

Modular Sulfondiimine Synthesis using a Stable Sulfinylamine Reagent

Ze-Xin Zhang, Thomas Q. Davies, and Michael C. Willis*

Department of Chemistry, Chemistry Research Laboratory, University of Oxford, Mansfield Road, Oxford, OX1 3TA, United Kingdom.

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1. Experimental

1.1 General Considerations

Reactions were performed under inert nitrogen atmosphere with anhydrous solvent unless otherwise stated. All glassware was oven dried at 200 °C and allowed to cool to room temperature under positive pressure of nitrogen. Reactions were monitored by TLC until deemed complete using aluminum backed silica plates. Plates were visualised under ultraviolet light (254 nm) and/or by staining with KMnO₄ solution. Cooling of reaction mixtures to 0 °C was achieved using an ice-water bath. Cooling of reaction mixtures between -20 °C and -78 °C was achieved using a dry ice-acetone bath.

Reagents were purchased from Sigma-Aldrich Chemical Co. Ltd., Alfa Aesar, Acros Organics Ltd., Fluorochem Ltd. or Strem Chemicals Inc. and were used as supplied. Grignard and organolithium reagents were titrated against salicylaldehyde phenylhydrazone.¹ Flash column chromatography was carried out using matrix 60 silica gel (particle size 0.040-0.063 nm). 'Petrol' refers to the fraction of light petroleum ether boiling in the range 40-60 °C.

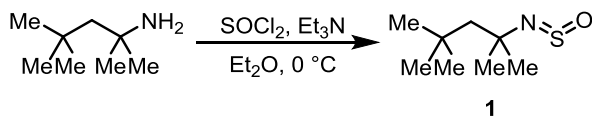
¹H-NMR spectra were obtained on a Bruker AVIII400 (400 MHz) spectrometer using the residual solvent as an internal standard. ¹³C-NMR spectra were obtained on a Bruker AVIII400 (100 MHz) using the residual solvent as an internal standard. ¹⁹F-NMR spectra were obtained on a Bruker AVIII400 (376 MHz) spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) with the multiplicities of the spectra reported as following: s, singlet; d, doublet; t, triplet; q, quartet; pent., quintet; m, multiplet; app., apparent; br., broad. Coupling constants (*J*) were given in Hertz (Hz).

Low resolution ESI mass spectra were recorded on a Waters LCT Premier spectrometer. High resolution mass spectrometry measurements were recorded on a Bruker Daltronics MicroTOF (ESI) spectrometer by the internal service at Chemistry Research Laboratory, University of Oxford. Samples for mass spectra were prepared as 1 mg/mL solution in MeOH (LRMS, HRMS-ESI).

Infrared spectra were recorded as thin films on a Bruker Tensor 27 FT-IR spectrometer. Melting points were determined using a Stuart Scientific Melting Point Apparatus SMP1.

1.2 Synthetic Procedures and Characterisation Data

1.2.1 Preparation of *N*-Sulfinyl-*tert*-octylamine



tert-Octylamine (5.11 g, 39.6 mmol, 1.0 equiv.) was dissolved in anhydrous diethyl ether (100 mL) in a 250 mL 3-necked round bottom flask. Anhydrous triethylamine (11.6 mL, 83.2 mmol, 2.1 equiv.) was added and the reaction was cooled to 0 °C. Freshly distilled thionyl chloride (3.00 mL, 41.3 mmol, 1.05 equiv.) was added dropwise. The reaction was stirred at 0 °C for 2 h. Filtration through Celite ® (washed with diethyl ether) and removal of solvent under reduced pressure at room temperature afforded *N*-sulfinyl-*tert*-octylamine **1** as a yellow oil (6.71 g, 97%).

Notes

1. *N*-Sulfinyl-*tert*-octylamine should be stored in the freezer (-20 °C) and can be used without loss of performance for at least 2 months.
2. **CAUTION: Hydrolysis of sulfinylamines results in the formation of toxic sulfur dioxide gas.** Evolution of SO₂ from *N*-sulfinyl-*tert*-octylamine has not been observed in the normal course of use, but avoidance of contact with water or prolonged storage at room temperature is advised.
3. *tert*-Octylamine was purchased from Sigma-Aldrich or Fluorochem (both £27 for 100 g) and used without further purification.
4. After evaporation of diethyl ether following filtration, it is advised not to redissolve the product in solvent. Doing so may result in decomposition and the formation of a solid impurity.
5. The product can be further purified by vacuum distillation at 65 °C/5 mbar, but is not necessary. High temperature during distillation may cause decomposition of the product.

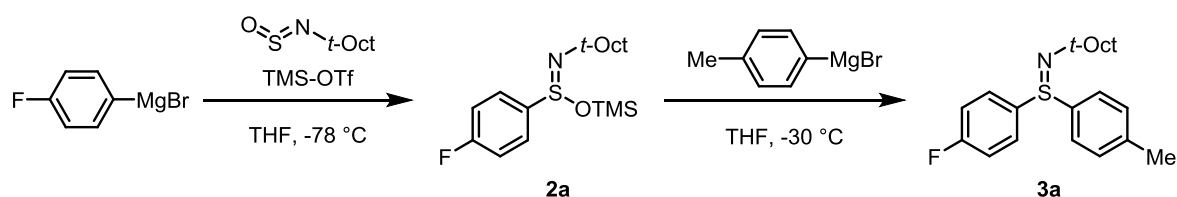
¹H NMR (400 MHz, CDCl₃): δ (ppm) = 1.72 (s, 2H), 1.59 (s, 6H), 1.01 (s, 9H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 67.6, 55.5, 32.1, 31.5, 31.2.

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 2980, 2888, 1382, 1252, 1152, 1073, 954.

HRMS (EI⁺) calcd. for C₈H₈NOS⁺ [M+H]⁺: 176.1104; found: 176.1106.

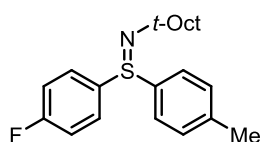
1.2.2 General Procedure A for Diaryl Sulfilimine Synthesis



N-Sulfinyl-*tert*-octylamine **1** (158 mg, 0.90 mmol, 1.05 equiv.) was dissolved in anhydrous THF (2 mL) in an oven-dried 25 mL round bottom flask. Then the mixture was cooled to -78 °C before TMSOTf (195 mg, 0.86 mmol, 1.0 equiv.) was added, and 4-fluorophenylmagnesium bromide (0.97 mL, 0.89 M in THF, 0.86 mmol, 1.0 equiv.) was added dropwise after 1 min. The reaction was stirred at -78 °C for 2 min and then the temperature was increased to -30 °C (**see note**). 4-Methylphenylmagnesium bromide (1.40 mL, 0.91 M in THF, 1.27 mmol, 1.5 equiv.) was then added quickly. The mixture was stirred at -30 °C for 10 min. Then the reaction was quenched with sat. aq. tetrasodium EDTA solution. Ethyl acetate (60 mL) was added and the organic phase was separated. The aqueous phase was further extracted with ethyl acetate (2 × 30 mL). The combined organic extracts were dried over anhydrous Na₂SO₄, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (petrol/ethyl acetate with 1% Et₃N, 4:1 to 1:1 to 0:1) to afford sulfilimine **3a** as a light yellow oil (252 mg, 85%).

Note: The reaction can be warmed from -78 °C to -30 °C through an addition of acetone to the dry ice-acetone bath over 5 min, or a quick replacement of the dry ice-acetone bath with an acetone bath at -30 °C.

1-(4-Fluorophenyl)-1-(*p*-tolyl)-*N*-(2,4,4-trimethylpentan-2-yl)-λ⁴-sulfanimine (**3a**)



¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.61-7.56 (m, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 7.08-7.02 (m, 2H), 2.33 (s, 3H), 1.63 (s, 2H), 1.31 (s, 6H), 0.95 (s, 9H).

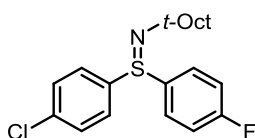
¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 163.6 (d, ¹*J*_{CF} = 250.2 Hz), 141.8, 140.9 (d, ⁴*J*_{CF} = 2.6 Hz), 140.4, 129.8, 128.8 (d, ³*J*_{CF} = 8.7 Hz), 126.7, 116.1 (d, ²*J*_{CF} = 22.2 Hz), 58.5, 58.4, 32.73, 32.70, 32.1, 31.8, 21.4.

^{19}F NMR (376 MHz, CDCl_3): δ (ppm) = -111.1 (tt, J = 9.0, 5.3 Hz).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2950, 1587, 1487, 1224, 1075, 1007, 833.

HRMS (ESI^+) calcd. for $\text{C}_{21}\text{H}_{29}\text{FNS}^+$ $[\text{M}+\text{H}]^+$: 346.1999; found: 346.1997.

1-(4-Chlorophenyl)-1-(4-fluorophenyl)-*N*-(2,4,4-trimethylpentan-2-yl)- λ^4 -sulfanimine (3g)



Prepared according to **General Procedure A** using *N*-sulfinyl-*tert*-octylamine **1** (164 mg, 0.934 mmol, 1.05 equiv.), TMSOTf (201 mg, 0.904 mmol, 1.0 equiv.), 4-chlorophenylmagnesium bromide (1.03 mL, 0.88 M in 2-methyltetrahydrofuran, 0.906 mmol, 1.0 equiv.) and 4-fluorophenylmagnesium bromide (1.42 mL, 0.96 M in THF, 1.36 mmol, 1.5 equiv.). Purification by flash column chromatography (petrol/ethyl acetate with 1% Et_3N , 7:1 to 1:1 to 0:1) afforded *sulfilimine* **3g** as a light yellow oil (262 mg, 79%).

^1H NMR (400 MHz, CDCl_3): δ (ppm) = 7.63-7.57 (m, 2H), 7.55 (d, J = 8.6 Hz, 2H), 7.35 (d, J = 8.6 Hz, 2H), 7.10-7.03 (m, 2H), 1.61 (s, 2H), 1.29 (s, 6H), 0.94 (s, 9H).

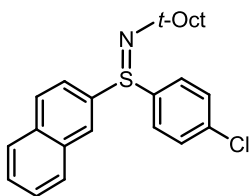
^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{CO}$): δ (ppm) = 164.8 (d, $^1J_{\text{CF}}$ = 248.5 Hz), 146.1, 142.7 (d, $^4J_{\text{CF}}$ = 2.9 Hz), 136.7, 130.3, 129.4 (d, $^3J_{\text{CF}}$ = 8.9 Hz), 128.6, 117.2 (d, $^2J_{\text{CF}}$ = 22.9 Hz), 59.2, 59.0, 33.84, 33.79, 32.82, 32.75.

^{19}F NMR (376 MHz, CDCl_3): δ (ppm) = -110.1 (tt, J = 8.4, 5.2 Hz).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1653, 1589, 1472, 1390, 1228, 1128, 1088, 1006, 963, 812, 736.

HRMS (ESI^+) calcd. for $\text{C}_{20}\text{H}_{26}\text{F}^{35}\text{Cl NS}^+$ $[\text{M}+\text{H}]^+$: 366.1453; found: 366.1446.

1-(4-Chlorophenyl)-1-(naphthalen-2-yl)-*N*-(2,4,4-trimethylpentan-2-yl)- λ^4 -sulfanimine (3h)



Prepared according to **General Procedure A** using *N*-sulfinyl-*tert*-octylamine **1** (366 mg, 2.09 mmol, 1.05 equiv.), TMSOTf (445 mg, 2.00 mmol, 1.0 equiv.), 2-naphthylmagnesium bromide (3.80 mL, 0.52 M in THF, 1.98 mmol, 1.0 equiv.) and 4-chlorophenylmagnesium bromide (3.60 mL, 0.83 M in 2-methyltetrahydrofuran, 2.99 mmol, 1.5 equiv.). Purification by flash column chromatography (petrol/ethyl acetate with 1% Et₃N, 7:1 to 5:1 to 0:1) afforded *sulfilimine 3h* as a light yellow oil (696 mg, 89%).

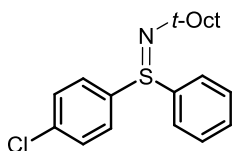
¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.30-8.27 (m, 1H), 7.94-7.89 (m, 1H), 7.84-7.78 (m, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.55-7.49 (m, 3H), 7.35 (d, *J* = 8.5 Hz, 2H), 1.71 (s, 2H), 1.38 (s, 6H), 0.99 (s, 9H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 143.6, 141.7, 136.1, 134.0, 132.9, 129.4, 129.2, 128.7, 128.1, 127.9, 127.5, 127.1, 126.7, 123.0, 58.7, 58.3, 32.84, 32.82, 32.1, 31.8.

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 1474, 1389, 1210, 1132, 1092, 1011, 857, 812, 763, 750.

HRMS (ESI⁺) calcd. for C₂₄H₂₉N³⁵ClS⁺ [M+H]⁺: 398.1704; found: 398.1701.

1-(4-Chlorophenyl)-1-phenyl-*N*-(2,4,4-trimethylpentan-2-yl)- λ^4 -sulfanimine (**3j**)



Prepared according to **General Procedure A** using *N*-sulfinyl-*tert*-octylamine **1** (337 mg, 1.93 mmol, 1.05 equiv.), TMSOTf (417 mg, 1.88 mmol, 1.0 equiv.), 4-chlorophenylmagnesium bromide (2.13 mL, 0.88 M in 2-methyltetrahydrofuran, 1.87 mmol, 1.0 equiv.) and phenyllithium (2.20 mL, 1.24 M in dibutyl ether, 2.73 mmol, 1.5 equiv.). Purification by flash column chromatography (petrol/ethyl acetate with 1% Et₃N, 3:1 to 1:1 to 0:1) afforded *sulfilimine 3j* as a light yellow oil (590 mg, 91%).

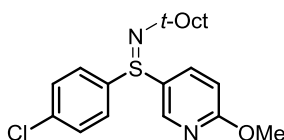
¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.61-7.57 (m, 2H), 7.55 (d, *J* = 8.6 Hz, 2H), 7.38- 7.30 (m, 5H), 1.62 (s, 2H), 1.30 (s, 6H), 0.94 (s, 9H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 144.1, 143.2, 136.1, 130.2, 129.2, 129.1, 128.0, 126.6, 58.6, 58.1, 32.6, 32.5, 31.9, 31.7.

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 1472, 1276, 1261, 1209, 1087, 1009, 817, 750, 702.

HRMS (ESI⁺) calcd. for C₂₀H₂₇N³⁵ClS⁺ [M+H]⁺: 348.1547; found: 348.1544.

1-(4-Chlorophenyl)-1-(6-methoxypyridin-3-yl)-N-(2,4,4-trimethylpentan-2-yl)- λ^4 -sulfanimine (3k)



Preparation of organolithium reagent

5-Bromo-2-methoxypyridine (458 mg, 2.44 mmol, 1.2 equiv.) and THF (5 mL) were added to an oven-dried reaction tube and were cooled to -78 °C. *n*-Butyllithium (1.09 mL, 2.24 M in hexanes, 2.44 mmol, 1.2 equiv.) was added dropwise and the mixture was stirred at the same temperature for 40 min.

Preparation of diaryl sulfilimine

N-Sulfinyl-*tert*-octylamine **1** (370 mg, 2.11 mmol, 1.05 equiv.) was dissolved in anhydrous THF (4.0 mL) in an oven-dried 25 mL round bottom flask. The mixture was cooled to -78 °C before the addition of TMSOTf (440 mg, 1.98 mmol, 1.0 equiv.). 4-Chlorophenylmagnesium bromide (2.25 mL, 0.88 M in 2-methyltetrahydrofuran, 1.98 mmol, 1.0 equiv.) was added dropwise after 1 min. The reaction was stirred at -78 °C for 2 min and then the temperature was increased to -30 °C. Then the organolithium reagent was by syringe. The mixture was stirred at -30 °C for 10 min, then warmed to room temperature and stirred for 1.5 h. The reaction was subsequently quenched with sat. aq. tetrasodium EDTA solution. Ethyl acetate (60 mL) was then added and the organic phase was separated. The aqueous phase was further extracted with ethyl acetate (2 × 30 mL). The combined extracts were dried over anhydrous Na₂SO₄, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (petrol/ethyl acetate with 1% Et₃N, 4:1 to 1:1 to 0:1) to afford *sulfilimine* **3k** as a light yellow oil (570 mg, 76%).

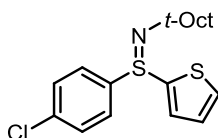
¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.26 (dd, *J* = 2.5, 0.7 Hz, 1H), 7.67 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.52 (d, *J* = 8.6 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 6.68 (dd, *J* = 8.7, 0.7 Hz, 1H), 3.86 (s, 3H), 1.58 (d, *J* = 14.4 Hz, 1H), 1.54 (d, *J* = 14.4 Hz, 1H), 1.25 (s, 3H), 1.24 (s, 3H), 0.89 (s, 9H).

^{13}C NMR (100 MHz, CDCl_3): δ (ppm) = 165.2, 145.9, 142.9, 137.0, 136.1, 133.9, 129.1, 127.5, 112.4, 58.5, 58.1, 53.9, 32.7, 32.5, 31.9, 31.7.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1587, 1473, 1362, 1276, 1261, 1010, 750.

HRMS (ESI^+) calcd. for $\text{C}_{20}\text{H}_{28}\text{O}^{35}\text{Cl N}_2\text{S}^+$ $[\text{M}+\text{H}]^+$: 379.1605; found: 379.1602.

1-(4-Chlorophenyl)-1-(thiophen-2-yl)-*N*-(2,4,4-trimethylpentan-2-yl)- λ^4 -sulfanimine (3l)



Prepared according to **General Procedure A** using *N*-sulfinyl-*tert*-octylamine **1** (372 mg, 2.12 mmol, 1.05 equiv.), TMSOTf (458 mg, 2.06 mmol, 1.0 equiv.), 4-chlorophenylmagnesium bromide (2.34 mL, 0.88 M in 2-methyltetrahydrofuran, 2.06 mmol, 1.0 equiv.) and 2-thienylmagnesium bromide (3.50 mL, 0.85 M in THF, 2.96 mmol, 1.5 equiv.). Purification by flash column chromatography (petrol/ethyl acetate with 1% Et_3N , 7:1 to 2:1 to 0:1) afforded *sulfilimine* **3l** as a light yellow oil (627 mg, 86%).

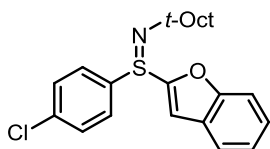
^1H NMR (400 MHz, CDCl_3): δ (ppm) = 7.66 (d, J = 8.6 Hz, 2H), 7.43 (dd, J = 5.0, 1.3 Hz, 1H), 7.37 (d, J = 8.6 Hz, 2H), 7.27-7.21 (m, 1H), 6.97 (dd, J = 5.0, 3.7 Hz, 1H), 1.63 (d, J = 14.5 Hz, 1H), 1.60 (d, J = 14.5 Hz, 1H), 1.32 (s, 3H), 1.31 (s, 3H), 0.95 (s, 9H).

^{13}C NMR (100 MHz, CDCl_3): δ (ppm) = 149.4, 143.0, 136.4, 130.6, 129.1, 128.8, 127.4, 127.2, 58.8, 57.9, 32.5, 32.4, 31.9, 31.7.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1471, 1276, 1261, 1209, 1087, 1008, 816, 766, 706.

HRMS (ESI^+) calcd. for $\text{C}_{18}\text{H}_{25}\text{N}^{35}\text{ClS}_2^+$ $[\text{M}+\text{H}]^+$: 354.1112; found: 354.1111.

1-(Benzofuran-2-yl)-1-(4-chlorophenyl)-N-(2,4,4-trimethylpentan-2-yl)- λ^4 -sulfanimine (3m)



Preparation of organolithium reagent

Benzofuran (317 mg, 2.69 mmol, 1.5 equiv.) and THF (5.0 mL) were added to an oven-dried reaction tube. The reaction was cooled to 0 °C. *n*-Butyllithium (1.20 mL, 2.24 M in hexanes, 2.69 mmol, 1.5 equiv.) was added dropwise and the mixture stirred at the room temperature for 1 h.

Preparation of diaryl sulfilimine

N-Sulfinyl-*tert*-octylamine **1** (312 mg, 1.78 mmol, 1.05 equiv.) was dissolved in anhydrous THF (3.6 mL) in an oven-dried 25 mL round bottom flask. Then the reaction was cooled to -78 °C before TMSOTf (386 mg, 1.74 mmol, 1.0 equiv.) was added, 4-chlorophenylmagnesium bromide (1.97 mL, 0.88 M in 2-methyltetrahydrofuran, 1.73 mmol, 1.0 equiv.) was added dropwise after 1 min. The reaction was stirred at -78 °C for 2 min and then the temperature was increased to -30 °C. Then the lithium reagent was added by syringe. The mixture was stirred at -30 °C for 10 min and then warmed to room temperature and stirred for 1.5 h. Then the reaction was quenched with saturated aqueous tetrasodium EDTA solution and poured into a 250 mL separating funnel. Ethyl acetate (60 mL) was then added and the organic phase was separated. The aqueous phase was further extracted with ethyl acetate (2 × 30 mL). The combined extracts were dried over anhydrous Na₂SO₄, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (petrol/ethyl acetate with 1% Et₃N, 7:1 to 1:1 to 0:1) to afford *sulfilimine* **3m** as a light yellow oil (584 mg, 87%).

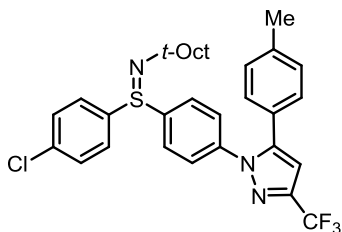
¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.75 (d, *J* = 8.6 Hz, 2H), 7.57-7.52 (m, 1H), 7.45-7.39 (m, 3H), 7.32-7.27 (m, 1H), 7.22 (app. td, *J* = 7.5, 1.1 Hz, 1H), 7.04 (d, *J* = 1.1 Hz, 1H), 1.68 (s, 2H), 1.39 (s, 3H), 1.37 (s, 3H), 0.98 (s, 9H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 156.6, 156.4, 139.4, 136.8, 129.3, 127.6, 127.0, 126.1, 123.6, 122.0, 112.0, 109.8, 58.7, 57.8, 32.6, 32.4, 31.9, 31.8.

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 1472, 1444, 1276, 1261, 1010, 816, 750.

HRMS (ESI⁺) calcd. for C₂₂H₂₇O³⁵ClNS⁺ [M+H]⁺: 388.1496; found: 388.1494.

1-(4-Chlorophenyl)-1-(4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)phenyl)-*N*-(2,4,4-trimethylpentan-2-yl)- λ^4 -sulfanimine (3n**)**



Preparation of organolithium reagent

1-(4-Bromophenyl)-5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazole² (413 mg, 1.09 mmol, 1.3 equiv.) and THF (2.0 mL) were added to an oven-dried reaction tube and were cooled to -78 °C. *n*-Butyllithium (0.48 mL, 2.24 M in hexanes, 1.1 mmol, 1.3 equiv.) was added dropwise and the mixture was stirred at the same temperature for 40 min.

Preparation of diaryl sulfilimine

N-Sulfinyl-*tert*-octylamine **1** (155 mg, 0.89 mmol, 1.05 equiv.) was dissolved in anhydrous THF (4.0 mL) in an oven-dried 25 mL round bottom flask. The mixture was cooled to -78 °C before the addition of TMSOTf (190 mg, 0.86 mmol, 1.0 equiv.). 4-Chlorophenylmagnesium bromide (0.97 mL, 0.88 M in 2-methyltetrahydrofuran, 0.85 mmol, 1.0 equiv.) was added dropwise after 1 min. The reaction was stirred at -78 °C for 2 min and then the temperature was increased to -30 °C. Then the organolithium reagent was added by syringe. The mixture was stirred at -30 °C for 10 min, then warmed to room temperature and stirred for 1.5 h. The reaction was subsequently quenched with sat. aq. tetrasodium EDTA solution. Ethyl acetate (50 mL) was then added and the organic phase was separated. The aqueous phase was further extracted with ethyl acetate (2 × 30 mL). The combined extracts were dried over anhydrous Na₂SO₄, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (petrol/ethyl acetate with 1% Et₃N, 3:1 to 1:1 to 0:1) to afford *sulfilimine* **3n** as a light yellow oil (413 mg, 85%).

¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.60 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 8.6 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 8.6 Hz, 2H), 7.11 (d, *J* = 8.3 Hz, 2H), 7.06 (d, *J* = 8.3 Hz, 2H), 6.70 (s, 1H), 2.35 (s, 3H), 1.61 (s, 2H), 1.32 (s, 6H), 0.94 (s, 9H).

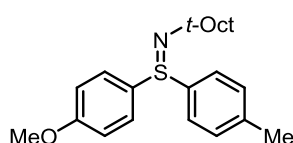
^{13}C NMR (100 MHz, CDCl_3): δ (ppm) = 145.1, 143.7 (q, $^2J_{\text{CF}} = 38.7$ Hz), 142.5, 140.8, 139.6, 136.7, 129.7, 129.5, 128.7, 128.1, 127.6, 125.92, 125.87, 125.5, 121.2 (q, $^1J_{\text{CF}} = 268.8$ Hz), 105.9, 58.9, 58.1, 32.7, 32.5, 32.0, 31.8, 21.4.

^{19}F NMR (376 MHz, CDCl_3): δ (ppm) = -62.3.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1472, 1276, 1261, 1235, 1161, 1133, 1094, 975, 750.

HRMS (ESI^+) calcd. for $\text{C}_{31}\text{H}_{34}^{35}\text{Cl N}_3\text{F}_3\text{S}^+$ $[\text{M}+\text{H}]^+$: 572.2109; found: 572.2097.

1-(4-Methoxyphenyl)-1-(*p*-tolyl)-*N*-(2,4,4-trimethylpentan-2-yl)- λ^4 -sulfanimine (3r**)**



Prepared according to **General Procedure A** using *N*-sulfinyl-*tert*-octylamine **1** (208 mg, 1.19 mmol, 1.05 equiv.), TMSOTf (252 mg, 1.13 mmol, 1.0 equiv.), 4-methoxyphenylmagnesium bromide (2.30 mL, 0.48 M in THF, 1.10 mmol, 1.0 equiv.) and 4-methylphenylmagnesium bromide (1.80 mL, 0.94 M in THF, 1.69 mmol, 1.5 equiv.). Purification by flash column chromatography (petrol/ethyl acetate with 1% Et_3N , 3:1 to 1:1 to 0:1) afforded *sulfilimine* **3r** as a light yellow oil (317 mg, 81%).

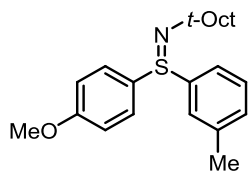
^1H NMR (400 MHz, CDCl_3): δ (ppm) = 7.50 (d, $J = 8.8$ Hz, 2H), 7.46 (d, $J = 8.2$ Hz, 2H), 7.15 (d, $J = 8.2$ Hz, 2H), 6.86 (d, $J = 8.8$ Hz, 2H), 3.74 (s, 3H), 2.30 (s, 3H), 1.63 (s, 2H), 1.302 (s, 3H), 1.298 (s, 3H), 0.94 (s, 9H).

^{13}C NMR (100 MHz, CDCl_3): δ (ppm) = 160.9, 142.0, 139.8, 136.4, 129.5, 128.4, 126.6, 114.3, 58.3, 58.2, 55.4, 32.62, 32.56, 32.0, 31.7, 21.2.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1592, 1491, 1392, 1249, 1129, 1030, 828, 730.

HRMS (ESI^+) calcd. for $\text{C}_{22}\text{H}_{32}\text{NOS}^+$ $[\text{M}+\text{H}]^+$: 358.2199; found: 358.2200.

1-(4-Methoxyphenyl)-1-(*m*-tolyl)-*N*-(2,4,4-trimethylpentan-2-yl)- λ^4 -sulfanimine (3s**)**



Prepared according to **General Procedure A** using *N*-sulfinyl-*tert*-octylamine **1** (305 mg, 1.74 mmol, 1.05 equiv.), TMSOTf (369 mg, 1.66 mmol, 1.0 equiv.), 4-methoxyphenylmagnesium bromide (3.45 mL, 0.48 M in THF, 1.66 mmol, 1.0 equiv.) and 3-methylphenylmagnesium chloride (3.10 mL, 0.80 M in THF, 2.48 mmol, 1.5 equiv.). Purification by flash column chromatography (petrol/ethyl acetate with 1% Et₃N, 3:1 to 1:1 to 0:1) afforded *sulfilimine* **3s** as a light yellow oil (445 mg, 78%).

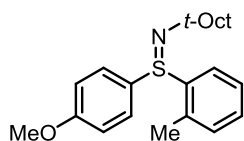
¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.50 (d, J = 8.8 Hz, 2H), 7.43 (app. br. s, 1H), 7.35-7.30 (m, 1H), 7.21 (t, J = 7.6 Hz, 1H), 7.13-7.08 (m, 1H), 6.86 (d, J = 8.8 Hz, 2H), 3.74 (s, 3H), 2.30 (s, 3H), 1.63 (s, 2H), 1.31 (s, 3H), 1.30 (s, 3H), 0.93 (s, 9H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 160.9, 144.9, 138.8, 136.3, 130.5, 128.51, 128.46, 126.8, 123.7, 114.3, 58.3, 58.2, 55.3, 32.63, 32.56, 32.0, 31.7, 21.4.

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 1491, 1249, 827.

HRMS (ESI⁺) calcd. for C₂₂H₃₂NOS⁺ [M+H]⁺: 358.2199; found: 358.2190.

1-(4-Methoxyphenyl)-1-(*o*-tolyl)-*N*-(2,4,4-trimethylpentan-2-yl)- λ^4 -sulfanimine (3t**)**



Prepared according to **General Procedure A** using *N*-sulfinyl-*tert*-octylamine **1** (266 mg, 1.52 mmol, 1.05 equiv.), TMSOTf (322 mg, 1.45 mmol, 1.0 equiv.), 4-methoxyphenylmagnesium bromide (3.00 mL, 0.48 M in THF, 1.44 mmol, 1.0 equiv.) and 2-methylphenylmagnesium chloride (3.00 mL, 0.73 M in THF, 2.19 mmol, 1.5 equiv.). Purification by flash column chromatography (petrol/ethyl acetate with 1% Et₃N, 3:1 to 1:1 to 0:1) afforded *sulfilimine* **3t** as a light yellow oil (400 mg, 78%).

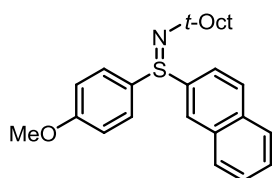
¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.10 (dd, J = 7.8, 1.5 Hz, 1H), 7.34-7.29 (m, 3H), 7.23 (td, J = 7.4, 1.5 Hz, 1H), 7.08-7.04 (m, 1H), 6.79 (d, J = 8.9 Hz, 2H), 3.68 (s, 3H), 2.27 (s, 3H), 1.63 (s, 2H), 1.28 (s, 6H), 0.93 (s, 9H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 160.6, 142.9, 135.3, 135.2, 130.2, 129.7, 128.7, 126.9, 126.8, 114.4, 58.4, 58.3, 55.2, 32.6, 32.3, 31.9, 31.6, 19.0.

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 1492, 1250, 827, 756.

HRMS (ESI⁺) calcd. for C₂₂H₃₂NOS⁺ [M+H]⁺: 358.2199; found: 358.2196.

1-(4-Methoxyphenyl)-1-(naphthalen-2-yl)-N-(2,4,4-trimethylpentan-2-yl)- λ^4 -sulfanimine (3u)



Prepared according to **General Procedure A** using *N*-sulfinyl-*tert*-octylamine **1** (358 mg, 2.04 mmol, 1.05 equiv.), TMSOTf (433 mg, 1.95 mmol, 1.0 equiv.), 4-methoxyphenylmagnesium bromide (4.05 mL, 0.48 M in THF, 1.94 mmol, 1.0 equiv.) and 2-naphthylmagnesium bromide (5.60 mL, 0.53 M in THF, 2.97 mmol, 1.5 equiv.). Purification by flash column chromatography (petrol/ethyl acetate with 1% Et₃N, 3:1 to 1:1 to 0:1) afforded *sulfilimine* **3u** as a light yellow oil (598 mg, 78%).

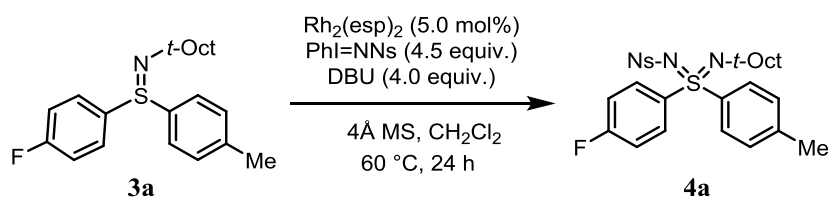
¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.33-8.30 (m, 1H), 7.93-7.87 (m, 1H), 7.81-7.74 (m, 2H), 7.57 (d, J = 8.8 Hz, 2H), 7.51-7.45 (m, 3H), 6.87 (d, J = 8.8 Hz, 2H), 3.72 (s, 3H), 1.73 (s, 2H), 1.40 (s, 3H), 1.39 (s, 3H), 0.99 (s, 9H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 161.0, 142.2, 136.0, 133.8, 132.9, 128.8, 128.6, 128.5, 127.8, 127.2, 126.8, 126.4, 123.1, 114.4, 58.5, 58.2, 55.3, 32.8, 32.6, 32.0, 31.7.

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 1591, 1492, 1382, 1249, 1129, 1029, 825, 730.

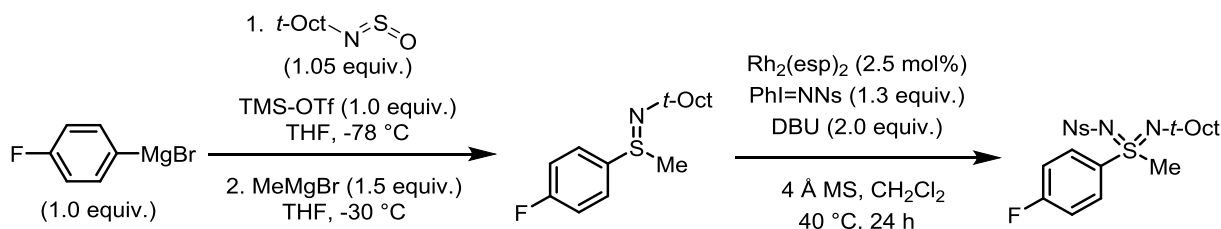
HRMS (ESI⁺) calcd. for C₂₅H₃₂NOS⁺ [M+H]⁺: 394.2199; found: 394.2191.

1.2.3 General Procedure B for Diaryl Sulfondiimine Synthesis



To a 10 mL vial containing $\text{Rh}_2(\text{esp})_2$ (9.0 mg, 0.012 mmol, 5.0 mol%), 4 Å MS (c. 0.2 g) and $\text{PhI}=\text{NNs}$ (136 mg, 0.337 mmol, 1.5 equiv.) was added a solution of sulfilimine **3a** (80 mg, 0.23 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (1.1 mL). DBU (0.14 mL, 0.93 mmol, 4.0 equiv.) was then quickly added at room temperature and the reaction was sealed and stirred at 60 °C for 8 h. Two portions of $\text{PhI}=\text{NNs}$ (2×137 mg, 0.678 mmol, 3.0 equiv.) were subsequently added at the 8th and 16th hour. The reaction mixture was then transferred to a 100 mL round bottom flask, to separate from the 4 Å MS, washing the vial several times with CH_2Cl_2 . The solvent was then removed under reduced pressure. The crude product was purified by flash column chromatography (petrol/ethyl acetate 6:1 to 4:1) to afford *sulfondiimine* **4a** as a light yellow solid (55 mg, 44%).

1.2.4 General Procedure C for Aryl-Alkyl and Dialkyl Sulfondiimine Synthesis



N-Sulfinyl-*tert*-octylamine **1** (240 mg, 1.37 mmol, 1.05 equiv.) was dissolved in anhydrous THF (2.7 mL) in an oven-dried 25 mL round bottom flask. The mixture was then cooled to -78 °C and TMSOTf (297 mg, 1.34 mmol, 1.0 equiv.) was added. Then 4-fluorophenylmagnesium bromide (1.47 mL, 0.91 M in THF, 1.34 mmol, 1.0 equiv.) was added dropwise after 1 min. The reaction was stirred at -78 °C for 2 min and then the temperature was increased to -30 °C (see **note 1**). Methylmagnesium bromide (0.67 mL, 3.0 M in diethyl ether, 2.0 mmol, 1.5 equiv.) was then added quickly. The mixture was stirred at -30 °C for 10 min. Then the reaction was quenched with sat. aq. tetrasodium EDTA solution (100 mL) and poured into a 250 mL separating funnel. Ethyl acetate (80 mL) was then added and the organic phase was separated. The aqueous phase was further extracted with ethyl acetate (2×40 mL). The combined extracts were dried over anhydrous Na_2SO_4 , filtered and concentrated under reduced pressure. The crude sulfilimine was dissolved in a mixture

of diethyl ether (15 mL) and petroleum ether (5 mL) and acidified by an 1 M aq. solution of 4-toluenesulfonic acid (35 mL). The organic layer was discarded. The aqueous phase was washed once with a mixture of diethyl ether (5 mL) and petroleum ether (15 mL). The aqueous phase was then extracted with CH₂Cl₂ (3 × 40 mL), combined CH₂Cl₂ extracts dried over Na₂SO₄, filtered and concentrated under reduced pressure to afford the 4-toluenesulfonic acid-sulfilimine salt **3ba** (c. 85% yield). The sulfilimine salt **3ba** was then dissolved in CH₂Cl₂ (50 mL) and treated with 1 M aq. NaOH (50 mL). The organic layer was separated and the aqueous phase was extracted with CH₂Cl₂ (2 × 50 mL). The combined organic extracts were dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure to afford *sulfilimine* **3b** as a light yellow oil (300 mg, 83%).

Notes:

1. The reaction can be warmed from -78 °C to -30 °C through an addition of acetone to the dry ice-acetone bath over 5 min, or a quick replacement of the dry ice-acetone bath with an acetone bath at -30 °C
2. Solvents were removed in a rotary evaporator below 30 °C due to instability of the sulfilimine **3b** at high temperatures.
3. After performing an acid-base workup as mentioned above, crude *S*-aryl-*S*-alkyl and *S,S*-dialkyl sulfilimines were used without further purification in the next step. For long-term storage, 4-toluenesulfonic acid salt would be preferred over the neutral sulfilimine due to enhanced stability.
4. EDTA solution is used to complex the magnesium salts present in the Grignard reagents, which otherwise emulsions may be formed and complicate the aqueous work-up if only water is used instead.
5. The *S*-aryl-*S*-alkyl and *S,S*-dialkyl sulfilimines are typically very polar and appear to be strongly basic, which often stay on the baseline of the TLC plate even when ethyl acetate is used as the eluent. When mixtures of ethyl acetate and methanol were used, the sulfilimine may travel further up the TLC plate but “streaking” is often observed. For sulfilimine **3b**, 3:1 petrol/ethyl acetate can be used to observe the by-products (which are removed during the diethyl ether/petroleum ether washes).

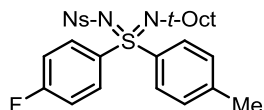
A solution of sulfilimine **3b** (300 mg, 1.11 mmol, 1.0 equiv.) in anhydrous CH₂Cl₂ (5.6 mL) was

added to a 25 mL vial containing Rh₂(esp)₂ (21 mg, 0.028 mmol, 2.5 mol%), 4 Å MS (c. 0.4 g) and PhI=NNs (583 mg, 1.44 mmol, 1.3 equiv.). DBU (0.34 mL, 2.2 mmol, 2.0 equiv.) was then added at room temperature quickly and the reaction was sealed and stirred at 40 °C for 24 h. The reaction mixture was then transferred to a 100 mL round bottom flask, to separate from the 4 Å MS, washing the vial several times with CH₂Cl₂. The solvent was then removed under reduced pressure. The crude product was purified by flash column chromatography (petrol/ethyl acetate, 4:1 to 2:1) to afford *sulfondiimine* **4b** as a light yellow solid (444 mg, 71% yield over two steps).

Notes:

1. The reaction was run under air.
2. The reaction is run for 24 hours as standard as some *S,S*-diaryl substrates need extended reaction times, but it may be finished sooner for *S*-aryl-*S*-alkyl and *S,S*-dialkyl substrates.
3. The protected sulfondiimines are stable towards air and moisture and do not need any special care to be taken when handling them.

***N*-((4-Fluorophenyl)(*p*-tolyl)((2,4,4-trimethylpentan-2-yl)imino)-λ⁶-sulfaneylidene)-4-nitrobenzenesulfonamide (**4a**)**



mp 169-171 °C (CH₂Cl₂)

R_f 0.50 (petrol/ethyl acetate, 3:1).

¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.08 (d, *J* = 8.9 Hz, 2H), 7.82-7.76 (m, 2H), 7.72 (d, *J* = 8.9 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.14 (d, *J* = 8.5 Hz, 2H), 7.08-6.99 (m, 2H), 2.37 (s, 3H), 1.60 (d, *J* = 14.6 Hz, 1H), 1.56 (d, *J* = 14.6 Hz, 1H), 1.38 (s, 3H), 1.35 (s, 3H), 1.08 (s, 9H).

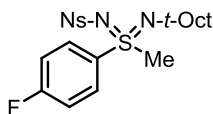
¹³C NMR (100 MHz, (CD₃)₂CO): δ (ppm) = 166.0 (d, ¹*J*_{CF} = 253.5 Hz), 150.9, 150.3, 145.0, 139.7, 139.3 (d, ⁴*J*_{CF} = 3.1 Hz), 132.2 (d, ³*J*_{CF} = 9.5 Hz), 130.8, 129.2, 128.6, 124.8, 117.2 (d, ²*J*_{CF} = 23.1 Hz), 61.0, 58.7, 32.7, 32.6, 32.54, 32.51, 21.5.

¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) = -105.2 (tt, *J* = 8.0, 4.9 Hz).

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 2980, 1528, 1488, 1349, 1301, 1222, 1152, 1074, 1029, 1005, 734, 612.

HRMS (ESI⁺) calcd. for C₂₇H₃₃FN₃O₄S₂⁺ [M+H]⁺: 546.1891; found: 546.1885.

***N*-((4-Fluorophenyl)(methyl)((2,4,4-trimethylpentan-2-yl)imino)- λ^6 -sulfaneylidene)-4-nitrobenzenesulfonamide (**4b**)**



mp 153-155 °C (CH₂Cl₂)

R_f 0.54 (petrol/ethyl acetate, 3:1).

¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.27 (d, *J* = 8.9 Hz, 2H), 8.07 (d, *J* = 8.9 Hz, 2H), 7.99-7.94 (m, 2H), 7.21-7.15 (m, 2H), 3.46 (s, 3H), 1.47 (d, *J* = 14.4 Hz, 1H), 1.41 (d, *J* = 14.4 Hz, 1H), 1.29 (s, 3H), 1.14 (s, 3H), 1.00 (s, 9H).

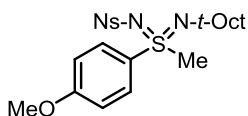
¹³C NMR (100 MHz, (CD₃)₂CO): δ (ppm) = 166.3 (d, ¹*J*_{CF} = 253.4 Hz), 151.4, 150.4, 139.6 (d, ⁴*J*_{CF} = 3.1 Hz), 131.7 (d, ³*J*_{CF} = 9.6 Hz), 128.6, 125.1, 117.4 (d, ²*J*_{CF} = 23.0 Hz), 60.3, 58.5, 49.2, 32.6, 32.5, 32.4, 32.3.

¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) = -104.6 (tt, *J* = 8.0, 4.9 Hz).

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 2953, 1589, 1528, 1487, 1349, 1293, 1223, 1149, 1035, 840.

HRMS (ESI⁺) calcd. for C₂₁H₂₉FN₃O₄S₂⁺ [M+H]⁺: 470.1578; found: 470.1577.

***N*-((4-Methoxyphenyl)(methyl)((2,4,4-trimethylpentan-2-yl)imino)- λ^6 -sulfaneylidene)-4-nitrobenzenesulfonamide (**4c**)**



Sulfilimine prepared according to **General Procedure C** using *N*-sulfinyl-*tert*-octylamine **1** (164 mg, 0.937 mmol, 1.05 equiv.), TMSOTf (202 mg, 0.909 mmol, 1.0 equiv.), 4-methoxyphenylmagnesium bromide (1.85 mL, 0.49 M in THF, 0.907 mmol, 1.0 equiv.) and methylmagnesium bromide (0.46 mL, 3.0 M in diethyl ether, 1.4 mmol, 1.5 equiv.). Following the general purification method, *sulfilimine 3c* was generated as light yellow oil with a crude yield of 84% (215 mg). Sulfondiimine prepared using Rh₂(esp)₂ (15 mg, 0.020 mmol, 2.5 mol%), PhI=NNs (400 mg, 0.990 mmol, 1.3 equiv.) and DBU (0.23 mL, 1.5 mmol, 2.0 equiv.). Purification by flash

column chromatography (petrol/ethyl acetate, 3:1 to 1:1) afforded *sulfondiimine 4c* as a light yellow solid (279 mg, 64% yield over two steps).

mp 117-119 °C (CH₂Cl₂)

R_f 0.5 (petrol/ethyl acetate, 1:1).

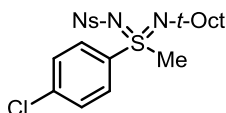
¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.25 (d, *J* = 8.9 Hz, 2H), 8.06 (d, *J* = 8.9 Hz, 2H), 7.84 (d, *J* = 9.0 Hz, 2H), 6.94 (d, *J* = 9.0 Hz, 2H), 3.84 (s, 3H), 3.42 (s, 3H), 1.47 (d, *J* = 14.4 Hz, 1H), 1.42 (d, *J* = 14.4 Hz, 1H), 1.30 (s, 3H), 1.16 (s, 3H), 1.00 (s, 9H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 163.4, 150.2, 149.3, 133.3, 129.6, 127.6, 124.0, 114.7, 59.8, 57.8, 55.8, 49.7, 32.0, 31.9, 31.83, 31.80.

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 2950, 1591, 1528, 1349, 1293, 1176, 1083, 1031, 855, 797.

HRMS (ESI⁺) calcd. for C₂₂H₃₁N₃NaO₅S₂⁺ [M+Na]⁺: 504.1597; found: 504.1596.

***N*-((4-Chlorophenyl)(methyl)((2,4,4-trimethylpentan-2-yl)imino)-λ⁶-sulfaneylidene)-4-nitrobenzenesulfonamide (4d)**



Sulfilimine prepared according to **General Procedure C** using *N*-sulfinyl-*tert*-octylamine **1** (316 mg, 1.81 mmol, 1.05 equiv.), TMSOTf (381 mg, 1.71 mmol, 1.0 equiv.), 4-chlorophenylmagnesium bromide (1.95 mL, 0.88 M in 2-methyltetrahydrofuran, 1.72 mmol, 1.0 equiv.) and methylmagnesium bromide (0.85 mL, 3.0 M in diethyl ether, 2.6 mmol, 1.5 equiv.). Following the general purification method, *sulfilimine 3d* was generated as light yellow oil with a crude yield of 78% (380 mg). Sulfondiimine prepared using Rh₂(esp)₂ (24 mg, 0.032 mmol, 2.5 mol%), PhI=NNs (726 mg, 1.80 mmol, 1.3 equiv.) and DBU (0.40 mL, 2.7 mmol, 2.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 7:1 to 3:1) afforded *sulfondiimine 4d* as a white solid (546 mg, 66% yield over two steps).

mp 153-155 °C (CH₂Cl₂)

R_f 0.6 (petrol / ethyl acetate = 2:1).

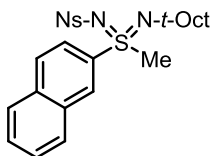
¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.25 (d, J = 8.9 Hz, 2H), 8.05 (d, J = 8.9 Hz, 2H), 7.87 (d, J = 8.7 Hz, 2H), 7.45 (d, J = 8.7 Hz, 2H), 3.44 (s, 3H), 1.45 (d, J = 14.4 Hz, 1H), 1.40 (d, J = 14.4 Hz, 1H), 1.28 (s, 3H), 1.13 (s, 3H), 0.98 (s, 9H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 149.8, 149.3, 141.1, 139.8, 129.7, 129.0, 127.5, 124.0, 60.0, 57.6, 49.3, 31.89, 31.87, 31.73, 31.71.

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 1527, 1349, 1294, 1221, 1149, 1089, 1075, 1035, 1006, 968, 855, 735.

HRMS (ESI⁺) calcd. for C₂₁H₂₈N₃Na³⁵ClO₄S₂⁺ [M+Na]⁺: 508.1102; found: 508.1104.

***N*-(Methyl(naphthalen-2-yl)((2,4,4-trimethylpentan-2-yl)imino)- λ^6 -sulfaneylidene)-4-nitrobenzenesulfonamide (4e)**



Sulfilimine prepared according to **General Procedure C** using *N*-sulfinyl-*tert*-octylamine **1** (249 mg, 1.42 mmol, 1.05 equiv.), TMSOTf (300 mg, 1.35 mmol, 1.0 equiv.), 2-naphthylmagnesium bromide (2.60 mL, 0.52 M in THF, 1.35 mmol, 1.0 equiv.) and methylmagnesium bromide (0.70 mL, 3.0 M in diethyl ether, 2.1 mmol, 1.5 equiv.). Following the general purification method, *sulfilimine 3e* was generated as light yellow oil with a crude yield of 78% (318 mg). Sulfondiimine prepared using Rh₂(esp)₂ (20 mg, 0.026 mmol, 2.5 mol%), PhI=NNs (524 mg, 1.30 mmol, 1.3 equiv.) and DBU (0.30 mL, 2.0 mmol, 2.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 4:1 to 2:1) afforded *sulfondiimine 4e* as a light yellow solid (356 mg, 53% yield over two steps).

mp 154-156 °C (CH₂Cl₂)

R_f 0.5 (petrol/ethyl acetate, 1.5:1).

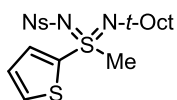
¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.47 (d, J = 1.8 Hz, 1H), 8.16 (d, J = 8.9 Hz, 2H), 8.04 (d, J = 8.9 Hz, 2H), 7.96-7.84 (m, 4H), 7.67-7.57 (m, 2H), 3.52 (s, 3H), 1.50 (s, 2H), 1.36 (s, 3H), 1.22 (s, 3H), 1.04 (s, 9H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 149.9, 149.1, 138.6, 134.8, 132.2, 129.7, 129.4, 129.3, 129.2, 127.91, 127.89, 127.6, 123.9, 122.1, 60.0, 57.7, 49.2, 32.0, 31.94, 31.90, 31.8.

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 1526, 1348, 1293, 1220, 1148, 1089, 1031, 1008, 969, 739.

HRMS (ESI⁺) calcd. for C₂₅H₃₂N₃O₄S₂⁺ [M+H]⁺: 502.1829; found: 502.1827.

***N*-(Methyl(thiophen-2-yl)((2,4,4-trimethylpentan-2-yl)imino)- λ^6 -sulfaneylidene)-4-nitrobenzenesulfonamide (4f)**



Sulfilimine prepared according to **General Procedure C** using *N*-sulfinyl-*tert*-octylamine **1** (295 mg, 1.69 mmol, 1.05 equiv.), TMSOTf (340 mg, 1.53 mmol, 1.0 equiv.), 2-thienylmagnesium bromide (1.80 mL, 0.85 M in THF, 1.53 mmol, 1.0 equiv.) and methylmagnesium bromide (0.77 mL, 3.0 M in diethyl ether, 2.3 mmol, 1.5 equiv.). Following the general purification method, *sulfilimine* **3f** was generated as light yellow oil with a crude yield of 76% (300 mg). Sulfondiimine prepared using Rh₂(esp)₂ (22 mg, 0.029 mmol, 2.5 mol%), PhI=NNs (621 mg, 1.54 mmol, 1.3 equiv.) and DBU (0.34 mL, 2.3 mmol, 2.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 7:1 to 3:1) afforded *sulfondiimine* **4f** as a white solid (414 mg, 60% yield over two steps).

mp 132-134 °C (CH₂Cl₂)

R_f 0.42 (petrol/ethyl acetate, 3:1).

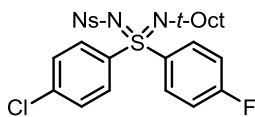
¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.28 (d, *J* = 8.9 Hz, 2H), 8.10 (d, *J* = 8.9 Hz, 2H), 7.64 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.60 (dd, *J* = 3.9, 1.3 Hz, 1H), 7.10 (dd, *J* = 5.1, 3.9 Hz, 1H), 3.58 (s, 3H), 1.47 (d, *J* = 14.4 Hz, 1H), 1.41 (d, *J* = 14.4 Hz, 1H), 1.34 (s, 3H), 1.19 (s, 3H), 1.00 (s, 9H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 149.9, 149.4, 144.2, 134.5, 132.1, 128.6, 127.5, 124.1, 60.3, 57.6, 51.1, 31.9, 31.8, 31.6, 31.5.

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 1527, 1349, 1293, 1241, 1220, 1149, 1090, 1028, 1008, 854, 738.

HRMS (ESI⁺) calcd. for C₁₉H₂₇N₃NaO₄S₃⁺ [M+Na]⁺: 480.1056; found: 480.1050.

***N*-((4-Chlorophenyl)(4-fluorophenyl)((2,4,4-trimethylpentan-2-yl)imino)- λ^6 -sulfaneylidene)-4-nitrobenzenesulfonamide (4g)**



Prepared according to **General Procedure B** using sulfilimine **3g** (152 mg, 0.416 mmol, 1.0 equiv.), $\text{Rh}_2(\text{esp})_2$ (16 mg, 0.021 mmol, 5.0 mol%), $\text{PhI}=\text{NNs}$ (3×262 mg, 1.95 mmol, 4.5 equiv.) and DBU (0.25 mL, 1.7 mmol, 4.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 12:1 to 4:1) afforded *sulfondiimine* **4g** as a white solid (111 mg, 47% yield).

mp 191-192 °C (CH_2Cl_2)

R_f 0.50 (petrol/ethyl acetate, 5:1).

^1H NMR (400 MHz, CDCl_3) = 8.14 (d, J = 8.9 Hz, 2H), 7.81-7.77 (m, 2H), 7.75 (d, J = 8.9 Hz, 2H), 7.69 (d, J = 8.8 Hz, 2H), 7.34 (d, J = 8.8 Hz, 2H), 7.14-6.99 (m, 2H), 1.57 (s, 2H), 1.35 (s, 3H), 1.34 (s, 3H), 1.07 (s, 9H).

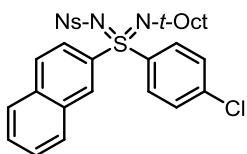
^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{CO}$): δ (ppm) = 166.2 (d, $^1J_{\text{CF}}$ = 253.6 Hz), 150.6, 150.4, 141.8, 139.9, 138.7 (d, $^4J_{\text{CF}}$ = 3.1 Hz), 132.3 (d, $^4J_{\text{CF}}$ = 9.6 Hz), 131.0, 130.4, 128.6, 124.9, 117.4 (d, $^2J_{\text{CF}}$ = 23.1 Hz), 61.2, 58.6, 32.6, 32.52, 32.48 ($2 \times \text{C}$).

^{19}F NMR (376 MHz, CDCl_3): δ (ppm) = -104.3 (ddd, J = 13.0, 8.0, 4.9 Hz).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1528, 1349, 1299, 1276, 1261, 1219, 1152, 1089, 1072, 1028, 1002, 750.

HRMS (ESI^+) calcd. for $\text{C}_{26}\text{H}_{29}\text{N}_3\text{F}^{35}\text{ClNaO}_4\text{S}_2^+$ [$\text{M}+\text{Na}$] $^+$: 588.1164; found: 588.1166.

***N*-((4-Chlorophenyl)(naphthalen-2-yl)((2,4,4-trimethylpentan-2-yl)imino)- λ^6 -sulfaneylidene)-4-nitrobenzenesulfonamide (4h)**



Prepared according to **General Procedure B** using sulfilimine **3h** (253 mg, 0.637 mmol, 1.0 equiv.), $\text{Rh}_2(\text{esp})_2$ (24 mg, 0.032 mmol, 5.0 mol%), $\text{PhI}=\text{NNs}$ (3×397 mg, 2.95 mmol, 4.5 equiv.) and DBU

(0.38 mL, 2.5 mmol, 4.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 7:1 to 4:1) afforded *sulfondiimine* **4h** as a white solid (125 mg, 33%).

mp 191-193 °C (CH₂Cl₂)

R_f 0.50 (petrol/ethyl acetate, 5:1).

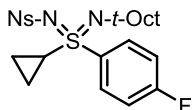
¹H NMR (400 MHz, CDCl₃) = 8.33 (d, *J* = 2.3 Hz, 1H), 7.91 (d, *J* = 8.9 Hz, 2H), 7.84 (app. d, *J* = 8.1 Hz, 1H), 7.81-7.73 (m, 4H), 7.69-7.54 (m, 5H), 7.35 (d, *J* = 8.9 Hz, 2H), 1.66 (d, *J* = 14.5 Hz, 1H), 1.60 (d, *J* = 14.5 Hz, 1H), 1.44 (s, 3H), 1.39 (s, 3H), 1.12 (s, 9H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 149.2, 148.9, 140.6, 139.5, 137.4, 134.7, 132.0, 129.9, 129.8, 129.6, 129.4, 129.30, 129.27, 128.0, 127.9, 127.6, 123.5, 122.7, 60.9, 58.0, 32.2, 32.10, 32.05, 32.0.

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 1527, 1348, 1300, 1276, 1261, 1216, 1152, 1088, 1026, 1003, 909, 750.

HRMS (ESI⁺) calcd. for C₃₀H₃₃N₃³⁵ClO₄S₂⁺ [M+H]⁺: 598.1596; found: 598.1592.

***N*-(Cyclopropyl(4-fluorophenyl)((2,4,4-trimethylpentan-2-yl)imino)-λ⁶-sulfaneylidene)-4-nitrobenzenesulfonamide (4i)**



Sulfilimine prepared according to **General Procedure C** using *N*-sulfinyl-*tert*-octylamine **1** (276 mg, 1.57 mmol, 1.05 equiv.), TMSOTf (334 mg, 1.50 mmol, 1.0 equiv.), cyclopropylmagnesium bromide (1.71 mL, 0.88 M in 2-methyltetrahydrofuran, 1.50 mmol, 1.0 equiv.) and 4-fluorophenylmagnesium bromide (2.30 mL, 0.96 M in THF, 2.21 mmol, 1.5 equiv.). Following the general purification method, *sulfilimine* **3i** was generated as light yellow oil with a crude yield of 65% (289 mg). Sulfondiimine prepared using Rh₂(esp)₂ (19 mg, 0.025 mmol, 2.5 mol%), PhI=NNs (531 mg, 1.31 mmol, 1.3 equiv.) and DBU (0.30 mL, 2.0 mmol, 2.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 5:1 to 3:1) afforded *sulfondiimine* **4i** as a light yellow solid (297 mg, 40% yield over two steps).

mp 87-89 °C (CH₂Cl₂)

R_f 0.62 (petrol/ethyl acetate, 2:1).

¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.26 (d, J = 8.9 Hz, 2H), 8.06 (d, J = 8.9 Hz, 2H), 7.98-7.91 (m, 2H), 7.19-7.11 (m, 2H), 2.32 (tt, J = 7.6, 4.6 Hz, 1H), 1.71 (ddt, J = 10.5, 6.3, 4.6 Hz, 1H), 1.53-1.39 (m, 3H), 1.36 (s, 3H), 1.14 (s, 3H), 1.12-1.02 (m, 2H), 0.97 (s, 9H).

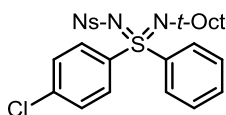
¹³C NMR (100 MHz, (CD₃)₂CO): δ (ppm) = 166.2 (d, $^1J_{\text{CF}}$ = 252.8 Hz), 151.9, 150.3, 140.3 (d, $^4J_{\text{CF}}$ = 2.8 Hz), 132.1 (d, $^3J_{\text{CF}}$ = 9.5 Hz), 128.6, 125.0, 117.2 (d, $^2J_{\text{CF}}$ = 22.5 Hz), 60.1, 58.8, 38.7, 32.8, 32.7, 32.5, 32.4, 9.5, 8.7.

¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) = -105.2 (tt, J = 8.0, 5.1 Hz).

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 1527, 1349, 1296, 1276, 1260, 1220, 1149, 1090, 1075, 1030, 1007, 765, 749.

HRMS (ESI⁺) calcd. for C₂₃H₃₀N₃FN₃O₄S₂⁺ [M+Na]⁺: 518.1554; found: 518.1560.

***N*-((4-Chlorophenyl)(phenyl)((2,4,4-trimethylpentan-2-yl)imino)- λ^6 -sulfaneylidene)-4-nitrobenzenesulfonamide (**4j**)**



Prepared according to **General Procedure B** using sulfilimine **3j** (251 mg, 0.723 mmol, 1.0 equiv.), Rh₂(esp)₂ (27 mg, 0.036 mmol, 5.0 mol%), PhI=NNs (3 × 438 mg, 3.25 mmol, 4.5 equiv.) and DBU (0.44 mL, 2.9 mmol, 4.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 7:1 to 3:1) afforded *sulfondiimine* **4j** as a light yellow solid (138 mg, 35%).

mp 145-147 °C (CH₂Cl₂)

R_f 0.50 (petrol/ethyl acetate = 5:1).

¹H NMR (400 MHz, CDCl₃) = 8.08 (d, J = 8.9 Hz, 2H), 7.75-7.68 (m, 6H), 7.52-7.46 (m, 1H), 7.39-7.31 (m, 4H), 1.61 (d, J = 14.6 Hz, 1H), 1.57 (d, J = 14.6 Hz, 1H), 1.38 (s, 3H), 1.35 (s, 3H), 1.08 (s, 9H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 149.4, 149.1, 141.4, 140.7, 139.5, 132.9, 129.7, 129.3, 129.2, 128.2, 127.6, 123.7, 60.7, 57.9, 32.04, 32.0, 31.97 (2 × C).

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 1527, 1348, 1300, 1276, 1261, 1217, 1151, 1088, 1071, 1030, 1006, 995, 749.

HRMS (ESI⁺) calcd. for C₂₆H₃₁N₃³⁵ClO₄S₂⁺ [M+H]⁺: 548.1439; found: 548.1441.

***N*-((4-Chlorophenyl)(6-methoxypyridin-3-yl)((2,4,4-trimethylpentan-2-yl)imino)- λ^6 -sulfaneylidene)-4-nitrobenzenesulfonamide (**4k**)**



Prepared according to **General Procedure B** using sulfilimine **3k** (230 mg, 0.608 mmol, 1.0 equiv.), $\text{Rh}_2(\text{esp})_2$ (23 mg, 0.030 mmol, 5.0 mol%), $\text{PhI}=\text{NNs}$ (3×370 mg, 2.75 mmol, 4.5 equiv.) and DBU (0.37 mL, 2.5 mmol, 4.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 7:1 to 3:1) afforded *sulfondiimine* **4k** as a white solid (199 mg, 57%).

mp 197-198 °C (CH_2Cl_2)

R_f 0.41 (petrol/ethyl acetate, 5:1).

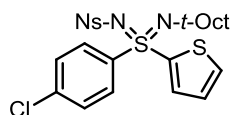
^1H NMR (400 MHz, CDCl_3) : δ (ppm) = 8.46 (d, J = 2.4 Hz, 1H), 8.13 (d, J = 8.8 Hz, 2H), 7.81 (dd, J = 8.9, 2.4 Hz, 1H), 7.76 (d, J = 8.8 Hz, 2H), 7.72 (d, J = 8.8 Hz, 2H), 7.35 (d, J = 8.8 Hz, 2H), 6.68 (d, J = 8.9 Hz, 1H), 3.92 (s, 3H), 1.57 (s, 2H), 1.37 (s, 3H), 1.35 (s, 3H), 1.06 (s, 9H).

^{13}C NMR (100 MHz, CDCl_3) : δ (ppm) = 166.4, 149.3, 149.2, 148.6, 140.6, 139.6, 137.9, 130.3, 129.46, 129.45, 127.6, 123.8, 111.5, 60.8, 57.9, 54.5, 32.03, 31.99, 31.95, 31.93.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1586, 1529, 1477, 1371, 1349, 1308, 1276, 1261, 1217, 1153, 1087, 1027, 1000, 908, 750.

HRMS (ESI^+) calcd. for $\text{C}_{26}\text{H}_{32}\text{N}_4^{35}\text{ClO}_5\text{S}_2^+$ [$\text{M}+\text{H}$] $^+$: 579.1497; found: 579.1485.

***N*-((4-Chlorophenyl)(thiophen-2-yl)((2,4,4-trimethylpentan-2-yl)imino)- λ^6 -sulfaneylidene)-4-nitrobenzenesulfonamide (**4l**)**



Prepared according to **General Procedure B** using sulfilimine **3l** (203 mg, 0.575 mmol, 1.0 equiv.), $\text{Rh}_2(\text{esp})_2$ (21 mg, 0.028 mmol, 5.0 mol%), $\text{PhI}=\text{NNs}$ (3×356 mg, 2.64 mmol, 4.5 equiv.) and DBU (0.35 mL, 2.3 mmol, 4.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 7:1 to 3:1) afforded *sulfondiimine* **4l** as a light yellow solid (128 mg, 40%).

mp 131-133 °C (CH₂Cl₂)

R_f 0.33 (petrol/ethyl acetate, 5:1).

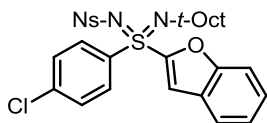
¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.15 (d, *J* = 8.8 Hz, 2H), 7.78 (d, *J* = 8.8 Hz, 2H), 7.70 (d, *J* = 8.9 Hz, 2H), 7.65 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.33-7.26 (m, 3H), 7.01 (dd, *J* = 5.1, 3.9 Hz, 1H), 1.64 (d, *J* = 14.5 Hz, 1H), 1.58 (d, *J* = 14.5 Hz, 1H), 1.49 (s, 3H), 1.38 (s, 3H), 1.08 (s, 9H).

¹³C NMR (100 MHz, (CD₃)₂CO): δ (ppm) = 150.6, 150.4, 144.6, 142.1, 139.7, 136.6, 134.7, 130.4, 130.2, 130.0, 128.5, 124.9, 61.4, 58.6, 32.63, 32.56, 32.5, 32.1.

(ATR): $\tilde{\nu}$ (cm⁻¹) = 1527, 1348, 1300, 1276, 1260, 1216, 1153, 1089, 1026, 1004, 749.

HRMS (ESI⁺) calcd. for C₂₈H₃₁N₃³⁵ClNaO₄S₃⁺ [M+Na]⁺: 576.0823; found: 576.0823.

***N*-(Benzofuran-2-yl(4-chlorophenyl)((2,4,4-trimethylpentan-2-yl)imino)-λ⁶-sulfaneylidene)-4-nitrobenzenesulfonamide (4m)**



Prepared according to **General Procedure B** using sulfilimine **3m** (240 mg, 0.620 mmol, 1.0 equiv.), Rh₂(esp)₂ (24 mg, 0.032 mmol, 5.0 mol%), PhI=NNs (3 × 385 mg, 2.86 mmol, 4.5 equiv.) and DBU (0.38 mL, 2.6 mmol, 4.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 7:1 to 3:1) afforded *sulfondiimine* **4m** as a light yellow solid (145 mg, 40%).

mp 201-202 °C (CH₂Cl₂)

R_f 0.44 (petrol/ethyl acetate, 5:1).

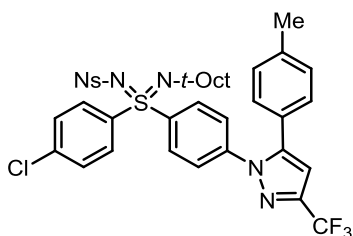
¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.08 (d, *J* = 8.9 Hz, 2H), 7.82 (d, *J* = 8.9 Hz, 2H), 7.79 (d, *J* = 8.9 Hz, 2H), 7.71-7.66 (m, 2H), 7.43-7.26 (m, 5H), 1.63 (d, *J* = 14.6 Hz, 1H), 1.58 (d, *J* = 14.6 Hz, 1H), 1.47 (s, 3H), 1.38 (s, 3H), 1.09 (s, 9H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 156.3, 149.6, 149.2, 149.0, 140.0, 137.4, 129.6, 129.5, 128.2, 127.7, 126.1, 124.7, 123.6, 123.2, 115.6, 112.2, 60.9, 57.5, 32.2, 31.92, 31.87, 31.1.

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 1525, 1349, 1301, 1261, 1223, 1152, 1077, 1030, 1006, 833, 746.

HRMS (ESI⁺) calcd. for C₂₈H₃₁N₃³⁵ClO₅S₂⁺ [M+H]⁺: 588.1388; found: 588.1387.

***N*-((4-Chlorophenyl)(4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)phenyl)((2,4,4-trimethylpentan-2-yl)imino)-λ⁶-sulfaneylidene)-4-nitrobenzenesulfonamide (4n)**



Prepared according to **General Procedure B** using sulfilimine **3n** (170 mg, 0.298 mmol, 1.0 equiv.), Rh₂(esp)₂ (12 mg, 0.016 mmol, 5.0 mol%), PhI=NNs (3 × 181 mg, 1.34 mmol, 4.5 equiv.) and DBU (0.18 mL, 1.2 mmol, 4.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 7:1 to 3:1) afforded *sulfondiimine* **4n** as a light blue oil (93 mg, 40%).

R_f 0.56 (petrol/ethyl acetate, 5:1).

¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.11 (d, *J* = 8.9 Hz, 2H), 7.78 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 8.9 Hz, 2H), 7.66 (d, *J* = 8.9 Hz, 2H), 7.39 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 8.9 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 6.73 (s, 1H), 2.38 (s, 3H), 1.61 (d, *J* = 14.5 Hz, 1H), 1.56 (d, *J* = 14.6 Hz, 1H), 1.38 (s, 3H), 1.34 (s, 3H), 1.07 (s, 9H).

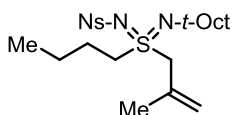
¹³C NMR (100 MHz, (CD₃)₂CO): δ (ppm) = 150.6, 150.4, 146.7, 144.4 (q, ²*J*_{CF} = 38.2 Hz), 143.9, 142.9, 141.3, 140.7, 140.0, 131.0, 130.53, 130.49, 130.4, 130.0, 128.6, 127.2, 126.9, 124.9, 122.5 (q, ¹*J*_{CF} = 266.5 Hz), 107.0, 61.4, 58.6, 32.63, 32.59, 32.5, 32.4, 21.5.

¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) = -62.5

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 1529, 1471, 1349, 1276, 1261, 1235, 1153, 1090, 1030, 1003, 827, 750.

HRMS (ESI⁺) calcd. for C₃₇H₃₈N₅F₃³⁵ClO₄S₂⁺ [M+H]⁺: 772.2000; found: 772.1997.

***N*-(Butyl(2-methylallyl)((2,4,4-trimethylpentan-2-yl)imino)-λ⁶-sulfaneylidene)-4-nitrobenzenesulfonamide (4o)**



Sulfilimine prepared according to **General Procedure C** using *N*-sulfinyl-*tert*-octylamine **1** (399 mg, 2.28 mmol, 1.05 equiv.), TMSOTf (486 mg, 2.19 mmol, 1.0 equiv.), *n*-butylmagnesium chloride (1.11 mL, 1.96 M in THF, 2.18 mmol, 1.0 equiv.) and 2-methyl-1-propenylmagnesium bromide (6.70 mL, 0.49 M in THF, 3.28 mmol, 1.5 equiv.). Following the general purification method, *sulfilimine* **3o** was generated as light yellow oil with a crude yield of 77% (454 mg). Sulfondiimine prepared using Rh₂(esp)₂ (31 mg, 0.041 mmol, 2.5 mol%), PhI=NNs (861 mg, 2.13 mmol, 1.3 equiv.) and DBU (0.50 mL, 3.4 mmol, 2.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 5:1 to 2:1) afforded *sulfondiimine* **4o** as a yellow solid (163 mg, 16% yield over two steps).

mp 113-115 °C (CH₂Cl₂)

R_f 0.65 (petrol/ethyl acetate, 3:1).

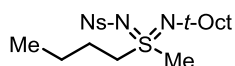
¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.25 (d, *J* = 8.9 Hz, 2H), 8.04 (d, *J* = 8.9 Hz, 2H), 4.92-4.86 (m, 2H), 4.16 (d, *J* = 19.3 Hz, 1H), 3.34 (d, *J* = 19.3 Hz, 1H), 2.91-2.81 (m, 1H), 2.79-2.70 (m, 1H), 2.00 (d, *J* = 14.6 Hz, 1H), 1.72 (s, 3H), 1.62 (d, *J* = 14.6 Hz, 1H), 1.47 (s, 3H), 1.30 (s, 3H), 1.27-1.15 (m, 4H), 0.97 (s, 9H), 0.73-0.68 (m, 3H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 150.8, 149.1, 144.1, 127.3, 123.9, 111.9, 66.6, 52.6, 51.8, 45.4, 31.8, 31.5, 28.5, 27.6, 25.7, 21.2, 20.7, 13.5.

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 1527, 1348, 1276, 1261, 1146, 1091, 979, 910, 854, 750.

HRMS (ESI⁺) calcd. for C₂₂H₃₈N₃O₄S₂⁺ [M+H]⁺: 472.2298; found: 472.2293.

***N*-(Butyl(methyl)((2,4,4-trimethylpentan-2-yl)imino)-λ⁶-sulfaneylidene)-4-nitrobenzenesulfonamide (4p)**



Sulfilimine prepared according to **General Procedure C** using *N*-sulfinyl-*tert*-octylamine **1** (307 mg, 1.75 mmol, 1.05 equiv.), TMSOTf (371 mg, 1.67 mmol, 1.0 equiv.), *n*-butylmagnesium chloride (0.85 mL, 1.96 M in THF, 1.7 mmol, 1.0 equiv.) and methylmagnesium bromide (0.84 mL, 3.0 M in diethyl ether, 2.5 mmol, 1.5 equiv.). Following the general purification method, *sulfilimine* **3p** was generated as light yellow oil with a crude yield of 77% (298 mg). Sulfondiimine prepared

using Rh₂(esp)₂ (22 mg, 0.029 mmol, 2.5 mol%), PhI=NNs (690 mg, 1.71 mmol, 1.3 equiv.) and DBU (0.40 mL, 2.7 mmol, 2.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 4:1 to 2:1) afforded *sulfondiimine* **4p** as a light yellow solid (187 mg, 26% yield over two steps).

mp 80-82 °C (CH₂Cl₂)

R_f 0.35 (petrol/ethyl acetate, 2:1).

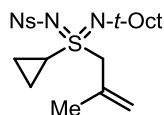
¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.26 (d, *J* = 8.9 Hz, 2H), 8.05 (d, *J* = 8.9 Hz, 2H), 3.43-3.37 (m, 2H), 3.17 (s, 3H), 1.81-1.71 (m, 2H), 1.45-1.37 (m, 2H), 1.37 (d, *J* = 14.4 Hz, 1H), 1.33 (d, *J* = 14.4 Hz, 1H), 1.27 (s, 3H), 1.23 (s, 3H), 0.93-0.87 (m, 12H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 150.2, 149.3, 127.5, 123.9, 60.0, 59.3, 57.6, 44.6, 32.3, 32.0, 31.8, 31.7, 25.6, 21.4, 13.6.

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 1528, 1349, 1276, 1261, 1220, 1146, 1089, 1029, 1008, 750.

HRMS (ESI⁺) calcd. for C₁₉H₃₃N₃NaO₄S₂⁺ [M+Na]⁺: 454.1805; found: 454.1798.

***N*-(Cyclopropyl(2-methylallyl)((2,4,4-trimethylpentan-2-yl)imino)-λ⁶-sulfaneylidene)-4-nitrobenzenesulfonamide (4q)**



Sulfilimine prepared according to **General Procedure C** using *N*-sulfinyl-*tert*-octylamine **1** (355 mg, 2.03 mmol, 1.05 equiv.), TMSOTf (444 mg, 2.00 mmol, 1.0 equiv.), cyclopropylmagnesium bromide (2.38 mL, 0.84 M in 2-methyltetrahydrofuran, 2.00 mmol, 1.0 equiv.) and 2-methyl-1-propenylmagnesium bromide (6.00 mL, 0.50 M in THF, 3.00 mmol, 1.5 equiv.). Following the general purification method, *sulfilimine* **3q** was generated as light yellow oil with a crude yield of 89% (455 mg). Sulfondiimine prepared using Rh₂(esp)₂ (33 mg, 0.044 mmol, 2.5 mol%), PhI=NNs (930 mg, 2.30 mmol, 1.3 equiv.) and DBU (0.53 mL, 3.6 mmol, 2.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 4:1 to 2:1) afforded *sulfondiimine* **4q** as a light brown solid (315 mg, 35% yield over two steps).

mp 119-121 °C (CH₂Cl₂)

R_f 0.54 (petrol/ethyl acetate, 3:1).

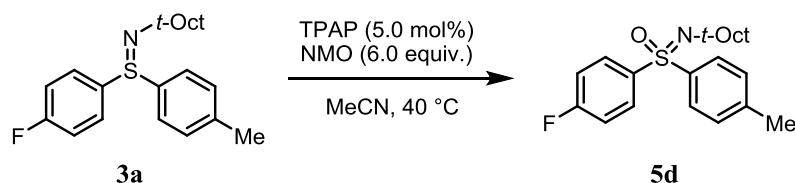
¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.24 (d, *J* = 8.9 Hz, 2H), 7.99 (d, *J* = 8.9 Hz, 2H), 4.93 (s, 1H), 4.86 (s, 1H), 4.08 (d, *J* = 19.3 Hz, 1H), 3.37 (d, *J* = 19.3 Hz, 1H), 2.20 (tt, *J* = 7.7, 4.8 Hz, 1H), 1.97 (d, *J* = 14.6 Hz, 1H), 1.69 (s, 3H), 1.63 (d, *J* = 14.6 Hz, 1H), 1.49 (s, 3H), 1.29 (s, 3H), 1.23-1.16 (m, 1H), 0.96 (s, 9H), 0.76-0.61 (m, 2H), 0.27-0.21 (m, 1H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 150.8, 149.0, 143.3, 127.2, 123.9, 111.2, 66.4, 51.8, 46.1, 31.7, 31.5, 29.6, 28.5, 27.5, 20.6, 3.9, 2.4.

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 1526, 1348, 1289, 1145, 1090, 1016, 973, 854, 768, 733.

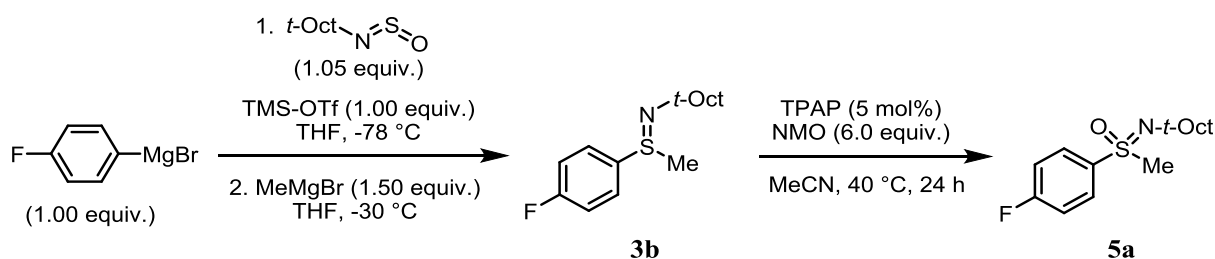
HRMS (ESI⁺) calcd. for C₂₁H₃₄N₃O₄S₂⁺ [M+H]⁺: 456.1985; found: 456.1979.

1.2.5 General Procedure D for Diaryl Sulfoximine Synthesis



Sulfilimine **3a** (471 mg, 1.37 mmol, 1.0 equiv.) was dissolved in anhydrous MeCN (7.0 mL) in an oven-dried 50 mL round bottom flask. Then the reaction was heated to 40 °C before TPAP (24 mg, 0.068 mmol, 5.0 mol%) was added, then NMO (1.01 g, 8.63 mmol, 6.0 equiv.) was added. The reaction was stirred at 40 °C for 24 h until completion of the reaction (TLC). The reaction was quenched with water and extracted with ethyl acetate (3 × 50 mL). The combined organic extracts were washed with brine, dried over anhydrous Na₂SO₄, and concentrated. The crude product was purified by flash column chromatography (petrol/ethyl acetate, 20:1 to 10:1) to afford *sulfoximine* **5d** as a colourless oil (490 mg, 99%).

1.2.6 General Procedure E for Aryl-Alkyl and Dialkyl Sulfoximine Synthesis

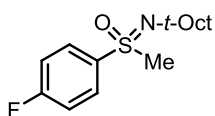


N-Sulfinyl-*tert*-octylamine **1** (248 mg, 1.42 mmol, 1.05 equiv.) was dissolved in anhydrous THF (3.0 mL) in an oven-dried 25 mL round bottom flask. Then the mixture was cooled to -78 °C and TMSOTf (310 mg, 1.37 mmol, 1.0 equiv.) was added. 4-Fluorophenylmagnesium bromide (1.57 mL, 0.87 M in THF, 1.37 mmol, 1.0 equiv.) was added dropwise after 1 min. The mixture was stirred at -78 °C for 2 min and then the temperature was increased to -30 °C. Methylmagnesium bromide (0.70 mL, 3.0 M in diethyl ether, 2.1 mmol, 1.5 equiv.) was then added quickly. The mixture was stirred at -30 °C for 10 min. Then the reaction was quenched with sat. aq. tetrasodium EDTA solution and poured into a 250 mL separating funnel. Ethyl acetate (80 mL) was then added and the organic phase was separated. The aqueous phase was further extracted with ethyl acetate (2 × 40 mL). The combined extracts were dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The crude sulfilimine was dissolved in a mixture of diethyl ether (15 mL) and petroleum ether (5 mL) and acidified by a 1 M aq. solution of 4-toluenesulfonic acid (35 mL) and the organic layer was then discarded. The aqueous phase was washed once with a mixture of diethyl ether (5 mL) and petroleum ether (15 mL). The aqueous phase was then extracted with CH₂Cl₂ (3 × 40 mL), dried over anhydrous Na₂SO₄, filtered and concentrated *in vacuo* to afford the 4-toluenesulfonic acid-sulfilimine salt **3ba** (c. 85% yield). The sulfilimine salt was then dissolved in CH₂Cl₂ (50 mL) and treated with 1M aq. NaOH solution (50 mL). The organic layer was separated and the aqueous phase was extracted with CH₂Cl₂ (2 × 50 mL). The combined organic extracts were dried over Na₂SO₄, filtered and concentrated under reduced pressure to afford *sulfilimine* **3b** as a light yellow oil (301 mg, 82%).

(Please see notes on **General Procedure C** for further guidance.)

Sulfilimine **3b** (301 mg, 1.12 mmol, 1.0 equiv.) was dissolved in anhydrous MeCN (6.0 mL) in an oven-dried 50 mL round bottom flask. Then the mixture was heated to 40 °C before TPAP (20 mg, 0.057 mmol, 5.0 mol%) was added, then NMO (787 mg, 6.73 mmol, 6.0 equiv.) was added. The reaction was stirred at 40 °C for 24 h until completion of the reaction (TLC). The reaction was quenched with water and extracted with ethyl acetate (3 × 50 mL). The combined extracts were washed with brine, dried over anhydrous Na₂SO₄, and concentrated. The crude product was purified by flash column chromatography (petrol/ethyl acetate, 5:1 to 3:1) to afford *sulfoximine* **5a** as a colourless oil (315 mg, 99%).

(4-Fluorophenyl)(methyl)((2,4,4-trimethylpentan-2-yl)imino)- λ^6 -sulfanone (5a)



R_f 0.33 (petrol/ethyl acetate, 4:1).

¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.97-7.89 (m, 2H), 7.18-7.11 (m, 2H), 2.97 (s, 3H), 1.51 (d, J = 14.3 Hz, 1H), 1.44 (d, J = 14.3 Hz, 1H), 1.26 (s, 3H), 1.11 (s, 3H), 1.03 (s, 9H).

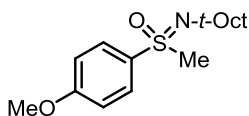
¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 164.9 (d, $^1J_{\text{CF}}$ = 253.0 Hz), 141.8 (d, $^4J_{\text{CF}}$ = 3.2 Hz), 130.4 (d, $^3J_{\text{CF}}$ = 9.2 Hz), 116.1 (d, $^2J_{\text{CF}}$ = 22.2 Hz), 58.8, 58.3, 48.7, 32.9, 32.7, 32.0, 31.9.

¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) = -107.5 (tt, J = 8.5, 5.2 Hz).

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 2956, 2903, 1589, 1491, 1363, 1226, 1150, 1090, 1077, 970, 838

HRMS (ESI⁺) calcd. for C₁₅H₂₅FNOS⁺ [M+H]⁺: 286.1635; found: 286.1637.

(4-Methoxyphenyl)(methyl)((2,4,4-trimethylpentan-2-yl)imino)- λ^6 -sulfanone (5b)



Sulfilimine prepared according to **General Procedure E** using *N*-sulfinyl-*tert*-octylamine **1** (135 mg, 0.770 mmol, 1.05 equiv.), TMSOTf (163 mg, 0.730 mmol, 1.0 equiv.), 4-methoxyphenylmagnesium bromide (1.5 mL, 0.49 M in THF, 0.74 mmol, 1.0 equiv.) and methylmagnesium bromide (0.37 mL, 3.0 M in diethyl ether, 1.1 mmol, 1.5 equiv.). Following the general purification method, sulfilimine **3c** was generated as light yellow oil with a crude yield of 83% (170 mg). Sulfoximine prepared using TPAP (11 mg, 0.031 mmol, 5.0 mol%), NMO (0.42 g, 3.6 mmol, 6.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 4:1 to 2:1) afforded *sulfoximine* **5b** as a colourless oil (164 mg, 75% yield over two steps).

R_f 0.45 (petrol/ethyl acetate, 2:1).

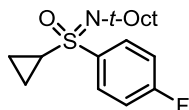
¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.85 (d, J = 8.9 Hz, 2H), 6.96 (d, J = 8.9 Hz, 2H), 3.85 (s, 3H), 2.96 (s, 3H), 1.52 (d, J = 14.3 Hz, 1H), 1.46 (d, J = 14.3 Hz, 1H), 1.26 (s, 3H), 1.13 (s, 3H), 1.04 (s, 9H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 162.5, 137.4, 129.8, 114.1, 58.7, 58.4, 55.6, 48.9, 32.9, 32.7, 32.1, 31.9.

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 2980, 2902, 1594, 1495, 1252, 1151, 1132, 1079, 969, 833.

HRMS (ESI⁺) calcd. for C₁₆H₂₈NO₂S⁺ [M+H]⁺: 298.1835; found: 298.1836.

Cyclopropyl(4-fluorophenyl)((2,4,4-trimethylpentan-2-yl)imino)- λ^6 -sulfanone (5c)



Sulfilimine prepared according to **General Procedure E** using *N*-sulfinyl-*tert*-octylamine **1** (231 mg, 1.32 mmol, 1.05 equiv.), TMSOTf (290 mg, 1.31 mmol, 1.0 equiv.), cyclopropylmagnesium bromide (1.55 mL, 0.84 M in 2-methyltetrahydrofuran, 1.30 mmol, 1.0 equiv.) and 4-fluorophenylmagnesium bromide (2.00 mL, 0.96 M in THF, 1.92 mmol, 1.5 equiv.). Following the general purification method, *sulfilimine 3i* was generated as light yellow oil with a crude yield of 78% (300 mg). Sulfoximine prepared using TPAP (18 mg, 0.050 mmol, 5.0 mol%), NMO (0.70 g, 6.0 mmol, 6.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 5:1 to 3:1) afforded *sulfoximine 5c* as a white solid (195 mg, 48% yield over two steps).

mp 77-79 °C (CH₂Cl₂)

R_f 0.5 (petrol/ethyl acetate, 3:1).

¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.91-7.86 (m, 2H), 7.17-7.11 (m, 2H), 2.39 (tt, J = 7.8, 4.8 Hz, 1H), 1.51 (d, J = 14.4 Hz, 1H), 1.46 (d, J = 14.4 Hz, 1H), 1.43-1.34 (m, 1H), 1.28 (s, 3H), 1.14 (s, 3H), 1.07-0.94 (m, 11H), 0.80-0.70 (m, 1H).

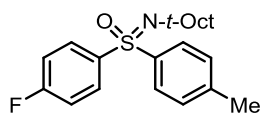
¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 164.7 (d, $^1J_{\text{CF}}$ = 252.7 Hz), 142.0 (d, $^4J_{\text{CF}}$ = 3.3 Hz), 130.5 (d, $^3J_{\text{CF}}$ = 8.8 Hz), 115.9 (d, $^2J_{\text{CF}}$ = 22.2 Hz), 58.5, 58.4, 36.3, 33.2, 33.0, 32.1, 32.0, 6.8, 5.5.

¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) = -108.1 (tt, J = 8.5, 5.2 Hz).

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 1588, 1490, 1276, 1261, 1226, 1149, 1114, 1077, 887, 836.

HRMS (ESI⁺) calcd. for C₁₇H₂₇ONFS⁺ [M+H]⁺: 312.1792; found: 312.1792.

(4-Fluorophenyl)(*p*-tolyl)((2,4,4-trimethylpentan-2-yl)imino)- λ^6 -sulfanone (5d)



R_f 0.65 (petrol / ethyl acetate = 9:1).

¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.97-7.90 (m, 2H), 7.80 (d, J = 8.3 Hz, 2H), 7.21 (d, J = 8.3 Hz, 2H), 7.09-7.02 (m, 2H), 2.36 (s, 3H), 1.58 (s, 2H), 1.28 (s, 6H), 1.08 (s, 9H).

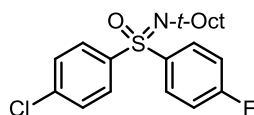
¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 164.5 (d, $^1J_{\text{CF}}$ = 252.7 Hz), 142.8, 142.3, 142.1 (d, $^4J_{\text{CF}}$ = 3.1 Hz), 130.5 (d, $^3J_{\text{CF}}$ = 9.5 Hz), 129.6, 128.0, 115.8 (d, $^2J_{\text{CF}}$ = 22.3 Hz), 59.0, 58.8, 33.1, 33.0, 32.11, 32.07, 21.5.

¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) = -108.3 (tt, J = 8.4, 5.2 Hz).

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 2953, 2903, 1589, 1488, 1363, 1259, 1218, 1150, 1090, 836, 813, 714, 672.

HRMS (ESI⁺) calcd. for C₂₁H₂₉FNOS⁺ [M+H]⁺: 362.1948; found: 362.1946.

(4-Chlorophenyl)(4-fluorophenyl)((2,4,4-trimethylpentan-2-yl)imino)- λ^6 -sulfanone (5e)



Prepared according to **General Procedure D** except reaction was carried out at 50 °C instead of 40 °C, using sulfilimine **3g** (140 mg, 0.384 mmol, 1.0 equiv.), TPAP (6.8 mg, 0.019 mmol, 5.0 mol%), NMO (270 mg, 2.31 mmol, 6.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 15:1) afforded *sulfoximine* **5e** as a colourless oil (113 mg, 78%).

R_f 0.45 (petrol/ethyl acetate, 7:1).

¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.96-7.90 (m, 2H), 7.85 (d, J = 8.7 Hz, 2H), 7.38 (d, J = 8.7 Hz, 2H), 7.13-7.05 (m, 2H), 1.58 (s, 2H), 1.28 (s, 3H), 1.27 (s, 3H), 1.07 (s, 9H).

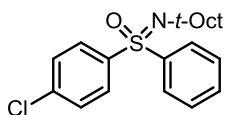
¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 164.7 (d, $^1J_{\text{CF}}$ = 253.6 Hz), 144.3, 141.3 (d, $^4J_{\text{CF}}$ = 3.2 Hz), 138.2, 130.6 (d, $^3J_{\text{CF}}$ = 9.3 Hz), 129.4, 129.2, 116.1 (d, $^2J_{\text{CF}}$ = 22.3 Hz), 59.2, 58.7, 33.1, 33.0, 32.10, 32.05.

¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) = -107.4 (tt, J = 8.2, 5.2 Hz).

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 1653, 1589, 1472, 1390, 1228, 1128, 1088, 1006, 963, 813, 736.

HRMS (ESI⁺) calcd. for C₂₀H₂₆F³⁵ClNOS⁺ [M+H]⁺: 382.1402; found: 382.1395.

(4-Chlorophenyl)(phenyl)((2,4,4-trimethylpentan-2-yl)imino)- λ^6 -sulfanone (5f)



Prepared according to **General Procedure D** except reaction was carried out at 50 °C instead of 40 °C, using sulfilimine **3j** (210 mg, 0.605 mmol, 1.0 equiv.), TPAP (11 mg, 0.031 mmol, 5.0 mol%), NMO (428 mg, 3.66 mmol, 6.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 10:1 to 6:1) afforded *sulfoximine* **5f** as a colourless oil (184 mg, 84%).

R_f 0.50 (petrol/ethyl acetate, 15:1).

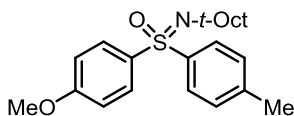
¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.95-7.91 (m, 2H), 7.88 (d, *J* = 8.7 Hz, 2H), 7.46-7.39 (m, 3H), 7.37 (d, *J* = 8.7 Hz, 2H), 1.59 (s, 2H), 1.283 (s, 3H), 1.278 (s, 3H), 1.08 (s, 9H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 145.3, 144.4, 138.0, 131.7, 129.5, 129.0, 128.9, 127.9, 59.1, 58.6, 33.1, 33.0, 32.1, 32.0.

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 1473, 1276, 1261, 1213, 1153, 1087, 1066, 1013, 827, 749, 701.

HRMS (ESI⁺) calcd. for C₂₀H₂₇O³⁵CINS⁺ [M+H]⁺: 364.1496; found: 364.1500.

(4-Methoxyphenyl)(*p*-tolyl)((2,4,4-trimethylpentan-2-yl)imino)- λ^6 -sulfanone (5g)



Prepared according to **General Procedure D** using sulfilimine **3r** (155 mg, 0.434 mmol, 1.0 equiv.), TPAP (8.1 mg, 0.023 mmol, 5.0 mol%), NMO (310 mg, 2.65 mmol, 6.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 7:1) afforded *sulfoximine* **5g** as a colourless oil (142 mg, 88%).

R_f 0.40 (petrol/ethyl acetate, 5:1).

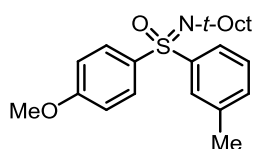
¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.86 (d, *J* = 8.9 Hz, 2H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.9 Hz, 2H), 3.78 (s, 3H), 2.33 (s, 3H), 1.58 (s, 2H), 1.28 (s, 3H), 1.27 (s, 3H), 1.09 (s, 9H).

¹³C NMR (100 MHz, (CD₃)₂CO): δ (ppm) = 163.3, 145.0, 142.9, 138.9, 130.8, 130.4, 128.7, 115.0, 59.6, 59.1, 56.2, 33.8, 33.7, 32.8, 32.7, 21.6.

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 1594, 1492, 1387, 1251, 1151, 1091, 1027, 951, 801, 716, 673.

HRMS (ESI⁺) calcd. for C₂₂H₃₂NO₂S⁺ [M+H]⁺: 374.2148; found: 374.2146.

(4-Methoxyphenyl)(*m*-tolyl)((2,4,4-trimethylpentan-2-yl)imino)-λ⁶-sulfanone (5h)



Prepared according to **General Procedure D** except reaction was carried out at 50 °C instead of 40 °C, using sulfilimine **3s** (135 mg, 0.378 mmol, 1.0 equiv.), TPAP (6.9 mg, 0.019 mmol, 5.0 mol%), NMO (263 mg, 2.25 mmol, 6.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 12:1) afforded *sulfoximine* **5h** as a colorless oil (128 mg, 91%).

R_f 0.46 (petrol/ethyl acetate, 9:1).

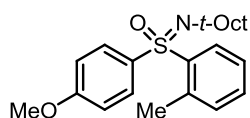
¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.87 (d, *J* = 8.9 Hz, 2H), 7.76-7.69 (m, 2H), 7.29-7.24 (m, 1H), 7.22-7.18 (m, 1H), 6.88 (d, *J* = 8.9 Hz, 2H), 3.78 (s, 3H), 2.35 (s, 3H), 1.59 (s, 2H), 1.282 (s, 3H), 1.277 (s, 3H), 1.09 (s, 9H).

¹³C NMR (100 MHz, (CD₃)₂CO): δ (ppm) = 163.4, 147.7, 139.8, 138.7, 133.0, 130.9, 129.7, 128.9, 125.9, 115.0, 59.6, 59.1, 56.2, 33.8, 33.7, 32.8, 32.7, 21.6.

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 1594, 1493, 1386, 1252, 1151, 1090, 955, 832, 694.

HRMS (ESI⁺) calcd. for C₂₂H₃₂NO₂S⁺ [M+H]⁺: 374.2148; found: 374.2140.

(4-Methoxyphenyl)(*o*-tolyl)((2,4,4-trimethylpentan-2-yl)imino)-λ⁶-sulfanone (5i)



Prepared according to **General Procedure D** using sulfilimine **3t** (60 mg, 0.17 mmol, 1.0 equiv.), TPAP (9.2 mg, 0.026 mmol, 15 mol%), NMO (117 mg, 1.00 mmol, 6.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 12:1) afforded *sulfoximine* **5i** as a colourless oil (45 mg, 72%).

R_f 0.50 (petrol/ethyl acetate, 9:1).

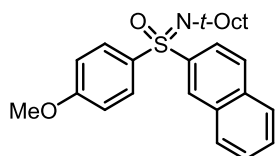
¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.36 (dd, J = 7.6, 1.9 Hz, 1H), 7.80 (d, J = 9.0 Hz, 2H), 7.37-7.28 (m, 2H), 7.12-7.08 (m, 1H), 6.88 (d, J = 9.0 Hz, 2H), 3.81 (s, 3H), 2.33 (s, 3H), 1.59 (s, 2H), 1.27 (s, 3H), 1.21 (s, 3H), 1.08 (s, 9H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 162.0, 143.9, 137.5, 136.6, 132.6, 131.7, 130.2, 130.1, 126.1, 113.7, 59.0, 58.7, 55.6, 32.7, 32.5, 32.14, 32.07, 20.2.

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 1594, 1494, 1251, 1151, 1083, 833, 803, 759, 717.

HRMS (ESI⁺) calcd. for C₂₂H₃₂NO₂S⁺ [M+H]⁺: 374.2148; found: 374.2138.

(4-Methoxyphenyl)(naphthalen-2-yl)((2,4,4-trimethylpentan-2-yl)imino)- λ^6 -sulfanone (5j**)**



Prepared according to **General Procedure D** using sulfilimine **3u** (153 mg, 0.389 mmol, 1.0 equiv.), TPAP (6.9 mg, 0.019 mmol, 5.0 mol%), NMO (277 mg, 2.37 mmol, 6.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 9:1) afforded *sulfoximine* **5j** as a white solid (146 mg, 92%).

mp 106-108 °C (CH₂Cl₂)

R_f 0.45 (petrol/ethyl acetate, 5:1).

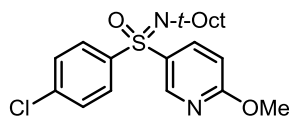
¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.61-8.55 (m, 1H), 7.98-7.91 (m, 3H), 7.87 (dd, J = 8.7, 1.8 Hz, 1H), 7.85-7.79 (m, 2H), 7.58-7.51 (m, 2H), 6.89 (d, J = 9.0 Hz, 2H), 3.78 (s, 3H), 1.66 (d, J = 14.4 Hz, 1H), 1.62 (d, J = 14.4 Hz, 1H), 1.35 (s, 3H), 1.30 (s, 3H), 1.14 (s, 9H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 162.2, 143.5, 137.1, 134.3, 132.6, 130.1, 129.3, 128.8, 128.4, 128.2, 127.8, 127.1, 124.0, 114.0, 58.9, 58.8, 55.6, 33.3, 33.0, 32.12, 32.10.

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 1593, 1493, 1386, 1254, 1152, 1083, 955, 832, 748.

HRMS (ESI⁺) calcd. for C₂₅H₃₂NO₂S⁺ [M+H]⁺: 410.2148; found: 410.2141.

(4-Chlorophenyl)(6-methoxypyridin-3-yl)((2,4,4-trimethylpentan-2-yl)imino)-λ⁶-sulfanone (5k)



Prepared according to **General Procedure D** using sulfilimine **3k** (96.6 mg, 0.256 mmol, 1.0 equiv.), TPAP (4.5 mg, 0.013 mmol, 5.0 mol%), NMO (180 mg, 1.54 mmol, 6.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 10:1) afforded *sulfoximine* **5k** as a colourless oil (88 mg, 88%).

R_f 0.50 (petrol/ethyl acetate, 5:1).

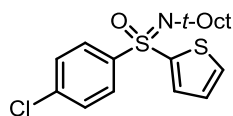
¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.72 (dd, *J* = 2.5, 0.7 Hz, 1H), 7.95 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.85 (d, *J* = 8.7 Hz, 2H), 7.38 (d, *J* = 8.7 Hz, 2H), 6.72 (dd, *J* = 8.8, 0.7 Hz, 1H), 3.94 (s, 3H), 1.57 (s, 2H), 1.28 (s, 3H), 1.26 (s, 3H), 1.06 (s, 9H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 165.9, 148.2, 144.4, 138.2, 138.1, 134.4, 129.3, 129.2, 111.2, 59.2, 58.6, 54.3, 33.2, 33.1, 32.1, 32.0.

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 1587, 1476, 1366, 1276, 1261, 1212, 1154, 1118, 1087, 1013, 823.

HRMS (ESI⁺) calcd. for C₂₀H₂₈³⁵ClO₂N₂S⁺ [M+H]⁺: 395.1555; found: 395.1553.

(4-Chlorophenyl)(thiophen-2-yl)((2,4,4-trimethylpentan-2-yl)imino)-λ⁶-sulfanone (5l)



Prepared according to **General Procedure D** except reaction was carried out at 50 °C instead of 40 °C, using sulfilimine **3l** (223 mg, 0.632 mmol, 1.0 equiv.), TPAP (12 mg, 0.034 mmol, 5.0 mol%), NMO (447 mg, 3.82 mmol, 6.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 11:1 to 6:1) afforded *sulfoximine* **5l** as a colourless oil (201 mg, 87%).

R_f 0.50 (petrol/ethyl acetate, 15:1).

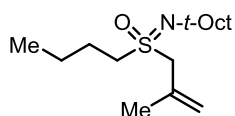
¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.95 (d, J = 8.7 Hz, 2H), 7.50 (dd, J = 5.0, 1.3 Hz, 1H), 7.43 (dd, J = 3.7, 1.3 Hz, 1H), 7.39 (d, J = 8.7 Hz, 2H), 6.98 (dd, J = 5.0, 3.7 Hz, 1H), 1.58 (s, 2H), 1.334 (s, 3H), 1.329 (s, 3H), 1.08 (s, 9H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 148.5, 144.6, 138.1, 132.5, 131.9, 129.1, 129.0, 127.8, 59.4, 58.5, 33.1, 32.7, 32.1, 32.0.

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 1473, 1276, 1261, 1212, 1154, 1088, 1012, 997, 826, 750.

HRMS (ESI⁺) calcd. for C₁₈H₂₅O³⁵ClNS₂⁺ [M+H]⁺: 370.1061; found: 370.1059.

Butyl(2-methylallyl)((2,4,4-trimethylpentan-2-yl)imino)- λ^6 -sulfanone (5m)



Sulfilimine prepared according to **General Procedure E** using *N*-sulfinyl-*tert*-octylamine **1** (512 mg, 2.92 mmol, 1.05 equiv.), TMSOTf (605 mg, 2.72 mmol, 1.0 equiv.), *n*-butylmagnesium chloride (1.39 mL, 1.96 M in THF, 2.72 mmol, 1.0 equiv.) and 2-methyl-1-propenylmagnesium bromide (8.00 mL, 0.49 M in THF, 3.92 mmol, 1.5 equiv.). Following the general purification method, sulfilimine **3o** was generated as light yellow oil with a crude yield of 81% (600 mg). Sulfoximine prepared using TPAP (39 mg, 0.11 mmol, 5.0 mol%), NMO (1.54 g, 13.2 mmol, 6.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 3:1 to 1:1) afforded *sulfoximine* **5m** as a light yellow oil (187 mg, 24% yield over two steps).

R_f 0.61 (petrol/ethyl acetate, 1:1).

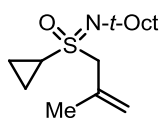
¹H NMR (400 MHz, CDCl₃): δ (ppm) = 4.93 (s, 1H), 4.84 (s, 1H), 3.98 (d, J = 19.6 Hz, 1H), 3.03 (d, J = 19.6 Hz, 1H), 2.55-2.38 (m, 2H), 1.76 (d, J = 14.7 Hz, 1H), 1.70 (s, 3H), 1.68 (d, J = 14.7 Hz, 1H), 1.62-1.47 (m, 2H), 1.43-1.31 (m, 5H), 1.22 (s, 3H), 0.95 (s, 9H), 0.87 (t, J = 7.3 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 145.6, 110.7, 63.6, 54.5, 53.1, 42.0, 31.9, 31.4, 29.3, 27.5, 25.9, 22.0, 20.7, 13.8.

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 1469, 1368, 1276, 1261, 1138, 1071, 1045, 895, 839, 763.

HRMS (ESI⁺) calcd. for C₁₆H₃₄NOS⁺ [M+H]⁺: 288.2356; found: 288.2354.

Cyclopropyl(2-methylallyl)((2,4,4-trimethylpentan-2-yl)imino)- λ^6 -sulfanone (**5n**)



Sulfilimine prepared according to **General Procedure E** using *N*-sulfinyl-*tert*-octylamine **1** (340 mg, 1.94 mmol, 1.05 equiv.), TMSOTf (416 mg, 1.87 mmol, 1.0 equiv.), cyclopropylmagnesium bromide (2.23 mL, 0.84 M in 2-methyltetrahydrofuran, 1.87 mmol, 1.0 equiv.) and 2-methyl-1-propenylmagnesium bromide (5.60 mL, 0.49 M in THF, 2.74 mmol, 1.5 equiv.). Following the general purification method, *sulfilimine* **3q** was generated as light yellow oil with a crude yield of 81% (387 mg). Sulfoximine prepared using TPAP (27 mg, 0.076 mmol, 5.0 mol%), NMO (1.07 g, 9.15 mmol, 6.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 4:1 to 2:1) afforded *sulfoximine* **5n** as a colourless oil (236 mg, 47% yield over two steps).

R_f 0.65 (petrol/ethyl acetate, 3:1).

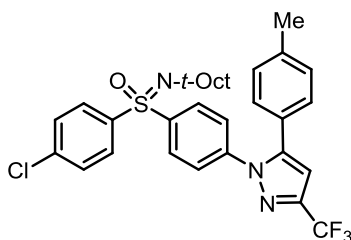
¹H NMR (400 MHz, CDCl₃): δ (ppm) = 4.96 (s, 1H), 4.78 (s, 1H), 3.88 (d, J = 19.8 Hz, 1H), 3.05 (d, J = 19.8 Hz, 1H), 1.88 (tt, J = 8.0, 5.0 Hz, 1H), 1.79 (d, J = 14.7 Hz, 1H), 1.65 (s, 3H), 1.64 (d, J = 14.7 Hz, 1H), 1.37 (s, 3H), 1.21 (s, 3H), 1.18-1.11 (m, 1H), 0.93 (s, 9H), 0.65-0.54 (m, 2H), 0.52-0.44 (m, 1H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 144.6, 110.2, 63.4, 53.3, 42.9, 31.9, 31.4, 30.1, 29.2, 27.6, 20.6, 2.7, -0.1.

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 1472, 1368, 1276, 1261, 1139, 1071, 1028, 896, 840, 818, 750.

HRMS (ESI⁺) calcd. for C₁₅H₃₀NOS⁺ [M+H]⁺: 272.2043; found: 272.2043.

(4-Chlorophenyl)(4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)phenyl)((2,4,4-trimethylpentan-2-yl)imino)- λ^6 -sulfanone (**5o**)



Prepared according to **General Procedure D** using sulfilimine **3n** (108 mg, 0.189 mmol, 1.0 equiv.), TPAP (3.4 mg, 0.010 mmol, 5.0 mol%), NMO (137 mg, 1.17 mmol, 6.0 equiv.). Purification by flash column chromatography (petrol/ethyl acetate, 10:1) afforded *sulfoximine 5o* as a colourless oil (83 mg, 75%).

R_f 0.5 (petrol/ethyl acetate, 9:1).

¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.90 (d, J = 8.7 Hz, 2H), 7.84 (d, J = 8.7 Hz, 2H), 7.40 (d, J = 6.1 Hz, 2H), 7.37 (d, J = 6.1 Hz, 2H), 7.13 (d, J = 7.8 Hz, 2H), 7.07 (d, J = 7.8 Hz, 2H), 6.71 (s, 1H), 2.37 (s, 3H), 1.58 (s, 2H), 1.28 (s, 3H), 1.27 (s, 3H), 1.06 (s, 9H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 145.2, 144.9, 144.0 (q, $^2J_{\text{CF}}$ = 38.3 Hz), 143.8, 141.8, 139.8, 138.4, 129.7, 129.6, 129.2, 129.0, 128.8, 125.9, 125.5, 121.2 (q, $^1J_{\text{CF}}$ = 269.2 Hz), 106.2, 59.3, 58.6, 33.1, 33.0, 32.1, 32.0, 21.5.

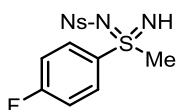
¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) = -62.4

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 1472, 1276, 1261, 1235, 1214, 1134, 1088, 975, 909, 750.

HRMS (ESI⁺) calcd. for C₃₁H₃₄O³⁵ClN₃F₃S⁺ [M+H]⁺: 588.2058; found: 588.2055.

1.2.7 Deprotection of Sulfondiimine

N-((4-Fluorophenyl)(imino)(methyl)- λ^6 -sulfaneylidene)-4-nitrobenzenesulfonamide (**6**)



Sulfondiimine **4b** (1.00 g, 2.14 mmol, 1.0 equiv.) was mixed with TFA (21 mL) and stirred at room temperature for 14 h. The mixture was concentrated *in vacuo* then diluted with CH₂Cl₂ and basified to pH 10-11 using 1 M aq. NaOH solution. The product was extracted with CH₂Cl₂ (3 × 50 mL). The combined extracts were washed with brine, dried over anhydrous Na₂SO₄, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (petrol/ethyl acetate, 1:1 to 1:3) to afford *sulfondiimine 6* as a white solid (737 mg, 97%).

mp 173-175 °C (CH₂Cl₂)

R_f 0.37 (petrol/ethyl acetate, 1:3).

¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.29 (d, J = 8.9 Hz, 2H), 8.13 (d, J = 8.9 Hz, 2H), 8.15-8.08 (m, 2H), 7.29-7.24 (m, 2H), 3.43 (s, 3H), 2.71 (br. s, 1H).

¹³C NMR (100 MHz, (CD₃)₂CO): δ (ppm) = 166.7 (d, $^1J_{\text{CF}}$ = 253.7 Hz), 151.5, 150.5, 138.5 (d, $^4J_{\text{CF}}$ = 3.2 Hz), 131.6 (d, $^3J_{\text{CF}}$ = 9.6 Hz), 129.0, 124.8, 117.4 (d, $^2J_{\text{CF}}$ = 23.1 Hz), 48.5.

¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) = -102.4 (tt, J = 8.0, 4.9 Hz).

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 2978, 1528, 1352, 1296, 1238, 1152, 1086, 1035, 1006, 968.

HRMS (ESI⁺) calcd. for C₁₃H₁₃FN₃O₄S₂⁺ [M+H]⁺: 358.0326; found: 358.0323.

1-(4-Fluorophenyl)-1-methyl-N-(2,4,4-trimethylpentan-2-yl)- λ^6 -sulfanediimine (7)



Under an atmosphere of nitrogen, sulfondiimines **4b** (1.50 g, 3.20 mmol, 1.0 equiv.) was dissolved in anhydrous MeCN (10 ml). 1-Dodecanethiol (3.80 ml, 15.8 mmol, 5.0 equiv.) was added at room temperature followed by DBU (2.30 mL, 15.4 mmol, 4.75 equiv.). The solution became yellow and was stirred for 20 min under nitrogen until completion of the reaction (TLC). The reaction mixture was then concentrated *in vacuo* to afford light yellow oil. The crude product was purified by flash column chromatography (petrol/ethyl acetate, 1:1 to 0:1) to afford corresponding *sulfondiimine* **7** as a colourless oil (806 mg, 89%).

R_f 0.44 (ethyl acetate).

¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.14-8.08 (m, 2H), 7.18-7.08 (m, 2H), 3.05 (s, 3H), 1.97 (br. s, 1H), 1.56 (d, J = 14.4 Hz, 1H), 1.52 (d, J = 14.4 Hz, 1H), 1.41 (s, 3H), 1.30 (s, 3H), 1.03 (s, 9H).

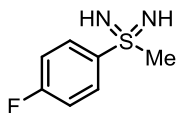
¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 164.6 (d, $^1J_{\text{CF}}$ = 252.7 Hz), 143.0 (d, $^4J_{\text{CF}}$ = 3.1 Hz), 129.8 (d, $^3J_{\text{CF}}$ = 9.1 Hz), 115.7 (d, $^2J_{\text{CF}}$ = 22.4 Hz), 58.72, 58.70, 51.8, 33.3, 32.3, 32.08, 32.05.

¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) = -108.7 (tt, J = 8.3, 5.2 Hz).

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 2954, 1589, 1488, 1219, 1188, 1152, 1087, 1001, 939.

HRMS (ESI⁺) calcd. for C₁₅H₂₆FN₂S⁺ [M+H]⁺: 285.1795; found: 285.1795.

(4-Fluorophenyl)(methyl)- λ^6 -sulfanediimine (8)



Under an atmosphere of nitrogen, sulfondiimines **6** (602 mg, 1.69 mmol, 1.0 equiv.) was dissolved in anhydrous MeCN (5.0 mL). 1-Dodecanethiol (2.00 mL, 8.35 mmol, 5.0 equiv.) was added at room temperature followed by DBU (1.20 mL, 8.02 mmol, 4.75 equiv.). The solution became yellow and was stirred for 20 min under nitrogen until completion of the reaction (TLC). The reaction mixture was concentrated *in vacuo* to afford light yellow oil. The crude product was purified by flash column chromatography (CH₂Cl₂/MeOH, 9:1) to afford *sulfondiimine 8* as a white solid (285 mg, 98%).

mp 103-105 °C (CH₂Cl₂)

R_f 0.48 (CH₂Cl₂/MeOH, 9:1).

¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.17-8.08 (m, 2H), 7.18-7.09 (m, 2H), 3.09 (s, 3H), 2.48 (br. s, 2H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 165.2 (d, ¹*J*_{CF} = 254.2 Hz), 140.4 (d, ⁴*J*_{CF} = 3.1 Hz), 129.9 (d, ³*J*_{CF} = 9.3 Hz), 116.1 (d, ²*J*_{CF} = 22.4 Hz), 50.6.

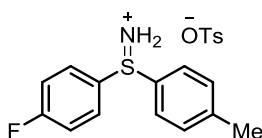
¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) = -106.7 (tt, *J* = 8.5, 5.1 Hz).

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 1589, 1490, 1227, 1057, 933, 839, 661.

HRMS (ESI⁺) calcd. for C₇H₁₀FN₂S⁺ [M+H]⁺: 173.0543; found: 173.0543.

1.2.8 Deprotection of Sulfilimine

(4-Fluorophenyl)(*p*-tolyl)- λ^4 -sulfaniminium-4-methylbenzenesulfonate (9)



In a 25 mL round bottom flask, sulfilimine **3a** (225 mg, 0.652 mmol, 1.0 equiv.) was dissolved in anhydrous CH₂Cl₂ (6.5 mL). Triflic acid (290 μ L, 3.29 mmol, 5.0 equiv.) was added and the

reaction was stirred at room temperature for 1 h. The mixture was diluted with CH₂Cl₂ and basified to pH 10-11 using 1 M aq. NaOH solution. The separated aqueous phase was extracted with CH₂Cl₂ (3 × 30 mL). The combined extracts were washed with brine, dried over anhydrous Na₂SO₄, and concentrated *in vacuo*. Then the crude sulfilimine was dissolved in CH₂Cl₂ (20 mL), TsOH·H₂O (123 mg, 0.715 mmol, 1.1 equiv.) was added and stirred at room temperature for 10 min until a homogeneous solution is formed. The mixture was then concentrated *in vacuo* and was purified by flash column chromatography (CH₂Cl₂/MeOH, 20:1 to 5:1) to afford *sulfiliminium salt* **9** as a waxy solid (255 mg, 97%).

R_f 0.62 (CH₂Cl₂/MeOH, 5:1).

¹H NMR (400 MHz, CD₃OD): δ (ppm) = 7.87-7.81 (m, 2H), 7.70-7.76 (m, 4H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.45-7.39 (m, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 2.44 (s, 3H), 2.34 (s, 3H).

¹³C NMR (100 MHz, CD₃OD): δ (ppm) = 166.9 (d, ¹*J*_{CF} = 255.7 Hz), 146.7, 143.5, 141.6, 132.4, 132.3 (d, ³*J*_{CF} = 9.7 Hz), 130.5, 130.0 (d, ⁴*J*_{CF} = 3.2 Hz), 129.8, 129.4, 126.9, 119.0 (d, ²*J*_{CF} = 23.3 Hz), 21.5, 21.3.

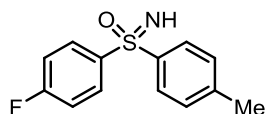
¹⁹F NMR (376 MHz, CD₃OD): δ (ppm) = -105.7 (tt, *J* = 8.2, 4.7 Hz).

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 2981, 2361, 2341, 1589, 1494, 1227, 1177, 1122, 1034, 1011, 814, 683.

HRMS (ESI⁺) calcd. for C₁₃H₁₃FNS⁺ [M+H]⁺: 234.0747; found: 234.0746.

1.2.9 Deprotection of Sulfoximine

(4-Fluorophenyl)(imino)(*p*-tolyl)-λ⁶-sulfanone (**10**)



Sulfoximine **5d** (69 mg, 0.19 mmol, 1.0 equiv.) was mixed with TFA (1.5 mL) and heated to 60 °C for 18 h. The mixture was concentrated *in vacuo* then diluted with CH₂Cl₂ and basified to pH 10-11 using 1 M aq. NaOH solution. The product was extracted with CH₂Cl₂ (3 × 30 mL). The combined extracts were washed with brine, dried over anhydrous Na₂SO₄, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (petrol/ethyl acetate, 3:1 to 1:2) to afford *sulfoximine* **10** as a colourless oil (47 mg, 99%).

R_f 0.41 (petrol/ethyl acetate, 1:1).

¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.05-8.00 (m, 2H), 7.89 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 7.14-7.08 (m, 2H), 2.90 (br. s, 1H), 2.37 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 165.2 (d, $^1J_{\text{CF}}$ = 254.4 Hz), 143.7, 140.5, 139.8 (d, $^4J_{\text{CF}}$ = 3.1 Hz), 130.7 (d, $^3J_{\text{CF}}$ = 9.5 Hz), 130.0, 128.0, 116.4 (d, $^2J_{\text{CF}}$ = 22.7 Hz), 21.6.

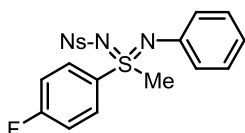
¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) = -106.2 (tt, J = 8.3, 5.1 Hz).

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 2981, 2888, 1588, 1489, 1382, 1229, 1130, 1094, 968, 839.

HRMS (ESI⁺) calcd. for C₁₃H₁₃FNOS⁺ [M+H]⁺: 250.0696; found: 250.0695.

1.2.10 *N*-Functionalization of Sulfondiimine

N-((4-Fluorophenyl)(methyl)(phenylimino)- λ^6 -sulfaneylidene)-4-nitrobenzenesulfonamide (11a)



Sulfondiimine **6** (50 mg, 0.14 mmol, 1.0 equiv.), phenylboronic acid (45 mg, 0.37 mmol, 2.5 equiv.), Cu(MeCN)₄PF₆ (26 mg, 0.070 mmol, 0.5 equiv.), *N*-methylpiperidine (123 mg, 1.24 mmol, 9.0 equiv.) were added to an oven-dried 10 mL vial and dissolved in MeCN (1.4 mL) under oxygen atmosphere. The reaction was stirred at room temperature for 24 h until completion of the reaction (TLC). The reaction was quenched with water and extracted with ethyl acetate (3 × 20 mL). The combined extracts were washed with brine, dried over anhydrous Na₂SO₄, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (petrol/ethyl acetate, 4:1 to 2:1) to afford *sulfondiimine 11a* as a white solid (51 mg, 84%).

mp 177-179 °C (CH₂Cl₂)

R_f 0.39 (petrol/ethyl acetate, 2:1).

¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.08-8.04 (m, 2H), 7.91 (d, J = 8.9 Hz, 2H), 7.81 (d, J = 8.9 Hz, 2H), 7.29-7.23 (m, 2H), 6.79-6.73 (m, 2H), 6.69-6.63 (m, 1H), 6.40-6.35 (m, 2H), 3.76 (s, 3H).

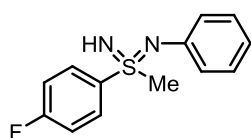
¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 166.3 (d, $^1J_{\text{CF}}$ = 258.6 Hz), 149.4, 147.5, 142.6, 131.9 (d, $^4J_{\text{CF}}$ = 3.2 Hz), 131.1 (d, $^3J_{\text{CF}}$ = 9.7 Hz), 128.7, 128.3, 123.5, 122.1, 121.9, 117.9 (d, $^2J_{\text{CF}}$ = 23.0 Hz), 49.1.

¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) = -101.9 (tt, J = 8.0, 4.8 Hz).

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 1592, 1527, 1487, 1350, 1294, 1260, 1156, 1065, 1002, 797, 737, 691

HRMS (ESI⁺) calcd. for C₁₉H₁₇FN₃O₄S₂⁺ [M+H]⁺: 434.0639; found: 434.0642.

1-(4-Fluorophenyl)-1-methyl-*N*-phenyl- λ^6 -sulfanediimine (**11**)



Under an atmosphere of nitrogen, sulfondiimines **11a** (42 mg, 0.10 mmol, 1.0 equiv.) was dissolved in anhydrous MeCN (1.0 mL). 1-Dodecanethiol (0.12 mL, 0.50 mmol, 5.0 equiv.) was added at room temperature followed by DBU (70 μ L, 0.47 mmol, 4.8 equiv.). The solution became yellow and was stirred for 20 min under nitrogen until completion of the reaction (TLC). The reaction mixture was concentrated *in vacuo* to afford light yellow oil. The crude product was purified by flash column chromatography (petrol/ethyl acetate, 1:1 to 0:1) to afford corresponding *sulfondiimine* **11** as a white solid (19 mg, 80%).

mp 122-123 °C (CH₂Cl₂)

R_f 0.39 (ethyl acetate).

¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.23-8.16 (m, 2H), 7.25-7.14 (m, 4H), 7.10-7.06 (m, 2H), 6.90 (tt, J = 7.5, 1.2 Hz, 1H), 3.25 (s, 3H), 2.17 (br. s, 1H).

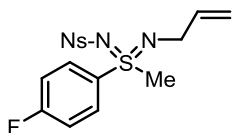
¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 165.5 (d, $^1J_{\text{CF}}$ = 254.8 Hz), 145.8, 138.0 (d, $^4J_{\text{CF}}$ = 3.1 Hz), 130.7 (d, $^3J_{\text{CF}}$ = 9.4 Hz), 129.2, 123.2, 121.3, 116.6 (d, $^2J_{\text{CF}}$ = 22.6 Hz), 48.6.

¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) = -106.1 (tt, J = 8.3, 5.2 Hz).

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 1590, 1486, 1390, 1254, 1153, 1081, 956, 839, 758.

HRMS (ESI⁺) calcd. for C₁₃H₁₄FN₂S⁺ [M+H]⁺: 249.0856; found: 249.0855.

***N*-((Allylimino)(4-fluorophenyl)(methyl)- λ^6 -sulfaneylidene)-4-nitrobenzenesulfonamide (12a)**



In an oven-dried flask, sulfondiimine **6** (64 mg, 0.18 mmol, 1.0 equiv.) was dissolved in anhydrous DMSO (0.40 mL). KOH (21 mg, 0.37 mmol, 2.0 equiv.) was added followed by allyl bromide (35 mg, 0.29 mmol, 1.5 equiv.). The reaction mixture was stirred at room temperature for 12 h until completion of the reaction (TLC). The reaction was quenched with water and extracted with CH₂Cl₂ (3 × 20 mL). The combined extracts were washed with brine, dried over anhydrous Na₂SO₄, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (petrol/ethyl acetate, 1:1) to afford *sulfondiimine 12a* as a light yellow oil (58 mg, 81%).

R_f 0.35 (petrol/ethyl acetate, 1:1).

¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.30 (d, J = 9.0 Hz, 2H), 8.18 (d, J = 9.0 Hz, 2H), 8.04-7.96 (m, 2H), 7.41-6.94 (m, 2H), 5.60 (ddt, J = 17.0, 10.3, 5.2 Hz, 1H), 5.05 (dq, J = 17.0, 1.8 Hz, 1H), 4.97 (dq, J = 10.3, 1.8 Hz, 1H), 3.59 (s, 3H), 3.12 (ddt, J = 15.5, 5.2, 1.7 Hz, 1H), 2.90 (ddt, J = 15.5, 5.2, 1.7 Hz, 1H).

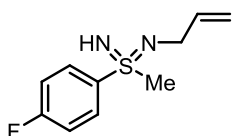
¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 166.2 (d, $^1J_{\text{CF}}$ = 258.0 Hz), 149.7, 149.6, 135.5, 132.4 (d, $^4J_{\text{CF}}$ = 3.2 Hz), 131.3 (d, $^3J_{\text{CF}}$ = 9.7 Hz), 128.3, 124.1, 117.5 (d, $^2J_{\text{CF}}$ = 22.7 Hz), 115.6, 47.6, 46.4.

¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) = -102.7 (tt, J = 8.0, 4.9 Hz).

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 1526, 1390, 1153, 1084, 956.

HRMS (ESI⁺) calcd. for C₁₆H₁₇FN₃O₄S₂⁺ [M+H]⁺: 398.0639; found: 398.0644.

***N*-Allyl-1-(4-fluorophenyl)-1-methyl- λ^6 -sulfanediimine (12)**



Under an atmosphere of nitrogen, sulfondiimines **12a** (45 mg, 0.11 mmol, 1.0 equiv.) was dissolved in anhydrous MeCN (1.1 mL). 1-Dodecanethiol (0.13 mL, 0.54 mmol, 5.0 equiv.) was added at room temperature followed by DBU (78 μ L, 0.52 mmol, 4.75 equiv.). The solution became yellow

and was stirred for 20 mins under nitrogen until completion of the reaction (TLC). The reaction mixture was concentrated *in vacuo* to afford light yellow oil. The crude product was purified by flash column chromatography (CH₂Cl₂/MeOH, 15:1 to 9:1) to afford corresponding *sulfondiimine* **12** as a light yellow oil (22 mg, 94%).

R_f 0.43 (CH₂Cl₂ / MeOH = 9:1).

¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.16-8.01 (m, 2H), 7.23-7.17 (m, 2H), 5.96 (ddt, J = 17.0, 10.1, 5.6 Hz, 1H), 5.25 (dq, J = 17.0, 1.8 Hz, 1H), 5.05 (dq, J = 10.1, 1.8 Hz, 1H), 3.68 (ddt, J = 15.2, 5.6, 1.6 Hz, 1H), 3.53 (ddt, J = 15.2, 5.6, 1.6 Hz, 1H), 3.12 (s, 3H), 2.25 (br. s, 1H).

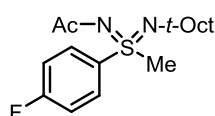
¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 165.3 (d, $^1J_{CF}$ = 254.1 Hz), 138.5, 137.6 (d, $^4J_{CF}$ = 3.0 Hz), 130.6 (d, $^3J_{CF}$ = 9.3 Hz), 116.4 (d, $^2J_{CF}$ = 22.5 Hz), 114.8, 48.5, 45.7.

¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) = -106.7 (tt, J = 8.3, 5.1 Hz).

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 1490, 1389, 1253, 1153, 1076, 956.

HRMS (ESI⁺) calcd. for C₁₀H₁₄FN₂S⁺ [M+H]⁺: 213.0856; found: 213.0860.

***N*-((4-Fluorophenyl)(methyl)((2,4,4-trimethylpentan-2-yl)imino)- λ^6 -sulfaneylidene)acetamide
(**13a**)**



Under an atmosphere of argon, sulfondiimine **7** (40 mg, 0.14 mmol, 1.0 equiv.) was dissolved in anhydrous CH₂Cl₂ (1.5 mL). Triethylamine (30 μ L, 0.22 mmol, 1.5 equiv.) was added at 0°C followed by acetic anhydride (20 μ L, 0.21 mmol, 1.5 equiv.) and DMAP (4.1 mg, 0.034 mmol, 0.25 equiv.). The reaction mixture was stirred at room temperature for 12 h. Sat. aq. NH₄Cl (30 mL) was added and the product was extracted with CH₂Cl₂ (3 x 10 mL). The combined extracts were washed with brine, dried over anhydrous Na₂SO₄, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (petrol/ethyl acetate, 1.5:1) to afford *sulfondiimine* **13a** as a white solid (45 mg, 99%).

mp 64-65 °C (CH₂Cl₂)

R_f 0.37 (petrol/ethyl acetate, 1.5:1).

¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.12-8.02 (m, 2H), 7.23-7.12 (m, 2H), 3.36 (s, 3H), 2.12 (s, 3H), 1.52 (d, J = 14.4 Hz, 1H), 1.47 (d, J = 14.4 Hz, 1H), 1.32 (s, 3H), 1.13 (s, 3H), 1.02 (s, 9H).

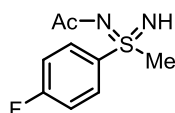
¹³C NMR (100 MHz, (CD₃)₂CO): δ (ppm) = 179.6, 166.0 (d, $^1J_{\text{CF}}$ = 251.7 Hz), 141.5 (d, $^4J_{\text{CF}}$ = 3.2 Hz), 131.6 (d, $^3J_{\text{CF}}$ = 9.1 Hz), 117.0 (d, $^2J_{\text{CF}}$ = 23.0 Hz), 59.6, 59.0, 47.9, 32.7, 32.6, 32.4, 32.2, 27.5.

¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) = -106.8 (tt, J = 8.1, 5.0 Hz).

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 2980, 1623, 1383, 1360, 1262, 1217, 1153, 1079, 1022, 969, 817

HRMS (ESI⁺) calcd. for C₁₇H₂₈FN₂OS⁺ [M+H]⁺: 327.1901; found: 327.1897.

***N*-((4-Fluorophenyl)(imino)(methyl)- λ^6 -sulfaneylidene)acetamide (**13**)**



Sulfondiimine **13a** (91 mg, 0.28 mmol, 1.0 equiv.) was mixed with TFA (2.8 mL) and stirred at room temperature for 14 h. The mixture was concentrated *in vacuo* then diluted with CH₂Cl₂ and basified to pH 10-11 using 1 M aq. NaOH solution. The product was extracted with CH₂Cl₂ (3 \times 20 mL). The combined extracts were washed with brine, dried over anhydrous Na₂SO₄, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (ethyl acetate, then CH₂Cl₂/MeOH, 5:1) to afford *sulfondiimine* **13** as a colourless oil (54 mg, 90%).

R_f 0.28 (ethyl acetate).

¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.01-7.93 (m, 2H), 7.24-7.17 (m, 2H), 3.16 (s, 3H), 3.04 (br. s, 1H), 2.07 (s, 3H).

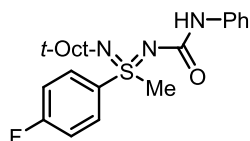
¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 181.8, 165.6 (d, $^1J_{\text{CF}}$ = 255.6 Hz), 137.6 (d, $^4J_{\text{CF}}$ = 3.1 Hz), 129.7 (d, $^3J_{\text{CF}}$ = 9.4 Hz), 117.0 (d, $^2J_{\text{CF}}$ = 22.9 Hz), 45.1, 26.0.

¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) = -105.0 (tt, J = 8.0, 5.1 Hz).

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 1587, 1490, 1365, 1281, 1233, 1157, 1083, 1047, 944, 818.

HRMS (ESI⁺) calcd. for C₉H₁₂FN₂OS⁺ [M+H]⁺: 215.0649; found: 215.0648.

1-((4-Fluorophenyl)(methyl)((2,4,4-trimethylpentan-2-yl)imino)- λ^6 -sulfaneylidene)-3-phenylurea (14a)



To a solution of sulfondiimine **7** (38 mg, 0.13 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (1.3 mL), the phenyl isocyanate (26 mg, 0.22 mmol, 1.5 equiv.) was added dropwise at room temperature under argon atmosphere. The reaction was stirred at room temperature for 24 h until completion of the reaction (TLC). The reaction was quenched with water and extracted with CH_2Cl_2 (3×20 mL). The combined extracts were washed with brine, dried over anhydrous Na_2SO_4 , and concentrated *in vacuo*. The crude product was purified by flash column chromatography (petrol/ethyl acetate, 3:1 to 2:1) to afford *sulfondiimine* **14a** as a white solid (53 mg, 98%).

mp 82-84 °C (CH_2Cl_2)

R_f 0.56 (petrol/ethyl acetate, 2:1).

¹H NMR (400 MHz, CDCl_3): δ (ppm) = 8.15-8.08 (m, 2H), 7.48 (dd, J = 8.6, 1.2 Hz, 1H), 7.27 (dd, J = 8.5, 7.3 Hz, 1H), 7.24-7.18 (m, 2H), 6.99 (tt, J = 7.3, 1.2 Hz, 1H), 6.90 (br. s, 1H), 3.43 (s, 3H), 1.56 (d, J = 14.3 Hz, 1H), 1.51 (d, J = 14.3 Hz, 1H), 1.37 (s, 3H), 1.17 (s, 3H), 1.04 (s, 9H).

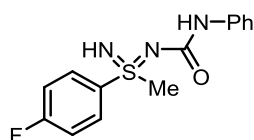
¹³C NMR (100 MHz, CDCl_3): δ (ppm) = 165.1 (d, $^1J_{\text{CF}}$ = 254.2 Hz), 159.2, 140.1 (d, $^4J_{\text{CF}}$ = 3.1 Hz), 139.9, 130.2 (d, $^3J_{\text{CF}}$ = 9.4 Hz), 129.0, 122.5, 118.7, 116.4 (d, $^2J_{\text{CF}}$ = 22.8 Hz), 59.4, 58.2, 48.8, 32.1, 32.0, 31.92, 31.89.

¹⁹F NMR (376 MHz, CDCl_3): δ (ppm) = -106.9. (ddd, J = 13.3, 8.5, 5.1 Hz).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1650, 1506, 1389, 1217, 1153, 1088, 962, 836.

HRMS (ESI^+) calcd. for $\text{C}_{22}\text{H}_{31}\text{FN}_3\text{OS}^+$ $[\text{M}+\text{H}]^+$: 404.2166; found: 404.1273.

1-((4-Fluorophenyl)(imino)(methyl)- λ^6 -sulfaneylidene)-3-phenylurea (14)



Sulfondiimine **14a** (50 mg, 0.12 mmol, 1.0 equiv.) was mixed with TFA (1.2 mL) and stirred at room temperature for 3 days. The mixture was concentrated *in vacuo* then diluted with CH₂Cl₂ and basified to pH 10-11 using 1 M aq. NaOH solution. The product was extracted with CH₂Cl₂ (3 × 20 mL). The combined extracts were washed with brine, dried over anhydrous Na₂SO₄, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (ethyl acetate) to afford *sulfondiimine 14* as a light yellow solid (31 mg, 86%).

mp 55-57 °C (CH₂Cl₂)

R_f 0.41 (ethyl acetate).

¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.07-8.01 (m, 2H), 7.37 (dd, *J* = 8.6, 1.2 Hz, 2H), 7.26-7.18 (m, 4H), 7.01 (br. s, 1H), 7.00-6.96 (m, 1H), 3.24 (s, 3H), 2.87 (br. s, 1H).

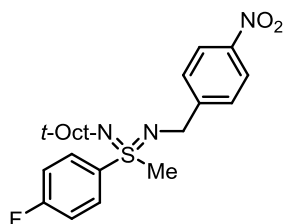
¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 165.7 (d, ¹*J*_{CF} = 255.5 Hz), 160.3, 139.3, 138.3(d, ⁴*J*_{CF} = 3.2 Hz), 130.0 (d, ³*J*_{CF} = 9.5 Hz), 129.0, 122.8, 118.8, 117.0 (d, ²*J*_{CF} = 22.7 Hz), 45.7.

¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) = -105.2 (ddd, *J* = 13.2, 8.3, 4.9 Hz).

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 1591, 1535, 1491, 1438, 1389, 1317, 1236, 1154, 1075, 960, 832.

HRMS (ESI⁺) calcd. for C₁₄H₁₅FN₃OS⁺ [M+H]⁺: 292.0914; found: 292.0915.

1-(4-Fluorophenyl)-1-methyl-N-(4-nitrobenzyl)-N-(2,4,4-trimethylpentan-2-yl)-λ⁶-sulfanediimine (15a)



Under an atmosphere of argon, sulfondiimine **7** (91 mg, 0.32 mmol, 1.0 equiv.) was dissolved in anhydrous DCE (1.5 mL). 4 Å Molecular sieves (0.1 g) were added followed by 4-nitrobenzaldehyde (71 mg, 0.47 mmol, 1.3 equiv.) and NaBH(OAc)₃ (199 mg, 0.940 mmol, 3.0 equiv.). The reaction mixture was stirred at 50 °C for 18 h. 1 M aq. NaOH solution (30 mL) was added, the product was extracted with CH₂Cl₂ (3 x 30 mL). The combined extracts were washed with brine, dried over anhydrous Na₂SO₄, and concentrated *in vacuo*. The crude product was

purified by flash column chromatography (petrol/ethyl acetate, 4:1 to 1.5:1) to afford *sulfondiimine* **15a** as a colourless oil (109 mg, 81%).

R_f 0.38 (petrol/ethyl acetate, 1.5:1).

¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.15 (d, J = 8.8 Hz, 2H), 8.08-8.01 (m, 2H), 7.55 (d, J = 8.8 Hz, 2H), 7.19-7.10 (m, 2H), 4.33 (d, J = 16.2 Hz, 1H), 4.08 (d, J = 16.2 Hz, 1H), 3.15 (s, 3H), 1.57 (s, 2H), 1.46 (s, 3H), 1.36 (s, 3H), 1.05 (s, 9H).

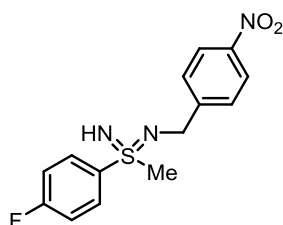
¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 165.2 (d, $^1J_{\text{CF}}$ = 254.5 Hz), 149.1, 146.9, 137.1 (d, $^4J_{\text{CF}}$ = 2.6 Hz), 131.0 (d, $^3J_{\text{CF}}$ = 9.2 Hz), 128.3, 123.6, 116.5 (d, $^2J_{\text{CF}}$ = 22.4 Hz), 58.9, 58.5, 48.2, 46.2, 32.6, 32.3, 32.04, 32.01.

¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) = -108.2 (ddd, J = 13.4, 8.4, 5.1 Hz).

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 1518, 1487, 1343, 1216, 1146, 1106, 839, 738.

HRMS (ESI⁺) calcd. for C₂₂H₃₁FN₃O₂S⁺ [M+H]⁺: 420.2116; found: 420.2114.

1-(4-Fluorophenyl)-1-methyl-N-(4-nitrobenzyl)- λ^6 -sulfanediimine (**15**)



Sulfondiimine **15a** (45 mg, 0.11 mmol, 1.0 equiv.) was mixed with TFA (1.1 mL) and stir at room temperature for 6 h. The mixture was concentrated *in vacuo* then diluted with ethyl acetate and basified to pH 10-11 using 1 M aq. NaOH solution. The product was extracted with ethyl acetate (3 × 20 mL). The combined extracts were washed with brine, dried over anhydrous Na₂SO₄, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (CH₂Cl₂/MeOH, 20:1) to afford *sulfondiimine* **15** as a light yellow solid (29 mg, 88%).

mp 131-133 °C (CH₂Cl₂)

R_f 0.36 (CH₂Cl₂/MeOH, 9:1).

¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.15 (d, J = 8.7 Hz, 2H), 8.13-8.08 (m, 2H), 7.55 (d, J = 8.7 Hz, 2H), 7.25-7.17 (m, 2H), 4.33 (d, J = 15.7 Hz, 1H), 4.18 (d, J = 15.7 Hz, 1H), 3.15 (s, 3H), 1.87 (br. s, 1H).

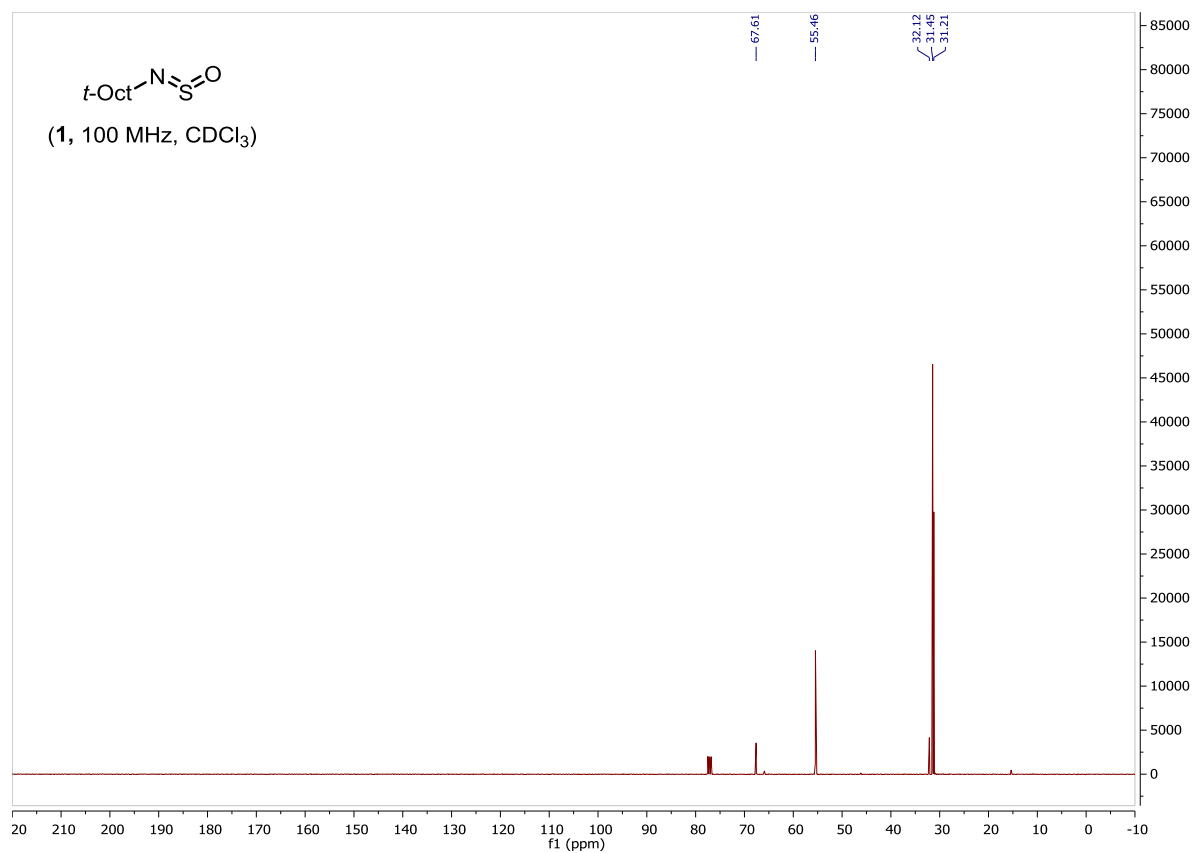
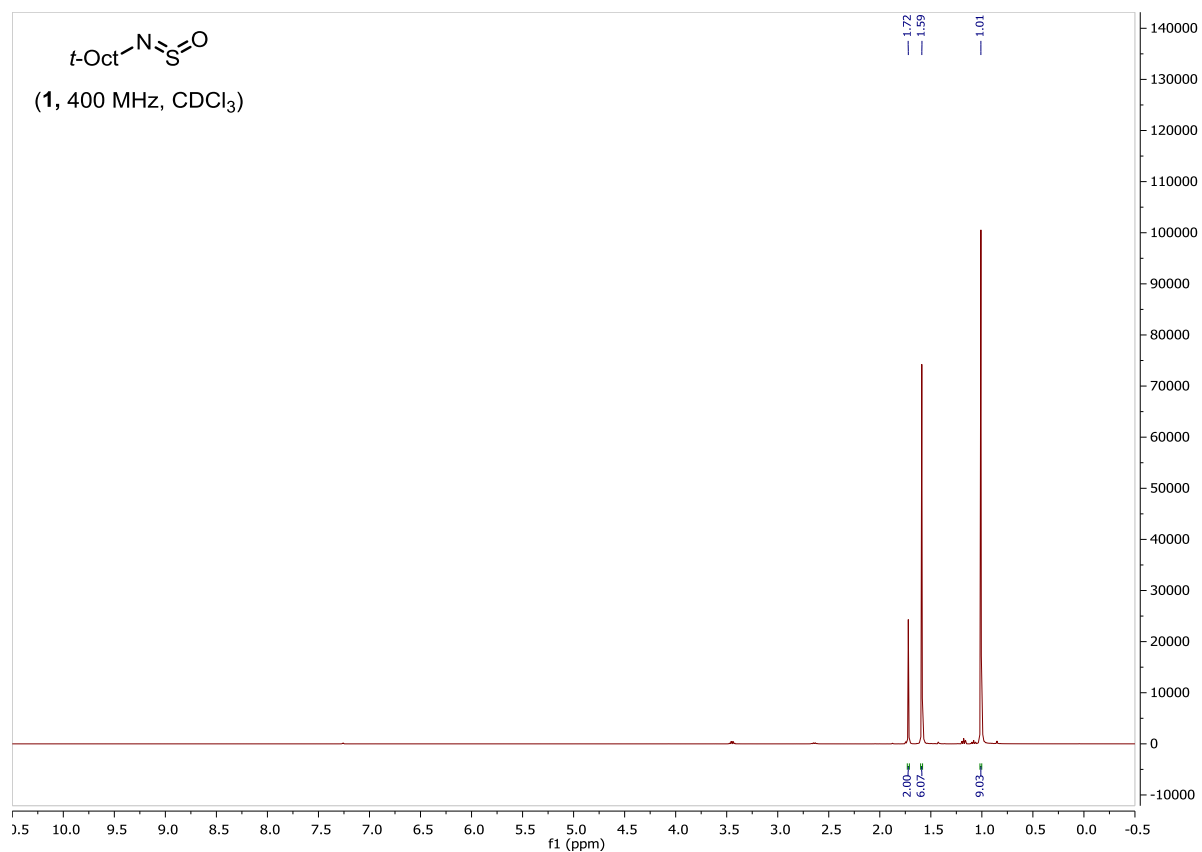
¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 165.4 (d, $^1J_{\text{CF}}$ = 254.8 Hz), 150.0, 146.8, 137.2 (d, $^4J_{\text{CF}}$ = 3.0 Hz), 130.6 (d, $^3J_{\text{CF}}$ = 9.4 Hz), 128.3, 123.7, 116.6 (d, $^2J_{\text{CF}}$ = 22.4 Hz), 48.6, 46.3.

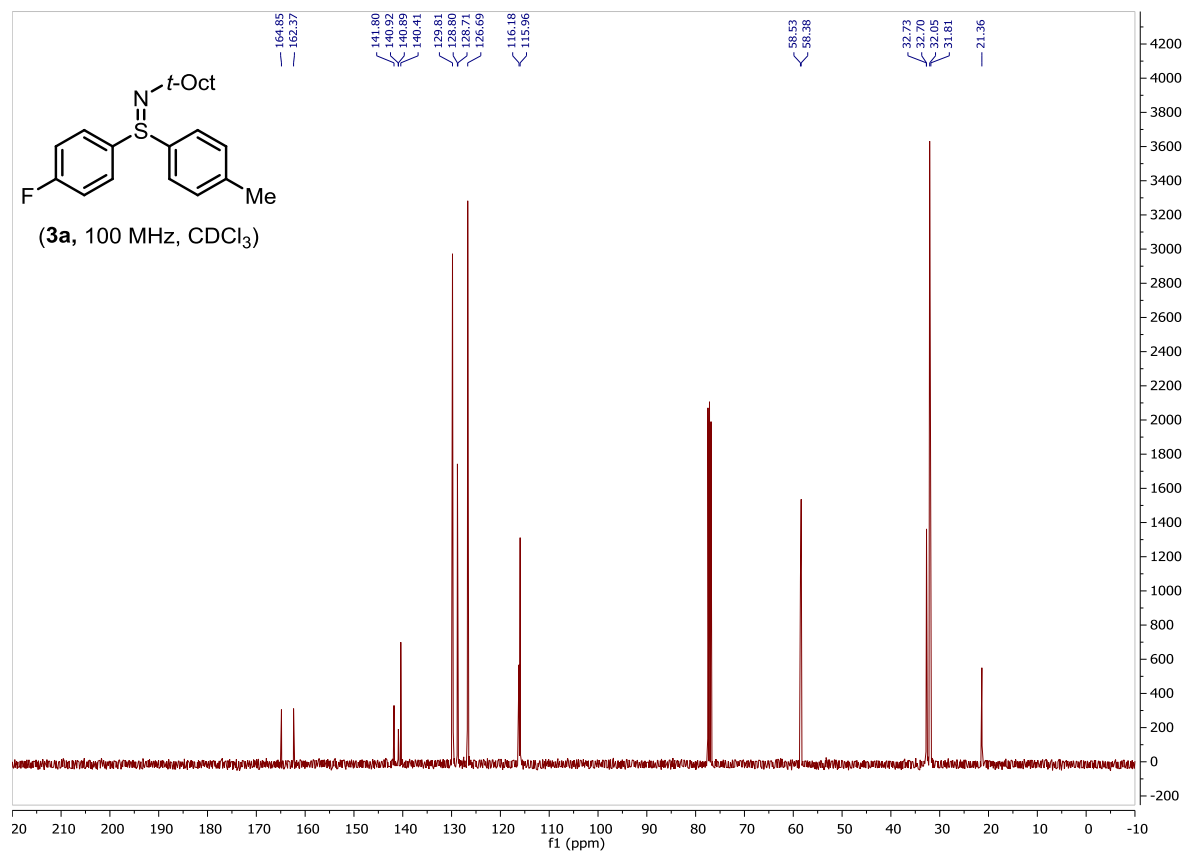
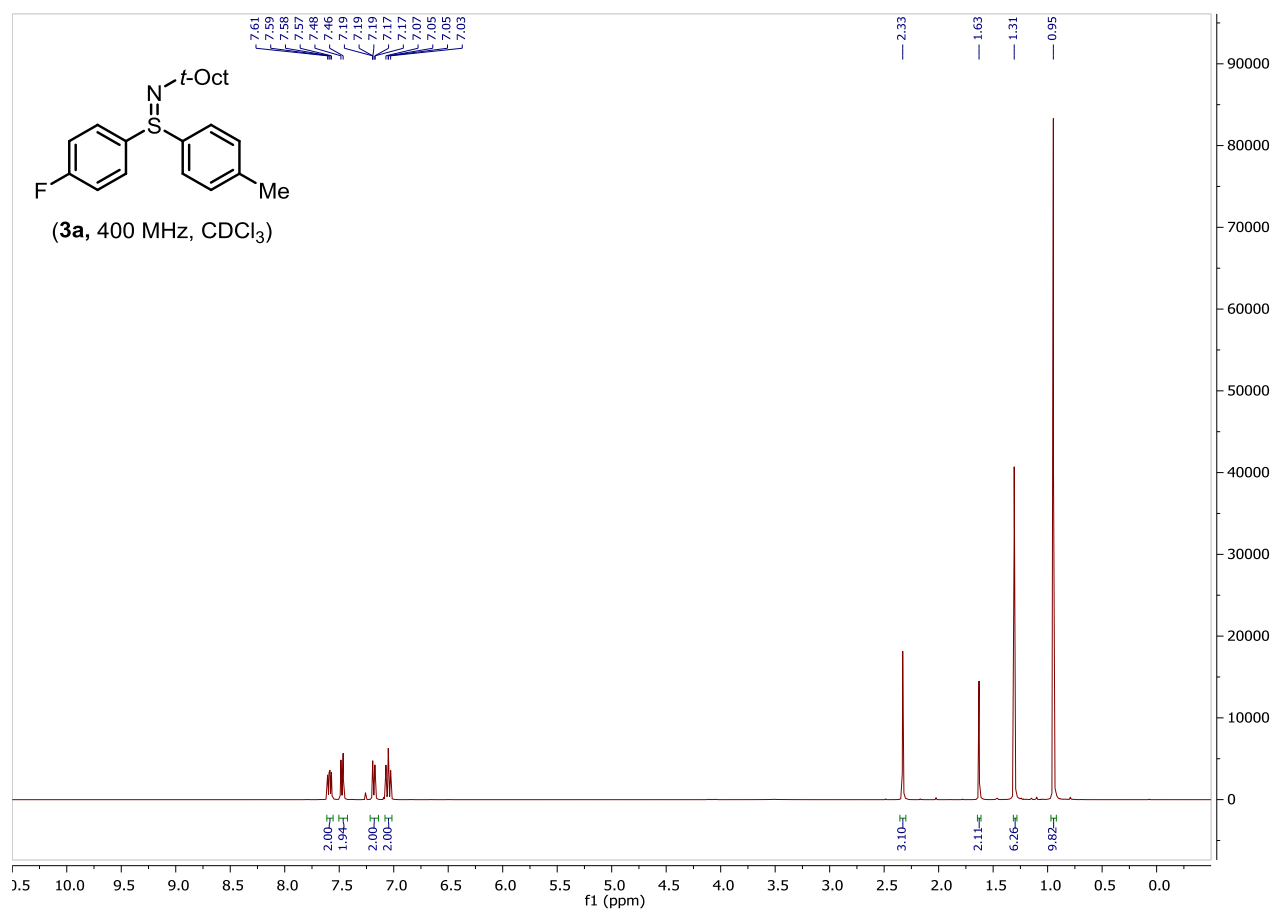
¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) = -106.0 (ddd, J = 13.3, 8.2, 5.1 Hz).

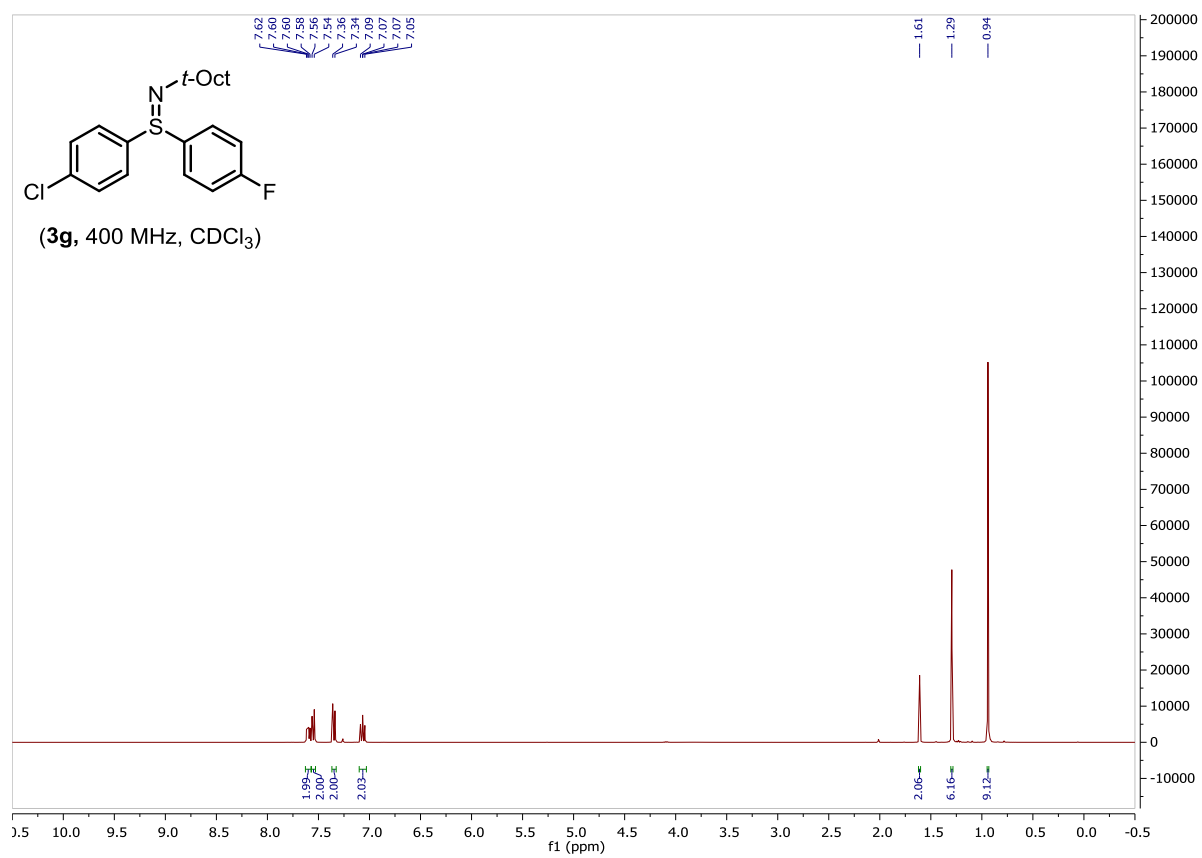
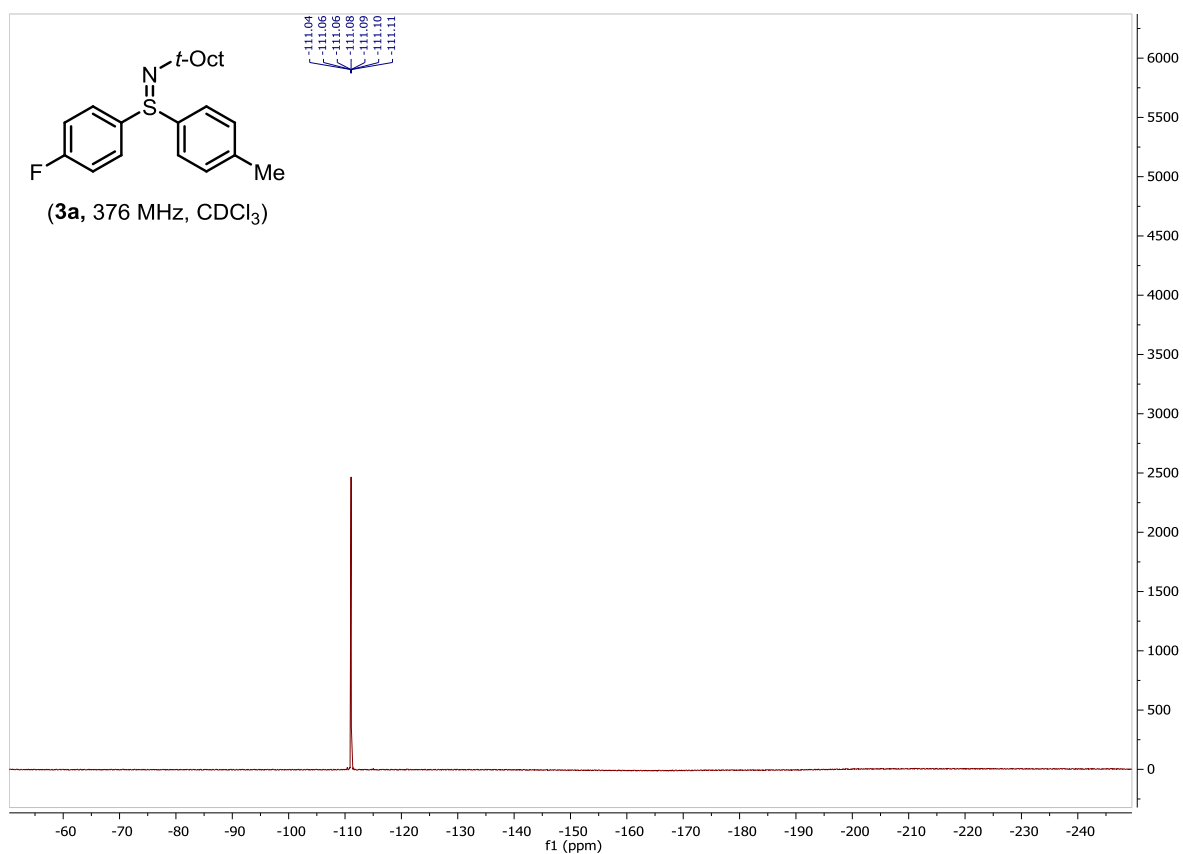
IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 1516, 1344, 1153, 839.

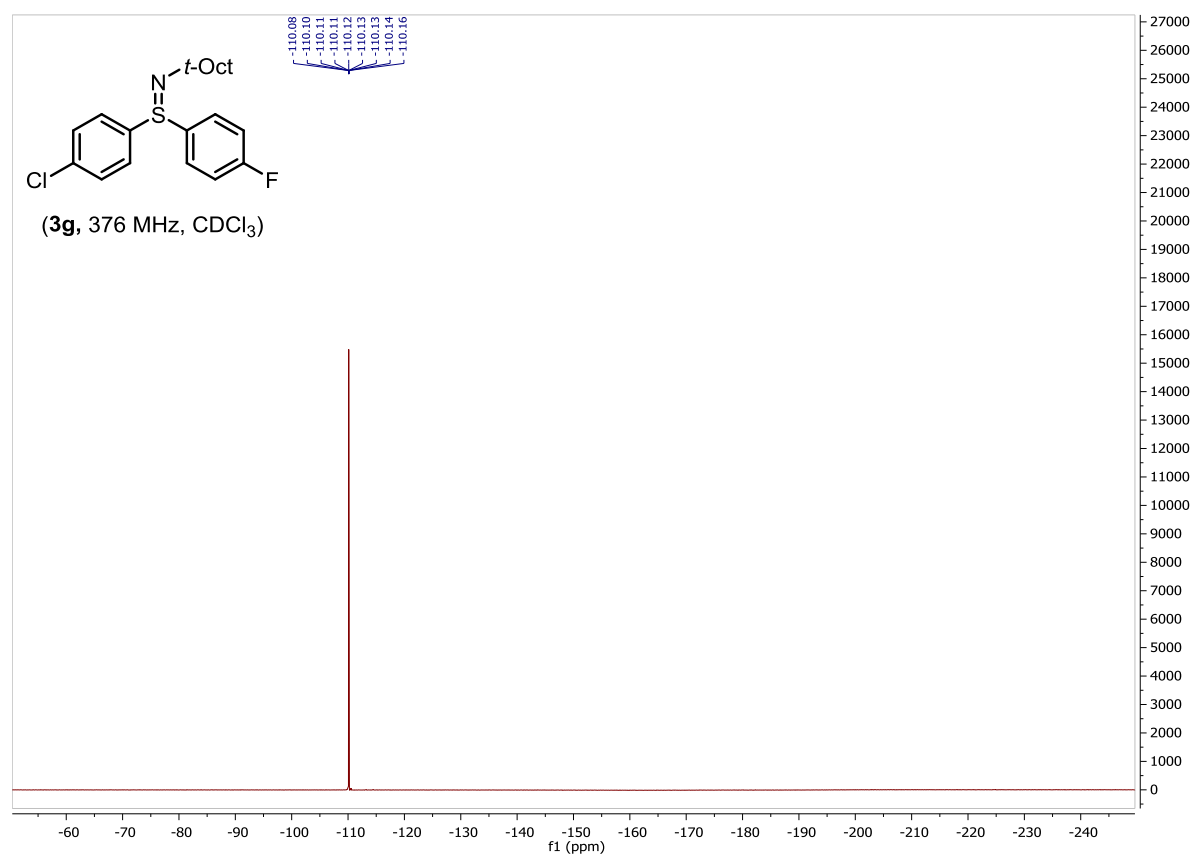
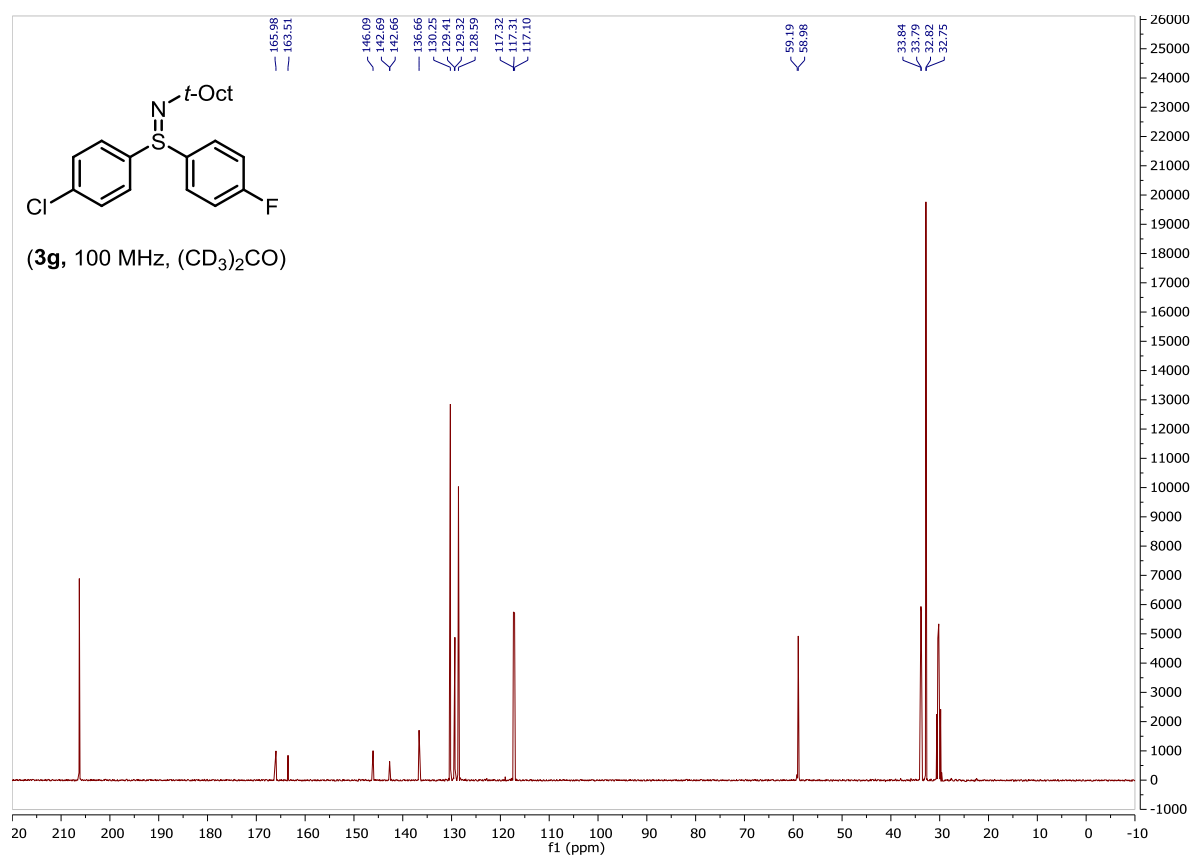
HRMS (ESI⁺) calcd. for C₁₄H₁₅FN₃O₂S⁺ [M+H]⁺: 308.0864; found: 308.0858.

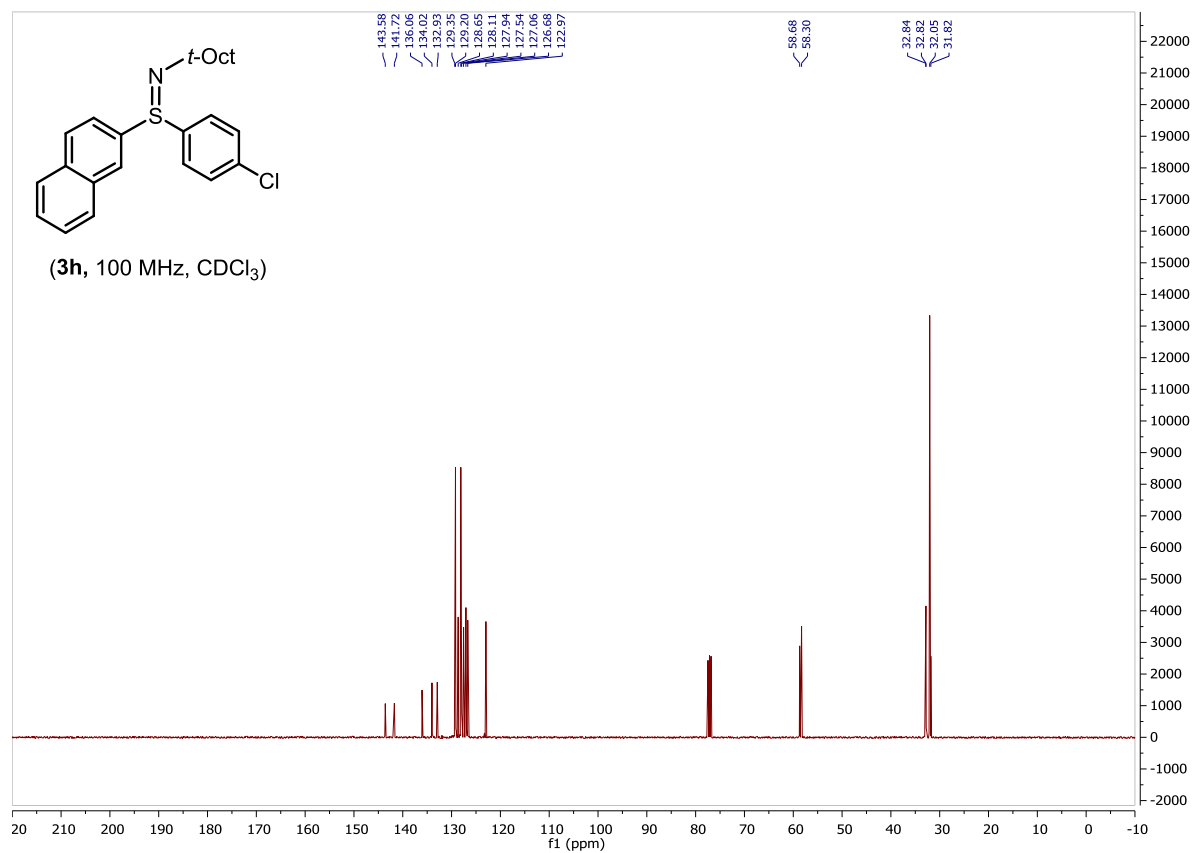
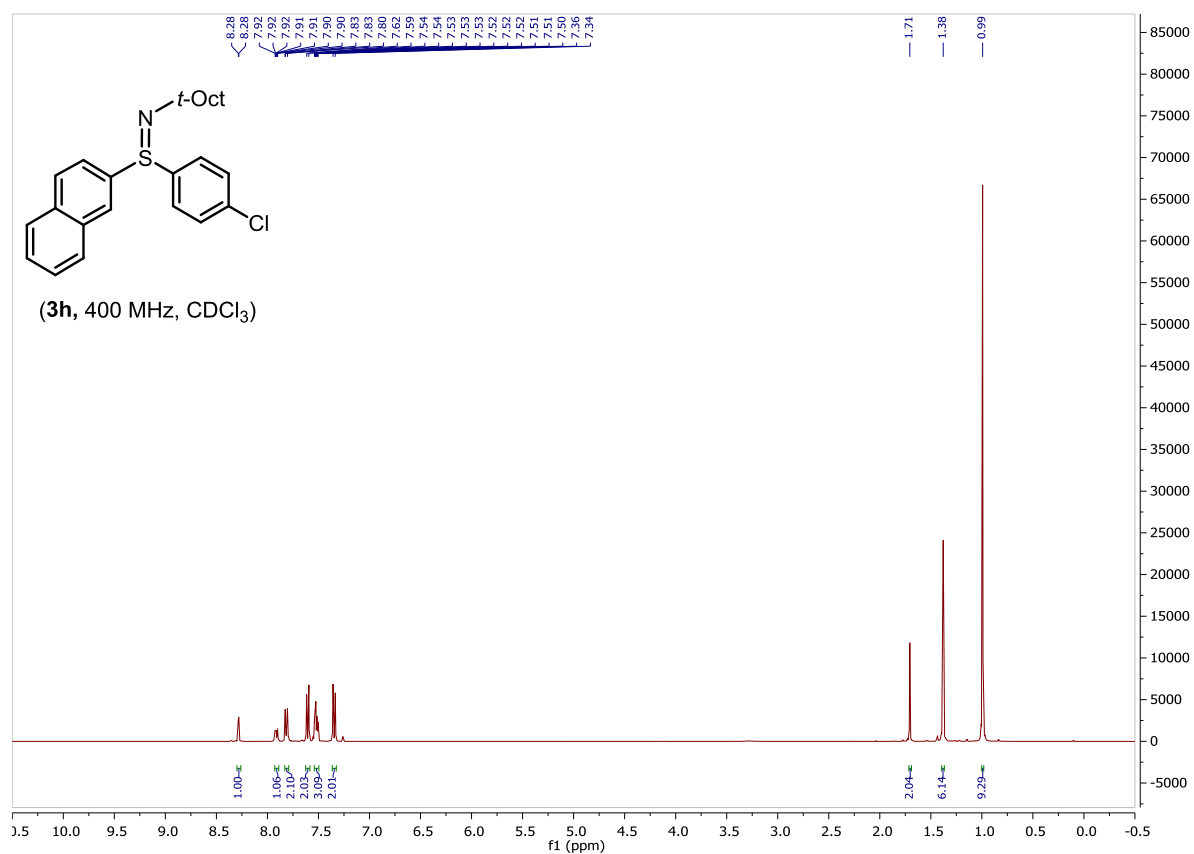
2. NMR Spectra

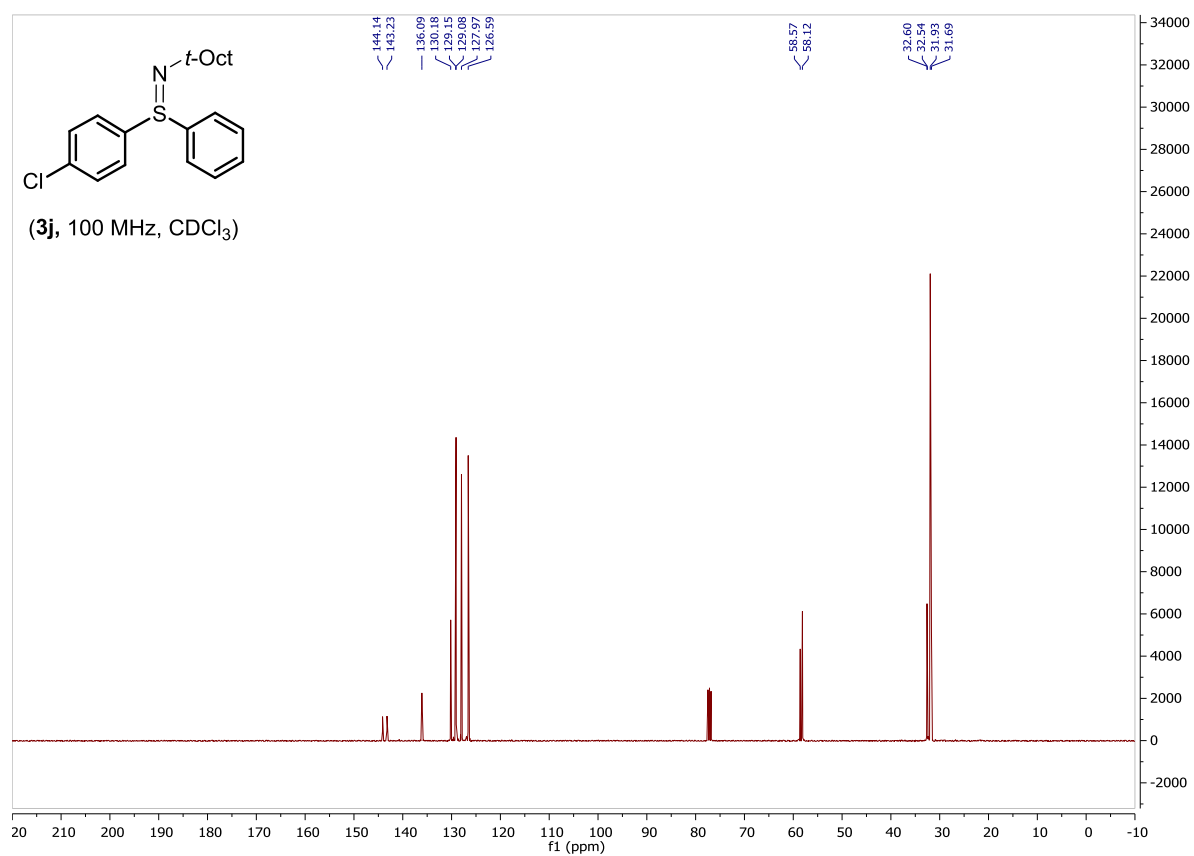
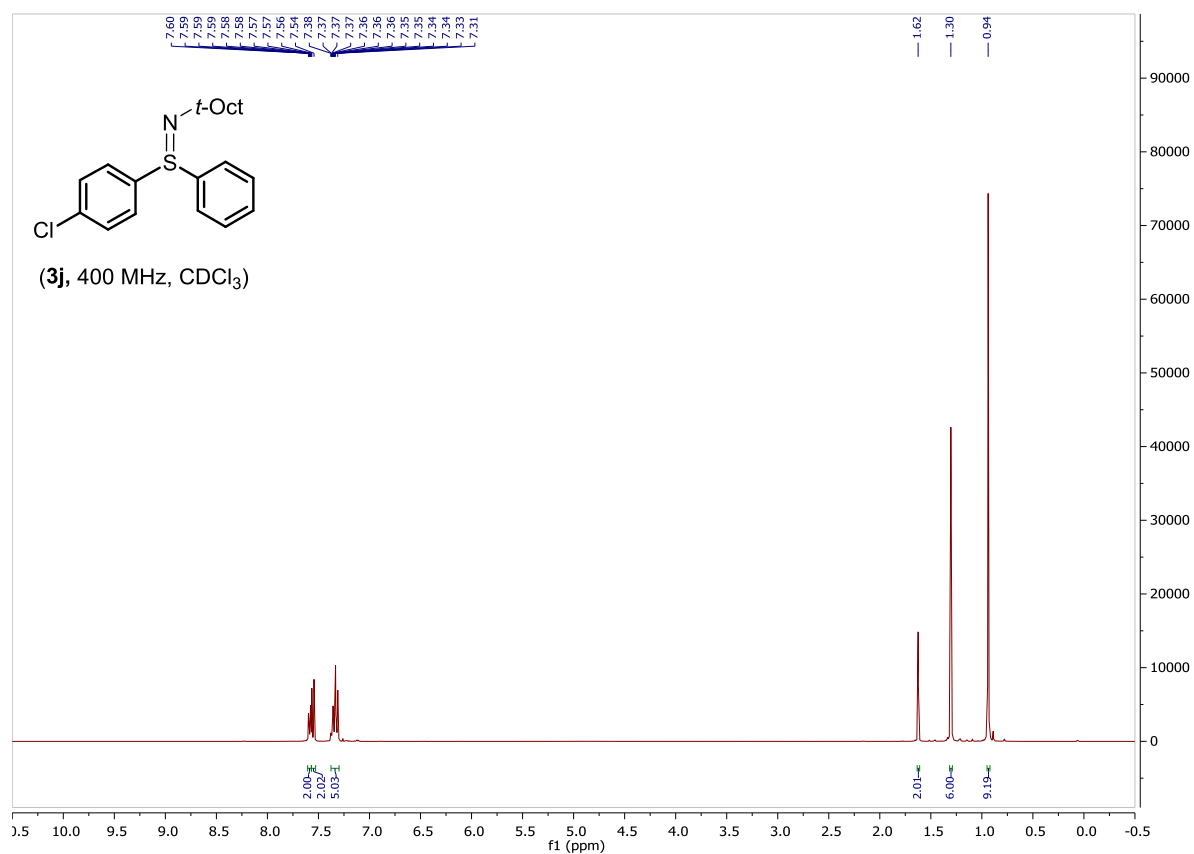


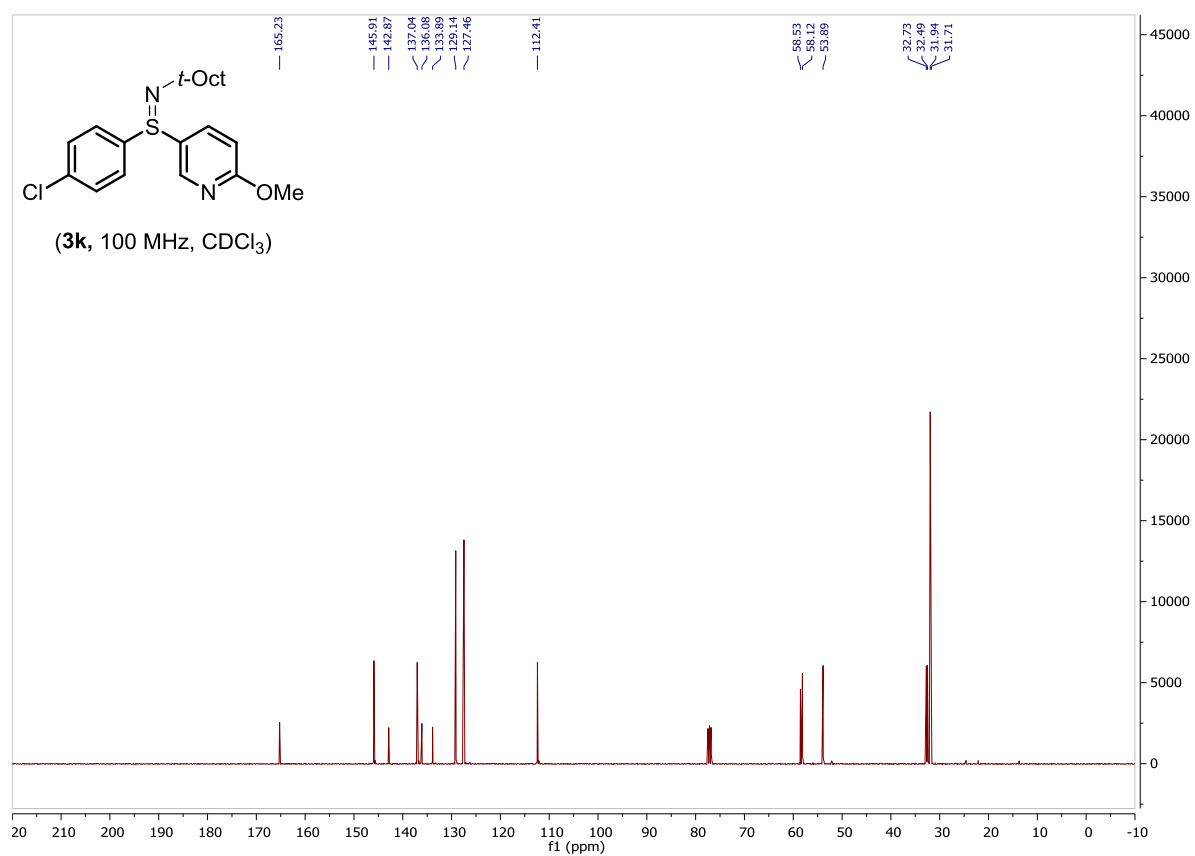
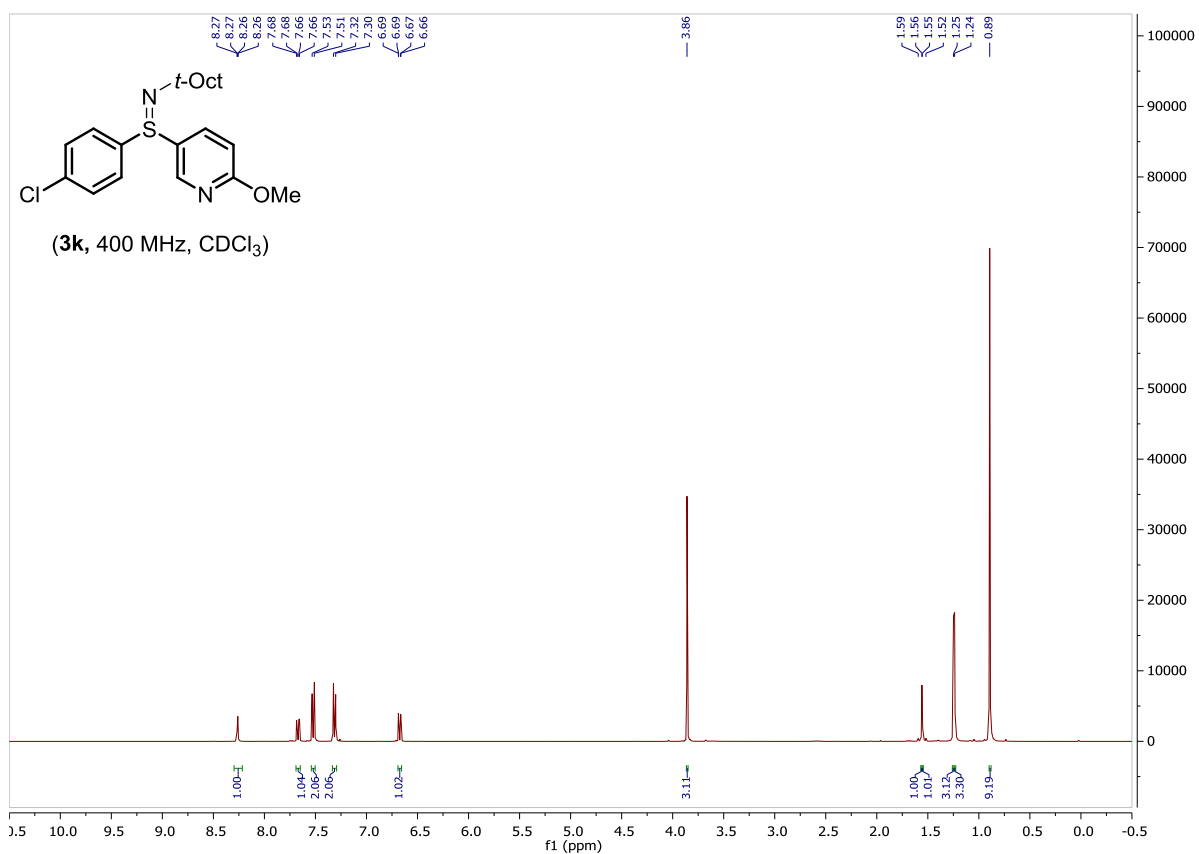


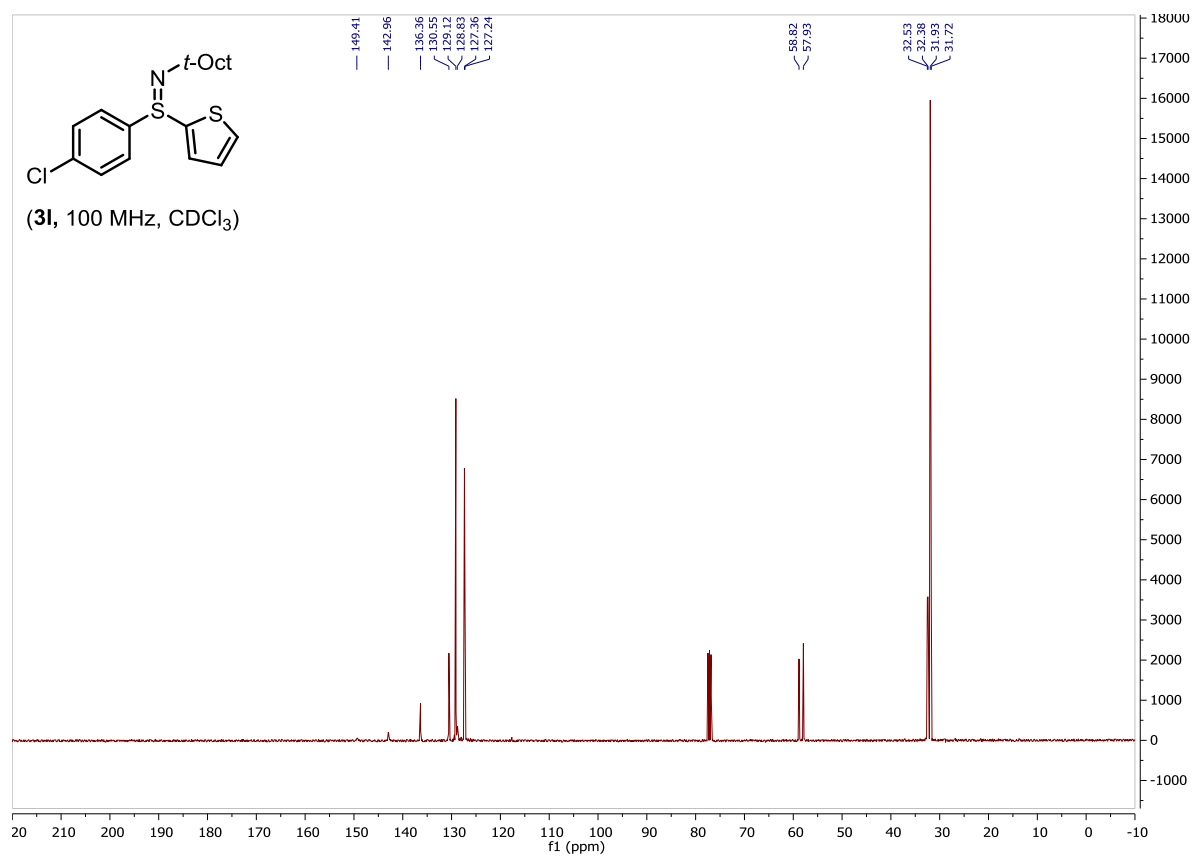
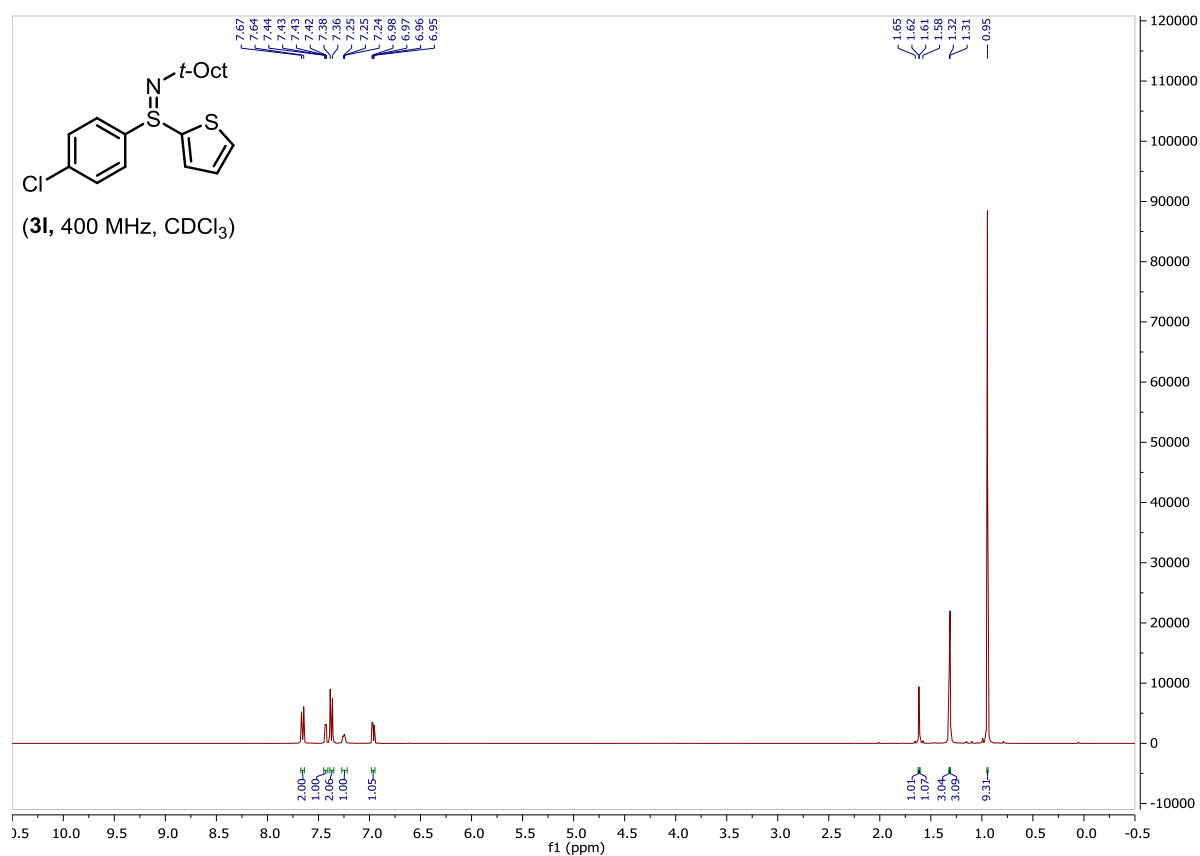


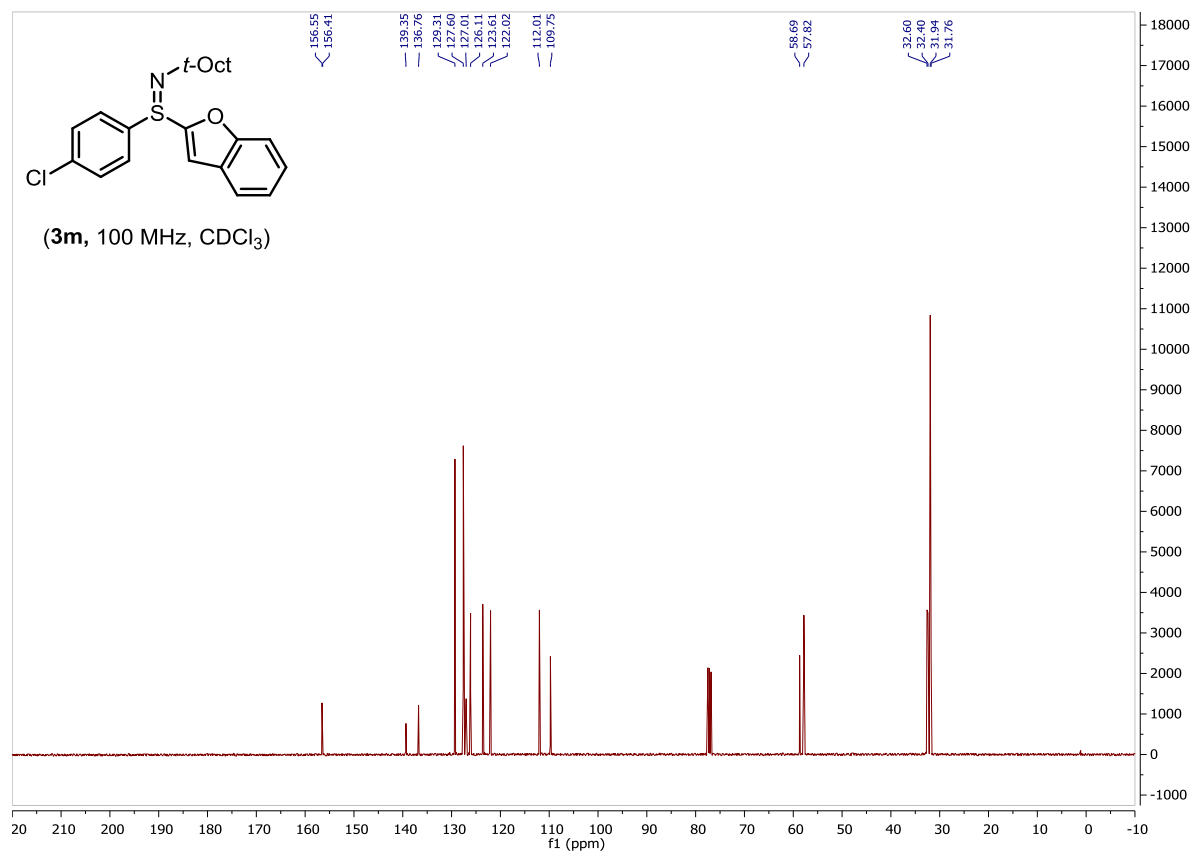
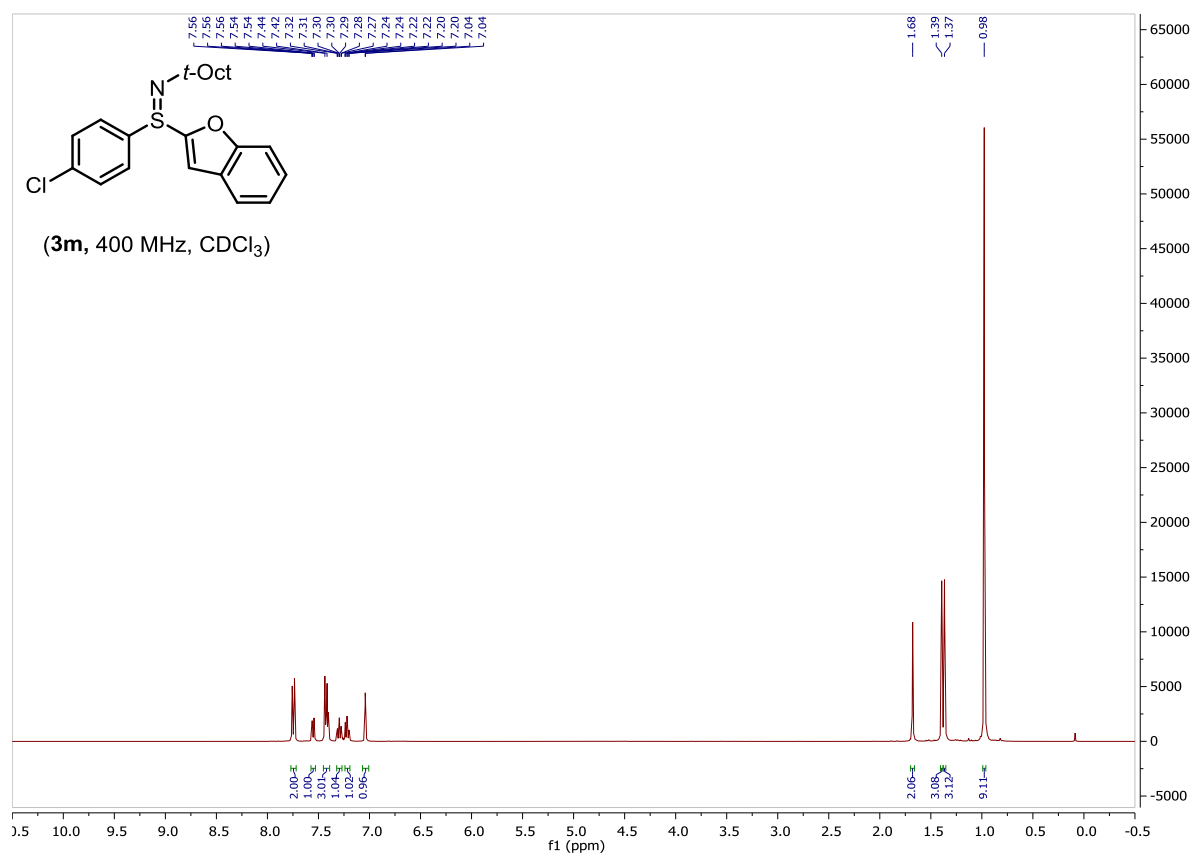


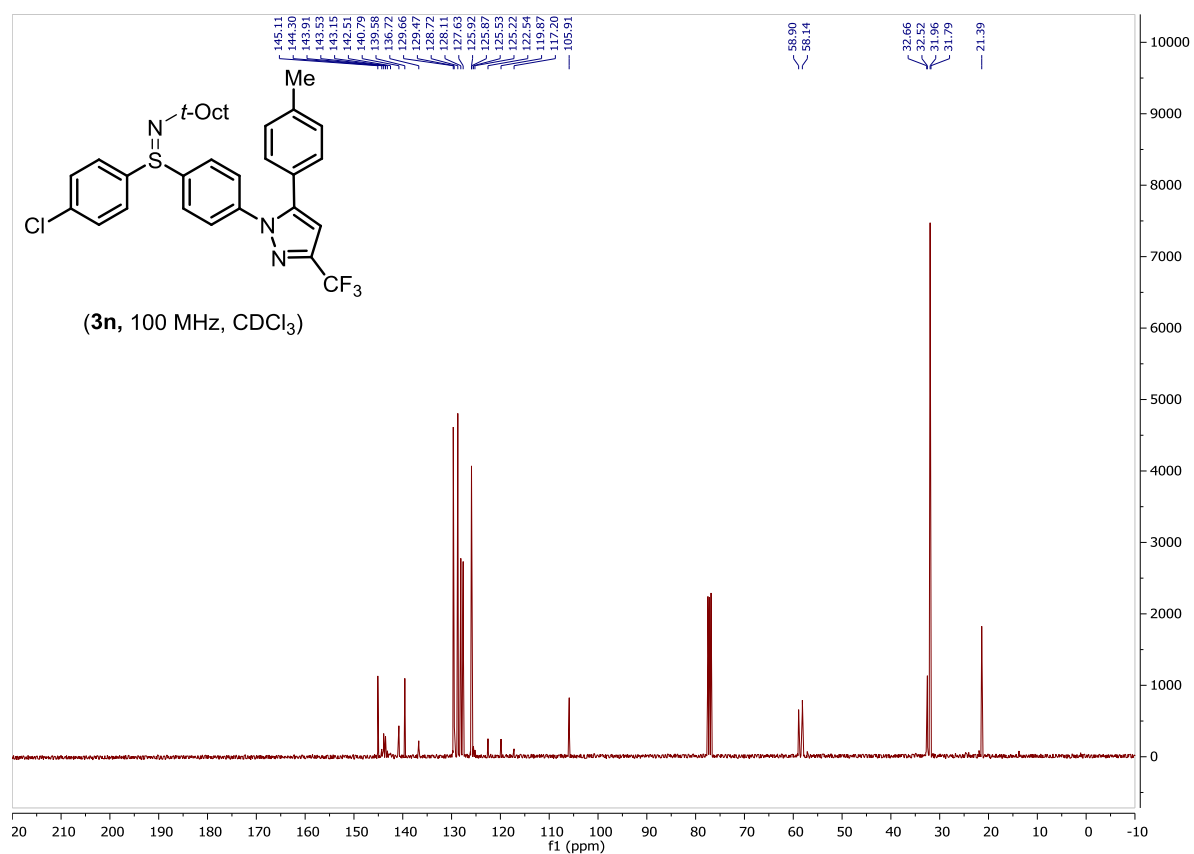
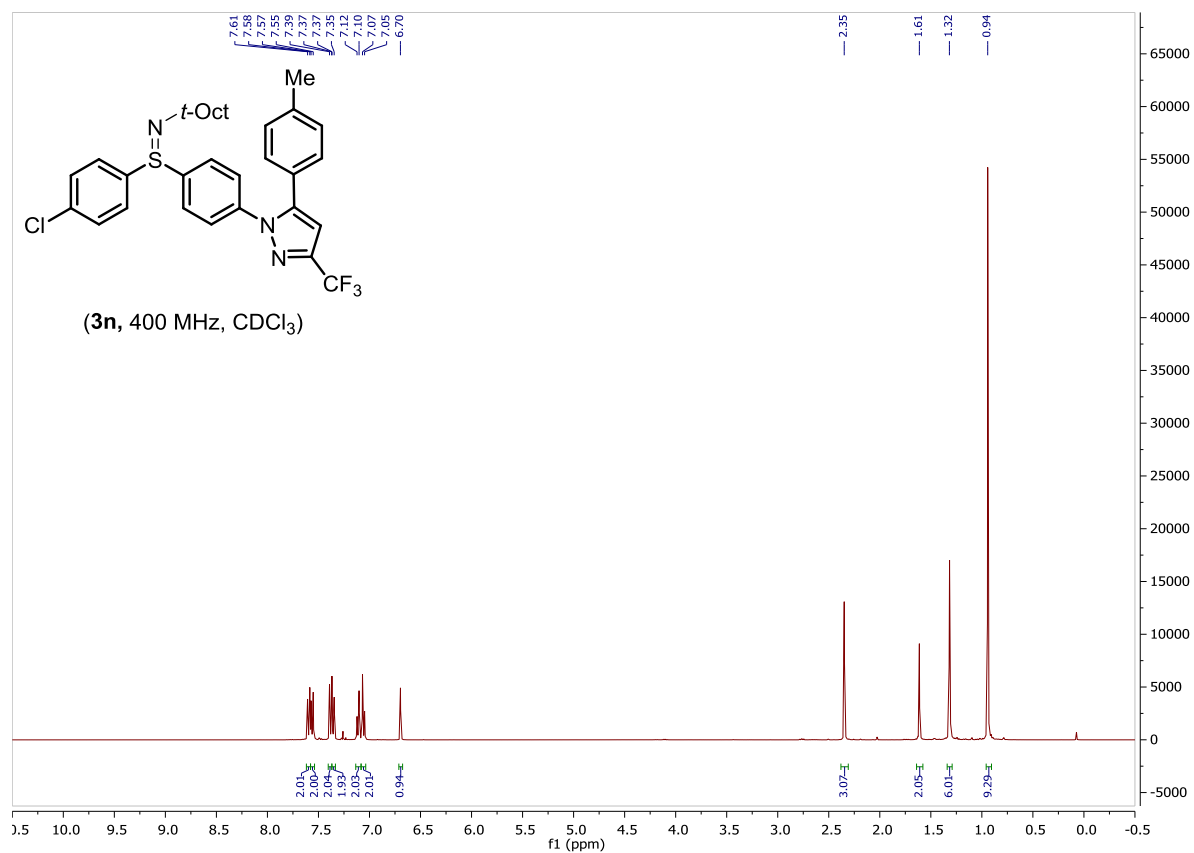


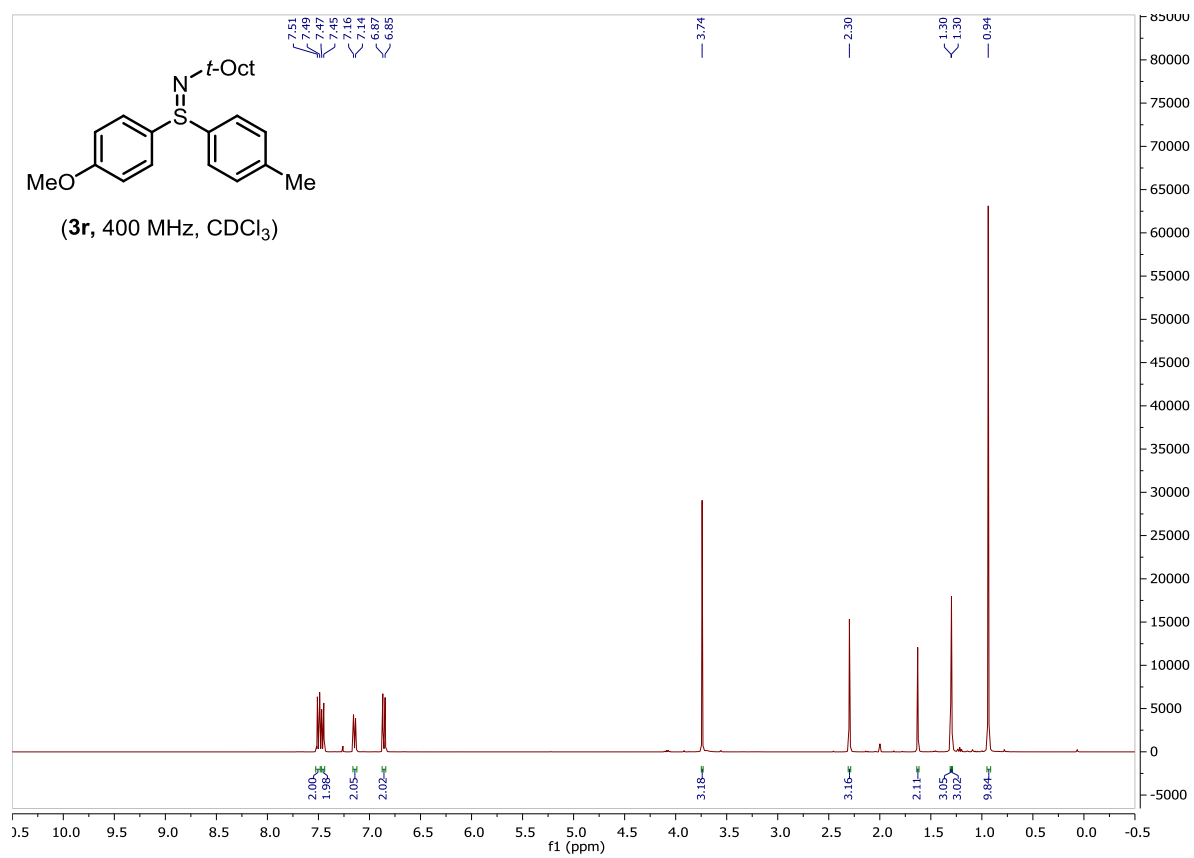
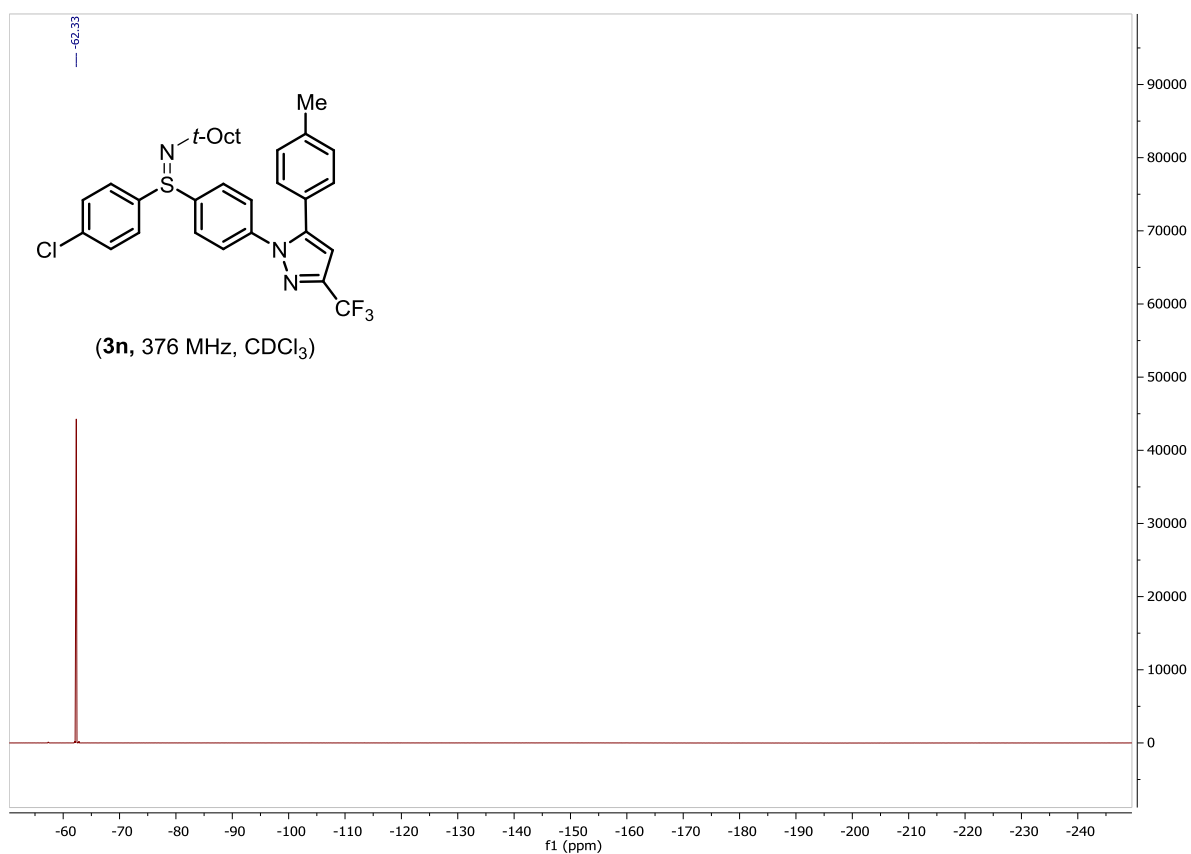


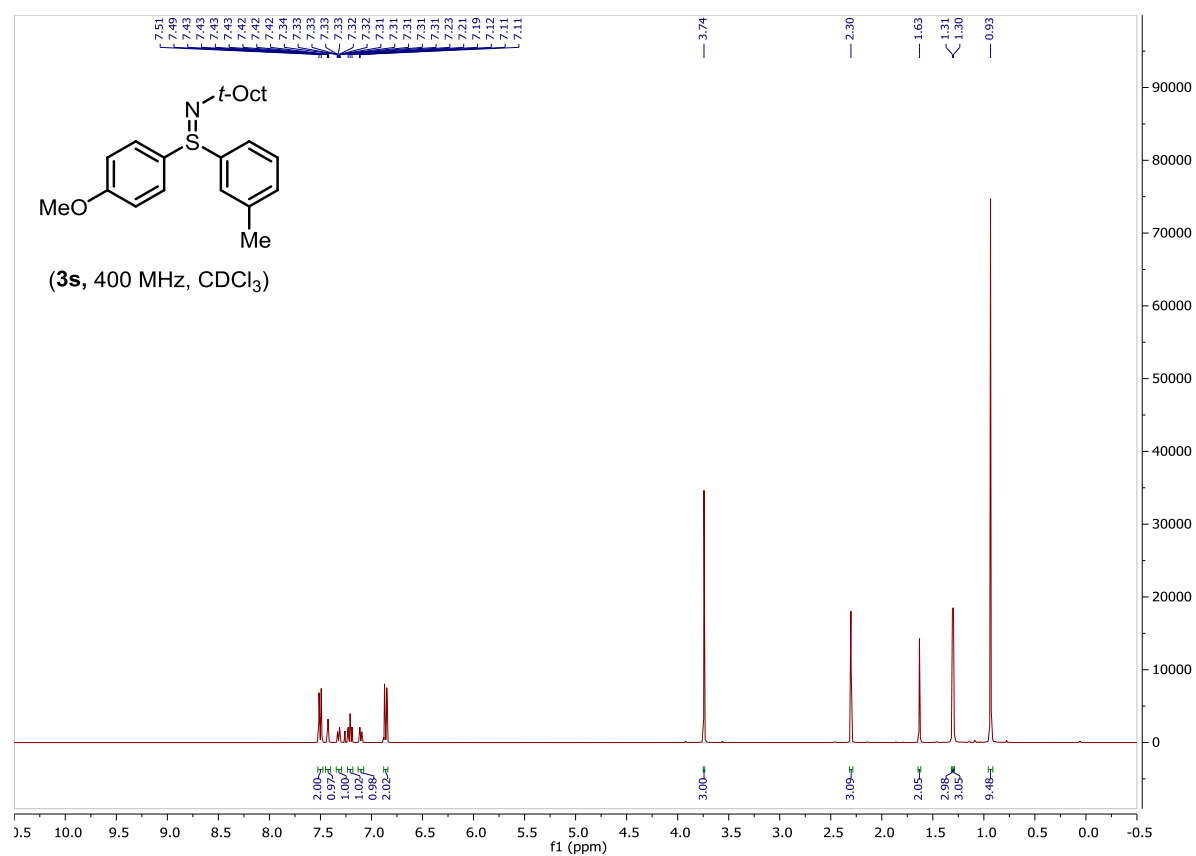
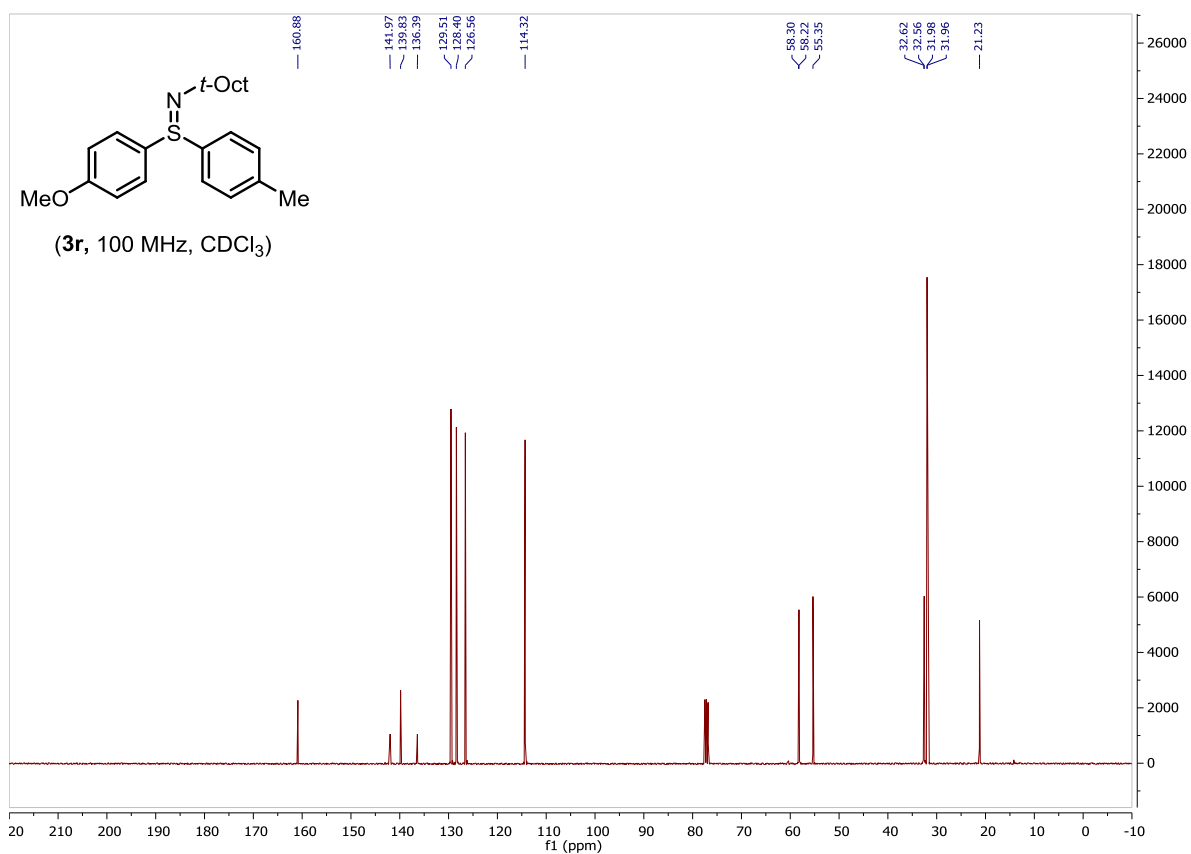


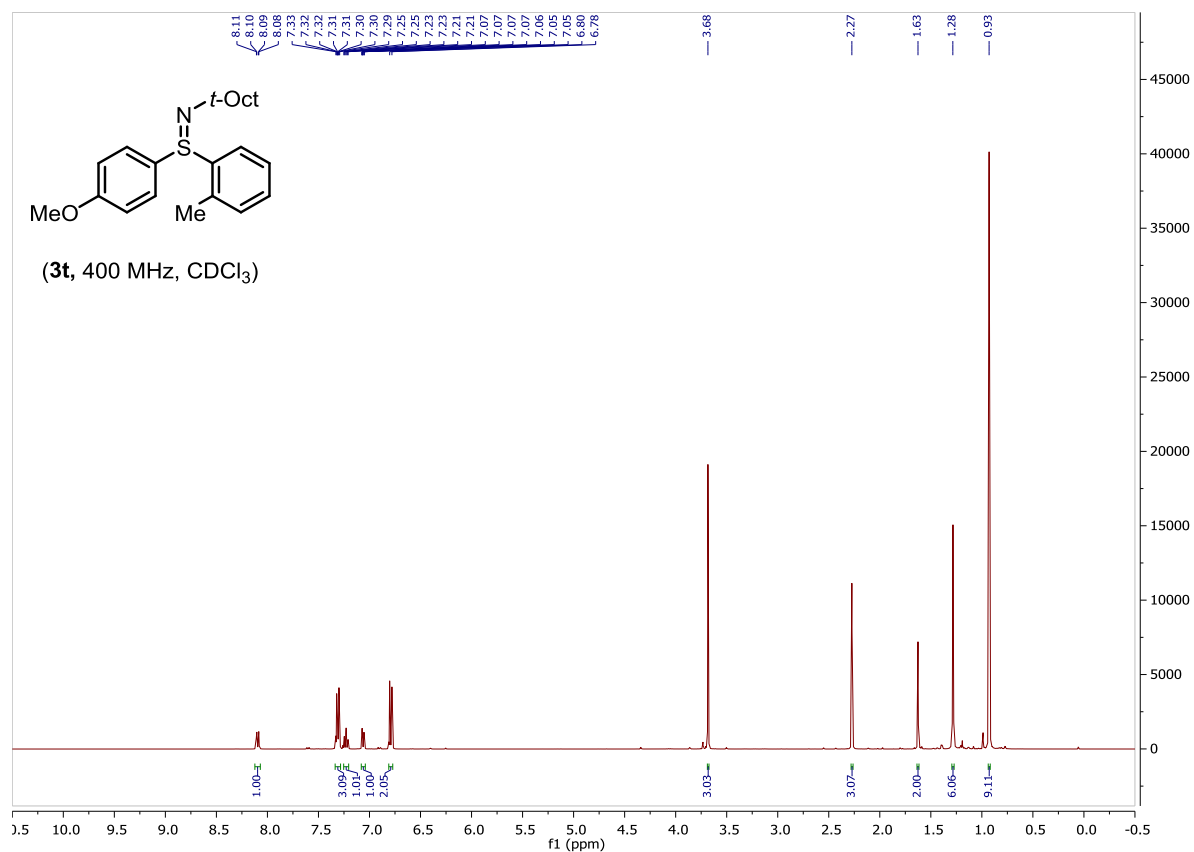
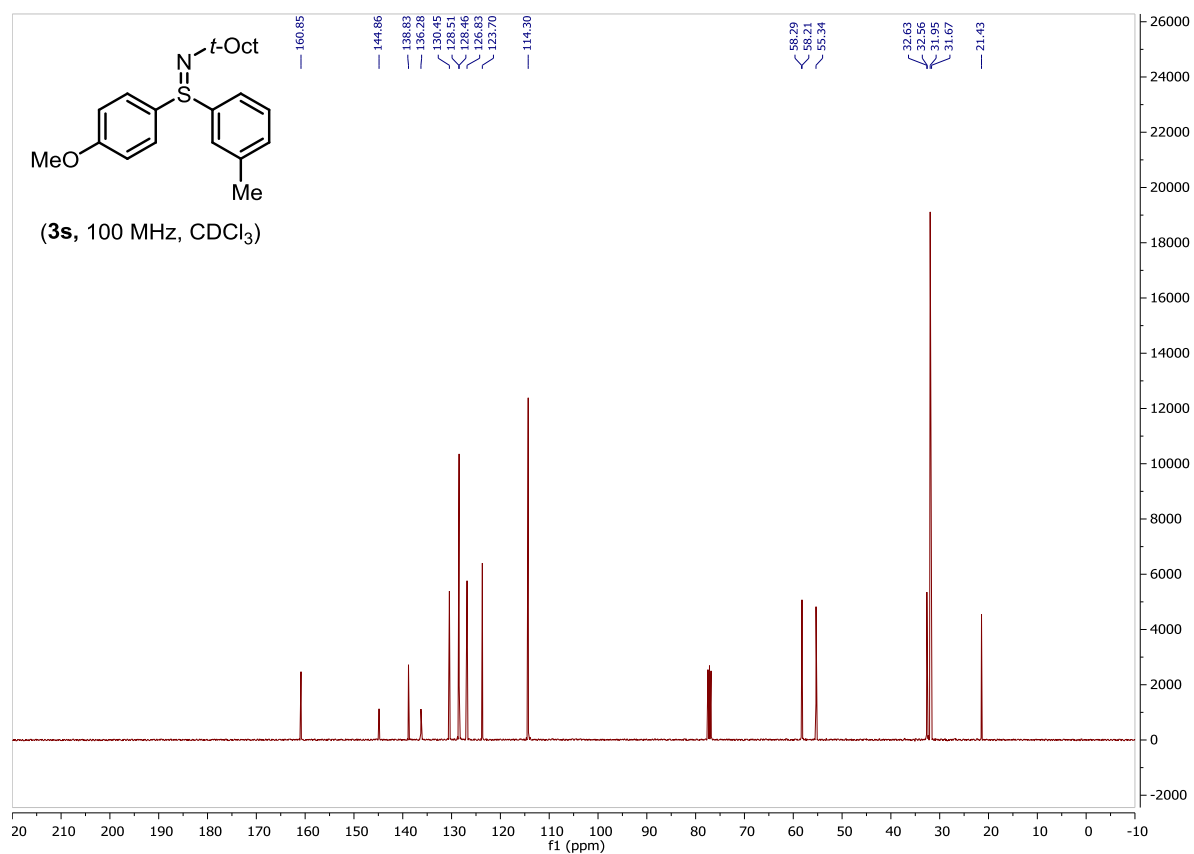


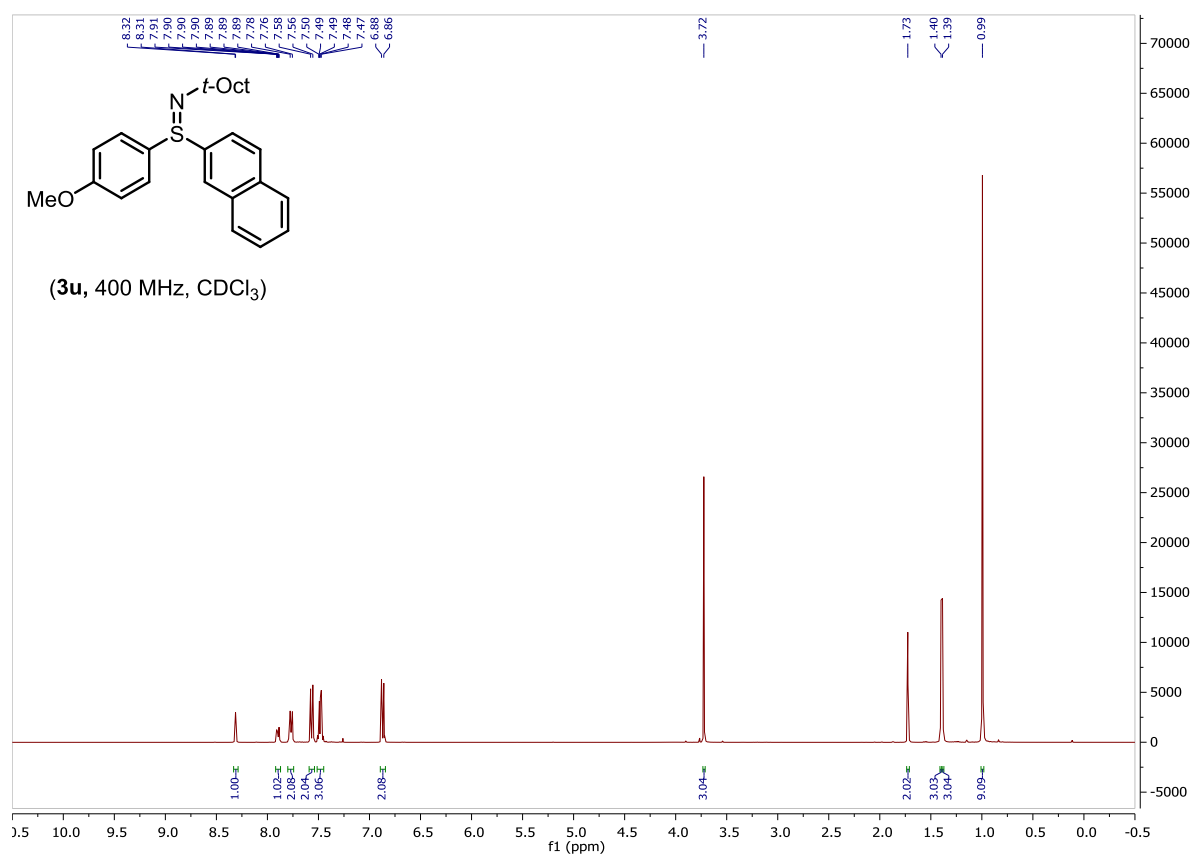
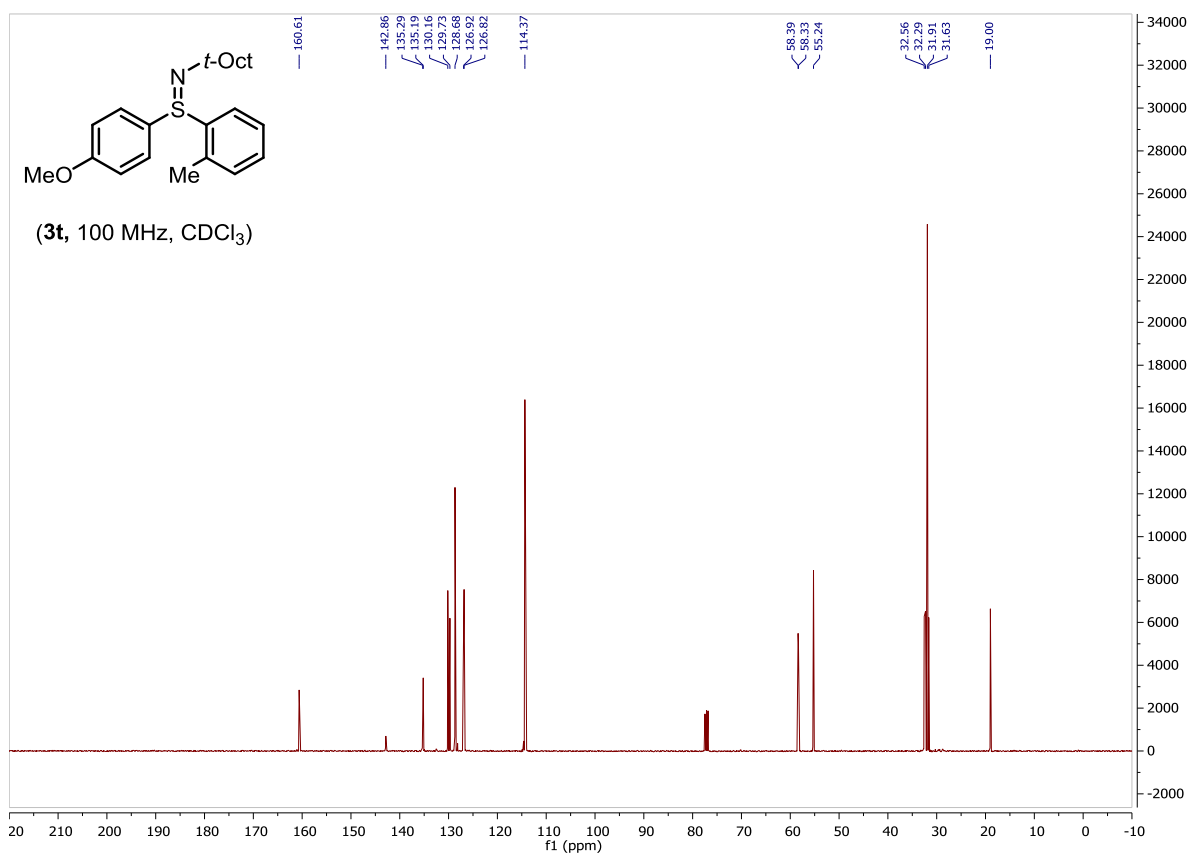


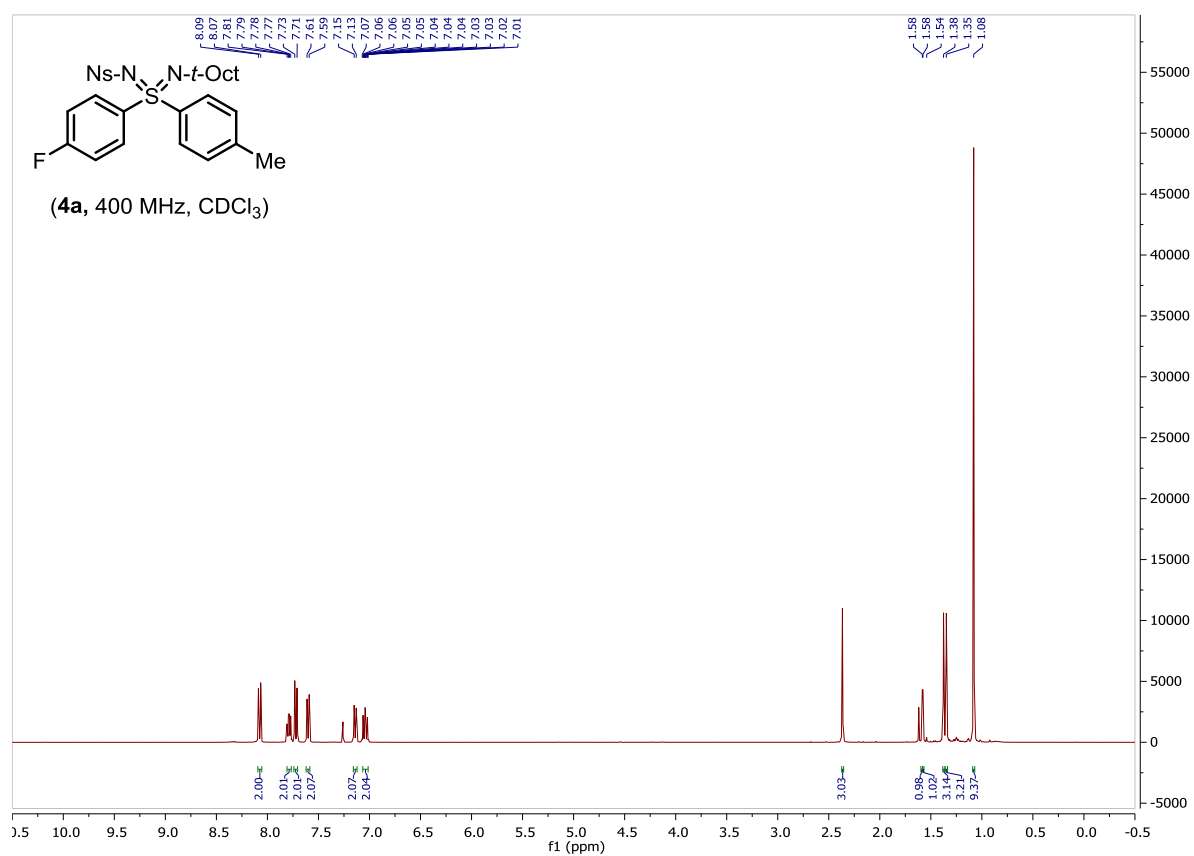
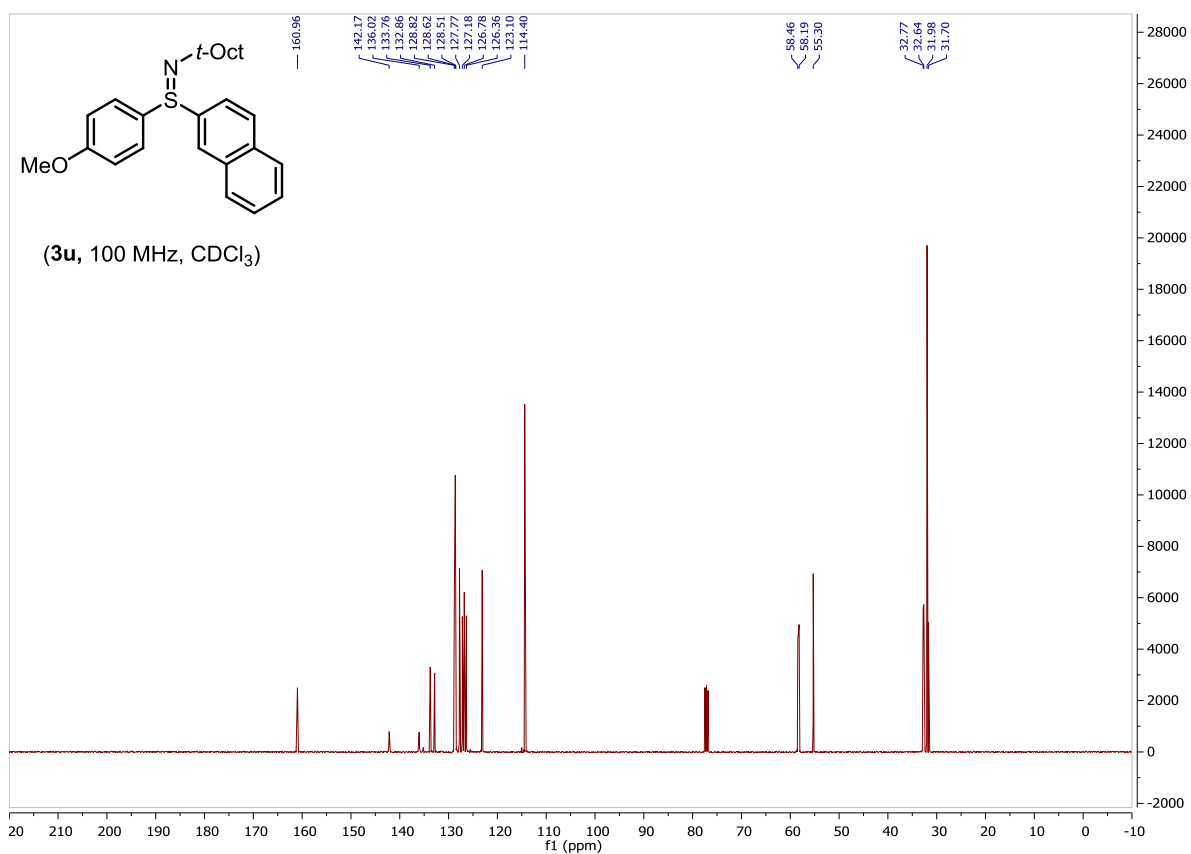


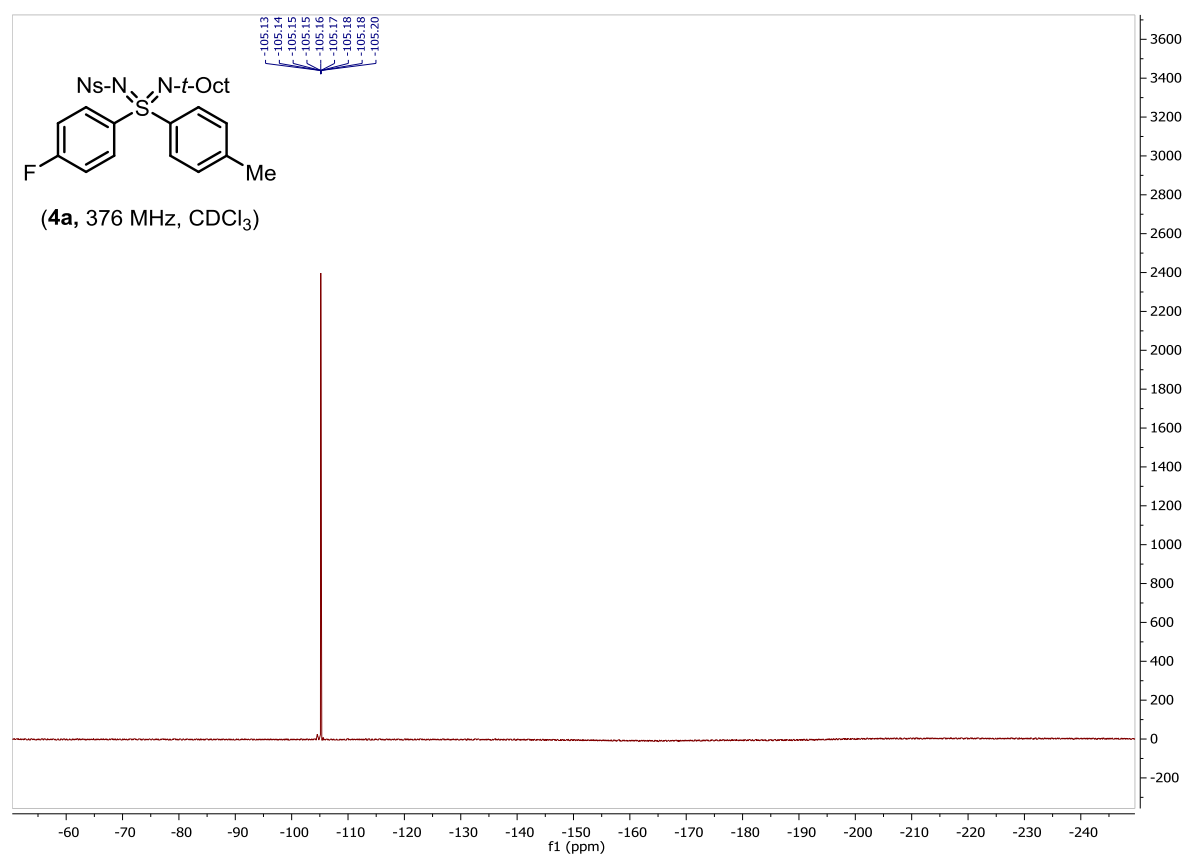
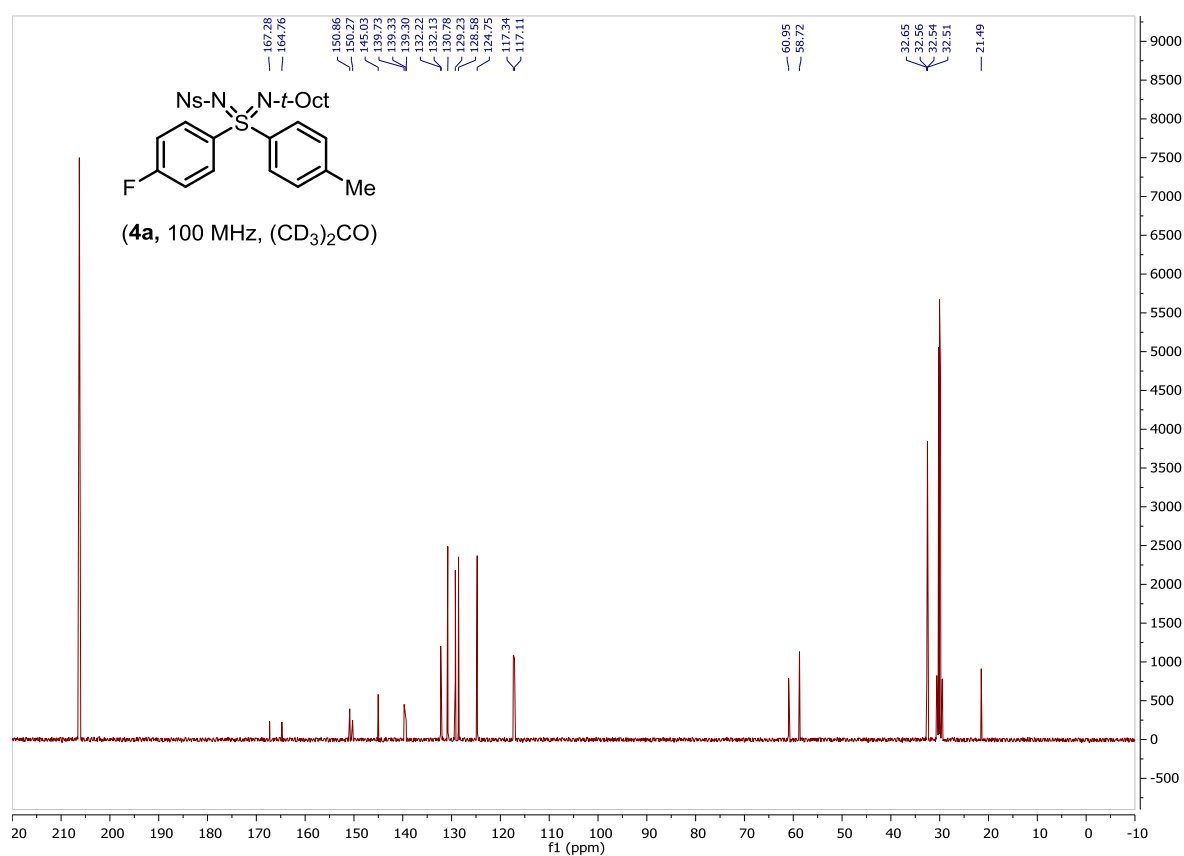


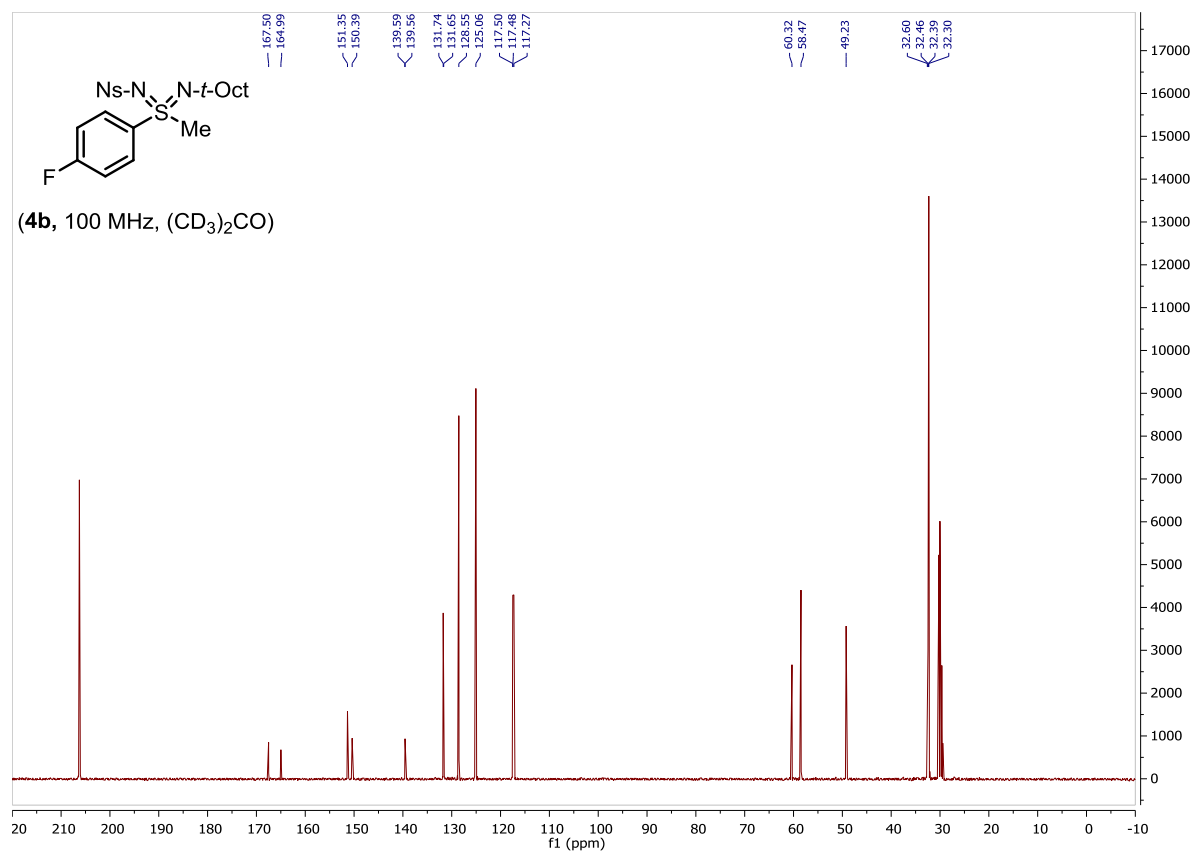
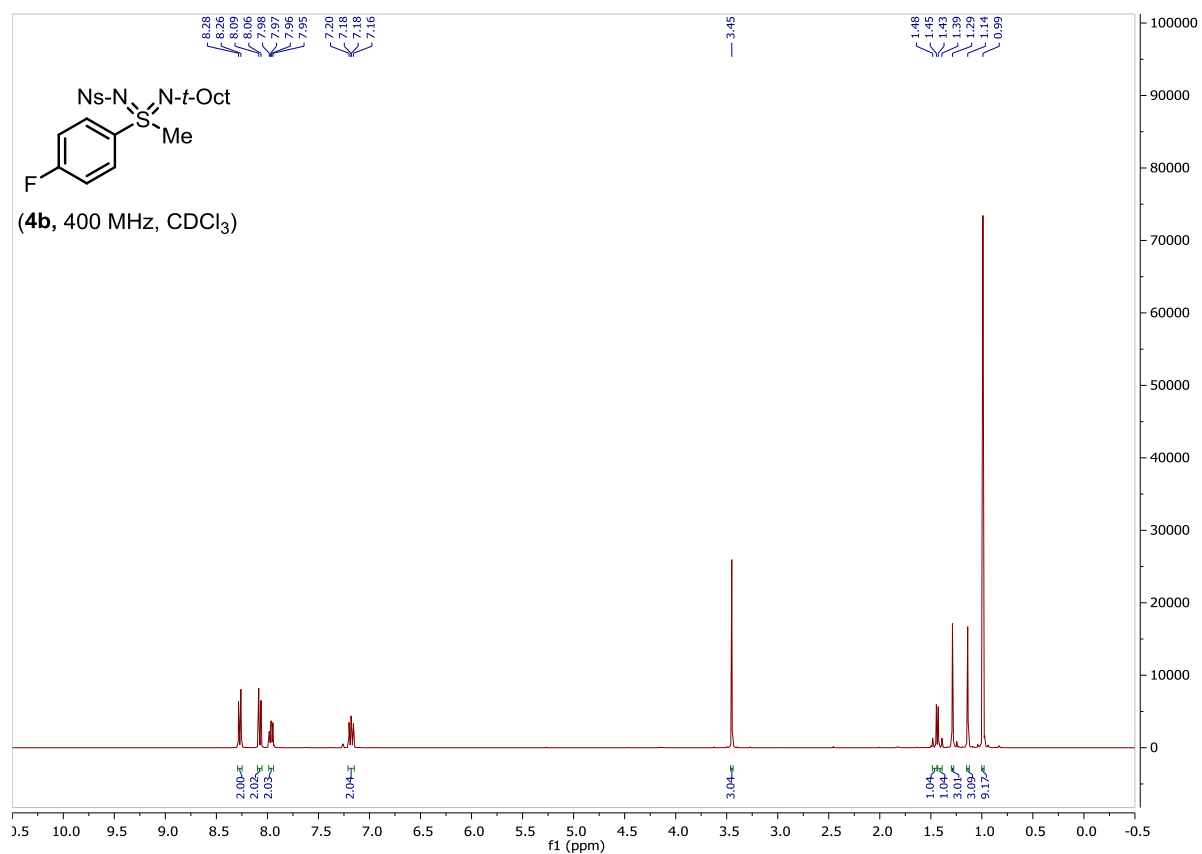


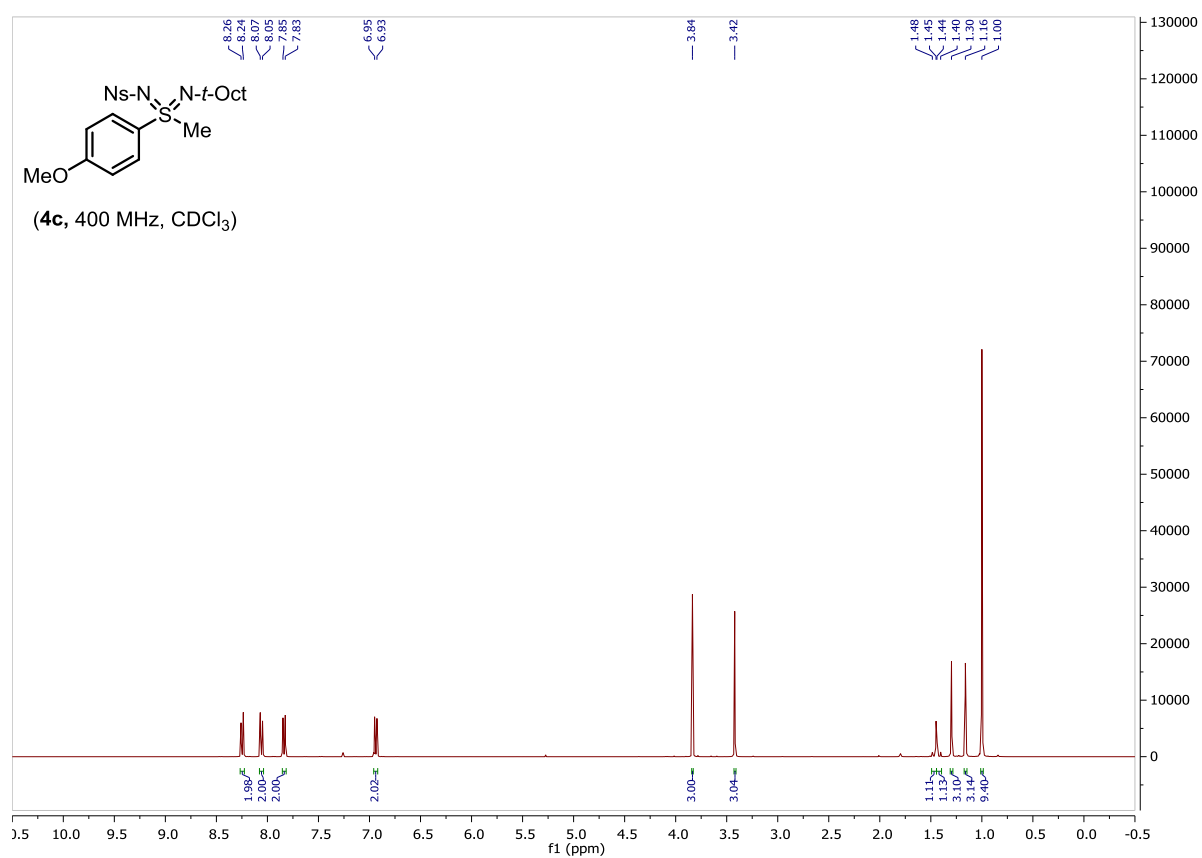
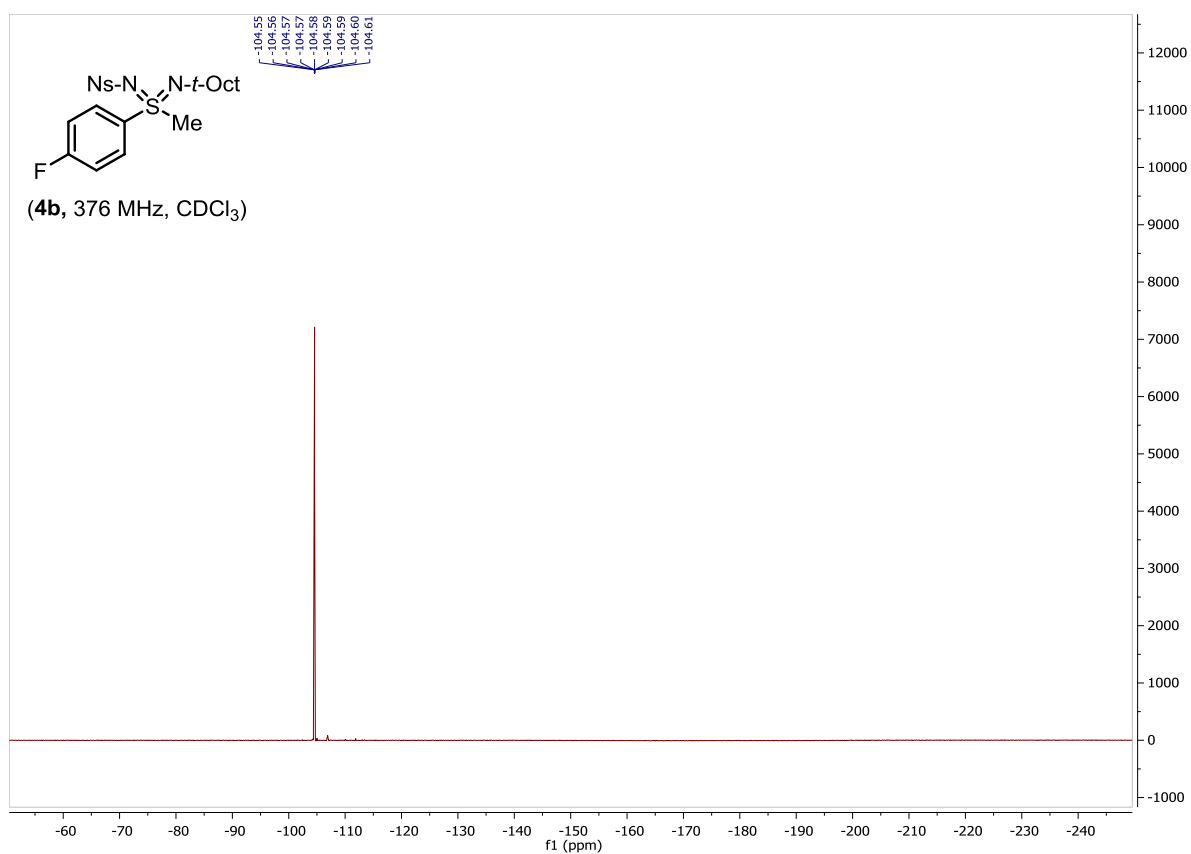


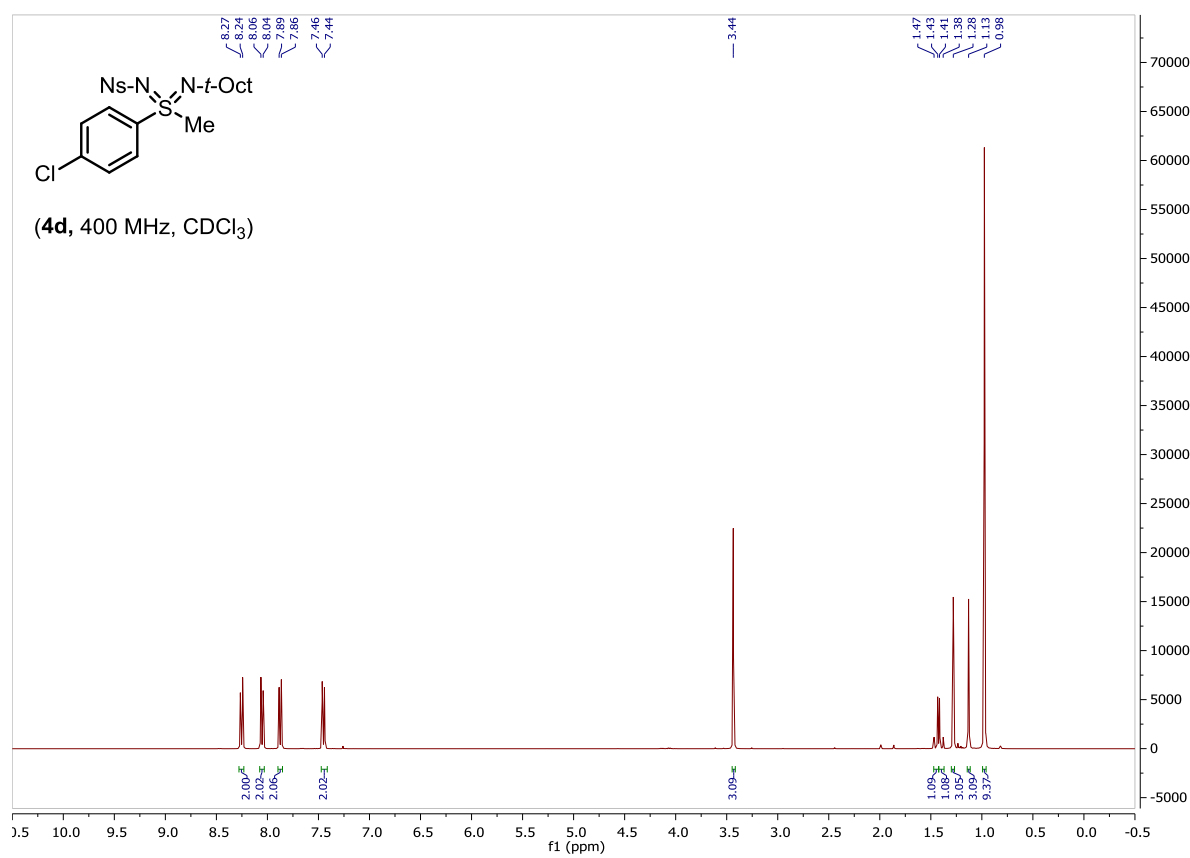
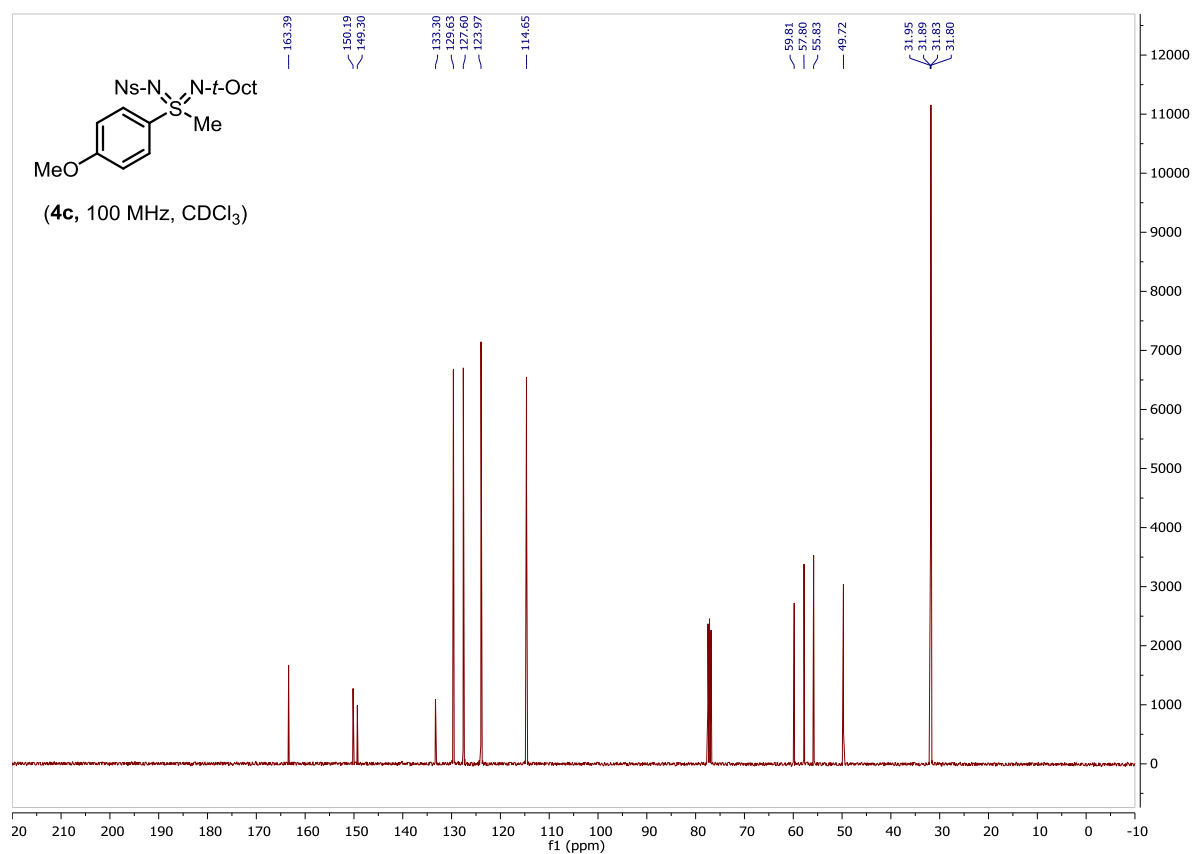


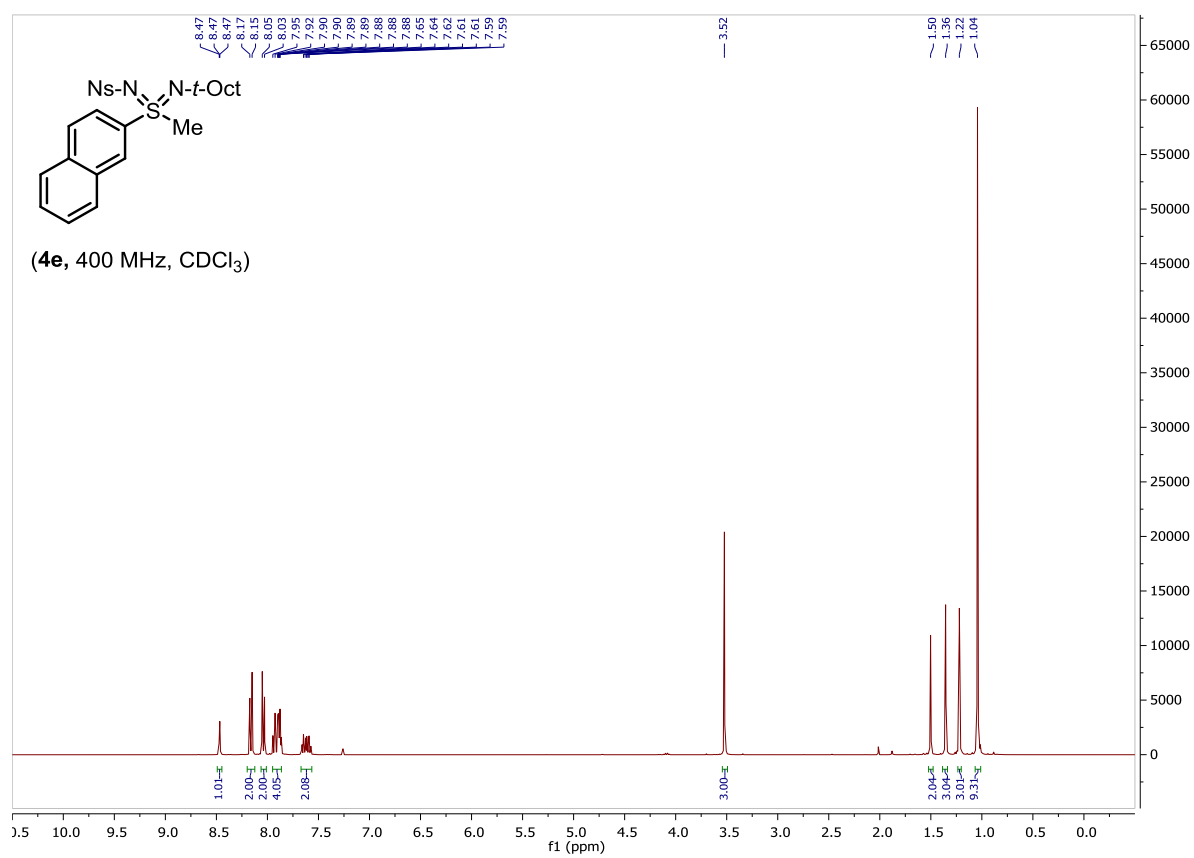
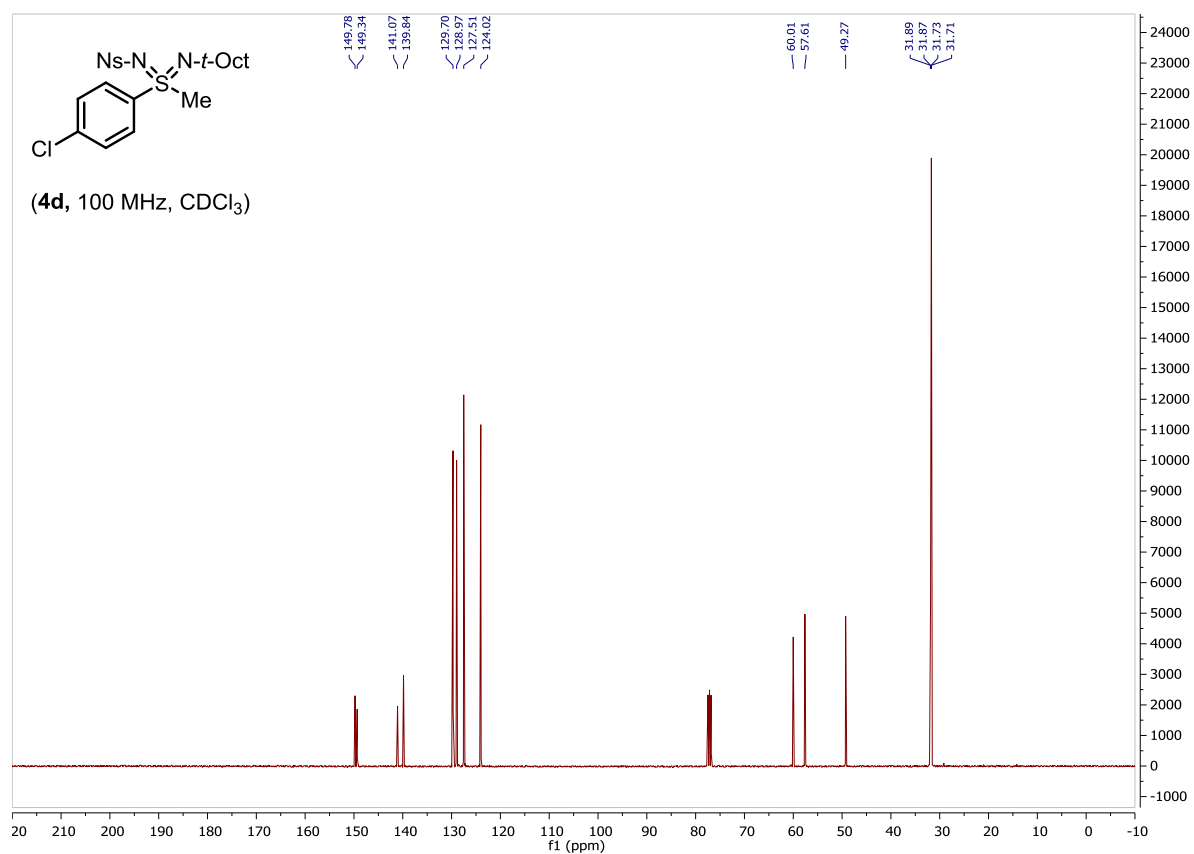


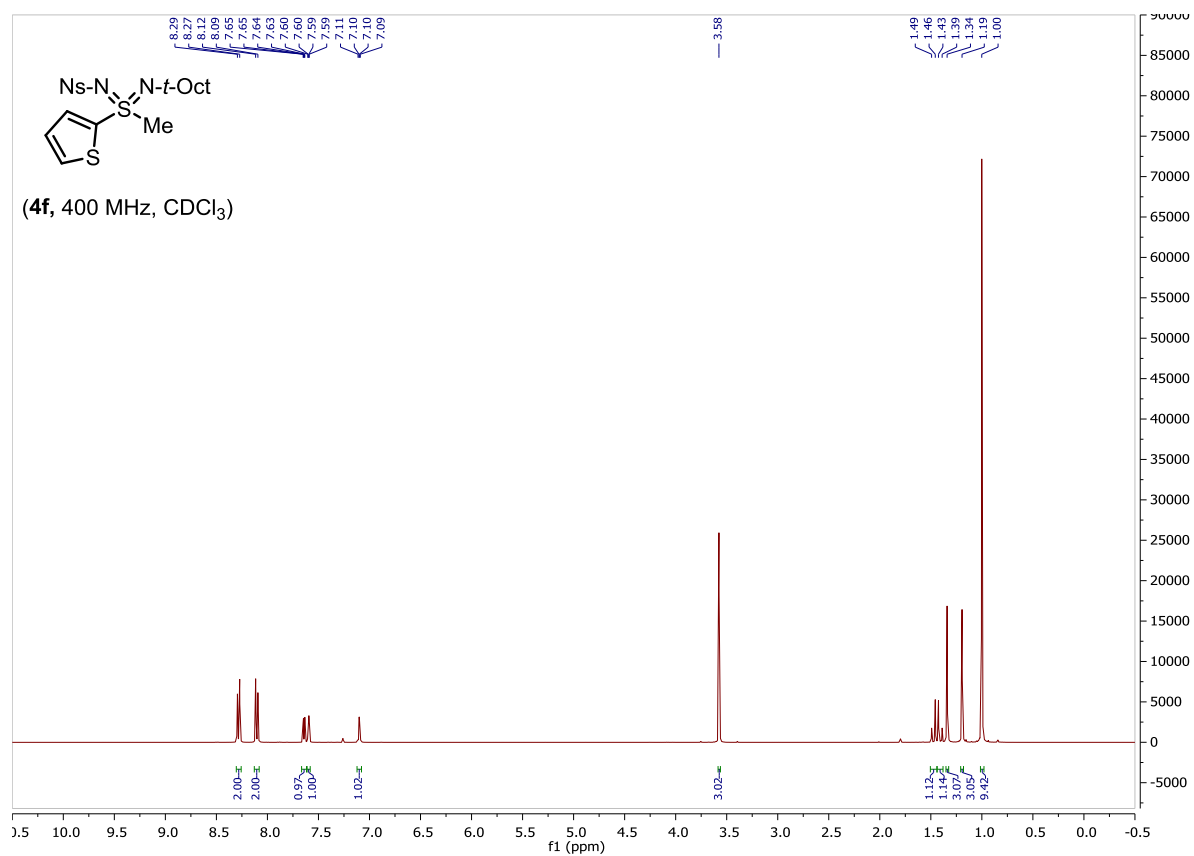
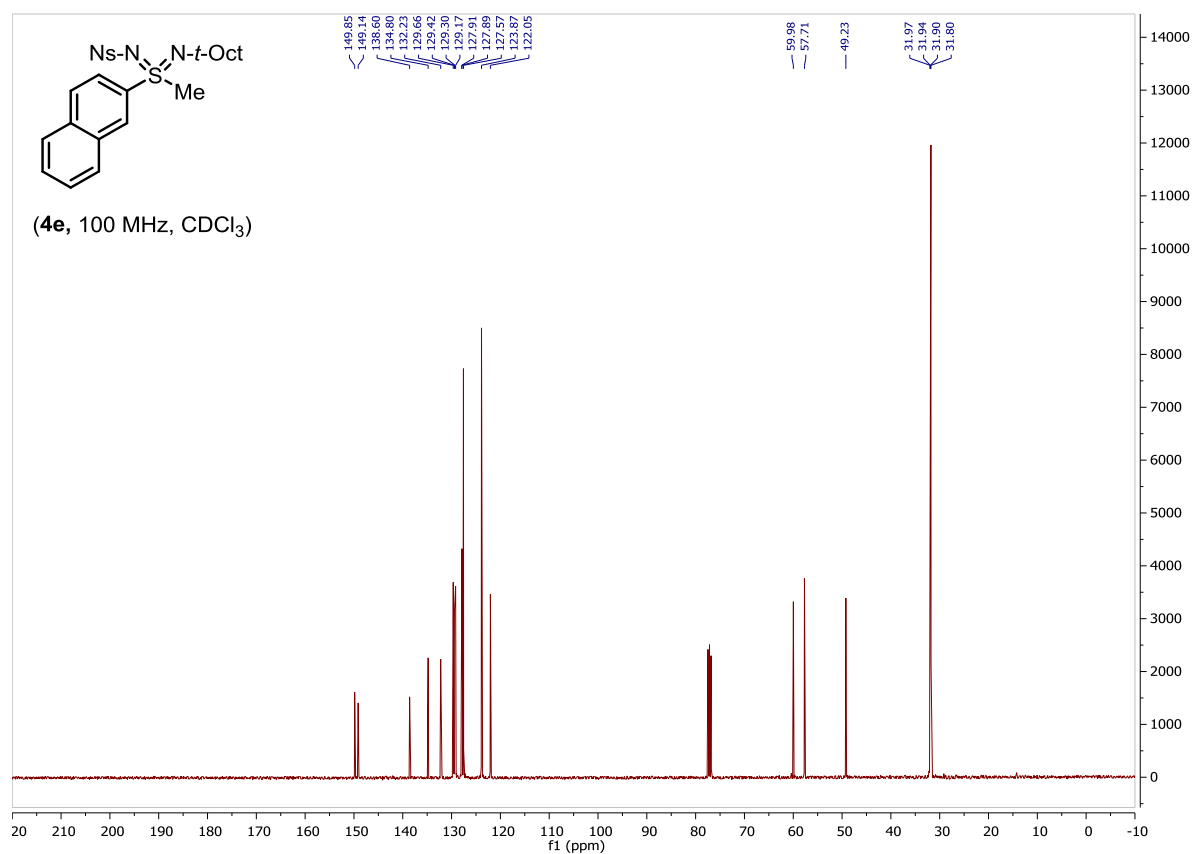


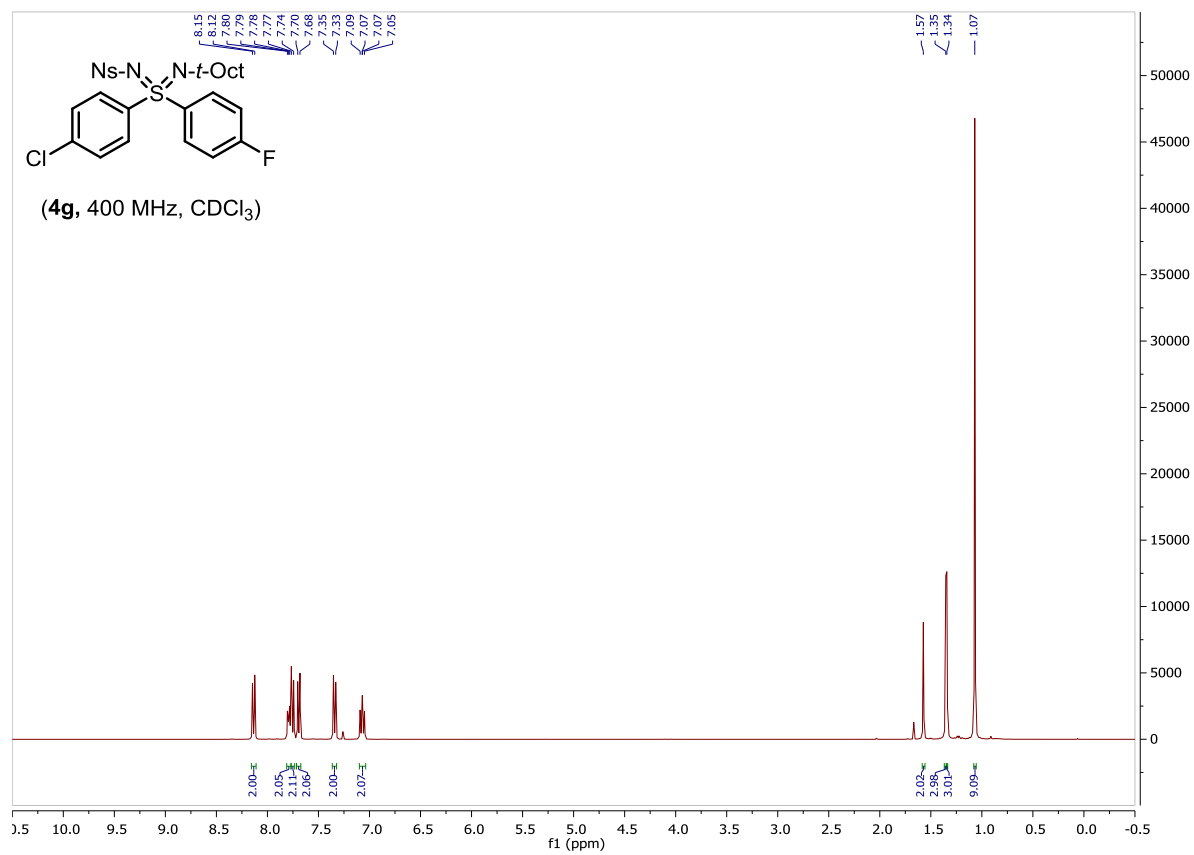
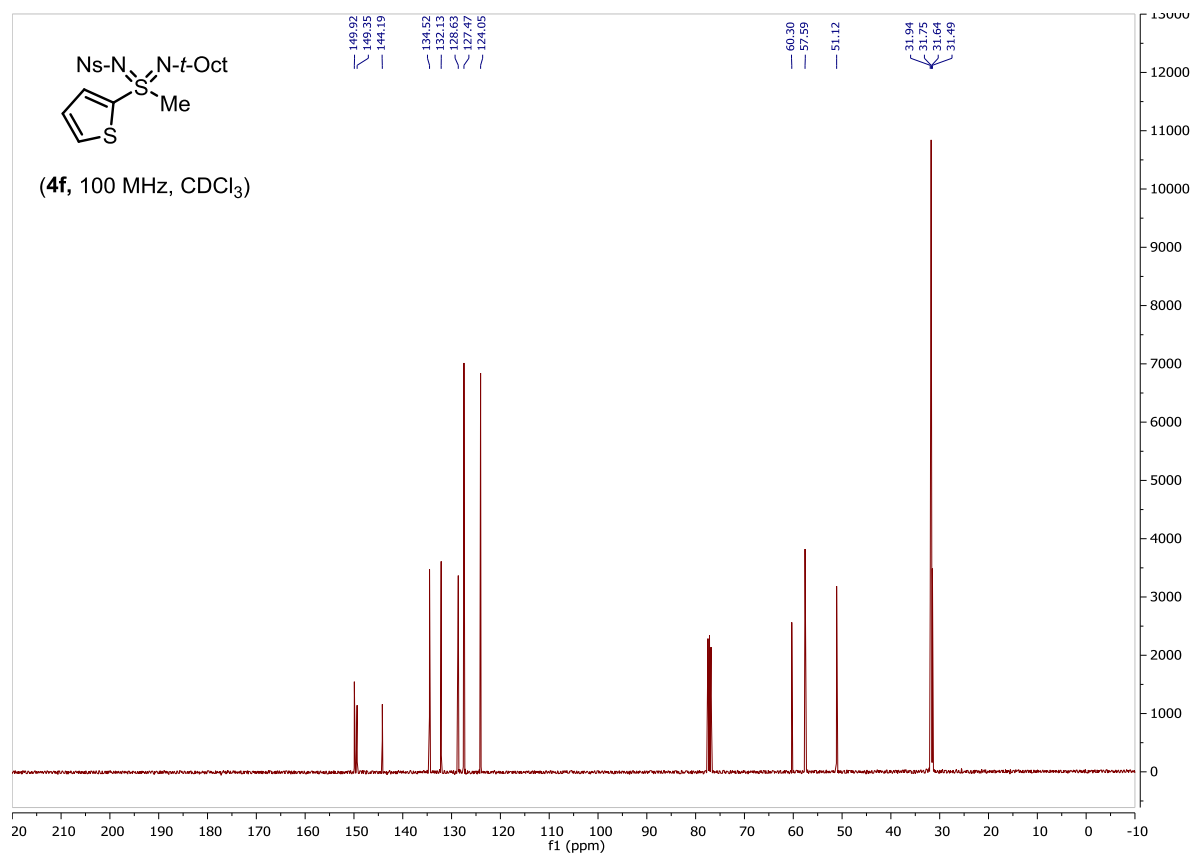


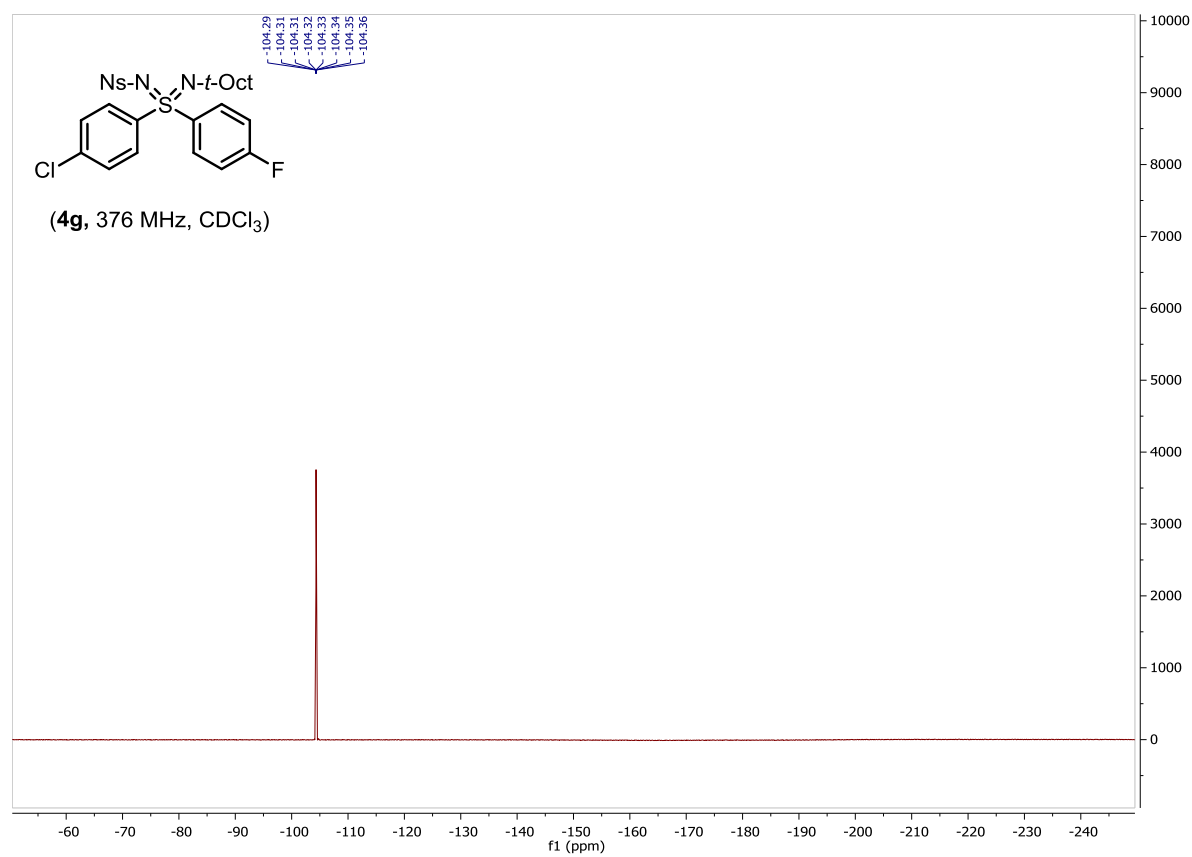
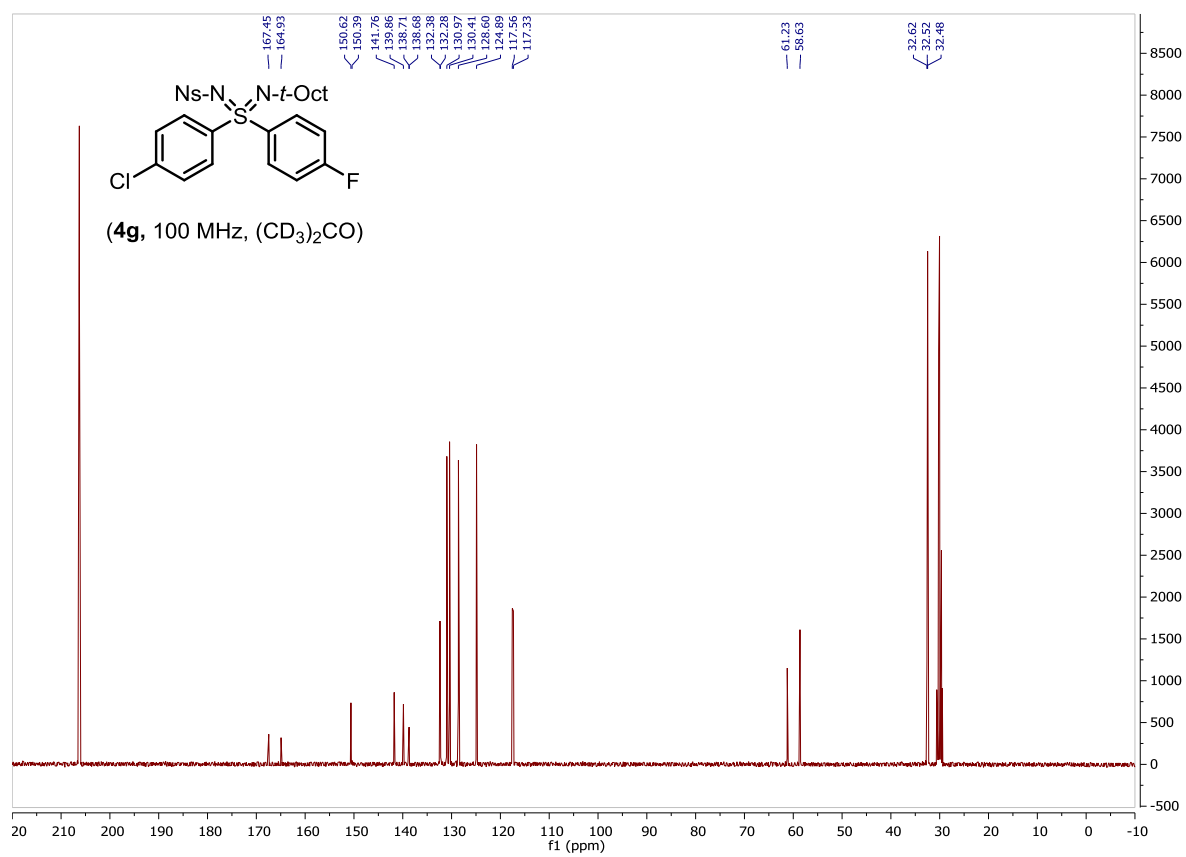


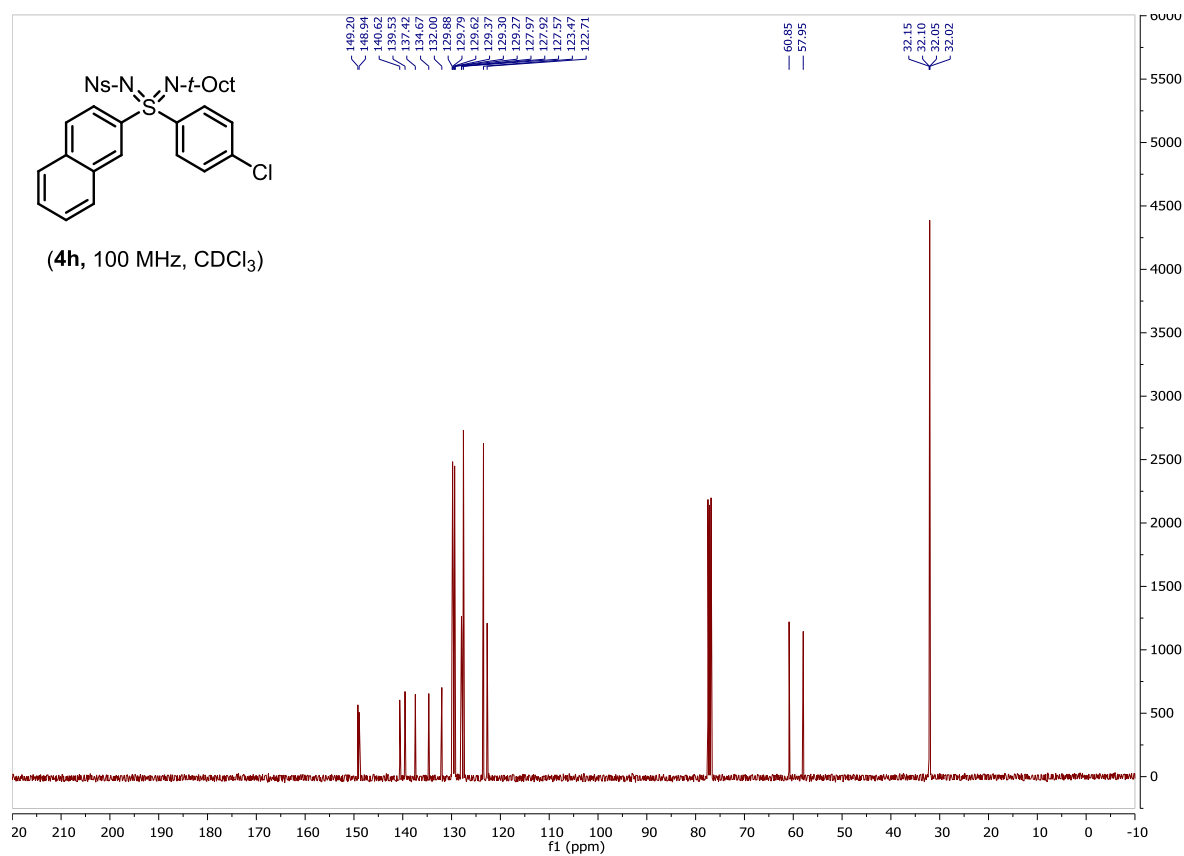
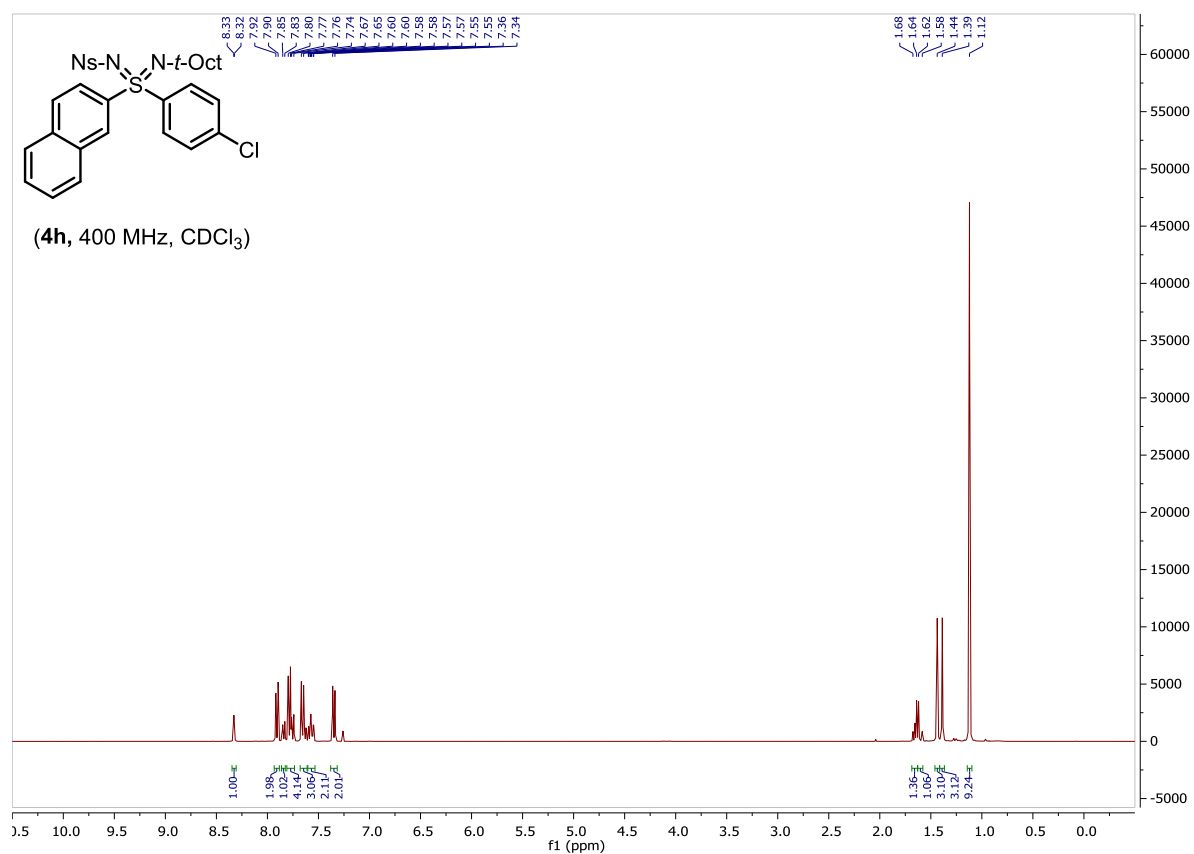


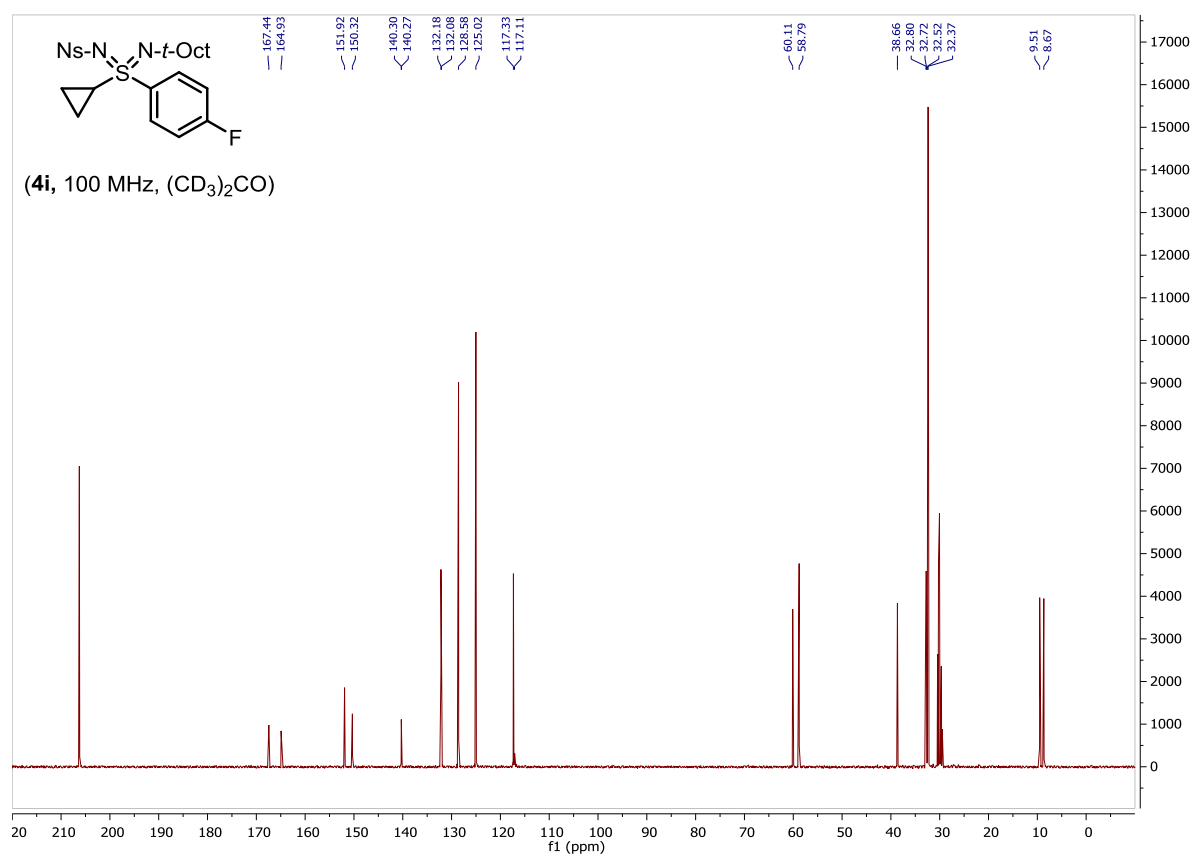
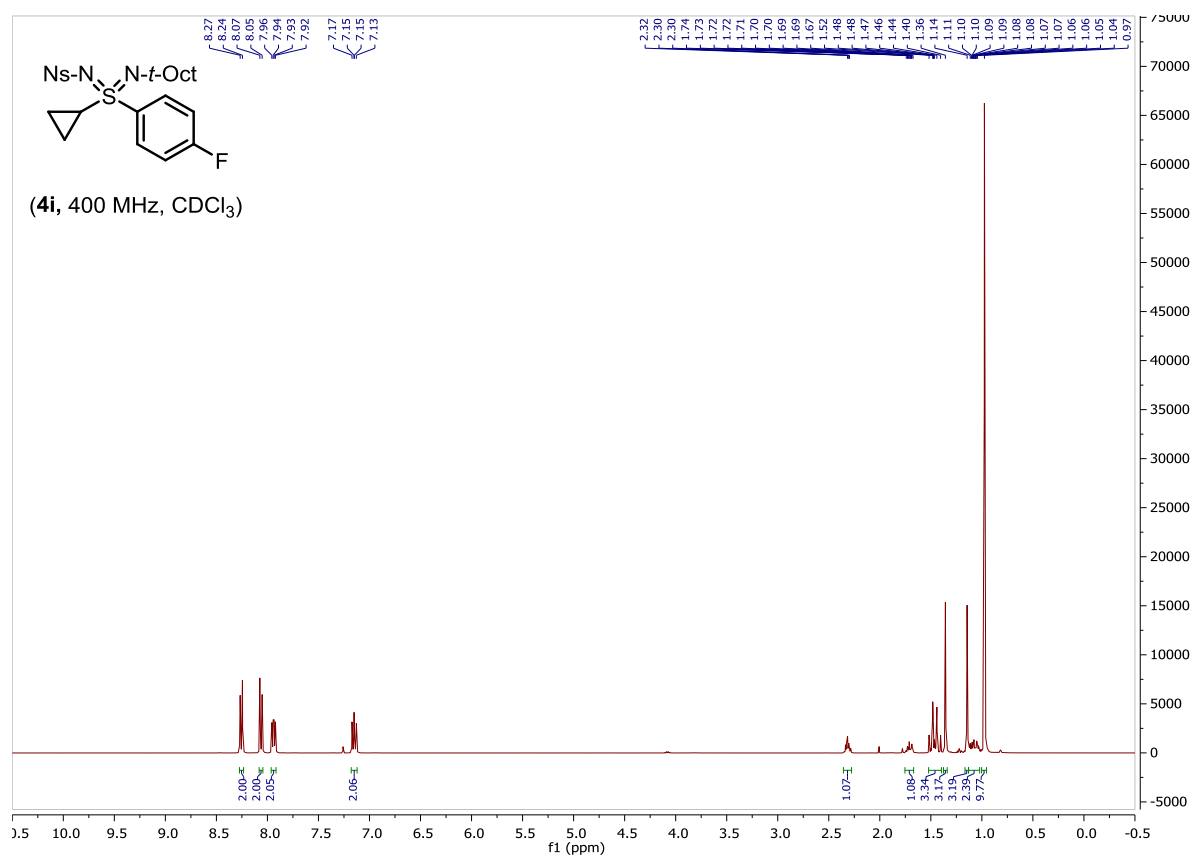


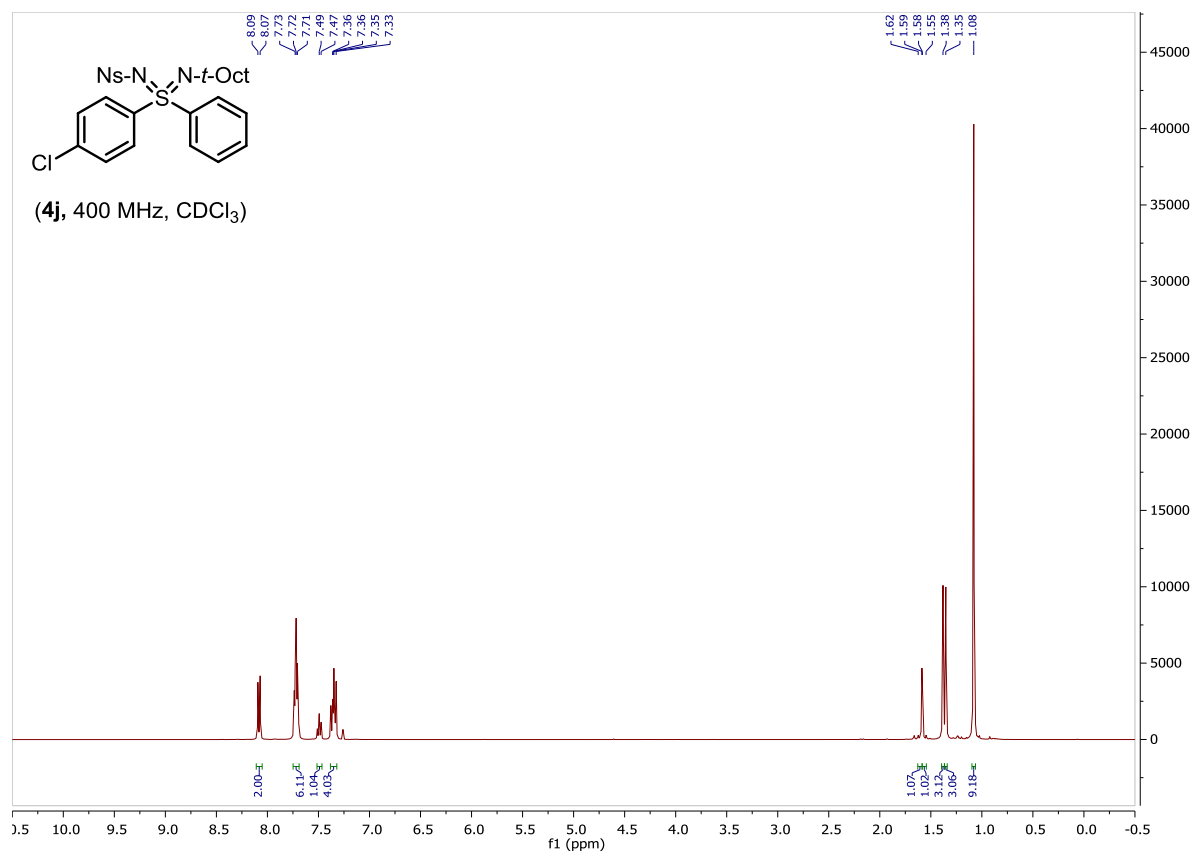
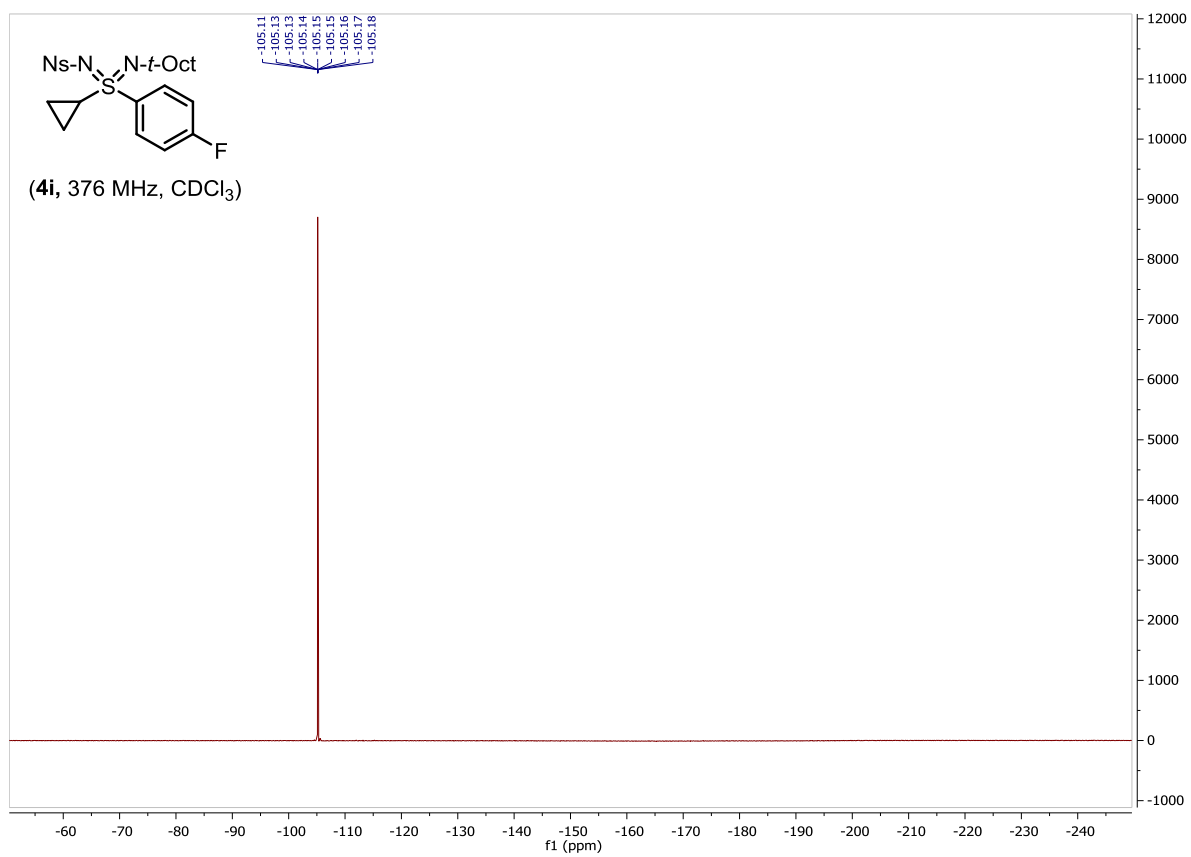


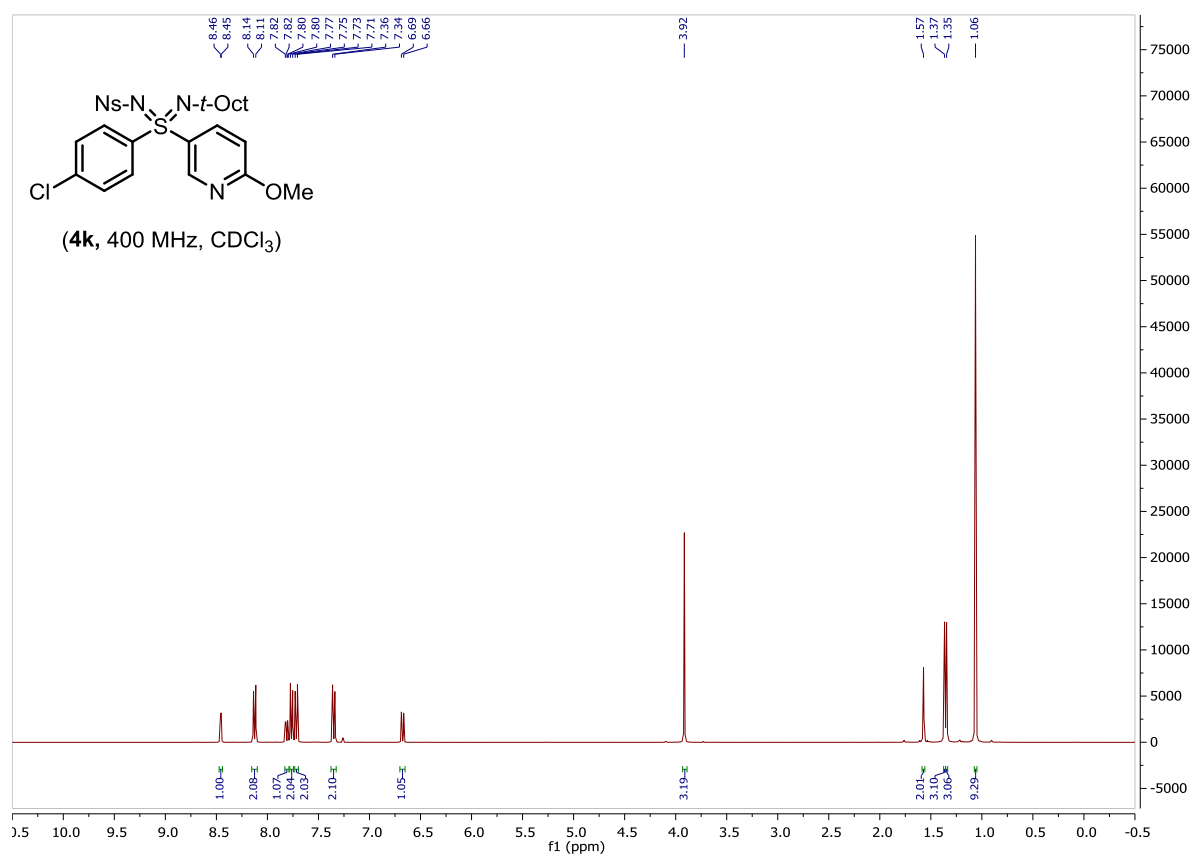
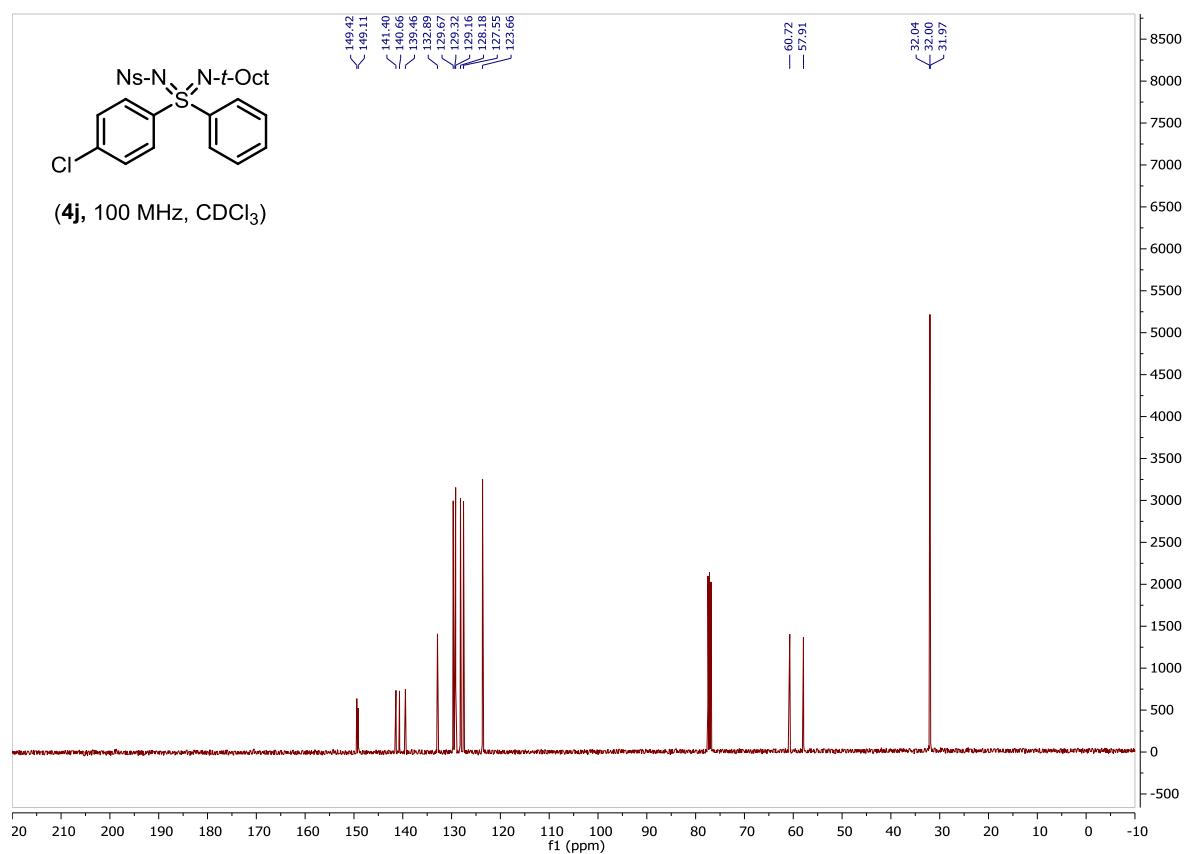


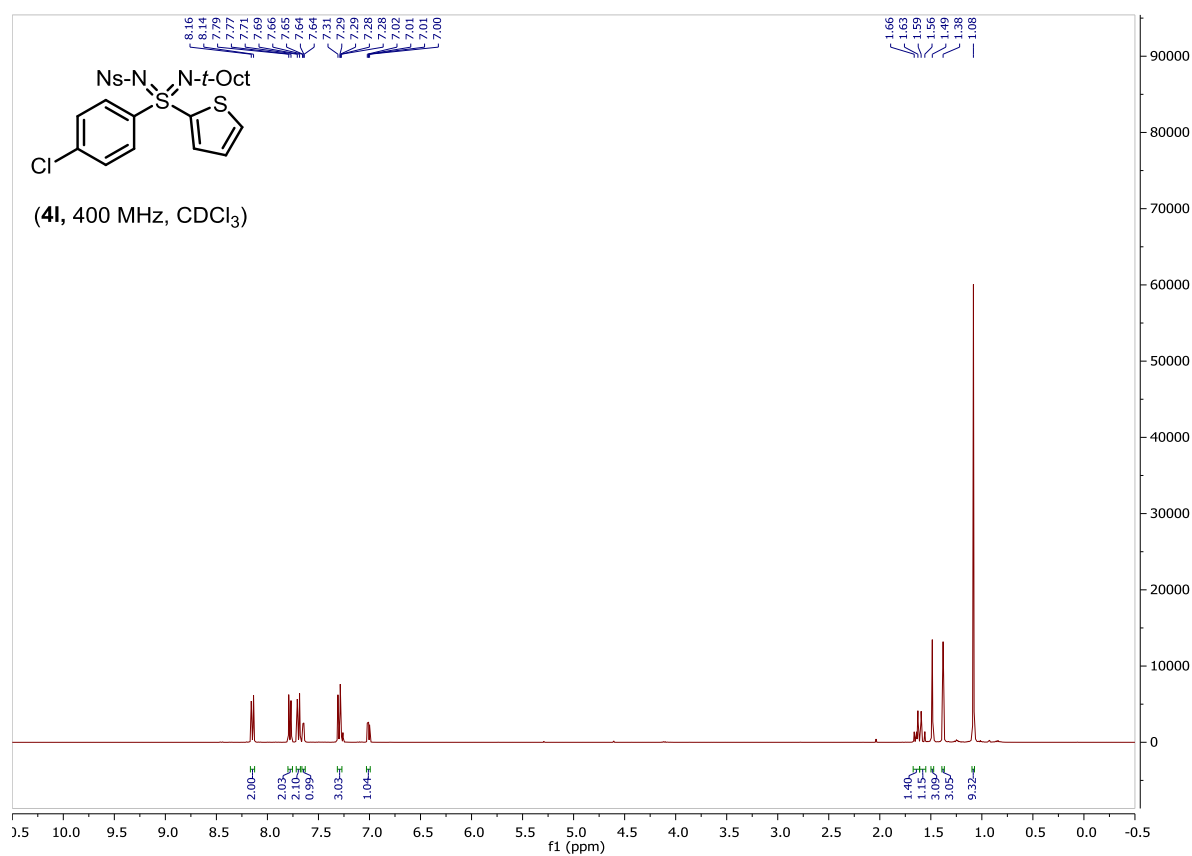
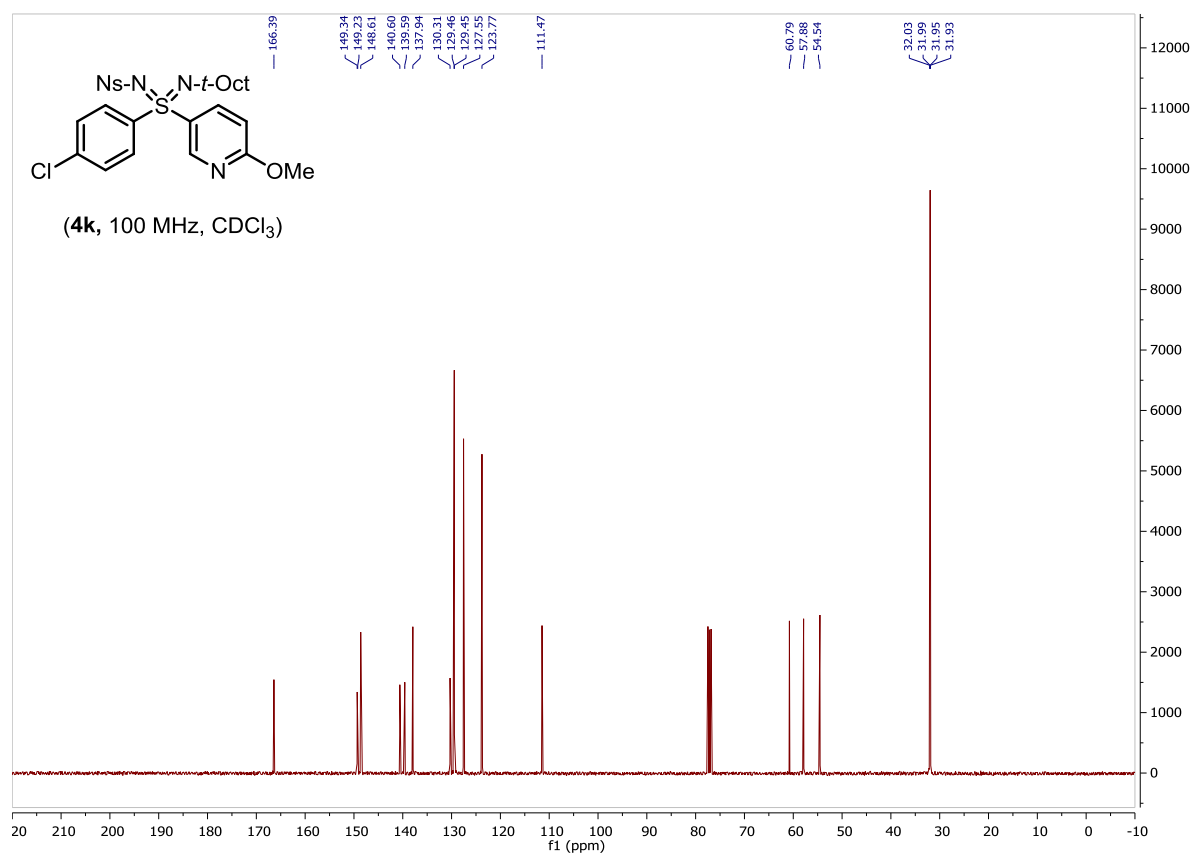


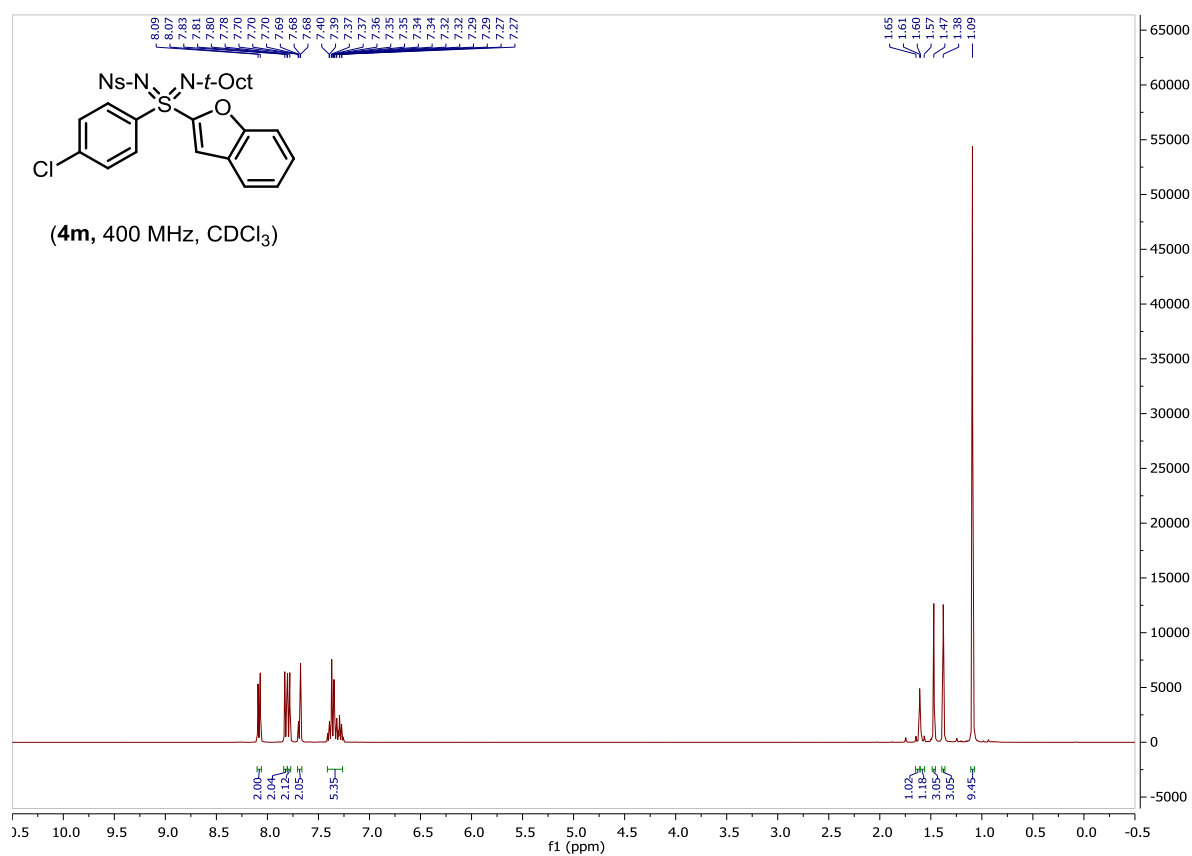
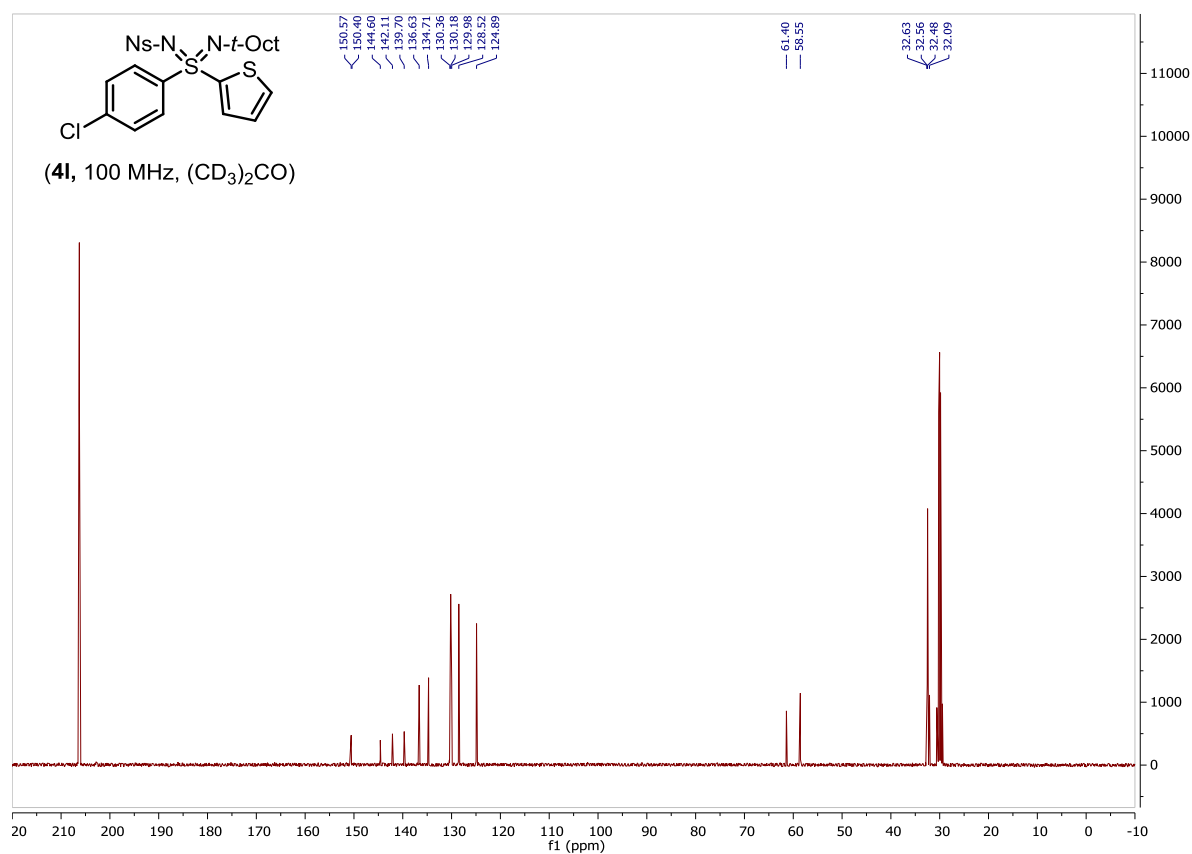


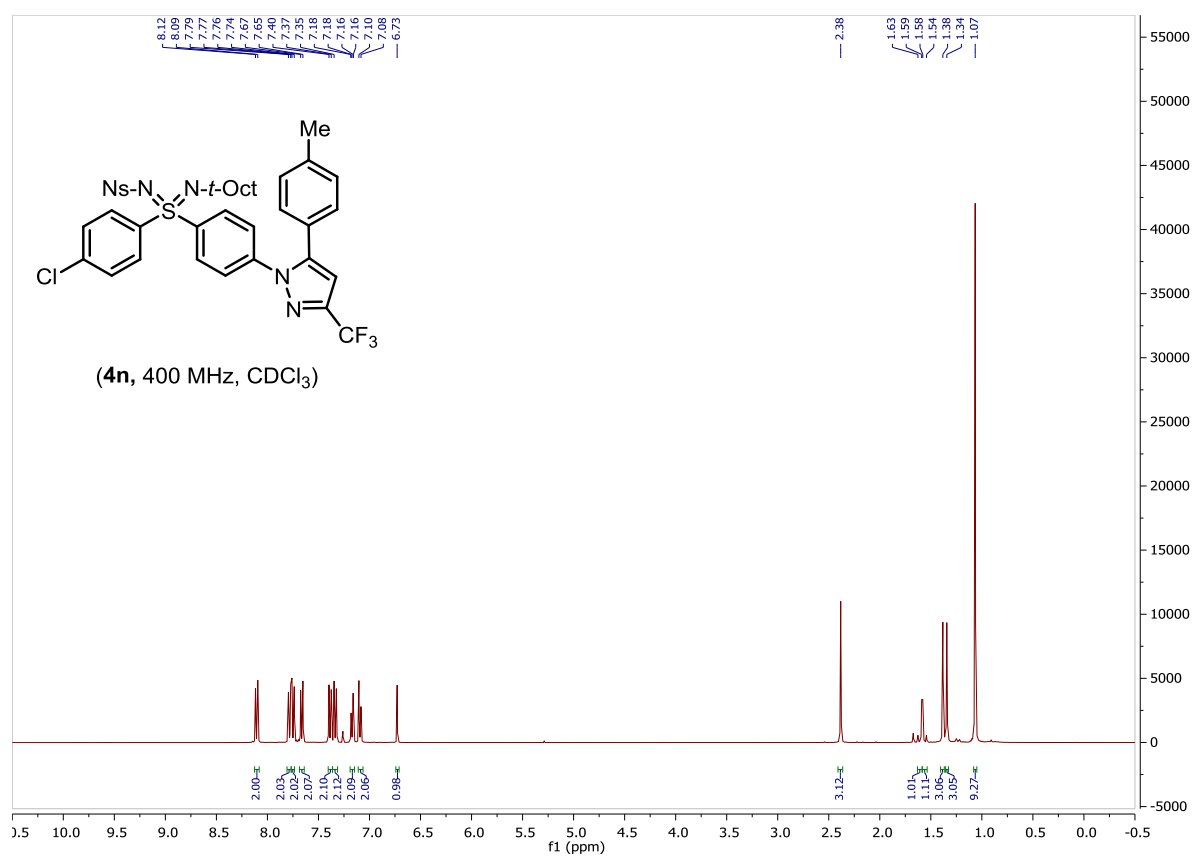
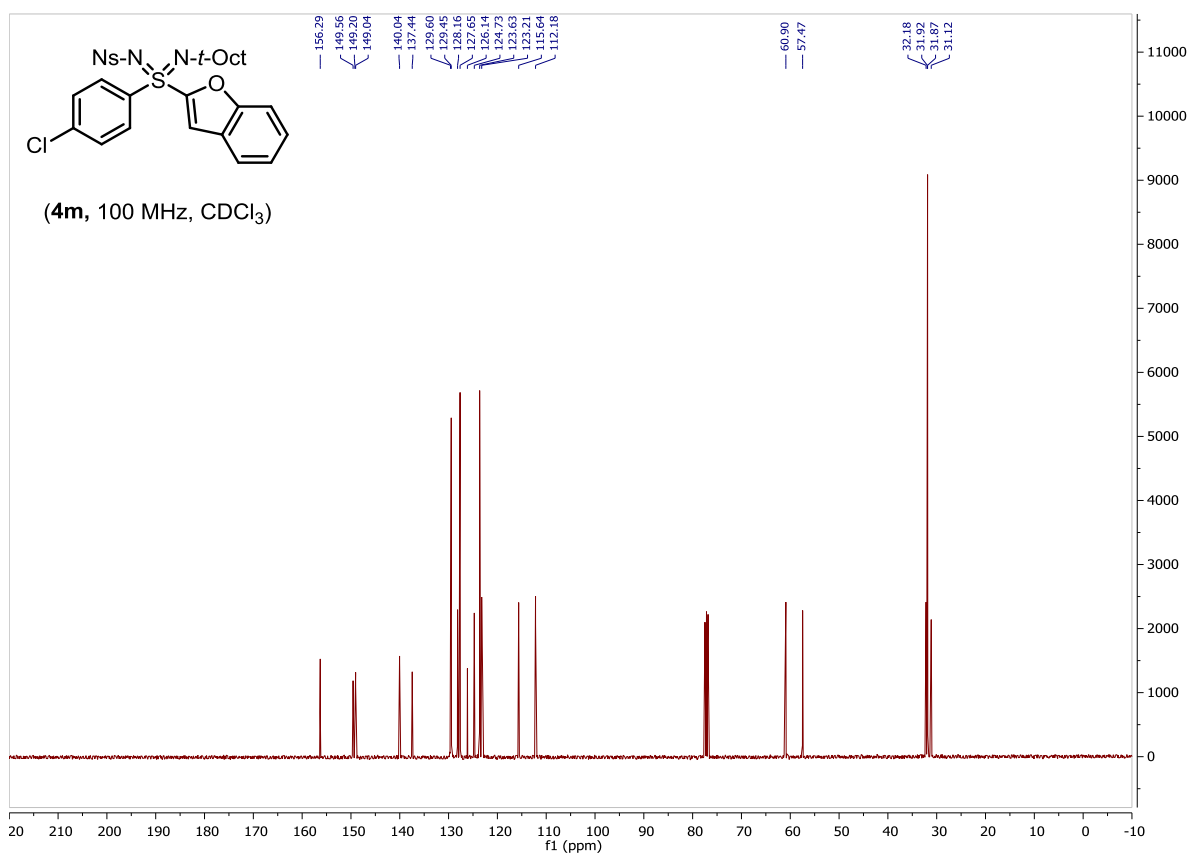


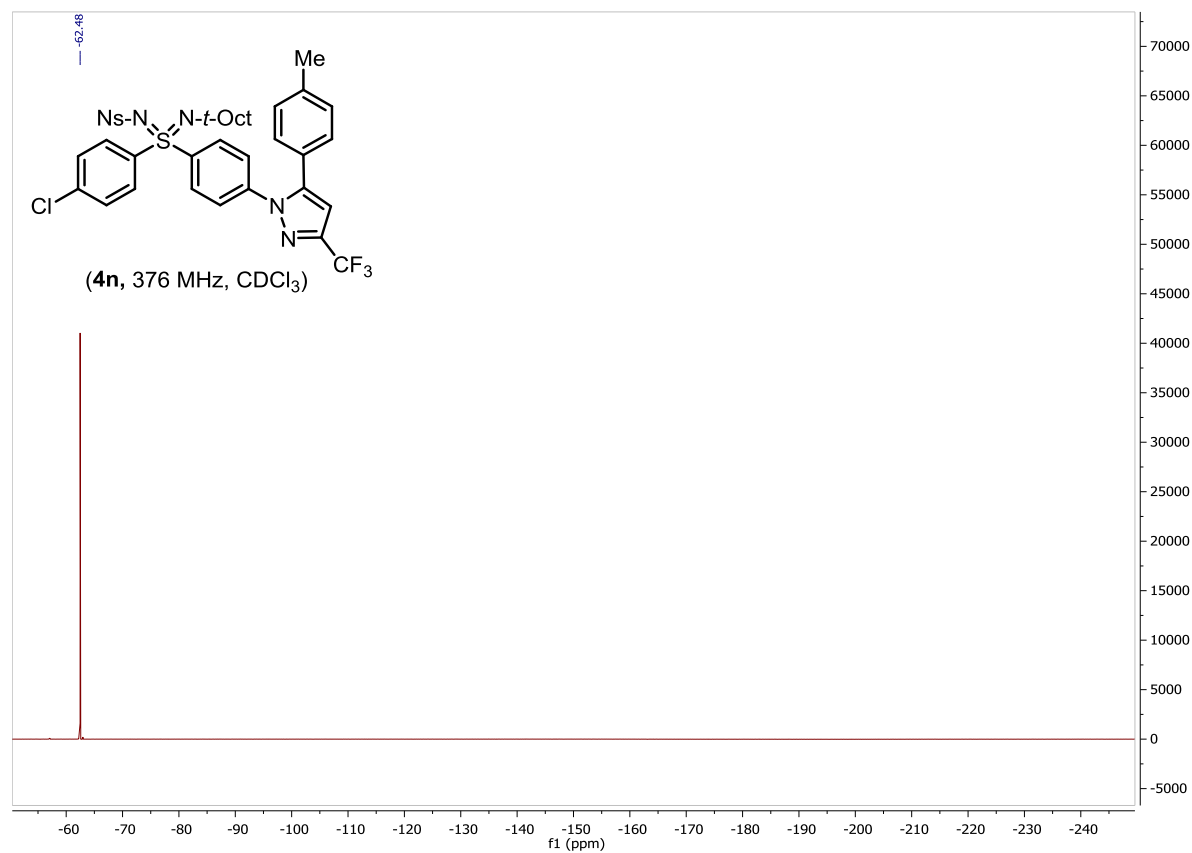
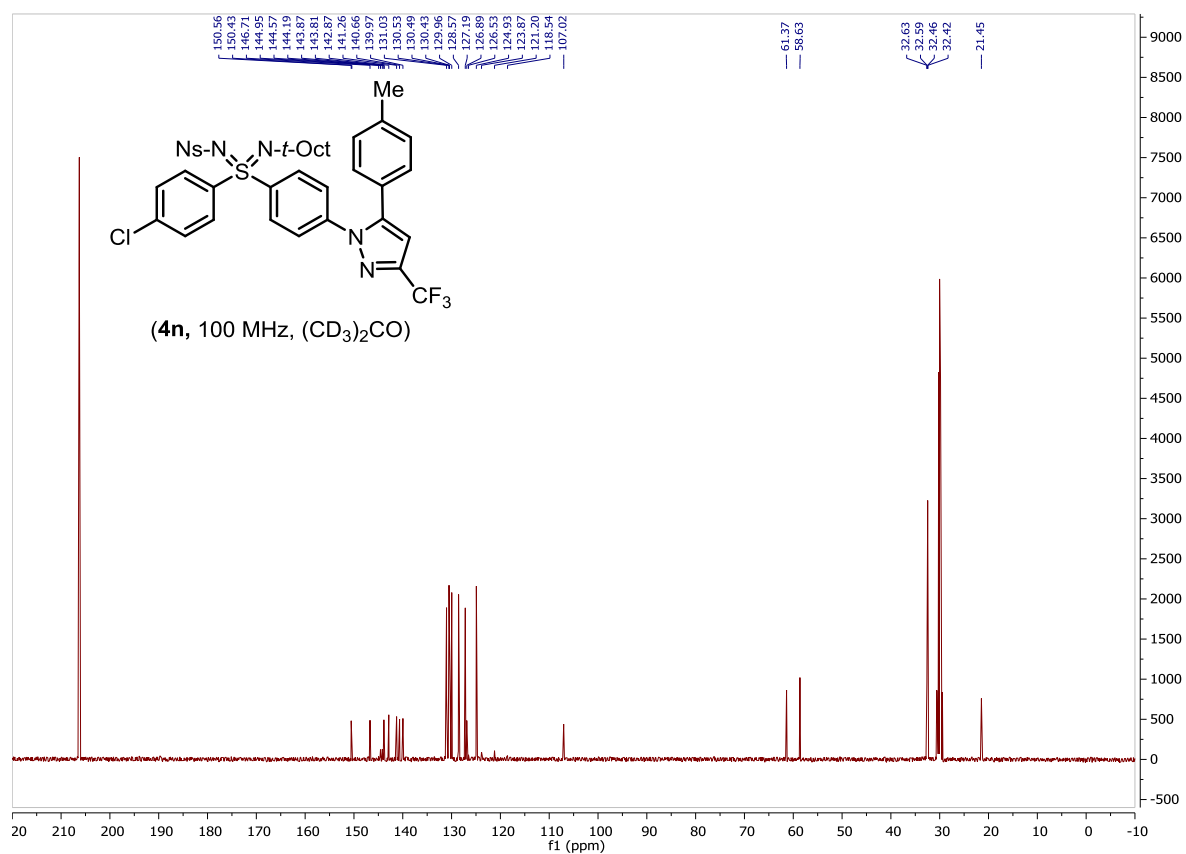


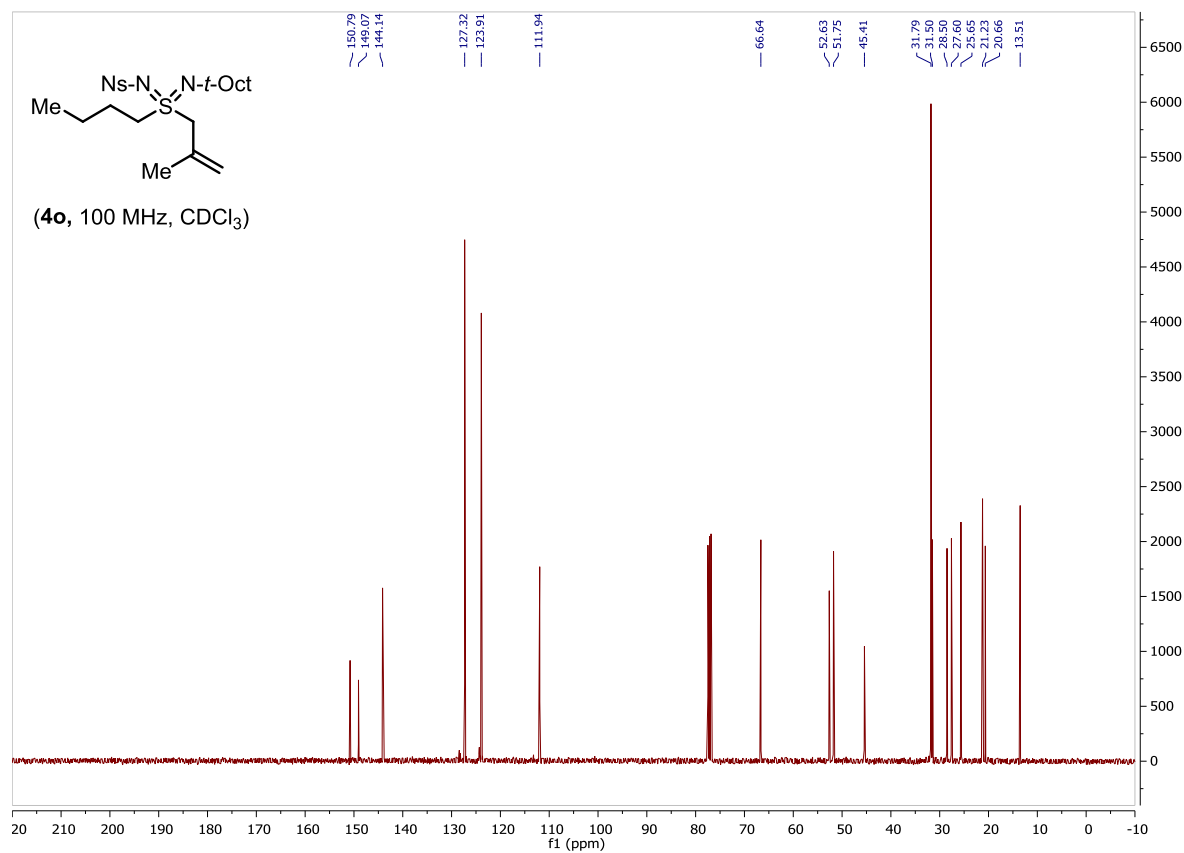
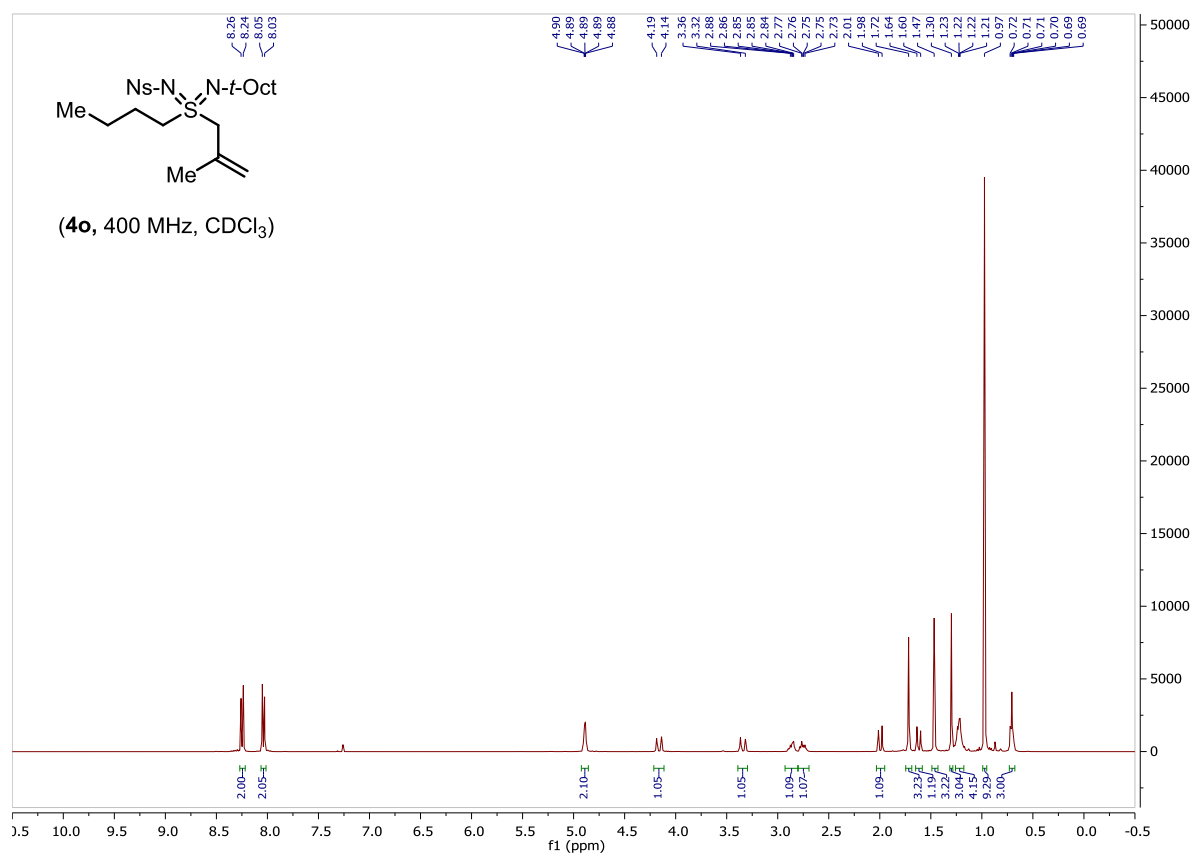


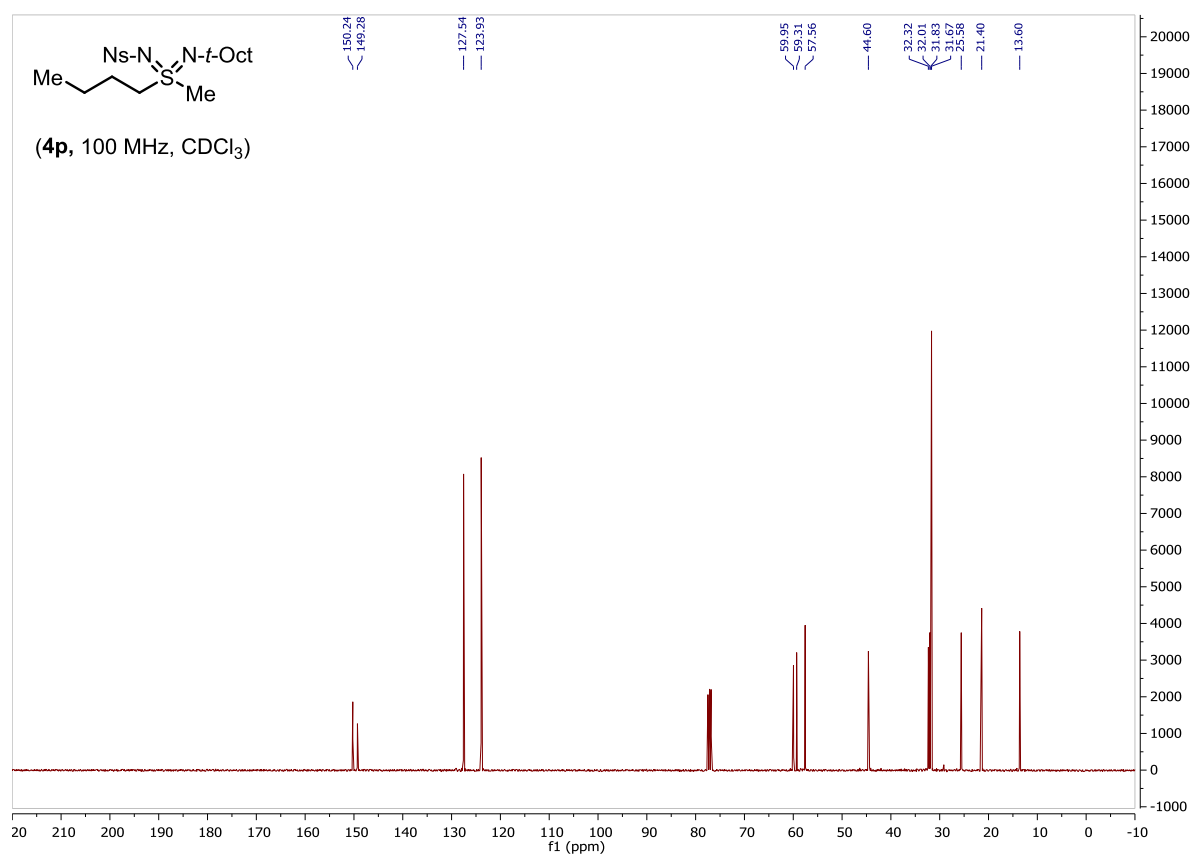
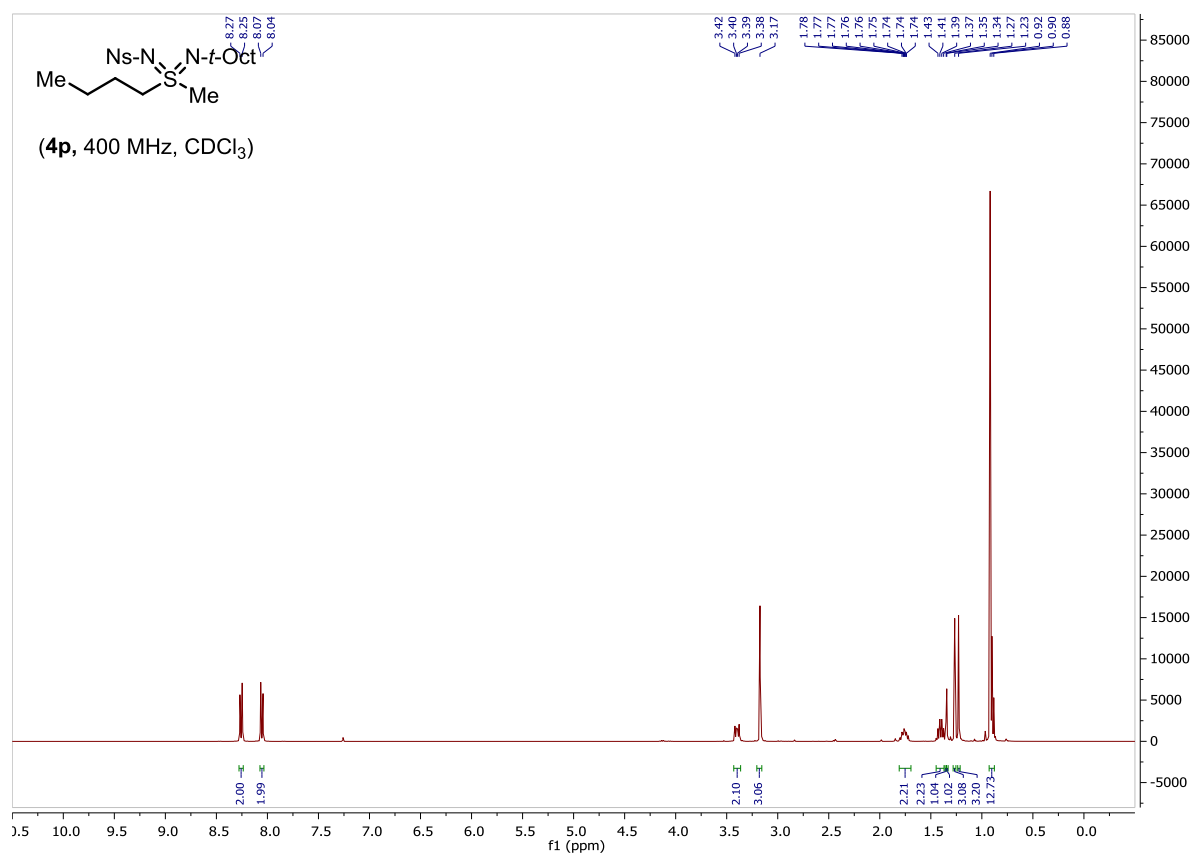


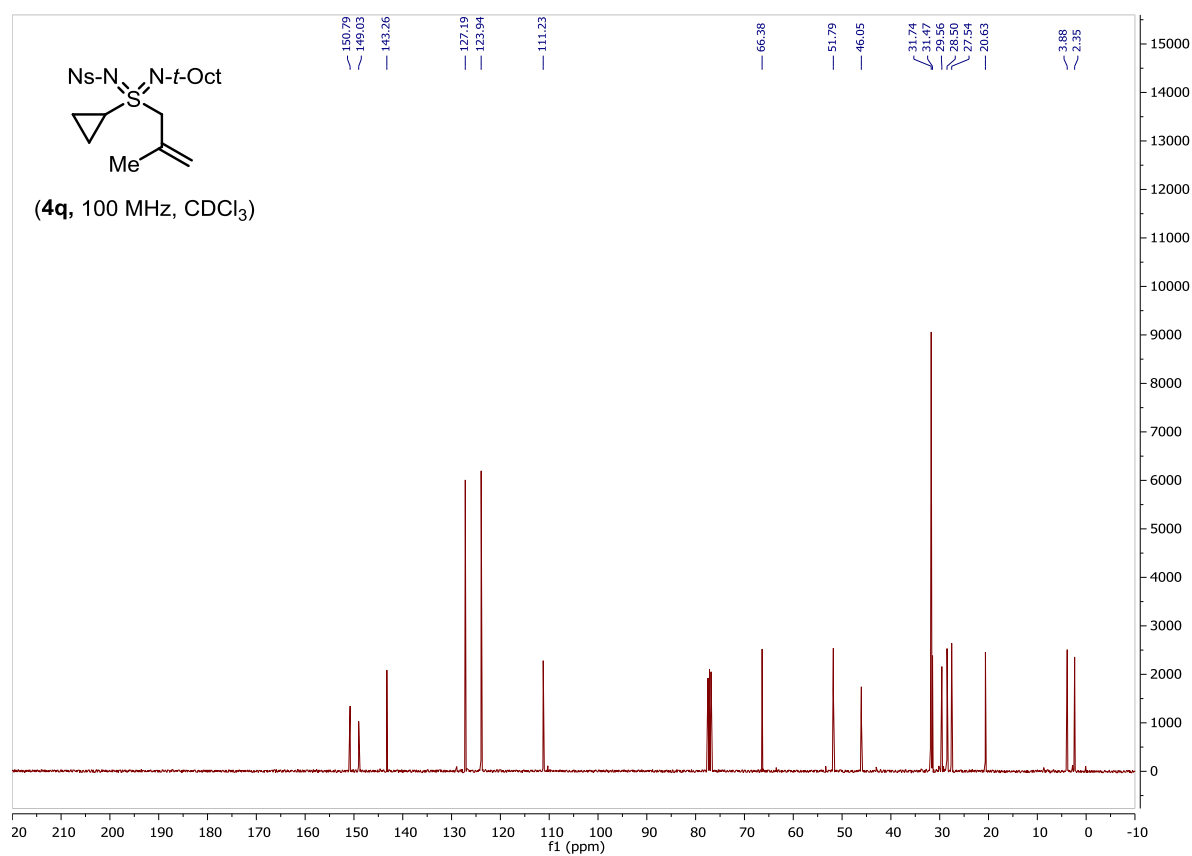
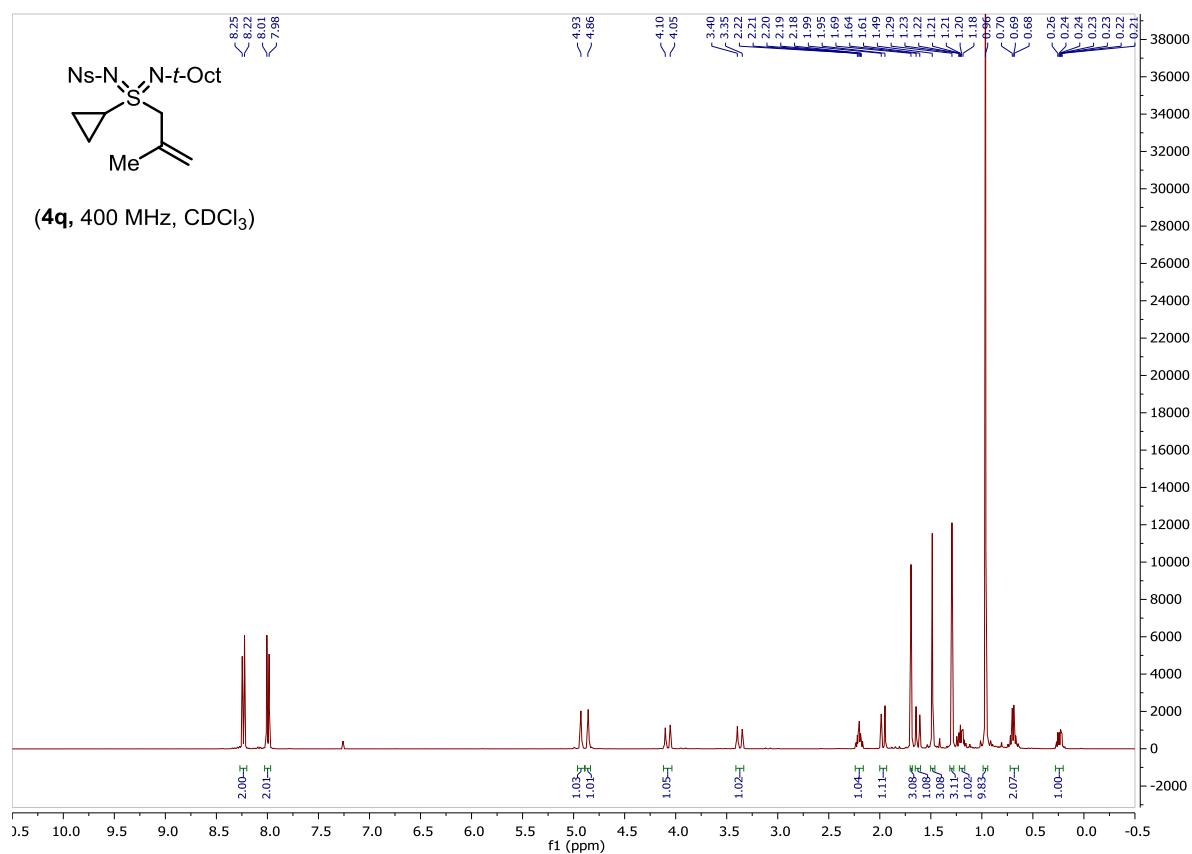


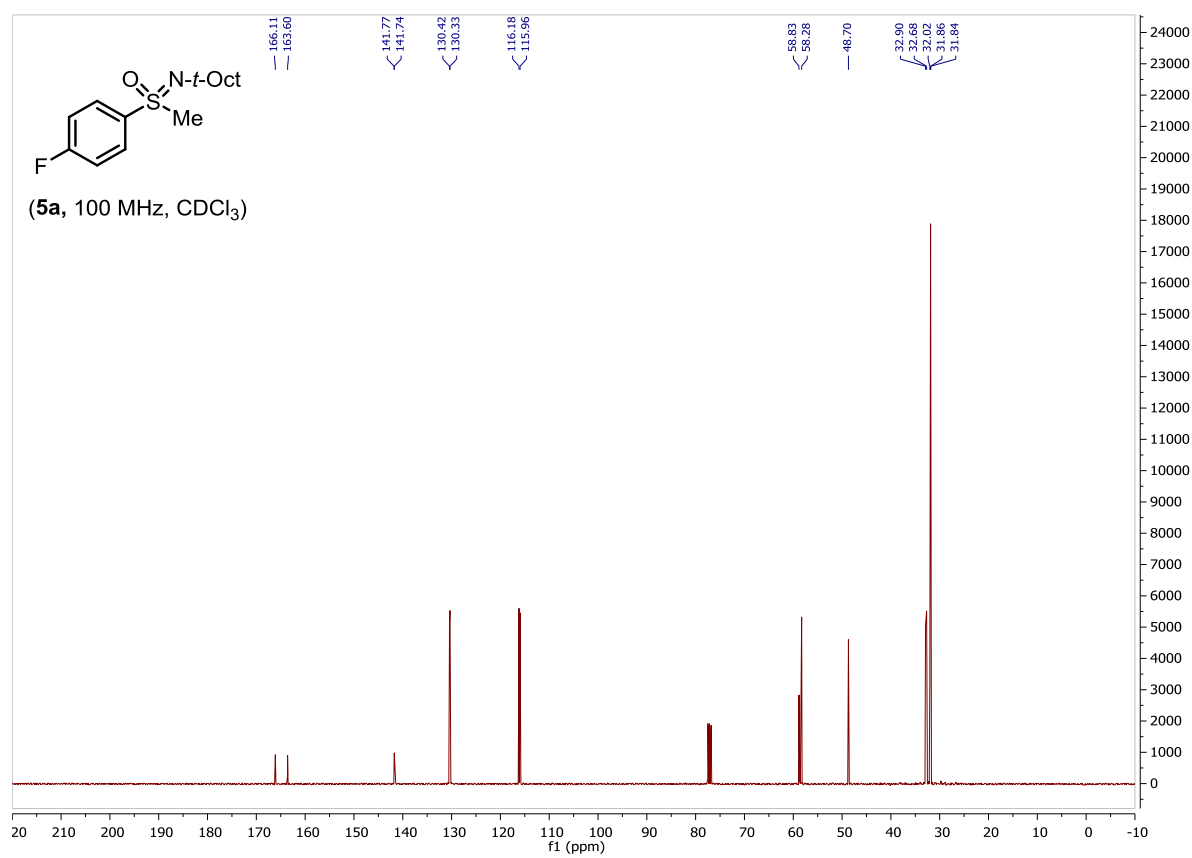
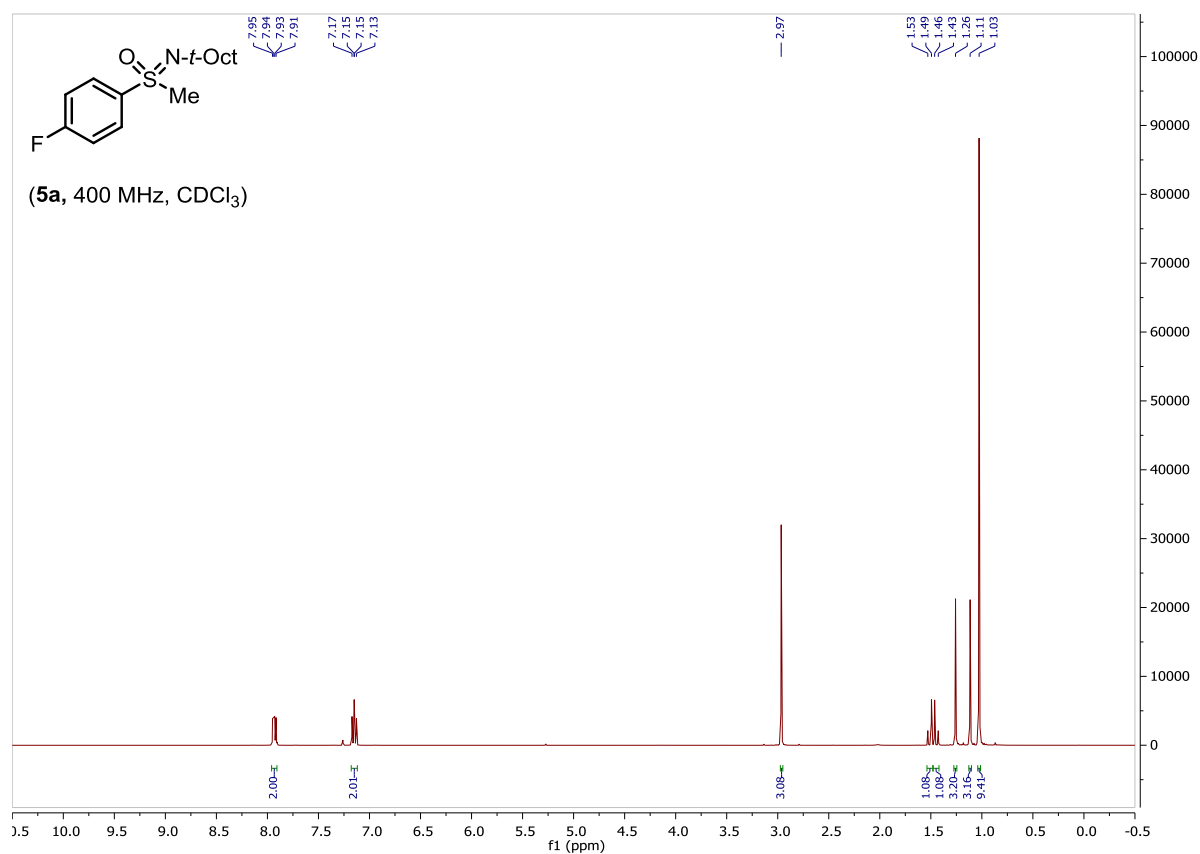


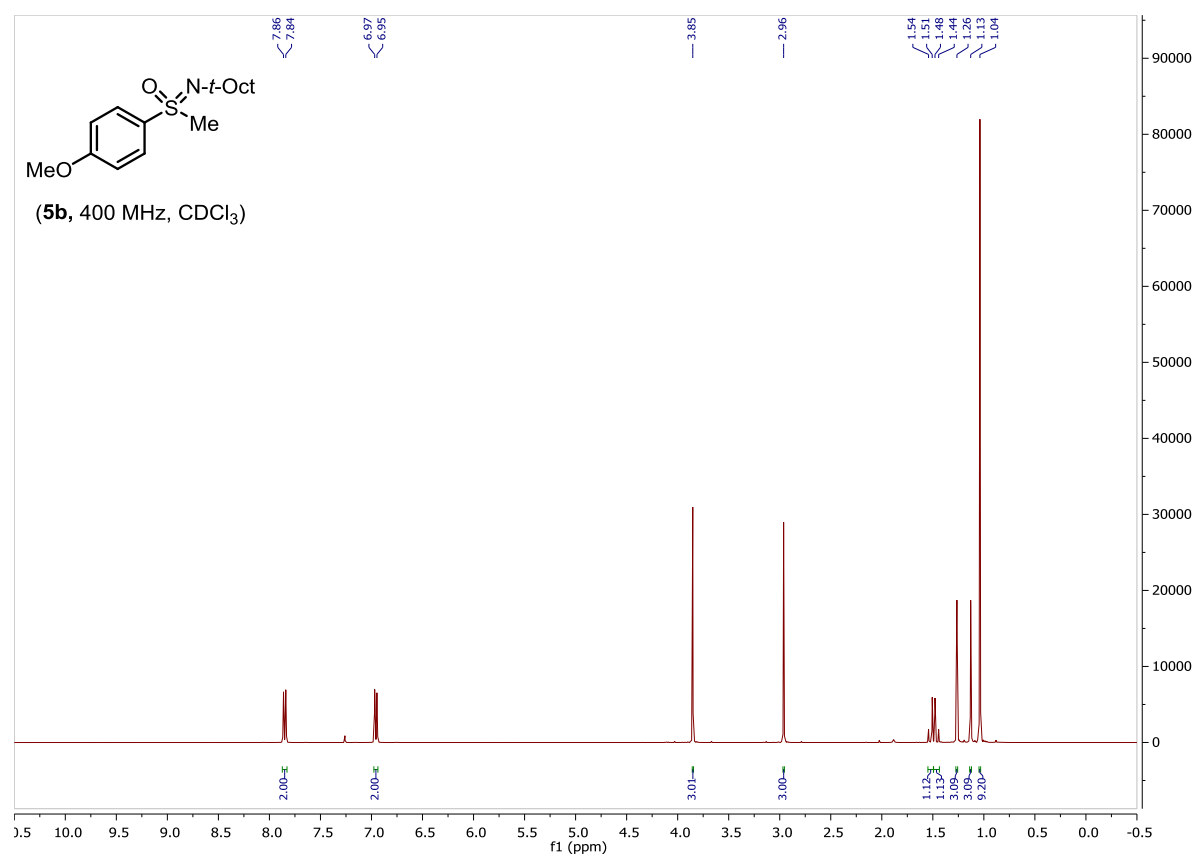
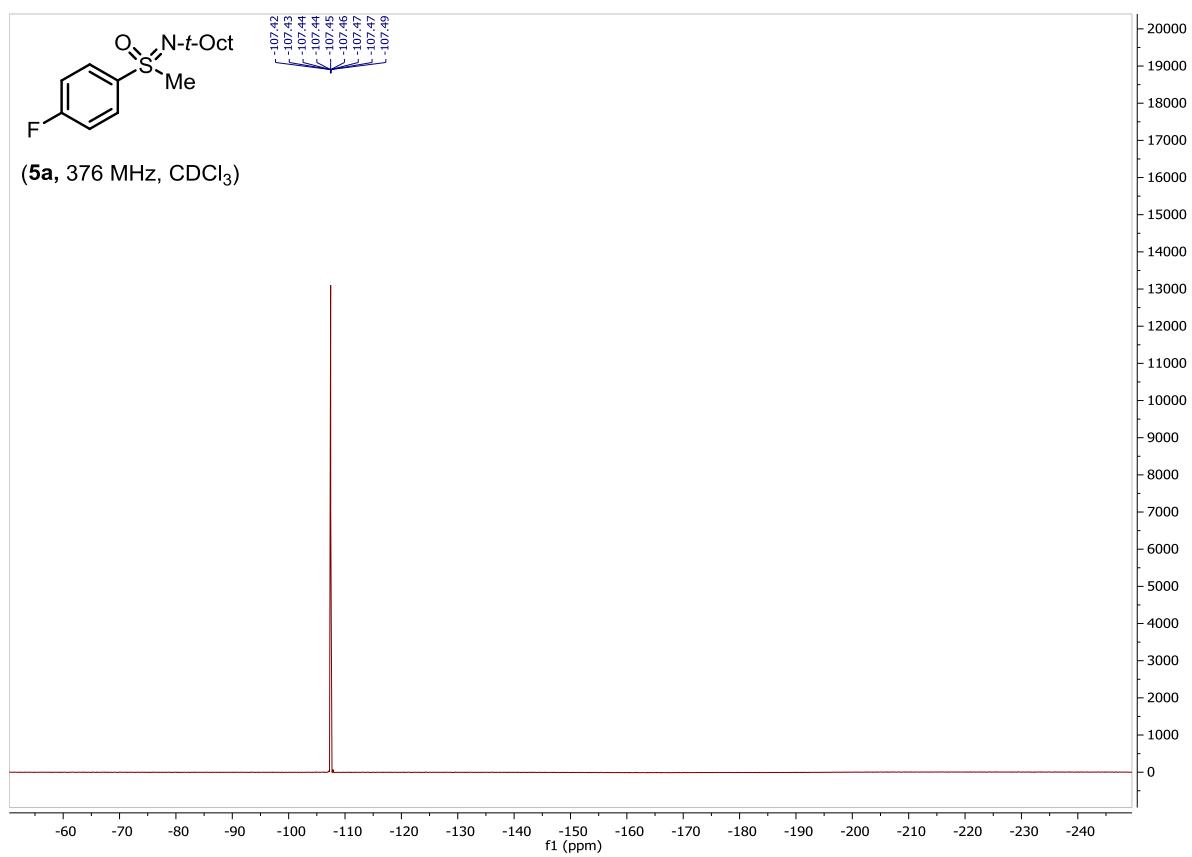


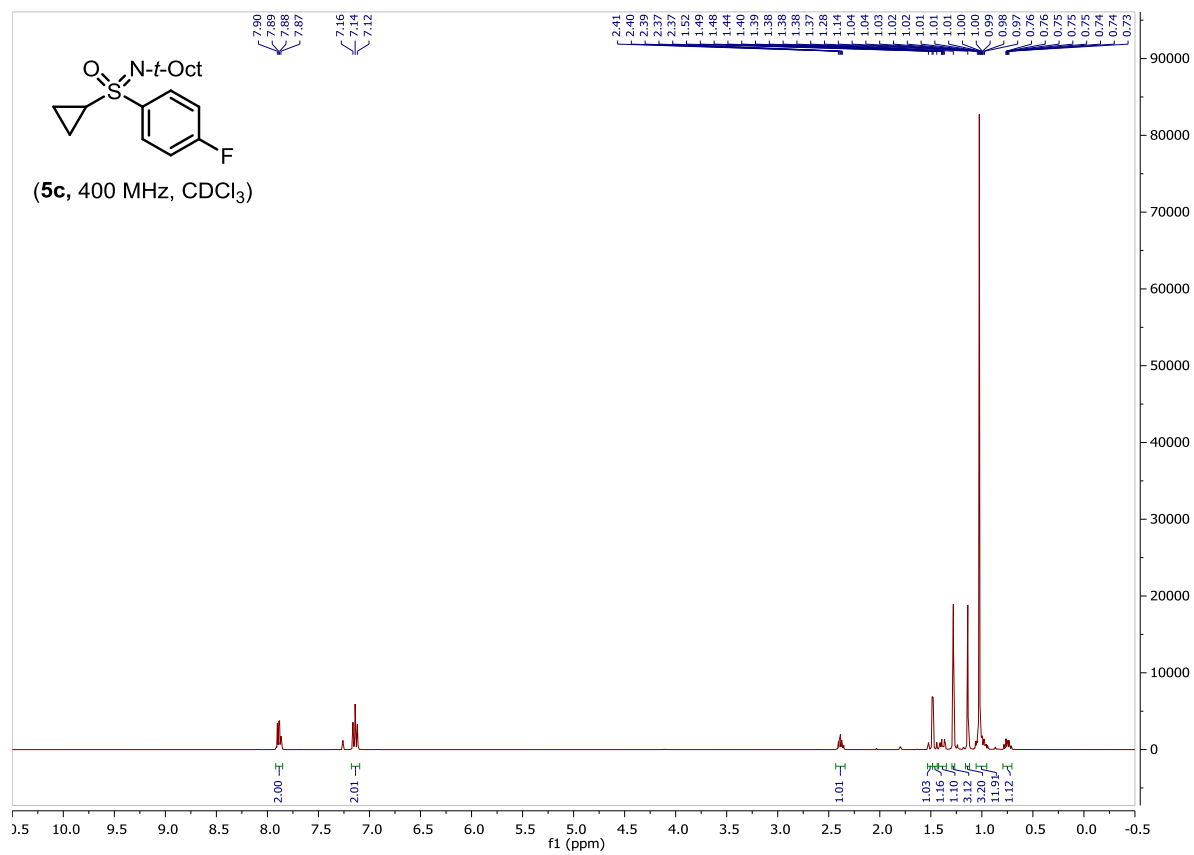
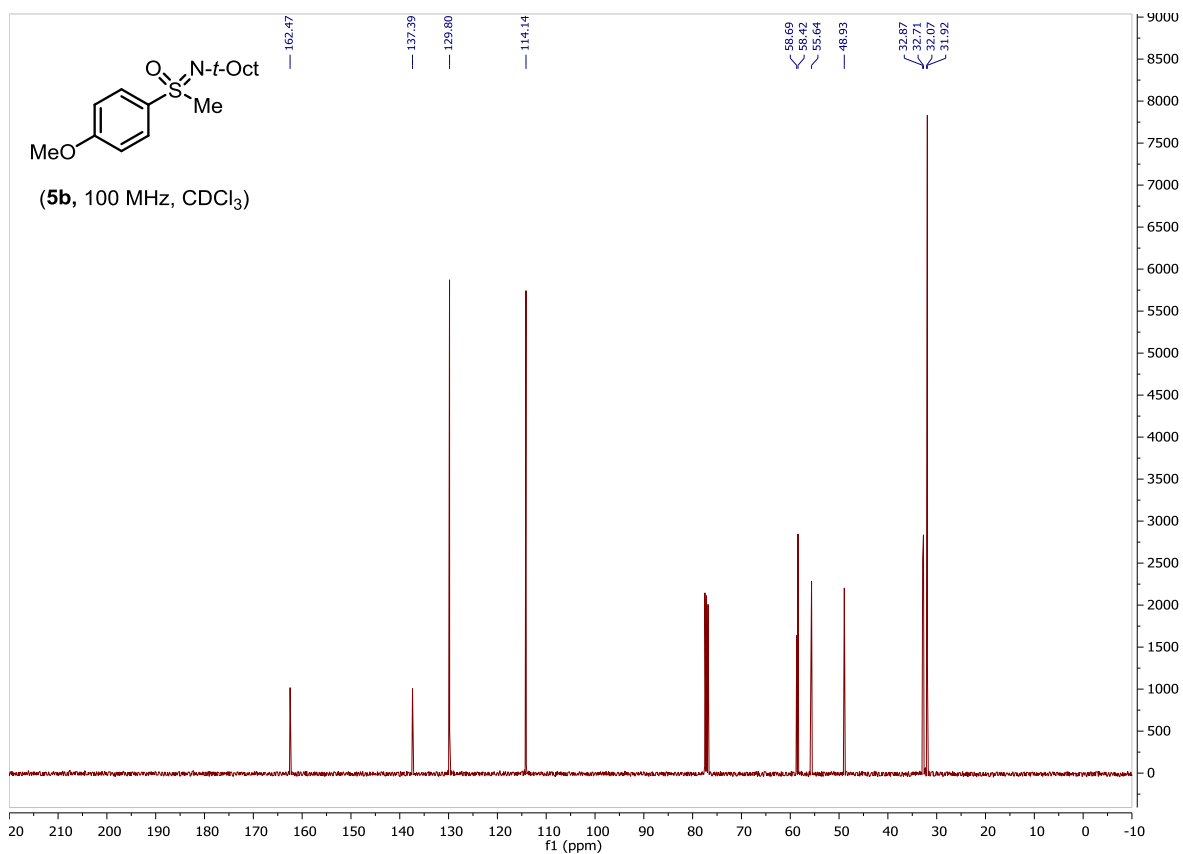


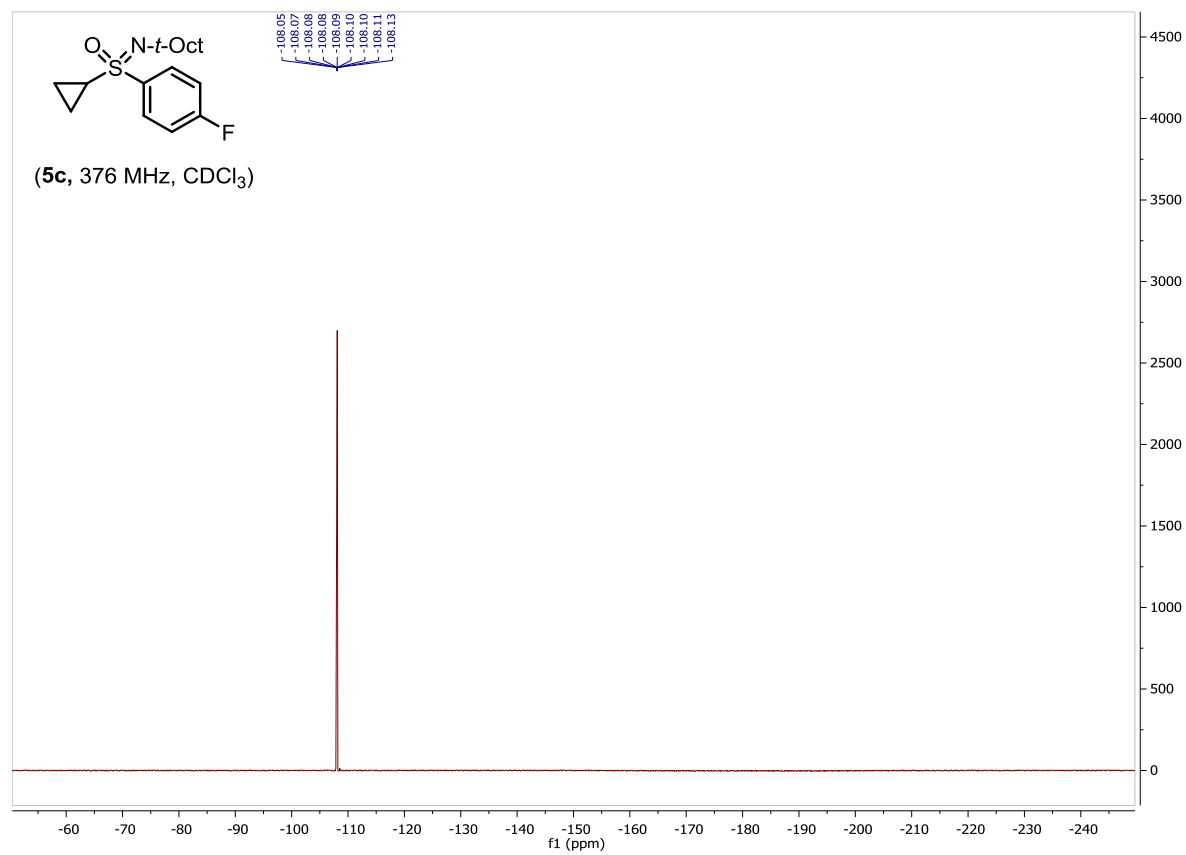
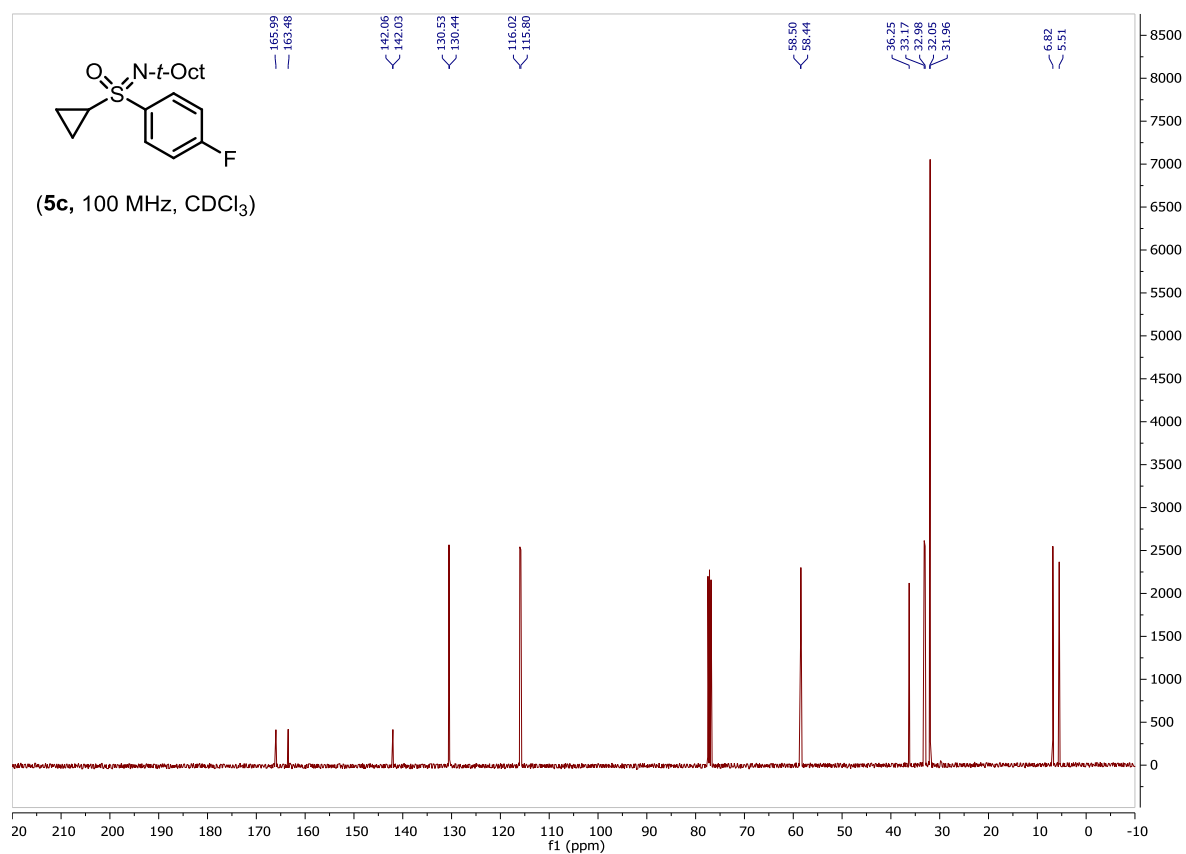


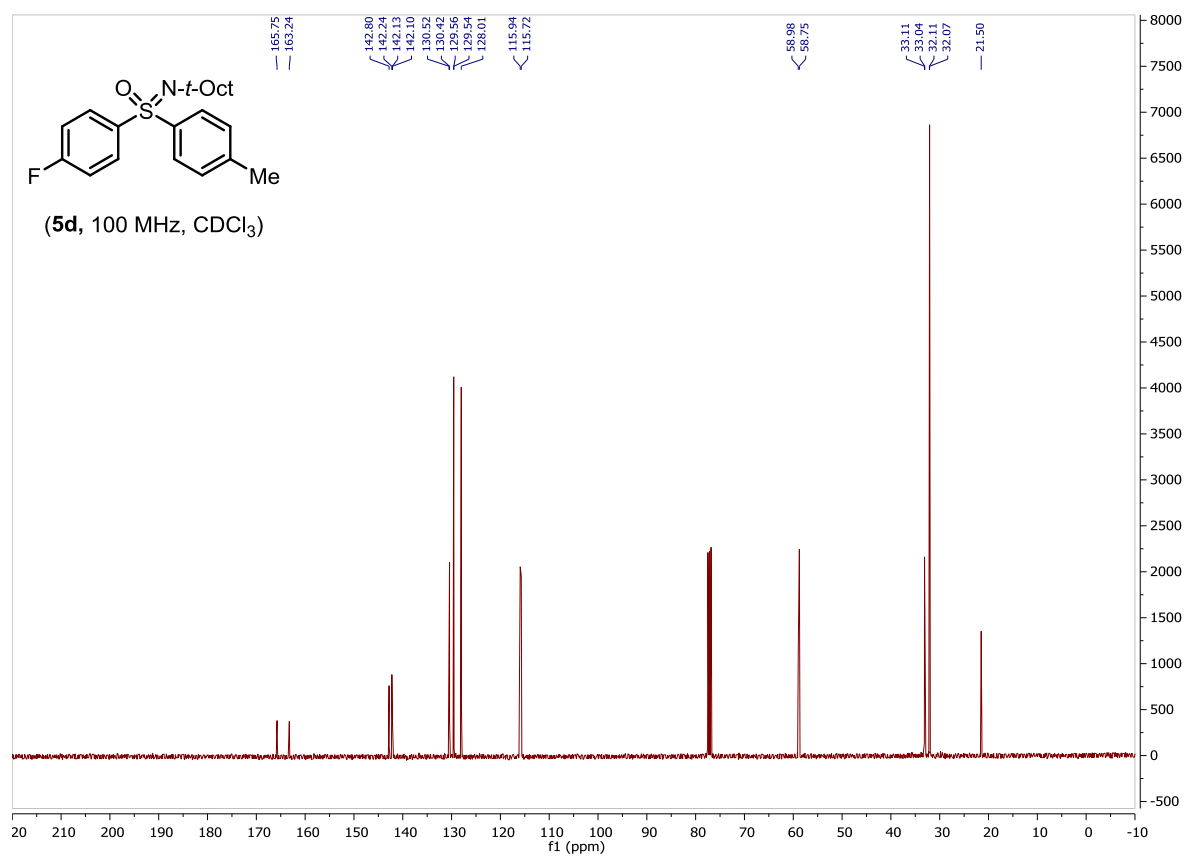
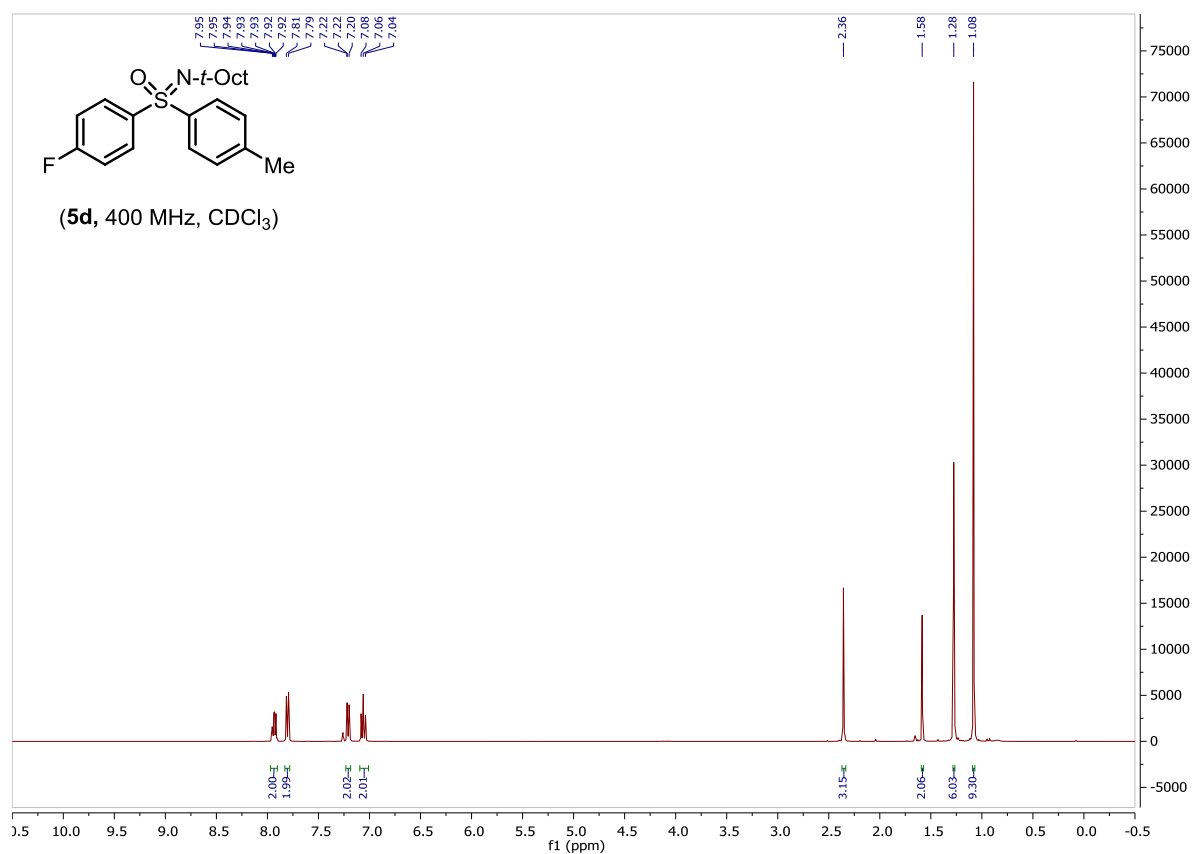


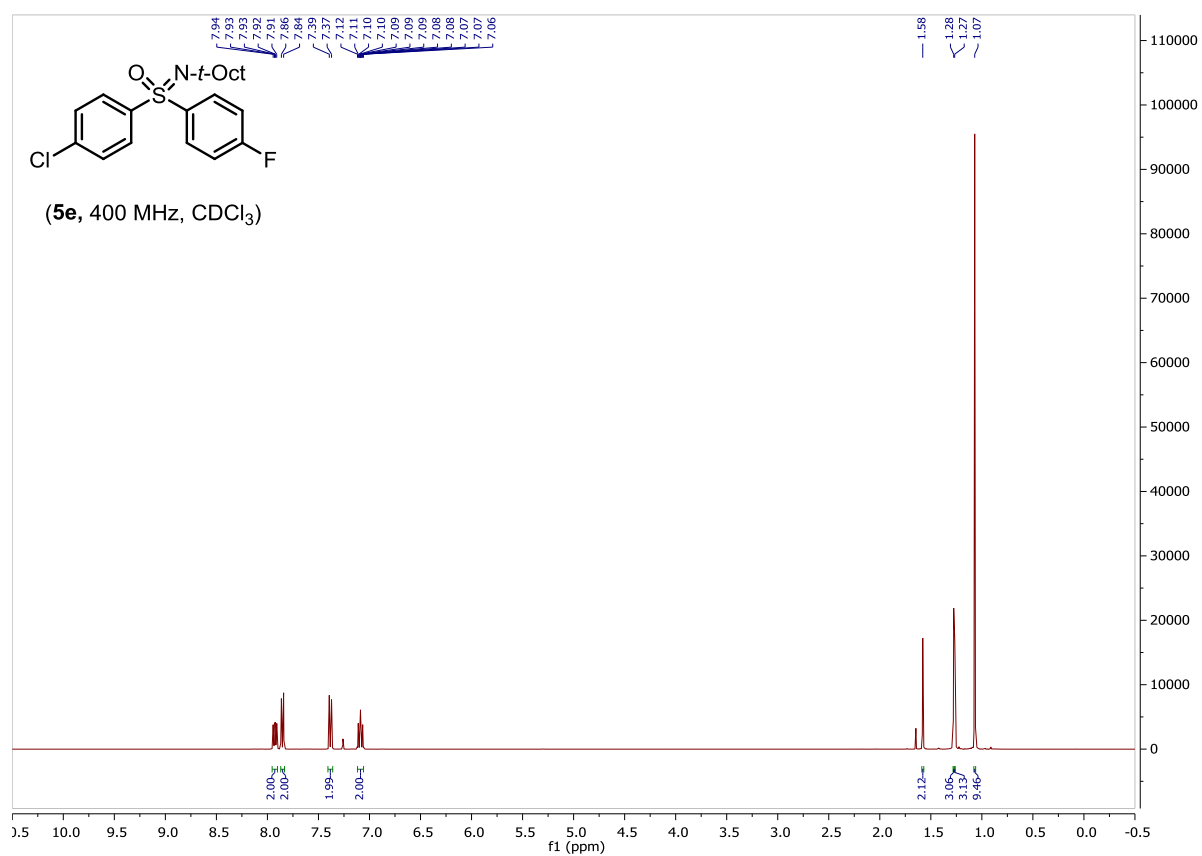
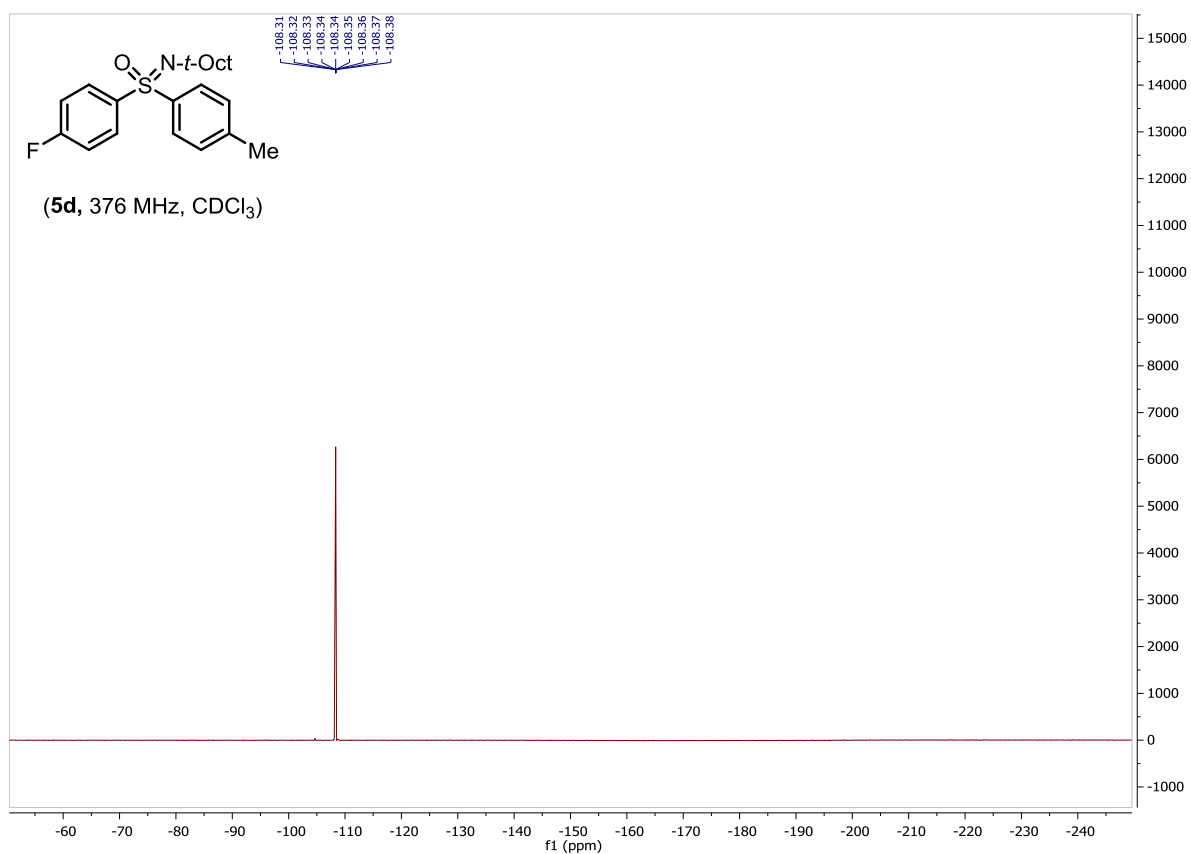


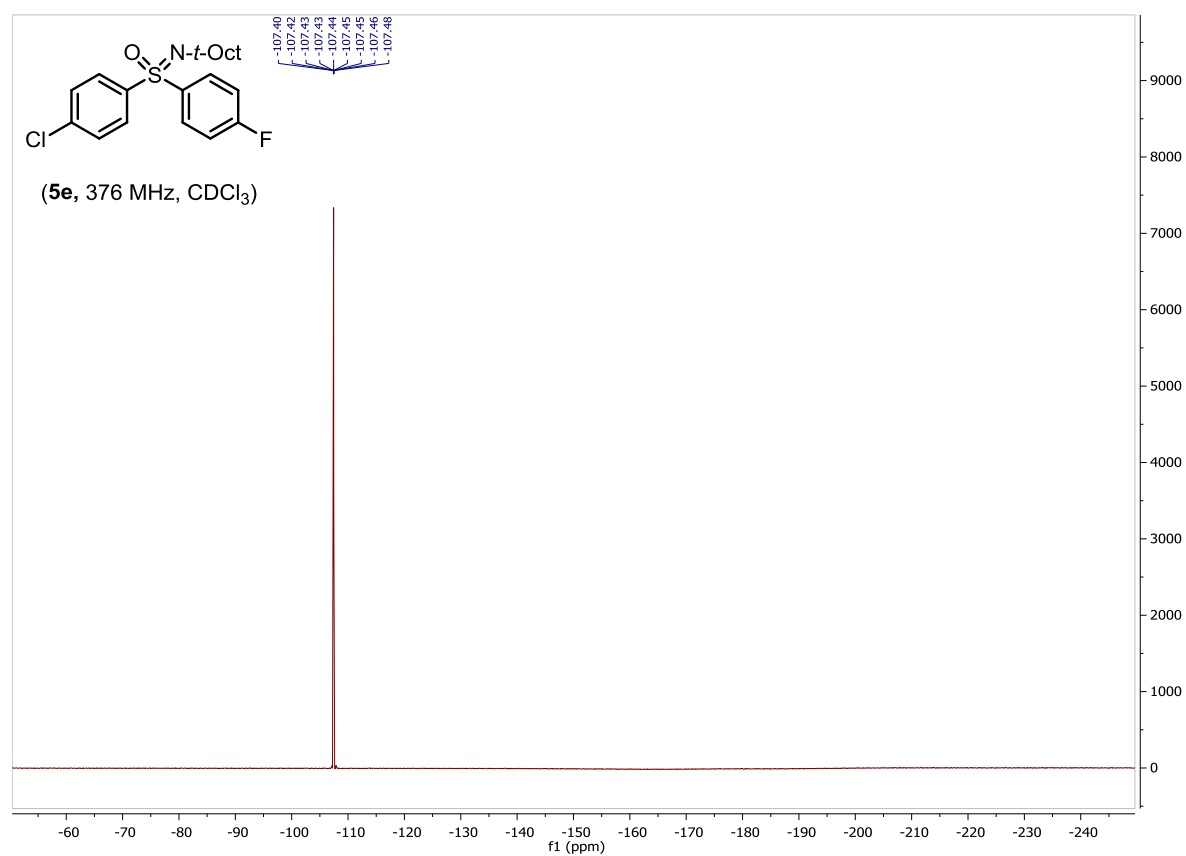
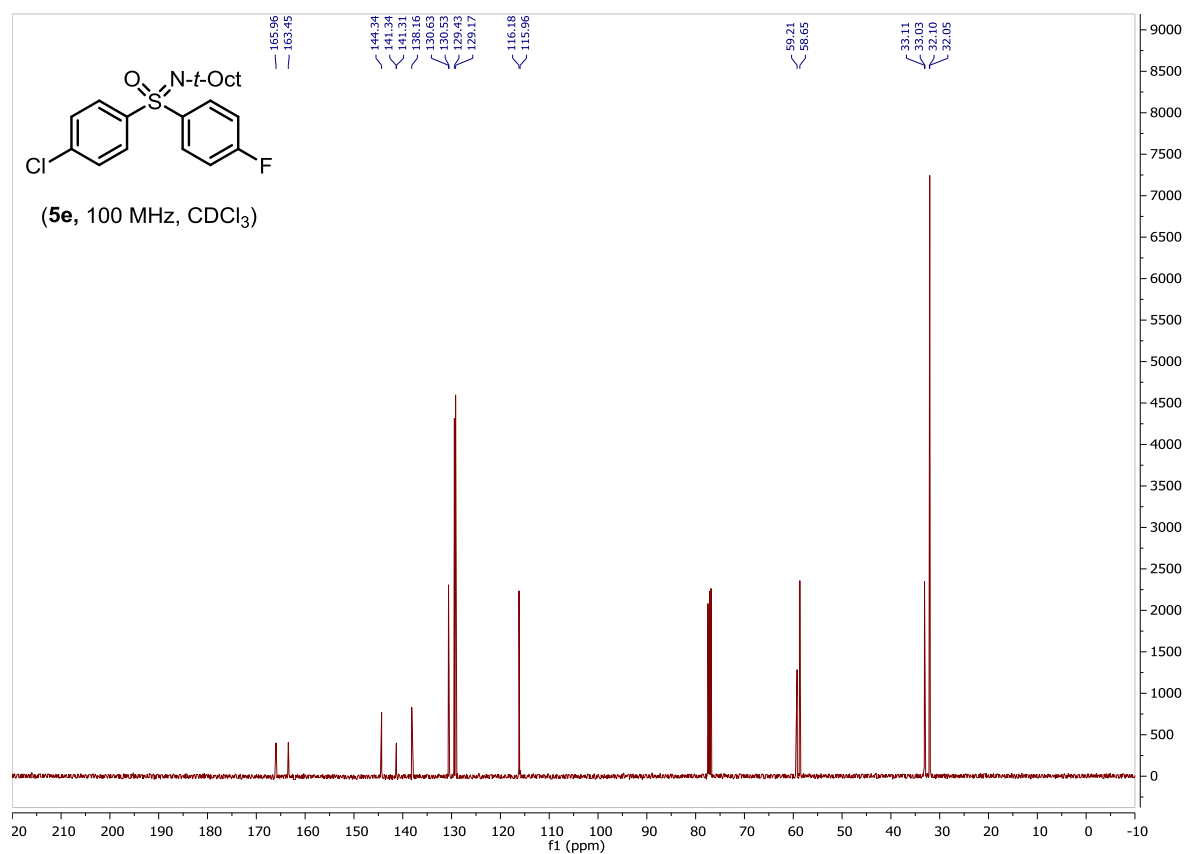


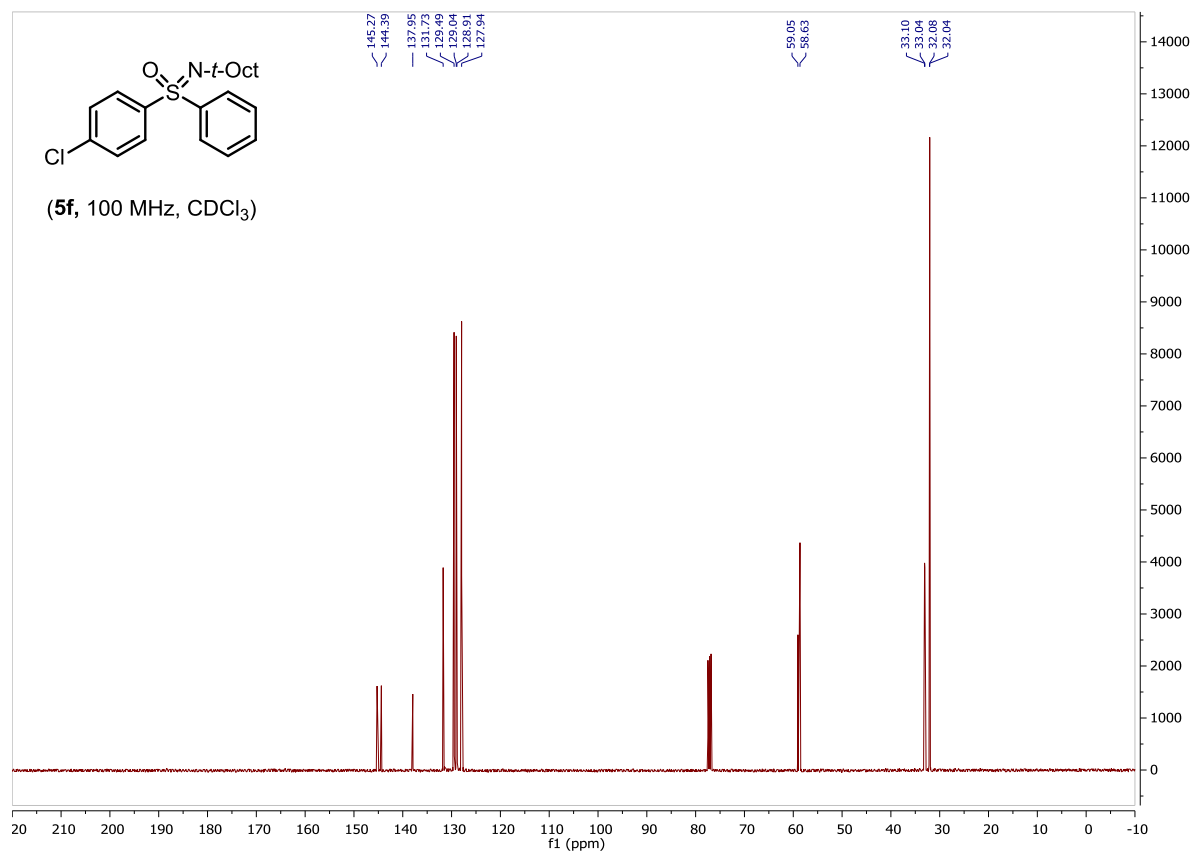
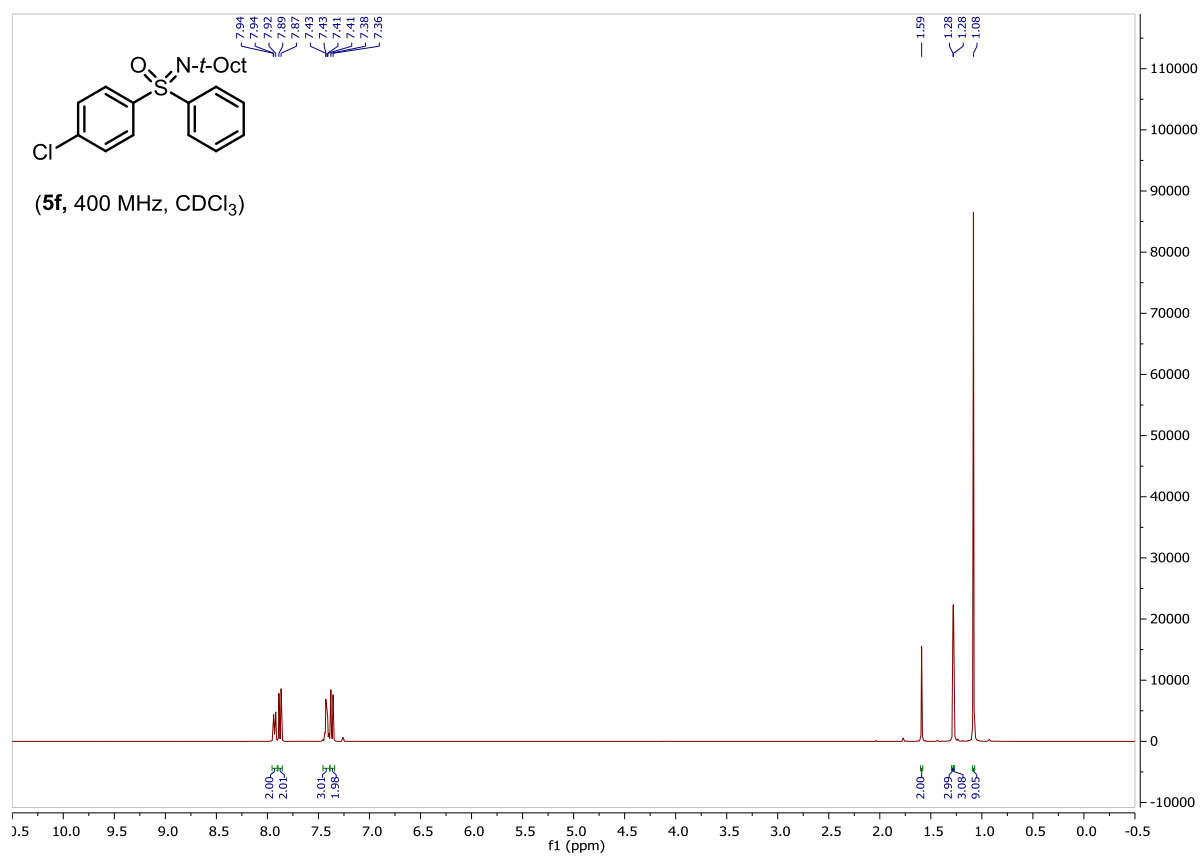


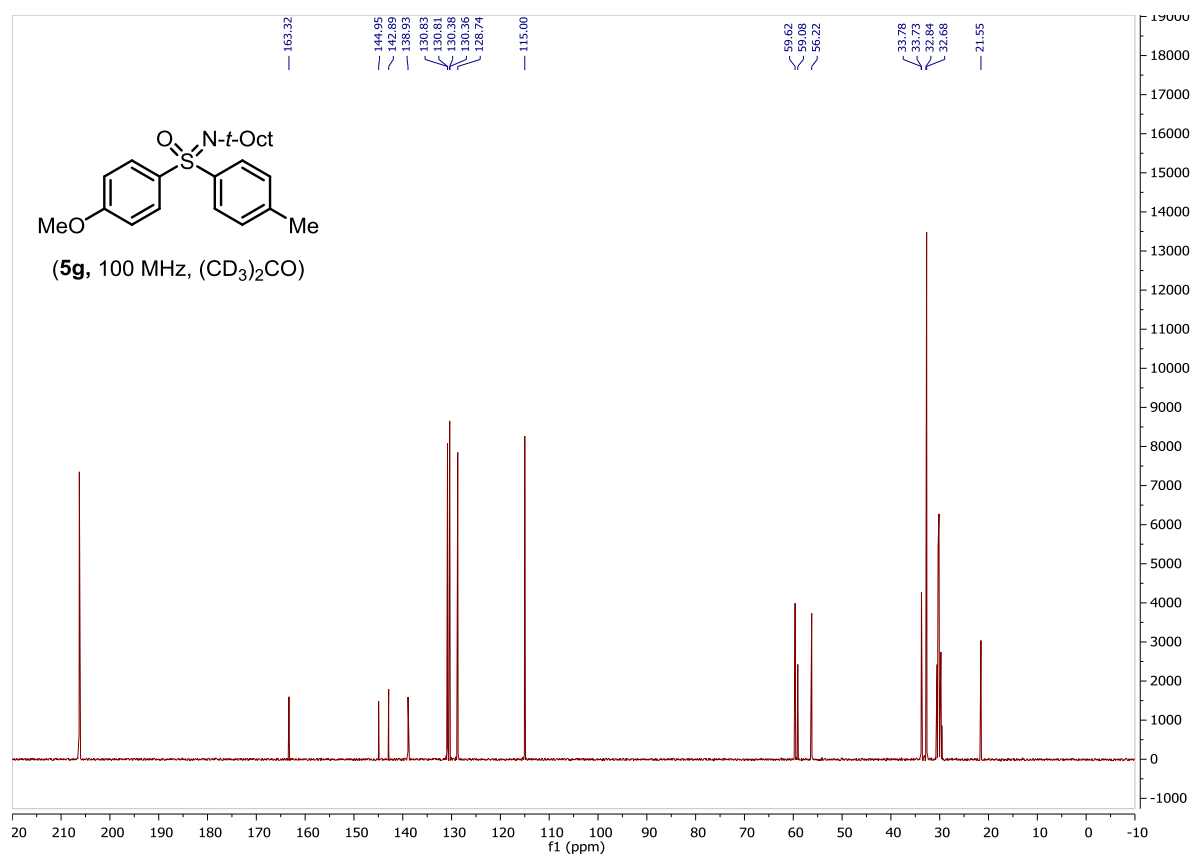
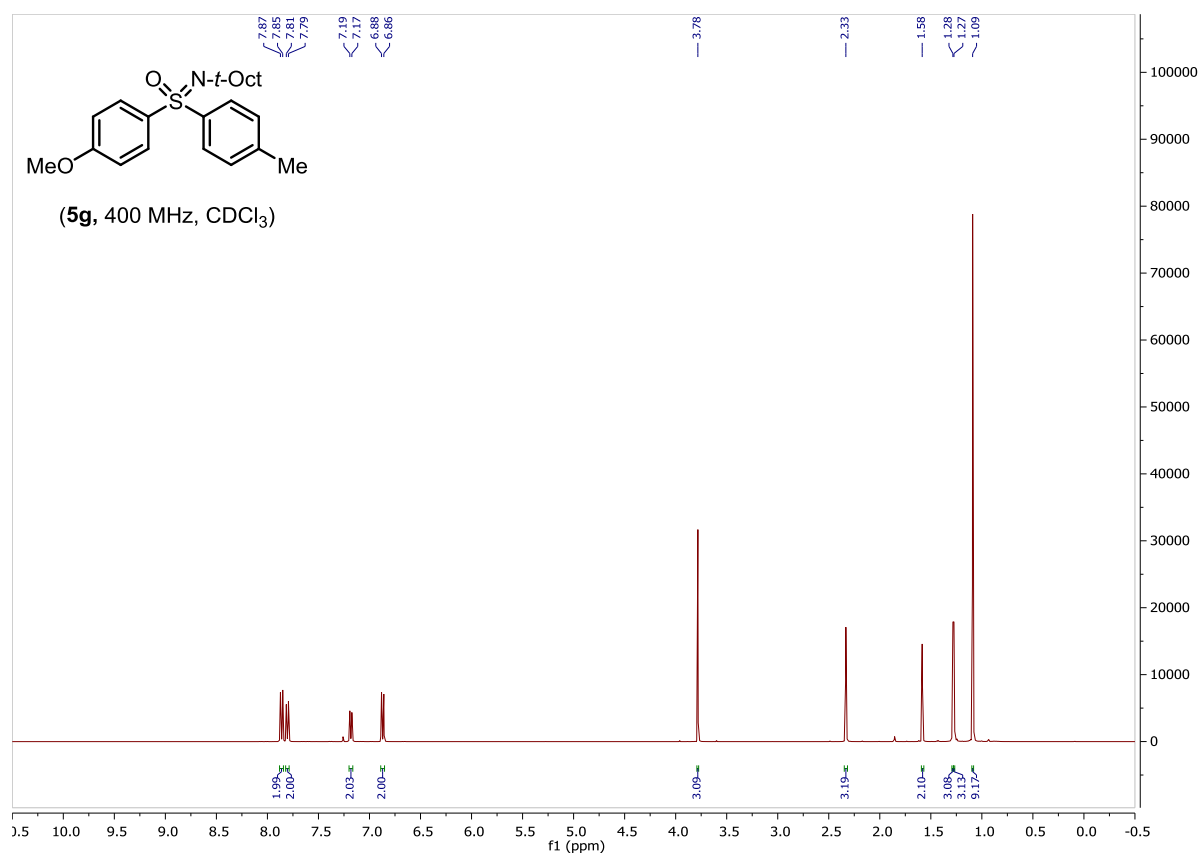


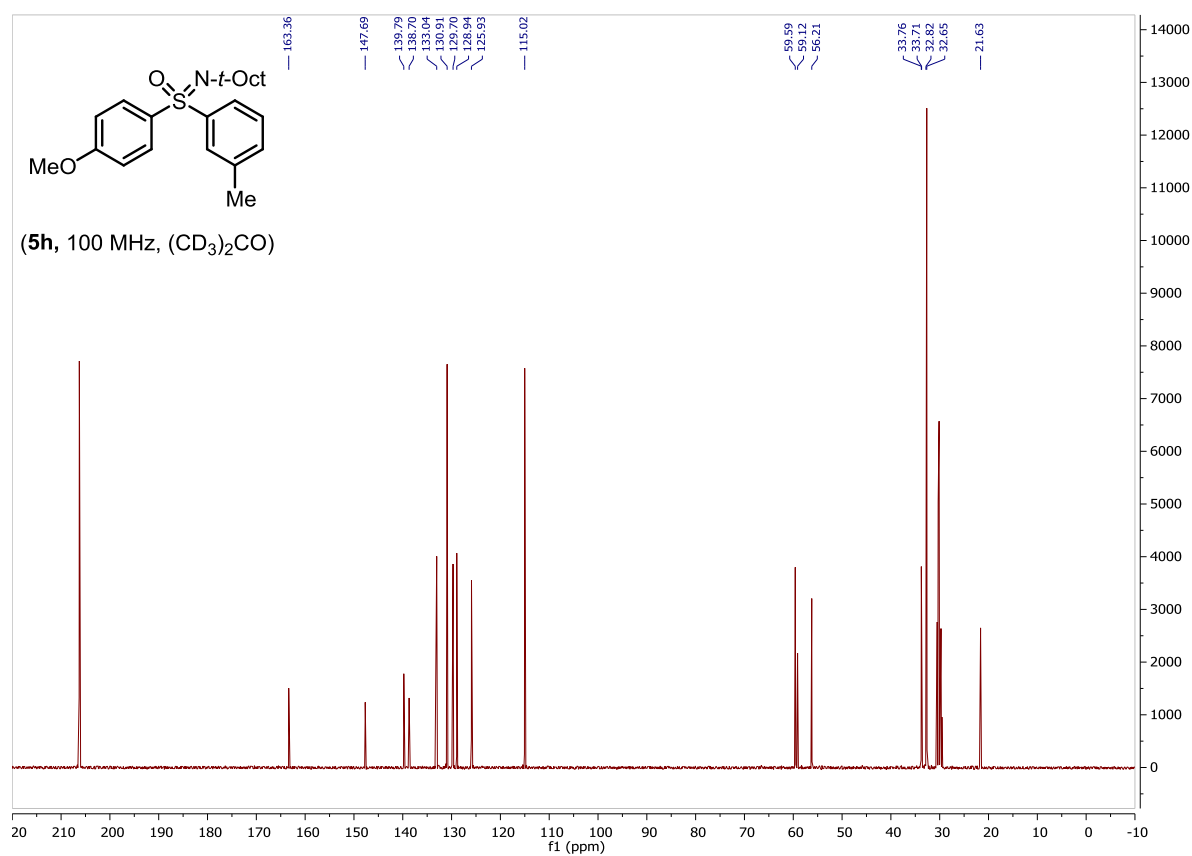
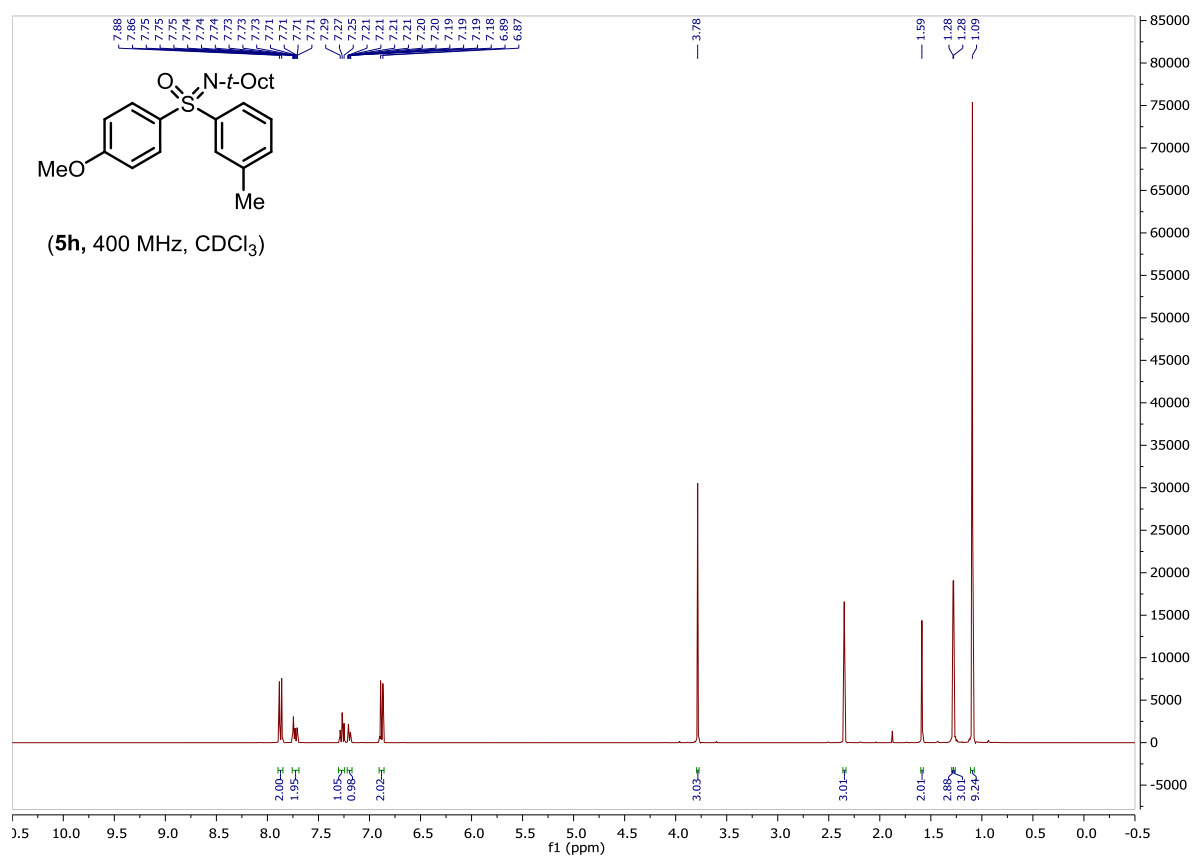


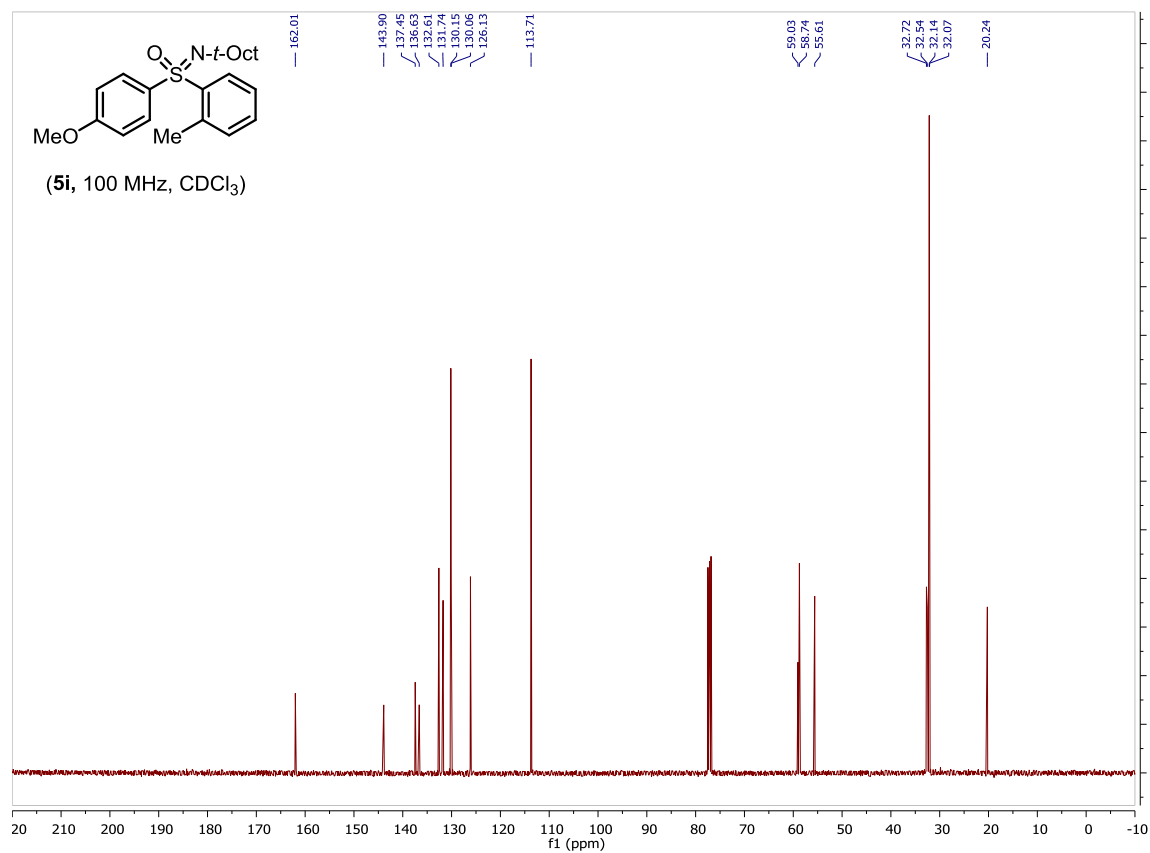
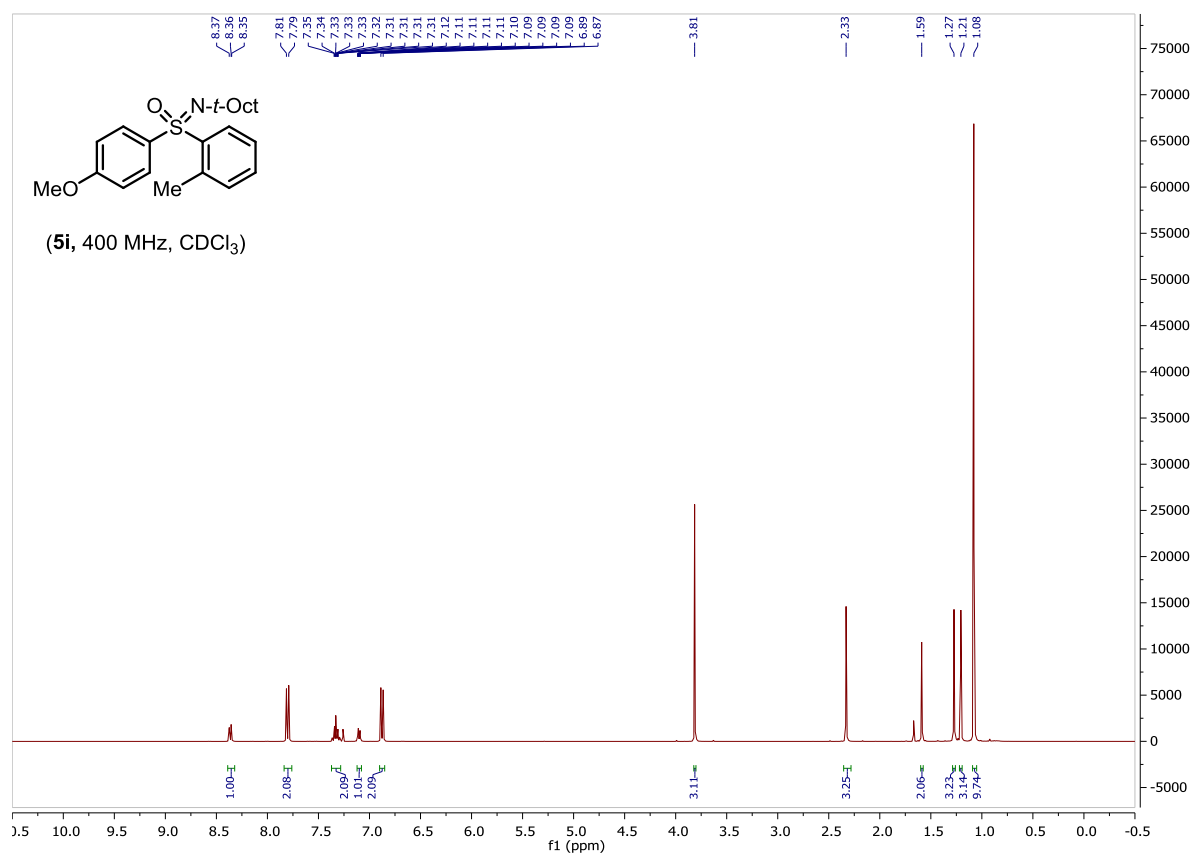


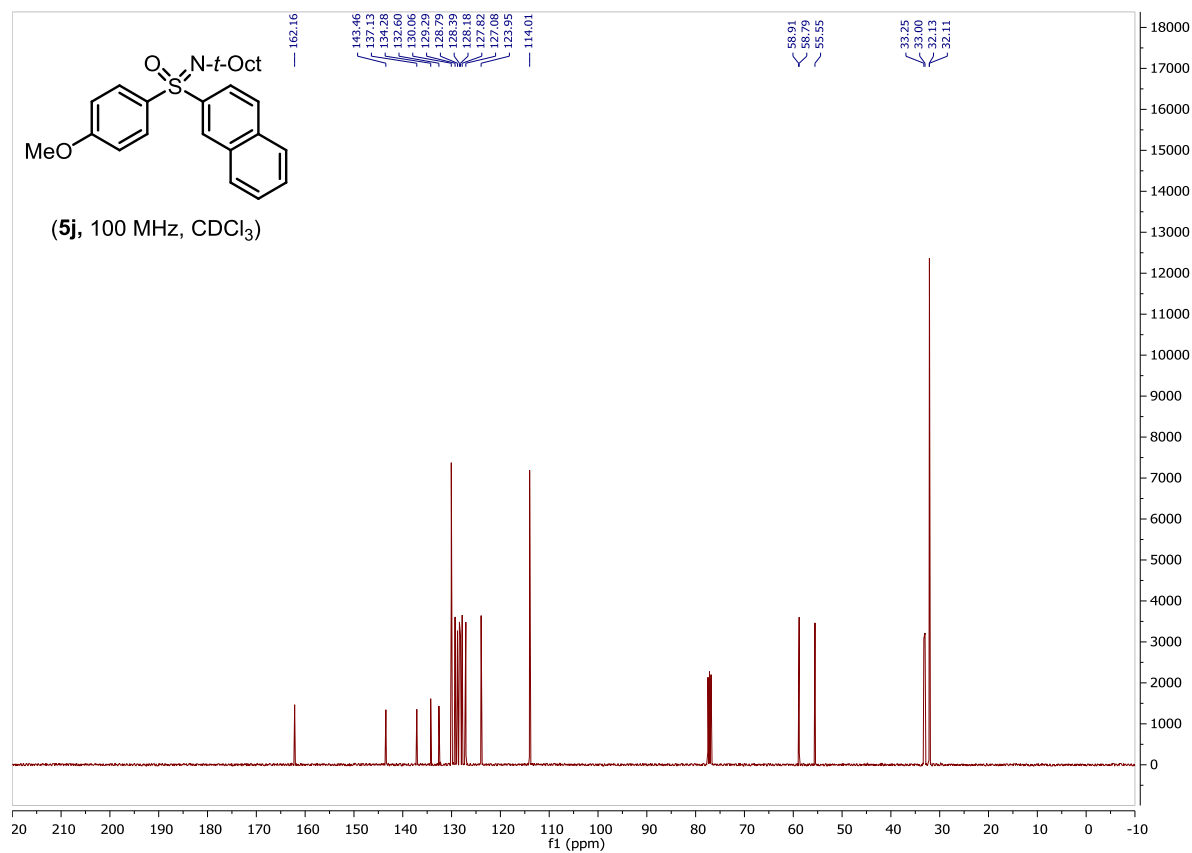
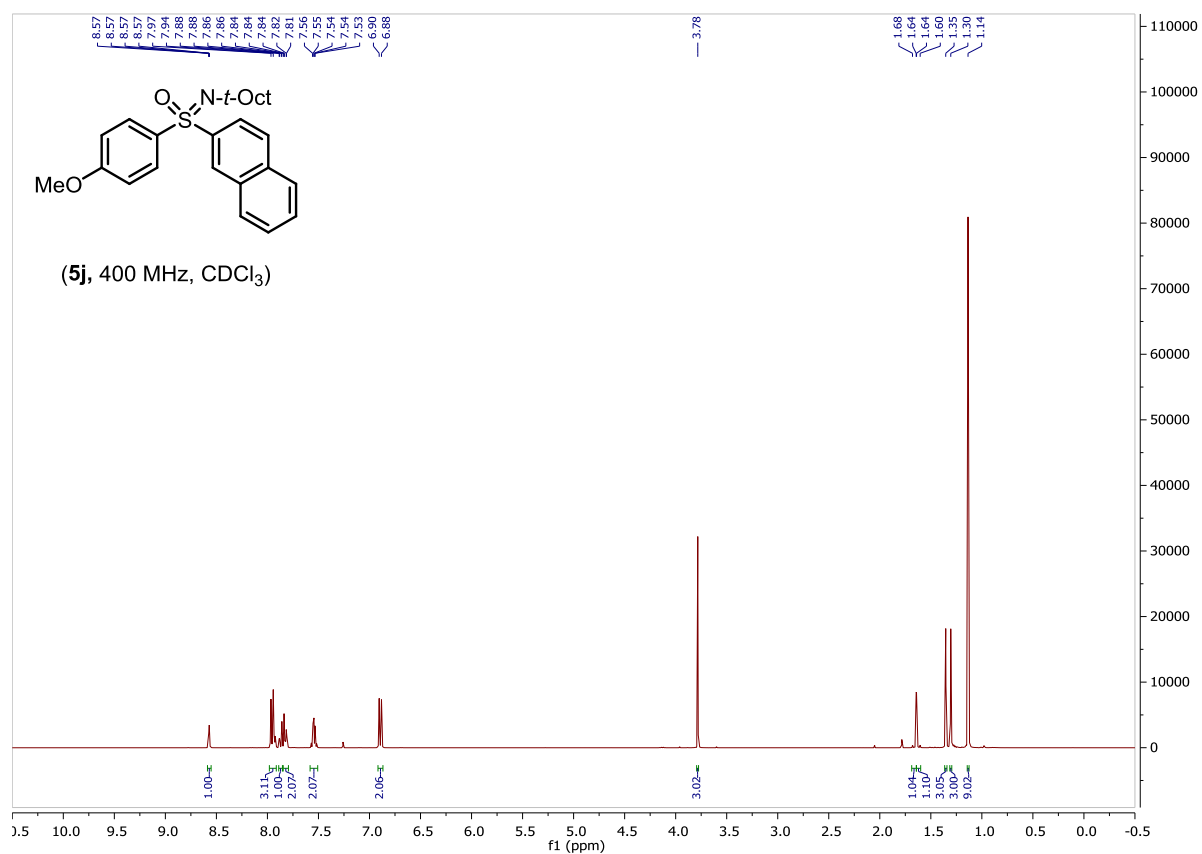


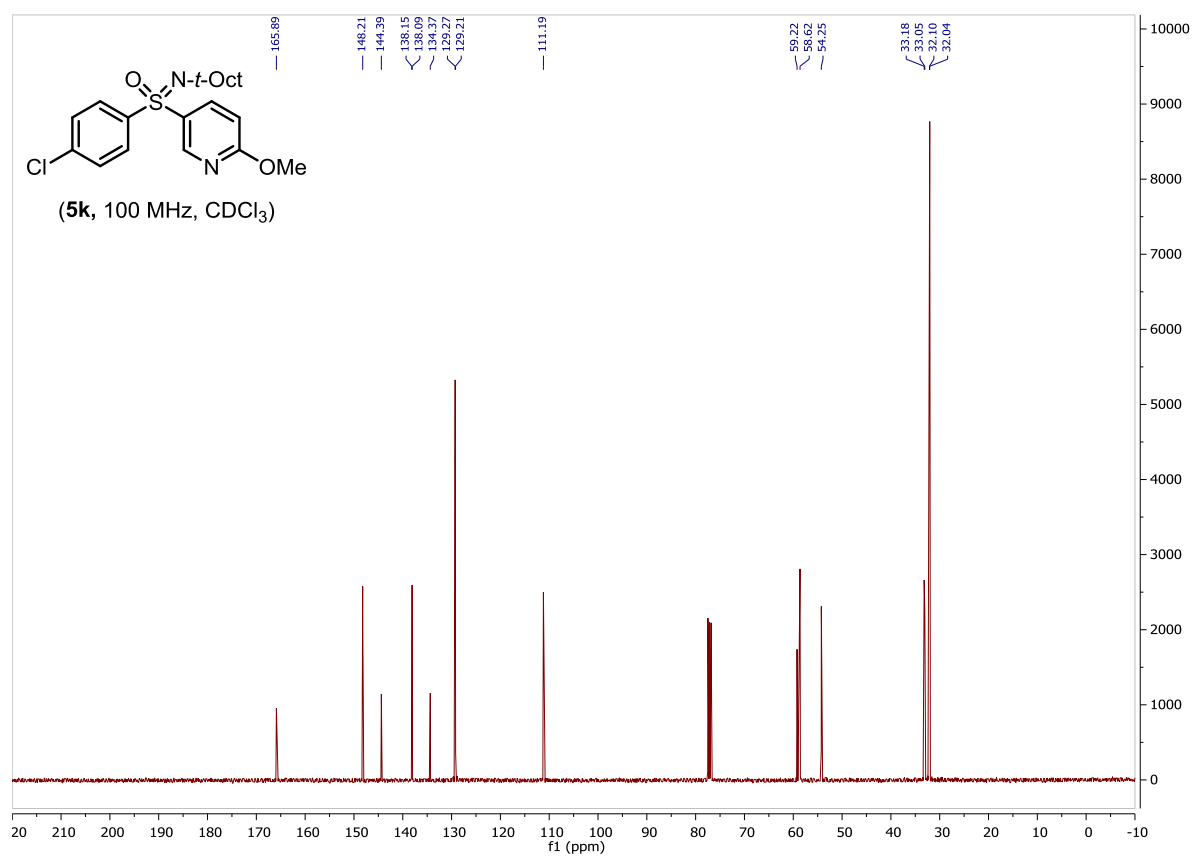
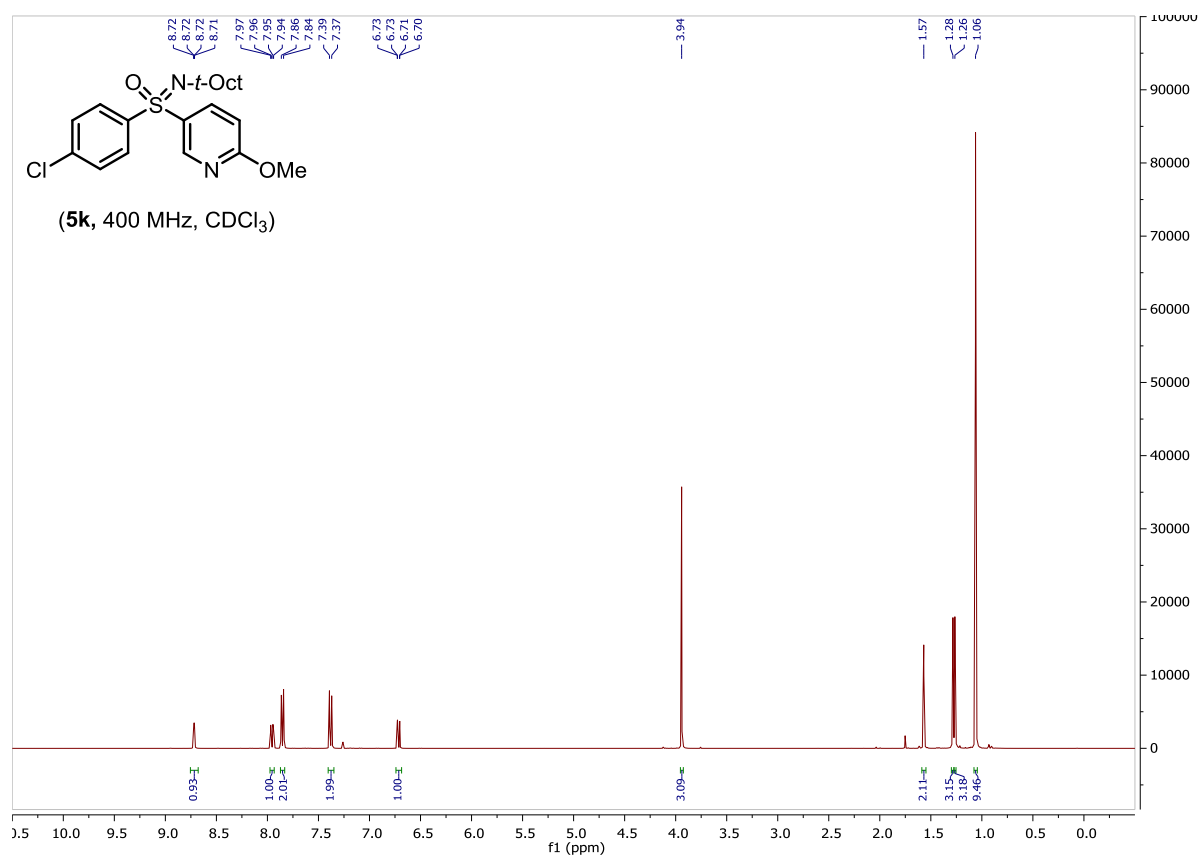


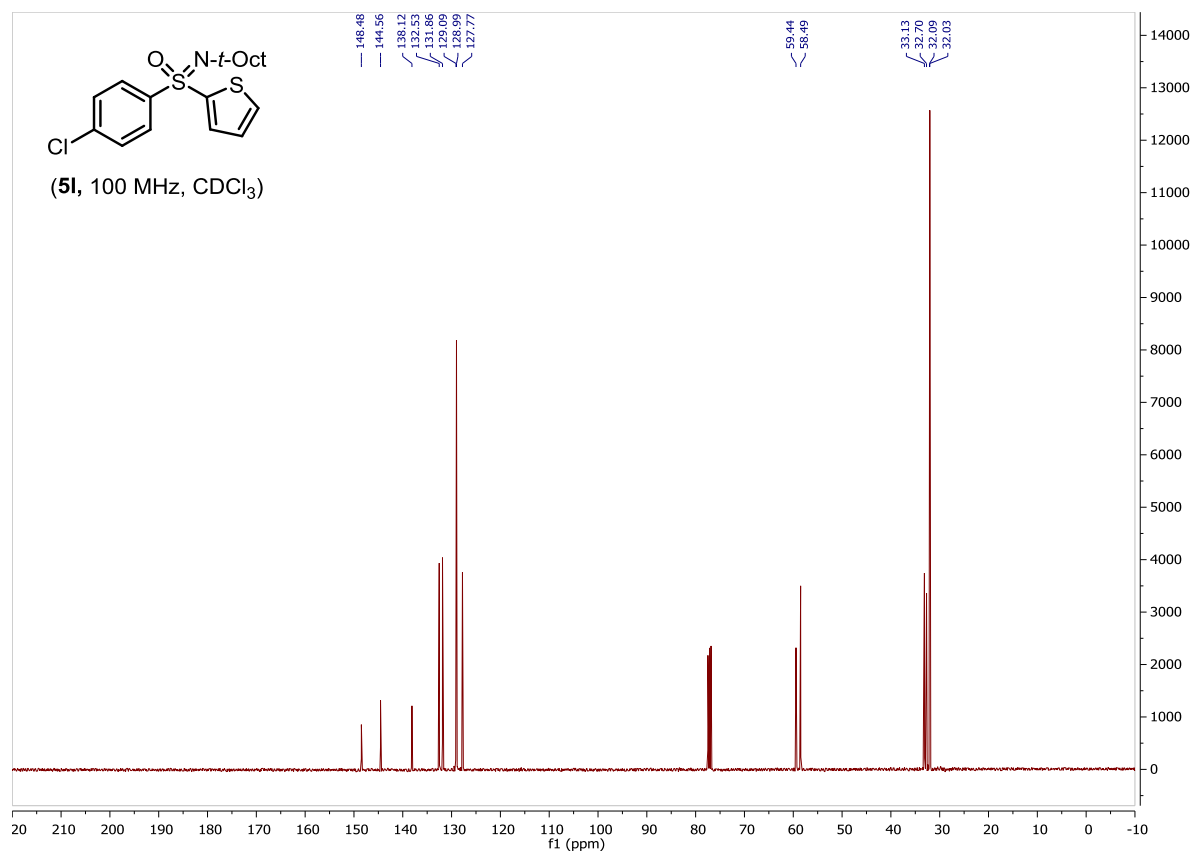
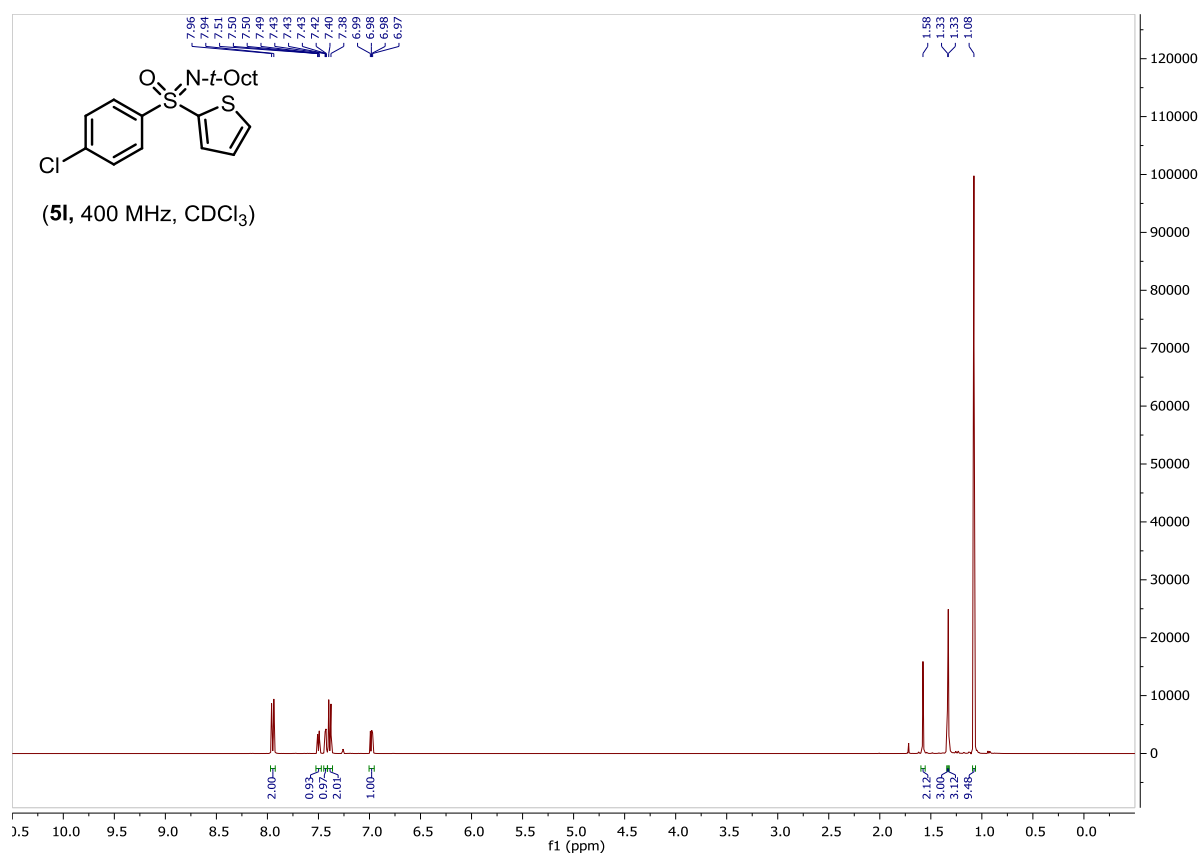


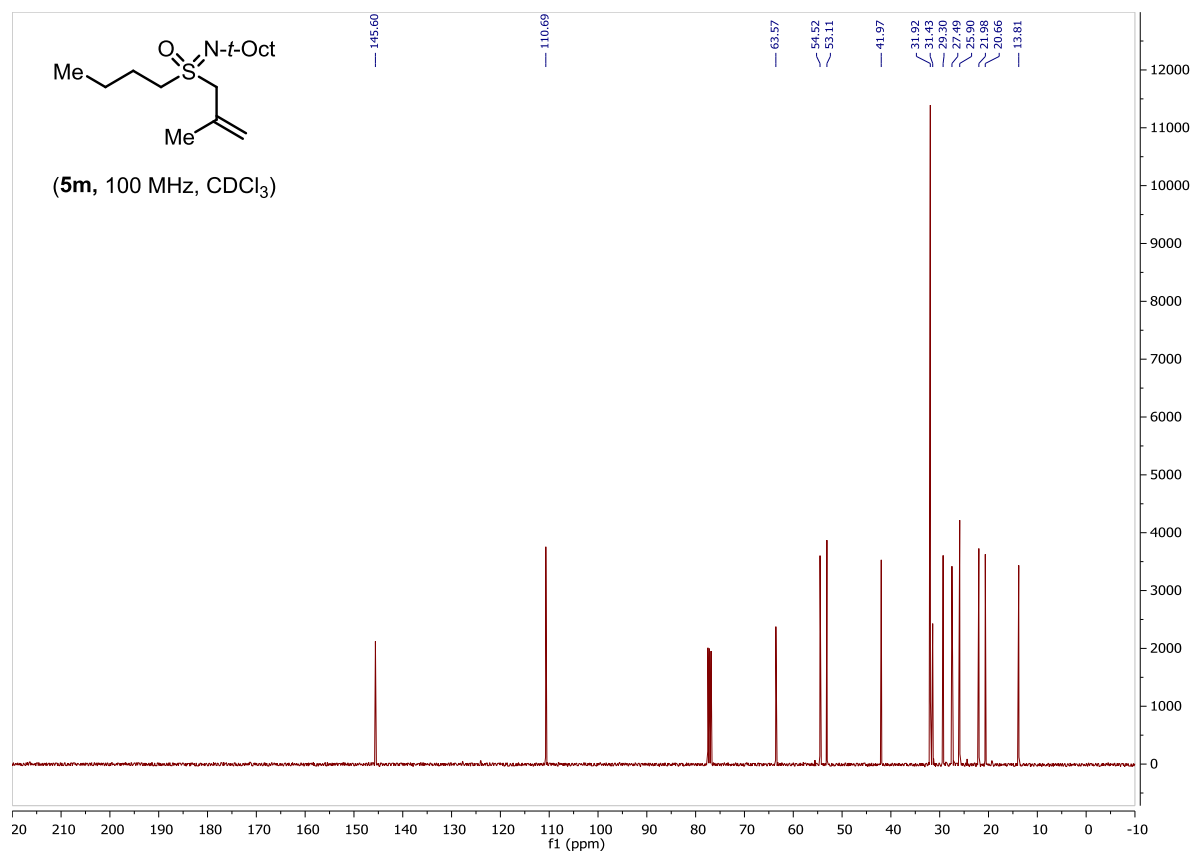
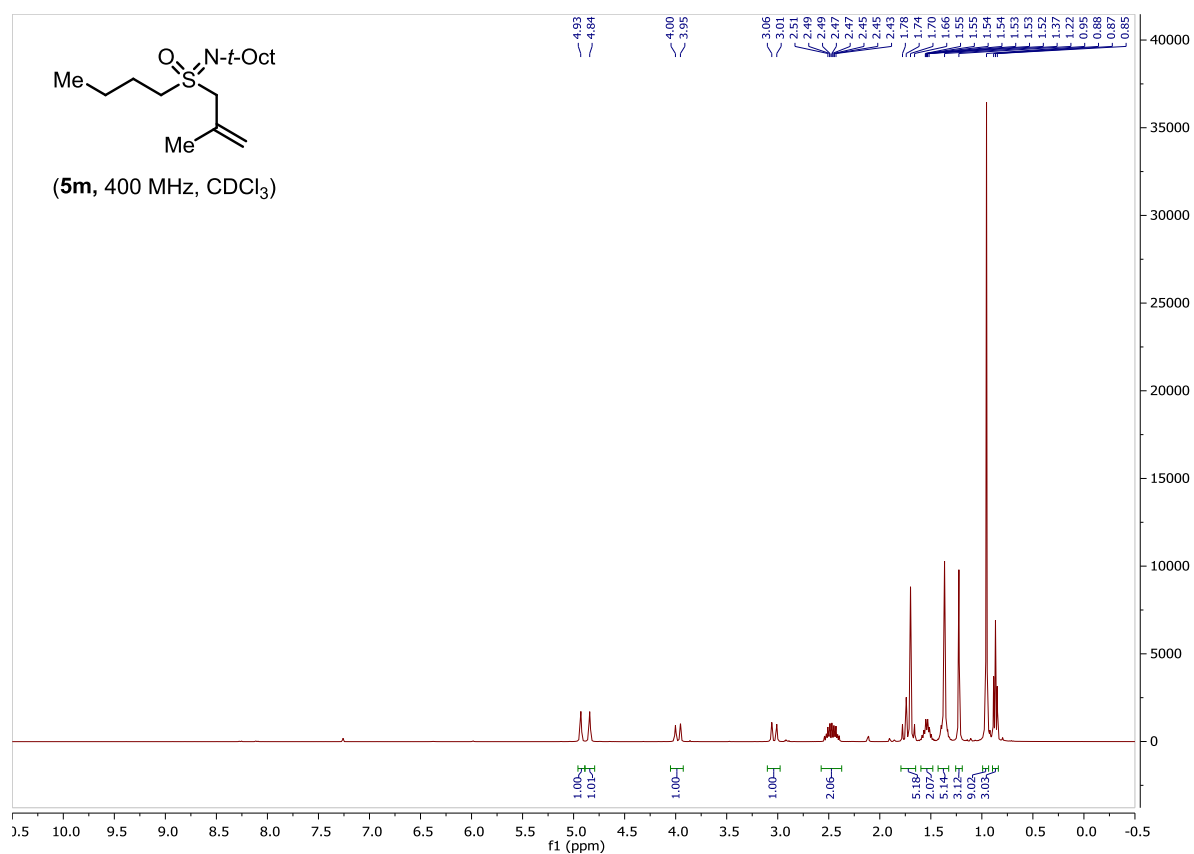


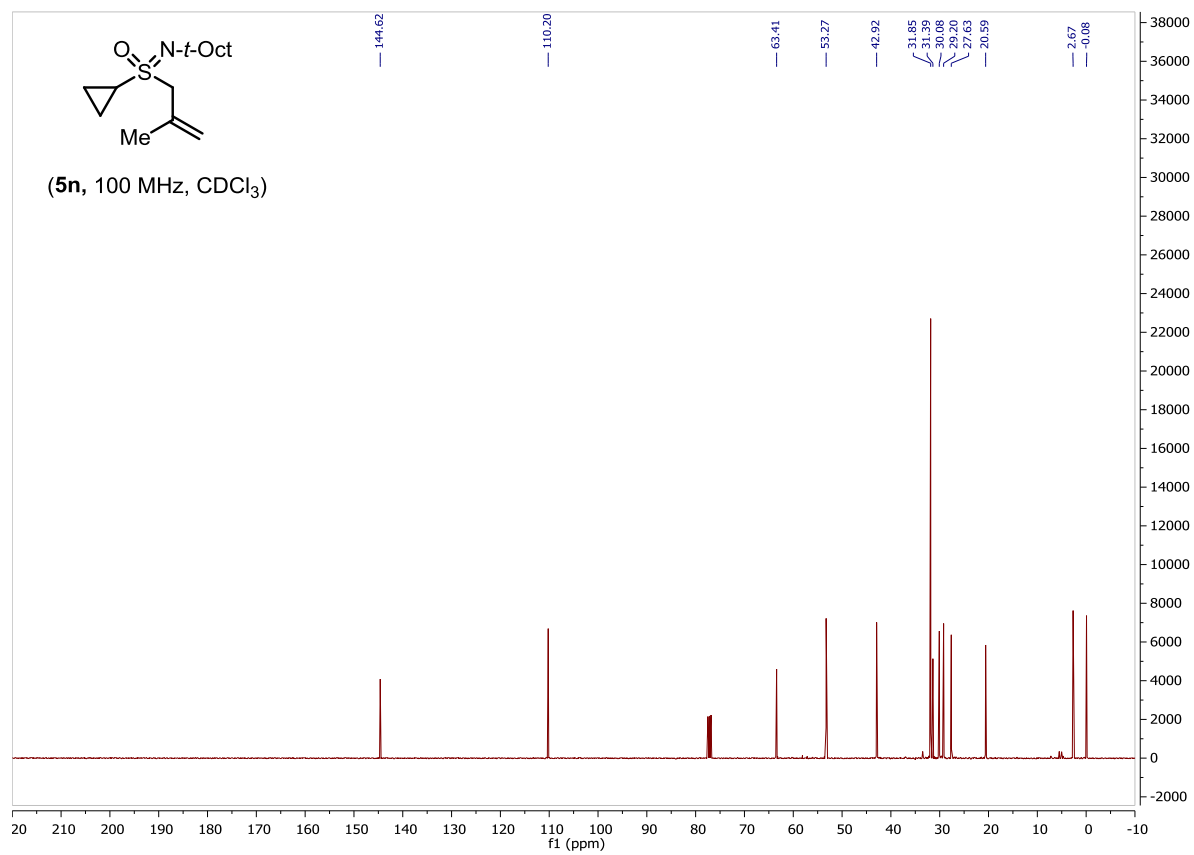
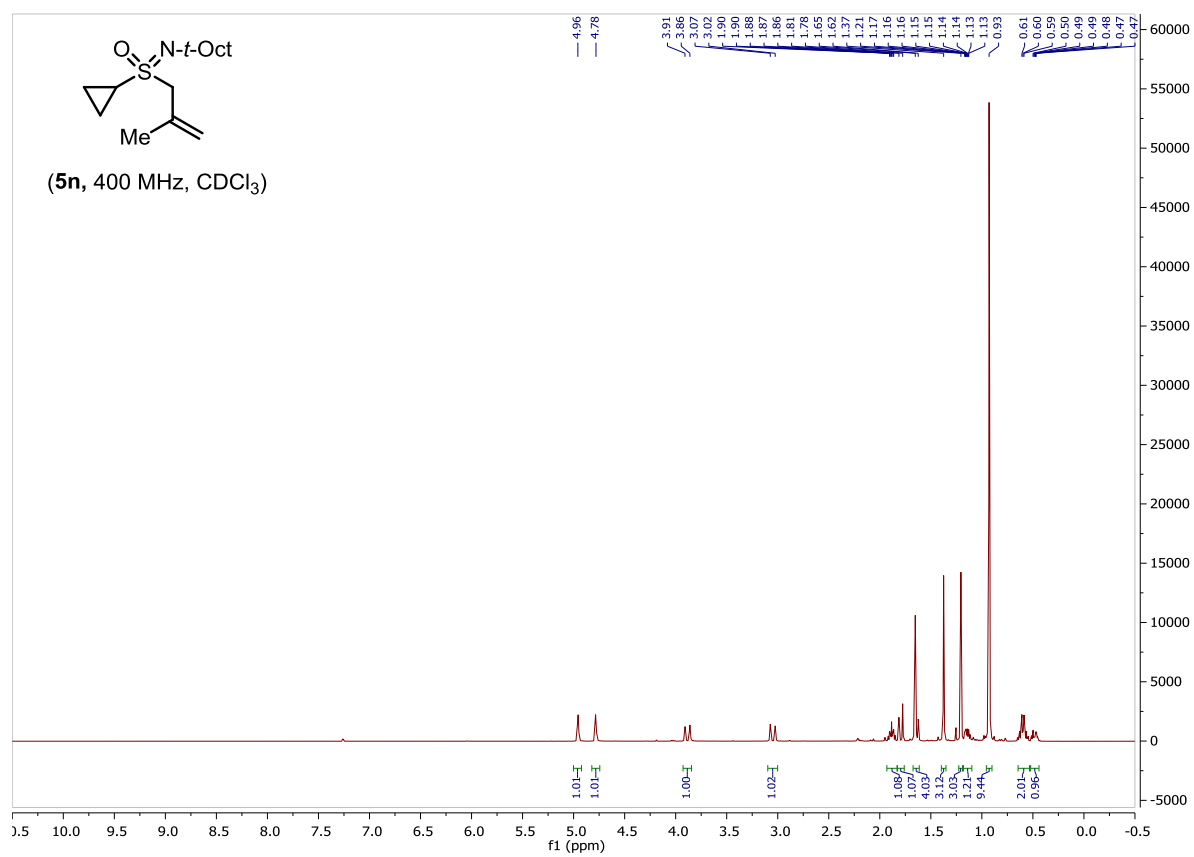


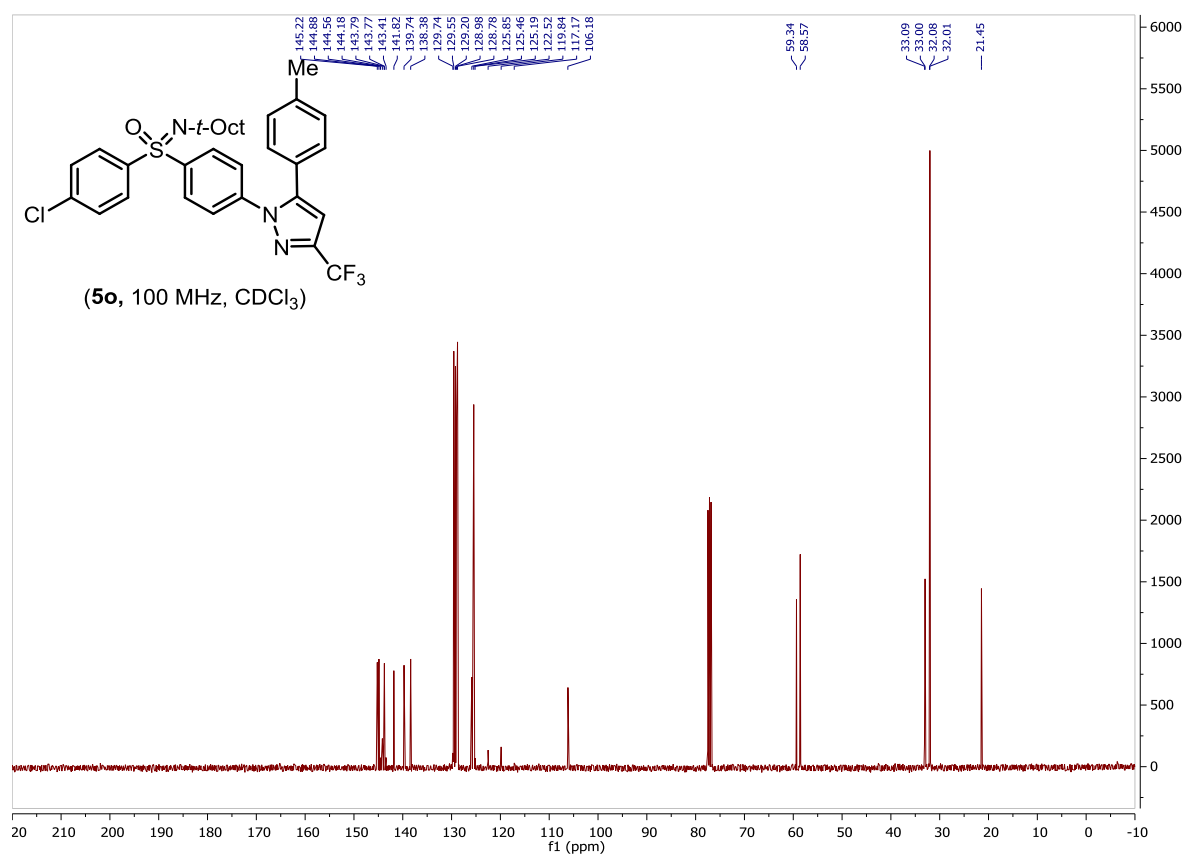
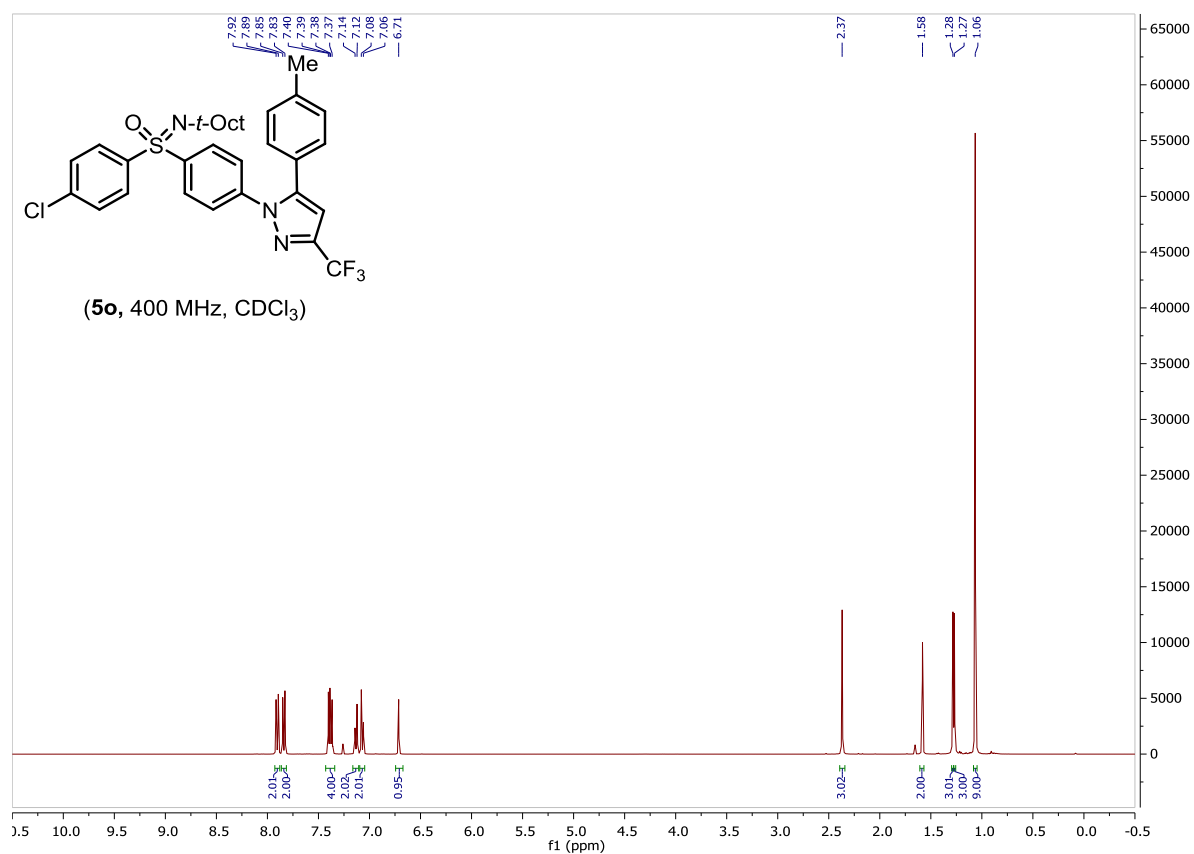


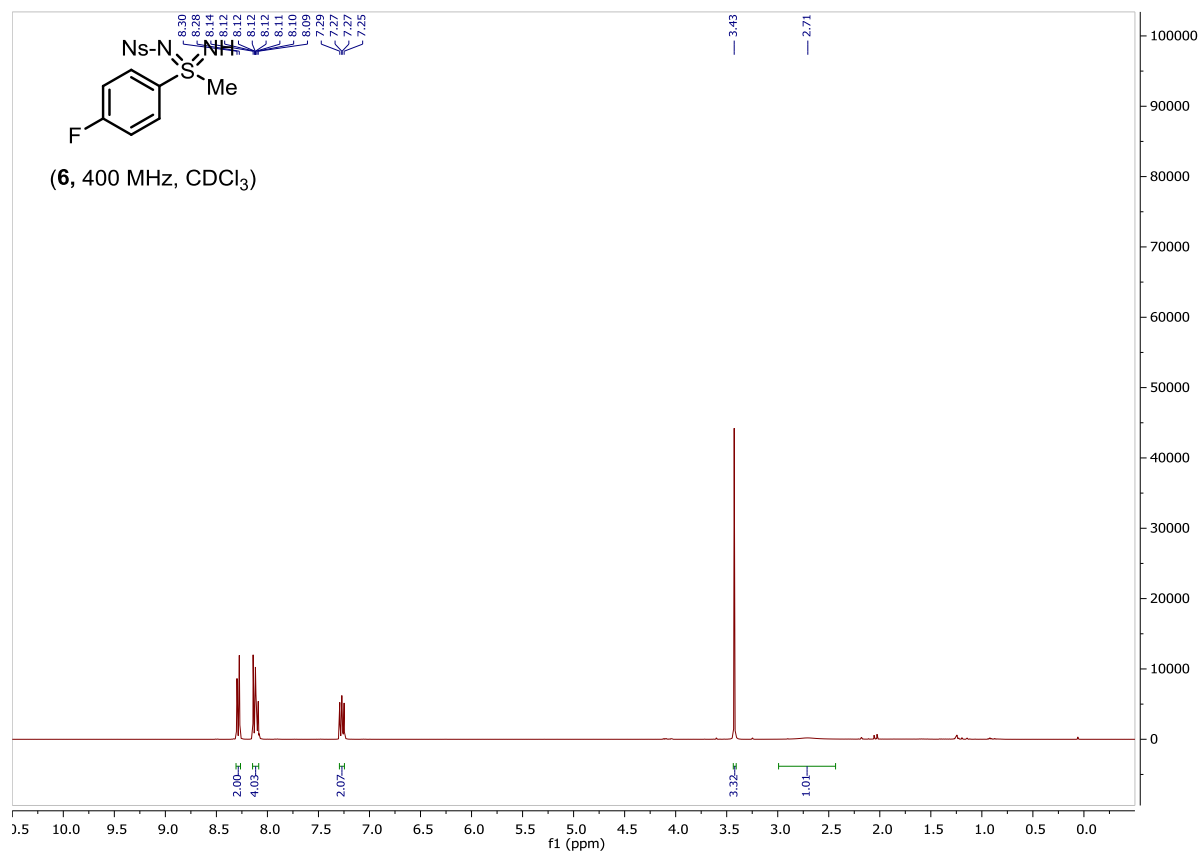
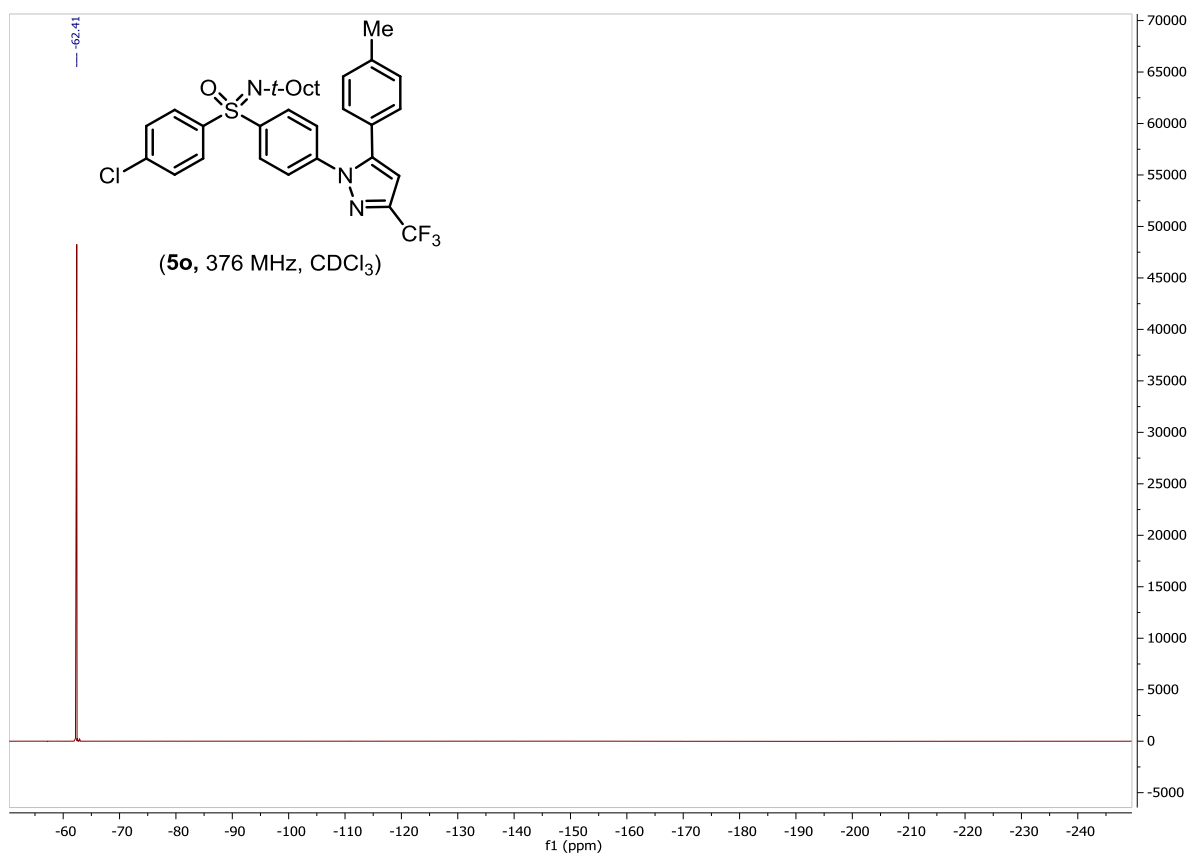


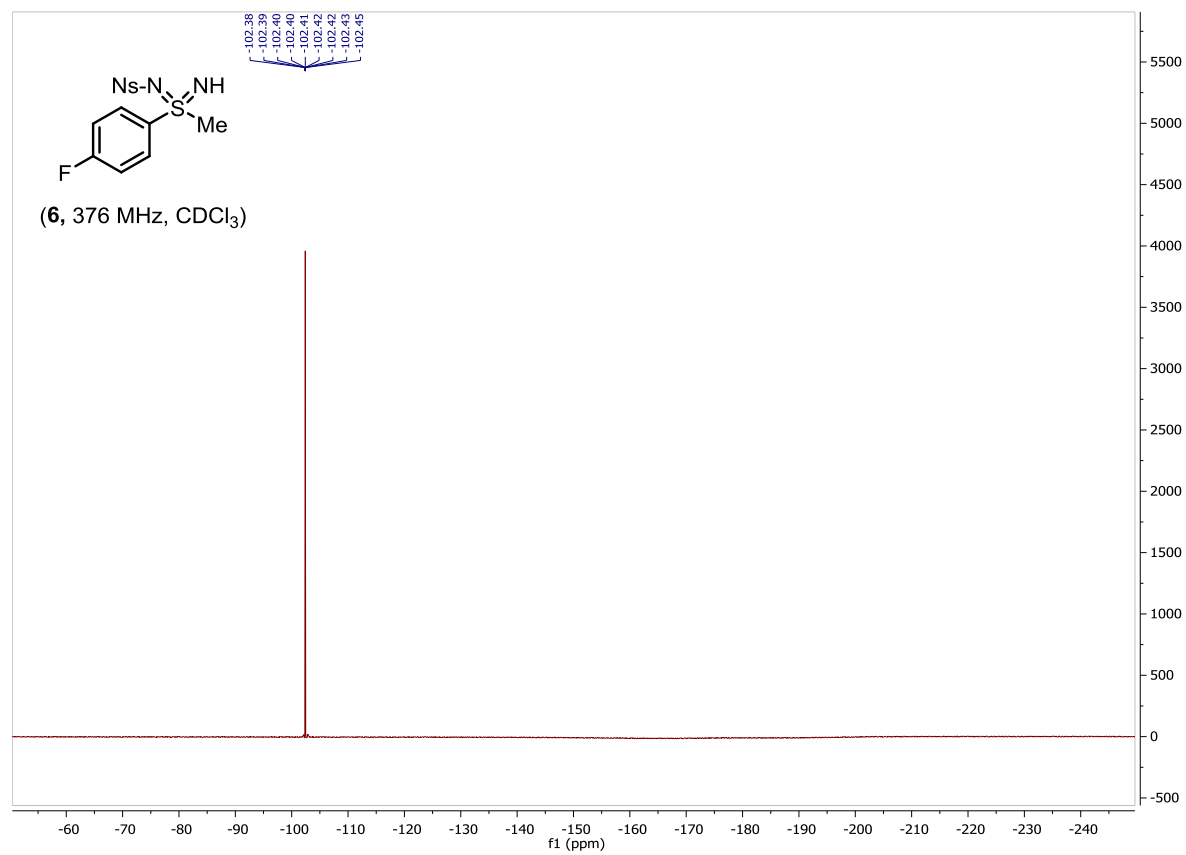
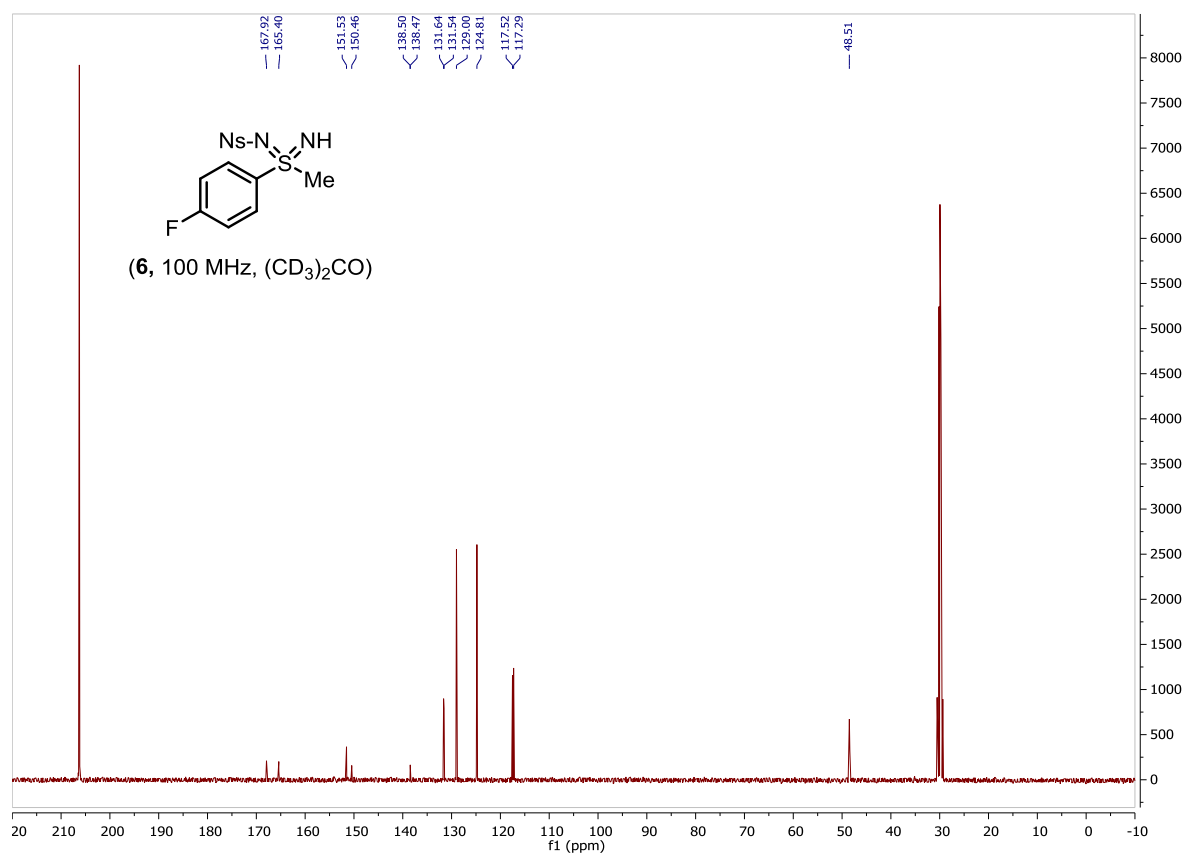


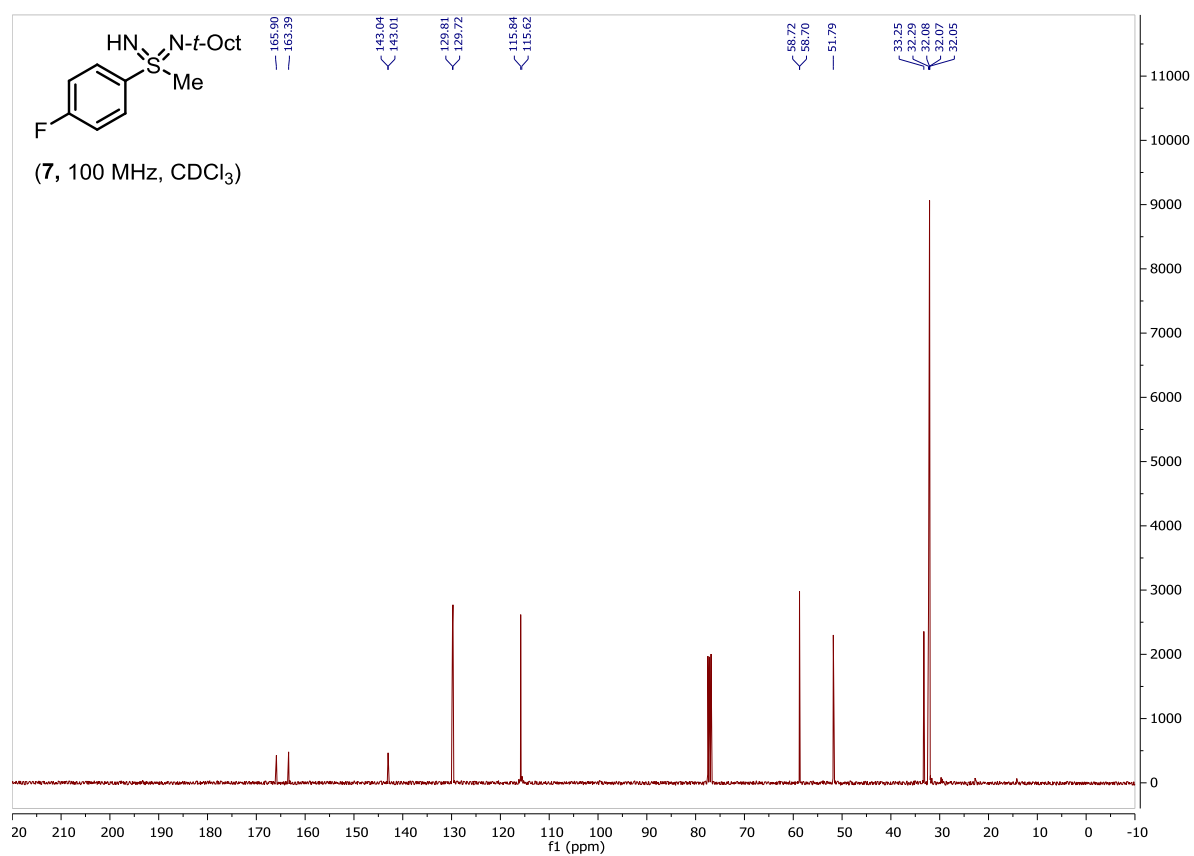
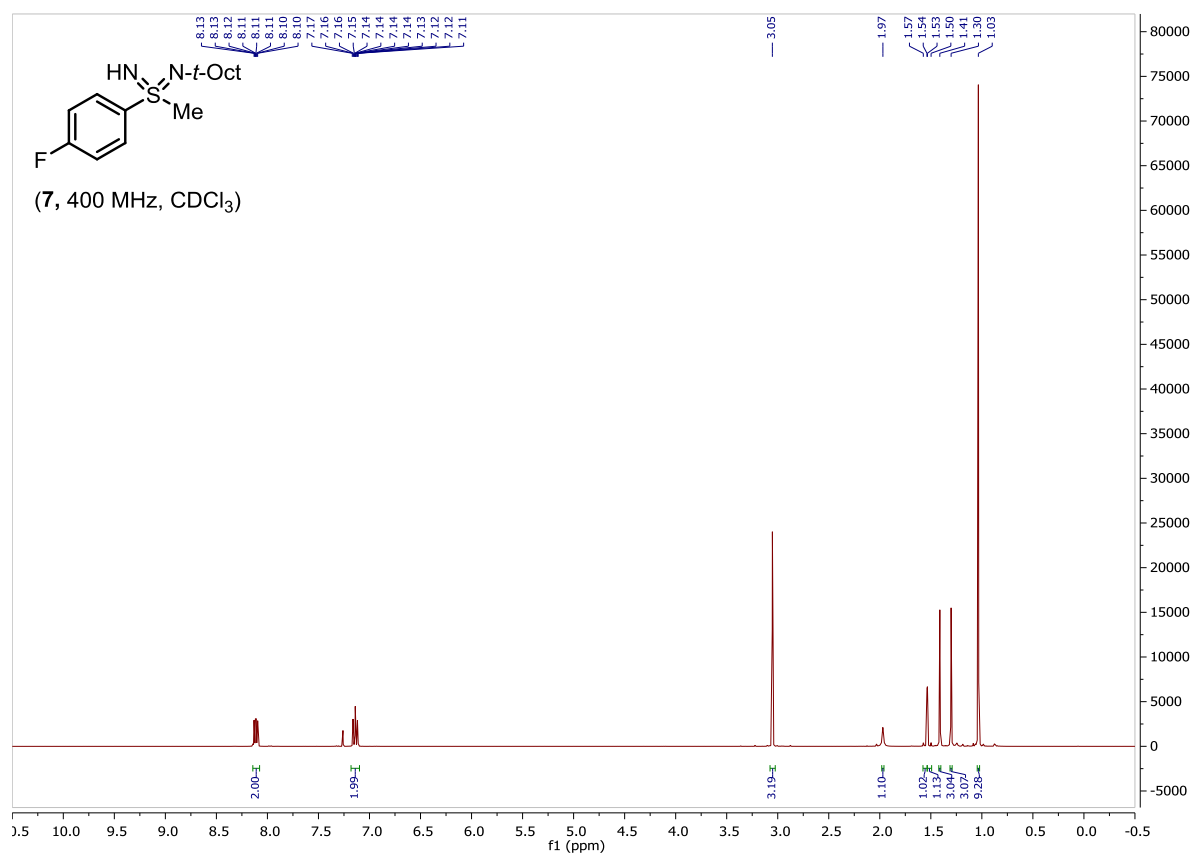


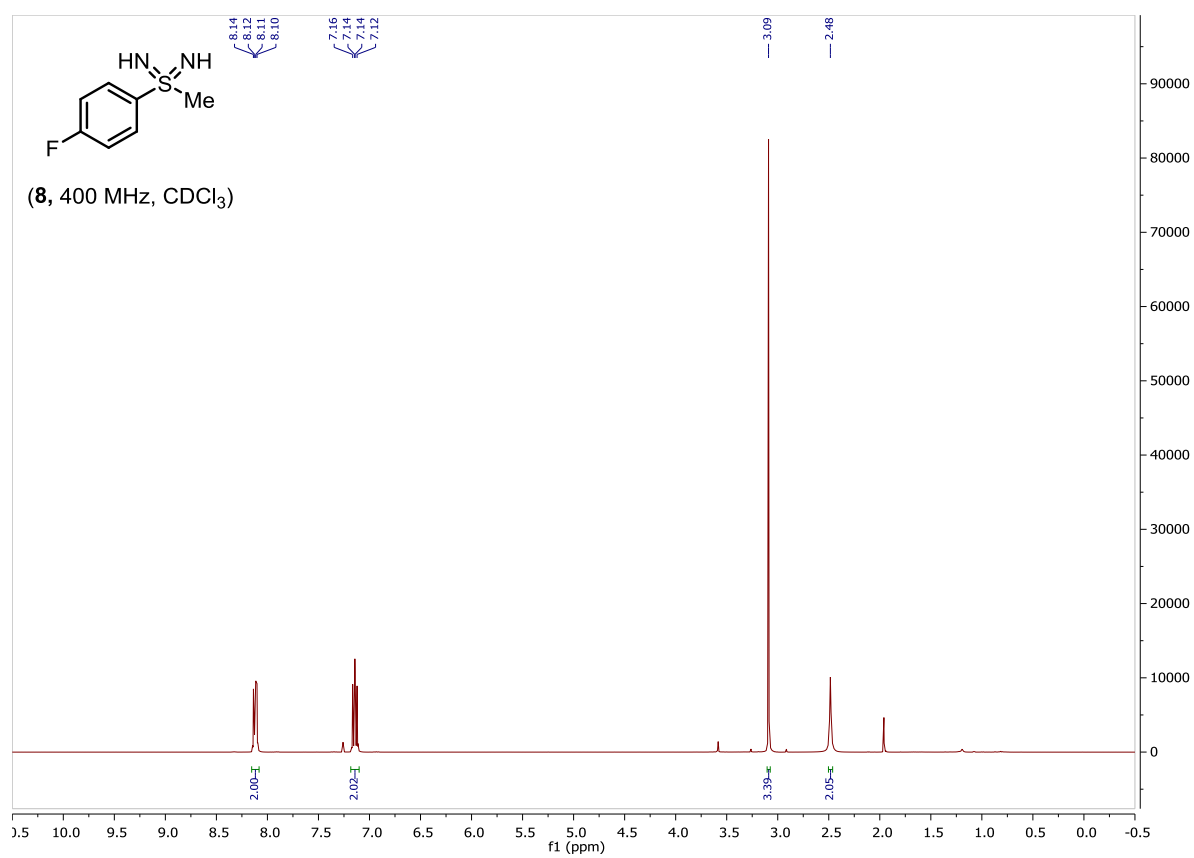
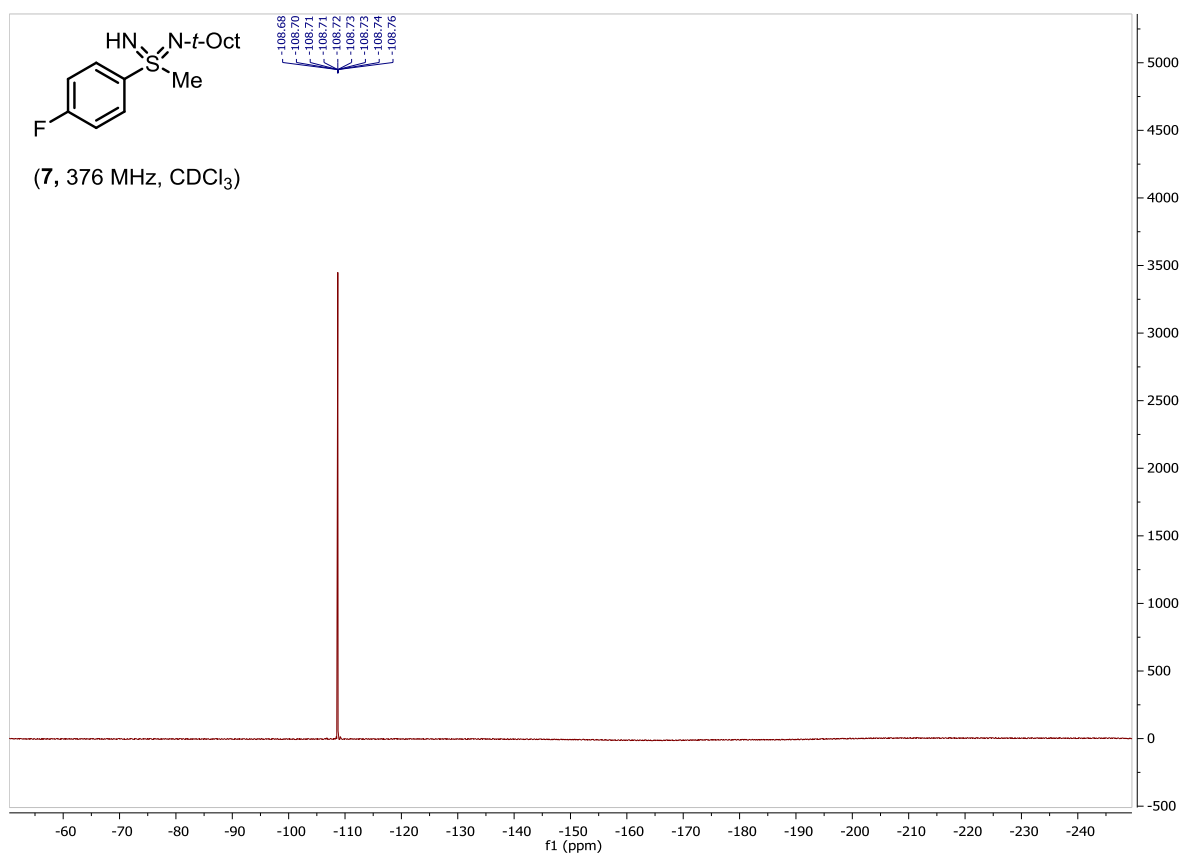


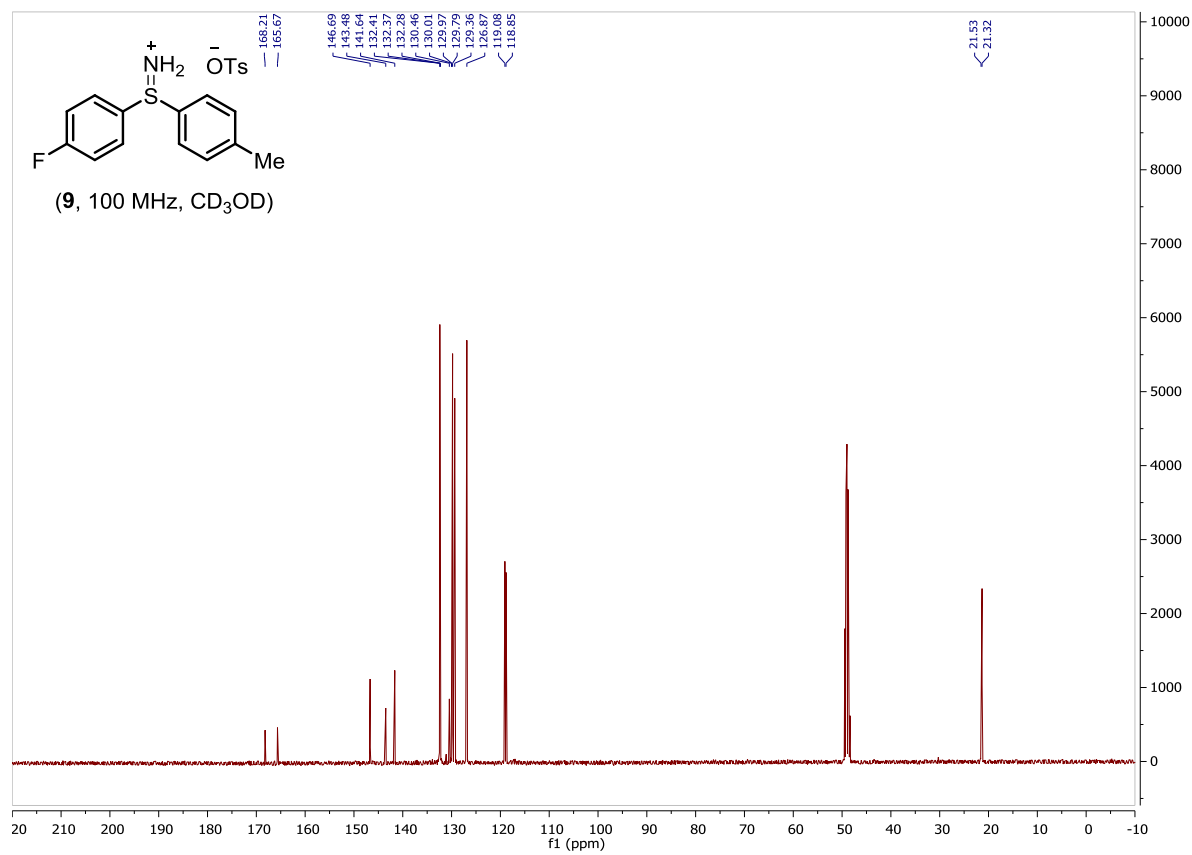
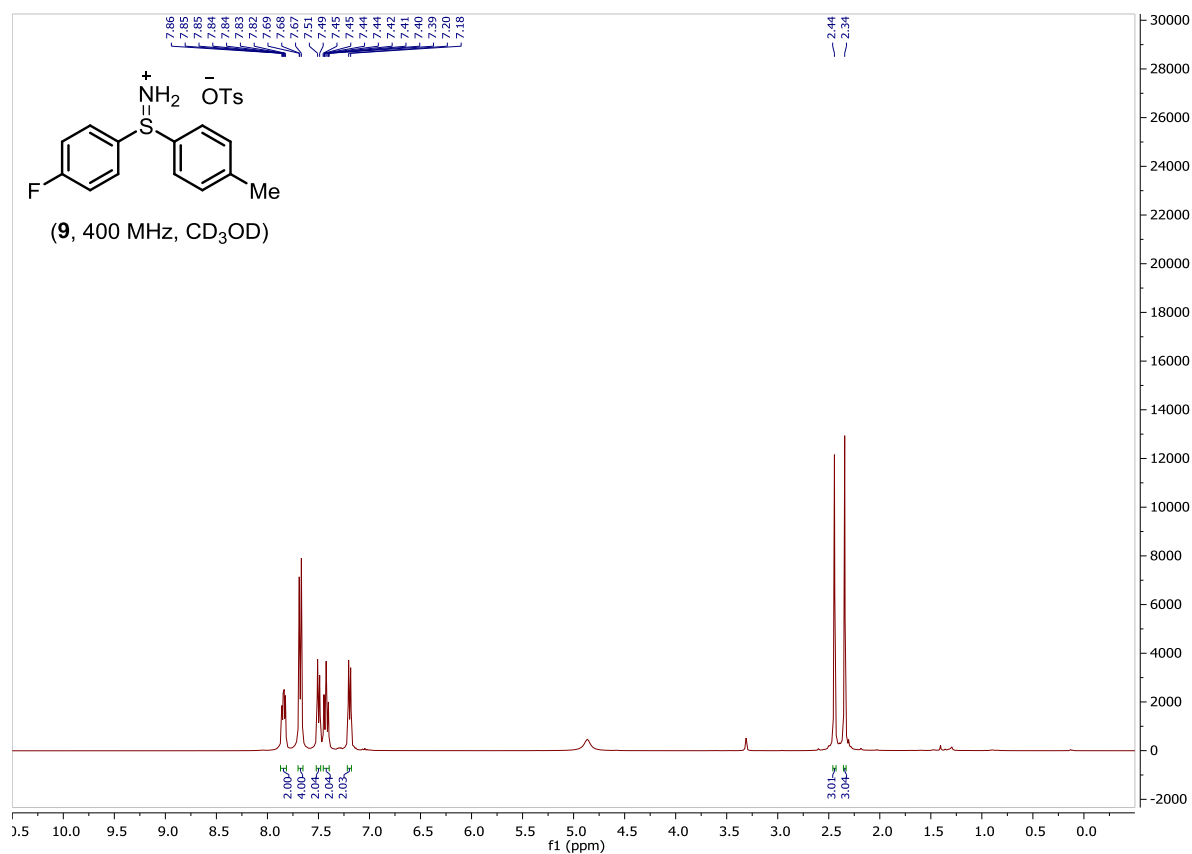


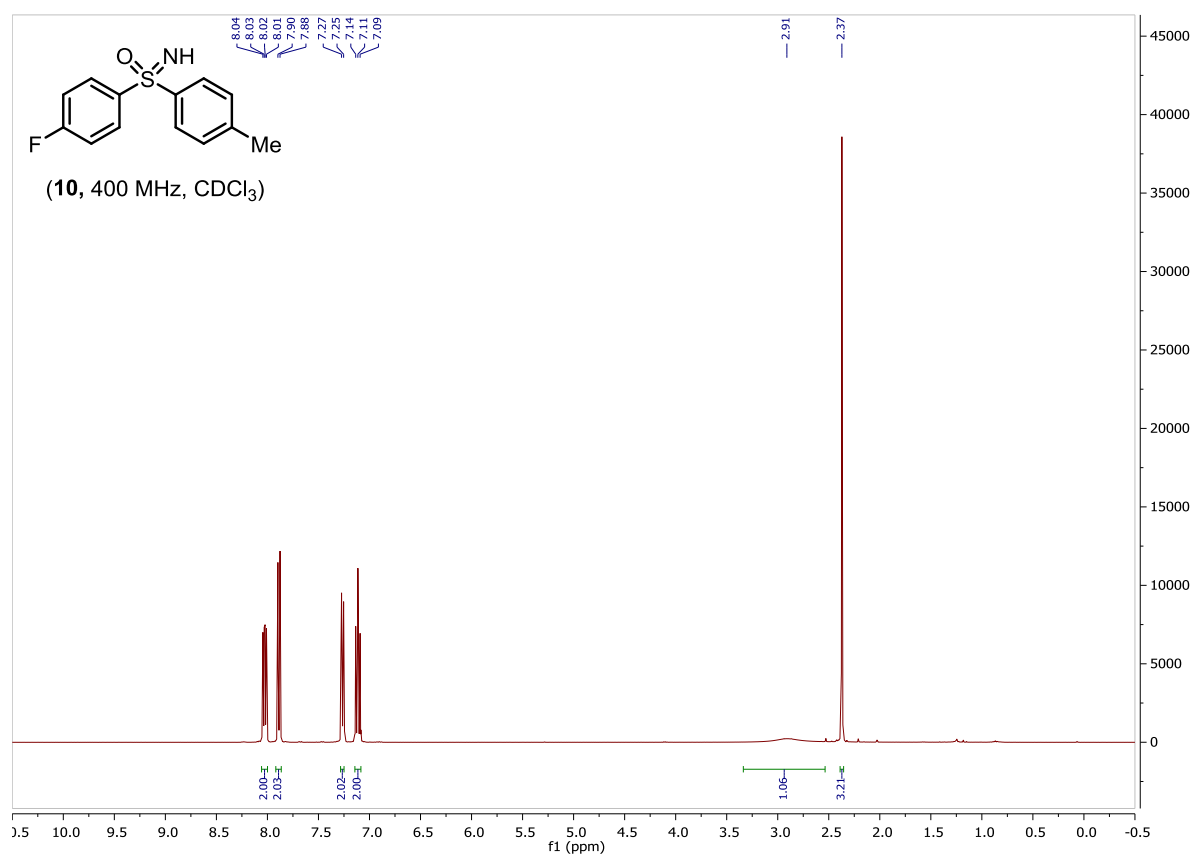
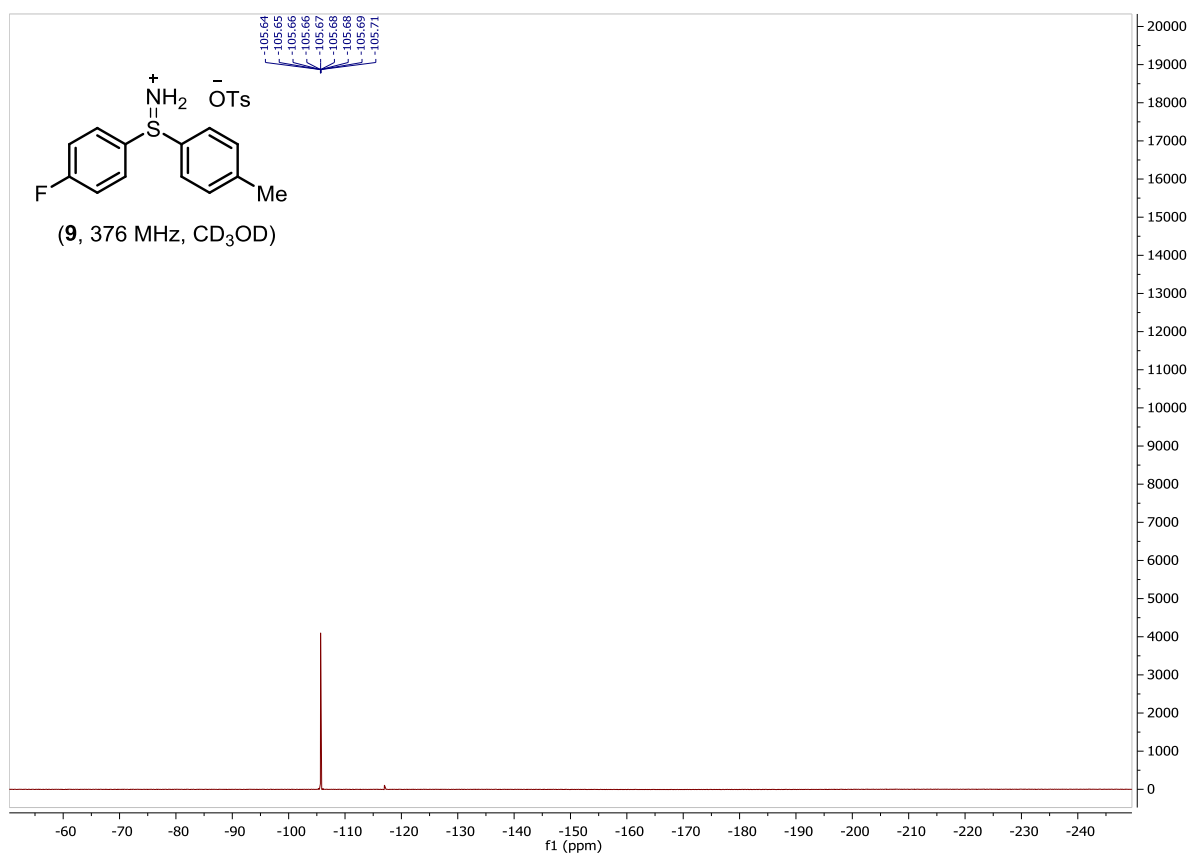


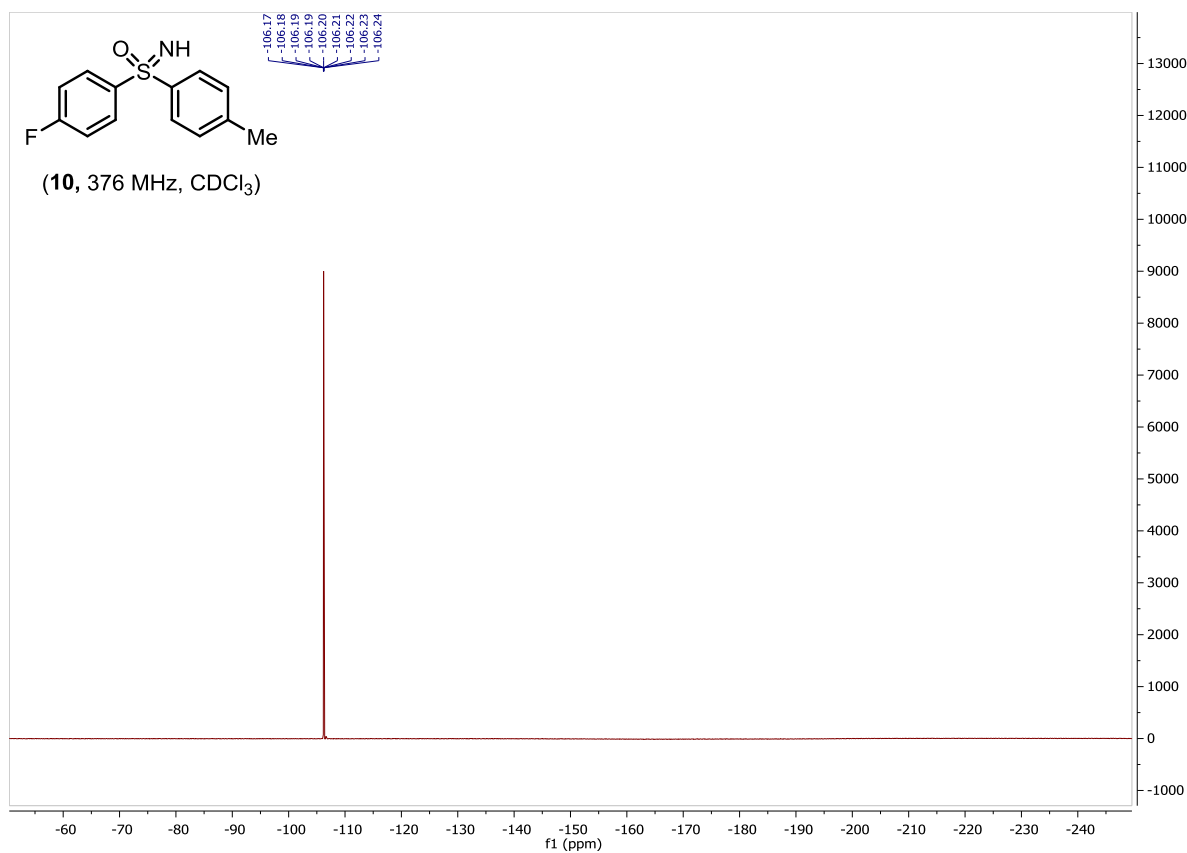
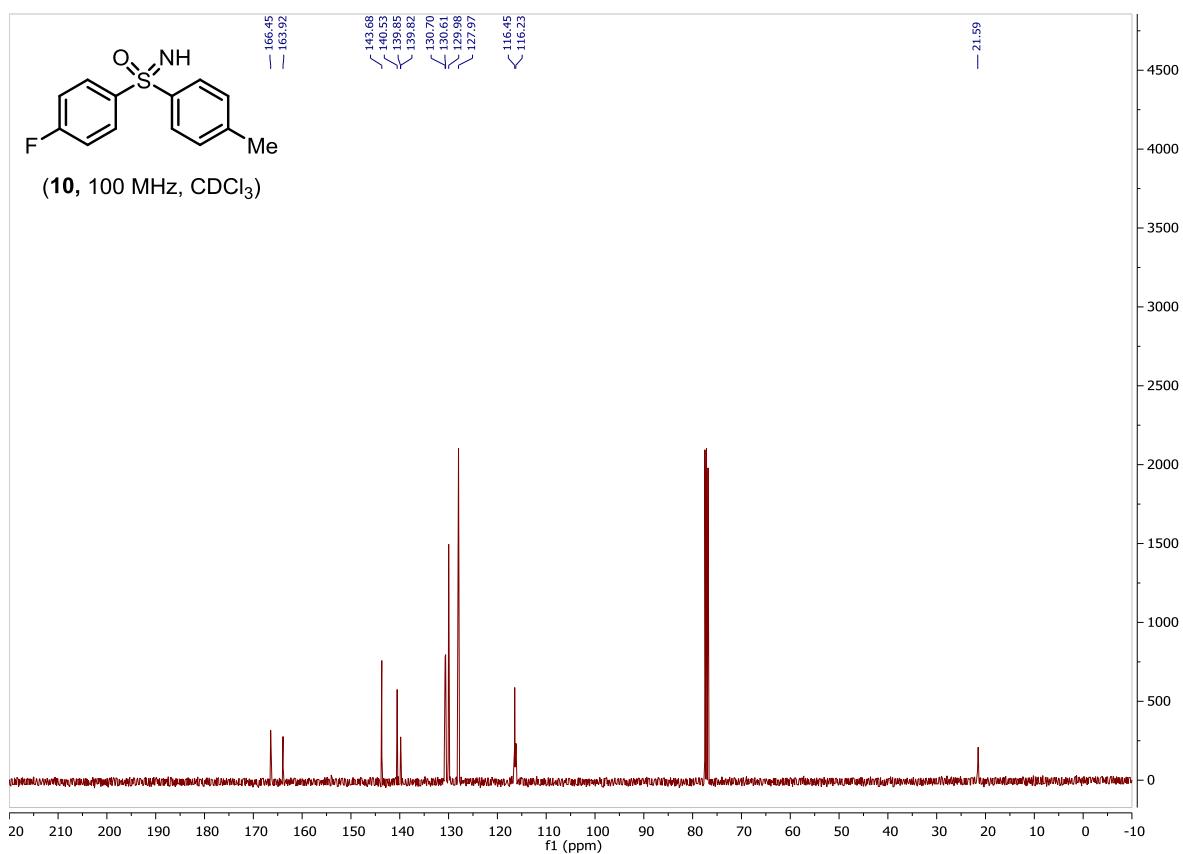


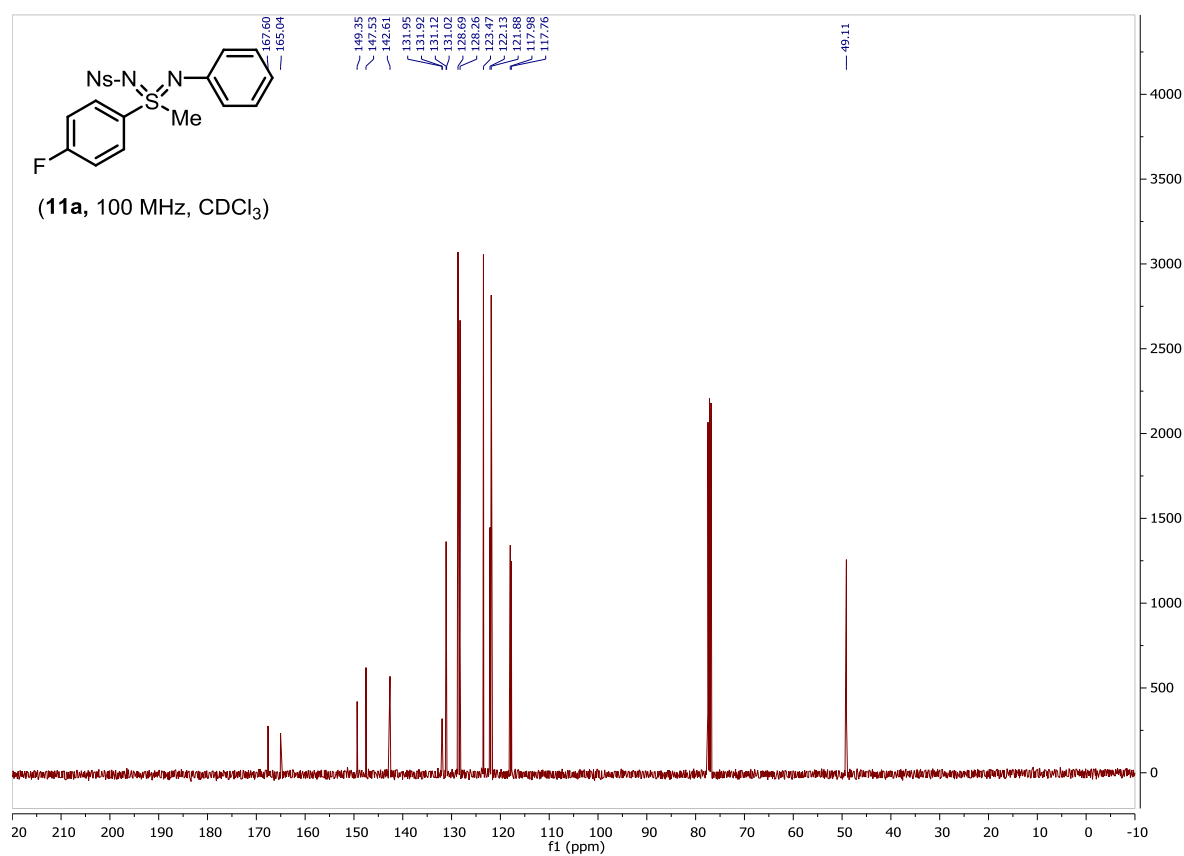
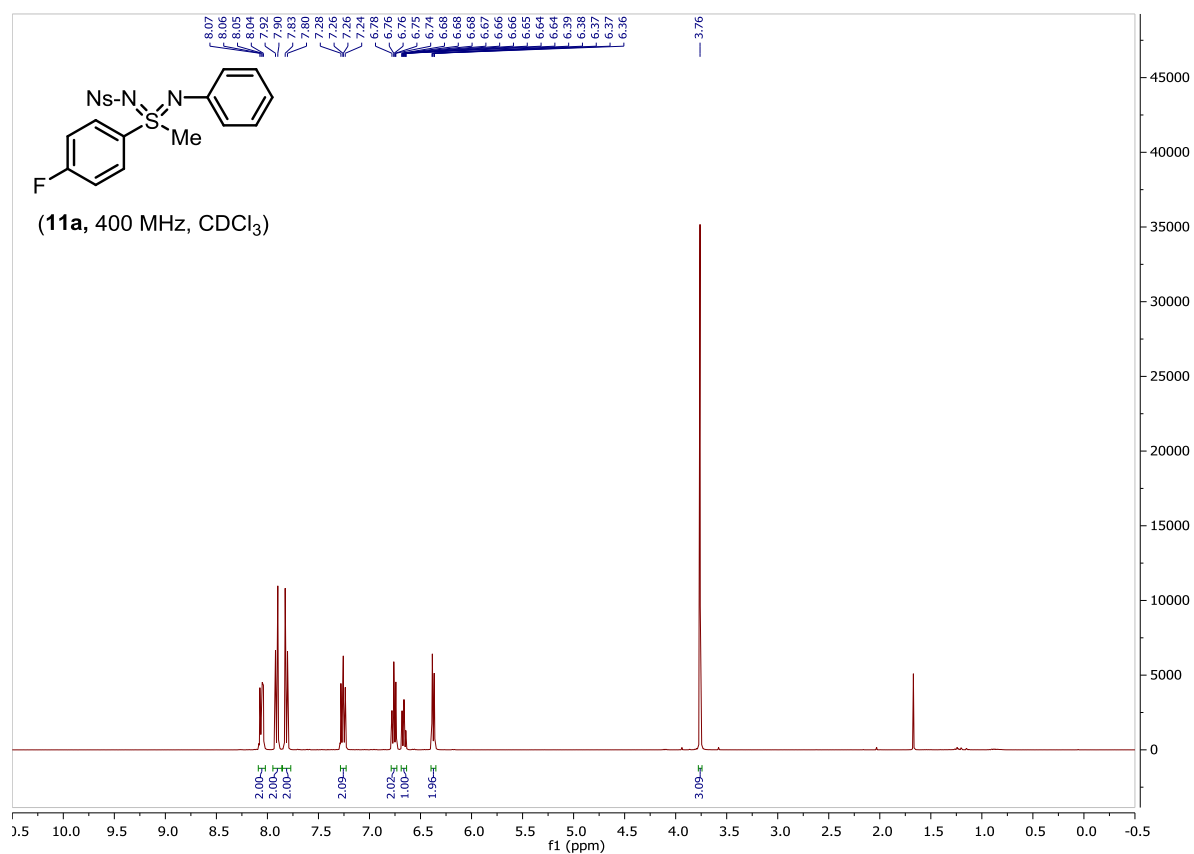


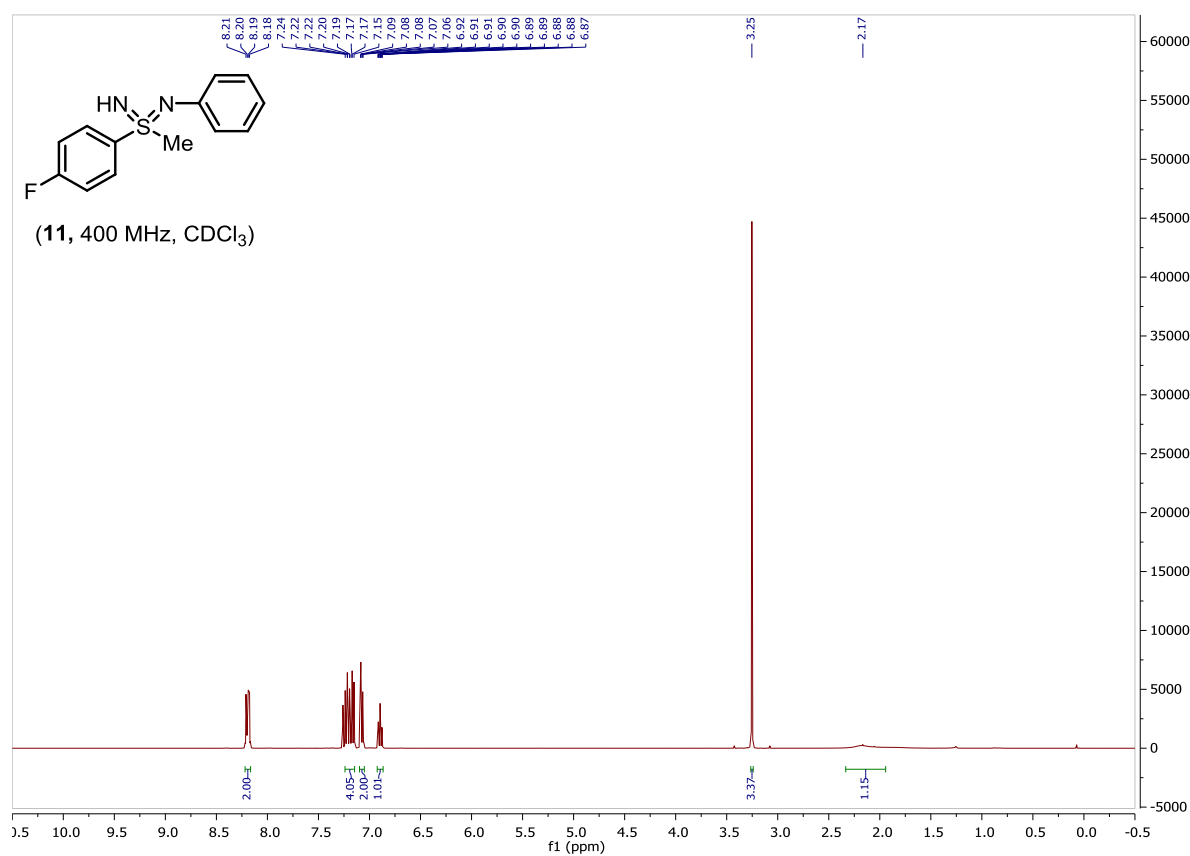
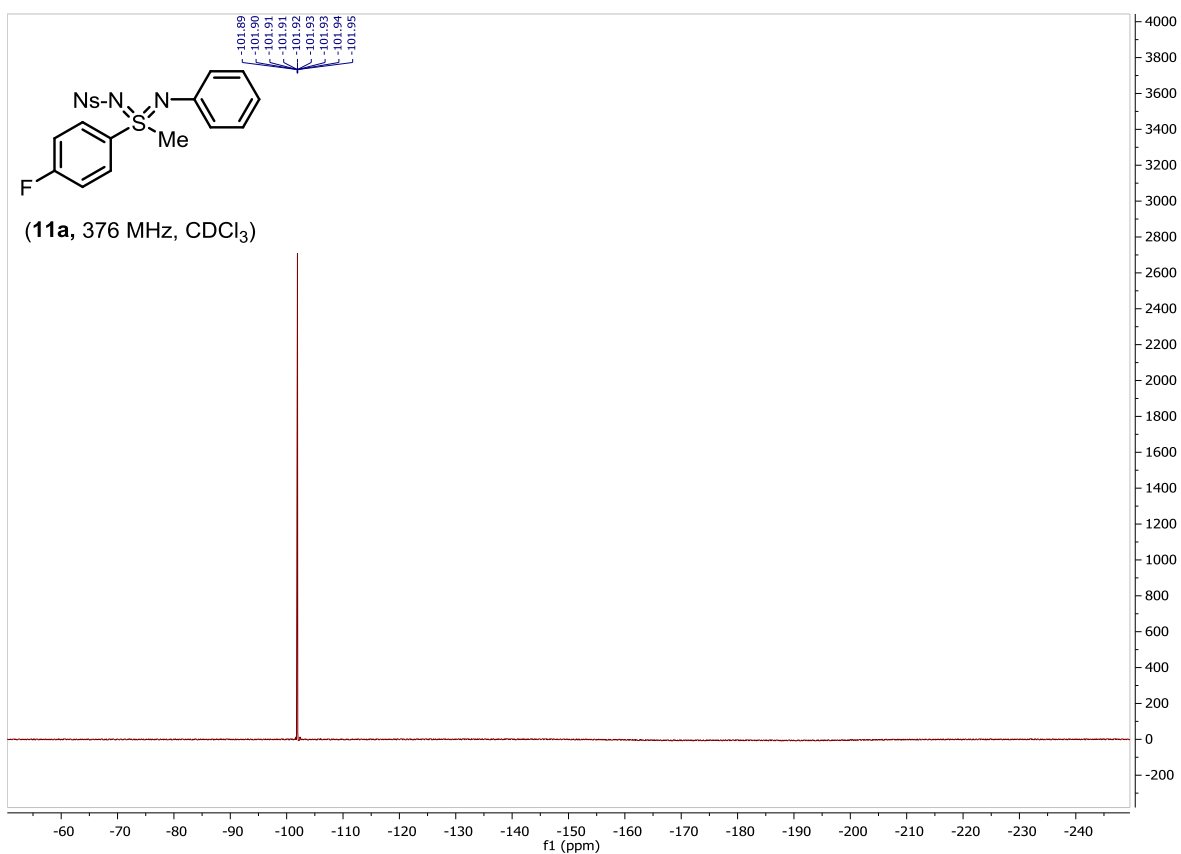


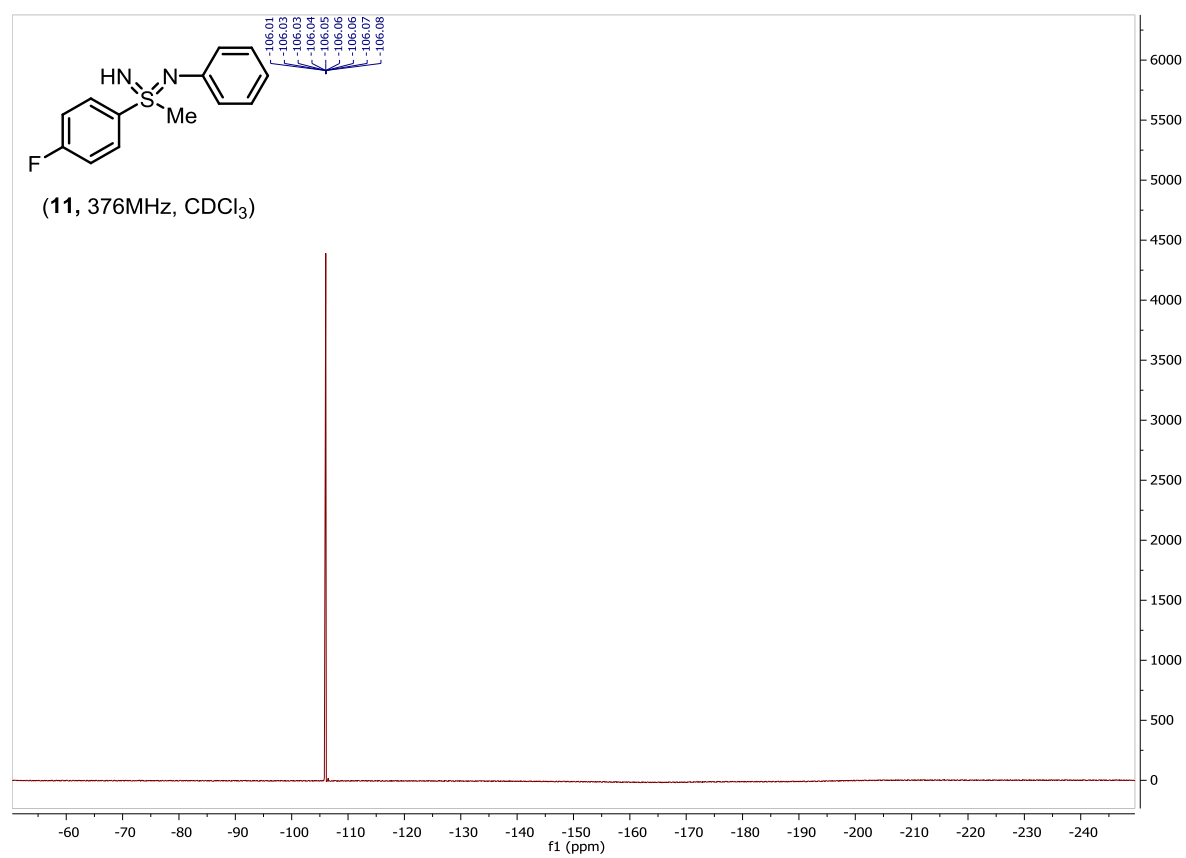
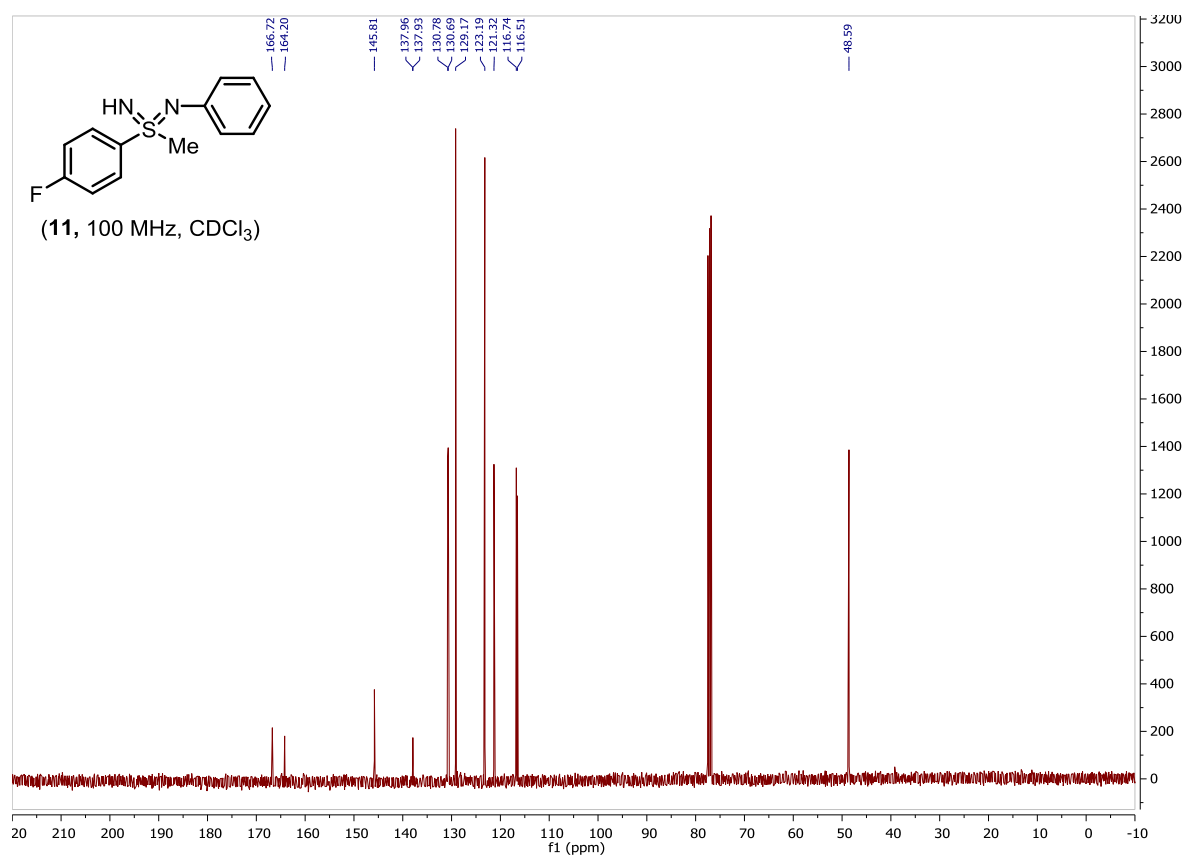


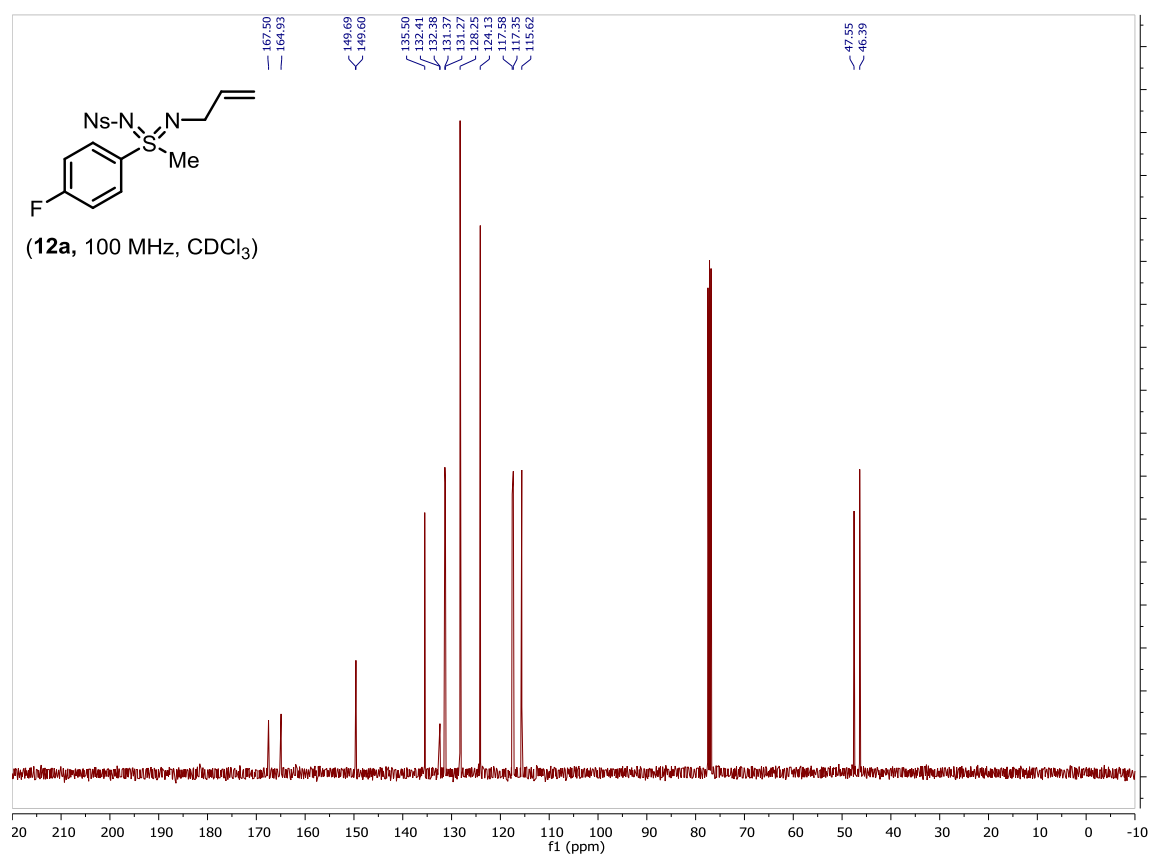
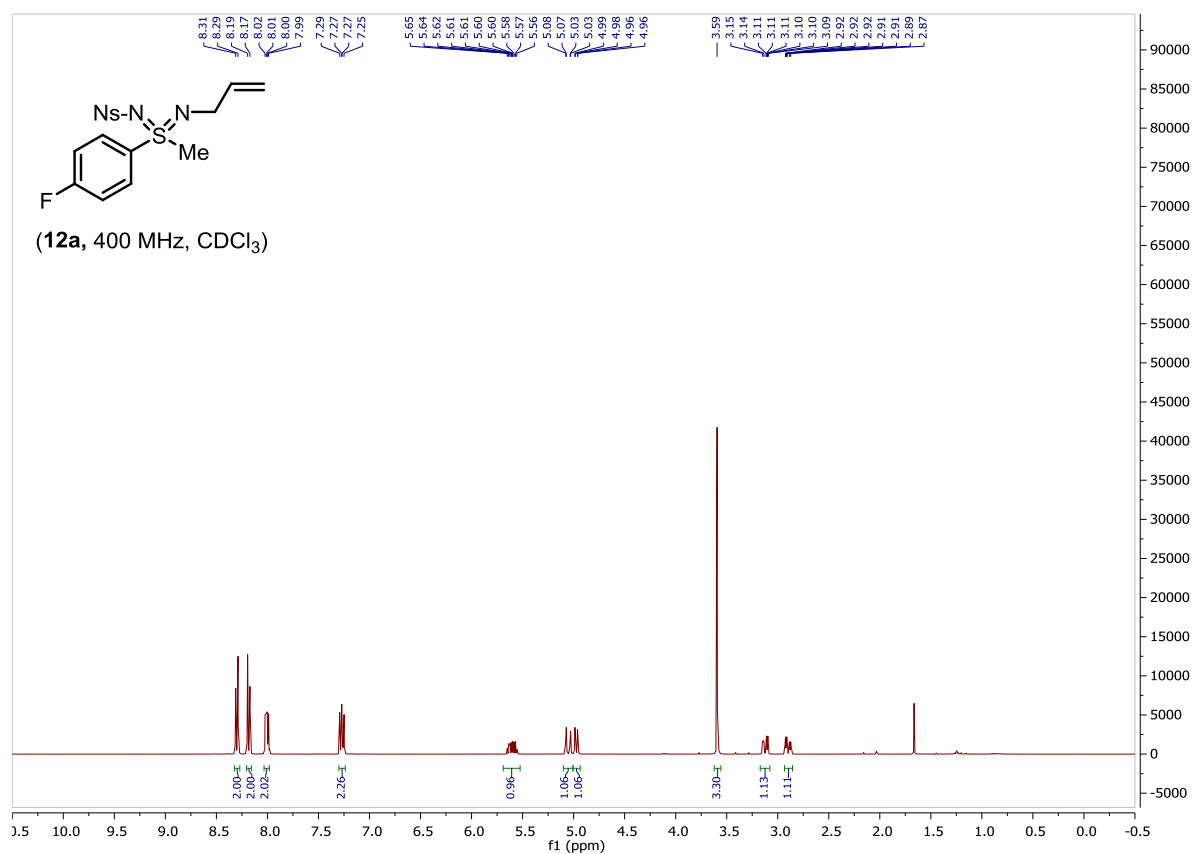


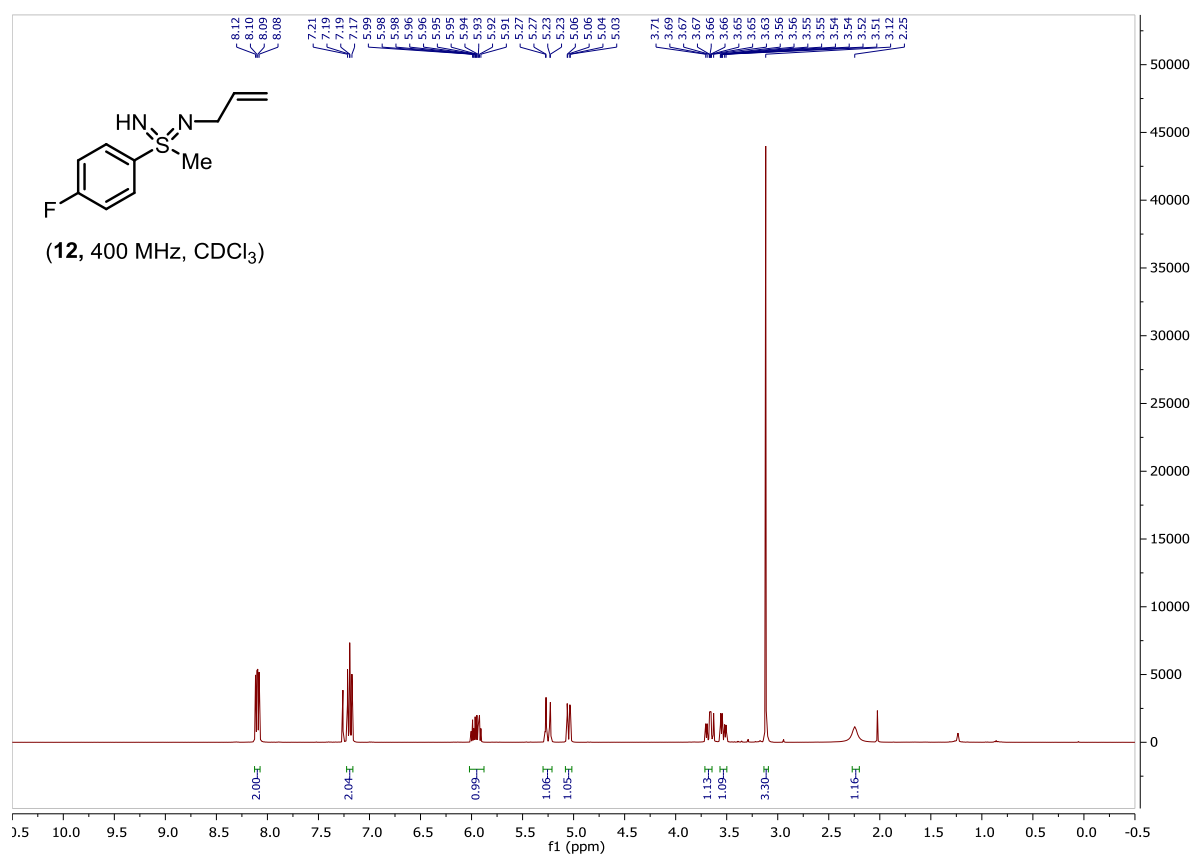
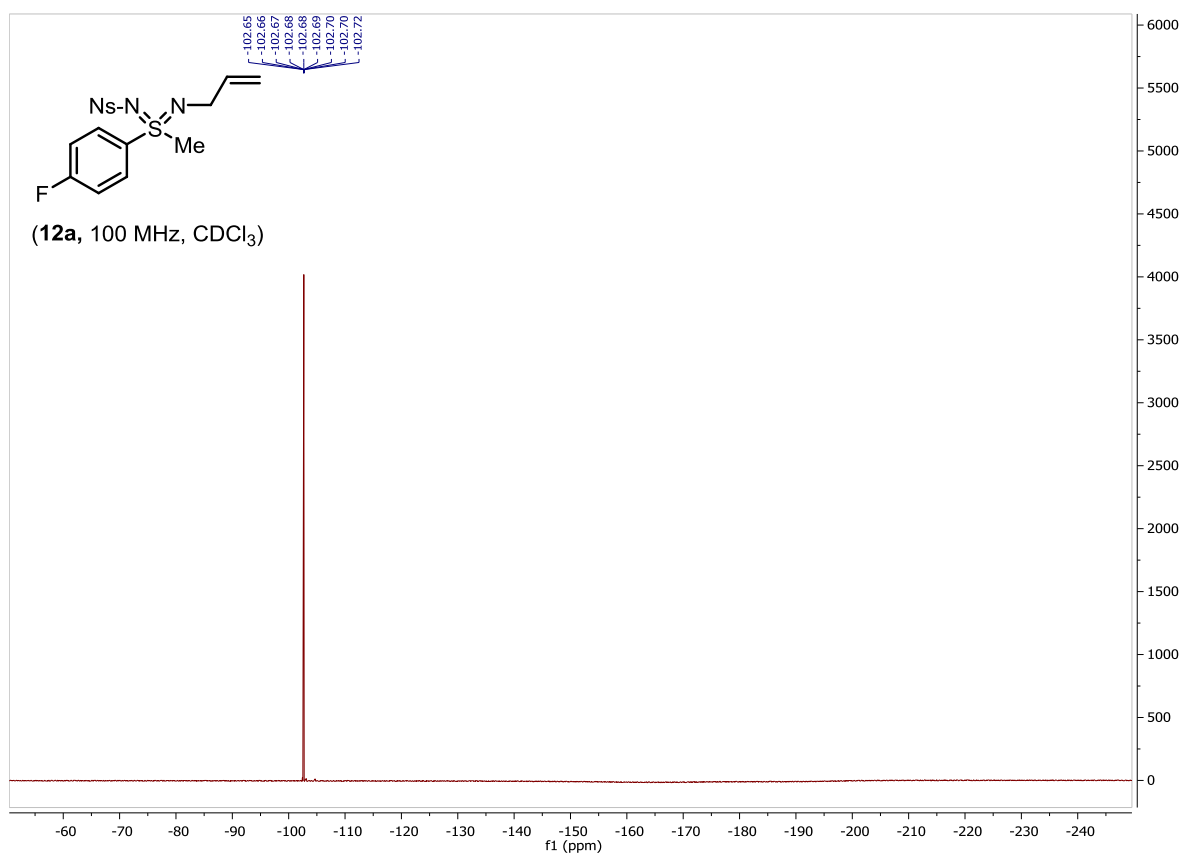


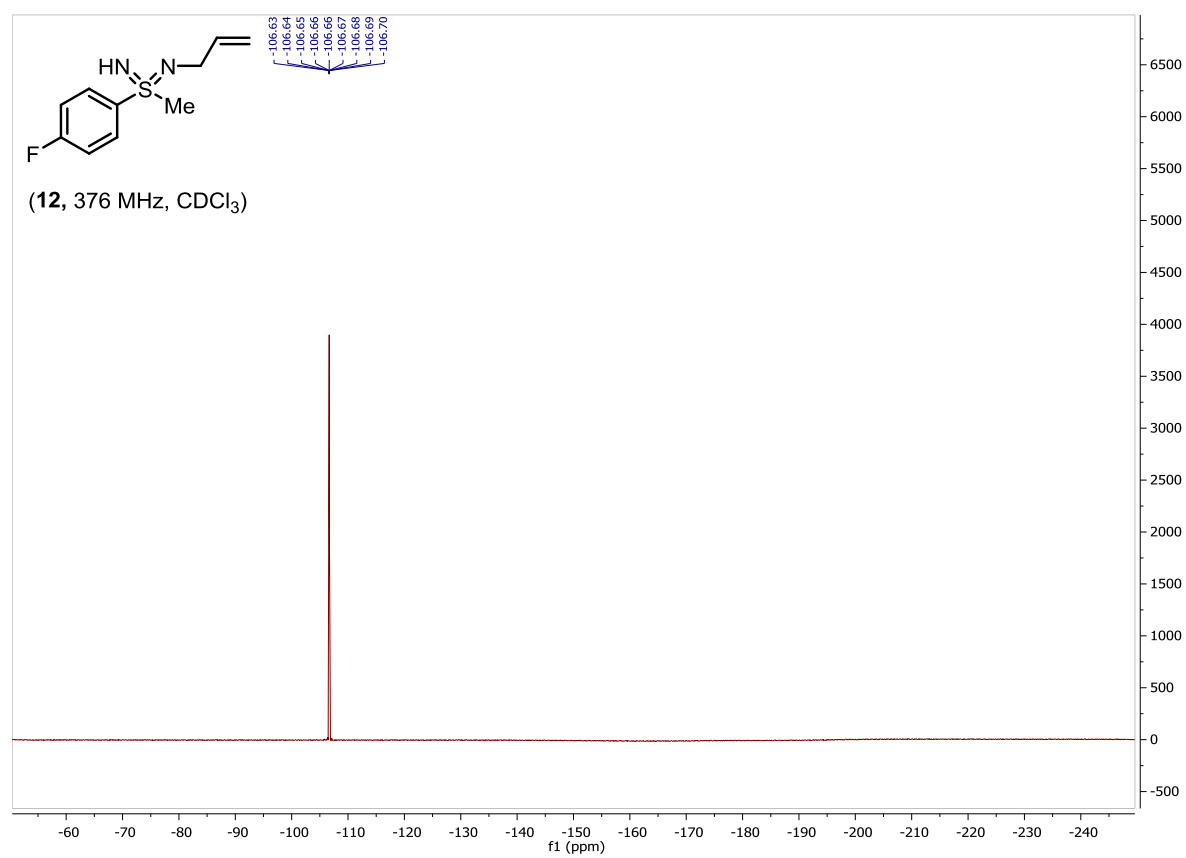
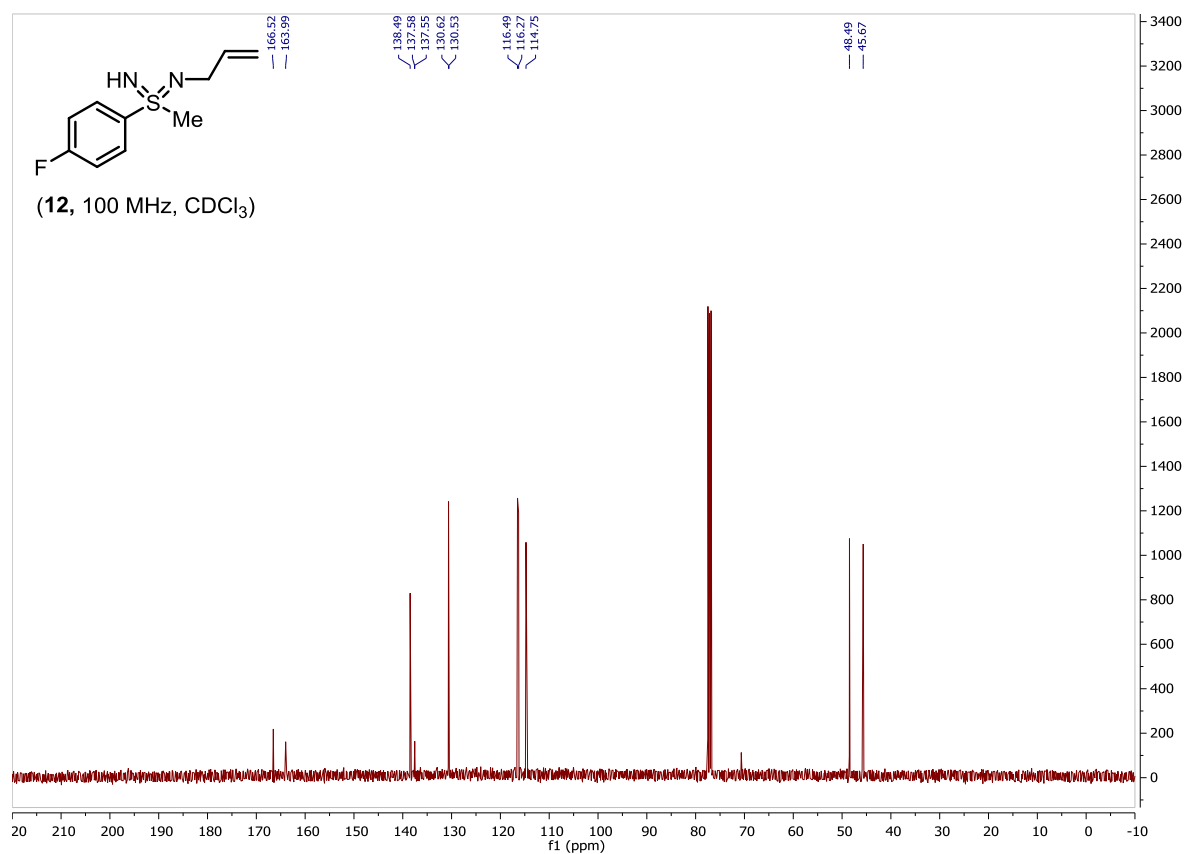


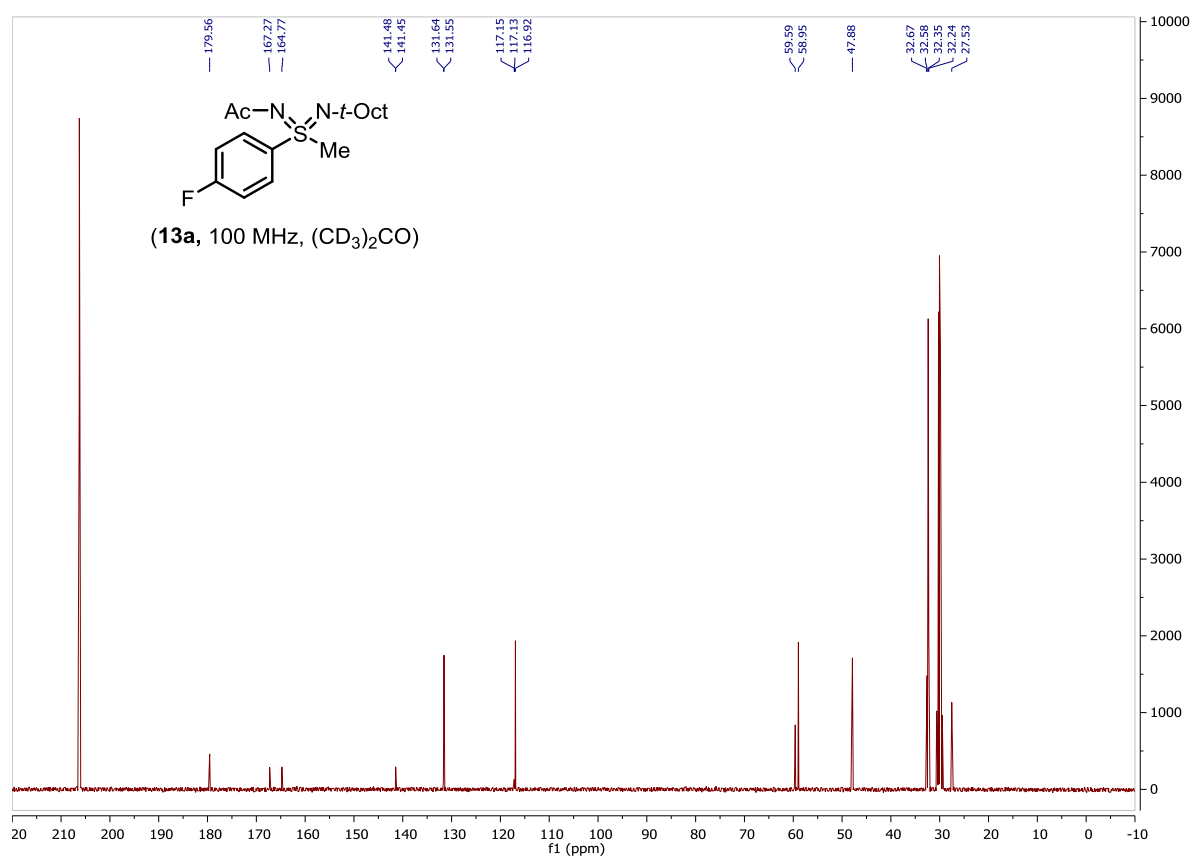
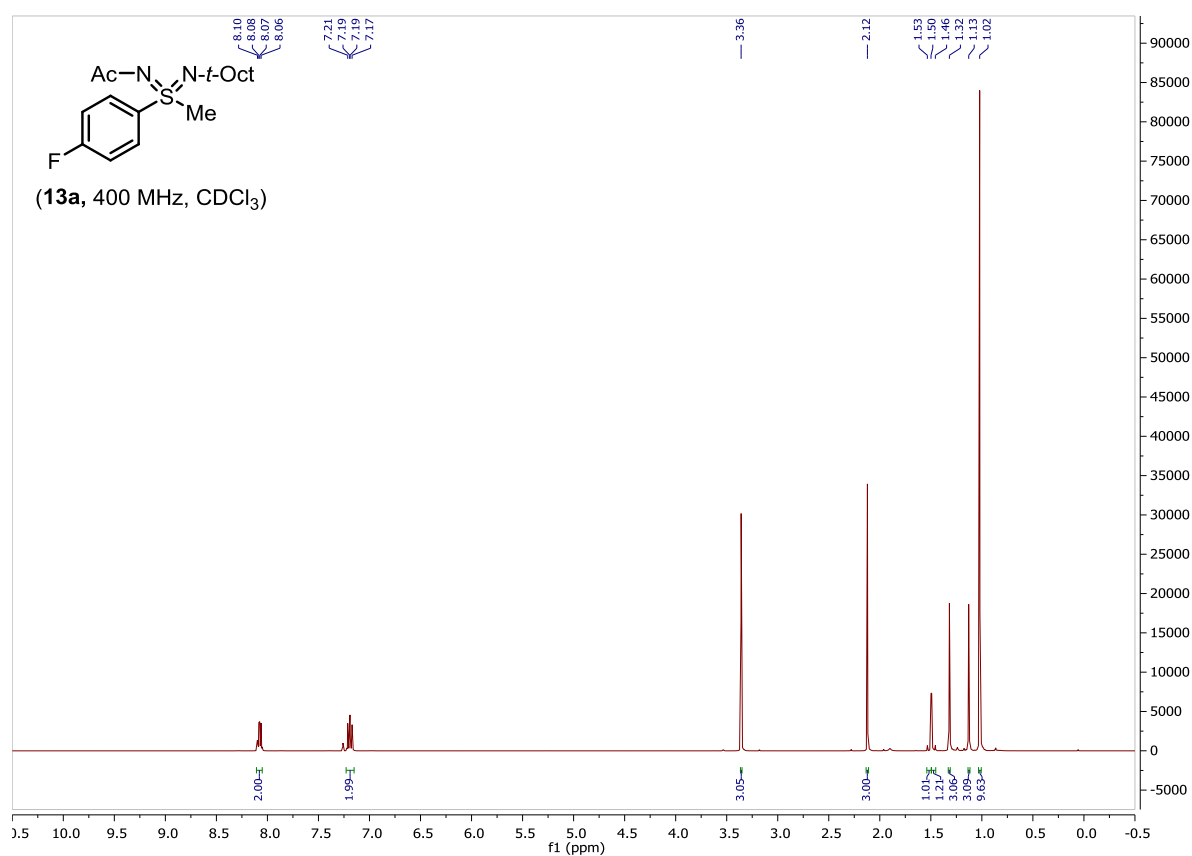


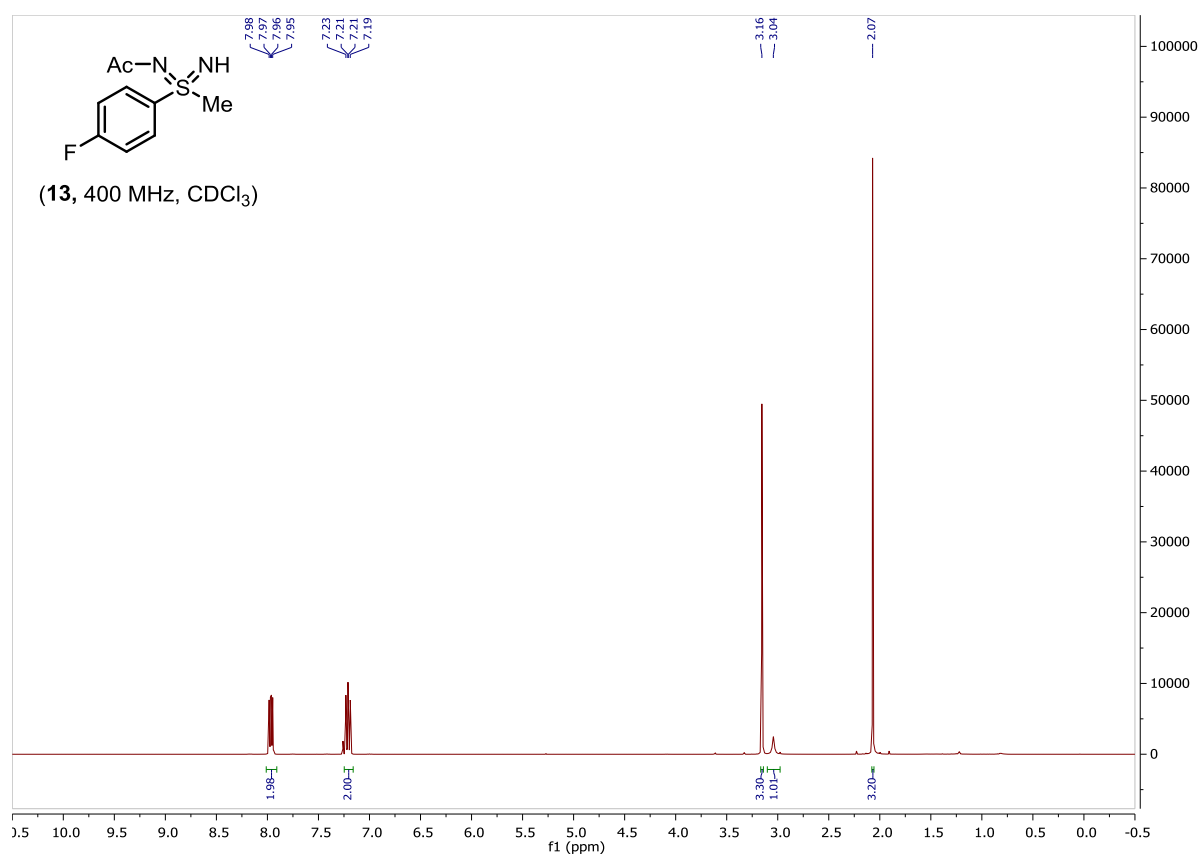
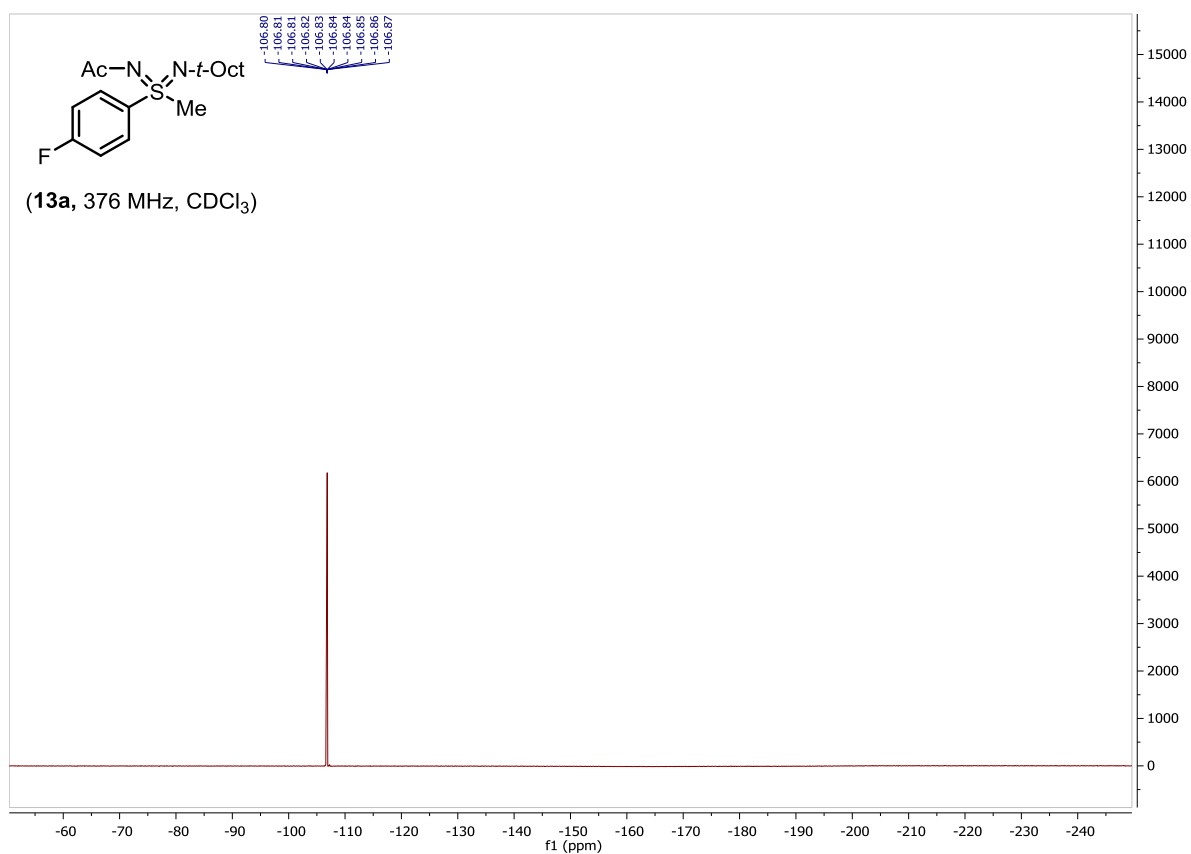


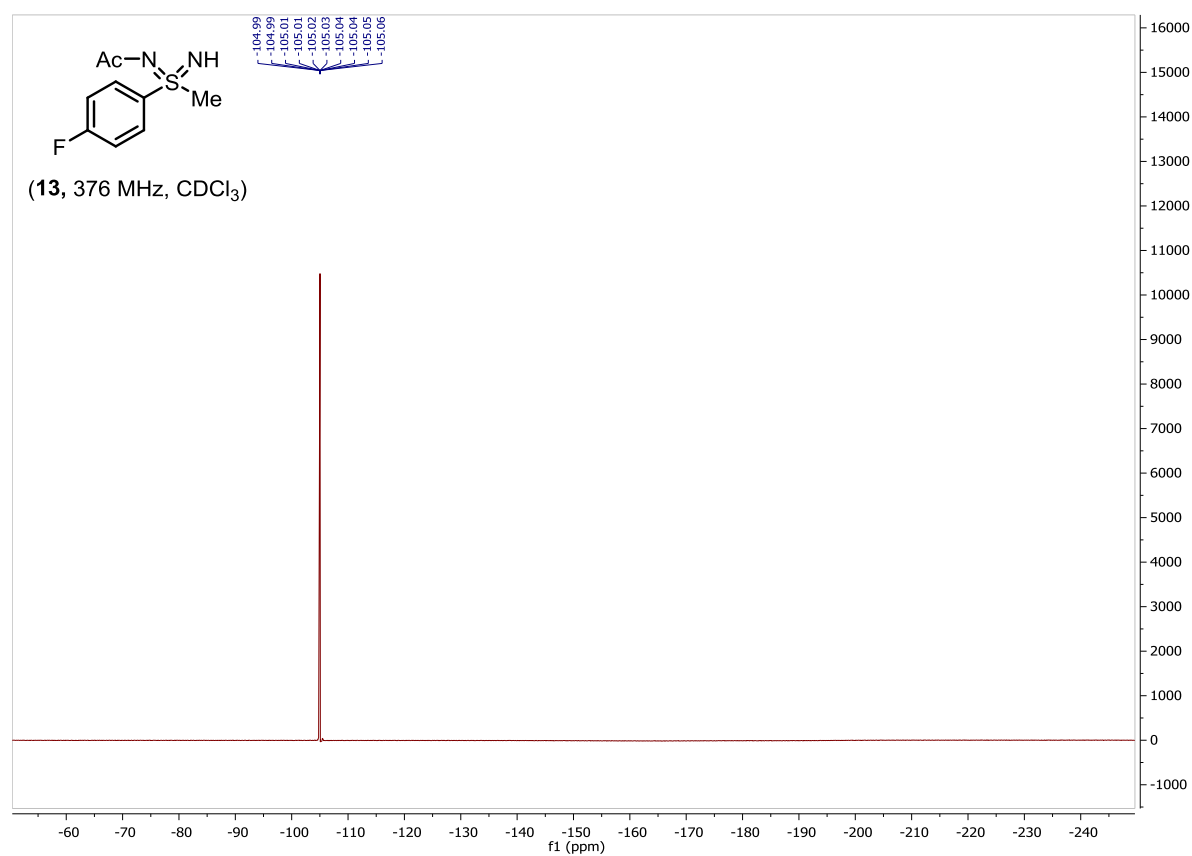
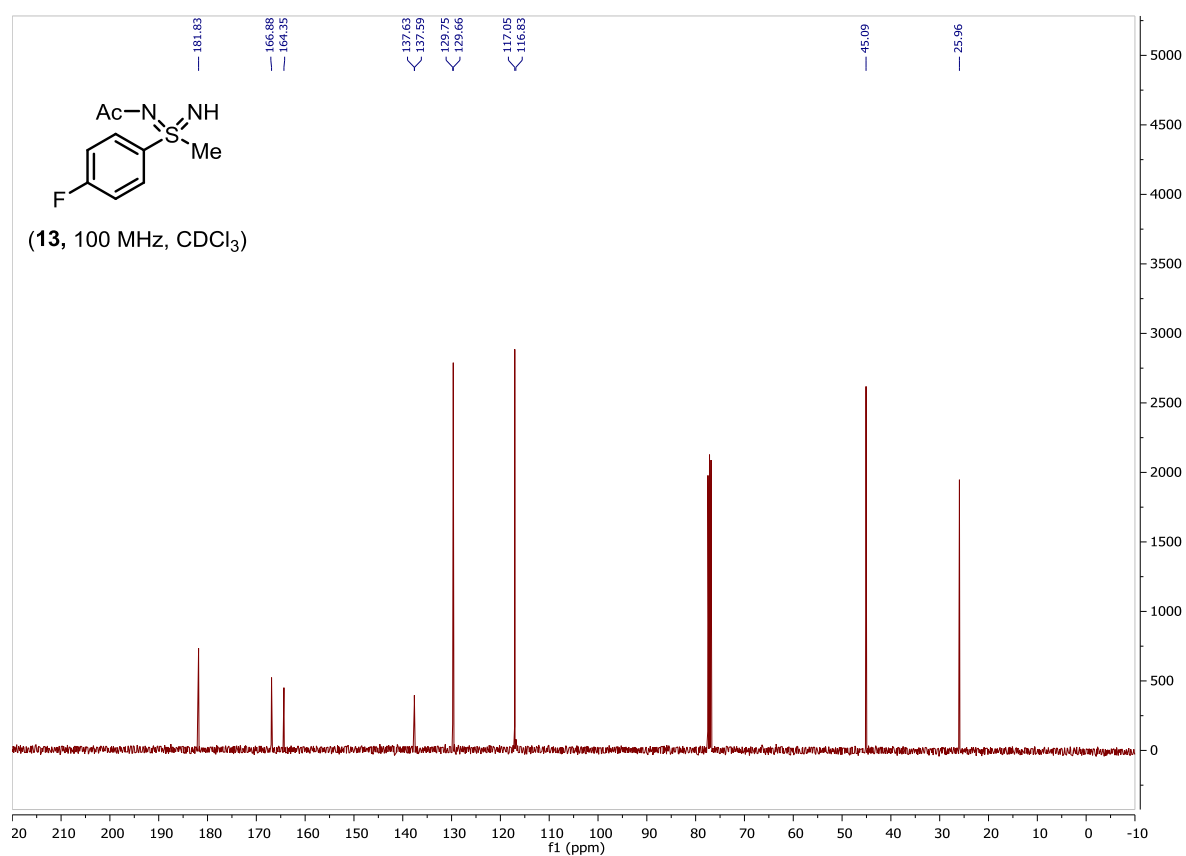


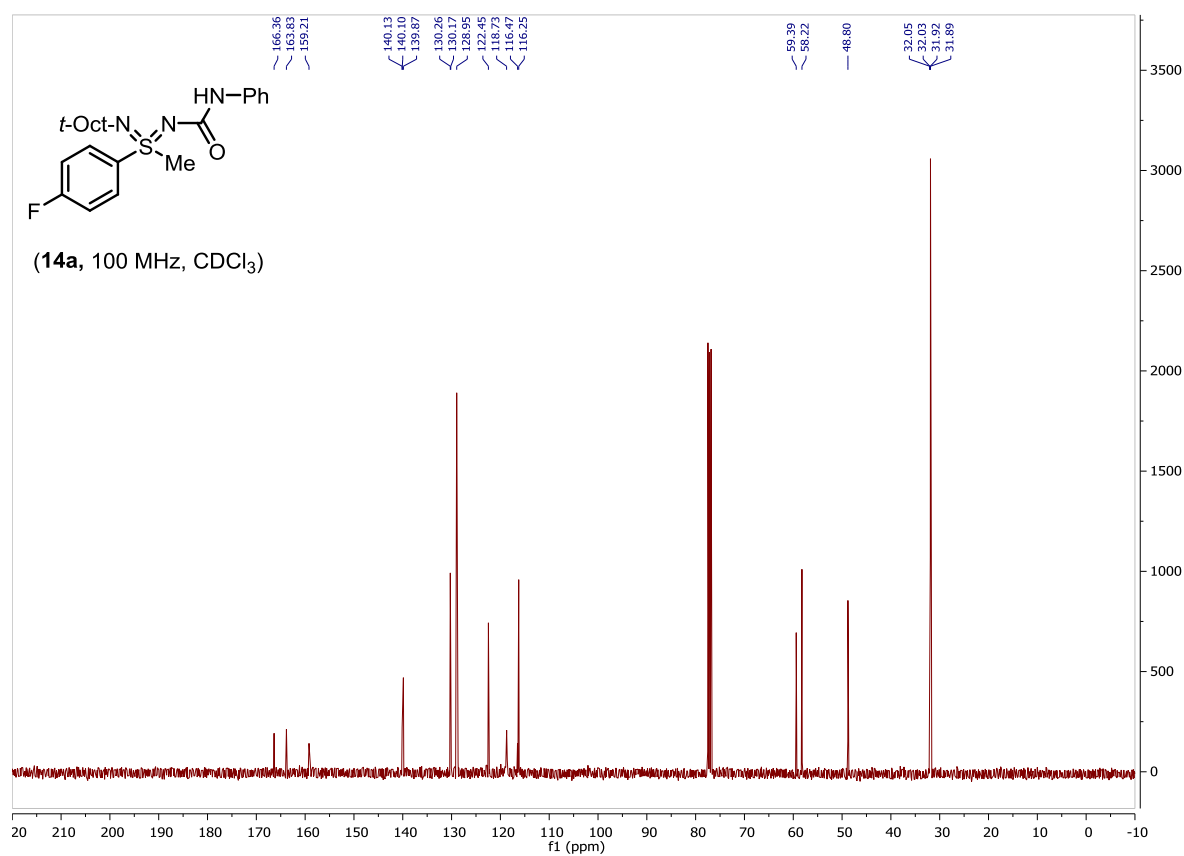
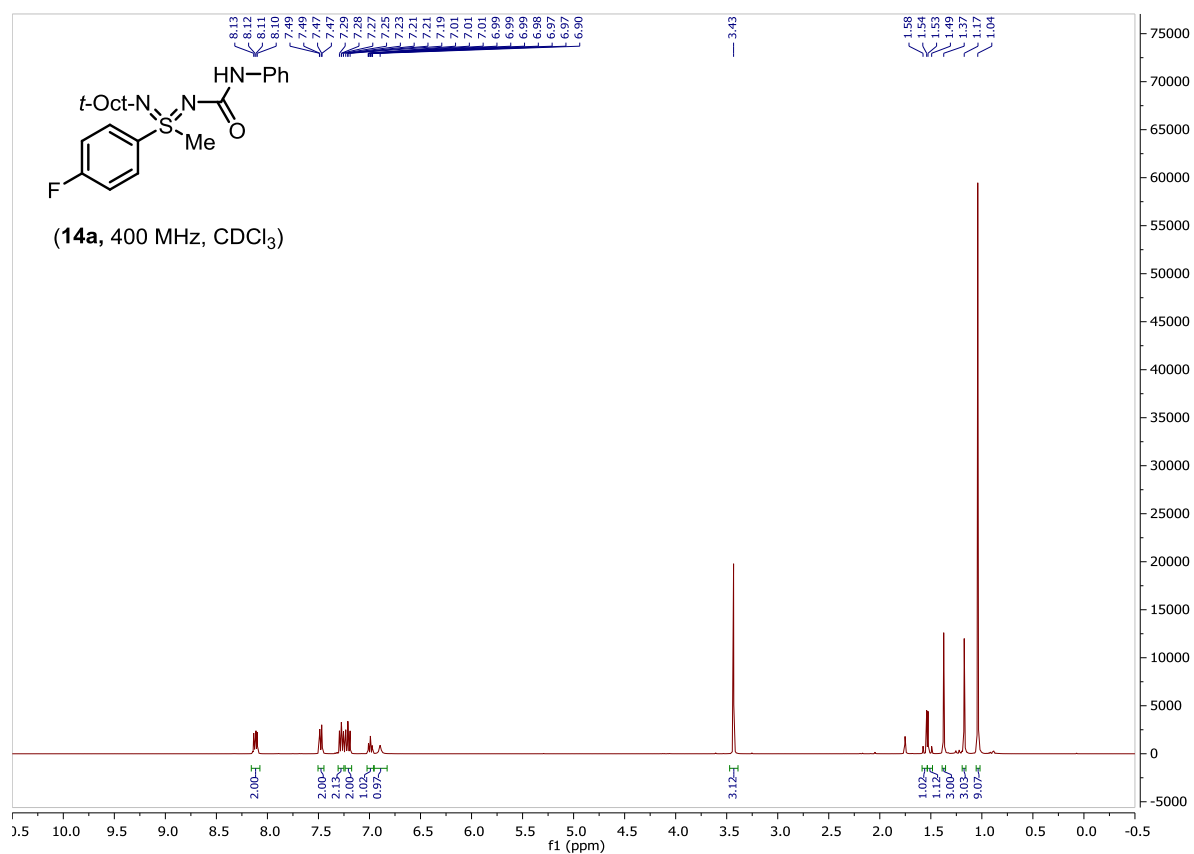


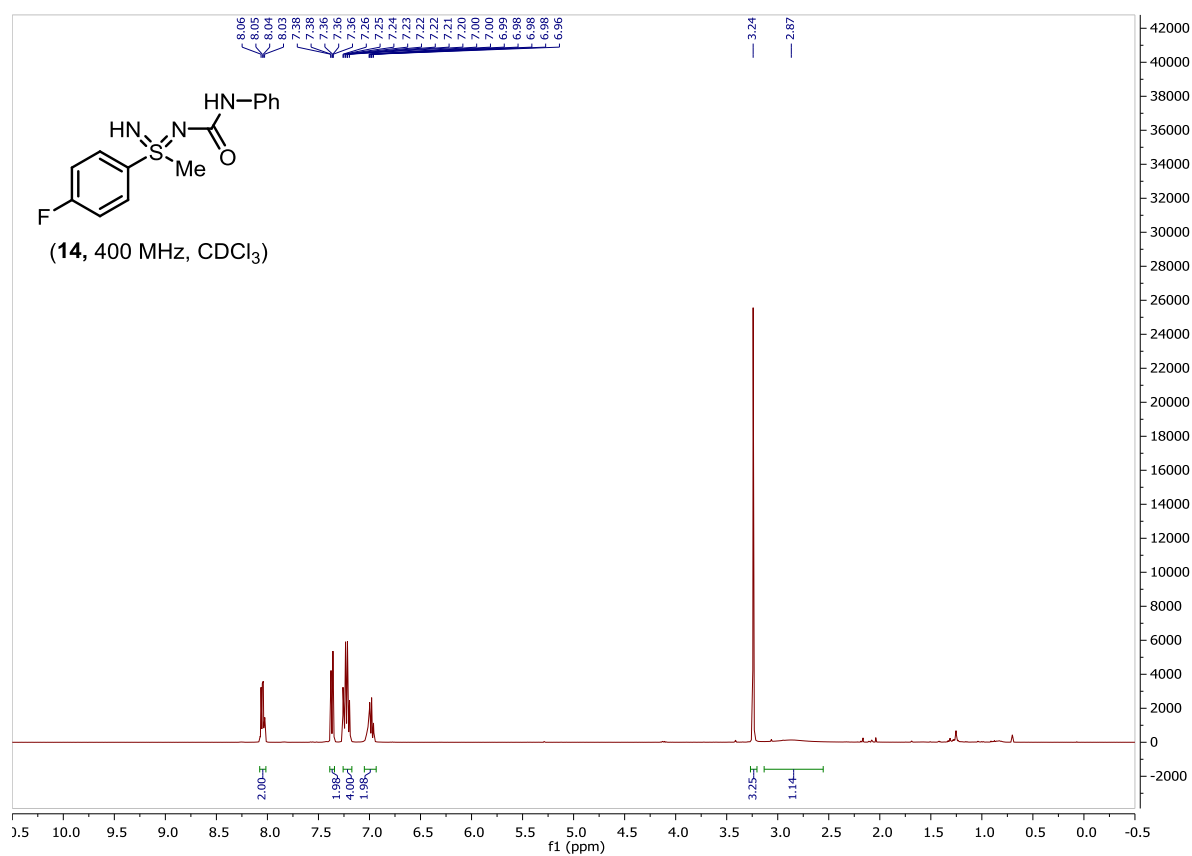
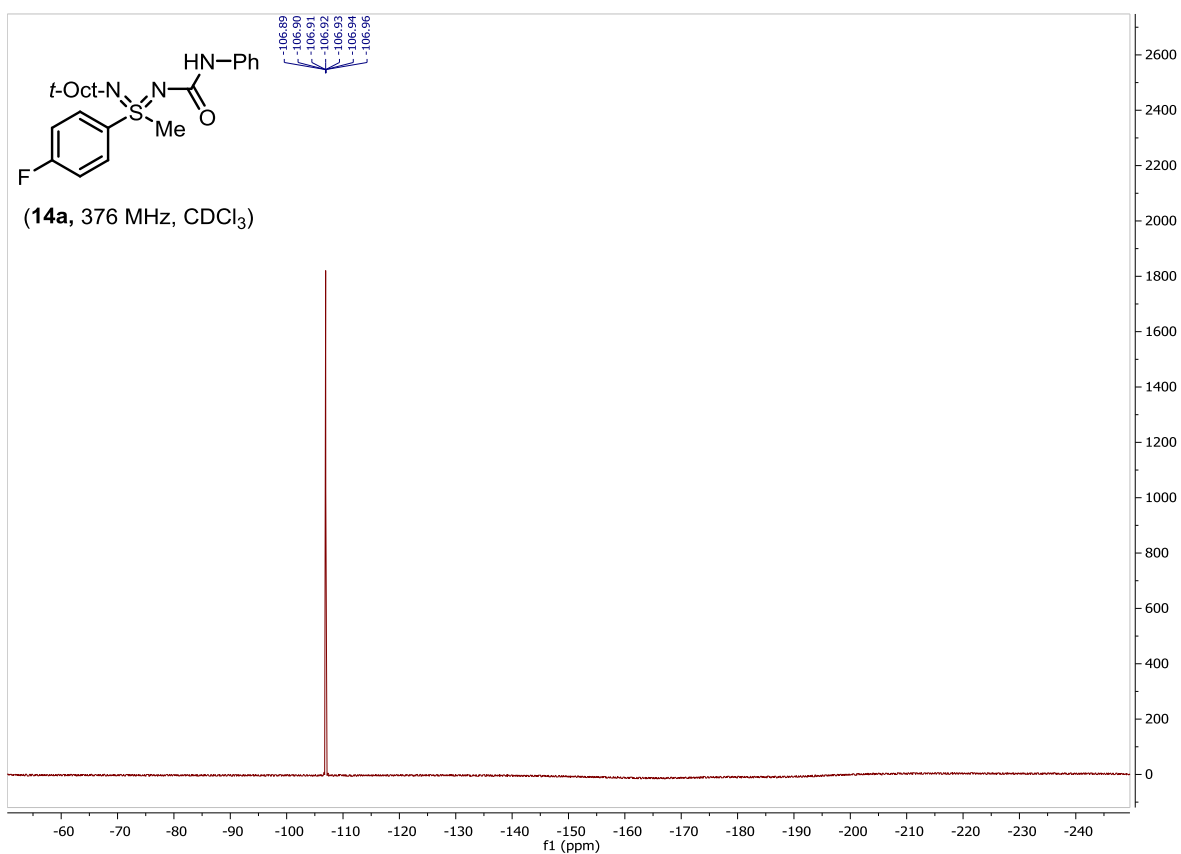


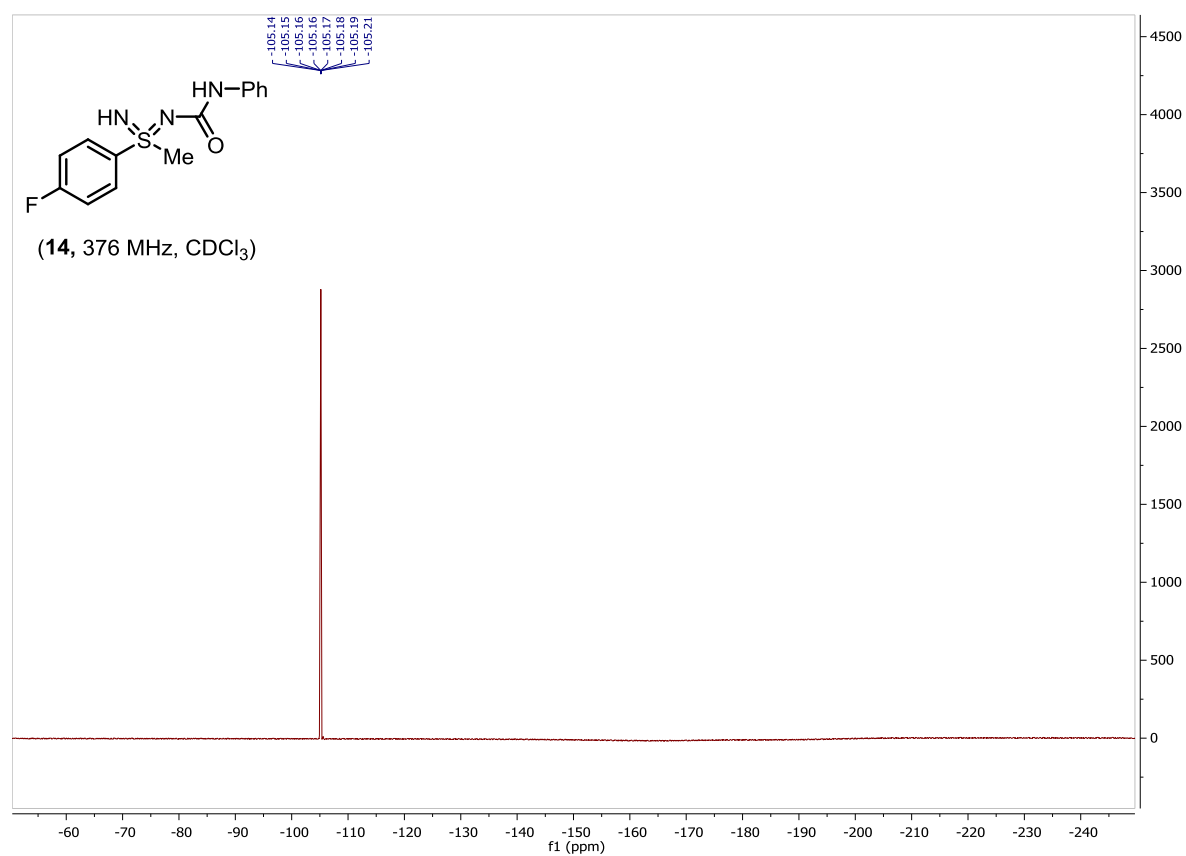
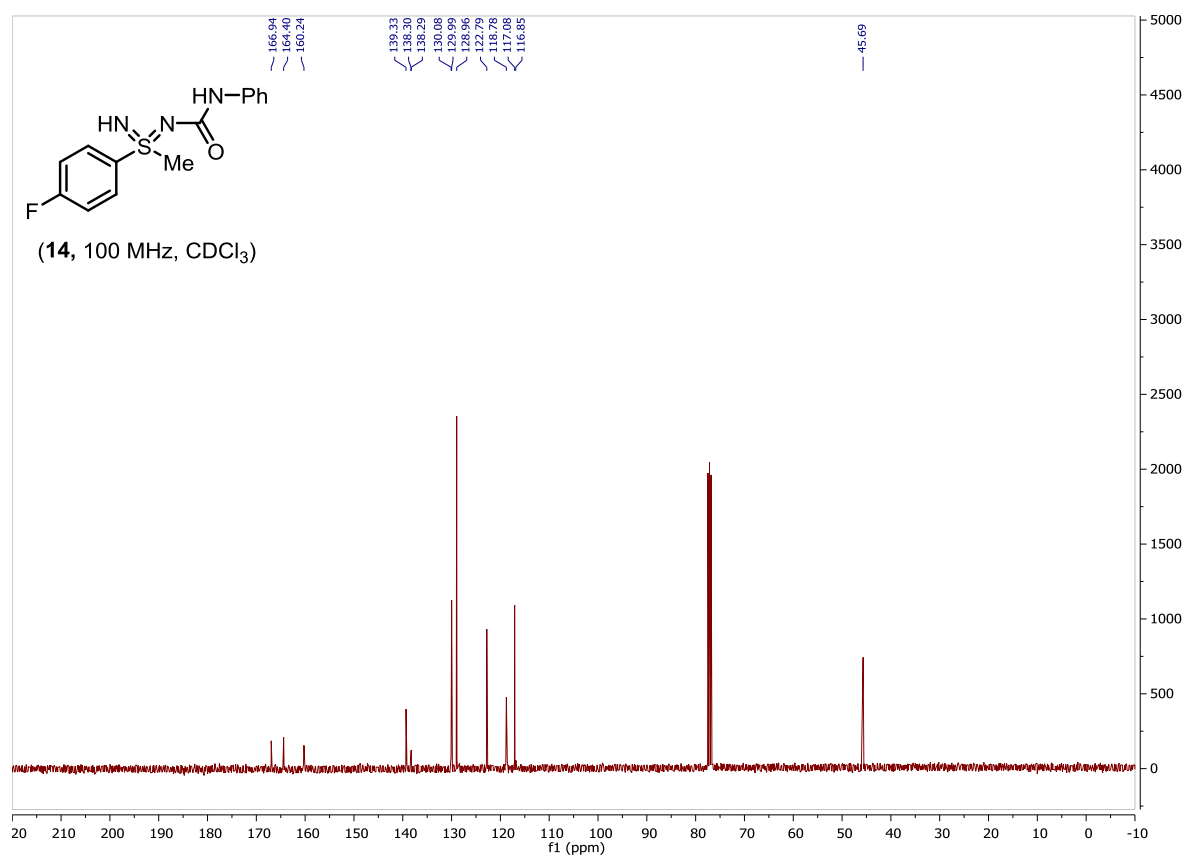


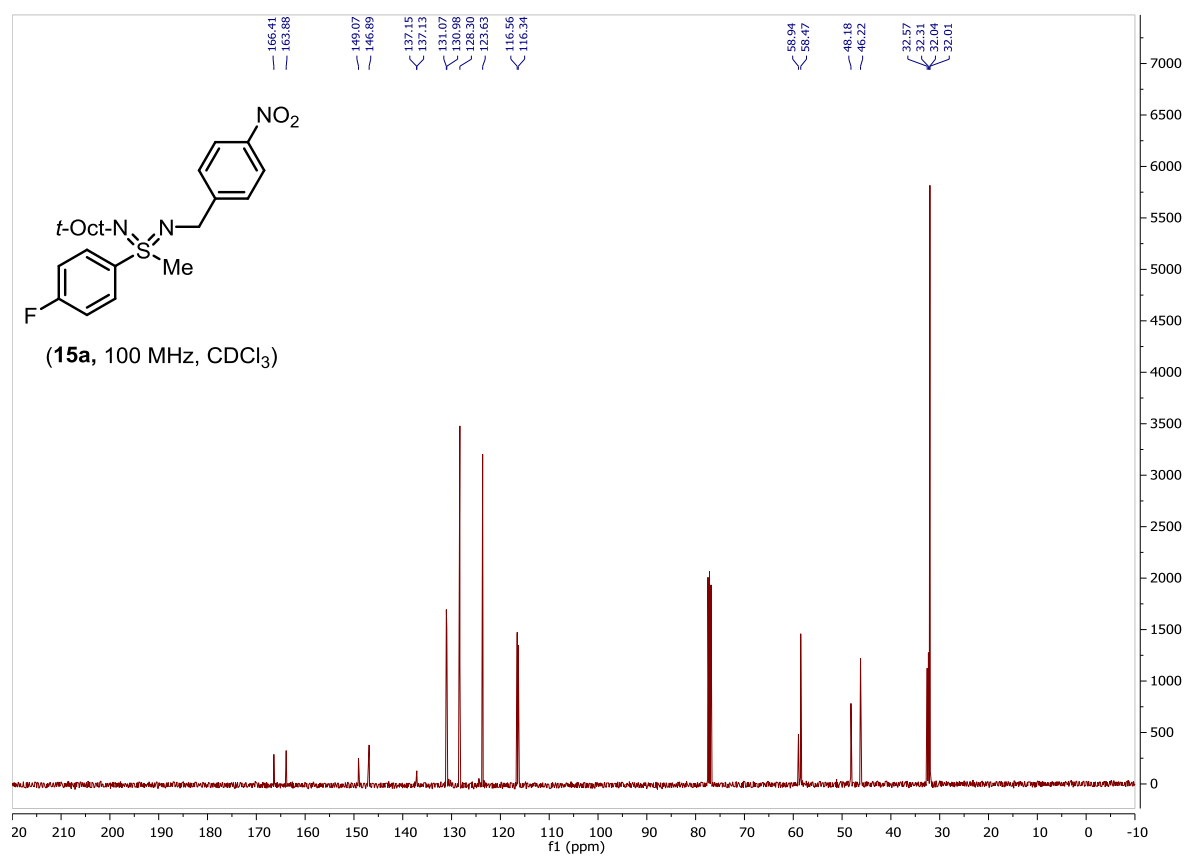
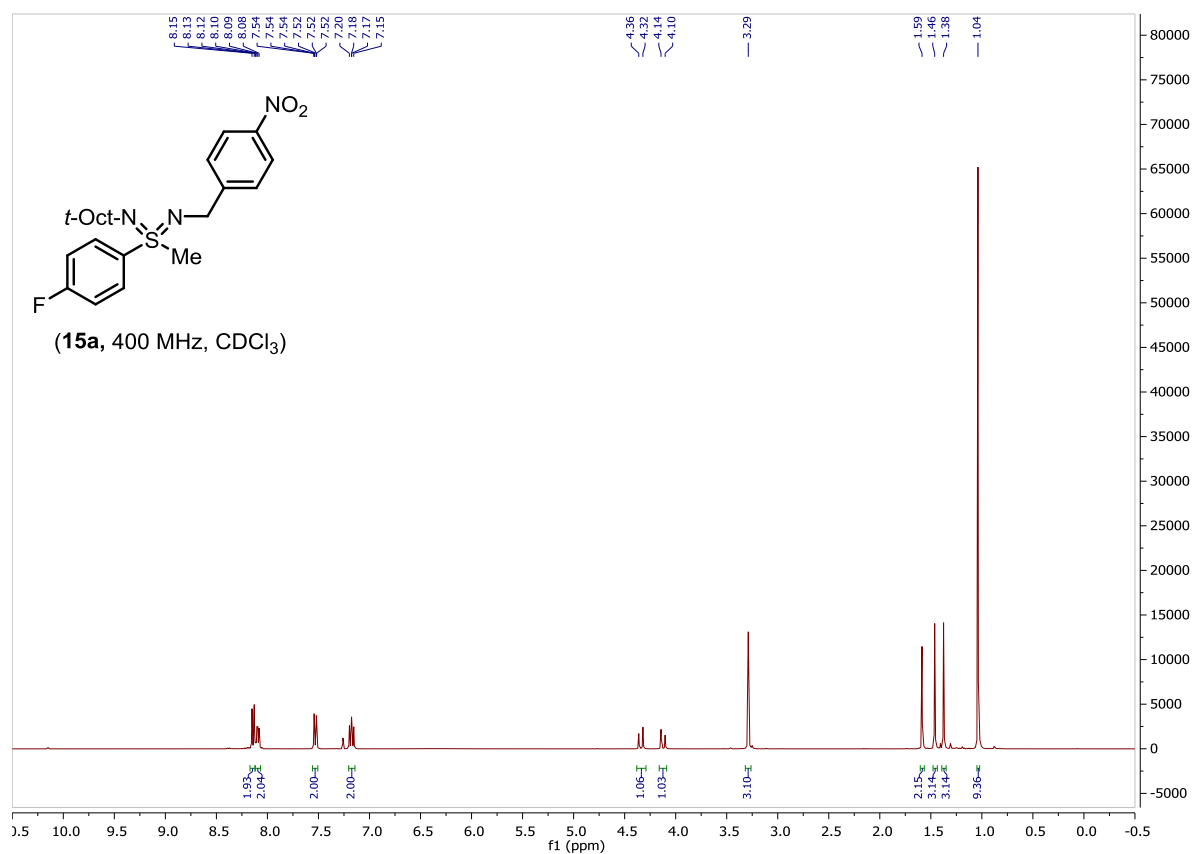


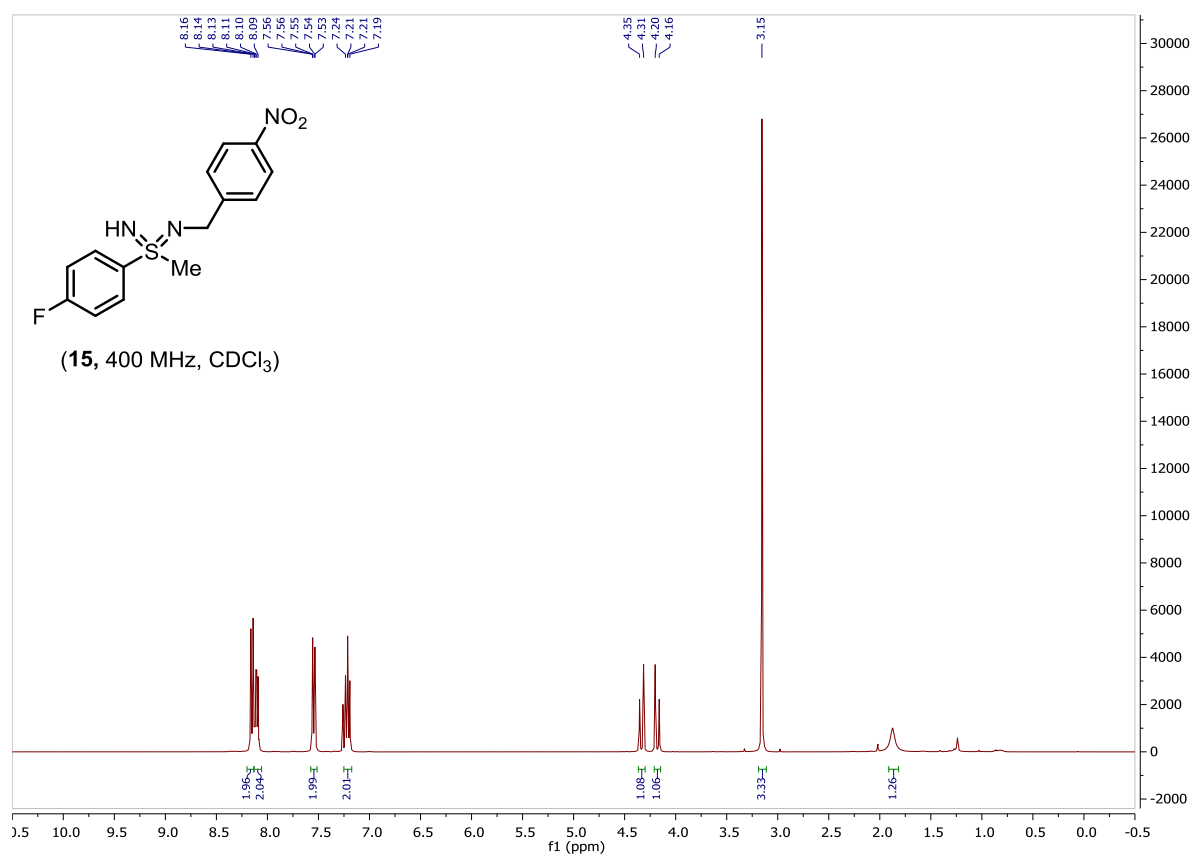
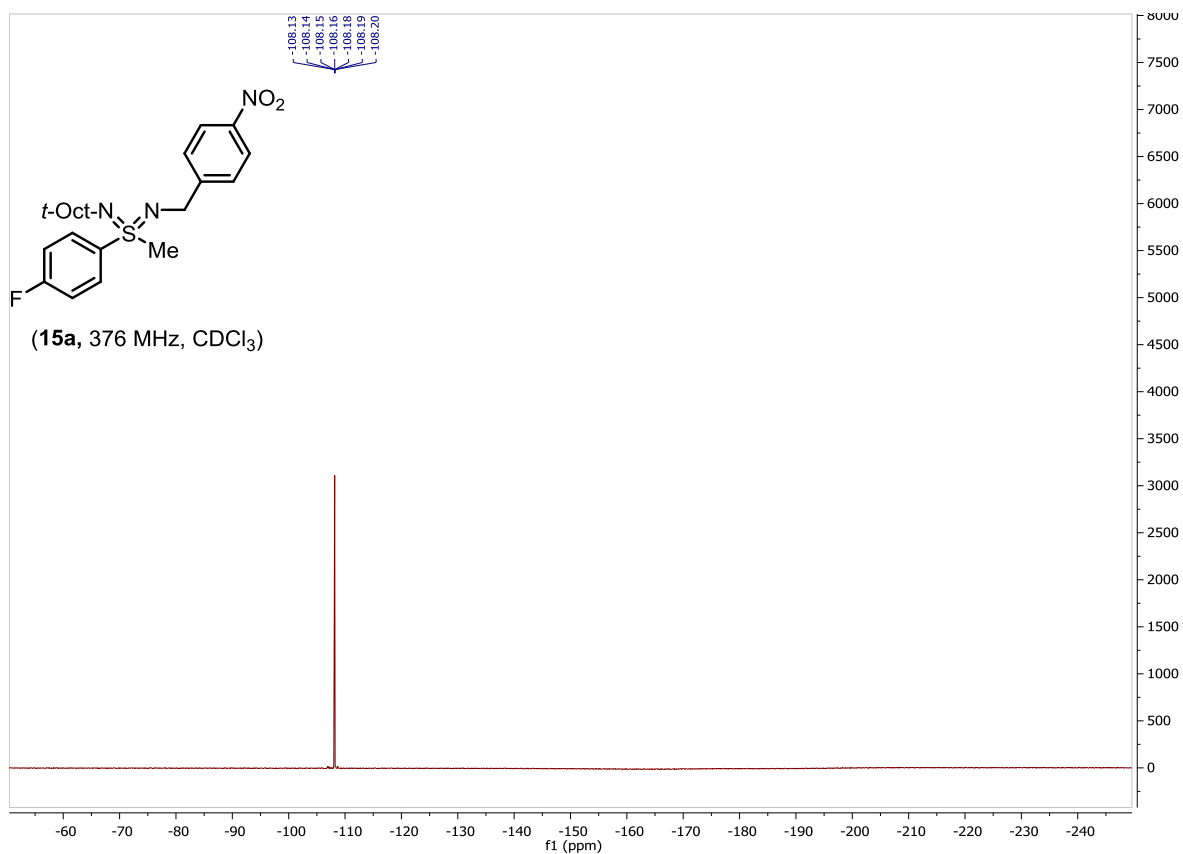


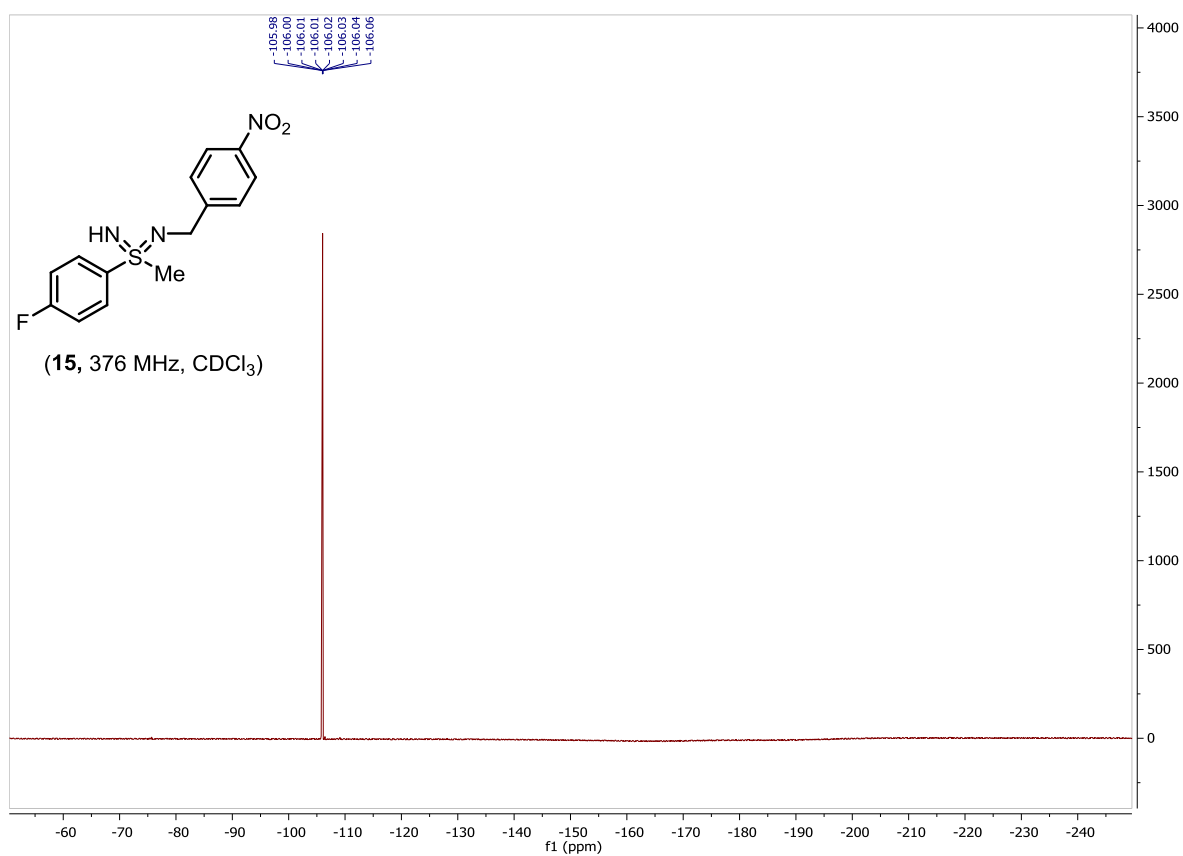
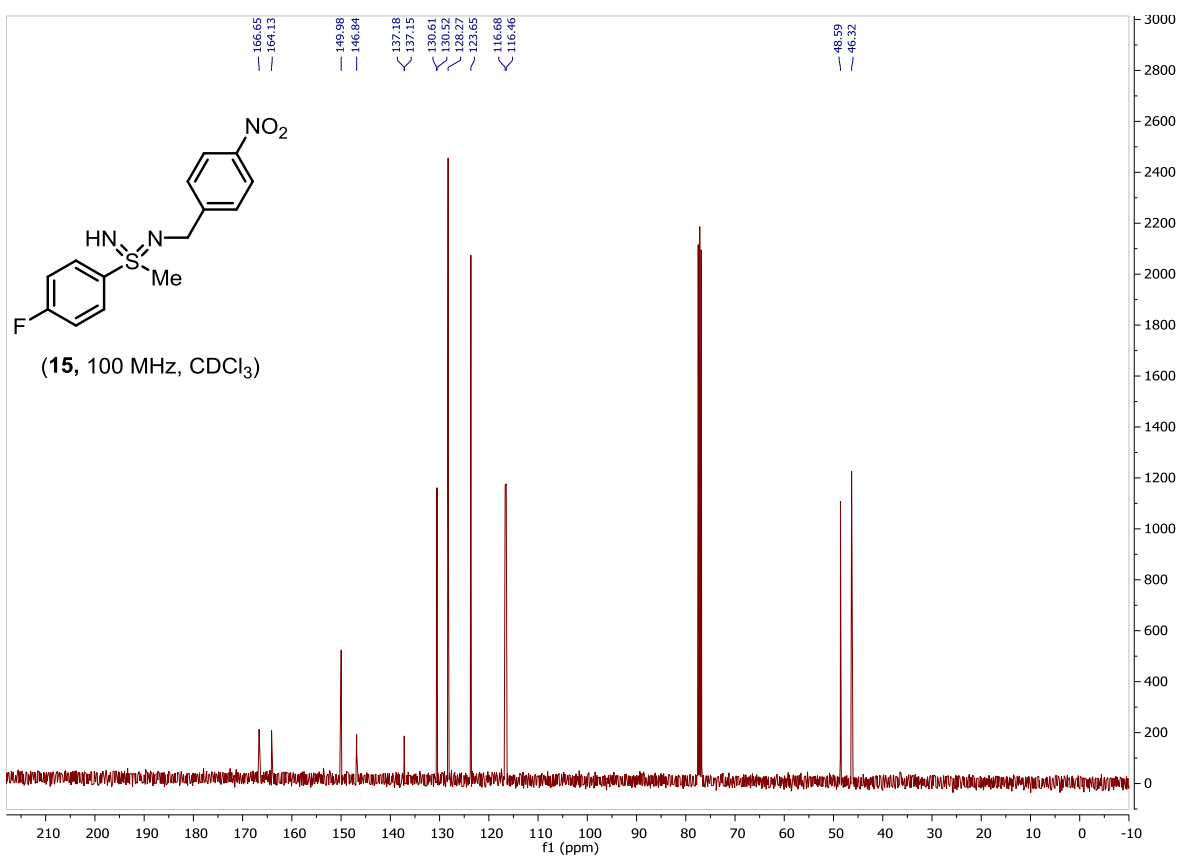












3. References

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