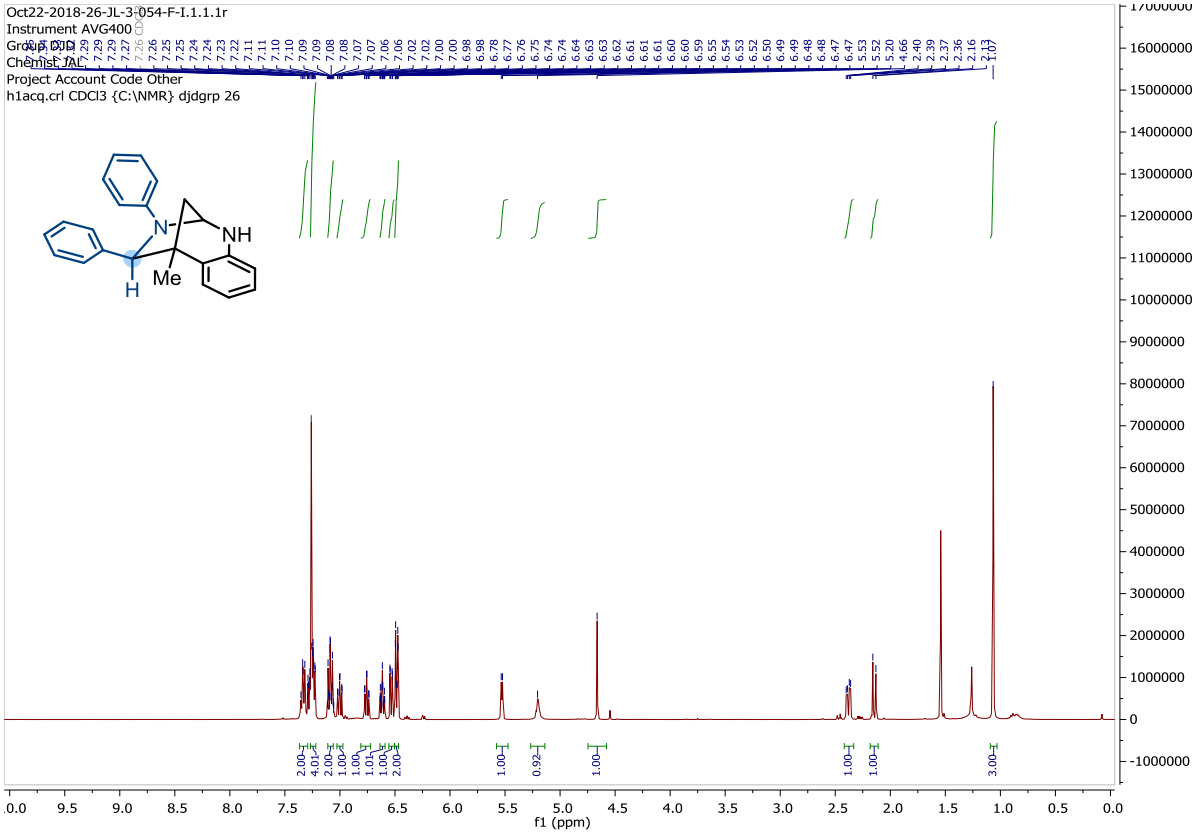
3r$_{(endo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



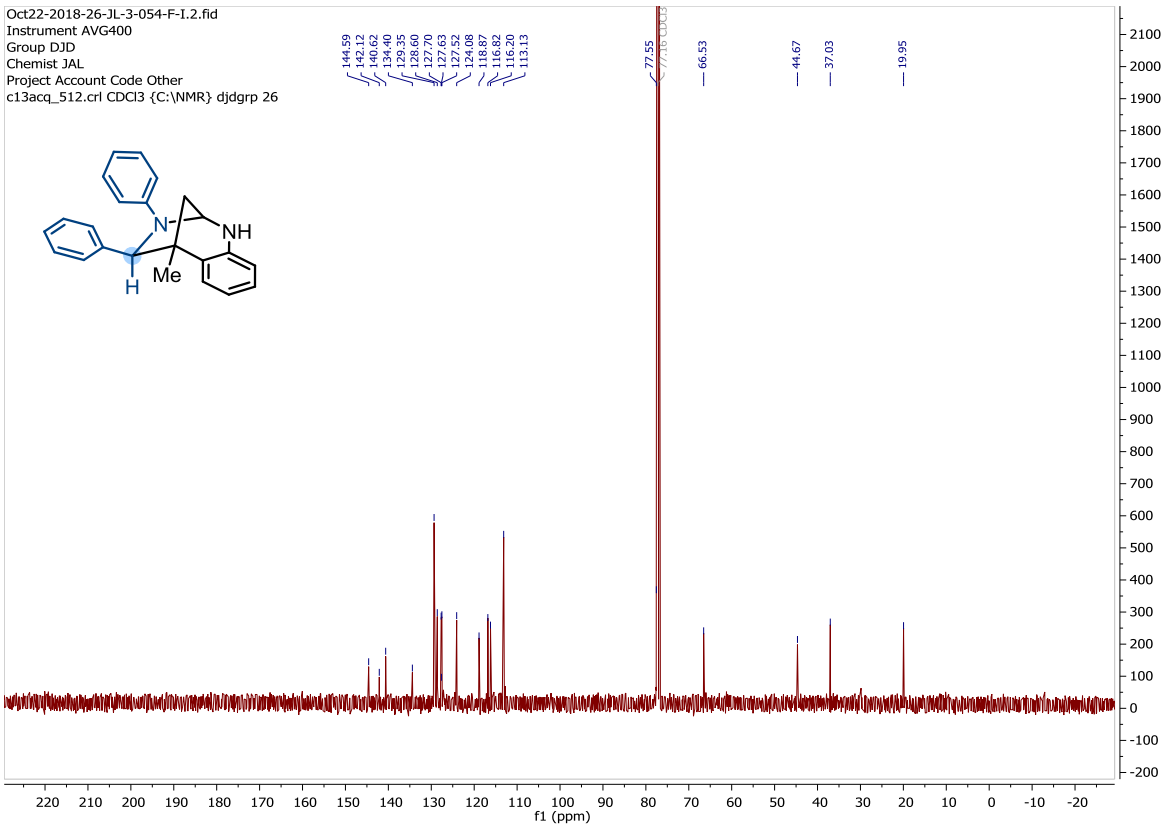
3r$_{(endo)}$ – ^{13}C NMR (126 MHz, $CDCl_3$)



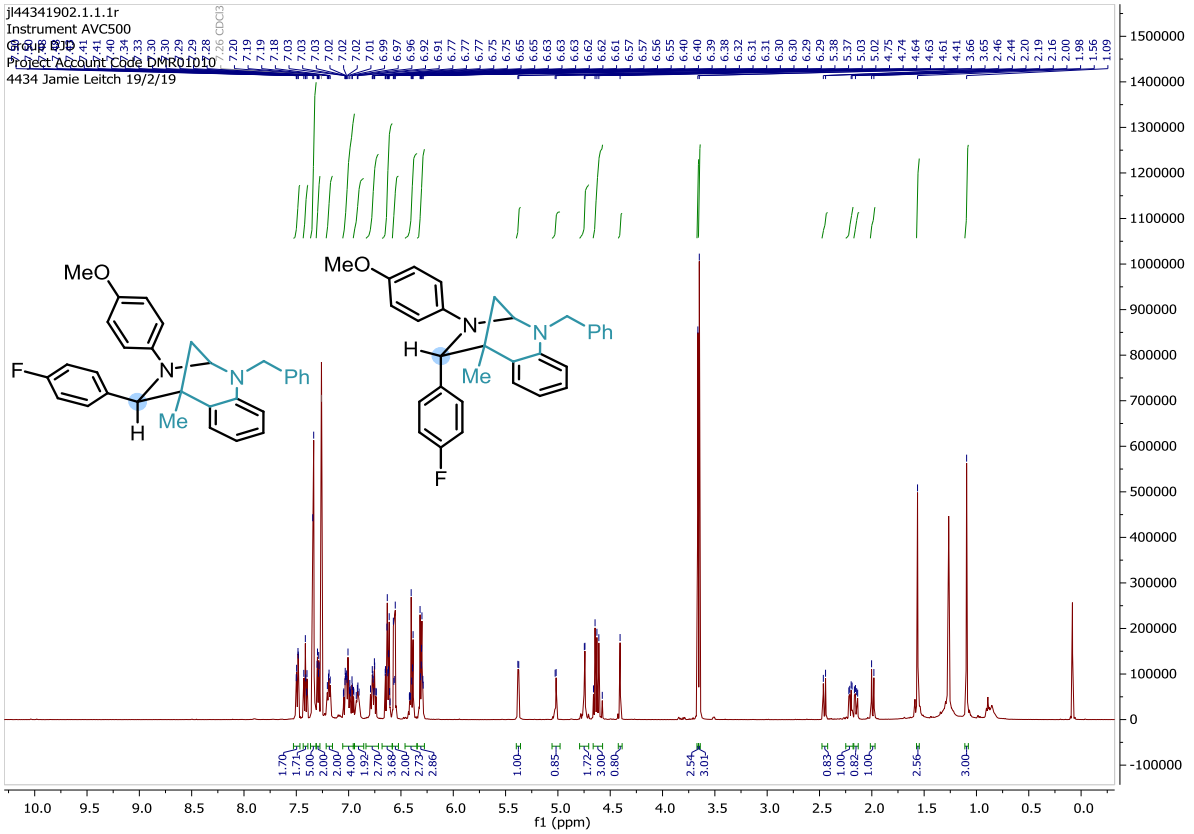
3r$_{(exo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



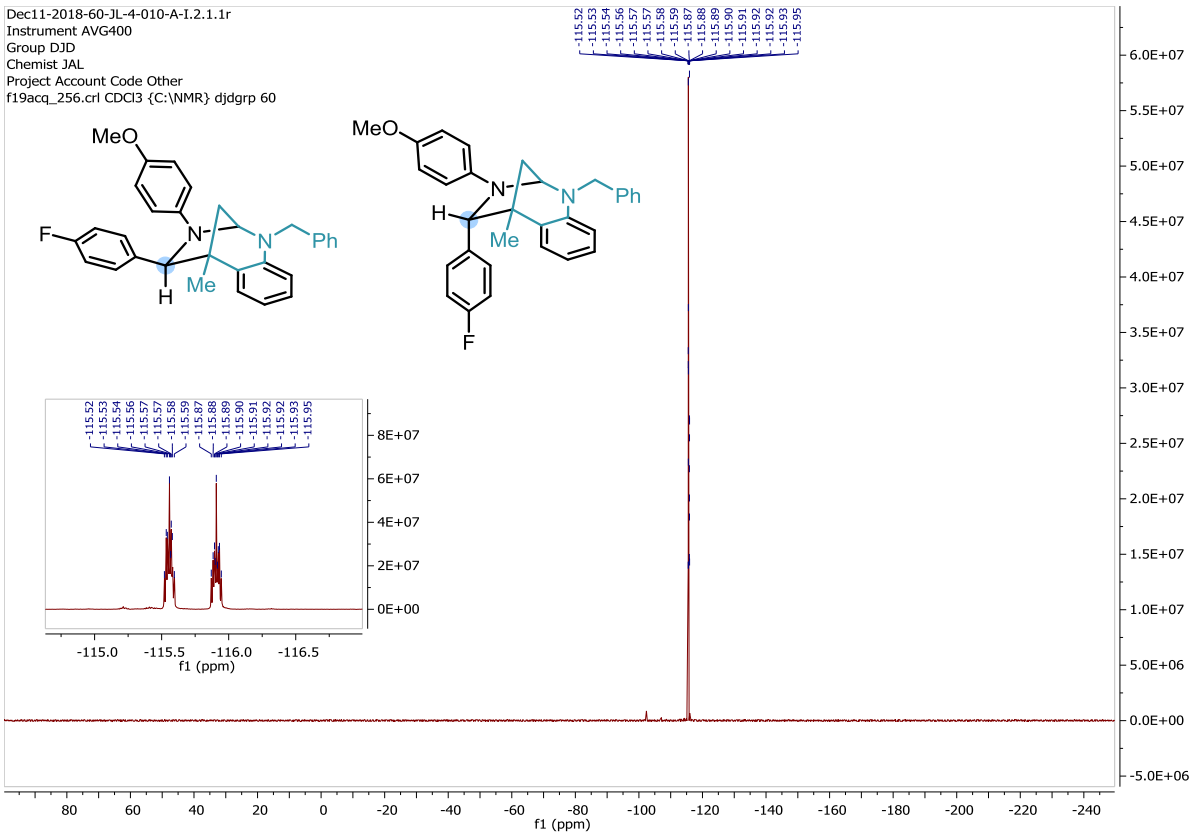
3r$_{(exo)}$ – ^{13}C NMR (101 MHz, $CDCl_3$)



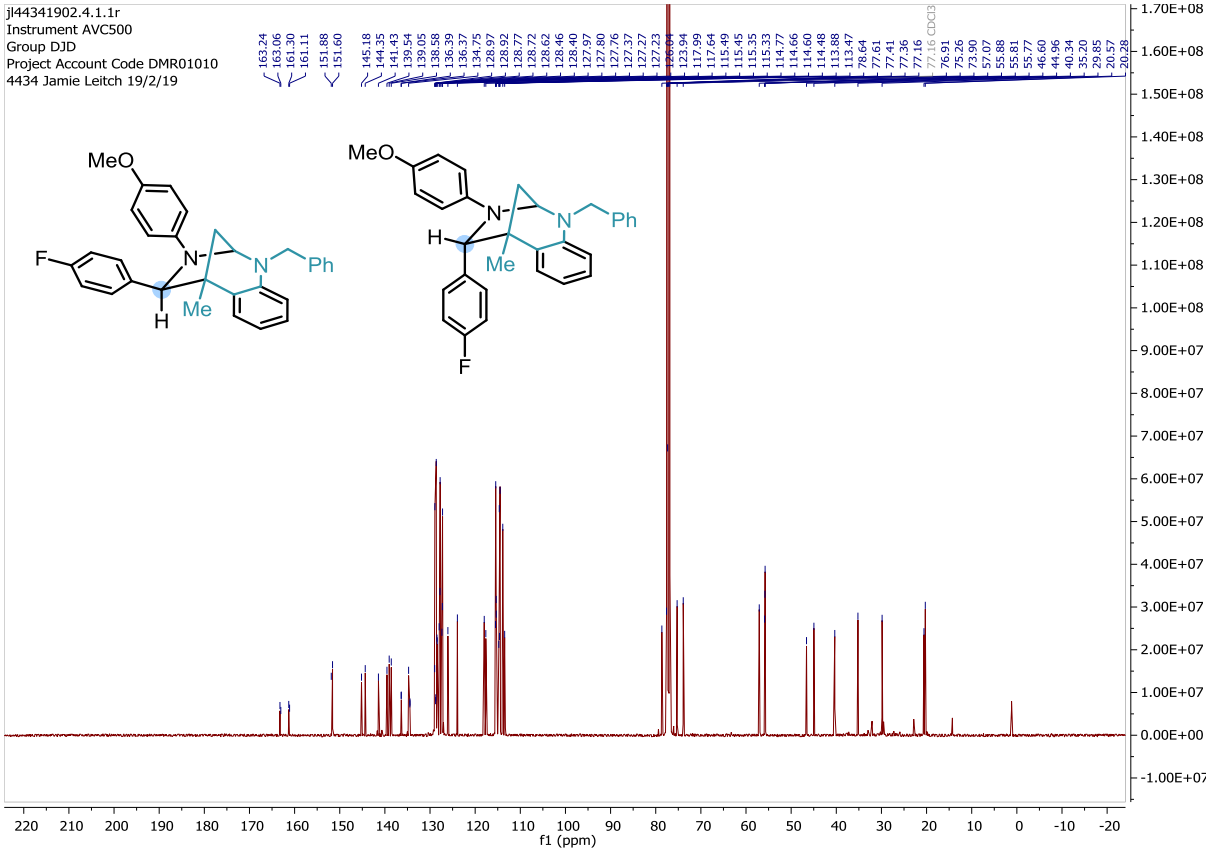
3al$_{(exo\ \&\ endo)}$- ^{1}H NMR (500 MHz, $CDCl_3$)



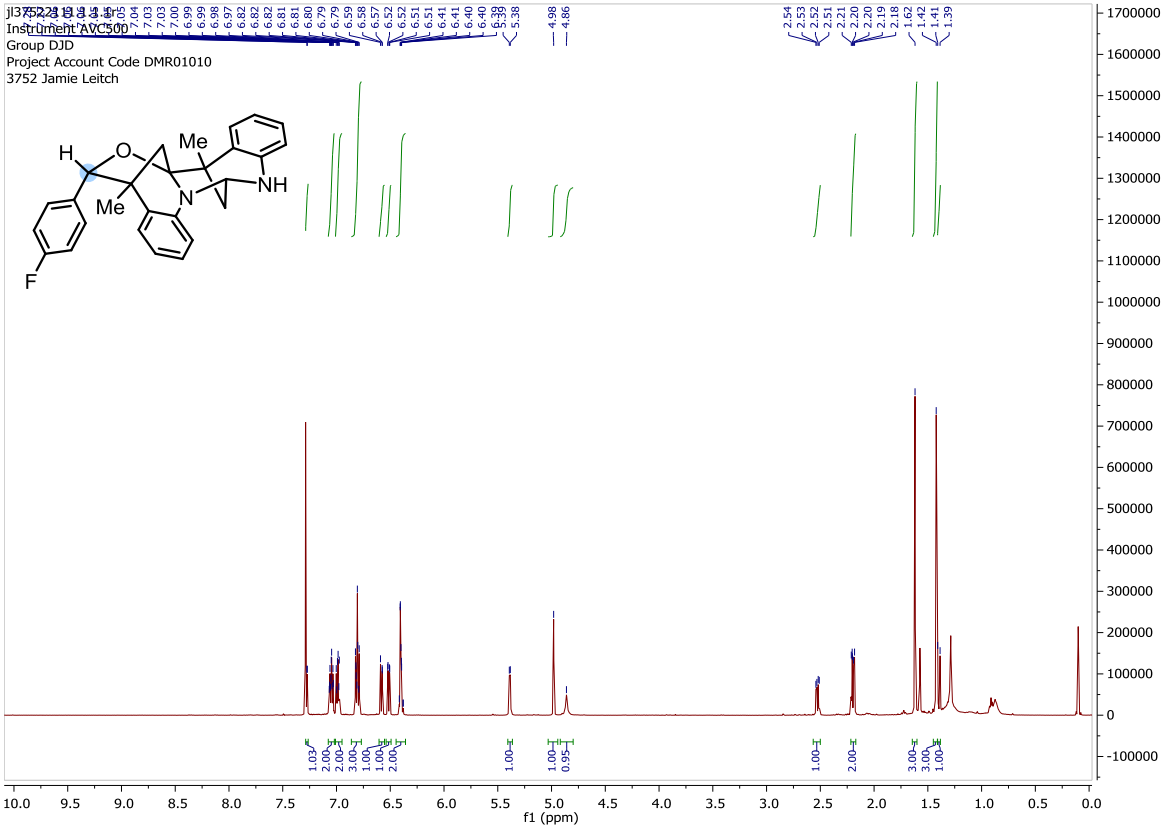
3al$_{(exo\ \&\ endo)}$- ^{19}F NMR (377 MHz, $CDCl_3$)



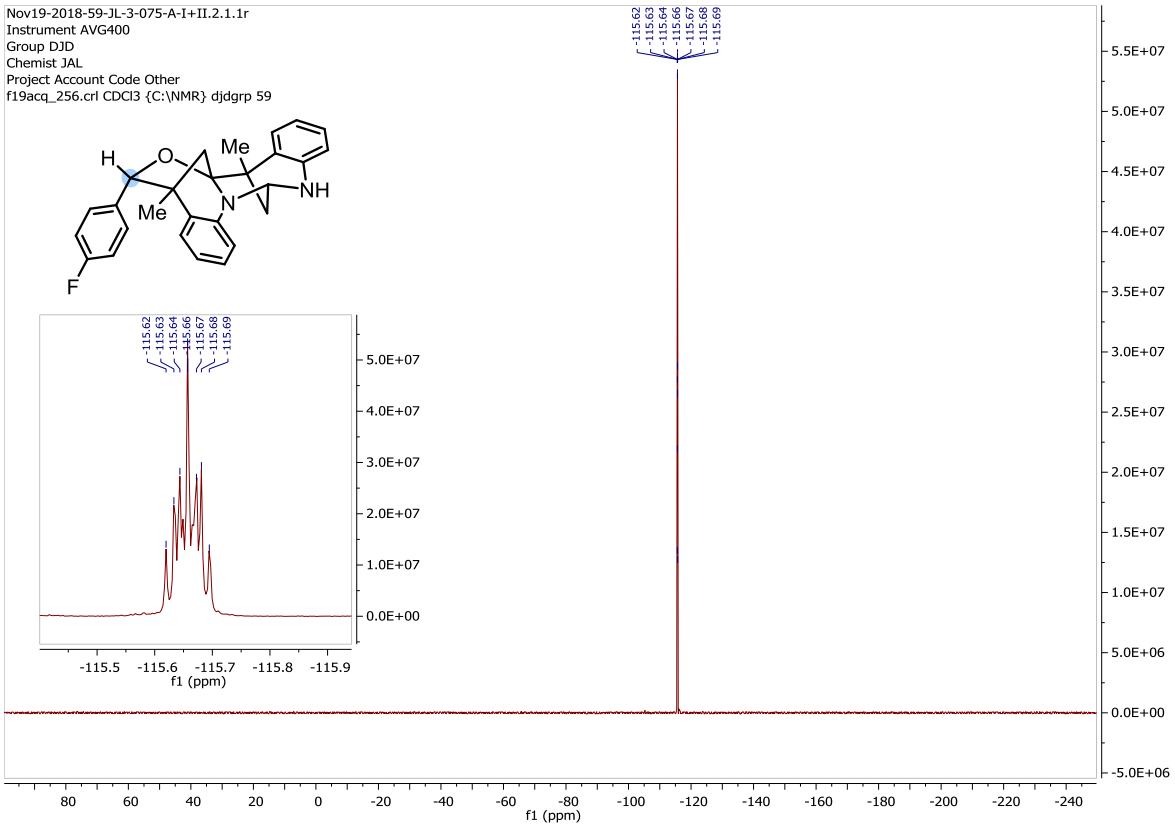
3al$_{(exo\ \&\ endo)}$- ^{13}C NMR (126 MHz, $CDCl_3$)



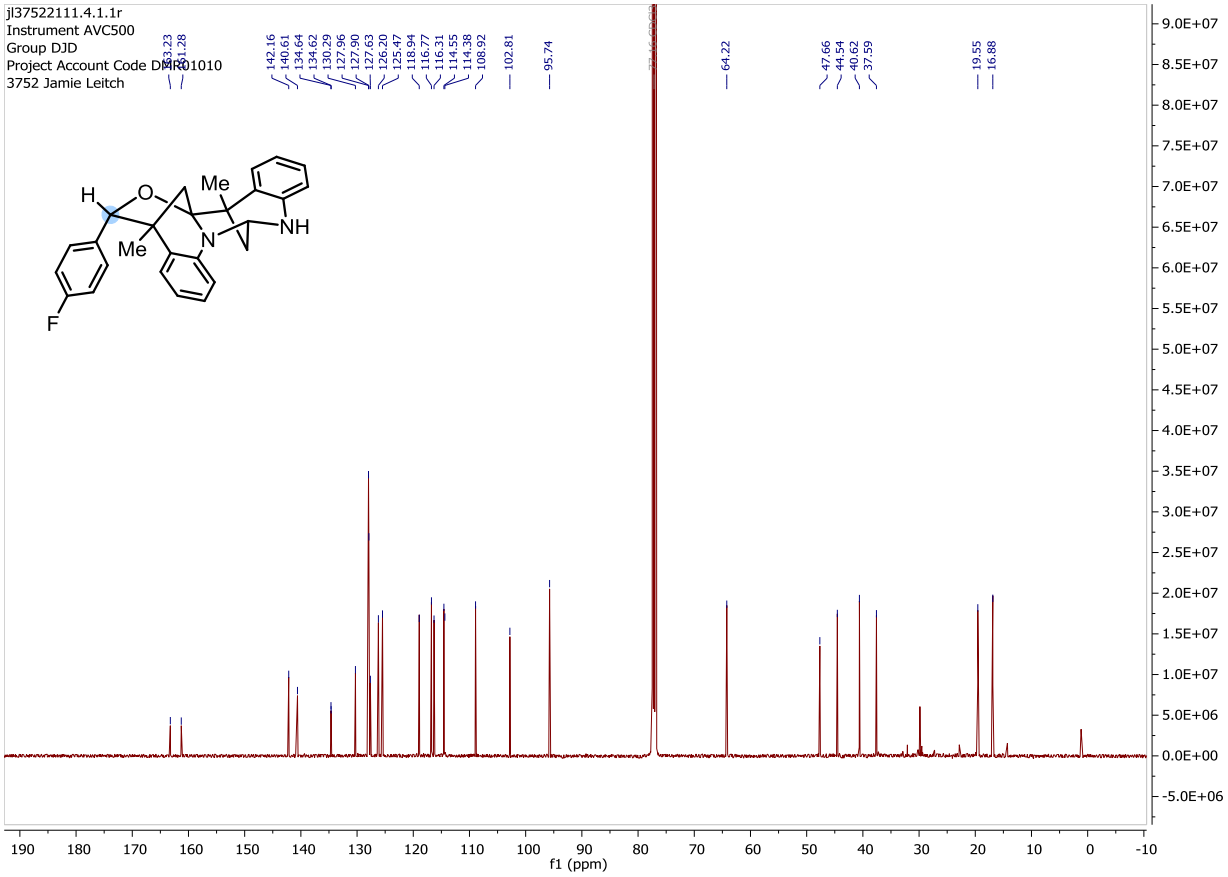
5a – ^{1}H NMR (500 MHz, $CDCl_3$)



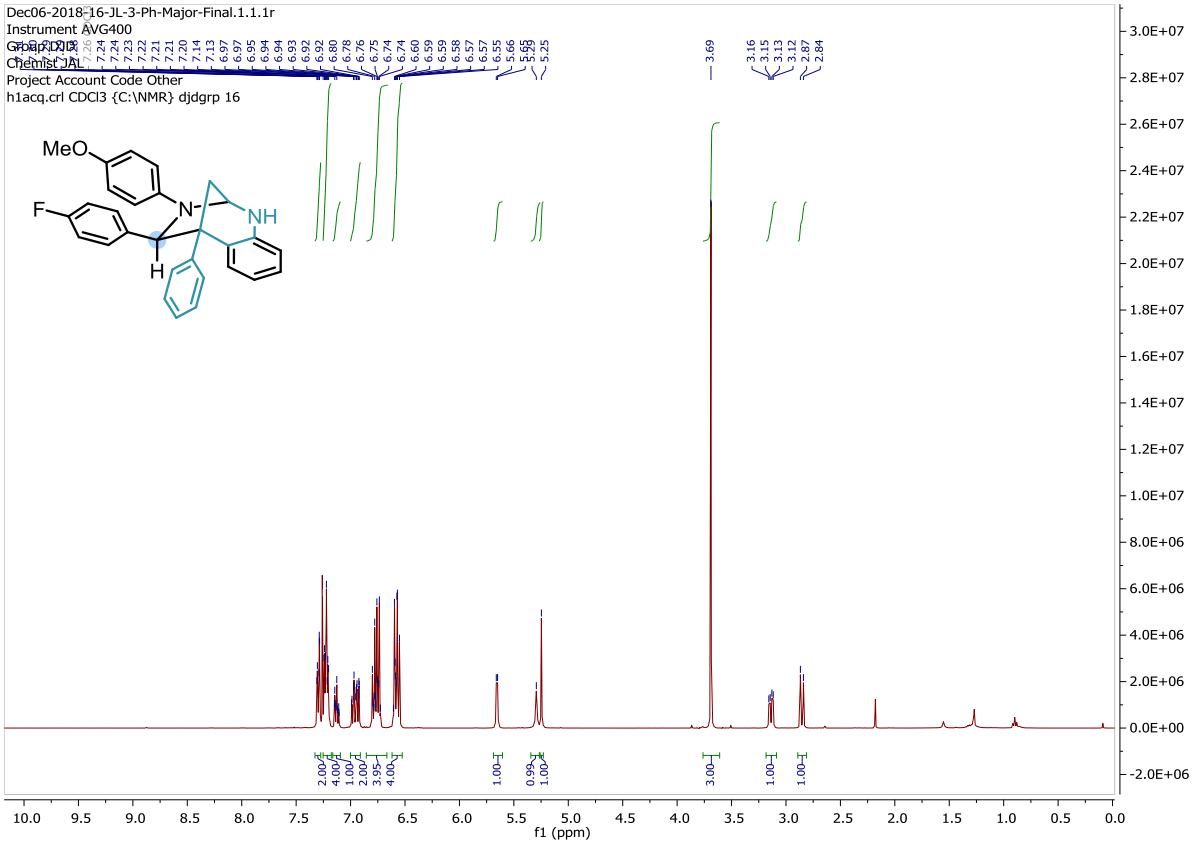
5a – ^{19}F NMR (377 MHz, $CDCl_3$)



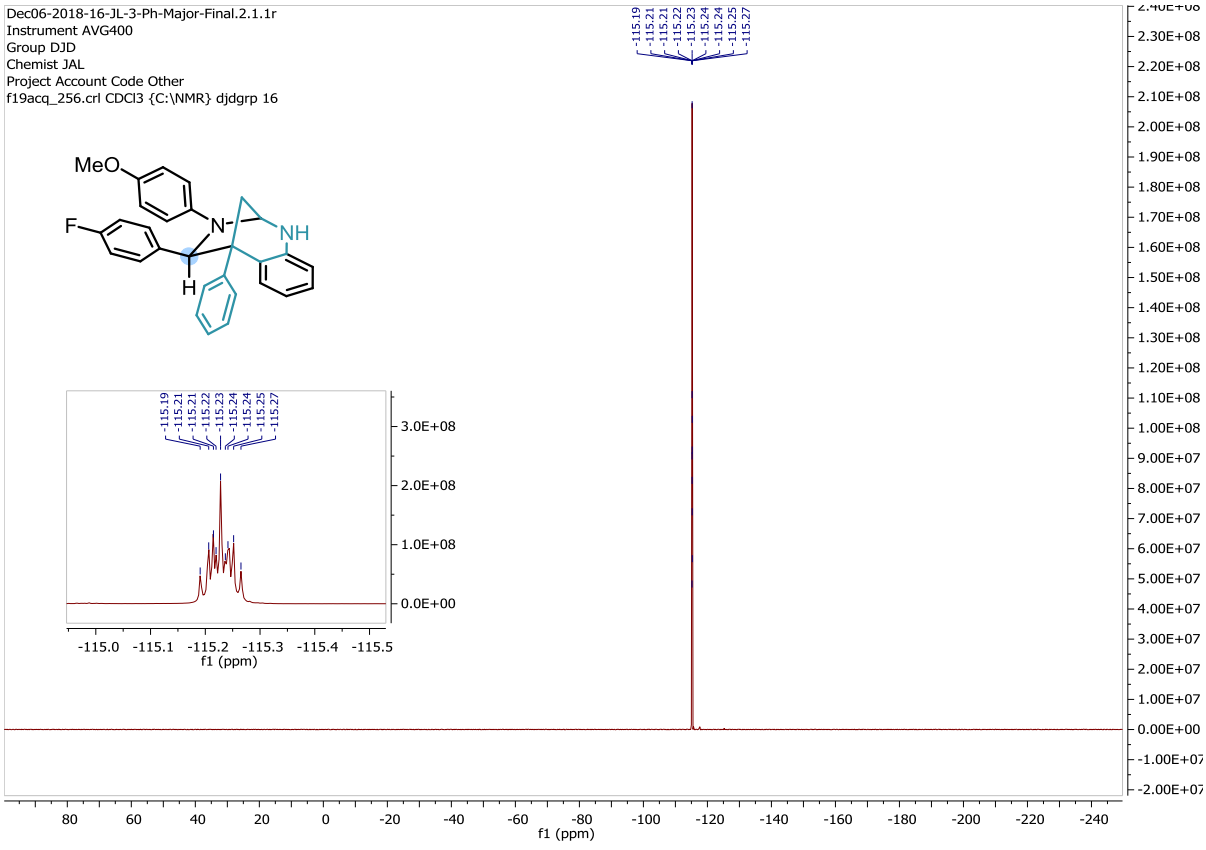
5a – ^{13}C NMR (126 MHz, $CDCl_3$)



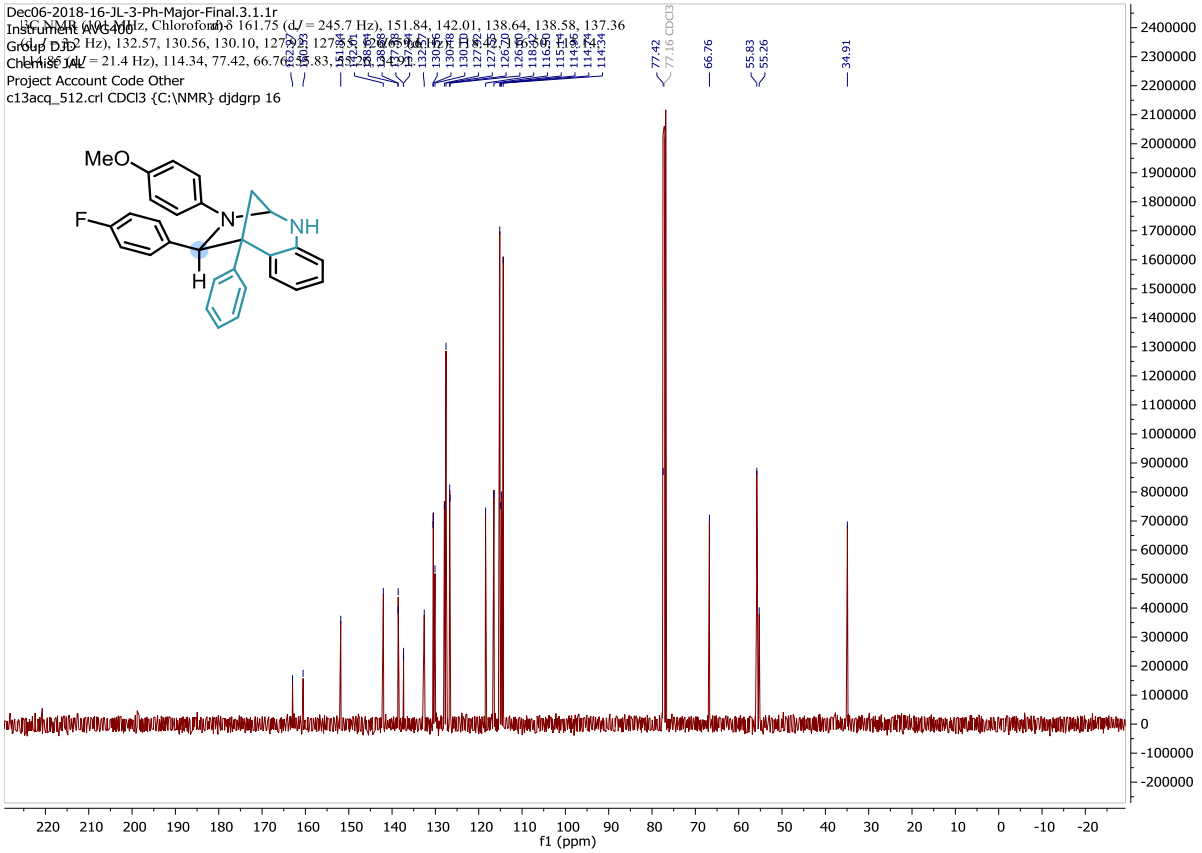
3am$_{(exo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



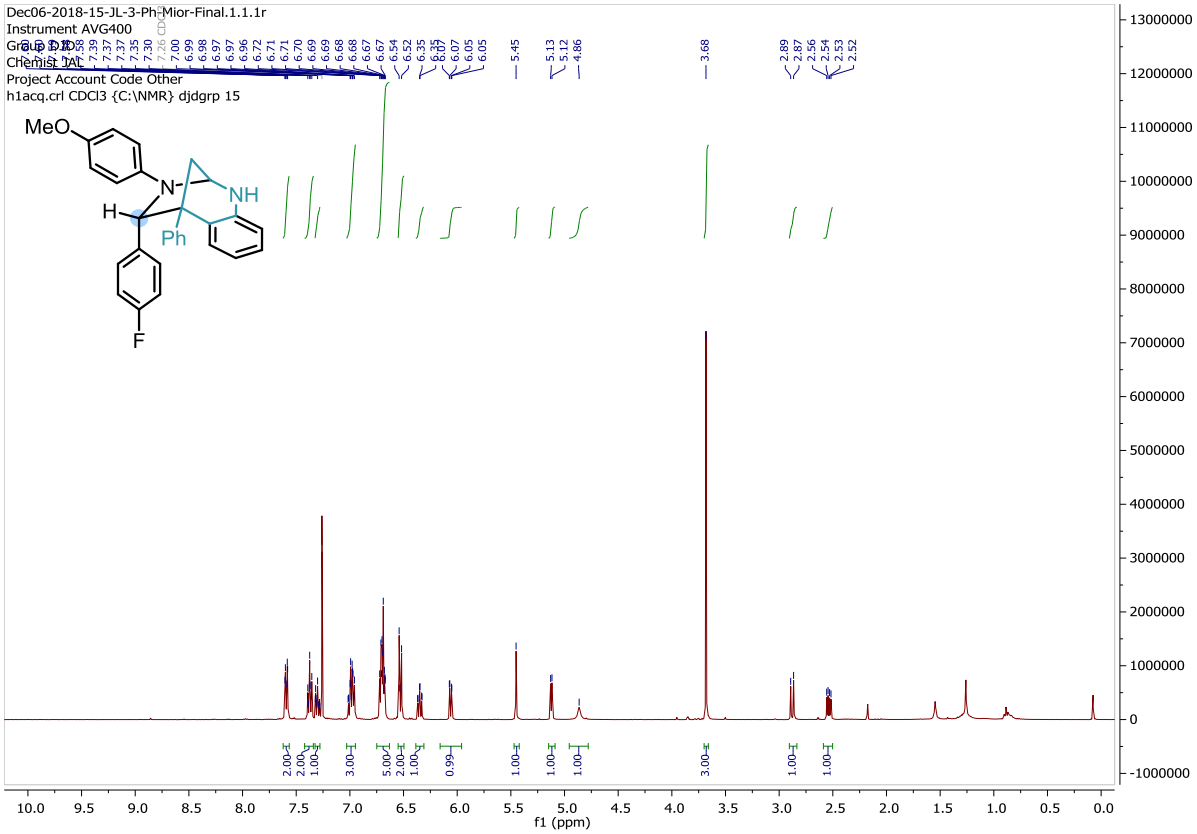
3am$_{(exo)}$ – ^{19}F NMR (377 MHz, $CDCl_3$)



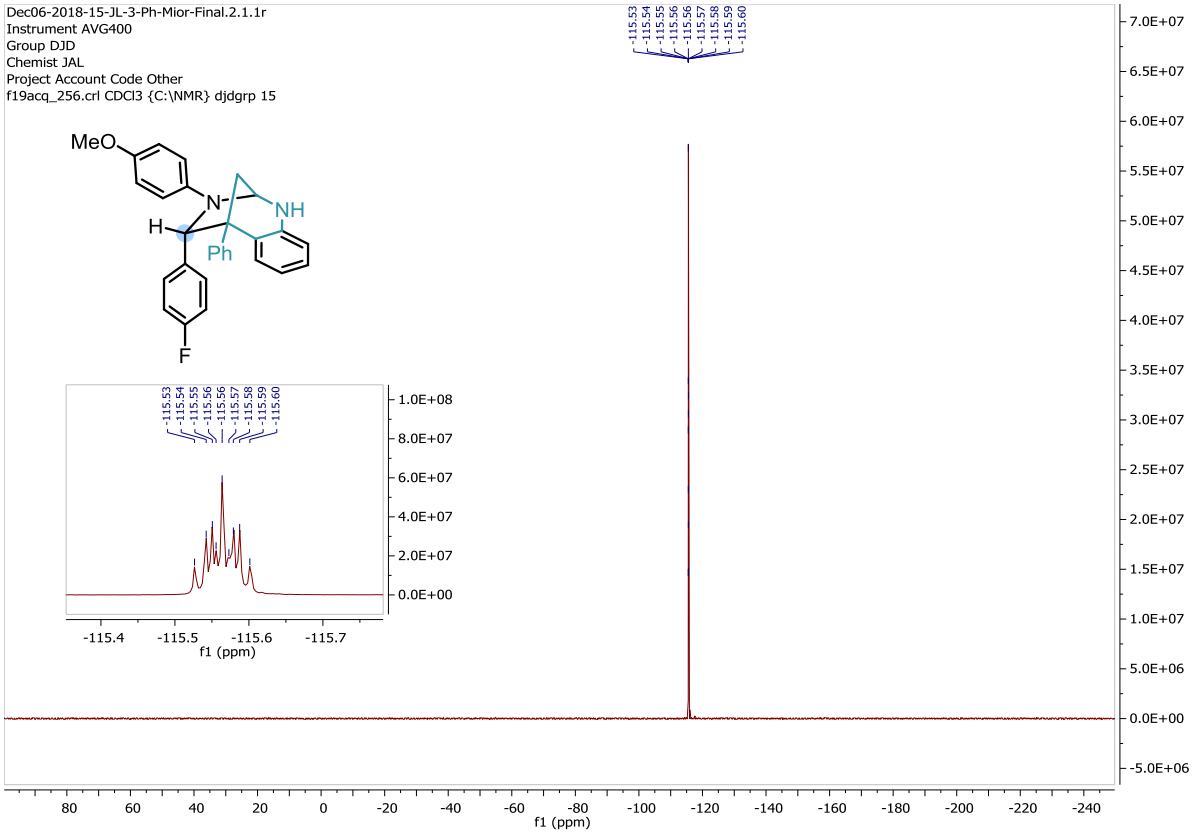
3am$_{(exo)}$ – ^{13}C NMR (101 MHz, $CDCl_3$)



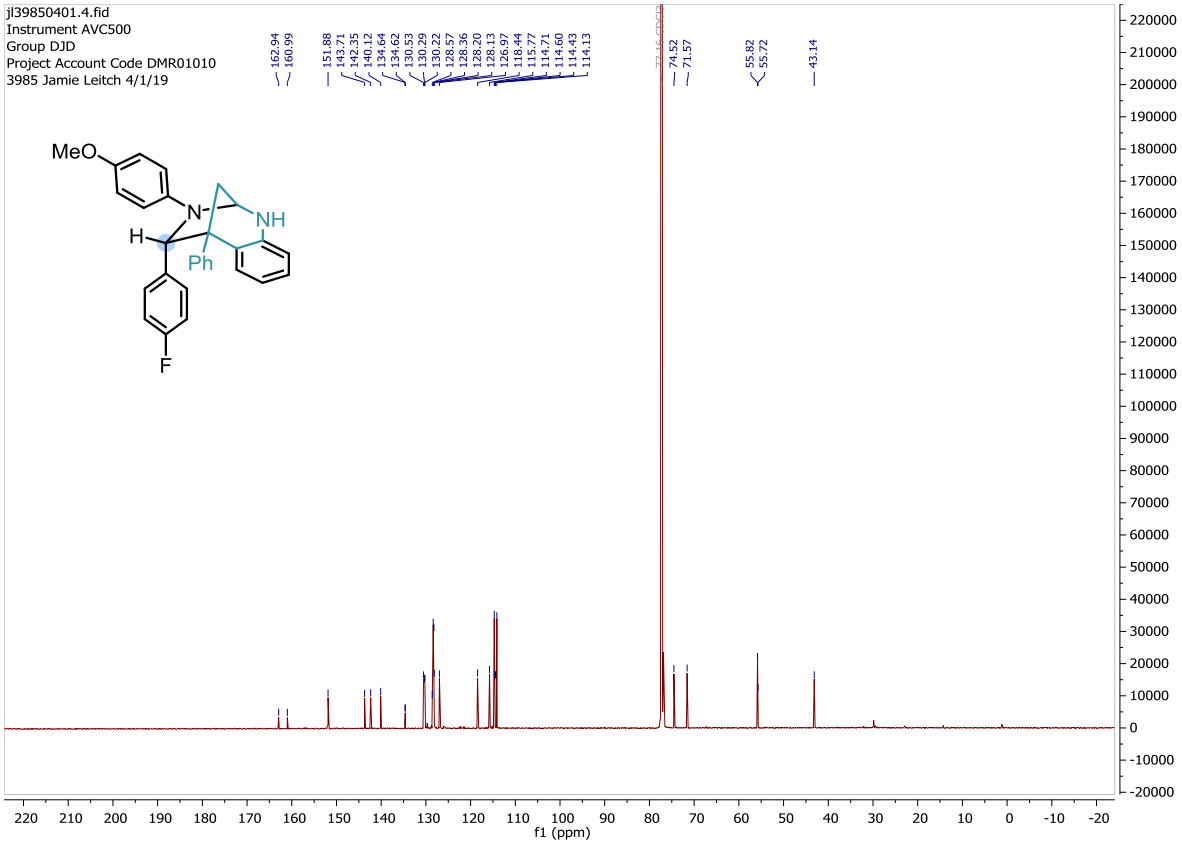
3am$_{(endo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



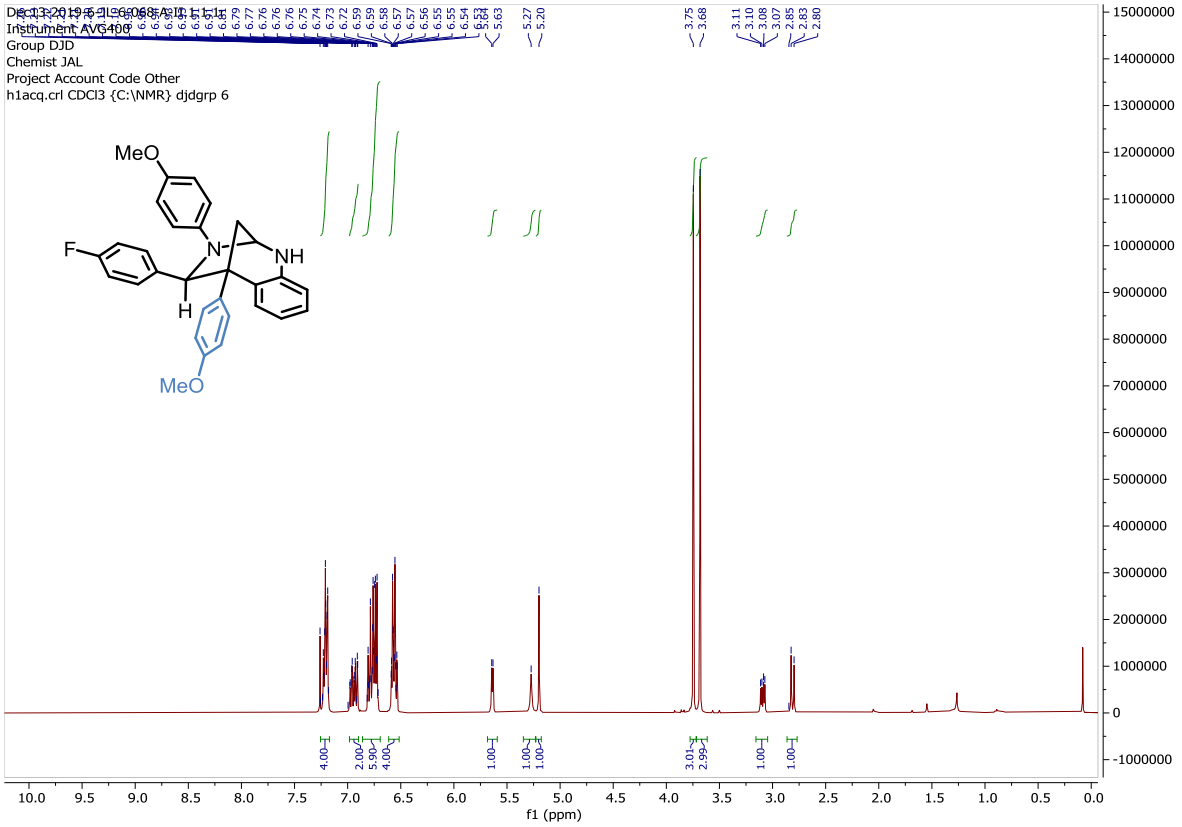
3am$_{(endo)}$ – ^{19}F NMR (377 MHz, $CDCl_3$)



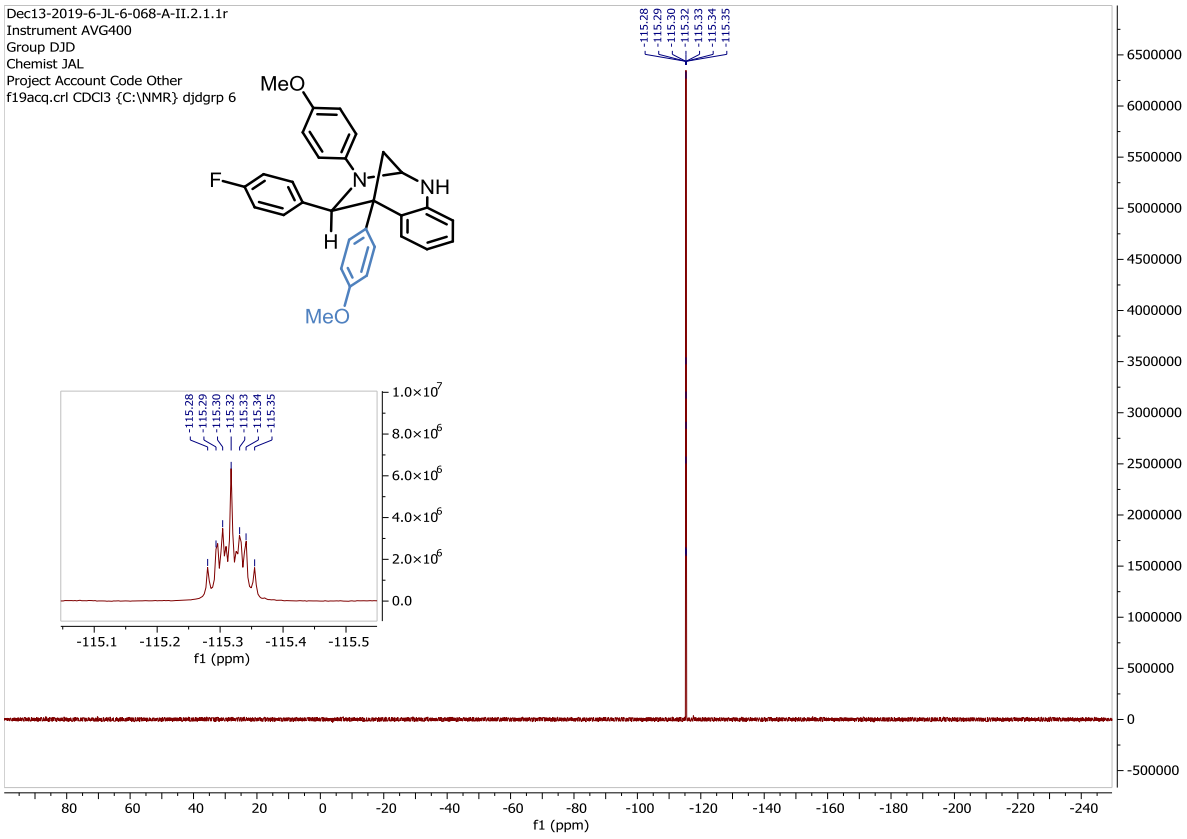
3am$_{(endo)}$ – ^{13}C NMR (126 MHz, $CDCl_3$)



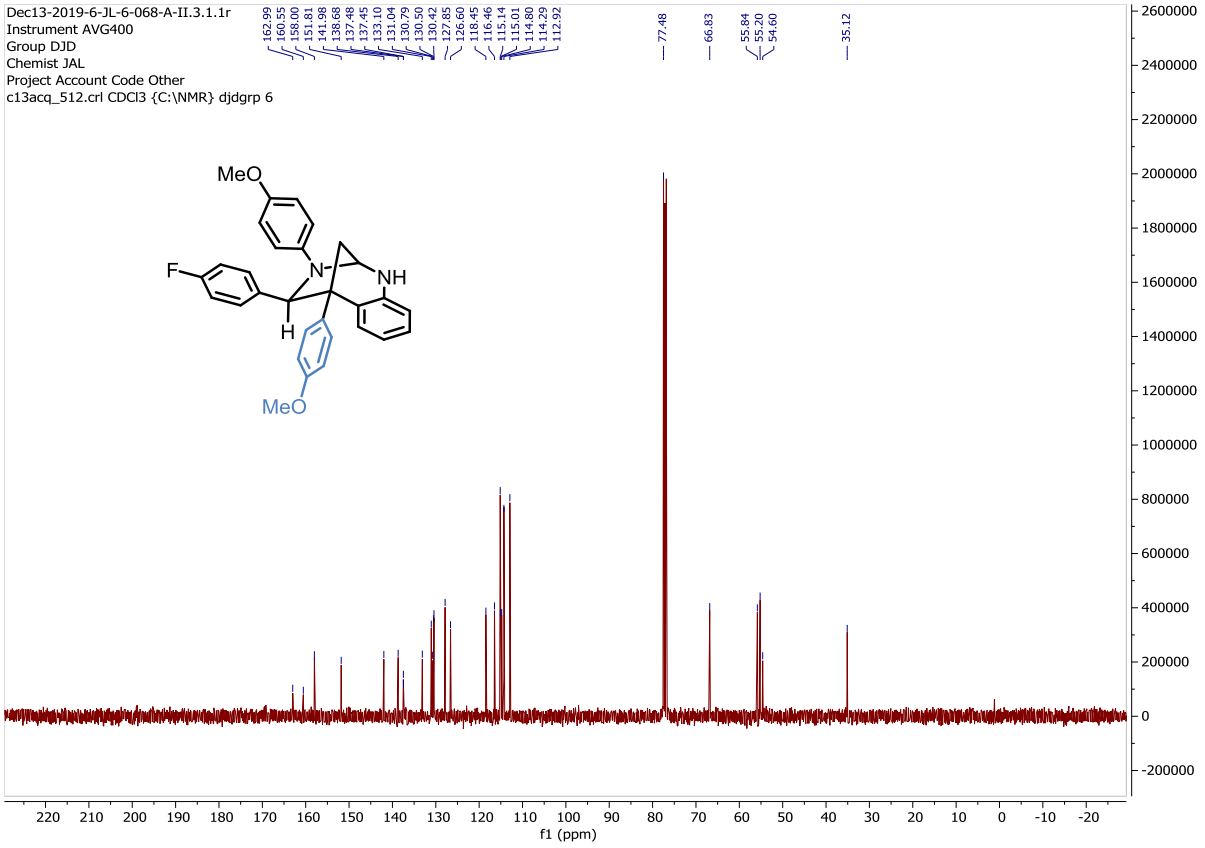
3an$_{(exo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



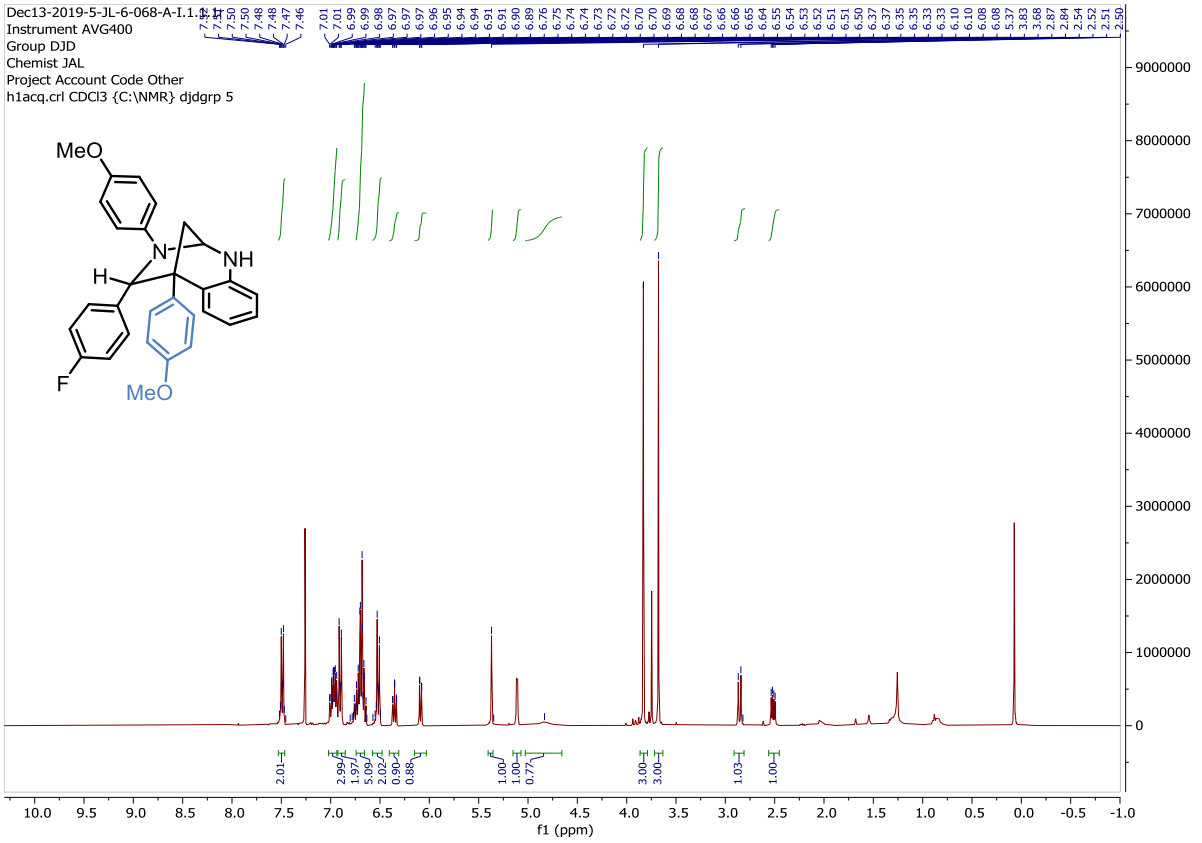
3an$_{(exo)}$ – ^{19}F NMR (377 MHz, $CDCl_3$)



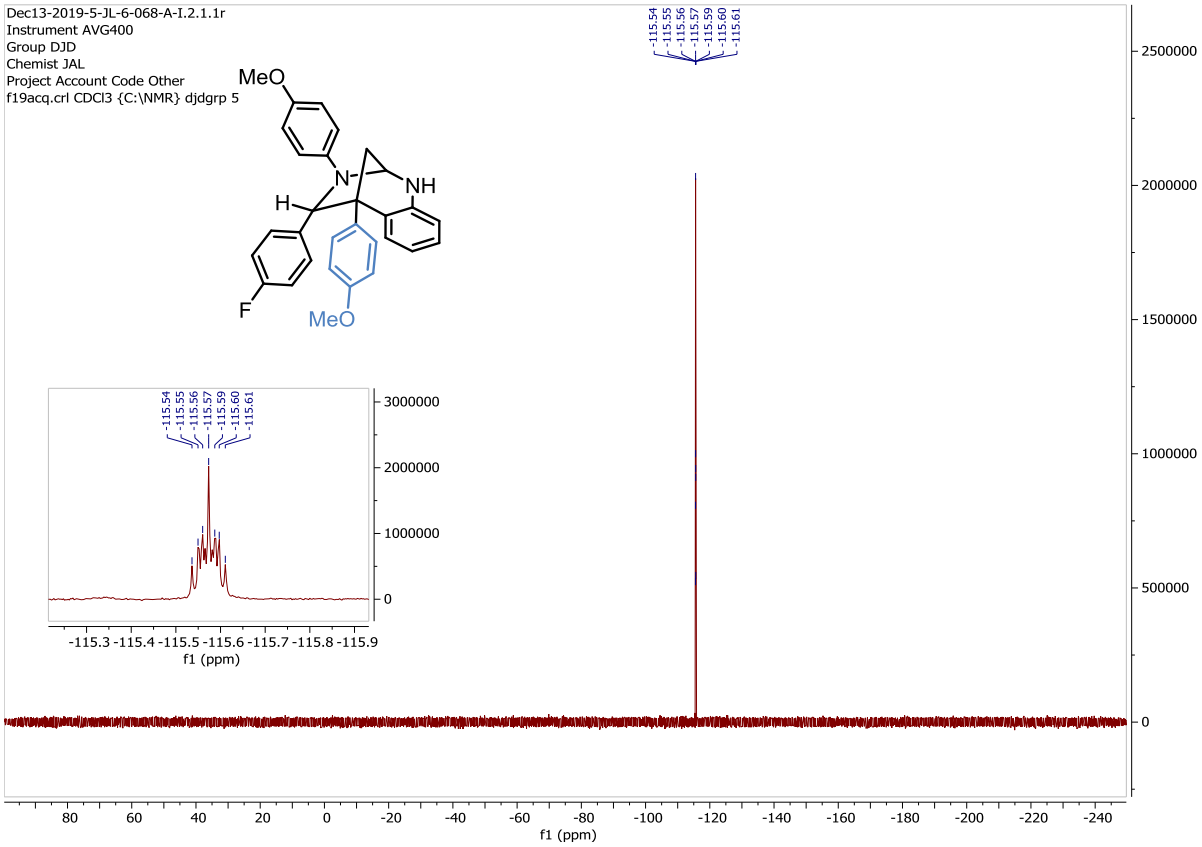
3an$_{(exo)}$ – ^{13}C NMR (126 MHz, $CDCl_3$)



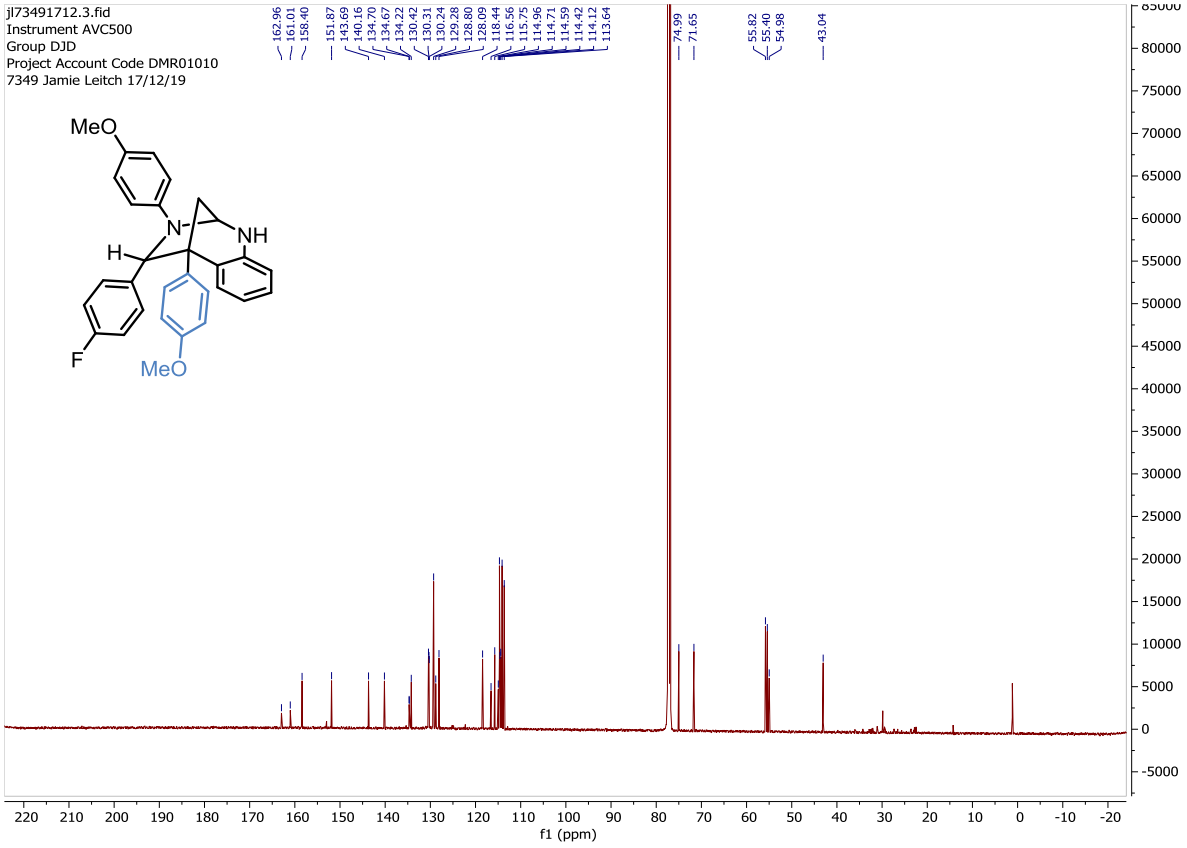
3an$_{(endo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



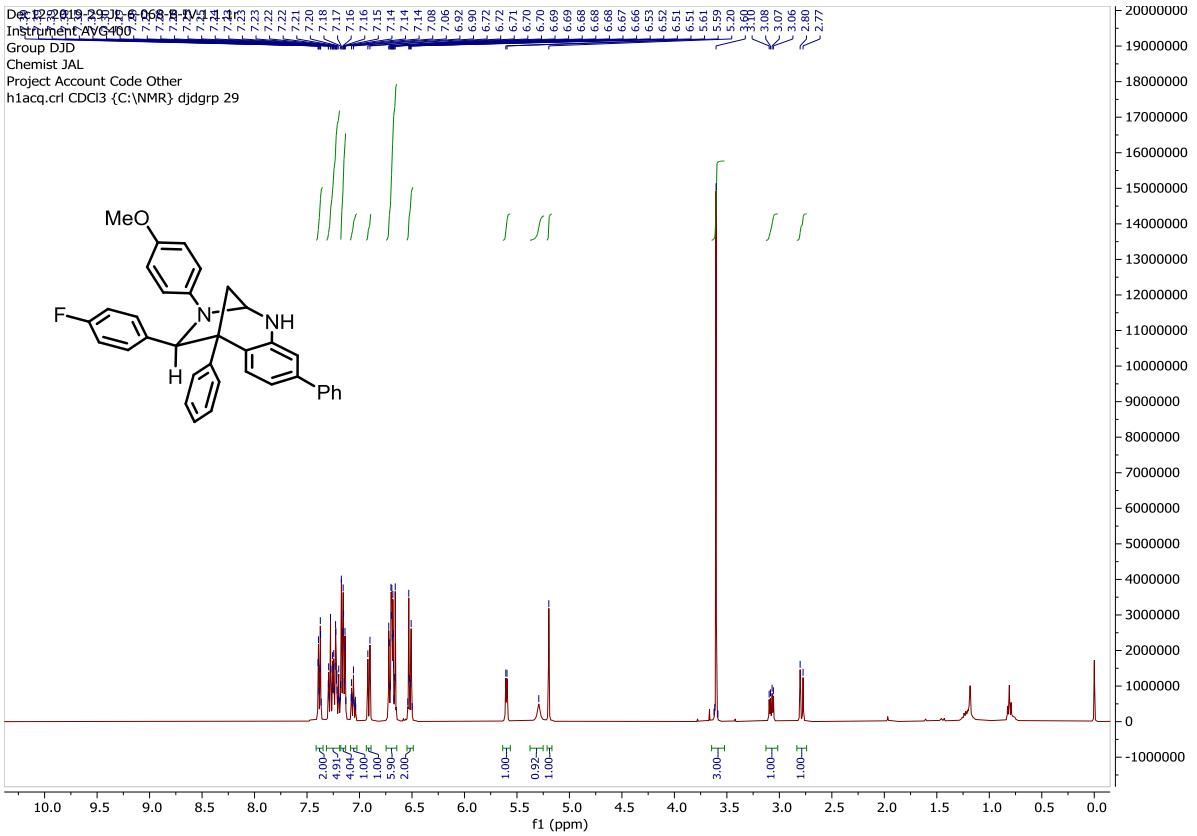
3an$_{(endo)}$ – ^{19}F NMR (377 MHz, $CDCl_3$)



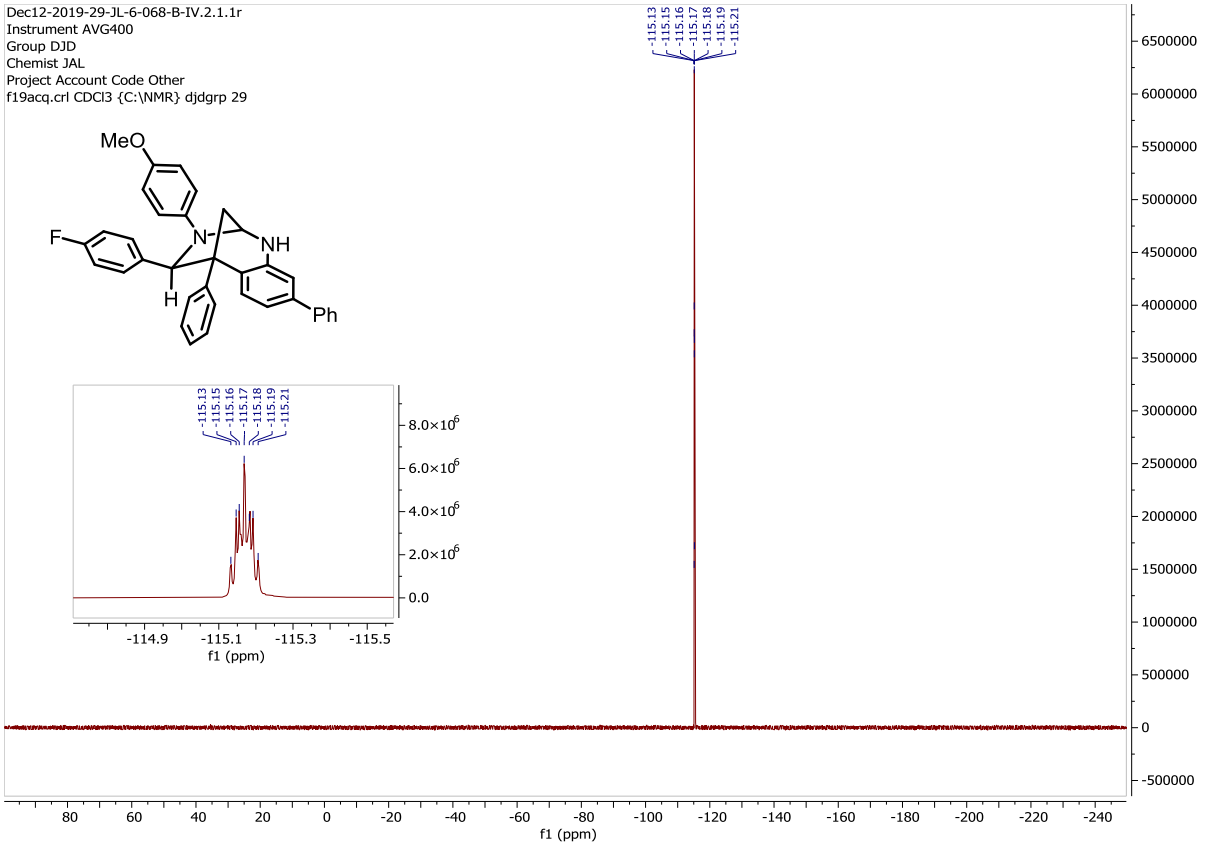
3an$_{(endo)}$ – ^{13}C NMR (126 MHz, $CDCl_3$)



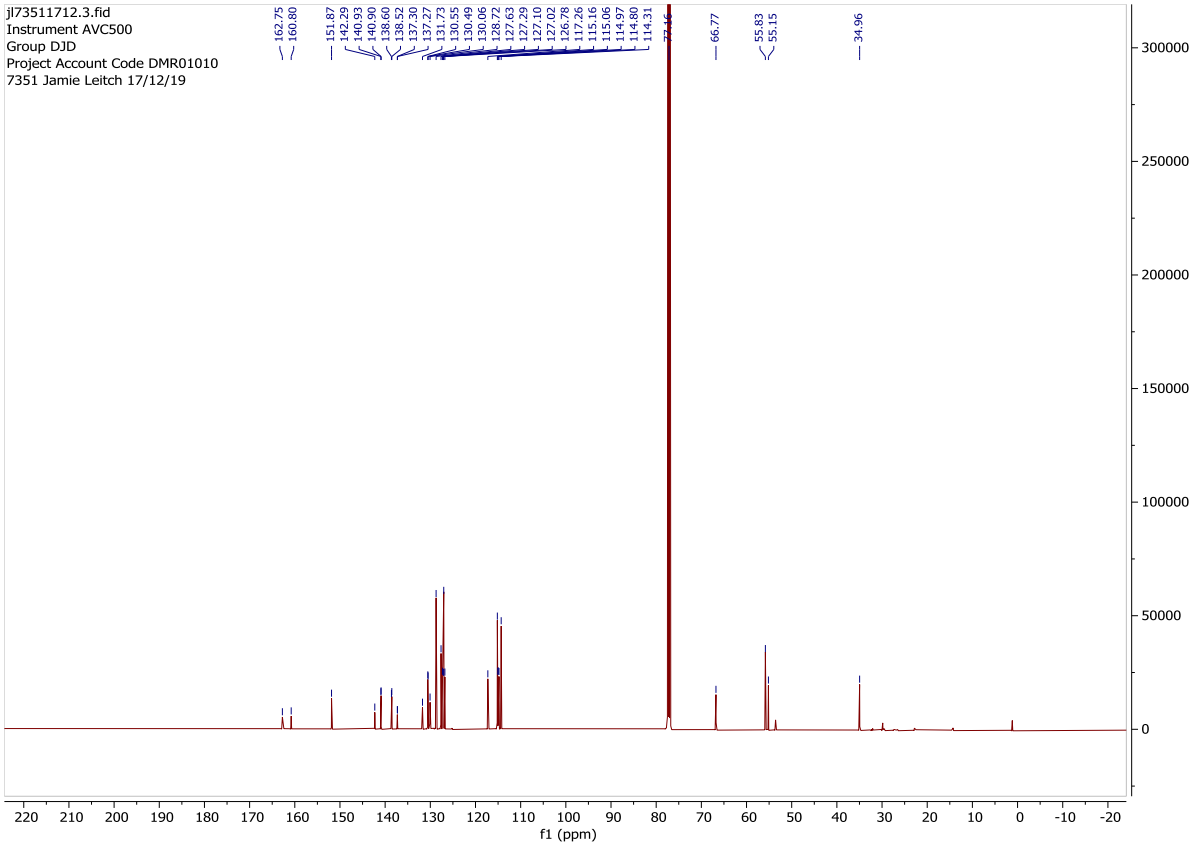
3ao$_{(exo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



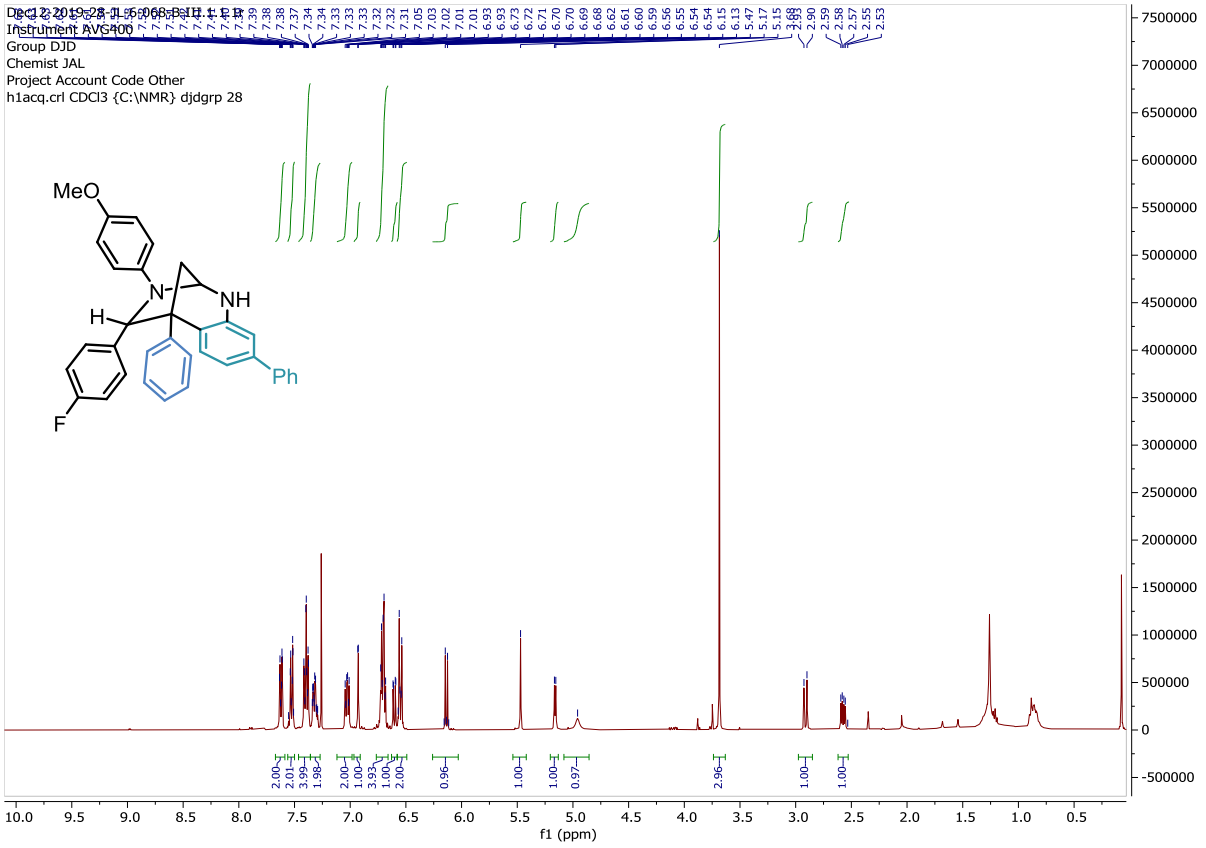
3ao$_{(exo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



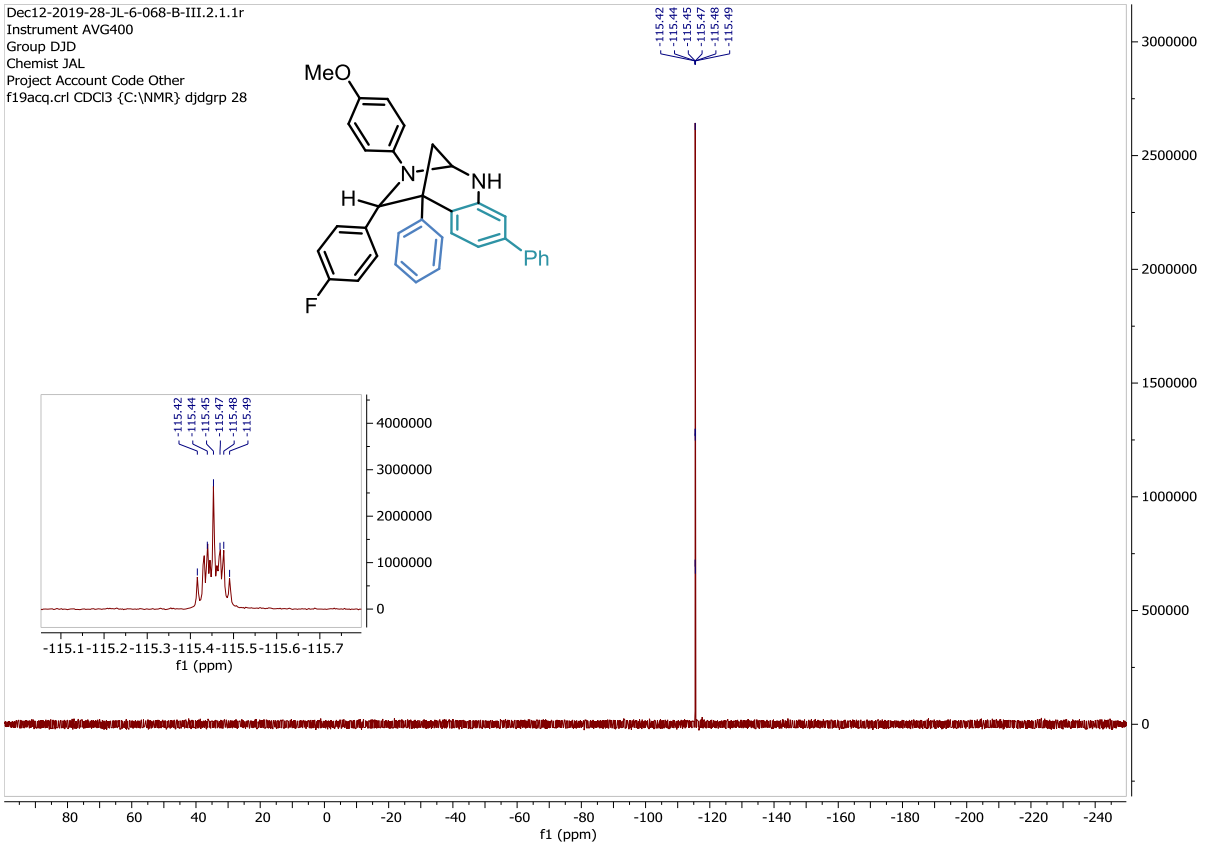
3ao$_{(exo)}$ – ^{13}C NMR (126 MHz, $CDCl_3$)



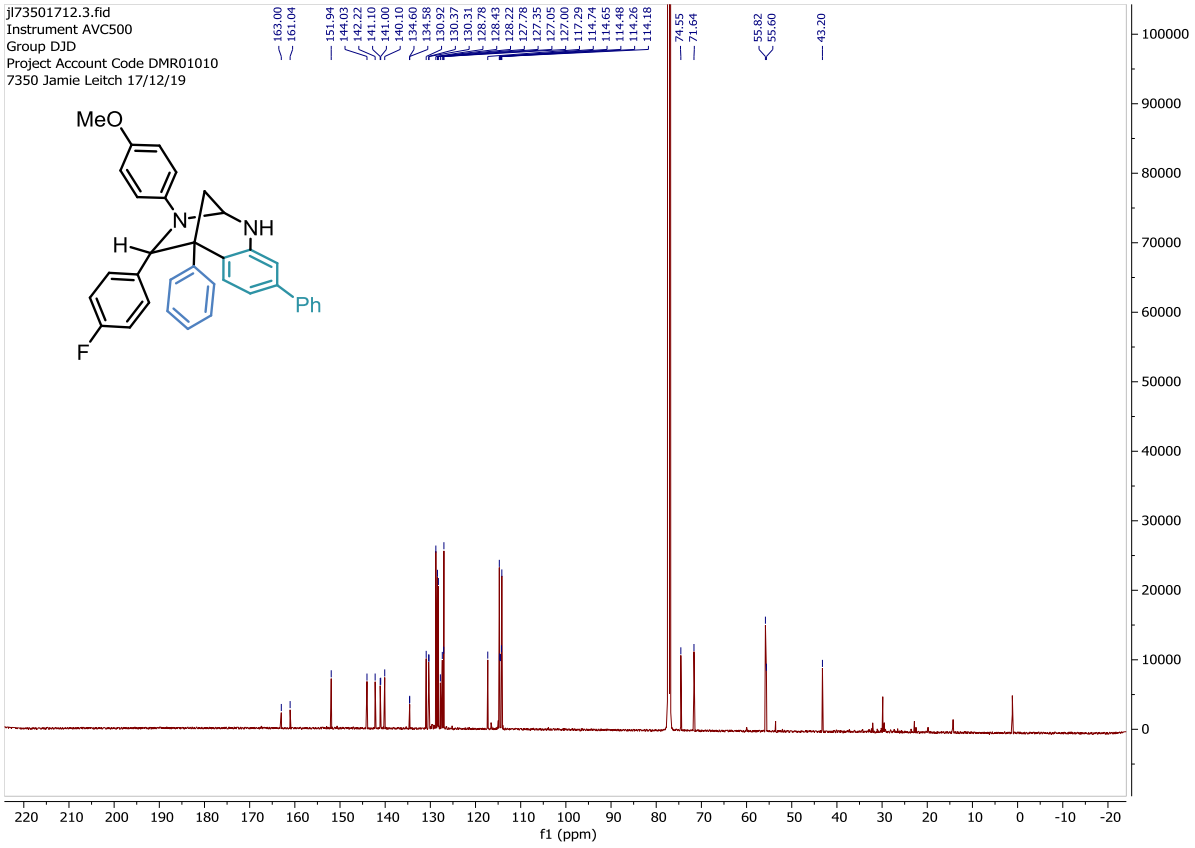
3ao$_{(endo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



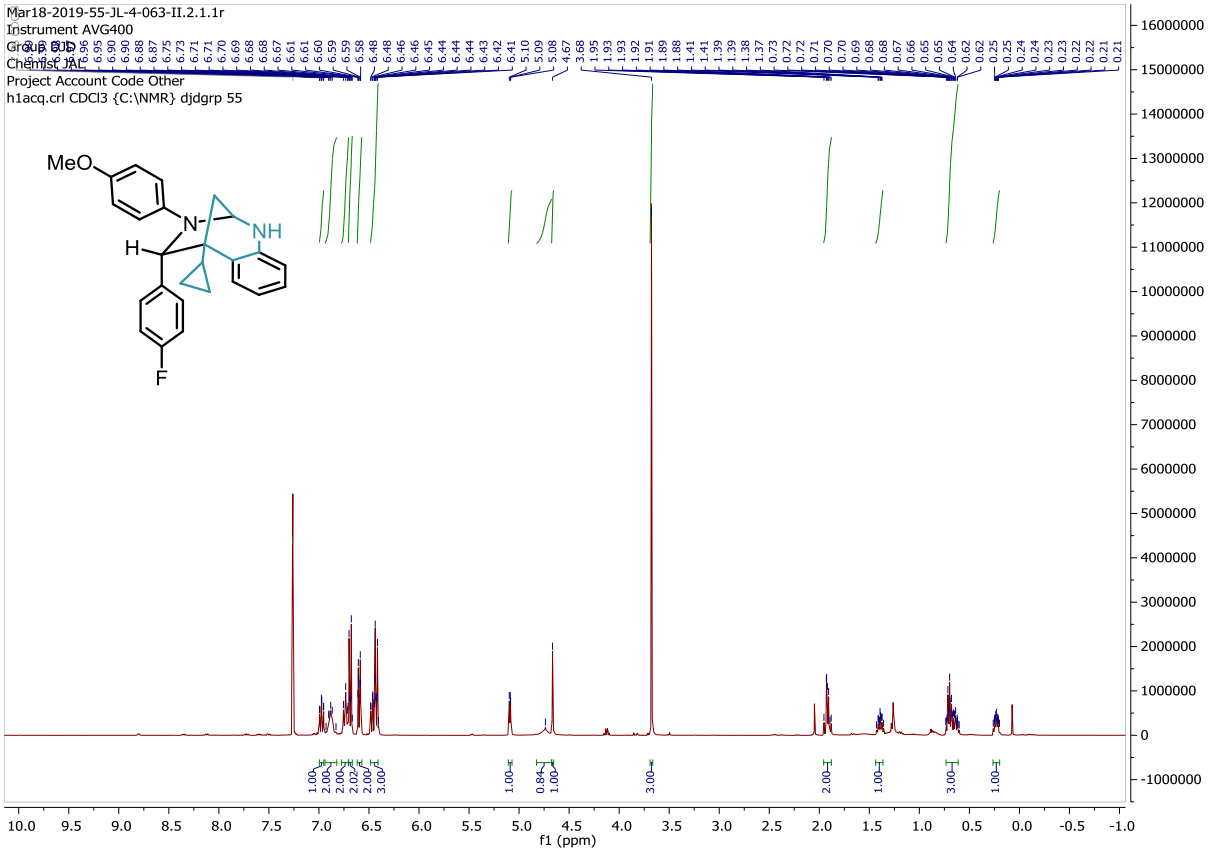
3ao$_{(endo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



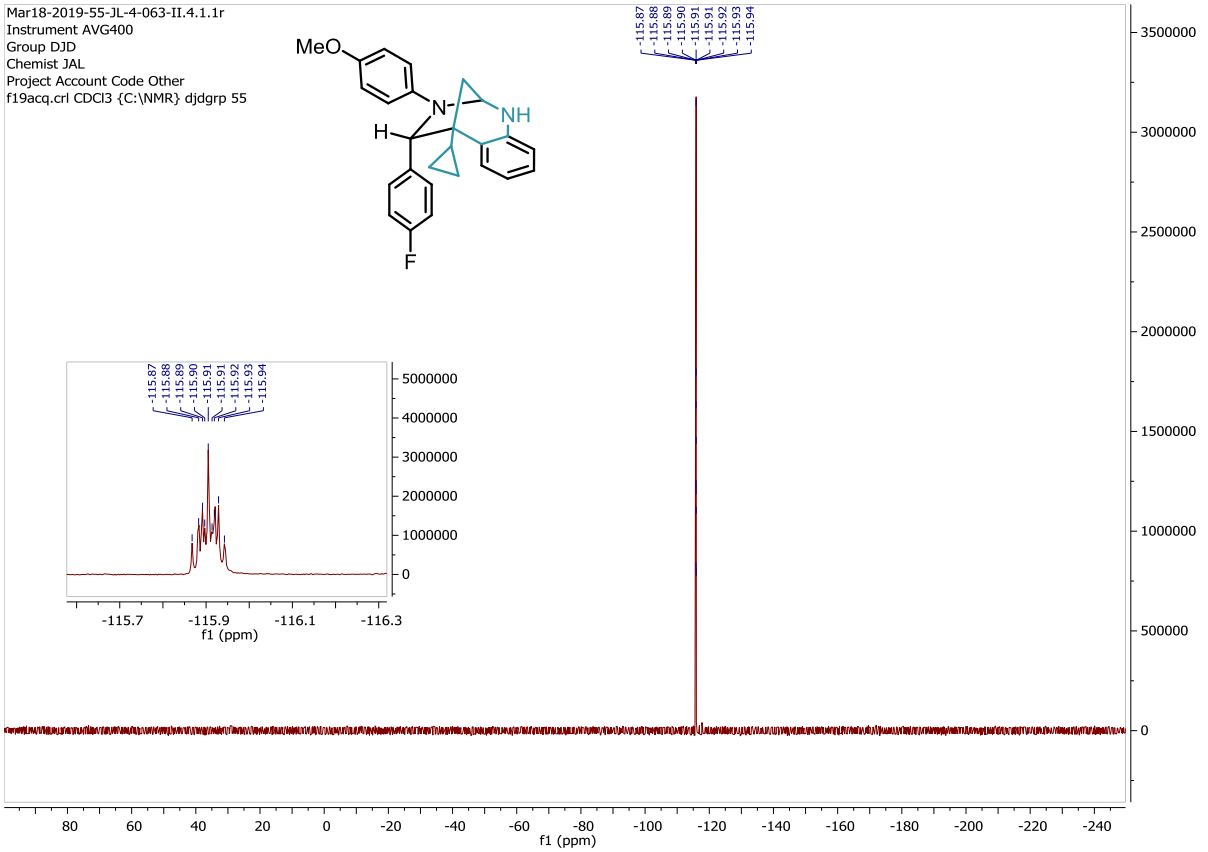
3ao$_{(endo)}$ – ^{13}C NMR (126 MHz, $CDCl_3$)



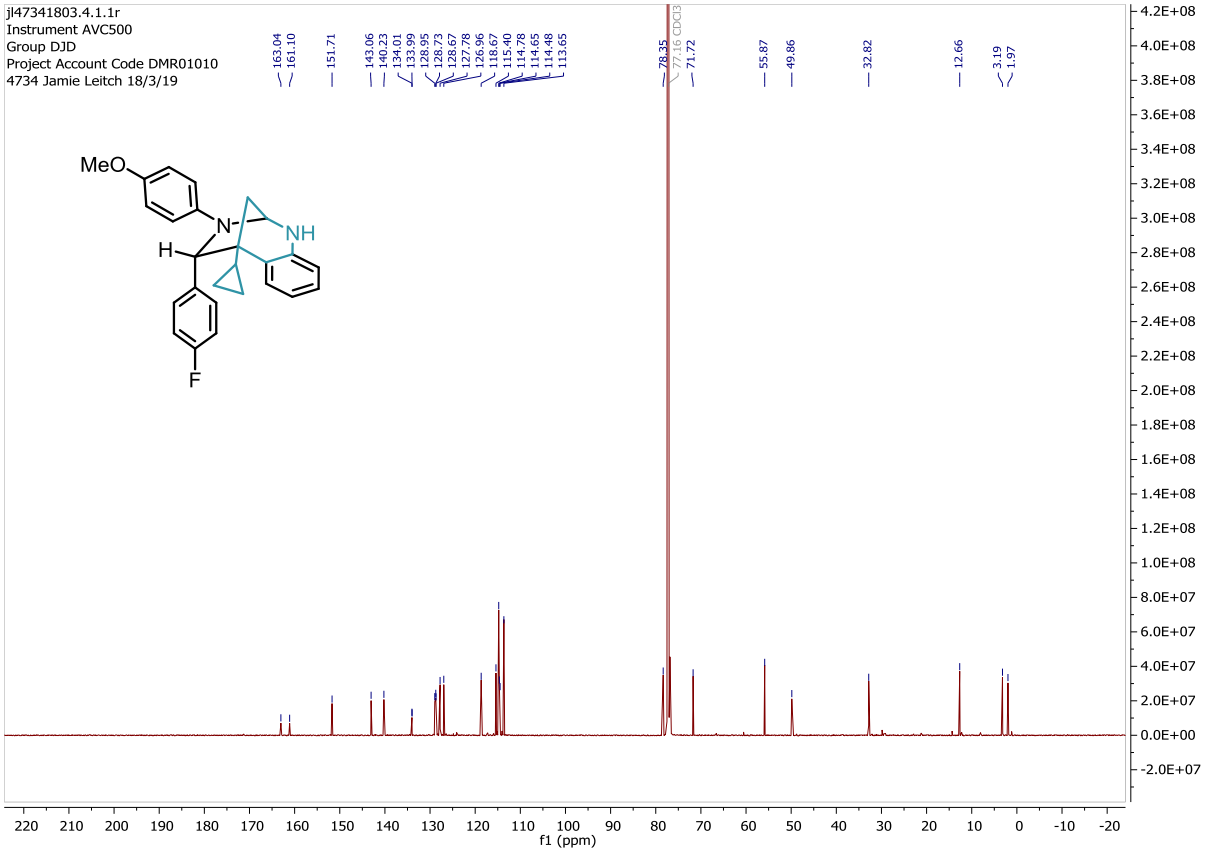
3ap$_{(endo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)

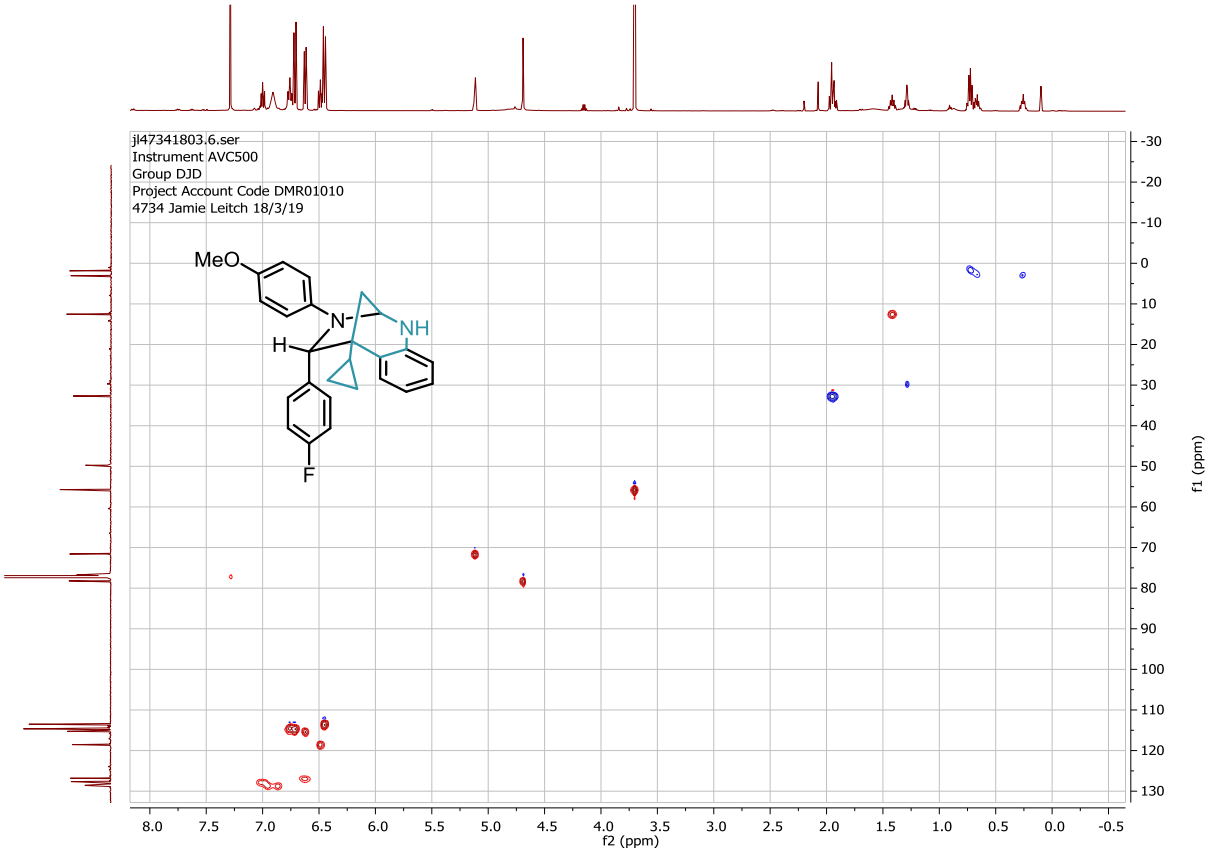


3ap$_{(endo)}$ – ^{19}F NMR (377 MHz, $CDCl_3$)

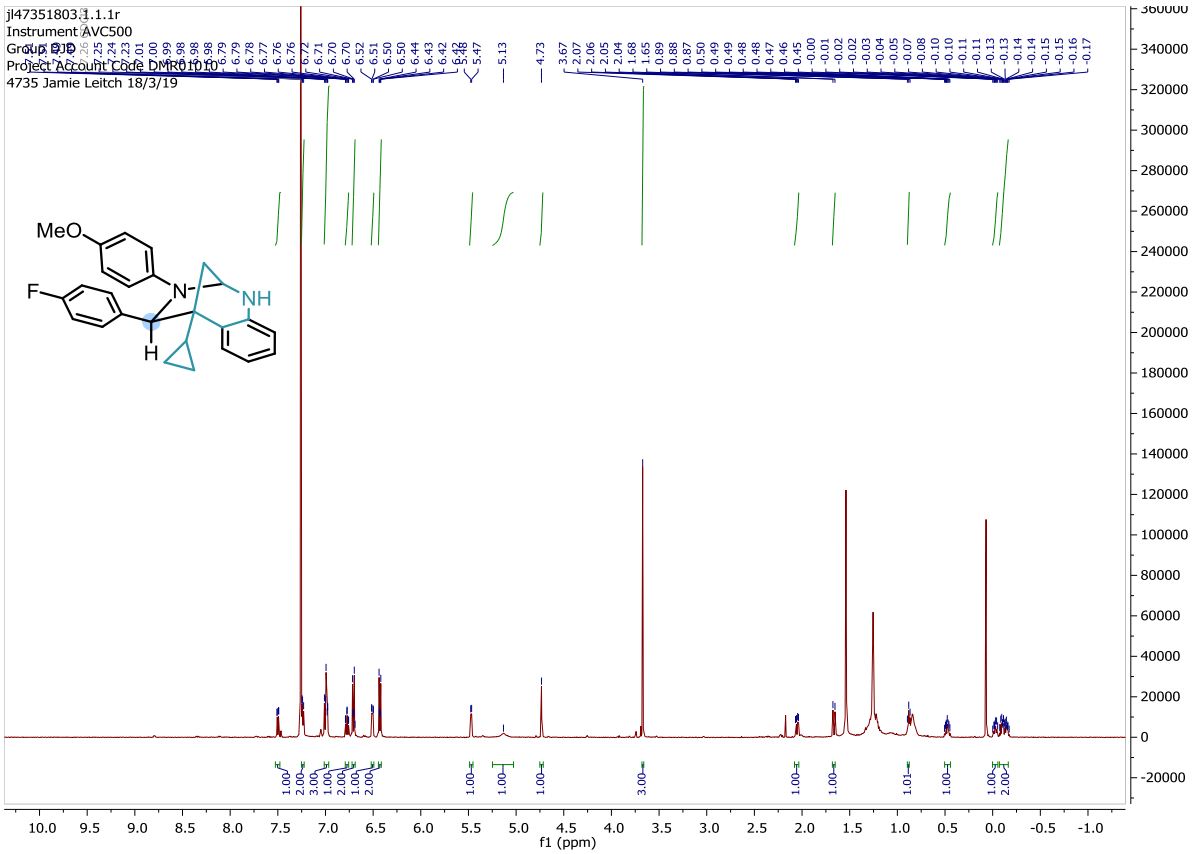


3ap$_{(endo)}$ – ^{13}C NMR (126 MHz, $CDCl_3$)

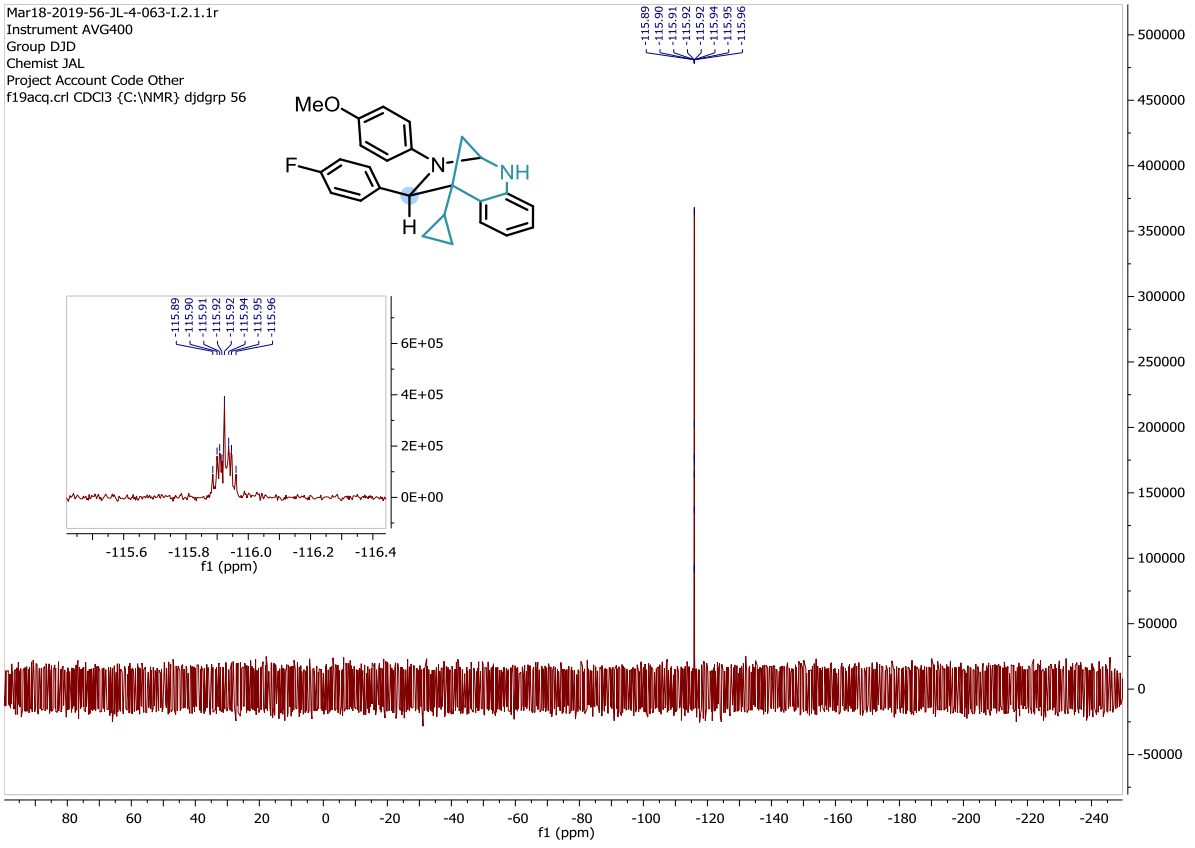




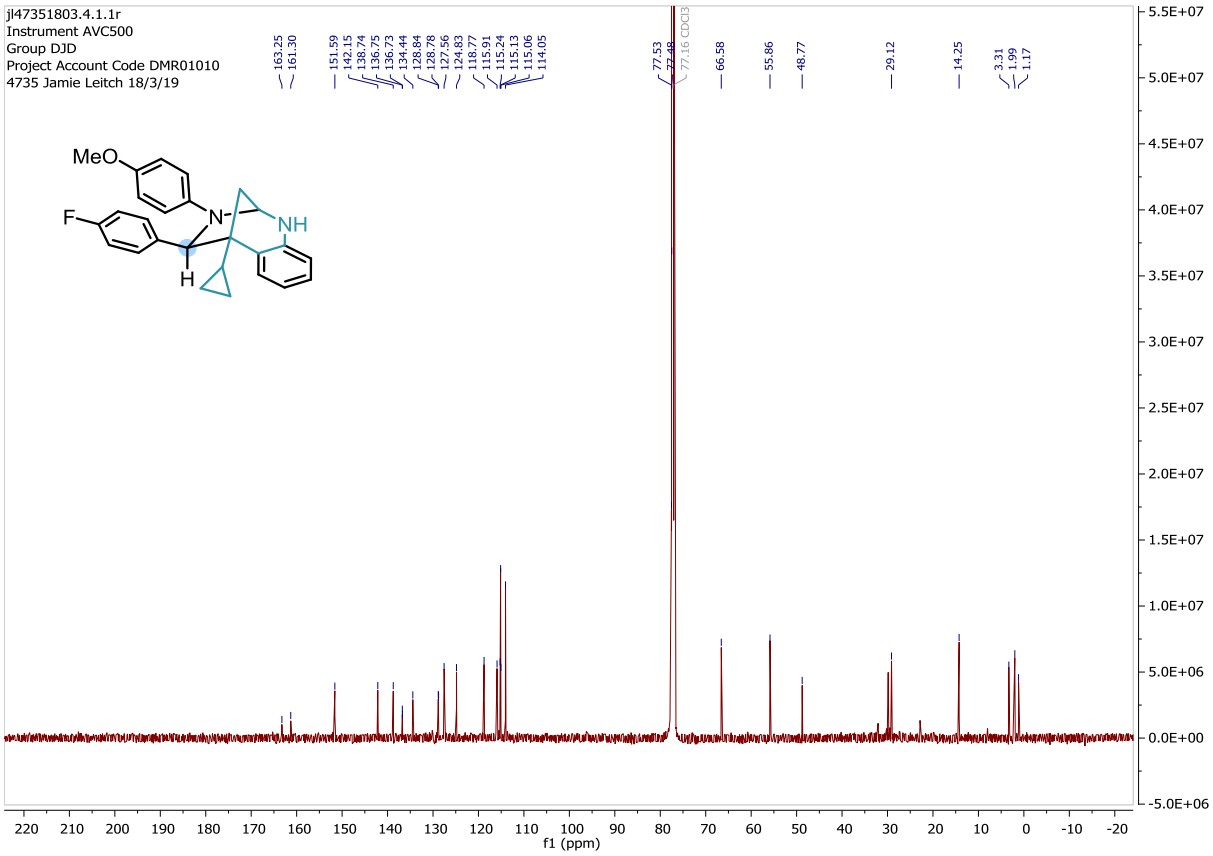
3ap$_{(exo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



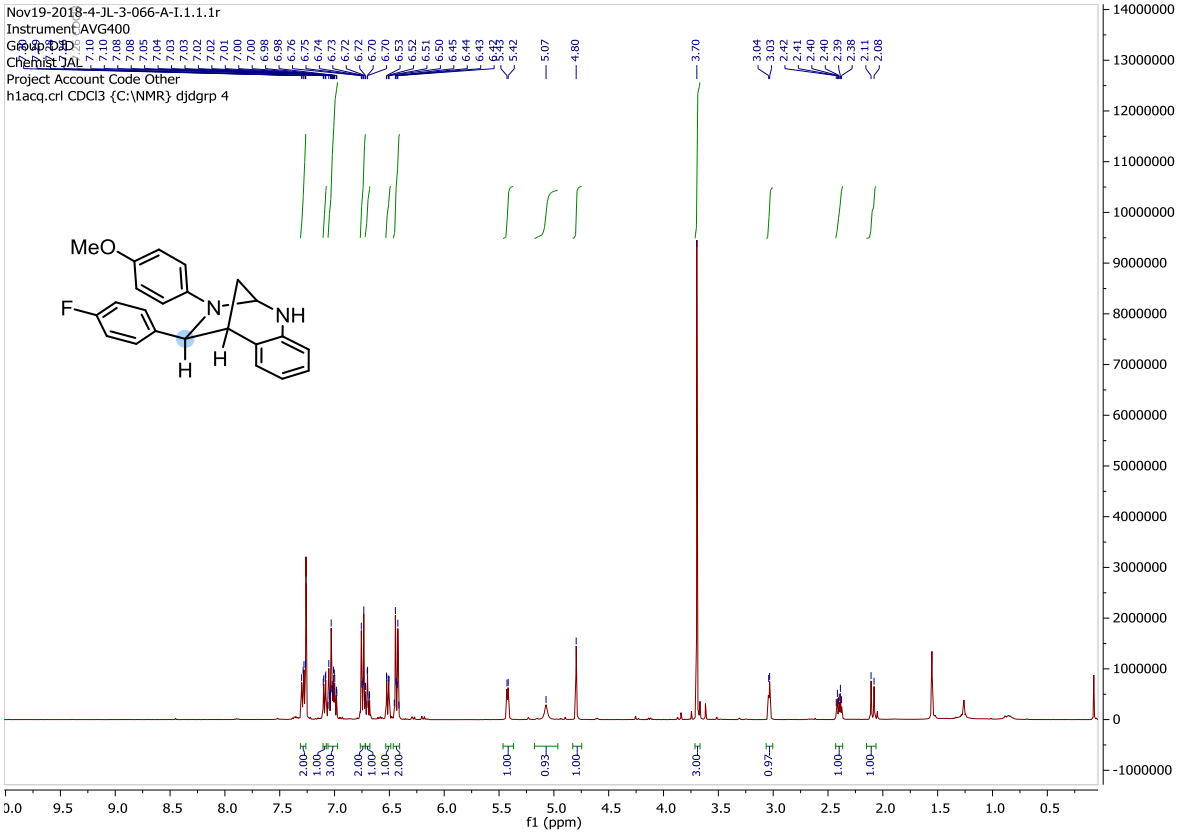
3ap$_{(exo)}$ – ^{19}F NMR (377 MHz, $CDCl_3$)



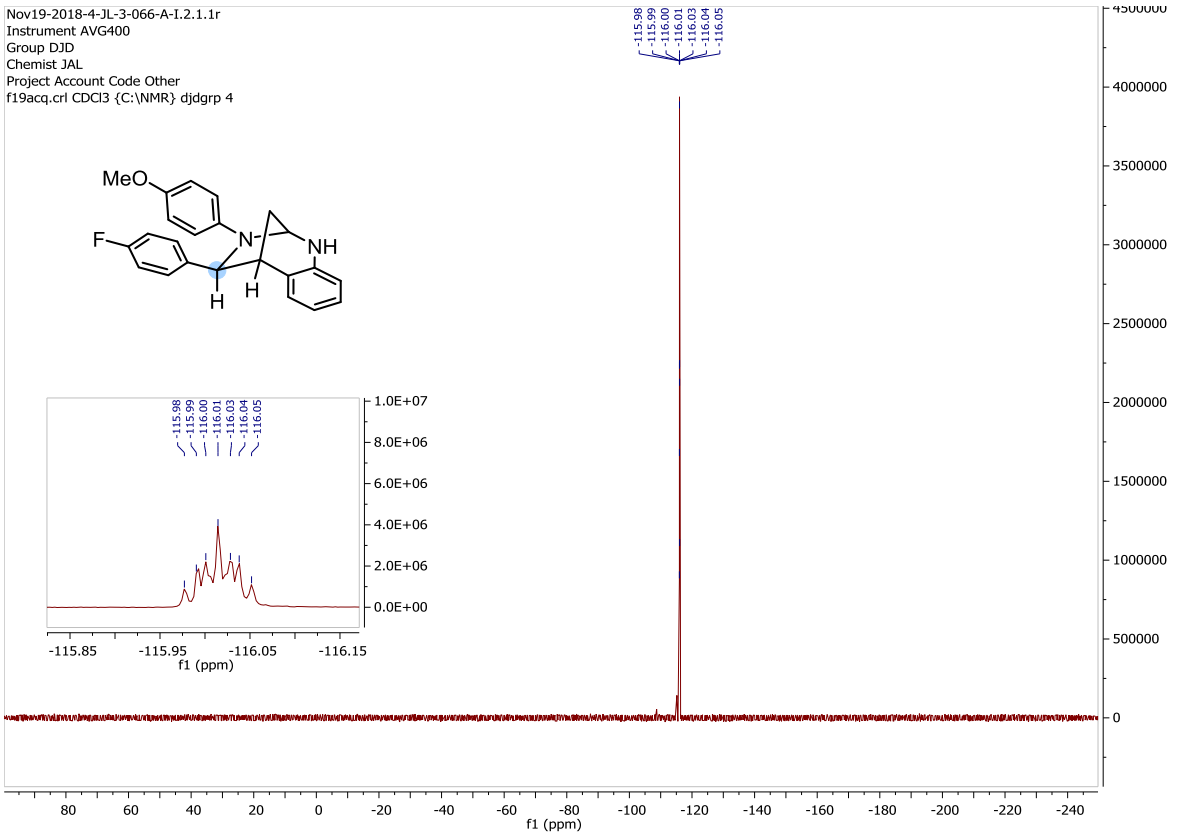
3ap$_{(exo)}$ – ^{13}C NMR (126 MHz, $CDCl_3$)



S3a$_{(exo)}$ – ^{1}H NMR (400 MHz, $CDCl_3$)



S3a$_{(exo)}$ – ^{19}F NMR (373 MHz, $CDCl_3$)



S3a$_{(exo)}$ – ^{13}C NMR (126 MHz, $CDCl_3$)