

SUPPORTING INFORMATION

Copper(I)@Carbon-Catalyzed Carboxylation of Terminal Alkynes with CO₂ at Atmospheric Pressure

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1. General Information

The starting materials were commercially available and were used without further purification except solvents. The products were isolated by column chromatography on silica gel (200-300 mesh) using petroleum ether (60-90 °C) and ethyl acetate. The test of Cu content was carried out in a TAS990 Atomic absorption spectrophotometer (BEIJING PURKINJE GENERAL INSTRUMENT CO.LTD), used graphite furnace atomic absorption spectrometry. X-ray photoelectron spectra were recorded using a PHI-5000 Versaprobe. All products were characterized by ^1H NMR, ^{13}C NMR and mass spectroscopy. ^1H NMR chemical shifts were referenced to residual solvent as determined relative to CDCl_3 (7.26 ppm). The ^{13}C NMR chemical shifts were reported in ppm relative to the carbon resonance of CDCl_3 (central peak is 77.00 ppm). ^1H NMR peaks are labeled as singlet (s), doublet (d), triplet (t), and multiplet (m). The coupling constants, J , are reported in Hertz (Hz). GC-MS data were performed on Finnigan HP G1800 A or Shimadzu GCMS-QP2010 SE. GC analyses were performed on a Shimadzu GC-2014 equipped with a capillary column (RTX-17 30 m \times 0.25 μm) using a flame ionization detector.

2. Preparation and Characterization of Catalysts

2.1 Preparation of supporter

To the aqueous solution of concentrated hydrochloric acid (8 mL), hydrofluoric acid (6 mL) and water (400 mL), coconut shell carbon (100~200 mesh, 20 g) was added. The mixture was stirred at room temperature for 24 h and then filtered. Subsequently, the solid was dried at 110 °C for 16 h under flowing nitrogen gas. The obtained solid was employed as supporter for the synthesis of catalyst.

2.2 Preparation of Catalysts using the Impregnation Method

CuCl@C: CuCl (0.3 g) was dissolved in the concentrated hydrochloric acid (1 g). Then the activated carbon (0.7 g) was added. After ultrasonic treatment for 1 h, the obtained catalyst was dried under vacuum at 100 °C.

CuBr@C: CuBr (0.3 g) was dissolved in the concentrated ammonium hydroxide (2 g). Then the activated carbon (0.7 g) was added. After ultrasonic treatment for 1 h, the obtained catalyst was dried under vacuum at 100 °C.

CuI@C: CuI (0.3 g) and KI (4.7 g) were dissolved in water (6 g). Then the activated carbon (0.7 g) was added. Distilled water was added (1 mL/min) under slowly stirring, facilitating the precipitation of CuI on the surface of supporter. After filtration, the obtained catalyst was dried under vacuum at 100 °C.

3. General Procedure for the Carboxylation of Terminal Alkynes

In a 20 mL Schlenk flask, terminal alkyne (1.0 mmol), Cs_2CO_3 (0.391 g, 1.2 mmol), indicated amount of catalyst, *n*-BuI (0.221 g, 1.2 mmol) and ethylene carbonate (3

mL) were added. The flask was capped with a stopper and sealed. Then the freeze-pump-thaw method was employed for gas exchanging process. The reaction mixture was stirred at 80 °C for desired time under the atmosphere of CO₂ (99.999%, balloon). After the reaction, the mixture was cooled to room temperature, extracted with *n*-hexane. The combined organic layers were washed with saturated NaCl solution then dried with anhydrous Na₂SO₄. The residue was purified by column chromatography (silica gel, petroleum ether/EtOAc) to afford the desired product alkyl 2-alkynoates.

4. Recycle of the Catalyst

In a 50 mL Schlenk flask, phenylacetylene (3.0 mmol), Cs₂CO₃ (3.6 mmol), Cu catalyst (10 mol%), *n*-BuI (3.6 mmol) and ethylene carbonate (5 mL) were added. The flask was capped with a stopper and sealed. Then the freeze-pump-thaw method was employed for gas exchanging process. The reaction mixture was stirred at 80 °C for 2 h under the atmosphere of CO₂ (99.999%, balloon). After the reaction, the mixture was cooled to room temperature, diluted with EtOAc. After centrifugation, the organic phase was analysed by GC to determine the yield of the reaction. The recycled catalyst was dried under vacuum then reused in the next run.

5. Characterization Data of the catalysts

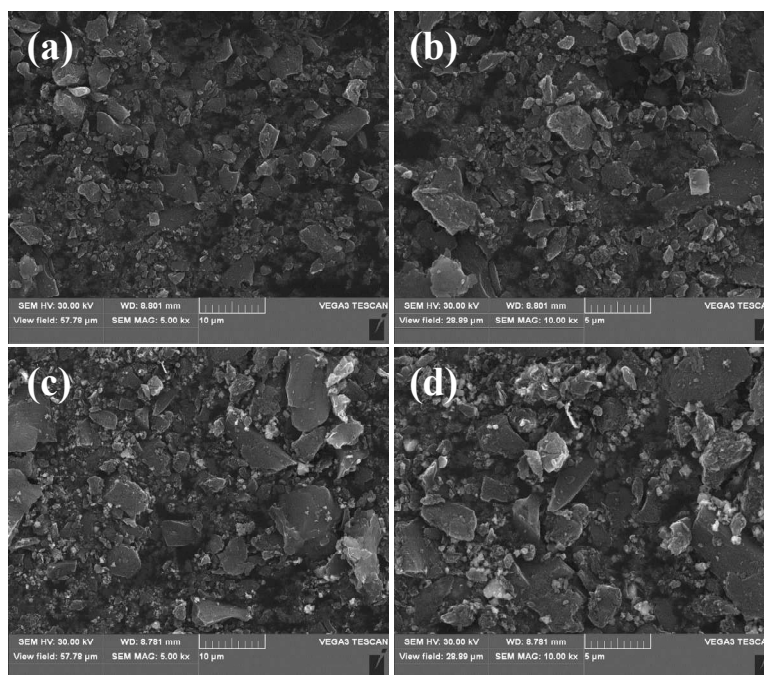
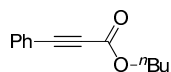


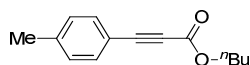
Figure S1. SEM images of CuBr@C before (a and b) and after (c and d) catalytic reaction

Table S1. Brunauer-Emmett-Teller (BET) analysis of catalysts

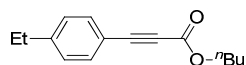
Catalysts	S _{BET} (m ² /g)	V _p (cm ³ /g)
Freshly prepared	868	0.39
Recycled	939	0.40

6. Characterization Data of Products

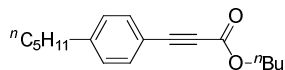
Compound **2a**: Colourless oil; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.62–7.59 (m, 2H), 7.48–7.37 (m, 3H), 4.26 (t, J = 6.7 Hz, 2H), 1.72 (quint, J = 6.8 Hz, 2H), 1.51–1.41 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 154.2, 132.9, 130.5, 128.5, 119.6, 86.0, 80.7, 65.9, 30.4, 19.0, 13.6; EI-MS, m/z (%): 129.10 (100), 201.08 (34) [M^+].



Compound **2b**: Light yellow solid; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.48 (d, J = 7.5 Hz, 2H), 7.17 (d, J = 7.6 Hz, 2H), 4.23 (t, J = 6.6 Hz, 2H), 2.37 (s, 3H), 1.69 (quint, J = 7.3 Hz, 2H), 1.51–1.36 (m, 2H), 0.96 (t, J = 7.5 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 154.3, 141.2, 132.9, 129.3, 116.5, 86.6, 80.3, 65.8, 30.5, 21.7, 19.0, 13.6; EI-MS, m/z (%): 116.20 (100), 216.25 (13) [M^+].

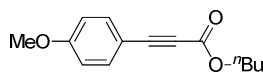


Compound **2c**: Yellow oil; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.52–7.40 (m, 2H), 7.21–7.14 (m, 2H), 4.23 (t, J = 6.7 Hz, 2H), 2.70–2.61 (m, 2H), 1.73–1.63 (m, 2H), 1.48–1.37 (m, 2H), 1.25–1.20 (m, 3H), 0.98–0.92 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 154.3, 147.4, 133.1, 128.1, 116.7, 86.6, 80.3, 65.8, 30.5, 28.9, 19.0, 15.1, 13.6; EI-MS, m/z (%): 130.20 (100), 230.20 (14) [M^+]; HRMS (ESI): C₁₅H₁₈O₂Na for [$M+Na$]⁺ calculated 253.1199, found 253.1196.

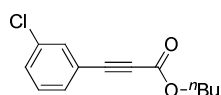


Compound **2d**: Yellow oil; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.50 (d, J = 8.1 Hz, 2H), 7.18 (d, J = 8.1 Hz, 2H), 4.23 (t, J = 6.7 Hz, 2H), 2.63–2.59 (m, 2H), 1.70–1.58 (m, 4H), 1.46–1.28 (m, 6H), 0.98–0.87 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 154.3, 146.2, 133.0, 128.6, 116.7, 86.6, 80.3, 65.8, 36.0, 31.4, 30.7, 30.5, 22.4,

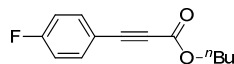
19.0, 14.0, 13.6; EI-MS, m/z (%): 172.25 (100), 272.30 (15) [M^+]; HRMS (ESI): $C_{18}H_{24}O_2Na$ for $[M+Na]^+$ calculated 295.1669, found 295.1664.



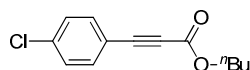
Compound **2e**: White solid; 1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.53 (d, $J = 8.8$ Hz, 2H), 6.87 (d, $J = 8.8$ Hz, 2H), 4.22 (t, $J = 6.7$ Hz, 2H), 3.82 (s, 3H), 1.69 (dt, $J = 14.7$, 6.8 Hz, 2H), 1.43 (dq, $J = 14.7$, 7.4 Hz, 2H), 0.95 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 161.4, 154.4, 134.9, 114.2, 111.4, 86.8, 80.1, 65.7, 55.3, 30.5, 19.0, 13.6; EI-MS, m/z (%): 132.15 (100), 232.20 (15) [M^+].



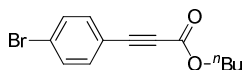
Compound **2f**: Yellow oil; 1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.57 (s, 1H), 7.47–7.41 (m, 2H), 7.33–7.29 (m, 1H), 4.24 (t, $J = 6.6$ Hz, 2H), 1.73–1.63 (m, 2H), 1.48–1.37 (m, 2H), 0.96 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 153.8, 134.5, 132.6, 131.0, 130.9, 129.8, 121.4, 84.1, 81.4, 66.1, 30.4, 19.0, 13.6; EI-MS, m/z (%): 163.10 (100), 235.15 (7) [M^+]; HRMS (ESI): $C_{13}H_{13}O_2ClNa$ for $[M+Na]^+$ calculated 259.0496, found 259.0493.



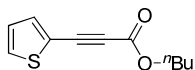
Compound **2g**: Yellow oil; 1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.59–7.56 (m, 2H), 7.08–7.04 (m, 2H), 4.23 (t, $J = 6.6$ Hz, 2H), 1.73–1.62 (m, 2H), 1.46–1.38 (m, 2H), 0.95 (t, $J = 7.8$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 165.1, 162.6, 154.1, 135.2, 116.1, 84.9, 80.6, 65.9, 30.4, 19.0, 13.6; EI-MS, m/z (%): 147.15 (100), 220.15 (5) [M^+]; HRMS (ESI): $C_{13}H_{13}FO_2Na$ for $[M+Na]^+$ calculated 243.0792, found 243.0786.



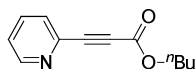
Compound **2h**: Yellow oil; 1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.51 (d, $J = 8.4$ Hz, 2H), 7.35 (d, $J = 8.5$ Hz, 2H), 4.23 (t, $J = 6.7$ Hz, 2H), 1.71–1.66 (m, 2H), 1.46–1.40 (m, 2H), 0.95 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 154.0, 136.9, 134.1, 129.0, 118.1, 84.7, 81.5, 66.0, 30.4, 19.0, 13.6; EI-MS, m/z (%): 163.10 (100), 236.10 (7) [M^+]; HRMS (ESI): $C_{13}H_{13}O_2ClNa$ for $[M+Na]^+$ calculated 259.0496, found 259.0494.



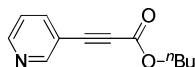
Compound **2i**: Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.52 (d, $J = 8.5$ Hz, 2H), 7.44 (d, $J = 8.5$ Hz, 2H), 4.23 (t, $J = 6.7$ Hz, 2H), 1.73–1.66 (m, 2H), 1.48–1.38 (m, 2H), 0.95 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 154.0, 134.2, 131.9, 125.3, 118.6, 84.7, 81.6, 66.1, 30.4, 19.0, 13.6; EI-MS, m/z (%): 180.00 (100), 280.10 (8) [M^+].



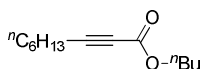
Compound **2j**: Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.48–7.45 (m, 2H), 7.04 (s, 1H), 4.23 (t, $J = 6.6$ Hz, 2H), 1.71–1.67 (m, 2H), 1.46–1.40 (m, 2H), 0.95 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 154.0, 136.4, 131.0, 127.5, 119.4, 84.9, 80.0, 65.9, 30.4, 19.0, 13.6; EI-MS, m/z (%): 108.19 (100), 207.90 (14) [M^+].



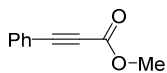
Compound **2k**: Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.64–8.62 (m, 1H), 7.72–7.68 (m, 1H), 7.57 (d, $J = 7.8$ Hz, 1H), 7.35–7.31 (m, 1H), 4.23 (t, $J = 6.6$ Hz, 2H), 1.70–1.63 (m, 2H), 1.44–1.36 (m, 2H), 0.93 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 153.5, 150.5, 140.6, 136.3, 128.5, 124.5, 83.7, 79.2, 66.1, 30.3, 18.9, 13.5; EI-MS, m/z (%): 130.10 (100), 202.15 (2) [M^+].



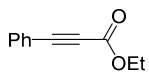
Compound **2l**: Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.80–8.79 (m, 1H), 8.65–8.63 (m, 1H), 7.87–7.84 (m, 1H), 7.33–7.30 (m, 1H), 4.24 (t, $J = 6.6$ Hz, 2H), 1.71–1.67 (m, 2H), 1.46–1.40 (m, 2H), 0.95 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 153.6, 153.3, 150.6, 139.8, 123.1, 117.1, 83.5, 82.2, 66.2, 30.4, 19.0, 13.6; EI-MS, m/z (%): 130.15 (100), 202.15 (10) [M^+].



Compound **2m**: Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ (ppm): 4.13 (t, $J = 6.7$ Hz, 2H), 2.30 (t, $J = 7.2$ Hz, 2H), 1.65–1.53 (m, 4H), 1.40–1.25 (m, 8H), 0.93–0.85 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 154.0, 89.4, 73.1, 65.5, 31.1, 30.4, 28.5, 27.4, 22.4, 19.0, 18.6, 13.9, 13.6; EI-MS, m/z (%): 67.19 (100), 211.02 (46) [M^+].

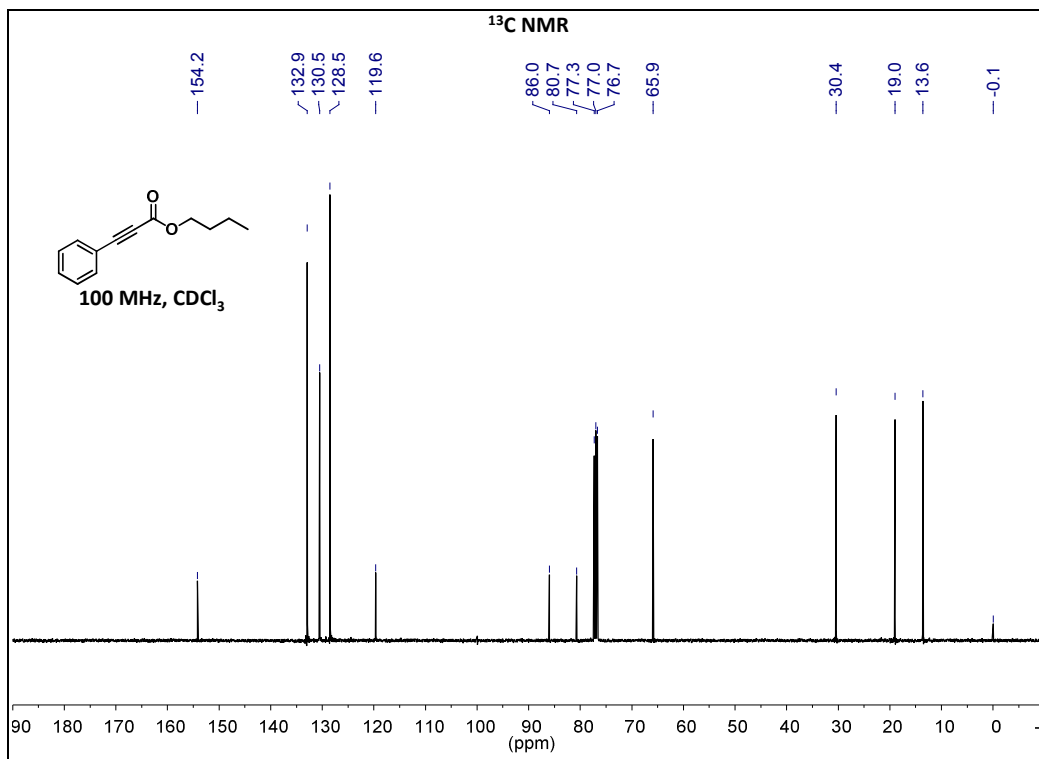
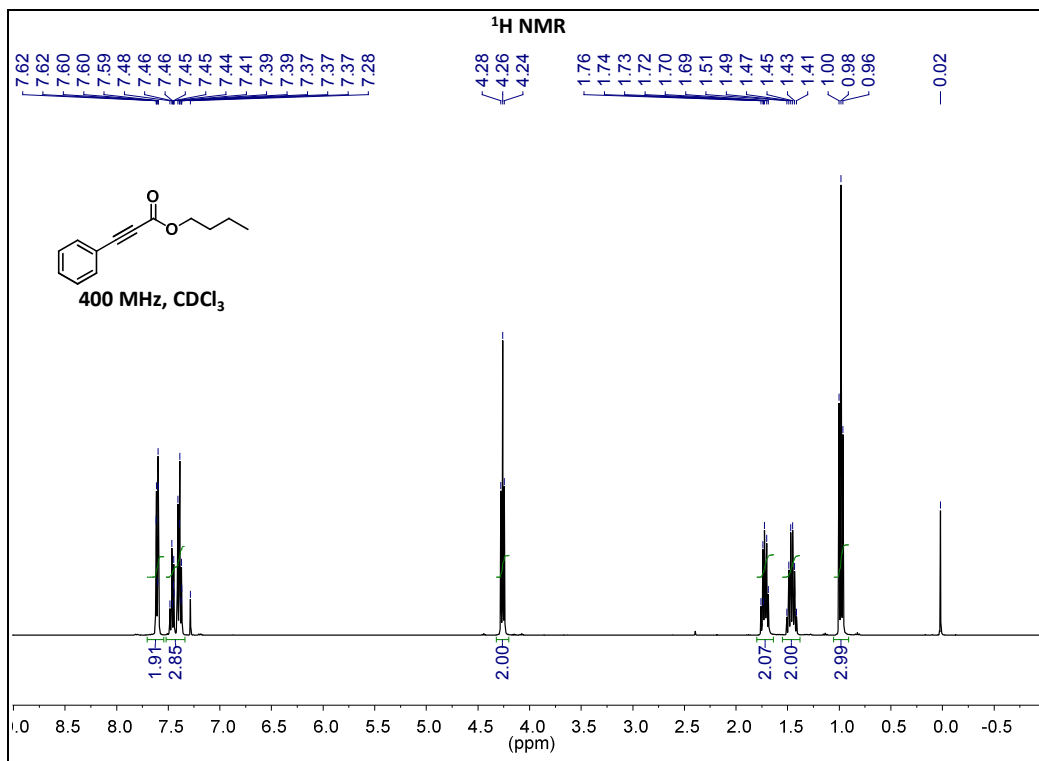


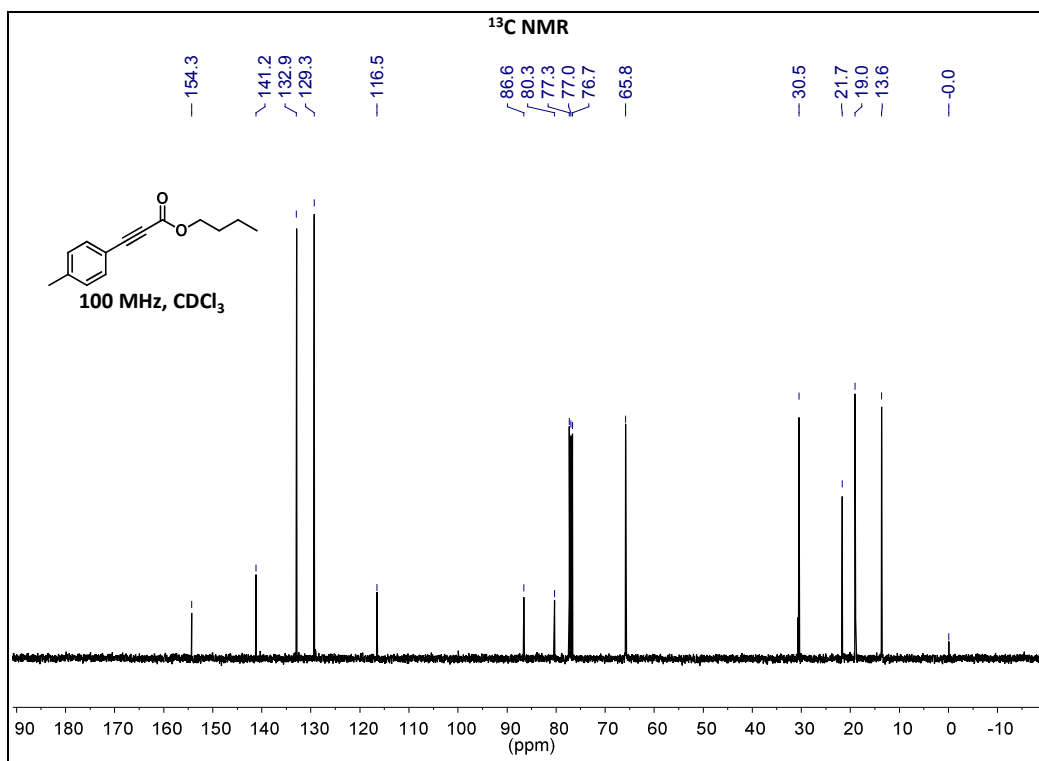
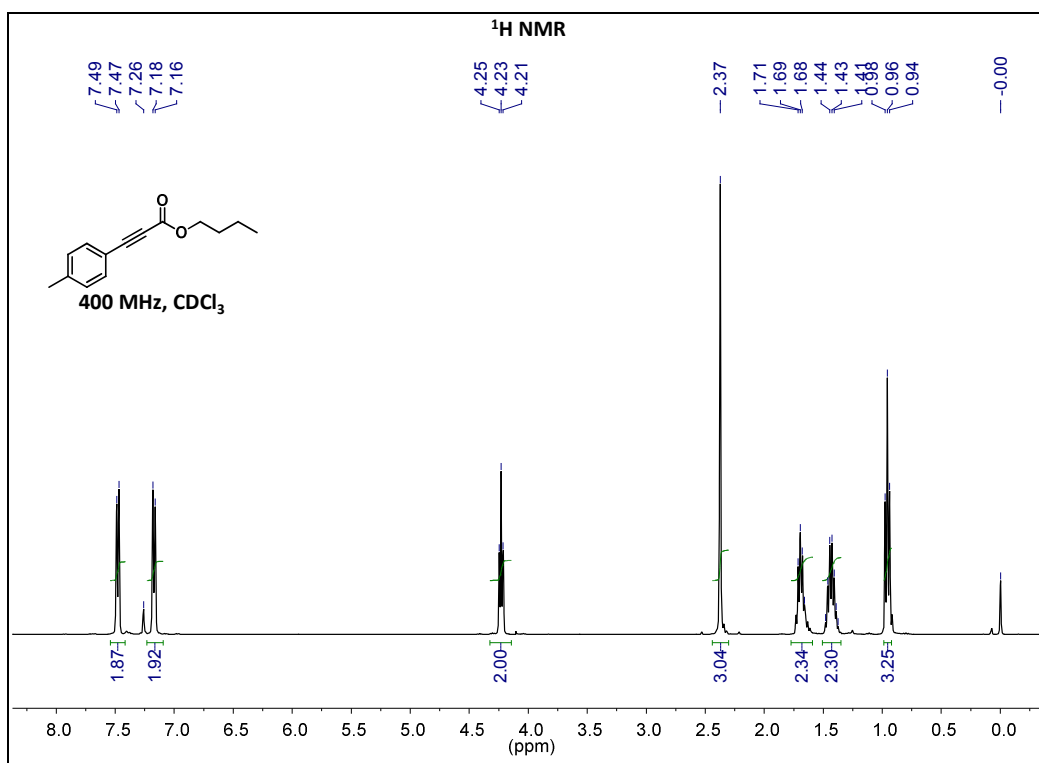
Compound **2n**: Colourless oil; ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.52–7.50 (m, 2H), 7.39–7.28 (m, 3H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 153.4, 132.0, 129.7, 127.6, 118.5, 85.5, 79.4, 51.8; EI-MS, m/z (%): 129.10 (100), 160 (27) $[\text{M}^+]$.

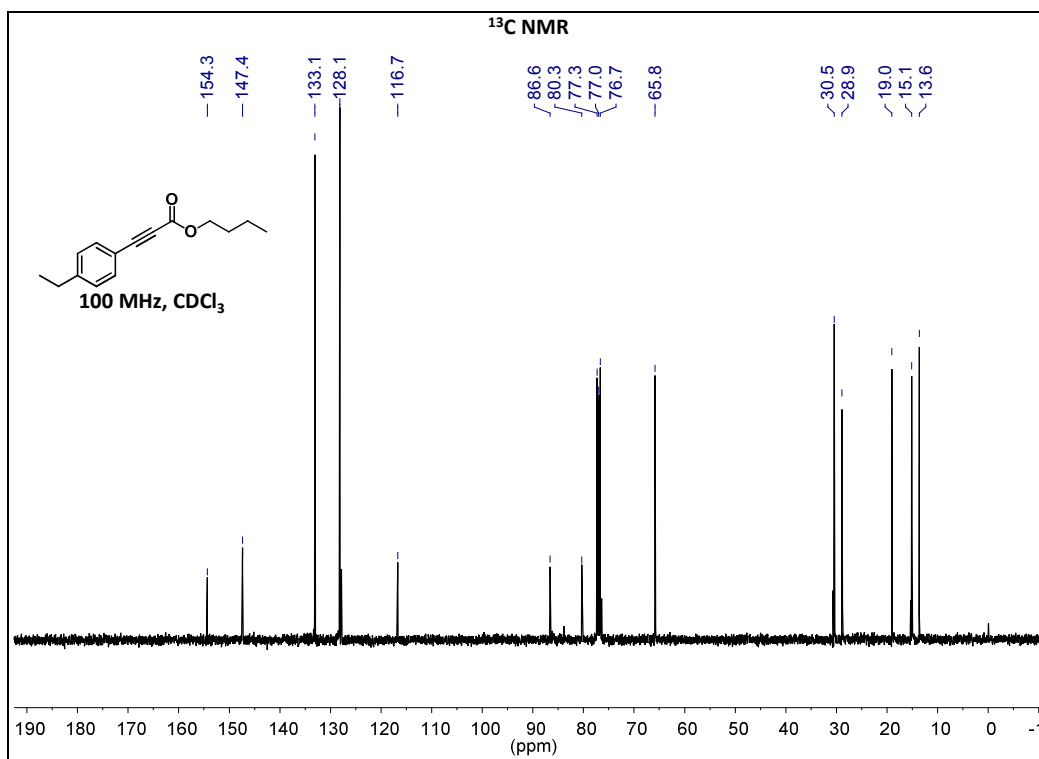
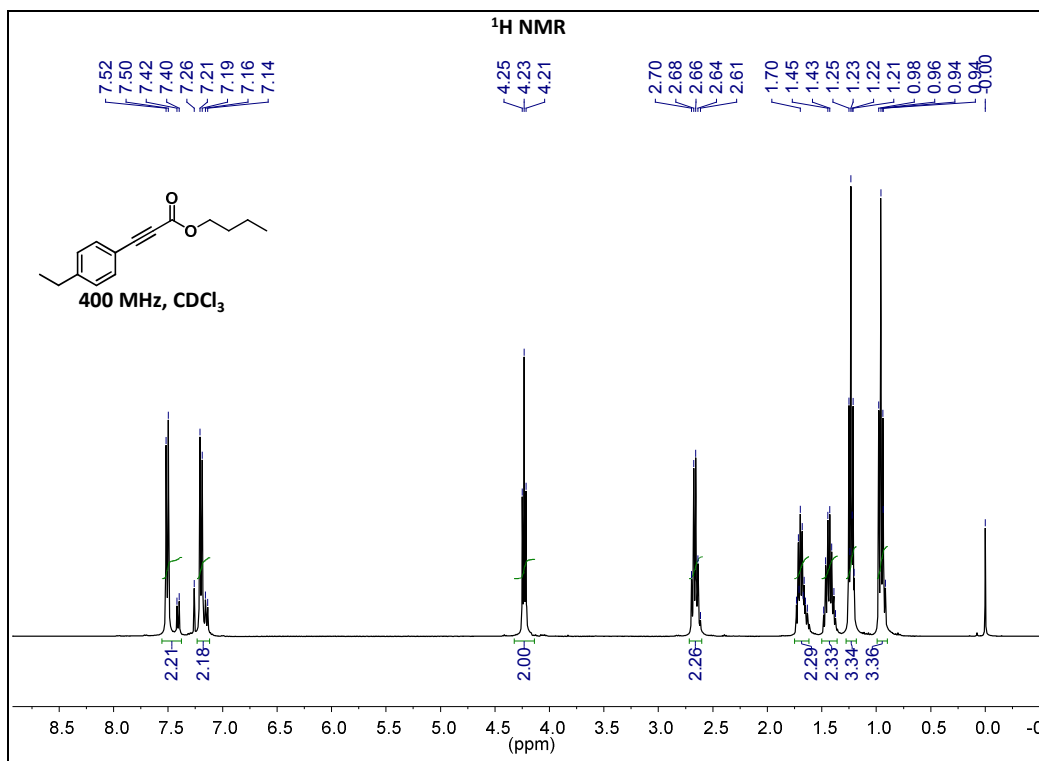


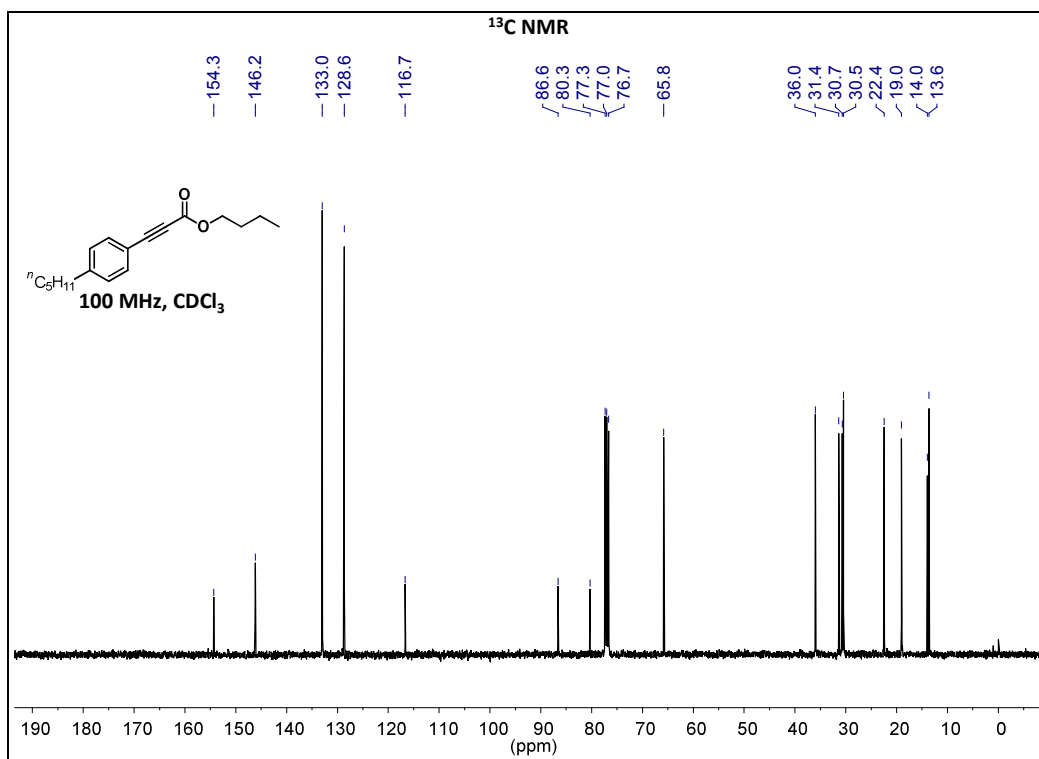
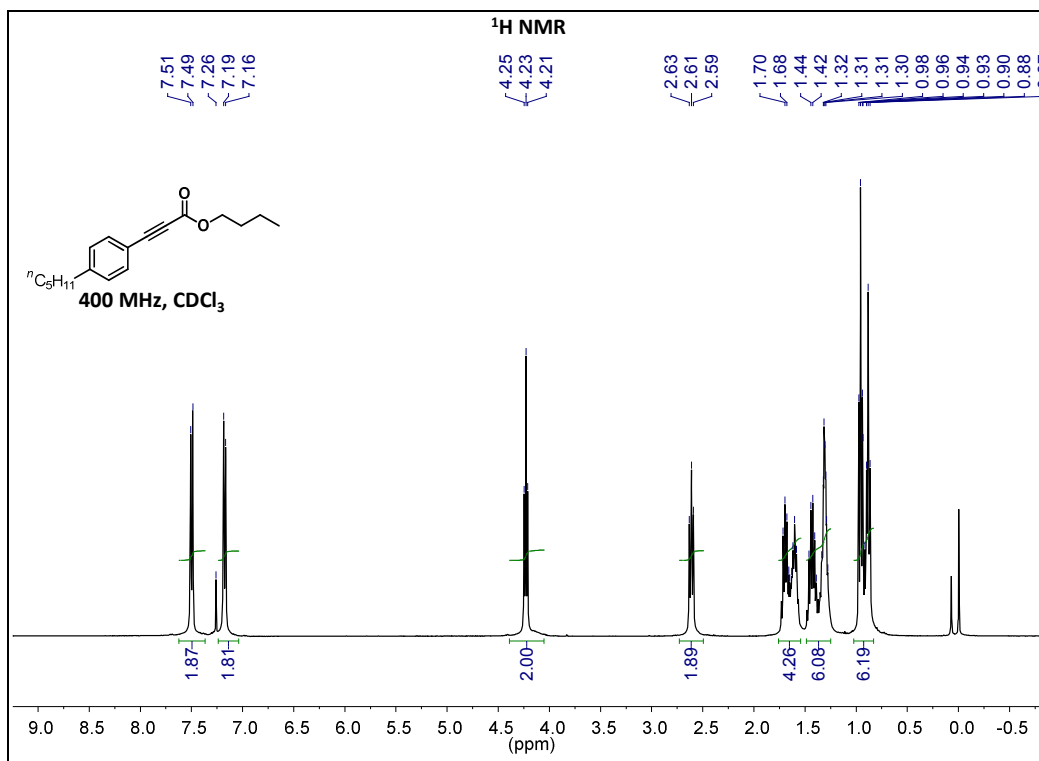
Compound **2o**: Colourless oil; ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.59–7.56 (m, 2H), 7.46–7.34 (m, 3H), 4.29 (q, 2H), 1.35 (t, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 153.0, 131.9, 129.6, 127.5, 118.6, 85.0, 79.7, 61.0, 13.1; EI-MS, m/z (%): 129.10 (100), 174.10 (17) $[\text{M}^+]$.

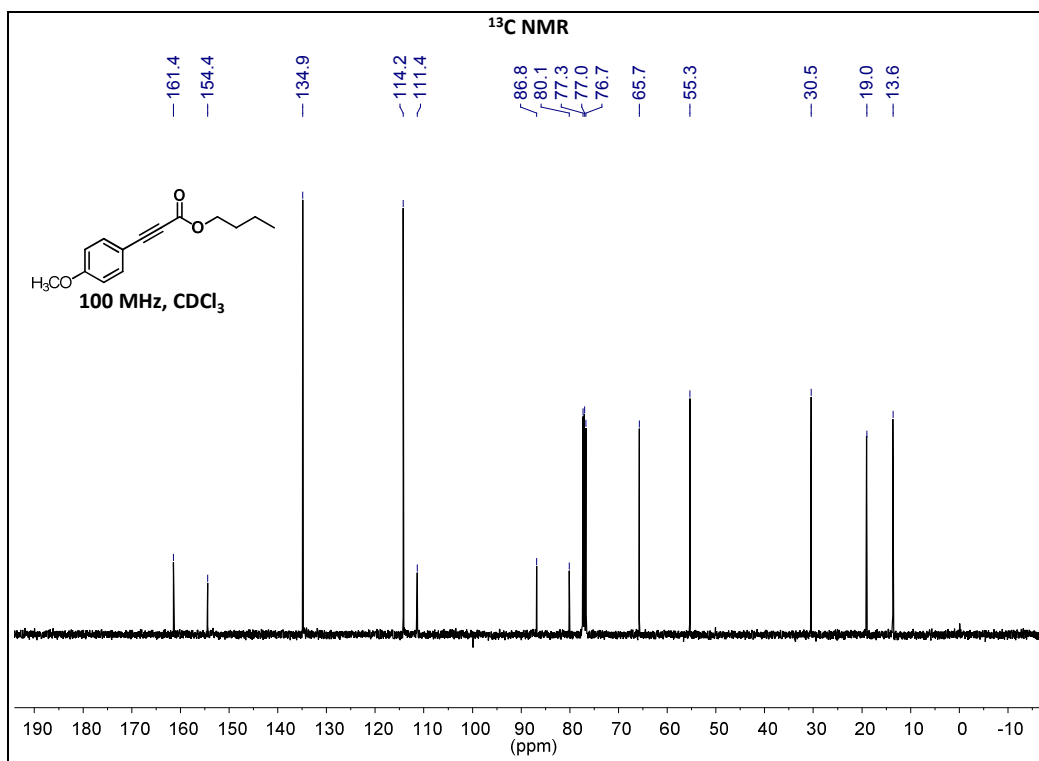
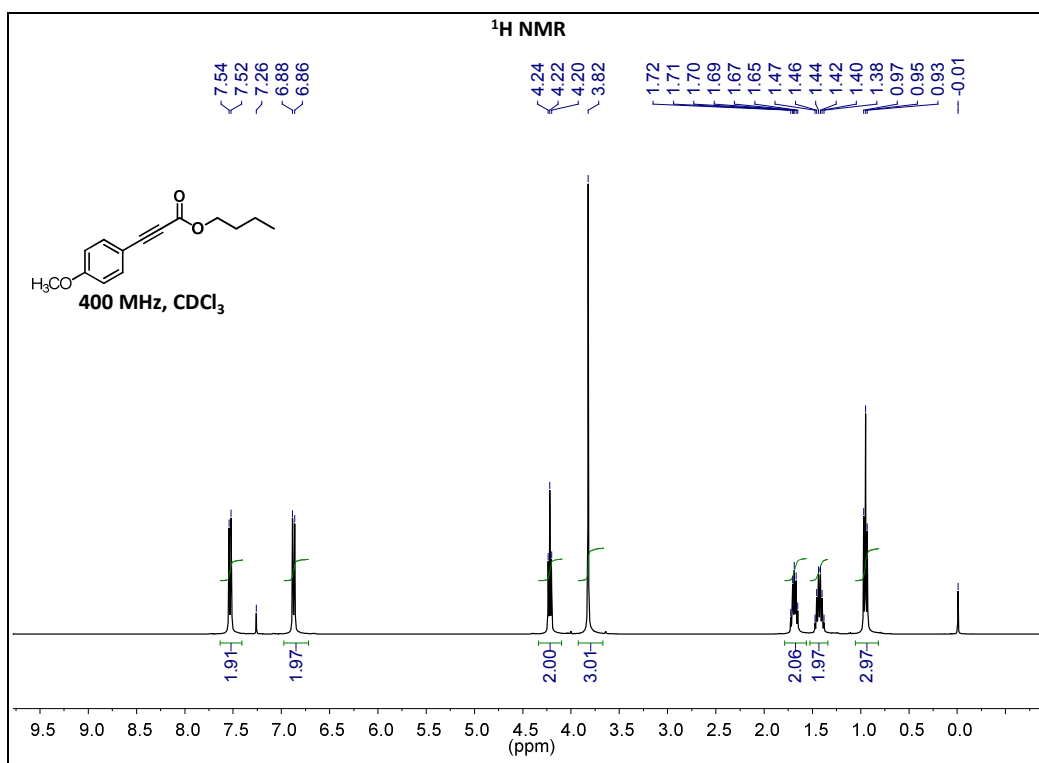
7. NMR Spectral Copies of the Products

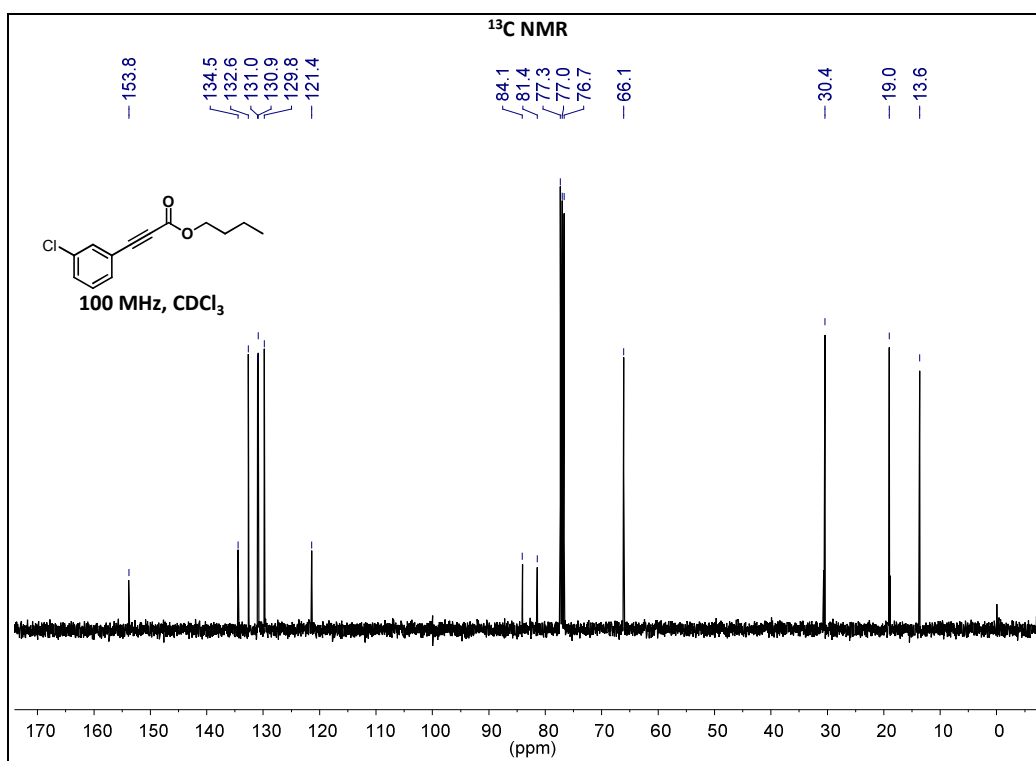
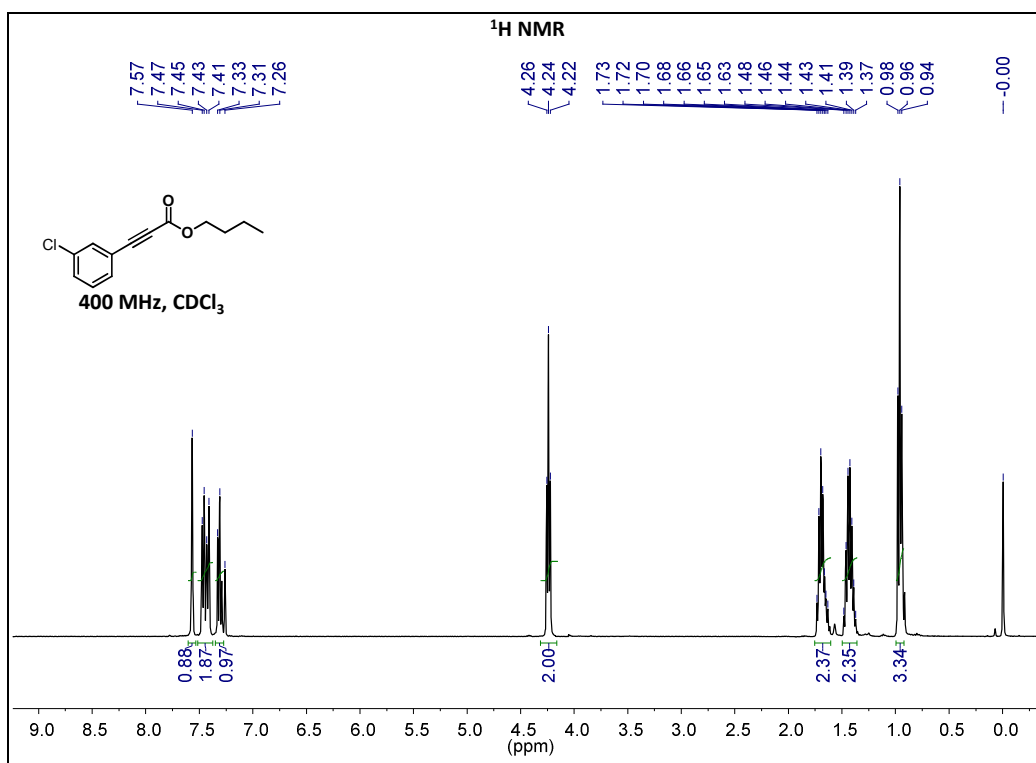


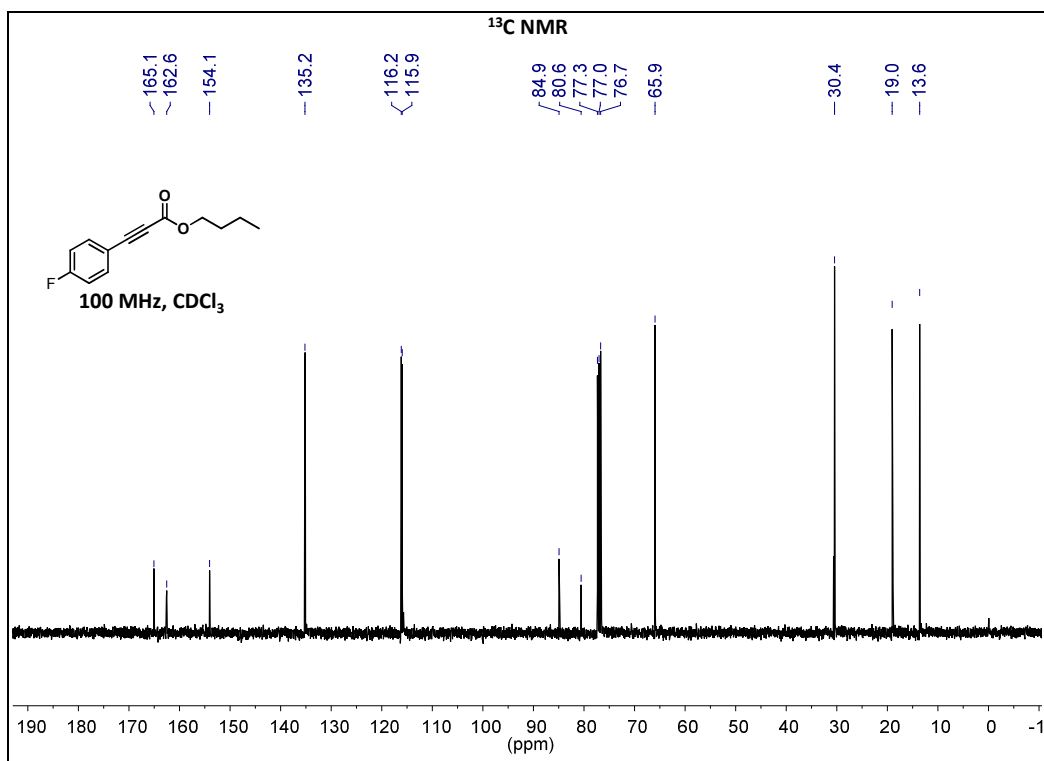
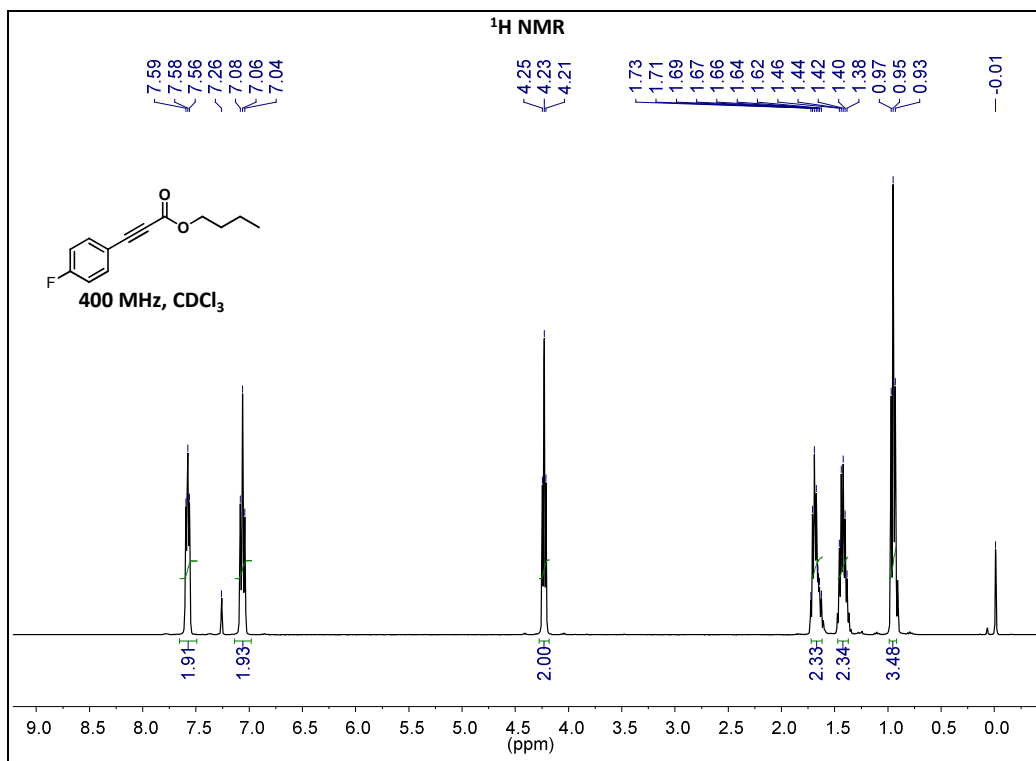


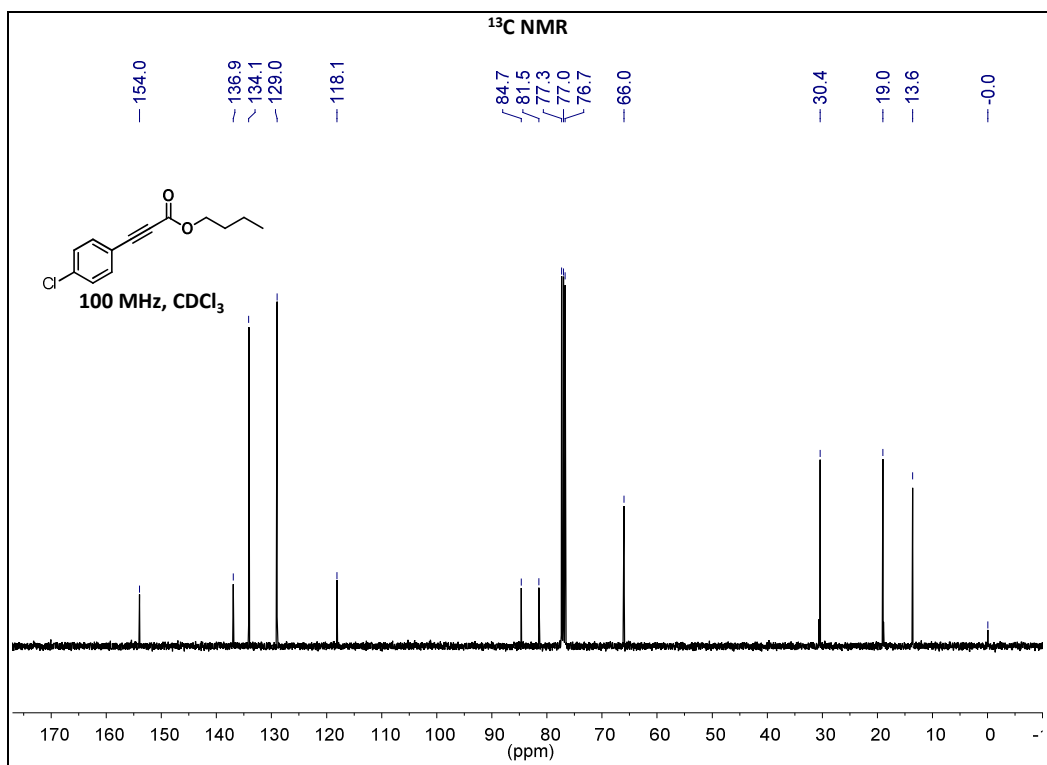
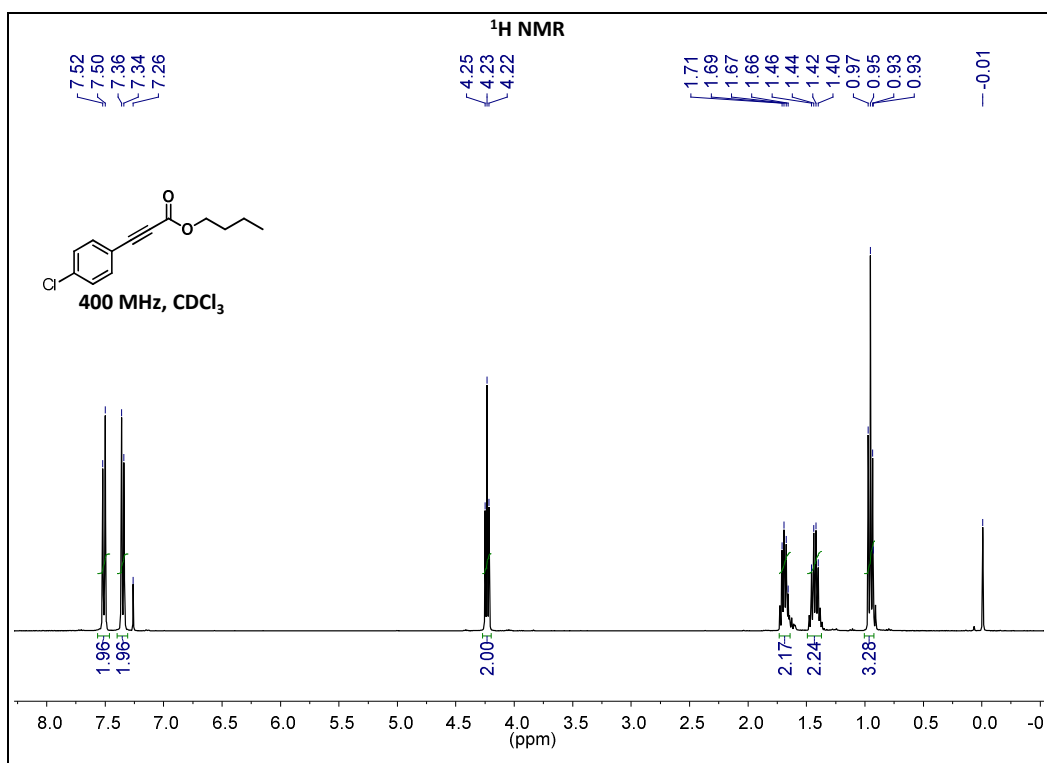


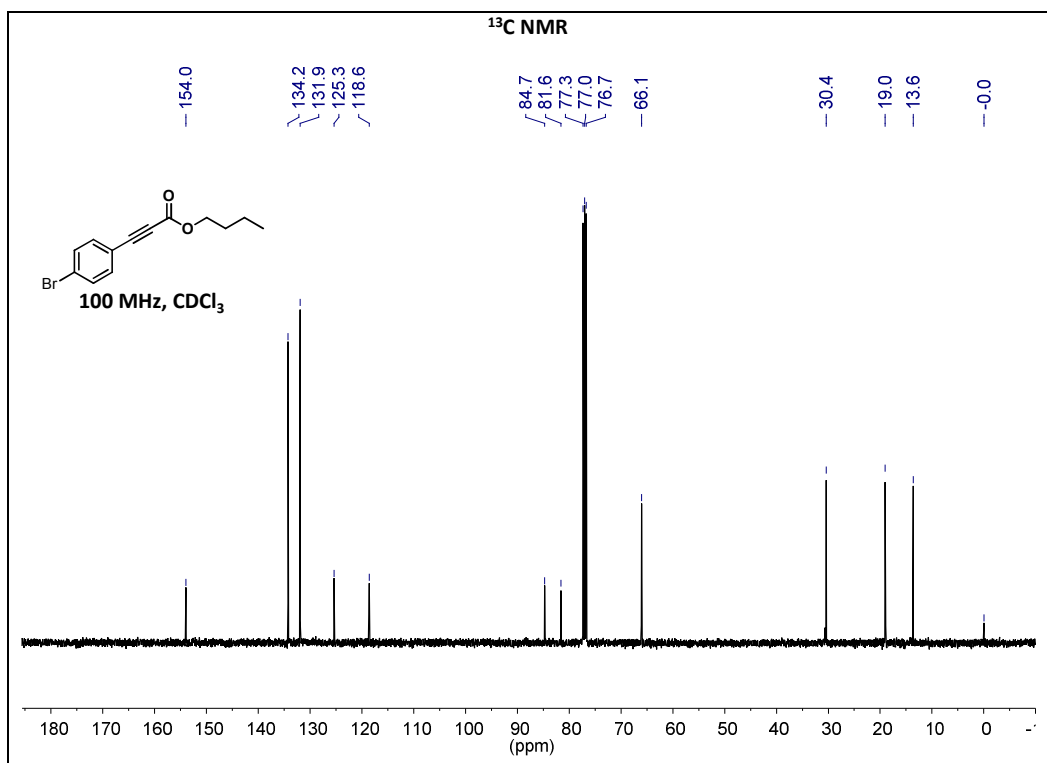
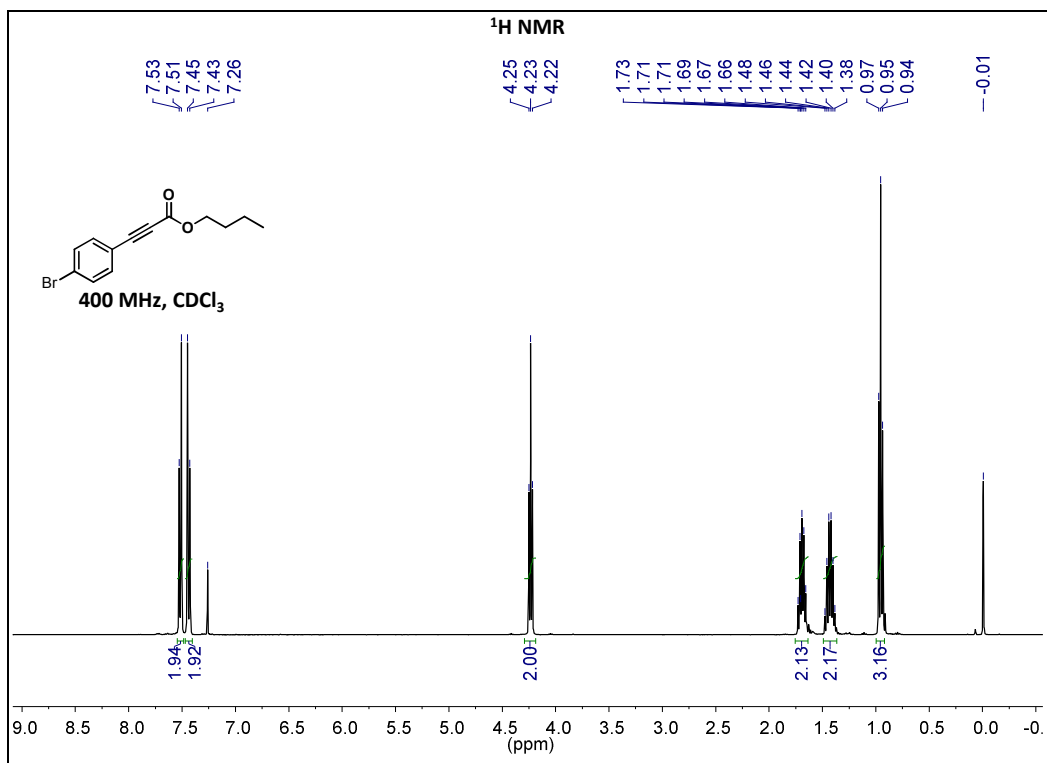


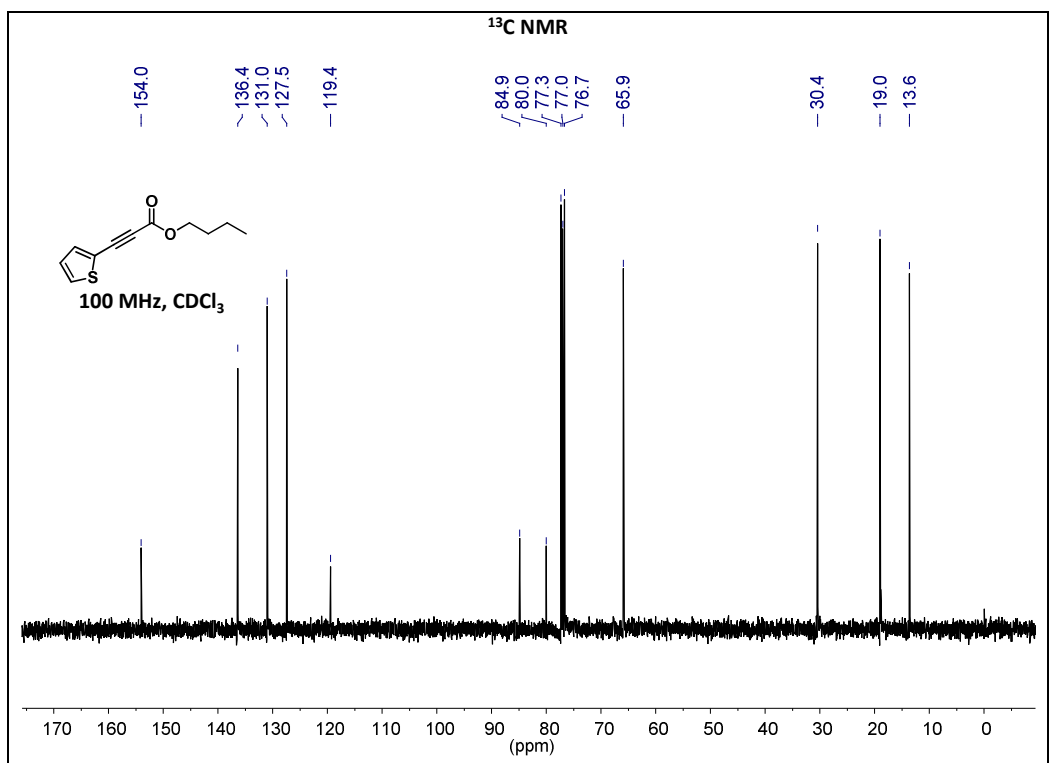
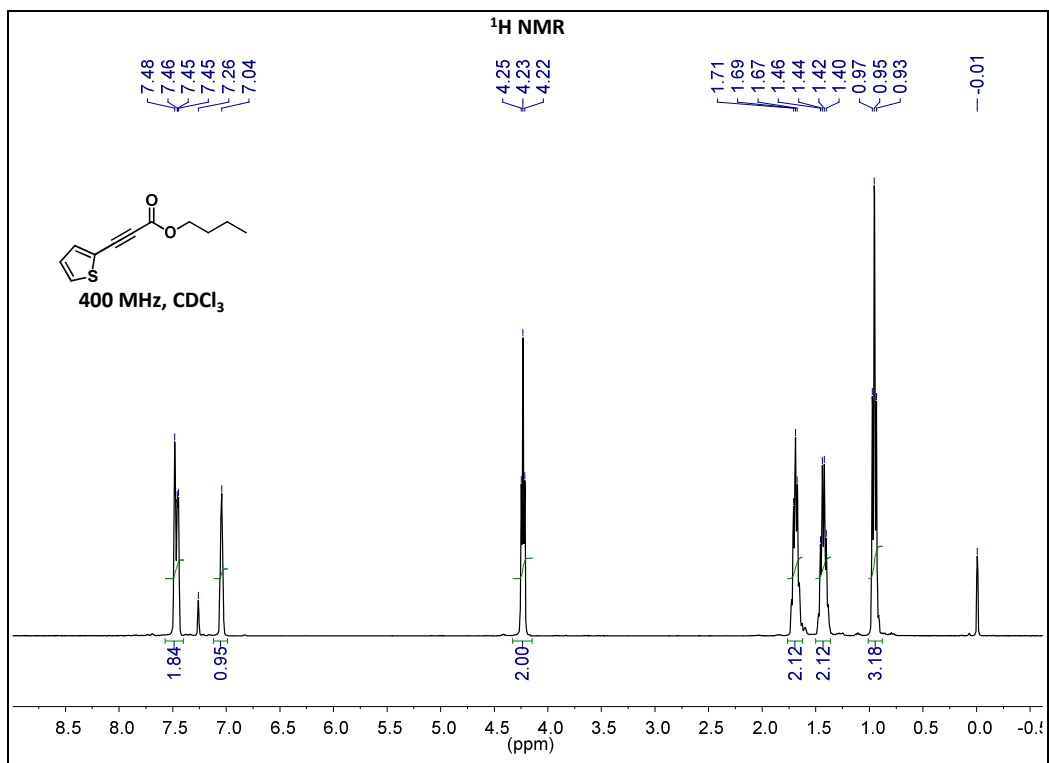


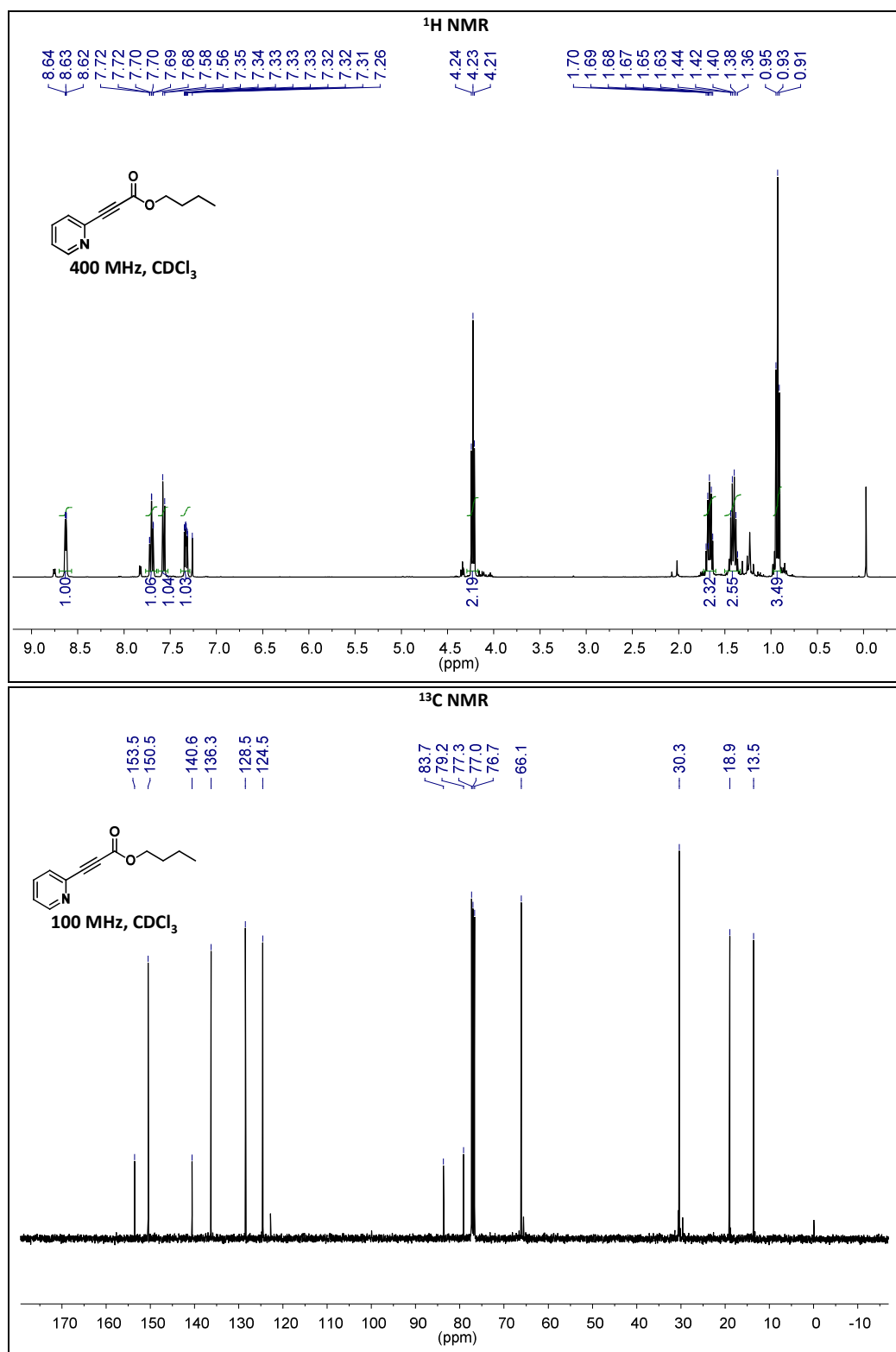


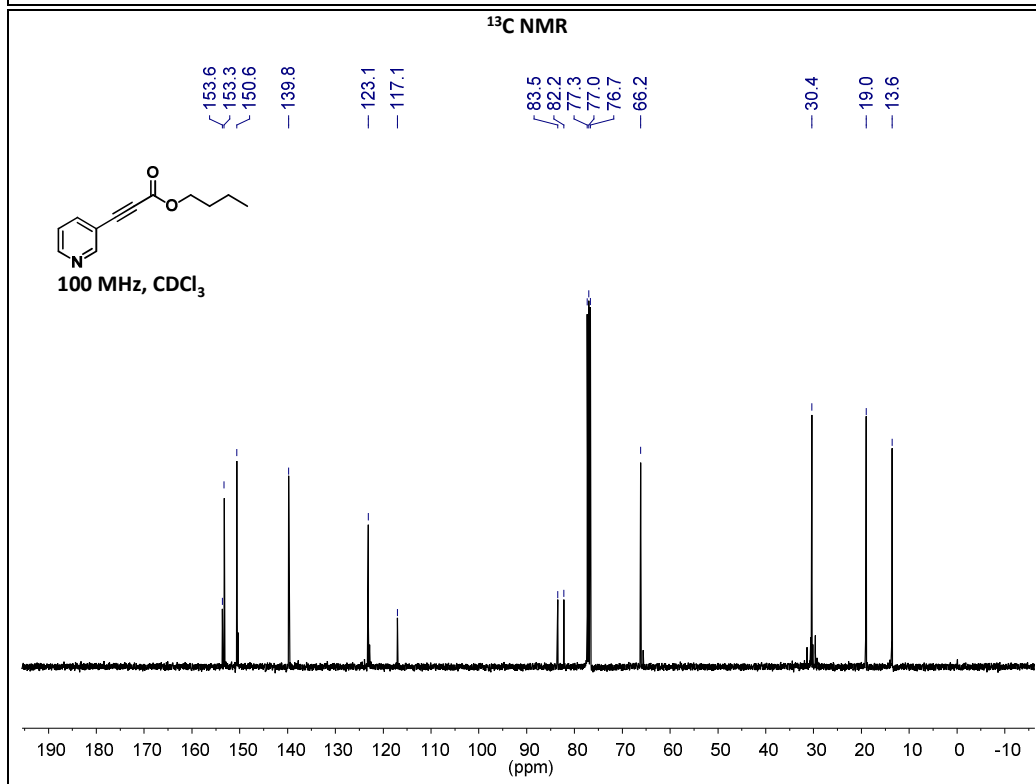
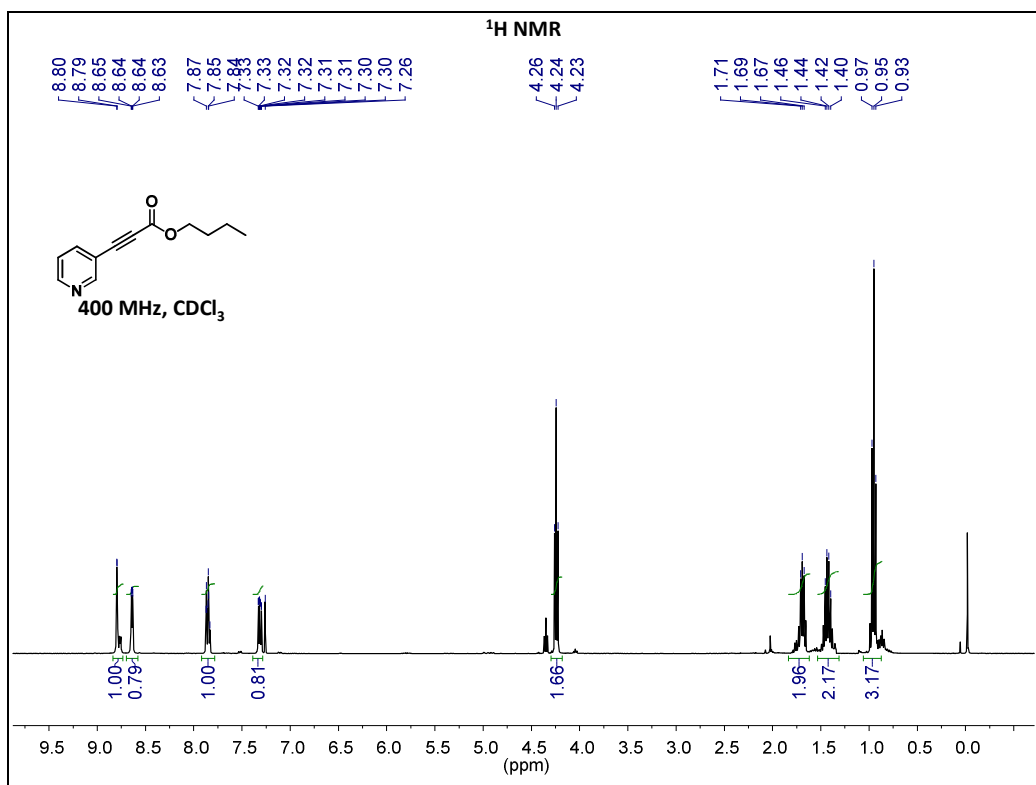


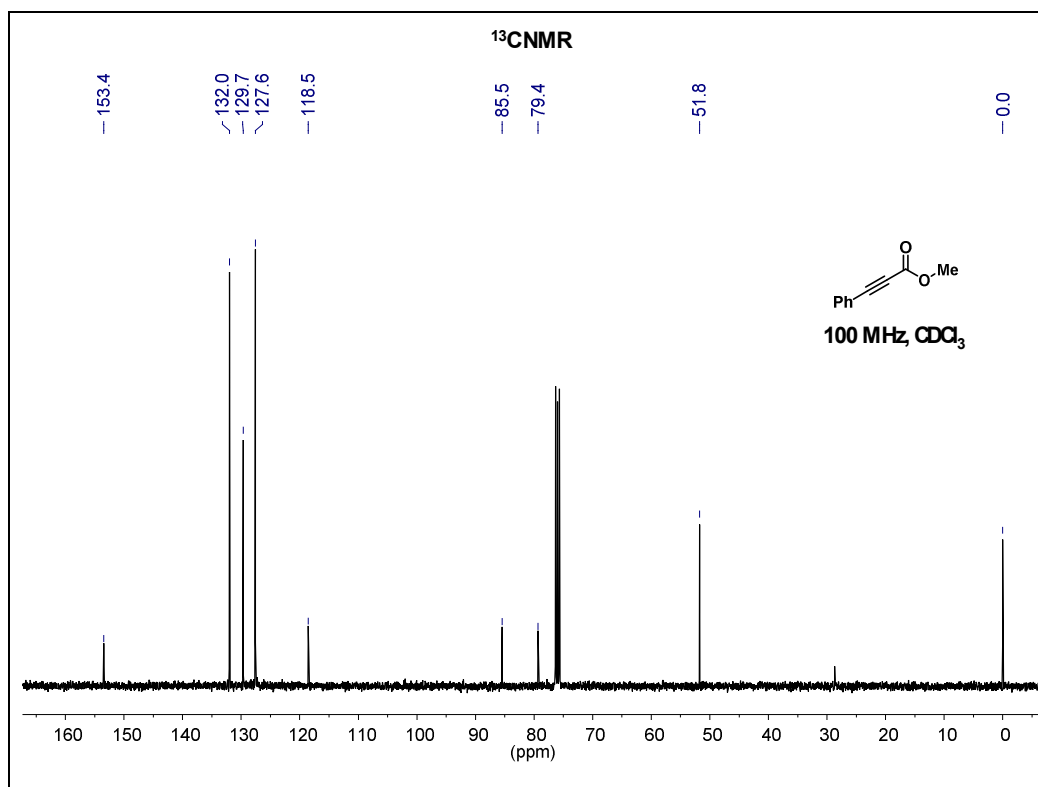
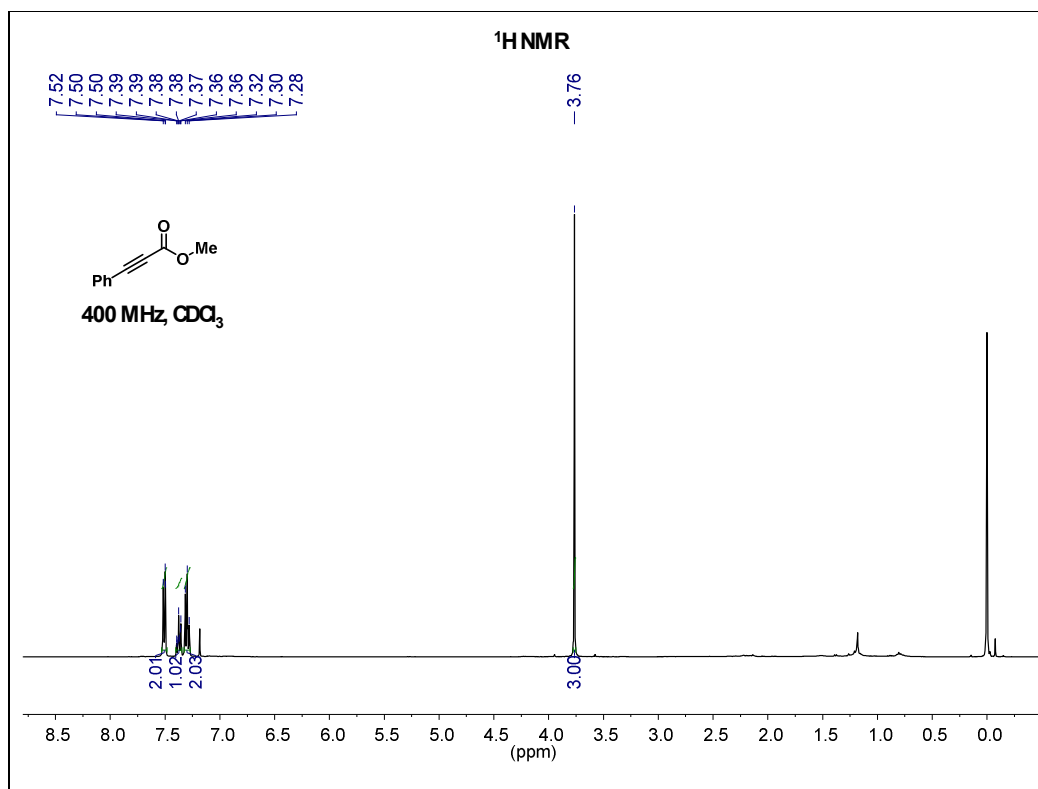


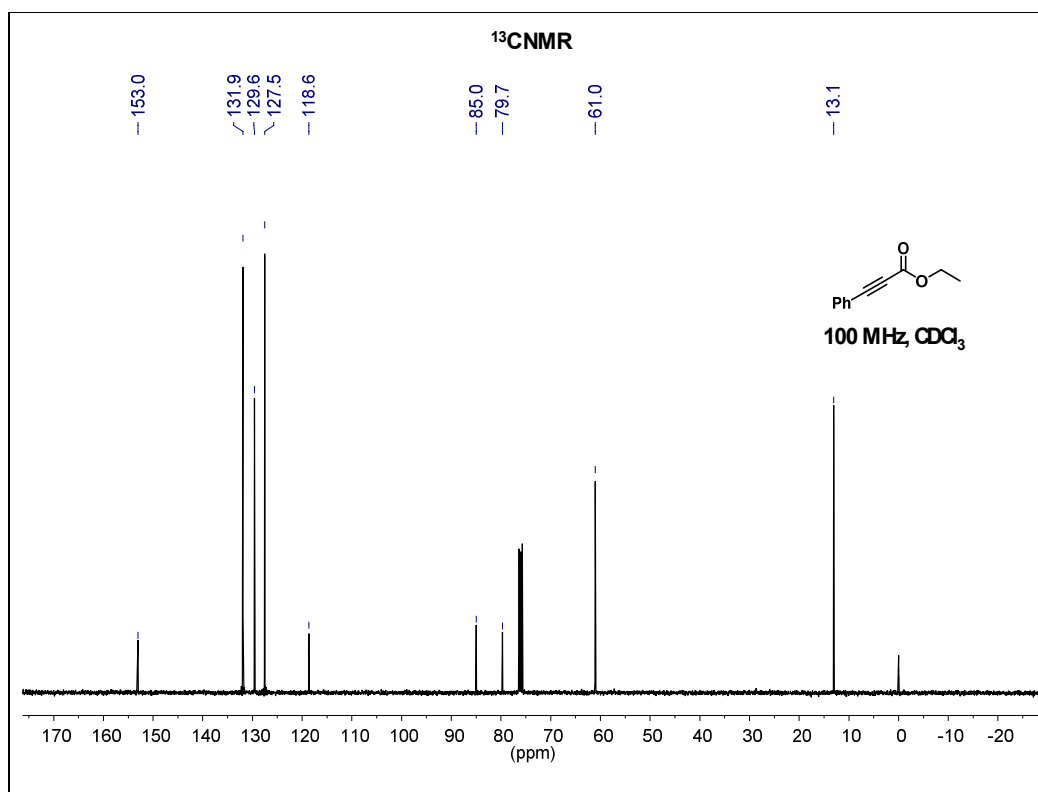
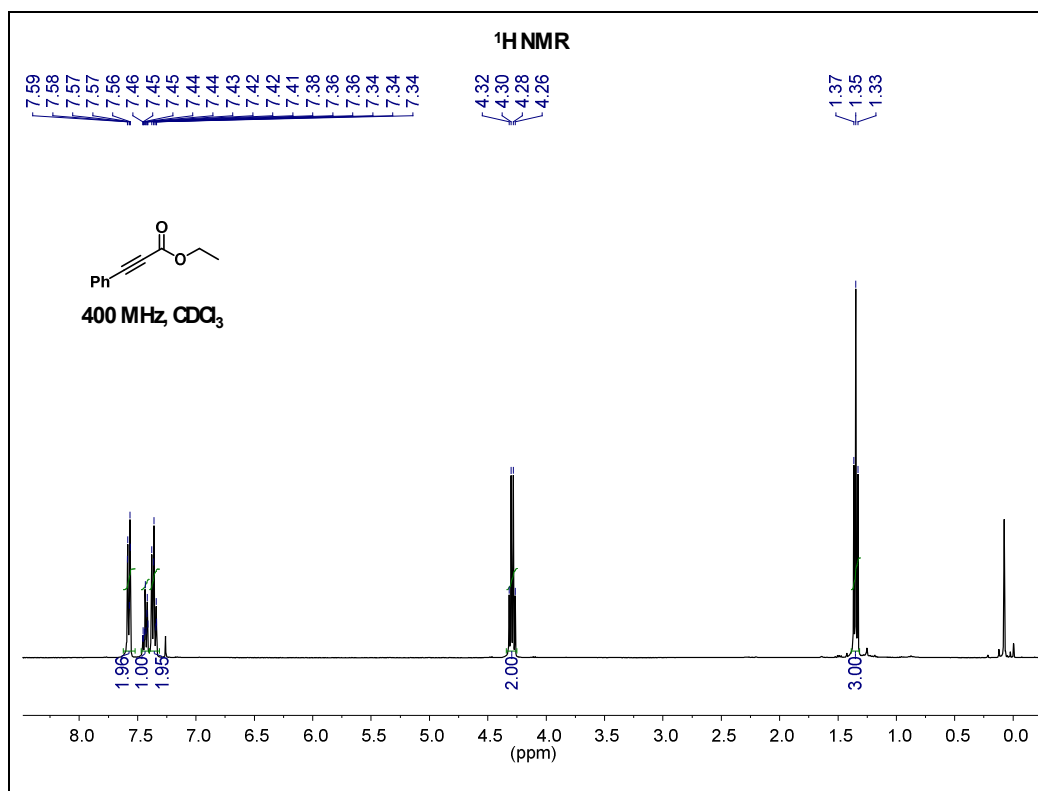




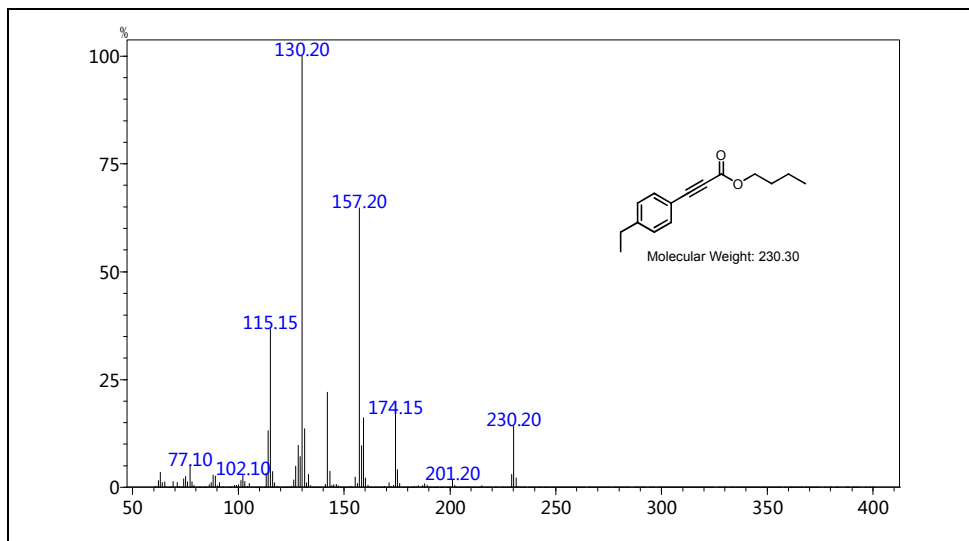
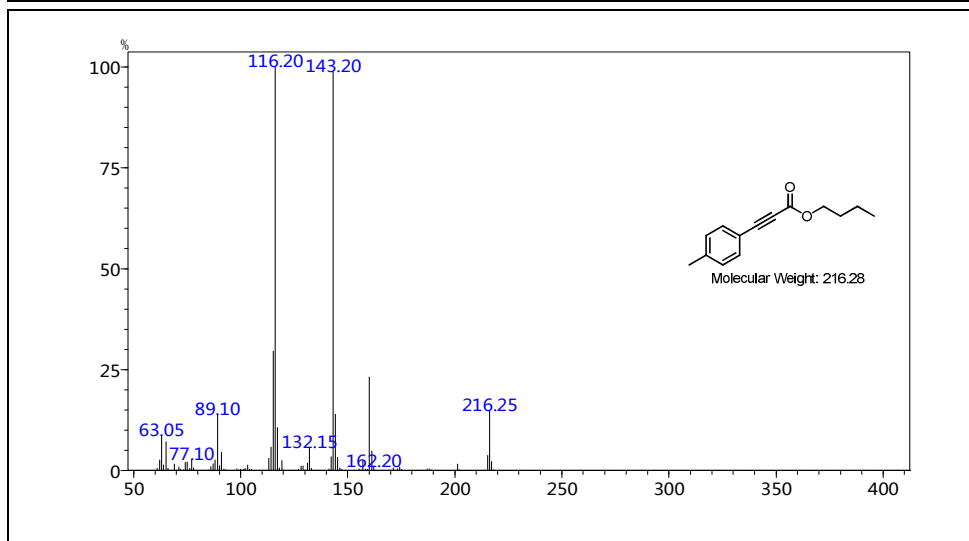
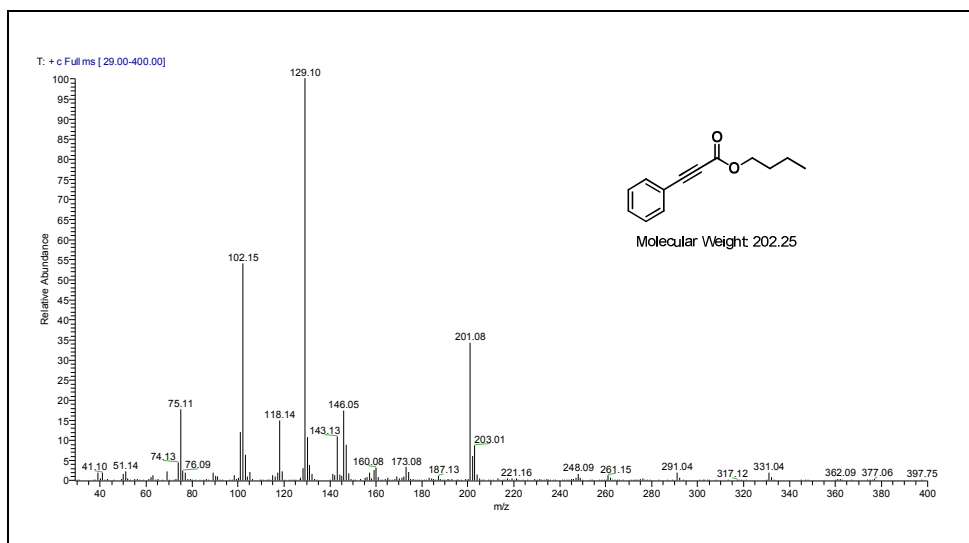


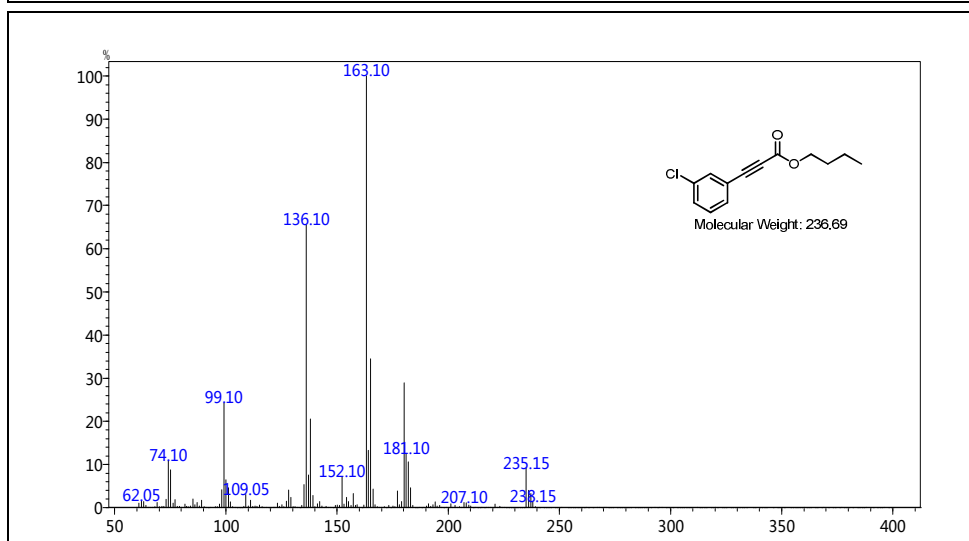
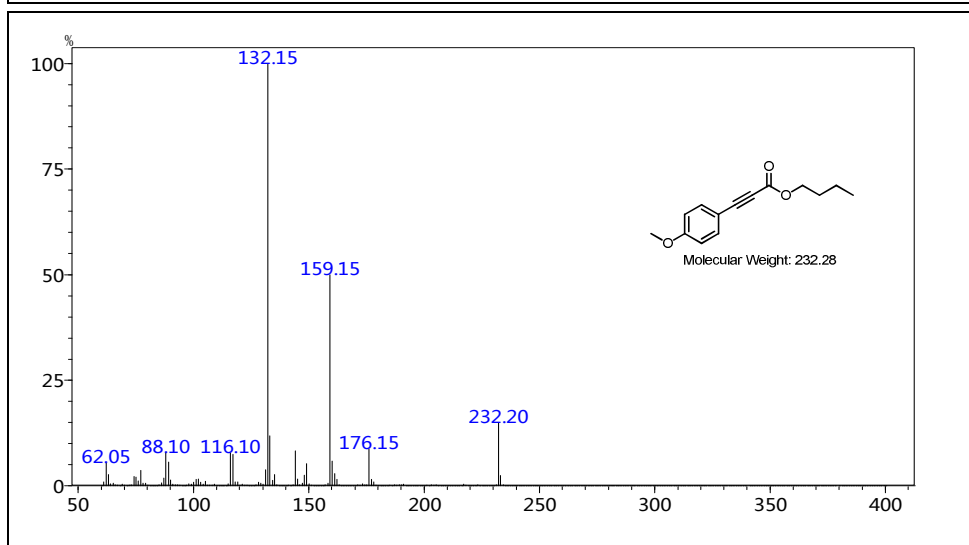
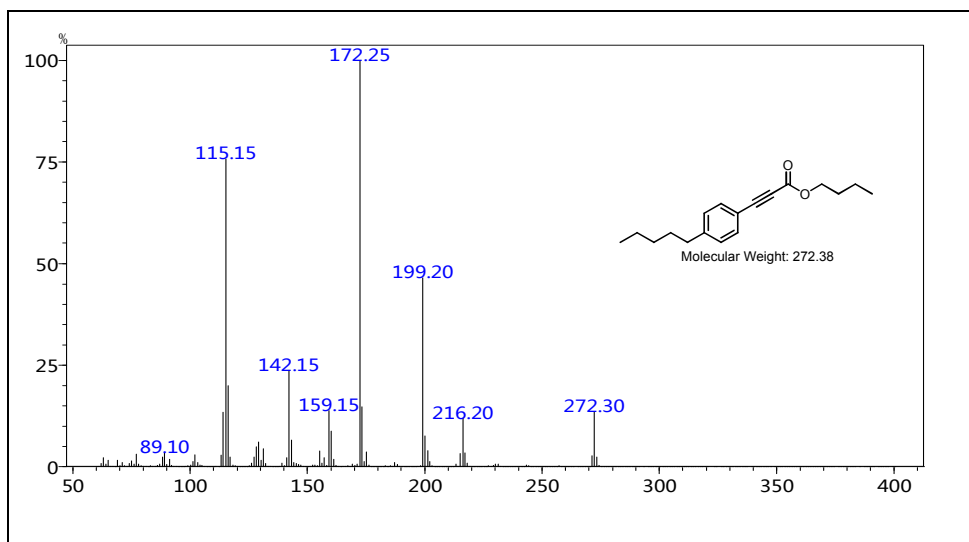


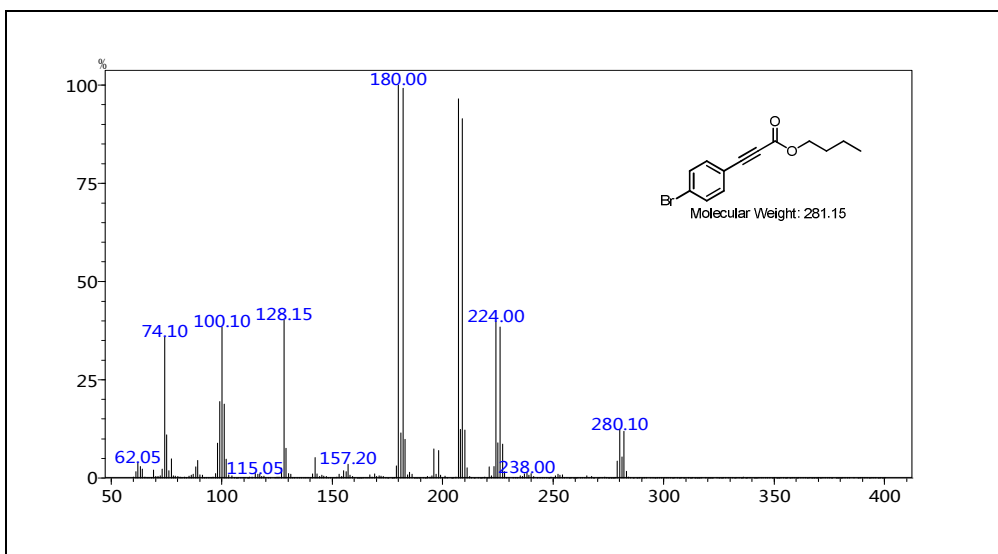
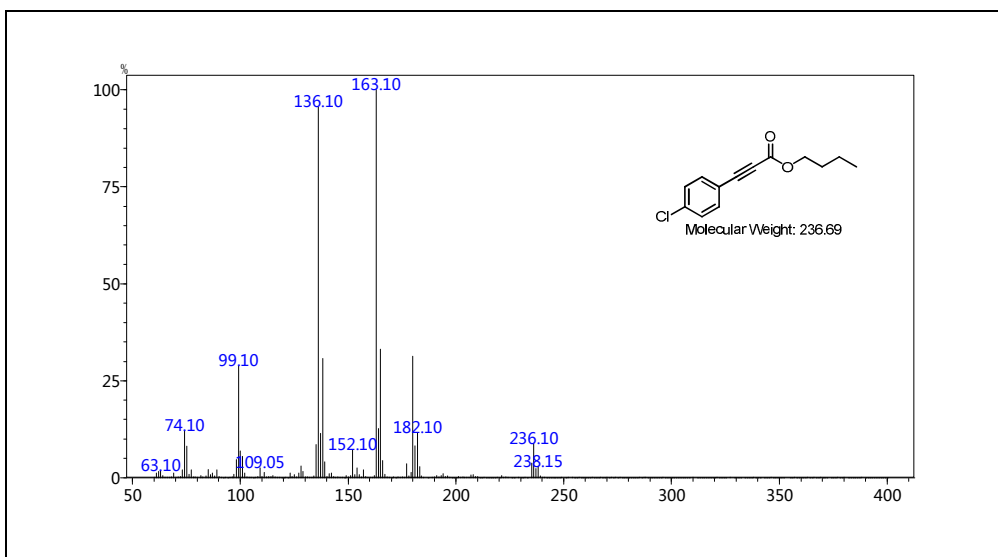
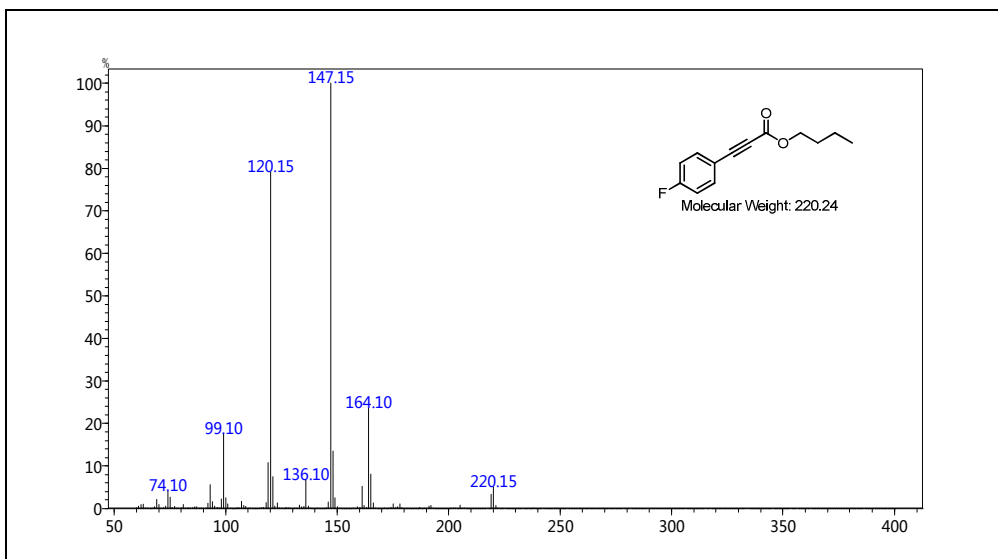




8. GC-MS Spectral Copies of the Products







T: + c Full ms [29.00-400.00]

