Electronic Supplementary Information

Facile access to α-silylmethylamidines by BF_3-catalyzed hydroamination of silylynamides with amines

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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. Amines **1** were commercially available and silylynamides **2** were prepared according to literature procedures. Other reagents were purchased commercially and used without further purification unless otherwise noted.

2. Preparation of Silylynamides

Silylynamides **2a-2o** were prepared according to literature procedures [1-4].

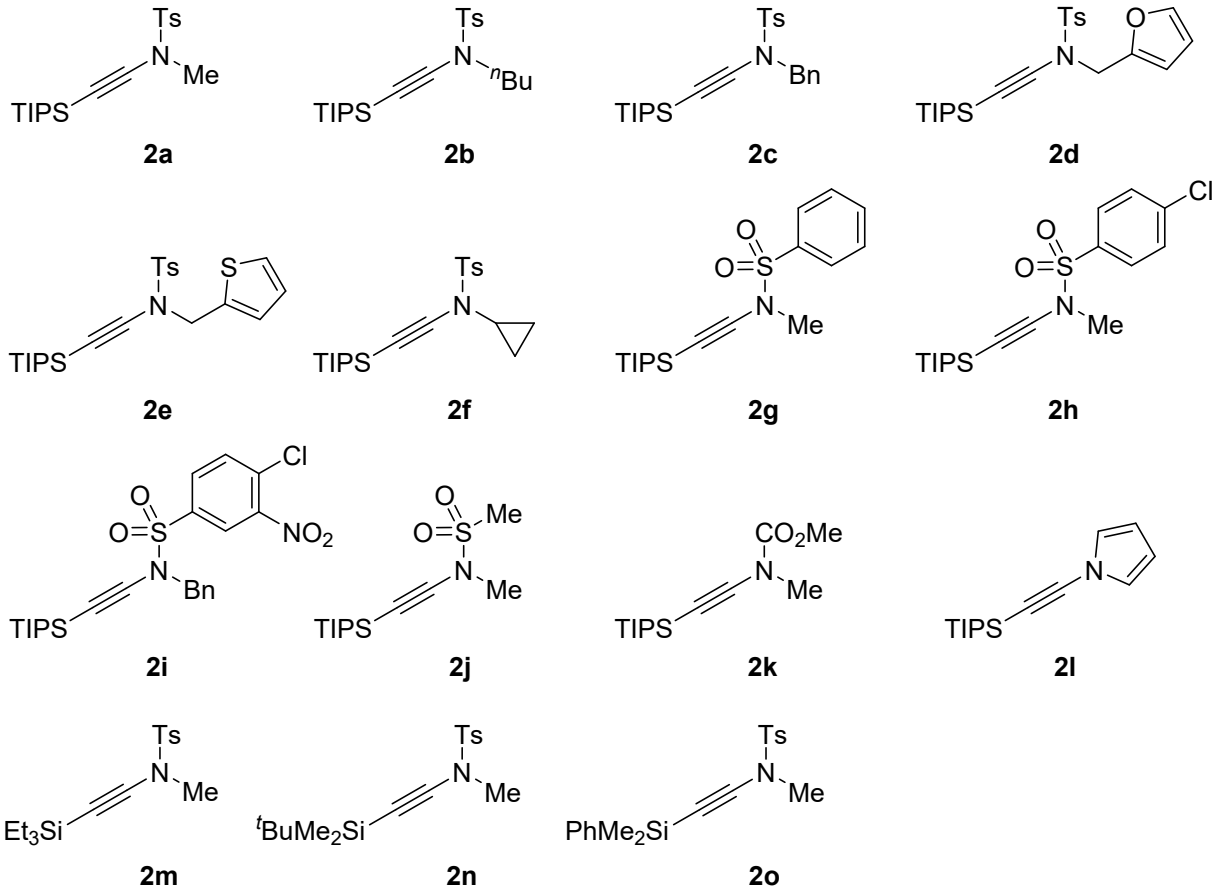
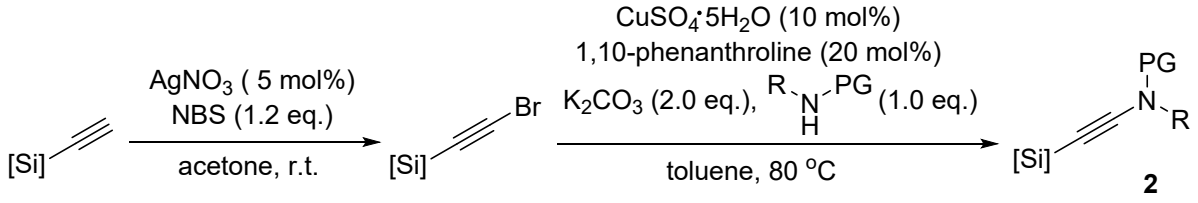


Figure S1. Silylynamides used in this work

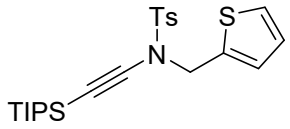
Synthetic procedure for silylynamides



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

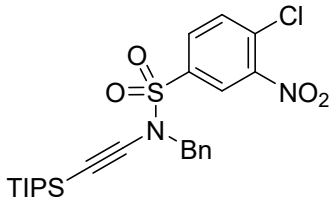
residue was then purified by chromatography on silica gel (eluent: PE/EA) to afford silylynamides **2**.

Analytical data of unkown ynamides:



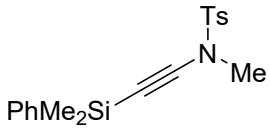
2e

4-Methyl-*N*-(thiophen-2-ylmethyl)-*N*-((triisopropylsilyl)ethynyl)benzenesulfonamide (2e), white solid, m.p. 50-52 °C (715.2 mg, 80% yield). PE/EA = 25:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.71 (d, J = 8.3 Hz, 2H), 7.25 (d, J = 7.9 Hz, 2H), 7.21 (q, J = 3.5, 1.0 Hz, 1H), 6.98 (d, J = 3.3 Hz, 1H), 6.89 (q, J = 8.6 Hz, 1H), 4.74 (s, 2H), 2.42 (s, 3H), 0.98 (s, 21H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 144.7, 136.4, 134.8, 129.6, 128.7, 128.0, 126.8, 126.6, 95.9, 71.0, 50.3, 21.8, 18.7, 11.5. **HRMS** (ESI, m/z) Calculated for $[C_{23}H_{34}NO_2S_2Si, M + H]^+$: 448.1802, found: 448.1795.



2i

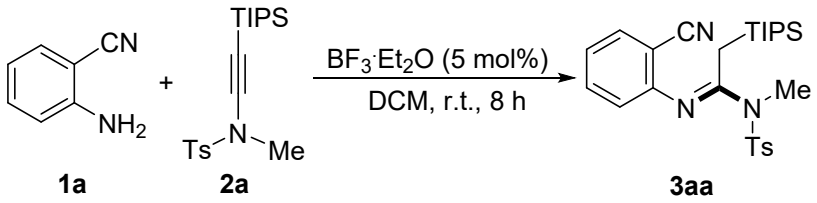
***N*-benzyl-4-chloro-3-nitro-*N*-((triisopropylsilyl)ethynyl)benzenesulfonamide (2i)**, white solid, m.p. 45-47 °C (799.4 mg, 78% yield). PE/EA = 25:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.08 (d, J = 2.0 Hz, 1H), 7.83 (dd, J = 8.5, 2.1 Hz, 1H), 7.59 (d, J = 9.4 Hz, 1H), 7.31-7.24 (m, 5H), 4.62 (s, 2H), 0.99 (d, J = 2.6 Hz, 21H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 147.7, 137.8, 133.7, 132.6, 132.5, 131.6, 129.1, 129.0, 128.8, 125.0, 95.6, 71.6, 56.6, 18.6, 11.4. **HRMS** (ESI, m/z) Calculated for $[C_{24}H_{32}ClN_2O_4SSi, M + H]^+$: 507.1546, found: 507.1535.



2o

***N*-((dimethyl(phenyl)silyl)ethynyl)-*N*,4-dimethylbenzenesulfonamide (2o)**, white solid, m.p. 53-55 °C (507.6 mg, 74% yield). PE/EA = 20:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.78 (d, J = 8.3 Hz, 2H), 7.61 (dd, J = 7.2, 1.6 Hz, 2H), 7.47-7.36 (m, 3H), 7.21 (d, J = 8.2 Hz, 2H), 2.98 (s, 3H), 2.35 (s, 3H), 0.31 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 144.9, 137.2, 133.7, 133.2, 129.8, 129.5, 128.0, 127.9, 98.3, 69.7, 39.1, 21.7, -0.7. **HRMS** (ESI, m/z) Calculated for $[C_{18}H_{22}NO_2SSi, M + H]^+$: 344.1143, found: 344.1135.

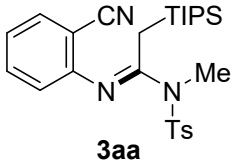
3. Typical Procedure for α-Silylmethylamidines



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

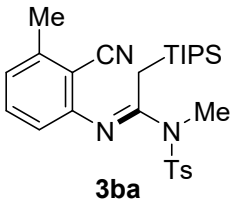
Typical procedure: A pre-dried 10.0 mL Schlenk tube was charged with stirring bar, $BF_3{\cdot}Et_2O$ (1.3 μL, 0.01 mmol, 0.05 eq.), 2-aminobenzonitrile (**1a**, 35.4 mg, 0.3 mmol, 1.5 eq.), *N*,4-dimethyl-*N*-((triisopropylsilyl)ethynyl) benzenesulfonamide (**2a**, 73.1 mg, 0.2 mmol, 1 eq.) and DCM (1.0 mL) under N_2 atmosphere. The mixture was stirred at rt for 8 h. Solvent was removed by rotary evaporation instrument and 1,3,5-trimethoxybenzene as the internal reference was added. The NMR yield (98%) is 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 = 10:1, R_f = 0.20) to give the analytical pure product **3aa** (92.7 mg, 96 % yield).

4. Characterization of α-Silylmethylamidines



3aa

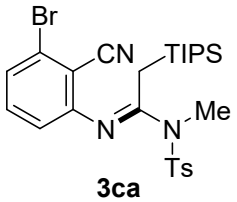
(*E*)-*N′*-(2-cyanophenyl)-*N*-methyl-*N*-tosyl-2-(triisopropylsilyl)acetimidamide (3aa), white solid, m.p. 147-149 °C (92.7 mg, 96% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 3.14 (s, 3H), 2.72 (s, 2H), 2.41 (s, 3H), 1.13-1.05 (m, 3H), 0.95 (d, *J* = 7.3 Hz, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 163.2, 151.6, 144.5, 134.0, 133.6, 133.4, 129.9, 127.9, 123.6, 121.4, 117.6, 105.1, 37.1, 21.7, 18.5, 17.5, 12.0. **HRMS** (ESI, m/z) Calculated for [$C_{26}H_{38}N_3O_2SSi$, M + H]$^+$: 484.2453, found: 484.2449.



3ba

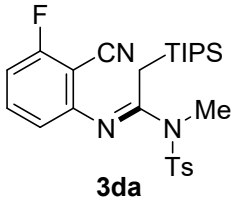
(*E*)-*N′*-(2-cyano-3-methylphenyl)-*N*-methyl-*N*-tosyl-2-(triisopropylsilyl)acetimidamide (3ba), white solid, m.p. 133-136 °C (91.4 mg, 92% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz,

$CDCl_3$): δ 7.77 (d, J = 8.2 Hz, 2H), 7.38-7.29 (m, 3H), 6.94 (d, J = 7.7 Hz, 1H), 6.56 (d, J = 8.1 Hz, 1H), 3.14 (s, 3H), 2.72 (s, 2H), 2.49 (s, 3H), 2.41 (s, 3H), 1.14-1.04 (m, 3H), 0.95 (d, J = 7.4 Hz, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 163.0, 151.9, 144.4, 143.2, 133.9, 132.9, 129.9, 127.9, 124.6, 118.1, 116.7, 105.8, 37.2, 21.7, 20.8, 18.5, 17.6, 12.0. **HRMS** (ESI, m/z) Calculated for [$C_{27}H_{40}N_3O_2SSi$, M + H]$^+$: 498.2613, found: 498.2605.



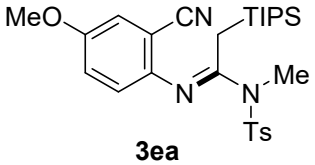
3ca

(*E*)-*N′*-(3-bromo-2-cyanophenyl)-*N*-methyl-*N*-tosyl-2-(triisopropylsilyl)acetimidamide (3ca), white solid, m.p. 172-175 ^{o}C (97.6 mg, 87% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.76 (d, J = 8.1 Hz, 2H), 7.43-7.27 (m, 4H), 6.69 (dd, J = 6.9, 1.2 Hz ,1H), 3.15 (s, 3H), 2.69 (s, 2H), 2.42 (s, 3H), 1.14-1.07 (m, 3H), 0.96 (d, J = 7.4 Hz, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 163.6, 153.4, 144.6, 134.1, 133.9, 130.0, 127.8, 127.2, 126.0, 119.9, 116.0, 108.4, 37.1, 21.8, 18.5, 17.7, 12.0. **HRMS** (ESI, m/z) Calculated for [$C_{26}H_{37}BrN_3O_2SSi$, M + H]$^+$: 562.1561, found: 562.1554.



3da

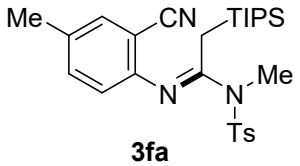
(*E*)-*N′*-(2-cyano-3-fluorophenyl)-*N*-methyl-*N*-tosyl-2-(triisopropylsilyl)acetimidamide (3da), white solid, m.p. 129-131 ^{o}C (96.3 mg, 96% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.77 (d, J = 8.3 Hz, 2H), 7.50-7.40 (m, 1H), 7.34 (d, J = 8.1 Hz, 2H), 6.83 (t, J = 8.5 Hz, 1H), 6.55 (d, J = 8.2 Hz, 1H), 3.14 (s, 3H), 2.71 (s, 2H), 2.42 (s, 3H), 2.41 (s, 3H), 1.15-1.06 (m, 3H), 0.96 (d, J = 7.4 Hz, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 165.1, 163.6, 163.0, 153.2, 144.6, 134.6 (d, J = 10.1 Hz), 134.0, 130.0, 127.8, 116.9 (d, J = 2.9 Hz), 112.7, 110.0 (d, J = 19.5 Hz), 93.9 (d, J = 16.0 Hz), 37.1, 18.5, 17.6, 12.0. **^{19}F NMR** (471 MHz, $CDCl_3$): δ -105.66. **HRMS** (ESI, m/z) Calculated for [$C_{27}H_{37}N_2O_2SSiNa$, M + H]$^+$: 502.2360, found: 502.2355.



3ea

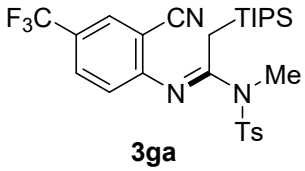
(*E*)-*N′*-(2-cyano-4-methoxyphenyl)-*N*-methyl-*N*-tosyl-2-(triisopropylsilyl)acetimidamide (3ea), white solid, m.p. 101-103 ^{o}C (95.6 mg, 93% yield). PE/EA = 10:1, R_f = 0.2. **^{1}H NMR** (500 MHz,

$CDCl_3$): δ 7.76 (d, J = 7.9 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.13-7.01 (m, 2H), 6.70 (d, J = 8.6 Hz ,1H), 3.78 (s, 3H), 3.11 (s, 3H), 2.74 (s, 2H), 2.40 (s, 3H), 1.12-1.04 (m, 3H), 0.95 (d, J = 7.3 Hz, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 163.7, 155.6, 145.2, 144.4, 133.8, 129.8, 127.9, 122.6, 121.0, 117.5, 116.5, 105.5, 56.0, 37.1, 21.7, 18.5, 17.6, 11.9. **HRMS** (ESI, m/z) Calculated for $[C_{27}H_{40}N_3O_3SSi, M + H]^+$: 514.2560, found: 514.2554.



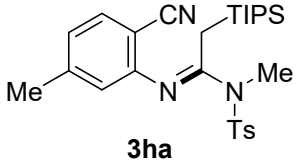
3fa

(*E*)-*N′*-(2-cyano-4-methylphenyl)-*N*-methyl-*N*-tosyl-2-(triisopropylsilyl)acetimidamide (3fa), white solid, m.p. 138-141 °C (94.6 mg, 95% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.77 (d, J = 8.2 Hz, 2H), 7.36 (s, 1H), 7.32 (d, J = 8.2 Hz, 2H), 7.29 (dd, J = 8.2, 1.6 Hz, 1H), 6.67 (d, J = 8.2 Hz, 1H), 3.12 (s, 3H), 2.72 (s, 2H), 2.41 (s, 3H), 2.31 (s, 3H), 1.13-1.03 (m, 3H), 0.95 (d, J = 7.3 Hz, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 163.3, 149.2, 144.4, 134.5, 133.9, 133.5, 133.3, 129.9, 127.9, 121.2, 117.8, 104.9, 37.1, 21.7, 20.6, 18.5, 17.6, 12.0. **HRMS** (ESI, m/z) Calculated for $[C_{27}H_{40}N_3O_2SSi, M + H]^+$: 498.2611, found: 498.2605.



3ga

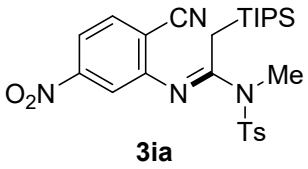
(*E*)-*N′*-(2-cyano-4-(trifluoromethyl)phenyl)-*N*-methyl-*N*-tosyl-2-(triisopropylsilyl)acetimidamide (3ga), white solid, m.p. 105-108 °C (102.3 mg, 98% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.82 (s, 1H), 7.77 (d, J = 8.3 Hz, 2H), 7.71 (dd, J = 8.5, 1.6 Hz ,1H), 7.34 (d, J = 8.0 Hz, 2H), 6.87 (d, J = 8.5 Hz, 1H), 3.17 (s, 3H), 2.67 (s, 2H), 2.43 (s, 3H), 1.13-1.05 (m, 3H), 0.94 (d, J = 7.3 Hz, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 163.4, 154.6, 144.7, 134.2, 130.4 (q, J = 3.8 Hz), 130.3 (q, J = 3.4 Hz), 130.0, 127.8, 125.8 (q, J = 34.0 Hz), 123.3 (q, J = 272.0 Hz), 122.2, 116.3, 105.3, 36.9, 21.7, 18.4, 17.5, 11.9. **^{19}F NMR** (471 MHz, $CDCl_3$): δ -62.45. **HRMS** (ESI, m/z) Calculated for $[C_{27}H_{37}F_3N_3O_2SSi, M + H]^+$: 552.2329, found: 552.2323.



3ha

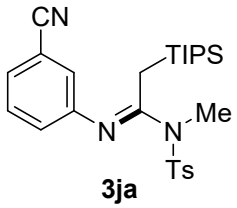
(*E*)-*N′*-(2-cyano-5-methylphenyl)-*N*-methyl-*N*-tosyl-2-(triisopropylsilyl)acetimidamide (3ha), white solid, m.p. 158-160 °C (89.6 mg, 90% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.79 (d, J = 8.2 Hz, 2H), 7.45 (d, J = 7.9 Hz, 1H), 7.34 (d, J = 8.2 Hz, 2H), 6.89 (d, J = 8.0 Hz, 1H), 6.57 (s, 1H), 3.12 (s, 3H), 2.69 (s, 2H), 2.41 (s, 3H), 2.35 (s, 3H), 1.14-1.06 (m, 3H),

0.96 (d, J = 7.3 Hz, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 163.0, 151.6, 144.6, 144.4, 134.0, 133.2, 129.9, 128.0, 124.6, 121.9, 117.9, 101.9, 37.1, 22.0, 21.7, 18.5, 17.6, 12.0. **HRMS** (ESI, m/z) Calculated for $[C_{27}H_{40}N_3O_2SSi, M + H]^+$: 498.2611, found: 498.2605.



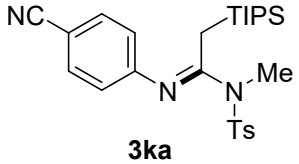
3ia

(*E*)-*N′*-(2-cyano-5-nitrophenyl)-*N*-methyl-*N*-tosyl-2-(triisopropylsilyl)acetimidamide (3ia), yellow solid, m.p. 48-51 °C (95.2 mg, 90% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.89 (dd, J = 8.3, 2.0 Hz, 1H), 7.78 (d, J = 8.3 Hz, 2H), 7.75 (d, J = 8.6 Hz, 1H), 7.55 (d, J = 1.9 Hz, 1H), 7.37 (d, J = 8.1 Hz, 2H), 3.19 (s, 3H), 2.68 (s, 2H), 2.44 (s, 3H), 1.13-1.05 (m, 3H), 0.95 (d, J = 7.4 Hz, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 164.4, 153.0, 150.6, 144.9, 134.4, 134.2, 130.1, 127.8, 117.5, 116.6, 115.9, 110.6, 37.0, 21.8, 18.4, 17.8, 12.0. **HRMS** (ESI, m/z) Calculated for $[C_{26}H_{37}N_4O_4SSi, M + H]^+$: 529.2307, found: 529.2300.



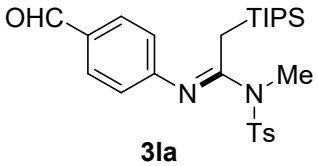
3ja

(*E*)-*N′*-(3-cyanophenyl)-*N*-methyl-*N*-tosyl-2-(triisopropylsilyl)acetimidamide (3ja), white solid, m.p. 78-80 °C (78.4 mg, 81% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.69 (d, J = 8.2 Hz, 2H), 7.36 (q, J = 7.8 Hz, 3H), 7.30 (d, J = 7.6 Hz, 1H), 6.85 (t, J = 8.3 Hz, 2H), 3.09 (s, 3H), 2.60 (s, 2H), 2.43 (s, 3H), 1.07-0.98 (m, 3H), 0.94 (d, J = 7.0 Hz, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 163.1, 149.5, 144.6, 133.7, 130.1, 129.8, 127.7, 127.0, 125.2, 123.8, 118.7, 113.0, 36.9, 21.7, 18.4, 17.4, 11.9. **HRMS** (ESI, m/z) Calculated for $[C_{26}H_{38}N_3O_2SSi, M + H]^+$: 484.2457, found: 484.2449.



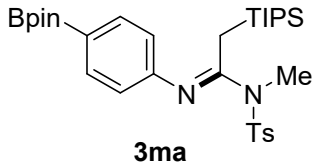
3ka

(*E*)-*N′*-(4-cyanophenyl)-*N*-methyl-*N*-tosyl-2-(triisopropylsilyl)acetimidamide (3ka), yellow solid, m.p. 108-109 °C (83.2 mg, 86% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.70 (d, J = 8.2 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 6.67 (d, J = 8.4 Hz, 2H), 3.08 (s, 3H), 2.59 (s, 2H), 2.43 (s, 3H), 1.07-1.00 (m, 3H), 0.94 (d, J = 7.1 Hz, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 152.8, 144.6, 133.8, 133.4, 129.8, 127.8, 121.2, 119.3, 106.6, 36.9, 21.7, 18.5, 17.7, 12.0. **HRMS** (ESI, m/z) Calculated for $[C_{26}H_{38}N_3O_2SSi, M + H]^+$: 484.2456, found: 484.2449.



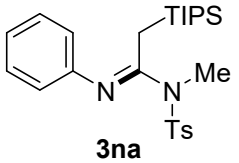
3la

(*E*)-*N′*-(4-formylphenyl)-*N*-methyl-*N*-tosyl-2-(triisopropylsilyl)acetimidamide (3la), yellow oil, (76.8 mg, 79% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.90 (s, 1H), 7.81 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 6.73 (d, J = 8.3 Hz, 2H), 3.09 (s, 3H), 2.62 (s, 2H), 2.43 (s, 3H), 1.09-1.01 (m, 3H), 0.93 (d, J = 7.2 Hz, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 191.3, 161.9, 154.5, 144.5, 133.7, 132.1, 131.4, 129.8, 127.8, 120.9, 37.0, 21.8, 18.5, 17.9, 12.0. **HRMS** (ESI, m/z) Calculated for $[C_{26}H_{39}N_2O_3SSi, M + H]^+$: 487.2452, found: 487.2445.



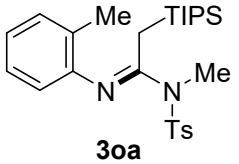
3ma

(*E*)-*N*-methyl-*N′*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-*N*-tosyl-2-(triisopropylsilyl)acetimidamide (3ma), yellow oil, (96.9 mg, 83% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.70 (d, J = 7.4 Hz, 4H), 7.31 (d, J = 8.1 Hz, 2H), 6.62 (d, J = 8.1 Hz, 2H), 3.04 (s, 3H), 2.64 (s, 2H), 2.40 (s, 3H), 1.34 (s, 12H), 1.08-1.01 (m, 3H), 0.94 (d, J = 7.1 Hz, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 161.9, 151.4, 144.2, 135.9, 133.2, 129.6, 128.0, 119.6, 83.8, 37.0, 25.0, 21.7, 18.5, 17.9, 11.9. **HRMS** (ESI, m/z) Calculated for $[C_{31}H_{50}BN_2O_4SSi, M + H]^+$: 585.3355, found: 585.3348.



3na

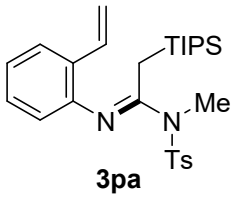
(*E*)-*N*-methyl-*N′*-phenyl-*N*-tosyl-2-(triisopropylsilyl)acetimidamide (3na), colorless oil, (89.8 mg, 98% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.66 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.22 (t, J = 7.7 Hz, 2H), 6.96 (t, J = 7.4 Hz, 1H), 6.59 (d, J = 7.7 Hz, 2H), 3.02 (s, 3H), 2.64 (s, 2H), 2.35 (s, 3H), 1.05-0.99 (m, 3H), 0.90 (d, J = 7.2 Hz, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 162.0, 148.7, 144.2, 133.3, 129.6, 129.1, 127.9, 123.5, 120.3, 37.0, 21.7, 18.5, 17.5, 11.9. **HRMS** (ESI, m/z) Calculated for $[C_{25}H_{39}N_2O_2SSi, M + H]^+$: 459.2509, found: 459.2496.



3oa

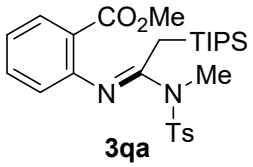
(*E*)-*N*-methyl-*N′*-(o-tolyl)-*N*-tosyl-2-(triisopropylsilyl)acetimidamide (3oa), white solid, m.p. 50-54 °C (93.6 mg, 99% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.74 (d, J =

7.9 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.10 (t, *J* = 7.5 Hz, 2H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.57 (d, *J* = 7.6 Hz, 1H), 3.16 (s, 3H), 2.61 (s, 2H), 2.40 (s, 3H), 1.97 (s, 3H), 1.10-1.04 (m, 3H), 0.95 (d, *J* = 7.2 Hz, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): *δ* 160.5, 146.9, 144.1, 134.1, 130.7, 129.7, 128.6, 127.9, 126.5, 123.7, 119.7, 37.0, 21.7, 18.5, 18.2, 17.2, 11.9. **HRMS** (ESI, m/z) Calculated for [$C_{26}H_{41}N_2O_2SSi$, M + H]$^+$: 473.2661, found: 473.2653.



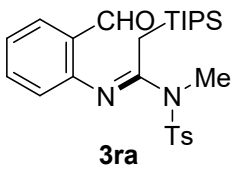
3pa

(*E*)-*N*-methyl-*N*-tosyl-2-(triisopropylsilyl)-*N′*-(2-vinylphenyl)acetimidamide (3pa), yellow solid, m.p. 48-52 °C (95.1 mg, 98% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* 7.76 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.57 (d, *J* = 7.8 Hz, 1H), 6.41 (q, *J* = 11.1 Hz, 1H), 5.57 (d, *J* = 17.7 Hz, 1H), 5.09 (d, *J* = 11.0 Hz, 1H), 3.20 (s, 3H), 2.58 (s, 2H), 2.42 (s, 3H), 1.07-1.00 (m, 3H), 0.92 (d, *J* = 7.3 Hz, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): *δ* 161.0, 145.9, 144.2, 134.4, 133.4, 129.7, 128.8, 128.5, 127.8, 125.7, 123.8, 120.5, 113.6, 36.9, 21.7, 18.5, 17.2, 11.9. **HRMS** (ESI, m/z) Calculated for [$C_{27}H_{41}N_2O_2SSi$, M + H]$^+$: 485.2661, found: 485.2653.



3qa

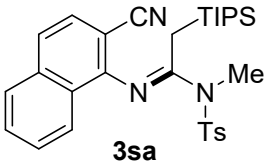
Methyl(*E*)-2-((1-((*N*,4-dimethylphenyl)sulfonamido)-2(triisopropylsilyl)ethylidene)amino)benzoate (3qa), yellow solid, m.p. 43-50 °C (83.7 mg, 81% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* 7.88 (d, *J* = 7.9 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.49-7.38 (m, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.57 (d, *J* = 8.0 Hz, 1H), 3.76 (s, 3H), 3.16 (s, 3H), 2.60 (s, 2H), 2.40 (s, 3H), 1.06-0.99 (m, 3H), 0.92 (d, *J* = 7.2 Hz, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): *δ* 166.5, 159.9, 148.9, 144.1, 134.2, 133.1, 131.6, 129.7, 128.0, 123.3, 121.5, 121.3, 51.9, 36.9, 21.7, 18.5, 17.5, 11.8. **HRMS** (ESI, m/z) Calculated for [$C_{27}H_{41}N_2O_4SSi$, M + H]$^+$: 517.2564, found: 517.2551.



3ra

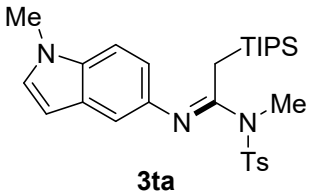
(*E*)-*N′*-(2-formylphenyl)-*N*-methyl-*N*-tosyl-2-(triisopropylsilyl)acetimidamide (3ra), yellow solid, m.p. 78-80 °C (81.8 mg, 84% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* 9.78 (s, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.33 (d, 8.2

Hz, 2H), 7.11 (t, *J* = 7.7 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 3.19 (s, 3H), 2.60 (s, 2H), 2.42 (s, 3H), 1.02-0.96 (m, 3H), 0.90 (d, *J* = 7.2 Hz, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): *δ* 190.7, 162.0, 151.0, 144.6, 135.1, 134.4, 129.8, 128.5, 127.7, 126.7, 123.9, 121.2, 36.8, 21.7, 18.4, 17.3, 12.0. **HRMS** (ESI, m/z) Calculated for $[C_{26}H_{39}N_2O_3SSi, M + H]^+$: 487.25453, found: 487.2445.



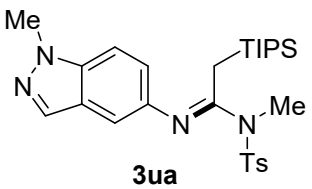
3sa

(*E*)-*N′*-(2-cyanonaphthalen-1-yl)-*N*-methyl-*N*-tosyl-2-(triisopropylsilyl)acetimidamide (3sa), white solid, m.p. 121-123 °C (93.8 mg, 88% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* 7.90 (d, *J* = 8.2 Hz, 2H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.69 (d, *J* = 8.5 Hz, 1H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.54-7.41 (m, 3H), 7.35 (d, *J* = 8.2 Hz, 2H), 3.41 (s, 3H), 2.61 (d, *J* = 13.0 Hz, 1H), 2.46 (d, *J* = 13.1 Hz, 1H), 2.43 (s, 3H), 0.93-0.87 (m, 3H), 0.85 (d, *J* = 6.6 Hz, 9H), 0.72 (d, *J* = 7.0 Hz, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): *δ* 162.2, 150.8, 144.4, 135.8, 129.9, 129.2, 128.1, 126.8, 126.6, 126.3, 125.0, 123.6, 118.7, 97.5, 36.8, 25.0, 21.7, 18.5, 18.3, 17.1, 11.8. **HRMS** (ESI, m/z) Calculated for $[C_{30}H_{40}N_3O_2SSi, M + H]^+$: 505.2599, found: 534.2605.



3ta

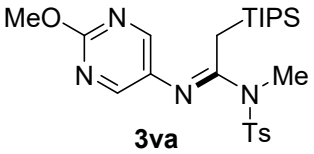
(*E*)-*N*-methyl-*N*′-(1-methyl-1*H*-indol-5-yl)-*N*-tosyl-2-(triisopropylsilyl)acetimidamide (3ta), yellow solid, m.p. 103-105 °C (50.1 mg, 49% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* 7.74 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 1H), 7.01 (d, *J* = 2.7 Hz, 1H), 6.86 (s, 1H), 6.57 (d, *J* = 8.5 Hz, 1H), 6.39 (d, *J* = 2.5 Hz, 1H), 3.76 (s, 3H), 3.07 (s, 3H), 2.76 (s, 2H), 2.39 (s, 3H), 1.08-1.01 (m, 3H), 0.92 (d, *J* = 7.3 Hz, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): *δ* 161.9, 144.0, 141.3, 134.1, 133.1, 129.6, 129.4, 129.0, 128.2, 115.7, 111.1, 109.6, 100.7, 37.0, 33.1, 21.7, 18.6, 17.8, 11.9. **HRMS** (ESI, m/z) Calculated for $[C_{28}H_{42}N_3O_2SSi, M + H]^+$: 512.2773, found: 512.2762.



3ua

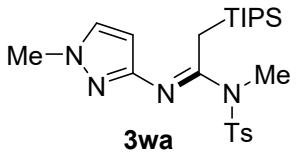
(*E*)-*N*-methyl-*N′*-(1-methyl-1*H*-indazol-5-yl)-*N*-tosyl-2-(triisopropylsilyl)acetimidamide (3ua), white oil, (41.0 mg, 40% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* 7.89 (s, 1H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 3H), 6.92 (d, *J* = 1 Hz, 1H), 6.76 (dd, *J* = 8.8, 1.7

Hz, 1H), 4.05 (s, 3H), 3.08 (s, 3H), 2.73 (s, 2H), 2.40 (s, 3H), 1.06-0.99 (m, 3H), 0.91 (d, J = 7.2 Hz, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 162.7, 144.2, 142.3, 137.5, 133.3, 132.4, 129.6, 128.0, 124.5, 121.6, 110.2, 109.5, 36.9, 35.8, 21.7, 18.5, 17.7, 11.9. **HRMS** (ESI, m/z) Calculated for $[C_{27}H_{41}N_4O_2SSi, M + H]^+$: 513.2718, found: 513.2714.



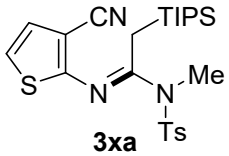
3va

(*E*)-*N′*-(2-methoxypyrimidin-5-yl)-*N*-methyl-*N*-tosyl-2-(triisopropylsilyl)acetimidamide (3va), yellow solid, m.p. 102-103 °C (96.0 mg, 98% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.86 (s, 2H), 7.65 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 3.93 (s, 3H), 3.07 (s, 3H), 2.63 (s, 2H), 2.38 (s, 3H), 1.04-0.97 (m, 3H), 0.92 (d, J = 6.9 Hz, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 164.8, 162.3, 150.9, 144.5, 137.6, 133.3, 129.7, 127.6, 55.0, 36.9, 21.6, 18.3, 17.5, 11.9. **HRMS** (ESI, m/z) Calculated for $[C_{24}H_{39}N_4O_3SSi, M + H]^+$: 491.2512, found: 491.2507.



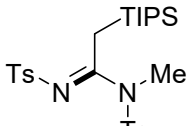
3wa

(*E*)-*N*-methyl-*N′*-(1-methyl-1*H*-pyrazol-3-yl)-*N*-tosyl-2-(triisopropylsilyl)acetimidamide (3wa), yellow oil, (89.8 mg, 97% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.64 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 2.1 Hz, 1H), 5.7 (d, J = 2.1 Hz, 1H), 3.74 (s, 3H), 3.03 (s, 2H), 3.01 (s, 3H), 2.34 (s, 3H), 1.10-1.03 (m, 3H), 0.96 (d, J = 7.1 Hz, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 164.1, 155.4, 143.9, 133.6, 130.7, 129.5, 128.0, 99.2, 39.0, 36.8, 21.6, 18.8, 18.5, 11.9. **HRMS** (ESI, m/z) Calculated for $[C_{23}H_{39}N_4O_2SSi, M + H]^+$: 463.2568, found: 463.2558.



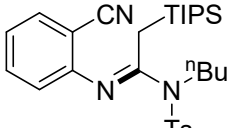
3xa

(*E*)-*N′*-(3-cyanothiophen-2-yl)-*N*-methyl-*N*-tosyl-2-(triisopropylsilyl)acetimidamide (3xa), green oil, (79.4 mg, 81% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.72 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 6.96 (d, J = 5.8 Hz, 1H), 6.91 (d, J = 5.8 Hz, 1H), 3.09 (s, 3H), 3.00 (s, 2H), 2.41 (s, 3H), 1.18-1.10 (m, 3H), 1.01 (d, J = 7.3 Hz, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 166.0, 160.8, 144.7, 133.5, 130.0, 127.8, 126.9, 119.4, 115.1, 99.0, 36.9, 21.7, 18.5, 12.2. **HRMS** (ESI, m/z) Calculated for $[C_{24}H_{36}N_3O_2S_2Si, M + H]^+$: 490.2018, found: 490.2013.



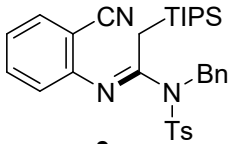
3ya

(*E*)-*N*-methyl-*N*, *N′*-ditosyl-2-(triisopropylsilyl)acetimidamide (3ya), white solid, m.p. 93-95 °C (94.5 mg, 88% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.65 (d, J = 8.2 Hz, 2H), 7.45 (d, J = 8.3 Hz, 2H), 7.24 (d, J = 8.1 Hz, 2H), 7.09 (d, J = 8.1 Hz, 2H), 3.18 (s, 3H), 3.13 (s, 2H), 2.43 (s, 3H), 2.37 (s, 3H), 1.47-1.37 (m, 3H), 1.13 (d, J = 7.5 Hz, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 172.0, 144.7, 142.9, 139.6, 134.6, 129.5, 129.2, 128.0, 126.7, 36.1, 22.2, 21.7, 21.6, 18.8, 12.4. **HRMS** (ESI, m/z) Calculated for $[C_{26}H_{41}N_2O_4S_2Si, M + H]^+$: 537.2281, found: 537.2272.



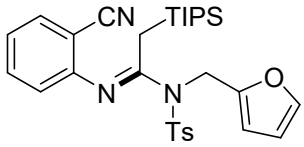
3ab

(*E*)-*N*-butyl-*N′*-(2-cyanophenyl)-*N*-tosyl-2-(triisopropylsilyl)acetimidamide (3ab), colorless oil, (95.5 mg, 91% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.80 (d, J = 8.3 Hz, 2H), 7.54 (dd, J = 7.8, 1.1 Hz, 1H), 7.46 (td, J = 8.2, 1.5 Hz, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.04 (td, J = 7.7, 0.9 Hz, 1H), 6.82 (d, J = 8.0 Hz, 1H), 3.77 (t, J = 7.9 Hz, 2H), 2.41 (s, 3H), 2.38 (s, 2H), 1.86-1.70 (m, 2H), 1.39-1.28 (m, 2H), 1.11-1.03 (m, 3H), 0.92 (t, J = 3.8 Hz, 21H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 159.9, 151.8, 144.0, 137.0, 133.5, 133.3, 129.6, 128.0, 123.0, 121.9, 117.8, 104.2, 48.7, 31.1, 21.7, 20.4, 18.7, 16.3, 13.8, 12.1. **HRMS** (ESI, m/z) Calculated for $[C_{29}H_{44}N_3O_2SSi, M + H]^+$: 526.2923, found: 526.2927.



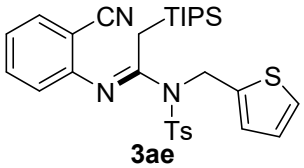
3ac

(*E*)-*N*-benzyl-*N′*-(2-cyanophenyl)-*N*-tosyl-2-(triisopropylsilyl)acetimidamide (3ac), white solid, m.p. 93-96 °C 100.8 mg, 95% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.67 (d, J = 8.2 Hz, 2H), 7.50 (d, J = 7.7 Hz, 1H), 7.40 (t, J = 6.3 Hz, 3H), 7.28-7.17 (m, 5H), 7.01 (t, J = 7.5 Hz, 1H), 6.71 (d, J = 8.2 Hz, 1H), 4.98 (s, 2H), 2.35 (s, 3H), 2.31 (s, 2H), 0.93-0.85 (m, 3H), 0.75 (d, J = 7.3 Hz, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 159.6, 151.5, 144.2, 136.5, 136.3, 133.5, 133.4, 129.5, 129.1, 128.4, 127.7, 123.1, 122.3, 117.8, 103.6, 51.2, 21.7, 18.5, 16.4, 12.1. **HRMS** (ESI, m/z) Calculated for $[C_{32}H_{42}N_3O_2SSi, M + H]^+$: 560.2770, found: 560.2762.



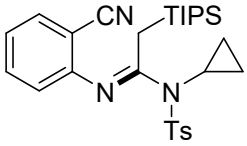
3ad

(*E*)-*N′*-(2-cyanophenyl)-*N*-(furan-2-ylmethyl)-*N*-tosyl-2-(triisopropylsilyl)acetimidamide (3ad), white oil, (101.2 mg, 92% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.65 (d, J = 8.0 Hz, 2H), 7.54 (d, J = 7.7 Hz, 1H), 7.46 (t, J = 7.8 Hz, 1H), 7.34 (s, 1H), 7.22 (d, J = 8.0 Hz, 2H), 7.06 (t, J = 7.6 Hz, 1H), 6.81 (d, J = 8.1 Hz, 1H), 6.38 (d, J = 2.8 Hz, 1H), 6.29 (s, 1H), 5.04 (s, 2H), 2.43 (s, 2H), 2.38 (s, 3H), 1.05-0.97 (m, 3H), 0.88 (d, J = 7.4 Hz, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 159.6, 151.3, 149.7, 144.0, 142.3, 136.5, 133.5, 133.3, 129.5, 128.1, 123.2, 122.0, 117.5, 110.54, 110.51, 104.0, 44.4, 21.6, 18.5, 16.4, 12.0. **HRMS** (ESI, m/z) Calculated for [$C_{30}H_{40}N_3O_3SSi$, M + H]$^+$: 550.2564, found: 550.2554.



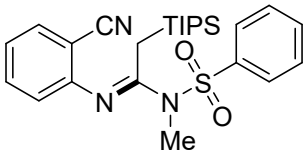
3ae

(*E*)-*N′*-(2-cyanophenyl)-*N*-(thiophen-2-ylmethyl)-*N*-tosyl-2-(triisopropylsilyl)acetimidamide (3ae), white solid, m.p. 115-116 ^{o}C (104.1 mg, 92% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.59 (d, J = 7.7 Hz, 1H), 7.48 (d, J = 8.3 Hz, 3H), 7.16 (q, J = 8.6 Hz, 4H), 7.09 (t, J = 7.6 Hz, 1H), 6.89 (q, J = 3.7 Hz, 1H), 6.82 (d, J = 8.1 Hz, 1H), 5.31 (s, 2H), 2.51 (s, 2H), 2.37 (s, 3H), 1.11-1.03 (m, 3H), 0.88 (d, J = 7.4 Hz, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 160.2, 151.2, 144.1, 138.4, 137.0, 133.6, 133.4, 129.7, 127.5, 127.1, 126.0, 123.3, 122.1, 117.8, 104.6, 47.5, 21.7, 18.6, 16.4, 12.2. **HRMS** (ESI, m/z) Calculated for [$C_{30}H_{40}N_3O_2S_2Si$, M + H]$^+$: 566.2335, found: 566.2326.



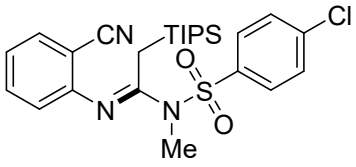
3af

(*E*)-*N′*-(2-cyanophenyl)-*N*-cyclopropyl-*N*-tosyl-2-(triisopropylsilyl)acetimidamide (3af), white solid, m.p. 98-102 ^{o}C (93.8 mg, 92% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.84 (d, J = 6.5 Hz, 2H), 7.57 (d, J = 7.8 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.29 (d, J = 8.1 Hz, 2H), 7.09 (t, J = 7.6 Hz, 1H), 6.92 (d, J = 8.1 Hz, 1H), 2.54 (s, 2H), 2.40 (s, 4H), 1.10 (s, 3H), 0.99 (d, J = 6.8 Hz, 18H), 0.87 (d, J = 5.3 Hz, 4H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 151.6, 144.3, 135.5, 133.5, 133.2, 129.5, 128.4, 123.6, 121.1, 117.8, 105.0, 31.1, 21.7, 18.8, 11.9, 9.3. **HRMS** (ESI, m/z) Calculated for [$C_{28}H_{40}N_3O_2SSi$, M + H]$^+$: 510.2612, found: 510.2605.



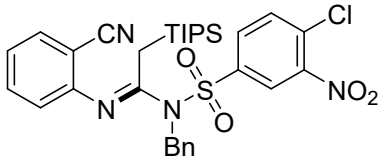
3ag

(*E*)-*N'*-(2-cyanophenyl)-*N*-methyl-*N*-(phenylsulfonyl)-2-(triisopropylsilyl)acetimidamide (3ag), white solid, m.p. 103-105 °C (79.9 mg, 85% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.90 (d, J = 7.4 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.58-7.51 (m, 3H), 7.50-7.44 (m, 1H), 7.08 (t, J = 7.6 Hz, 1H), 6.75 (d, J = 8.1 Hz, 1H), 3.16 (s, 3H), 2.71 (s, 2H), 1.13-1.05 (m, 3H), 0.94 (d, J = 7.4 Hz, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 162.9, 151.4, 136.9, 133.6, 133.5, 133.3, 129.3, 127.8, 123.6, 121.3, 117.5, 104.9, 37.1, 18.5, 17.5, 11.9. **HRMS** (ESI, m/z) Calculated for $[C_{25}H_{36}N_3O_2SSi, M + H]^+$: 470.2300, found: 470.2292.



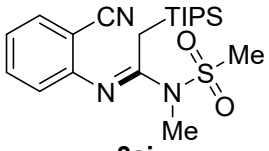
3ah

(*E*)-*N*-((4-chlorophenyl)sulfonyl)-*N'*-(2-cyanophenyl)-*N*-methyl-2-(triisopropylsilyl)acetimidamide (3ah), white solid, m.p. 144-150 °C (92.7 mg, 92% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.85 (d, J = 8.5 Hz, 2H), 7.58 (d, J = 7.7 Hz, 1H), 7.51 (d, J = 8.6 Hz, 2H), 7.49 (d, J = 8.1 Hz, 1H), 7.10 (t, J = 7.6 Hz, 1H), 6.80 (d, J = 8.1 Hz, 1H), 3.15 (s, 3H), 2.66 (s, 2H), 1.11-1.04 (m, 3H), 0.94 (d, J = 7.3 Hz, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 162.9, 151.3, 140.1, 135.3, 133.7, 133.4, 129.6, 129.5, 123.8, 121.4, 117.6, 104.6, 37.1, 18.5, 17.6, 11.9. **HRMS** (ESI, m/z) Calculated for $[C_{25}H_{35}ClN_3O_2SSi, M +H]^+$: 504.1910, found: 504.1903.



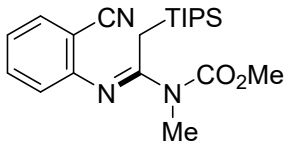
3ai

(*E*)-*N*-benzyl-*N*-((4-chloro-3-nitrophenyl)sulfonyl)-*N'*-(2-cyanophenyl)-2-(triisopropylsilyl)acetimidamide (3ai), white solid, m.p. 126-130 °C (116.3 mg, 93% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.00 (d, J = 1.7 Hz, 1H), 7.72 (dd, J = 8.2, 1.4 Hz ,1H), 7.56 (d, J = 7.7 Hz, 1H), 7.53 (t, J = 7.8 Hz, 1H), 7.46 (d, J = 8.5 Hz, 1H), 7.40-7.28 (m, 5H), 7.12 (t, J = 7.6 Hz, 1H), 6.94 (d, J = 8.1 Hz, 1H), 5.16 (s, 2H), 2.16 (s, 2H), 1.08-1.01 (m, 3H), 0.89 (d, J = 7.4 Hz, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 159.3, 150.7, 147.0, 139.7, 135.2, 133.8, 133.3, 133.1, 131.9, 131.8, 129.0, 128.4, 127.9, 126.8, 123.7, 122.1, 117.5, 103.5, 51.4, 18.5, 15.4, 11.9. **HRMS** (ESI, m/z) Calculated for $[C_{31}H_{38}ClN_4O_4SSi, M + H]^+$: 625.2073, found: 625.2066.



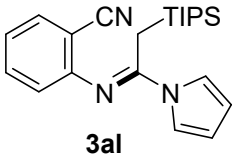
3aj

(*E*)-*N′*-(2-cyanophenyl)-*N*-methyl-*N*-(methylsulfonyl)-2-(triisopropylsilyl)acetimidamide (3aj), white solid, m.p. 75-78 °C (63.6 mg, 78% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.60 (d, J = 7.7 Hz, 1H), 7.52 (t, J = 7.6 Hz, 1H), 7.11 (t, J = 7.6 Hz, 1H), 6.95 (d, J = 8.1 Hz, 1H), 3.33 (s, 3H), 3.17 (s, 3H), 2.43 (s, 2H), 1.10-1.01 (m, 3H), 0.92 (d, J = 7.4 Hz, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 163.2, 151.8, 133.8, 133.1, 123.6, 121.8, 117.8, 103.9, 38.3, 36.5, 18.4, 17.0, 11.9. **HRMS** (ESI, m/z) Calculated for $[C_{20}H_{34}N_3O_2SSi, M + H]^+$: 408.2145, found: 408.2136.



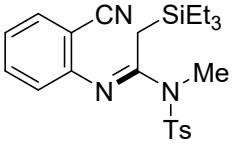
3ak

methyl(*E*)-(1-((2-cyanophenyl)imino)-2-(triisopropylsilyl)ethyl)(methyl)carbamate (3ak), white solid, m.p. 88-91 °C (69.1 mg, 89% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.59 (d, J = 7.7 Hz, 1H), 7.49 (t, J = 7.7 Hz, 1H), 7.07 (t, J = 7.6 Hz, 1H), 6.90 (d, J = 5.6 Hz, 1H), 3.79 (s, 3H), 3.40 (s, 3H), 2.84 (s, 2H), 0.91 (s, 21H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 152.3, 133.5, 133.3, 123.2, 121.5, 117.8, 53.4, 35.3, 18.5, 15.4, 11.9. **HRMS** (ESI, m/z) Calculated for [$C_{21}H_{34}N_3O_2Si, M + H]^+$: 388.2419, found: 388.2415.



3al

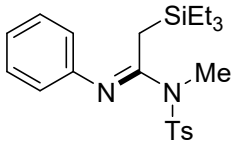
(*E*)-2-((1-(1*H*-pyrrol-1-yl)-2-(triisopropylsilyl)ethylidene)amino)benzonitrile (3al), white solid, m.p. 99-103 °C (71.7 mg, 98% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.63 (d, J = 7.6 Hz, 1H), 7.53 (t, J = 7.7 Hz, 1H), 7.44 (s, 2H), 7.11 (t, J = 7.6 Hz, 1H), 6.97 (d, J = 7.9 Hz, 1H), 6.29 (s, 2H), 2.39 (s, 2H), 1.03-0.95 (m, 3H), 0.85 (d, J = 7.2 Hz, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 156.9, 152.4, 133.7, 133.5, 123.3, 121.8, 119.7, 117.6, 112.0, 105.2, 18.3, 13.2, 11.7. **HRMS** (ESI, m/z) Calculated for $[C_{22}H_{32}N_3Si, M + H]^+$: 366.2366, found: 366.2360.



3am

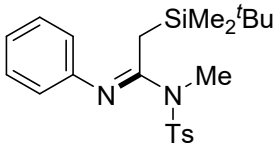
(*E*)-*N′*-(2-cyanophenyl)-*N*-methyl-*N*-tosyl-2-(triethylsilyl)acetimidamide (3am), white solid, m.p. 103-107 °C (62.8 mg, 71% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): 7.78

(d, *J* = 8.3 Hz, 2H), 7.57 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.48 (td, *J* = 8.1, 1.4 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 8.1 Hz, 1H), 3.18 (s, 3H), 2.60 (s, 2H), 2.42 (s, 3H), 0.80 (t, *J* = 7.9 Hz, 9H), 0.57 (q, *J* = 7.7 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$): *δ* 162.5, 151.9, 144.4, 134.6, 133.5, 133.2, 130.0, 127.7, 123.5, 121.5, 117.6, 104.9, 36.6, 21.7, 20.0, 7.1, 4.1. **HRMS** (ESI, m/z) Calculated for $[C_{23}H_{32}N_3O_2SSi, M + H]^+$: 442.1987, found: 442.1979.



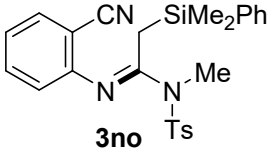
3nm

(*E*)-*N*-methyl-*N′*-phenyl-*N*-tosyl-2-(triethylsilyl)acetimidamide (3nm), yellow oil, (73.2 mg, 88% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* 7.72 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.27 (t, *J* = 7.9 Hz, 2H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.59 (d, *J* = 7.5 Hz, 2H), 3.10 (s, 3H), 2.55 (s, 2H), 2.42 (s, 3H), 0.83 (t, *J* = 8.0 Hz, 9H), 0.54 (q, *J* = 7.8 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$): *δ* 161.0, 149.0, 144.2, 134.1, 129.7, 129.1, 127.8, 123.4, 120.2, 36.5, 21.7, 20.1, 7.2, 4.1. **HRMS** (ESI, m/z) Calculated for $[C_{22}H_{33}N_2O_2SSi, M + H]^+$: 417.2034, found: 417.2027.



3nn

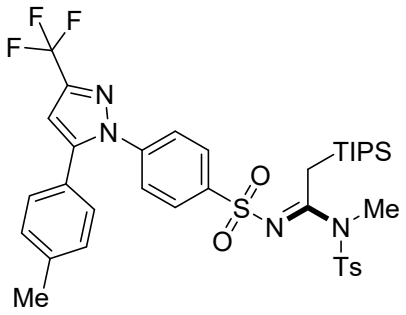
(*E*)-2-(tert-butyldimethylsilyl)-*N*-methyl-*N′*-phenyl-*N*-tosylacetimidamide (3nn), white solid, m.p. 88-90 °C (81.7 mg, 98% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* 7.73 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.27 (t, *J* = 7.7 Hz, 2H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.59 (d, *J* = 7.4 Hz, 2H), 3.07 (s, 3H), 2.61 (s, 2H), 2.42 (s, 3H), 0.72 (s, 9H), 0.06 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$): *δ* 161.5, 148.9, 144.2, 133.6, 129.6, 129.1, 127.9, 123.5, 120.2, 36.6, 26.1, 21.7, 20.8, 17.0, -4.9. **HRMS** (ESI, m/z) Calculated for $[C_{22}H_{33}N_2O_2SSi, M + H]^+$: 417.2033, found: 417.2027.



3no

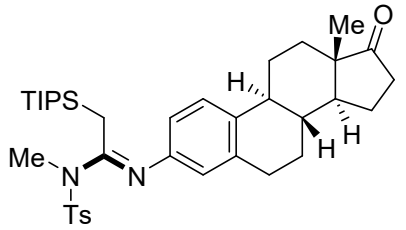
(*E*)-*N′*-(2-cyanophenyl)-2-(dimethyl(phenyl)silyl)-*N*-methyl-*N*-tosylacetimidamide (3no), colorless oil (61.8 mg, 67% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* 7.78 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.39-7.32 (m, 5H), 7.31-7.22 (m, 3H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.29 (d, *J* = 8.0 Hz, 1H), 3.10 (s, 3H), 2.79 (s, 2H), 2.42 (s, 3H), 0.41 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$): *δ* 161.2, 151.6, 144.5, 137.2, 134.7, 133.7, 133.3, 133.0, 130.1, 129.6, 128.1, 127.7, 123.3, 121.4, 117.6, 104.5, 36.4, 24.5, 21.7, -2.1. **HRMS** (ESI, m/z) Calculated for [$C_{25}H_{28}N_3O_2SSi$,

M + H]$^+$: 462.1665, found: 462.1666.



5

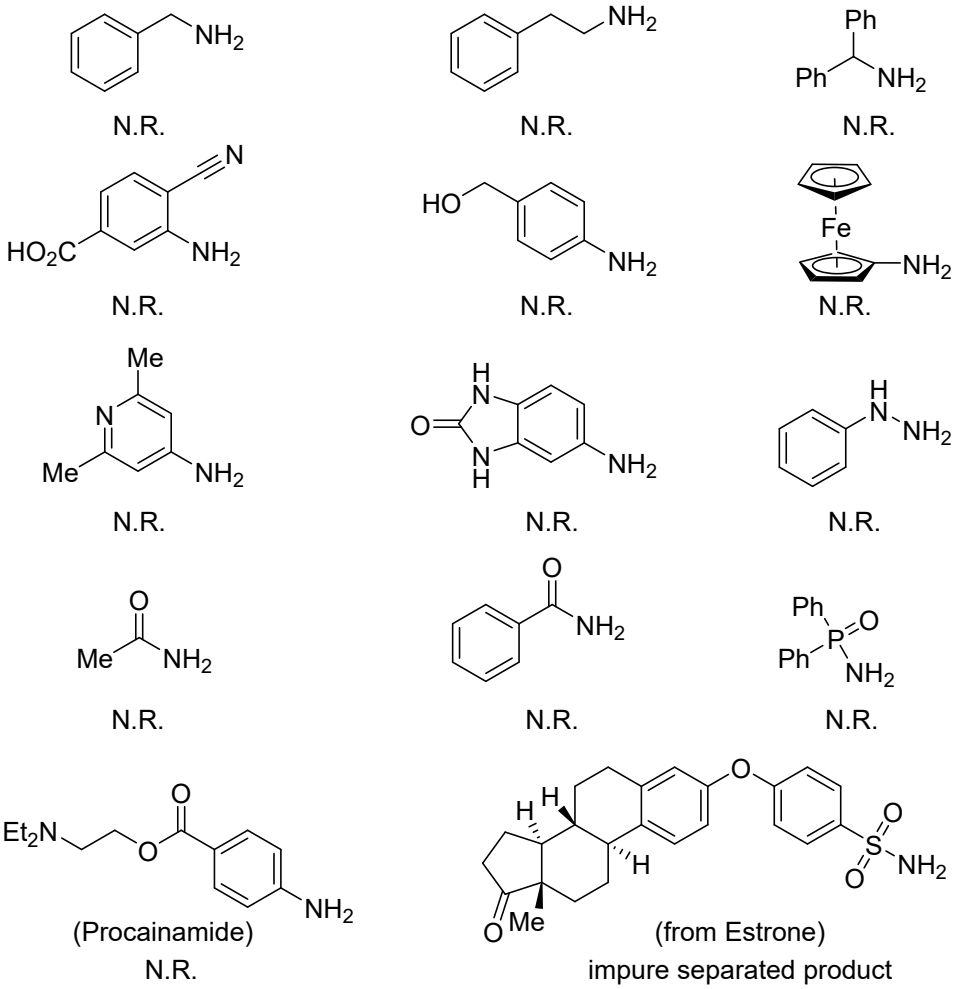
(*E*)-*N*-methyl-*N′*-((4-(5-(p-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)phenyl)sulfonyl)-*N*-tosyl-2-(triisopropylsilyl)acetimidamide (5), white solid, m.p. 74-79 °C (131.5 mg, 88% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.75 (d, J = 8.6 Hz, 2H), 7.41 (t, J = 9.4 Hz, 4H), 7.16-7.08 (m, 6H), 6.75 (s, 1H), 3.23 (s, 3H), 3.08 (s, 2H), 2.36 (d, J = 10.1 Hz, 6H), 1.44-1.37 (m, 3H), 1.12 (d, J = 7.5 Hz, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 172.3, 145.3, 145.1, 144.1 (q, J = 38.5 Hz), 142.2, 141.9, 139.8, 134.8, 129.9, 129.6, 128.8, 127.9, 127.7, 125.9, 125.2, 121.2 (q, J = 269.1 Hz), 106.2, 36.0, 22.2, 21.6, 21.4, 18.7, 12.4. **^{19}F NMR** (471 MHz, $CDCl_3$): δ -62.39. **HRMS** (ESI, m/z) Calculated for [$C_{36}H_{46}F_3N_4O_4S_2Si$, M + H]$^+$: 747.2685, found: 747.2677.



6

(*E*)-*N*-methyl-*N′*-((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl)-*N*-tosyl-2-(triisopropylsilyl)acetimidamide (6), white solid, m.p. 59-63 °C (108.0 mg, 85% yield). PE/EA = 10:1, R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.70 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 7.17 (d, J = 8.1 Hz, 1H), 6.38 (t, J = 8.4 Hz, 2H), 3.04 (s, 3H), 2.83 (t, J = 4.8 Hz, 2H), 2.64 (s, 2H), 2.50 (q, J = 8.7 Hz, 1H), 2.40 (s, 3H), 2.25 (s, 1H), 2.19-2.10 (m, 1H), 2.09-1.92 (m, 3H), 1.72-1.35 (m, 7H), 1.07-1.01 (m, 3H), 0.94 (d, J = 6.9 Hz, 18H), 0.91 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 161.9, 146.6, 144.1, 137.2, 135.0, 133.4, 129.6, 128.0, 126.0, 120.6, 117.6, 50.6, 48.1, 44.2, 38.5, 36.9, 36.0, 31.7, 29.6, 26.6, 26.1, 21.7, 18.5, 17.5, 14.0, 12.0. **HRMS** (ESI, m/z) Calculated for [$C_{37}H_{55}N_2O_3SSi$, M + H]$^+$: 635.3701, found: 635.3697.

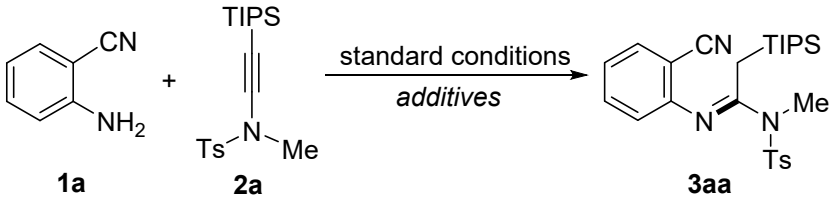
5. Failed Examples of Substrate 1 with 2a



Note: N.R. = no reaction

Figure S2. Failed Examples of Substrate **1**

6. Control Experiments



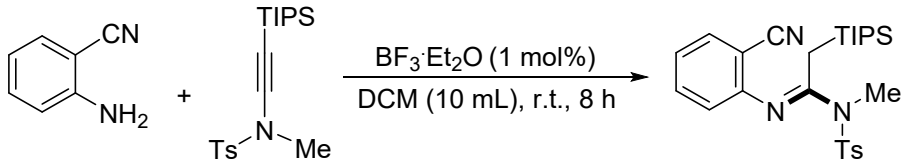
Following the typical procedure for α-silylmethylamidines, a pre-dried 10.0 mL Schlenk tube was charged with stirring bar, $BF_3{\cdot}Et_2O$ (1.3 μL, 0.01 mmol, 0.05 eq.), 2-aminobenzonitrile (**1a**, 35.4 mg, 0.3 mmol, 1.5 eq.), *N*,4-dimethyl-*N*-((triisopropylsilyl)ethynyl)benzenesulfonamide (**2a**, 73.1 mg, 0.2 mmol, 1 eq.), 2,2,6,6-tetramethylpiperidinyloxyl (TEMPO, 3.1 mg, 0.02 mmol, 0.1 eq.) and DCM (1.0 mL) under N_2 atmosphere. The mixture was stirred at rt for 8 h. Solvent was removed by rotary evaporation instrument and 1,3,5-trimethoxybenzene as the internal reference was added. The NMR yield (92%) is 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 = 10:1, R_f = 0.20) to give the analytical pure product **3aa** (87.9 mg, 91 % yield).

Following the typical procedure for α-silylmethylamidines, a pre-dried 10.0 mL Schlenk tube was charged with stirring bar, $BF_3{\cdot}Et_2O$ (1.3 μL, 0.01 mmol, 0.05 eq.), 2-aminobenzonitrile (**1a**, 35.4 mg, 0.3 mmol, 1.5 eq.), *N*,4-dimethyl-*N*-((triisopropylsilyl)ethynyl)benzenesulfonamide (**2a**, 73.1 mg, 0.2 mmol, 1 eq.), 2,2,6,6-tetramethylpiperidinyloxyl (TEMPO, 15.6 mg, 0.1 mmol, 0.5 eq.) and DCM (1.0 mL) under N_2 atmosphere. The mixture was stirred at rt for 8 h. Solvent was removed by rotary evaporation instrument and 1,3,5-trimethoxybenzene as the internal reference was added. The NMR yield (82%) is 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 = 10:1, R_f = 0.20) to give the analytical pure product **3aa** (77.3 mg, 80 % yield).

7. Large-Scale Experiment and Product Transformation

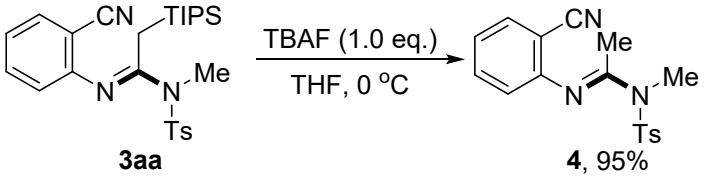
(a) Large-scale experiment



1a, 3 mmol **2a**, 2 mmol **3aa**, 86%, 0.83 g

A pre-dried 50.0 mL Schlenk tube was charged with stirring bar, $BF_3{\cdot}Et_2O$ (2.5 μL, 0.02 mmol, 0.01 eq.), 2-aminobenzonitrile (**1a**, 354.4 mg, 3 mmol, 1.5 eq.), *N*,4-dimethyl-*N*-((triisopropylsilyl)ethynyl) benzenesulfonamide (**2a**, 730.4 mg, 2 mmol, 1 eq.) and DCM (10.0 mL). The mixture was stirred at rt for 8 h. Solvent was removed by rotary evaporation instrument. The mixture was transferred to a column and purified by flash chromatography on silica gel (PE/EA = 10:1, R_f = 0.20) to give the analytical pure product **3aa** (0.83g, 86 % yield).

(b) Product transformation



3aa **4**, 95%

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

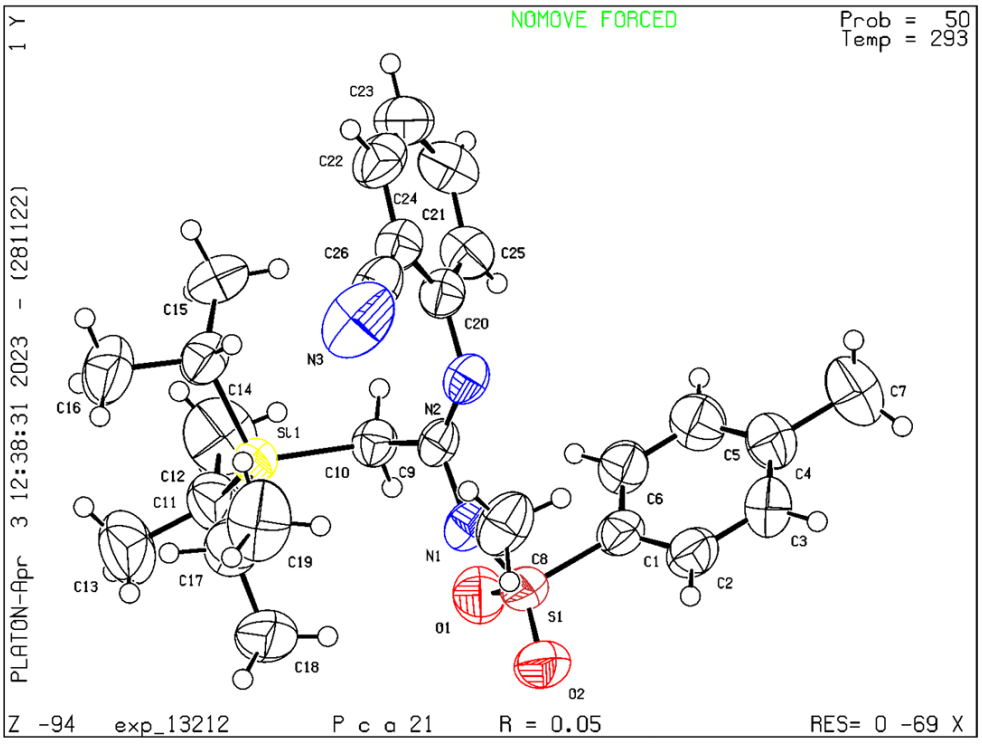
transferred to a column and purified by flash chromatography on silica gel (PE/EA = 5:1, R_f = 0.20) to give product **(*E*)-*N*'-(2-cyanophenyl)-*N*-methyl-*N*-tosylacetimidamide** (**4**, 62.1 mg, 95% yield, white solid, m.p. 69-74 °C). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.75 (d, J = 8.2 Hz, 2H), 7.54 (d, J = 7.7 Hz, 1H), 7.48 (t, J = 7.9 Hz, 1H), 7.35 (d, J = 8.1 Hz, 2H), 7.08 (t, J = 7.6 Hz, 1H), 6.74 (d, J = 8.2 Hz, 1H), 3.37 (s, 3H), 2.43 (s, 3H), 2.20 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 157.5, 151.9, 144.6, 136.1, 133.7, 132.9, 130.2, 127.0, 123.5, 121.1, 117.2, 104.3, 35.6, 21.6, 19.0. **HRMS** (ESI, m/z) Calculated for [$C_{18}H_{18}N_3O_2S$, M + H]$^+$: 328.1120, found: 328.1114.

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.
4. Li, Z.; Lu, F.; Xu, Q.; Liu, G.; Zhao, X.; Wang, G. *Green Chem.*, **2024**, *26*, 259-263.

9. Crystal Data and Structure Refinement for 3aa.

ORTEP drawing of **3aa** (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 = 0.0092 A	Wavelength=1.54184	
Cell:	a=19.9676(6)	b=7.9854(2)	c=16.9860(6)
	alpha=90	beta=90	gamma=90
Temperature:	293 K		

	Calculated	Reported
Volume	2708.41(14)	2708.40(14)
Space group	P c a 21	P c a 21
Hall group	P 2c -2ac	P 2c -2ac
Moiety formula	C26 H37 N3 O2 S Si	?
Sum formula	C26 H37 N3 O2 S Si	C26 H37 N3 O2 S Si
Mr	483.74	483.73
Dx,g cm-3	1.186	1.186
Z	4	4
Mu (mm-1)	1.688	1.688
F000	1040.0	1040.0
F000'	1044.84	
h,k,lmax	23,9,20	23,9,20
Nref	4861[2522]	4818
Tmin,Tmax	0.817,0.831	0.614,1.000
Tmin'	0.817	

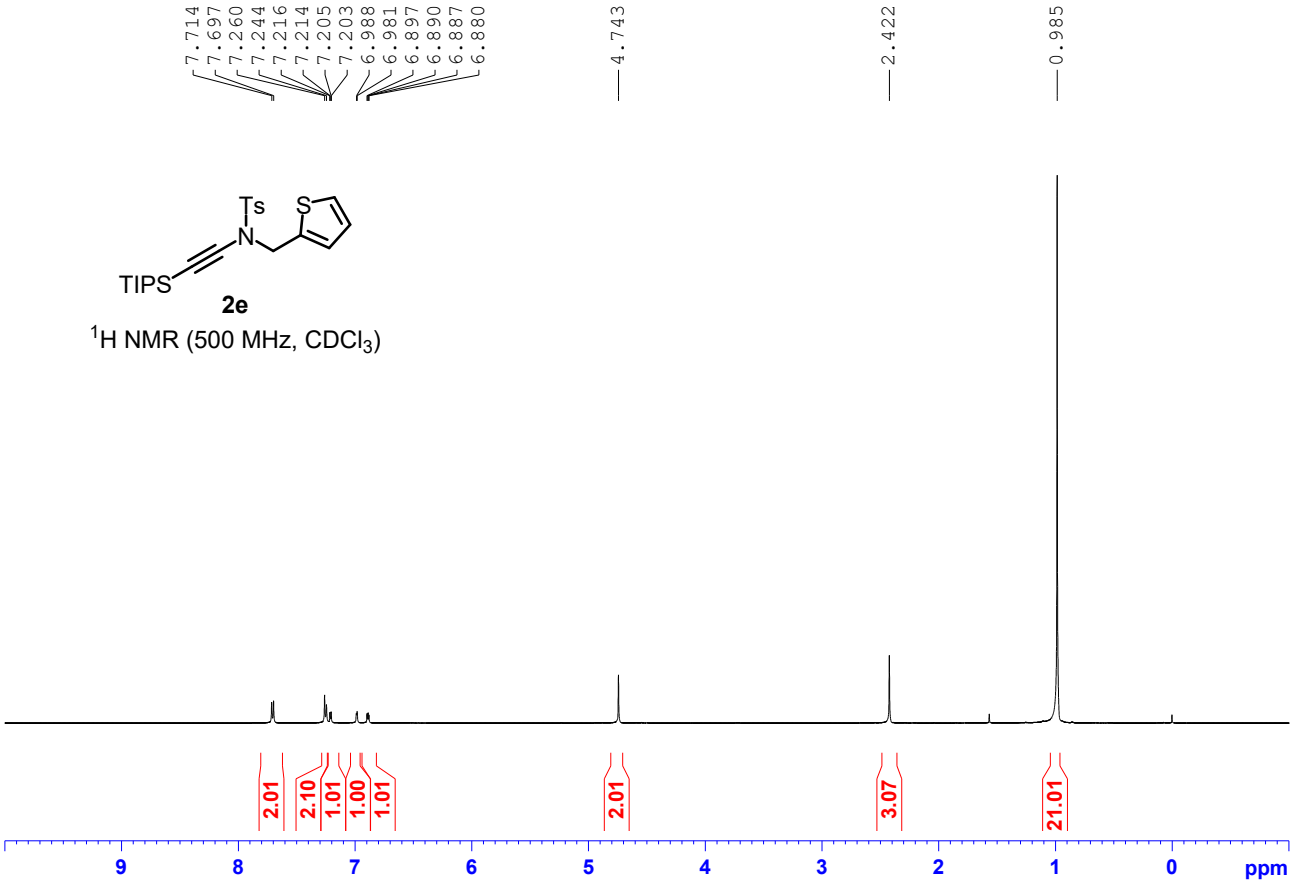
Correction method= # Reported T Limits: Tmin=0.614 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.91/0.99 Theta(max)= 67.240

R(reflections)= 0.0477(3758) wR2(reflections)= 0.1408(4818)

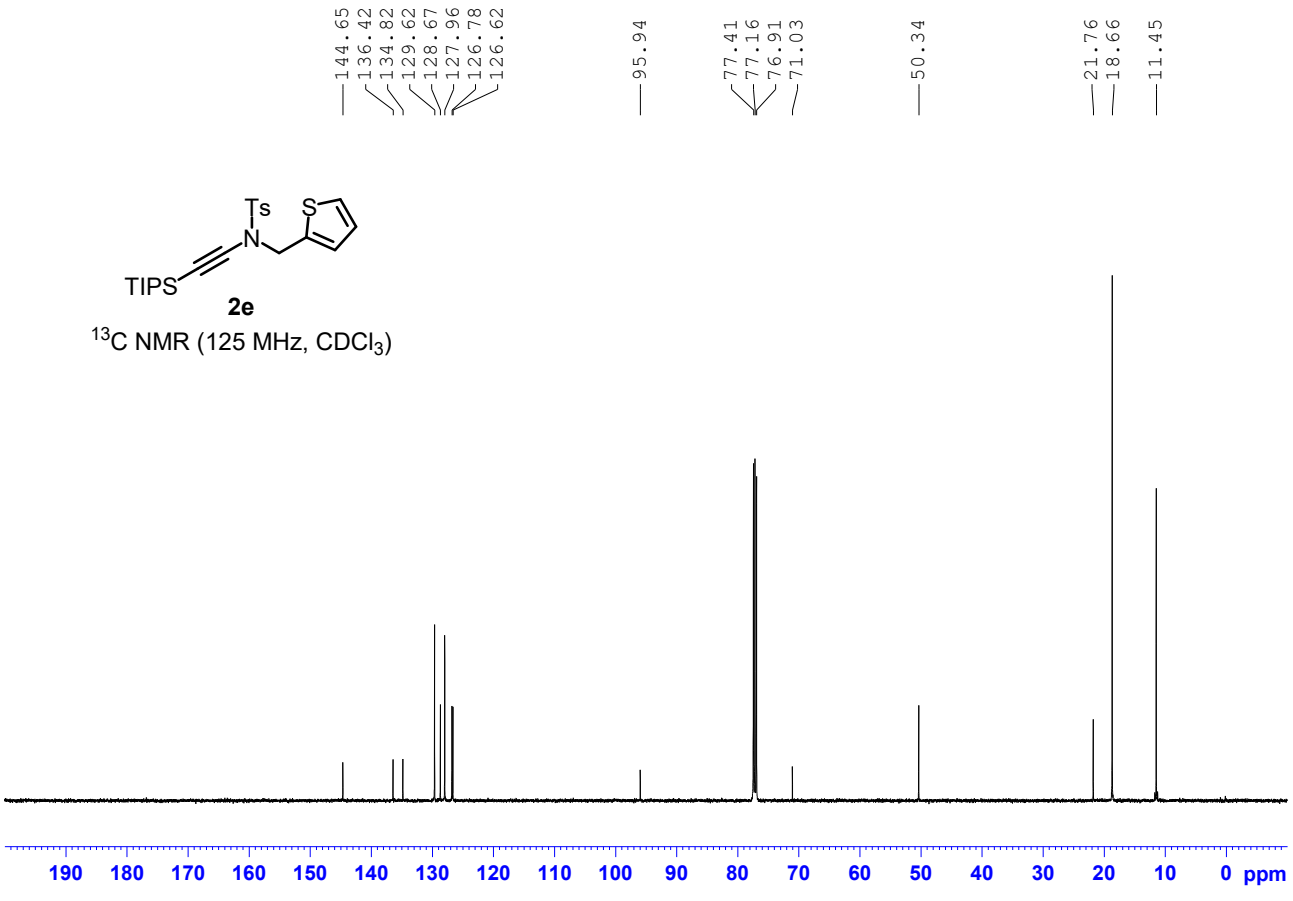
S = 1.066 Npar= 307

10. NMR Spectra



2e

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



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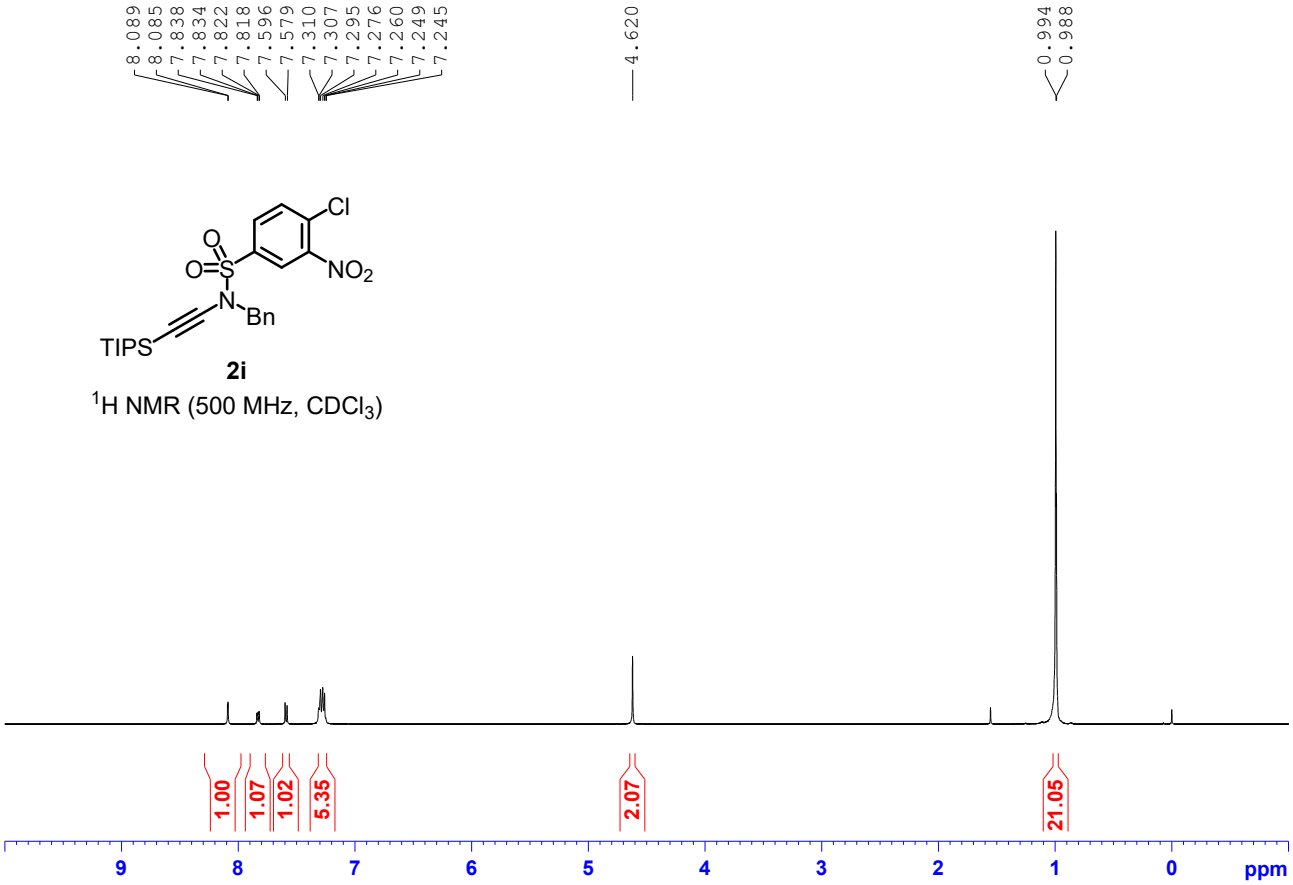
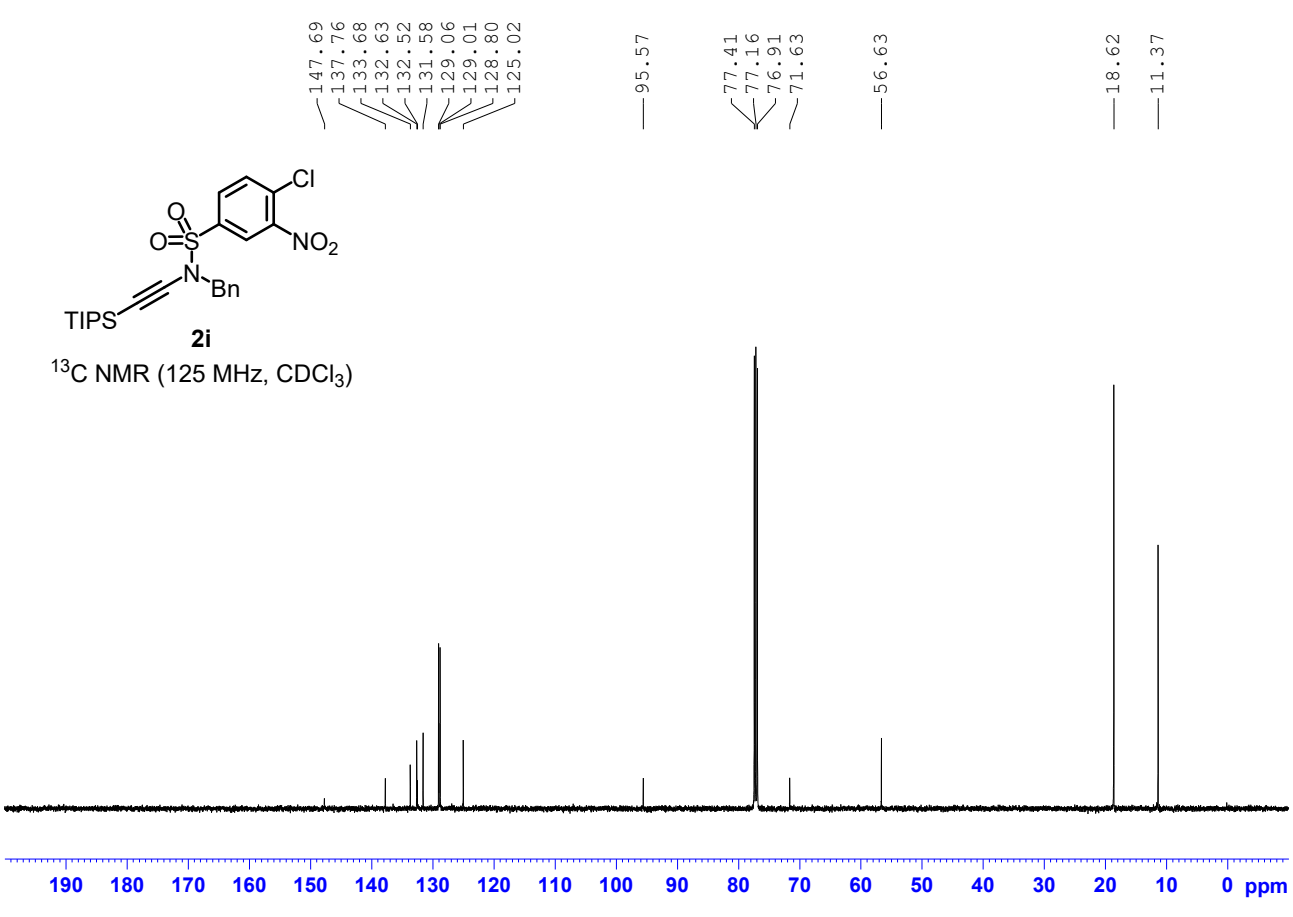
^{13}C NMR (125 MHz, $CDCl_3$)



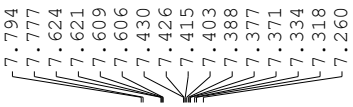
2i

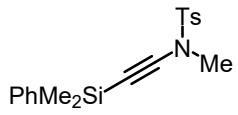
^{1}H NMR (500 MHz, $CDCl_3$)



2i

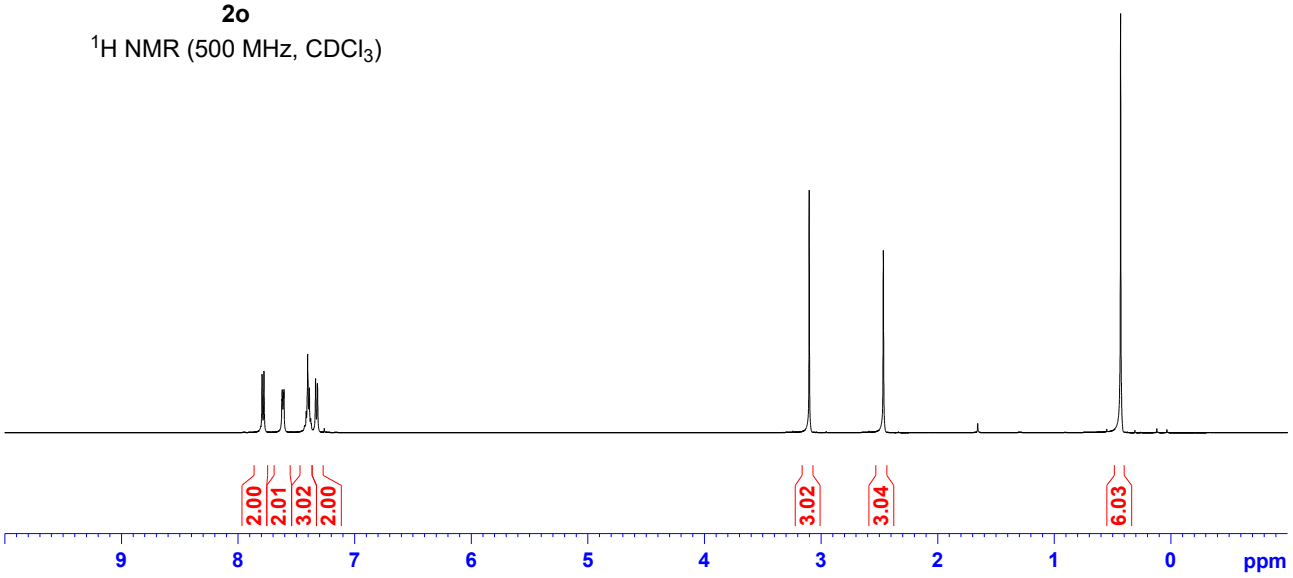
^{13}C NMR (125 MHz, $CDCl_3$)

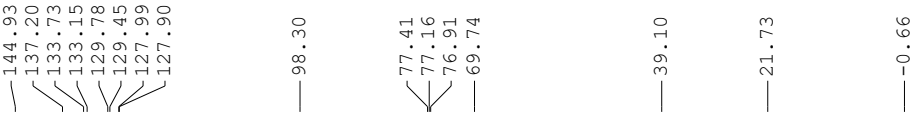


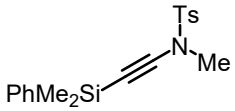


2o

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

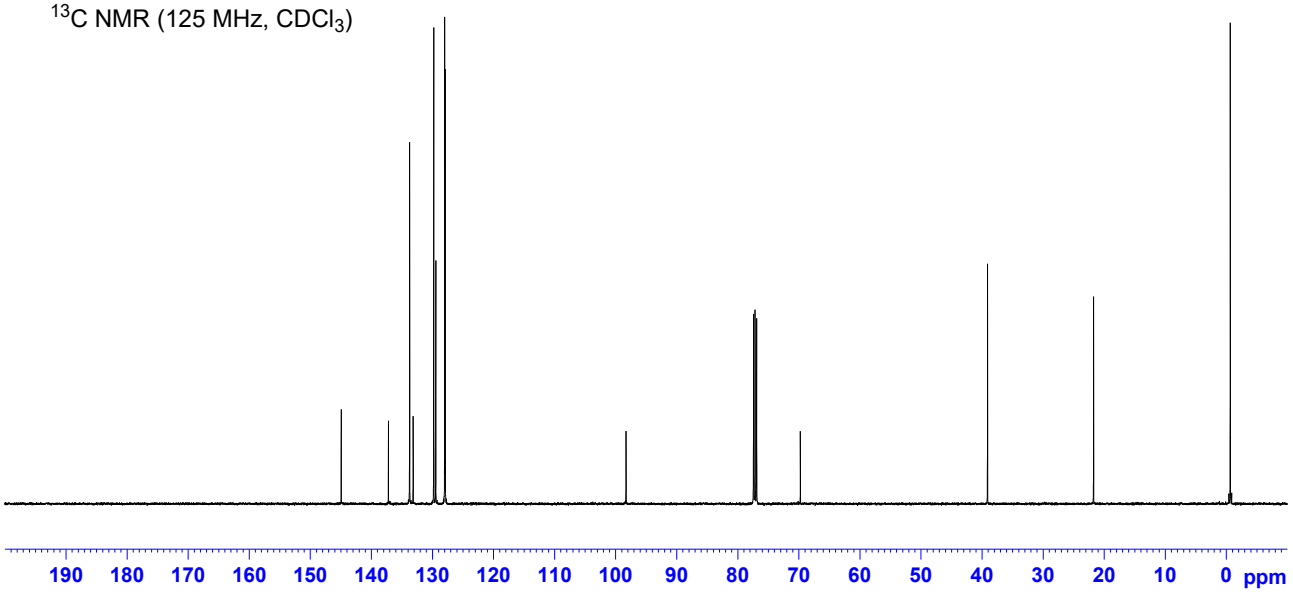


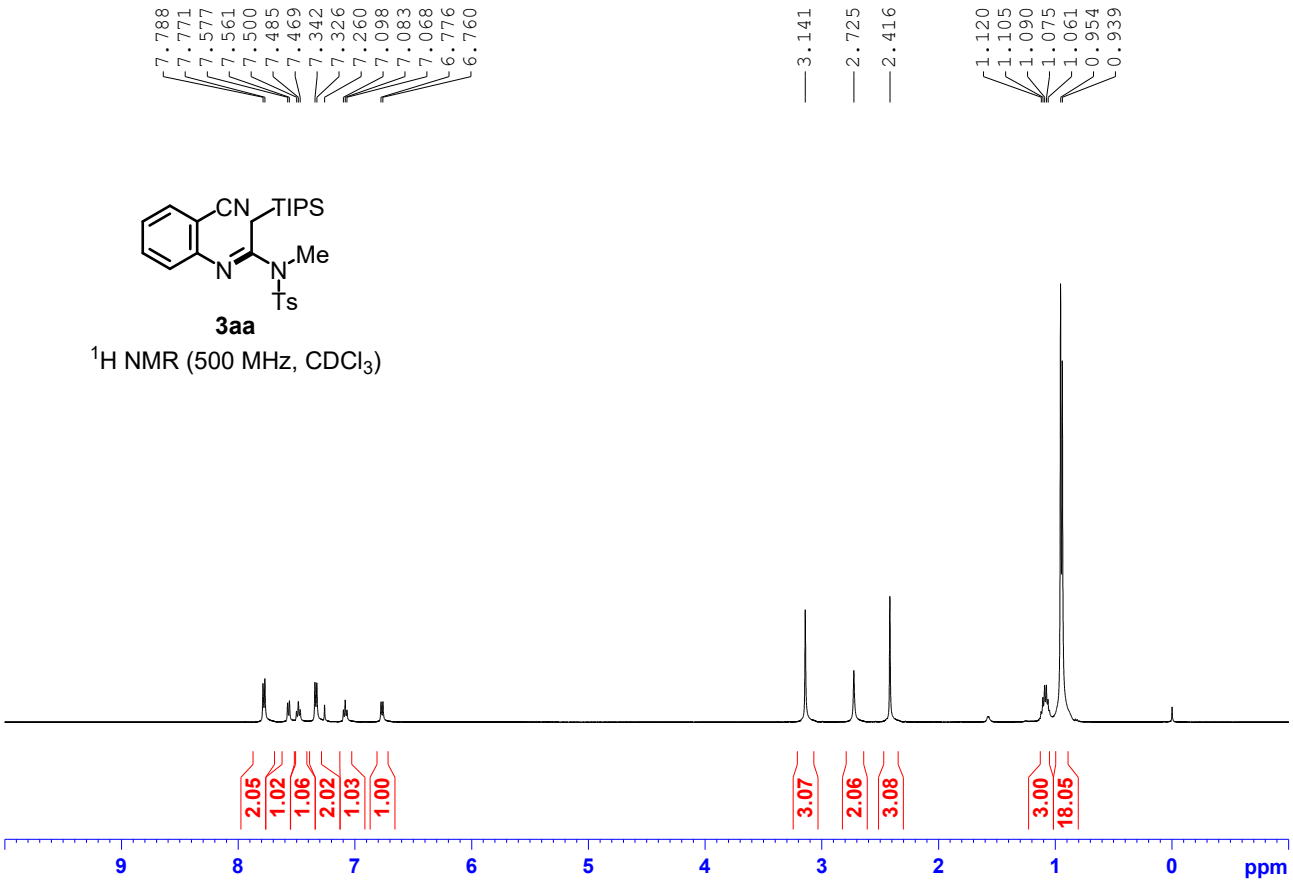




2o

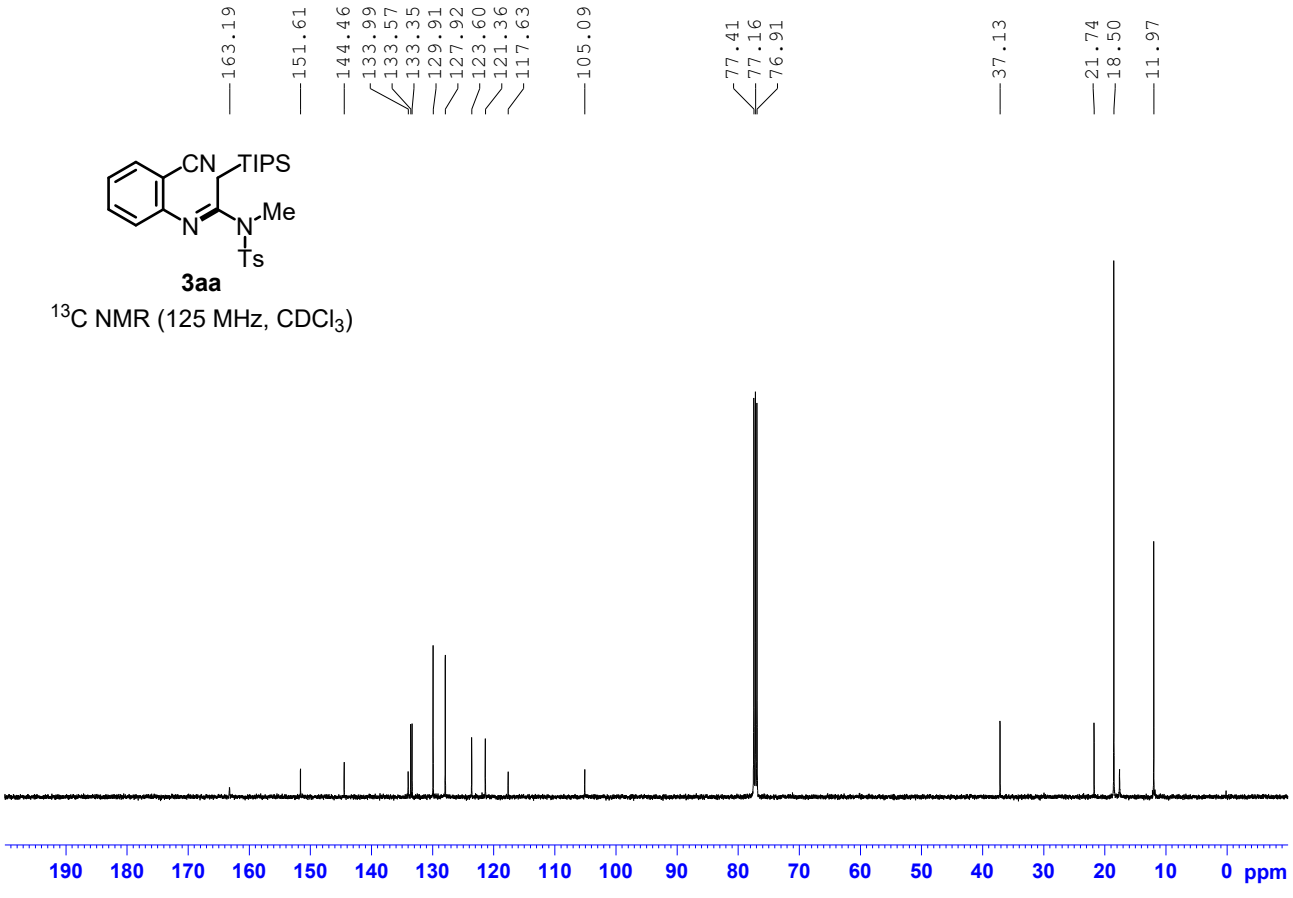
^{13}C NMR (125 MHz, $CDCl_3$)





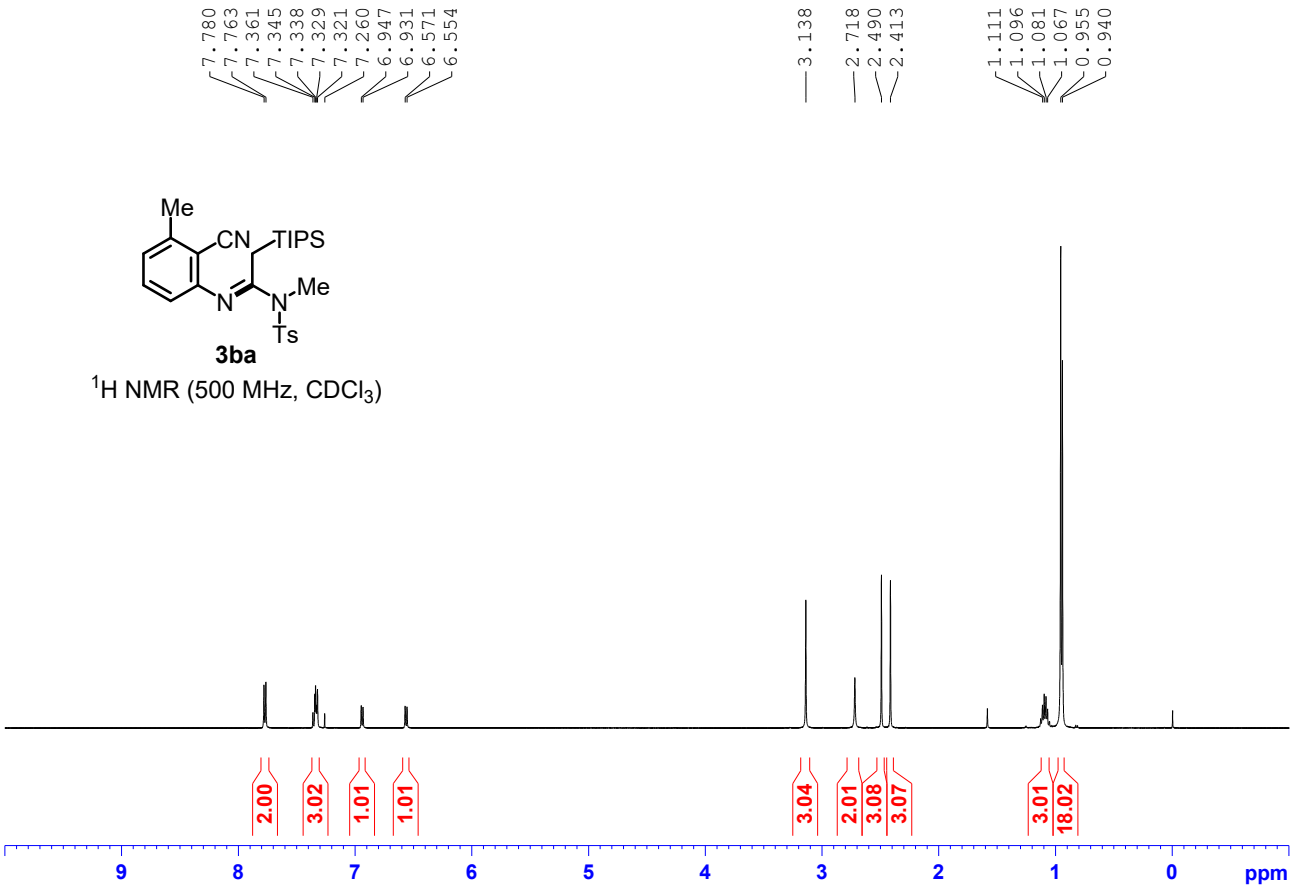
3aa

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



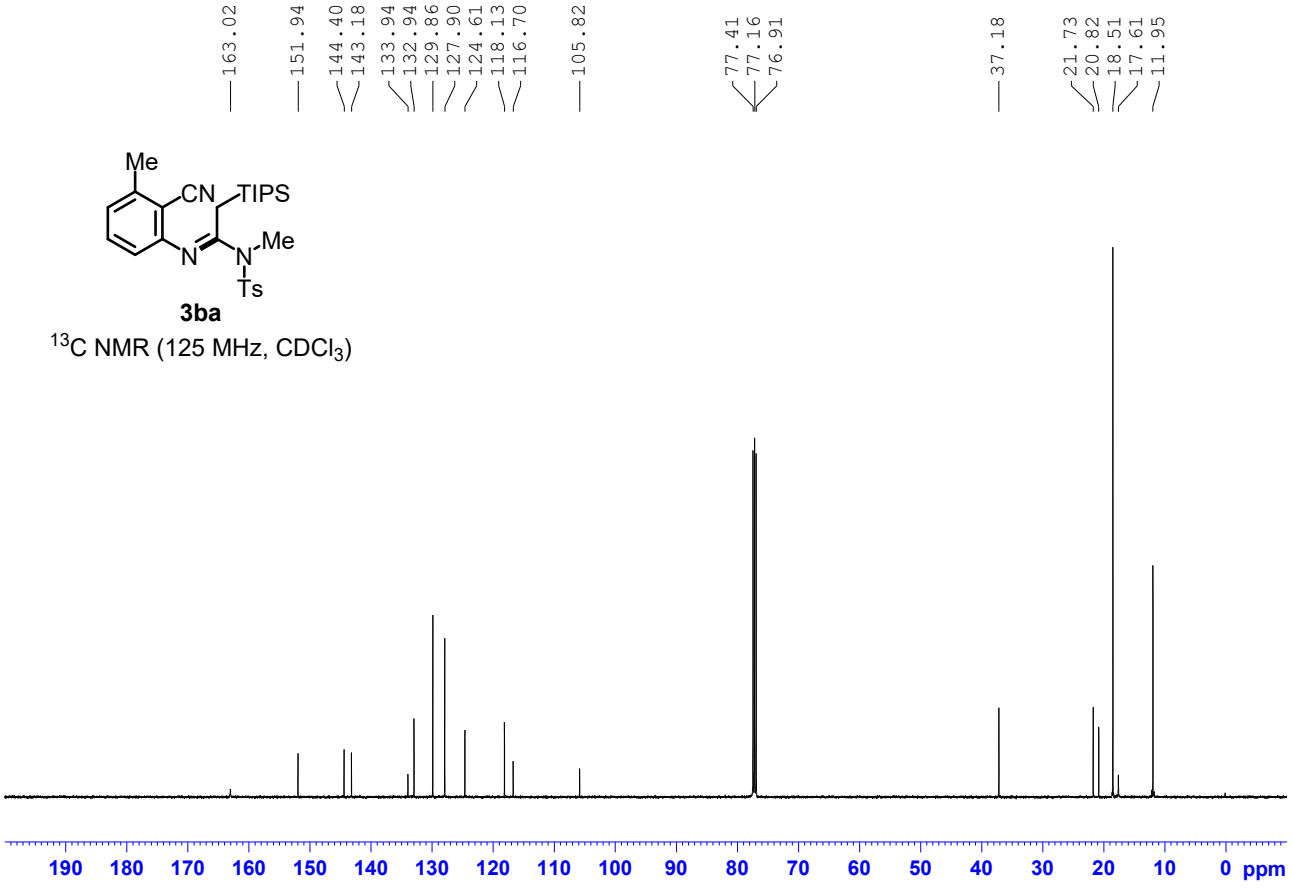
3aa

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



3ba

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



3ba

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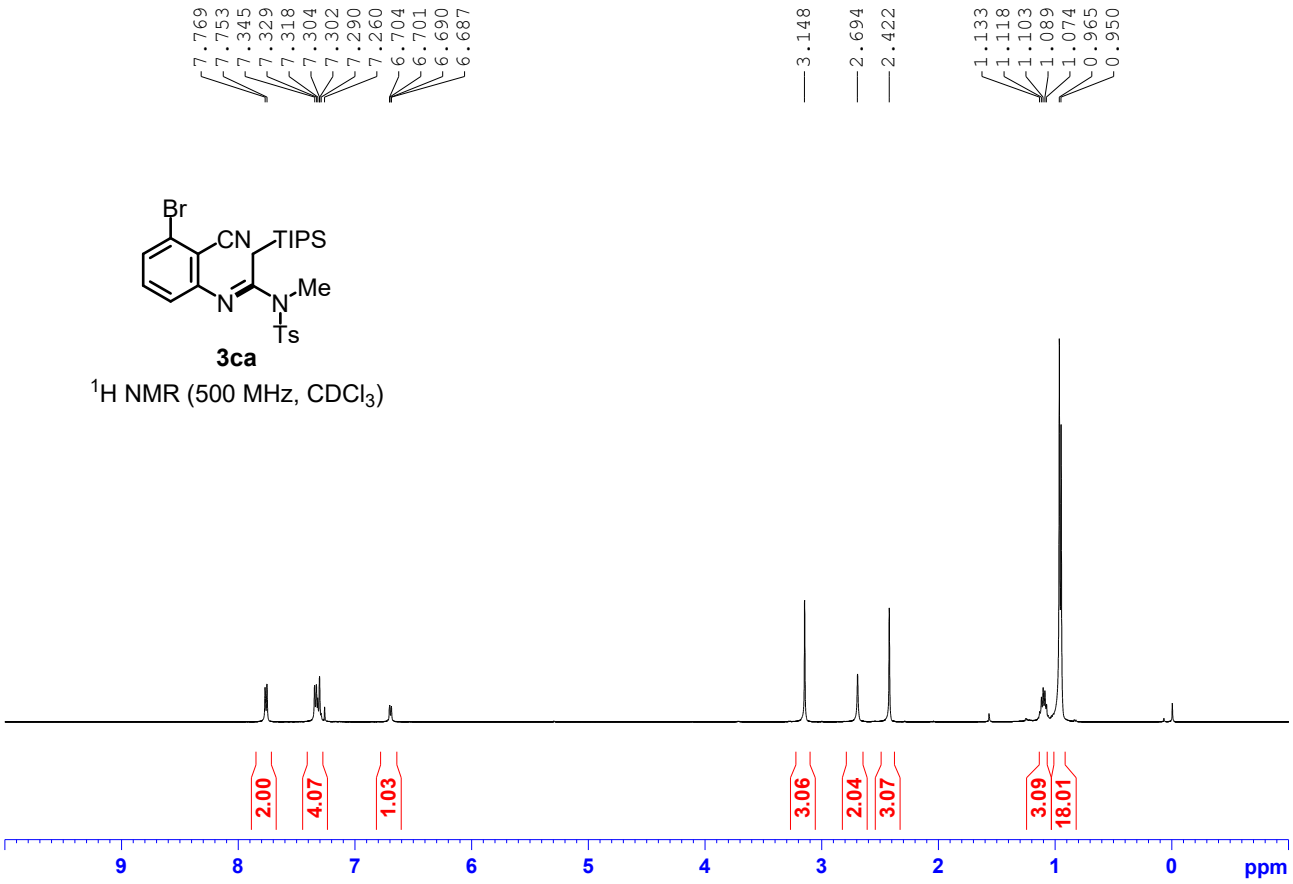

3ca

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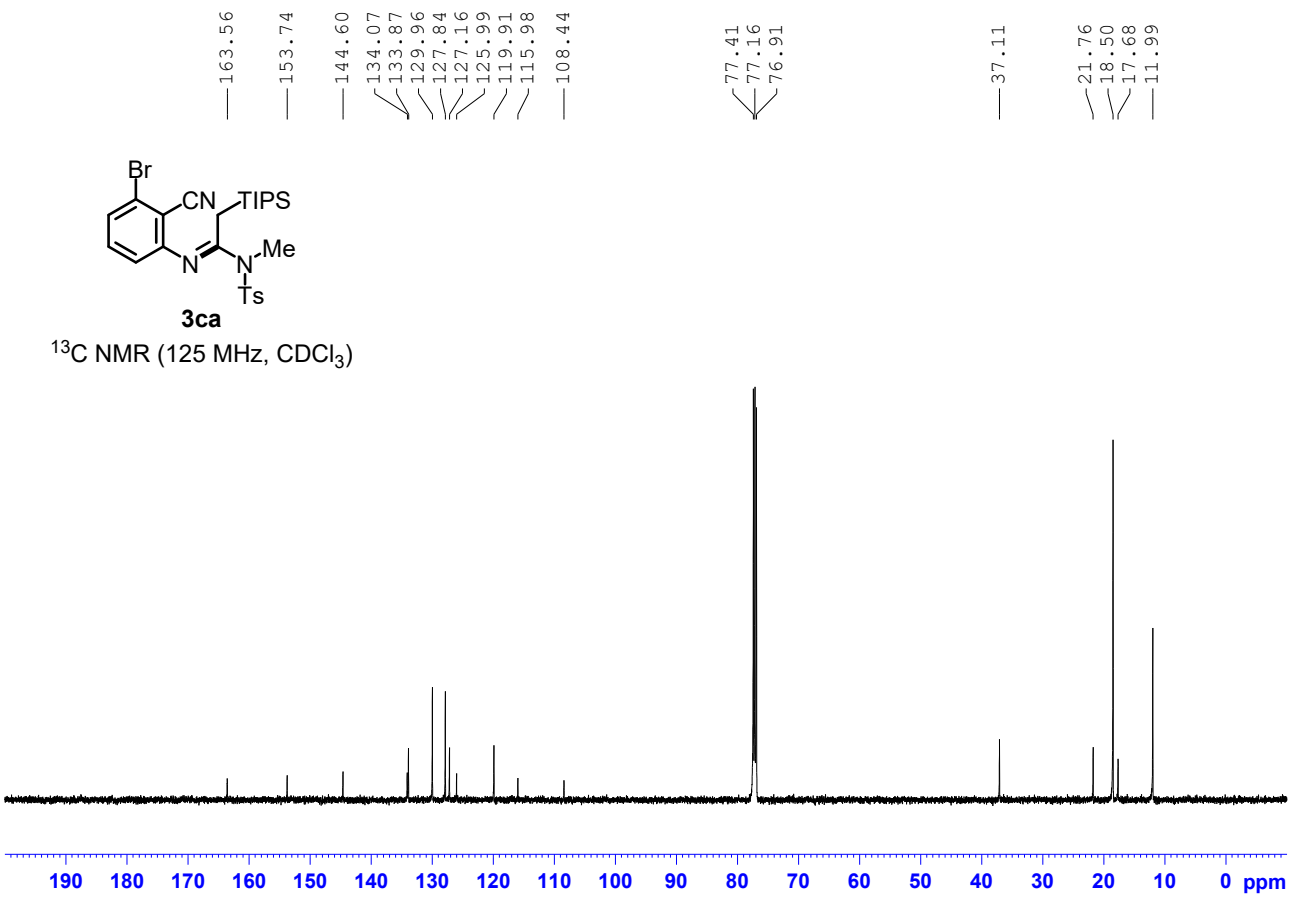

3ca

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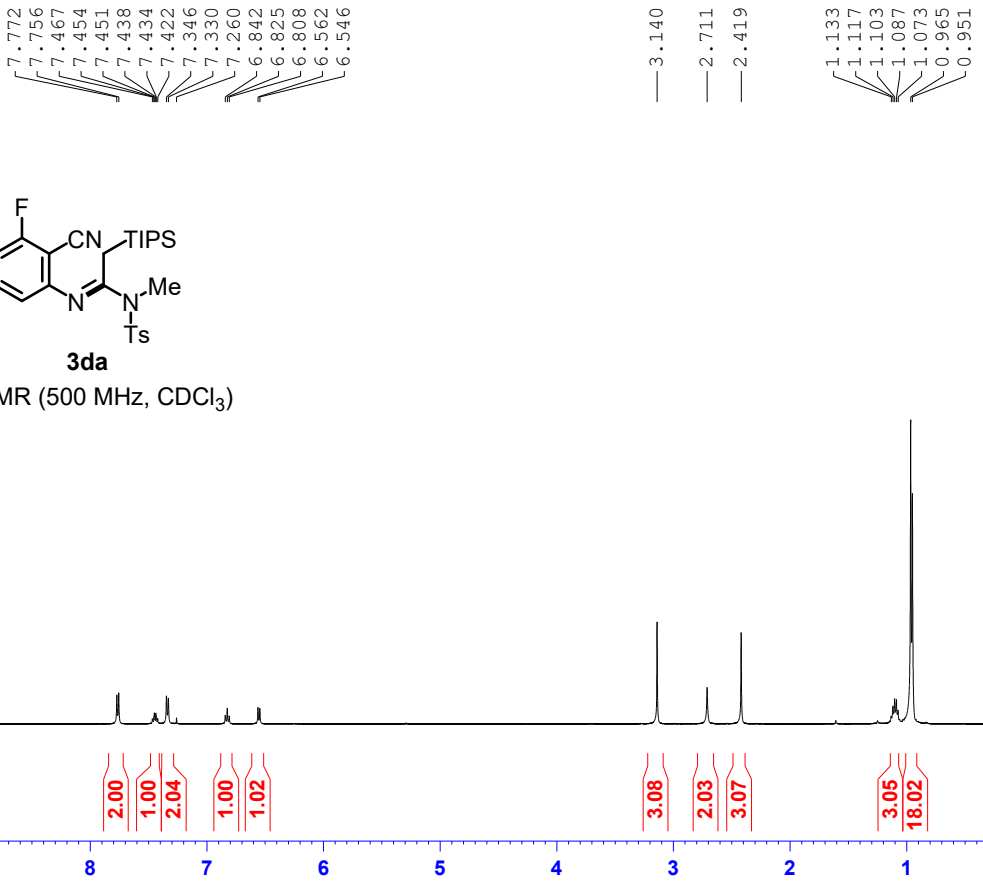

3da

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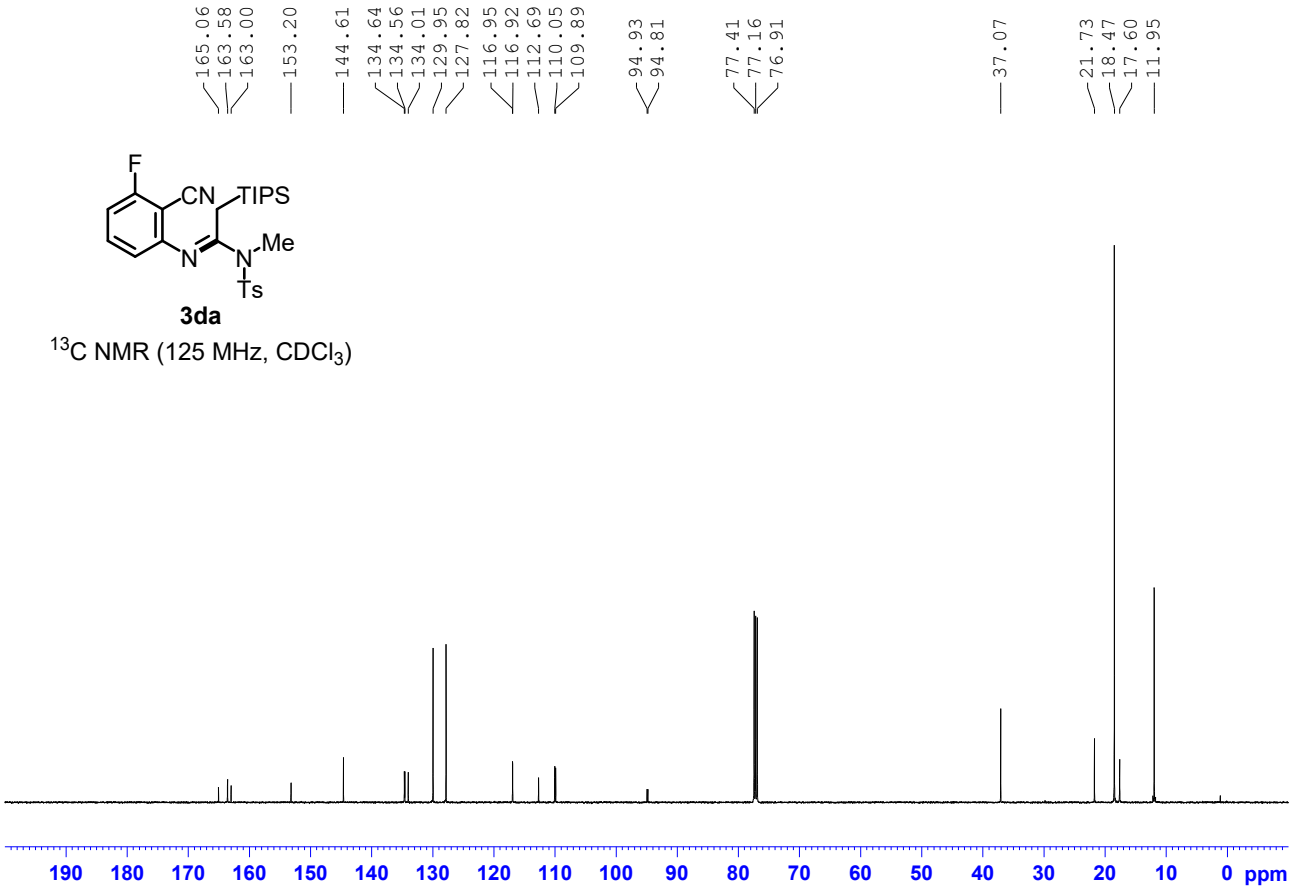

3da

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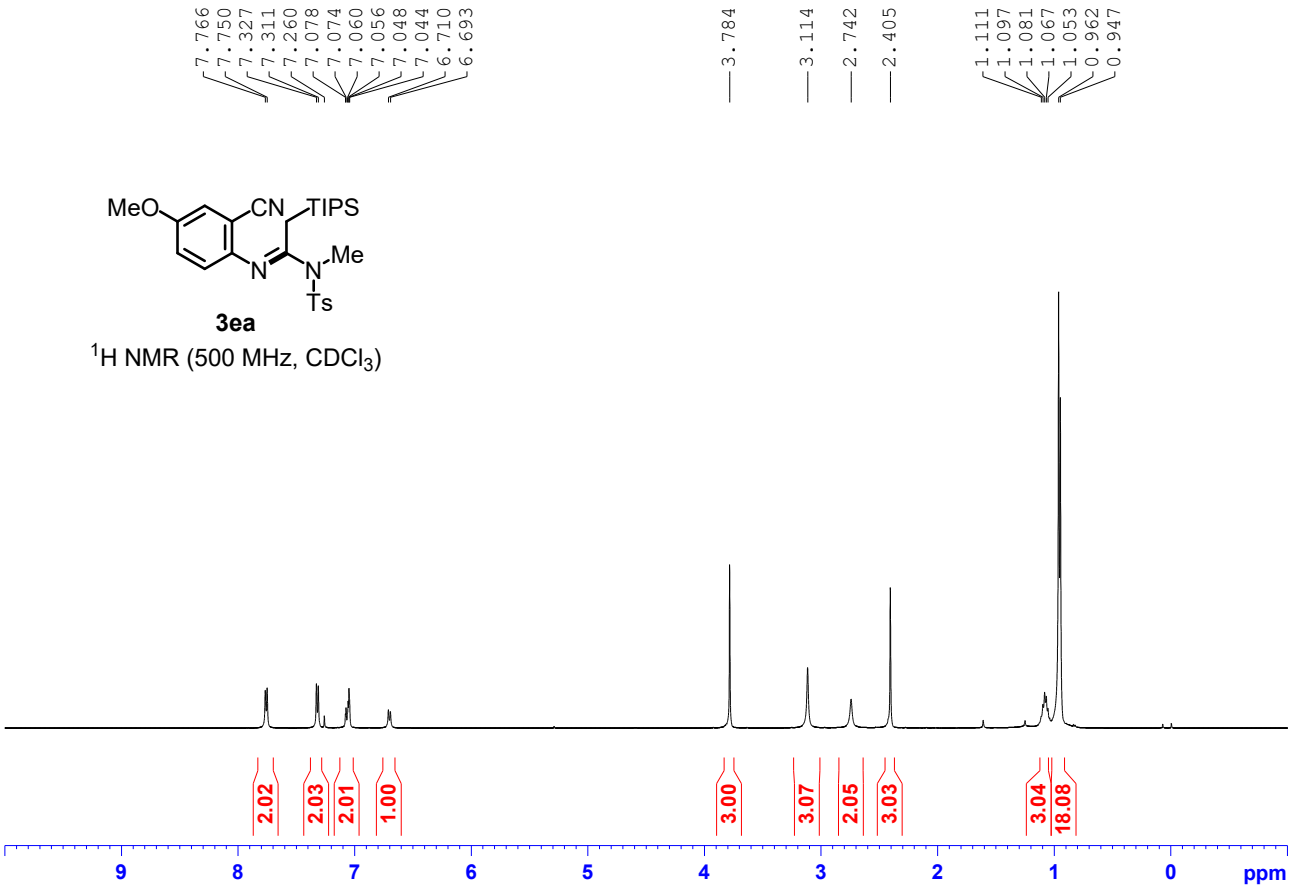
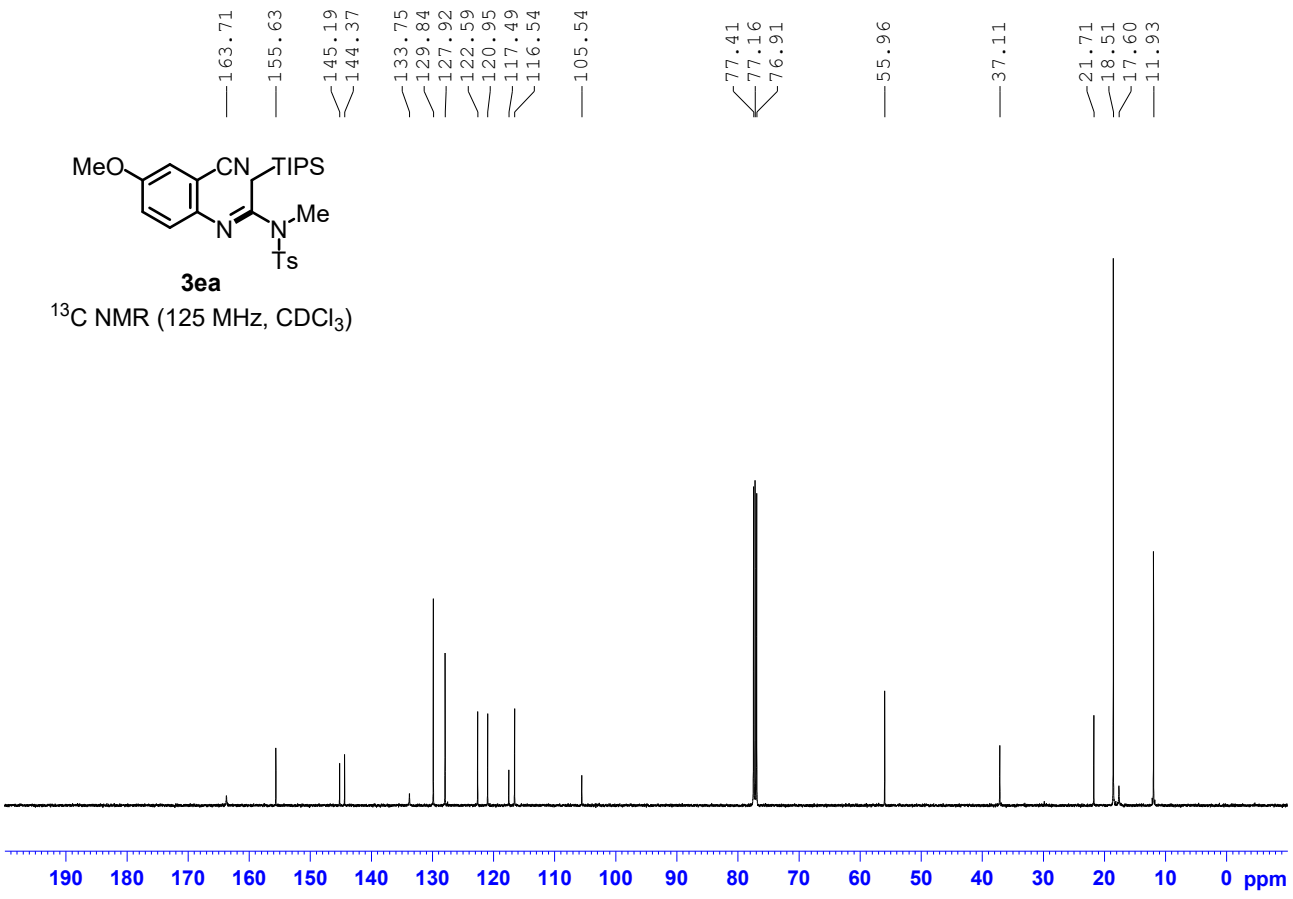


3ea

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



3ea

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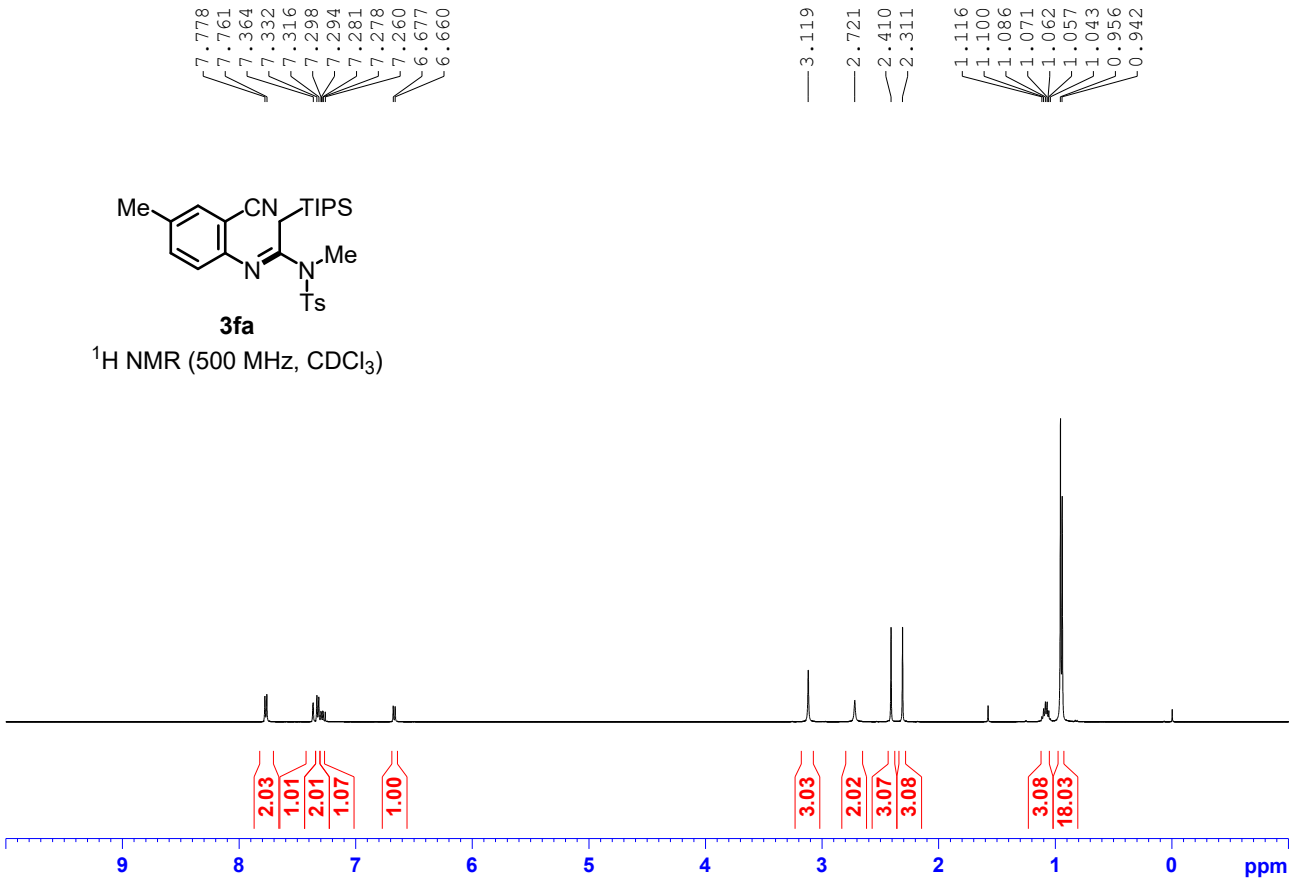

3fa

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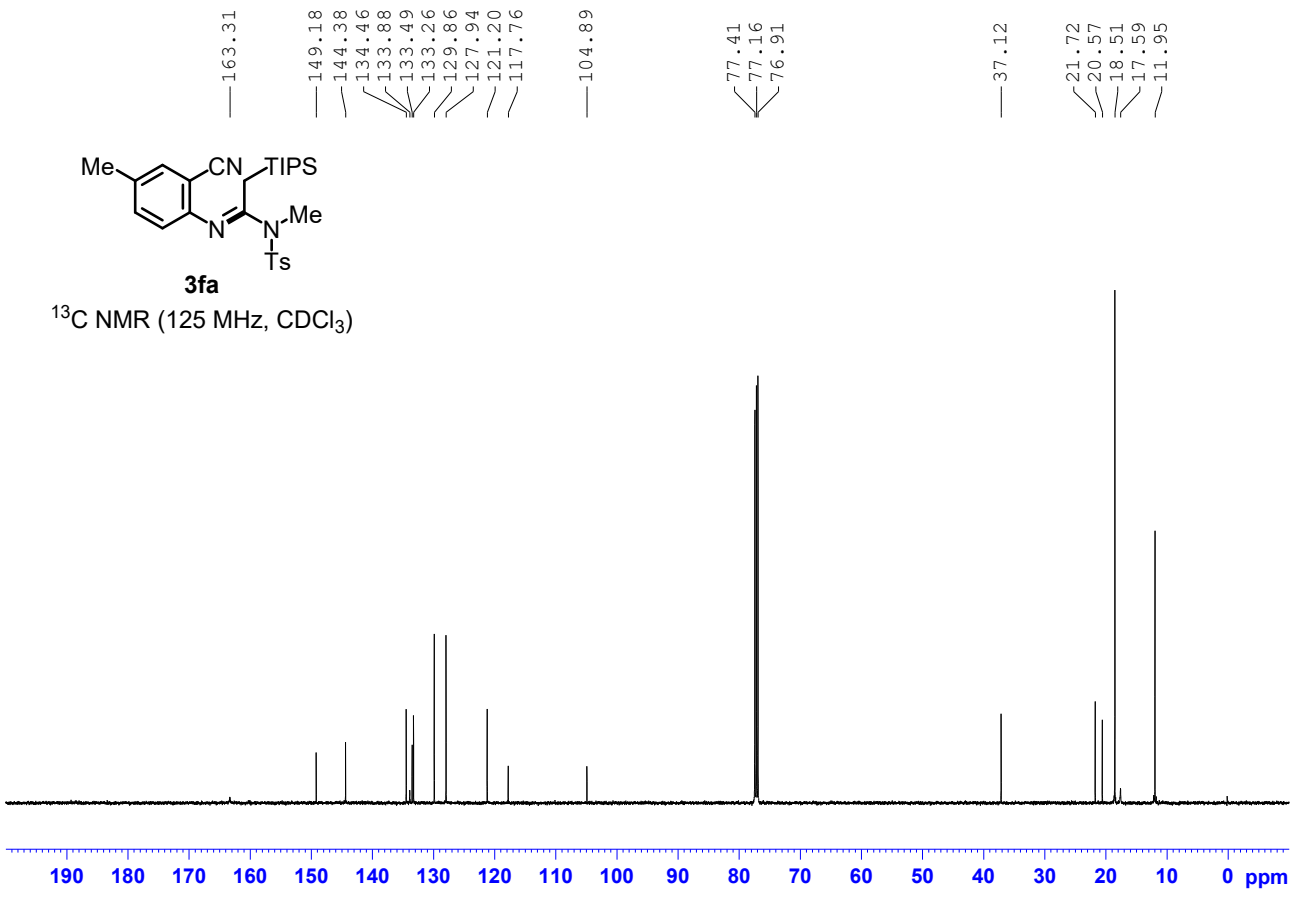

3fa

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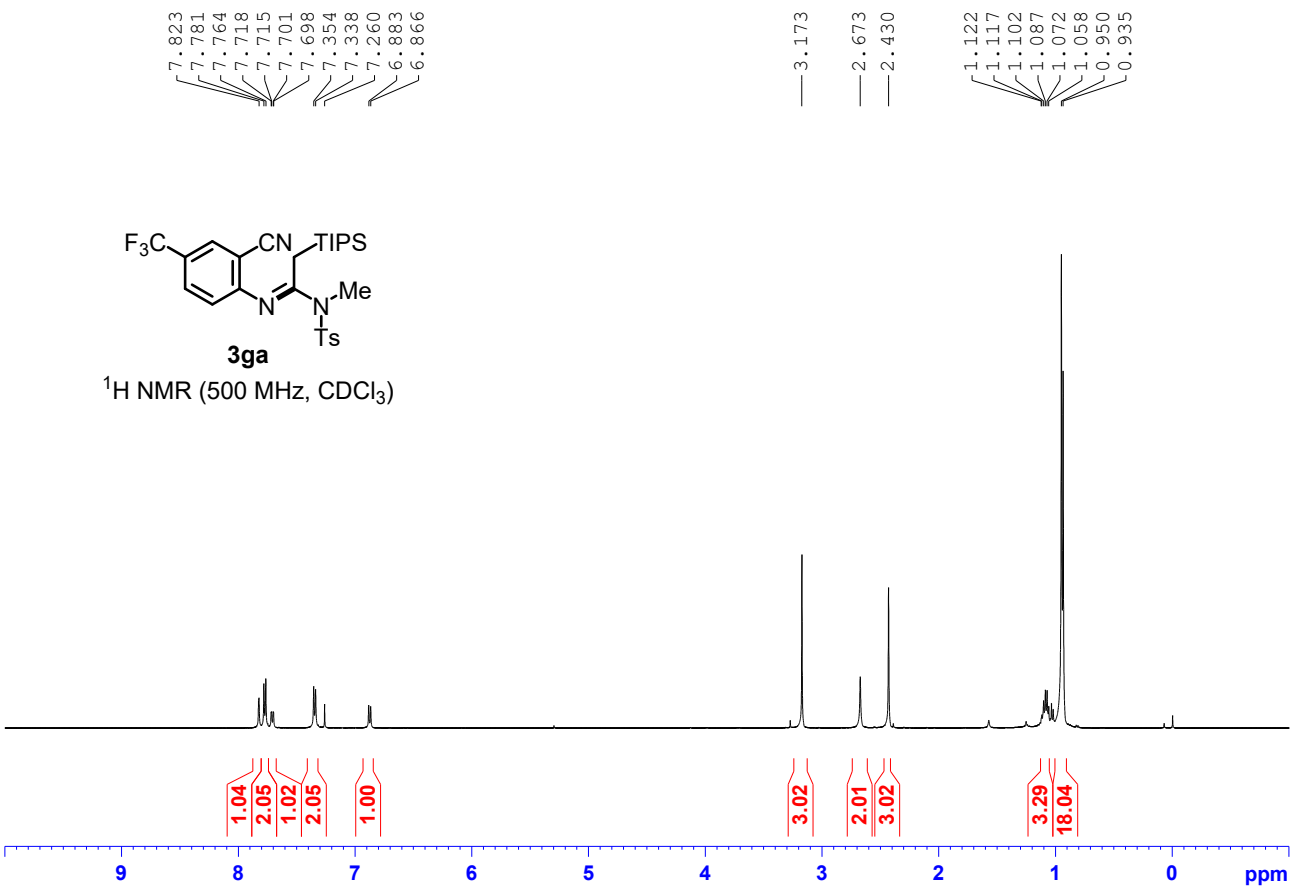
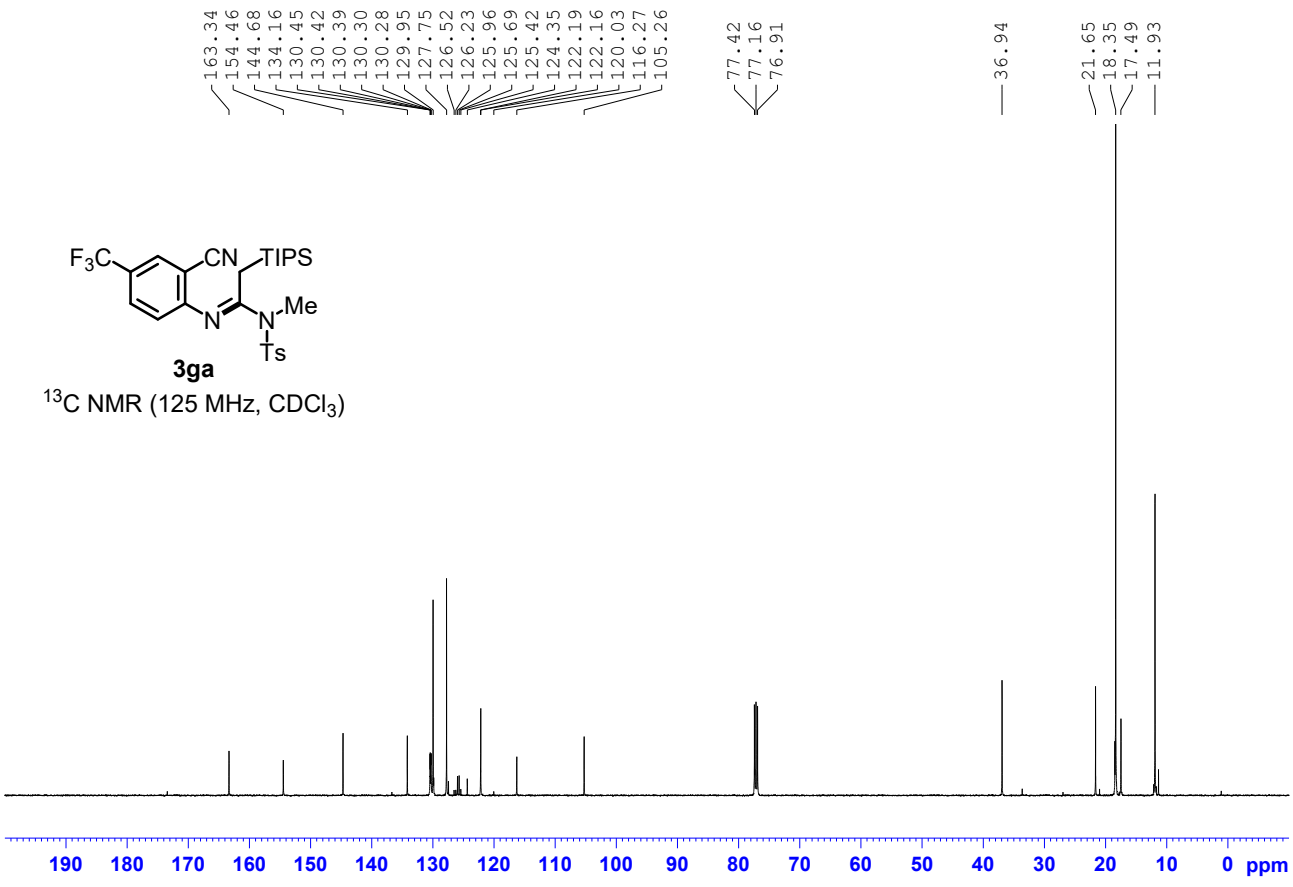


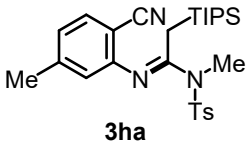
3ga

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



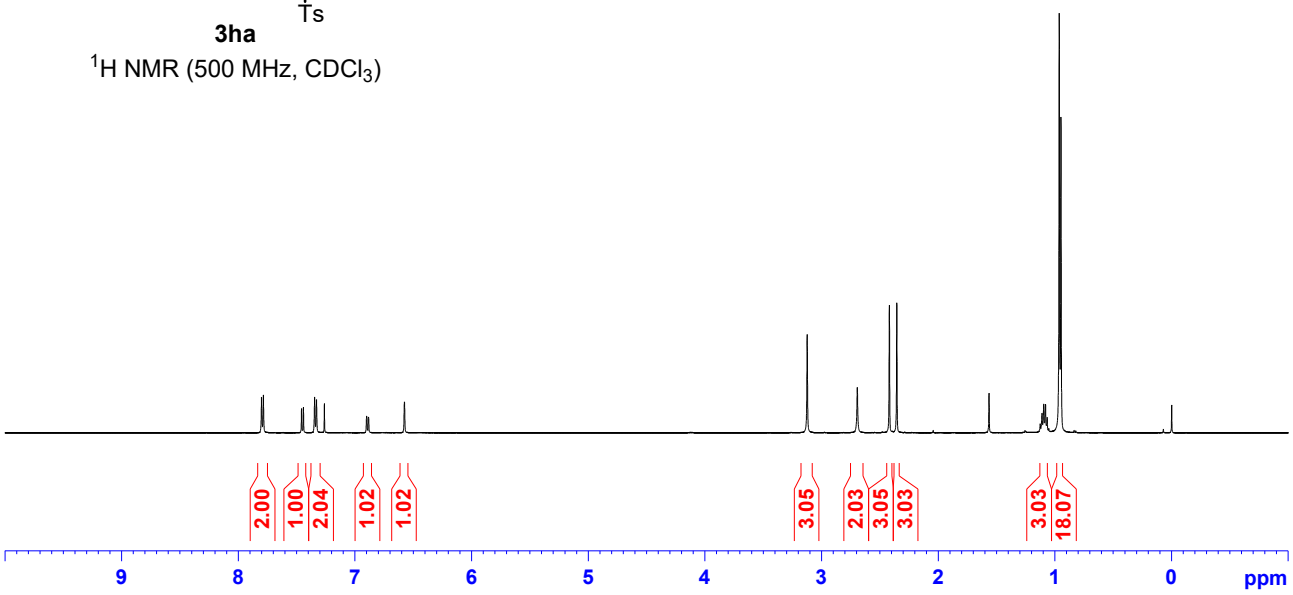
3ga

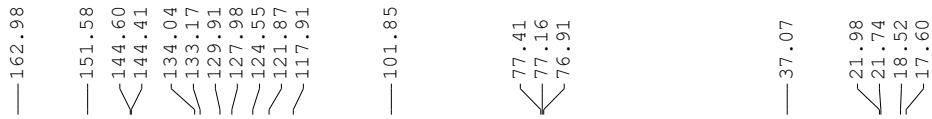
^{13}C NMR (125 MHz, $CDCl_3$)

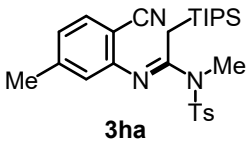


3ha

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

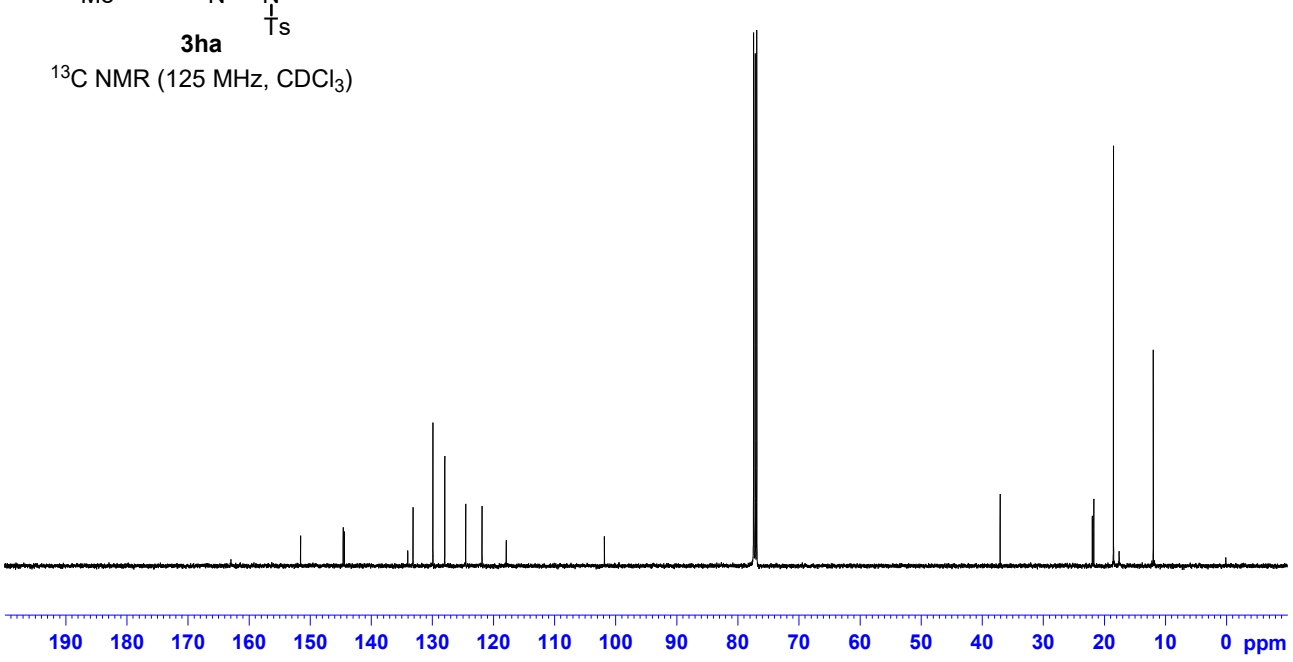


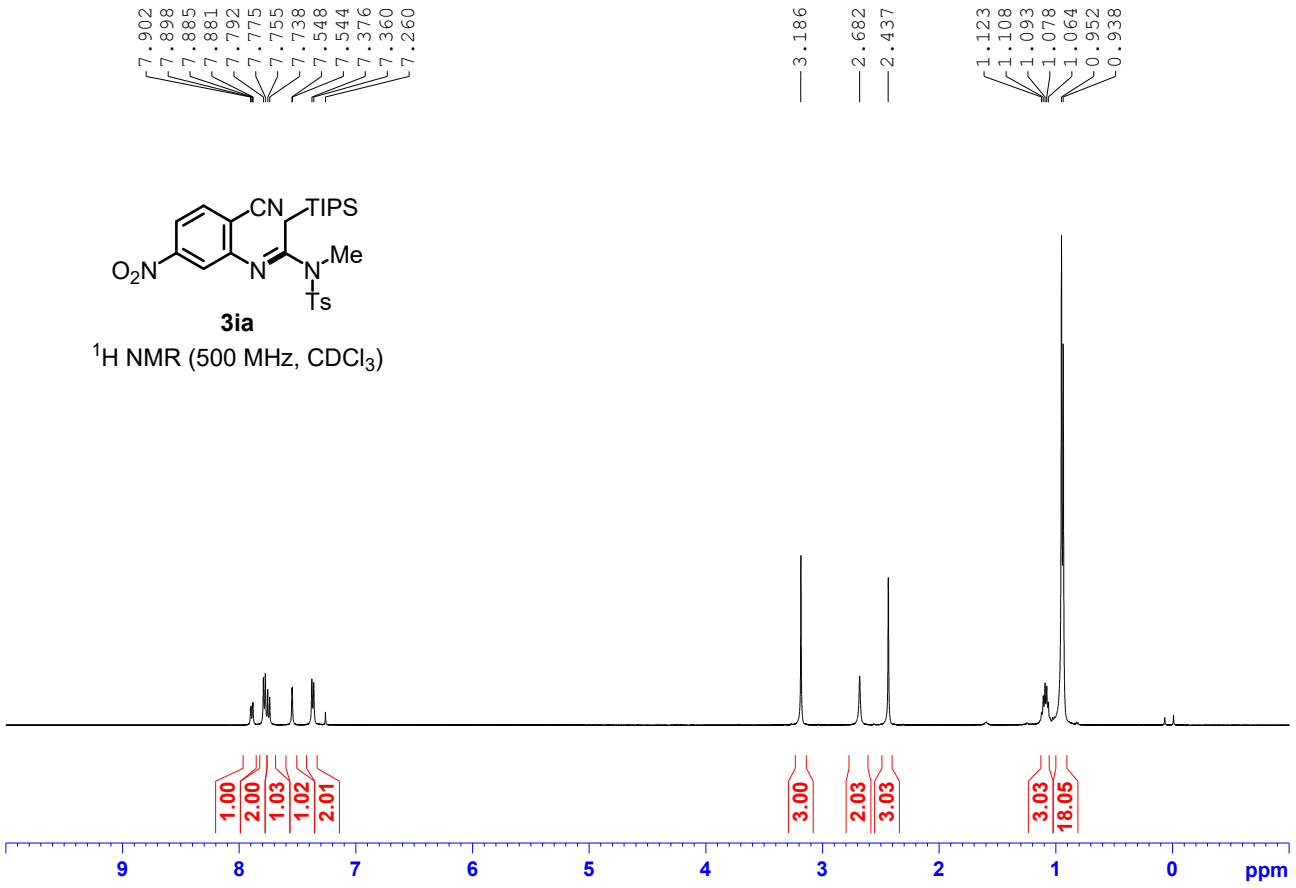




3ha

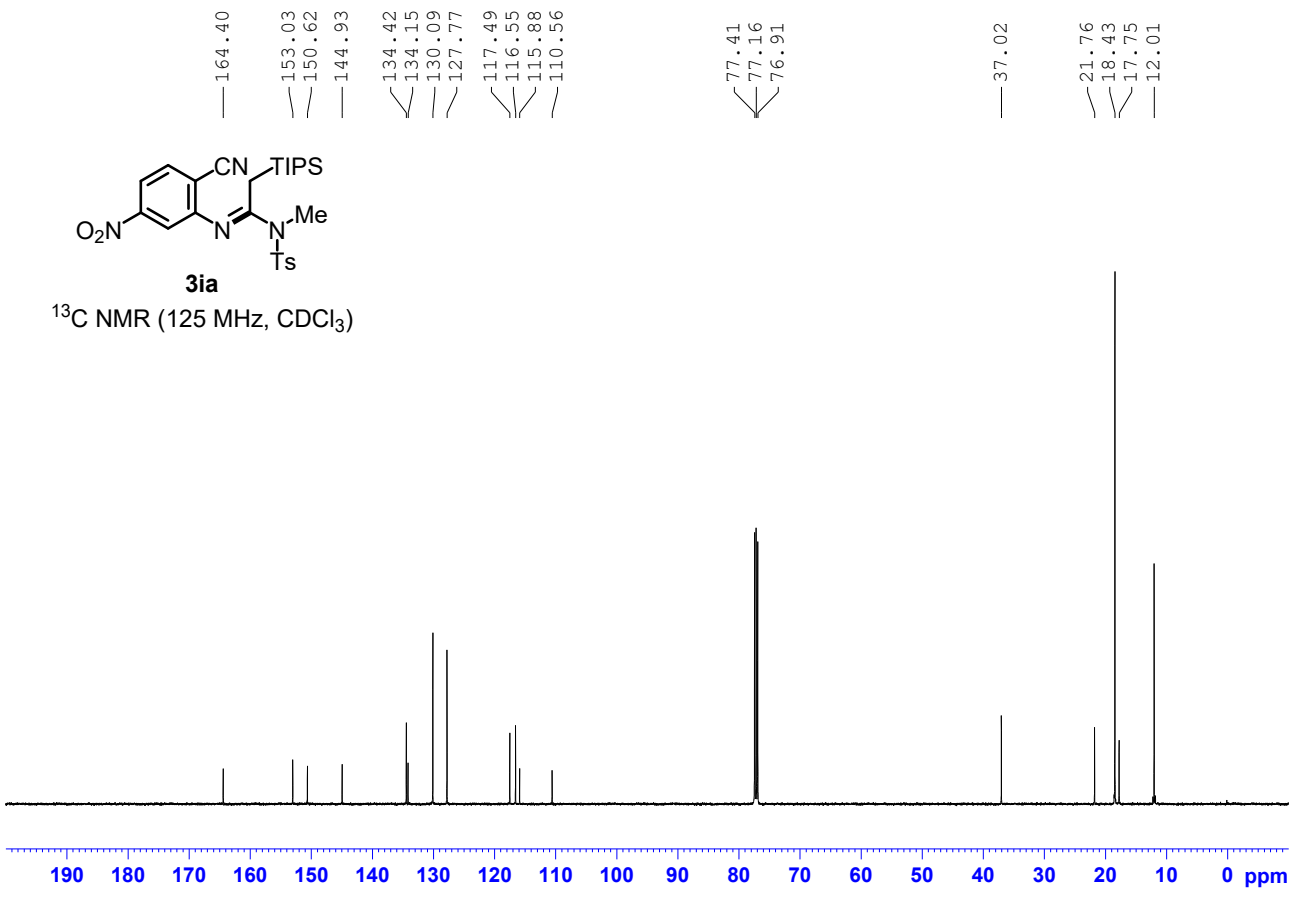
^{13}C NMR (125 MHz, $CDCl_3$)





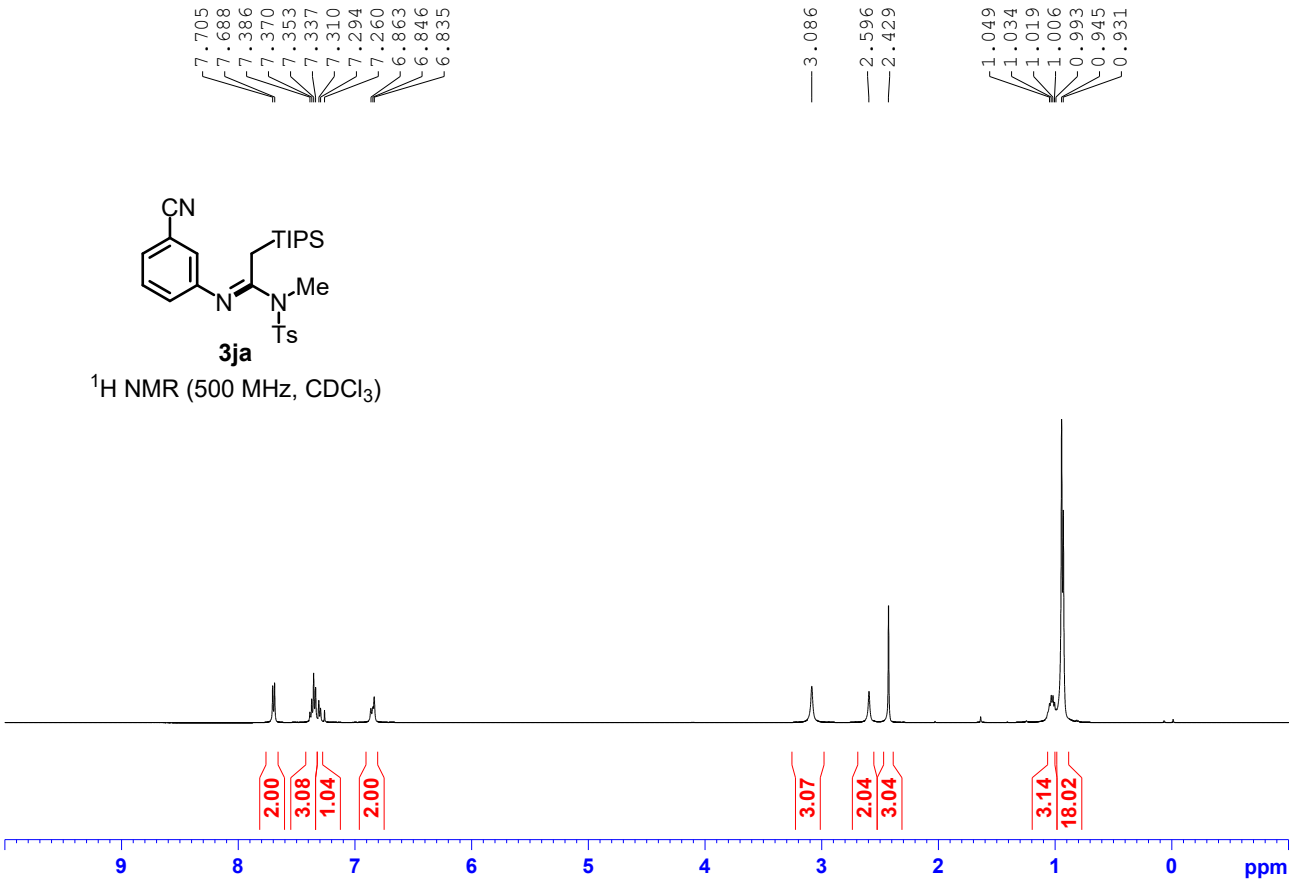
3ia

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



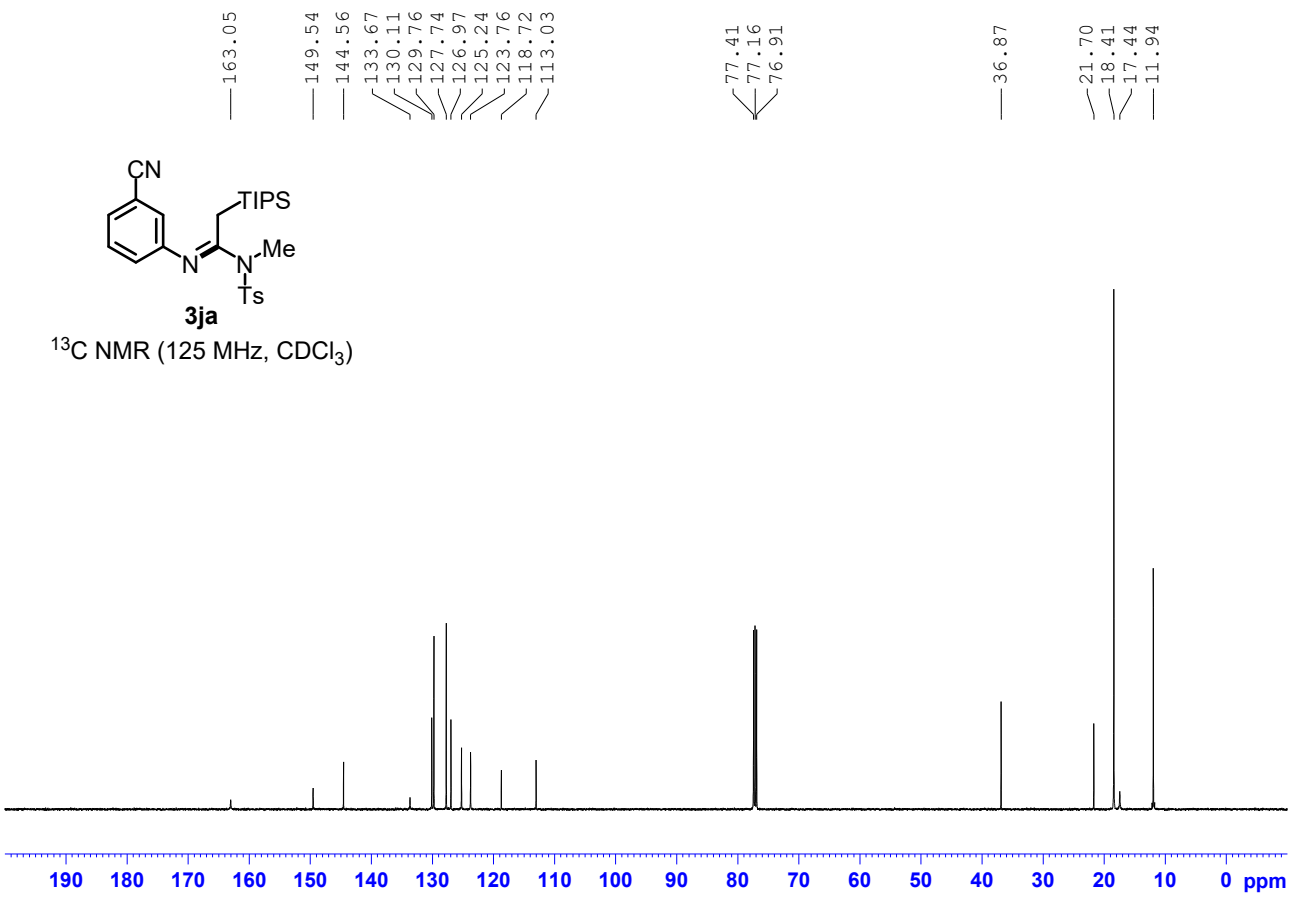
3ia

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



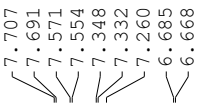
3ja

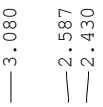
^{1}H NMR (500 MHz, $CDCl_3$)

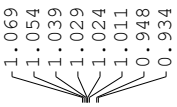


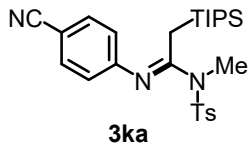
3ja

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



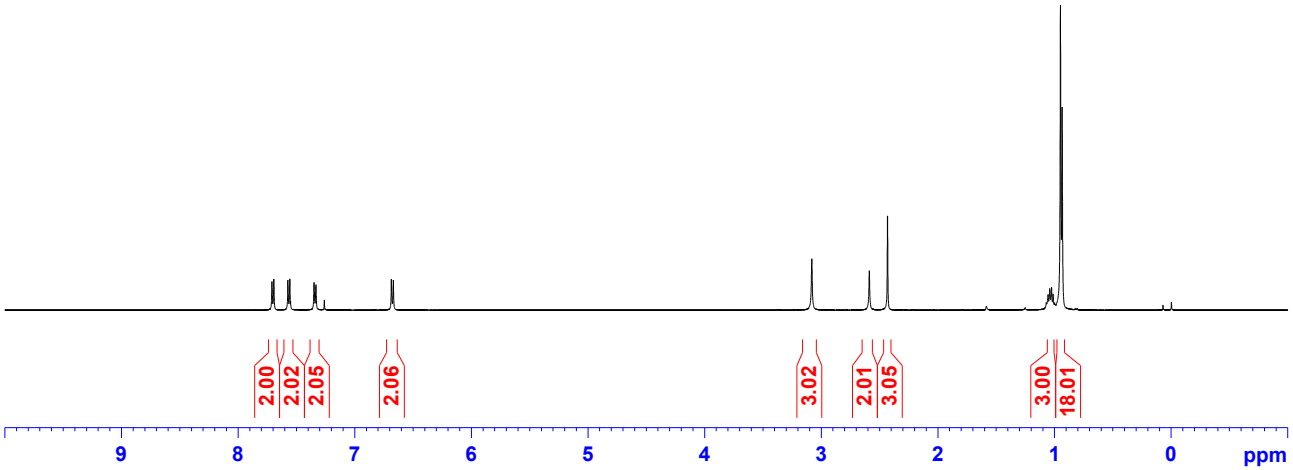


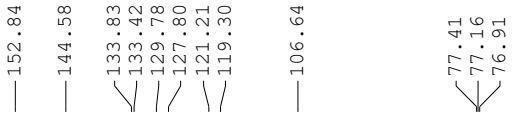


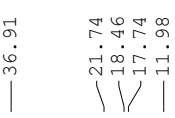


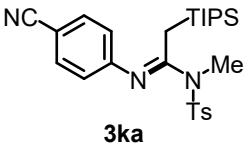
3ka

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



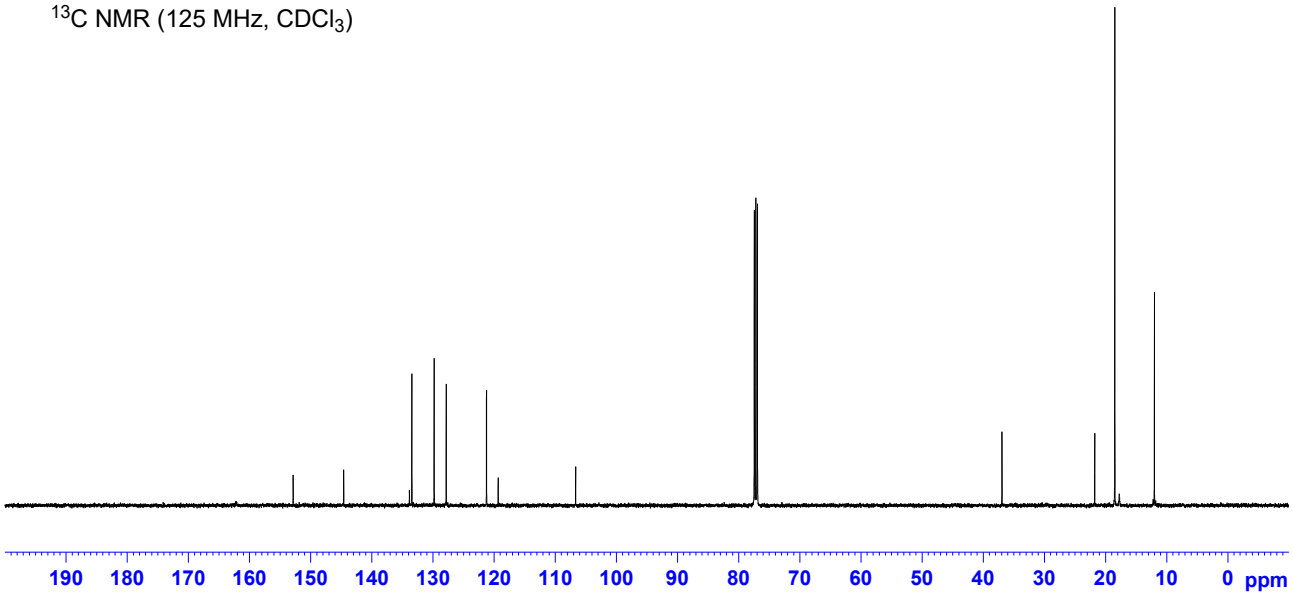


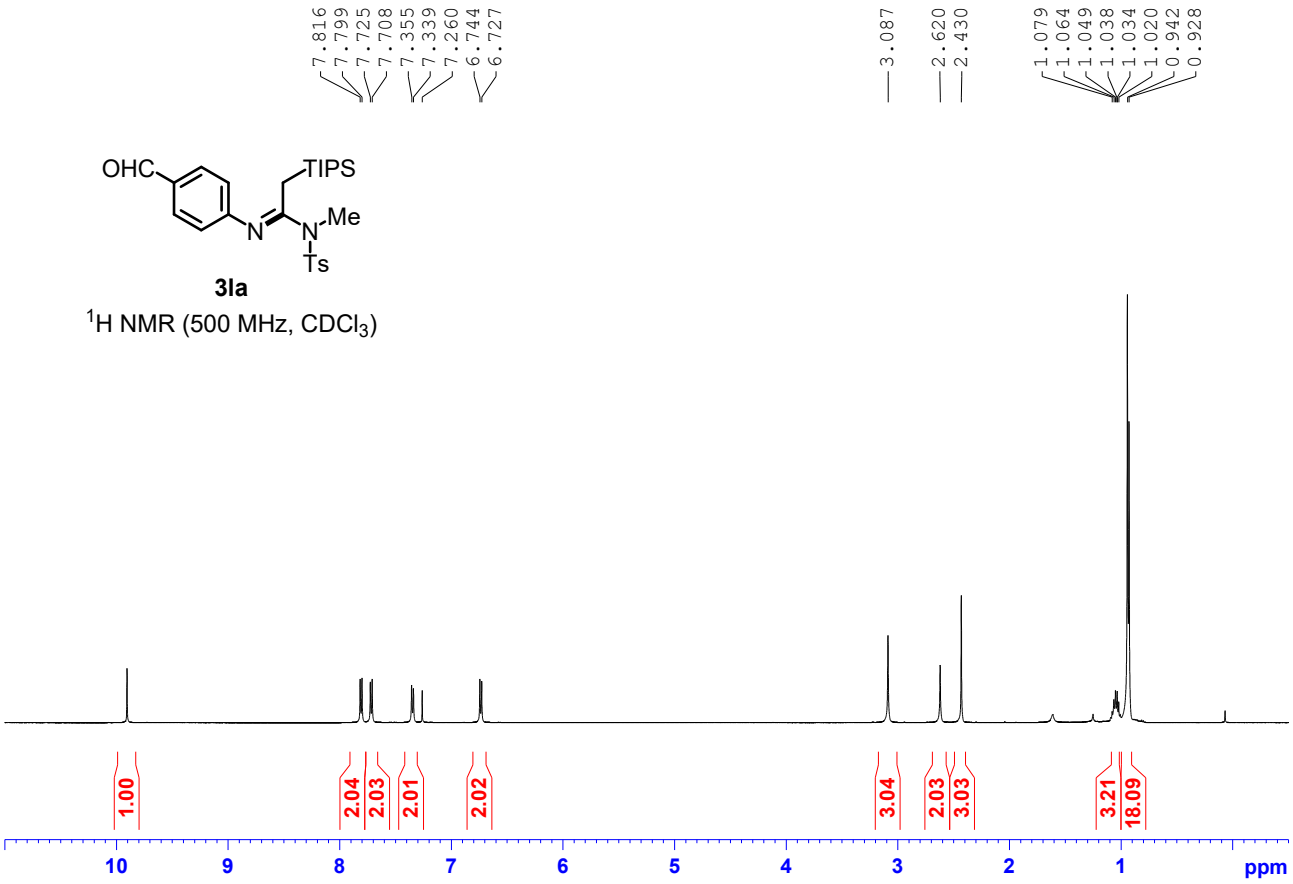




3ka

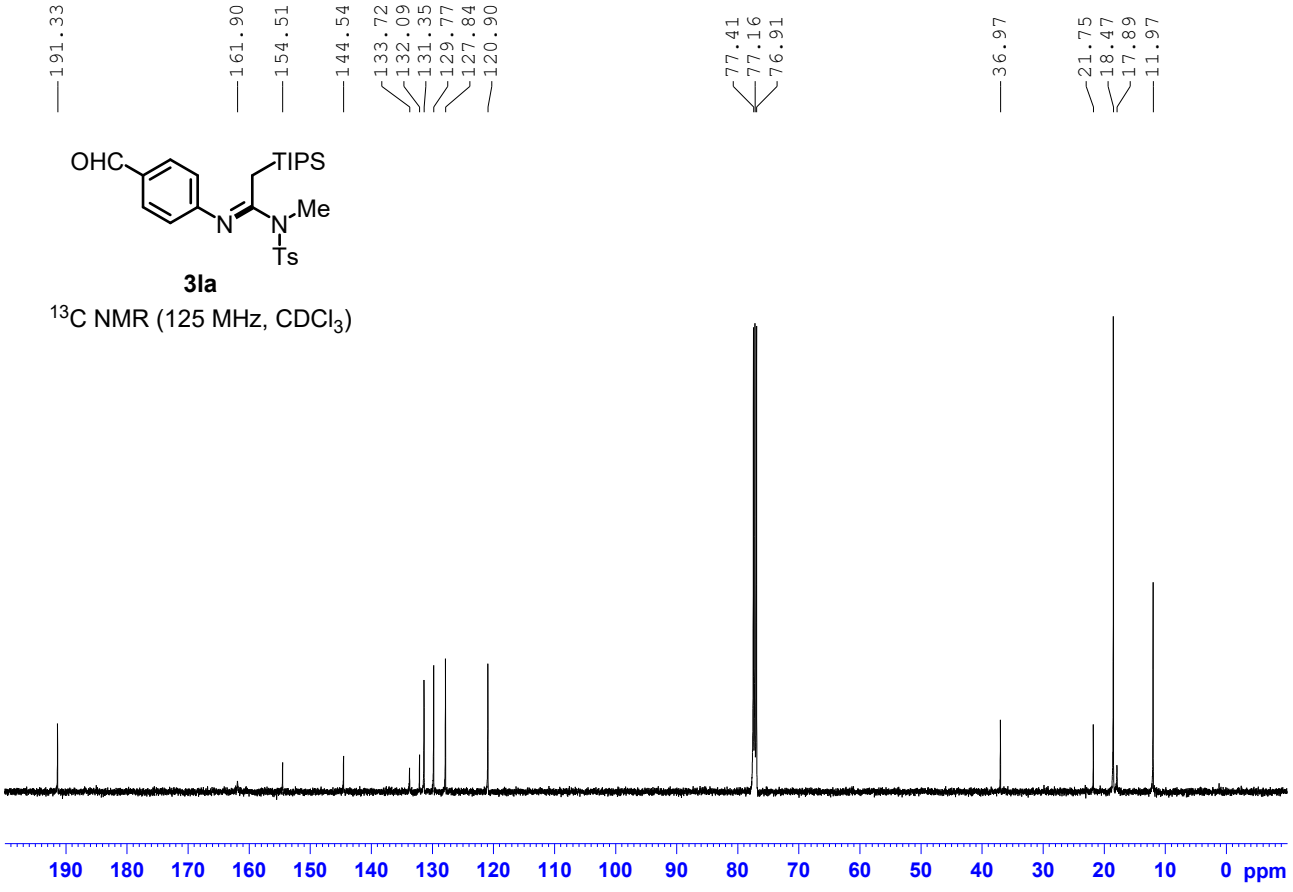
^{13}C NMR (125 MHz, $CDCl_3$)





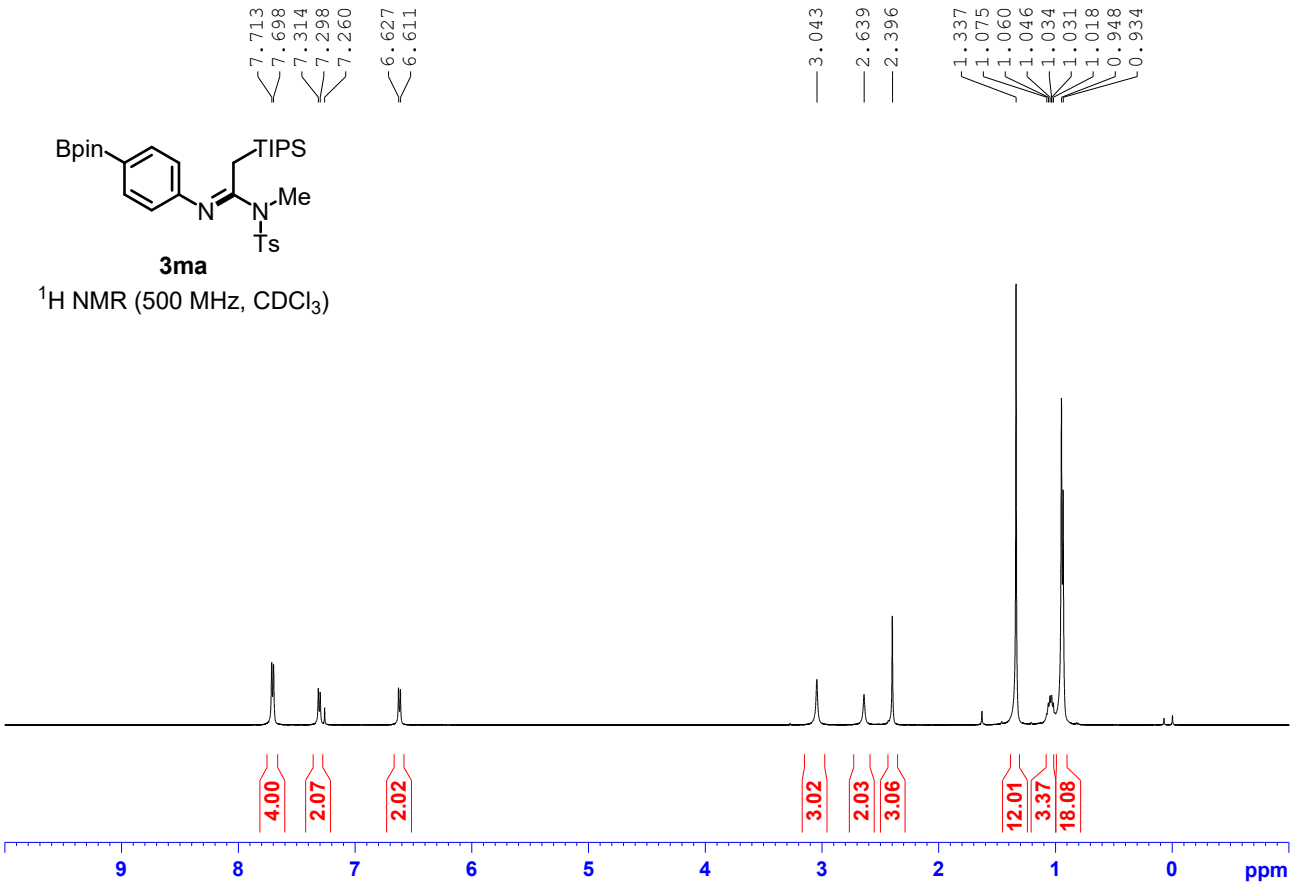
3la

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



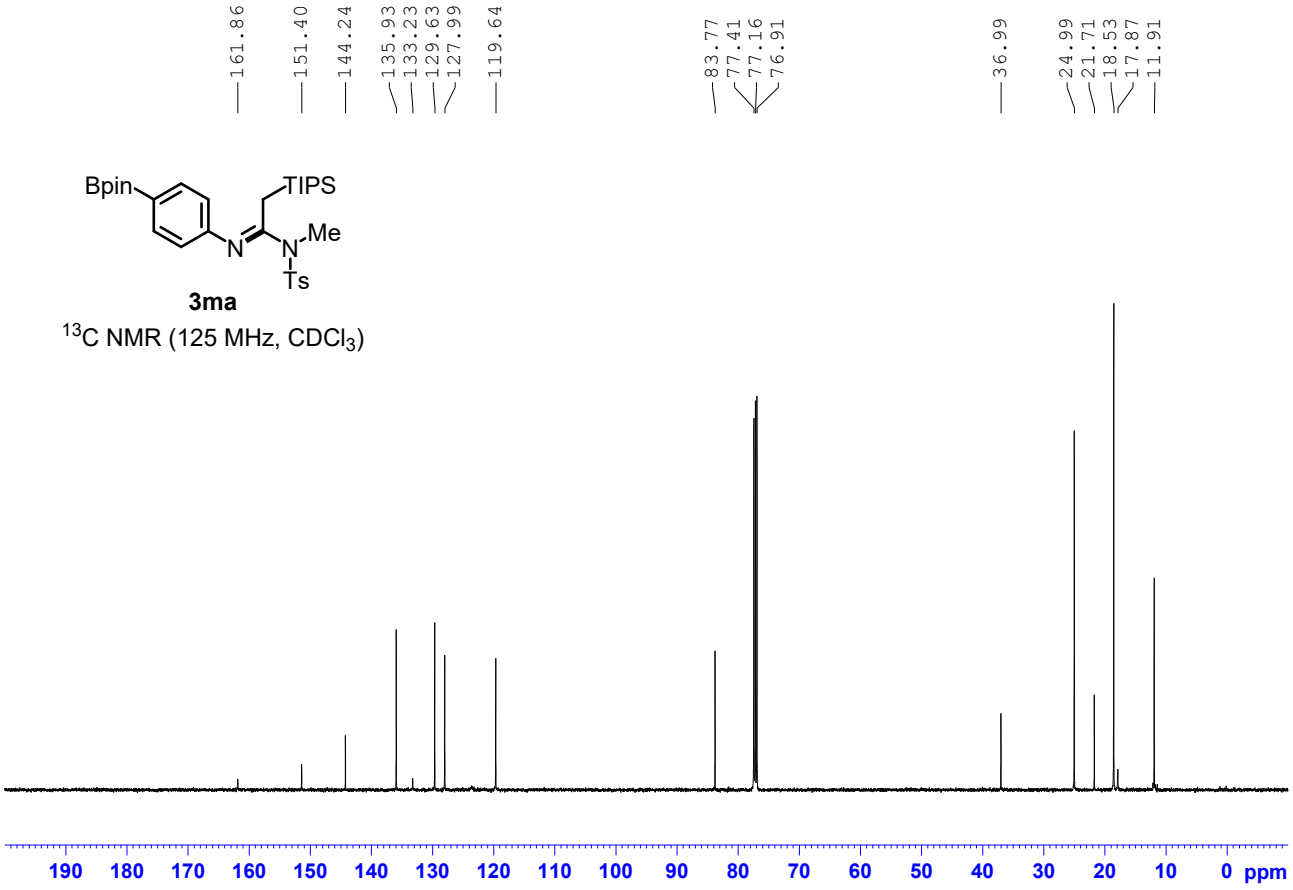
3la

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



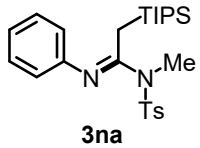
3ma

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



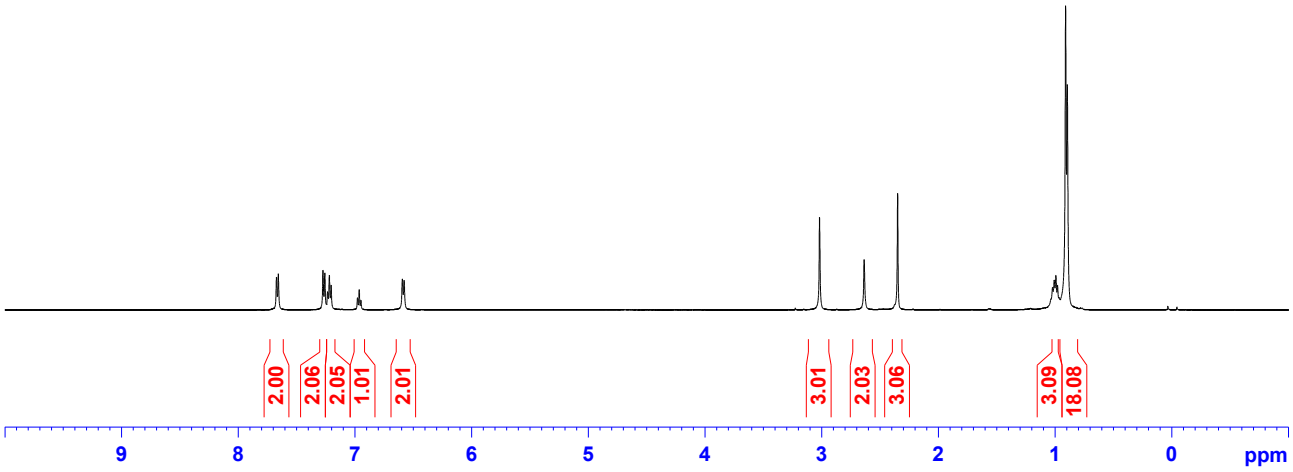
3ma

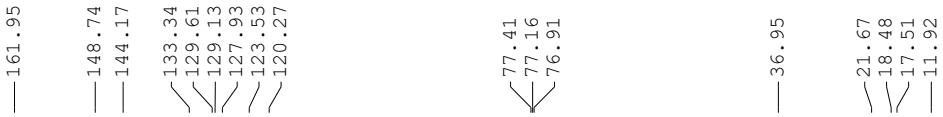
^{13}C NMR (125 MHz, $CDCl_3$)

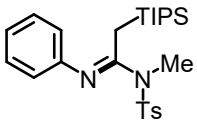


3na

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

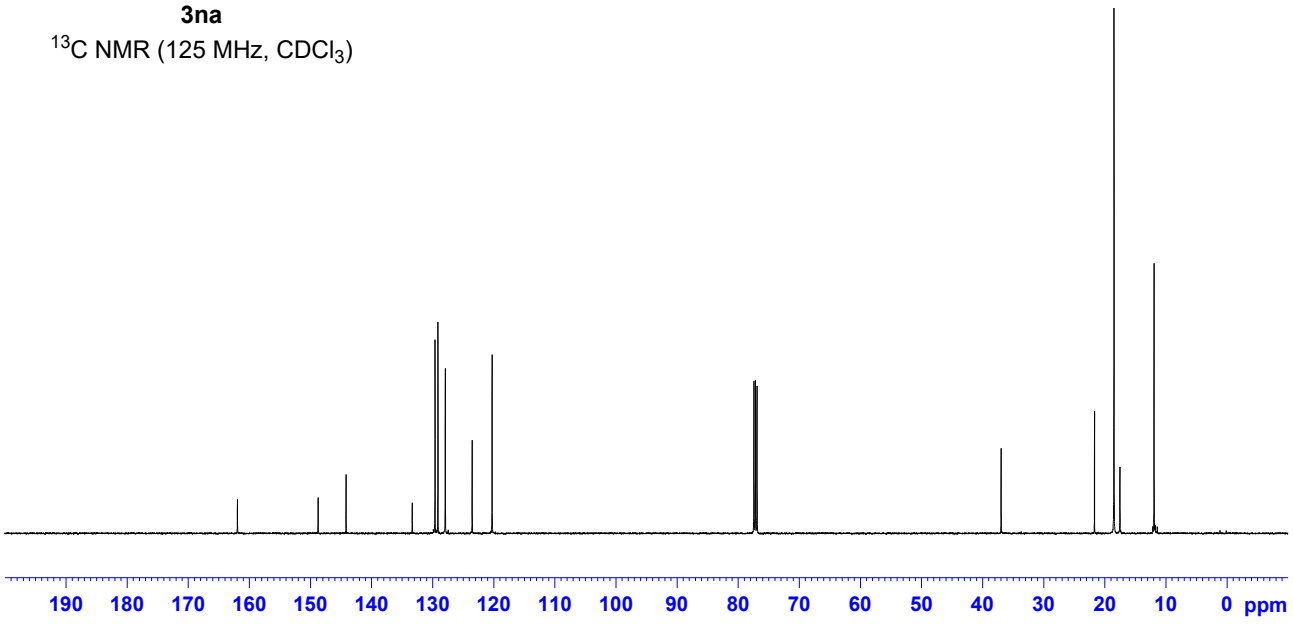


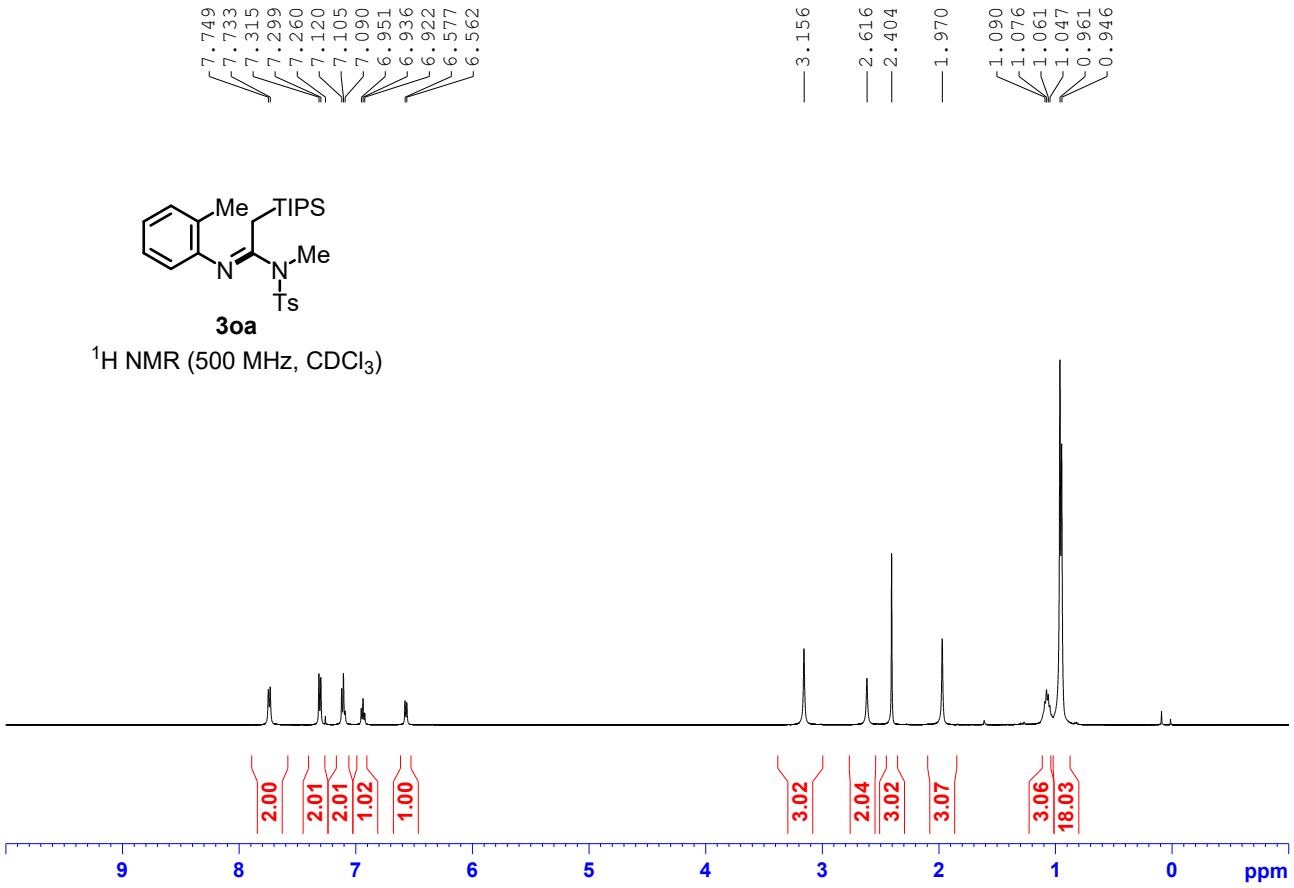




3na

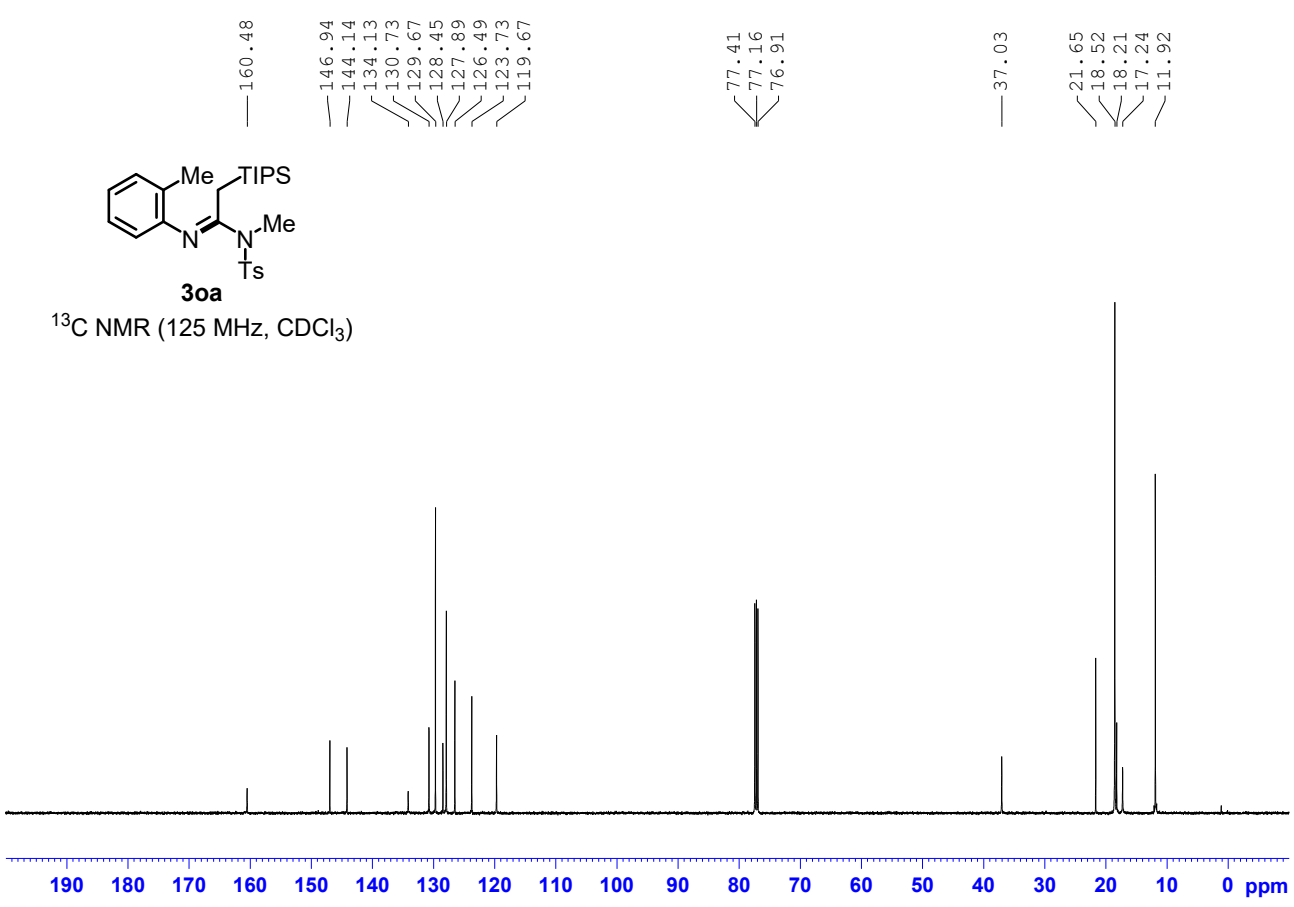
^{13}C NMR (125 MHz, $CDCl_3$)





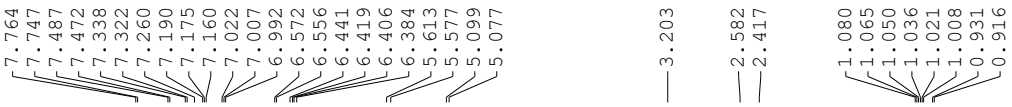
3oa

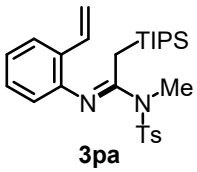
^{1}H NMR (500 MHz, $CDCl_3$)



3oa

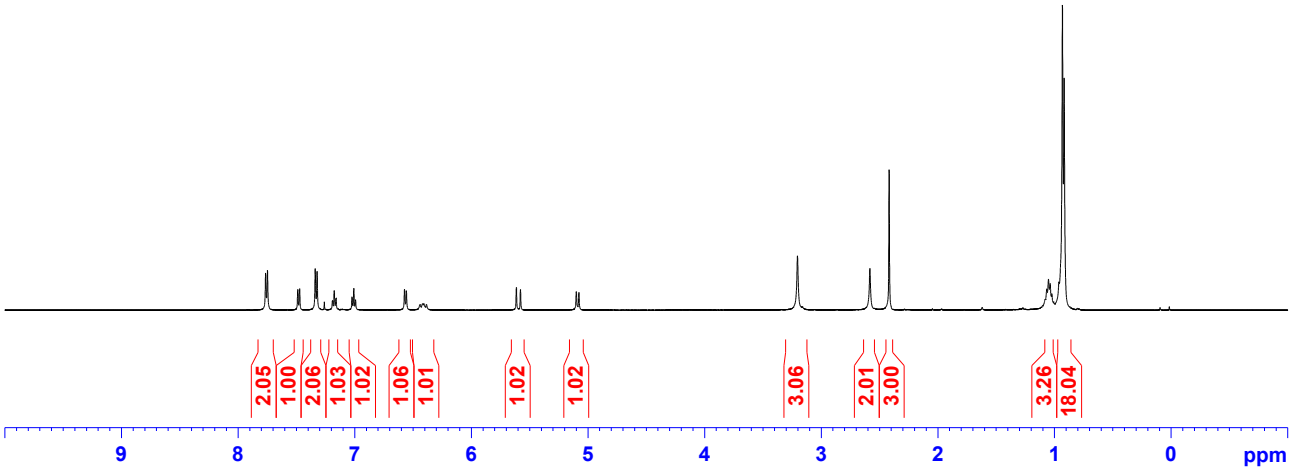
^{13}C NMR (125 MHz, $CDCl_3$)

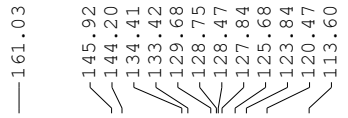


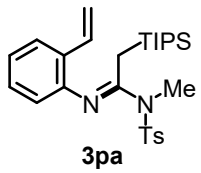


3pa

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

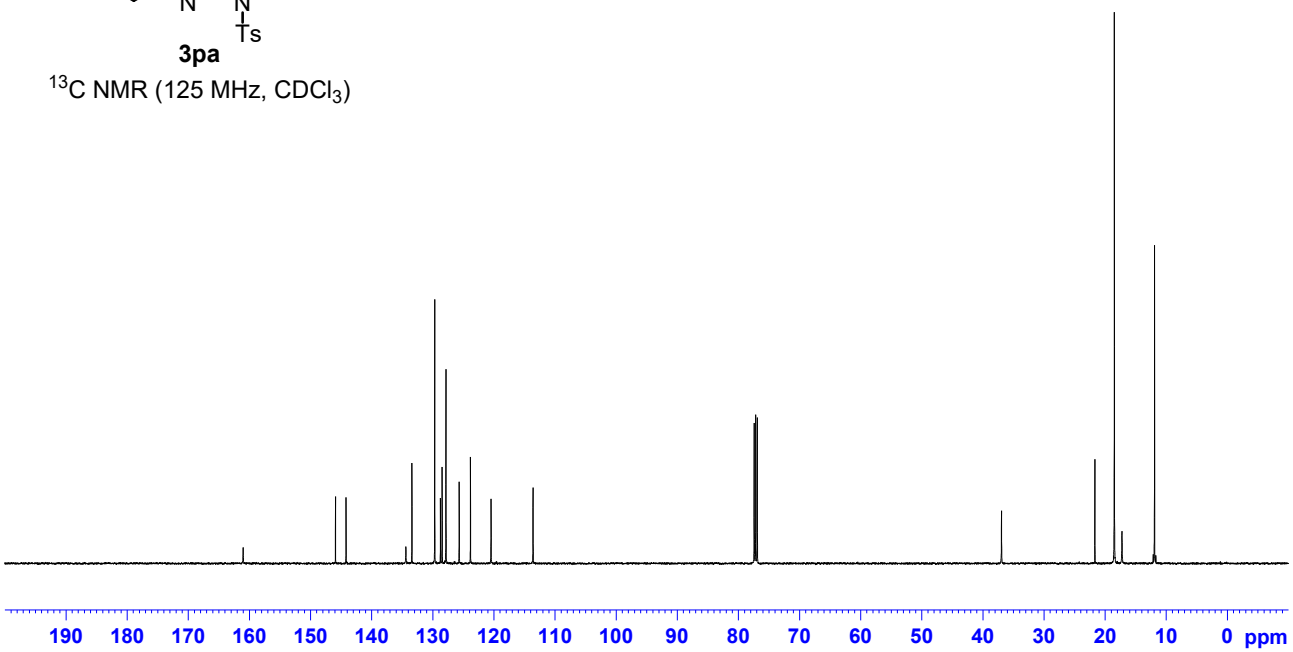


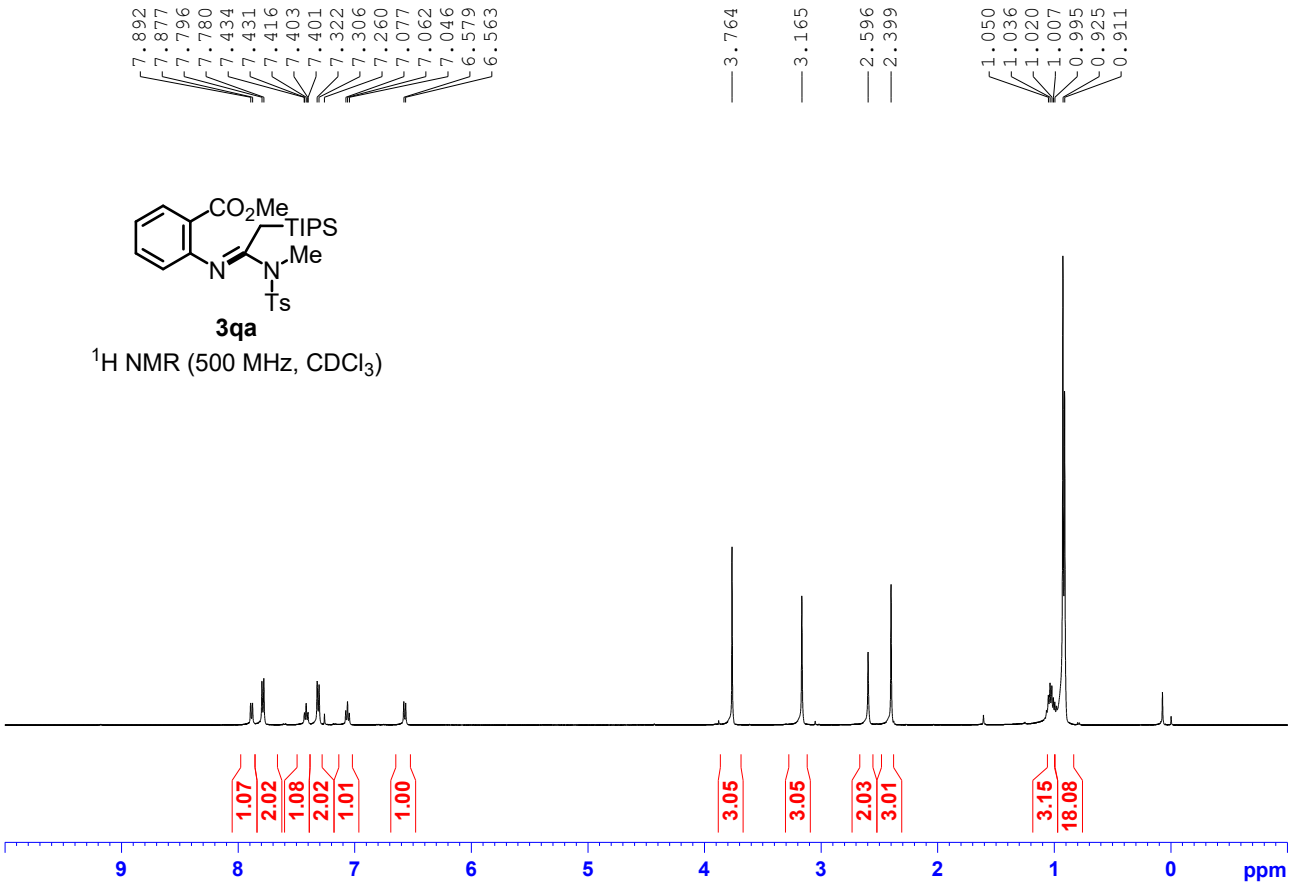




3pa

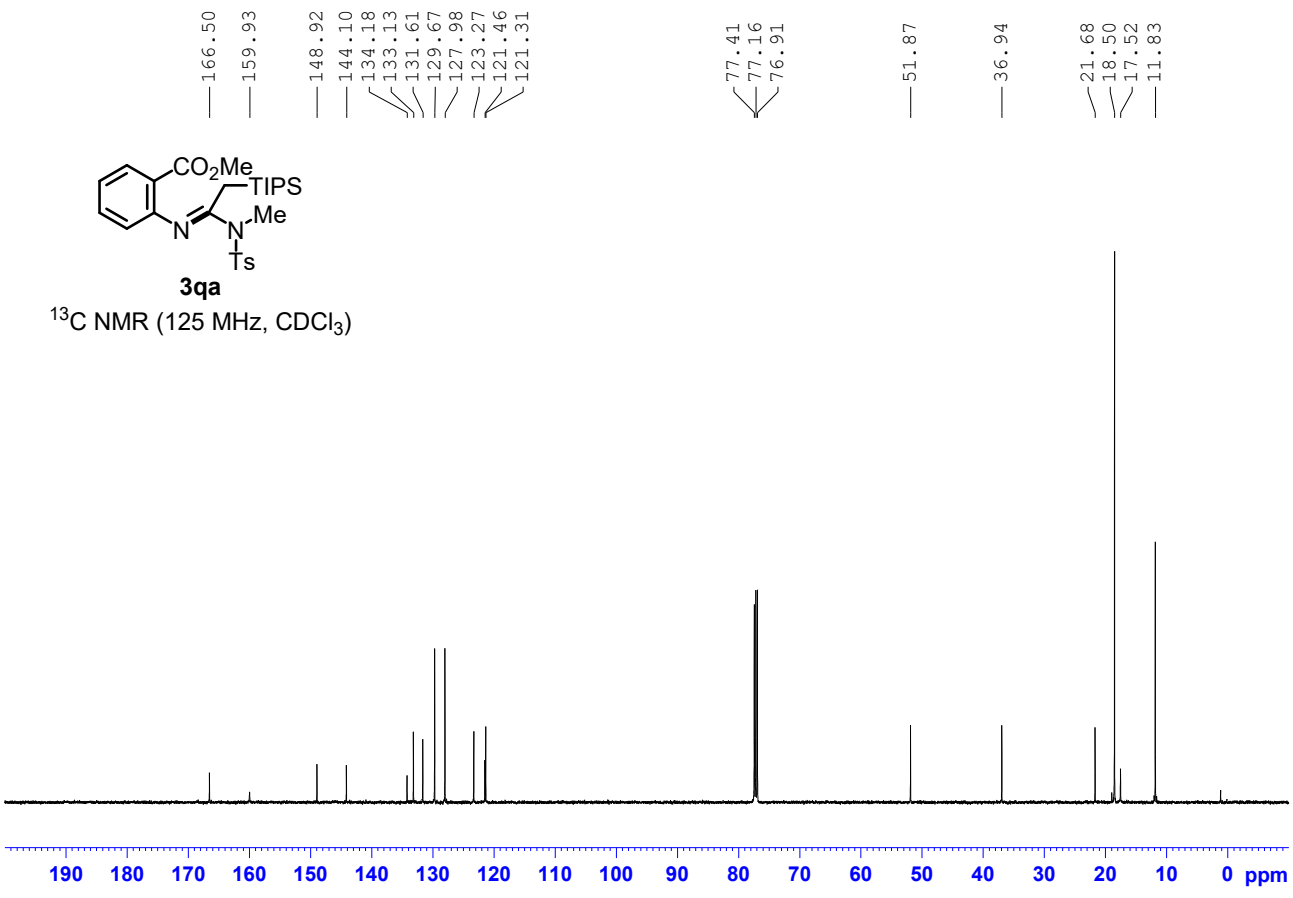
^{13}C NMR (125 MHz, $CDCl_3$)





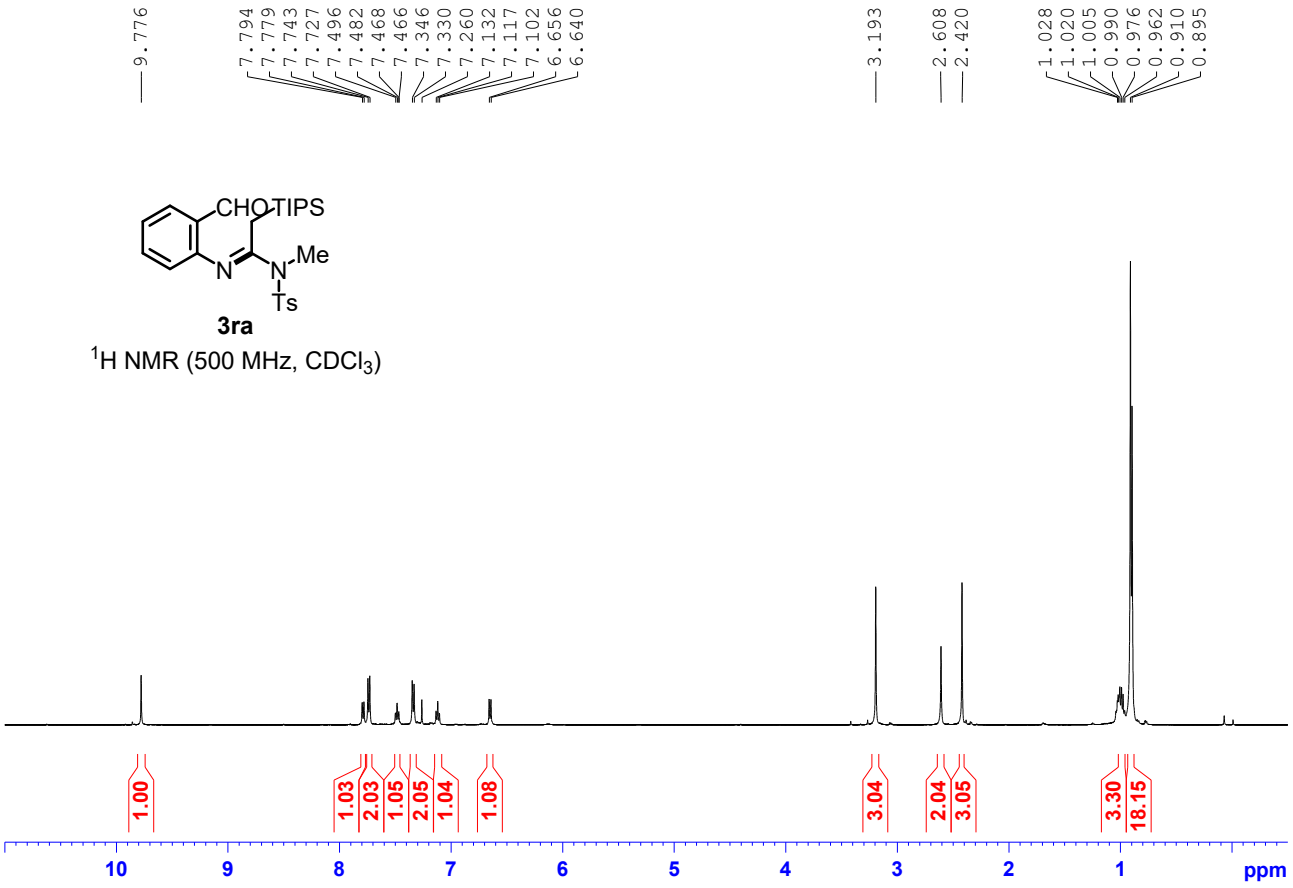
3qa

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



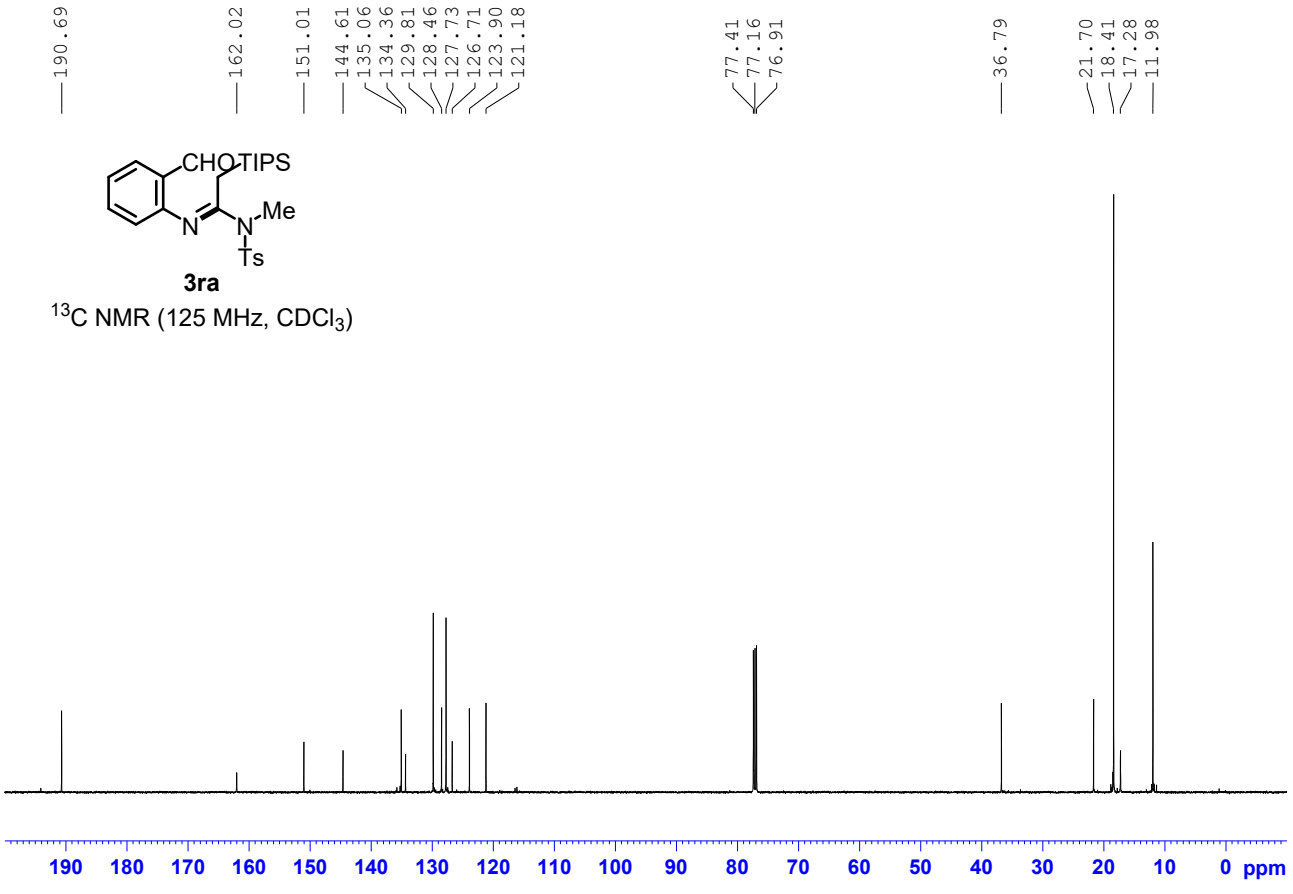
3qa

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



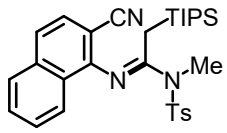
3ra

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



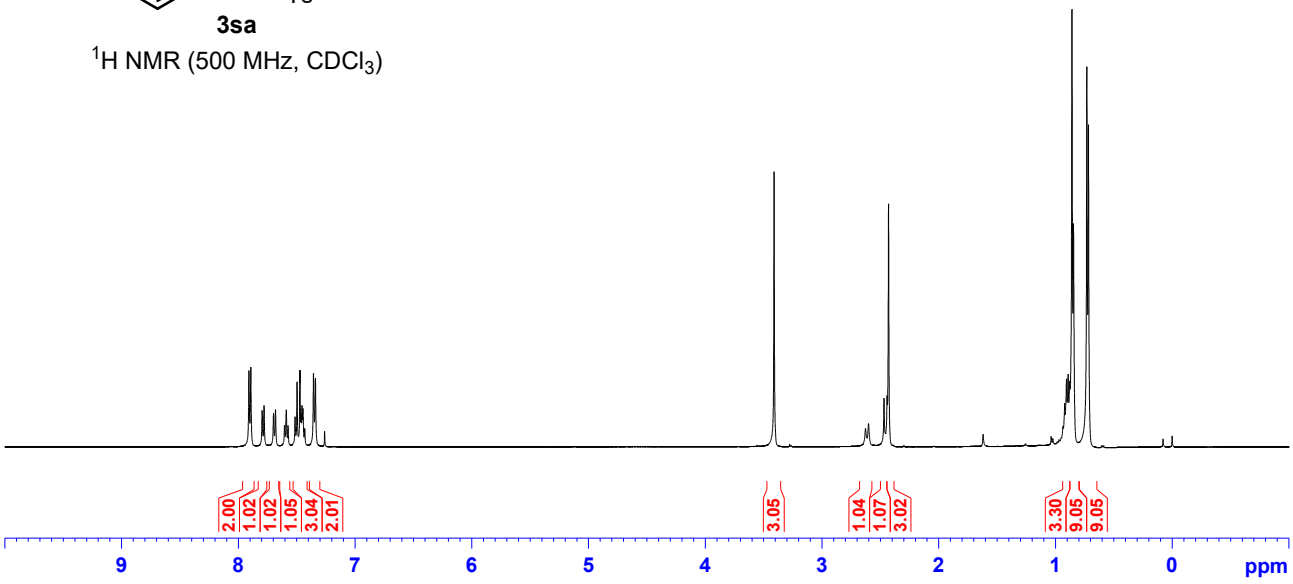
3ra

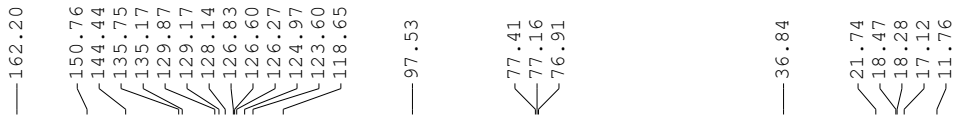
^{13}C NMR (125 MHz, $CDCl_3$)

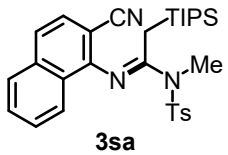


3sa

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

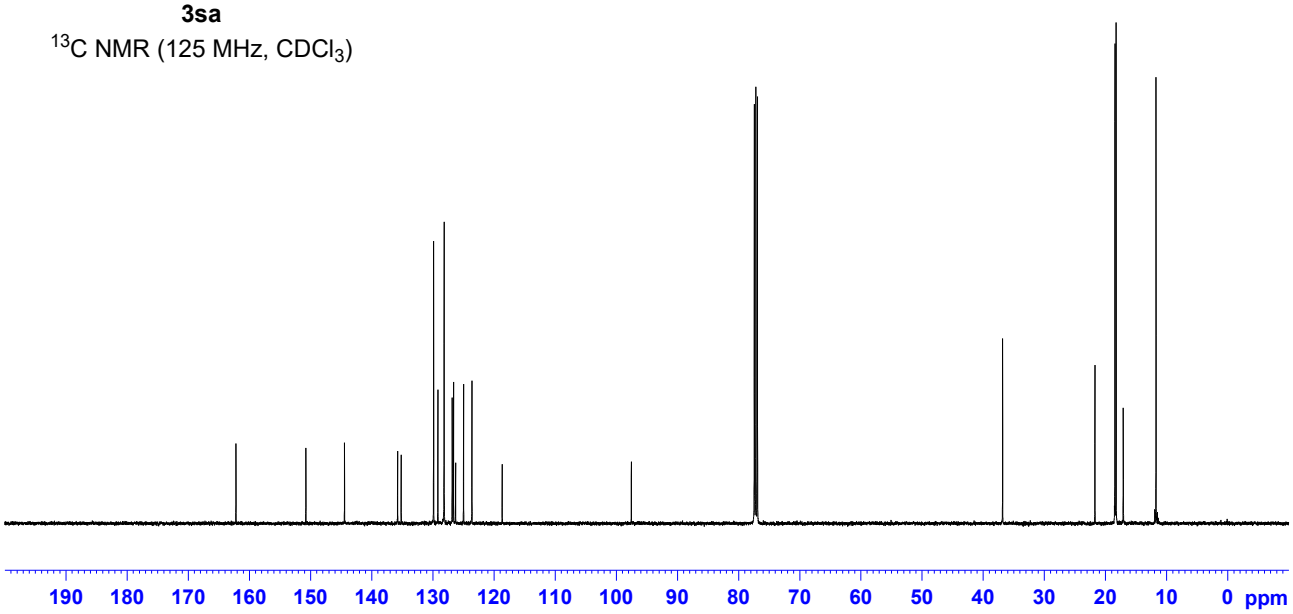


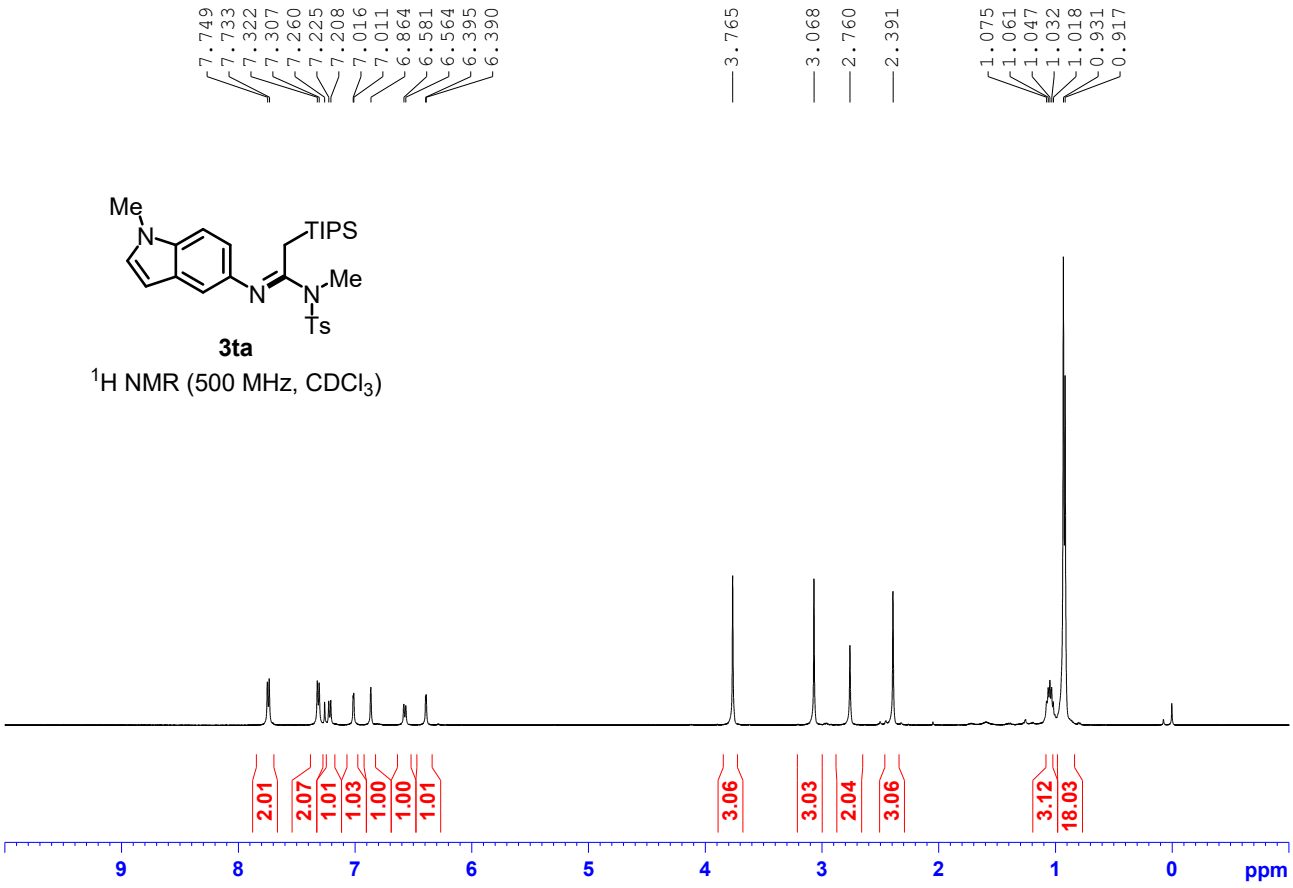




3sa

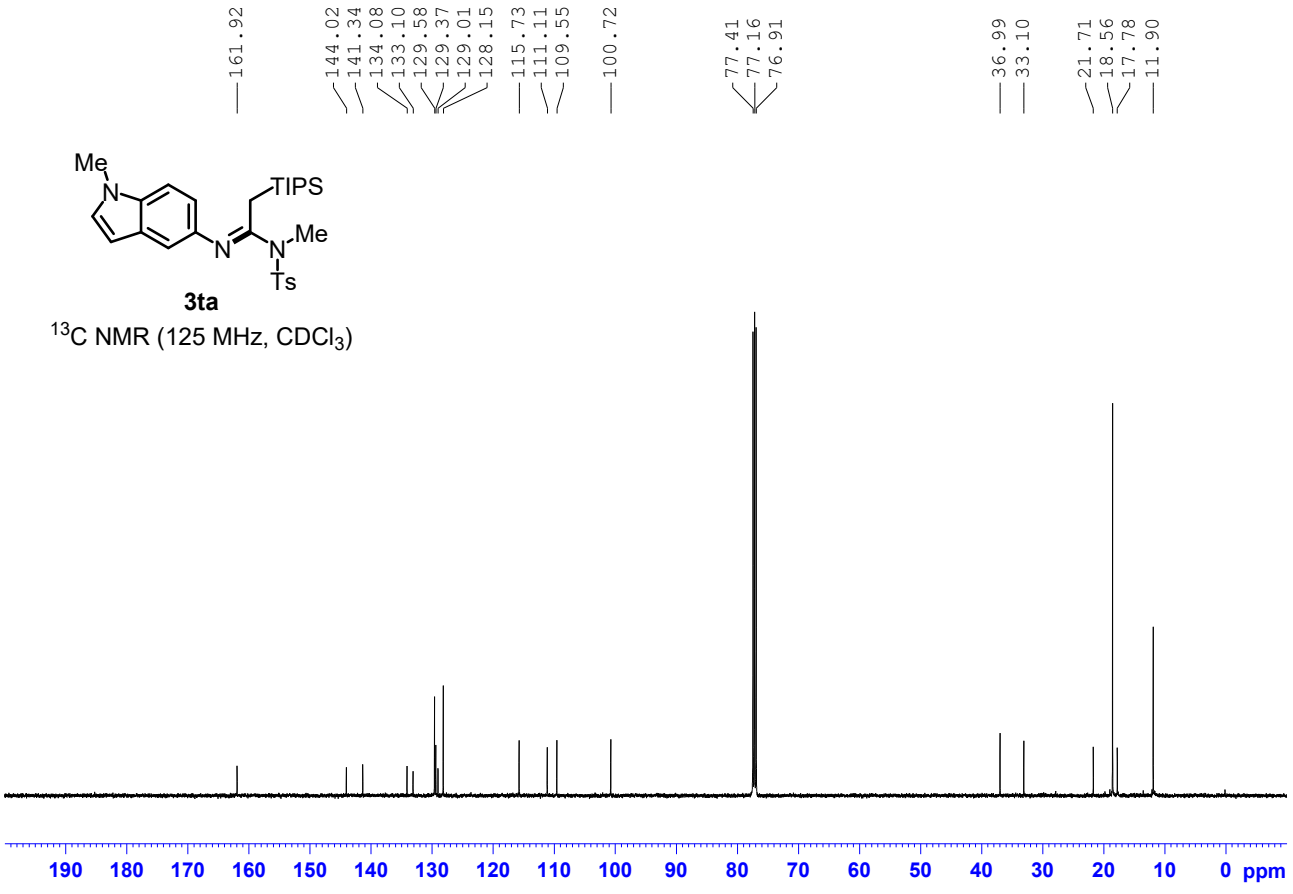
^{13}C NMR (125 MHz, $CDCl_3$)





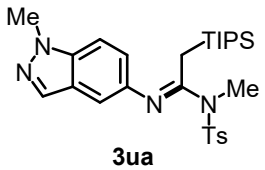
3ta

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



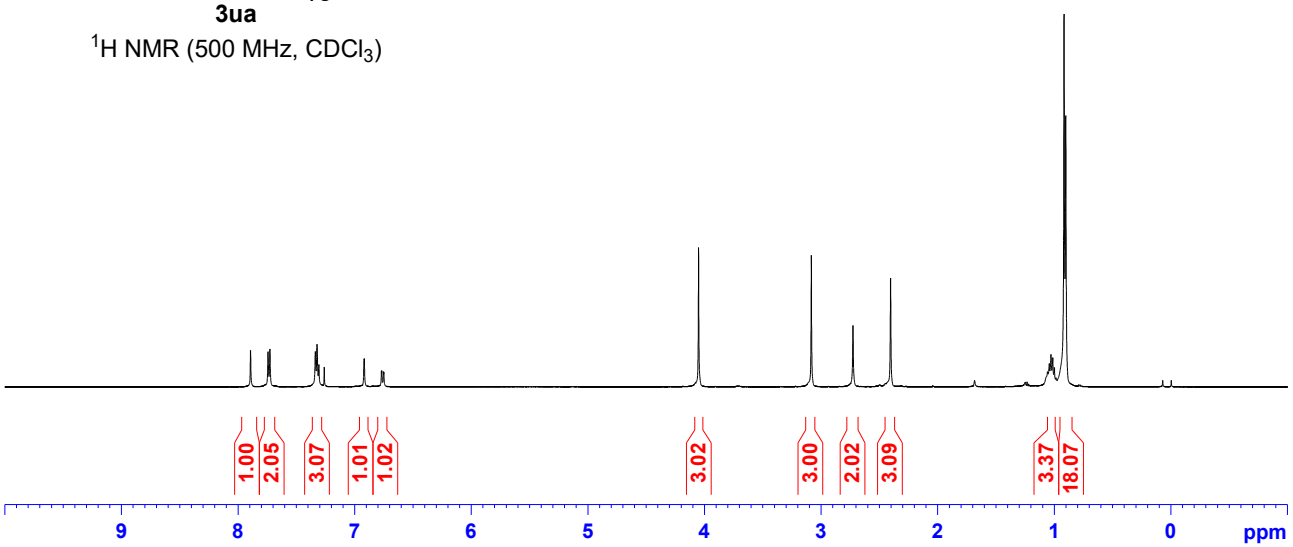
3ta

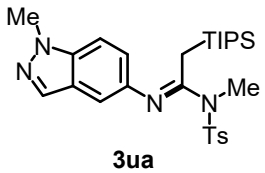
^{13}C NMR (125 MHz, $CDCl_3$)



3ua

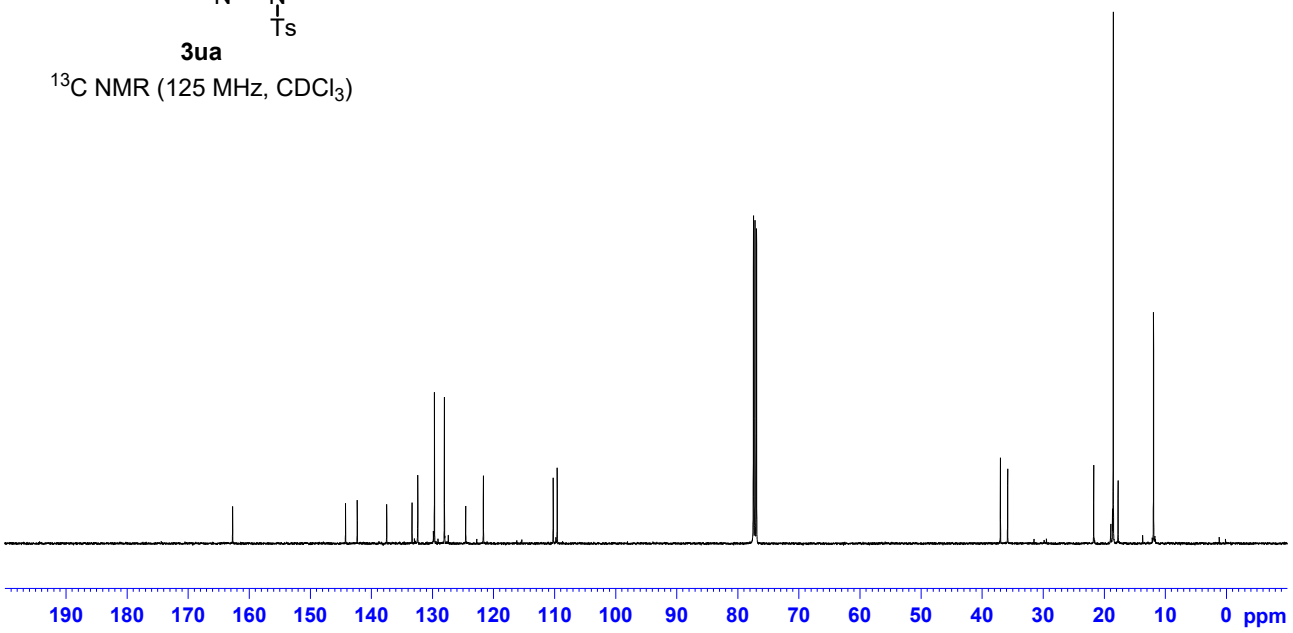
^{1}H NMR (500 MHz, $CDCl_3$)

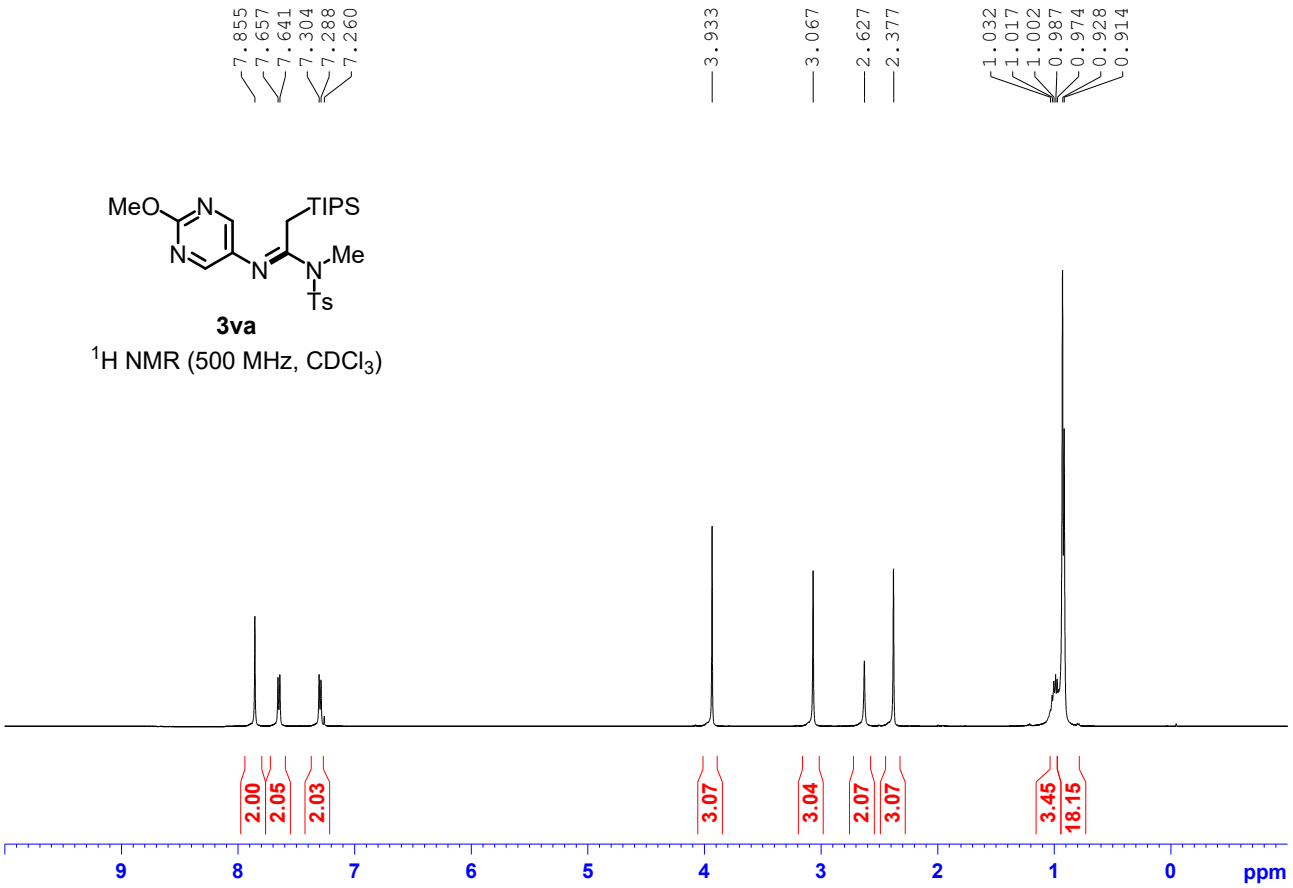




3ua

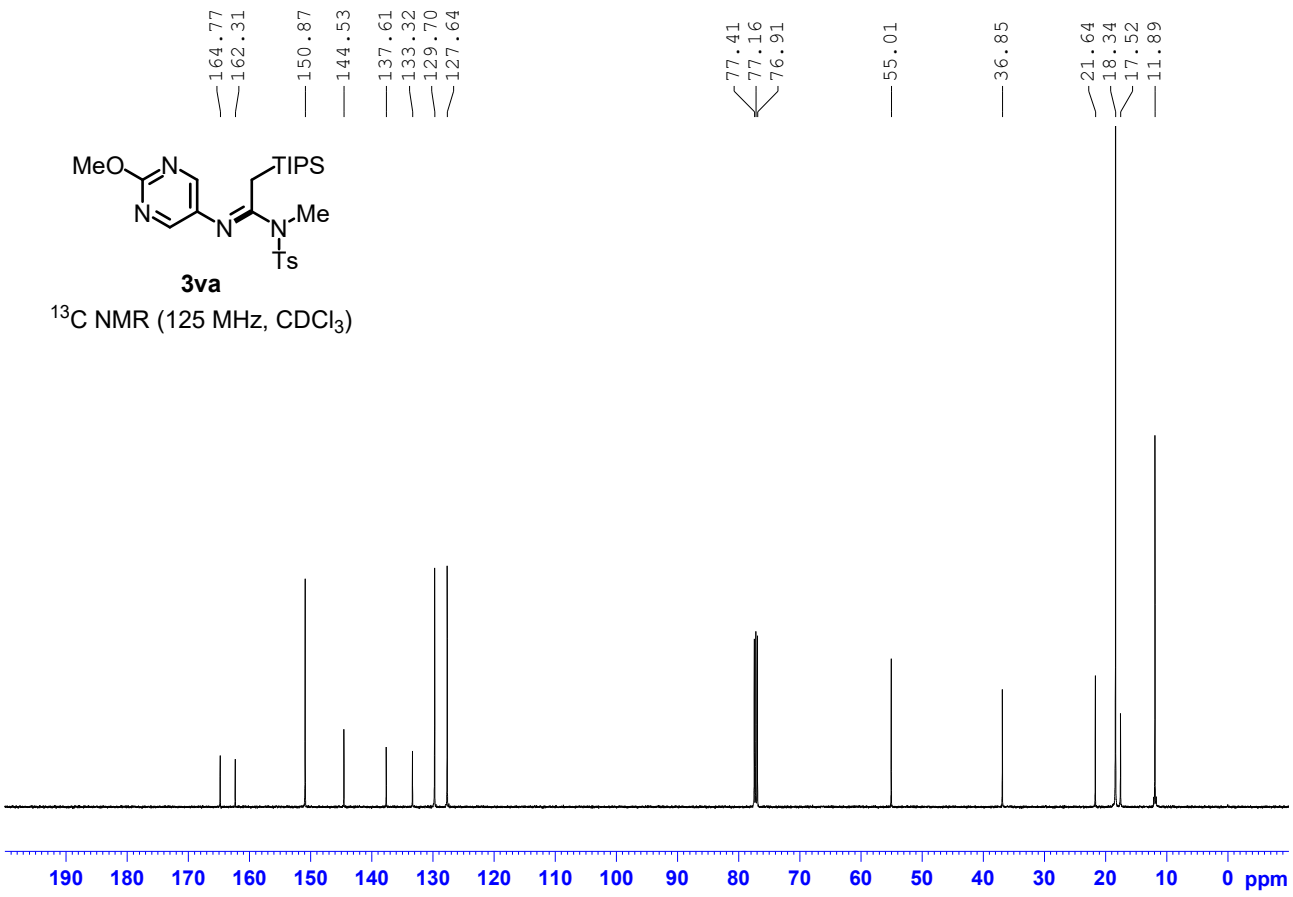
^{13}C NMR (125 MHz, $CDCl_3$)





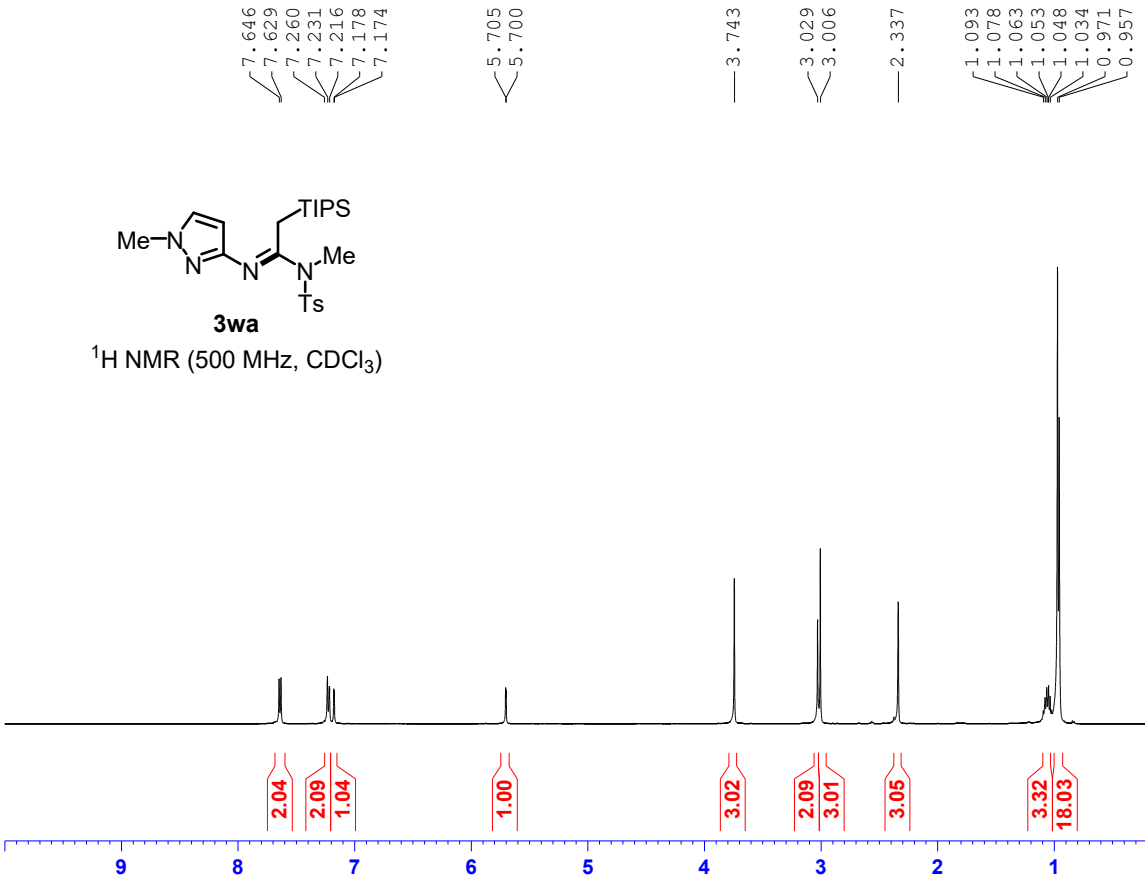
3va

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



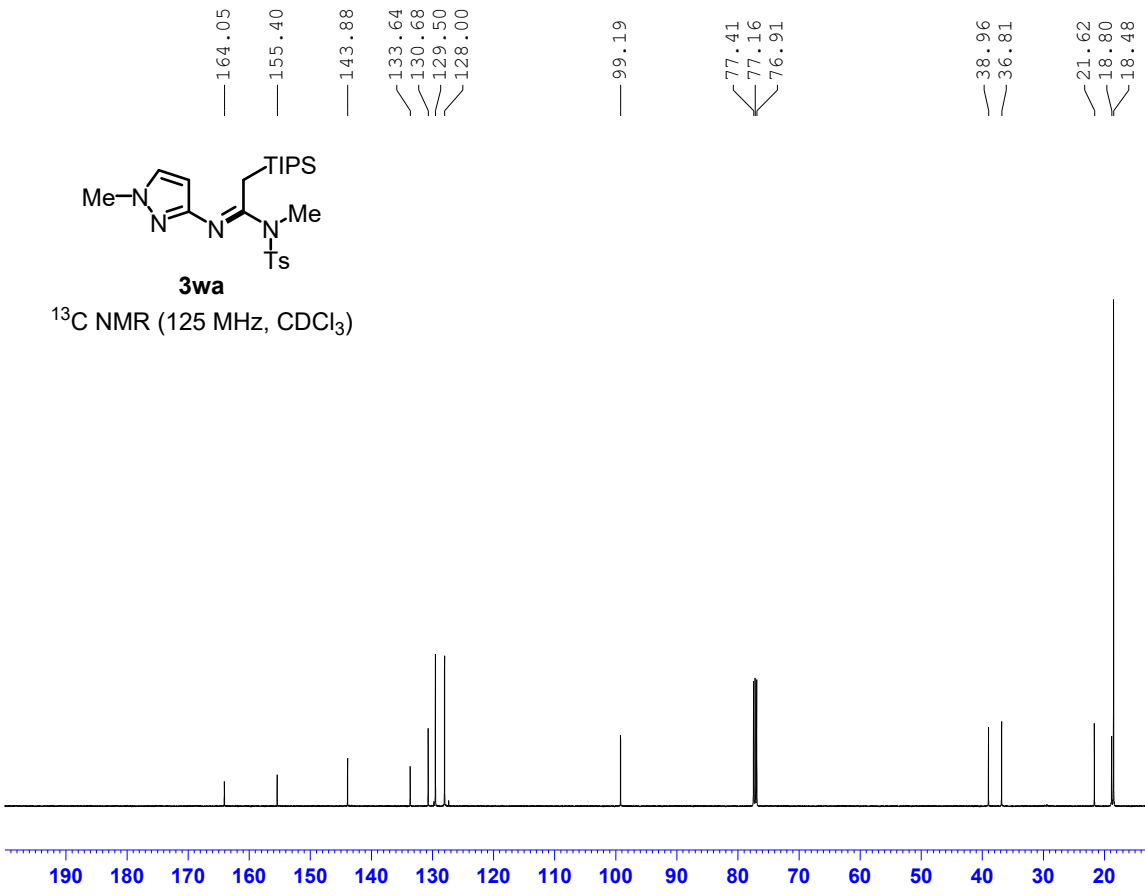
3va

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



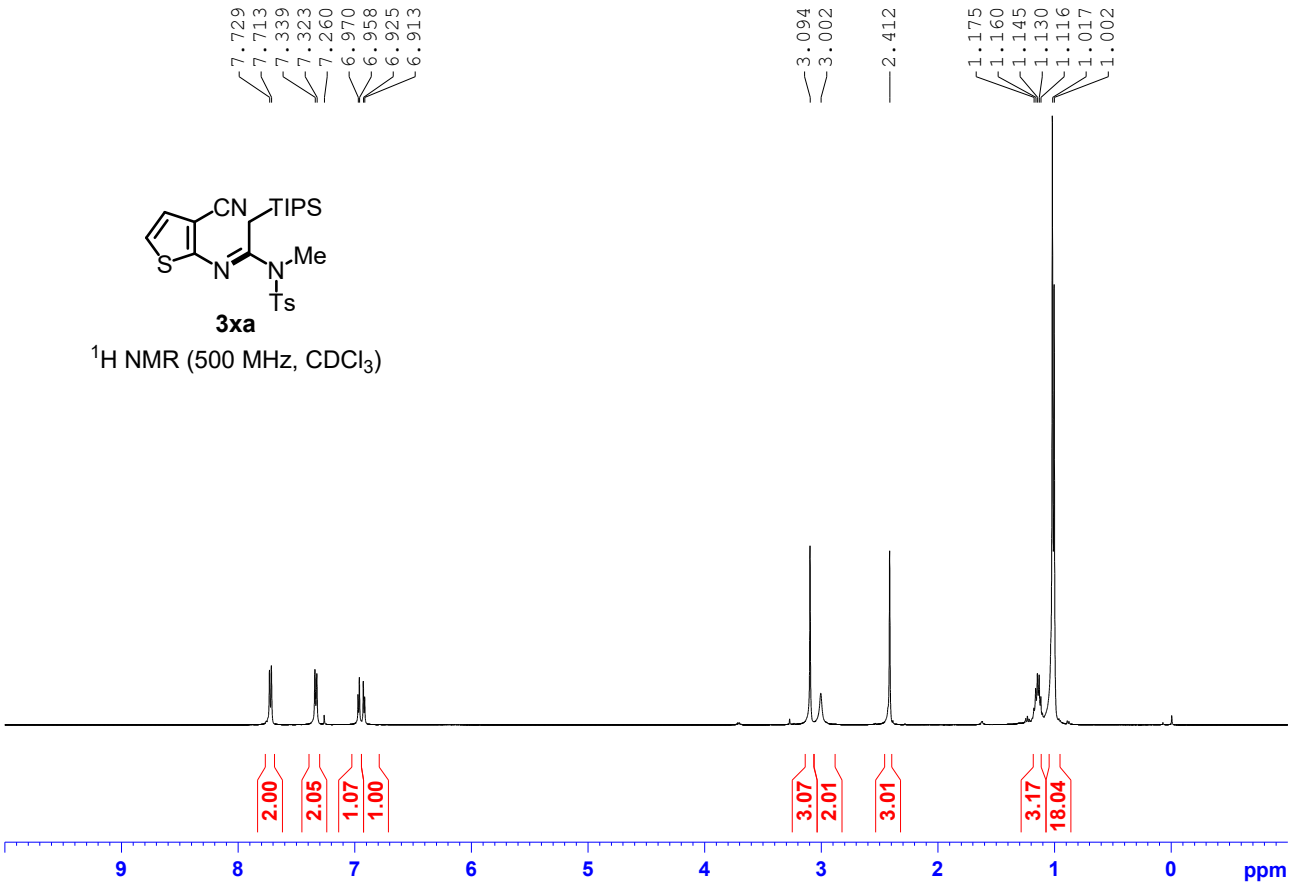
3wa

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



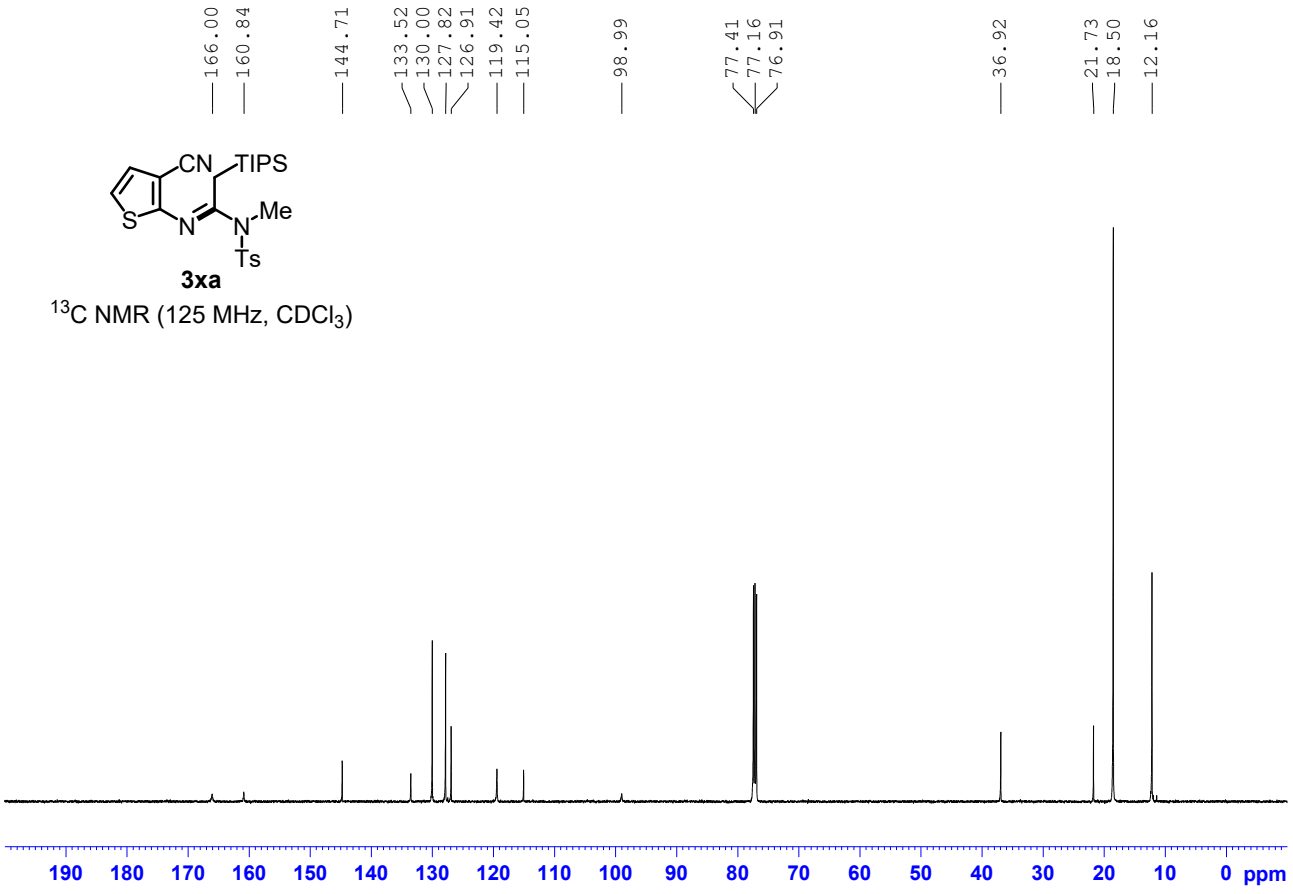
3wa

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



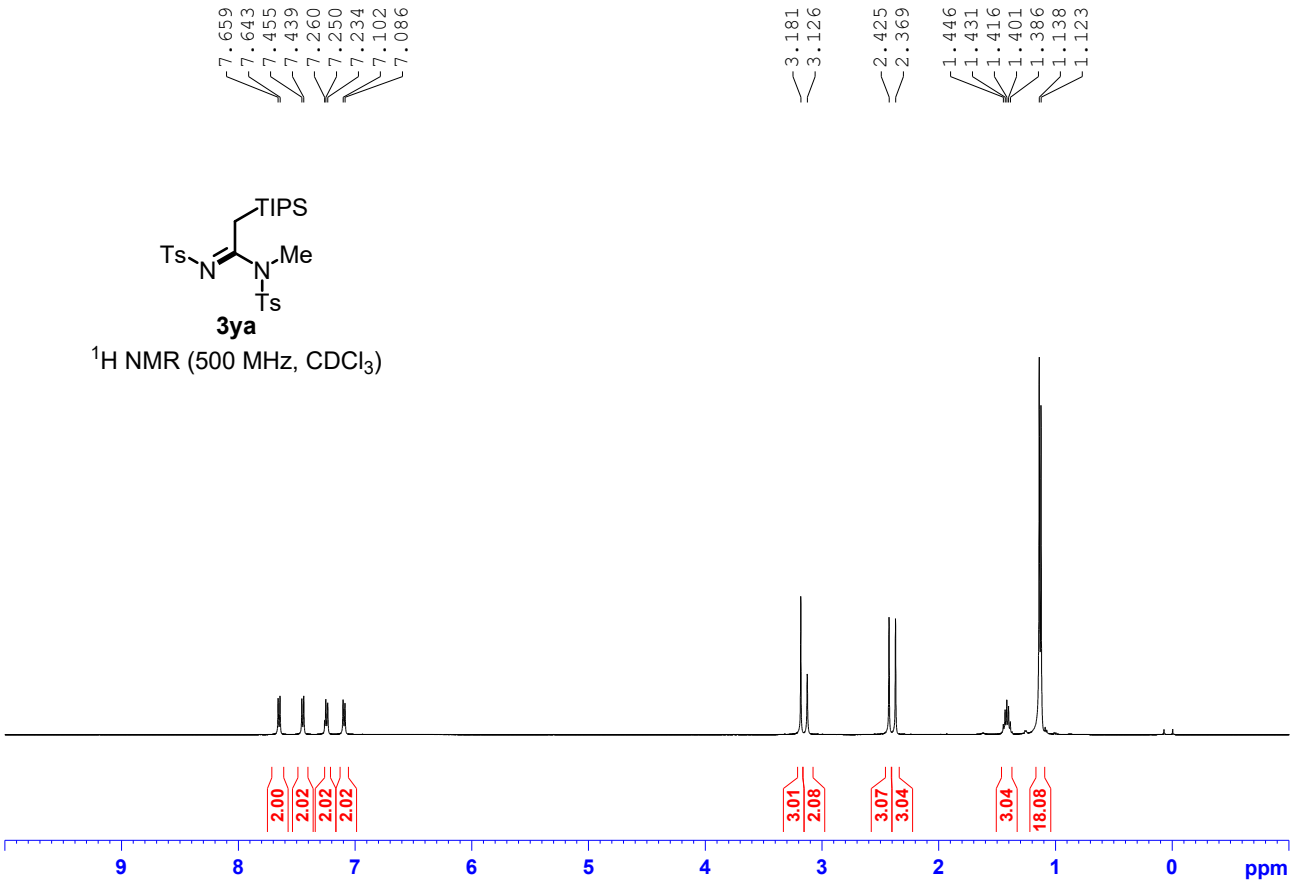
3xa

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



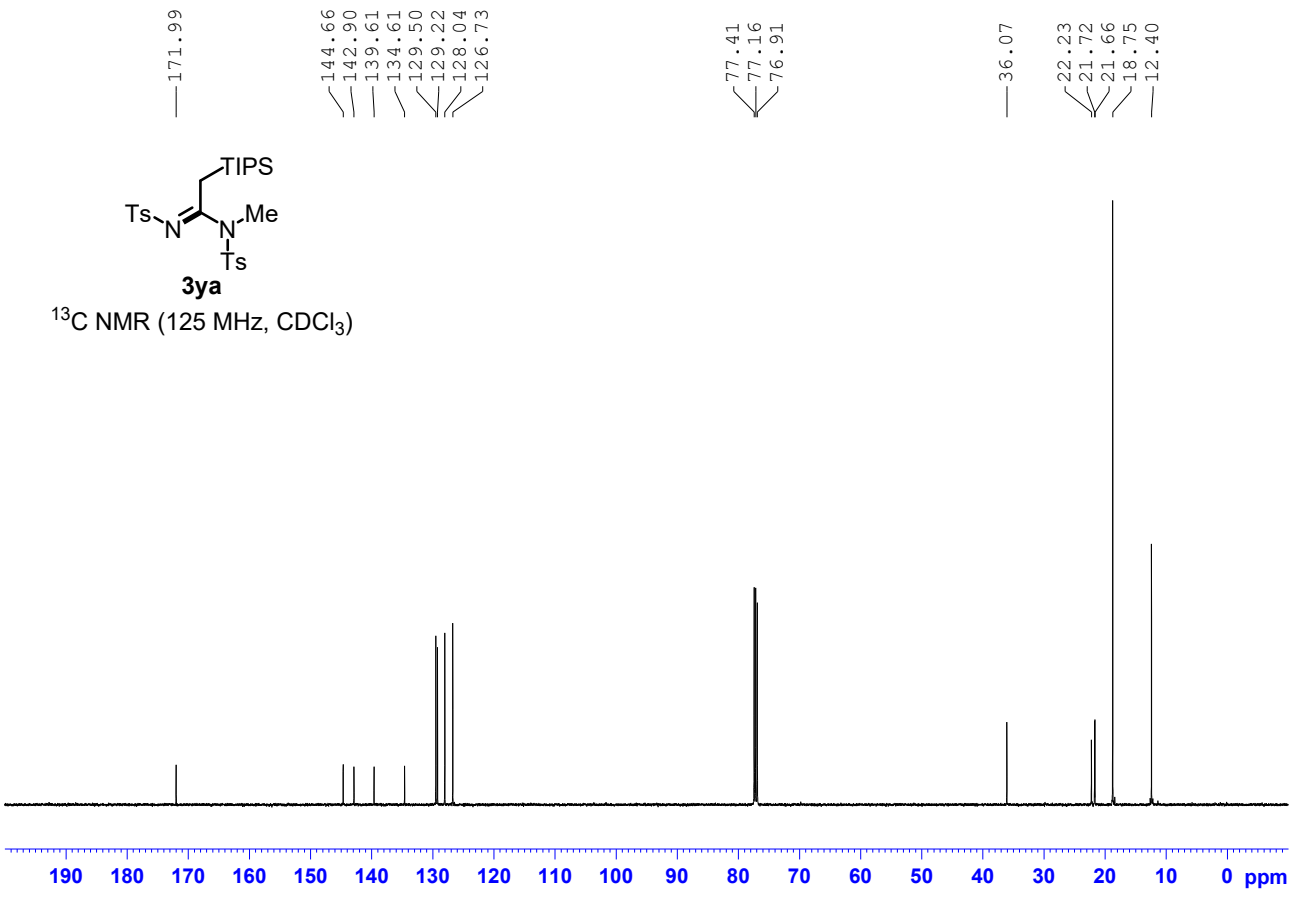
3xa

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



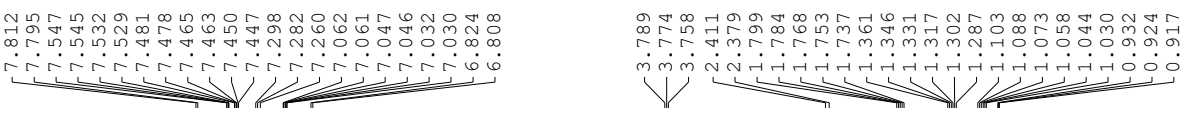
3ya

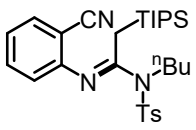
^{1}H NMR (500 MHz, $CDCl_3$)



3ya

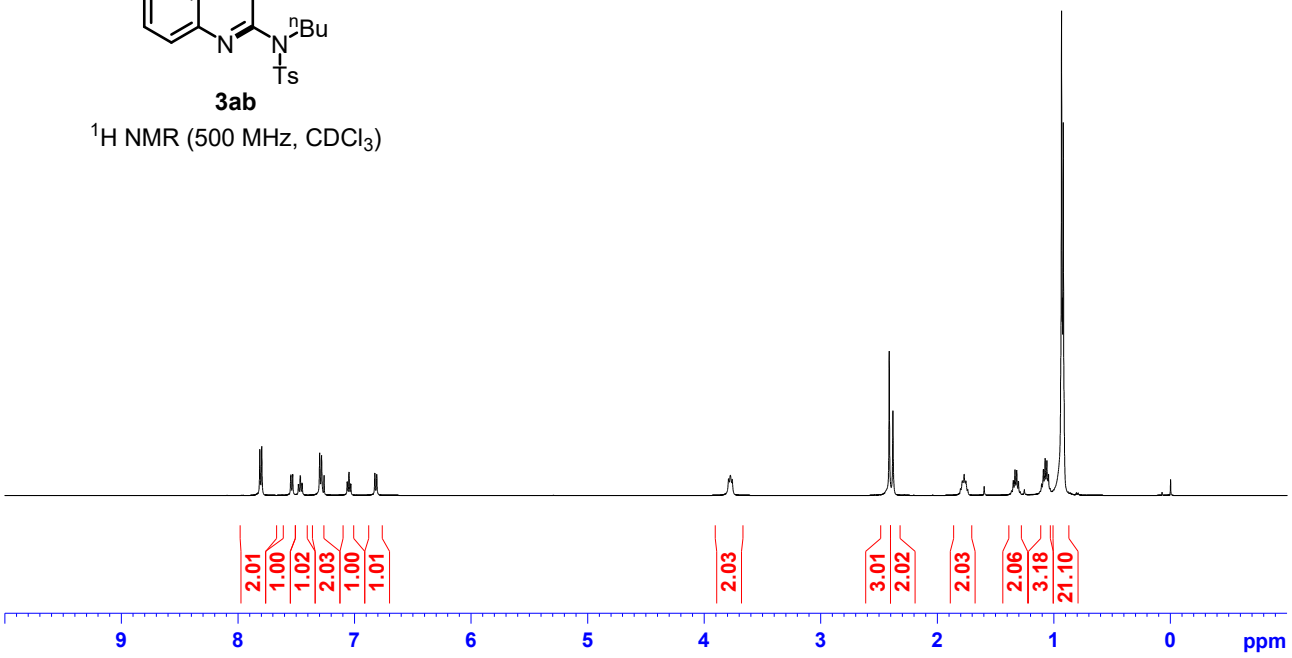
^{13}C NMR (125 MHz, $CDCl_3$)

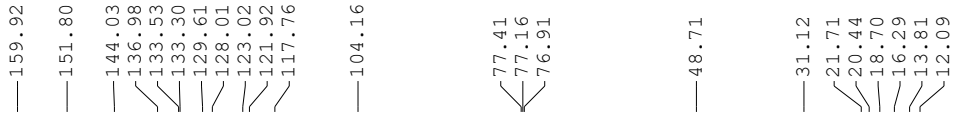


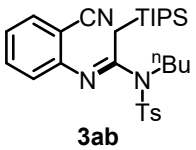


3ab

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

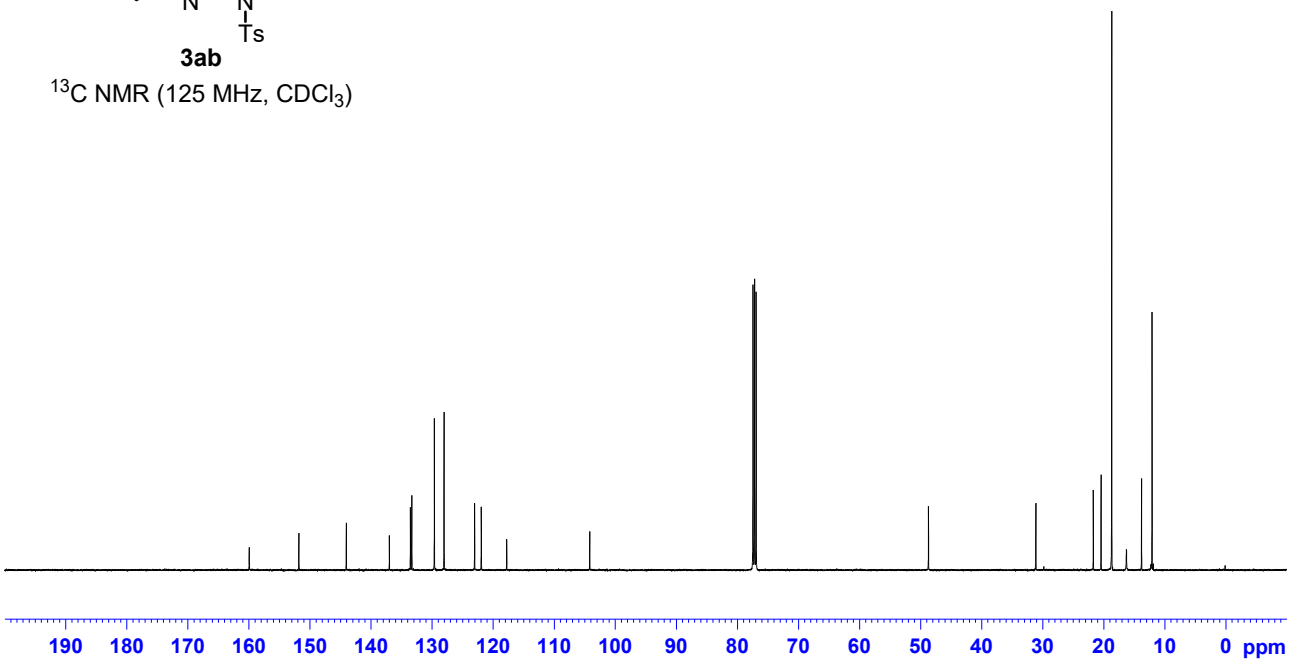


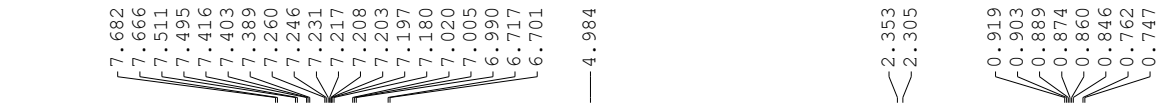


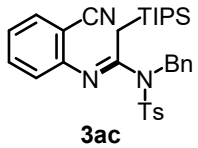


3ab

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

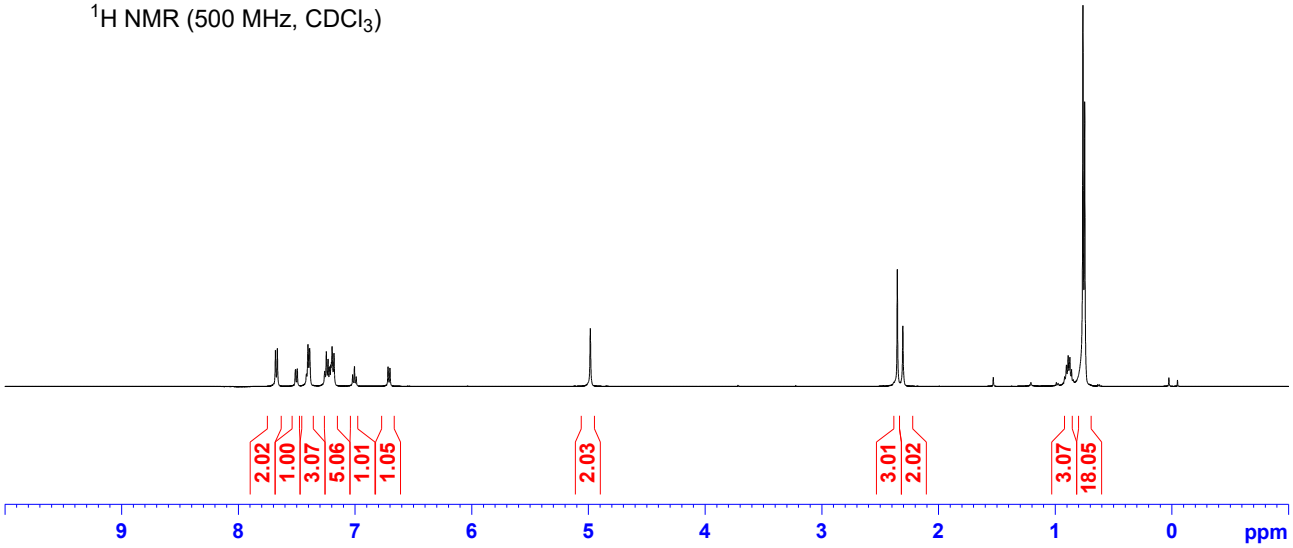


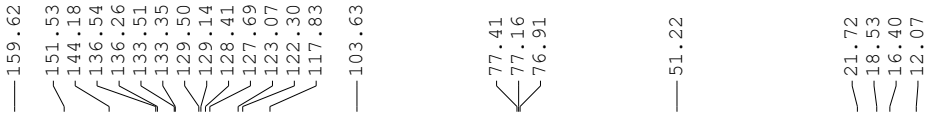


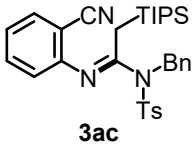


3ac

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

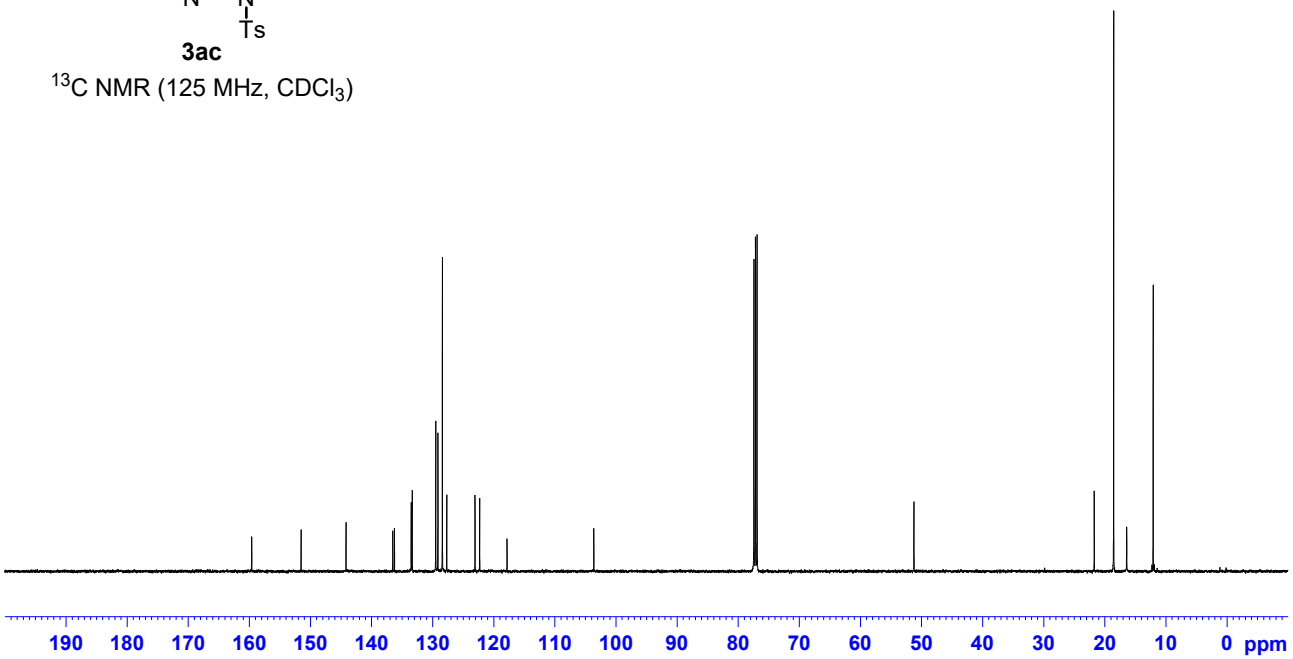


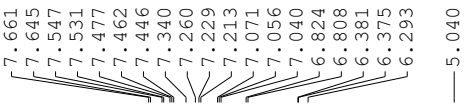


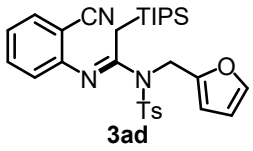


3ac

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

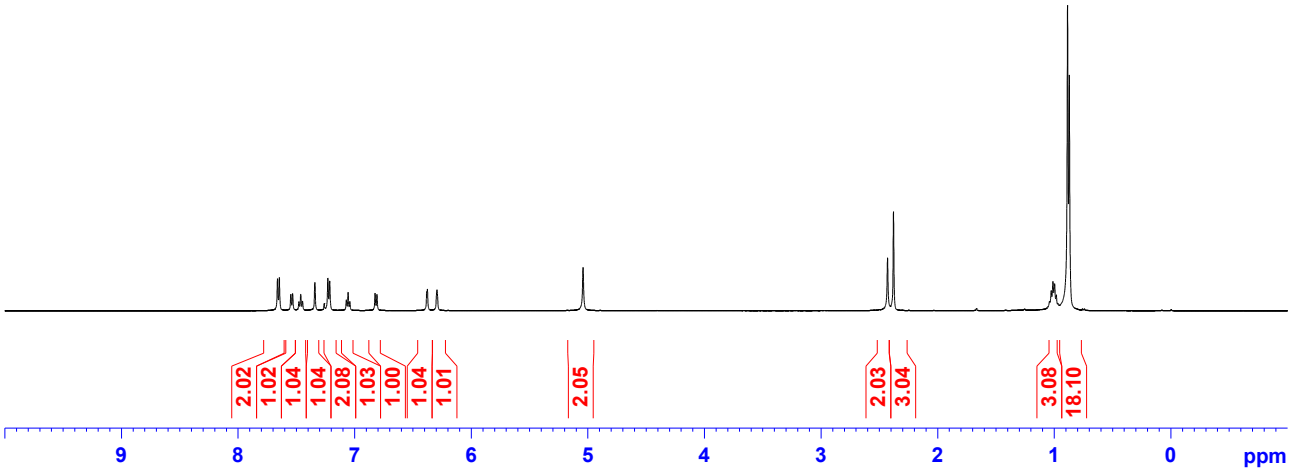


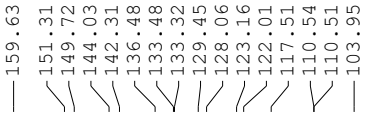


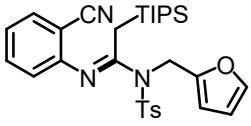


3ad

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

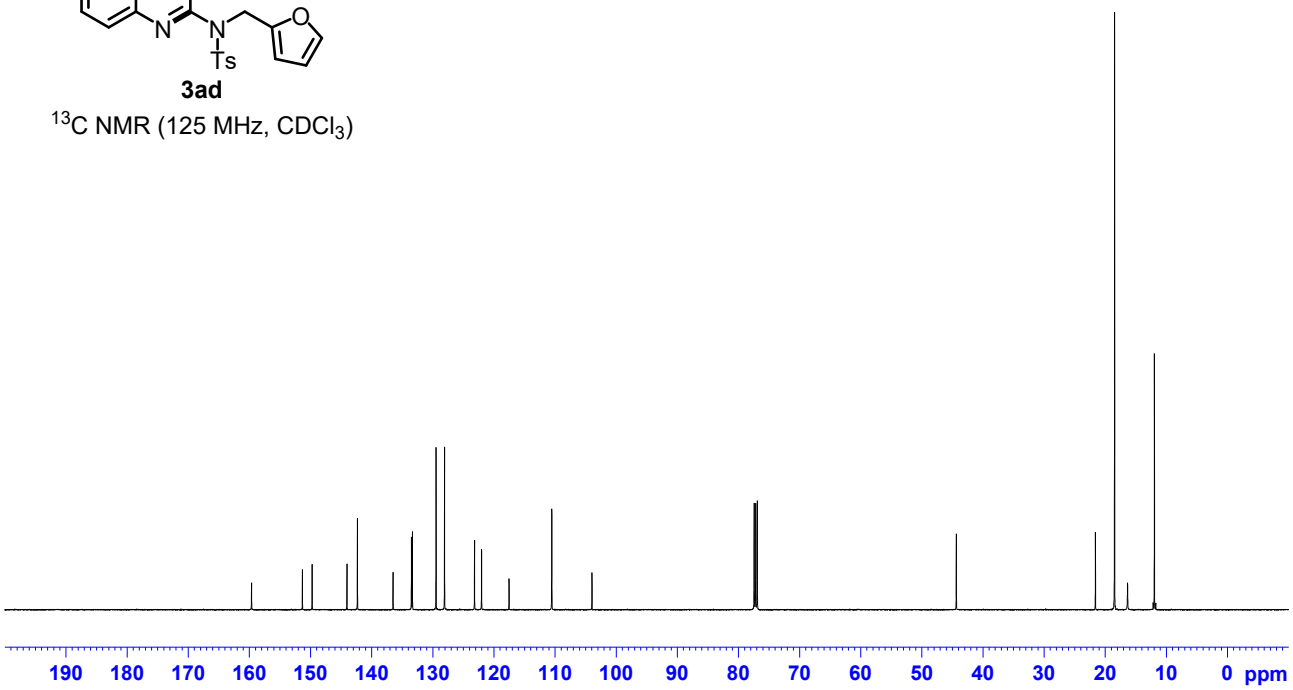


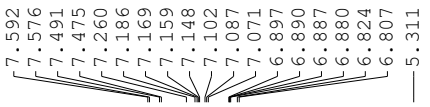


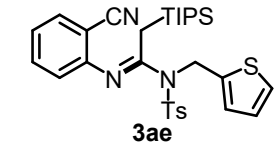


3ad

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

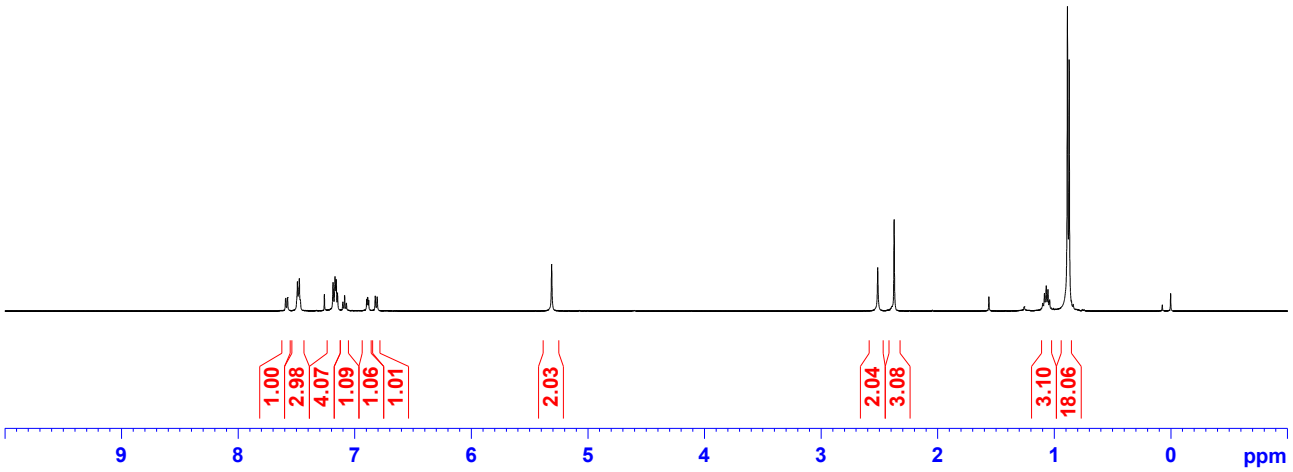


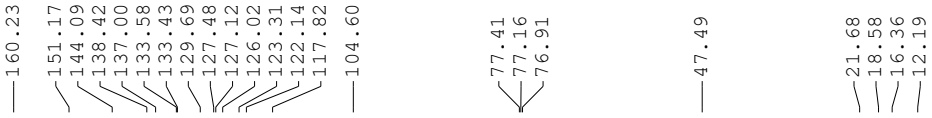


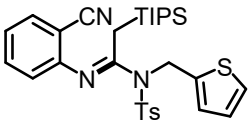


3ae

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

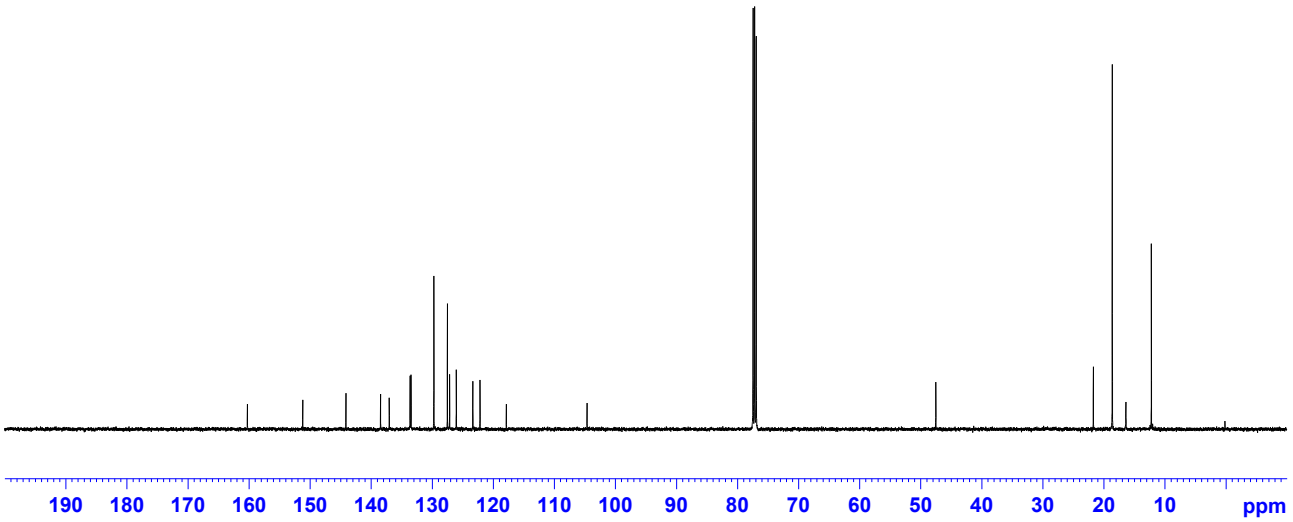


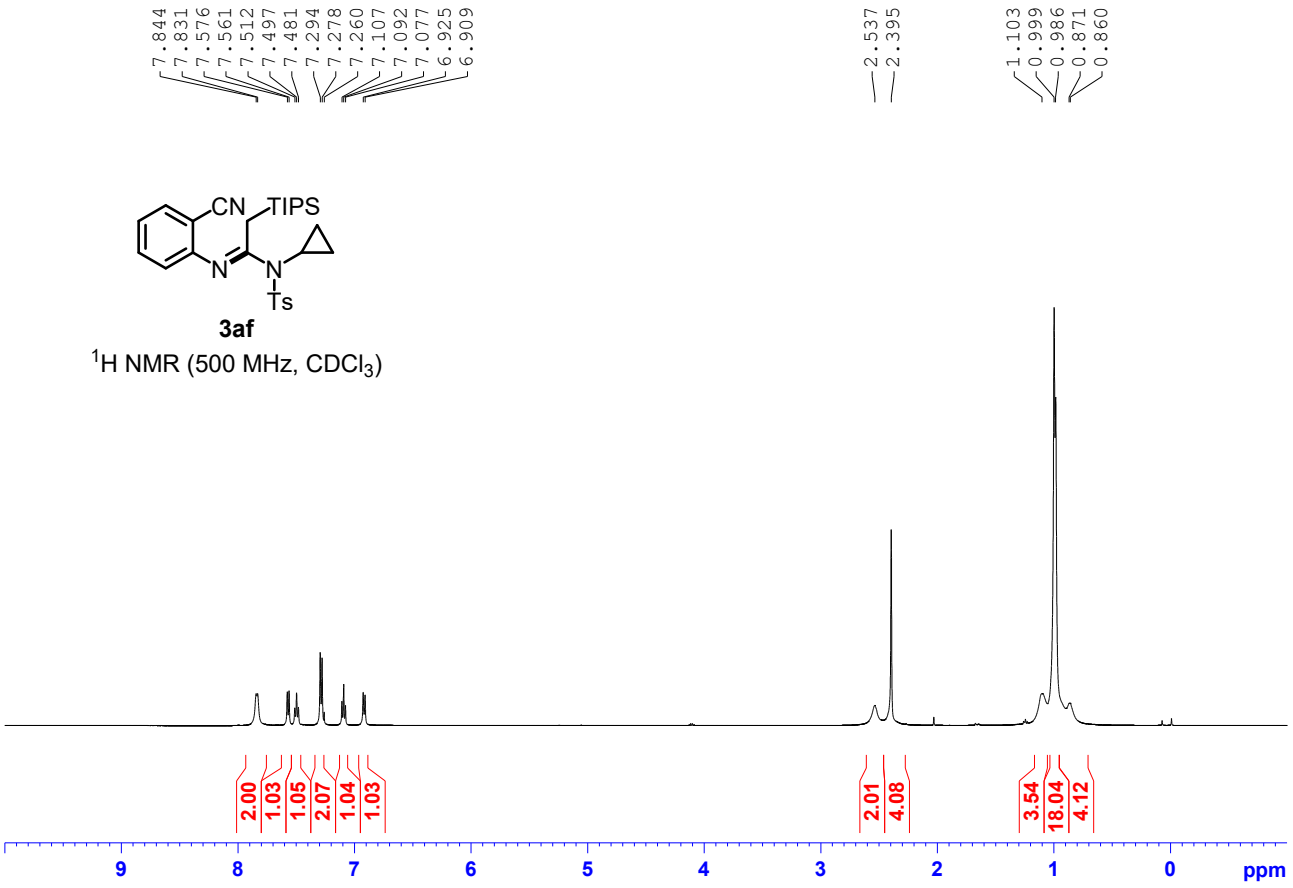




3ae

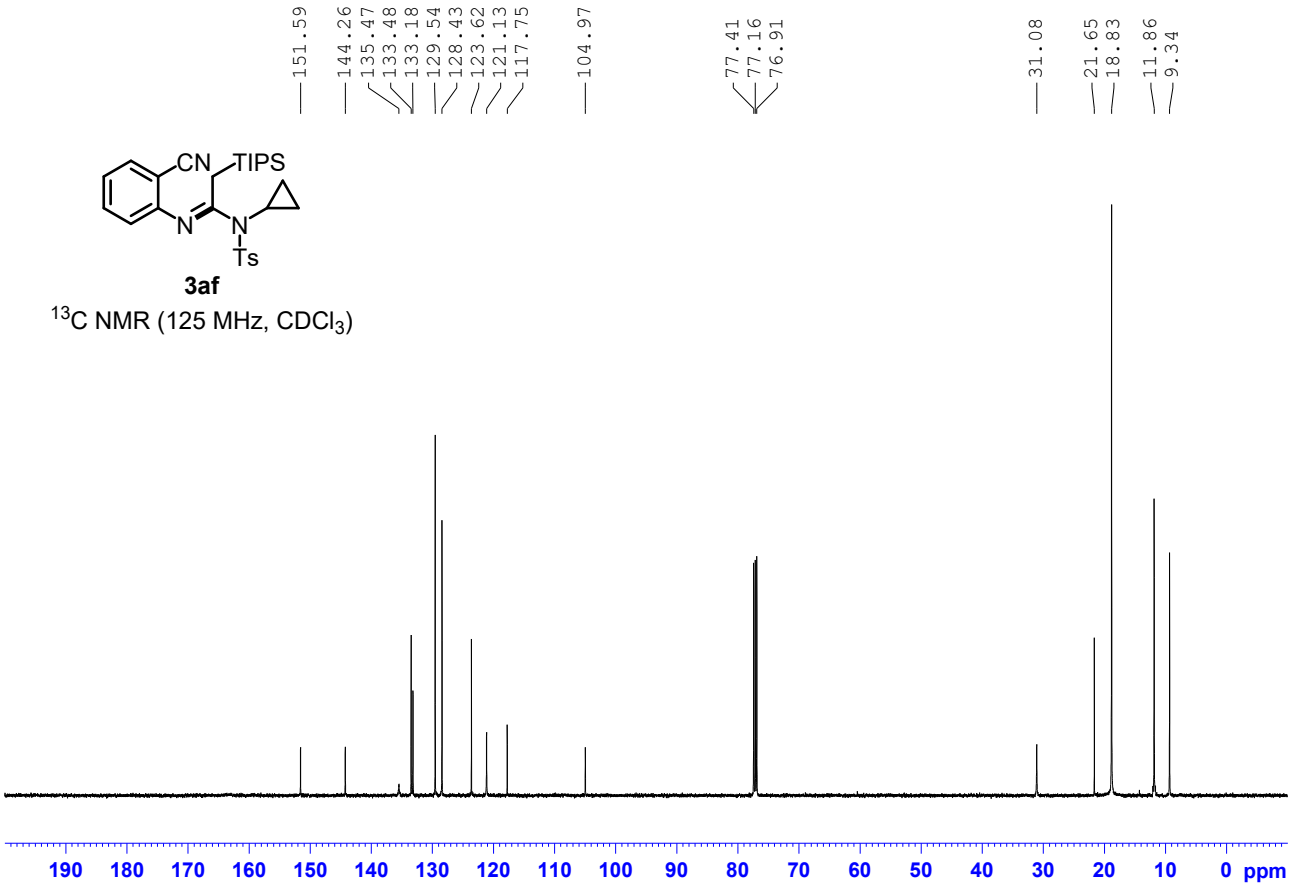
^{13}C NMR (125 MHz, $CDCl_3$)





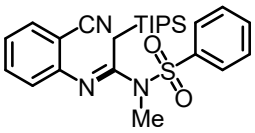
3af

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



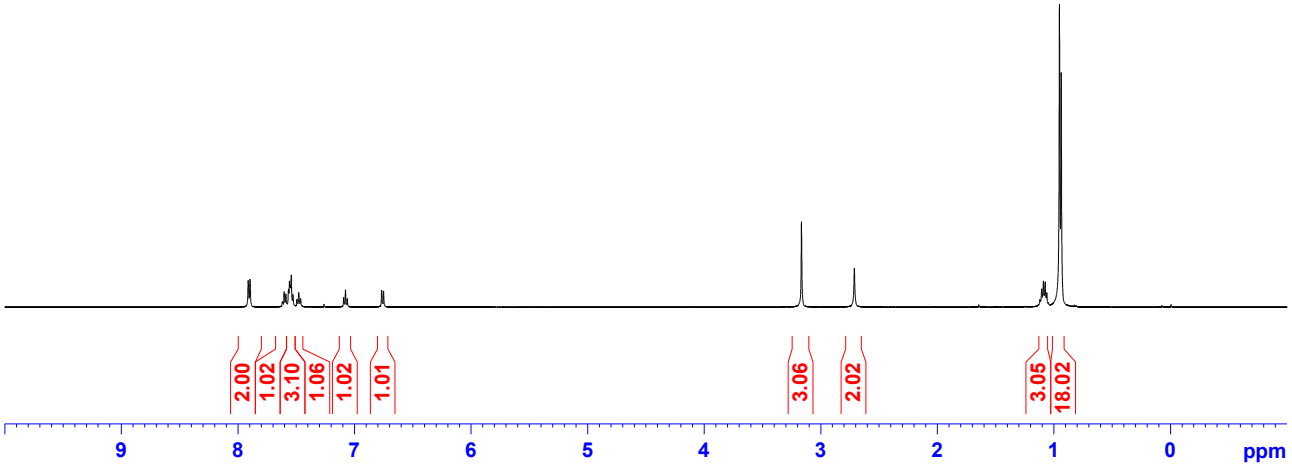
3af

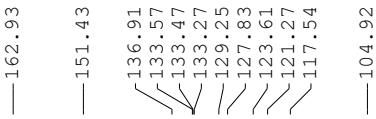
^{13}C NMR (125 MHz, $CDCl_3$)

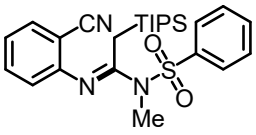


3ag

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

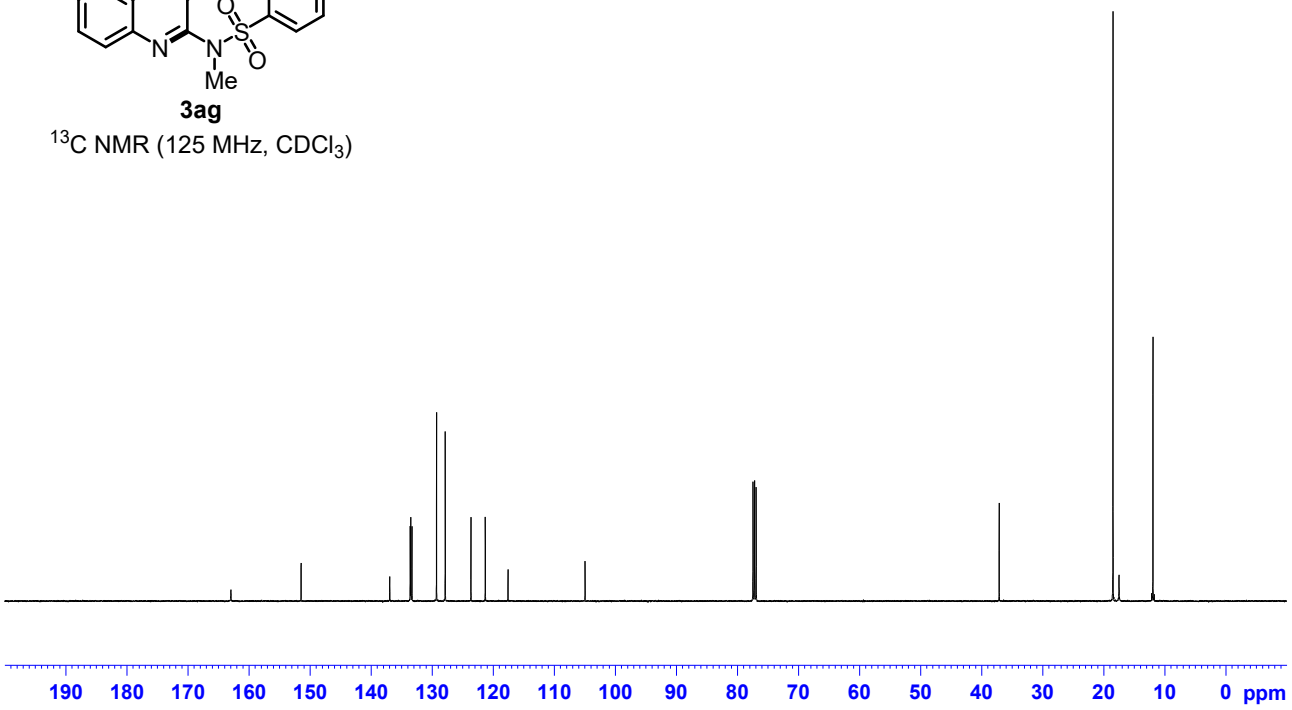


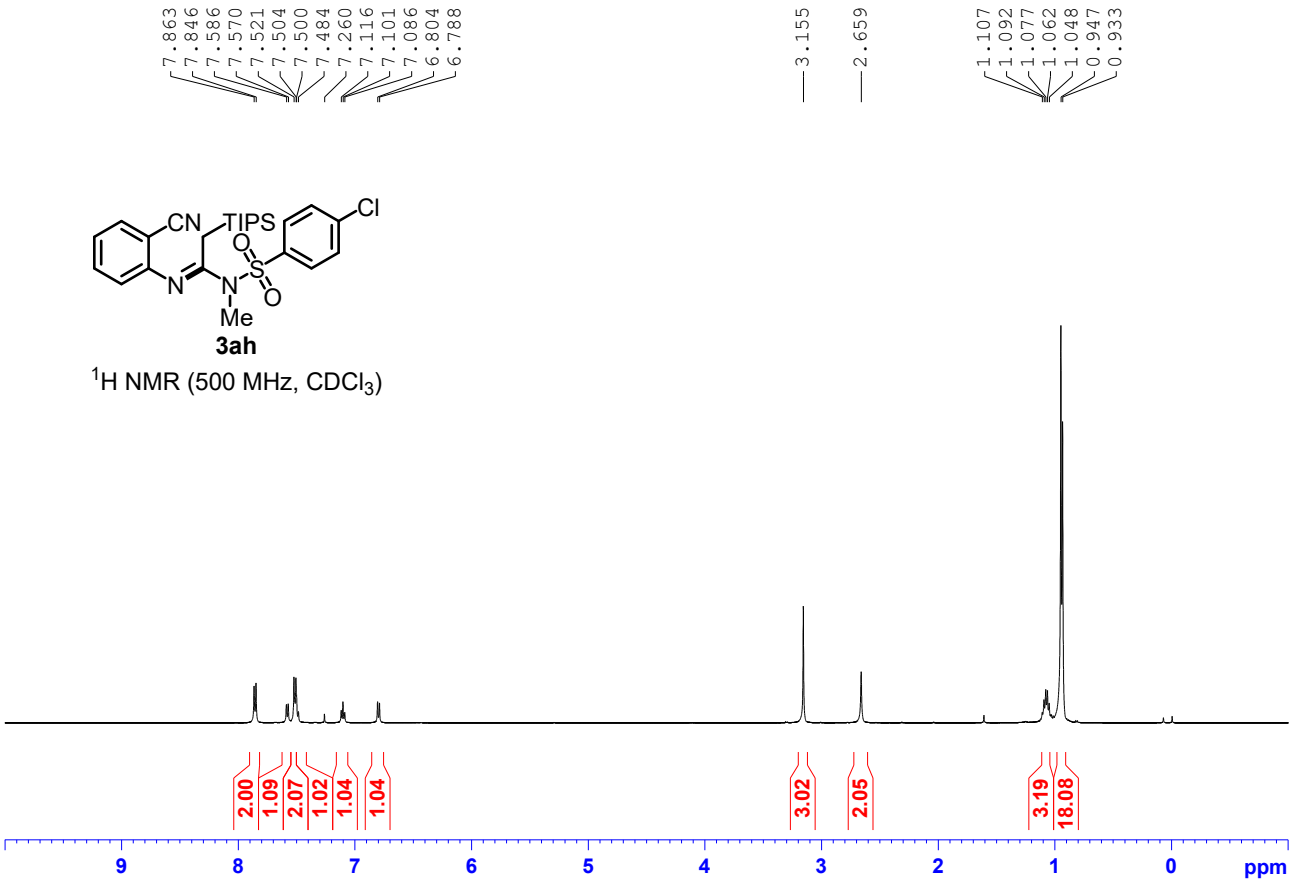




3ag

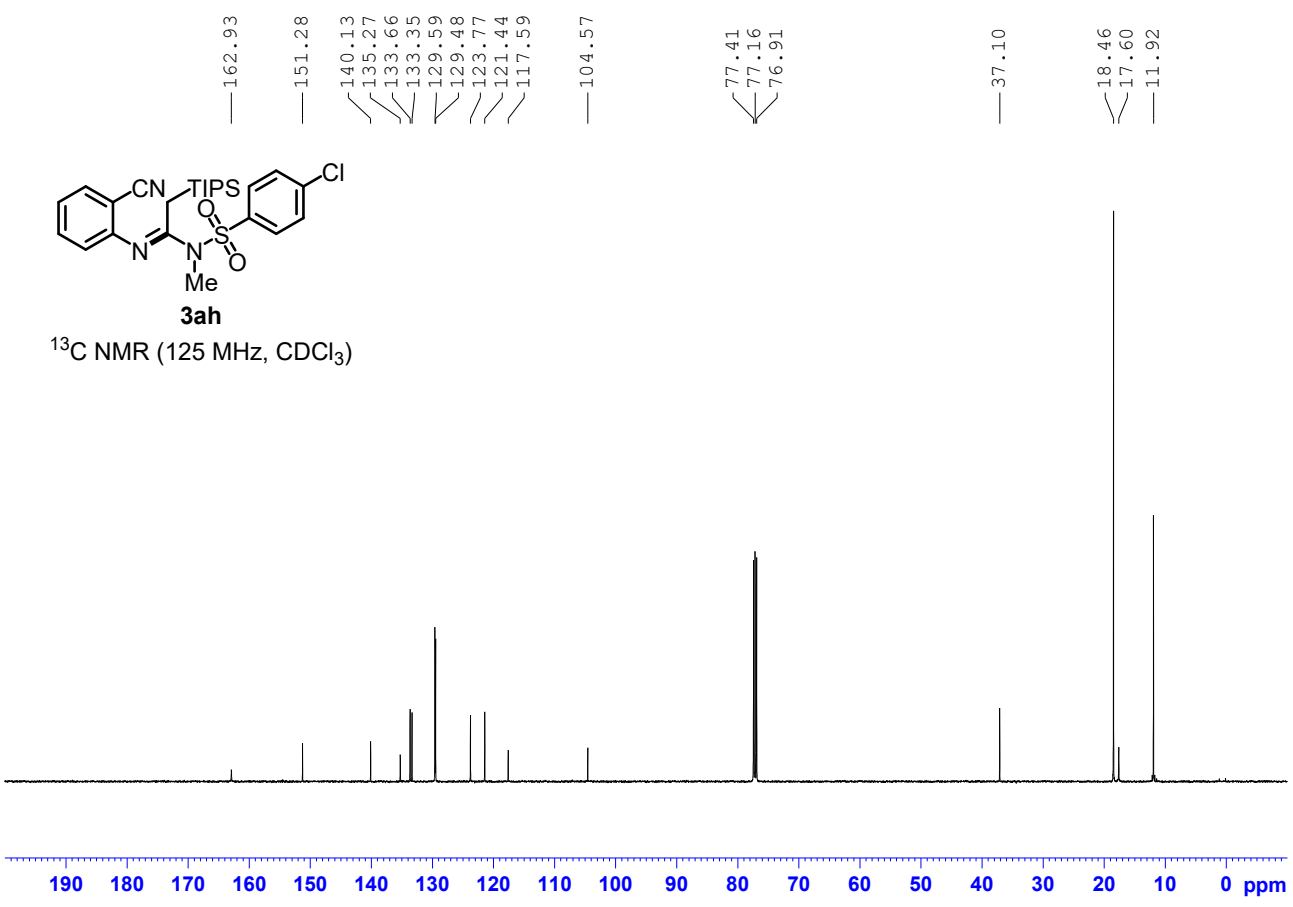
^{13}C NMR (125 MHz, $CDCl_3$)





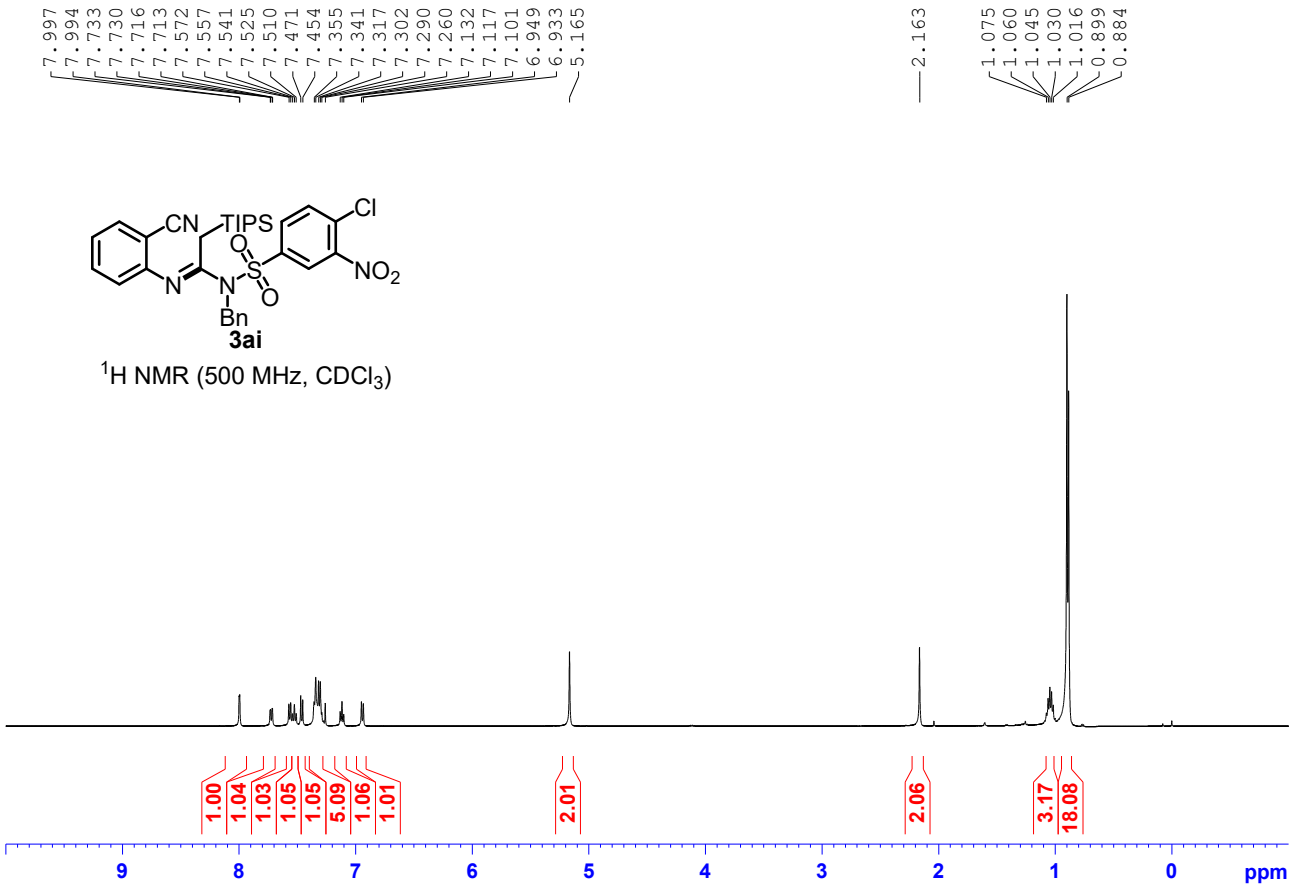
3ah

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



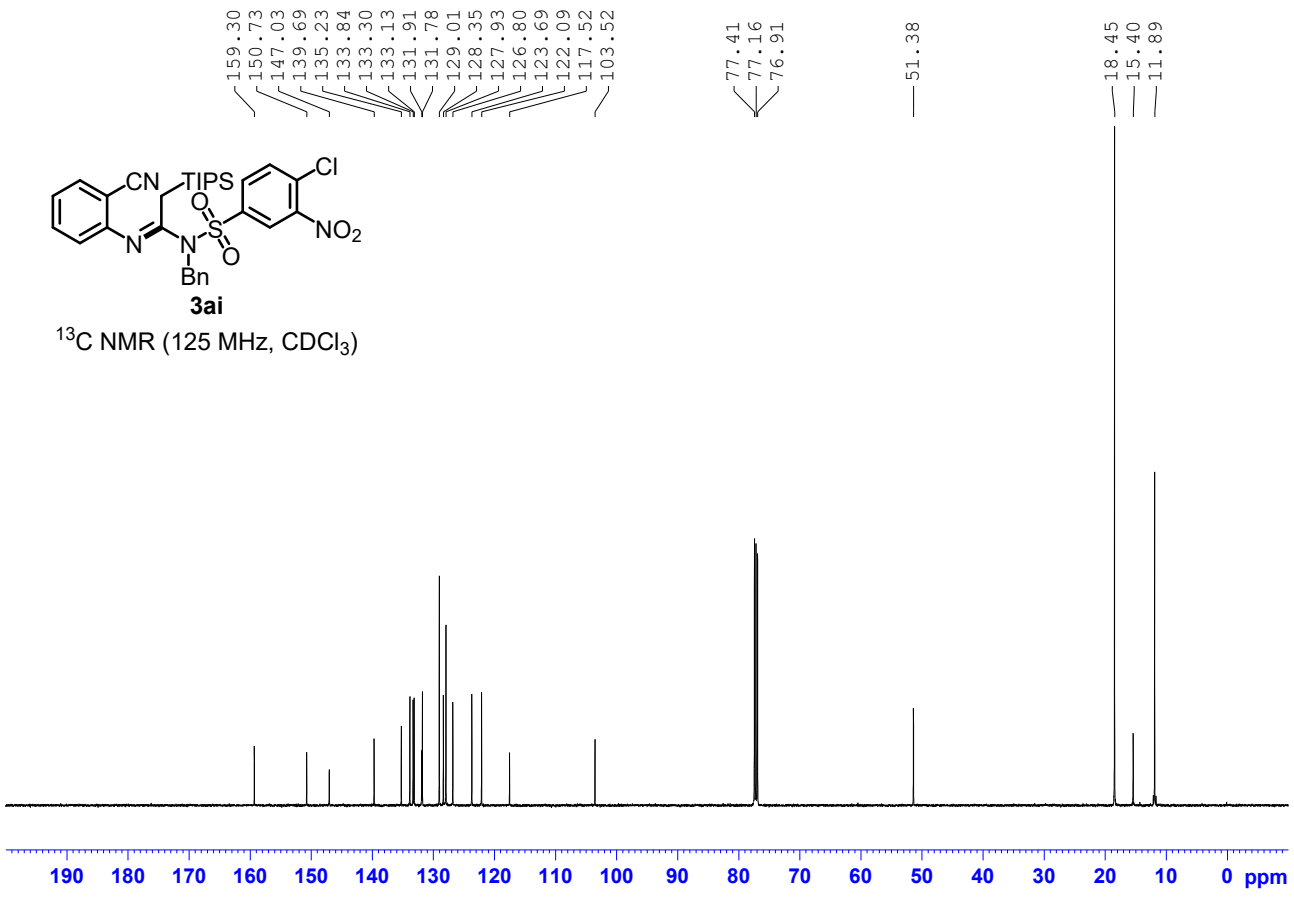
3ah

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



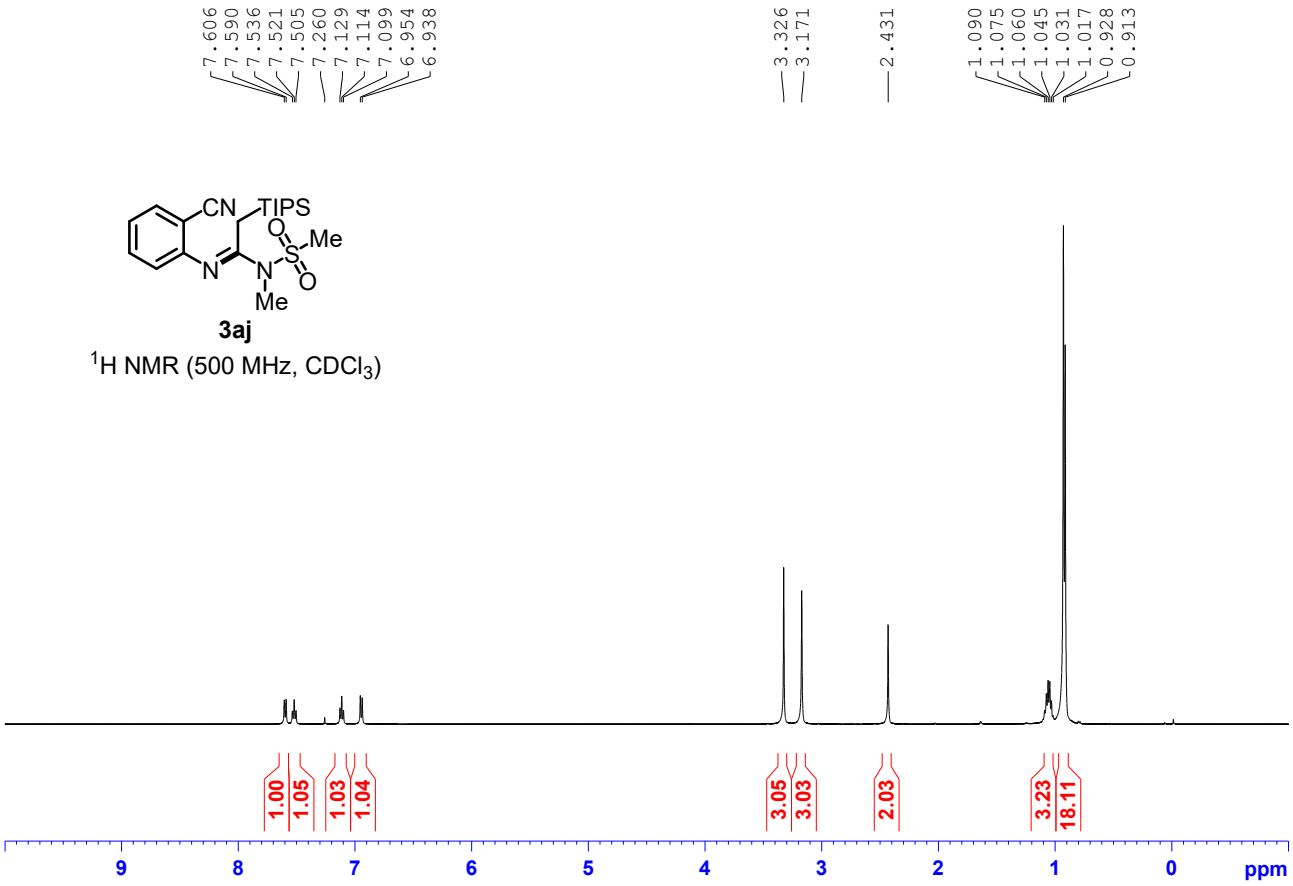
3ai

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



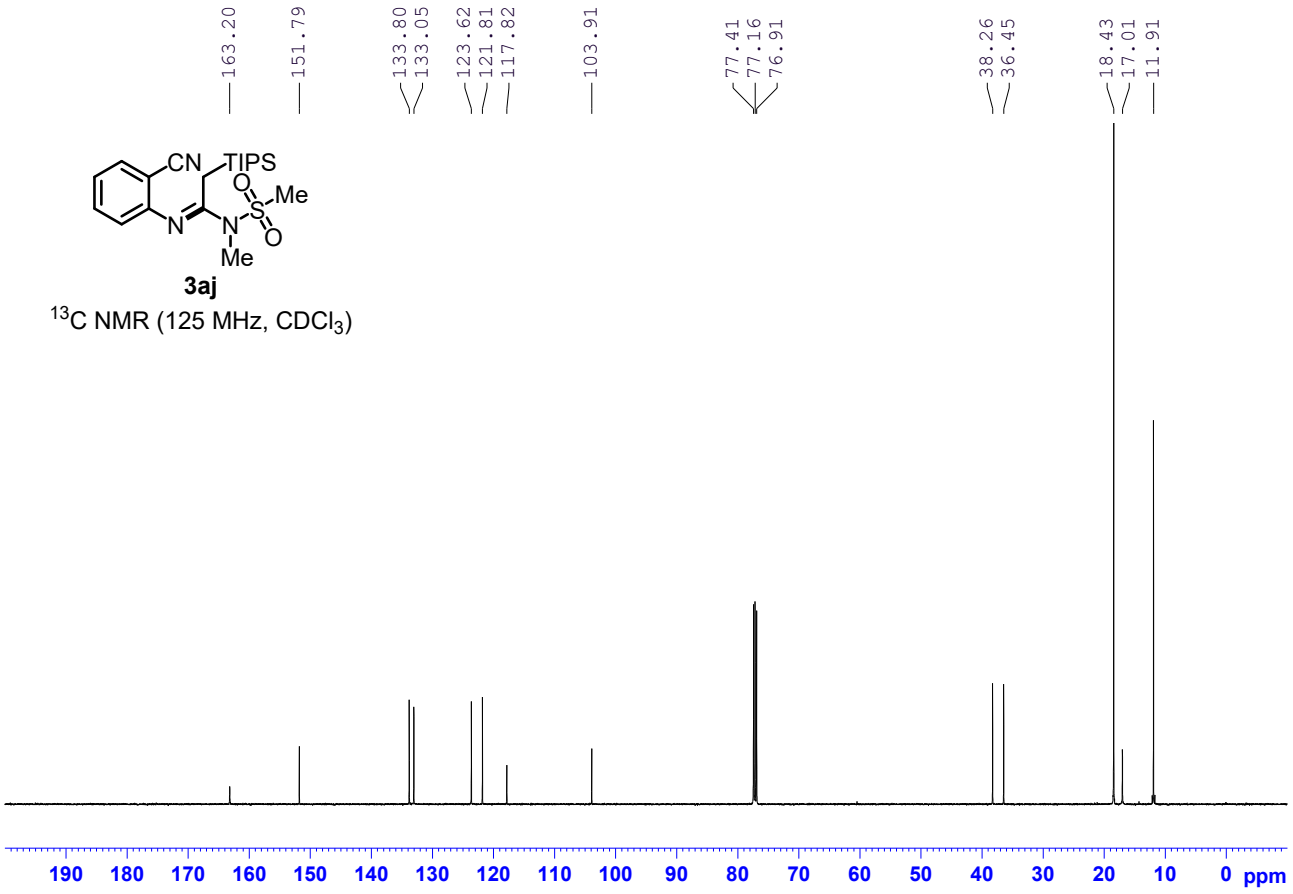
3ai

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



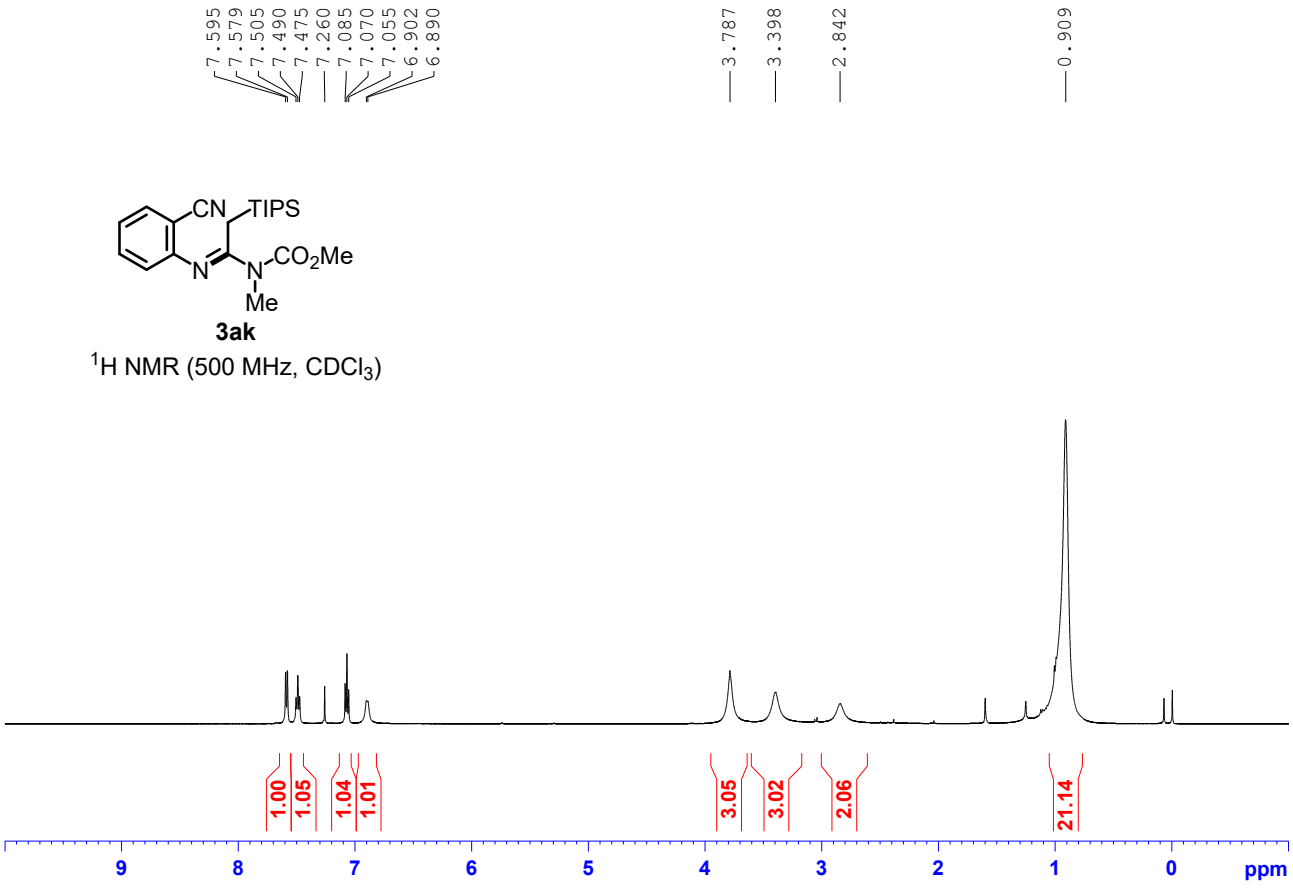
3aj

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



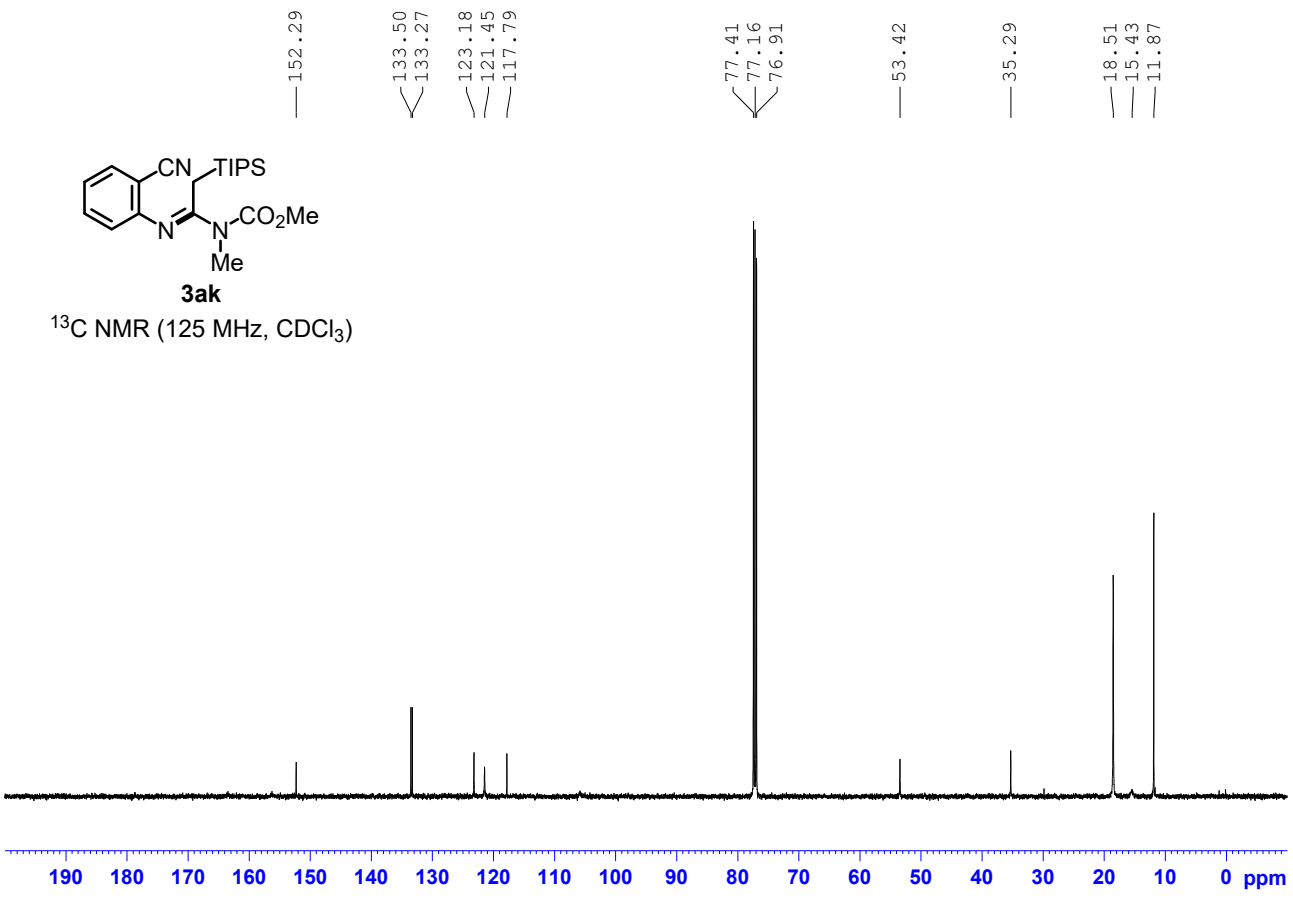
3aj

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



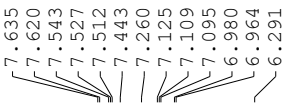
3ak

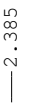
^{1}H NMR (500 MHz, $CDCl_3$)

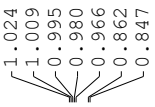


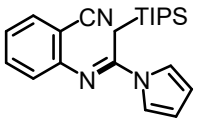
3ak

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



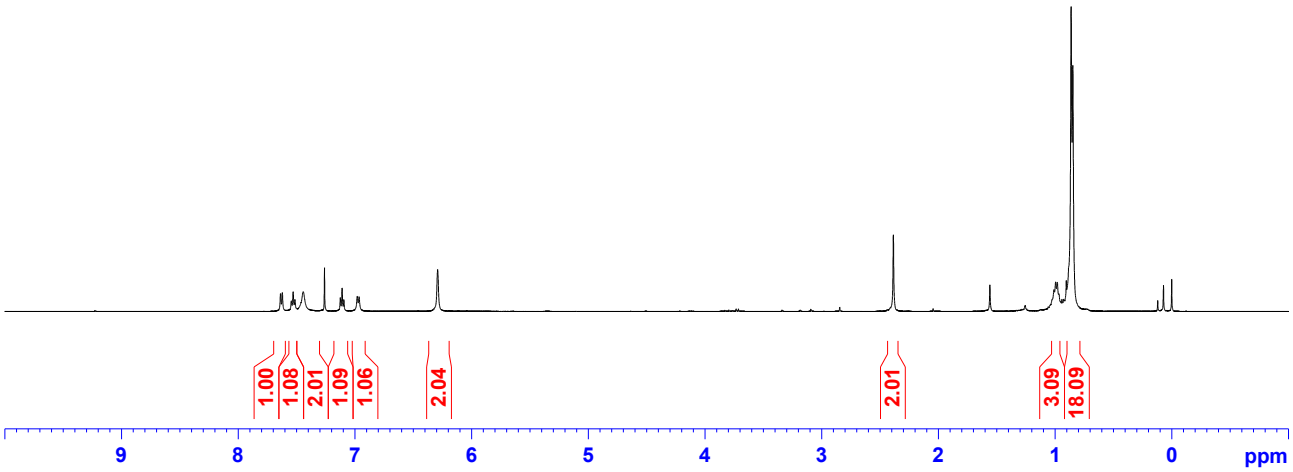


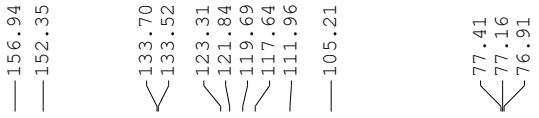


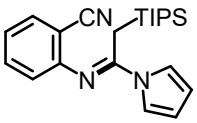


3al

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

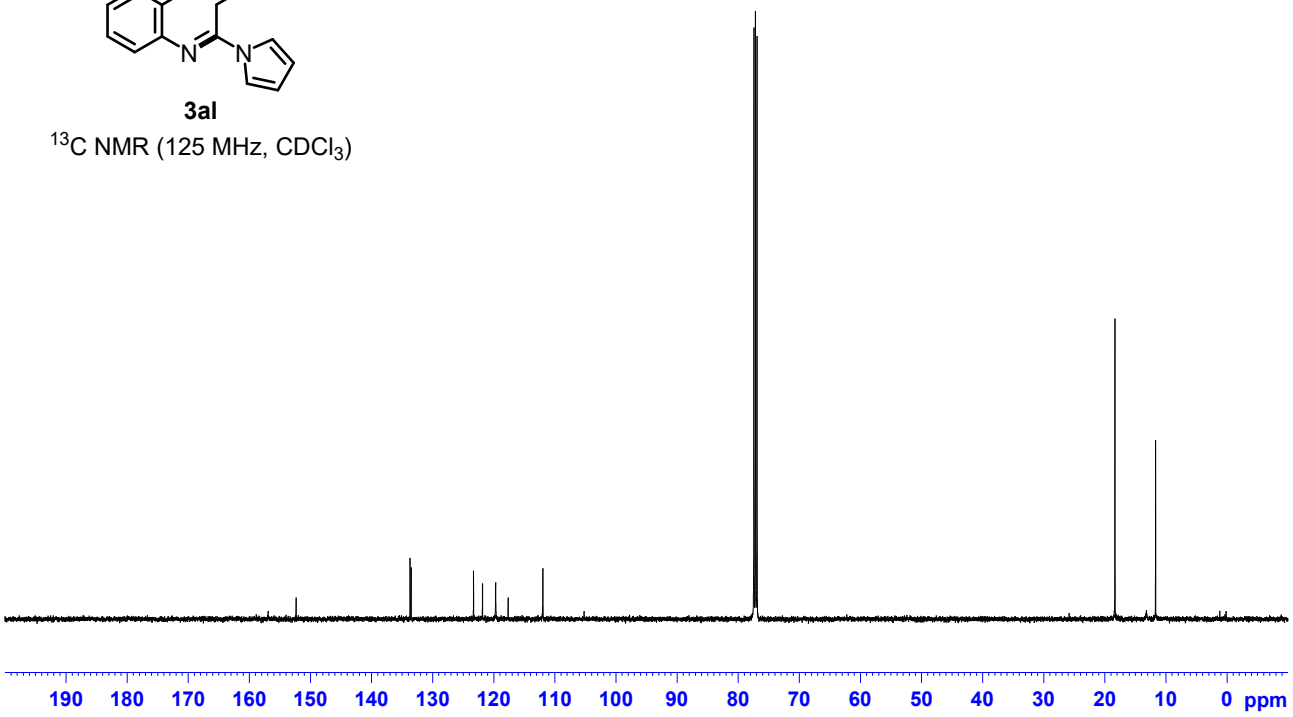


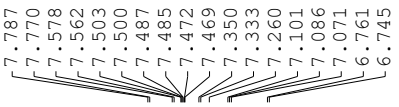


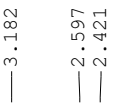


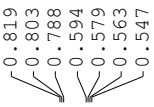
3al

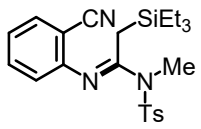
^{13}C NMR (125 MHz, $CDCl_3$)





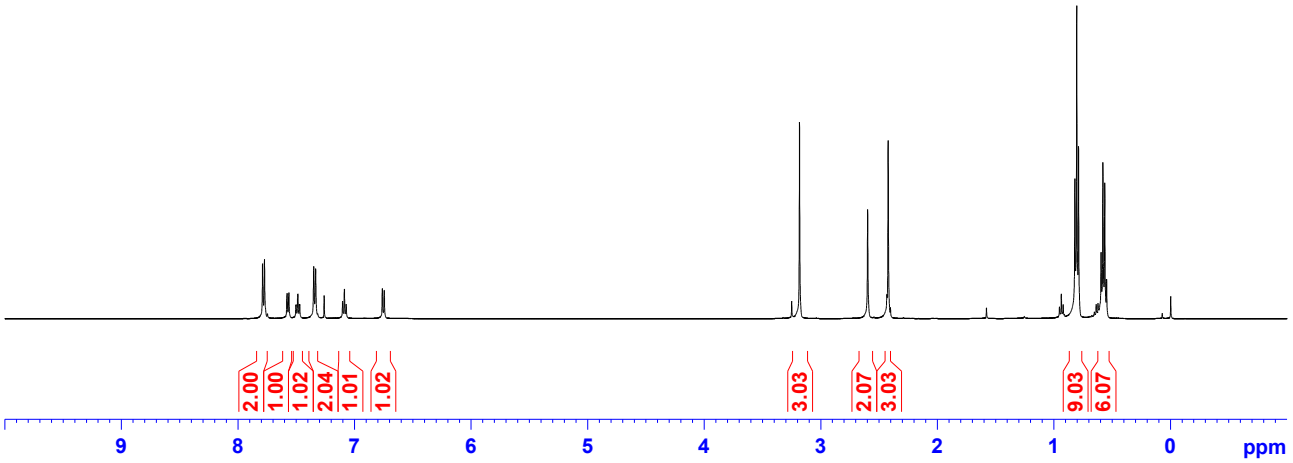


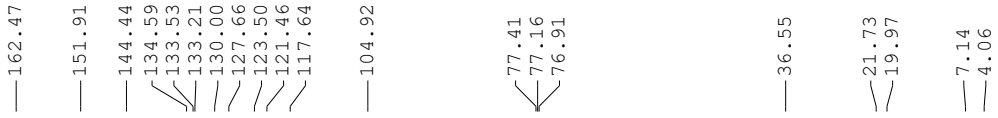


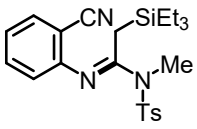


3am

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

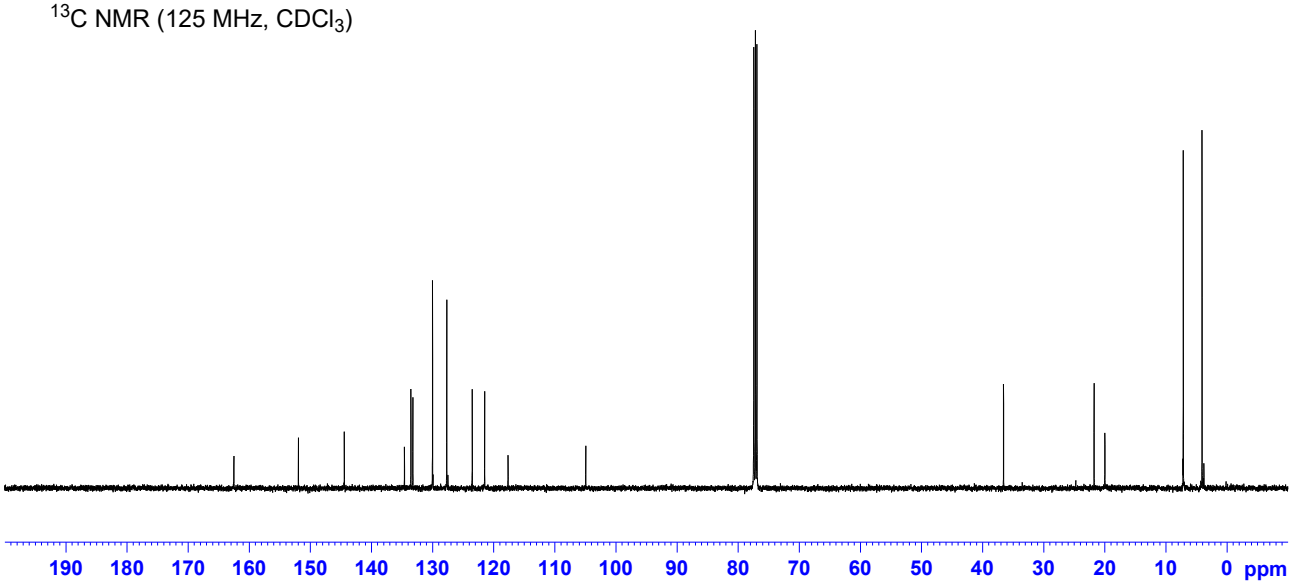


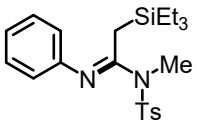




3am

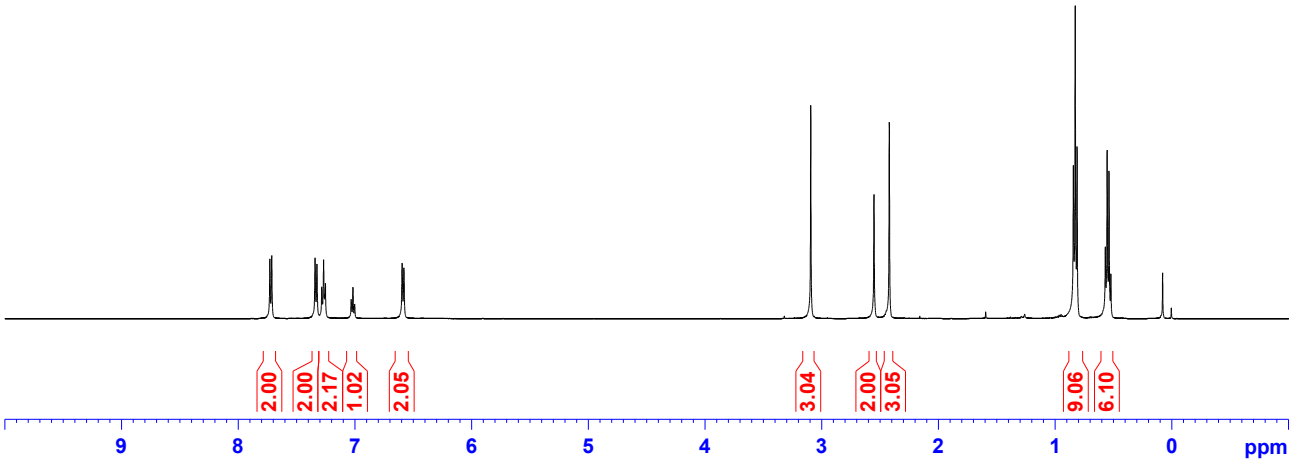
^{13}C NMR (125 MHz, $CDCl_3$)

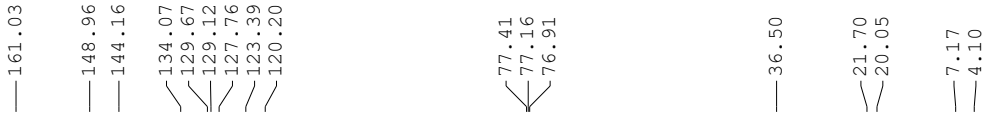


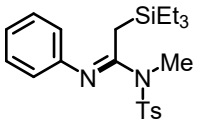


3nm

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

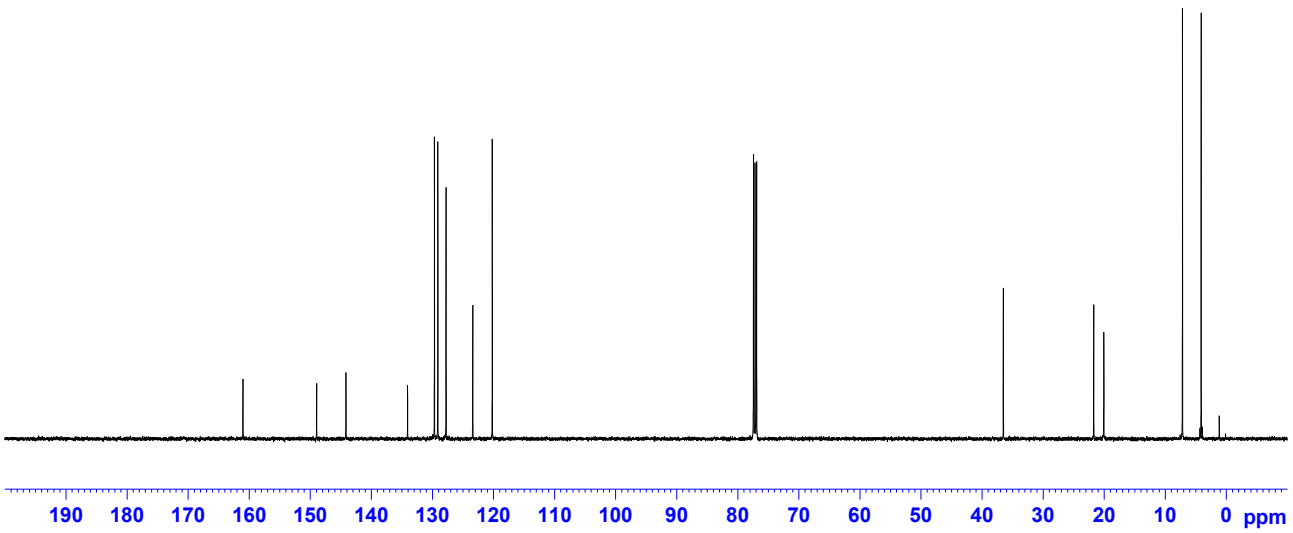


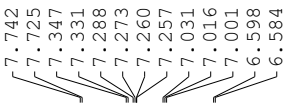


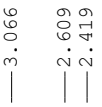


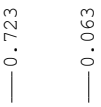
3nm

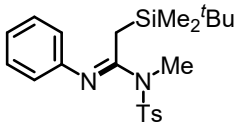
^{13}C NMR (125 MHz, $CDCl_3$)





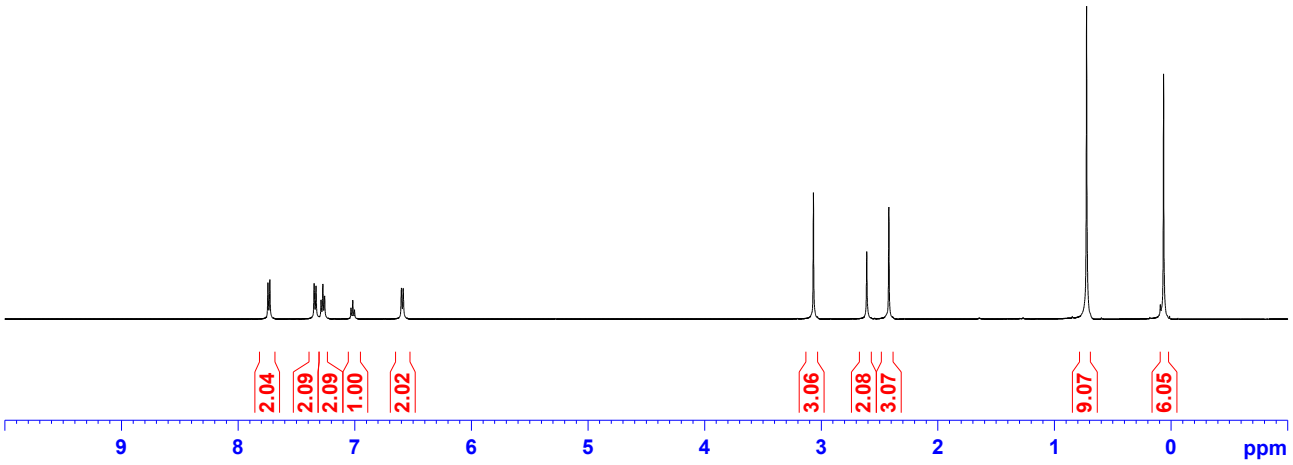


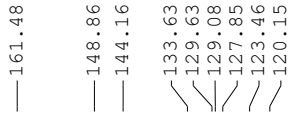


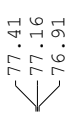


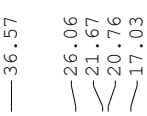
3nn

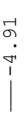
^{1}H NMR (500 MHz, $CDCl_3$)

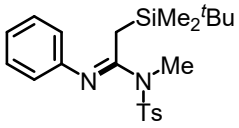






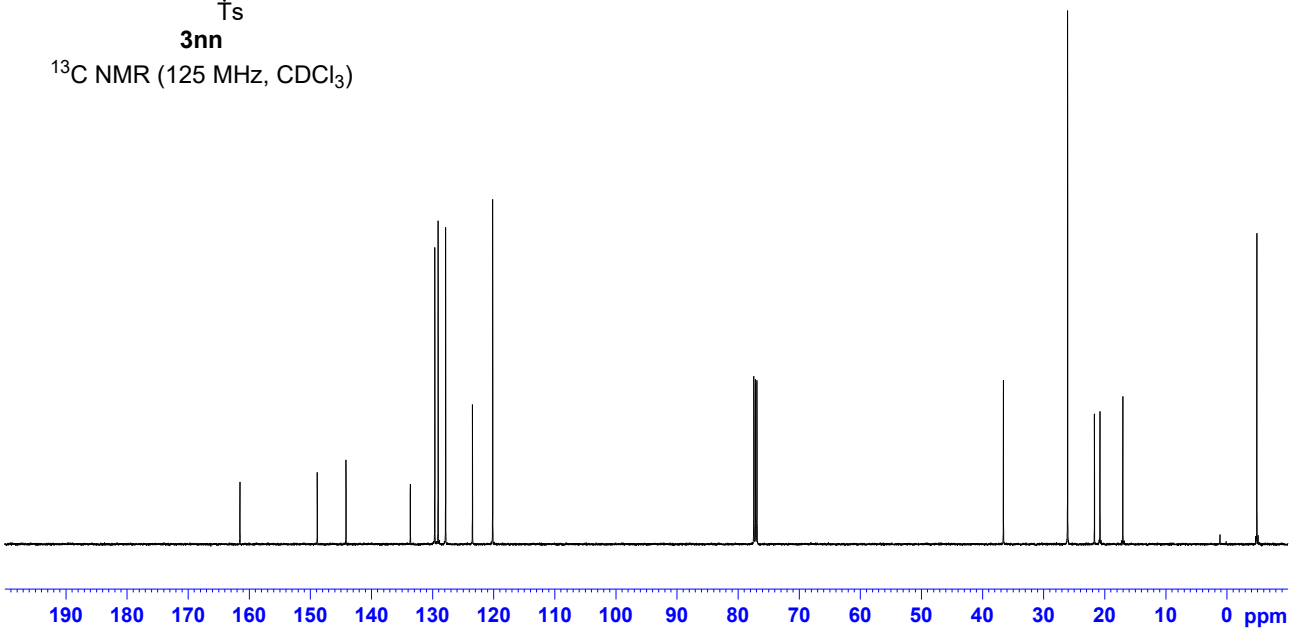


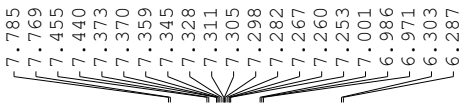


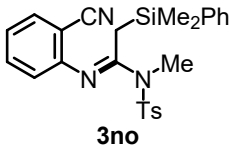


3nn

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

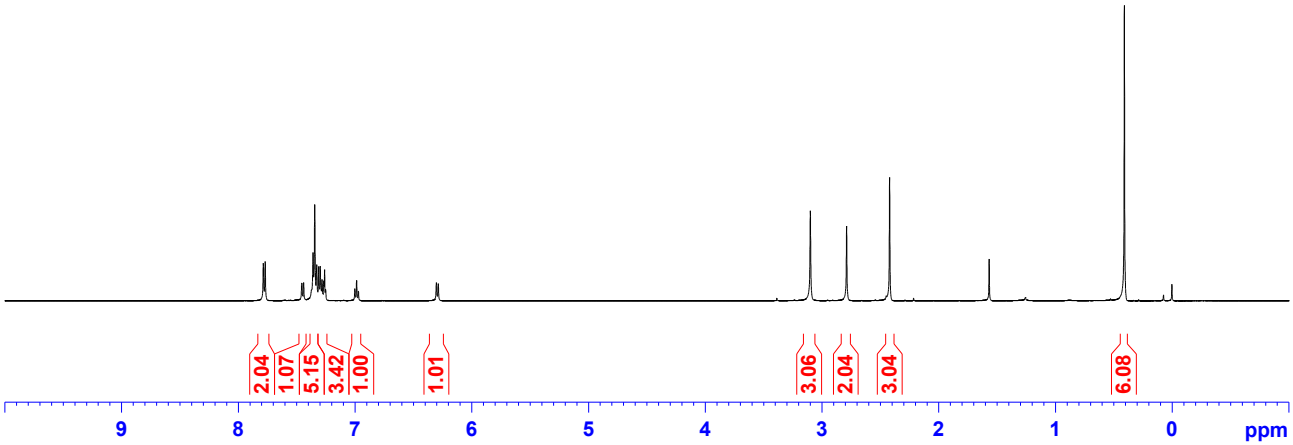


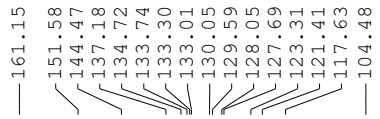




3no

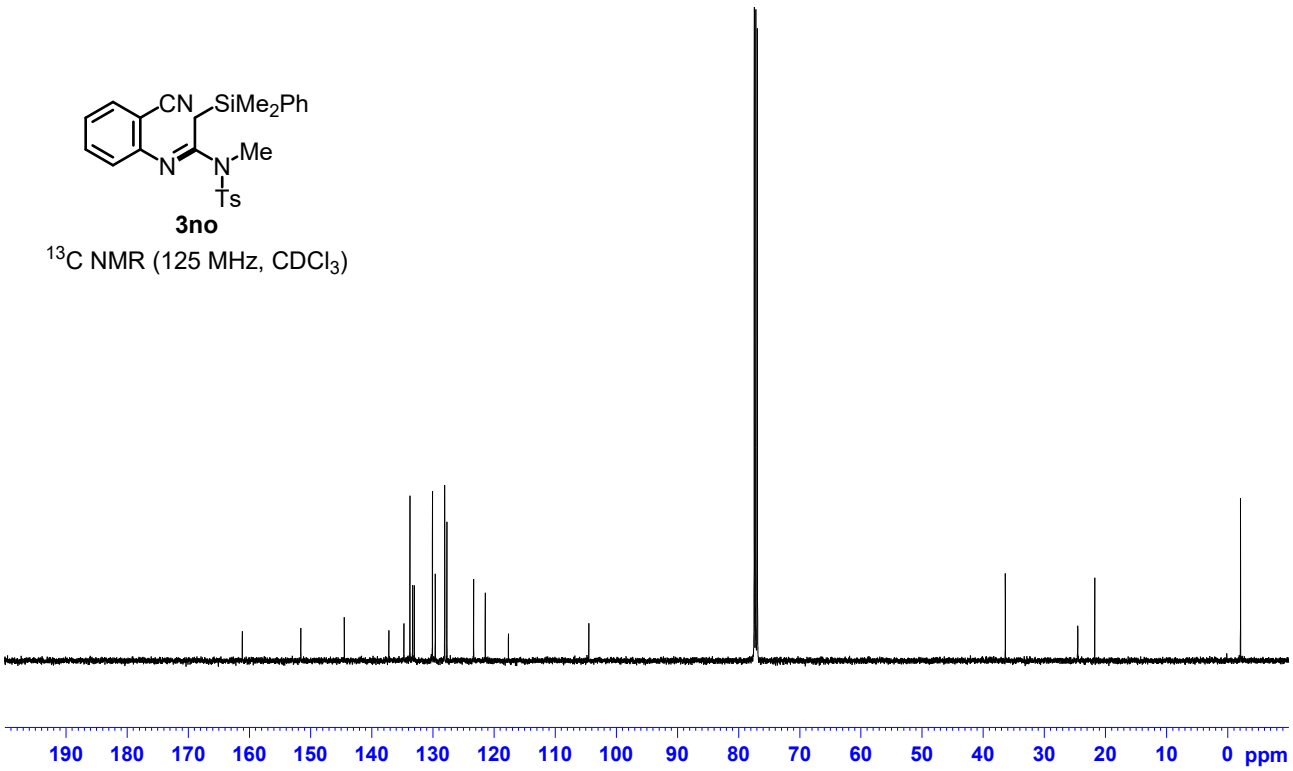
^{1}H NMR (500 MHz, $CDCl_3$)

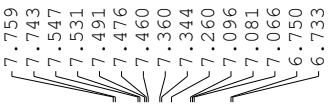


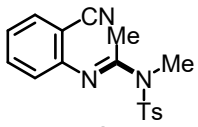


3no

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

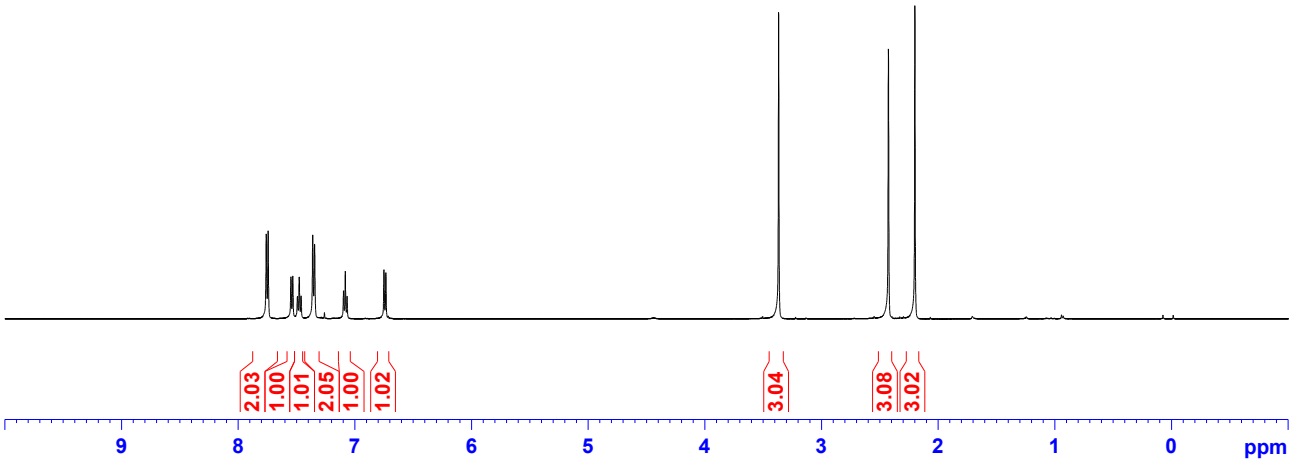


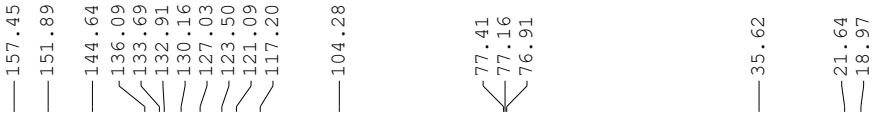


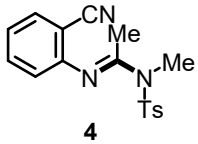


4

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

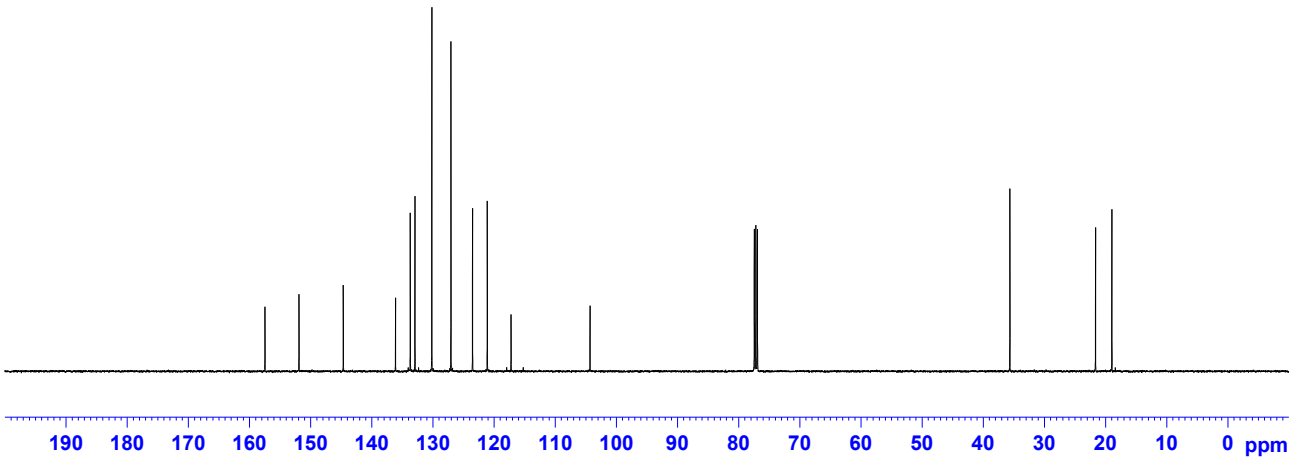


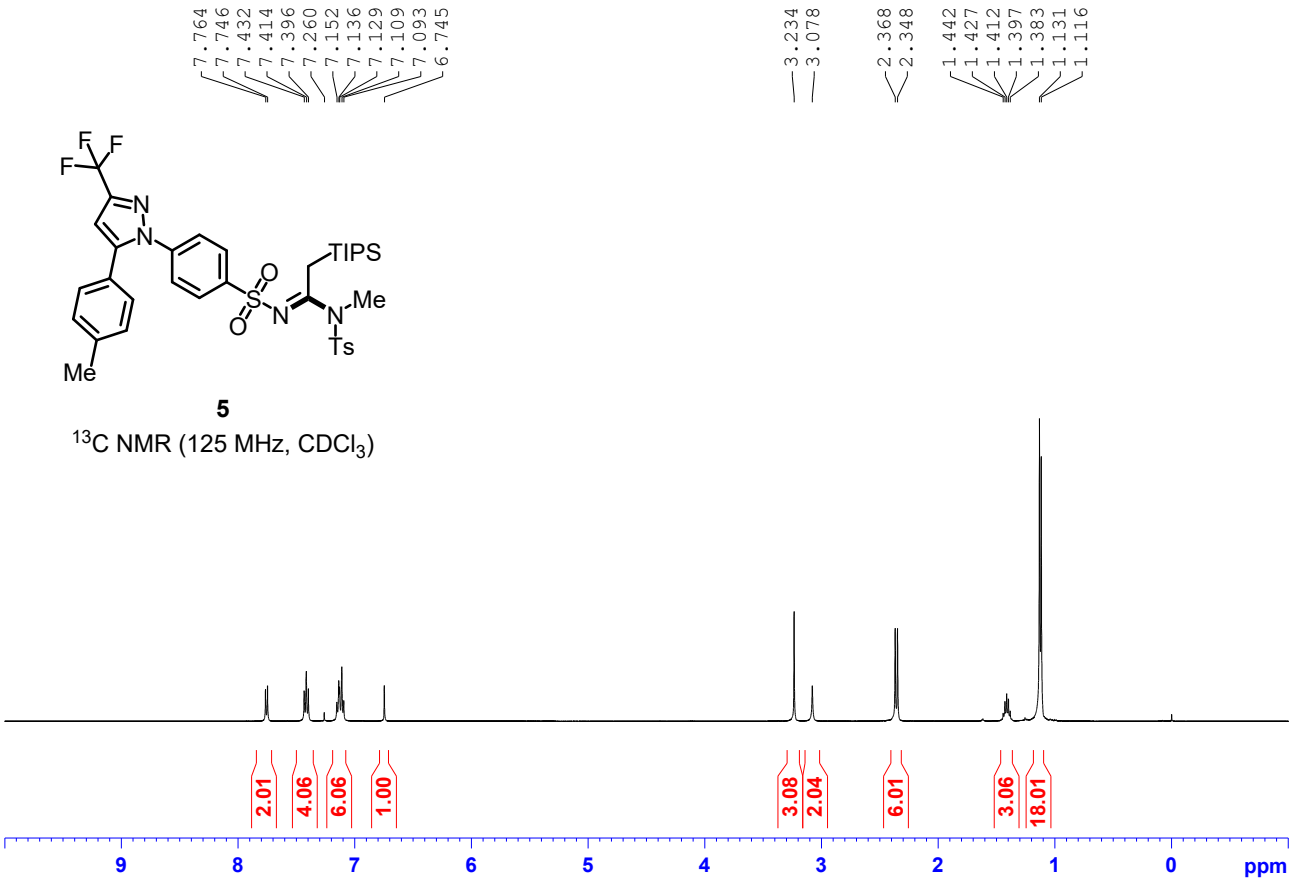




4

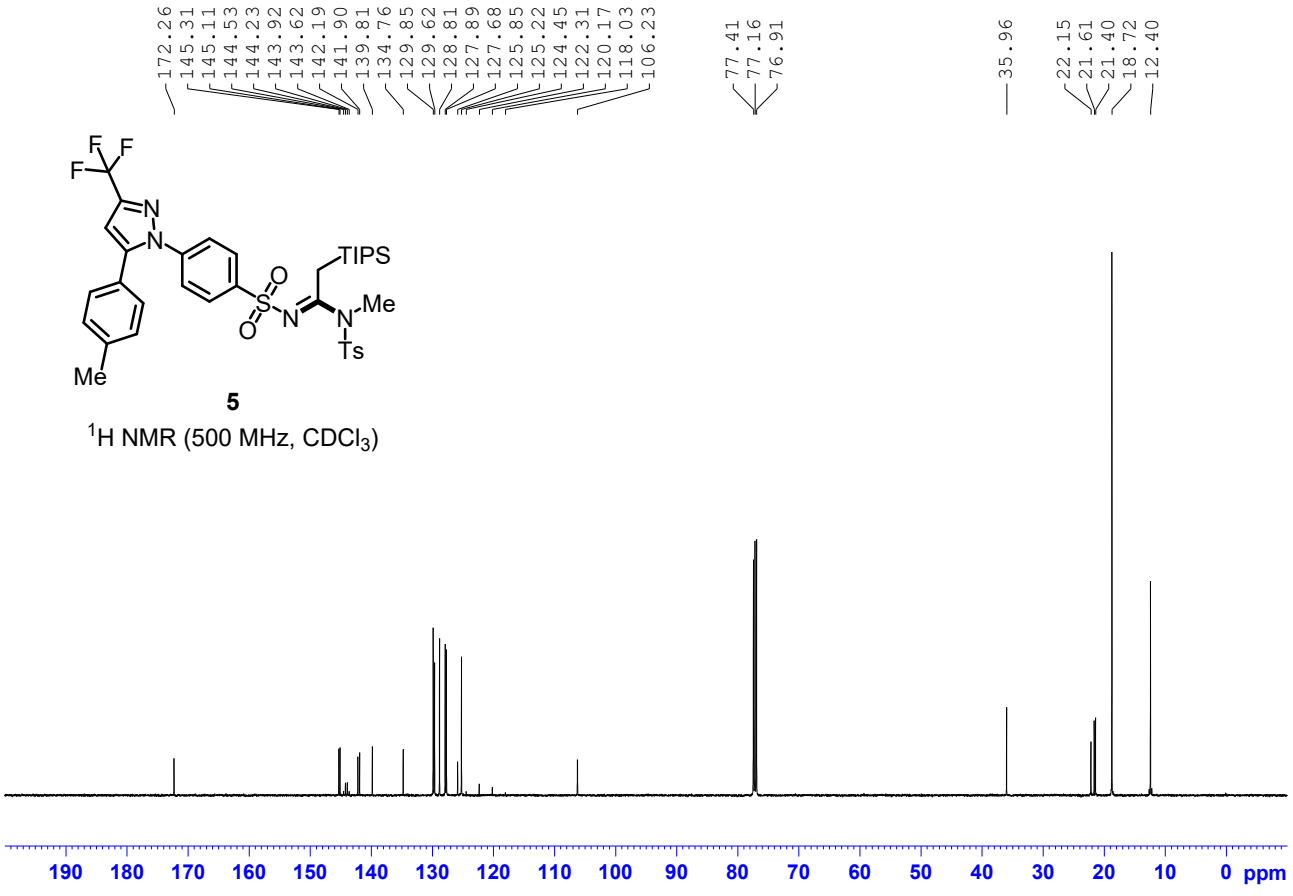
^{13}C NMR (125 MHz, $CDCl_3$)





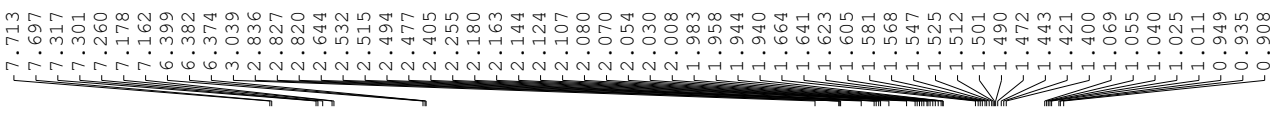
5

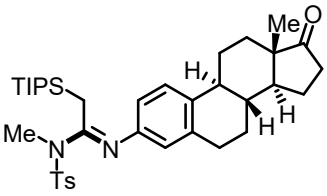
^{13}C NMR (125 MHz, $CDCl_3$)



5

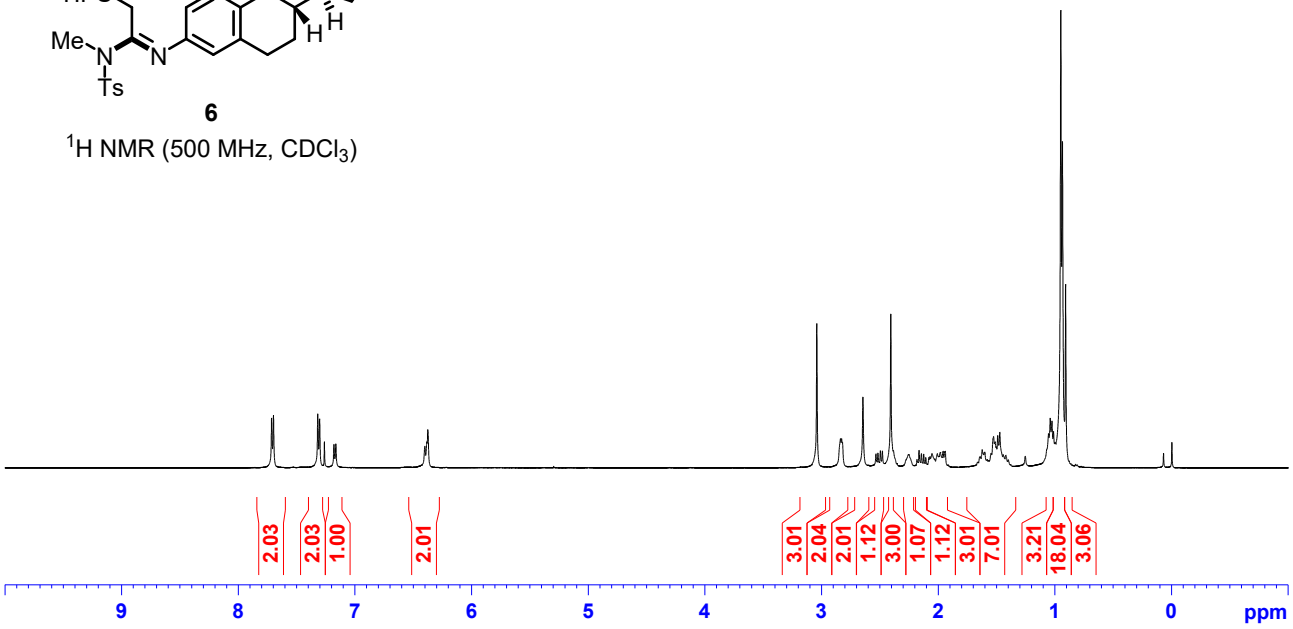
^{1}H NMR (500 MHz, $CDCl_3$)

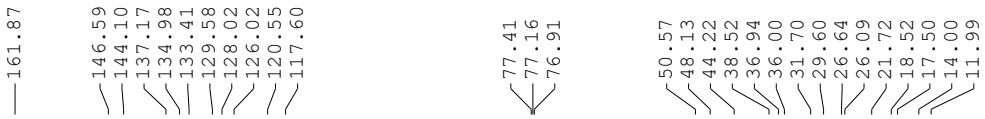


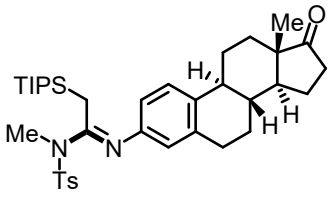


6

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







6

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