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1. General Information

Acetonitrile was obtained by distillation under argon from calcium hydride. Flash column chromatography was performed with silica gel (230–400 mesh). NMR spectra were recorded on Bruker AV-400 and Bruker AV-500 instruments. Data were reported as chemical shifts in ppm relative to TMS (0.00 ppm) for ^1H and CDCl_3 (77.2 ppm) for ^{13}C , respectively. The abbreviations used for explaining the multiplicities were as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High resolution mass spectra (ESI HRMS) were recorded on a Micromass QTOF2 Quadruple/Time-of-Flight Tandem mass spectrometer by the instrumentation center of Department of Chemistry, Xiamen University. Cyclic voltammograms were obtained on a CHI 760E potentiostat. Infrared spectra (IR) were recorded on a Nicolet AVATER FTIR330 spectrometer.

2. General Procedure for the Photoelectrolysis

A 10 mL Schlenk tube (Figure S1a) equipped with a RVC (100 PPI, 1.2 cm x 2 cm x 0.5 cm) anode and a Pt plate (1 cm x 1cm) cathode was charged with arene (0.5 mmol), carbamate or azole (1.0 mmol), DDQ (20 mol%), Et_4NBF_4 (0.05 mmol) and MeCN (6 mL) under argon. The electrolysis cell was suspended 6 mm above the blue LEDs (25 W). A reflector was employed to increase reaction efficiency (Figure S1b). The photoelectrolysis was carried out at rt (cooled by the axial fan) using a constant current of 2 mA. Upon completion, the reaction mixture was concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/hexanes to give the final product.

The gram scale reaction was conducted in a 200 mL beaker-type cell equipped with a RVC anode (100 PPI, 1.2 cm x 5 cm x 5 cm) and a Pt plate (3 cm x 3 cm) cathode. The cell was charged with **1** (1.01 g, 13 mmol, 1.0 equiv), **2** (3.04 g, 26 mmol, 2.0 equiv), DDQ (0.59 g, 20 mol%), Et_4NBF_4 (0.28 g, 1.3 mmol, 0.1 equiv), and MeCN (156 mL). 5 blue LEDs (25 W each) were placed around the cell within about 6 mm (Figure S1c). The photoelectrolysis was carried out at rt using a constant current of 52 mA. Upon completion, the reaction mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with ethyl acetate/hexanes to afford **3** as a white solid (1.62 g, 65% yield).

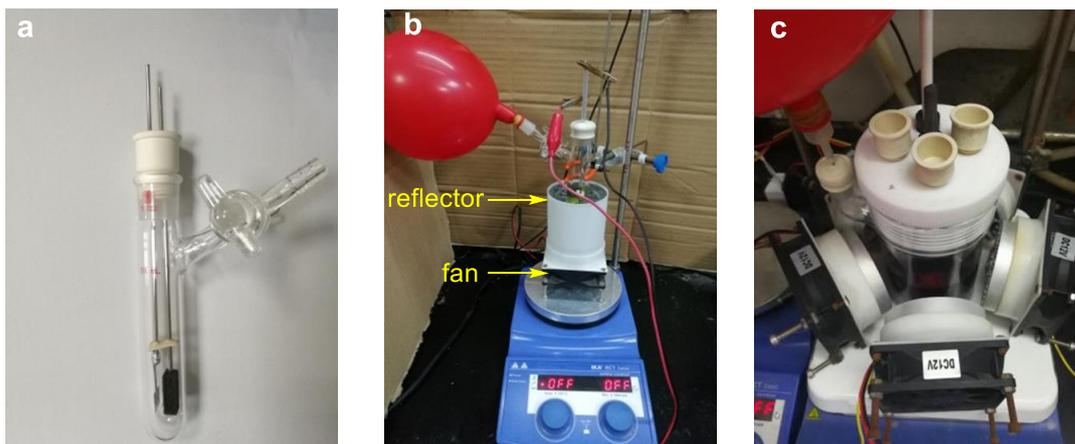
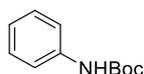


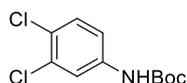
Figure S1. a. The assembled electrolysis cell. b. Reaction setup for small scale reaction. c. Reaction setup for the gram scale reaction.

3. Characterization Data for the Photoelectrolysis Products

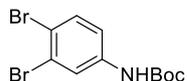
The compounds **3**, **4**, **5**, **6**, **7**, **8**, **9**, **10**, **11**, **12**, **15**, **16**, **17**, **18**, **20**, **21**, **23**, **24**, **25**, **27** and **28** are known in the literature.



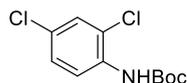
tert-Butyl phenylcarbamate (3). Yield = 83%; White solid; ^1H NMR (500 MHz, CDCl_3) δ 7.35 (d, J = 8.0 Hz, 2H), 7.30–7.26 (m, 2H), 7.04–7.00 (m, 1H), 6.52 (s, 1H), 1.52 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 152.9, 138.5, 129.1, 123.2, 118.7, 80.6, 28.5.



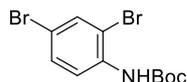
tert-Butyl (3,4-dichlorophenyl)carbamate (4). Yield = 70%; White solid; ^1H NMR (500 MHz, CDCl_3) δ 7.62 (d, J = 2.6 Hz, 1H), 7.31 (d, J = 8.7 Hz, 1H), 7.13 (dd, J = 8.7, 2.6 Hz, 1H), 6.59 (s, 1H), 1.51 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 152.5, 138.1, 132.9, 130.5, 126.2, 120.3, 117.9, 81.5, 28.4.



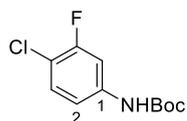
tert-Butyl (3,4-dibromophenyl)carbamate (5). Yield = 58%; White solid; ^1H NMR (500 MHz, CDCl_3) δ 7.78 (d, J = 2.6 Hz, 1H), 7.47 (d, J = 8.7 Hz, 1H), 7.13 (dd, J = 8.7, 2.6 Hz, 1H), 6.54 (s, 1H), 1.51 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 152.4, 138.7, 133.7, 125.1, 123.3, 118.7, 117.8, 81.5, 28.4.



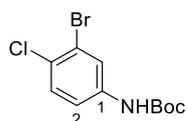
tert-Butyl (2,4-dichlorophenyl)carbamate (6). Yield = 60%; White solid; ^1H NMR (500 MHz, CDCl_3) δ 8.13 (d, $J = 9.0$ Hz, 1H), 7.33 (d, $J = 2.4$ Hz, 1H), 7.21 (dd, $J = 9.0, 2.4$ Hz, 1H), 6.95 (s, 1H), 1.53 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 152.3, 134.2, 128.8, 127.9, 127.8, 122.4, 120.6, 81.6, 28.4.



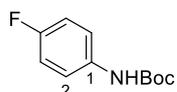
tert-Butyl (2,4-dibromophenyl)carbamate (7). C1:C2 = 1:1. Yield = 46%; White solid; ^1H NMR (500 MHz, CDCl_3) δ 8.06 (d, $J = 8.9$ Hz, 1H), 7.64 (d, $J = 2.2$ Hz, 1H), 7.39 (dd, $J = 8.9, 2.2$ Hz, 1H), 6.96 (s, 1H), 1.53 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 152.3, 135.8, 134.5, 131.4, 121.2, 115.3, 112.8, 81.7, 28.4.



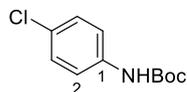
tert-Butyl (4-chloro-3-fluorophenyl)carbamate and tert-butyl (3-chloro-4-fluorophenyl)carbamate (8). C1:C2 = 4.5:1. Yield = 38%; White solid; ^1H NMR (400 MHz, CDCl_3) δ 7.59–7.41 (m, 1H), 7.28–7.10 (m, 1H), 7.07–6.92 (m, 1H), 6.59–6.39 (m, 1H), 1.52 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 158.4 (d, $J = 247.0$ Hz), 152.4, 138.7 (d, $J = 9.9$ Hz), 130.6, 116.7 (d, $J = 22.1$ Hz), 114.6, 107.2 (d, $J = 26.0$ Hz), 81.5, 28.4; ^{19}F NMR (376 MHz, CDCl_3) δ -113.7, -122.8.



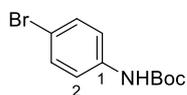
tert-Butyl (3-bromo-4-chlorophenyl)carbamate and tert-butyl (4-bromo-3-chlorophenyl)carbamate (9). C1:C2 = 1:1. Yield = 33%; White solid; ^1H NMR (500 MHz, CDCl_3) δ 7.77 (d, $J = 2.5$ Hz, 0.5H), 7.63 (d, $J = 2.5$ Hz, 0.5H), 7.47 (d, $J = 8.7$ Hz, 0.5H), 7.32 (d, $J = 8.7$ Hz, 0.5H), 7.19 (dd, $J = 8.7, 2.6$ Hz, 0.5H), 7.07 (dd, $J = 8.8, 2.6$ Hz, 0.5H), 6.65 – 6.52 (m, 1H), 1.51 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 152.5, 152.4, 138.8, 138.1, 134.9, 133.8, 130.4, 128.2, 123.4, 122.7, 120.1, 118.6, 118.0, 115.4, 81.5, 28.4.



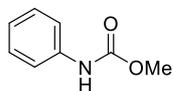
***tert*-Butyl (4-fluorophenyl)carbamate and *tert*-butyl (3-fluorophenyl)carbamate (10).** C1:C2 = 1.2:1. Yield = 49%; White solid; ^1H NMR (500 MHz, CDCl_3) δ 7.36–7.27 (m, 1.5H), 7.20 (td, $J = 8.3, 6.5$ Hz, 0.5H), 7.05–6.94 (m, 1.5H), 6.71 (td, $J = 8.3, 2.5$ Hz, 0.5H), 6.67–6.46 (m, 1H), 1.53–1.49 (m, 9H); ^{19}F NMR (471 MHz, CDCl_3) δ -111.8 (dt, $J = 10.9, 7.4$ Hz), -120.2.



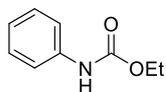
***tert*-Butyl (4-chlorophenyl)carbamate and *tert*-butyl (3-chlorophenyl)carbamate (11).** C1:C2 = 7.5:1. Yield = 71%; White solid; ^1H NMR (500 MHz, CDCl_3) δ 7.52–6.92 (m, 4H), 6.70–6.51 (m, 1H), 1.54–1.49 (m, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 152.8, 137.1, 130.0, 129.1, 129.0, 128.1, 127.8, 123.4, 123.1, 119.9, 81.0 (2C), 28.5, 28.4.



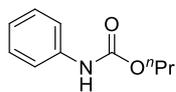
***tert*-Butyl (4-bromophenyl)carbamate and *tert*-butyl (3-bromophenyl)carbamate (12).** C1:C2 = 8:1. Yield = 62%; White solid; ^1H NMR (500 MHz, CDCl_3) δ 7.67–7.09 (m, 4H), 6.66–6.52 (m, 1H), 1.54–1.48 (m, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 152.7, 137.6, 132.0, 130.3, 126.1, 120.2, 115.5, 81.0, 28.5, 28.4.



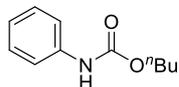
Methyl phenylcarbamate (15). Yield = 74%; White solid; ^1H NMR (500 MHz, CDCl_3) δ 7.38 (d, $J = 8.2$ Hz, 2H), 7.29 (dd, $J = 8.2, 7.3$ Hz, 2H), 7.05 (t, $J = 7.3$ Hz, 1H), 6.84 (s, 1H), 3.76 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 154.3, 138.0, 129.1, 123.6, 118.9, 52.5.



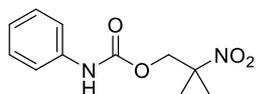
Ethyl phenylcarbamate (16). Yield = 78%; White solid; ^1H NMR (500 MHz, CDCl_3) δ 7.38 (d, $J = 8.2$ Hz, 2H), 7.28 (dd, $J = 8.2, 7.3$ Hz, 2H), 7.04 (t, $J = 7.2$ Hz, 1H), 6.78 (s, 1H), 4.22 (q, $J = 7.1$ Hz, 2H), 1.29 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 153.9, 138.1, 129.1, 123.4, 118.8, 61.3, 14.7.



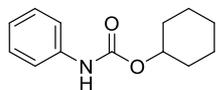
Propyl phenylcarbamate (17). Yield = 71%; White solid; ^1H NMR (500 MHz, CDCl_3) δ 7.39 (d, $J = 8.0$ Hz, 2H), 7.31–7.26 (m, 2H), 7.04 (t, $J = 7.4$ Hz, 1H), 6.77 (s, 1H), 4.12 (t, $J = 6.7$ Hz, 2H), 1.73–1.65 (m, 2H), 0.97 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 153.9, 138.1, 129.1, 123.4, 118.8, 67.0, 22.4, 10.5.



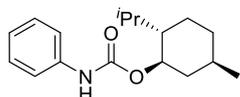
Butyl phenylcarbamate (18). Yield = 71%; White solid; ^1H NMR (500 MHz, CDCl_3) δ 7.38 (d, $J = 8.0$ Hz, 2H), 7.31–7.25 (m, 2H), 7.04 (t, $J = 7.4$ Hz, 1H), 6.80 (s, 1H), 4.16 (t, $J = 6.7$ Hz, 2H), 1.68–1.61 (m, 2H), 1.44–1.36 (m, 2H), 0.94 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 154.0, 138.2, 129.1, 123.4, 118.8, 65.2, 31.1, 19.2, 13.8.



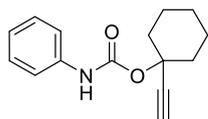
2-Methyl-2-nitropropyl phenylcarbamate (19). Yield = 57%; White solid; ^1H NMR (500 MHz, CDCl_3) δ 7.42–7.32 (m, 2H), 7.32–7.28 (m, 2H), 7.10–7.05 (m, 1H), 6.84 (s, 1H), 4.50 (s, 2H), 1.64 (s, 6H); ^{13}C NMR (126 MHz, CDCl_3) δ 152.6, 137.4, 129.2, 124.1, 119.0, 86.7, 69.0, 23.1; IR (neat, cm^{-1}): 3397, 1636, 1543, 1444, 1219, 1070, 692; ESI HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 261.0846, obsd 261.0849.



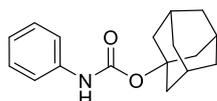
Cyclohexyl phenylcarbamate (20). Yield = 81%; White solid; ^1H NMR (500 MHz, CDCl_3) δ 7.38 (d, $J = 8.0$ Hz, 2H), 7.30–7.26 (m, 2H), 7.03 (t, $J = 7.4$ Hz, 1H), 6.73 (s, 1H), 4.79–4.71 (m, 1H), 1.96–1.90 (m, 2H), 1.76–1.70 (m, 2H), 1.57–1.51 (m, 1H), 1.48–1.34 (m, 4H), 1.29–1.21 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 153.4, 138.3, 129.1, 123.3, 118.7, 73.7, 32.0, 25.5, 23.9.



(1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl phenylcarbamate (21). Yield = 67%; White solid; ^1H NMR (500 MHz, CDCl_3) δ 7.40 (d, $J = 8.0$ Hz, 2H), 7.31–7.26 (m, 2H), 7.06–7.01 (m, 1H), 6.69 (s, 1H), 4.66 (td, $J = 10.9, 4.3$ Hz, 1H), 2.13–2.07 (m, 1H), 2.01–1.93 (m, 1H), 1.71–1.64 (m, 2H), 1.53–1.44 (m, 1H), 1.39–1.32 (m, 1H), 1.11–0.96 (m, 2H), 0.94–0.82 (m, 7H), 0.81 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 153.5, 138.3, 129.1, 123.3, 118.6, 75.2, 47.4, 41.5, 34.4, 31.5, 26.4, 23.6, 22.2, 21.0, 16.6.



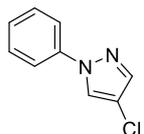
1-Ethynylcyclohexyl phenylcarbamate (22). Yield = 59%; White solid; ^1H NMR (500 MHz, CDCl_3) δ 7.40 (d, J = 8.0 Hz, 2H), 7.30–7.26 (m, 2H), 7.03 (t, J = 7.4 Hz, 1H), 6.67 (s, 1H), 2.64 (s, 1H), 2.24–2.17 (m, 2H), 1.97–1.88 (m, 2H), 1.69–1.61 (m, 4H), 1.57–1.50 (m, 1H), 1.38–1.30 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 151.7, 138.0, 129.1, 123.4, 118.7, 83.9, 75.8, 74.6, 37.4, 25.2, 22.7; IR (neat, cm^{-1}): 3305, 2936, 1712, 1523, 1442, 1313, 1220, 1052, 751; ESI HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 266.1151, obsd 266.1158.



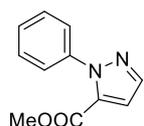
(3R,5R)-Adamantan-1-yl phenylcarbamate (23). Yield = 87%; White solid; ^1H NMR (500 MHz, CDCl_3) δ 7.35 (d, J = 8.1 Hz, 2H), 7.29–7.25 (m, 2H), 7.01 (t, J = 7.4 Hz, 1H), 6.56 (s, 1H), 2.20–2.15 (m, 9H), 1.71–1.63 (m, 6H); ^{13}C NMR (126 MHz, CDCl_3) δ 152.5, 138.5, 129.0, 123.1, 118.6, 80.5, 41.7, 36.3, 31.0.



4-Bromo-1-phenyl-1H-pyrazole (24). Yield = 65%; White solid; ^1H NMR (500 MHz, CDCl_3) δ 7.91 (s, 1H), 7.66 (s, 1H), 7.64–7.60 (m, 2H), 7.46–7.41 (m, 2H), 7.32–7.28 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 141.6, 139.8, 129.7, 127.2, 127.1, 119.1, 95.8.

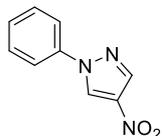


4-Chloro-1-phenyl-1H-pyrazole (25). Yield = 69%; White solid; ^1H NMR (500 MHz, CDCl_3) δ 7.88 (s, 1H), 7.64–7.60 (m, 3H), 7.46–7.41 (m, 2H), 7.29 (t, J = 7.5 Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 139.9, 139.6, 129.7, 127.1, 124.9, 119.1, 112.5.

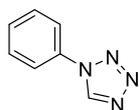


Methyl 1-phenyl-1H-pyrazole-5-carboxylate (26). Yield = 62%; White solid; ^1H NMR (500 MHz, CDCl_3) δ 7.68 (d, J = 2.0 Hz, 1H), 7.49–7.40 (m, 5H), 7.01 (d, J = 2.0 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 159.7, 140.3, 139.8, 133.1, 128.8, 128.7, 126.0, 112.7,

52.1; IR (neat, cm^{-1}): 2920, 1733, 1501, 1316, 1238, 1103, 760; ESI HRMS m/z ($\text{M}+\text{Na}$)⁺ calcd 225.0634, obsd 225.0626.



4-Nitro-1-phenyl-1H-pyrazole (27). Yield = 53%; White solid; ¹H NMR (400 MHz, CDCl_3) δ 8.63 (s, 1H), 8.27 (s, 1H), 7.75–7.67 (m, 2H), 7.57–7.50 (m, 2H), 7.47–7.41 (m, 1H); ¹³C NMR (151 MHz, CDCl_3) δ 138.8, 137.5, 136.9, 130.1, 128.9, 126.0, 120.0.



Phenyl-1H-tetrazole (28). Yield = 36%; White solid; ¹H NMR (400 MHz, CDCl_3) δ 9.03 (s, 1H), 7.77–7.69 (m, 2H), 7.64–7.52 (m, 3H); ¹³C NMR (101 MHz, CDCl_3) δ 140.7, 134.0, 130.4, 130.2, 121.4.

4. Cyclic Voltammetry Studies

The cyclic voltammogram of DDQ (3 mM) was recorded in an electrolyte of Et_4NPF_6 (0.1 M) in MeCN (5 mL) using a glassy carbon disk working electrode (diameter, 1 mm), a Pt wire auxiliary electrode and a SCE reference electrode. The scan rate is 100 mV/s.

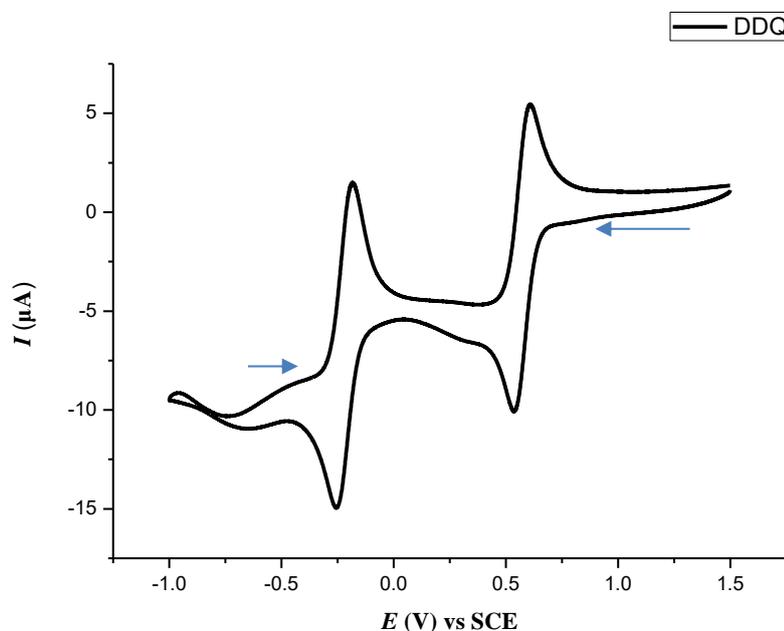
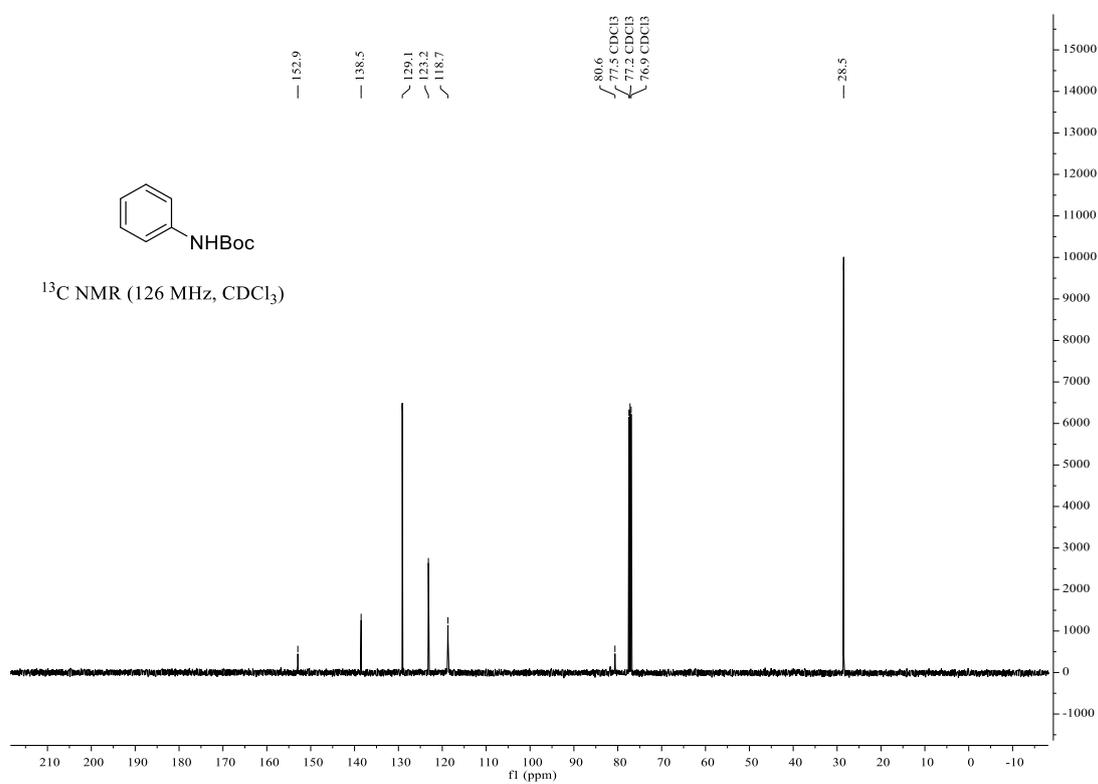
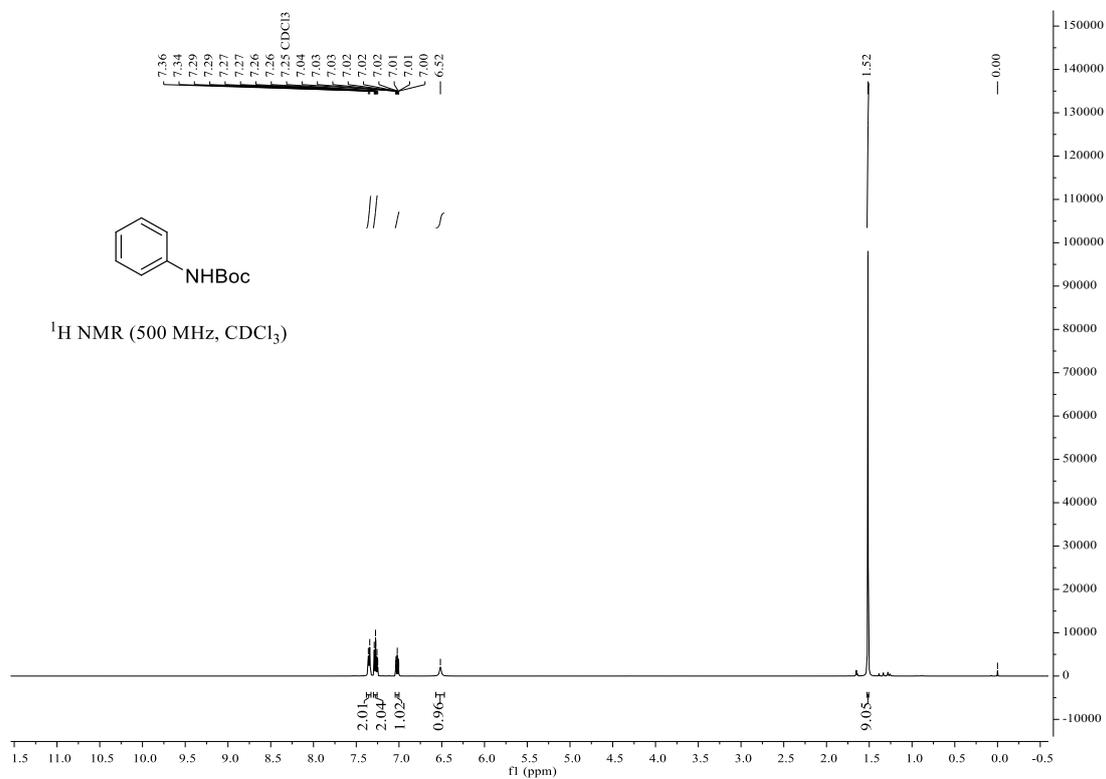


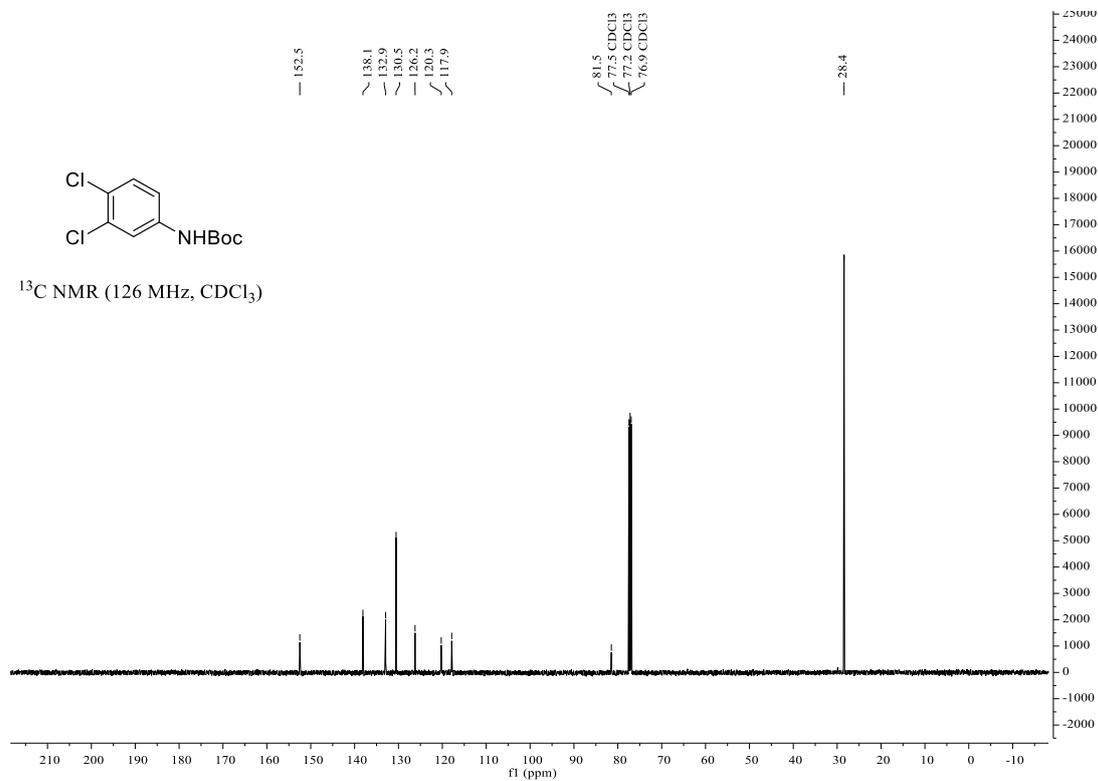
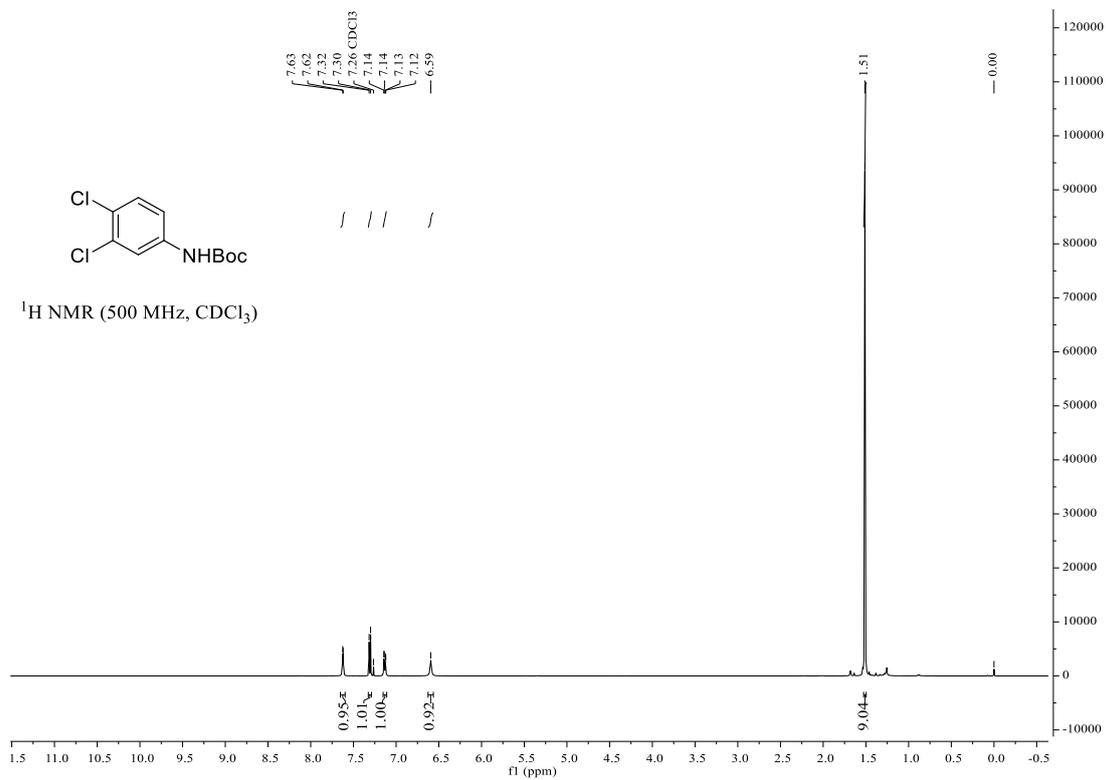
Figure S2. Cyclic voltammogram of DDQ (3 mM).

5. NMR Spectra for Photoelectrolysis Products

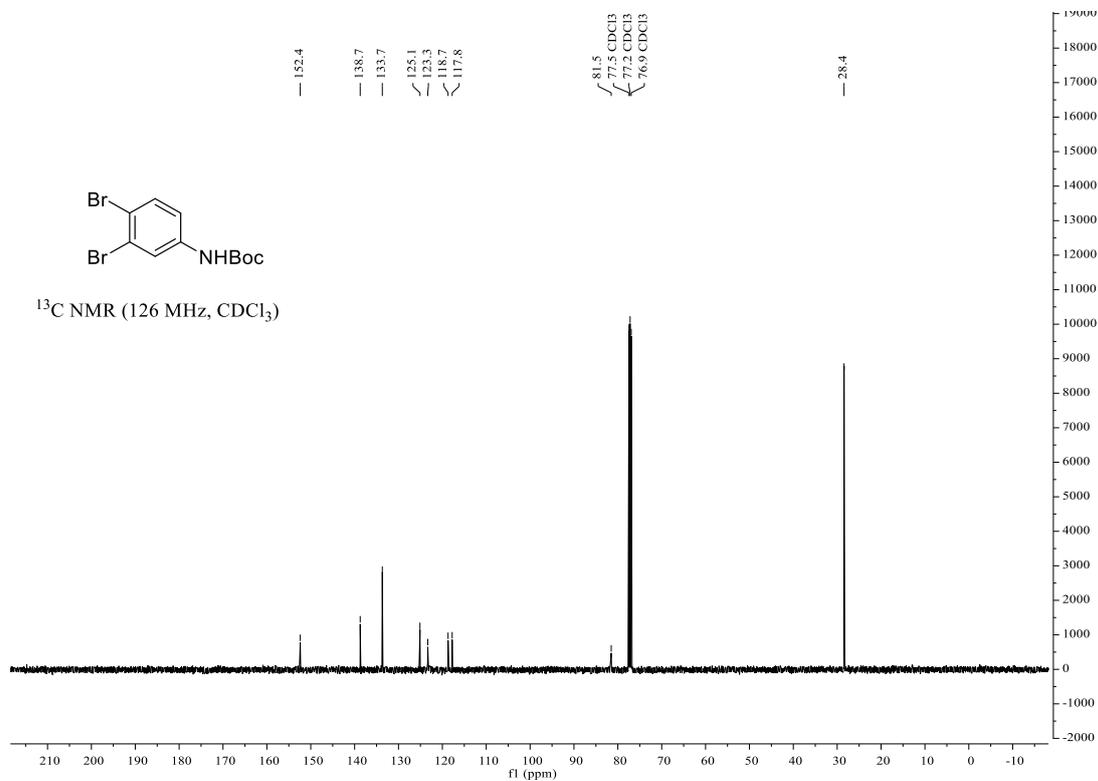
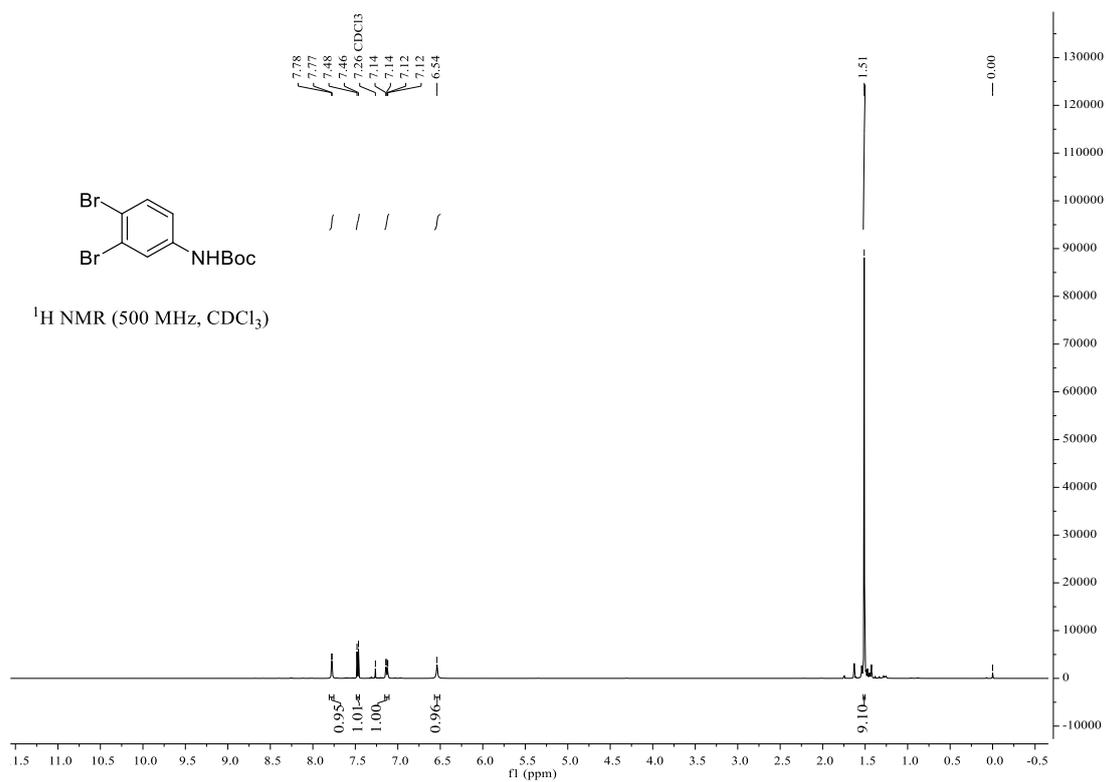
Compound 3



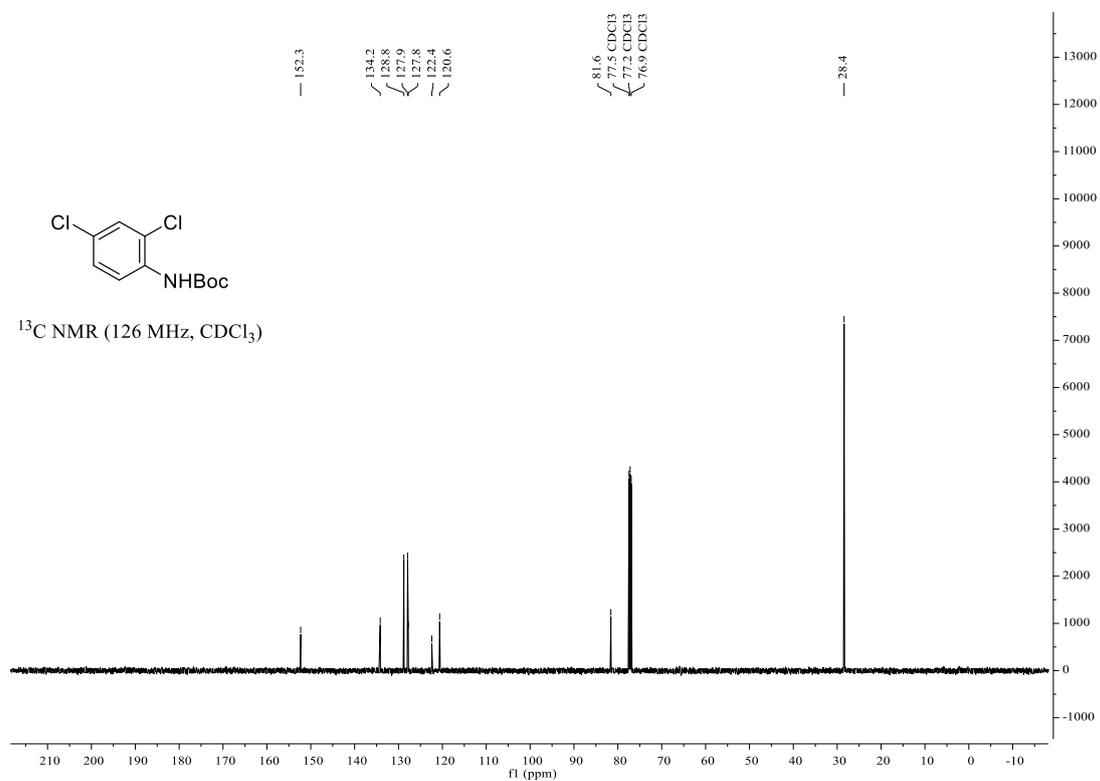
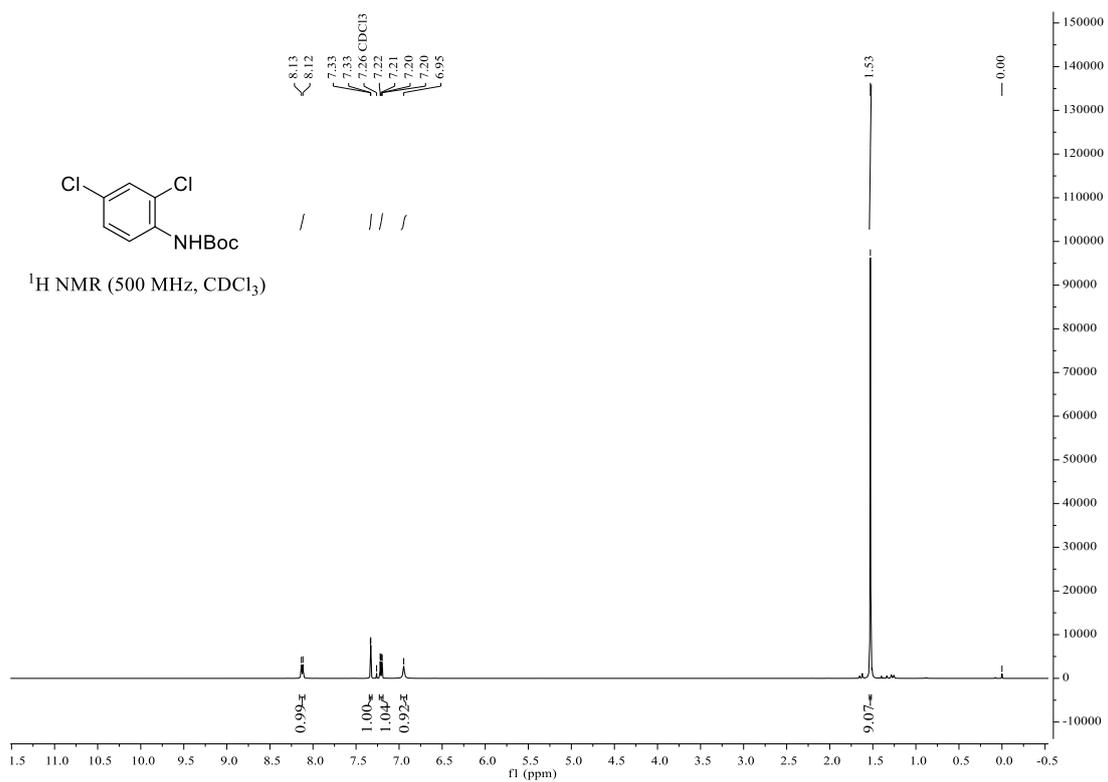
Compound 4



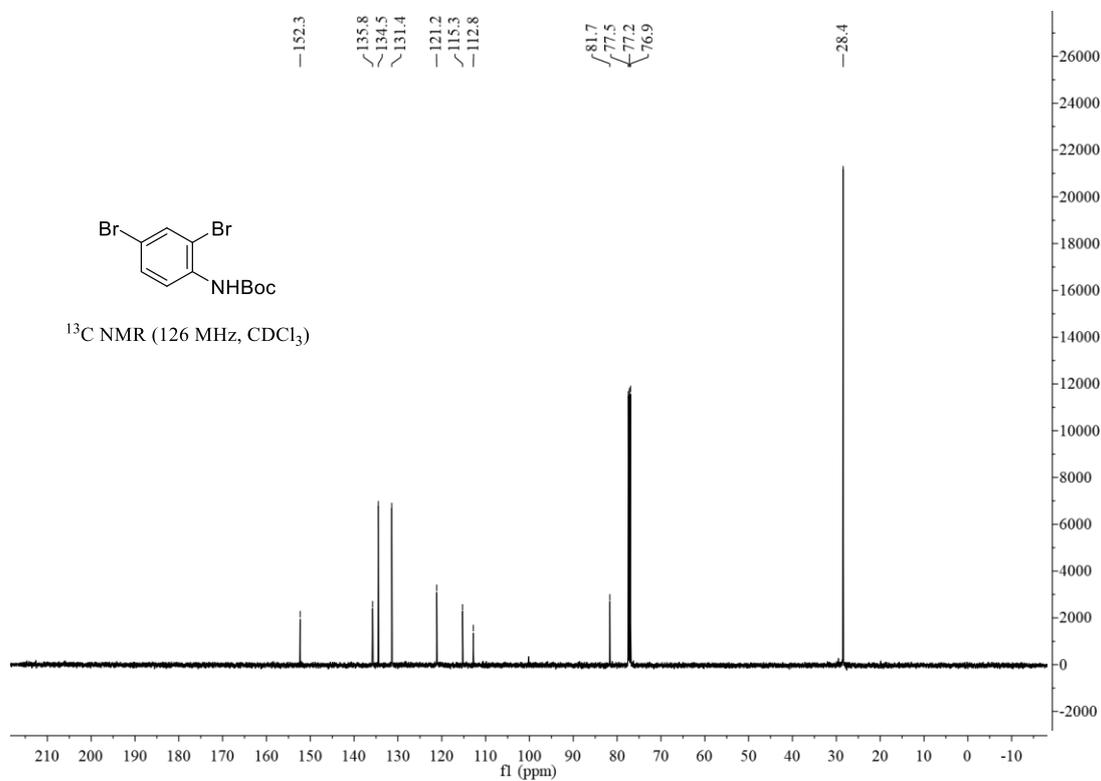
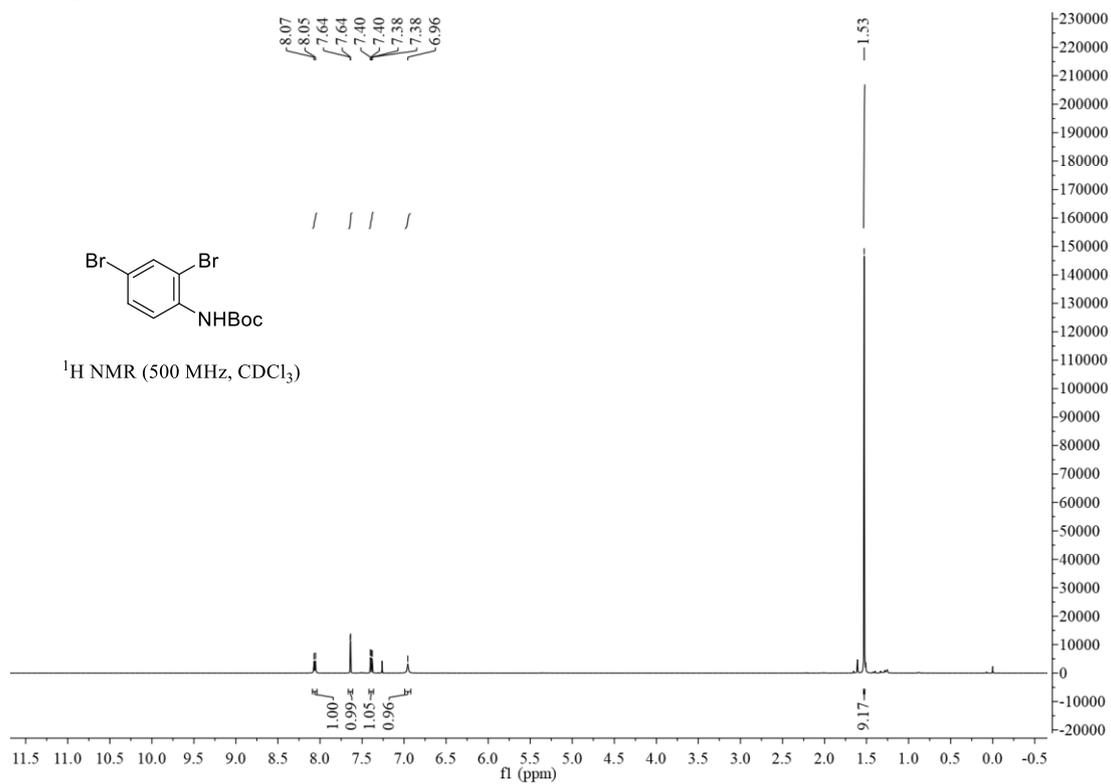
Compound 5



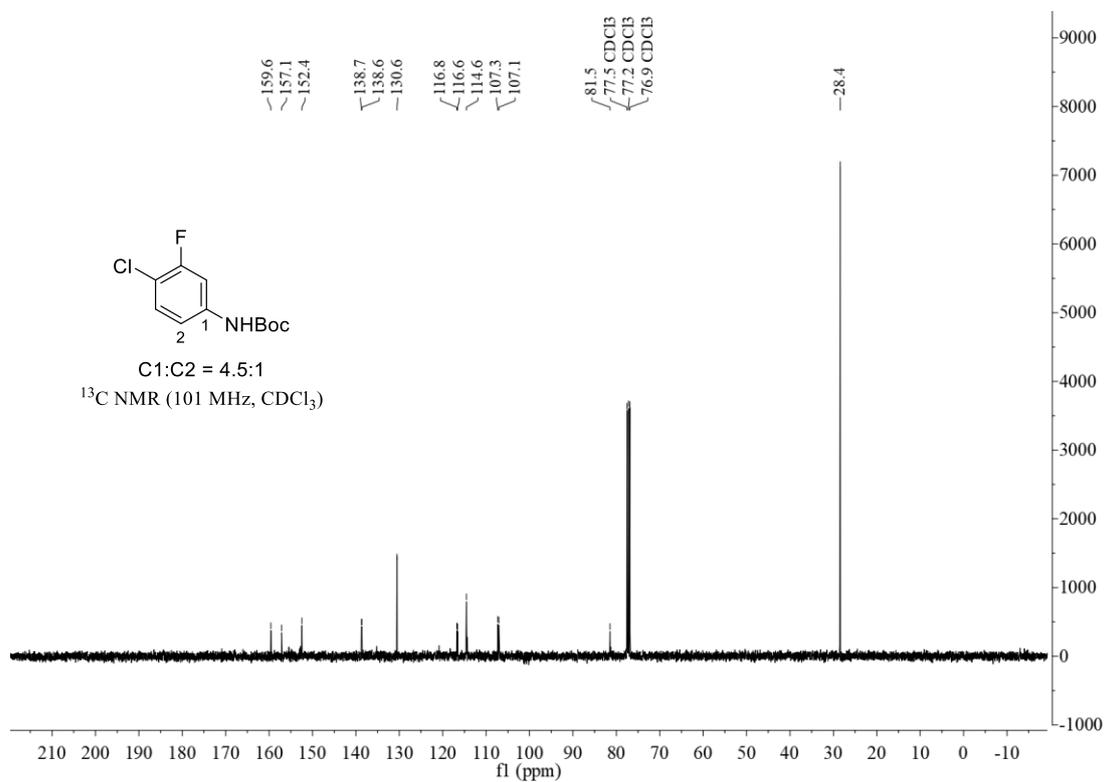
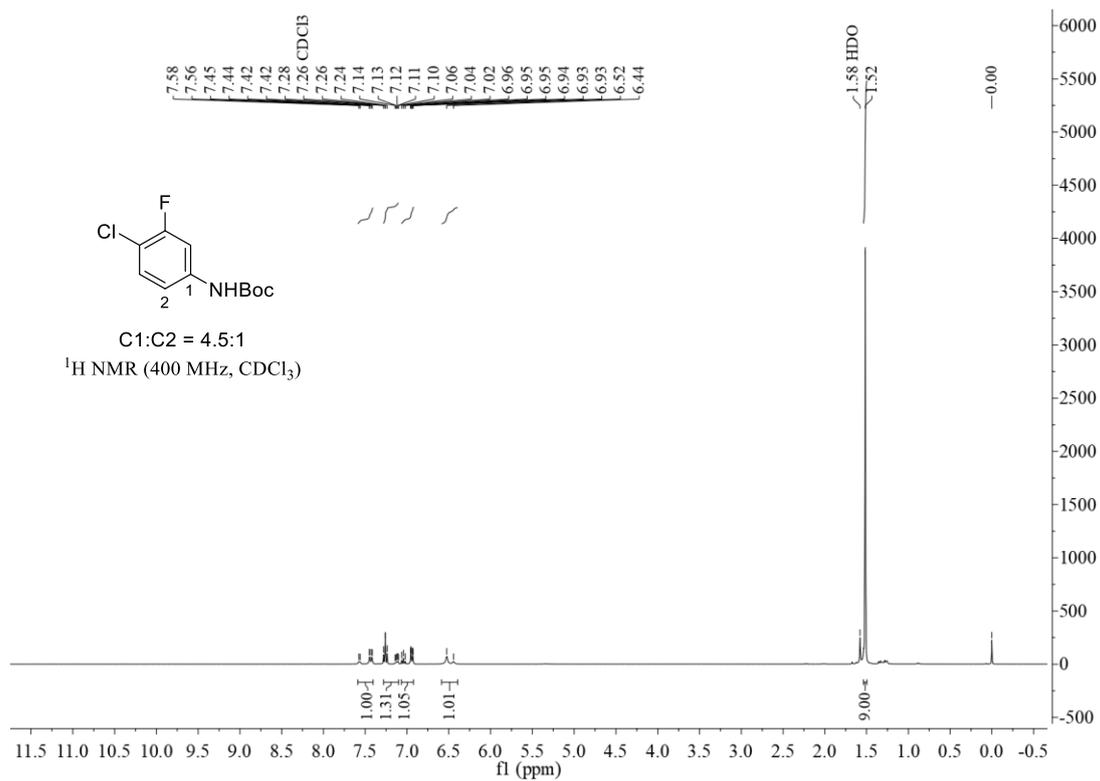
Compound 6

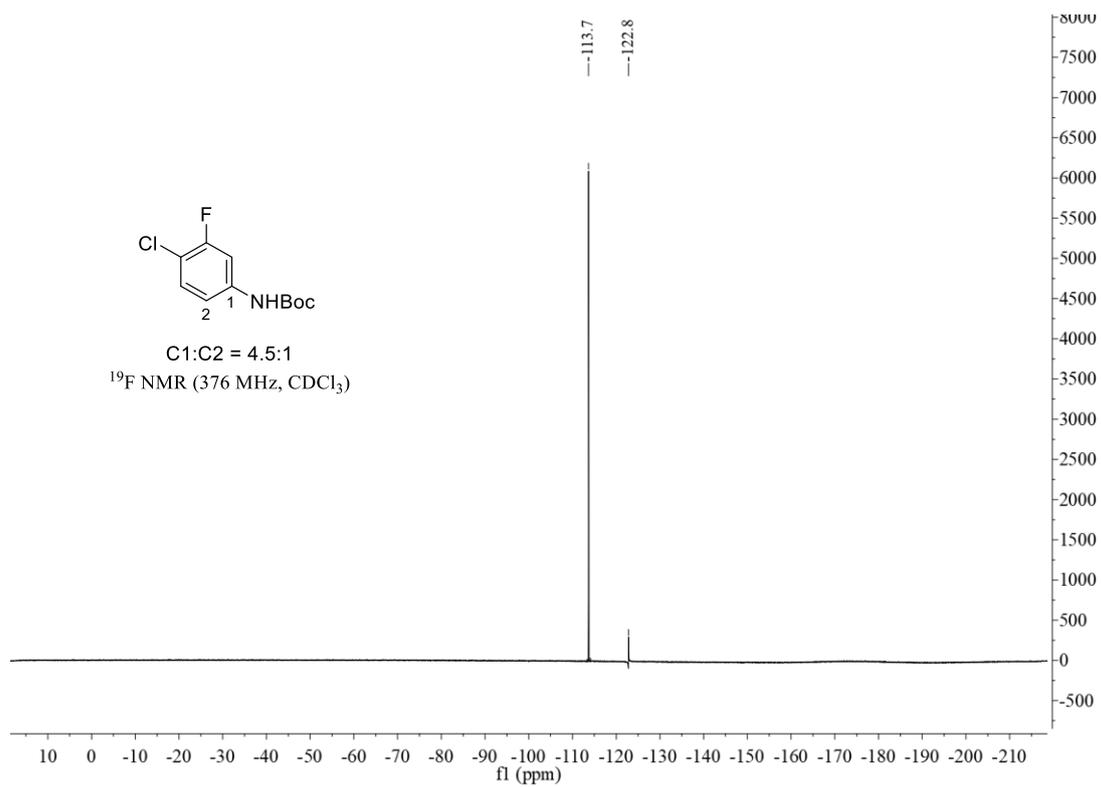


Compound 7

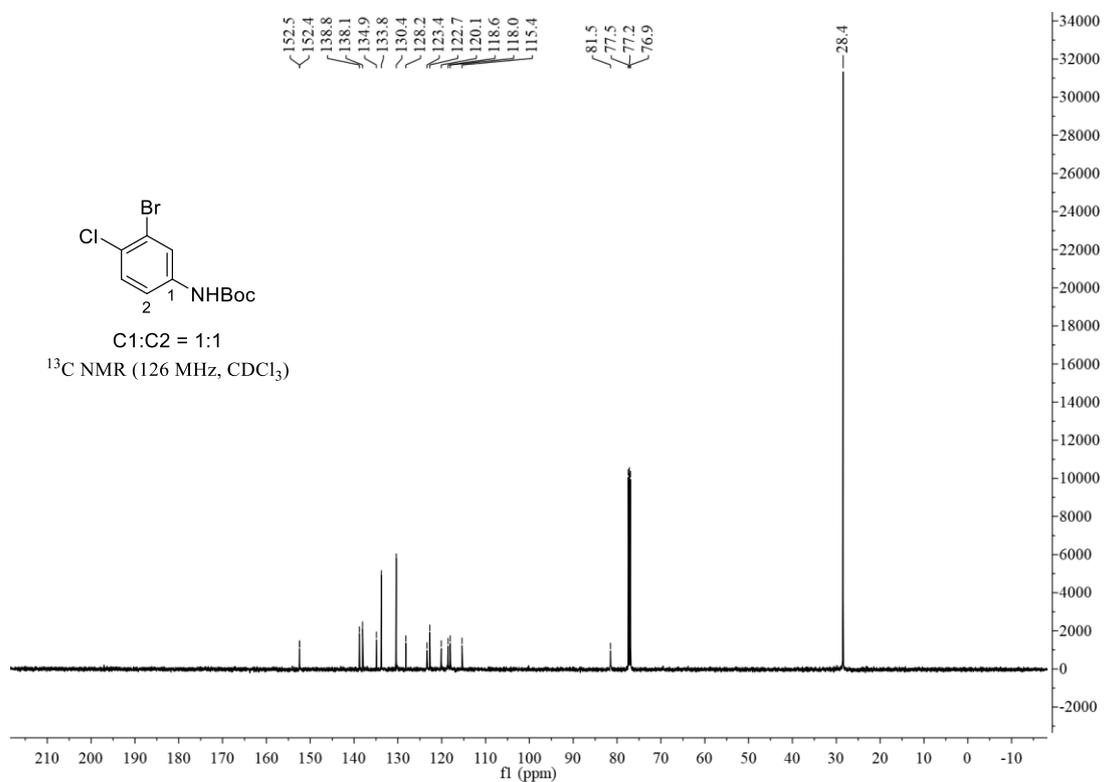
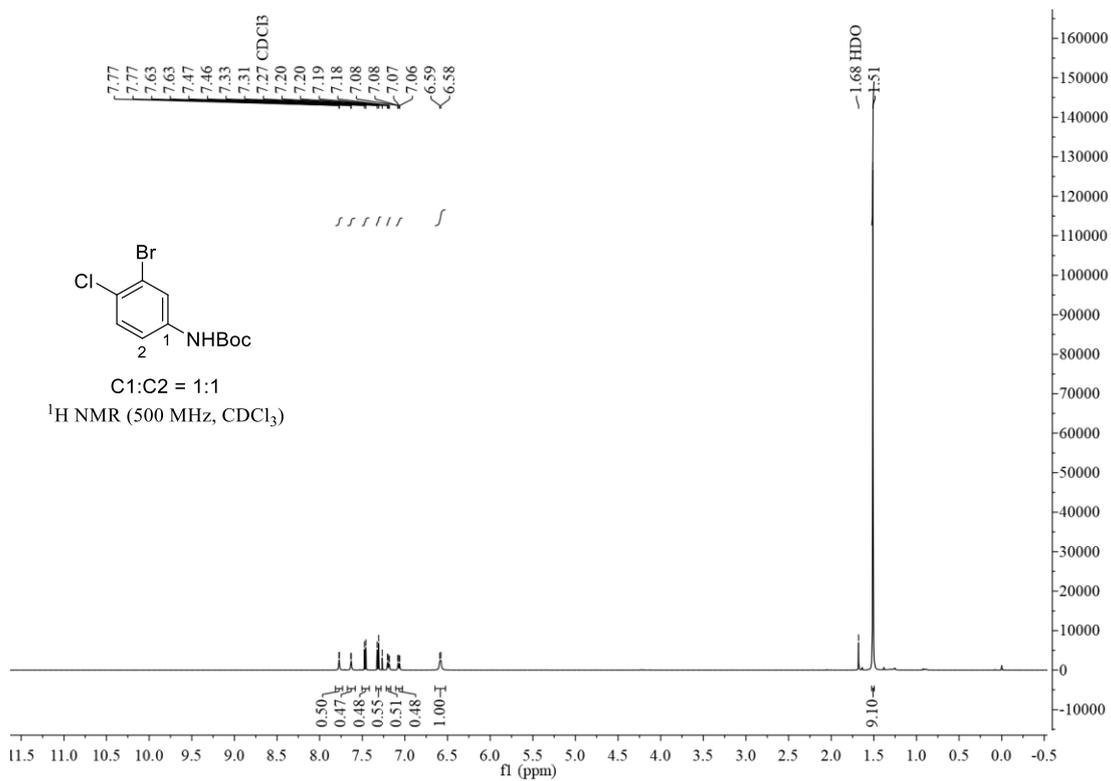


Compound 8

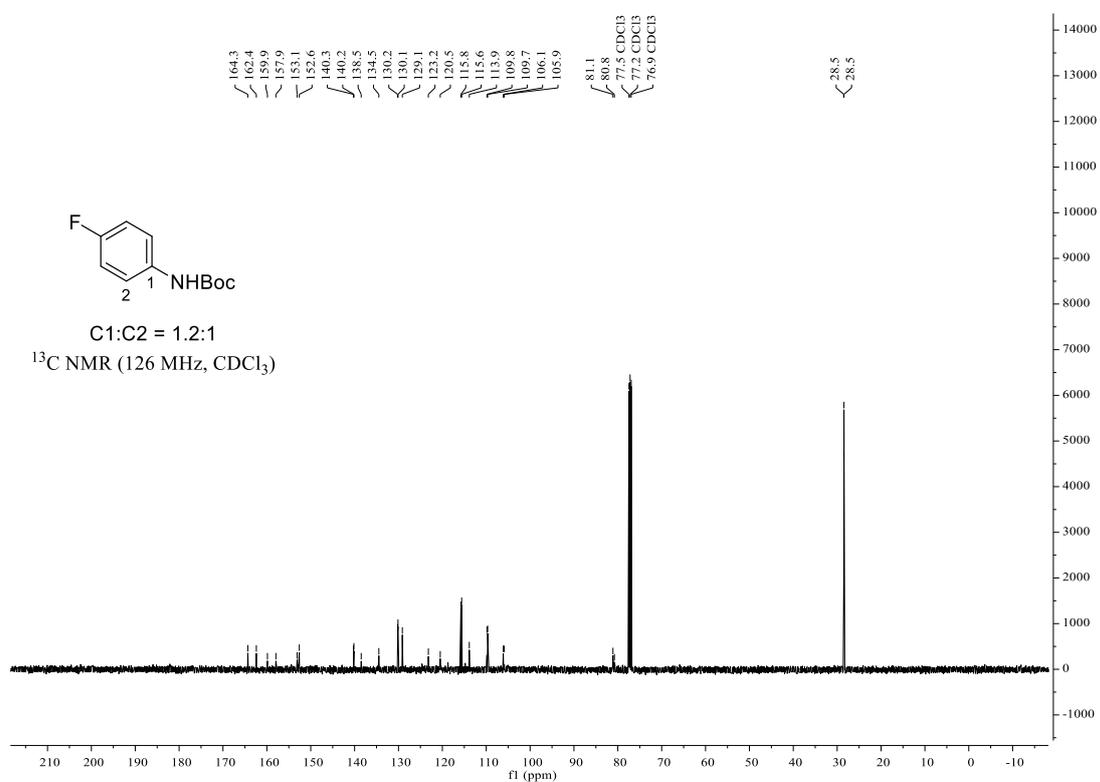
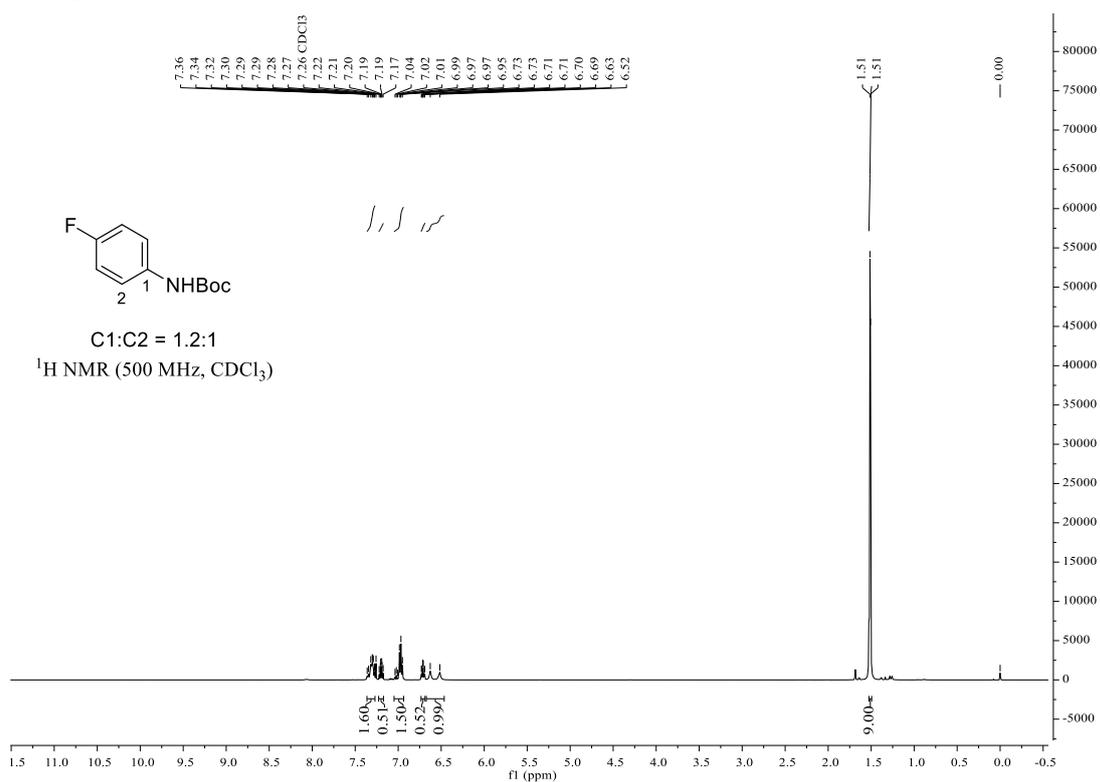


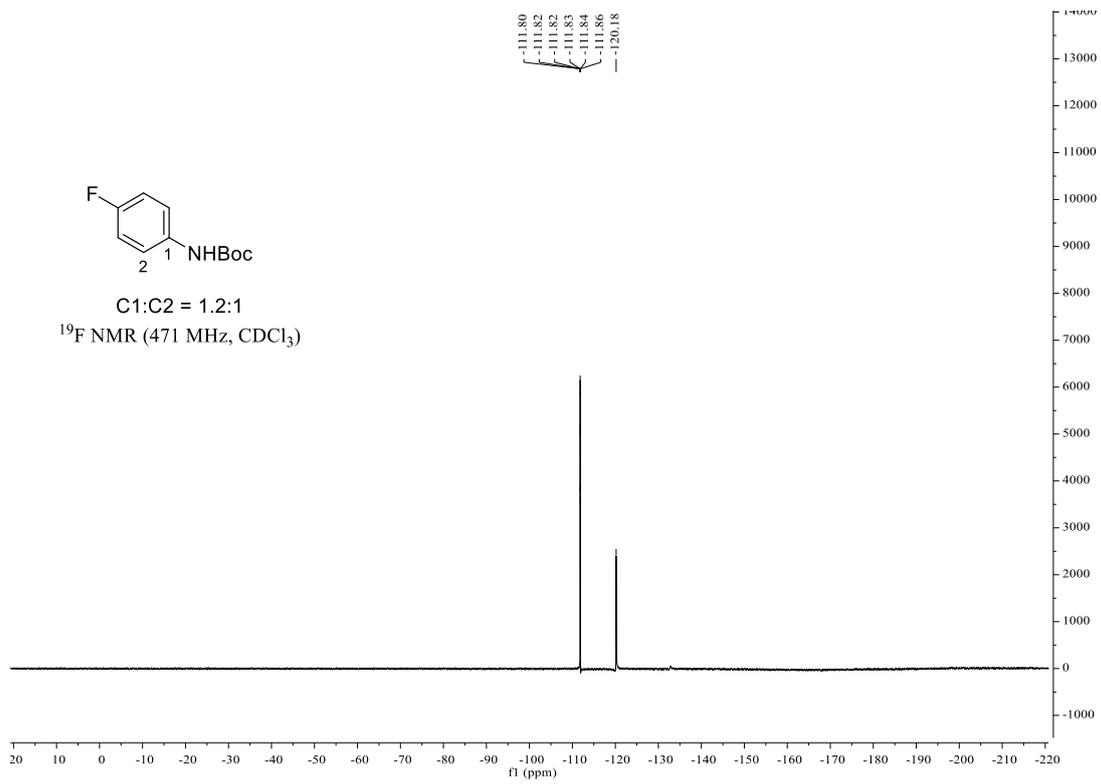


Compound 9

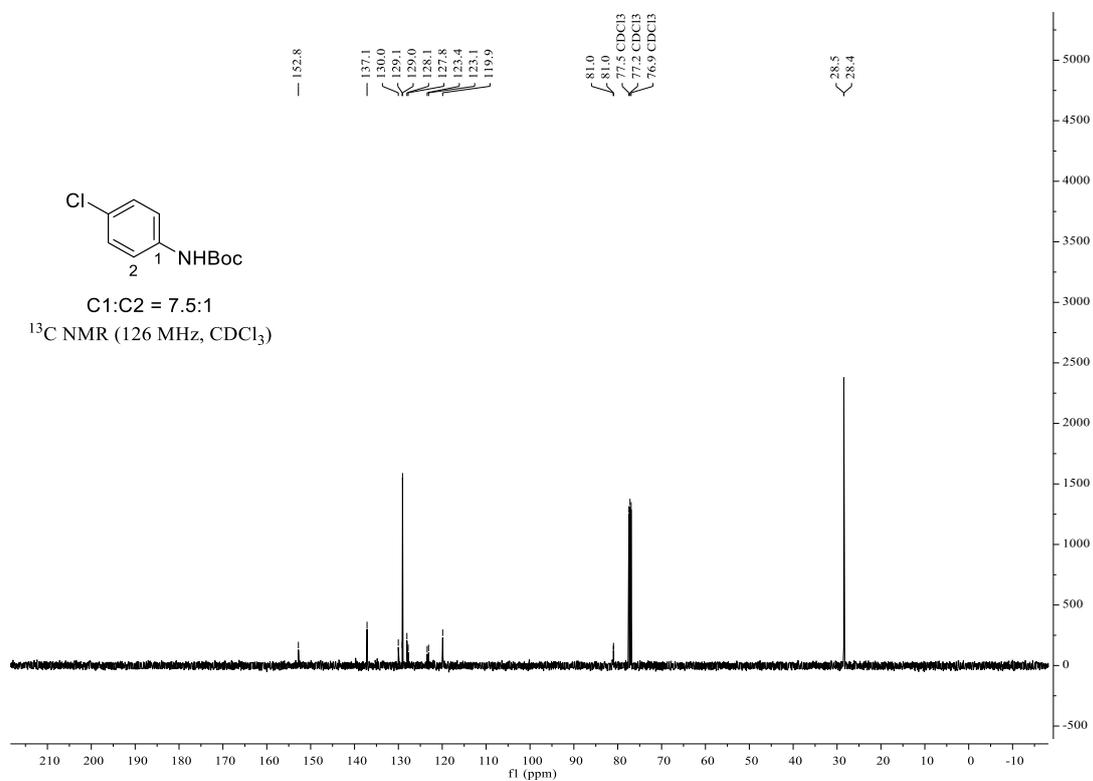
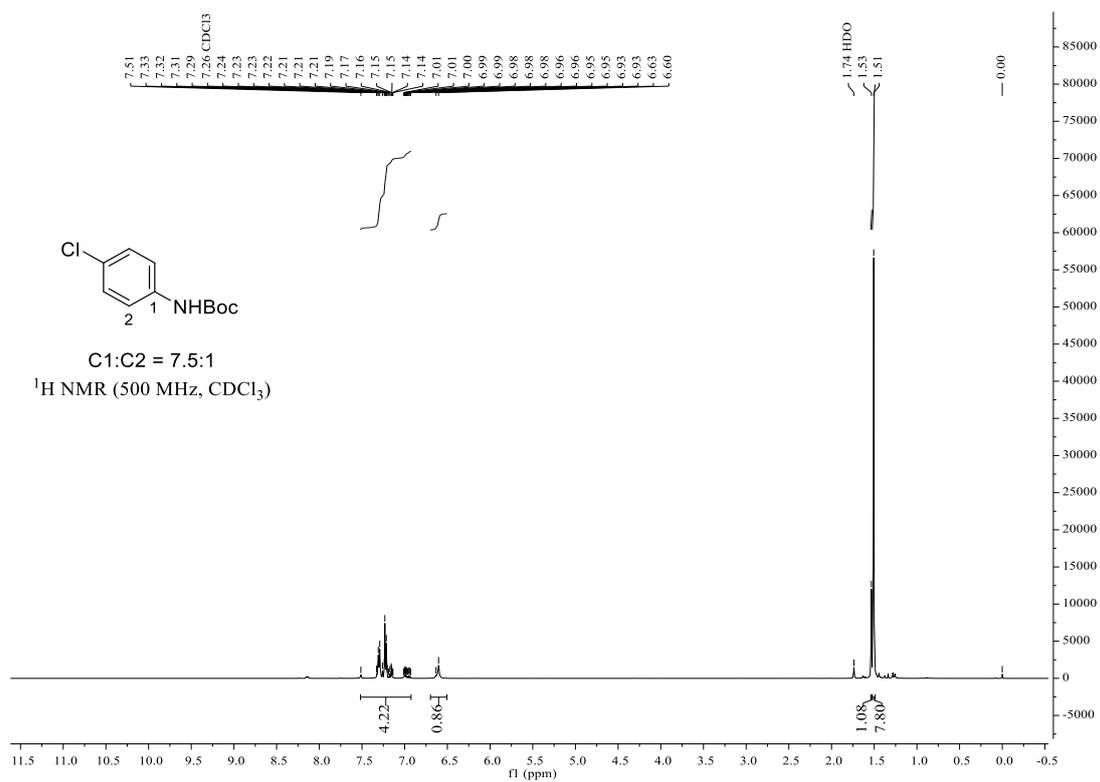


Compound 10

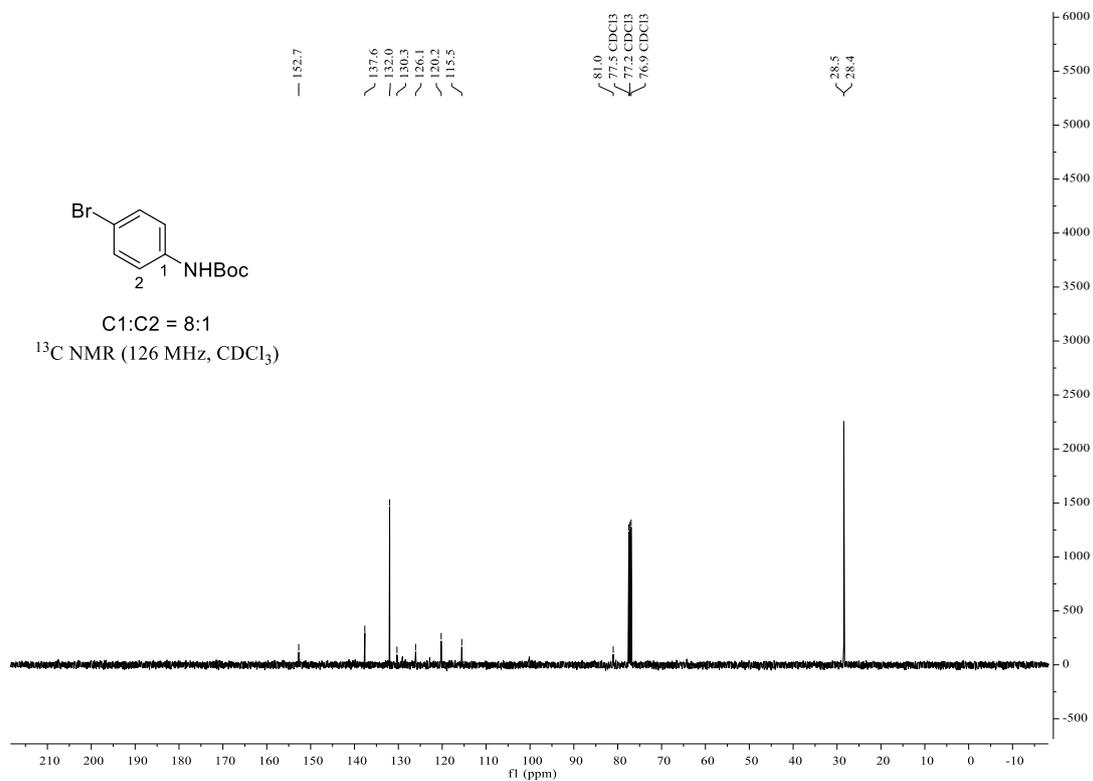
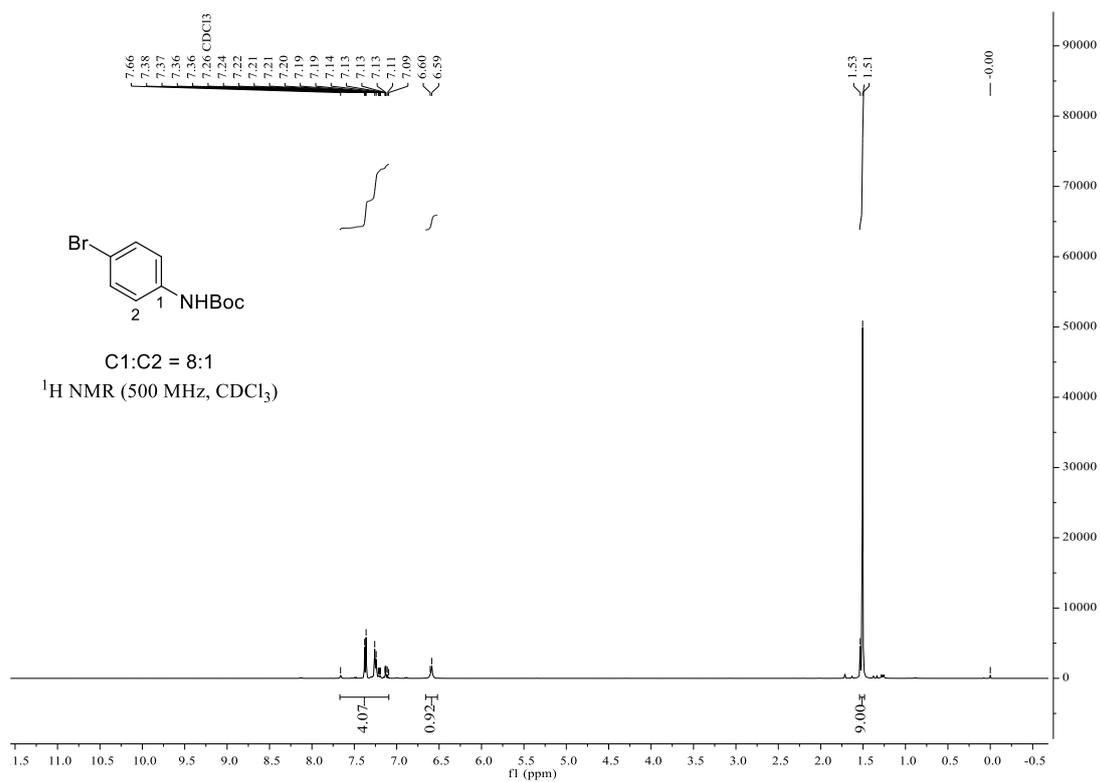




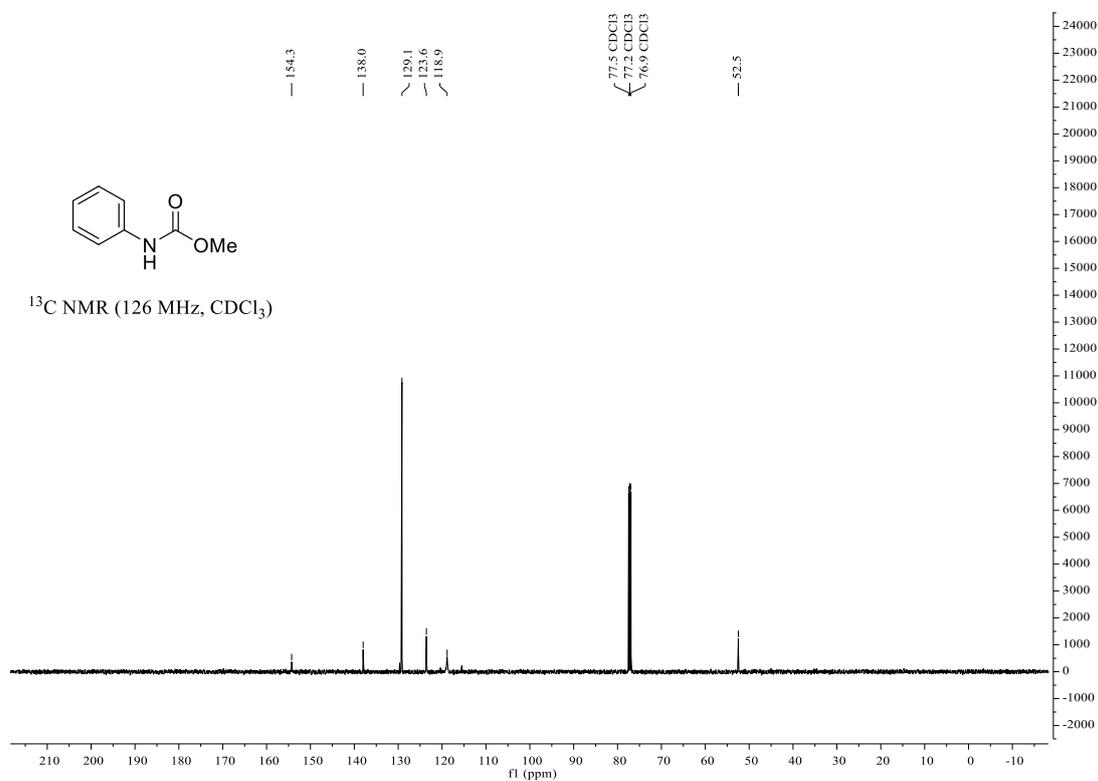
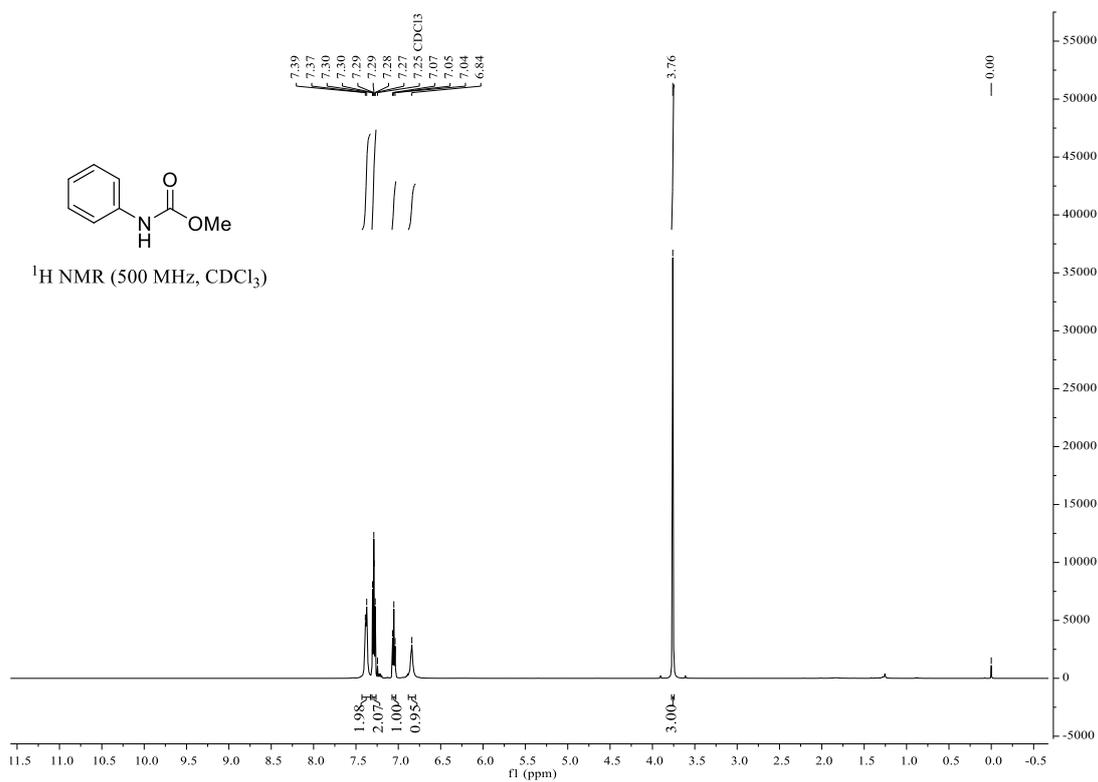
Compound 11



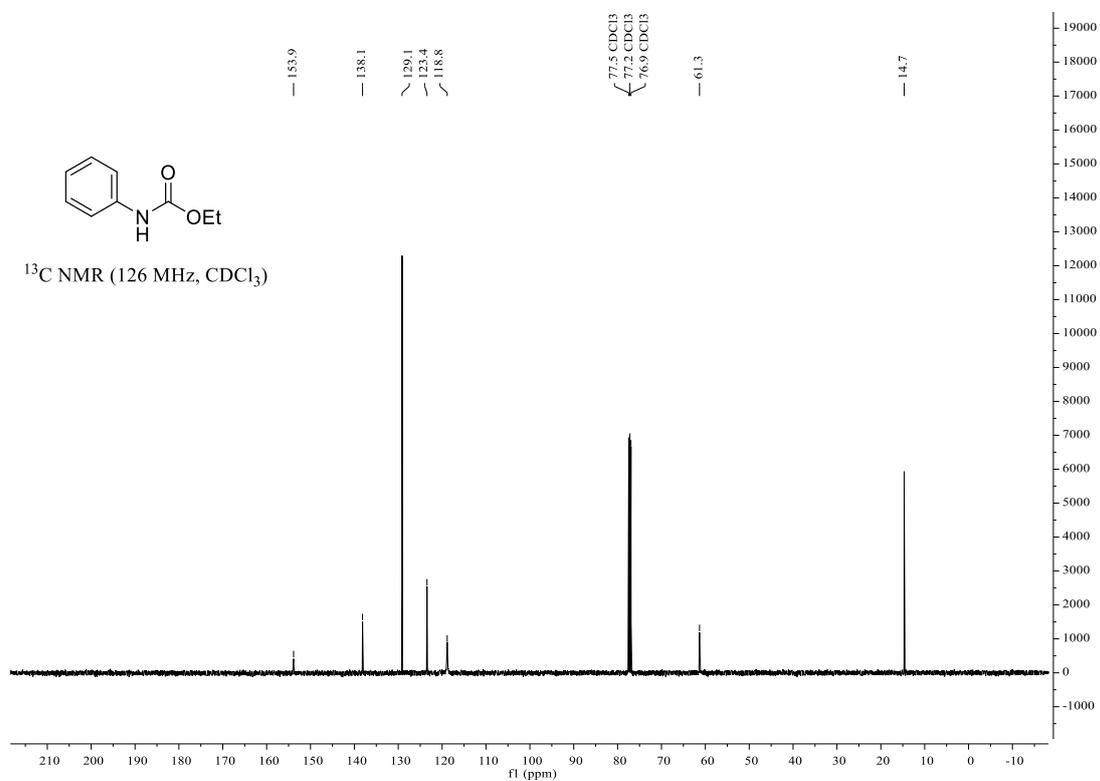
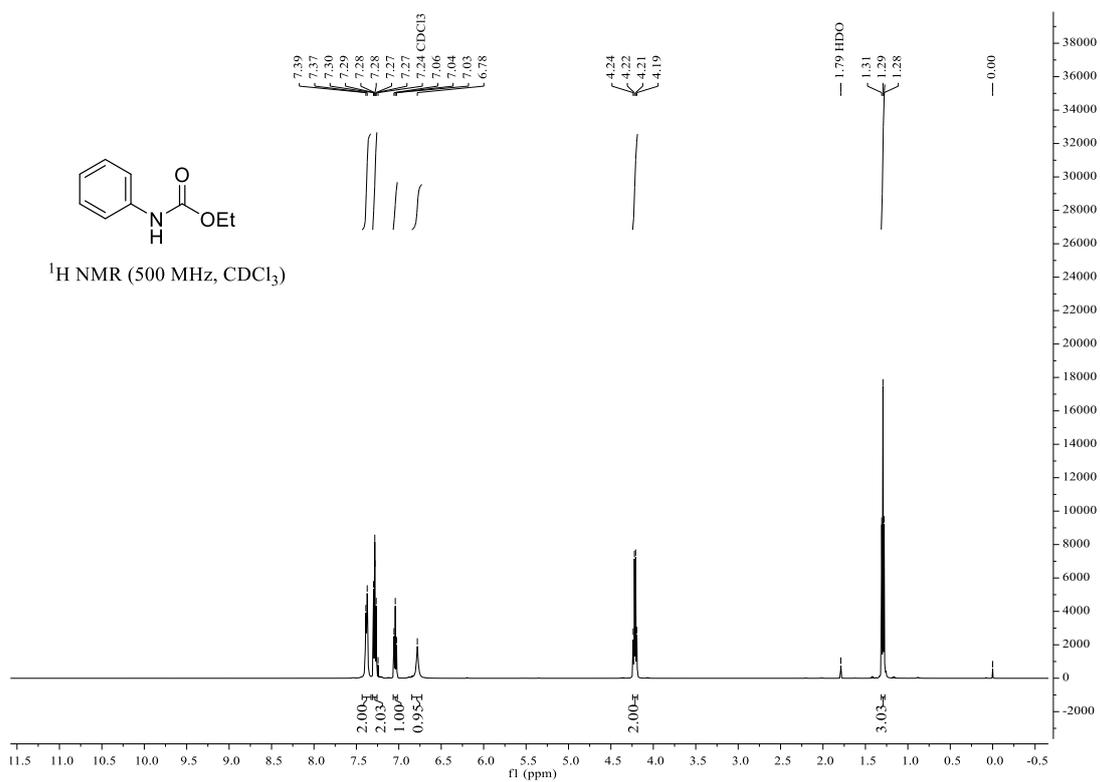
Compound 12



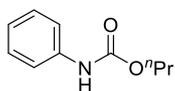
Compound 15



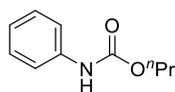
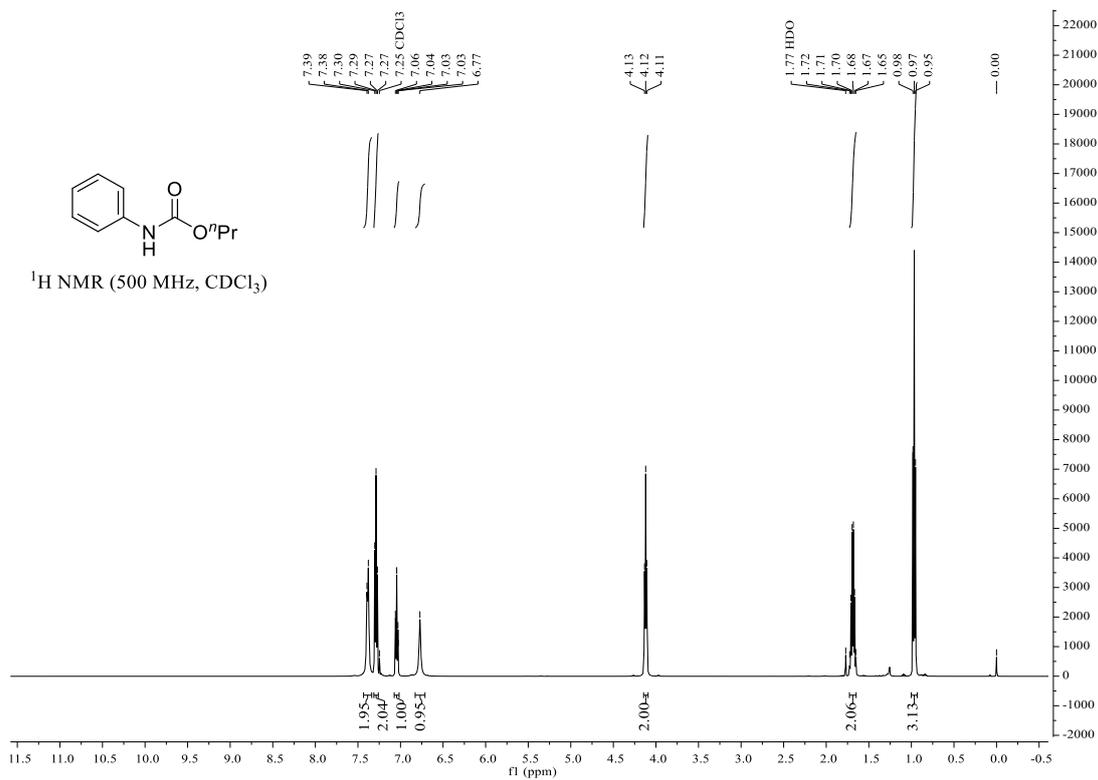
Compound 16



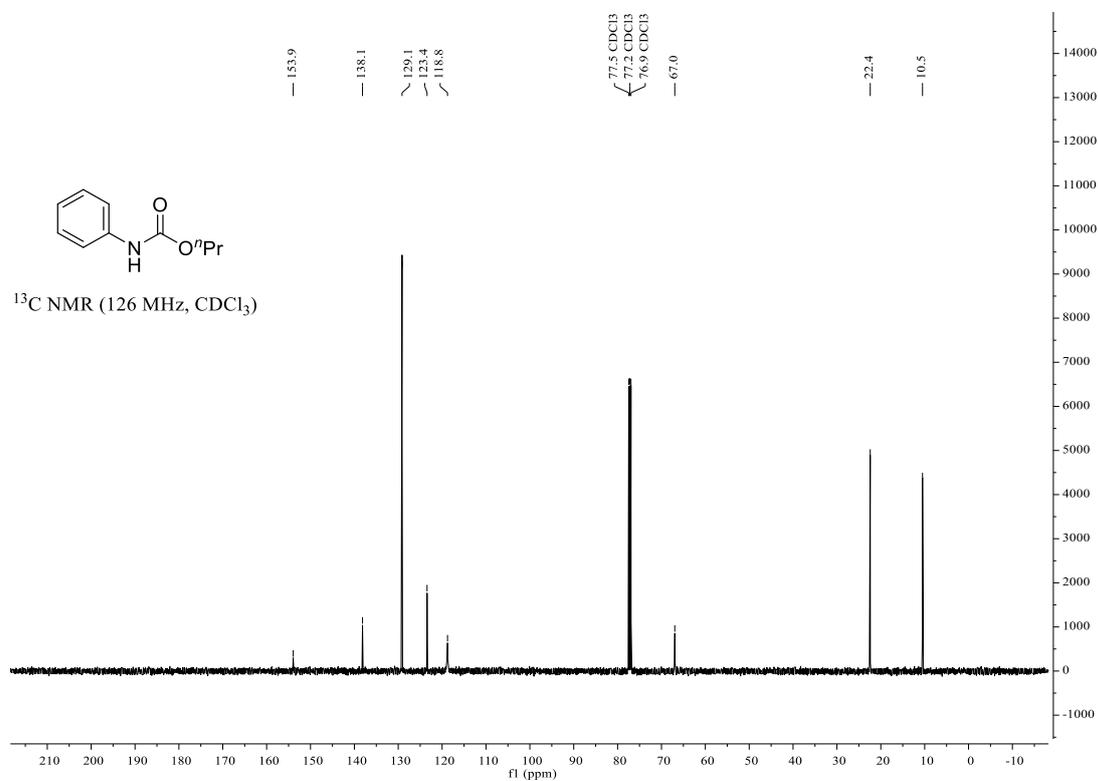
Compound 17



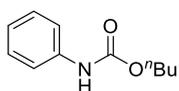
$^1\text{H NMR}$ (500 MHz, CDCl_3)



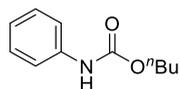
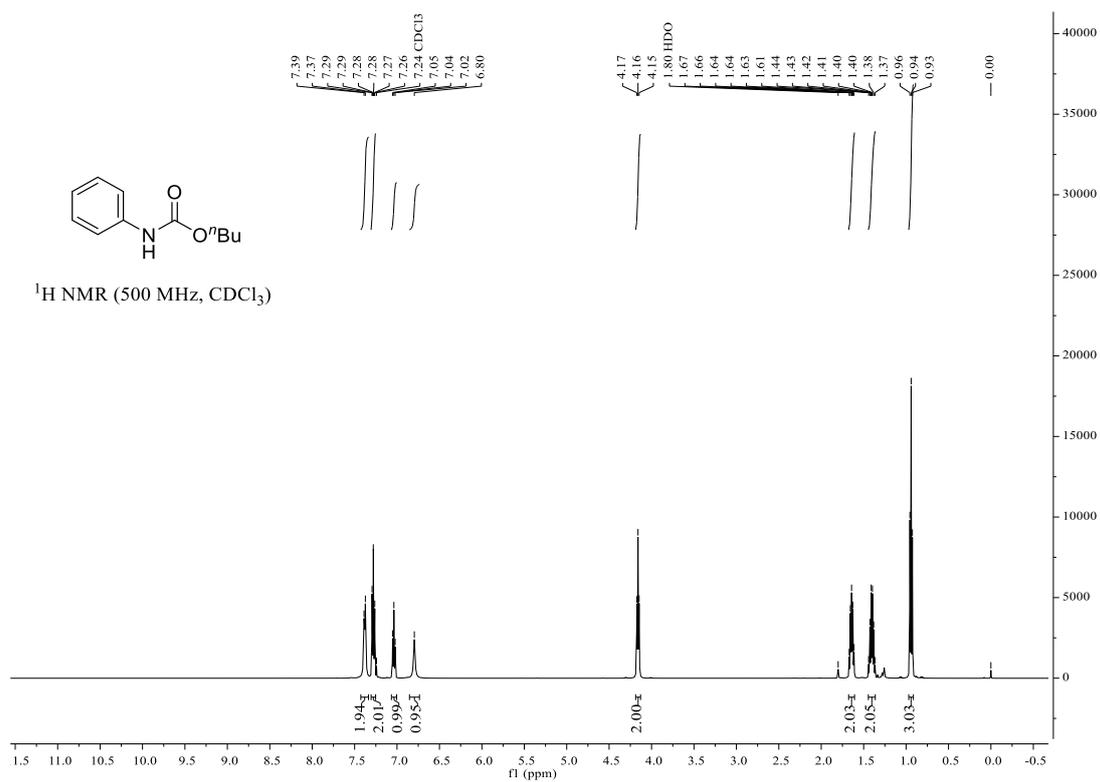
$^{13}\text{C NMR}$ (126 MHz, CDCl_3)



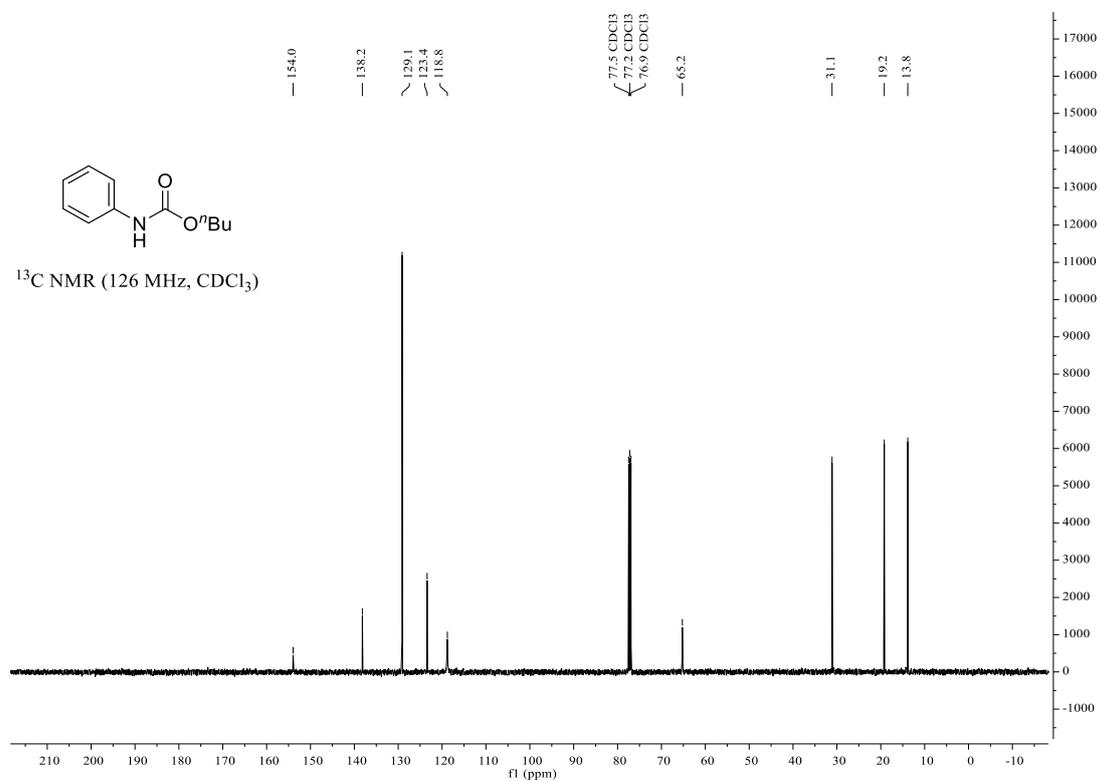
Compound 18



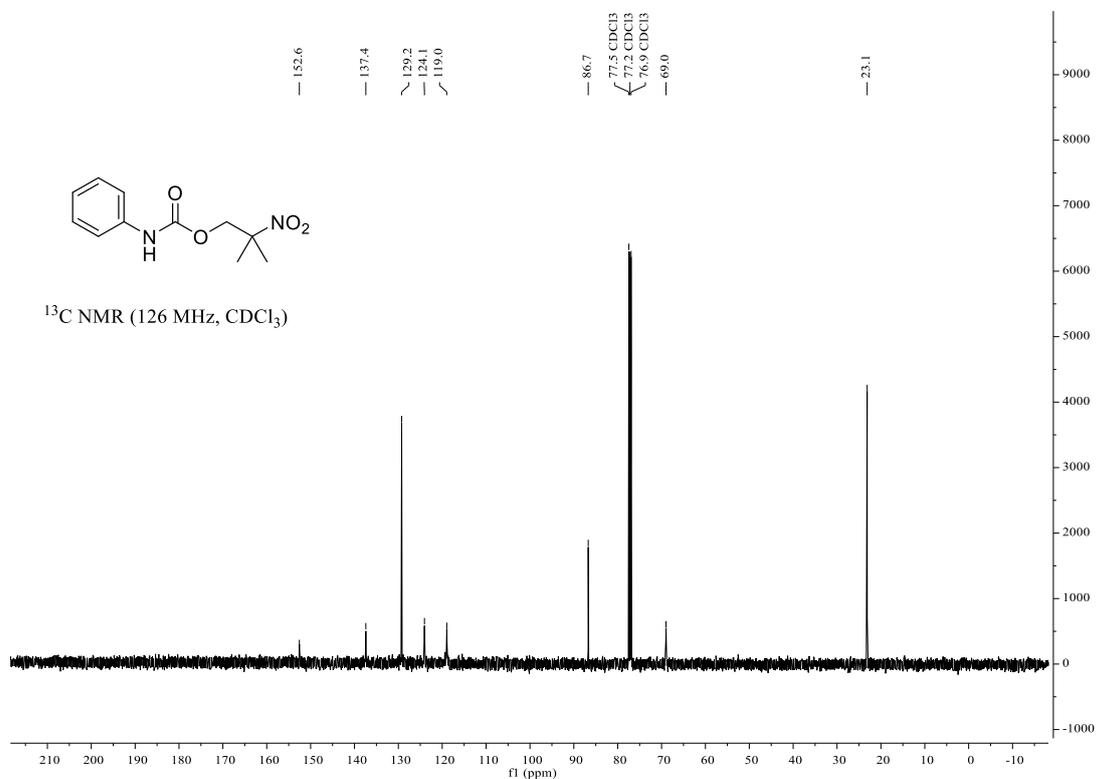
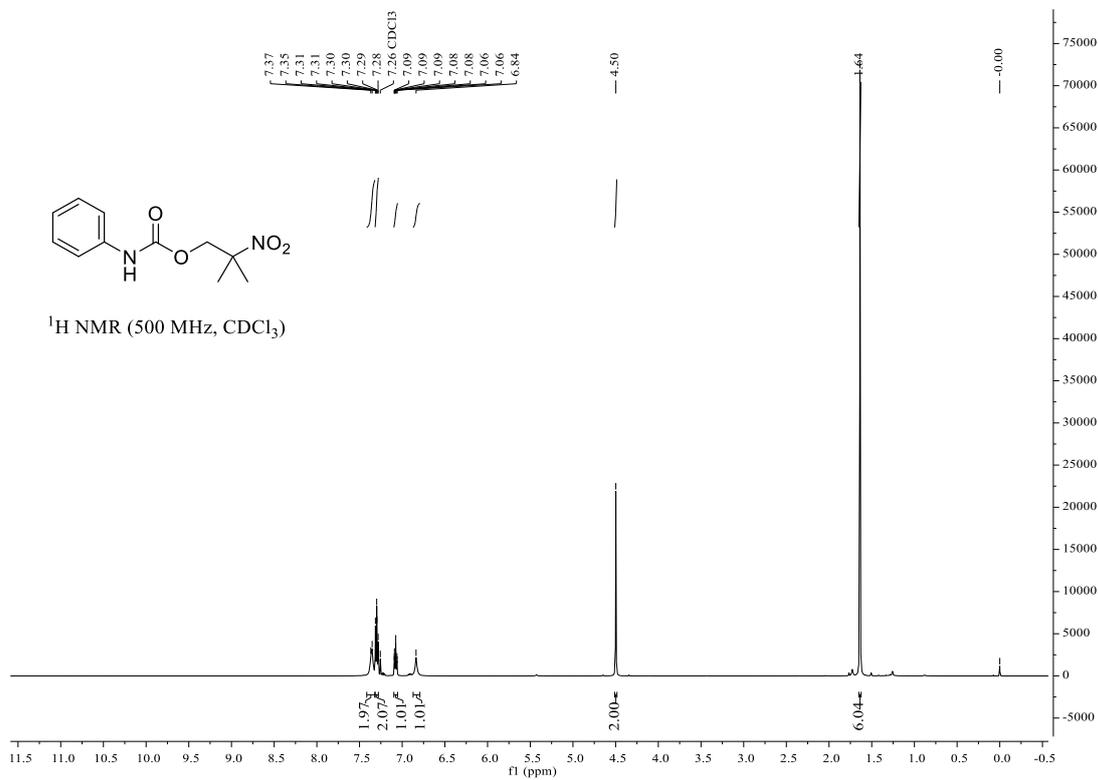
$^1\text{H NMR}$ (500 MHz, CDCl_3)



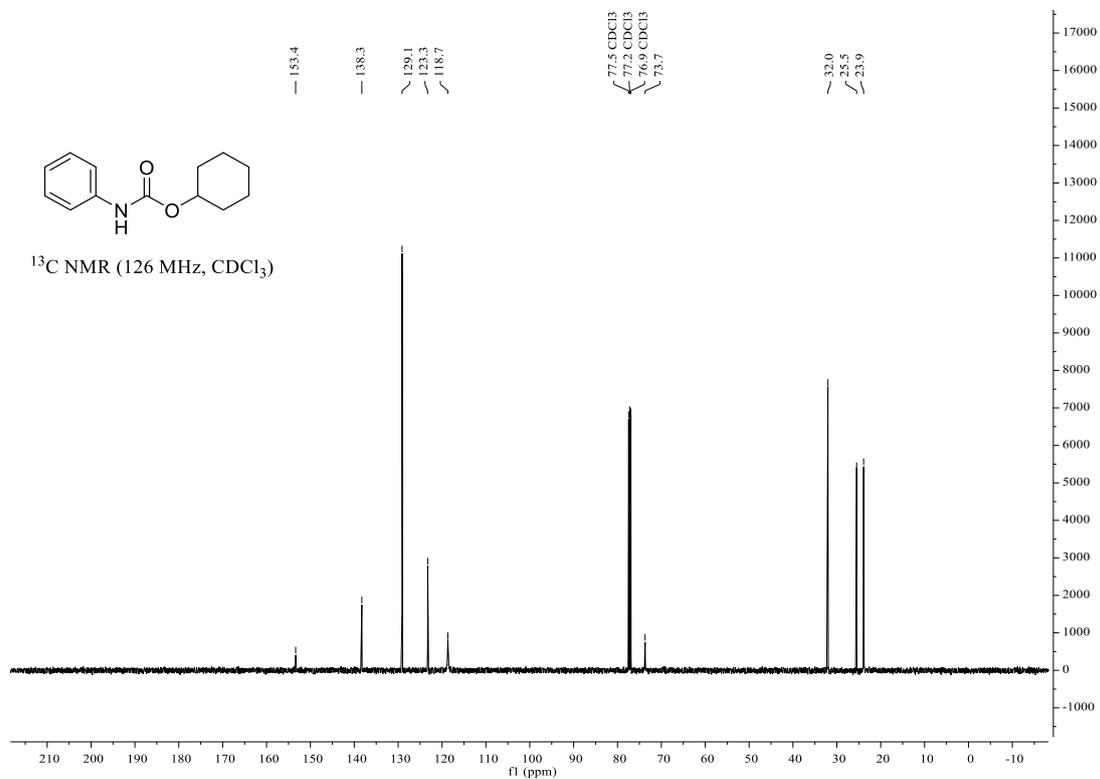
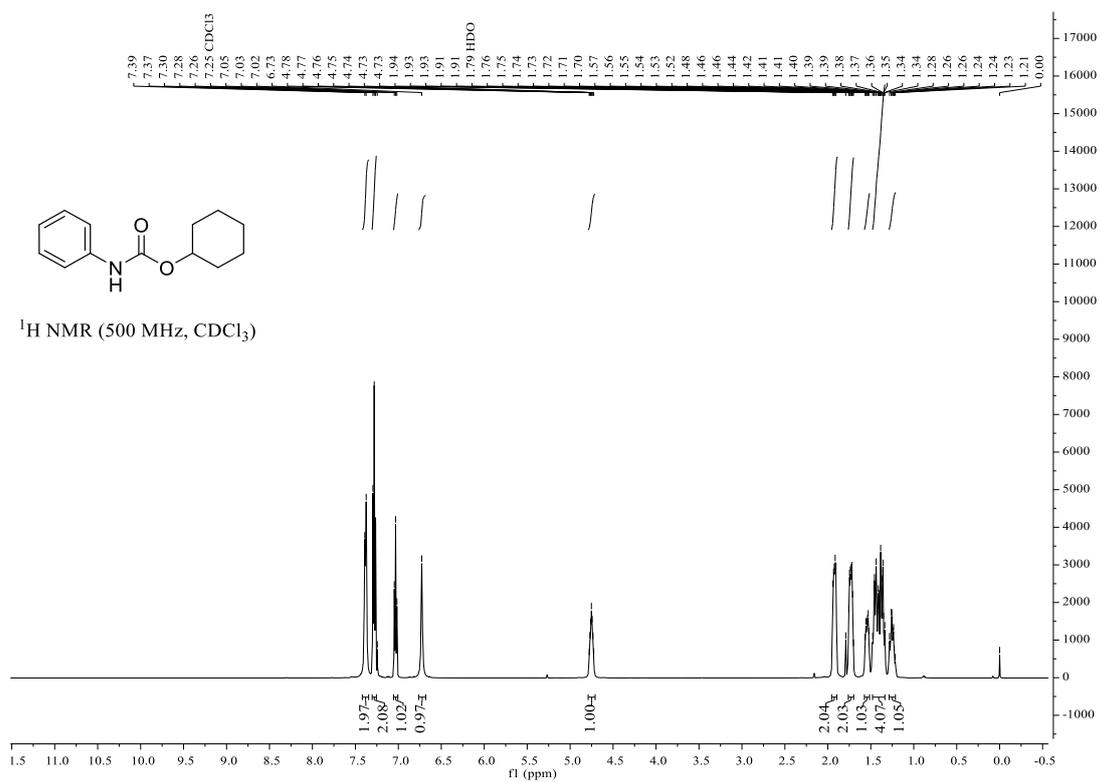
$^{13}\text{C NMR}$ (126 MHz, CDCl_3)



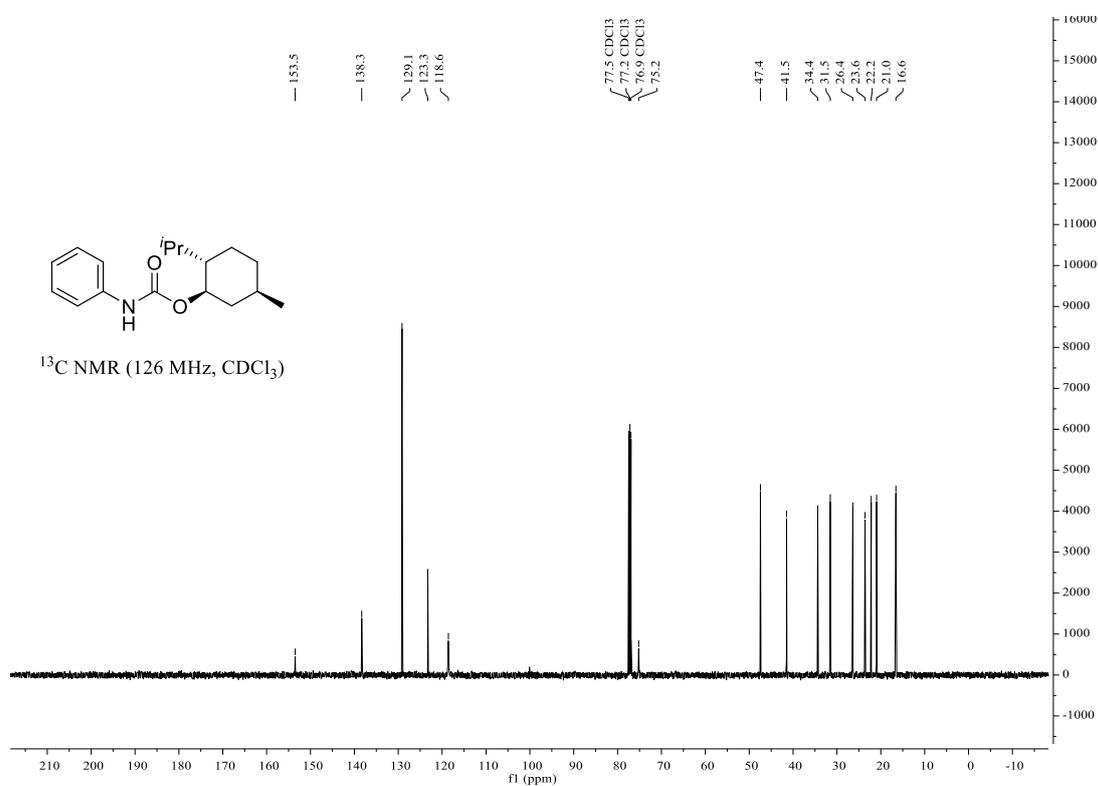
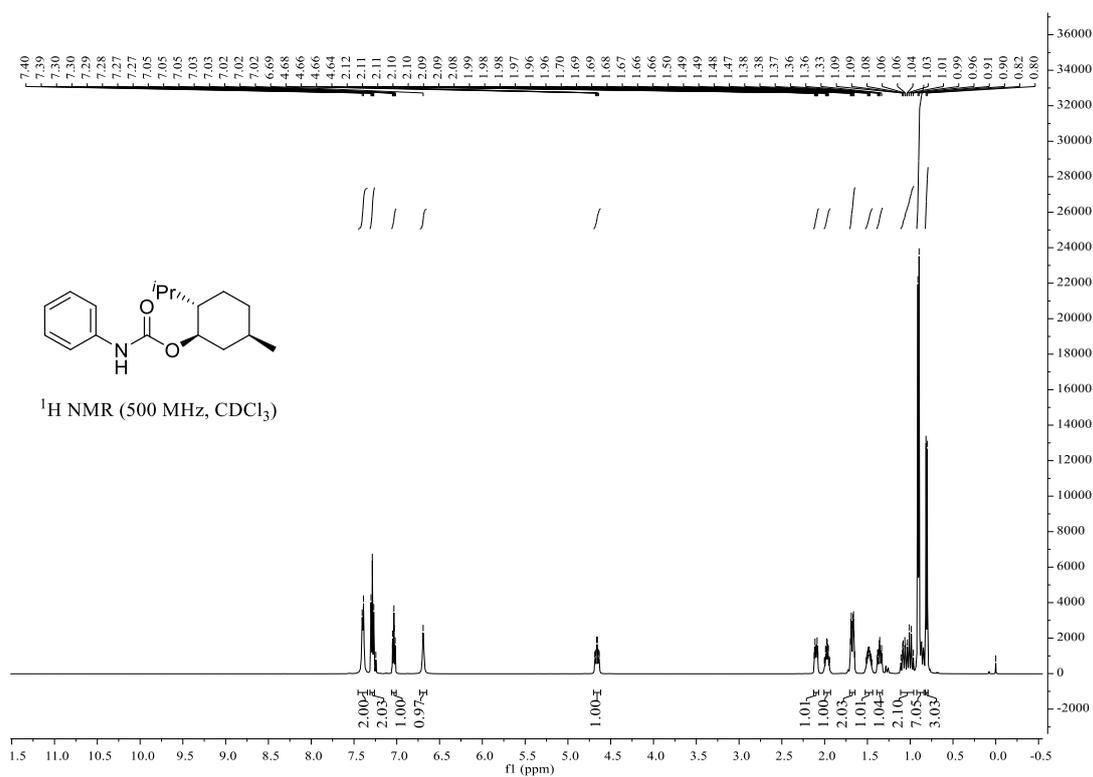
Compound 19



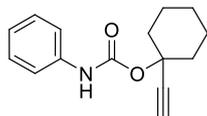
Compound 20



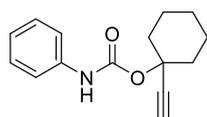
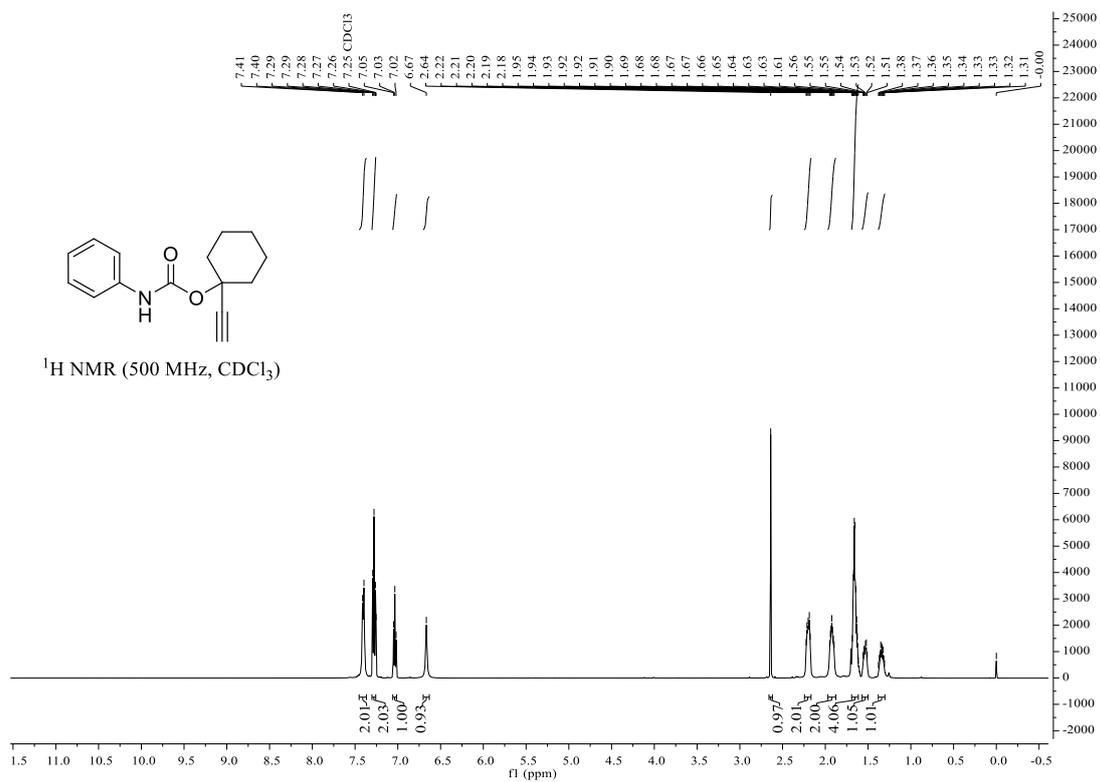
Compound 21



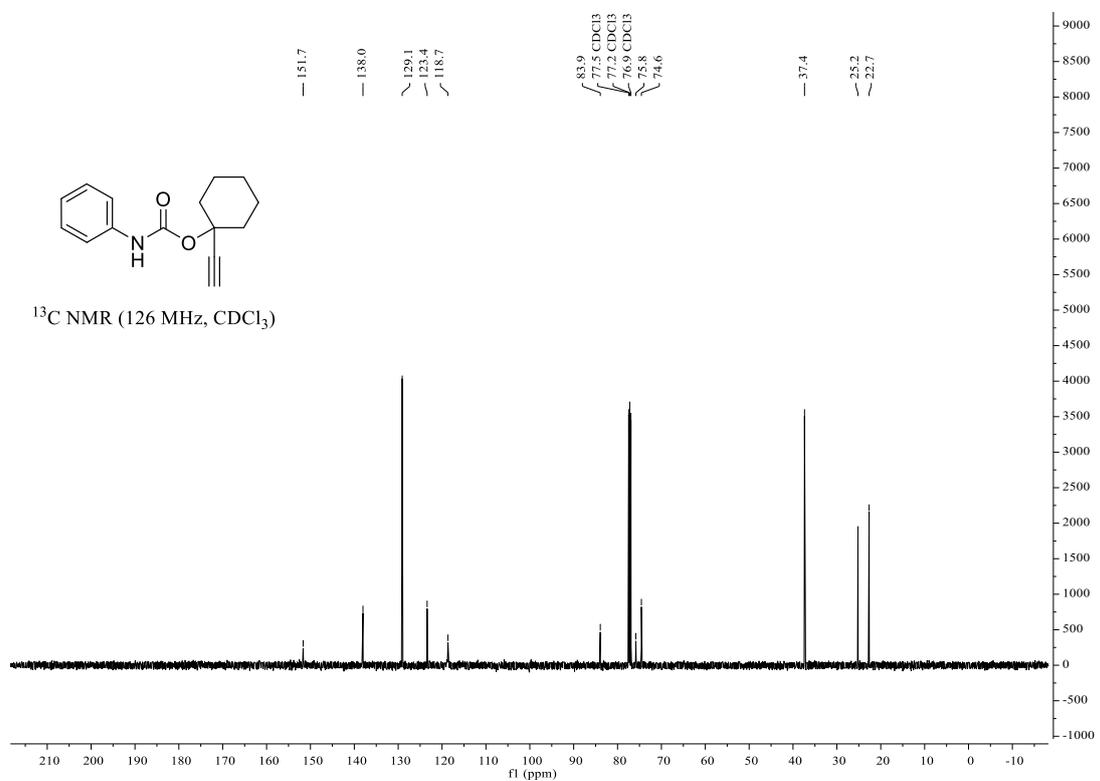
Compound 22



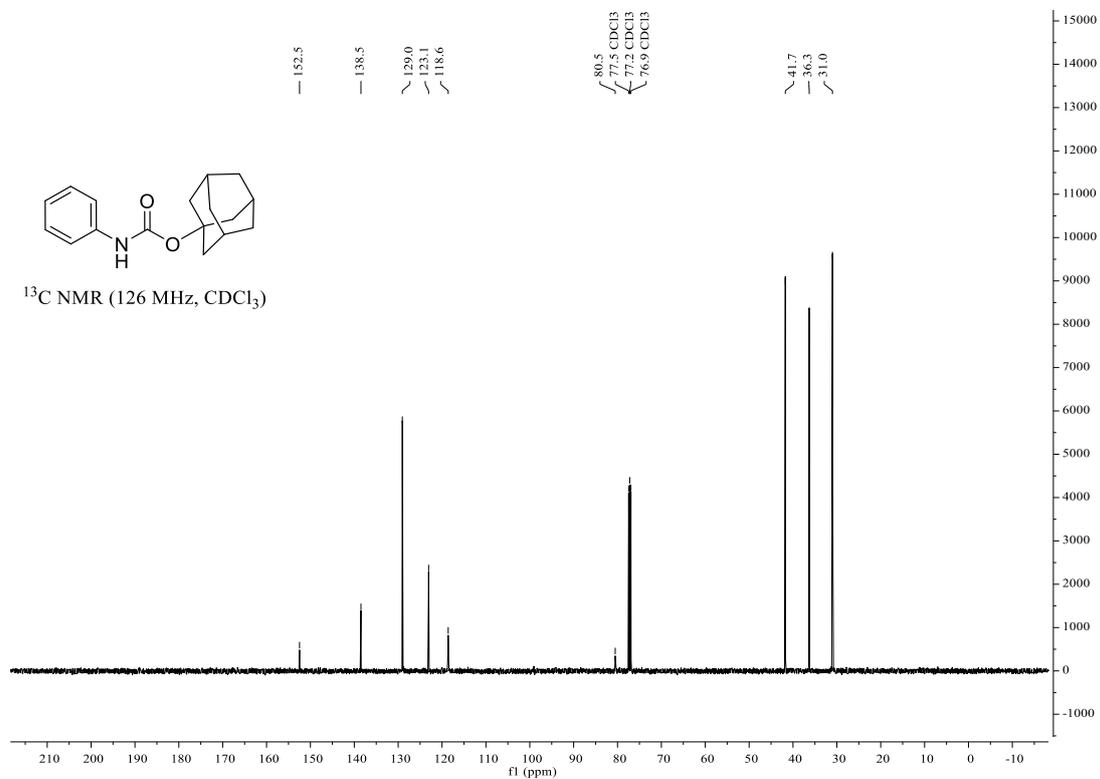
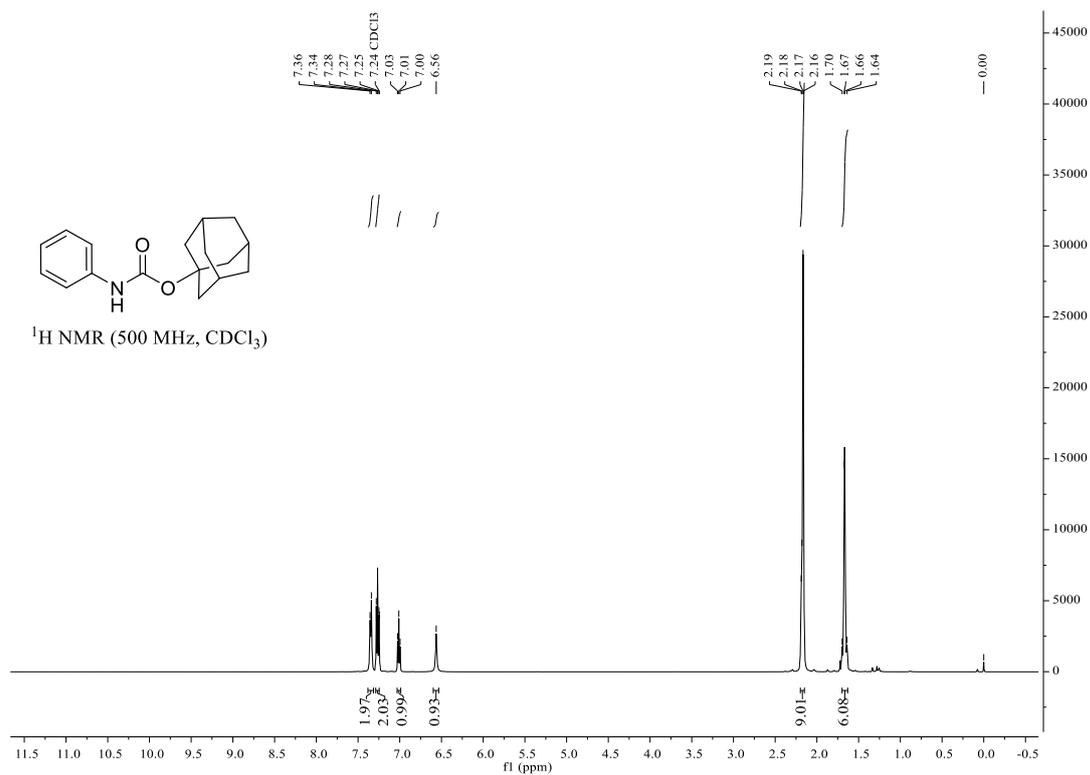
$^1\text{H NMR}$ (500 MHz, CDCl_3)



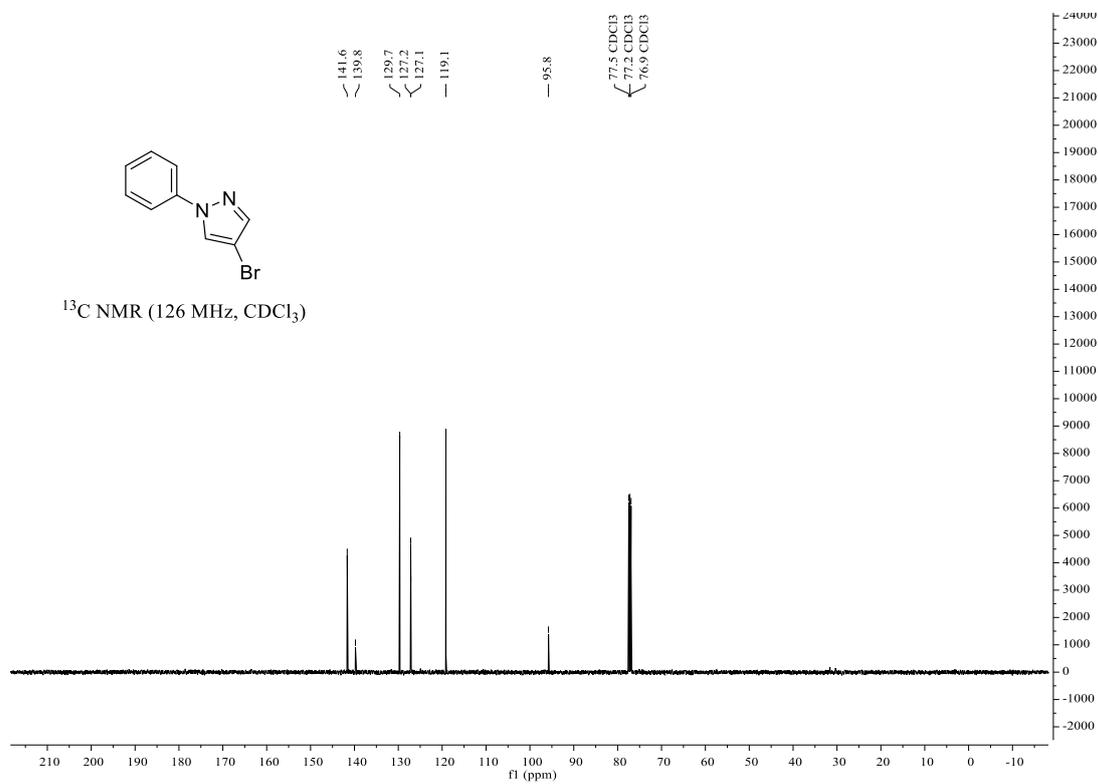
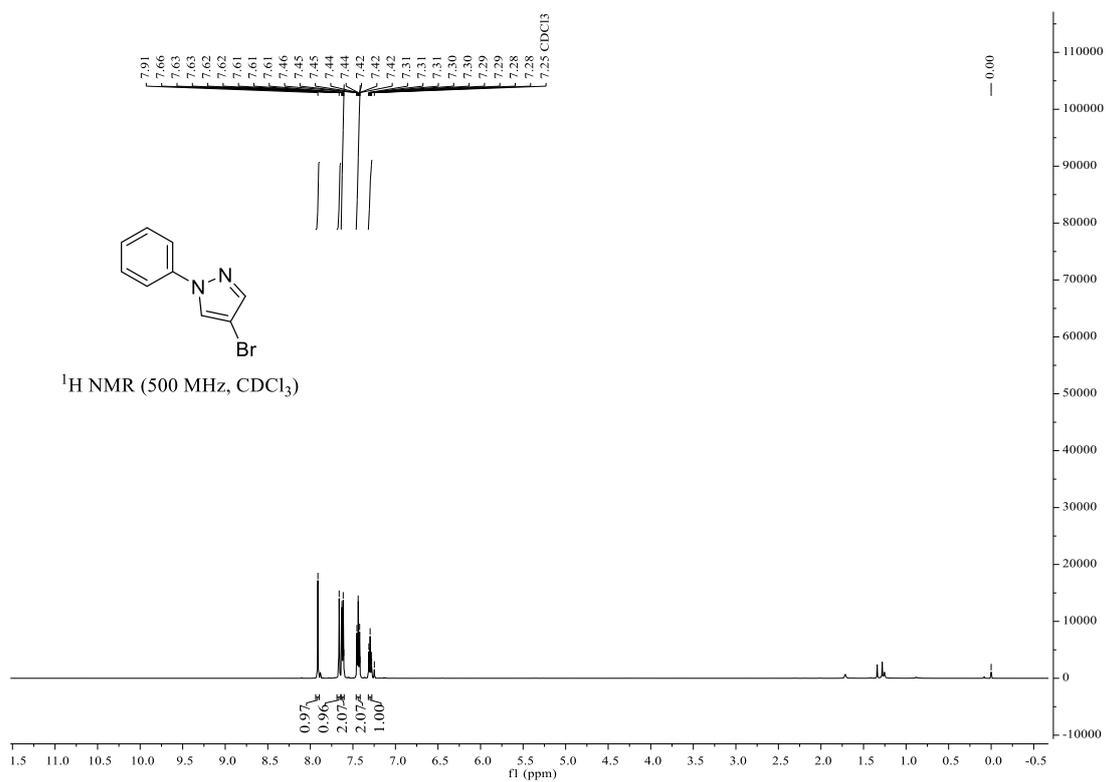
$^{13}\text{C NMR}$ (126 MHz, CDCl_3)



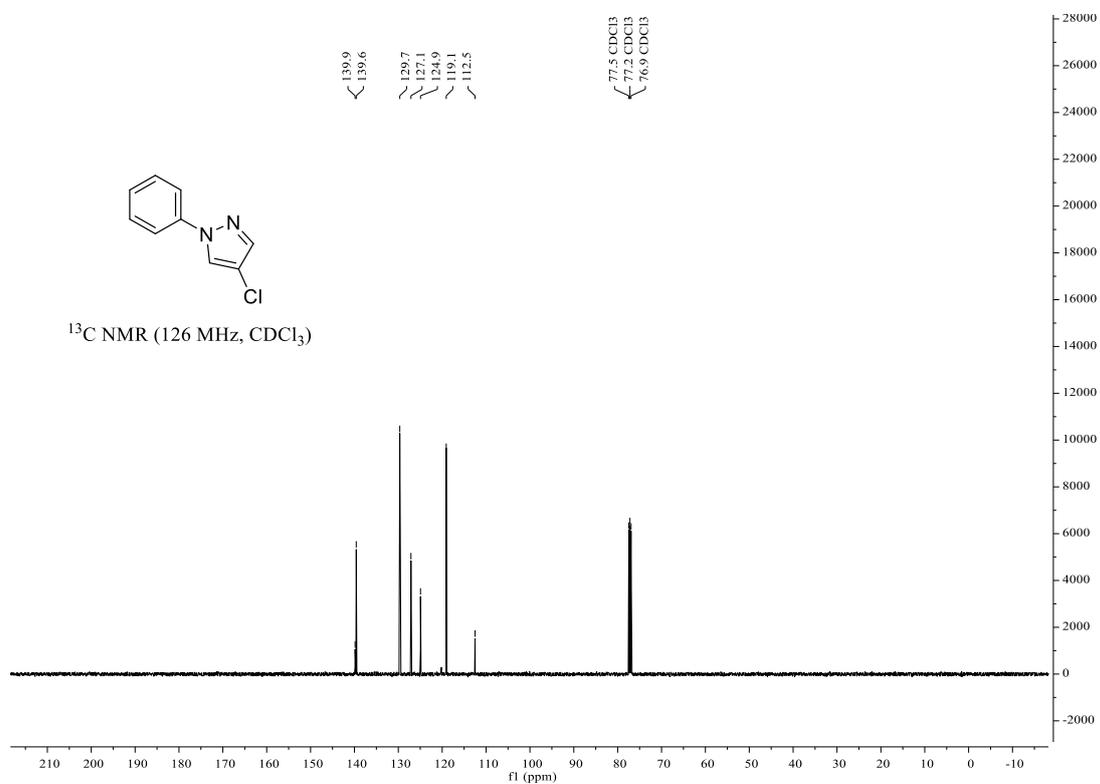
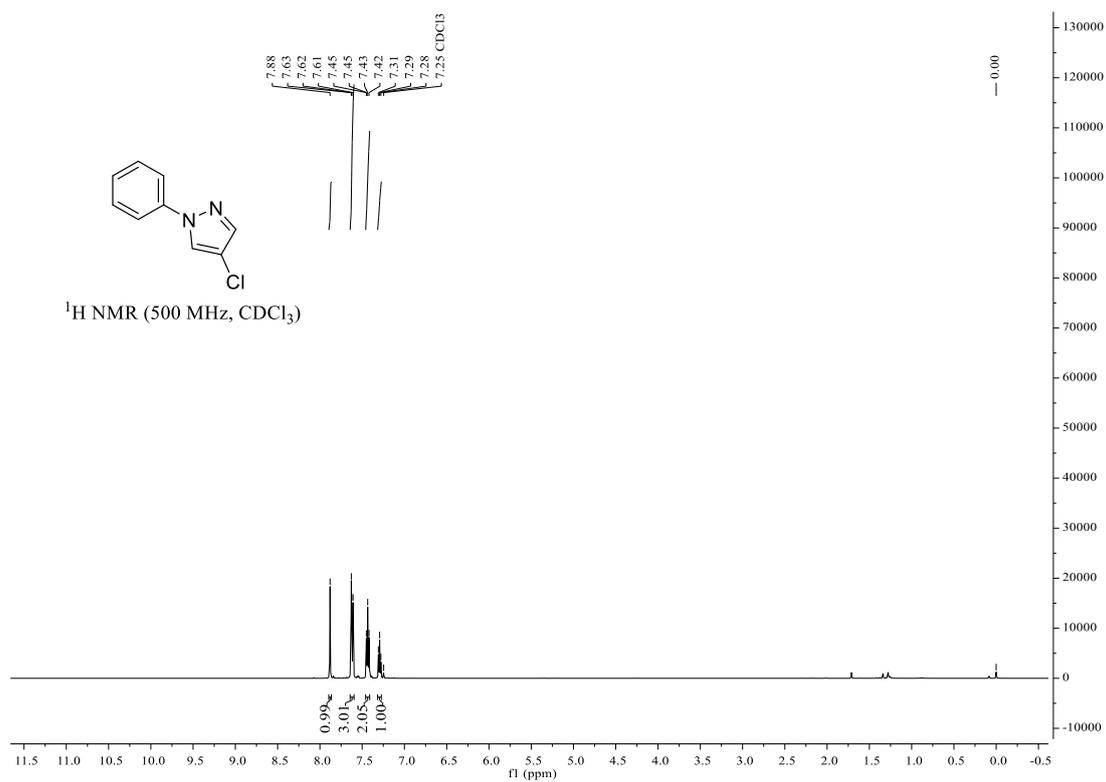
Compound 23



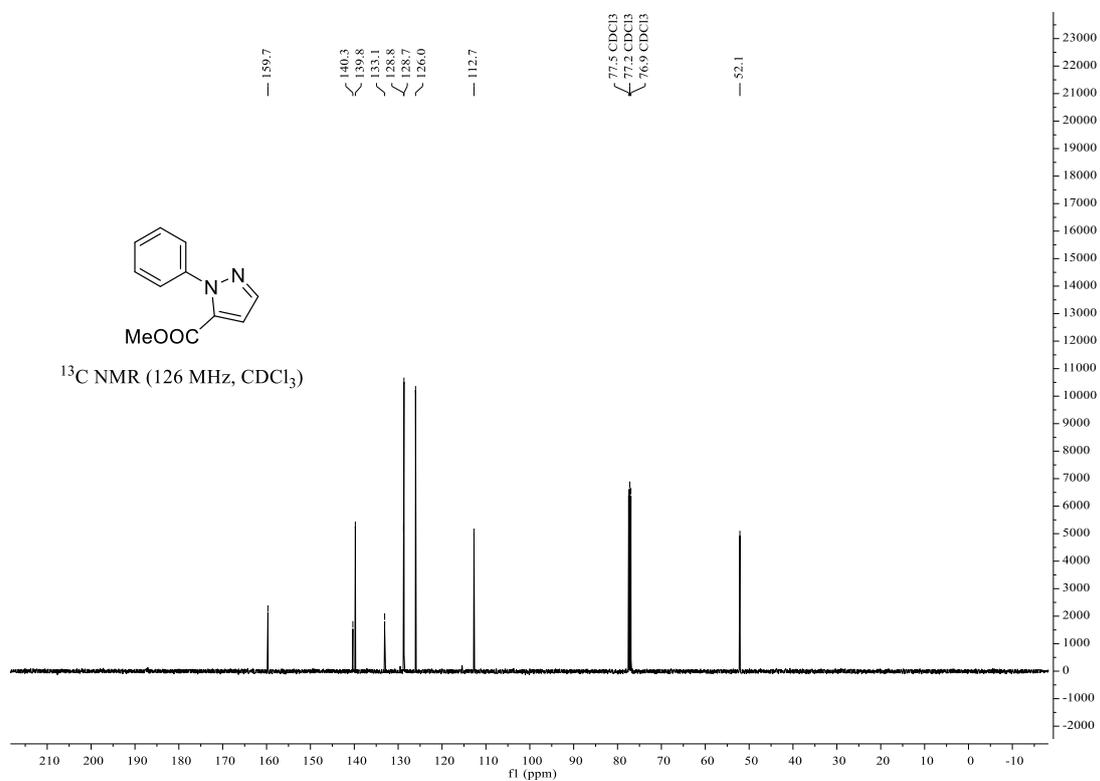
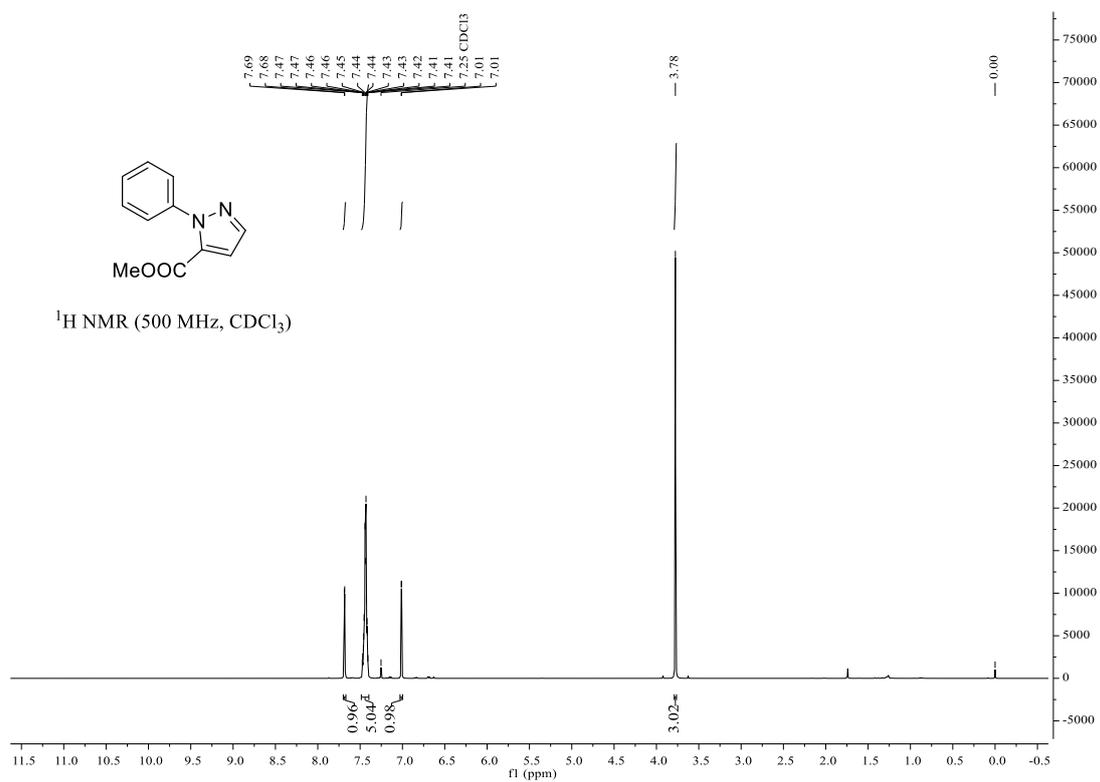
Compound 24



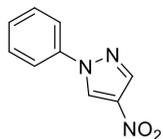
Compound 25



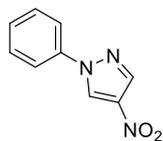
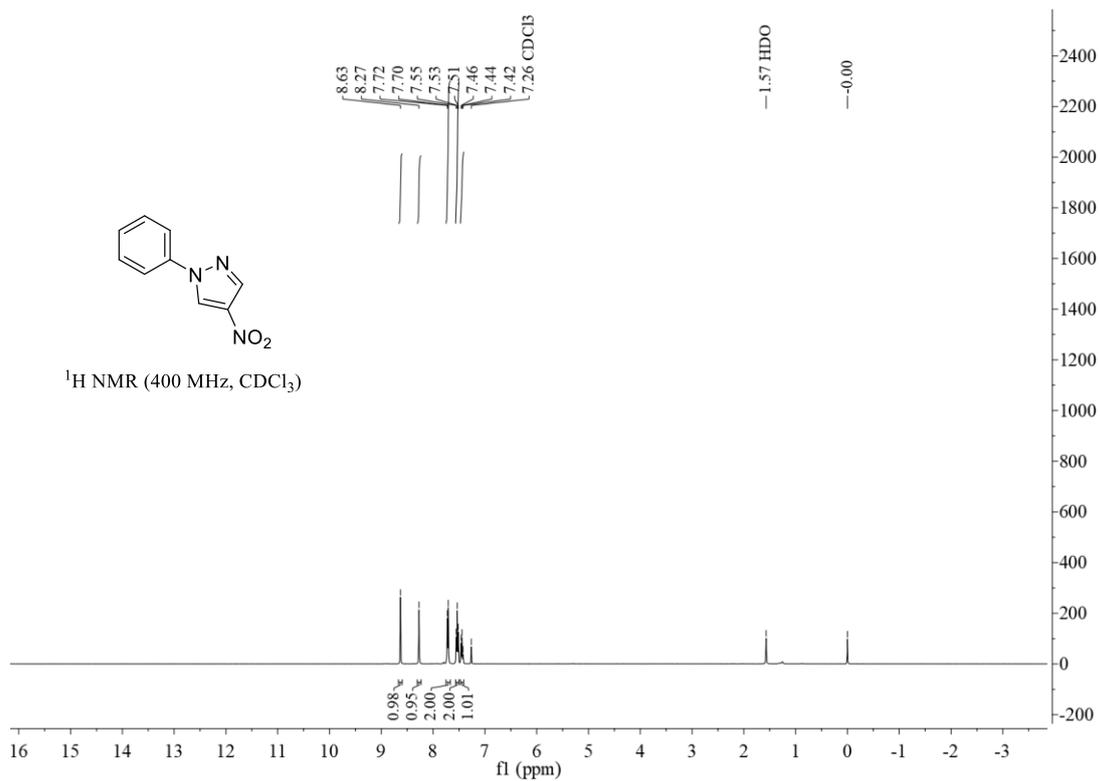
Compound 26



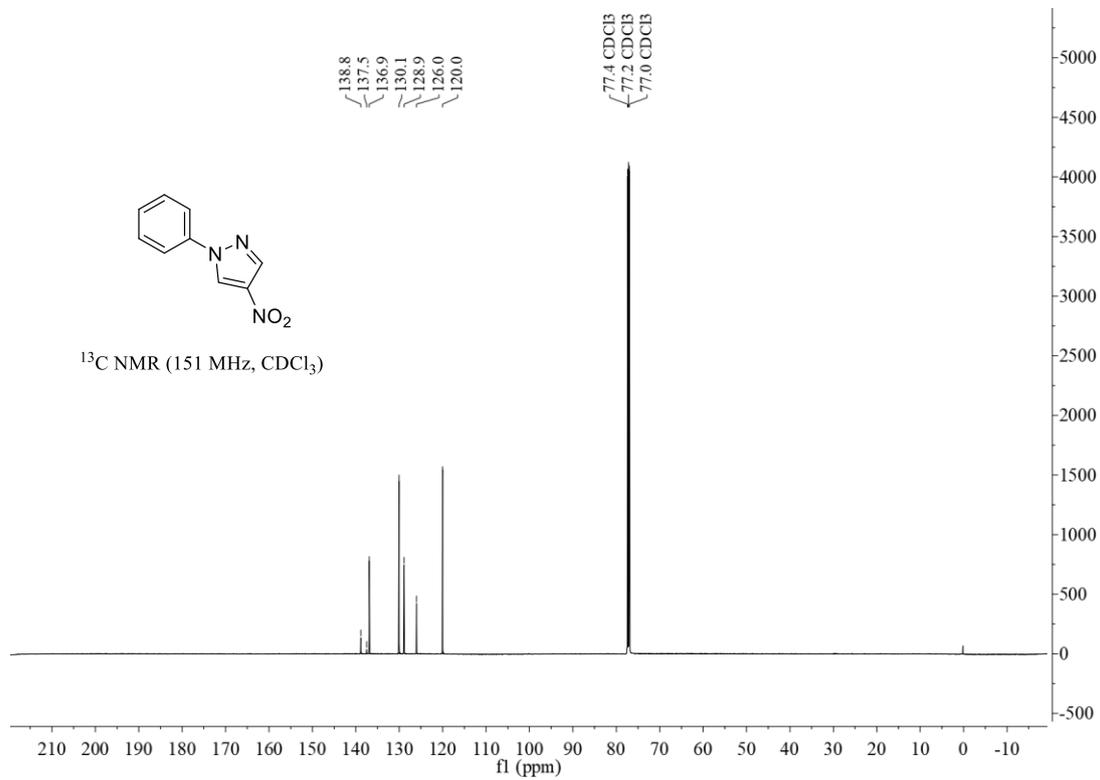
Compound 27



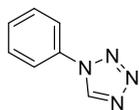
¹H NMR (400 MHz, CDCl₃)



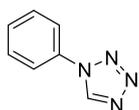
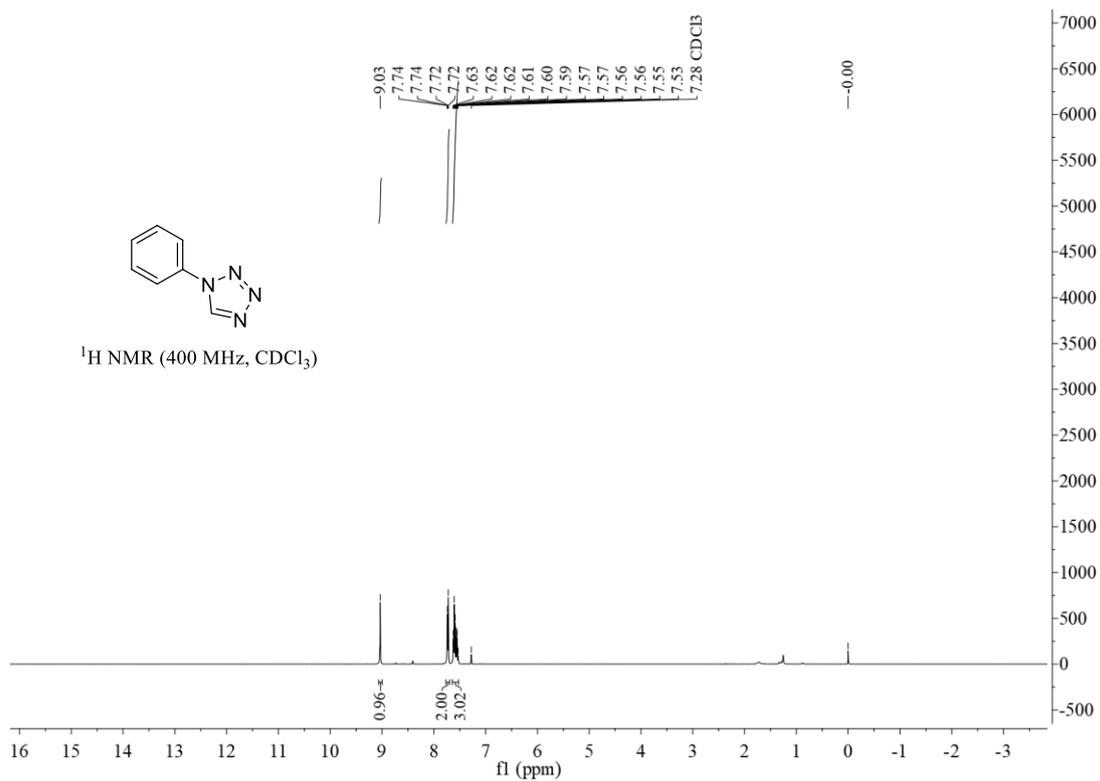
¹³C NMR (151 MHz, CDCl₃)



Compound 28



¹H NMR (400 MHz, CDCl₃)



¹³C NMR (101 MHz, CDCl₃)

