

**Supplementary Material (ESI) for Chemical Communications**

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# **Supporting Information**

## **Cluster-based MOFs with accelerating chemical conversion of CO<sub>2</sub> through C-C bond formation**

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### **1. General information**

#### **Materials**

The reagents for the synthesis of MOFs are from Tianjin Guangfu Fine chemical research institute. Reagents used in the carboxylative reaction were commercially available. All were used without further purification except solvents. The carboxylation products were isolated by column chromatography on silica gel (200-300 mesh) using petroleum ether (60-90 °C) and ethyl acetate.

#### **Measurement techniques**

Powder X-ray diffraction was carried on the Rigaku Ultima IV multipurpose X-ray diffraction system. The elemental analyses (C, H and N) were carried out applying a Perkin-Elmer 240C elemental analyzer; TG-DTA analyzer from room temperature to 800 °C under nitrogen atmosphere with heating rate of 10 °C min<sup>-1</sup>. IR spectra were recorded in the range of 400 - 4000 cm<sup>-1</sup> on a Nicolet IR-6700 spectrophotometer using KBr pellets. The X-ray photoelectron spectroscopy (XPS) was measured with a Kratos Axis Ultra DLD spectrometer. CO<sub>2</sub> adsorption measurements were performed on Autosorb iQ Station 2. All carboxylative compounds were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR and mass spectroscopy, which are consistent with those reported in

the literature. NMR spectra were determined on Bruker 400 in  $\text{CDCl}_3$ .  $^1\text{H}$  NMR chemical shifts were referenced to residual solvent as determined relative to  $\text{CDCl}_3$  (7.26 ppm). The  $^{13}\text{C}$  NMR chemical shifts were reported in ppm relative to the carbon resonance of  $\text{CDCl}_3$  (central peak is 77.0 ppm).  $^1\text{H}$  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  $\mu\text{m}$ ) using a flame ionization detector.

## 2. Experimental Section

### Synthesis of I

A mixture of 0.5 mmol  $\text{CuI}$ , 0.5 mmol  $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , 0.5 mmol isonicotinic acid and 10 mL DMF were sealed in a Teflon lined stainless steel container and heated at 125  $^\circ\text{C}$  for 24 h, and then cooled slowly controlled procedures to room temperature during 24 h. Finally, light green block crystals were collected with a yield of about 60% (based on  $\text{CuI}$ ). Anal. Calcd. for  $\text{C}_{65}\text{H}_{56.5}\text{Cu}_4\text{Gd}_4\text{I}_3\text{N}_{11.5}\text{O}_{29}$  (%): C: 34.02, H: 2.48, N: 7.02. Found: C:33.98, H: 2.46, N: 6.99. FT-IR (KBr,  $\text{cm}^{-1}$ ): 3215w, 2822w, 1623m, 1561s, 1542s, 1414s, 1235w, 1126w, 1089w, 1059w, 843w, 774m, 706m, 664m .

### Synthesis of II

A mixture of 0.5 mmol  $\text{CuI}$ , 0.5 mmol  $\text{Gd}_2\text{O}_3$ , 1 mmol isonicotinic acid , 10 mL DMF (N, N-Dimethylformamide) and 160  $\mu\text{L}$   $\text{HNO}_3$  were sealed in a Teflon lined stainless steel container and heated at 155  $^\circ\text{C}$  for 96 h, and then cooled slowly controlled procedures to room temperature during 96 h. Finally, light yellow block crystals were collected with a yield of 71% (based on  $\text{CuI}$ ). Anal. Calcd. for  $\text{C}_{69}\text{H}_{71}\text{Cu}_{12}\text{Gd}_3\text{I}_{12}\text{N}_{14}\text{O}_{23}$  (%): C:19.59, H: 1.65, N: 4.60; Found: C: 19.63, H: 1.70, N: 4.64. FT-IR (KBr,  $\text{cm}^{-1}$ ): 3306w, 2933w, 1639s, 1524s, 1423s, 1246w, 1189w, 1058w, 996w, 823w, 763m.

### General procedure for the carboxylation of terminal alkynes with $\text{CO}_2$ .

In a 20 mL Schlenk flask, terminal alkyne (1.0 mmol), Cs<sub>2</sub>CO<sub>3</sub> (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 CO<sub>2</sub> (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 Na<sub>2</sub>SO<sub>4</sub>. The residue was purified by column chromatography (silica gel, petroleum ether/EtOAc) to afford the desired product alkyl 2-alkynoates. The products were further identified by NMR and MS (see the Supporting Information), which are consistent with those reported in the literature and in good agreement with the assigned structures.

### 3. Characterization of catalysts

#### Crystallographic Study

A suitable single crystal of **I** or **II** was selected and settled on a SuperNova Single Crystal Diffractometer equipped with graphite-monochromatic Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) using the  $\omega - \phi$  scan technique, respectively. The crystal was kept at about 123 K in the process of data collection. The structure was solved with the XS structure solution program using Direct Methods and refined with the XL refinement package using Least Squares minimisation in shelxtl program package<sup>1</sup>. Details of the crystal parameters, data collection, and refinements for **I** and **II** are summarized in Table S1. CCDC: 920370 for **I** and 920369 for **II** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Table S1** Crystallographic data and structure refinements for compounds **I** and **II**.

Compound	<b>I</b>	<b>II</b>
Empirical formula	C <sub>69</sub> H <sub>71</sub> Cu <sub>12</sub> Gd <sub>3</sub> I <sub>12</sub> N <sub>14</sub> O <sub>23</sub>	C <sub>65</sub> H <sub>56.5</sub> Cu <sub>4</sub> Gd <sub>4</sub> I <sub>3</sub> N <sub>11.5</sub> O <sub>29</sub>
Formula weight	4221.43	2726.58
Temperature/K	124.8(2)	128.55(10)
Crystal system	monoclinic	orthorhombic

Space group	$P2_1/c$	$Pnma$
$a/\text{\AA}$	15.1074(3)	16.9302(4)
$b/\text{\AA}$	25.0187(5)	19.9756(3)
$c/\text{\AA}$	28.8461(4)	28.9303(10)
$\alpha/^\circ$	90.00	90.00
$\beta/^\circ$	102.080(2)	90.00
$\gamma/^\circ$	90.00	90.00
Volume/ $\text{\AA}^3$	10661.5(3)	9784.0(4)
Z	4	4
$\rho_{\text{calc}}/\text{mg}/\text{mm}^3$	2.630	1.851
$m/\text{mm}^{-1}$	7.717	4.541
F(000)	7772.0	5160.0
Crystal size/ $\text{mm}^3$	$0.35 \times 0.30 \times 0.30$	$0.25 \times 0.25 \times 0.2$
$2\theta$ range for data collection	5.84 to 50.02°	5.64 to 50.02
Index ranges	$-10 \leq h \leq 17, -22 \leq k \leq 29, -33 \leq l \leq 34$	$-18 \leq h \leq 20, -23 \leq k \leq 15, -34 \leq l \leq 31$
Reflections collected	46278	26284
Independent reflections	18756 [ $R_{\text{int}} = 0.0297$ ]	8834 [ $R_{\text{int}} = 0.0303$ ]
Data/restraints/parameters	18756/6/1208	8834/394/672
Goodness-of-fit on $F^2$	1.046	1.162
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0303, wR_2 = 0.0629$	$R_1 = 0.0512, wR_2 = 0.1090$
Final R indexes [all data]	$R_1 = 0.0400, wR_2 = 0.0678$	$R_1 = 0.0620, wR_2 = 0.1141$
Largest diff. peak/hole / $e \text{\AA}^{-3}$	1.923/-1.115	1.136/-2.063

## Reusability experiment of the catalyst II

The stability and reusability of the catalysts were further studied by using **II** as an example in the model reaction (Table S2). After the first catalytic cycle, the catalyst was separated from solution by centrifugation, washed with DMF and ethanol for several times, dried under vacuum, and then reused in next reaction. The results exhibited that **II** can be reused for two times with high catalytic activity. After the second run, the XPS of **II** was further investigated, and the oxidation state of Cu still keeps +1 (Fig. S15). Furthermore, the PXRD of Cat-I and Cat-II after the catalytic reaction have been presented in Figure S16. From the PXRD patterns, the well consistence between simulated and experimental PXRD indicates that the structures of the two catalysts still keep intact.

**Table S2** Reusability of the catalyst **II** in the carboxylation of phenylacetylene<sup>a</sup>

$\text{Ph}-\text{C}\equiv\text{C}-\text{H} + \text{CO}_2 \xrightarrow[\text{EC}]{\text{Cat-II (4 mol\%)} \atop \text{Cs}_2\text{CO}_3 (1.2 \text{ equiv.}) \atop n\text{Bul (1.2 equiv.)}} \text{Ph}-\text{C}\equiv\text{C}-\text{C}(=\text{O})-\text{O}-n\text{Bu}$

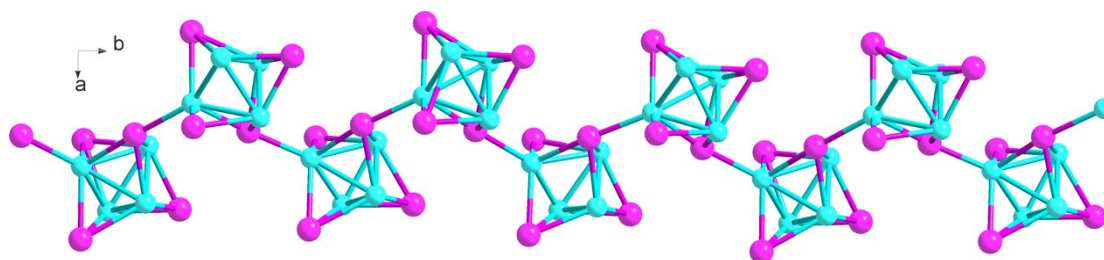
**1a** (*Balloon*)  **2a**

Entry	Run	Yield <sup>b</sup> (%)
1	1st	80
2	2nd	70

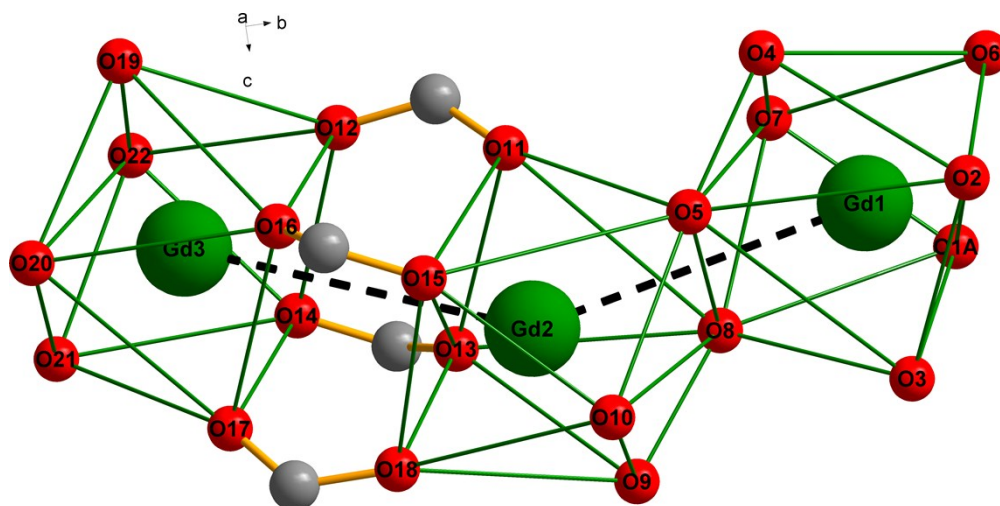
<sup>a</sup> Reaction conditions: Phenylacetylene (51 mg, 0.5 mmol), Cs<sub>2</sub>CO<sub>3</sub> (196 mg, 0.6 mmol), **II** (4 mol%), *n*-Bul (110 mg, 0.6 mmol), EC (3 mL), CO<sub>2</sub> (99.999%, balloon), 80 °C, 4 h.

<sup>b</sup> The yields were determined by GC with biphenyl as internal standard.

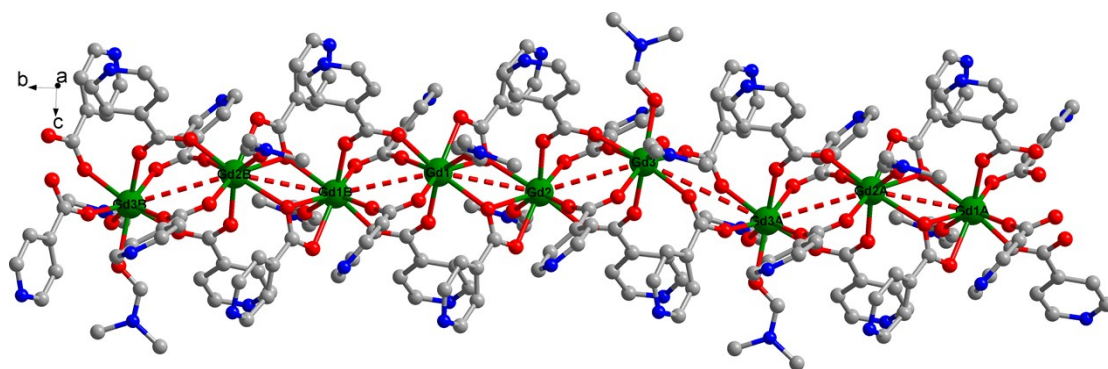
### Structure description graphs



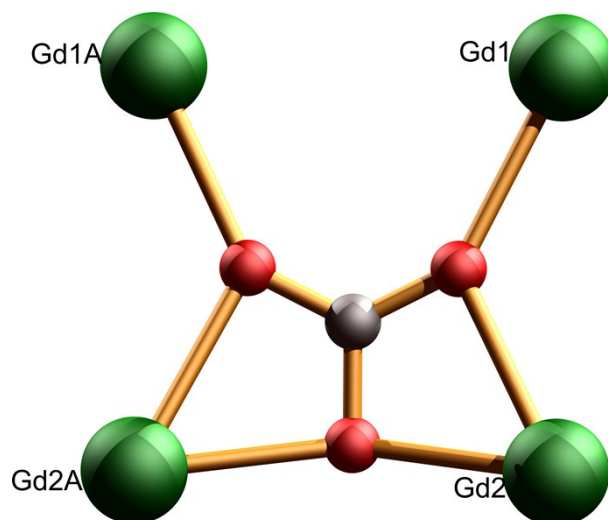
**Fig. S1** Cu-I chain comprised by [Cu<sub>4</sub>I<sub>4</sub>] clusters along *b* axis in **I**.



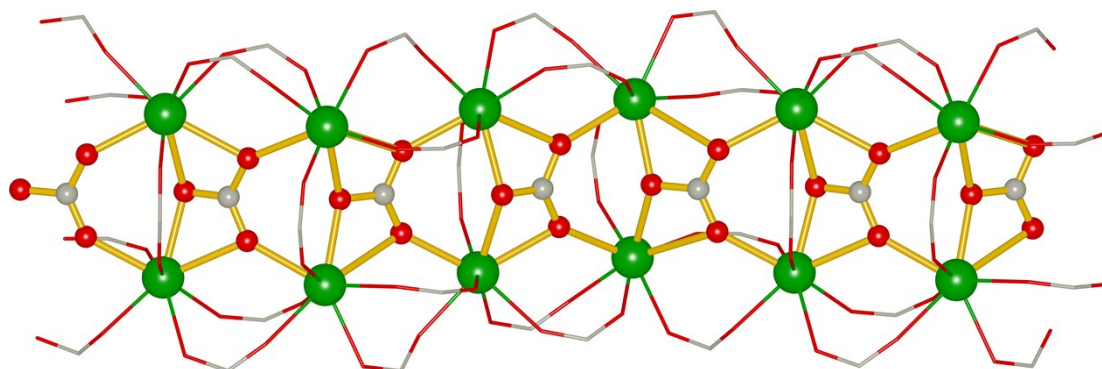
**Fig. S2** The coordination geometric configurations of Gd<sup>III</sup> cations in **I**. A=2-x, 2-y, 1-z.



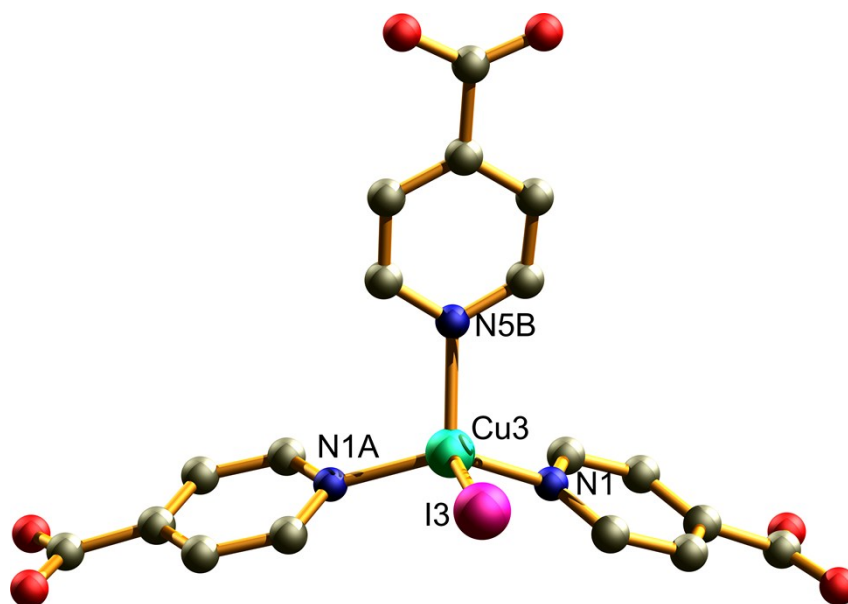
**Fig. S3** One-dimensional chain constructed by tri-nuclear  $[\text{Gd}_3(\text{IN})_9(\text{DMF})_4]$  units in **I** along  $b$  axis.  $A = 2-x, 1-y, 1-z$ ;  $B = 2-x, 2-y, 1-z$ .



**Fig. S4** The coordination mode  $\mu_4: \eta^2, \eta^2, \eta^2$  of  $\text{CO}_3^{2-}$  anion in **II**.  $A = x, 0.5-y, z$ .

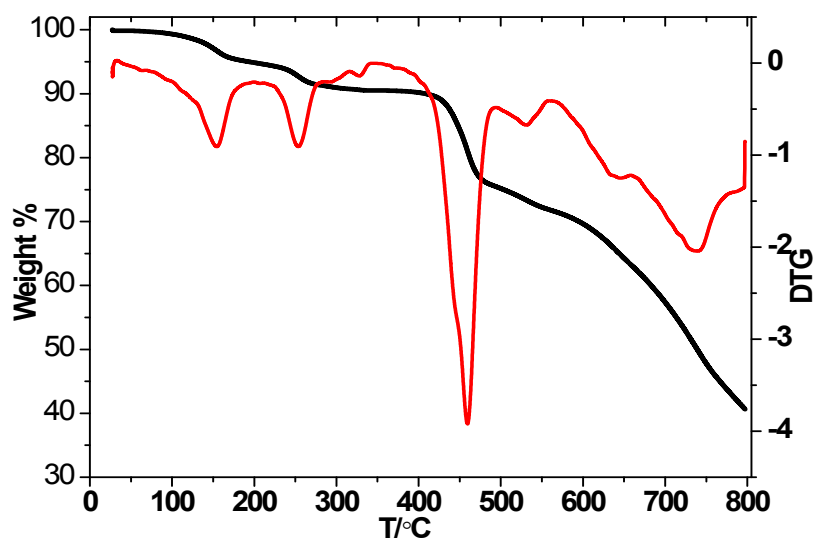


**Fig. S5** The  $\text{Gd}_4(\text{CO}_3)_2$  chain in **II**. Green, red and gray balls stand for gadolinium, oxygen and carbon atoms, respectively.



**Fig. S6** The triangle [CuI] unit in **II**.  $A=x, 1.5-y, z$ .  $B=1-x, 0.5+y, 1-z$ .

### TGA of I and II



**Fig. S7** TGA curve of **I**

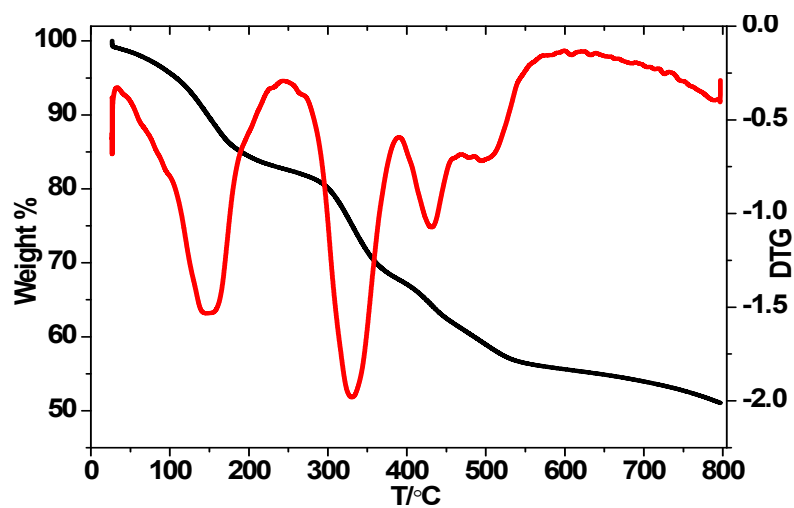


Fig. S8 TGA curve of II

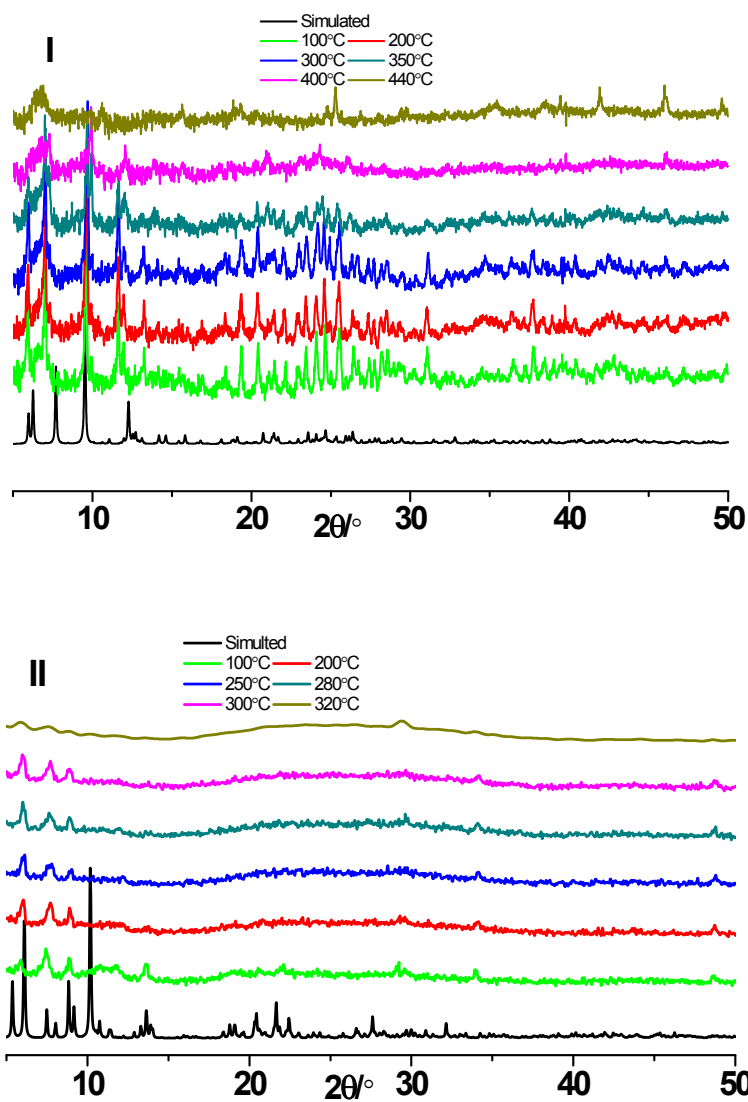
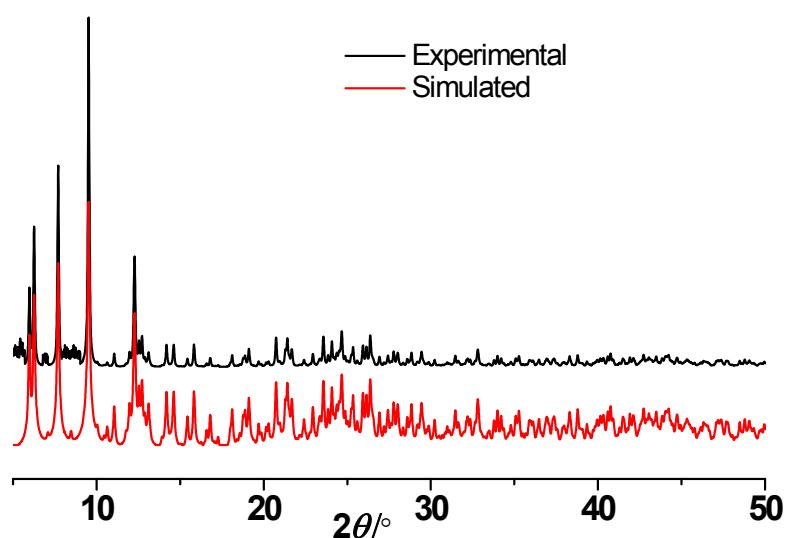


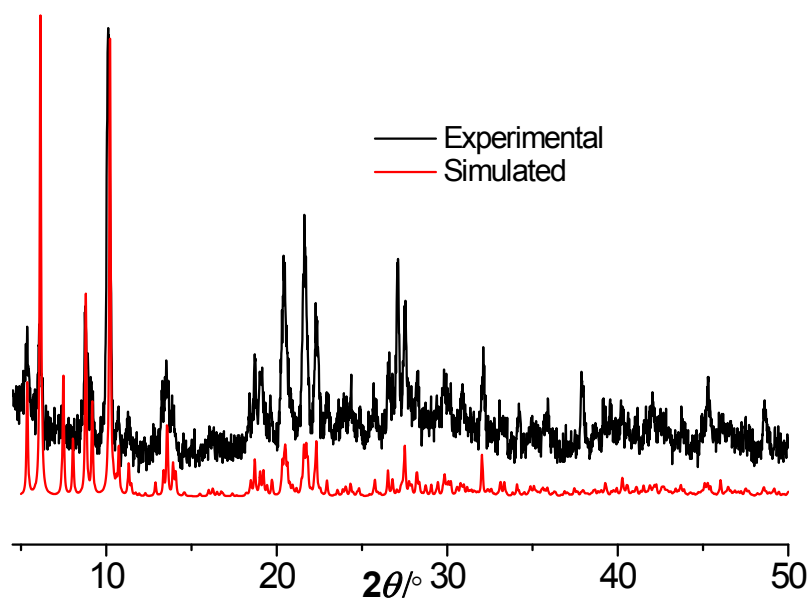
Fig. S9 Variable-temperature PXRD patterns of Cat-I and Cat-II.



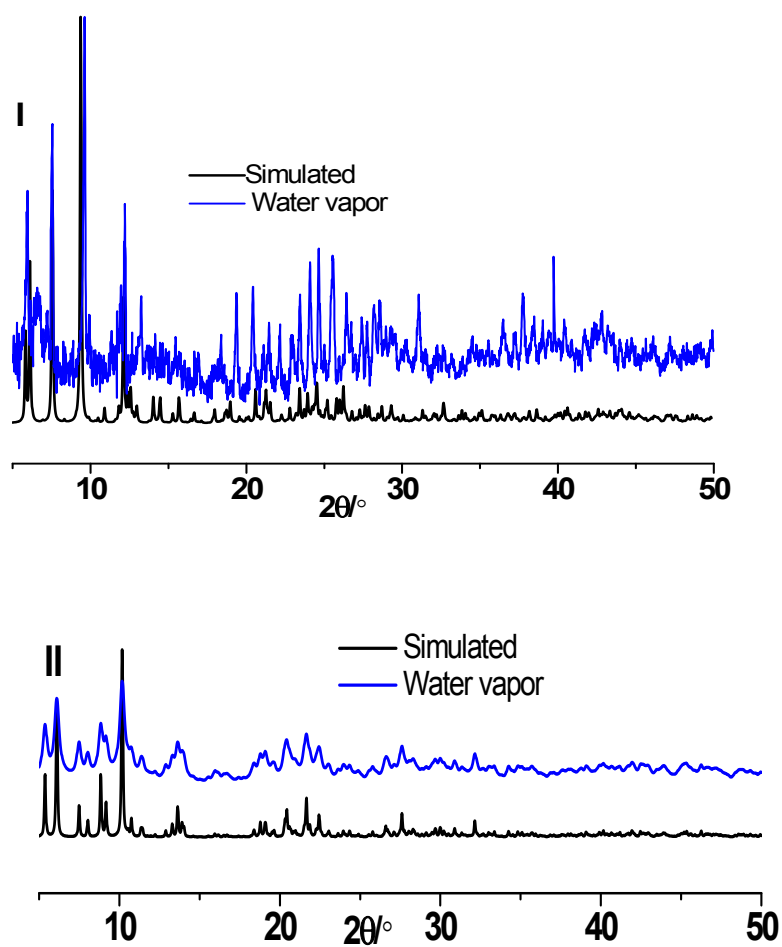
The thermal stabilities of **I** and **II** were performed by TGA (Fig. S7 and S8). Before 260 °C, **I** lost weight of about 8.54%, in consistence with the sum (8.63%) of one isolated DMF and four coordinated DMF molecules, and the structural decomposition temperature of **I** is about 400°C. For Cat II, when the temperature was heated to 140 °C, the lost weight is 9.05%, in according to all of DMF, H<sub>2</sub>O and half HIN ligand (8.91%) in **II**. When **II** was been heated to about 300°C, the structural decomposition happened. The thermal stabilities of **I** and **II** were also determined by variable-temperature PXRD (Fig. S9), which consisted with those obtained from TGA.



**Fig. S10** The experimental and simulated PXRD of **I** after dipped in the ethanol, acetonitrile, DMF (100 °C), hexane and ethylene carbonate (EC) (100 °C).



**Fig. S11** The experimental and simulated PXRD of **II** after dipped in the ethanol, acetonitrile, DMF (100 °C), hexane and ethylene carbonate (EC) (100 °C).



**Fig. S12** The experimental and simulated PXRD of **I** and **II** exposed to water vapor for one hour.

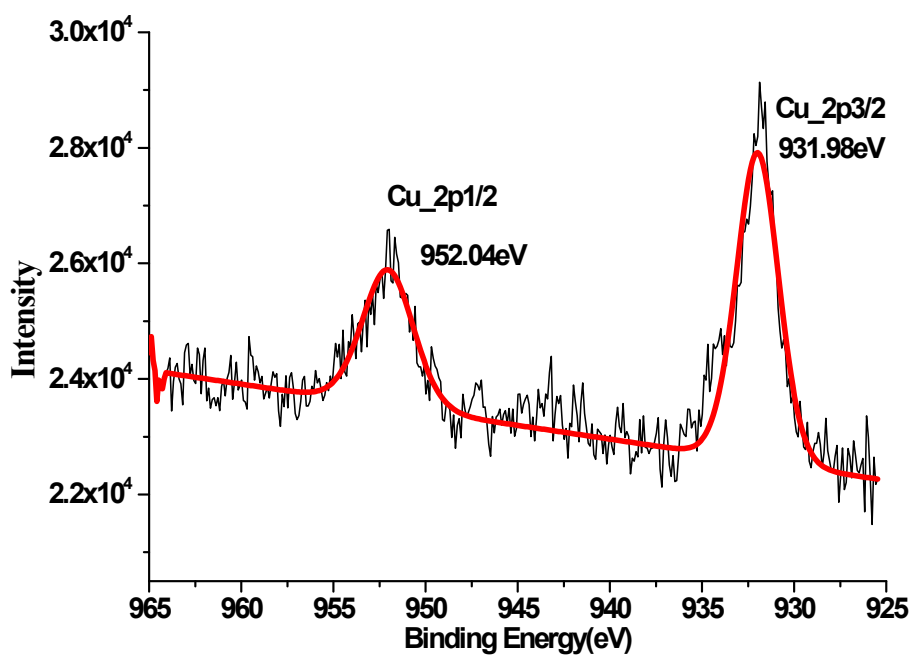


Fig. S13 The Cu 2p XPS spectrum of I.

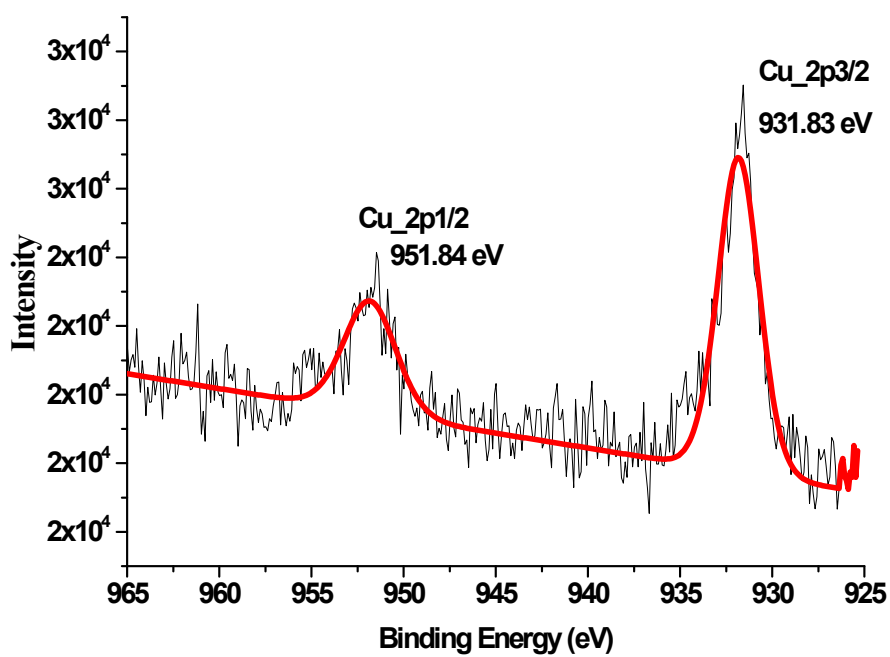


Fig. S14 The Cu 2p XPS spectrum of II.

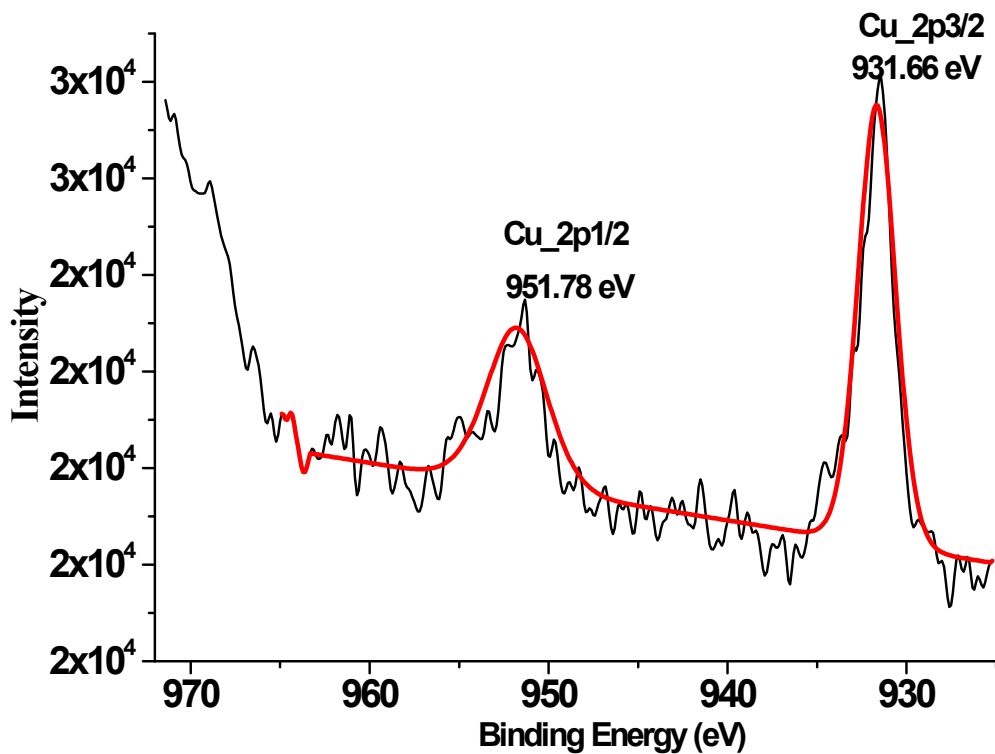


Fig. S15 The Cu 2p XPS spectrum of **II** after two catalysis cycles.

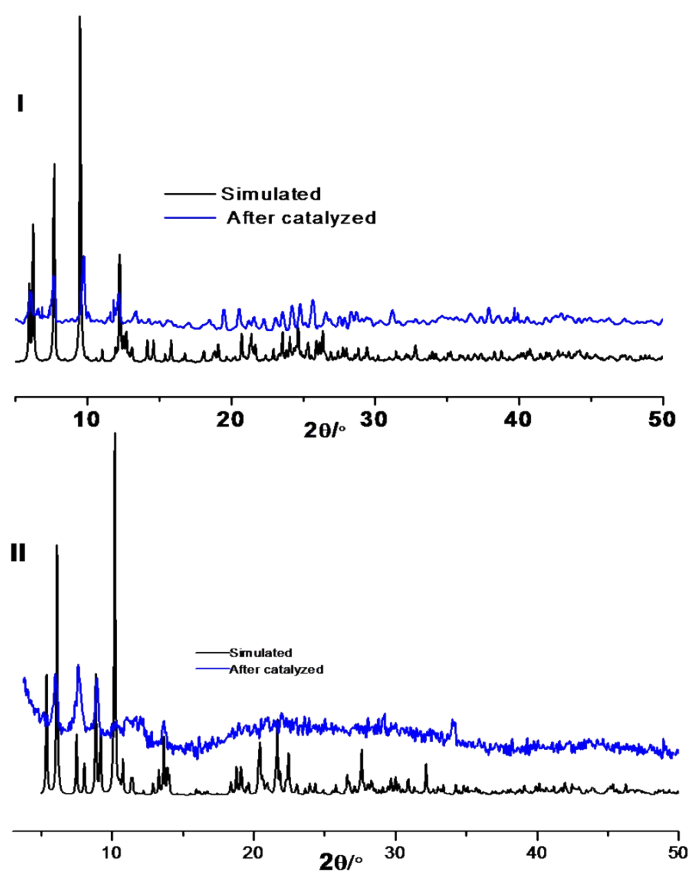
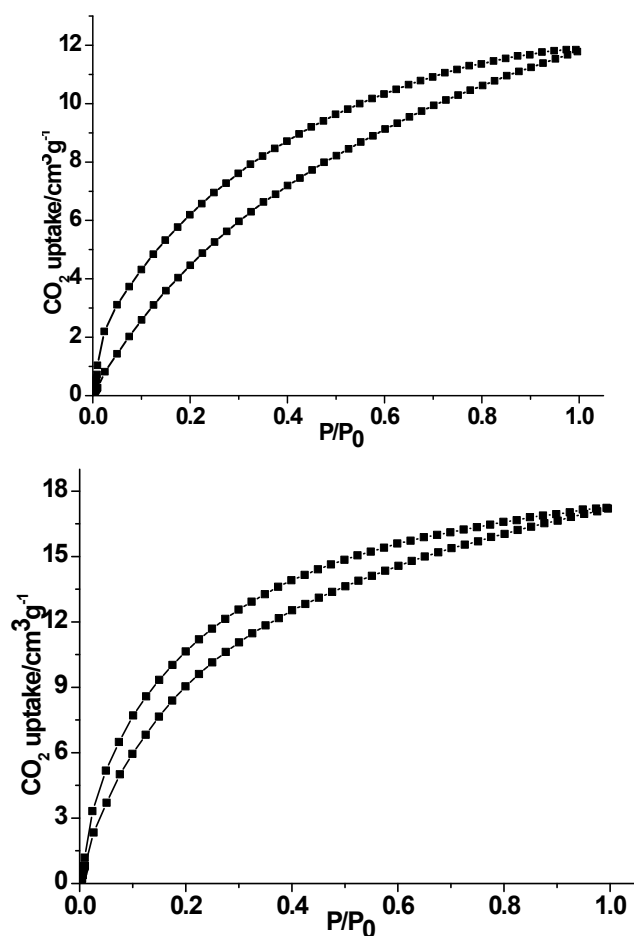
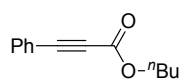


Fig. S16 PXRD patterns of Cat-I and Cat-II after catalyzed.

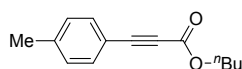


**Fig. S17** The CO<sub>2</sub> adsorption behaviors of **I** (Top) and **II** (Bottom) at 273 K.

## Characterization data of carboxylation products

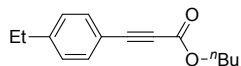


**Compound 2a:** Colourless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 7.62–7.59 (m, 2H), 7.48–7.37 (m, 3H), 4.26 (t, *J* = 6.7 Hz, 2H), 1.72 (quint, *J* = 6.8 Hz, 2H), 1.51–1.41 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm): 154.2, 132.9, 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<sup>+</sup>].

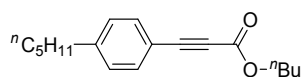


**Compound 2b:** Light yellow solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 7.48 (d, *J* = 7.5 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 2H), 4.23 (t, *J* = 6.6 Hz, 2H), 2.37 (s, 3H), 1.69

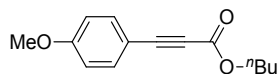
(quint,  $J = 7.3$  Hz, 2H), 1.51–1.36 (m, 2H), 0.96 (t,  $J = 7.5$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 154.3, 141.2, 132.9, 129.3, 116.5, 86.6, 80.3, 65.8, 30.5, 21.7, 19.0, 13.6; EI-MS,  $m/z$  (%): 116.20 (100), 216.25 (13) [ $\text{M}^+$ ].



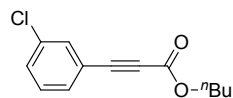
**Compound 2c:** Yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.52–7.40 (m, 2H), 7.21–7.14 (m, 2H), 4.23 (t,  $J = 6.7$  Hz, 2H), 2.70–2.61 (m, 2H), 1.73–1.63 (m, 2H), 1.48–1.37 (m, 2H), 1.25–1.20 (m, 3H), 0.98–0.92 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (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) [ $\text{M}^+$ ]; HRMS (ESI):  $\text{C}_{15}\text{H}_{18}\text{O}_2\text{Na}$  for [ $\text{M}+\text{Na}$ ] $^+$  calculated 253.1199, found 253.1196.



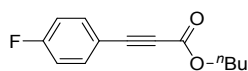
**Compound 2d:** Yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.50 (d,  $J = 8.1$  Hz, 2H), 7.18 (d,  $J = 8.1$  Hz, 2H), 4.23 (t,  $J = 6.7$  Hz, 2H), 2.63–2.59 (m, 2H), 1.70–1.58 (m, 4H), 1.46–1.28 (m, 6H), 0.98–0.87 (m, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (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) [ $\text{M}^+$ ]; HRMS (ESI):  $\text{C}_{18}\text{H}_{24}\text{O}_2\text{Na}$  for [ $\text{M}+\text{Na}$ ] $^+$  calculated 295.1669, found 295.1664.



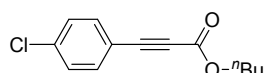
**Compound 2e:** White solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.53 (d,  $J = 8.8$  Hz, 2H), 6.87 (d,  $J = 8.8$  Hz, 2H), 4.22 (t,  $J = 6.7$  Hz, 2H), 3.82 (s, 3H), 1.69 (dt,  $J = 14.7$ , 6.8 Hz, 2H), 1.43 (dq,  $J = 14.7$ , 7.4 Hz, 2H), 0.95 (t,  $J = 7.4$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (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) [ $\text{M}^+$ ].



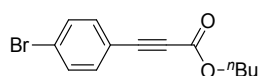
**Compound 2f:** Yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.57 (s, 1H), 7.47–7.41 (m, 2H), 7.33–7.29 (m, 1H), 4.24 (t,  $J = 6.6$  Hz, 2H), 1.73–1.63 (m, 2H), 1.48–1.37 (m, 2H), 0.96 (t,  $J = 7.4$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (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) [ $\text{M}^+$ ]; HRMS (ESI):  $\text{C}_{13}\text{H}_{13}\text{O}_2\text{ClNa}$  for [ $\text{M}+\text{Na}$ ] $^+$  calculated 259.0496, found 259.0493.



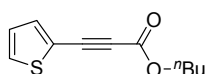
**Compound 2g:** Yellow oil;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.59–7.56 (m, 2H), 7.08–7.04 (m, 2H), 4.23 (t,  $J = 6.6$  Hz, 2H), 1.73–1.62 (m, 2H), 1.46–1.38 (m, 2H), 0.95 (t,  $J = 7.8$  Hz, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 165.1, 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)  $[\text{M}^+]$ ; HRMS (ESI):  $\text{C}_{13}\text{H}_{13}\text{FO}_2\text{Na}$  for  $[\text{M}+\text{Na}]^+$  calculated 243.0792, found 243.0786.



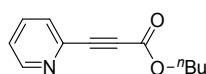
**Compound 2h:** Yellow oil;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.51 (d,  $J = 8.4$  Hz, 2H), 7.35 (d,  $J = 8.5$  Hz, 2H), 4.23 (t,  $J = 6.7$  Hz, 2H), 1.71–1.66 (m, 2H), 1.46–1.40 (m, 2H), 0.95 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (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)  $[\text{M}^+]$ ; HRMS (ESI):  $\text{C}_{13}\text{H}_{13}\text{O}_2\text{ClNa}$  for  $[\text{M}+\text{Na}]^+$  calculated 259.0496, found 259.0494.



**Compound 2i:** Yellow oil;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (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);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (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)  $[\text{M}^+]$ .

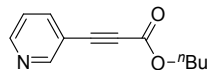


**Compound 2j:** Yellow oil;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.48–7.45 (m, 2H), 7.04 (s, 1H), 4.23 (t,  $J = 6.6$  Hz, 2H), 1.71–1.67 (m, 2H), 1.46–1.40 (m, 2H), 0.95 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 154.0, 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)  $[\text{M}^+]$ .

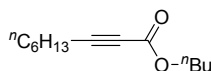


**Compound 2k:** Yellow oil;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 8.64–8.62 (m, 1H), 7.72–7.68 (m, 1H), 7.57 (d,  $J = 7.8$  Hz, 1H), 7.35–7.31 (m, 1H), 4.23 (t,  $J = 6.6$  Hz,

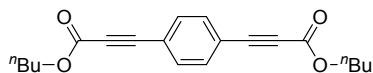
2H), 1.70–1.63 (m, 2H), 1.44–1.36 (m, 2H), 0.93 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 153.5, 150.5, 140.6, 136.3, 128.5, 124.5, 83.7, 79.2, 66.1, 30.3, 18.9, 13.5; EI-MS,  $m/z$  (%): 130.10 (100), 202.15 (2) [ $\text{M}^+$ ].



**Compound 2l:** Yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (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).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (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) [ $\text{M}^+$ ].



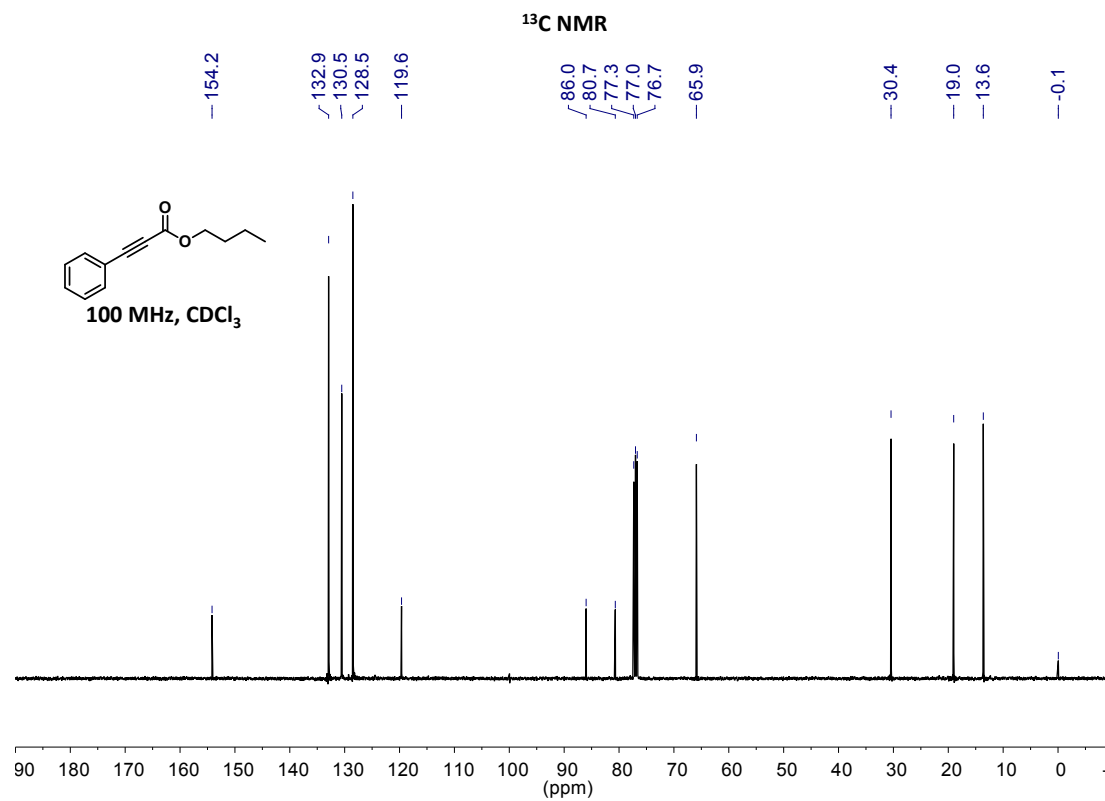
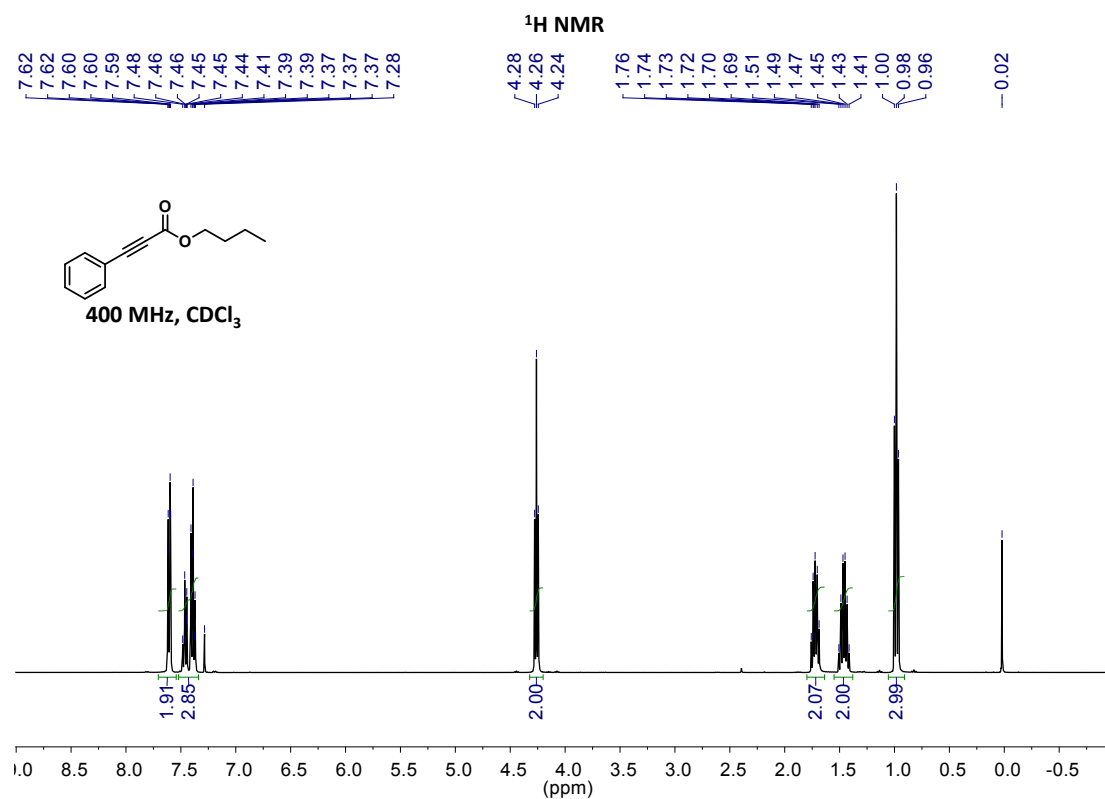
**Compound 2m:** Yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 4.13 (t,  $J = 6.7$  Hz, 2H), 2.30 (t,  $J = 7.2$  Hz, 2H), 1.65–1.53 (m, 4H), 1.40–1.25 (m, 8H), 0.93–0.85 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 154.0, 89.4, 73.1, 65.5, 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) [ $\text{M}^+$ ].

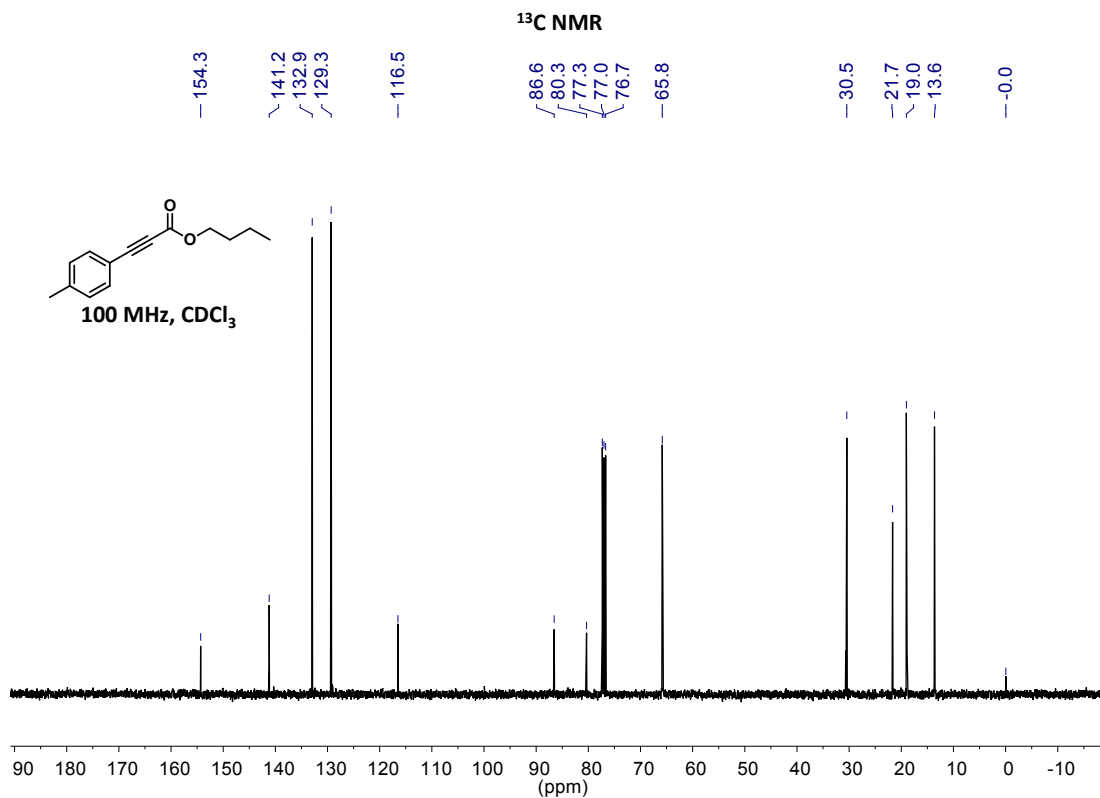
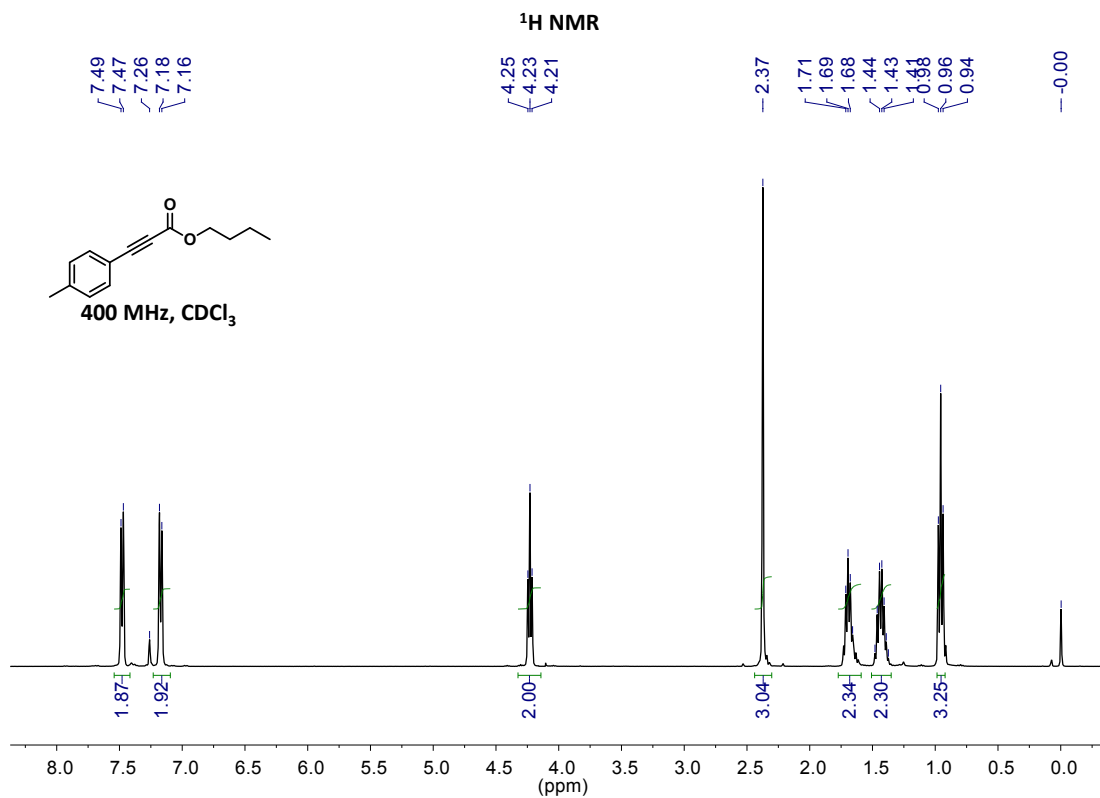


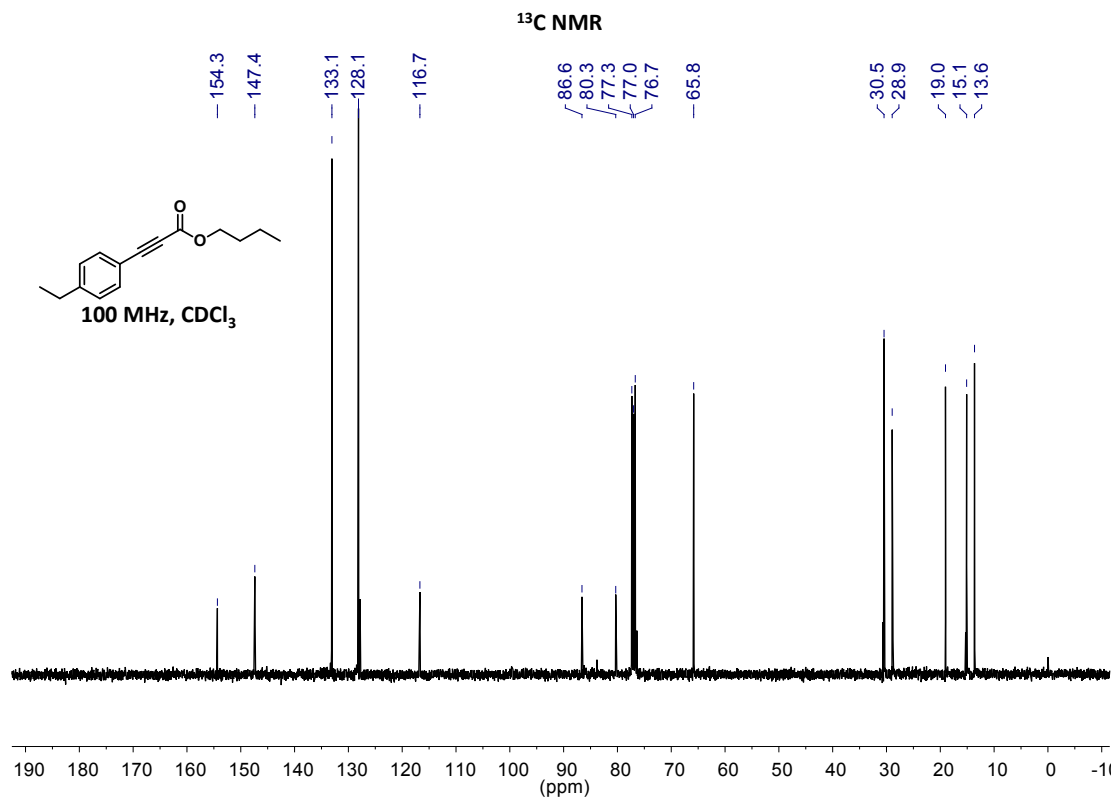
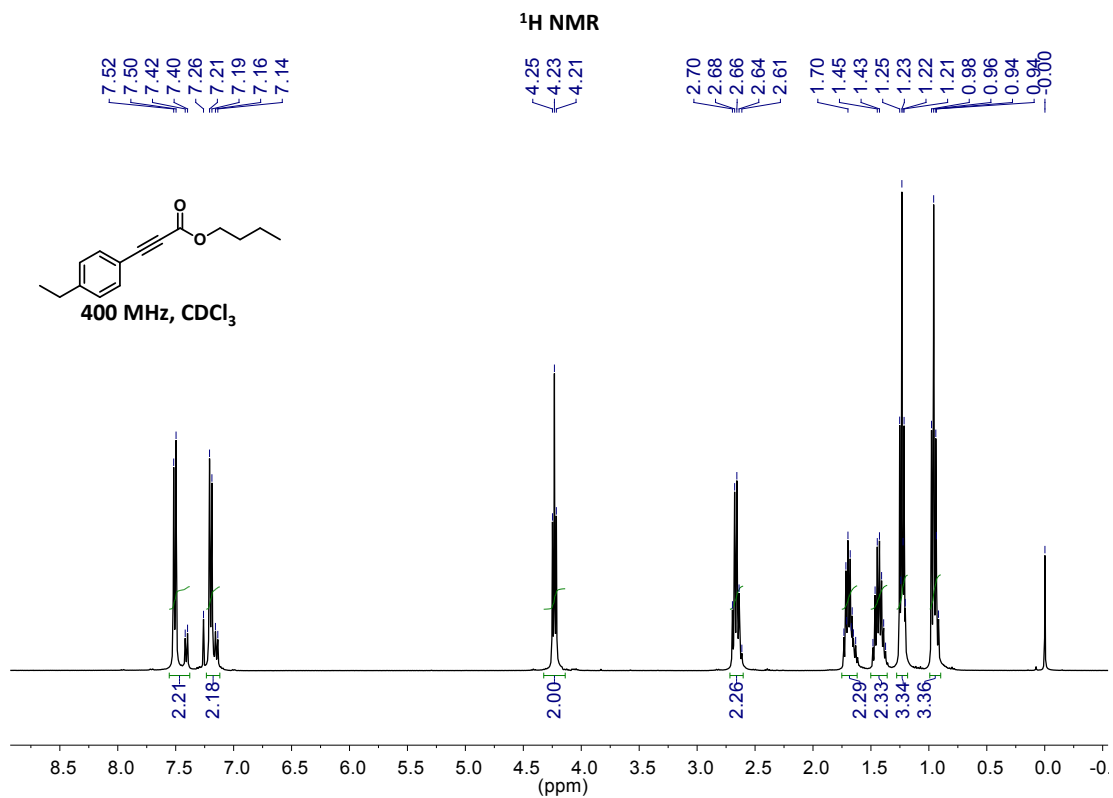
**Compound 2n:** White solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.58 (s, 4H), 4.24 (t,  $J = 6.7$  Hz, 4H), 1.72–1.68 (m, 4H), 1.46–1.41 (m, 4H), 0.96 (t,  $J = 7.4$  Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 153.8, 132.9, 121.8, 84.4, 82.9, 66.2, 30.4, 19.0, 13.6; EI-MS,  $m/z$  (%): 126.15 (100), 326.25 (16) [ $\text{M}^+$ ].

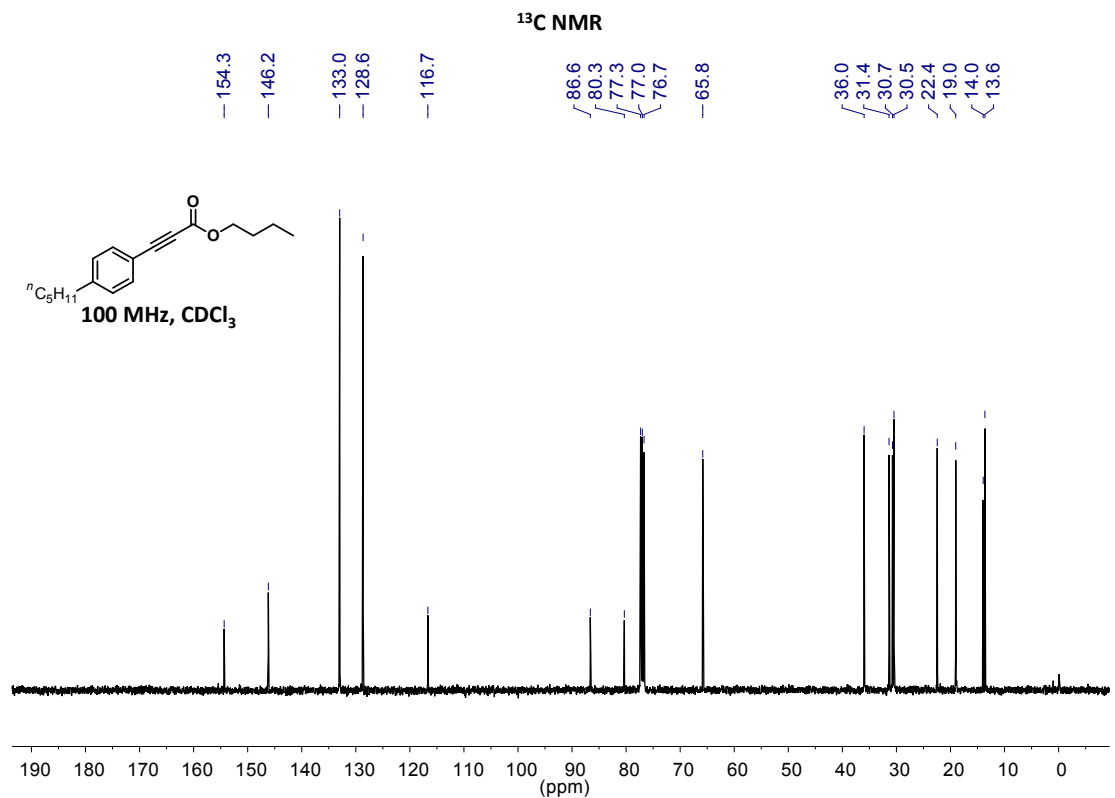
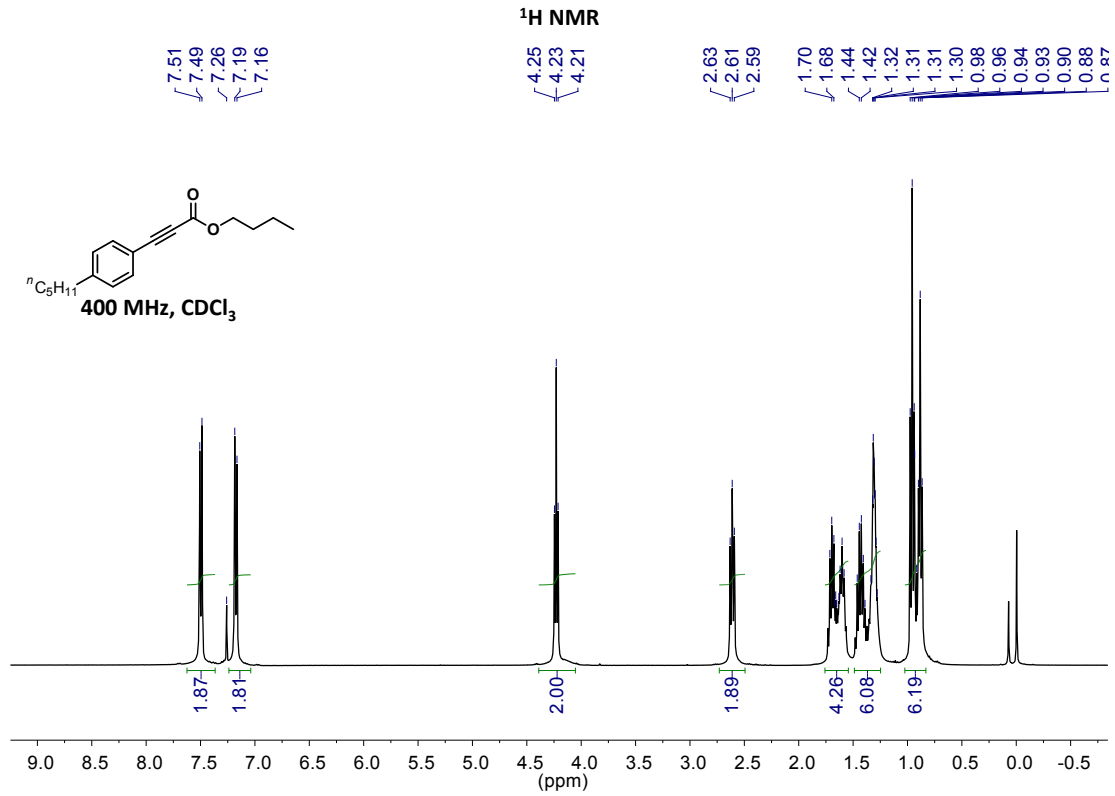


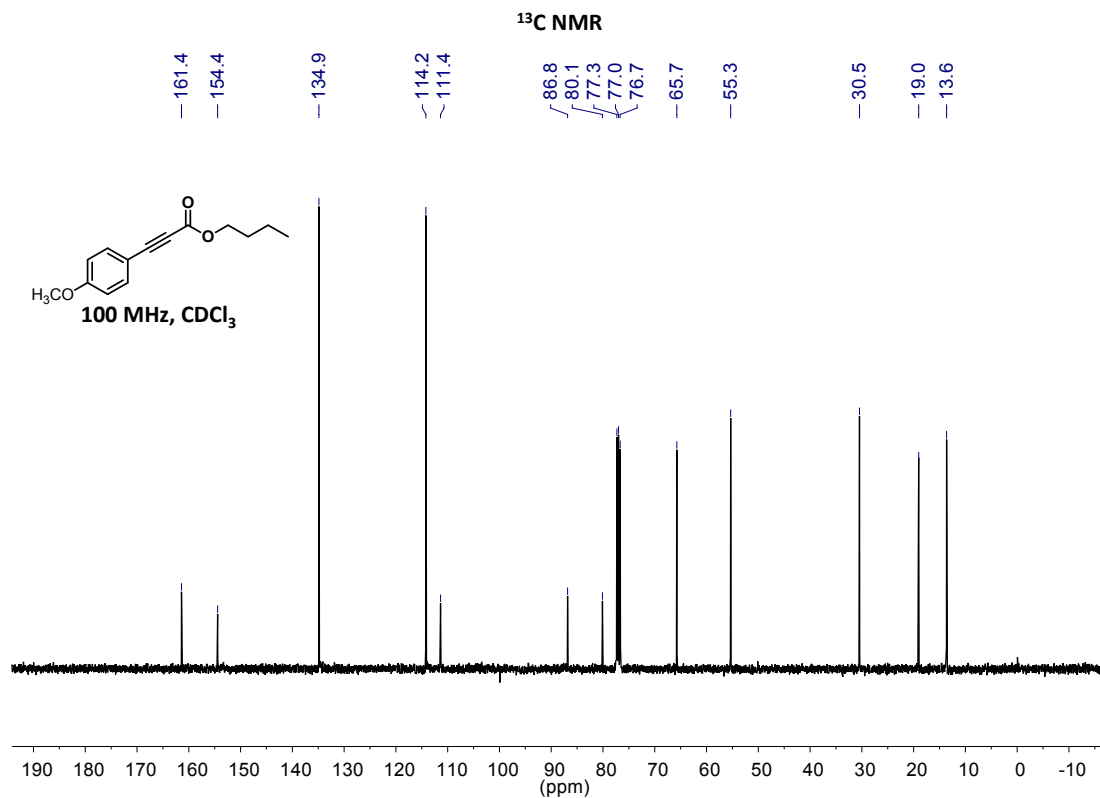
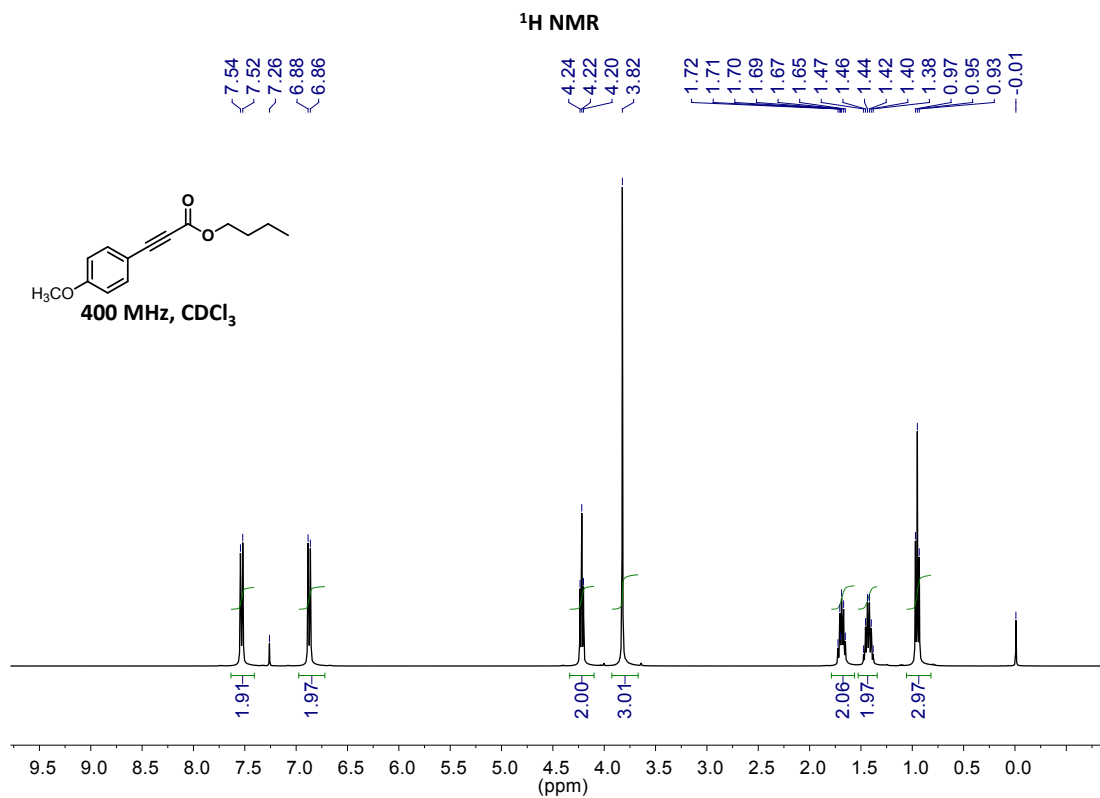
## 5. NMR spectral copies of carboxylation products

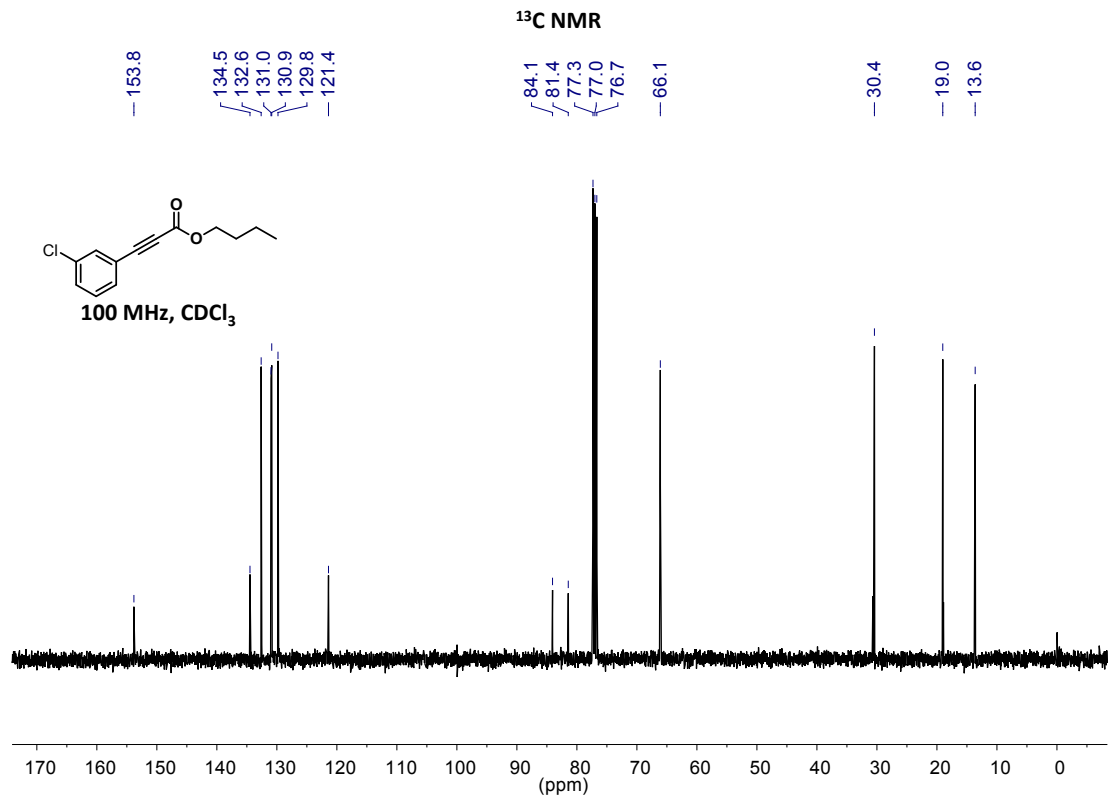
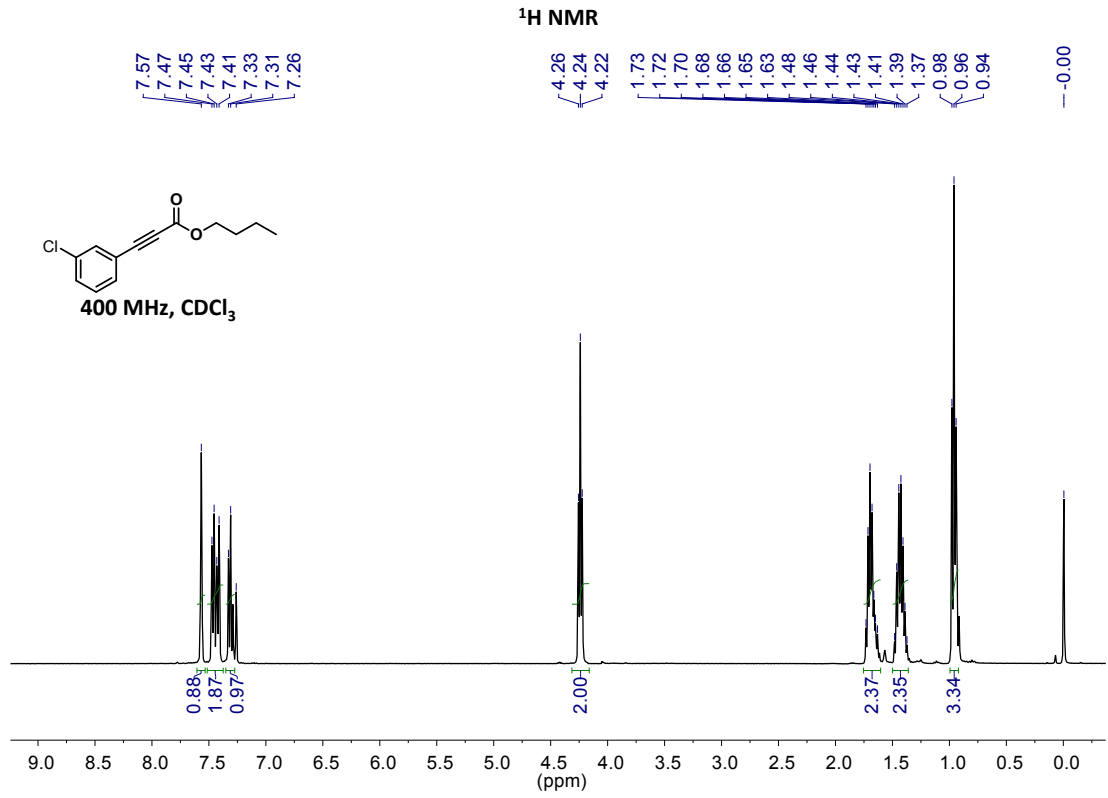


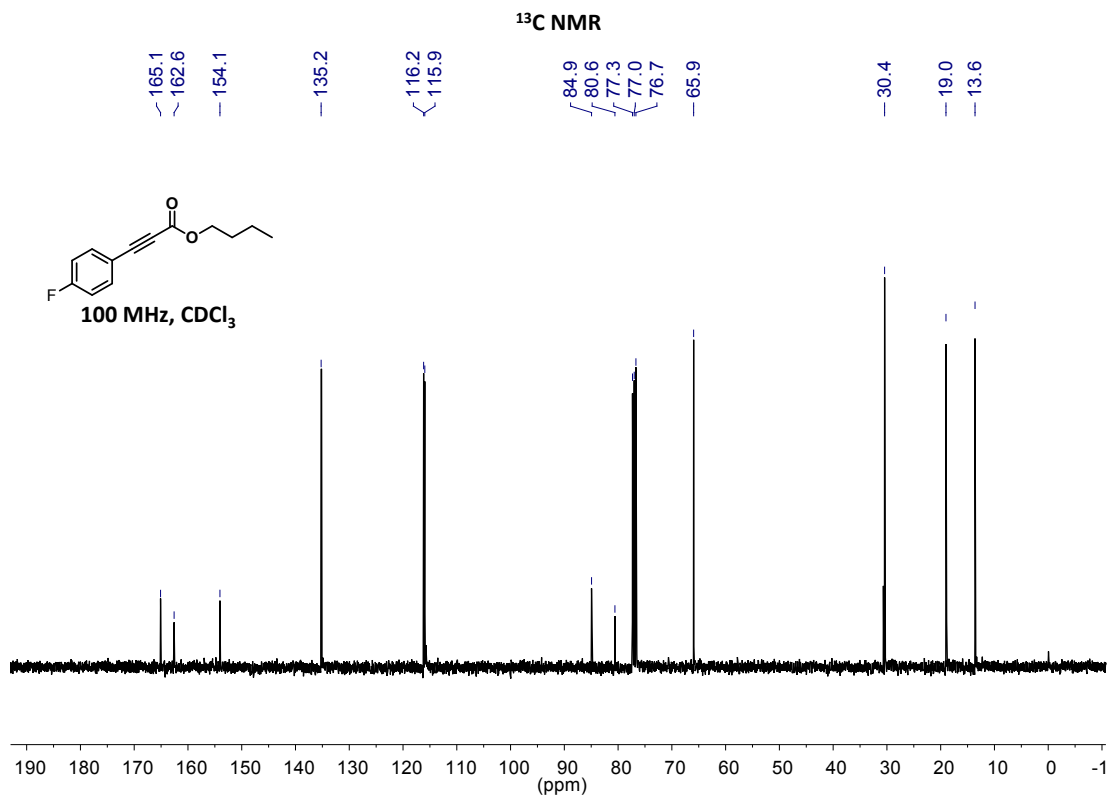
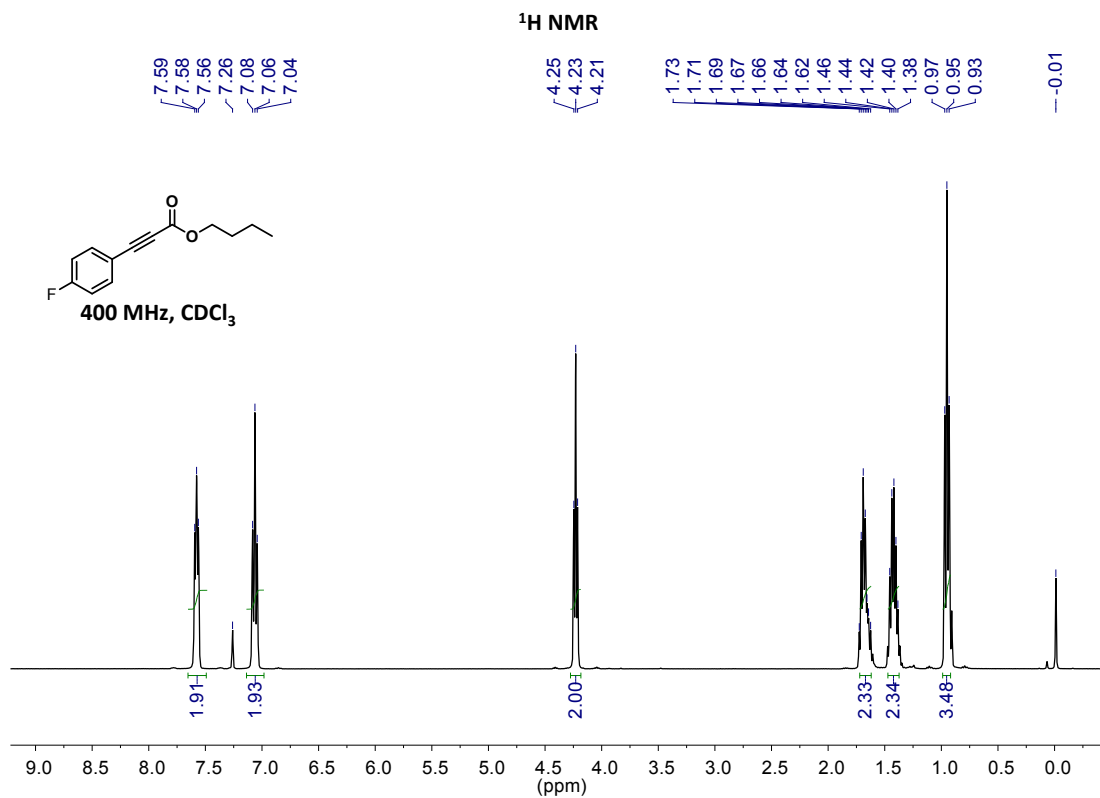


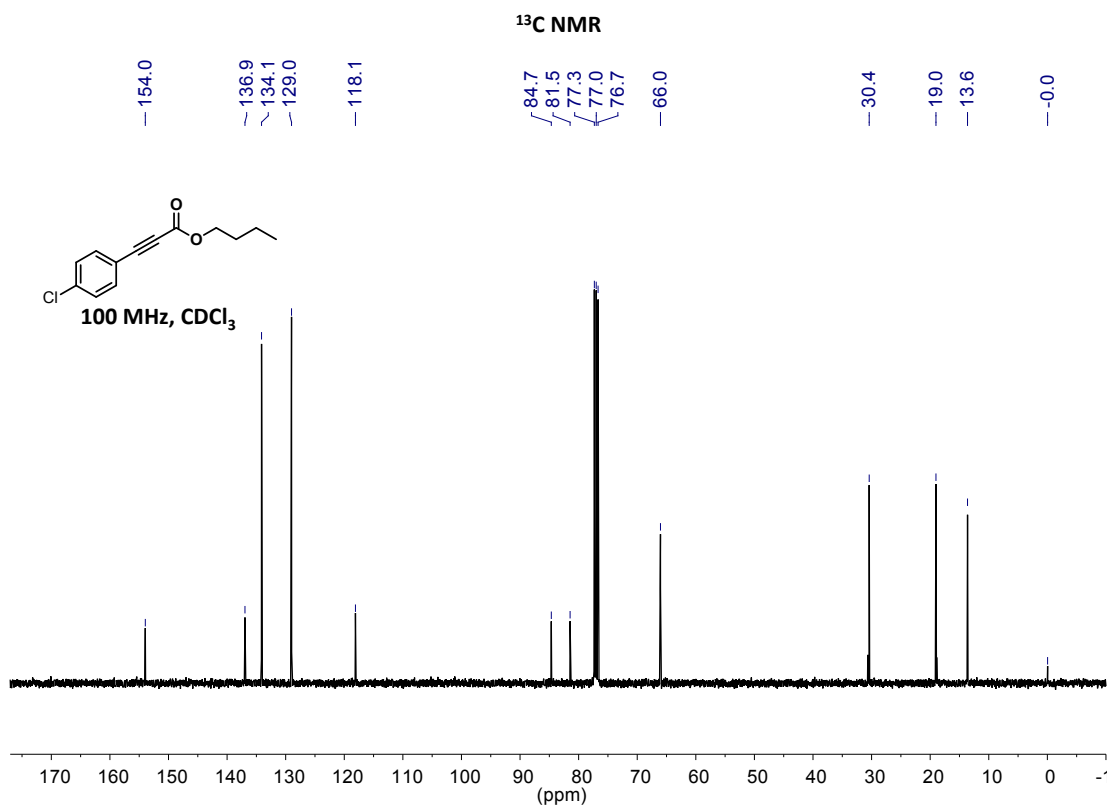
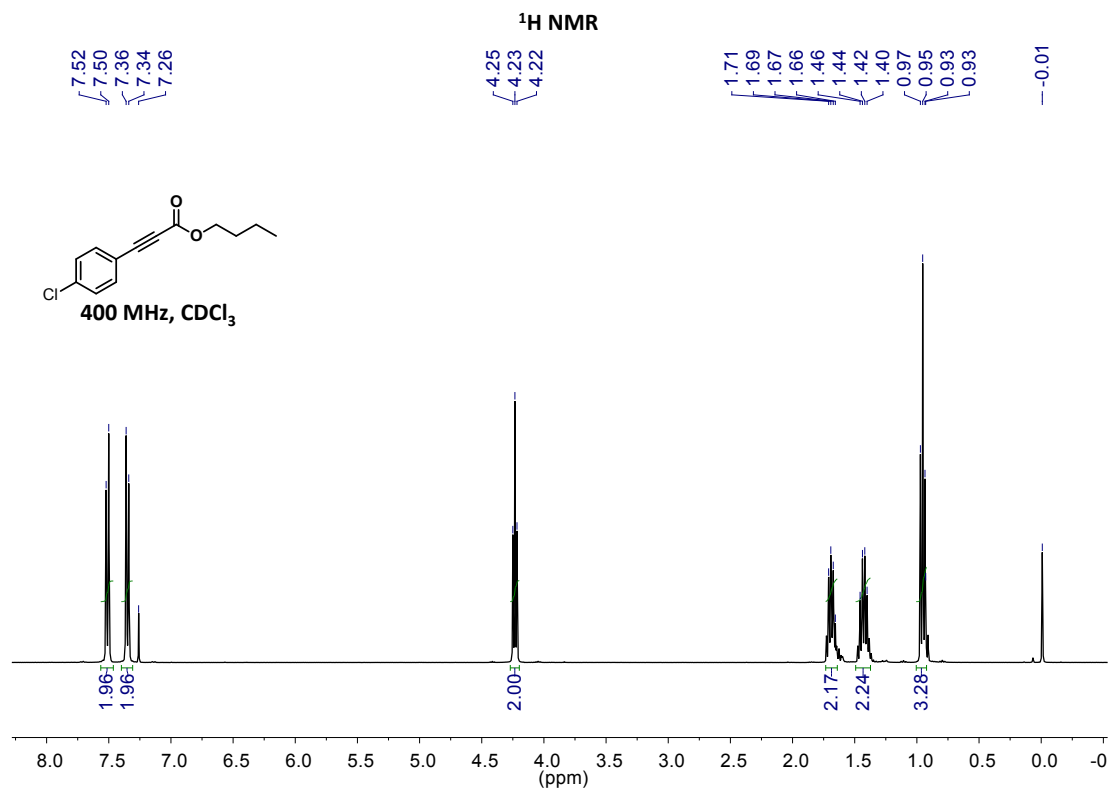




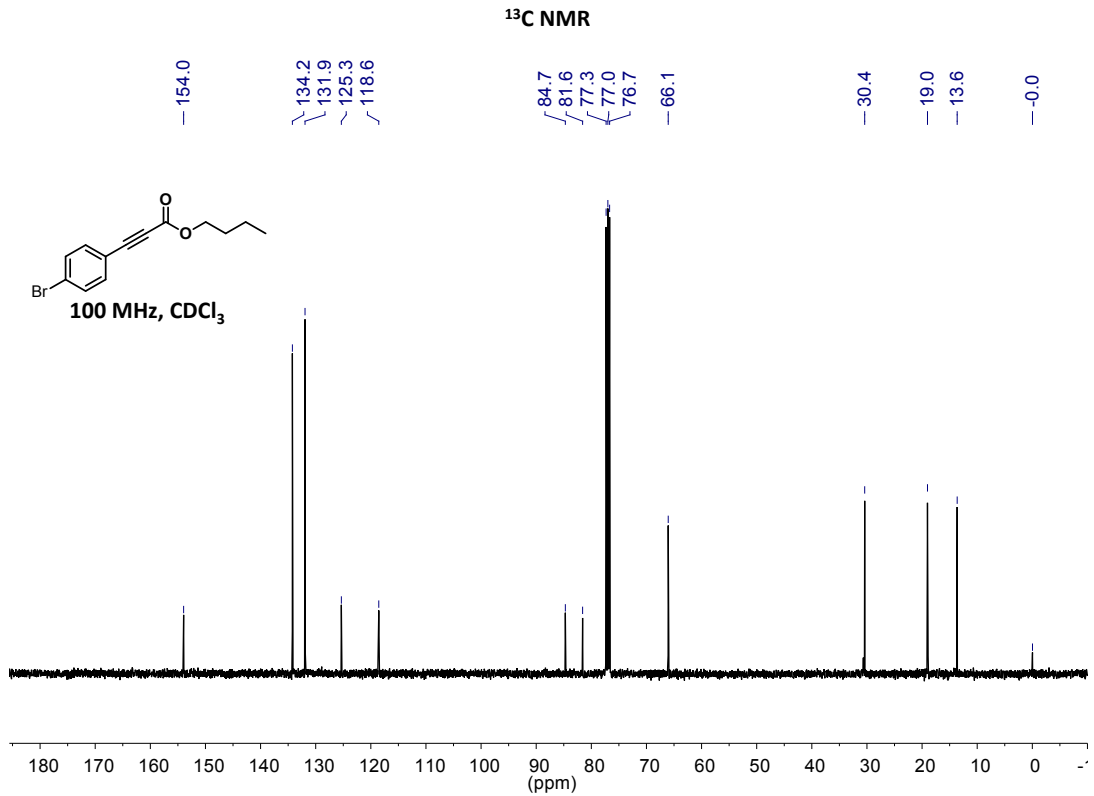
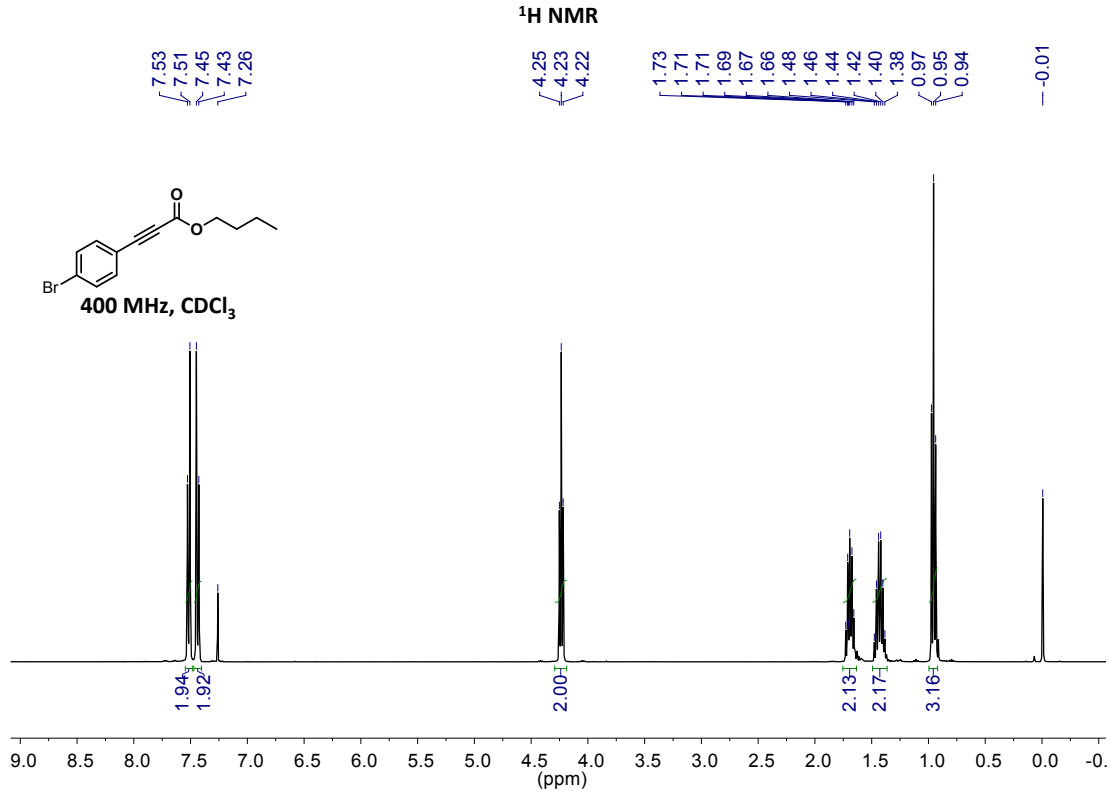


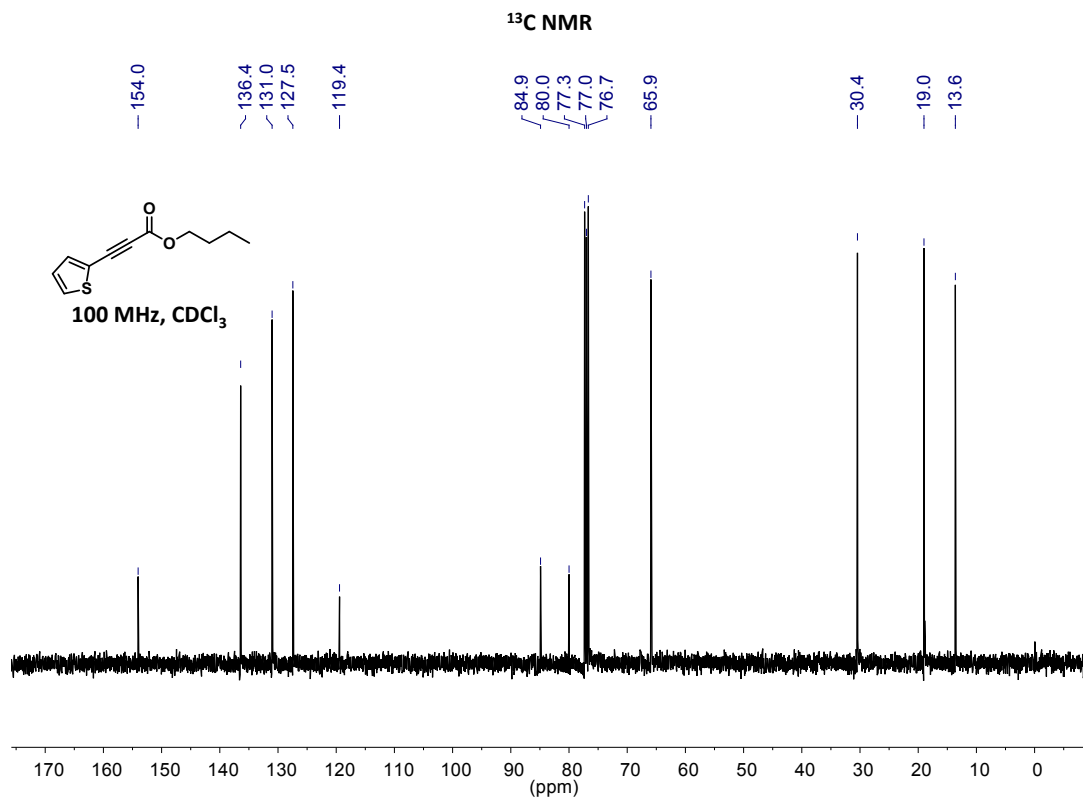
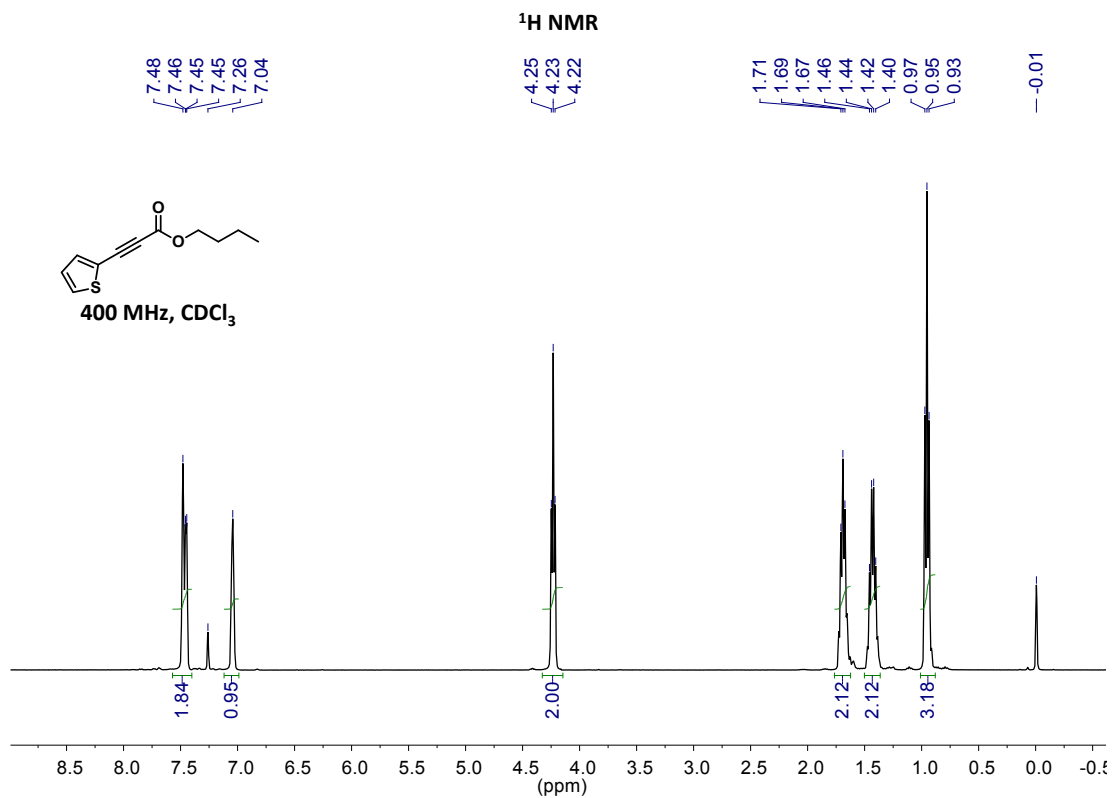


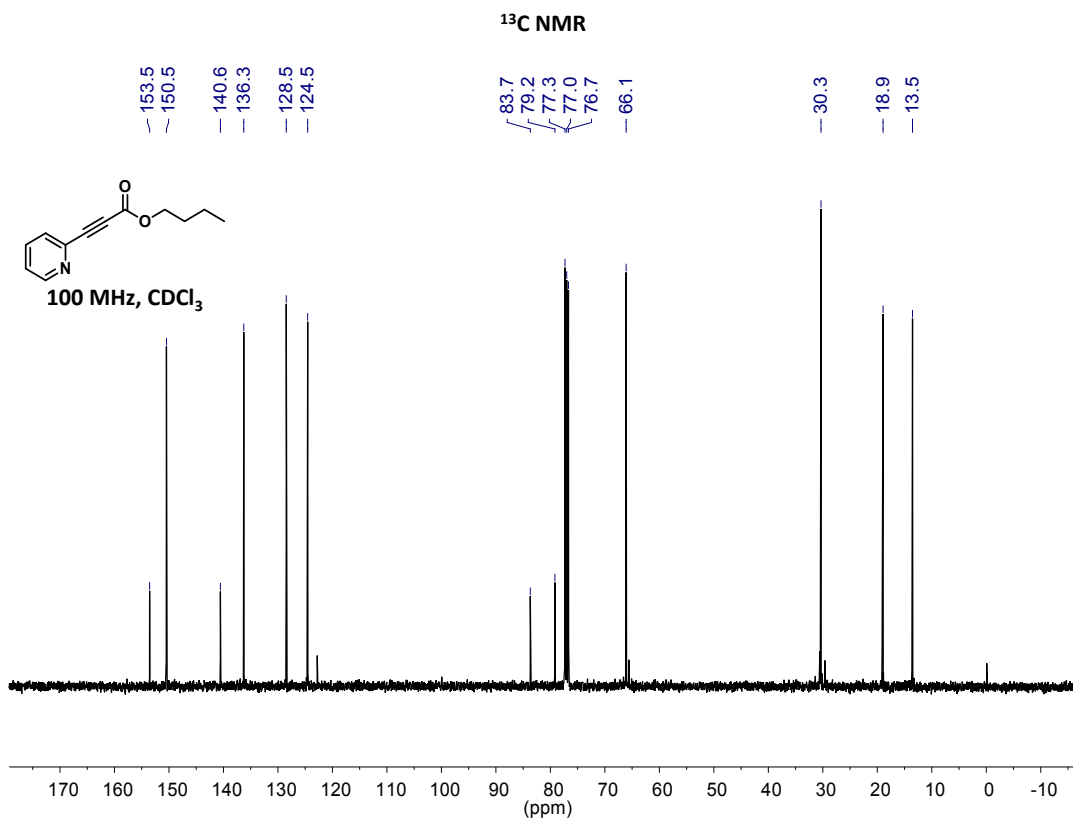
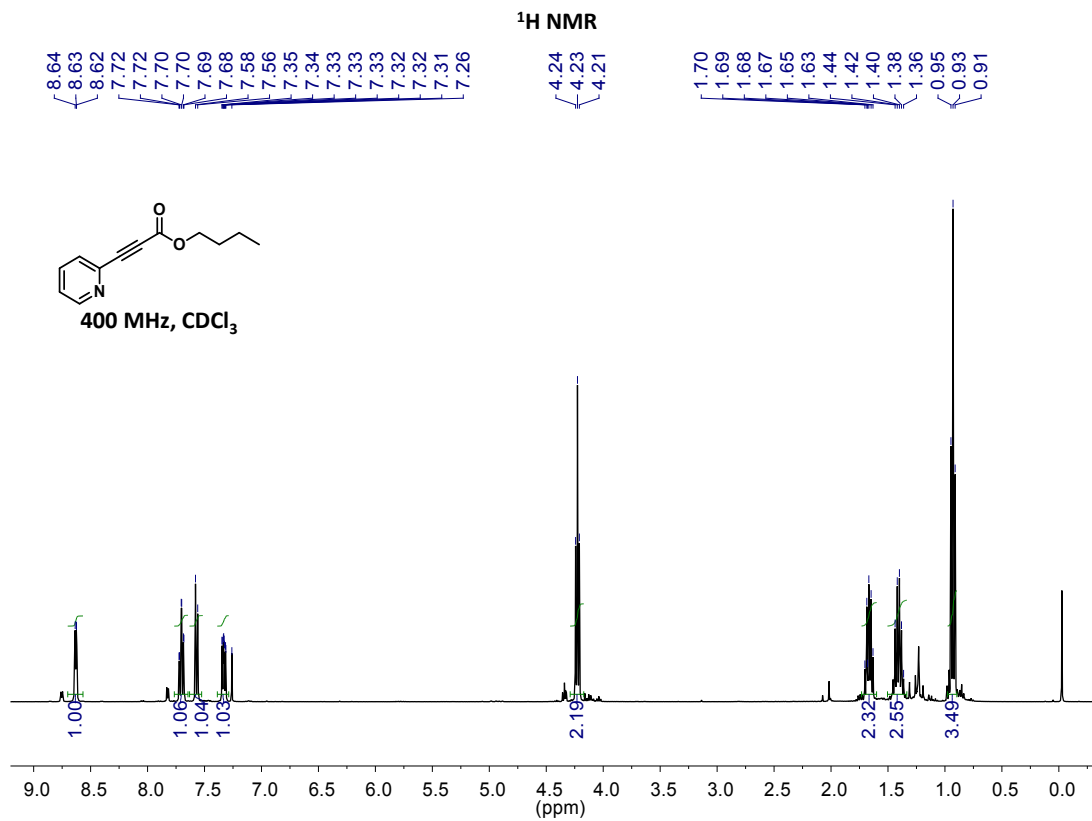


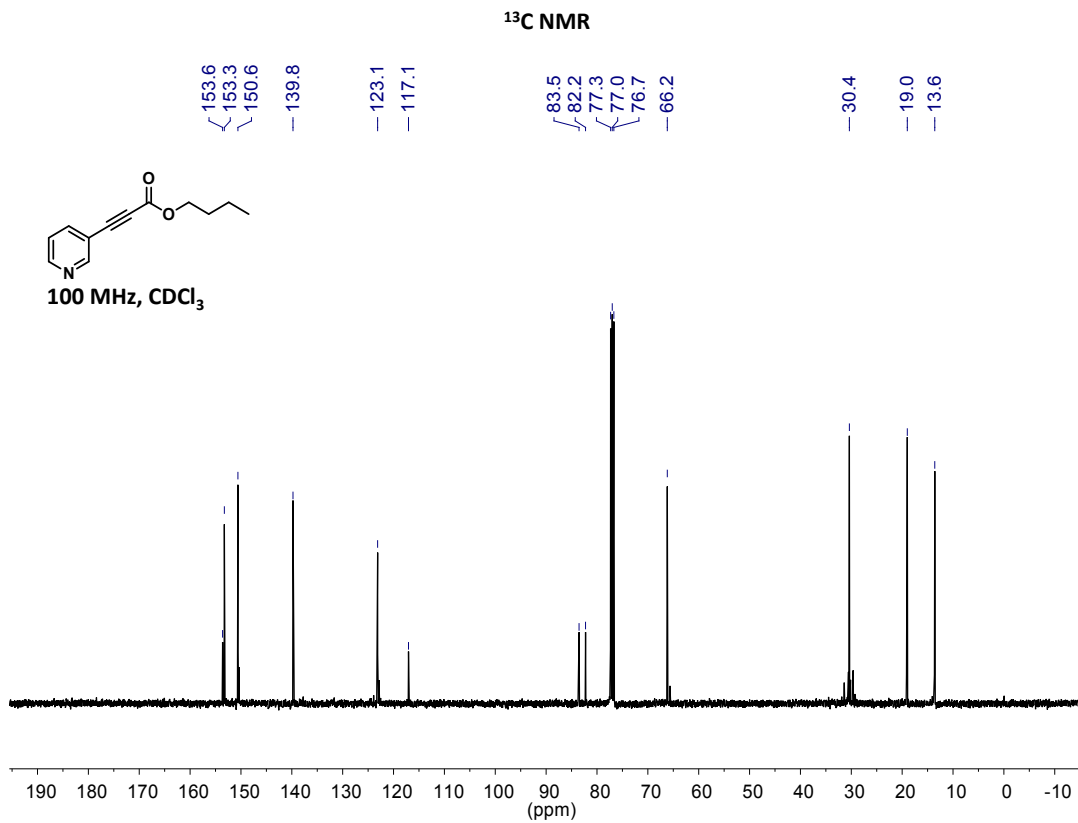
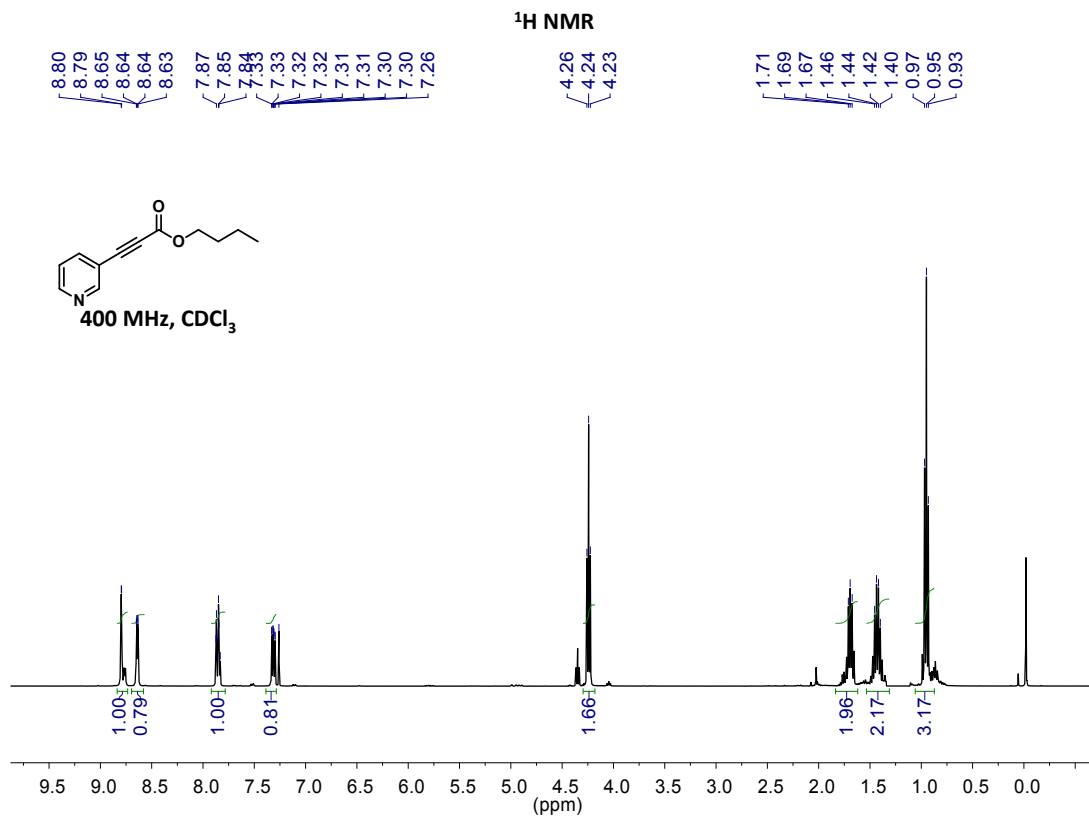


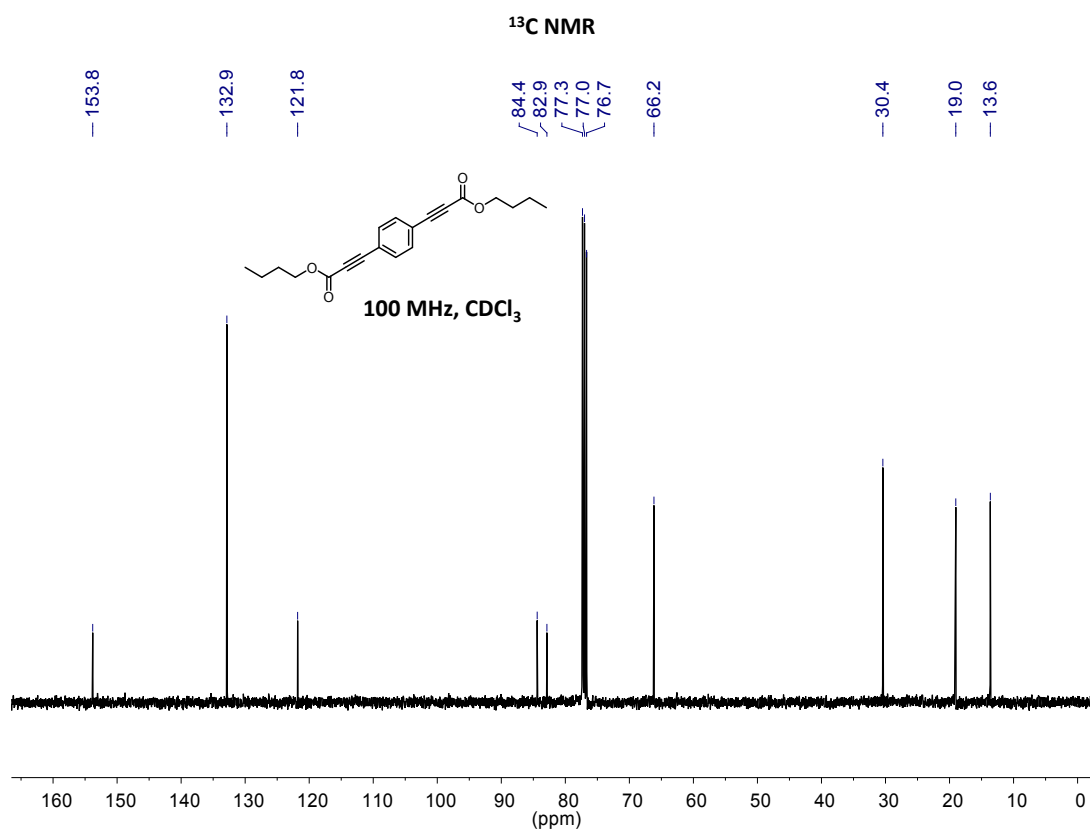
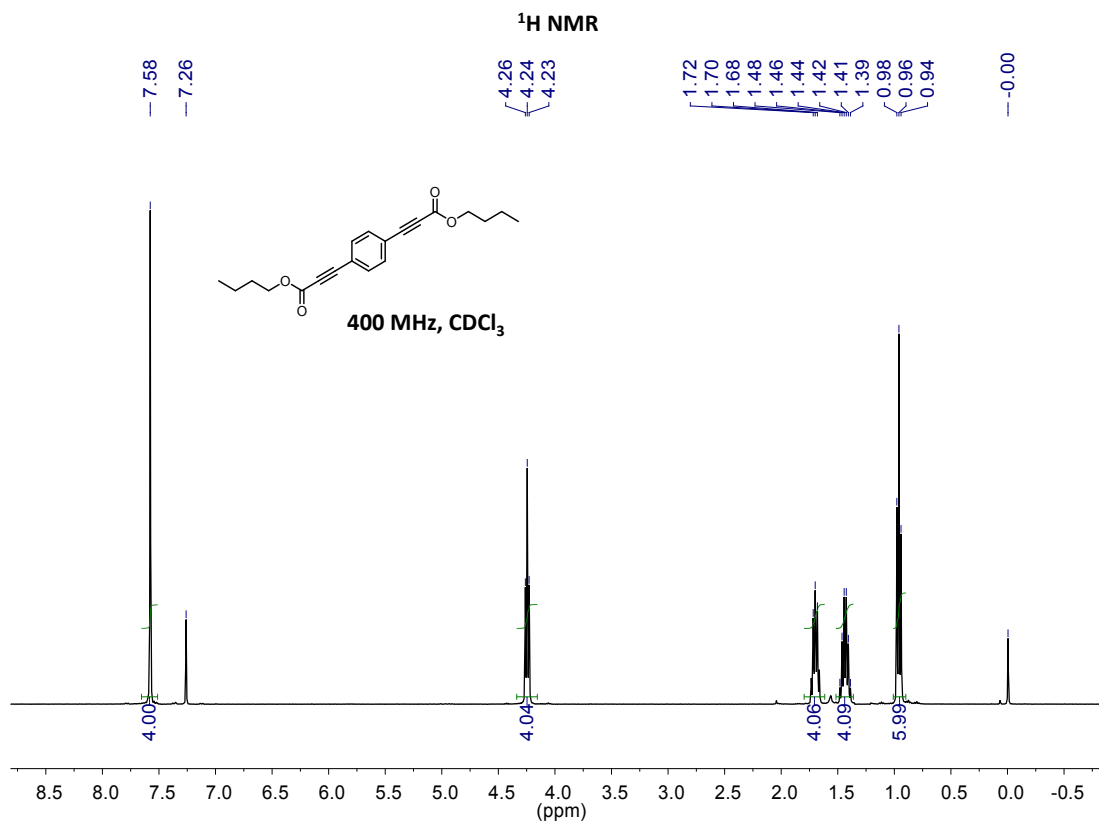






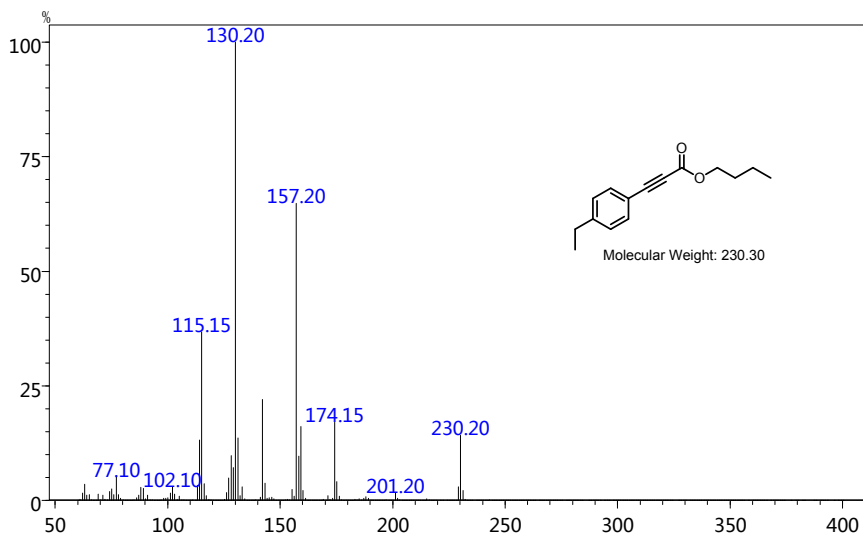
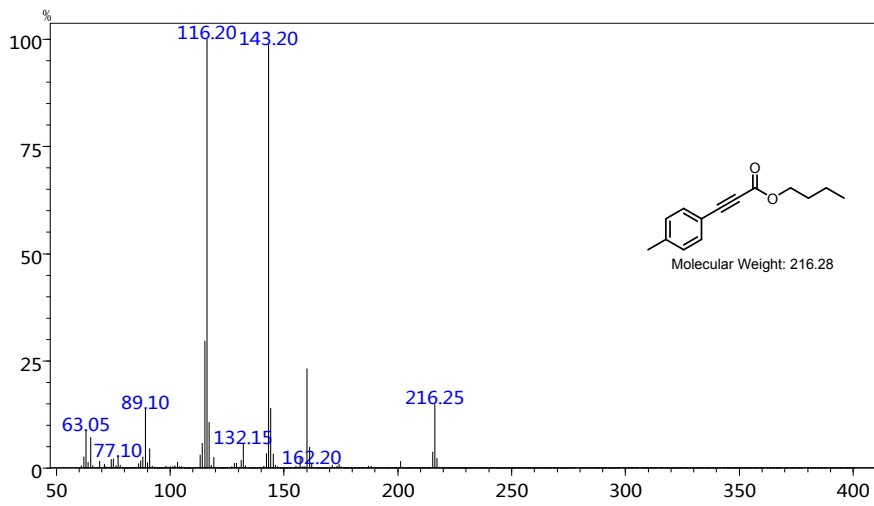
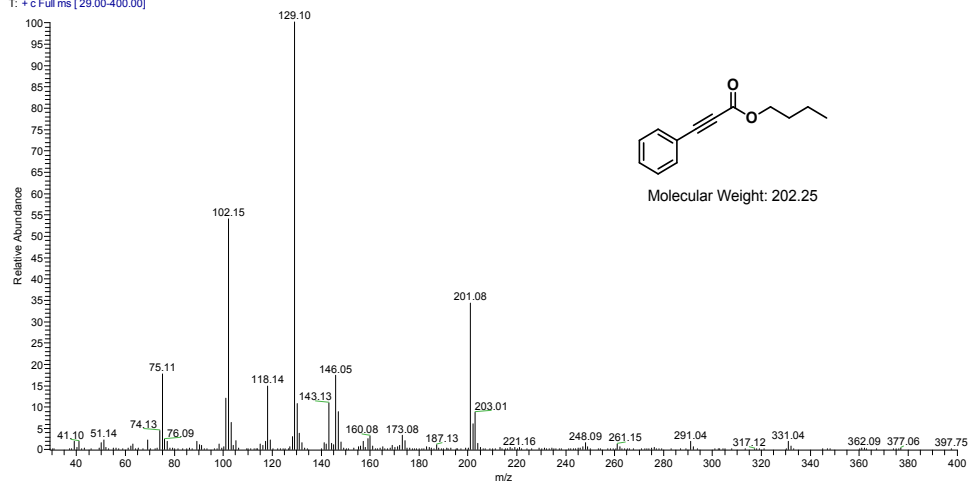


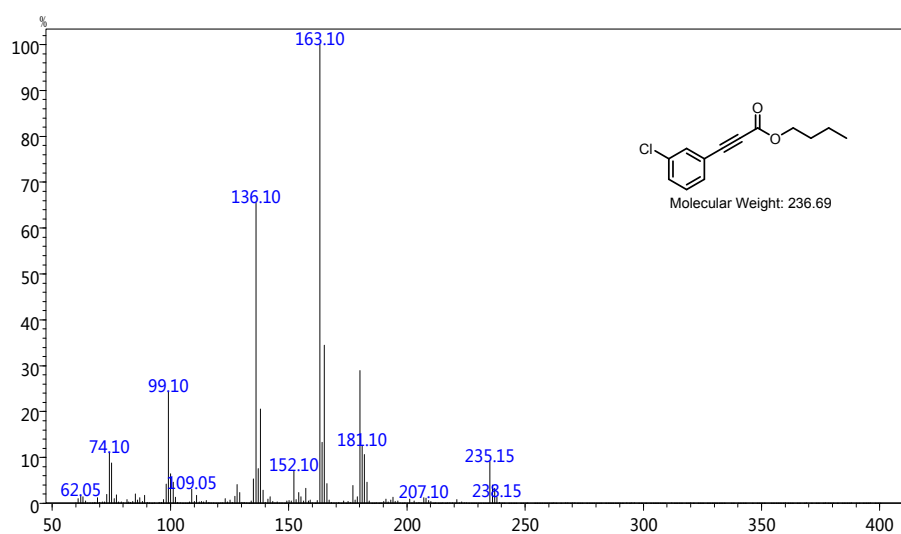
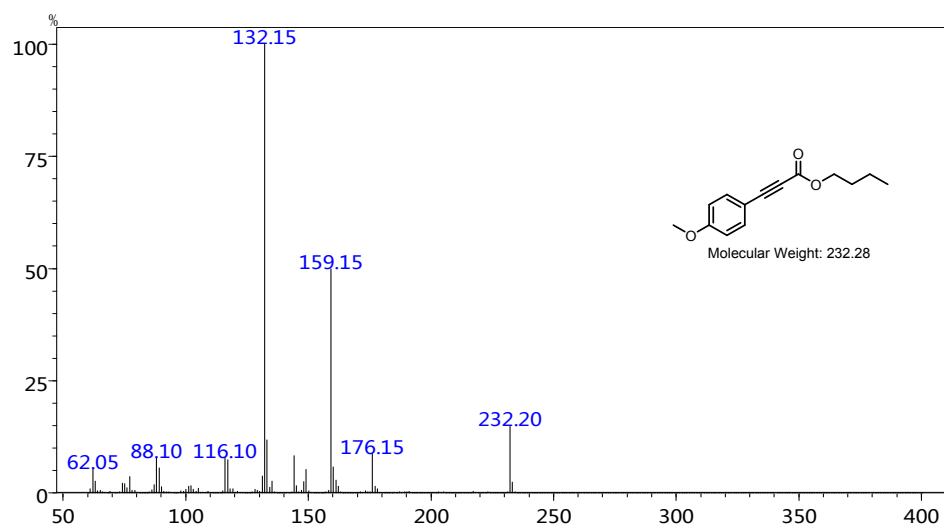
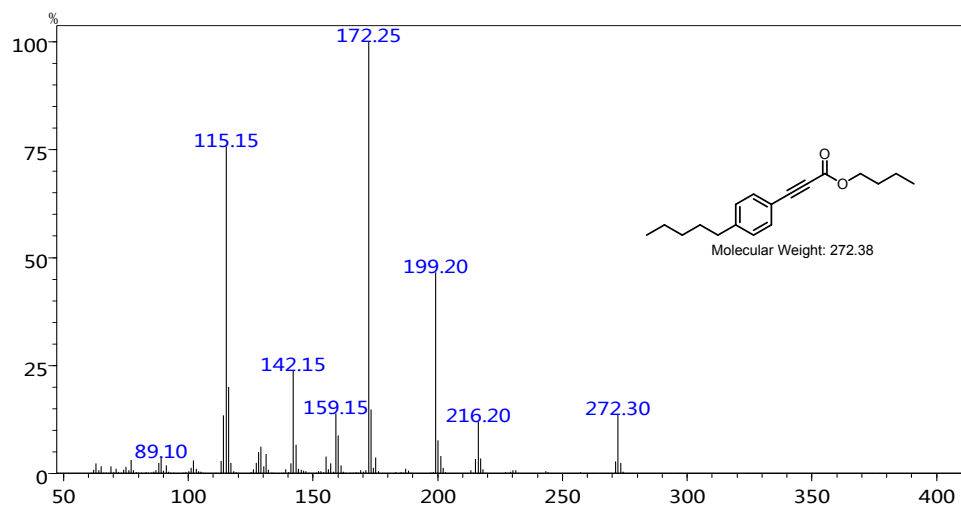


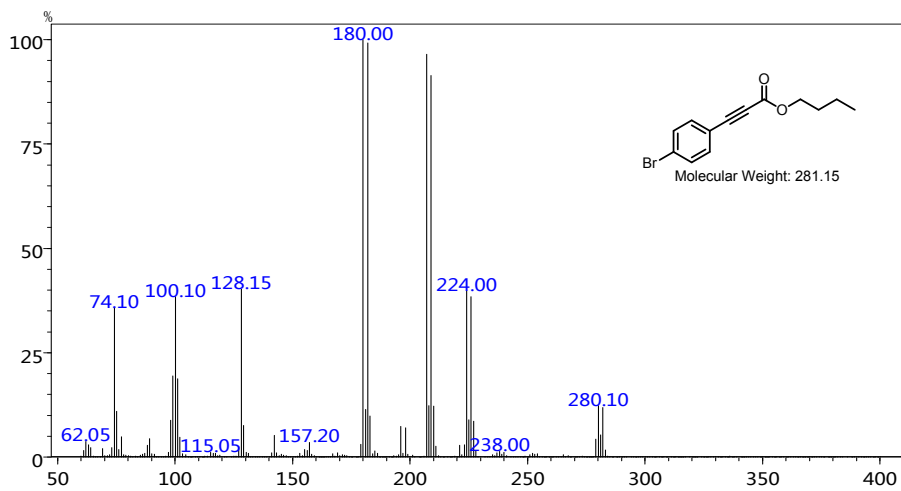
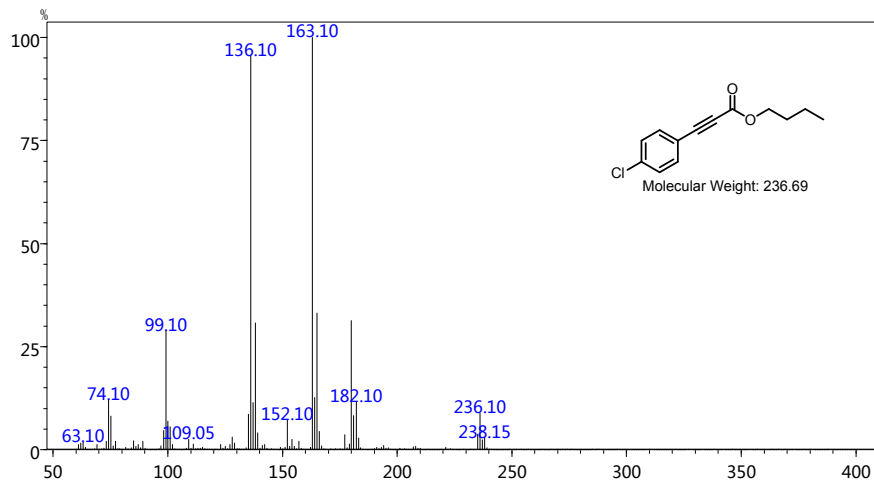
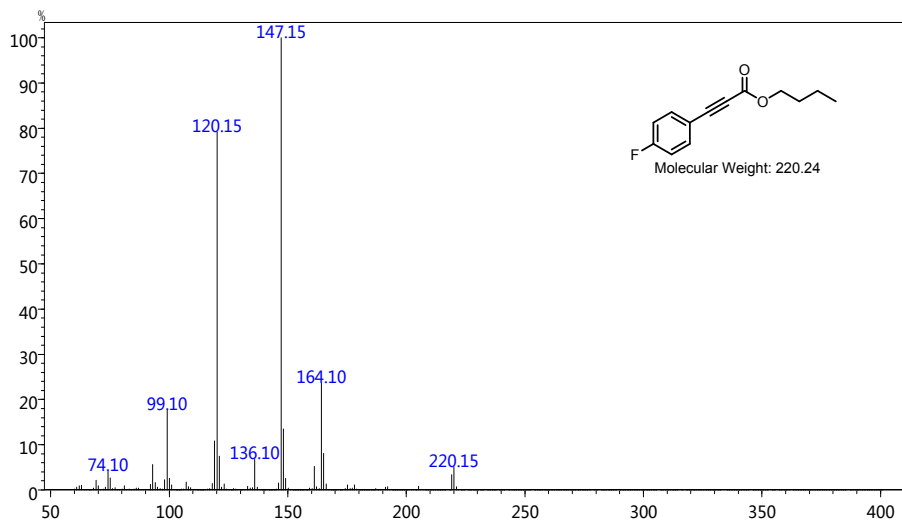


## 6. GC-MS spectral copies of the products

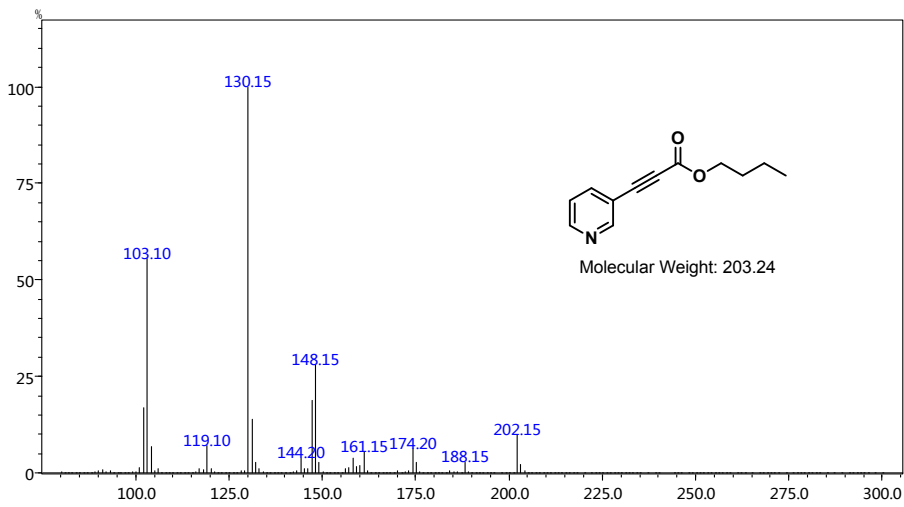
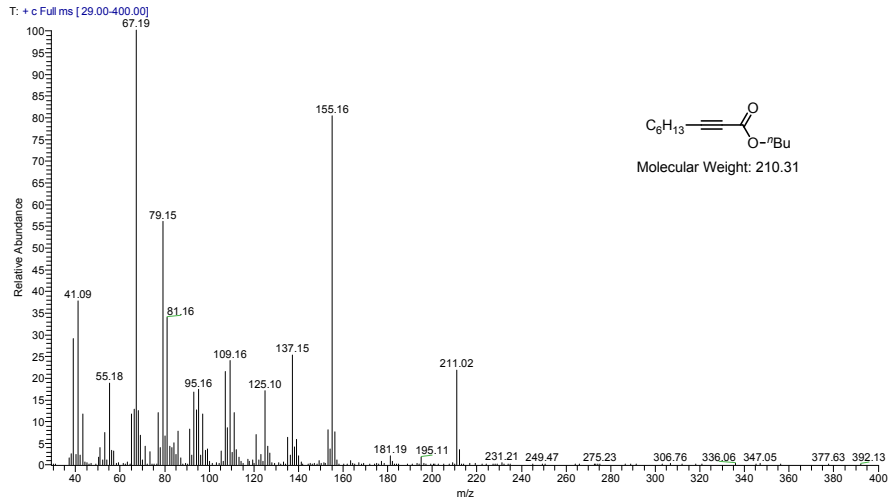
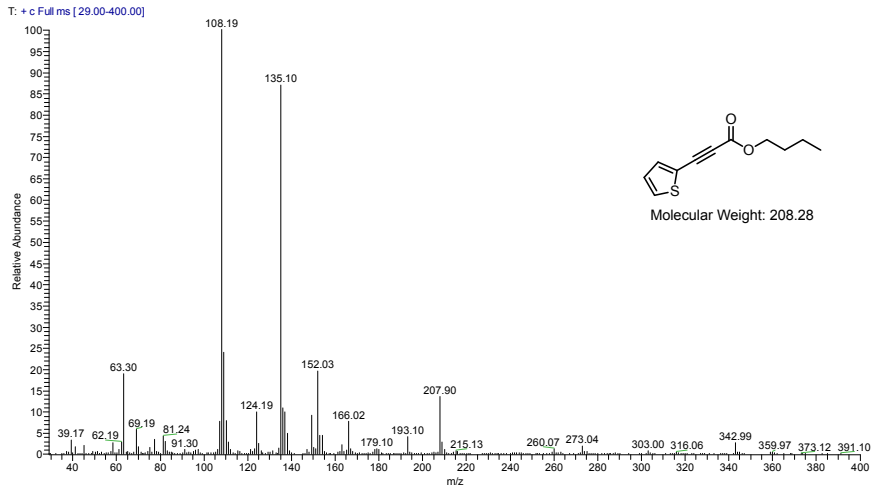
T: + c Full ms [29.00-400.00]

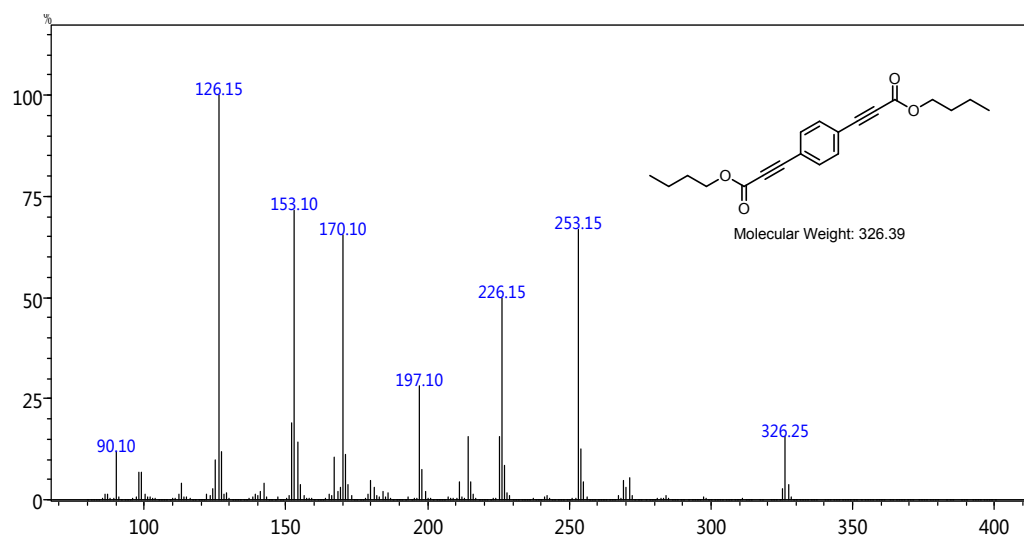
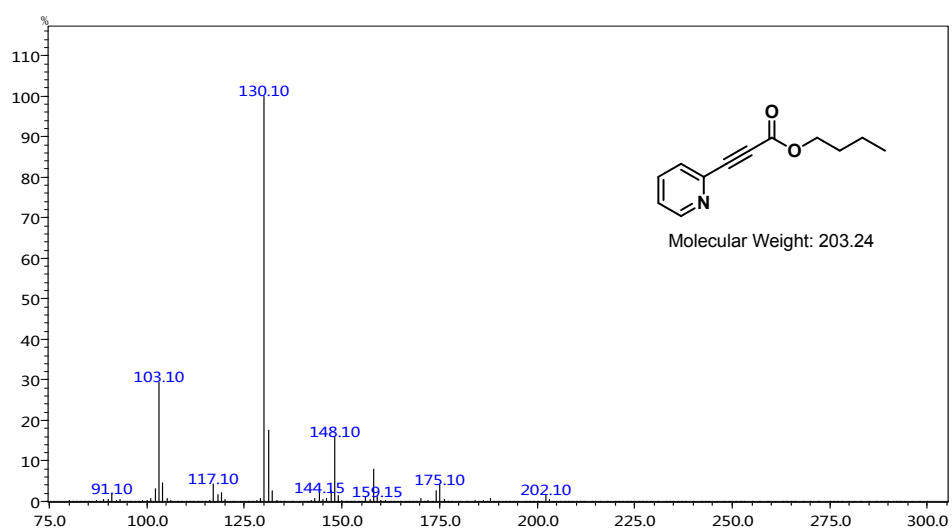












## Reference

[1] G. M. Sheldrick, Acta Cryst. 2008, **A64**, 112.