Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Direct synthesis of C3-alkynyl pyrroloindolines from tryptamines via a visible-light-induced radical cascade reaction

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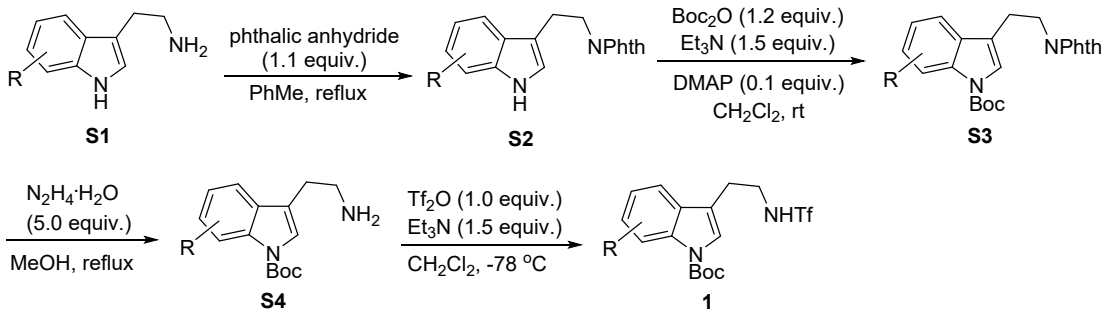
Table of Contents

1. General information

All the reaction were performed under argon atmosphere unless other noted. Unless otherwise noted, all other reagents and starting materials were purchased from commercial source and used without further purification. Thin layer chromatography was carried out on GF254 plates (0.25 mm layer thickness). Flash chromatography was performed with 200-300 mesh silica gels. Reactions were monitored by TLC and visualized by a dual short wave/long wave UV lamp. Photochemical reactions were carried with two 18 W LEDs (composed of 18 LED units each with 1.0 W). ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker Avance 500 or 600 MHz spectrophotometers. Chemical shifts in ^{1}H NMR spectra were reported in parts per million (ppm) on the δ scale. Data for ^{1}H NMR were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br. s = broad singlet), coupling constant in Herts (Hz) and integration. Data for ^{13}C NMR spectra were reported in terms of chemical shift in ppm. HR-ESI-MS were taken on Agilent 6540 Q-TOF spectrometer. The emission spectra were recorded in a Hitachi F-7000 fluorescence spectrometer.

2. General procedure A for the synthesis of typtamine derivate 1.



Scheme S1. Reaction sequence for the preparation of typtamine derivate **1**.

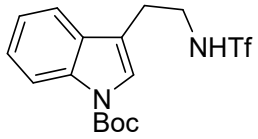
A mixture of tryptamine **S1** (10.0 mmol, 1.0 equiv.) and phthalic anhydride (1.63 g, 11.0 mmol, 1.1 equiv.) in toluene (80 mL) was refluxed overnight. The mixture was concentrated under reduced pressure to give a residual solid, which was recrystallized from CH_2Cl_2 and hexanes to afford Phth-protected **S2** as yellow crystals.[1]

To a solution of the Phth-protected **S2** (10.0 mmol, 1.0 equiv.) in CH_2Cl_2 (50 mL) was added Et_3N (2.08 mL, 15.0 mmol, 1.5 equiv.), $(Boc)_2O$ (2.76 mL, 12.0 mmol, 1.2 equiv.) and DMAP (122.2 mg, 1.0 mmol, 0.1 equiv.) at 25 ℃. After stirring for 20 min, saturated NH_4Cl solution (50 mL) was added to quench the reaction. The mixture was extracted with CH_2Cl_2 (50 mL × 2). The combined organic layers were washed with brine (100 mL × 1), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography to give the Boc-protetected **S3** as yellow oil.

To a solution of the Boc-protected **S3** (10.0 mmol, 1.0 equiv.) in methanol (80 mL) was added $N_2H_4·H_2O$ (2.43 mL, 50.0 mmol, 5.0 equiv.). After stirring for 3 h at reflux, 2 N NaOH was added at 25 ℃ to quench the reaction. The mixture was extracted with CH_2Cl_2 (50 mL × 3), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The resulting crude amine **S4** was used in the subsequent step without further purification.[2]

To a stirred solution of the above crude amine **S4** (10.0 mmol, 1.0 equiv.) in CH_2Cl_2 (50 mL) and Et_3N (2.08 mL, 15.0 mmol, 1.5 equiv.) was added dropwise Tf_2O (1.68 mL, 10.0 mmol, 1.0 equiv.) at −78 °C. The reaction mixture was allowed to stir at room temperature for 30 min and was then quenched with saturated aqueous $NaHCO_3$ (20 mL). The reaction mixture was extracted with CH_2Cl_2 (50 mL × 3). The combined organic layers were washed with saturated brine (100 mL), dried over Na_2SO_4, filtered, and concentrated. The cured mixture was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 20/1) to give the Tf-protected tryptamine **1** as light yellow oil.[3]

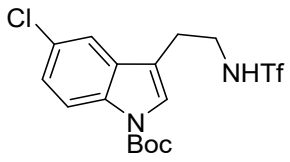
***tert*-butyl 3-(2-((trifluoromethyl)sulfonamido)ethyl)-1*H*-indole-1-carboxylate (1a)**



1a

Following the general procedure A, **1a** was isolated as light yellow oil (2.04 g, 52% yield over four steps from tryptamine) by flash column chromatography (petroleum ether/AcOEt = 20/1, V/V). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 7.4 Hz, 1H), 7.55 – 7.43 (m, 2H), 7.39 – 7.32 (m, 1H), 7.31 – 7.24 (m, 1H), 5.00 (t, J = 5.5 Hz, 1H), 3.63 (q, J = 6.6 Hz, 2H), 3.02 (t, J = 6.67 Hz, 2H), 1.68 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 136.0, 129.9, 125.2, 124.1, 123.1, 119.9 (q, J_{CF} = 319.0 Hz), 118.8, 115.8, 115.7, 84.3, 44.1, 28.5, 26.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -77.394 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{16}H_{18}F_3N_2O_4S$ $[M - H]^-$ 391.0945, found 391.0950.

***tert*-butyl 5-chloro-3-(2-((trifluoromethyl)sulfonamido)ethyl)-1*H*-indole-1-carboxylate (1b)**

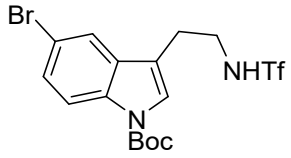


1b

Following the general procedure A, **1b** was isolated as light yellow oil (2.00 g, 47%

yield over four steps from 5-chlorotryptamine) by flash column chromatography (petroleum ether/AcOEt = 20/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (br. s, 1H), 7.48 (br. s, 1H), 7.44 (d, *J* = 2.0 Hz, 1H), 7.28 (dd, *J* = 8.8, 2.0 Hz, 1H), 5.19 (t, *J* = 5.7 Hz, 1H), 3.61 (q, *J* = 6.8 Hz, 2H), 2.97 (t, *J* = 6.8 Hz, 2H), 1.66 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.5, 134.3, 131.2, 128.9, 125.35, 125.31, 119.9 (q, J_{CF} = 319.1 Hz), 118.5, 116.8, 115.2, 84.8, 43.9, 28.4, 26.5; ^{19}F NMR (564 MHz, $CDCl_3$) δ -77.4 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{16}H_{18}ClF_3N_2O_4SNa$ $[M + Na]^+$ 449.0520, found 449.0522.

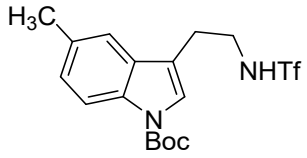
***tert*-butyl 5-bromo-3-(2-((trifluoromethyl)sulfonamido)ethyl)-1*H*-indole-1-carboxylate (1c)**



1c

Following the general procedure A, **1c** was isolated as light yellow oil (2.40 g, 51% yield over four steps from 5-bromotryptamine) by flash column chromatography (petroleum ether/AcOEt = 20/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (br. s, 1H), 7.60 (d, *J* = 1.7 Hz, 1H), 7.46 (br. s, 1H), 7.42 (dd, *J* = 8.8, 1.7 Hz, 1H), 5.19 (t, *J* = 5.6 Hz, 1H), 3.61 (q, *J* = 6.8 Hz, 2H), 2.97 (t, *J* = 6.8 Hz, 2H), 1.66 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.5, 134.6, 131.7, 128.0, 125.2, 121.5, 119.9 (q, J_{CF} = 319.4 Hz), 117.2, 116.5, 115.1, 84.8, 43.9, 28.4, 26.4; ^{19}F NMR (564 MHz, $CDCl_3$) δ -77.4 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{16}H_{18}BrF_3N_2O_4SNa$ $[M + Na]^+$ 493.0015, found 493.0019.

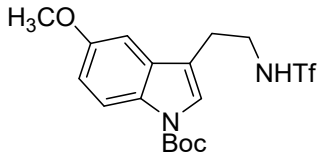
***tert*-butyl 5-methyl-3-(2-((trifluoromethyl)sulfonamido)ethyl)-1*H*-indole-1-carboxylate (1d)**



1d

Following the general procedure A, **1d** was isolated as light yellow oil (1.75 g, 43% yield over four steps from 5-methyltryptamine) by flash column chromatography (petroleum ether/AcOEt = 20/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (br. s, 1H), 7.43 (br. s, 1H), 7.28 (s, 1H), 7.17 (d, J = 8.5 Hz, 1H), 5.27 (br. s, 1H), 3.62 (t, J = 6.8 Hz, 2H), 2.99 (t, J = 6.8 Hz, 2H), 2.46 (s, 3H), 1.67 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.9, 134.1, 132.6, 130.1, 126.5, 124.1, 119.9 (q, J_{CF} = 319.4 Hz), 118.7, 115.6, 115.4, 84.1, 44.0, 28.4, 26.5, 21.6; ^{19}F NMR (564 MHz, $CDCl_3$) δ -77.4 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{17}H_{21}F_3N_2O_4SNa$ $[M + Na]^+$ 429.1066, found 429.1068.

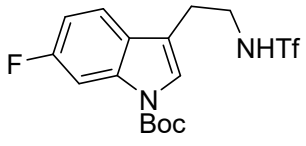
***tert*-butyl 5-methoxy-3-(2-((trifluoromethyl)sulfonamido)ethyl)-1*H*-indole-1-carboxylate (1e)**



1e

Following the general procedure A, **1e** was isolated as light yellow oil (2.03 g, 48% yield over four steps from 5-methoxytryptamine) by flash column chromatography (petroleum ether/AcOEt = 15/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (br. s, 1H), 7.42 (br. s, 1H), 6.95 – 6.92 (m, 2H), 5.38 (t, J = 5.4 Hz, 1H), 3.84 (s, 3H), 3.61 (q, J = 6.8 Hz, 2H), 2.97 (t, J = 6.8 Hz, 2H), 1.65 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.2, 149.8, 130.8, 124.6, 119.9 (q, J_{CF} = 319.1 Hz), 116.5, 115.6, 113.6, 110.4, 101.7, 84.2, 56.0, 44.0, 28.4, 26.6; ^{19}F NMR (564 MHz, $CDCl_3$) δ -77.4 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{17}H_{21}F_3N_2O_5SNa$ $[M + Na]^+$ 445.1015, found 445.1015.

***tert*-butyl 6-fluoro-3-(2-((trifluoromethyl)sulfonamido)ethyl)-1*H*-indole-1-carboxylate (1f)**

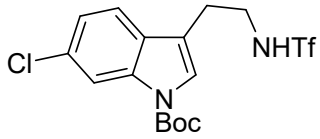


1f

Following the general procedure A, **1f** was isolated as light yellow oil (1.68 g, 41%

yield over four steps from 6-fluorotryptamine) by flash column chromatography (petroleum ether/AcOEt = 20/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (br. s, 1H), 7.43 (s, 1H), 7.40 (dd, *J* = 8.8, 5.2 Hz, 1H), 7.01 (td, *J* = 8.8, 2.2 Hz, 1H), 5.25-5.02 (m, 1H), 3.61 (t, *J* = 6.8 Hz, 2H), 2.99 (t, *J* = 6.8 Hz, 2H), 1.67 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.5 (d, J_{CF} = 239.0 Hz), 149.6, 136.2, 126.2, 124.2, 119.9 (q, J_{CF} = 318.9 Hz), 119.5 (d, J_{CF} = 9.9 Hz), 115.7, 111.4 (d, J_{CF} = 24.3 Hz), 103.2 (d, J_{CF} = 28.2 Hz), 84.8, 44.0, 28.4, 26.6; ^{19}F NMR (564 MHz, $CDCl_3$) δ -77.4 (s, 3F), -116.6 (s, 1F); HR-ESI-MS (*m/z*): calcd. for $C_{16}H_{18}F_4N_2O_4SNa$ $[M + Na]^+$ 433.0816, found 433.0817.

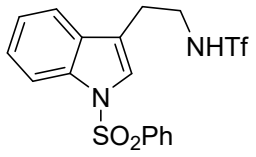
tert-butyl 6-chloro-3-(2-((trifluoromethyl)sulfonamido)ethyl)-1*H*-indole-1-carboxylate (1g)



1g

Following the general procedure A, **1g** was isolated as light yellow oil (1.87 g, 44% yield over four steps from 6-chlorotryptamine) by flash column chromatography (petroleum ether/AcOEt = 20/1, V/V). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (br. s, 1H), 7.44 (s, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.23 (dd, *J* = 8.4, 1.9 Hz, 1H), 5.05 (br. s, 1H), 3.61 (q, *J* = 6.5 Hz, 2H), 2.99 (t, *J* = 6.5, 6.3 Hz, 2H), 1.67 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 136.3, 131.3, 128.4, 124.5, 123.7, 119.9 (q, J_{CF} = 319.2 Hz), 119.5, 116.1, 115.6, 84.9, 44.0, 28.4, 26.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -77.4 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{16}H_{18}ClF_3N_2O_4SNa$ $[M + Na]^+$ 449.0520, found 449.0523.

1,1,1-trifluoro-*N*-(2-(1-(phenylsulfonyl)-1*H*-indol-3-yl)ethyl)methanesulfonamide (1h)

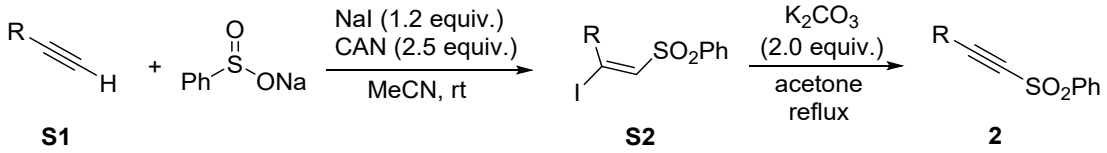


1h

Following the general procedure A, **1h** was isolated as light gray solids (2.03 g, 47%

yield over four steps from tryptamine) by flash column chromatography (petroleum ether/AcOEt = 15/1, V/V). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.3 Hz, 1H), 7.88 (d, J = 7.8 Hz, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.50 – 7.41 (m, 4H), 7.36 (t, J = 7.8 Hz, 1H), 7.27 (t, J = 7.6 Hz, 1H), 5.14 (br. s, 1H), 3.59 (q, J = 6.7 Hz, 2H), 2.99 (t, J = 6.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 135.6, 134.3, 130.3, 129.7, 127.0, 125.6, 124.3, 123.9, 119.8 (q, J_{CF} = 319.4 Hz), 119.4, 118.2, 114.2, 43.8, 26.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -77.4 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{17}H_{15}F_3N_2O_4S_2Na$ $[M + Na]^+$ 455.0318, found 455.0316.

3. General procedure B for the synthesis of alkynyl sulfones 2.



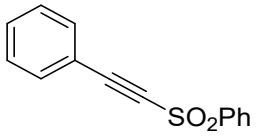
Scheme S2. Reaction sequence for the preparation of alkynyl sulfones **2**.[4]

Alkynyl sulfones were prepared according to the known procedures. To a stirred solution of alkyne **S1** (5.0 mmol, 1.0 equiv.) in dry MeCN (50 mL) at 0 ℃ was slowly added sodium benzenesulfinate (985.0 mg, 6.0 mmol, 1.2 equiv.), NaI (899.3 mg, 6.0 mmol, 1.2 equiv.) and CAN (6.58 g, 12.5 mmol, 2.5 equiv.) under argon atmosphere. Then, the mixture was vigorous stirred at room temperature overnight. After the completion of the reaction, it was quenched with sat. aqueous $Na_2S_2O_3$(30 mL). The quenched mixture was poured into H_2O (30 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were washed with brine (90 mL), dried over $MgSO_4$, filtered, and concentrated by rotary evaporation to afford cured iodosulfone **S2** without any purification.

The cured iodosulfone **S2** were dissolved in dry acetone (50 mL) and refluxed with K_2CO_3 (1.38 g, 10.0 mmol, 2.0 equiv.) for about 5 hours. Upon completion, the reaction was quenched with sat. aqueous NH_4Cl solution (30 mL), and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine (90 mL), dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The residue was purified by

column chromatography to afford the desired alkynyl sulfones **2**.

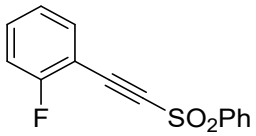
((phenylethynyl)sulfonyl)benzene (2a)



2a

Following the general procedure B, **2a** was isolated as pale solids (774.5 mg, 64% yield over two steps from ethynylbenzene) by flash column chromatography (petroleum ether/AcOEt = 15/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 – 8.06 (m, 2H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.60 (t, *J* = 7.8 Hz, 2H), 7.55 – 7.51 (m, 2H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.2, 134.4, 133.1, 131.9, 129.7, 129.0, 127.7, 118.2, 93.8, 85.7; HR-ESI-MS (*m/z*): calcd. for $C_{14}H_{10}O_2SNa$ $[M + Na]^+$ 265.0294, found 265.0293.

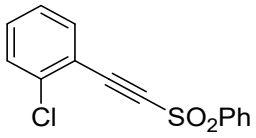
1-fluoro-2-((phenylsulfonyl)ethynyl)benzene (2b)



2b

Following the general procedure B, **2b** was isolated as pale solids (871.1 mg, 67% yield over two steps from 1-ethynyl-2-fluorobenzene) by flash column chromatography (petroleum ether/AcOEt = 15/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.6 Hz, 2H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 2H), 7.52 – 7.43 (m, 2H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.7 (d, J_{CF} = 255.9 Hz), 141.9, 134.6, 134.4, 134.0 (d, J_{CF} = 8.0 Hz), 129.7, 127.7, 124.7 (d, J_{CF} = 3.8 Hz), 116.3 (d, J_{CF} = 20.0 Hz), 107.2 (d, J_{CF} = 15.3 Hz), 90.0, 87.4; ^{19}F NMR (564 MHz, $CDCl_3$) δ -106.2 (s, 1F); HR-ESI-MS (*m/z*): calcd. for $C_{14}H_{10}FO_2S$ $[M + H]^+$ 261.0380, found 261.0378.

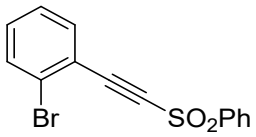
1-chloro-2-((phenylsulfonyl)ethynyl)benzene (2c)



2c

Following the general procedure B, **2c** was isolated as pale solids (979.8 mg, 71% yield over two steps from 1-chloro-2-ethynylbenzene) by flash column chromatography (petroleum ether/AcOEt = 15/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 – 8.07 (m, 2H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.8 Hz, 2H), 7.56 – 7.51 (m, 1H), 7.44 – 7.37 (m, 2H), 7.29 – 7.24 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.7, 137.6, 134.3, 132.6, 129.8, 129.4, 127.5, 126.8, 118.4, 90.0, 89.5; HR-ESI-MS (*m/z*): calcd. for $C_{14}H_9ClO_2SNa$ $[M + Na]^+$ 298.9904, found 298.9906.

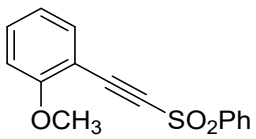
1-bromo-2-((phenylsulfonyl)ethynyl)benzene (2d)



2d

Following the general procedure B, **2d** was isolated as pale solids (991.8 mg, 62% yield over two steps from 1-bromo-2-ethynylbenzene) by flash column chromatography (petroleum ether/AcOEt = 15/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.6 Hz, 2H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.63 – 7.55 (m, 3H), 7.53 – 7.48 (m, 1H), 7.34 – 7.27 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.0, 134.7, 134.57, 133.17, 132.87, 129.67, 127.7, 127.6, 126.8, 120.9, 91.8, 89.1; HR-ESI-MS (*m/z*): calcd. for $C_{14}H_{10}BrO_2S$ $[M + H]^+$ 320.9579, found 320.9575.

1-methoxy-2-((phenylsulfonyl)ethynyl)benzene (2e)

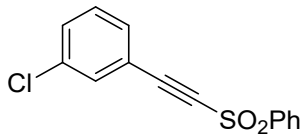


2e

Following the general procedure B, **2e** was isolated as pale solids (802.5 mg, 59% yield over two steps from 1-ethynyl-2-methoxybenzene) by flash column chromatography

(petroleum ether/AcOEt = 15/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 – 8.06 (m, 2H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.8 Hz, 2H), 7.47 – 7.38 (m, 2H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.1, 142.6, 134.7, 134.1, 133.6, 129.5, 127.6, 120.8, 111.3, 107.5, 91.9, 89.2, 56.1; HR-ESI-MS (*m/z*): calcd. for $C_{15}H_{12}O_3SNa$ $[M + Na]^+$ 295.0399, found 295.0402.

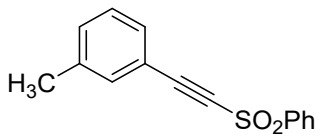
1-chloro-3-((phenylsulfonyl)ethynyl)benzene (2f)



2f

Following the general procedure B, **2f** was isolated as pale solids (841.8 mg, 61% yield over two steps from 1-chloro-3-ethynylbenzene) by flash column chromatography (petroleum ether/AcOEt = 15/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 – 8.05 (m, 2H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 8.0 Hz, 2H), 7.49 (s, 1H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.7, 135.0, 134.7, 132.6, 132.1, 131.1, 130.3, 129.7, 127.8, 119.8, 91.6, 86.4; HR-ESI-MS (*m/z*): calcd. for $C_{14}H_9ClO_2SNa$ $[M + Na]^+$ 298.9904, found 298.9906.

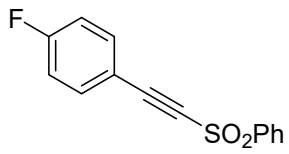
1-methyl-3-((phenylsulfonyl)ethynyl)benzene (2g)



2g

Following the general procedure B, **2g** was isolated as pale solids (934.6 mg, 73% yield over two steps from 1-ethynyl-3-methylbenzene) by flash column chromatography (petroleum ether/AcOEt = 15/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 – 8.05 (m, 2H), 7.71 – 7.66 (m, 1H), 7.62 – 7.57 (m, 2H), 7.36 – 7.30 (m, 2H), 7.29 – 7.22 (m, 1H), 2.32 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.2, 138.9, 134.4, 133.4, 132.8, 130.2, 129.6, 128.9, 127.69, 117.9, 94.2, 85.3, 21.4; HR-ESI-MS (*m/z*): calcd. for $C_{15}H_{12}O_2SNa$ $[M + Na]^+$ 279.0450, found 279.0450.

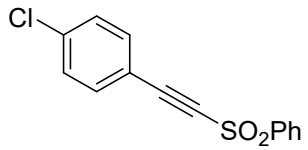
1-fluoro-4-((phenylsulfonyl)ethynyl)benzene (2h)



2h

Following the general procedure B, **2g** was isolated as pale solids (754.1 mg, 58% yield over two steps from 1-ethynyl-4-fluorobenzene) by flash column chromatography (petroleum ether/AcOEt = 15/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 – 8.04 (m, 2H), 7.72 – 7.67 (m, 1H), 7.63 – 7.58 (m, 2H), 7.56 – 7.51 (m, 2H), 7.10 – 7.04 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.7 (d, J_{CF} = 253.7 Hz), 141.9, 135.4 (d, J_{CF} = 9.1 Hz), 134.5, 129.7, 127.7, 116.6 (d, J_{CF} = 22.2 Hz), 114.3, 92.6, 85.5; ^{19}F NMR (564 MHz, $CDCl_3$) δ -104.3 (s, 1F); HR-ESI-MS (*m/z*): calcd. for $C_{14}H_9FO_2SNa$ $[M + Na]^+$ 283.0199, found 283.0202.

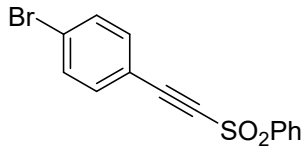
1-chloro-4-((phenylsulfonyl)ethynyl)benzene (2i)



2i

Following the general procedure B, **2i** was isolated as pale solids (883.2 mg, 64% yield over two steps from 1-chloro-4-ethynylbenzene) by flash column chromatography (petroleum ether/AcOEt = 15/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 – 8.05 (m, 2H), 7.70 (t, J = 7.6 Hz, 1H), 7.64 – 7.58 (m, 2H), 7.48 – 7.43 (m, 2H), 7.38 – 7.32 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.8, 138.4, 134.6, 134.2, 129.7, 129.5, 127.8, 116.6, 92.3, 86.4; HR-ESI-MS (*m/z*): calcd. for $C_{14}H_9ClO_2SNa$ $[M + Na]^+$ 298.9904, found 298.9903.

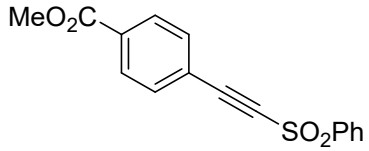
1-bromo-4-((phenylsulfonyl)ethynyl)benzene (2j)



2j

Following the general procedure B, **2j** was isolated as pale solids (991.8 mg, 62% yield over two steps from 1-bromo-4-ethynylbenzene) by flash column chromatography (petroleum ether/AcOEt = 15/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 – 8.04 (m, 2H), 7.72 – 7.67 (m, 1H), 7.61 (t, *J* = 7.8 Hz, 2H), 7.54 – 7.49 (m, 2H), 7.40 – 7.35 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.9, 134.6, 134.3, 132.4, 129.7, 127.7, 126.8, 117.1, 92.4, 86.6; HR-ESI-MS (*m/z*): calcd. for $C_{14}H_9BrO_2SNa$ $[M + Na]^+$ 342.9399, found 342.9400.

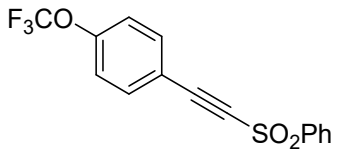
4-((phenylsulfonyl)ethynyl)phenyl acetate (2k)



2k

Following the general procedure B, **2k** was isolated as pale solids (840.1 mg, 56% yield from over two steps methyl 4-ethynylbenzoate) by flash column chromatography (petroleum ether/AcOEt = 8/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.0 Hz, 2H), 8.02 (d, *J* = 8.0 Hz, 2H), 7.71 (t, *J* = 7.4 Hz, 1H), 7.65 – 7.56 (m, 4H), 3.92 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.0, 141.7, 134.7, 132.9, 132.8, 129.9, 129.8, 127.8, 122.5, 91.9, 87.6, 52.8; HR-ESI-MS (*m/z*): calcd. for $C_{16}H_{13}O_4S$ $[M + H]^+$ 301.0529, found 301.0528.

1-((phenylsulfonyl)ethynyl)-4-(trifluoromethoxy)benzene (2l)

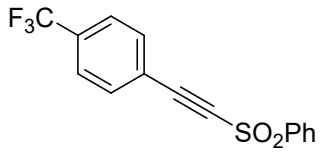


2l

Following the general procedure B, **2l** was isolated as pale solids (978.1 mg, 60% yield over two steps from 1-ethynyl-4-(trifluoromethoxy)benzene) by flash column

chromatography (petroleum ether/AcOEt = 10/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 – 8.05 (m, 2H), 7.72 – 7.67 (m, 1H), 7.63 – 7.57 (m, 2H), 7.58 – 7.54 (m, 2H), 7.21 (d, J = 8.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.6, 141.9, 134.9, 134.6, 129.7, 127.7, 121.2, 120.5 (q, J_{CF} = 257.4 Hz), 116.7, 91.8, 86.4; HR-ESI-MS (*m/z*): calcd. for $C_{16}H_{14}O_3SNa$ $[M + Na]^+$ 309.0556, found 309.0555. ^{19}F NMR (564 MHz, $CDCl_3$) δ -57.7 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{15}H_{19}F_3O_3SNa$ $[M + Na]^+$ 349.0117, found 349.0116.

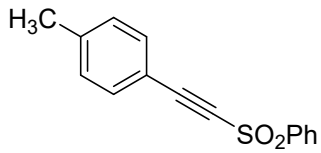
1-((phenylsulfonyl)ethynyl)-4-(trifluoromethyl)benzene (2m)



2m

Following the general procedure B, **2m** was isolated as pale solids (821.6 mg, 53% yield over two steps from 1-ethynyl-4-(trifluoromethyl)benzene) by flash column chromatography (petroleum ether/AcOEt = 12/1, V/V). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.06 (m, 2H), 7.75 – 7.69 (m, 1H), 7.68 – 7.59 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 134.8, 133.4, 133.3 (q, J_{CF} = 32.8 Hz), 129.8, 127.9, 125.9 (q, J_{CF} = 3.7 Hz), 123.6 (q, J_{CF} = 271.1 Hz), 122.0, 91.1, 87.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.3 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{15}H_{10}F_3O_2S$ $[M + H]^+$ 311.0348, found 311.0350.

1-methyl-4-((phenylsulfonyl)ethynyl)benzene (2n)

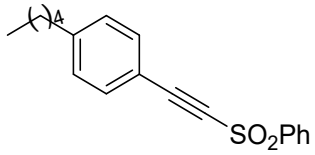


2n

Following the general procedure B, **2n** was isolated as pale solids (832.2 mg, 65% yield over two steps from 1-ethynyl-4-methylbenzene) by flash column chromatography (petroleum ether/AcOEt = 15/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 – 8.05 (m, 2H), 7.68 (t, J = 7.6 Hz, 1H), 7.60 (t, J = 7.6 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 7.17 (d,

J = 8.0 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.7, 142.3, 134.3, 133.0, 129.8, 129.6, 127.6, 115.0, 94.5, 85.2, 22.1; HR-ESI-MS (*m/z*): calcd. for $C_{15}H_{12}O_2SNa$ $[M + Na]^+$ 279.0450, found 279.0450.

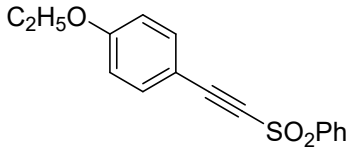
1-pentyl-4-((phenylsulfonyl)ethynyl)benzene (2o)



2o

Following the general procedure B, **2o** was isolated as pale solids (952.0 mg, 61% yield over two steps from 1-ethynyl-4-pentylbenzene) by flash column chromatography (petroleum ether/AcOEt = 15/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 – 8.05 (m, 2H), 7.67 (t, J = 7.6 Hz, 1H), 7.59 (t, J = 7.6 Hz, 2H), 7.43 (d, J = 8.2 Hz, 2H), 7.17 (d, J = 8.2 Hz, 2H), 2.60 (t, J = 7.6 Hz, 2H), 1.62 – 1.54 (m, 2H), 1.35 – 1.23 (m, 4H), 0.87 (t, J = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.7, 142.3, 134.3, 133.0, 129.6, 129.1, 127.6, 115.2, 94.6, 85.3, 36.3, 31.6, 30.9, 22.7, 14.2; HR-ESI-MS (*m/z*): calcd. for $C_{19}H_{20}O_2SNa$ $[M + Na]^+$ 335.1076, found 335.1076.

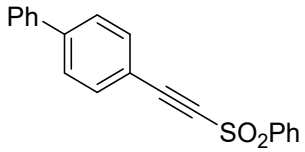
1-ethoxy-4-((phenylsulfonyl)ethynyl)benzene (2p)



2p

Following the general procedure B, **2p** was isolated as pale solids (944.0 mg, 66% yield over two steps from 1-ethoxy-4-ethynylbenzene) by flash column chromatography (petroleum ether/AcOEt = 10/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, J = 7.6 Hz, 2H), 7.66 (t, J = 7.6 Hz, 1H), 7.58 (t, J = 7.6 Hz, 2H), 7.45 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 4.04 (q, J = 7.0 Hz, 2H), 1.40 (t, J = 7.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.9, 142.4, 135.0, 134.2, 129.6, 127.5, 115.1, 109.5, 95.1, 84.8, 64.1, 14.8; HR-ESI-MS (*m/z*): calcd. for $C_{16}H_{14}O_3SNa$ $[M + Na]^+$ 309.0556, found 309.0555.

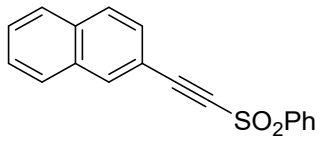
4-((phenylsulfonyl)ethynyl)-1,1'-biphenyl (2q)



2q

Following the general procedure B, **2q** was isolated as pale solids (1.15 g, 72% yield over two steps from 4-ethynyl-1,1'-biphenyl) by flash column chromatography (petroleum ether/AcOEt = 12/1, V/V). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.08 (m, 2H), 7.74 – 7.67 (m, 1H), 7.66 – 7.53 (m, 8H), 7.50 – 7.42 (m, 2H), 7.42 – 7.36 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 142.1, 139.7, 134.5, 133.5, 129.7, 129.3, 128.7, 127.7, 127.6. 127.4, 116.7, 93.9, 86.1; HR-ESI-MS (*m/z*): calcd. for $C_{20}H_{14}O_2SNa$ $[M + Na]^+$ 341.0607, found 341.0607.

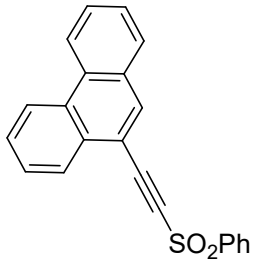
2-((phenylsulfonyl)ethynyl)naphthalene (2r)



2r

Following the general procedure B, **2r** was isolated as pale solids (1.11 g, 76% yield over two steps from 2-ethynylnaphthalene) by flash column chromatography (petroleum ether/AcOEt = 12/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 – 8.09 (m, 3H), 7.83 (t, *J* = 8.6 Hz, 3H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 2H), 7.60 – 7.52 (m, 2H), 7.50 (dd, *J* = 8.6, 1.5 Hz, 1H); ^{13}N MR (150 MHz) δ 142.0, 134.4, 134.2, 134.1, 132.4, 129.4, 128.6, 128.5, 128.3, 127.9, 127.5, 127.4, 127.3, 115.0, 94.0, 85.6; HR-ESI-MS (*m/z*): calcd. for $C_{18}H_{12}O_2SNa$ $[M + Na]^+$ 315.0450, found 315.0448.

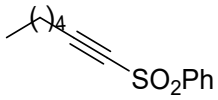
9-((phenylsulfonyl)ethynyl)phenanthrene (2s)



2s

Following the general procedure B, **2s** was isolated as pale solids (1.50 g, 73% yield over two steps from 9-ethynylphenanthrene) by flash column chromatography (petroleum ether/AcOEt = 12/1, V/V). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (t, *J* = 8.4 Hz, 2H), 8.24 – 8.17 (m, 2H), 8.15 – 8.09 (m, 1H), 8.07 (s, 1H), 7.81 (d, *J* = 7.7 Hz, 1H), 7.75 – 7.57 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 136.1, 134.5, 131.7, 130.4, 130.2, 130.1, 129.7, 129.6, 129.5, 128.02, 127.96, 127.7, 127.6, 126.3, 123.2, 123.0, 114.5, 93.0, 89.6; HR-ESI-MS (*m/z*): calcd. for $C_{22}H_{15}O_2S$ $[M + H]^+$ 343.0787, found 343.0791.

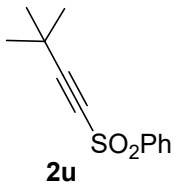
(hept-1-yn-1-ylsulfonyl)benzene (2t)



2t

Following the general procedure B, **2t** was isolated as pale solids (625.5 mg, 53% yield over two steps from hept-1-yne) by flash column chromatography (petroleum ether/AcOEt = 50/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 – 7.96 (m, 2H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 2H), 2.35 (t, *J* = 7.2 Hz, 2H), 1.57 – 1.49 (m, 2H), 1.32 – 1.24 (m, 4H), 0.85 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.4, 134.2, 129.5, 127.4, 98.3, 78.5, 31.1, 26.9, 22.2, 19.2, 14.0; HR-ESI-MS (*m/z*): calcd. for $C_{13}H_{17}O_2S$ $[M + H]^+$ 237.0944, found 237.0947.

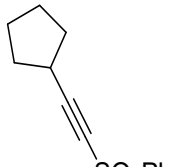
((3,3-dimethylbut-1-yn-1-yl)sulfonyl)benzene (2u)



2u

Following the general procedure B, **2u** was isolated as pale solids (732.8 mg, 55% yield over two steps from 3,3-dimethylbut-1-yne) by flash column chromatography (petroleum ether/AcOEt = 50/1, V/V). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.95 (m, 2H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 2H), 1.24 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 134.1, 129.5, 127.4, 104.5, 77.1, 29.7, 28.2; HR-ESI-MS (*m/z*): calcd. for $C_{12}H_{15}O_2S$ $[M + H]^+$ 223.0787, found 223.0789.

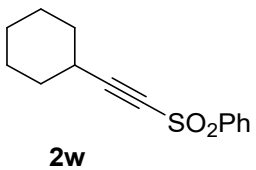
((cyclopentylethynyl)sulfonyl)benzene (2v)



2v

Following the general procedure B, **2v** was isolated as pale solids (884.8 mg, 63% yield over two steps from ethynylcyclopentane) by flash column chromatography (petroleum ether/AcOEt = 50/1, V/V). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.93 (m, 2H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 2H), 2.83 – 2.68 (m, 1H), 2.03 – 1.85 (m, 2H), 1.76 – 1.50 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 134.1, 129.5, 127.3, 102.0, 77.7, 32.9, 30.0, 25.5;

((cyclohexylethynyl)sulfonyl)benzene (2w)

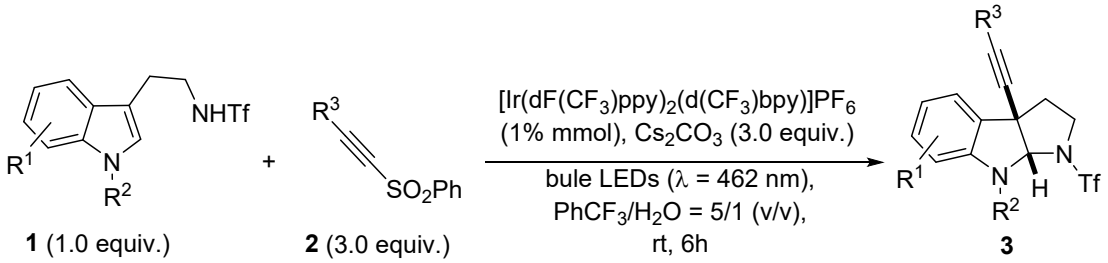


2w

Following the general procedure B, **2w** was isolated as pale solids (744.3 mg, 60% yield over two steps from ethynylcyclohexane) by flash column chromatography (petroleum

ether/AcOEt = 50/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.4 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 2H), 2.58 – 2.49 (m, 1H), 1.82 – 1.72 (m, 2H), 1.69 – 1.58 (m, 2H), 1.53 – 1.43 (m, 3H), 1.35 – 1.24 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.6, 134.1, 129.5, 127.3, 101.3, 78.5, 31.1, 29.3, 25.6, 24.7; HR-ESI-MS (*m/z*): calcd. for $C_{14}H_{17}O_2S$ $[M + H]^+$ 249.0944, found 249.0945.

4. General procedure C for the synthesis of pyrroloindoline product 3.



1 (1.0 equiv.) **2** (3.0 equiv.) **3**

Scheme S3. Reaction for the preparation of pyrroloindoline product **3**.

To a 10 mL Schlenk reaction tube equipped with a magnetic stir bar, typtamine derivate **1** (0.30 mmol, 1.0 equiv.), acetylenic sulfone **2** (0.90 mmol, 3.0 equiv.) $[Ir(dF(CF_3)ppy)_2(d(CF_3)bpy)]PF_6$ (0.003 mmol, 0.01 equiv.), Cs_2CO_3 (0.90 mmol, 3.0 equiv.), $PhCF_3$ (5.0 mL) and H_2O (1.0 mL) were sequentially added. The reaction mixture was degassed three times by freeze-pump-thaw method. The tube was stirred and irradiated with two 18W light emitting diode (LED) lamps from approximately 10 cm away at room temperature for 6 h under argon atmosphere. After completion of the reaction (by TLC analysis), it was quenched with sat. aqueous NH_4Cl solution (10 mL), and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by column chromatography to afford the desired pyrroloindoline product **3**.

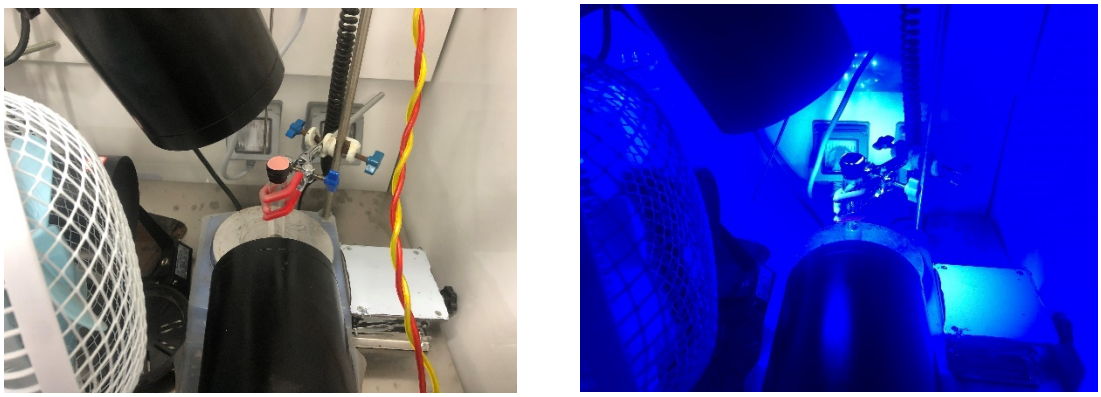


Figure S1. Details for the photochemical reaction setup at room temperature.

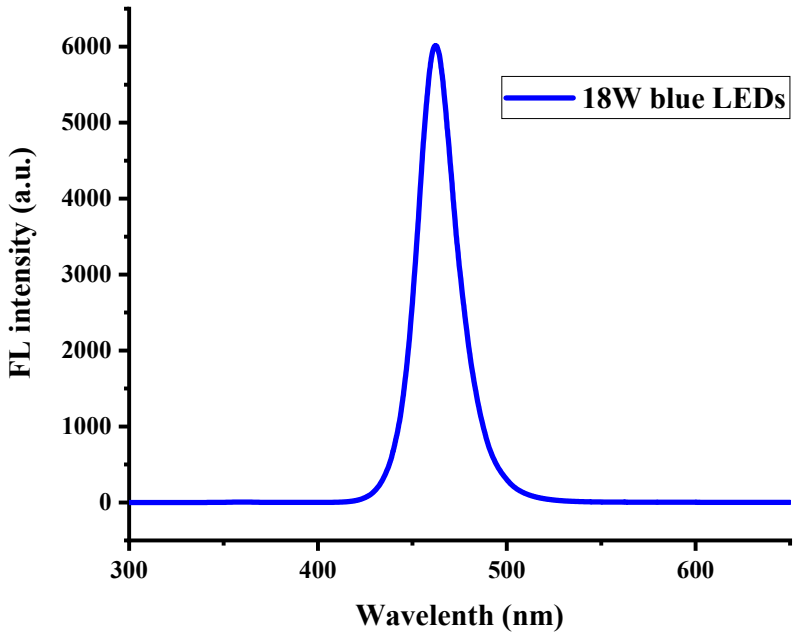


Figure S2. Emission spectra of the 18W blue LED lamps (λmax = 462 nm)

5. Mechanistic investigations

5.1 Luminescence quenching experiments

Fluorescence quenching experiments were performed on a Hitchi F-7000 fluorescence spectrometer. All $[Ir(dF(CF_3)ppy)_2(d(CF_3)bpy)]PF_6$ (**PC5**) solution were excited at 400 nm and the emission intensity was collected from 410 to 780 nm. In a typical experiment, to a 5×10^{-5} M solution of $[Ir(dF(CF_3)ppy)_2(d(CF_3)bpy)]PF_6$ in $PhCF_3/H_2O$ = 5/1 (v/v) (rigorously degassed by freeze/pump/thaw) was added the

appropriate amount of quencher in a 10 x 10 nm light path quartz fluorescence cuvette. After degassing the sample with a stream of argon for 10 minutes, the emission of the sample was collected.

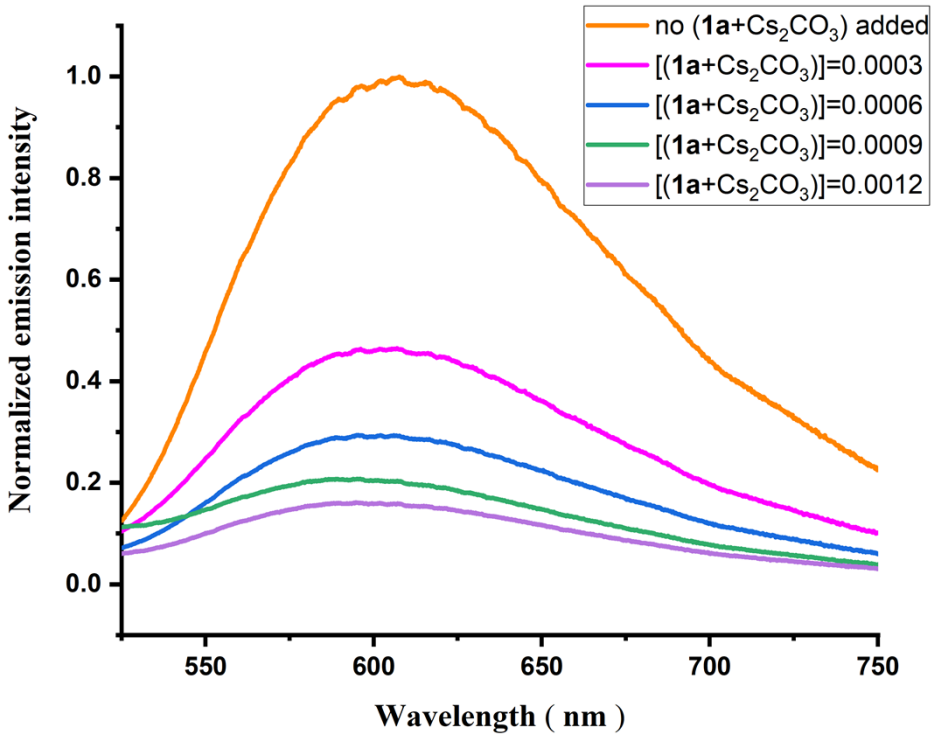


Figure S3. Quenching of $[Ir(dF(CF_3)ppy)_2(d(CF_3)bpy)]PF_6$ emission (5×10^{-5} M in $PhCF_3/H_2O$ = 5/1 (v/v)) in the presence of increasing amounts of deprotonated **1a**.

5.2 The light on-off experiment

Following the general procedure **C**, the photochemical reaction was conducted for light-dark experiment. Aliquots of samples were taken out at various time points during the reaction. The crude NMR was taken on the concentrated crude reaction mixture and analyzed by ^1H NMR using diphenylacetonitrile as an internal standard.

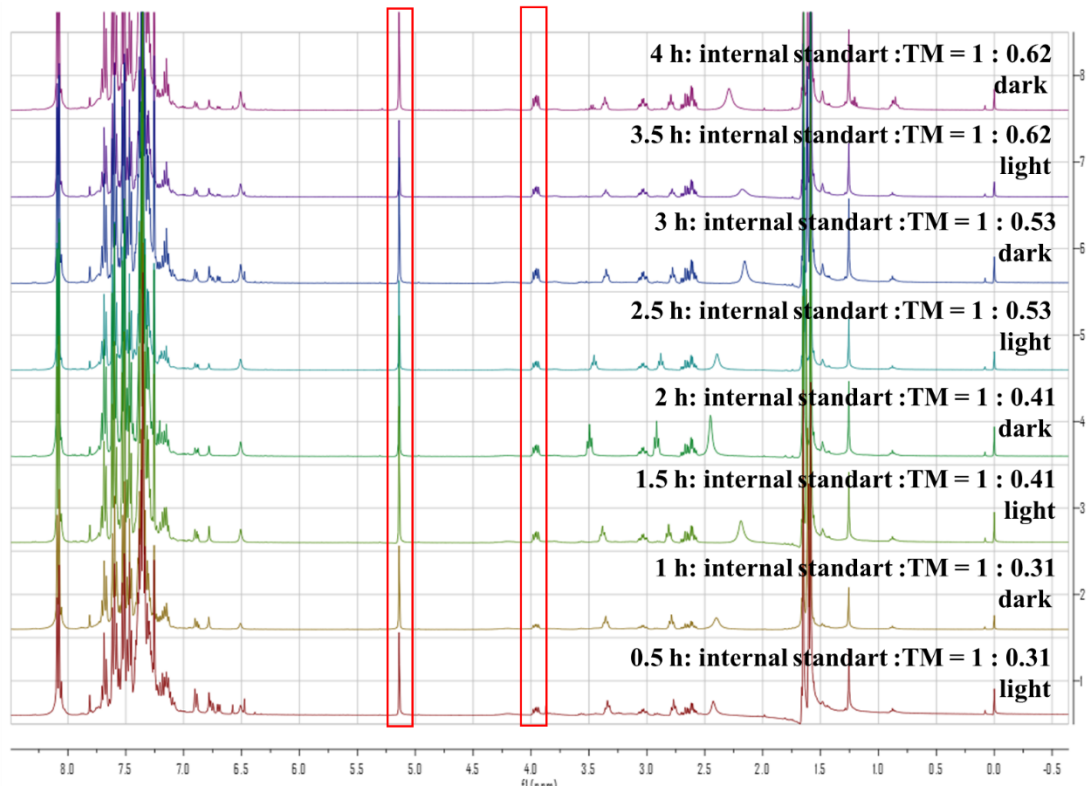


Figure S4. The light on–off experiment analyzed by ^{1}H NMR.

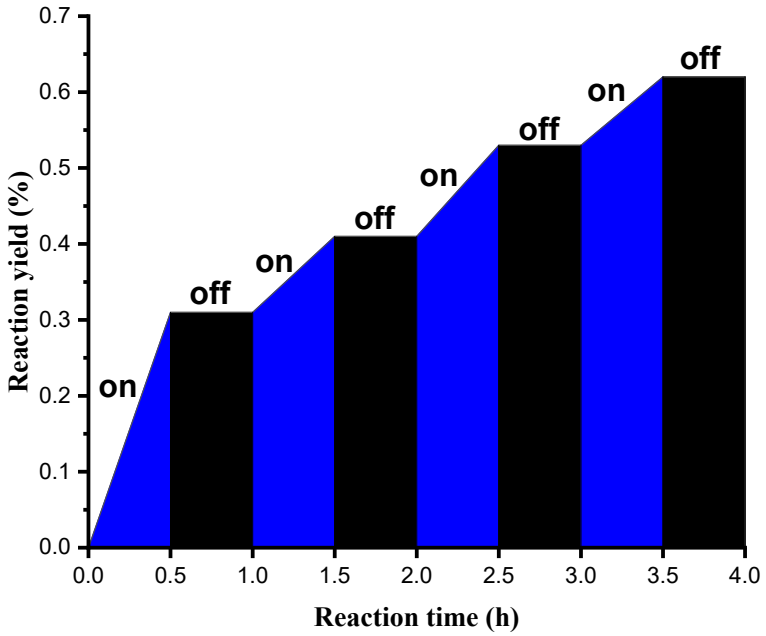
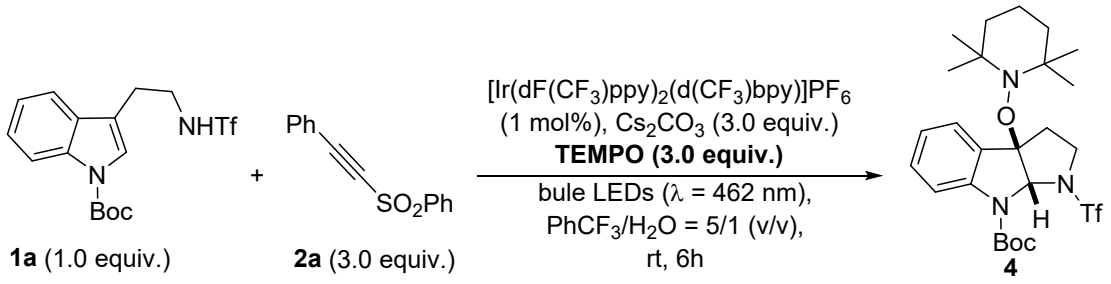


Figure S5. The light on–off experiment.

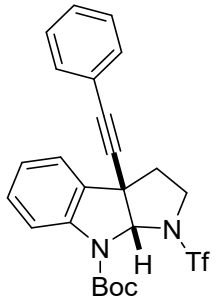
5.3 Controlled experiments



Scheme S4. Inhibition experiments with TEMPO.

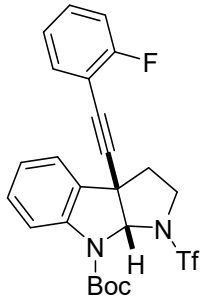
To a 10 mL Schlenk reaction tube equipped with a magnetic stir bar, typtamine derivate **1a** (117.6 mg, 0.30 mmol, 1.0 equiv.), acetylenic sulfone **2a** (217.8 mg, 0.90 mmol, 3.0 equiv.) $[Ir(dF(CF_3)ppy)_2(d(CF_3)bpy)]PF_6$ (3.4 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO_3 (293.2 mg, 0.90 mmol, 3.0 equiv.), TEMPO (140.6 mg, 0.90 mmol, 3.00 equiv), $PhCF_3$ (5.0 mL) and H_2O (1.0 mL) were sequentially added. The reaction mixture was degassed three times by freeze-pump-thaw method. The tube was stirred and irradiated with two 18W light emitting diode (LED) lamps from approximately 10 cm away at room temperature for 6 h under argon atmosphere. After completion of the reaction (by TLC analysis), it was quenched with sat. aqueous NH_4Cl solution (10 mL), and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by column chromatography (petroleum ether/ethyl acetate = 30/1, V/V) to afford the TEMPO-trapped pyrroloindoline compound **4** (142.3 mg, 0.26 mmol, 87 %) as colorless powders. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (br. s, 1H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 6.99 (s, 1H), 3.97 (dd, *J* = 11.4, 7.8 Hz, 1H), 2.98 (td, *J* = 11.4, 4.6 Hz, 1H), 2.75 (td, *J* = 12.5, 7.8 Hz, 1H), 2.44 (dd, *J* = 12.5, 4.6 Hz, 1H), 1.56 (s, 9H), 1.55 – 1.49 (m, 2H), 1.45 – 1.38 (m, 2H), 1.34 – 1.26 (m, 2H), 1.13 (s, 3H), 1.11 (s, 3H), 0.99 (s, 3H), 0.37 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.1, 144.0, 132.6, 130.5, 124.6, 124.3, 119.8 (q, J_{CF} = 320.0 Hz), 117.0, 95.9, 82.6, 80.2, 60.8, 59.8, 49.3, 41.1, 40.8, 33.8, 33.0, 28.3, 20.7, 20.5, 17.1; ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.9 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{25}H_{36}F_3N_3O_5SNa$ $[M + Na]^+$, 570.2220, found 570.2222.

6. Characterization of products



3aa

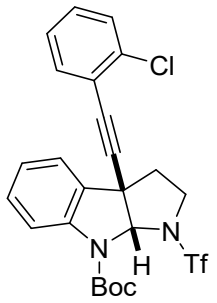
Prepared according to the general procedure **C**, **3aa** was isolated as pale solids (134.4 mg, 91% yield) by flash column chromatography (petroleum ether/ethyl acetate = 30/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.75 (br. s, 1H), 7.41 – 7.28 (m, 7H), 7.15 (t, *J* = 7.4 Hz, 1H), 6.51 (s, 1H), 3.96 (dd, *J* = 12.0, 7.0 Hz, 1H), 3.04 (td, *J* = 12.0, 4.6 Hz, 1H), 2.66 (td, *J* = 12.6, 7.0 Hz, 1H), 2.60 (dd, *J* = 12.6, 4.6 Hz, 1H), 1.59 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.8, 141.8, 131.9, 131.5, 130.0, 128.8, 128.5, 124.7, 123.5, 122.3, 119.8 (q, J_{CF} = 320.0 Hz), 117.0, 87.4, 85.7, 84.0, 83.4, 51.4, 49.1, 40.6, 28.2; ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.5 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{24}H_{23}F_3N_2O_4SNa$ $[M + Na]^+$, 515.1223, found 515.1226.



3ab

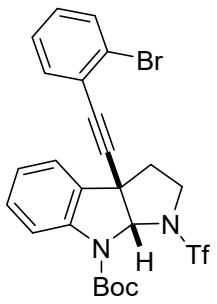
Prepared according to the general procedure **C**, **3ab** was isolated as pale solids (140.8 mg, 92% yield) by flash column chromatography (petroleum ether/ethyl acetate = 30/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (br. s, 1H), 7.40 – 7.27 (m, 4H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.6, 4.5 Hz, 1H), 7.05 (t, *J* = 8.2 Hz, 1H), 6.53 (s, 1H), 3.97 (dd, *J* = 11.4, 7.1 Hz, 1H), 3.06 (td, *J* = 11.4, 4.6 Hz, 1H), 2.69 (td, *J* = 12.6, 7.1 Hz, 1H), 2.62 (dd, *J* = 12.6, 4.6 Hz, 1H), 1.59 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.0

(d, J_{CF} = 250.8 Hz), 151.8, 141.9, 133.6, 131.1, 130.6 (d, J_{CF} = 8.0 Hz), 130.0, 124.7, 124.1 (d, J_{CF} = 3.8 Hz), 123.6, 119.9 (q, J_{CF} = 320.1 Hz), 117.1, 115.7 (d, J_{CF} = 20.7 Hz), 111.0 (d, J_{CF} = 15.8 Hz), 92.5, 84.0, 83.4, 79.3, 51.6, 49.1, 40.4, 28.2; ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.4 (s, 3F), -109.8 (s, 1F); HR-ESI-MS (*m/z*): calcd. for $C_{24}H_{22}F_4N_2O_4SNa$ $[M + Na]^+$, 533.1129, found 533.1127.



3ac

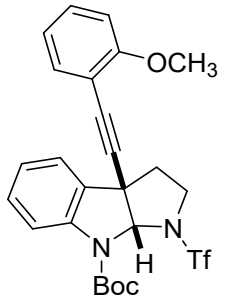
Prepared according to the general procedure **C**, **3ac** was isolated as pale solids (138.9 mg, 88% yield) by flash column chromatography (petroleum ether/ethyl acetate = 30/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (br. s, 1H), 7.43 – 7.36 (m, 3H), 7.34 (t, *J* = 7.8, 1H), 7.25 (td, *J* = 7.8, 1.6, 1H), 7.19 (td, *J* = 7.6, 1.0 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 6.56 (s, 1H), 3.98 (dd, *J* = 11.4, 7.1 Hz, 1H), 3.08 (td, *J* = 11.4, 4.6 Hz, 1H), 2.70 (td, *J* = 12.6, 7.1 Hz, 1H), 2.63 (dd, *J* = 12.6, 4.6 Hz, 1H), 1.59 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.7, 141.9, 136.5, 133.2, 131.0, 130.0, 129.4, 126.6, 124.7, 123.6, 122.2, 119.8 (q, J_{CF} = 320.4 Hz), 117.1, 92.6, 84.0, 83.3, 82.7, 51.6, 49.1, 40.1, 28.2; ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.4 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{24}H_{22}ClF_3N_2O_4SNa$ $[M + Na]^+$, 549.0833, found 549.0836.



3ad

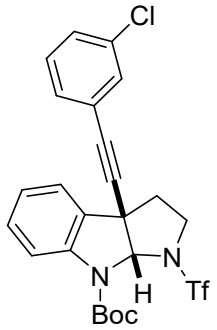
Prepared according to the general procedure **C**, **3ad** was isolated as pale solids (155.6

mg, 91% yield) by flash column chromatography (petroleum ether/ethyl acetate = 30/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (br. s, 1H), 7.56 (dd, *J* = 8.0, 0.7 Hz, 1H), 7.56 (dd, *J* = 8.2, 0.7 Hz, 1H), 7.42 – 7.37 (m, 2H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.24 (td, *J* = 7.6, 1.0 Hz, 1H), 7.19 – 7.13 (m, 2H), 6.57 (s, 1H), 3.97 (dd, *J* = 11.4, 7.1 Hz, 1H), 3.08 (td, *J* = 11.4, 4.6 Hz, 1H), 2.71 (td, *J* = 12.6, 7.1 Hz, 1H), 2.63 (dd, *J* = 12.6, 4.6 Hz, 1H), 1.59 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.7, 142.0, 133.2, 132.6, 131.0, 130.0, 130.0, 127.2, 126.3, 124.7, 124.4, 123.6, 120.0 (q, J_{CF} = 320.4 Hz), 117.2, 92.0, 84.60, 84.0, 83.3, 51.6, 49.1, 40.0, 28.20; ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.4 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{24}H_{22}BrF_3N_2O_4SNa$ [M + Na]$^+$, 593.0328, found 593.0331.



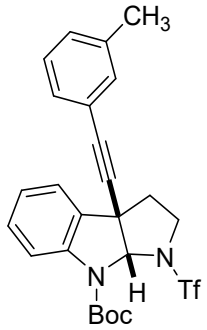
3ae

Prepared according to the general procedure **C**, **3ae** was isolated as pale solids (148.8 mg, 95% yield) by flash column chromatography (petroleum ether/ethyl acetate = 25/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (br. s, 1H), 7.38 (d, *J* = 7.6, 1H), 7.35 – 7.26 (m, 3H), 7.14 (td, *J* = 7.6, 0.8 Hz, 1H), 6.87 (td, *J* = 7.6, 0.8 Hz, 1H), 6.85 (d, *J* = 8.4, 1H), 6.53 (s, 1H), 3.96 (dd, *J* = 11.4, 7.1 Hz, 1H), 3.84 (s, 3H), 3.04 (td, *J* = 11.4, 4.6 Hz, 1H), 2.70 (td, *J* = 12.6, 7.1 Hz, 1H), 2.61 (dd, *J* = 12.6, 4.6 Hz, 1H), 1.59 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.4, 151.8, 141.9, 133.7, 131.6, 130.3, 129.7, 124.6, 123.6, 120.5, 119.8 (q, J_{CF} = 320.7 Hz), 117.0, 111.6, 110.9, 91.4, 84.1, 83.2, 82.1, 55.9, 51.8, 49.1, 40.6, 28.2; ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.5 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{25}H_{25}F_3N_2O_5SNa$ [M + Na]$^+$, 545.1328, found 545.1327.



3af

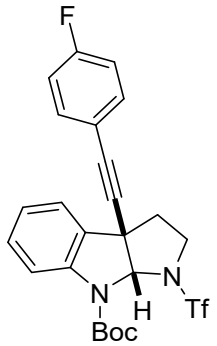
Prepared according to the general procedure **C**, **3af** was isolated as pale solids (151.5 mg, 96% yield) by flash column chromatography (petroleum ether/ethyl acetate = 30/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (br. s, 1H), 7.40 – 7.26 (m, 5H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 6.50 (s, 1H), 3.97 (dd, *J* = 11.4, 7.1 Hz, 1H), 3.04 (td, *J* = 11.4, 4.6 Hz, 1H), 2.65 (td, *J* = 12.6, 7.1 Hz, 1H), 2.59 (dd, *J* = 12.5, 4.6 Hz, 1H), 1.59 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.7, 141.8, 134.3, 131.8, 131.0, 130.0, 129.7, 129.1, 124.7, 123.9, 123.5, 119.8 (q, J_{CF} = 320.7 Hz), 117.0, 88.6, 84.3, 83.9, 83.5, 51.3, 49.0, 40.6, 28.2; ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.5 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{24}H_{22}ClF_3N_2O_4SNa$ $[M + Na]^+$, 549.0833, found 549.0837.



3ag

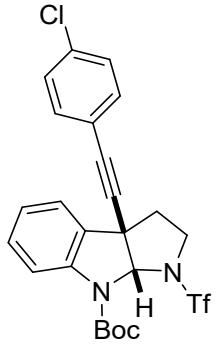
Prepared according to the general procedure **C**, **3ag** was isolated as pale solids (14.3 mg, 95% yield) by flash column chromatography (petroleum ether/ethyl acetate = 30/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (br. s, 1H), 7.38 – 7.32 (m, 2H), 7.23 (s, 1H), 7.21 – 7.13 (m, 4H), 6.51 (s, 1H), 3.97 (dd, *J* = 11.4, 7.0 Hz, 1H), 3.04 (td, *J* = 11.4, 4.6 Hz, 1H), 2.66 (td, *J* = 12.6, 7.0 Hz, 1H), 2.60 (dd, *J* = 12.6, 4.6 Hz, 1H), 2.32 (s, 3H), 1.60 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.8, 141.8, 138.2, 132.5, 131.4, 129.8,

129.7, 128.9, 128.3, 124.7, 123.5, 122.0, 119.8 (q, J_{CF} = 320.6 Hz), 117.0, 87.0, 85.8, 84.0, 83.3, 51.4, 49.1, 40.6, 28.2, 21.3; ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.5 (s, 3F); calcd. for $C_{25}H_{25}ClF_3N_2O_4SNa$ [M + Na]$^+$, 529.1379, found 529.1376.



3ah

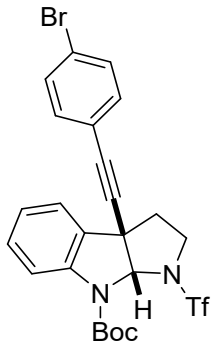
Prepared according to the general procedure **C**, **3ah** was isolated as pale solids (148.4 mg, 97% yield) by flash column chromatography (petroleum ether/ethyl acetate = 30/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (br. s, 1H), 7.40 – 7.31 (m, 4H), 7.15 (t, J = 7.5 Hz, 1H), 6.99 (t, J = 8.6 Hz, 2H), 6.50 (s, 1H), 3.97 (dd, J = 11.4, 7.0 Hz, 1H), 3.03 (td, J = 11.4, 4.6 Hz, 1H), 2.65 (td, J = 12.5, 7.0 Hz, 1H), 2.59 (dd, J = 12.5, 4.6 Hz, 1H), 1.59 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.8 (d, J_{CF} = 248.7 Hz), 151.7, 141.8, 133.8 (d, J_{CF} = 8.3 Hz), 131.3, 129.8, 124.7, 123.5, 119.8 (q, J_{CF} = 320.1 Hz), 118.3, 117.0, 115.8 (d, J_{CF} = 22.1 Hz), 87.1, 84.6, 83.9, 83.4, 51.3, 49.0, 40.6, 28.2; ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.5 (s, 3F), -110.2 (s, 1F); HR-ESI-MS (*m/z*): calcd. for $C_{24}H_{22}F_4N_2O_4SNa$ [M + Na]$^+$, 533.1129, found 533.1128.



3ai

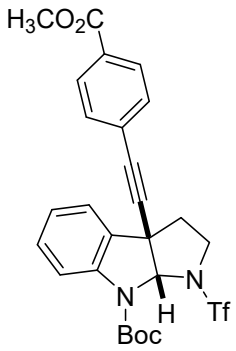
Prepared according to the general procedure **C**, **3ai** was isolated as pale solids (146.8

mg, 93% yield) by flash column chromatography (petroleum ether/ethyl acetate = 30/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (br. s, 1H), 7.37 – 7.31 (m, 4H), 7.29 – 7.26 (m, 2H), 7.15 (td, *J* = 7.5, 0.8 Hz, 1H), 6.50 (s, 1H), 3.97 (dd, *J* = 11.4, 7.0 Hz, 1H), 3.03 (td, *J* = 11.4, 4.6 Hz, 1H), 2.65 (td, *J* = 12.5, 7.0 Hz, 1H), 2.59 (dd, *J* = 12.5, 4.6 Hz, 1H), 1.59 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.7, 141.8, 135.0, 133.1, 132.7, 129.9, 128.8, 124.7, 123.6, 120.7, 119.8 (q, J_{CF} = 320.4 Hz), 117.0, 88.4, 84.6, 83.9, 83.5, 51.5, 49.0, 40.5, 28.2; ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.5 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{24}H_{22}ClF_3N_2O_4SNa$ [M + Na]$^+$, 549.0833, found 549.0835.



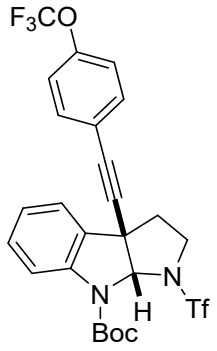
3aj

Prepared according to the general procedure **C**, **3aj** was isolated as pale solids (155.6 mg, 91% yield) by flash column chromatography (petroleum ether/ethyl acetate = 30/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (br. s, 1H), 7.46 – 7.41 (m, 2H), 7.34 (t, *J* = 8.2 Hz, 2H), 7.27 – 7.23 (m, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.50 (s, 1H), 3.96 (dd, *J* = 11.4, 7.0 Hz, 1H), 3.03 (td, *J* = 11.4, 4.7 Hz, 1H), 2.65 (td, *J* = 12.5, 7.0 Hz, 1H), 2.59 (dd, *J* = 12.5, 4.7 Hz, 1H), 1.59 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.7, 141.8, 133.3, 131.7, 131.1, 129.9, 124.7, 123.5, 123.2, 121.2, 119.8 (q, J_{CF} = 320.3 Hz),, 117.0, 88.6, 84.7, 83.8, 83.4, 51.4, 49.0, 40.6, 28.2; ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.5 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{24}H_{22}BrF_3N_2O_4SNa$ [M + Na]$^+$, 593.0328, found 593.0328.



3ak

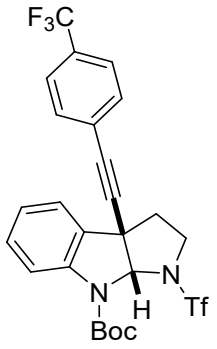
Prepared according to the general procedure **C**, **3ak** was isolated as pale solids (153.5 mg, 93% yield) by flash column chromatography (petroleum ether/ethyl acetate = 20/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.2 Hz, 2H), 7.74 (br. s, 1H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.32 (m, 2H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.53 (s, 1H), 3.97 (dd, *J* = 11.4, 7.0 Hz, 1H), 3.90 (s, 3H), 3.05 (td, *J* = 11.4, 4.6 Hz, 1H), 2.67 (td, *J* = 12.5, 7.0 Hz, 1H), 2.61 (dd, *J* = 12.5, 4.6 Hz, 1H), 1.59 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.5, 151.7, 141.8, 131.8, 131.0, 130.2, 129.9, 129.6, 126.9, 124.7, 123.5, 119.8 (q, J_{CF} = 321.0 Hz), 117.1, 90.3, 85.0, 83.9, 83.4, 52.3, 51.4, 49.0, 40.5, 28.2; ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.5 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{26}H_{25}F_3N_2O_6SNa$ [M + Na]$^+$, 573.1278, found 573.1278.



3al

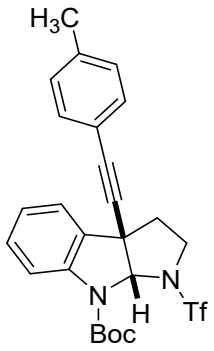
Prepared according to the general procedure **C**, **3al** was isolated as pale solids (164.2 mg, 95% yield) by flash column chromatography (petroleum ether/ethyl acetate = 25/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.45 – 7.39 (m, 2H), 7.36 – 7.392 (m, 2H), 7.17 – 7.13 (m, 3H), 6.51 (s, 1H), 3.97 (dd, *J* = 11.4, 7.0 Hz, 1H), 3.04 (td, *J* = 11.4, 4.6 Hz, 1H), 2.65 (td, *J* = 12.5, 7.0 Hz, 1H), 2.59 (dd, *J* = 12.5, 4.6 Hz, 1H),

1.59 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.7, 149.4, 141.9, 133.5, 131.1, 129.9, 124.7, 123.5, 121.0, 120.9, 120.5 (q, J = 256.1 Hz), 119.8 (q, J_{CF} = 320.0 Hz), 117.1, 88.3, 84.3, 83.9, 83.5, 51.3, 49.0, 40.6, 28.2; ^{19}F NMR (564 MHz, $CDCl_3$) δ -57.9 (s, 3F), -76.5 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{25}H_{22}F_6N_2O_5SNa$ [M + Na]$^+$, 599.1046, found 599.1045.



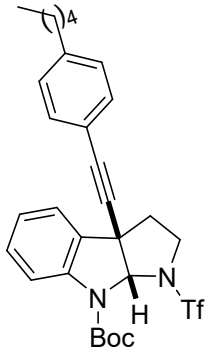
3am

Prepared according to the general procedure **C**, **3am** was isolated as pale solids (158.0 mg, 94% yield) by flash column chromatography (petroleum ether/ethyl acetate = 30/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (br. s, 1H), 7.56 (d, J = 8.2 Hz, 2H), 7.50 (d, J = 8.2 Hz, 2H), 7.38 – 7.31 (m, 2H), 7.16 (td, J = 7.6, 0.7 Hz, 1H), 6.53 (s, 1H), 3.98 (dd, J = 11.4, 7.0 Hz, 1H), 3.05 (td, J = 11.4, 4.7 Hz, 1H), 2.67 (td, J = 12.5, 7.0 Hz, 1H), 2.61 (dd, J = 12.5, 4.7 Hz, 1H), 1.59 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.7, 141.9, 132.2, 130.9, 130.0, 126.1, 125.4 (q, J = 3.9 Hz), 124.8, 123.9 (q, J = 270.3 Hz), 123.5, 119.8 (q, J_{CF} = 320.3 Hz), 117.1, 89.9, 84.4, 83.9, 83.59, 51.3, 49.0, 40.6, 28.2; ^{19}F NMR (564 MHz, $CDCl_3$) δ -63.0 (s, 3F), -76.5 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{25}H_{22}F_6N_2O_4SNa$ [M + Na]$^+$, 583.1097, found 583.1101.



3an

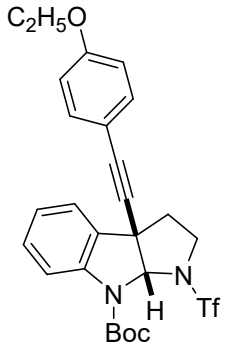
Prepared according to the general procedure **C**, **3an** was isolated as pale solids (141.2 mg, 93% yield) by flash column chromatography (petroleum ether/ethyl acetate = 30/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (br. s, 1H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.15 (td, *J* = 7.5, 0.7 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.50 (s, 1H), 3.96 (dd, *J* = 11.4, 7.0 Hz, 1H), 3.04 (td, *J* = 11.4, 4.6 Hz, 1H), 2.66 (td, *J* = 12.5, 7.0 Hz, 1H), 2.59 (dd, *J* = 12.5, 4.6 Hz, 1H), 2.34 (s, 3H), 1.59 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.8, 141.8, 139.0, 131.8, 131.5, 129.7, 129.2, 124.6, 123.5, 119.8 (q, J_{CF} = 320.4 Hz), 119.2, 117.0, 86.7, 85.8, 84.0, 83.30, 51.5, 49.1, 40.6, 28.2, 21.6; ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.5 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{25}H_{25}F_3N_2O_4SNa$ $[M + Na]^+$, 529.1379, found 529.1379.



3ao

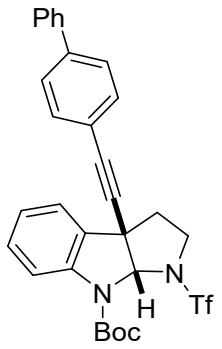
Prepared according to the general procedure **C**, **3ao** was isolated as pale solids (150.1 mg, 89% yield) by flash column chromatography (petroleum ether/ethyl acetate = 30/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (br. s, 1H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.33(t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 8.1 Hz, 2H), 6.49 (s, 1H), 3.96 (dd, *J* = 11.4, 7.0 Hz, 1H), 3.03 (td, *J* = 11.4, 4.6 Hz, 1H), 2.66

(td, J = 12.5, 7.0 Hz, 1H), 2.61 – 2.56 (m, 3H), 1.59 (s, 9H), 1.58 – 1.55 (m, 2H), 1.34 – 1.26 (m, 4H), 0.88 (t, J = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.8, 144.1, 141.9, 131.89, 131.6, 129.7, 128.6, 124.7, 123.5, 119.8 (q, J_{CF} = 320.0 Hz), 119.4, 117.0, 86.7, 85.9, 84.1, 83.3, 51.5, 49.1, 40.6, 36.0, 31.5, 31.0, 28.2, 22.6, 14.1; ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.5 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{29}H_{33}F_3N_2O_4SNa$ $[M + Na]^+$, 585.2005, found 585.2007.



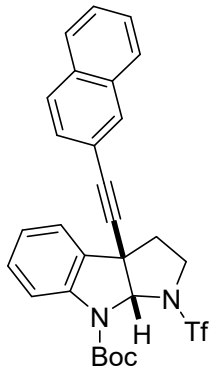
3ap

Prepared according to the general procedure **C**, **3ap** was isolated as pale solids (148.0 mg, 92% yield) by flash column chromatography (petroleum ether/ethyl acetate = 25/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (br. s, 1H), 7.35 (d, J = 7.5 Hz, 1H), 7.34 – 7.30 (m, 3H), 7.14 (td, J = 7.5, 0.7 Hz, 1H), 6.81 (td, J = 8.4, 2.0 Hz, 2H), 6.49 (s, 1H), 4.02 (q, J = 7.0 Hz, 2H), 3.95 (dd, J = 11.4, 7.0 Hz, 1H), 3.03 (td, J = 11.4, 4.6 Hz, 1H), 2.65 (td, J = 12.5, 7.0 Hz, 1H), 2.58 (dd, J = 12.5, 4.6 Hz, 1H), 1.59 (s, 9H), 1.40 (t, J = 7.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.4, 151.8, 141.8, 133.3, 131.6, 129.7, 124.6, 123.5, 119.8 (q, J_{CF} = 319.5 Hz), 117.0, 114.6, 114.1, 85.9, 85.7, 84.0, 83.3, 63.7, 51.5, 49.1, 40.6, 28.2, 14.8; ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.5 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{26}H_{27}F_3N_2O_5SNa$ $[M + Na]^+$, 559.1485, found 559.1493.



3aq

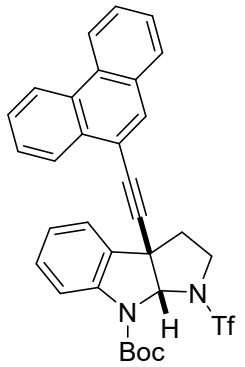
Prepared according to the general procedure **C**, **3aq** was isolated as pale solids (168.7 mg, 99% yield) by flash column chromatography (petroleum ether/ethyl acetate = 30/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (br. s, 1H), 7.59 – 7.53 (m, 4H), 7.49 – 7.41 (m, 4H), 7.40 – 7.33 (m, 3H), 7.17 (td, *J* = 7.5, 0.8 Hz, 1H), 6.54 (s, 1H), 3.98 (dd, *J* = 11.4, 7.0 Hz, 1H), 3.06 (td, *J* = 11.4, 4.6 Hz, 1H), 2.69 (td, *J* = 12.5, 7.0 Hz, 1H), 2.62 (dd, *J* = 12.5, 4.6 Hz, 1H), 1.61 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.8, 141.9, 141.6, 140.3, 132.3, 131.4, 129.8, 129.0, 127.9, 127.2, 127.1, 124.7, 123.6, 121.16, 119.8 (q, J_{CF} = 320.1 Hz), 117.1, 88.0, 85.6, 84.0, 83.4, 51.5, 49.1, 40.6, 28.2; ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.4 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{30}H_{27}F_3N_2O_4SNa$ [M + Na]$^+$, 591.1536, found 591.1532.



3ar

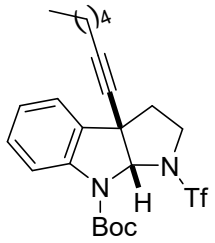
Prepared according to the general procedure **C**, **3ar** was isolated as pale solids (152.9 mg, 94% yield) by flash column chromatography (petroleum ether/ethyl acetate = 30/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.84 – 7.73 (m, 4H), 7.52 – 7.47 (m, 2H), 7.43 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.36 (td, *J* = 7.6 Hz, 1.2, 1H), 7.18 (td, *J* = 7.6, 0.8 Hz, 1H), 6.57 (s, 1H), 3.99 (dd, *J* = 11.4, 7.0 Hz, 1H), 3.07

(td, J = 11.4, 4.6 Hz, 1H), 2.72 (td, J = 12.6, 7.0 Hz, 1H), 2.64 (dd, J_{CF} = 12.6, 4.6 Hz, 1H), 1.61 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.8, 141.9, 133.1, 133.0, 132.0, 131.4, 129.8, 128.4, 128.2, 127.9, 127.0, 126.8, 124.7, 123.6, 119.8 (q, J = 321.0 Hz), 119.5, 117.1, 87.7, 86.1, 84.0, 83.4, 51.5, 49.1, 40.7, 28.2; ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.4 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{28}H_{25}F_3N_2O_4SNa$ $[M + Na]^+$, 565.1379, found 565.1384.



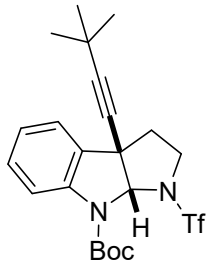
3as

Prepared according to the general procedure **C**, **3as** was isolated as pale solids (161.7 mg, 91% yield) by flash column chromatography (petroleum ether/ethyl acetate = 30/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.67 (d, J = 8.2 Hz, 1H), 8.63 (d, J = 8.2 Hz, 1H), 8.22 (d, J = 7.9 Hz, 1H), 7.96 (s, 1H), 7.83 (m, 2H), 7.71 – 7.63 (m, 3H), 7.60 (t, J = 7.4 Hz, 1H), 7.48 (d, J = 7.4 Hz, 1H), 7.39 (t, J = 7.9 Hz, 1H), 7.22 (t, J = 7.4 Hz, 1H), 6.67 (s, 1H), 4.04 (dd, J = 11.4, 7.1 Hz, 1H), 3.14 (td, J = 11.4, 4.4 Hz, 1H), 2.82 (td, J = 12.5, 7.1 Hz, 1H), 2.74 (dd, J = 12.5, 4.4 Hz, 1H), 1.62 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.8, 142.0, 132.5, 131.4, 131.1, 131.0, 130.6, 130.2, 129.9, 128.7, 127.9, 127.3, 127.2, 126.6, 124.8, 123.5, 123.0, 122.8, 119.9 (q, J_{CF} = 319.5 Hz), 118.5, 117.3, 91.8, 84.3, 84.2, 83.4, 51.8, 49.2, 40.4, 28.2; ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.4 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{32}H_{27}F_3N_2O_6SNa$ $[M + Na]^+$, 615.1536, found 615.1538.



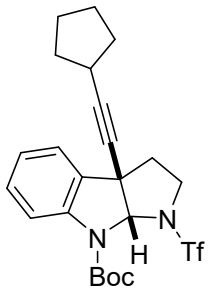
3at

Prepared according to the general procedure **C**, **3at** was isolated as pale solids (121.1 mg, 83% yield) by flash column chromatography (petroleum ether/ethyl acetate = 40/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (br. s, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.34 (s, 1H), 3.89 (dd, *J* = 11.4, 6.6 Hz, 1H), 2.97 (td, *J* = 11.4, 5.2 Hz, 1H), 2.57 – 2.43 (m, 2H), 2.15 (t, *J* = 7.2 Hz, 2H), 1.57 (s, 9H), 1.51 – 1.42 (m, 2H), 1.33 – 1.27 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.8, 141.7, 132.1, 129.5, 124.5, 123.3, 119.8 (q, J_{CF} = 319.2 Hz), 117.0, 86.6, 84.3, 83.1, 78.6, 51.0, 49.1, 40.4, 31.1, 28.2, 28.2, 22.2, 18.9, 14.1; ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.5 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{23}H_{29}F_3N_2O_4SNa$ $[M + Na]^+$, 509.1692, found 509.1693.



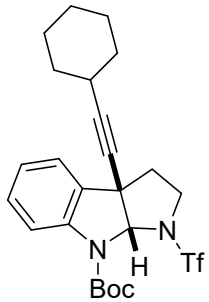
3au

Prepared according to the general procedure **C**, **3au** was isolated as pale solids (126.1 mg, 89% yield) by flash column chromatography (petroleum ether/ethyl acetate = 40/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (br. s, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.32 (s, 1H), 3.88 (dd, *J* = 11.4, 6.6 Hz, 1H), 2.96 (td, *J* = 11.4, 5.2 Hz, 1H), 2.57 – 2.40 (m, 2H), 1.57 (s, 9H), 1.16 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.9, 141.7, 132.4, 129.4, 124.6, 123.3, 119.9 (q, J_{CF} = 321.0 Hz), 117.0, 94.6, 84.6, 83.1, 51.0, 49.0, 40.7, 31.0, 28.2, 27.6; ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.5 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{22}H_{27}F_3N_2O_4SNa$ $[M + Na]^+$, 495.1536, found 495.1531.



3av

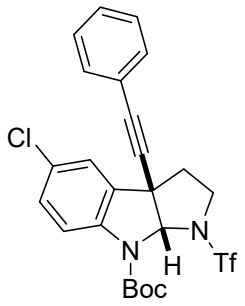
Prepared according to the general procedure **C**, **3av** was isolated as pale solids (126.4 mg, 87% yield) by flash column chromatography (petroleum ether/ethyl acetate = 40/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (br. s, 1H), 7.29 (td, *J* = 7.6, 1.0 Hz, 1H), 7.27 – 7.25 (m, 1H), 7.29 (td, *J* = 7.6, 1.0 Hz, 1H), 6.33 (s, 1H), 3.88 (dd, *J* = 11.4, 6.6 Hz, 1H), 2.96 (td, *J* = 11.4, 5.2 Hz, 1H), 2.60 – 2.54 (m, 1H), 2.53 – 2.44 (m, 2H), 1.91 – 1.80 (m, 2H), 1.72 – 1.62 (m, 2H), 1.57 (s, 9H), 1.55 – 1.48 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.9, 141.7, 132.3, 129.5, 124.6, 123.3, 119.8 (q, J_{CF} = 319.5 Hz), 117.0, 90.7, 84.4, 83.1, 78.1, 51.1, 49.1, 40.6, 33.9, 30.3, 28.2, 25.1; ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.5 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{23}H_{27}F_3N_2O_4SNa$ [M + Na]$^+$, 507.1536, found 507.1534.



3aw

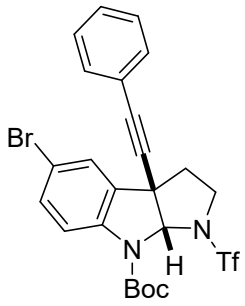
Prepared according to the general procedure **C**, **3aw** was isolated as pale solids (125.5 mg, 84% yield) by flash column chromatography (petroleum ether/ethyl acetate = 40/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (br. s, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.34 (s, 1H), 3.88 (dd, *J* = 11.4, 6.6 Hz, 1H), 2.97 (td, *J* = 11.4, 5.4 Hz, 1H), 2.56 – 2.44 (m, 2H), 2.39 – 2.31 (m, 1H), 1.74 – 1.68 (m, 2H), 1.66 – 1.61 (m, 2H), 1.57 (s, 9H), 1.51 – 1.44 (m, 1H), 1.41 – 1.35 (m, 2H), 1.32 – 1.26 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.9, 141.7, 132.3, 129.5, 124.6,

123.3, 119.9 (q, J_{CF} = 319.5 Hz), 117.0, 90.5, 84.5, 83.1, 78.8, 51.1, 49.1, 40.5, 32.5, 29.1, 28.2, 26.0, 24.8; ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.5 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{24}H_{29}F_3N_2O_4SNa$ [M + Na]$^+$, 521.1692, found 521.1691.



3ba

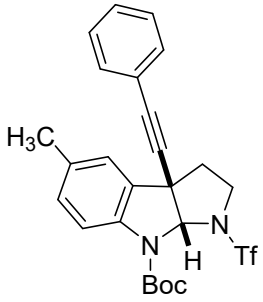
Prepared according to the general procedure **C**, **3ba** was isolated as pale solids (153.1 mg, 97% yield) by flash column chromatography (petroleum ether/ethyl acetate = 30/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (br. s, 1H), 7.43 – 7.39 (m, 2H), 7.35 – 7.28 (m, 5H), 6.49 (s, 1H), 3.98 (dd, *J* = 11.4, 7.1 Hz, 1H), 3.06 (td, *J* = 11.4, 4.6 Hz, 1H), 2.66 (td, *J* = 12.6, 7.1 Hz, 1H), 2.58 (dd, *J* = 12.6, 4.6 Hz, 1H), 1.58 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.5, 140.5, 133.2, 131.9, 129.9, 129.7, 129.1, 128.5, 123.8, 122.0, 119.8 (q, J_{CF} = 320.6 Hz), 118.1, 86.6, 86.2, 84.2, 83.8, 51.4, 49.0, 40.5, 28.2; ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.4 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{24}H_{22}ClF_3N_2O_4SNa$ [M + Na]$^+$, 549.0833, found 549.0831.



3ca

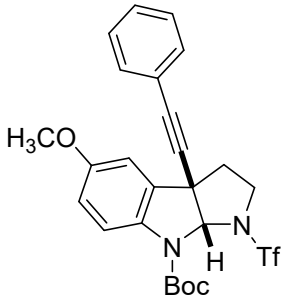
Prepared according to the general procedure **C**, **3ca** was isolated as pale solids (162.5 mg, 95% yield) by flash column chromatography (petroleum ether/ethyl acetate = 30/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (br. s, 1H), 7.48 (d, *J* = 1.9 Hz, 1H), 7.44 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.43 – 7.39 (m, 2H), 7.35 – 7.29 (m, 3H), 6.48 (s, 1H), 3.98

(dd, J = 11.4, 7.1 Hz, 1H), 3.06 (td, J = 11.4, 4.6 Hz, 1H), 2.66 (td, J = 12.6, 7.1 Hz, 1H), 2.58 (dd, J = 12.6, 4.6 Hz, 1H), 1.58 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.5, 141.0, 133.5, 132.8, 131.9, 129.1, 128.5, 126.7, 121.9, 119.8 (q, J_{CF} = 320.1 Hz), 118.5, 117.0, 86.6, 86.3, 84.2, 83.8, 51.3, 49.0, 40.5, 28.2; ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.4 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{24}H_{22}BrF_3N_2O_4SNa$ [M + Na]$^+$, 593.0328, found 593.0327.



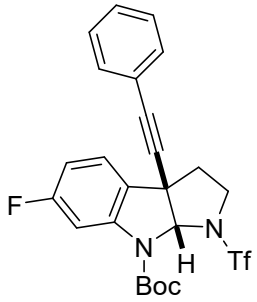
3da

Prepared according to the general procedure **C**, **3da** was isolated as pale solids (141.2 mg, 93% yield) by flash column chromatography (petroleum ether/ethyl acetate = 30/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (br. s, 1H), 7.40 (dd, J = 7.6, 1.9 Hz, 2H), 7.34 – 7.29 (m, 3H), 7.16 (s, 1H), 7.14 (d, J = 8.6 Hz, 1H), 6.49 (s, 1H), 3.96 (dd, J = 11.4, 7.0 Hz, 1H), 3.05 (td, J = 11.4, 4.6 Hz, 1H), 2.65 (td, J = 12.5, 7.0 Hz, 1H), 2.59 (dd, J = 12.5, 4.6 Hz, 1H), 2.36 (s, 3H), 1.58 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.8, 139.6, 134.5, 131.9, 131.3, 130.4, 128.8, 128.4, 123.9, 122.3, 119.8 (q, J_{CF} = 321.0 Hz), 116.8, 87.5, 85.5, 84.2, 83.1, 51.4, 49.0, 40.5, 28.2, 21.1; ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.5 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{25}H_{25}F_3N_2O_4SNa$ [M + Na]$^+$, 529.1379, found 529.1381.



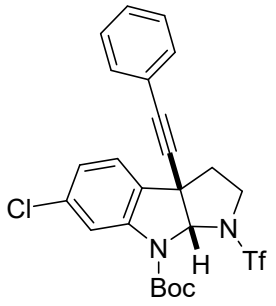
3ea

Prepared according to the general procedure **C**, **3aa** was isolated as pale solids (126.9 mg, 81% yield) by flash column chromatography (petroleum ether/ethyl acetate = 25/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (br. s, 1H), 7.39 (dd, *J* = 7.6, 1.9 Hz, 2H), 7.35 – 7.28 (m, 3H), 6.91 – 6.85 (m, 2H), 6.48 (s, 1H), 3.96 (dd, *J* = 11.4, 7.1 Hz, 1H), 3.82 (s, 3H), 3.06 (td, *J* = 11.4, 4.6 Hz, 1H), 2.64 (td, *J* = 12.5, 7.1 Hz, 1H), 2.58 (dd, *J* = 12.5, 4.6 Hz, 1H), 1.58 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.3, 151.9, 135.3, 132.6, 131.9, 128.9, 128.5, 122.2, 119.8 (q, J_{CF} = 321.4 Hz), 117.9, 114.76 (s, 8H), 109.3, 87.1, 85.8, 84.3, 83.1, 56.0, 51.7, 49.0, 40.2, 28.2; ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.5 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{25}H_{25}F_3N_2O_5SNa$ $[M + Na]^+$, 545.1328, found 545.1337.



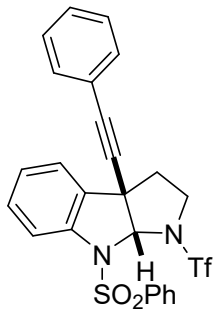
3fa

Prepared according to the general procedure **C**, **3fa** was isolated as pale solids (142.3 mg, 93% yield) by flash column chromatography (petroleum ether/ethyl acetate = 30/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (br. s, 1H), 7.41 – 7.37 (m, 2H), 7.35 – 7.27 (m, 4H), 6.84 (td, *J* = 8.5, 2.4 Hz, 1H), 6.50 (s, 1H), 3.98 (dd, *J* = 11.4, 7.0 Hz, 1H), 3.06 (td, *J* = 11.4, 4.6 Hz, 1H), 2.65 (td, *J* = 12.6, 7.0 Hz, 1H), 2.56 (dd, *J* = 12.6, 4.6 Hz, 1H), 1.59 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.7, 163.0, 151.4, 131.9, 129.0, 128.5, 126.9, 124.4 (d, J_{CF} = 9.8 Hz), 122.1, 119.8 (q, J_{CF} = 320.0 Hz), 111.5 (d, J_{CF} = 23.4 Hz), 105.1 (d, J_{CF} = 30.0 Hz), 87.2, 85.9, 84.6, 84.0, 51.0, 49.1, 40.8, 28.2; ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.5 (s, 3F), -110.8 (s, 1F); HR-ESI-MS (*m/z*): calcd. for $C_{24}H_{22}F_4N_2O_4SNa$ $[M + Na]^+$, 533.1129, found 533.1128.



3ga

Prepared according to the general procedure **C**, **3ga** was isolated as pale solids (115.2 mg, 73% yield) by flash column chromatography (petroleum ether/ethyl acetate = 30/1, V/V). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (br. s, 1H), 7.34 – 7.29 (m, 2H), 7.27 – 7.18 (m, 4H), 7.05 (dd, *J* = 8.0, 1.9 Hz, 1H), 6.42 (s, 1H), 3.91 (dd, *J* = 11.4, 7.0 Hz, 1H), 2.98 (td, *J* = 11.4, 4.7 Hz, 1H), 2.58 (td, *J* = 12.6, 7.0 Hz, 1H), 2.49 (dd, *J* = 12.6, 4.7 Hz, 1H), 1.52 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 142.9, 135.7, 131.9, 129.9, 129.0, 128.5, 124.8, 124.4, 122.0, 119.7 (q, J_{CF} = 320.2 Hz), 117.4, 86.8, 86.0, 84.3, 84.0, 51.1, 49.1, 40.6, 28.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.5 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{24}H_{22}ClF_3N_2O_4SNa$ $[M + Na]^+$, 549.0833, found 549.0832.



3ha

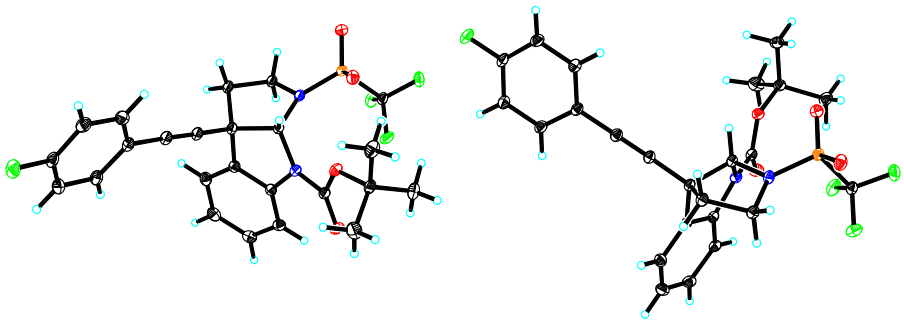
Prepared according to the general procedure **C**, **3ga** was isolated as pale solids (122.9 mg, 77% yield) by flash column chromatography (petroleum ether/ethyl acetate = 20/1, V/V). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.29 – 7.11 (m, 9H), 6.33 (s, 1H), 3.96 (dd, *J* = 11.4, 7.2 Hz, 1H), 2.96 (td, *J* = 11.4, 4.5 Hz, 1H), 2.57 (td, *J* = 12.6, 7.2 Hz, 1H), 2.46 (dd, *J* = 12.6, 4.5 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.0, 137.1, 133.8, 133.4, 131.9, 130.1, 129.0, 128.9, 128.3, 127.9, 126.9, 124.0, 122.0, 119.7 (q, J_{CF} = 319.2 Hz), 118.3, 86.5, 86.1, 52.4, 48.7, 40.7, 28.2; ^{19}F NMR (564 MHz, $CDCl_3$)

δ -75.9 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{25}H_{19}F_3N_2O_4S_2Na$ $[M + Na]^+$, 555.0631, found 555.0627.

7. Crystal Data and Structure Refinement for pyrroloindoline product 3ah.

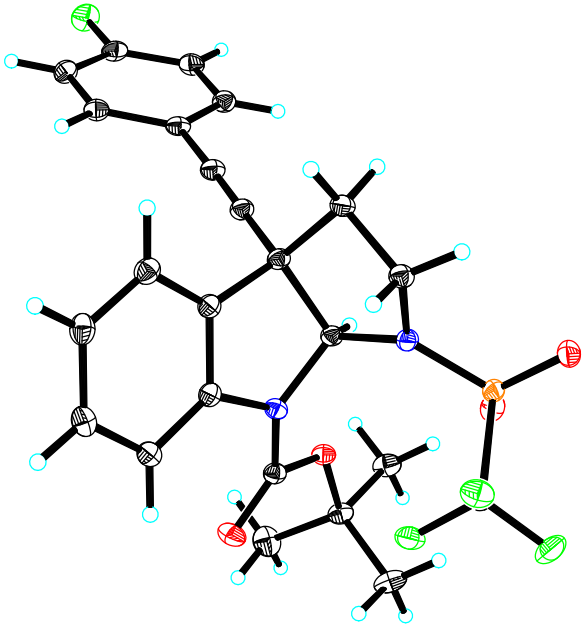
Single crystal of **3ah** was obtained from a mixed solution of ethyl acetate/petroleum ether (1/10) at room temperature with slow volatilization. The relative configuration of **3ah** was determined by X-ray diffraction analysis of a single crystal (Bruker D8 Quest diffractometer). The X-ray data have been deposited at the Cambridge Crystallographic Data Center (***CCDC***). The stereochemistry of other products was assumed by analogy.

Crystal data for **3ah**: $C_{24}H_{22}F_4N_2O_4S$, $M = 510.49$, $a = 10.1699(3)$ Å, $b = 10.9182(3)$ Å, $c = 22.3255(7)$ Å, $\alpha = 76.1900(10)°$, $\beta = 83.8180(10)°$, $\gamma = 75.0440(10)°$, $V = 2322.94(12)$ Å^3, $T = 100.(2)$ K, space group P-1, $Z = 4$, μ(Cu Kα) = 1.842 mm^{-1}, 42065 reflections measured, 9080 independent reflections ($R_{int} = 0.0325$). The final R_1 values were 0.0503 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1467 ($I > 2\sigma(I)$). The final R_1 values were 0.0647 (all data). The final $wR(F^2)$ values were 0.1632 (all data). The goodness of fit on F^2 was 1.492.



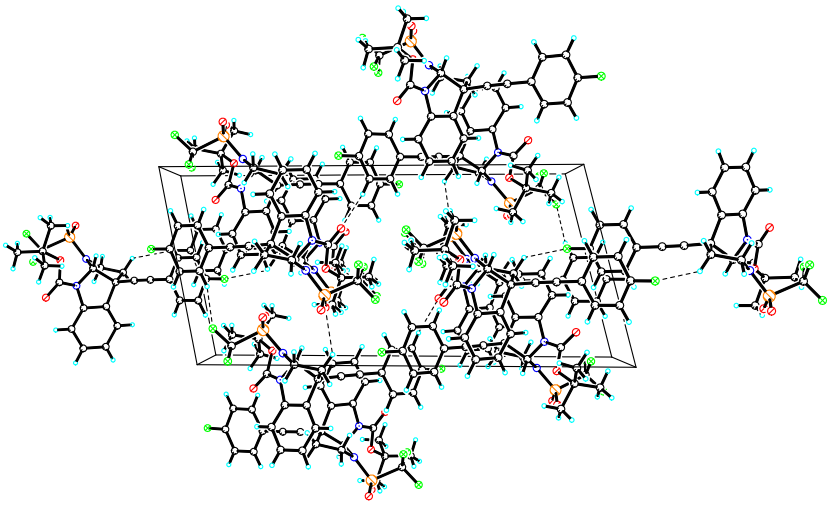
View of the molecules in an asymmetric unit.

Displacement ellipsoids are drawn at the 30% probability level.



View of a molecule of **3ah** with the atom-labelling scheme.

Displacement ellipsoids are drawn at the 30% probability level.



View of the pack drawing of **3ah**.

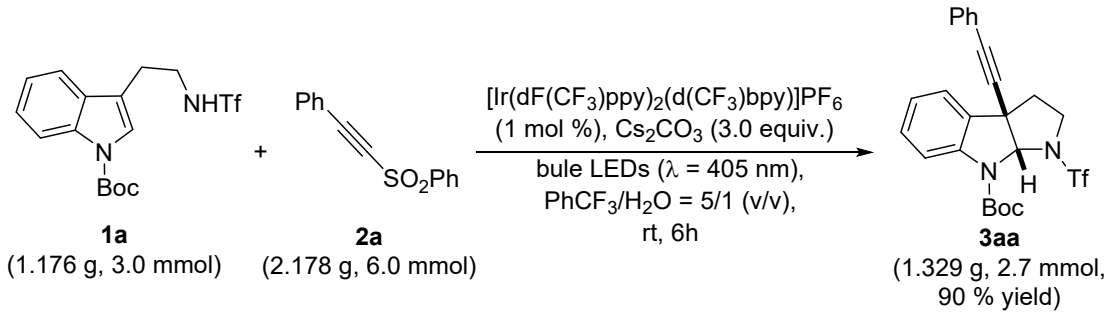
Hydrogen-bonds are shown as dashed lines.

Table S1. Crystal data and structure refinement for 3ah_0m.

Identification code	global
Empirical formula	C24 H22 F4 N2 O4 S
Formula weight	510.49

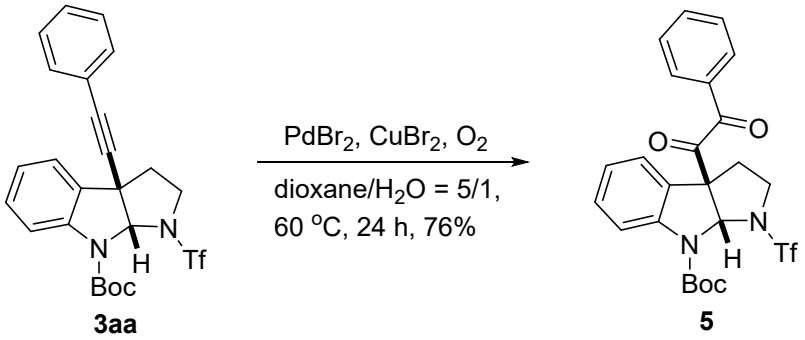
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.1699(3) Å	a= 76.1900(10)°.
	b = 10.9182(3) Å	b= 83.8180(10)°.
	c = 22.3255(7) Å	g = 75.0440(10)°.
Volume	2322.94(12) $Å^3$	
Z	4	
Density (calculated)	1.460 Mg/m^3	
Absorption coefficient	1.842 mm^{-1}	
F(000)	1056	
Crystal size	0.540 x 0.280 x 0.250 mm^3	
Theta range for data collection	2.04 to 72.36°.	
Index ranges	-12<=h<=12, -13<=k<=13, -27<=l<=26	
Reflections collected	42065	
Independent reflections	9080 [R(int) = 0.0325]	
Completeness to theta = 72.36°	98.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.66 and 0.37	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9080 / 0 / 638	
Goodness-of-fit on F^2	1.492	
Final R indices [I>2sigma(I)]	R1 = 0.0503, wR2 = 0.1467	
R indices (all data)	R1 = 0.0647, wR2 = 0.1632	
Extinction coefficient	0.0280(11)	
Largest diff. peak and hole	1.255 and -1.188 $e.Å^{-3}$	

8. Gram-scale synthesis and several transformations of pyrroloindoline product 3aa.



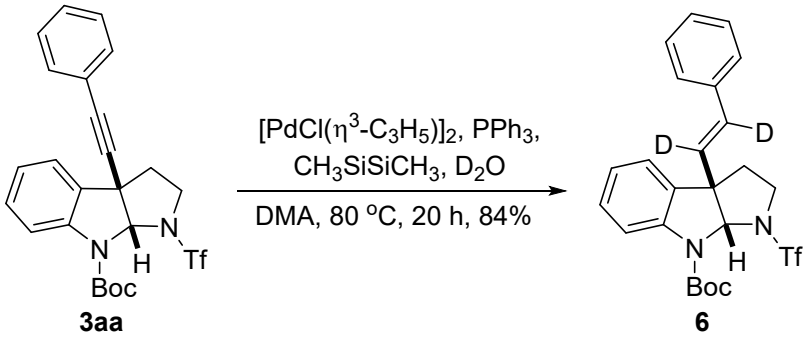
Scheme S5. Gram-scale reaction for the pyrroloindoline product **3aa.**

To a 100 mL round-bottom flask equipped with a magnetic stir bar, typtamine derivate **1a** (1.176 g, 3.00 mmol, 1.0 equiv.), acetylenic sulfone **2a** (2.178 g, 9.00 mmol, 3.0 equiv.) $[Ir(dF(CF_3)ppy)_2(d(CF_3)bpy)]PF_6$ (34.4 mg, 0.03 mmol, 0.01 equiv.), Cs_2CO_3 (2.932 g, 9.00 mmol, 3.0 equiv.), $PhCF_3$ (20 mL) and H_2O (4 mL) were sequentially added. The reaction mixture was degassed three times by freeze-pump-thaw method. The tube was stirred and irradiated with two 18W light emitting diode (LED) lamps from approximately 10 cm away at room temperature for 6 h under argon atmosphere. After completion of the reaction (by TLC analysis), it was quenched with sat. aqueous NH_4Cl solution (30 mL), and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine (60 mL), dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by column chromatography (petroleum ether/ethyl acetate = 30/1, V/V) to afford the the pyrroloindoline product **3aa** (1.329 g, 2.70 mmol, 90 %) as colorless powders. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.75 (br. s, 1H), 7.41 – 7.28 (m, 7H), 7.15 (t, J = 7.4 Hz, 1H), 6.51 (s, 1H), 3.96 (dd, J = 12.0, 7.0 Hz, 1H), 3.04 (td, J = 12.0, 4.6 Hz, 1H), 2.66 (td, J = 12.6, 7.0 Hz, 1H), 2.60 (dd, J = 12.6, 4.6 Hz, 1H), 1.59 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.8, 141.8, 131.9, 131.5, 130.0, 128.8, 128.5, 124.7, 123.5, 122.3, 119.8 (q, J_{CF} = 320.0 Hz), 117.0, 87.4, 85.7, 84.0, 83.4, 51.4, 49.1, 40.6, 28.2; ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.5 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{24}H_{23}F_3N_2O_4SNa$ [M + Na]$^+$, 515.1223, found 515.1226.



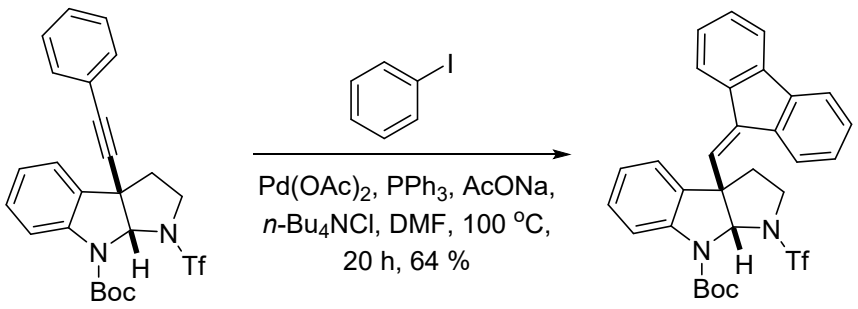
Scheme S6. Oxidation of alkynyl pyrroloindoline **3aa** into 1,2-diketone compound **5**.[5]

Alkynyl pyrroloindoline **3aa** (49.2 mg, 0.10 mmol, 1.0 equiv.), $PdBr_2$ (1.3 mg, 0.005 mmol, 0.05 equiv.), and $CuBr_2$ (2.2 mg, 0.01 mmol, 0.1 equiv.) were added to a Schlenck tube under air. The septum-sealed tube was evacuated and refilled with O_2 thrice. Dioxane (4 mL) and H_2O (0.8 mL) were added via syringe. The reaction mixture was heated in an oil bath at 60 ℃ for 24 h. After the reaction completed, water (10 mL) was added and the resulting mixture was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (30 mL), dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by column chromatography (petroleum ether/ethyl acetate = 10/1, V/V) to afford 1,2-diketone compound **5** (39.8 mg, 0.076 mmol, 76 %) as colorless powders. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (br. s, 1H), 7.71 (d, J = 7.8 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 7.8 Hz, 2H), 7.29 (t, J = 7.8 Hz, 1H), 7.18 (d, J = 7.4 Hz, 1H), 7.01 (t, J = 7.4 Hz, 1H), 6.96 (s, 1H), 4.04 (dd, J = 11.4, 7.3 Hz, 1H), 3.13 (td, J = 11.4, 4.4 Hz, 1H), 2.81 (td, J = 12.7, 7.3 Hz, 1H), 2.59 (dd, J = 12.7, 4.4 Hz, 1H), 1.59 (s, 8H)； ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.3, 191.6, 151.7, 143.6, 135.2, 132.2, 130.8, 130.0, 129.0, 126.3, 124.5, 124.2, 119.8 (q, J_{CF} = 320.6 Hz), 117.8, 83.4, 80.8, 66.9, 48.9, 35.5, 28.1; ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.6 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{24}H_{23}F_3N_2O_6SNa$ [M + Na]$^+$, 547.1121, found 547.1120.



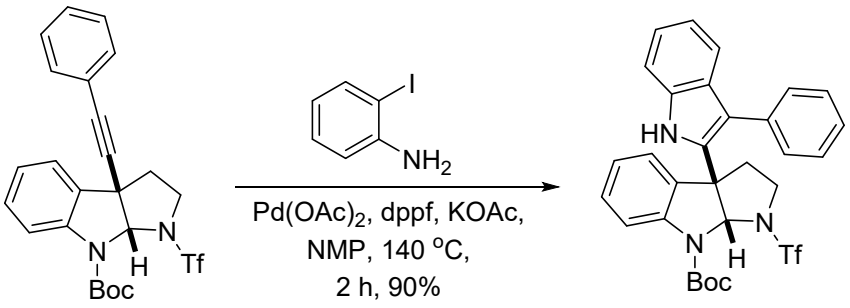
Scheme S7. Reduction of alkynyl pyrroloindoline **3aa** into 1,2-dideuterioalkene compound **6**.[6]

A solution of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (0.9 mg, 0.0025 mmol, 0.025 equiv.) and PPh_3 (2.6 mg, 0.01 mmol, 0.1 equiv.) in DMA (4 mL) was stirred at room temperature for 10 min. To the resulting mixture were added alkynyl pyrroloindoline **3aa** (49.2 mg, 0.10 mmol, 1.0 equiv.), hexamethyldisilane (22.0 mg, 0.15 mmol, 1.5 equiv.) and D_2O (18.1 μL, 1.00 mmol, 10.0 equiv.). After stirring at 80 ℃ for 20 h, water (10 mL) was added and the resulting mixture was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (30 mL), dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by column chromatography (petroleum ether/ethyl acetate = 30/1, V/V) to afford 1,2-dideuterioalkene compound **6** (41.7 mg, 0.084 mmol, 84 %) as colorless powders. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (br. s, 1H), 7.38 – 7.29 (m, 5H), 7.28 – 7.24 (m, 1H), 7.19 (d, J = 7.6 Hz, 1H), 7.15 (t, J = 7.6 Hz, 1H), 6.23 (s, 1H), 3.97 (dd, J = 11.4, 7.0 Hz, 1H), 3.12 (td, J = 11.4, 5.0 Hz, 1H), 2.47 (td, J = 12.5, 7.0 Hz, 1H), 2.59 (dd, J = 12.5, 5.0 Hz, 1H) 1.56 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.9, 142.5, 136.0, 132.0, 129.5, 128.8, 128.7, 128.3, 128.2, 126.7, 124.4, 124.1, 119.9 (q, J_{CF} = 321.0 Hz), 117.3, 83.5, 83.1, 60.0, 49.8, 37.8, 28.2; ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.5 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{24}H_{23}D_2F_3N_2O_6SNa$ $[M + Na]^+$, 519.1505, found 519.1507.



Scheme S8. Synthesis of 9-alkylidene-9*H*-fluorene compound **7** from alkynyl pyrroloindoline **3aa.**[7]

Alkynyl pyrroloindoline **3aa** (49.2 mg, 0.10 mmol, 1.0 equiv.), iodobenzene (20.4 mg, 0.10 mmol, 1.0 equiv.), palladium acetate (1.1 mg, 0.005 mmol, 0.05 equiv.), PPh_3 (2.6 mg, 0.01 mmol, 0.1 equiv.), NaOAc (16.4 mg, 0.20 mmol, 2.0 equiv.), *n*-Bu_4NCl (27.8 mg, 0.10 mmol, 1.0 equiv.) and 4 mL of DMF were placed in a 25 mL round-bottom flask equipped with a magnetic stir bar. The reaction mixture was heated in an oil bath at 100 ℃ for 20 h. After completion of the reaction, it was quenched with sat. aqueous NH_4Cl solution (10 mL), and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (30 mL), dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by column chromatography (petroleum ether/ethyl acetate = 30/1, V/V) to afford 9-alkylidene-9*H*-fluorene compound **7** (36.4 mg, 0.064 mmol, 64 %) as colorless powders. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (br. s, 1H), 7.75 (d, *J* = 7.0 Hz, 1H), 7.68 (d, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.0 Hz, 2H), 7.44 – 7.32 (m, 5H), 7.28 – 7.20 (m, 2H), 6.86 (s, 1H), 6.68 (s, 1H), 4.16 (dd, *J* = 11.4, 7.4 Hz, 1H), 3.25 (td, *J* = 11.4, 4.9 Hz, 1H), 3.11 (td, *J* = 12.6, 7.4 Hz, 1H), 2.55 (dd, *J* = 12.6, 4.9 Hz, 1H), 1.43 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7, 142.1, 141.8, 139.5, 139.2, 138.8, 135.8, 134.4, 129.7, 129.3, 128.9, 128.8, 127.6, 127.4, 125.9, 125.1, 123.1, 120.4, 120.3, 119.8 (q, J_{CF} = 320.5 Hz), 119.7, 117.1, 83.1, 82.5, 58.7, 49.9, 38.0, 28.0; ^{19}F NMR (564 MHz, $CDCl_3$) δ -76.5 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{30}H_{27}F_3N_2O_4SNa$ $[M + Na]^+$, 591.1536, found 591.1537.



Scheme S9. Synthesis of 2,3-disubstituted indole **8** from alkynyl pyrroloindoline **3aa.**[8]

2-Iodoaniline (21.5 mg, 0.10 mmol, 1.0 equiv.), alkynyl pyrroloindoline **3aa** (59.1 mg, 0.12 mmol, 1.2 equiv.), palladium acetate (1.1 mg, 0.005 mmol, 0.05 equiv.), 1,1'-bis(diphenylphosphino)-ferrocene (4.4 mg, 0.008 mmol, 0.08 equiv.), KOAc (49.1 mg, 0.50 mmol, 5.0 equiv.) and 2 mL of anhydrous NMP were placed in a 25 mL round-bottom flask equipped with a magnetic stir bar. The resulting dark mixture was heated in an oil bath at 140 ℃ for 2 h. After completion of the reaction, it was cooled to room temperature, filtered through a pad of Celite, which was rinsed with EtOAc. Then, it was diluted with H_2O (20 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (30 mL), dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by column chromatography (petroleum ether/ethyl acetate = 10/1, V/V) to afford 2,3-disubstituted indole **8** (58.3 mg, 0.09 mmol, 90 %) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.3 Hz, 1H), 7.65 (br. s, 1H), 7.54 – 7.36 (m, 2H), 7.46 – 7.38 (m, 4H), 7.36 – 7.24 (m, 3H), 7.24 – 7.17 (m, 2H), 7.13 – 7.07 (m, 1H), 6.56 (s, 1H), 3.78 (dd, *J* = 11.3, 7.2 Hz, 1H), 2.98 (td, *J* = 11.3, 4.4 Hz, 1H), 2.73 (td, *J* = 12.5, 7.2 Hz, 1H), 2.29 (dd, *J* = 12.5, 4.4 Hz, 1H), 1.54 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7, 142.7, 134.6, 134.3, 131.7, 131.6, 131.0, 130.5, 130.2, 129.0, 127.8, 124.9, 124.3, 123.2, 120.6, 119.77 (q, J_{CF} = 322.8 Hz), 119.76, 117.7, 116.4, 111.0, 84.5, 83.7, 58.1, 49.6, 37.5, 28.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.9 (s, 3F); HR-ESI-MS (*m/z*): calcd. for $C_{30}H_{27}F_3N_3O_4S$ $[M-H]^-$, 582.1680, found 582.1682.

9. References

(1) P. Feng, Y. Fan, F. Xue, W. Liu, S. Li, Y. Shi. Org. Lett. 2011, 13, 5827.

(2) K. Li, J. Ou, S. Gao. Angew. Chem., Int. Ed. 2016, 55, 14778.

(3) J. Zhang, F.-S. Han. J. Org. Chem. 2019, 84, 13890.

(4) V. Nair, A. Augustine, T. D. Suja. Synthesis 2002, 2259.

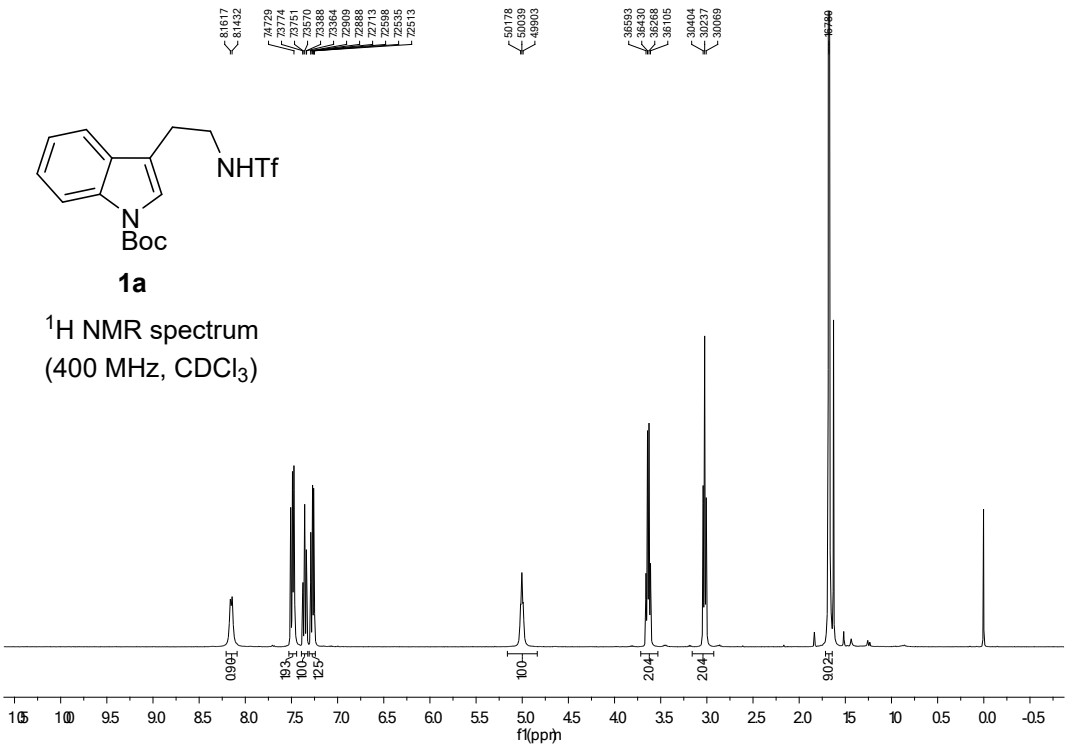
(5) W. Ren, Y. Xia, S.-J. Ji, Y. Zhang, X. Wan, J. Zhao. Org. Lett. 2009, 11, 1841.

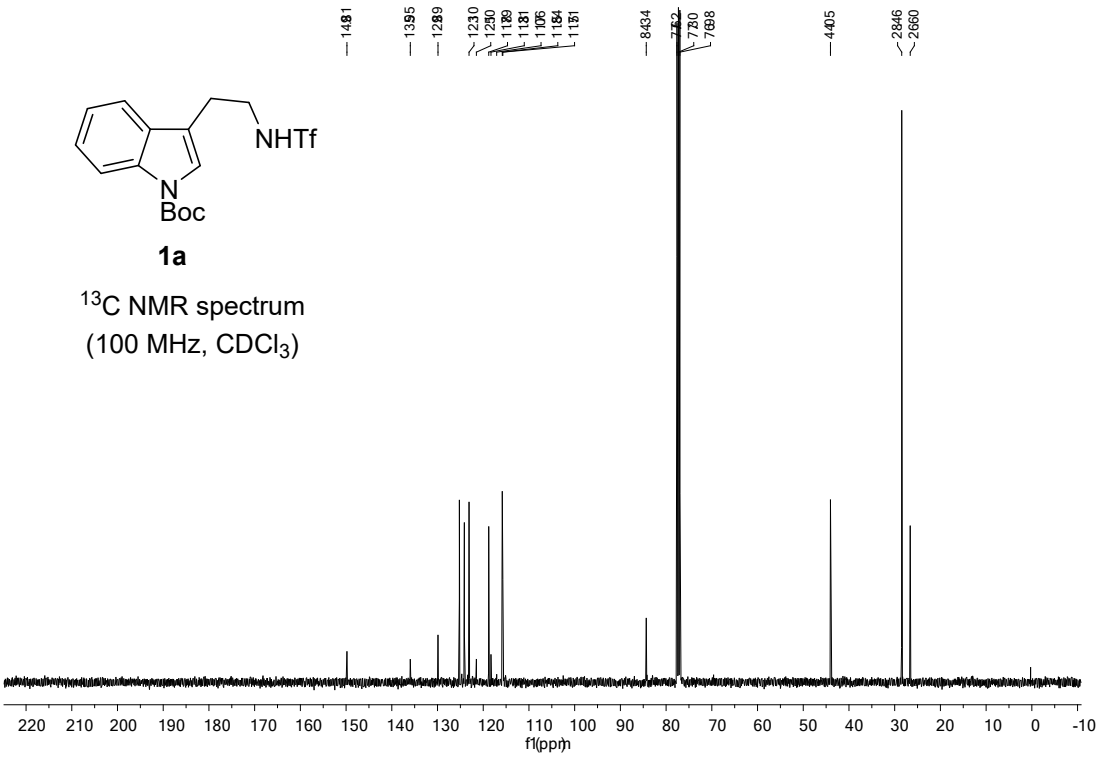
(6) E. Shirakawa, H. Otsuka, T. Hayashi. Chem. Commun. 2005, 5885.

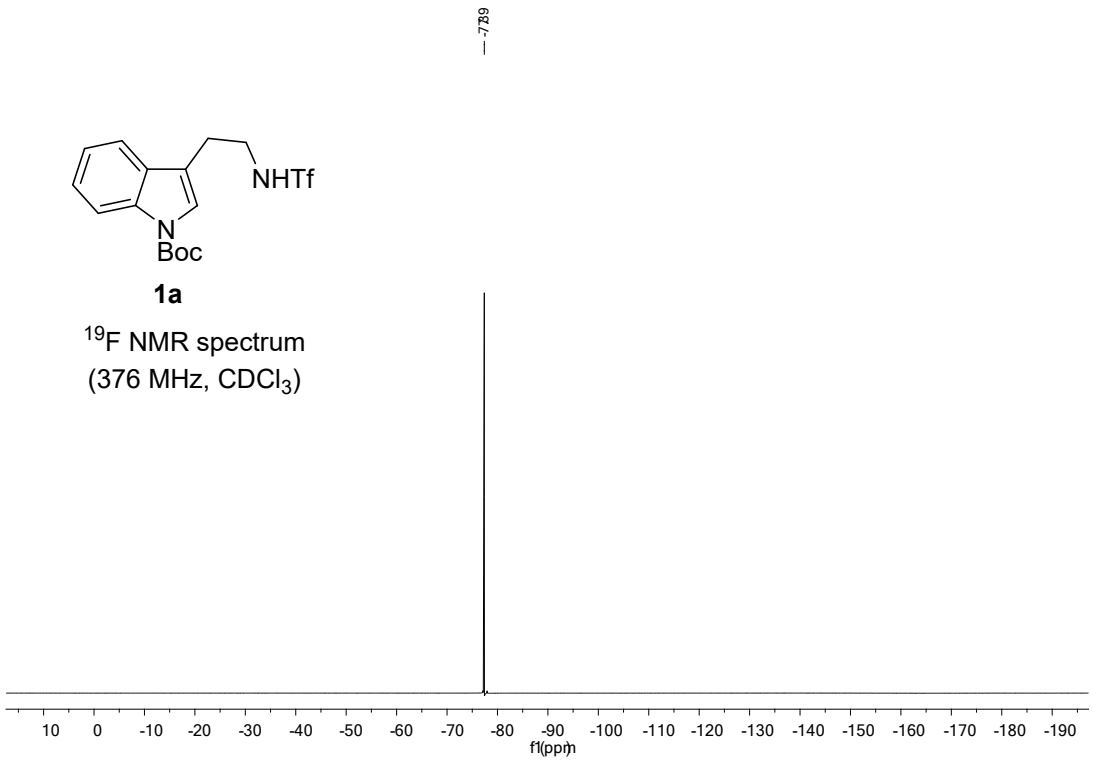
(7) Q. Tian, R. C. Larock. Org. Lett. 2000, 2, 3329.

(8) F. Roschangar, J. Liu, E. Esstanove, M. Dufour, S. Rodríguez, V. Farina, E. Hickey, A. Hossain, P. -J. Jones, H. Lee, B. Z. Lu, R. Varsolona, J. Schröder, P. Beaulieu, J. Gillard, C. H. Senanayake. Tetrahedron Lett. 2008, 49, 363.

10. Copies of NMR spectra







1a

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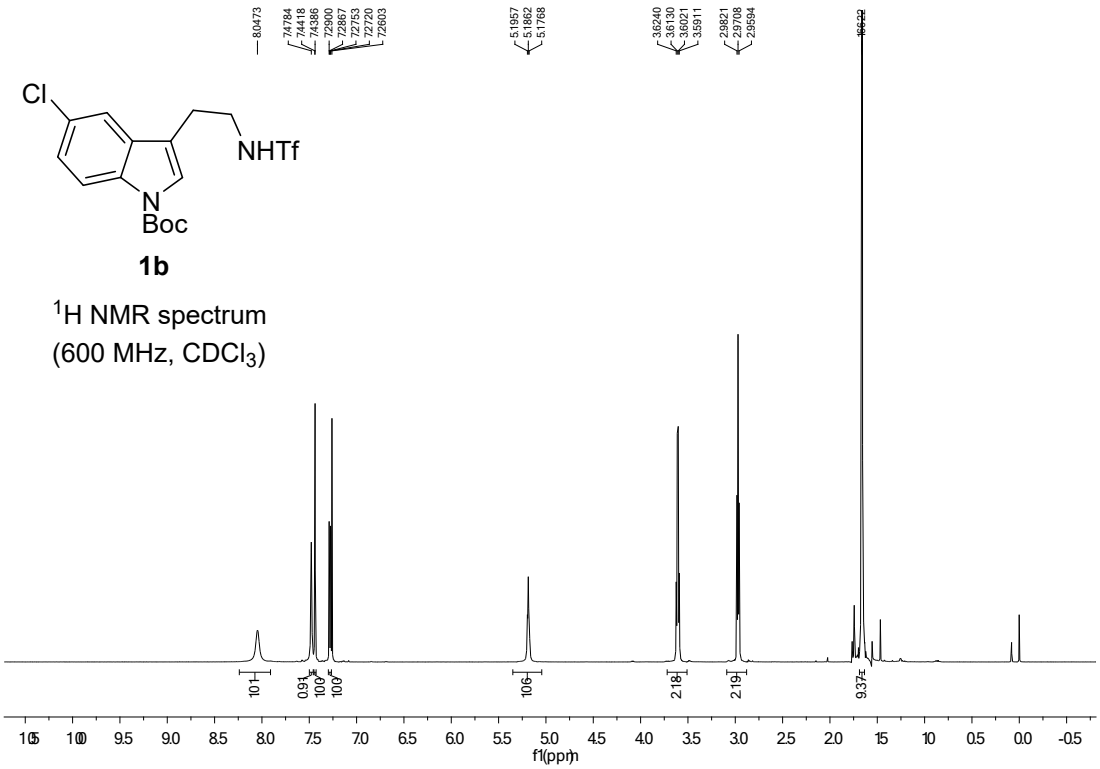
(376 MHz, $CDCl_3$)



1b

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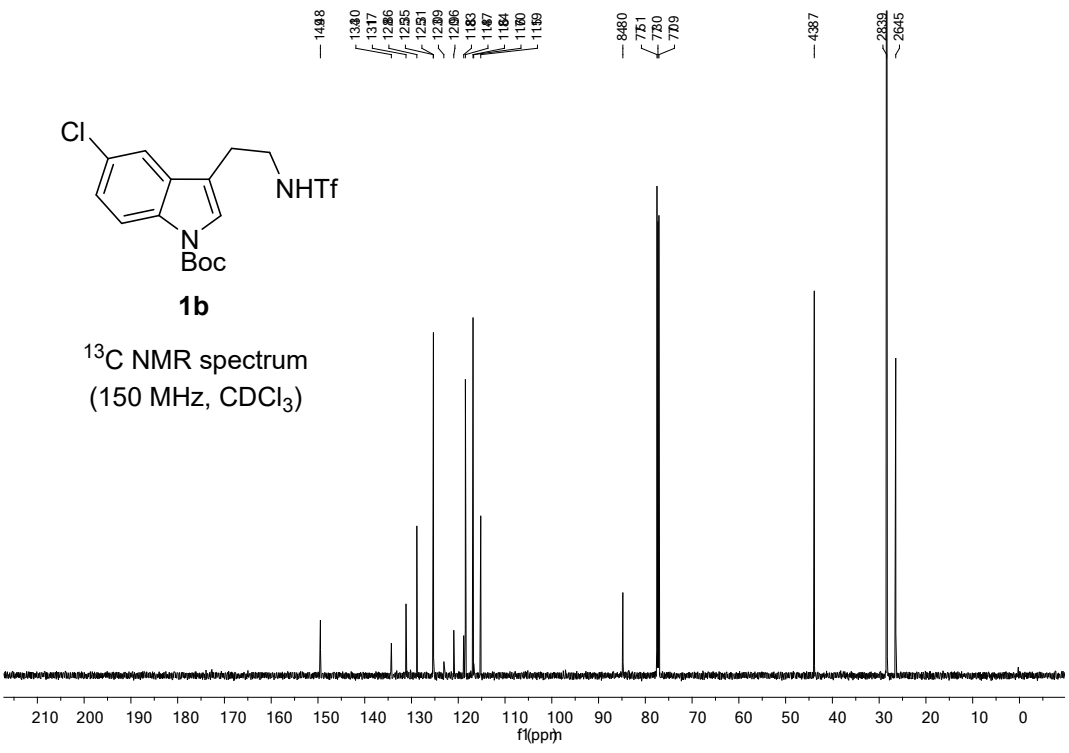

1b

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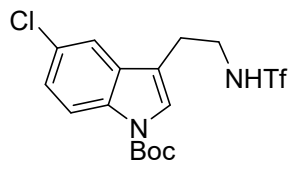
(150 MHz, $CDCl_3$)



1b

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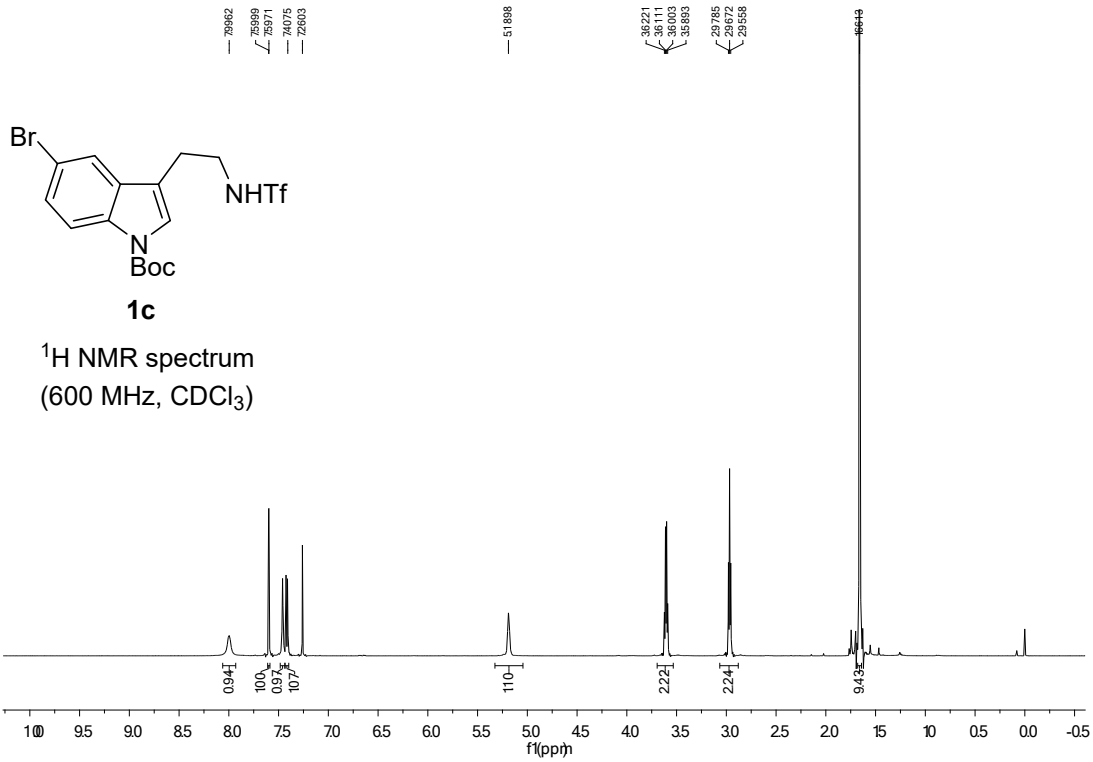
(564 MHz, $CDCl_3$)



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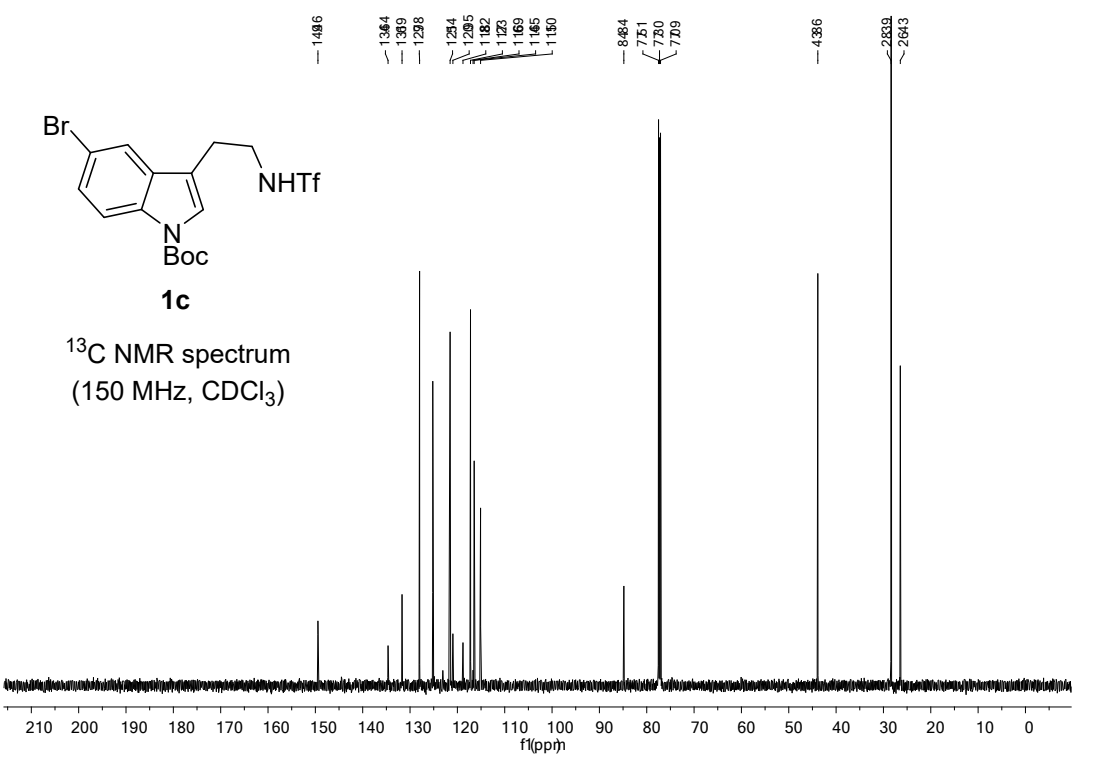
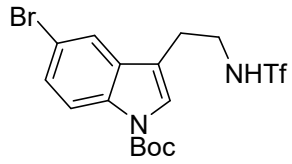


1c

^{13}C NMR spectrum
(150 MHz, $CDCl_3$)



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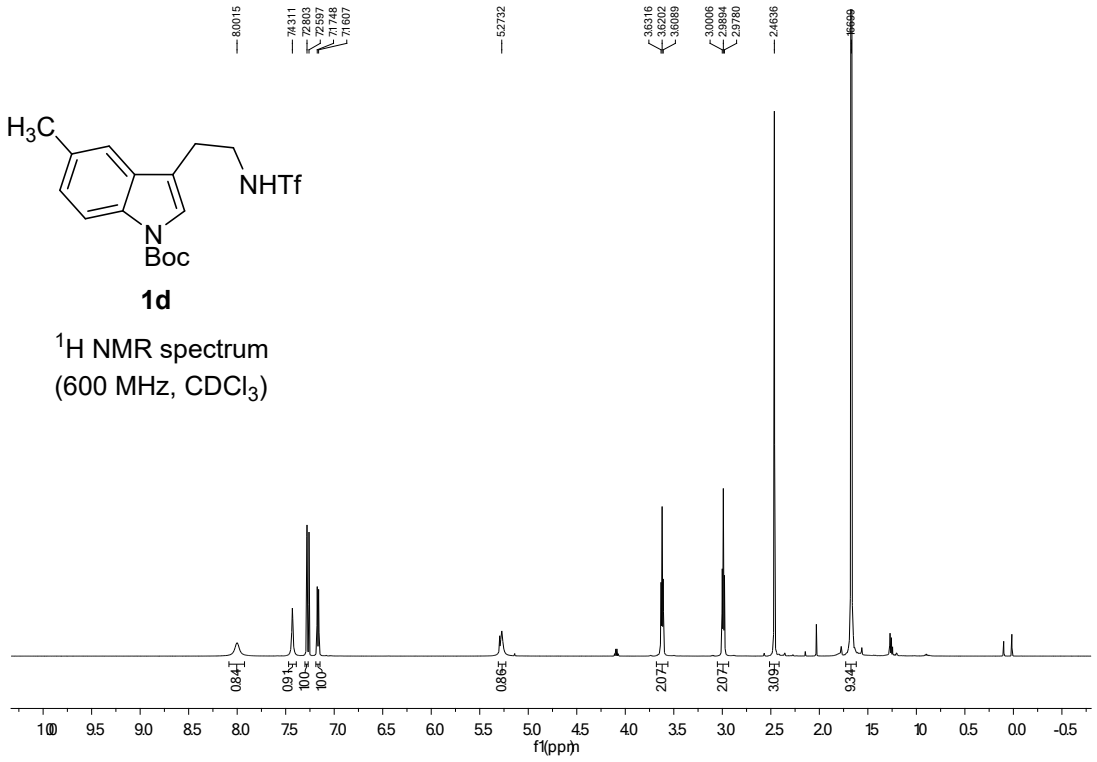

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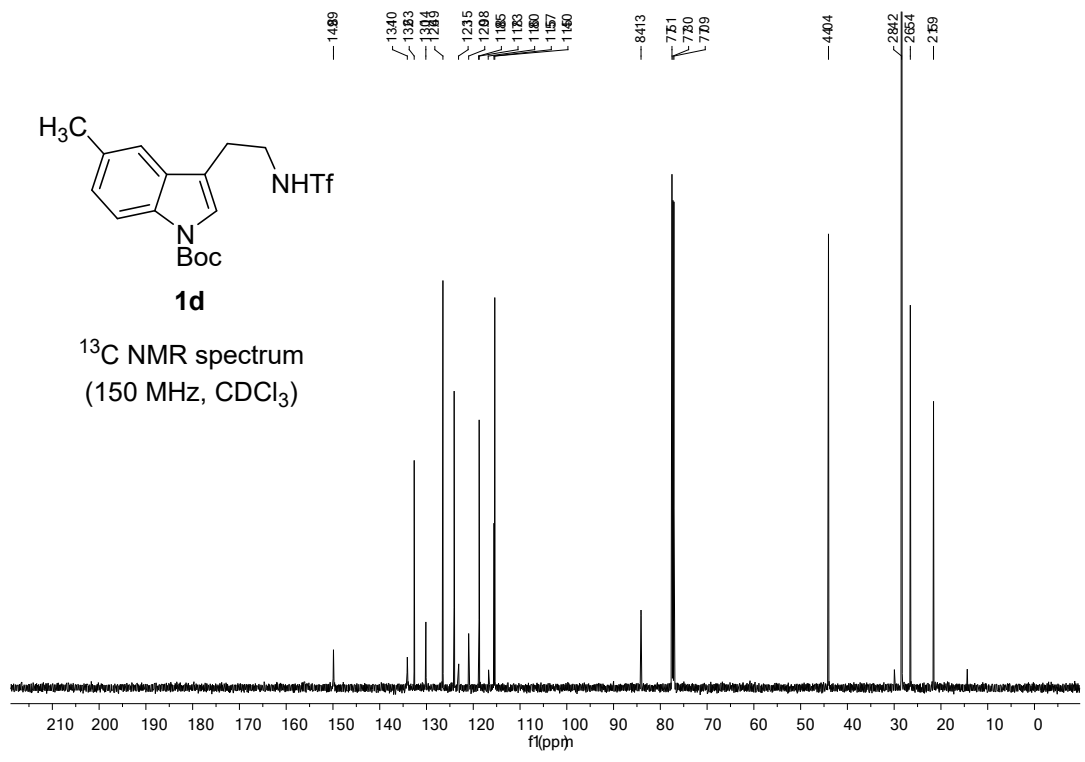

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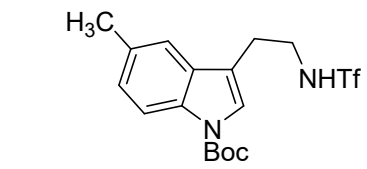
(150 MHz, $CDCl_3$)



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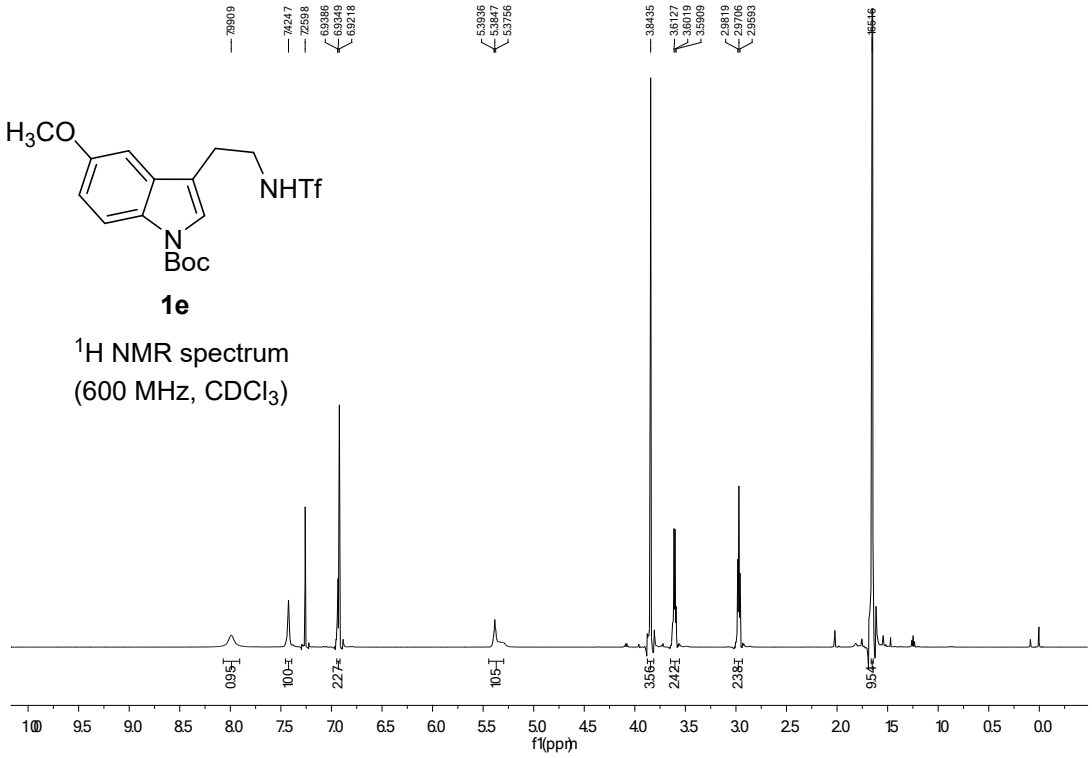
(564 MHz, $CDCl_3$)



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^{1}H NMR spectrum
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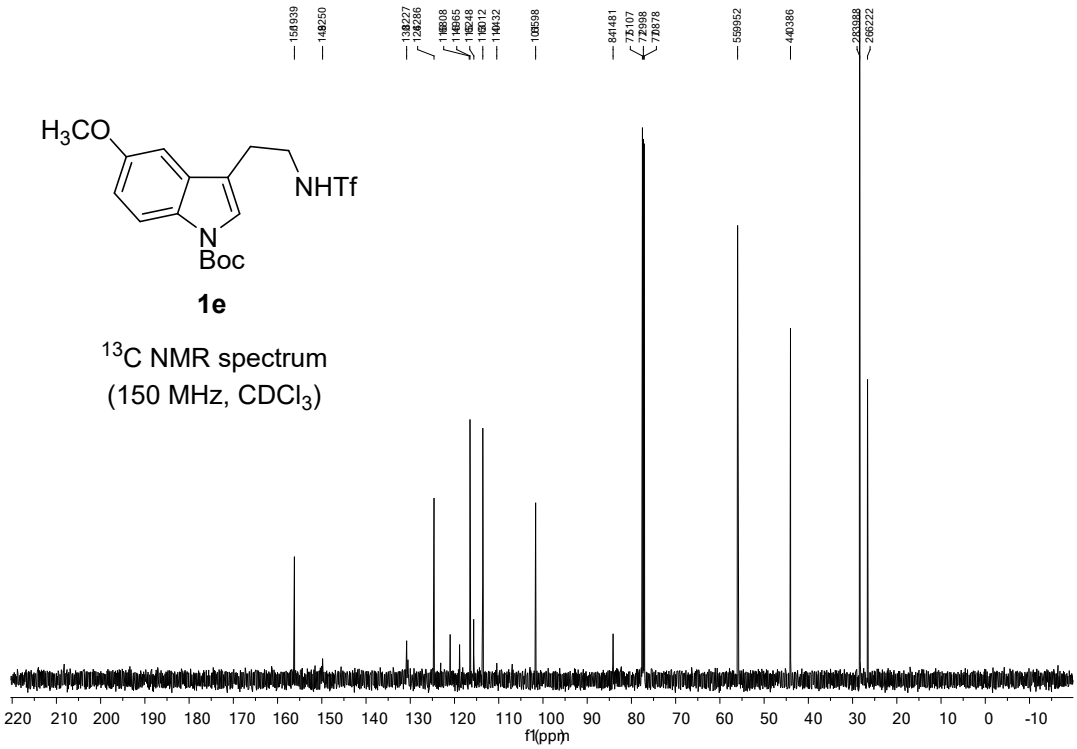

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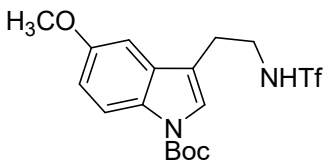

1e

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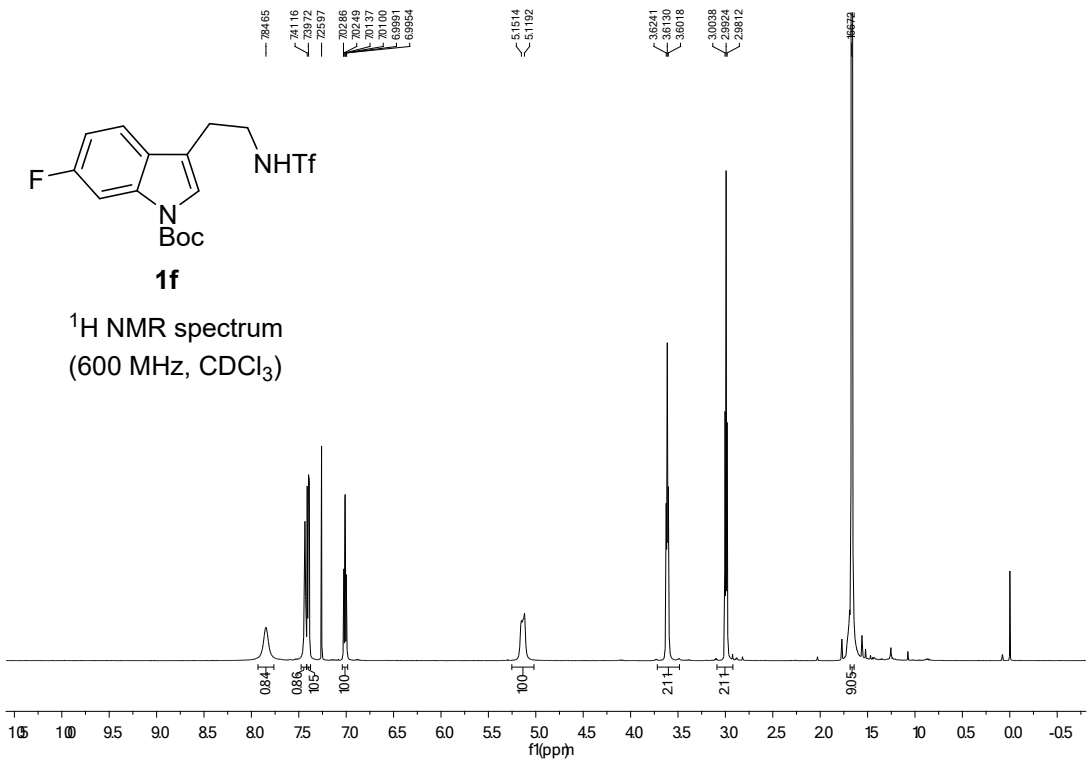
(564 MHz, $CDCl_3$)



1f

^{1}H NMR spectrum
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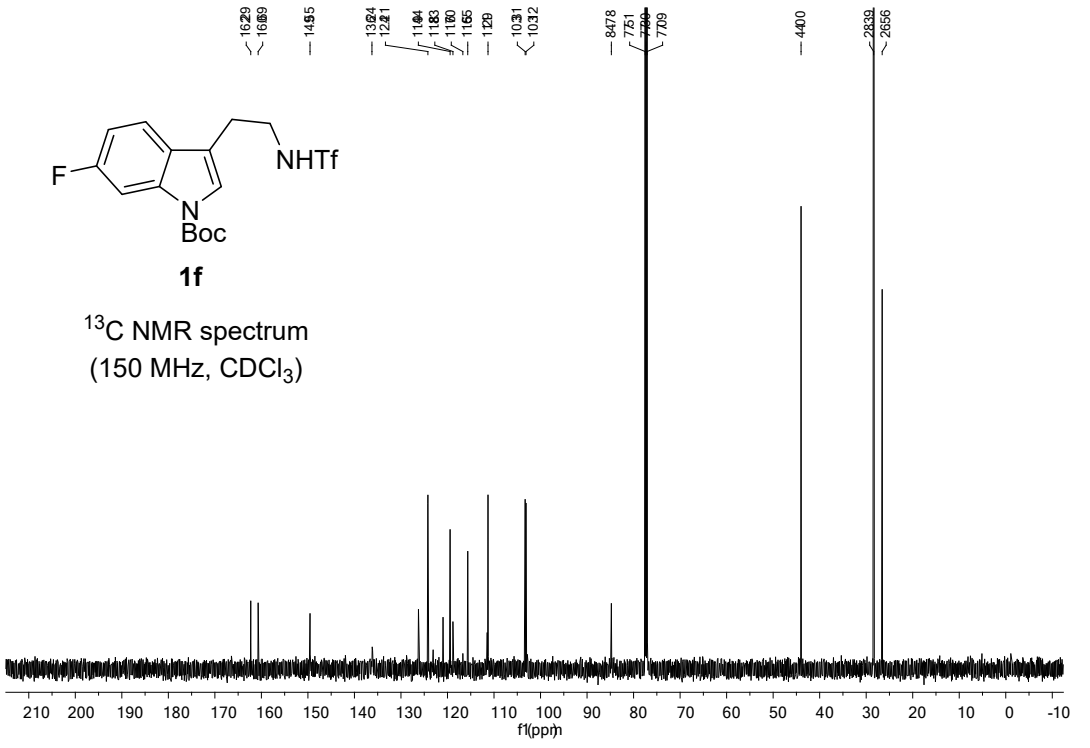

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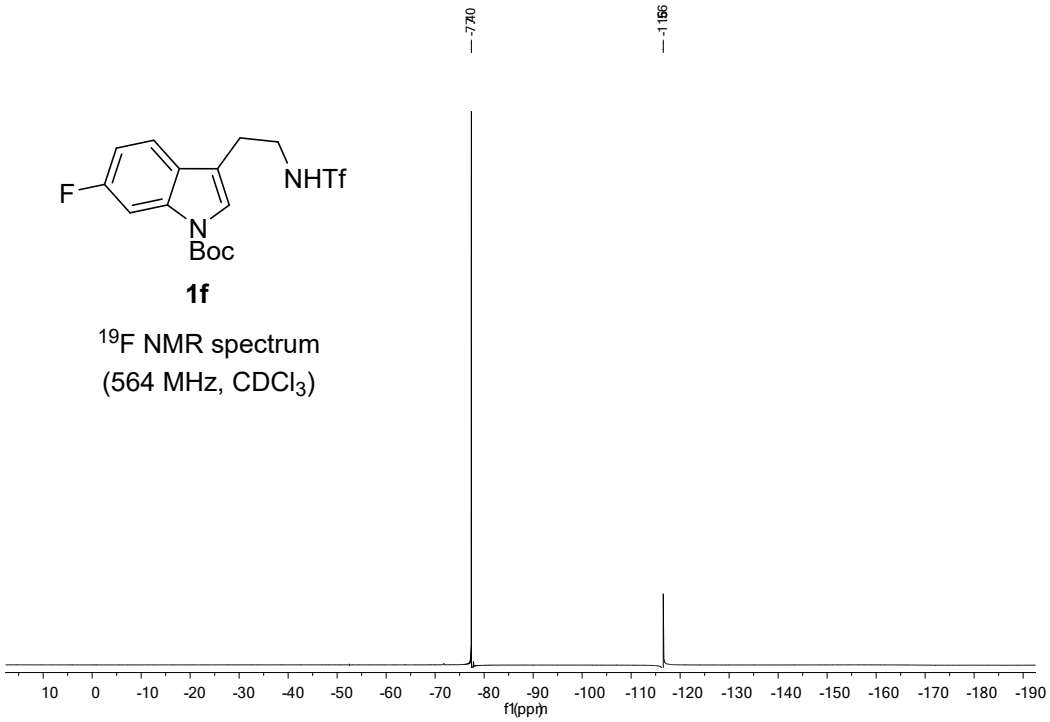

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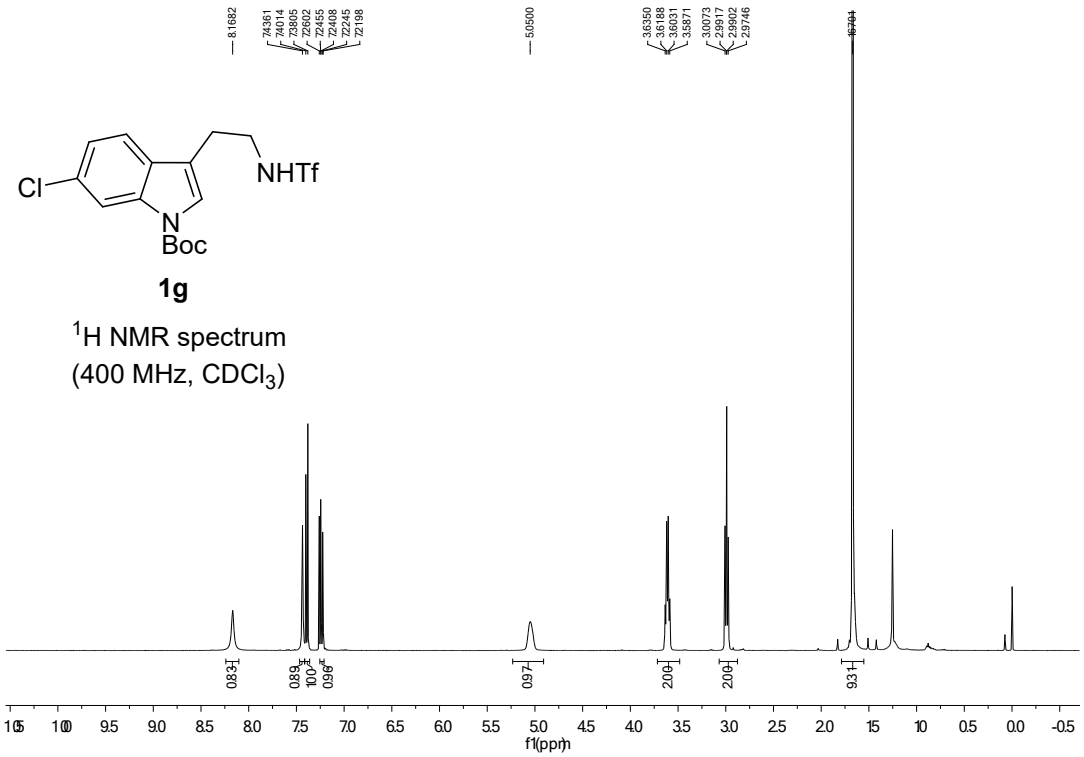

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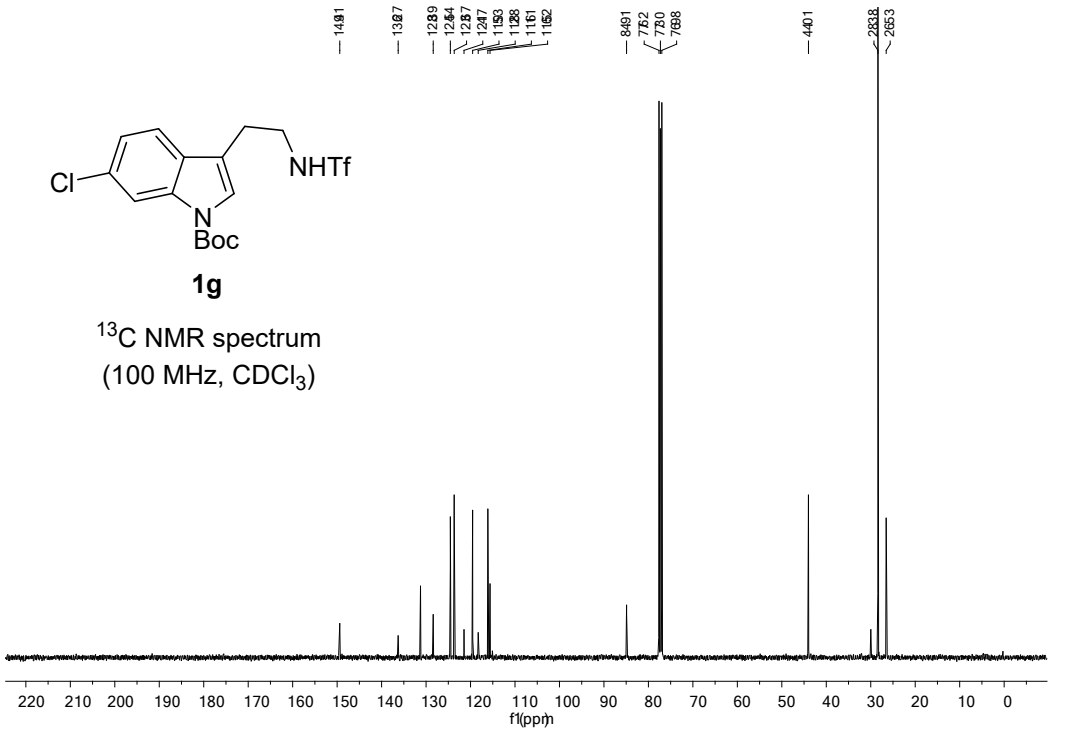

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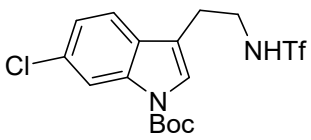

1g

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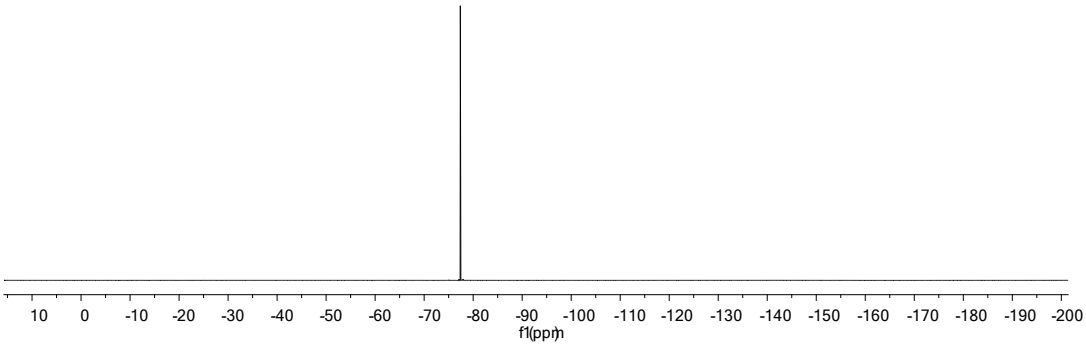
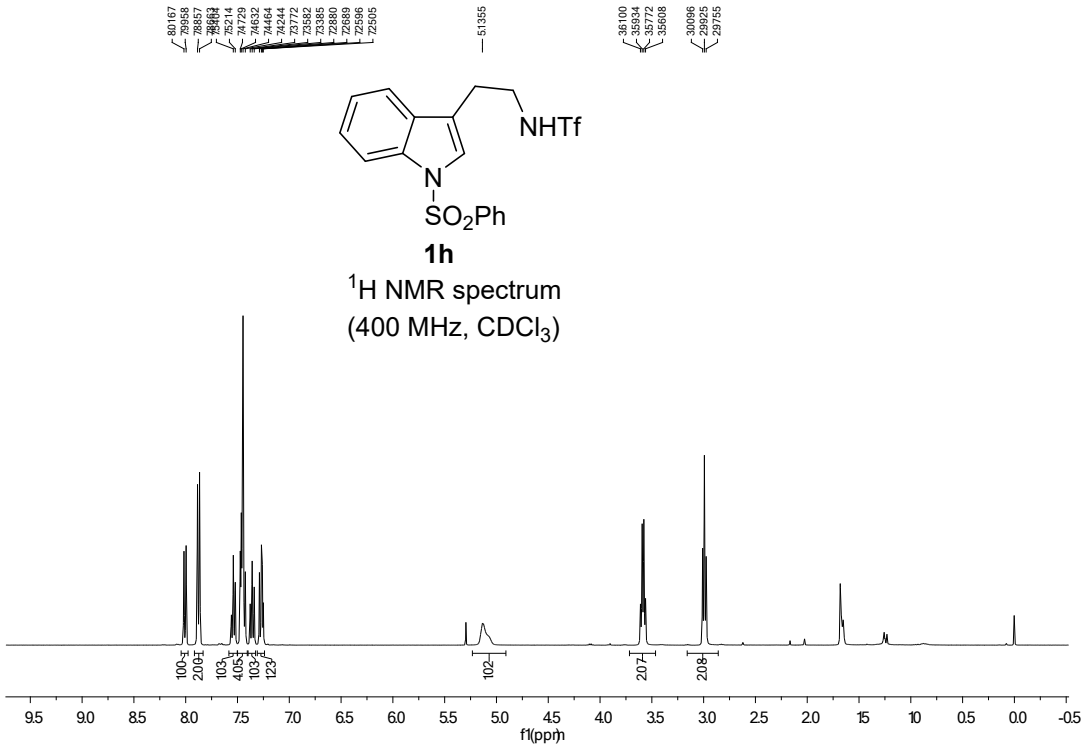
(376 MHz, $CDCl_3$)





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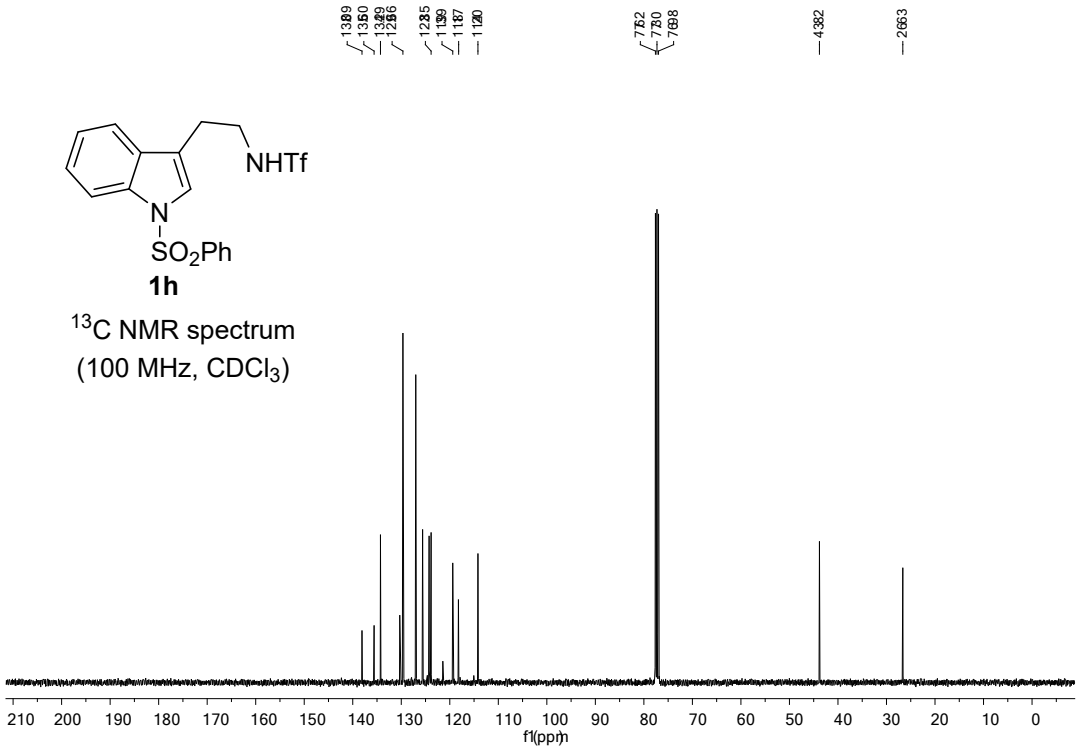

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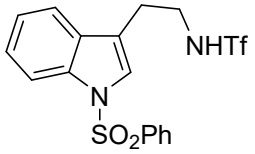

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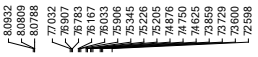
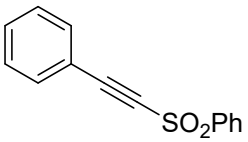
(376 MHz, $CDCl_3$)





2a

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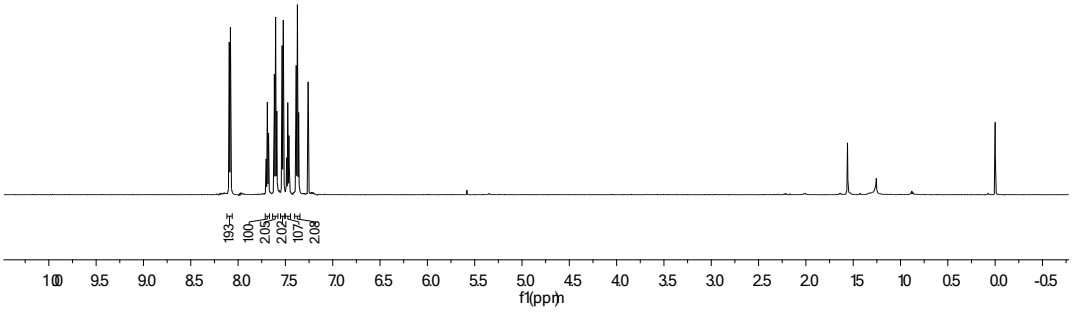
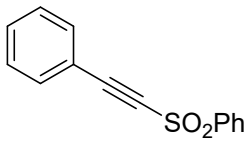
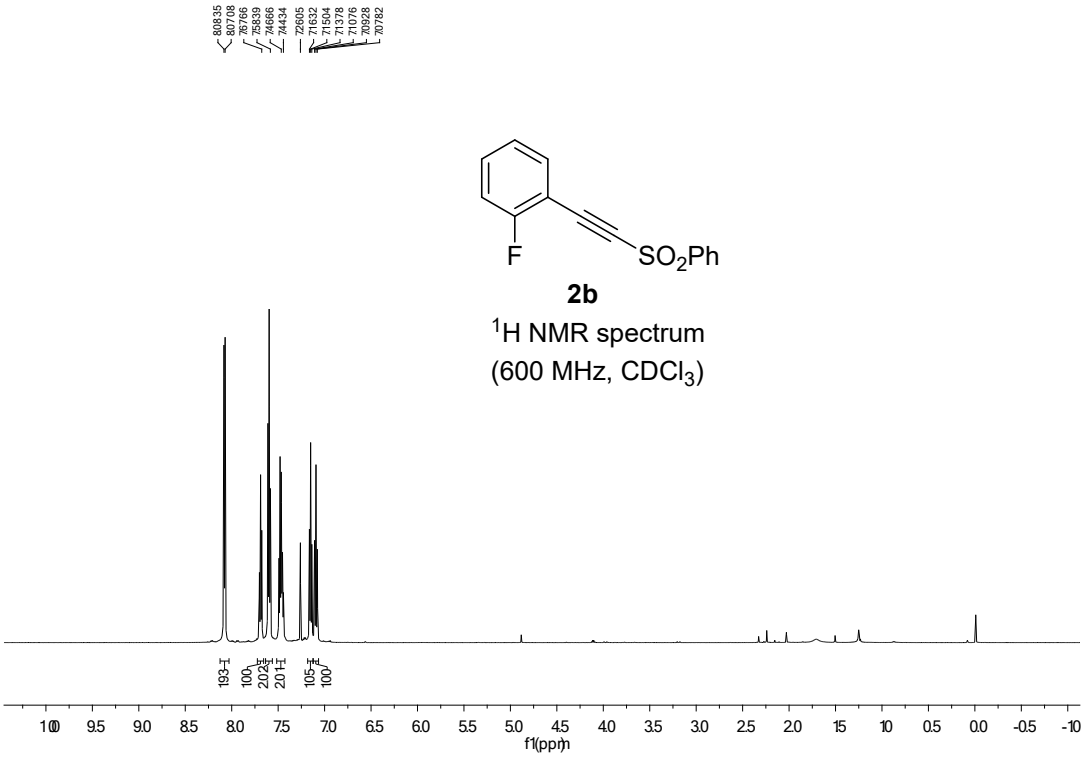
(600 MHz, $CDCl_3$)

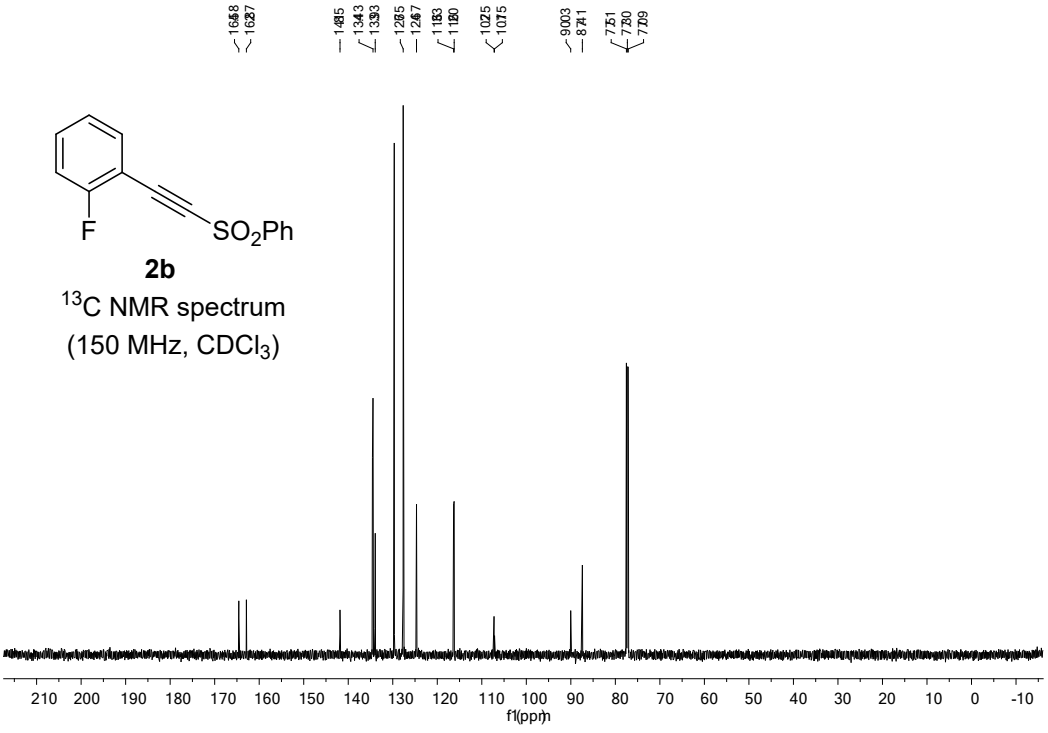


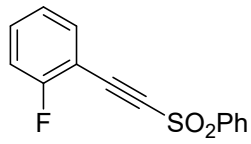


2a

^{13}C NMR spectrum
(150 MHz, $CDCl_3$)

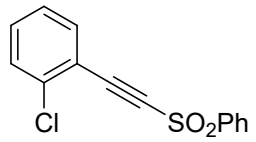

F
SO2Ph
2b
1H NMR spectrum
(600 MHz, CDCl3)
f1(ppm)


F
SO2Ph
2b
13C NMR spectrum
(150 MHz, CDCl3)
f1(ppm)



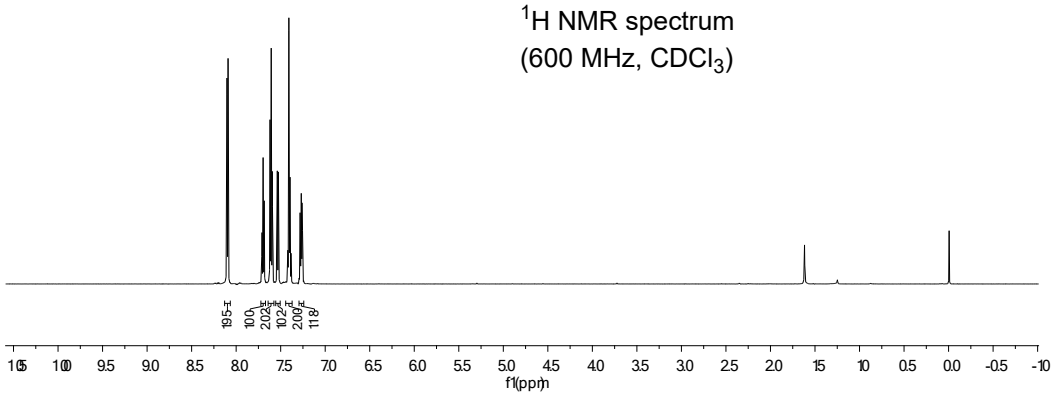
2b

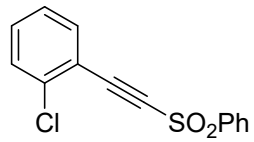
^{19}F NMR spectrum
(564 MHz, $CDCl_3$)



2c

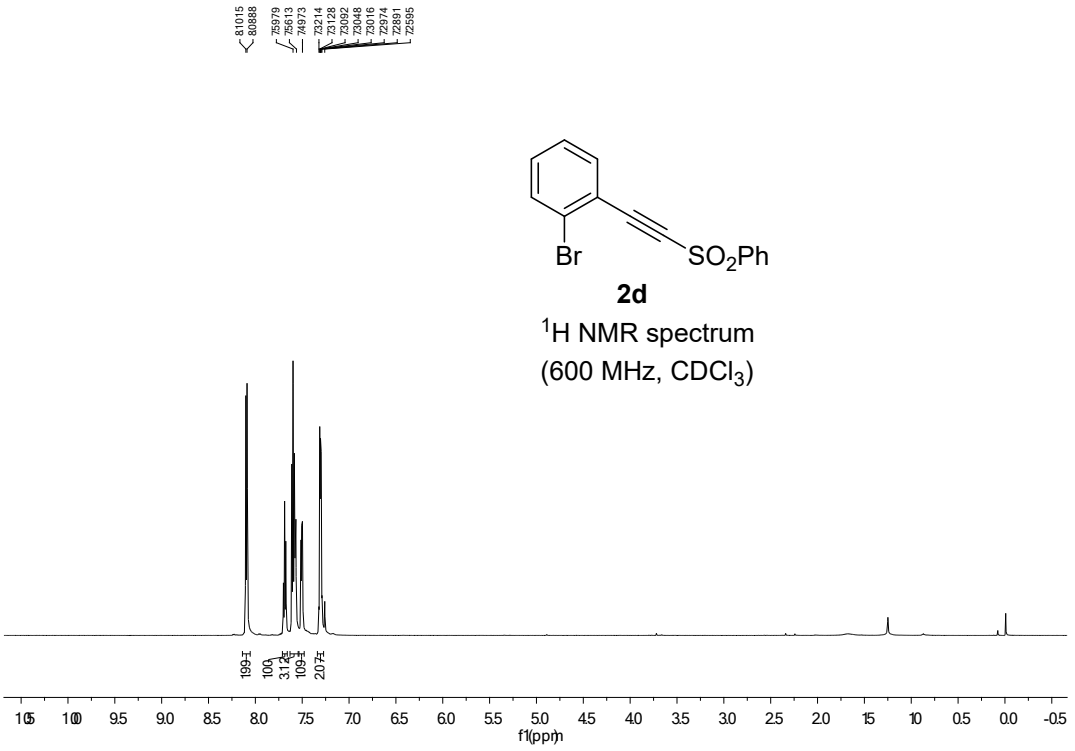
^{1}H NMR spectrum
(600 MHz, $CDCl_3$)

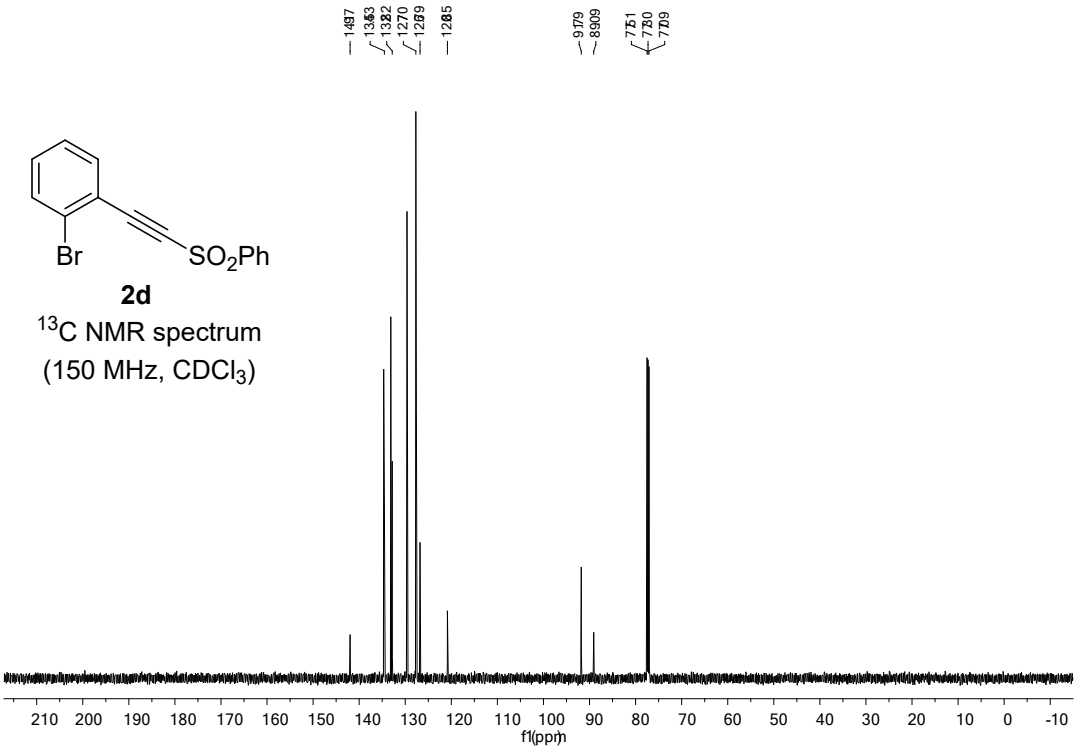


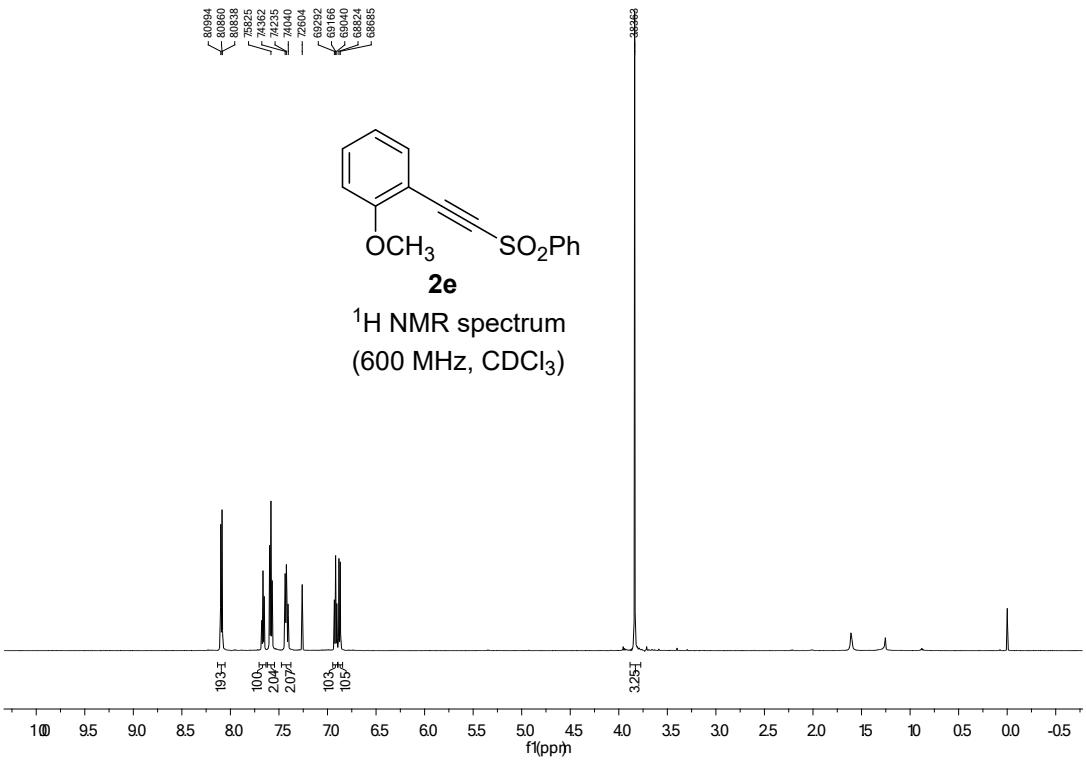


2c

^{13}C NMR spectrum
(150 MHz, $CDCl_3$)

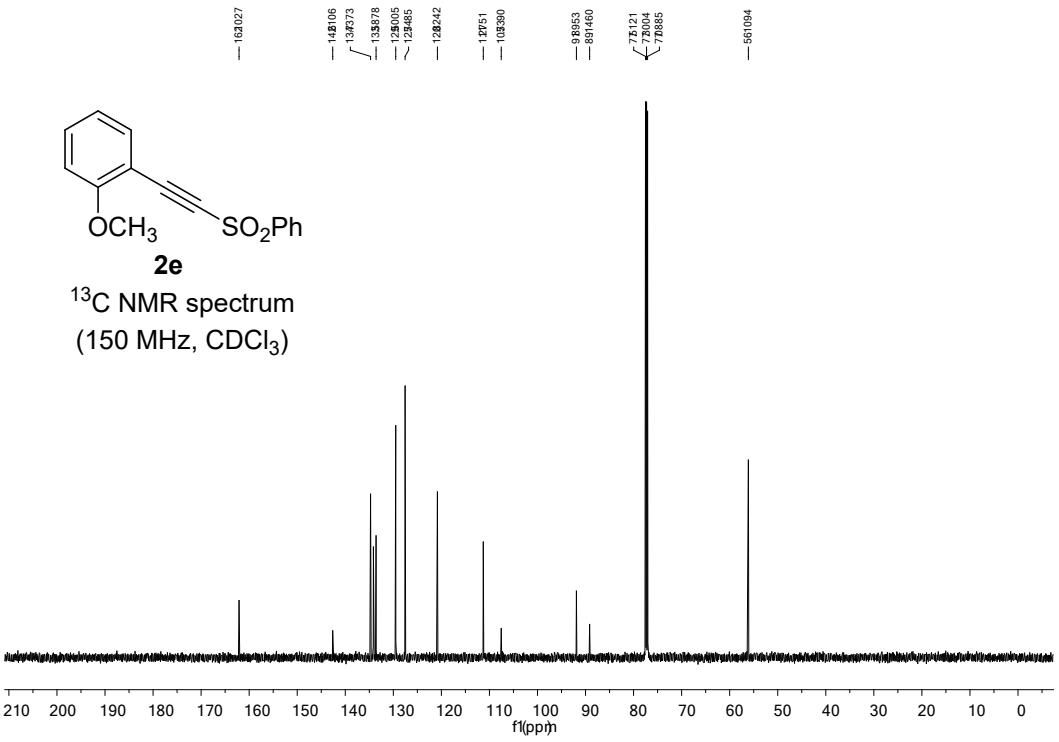

Br
SO2Ph
2d
1H NMR spectrum
(600 MHz, CDCl3)
f1(ppm)


Br
SO2Ph
2d
13C NMR spectrum
(150 MHz, CDCl3)
f1(ppm)



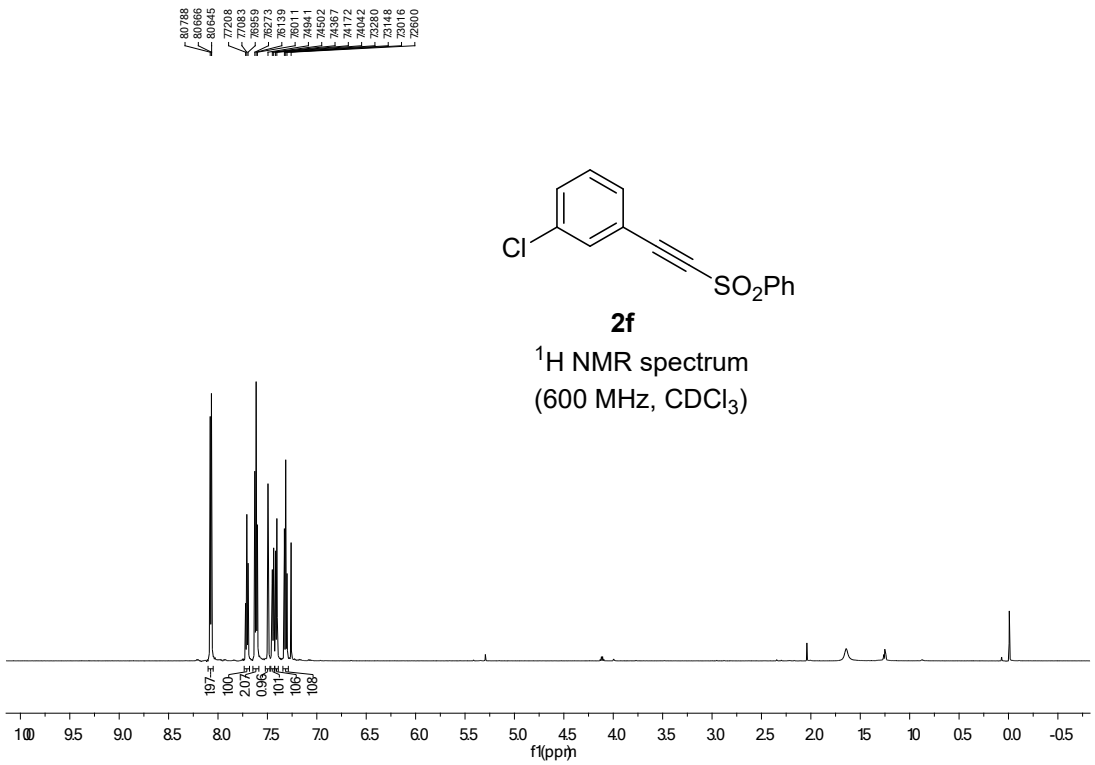
2e

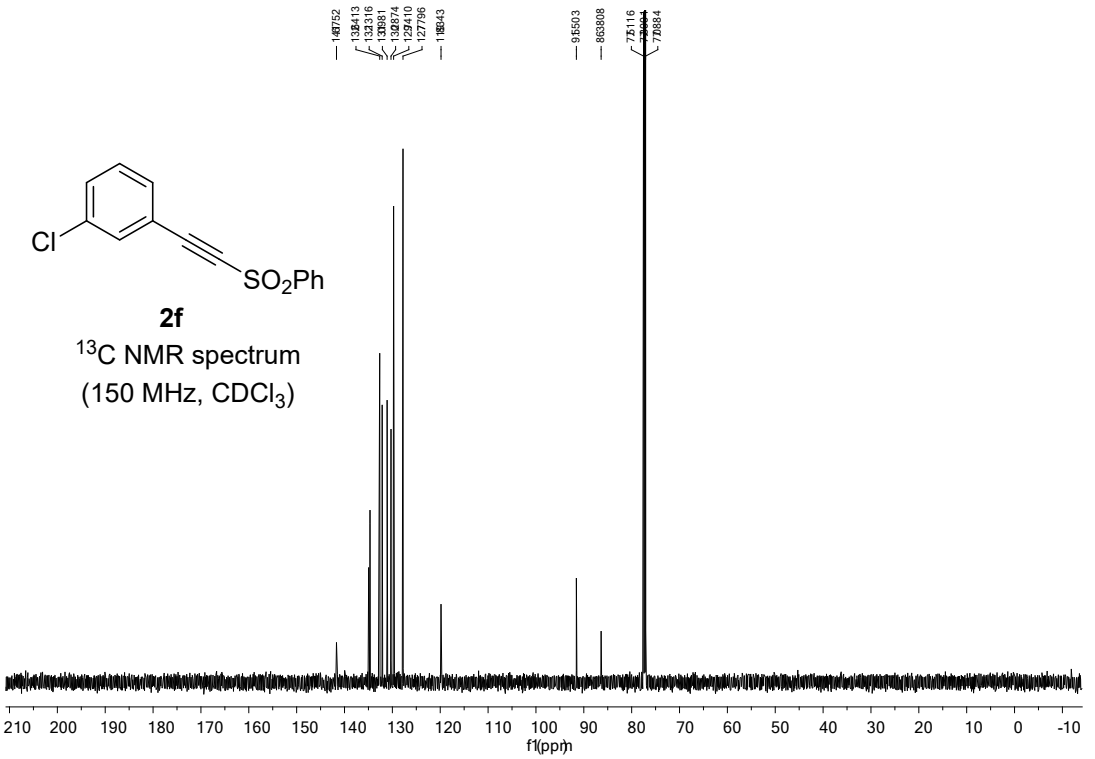
^{1}H NMR spectrum
(600 MHz, $CDCl_3$)

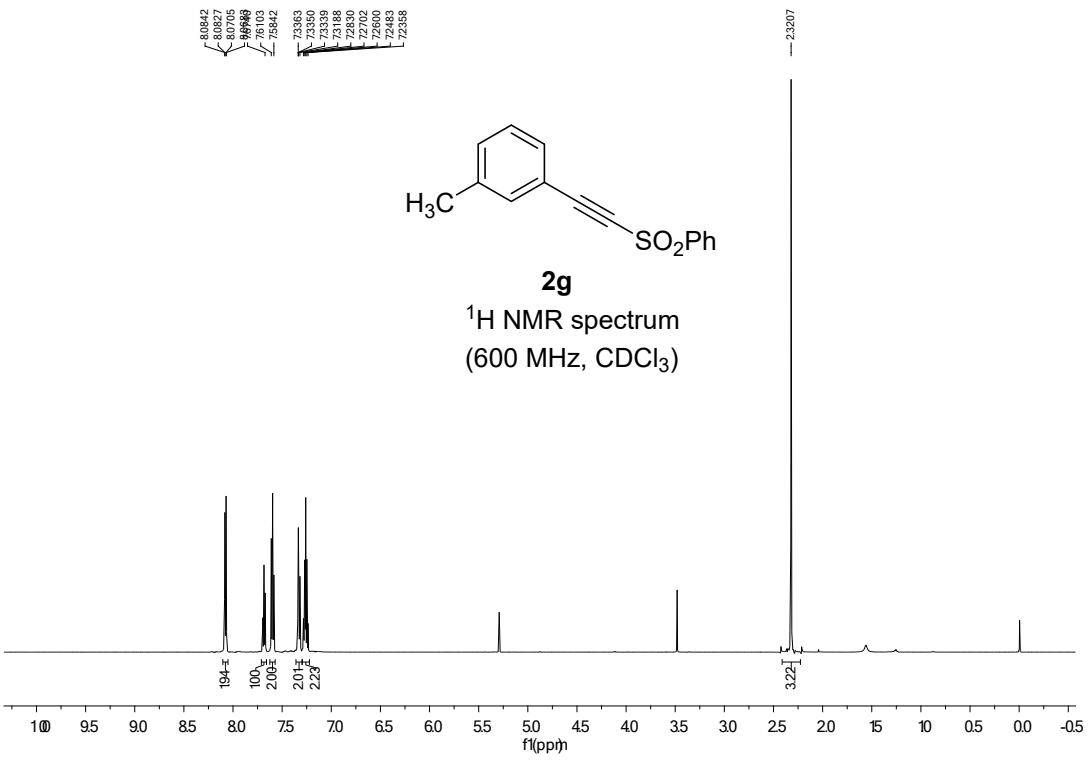


2e

^{13}C NMR spectrum
(150 MHz, $CDCl_3$)


Cl
SO2Ph
2f
1H NMR spectrum
(600 MHz, CDCl3)
f1(ppm)

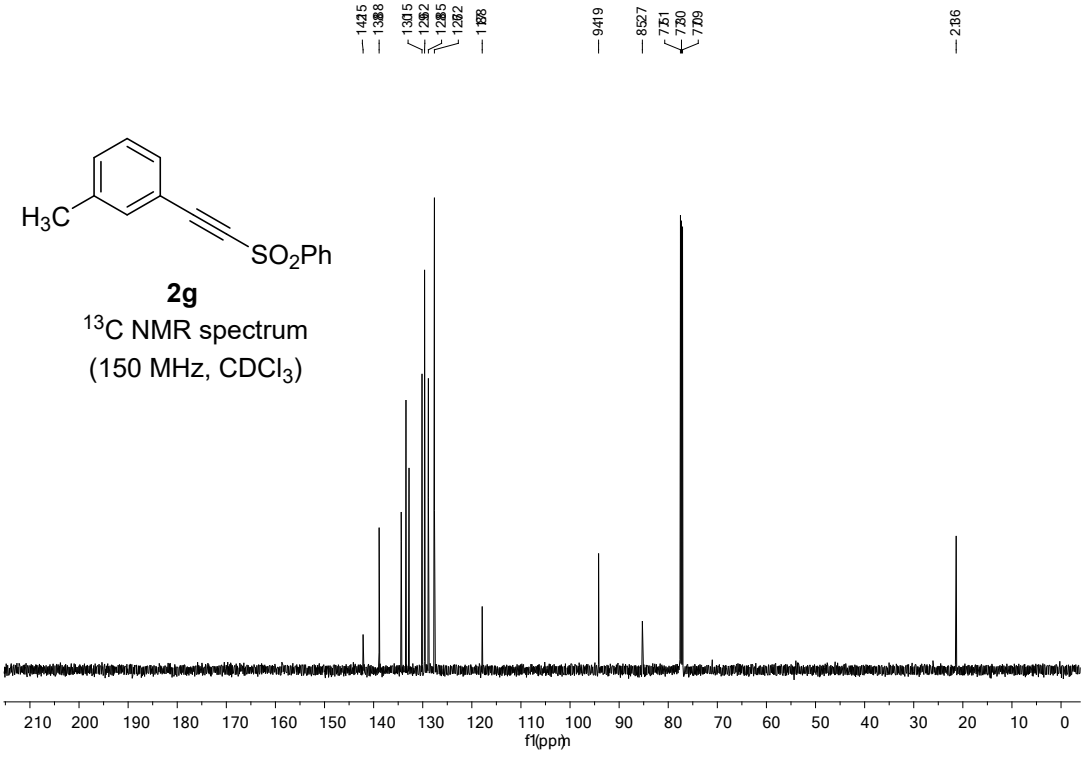

Cl
SO2Ph
2f
13C NMR spectrum
(150 MHz, CDCl3)
f1(ppm)



2g

^{1}H NMR spectrum

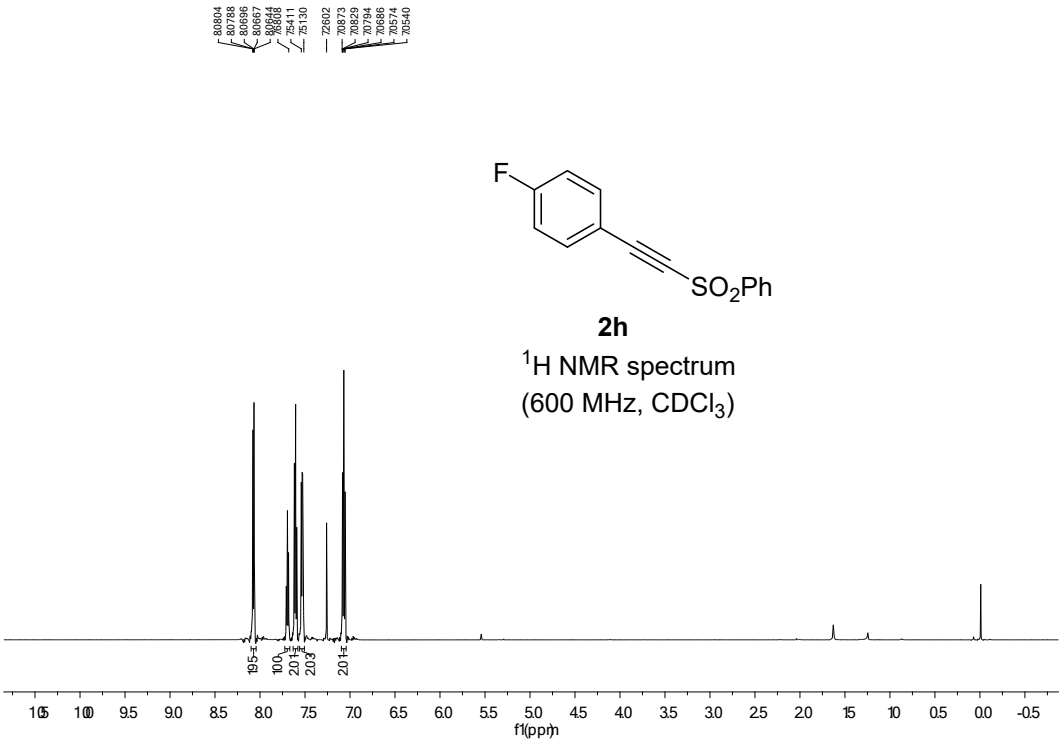
(600 MHz, $CDCl_3$)

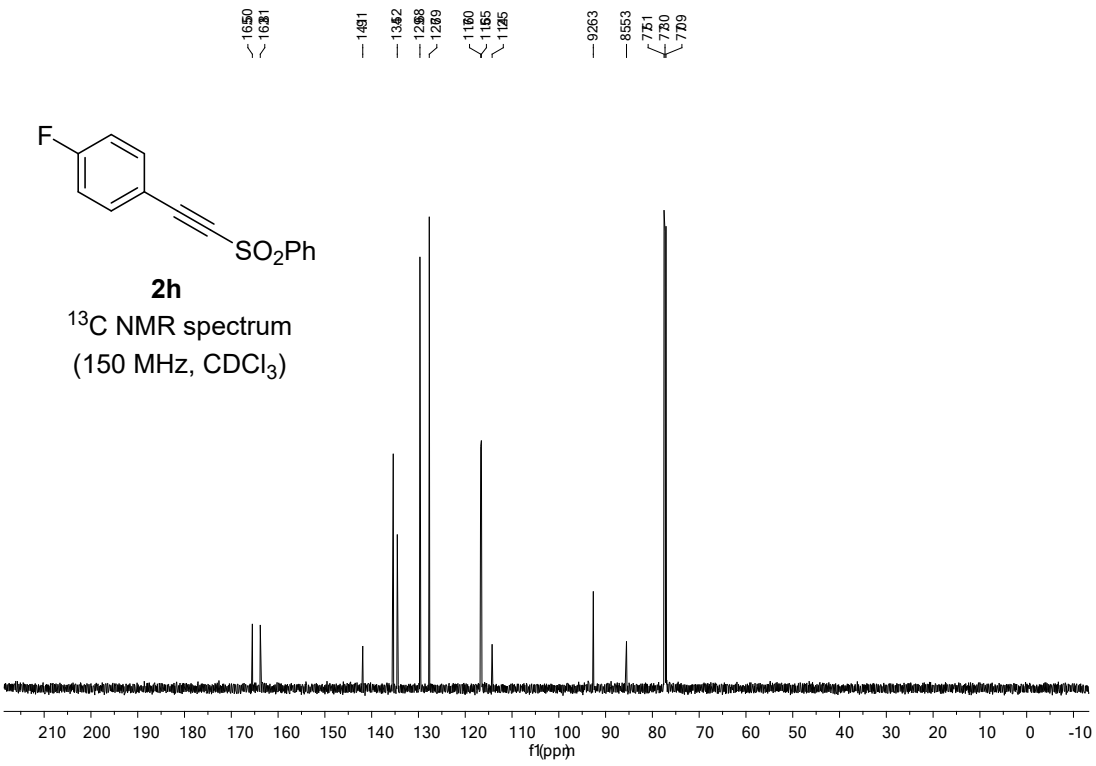


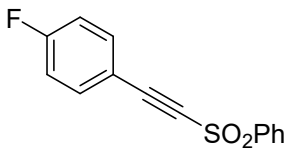
2g

^{13}C NMR spectrum

(150 MHz, $CDCl_3$)


F
SO2Ph
2h
1H NMR spectrum
(600 MHz, CDCl3)
f1(ppm)

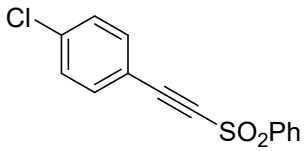

F
SO2Ph
2h
13C NMR spectrum
(150 MHz, CDCl3)
f1(ppm)



2h

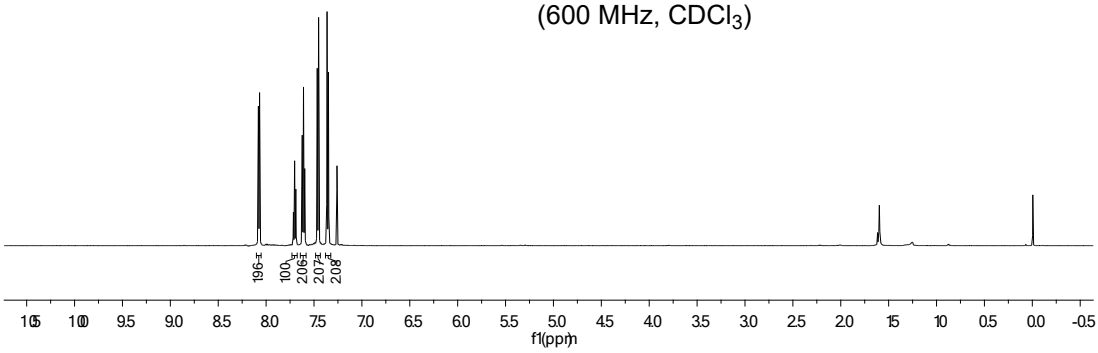
^{19}F NMR spectrum

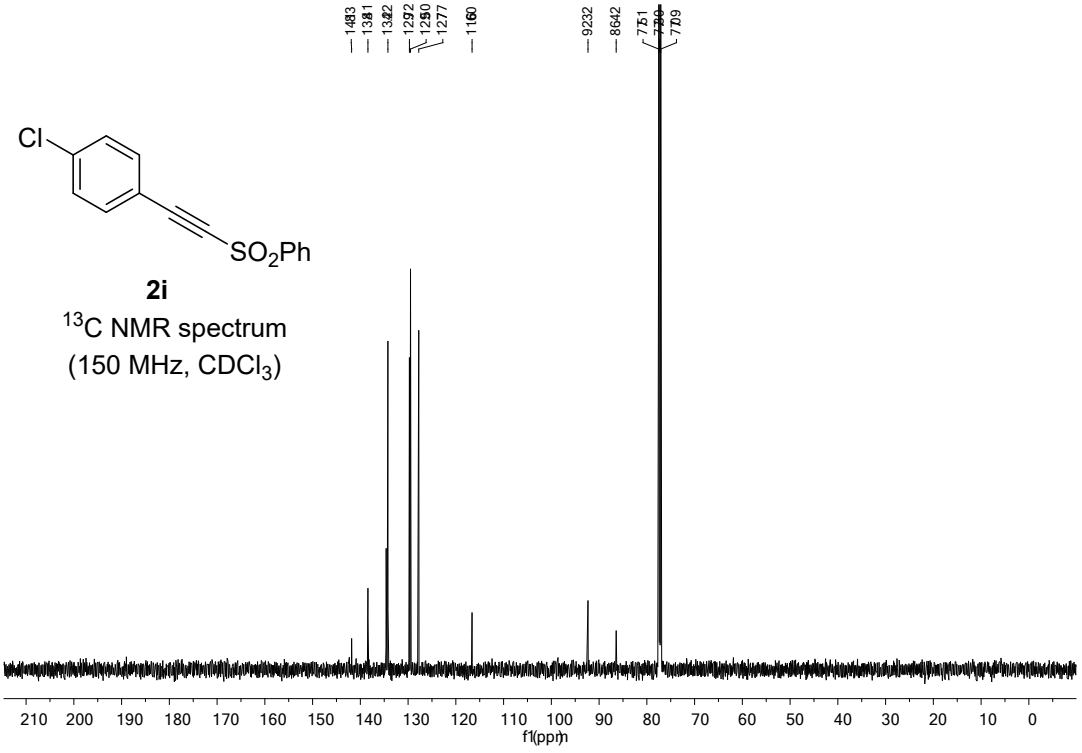
(564 MHz, $CDCl_3$)



2i

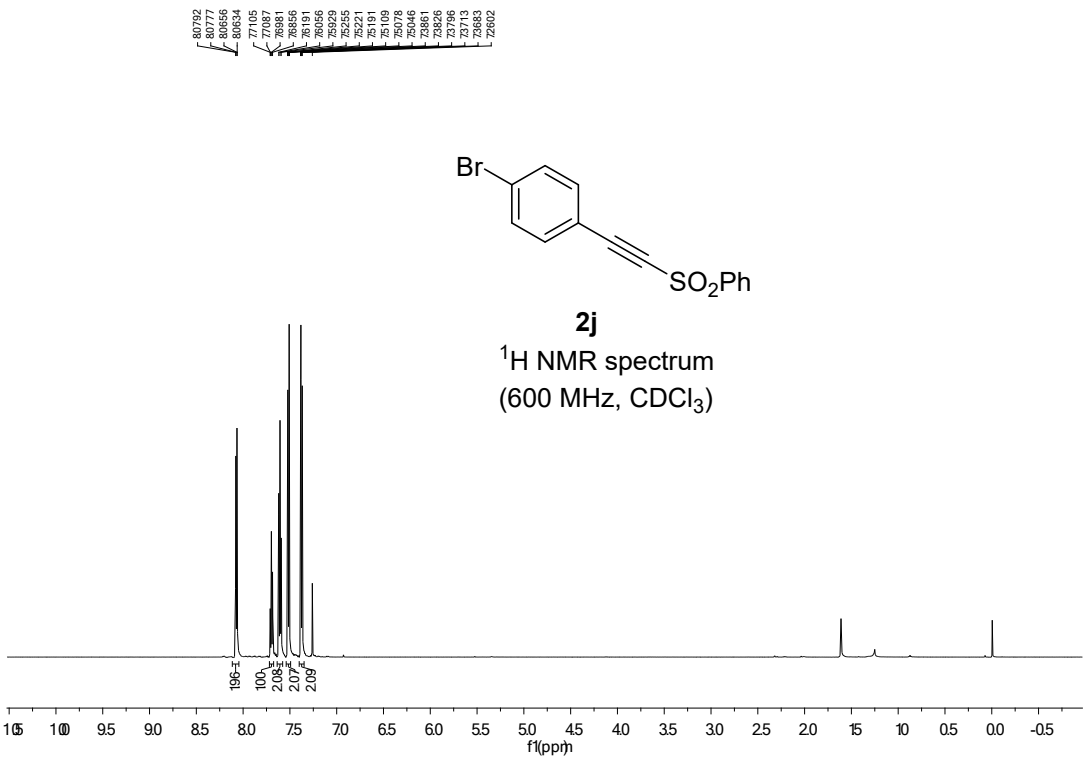
^{1}H NMR spectrum
(600 MHz, $CDCl_3$)

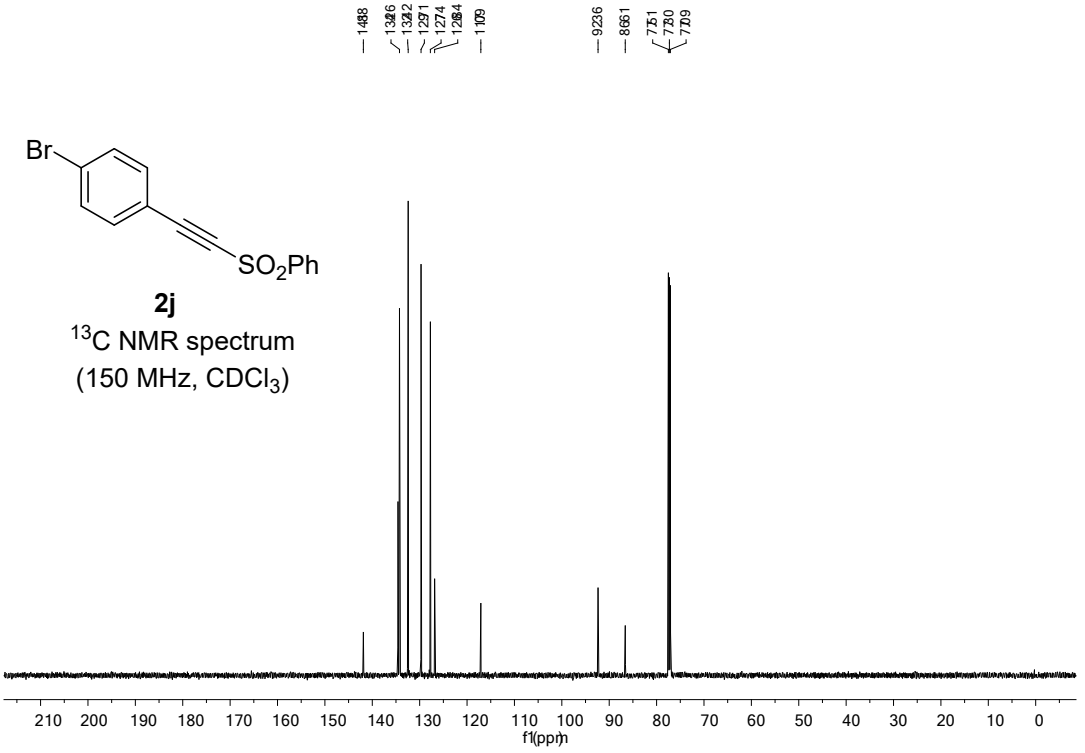


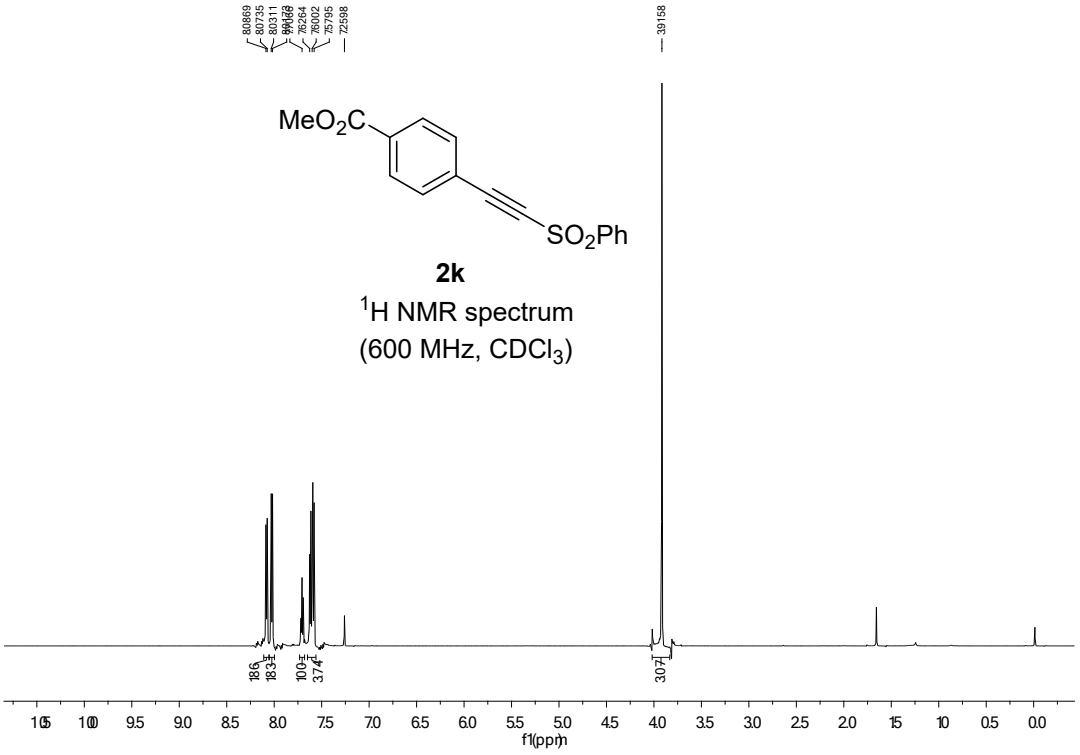


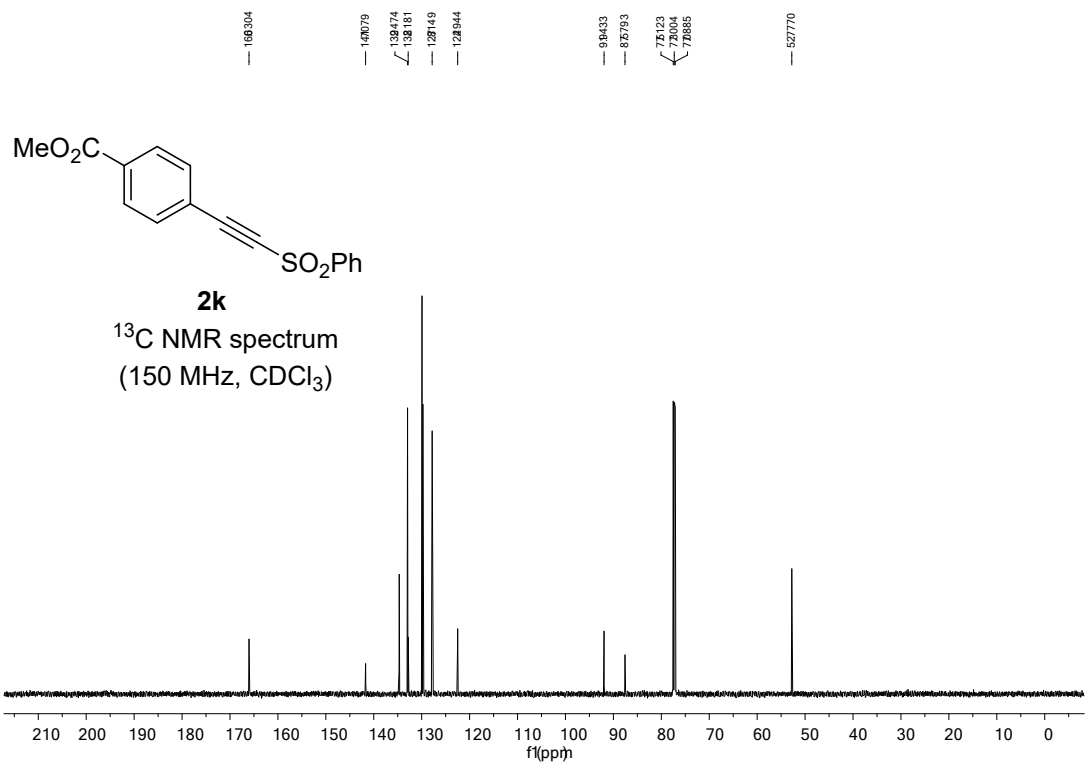
2i

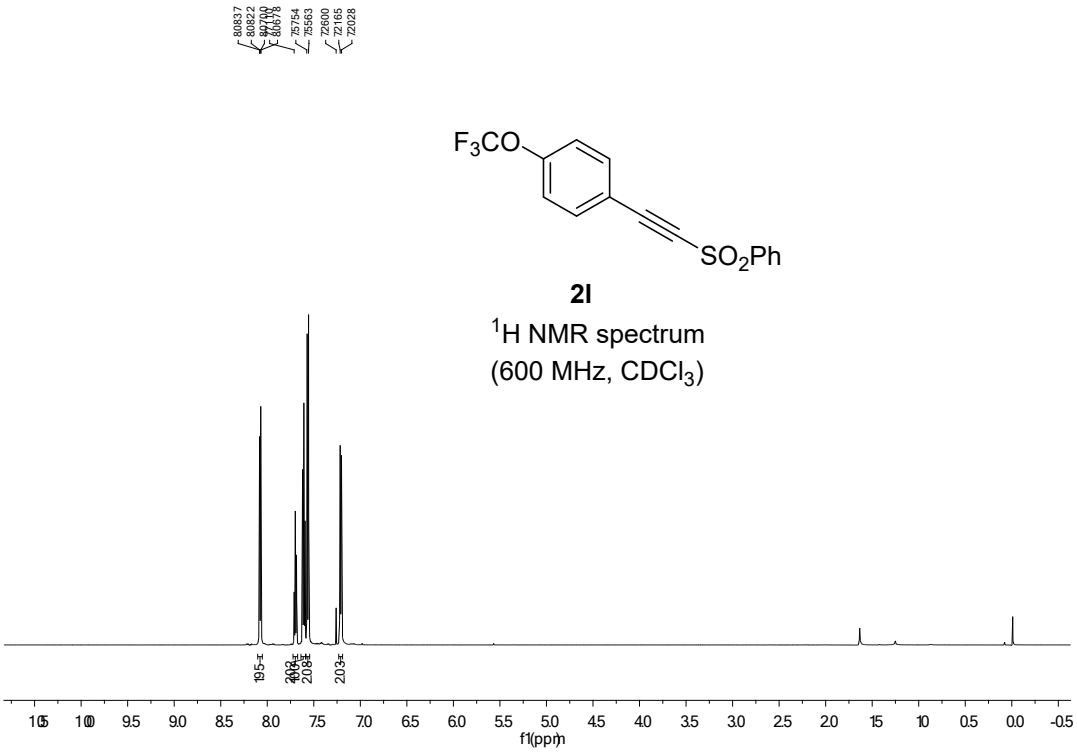
^{13}C NMR spectrum
(150 MHz, $CDCl_3$)

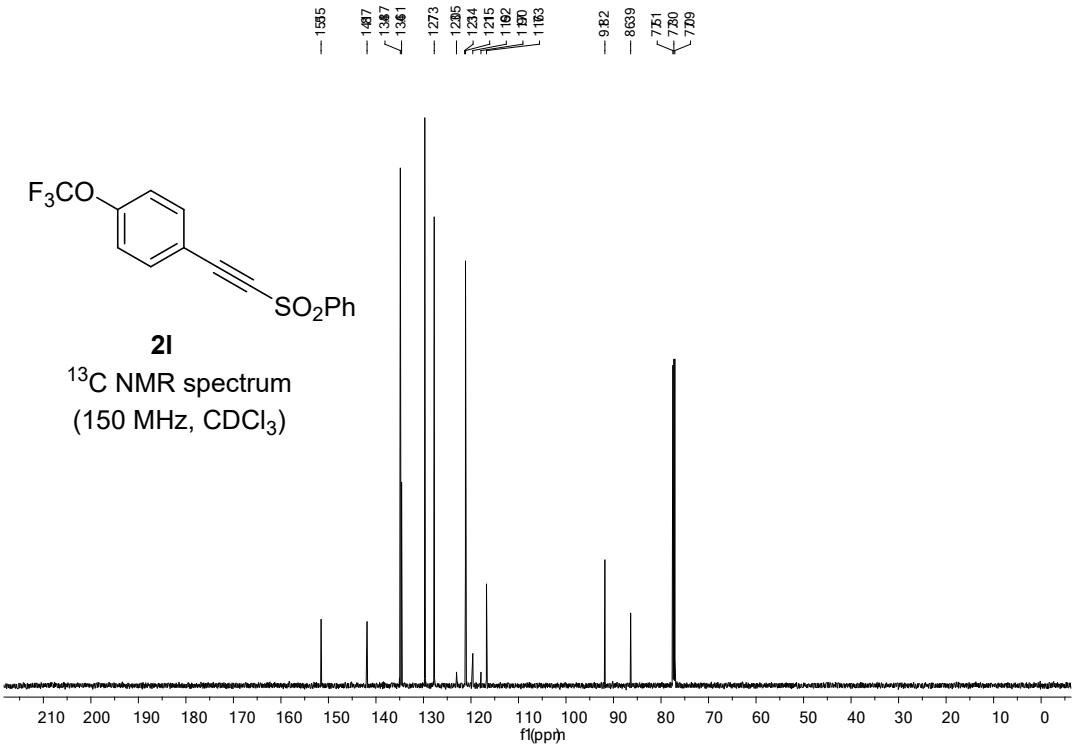

Br
SO2Ph
2j
1H NMR spectrum
(600 MHz, CDCl3)
f1(ppm)

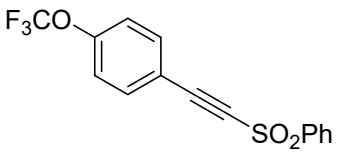

Br
SO2Ph
2j
13C NMR spectrum
(150 MHz, CDCl3)
f1(ppm)


MeO2C
SO2Ph
2k
1H NMR spectrum
(600 MHz, CDCl3)
f1(ppm)


MeO2C
SO2Ph
2k
13C NMR spectrum
(150 MHz, CDCl3)
f1(ppm)


F3CO
SO2Ph
2l
1H NMR spectrum
(600 MHz, CDCl3)
f1(ppm)

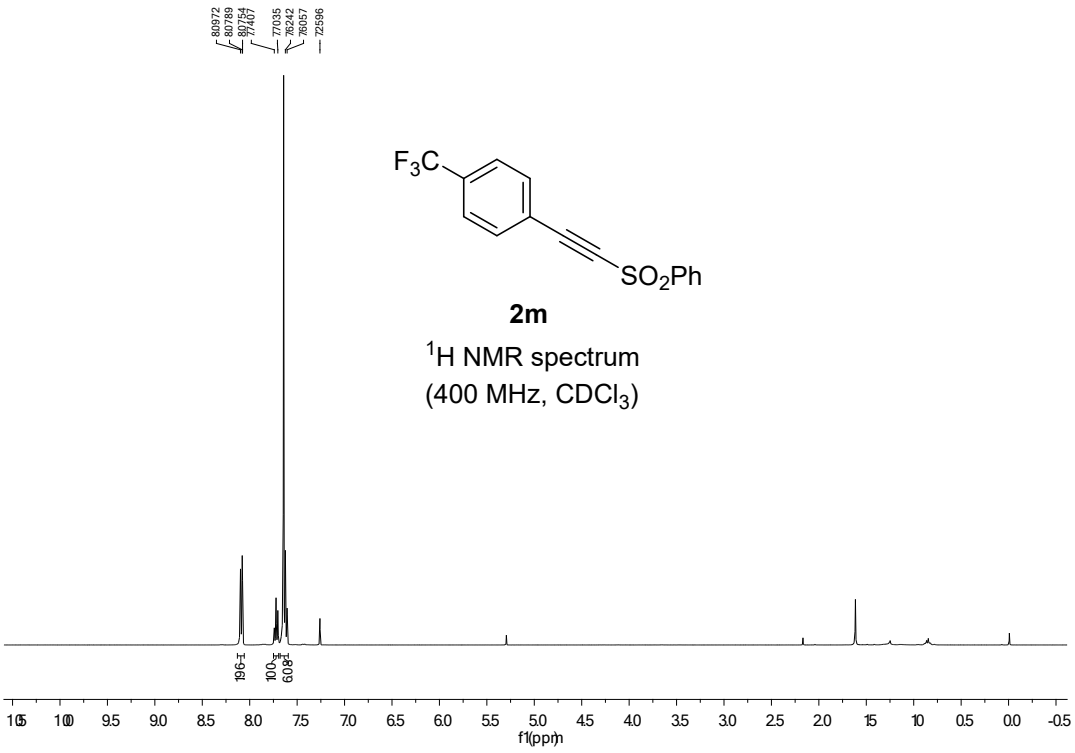

F3CO
SO2Ph
2l
13C NMR spectrum
(150 MHz, CDCl3)
f1(ppm)

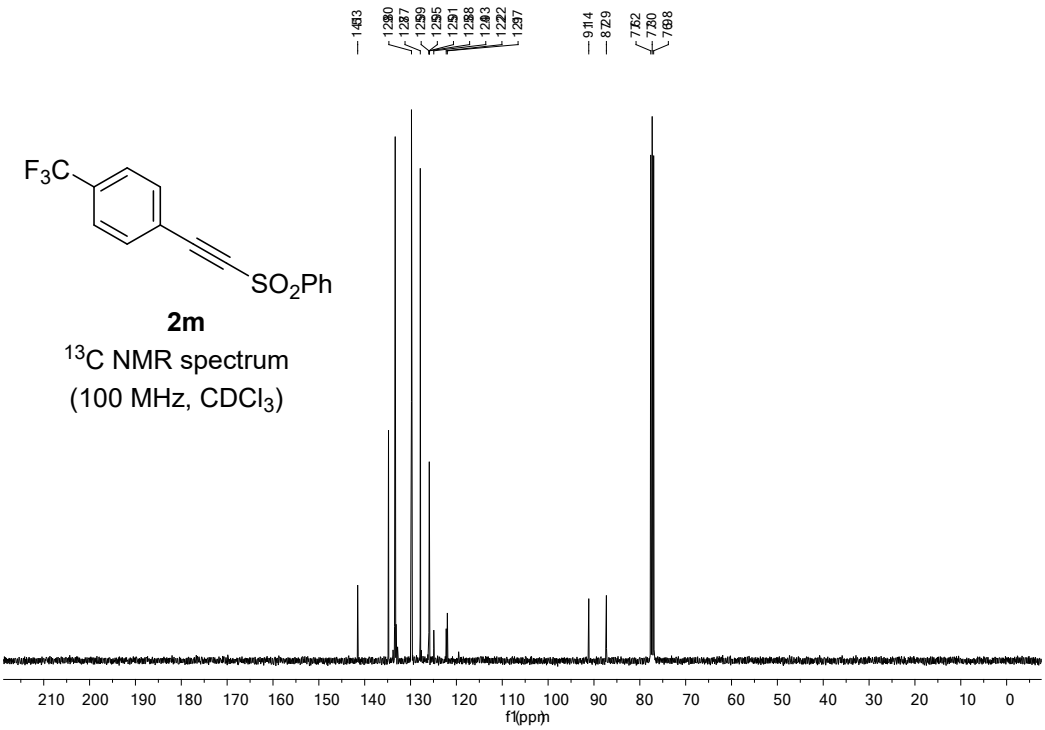


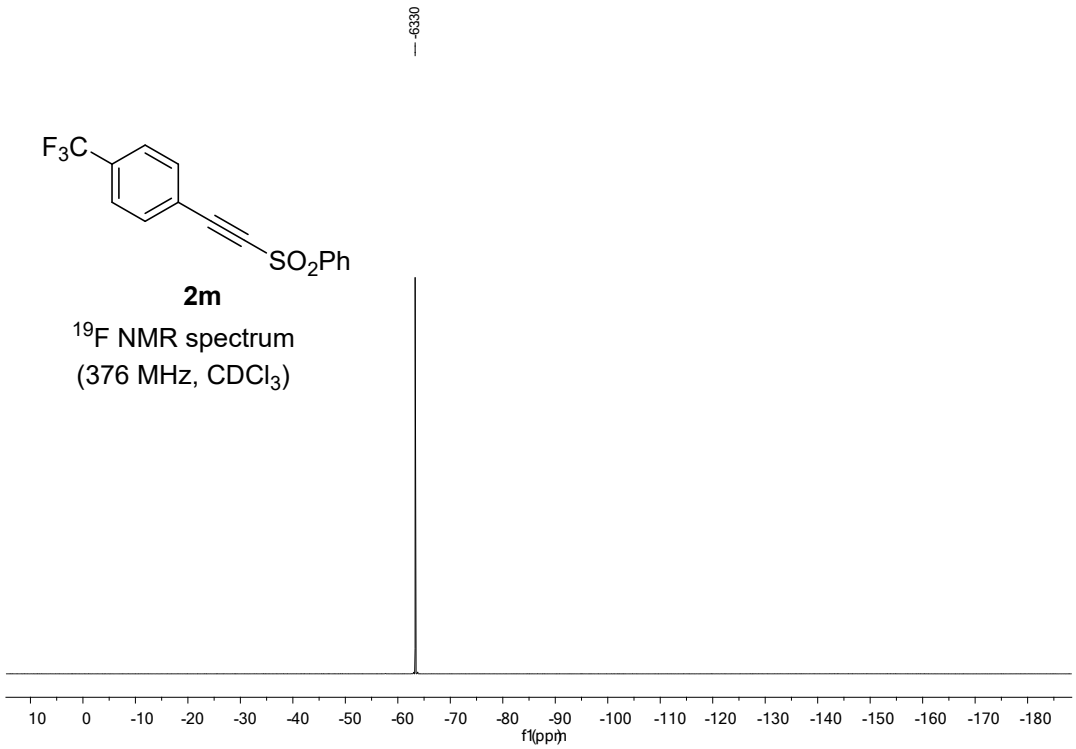
2l

^{19}F NMR spectrum

(564 MHz, $CDCl_3$)


F3C
SO2Ph
2m
1H NMR spectrum
(400 MHz, CDCl3)
f1(ppm)

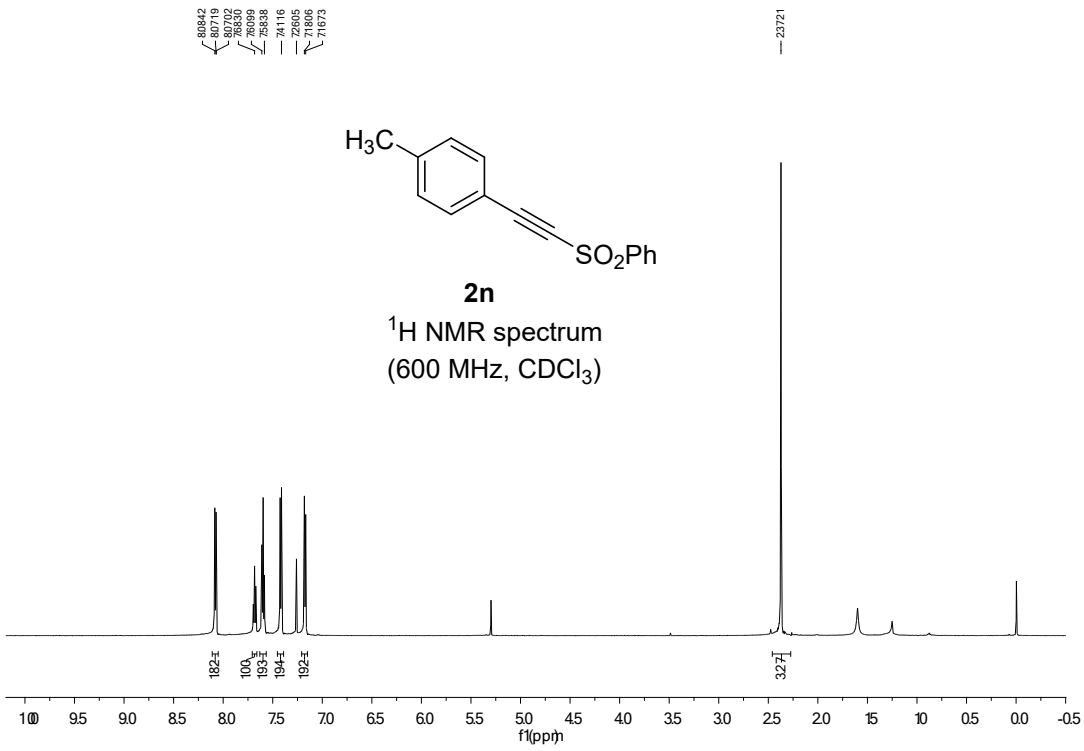

F3C
SO2Ph
2m
13C NMR spectrum
(100 MHz, CDCl3)
f1(ppm)



2m

^{19}F NMR spectrum

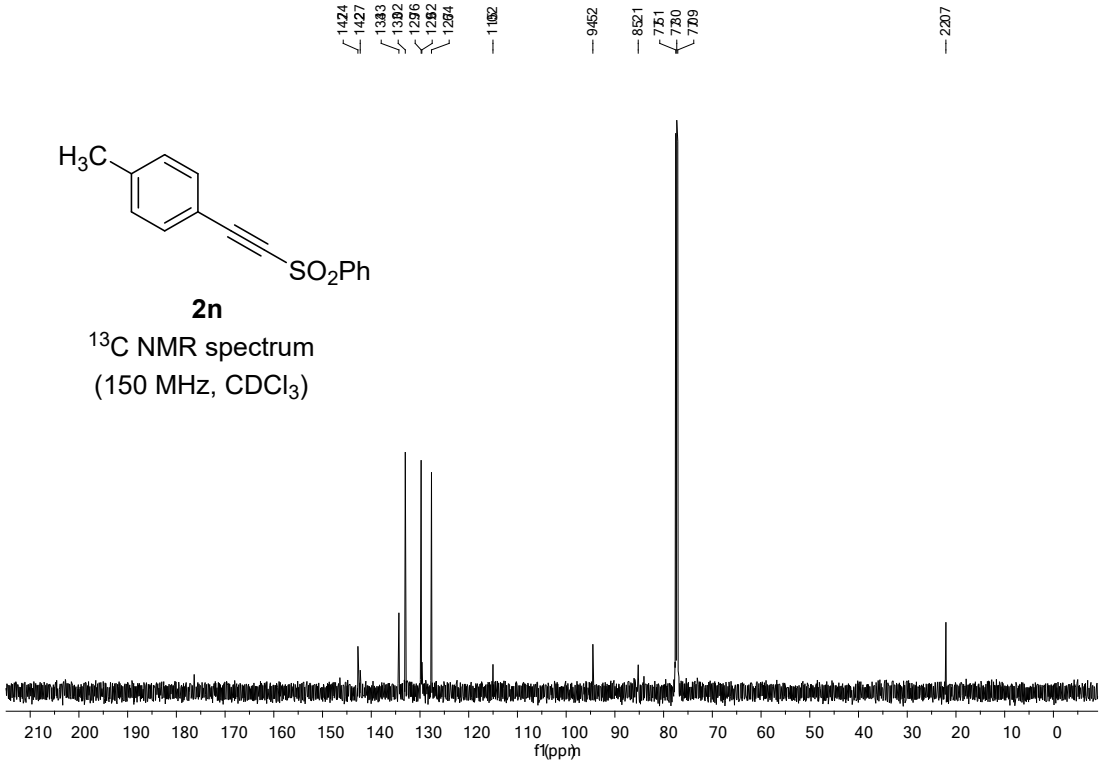
(376 MHz, $CDCl_3$)



2n

^{1}H NMR spectrum

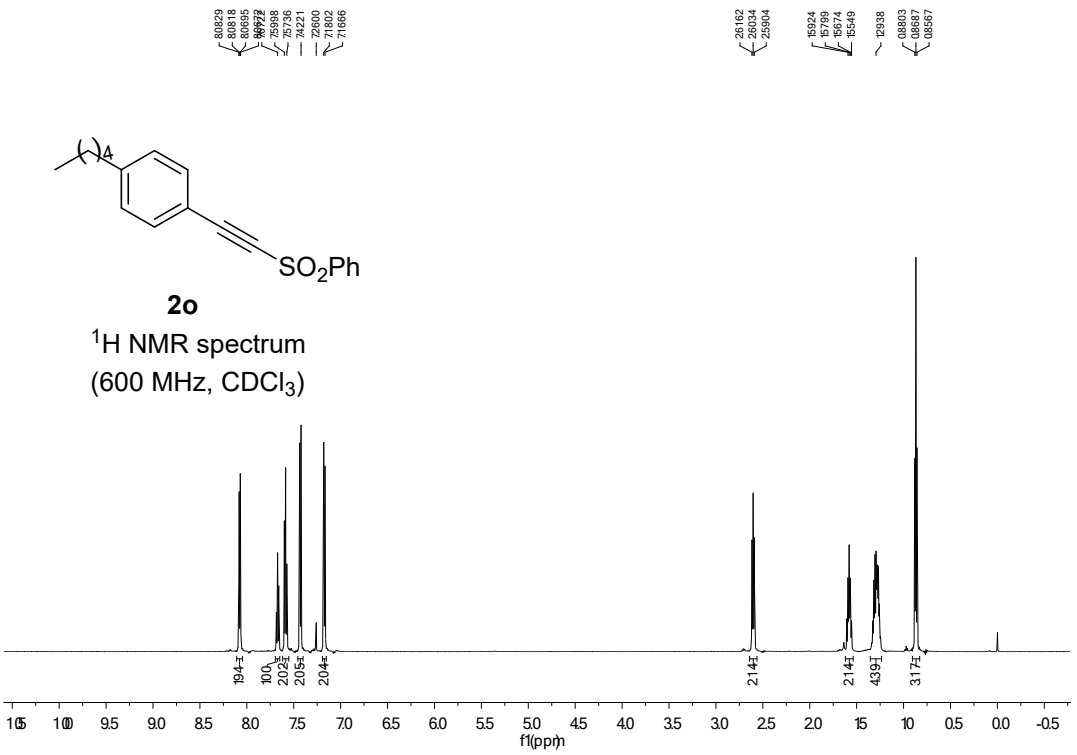
(600 MHz, $CDCl_3$)



2n

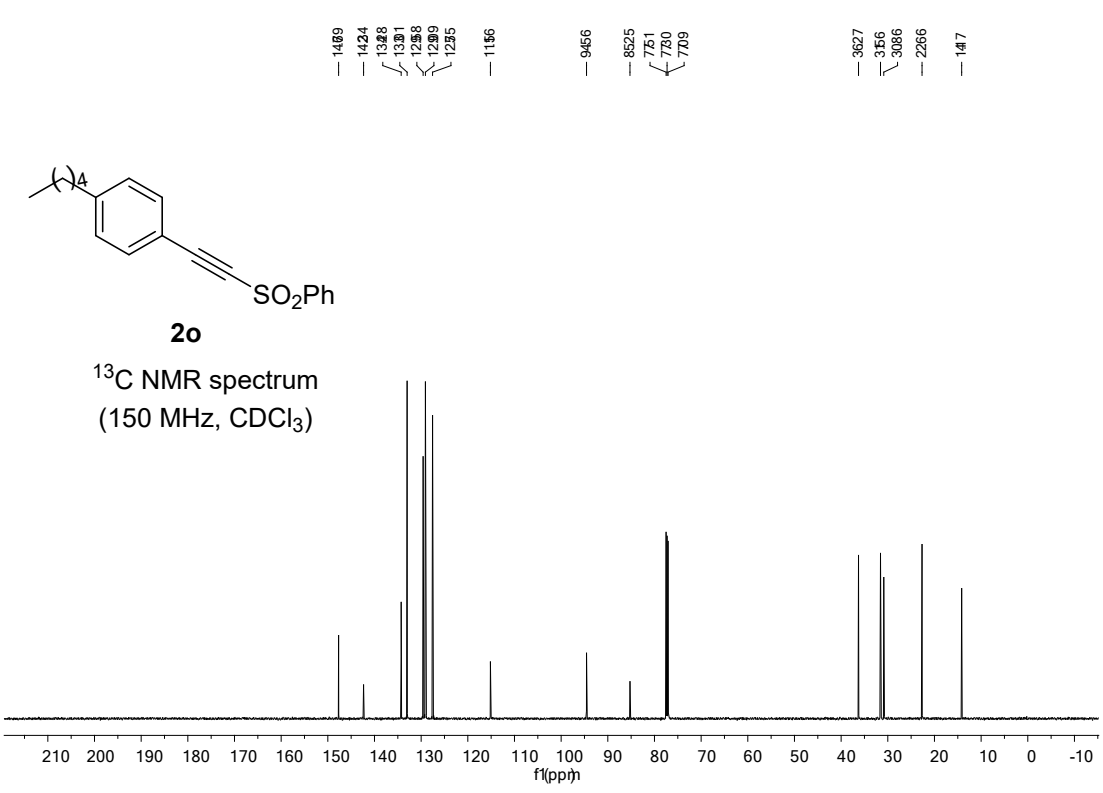
^{13}C NMR spectrum

(150 MHz, $CDCl_3$)



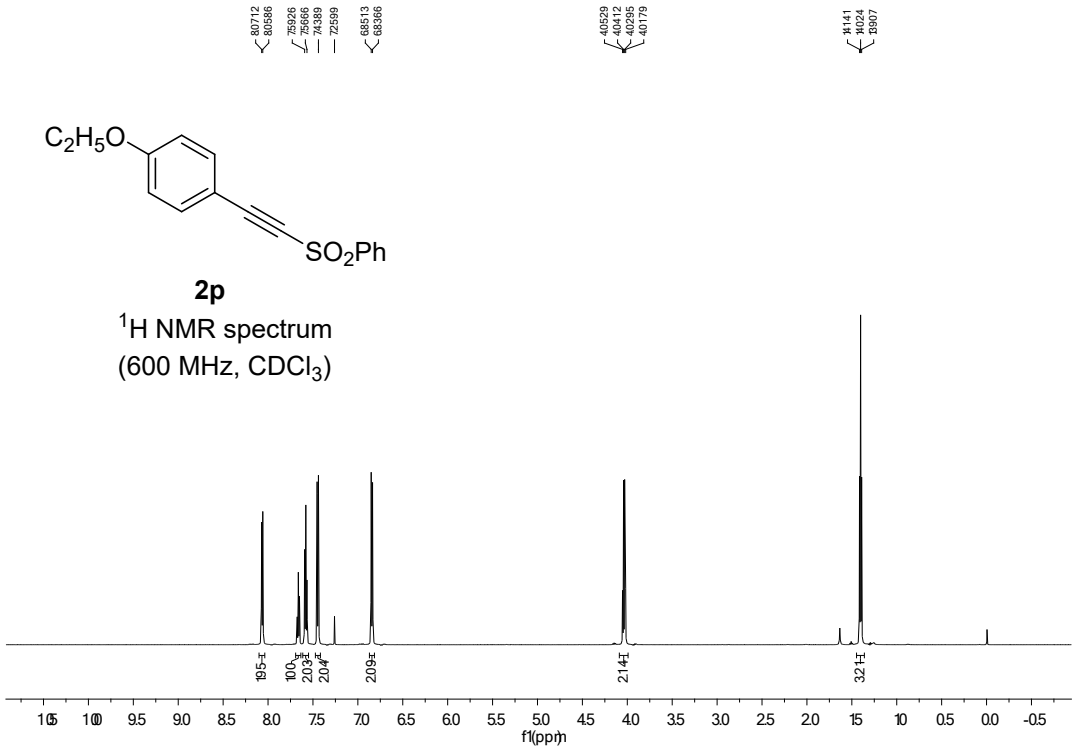
2o

^{1}H NMR spectrum
(600 MHz, $CDCl_3$)



2o

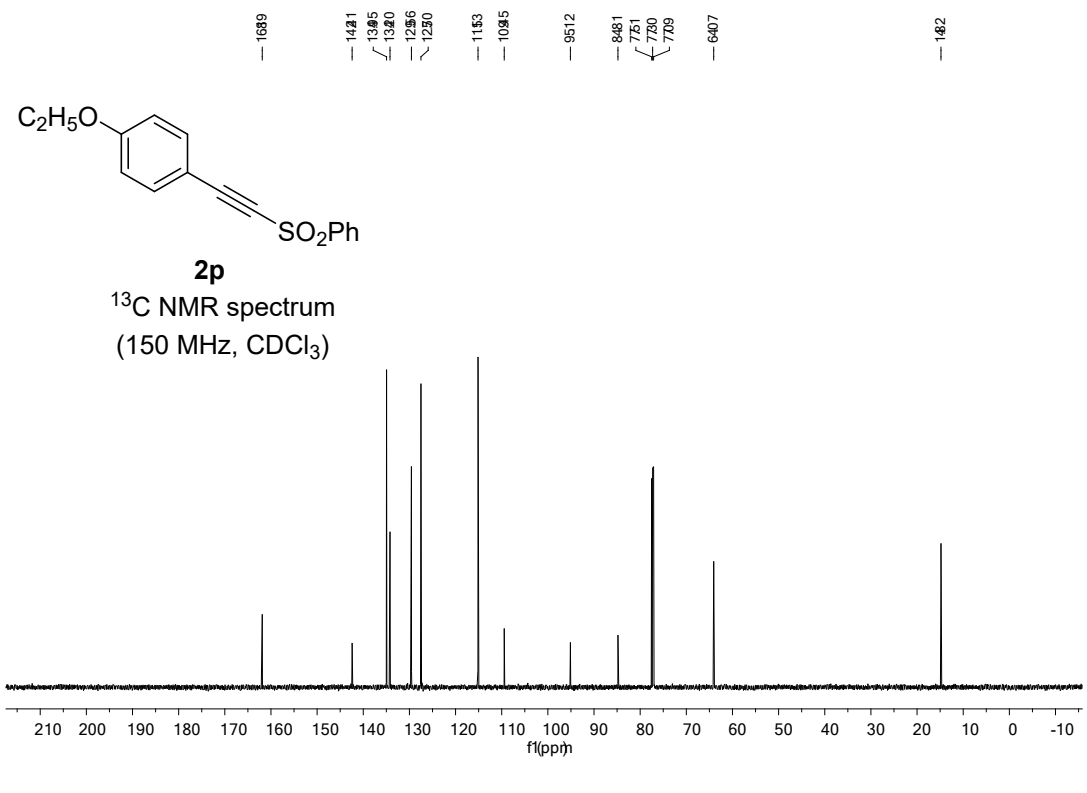
^{13}C NMR spectrum
(150 MHz, $CDCl_3$)



2p

^{1}H NMR spectrum

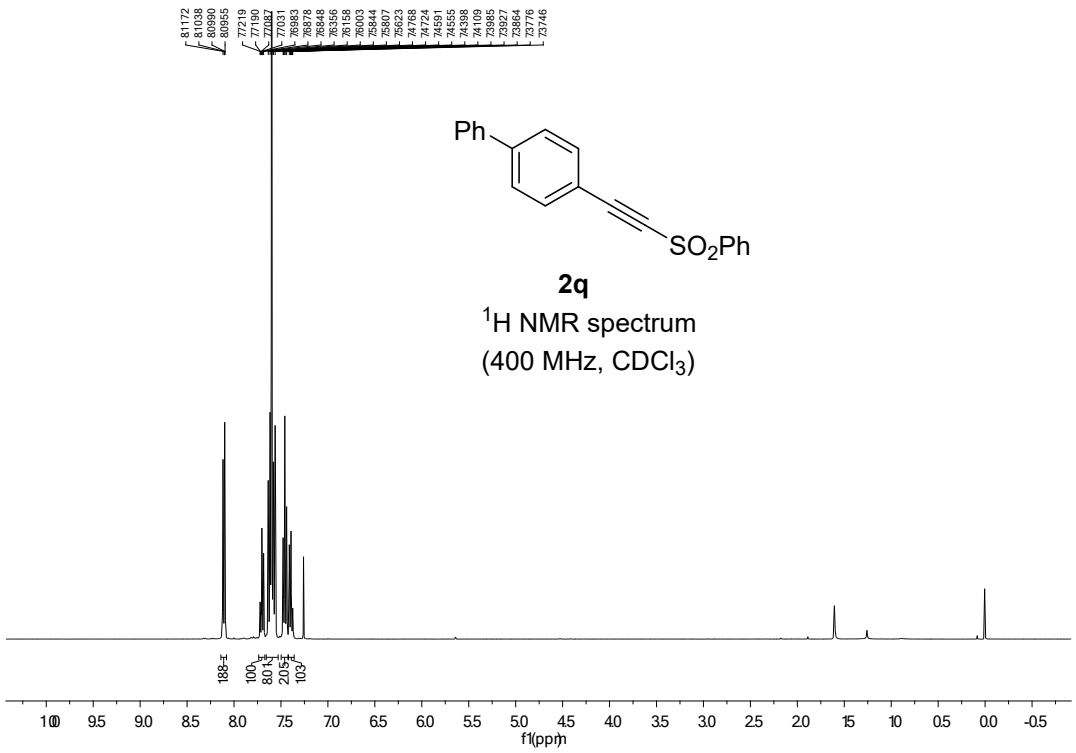
(600 MHz, $CDCl_3$)



2p

^{13}C NMR spectrum

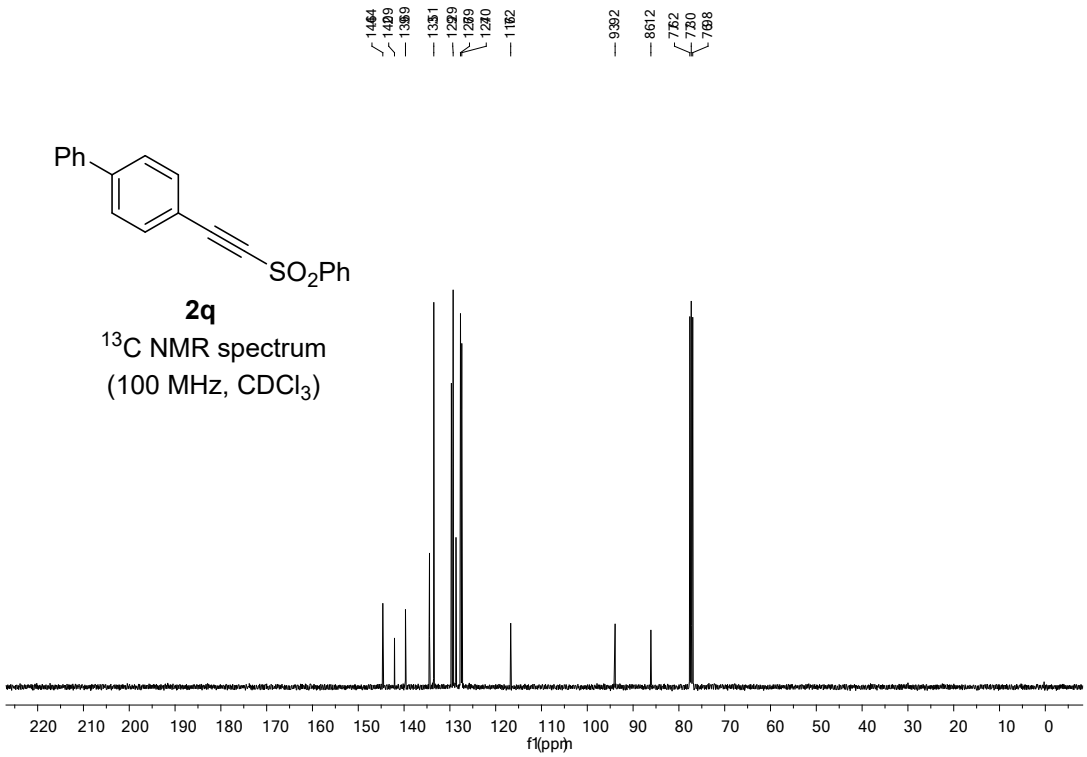
(150 MHz, $CDCl_3$)



2q

^{1}H NMR spectrum

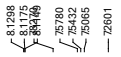
(400 MHz, $CDCl_3$)

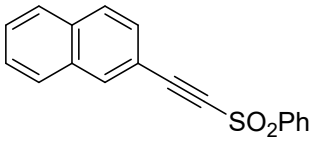


2q

^{13}C NMR spectrum

(100 MHz, $CDCl_3$)

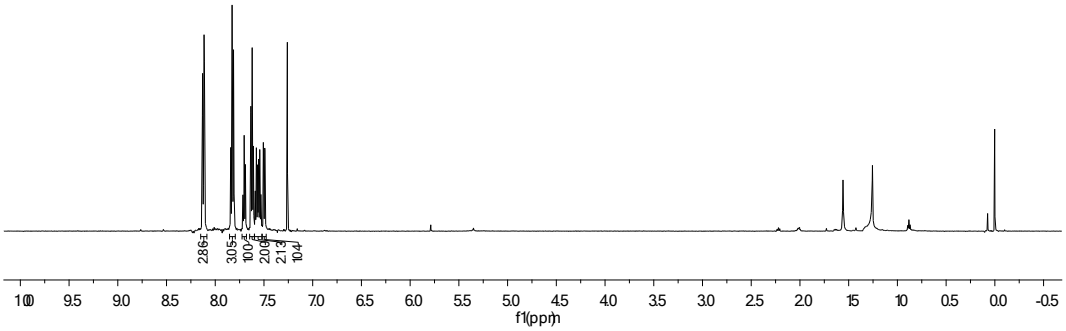


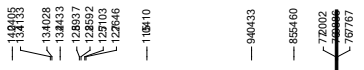


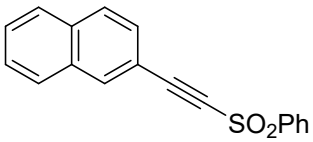
2r

^{1}H NMR spectrum

(600 MHz, $CDCl_3$)



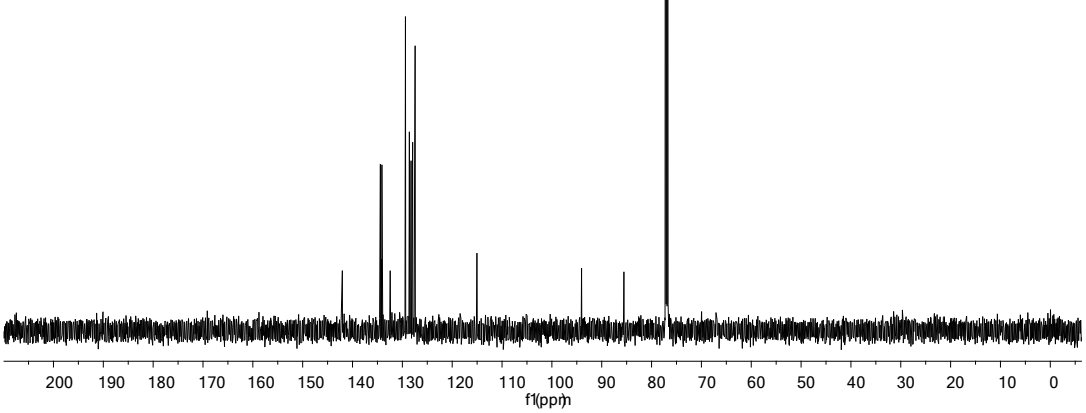


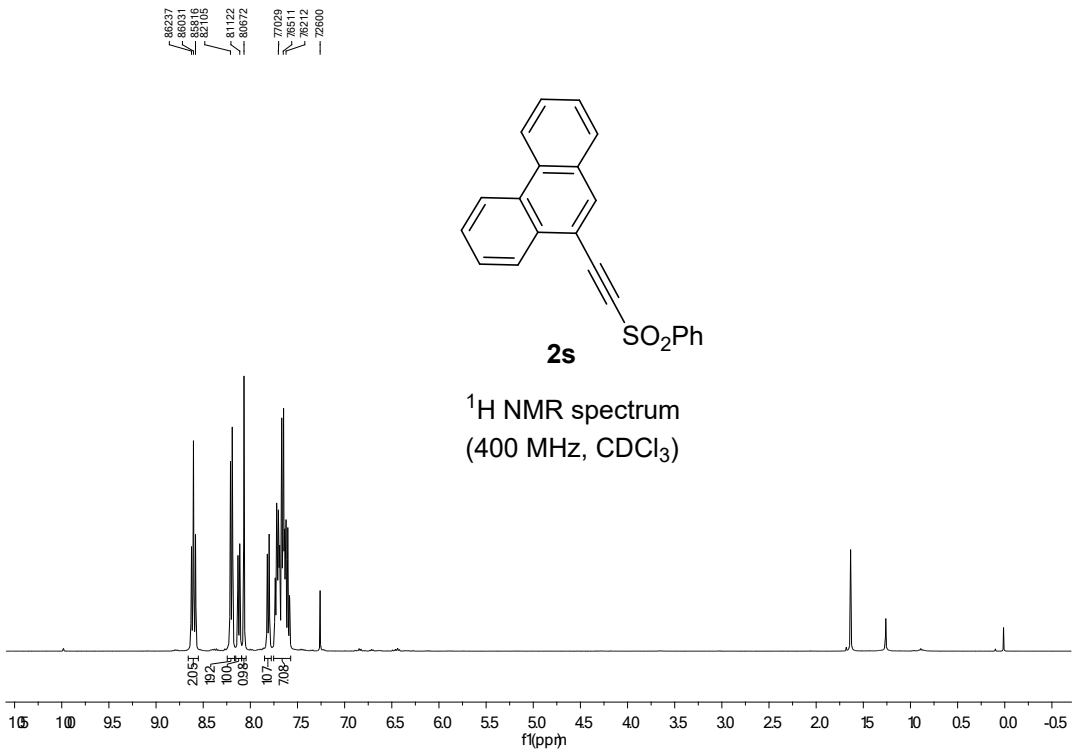


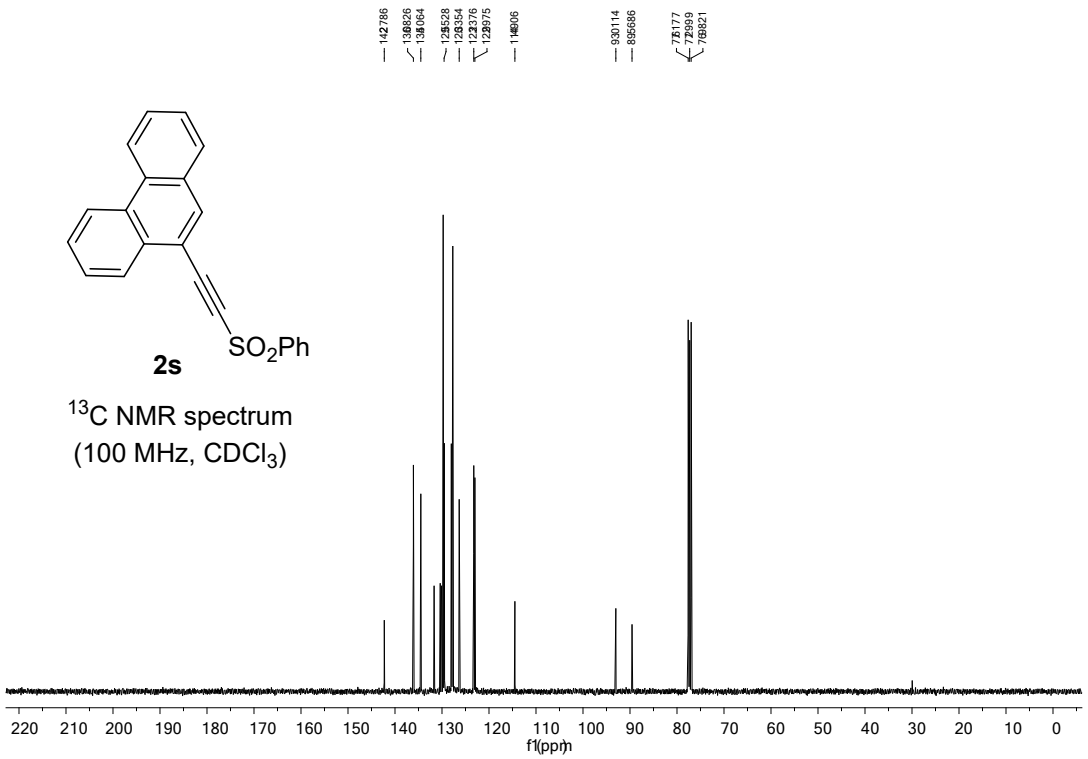
2r

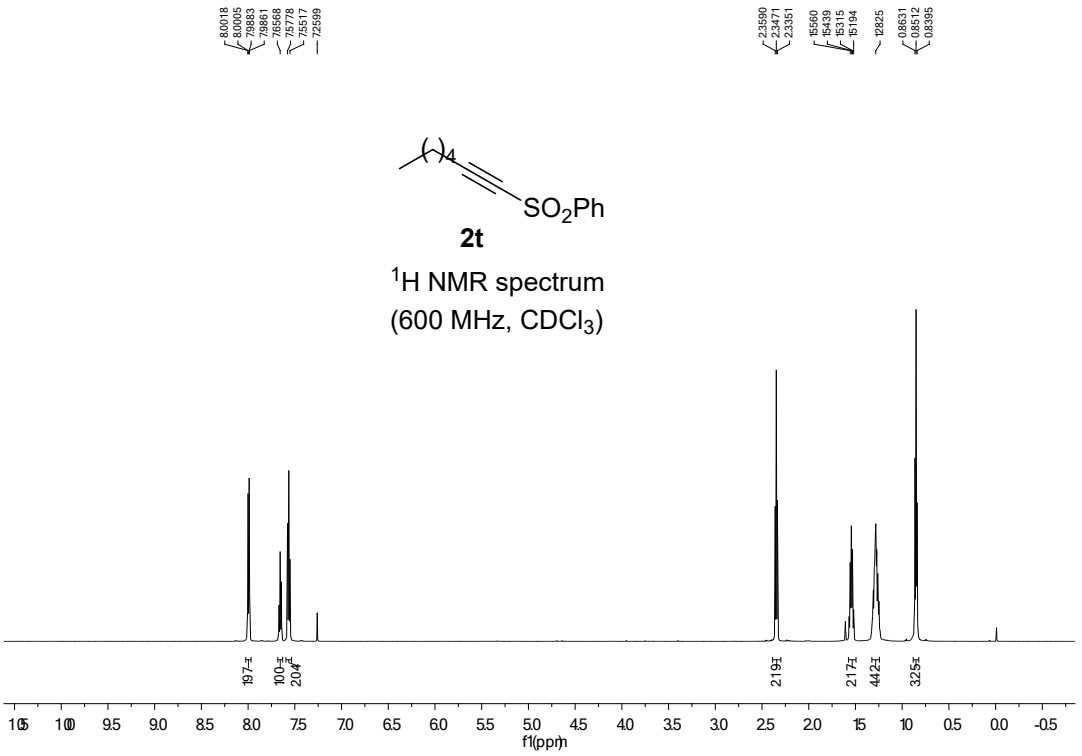
^{13}C NMR spectrum

(150 MHz, $CDCl_3$)




SO2Ph
2s
1H NMR spectrum
(400 MHz, CDCl3)
f1(ppm)


SO2Ph
2s
13C NMR spectrum
(100 MHz, CDCl3)
f1(ppm)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7.99861
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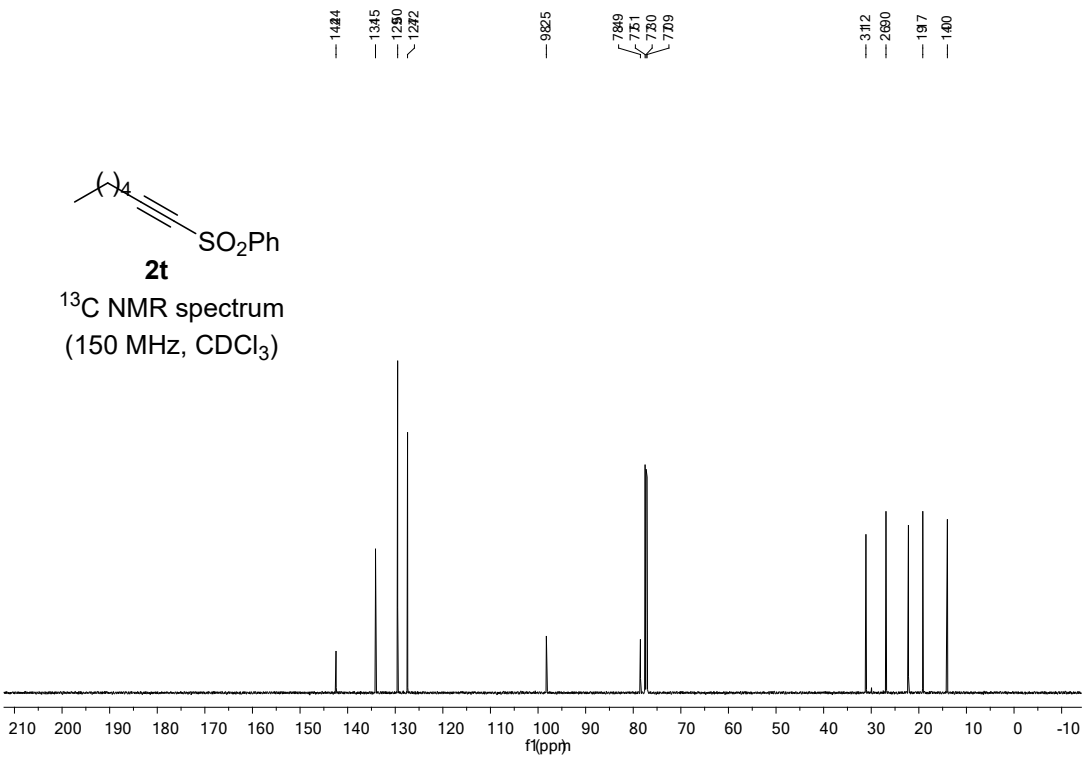
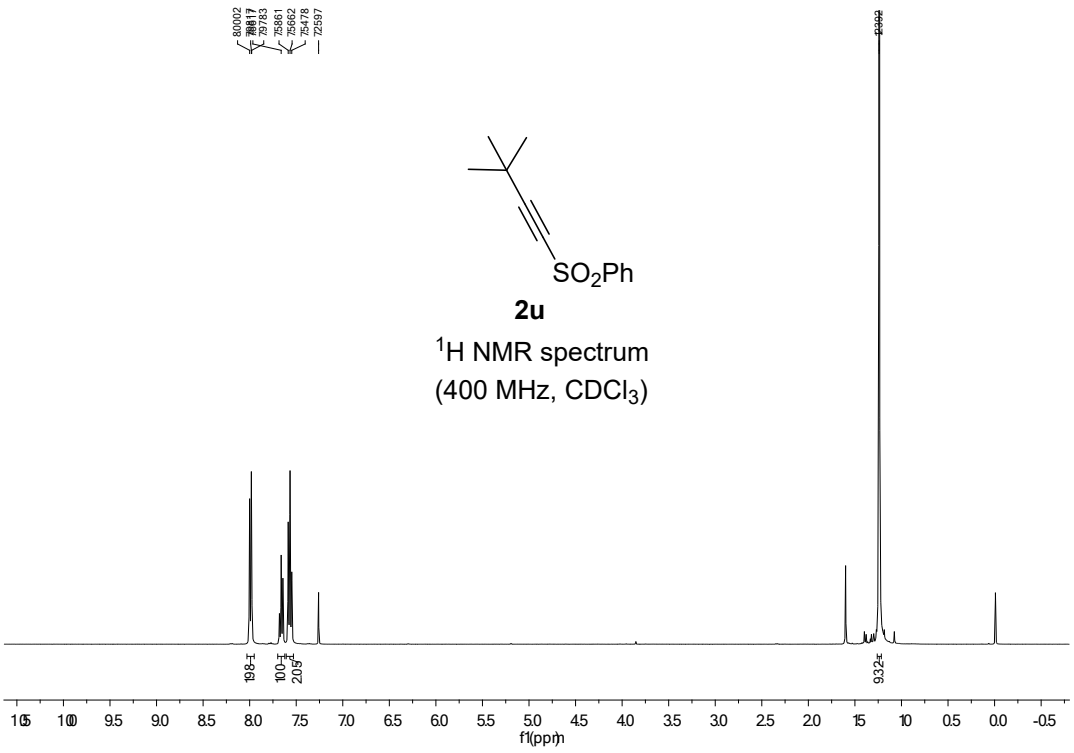
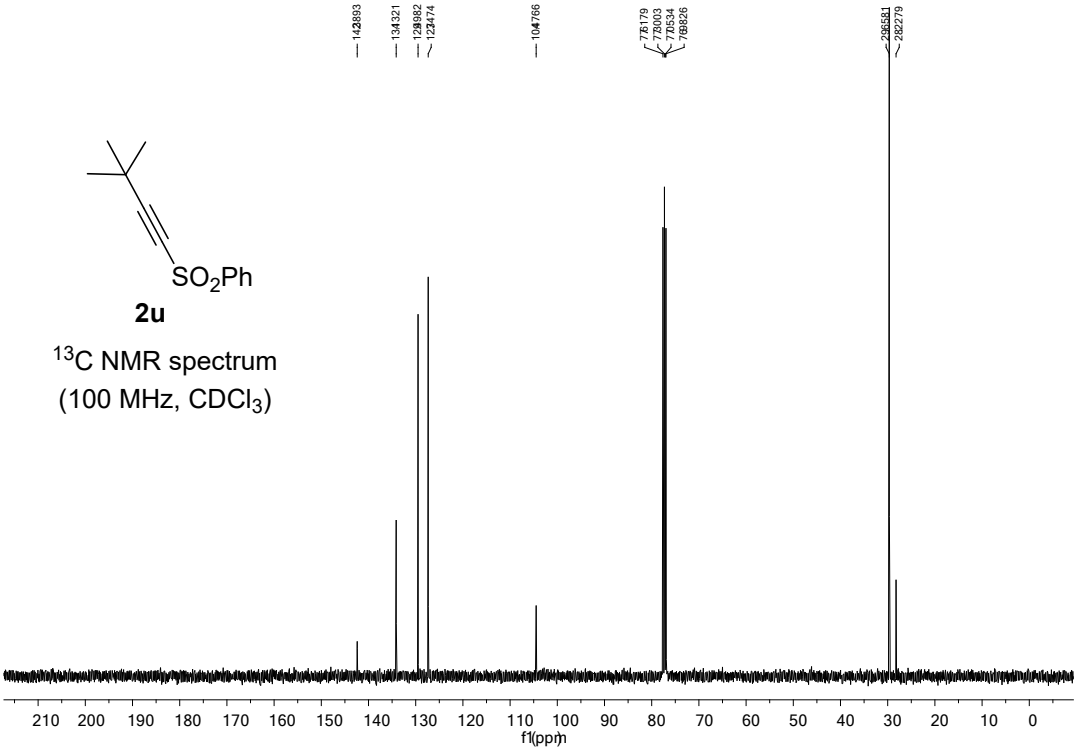
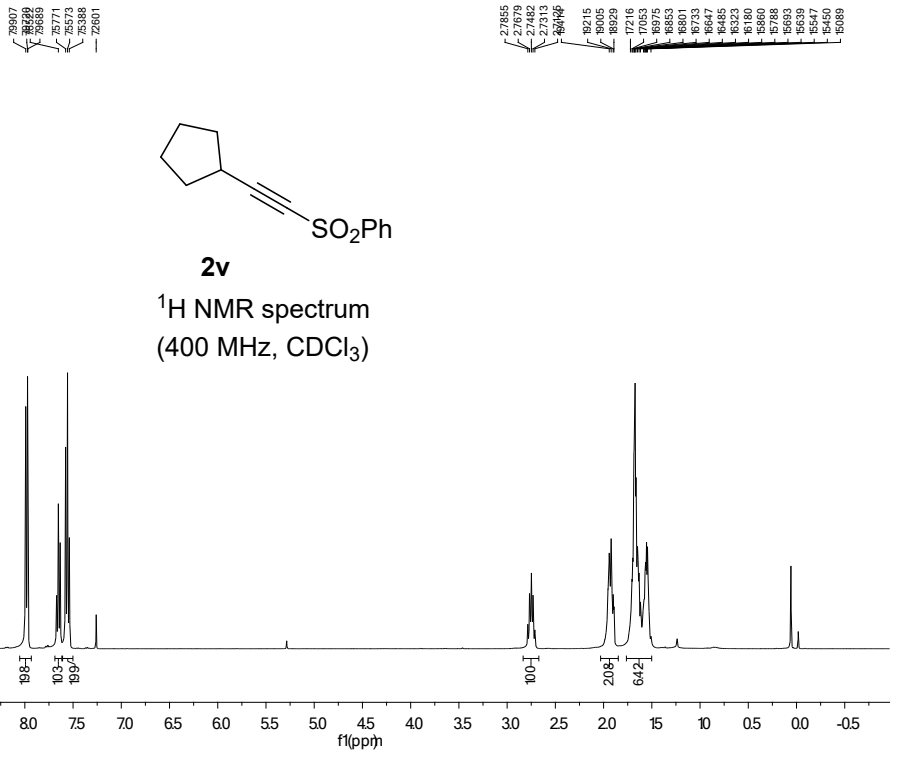
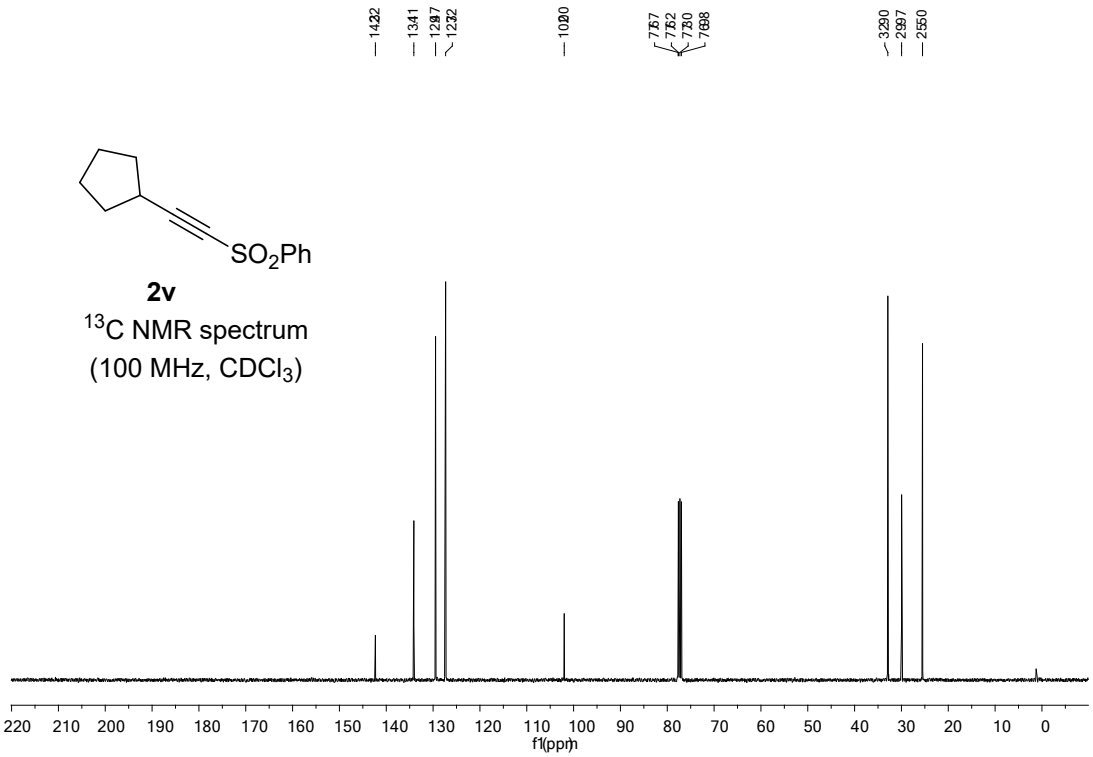
7.75778
7.75517
7.72599
2.35590
2.34471
2.33351
1.55560
1.55439
1.55315
1.55194
1.12825
0.98631
0.98512
0.98395
SO2Ph
2t
1H NMR spectrum
(600 MHz, CDCl3)
1.97
1.00
2.04
2.19
2.17
4.42
3.25
f1(ppm)

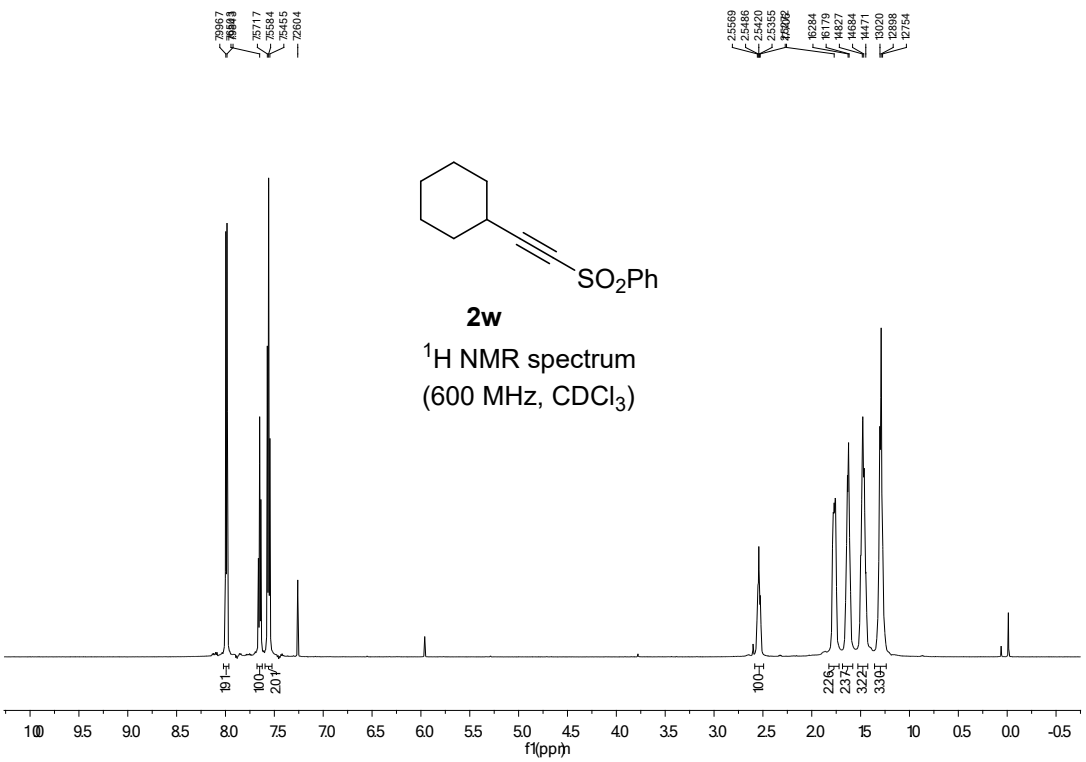

143.44
134.45
129.90
129.72
98.25
78.49
77.51
77.30
77.09
31.12
26.90
19.17
14.00
SO2Ph
2t
13C NMR spectrum
(150 MHz, CDCl3)
f1(ppm)

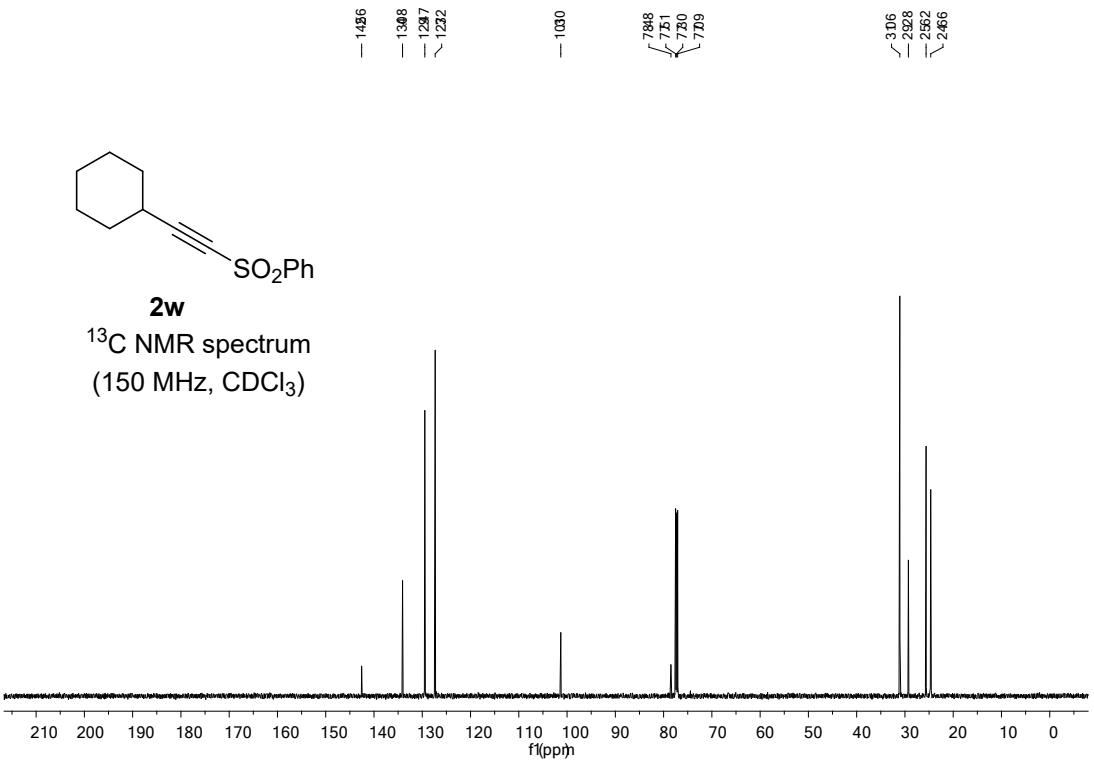

SO2Ph
2u
1H NMR spectrum
(400 MHz, CDCl3)
f1(ppm)

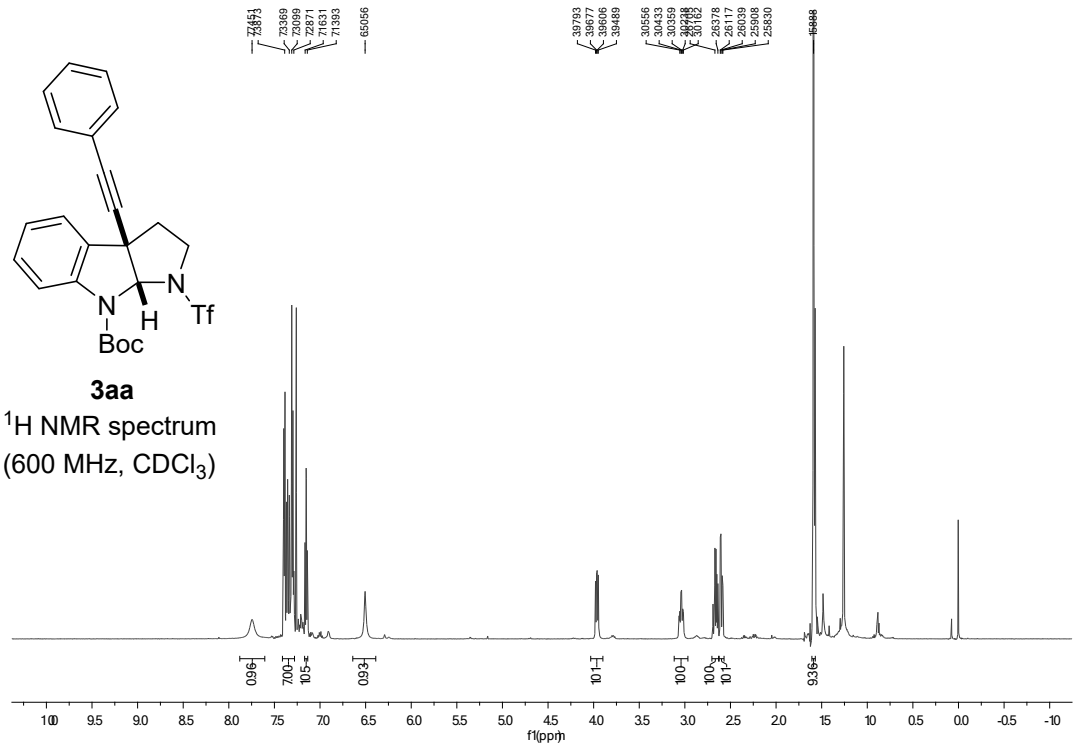

SO2Ph
2u
13C NMR spectrum
(100 MHz, CDCl3)
f1(ppm)


SO2Ph
2v
1H NMR spectrum
(400 MHz, CDCl3)
f1(ppm)


SO2Ph
2v
13C NMR spectrum
(100 MHz, CDCl3)
f1(ppm)


SO2Ph
2w
1H NMR spectrum
(600 MHz, CDCl3)
f1(ppm)

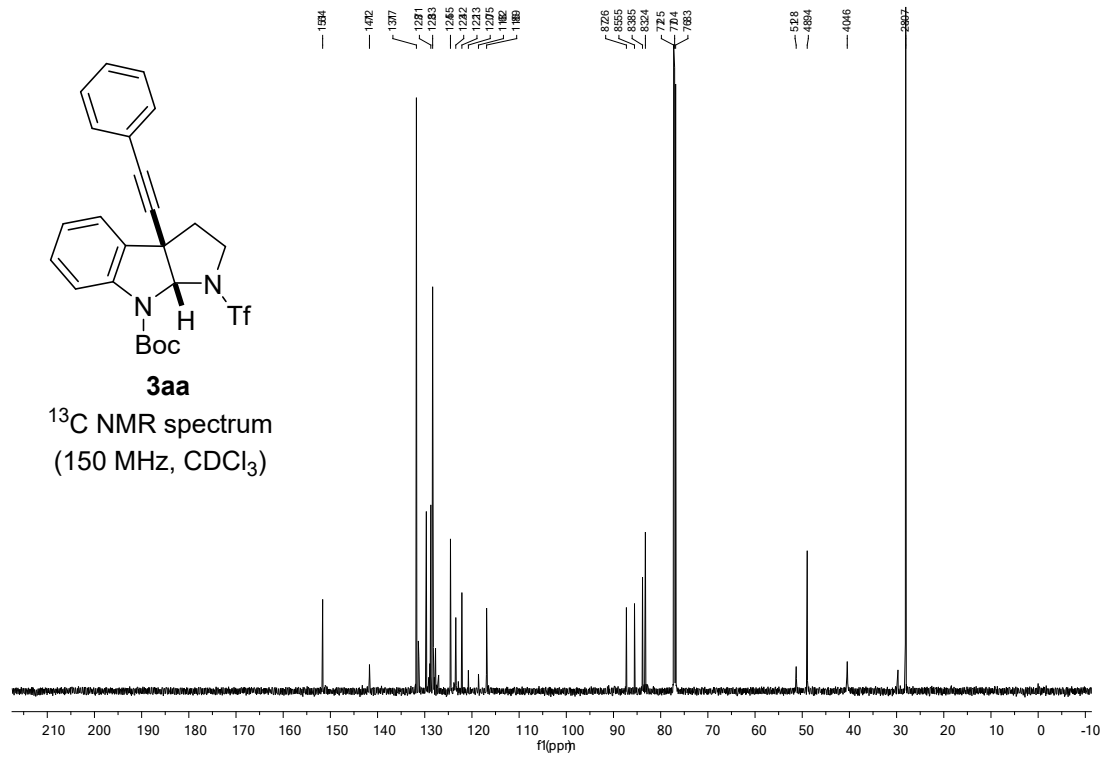

SO2Ph
2w
13C NMR spectrum
(150 MHz, CDCl3)
f1(ppm)



3aa

^{1}H NMR spectrum

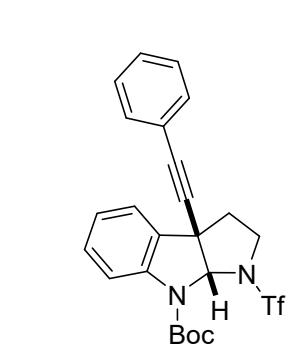
(600 MHz, $CDCl_3$)



3aa

^{13}C NMR spectrum

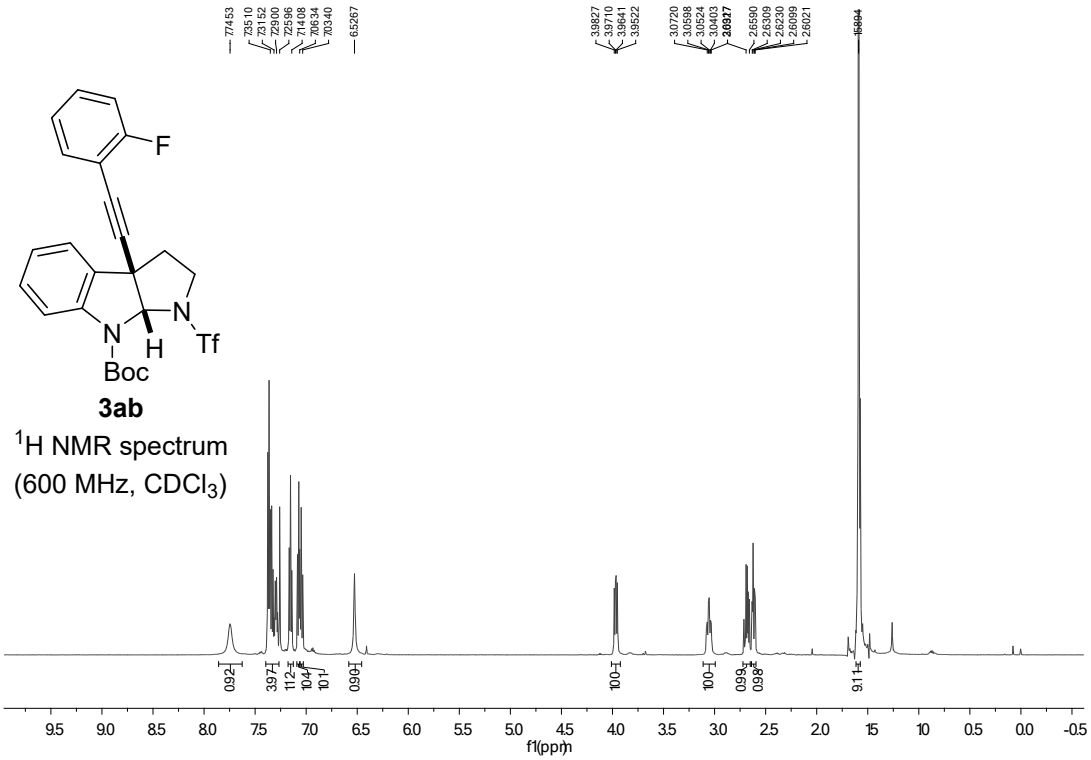
(150 MHz, $CDCl_3$)



3aa

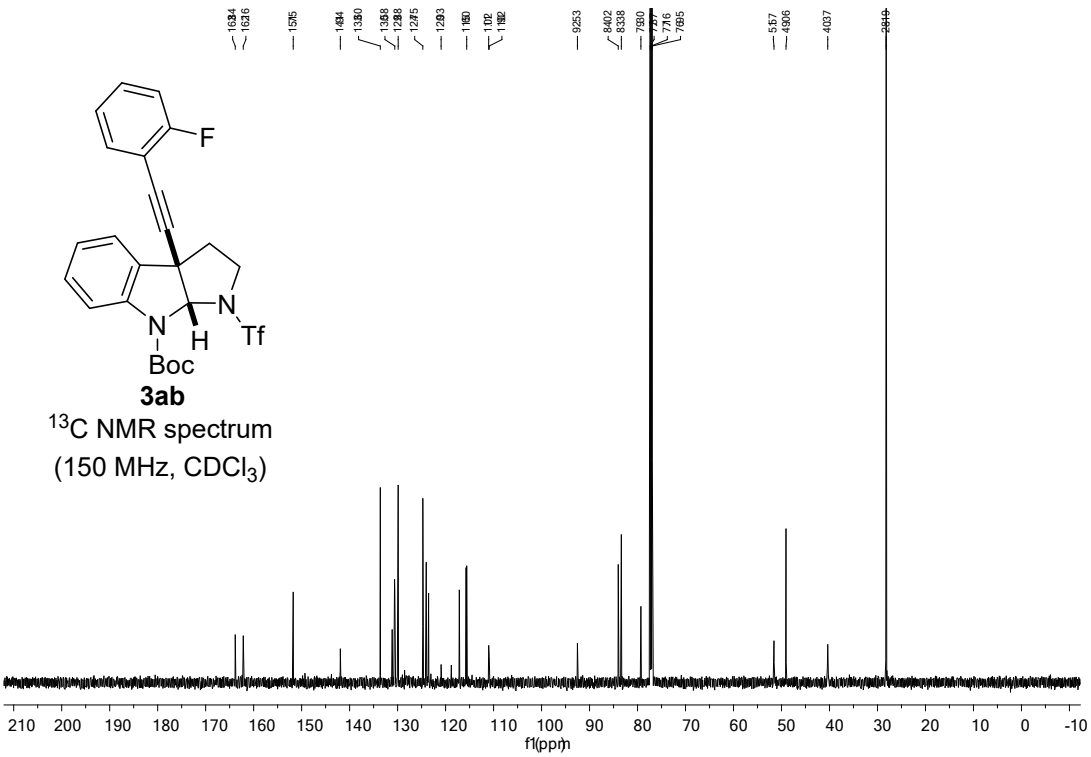
^{19}F NMR spectrum

(564 MHz, $CDCl_3$)



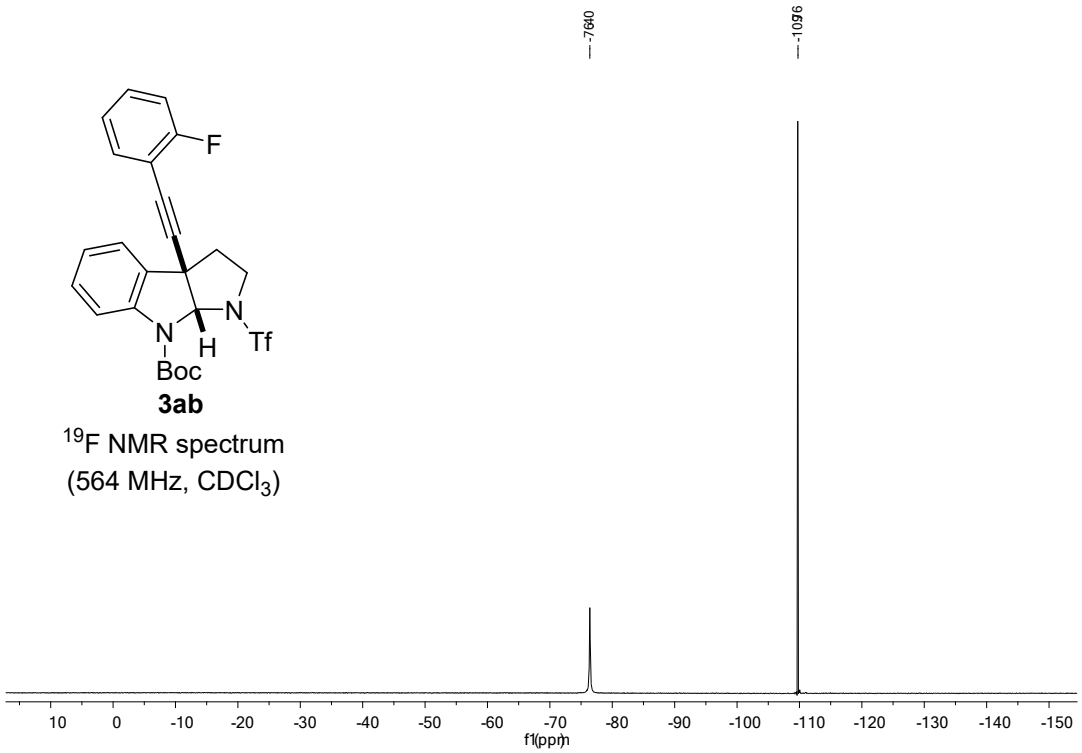
3ab

^{1}H NMR spectrum
(600 MHz, $CDCl_3$)



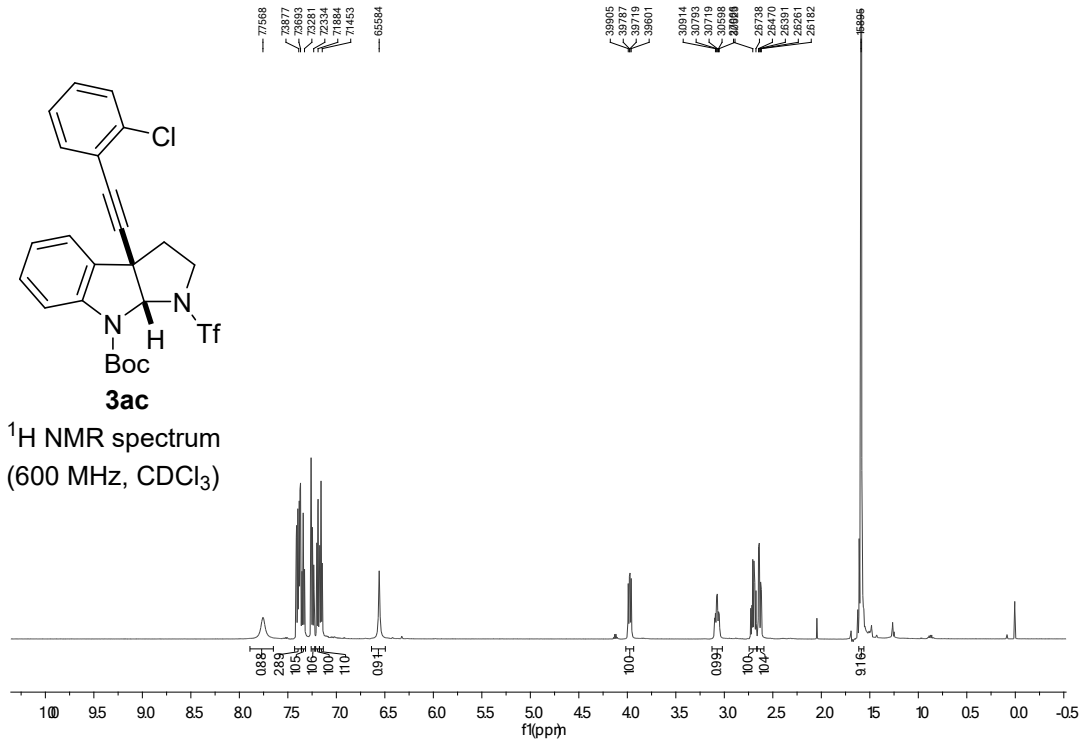
3ab

^{13}C NMR spectrum
(150 MHz, $CDCl_3$)



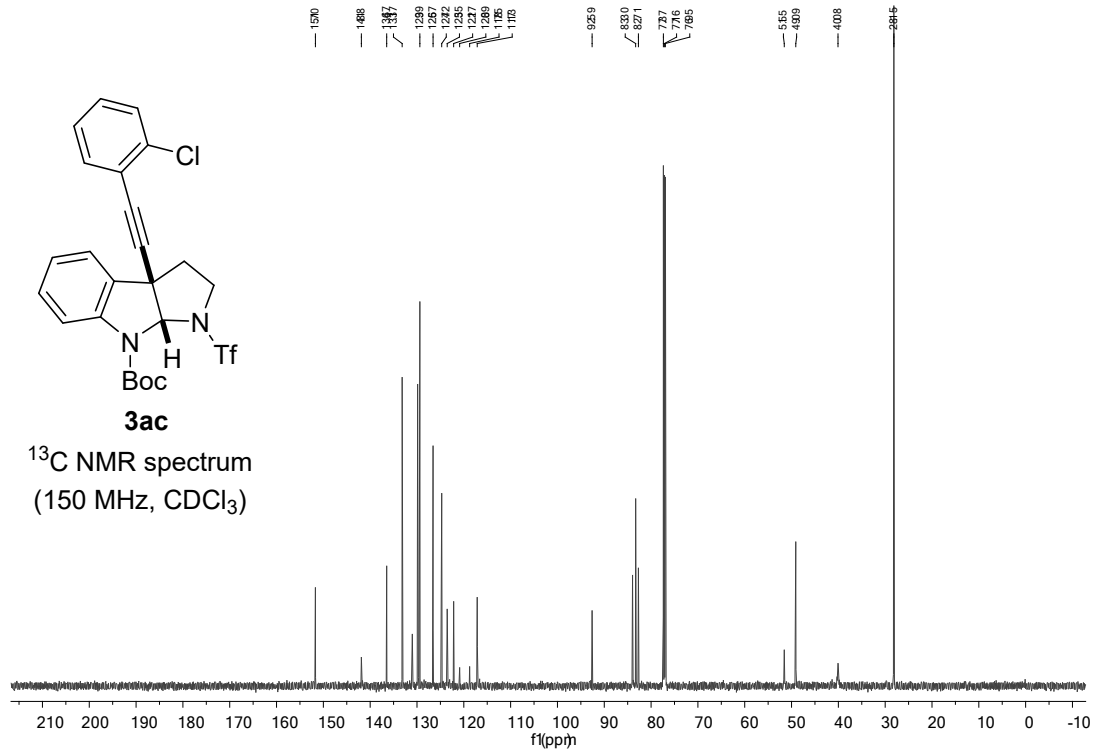
3ab

^{19}F NMR spectrum
(564 MHz, $CDCl_3$)



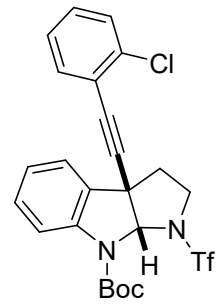
3ac

^{1}H NMR spectrum
(600 MHz, $CDCl_3$)



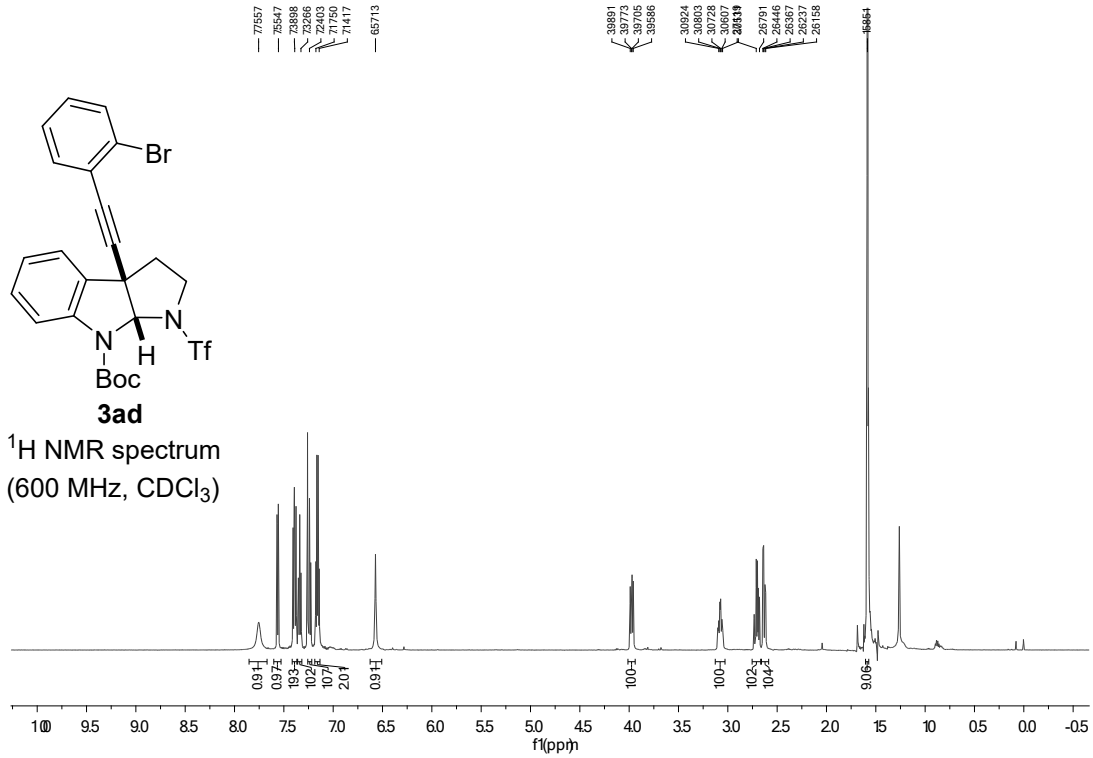
3ac

^{13}C NMR spectrum
(150 MHz, $CDCl_3$)



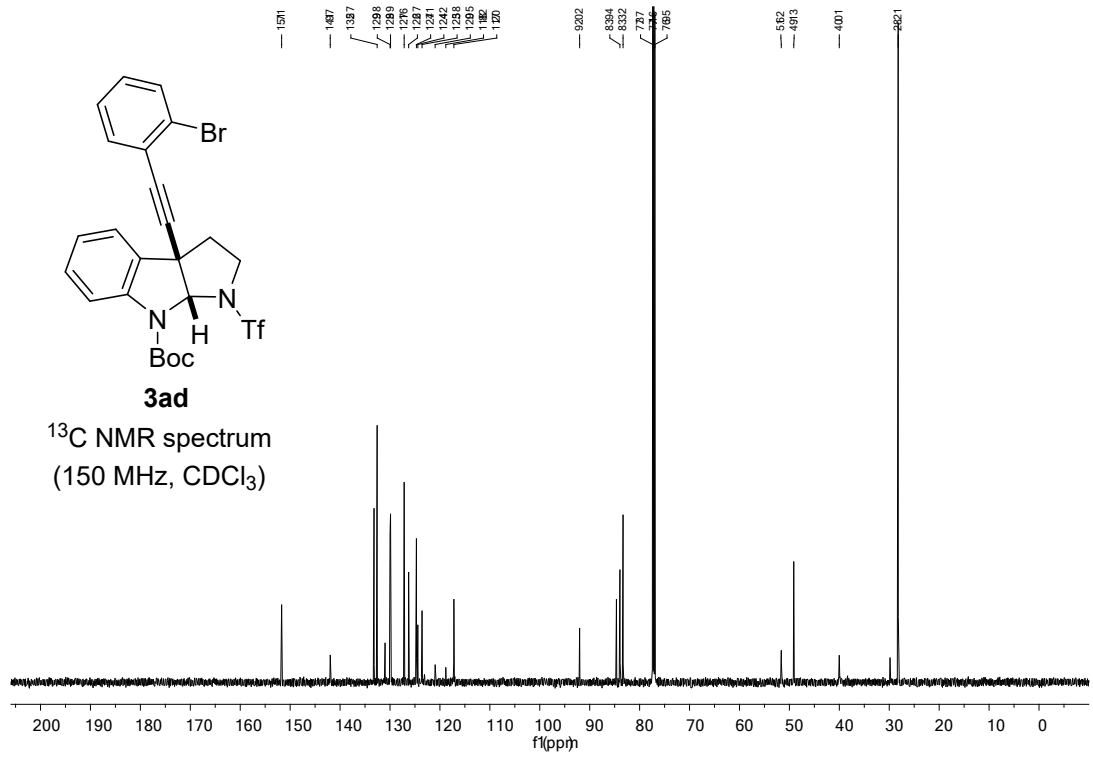
3ac

^{19}F NMR spectrum
(564 MHz, $CDCl_3$)



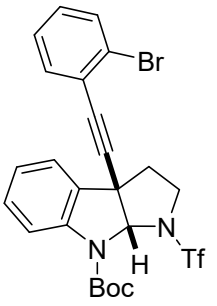
3ad

^{1}H NMR spectrum
(600 MHz, $CDCl_3$)



3ad

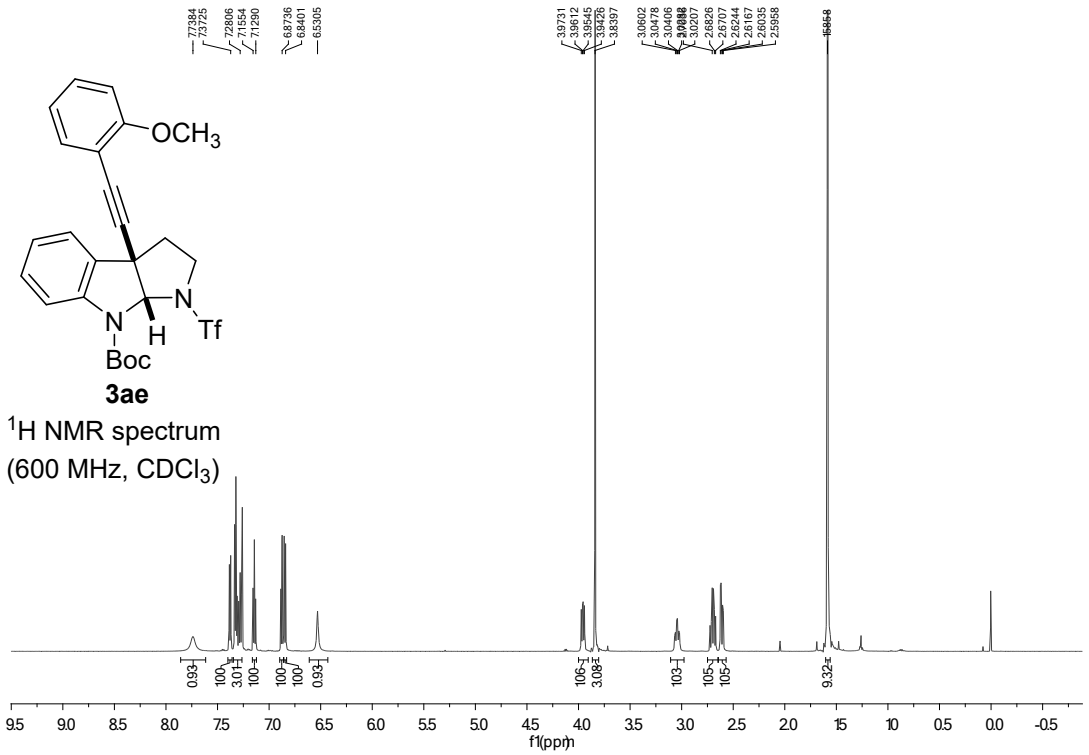
^{13}C NMR spectrum
(150 MHz, $CDCl_3$)



3ad

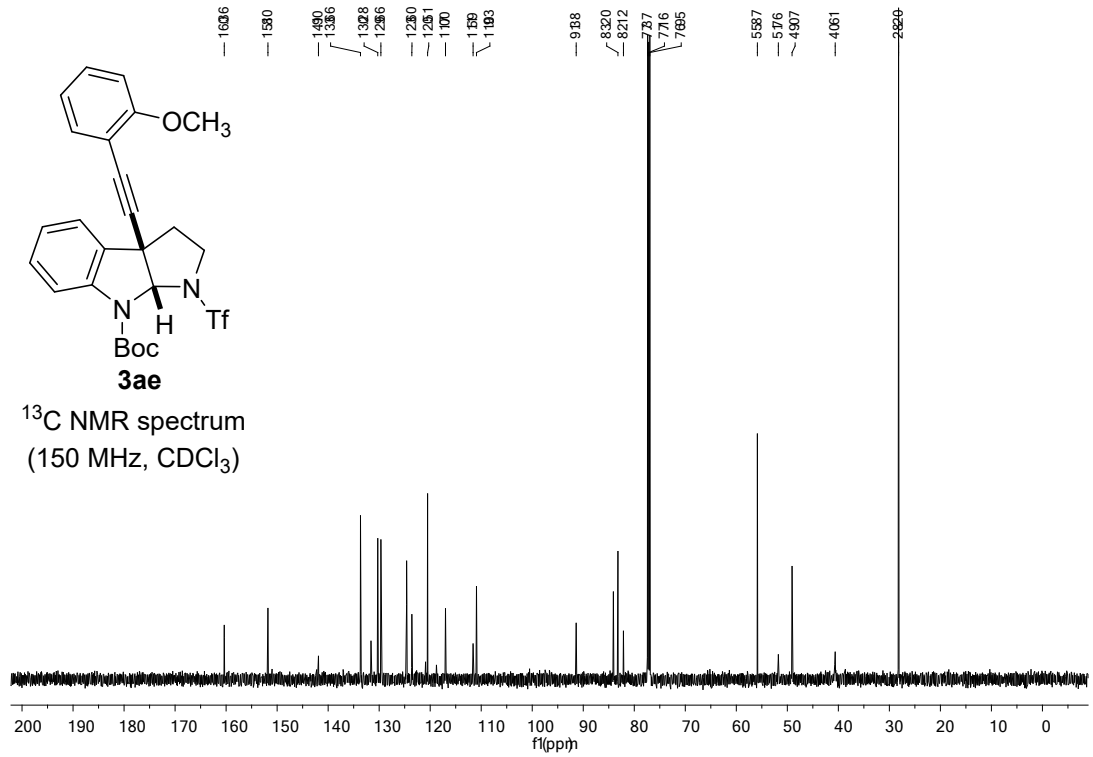
^{19}F NMR spectrum

(564 MHz, $CDCl_3$)



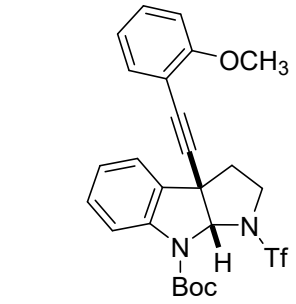
3ae

^{1}H NMR spectrum
(600 MHz, $CDCl_3$)



3ae

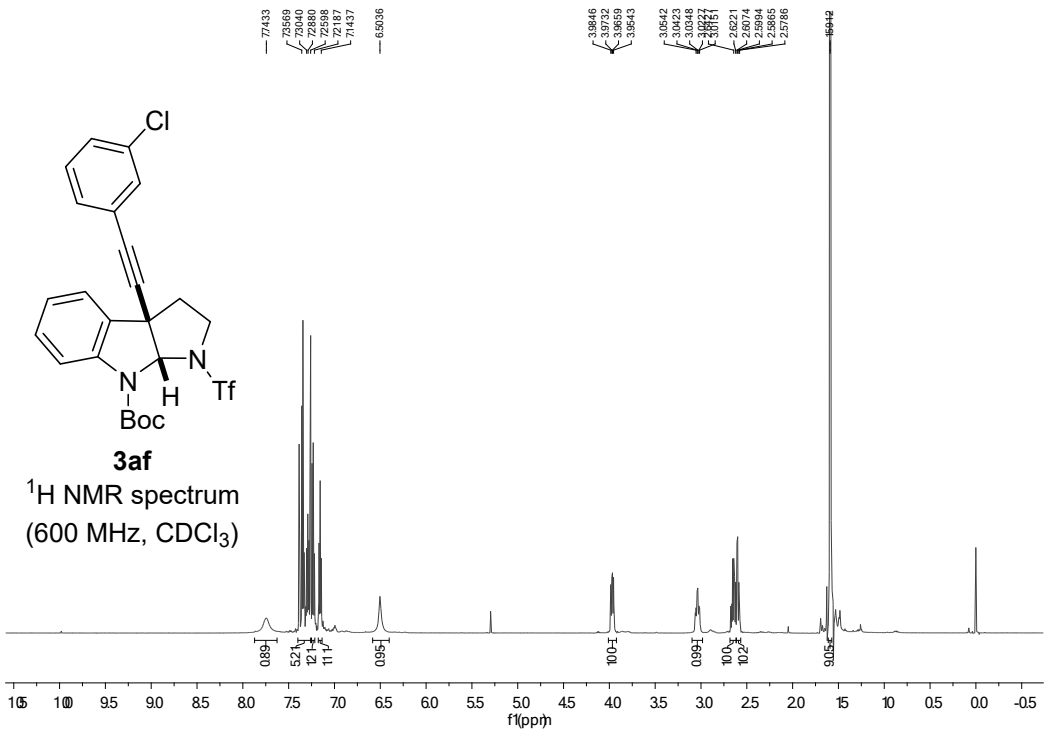
^{13}C NMR spectrum
(150 MHz, $CDCl_3$)



3ae

^{19}F NMR spectrum

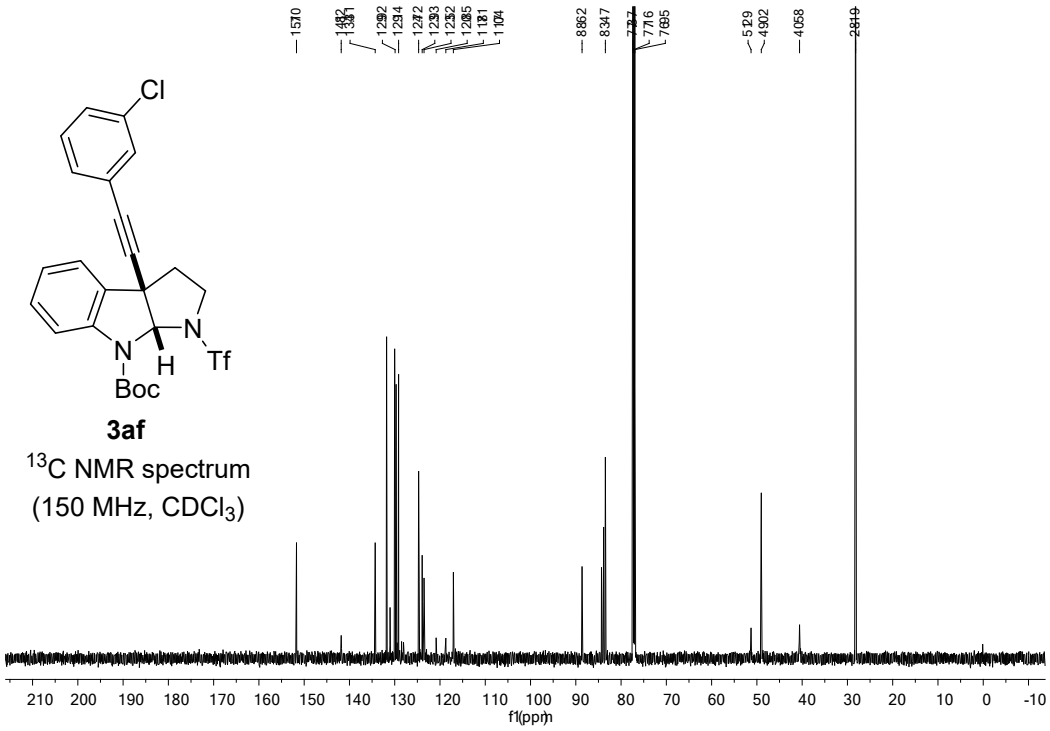
(564 MHz, $CDCl_3$)



3af

^{1}H NMR spectrum

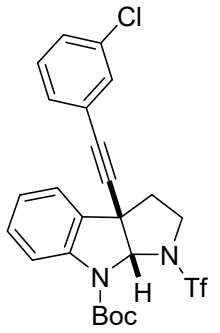
(600 MHz, $CDCl_3$)



3af

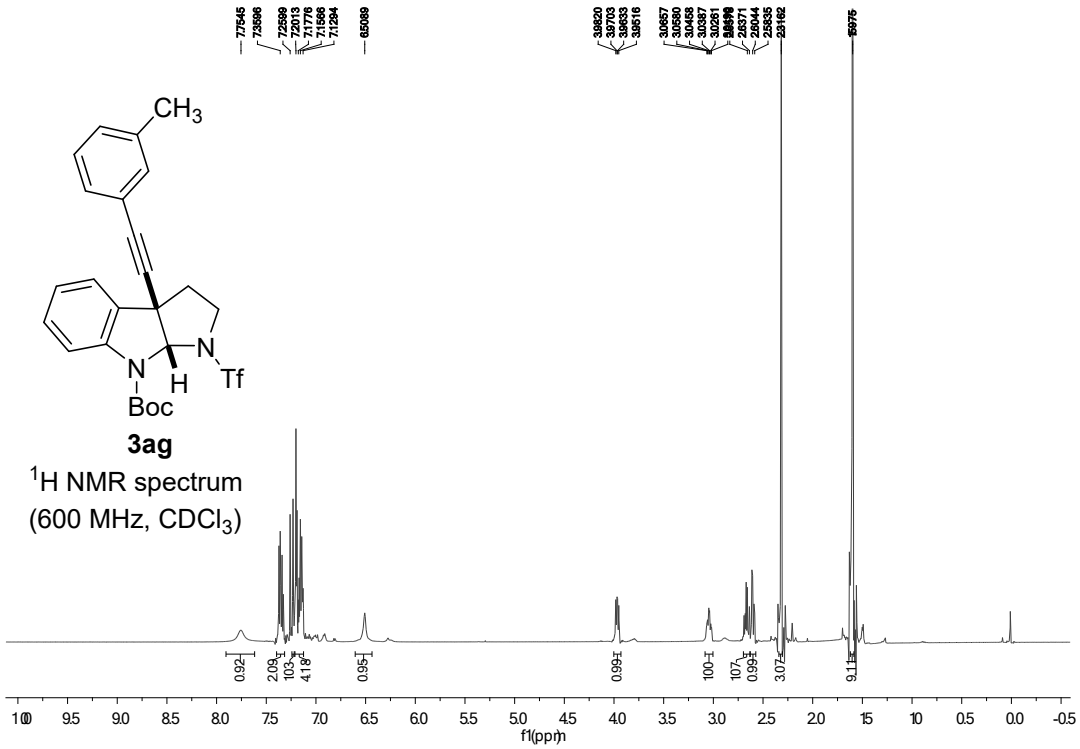
^{13}C NMR spectrum

(150 MHz, $CDCl_3$)



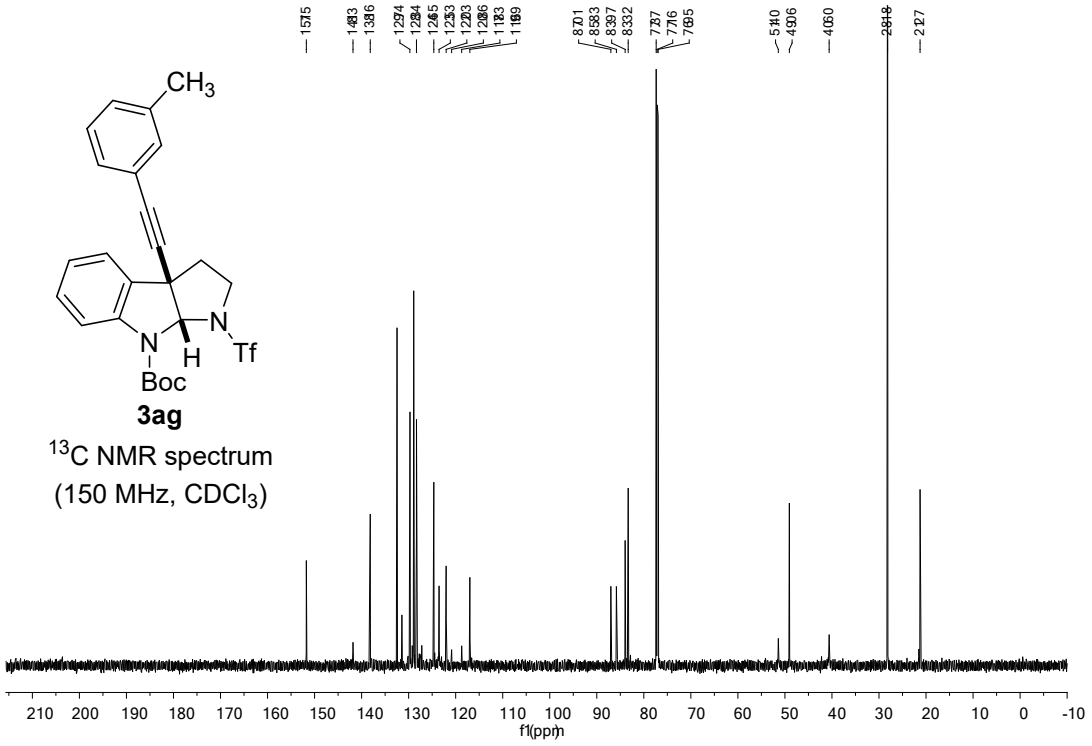
3af

^{19}F NMR spectrum
(564 MHz, $CDCl_3$)



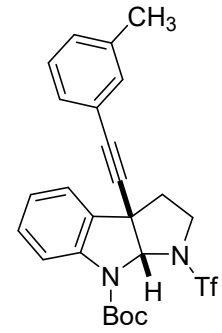
3ag

^{1}H NMR spectrum
(600 MHz, $CDCl_3$)



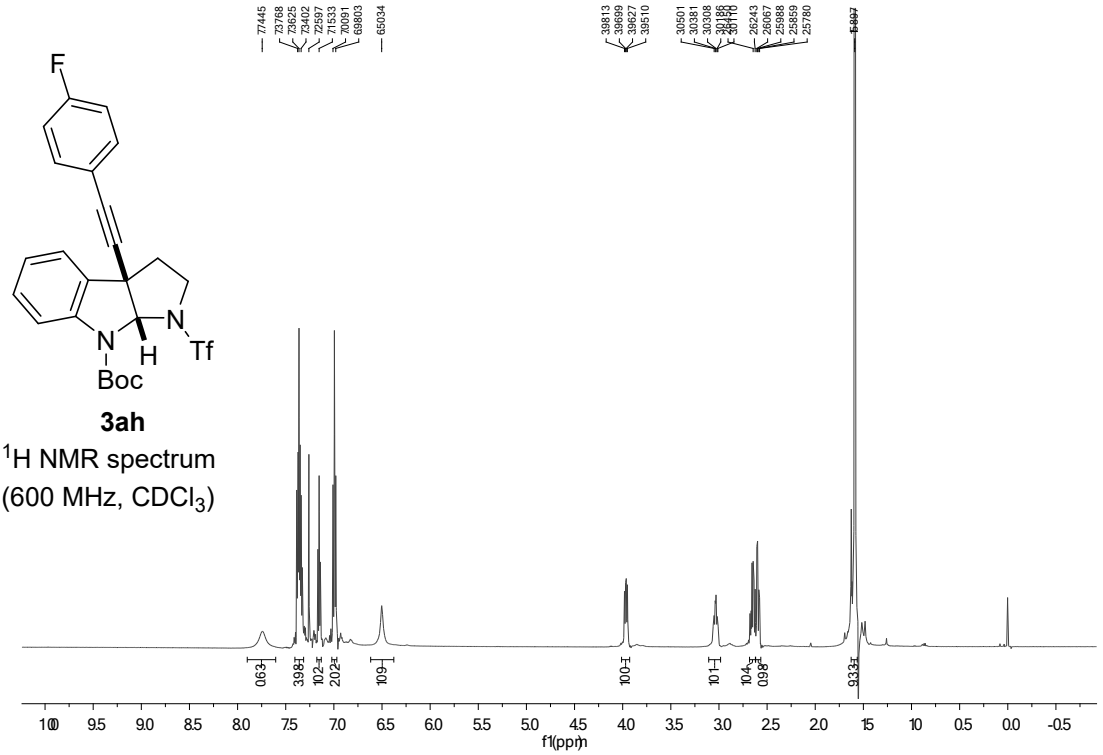
3ag

^{13}C NMR spectrum
(150 MHz, $CDCl_3$)



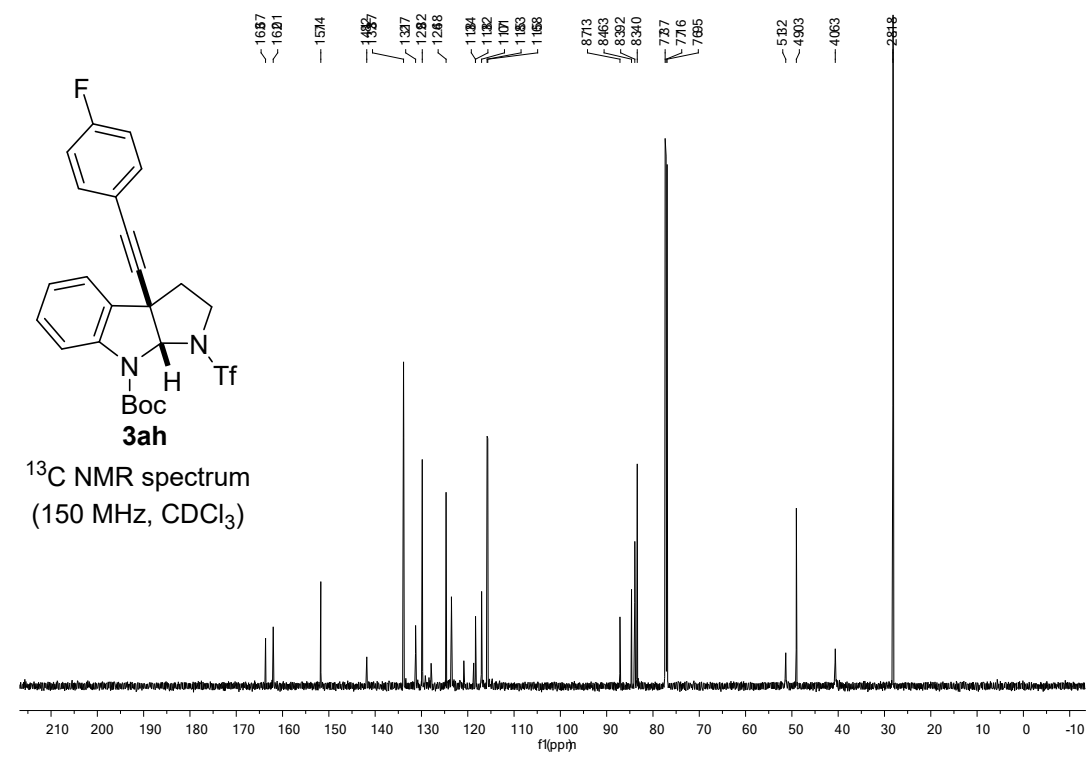
3ag

^{19}F NMR spectrum
(564 MHz, $CDCl_3$)



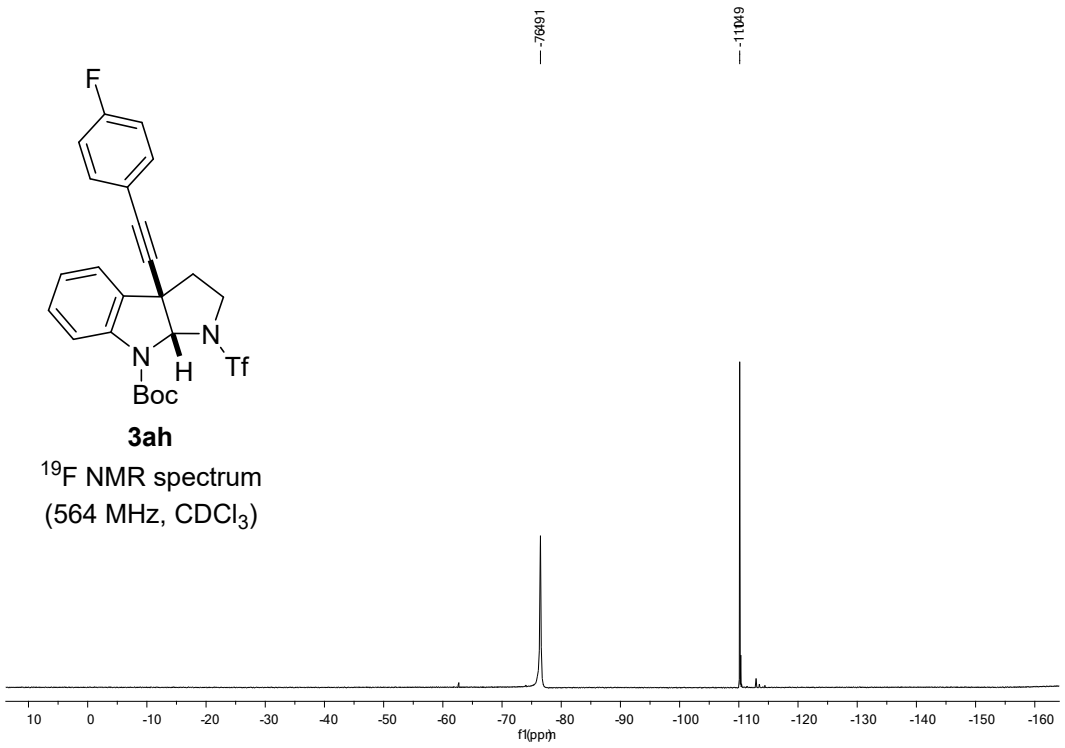
3ah

^{1}H NMR spectrum
(600 MHz, $CDCl_3$)



3ah

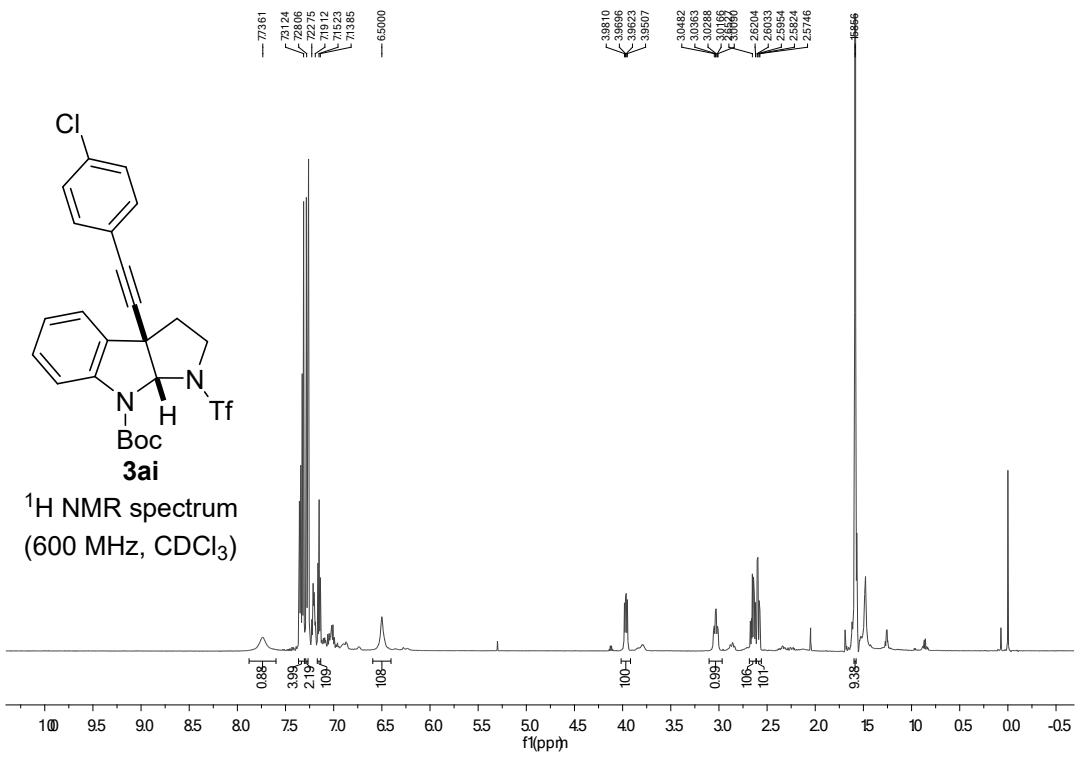
^{13}C NMR spectrum
(150 MHz, $CDCl_3$)

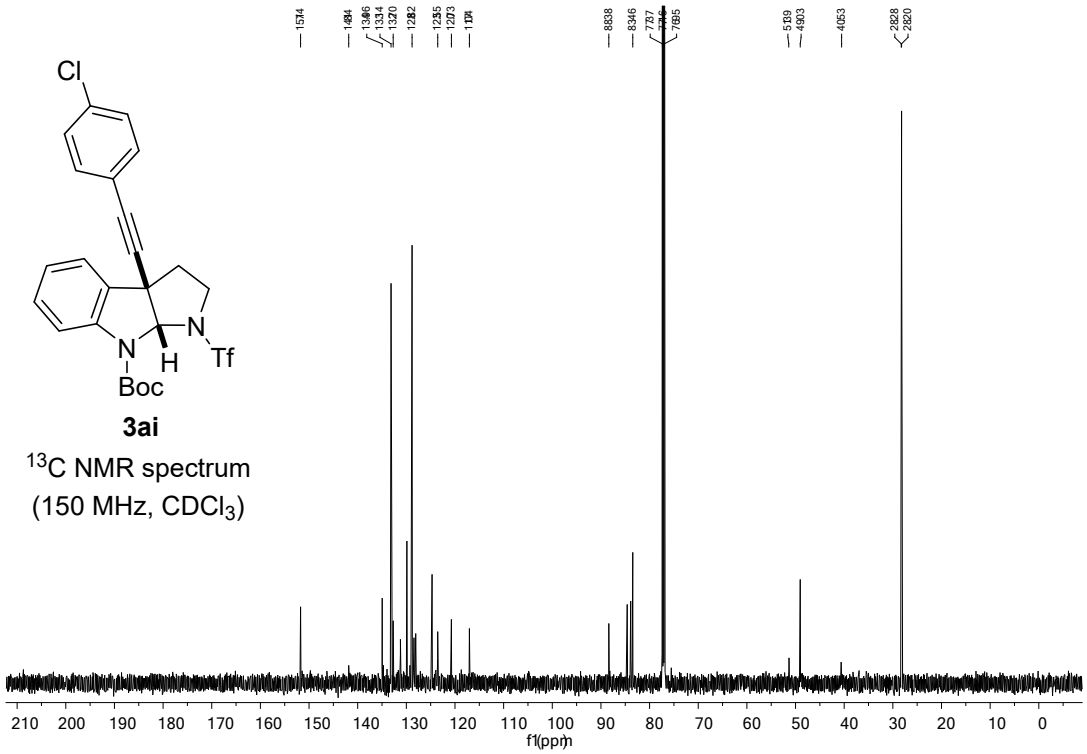


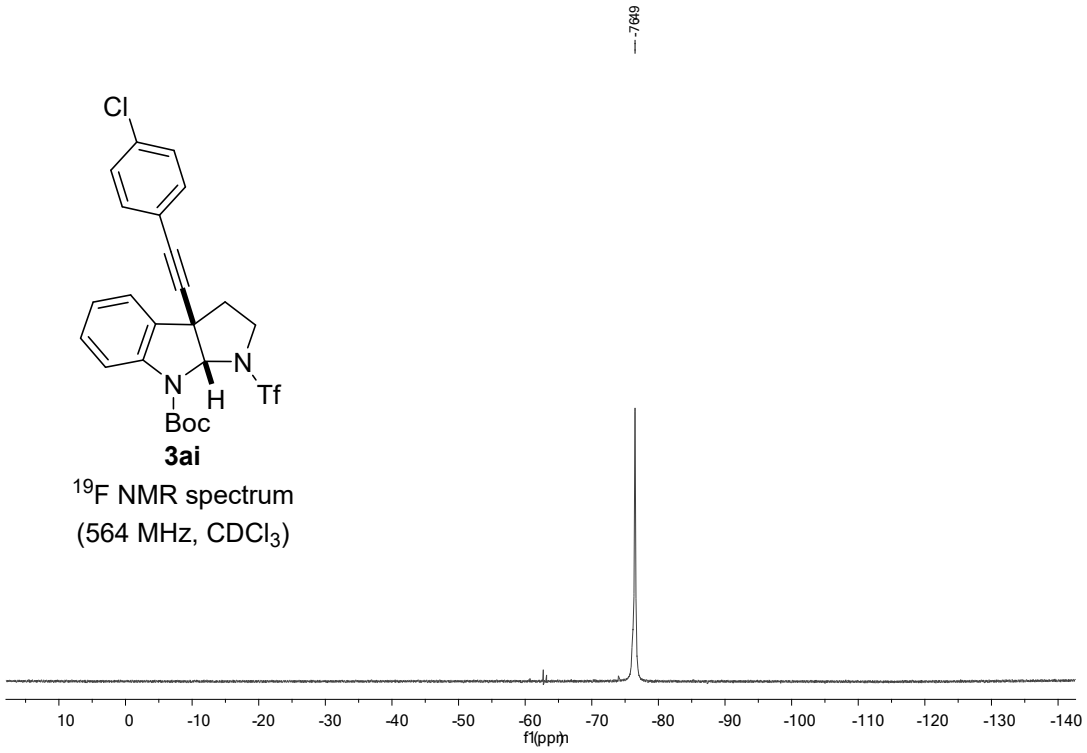
3ah

^{19}F NMR spectrum

(564 MHz, $CDCl_3$)


Cl
N
N
H
Tf
Boc
3ai
1H NMR spectrum
(600 MHz, CDCl3)
f1(ppm)

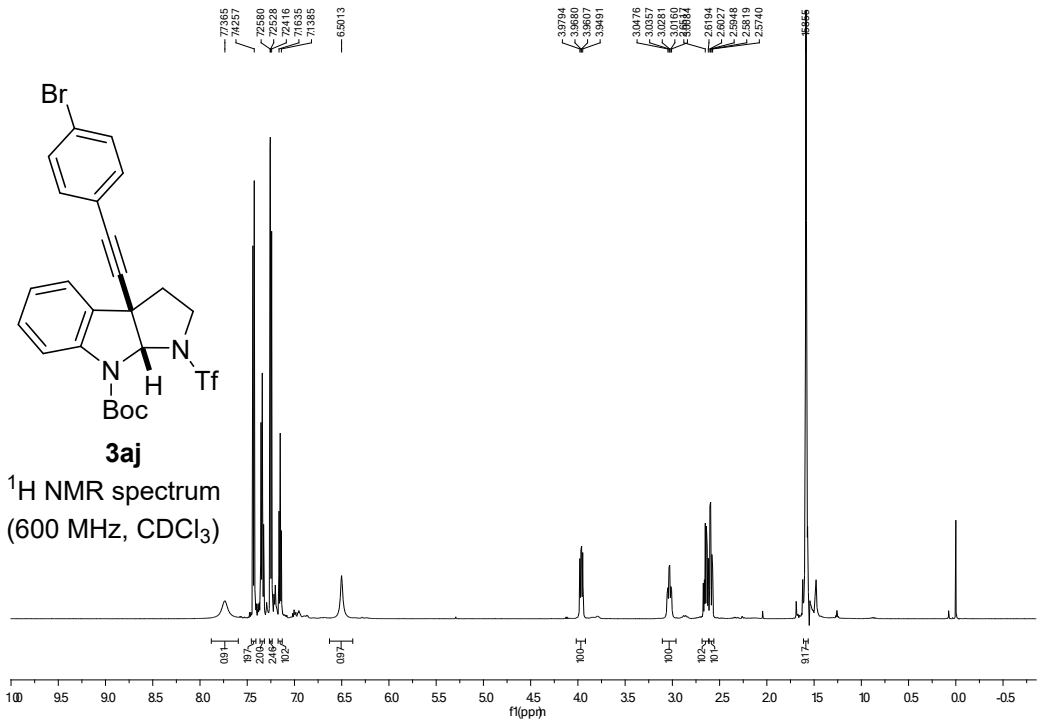

Cl
N
N
H
Tf
Boc
3ai
13C NMR spectrum
(150 MHz, CDCl3)
f1(ppm)

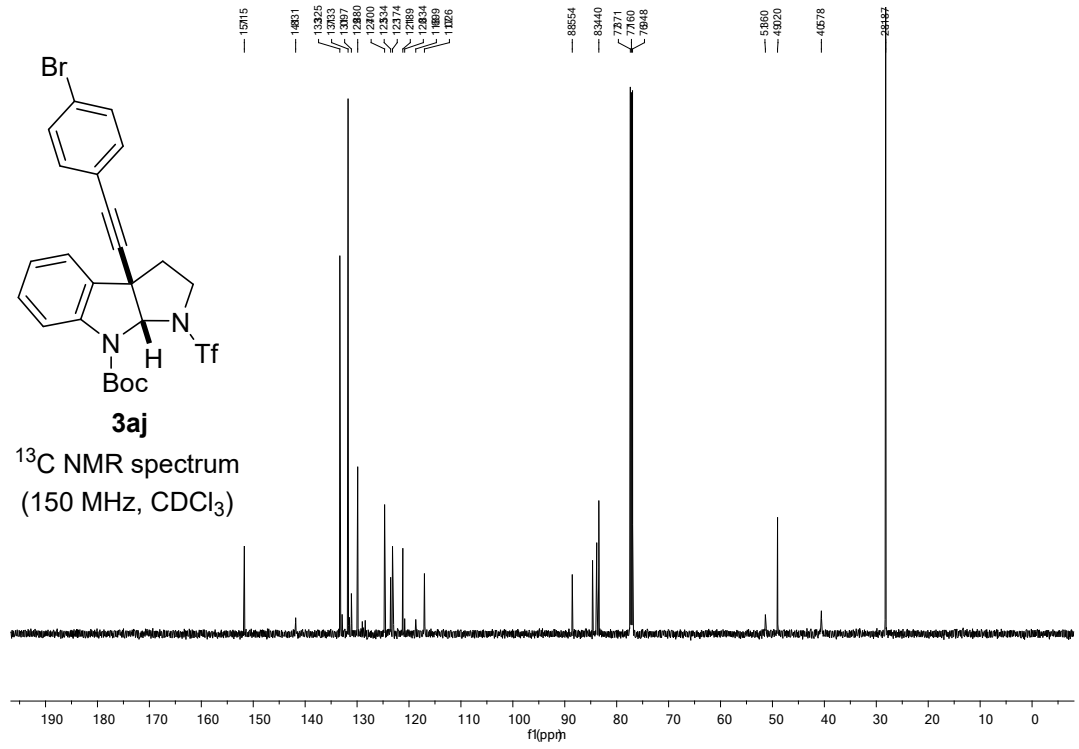


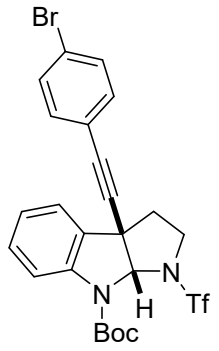
3ai

^{19}F NMR spectrum

(564 MHz, $CDCl_3$)

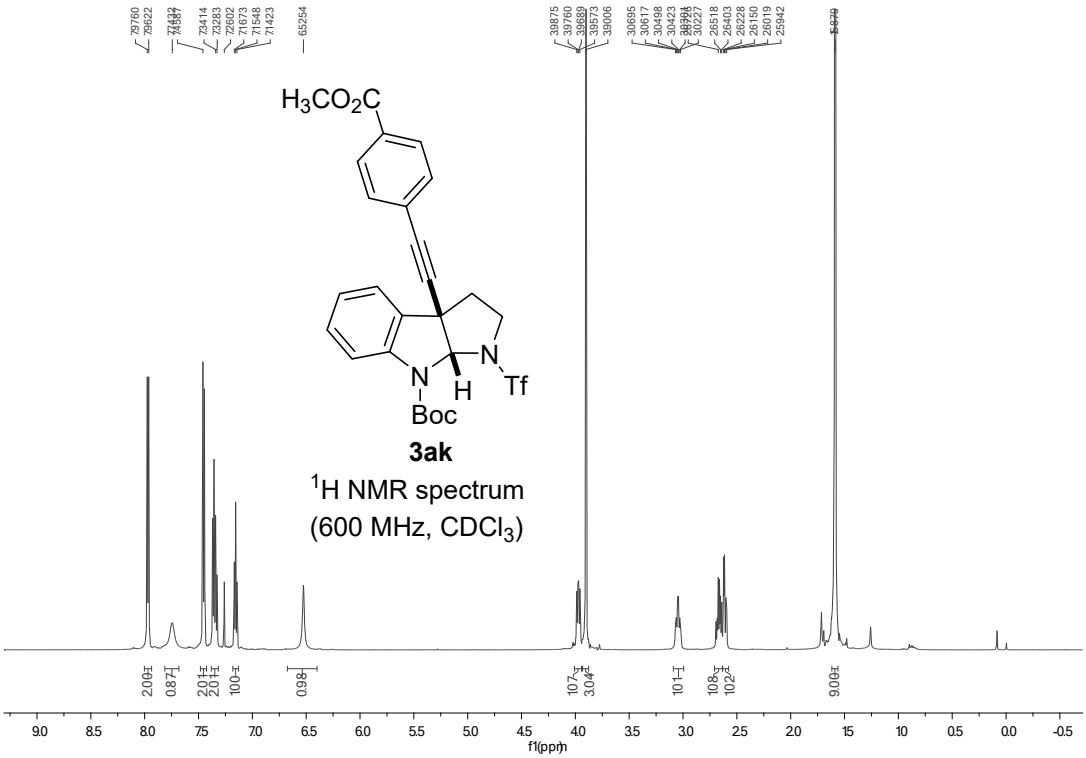

Br
N
N
H
Tf
Boc
3aj
1H NMR spectrum
(600 MHz, CDCl3)
f1(ppm)

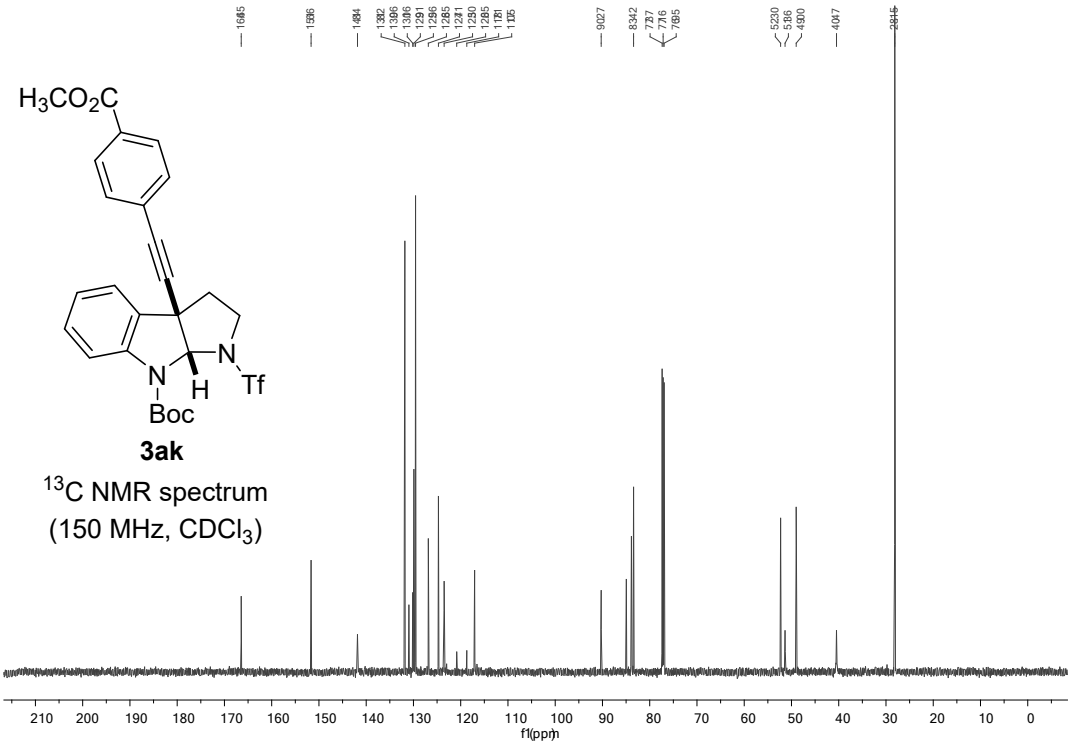

Br
N
N
H
Tf
Boc
3aj
13C NMR spectrum
(150 MHz, CDCl3)
f1(ppm)

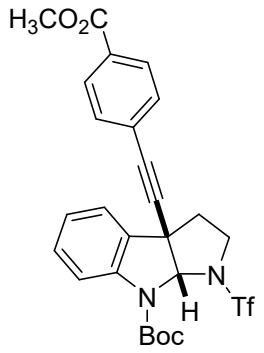


3aj

^{19}F NMR spectrum
(564 MHz, $CDCl_3$)

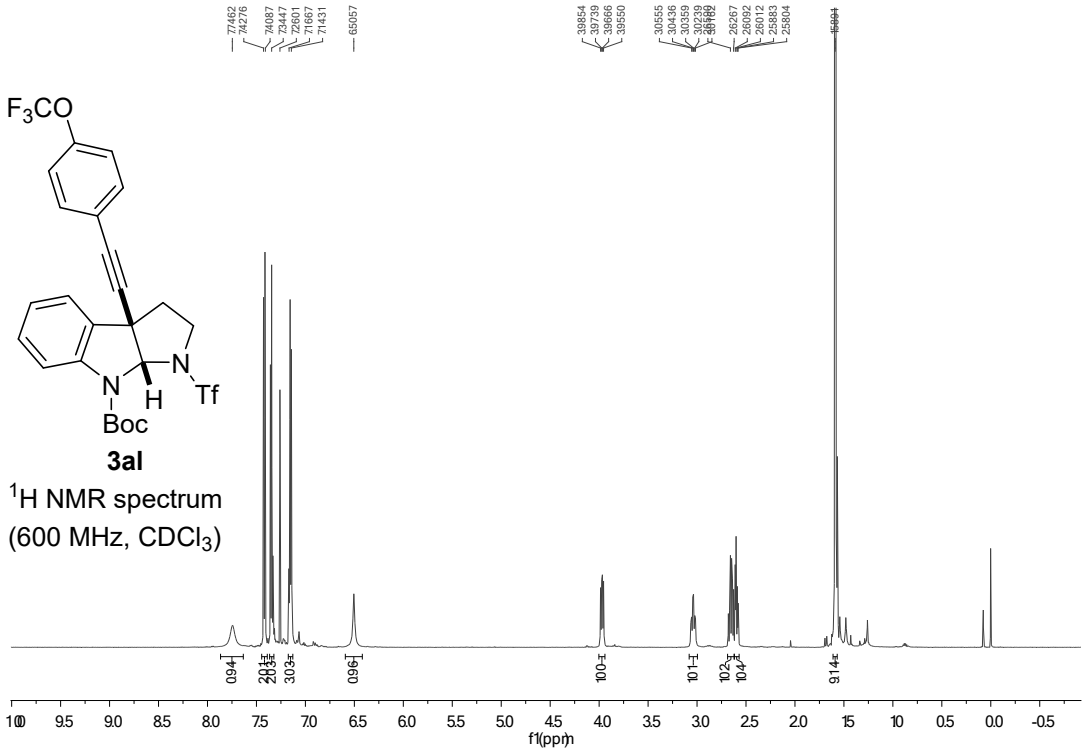

H3CO2C
N
N
H
Tf
Boc
3ak
1H NMR spectrum
(600 MHz, CDCl3)
f1(ppm)


H3CO2C
N
N
H
Tf
Boc
3ak
13C NMR spectrum
(150 MHz, CDCl3)
f1(ppm)



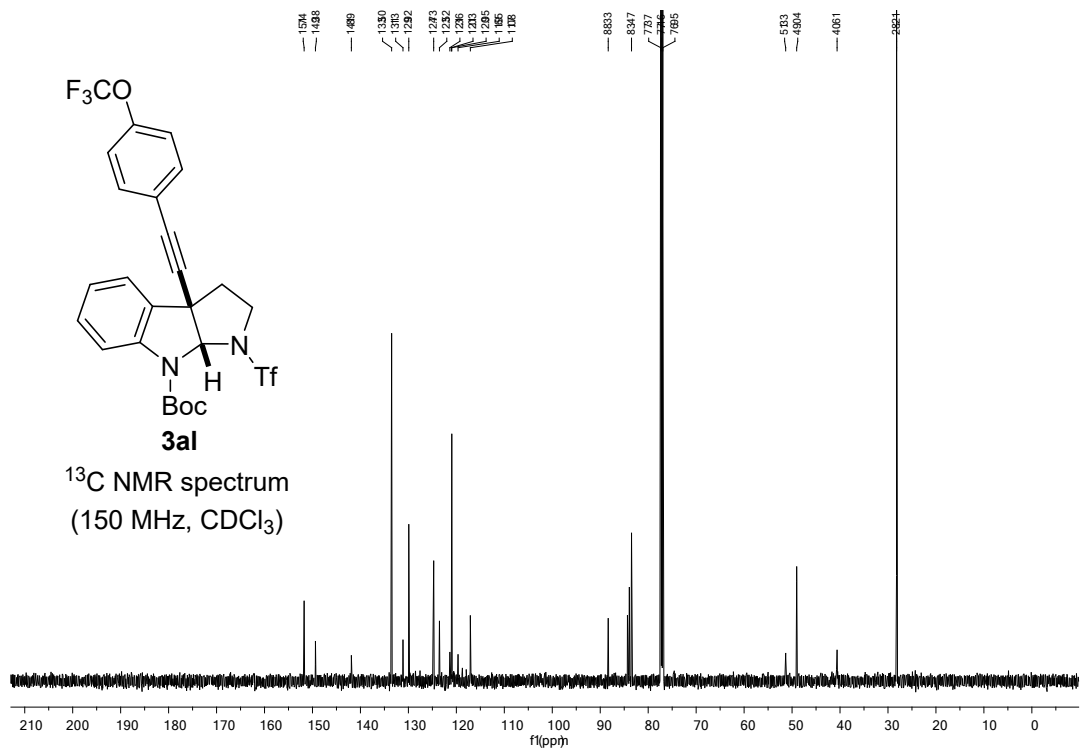
3ak

^{19}F NMR spectrum
(564 MHz, $CDCl_3$)



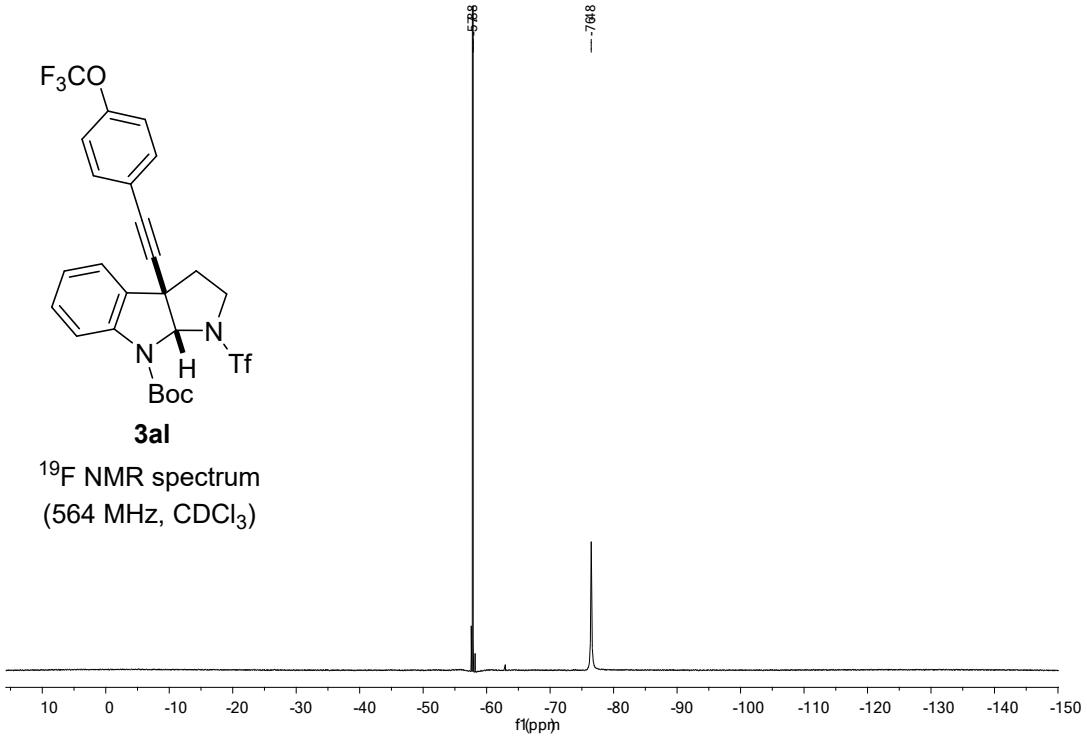
3al

^{1}H NMR spectrum
(600 MHz, $CDCl_3$)



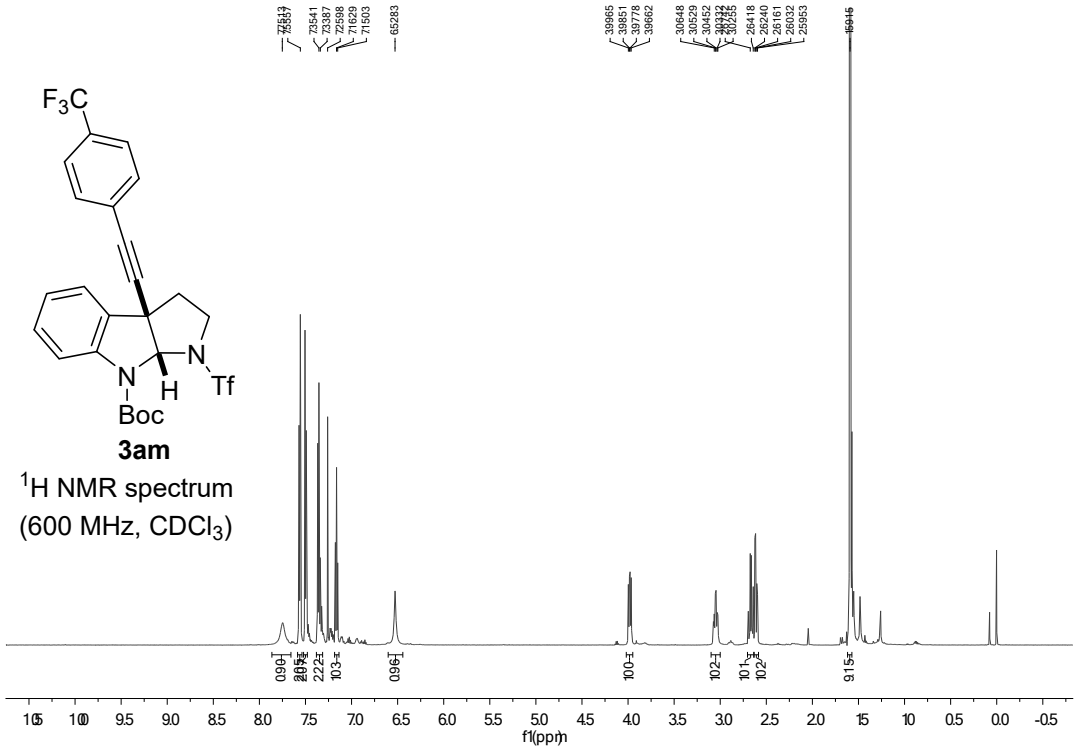
3al

^{13}C NMR spectrum
(150 MHz, $CDCl_3$)



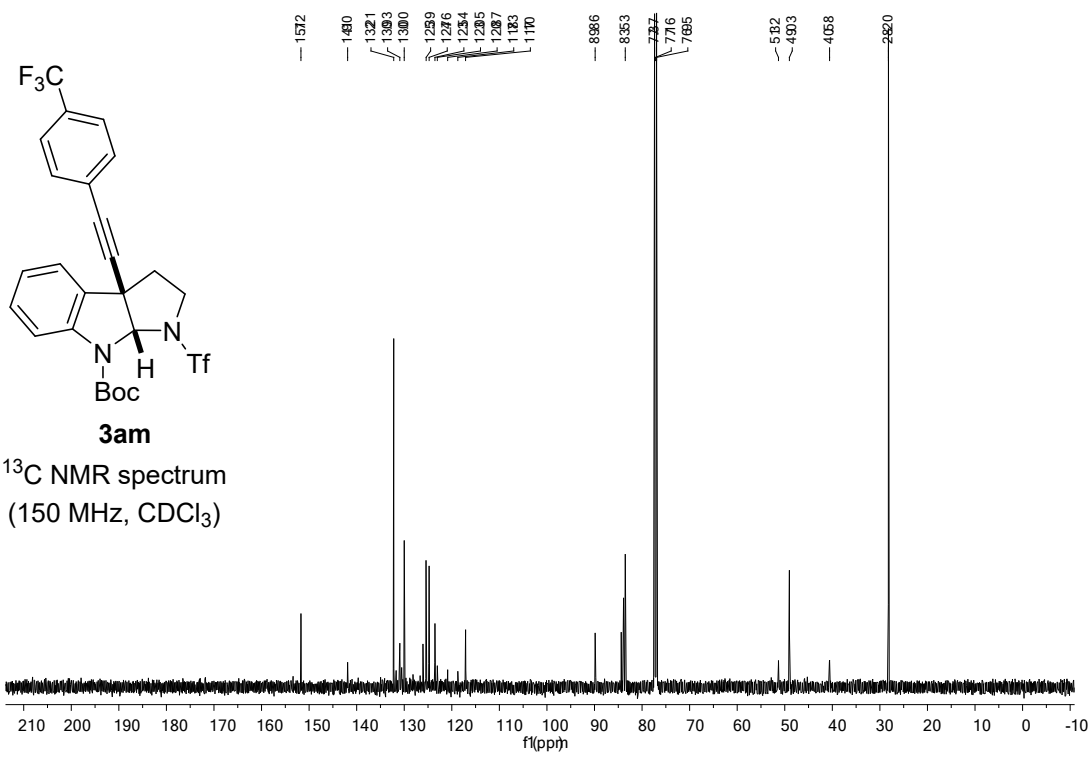
3al

^{19}F NMR spectrum
(564 MHz, $CDCl_3$)



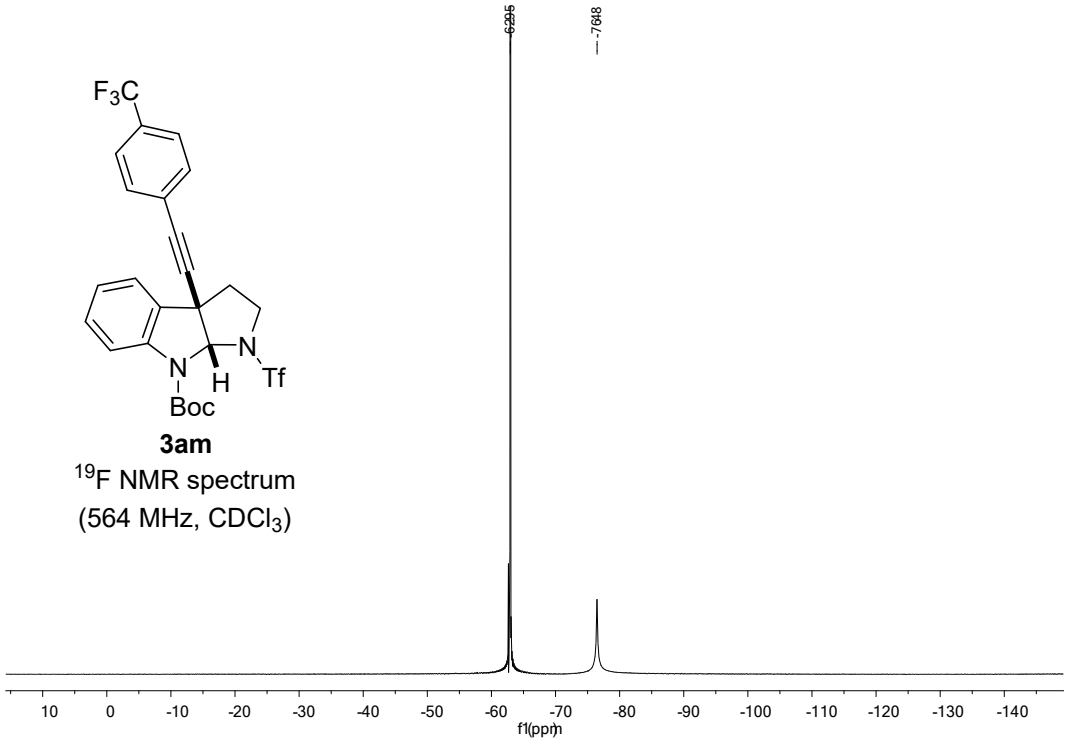
3am

^{1}H NMR spectrum
(600 MHz, $CDCl_3$)



3am

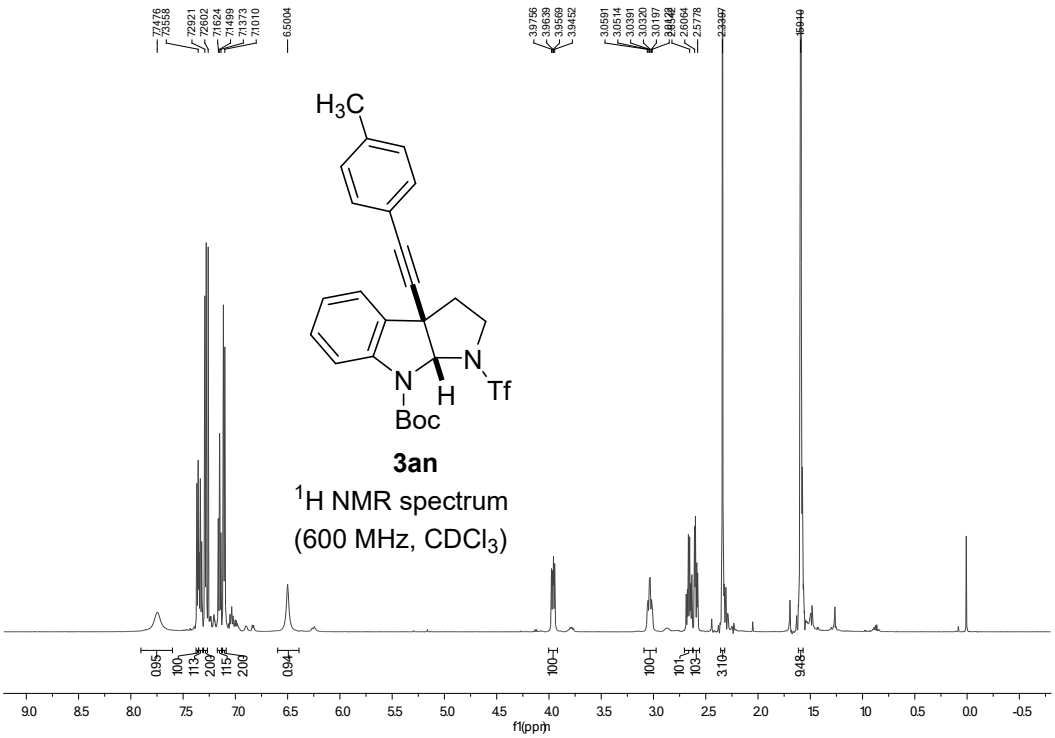
^{13}C NMR spectrum
(150 MHz, $CDCl_3$)

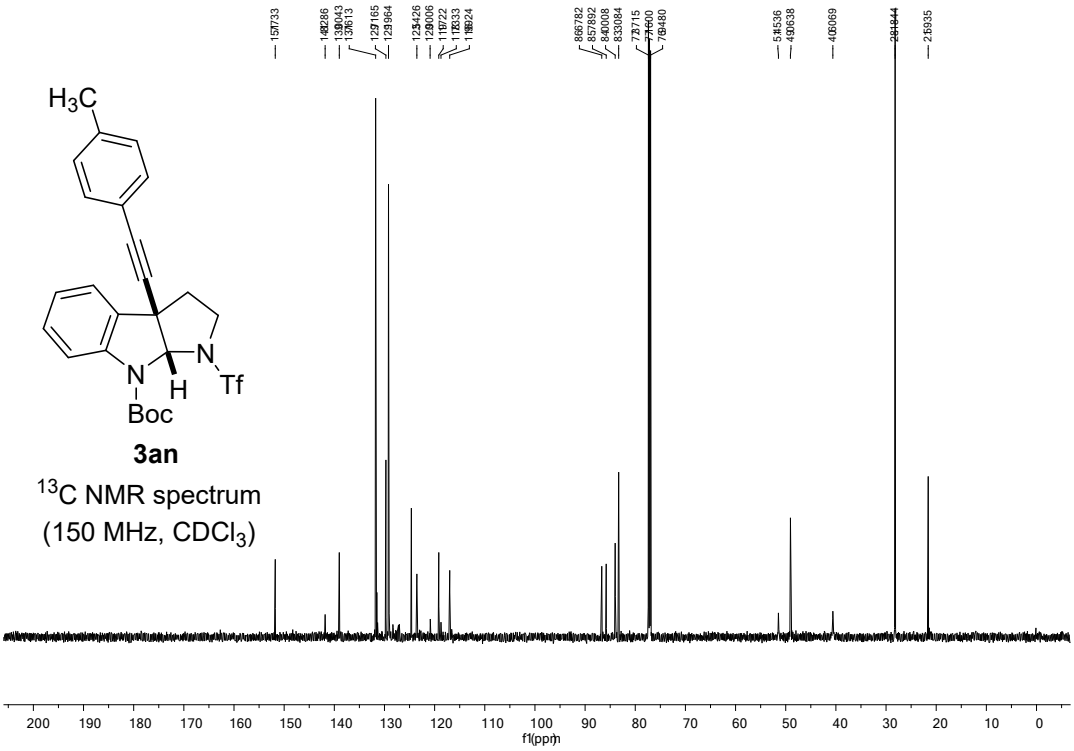


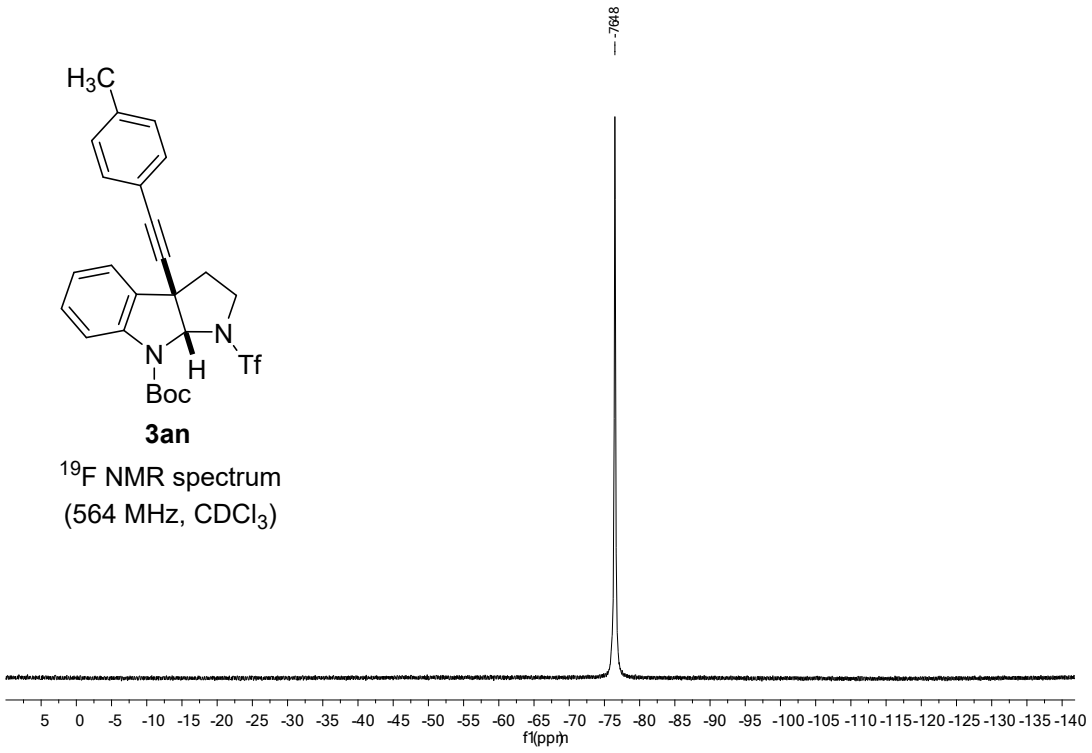
3am

^{19}F NMR spectrum

(564 MHz, $CDCl_3$)

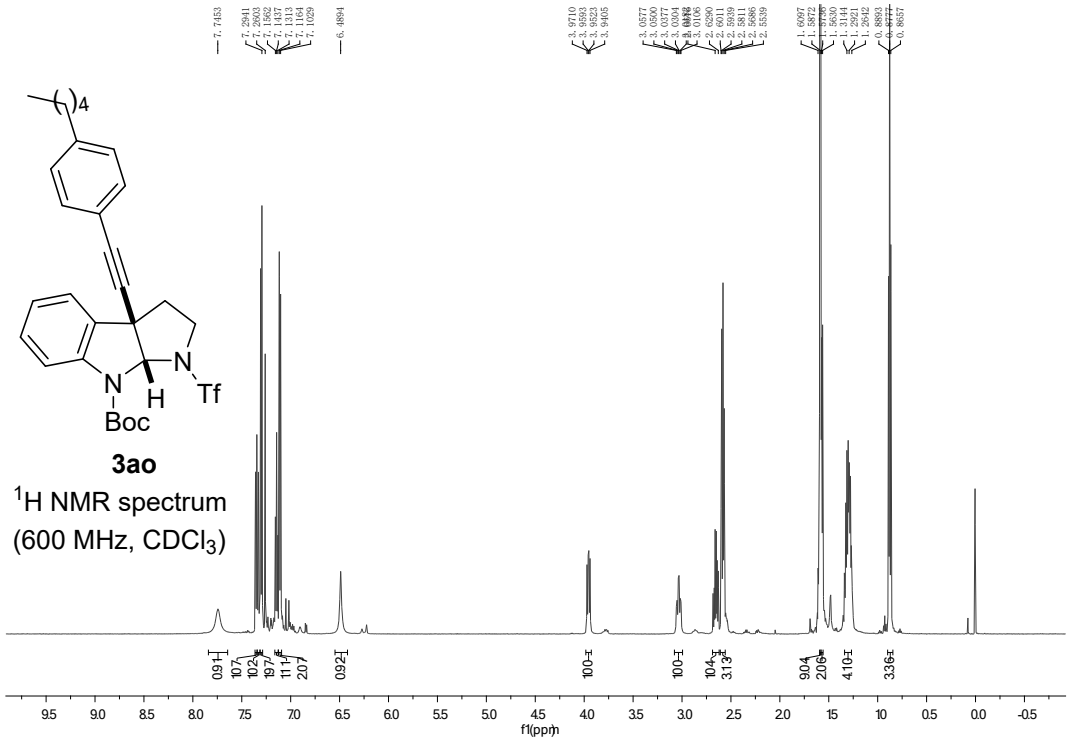

H3C
N
N
Tf
H
Boc
3an
1H NMR spectrum
(600 MHz, CDCl3)
f1(ppm)


H3C
N
N
Tf
H
Boc
3an
13C NMR spectrum
(150 MHz, CDCl3)
f1(ppm)



3an

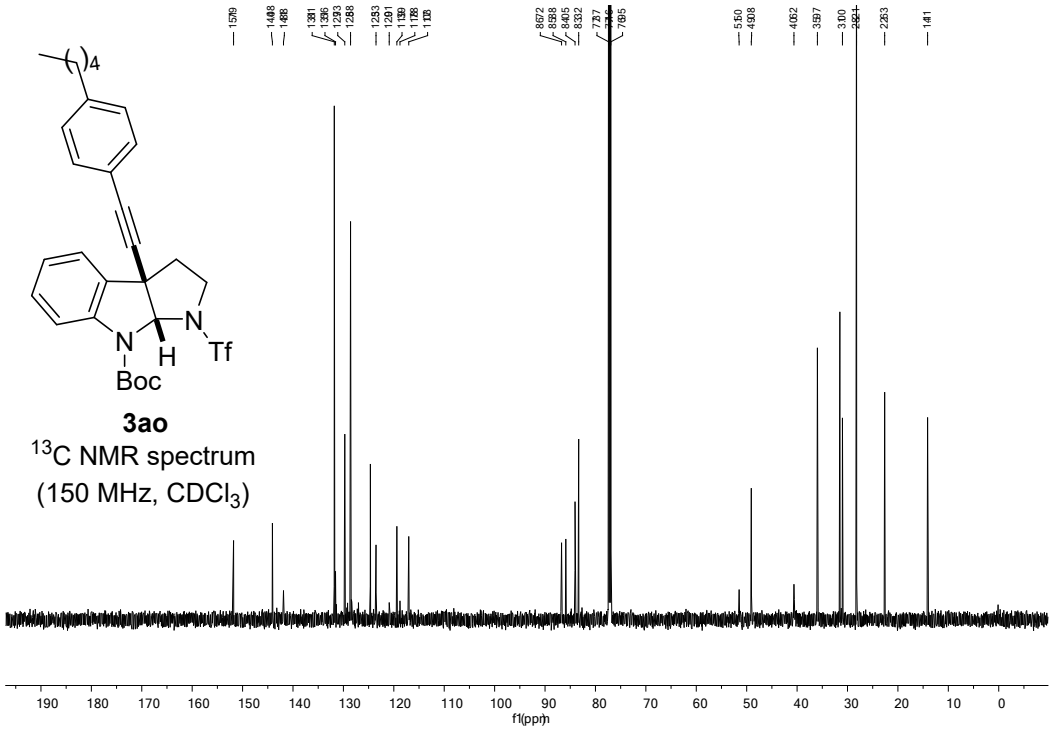
^{19}F NMR spectrum
(564 MHz, $CDCl_3$)



3ao

^{1}H NMR spectrum

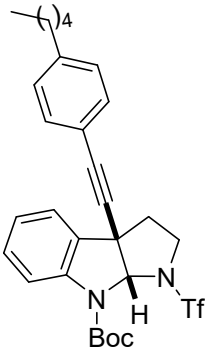
(600 MHz, $CDCl_3$)



3ao

^{13}C NMR spectrum

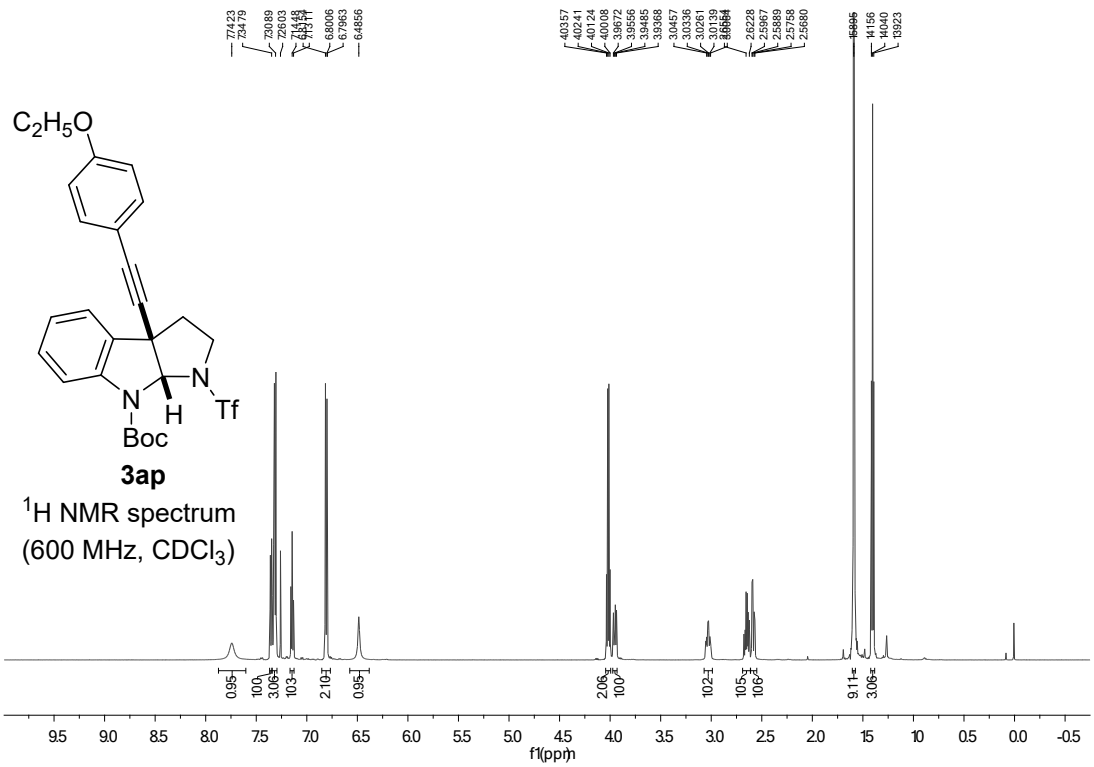
(150 MHz, $CDCl_3$)

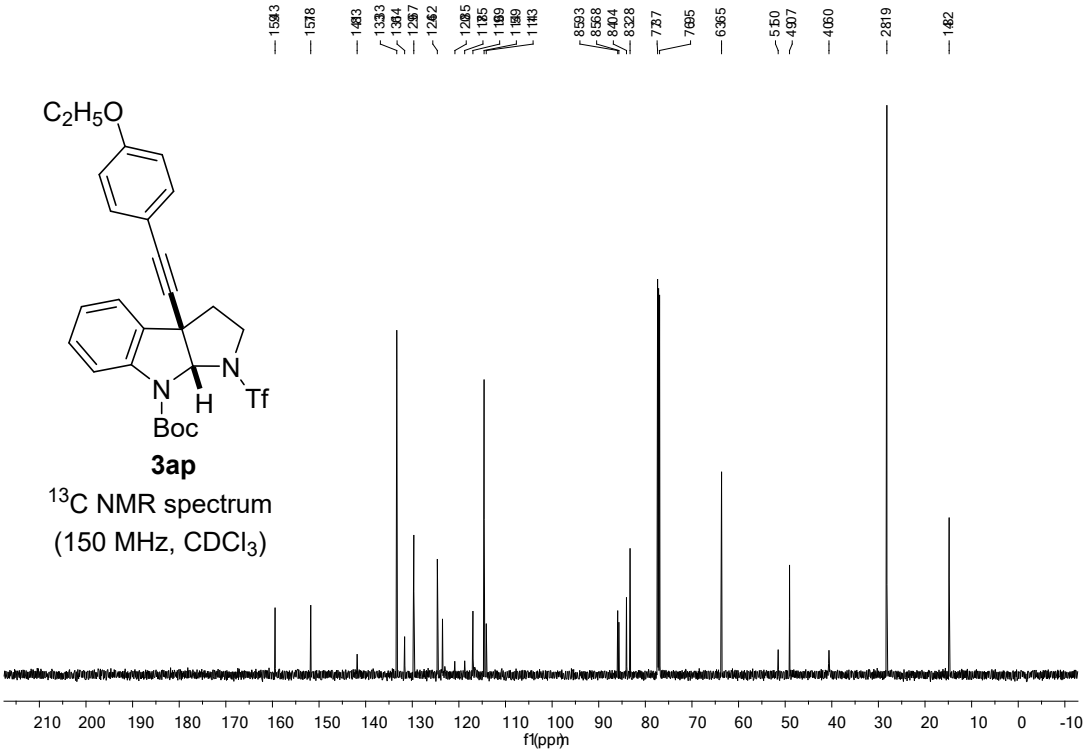


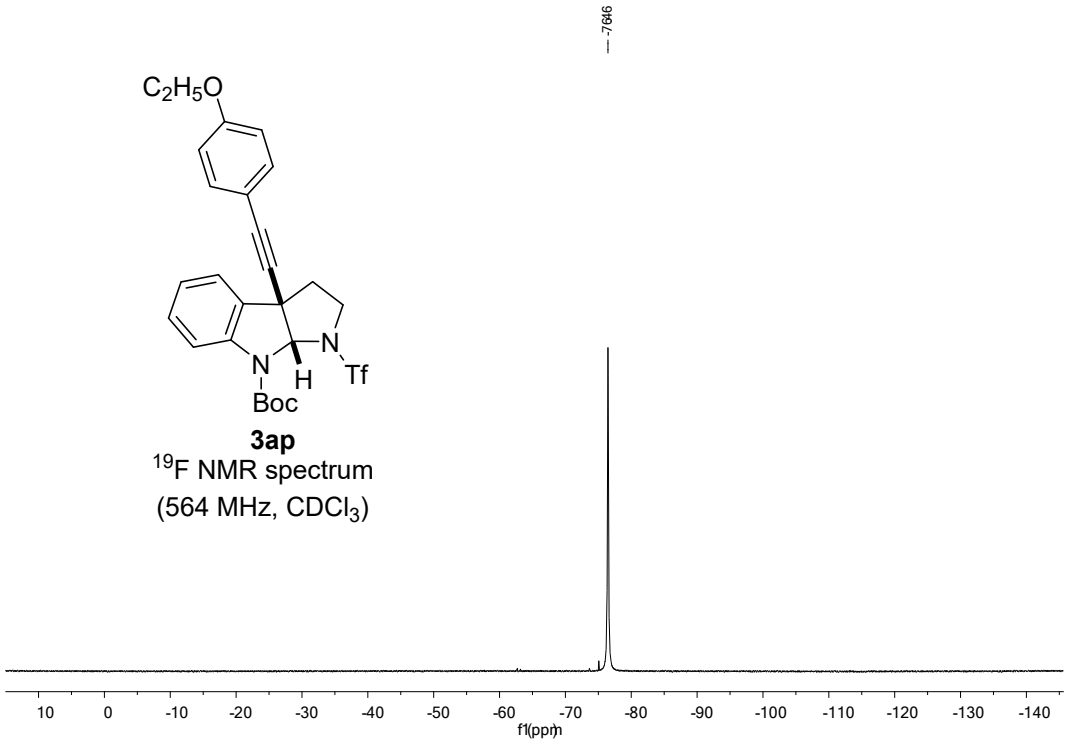
3ao

^{19}F NMR spectrum

(564 MHz, $CDCl_3$)


C2H5O
N
N
H
Tf
Boc
3ap
1H NMR spectrum
(600 MHz, CDCl3)
f1(ppm)

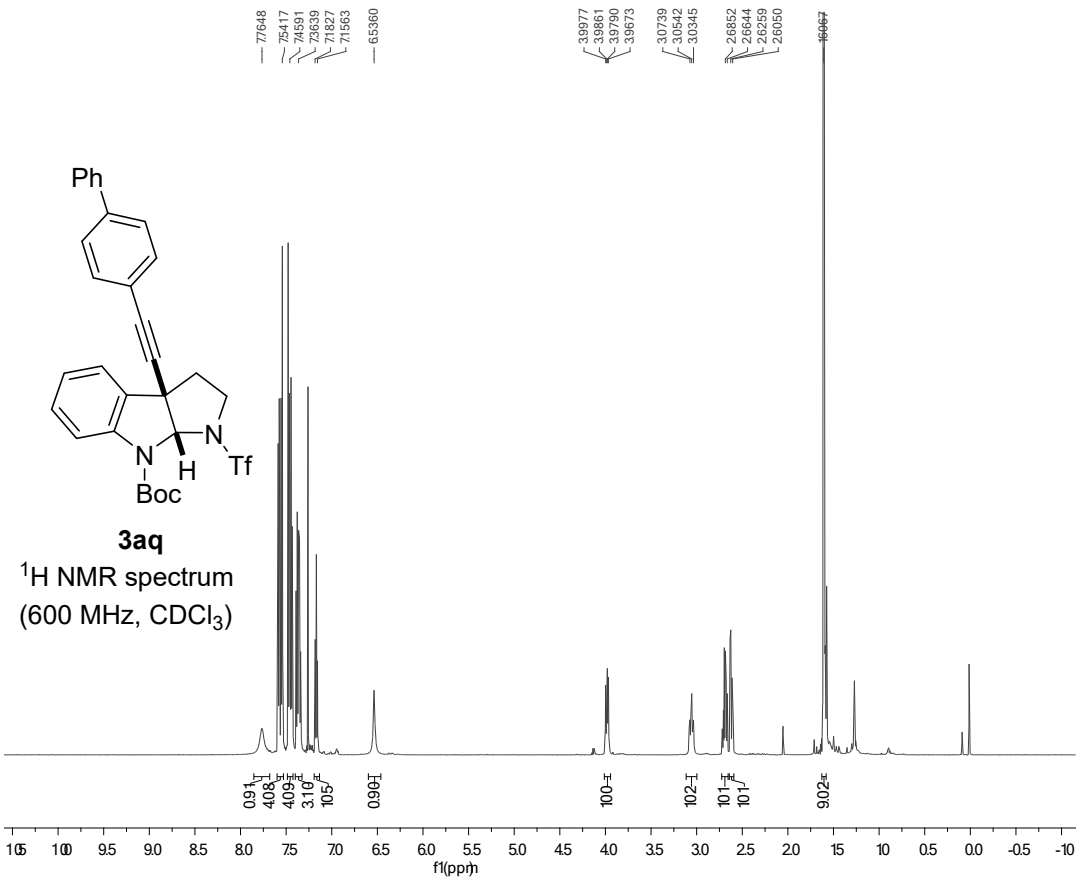

C2H5O
N
N
H
Tf
Boc
3ap
13C NMR spectrum
(150 MHz, CDCl3)
f1(ppm)



3ap

^{19}F NMR spectrum

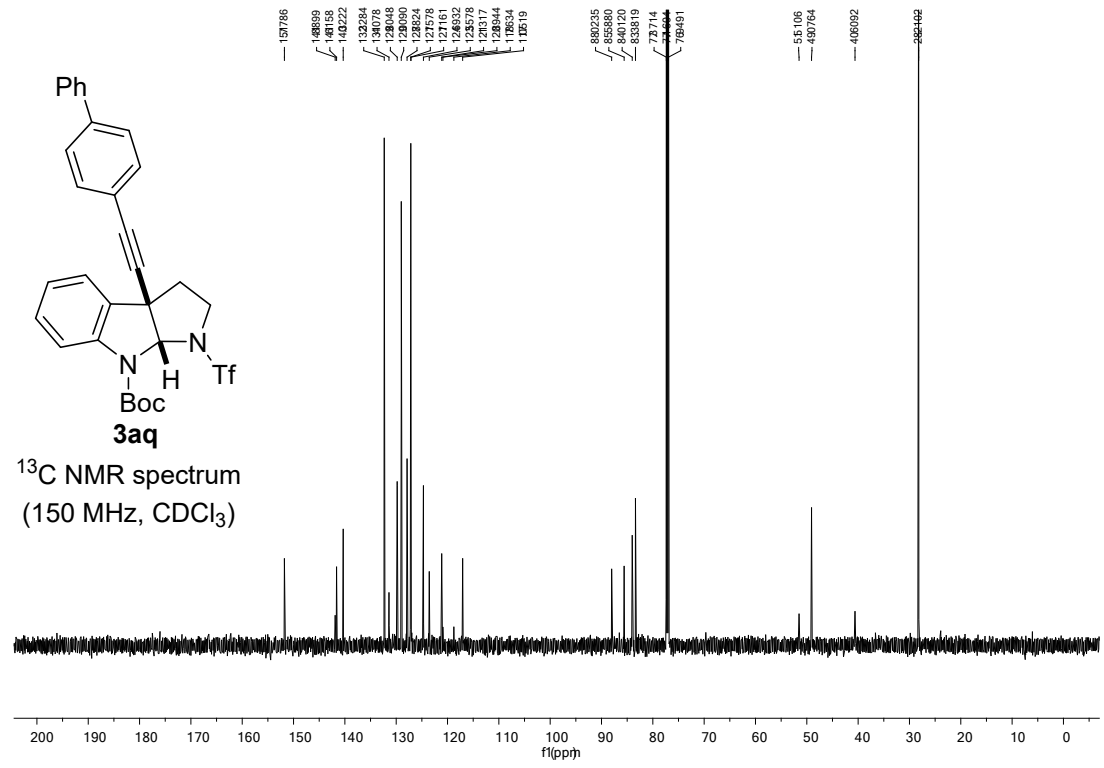
(564 MHz, $CDCl_3$)



3aq

^{1}H NMR spectrum

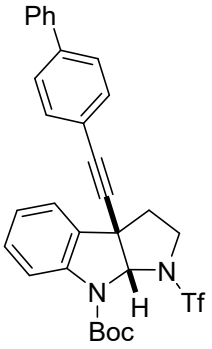
(600 MHz, $CDCl_3$)



3aq

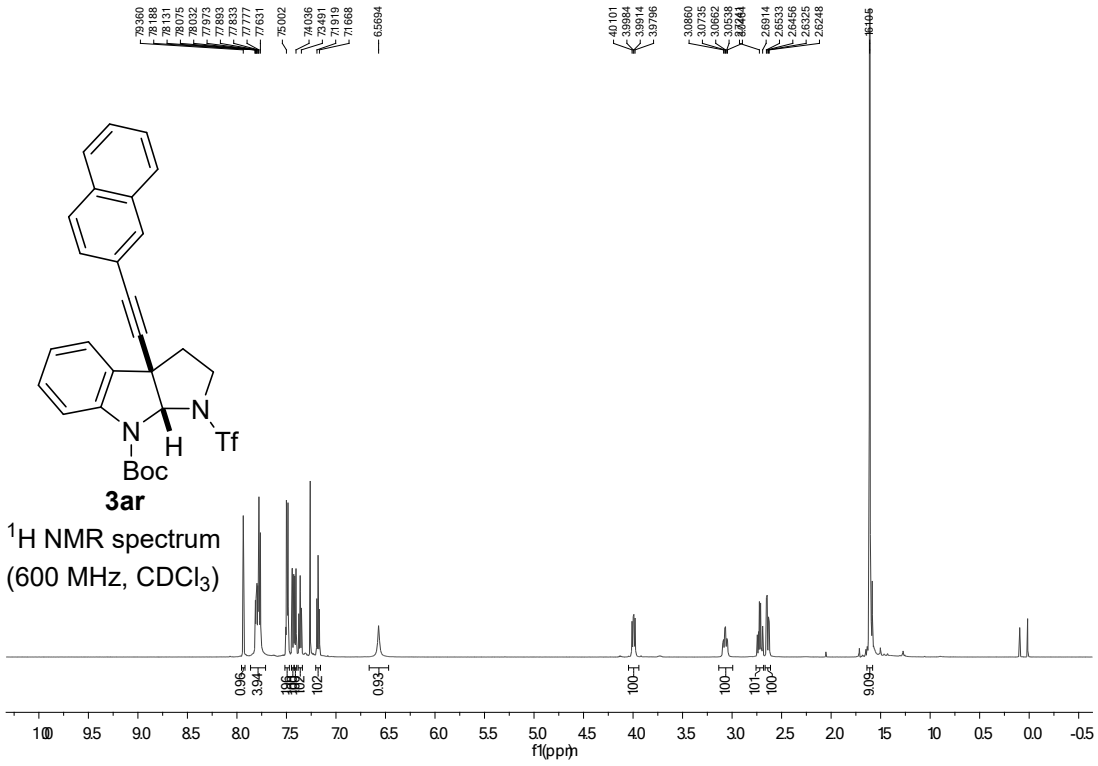
^{13}C NMR spectrum

(150 MHz, $CDCl_3$)



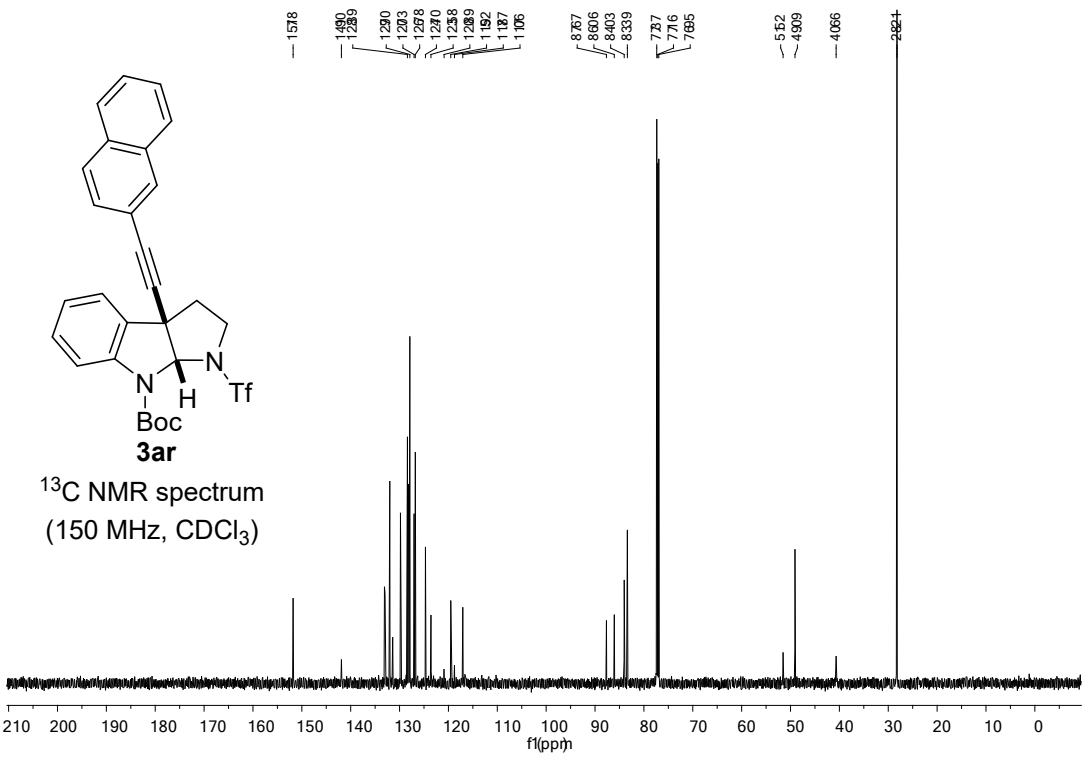
3aq

^{19}F NMR spectrum
(564 MHz, $CDCl_3$)



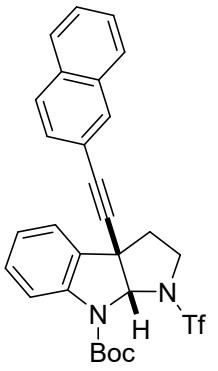
3ar

^{1}H NMR spectrum
(600 MHz, $CDCl_3$)



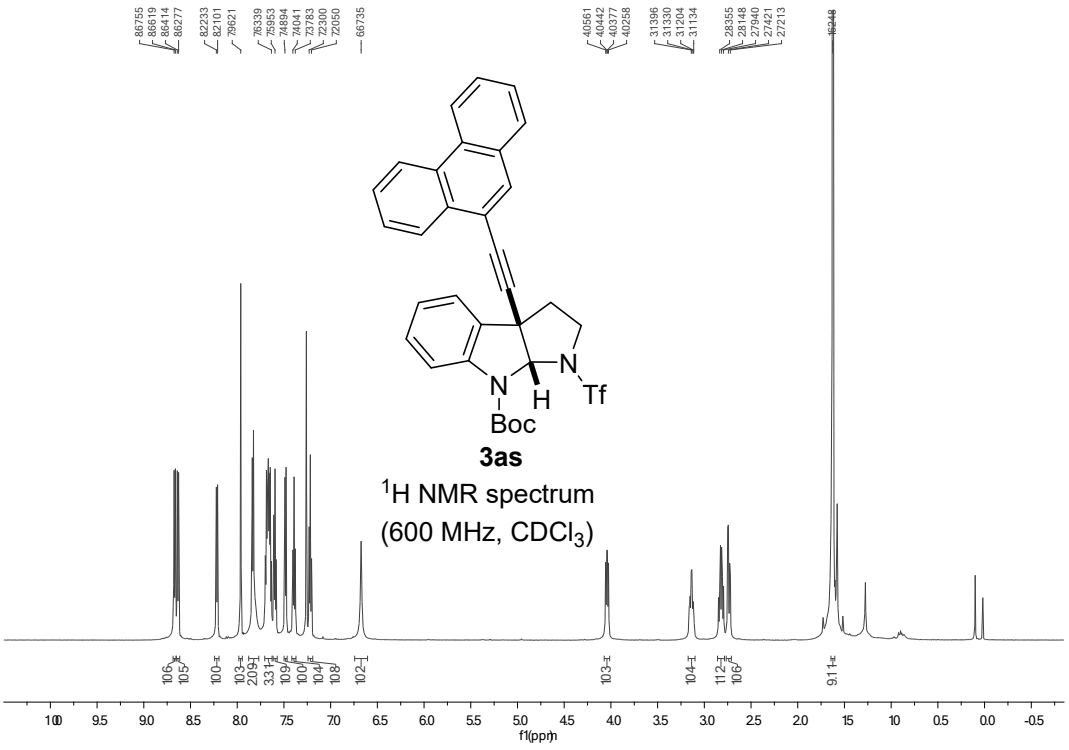
3ar

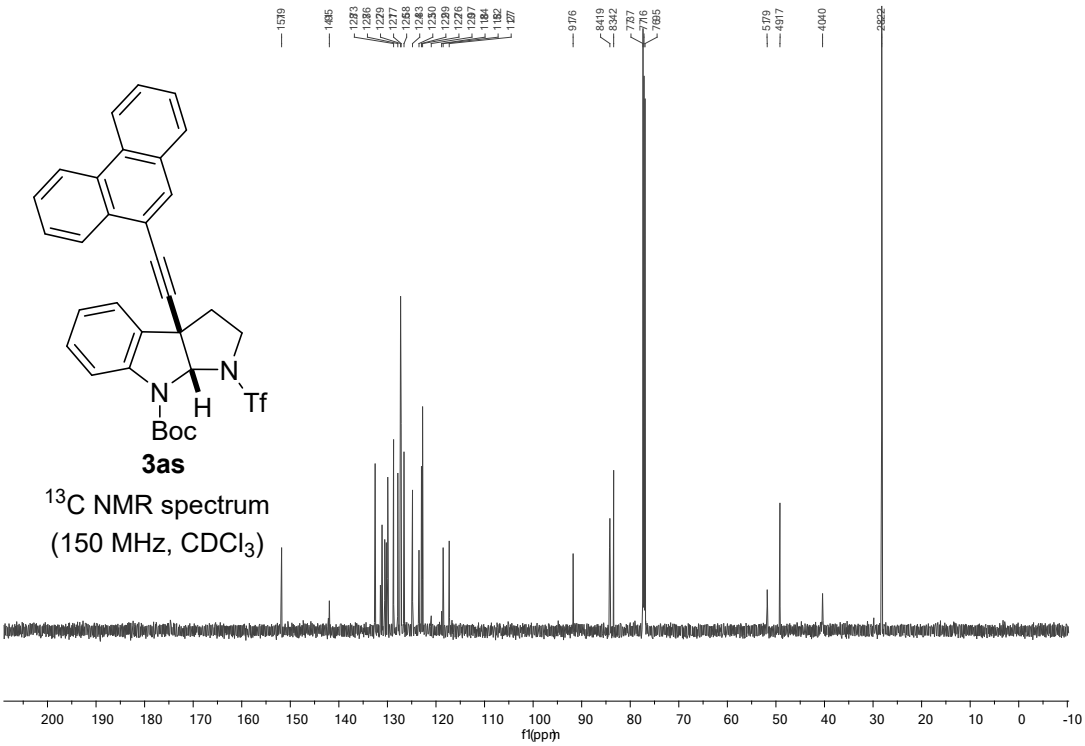
^{13}C NMR spectrum
(150 MHz, $CDCl_3$)

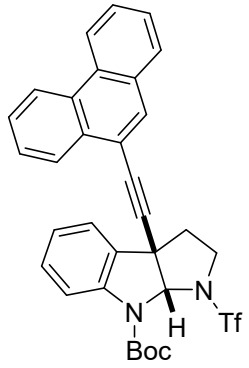


3ar

^{19}F NMR spectrum
(564 MHz, $CDCl_3$)


N
H
Tf
Boc
3as
1H NMR spectrum
(600 MHz, CDCl3)
f1(ppm)

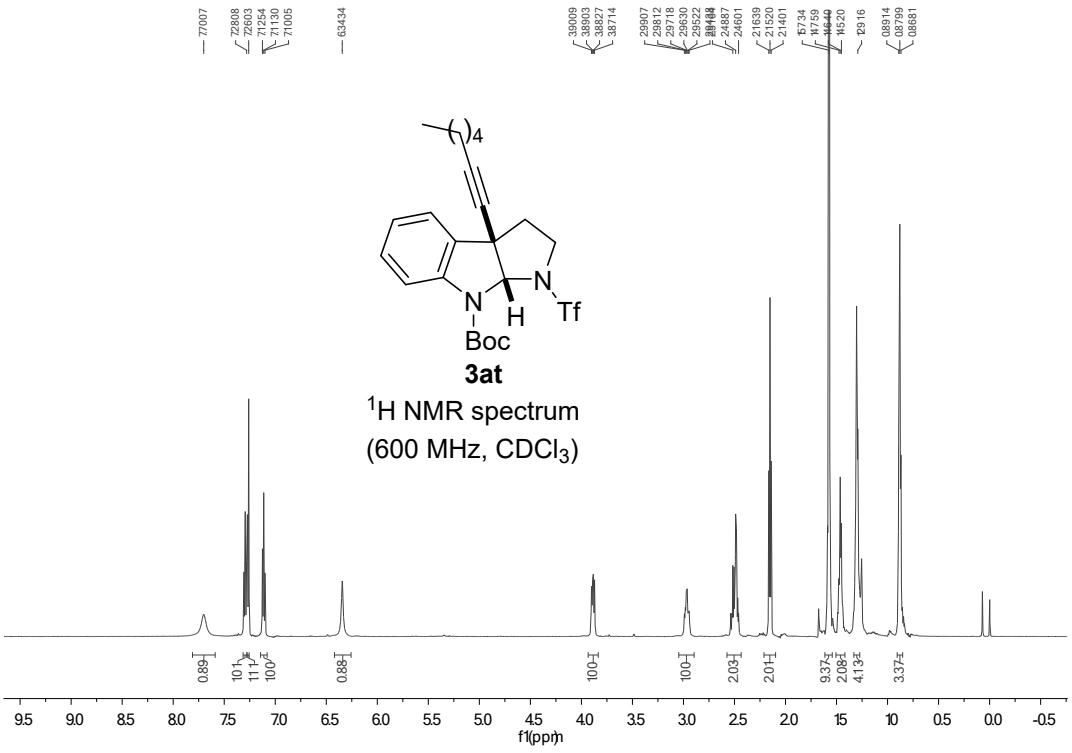

N
H
Tf
Boc
3as
13C NMR spectrum
(150 MHz, CDCl3)
f1(ppm)



3as

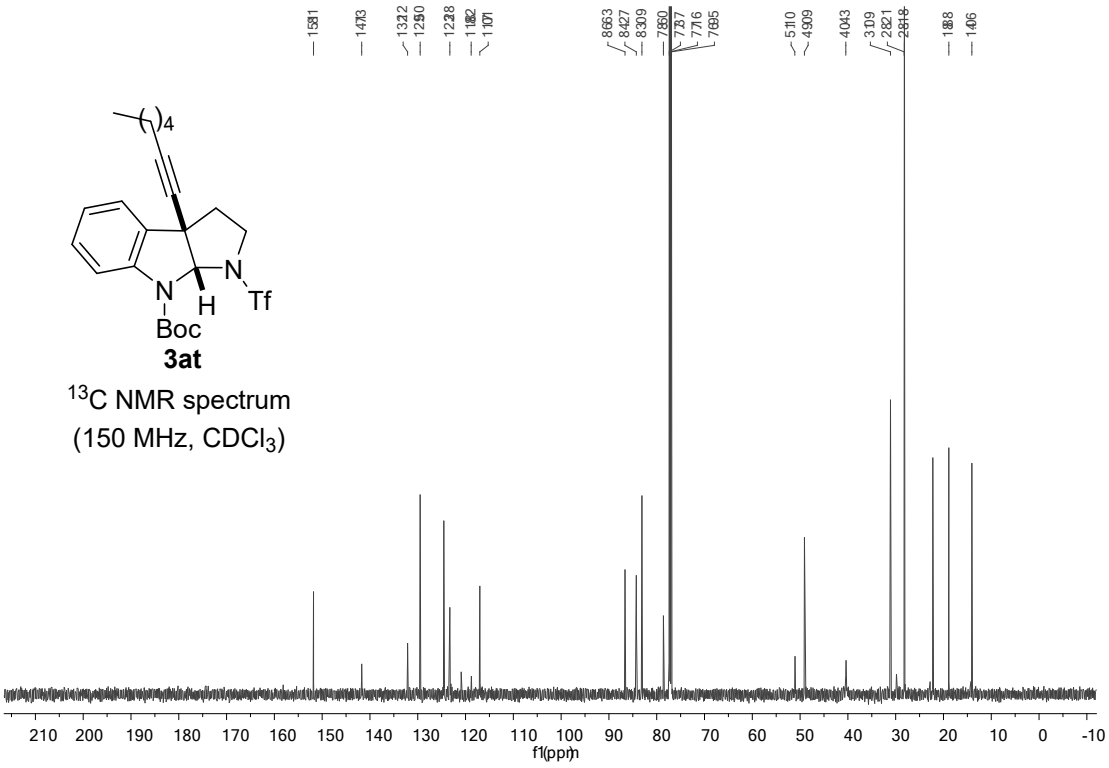
^{19}F NMR spectrum

(564 MHz, $CDCl_3$)



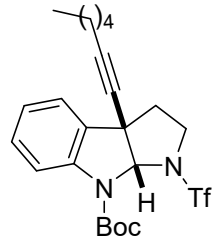
3at

^{1}H NMR spectrum
(600 MHz, $CDCl_3$)



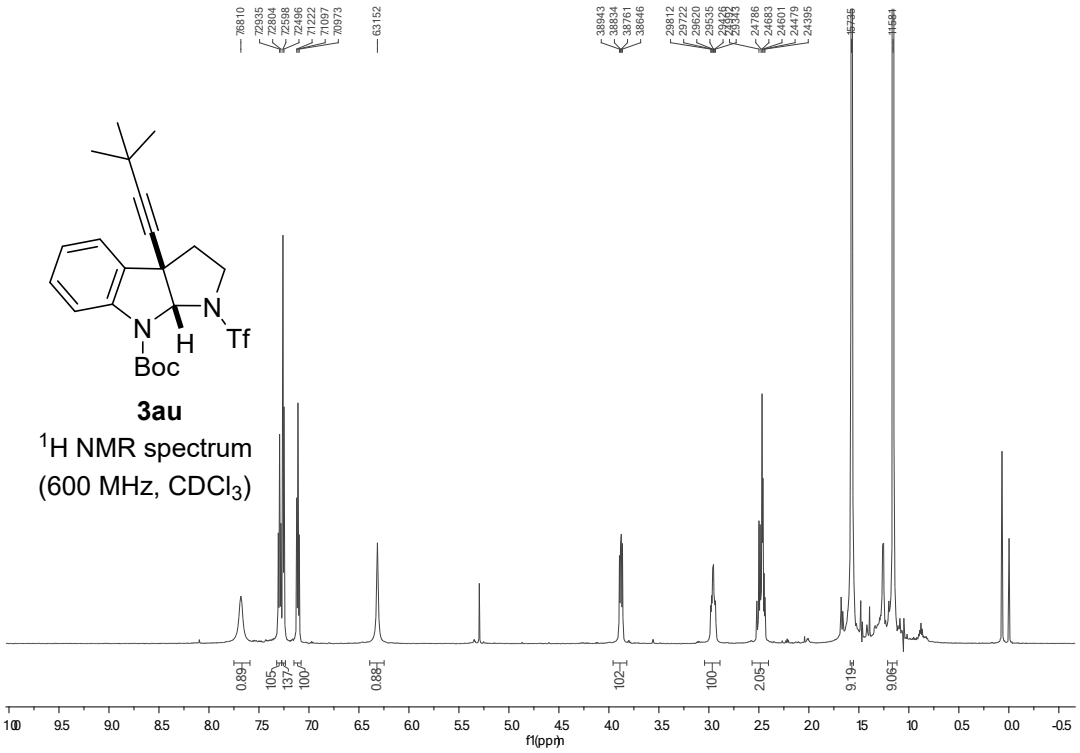
3at

^{13}C NMR spectrum
(150 MHz, $CDCl_3$)



3at

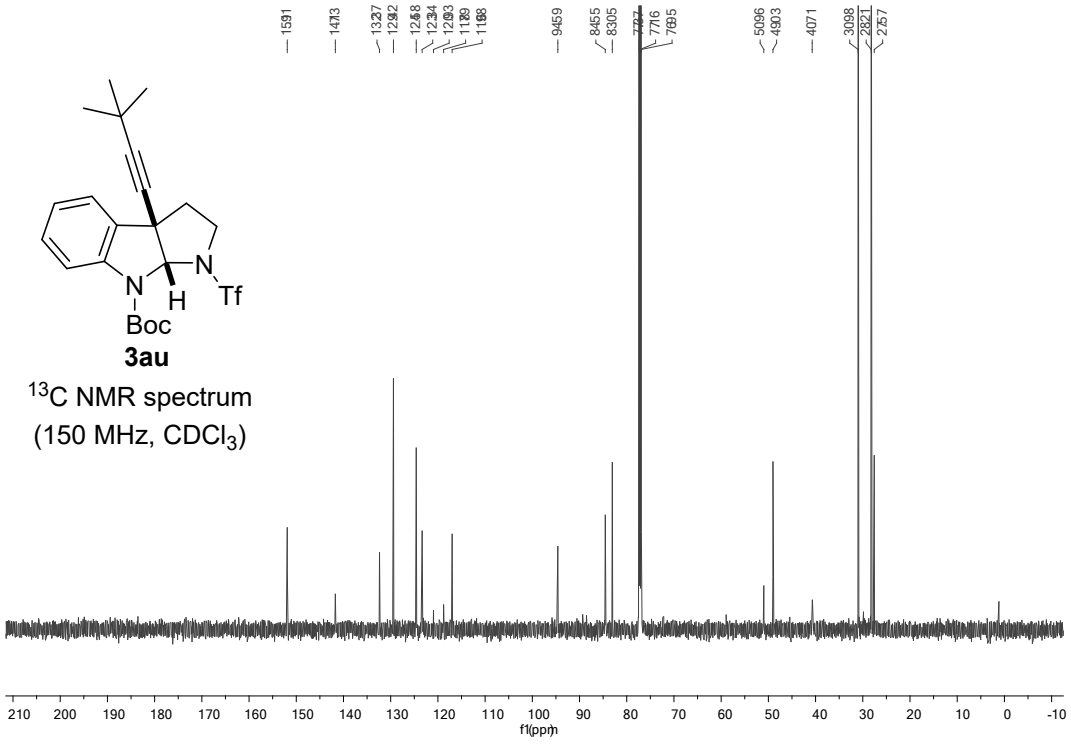
^{19}F NMR spectrum
(564 MHz, $CDCl_3$)



3au

^{1}H NMR spectrum

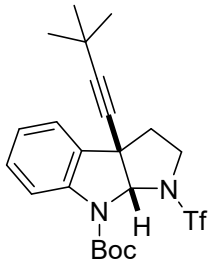
(600 MHz, $CDCl_3$)



3au

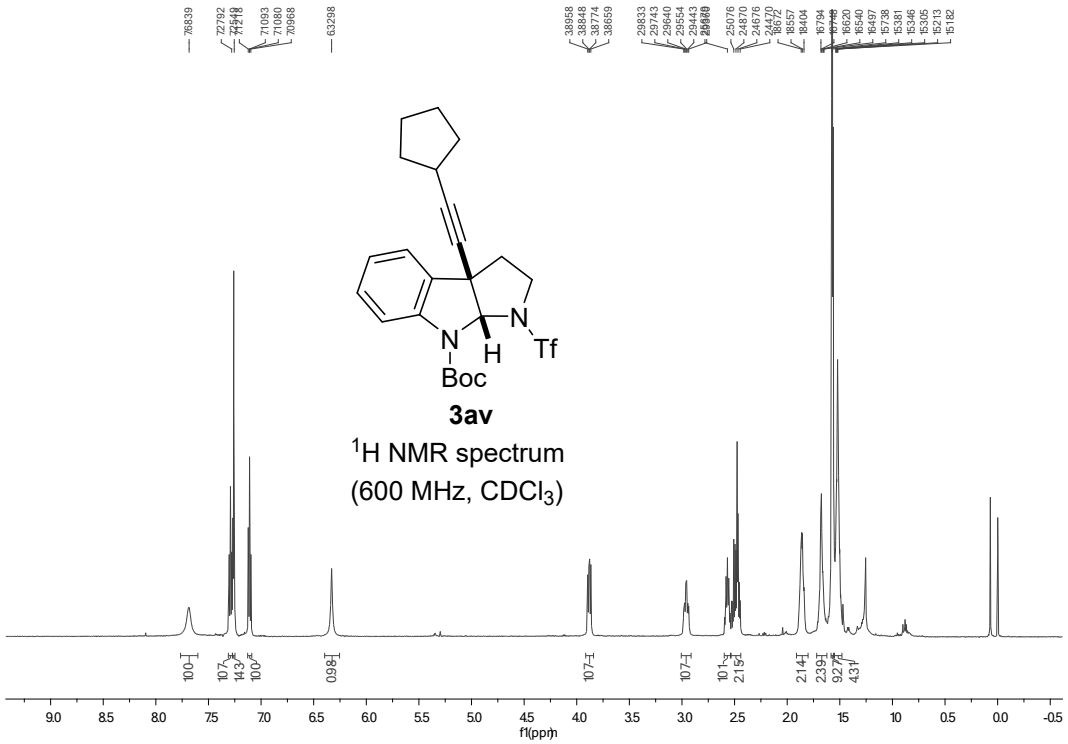
^{13}C NMR spectrum

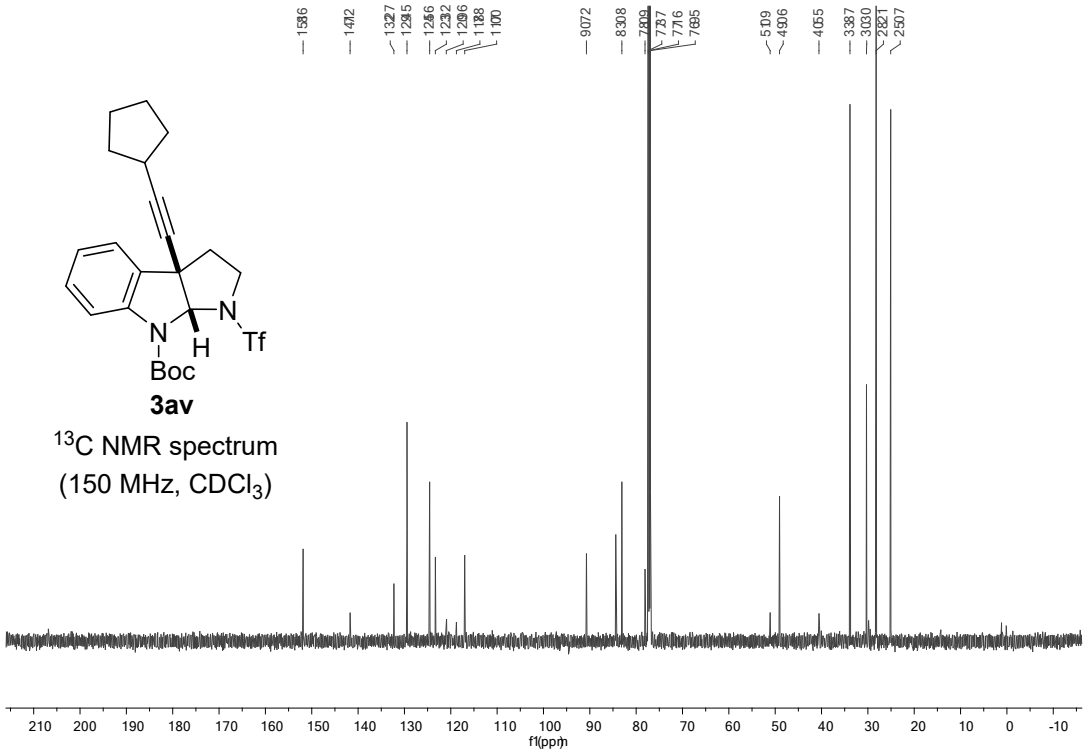
(150 MHz, $CDCl_3$)

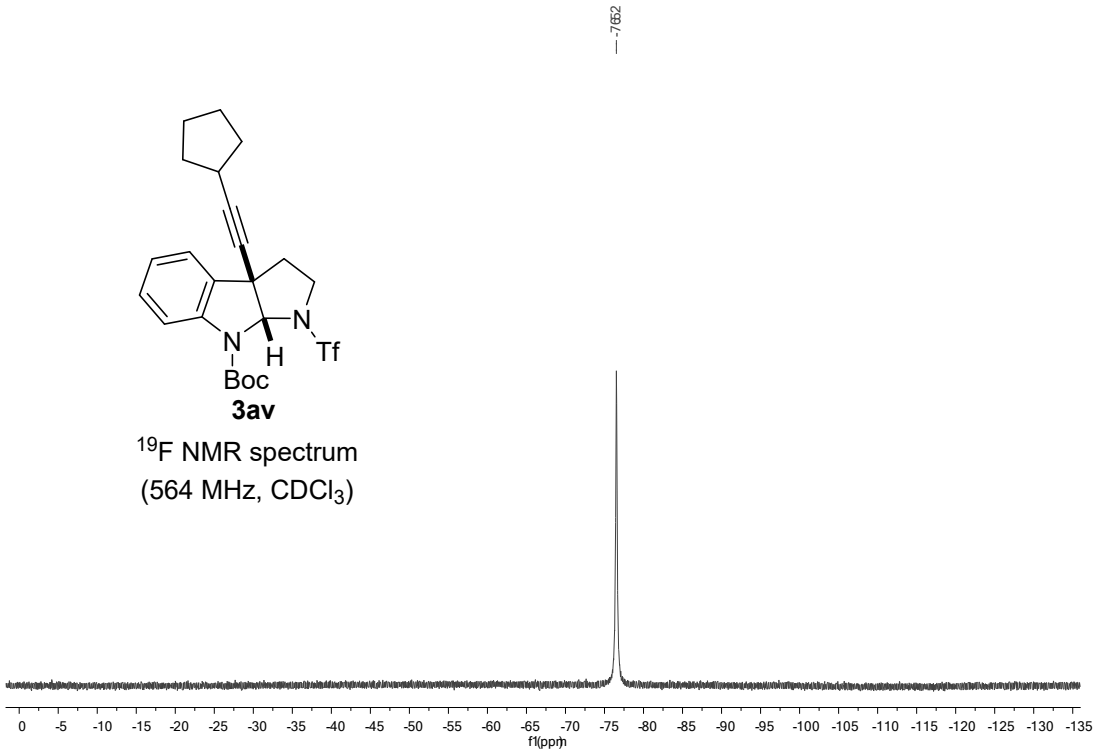


3au

^{19}F NMR spectrum
(564 MHz, $CDCl_3$)

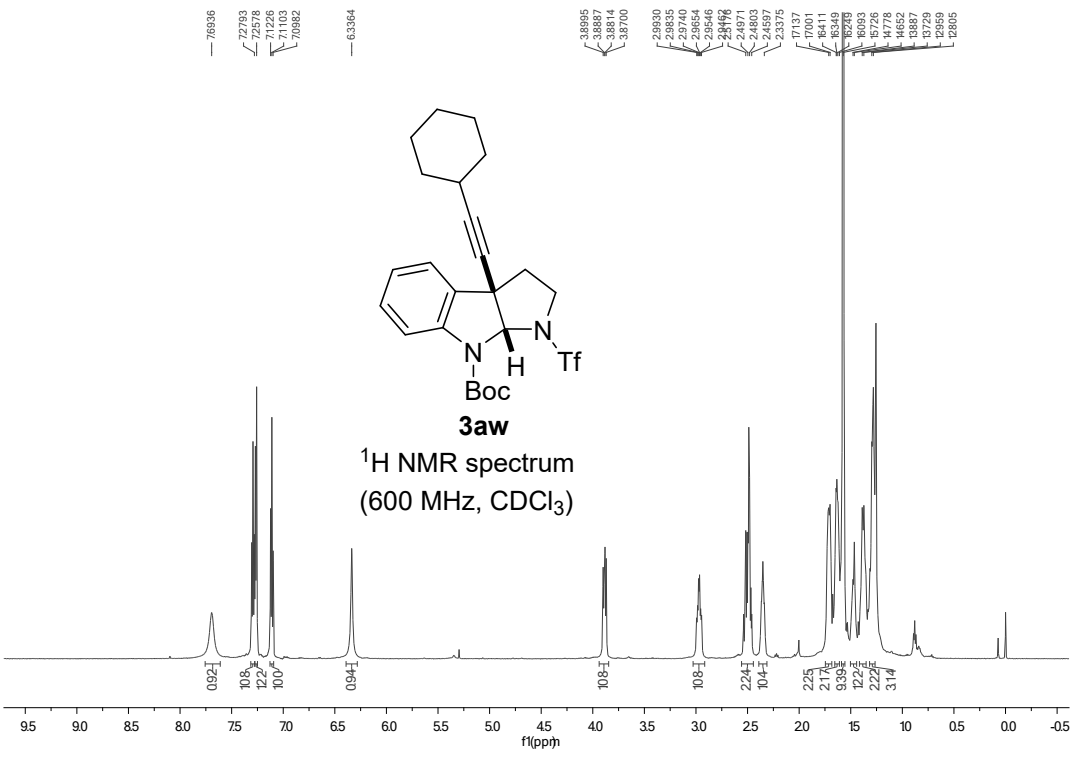

Boc
N
H
N
Tf
3av
1H NMR spectrum
(600 MHz, CDCl3)
f1(ppm)

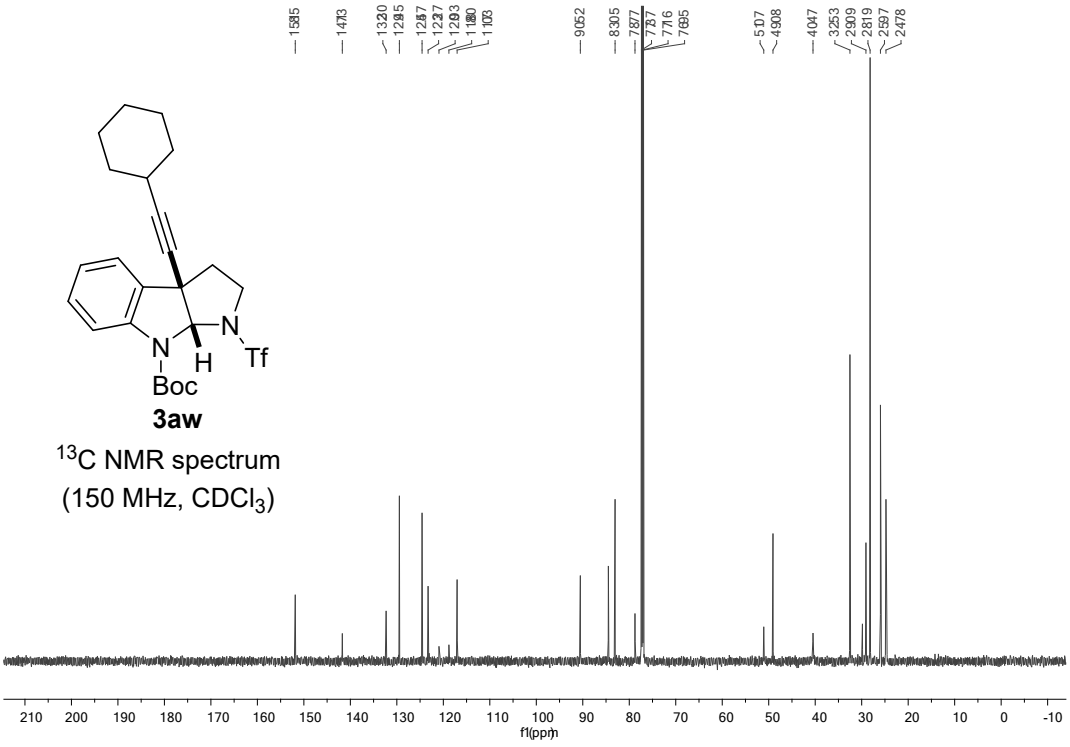

Boc
N
H
N
Tf
3av
13C NMR spectrum
(150 MHz, CDCl3)
f1(ppm)

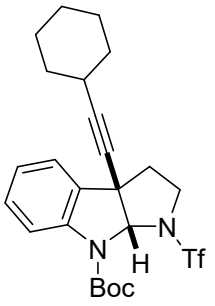


3av

^{19}F NMR spectrum
(564 MHz, $CDCl_3$)

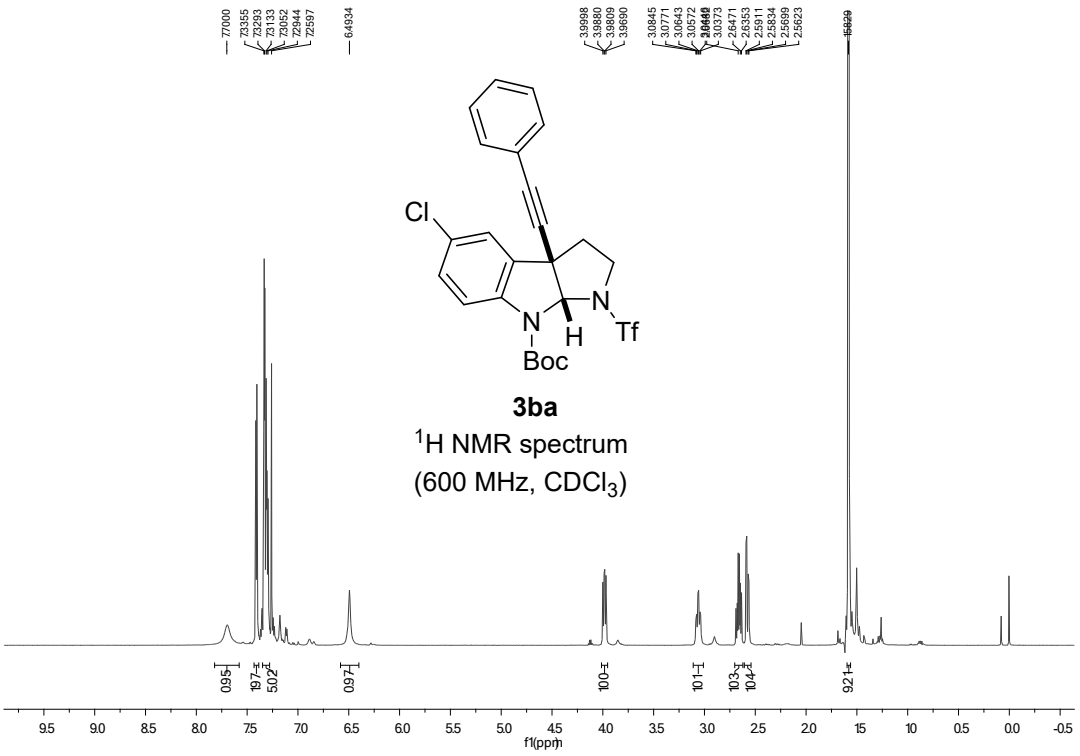

Boc
N
H
N
Tf
3aw
1H NMR spectrum
(600 MHz, CDCl3)
f1(ppm)


Boc
N
H
N
Tf
3aw
13C NMR spectrum
(150 MHz, CDCl3)
f1(ppm)



3aw

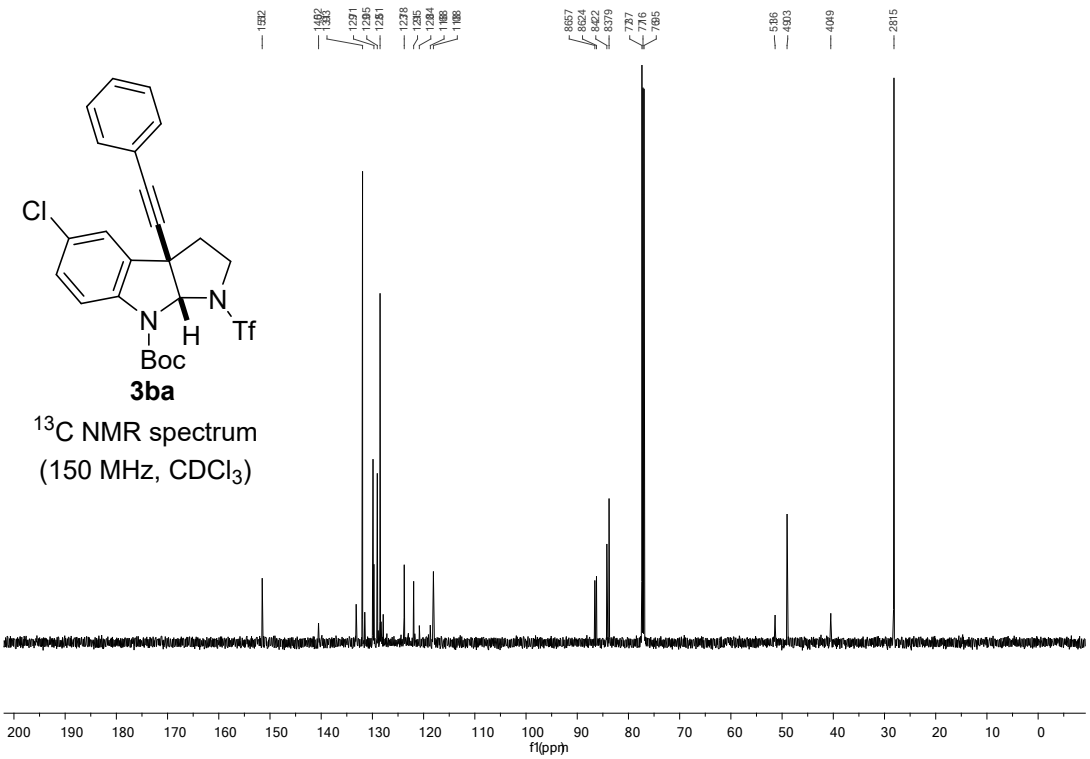
^{19}F NMR spectrum
(564 MHz, $CDCl_3$)



3ba

^{1}H NMR spectrum

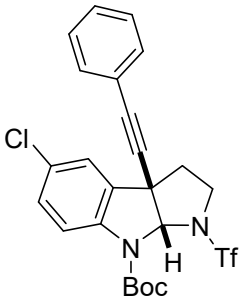
(600 MHz, $CDCl_3$)



3ba

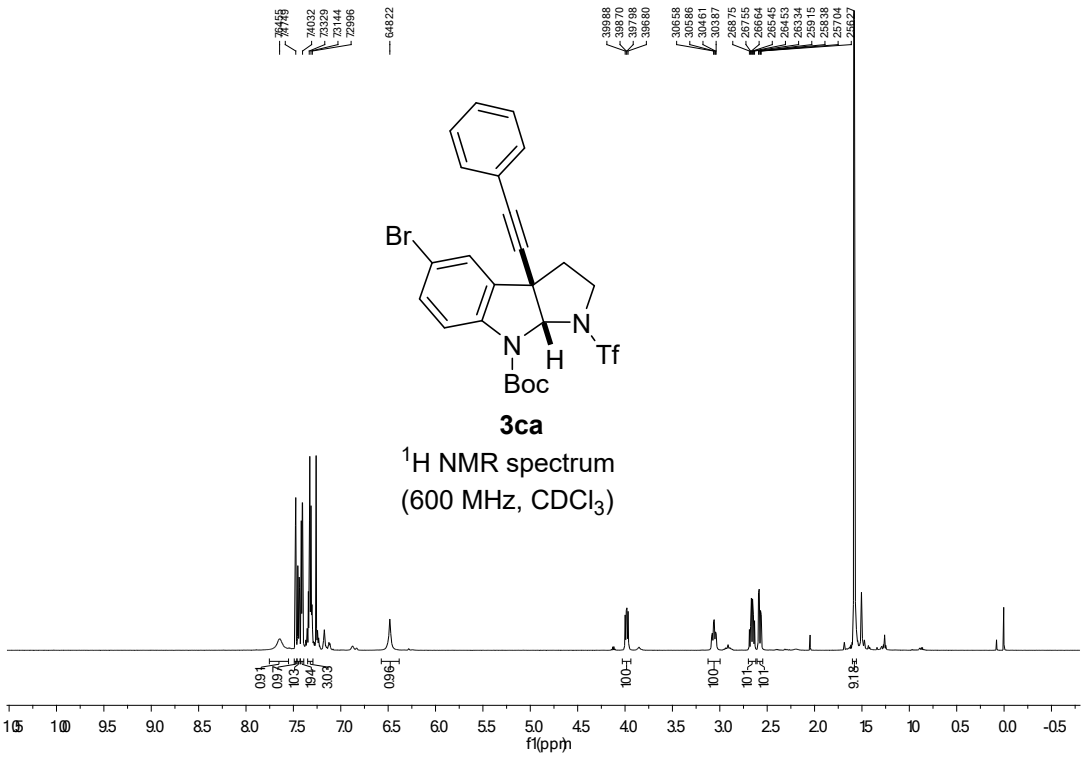
^{13}C NMR spectrum

(150 MHz, $CDCl_3$)



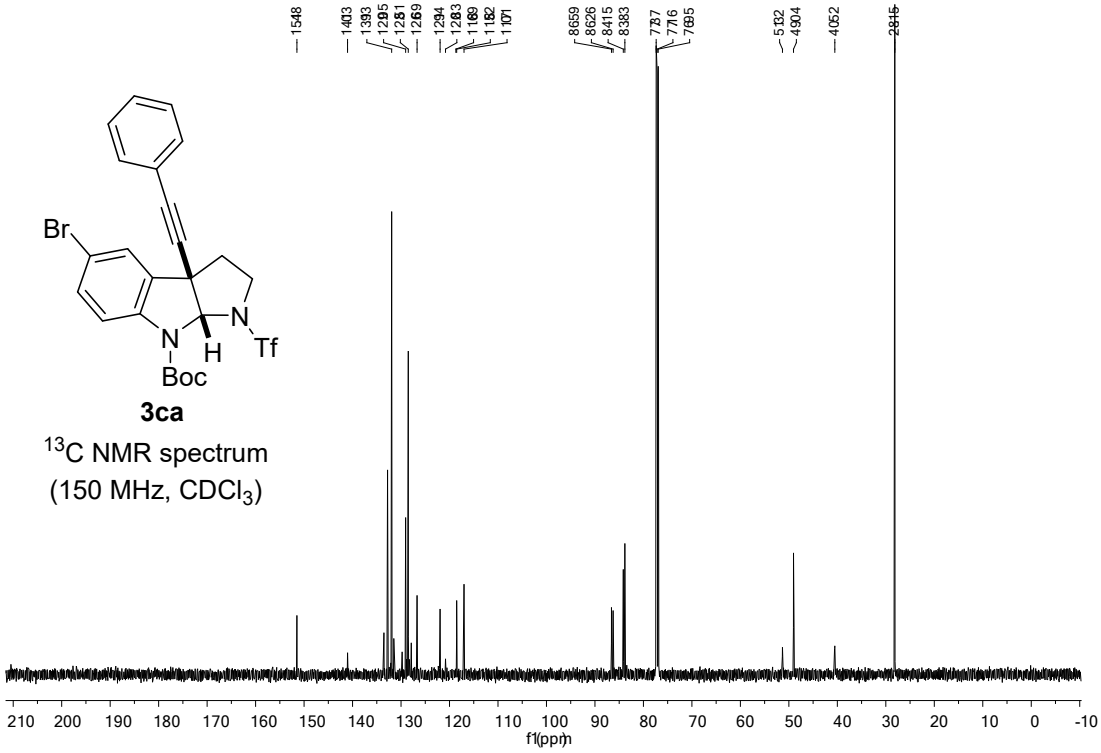
3ba

^{19}F NMR spectrum
(564 MHz, $CDCl_3$)



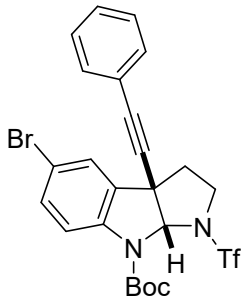
3ca

^{1}H NMR spectrum
(600 MHz, $CDCl_3$)



3ca

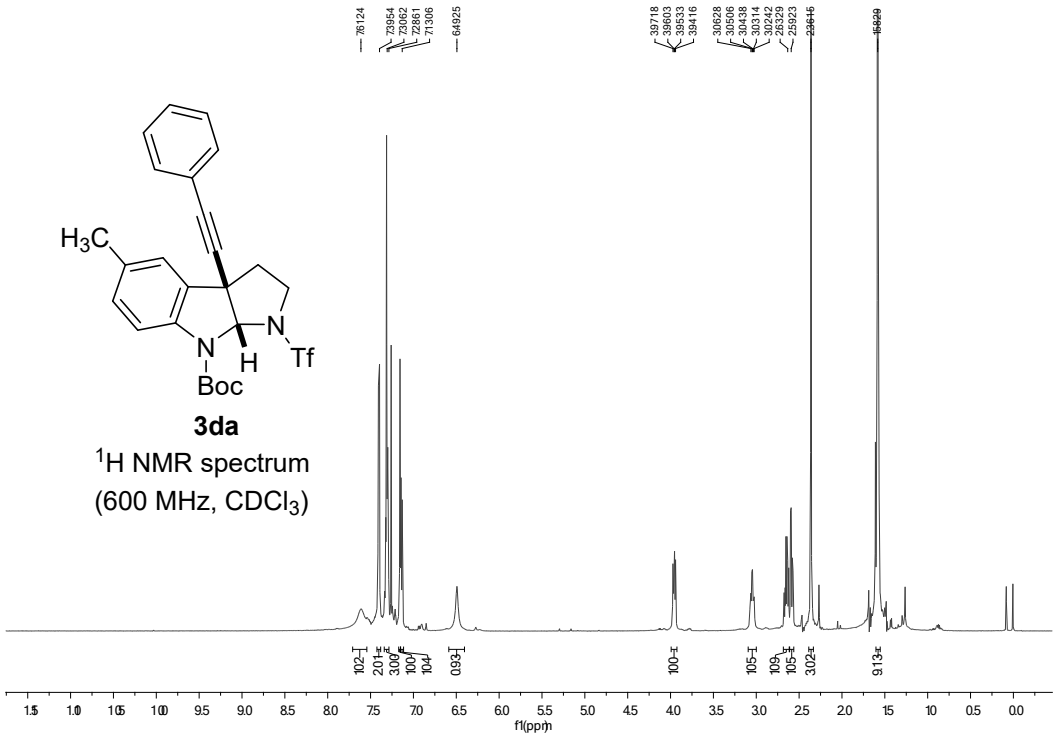
^{13}C NMR spectrum
(150 MHz, $CDCl_3$)



3ca

^{19}F NMR spectrum

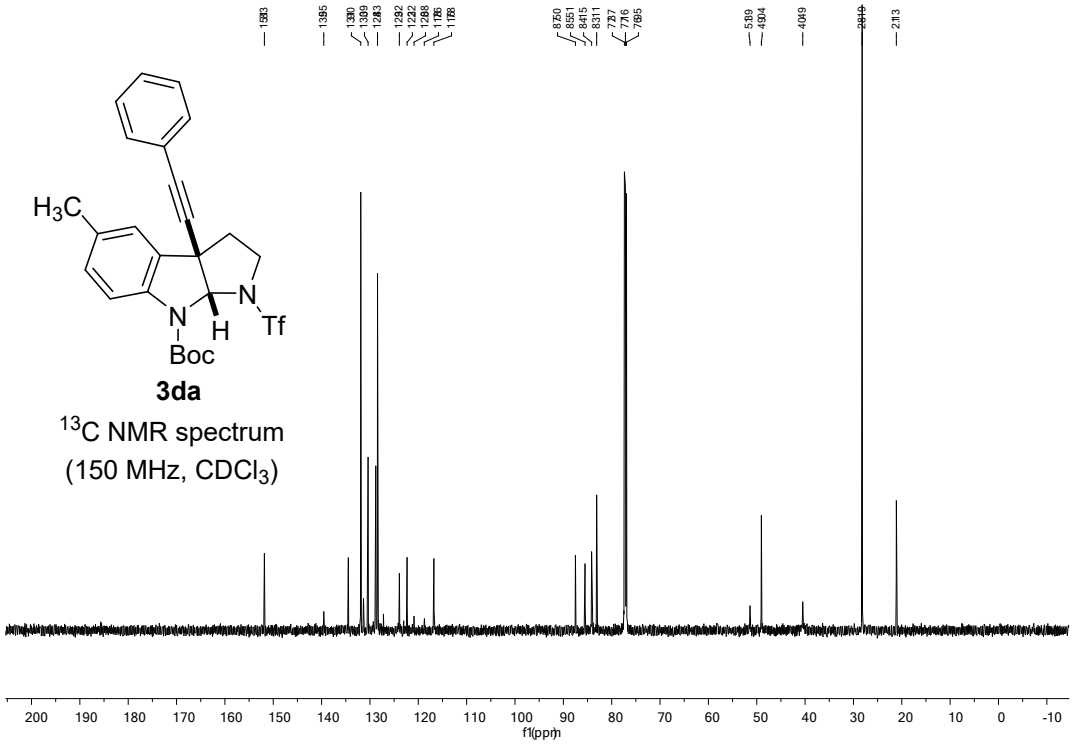
(564 MHz, $CDCl_3$)



3da

^{1}H NMR spectrum

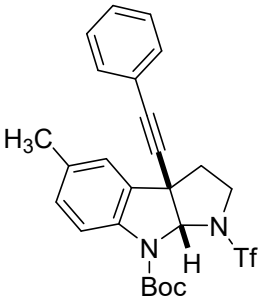
(600 MHz, $CDCl_3$)



3da

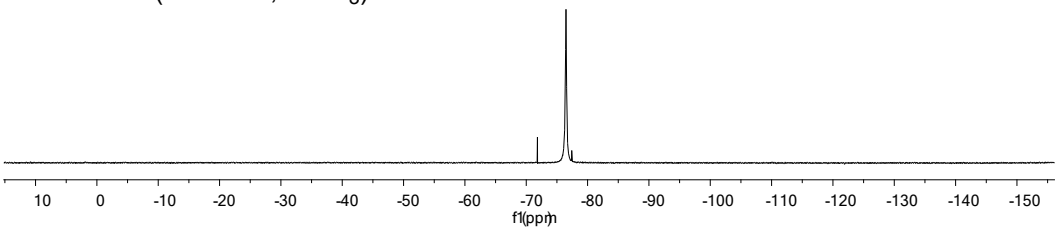
^{13}C NMR spectrum

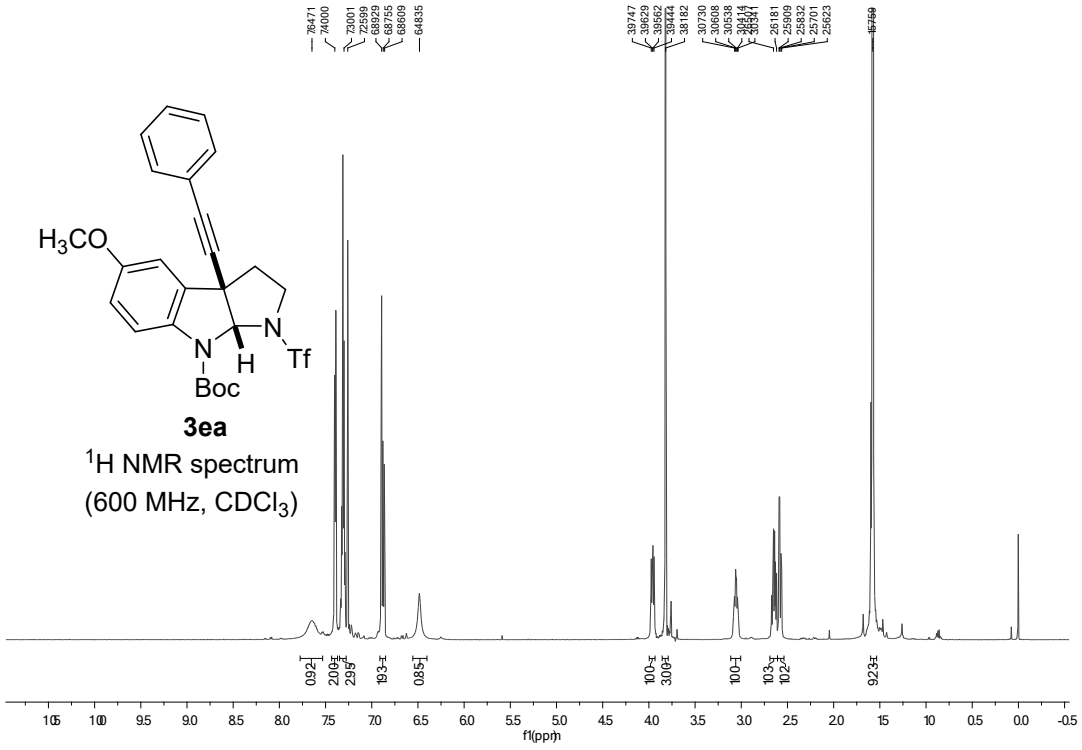
(150 MHz, $CDCl_3$)



3da

^{19}F NMR spectrum
(564 MHz, $CDCl_3$)

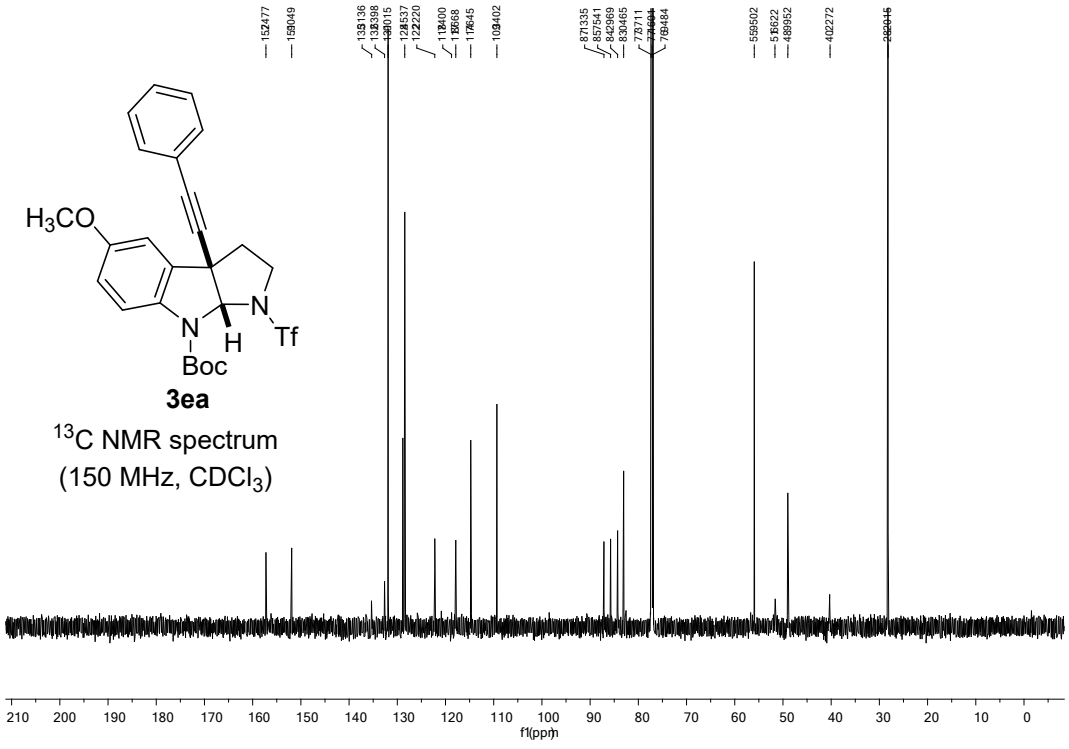




3ea

^{1}H NMR spectrum

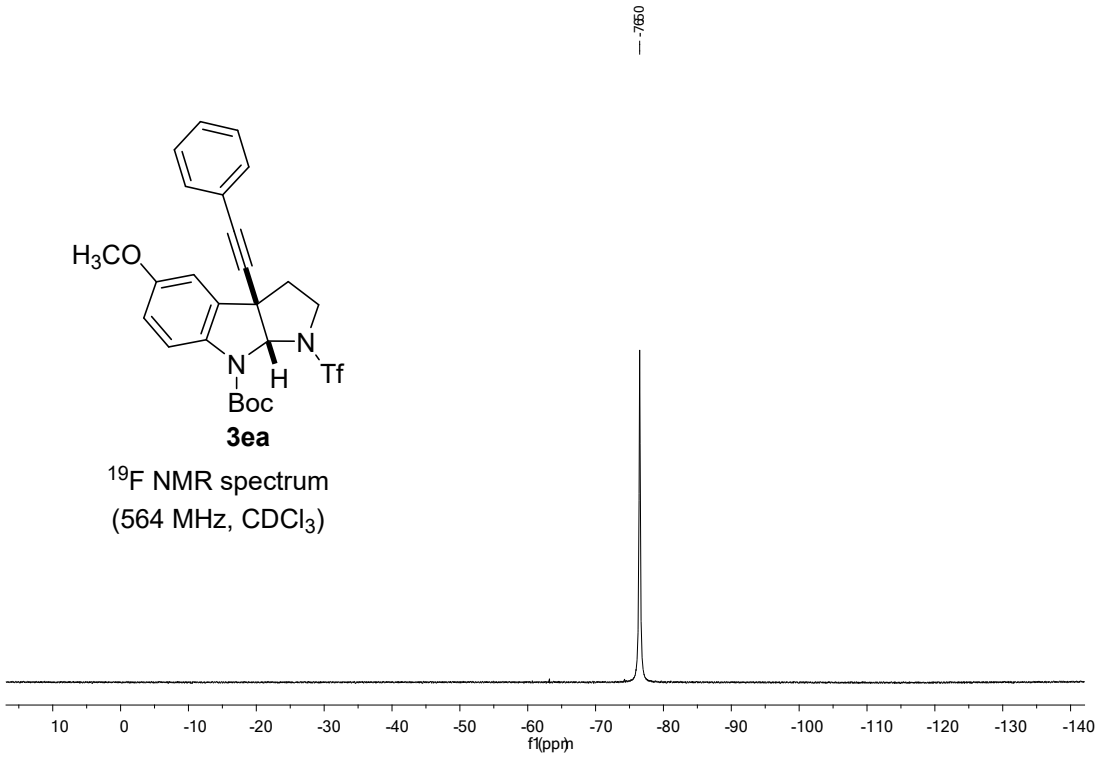
(600 MHz, $CDCl_3$)



3ea

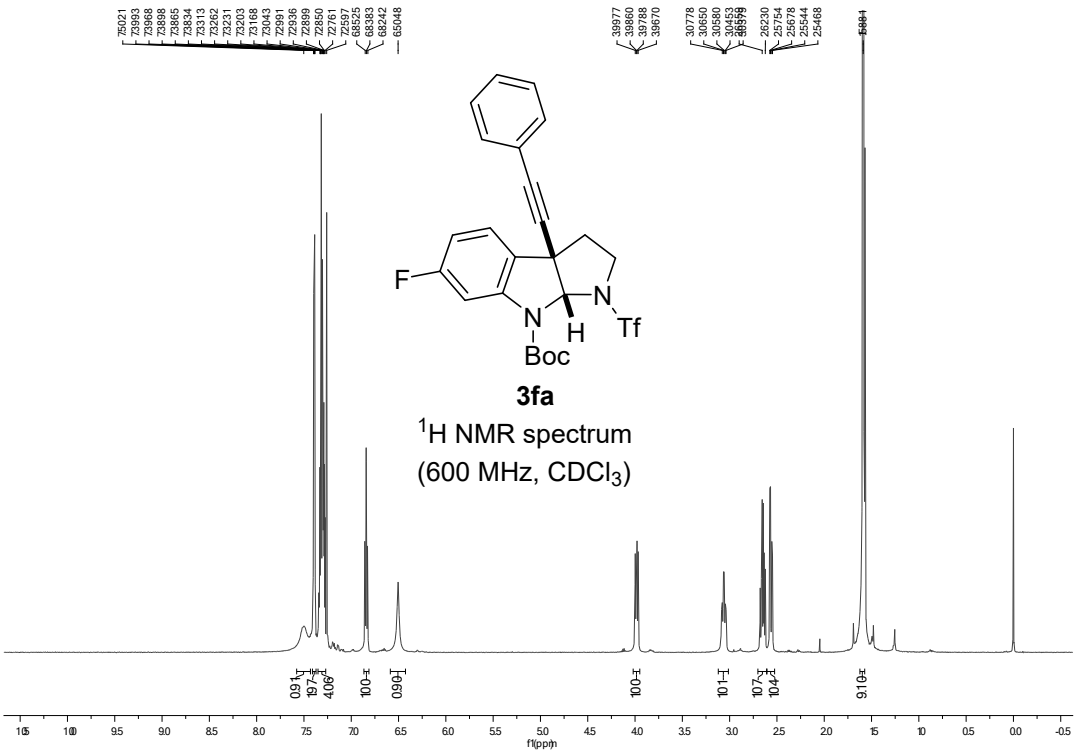
^{13}C NMR spectrum

(150 MHz, $CDCl_3$)



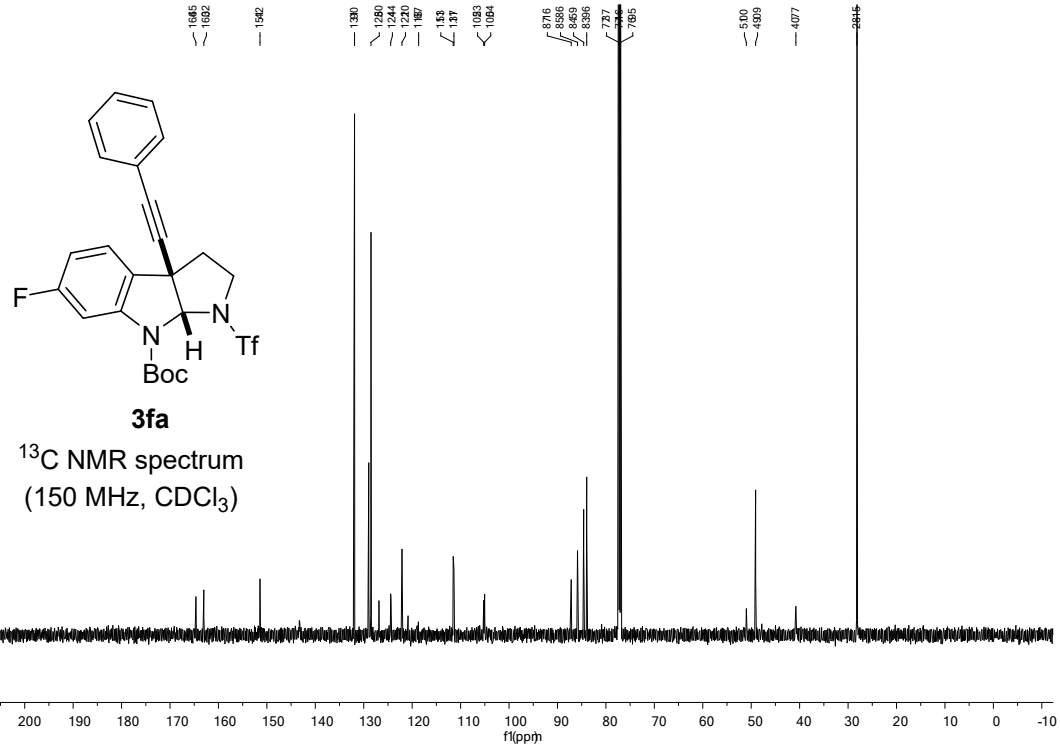
3ea

^{19}F NMR spectrum
(564 MHz, $CDCl_3$)



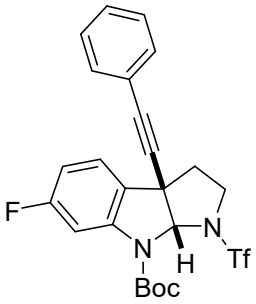
3fa

^{1}H NMR spectrum
(600 MHz, $CDCl_3$)



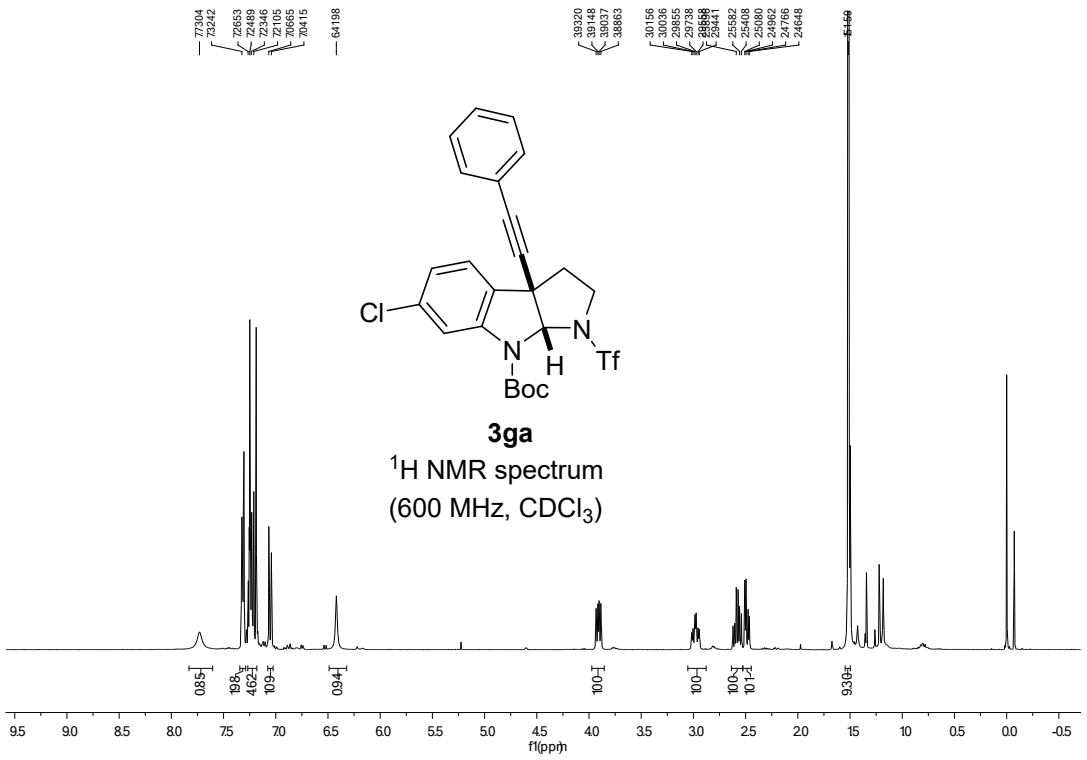
3fa

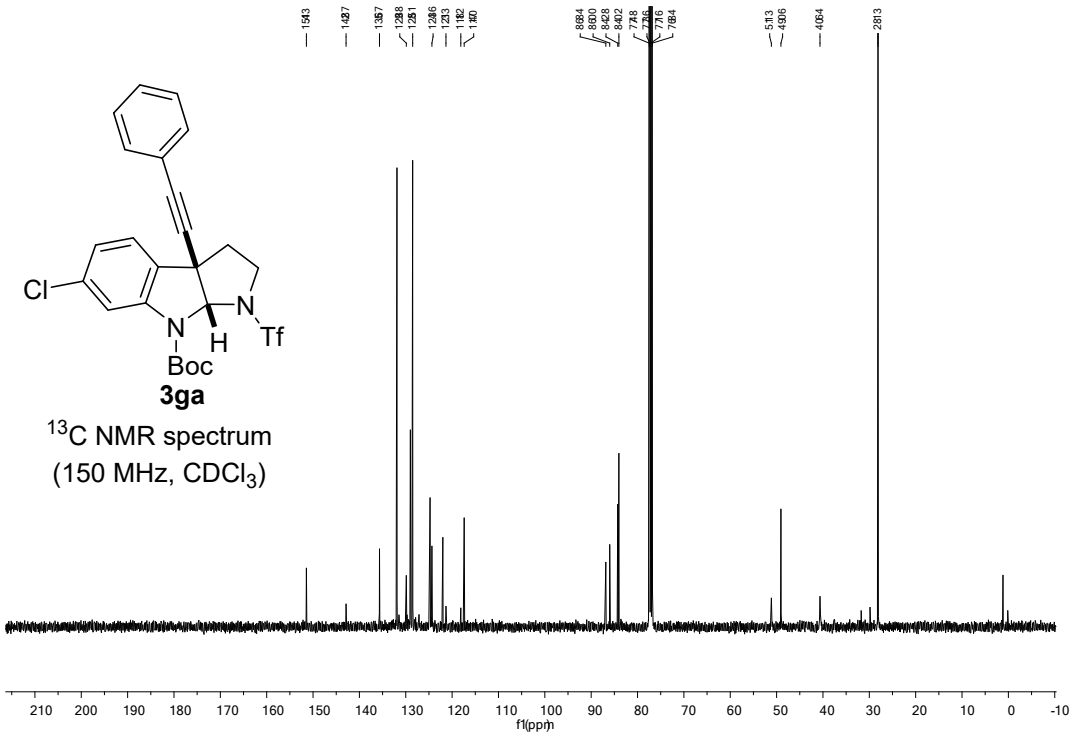
^{13}C NMR spectrum
(150 MHz, $CDCl_3$)

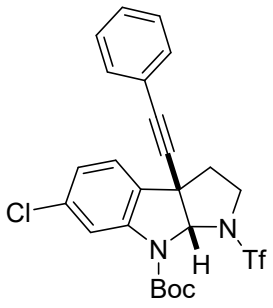


3fa

^{19}F NMR spectrum
(564 MHz, $CDCl_3$)


Cl
N
H
Tf
Boc
3ga
1H NMR spectrum
(600 MHz, CDCl3)
f1(ppm)

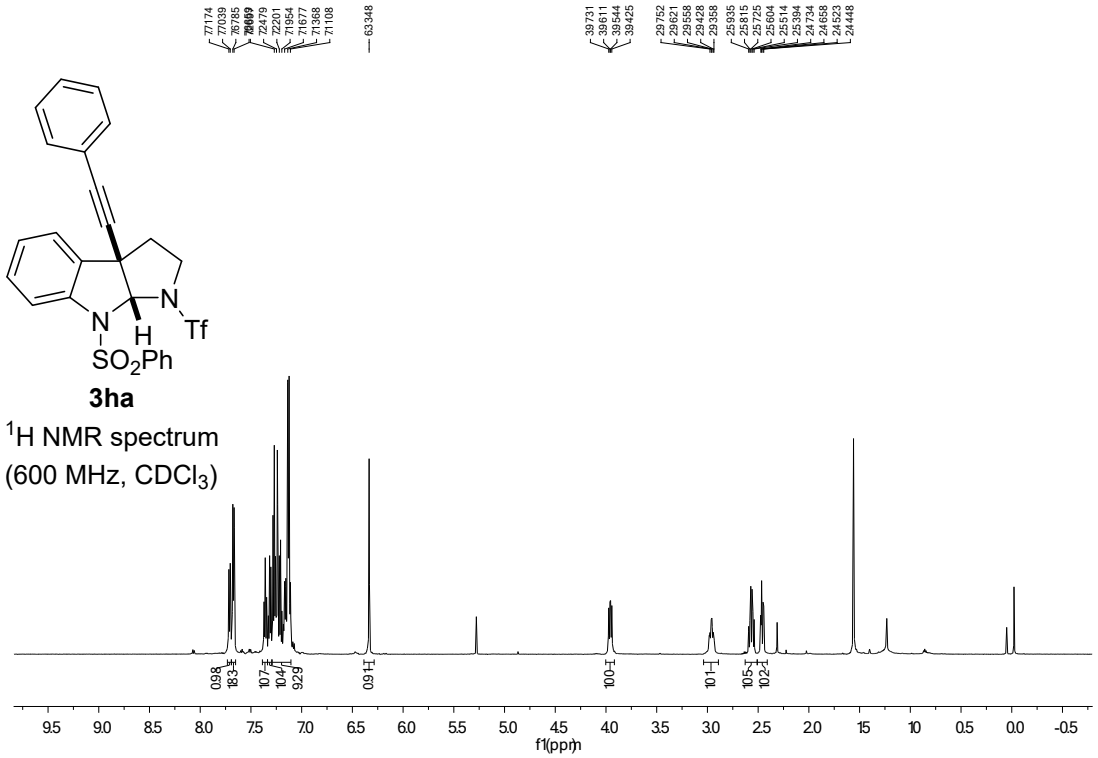

Cl
N
H
Tf
Boc
3ga
13C NMR spectrum
(150 MHz, CDCl3)
f1(ppm)

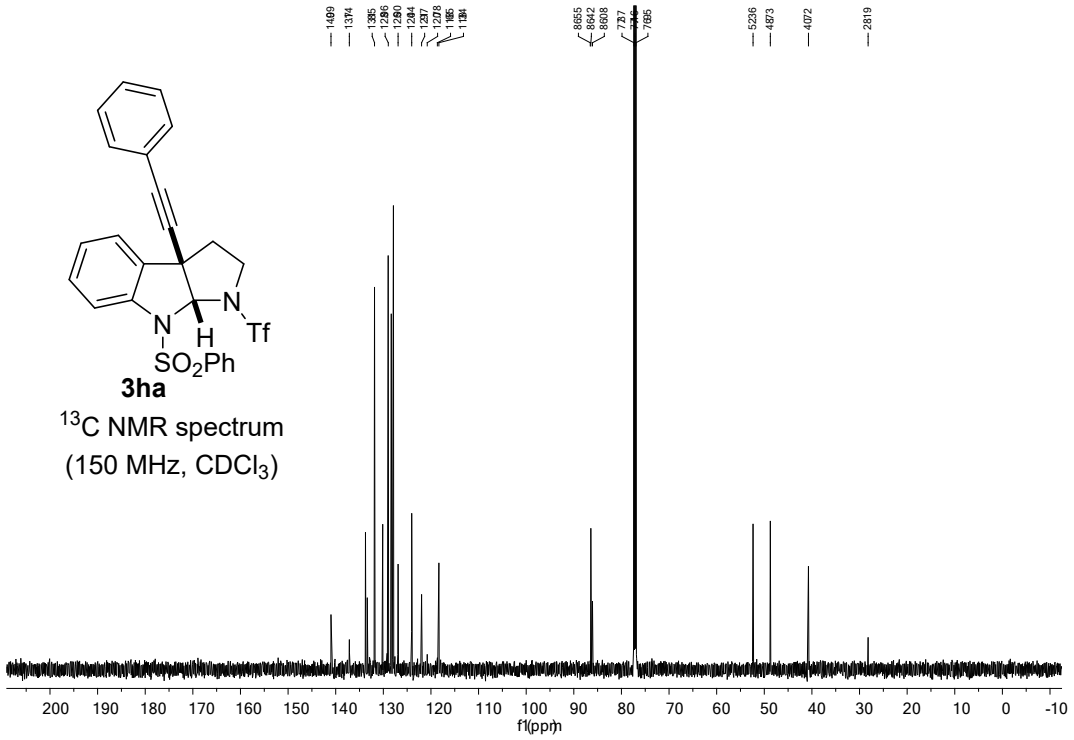


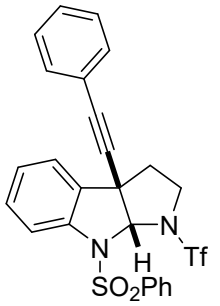
3ga

^{19}F NMR spectrum

(564 MHz, $CDCl_3$)

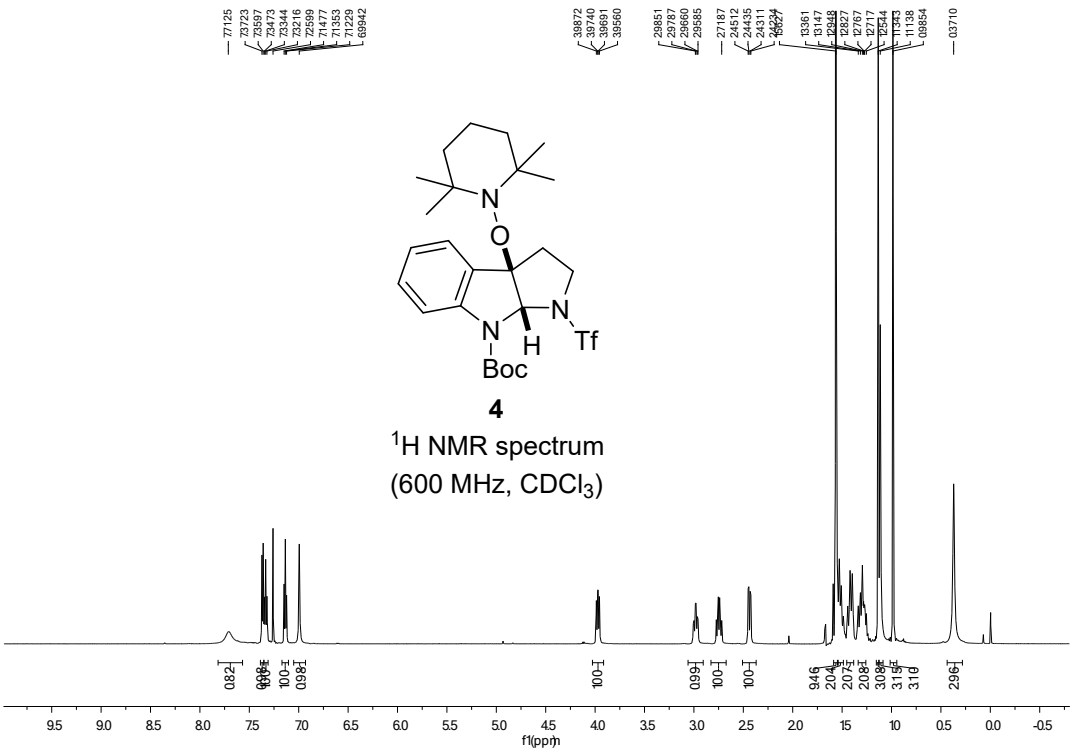

N
N
H
Tf
SO2Ph
3ha
1H NMR spectrum
(600 MHz, CDCl3)
f1(ppm)


N
N
H
Tf
SO2Ph
3ha
13C NMR spectrum
(150 MHz, CDCl3)
f1(ppm)



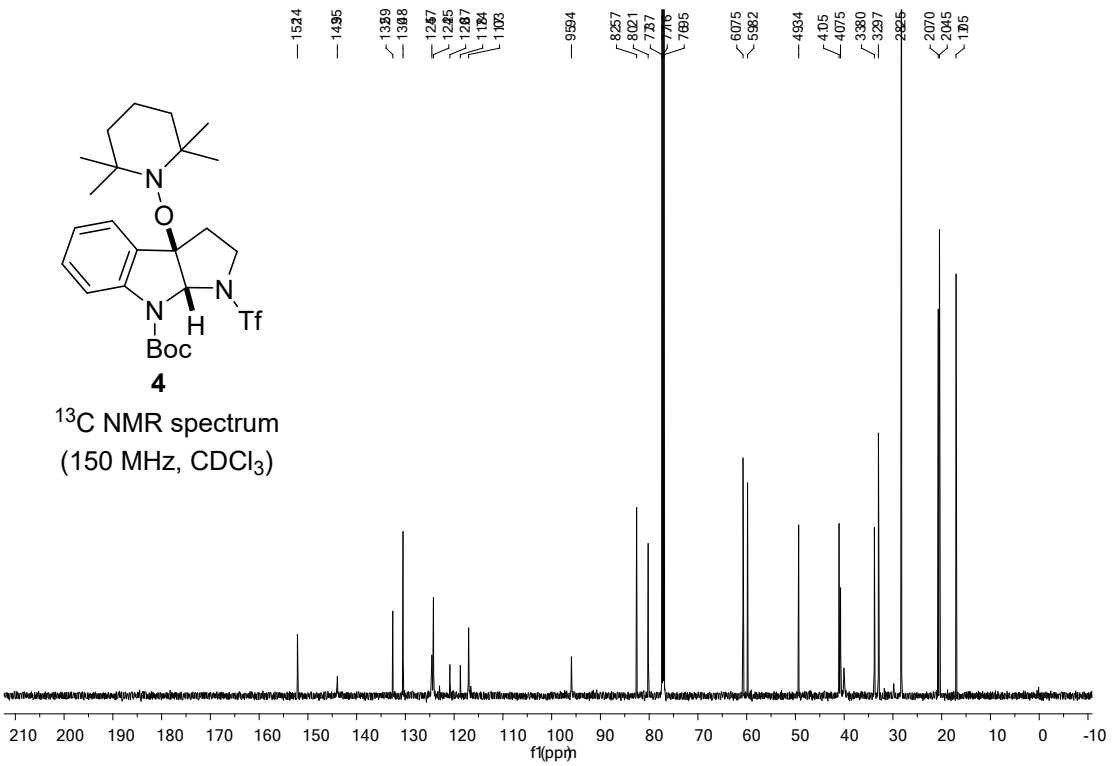
3ha

^{19}F NMR spectrum
(564 MHz, $CDCl_3$)



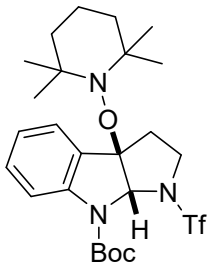
4

^{1}H NMR spectrum
(600 MHz, $CDCl_3$)



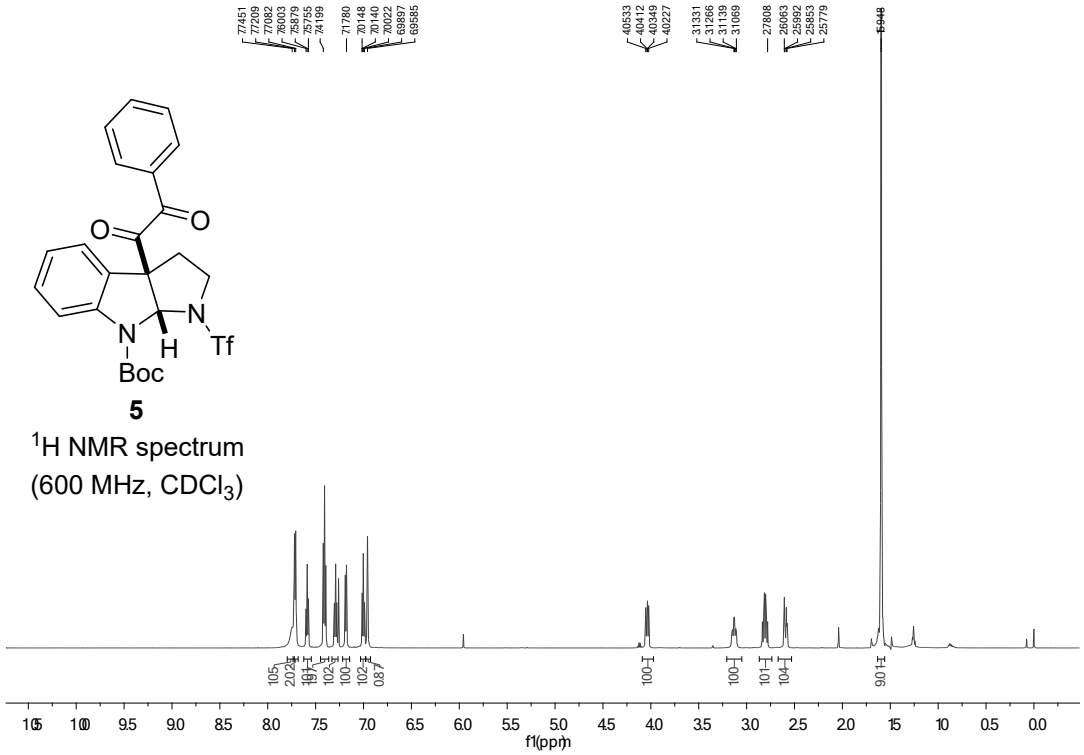
4

^{13}C NMR spectrum
(150 MHz, $CDCl_3$)



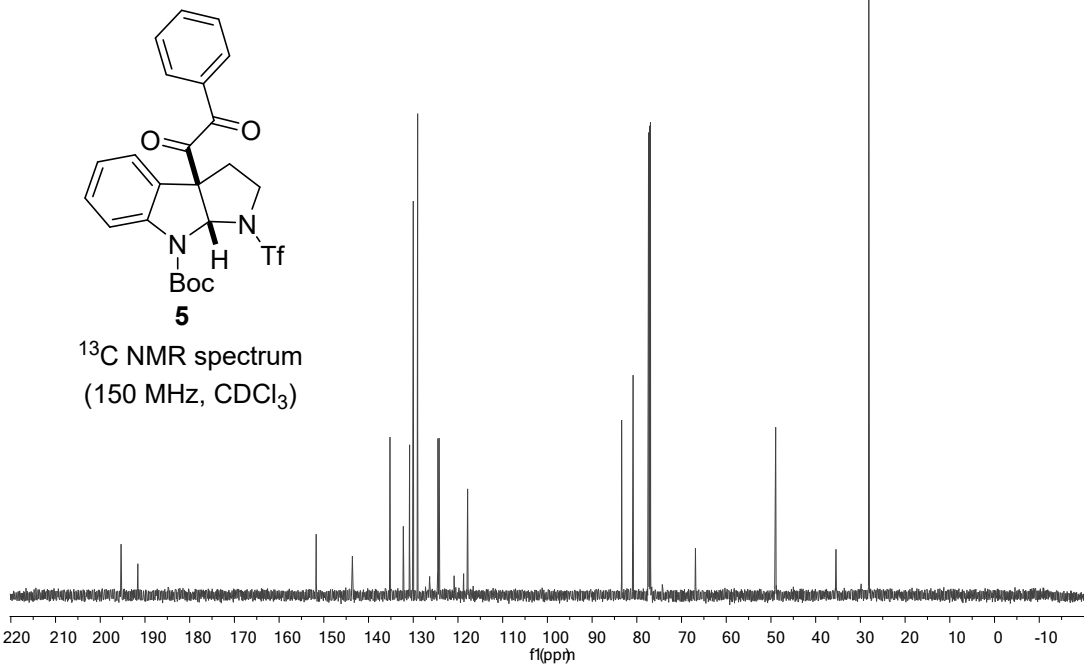
4

^{19}F NMR spectrum
(564 MHz, $CDCl_3$)



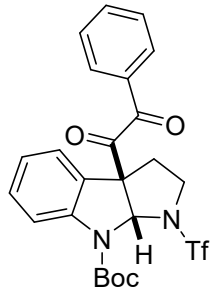
5

^{1}H NMR spectrum
(600 MHz, $CDCl_3$)



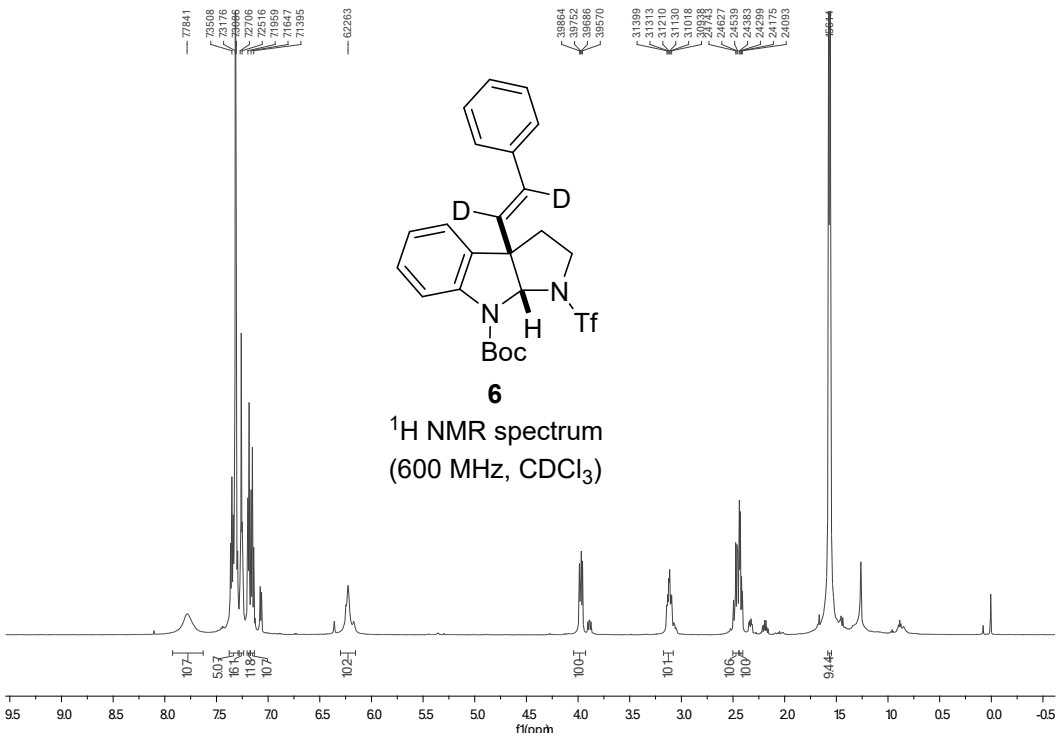
5

^{13}C NMR spectrum
(150 MHz, $CDCl_3$)



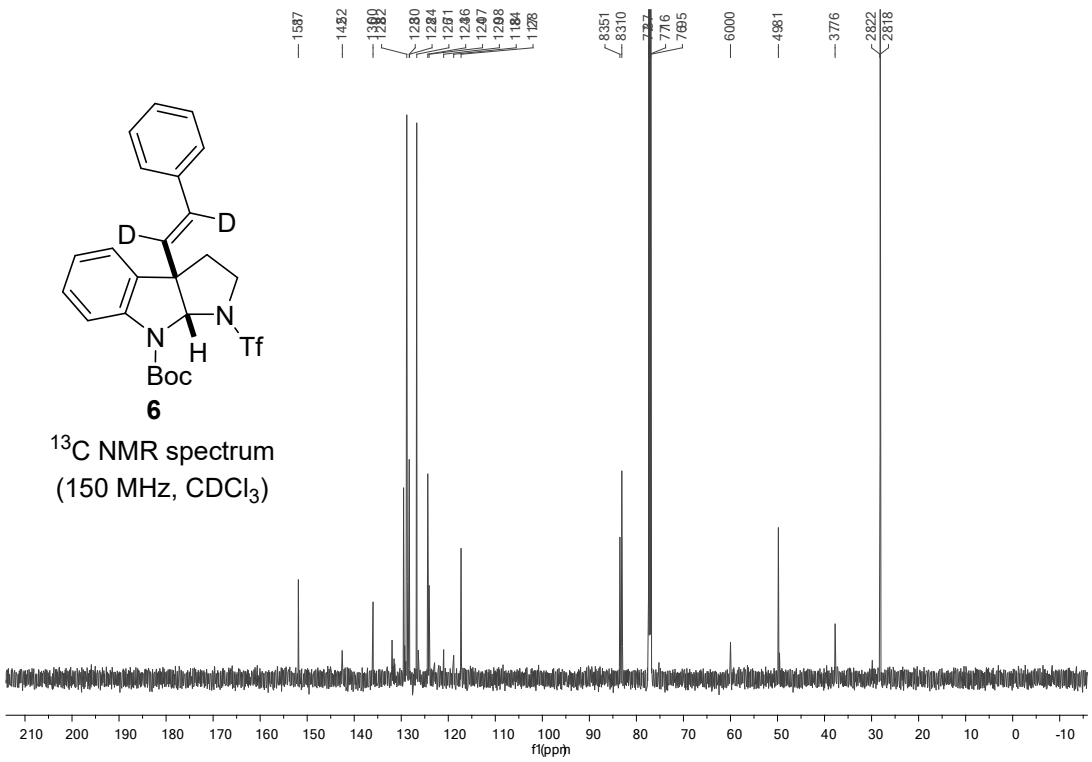
5

^{19}F NMR spectrum
(564 MHz, $CDCl_3$)



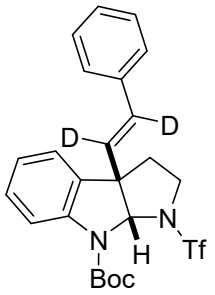
6

^{1}H NMR spectrum
(600 MHz, $CDCl_3$)



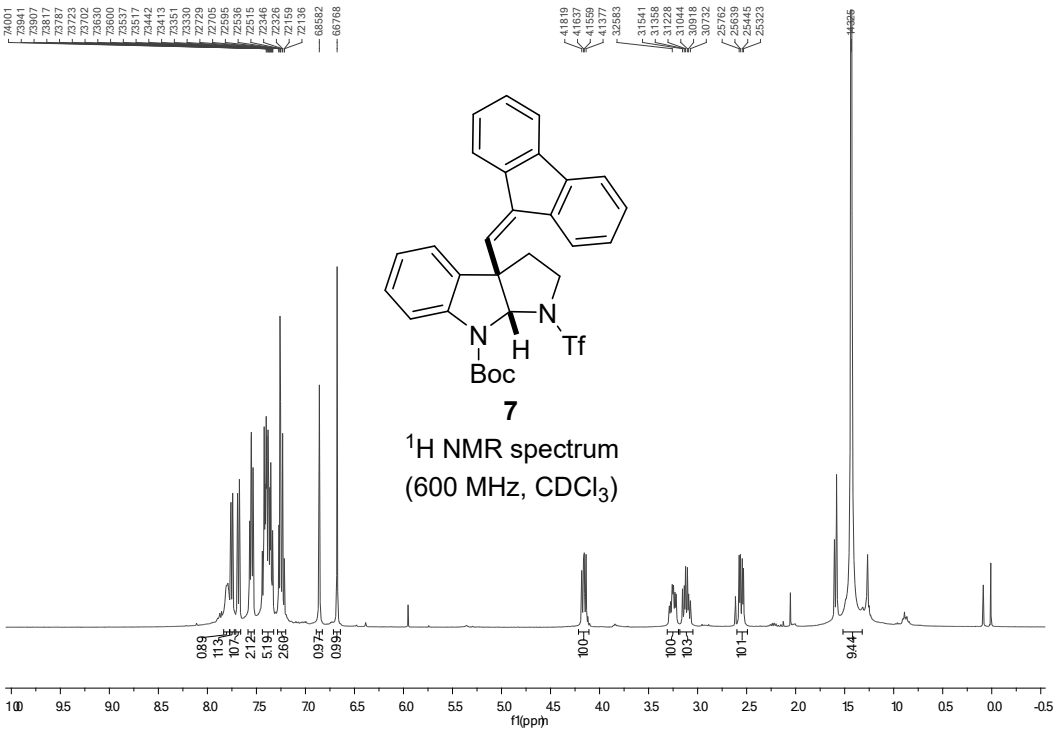
6

^{13}C NMR spectrum
(150 MHz, $CDCl_3$)



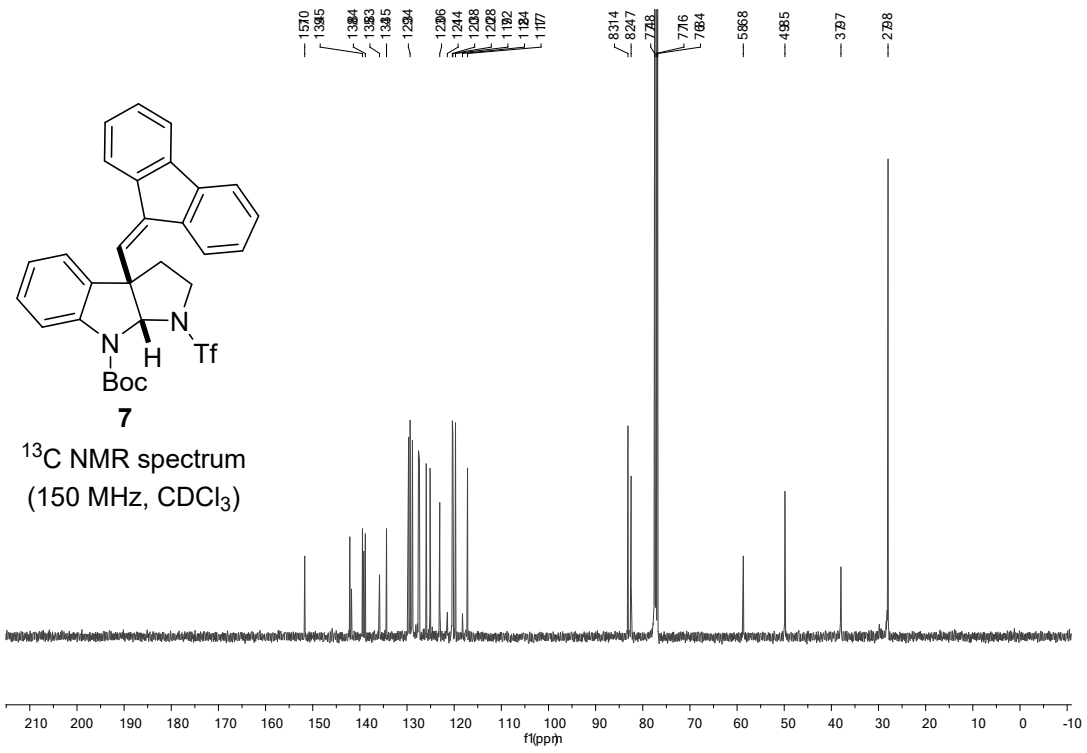
6

^{19}F NMR spectrum
(564 MHz, $CDCl_3$)



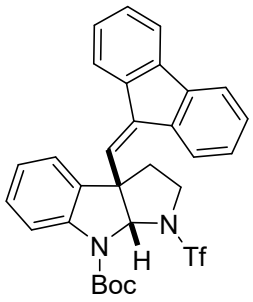
7

^{1}H NMR spectrum
(600 MHz, $CDCl_3$)



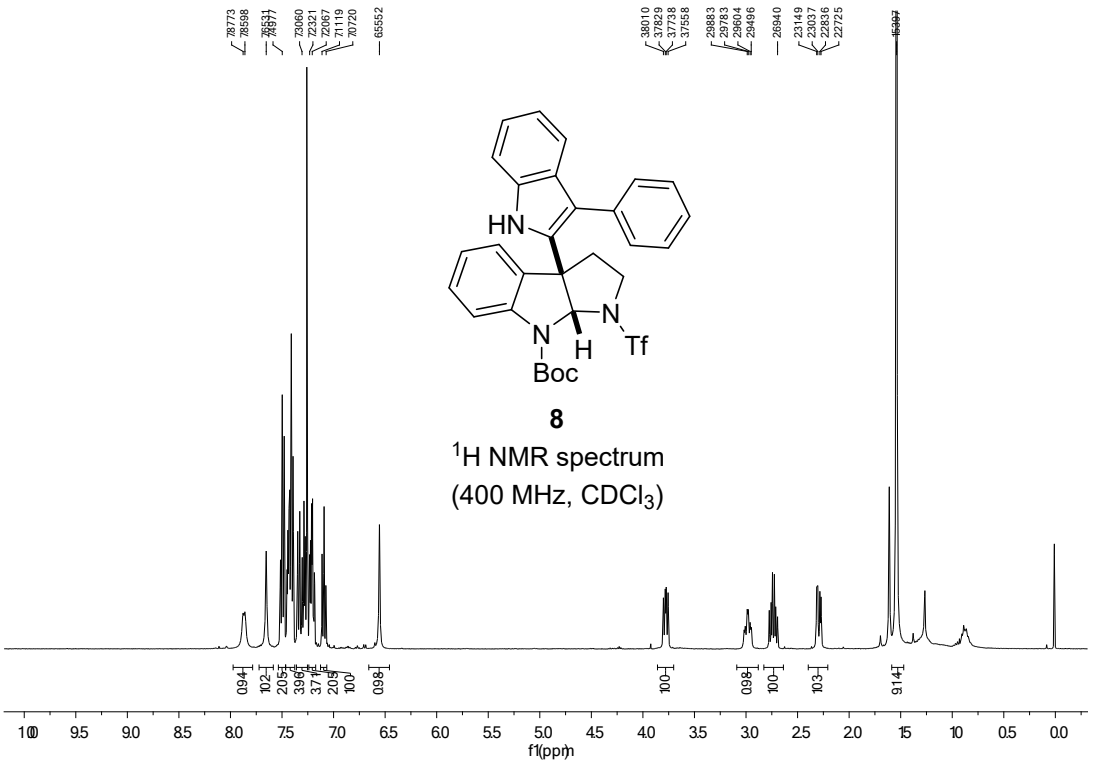
7

^{13}C NMR spectrum
(150 MHz, $CDCl_3$)



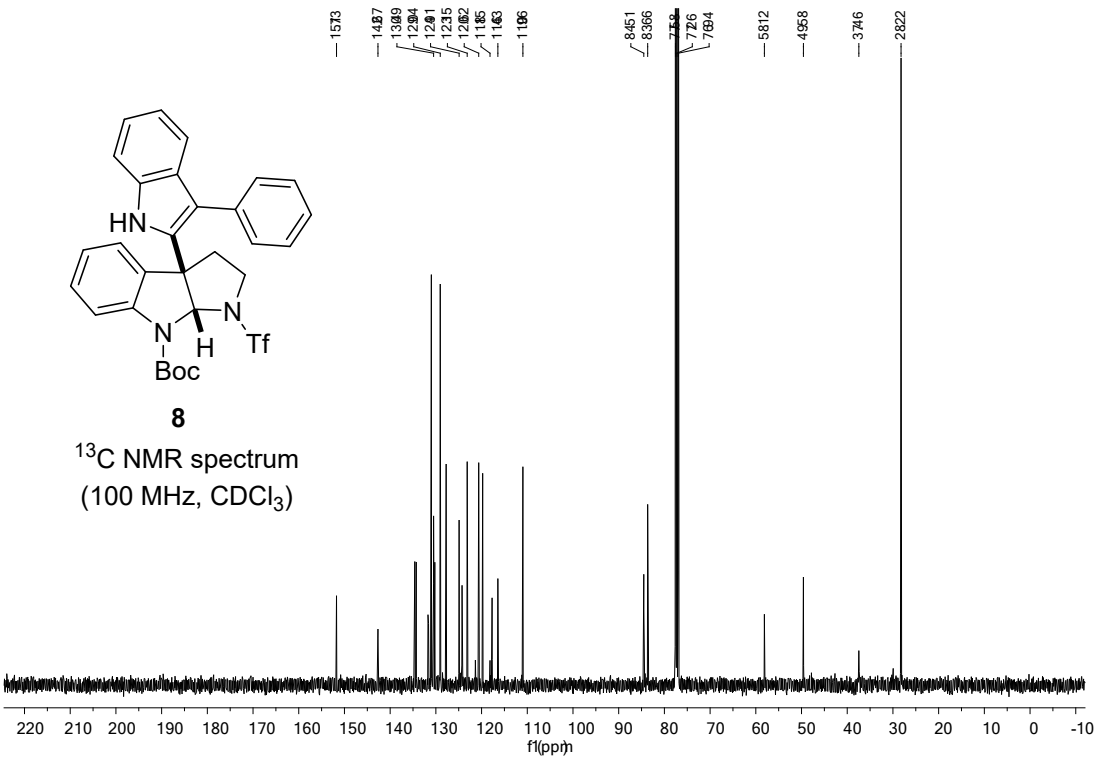
7

^{19}F NMR spectrum
(564 MHz, $CDCl_3$)



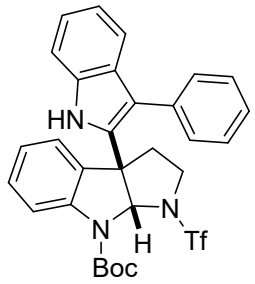
8

^{1}H NMR spectrum
(400 MHz, $CDCl_3$)



8

^{13}C NMR spectrum
(100 MHz, $CDCl_3$)



8

^{19}F NMR spectrum
(376 MHz, $CDCl_3$)