Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Exploiting the Dual Role of Ethynylbenziodoxolones in Gold-Catalyzed C(sp)-C(sp) Cross-Coupling Reactions

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Contents

1. General information

1.1 Practical Considerations:

Unless otherwise specified, all reactions were carried out in oven dried vials or reaction vessels with magnetic stirring under nitrogen atmosphere. The gold catalyzed cross-coupling reactions were performed in 2.5 mL glass vials with a PTFE-lined cap and all other reactions for the preparation of starting materials were performed in round-bottom flasks with rubber septa. All experiments were monitored by analytical thin layer chromatography (TLC) or Gas Chromatography by using biphenyl as an internal standard. TLC was performed on pre-coated silica gel plates. After elution, the plate was visualized under UV illumination at 254 nm for UV active materials. Further visualization was achieved by staining iodine, potassium permanganate solution and charring on a hot plate. Solvents were removed in vacuo and heated with a water bath at 35 °C. Silica gel finer than 200 mesh was used for flash column chromatography. Columns were packed as slurry of silica gel in pet. ether and equilibrated with the appropriate solvent mixture prior to use. The compounds were loaded neat or as a concentrated solution using the appropriate solvent system. The elution was assisted by applying pressure with an air pump.

1.2 Materials:

Unless otherwise noted, material obtained from commercial suppliers was used without further purification. DCE, ACN, 1,4-dioxane, toluene were dried by using standard protocols under N_2. Gold salts, silver salts, 1,10-phenanthroline (phen) and 2,2′-bipyridine (bipy) ligands were purchased from Sigma-Aldrich and stored under inert atmosphere. All deuterated solvents were used as supplied by Sigma–Aldrich.

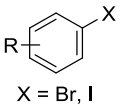
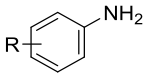
1.3 Instrumentation:

Melting points are uncorrected and recorded using digital Büchi B-540 melting point apparatus. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded on Bruker AV 500 or JEOL 400 MHz spectrometers in appropriate solvents using TMS as internal standard or the solvent signals as secondary standards and the chemical shifts are shown in δ scales. Multiplicities of ^{1}H NMR signals are designated as s (singlet), d (doublet), dd (doublet of doublet), dt (doublet of triplet), t

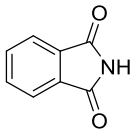
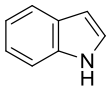
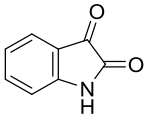
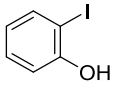
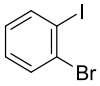
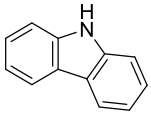
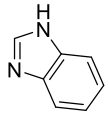
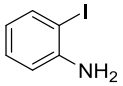
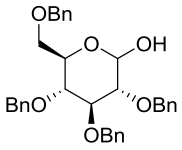
(triplet), quin (quintet), br. s. (broad signal), m (multiplet) etc. HRMS (ESI) data were recorded on a Thermo Scientific Q-Exactive, Accela 1250 pump. Gas chromatography (GC) was performed on a Perkin Elmer Arnel Clarus 500 instrument equipped with a hydrogen flame ionization detector; HP5 columns (polar) (12 m×0.32 mm×1.0 μm) were used with helium as the carrier gas at a flow rate of 1 mL/min. Elemental analysis was performed on Thermo Finnigan FLASH EA 1112 series analyzer. MALDI-TOF mass spectrometric analysis was performed on AB SCIEX TOF/TOF 5800 system.

2. Representative procedure for the synthesis of EBX reagents and terminal alkynes

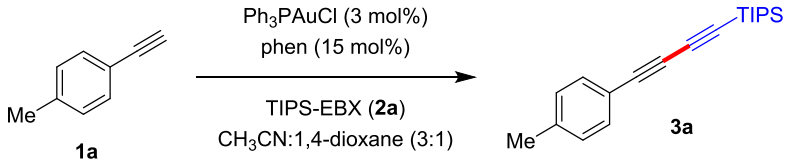
Ethynylbenziodoxolone (EBX) reagents **2a-d** were prepared by following Waser's methods.[1a] **2e** was synthesized by method described by Xiao.[1b] The terminal alkynes **1a, 1b, 1c, 1f**, **1h**, **1v**, **1w**, **1ah** and **1ak** have been purchased from Sigma-Aldrich and were directly used without further purification. The rest of the alkynes were prepared by literature methods. The references for the representative procedures are given in tabular form below.

Terminal alkynes (Starting materials)	**Starting from**	**Overall yields**	**References**
1d-e, **1g**, **1i-m**, **1o**, **1af**	 X = Br, I	84-90% (2 steps)	*Angew. Chem. Int. Ed.*, 2010, **49**, 9891
1n, 1q, **1t-u**	R-CHO	80-87% (2 steps)	*Chem. Commun.*, 2014, **50**, 8966
1p, 1r, 1s		71-75% (3 steps)	*Synthesis*, 2015, **47**, 1633
1y, **1aj**	R_1NHR_2 and R_3CO_2H	75-82% (1 step)	*Chem. Eur. J.* , 2014, **20**, 11101

[1] (a) J. P. Brand, C. Chevalley, R. Scopelliti and J. Waser, *Chem. Eur. J.*, 2012, **18**, 5655; (b) Q.-Q. Zhou, W. Guo,W. Ding, X. Wu, X. Chen, L.-Q. Lu and W.- J. Xiao, *Angew. Chem. Int. Ed.*, 2015, **54**, 11196.

1x		71% (2 steps)	*Adv. Synth. Catal*. 2010, **352**, 2881
1z		90% (3 steps)	*Tetrahedron*, 2016, **72**, 8106
1aa		69% (1 step)	*Chem. Commun*., 2012, **48**, 10132
1ab		80% (3 steps)	*J. Org. Chem*., 2004, **69**, 2084
1ac		51% (3 steps)	*Chem. Commun*., 2014, **50**, 5451
1ad		54% (4 steps)	*J. Am. Chem. Soc.*, 2006, **128**, 5592
1ae		50% (2 steps)	*J. Org. Chem*., 2010, **75**, 980
1ag		66% (2 steps)	*Tetrahedron*, 2008, **64**, 53
1ai		45% (5 steps)	*Bioorg. Med. Chem. Lett*., 2012, **22**, 642

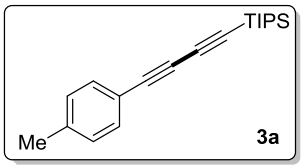
3. Representative procedure for synthesis and characterization of 1,3-diynes



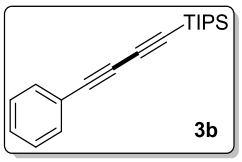
To an oven-dried screw-cap vial containing a stir bar were added 4-ethynyltoluene (**1a**) (25 μL, 0.20 mmol), TIPS-EBX (**2a**) (94 mg, 0.22 mmol, 1.1 equiv), Ph_3PAuCl (3.0 mg, 3

mol%), phen (6.0 mg, 15 mol%) and degassed CH_3CN:1,4-dioxane (1.8 mL : 0.6 mL). The reaction vial was fitted with a cap, evacuated and back filled with N_2 and heated at 60 °C for 12 h. The reaction mixture was allowed to cool at ambient temperature. The reaction mixture was diluted with EtOAc and washed with $NaHCO_3$ followed by brine. The collective organic layer dried over Na_2SO_4 and the solvent was removed under vacuo. The resulting residue was purified by flash column chromatography on silica gel (eluent: pet. ether/EtOAc) to give the product **3a** as yellow liquid (87% yield).

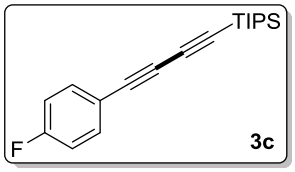
Characterization data:



Compound 3a: $\mathbf{R_f}$: 0.80 (pet. ether); 51 mg, **yield**: 87%; **physical appearance**: yellow liquid; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**): δ = 7.39 - 7.44 (m, *J* = 8.0 Hz, 2 H), 7.11 - 7.15 (m, *J* = 8.0 Hz, 2 H), 2.37 (s, 3 H), 1.13 (s, 21 H) ppm; **^{13}C NMR** (**125 MHz**, **$CDCl_3$**): δ = 139.8, 132.9, 129.4, 118.6, 89.9, 87.6, 76.1, 74.3, 21.8, 18.8, 11.6 ppm.



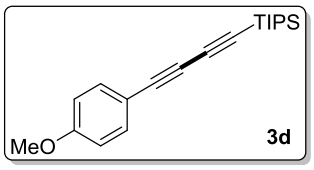
Compound 3b[2]: $\mathbf{R_f}$: 0.75 (pet. ether); 45 mg, **yield**: 81%; **physical appearance**: colourless liquid; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**): δ = 7.52 (m, 2 H), 7.33 (m, 3 H), 1.14 (s, 21 H) ppm; **^{13}C NMR** (**125 MHz**, **$CDCl_3$**): δ = 132.7, 129.2, 128.4, 121.5, 89.5, 87.9, 75.5, 74.7, 18.6, 11.3 ppm.



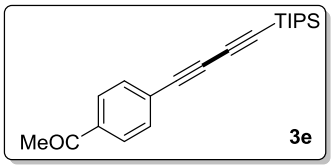
Compound 3c[3]: $\mathbf{R_f}$: 0.70 (pet. ether); 38 mg, **yield**: 64%; **physical appearance**: colourless liquid; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**): δ = 7.50 (dd, *J* = 8.8, 5.3 Hz, 2 H), 7.02 (t, *J* = 8.8 Hz, 2

[2] P. Bichler, W. A. Chalifoux, S. Eisler, A. L. K. Shi Shun, E. T. Chernick and R. R. Tykwinski, *Org. Lett*., 2009, **11**, 519.

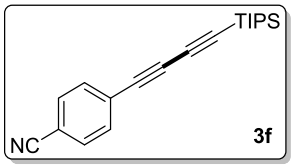
H), 1.12 (s, 21 H) ppm; **^{13}C NMR** (**125 MHz**, **$CDCl_3$**): δ = 164.2 and 162.2 (d, $^{1}J_{C\text{-}F}$ = 251.8 Hz), 134.9 (d, $^{3}J_{C\text{-}F}$ = 8.58 Hz), 117.9 (d, $^{4}J_{C\text{-}F}$ = 3.81 Hz), 116.2 (d, $^{2}J_{C\text{-}F}$ = 21.93 Hz), 89.6, 88.2, 74.7, 74.6, 18.8, 11.5 ppm.



Compound 3d[2]: **R_f**: 0.50 (pet. ether); 53 mg, **yield**: 85%; **physical appearance**: colourless liquid; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**): δ = 7.43 - 7.49 (m, *J* = 8.8 Hz, 2 H), 6.82 - 6.87 (m, *J* = 8.8 Hz, 2 H), 3.82 (s, 3 H), 1.13 (s, 21 H) ppm; **^{13}C NMR** (**125 MHz**, **$CDCl_3$**): δ = 160.6, 134.6, 114.4, 113.7, 90.1, 87.3, 76.0, 73.8, 55.5, 18.8, 11.6 ppm; **HRMS**: (**ESI**) calcd 313.1982 for $C_{20}H_{29}OSi$ $[M + H]^+$ found 313.1984.



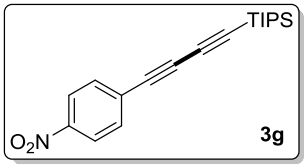
Compound 3e: **R_f**: 0.60 (pet. ether/EtOAc = 98/02); 49 mg, **yield**: 76%; **physical appearance**: colourless liquid; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**): δ = 7.87 - 7.94 (m, *J* = 8.4 Hz, 2 H), 7.56 - 7.62 (m, *J* = 8.4 Hz, 2 H), 2.60 (s, 3 H), 1.13 (s, 21 H) ppm; **^{13}C NMR** (**125 MHz**, **$CDCl_3$**): δ = 197.3, 137.1, 133.0, 128.5, 126.7, 90.4, 89.3, 77.9, 74.7, 26.9, 18.8, 11.5 ppm; **HRMS**: (**ESI**) calcd 325.1982 for $C_{21}H_{29}OSi$ $[M + H]^+$ found 325.1985.



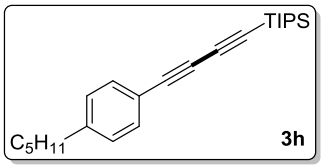
Compound 3f: **R_f**: 0.40 (pet. ether/EtOAc = 95/05); 43 mg, **yield**: 70%; **physical appearance**: white solid; **mp**: 70-72 °C; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**): δ = 7.60 (q, *J* = 8.4 Hz, 4 H), 1.12 (s, 21 H) ppm; **^{13}C NMR** (**125 MHz**, **$CDCl_3$**): δ = 133.3, 132.3, 126.8, 118.4, 112.6, 91.4, 88.9,

[3] T. Luu , R. McDonald and R. R. Tykwinski, *Org. Lett*., 2006, **8**, 6035.

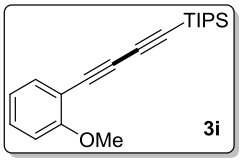
78.9, 73.6, 18.8, 11.5 ppm; **HRMS**: (**ESI**) calcd 308.1830 for $C_{20}H_{26}NSi$ $[M + H]^+$ found 308.1829.



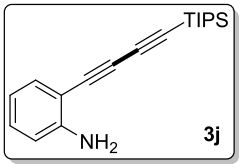
Compound 3g: $\mathbf{R_f}$: 0.50 (pet. ether); 51 mg, **yield**: 70%; **physical appearance**: bright yellow solid; **mp**: 70-72 °C; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**): δ = 8.17 - 8.22 (m, *J* = 8.8 Hz, 2 H), 7.63 - 7.68 (m, *J* = 8.8 Hz, 2 H), 1.13 (s, 21 H) ppm; **^{13}C NMR** (**125 MHz**, **$CDCl_3$**): δ = 147.8, 133.6, 128.8, 123.9, 92.0, 88.9, 79.7, 73.4, 18.8, 11.5 ppm; **HRMS**: (**ESI**) calcd 328.1727 for $C_{19}H_{26}NO_2Si$ $[M + H]^+$ found 328.1724.



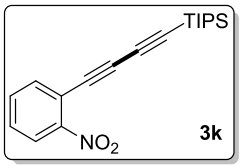
Compound 3h: $\mathbf{R_f}$: 0.90 (pet. ether); 52 mg, **yield**: 74%; **physical appearance**: colourless liquid; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**): δ = 7.40 - 7.45 (m, *J* = 8.0 Hz, 2 H), 7.11 - 7.16 (m, *J* = 8.0 Hz, 2 H), 2.60 (t, *J* = 7.6 Hz, 2 H), 1.61 (quin, *J* = 7.4 Hz, 2 H), 1.29 - 1.37 (m, 4 H), 1.13 (s, 21 H), 0.90 (t, *J* = 6.9 Hz, 3 H) ppm; **^{13}C NMR** (**125 MHz**, **$CDCl_3$**): δ = 144.9, 132.9, 128.8, 118.8, 89.9, 87.6, 76.2, 74.3, 36.2, 31.7, 31.1, 22.7, 18.8, 14.2, 11.6 ppm; **HRMS**: (**ESI**) calcd 353.2659 for $C_{24}H_{37}Si$ $[M + H]^+$ found 353.2665.



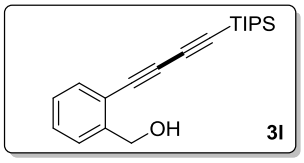
Compound 3i: $\mathbf{R_f}$: 0.50 (pet. ether); 46 mg, **yield**: 73%; **physical appearance**: yellow liquid; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**): δ = 7.46 - 7.51 (m, 1 H), 7.30 - 7.35 (m, 1 H), 6.90 - 6.93 (m, 1 H), 6.88 (d, *J* = 8.4 Hz, 1 H), 3.90 (s, 3 H), 1.12 (s, 21 H) ppm; **^{13}C NMR** (**125 MHz**, **$CDCl_3$**): δ = 161.8, 135.0, 130.9, 120.7, 111.0, 110.8, 89.9, 88.5, 78.7, 71.6, 56.0, 18.8, 11.6 ppm; **HRMS**: (**ESI**) calcd 313.1982 for $C_{20}H_{29}OSi$ $[M + H]^+$ found 313.1982.



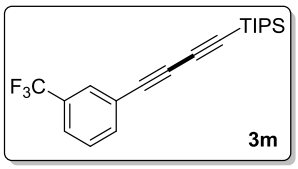
Compound 3j: **R_f**: 0.50 (pet. ether/EtOAc = 98/02); 35 mg, **yield**: 60%; **physical appearance**: brown liquid; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**): δ = 7.34 (d, *J* = 7.2 Hz, 1 H), 7.10 - 7.18 (m, 1 H), 6.63 - 6.71 (m, 2 H), 4.31 (br. s., 2 H), 1.13 (s, 21 H) ppm; **^{13}C NMR** (**125 MHz**, **$CDCl_3$**): δ = 149.6, 133.1, 130.3, 117.6, 114.1, 105.5, 89.2, 88.7, 79.5, 72.4, 18.3, 11.1 ppm; **HRMS**: (**ESI**) calcd 298.1986 for $C_{19}H_{28}NSi$ $[M + H]^+$ found 298.1989.



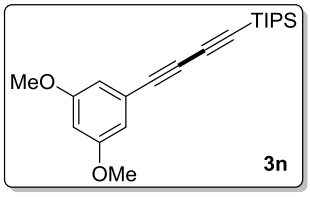
Compound 3k: **R_f**: 0.90 (pet. ether/EtOAc = 98/02); 43 mg, **yield**: 66%; **physical appearance**: yellow liquid; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**): δ = 8.10 (d, *J* = 8.0 Hz, 1 H), 7.74 (d, *J* = 8.0 Hz, 1 H), 7.58 - 7.63 (m, 1 H), 7.48 - 7.53 (m, 1 H), 1.11 - 1.15 ppm (m, 21 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**): δ = 150.2, 136.1, 132.9, 129.3, 124.9, 117.6, 92.2, 89.0, 82.1, 70.0, 18.5, 11.3 ppm; **HRMS**: (**ESI**) calcd 328.1727 for $C_{19}H_{26}NO_2Si$ $[M + H]^+$ found 328.1724.



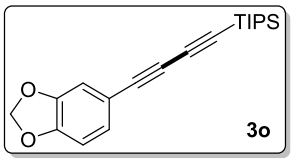
Compound 3l: **R_f**: 0.60 (pet. ether/EtOAc = 80/20); 33 mg, **yield**: 53%; **physical appearance**: colourless liquid; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**): δ = 7.56 (d, *J* = 7.6 Hz, 1 H), 7.51 (d, *J* = 7.6 Hz, 1 H), 7.38 - 7.45 (m, 1 H), 7.28 - 7.31 (m, 1 H), 4.90 (s, 2 H), 2.00 (br. s., 1 H), 1.15 (s, 21 H) ppm; **^{13}C NMR** (**125 MHz**, **$CDCl_3$**): δ = 144.3, 133.6, 129.6, 127.5, 127.3, 119.6, 89.4, 89.1, 79.0, 72.9, 63.6, 18.6, 11.3 ppm; **HRMS**: (**ESI**) calcd 313.1982 for $C_{20}H_{29}OSi$ $[M + H]^+$ found 313.1979.



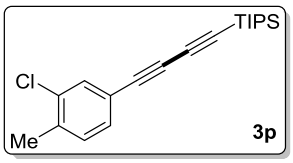
Compound 3m: $\mathbf{R_f}$: 0.80 (pet. ether); 45 mg, **yield**: 64%; **physical appearance**: colourless liquid; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**): δ = 7.78 (s, 1 H), 7.68 (d, *J* = 7.6 Hz, 1 H), 7.61 (d, *J* = 7.6 Hz, 1 H), 7.46 (t, *J* = 7.6 Hz, 1 H), 1.13 (s, 21 H) ppm; **^{13}C NMR** (**125 MHz**, **$CDCl_3$**): δ 135.6, 131.2 and 131.1($^2J_{C\text{-}F}$ = 33.38 Hz), 129.4(q, $^3J_{C\text{-}F}$ = 7.63 Hz), 129.0, 125.7($^4J_{C\text{-}F}$ = 3.81 Hz), 124.6 and 122.4 (q, $^1J_{C\text{-}F}$ = 272.7 Hz), 122.6, 89.4, 88.9, 76.1, 73.7, 18.5, 11.3 ppm; **HRMS**: (**ESI**) calcd 351.1750 for $C_{20}H_{26}F_3Si$ $[M + H]^+$ found 351.1766.



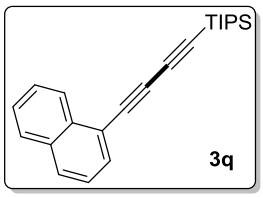
Compound 3n: $\mathbf{R_f}$: 0.50 (pet. ether/EtOAc = 98/02); 43 mg, **yield**: 63%; **physical appearance**: colourless liquid; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**): δ = 6.67 (d, *J* = 2.3 Hz, 2 H), 6.49 (s, 1 H), 3.78 (s, 6 H), 1.12 (s, 21 H) ppm; **^{13}C NMR** (**125 MHz**, **$CDCl_3$**): δ = 160.7, 123.0, 110.5, 103.3, 89.6, 88.2, 75.8, 74.4, 55.7, 18.8, 11.5 ppm; **HRMS**: (**ESI**) calcd 343.2088 for $C_{21}H_{31}O_2Si$ $[M + H]^+$ found 343.2087.



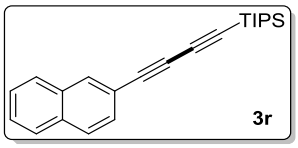
Compound 3o: $\mathbf{R_f}$: 0.70 (pet. ether); 63 mg, **yield**: 80%; **physical appearance**: yellow liquid; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**): δ = 7.07 (dd, *J* = 8.0, 1.5 Hz, 1 H), 6.91 - 6.97 (m, 1 H), 6.75 (d, *J* = 8.0 Hz, 1 H), 5.99 (s, 2 H), 1.12 (s, 21 H) ppm; **^{13}C NMR** (**125 MHz**, **$CDCl_3$**): δ = 148.8, 147.4, 128.0, 114.6, 112.2, 108.6, 101.5, 89.6, 87.4, 75.6, 73.3, 18.6, 11.3 ppm; **HRMS**: (**ESI**) calcd 327.1775 for $C_{20}H_{27}O_2Si$ $[M + H]^+$ found 327.1774.



Compound 3p: **R_f**: 0.80 (pet. ether); 50 mg, **yield**: 75%; **physical appearance**: colourless liquid; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**): δ = 7.48 - 7.51 (m, 1 H), 7.28 - 7.32 (m, 1 H), 7.17 (d, *J* = 7.6 Hz, 1 H), 2.38 (s, 3 H), 1.13 (s, 21 H) ppm; **^{13}C NMR** (**125 MHz**, **$CDCl_3$**): δ = 138.1, 134.6, 133.1, 131.1, 131.0, 120.7, 89.5, 88.7,75.3, 74.4, 20.4, 18.8, 11.5 ppm.

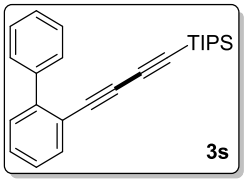


Compound 3q[4]: **R_f**: 0.70 (pet. ether); 44 mg, **yield**: 66%; **physical appearance**: colourless liquid; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**): δ = 8.37 (d, *J* = 8.4 Hz, 1 H), 7.87 (d, *J* = 8.0 Hz, 2 H), 7.79 (d, *J* = 7.2 Hz, 1 H), 7.61 (t, *J* = 7.2 Hz, 1 H), 7.55 (t, *J* = 7.4 Hz, 1 H), 7.43 (t, *J* = 7.8 Hz, 1 H), 1.18 (s, 21 H) ppm; **^{13}C NMR** (**125 MHz**, **$CDCl_3$**): δ = 134.3, 133.3, 132.6, 129.9, 128.6, 127.4, 126.9, 126.4, 125.4, 119.5, 89.9, 89.2, 79.5, 74.1, 18.9, 11.6 ppm; **HRMS**: (**ESI**) calcd 333.2033 for $C_{23}H_{29}Si$ $[M + H]^+$ found 333.2026.

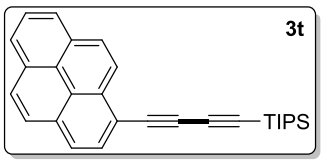


Compound 3r: **R_f**: 0.80 (pet. ether); 57 mg, **yield**: 86%; **physical appearance**: white solid; **mp**: 56-58 °C; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**): δ = 8.07 (s, 1 H), 7.75 - 7.86 (m, 3 H), 7.52 (t, *J* = 8.6 Hz, 3 H), 1.15 (s, 21 H) ppm; **^{13}C NMR** (**125 MHz**, **$CDCl_3$**): δ = 133.3, 133.2, 132.8, 128.6, 128.1, 127.8, 127.8, 127.2, 126.7, 118.8, 89.6, 88.1, 77.3, 76.7, 76.0, 75.0, 18.6, 11.3 ppm; **HRMS**: (**ESI**) calcd 333.2033 for $C_{23}H_{29}Si$ $[M + H]^+$ found 333.2033.

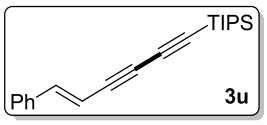
[4] M. A. Heuft, S. K. Collins, G. P. A. Yap and A. G. Fallis, *Org. Lett.*, 2001, **3**, 2883.



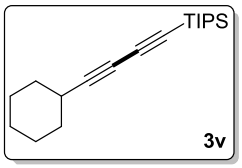
Compound 3s: **R_f**: 0.50 (pet. ether); 48 mg, **yield**: 68%; **physical appearance**: colourless liquid; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**): δ = 7.66 (d, *J* = 7.6 Hz, 1 H), 7.63 (d, *J* = 7.2 Hz, 2 H), 7.45 - 7.50 (m, 2 H), 7.38 - 7.44 (m, 3 H), 7.29 - 7.34 (m, 1 H), 1.10 (s, 21 H) ppm; **^{13}C NMR** (**125 MHz**, **$CDCl_3$**): δ = 145.4, 140.1, 134.8, 129.8, 129.6, 129.3, 128.4, 128.0, 127.3, 120.1, 89.9, 88.4, 75.5, 18.8, 11.5 ppm; **HRMS**: (**ESI**) calcd 359.2190 for $C_{25}H_{31}Si$ $[M + H]^+$ found 359.2193.



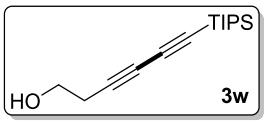
Compound 3t: **R_f**: 0.50 (pet. ether); 45 mg, **yield**: 56%; **physical appearance**: light yellow solid; **mp**: 96-98 °C; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**): δ = 8.57 (d, *J* = 9.2 Hz, 1 H), 8.20 (d, *J* = 7.6 Hz, 1 H), 8.23 (d, *J* = 7.6 Hz, 1 H), 8.18 (d, *J* = 8.4 Hz, 2 H), 8.06 - 8.13 (m, 2 H), 7.99 - 8.06 (m, 2 H), 1.21 (s, 21 H) ppm; **^{13}C NMR** (**125 MHz**, **$CDCl_3$**): δ = 133.5, 131.8, 131.1, 131.0, 130.8, 128.8, 128.7, 127.1, 126.3, 125.9, 125.8, 125.4, 124.4, 124.3, 124.1, 115.8, 89.9, 89.5, 80.0, 75.0, 18.7, 11.4 ppm; **MALDI-TOF**: calcd 406.21 for $C_{29}H_{31}Si$ $[M + H]^+$ found 406.1317.



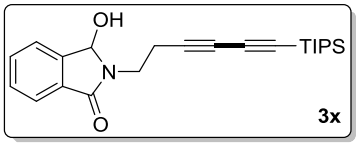
Compound 3u[2]: **R_f**: 0.80 (pet. ether); 33 mg, **yield**: 53%; **physical appearance**: yellow liquid; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**): δ = 7.38 - 7.41 (m, 2 H), 7.31 - 7.37 (m, 3 H), 7.13 (d, *J* = 16.0 Hz, 1 H), 6.19 (d, *J* = 16.0 Hz, 1 H), 1.12 (s, 21 H) ppm; **^{13}C NMR** (**125 MHz**, **$CDCl_3$**): δ = 145.0, 135.7, 129.3, 128.8, 126.4, 106.5, 89.7, 88.6, 76.8, 75.4, 18.6, 11.3 ppm.



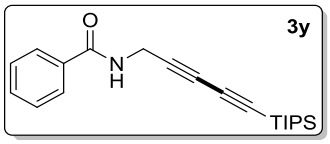
Compound 3v: **R_f**: 0.50 (pet. ether/EtOAc = 90/10); 24 mg, **yield**: 42%; **physical appearance**: brownish liquid; **^{1}H NMR**: (**500 MHz**, **$CDCl_3$**) δ = 1.84 - 2.08 (m, 3 H), 1.66 - 1.74 (m, 2 H), 1.47 - 1.66 (m, 6 H), 1.09 (s, 21 H) ppm; **^{13}C NMR** (**125 MHz**, **$CDCl_3$**): δ = 89.0, 84.4, 80.0, 69.5, 39.6, 29.7, 25.0, 23.0, 18.5, 11.3 ppm.



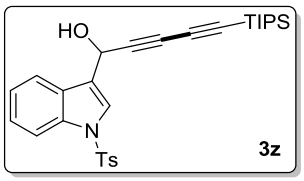
Compound 3w: **R_f**: 0.40 (pet. ether/EtOAc = 90/10); 23 mg, **yield**: 46%; **physical appearance**: yellow liquid; **^{1}H NMR**: (**500 MHz**, **$CDCl_3$**) δ = 3.77 (t, *J* = 6.1 Hz, 2 H), 2.56 (t, *J* = 6.3 Hz, 2 H), 1.08 (s, 21 H) ppm; **^{13}C NMR**: (**125 MHz**, **$CDCl_3$**) δ = 89.6, 81.1, 75.1, 67.6, 60.7, 23.7, 18.5, 11.2 ppm; **HRMS**: (**ESI**) calcd 251.1826 for $C_{15}H_{27}OSi$ $[M + H]^+$ found 251.1828.



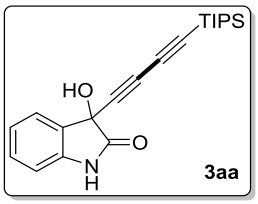
Compound 3x: **R_f**: 0.90 (pet. ether/EtOAc = 60/40); 55 mg, **yield**: 71%; **physical appearance**: white solid; **mp**: 110-112 °C; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**): δ = 7.55 - 7.66 (m, 3 H), 7.42 - 7.51 (m, 1 H), 5.89 (s, 1 H), 3.56 (dt, *J* = 10.6, 6.9 Hz, 2 H), 2.57 - 2.69 (m, 2 H), 1.07 (s, 21 H) ppm; **^{13}C NMR** (**125 MHz**, **$CDCl_3$**): δ = 167.5, 143.9, 132.5, 131.1, 129.9, 123.4, 123.3, 89.5, 82.4, 81.4, 75.4, 67.5, 38.0, 19.3, 18.5, 11.2 ppm; **HRMS**: (**ESI**) calcd 382.2197 for $C_{23}H_{32}NO_2Si$ $[M + H]^+$ found 382.2208.



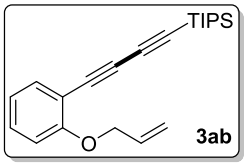
Compound 3y: **R_f**: 0.60 (pet. ether/EtOAc = 95/05); 36 mg, **yield**: 52%; **physical appearance**: colourless liquid; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**): δ = 7.99 (d, *J* = 7.6 Hz, 2 H), 7.54 (d, *J* =7.6 Hz, 1 H), 7.43 - 7.49 (m, 2 H), 5.46 (t, *J* = 3.1 Hz, 1 H), 4.85 (d, *J* = 3.1 Hz, 2 H), 1.11 (s, 21 H) ppm; **^{13}C NMR** (**125 MHz**, **$CDCl_3$**): δ = 166.0, 132.1, 128.6, 128.1, 126.3, 101.9, 95.2, 82.7, 59.2, 29.7, 18.6, 11.2 ppm; **HRMS**: (**ESI**) calcd 340.2091 for $C_{21}H_{30}NOSi$ $[M + H]^+$ found 340.2105.



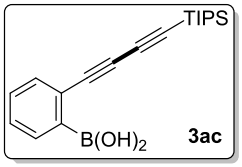
Compound 3z: $\mathbf{R_f}$: 0.50 (pet. ether/EtOAc = 80/20); 60 mg, **yield**: 59%; **physical appearance**: colourless liquid; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**): δ = 7.96 (d, *J* = 8.4 Hz, 1 H), 7.75 - 7.81 (m, *J* = 8.4 Hz, 2 H), 7.68 - 7.74 (m, 2 H), 7.31 - 7.36 (m, 1 H), 7.23 - 7.26 (m, 1 H), 7.19 - 7.23 (m, *J* = 8.0 Hz, 2 H), 5.72 (s, 1 H), 2.33 (s, 3 H), 1.09 (s, 21 H) ppm; **^{13}C NMR**: (**125 MHz**, **$CDCl_3$**): δ = 145.2, 135.4, 135.0, 130.0, 128.1, 126.9, 125.2, 124.2, 123.4, 121.3, 120.3, 113.6, 88.5, 86.3, 74.4, 71.3, 58.4, 21.5, 18.5, 11.2 ppm.



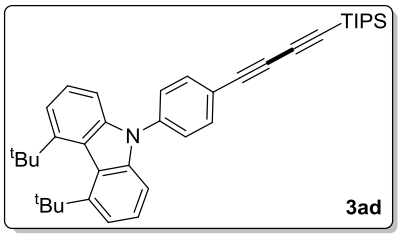
Compound 3aa: $\mathbf{R_f}$: 0.50 (pet. ether/EtOAc = 70/30); 57 mg, **yield**: 74%; **physical appearance**: white solid; **mp**: 230-232 °C; **^{1}H NMR** (**500 MHz**, **DMSO-d_6:$CDCl_3$ (1:4)**): δ = 10.43 (br. s., 1 H), 7.36 (d, *J* = 7.2 Hz, 1 H), 7.19 (t, *J* = 7.4 Hz, 1 H), 7.07 (s, 1 H), 6.96 (t, *J* = 7.2 Hz, 1 H), 6.79 (d, *J* = 7.6 Hz, 1 H), 1.00 (br. s., 21 H) ppm; **^{13}C NMR** (**125 MHz**, **DMSO-d_6:$CDCl_3$ (1:4)**); δ = 173.5, 141.1, 129.7, 129.5, 124.2, 122.0, 110.0, 88.4, 85.0, 78.5, 78.2, 78.0, 74.6, 69.3, 68.9, 18.0, 10.5 ppm; **HRMS**: (**ESI**) calcd 354.1884 for $C_{21}H_{28}NO_2Si$ $[M + H]^+$ found 354.1896.



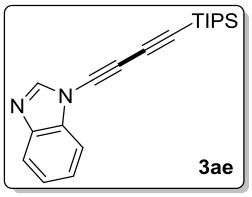
Compound 3ab: $\mathbf{R_f}$: 0.60 (pet. ether/EtOAc = 95/05); 47 mg, **yield**: 67%; **physical appearance**: colourless liquid; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**): δ = 7.48 (dd, *J* = 7.6, 1.1 Hz, 1 H), 7.27 - 7.32 (m, 1 H), 6.84 - 6.93 (m, 2 H), 5.97 - 6.17 (m, 1 H), 5.41 - 5.56 (m, 1 H), 5.21 - 5.36 (m, 1 H), 4.64 (d, *J* = 4.6 Hz, 2 H), 1.13 (s, 21 H) ppm; **^{13}C NMR** (**125 MHz**, **$CDCl_3$**): δ = 160.7, 134.7, 132.8, 130.5, 120.7, 117.4, 112.3, 111.4, 89.9, 88.1, 72.1, 69.3, 18.6, 11.3 ppm; **HRMS**: (**ESI**) calcd 339.2139 for $C_{22}H_{31}OSi$ $[M + H]^+$ found 339.2136.



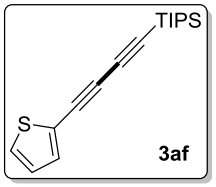
Compound 3ac: **R_f**: 0.40 (pet. ether/EtOAc = 80/20); 31 mg, **yield**: 47%; **physical appearance**: colourless liquid; **^{1}H NMR** (**400 MHz**, **$CDCl_3$**): δ = 7.98 (br. s., 1 H), 7.56 - 7.63 (m, 1 H), 7.40 - 7.48 (m, 2 H), 5.56 (s, 2 H), 1.13 ppm (br. s., 21 H); **^{13}C NMR**: (**100 MHz**, **$CDCl_3$**): δ = 135.8, 134.1, 132.7, 130.8, 129.1, 125.0, 91.0, 88.1, 78.5, 75.6, 18.5, 11.3 ppm; **^{11}B NMR** (**128 MHz**, **$CDCl_3$**): δ = 28.9 ppm; **HRMS**: (**ESI**) calcd 327.1946 for $C_{19}H_{28}BO_2Si$ $[M + H]^+$ found 327.1947.



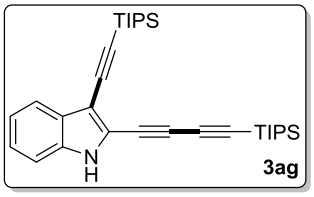
Compound 3ad: **R_f**: 0.70 (pet. ether); 91 mg, **yield**: 81%; **physical appearance**: colourless solid; **mp**: 171-173 °C; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**): δ = 8.15 (br. s., 2 H), 7.69 - 7.75 (m, *J* = 7.6 Hz, 2 H), 7.52 - 7.59 (m, *J* = 7.6 Hz, 2 H), 7.45 - 7.51 (m, *J* = 8.4 Hz, 2 H), 7.36 - 7.42 (m, *J* = 8.4 Hz, 2 H), 1.49 (s, 18 H), 1.17 (br. s., 21 H) ppm; **^{13}C NMR** (**125 MHz**, **$CDCl_3$**); δ = 143.4, 139.0, 138.7, 134.1, 126.2, 123.8, 123.7, 119.7, 116.3, 109.2, 89.5, 88.5, 75.3, 75.0, 34.7, 32.0, 18.6, 11.3 ppm; **MALDI-TOF**: calcd 559.36 for $C_{39}H_{50}NSi$ $[M + H]^+$ found 559.2845



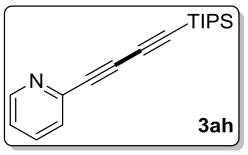
Compound 3ae: **R_f**: 0.50 (pet. ether/EtOAc = 95/05); 30 mg, **yield**: 45%; **physical appearance**: colorless liquid; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**): δ = 8.11 (s, 1 H), 7.82 (d, *J* = 8.0 Hz, 1 H), 7.67 (d, *J* = 7.6 Hz, 1 H), 7.43 (t, *J* = 7.6 Hz, 1 H), 7.38 (t, *J* = 7.6 Hz, 1 H), 1.15 (s, 21 H) ppm; **^{13}C NMR** (**125 MHz**, **$CDCl_3$**): δ = 143.9, 141.6, 134.4, 125.2, 124.5, 121.0, 111.2, 90.5, 87.6, 61.7, 61.4, 18.5, 11.2 ppm; **HRMS**: (**ESI**) calcd 323.1938 for $C_{20}H_{27}N_2Si$ $[M + H]^+$ found 323.1941.



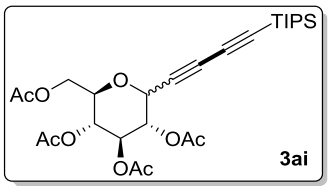
Compound 3af[4]: **R_f**: 0.80 (pet. ether/EtOAc = 98/02); 44 mg, **yield**: 66%; **physical appearance**: colorless liquid; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**): δ = 7.34 (d, *J* = 3.1 Hz, 1 H), 7.30 (d, *J* = 5.3 Hz, 1 H), 6.96 - 7.01 (m, 1 H), 1.12 (s, 21 H) ppm; **^{13}C NMR** (**125 MHz**, **$CDCl_3$**): δ = 134.8, 128.9, 127.3, 122.1, 90.6, 89.5, 79.0, 68.9, 18.8, 11.5 ppm.



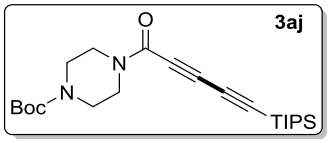
Compound 3ag: **R_f**: 0.50 (pet. ether/EtOAc = 95/05); 36 mg, **yield**: 56%; **physical appearance**: brown liquid; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**): δ = 8.16 (s, 1 H), 7.69 (d, *J* = 8.0 Hz, 1 H), 7.25 - 7.33 (m, 2 H), 7.18 - 7.24 (m, 1 H), 1.20 (s, 21 H), 1.14 (s, 21 H) ppm; **^{13}C NMR** (**125 MHz**, **$CDCl_3$**): δ = 135.1, 128.0, 125.2, 121.7, 121.4, 120.5, 111.1, 108.9, 98.8, 97.0, 91.9, 89.1, 82.2, 66.3, 18.7, 18.5, 11.3, 11.3 ppm; **MALDI-TOF** calcd 501.32 for $C_{32}H_{48}NSi_2$ $[M + H]^+$ found 501.2562.



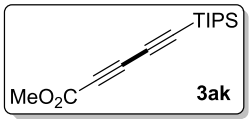
Compound 3ah: **R_f**: 0.40 (pet. ether/EtOAc = 95/05); 36 mg, **yield**: 64%; **physical appearance**: yellow liquid; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**): δ = 8.60 (d, *J* = 4.6 Hz, 1 H), 7.67 (dt, *J* = 7.6, 1.5 Hz, 1 H), 7.51 (d, *J* = 8.0 Hz, 1 H), 7.27 - 7.32 (m, 1 H), 1.13 (s, 21 H) ppm; **^{13}C NMR** (**125 MHz**, **$CDCl_3$**): δ = 150.6, 142.3, 136.3, 128.3, 123.7, 89.8, 89.3, 74.6, 74.4, 18.7, 11.4 ppm; **HRMS**: (**ESI**) calcd 284.1829 for $C_{18}H_{26}NSi$ $[M + H]^+$ found 284.1833.



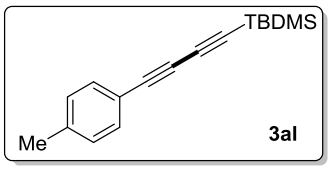
Compound 3ai: $\mathbf{R_f}$: 0.60 (pet. ether/EtOAc = 60/40); 68 mg, **yield**: 60%; (1:1 mixture of C-1 anomers); **physical appearance**: colourless liquid; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**): δ = 5.25 - 5.32 (m, 1 H), 5.15 - 5.23 (m, 1 H), 5.03 - 5.14 (m, 2 H), 4.96 (dt, *J* = 9.2, 5.0 Hz, 2 H), 4.37 - 4.44 (m, 1 H), 4.20 - 4.31 (m, 2 H), 4.12 (d, *J*=12.2 Hz, 2 H), 3.87 (t, *J* = 6.3 Hz, 1 H), 3.58 - 3.72 (m, 2 H), 2.06 - 2.13 (m, 12 H), 1.99 - 2.05 (m, 12 H), 1.07 (s, 42 H) ppm; **^{13}C NMR** (**125 MHz**, **$CDCl_3$**): δ = 170.8, 170.7, 170.3, 170.0, 169.8, 169.6, 169.5, 169.5, 89.6, 89.5, 81.7, 81.6, 75.8, 75.6, 73.9, 72.7, 72.4, 71.8, 70.7, 69.8, 69.7, 69.6, 68.4, 68.4, 68.1, 67.7, 62.1, 61.9, 20.8, 20.7, 20.7, 20.6, 18.5, 11.2 ppm; **HRMS**: (**ESI**) calcd 537.2514 for $C_{27}H_{41}O_9Si$ $[M + H]^+$ found 537.2513.



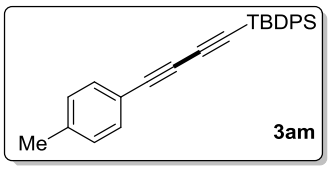
Compound 3aj: $\mathbf{R_f}$: 0.60 (pet. ether/EtOAc = 70/30); 51 mg, **yield**: 62%; **physical appearance**: colourless liquid; **^{1}H NMR** (**5c00 MHz**, **$CDCl_3$**): δ = 3.71 (t, *J* = 5.34 Hz, 2 H, 2 H), 3.60 (t, *J* = 5.34 Hz, 2 H), 3.49 (t, *J* = 4.58 Hz, 2 H), 3.42 (t, *J* = 4.58 Hz, 2 H), 1.47 (s, 9 H), 1.06 - 1.11 ppm (m, 21 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**): δ = 154.4, 151.8, 92.8, 87.4, 80.5, 76.4, 65.9, 46.7, 41.5, 28.3, 18.4, 11.1 ppm; **HRMS**: (**ESI**) calcd 419.2724 for $C_{23}H_{39}N_2O_3Si$ $[M + H]^+$ found 419.2739.



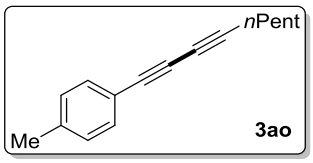
Compound 3ak: $\mathbf{R_f}$: 0.30 (pet. ether); 33 mg, **yield**: 63%; **physical appearance**: yellow liquid; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**): δ = 3.80 (s, 3 H), 1.10 (s, 21 H) ppm; **^{13}C NMR** (**125 MHz**, **$CDCl_3$**): δ = 153.2, 92.6, 87.3, 65.5, 53.0, 18.4, 11.1 ppm; **HRMS**: (**ESI**) calcd 265.1618 for $C_{15}H_{25}O_2Si$ $[M + H]^+$ found 265.1621.



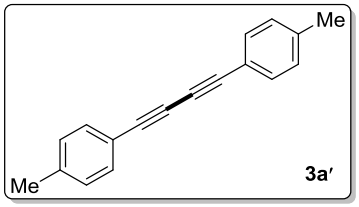
Compound 3al: R_f: 0.70 (pet. ether); 37 mg, **yield**: 73%; **physical appearance**: yellow solid; **mp**: 59-61 °C; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**): δ = 7.32 - 7.49 (m, *J*=8.0 Hz, 2 H), 7.03 - 7.18 (m, *J*=8.0 Hz, 2 H), 2.36 (s, 3 H), 0.99 (s, 9 H), 0.18 ppm (s, 6 H); **^{13}C NMR** (**125 MHz**, **$CDCl_3$**): δ = 139.7, 132.6, 129.2, 118.3, 88.9, 88.6, 76.5, 73.8, 26.1, 21.6, 16.8, -4.8 ppm; **HRMS**: (**ESI**) calcd 255.1564 for $C_{17}H_{23}Si$ $[M + H]^+$ found 255.1574.



Compound 3am: R_f: 0.50 (pet. ether); 42 mg, **yield**: 56%; **physical appearance**: yellow liquid; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**): δ = 7.76 - 7.89 (m, 4 H), 7.38 - 7.51 (m, 8 H), 7.17 (d, *J* = 6.9 Hz, 2 H), 2.39 (s., 3 H), 1.16 (s., 9 H) ppm; **^{13}C NMR** (**125 MHz**, **$CDCl_3$**): δ = 139.9, 135.6, 132.7, 132.6, 129.7, 129.3, 127.8, 118.0, 91.8, 85.5, 76.7, 74.0, 27.1, 21.6, 18.9 ppm; **HRMS**: (**ESI**) calcd 379.1877 for $C_{27}H_{27}Si$ $[M + H]^+$ found 379.1873.



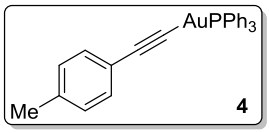
Compound 3ao: R_f: 0.60 (pet. ether); 21 mg, **yield**: 51%; **physical appearance**: colourless liquid; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**): δ = 7.34 - 7.42 (m, *J* = 7.6 Hz, 2 H), 7.08 - 7.15 (m, *J* = 7.6 Hz, 2 H), 2.27 - 2.40 (m, 5 H), 1.56 - 1.62 (m, 2 H), 1.38 - 1.45 (m, 2 H), 1.32 - 1.37 (m, 2 H), 0.92 (t, *J* = 7.2 Hz, 3 H) ppm; **^{13}C NMR** (**125 MHz**, **$CDCl_3$**): δ = 139.1, 132.4, 129.1, 119.0, 84.5, 75.0, 73.8, 65.1, 31.0, 28.0, 21.6, 19.6, 13.9 ppm; **HRMS**: (**ESI**) calcd 211.1481 for $C_{16}H_{19}$ $[M + H]^+$ found 211.1491.



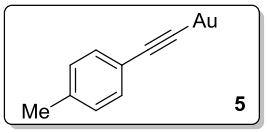
Compound 3a′[5]: **R_f**: 0.40 (pet. ether); **physical appearance**: white solid; **mp**: 177-178 °C; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**) δ = 7.43 (d, *J* = 8.0 Hz, 4 H), 7.15 (d, *J* = 8.0 Hz, 4 H), 2.38 (s, 6 H) ppm; **^{13}C NMR**: (**125 MHz**, **$CDCl_3$**) δ = 139.5, 132.4, 129.2, 118.8, 81.5, 73.4, 21.6 ppm.

3. Synthesis and characterization of gold acetylides 4 and 5:

The gold acetylides **4**[6] and **5**[7] were prepared in accordance with literature known methods.



Complex 4[8]: **physical appearance**: white solid; **^{1}H NMR** (**500 MHz**, **$CDCl_3$**): δ = 7.38 - 7.61 (m, 17 H), 7.07 (d, *J* = 8.0 Hz, 2 H), 2.33 (s, 3 H) ppm; **^{31}P NMR (202 MHz**, **$CDCl_3$)**: δ = 42.38 ppm.

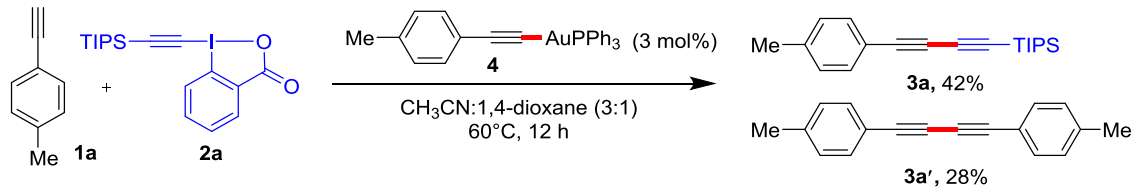


Complex 5: **physical appearance**: yellow solid; **mp**: 178-180 °C (decomp.); Anal. Calcd. for C_9H_7Au: C, 34.63; H, 2.26; Found: C, 34.34; H, 1.97.

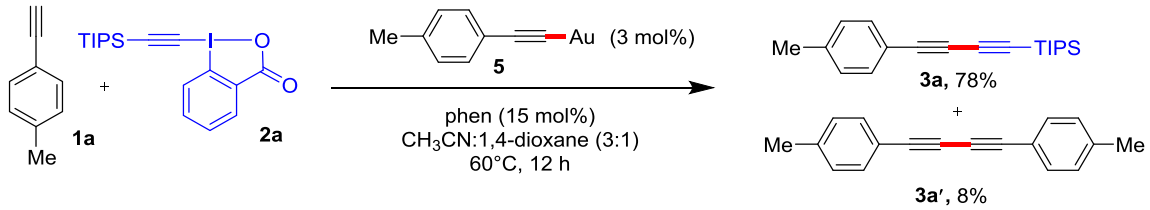
[5] J. M. Pérez, R. Cano, M. Yus and D. J. Ramón, *Synthesis*, 2013, **45**, 1373.
[6] D. Zhang, Z. Xu, J. Yuan, Y.-X. Zhao, Z.-Y. Qiao, Y.-J. Gao, G.-A. Yu, J. Li and H. Wang, *J. Med. Chem.*, 2014, **57**, 8132.
[7] K. J. Kilpin, R. Horvath, G. B. Jameson, S. G. Telfer, K. C. Gordon and J. D. Crowley, *Organometallics*, 2010, **29**, 6186.
[8] T. Lauterbach, M. Livendahl, A. Rosellón, P. Espinet and A. M. Echavarren, *Org. Lett.*, 2010, **13**, 3006.

4. Mechanistic studies:

4.1 Investigation on the role of phen



To an oven-dried screw-cap vial containing a stir bar was charged sequentially with 4-ethynyltoluene (**1a**) (25 µL, 0.20 mmol), TIPS-EBX (**2a**) (94 mg, 0.22 mmol, 1.1 equiv), **4** (3.1 mg, 0.006 mmol, 3 mol%), and degassed CH_3CN:1,4-dioxane (1.8 mL : 0.6 mL) under nitrogen. The reaction vial was fitted with a cap, evacuated and back filled with N_2 and heated at 60 °C for 12 h. Then the reaction mixture was filtered through a pad of silica gel (eluent: DCM). The solvent was evaporated under the reduced pressure and the residue was dissolved in DCM (1 mL). The GC yields were obtained from the crude mixture using biphenyl (0.20 mmol, 31 mg , 1.0 equiv) as the internal standard. The cross-coupled product **3a** was obtained in 42% yield and the homo-coupled product **3a′** was in 28% yield. Due to the poor selectivity and lower reaction rate of the reaction, it can be concluded from the results that Ph_3P –ligated gold catalyst is not the active catalyst.



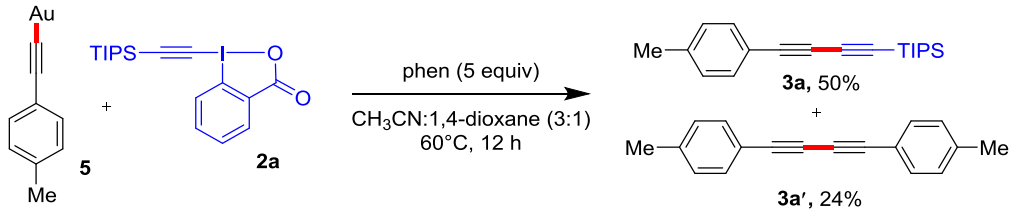
To an oven-dried screw-cap vial containing a stir bar was sequentially charged with 4-ethynyltoluene (**1a**) (25 µL, 0.20 mmol), TIPS-EBX (**2a**) (94 mg, 0.22 mmol, 1.1 equiv), **5** (0.006 mmol, 1.8 mg, 3 mol%), phen (6 mg, 15 mol%) and degassed CH_3CN:1,4-dioxane (1.8 mL : 0.6 mL) under nitrogen. The reaction vial was fitted with a cap, evacuated and back filled with N_2 and heated at 60 °C for 12 h with vigorous stirring. Then the reaction mixture was filtered through a pad of silica gel (eluent: DCM). The solvent was evaporated under the reduced pressure and the residue was dissolved in DCM (1 mL). The GC yields were obtained from the crude mixture using biphenyl (0.20 mmol, 31 mg, 1.0 equiv) as the internal standard. The cross-

coupled product **3a** was obtained in 78% yield and the homo-coupled product **3a′** was in 8% yield.

The higher heteroselectivity observed in this case imply that phen possibly acts as the effective ligand in improving the selectivity of the reaction.

4.2 Investigation of favoured reaction pathway via stoichiometric reactions of 5

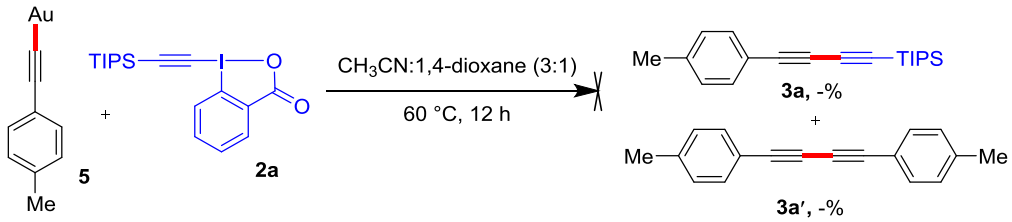
Stoichiometric reaction A: **Reaction of 5 with 2a in the presence of phen**



To an oven-dried screw-cap vial containing a stir bar was sequentially charged with **5** (31 mg, 0.1 mmol), **2a** (47 mg, 0.11 mmol), phen (100 mg, 0.5 mmol, 5 equiv), CH_3CN:1,4-dioxane (1.8 mL : 0.6 mL) under nitrogen. The reaction vial was fitted with a cap, evacuated and back filled with N_2 and heated at 60 °C for 12 h with vigorous stirring. Then the reaction mixture was filtered through a pad of silica gel (eluent: DCM). The solvent was evaporated under the reduced pressure and the residue was dissolved in DCM (1 mL). The GC yields were obtained from the crude mixture using biphenyl (0.10 mmol, 15.4 mg, 1.0 equiv) as the internal standard. The cross-coupled product **3a** was obtained in 50% yield and the homo-coupled product **3a′** was obtained in 24% yield.

Although the heteroselectivity is lowered here as compared to the corresponding catalytic reaction (see text, Scheme 2b), the cross-coupled product **3a** was obtained in 50% yield, which supported the feasibility of a direct oxidation of phen-ligated gold(I) acetylide **B** to **D** by EBX reagents and thus favoring cycle b (see text, Scheme 3, cycle b).

Stoichiometric reaction B: **Reaction of 5 with 2a in the absence of phen**

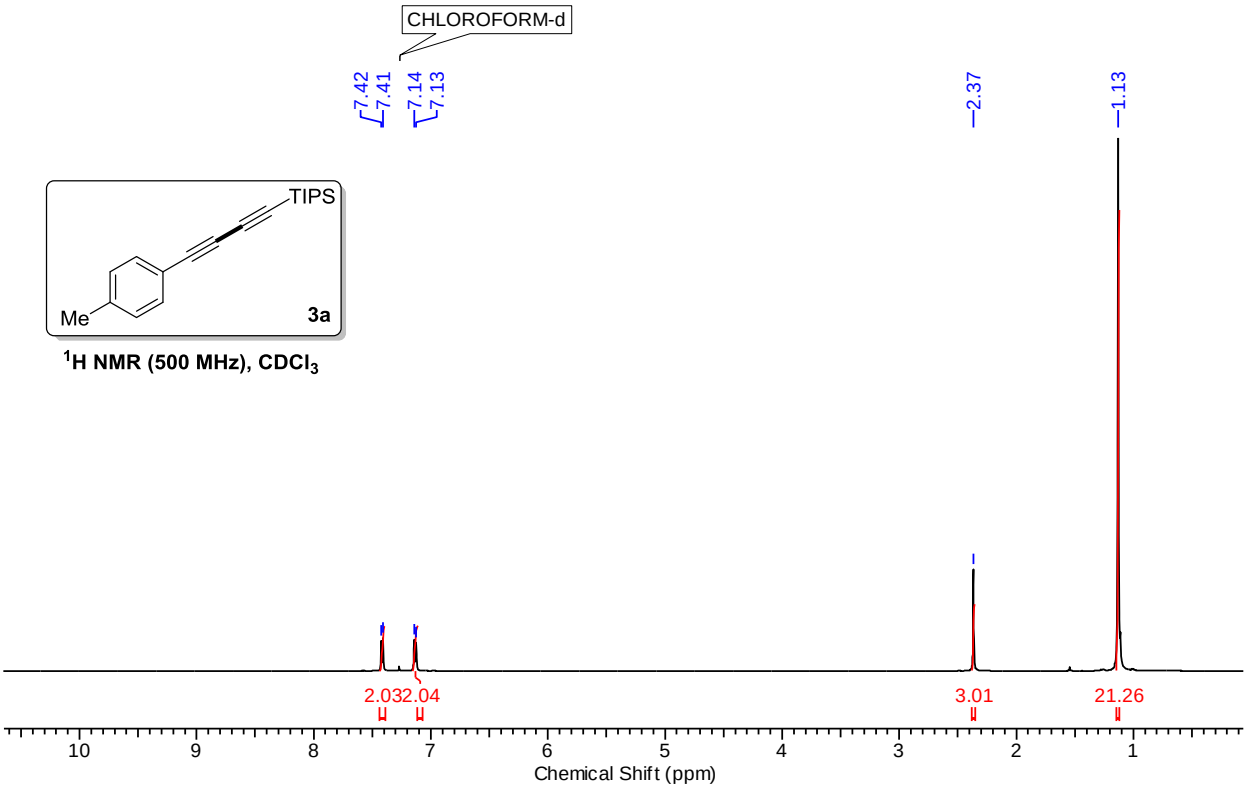


To an oven-dried screw-cap vial containing a stir bar was charged with with **5** (31 mg, 0.1 mmol), **2a** (47 mg, 0.11 mmol), CH_3CN:1,4-dioxane (1.8 mL : 0.6 mL) under nitrogen. The reaction vial was fitted with a cap, evacuated and back filled with N_2 and heated at 60 °C for 12 h with vigorous stirring. No reaction was observed on TLC even after 12 h. Then the reaction mixture was filtered through a pad of silica gel (eluent: DCM). The solvent was evaporated under the reduced pressure and the residue was dissolved in DCM (1 mL). The GC yields were obtained from the crude mixture using biphenyl (0.10 mmol, 15.4 mg, 1.0 equiv) as the internal standard. Neither **3a** nor **3a′** could be observed by GC.

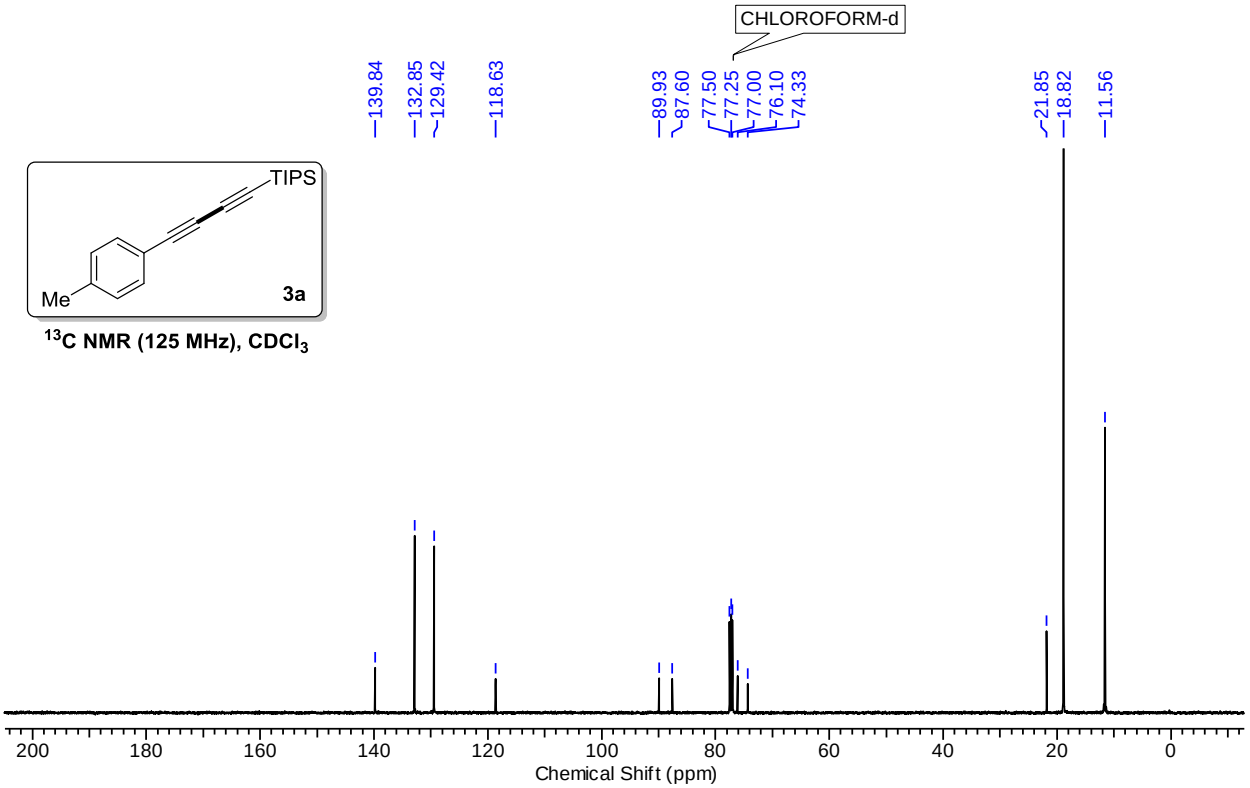
4.3 Determination of $[(phen)AuPPh_3]^+$ by MALDI-TOF studies:

To an oven-dried screw-cap vial containing a stir bar was charged sequentially with Ph_3PAuCl (10 mg, 0.02 mmol), phen (4 mg, 0.02 mmol) and CD_3CN (0.5 mL) under nitrogen. The resulting solution was stirred at 60 °C for 5 min. The formation of $[(phen)AuPPh_3]^+$ was confirmed by MALDI-TOF. For $[(phen)AuPPh_3]^+$: calcd 639.13, found 639.0679.

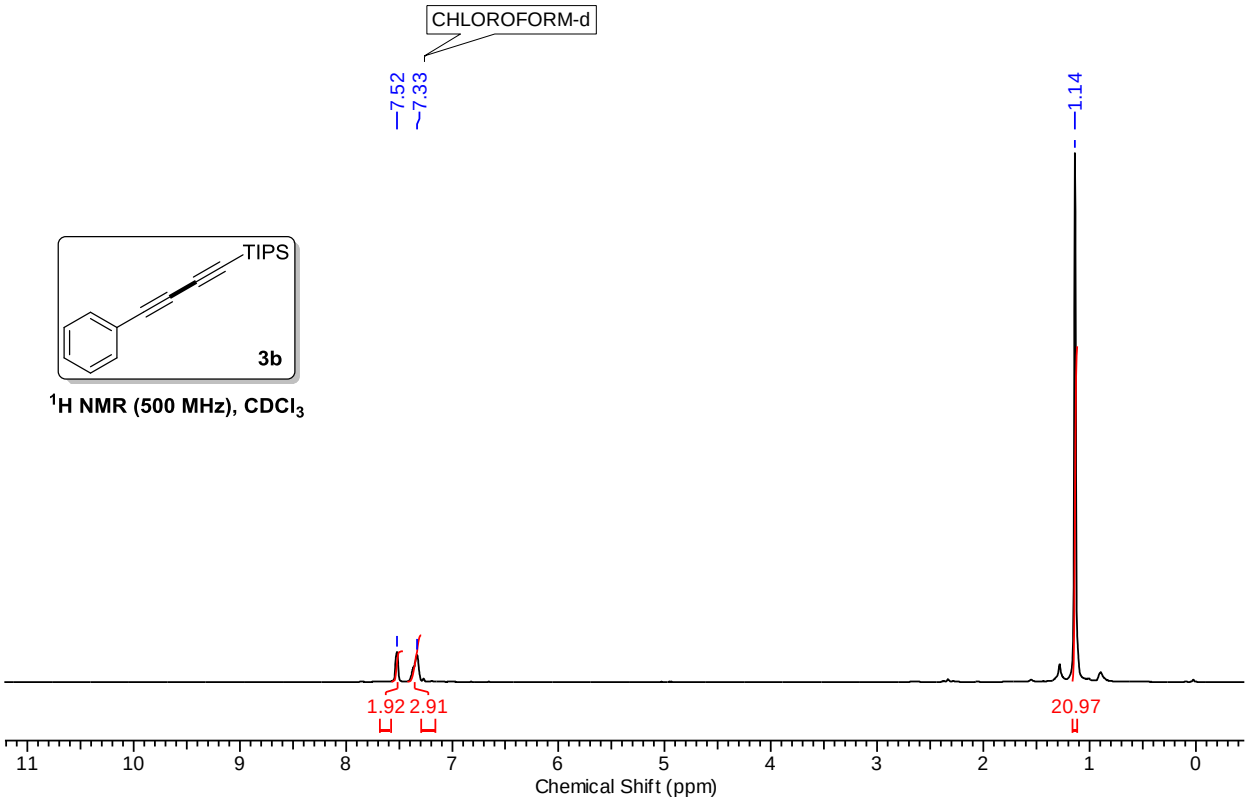
5. NMR spectra



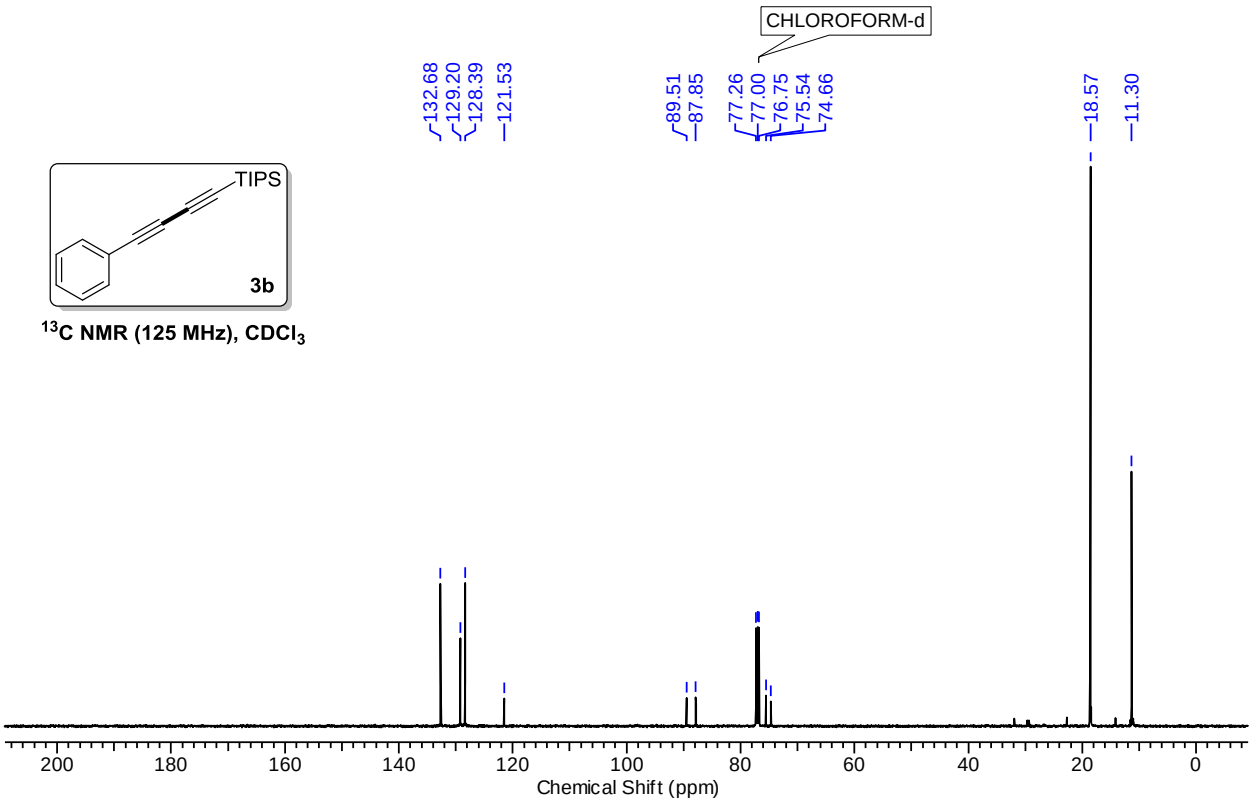
^{1}H NMR (500 MHz), $CDCl_3$



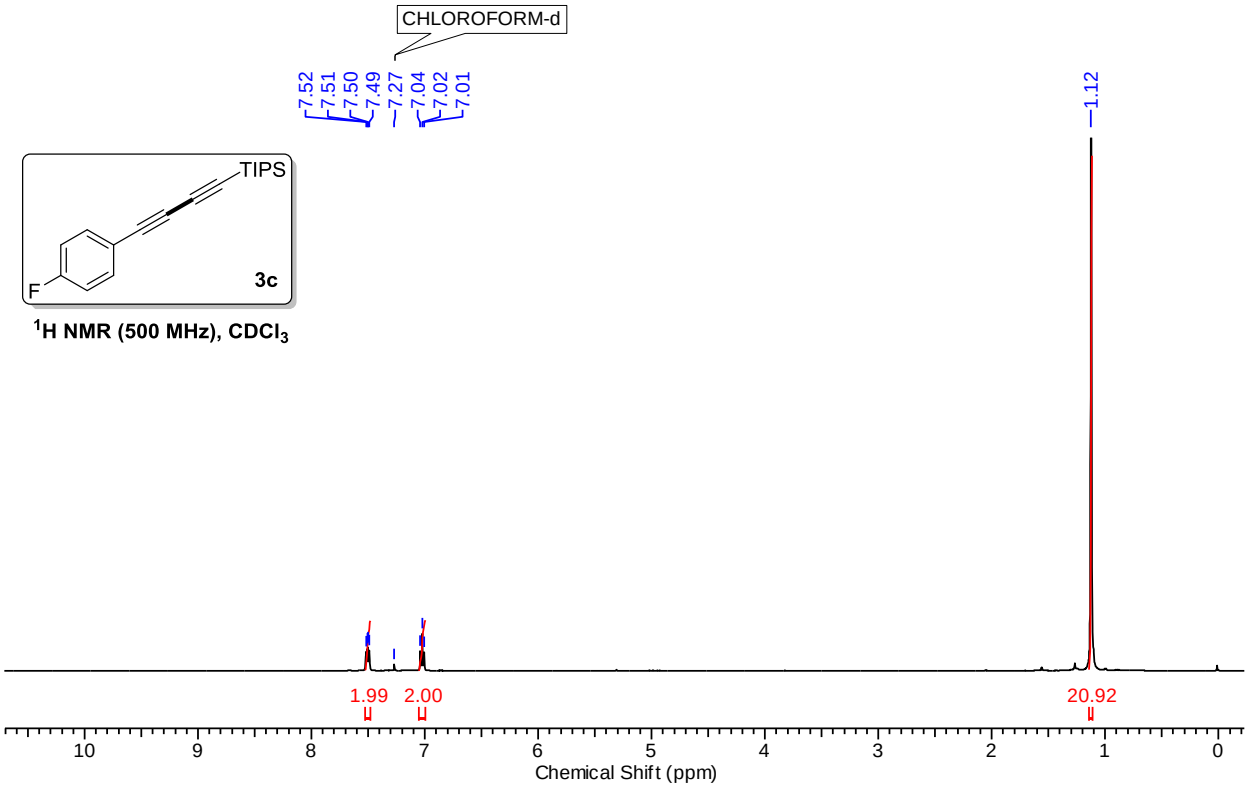
^{13}C NMR (125 MHz), $CDCl_3$



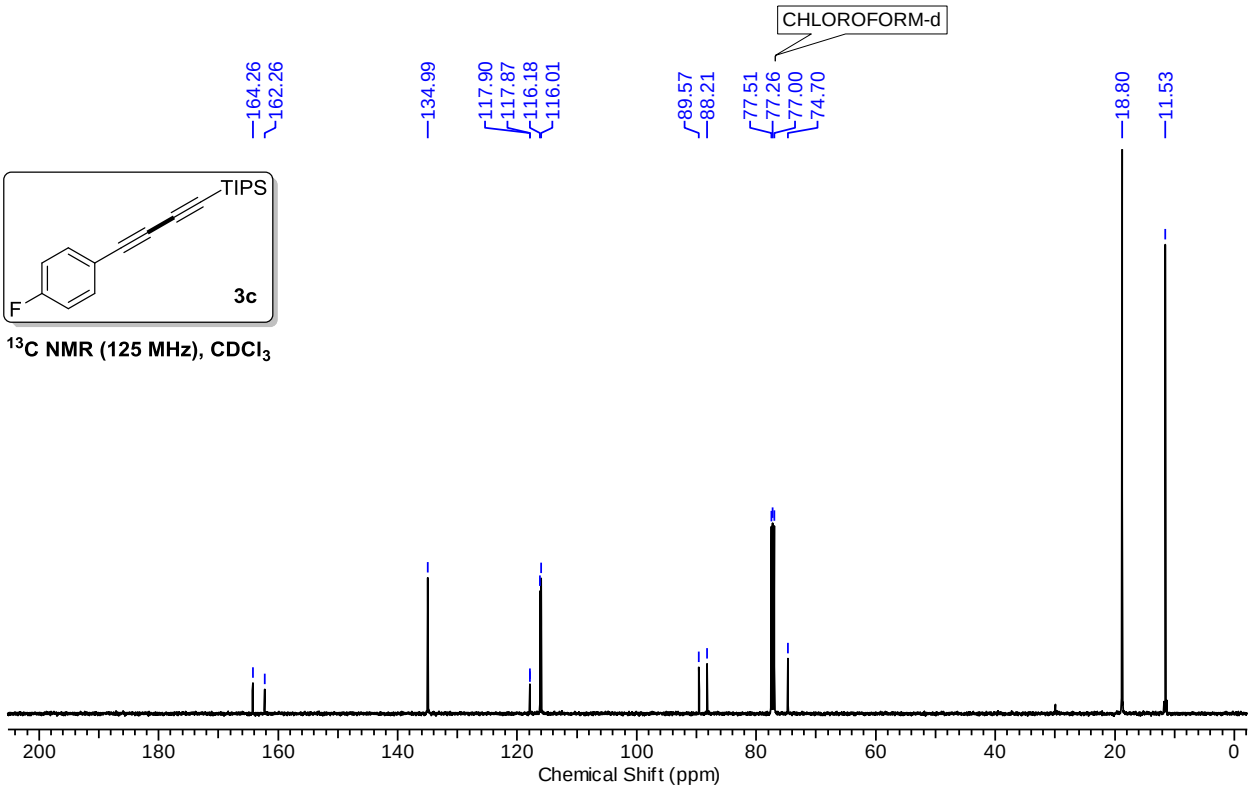
^{1}H NMR (500 MHz), $CDCl_3$



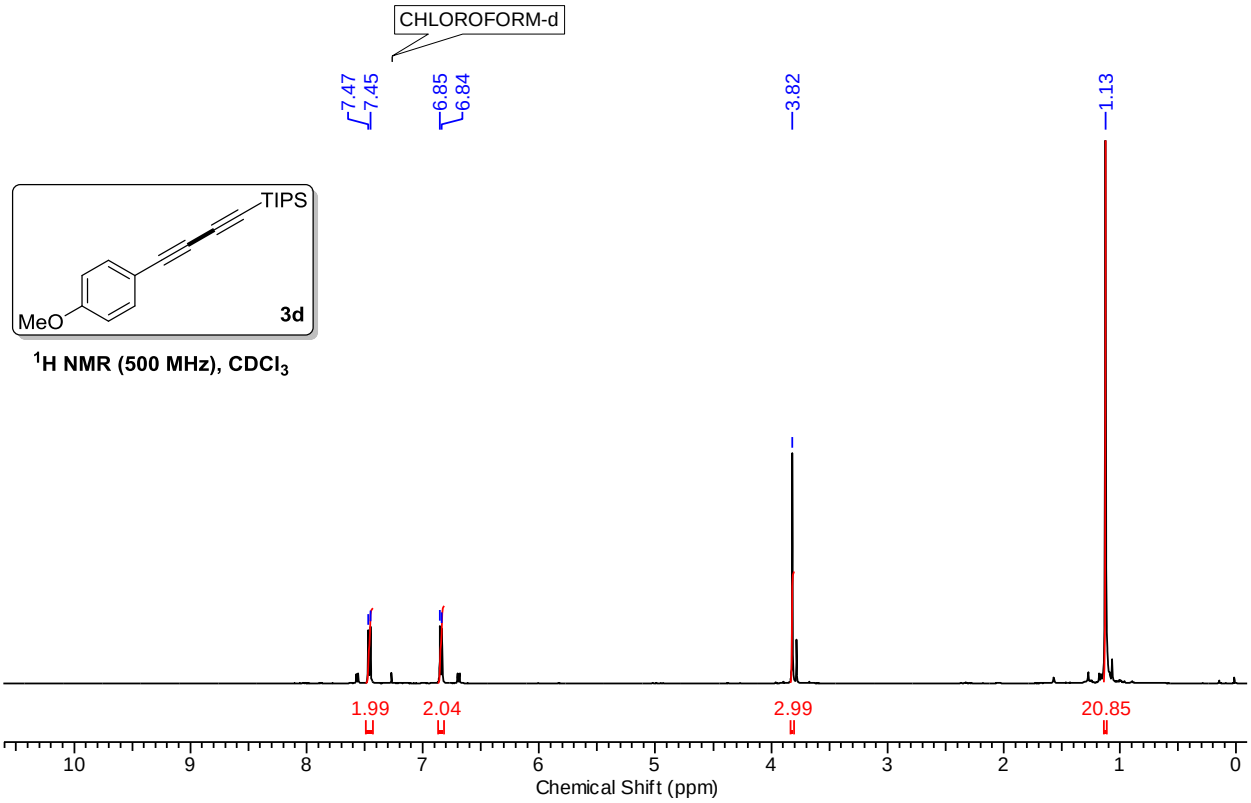
^{13}C NMR (125 MHz), $CDCl_3$



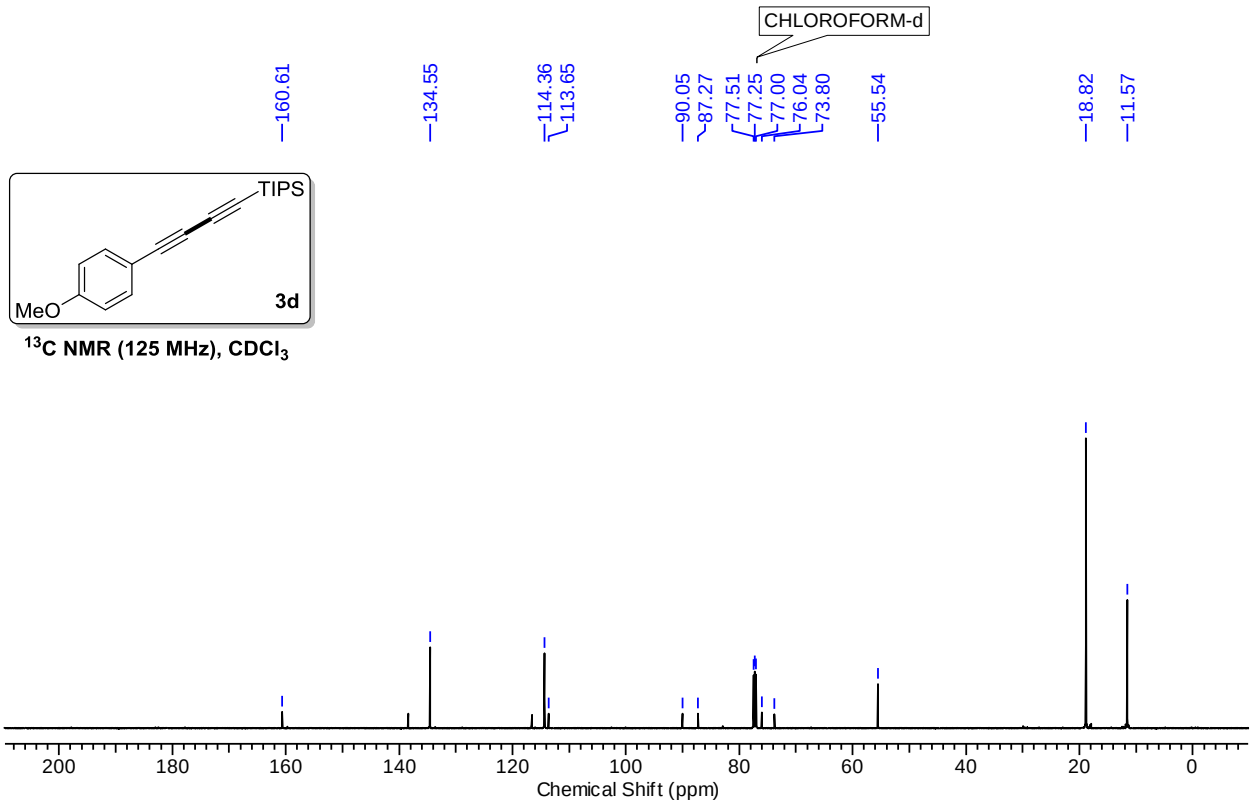
^{1}H NMR (500 MHz), $CDCl_3$



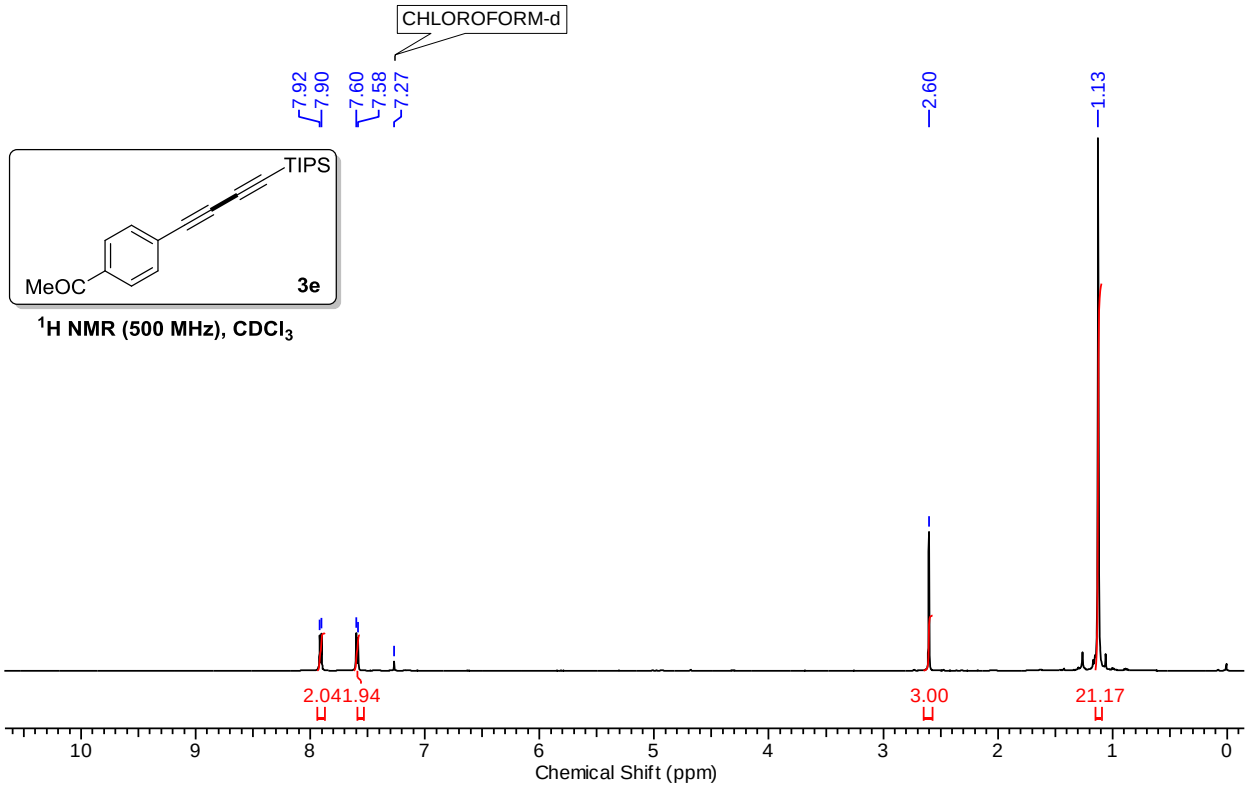
^{13}C NMR (125 MHz), $CDCl_3$



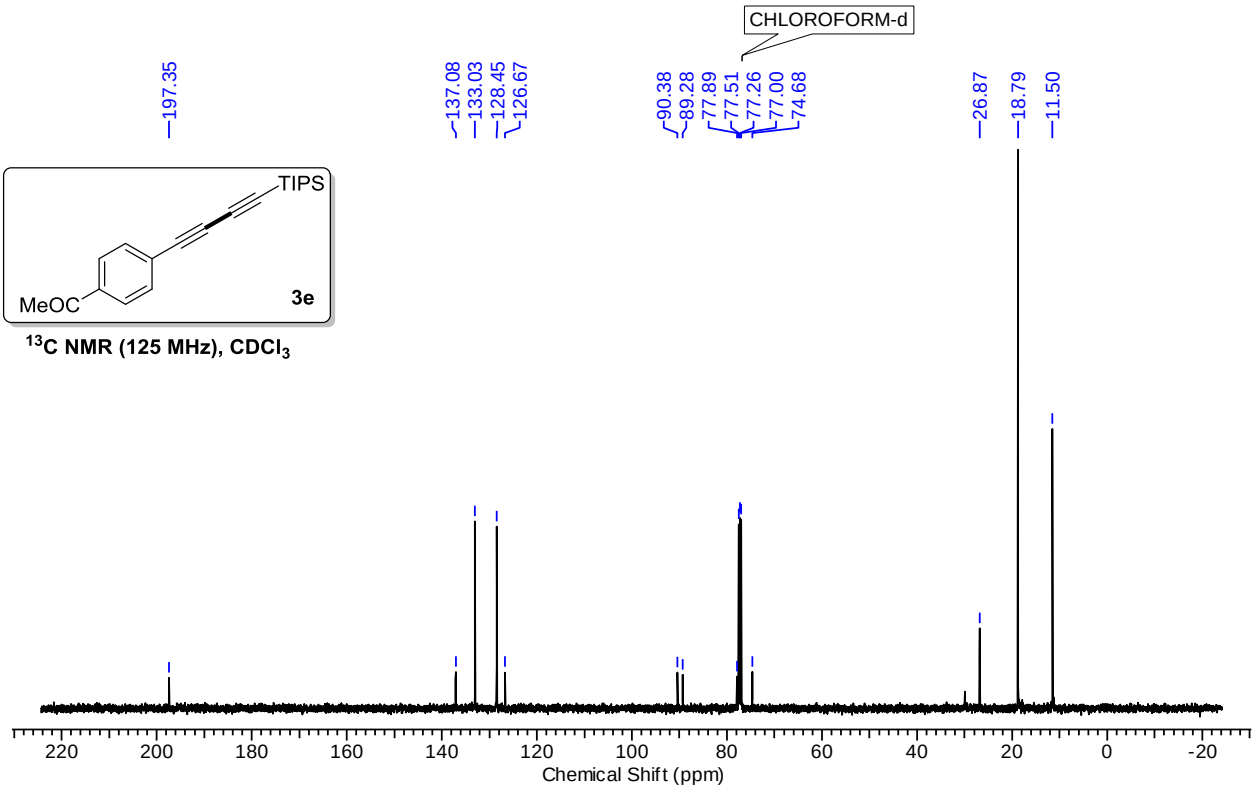
^{1}H NMR (500 MHz), $CDCl_3$



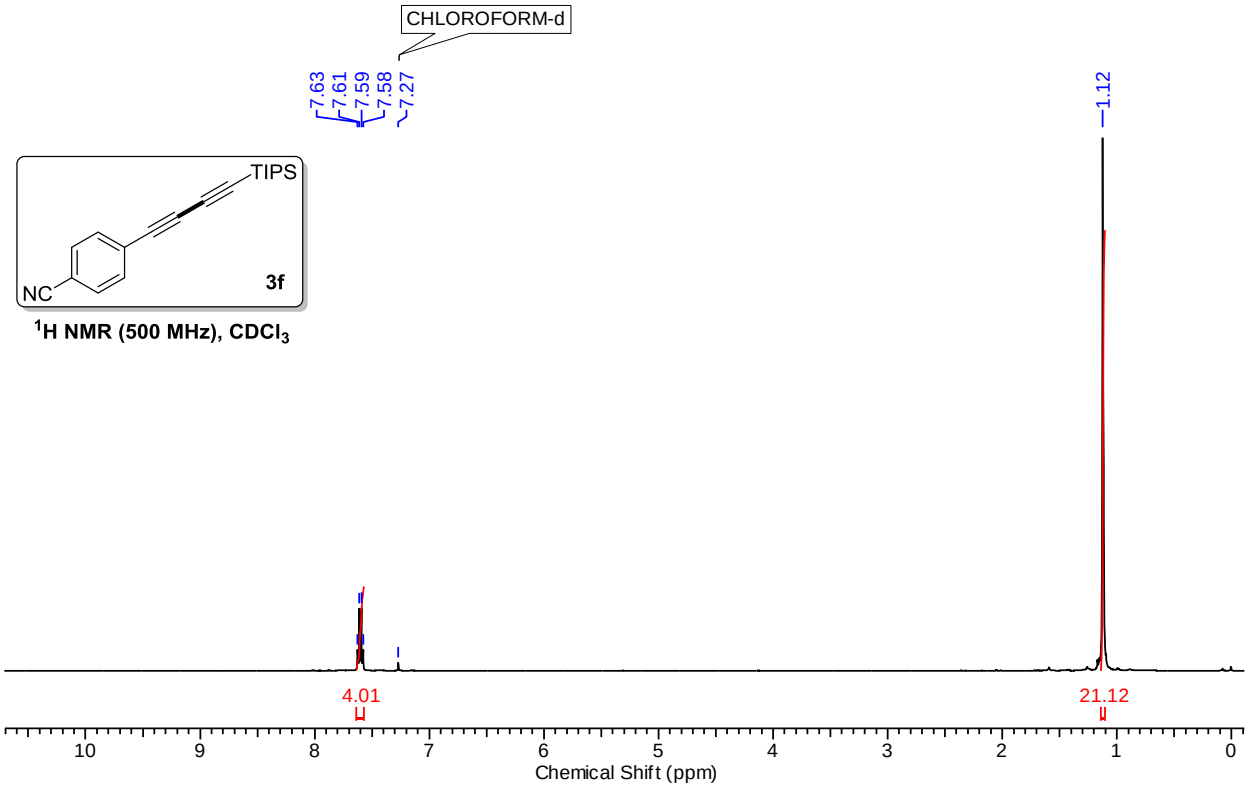
^{13}C NMR (125 MHz), $CDCl_3$



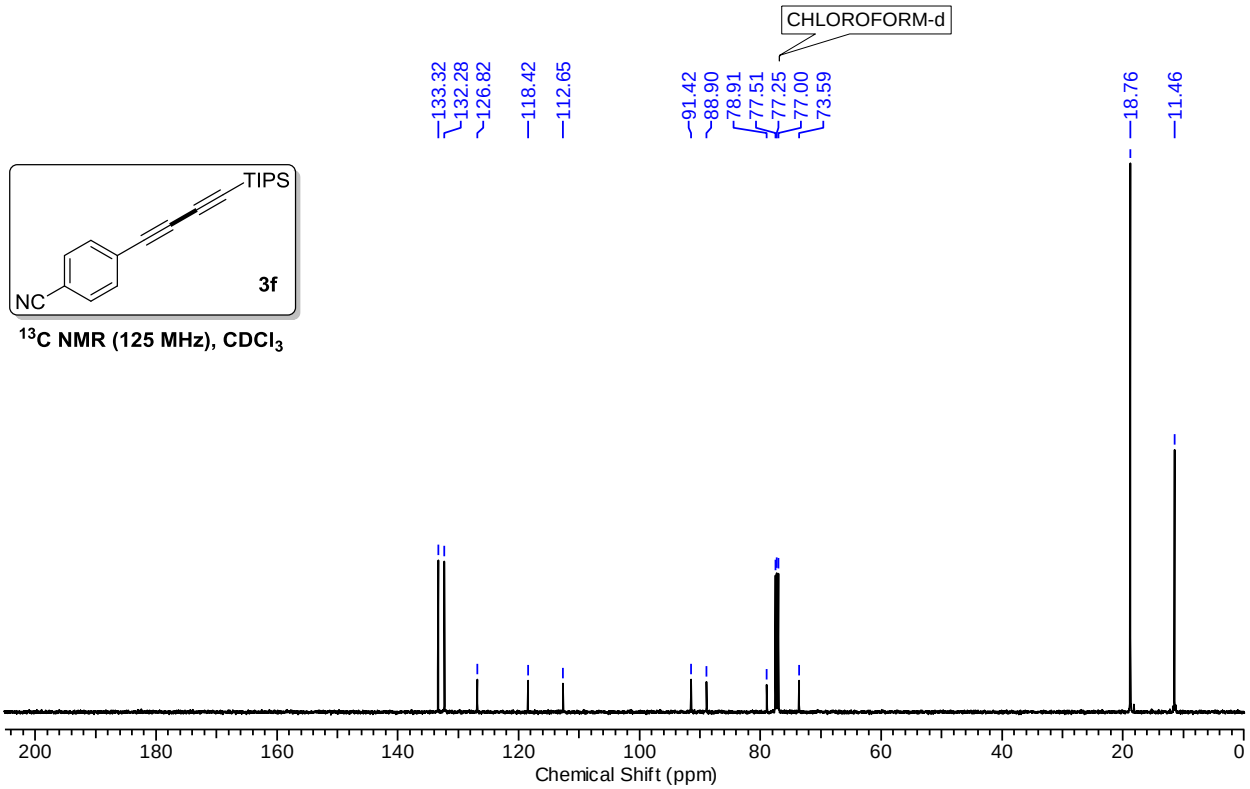
^{1}H NMR (500 MHz), $CDCl_3$



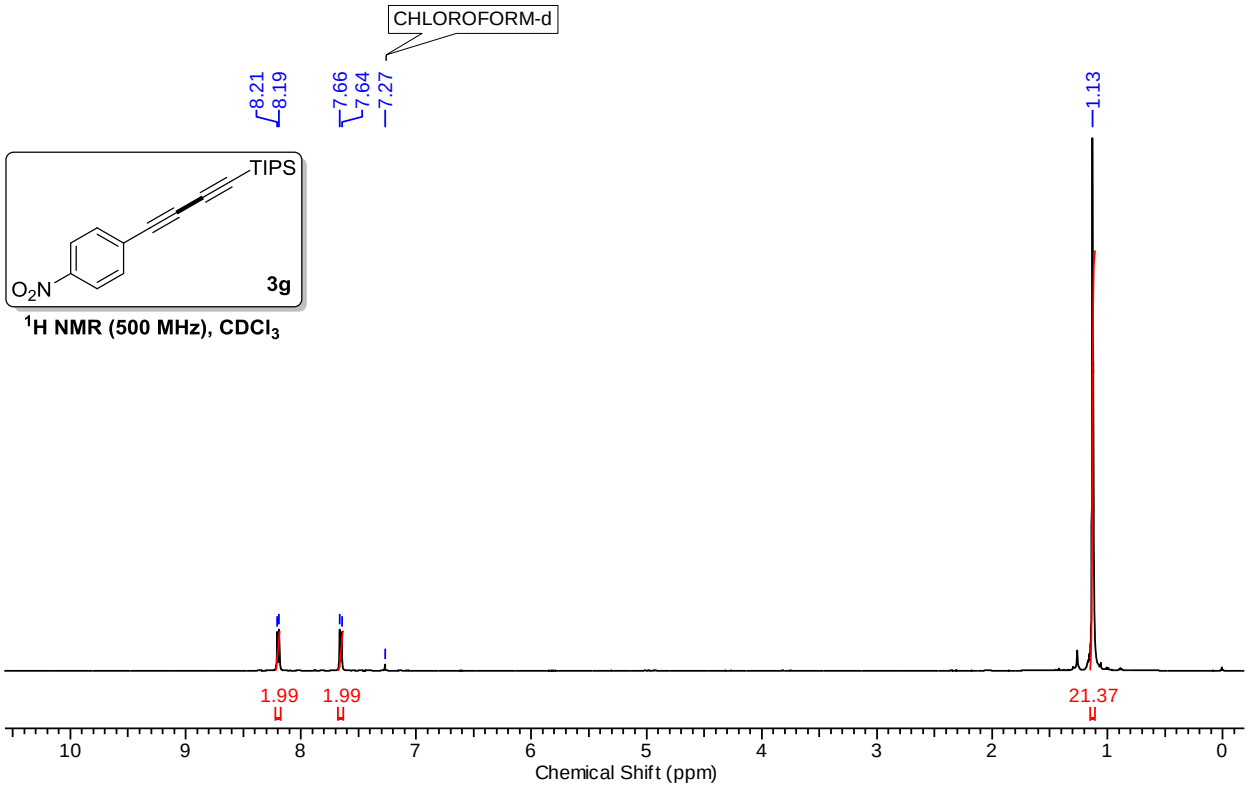
^{13}C NMR (125 MHz), $CDCl_3$

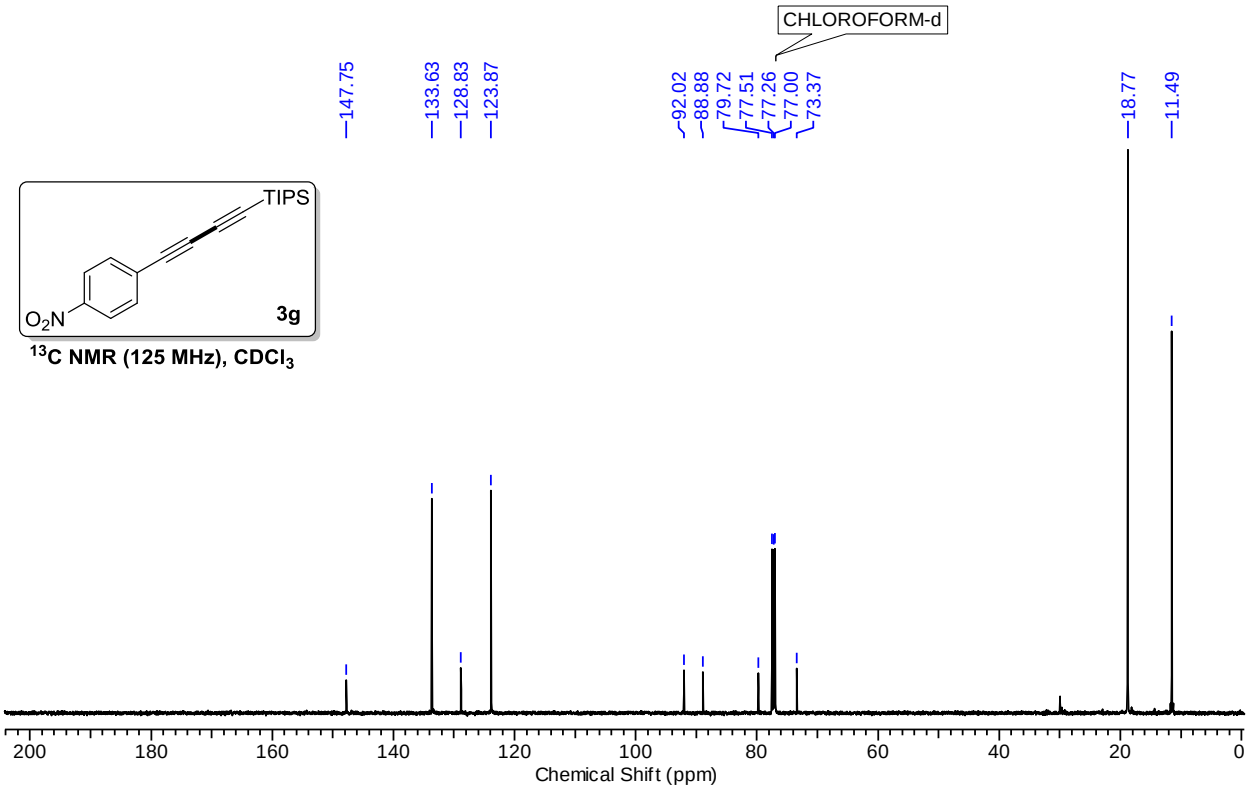


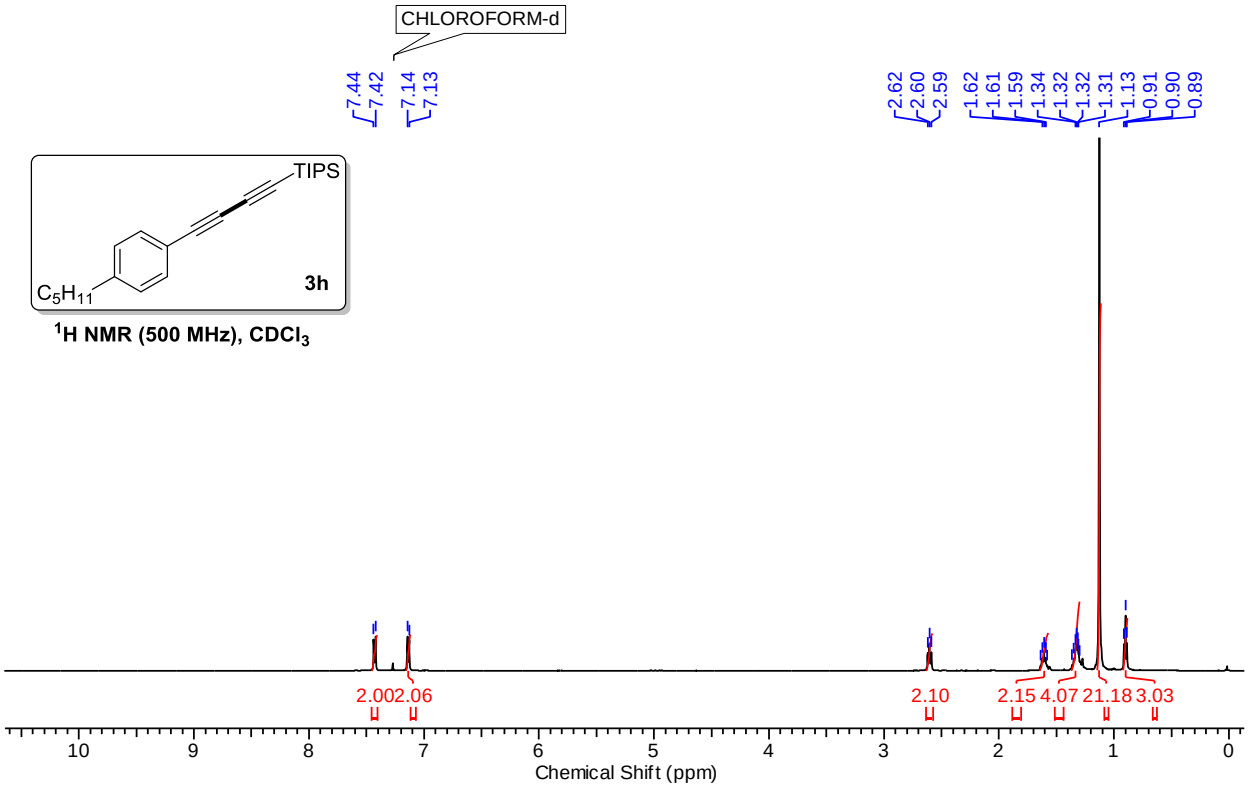
^{1}H NMR (500 MHz), $CDCl_3$



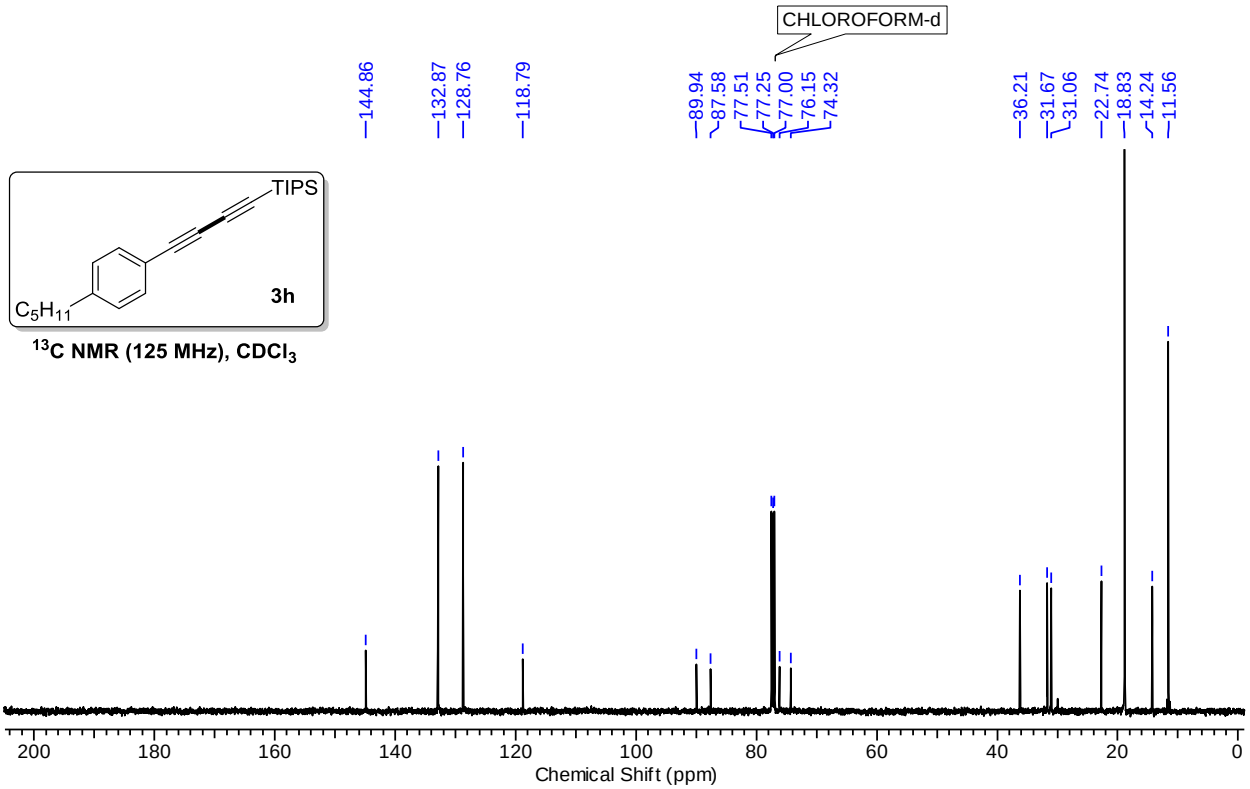
^{13}C NMR (125 MHz), $CDCl_3$


CHLOROFORM-d
8.21
8.19
7.66
7.64
7.27
1.13
TIPS
O2N
3g
1H NMR (500 MHz), CDCl3
1.99
1.99
21.37
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

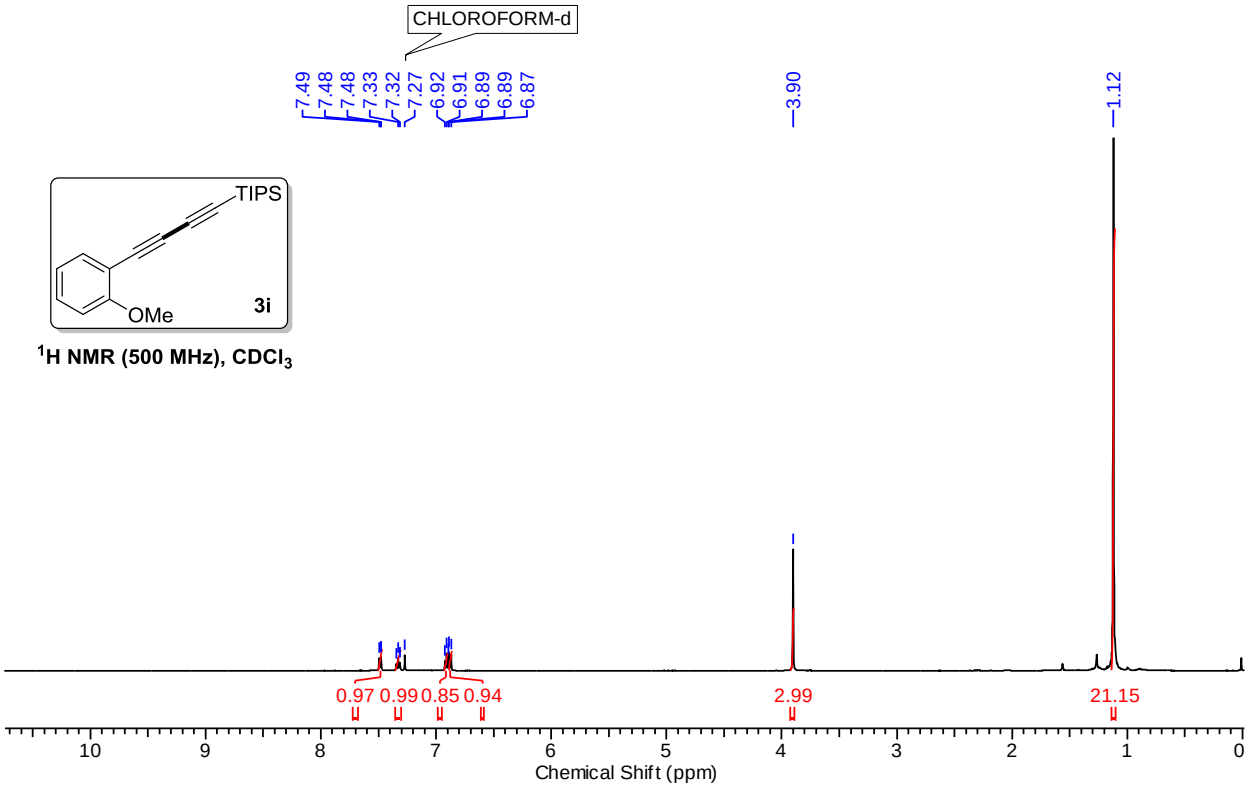

CHLOROFORM-d
147.75
133.63
128.83
123.87
92.02
88.88
79.72
77.51
77.26
77.00
73.37
18.77
11.49
TIPS
O2N
3g
13C NMR (125 MHz), CDCl3
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)



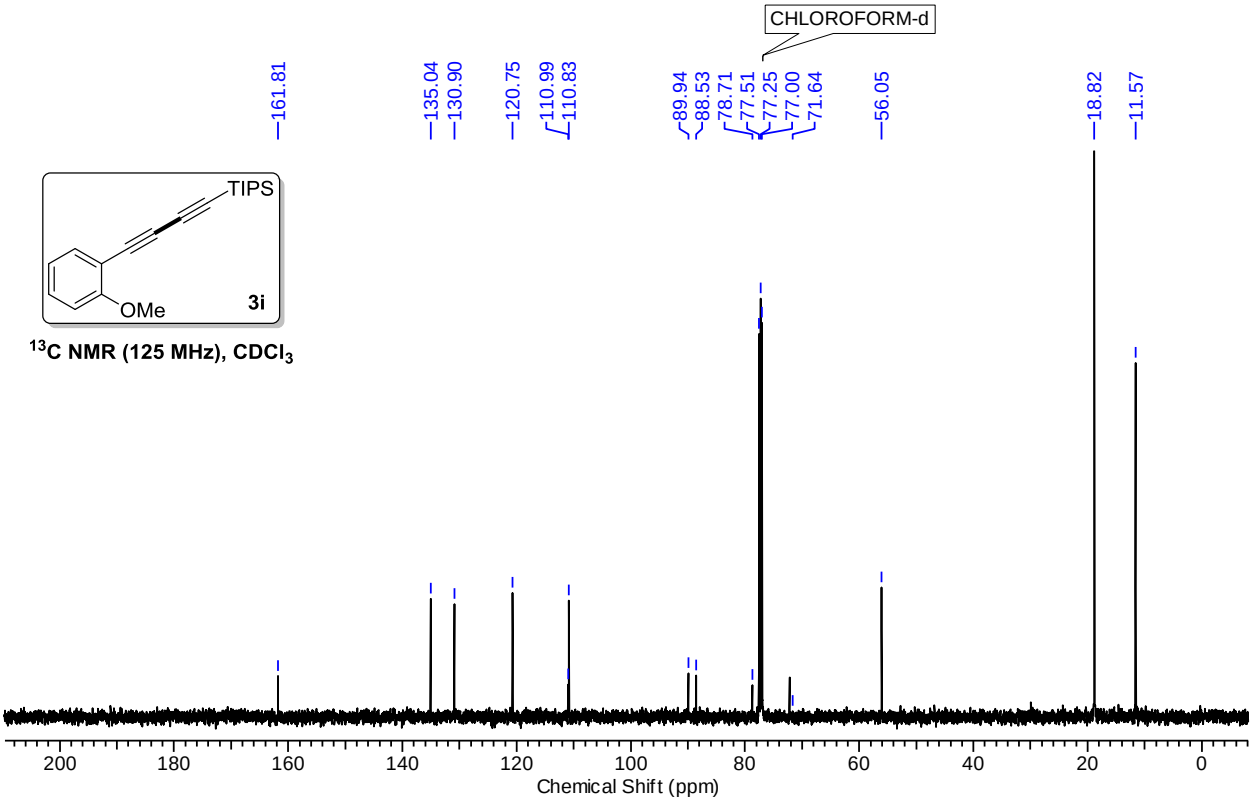
^{1}H NMR (500 MHz), $CDCl_3$



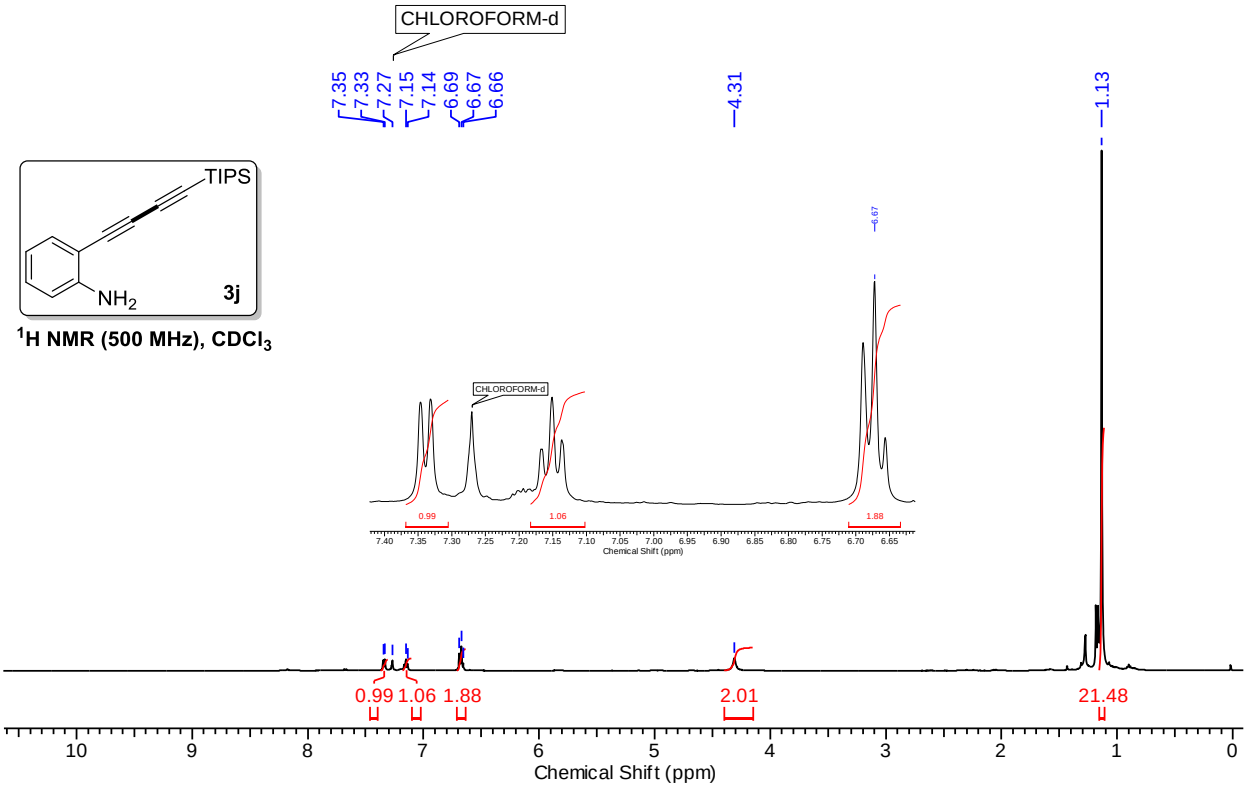
^{13}C NMR (125 MHz), $CDCl_3$



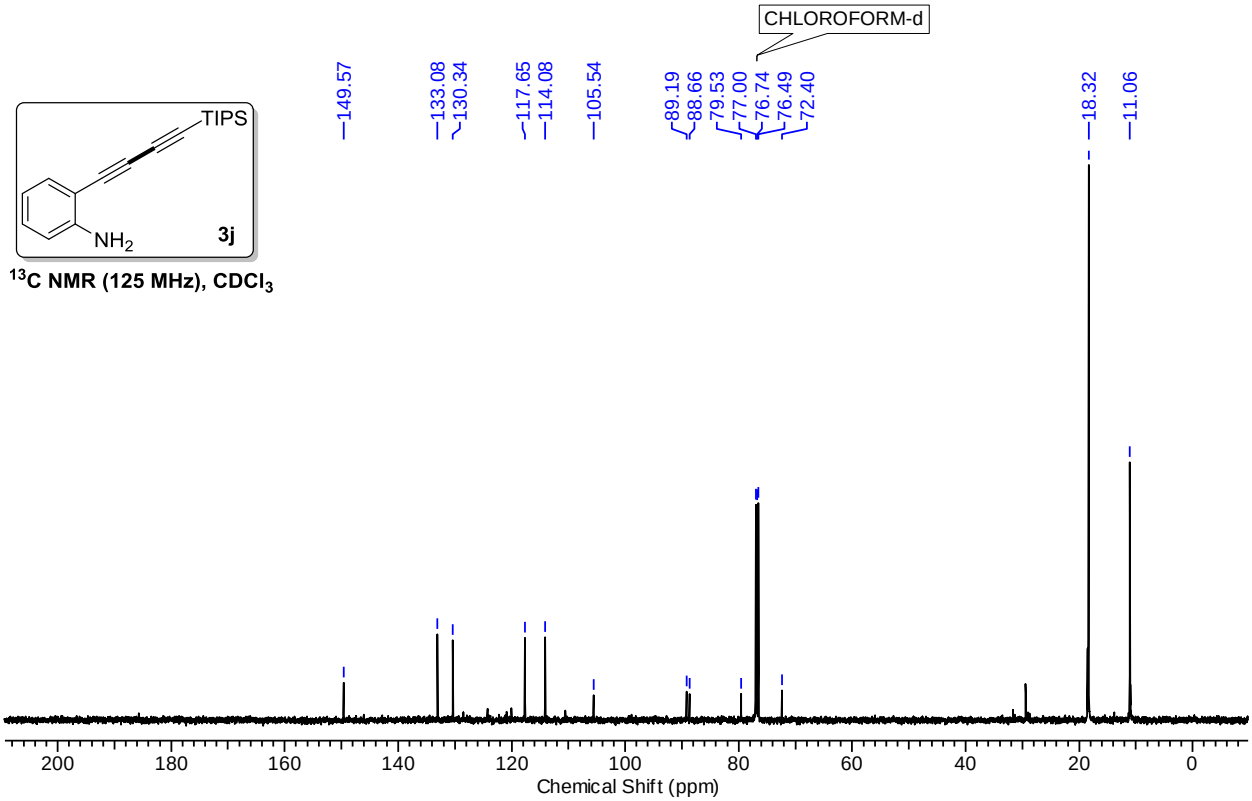
^{1}H NMR (500 MHz), $CDCl_3$



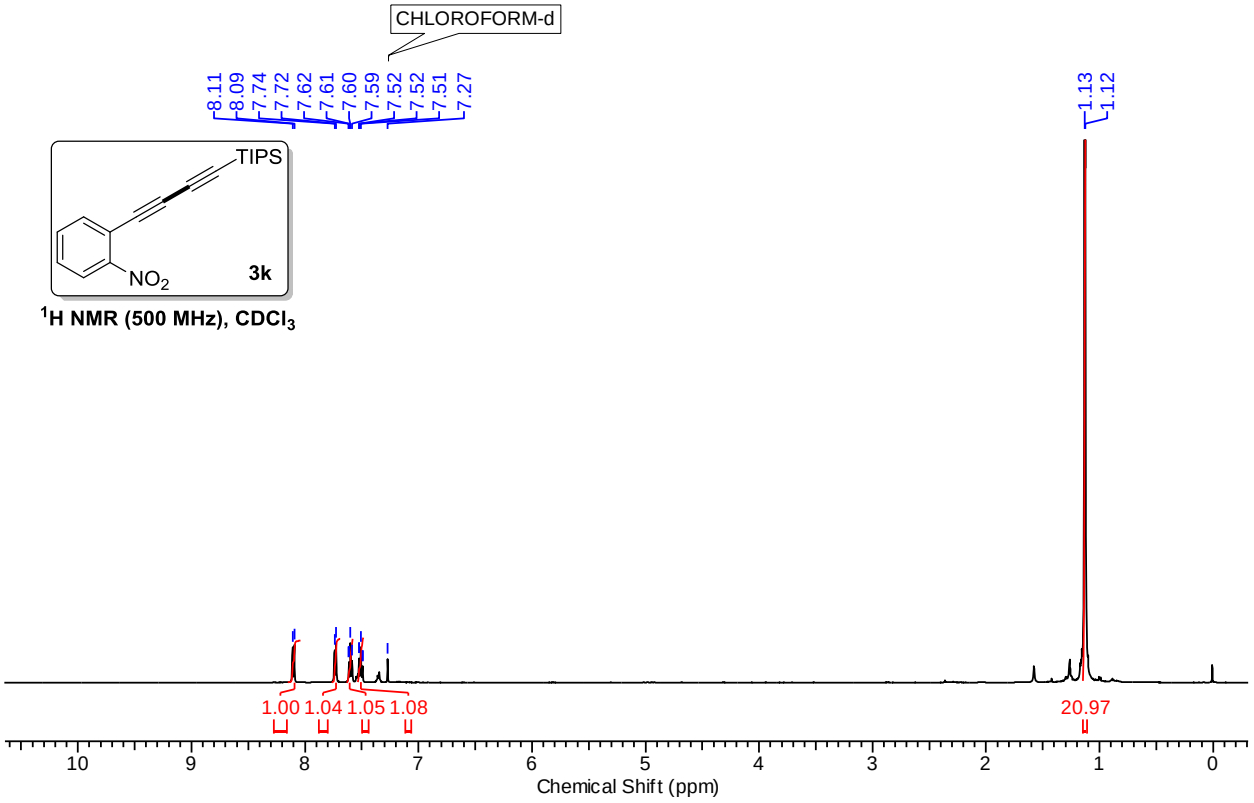
^{13}C NMR (125 MHz), $CDCl_3$



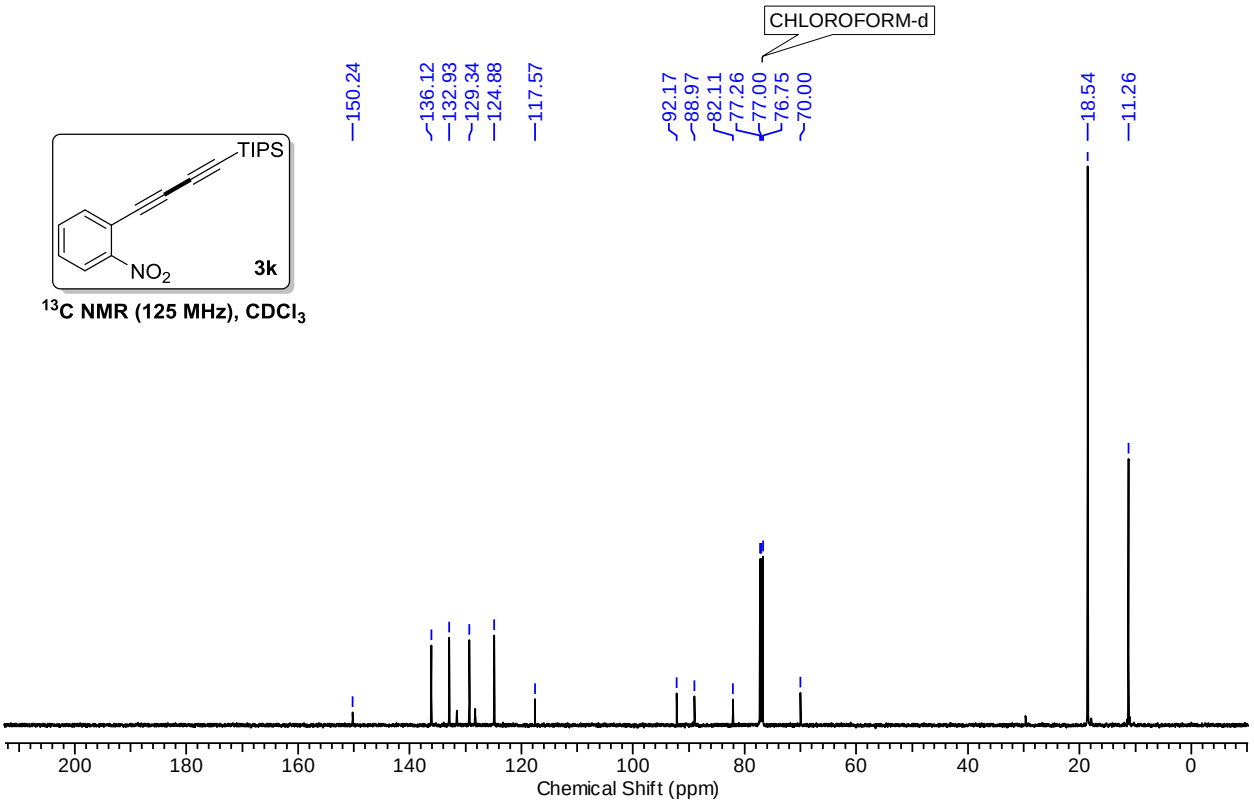
^{1}H NMR (500 MHz), $CDCl_3$



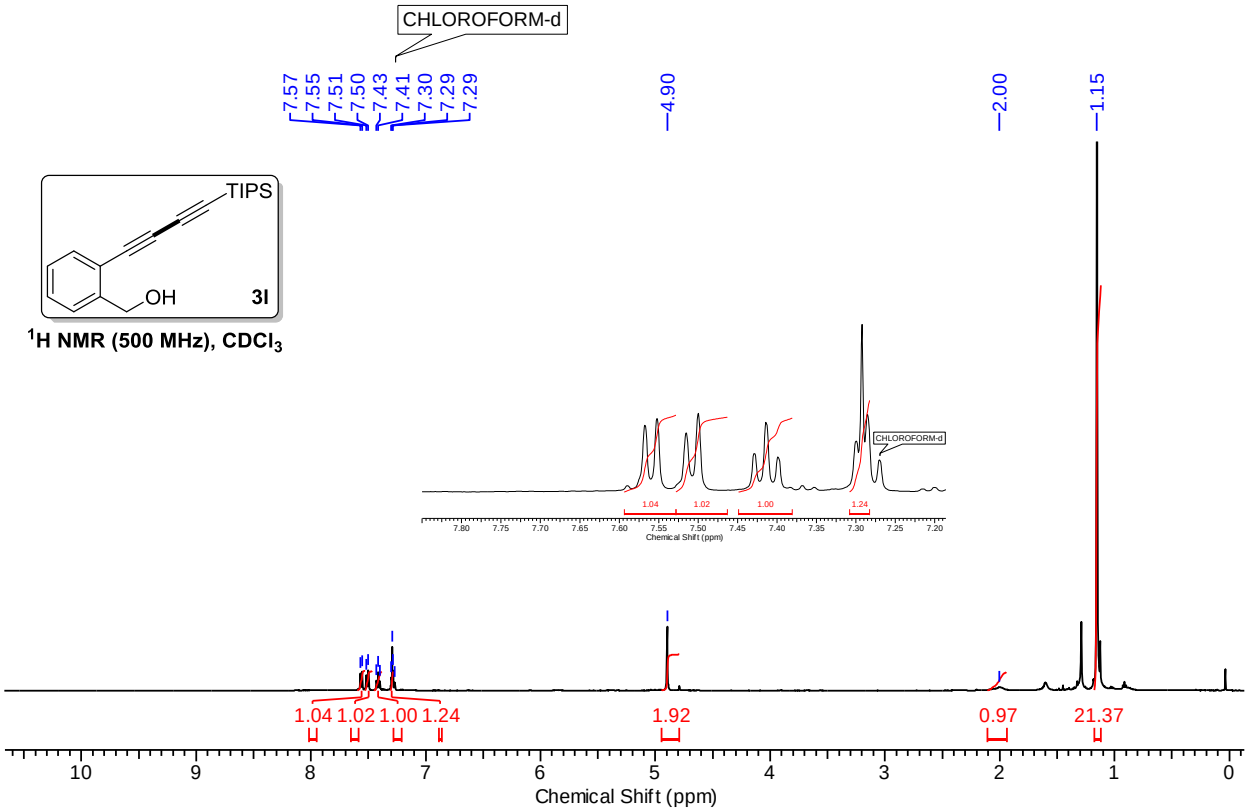
^{13}C NMR (125 MHz), $CDCl_3$



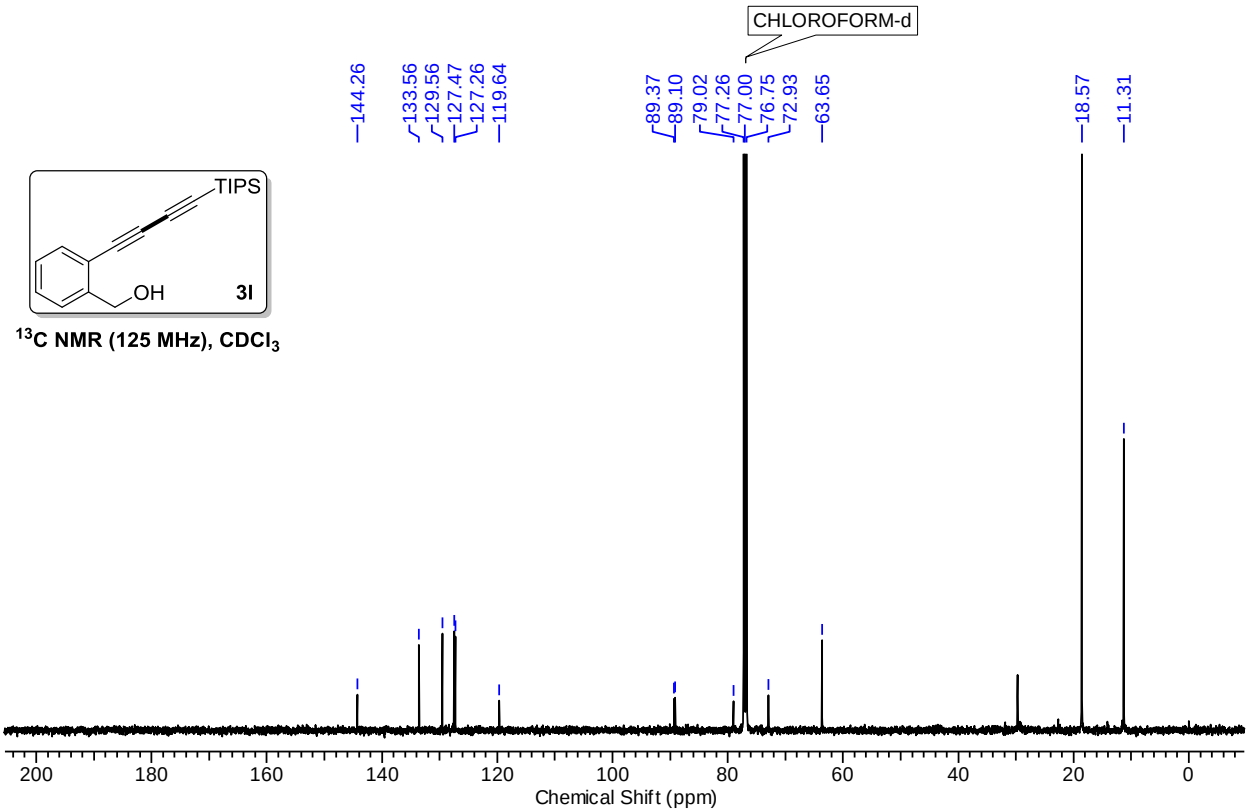
^{1}H NMR (500 MHz), $CDCl_3$



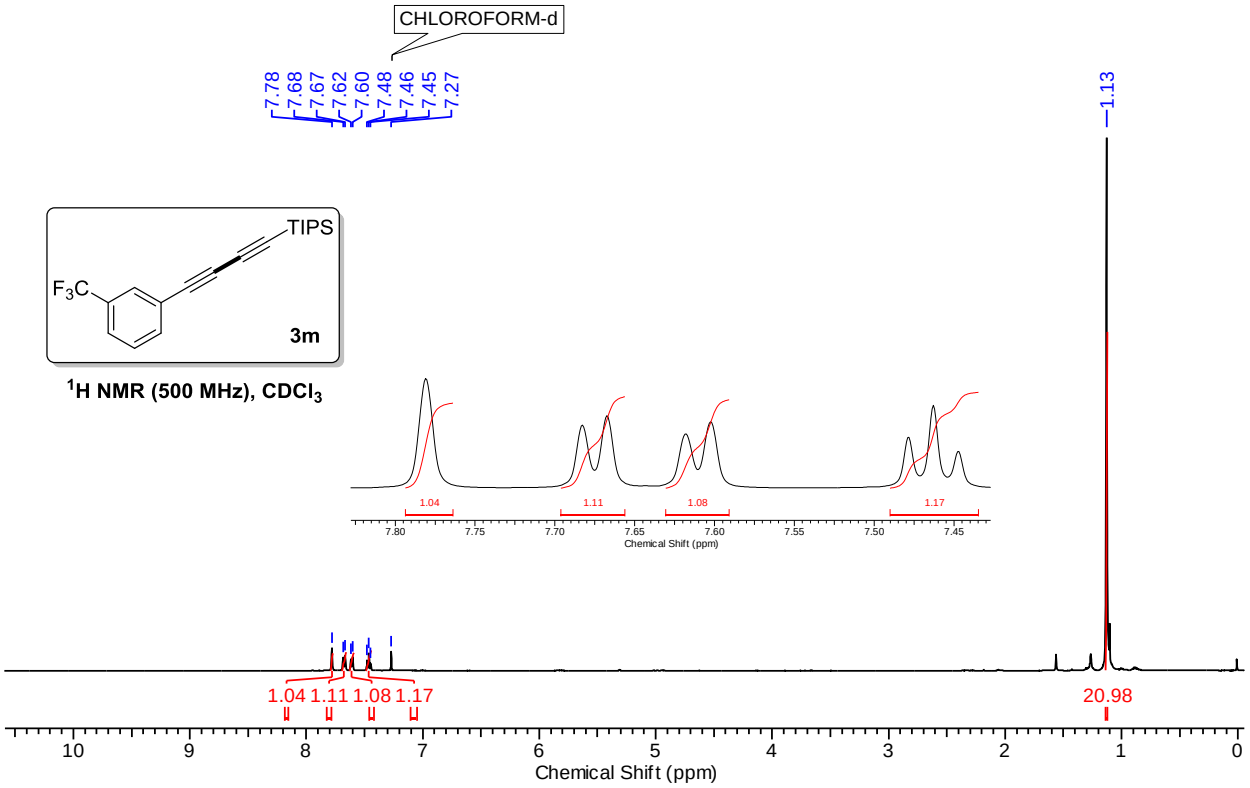
^{13}C NMR (125 MHz), $CDCl_3$

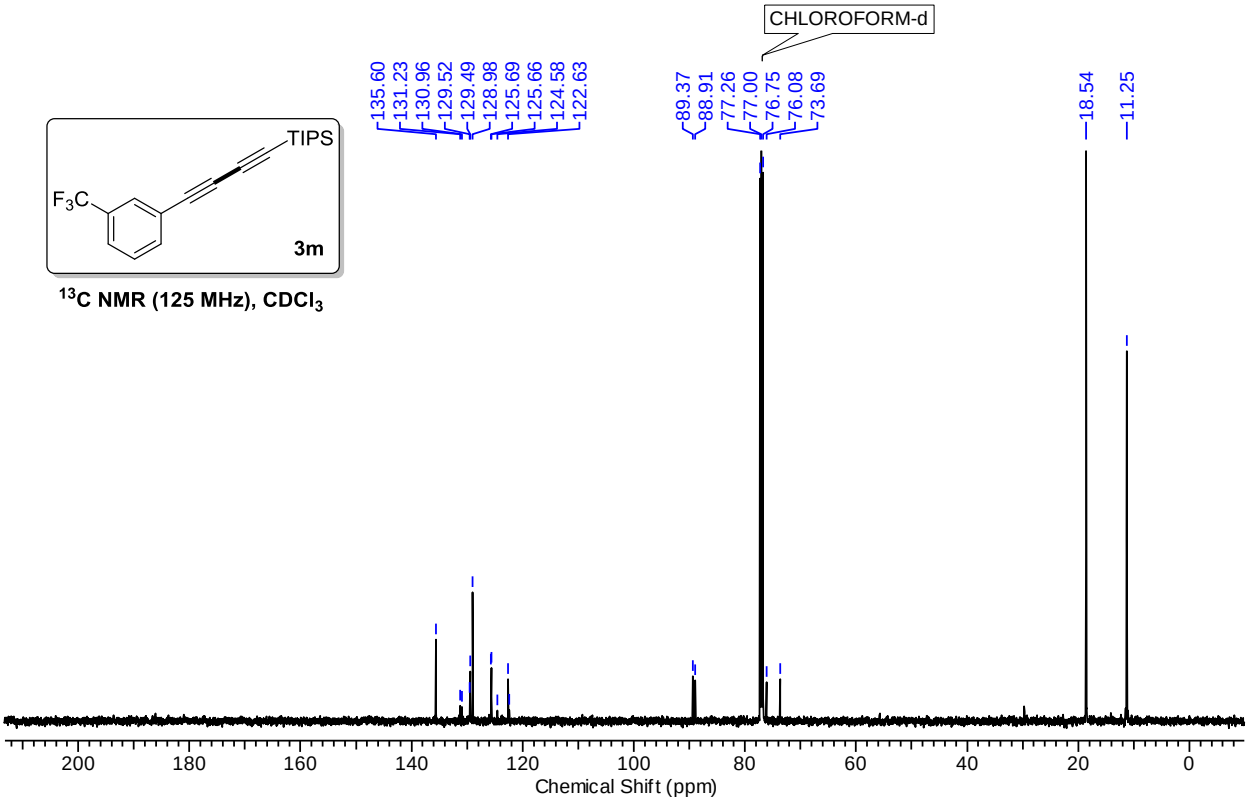


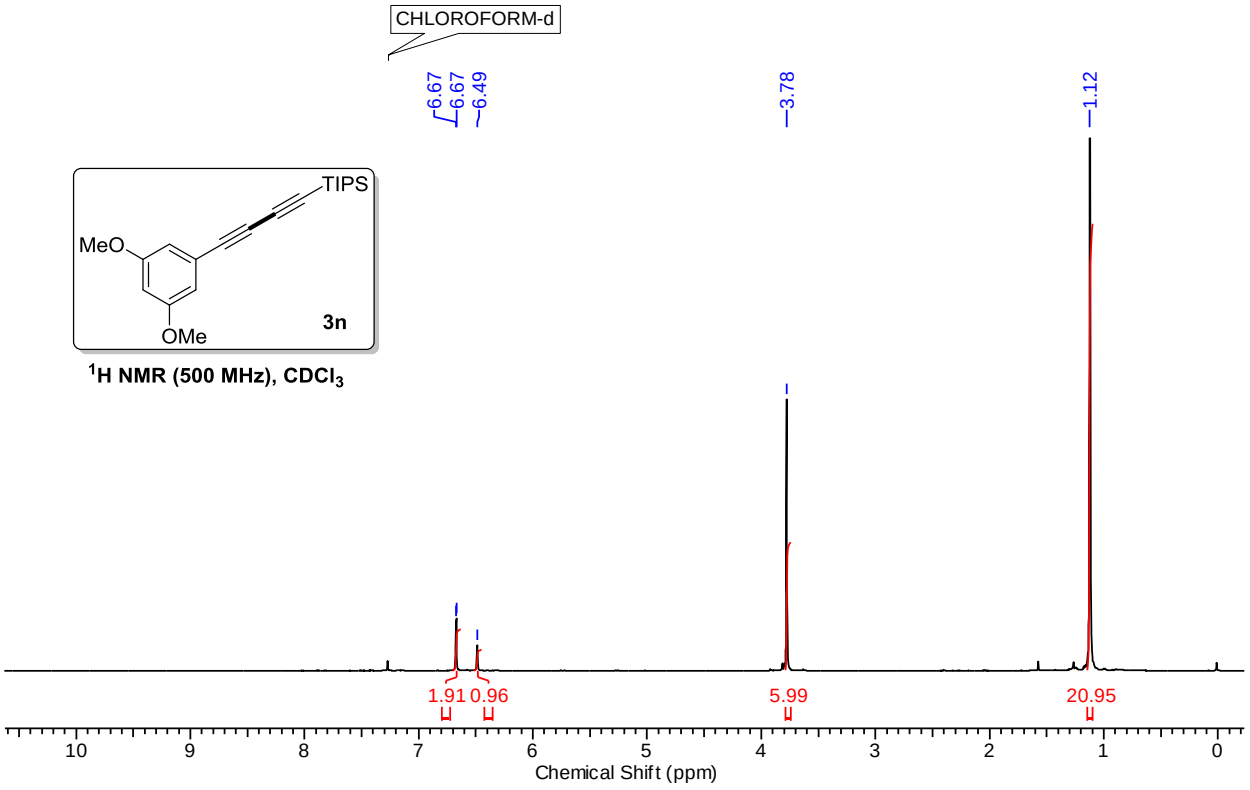
^{1}H NMR (500 MHz), $CDCl_3$



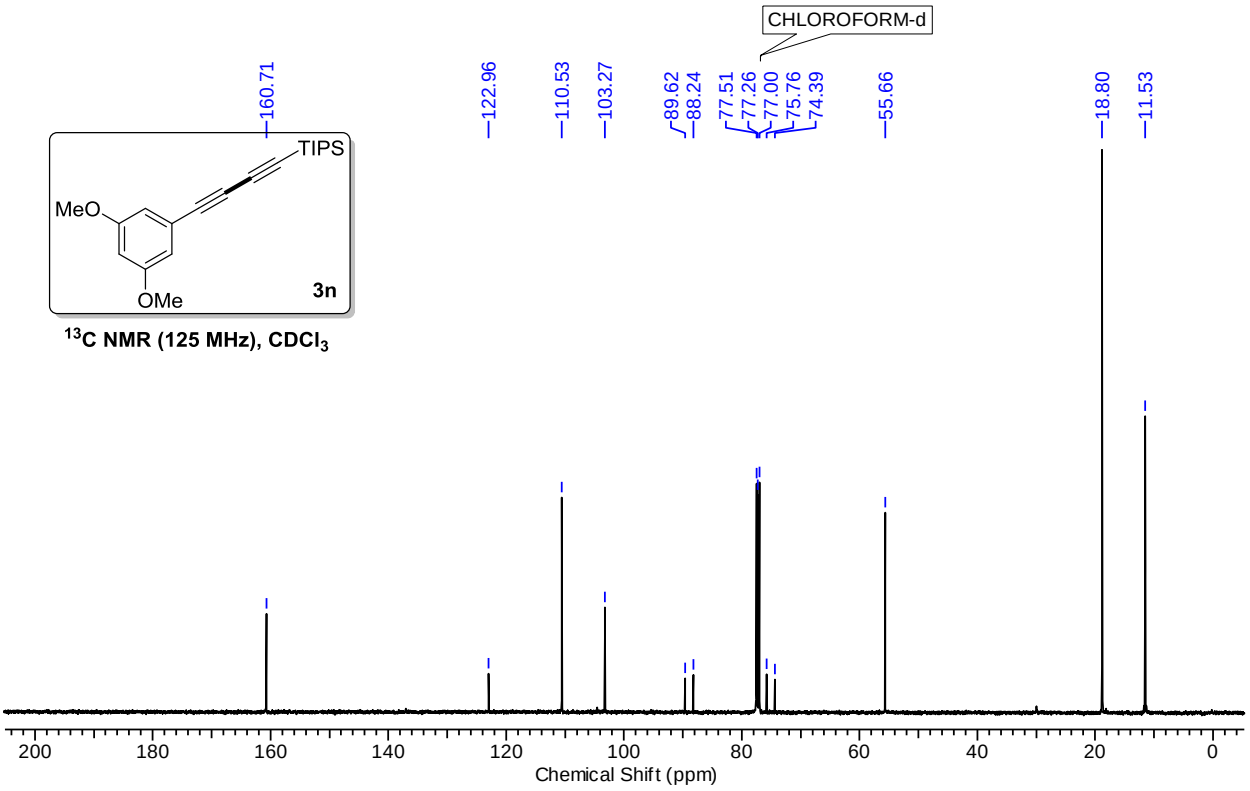
^{13}C NMR (125 MHz), $CDCl_3$


CHLOROFORM-d
7.78
7.68
7.67
7.62
7.60
7.48
7.46
7.45
7.27
1.13
TIPS
F3C
3m
1H NMR (500 MHz), CDCl3
1.04
1.11
1.08
1.17
Chemical Shift (ppm)
1.04 1.11 1.08 1.17
20.98
Chemical Shift (ppm)

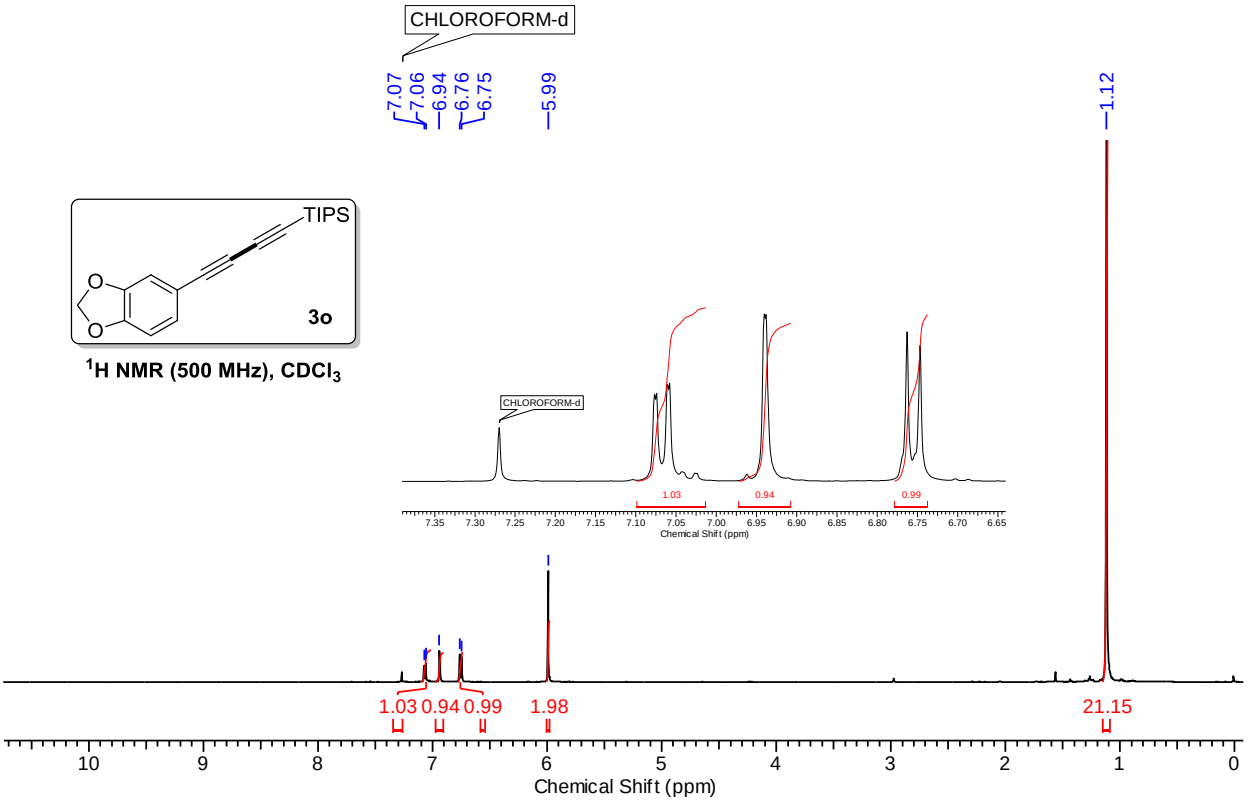

CHLOROFORM-d
135.60
131.23
130.96
129.52
129.49
128.98
125.69
125.66
124.58
122.63
89.37
88.91
77.26
77.00
76.75
76.08
73.69
18.54
11.25
TIPS
F3C
3m
13C NMR (125 MHz), CDCl3
Chemical Shift (ppm)

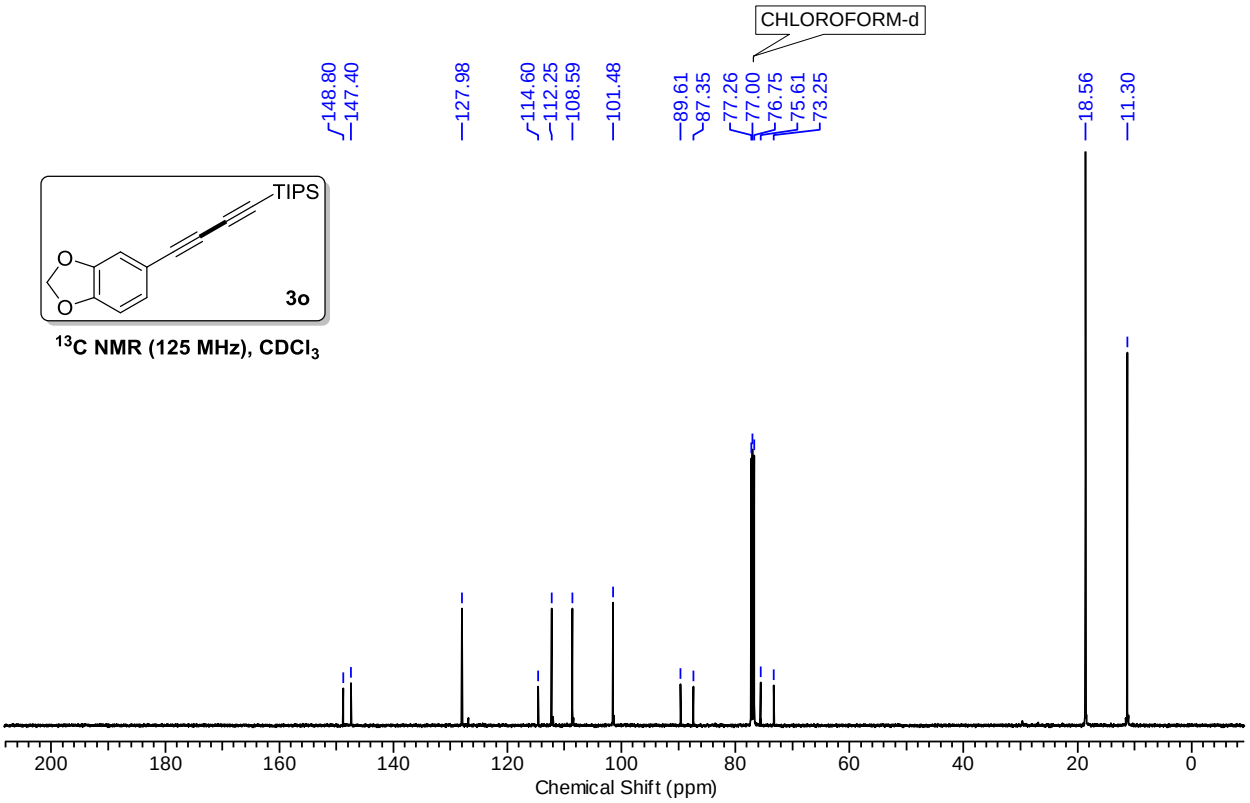


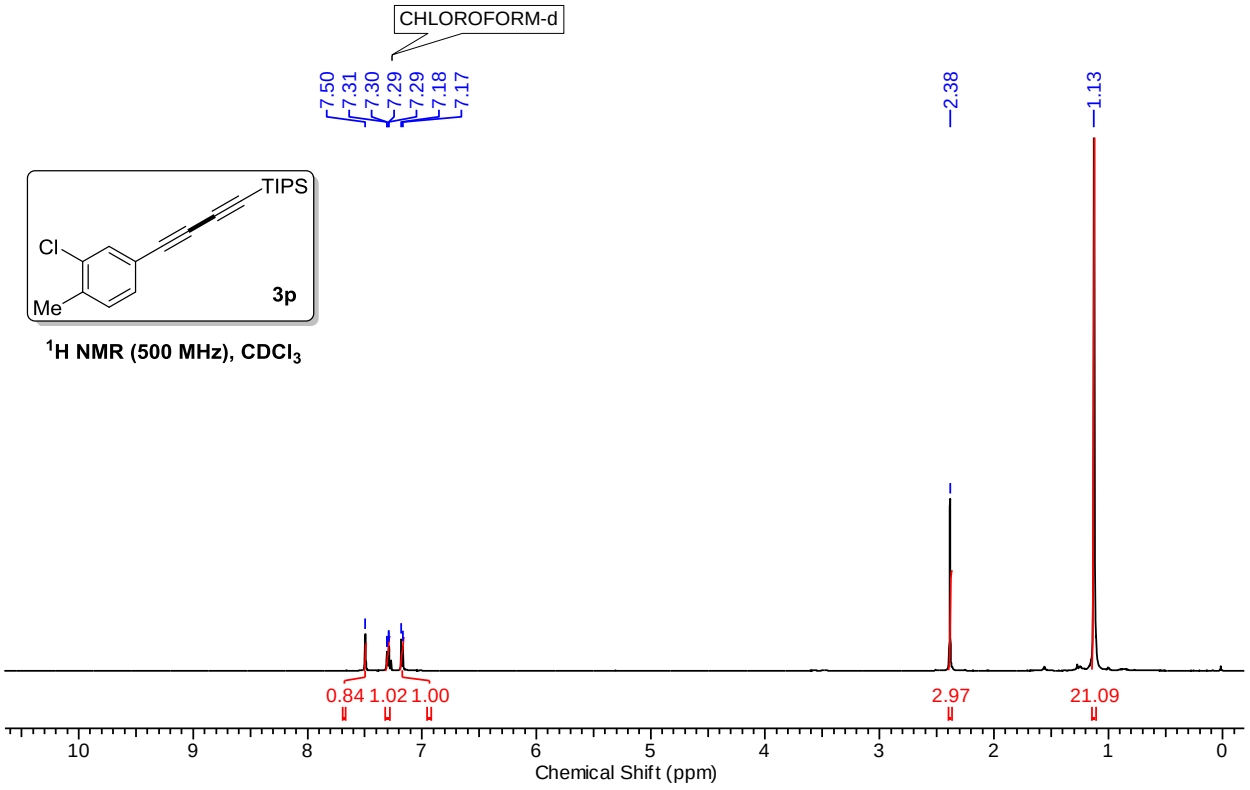
^{1}H NMR (500 MHz), $CDCl_3$



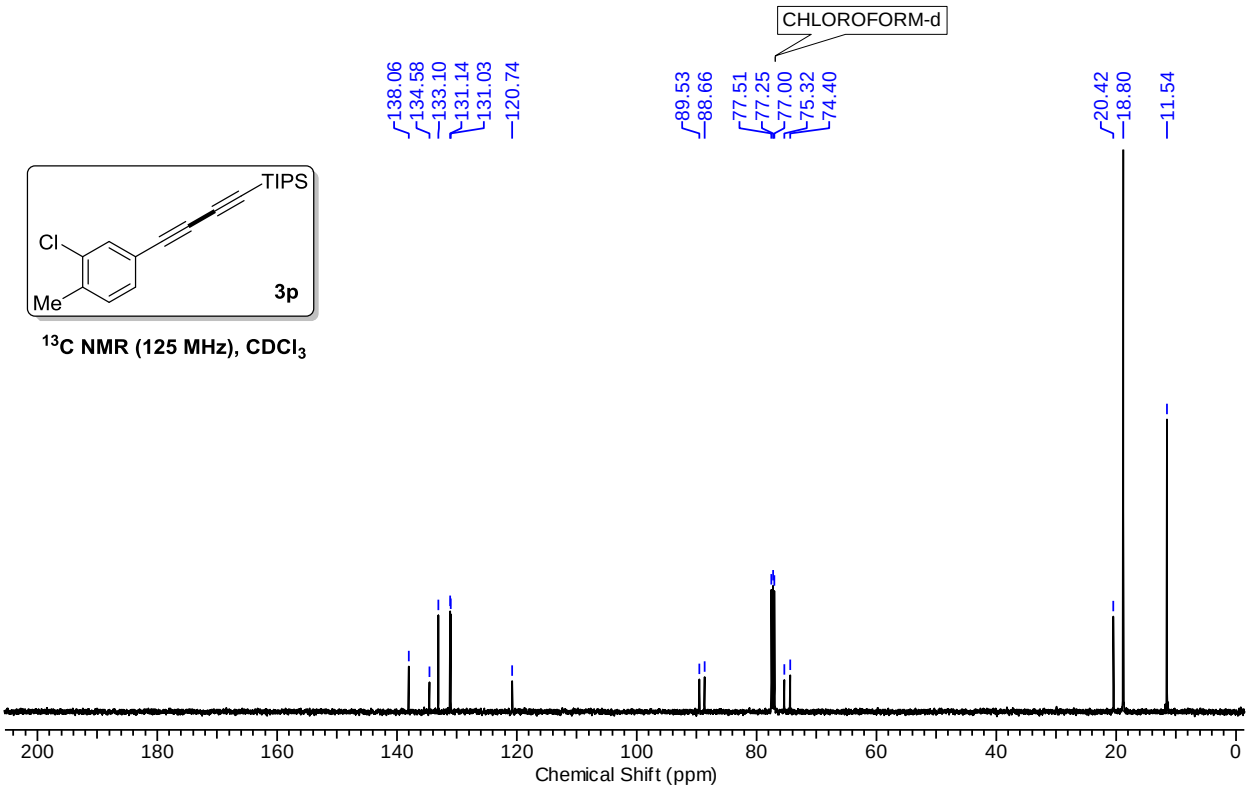
^{13}C NMR (125 MHz), $CDCl_3$


CHLOROFORM-d
7.07
7.06
6.94
6.76
6.75
5.99
1.12
TIPS
O
O
3o
1H NMR (500 MHz), CDCl3
CHLOROFORM-d
1.03
0.94
0.99
Chemical Shift (ppm)
1.03 0.94 0.99
1.98
21.15
Chemical Shift (ppm)

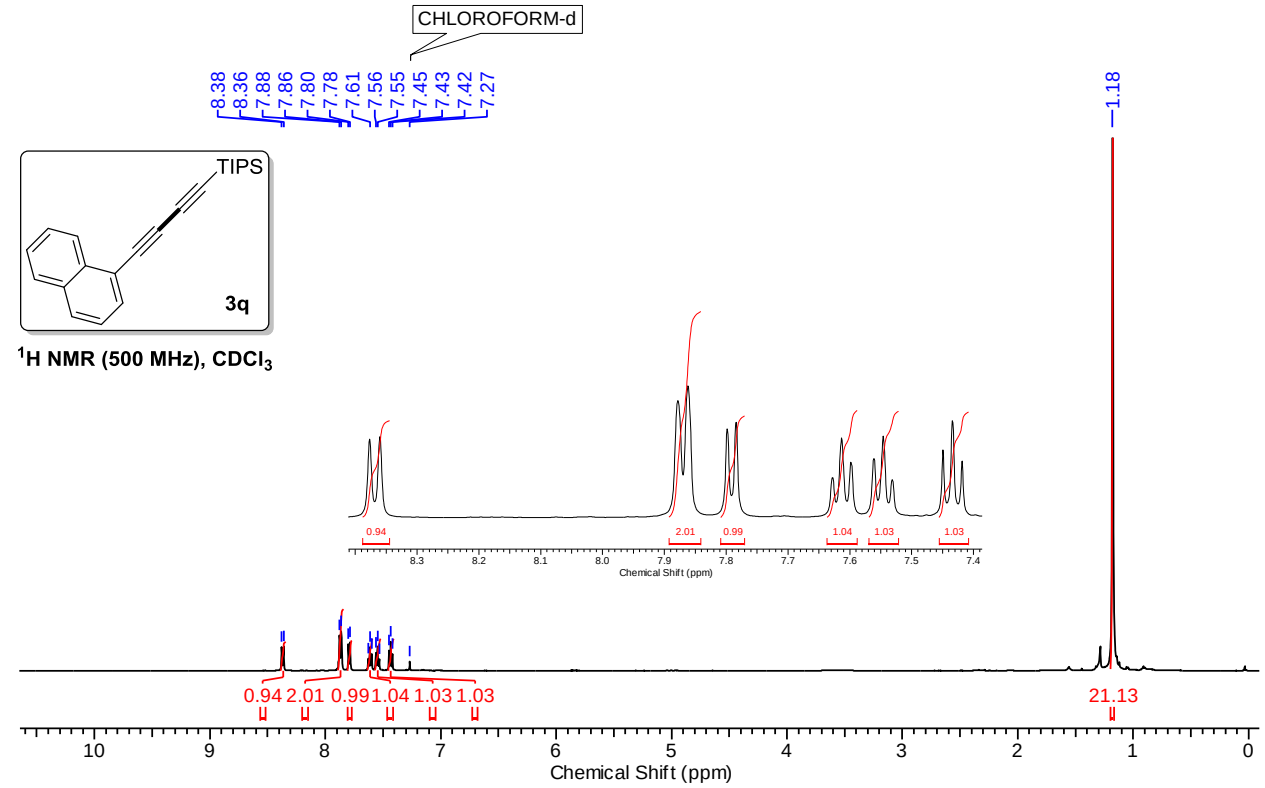

CHLOROFORM-d
148.80
147.40
127.98
114.60
112.25
108.59
101.48
89.61
87.35
77.26
77.00
76.75
75.61
73.25
18.56
11.30
TIPS
O
O
3o
13C NMR (125 MHz), CDCl3
Chemical Shift (ppm)



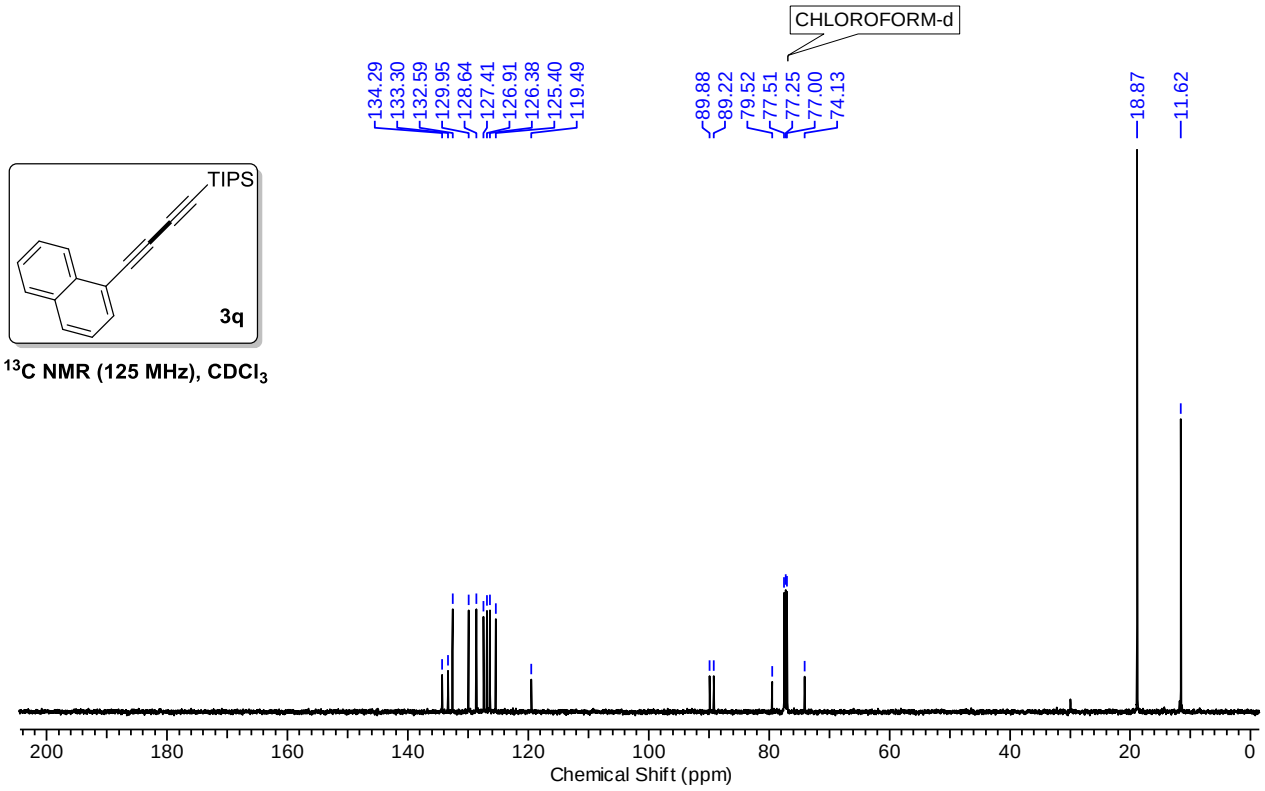
^{1}H NMR (500 MHz), $CDCl_3$



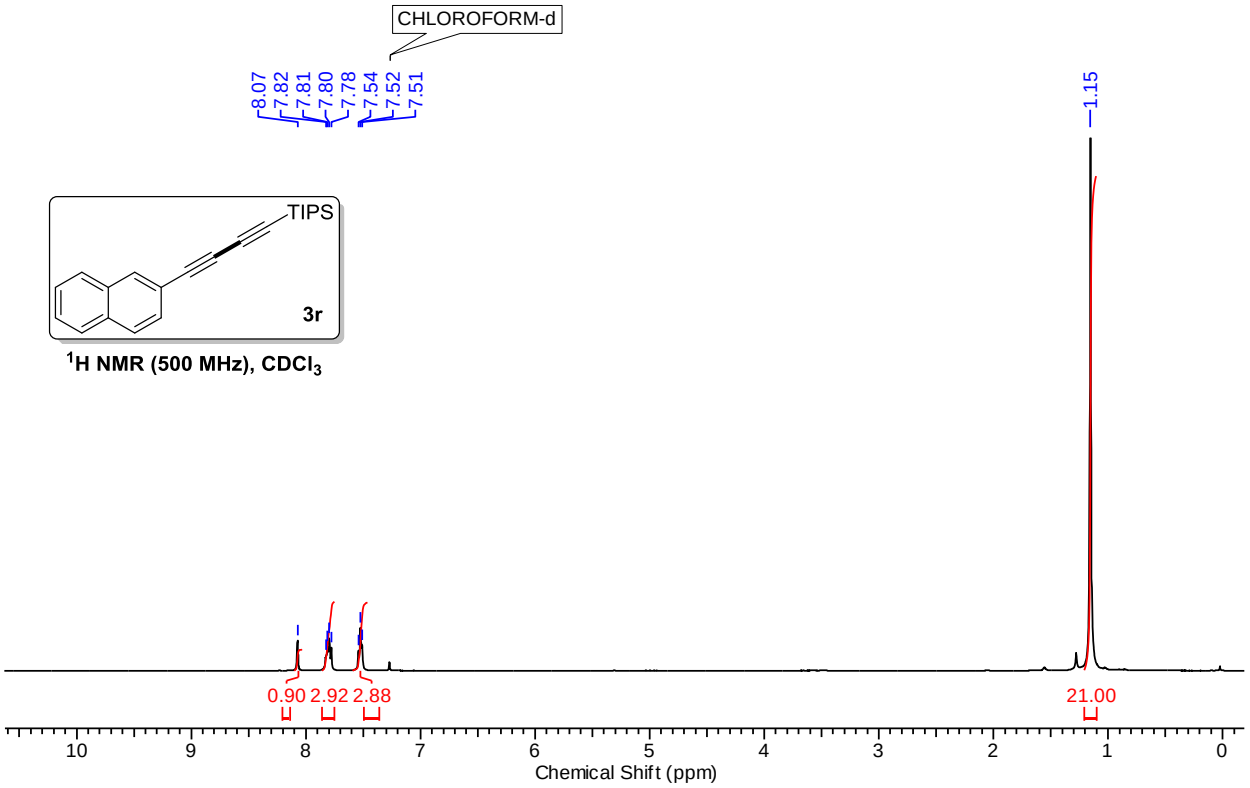
^{13}C NMR (125 MHz), $CDCl_3$



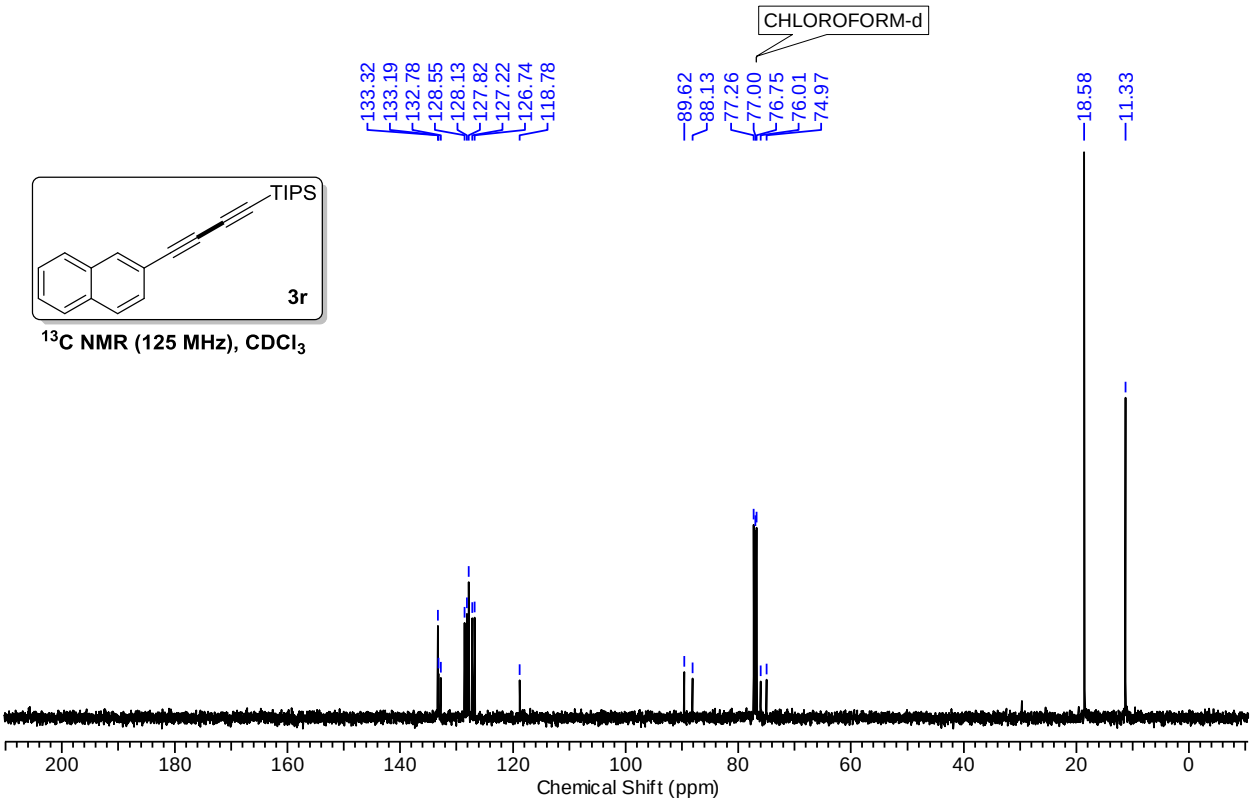
^{1}H NMR (500 MHz), $CDCl_3$



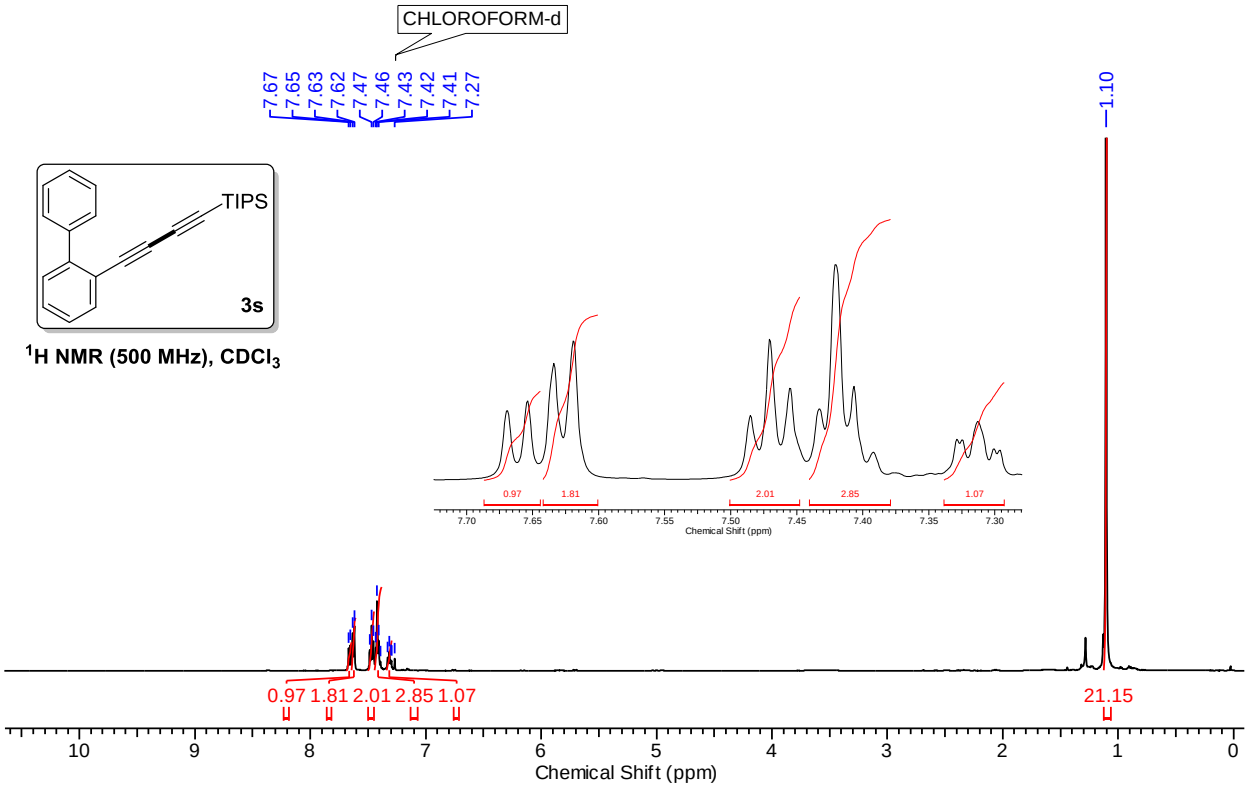
^{13}C NMR (125 MHz), $CDCl_3$



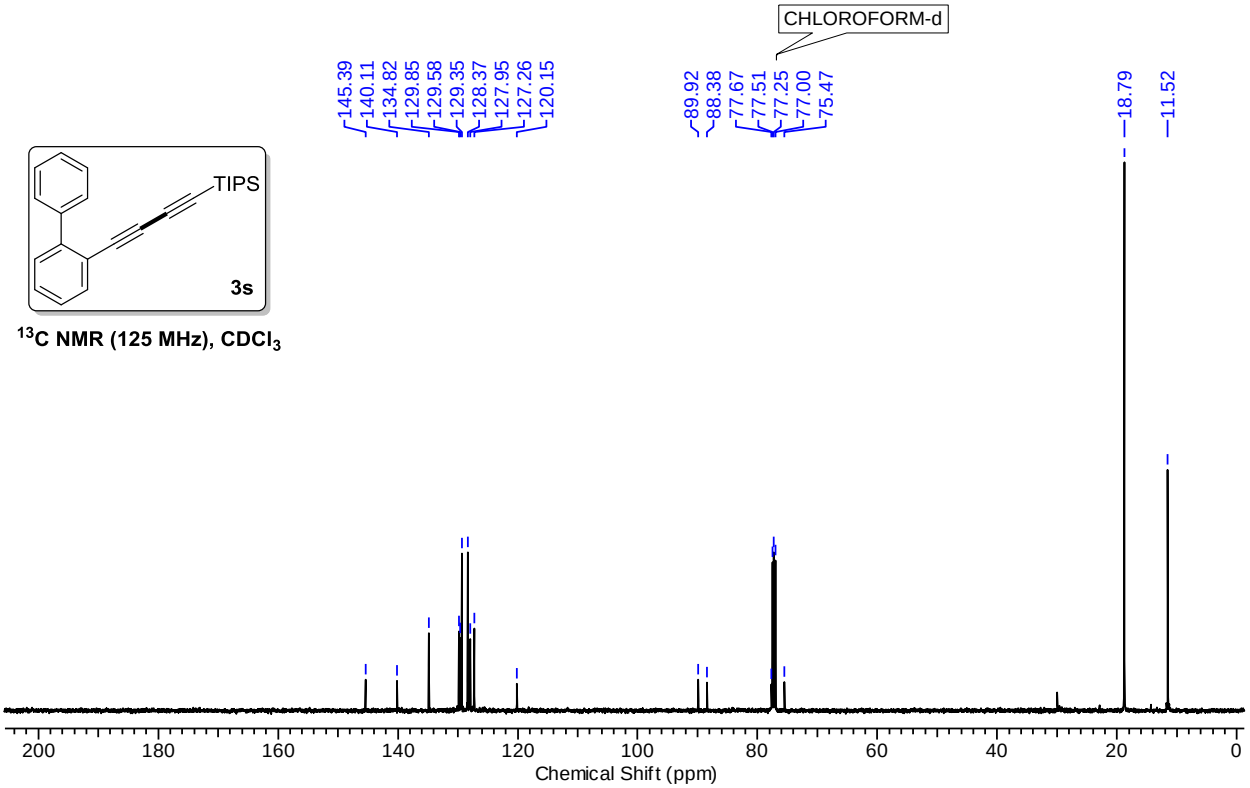
^{1}H NMR (500 MHz), $CDCl_3$



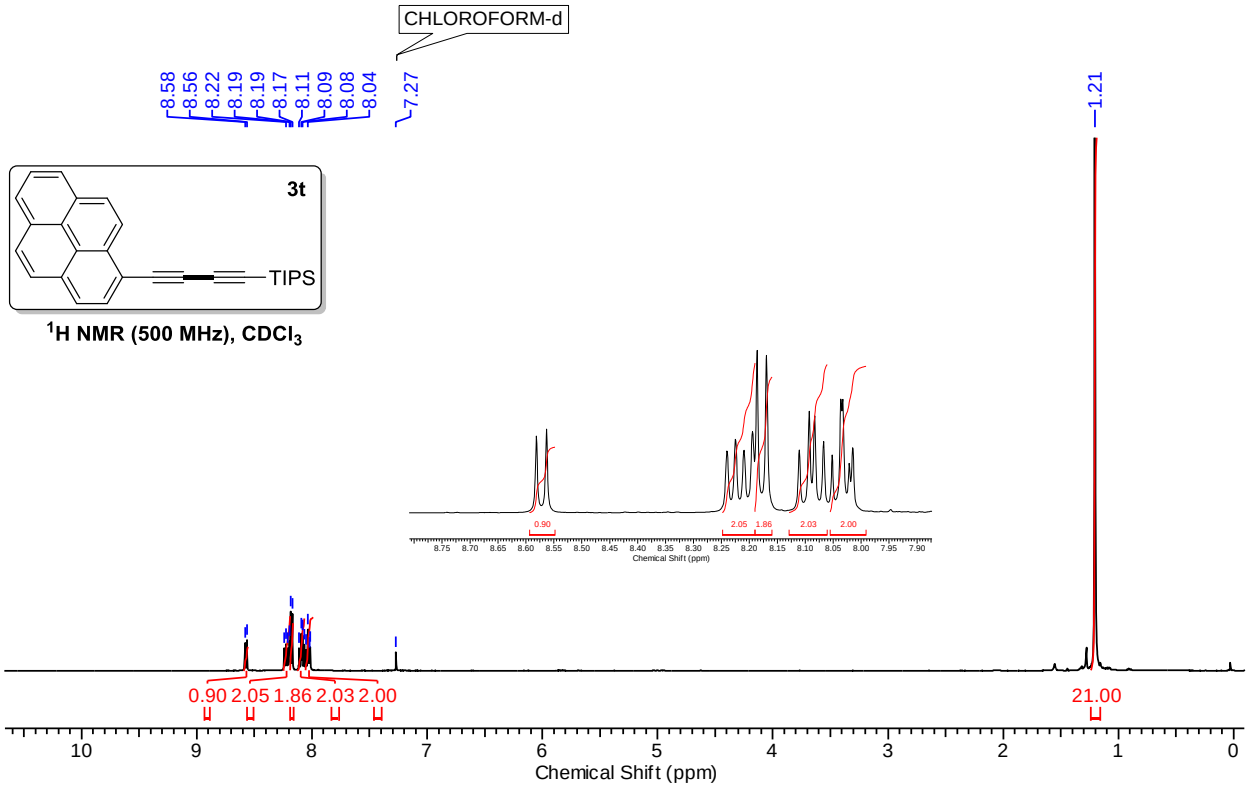
^{13}C NMR (125 MHz), $CDCl_3$



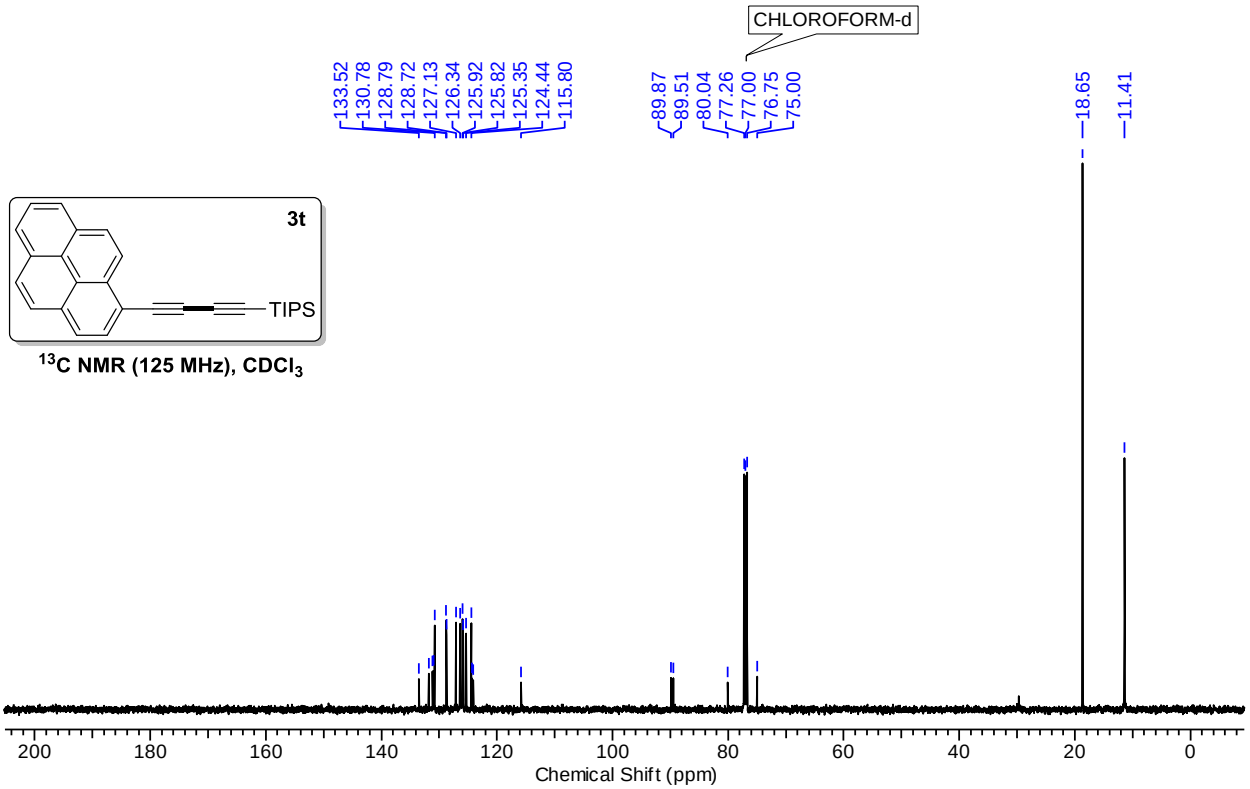
^{1}H NMR (500 MHz), $CDCl_3$



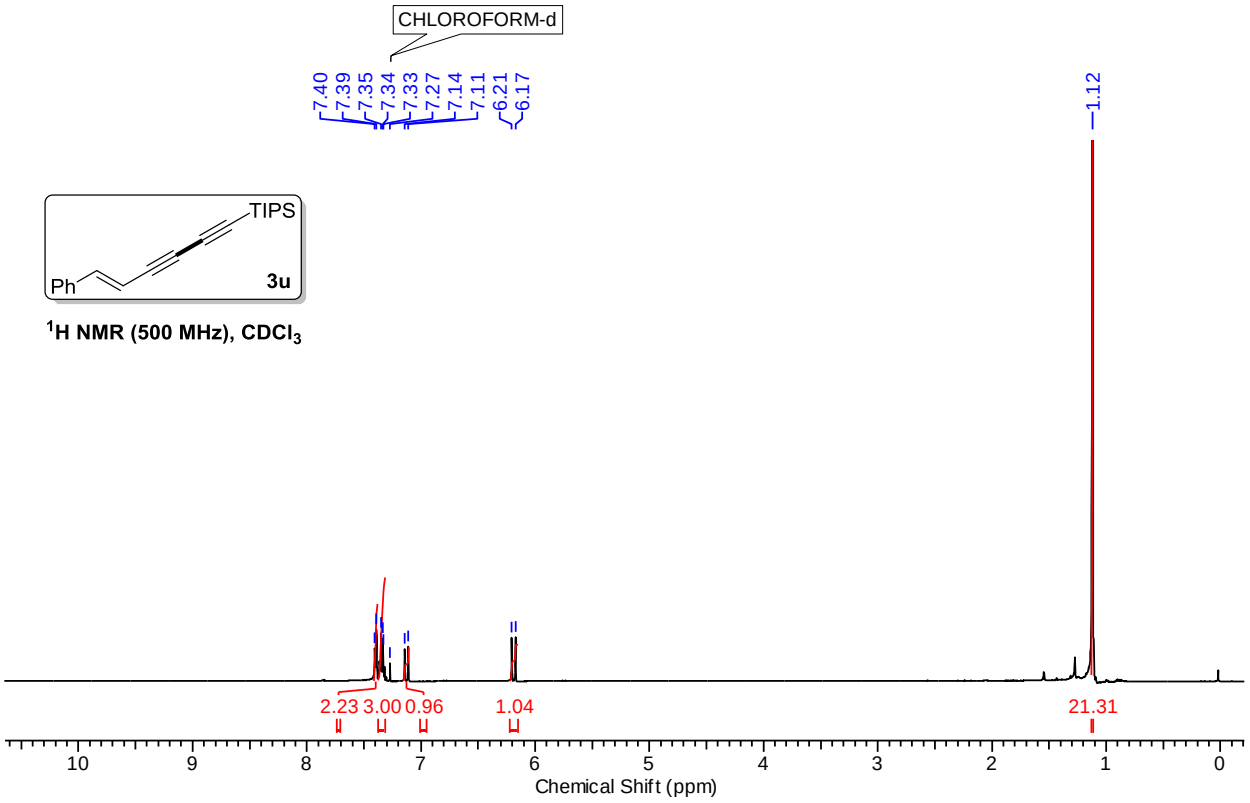
^{13}C NMR (125 MHz), $CDCl_3$



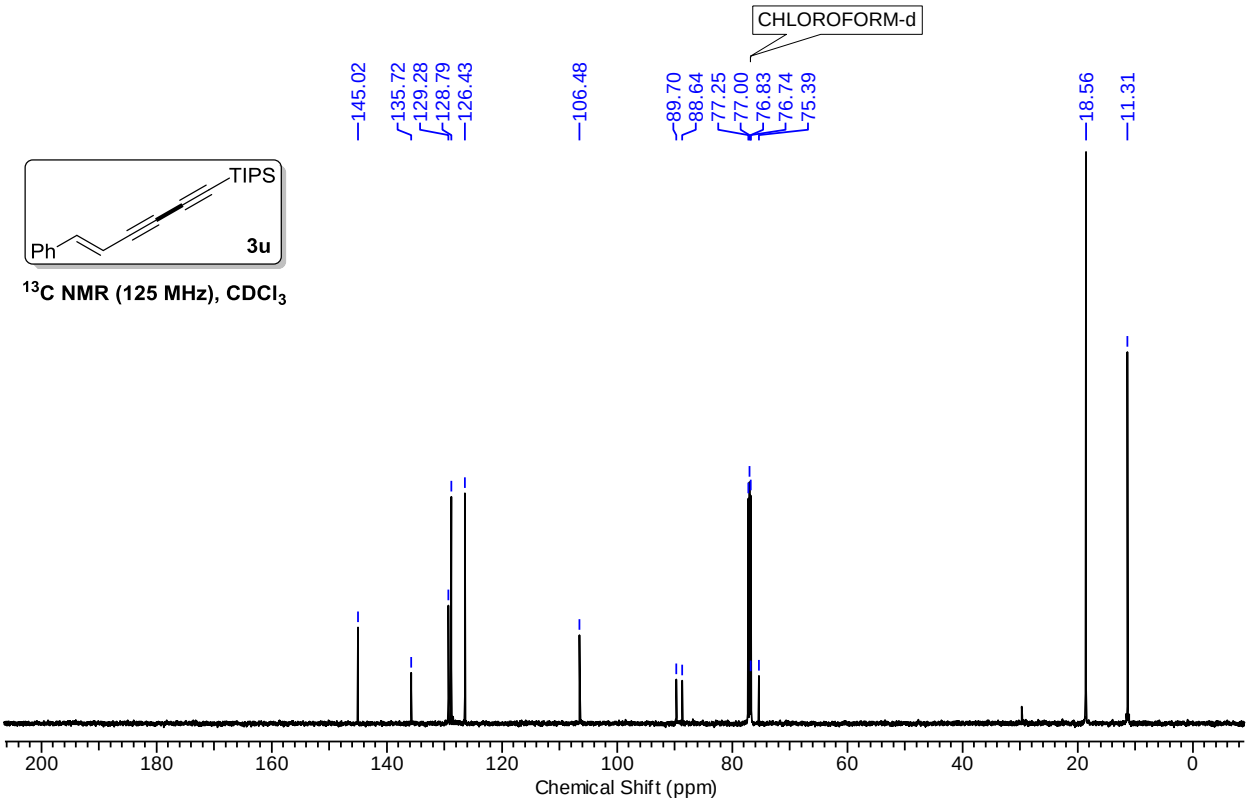
^{1}H NMR (500 MHz), $CDCl_3$



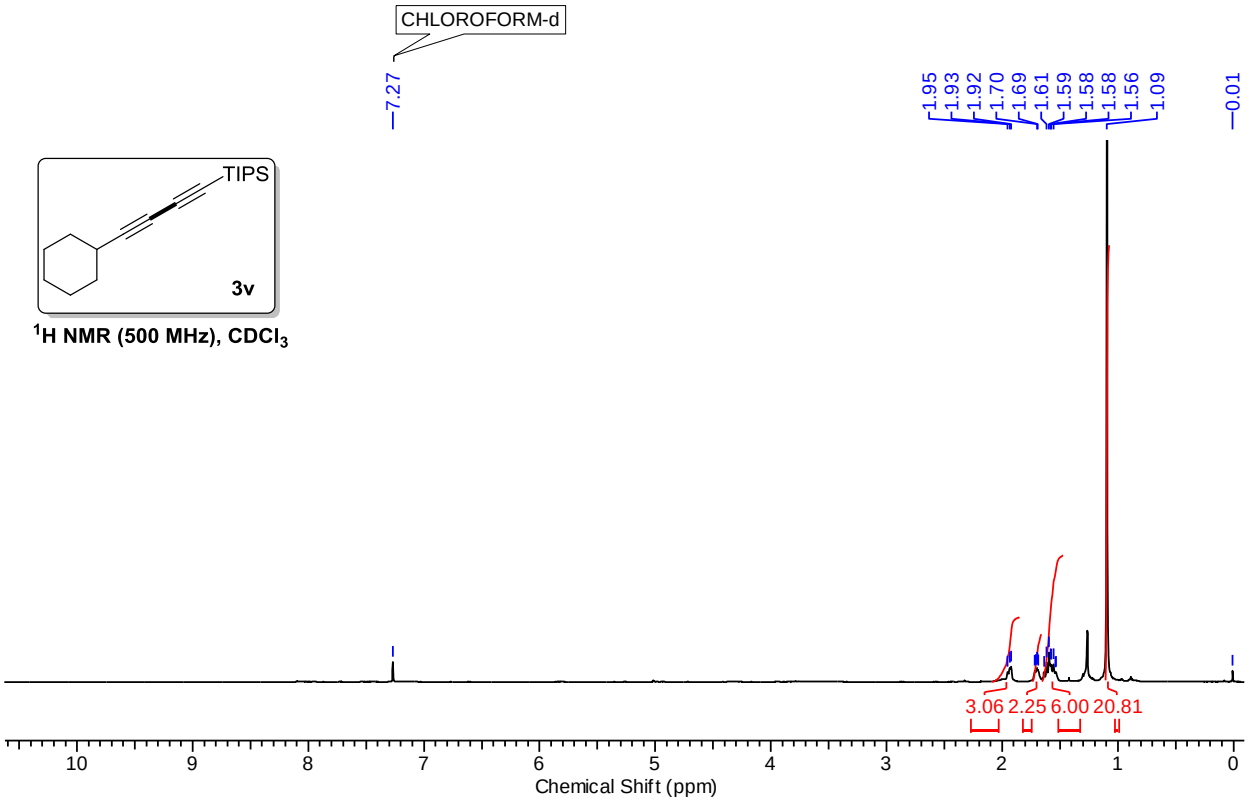
^{13}C NMR (125 MHz), $CDCl_3$



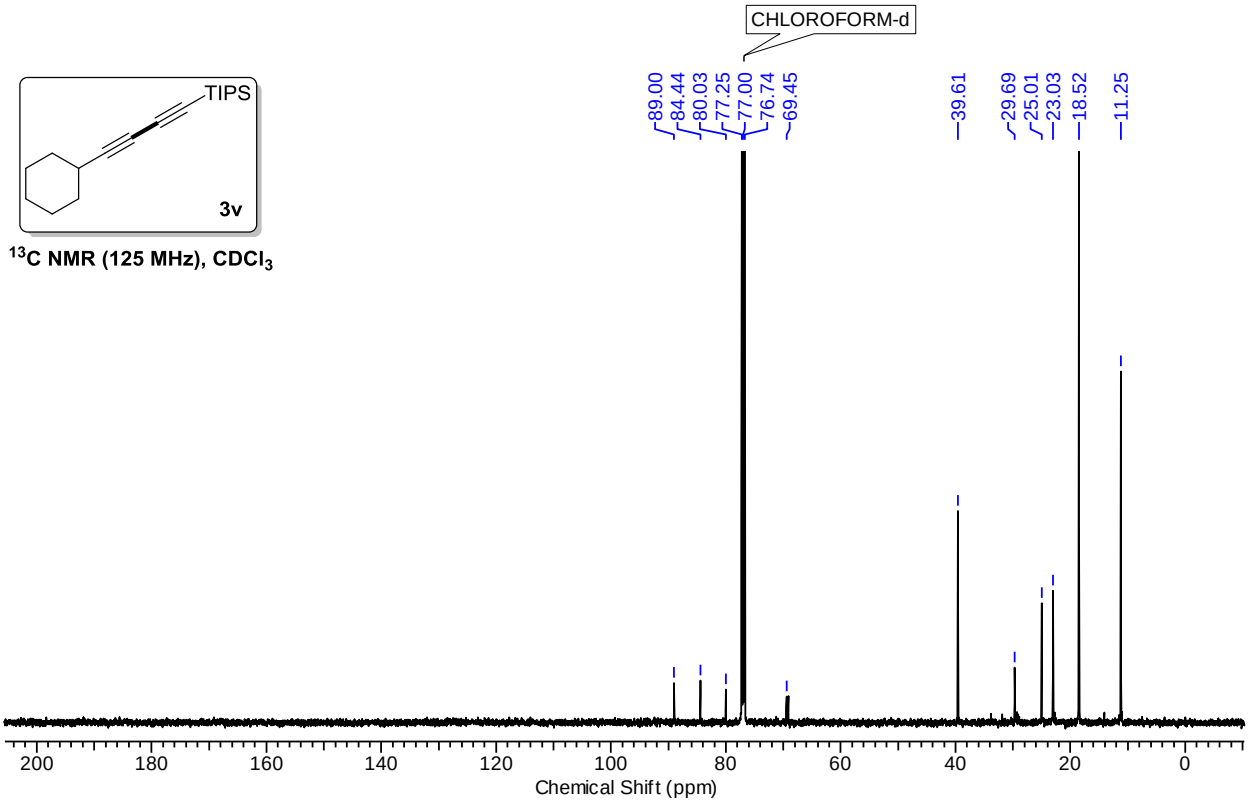
^{1}H NMR (500 MHz), $CDCl_3$



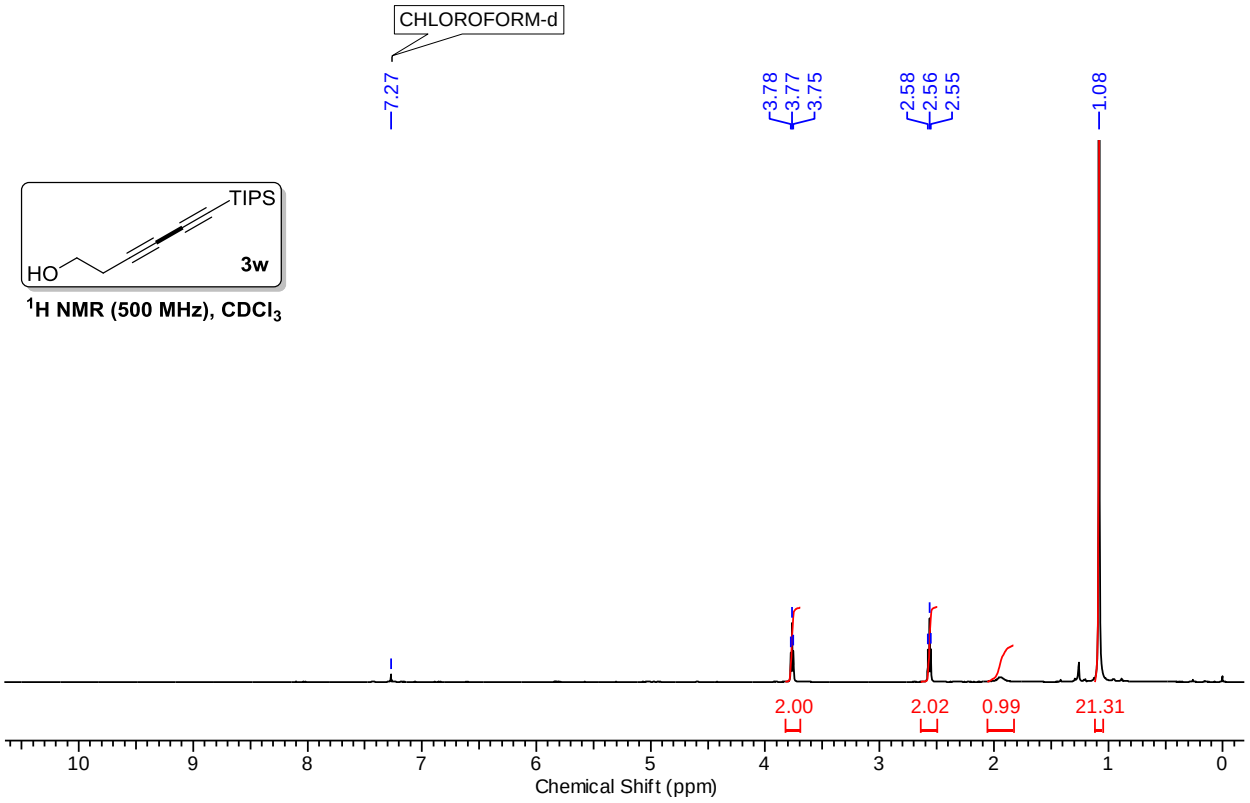
^{13}C NMR (125 MHz), $CDCl_3$



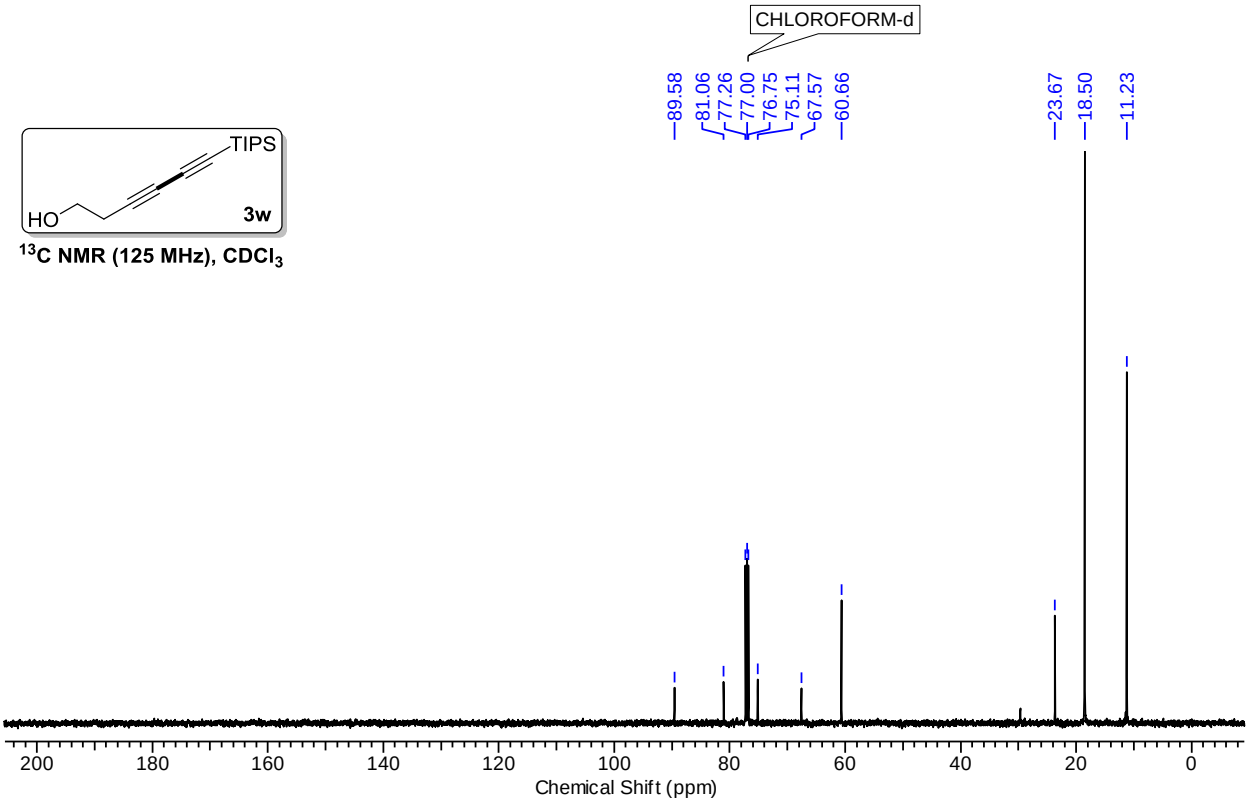
^{1}H NMR (500 MHz), $CDCl_3$



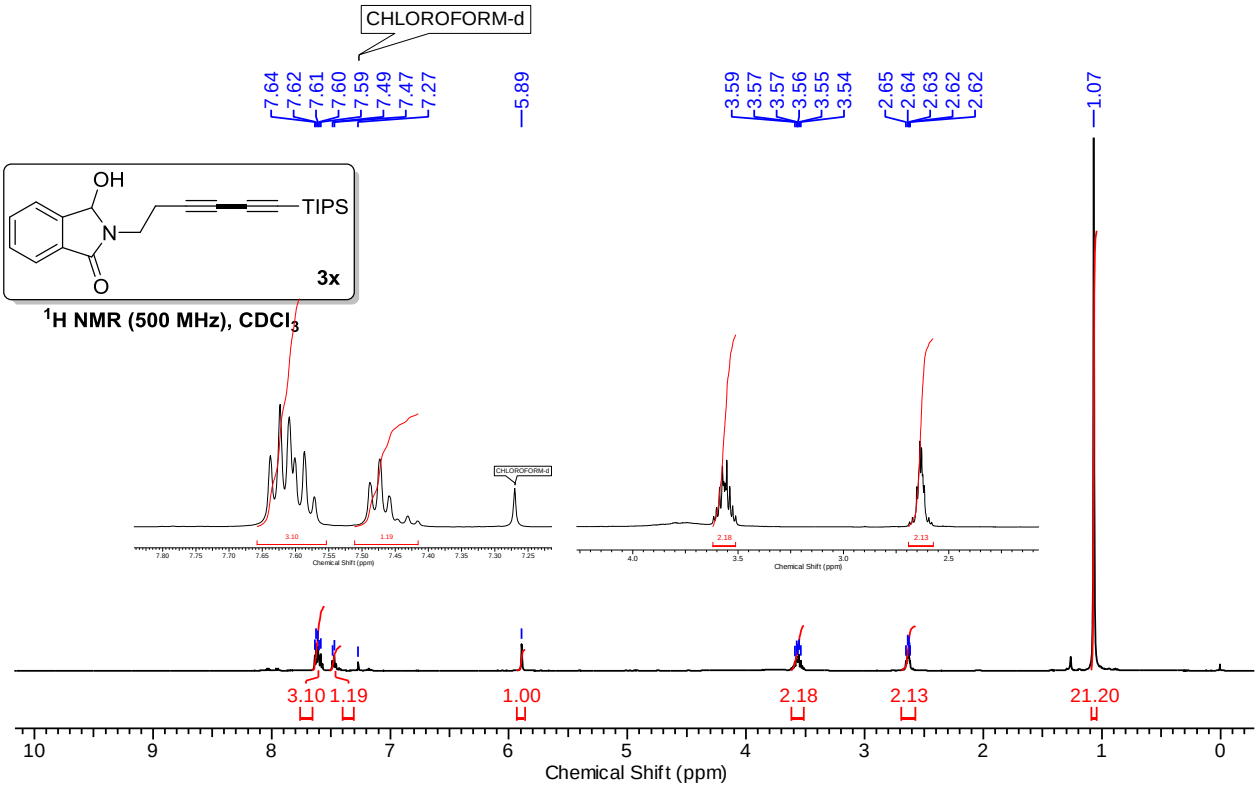
^{13}C NMR (125 MHz), $CDCl_3$



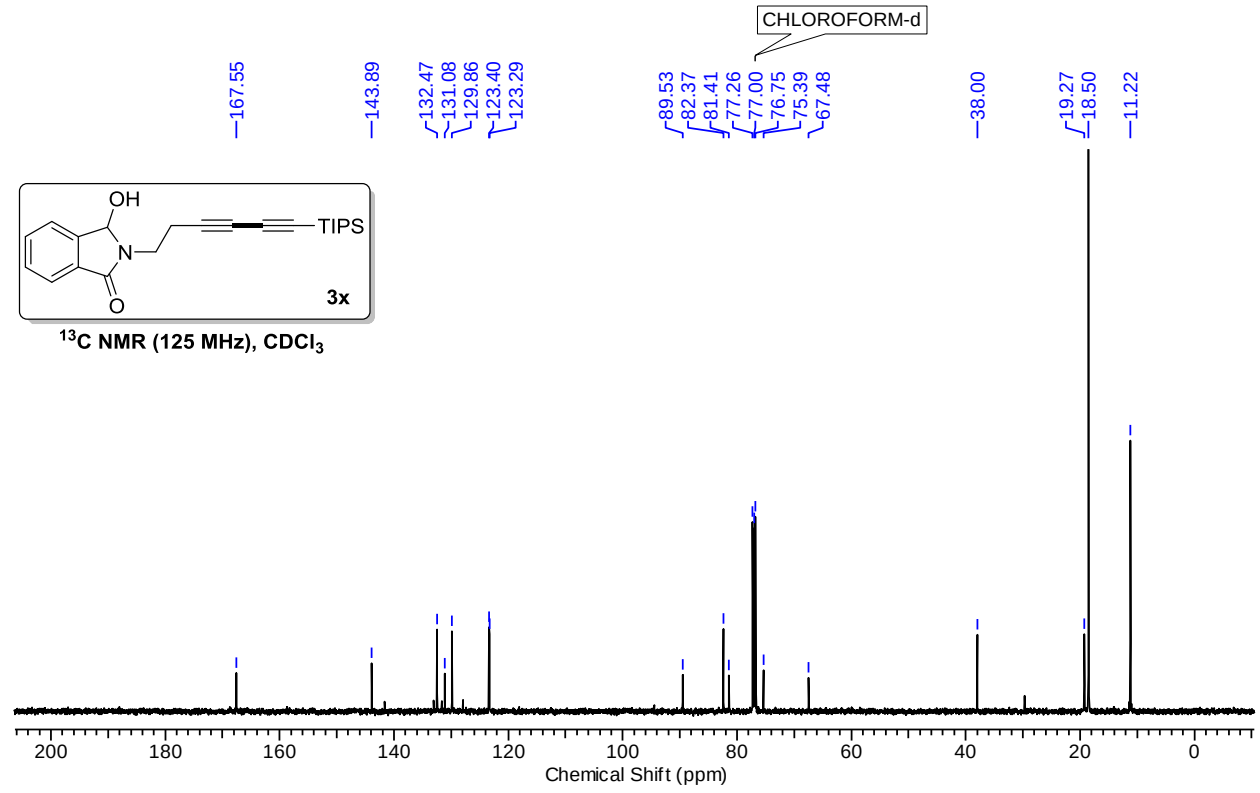
^{1}H NMR (500 MHz), $CDCl_3$



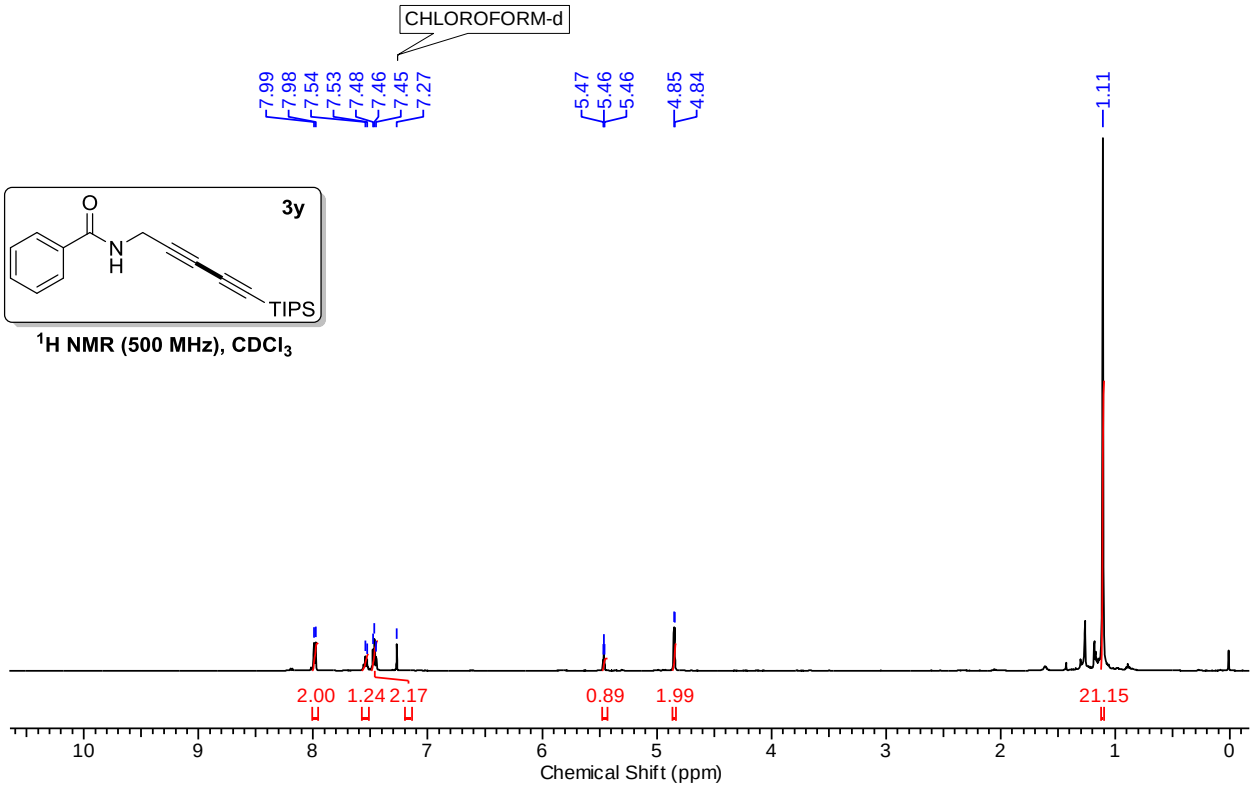
^{13}C NMR (125 MHz), $CDCl_3$



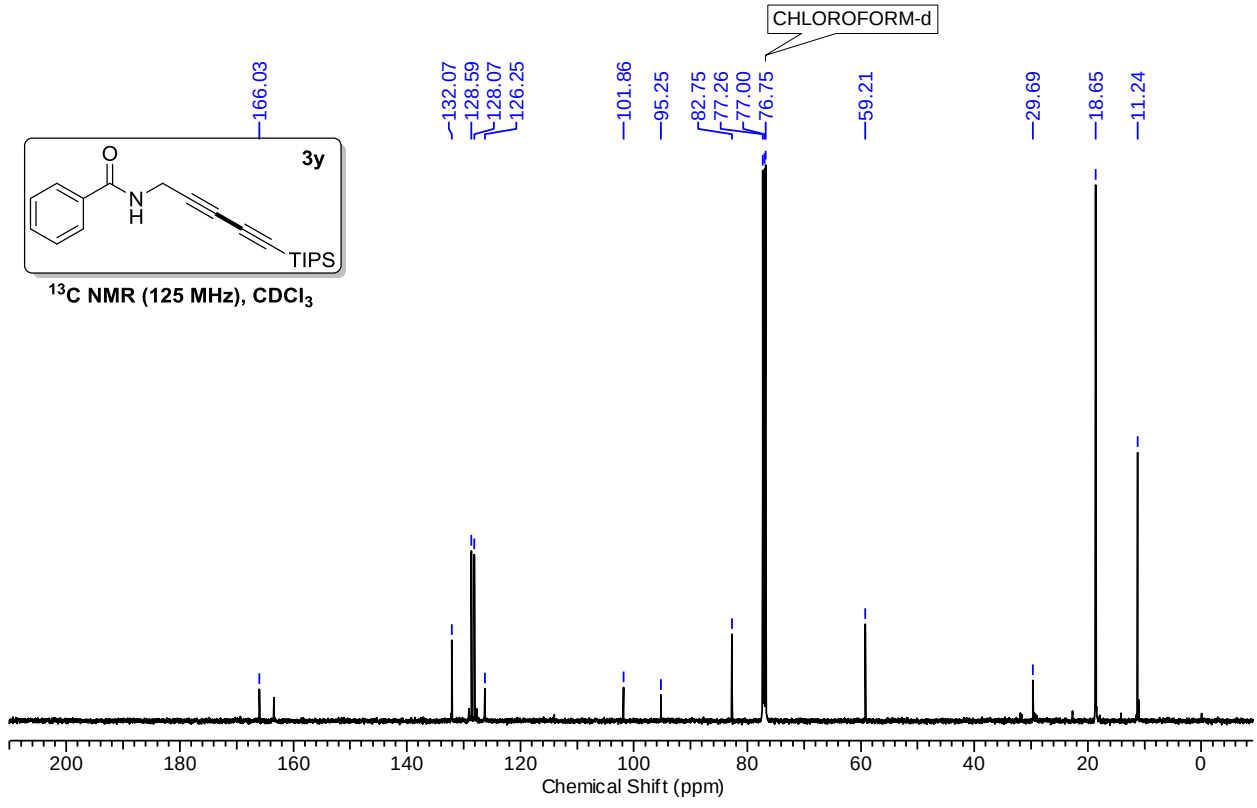
^{1}H NMR (500 MHz), $CDCl_3$



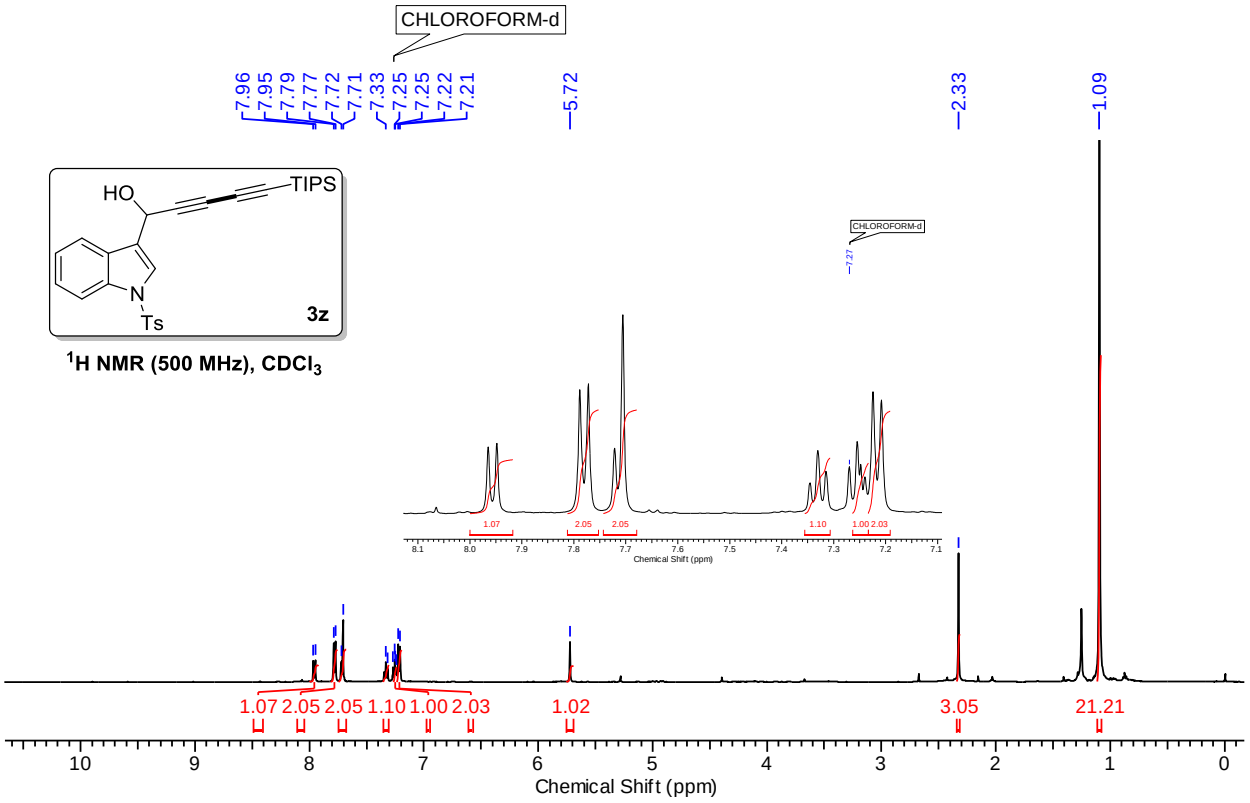
^{13}C NMR (125 MHz), $CDCl_3$

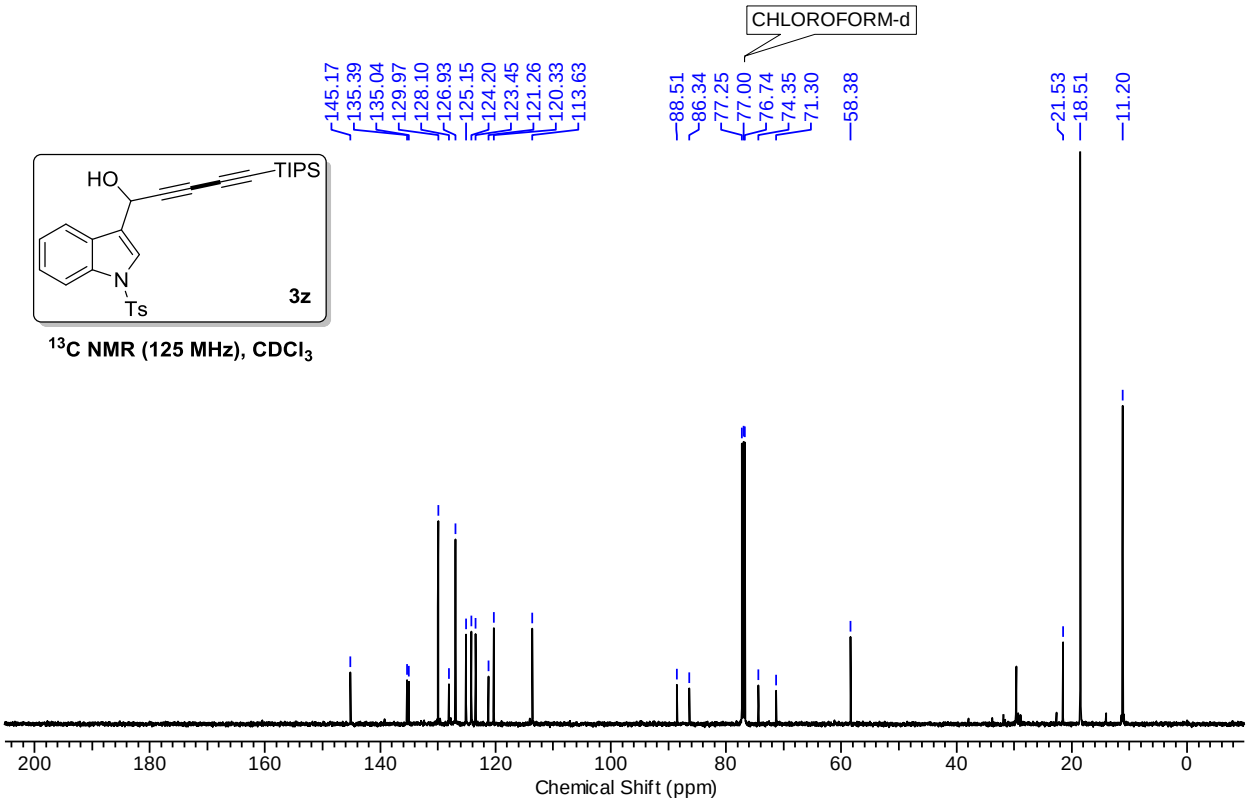


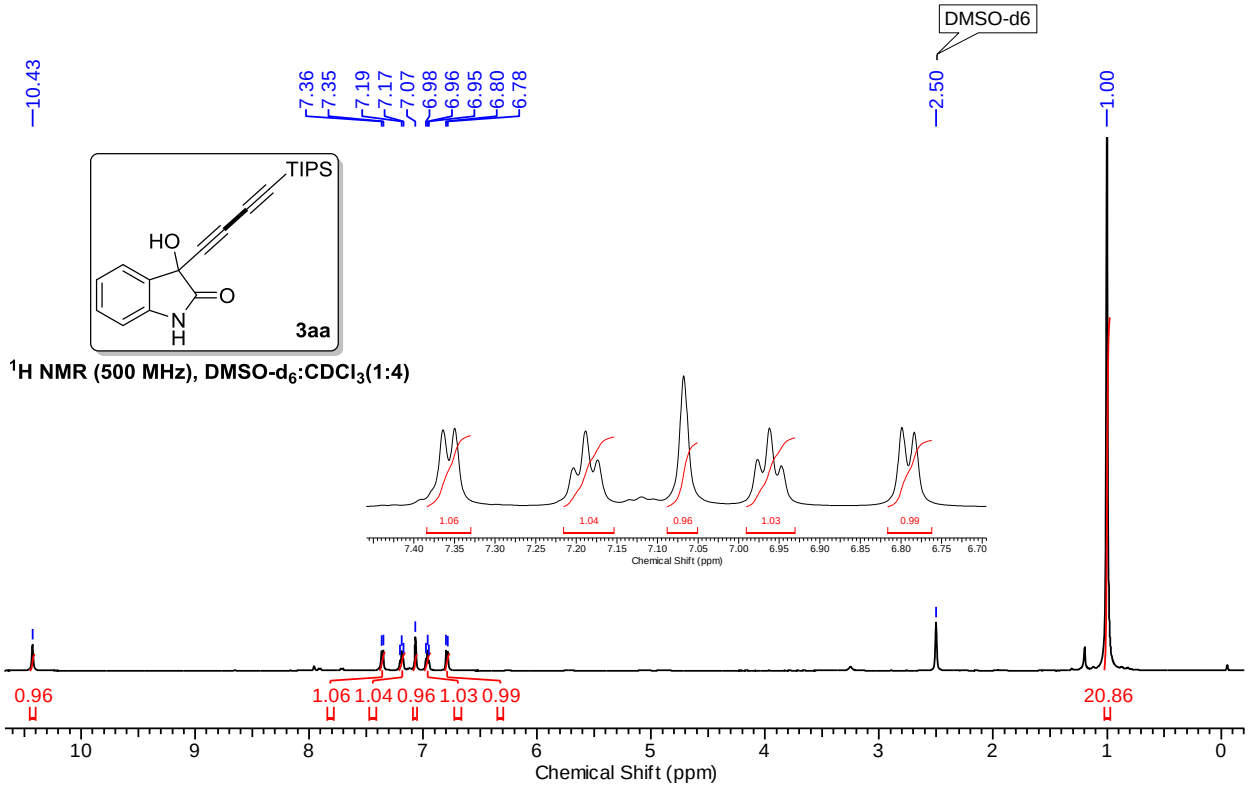
^{1}H NMR (500 MHz), $CDCl_3$

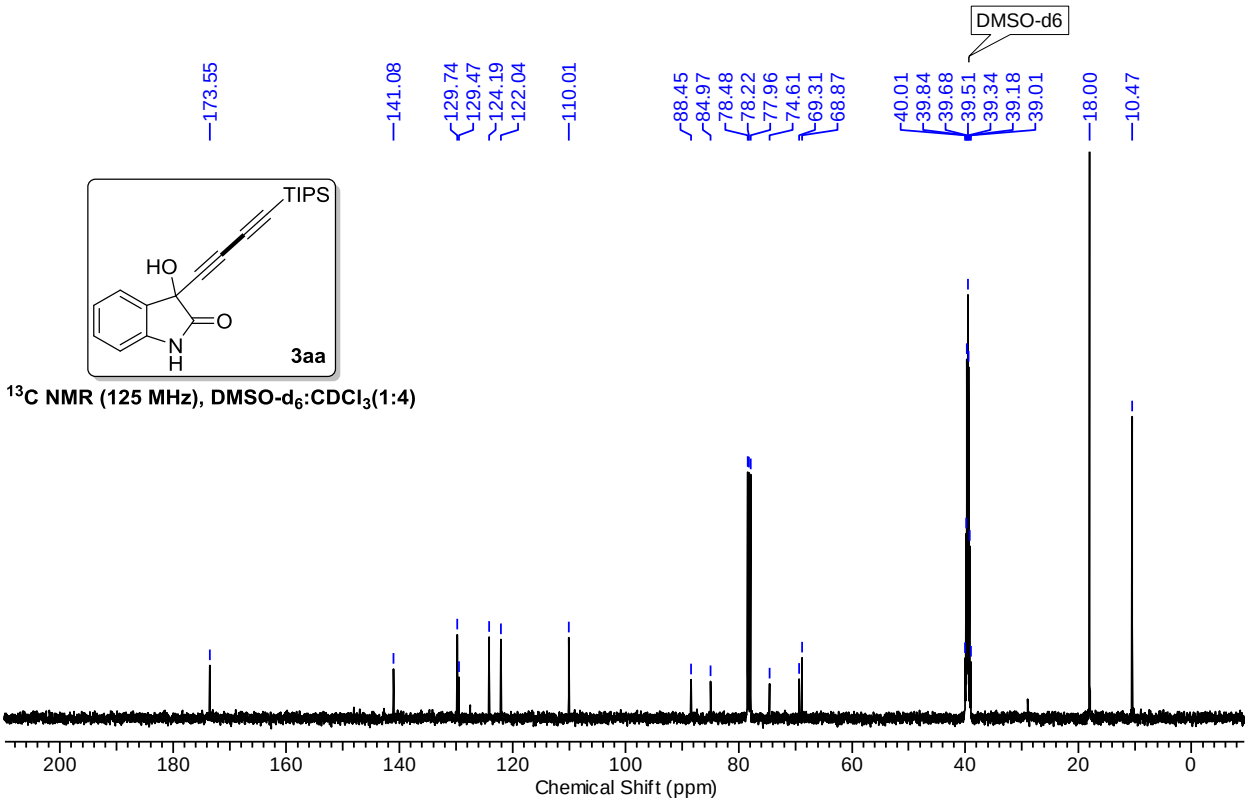


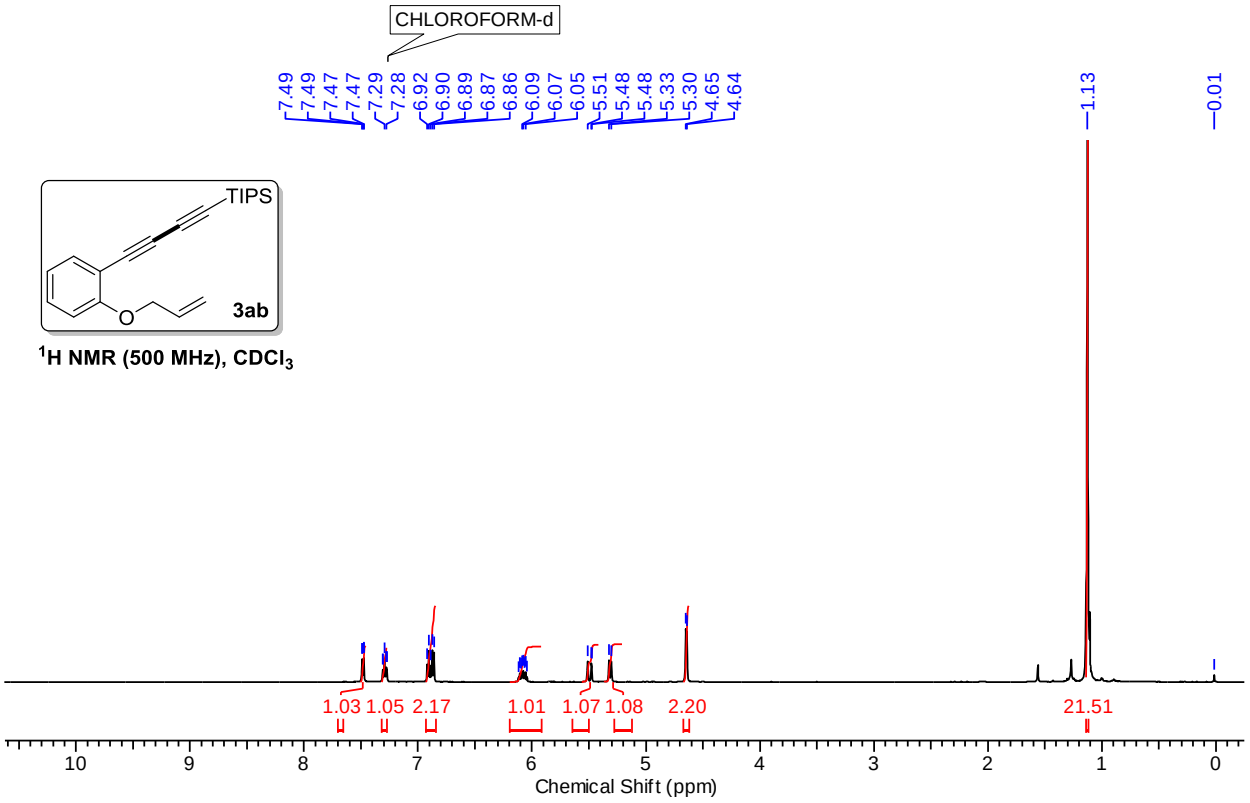
^{13}C NMR (125 MHz), $CDCl_3$


CHLOROFORM-d
7.96
7.95
7.79
7.77
7.72
7.71
7.33
7.25
7.25
7.22
7.21
5.72
2.33
1.09
HO
TIPS
N
Ts
3z
1H NMR (500 MHz), CDCl3
1.07 2.05 2.05 1.10 1.00 2.03
1.02
3.05
21.21
Chemical Shift (ppm)

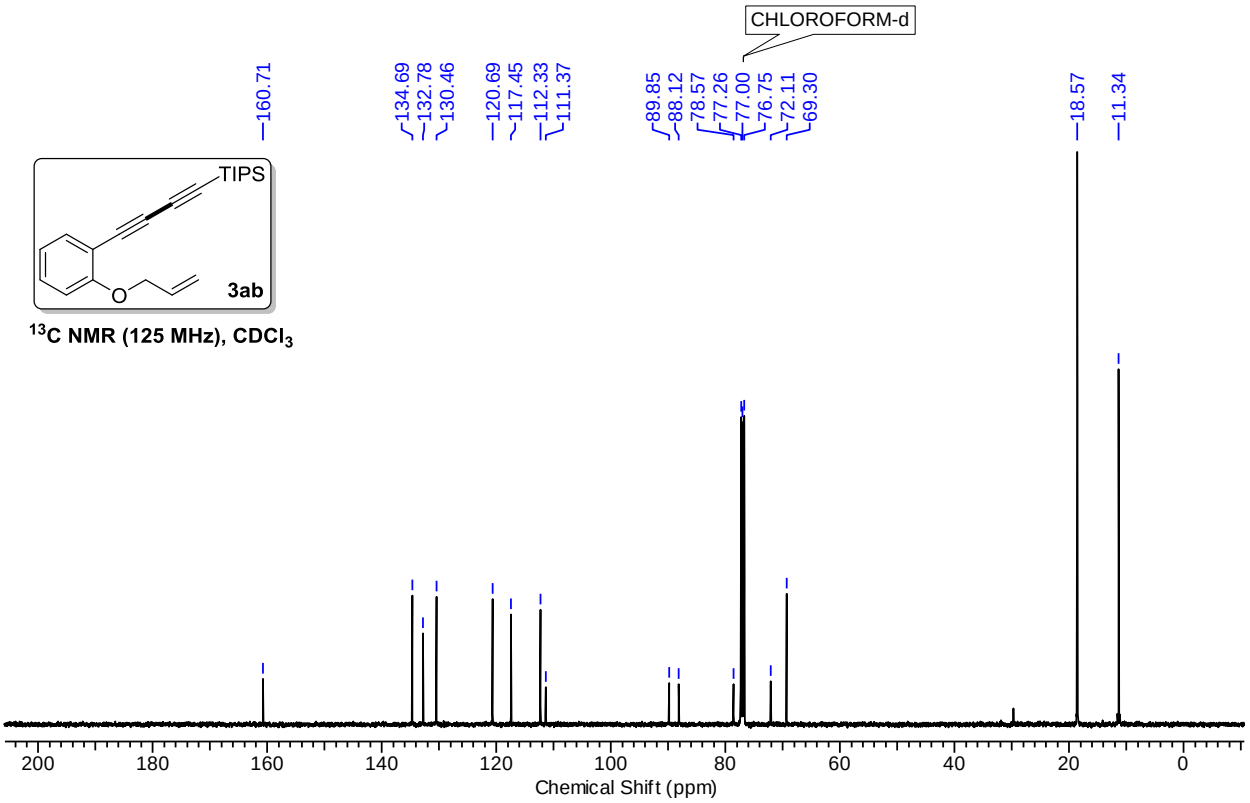

CHLOROFORM-d
145.17
135.39
135.04
129.97
128.10
126.93
125.15
124.20
123.45
121.26
120.33
113.63
88.51
86.34
77.25
77.00
76.74
74.35
71.30
58.38
21.53
18.51
11.20
HO
TIPS
N
Ts
3z
13C NMR (125 MHz), CDCl3
Chemical Shift (ppm)


DMSO-d6
10.43
7.36
7.35
7.19
7.17
7.07
6.98
6.96
6.95
6.80
6.78
2.50
1.00
TIPS
HO
O
N
H
3aa
1H NMR (500 MHz), DMSO-d6:CDCl3(1:4)
1.06
1.04
0.96
1.03
0.99
0.96
1.06 1.04 0.96 1.03 0.99
20.86
Chemical Shift (ppm)

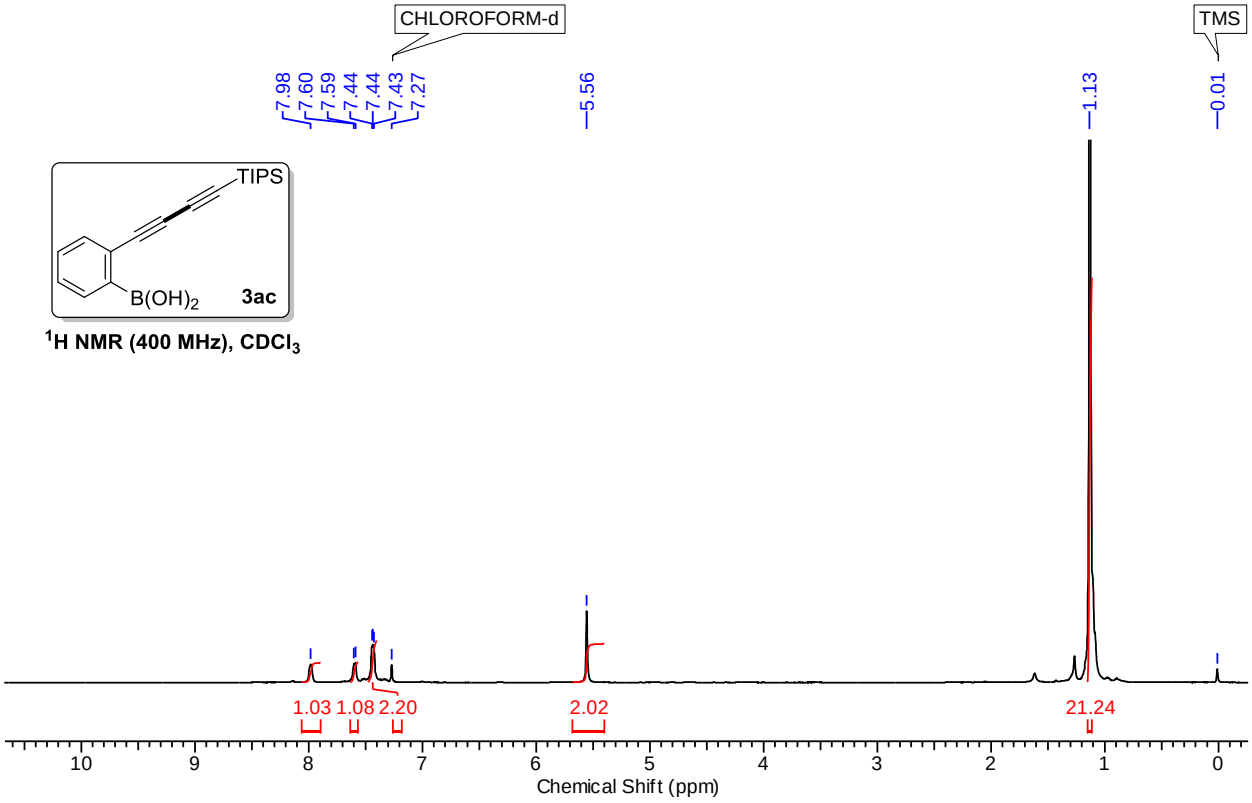

DMSO-d6
173.55
141.08
129.74
129.47
124.19
122.04
110.01
88.45
84.97
78.48
78.22
77.96
74.61
69.31
68.87
40.01
39.84
39.68
39.51
39.34
39.18
39.01
18.00
10.47
TIPS
HO
O
N
H
3aa
13C NMR (125 MHz), DMSO-d6:CDCl3(1:4)
Chemical Shift (ppm)



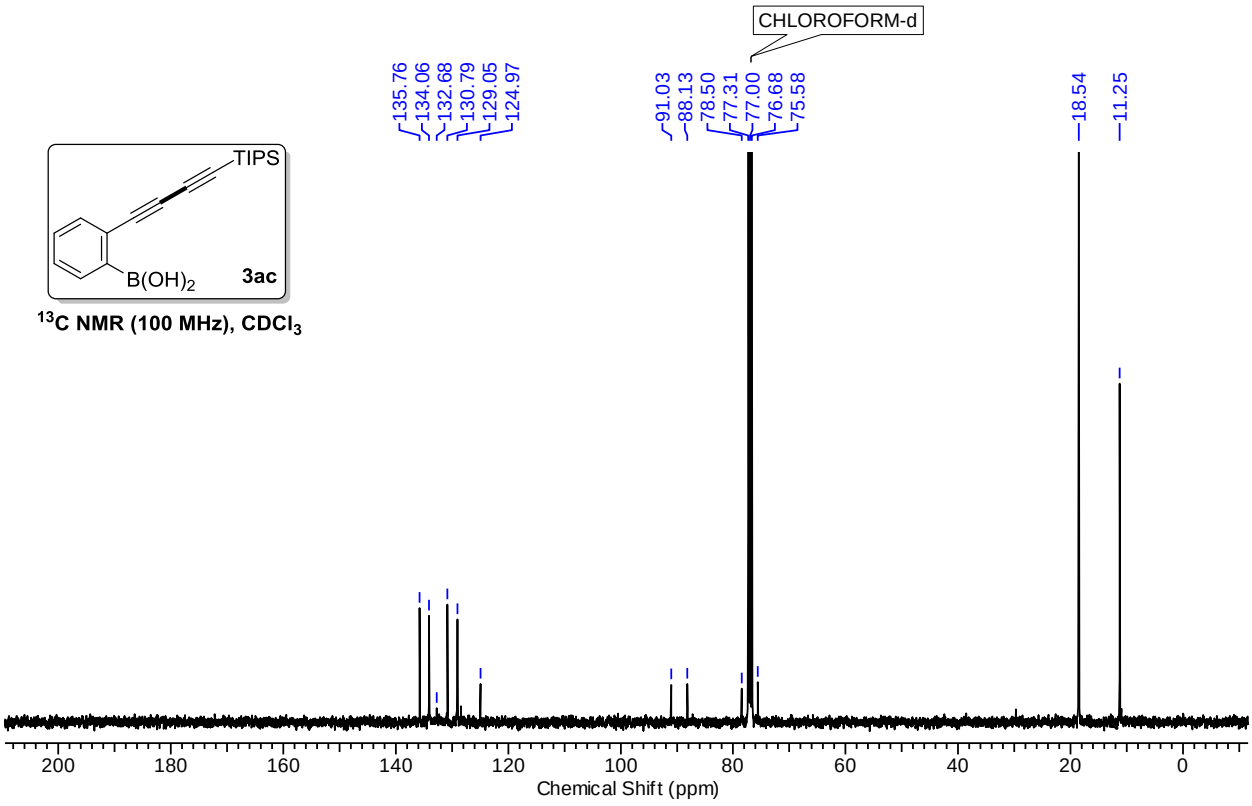
^{1}H NMR (500 MHz), $CDCl_3$



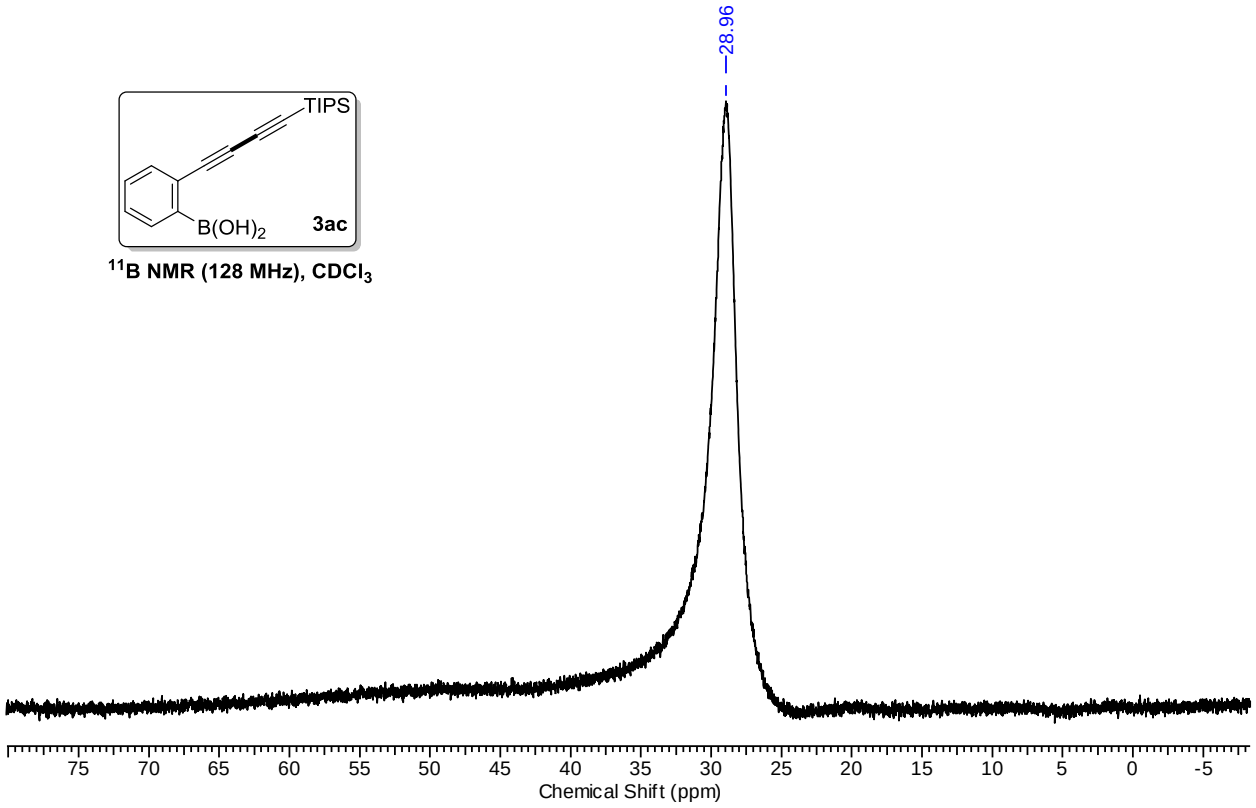
^{13}C NMR (125 MHz), $CDCl_3$

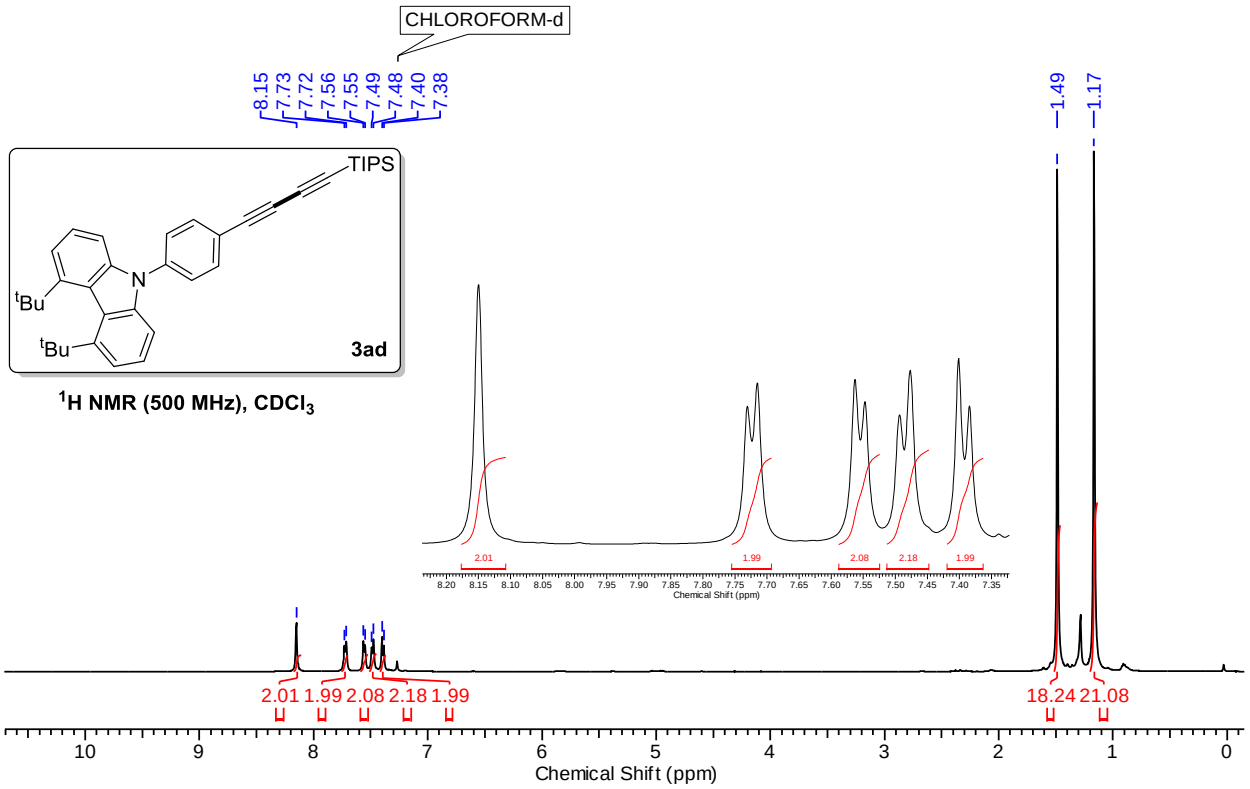


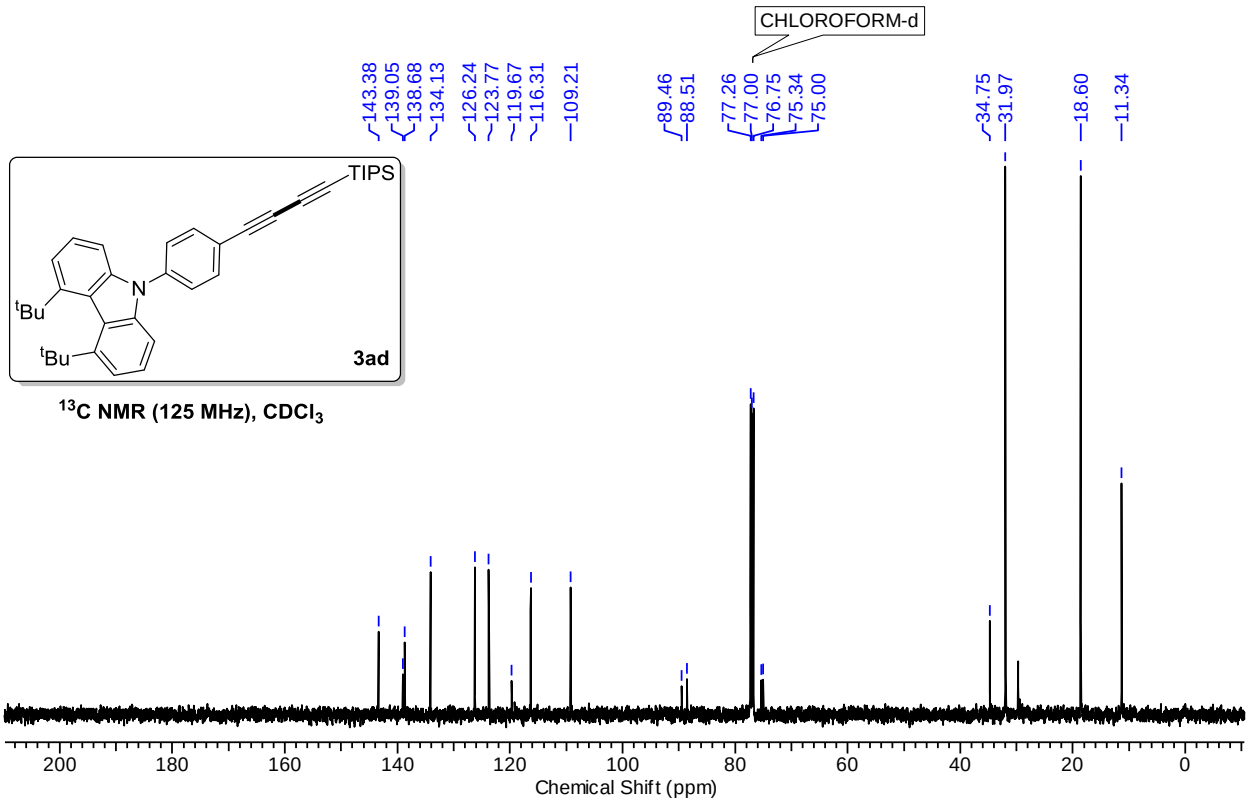
^{1}H NMR (400 MHz), $CDCl_3$

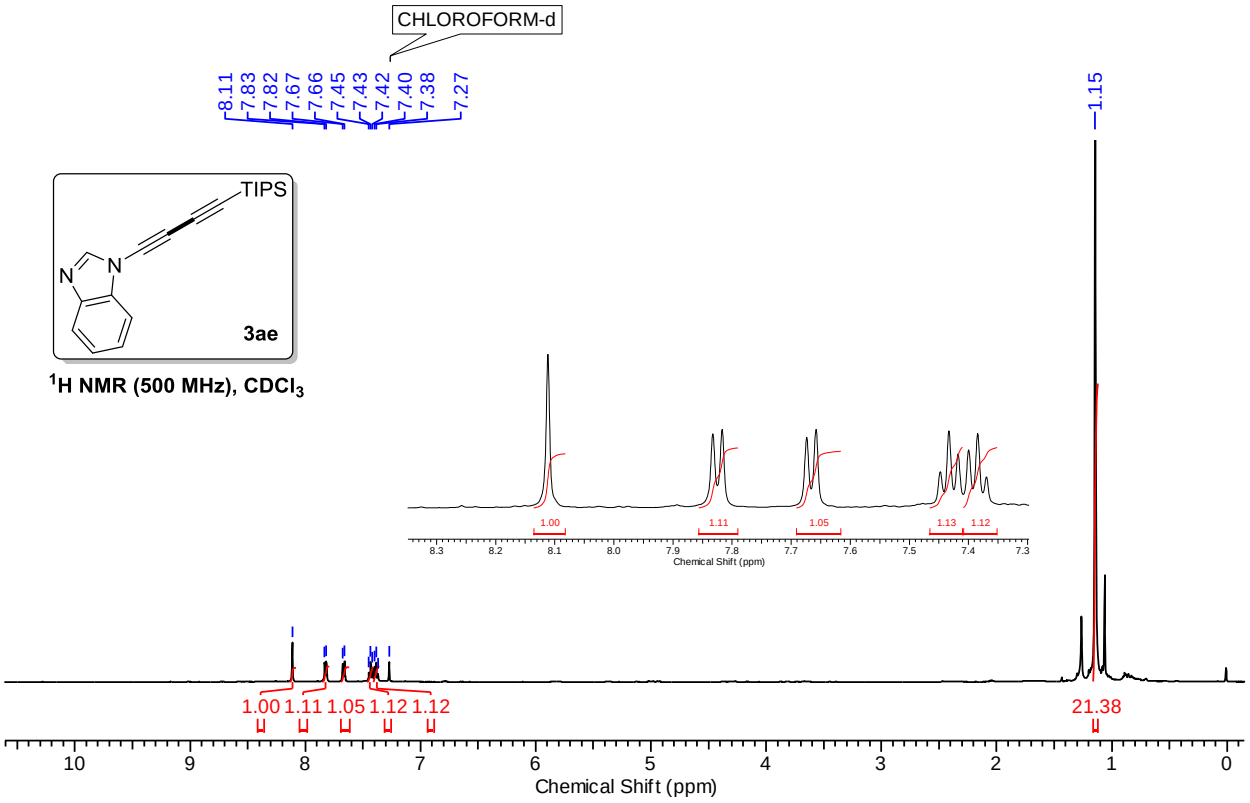


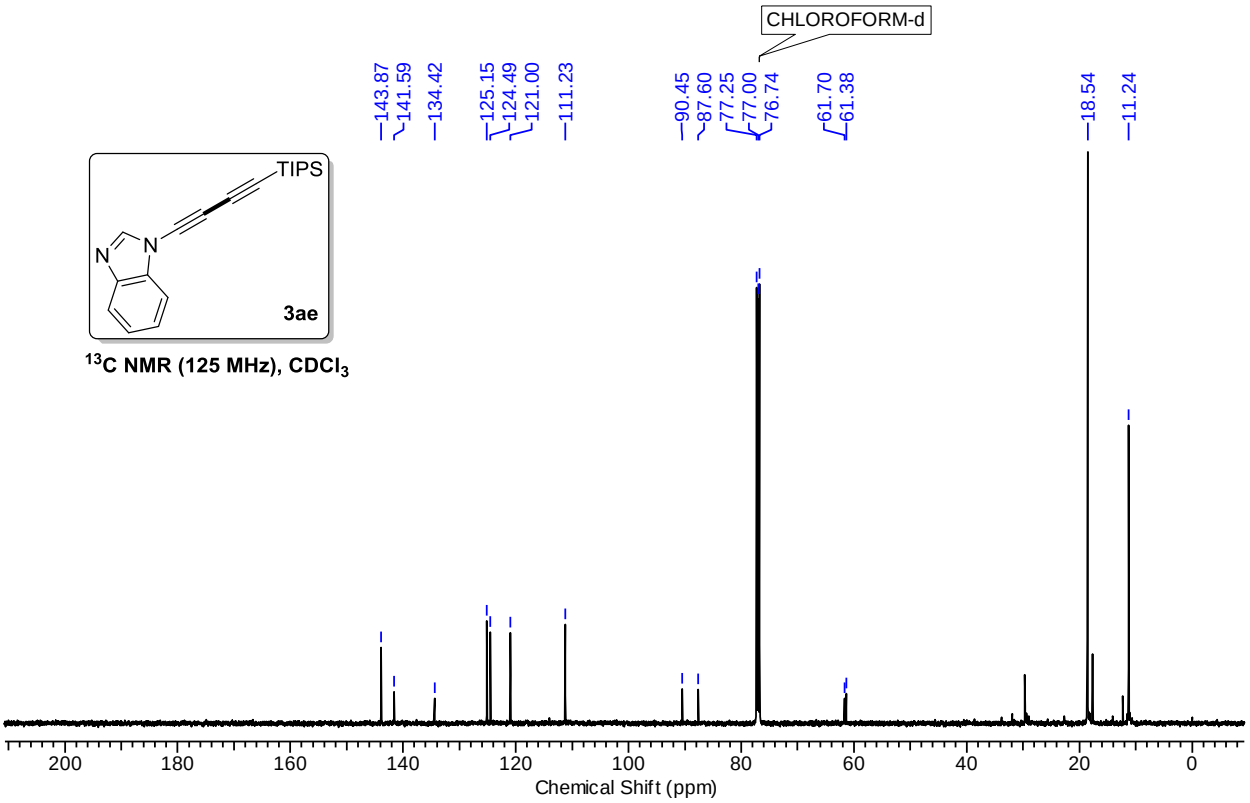
^{13}C NMR (100 MHz), $CDCl_3$

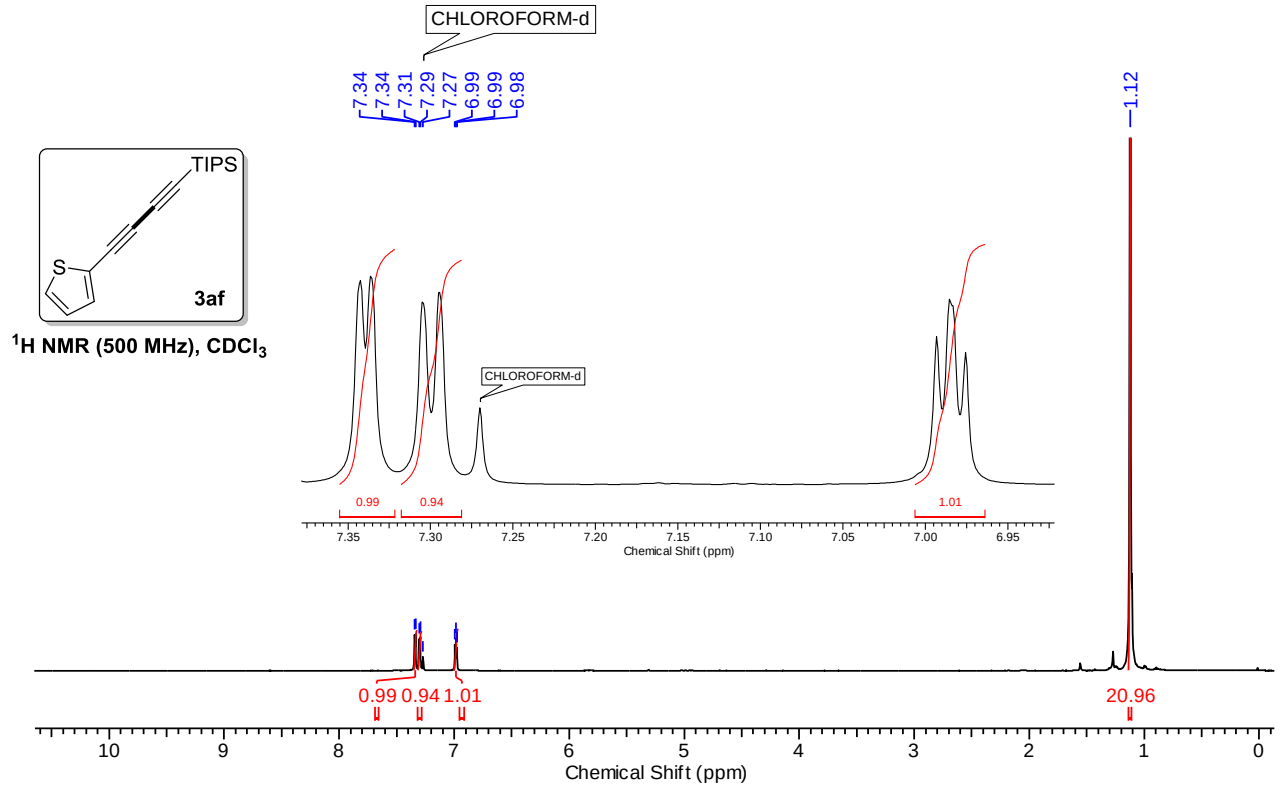

28.96
TIPS
B(OH)2
3ac
11B NMR (128 MHz), CDCl3
75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5
Chemical Shift (ppm)


CHLOROFORM-d
8.15
7.73
7.72
7.56
7.55
7.49
7.48
7.40
7.38
1.49
1.17
TIPS
tBu
tBu
N
3ad
1H NMR (500 MHz), CDCl3
2.01 1.99 2.08 2.18 1.99
18.24 21.08
Chemical Shift (ppm)

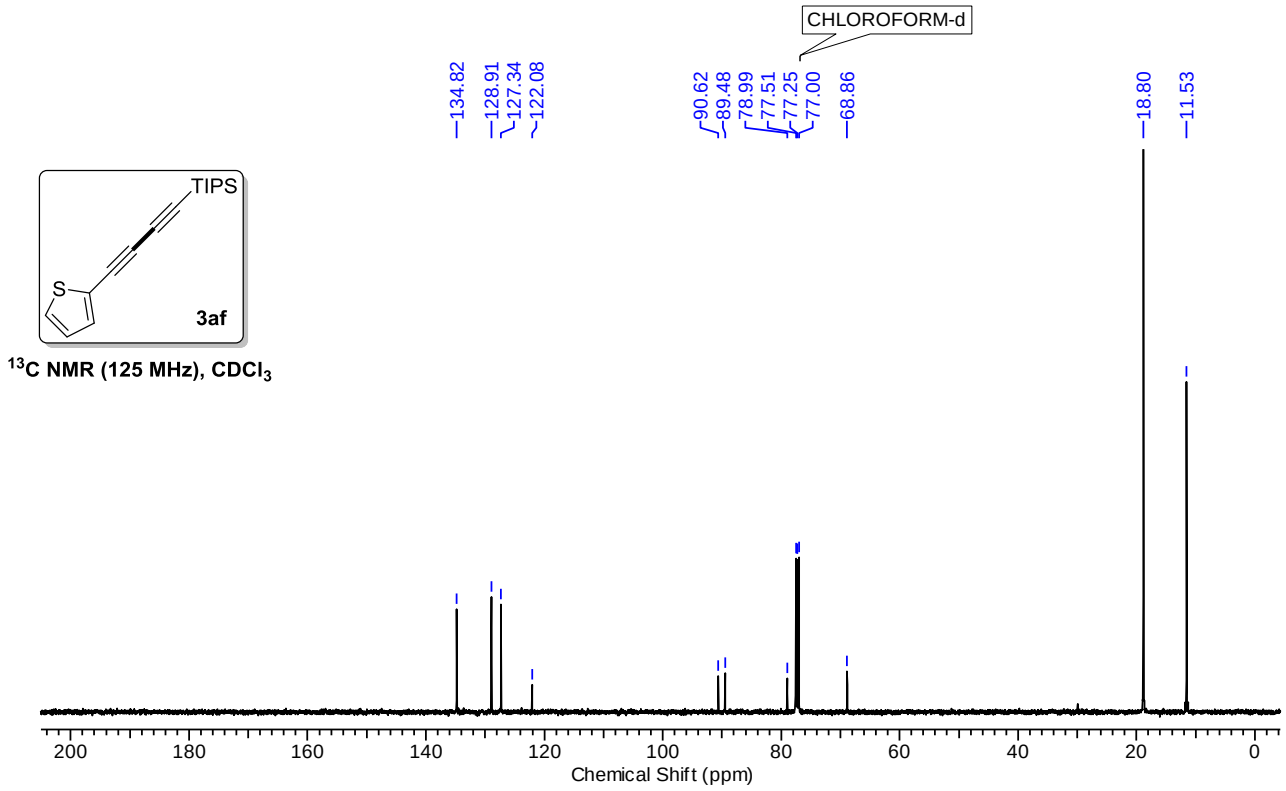

CHLOROFORM-d
143.38
139.05
138.68
134.13
126.24
123.77
119.67
116.31
109.21
89.46
88.51
77.26
77.00
76.75
75.34
75.00
34.75
31.97
18.60
11.34
TIPS
tBu
tBu
N
3ad
13C NMR (125 MHz), CDCl3
Chemical Shift (ppm)


CHLOROFORM-d
8.11
7.83
7.82
7.67
7.66
7.45
7.43
7.42
7.40
7.38
7.27
1.15
TIPS
N
N
3ae
1H NMR (500 MHz), CDCl3
1.00
1.11
1.05
1.13
1.12
Chemical Shift (ppm)
1.00 1.11 1.05 1.12 1.12
21.38
Chemical Shift (ppm)

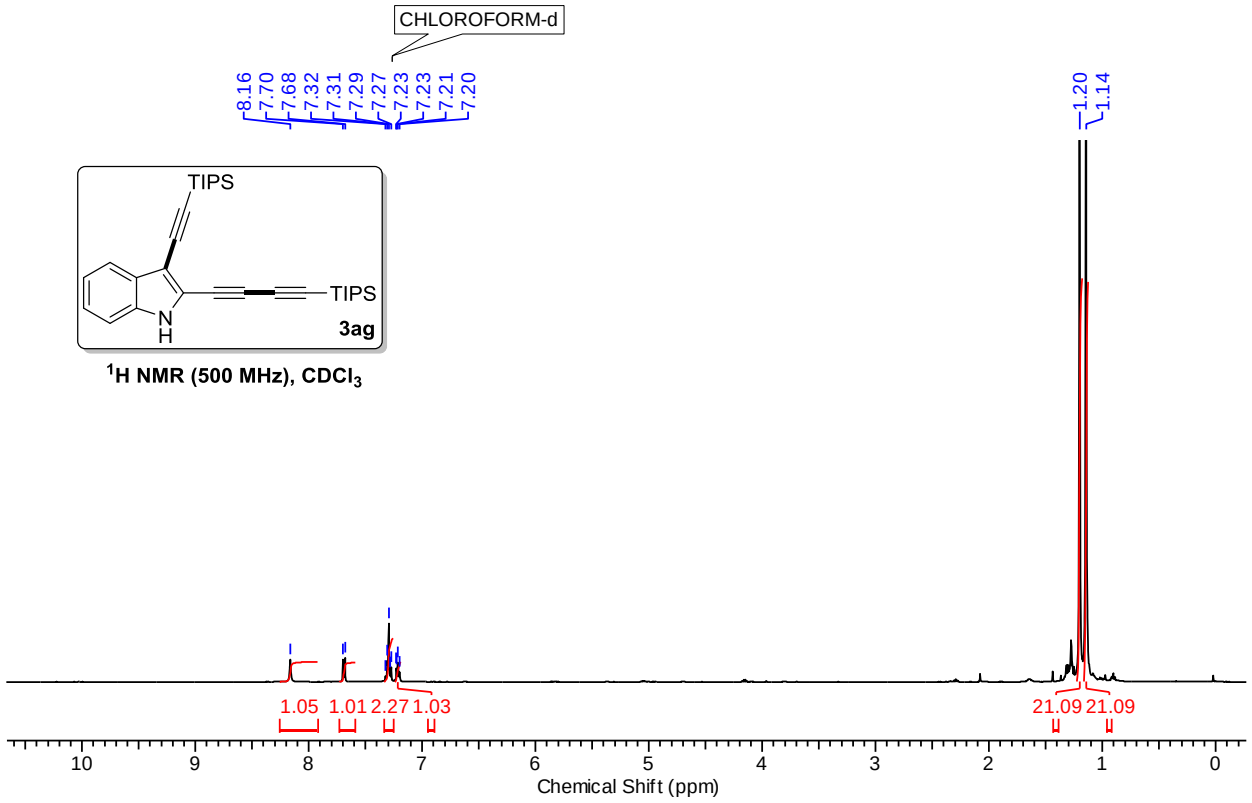

CHLOROFORM-d
143.87
141.59
134.42
125.15
124.49
121.00
111.23
90.45
87.60
77.25
77.00
76.74
61.70
61.38
18.54
11.24
TIPS
N
N
3ae
13C NMR (125 MHz), CDCl3
Chemical Shift (ppm)



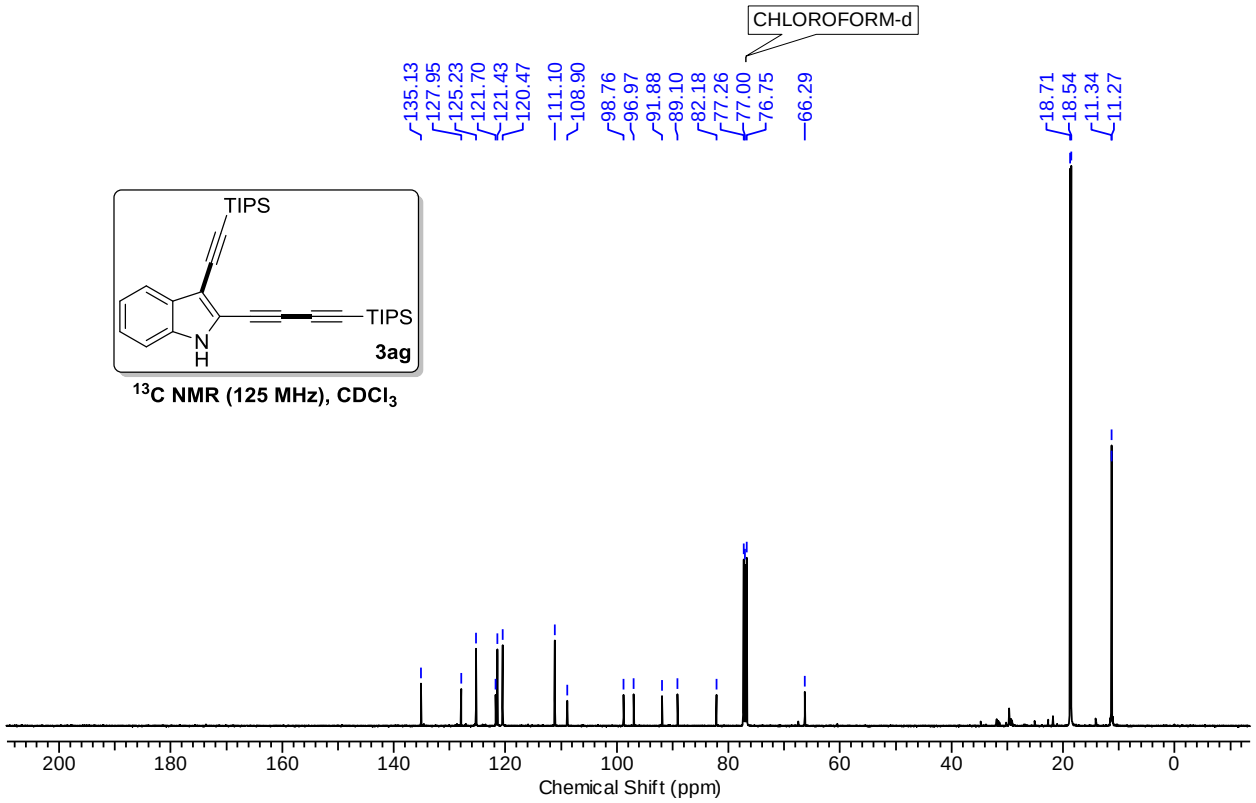
^{1}H NMR (500 MHz), $CDCl_3$



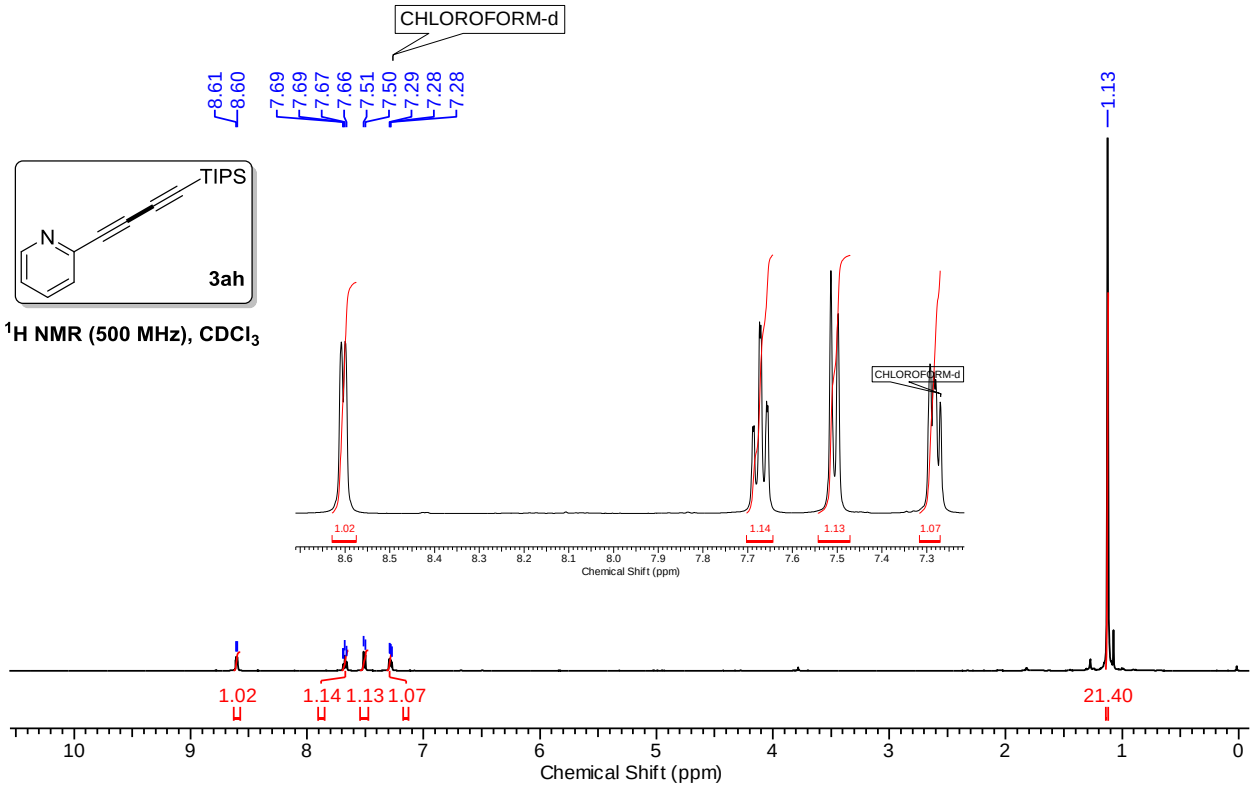
^{13}C NMR (125 MHz), $CDCl_3$



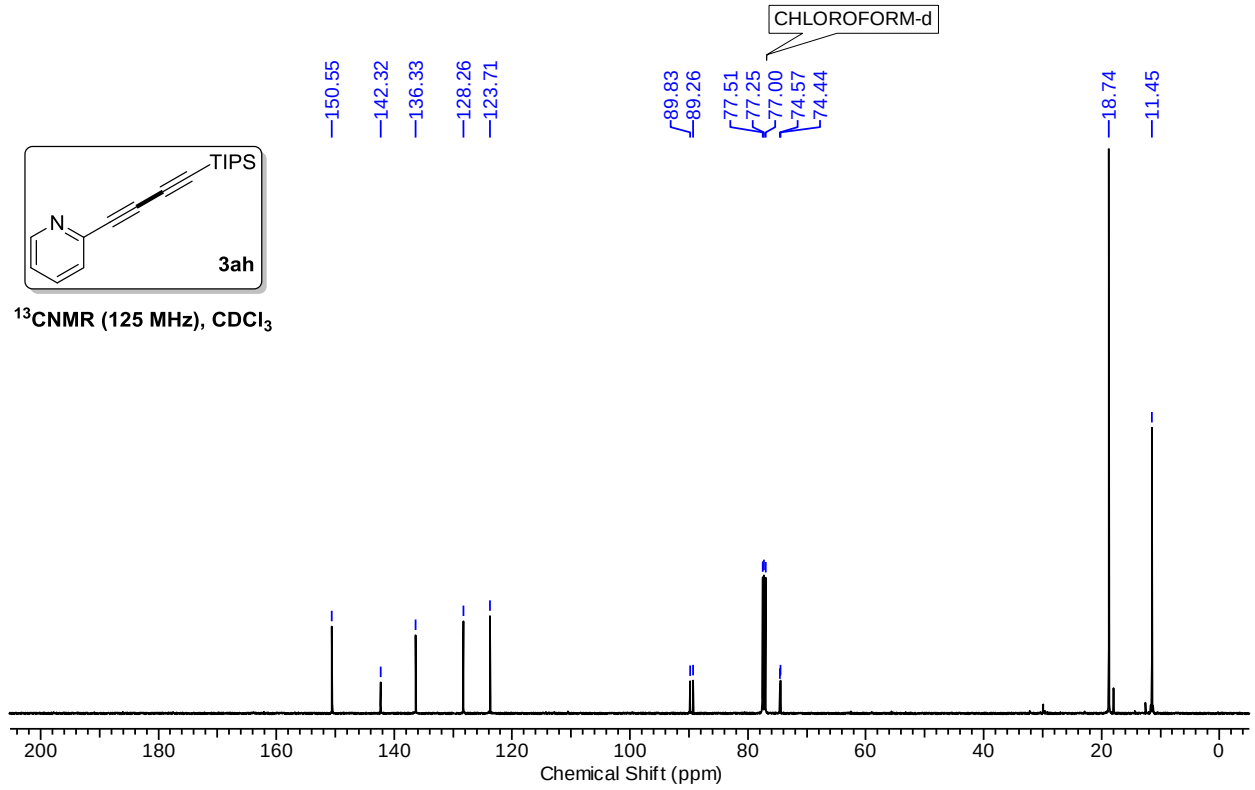
^{1}H NMR (500 MHz), $CDCl_3$



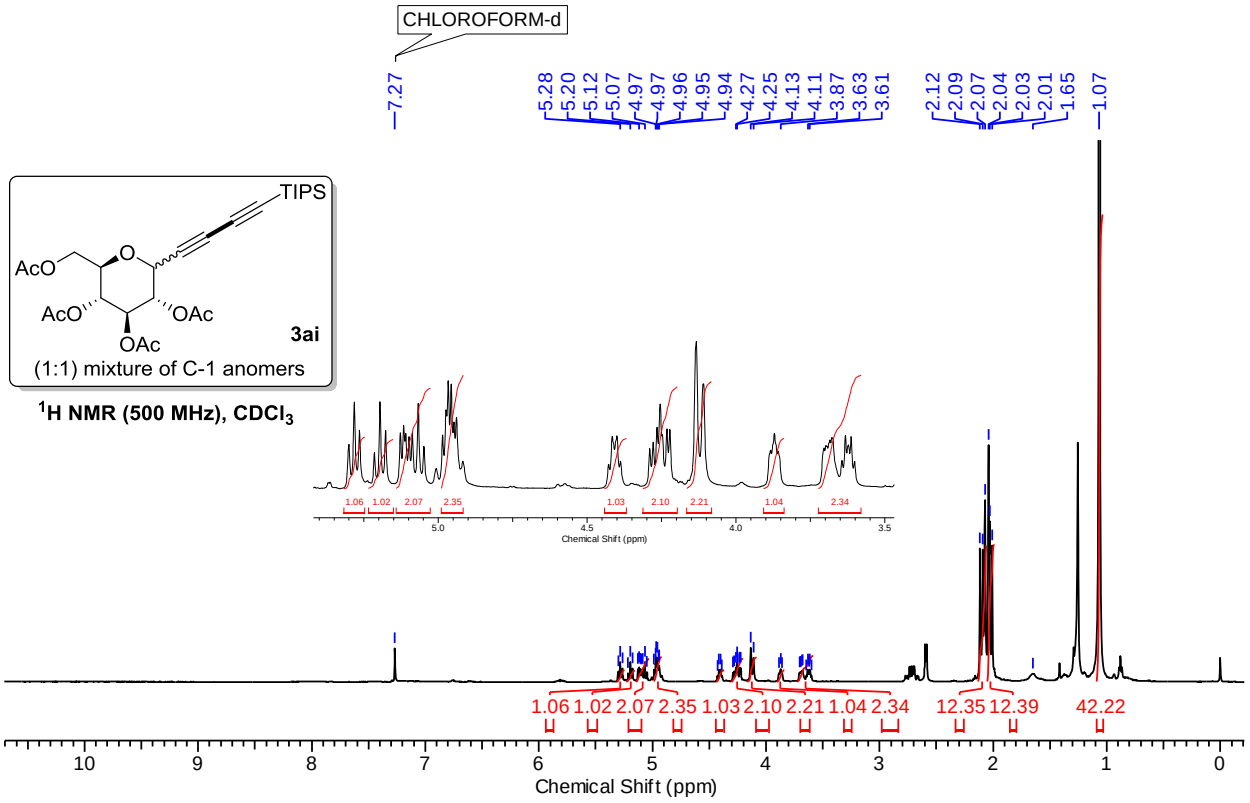
^{13}C NMR (125 MHz), $CDCl_3$



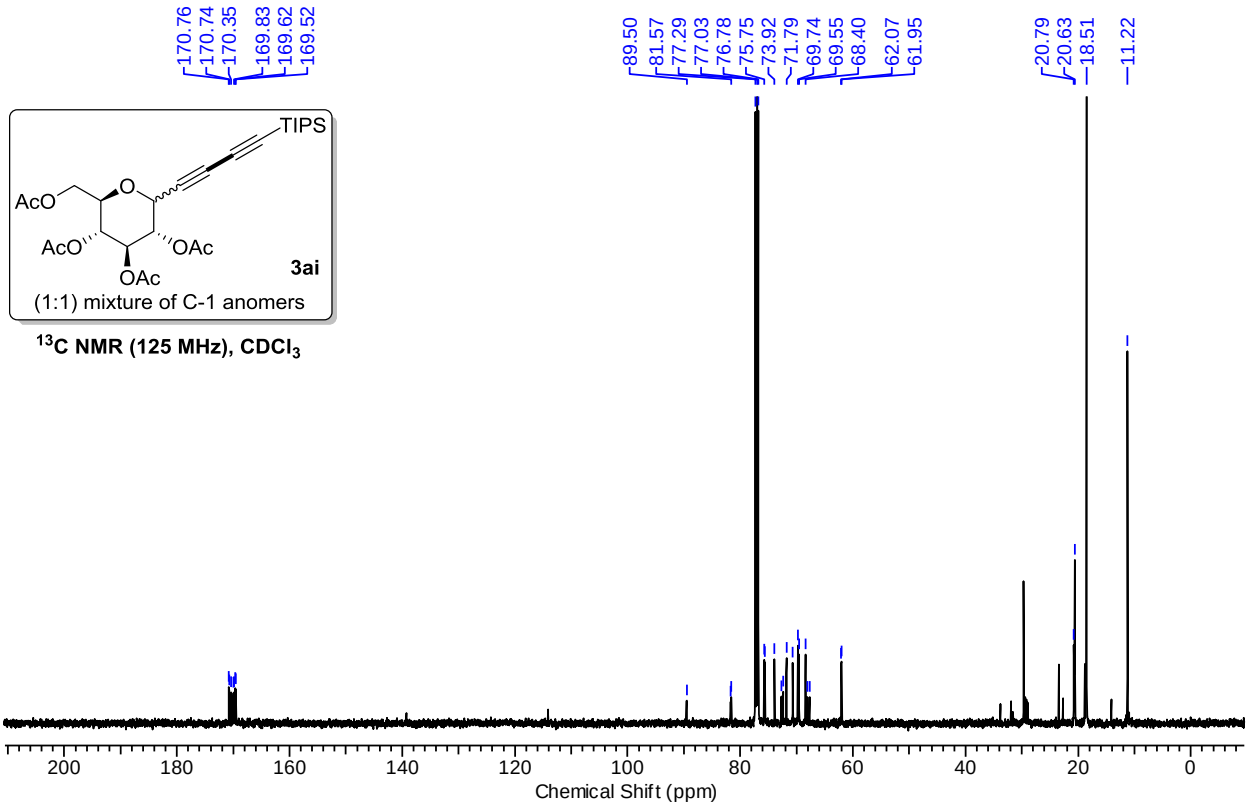
^{1}H NMR (500 MHz), $CDCl_3$



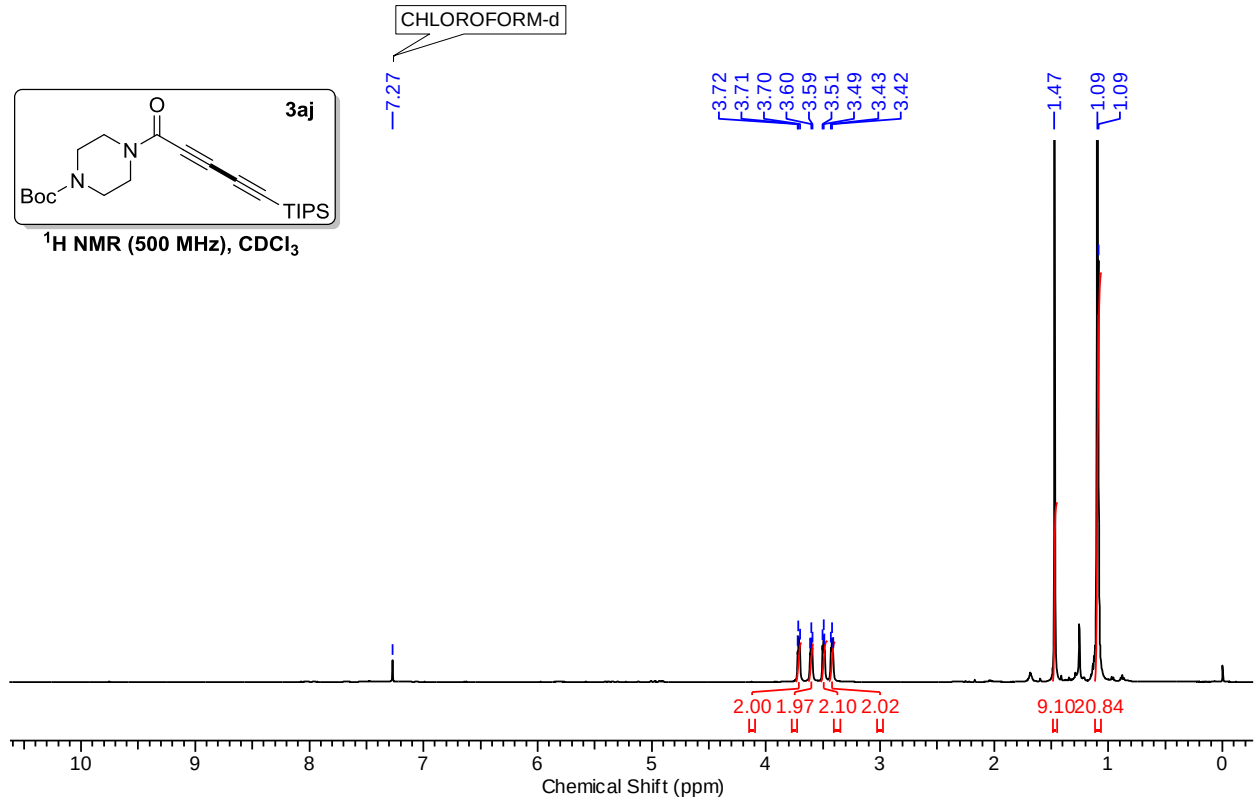
^{13}CNMR (125 MHz), $CDCl_3$



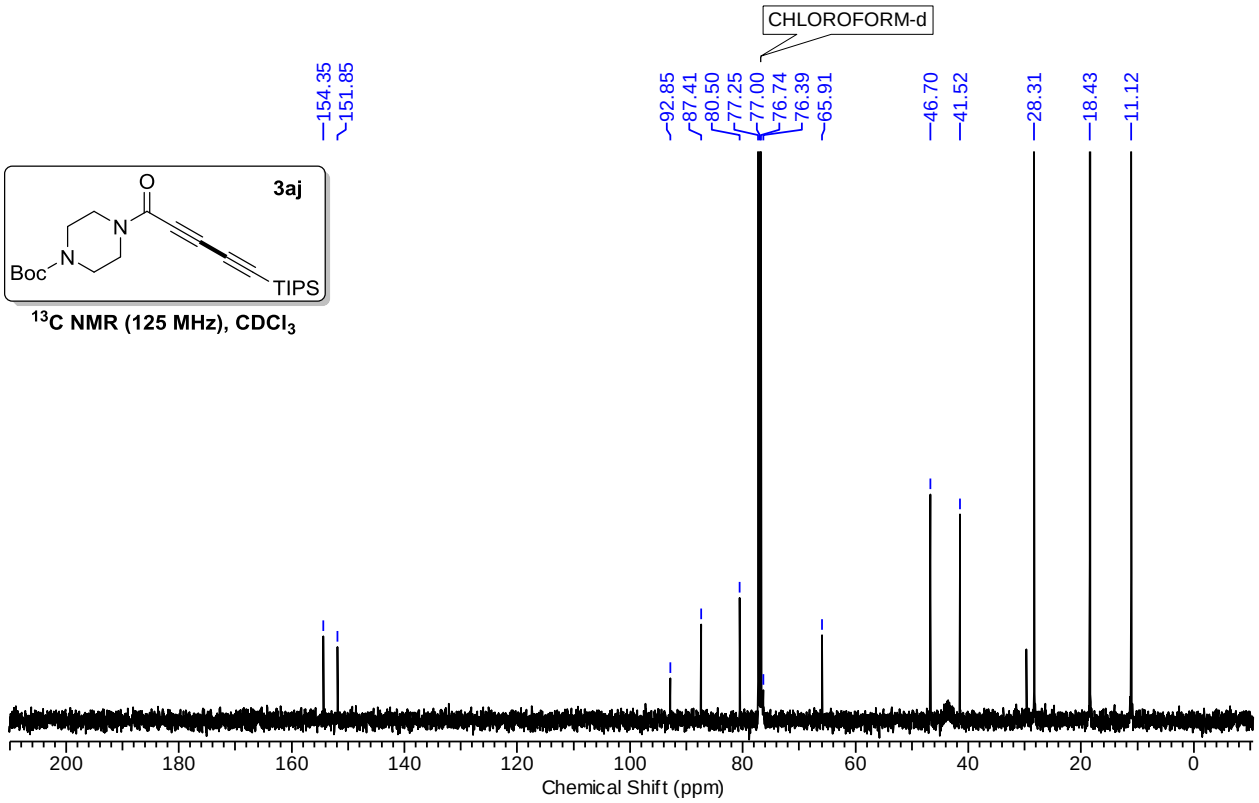
^{1}H NMR (500 MHz), $CDCl_3$



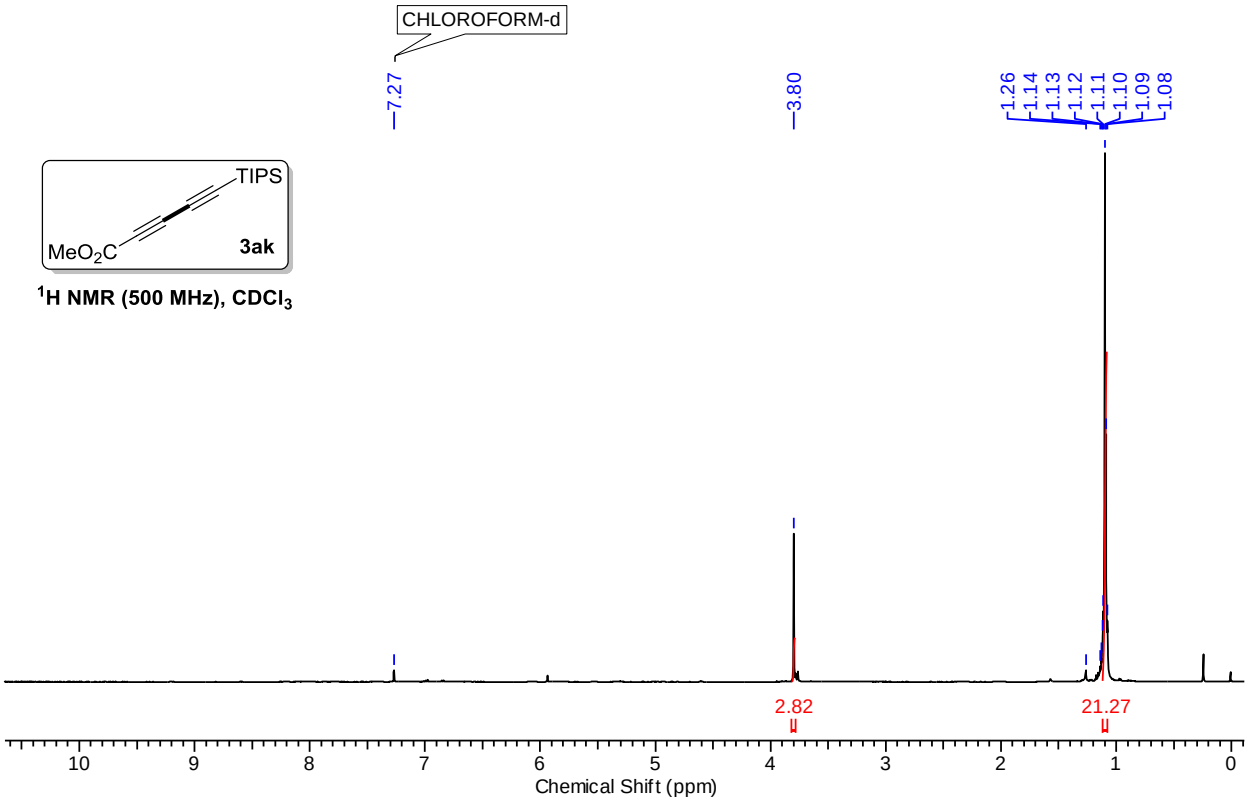
^{13}C NMR (125 MHz), $CDCl_3$



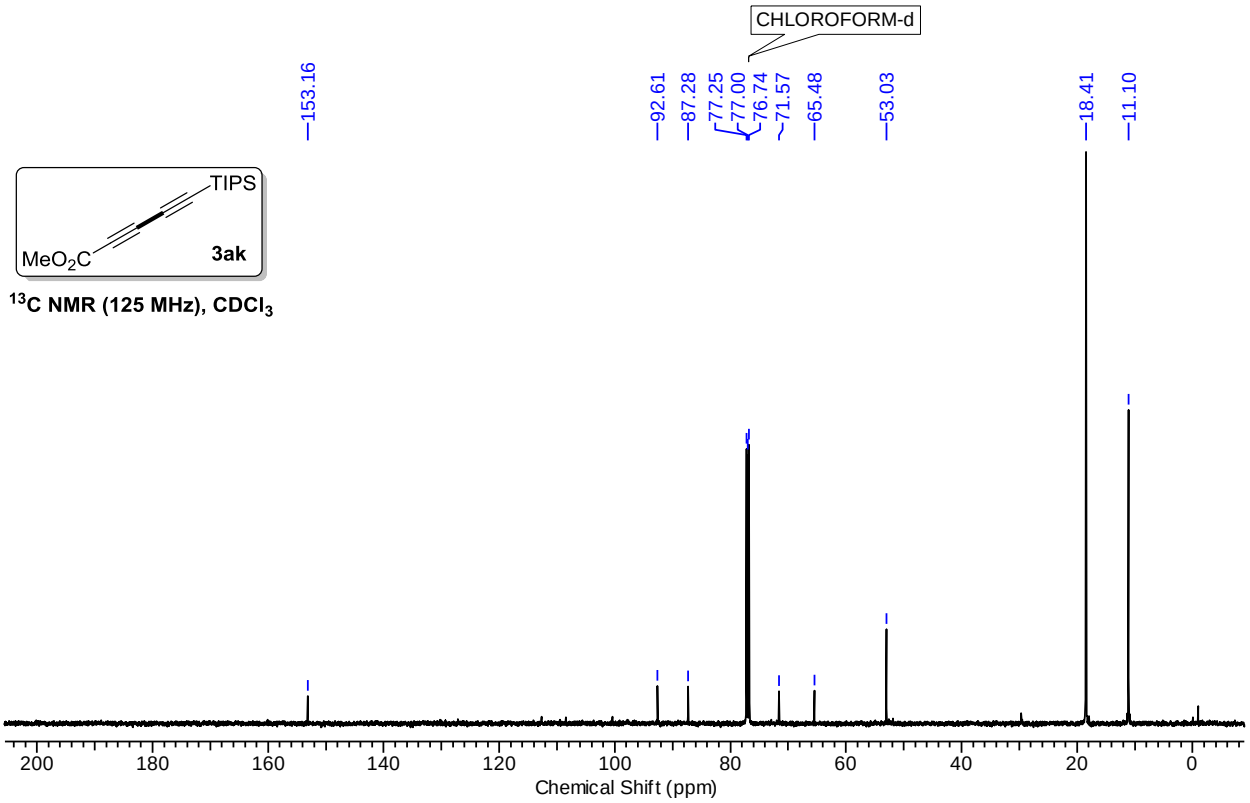
^{1}H NMR (500 MHz), $CDCl_3$



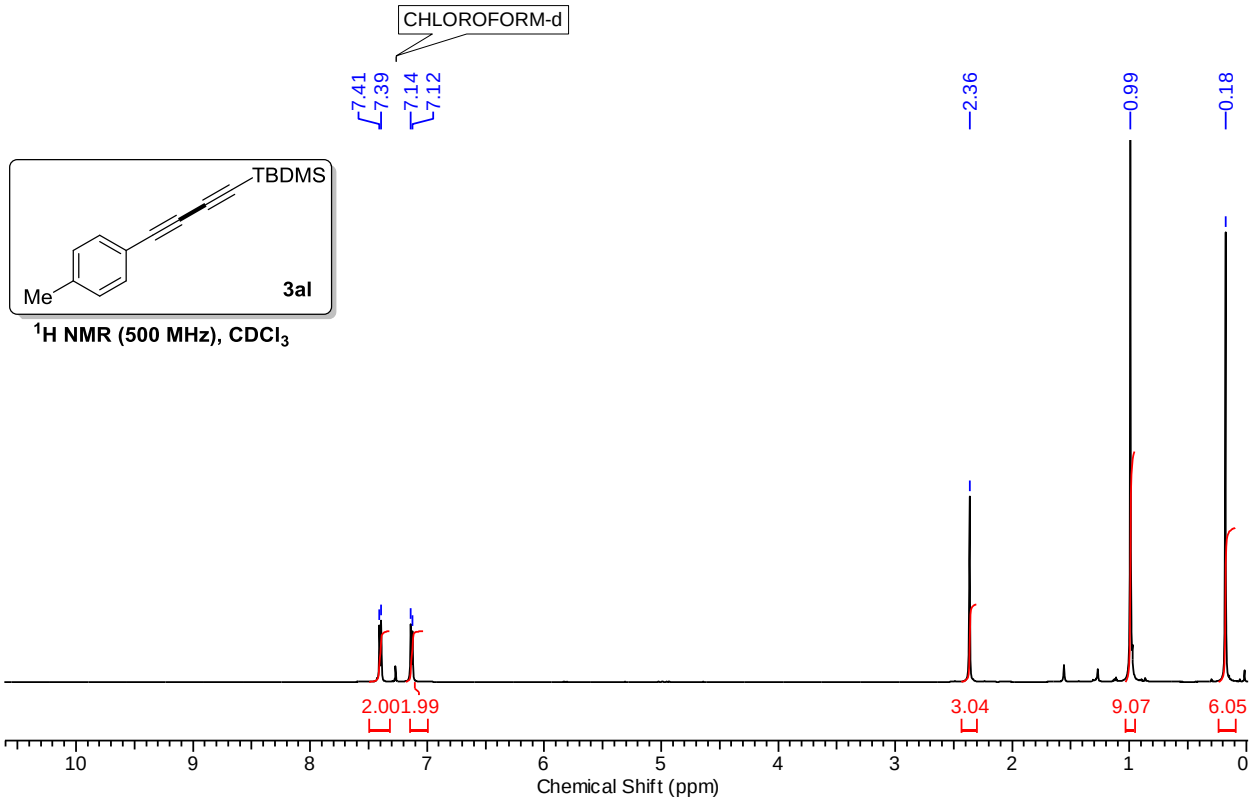
^{13}C NMR (125 MHz), $CDCl_3$



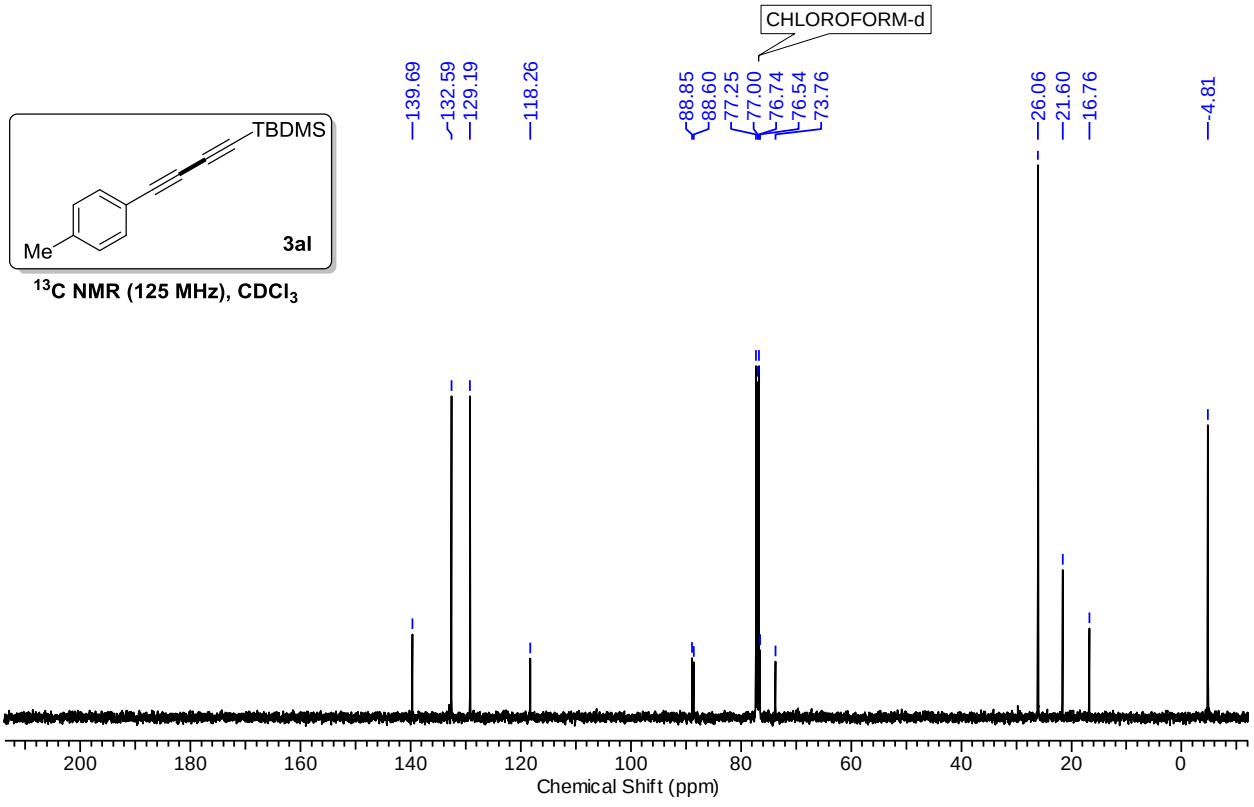
^{1}H NMR (500 MHz), $CDCl_3$



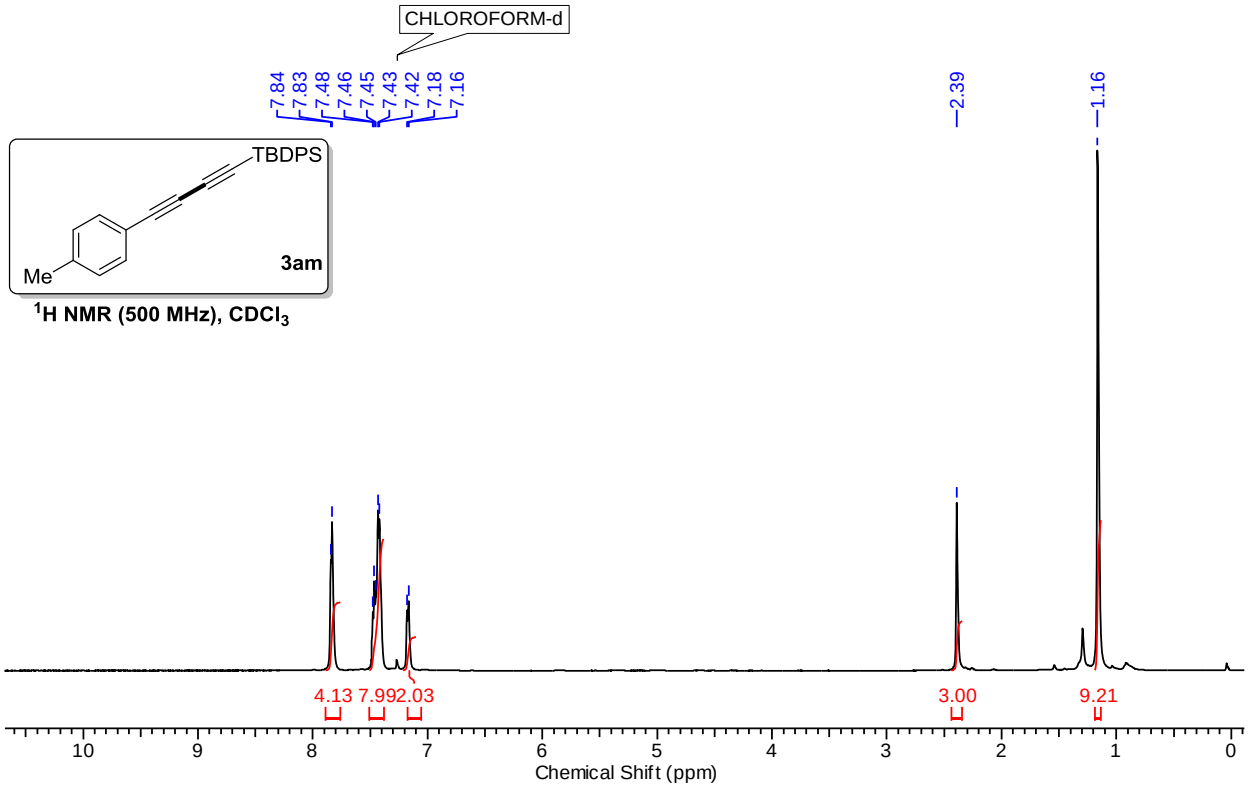
^{13}C NMR (125 MHz), $CDCl_3$



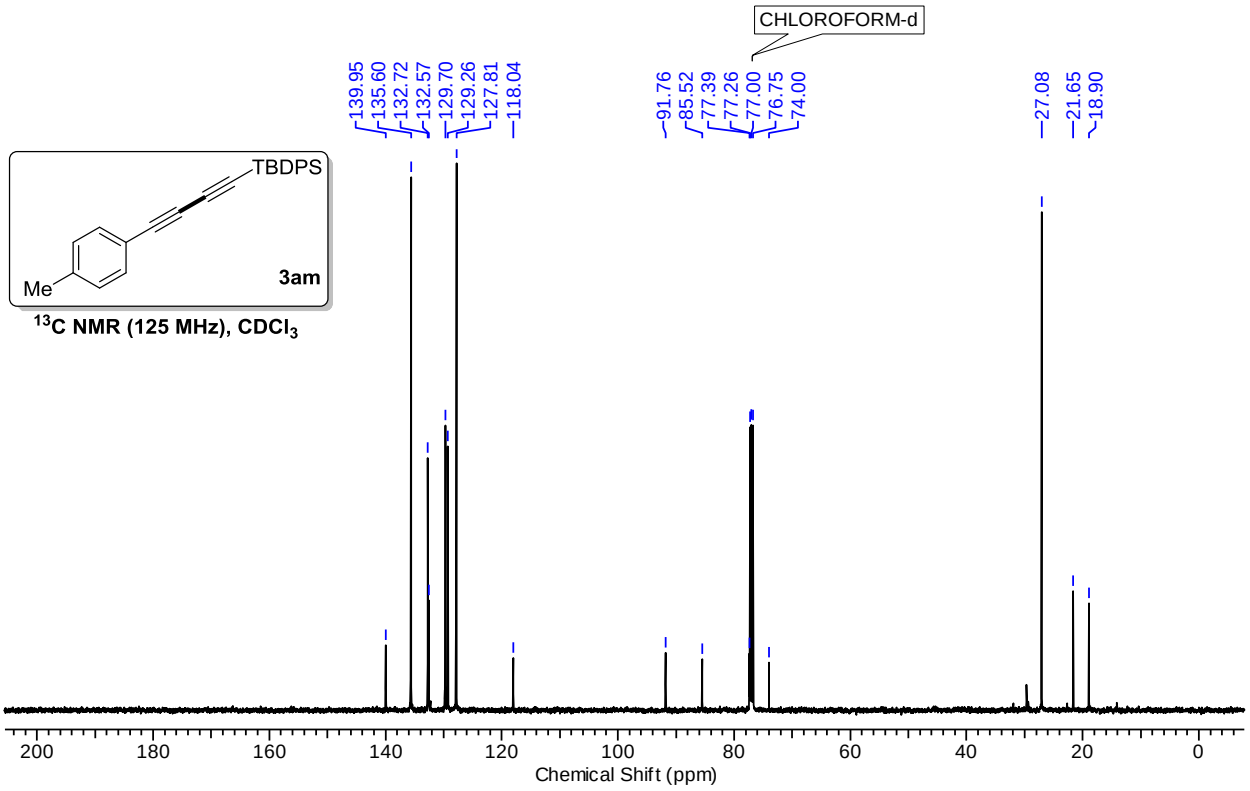
^{1}H NMR (500 MHz), $CDCl_3$



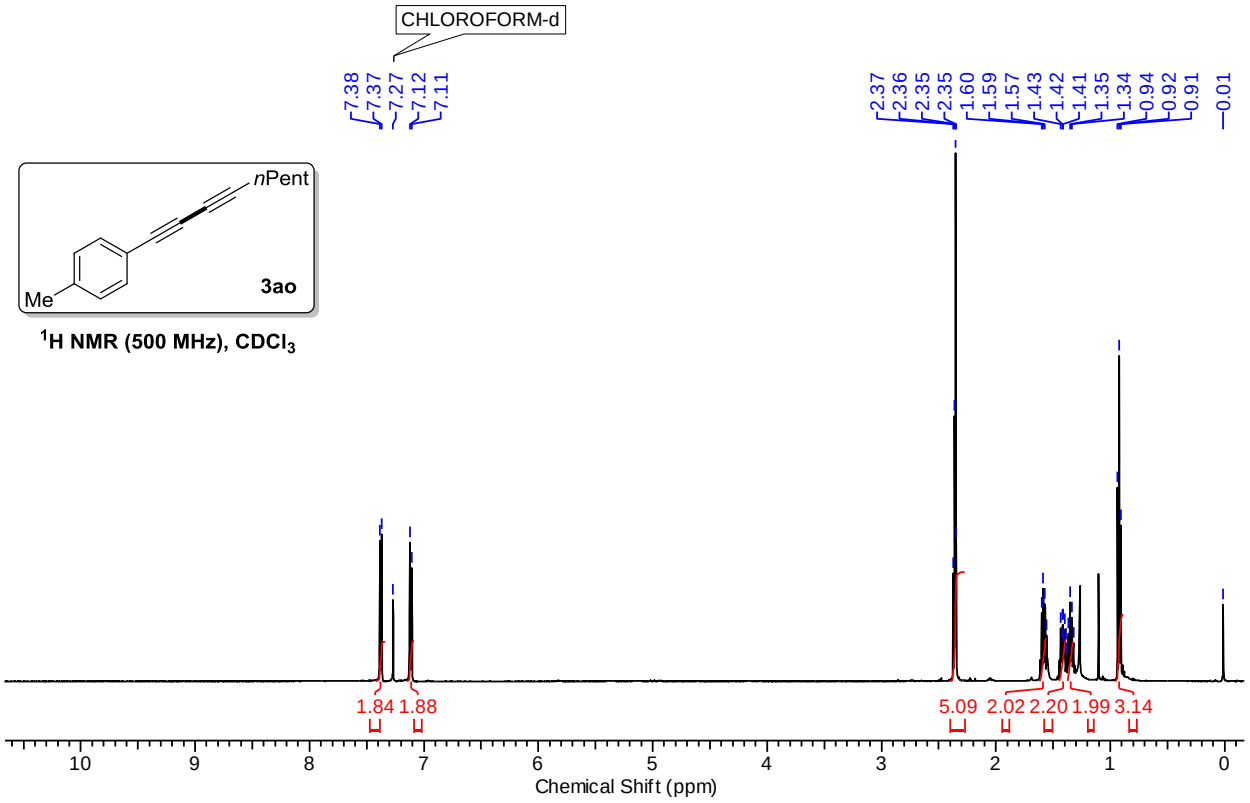
^{13}C NMR (125 MHz), $CDCl_3$



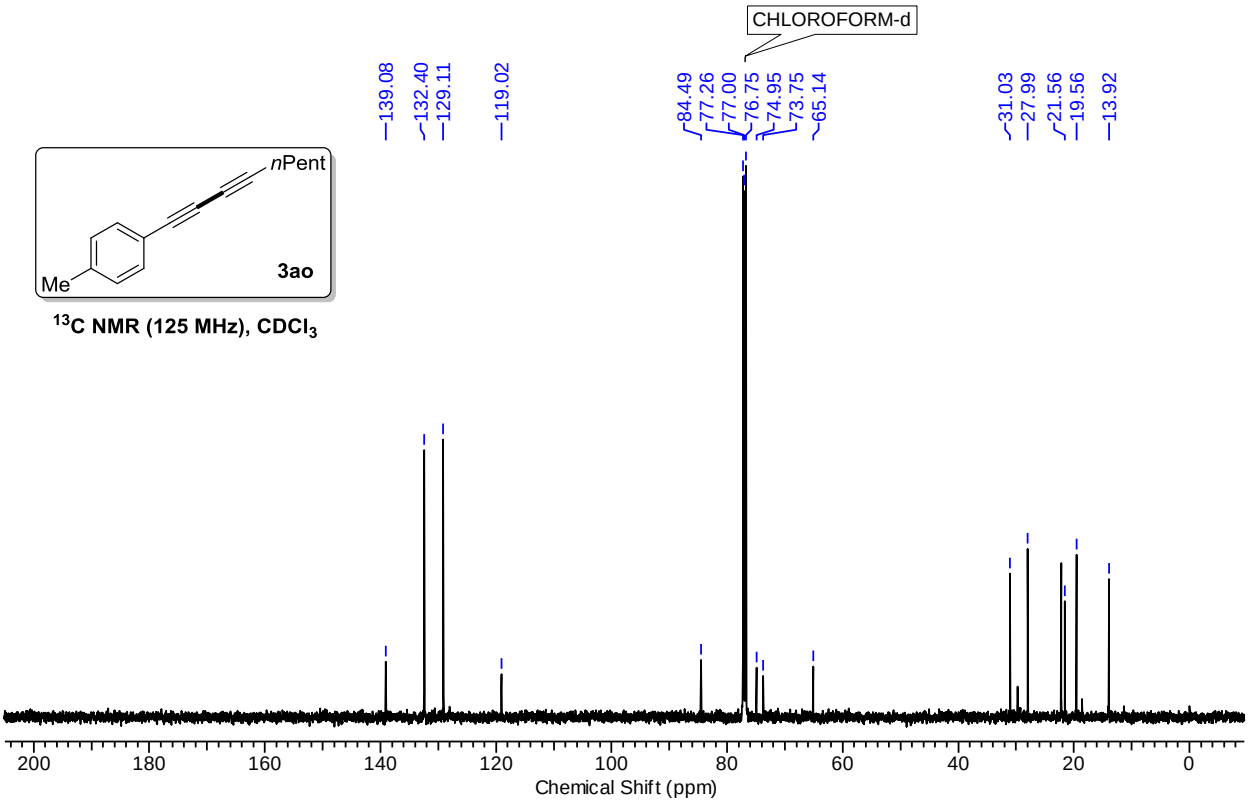
^{1}H NMR (500 MHz), $CDCl_3$



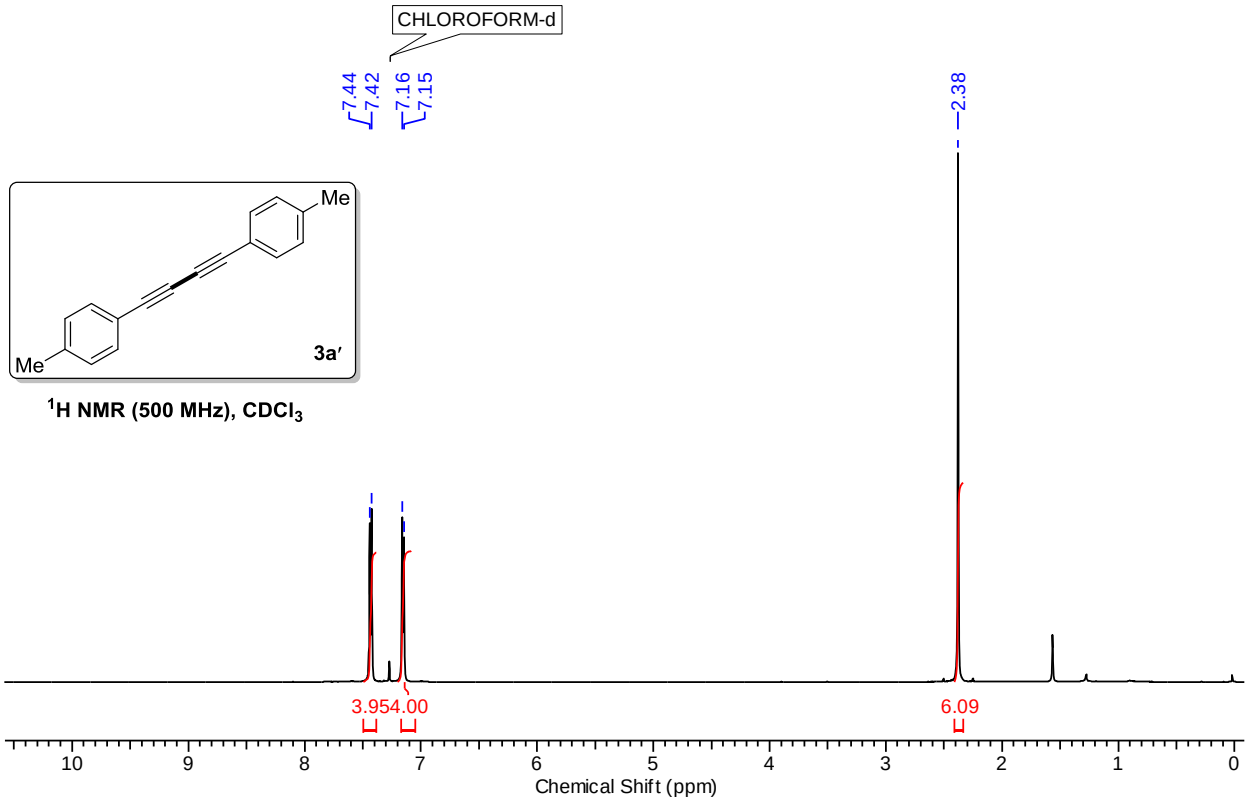
^{13}C NMR (125 MHz), $CDCl_3$



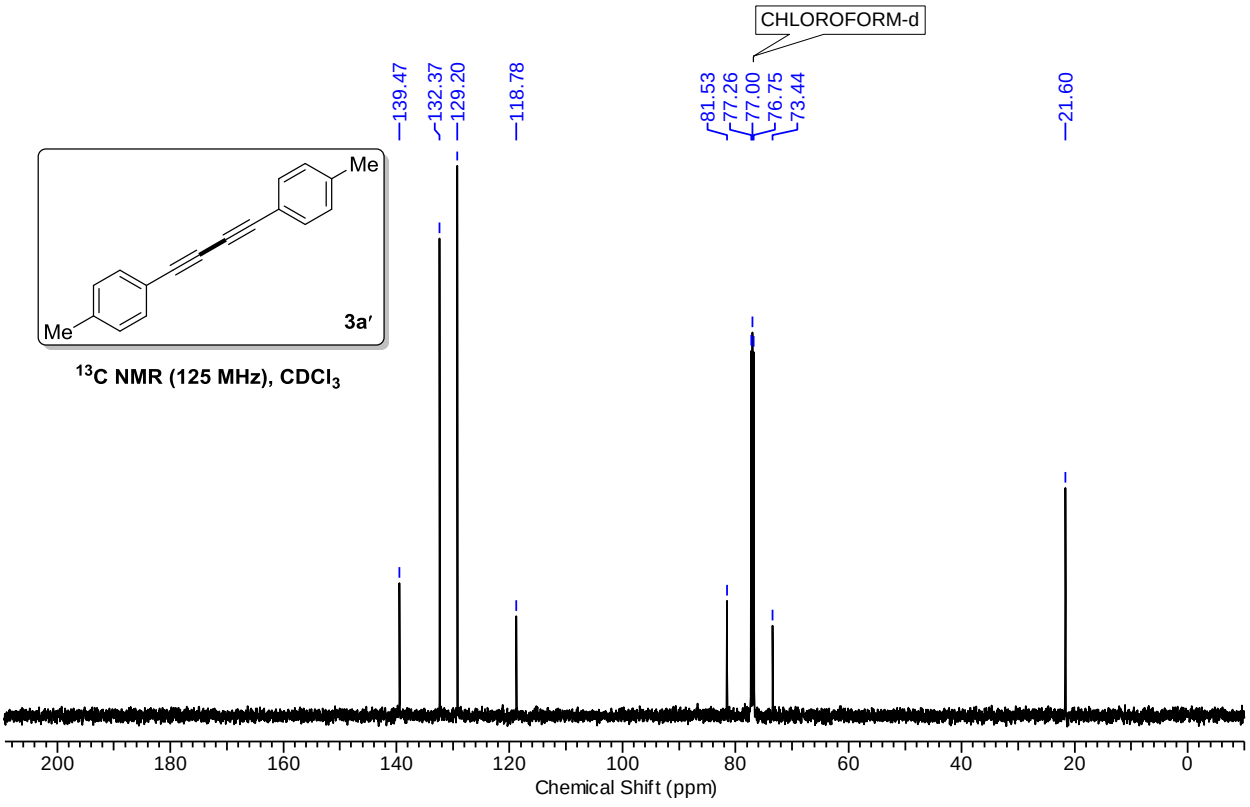
^{1}H NMR (500 MHz), $CDCl_3$



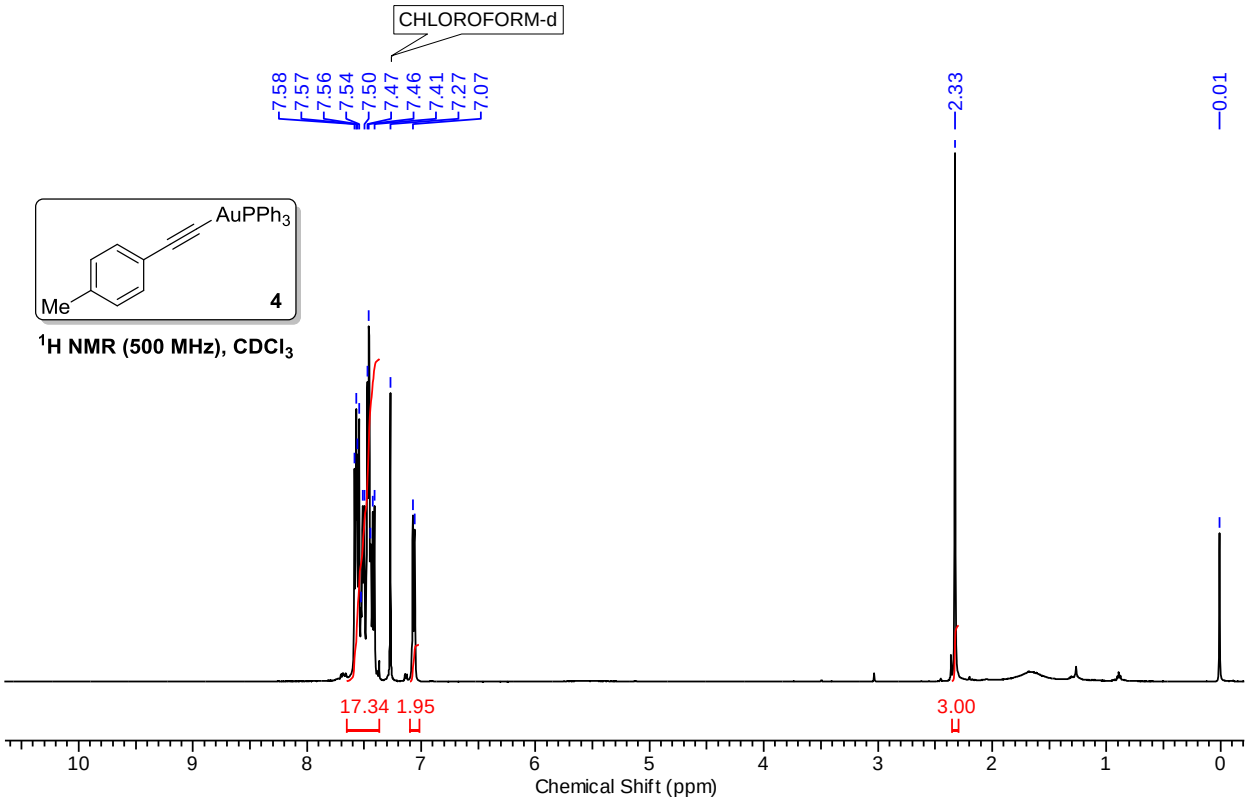
^{13}C NMR (125 MHz), $CDCl_3$



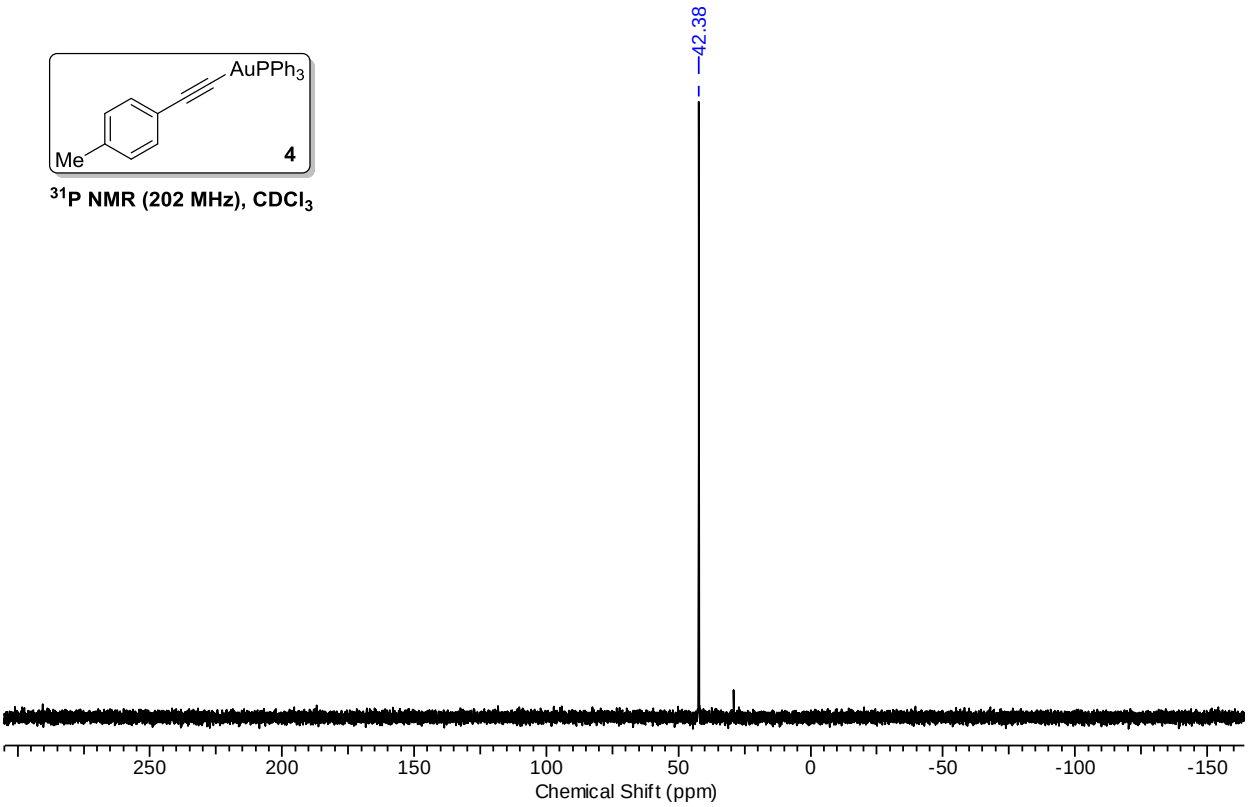
^{1}H NMR (500 MHz), $CDCl_3$



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



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



^{31}P NMR (202 MHz), $CDCl_3$