Electronic Supplementary Information

Unexpected stereoselective $CuBr_2$-catalyzed cascade reaction of 2-ethynylanilines with silylynamides: facile and atom-economical access to N-vinylsilylindoles

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1. General Information

Unless otherwise noted, all reactions were carried out in a flame-dried, sealed Schlenk reaction tube under an atmosphere of nitrogen with magnetic stirring. The oil bath acts as heat source for reactions that require heating. Reactions were monitored by analytical thin-layer chromatography (TLC). TLC was performed using Huanghai 8 ±0.2 μm precoated glass plates (0.25 mm 230-400 mesh silica gel) and visualized by UV fluorescence quenching, $KMnO_4$, or phosphomolybdic acid staining. Visualization was accomplished by exposure to a UV lamp. All the products in this article are compatible with standard silica gel chromatography unless otherwise noted. Column chromatography was performed on silica gel (200-300 mesh) using standard methods.

Melting points are recorded using DBK programmable melting point apparatus in capillary tubes and are uncorrected. ^{1}H NMR and proton decoupled ^{13}C NMR spectra were recorded on Bruker Avance 500 MHz spectrometers at ambient temperature. NMR standards were used as follows: ^{1}H NMR spectroscopy: δ = 7.26 ppm ($CDCl_3$). ^{13}C NMR spectroscopy: δ = 77.16 ppm ($CDCl_3$). Data for ^{1}H NMR were reported as chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration) using standard abbreviations for multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, dt = doublet of triplet, m = multiplet, and bs = broad signal. Data for ^{13}C NMR were reported in terms of chemical shifts (δ ppm) (multiplicity, coupling constant (Hz)) using standard abbreviations for multiplicities: d = doublet, q = quartet. Data for ^{19}F NMR were reported in terms of chemical shifts (δ ppm). High resolution mass spectra (HRMS) were recorded on Bruker 15T SolariX FTICR mass spectrometer instrument in an electrospray ionization mode (ESI+) or Thermo fisher Q-Exactive Orbitrap mass spectrometer instrument in an atmospheric pressure chemical ionization mode (APCI). X-ray diffraction analysis was recorded on an Agilent Gemini E X-ray single crystal diffractometer.

Petroleum ester (PE, 60~90 ^{o}C) and ethyl acetate (EA) were used as eluent for silica gel chromatography. Solvents were distilled under nitrogen from calcium hydride or sodium/benzophenone. 2-Ethynylanilines **1** were commercially available or prepared according to literature procedures. Ynamides **2** were prepared according to literature procedures. Other reagents were purchased commercially and used without further purification unless otherwise noted.

2. Preparation of 2-Ethynylanilines

2-Ethynylanilines **1a-1t** were prepared according to literature procedures[1,2].

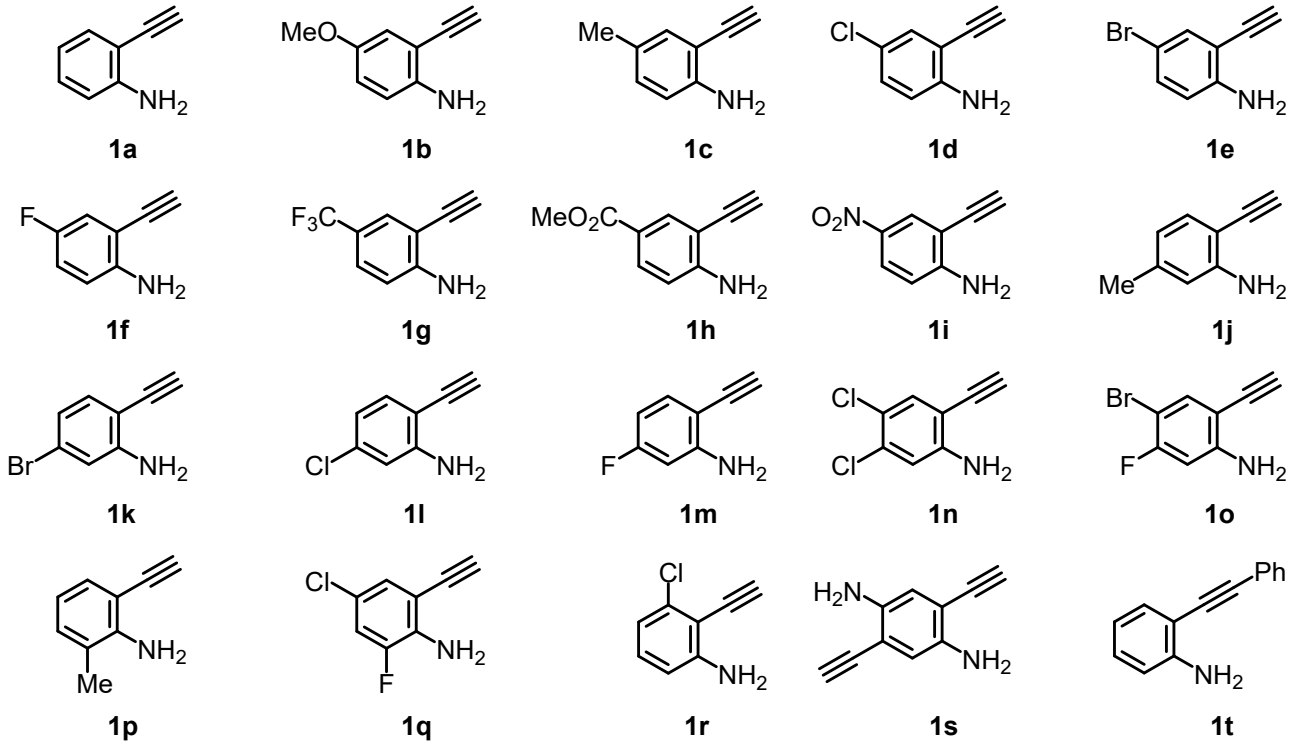
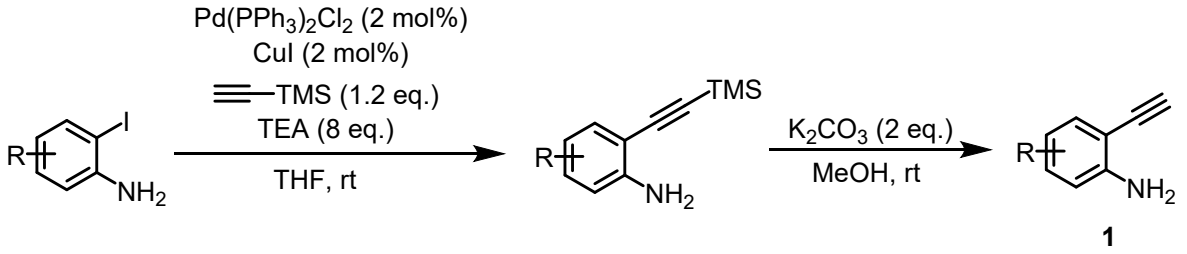


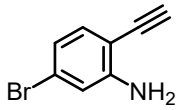
Figure S1. 2-Ethynylanilines used in this work

Synthetic procedure for substituted 2-ethynylanilines



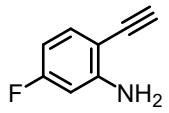
A mixture of 2-iodoaniline (3.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.06 mmol), CuI (0.06 mmol), ethynyltrimethylsilane (3.6 mmol), and TEA (24.0 mmol) in THF (5.0 mL) was stirred at room temperature overnight under nitrogen. When the reaction was complete, TEA and THF was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (eluent: PE/EA). To a solution of this intermediate in MeOH (10.0 mL), K_2CO_3 (6.0 mmol) was added. The resulting mixture was then stirred at room temperature for 30 min and concentrated in vacuo. The residue was extracted with ethyl acetate (15 mL × 3), and the combined organic layer was washed with brine, dried over anhydrous Na_2SO_4. Finally, the solvent was removed under vacuo to give compound **1.**

Analytical data of unkown 2-ethynylanilines:



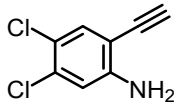
1k

5-Bromo-2-ethynylaniline (1k), pale yellow solid, m.p. 59-61 °C (548.5 mg, 93 % yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.16 (d, J = 8.2 Hz, 1H), 6.84 (d, J = 1.7 Hz, 1H), 6.79 (dd, J = 8.2, 1.8 Hz, 1H), 4.31 (s, 2H), 3.43 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 149.6, 133.7, 124.1, 120.8, 117.0, 105.5, 83.6, 79.8. **HRMS** (APCI, m/z) Calculated for $[C_8H_5BrN, M - H]^+$: 193.9611, found: 193.9606.



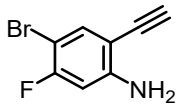
1m

2-Ethynyl-5-fluoroaniline (1m), pale yellow oil (356.4 mg, 88 % yield). PE/EA = 10:1, R_f = 0.25. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.29-7.26 (m, 1H), 6.40-6.36 (m, 2H), 4.36 (s, 2H), 3.35 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 164.1 (d, J = 248.0 Hz), 150.4 (d, J = 11.8 Hz), 134.4 (d, J = 10.3 Hz), 106.3 (d, J = 22.4 Hz), 102.8 (d, J = 2.6 Hz), 101.1 (d, J = 25.7 Hz), 82.3 (d, J = 1.3 Hz), 79.9. **^{19}F NMR** (471 MHz, $CDCl_3$): δ -109.25. **HRMS** (ESI, m/z) Calculated for $[C_6H_7FN, M + H]^+$: 136.0557, found: 136.0557.



1n

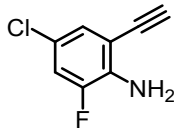
4,5-Dichloro-2-ethynylaniline (1n), colorless solid, m.p. 117-119 °C (482.8 mg, 87% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.36 (s, 1H), 6.79 (s, 1H), 4.29 (s, 2H), 3.43 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 147.9, 134.1, 133.5, 120.5, 115.6, 106.8, 84.2, 78.7. **HRMS** (APCI, m/z) Calculated for $[C_8H_4Cl_2N, M - H]^+$: 183.9726, found: 183.9720.



1o

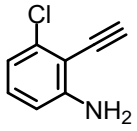
4-Bromo-2-ethynyl-5-fluoroaniline (1o), colorless solid, m.p. 58-60 °C, (527.9 mg, 83 % yield). PE/EA = 9:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.45 (d, J = 7.5 Hz, 1H), 6.46 (d, J = 10.1 Hz, 1H), 4.38 (s, 2H), 3.38 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 160.1 (d, J = 248.1 Hz), 149.5

(d, J = 10.6 Hz), 136.7 (d, J = 2.5 Hz), 104.5 (d, J = 3.0 Hz), 102.2, 102.0, 95.6 (d, J = 22.4 Hz), 83.3, 78.6. **^{19}F NMR** (471 MHz, $CDCl_3$): δ -104.06. **HRMS** (APCI, m/z) Calculated for [C_8H_4BrFN, M - H]$^+$: 211.9516, found: 211.9511.



1q

4-Chloro-2-ethynyl-6-fluoroaniline (1q), white solid, m.p. 52-54 °C (400.5 mg, 79 % yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.10-7.09 (m, 1H), 7.00 (dd, J = 10.6, 2.3 Hz, 1H), 4.27 (s, 2H), 3.46 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 150.7 (d, J = 242.5 Hz), 136.4 (d, J = 13.8 Hz), 127.4 (d, J = 3.6 Hz), 121.2 (d, J = 10.4 Hz), 116.9 (d, J = 21.7 Hz), 109.3 (d, J = 6.3 Hz), 84.5, 78.3 (d, J = 4.7 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$): δ -131.84. **HRMS** (APCI, m/z) Calculated for [C_8H_4ClFN, M - H]$^+$: 168.0022, found: 168.0015.

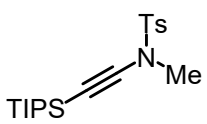


1r

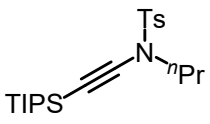
3-Chloro-2-ethynylaniline (1r), pale yellow oil (362.4 mg, 80% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.04 (t, J = 8.1 Hz, 1H), 6.75 (dd, J = 8.0, 0.7 Hz, 1H), 6.59 (dd, J = 8.2, 0.7 Hz, 1H), 4.38 (s, 2H), 3.68 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 150.2, 136.6, 130.2, 118.4, 112.4, 106.9, 87.5, 77.6. **HRMS** (APCI, m/z) Calculated for [C_8H_5ClN, M - H]$^+$: 150.0116, found: 150.0105.

3. Preparation of Ynamides

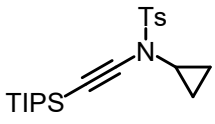
Ynamides **2a-2j** were prepared according to literature procedures[1,3].



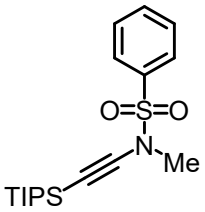
2a



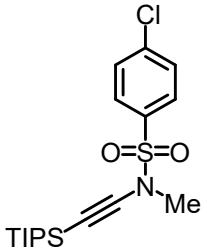
2b



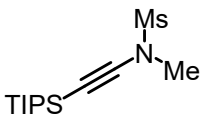
2c



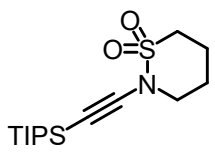
2d



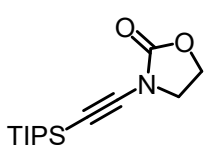
2e



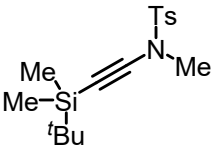
2f



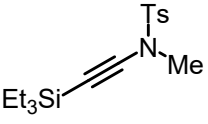
2g



2h



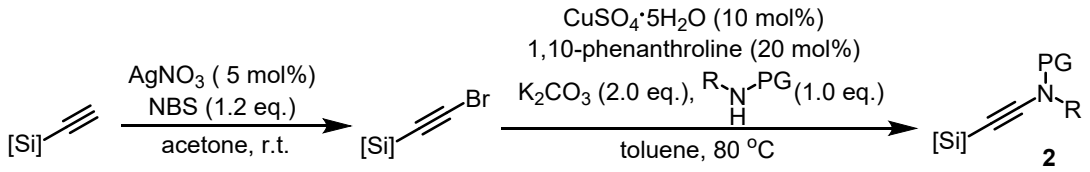
2i



2j

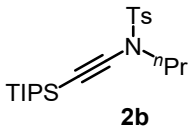
Figure S2. Ynamides used in this work

Synthetic procedure for ynamides



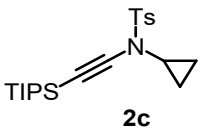
A mixture of terminal alkyne (3.0 mmol), NBS (3.6 mmol) and $AgNO_3$ (0.15 mmol) in acetone (10 mL) was stirred under N_2 at room temperature for 3 hours. Then the excess acetone was removed under vacuo. The residue was diluted with petroleum ether (25 mL), filtered through a pad of Celite, and the filtrate was concentrated in vacuo to give the bromoalkynes. To a solution of the bromoalkyne (3.0 mmol) in toluene (10 ml) sulfonamides (3.0 mmol), $CuSO_4{\cdot}5H_2O$ (0.3 mmol), 1,10-phenanthroline (0.6 mmol) and K_2CO_3 (6.0 mmol) were added. The resulting mixture was stirred at 80 °C overnight under N_2. After completion, the toluene was removed in vacuo. The residue was diluted with Et_2O, filtered through Celite, and the filtrate was concentrated in vacuo. The resulting residue was then purified by chromatography on silica gel (eluent: PE/EA) to afford ynamide **2**.

Analytical data of unkown ynamides:



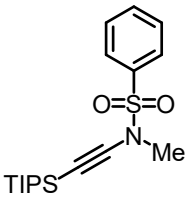
2b

4-Methyl-N-propyl-N-(triisopropylsilyl)benzenesulfonamide (2b), white solid, m.p. 49-51 °C (884.3 mg, 80% yield). PE/EA = 25:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.79 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 3.28 (t, J = 7.1 Hz, 2H), 2.44 (s, 3H), 1.70-1.65 (m, 2H), 1.04 (s, 21H), 0.91 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 144.6, 134.8, 129.7, 127.8, 96.4, 69.3, 53.1, 21.8, 21.3, 18.7, 18.6, 11.5, 11.4, 11.0. **HRMS** (ESI, m/z) Calculated for $[C_{21}H_{36}NO_2SSi, M + H]^+$: 394.2231, found: 394.2230.



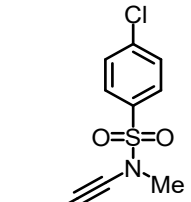
2c

N-cyclopropyl-4-methyl-N-((triisopropylsilyl)ethynyl)benzenesulfonamide (2c), white solid, m.p. 51-53 °C (915.4 mg, 78% yield). PE/EA = 25:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.83 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 2.85-2,81 (m, 1H), 2.45 (s, 3H), 1.04 (s, 21H), 0.82-0.81 (m, 2H), 0.79-0.72 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 144.8, 134.1,129.7, 128.2, 95.4, 69.5, 32.6, 21.8, 18.7, 11.5, 6.2. **HRMS** (ESI, m/z) Calculated for $[C_{21}H_{34}NO_2SSi, M + H]^+$: 392.2074, found: 392.2072.



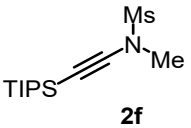
2d

N-methyl-N-((triisopropylsilyl)ethynyl)benzenesulfonamide (2d), colorless oil (937.7 mg, 89% yield). PE/EA = 25:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.92-7.90 (m, 2H), 7.67-7.64 (m, 1H), 7.55 (t, J = 8.0 Hz, 2H), 3.09 (s, 3H), 1.03 (s, 21H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 136.3, 133.8, 129.2, 127.9, 97.9, 67.8, 39.5, 18.7, 11.4. **HRMS** (ESI, m/z) Calculated for [$C_{18}H_{30}NO_2SSi$, M + H]$^+$: 352.1761, found: 352.1759.



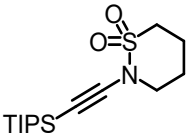
2e

4-Chloro-N-methyl-N-((triisopropylsilyl)ethynyl)benzenesulfonamide (2e), white solid, m.p. 48-50 ^{o}C (993.5 mg, 86% yield). PE/EA = 25:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.86-7.84 (m, 2H), 7.54-7.51 (m, 2H), 3.10 (s, 3H), 1.04 (s, 21H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 140.6, 134.8, 129.6, 129.4, 97.5, 68.2, 39.6, 18.7, 11.4. **HRMS** (ESI, m/z) Calculated for [$C_{18}H_{29}ClNO_2SSi$, M + H]$^+$: 386.1372, found: 386.1369.



2f

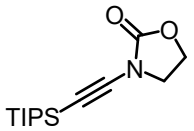
N-methyl-N-((triisopropylsilyl)ethynyl)methanesulfonamide (2f), **c**olorless oil (780.8 mg, 90% yield). PE/EA = 25:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): 3.21 (s, 3H), 3.07 (s, 3H), 1.07 (s, 21H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 97.6, 68.5, 39.3, 36.5, 18.7, 11.4. **HRMS** (ESI, m/z) Calculated for [$C_{13}H_{28}NO_2SSi$, M + H]$^+$: 290.1605, found: 290.1603.



2g

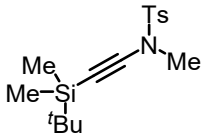
2-((Triisopropylsilyl)ethynyl)-1,2-thiazinane 1,1-dioxide (2g), colorless oil (765.9 mg, 81% yield). PE/EA = 25:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 3.75 (t, J = 5.5 Hz, 2H), 3.21 (t, J = 6.1 Hz, 2H), 2.25-2.18 (m, 2H), 1.84-1.77 (m, 2H), 1.07 (s, 21H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 97.5, 67.6,

55.6, 47.7, 23.9, 20.8, 18.8, 11.4. **HRMS** (ESI, m/z) Calculated for $[C_{15}H_{30}NO_2SSi, M + H]^+$: 316.1761, found: 316.1760.



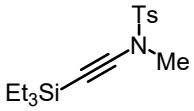
2h

3-((Triisopropylsilyl)ethynyl)oxazolidin-2-one (2h), white solid, m.p. 54-56 °C (641.28 mg, 80% yield). PE/EA = 25:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 4.43-4.40 (m, 2H), 3.94-3.91 (m, 2H), 1,07 (s, 21H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 156.0, 93.2, 70.1, 62.9, 47.1, 18.7, 11.3. **HRMS** (ESI, m/z) Calculated for $[C_{14}H_{26}NO_2Si, M + H]^+$: 268.1728, found: 268.1726.



2i

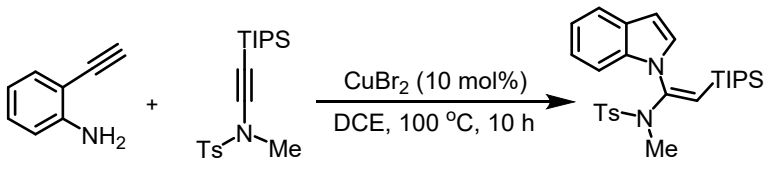
N-((tert-butyldimethylsilyl)ethynyl)-N,4-dimethylbenzenesulfonamide (2i), white solid, m.p. 58-59 °C (755.8 mg, 78 % yield). PE/EA = 20:1, R_f = 0.25. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.79 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 3.06 (s, 3H), 2.46 (s, 3H), 0.91 (s, 9H), 0.08 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 144.9, 133.4, 129.8, 128.0, 97.1, 69.8, 39.3, 26.2, 21.8, 16.9, -4.4 **HRMS** (ESI, m/z) Calculated for $[C_{16}H_{26}NO_2SSi, M + H]^+$: 324.1448, found: 324.1447.



2j

N,4-dimethyl-N-((triethylsilyl)ethynyl)benzenesulfonamide (2j), colorless oil (843.2 mg, 84% yield). PE/EA = 25:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.79 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 3.06 (s, 3H), 2.45 (s, 3H), 0.95 (t, J = 7.9 Hz, 9H), 0.57 (q, J = 7.8 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 144.9, 133.4, 129.8, 128.0, 97.7, 68.8, 39.3, 21.8, 7.5, 4.6. **HRMS** (ESI, m/z) Calculated for $[C_{16}H_{26}NO_2SSi, M + H]^+$: 324.1448, found: 324.1447.

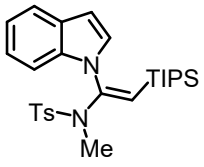
4. Typical Procedure for N-Vinylindoles



1a **2a** **3aa**

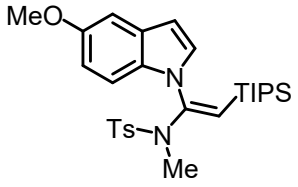
Typical procedure: A pre-dried 10.0 mL Schlenk tube was charged with stirring bar, $CuBr_2$ (4.5 mg, 0.02 mmol, 0.1 eq.), 2-ethynylaniline (**1a**, 35.2 mg, 0.3 mmol, 1.5 eq.), N,4-dimethyl-N-((triisopropylsilyl)ethynyl) benzenesulfonamide (**2a**, 73.1 mg, 0.2 mmol, 1 eq.) and DCE (1.0 mL). The mixture was stirred at 100 °C for 10 h. After cooling to room temperature, solvent was removed by rotary evaporation instrument and 1,3,5-trimethoxybenzene as the internal reference was added. The NMR yield (96%) and *E/Z* ratio (>30:1) are determined by the ^{1}H NMR spectroscopy. Finally, the mixture was transferred to a column and purified by flash chromatography on silica gel (PE/EA = 20:1, R_f = 0.30) to give the analytical pure product **3aa** (91.6 mg, 95 % yield).

5. Characterization of N-Vinylindoles



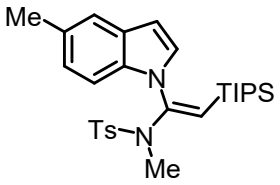
3aa

(E)-N-(1-(1H-indol-1-yl)-2-(triisopropylsilyl)vinyl)-N,4-dimethylbenzenesulfonamide (3aa), white solid, m.p. 78-80 °C (91.6 mg, 95% yield). PE/EA = 20:1, R_f = 0.25. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.53-7.51 (m, 3H), 7.29-7.27 (m, 1H), 7.16 (d, J = 8.2 Hz, 2H), 7.12-7.07 (m, 2H), 7.03 (d, J = 3.3 Hz, 1H), 6.48 (d, J = 3.2 Hz, 1H), 5.21 (s, 1H), 2.99 (s, 3H), 2.38 (s, 3H), 0.90-0.85 (m, 21H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 144.6, 143.8, 136.4, 135.6, 129.7, 129.5, 129.0, 127.3, 122.6, 120.9, 120.7, 112.5, 111.8, 103.4, 37.1, 21.6, 18.9, 12.0. **HRMS** (ESI, m/z) Calculated for $[C_{27}H_{38}N_2O_2SSiNa, M + Na]^+$: 505.2315, found: 505.2319.



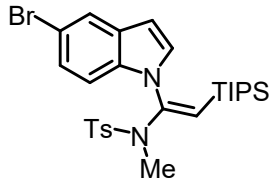
3ba

(E)-N-(1-(5-methoxy-1H-indol-1-yl)-2-(triisopropylsilyl)vinyl)-N,4-dimethylbenzene sulfonamide (3ba), pale yellow solid, m.p. 102-104 °C (94.3 mg, 92% yield). PE/EA = 20:1, R_f = 0.30. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.54 (d, J = 8.3 Hz, 2H), 7.21-7.15 (m, 3H), 7.02-6.98 (m, 2H), 6.74 (dd, J = 8.8, 2.5 Hz, 1H), 6.41 (d, J = 3.2 Hz, 1H), 5.13 (s, 1H), 3.83 (s, 3H), 2.97 (s, 3H), 2.39 (s, 3H), 0.89-0.83 (m, 21H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 154.8, 144.7, 143.8, 135.7, 131.5, 130.3,129.7, 129.5, 127.3, 112.6, 112.5, 111.6, 103.2, 102.7, 55.8, 37.0, 21.6, 18.9, 12.0. **HRMS** (ESI, m/z) Calculated for $[C_{28}H_{40}N_2O_3SSiNa, M + Na]^+$: 535.2421, found: 535.2428.



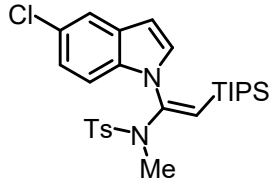
3ca

(E)-N,4-dimethyl-N-(1-(5-methyl-1H-indol-1-yl)-2-(triisopropylsilyl)vinyl)benzenesulfonamide (3ca), pale yellow solid, m.p. 102-103 °C (79.4 mg, 80% yield). PE/EA = 20:1, R_f = 0.30. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.54 (d, J = 8.2 Hz, 2H), 7.30 (s, 1H), 7.18 (d, J = 8.1 Hz, 3H), 6.98 (d, J = 3.3 Hz, 1H), 6.91 (d, J = 8.5 Hz, 1H), 6.40 (d, J = 3.2 Hz, 1H), 5.16 (s, 1H), 2.95 (s, 3H), 2.40 (d, J = 7.3 Hz, 6H), 0.89-0.88 (m, 21H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 144.7, 143.8, 135.7, 134.8, 130.0, 129.7, 129.5, 129.4, 127.4, 124.2, 120.7, 111.8, 111.5, 103.1, 36.9, 21.6, 21.5, 18.9, 12.0. **HRMS** (ESI, m/z) Calculated for $[C_{28}H_{40}N_2O_2SSiNa, M + Na]^+$: 519.2472, found: 519.2480.



3da

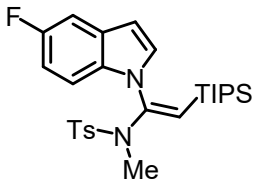
(E)-N-(1-(5-bromo-1H-indol-1-yl)-2-(triisopropylsilyl)vinyl)-N,4-dimethylbenzenesulfonamide (3da), yellow oil (90.7 mg, 81% yield). PE/EA = 20:1, R_f = 0.30. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.63 (d, J = 1.8 Hz, 1H), 7.43 (d, J = 8.3 Hz, 2H), 7.16-7.11 (m, 3H), 7.10-7.05 (m, 2H), 6.43 (d, J = 3.2 Hz, 1H), 5.19 (s, 1H), 3.06 (s, 3H), 2.39 (s, 3H), 0.94-0.91 (m, 21H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 144.5, 144.1, 135.3, 135.0, 131.0, 130.7, 129.5, 127.1, 125.4, 123.5, 114.1, 113.1, 112.8, 102.9, 37.6, 21.7, 18.9, 12.0. **HRMS** (ESI, m/z) Calculated for $[C_{27}H_{37}BrN_2O_2SSiNa, M + Na]^+$: 583.1420, found: 583.1432.



3ea

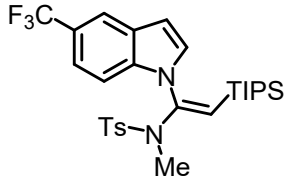
(E)-N-(1-(5-chloro-1H-indol-1-yl)-2-(triisopropylsilyl)vinyl)-N,4-dimethylbenzenesulfonamide (3ea), pale yellow solid, m.p. 99-100 °C (98.0 mg, 95% yield). PE/EA = 20:1, R_f = 0.30. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.48 (d, J = 1.9 Hz, 1H), 7.45 (d, J = 8.3 Hz, 2H), 7.16-7.11 (m, 3H), 7.10 (d, J = 3.3 Hz, 1H), 7.01 (dd, J = 8.6, 1.9 Hz, 1H), 6.43 (d, J = 3.2 Hz, 1H), 5.19 (s, 1H), 3.05 (s, 3H), 2.38 (s, 3H), 0.90-0.85 (m, 21H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 144.5, 144.0, 135.3, 134.7, 131.2,

130.1, 129.5, 127.1, 126.4, 122.9, 120.4, 112.7, 112.6, 103.0, 37.5, 21.6, 18.9, 12.0. **HRMS** (ESI, m/z) Calculated for $[C_{27}H_{37}ClN_2O_2SSiNa, M + Na]^+$: 539.1926, found: 539.1932.



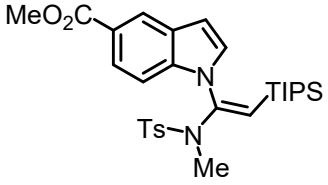
3fa

(E)-N-(1-(5-fluoro-1H-indol-1-yl)-2-(triisopropylsilyl)vinyl)-N,4-dimethylbenzenesulfonamide (3fa), pale yellow solid, m.p. 105-106 °C (95.9 mg, 96% yield). PE/EA = 20:1, R_f = 0.25. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.49 (d, J = 8.2 Hz, 2H), 7.21-7.13 (m, 4H), 7.10 (d, J = 3.2 Hz, 1H), 6.87-6.77 (m, 1H), 6.44 (d, J = 3.2 Hz, 1H), 5.16 (s, 1H), 3.03 (s, 3H), 2.38 (s, 3H), 0.88-0.87 (m, 21H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 158.5 (d, J = 235.7 Hz), 144.6, 144.0, 135.5, 132.9, 131.4, 129.5, 127.3, 112.5 (d, J = 9.3 Hz), 110.9 (d, J = 20.0 Hz), 103.3 (d, J = 4.4 Hz), 37.3, 21.6, 18.9, 12.0. **^{19}F NMR** (471 MHz, $CDCl_3$): δ -124.00. **HRMS** (ESI, m/z) Calculated for $[C_{27}H_{37}FN_2O_2SSiNa, M + Na]^+$: 523.2221, found: 523.2229.



3ga

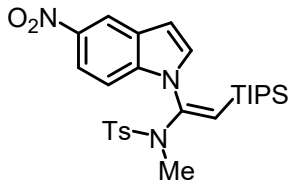
(E)-N,4-dimethyl-N-(1-(5-(trifluoromethyl)-1H-indol-1-yl)-2-(triisopropylsilyl)vinyl)benzene sulfonamide (3ga), pale yellow solid, m.p. 81-83 °C (100.1 mg, 91% yield). PE/EA = 25:1, R_f = 0.30. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.79 (s, 1H), 7.36 (d, J = 8.3 Hz, 2H), 7.26-7.24 (m, 1H), 7.24-7.19 (m, 2H), 7.06 (d, J = 8.0 Hz, 2H), 6.57 (d, J = 3.2 Hz, 1H), 5.24 (s, 1H), 3.14 (s, 3H), 2.33 (s, 3H), 0.88-0.85 (m, 21H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 144.5, 144.0, 137.6, 135.2, 131.7, 129.4, 128.4, 127.0, 125.3 (q, J = 271.3 Hz), 123.0 (q, J = 31.8 Hz), 119.2 (q, J = 3.5 Hz), 118.6 (q, J = 4.0 Hz), 113.3, 111.9, 103.9, 37.9, 21.5, 120.7, 18.9, 12.0. **^{19}F NMR** (471 MHz, $CDCl_3$): δ -60.47. **HRMS** (ESI, m/z) Calculated for $[C_{28}H_{37}F_3N_2O_2SSiNa, M + Na]^+$: 573.2189, found: 573.2198.



3ha

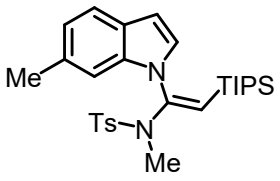
Methyl(E)-1-(1-((N,4-dimethylphenyl)sulfonamido)-2-(triisopropylsilyl)vinyl)-1H-indole-5-carboxylate (3ha), white solid, m.p. 127-129 °C (91.8 mg, 85% yield). PE/EA = 20:1, R_f = 0.30. **^{1}H**

NMR (500 MHz, $CDCl_3$): δ 8.28 (s, 1H), 7.77 (dd, J = 8.7, 1.6 Hz, 1H), 7.44 (d, J = 8.3 Hz, 2H), 7.21 (d, J = 8.7 Hz, 1H), 7.14 (d, J = 3.3 Hz, 1H), 7.11 (d, J = 8.1 Hz, 2H), 6.58 (d, J = 2.8 Hz, 1H), 5.27 (s, 1H), 3.93 (s, 3H), 3.08 (s, 3H), 2.34 (s, 3H), 0.87-0.86 (m, 21H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 168.1, 144.3, 144.0, 138.9, 135.3, 131.2, 129.5, 128.6, 127.2, 123.9, 123.8, 122.8, 133.8, 111.3, 104.5, 52.0, 37.6, 21.6, 18.9, 11.9. **HRMS** (ESI, m/z) Calculated for [$C_{29}H_{41}N_2O_4SSi$, M + H]$^+$: 541.2551, found: 541.2561.



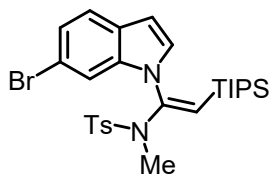
3ia

(E)-N,4-dimethyl-N-(1-(5-nitro-1H-indol-1-yl)-2-(triisopropylsilyl)vinyl)benzenesulfonamide (3ia), yellow oil (91.6 mg, 87% yield). PE/EA = 20:1, R_f = 0.30. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.47 (d, J = 2.2 Hz, 1H), 7.96 (dd, J = 9.1, 2.2 Hz, 1H), 7.42 (d, J = 8.3 Hz, 2H), 7.25-7.24 (m, 2H), 7.11 (d, J = 8.1 Hz, 2H), 6.66 (d, J = 3.3 Hz, 1H), 5.21 (s, 1H), 3.11 (s, 3H), 2.32 (s, 3H), 0.85-0.82 (m, 21H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 144.4, 144.1, 142.6, 139.1, 134.8, 133.1, 129.6, 128.4, 127.2, 118.1, 118.0, 114.5, 111.7, 105.1, 38.0, 21.6, 18.9, 11.9. **HRMS** (ESI, m/z) Calculated for [$C_{27}H_{37}N_3O_4SSiNa$, M + Na]$^+$: 550.2166, found: 550.2181.



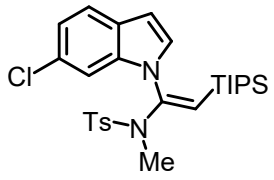
3ja

(E)-N,4-dimethyl-N-(1-(6-methyl-1H-indol-1-yl)-2-(triisopropylsilyl)vinyl)benzenesulfonamide (3ja), yellow oil (90.3 mg, 91% yield). PE/EA = 20:1, R_f = 0.30. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.51 (d, J = 8.2 Hz, 2H), 7.38 (d, J = 8.0 Hz, 1H), 7.15 (d, J = 8.1 Hz, 2H), 6.97 (s, 1H), 6.92 (d, J = 3.3 Hz, 1H), 6.89 (d, J = 8.0 Hz, 1H), 6.42 (d, J = 3.2 Hz, 1H), 5.25 (s, 1H), 2.98 (s, 3H), 2.38 (s, 3H), 2.35 (s, 3H), 0.89-0.87 (m, 21H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 144.4, 143.7, 136.9, 135.8, 132.2, 129.5, 129.0, 127.3, 126.8, 122.0, 120.5, 112.1, 111.7, 103.3, 36.9, 21.9, 21.6, 18.9, 12.0. **HRMS** (ESI, m/z) Calculated for [$C_{28}H_{40}N_2O_2SSiNa$, M + Na]$^+$: 519.2472, found: 519.2482.



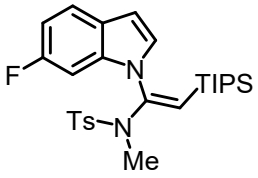
3ka

(E)-N-(1-(6-bromo-1H-indol-1-yl)-2-(triisopropylsilyl)vinyl)-N,4-dimethylbenzenesulfonamide (3ka), yellow oil (89.6 mg, 80% yield). PE/EA = 20:1, R_f = 0.30. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.39 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.3 Hz, 1H), 7.18 (s, 1H), 7.13 (dd, J = 8.4, 1.7 Hz, 1H), 7.10 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 3.3 Hz, 1H), 6.46 (d, J = 3.2 Hz, 1H), 5.25 (s, 1H), 3.12 (s, 3H), 2.36 (s, 3H), 0.89-0.86 (m, 21H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 144.2, 144.0, 137.1, 135.1, 130.5, 129.5, 127.8, 127.0, 123.9, 122.1, 116.0, 114.5, 112.9, 103.4, 37.8, 21.6, 18.9, 12.0. **HRMS** (ESI, m/z) Calculated for $[C_{27}H_{38}BrN_2O_2SSi, M + H]^+$: 561.1601, found: 561.1598.



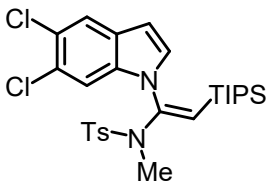
3la

(E)-N-(1-(6-chloro-1H-indol-1-yl)-2-(triisopropylsilyl)vinyl)-N,4-dimethylbenzenesulfonamide (3la), yellow oil (90.8 mg, 88% yield). PE/EA = 20:1, R_f = 0.30. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.30-7.26 (m, 1H), 7.23 (d, J = 8.3 Hz, 2H), 7.15 (d, J = 3.3 Hz, 1H), 6.91-6.82 (m, 4H), 6.41 (d, J = 3.3 Hz, 1H), 5.17 (s, 1H), 3.38 (s, 3H), 2.21 (s, 3H), 0.99-0.92 (m, 9H), 0.84-0.77 (m, 12H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 145.7, 143.2, 135.4, 133.9, 132.3, 132.0, 128.7, 126.3,123.7, 121.0, 119.6, 117.3, 111.4, 102.8, 39.2, 21.5, 19.0, 18.7, 11.8. **HRMS** (ESI, m/z) Calculated for $[C_{27}H_{37}ClN_2O_2SSiNa, M + Na]^+$: 539.1926, found: 539.1934.



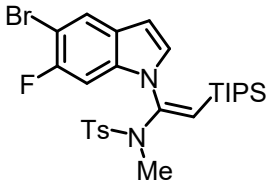
3ma

(E)-N-(1-(6-fluoro-1H-indol-1-yl)-2-(triisopropylsilyl)vinyl)-N,4-dimethylbenzenesulfonamide (3ma), white solid, m.p. 96-97 ^{o}C (95.0 mg, 95% yield). PE/EA = 20:1, R_f = 0.30. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.47 (d, J = 8.3 Hz, 2H), 7.44-7.38 (m, 1H), 7.14 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 3.3 Hz, 1H), 6.85-6.79 (m, 2H), 6.46 (d, J = 3.3 Hz, 1H), 5.19 (s, 1H), 3.06 (s, 3H), 2.37 (s, 3H), 0.91-0.85 (m, 21H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 159.9 (d, J = 238.3 Hz), 144.5, 144.0, 136.4 (d, J = 12.2 Hz), 135.2, 130.3 (d, J = 3.7 Hz), 129.5, 127.2, 125.4, 121.6 (d, J = 10.1 Hz), 112.7, 109.4, 109.2, 103.3, 98.3 (d, J = 26.9 Hz), 37.5, 21.6, 18.9, 12.0. **^{19}F NMR** (471MHz, $CDCl_3$): δ -119.97. **HRMS** (ESI, m/z) Calculated for $[C_{27}H_{37}FN_2O_2SSiNa, M + Na]^+$: 523.2221, found: 523.2229.



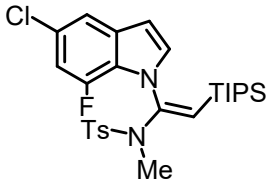
3na

(E)-N-(1-(5,6-dichloro-1H-indol-1-yl)-2-(triisopropylsilyl)vinyl)-N,4 dimethylbenzene sulfona mide (3na), white solid, m.p. 112-113 °C (103.4 mg, 94% yield). PE/EA = 20:1, R_f = 0.30. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.56 (s, 1H), 7.34 (d, J = 8.3 Hz, 2H), 7.14 (d, J = 3.3 Hz, 1H), 7.10-7.06 (m, 3H), 6.42 (d, J = 2.8 Hz, 1H), 5.21 (s, 1H), 3.17 (s, 3H), 2.36 (s, 3H), 0.93-0.84 (m, 21H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 144.23, 144.20, 135.1, 135.0, 132.0, 129.4, 128.6, 126.9, 126.2, 124.8, 121.8, 113.1, 112.7, 102.8, 38.1, 21.6, 18.9, 12.0. **HRMS** (ESI, m/z) Calculated for [$C_{27}H_{36}Cl_2N_2O_2SSiNa$, M + Na]$^+$: 573.1536, found: 573.1547.



3oa

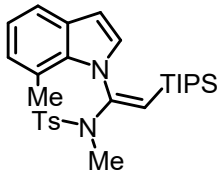
(E)-N-(1-(5-bromo-6-fluoro-1H-indol-1-yl)-2-(triisopropylsilyl)vinyl)-N,4-dimethylbenzenesul fonamide (3oa), pale yellow solid, m.p. 133-134 °C (105.2 mg, 91% yield). PE/EA = 20:1, R_f = 0.30. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.64 (d, J = 6.7 Hz, 1H), 7.40 (d, J = 8.2 Hz, 2H), 7.16-7.08 (m, 3H), 6.84 (d, J = 9.4 Hz, 1H), 6.42 (d, J = 3.2 Hz, 1H), 5.18 (s, 1H), 3.13 (s, 3H), 2.38 (s, 3H), 0.92-0.84 (m, 21H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 155.3 (d, J = 239.7 Hz), 144.3 (d, J = 17.7 Hz), 135.3 (d, J = 11.0 Hz), 135.0, 131.4 (d, J = 3.7 Hz), 129.5, 127.0, 126.5, 124.6, 112.7, 102.7, 102.2 (d, J = 23.1 Hz), 99.3 (d, J = 28.0 Hz), 37.9, 21.7, 18.9, 12.0. **^{19}F NMR** (471 MHz, $CDCl_3$): δ -113.78. **HRMS** (ESI, m/z) Calculated for [$C_{27}H_{36}BrFN_2O_2SSiNa$, M + Na]$^+$: 601.1336, found: 601.1326.



3pa

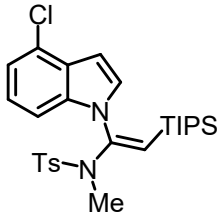
(E)-N-(1-(5-chloro-7-fluoro-1H-indol-1-yl)-2-(triisopropylsilyl)vinyl)-N,4-dimethylbenzenesul-fonamide (3pa), pale yellow solid, m.p. 93-94 °C (99.3 mg, 93% yield). PE/EA = 20:1, R_f = 0.30. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.24 (d, J = 8.3 Hz, 2H), 7.21-7.20 (m, 2H), 6.96 (d, J = 8.0 Hz, 2H), 6.65 (d, J = 11.5 Hz, 1H), 6.41-6.40 (m, 1H), 5.11 (s, 1H), 3.33 (s, 3H), 2.31 (s, 3H), 0.97-0.80 (m, 21H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 149.1 (d, J = 247.9 Hz), 146.0, 143.8, 134.9, 133.7, 133.3 (d,

J = 5.7 Hz), 129.0, 126.5, 126.7 (d, J = 8.9 Hz), 122.8 (d, J = 10.0 Hz), 116.3 (d, J = 3.6 Hz), 109.2 (d, J = 22.2 Hz), 102.7, 39.6, 21.5, 18.8, 11.9. **^{19}F NMR** (471 MHz, $CDCl_3$): δ -130.01. **HRMS** (ESI, m/z) Calculated for $[C_{27}H_{36}ClFN_2O_2SSiNa, M + Na]^+$: 557.1831, found: 557.1843.



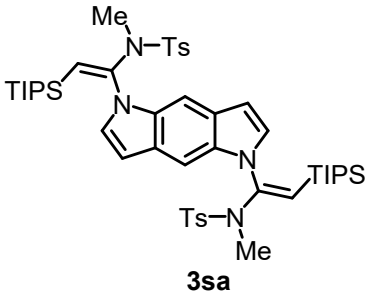
3qa

(E)-N,4-dimethyl-N-(1-(7-methyl-1H-indol-1-yl)-2-(triisopropylsilyl)vinyl)benzenesulfonamide (3qa), yellow oil, (89.3 mg, 90% yield). PE/EA = 20:1, R_f = 0.30. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.22 (d, J = 8.3 Hz, 2H), 7.07 (d, J = 3.2 Hz, 1H), 7.04 (d, J = 7.4 Hz, 1H), 6.95-6.85 (m, 3H), 6.38 (d, J = 3.2 Hz, 1H), 6.36 (d, J = 7.8 Hz, 1H), 5.08 (s, 1H), 3.71 (s, 3H), 3.28 (s, 3H), 2.25 (s, 3H), 0.98-0.96 (m, 9H), 0.78 (s, 12H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 147.4, 146.9, 143.1, 135.5, 132.1, 131.4, 128.7, 126.5, 126.2, 121.0, 113.6, 111.4, 103.0, 102.5, 55.1, 39.3, 21.5, 19.0, 18.6, 11.9. **HRMS** (ESI, m/z) Calculated for $[C_{28}H_{41}N_2O_2SSi, M + H]^+$: 497.2653, found: 497.2665.



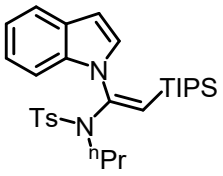
3ra

(E)-N-(1-(4-chloro-1H-indol-1-yl)-2-(triisopropylsilyl)vinyl)-N,4-dimethylbenzenesulfonamide (3ra), pale yellow solid, m.p. 85-86 ^{o}C (85.6 mg, 83% yield). PE/EA = 20:1, R_f = 0.30. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.46 (d, J = 8.3 Hz, 2H), 7.17-7.12 (m, 3H), 7.09 (d, J = 3.3 Hz, 1H), 7.06 (d, J = 7.0 Hz, 1H), 7.02-6.96 (m, 1H), 6.58 (d, J = 3.2 Hz, 1H), 5.24 (s, 1H), 3.05 (s, 3H), 2.37 (s, 3H), 0.89-0.87 (m, 21H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 144.4, 144.0, 137.0, 135.4, 130.3, 129.4, 127.7, 127.1, 126.1, 123.2, 120.5, 113.4, 110.4, 101.9, 37.5, 21.6, 18.9, 12.0. **HRMS** (ESI, m/z) Calculated for $[C_{27}H_{37}ClN_2O_2SSiNa, M + Na]^+$: 539.1926, found: 539.1938.



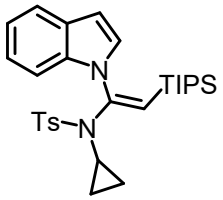
3sa

N,N'-((1E,1'E)-pyrrolo[2,3-f]indole-1,5-diylbis(2-(triisopropylsilyl)ethene-1,1-diyl))bis(N,4-dimethylbenzenesulfonamide) (3sa), pale yellow solid, m.p. 200-201 °C (124.1 mg, 70% yield). PE/EA = 20:1, R_f = 0.30. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.63 (d, J = 8.1 Hz, 4H), 7.39 (s, 2H), 7.23 (d, J = 8.1 Hz, 4H), 6.99 (d, J = 3.3 Hz, 2H), 6.44 (d, J = 3.3 Hz, 2H), 5.19 (s, 2H), 2.97 (s, 6H), 2.40 (s, 6H), 0.85 (s, 42H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 144.7, 143.9, 135.9, 133.7, 130.1, 129.6, 127.6, 127.0, 111.8, 103.2, 101.9, 36.7, 21.7, 18.9, 12.0. **HRMS** (ESI, m/z) Calculated for $[C_{48}H_{74}N_5O_4S_2Si_2, M + NH_4]^+$: 904.4715, found: 904.4728.



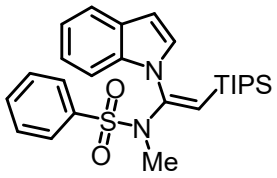
3ab

(E)-N-(1-(1H-indol-1-yl)-2-(triisopropylsilyl)vinyl)-4-methyl-N-propylbenzenesulfonamide (3ab), yellow oil (66.3 mg, 65% yield). PE/EA = 20:1, R_f = 0.30. **^{1}H NMR** (500 MHz,$CDCl_3$): δ 7.73 (d, J = 8.3 Hz, 2H), 7.55-7.51 (m, 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.30-7.26 (m, 2H), 7.15-7.08 (m, 2H), 6.93 (d, J = 3.3 Hz, 1H), 6.47 (d, J = 3.0 Hz, 1H), 5.56 (s, 1H), 3.01-2.91 (m, 2H), 2.43 (s, 3H), 1.54-1.46 (m, 2H), 0.98-0.80 (m, 21H), 7.46 (t, J = 14.8, 7.4 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 143.8, 141.5, 137.8, 136.6, 129.7, 129.3, 128.8, 127.6, 122.7, 120.9, 115.7, 111.9, 103.7, 49.8, 22.4, 21.7, 19.0, 12.1, 11.3. **HRMS** (ESI, m/z) Calculated for $[C_{29}H_{42}N_2O_2SSiNa, M + Na]^+$: 533.2628, found: 533.2627.



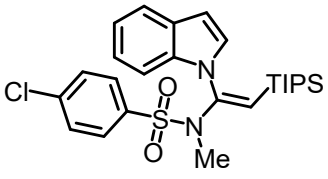
3ac

(E)-N-(1-(1H-indol-1-yl)-2-(triisopropylsilyl)vinyl)-N-cyclopropyl-4-methylbenzenesulfonamide (3ac), yellow oil (72.2 mg, 71% yield). PE/EA = 20:1, R_f = 0.30. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.50-7.46 (m, 3H), 7.25-7.21 (m, 1H), 7.12 (d, J = 3.3 Hz, 1H), 7.09 (d, J = 9.1 Hz, 2H), 7.06-7.02 (m, 2H), 6.48 (d, J = 3.3 Hz, 1H), 5.28 (s, 1H), 2.51-2.47 (m, 1H), 2.34 (s, 3H), 0.99-0.89 (m, 23H), 0.89-0.80 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 144.7, 143.8, 136.5, 135.8, 130.1, 129.2, 129.1, 127.7, 122.3, 120.8, 120.5, 112.7, 111.7, 103.3, 30.9, 21.6, 19.0, 12.1, 9.3. **HRMS** (ESI, m/z) Calculated for $[C_{29}H_{40}N_2O_2SSiNa, M + Na]^+$: 531.2472, found: 531.2478.



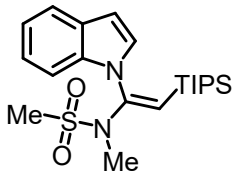
3ad

(E)-N-(1-(1H-indol-1-yl)-2-(triisopropylsilyl)vinyl)-N-methylbenzenesulfonamide (3ad), pale yellow solid, m.p. 67-68 °C (86.0 mg, 92% yield). PE/EA = 20:1, Rf = 0.30. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.70-7.60 (m, 2H), 7.55-7.48 (m, 2H), 7.43-7.35 (m, 2H), 7.31-7.26 (m, 1H), 7.12-7.05 (m, 2H), 7.04 (d, J = 3.3 Hz, 1H), 6.49 (d, J = 3.1 Hz, 1H), 5.22 (s, 1H), 3.02 (s, 3H), 0.89-0.87 (m, 21H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 144.5, 138.6, 136.4, 132.9, 129.6, 129.0, 128.9, 127.3, 122.7, 121.0, 120.8, 112.9, 111.7, 103.5, 37.1, 18.9, 12.0. **HRMS** (ESI, m/z) Calculated for $[C_{26}H_{36}N_2O_2SSiNa$, M + Na$]^+$: 491.2159, found: 491.2173.



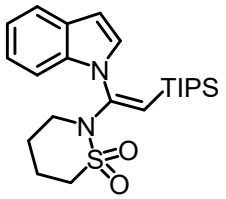
3ae

(E)-N-(1-(1H-indol-1-yl)-2-(triisopropylsilyl)vinyl)-4-chloro-N-methylbenzenesulfonamide (3ae), yellow oil (65.3 mg, 65%). PE/EA = 25:1, R_f = 0.30. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.50 (d, J = 7.3 Hz, 1H), 7.39 (d, J = 8.6 Hz, 2H), 7.20 (d, J = 8.6 Hz, 2H), 7.12 (d, J = 7.9 Hz, 1H), 7.10-7.00 (m, 3H), 6.48 (d, J = 3.2 Hz, 1H), 5.26 (s, 1H), 3.13 (s, 3H), 0.90-0.86 (m, 21H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 144.6, 139.3, 137.0, 136.2, 129.8, 128.9, 128.3, 122.7, 121.0, 120.8, 113.0, 111.5, 103.5, 37.7, 18.9, 12.0. **HRMS** (ESI, m/z) Calculated for $[C_{26}H_{35}ClN_2O_2SSiNa$, M + Na$]^+$: 525.1769, found: 525.1787.



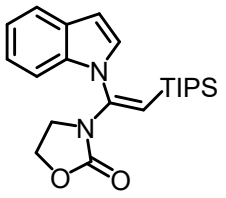
3af

(E)-N-(1-(1H-indol-1-yl)-2-(triisopropylsilyl)vinyl)-N-methylmethanesulfonamide (3af), pale yellow solid, m.p. 45-46 °C (72.3 mg, 89% yield). PE/EA = 20:1, R_f = 0.30. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.59 (d, J = 7.8 Hz, 1H), 7.36 (d, J = 8.2 Hz, 1H), 7.24-7.18 (m, 2H), 7.17-7.12 (m, 1H), 6.52 (d, J = 3.0 Hz, 1H), 5.43 (s, 1H), 3.14 (s, 3H), 2.43 (s, 3H), 0.99-0.85 (m, 21H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 144.6, 136.2, 130.4, 129.1, 122.9, 121.4, 121.1, 112.8, 111.5, 103.3, 40.0, 37.2, 19.0, 11.9. **^{19}F NMR** (471MHz, $CDCl_3$): δ -61.98. **HRMS (ESI, m/z)** Calculated for $[C_{21}H_{34}N_2O_2SSiNa$, M + Na$]^+$: 429.2002, found: 429.2004.



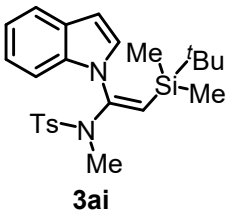
3ag

(E)-2-(1-(1H-indol-1-yl)-2-(triisopropylsilyl)vinyl)-1,2-thiazinane 1,1-dioxide (3ag), yellow oil (73.4 mg, 85% yield). PE/EA = 20:1, Rf = 0.30. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.59 (d, *J* = 7.8 Hz, 1H), 7.56 (d, J = 8.2 Hz, 1H), 7.21 (t, *J* = 7.9 Hz, 1H), 7.17-7.11 (m, 2H), 6.52 (d, *J* = 3.2 Hz, 1H), 5.56 (s, 1H), 3.26-3.22 (m, 2H), 3.18-3.12 (m, 2H), 2.20-2.10 (m, 2H), 1.41-1.35 (m, 2H), 1.00-0.90 (m, 21H). **^{13}C NMR** (125 MHz, $CDCl_3$): *δ* 141.0, 136.3, 130.1, 129.3, 122.6, 121.2, 120.9, 114.1, 112.5, 103.4, 51.0, 49.9, 24.2, 23.9, 18.9, 12.0. **HRMS** (ESI, m/z) Calculated for [$C_{23}H_{36}N_2O_2SSiNa$, M +Na]$^+$: 455.2159, found: 455.2173.



3ah

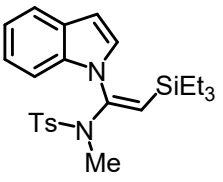
(E)-3-(1-(1H-indol-1-yl)-2-(triisopropylsilyl)vinyl)oxazolidin-2-one (3ah), yellow oil (33.6 mg, 45% yield). PE/EA = 20:1, R_f = 0.30. **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* 7.61 (d, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.25-7.20 (m, 1H), 7.19-7.13 (m, 1H), 7.11 (d, *J* = 3.3 Hz, 1H), 6.55 (d, *J* = 3.3 Hz, 1H), 5.93 (s, 1H), 4.15 (t, *J* = 7.9 Hz, 2H), 3.09 (t, *J* = 8.1 Hz, 2H), 0.98-0.88 (m, 21H). **^{13}C NMR** (125 MHz, $CDCl_3$): *δ* 155.7, 138.5, 136.1, 128.9, 128.8, 123.2, 121.3, 121.1, 111.9, 111.0, 103.6, 61.3, 43.7, 18.9, 11.8. **HRMS** (ESI, m/z) Calculated for [$C_{22}H_{32}N_2O_2SiNa$, M + Na]$^+$: 407.2125, found: 407.2139.



3ai

(E)-N-(2-(tert-butyldimethylsilyl)-1-(1H-indol-1-yl)vinyl)-N,4-dimethylbenzenesulfonamide (3ai), yellow oil (80.1 mg, 91% yield, mixture, *E/Z* = 11:1). PE/EA = 20:1, R_f = 0.30. **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* 7.56 (d, *J* = 8.2 Hz, 2H), 7.64-7.51 (m, 1H), 7.20 (d, *J* = 8.1 Hz, 3H), 7.13-7.07 (m, 2H), 6.78 (d, *J* = 3.3 Hz, 1H), 6.47 (d, *J* = 3.3 Hz, 1H), 5.61 (s, 1H), 2.89 (s, 3H), 2.40 (s, 3H), 0.87 (s, 9H), -0.43 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$): *δ* 143.9, 143.2, 137.0, 136.3, 129.6, 128.8, 128.5,

127.3, 122.7, 120.9, 120.7, 115.8, 111.1, 103.6, 35.9, 26.5, 21.7, 17.0, -6.2. **HRMS** (ESI, m/z) Calculated for $[C_{24}H_{32}N_2O_2SSiNa, M + Na]^+$: 463.1846, found: 463.1857.

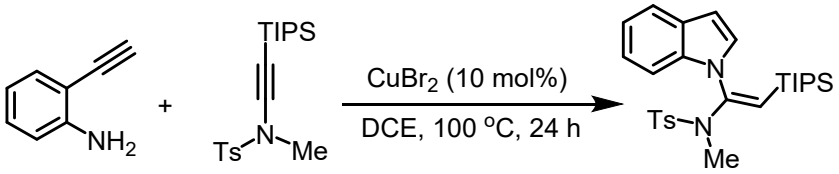


3aj

(E)-N-(1-(1H-indol-1-yl)-2-(triethylsilyl)vinyl)-N,4-dimethylbenzenesulfonamide (3aj), yellow oil (42.2 mg, 48% yield, the *E/Z* ratio of the unpurified reaction mixture was 1.7:1, while only (**E**)-**3aj** was isolated after column chromatography). PE/EA = 20:1, R_f = 0.30. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.58-7.50 (m, 3H), 7.23-7.17 (m, 3H), 7.12-7.06 (m, 2H), 6.85 (d, J = 3.3 Hz, 1H), 6.48 (d, J = 3.3 Hz, 1H), 5.43 (s, 1H), 2.94 (s, 3H), 2.40 (s, 3H), 0.77 (t, J = 7.9 Hz, 9H), 0.25 (q, J = 7.9 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 144.0, 143.5, 136.8, 135.8, 129.6, 128.9, 128.7, 127.5, 122.6, 120.9, 120.7, 114.5, 111.2, 103.7, 36.3, 21.7, 7.4, 3.5. **HRMS** (ESI, m/z) Calculated for $[C_{24}H_{32}N_2O_2SSiNa, M + Na]^+$: 463.1846, found: 463.1862.

6. Large-Scale Experiment and Product Transformations

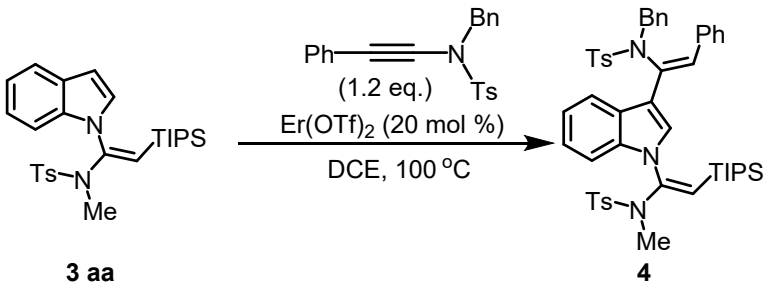
(a) Large-scale experiments



1a, 3 mmol **2a**, 2 mmol **3aa**, 90%, 0.87 g

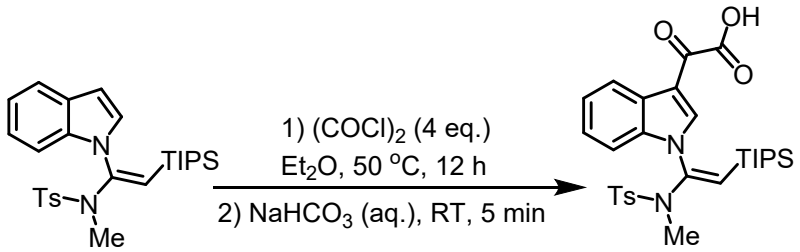
A pre-dried 50.0 mL Schlenk tube was charged with stirring bar, $CuBr_2$ (44.7 mg, 0.2 mmol, 0.1 eq.), **1a** (351.2 mg, 3.0 mmol, 1.5 eq.), N,4-dimethyl-N-((triisopropylsilyl)ethynyl) benzenesulfonamide **2a** (730.4 mg, 2.0 mmol, 1 eq.) and DCE (10.0 mL). The mixture was stirred at 100 °C for 24 h. After cooling to room temperature, the mixture was transferred to a column and purified by flash chromatography on silica gel (PE/EA = 20:1, R_f = 0.30) to give the analytical pure product **3aa** (0.87 g, 90 % yield).

(b) Product transformations



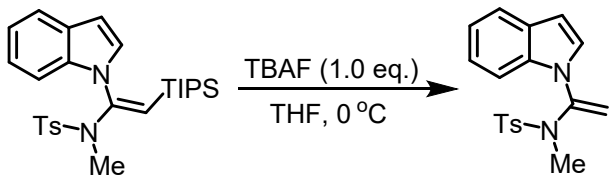
3 aa **4**

A round bottom flask equipped with a magnetic stir bar was charged with $Er(OTf)_2$ (24.5 mg, 0.04 mmol, 0.2 eq.), **3aa** (96.4 mg, 0.20 mmol, 1.0 eq.), N-benzyl-4-methyl-N-(phenylethynyl) benzenesulfonamide (86.6 mg, 0.24 mmol, 1.2 eq.) and 1,2-DCE (1.0 mL). The mixture was stirred at 100 °C for 10 h. After cooling to room temperature, the mixture was extracted with ethyl acetate and concentrated, and the residue was purified by chromatography on silica gel (eluent: PE/EA=10:1, R_f = 0.30.) to give the desired product **(1-(1H-indol-1-yl)vinyl)-N,4-dimethylbenzenesulfonamide** (**4**, 84.3 mg, 50% yield, mixture, *Z/E* = 14:1, colorless oil). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.2 Hz, 3H), 7.43 (t, *J* = 15.5, 8.1 Hz, 3H), 7.31-7.24 (m, 3H), 7.22-7.18 (m, 2H), 7.18-7.13 (m, 3H), 7.12-7.08 (m, 3H), 7.00 (t, *J* = 15.2, 7.7 Hz, 2H), 6.92 (d, *J* = 6.9 Hz, 2H), 6.79 (d, *J* = 6.5 Hz, 3H), 5.22 (s, 1H), 4.60-4.50 (m, 2H), 2.96 (s, 3H), 2.38 (d, *J* = 9.6 Hz, 6H), 0.92-0.84 (m, 21H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 144.0, 143.8, 143.5, 137.4, 137.2, 135.9, 135.8, 135.2, 131.1, 130.3, 130.0, 129.7, 129.4, 128.7, 128.5, 128.3, 128.2, 128.0, 127.6, 127.5, 127.1, 123.3, 121.5, 120.1, 115.7, 114.1, 112.4, 51.3, 37.3, 21.7, 21.7, 19.0, 19.0, 12.0. **HRMS** (ESI, m/z) Calculated for $[C_{49}H_{57}N_3O_4S_2SiNa, M + Na]^+$: 866.3452, found: 866.3445.



3 aa **5**

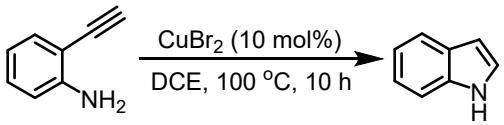
To a 10 mL Schlenk tube was added **3aa** (96.5 mg, 0.2 mmol, 1 eq.) and anhydrous Et_2O (1.0 mL). The solution was cooled to 0 °C and oxalyl chloride (100.7 mg, 0.8 mmol, 4 eq.) was dropwise added over a period of 5 minutes. The mixture was warmed to 50 °C and stirred for 12 hours. The suspension was then cooled to room temperature and a saturated $NaHCO_3$ solution (5.0 mL) was dropwise added and stirred for 5 minutes. Then the product was collected using vacuum filtration and washed with Et_2O to give **(E)-1-(1-((N,4-dimethylphenyl)sulfonamido)-2-(triisopropylsilyl)vinyl)-1H-indole-3-carboperoxoic acid** (**5**, 105.3 mg, 95% yield, white solid, m.p. 126-127 °C). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.93 (s, 1H), 8.32 (d, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 1H), 7.37 (t, *J* = 14.6, 7.2 Hz, 1H), 7.32 (t, *J* = 14.9, 7.4 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 5.24 (s, 1H), 3.17 (s, 3H), 2.41 (s, 3H), 0.88 (s, 21H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 176.6, 160.7, 144.7, 144.0, 143.6, 136.8, 133.8, 129.8, 127.5, 126.9, 125.4, 124.6, 122.7, 116.6, 112.7, 112.0, 38.3, 21.7, 18.8, 11.9. **HRMS** (ESI, m/z) Calculated for $[C_{29}H_{38}N_2O_2SSiNa, M + Na]^+$: 577.2163, found: 577.2165.



3 aa **6**

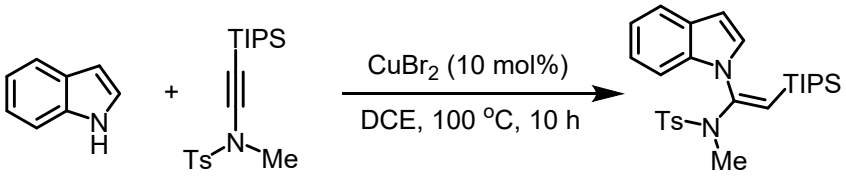
A flame-dried Schlenk flask with stir bar under N_2 was charged with **3aa** (96.4 mg, 0.2 mmol, 1.0 eq.) and anhydrous THF (2.0 mL). The suspension was cooled to 0 °C, and dropwise added with a solution of tetrabutylammonium fluoride trihydrate (63.1 mg, 0.2 mmol, 1.0 eq.) in THF (1.0 mL). Then the mixture was raised to room temperature and held for 5 minutes. Finally, the mixture was transferred to a column and purified by flash chromatography on silica gel (PE/EA = 15:1, R_f = 0.30) to give product **N-(1-(1H-indol-1-yl)vinyl)-N,4-dimethylbenzenesulfonamide** (**6**, 63.2 mg, 97% yield, white solid, m.p. 72-73 °C). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.70 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 7.7 Hz, 1H), 7.54-7.48 (m, 1H), 7.30 (d, J = 8.1 Hz, 2H), 7.23-7.17 (m, 1H), 7.16-7.10 (m, 1H), 7.08 (d, J = 3.4 Hz, 1H), 6.54 (d, J = 3.2 Hz, 1H), 5.07 (d, J = 1.8 Hz, 1H), 4.88 (d, J = 1.8 Hz, 1H), 3.05 (s, 3H), 2.44 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 144.3, 140.5, 136.0, 134.8, 129.8, 129.7, 128.0, 126.8, 122.9, 121.2, 121.0, 111.3, 104.5, 101.3, 26.9, 21.7, 17.9, 12.4. **HRMS** (ESI, m/z) Calculated for $[C_{18}H_{18}N_2O_2SNa, M + Na]^+$: 349.0981, found: 349.0986.

7. Control Experiments



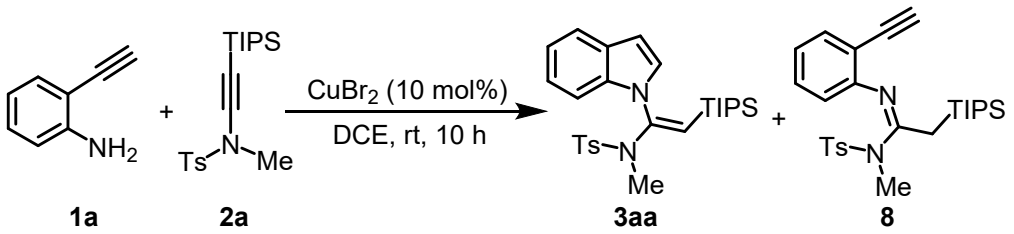
1a **7**

A pre-dried 10.0 mL Schlenk tube was charged with stirring bar, $CuBr_2$ (4.5 mg, 0.02 mmol, 0.1 eq.), **1a** (35.2 mg, 0.3 mmol, 1.5 eq.) and DCE (1.0 mL). The mixture was stirred at 100 °C for 10 h. After cooling to room temperature, solvent was removed by rotary evaporation instrument and 1,3,5-trimethoxybenzene as the internal reference was added. The NMR conversion rate (100%) and NMR yield (30%) are determined by the ^{1}H NMR. The mixture was transferred to a column and purified by flash chromatography on silica gel (PE/EA = 10:1, Rf = 0.25) to give the analytical pure products 1H-indole (**7**, white solid, 6.1 mg, 26% yield).

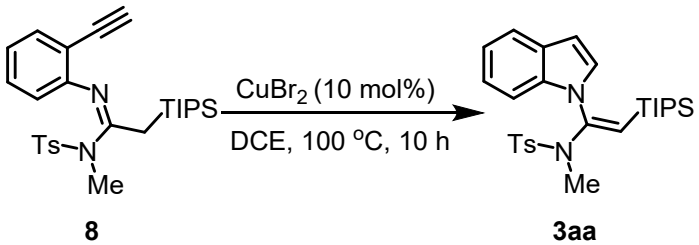


7 **2a** **3aa**

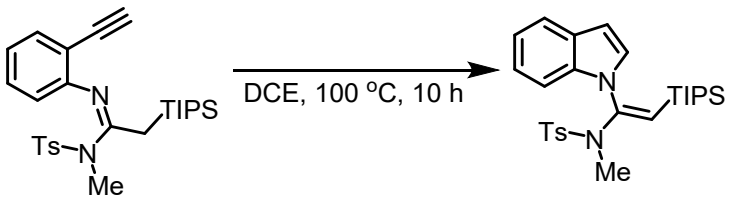
A pre-dried 10.0 mL Schlenk tube was charged with stirring bar, $CuBr_2$ (4.5 mg, 0.02 mmol, 0.1 eq.), **7** (35.2 mg, 0.3 mmol, 1.5 eq.), **2a** (73.1 mg, 0.2 mmol, 1.0 eq.) and DCE (1.0 mL). The mixture was stirred at 100 °C for 10 h. After cooling to room temperature, solvent was removed by rotary evaporation instrument. The residue was detected by TLC and ^{1}H NMR spectroscopy, and no **3aa** was found.



A pre-dried 10.0 mL Schlenk tube was charged with stirring bar, $CuBr_2$ (4.5 mg, 0.02 mmol, 0.1 eq.), **1a** (35.2 mg, 0.3 mmol, 1.5 eq.), **2a** (73.1 mg, 0.2 mmol, 1 eq.) and DCE (1.0 mL). The mixture was stirred at room temperature for 10 h. Subsequently the solvent was removed by rotary evaporation instrument and 1,3,5-trimethoxybenzene as the internal reference was added. The NMR yield (**3aa**, 5%) and NMR yield (**8**, 93%) were determined by the ^{1}H NMR spectroscopy. Finally, the mixture was transferred to a column and purified by flash chromatography on silica gel (PE/EA = 20:1, R_f = 0.30) to give the analytical pure product **(Z)-N'-(2-ethynylphenyl)-N-methyl-N-tosyl-2-(triisopropylsilyl)acetimidamide** (**8**, 89.5 mg, 93% yield, colorless oil). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.79 (d, J = 8.1 Hz, 2H), 7.44 (d, J = 7.6 Hz, 1H), 7.30 (d, J = 8.1 Hz, 2H), 7.28-7.24 (m, 1H), 6.98 (t, J = 7.6 Hz, 1H), 6.64 (d, J = 8.0 Hz, 1H), 3.13 (s, 3H), 3.10 (s, 1H), 2.69 (s, 2H), 2.40 (s, 3H), 1.15-1.07 (m, 3H), 1.00-0.90 (m, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 150.6, 144.2, 133.8, 129.7, 128.0, 127.2, 123.4, 120.7, 113.9, 81.9, 81.3, 37.2, 21.7, 18.6, 11.9. **HRMS** (ESI, m/z) Calculated for $[C_{27}H_{38}N_2O_2SSiNa, M + Na]^+$: 505.2315, found: 505.2320.



A pre-dried 10.0 mL Schlenk tube was charged with stirring bar, $CuBr_2$ (4.5 mg, 0.02 mmol, 0.1 eq.), **8** (96.5 mg, 0.2 mmol, 1eq.), and DCE (1.0 mL). The mixture was stirred at 100 °C for 10 h. Subsequently the solvent was removed by rotary evaporation instrument and 1,3,5-trimethoxybenzene as the internal reference was added. The NMR yield (100%) are determined by the ^{1}H NMR spectroscopy.



8 **3aa**

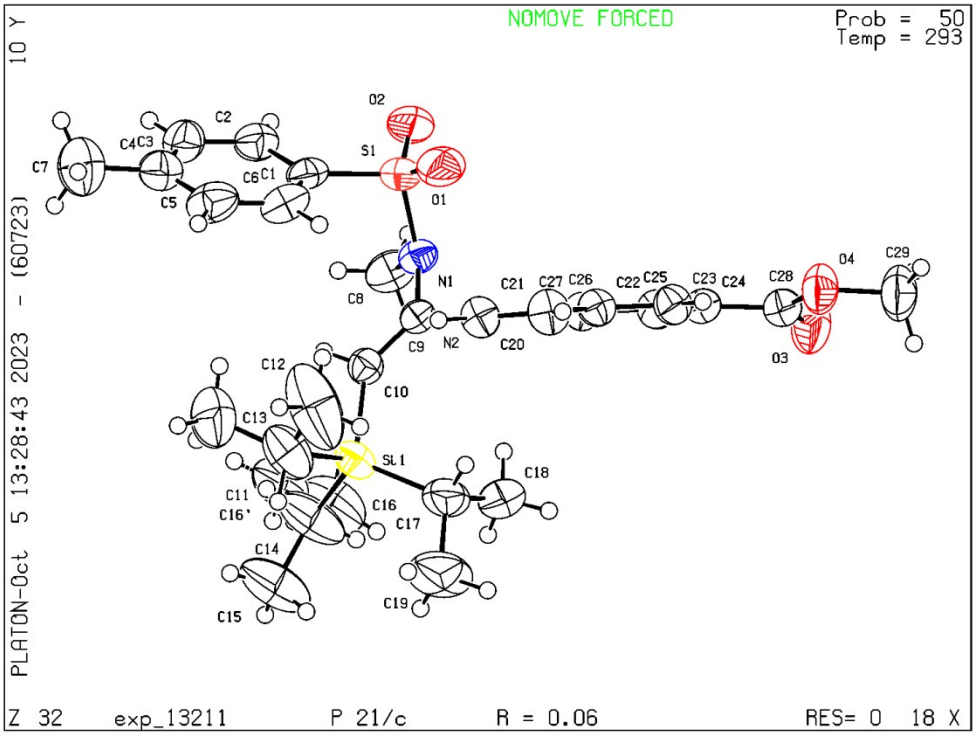
A pre-dried 10.0 mL Schlenk tube was charged with stirring bar, (Z)-N'-(2-ethynylphenyl)-N-methyl-**8** (96.5 mg, 0.2 mmol, 1eq.), and DCE (1.0 mL). The mixture was stirred at 100 °C 10 h. Subsequently the solvent was removed by rotary evaporation instrument and 1,3,5-trimethoxybenzene as the internal reference was added. The NMR conversion rate (0%) are determined by the ^{1}H NMR spectroscopy.

8. References

1. Zhao, X.; Song, X.; Jin, H.; Zeng, Z.; Wang, Q.; Rudolph, M.; Rominger, F.; Hashmi, A.S.K. *Adv. Synth. Catal.* **2018**, *360*, 2720−2726.
2. Matsuoka J.; Matsuda,Y.; Kawada, Y.; Oishi, S.; Ohno, H. *Angew. Chem. Int. Ed.* **2017**, *56*, 7444-7448.
3. Zhang, Y.; Hsung, R. P.; Tracey, M. R.; Kurtz, K. C. M.; Vera, E. L. *Org. Lett.*, **2004**, *6*, 1151-1154.

9. Crystal Data and Structure Refinement for 3ha.

ORTEP drawing of **3ha** (thermal ellipsoids set at 50% probability). Recrystallization from *n*-hexane/DCM afforded the single crystal suitable for X-ray diffraction analysis.



Bond precision:	C-C = 0.0048 A	Wavelength=1.54184	
Cell:	a=12.2243(4)	b=10.5039(3)	c=23.3691(8)
	alpha=90	beta=91.697(3)	gamma=90
Temperature:	293 K		

	Calculated	Reported
Volume	2999.34(17)	2999.34(17)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C29 H40 N2 O4 S Si	?
Sum formula	C29 H40 N2 O4 S Si	C29 H40 N2 O4 S Si
Mr	540.78	540.78
Dx,g cm-3	1.198	1.198
Z	4	4
Mu (mm-1)	1.618	1.618
F000	1160.0	1160.0
F000'	1165.33	
h,k,lmax	14,12,27	14,12,27
Nref	5387	5363
Tmin,Tmax	0.810,0.824	0.782,1.000
Tmin'	0.810	

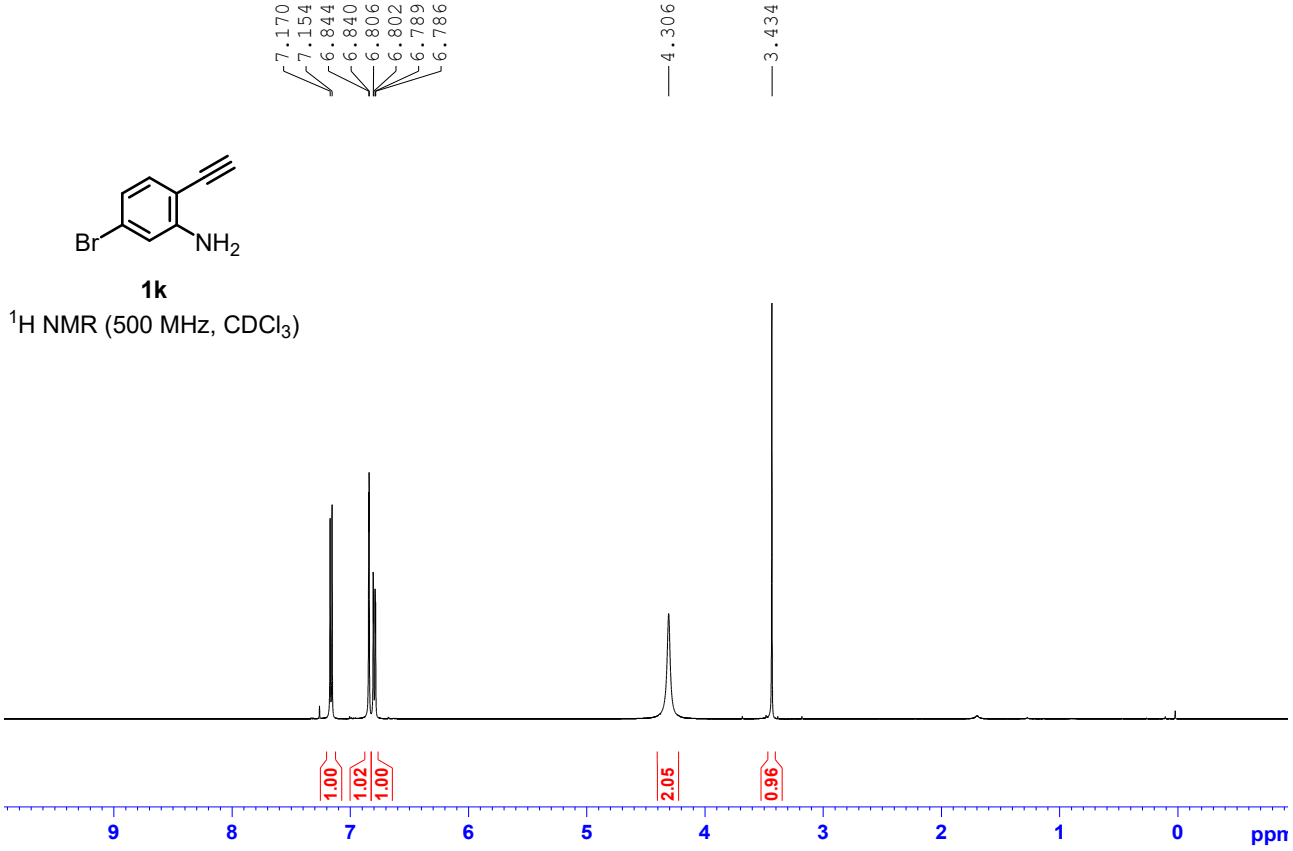
Correction method= # Reported T Limits: Tmin=0.782 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.996 Theta(max)= 67.245

R(reflections)= 0.0615(4100) wR2(reflections)= 0.1835(5363)

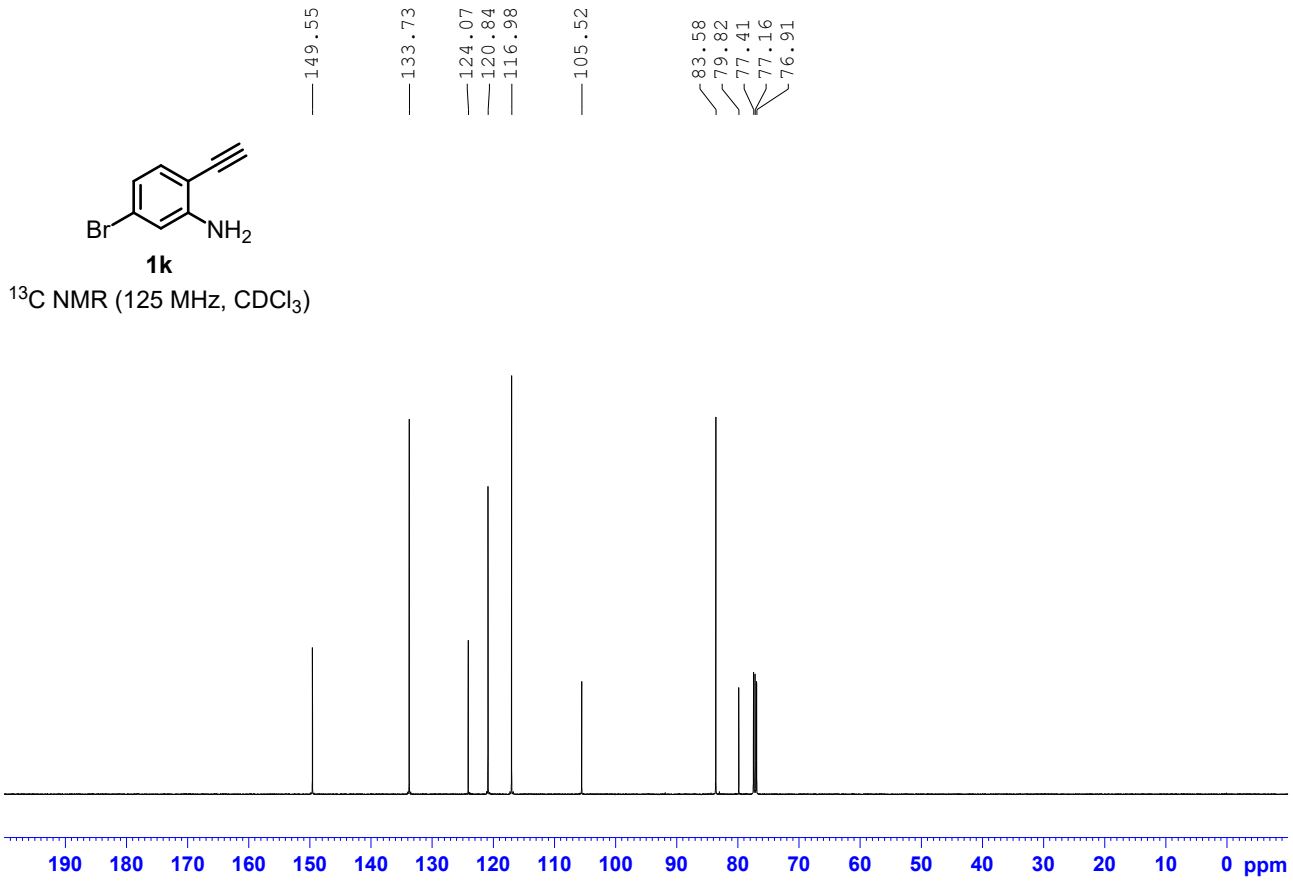
S = 1.036 Npar= 352

10. NMR Spectra



1k

^{1}H NMR (500 MHz, $CDCl_3$)



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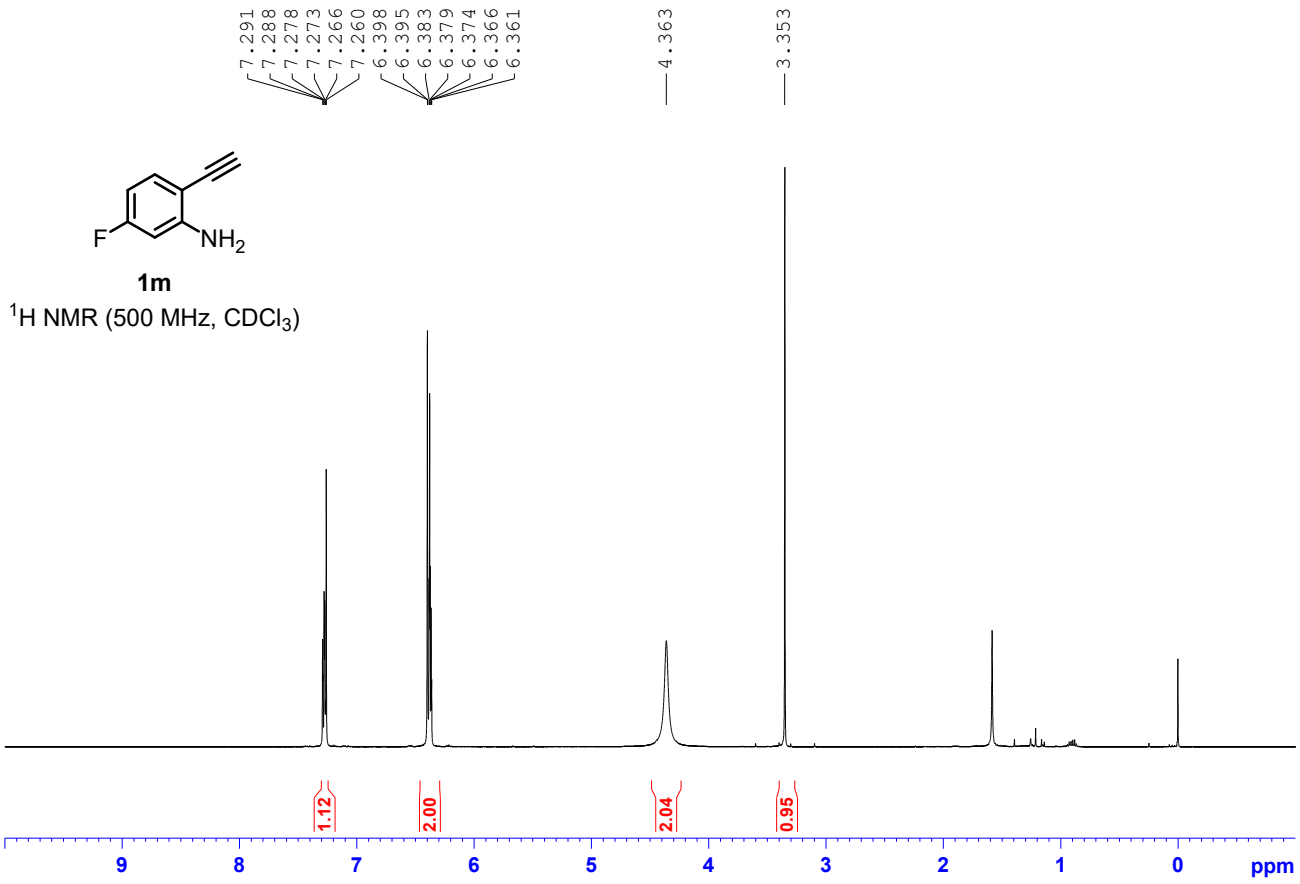
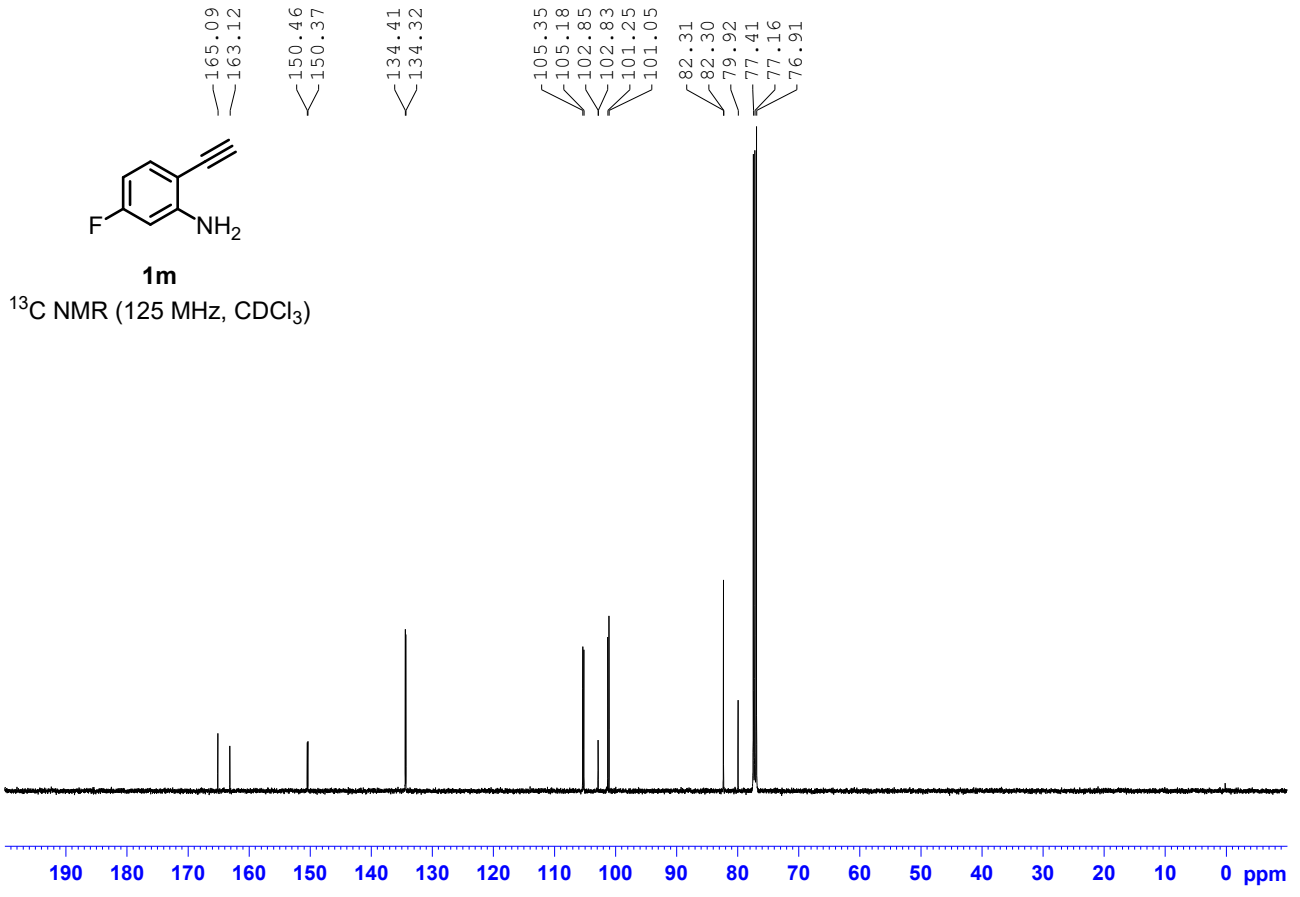


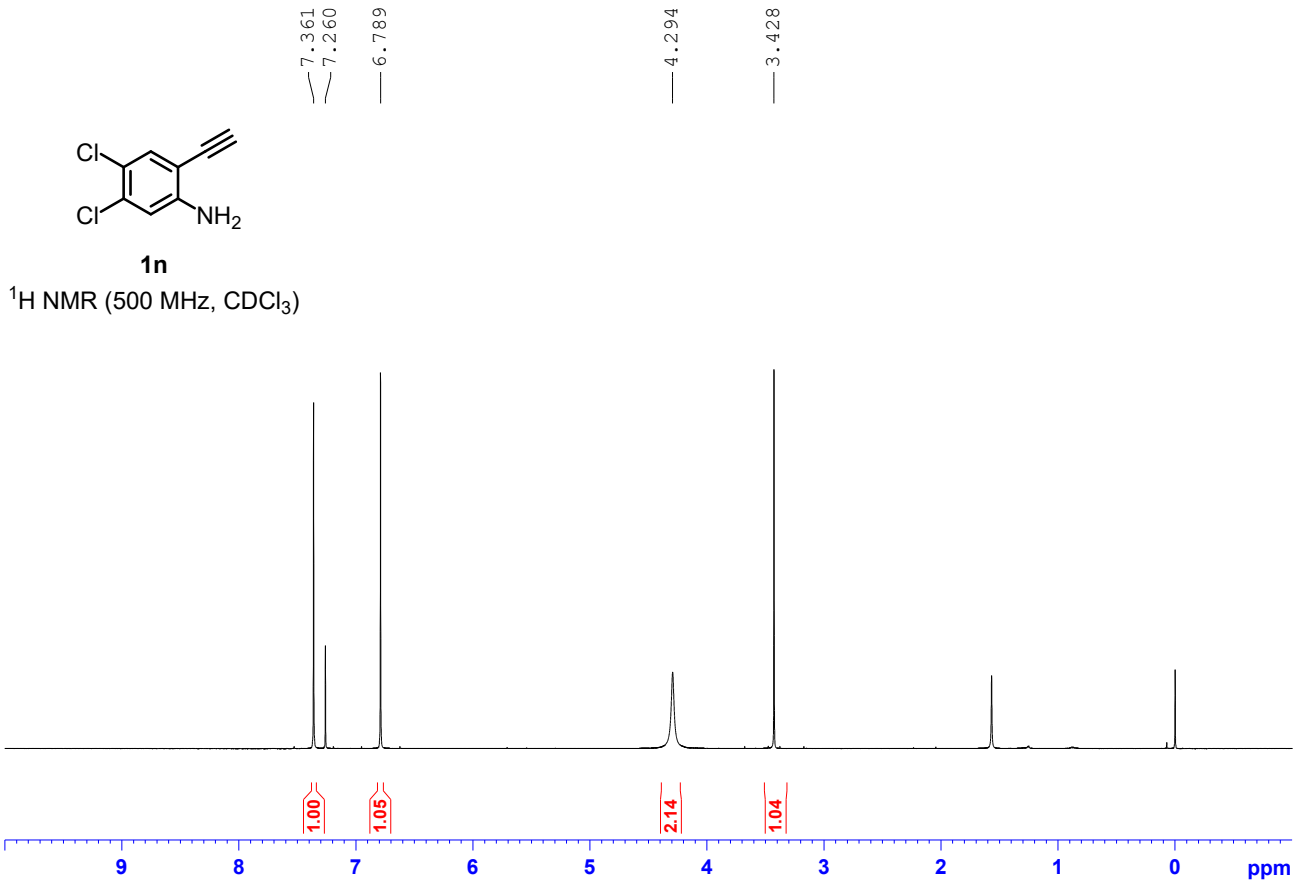
1m

^{1}H NMR (500 MHz, $CDCl_3$)



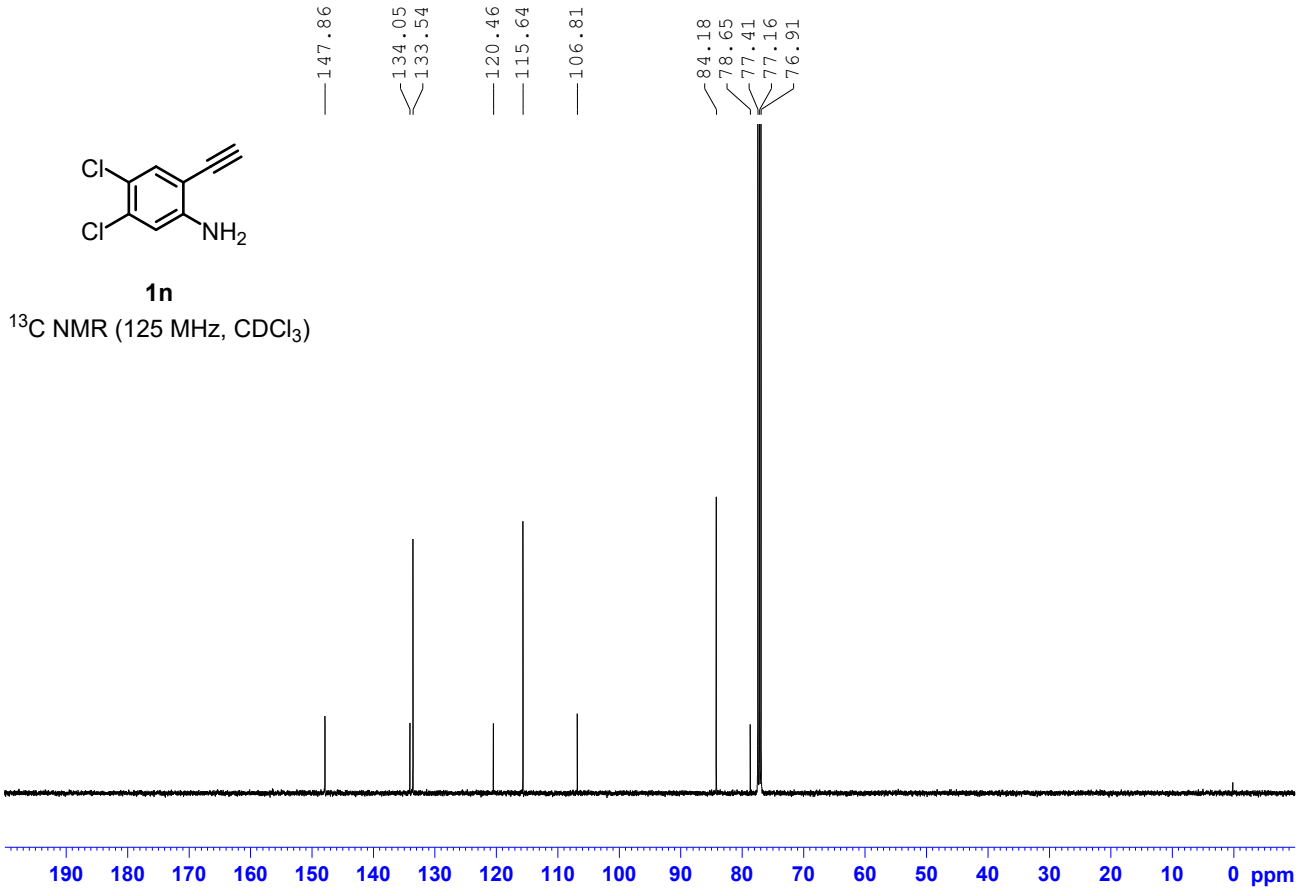
1m

^{13}C NMR (125 MHz, $CDCl_3$)



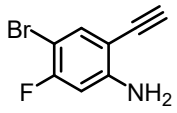
1n

^{1}H NMR (500 MHz, $CDCl_3$)



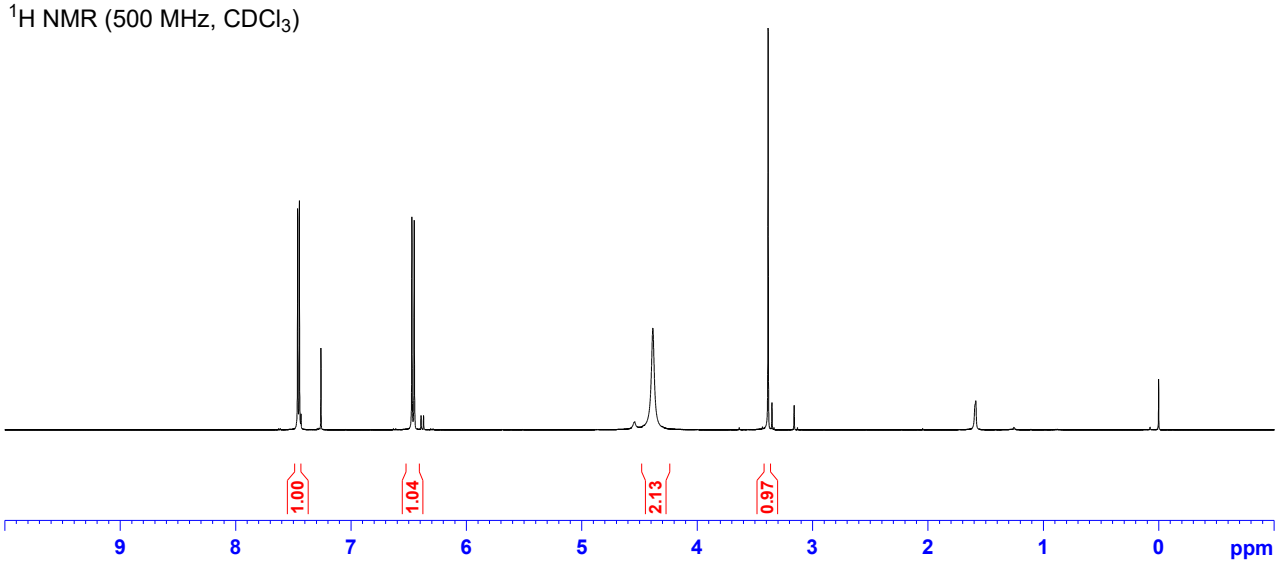
1n

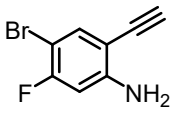
^{13}C NMR (125 MHz, $CDCl_3$)



1o

^{1}H NMR (500 MHz, $CDCl_3$)





1o

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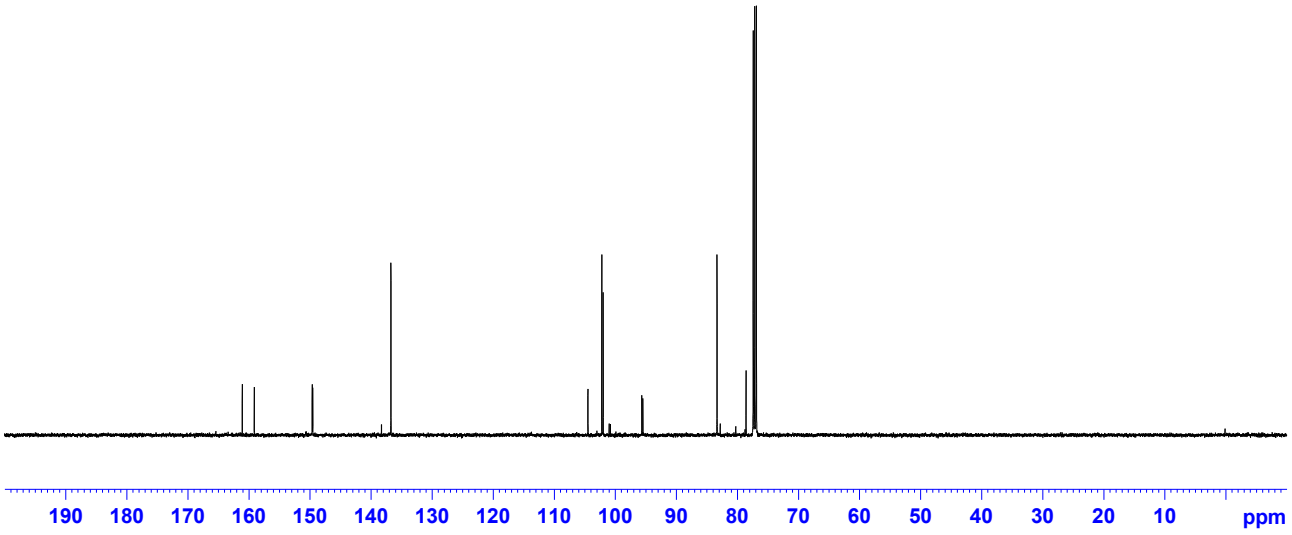

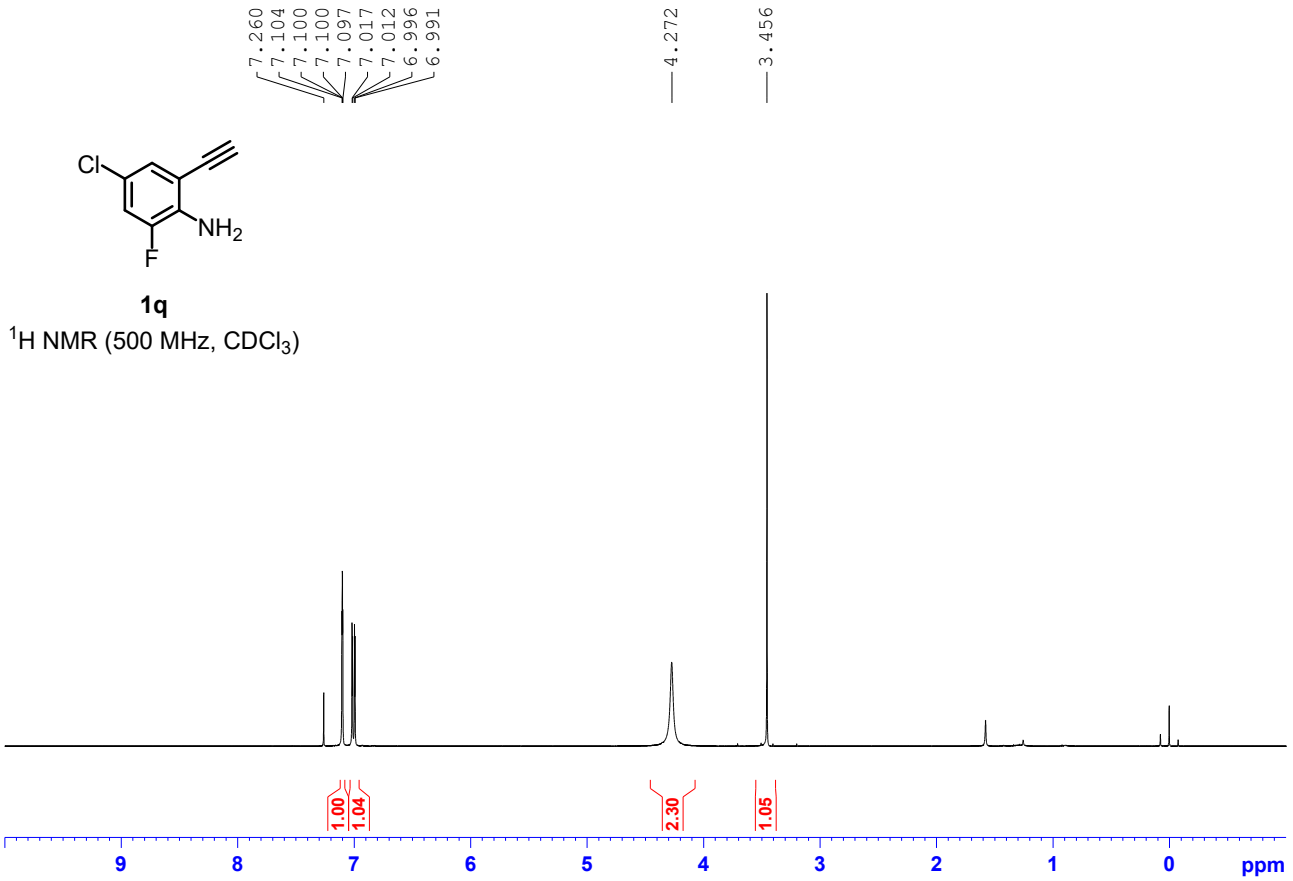

1q

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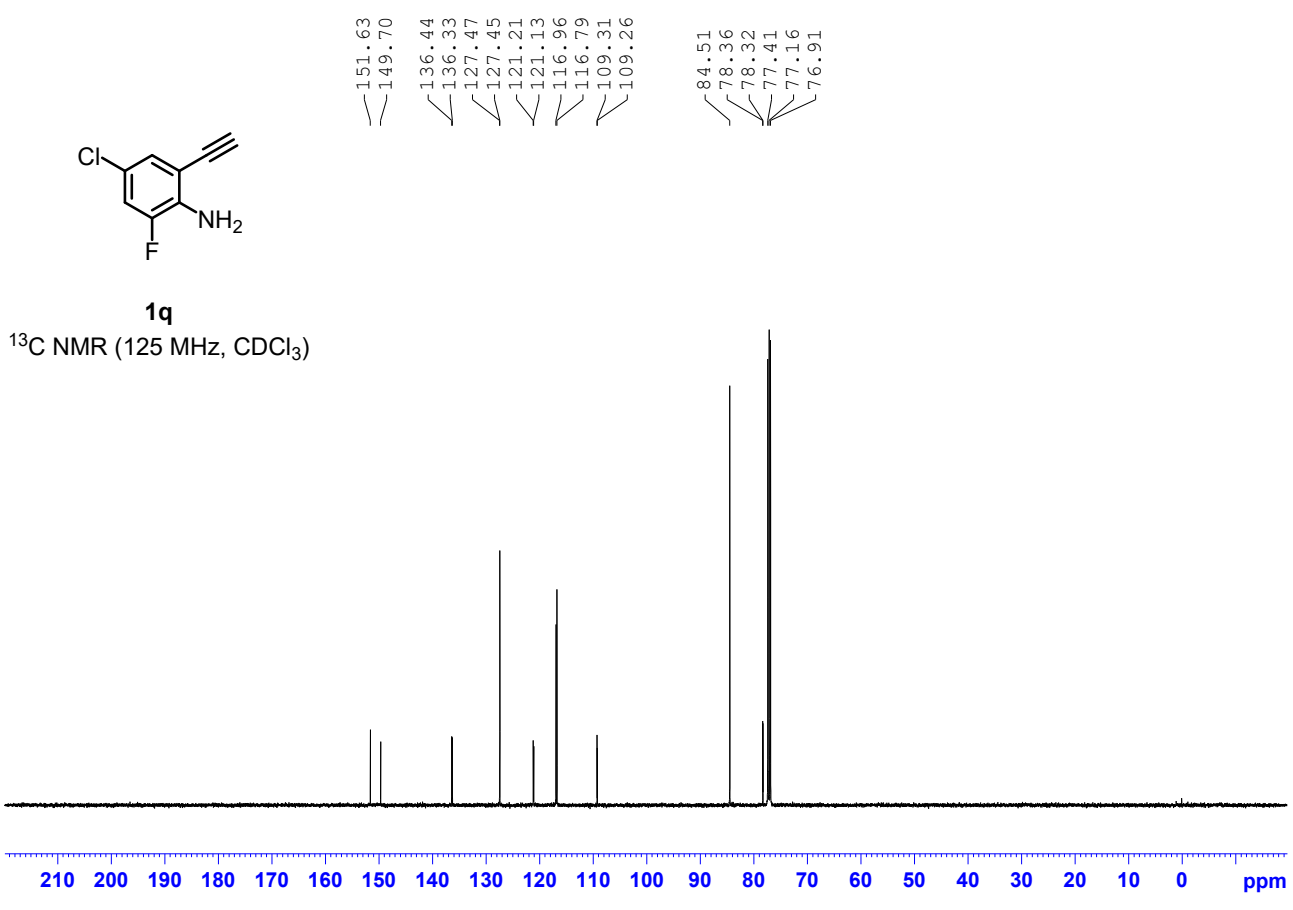

1q

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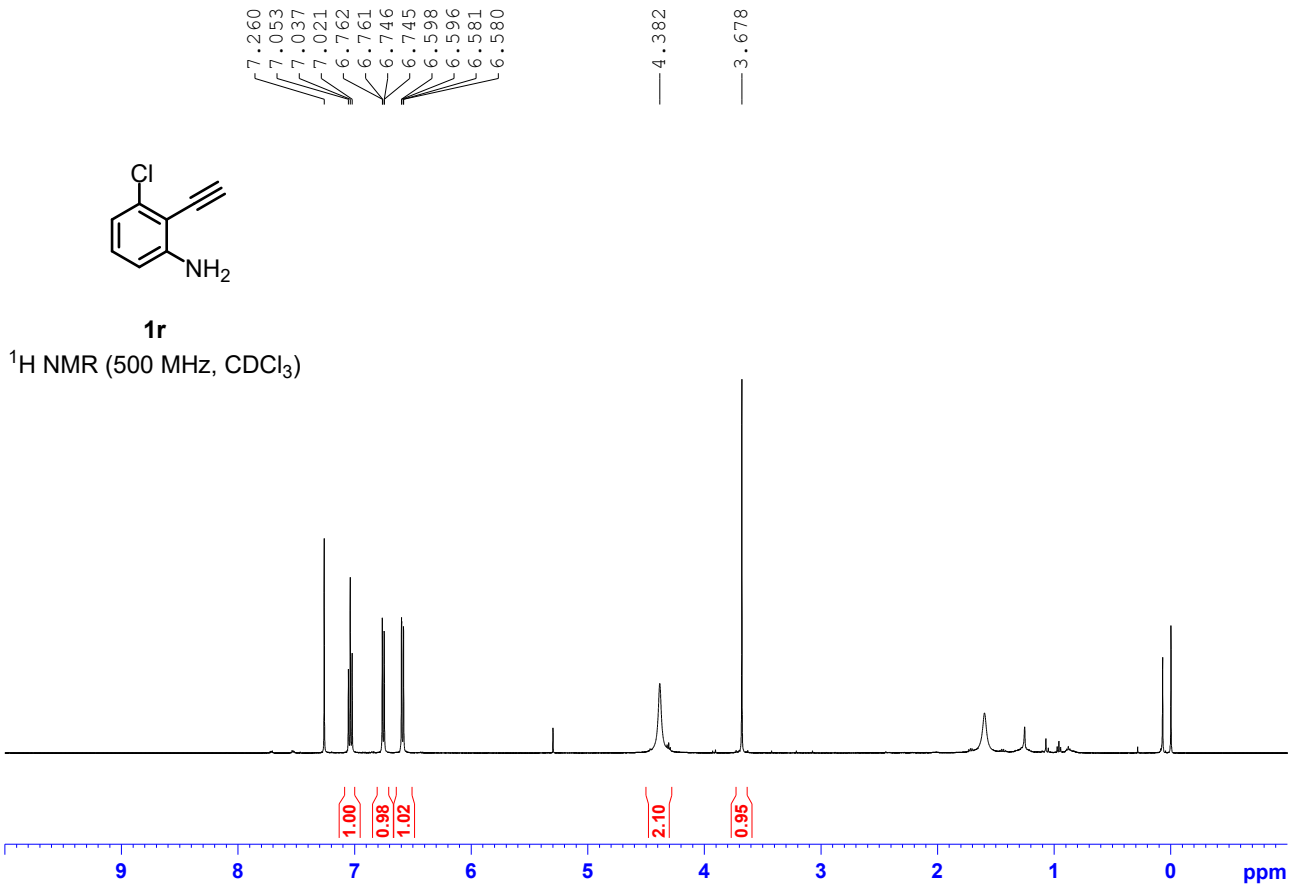
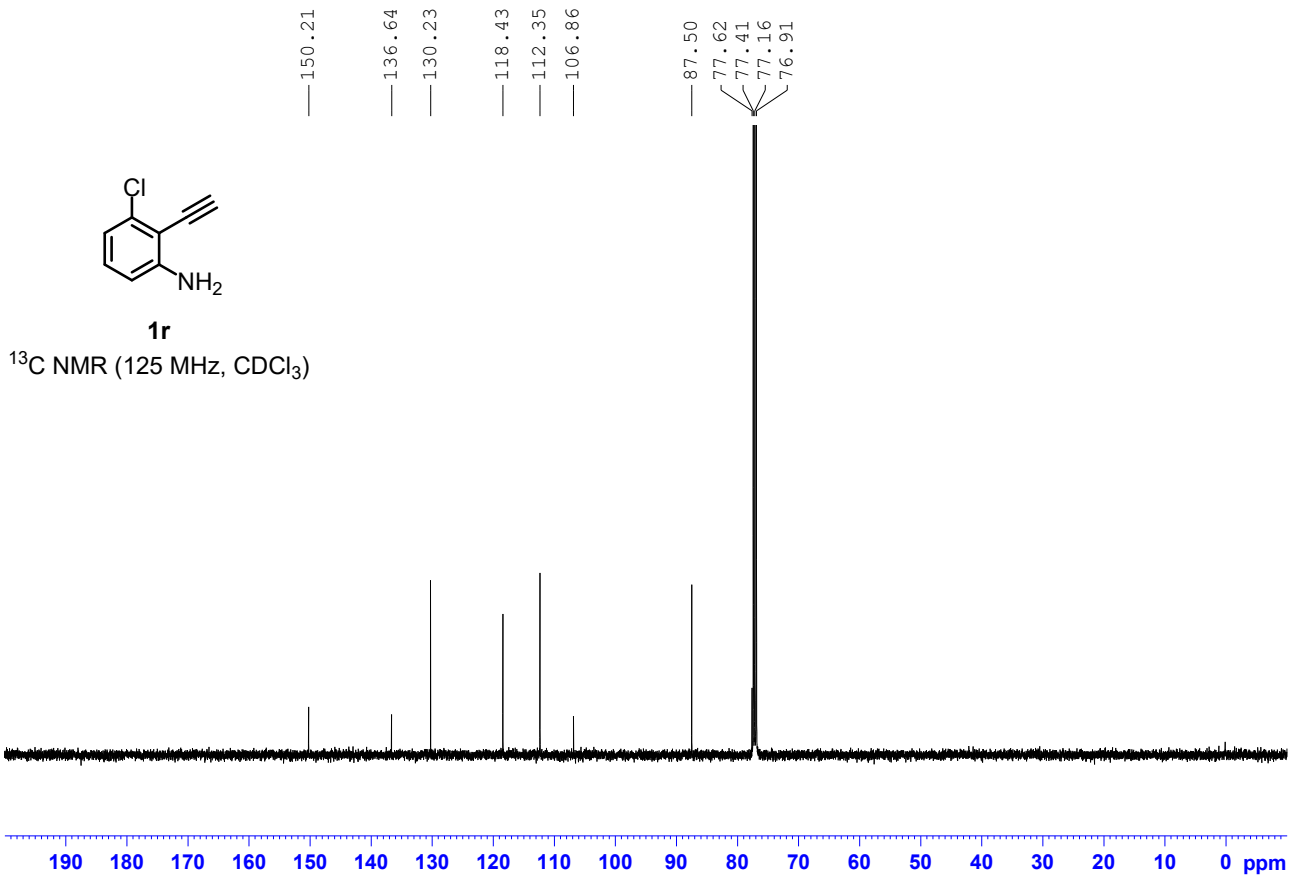


1r

^{1}H NMR (500 MHz, $CDCl_3$)



1r

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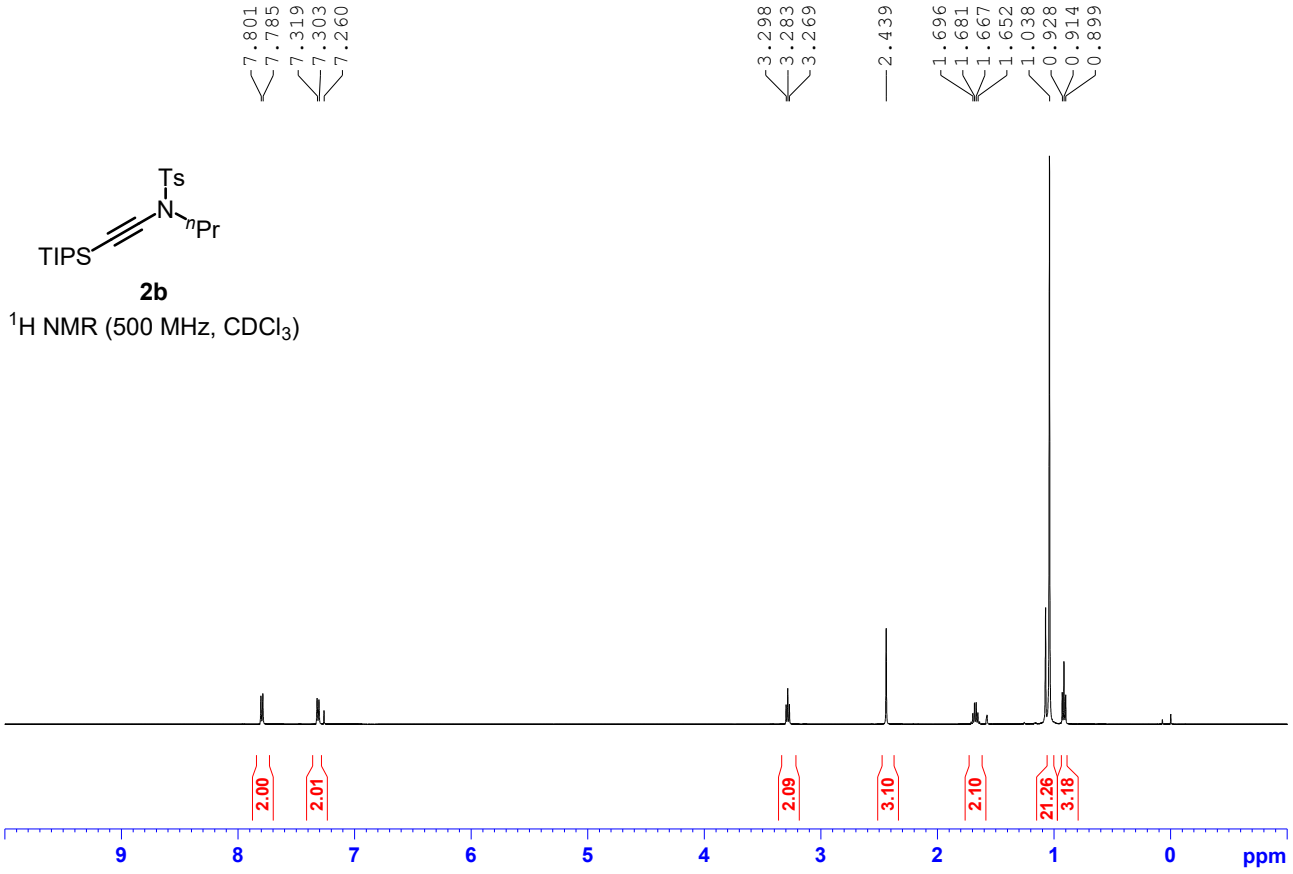
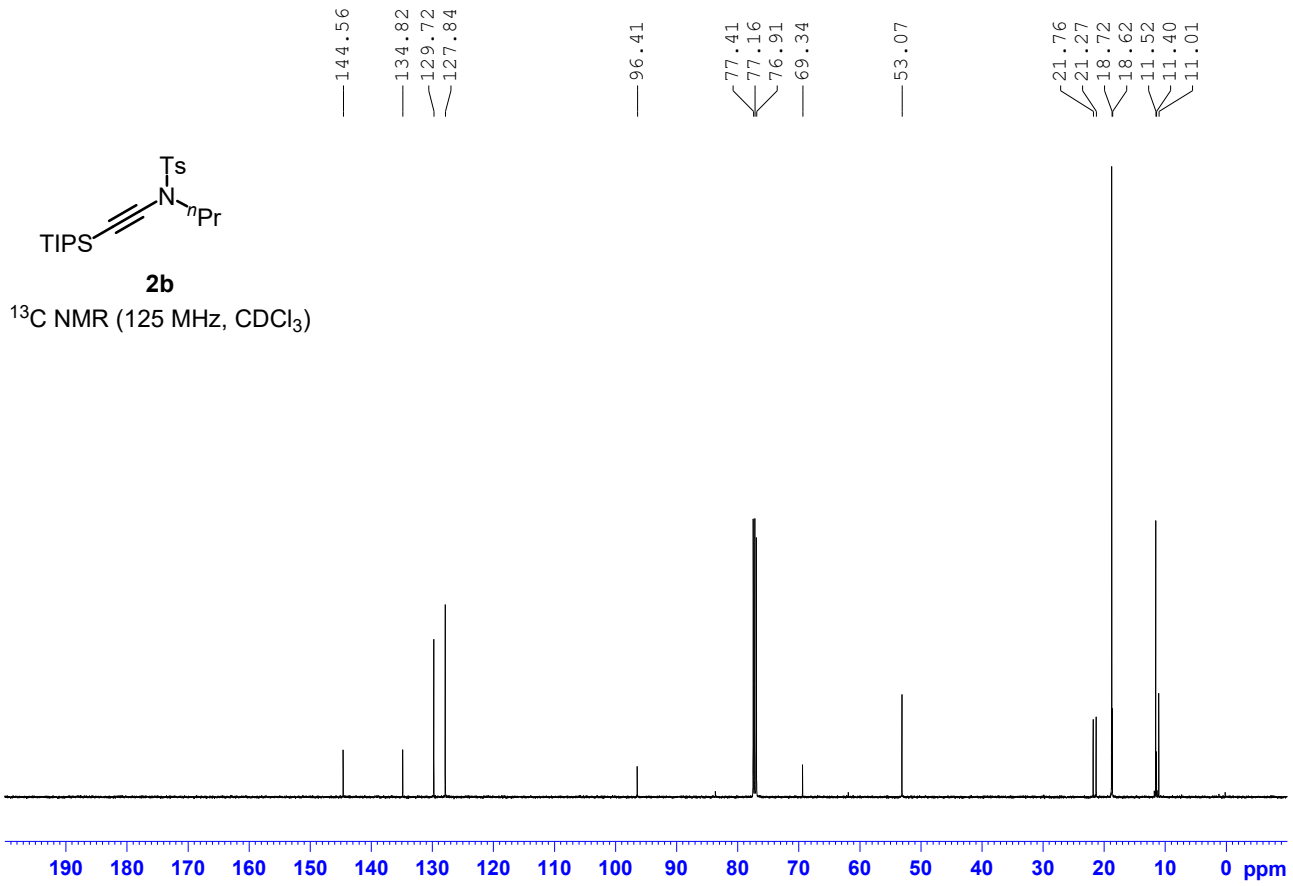


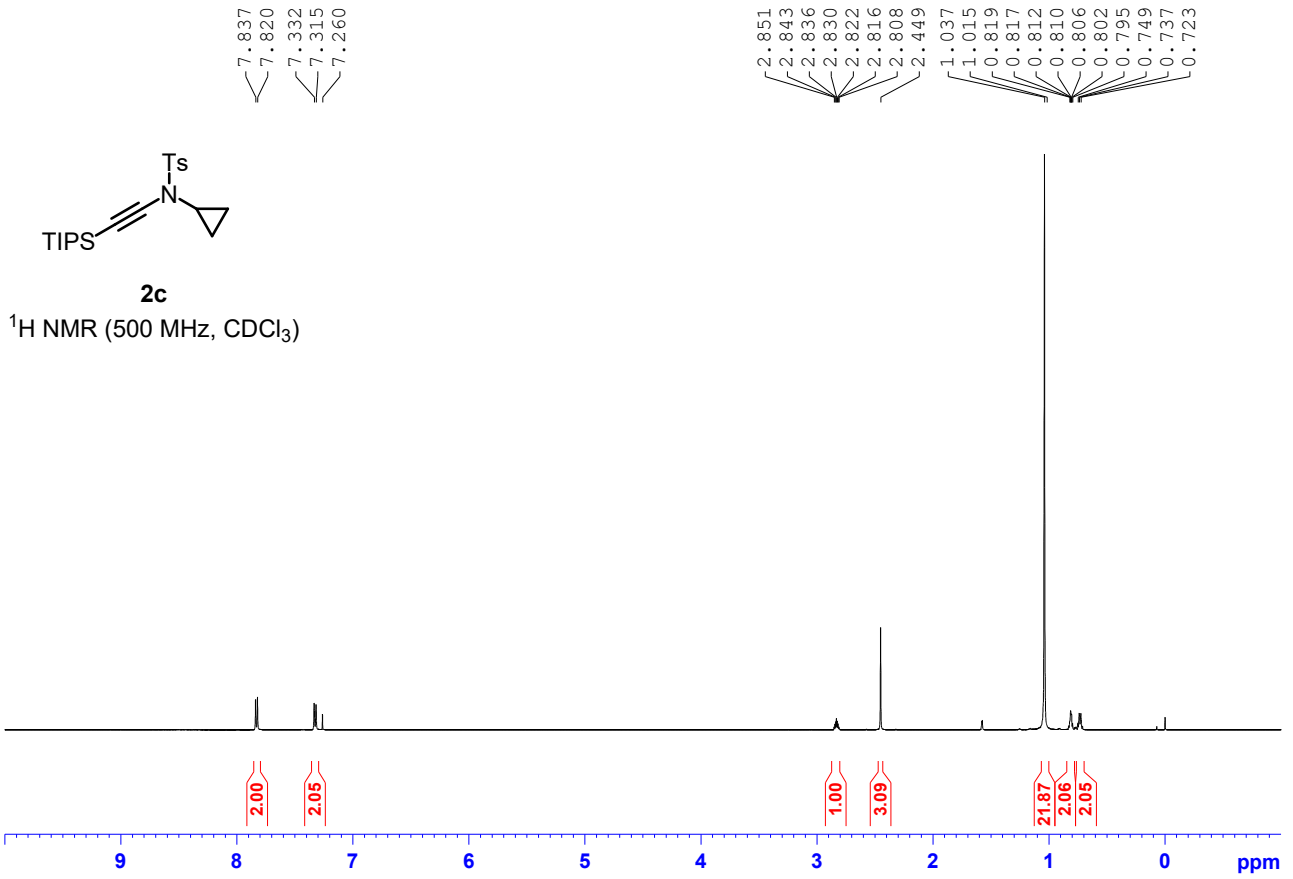
2b

^{1}H NMR (500 MHz, $CDCl_3$)



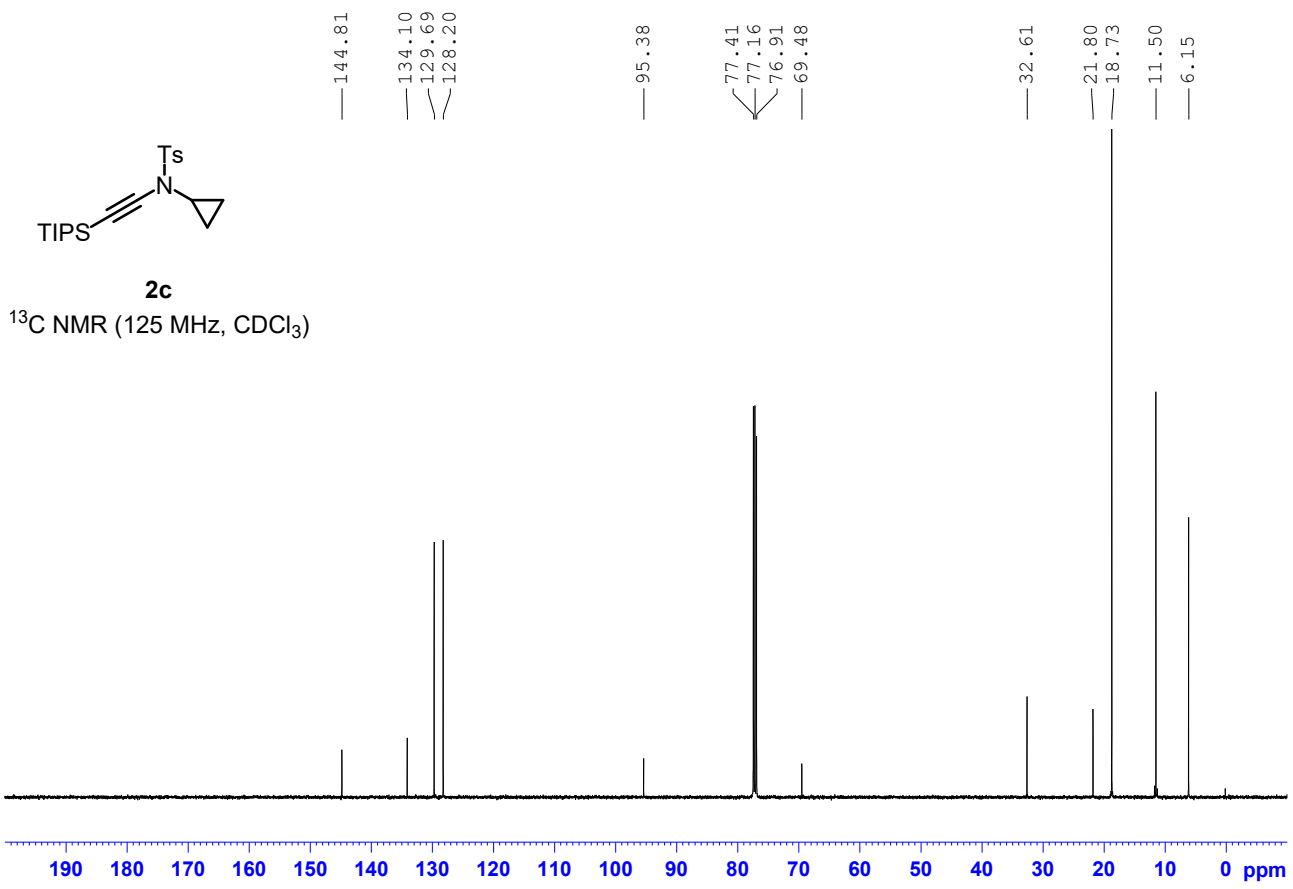
2b

^{13}C NMR (125 MHz, $CDCl_3$)



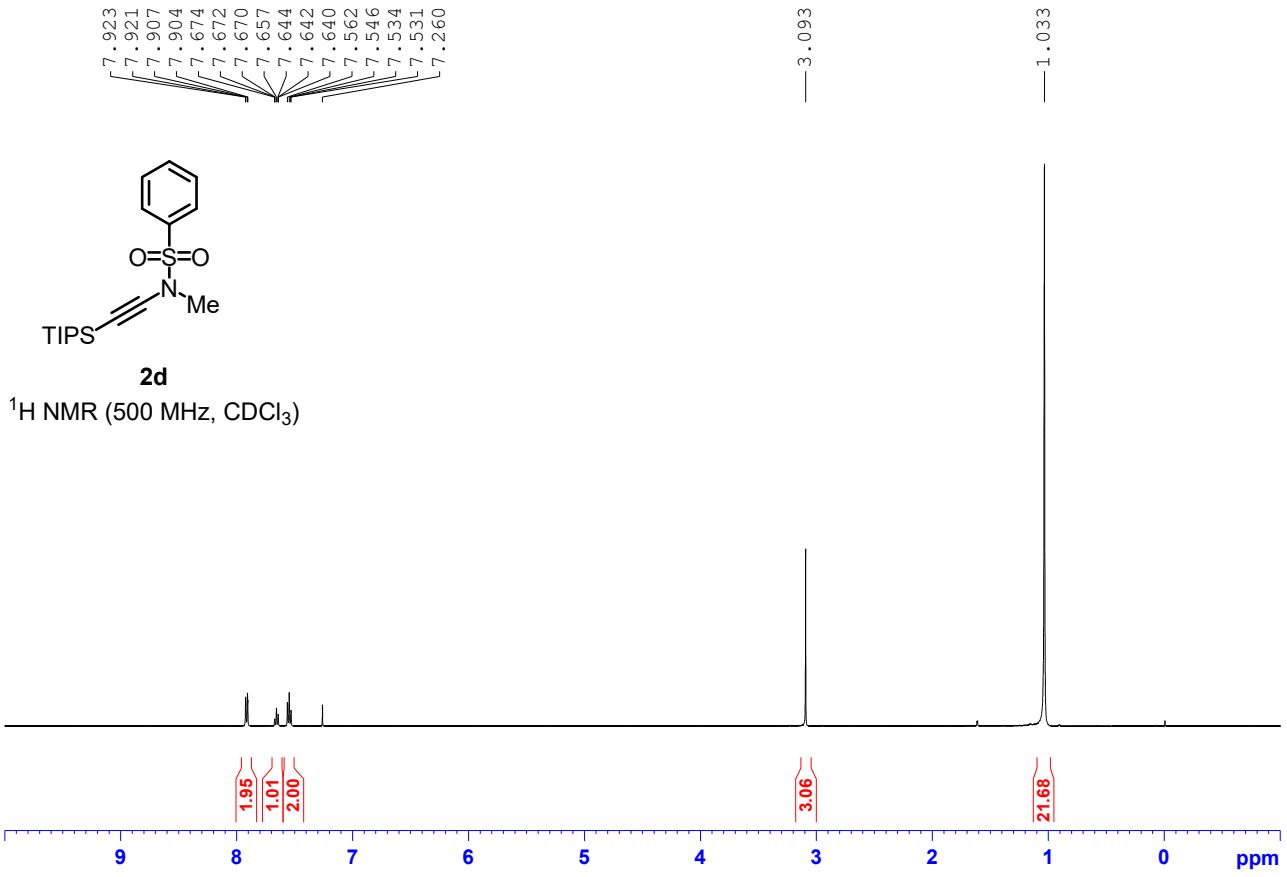
2c

^{1}H NMR (500 MHz, $CDCl_3$)



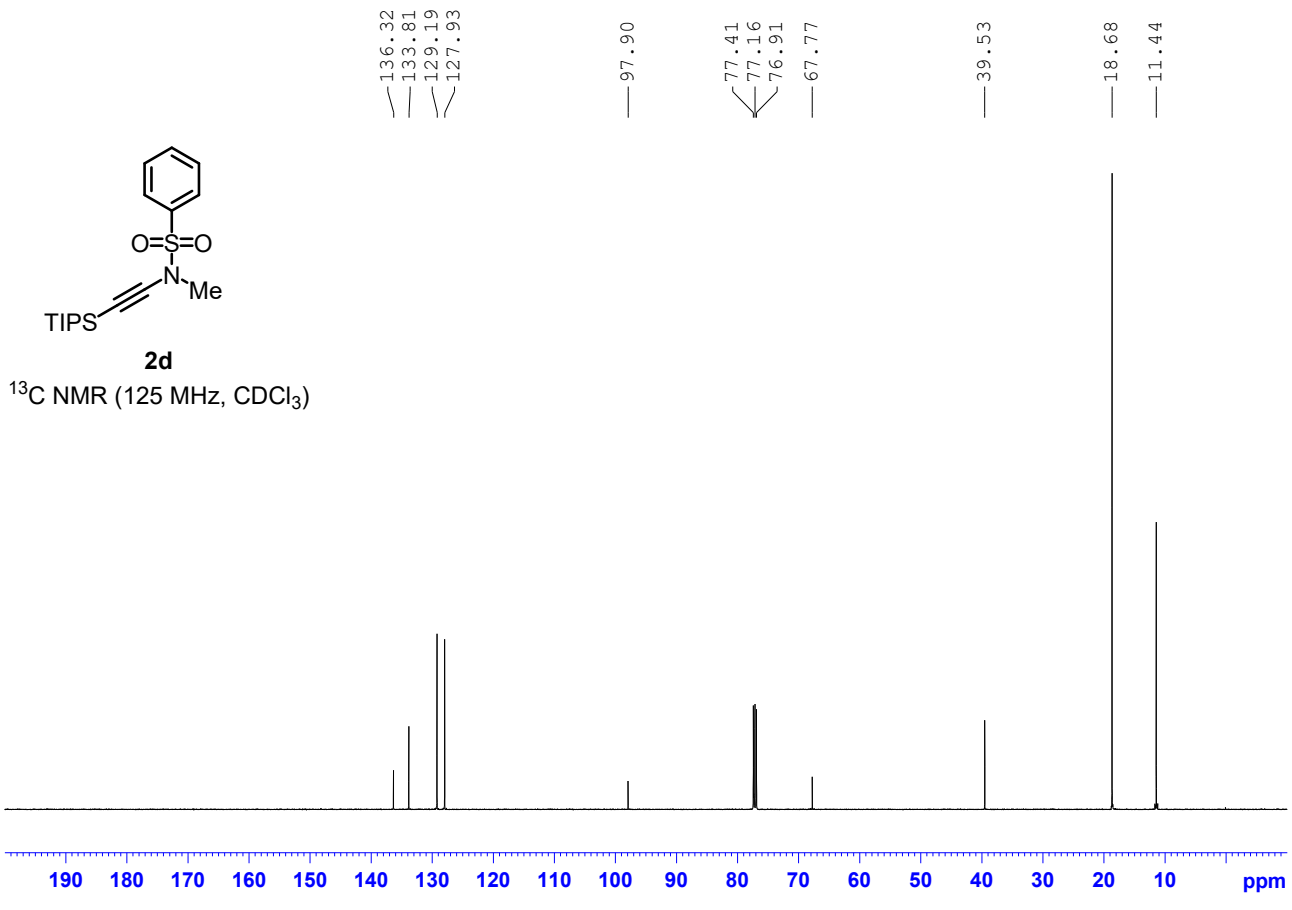
2c

^{13}C NMR (125 MHz, $CDCl_3$)



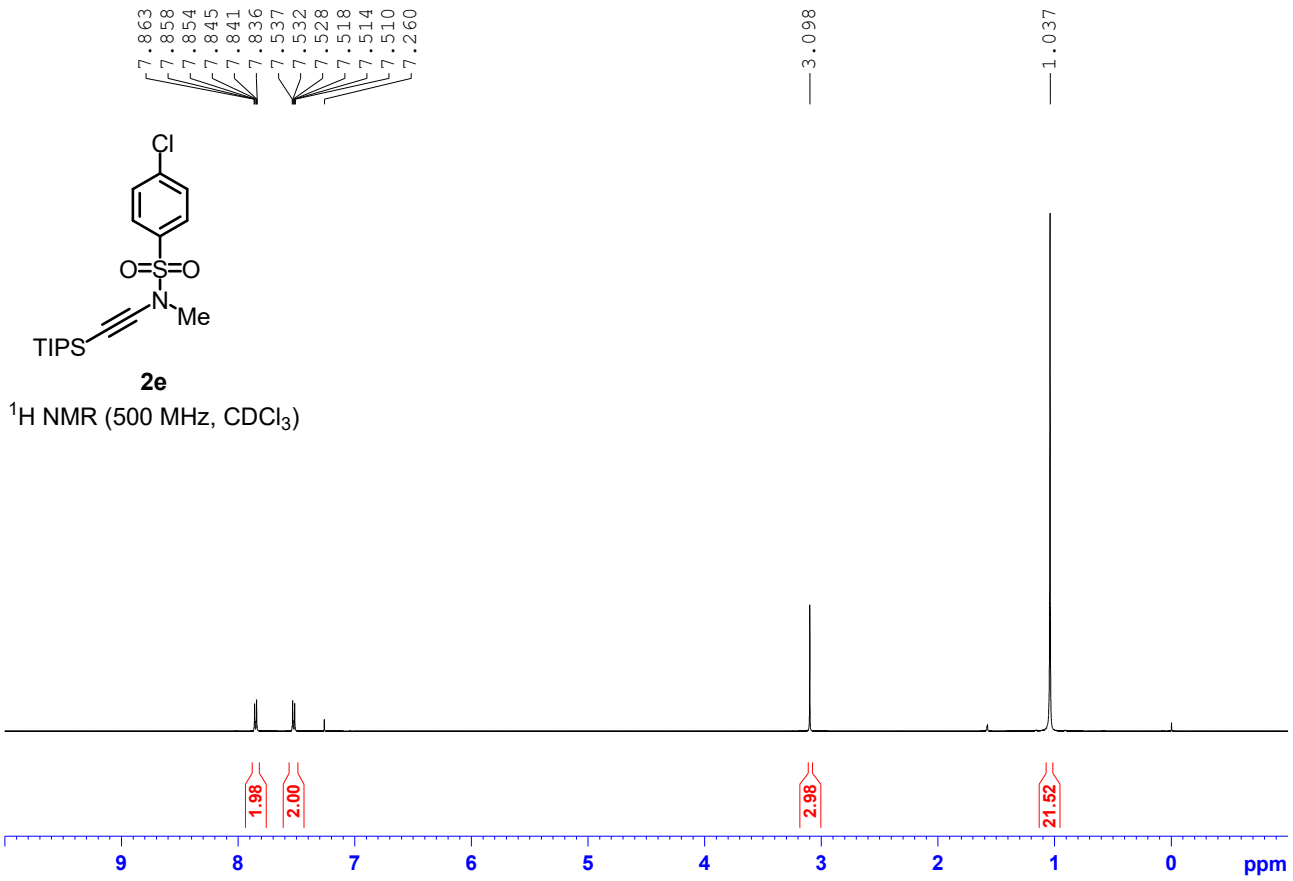
2d

^{1}H NMR (500 MHz, $CDCl_3$)



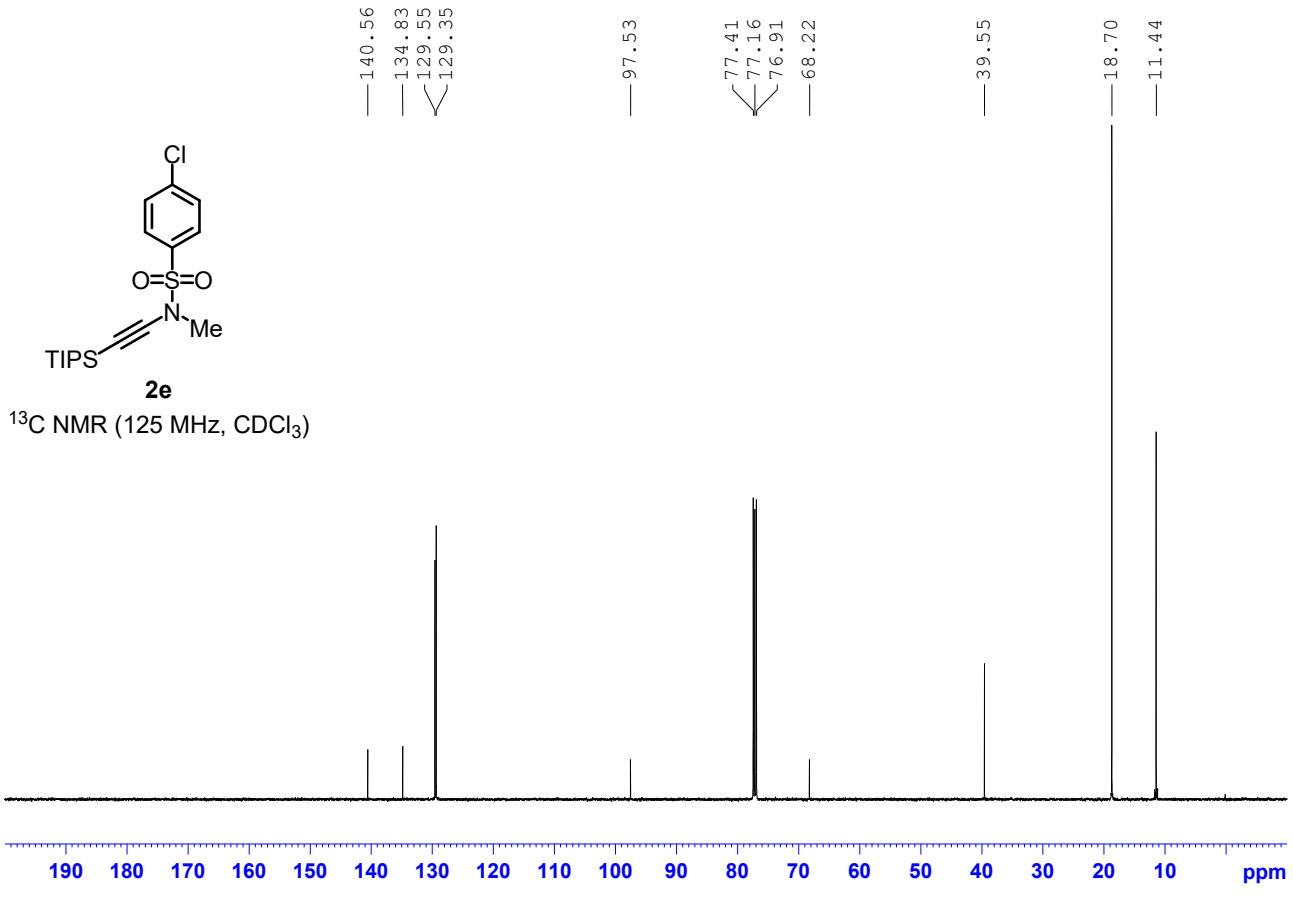
2d

^{13}C NMR (125 MHz, $CDCl_3$)



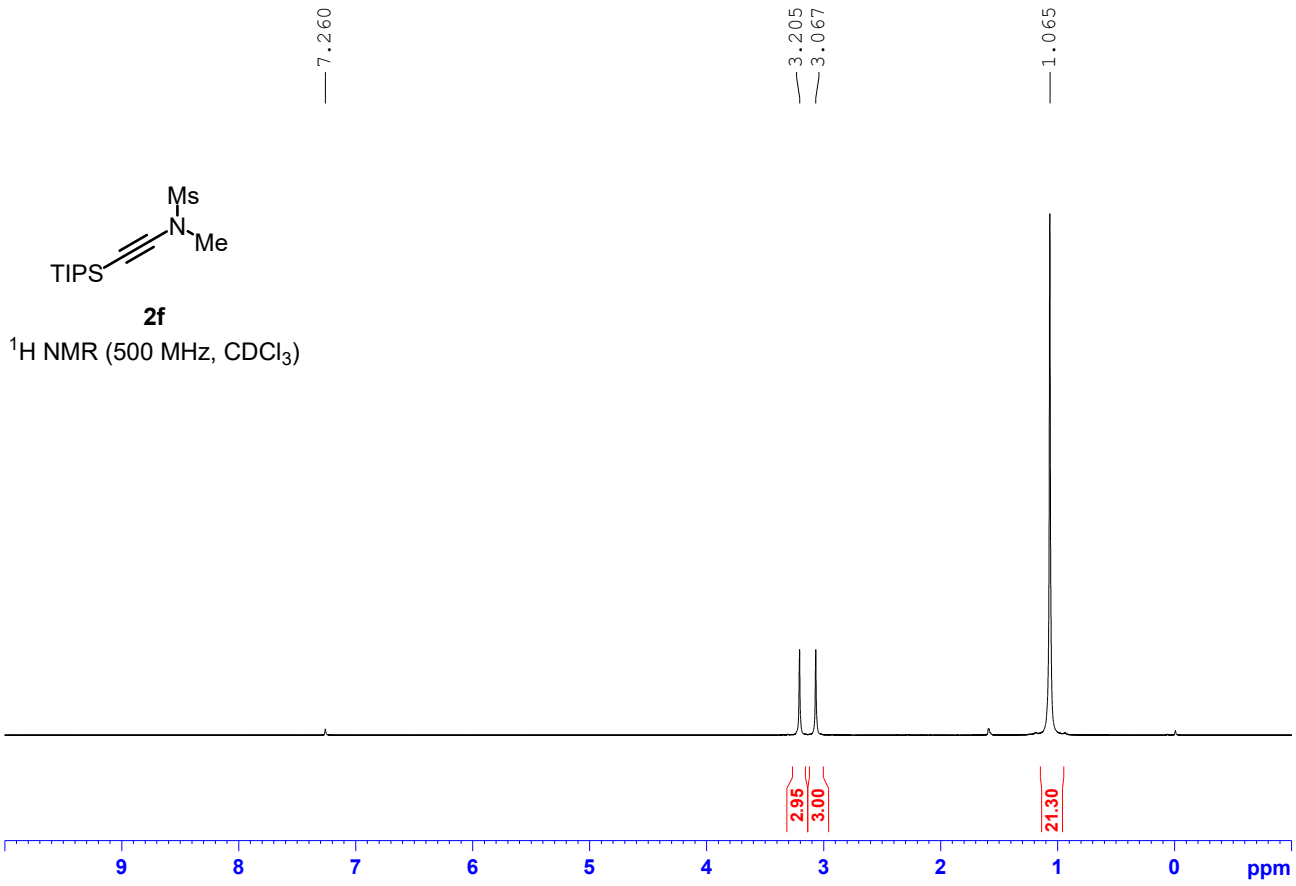
2e

^{1}H NMR (500 MHz, $CDCl_3$)



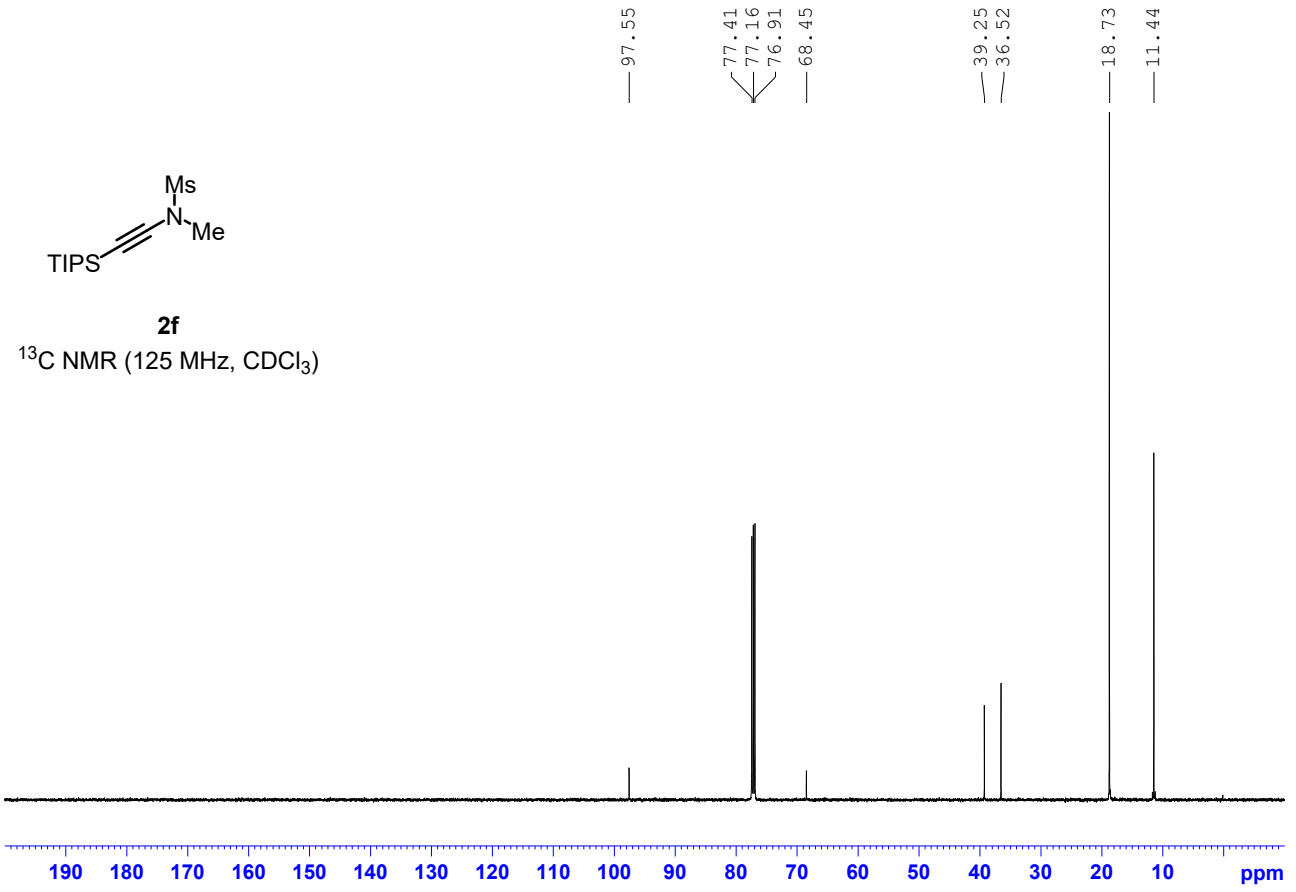
2e

^{13}C NMR (125 MHz, $CDCl_3$)



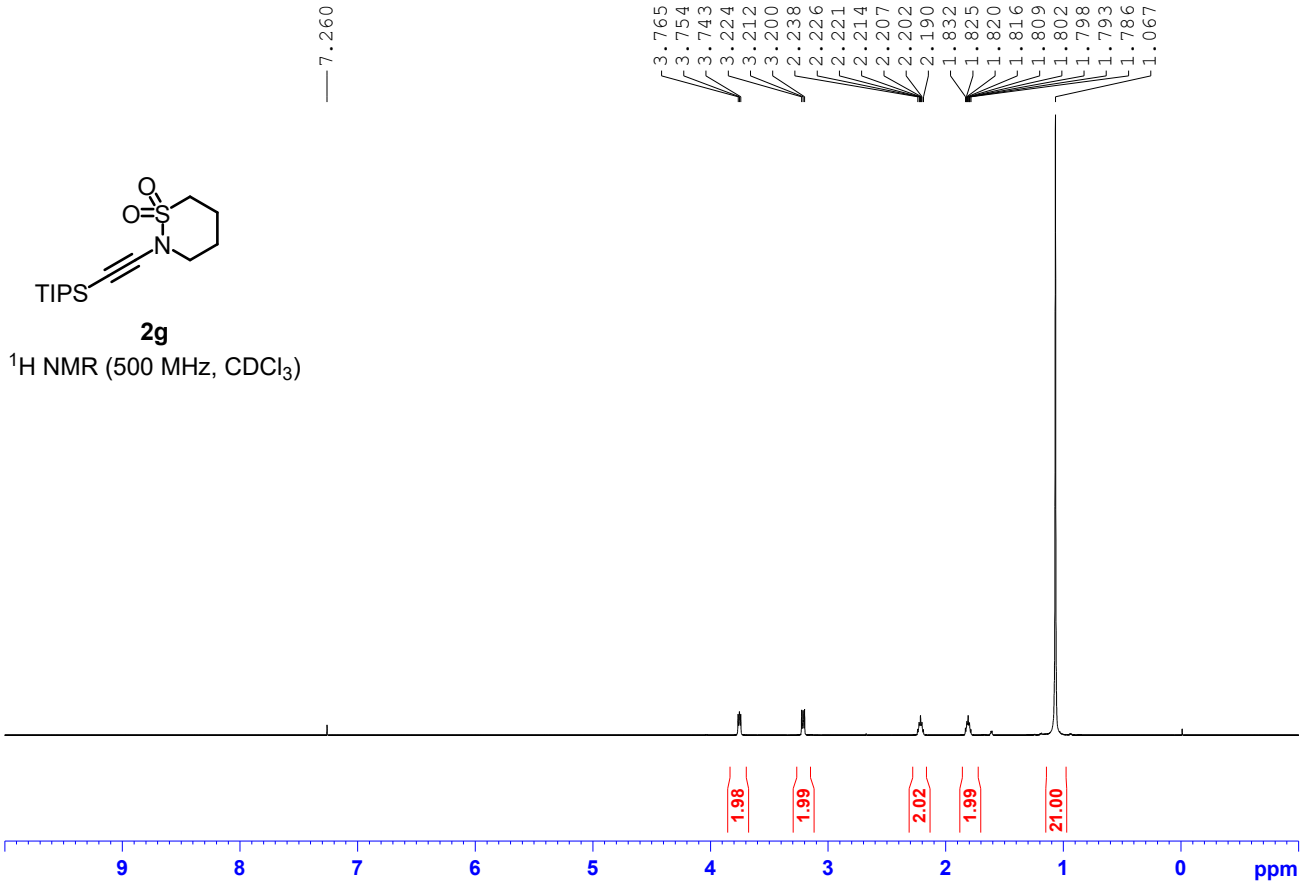
2f

^{1}H NMR (500 MHz, $CDCl_3$)



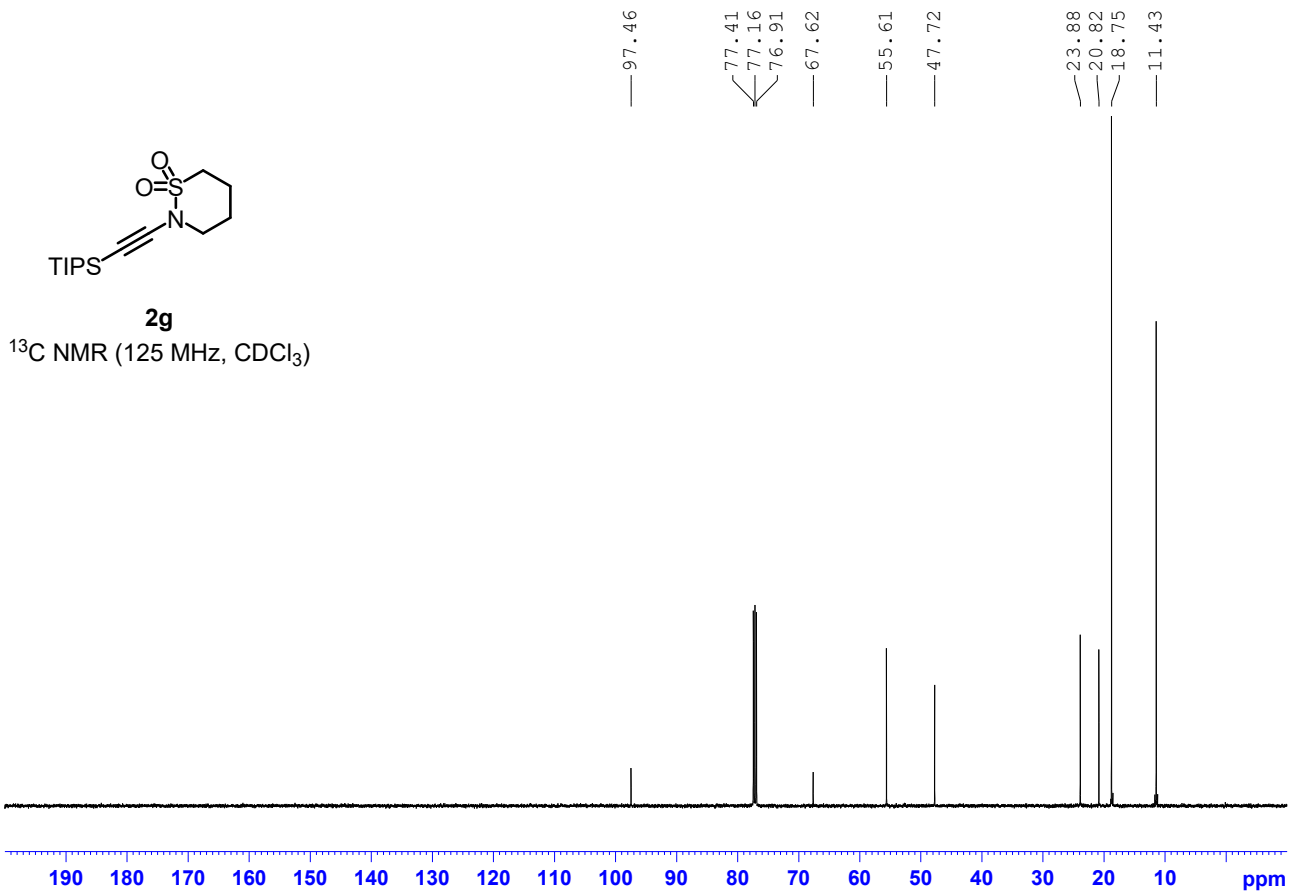
2f

^{13}C NMR (125 MHz, $CDCl_3$)



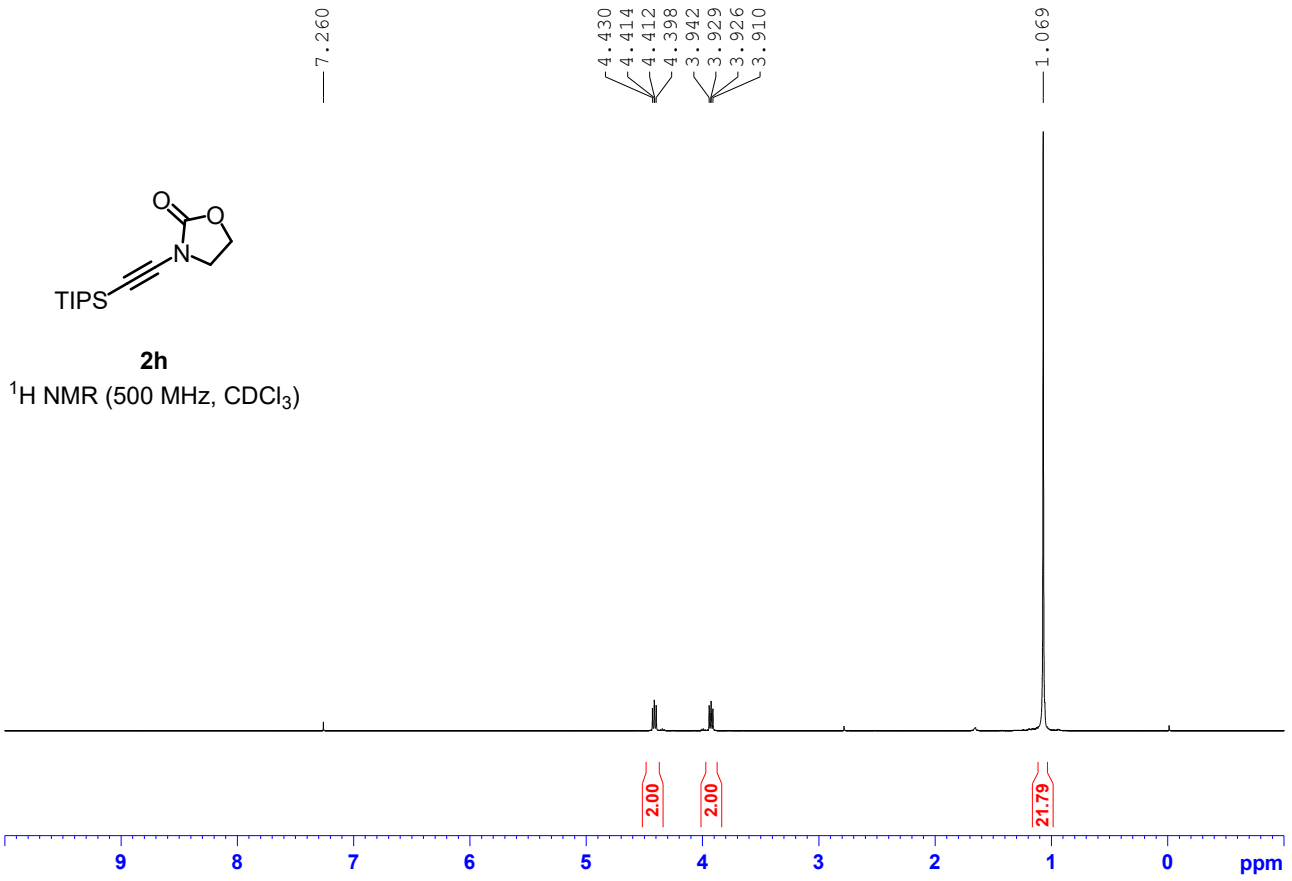
2g

^{1}H NMR (500 MHz, $CDCl_3$)



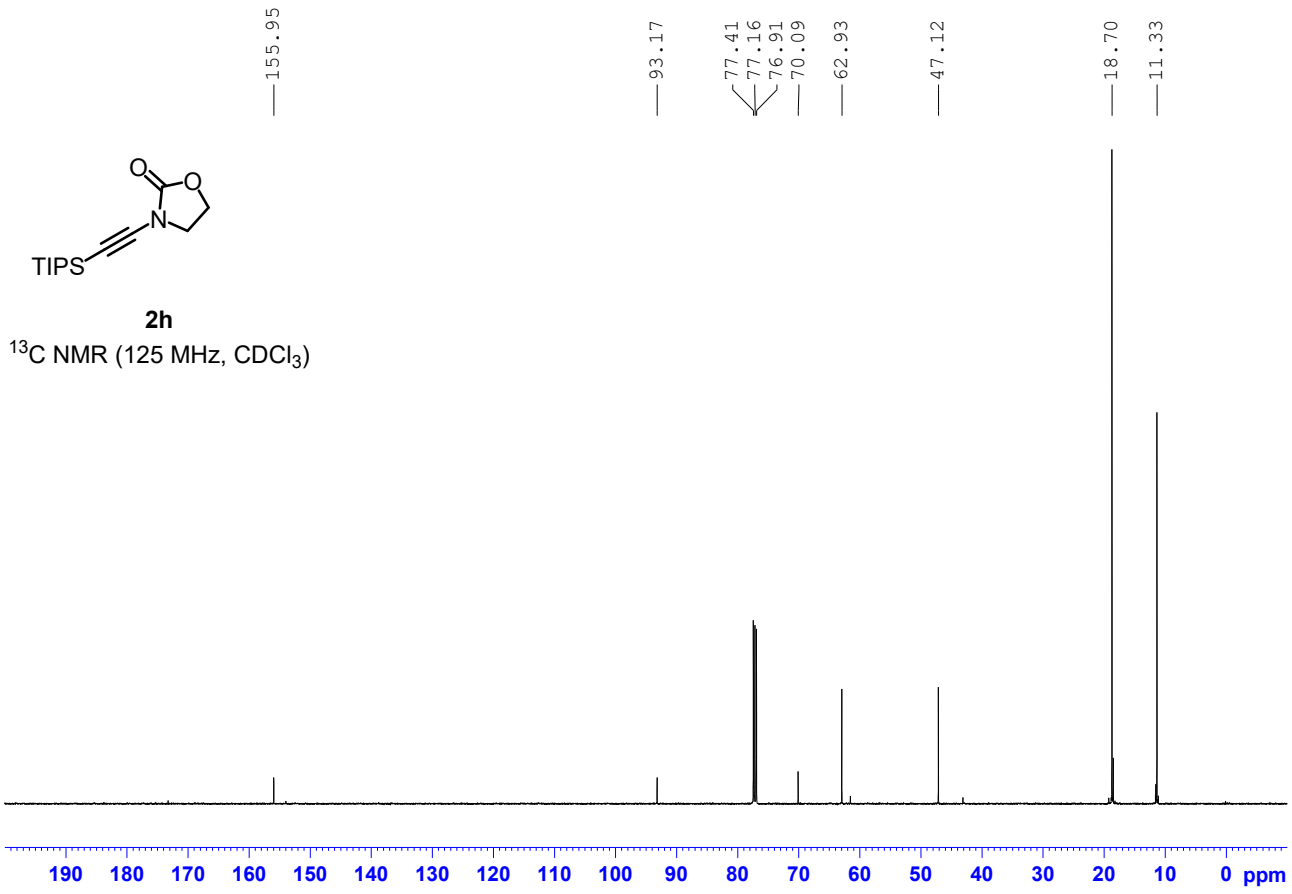
2g

^{13}C NMR (125 MHz, $CDCl_3$)



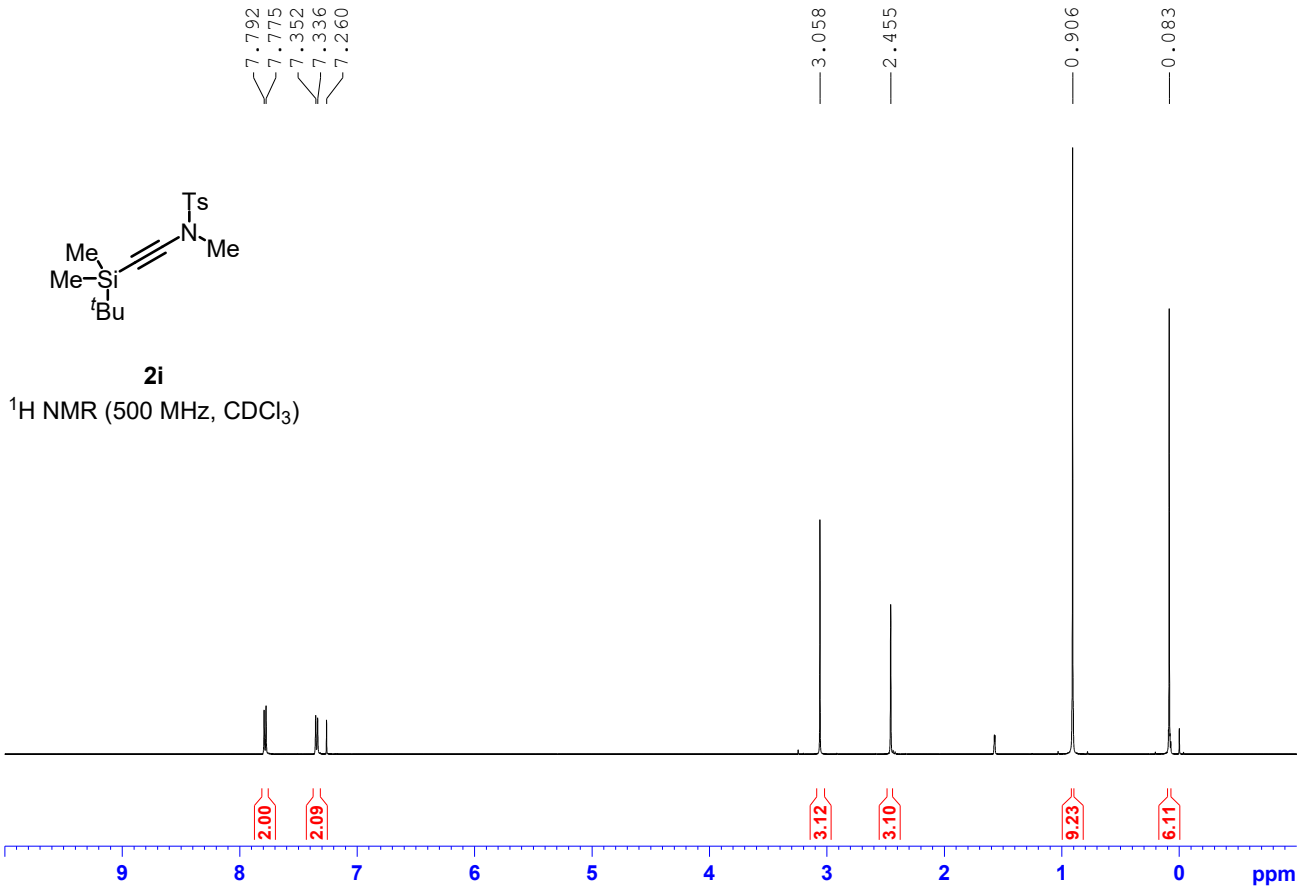
2h

^{1}H NMR (500 MHz, $CDCl_3$)



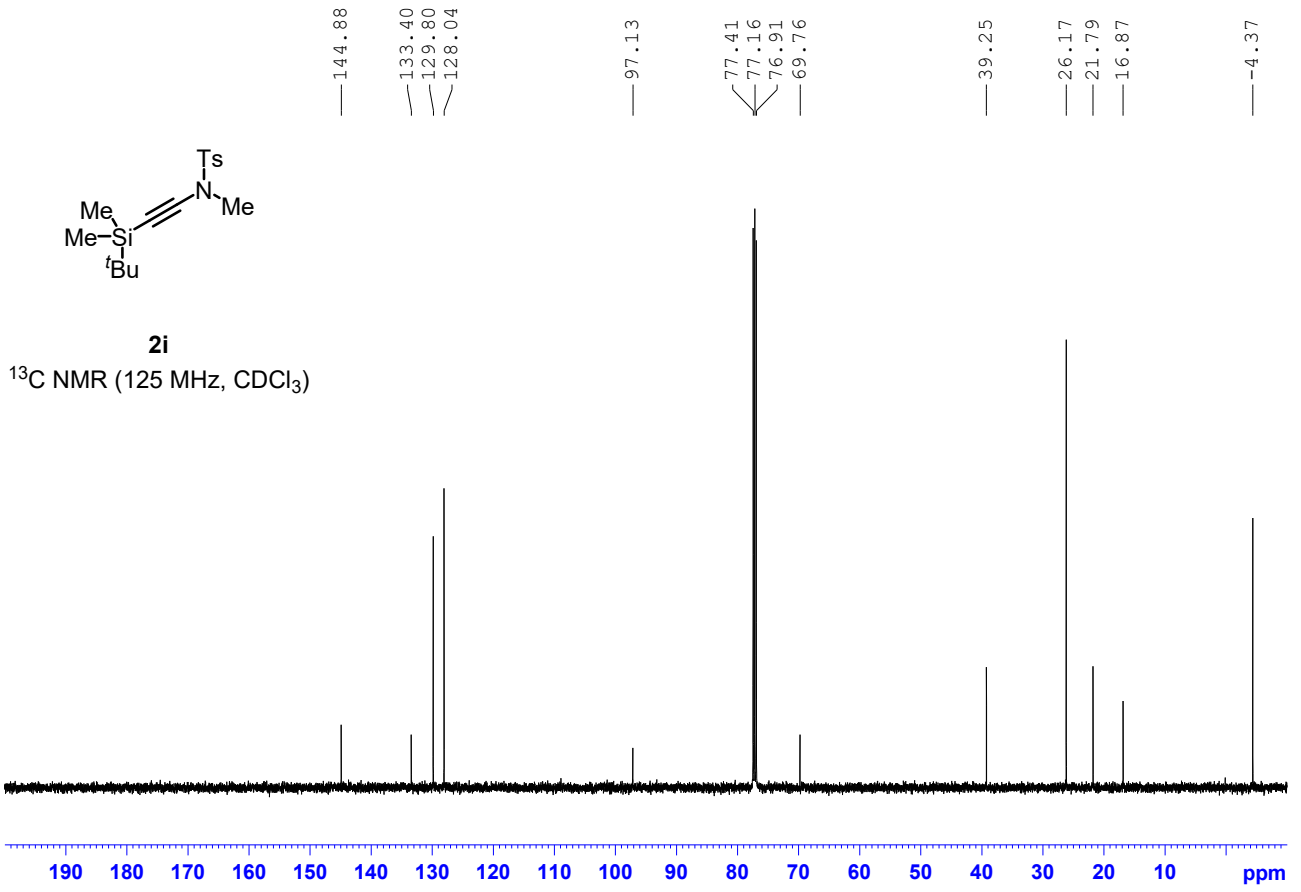
2h

^{13}C NMR (125 MHz, $CDCl_3$)



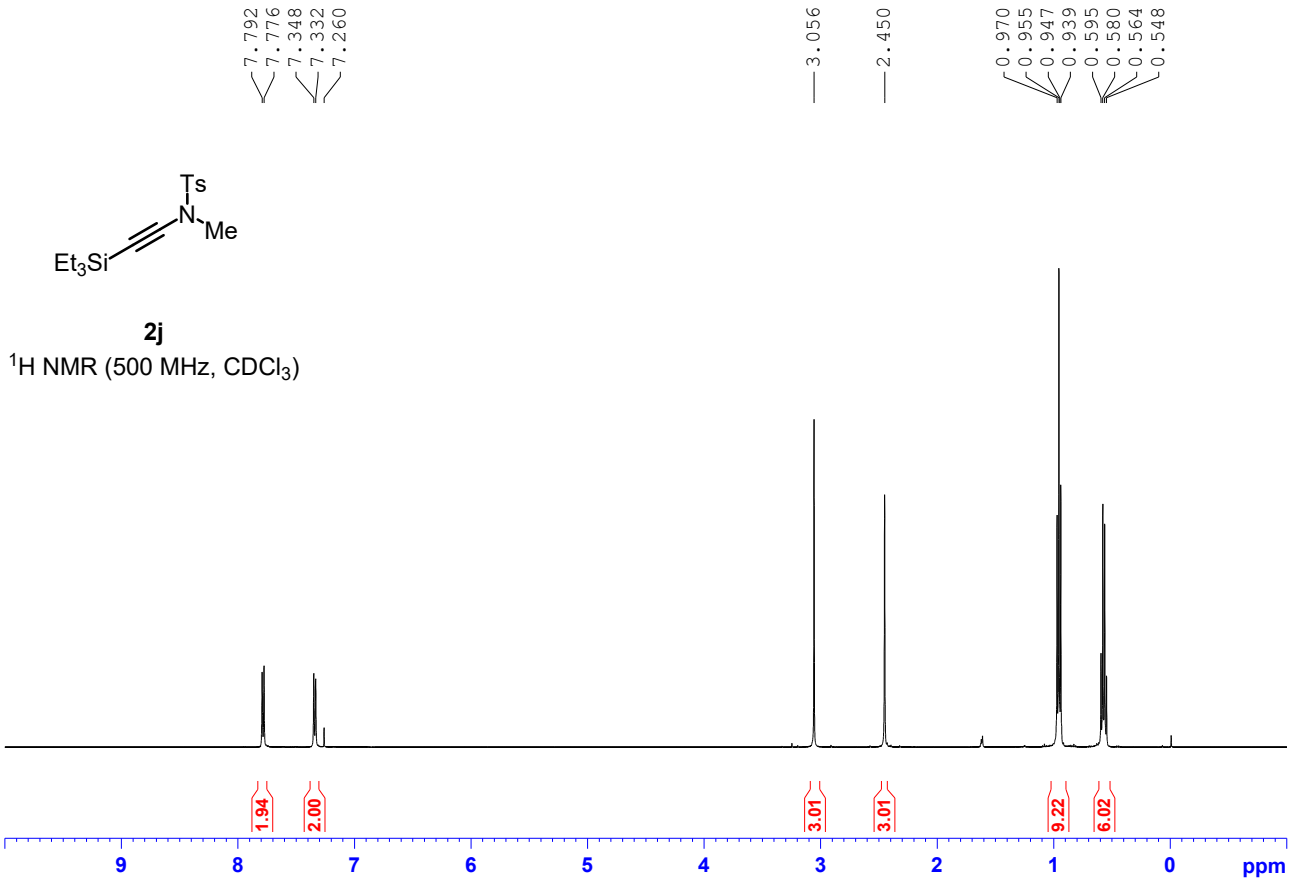
2i

^{1}H NMR (500 MHz, $CDCl_3$)



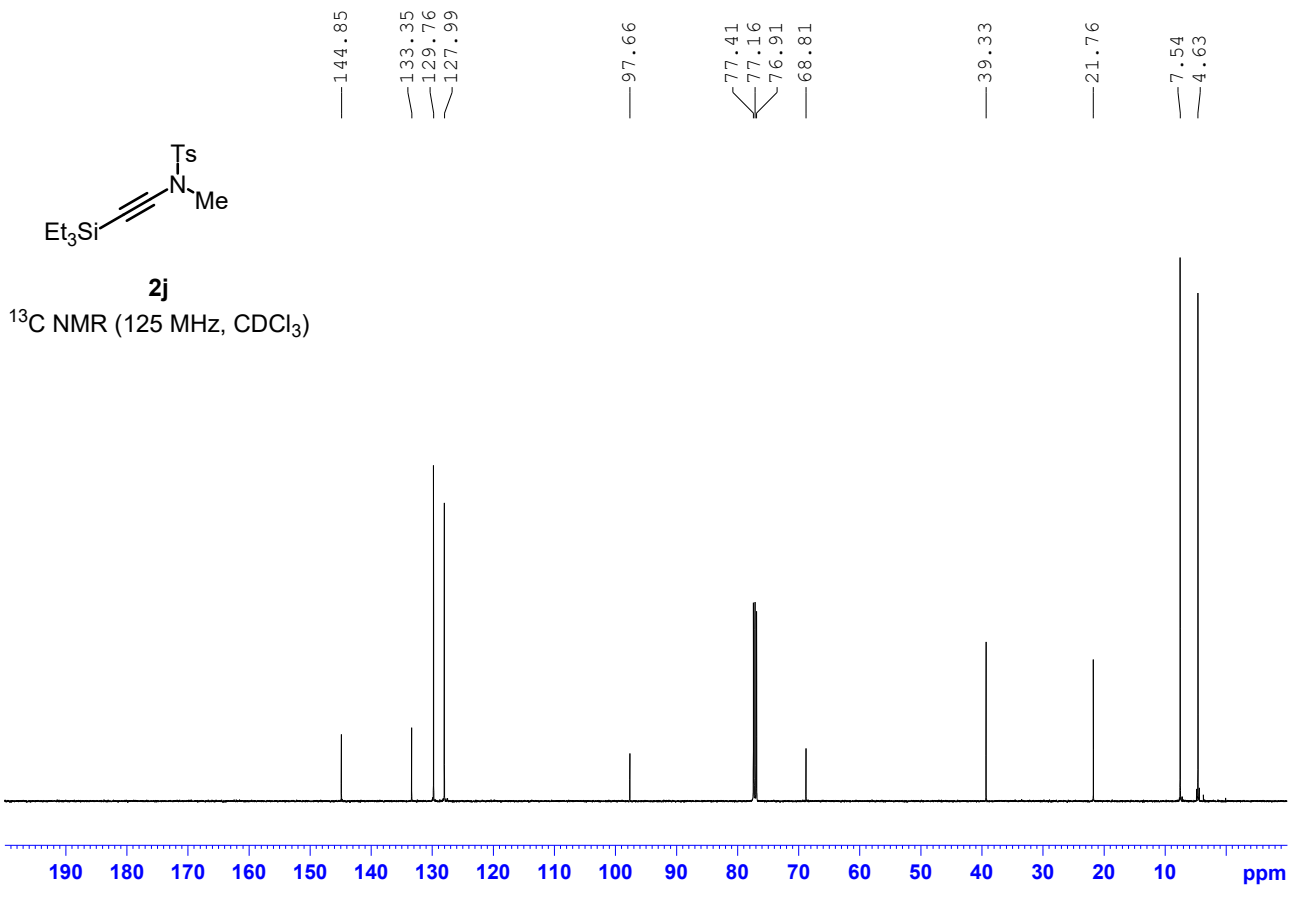
2i

^{13}C NMR (125 MHz, $CDCl_3$)



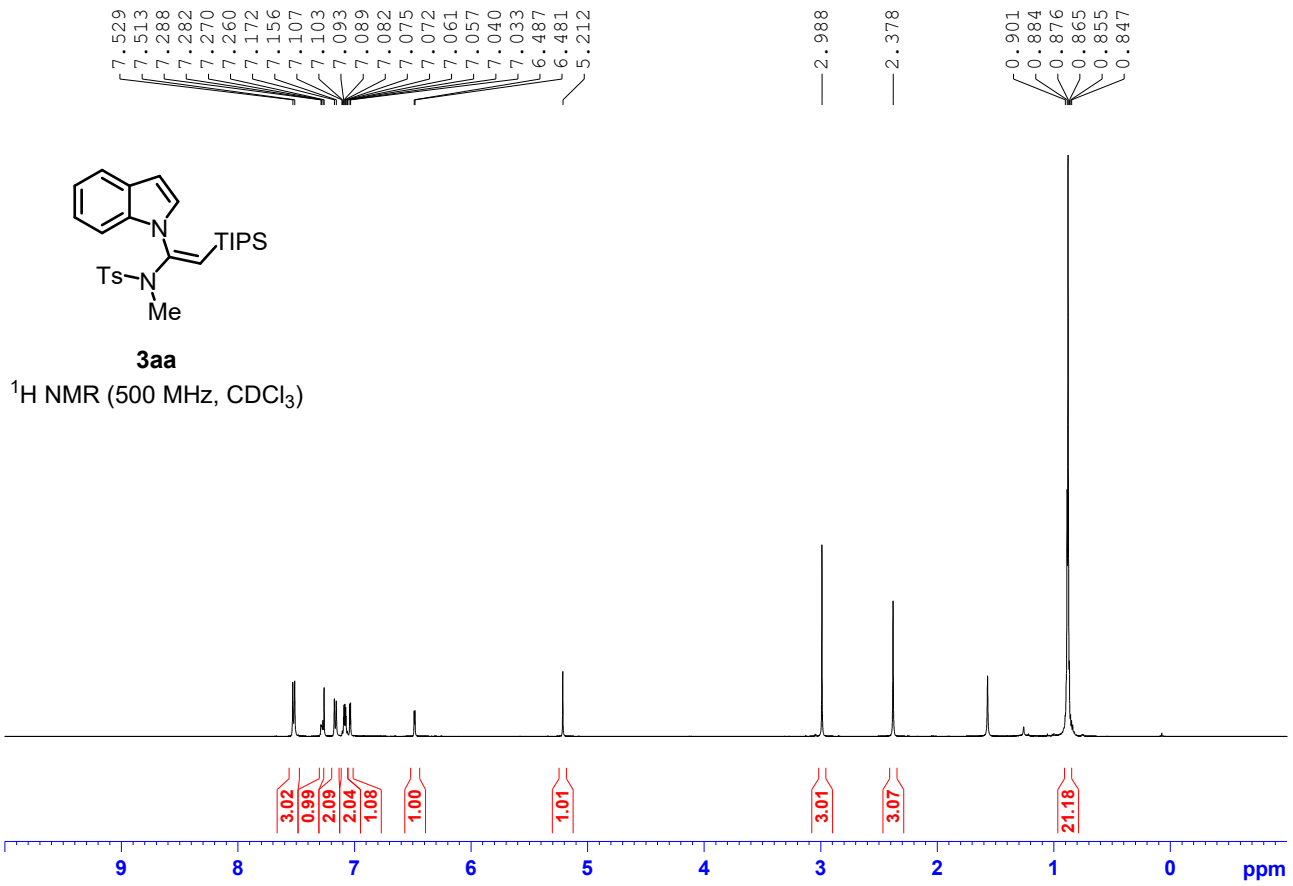
2j

^{1}H NMR (500 MHz, $CDCl_3$)



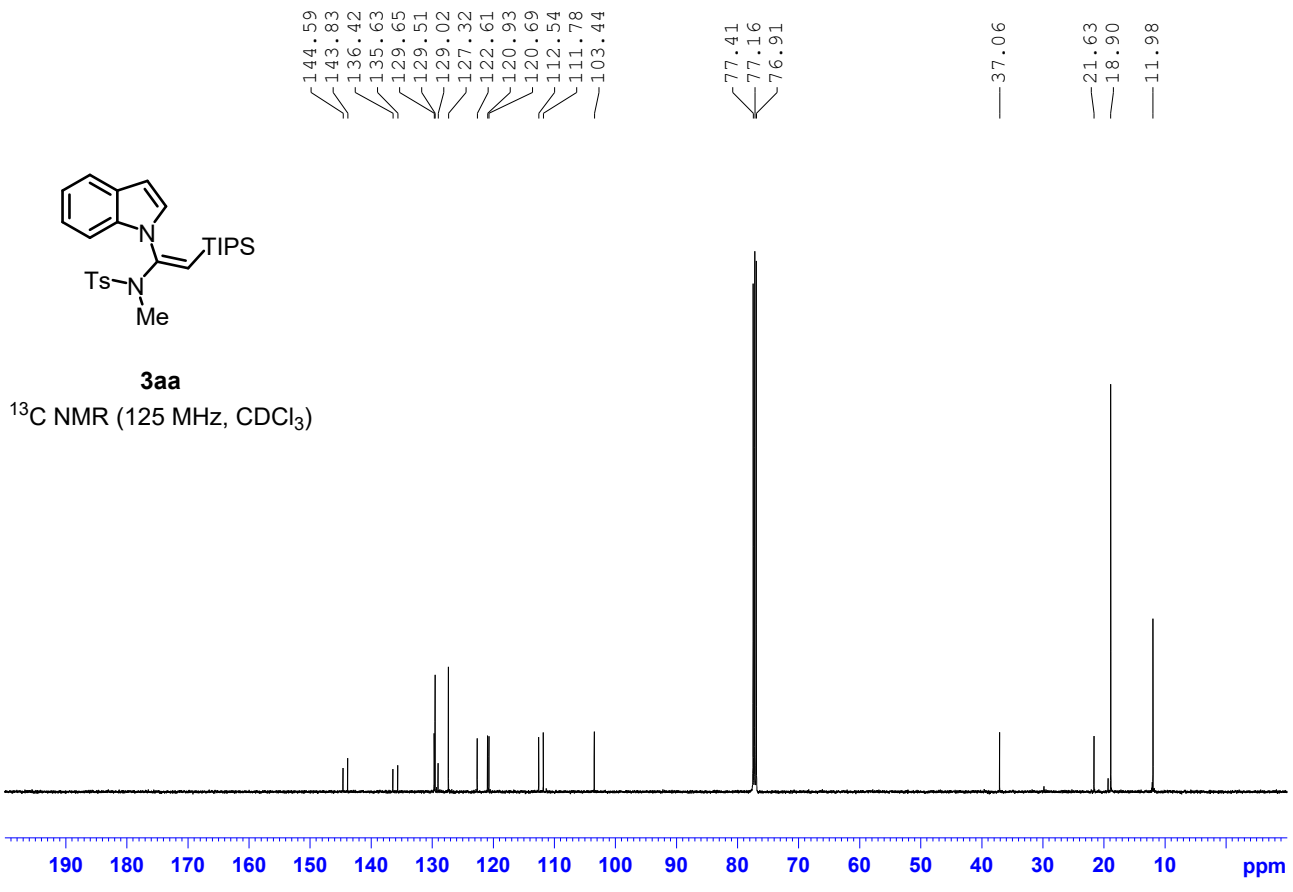
2j

^{13}C NMR (125 MHz, $CDCl_3$)



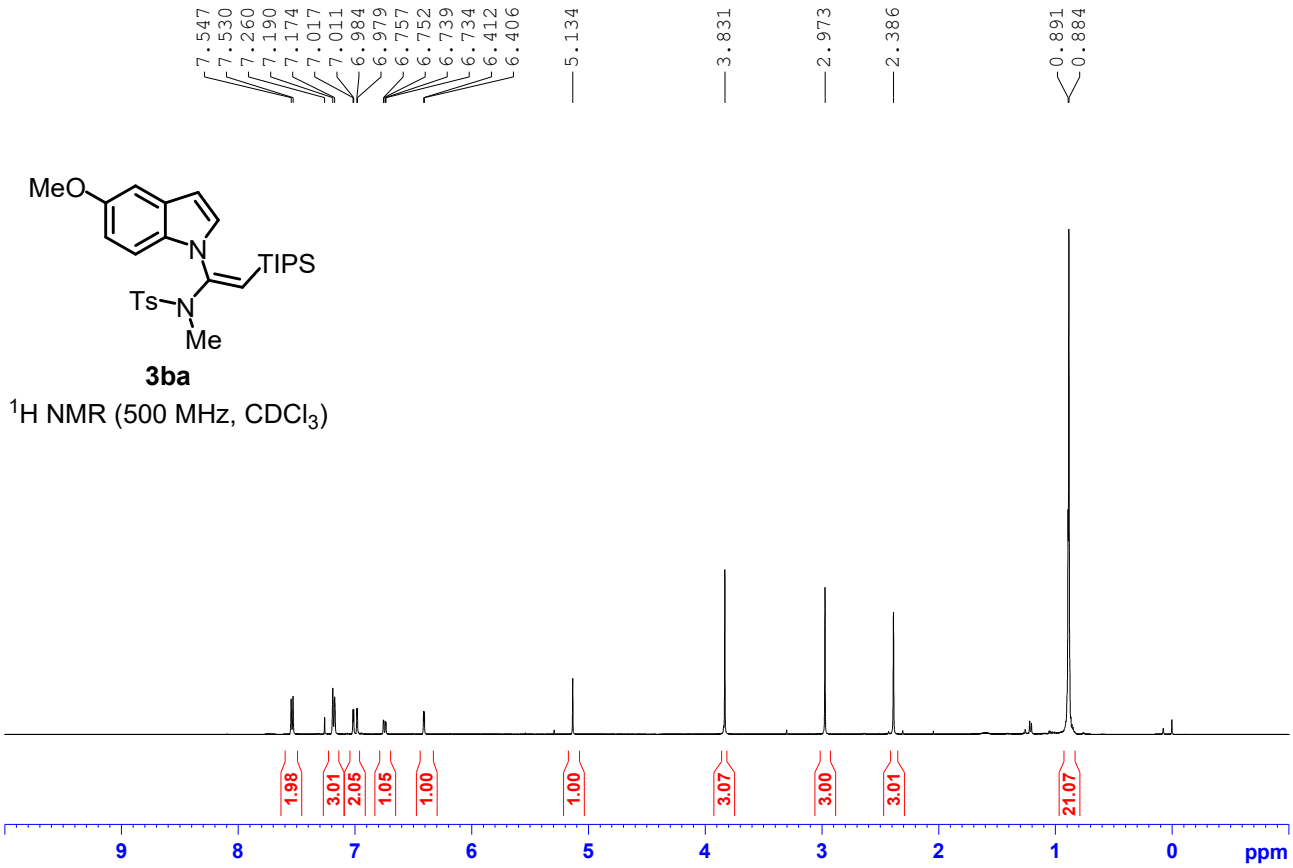
3aa

^{1}H NMR (500 MHz, $CDCl_3$)



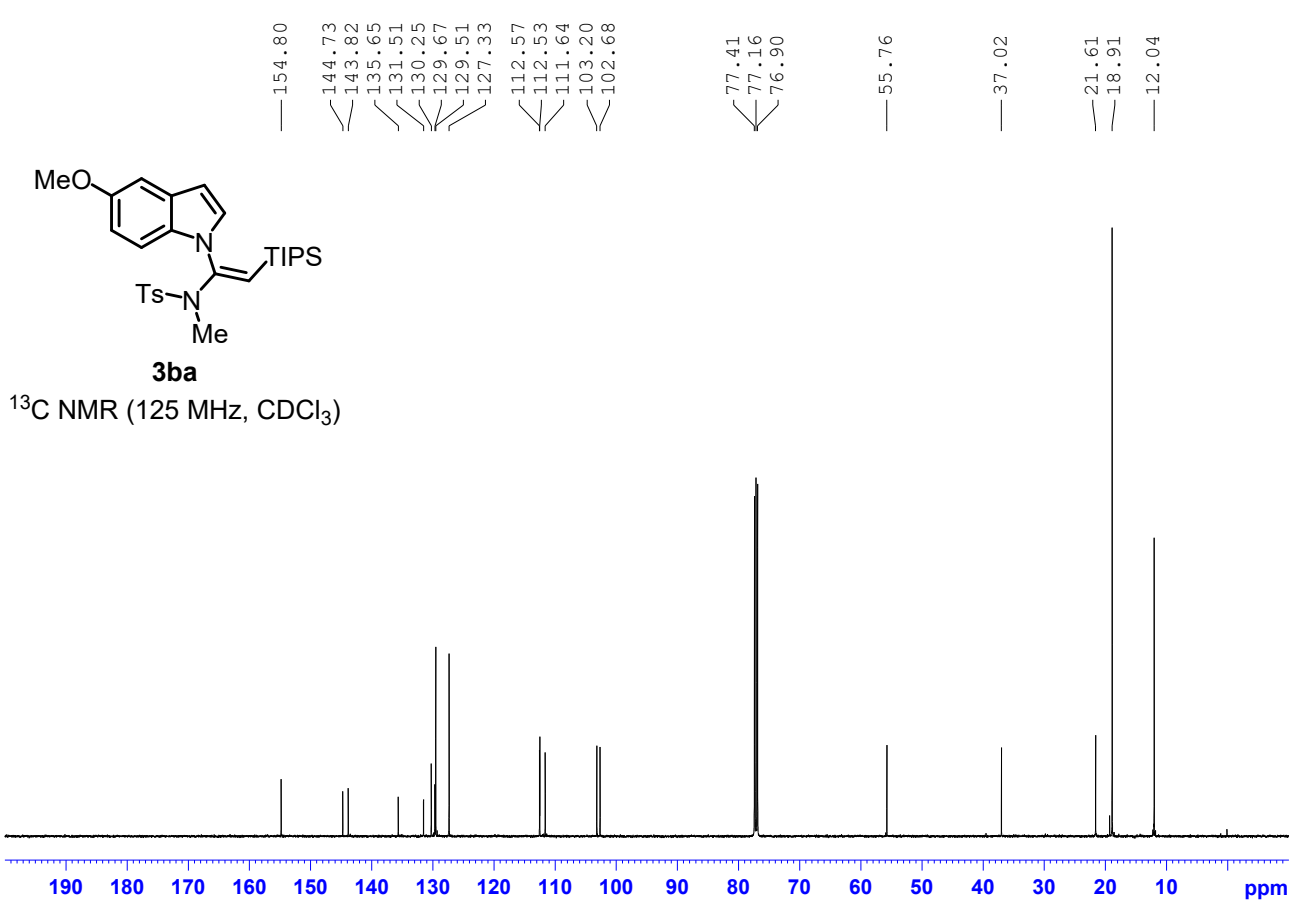
3aa

^{13}C NMR (125 MHz, $CDCl_3$)



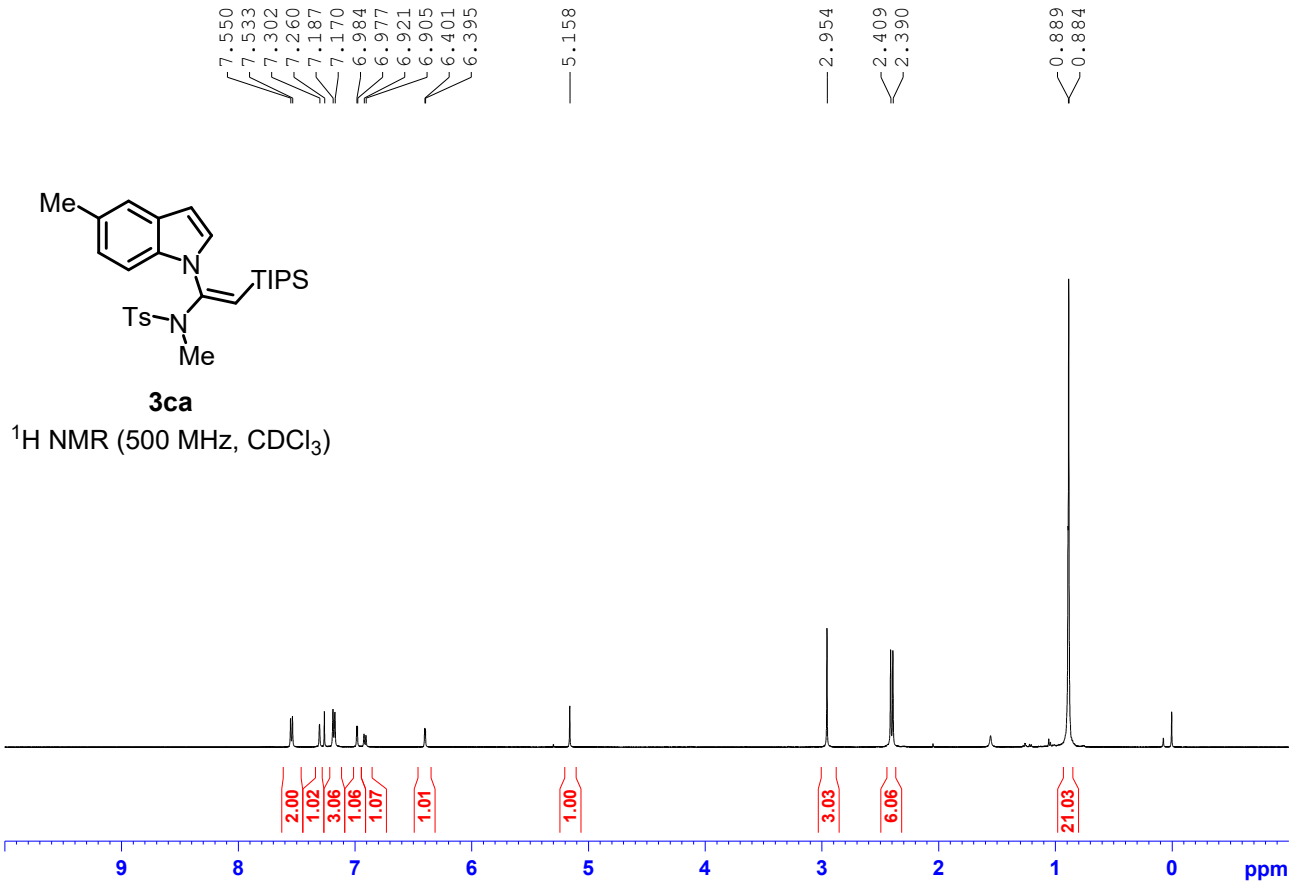
3ba

^{1}H NMR (500 MHz, $CDCl_3$)



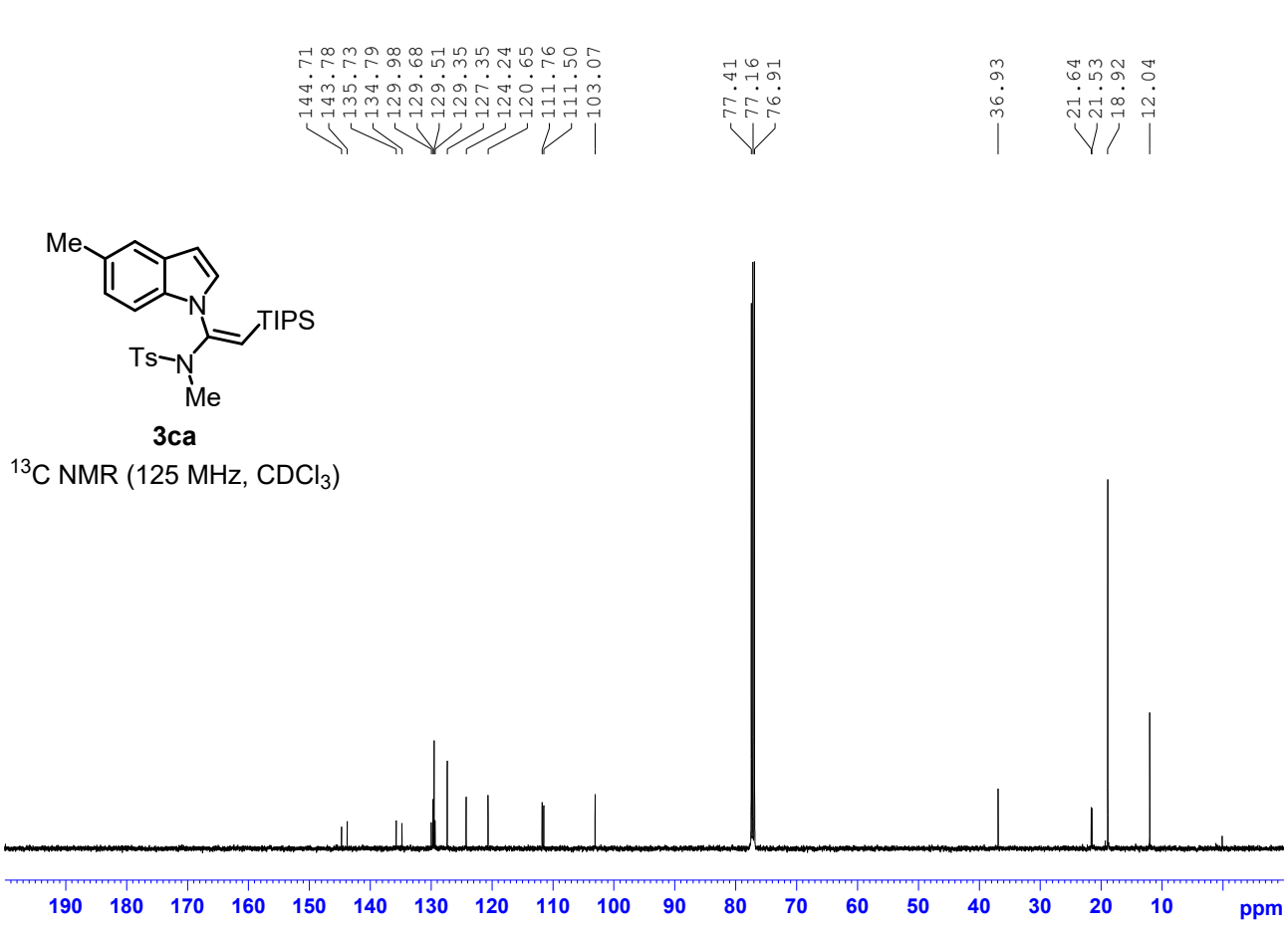
3ba

^{13}C NMR (125 MHz, $CDCl_3$)



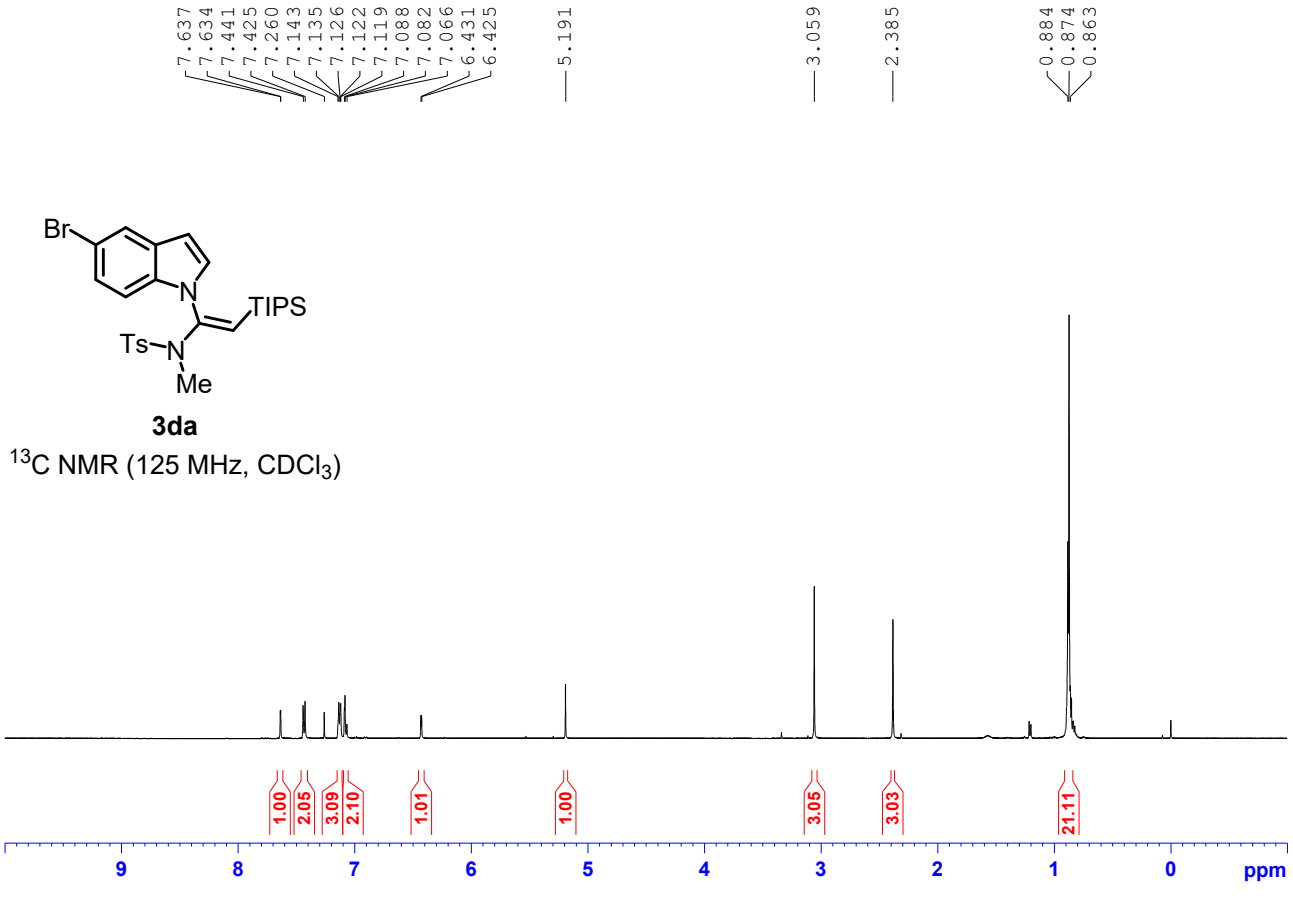
3ca

^{1}H NMR (500 MHz, $CDCl_3$)



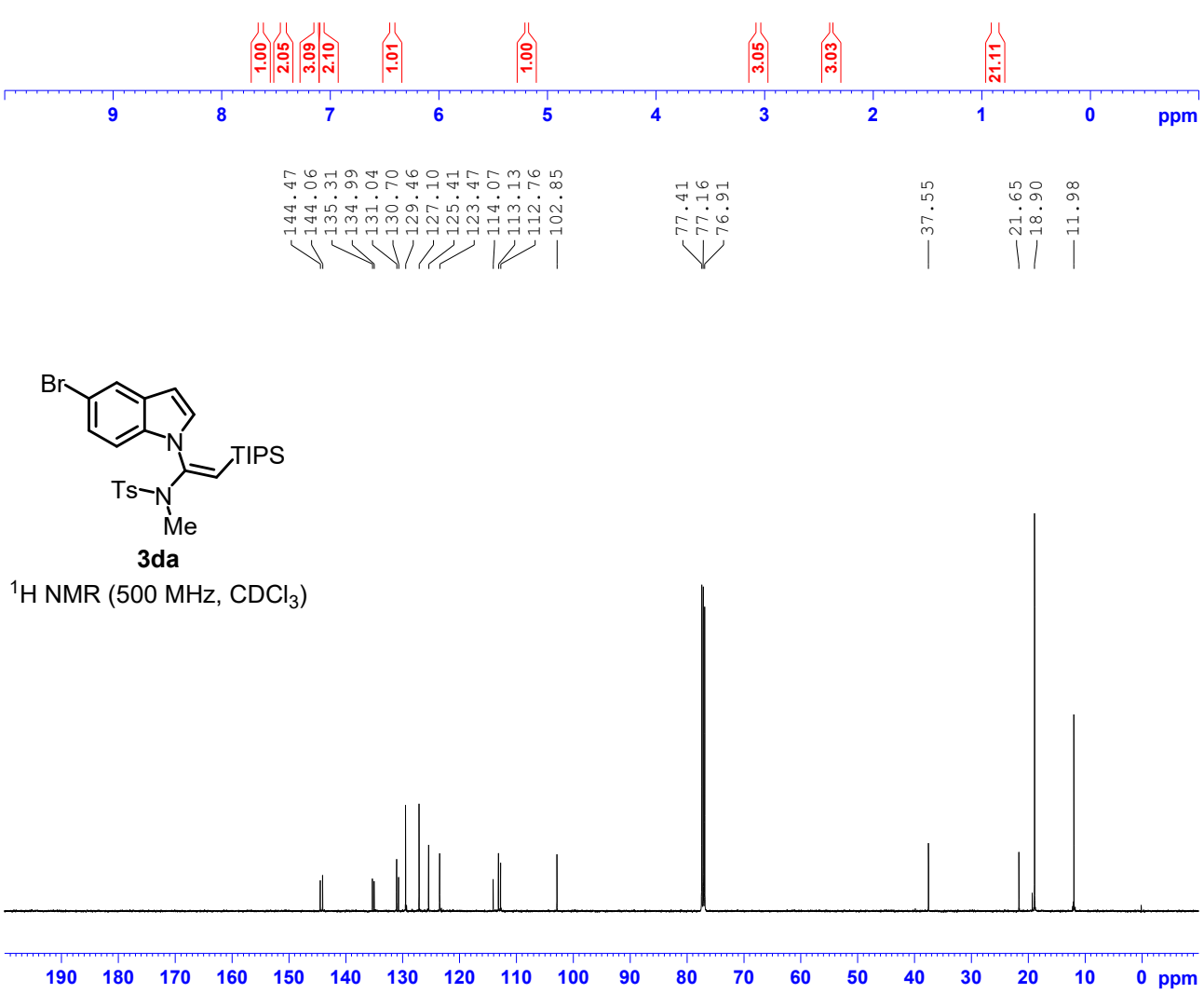
3ca

^{13}C NMR (125 MHz, $CDCl_3$)



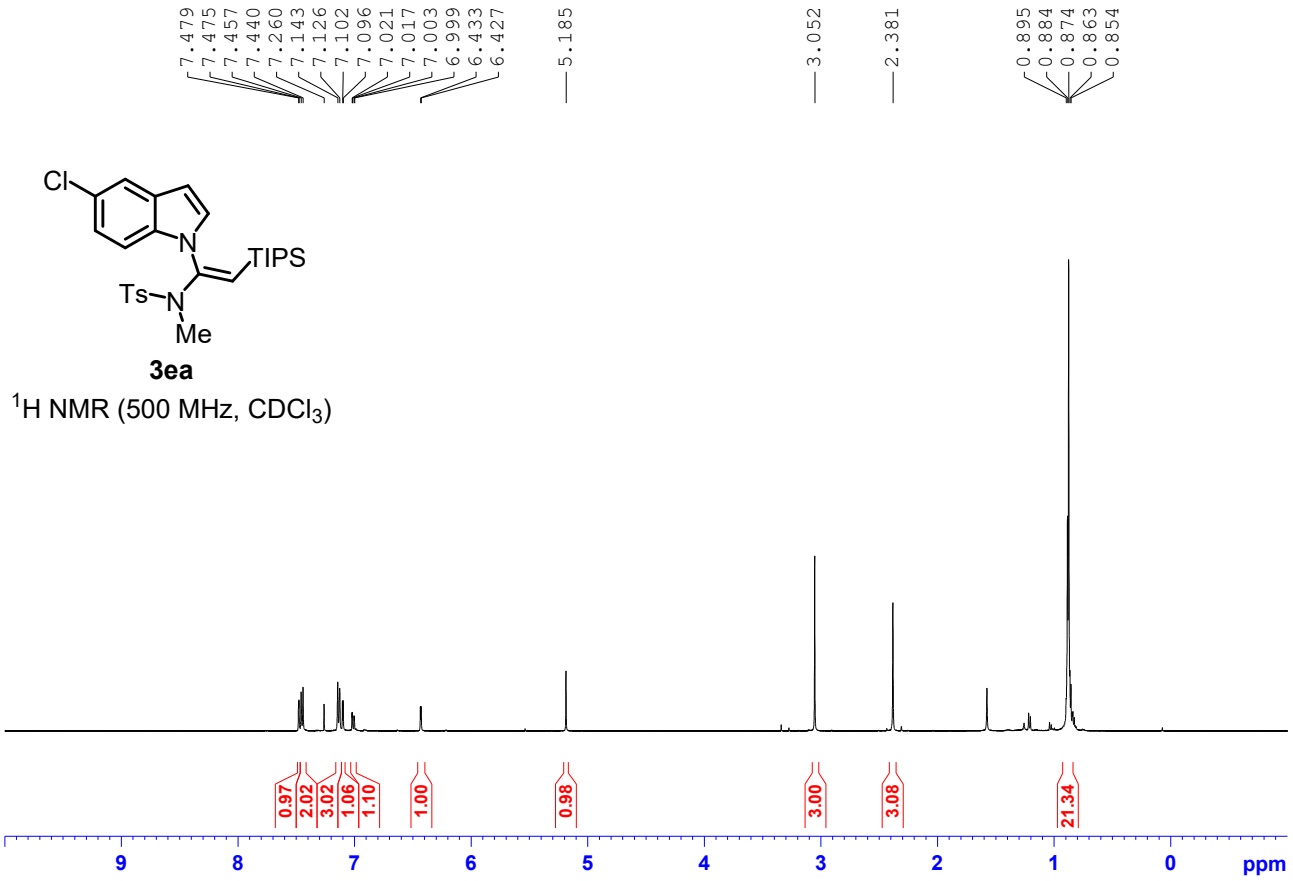
3da

^{13}C NMR (125 MHz, $CDCl_3$)



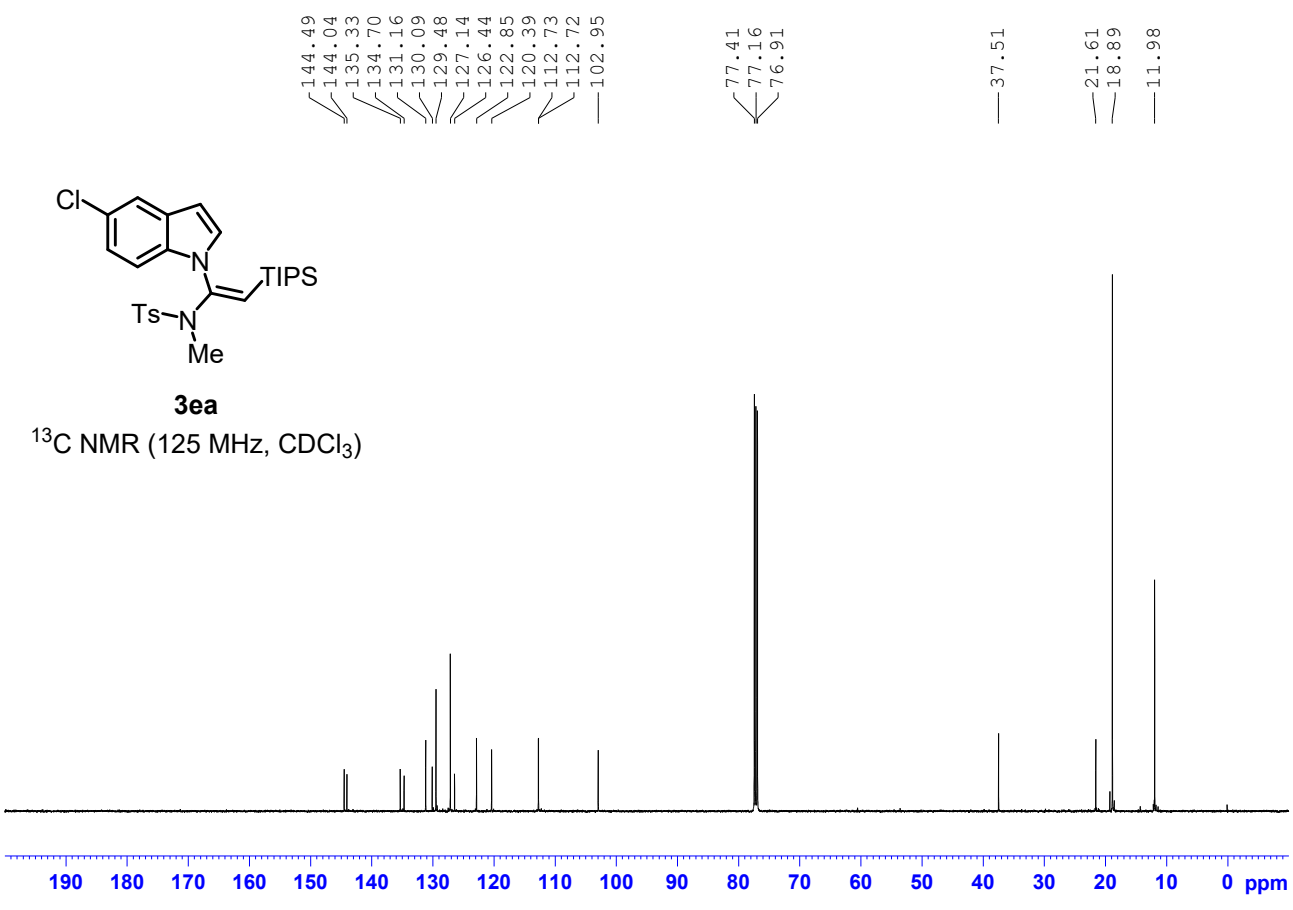
3da

^{1}H NMR (500 MHz, $CDCl_3$)



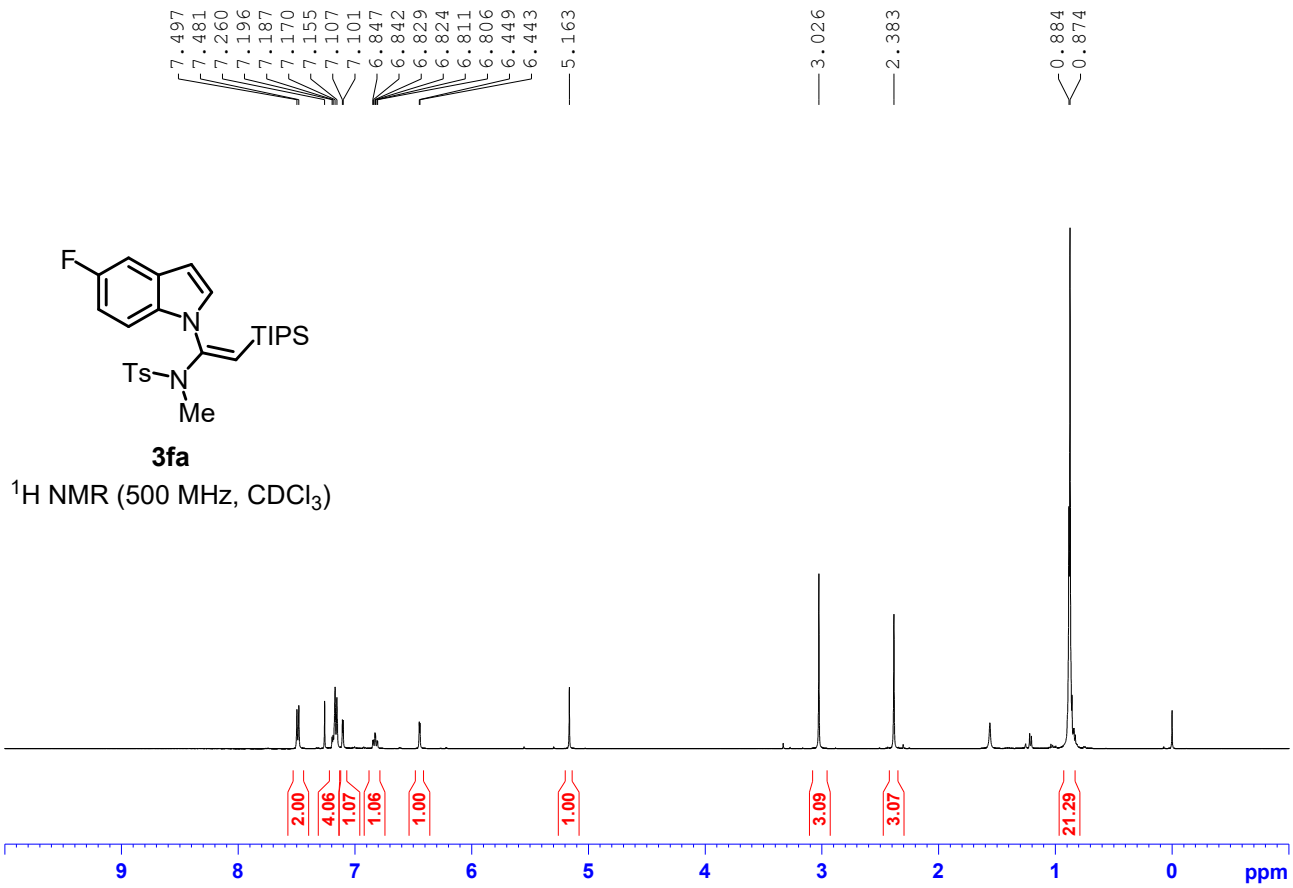
3ea

^{1}H NMR (500 MHz, $CDCl_3$)



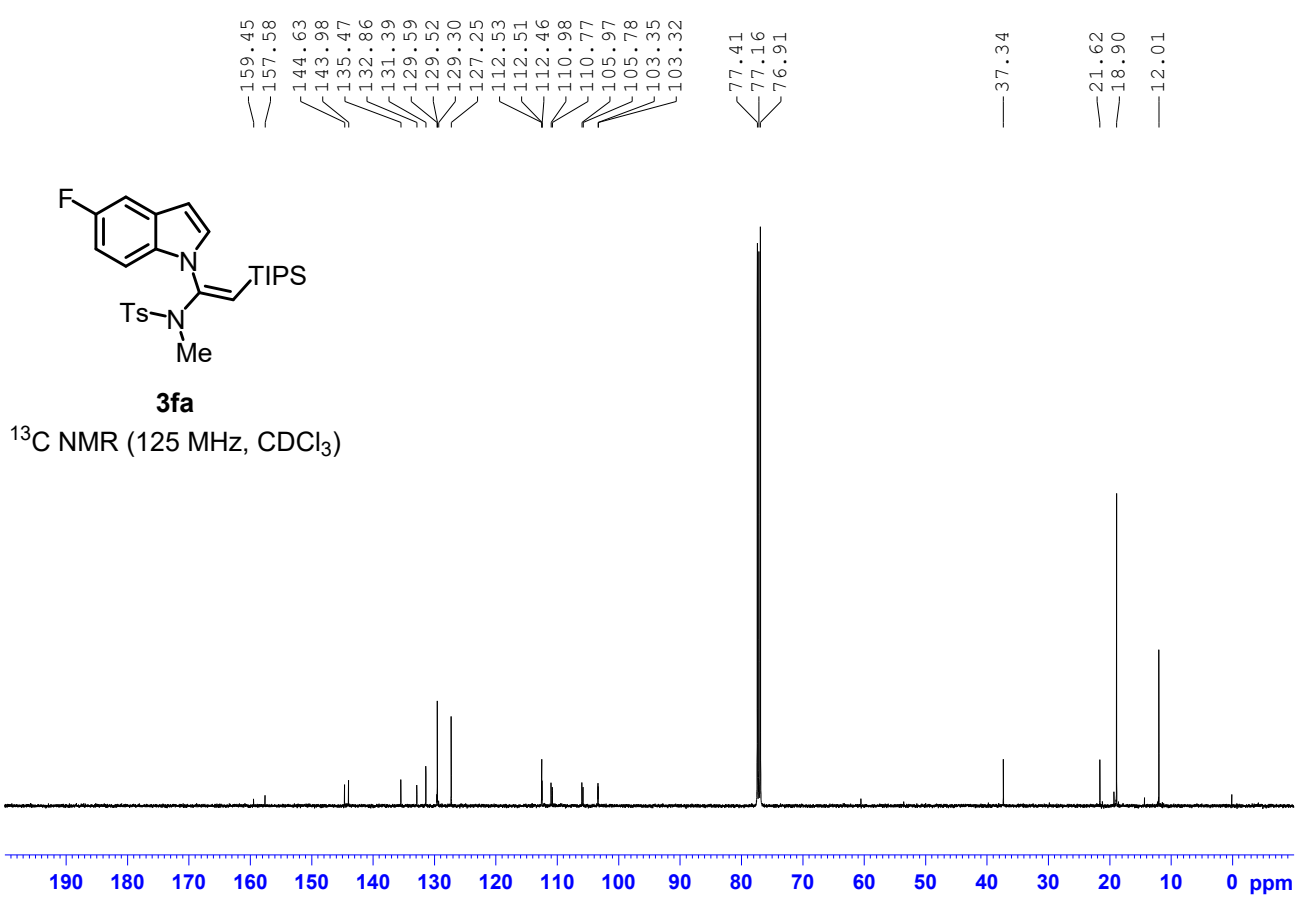
3ea

^{13}C NMR (125 MHz, $CDCl_3$)



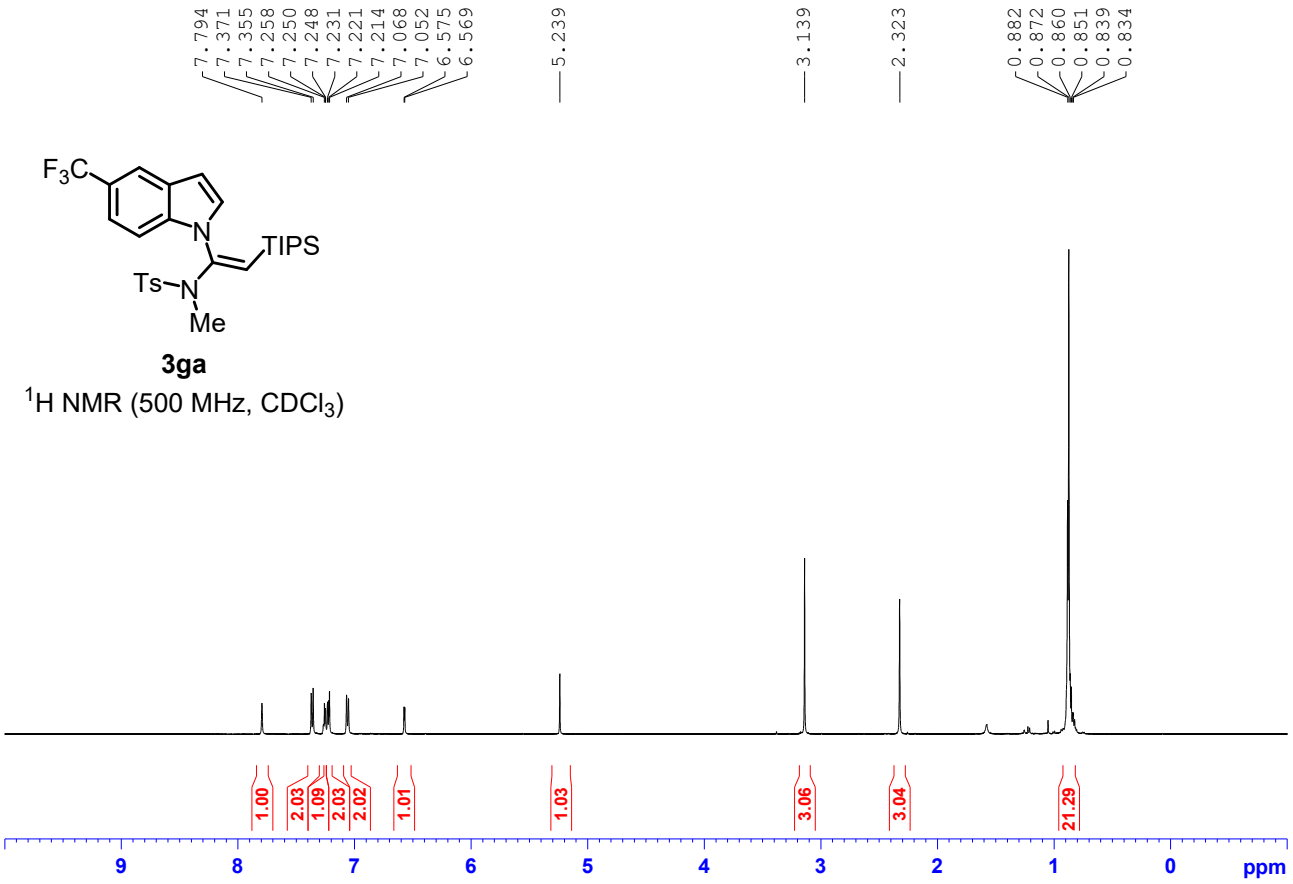
3fa

^{1}H NMR (500 MHz, $CDCl_3$)



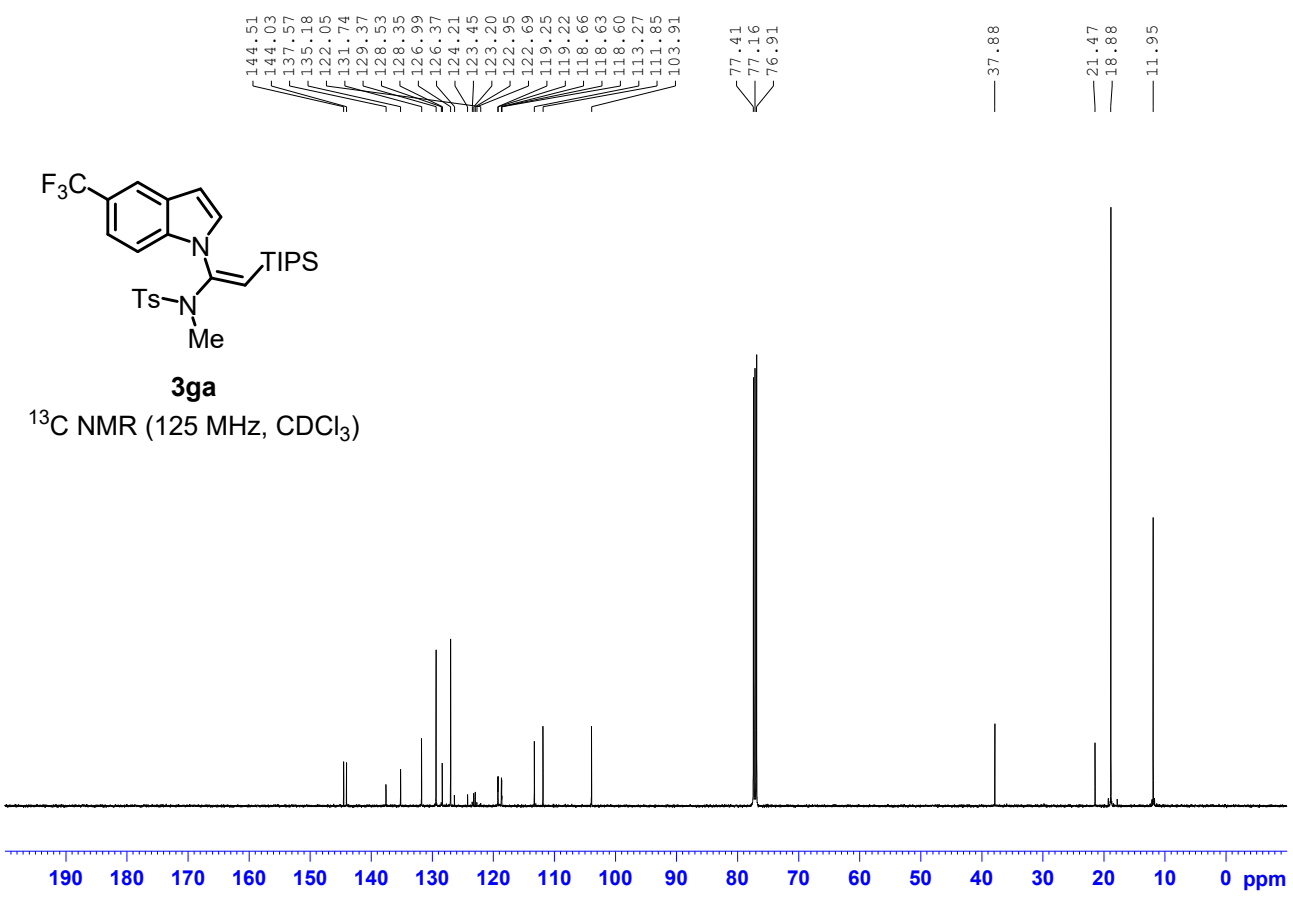
3fa

^{13}C NMR (125 MHz, $CDCl_3$)



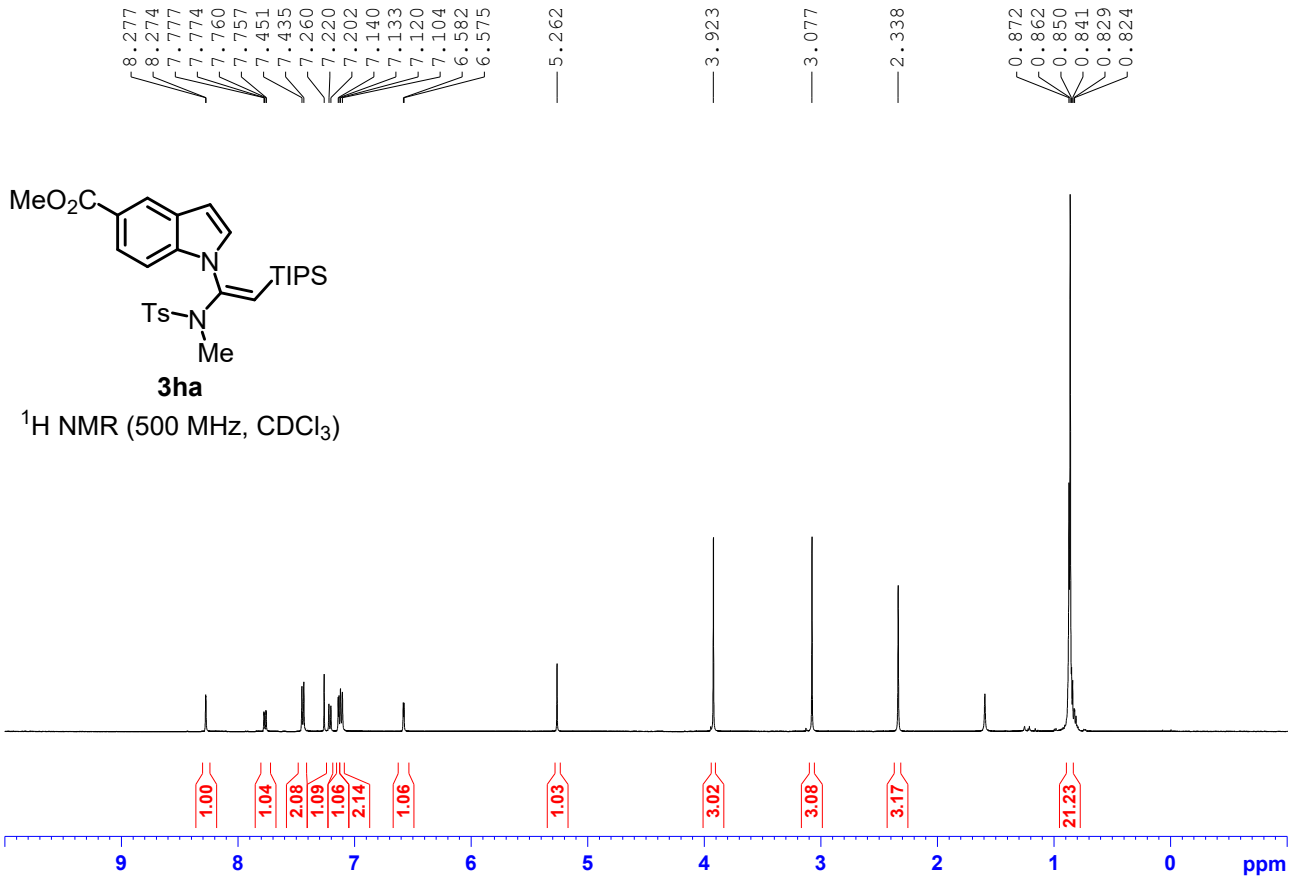
3ga

^{1}H NMR (500 MHz, $CDCl_3$)



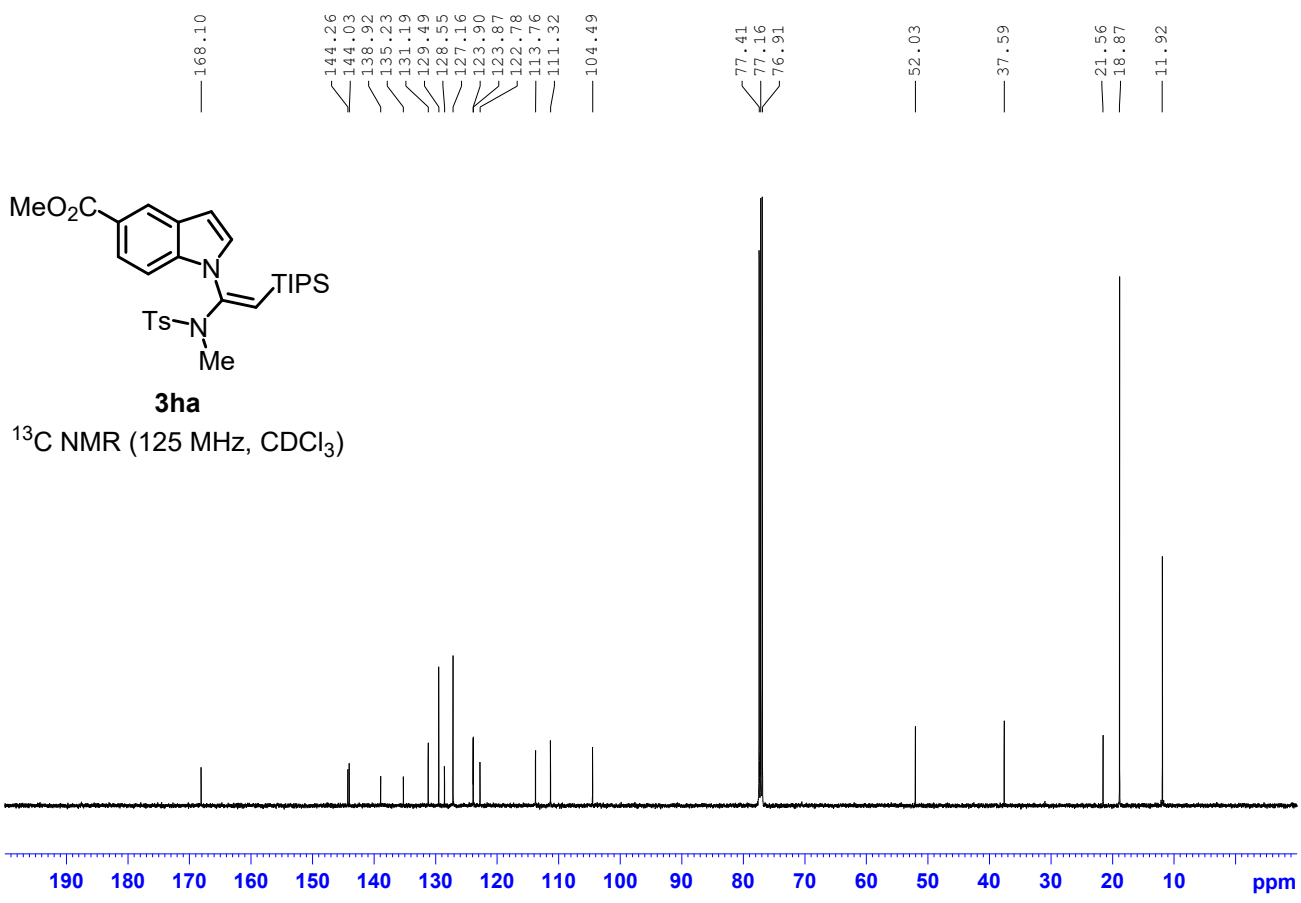
3ga

^{13}C NMR (125 MHz, $CDCl_3$)



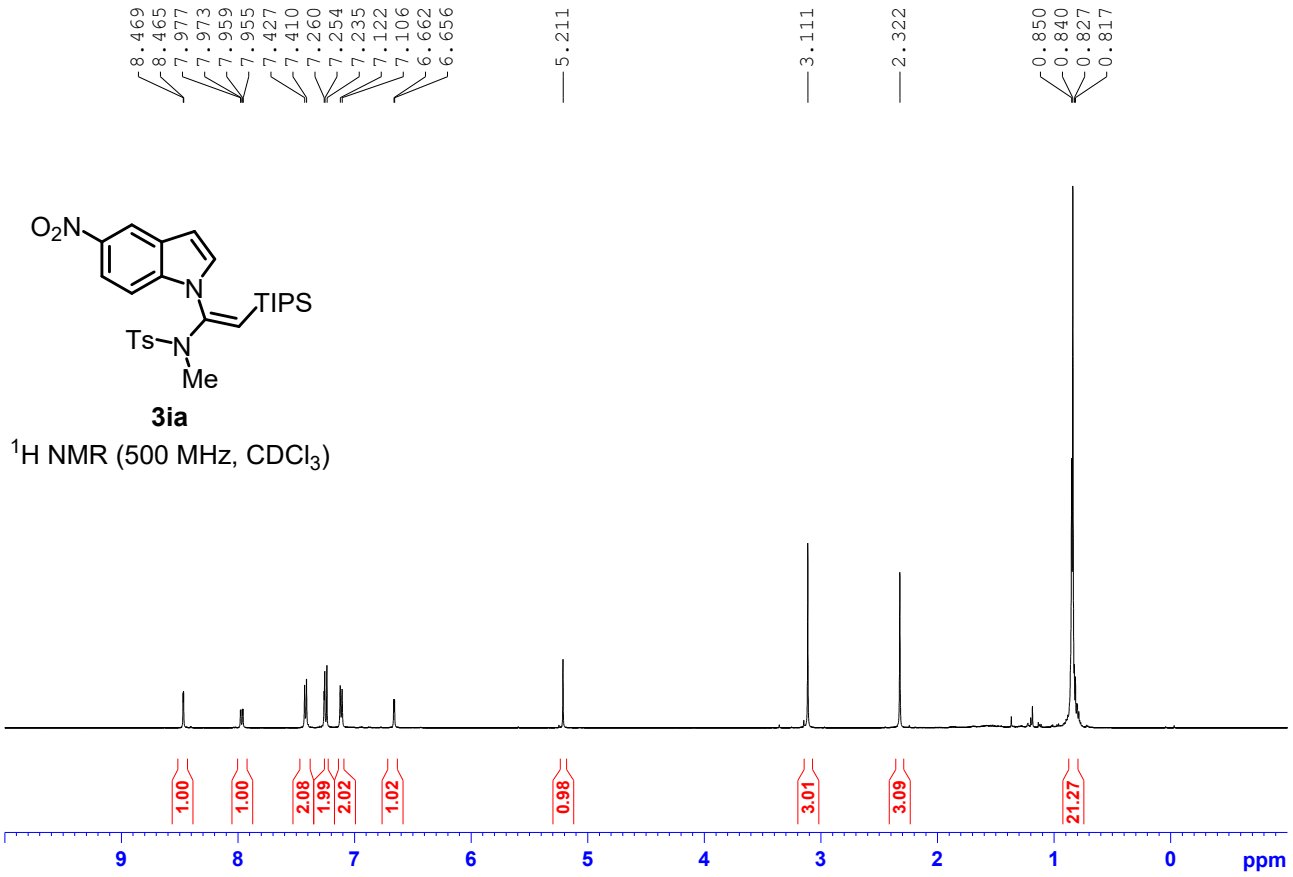
3ha

^{1}H NMR (500 MHz, $CDCl_3$)



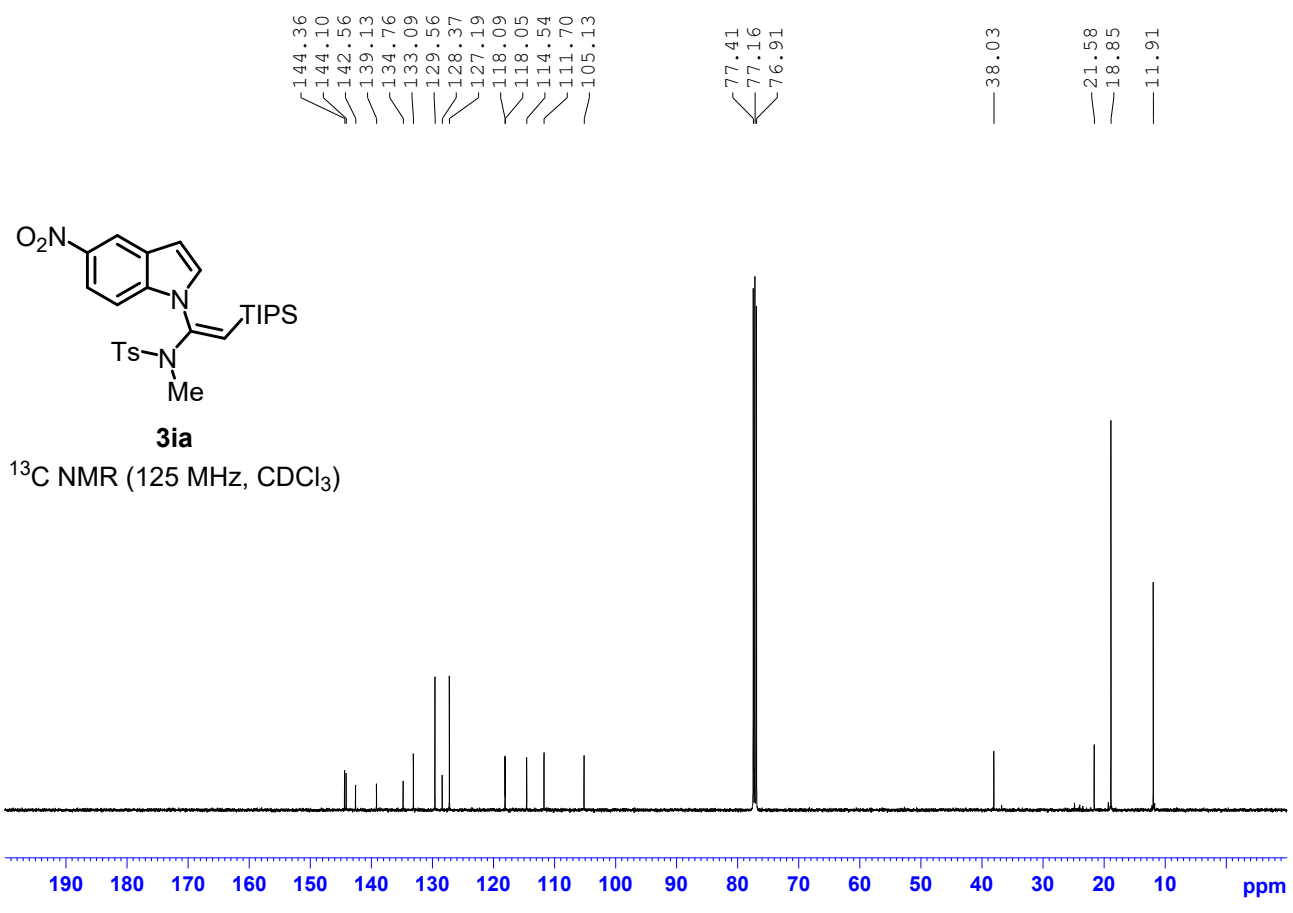
3ha

^{13}C NMR (125 MHz, $CDCl_3$)



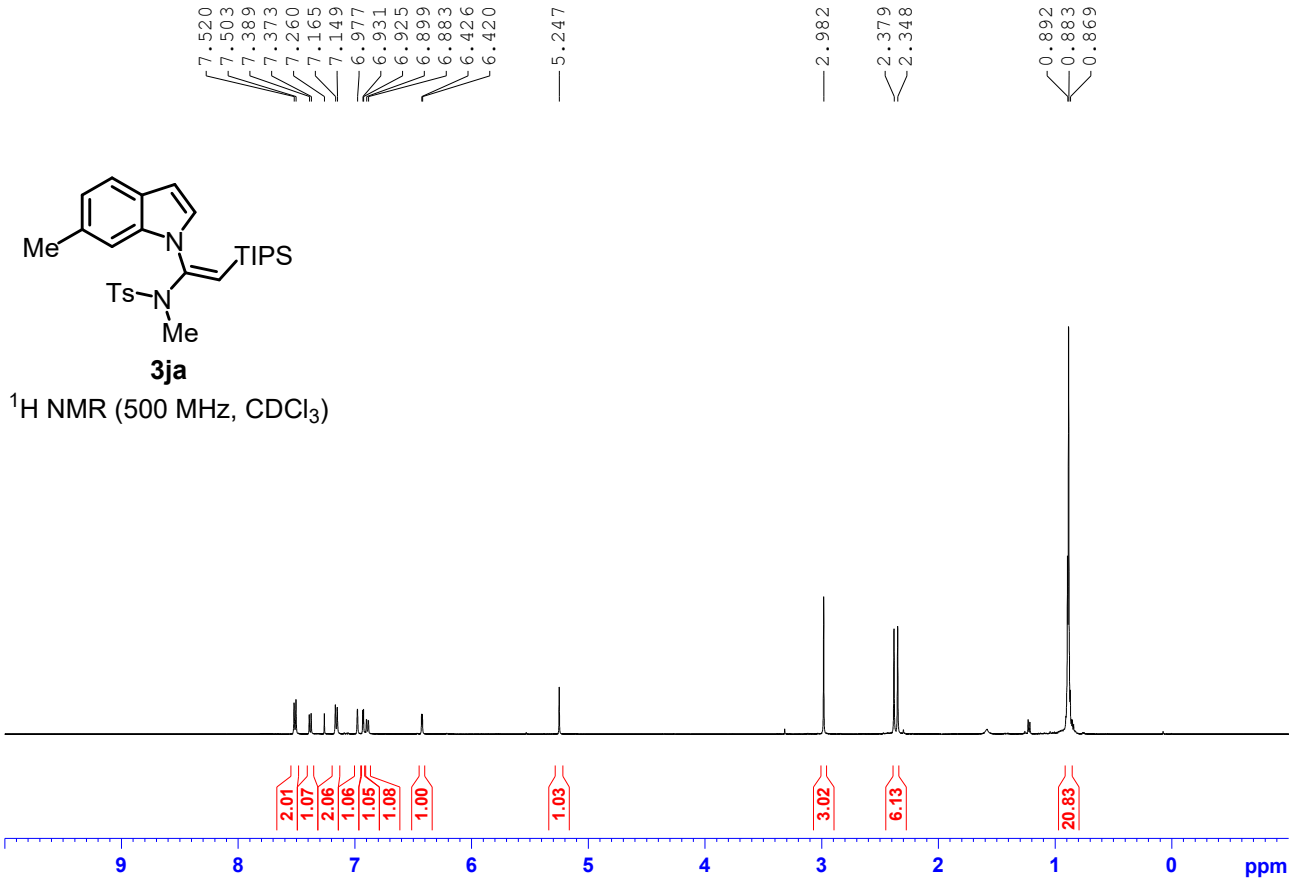
3ia

^{1}H NMR (500 MHz, $CDCl_3$)



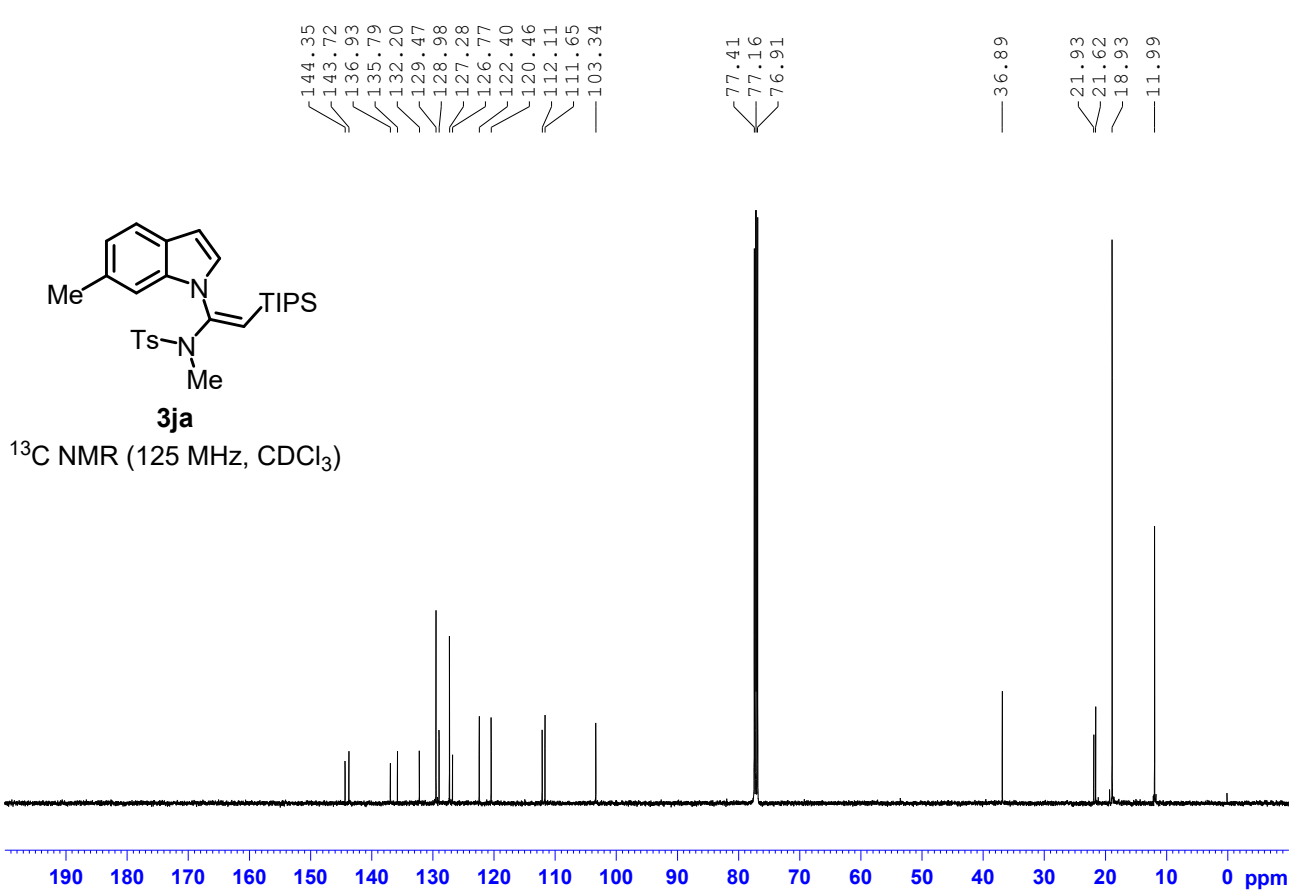
3ia

^{13}C NMR (125 MHz, $CDCl_3$)



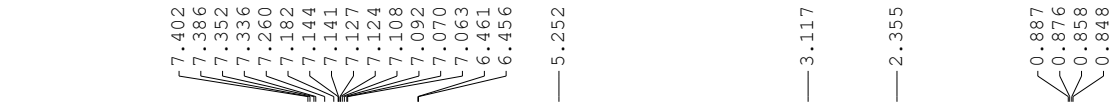
3ja

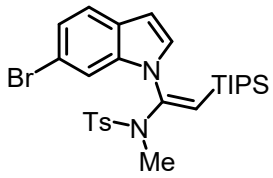
^{1}H NMR (500 MHz, $CDCl_3$)



3ja

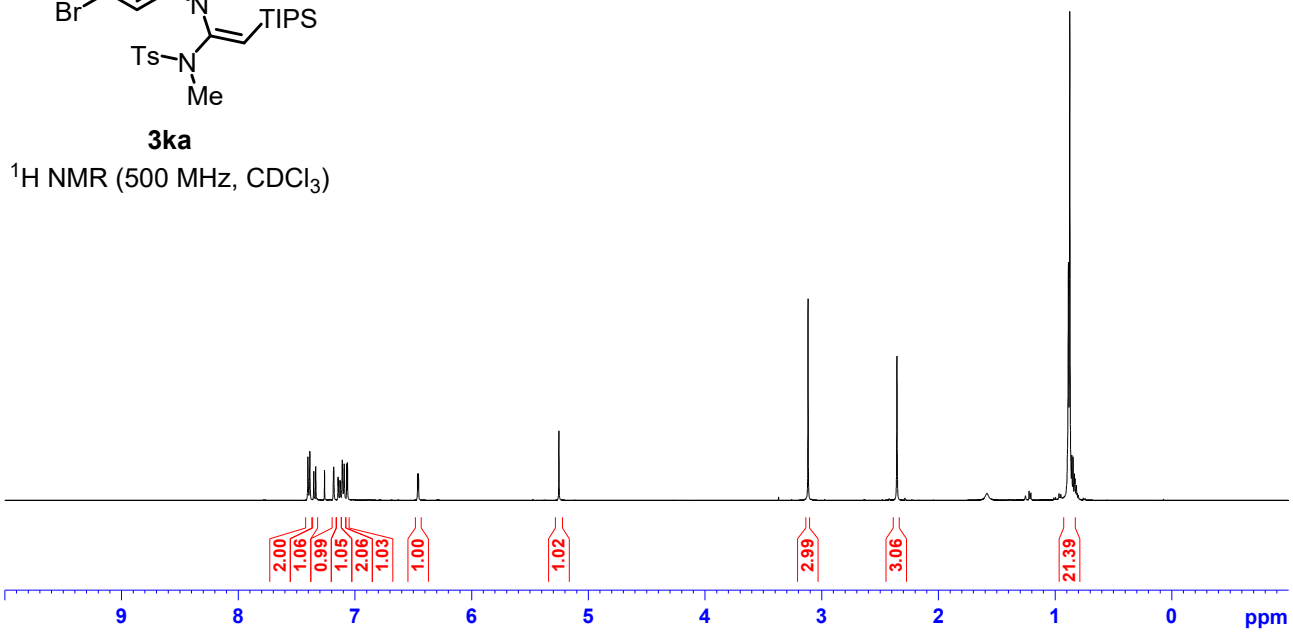
^{13}C NMR (125 MHz, $CDCl_3$)

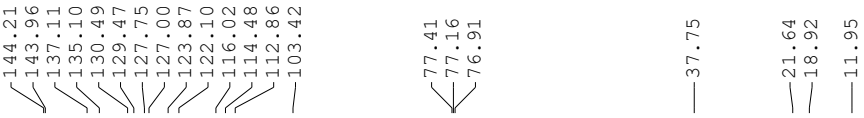


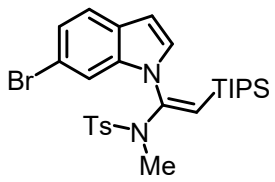


3ka

^{1}H NMR (500 MHz, $CDCl_3$)

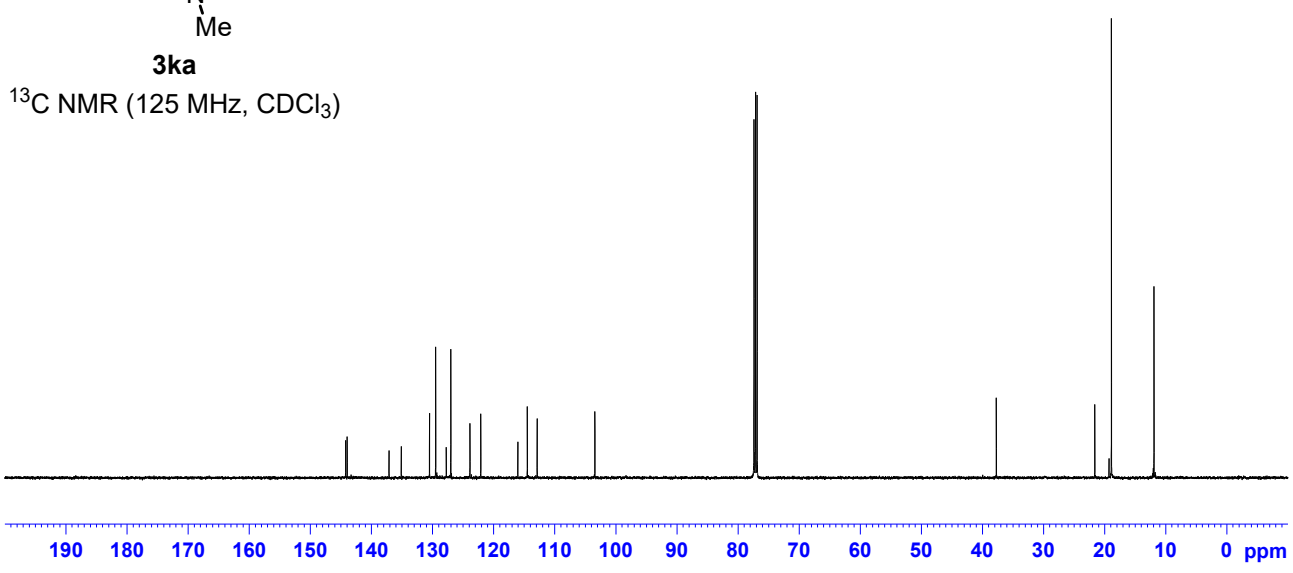


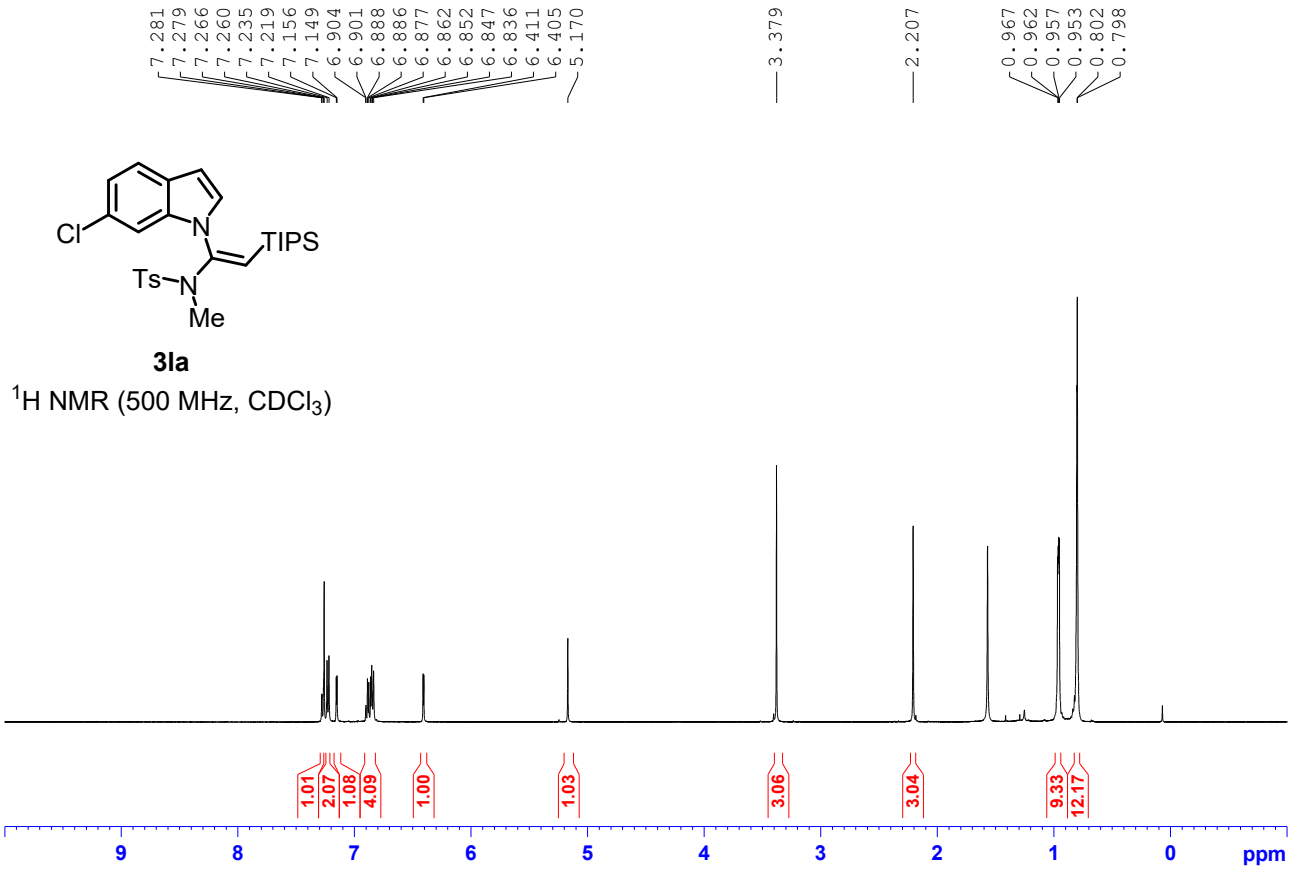




3ka

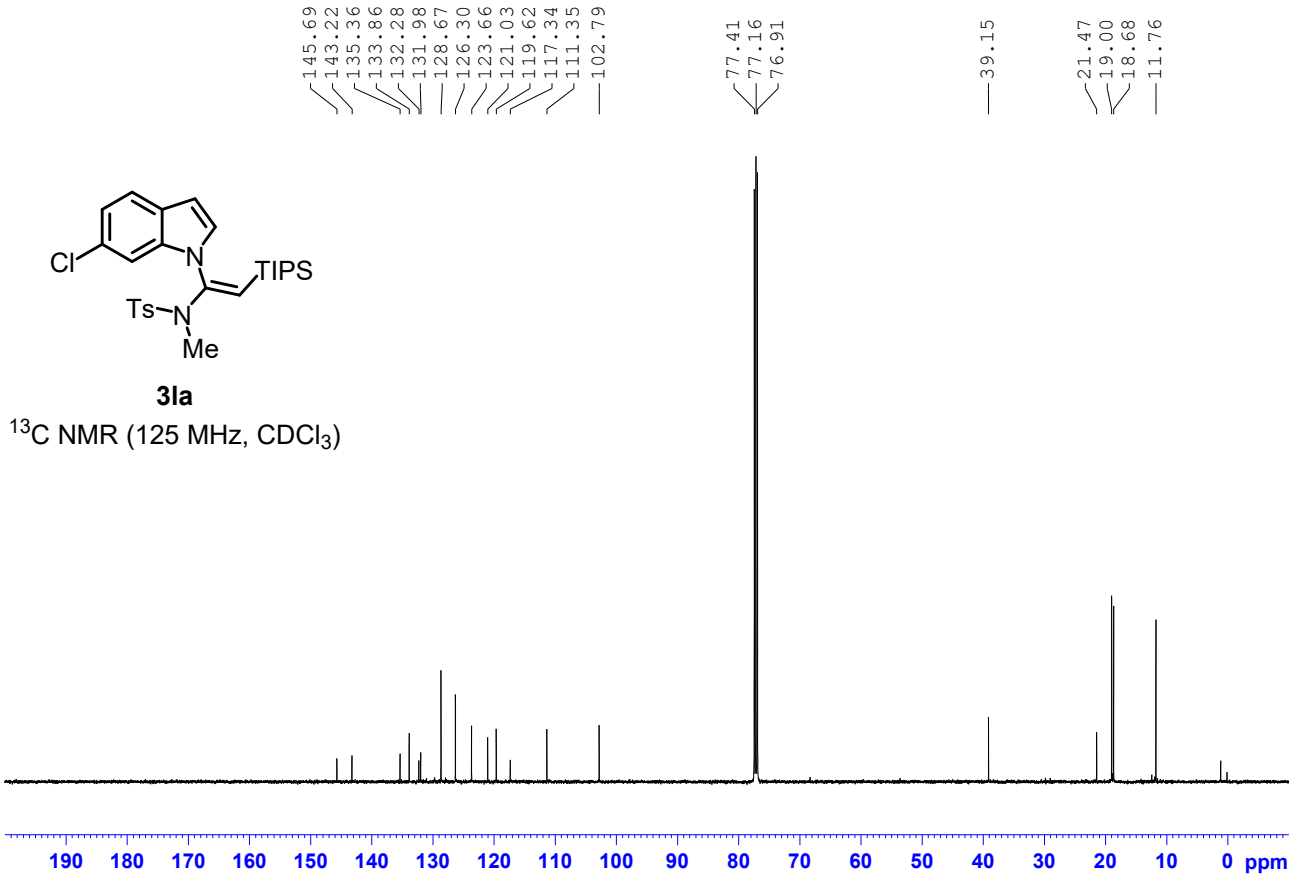
^{13}C NMR (125 MHz, $CDCl_3$)





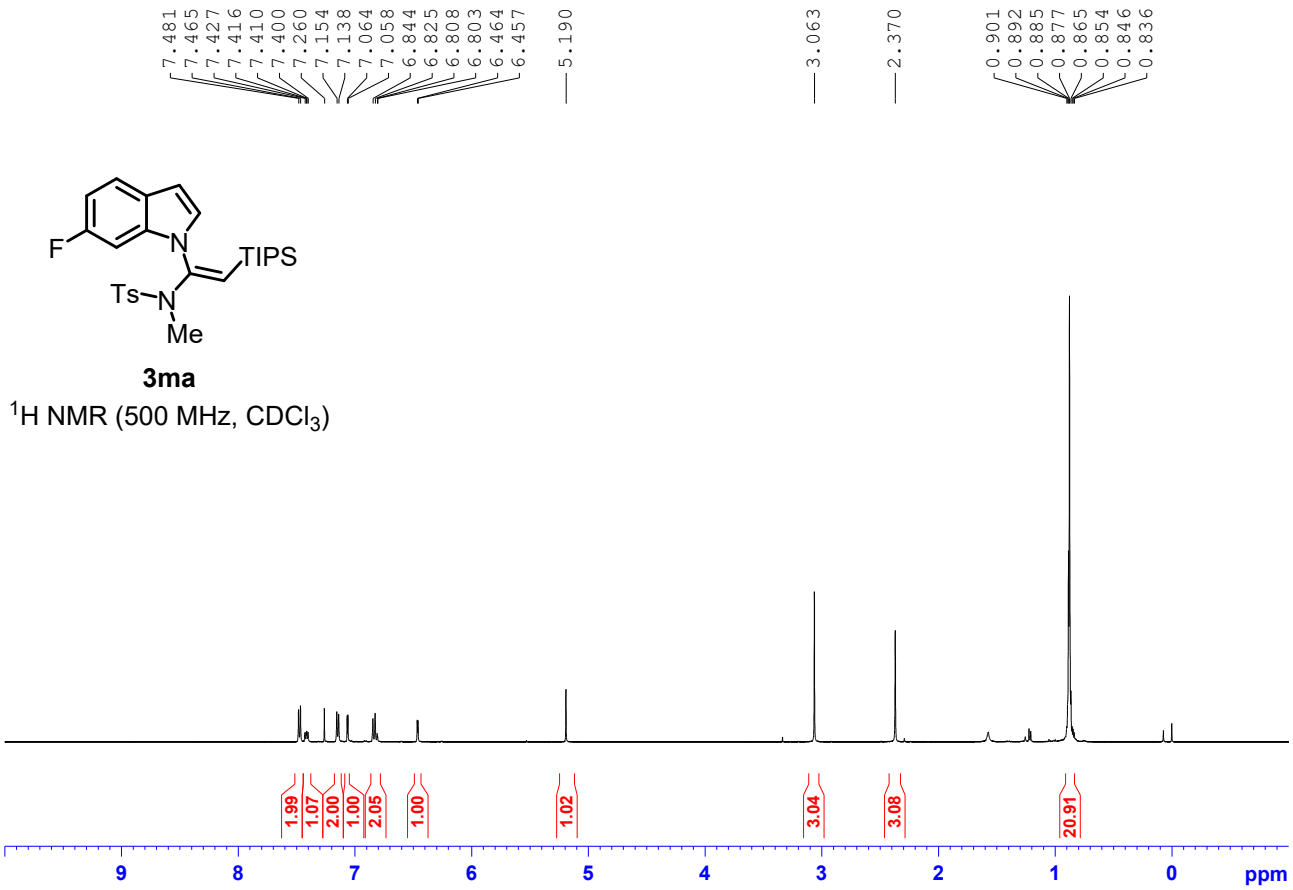
3la

^{1}H NMR (500 MHz, $CDCl_3$)



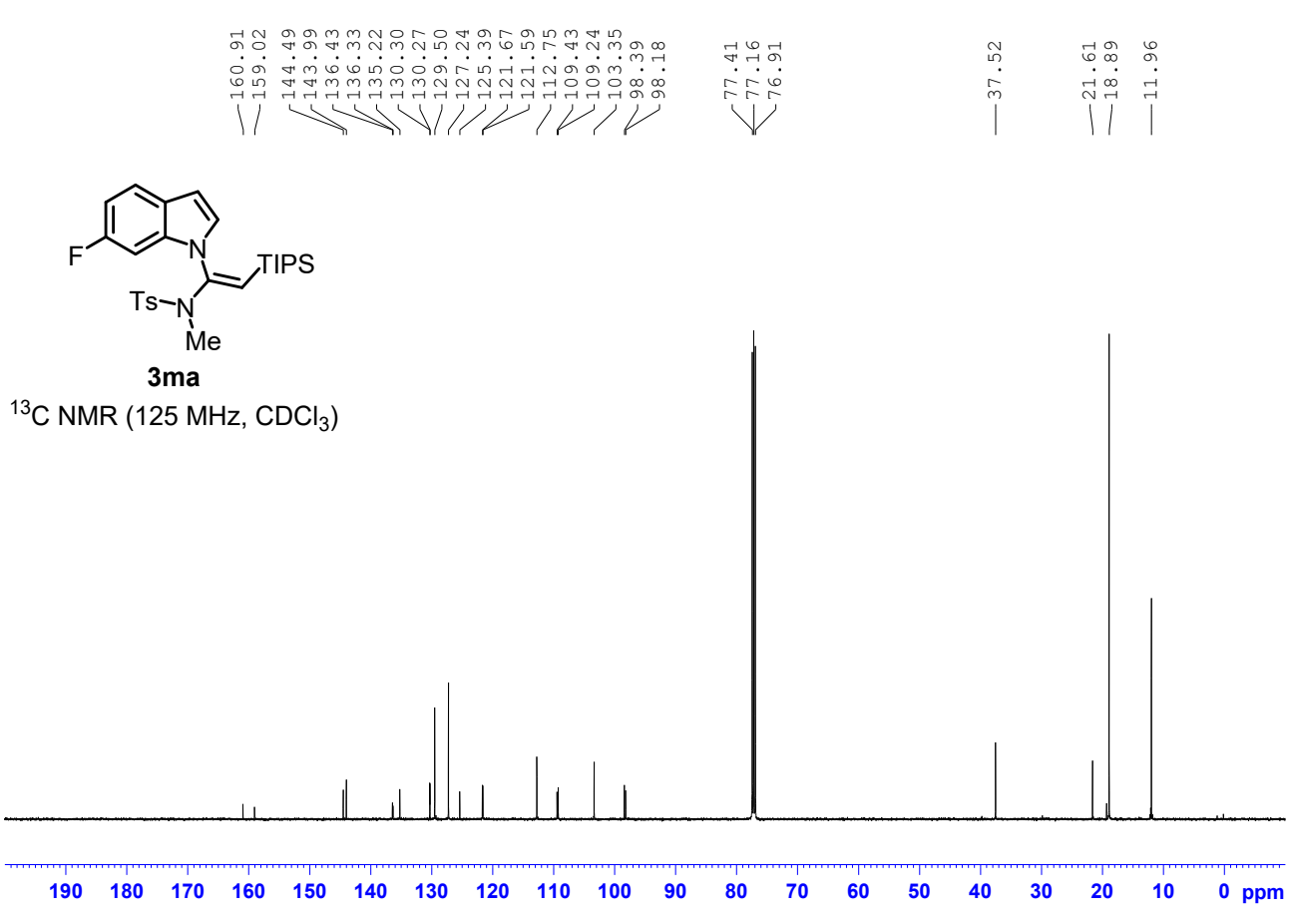
3la

^{13}C NMR (125 MHz, $CDCl_3$)



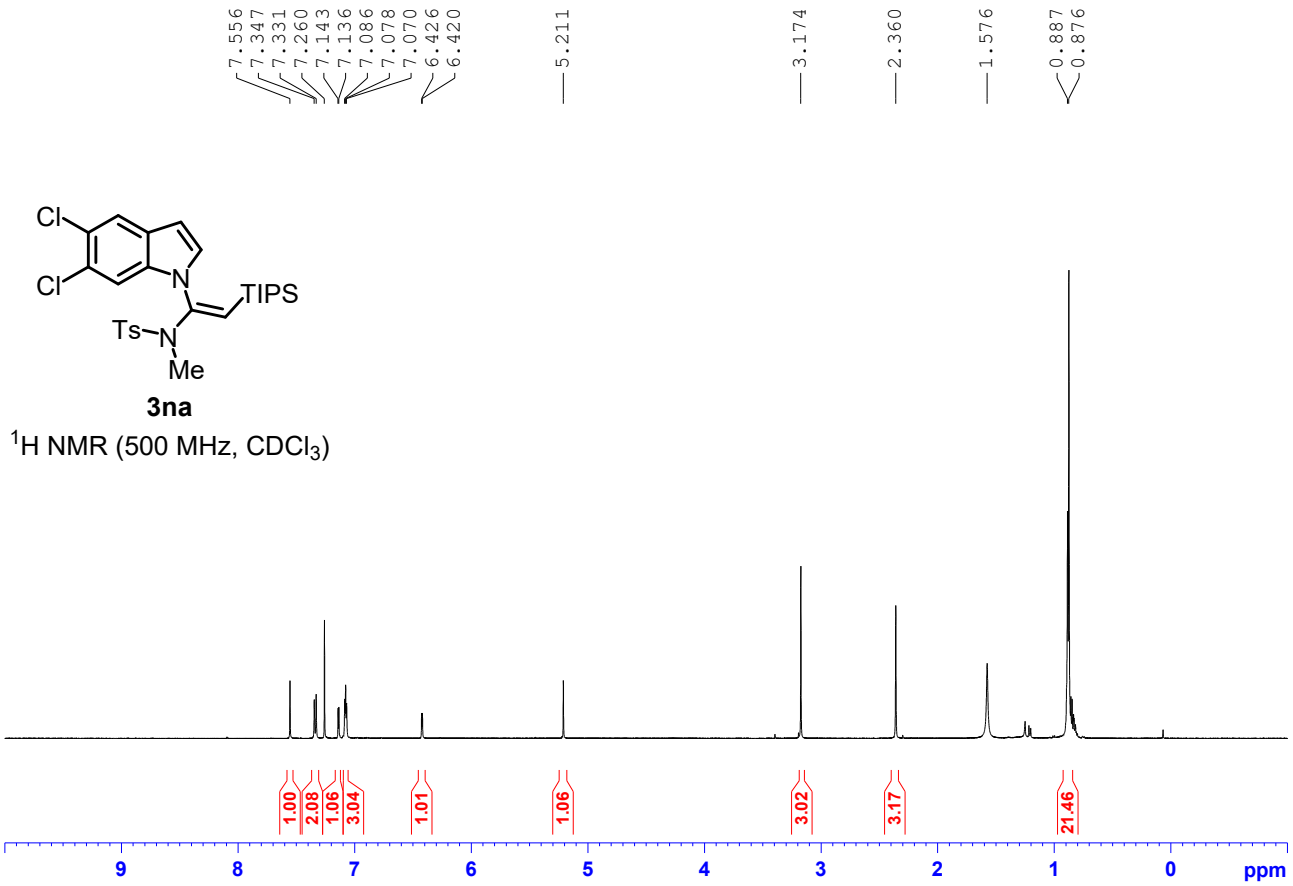
3ma

^{1}H NMR (500 MHz, $CDCl_3$)



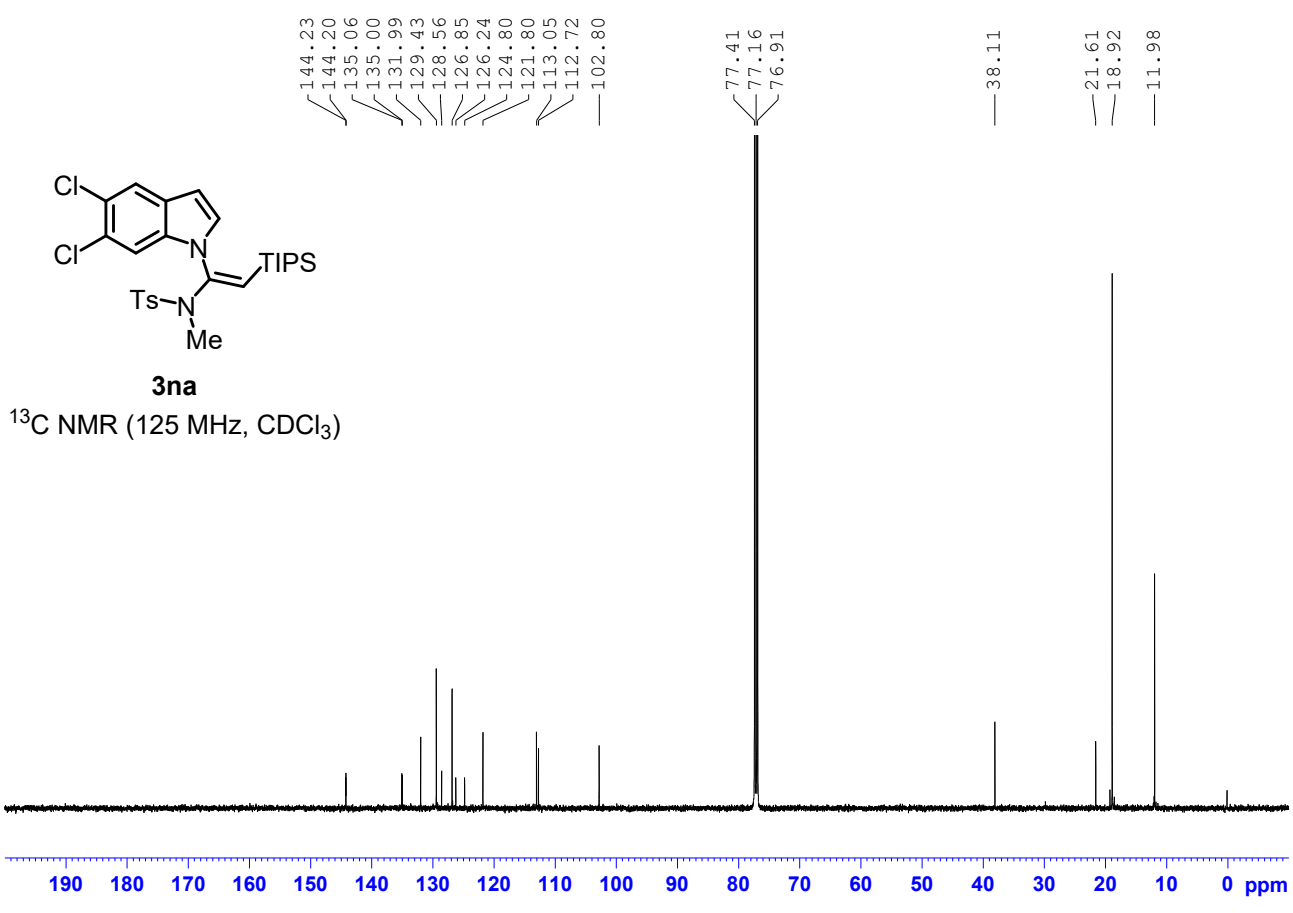
3ma

^{13}C NMR (125 MHz, $CDCl_3$)



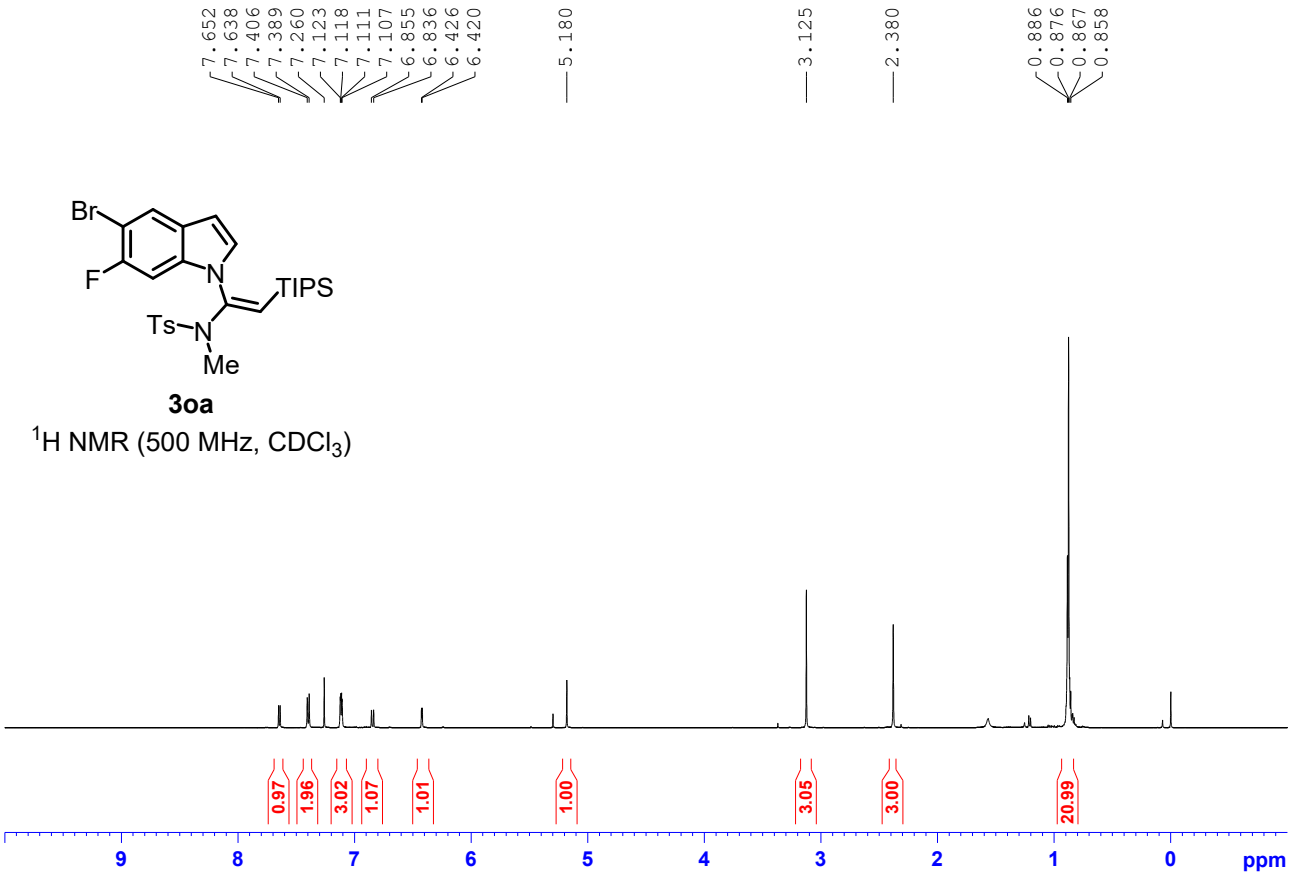
3na

^{1}H NMR (500 MHz, $CDCl_3$)



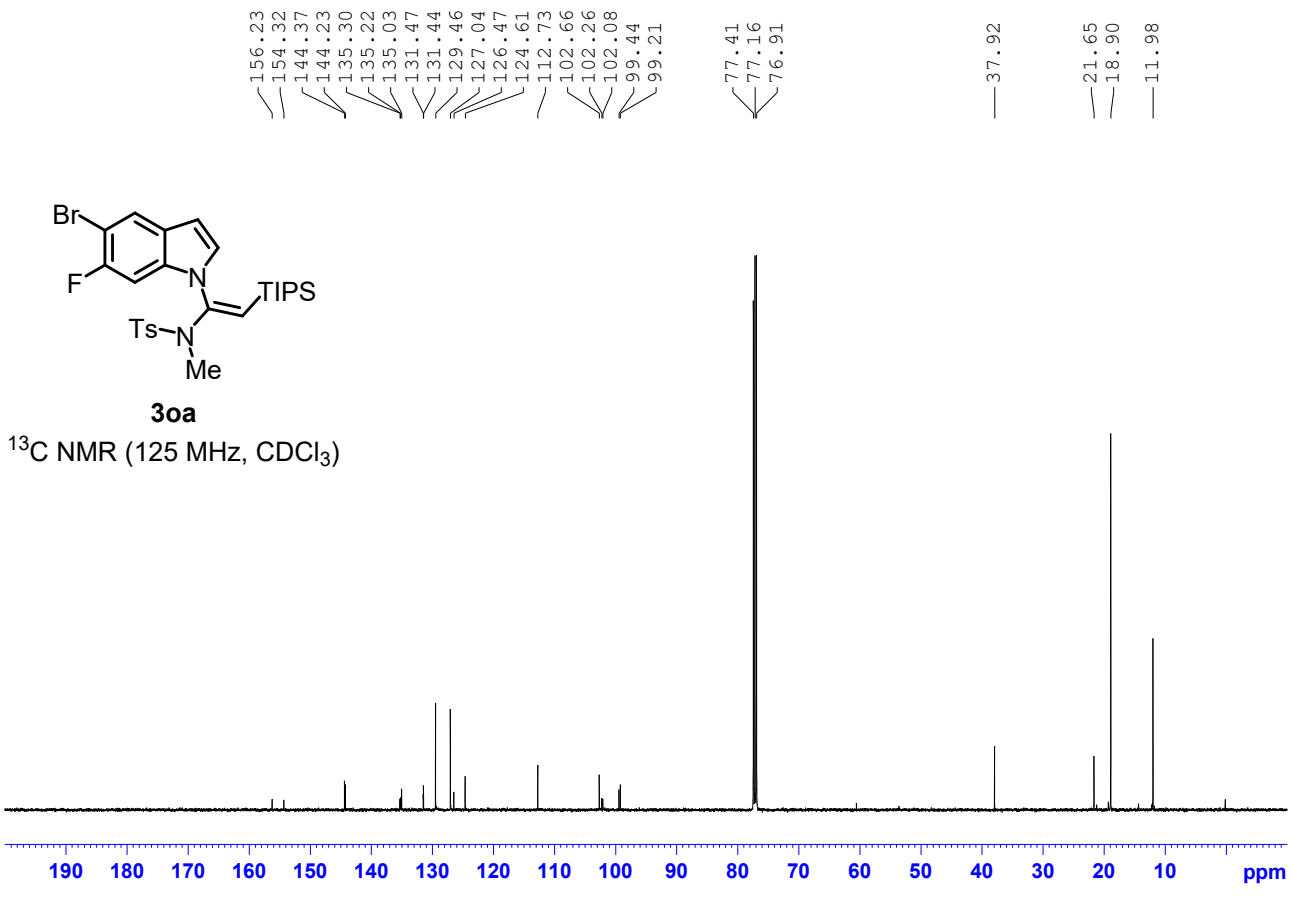
3na

^{13}C NMR (125 MHz, $CDCl_3$)



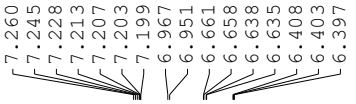
3oa

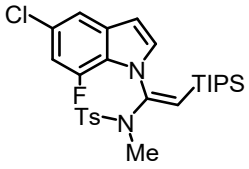
^{1}H NMR (500 MHz, $CDCl_3$)



3oa

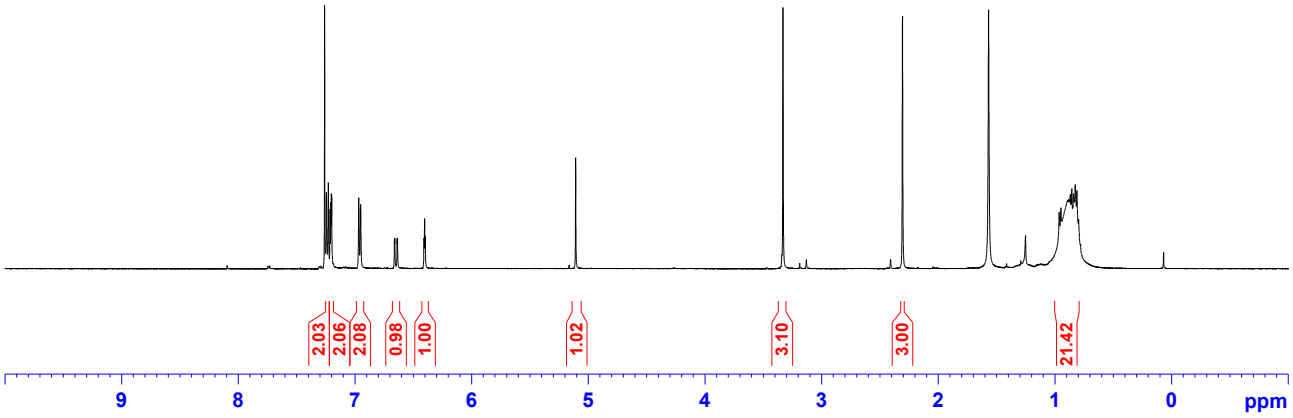
^{13}C NMR (125 MHz, $CDCl_3$)

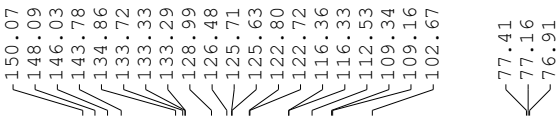


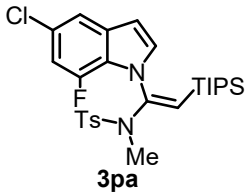


3pa

^{1}H NMR (500 MHz, $CDCl_3$)

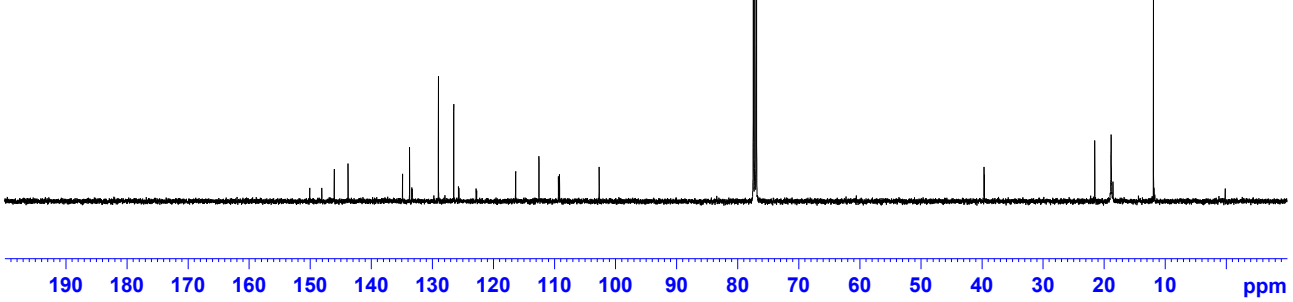


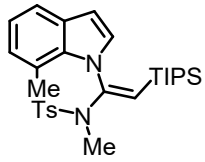




3pa

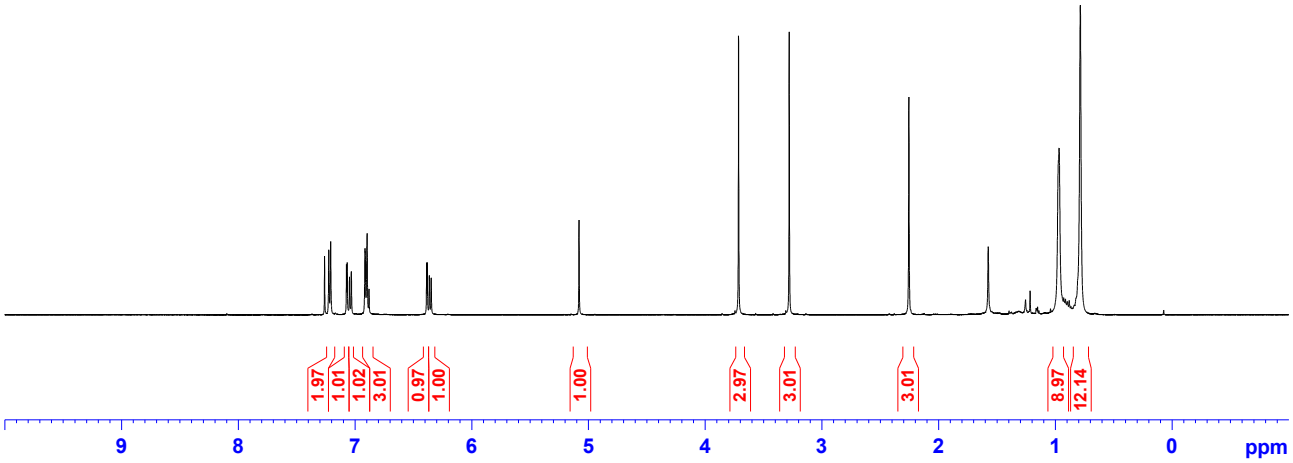
^{13}C NMR (125 MHz, $CDCl_3$)

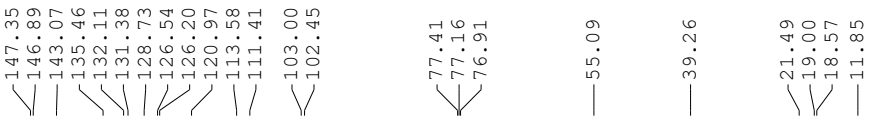


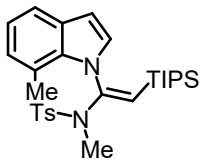


3qa

^{1}H NMR (500 MHz, $CDCl_3$)

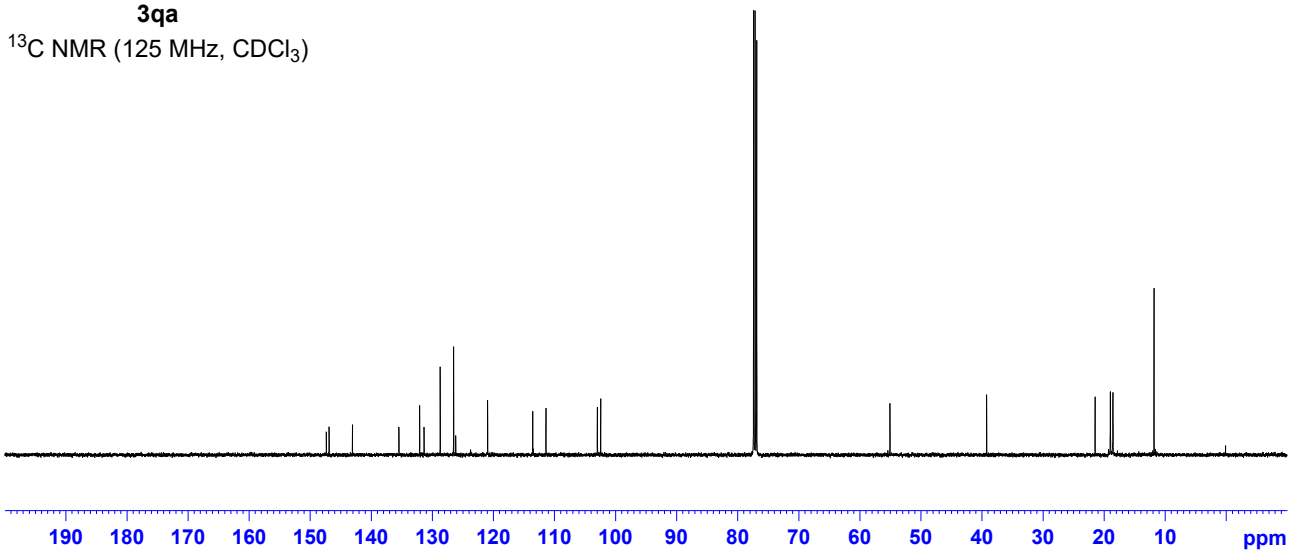


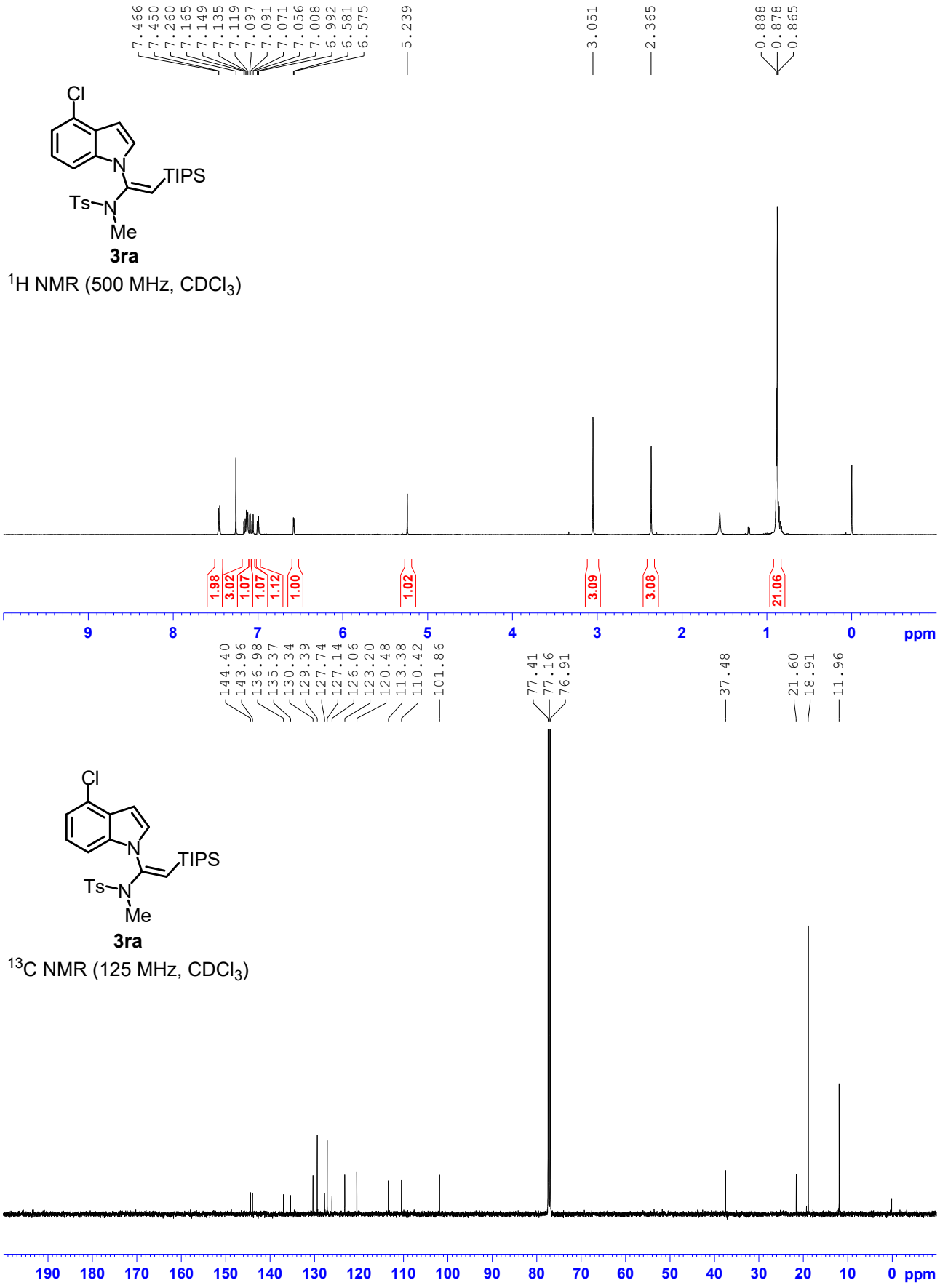




3qa

^{13}C NMR (125 MHz, $CDCl_3$)

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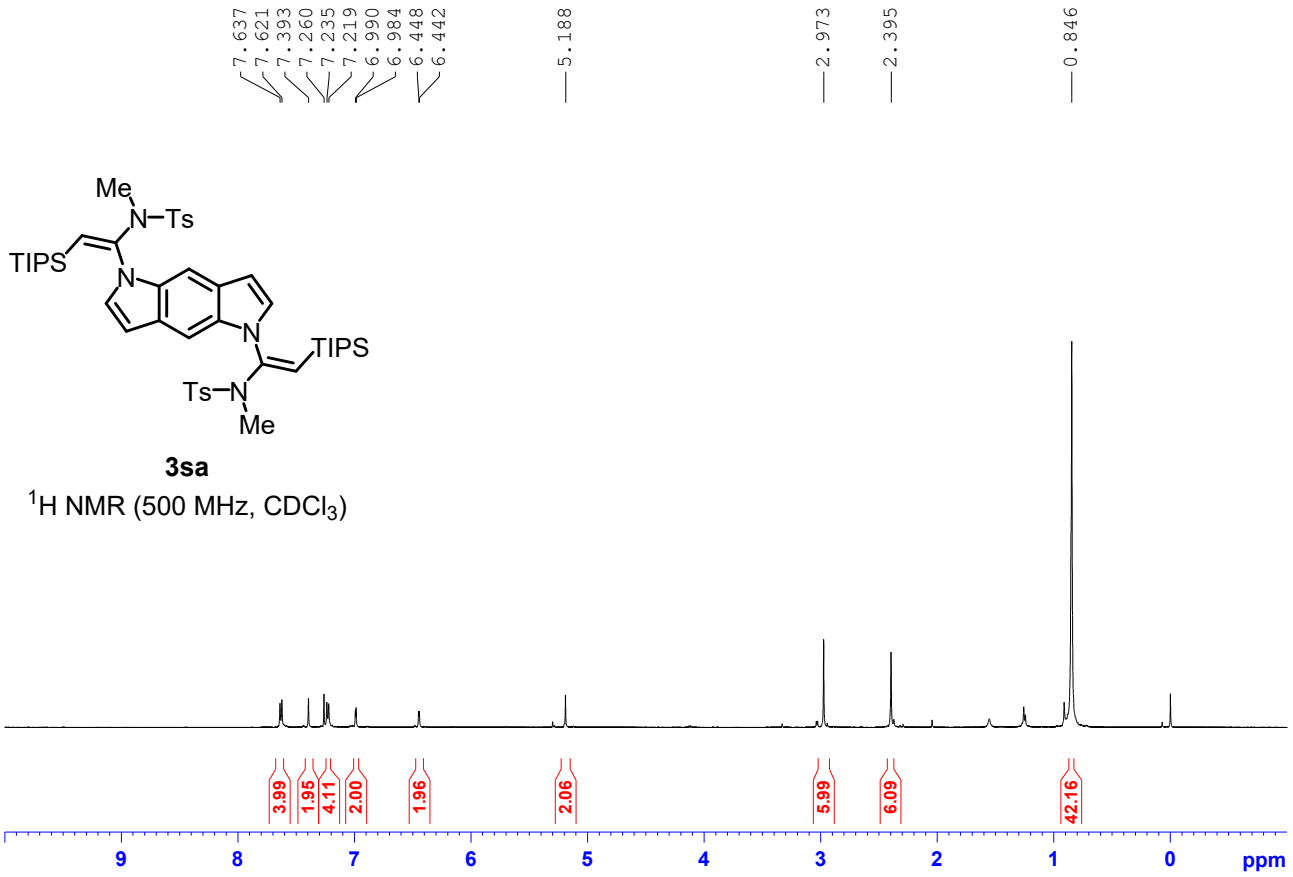
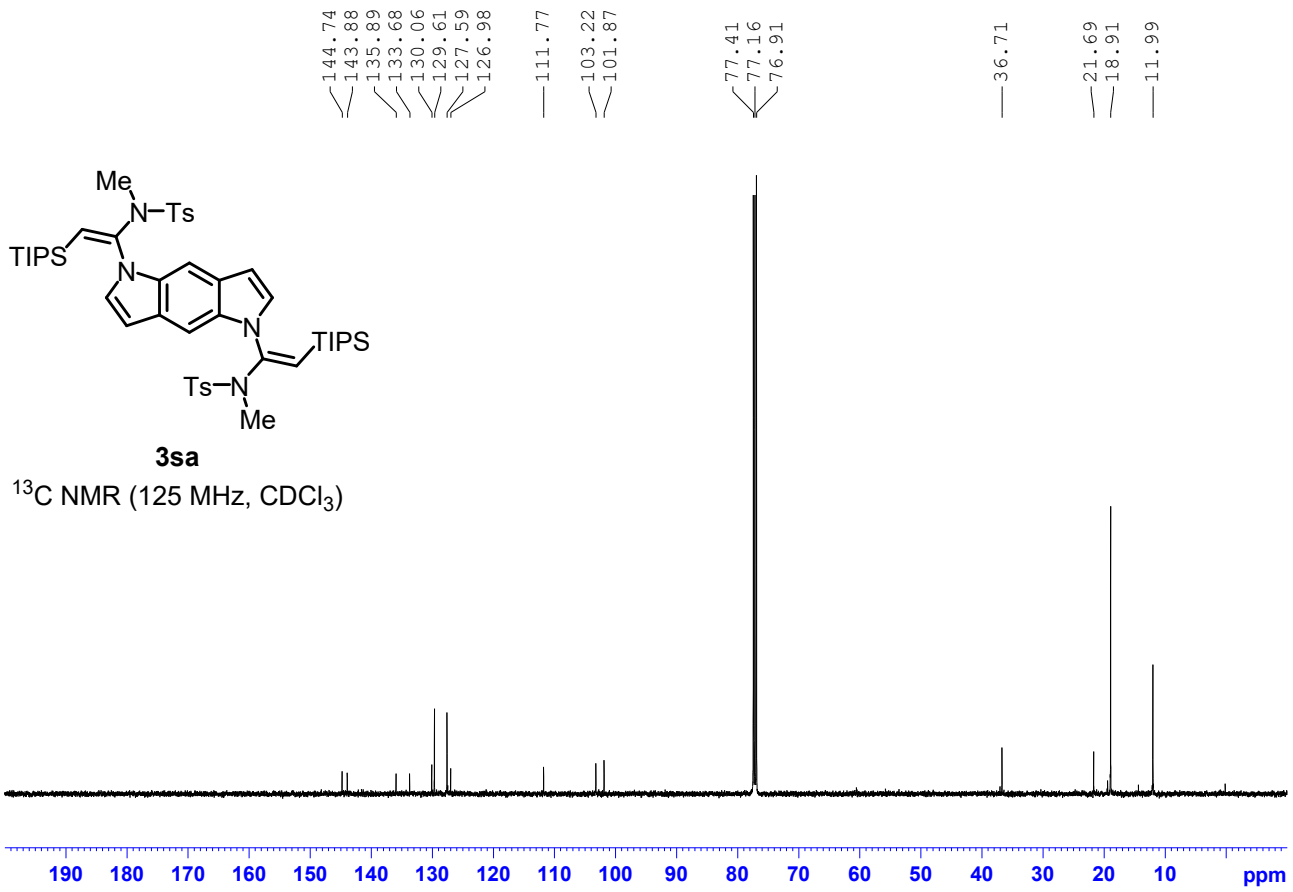
7.450
7.260
7.165
7.149
7.135
7.119
7.097
7.091
7.071
7.056
7.008
6.992
6.581
6.575
5.239
3.051
2.365
0.888
0.878
0.865
Cl
N
TIPS
Ts
N
Me
3ra
1H NMR (500 MHz, CDCl3)
1.98
3.02
1.07
1.07
1.12
1.00
1.02
3.09
3.08
21.06
9
8
7
6
5
4
3
2
1
0
ppm
144.40
143.96
136.98
135.37
130.34
129.39
127.74
127.14
126.06
123.20
120.48
113.38
110.42
101.86
77.41
77.16
76.91
37.48
21.60
18.91
11.96
Cl
N
TIPS
Ts
N
Me
3ra
13C NMR (125 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



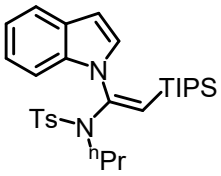
3sa

^{1}H NMR (500 MHz, $CDCl_3$)



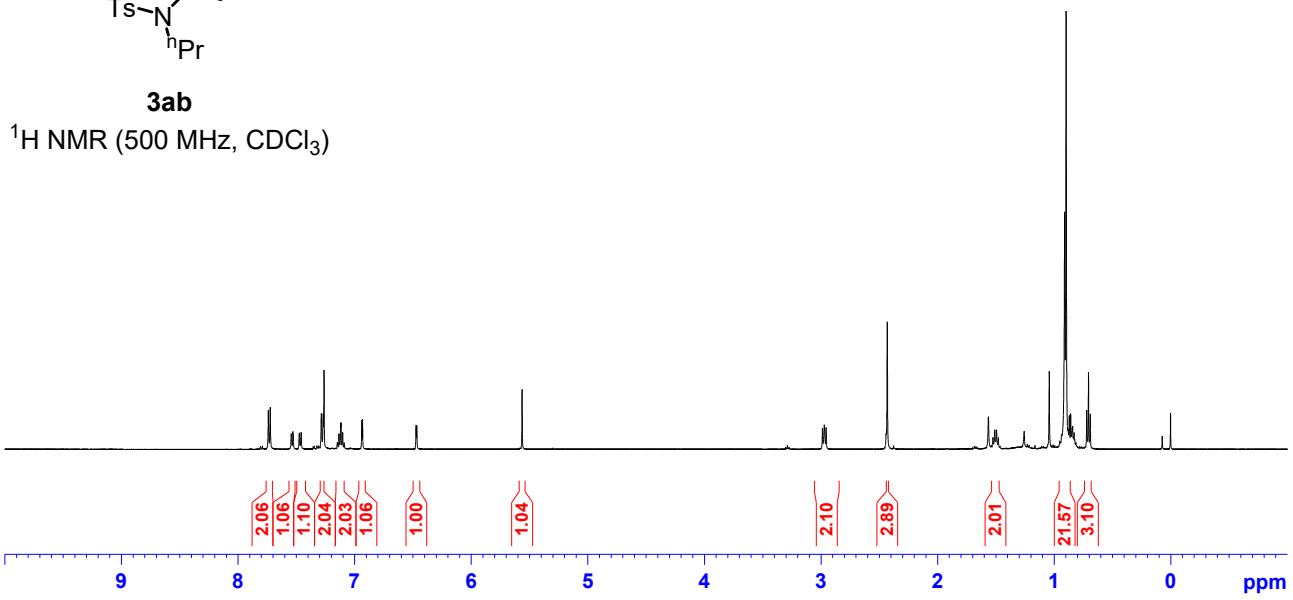
3sa

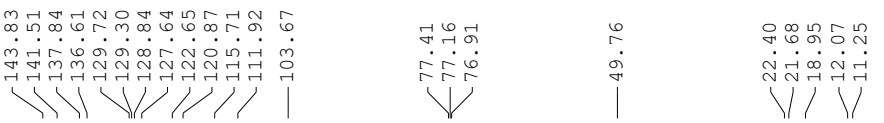
^{13}C NMR (125 MHz, $CDCl_3$)

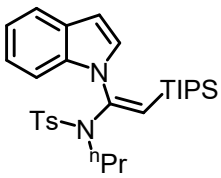


3ab

^{1}H NMR (500 MHz, $CDCl_3$)

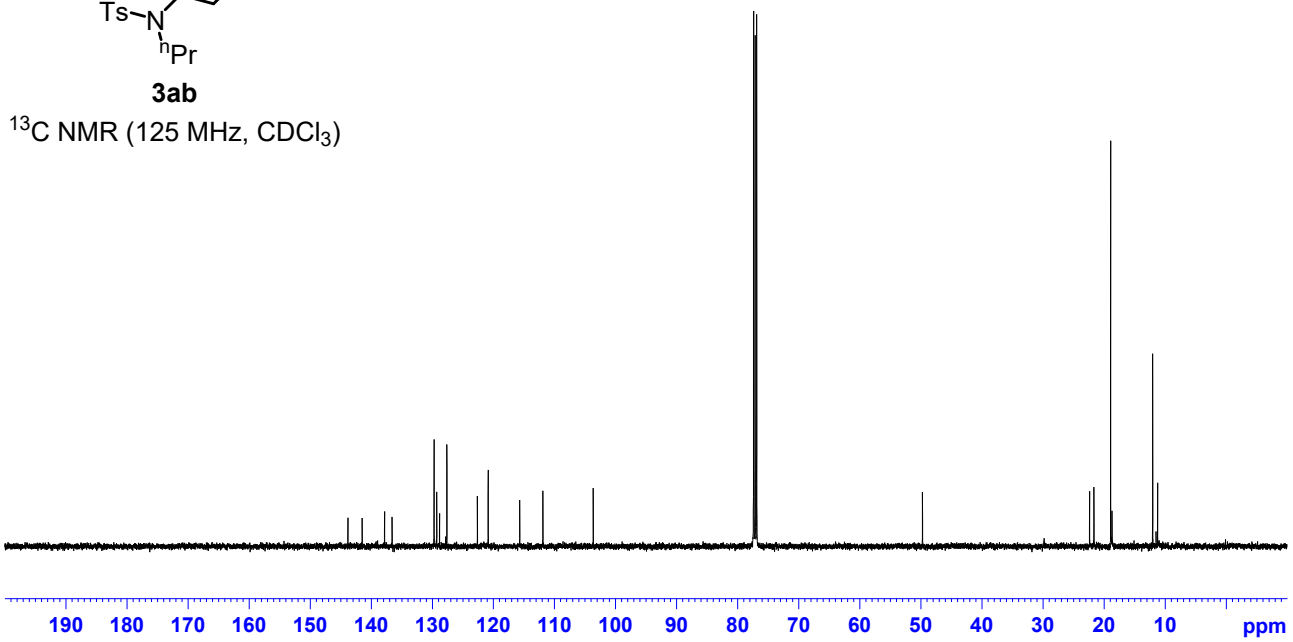


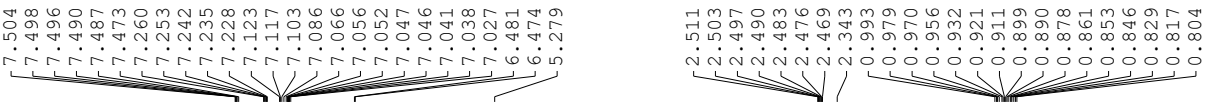


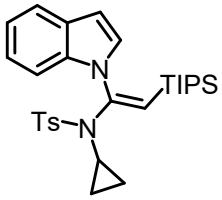


3ab

^{13}C NMR (125 MHz, $CDCl_3$)

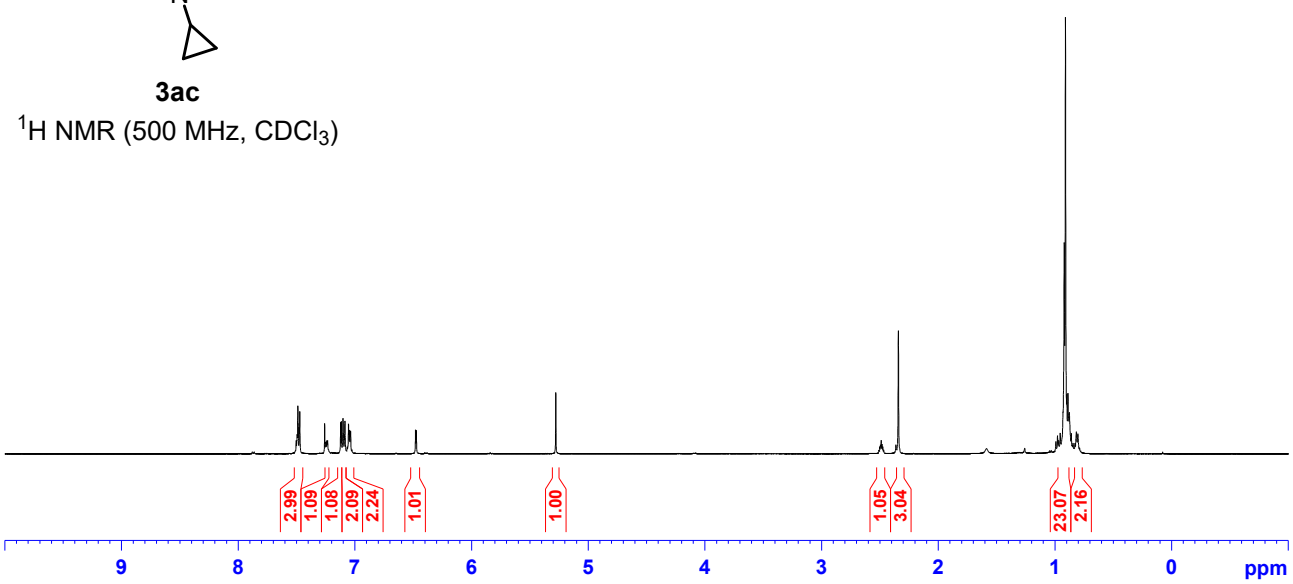


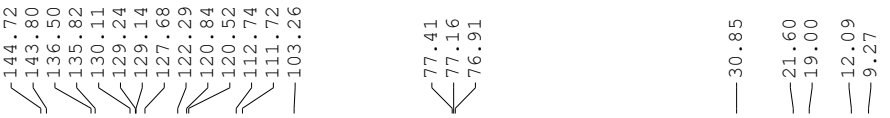


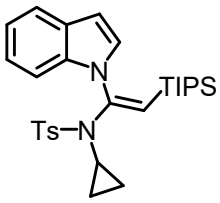


3ac

^{1}H NMR (500 MHz, $CDCl_3$)

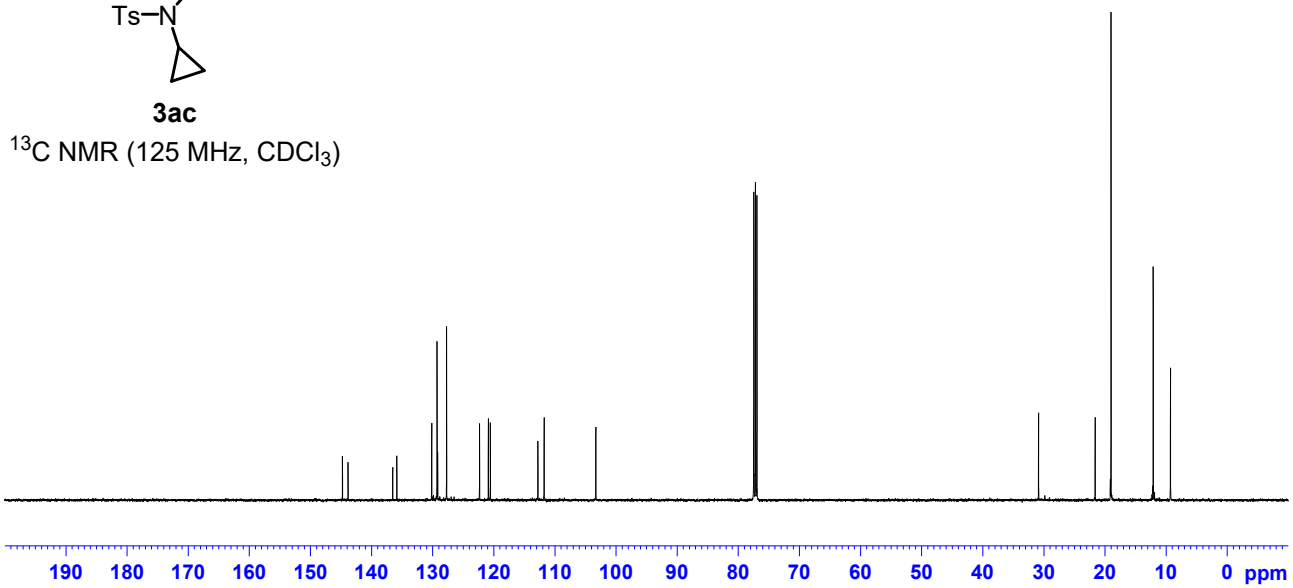


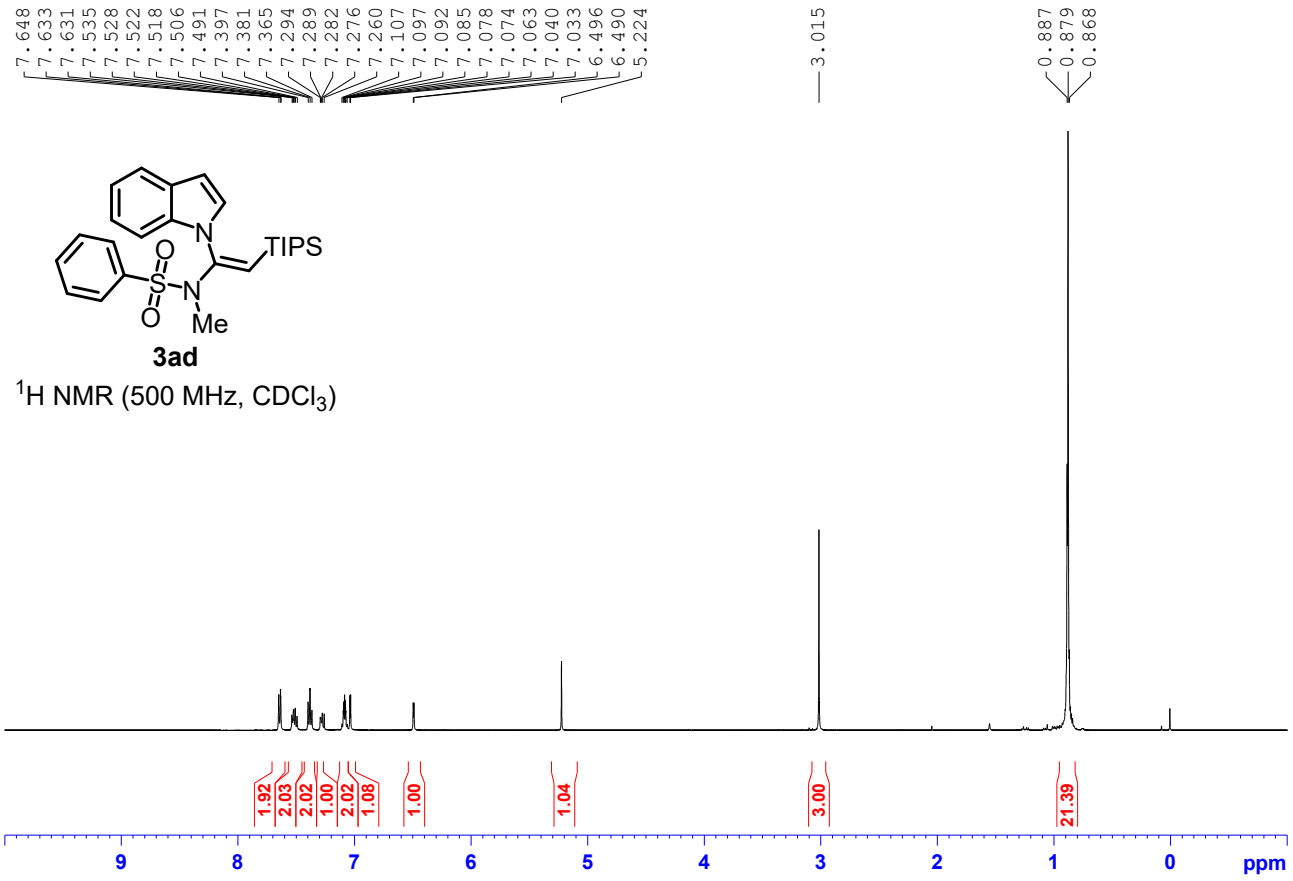




3ac

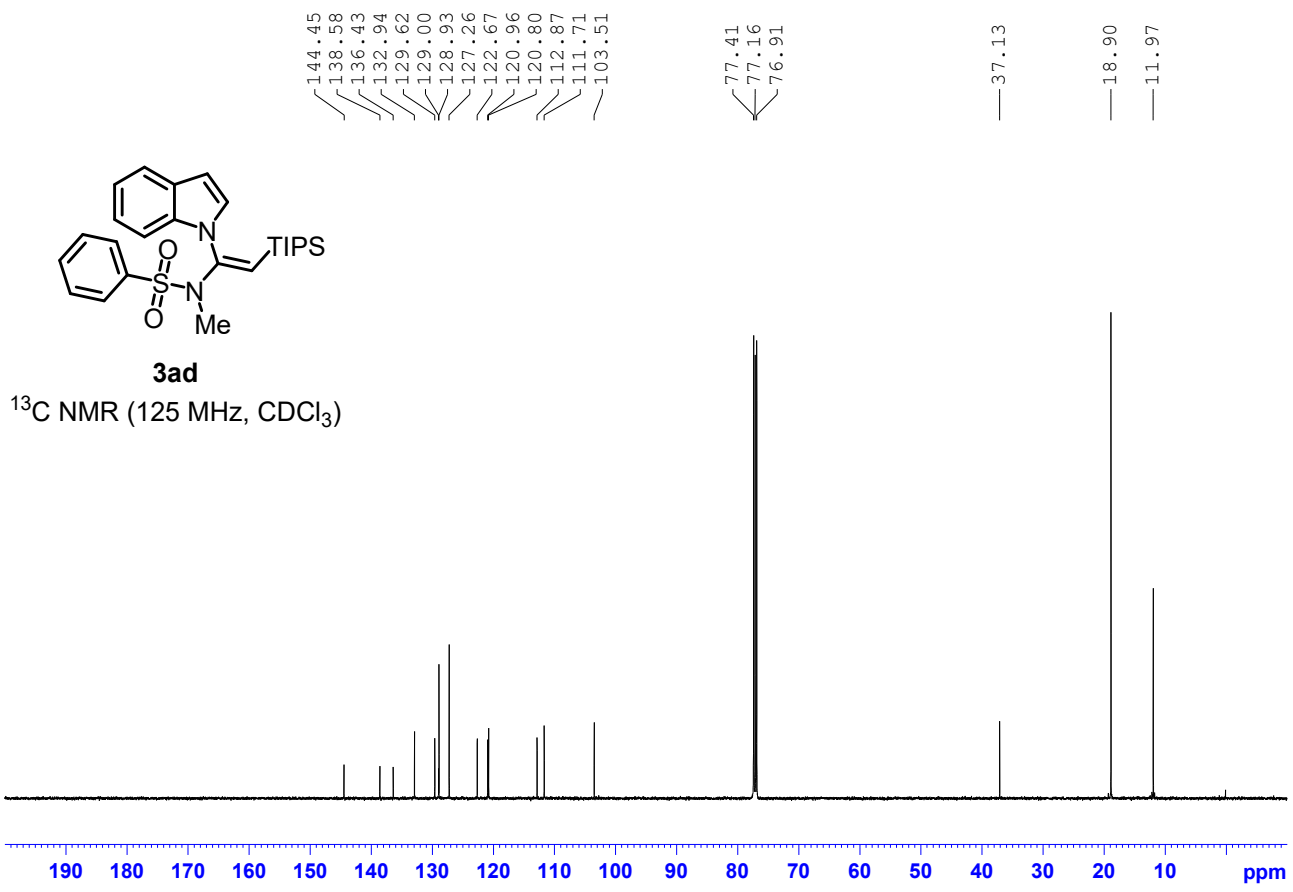
^{13}C NMR (125 MHz, $CDCl_3$)





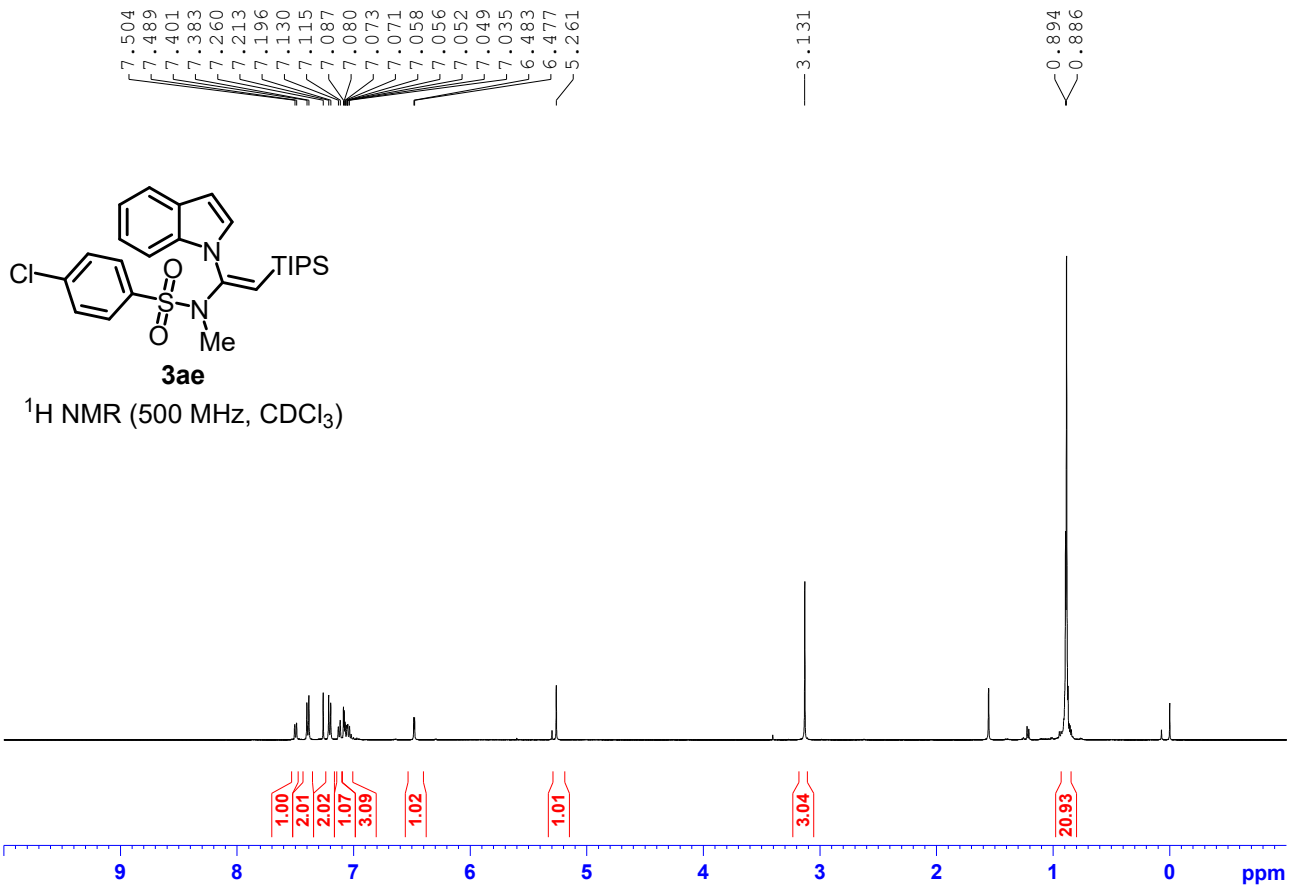
3ad

^{1}H NMR (500 MHz, $CDCl_3$)



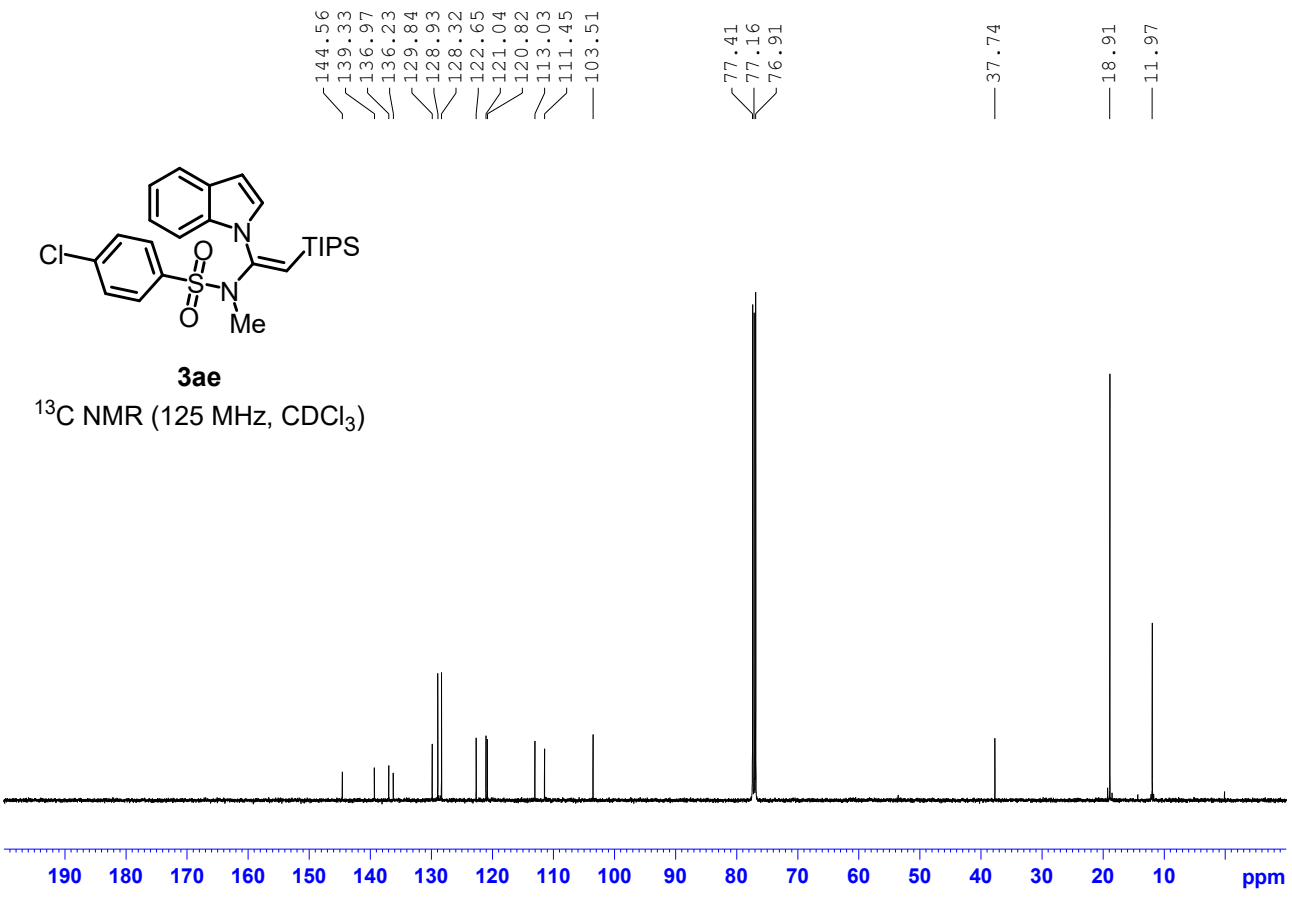
3ad

^{13}C NMR (125 MHz, $CDCl_3$)



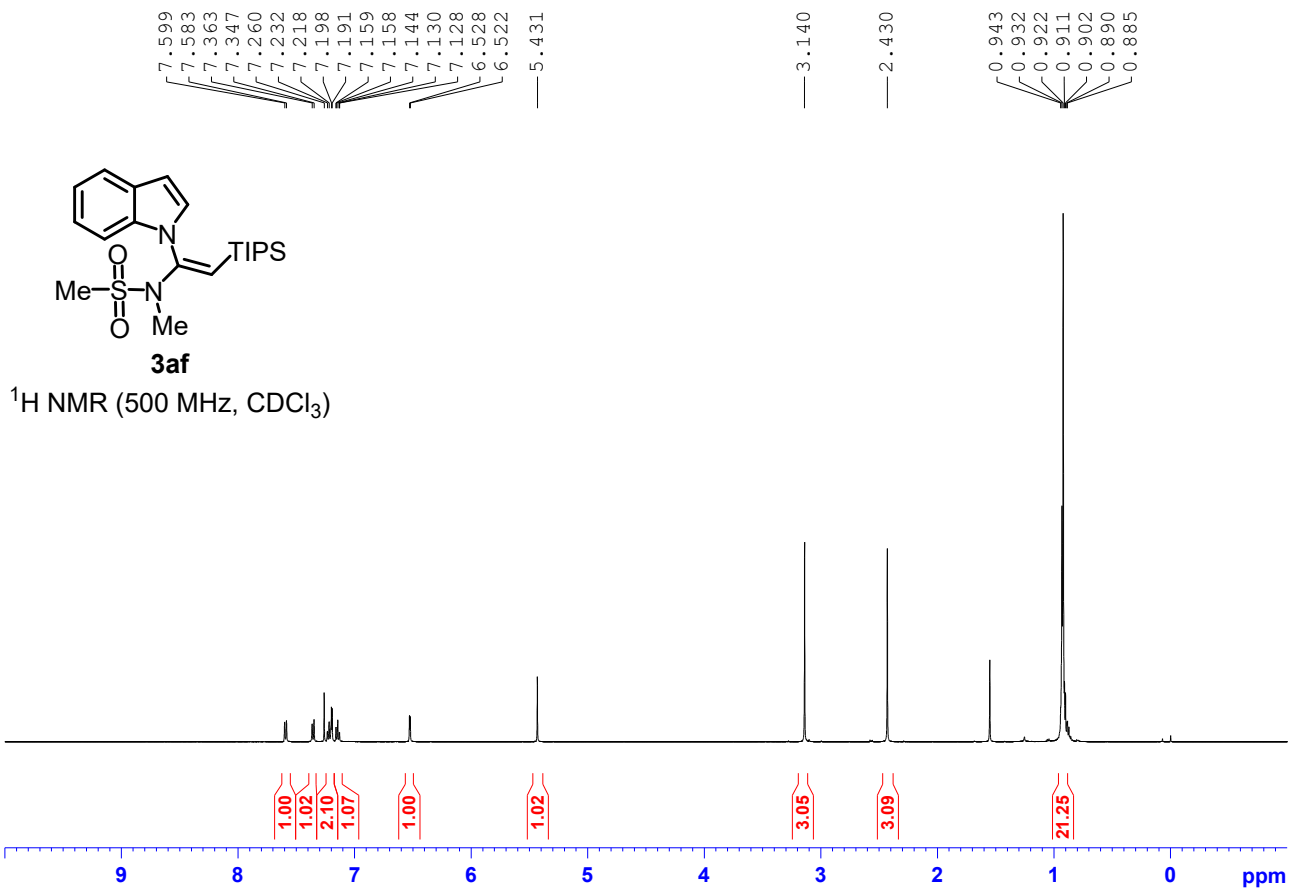
3ae

^{1}H NMR (500 MHz, $CDCl_3$)



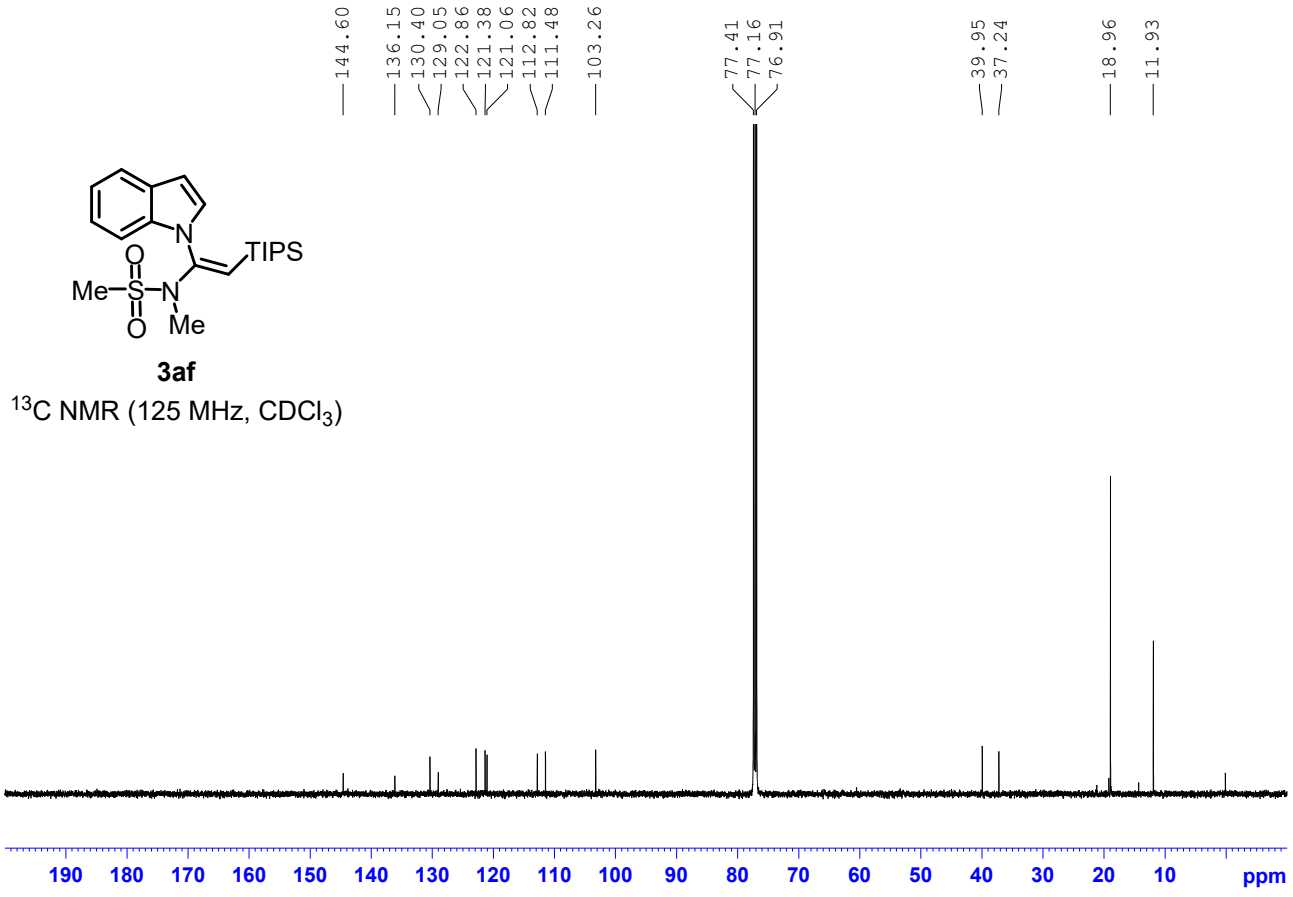
3ae

^{13}C NMR (125 MHz, $CDCl_3$)



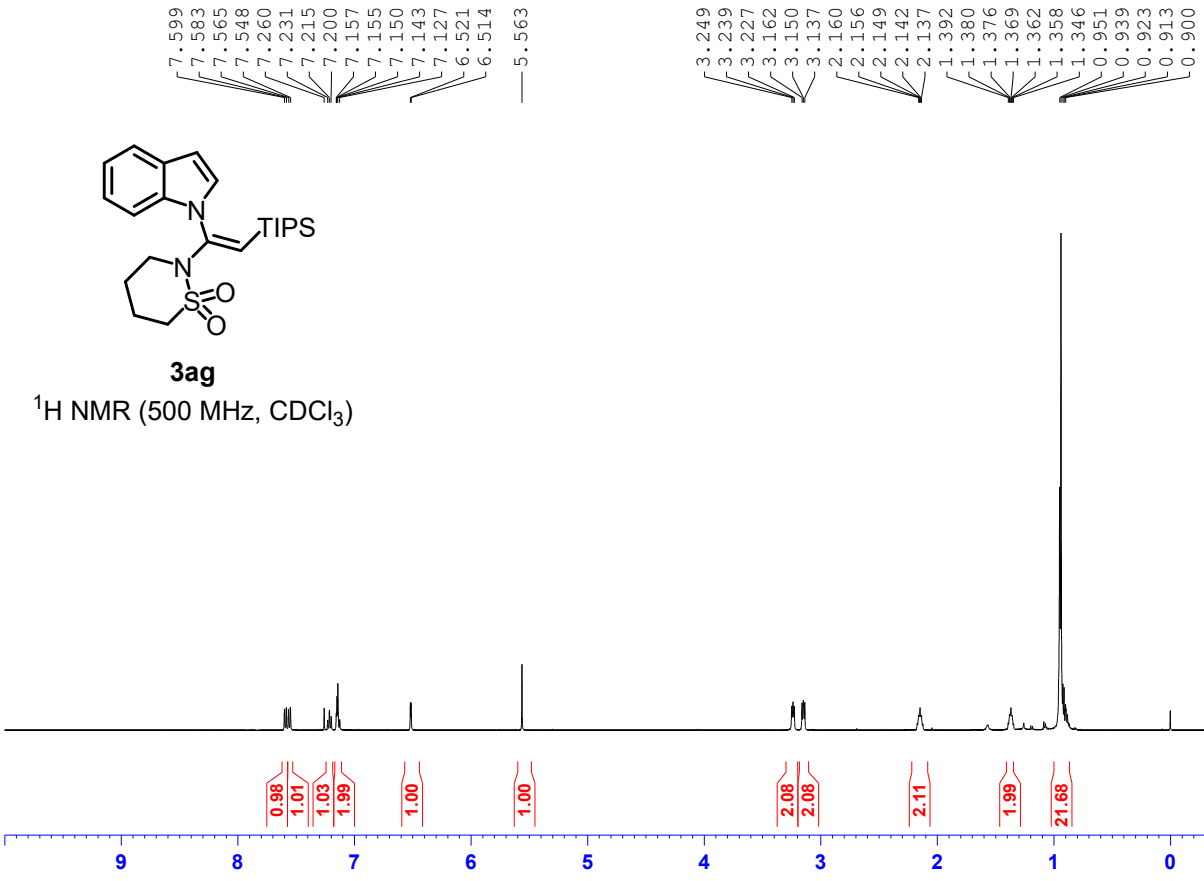
3af

^{1}H NMR (500 MHz, $CDCl_3$)



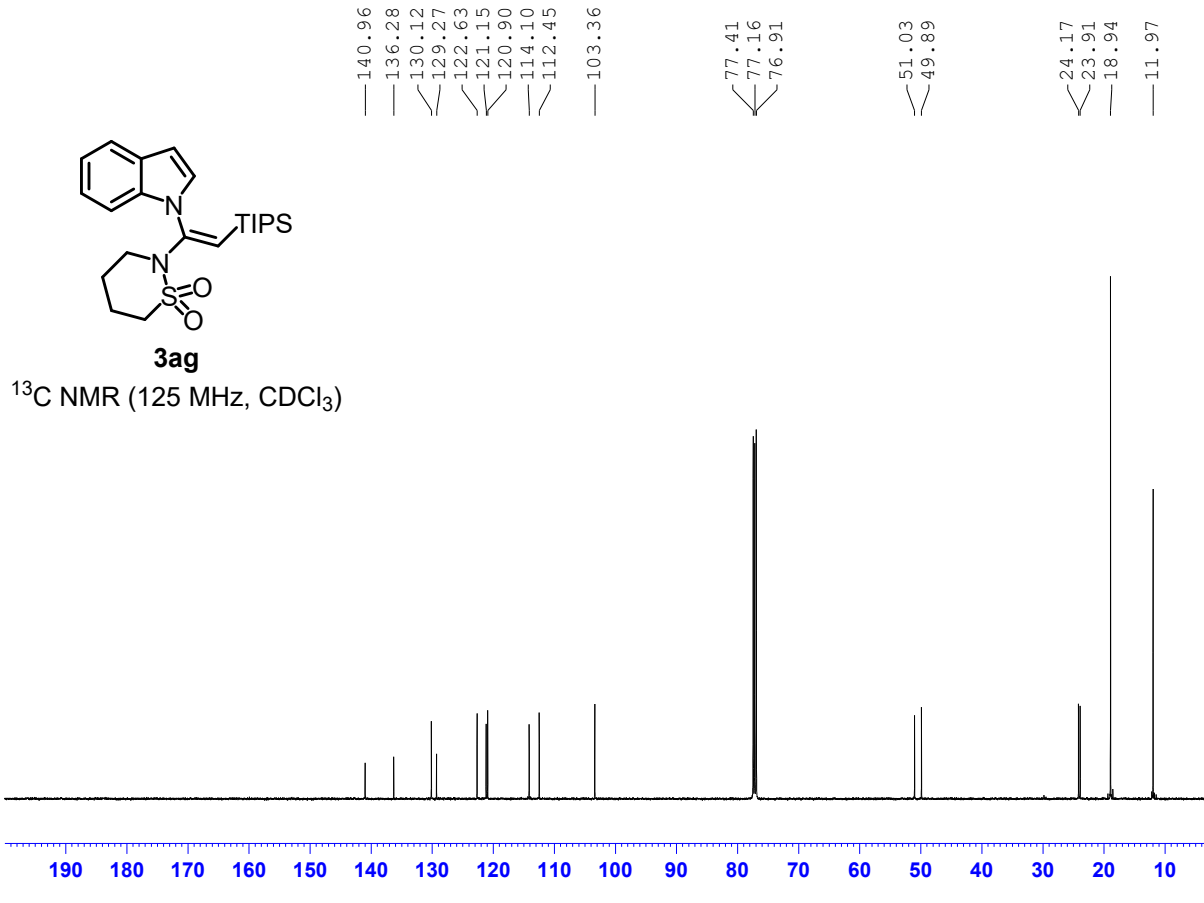
3af

^{13}C NMR (125 MHz, $CDCl_3$)



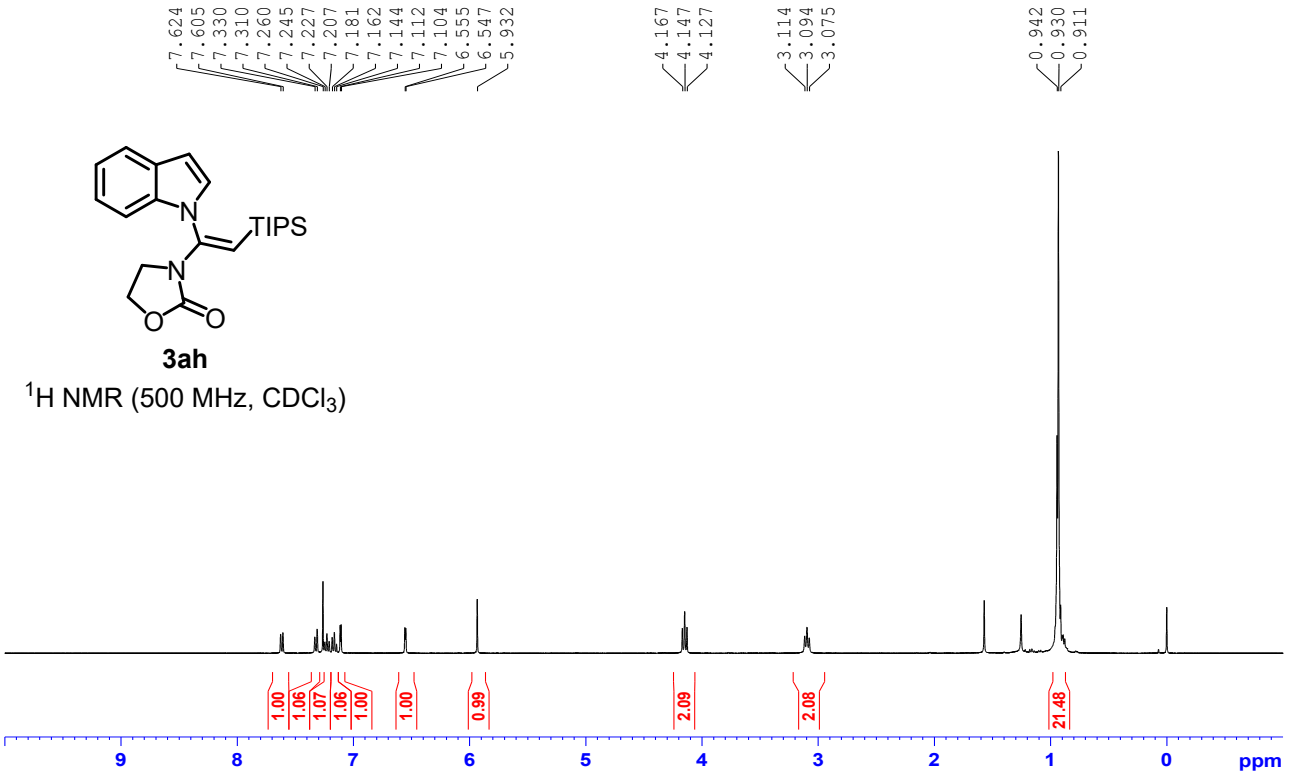
3ag

^{1}H NMR (500 MHz, $CDCl_3$)



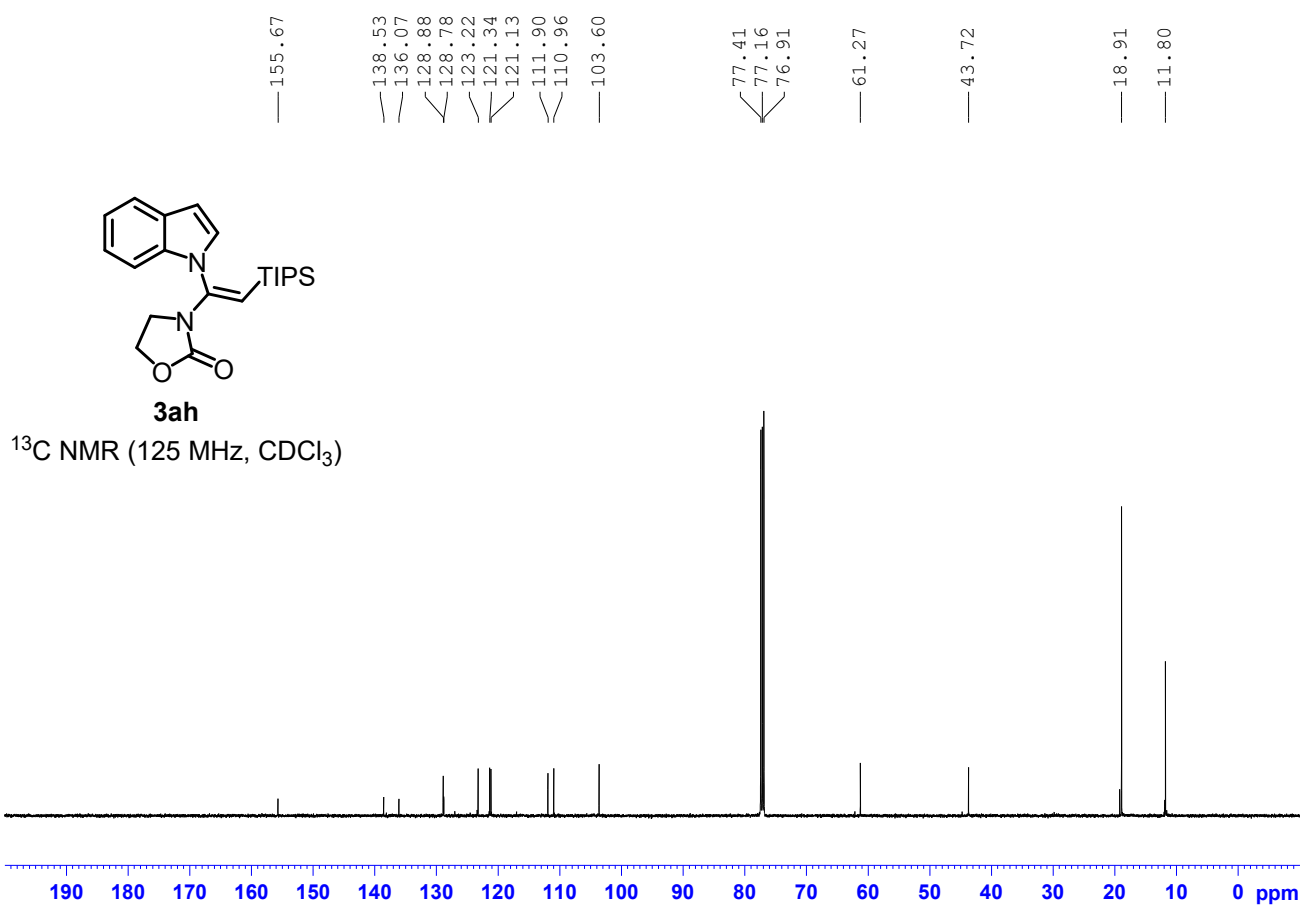
3ag

^{13}C NMR (125 MHz, $CDCl_3$)



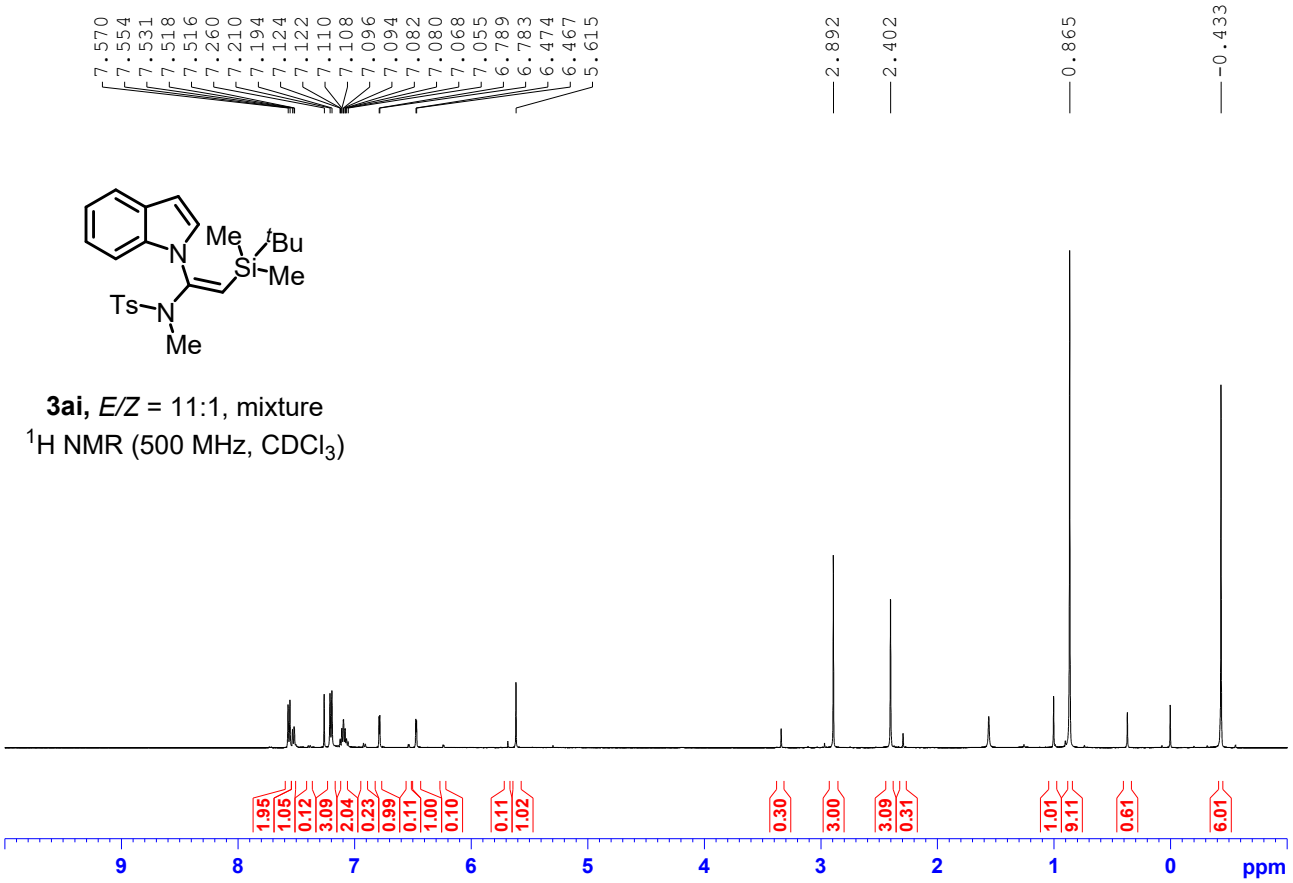
3ah

^{1}H NMR (500 MHz, $CDCl_3$)

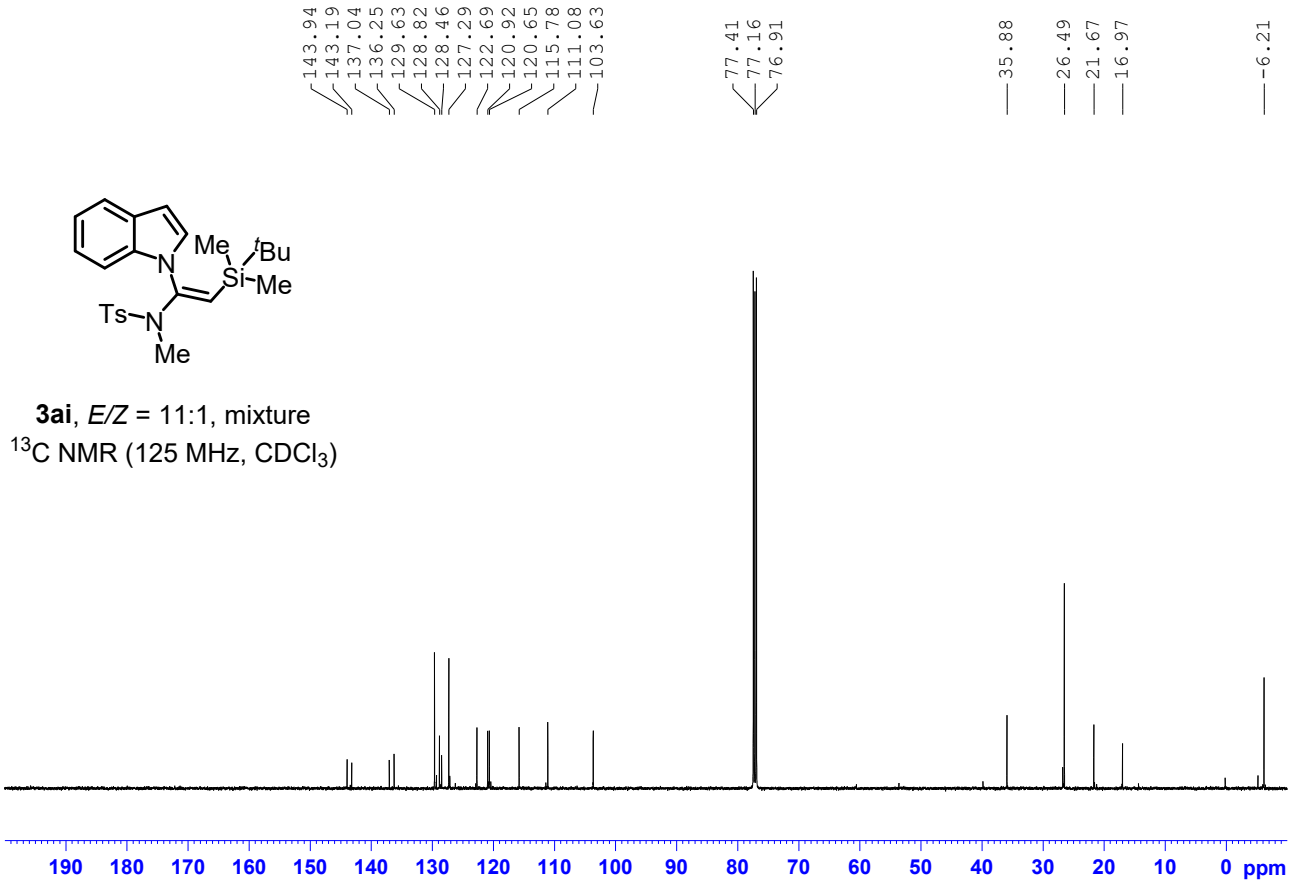


3ah

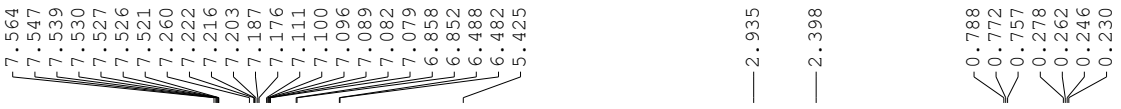
^{13}C NMR (125 MHz, $CDCl_3$)

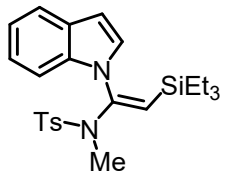


3ai, *E/Z* = 11:1, mixture
^{1}H NMR (500 MHz, $CDCl_3$)



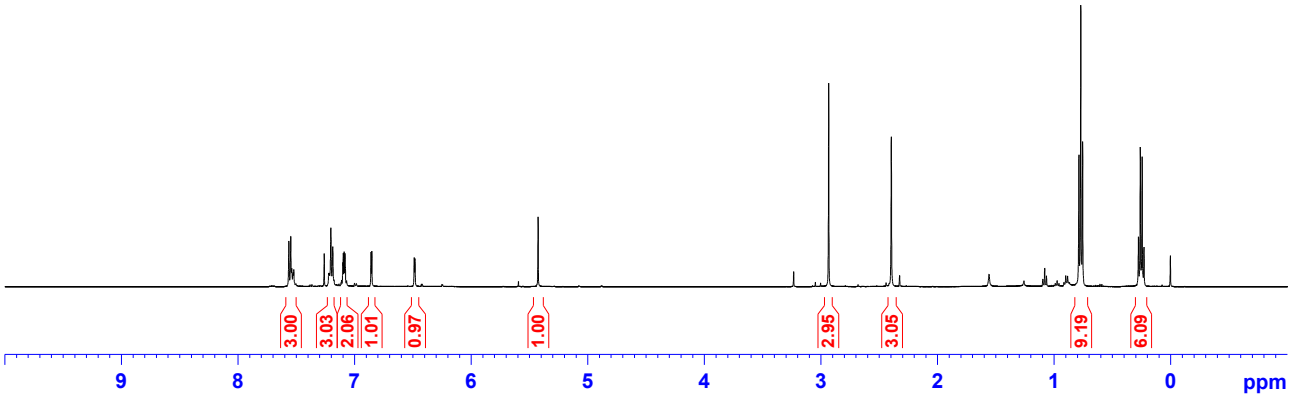
3ai, *E/Z* = 11:1, mixture
^{13}C NMR (125 MHz, $CDCl_3$)

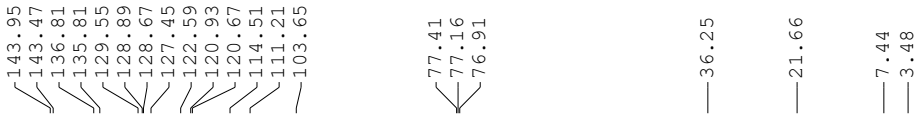


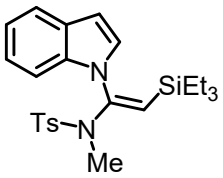


3aj

^{1}H NMR (125 MHz, $CDCl_3$)

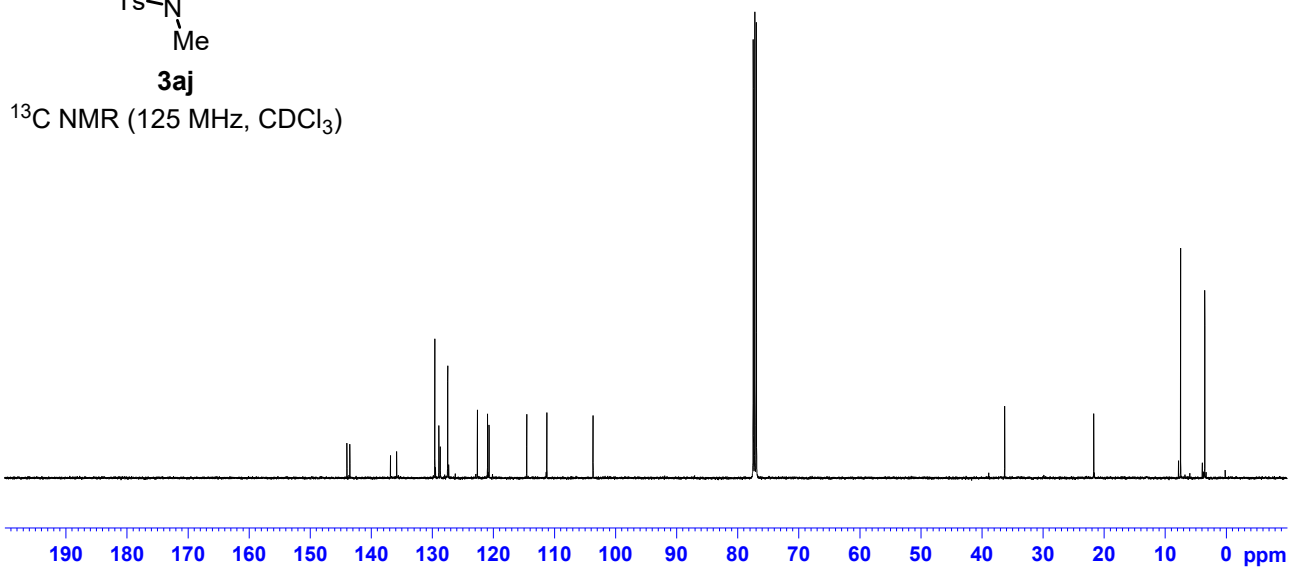


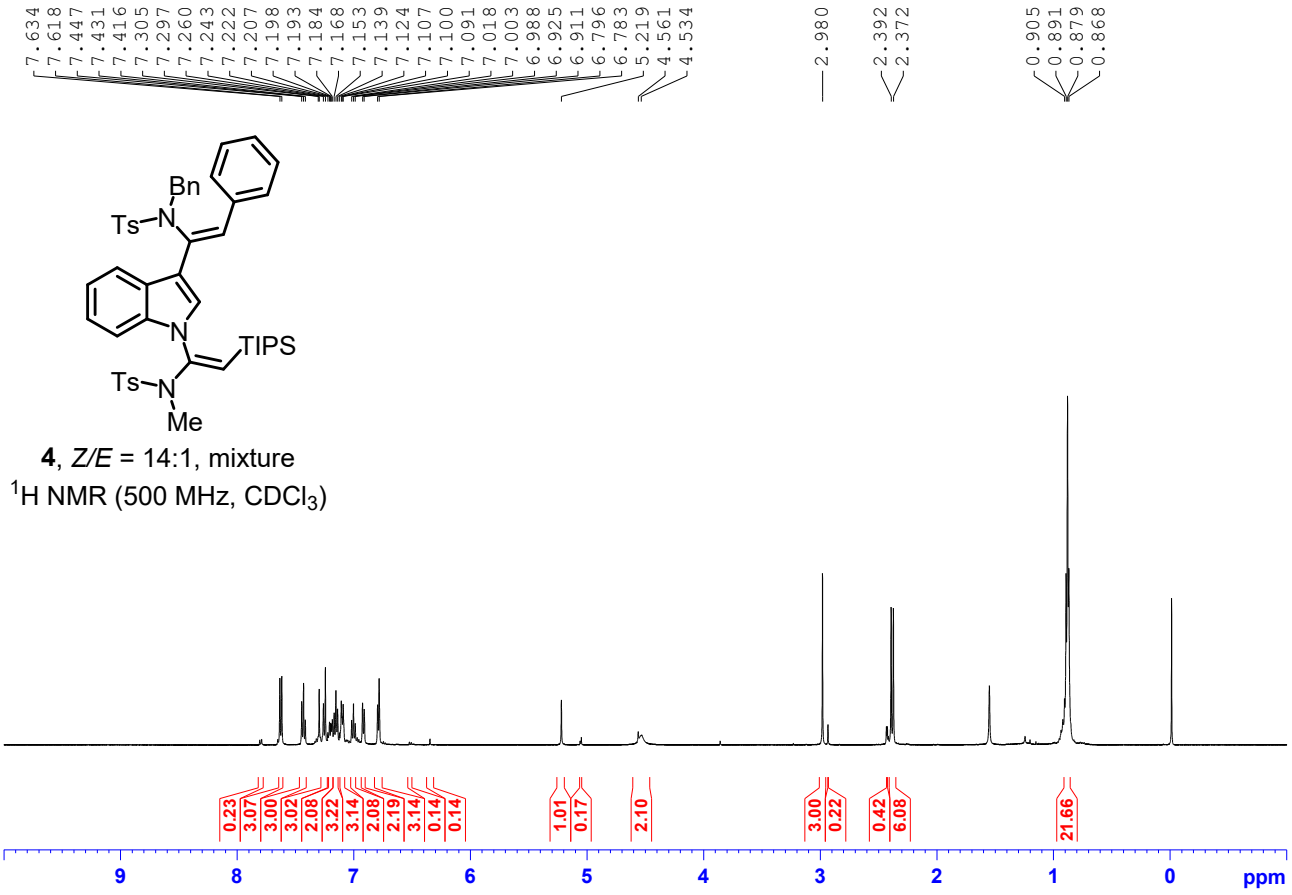




3aj

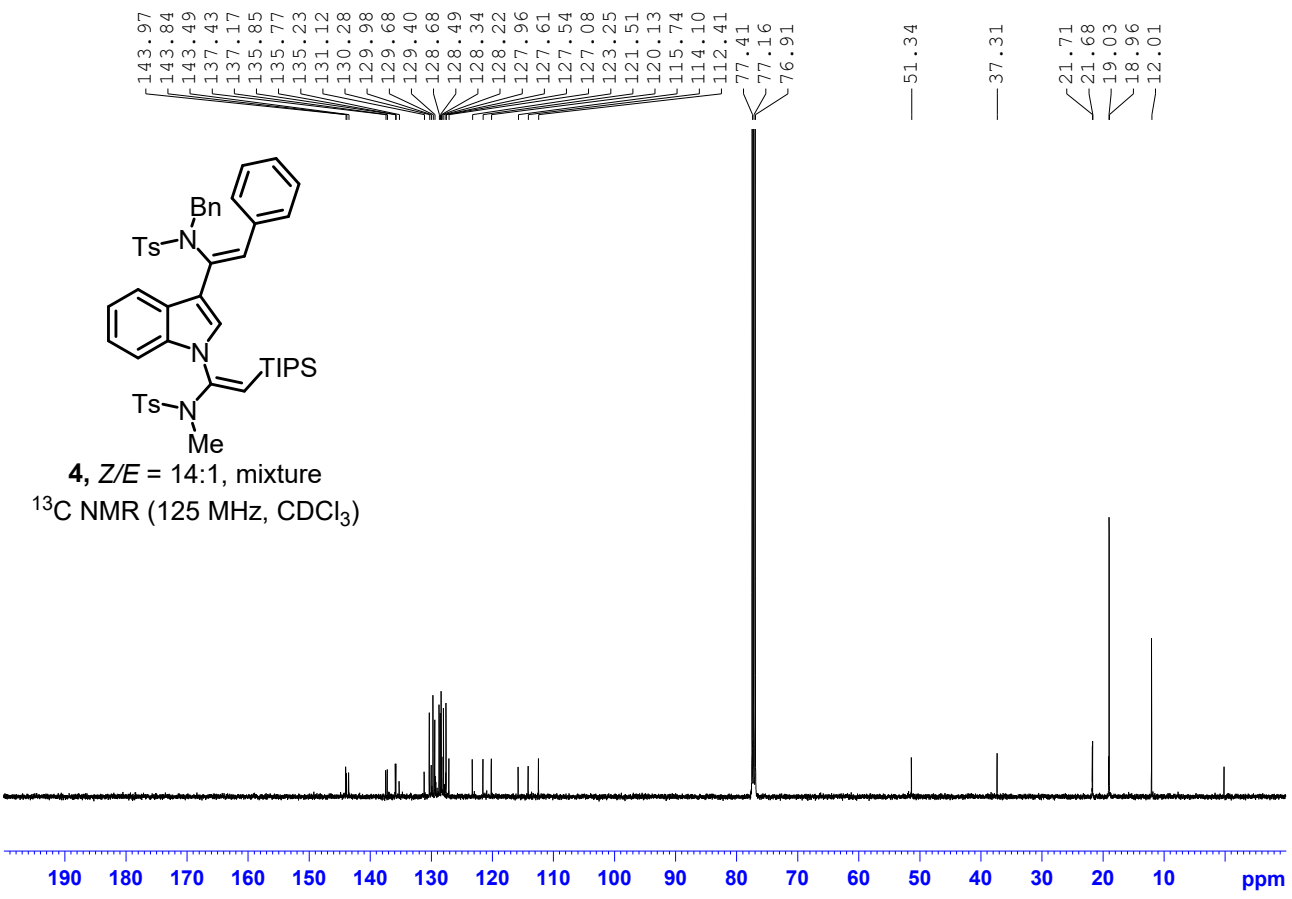
^{13}C NMR (125 MHz, $CDCl_3$)





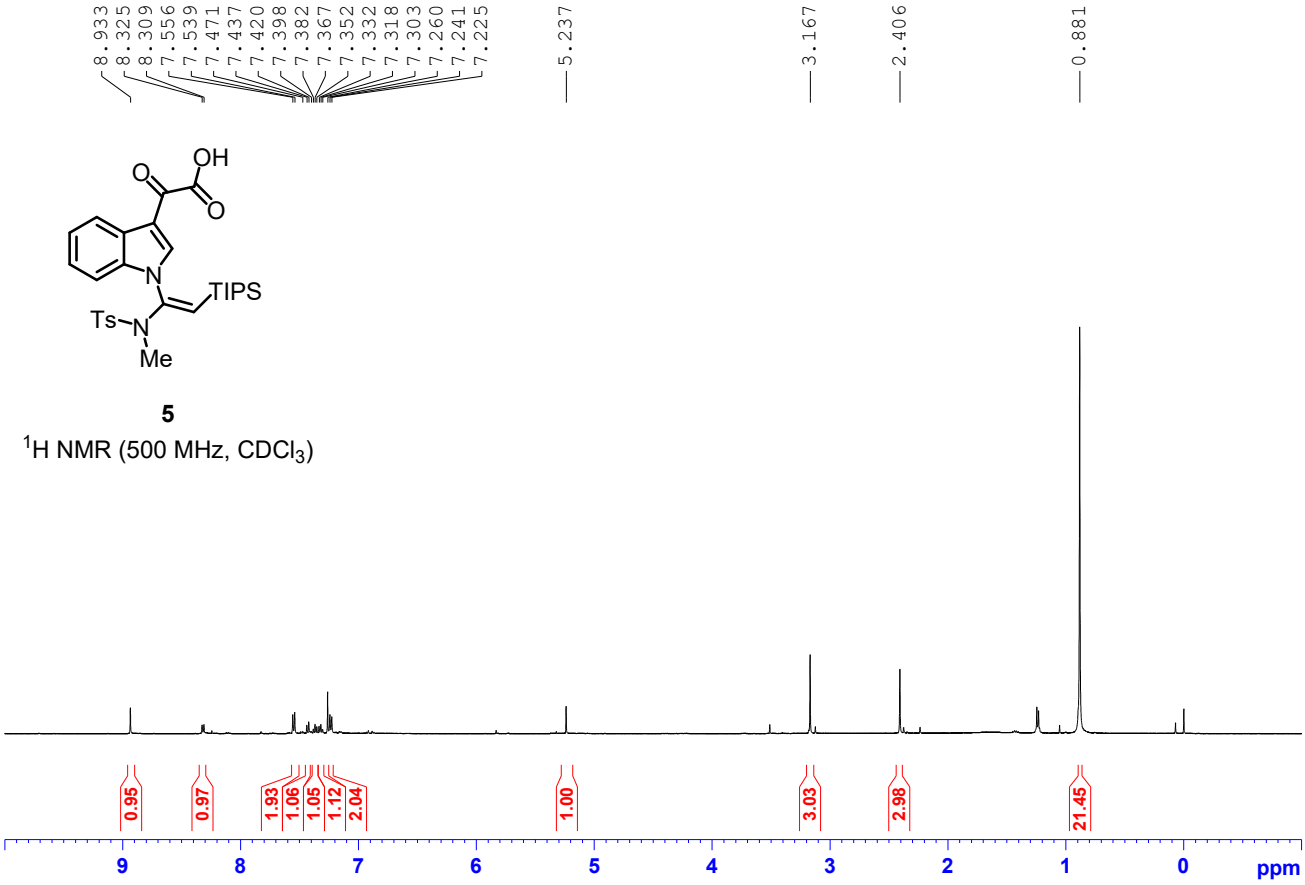
4, *Z/E* = 14:1, mixture

^{1}H NMR (500 MHz, $CDCl_3$)



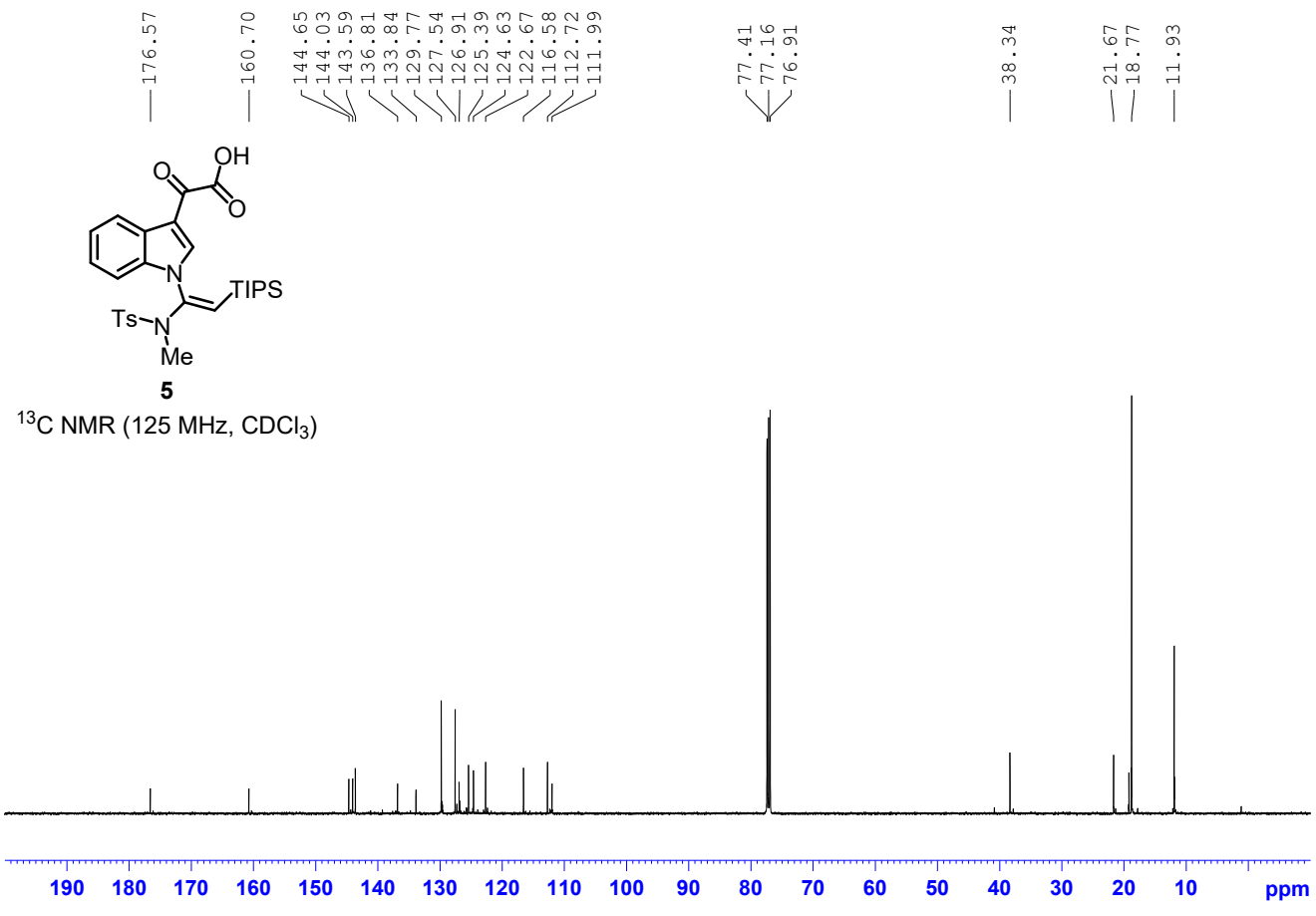
4, *Z/E* = 14:1, mixture

^{13}C NMR (125 MHz, $CDCl_3$)



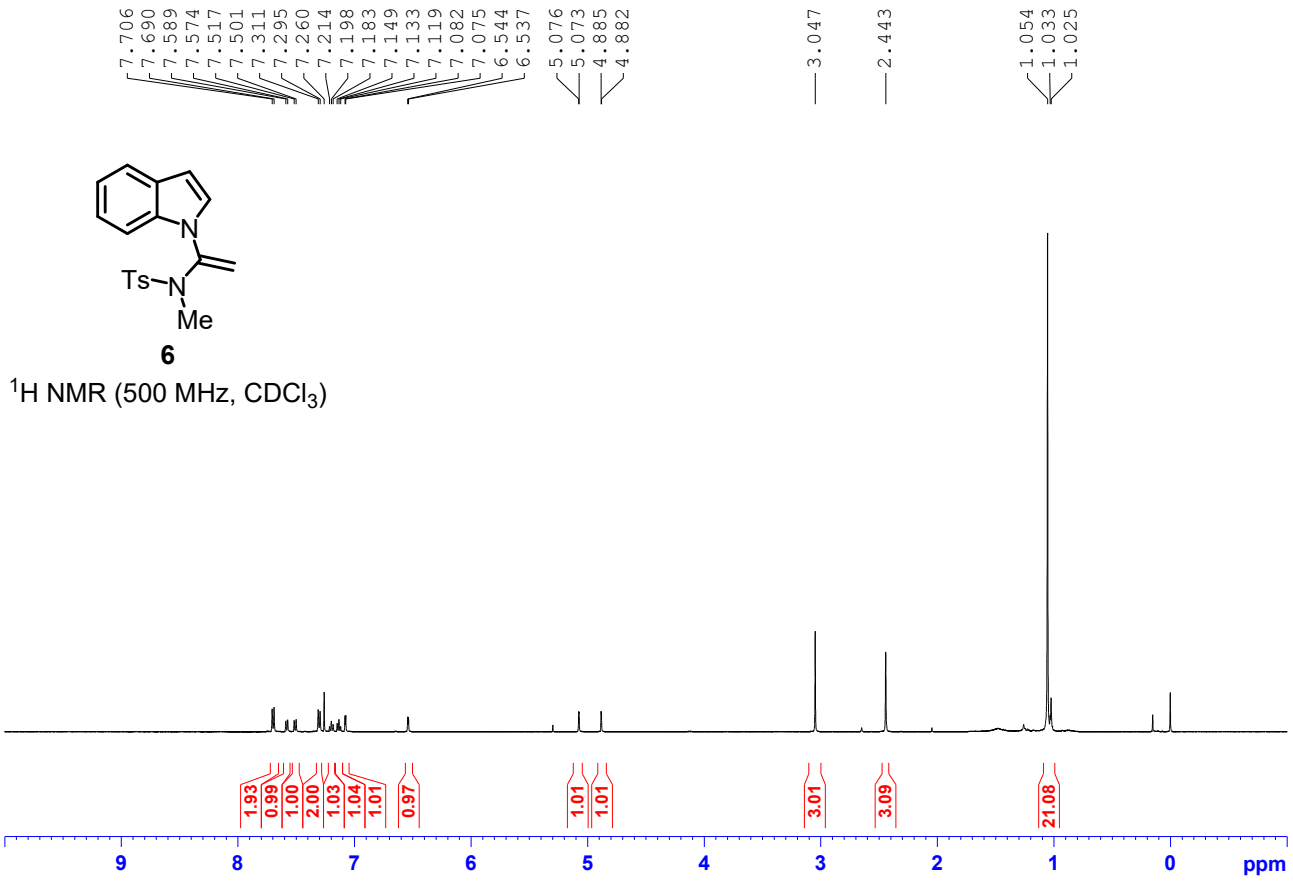
5

^{1}H NMR (500 MHz, $CDCl_3$)



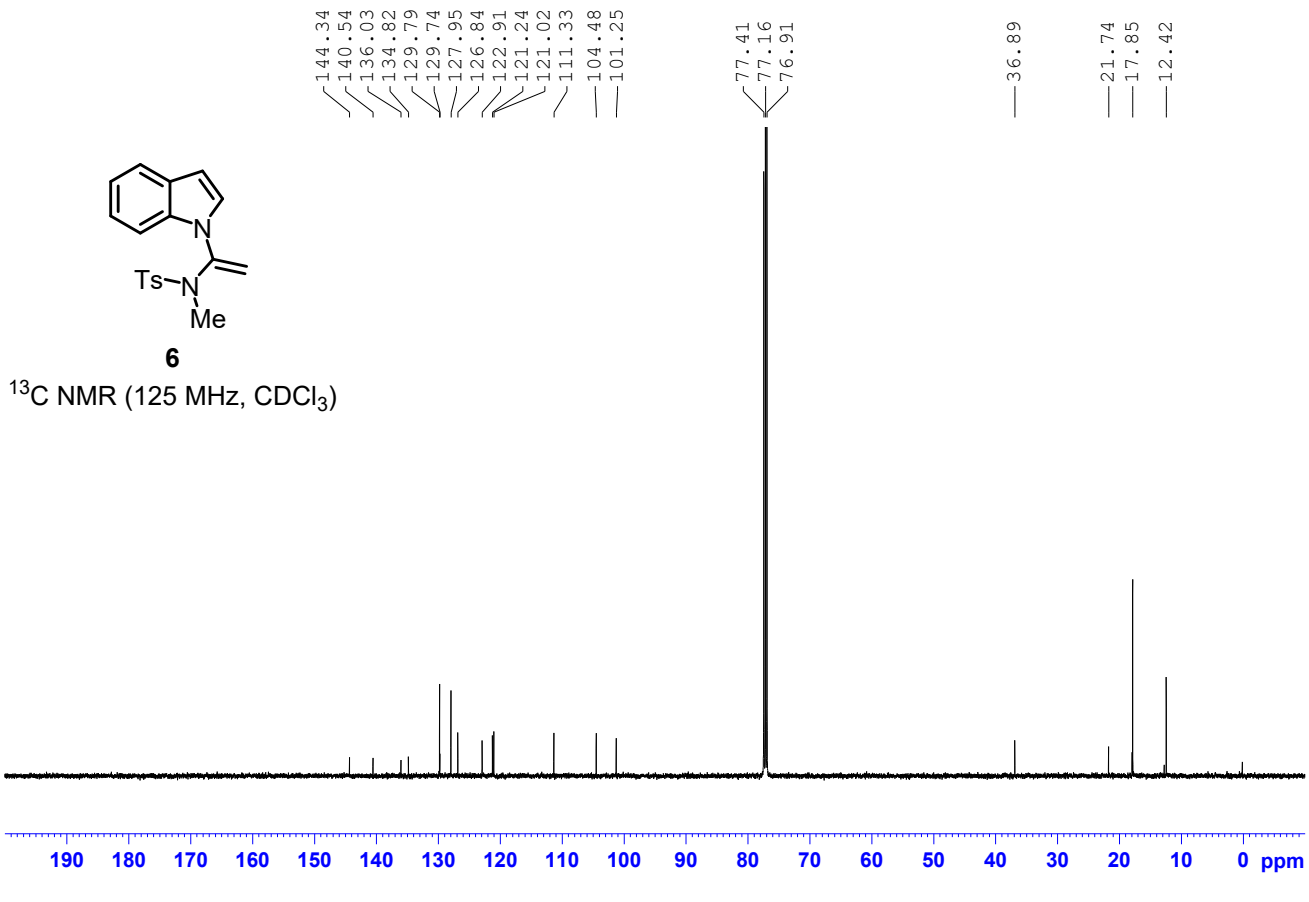
5

^{13}C NMR (125 MHz, $CDCl_3$)



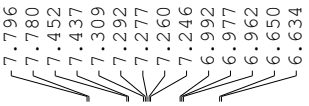
6

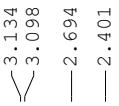
^{1}H NMR (500 MHz, $CDCl_3$)

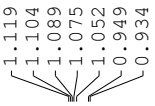


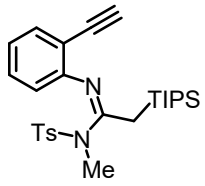
6

^{13}C NMR (125 MHz, $CDCl_3$)



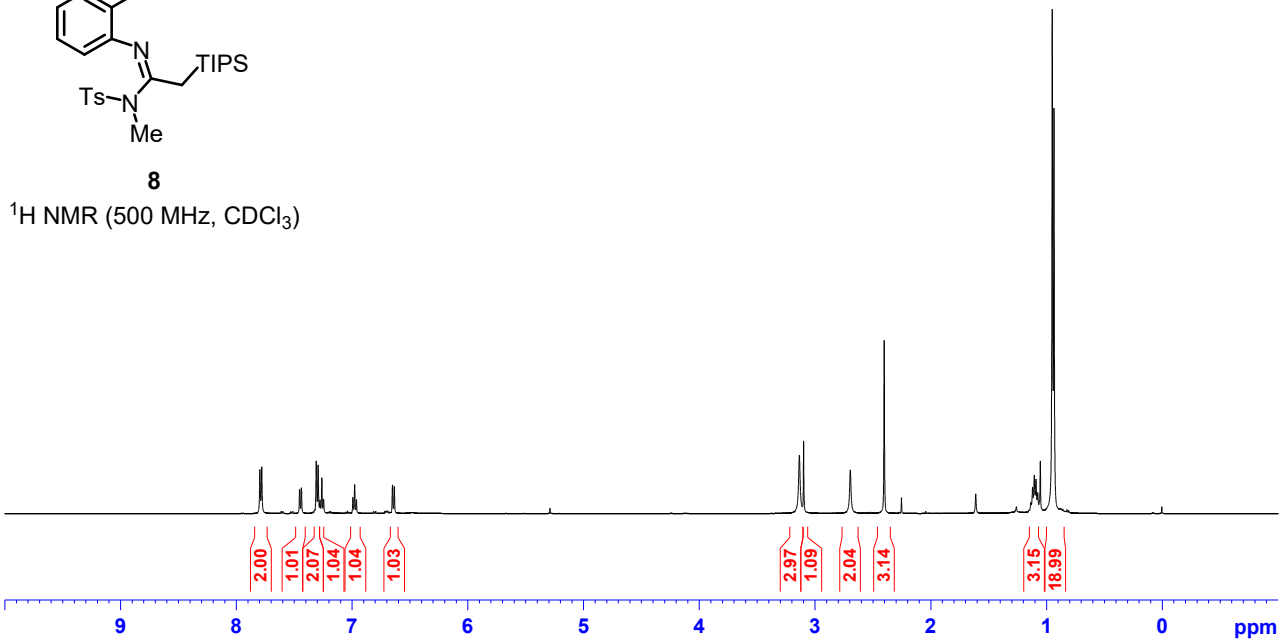


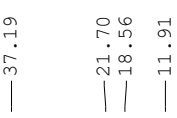


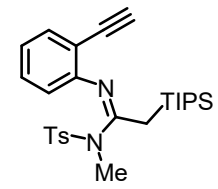


8

^{1}H NMR (500 MHz, $CDCl_3$)







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^{13}C NMR (125 MHz, $CDCl_3$)