Supporting Information

Directed Alkynylation of Unactivated C(sp^3)–H bonds with Ethynylbenziodoxolones Mediated by DTBP

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1. General

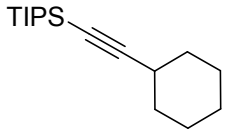
All the reactions were conducted in oven-dried Schlenk tubes. All solvents were obtained from commercial suppliers and used without further purification. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh).

^{1}H NMR and ^{13}C NMR spectra were recorded on a 600 MHz spectrometer in $CDCl_3$ and $(CD_3)_2SO$. Data for ^{1}H NMR are reported as follows: chemical shift (ppm, scale), multiplicity, coupling constant (Hz), and integration. Data for ^{13}C NMR are reported in terms of chemical shift (ppm, scale), multiplicity, and coupling constant (Hz). Gas chromatographic (GC) analyses were performed on a GC equipped with a flameionization detector and an Rtx@-65 (30 m × 0.32 mm ID × 0.25 μm df) column. GC-MS analyses were performed on a GC-MS with an EI mode. High-resolution mass spectra were obtained by ESI on a TOF mass analyzer.

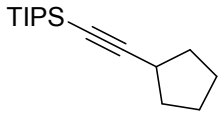
2. General procedure for alkynylation of C-H bonds

A sealed 25 mL Schlenk tube with a magnetic stir bar charged with ethynylbenziodoxolones (0.2 mmol), DTBP (di-tert-butyl peroxide, 1.0 equiv), solvent (1 mL), and the reaction mixture was heated under argon atmosphere for 16 h. The reaction mixture was then allowed to cool to room temperature, diluted with ethyl acetate, washed with water, and then the organic layer was dried over Mg_2SO_4. After concentrated in vacuo, the crude product was purified by column chromatography on silica gel (ethyl acetate : petroleum ether).

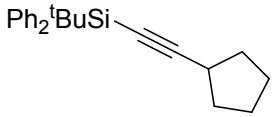
3. The spectral data of all products



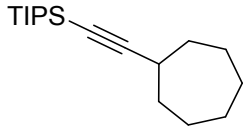
(Cyclohexylethynyl)triisopropylsilane (3aa)[1] : Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether) and **1a** : **2a** = 1:46, obtained in 83 % yield as a colorless oil (43.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.44 (s, 1H), 1.81 – 1.65 (m, 4H), 1.46 (dd, J = 18.6, 9.1 Hz, 3H), 1.35 – 1.26 (m, 3H), 1.10 – 0.94 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 113.5, 79.5, 32.7, 29.7, 25.9, 24.4, 18.6, 11.2.



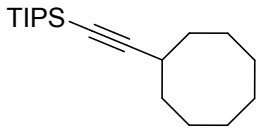
(Cyclopentylethynyl)triisopropylsilane (3ab)[1] : Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether) and **1a** : **2b** = 1:54, obtained in 83 % yield as a colorless oil (36 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.70 – 2.59 (m, 1H), 1.93 – 1.83 (m, 2H), 1.72 (s, 2H), 1.67 – 1.59 (m, 2H), 1.54 (s, 2H), 1.12 – 0.92 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 114.0, 79.0, 34.2, 31.2, 24.9, 18.6, 11.2.



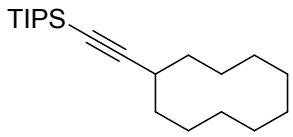
tert-butyl(cyclopentylethynyl)diphenylsilane (3bb) : Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether) and **1b** : **2b** = 1:54, obtained in 41 % yield as a colorless oil (27.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, J = 6.3 Hz, 4H), 7.37 (t, J = 7.3 Hz, 6H), 2.88 – 2.78 (m, 1H), 2.04 – 1.96 (m, 2H), 1.86 – 1.73 (m, 4H), 1.62 (d, J = 3.7 Hz, 2H), 1.07 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 135.5, 134.0, 129.2, 127.5, 116.5, 78.4, 34.0, 31.3, 27.0, 25.0, 18.5. HRMS calcd for $C_{23}H_{28}Si$ $[M + H]^+$ 332.1960; found: 332.1962.



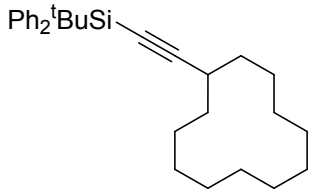
(cycloheptylethynyl)triisopropylsilane (3ac)[2] : Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether) and **1a** : **2c** = 1:41, obtained in 52 % yield as a colorless oil (28.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.65 (s, 1H), 1.78 (dd, J = 11.1, 3.7 Hz, 2H), 1.70 (dd, J = 11.8, 7.0 Hz, 4H), 1.60 – 1.46 (m, 6H), 1.03 (dd, J = 18.2, 5.9 Hz, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 114.1, 79.7, 34.7, 31.9, 27.7, 25.4, 18.6, 11.3.



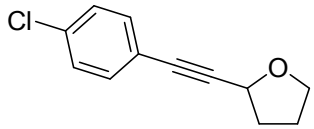
(cyclooctylethynyl)triisopropylsilane (3ad) : Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether) and **1a** : **2d** = 1:37, obtained in 71 % yield as a colorless oil (41.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.62 (td, J = 8.1, 4.1 Hz, 1H), 1.88 – 1.80 (m, 2H), 1.77 – 1.63 (m, 4H), 1.60 – 1.40 (m, 8H), 1.11 – 0.96 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 114.5, 79.3, 31.6, 31.2, 27.4, 25.3, 24.3, 18.6, 11.3. HRMS calcd for $C_{19}H_{36}Si$ $[M + H]^+$ 292.2586; found: 292.2588.



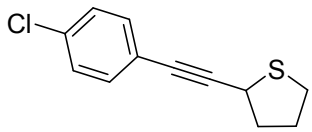
(cyclodecylethynyl)triisopropylsilane (3ae) : Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether) and **1a** : **2e** = 1:31, obtained in 67 % yield as a colorless oil (42.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.78 – 2.56 (m, 1H), 1.78 – 1.63 (m, 6H), 1.51 (s, 12H), 1.08 – 1.02 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 114.4, 78.8, 30.3, 29.9, 25.1, 24.9, 24.3, 23.3, 18.6, 11.2. HRMS calcd for $C_{19}H_{36}Si$ $[M + H]^+$ 320.2899; found: 320.2897.



tert-butyl(cyclododecylethynyl)diphenylsilane (3bf) : Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether) and **1b** : **2f** = 1:5, obtained in 53 % yield as a pale yellow oil (45.6 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, J = 6.6 Hz, 4H), 7.37 (d, J = 7.0 Hz, 6H), 2.70 – 2.65 (m, 1H), 1.74 (dd, J = 13.4, 6.7 Hz, 2H), 1.65 – 1.58 (m, 4H), 1.37 (dd, J = 32.0, 8.8 Hz, 16H), 1.10 (d, J = 22.3 Hz, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 135.5, 134.0, 129.2, 127.5, 116.6, 78.4, 29.9, 28.2, 27.0, 23.9, 23.4, 22.2. HRMS calcd for $C_{30}H_{42}Si$ $[M + H]^+$ 430.3056; found: 430.3053.

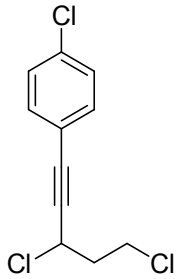


2-((4-chlorophenyl)ethynyl)tetrahydrofuran (3cg)[3] : Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether) and **1c** : **2g** = 1:69, obtained in 70 % yield as a pale yellow oil (28.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (d, J = 8.4 Hz, 2H), 7.28 – 7.25 (m, 2H), 4.82 – 4.77 (m, 1H), 4.00 (dd, J = 14.6, 7.1 Hz, 1H), 3.85 (dd, J = 13.6, 7.8 Hz, 1H), 2.26 – 2.19 (m, 1H), 2.11 – 2.04 (m, 2H), 1.95 (dd, J = 13.3, 5.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.2, 132.9, 128.5, 121.2, 90.0, 83.3, 68.5, 67.9, 33.3, 25.4.

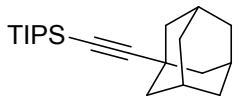


2-((4-chlorophenyl)ethynyl)tetrahydrothiophene (3ch) : Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether) and **1c** : **2h** = 1:57, obtained in 45 % yield as a pale yellow oil (19.9

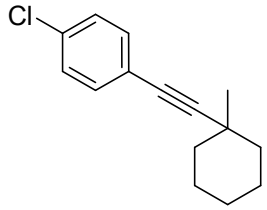
mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (d, J = 8.3 Hz, 2H), 7.25 (d, J = 8.7 Hz, 2H), 4.25 (t, J = 5.3 Hz, 1H), 3.15 – 3.07 (m, 1H), 2.94 (d, J = 5.9 Hz, 1H), 2.23 (d, J = 6.6 Hz, 2H), 2.15 (dd, J = 11.8, 5.9 Hz, 1H), 2.10 – 2.05 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 133.9, 132.8, 128.4, 121.7, 91.7, 81.7, 38.8, 36.8, 32.9, 30.4. HRMS calcd for $C_{12}H_{11}ClS$ $[M + H]^+$ 222.0270; found: 222.0272.



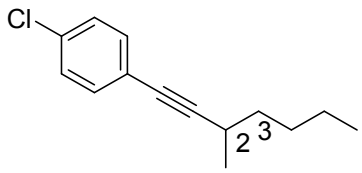
1-chloro-4-(3,5-dichloropent-1-ynyl)benzene (3ci) : Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether) and **1c** : **2i** = 1:53, obtained in 61 % yield as a pale yellow oil (29.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (t, J = 10.3 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 5.00 (t, J = 6.8 Hz, 1H), 3.78 (ddd, J = 16.9, 10.1, 4.7 Hz, 2H), 2.47 (q, J = 6.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 135.1, 133.0, 128.7, 120.2, 86.9, 85.6, 45.9, 41.4, 40.8. HRMS calcd for $C_{11}H_9Cl_3$ $[M + H]^+$ 245.9770; found: 245.9772.



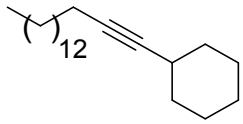
(Adamantan-1-ylethynyl)triisopropylsilane (3aj)[4] : Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether) and **1a** : **2j** = 1:5, obtained in 59 % yield as a colorless oil (37.3 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.94 (s, 3H), 1.88 (s, 6H), 1.75 (s, 2H), 1.68 (s, 4H), 1.11 – 0.98 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 118.0, 77.4, 43.0, 36.4, 30.3, 28.0, 18.6, 11.2.



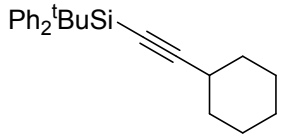
1-Chloro-4-((1-methylcyclohexyl)ethynyl)benzene (3ck)[1] : Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether) and **1c** : **2k** = 1:39, obtained in 65 % yield as a colorless oil (30.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (d, J = 8.4 Hz, 2H), 7.24 (dd, J = 9.1, 4.3 Hz, 2H), 1.80 (d, J = 12.6 Hz, 2H), 1.71 – 1.64 (m, 3H), 1.60 (dd, J = 10.0, 3.4 Hz, 2H), 1.26 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 133.2, 132.7, 128.3, 122.7, 97.8, 80.7, 39.4, 33.1, 30.1, 25.8, 23.4.



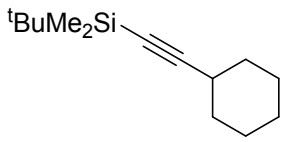
1-chloro-4-(3-methylhept-1-ynyl)benzene, 1-chloro-4-(3-ethylhex-1-ynyl)benzene (3cl) : Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether) and **1c** : **2l** = 1:40, obtained in 54 % yield as a colorless oil (23.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 8.4, 2.2 Hz, 3H), 7.26 – 7.22 (m, 4H), 2.62 (dd, *J* = 13.2, 6.6 Hz, 1H), 2.47 (t, *J* = 6.7 Hz, 0.62H), 1.62 – 1.54 (m, 3H), 1.50 (d, *J* = 4.4 Hz, 6H), 1.37 – 1.31 (m, 3H), 1.28 – 1.21 (m, 9H), 1.04 (t, *J* = 7.4 Hz, 2H), 0.97 – 0.85 (m, 7H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 133.2, 132.7, 132.7, 128.4, 124.2, 122.6, 95.9, 94.7, 80.7, 79.5, 36.8, 36.6, 33.7, 28.0, 26.5, 22.5, 20.9, 20.6, 14.0, 11.8. HRMS calcd for $C_{14}H_{17}Cl$ $[M + H]^+$ 220.1019; found: 220.1016.



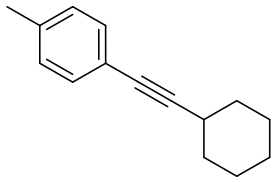
pent-1-ynylcyclohexane (4a) : Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether) and **1a** : **2a** = 1:46, obtained in 55 % yield as a pale yellow oil (33.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.14 (dd, *J* = 14.1, 6.7 Hz, 2H), 1.73 (dd, *J* = 45.9, 8.3 Hz, 3H), 1.47 (dd, *J* = 14.4, 7.2 Hz, 3H), 1.37 (d, *J* = 6.9 Hz, 4H), 1.26 (s, 24H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 84.6, 80.2, 33.2, 31.9, 29.7, 29.6, 29.5, 29.3, 29.1, 28.8, 28.5, 25.9, 24.9, 22.6, 20.8, 18.7, 14.1. HRMS calcd for $C_{22}H_{40}$ $[M + H]^+$ 304.3130; found: 304.3132.



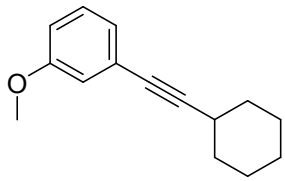
tert-butyl(cyclohexylethynyl)diphenylsilane (4b) : Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether) and **1b** : **2a** = 1:46, obtained in 49 % yield as a colorless oil (33.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 – 7.81 (m, 4H), 7.40 (t, *J* = 9.4 Hz, 6H), 2.63 (s, 1H), 1.91 (d, *J* = 4.5 Hz, 2H), 1.81 (dd, *J* = 6.3, 2.3 Hz, 2H), 1.65 (d, *J* = 9.2 Hz, 2H), 1.54 (s, 1H), 1.40 (d, *J* = 10.0 Hz, 3H), 1.10 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 135.5, 133.9, 129.2, 127.5, 116.0, 78.8, 32.5, 30.0, 27.0, 25.9, 24.6, 18.5. HRMS calcd for $C_{24}H_{30}Si$ $[M + H]^+$346.2117; found: 346.2119.



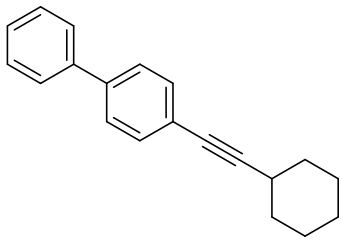
tert-butyl(cyclohexylethynyl)dimethylsilane (4c)[2] : Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether) and **1c** : **2a** = 1:46, obtained in 62 % yield as a colorless oil (27.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.41 (s, 1H), 1.76 (d, *J* = 8.7 Hz, 2H), 1.74 – 1.67 (m, 2H), 1.52 – 1.42 (m, 3H), 1.31 (d, *J* = 6.1 Hz, 3H), 0.92 (s, 9H), 0.07 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 112.3, 81.8, 32.6, 29.8, 26.0, 25.8, 24.6, 16.5, -4.4.



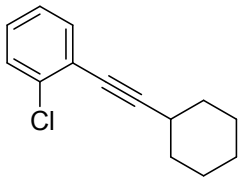
1-(cyclohexylethynyl)-4-methylbenzene (4d)[5] : Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether) and **1d** : **2a** = 1:46, obtained in 70 % yield as a colorless oil (27.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.8 Hz, 2H), 7.08 (d, *J* = 7.7 Hz, 2H), 2.57 (s, 1H), 2.32 (s, 3H), 1.87 (d, *J* = 10.5 Hz, 2H), 1.75 (d, *J* = 4.2 Hz, 2H), 1.53 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.3, 131.3, 128.8, 120.9, 93.6, 80.4, 32.7, 29.6, 25.9, 24.9, 21.3.



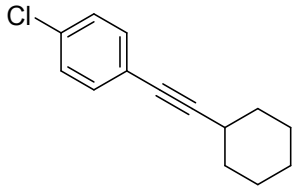
1-(cyclohexylethynyl)-3-methoxybenzene (4e) : Following general procedure, The product was purified by flash column chromatography on silica gel (ethyl acetate:petroleum ether = 1:50) and **1e** : **2a** = 1:46, obtained in 42 % yield as a colorless oil (17.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.9 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.92 (s, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 3.79 (s, 3H), 2.58 (s, 1H), 1.92 – 1.84 (m, 2H), 1.76 (d, *J* = 4.7 Hz, 2H), 1.53 (d, *J* = 9.5 Hz, 3H), 1.35 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.2, 129.1, 125.1, 124.1, 116.3, 114.0, 94.3, 80.4, 55.2, 32.6, 29.6, 25.9, 24.9. HRMS calcd for $C_{15}H_{18}O$ $[M + H]^+$214.1358; found: 214.1361.



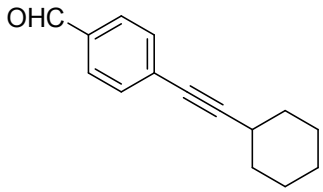
4-(cyclohexylethynyl)biphenyl (4f) : Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether) and **1f** : **2a** = 1:46, obtained in 60 % yield as a pale yellow oil (31.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.3 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 2.63 (s, 1H), 1.99 – 1.87 (m, 2H), 1.79 (s, 2H), 1.57 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.5, 140.0, 131.9, 128.7, 127.4, 126.9, 126.8, 123.0, 95.1, 80.3, 32.7, 29.7, 25.9, 24.9. HRMS calcd for $C_{20}H_{20}$ $[M + H]^+$260.1565; found: 260.1567.



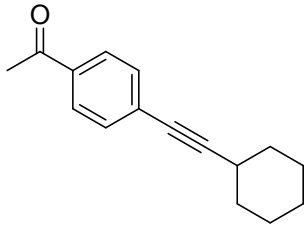
1-chloro-2-(cyclohexylethynyl)benzene (4g) : Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether) and **1g** : **2a** = 1:46, obtained in 58 % yield as a pale yellow oil (25.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.41 (m, 1H), 7.36 (d, *J* = 8.5 Hz, 1H), 7.20 – 7.14 (m, 2H), 2.68 (s, 1H), 1.88 (d, *J* = 7.8 Hz, 2H), 1.79 (dd, *J* = 9.4, 3.4 Hz, 2H), 1.60 (d, *J* = 10.4 Hz, 3H), 1.39 (d, *J* = 8.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 135.8, 133.1, 129.0, 128.3, 126.2, 123.9, 100.1, 32.4, 29.7, 25.9, 24.6. HRMS calcd for $C_{14}H_{15}Cl$ $[M + H]^+$218.0862; found: 218.0864.



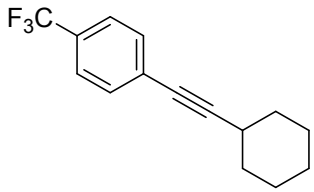
1-chloro-4-(2-cyclohexylethynyl)benzene (4h)[6] : Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether) and **1h** : **2a** = 1:46, obtained in 54 % yield as a colorless oil (23.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 2.56 (s, 1H), 1.87 (d, *J* = 10.9 Hz, 2H), 1.80 – 1.69 (m, 2H), 1.53 (dd, *J* = 23.9, 13.0 Hz, 3H), 1.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.2, 132.7, 128.4, 122.6, 95.5, 79.4, 32.5, 29.6, 25.8, 24.8.



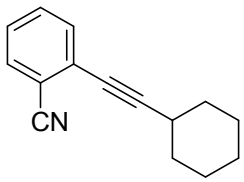
4-(cyclohexylethynyl)benzaldehyde (4i) : Following general procedure, The product was purified by flash column chromatography on silica gel (ethyl acetate:petroleum ether = 1:50) and **1i** : **2a** = 1:46, obtained in 39 % yield as a pale yellow oil (16.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 2.62 (s, 1H), 1.89 (d, *J* = 10.3 Hz, 2H), 1.75 (dd, *J* = 9.1, 4.2 Hz, 2H), 1.59 – 1.49 (m, 3H), 1.36 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.5, 132.4, 132.0, 130.6, 129.4, 99.2, 80.0, 32.4, 29.6, 25.8, 24.8. HRMS calcd for $C_{15}H_{16}O$ $[M + H]^+$212.1201; found:212.1204.



(p-Anisyl)cyclohexylacetylene (4j)[7] : Following general procedure, The product was purified by flash column chromatography on silica gel (ethyl acetate:petroleum ether = 1:50) and **1j** : **2a** = 1:46, obtained in 41 % yield as a pale yellow oil (18.5 mg). ^{1}H NMR (600 MHz, DMSO) δ 7.89 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 2.66 (s, 1H), 2.55 (s, 3H), 1.81 (s, 2H), 1.66 (s, 2H), 1.53 – 1.42 (m, 3H), 1.32 (d, *J* = 8.1 Hz, 3H). ^{13}C NMR (151 MHz, DMSO) δ 197.1, 131.9, 131.4, 128.3, 125.8, 97.9, 84.3, 39.7, 31.9, 28.8, 26.6, 25.2.



1-(Cyclohexylethynyl)-4-(trifluoromethyl)benzene (4k)[8] : Following general procedure, The product was purified by flash column chromatography on silica gel (petroleum ether) and **1k** : **2a** = 1:46, obtained in 70 % yield as a pale yellow solid (35.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 8.1 Hz, 2H), 2.60 (s, 1H), 1.93 – 1.84 (m, 2H), 1.80 – 1.71 (m, 2H), 1.54 (d, *J* = 10.7 Hz, 3H), 1.36 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 131.7, 129.2, 128.0, 125.04 (q, *J* = 3.7 Hz), 124.2, 97.2, 79.4, 32.5, 29.6, 25.8, 24.8.



2-(cyclohexylethynyl)benzonitrile (4l) : Following general procedure, The product was purified by flash column chromatography on silica gel (ethyl acetate:petroleum ether = 1:50) and **1l** : **2a** = 1:46, obtained in 61 % yield as a pale yellow oil (25.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 2.6 Hz, 2H), 7.33 (dd, *J* = 10.6, 5.7 Hz, 1H), 2.69 (s, 1H), 1.90 (d, *J* = 7.5 Hz, 2H), 1.82 – 1.75 (m, 2H), 1.65 – 1.54 (m, 3H), 1.39 (d, *J* = 8.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 132.4, 132.1 (d, *J* = 8.3 Hz), 128.1, 127.4, 117.7, 115.4, 101.8, 77.2, 32.2, 29.7, 25.8, 24.6. HRMS calcd for $C_{15}H_{15}N$ $[M + H]^+$209.1204; found:209.1206.

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3. Wan, M.; Meng, Z.; Lou, H.; Liu, L. *Angew. Chem. Int. Ed.* **2014**, *126*, 14065.
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5. Jia, K.; Zhang, F.; Huang, H.; Chen, Y. *J. Am. Chem. Soc.* **2016**, *138*, 1514.
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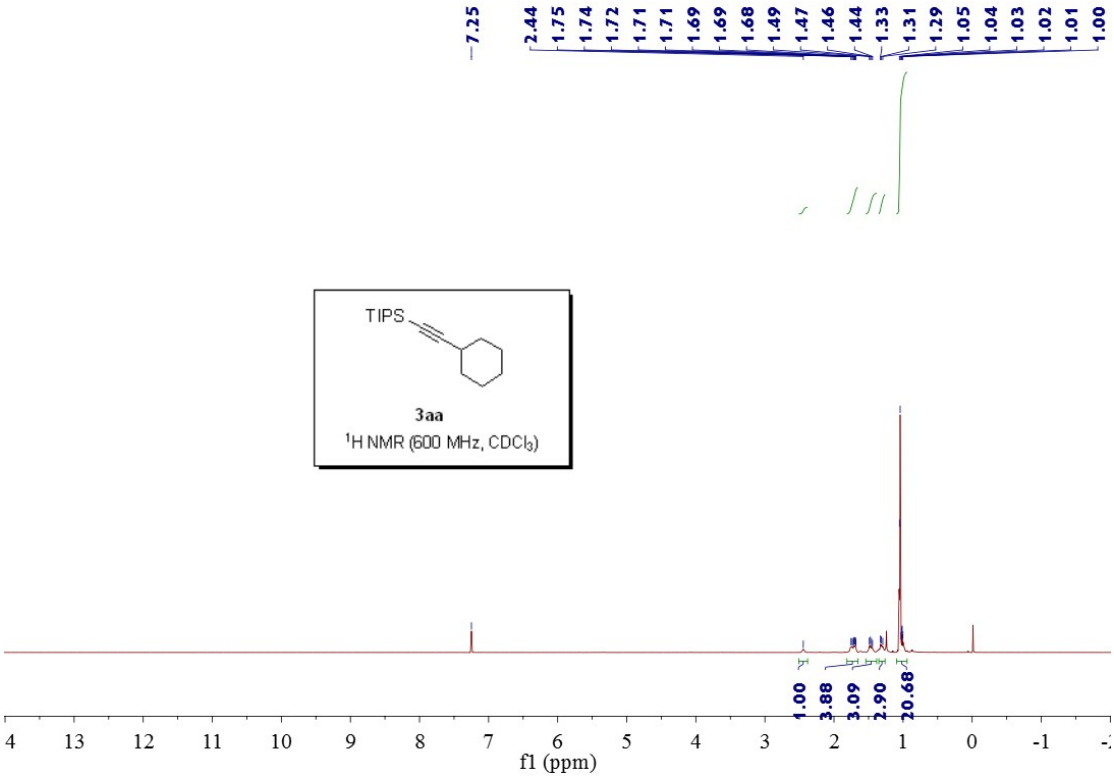
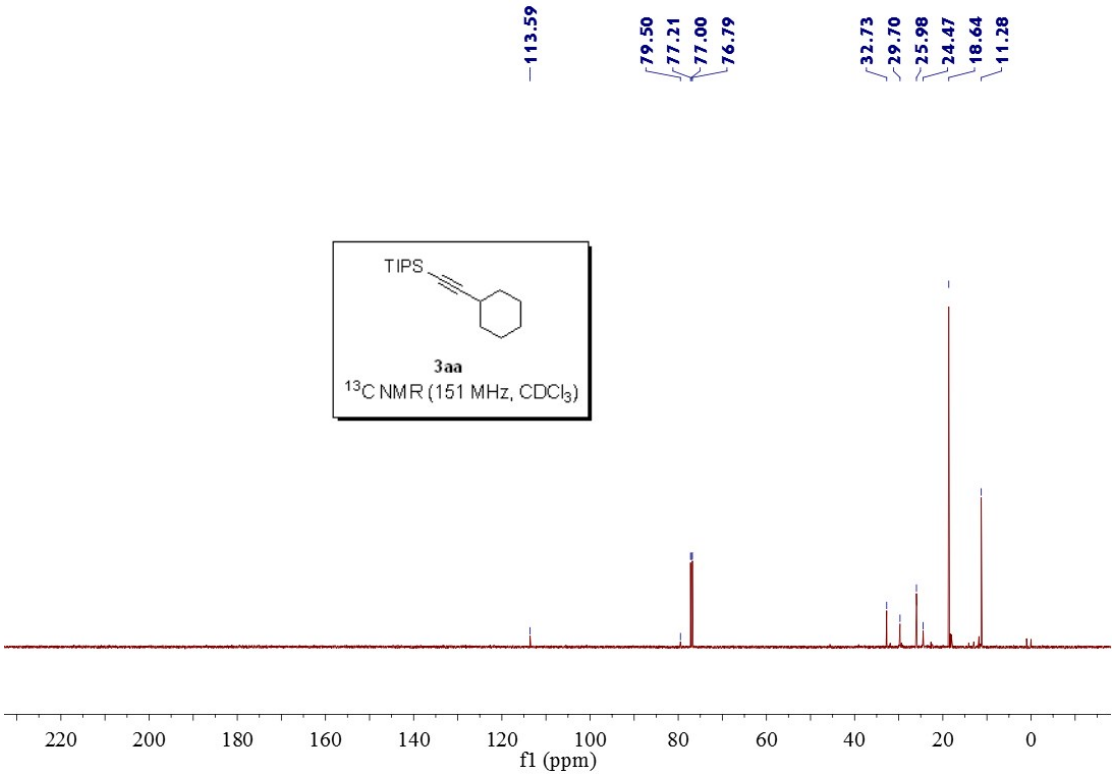
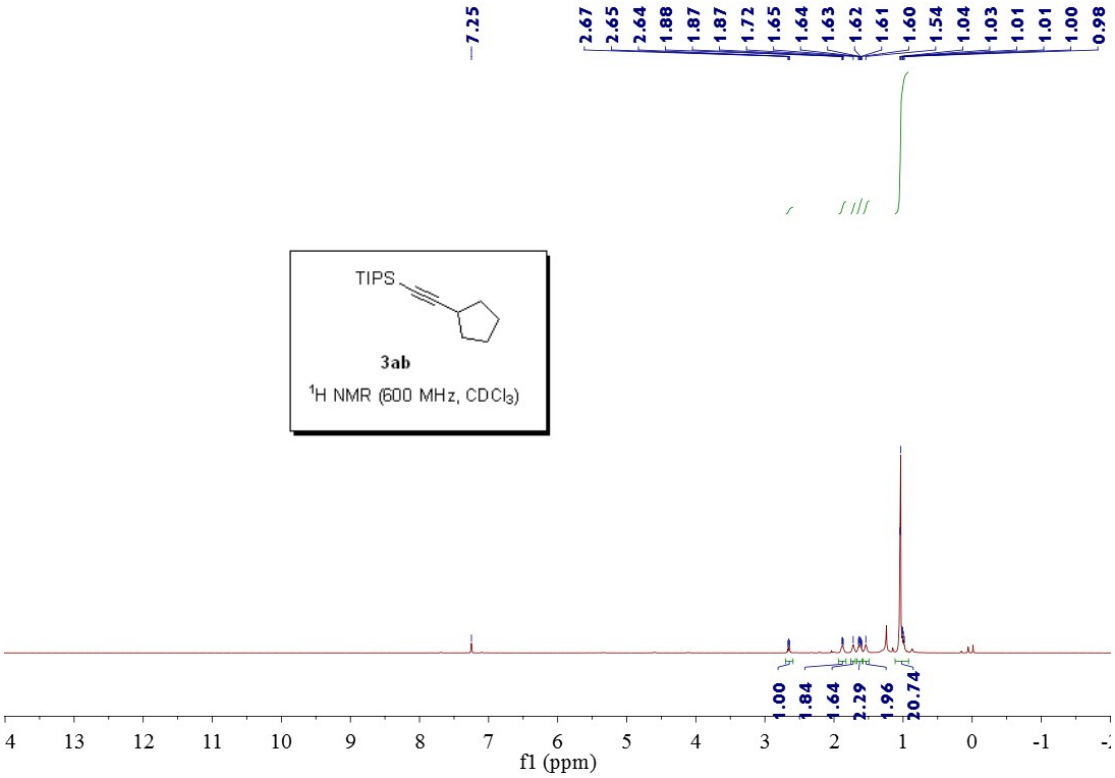
8. Melzig, L.; Metzger, A.; Knochel, P. *Chem. Eur. J*. **2011**, *17*, 2948

^{1}H NMR, ^{13}C NMR Spectra of products



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1.64
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1.62
1.61
1.60
1.54
1.04
1.03
1.01
1.01
1.00
0.98
TIPS
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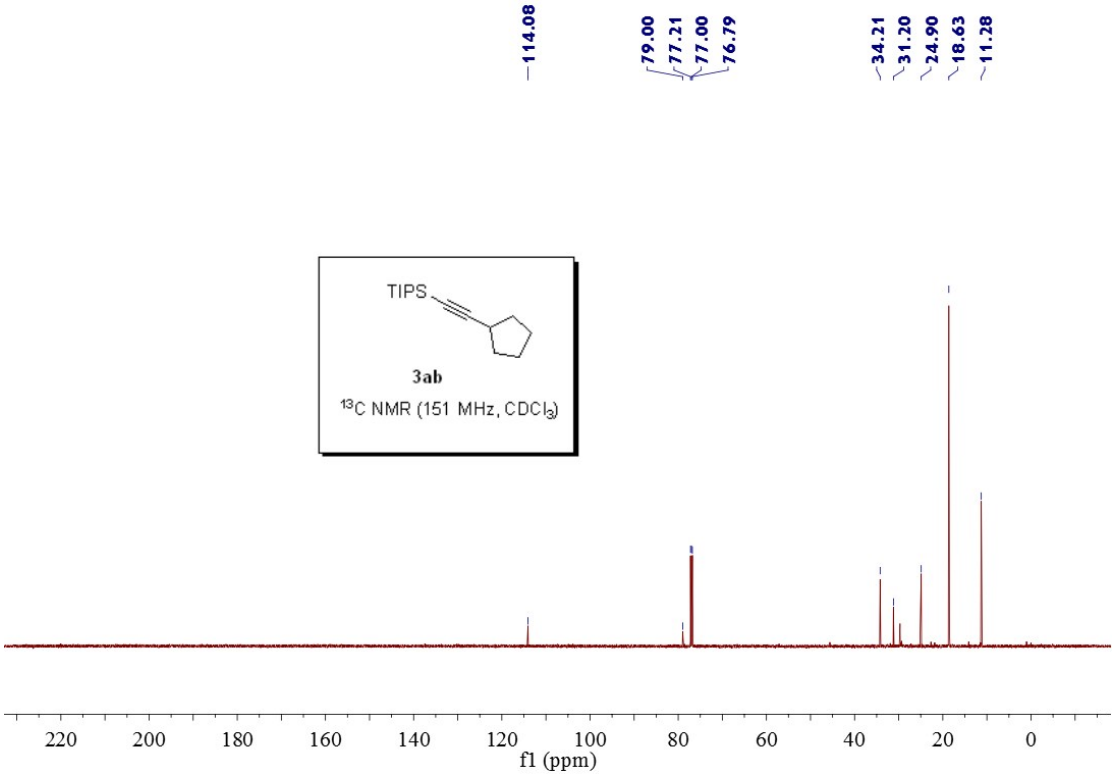
20.74
fl (ppm)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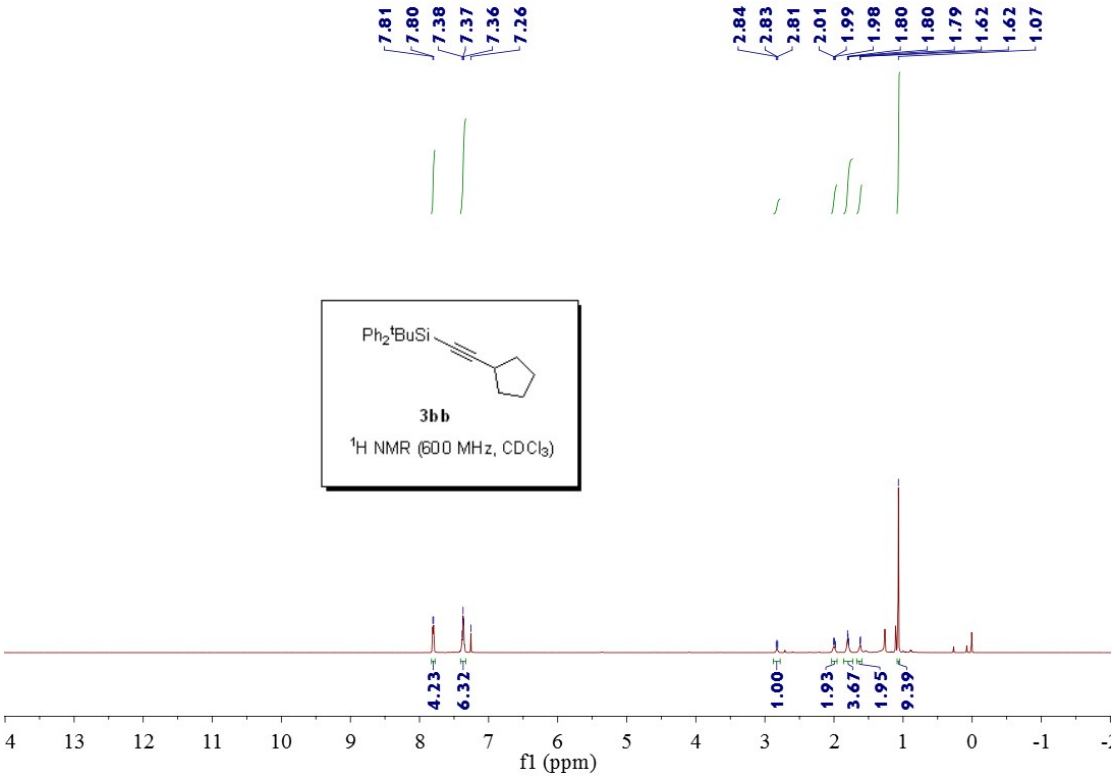
fl (ppm)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1.80
1.80
1.79
1.62
1.62
1.07
Ph2tBuSi
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1.93
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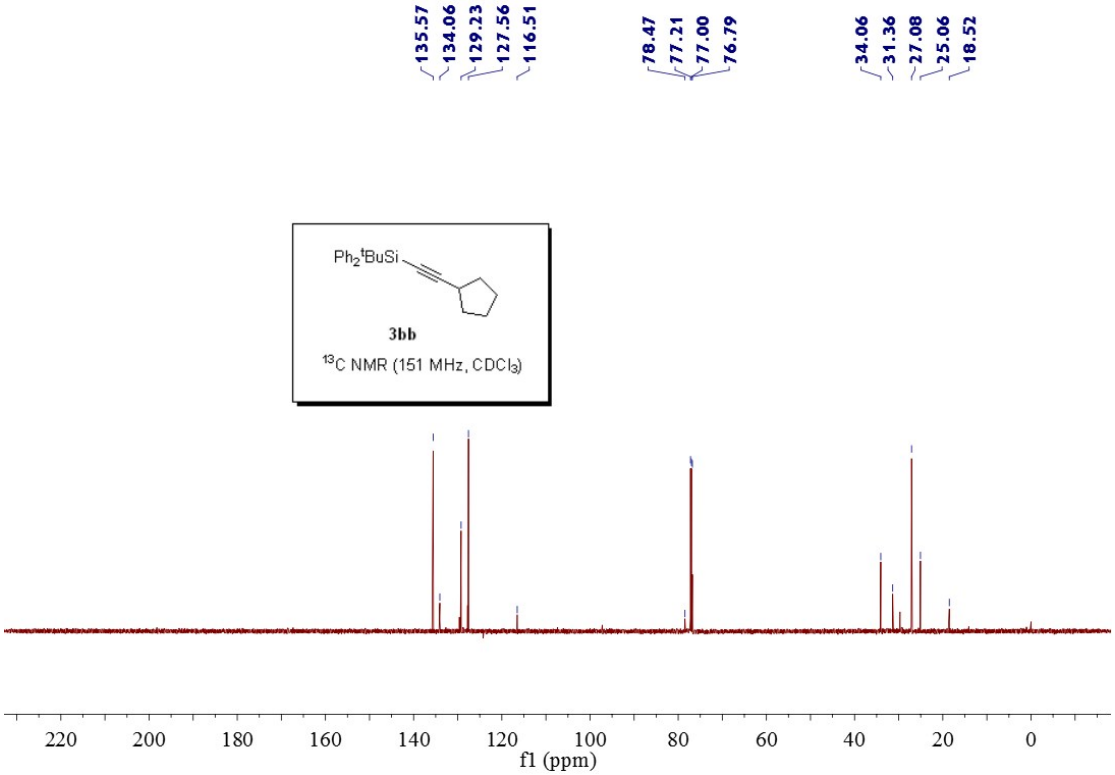
1.95
9.39
fl (ppm)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77.00
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31.36
27.08
25.06
18.52
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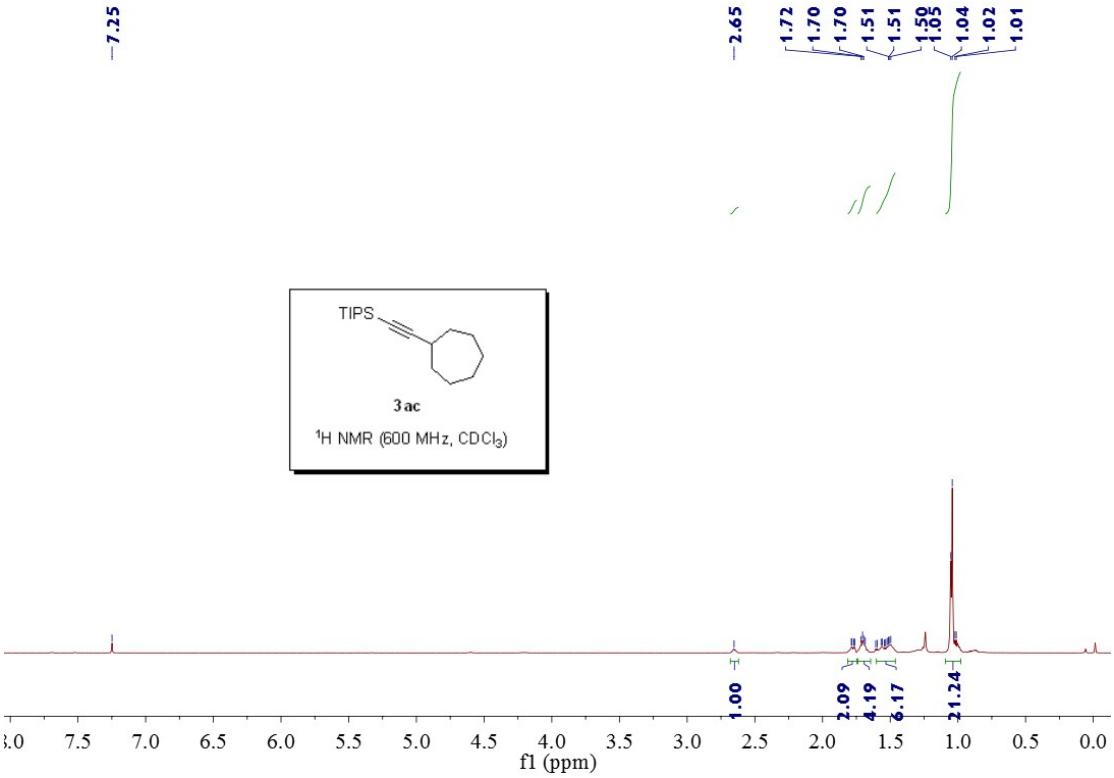
3bb
13C NMR (151 MHz, CDCl3)
fl (ppm)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1.70
1.51
1.51
1.50
1.05
1.04
1.02
1.01
TIPS
3ac
1H NMR (600 MHz, CDCl3)
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2.09
4.19
6.17
21.24
7.5
7.0
6.5
6.0
5.5
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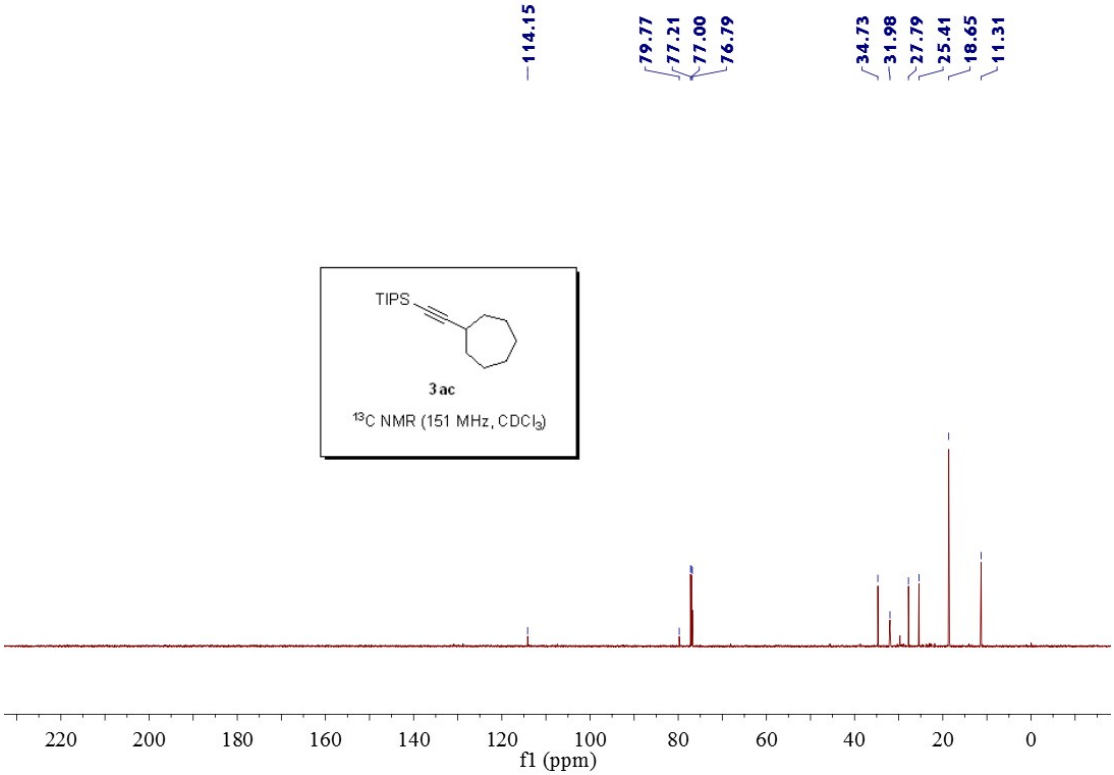
f1 (ppm)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180
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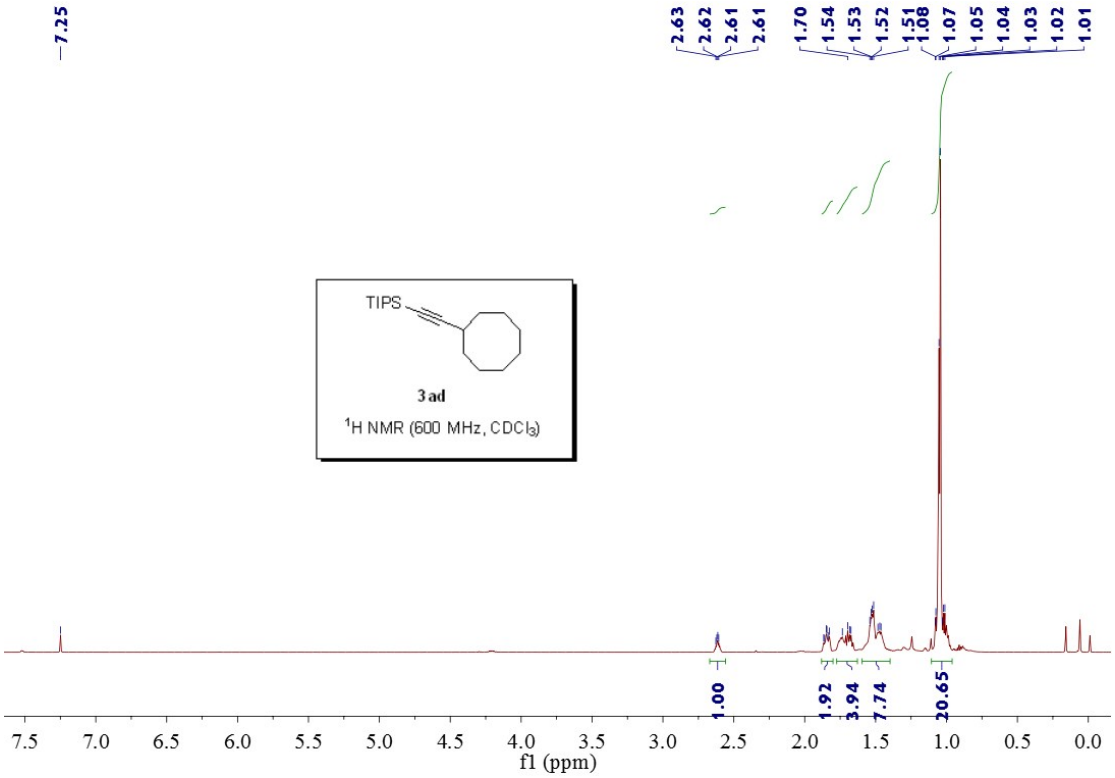
100
80
60
40
20
0
f1 (ppm)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2.61
1.70
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1.53
1.52
1.51
1.08
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1.05
1.04
1.03
1.02
1.01
TIPS
3ad
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1.92
3.94
7.74
20.65
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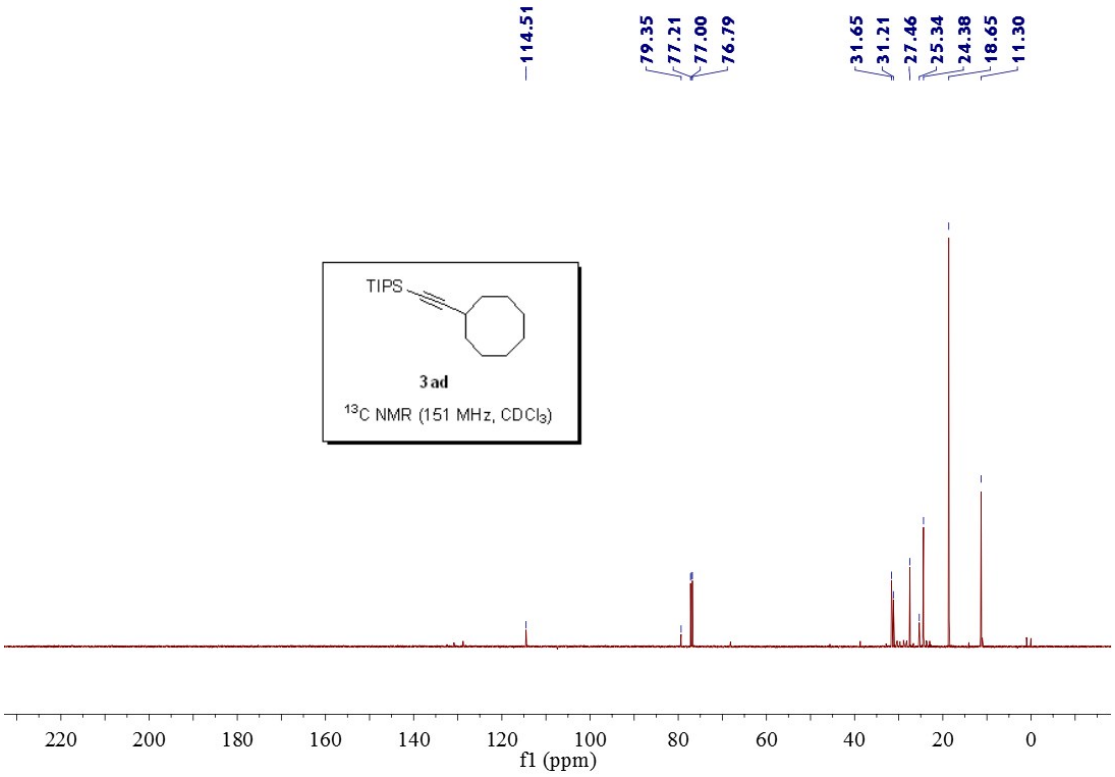
f1 (ppm)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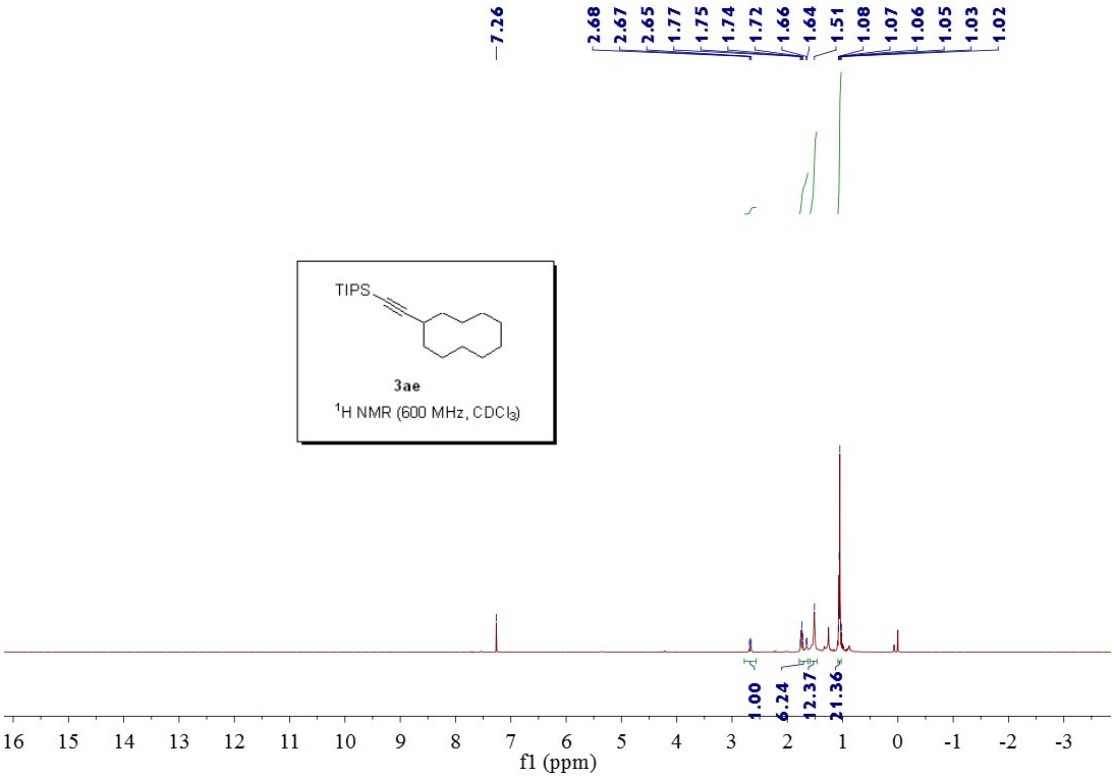
f1 (ppm)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1.07
1.06
1.05
1.03
1.02
TIPS
3ae
1H NMR (600 MHz, CDCl3)
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6.24
12.37
21.36
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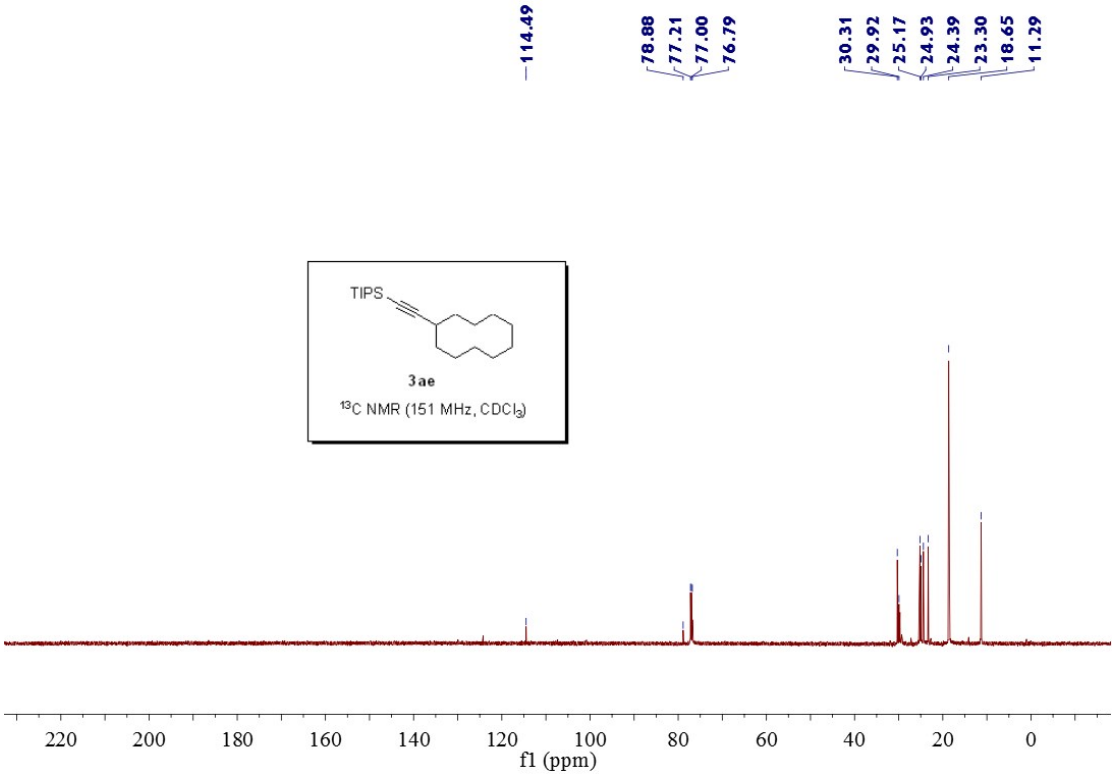
f1 (ppm)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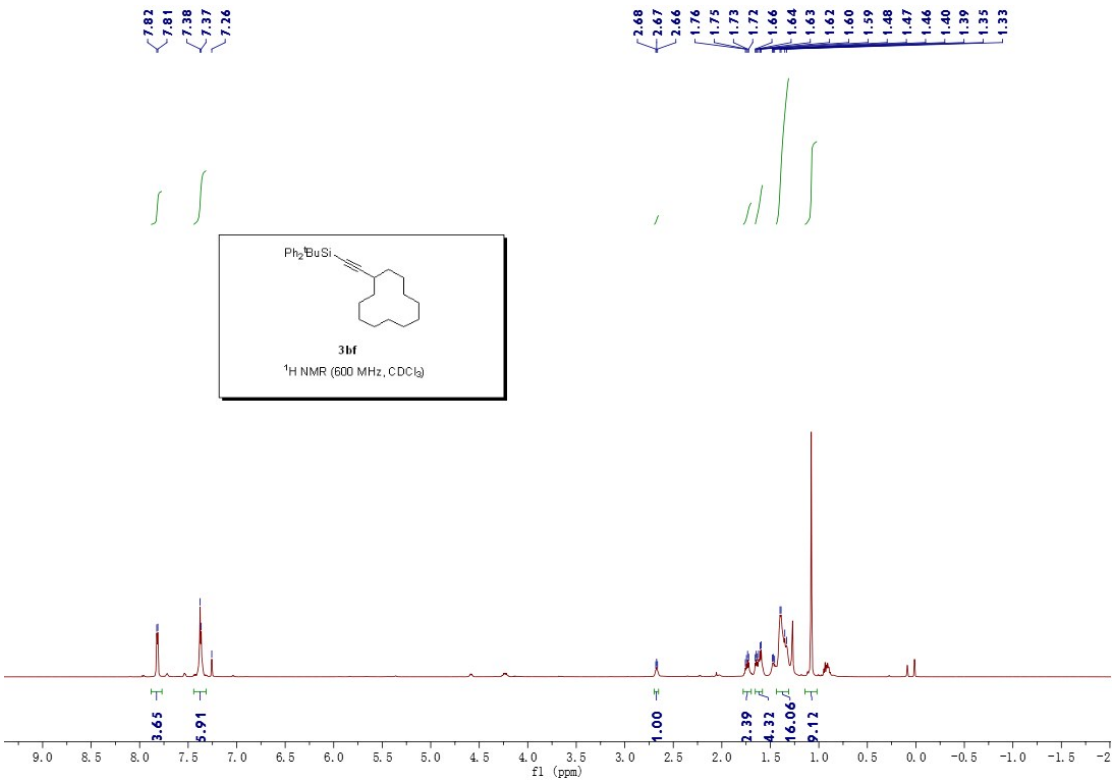
f1 (ppm)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1.64
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1.62
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1.59
1.48
1.47
1.46
1.40
1.39
1.35
1.33
Ph2tBuSi
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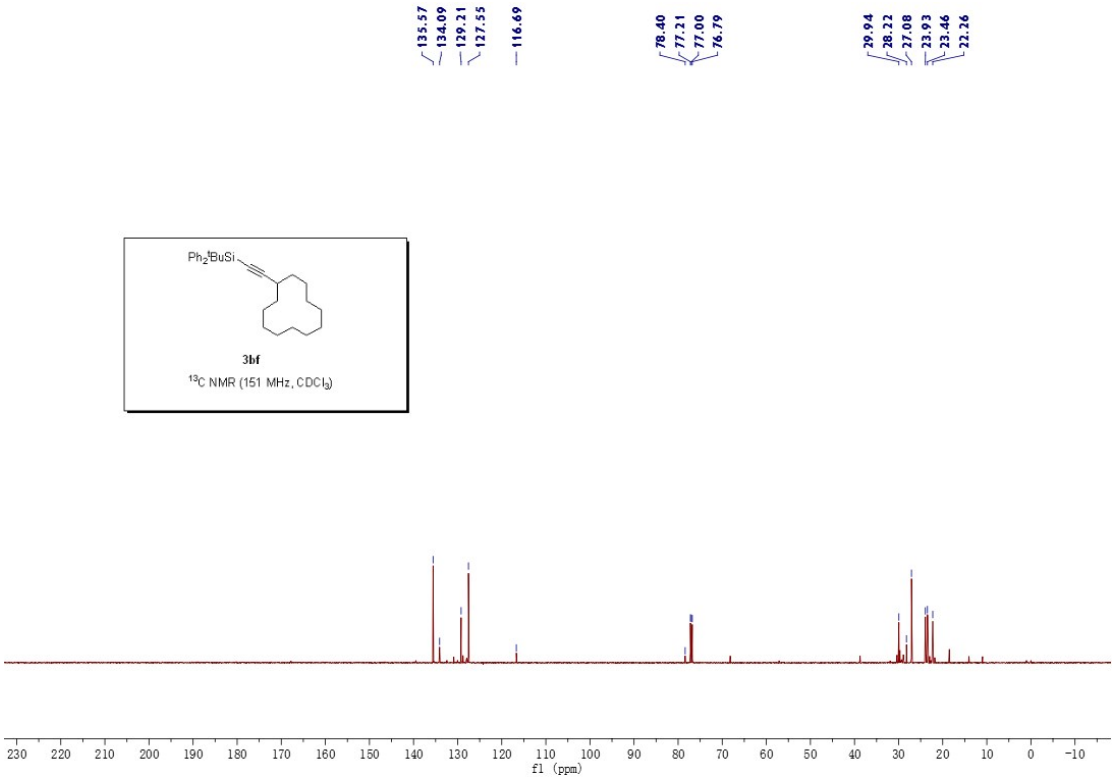
f1 (ppm)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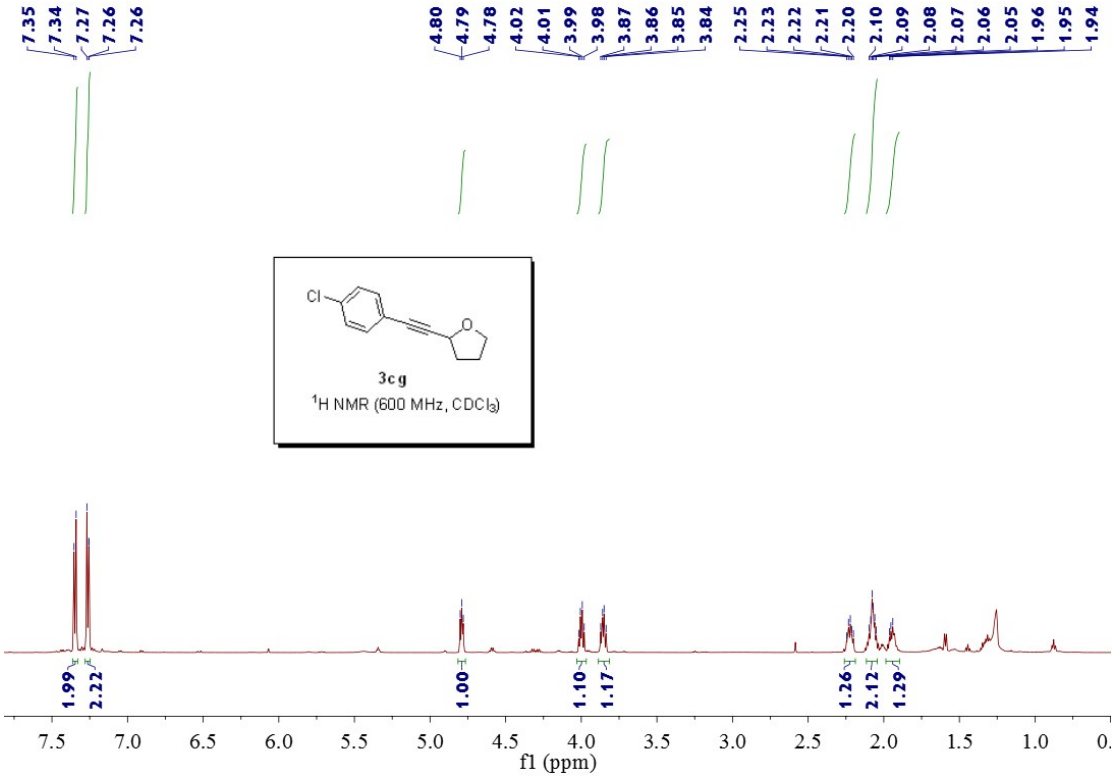
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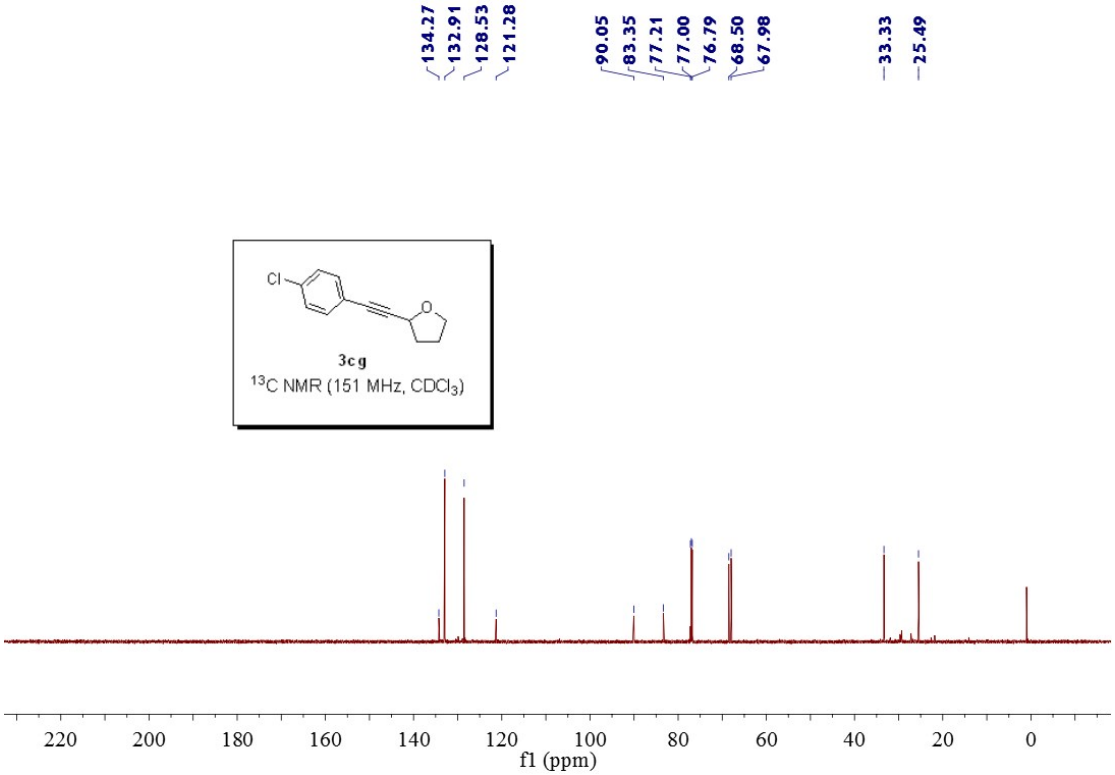
f1 (ppm)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Cl
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100
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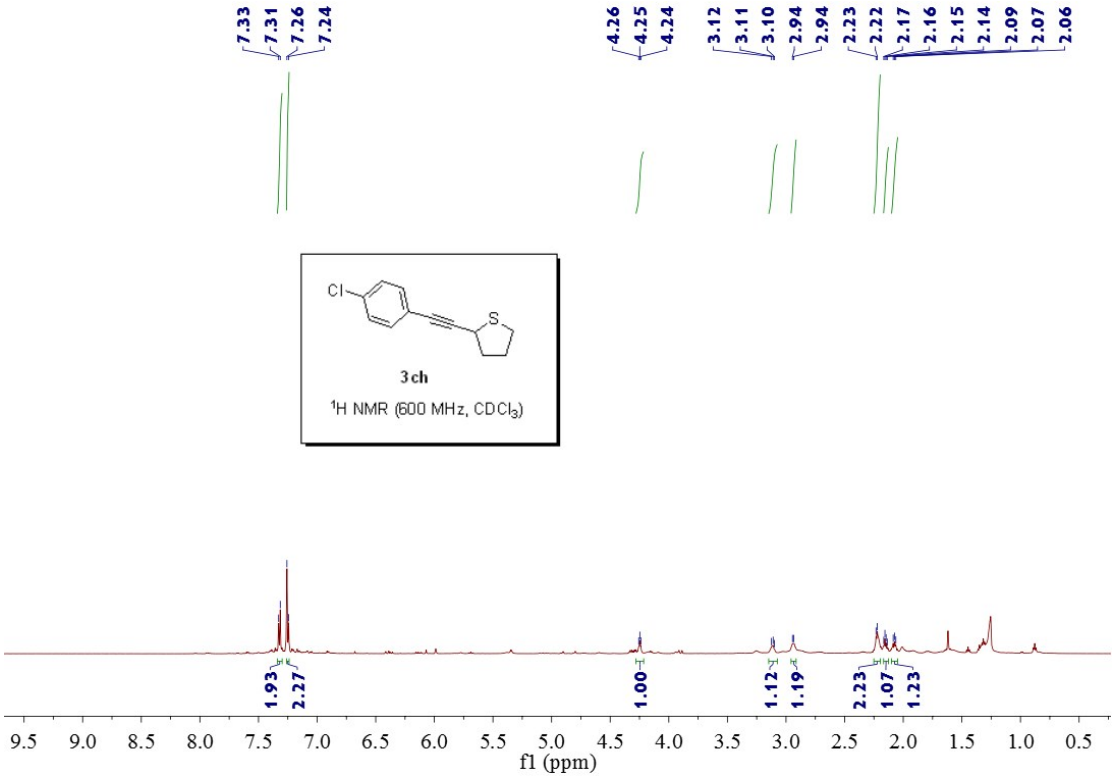
f1 (ppm)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2.22
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2.15
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2.09
2.07
2.06
Cl
S
3ch
1H NMR (600 MHz, CDCl3)
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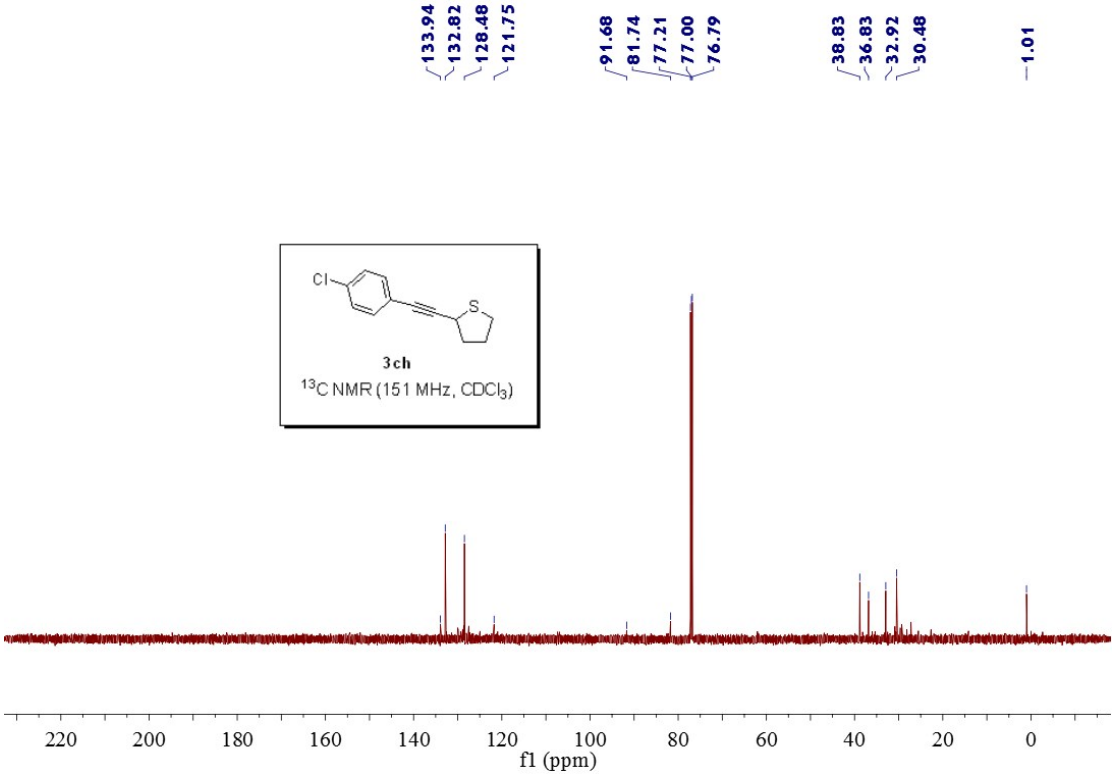
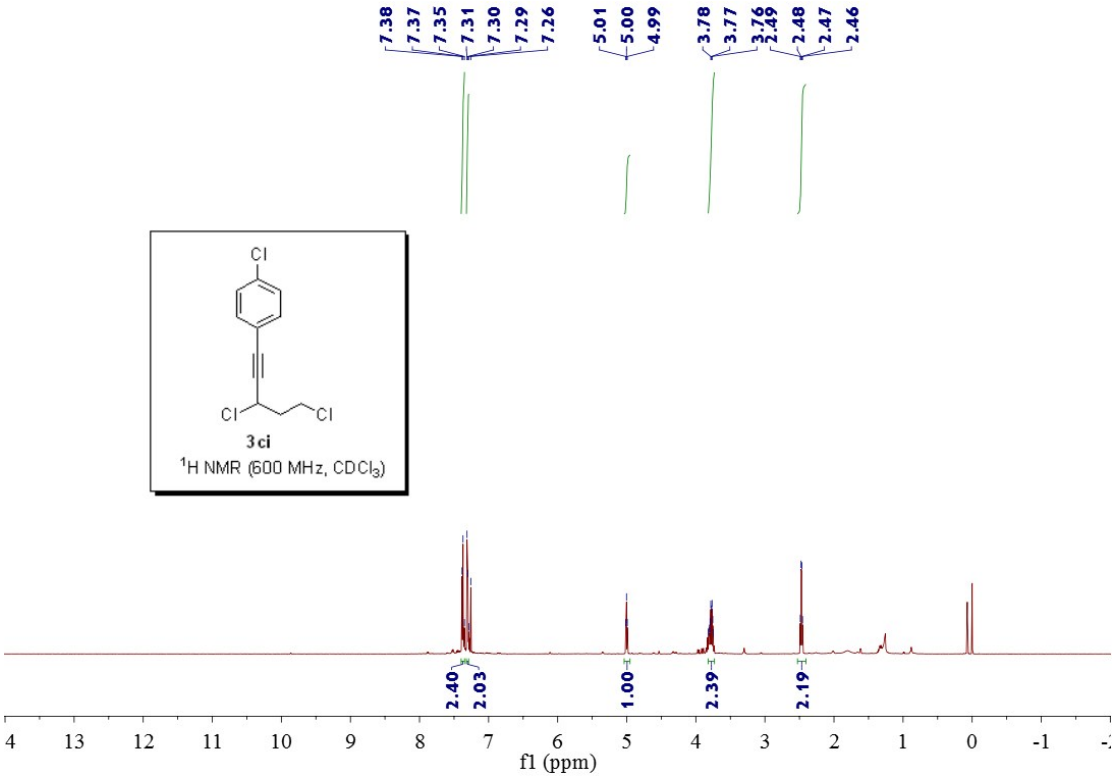
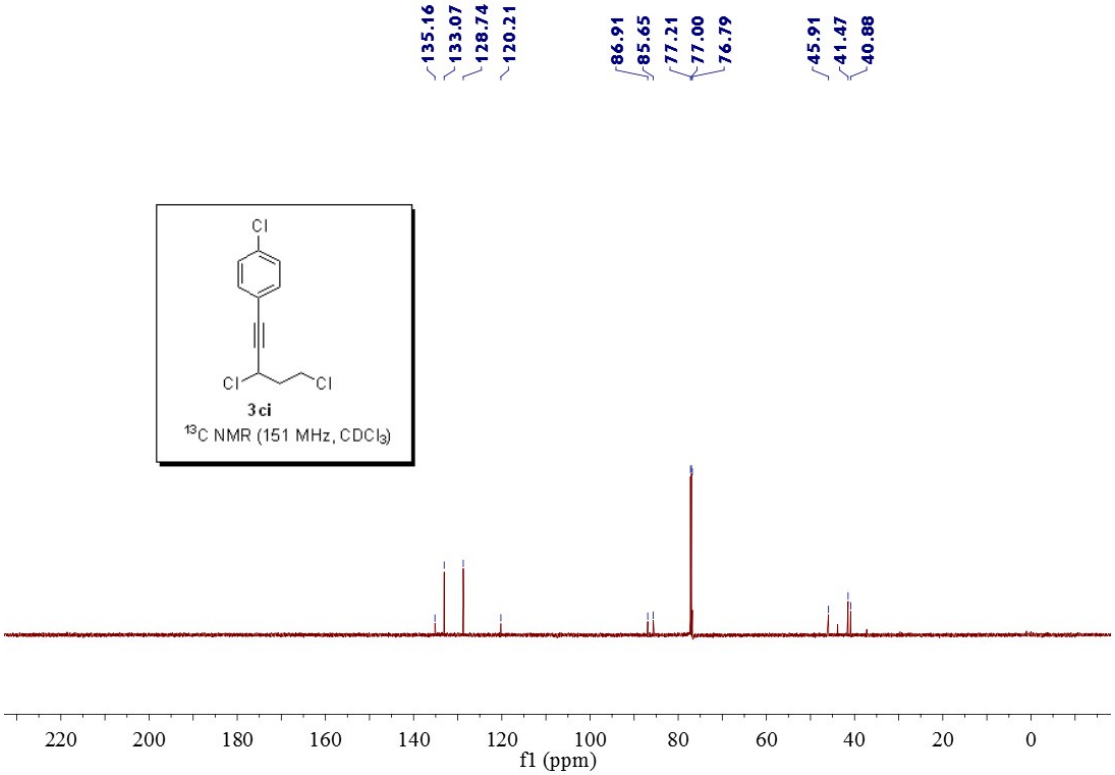
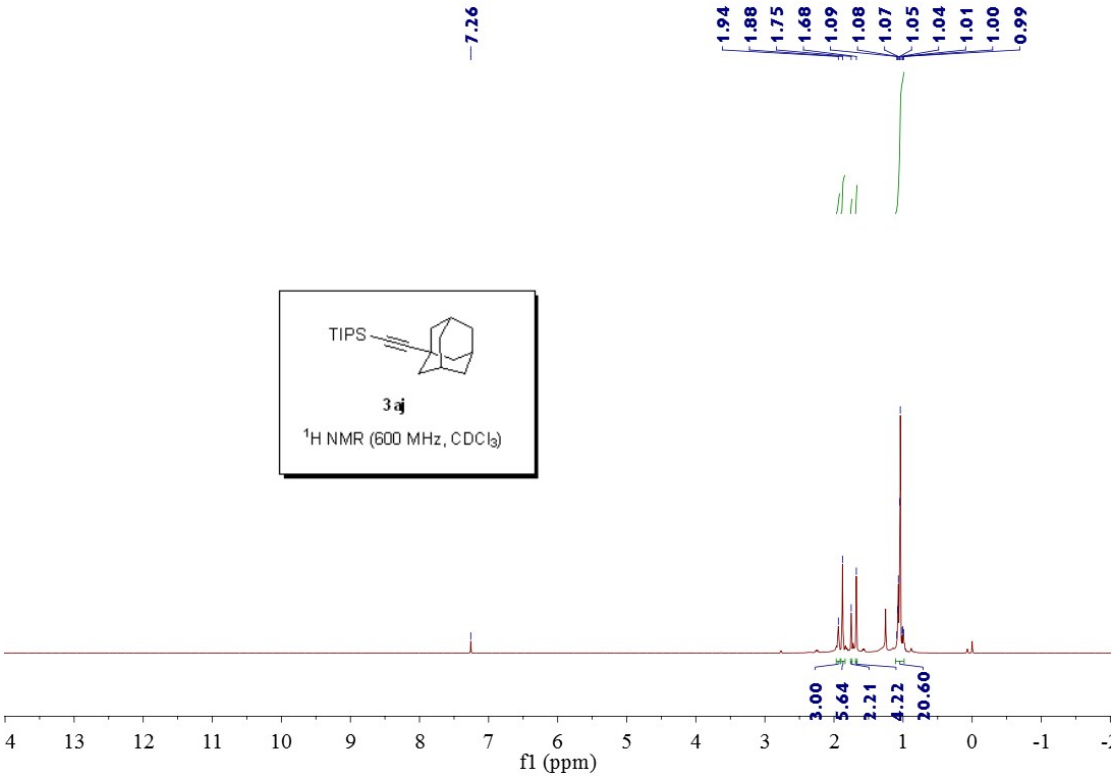
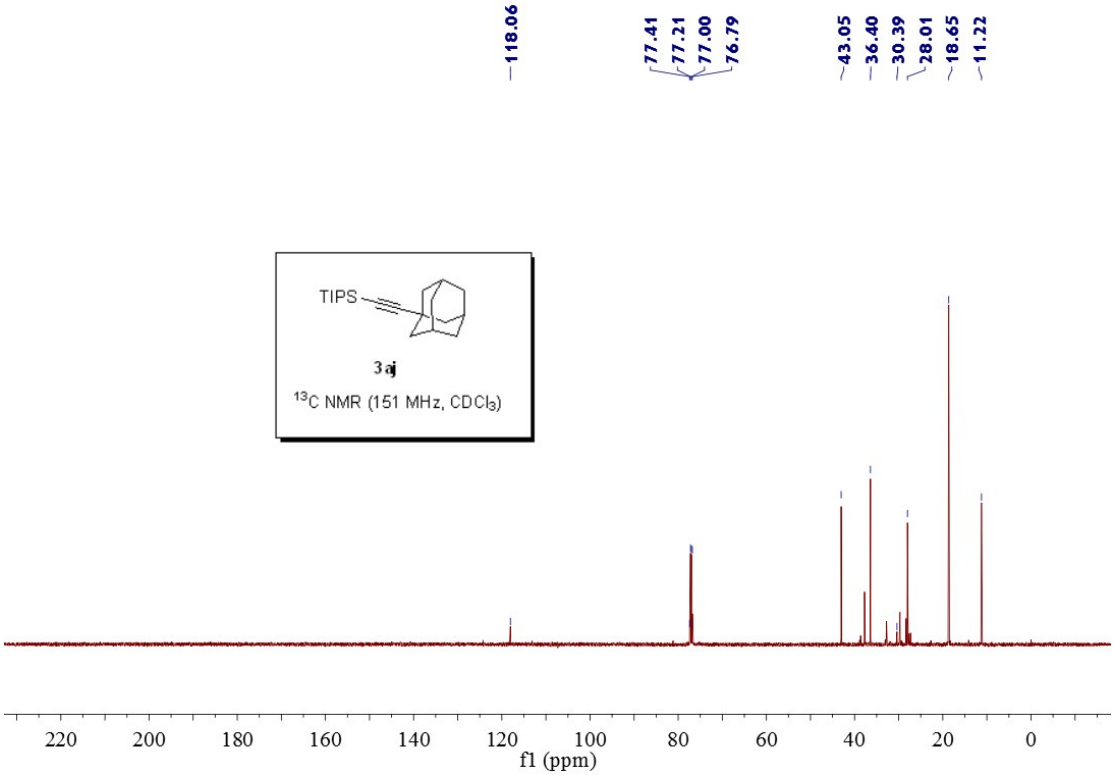
2.27
1.00
1.12
1.19
2.23
1.07
1.23
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

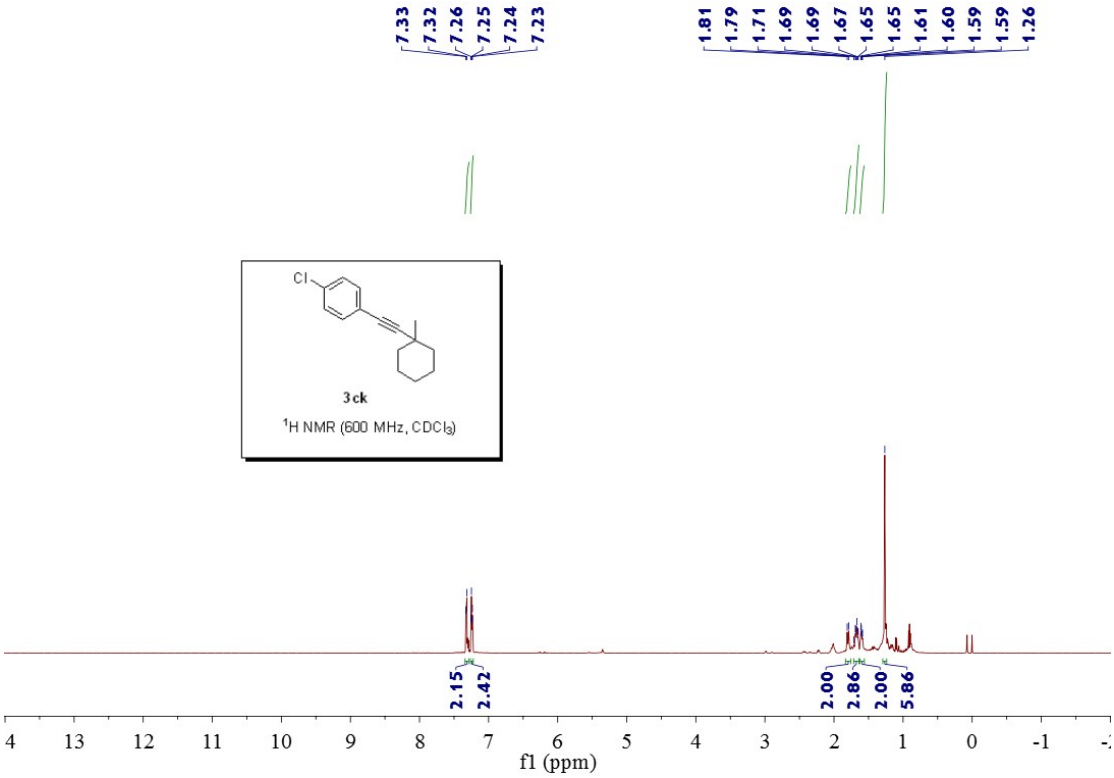

133.94
132.82
128.48
121.75
91.68
81.74
77.21
77.00
76.79
38.83
36.83
32.92
30.48
1.01
Cl
S
3ch
13C NMR (151 MHz, CDCl3)
220 200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

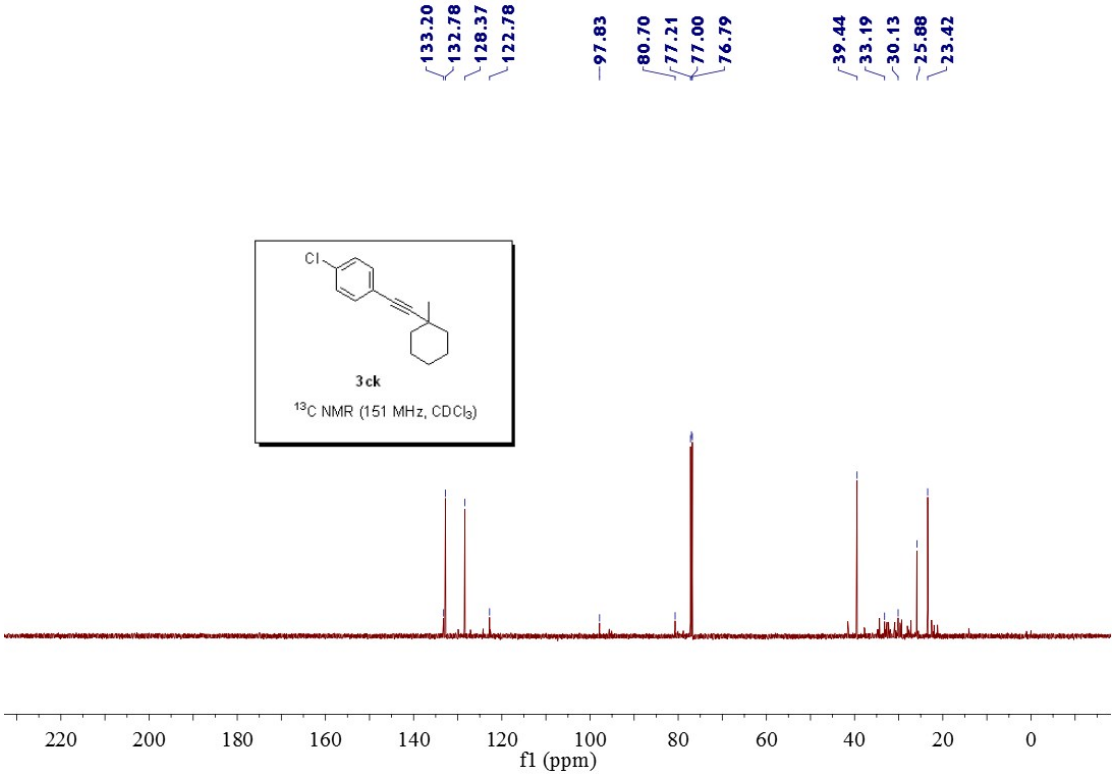

7.38
7.37
7.35
7.31
7.30
7.29
7.26
5.01
5.00
4.99
3.78
3.77
3.76
2.49
2.48
2.47
2.46
Cl
Cl
Cl
3ci
1H NMR (600 MHz, CDCl3)
2.40
2.03
1.00
2.39
2.19
4 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

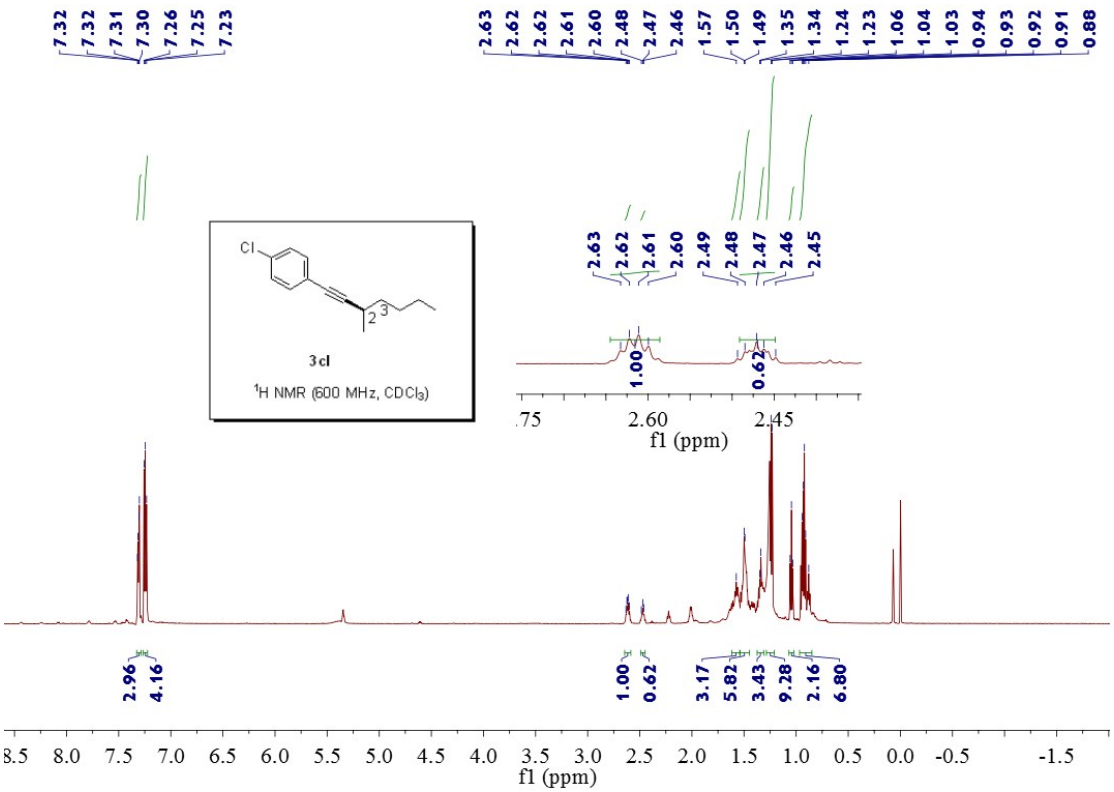

135.16
133.07
128.74
120.21
86.91
85.65
77.21
77.00
76.79
45.91
41.47
40.88
Cl
Cl
Cl
3ci
13C NMR (151 MHz, CDCl3)
220 200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

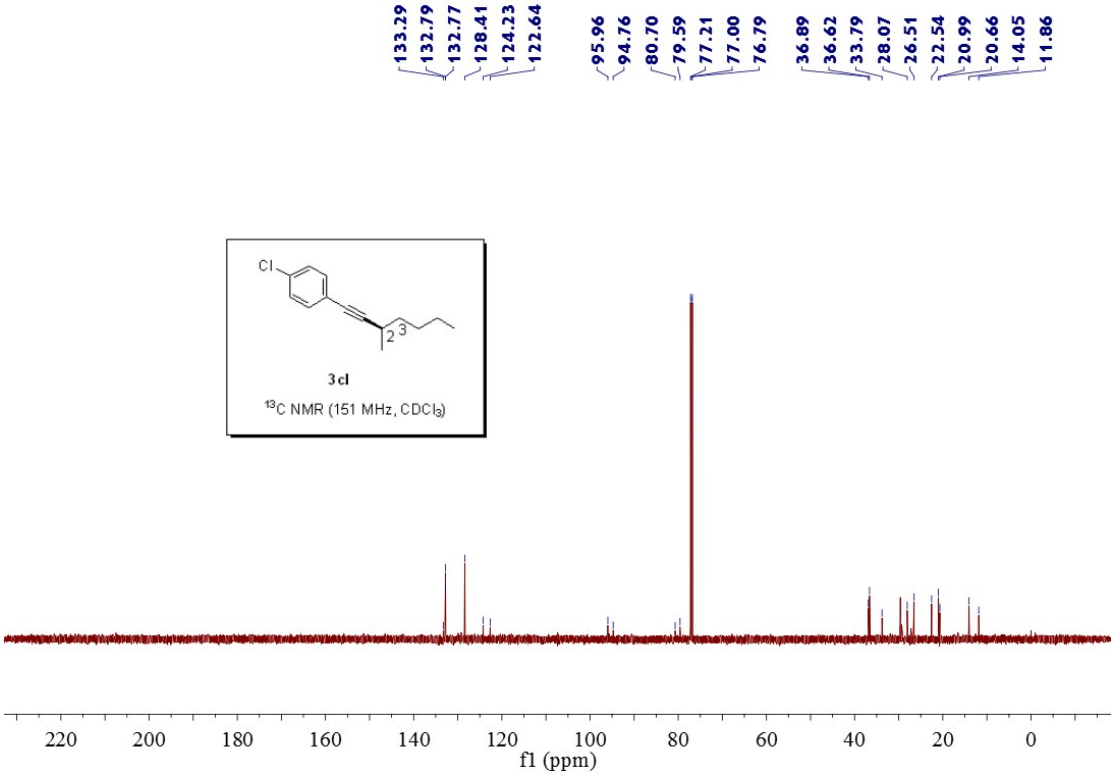

7.26
1.94
1.88
1.75
1.68
1.09
1.08
1.07
1.05
1.04
1.01
1.00
0.99
TIPS
3aj
1H NMR (600 MHz, CDCl3)
3.00
5.64
2.21
4.22
20.60
f1 (ppm)

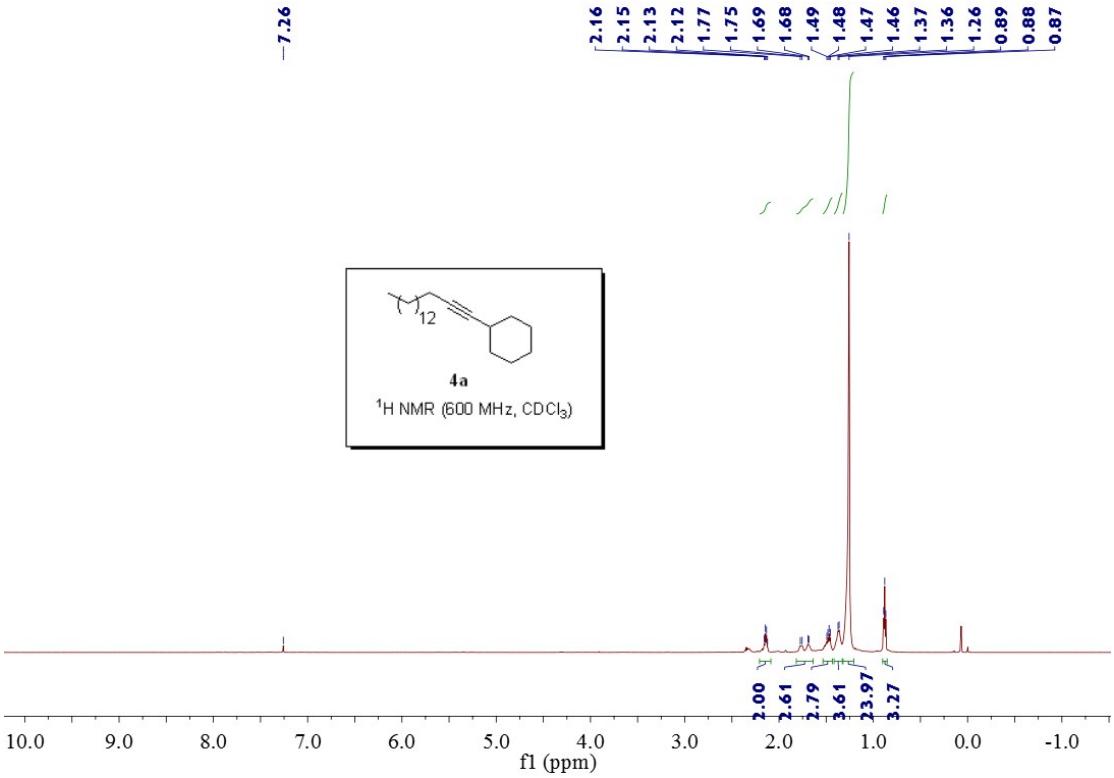

118.06
77.41
77.21
77.00
76.79
43.05
36.40
30.39
28.01
18.65
11.22
TIPS
3aj
13C NMR (151 MHz, CDCl3)
f1 (ppm)

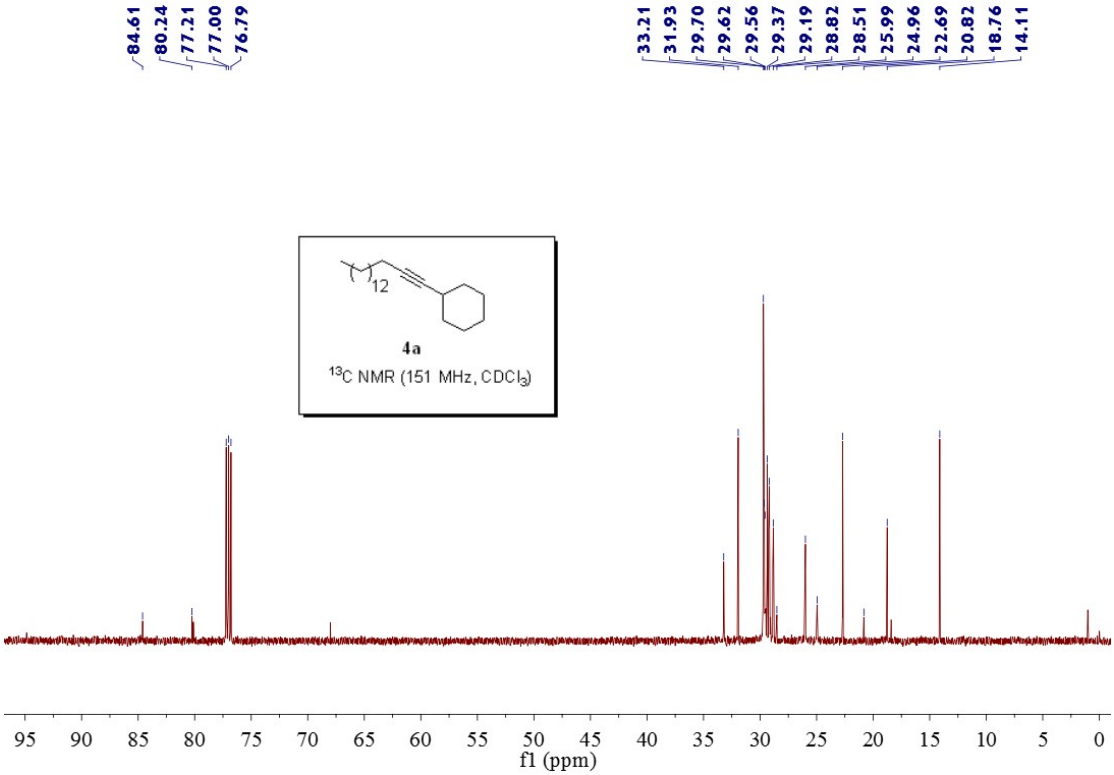

7.33
7.32
7.26
7.25
7.24
7.23
1.81
1.79
1.71
1.69
1.69
1.67
1.65
1.65
1.61
1.60
1.59
1.59
1.26
Cl
3ck
1H NMR (600 MHz, CDCl3)
2.15
2.42
2.00
2.86
2.00
5.86
f1 (ppm)

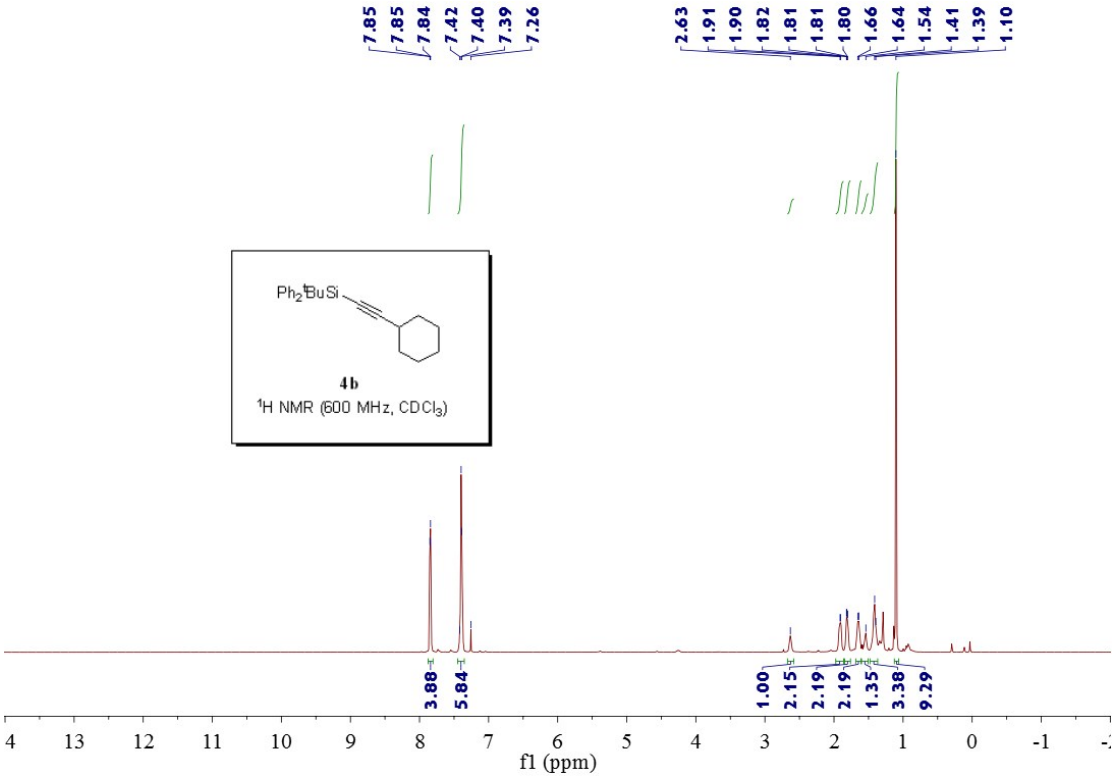

133.20
132.78
128.37
122.78
97.83
80.70
77.21
77.00
76.79
39.44
33.19
30.13
25.88
23.42
Cl
3ck
13C NMR (151 MHz, CDCl3)
f1 (ppm)

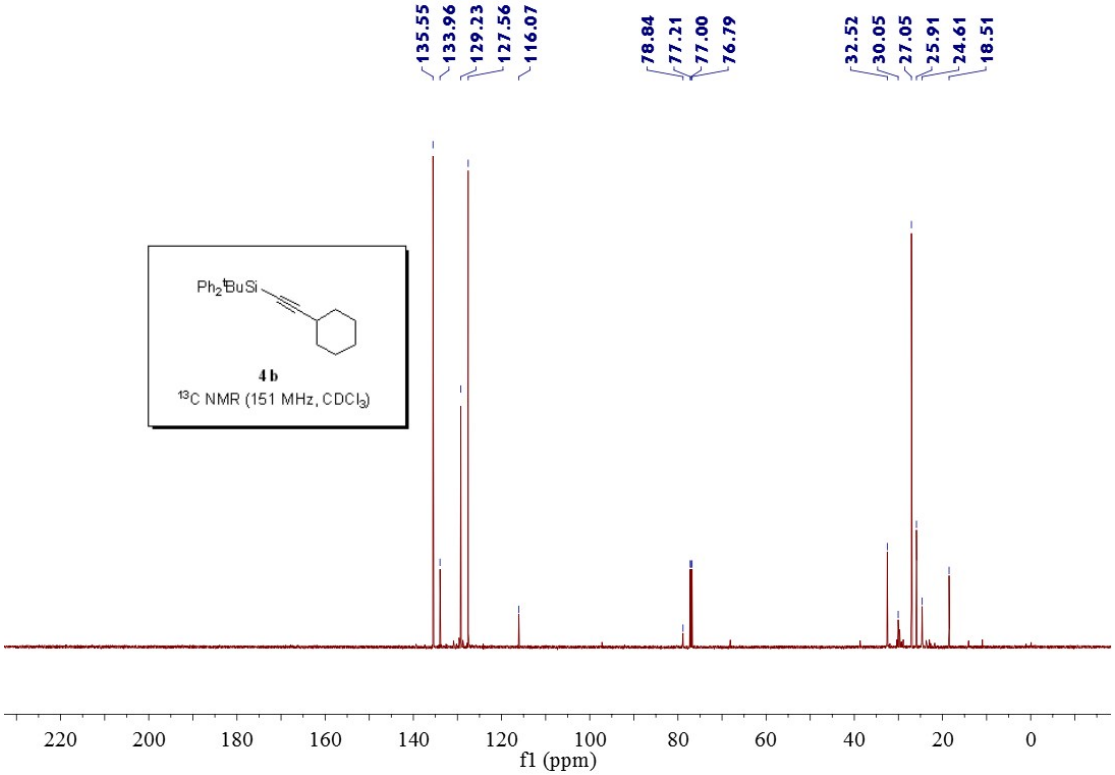

3cl
^{1}H NMR (600 MHz, $CDCl_3$)
f1 (ppm)

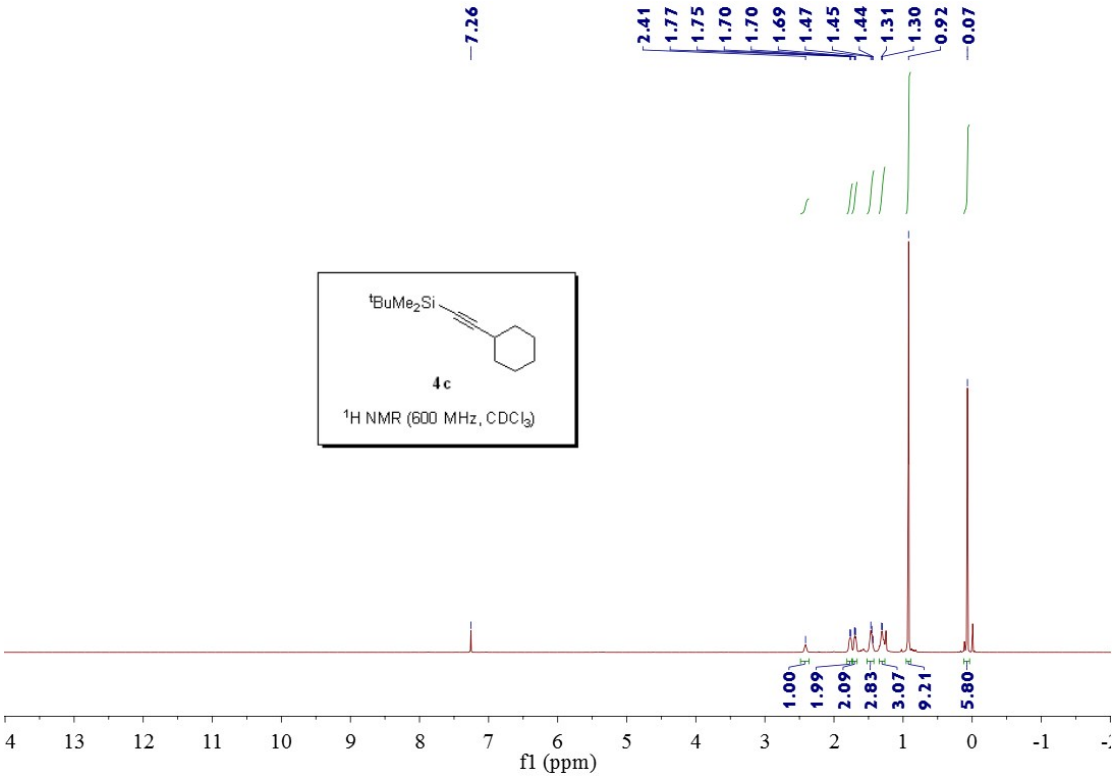

3cl
^{13}C NMR (151 MHz, $CDCl_3$)
f1 (ppm)

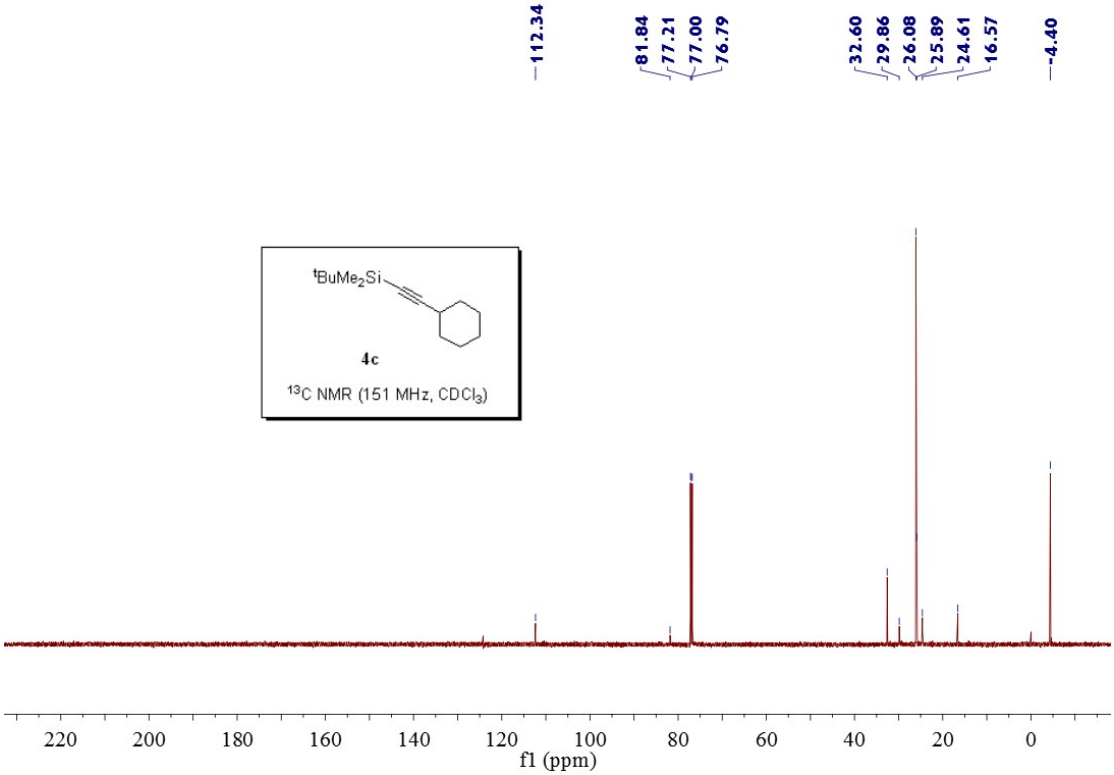

7.26
2.16
2.15
2.13
2.12
1.77
1.75
1.69
1.68
1.49
1.48
1.47
1.46
1.37
1.36
1.26
0.89
0.88
0.87
12
4a
1H NMR (600 MHz, CDCl3)
2.00
2.61
2.79
3.61
23.97
3.27
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

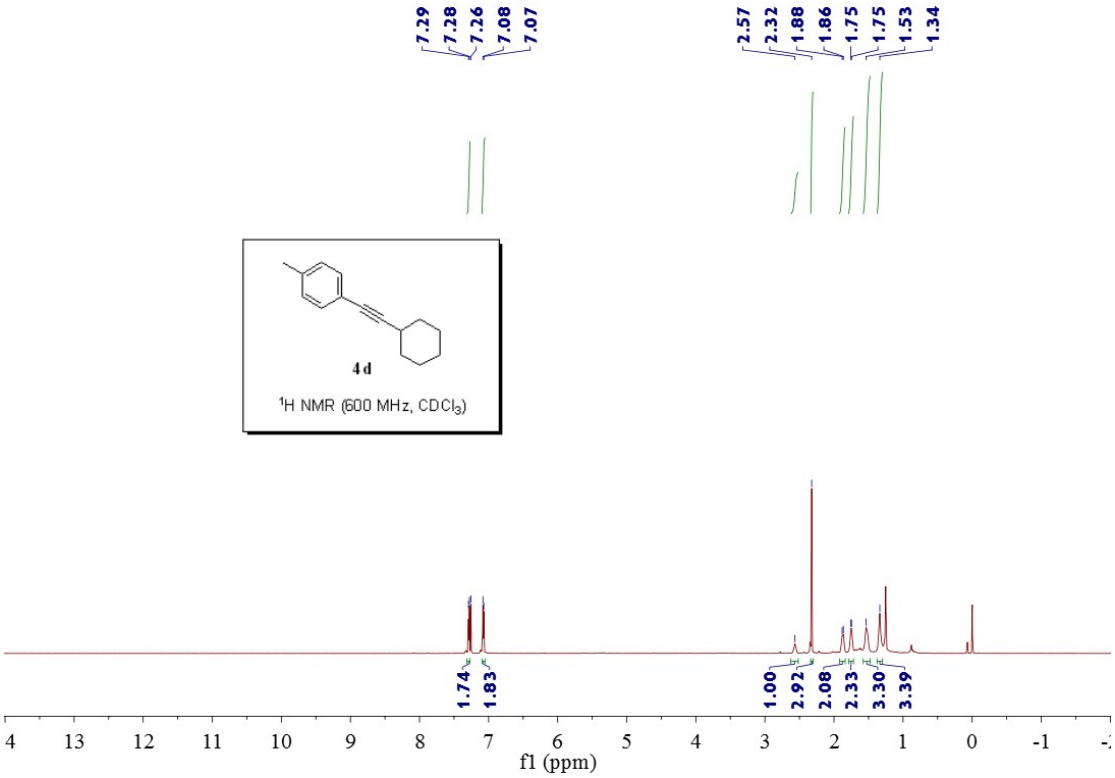

84.61
80.24
77.21
77.00
76.79
33.21
31.93
29.70
29.62
29.56
29.37
29.19
28.82
28.51
25.99
24.96
22.69
20.82
18.76
14.11
12
4a
13C NMR (151 MHz, CDCl3)
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)

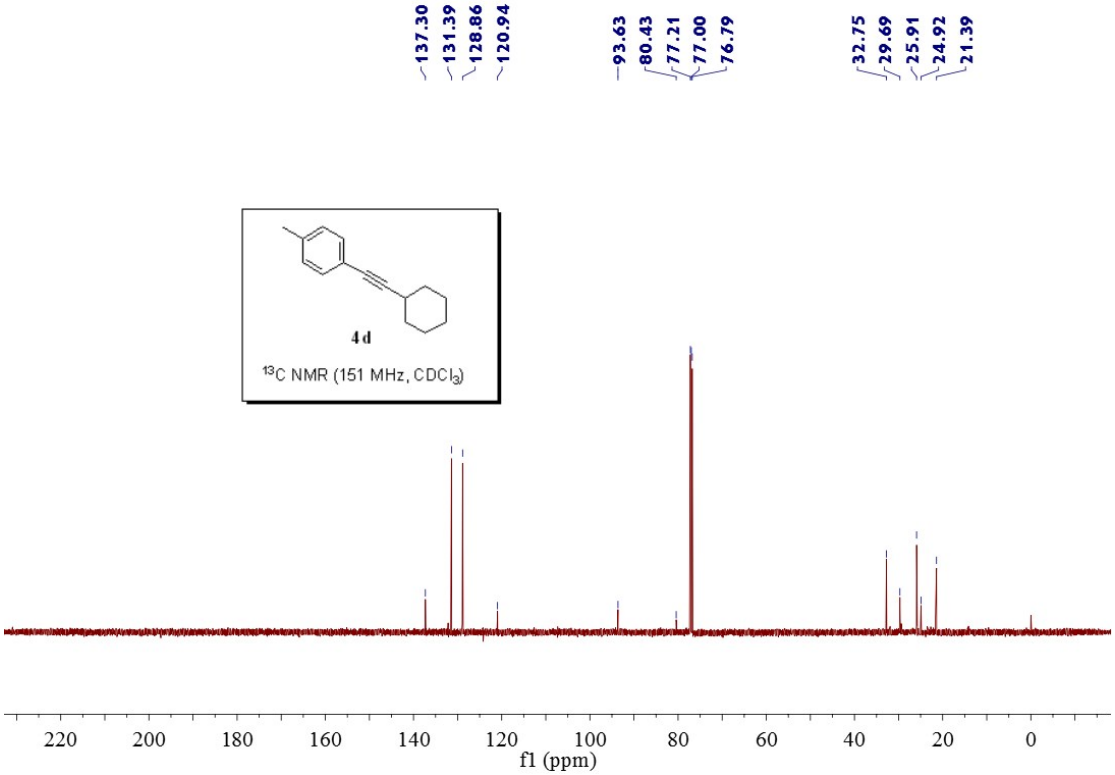

7.85
7.85
7.84
7.42
7.40
7.39
7.26
2.63
1.91
1.90
1.82
1.81
1.81
1.80
1.66
1.64
1.54
1.41
1.39
1.10
Ph2tBuSi
4b
1H NMR (600 MHz, CDCl3)
3.88
5.84
1.00
2.15
2.19
2.19
1.35
3.38
9.29
f1 (ppm)

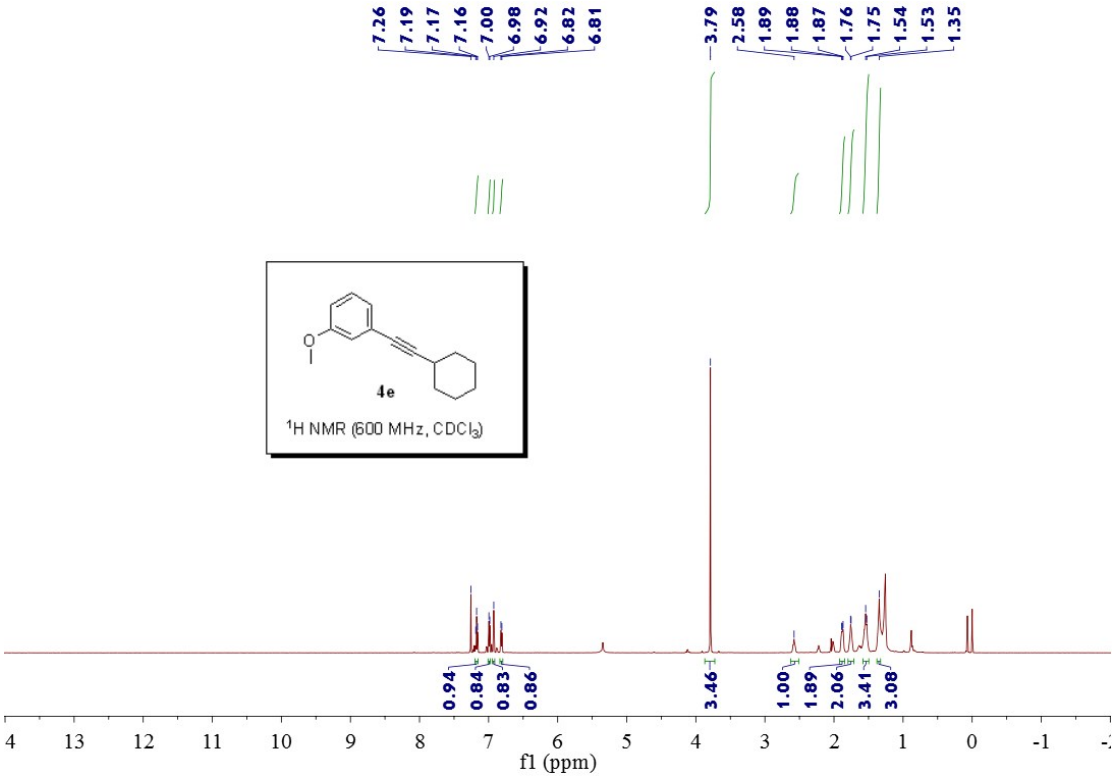

135.55
133.96
129.23
127.56
116.07
78.84
77.21
77.00
76.79
32.52
30.05
27.05
25.91
24.61
18.51
Ph2tBuSi
4b
13C NMR (151 MHz, CDCl3)
f1 (ppm)

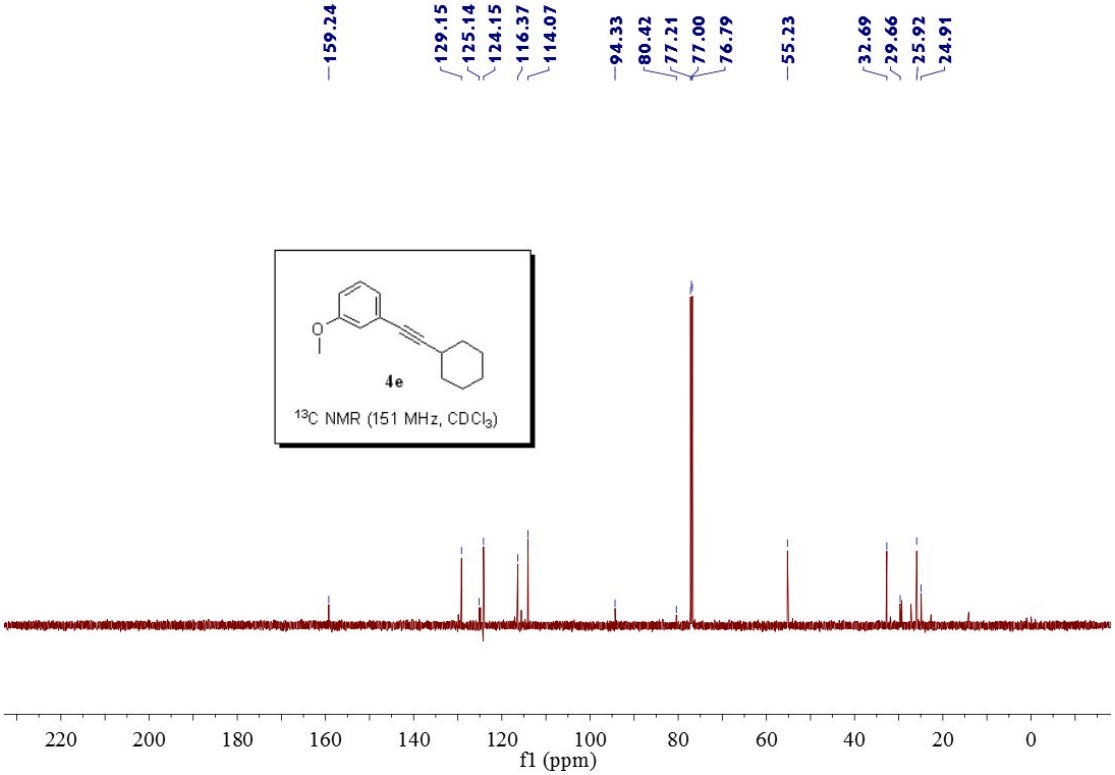

7.26
2.41
1.77
1.75
1.70
1.70
1.69
1.47
1.45
1.44
1.31
1.30
0.92
0.07
tBuMe2Si
4c
1H NMR (600 MHz, CDCl3)
1.00
1.99
2.09
2.83
3.07
9.21
5.80
f1 (ppm)

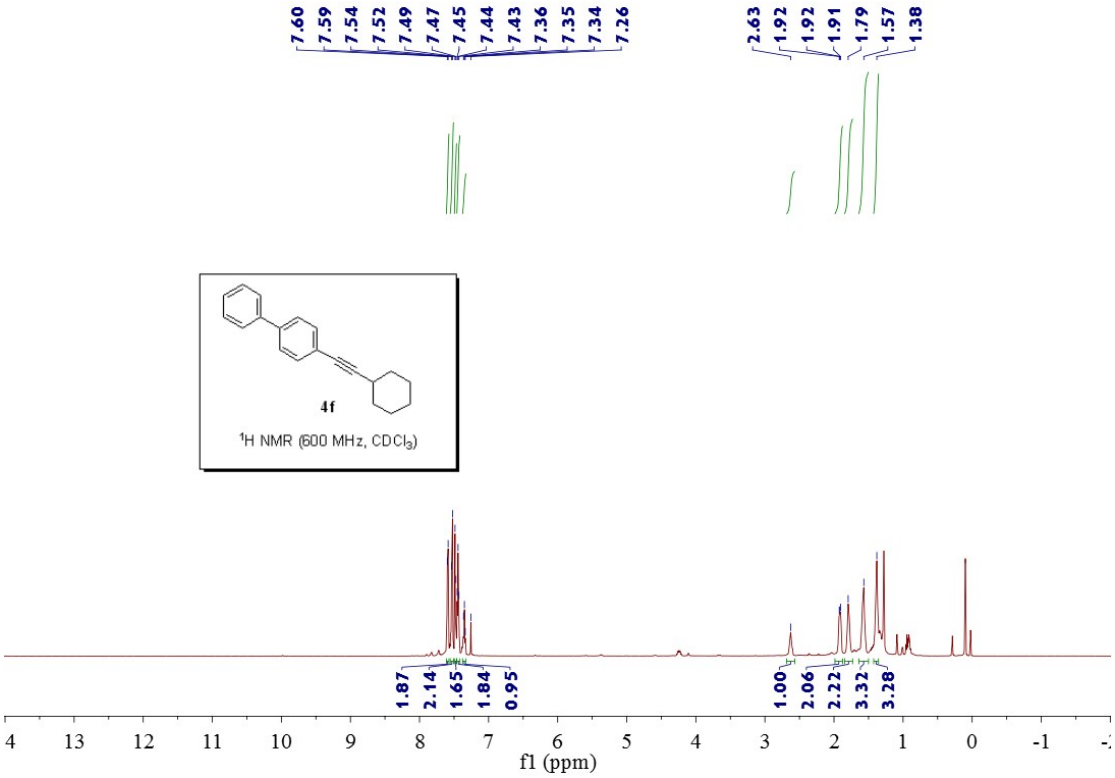

112.34
81.84
77.21
77.00
76.79
32.60
29.86
26.08
25.89
24.61
16.57
-4.40
tBuMe2Si
4c
13C NMR (151 MHz, CDCl3)
f1 (ppm)

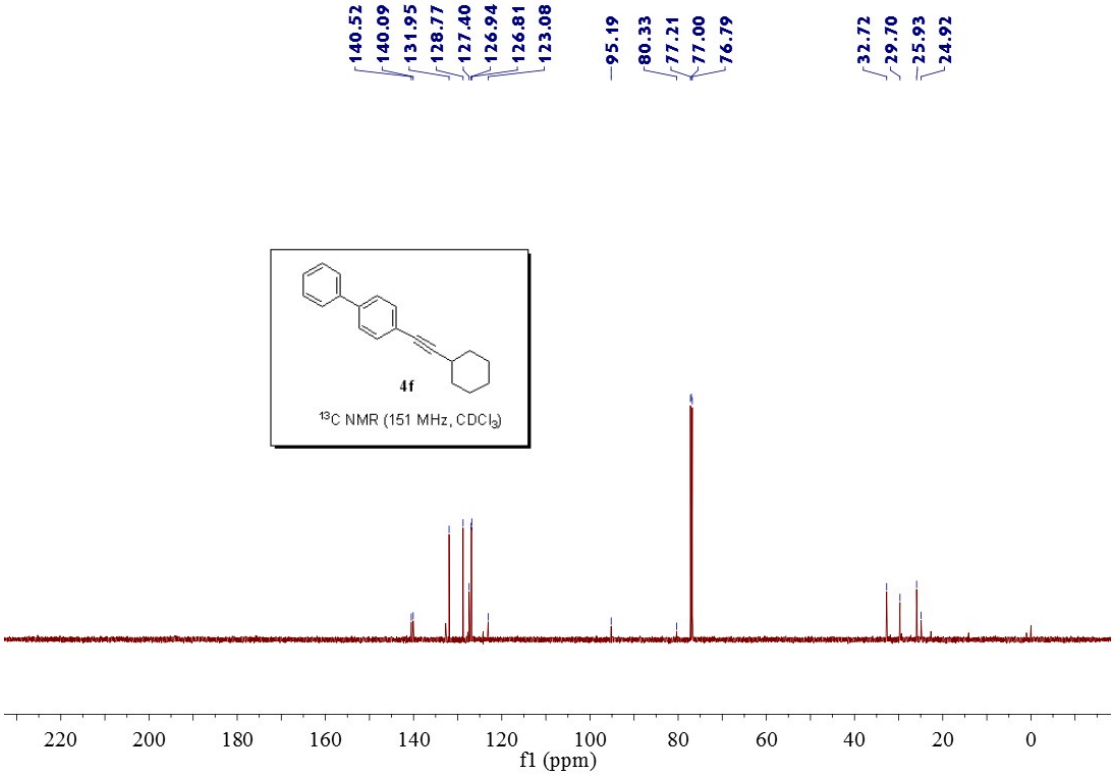

7.29
7.28
7.26
7.08
7.07
2.57
2.32
1.88
1.86
1.75
1.75
1.53
1.34
4d
1H NMR (600 MHz, CDCl3)
1.74
1.83
1.00
2.92
2.08
2.33
3.30
3.39
f1 (ppm)

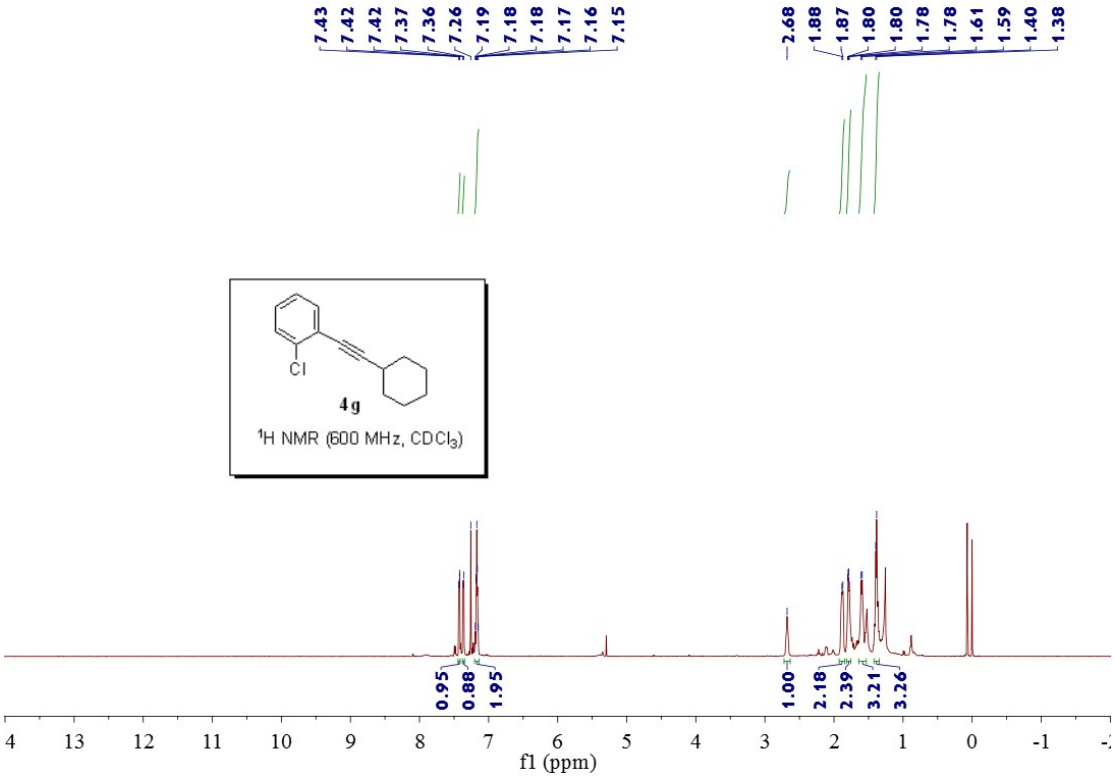

137.30
131.39
128.86
120.94
93.63
80.43
77.21
77.00
76.79
32.75
29.69
25.91
24.92
21.39
4d
13C NMR (151 MHz, CDCl3)
f1 (ppm)

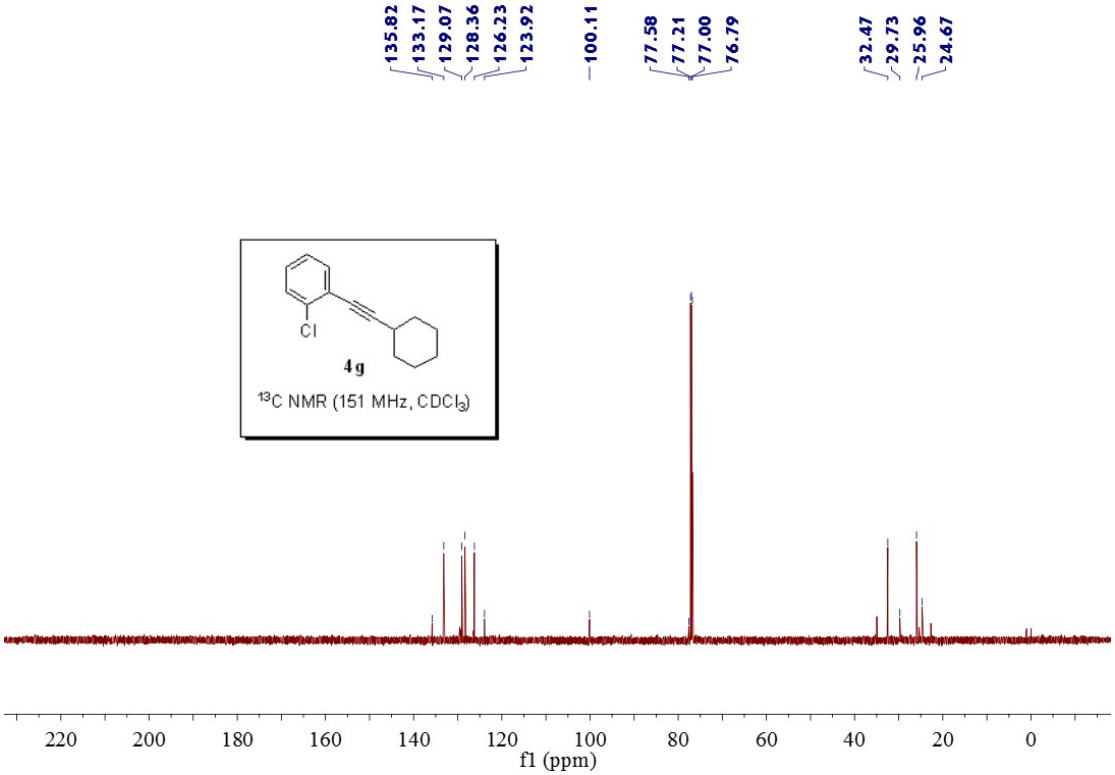

7.26
7.19
7.17
7.16
7.00
6.98
6.92
6.82
6.81
3.79
2.58
1.89
1.88
1.87
1.76
1.75
1.54
1.53
1.35
4e
^{1}H NMR (600 MHz, $CDCl_3$)
0.94
0.84
0.83
0.86
3.46
1.00
1.89
2.06
3.41
3.08
f1 (ppm)

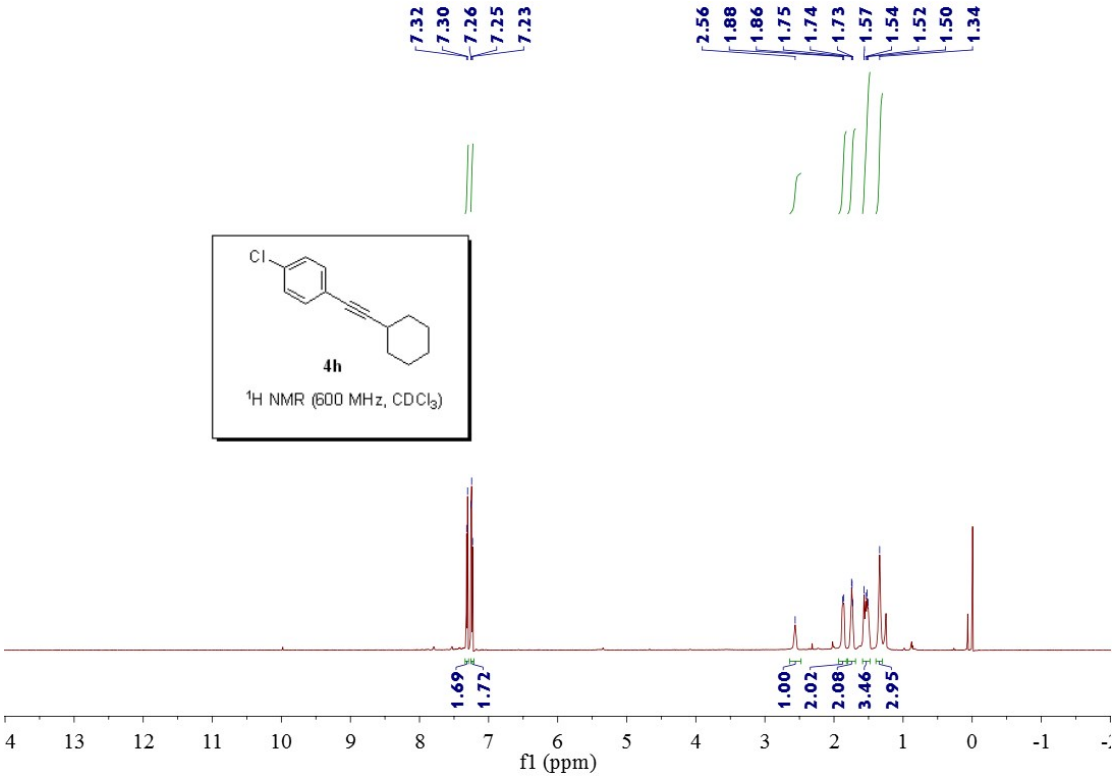

159.24
129.15
125.14
124.15
116.37
114.07
94.33
80.42
77.21
77.00
76.79
55.23
32.69
29.66
25.92
24.91
4e
^{13}C NMR (151 MHz, $CDCl_3$)
f1 (ppm)

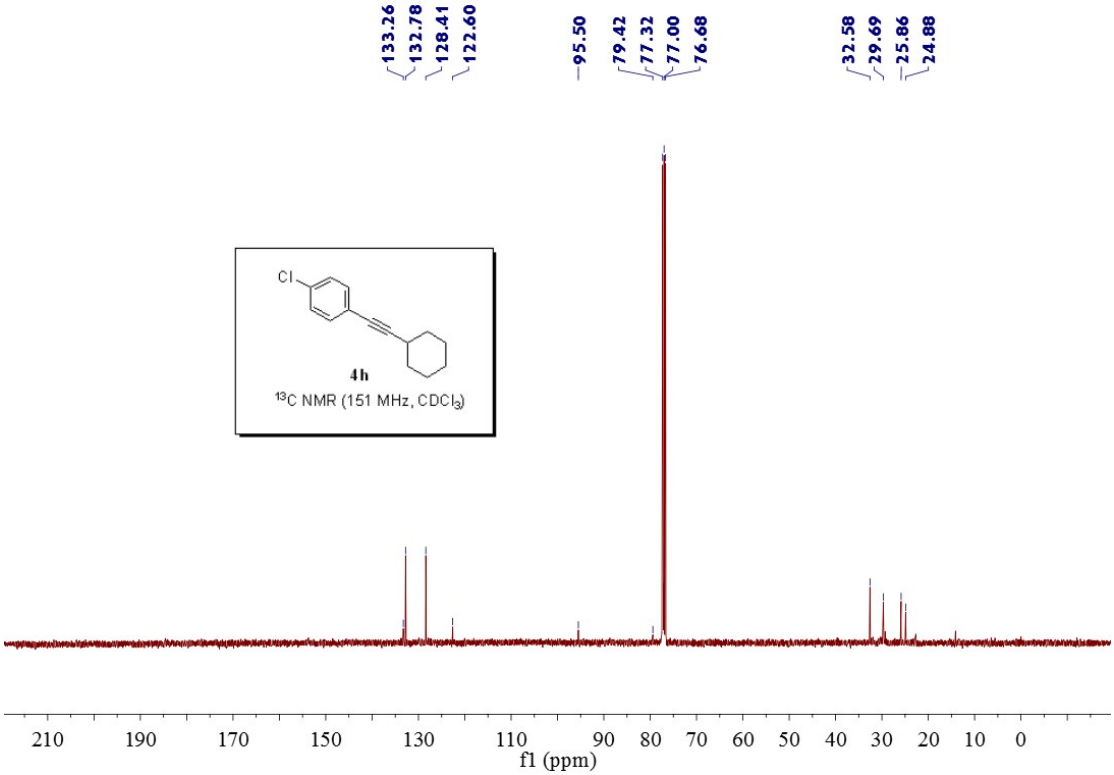

7.60
7.59
7.54
7.52
7.49
7.47
7.45
7.44
7.43
7.36
7.35
7.34
7.26
2.63
1.92
1.92
1.91
1.79
1.57
1.38
4f
¹H NMR (600 MHz, CDCl₃)
1.87
2.14
1.65
1.84
0.95
1.00
2.06
2.22
3.32
3.28
f1 (ppm)

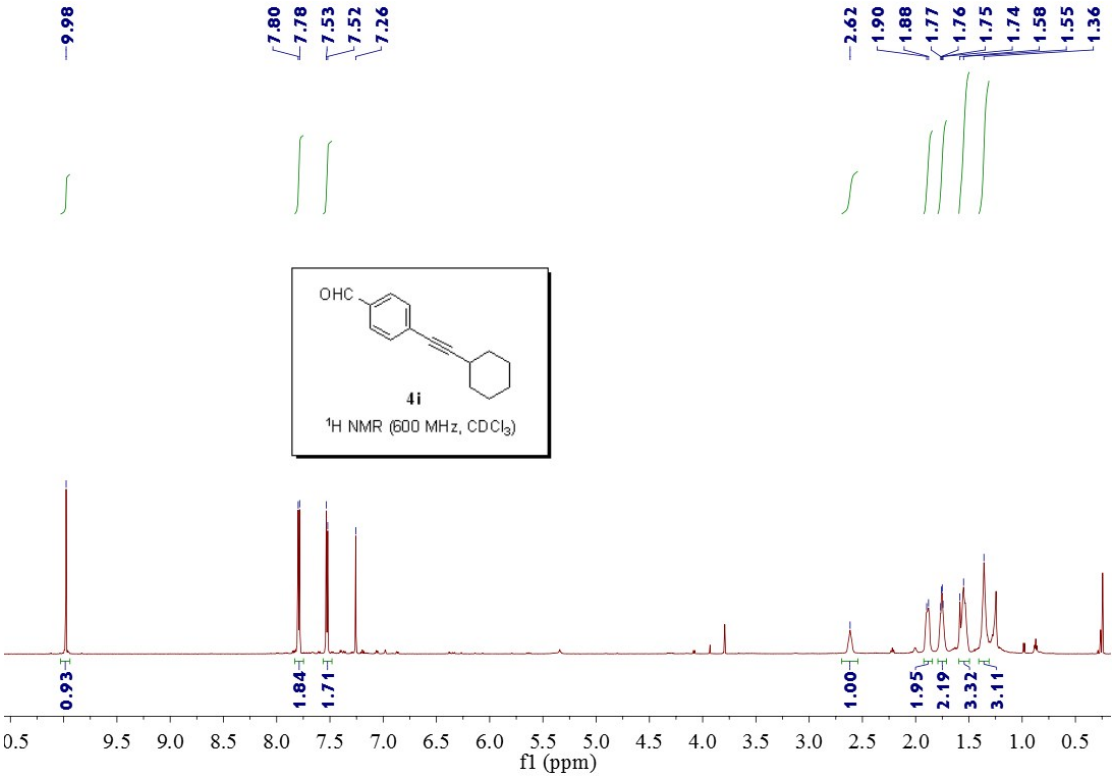

140.52
140.09
131.95
128.77
127.40
126.94
126.81
123.08
95.19
80.33
77.21
77.00
76.79
32.72
29.70
25.93
24.92
4f
¹³C NMR (151 MHz, CDCl₃)
f1 (ppm)

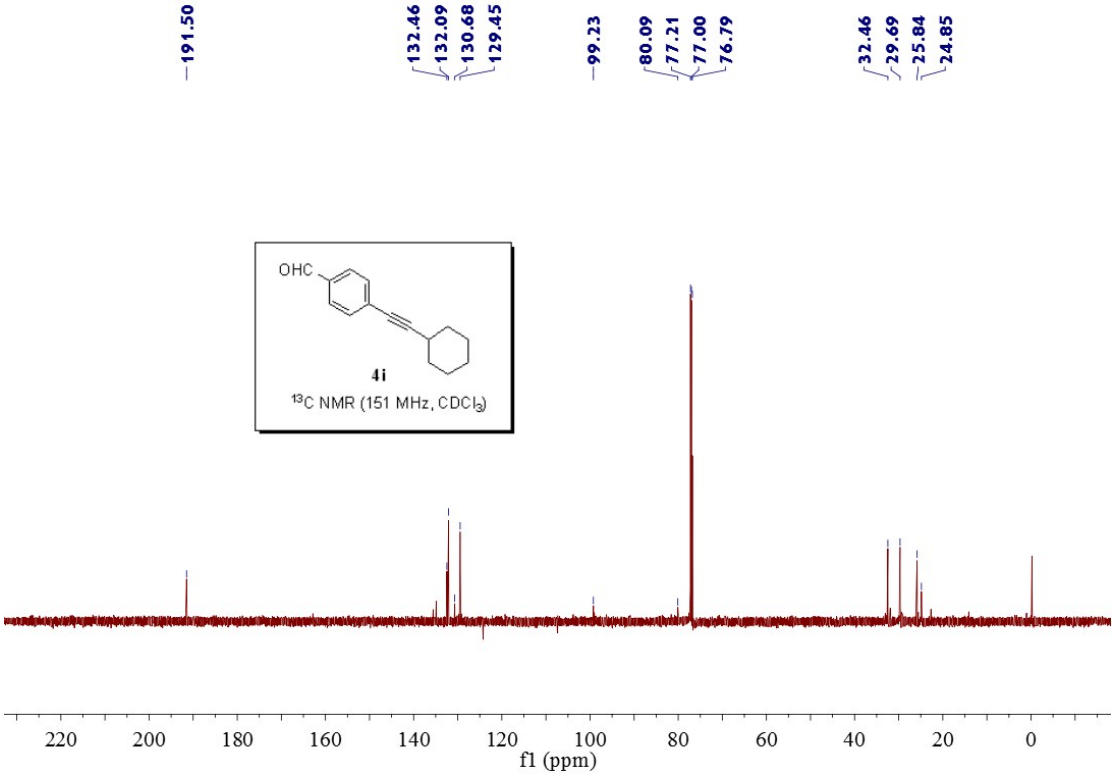

7.43
7.42
7.42
7.37
7.36
7.26
7.19
7.18
7.18
7.17
7.16
7.15
2.68
1.88
1.87
1.80
1.80
1.78
1.78
1.61
1.59
1.40
1.38
Cl
4g
¹H NMR (600 MHz, CDCl₃)
0.95
0.88
1.95
1.00
2.18
2.39
3.21
3.26
fl (ppm)

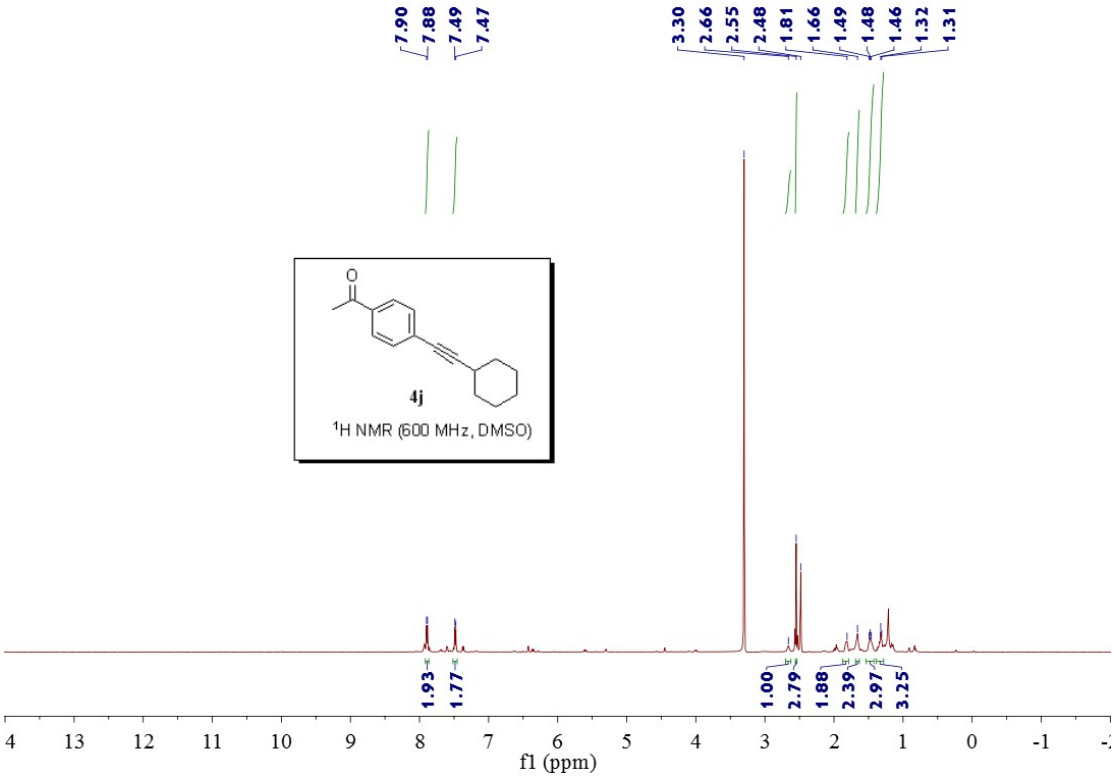

135.82
133.17
129.07
128.36
126.23
123.92
100.11
77.58
77.21
77.00
76.79
32.47
29.73
25.96
24.67
Cl
4g
¹³C NMR (151 MHz, CDCl₃)
fl (ppm)

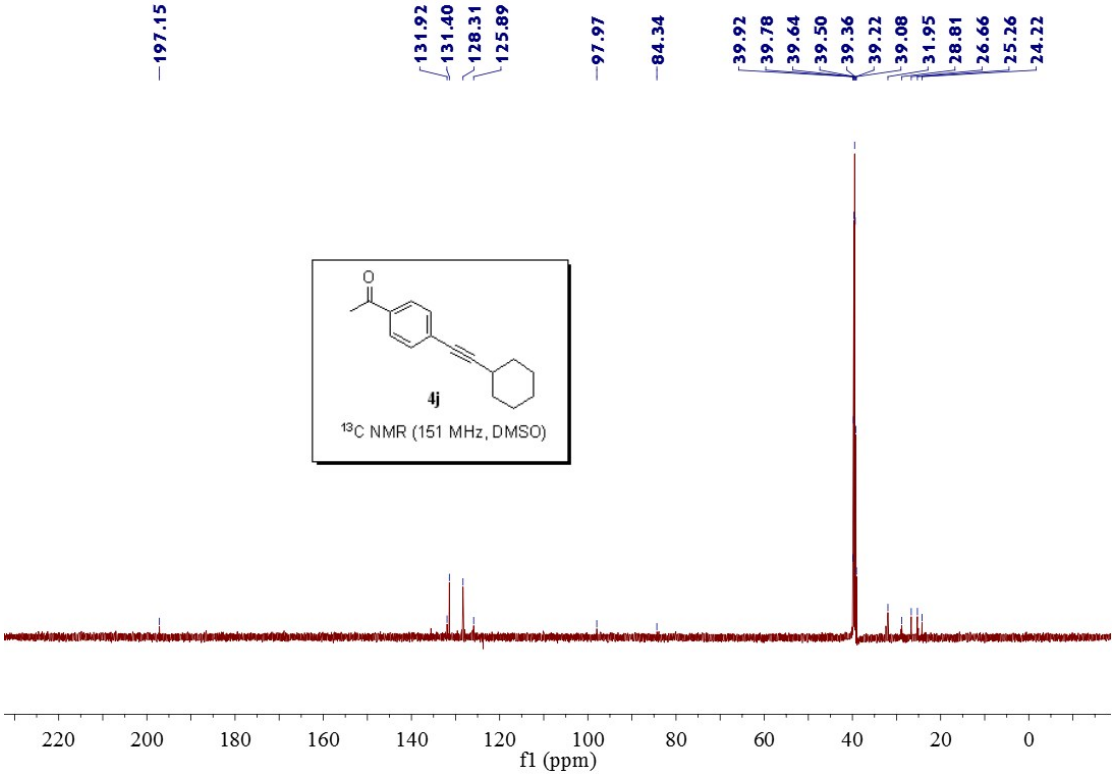

7.32
7.30
7.26
7.25
7.23
2.56
1.88
1.86
1.75
1.74
1.73
1.57
1.54
1.52
1.50
1.34
Cl
4h
¹H NMR (600 MHz, CDCl₃)
1.69
1.72
1.00
2.02
2.08
3.46
2.95
f1 (ppm)

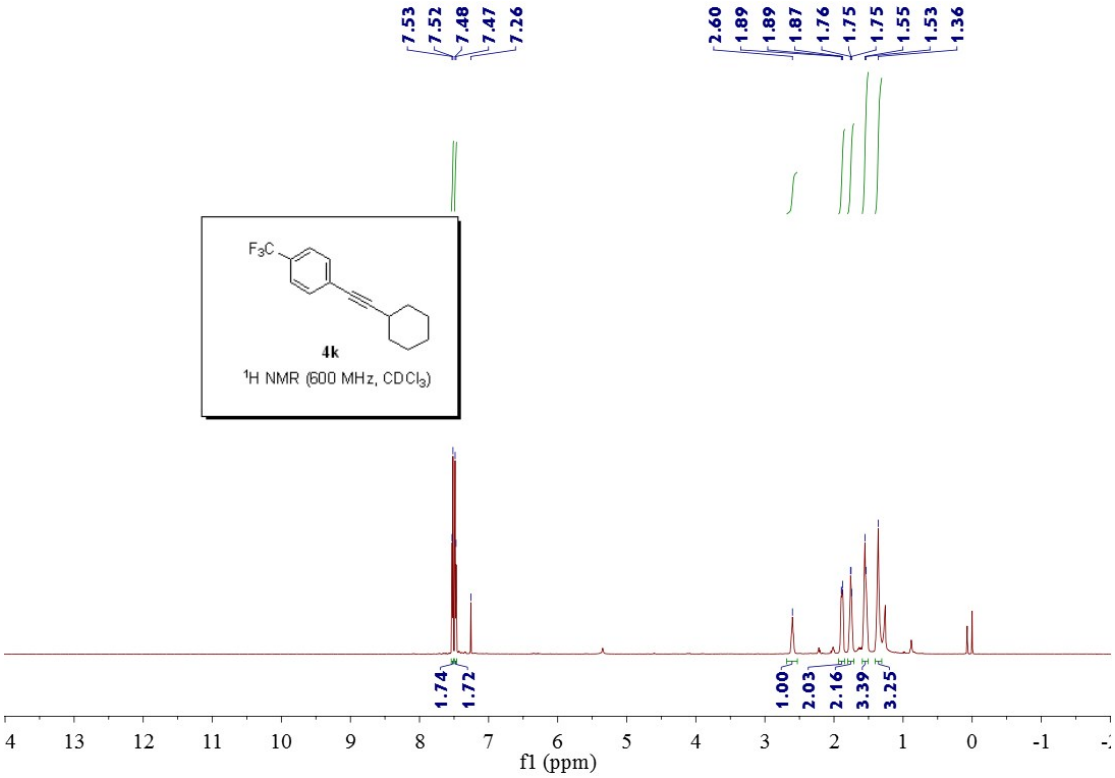

133.26
132.78
128.41
122.60
95.50
79.42
77.32
77.00
76.68
32.58
29.69
25.86
24.88
Cl
4h
¹³C NMR (151 MHz, CDCl₃)
f1 (ppm)

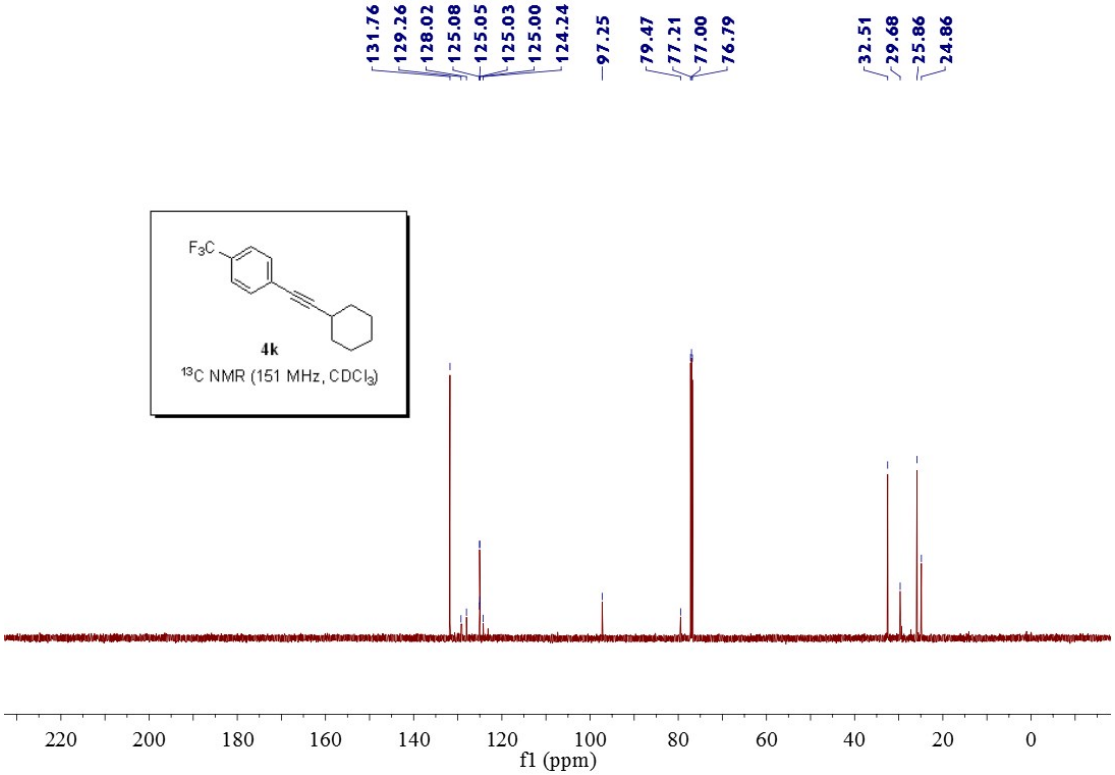

9.98
7.80
7.78
7.53
7.52
7.26
2.62
1.90
1.88
1.77
1.76
1.75
1.74
1.58
1.55
1.36
OHC
4i
1H NMR (600 MHz, CDCl3)
0.93
1.84
1.71
1.00
1.95
2.19
3.32
3.11
f1 (ppm)

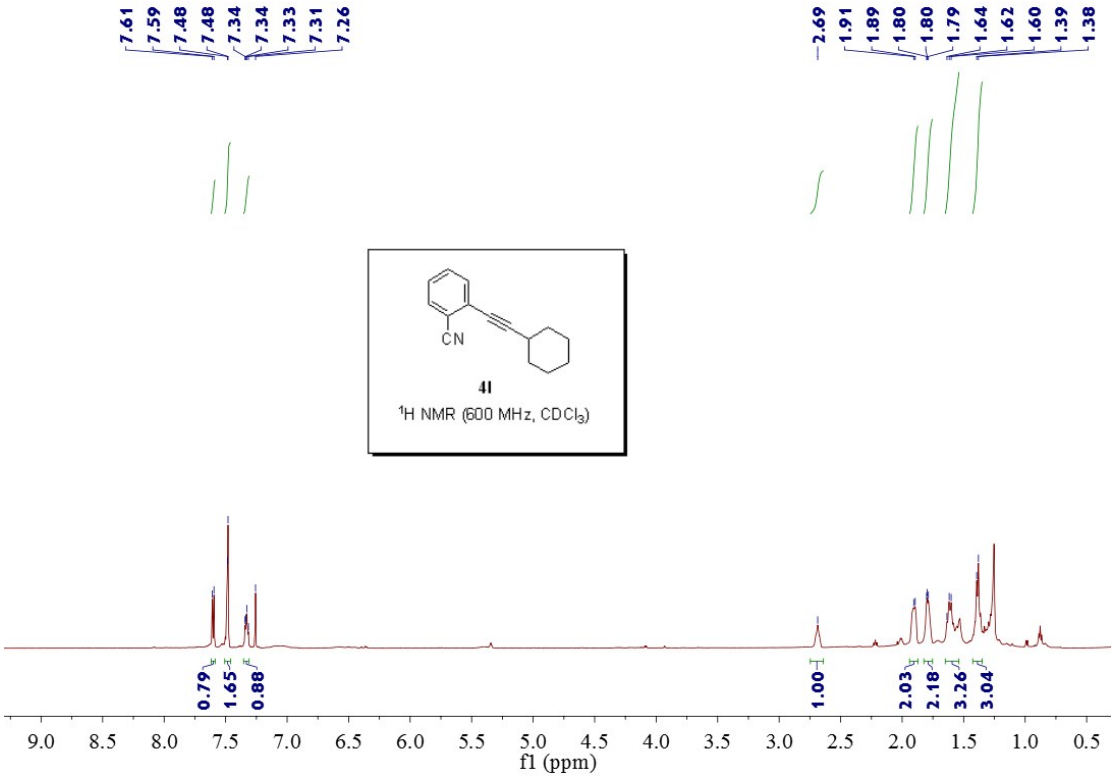

191.50
132.46
132.09
130.68
129.45
99.23
80.09
77.21
77.00
76.79
32.46
29.69
25.84
24.85
OHC
4i
13C NMR (151 MHz, CDCl3)
f1 (ppm)

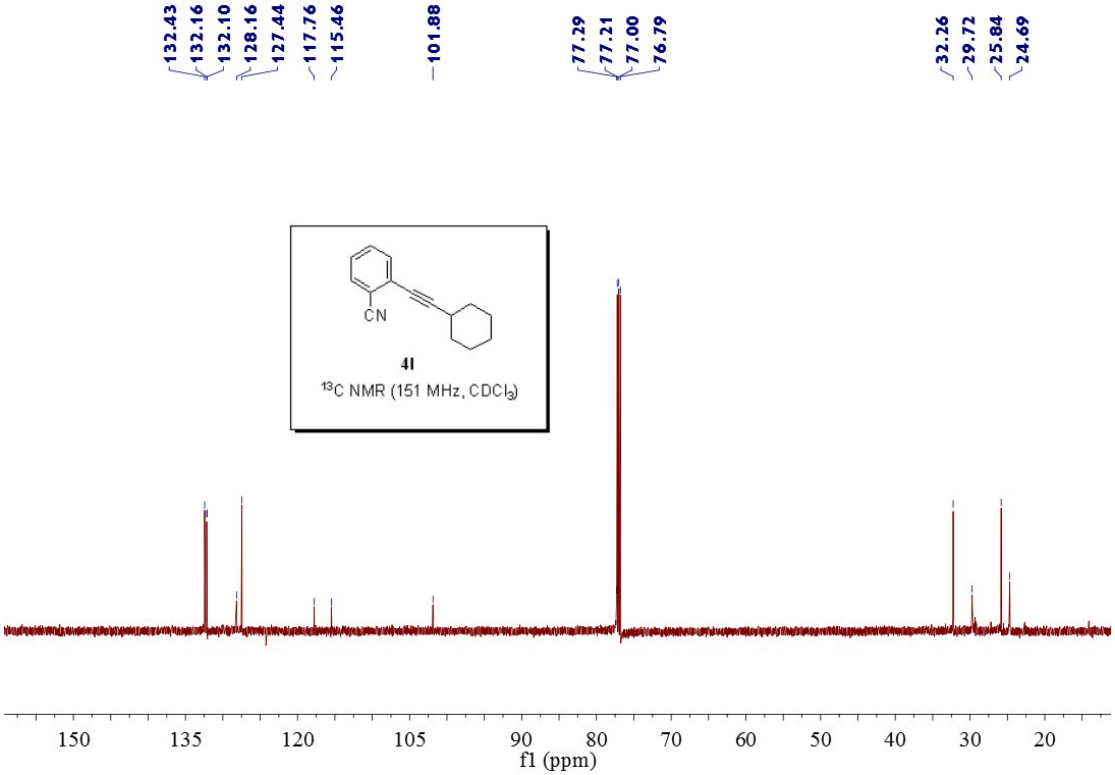

7.90
7.88
7.49
7.47
3.30
2.66
2.55
2.48
1.81
1.66
1.49
1.48
1.46
1.32
1.31
4j
1H NMR (600 MHz, DMSO)
1.93
1.77
1.00
2.79
1.88
2.39
2.97
3.25
f1 (ppm)

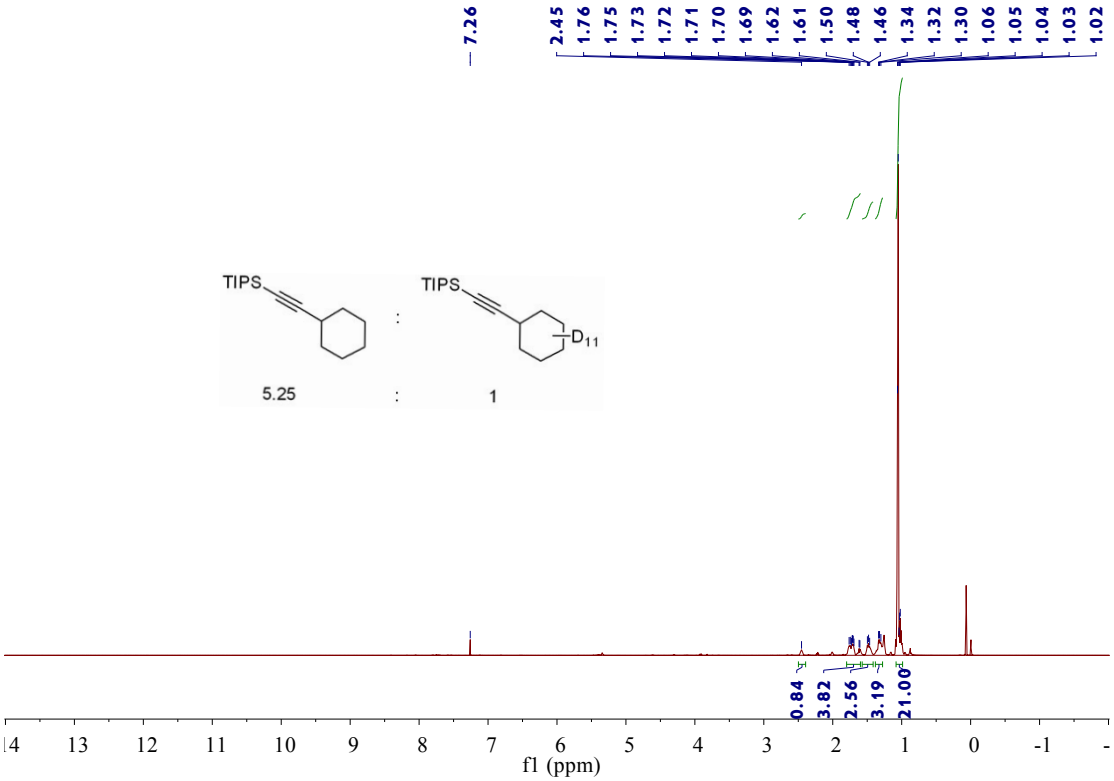

197.15
131.92
131.40
128.31
125.89
97.97
84.34
39.92
39.78
39.64
39.50
39.36
39.22
39.08
31.95
28.81
26.66
25.26
24.22
4j
13C NMR (151 MHz, DMSO)
f1 (ppm)


7.53
7.52
7.48
7.47
7.26
2.60
1.89
1.89
1.87
1.76
1.75
1.75
1.55
1.53
1.36
F3C
4k
1H NMR (600 MHz, CDCl3)
1.74
1.72
1.00
2.03
2.16
3.39
3.25
f1 (ppm)


131.76
129.26
128.02
125.08
125.05
125.03
125.00
124.24
97.25
79.47
77.21
77.00
76.79
32.51
29.68
25.86
24.86
F3C
4k
13C NMR (151 MHz, CDCl3)
f1 (ppm)


7.61
7.59
7.48
7.48
7.34
7.34
7.33
7.31
7.26
2.69
1.91
1.89
1.80
1.80
1.79
1.64
1.62
1.60
1.39
1.38
CN
4l
1H NMR (600 MHz, CDCl3)
0.79
1.65
0.88
1.00
2.03
2.18
3.26
3.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


132.43
132.16
132.10
128.16
127.44
117.76
115.46
101.88
77.29
77.21
77.00
76.79
32.26
29.72
25.84
24.69
CN
4l
13C NMR (151 MHz, CDCl3)
150 135 120 105 90 80 70 60 50 40 30 20
f1 (ppm)


7.26
2.45
1.76
1.75
1.73
1.72
1.71
1.70
1.69
1.62
1.61
1.50
1.48
1.46
1.34
1.32
1.30
1.06
1.05
1.04
1.03
1.02
TIPS
TIPS
D11
5.25 : 1
0.84
3.82
2.56
3.19
21.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)