

SUPPORTING INFORMATION

A NCS mediated oxidative C-H bond functionalization: direct esterification between C(sp³)-H bond and carboxylic acids

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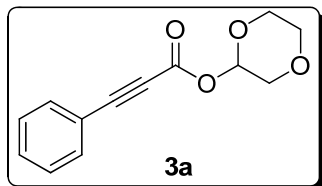
General experimental: All reactions were carried out in air. Carboxylic acids, *N*-Chlorosuccinimide (NCS), base, and the solvent used in this reaction were obtained from commercial sources and used without further purification. Flash column chromatography was performed using silica gel (300-400 mesh). Analytical thin-layer chromatography was performed using glass plates pre-coated with 200-300 mesh silica gel impregnated with a fluorescent indicator (254 nm). NMR spectra were recorded in CDCl₃ on a Varian Inova-400 NMR spectrometer (400 MHz); chemical shifts were reported in ppm with the solvent signals as reference, and coupling constants (J) were given in Hertz. The peak information was described as: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = composite. Products were characterized by comparison of ¹H NMR, ¹³C NMR and TOF-MS data in the literatures.

General Procedure for the NCS-Promoted Oxidative Coupling Esterfication.

To a Schlenk tube equipped with a magnetic stir bar was added carboxylic acids (**1**, 0.30 mmol), NCS (*N*-Chlorosuccinimide, 68.1 mg, 0.51 mmol), base (0.51 mmol), and ether **2** (2.0 mL). The reaction mixture was stirred at 80 °C for 12 hours. At the end of the reaction, the reaction mixture was cooled to room temperature. After removal of the solvent, the residue was purified by column chromatography on silica gel (eluent: hexanes:EtOAc = 6:1) to afford the pure products.

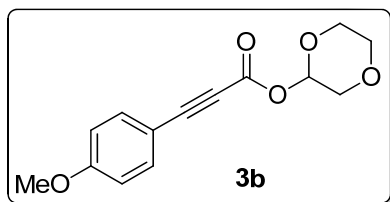
Characterization of the Corresponding Products:

1,4-Dioxan-2-yl 3-phenylpropiolate



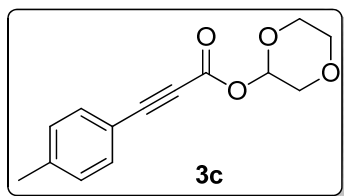
White oil; 53.8 mg; 77% yield; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.61 (dd, $J = 8.3$ Hz, 1.3 Hz, 2H), 7.47 (ddd, $J = 6.6$ Hz, 3.9 Hz, 1.3 Hz, 1H), 7.41-7.37 (m, 2H), 5.99 (s, 1H), 4.26-4.20 (m, 2H), 3.85-3.80 (comp, 4H), 3.67 (dt, $J = 11.7$ Hz, 2.3 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 152.8, 133.1, 130.9, 128.6, 119.4, 90.7, 87.5, 80.3, 67.5, 66.0, 61.6; HRMS (TOF MS Cl^+) calculated for $\text{C}_{13}\text{H}_{13}\text{O}_4$ $[\text{M}+\text{H}]^+$: 233.0814, found 233.0817.

1,4-Dioxan-2-yl 3-(4-methoxyphenyl)propiolate



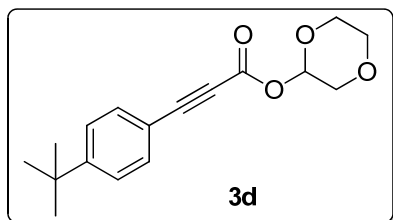
White oil; 56.0 mg; 71% yield; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.57 (d, $J = 8.8$ Hz, 2H), 6.90 (d, $J = 8.8$ Hz, 2H), 5.98 (s, 1H), 4.26-4.20 (m, 1H), 3.87-3.80 (comp, 7H), 3.69-3.65 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 161.7, 153.0, 135.1, 114.3, 111.1, 90.5, 88.5, 79.8, 67.5, 66.0, 61.6, 55.4; HRMS (TOF MS Cl^+) calculated for $\text{C}_{14}\text{H}_{15}\text{O}_5$ $[\text{M}+\text{H}]^+$: 263.0919, found 263.0928.

1,4-Dioxan-2-yl 3-*p*-tolylpropiolate



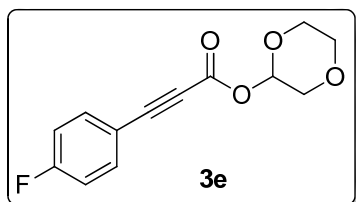
White oil; 54.0 mg; 73% yield; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.52 (d, $J = 8.0$ Hz, 2H), 7.20 (d, $J = 8.0$ Hz, 2H), 5.99 (s, 1H), 4.27-4.21 (m, 1H), 3.85-3.81 (comp, 4H), 3.67 (dt, $J = 11.7$ Hz, 2.2 Hz, 1H), 2.40 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 152.9, 141.6, 133.2, 129.4, 116.3, 90.6, 88.1, 80.0, 67.5, 66.0, 61.6, 21.7; HRMS (TOF MS Cl^+) calculated for $\text{C}_{14}\text{H}_{15}\text{O}_4$ $[\text{M}+\text{H}]^+$: 247.0970, found 247.0960.

1,4-Dioxan-2-yl 3-(4-*tert*-butylphenyl)propiolate



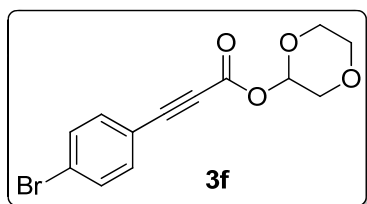
White oil; 72.0 mg; 83% yield; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.58-7.55 (m, 2H), 7.43-7.41 (m, 2H), 6.00 (s, 1H), 4.28-4.22 (m, 1H), 3.86-3.82 (comp, 4H), 3.68 (dt, $J = 11.7$ Hz, 2.4 Hz, 1H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 154.6, 153.0, 133.1, 125.7, 116.3, 90.6, 88.1, 80.0, 67.5, 66.1, 61.6, 35.1, 31.0; HRMS (TOF MS Cl^+) calculated for $\text{C}_{17}\text{H}_{21}\text{O}_4$ $[\text{M}+\text{H}]^+$: 289.1440, found 289.1441.

1,4-Dioxan-2-yl 3-(4-fluorophenyl)propiolate



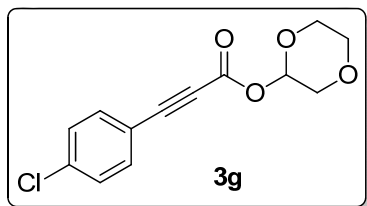
White oil; 48.9 mg; 65% yield; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.65-7.61 (comp, 2H), 7.10 (t, $J=8.6$, 2H), 6.00 (s, 1H), 4.27-4.20 (m, 1H), 3.86-3.82 (comp, 4H), 3.68 (dt, $J = 11.8$ Hz, 2.3 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 164.0 (d, $J = 250.0$ Hz), 152.7, 135.5 (d, $J = 9.0$ Hz), 116.2 (d, $J = 23.0$ Hz), 115.5, 90.7, 86.4, 80.2, 67.5, 66.0, 61.6; HRMS (TOF MS Cl^+) calculated for $\text{C}_{13}\text{H}_{12}\text{FO}_4$ $[\text{M}+\text{H}]^+$: 251.0720, found 251.0728.

1,4-Dioxan-2-yl 3-(4-bromophenyl)propiolate



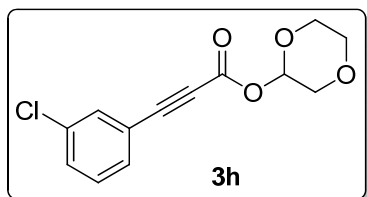
White oil; 60.6 mg; 65% yield; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.55 (d, $J = 8.5$ Hz, 2H), 7.48 (d, $J = 8.5$ Hz, 2H), 6.00 (s, 1H), 4.27-4.20 (m, 1H), 3.86-3.82 (comp, 4H), 3.68 (dt, $J = 11.7$ Hz, 2.1 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 152.6, 134.4, 132.1, 125.7, 118.3, 90.8, 86.2, 81.2, 67.4, 66.0, 61.6; HRMS (TOF MS Cl^+) calculated for $\text{C}_{13}\text{H}_{12}\text{BrO}_4$ $[\text{M}+\text{H}]^+$: 310.9919, found 310.9921.

1,4-Dioxan-2-yl 3-(4-chlorophenyl)propiolate



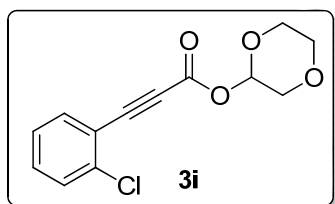
White oil; 49.7 mg; 62% yield; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.57-7.54 (m, 2H), 7.40-7.37 (m, 2H), 6.00 (s, 1H), 4.27-4.20 (m, 1H), 3.86-3.82 (comp, 4H), 3.68 (dt, $J = 11.8$ Hz, 2.3 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 152.6, 137.3, 134.3, 129.1, 117.9, 90.8, 86.1, 81.1, 67.4, 66.0, 61.6; HRMS (TOF MS Cl^+) calculated for $\text{C}_{13}\text{H}_{12}\text{ClO}_4$ $[\text{M}+\text{H}]^+$: 267.0424, found 267.0429.

1,4-Dioxan-2-yl 3-(3-chlorophenyl)propiolate



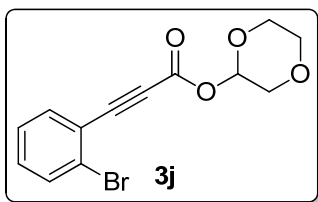
White oil; 51.3 mg; 64% yield; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.61 (t, $J = 1.7$ Hz, 1H), 7.51 (dt, $J = 7.6$ Hz, 1.3 Hz, 1H), 7.47-7.44 (m, 1H), 7.34 (t, $J = 7.9$ Hz, 1H), 6.00 (s, 1H), 4.27-4.20 (m, 1H), 3.86-3.82 (comp, 4H), 3.68 (dt, $J = 11.8$ Hz, 2.3 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 152.5, 134.6, 132.8, 131.2, 129.9, 121.1, 90.9, 85.5, 81.0, 67.4, 66.0, 61.6; HRMS (TOF MS Cl^+) calculated for $\text{C}_{13}\text{H}_{12}\text{ClO}_4$ $[\text{M}+\text{H}]^+$: 267.0424, found 267.0425.

1,4-Dioxan-2-yl 3-(2-chlorophenyl)propiolate



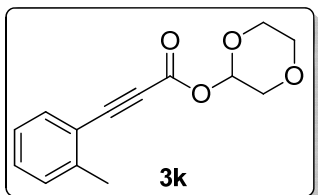
White oil; 61.7 mg; 77% yield; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.64-7.62 (m, 1H), 7.47-7.45 (m, 1H), 7.43-7.38 (m, 1H), 7.32-7.28 (m, 1H), 6.01 (s, 1H), 4.27-4.21 (m, 1H), 3.87-3.81 (comp, 4H), 3.68 (dt, $J = 11.9$ Hz, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 152.5, 137.5, 134.8, 131.8, 129.7, 126.7, 119.8, 90.9, 84.4, 83.7, 67.4, 66.0, 61.7; HRMS (TOF MS Cl^+) calculated for $\text{C}_{13}\text{H}_{12}\text{ClO}_4$ $[\text{M}+\text{H}]^+$: 267.0424, found 267.0414.

1,4-Dioxan-2-yl 3-(2-bromophenyl)propiolate



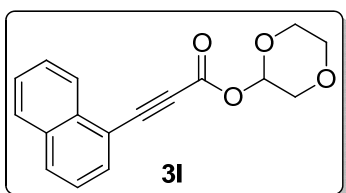
White oil; 66.1 mg; 71% yield; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.65-7.61 (m, 2H), 7.37-7.30 (m, 2H), 6.01 (s, 1H), 4.27-4.20 (m, 1H), 3.90-3.78 (comp, 4H), 3.68 (dt, $J = 11.8$ Hz, 2.4, 1H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 152.5, 134.9, 132.8, 131.9, 127.3, 126.6, 122.0, 90.9, 85.2, 83.8, 67.4, 66.0, 61.7; HRMS (TOF MS Cl^+) calculated for $\text{C}_{13}\text{H}_{12}\text{BrO}_4$ $[\text{M}+\text{H}]^+$: 310.9919, found 310.9929.

1,4-Dioxan-2-yl 3-*o*-tolylpropiolate



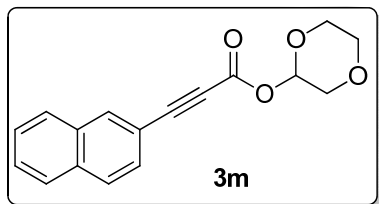
White oil; 51.9 mg; 70% yield; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.58 (d, $J = 7.1$ Hz, 1H), 7.37 (td, $J = 7.6$ Hz, 1.1 Hz, 1H), 7.24 (dt, $J = 15.1$ Hz, 5.4 Hz, 2H), 6.01 (s, 1H), 4.28-4.21 (m, 1H), 3.82-3.87 (comp, 4H), 3.69 (dt, $J = 11.8$ Hz, 2.4 Hz, 1H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 152.4, 142.0, 133.0, 130.4, 129.3, 125.3, 118.7, 90.2, 86.2, 83.5, 67.0, 65.5, 61.2, 20.1; HRMS (TOF MS Cl^+) calculated for $\text{C}_{14}\text{H}_{15}\text{O}_4$ $[\text{M}+\text{H}]^+$: 247.0970, found 247.0974.

1,4-Dioxan-2-yl 3-(naphthalen-1-yl)propiolate



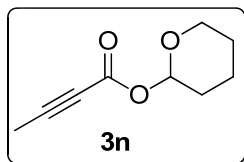
White oil; 53.5 mg; 63% yield; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 8.38 (d, $J = 8.4$ Hz, 1H), 7.98 (d, $J = 8.4$ Hz, 1H), 7.93-7.87 (comp, 2H), 7.68-7.64 (m, 1H), 7.61-7.57 (m, 1H), 7.51-7.47 (m, 1H), 6.07 (s, 1H), 4.33-4.27 (m, 1H), 3.96-3.82 (comp, 4H), 3.72 (dt, $J = 11.7$ Hz, 2.3 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 152.4, 133.2, 132.9, 132.5, 131.1, 128.0, 127.3, 126.5, 125.3, 124.6, 116.5, 90.3, 85.5, 84.4, 67.0, 65.6, 61.2; HRMS (TOF MS Cl^+) calculated for $\text{C}_{17}\text{H}_{14}\text{O}_4$ $[\text{M}+\text{H}]^+$: 283.0970, found 283.0965.

1,4-Dioxan-2-yl 3-(naphthalen-2-yl)propiolate



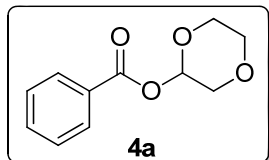
White oil; 46.7 mg; 55% yield; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 8.24 (s, 1H), 7.90-7.87 (comp, 3H), 7.66-7.57 (comp, 3H), 6.07 (s, 1H), 4.35-4.28 (m, 1H), 3.96-3.84 (comp, 4H), 3.74 (dt, $J = 11.7$ Hz, 2.3 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 152.4, 134.1, 133.5, 132.1, 128.0, 127.8, 127.7, 127.6, 127.4, 126.6, 116.1, 90.2, 87.6, 80.0, 67.0, 65.6, 61.1; HRMS (TOF MS Cl^+) calculated for $\text{C}_{17}\text{H}_{15}\text{O}_4$ $[\text{M}+\text{H}]^+$: 283.0970, found 283.0967.

1,4-Dioxan-2-yl but-2-ynoate



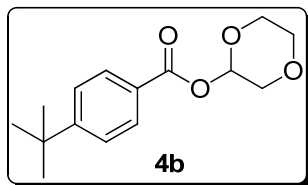
White oil; 31.8 mg; 62% yield; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 5.90 (s, 1H), 4.20-4.14 (m, 1H), 3.80-3.78 (comp, 4H), 3.64 (dt, $J = 11.9$ Hz, 2.4 Hz, 1H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 151.9, 89.9, 86.6, 71.6, 66.9, 65.5, 61.1, 3.4; HRMS (TOF MS Cl^+) calculated for $\text{C}_8\text{H}_{10}\text{O}_4$ $[\text{M}+\text{H}]^+$: 171.0657, found 171.0660.

1,4-Dioxan-2-yl benzoate



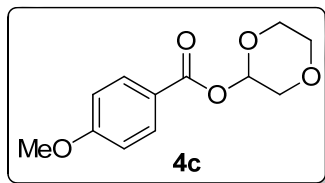
White oil; 46.4 mg; 74% yield; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 8.19-8.17 (m, 2H), 7.66-7.62 (m, 1H), 7.53-7.49 (m, 2H), 6.15 (t, $J = 1.9$ Hz, 1H), 4.31-4.25 (m, 1H), 3.95 (d, $J = 2.0$ Hz, 2H), 3.88 (dd, $J = 6.8$ Hz, 2.6 Hz, 2H), 3.73 (dt, $J = 11.8$ Hz, 2.6 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 164.8, 132.9, 129.4, 129.2, 128.0, 89.3, 67.4, 65.7, 61.3; HRMS (TOF MS Cl^+) calculated for $\text{C}_{11}\text{H}_{13}\text{O}_4$ $[\text{M}+\text{H}]^+$: 209.0814, found 209.0810.

1,4-Dioxan-2-yl 4-*tert*-butylbenzoate



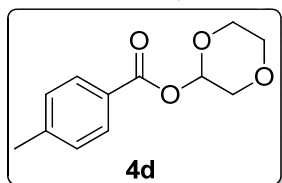
White oil; 74.7 mg; 94% yield; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 8.12-8.09 (m, 2H), 7.54-7.51 (m, 2H), 6.14 (t, $J = 1.8$ Hz, 1H), 4.30-4.23 (m, 1H), 3.94-3.93 (m, 2H), 3.87 (dd, $J = 6.7$ Hz, 2.6 Hz, 2H), 3.72 (dt, $J = 11.7$ Hz, 2.6 Hz, 1H), 1.39 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 164.7, 156.7, 129.3, 126.5, 124.9, 89.1, 67.4, 65.7, 61.3, 34.7, 30.6; HRMS (TOF MS Cl^+) calculated for $\text{C}_{15}\text{H}_{21}\text{O}_4$ $[\text{M}+\text{H}]^+$: 265.1440, found 265.1445.

1,4-Dioxan-2-yl 4-methoxybenzoate



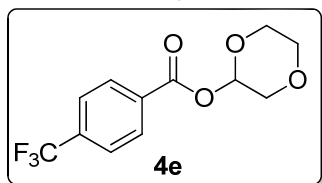
White oil; 43.1 mg; 60% yield; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 8.11-8.08 (m, 2H), 6.97-6.93 (m, 2H), 6.09 (t, $J = 1.9$ Hz, 1H), 4.26-4.19 (m, 1H), 3.90-3.82 (comp, 7H), 3.69 (dt, $J = 11.8$ Hz, 2.7 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 164.9, 163.8, 132.0, 122.0, 113.7, 89.5, 67.9, 66.2, 61.8, 55.5; HRMS (TOF MS Cl^+) calculated for $\text{C}_{12}\text{H}_{15}\text{O}_5$ $[\text{M}+\text{H}]^+$: 239.0919, found 239.0918.

1,4-Dioxan-2-yl 4-methylbenzoate



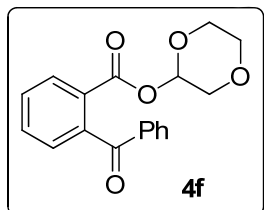
White oil; 53.5 mg; 80% yield; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 8.07 (d, $J = 8.2$ Hz, 2H), 7.32-7.30 (m, 2H), 6.14 (t, $J = 1.9$ Hz, 1H), 4.30-4.24 (m, 1H), 3.94 (m, 2H), 3.88 (dd, $J = 6.8$ Hz, 2.6 Hz, 2H), 3.73 (dt, $J = 11.7$ Hz, 2.7 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 164.8, 143.7, 129.5, 128.7, 126.5, 89.2, 67.4, 65.7, 61.3, 21.2; HRMS (TOF MS Cl^+) calculated for $\text{C}_{12}\text{H}_{15}\text{O}_4$ $[\text{M}+\text{H}]^+$: 223.0970, found 223.0973.

1,4-Dioxan-2-yl 4-(trifluoromethyl)benzoate



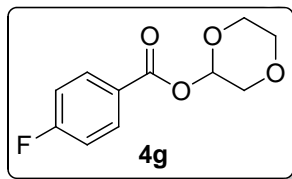
White oil; 70.6 mg; 85% yield; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 8.25 (d, $J = 8.1$ Hz, 2H), 7.74 (d, $J = 8.2$ Hz, 2H), 6.13 (s, 1H), 4.26-4.20 (m, 1H), 3.92 (d, $J = 1.8$ Hz, 2H), 3.86 (dd, $J = 6.8$ Hz, 2.3, 2H), 3.71 (dt, $J = 11.8$ Hz, 2.4, 1H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 164.1, 134.9 (d, $J = 33.0$ Hz), 133.0, 130.3, 125.5 (q, $J = 3.7$ Hz), 122.2, 90.4, 67.1, 66.1, 61.8; HRMS (TOF MS Cl^+) calculated for $\text{C}_{12}\text{H}_{12}\text{F}_3\text{O}_4$ $[\text{M}+\text{H}]^+$: 277.0688, found 277.0685.

1,4-Dioxan-2-yl 2-benzoylbenzoate



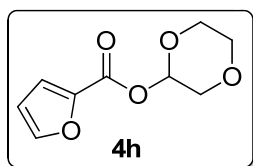
White oil; 77.0 mg; 82% yield; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 8.18 (dd, $J = 7.8$ Hz, 1.0 Hz, 1H), 7.81-7.79 (m, 2H), 7.67 (td, $J = 7.5$ Hz, 1.3 Hz, 1H), 7.62-7.53 (m, 2H), 7.47-7.39 (m, 3H), 5.85 (s, 1H), 3.88-3.82 (m, 1H), 3.70-3.60 (comp, 3H), 3.51-3.47 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 196.2, 164.1, 141.6, 136.4, 132.8, 132.2, 130.2, 129.3, 129.0, 128.1, 127.9, 127.1, 90.1, 66.7, 65.3, 61.1; HRMS (TOF MS Cl^+) calculated for $\text{C}_{18}\text{H}_{17}\text{O}_5$ $[\text{M}+\text{H}]^+$: 313.1076, found 313.1077.

1,4-Dioxan-2-yl 4-fluorobenzoate



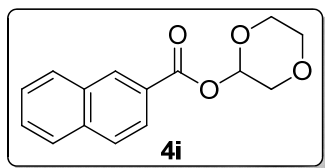
White oil; 68.1 mg; 65% yield; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 8.18-8.13 (m, 2H), 7.17-7.12 (m, 2H), 6.10 (s, 1H), 4.25-4.19 (m, 1H), 3.90 (d, $J = 1.9$ Hz, 2H), 3.84 (dd, $J = 6.8$ Hz, 2.5 Hz, 2H), 3.70 (dt, $J = 11.8$ Hz, 2.5 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 166.0 (d, $J = 250.0$ Hz), 164.3, 132.5 (d, $J = 9.4$ Hz), 126.0 (d, $J = 2.9$ Hz), 115.7 (d, $J = 21.9$ Hz), 89.9, 67.8, 66.1, 61.8; HRMS (TOF MS Cl^+) calculated for $\text{C}_{11}\text{H}_{12}\text{FO}_4$ $[\text{M}+\text{H}]^+$: 227.0720, found 227.0724.

1,4-Dioxan-2-yl furan-2-carboxylate



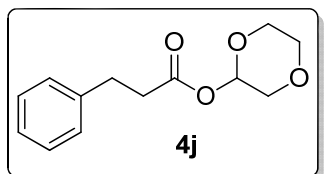
White oil; 44.2 mg; 74% yield; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.66 (m, 1H), 7.35-7.33 (m, 1H), 6.58-6.57 (m, 1H), 6.11 (s, 1H), 4.28-4.21 (m, 1H), 3.91 (d, $J = 1.9$ Hz, 2H), 3.87-3.85 (m, 2H), 3.71 (dt, $J = 11.7$ Hz, 2.5 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 156.8, 146.4, 143.6, 118.5, 111.5, 89.3, 67.2, 65.6, 61.3; HRMS (TOF MS Cl^+) calculated for $\text{C}_9\text{H}_{11}\text{O}_5$ $[\text{M}+\text{H}]^+$: 199.0606, found 199.0609.

1,4-Dioxan-2-yl 2-naphthoate



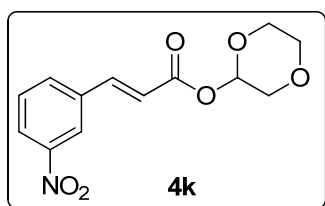
White oil; 55.2 mg; 71% yield; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 8.76 (s, 1H), 8.19 (dd, $J = 8.6$ Hz, 1.7 Hz, 1H), 8.04 (d, $J = 8.0$ Hz, 1H), 7.96-7.93 (m, 2H), 7.68-7.59 (m, 2H), 6.23 (t, $J = 1.9$ Hz, 1H), 4.37-4.31 (m, 1H), 4.01-4.00 (m, 2H), 3.93-3.91 (m, 2H), 3.77 (dt, $J = 11.8$ Hz, 2.6 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 164.9, 135.3, 132.0, 131.1, 129.0, 128.0, 127.8, 127.3, 126.5, 126.3, 124.9, 89.4, 67.5, 65.7, 61.4; HRMS (TOF MS Cl^+) calculated for $\text{C}_{15}\text{H}_{15}\text{O}_4$ $[\text{M}+\text{H}]^+$: 259.0970, found 259.0961.

1,4-Dioxan-2-yl 3-phenylpropanoate



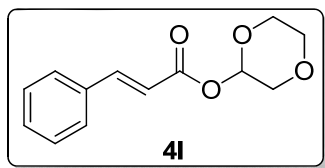
White oil; 59.0 mg; 83% yield; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.37-7.31 (m, 2H), 7.28-7.24 (comp, 3H), 5.91 (t, $J = 2.0$ Hz, 1H), 4.12-4.04 (m, 1H), 3.84-3.71 (m, 4H), 3.64 (dt, $J = 11.8$ Hz, 2.7 Hz, 1H), 3.05 (t, $J = 7.8$ Hz, 2H), 2.81-2.77 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 171.2, 139.7, 128.1, 127.8, 125.9, 88.8, 67.2, 65.6, 61.2, 35.4, 30.3; HRMS (TOF MS Cl^+) calculated for $\text{C}_{13}\text{H}_{17}\text{O}_4$ $[\text{M}+\text{H}]^+$: 237.1127, found 237.1124.

(*E*)-1,4-Dioxan-2-yl 3-(3-nitrophenyl)acrylate



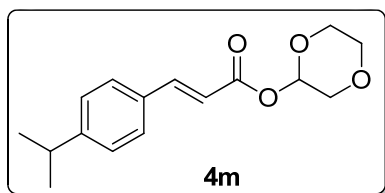
Yellow oil; 69.7 mg; 83% yield; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 8.41 (s, 1H), 8.26 (dd, $J = 8.2$ Hz, 1.3, 1H), 7.87-7.80 (m, 2H), 7.61 (t, $J = 8.0$ Hz, 1H), 6.65 (d, $J = 16.0$ Hz, 1H), 6.01 (s, 1H), 4.24-4.18 (m, 1H), 3.90-3.82 (comp, 4H), 3.69 (dt, $J = 11.8$ Hz, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 164.2, 148.2, 142.6, 135.4, 133.2, 129.6, 124.3, 122.1, 120.2, 89.3, 67.3, 65.6, 61.2; HRMS (TOF MS Cl^+) calculated for $\text{C}_{13}\text{H}_{14}\text{NO}_6$ $[\text{M}+\text{H}]^+$: 280.0821, found 280.0824.

1,4-Dioxan-2-yl cinnamate



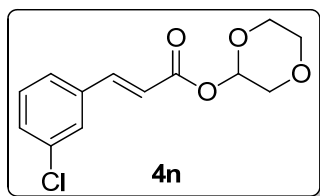
White oil; 42.3 mg; 60% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) (δ , ppm) 7.81 (d, $J = 16.0$ Hz, 1H), 7.58-7.56 (m, 2H), 7.43-7.42 (comp, 3H), 6.54 (d, $J = 16.0$ Hz, 1H), 6.02 (t, $J = 1.8$ Hz, 1H), 4.25-4.19 (m, 1H), 3.91-3.83 (comp, 4H), 3.69 (dt, $J = 11.7$ Hz, 2.6 Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) (δ , ppm) 165.6, 146.2, 134.2, 130.6, 129.0, 128.3, 117.4, 89.4, 67.9, 66.2, 61.7; HRMS (TOF MS Cl^+) calculated for $\text{C}_{13}\text{H}_{15}\text{O}_4$ $[\text{M}+\text{H}]^+$: 235.0970, found 235.0979.

(*E*)-1,4-Dioxan-2-yl 3-(4-isopropylphenyl)acrylate



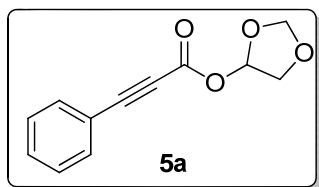
White oil; 59.0 mg; 71% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) (δ , ppm) 7.82 (d, $J = 16.0$ Hz, 1H), 7.53 (d, $J = 8.2$ Hz, 2H), 7.31 (d, $J = 8.2$ Hz, 2H), 6.53 (d, $J = 16.0$ Hz, 1H), 6.04 (t, $J = 1.9$ Hz, 1H), 4.27-4.21 (m, 1H), 3.93-3.85 (comp, 4H), 3.72 (dt, $J = 11.7$ Hz, 2.7 Hz, 1H), 3.03-2.93 (m, 1H), 1.32-1.30 (comp, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) (δ , ppm) 165.3, 151.5, 145.7, 131.4, 127.9, 126.6, 115.9, 88.8, 67.4, 65.7, 61.3, 33.6, 23.3; HRMS (TOF MS Cl^+) calculated for $\text{C}_{16}\text{H}_{21}\text{O}_4$ $[\text{M}+\text{H}]^+$: 277.1440, found 277.1437.

(*E*)-1,4-Dioxan-2-yl 3-(3-chlorophenyl)acrylate



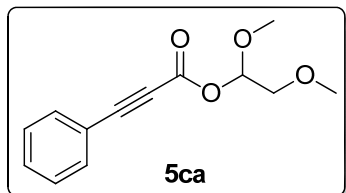
White oil; 51.6 mg; 64% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3) (δ , ppm) 7.75 (d, $J = 16.0$ Hz, 1H), 7.57 (m, 1H), 7.46 (dt, $J = 7.1$ Hz, 1.5 Hz, 1H), 7.43-7.36 (m, 2H), 6.56 (d, $J = 16.0$ Hz, 1H), 6.03 (t, $J = 1.9$ Hz, 1H), 4.26-4.20 (m, 1H), 3.93-3.85 (comp, 4H), 3.71 (dt, $J = 11.7$ Hz, 2.6 Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) (δ , ppm) 164.6, 143.9, 135.5, 134.5, 129.9, 129.7, 127.5, 125.9, 118.5, 89.1, 67.3, 65.6, 61.2; HRMS (TOF MS Cl^+) calculated for $\text{C}_{13}\text{H}_{14}\text{ClO}_4$ $[\text{M}+\text{H}]^+$: 269.0581, found 269.0584.

1,3-Dioxolan-4-yl 3-phenylpropiolate



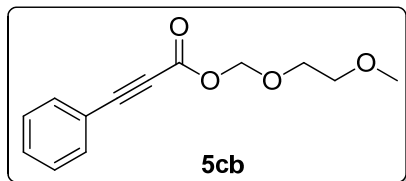
White oil; 19.7 mg; 30% yield; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.66-7.64 (m, 2H), 7.55-7.50 (m, 1H), 7.46-7.42 (m, 2H), 6.51 (dd, $J = 3.9$ Hz, 2.0 Hz, 1H), 5.25 (s, 1H), 5.19 (s, 1H), 4.19-4.12 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 152.6, 132.7, 130.5, 128.2, 118.7, 95.7, 94.7, 87.3, 79.6, 70.0; HRMS (TOF MS Cl^+) calculated for $\text{C}_{12}\text{H}_{11}\text{O}_4$ $[\text{M}+\text{H}]^+$: 219.0657, found 219.0655.

1,2-Dimethoxyethyl 3-phenylpropiolate

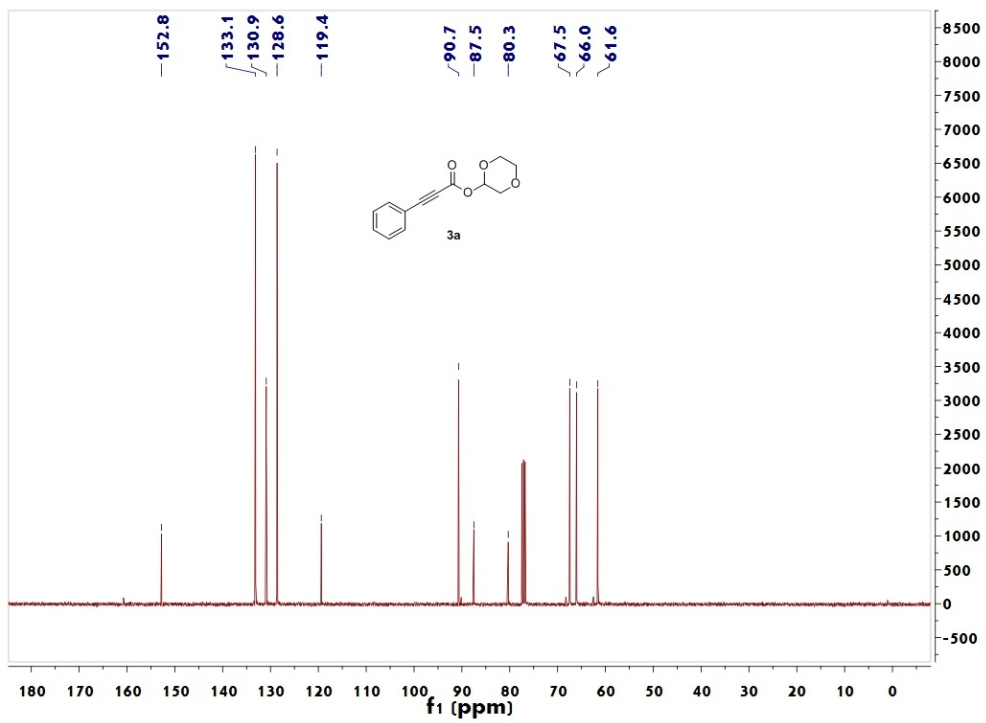
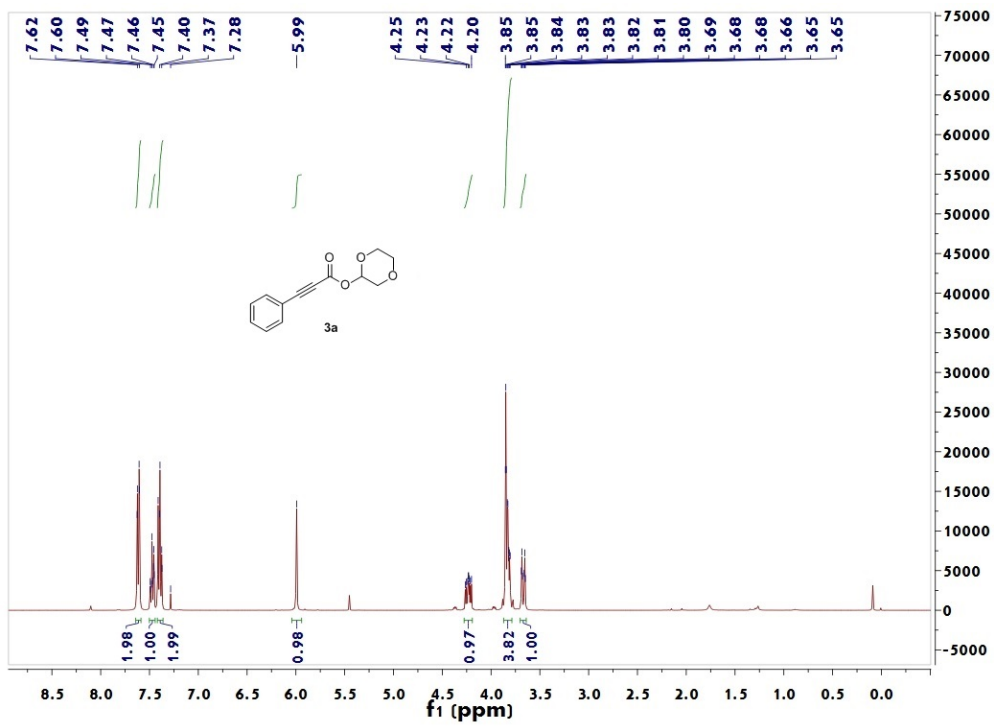


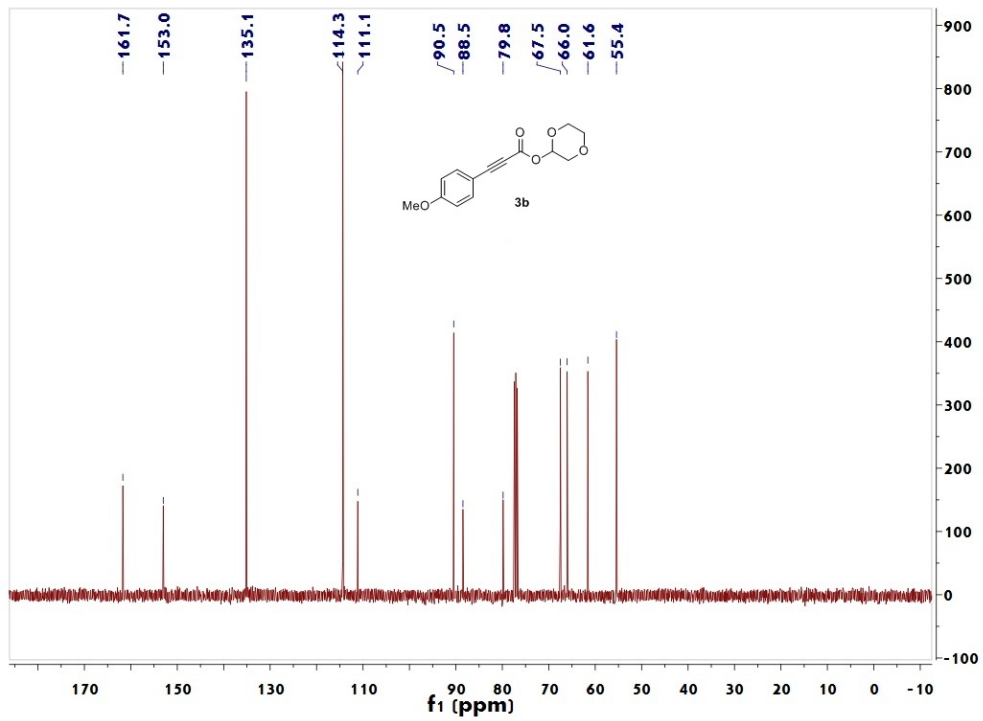
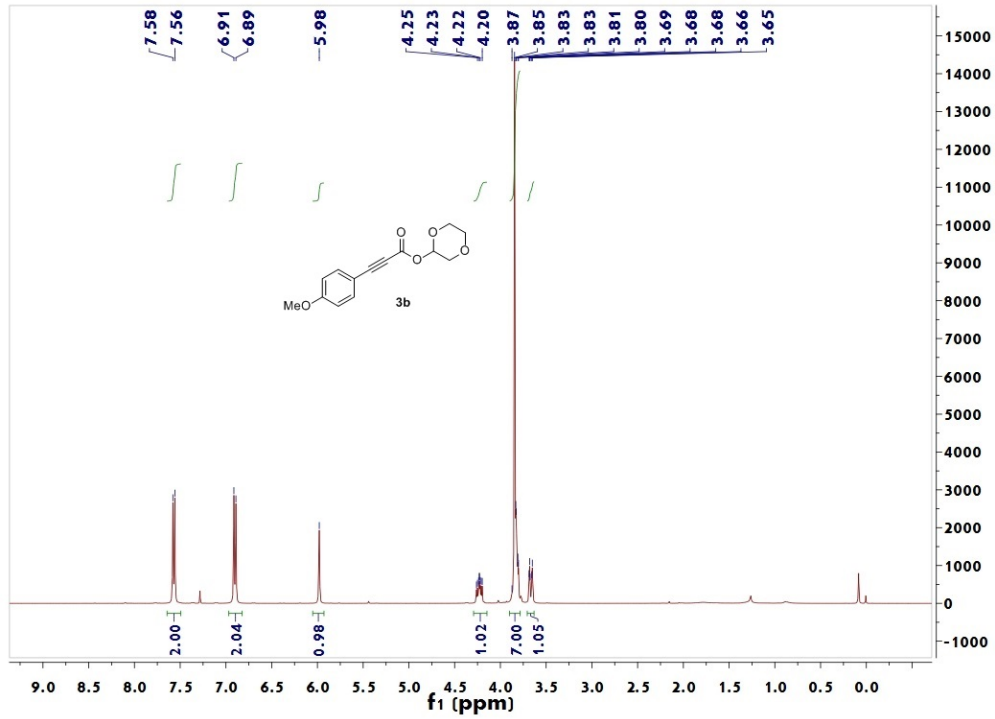
White oil; 26.5 mg; 37% yield; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.61-7.59 (m, 2H), 7.49-7.45 (m, 1H), 7.39 (t, $J = 7.4$ Hz, 2H), 6.01 (t, $J = 4.9$ Hz, 1H), 3.59-3.57 (m, 2H), 3.55 (s, 3H), 3.44 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 153.6, 133.1, 130.9, 128.6, 119.4, 98.4, 87.6, 80.0, 72.4, 59.6, 57.5; HRMS (TOF MS Cl^+) calculated for $\text{C}_{13}\text{H}_{15}\text{O}_4$ $[\text{M}+\text{H}]^+$: 235.0970, found 239.0962.

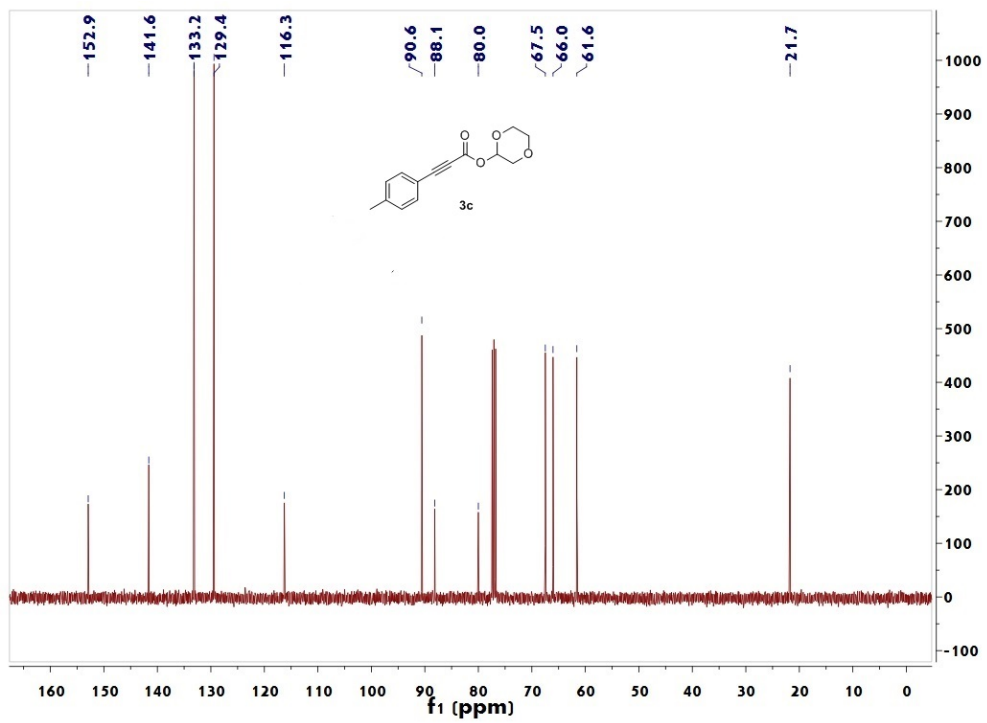
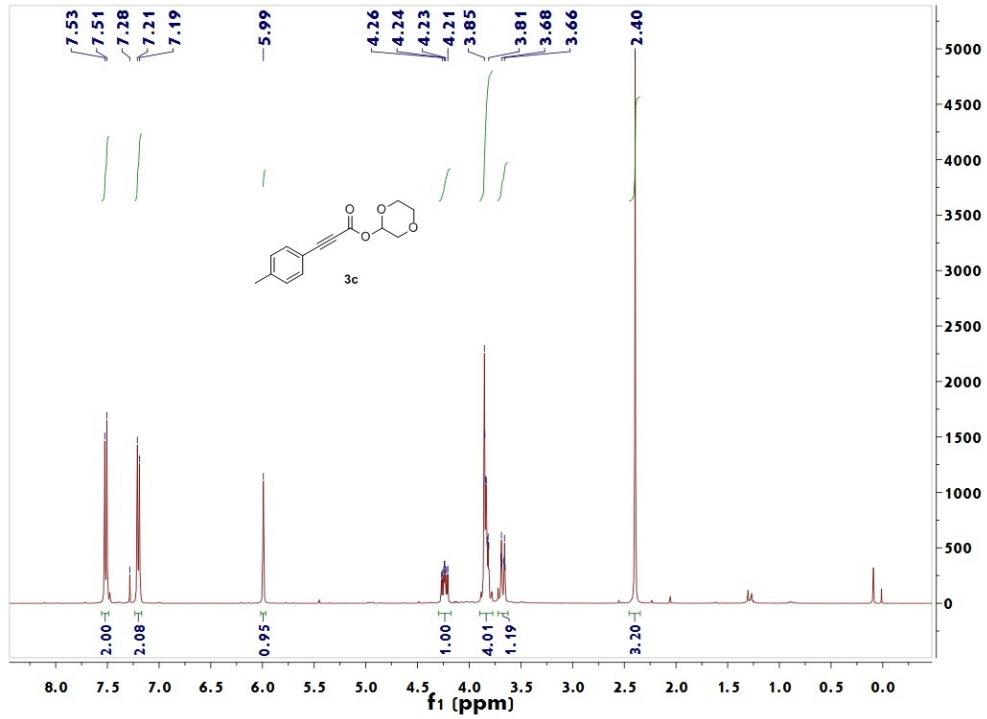
(2-Methoxyethoxy)methyl 3-phenylpropiolate

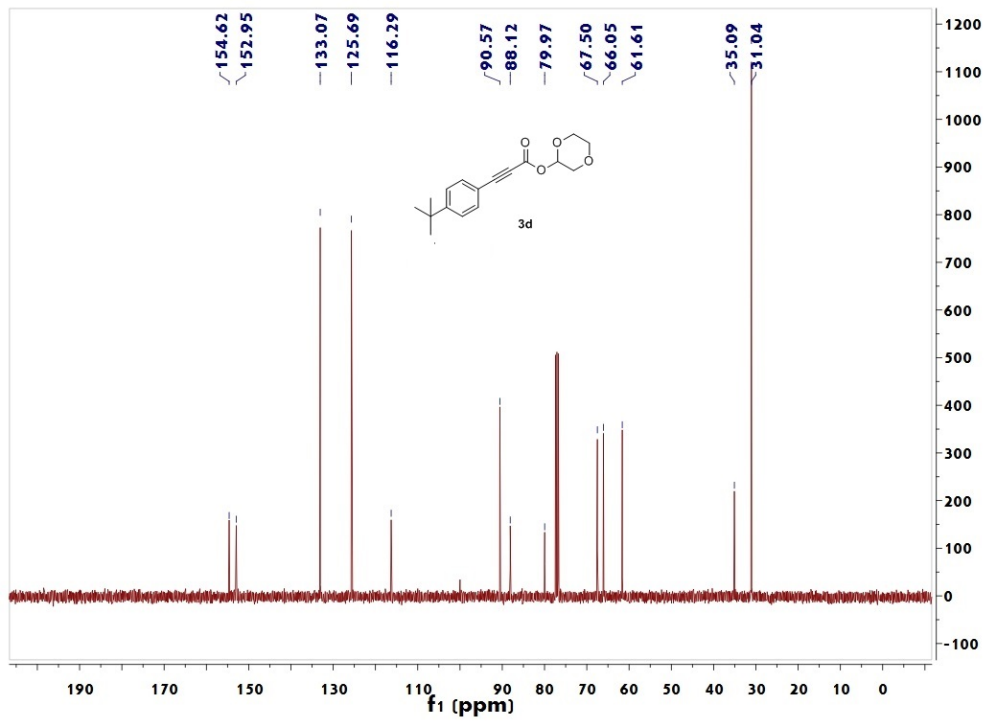
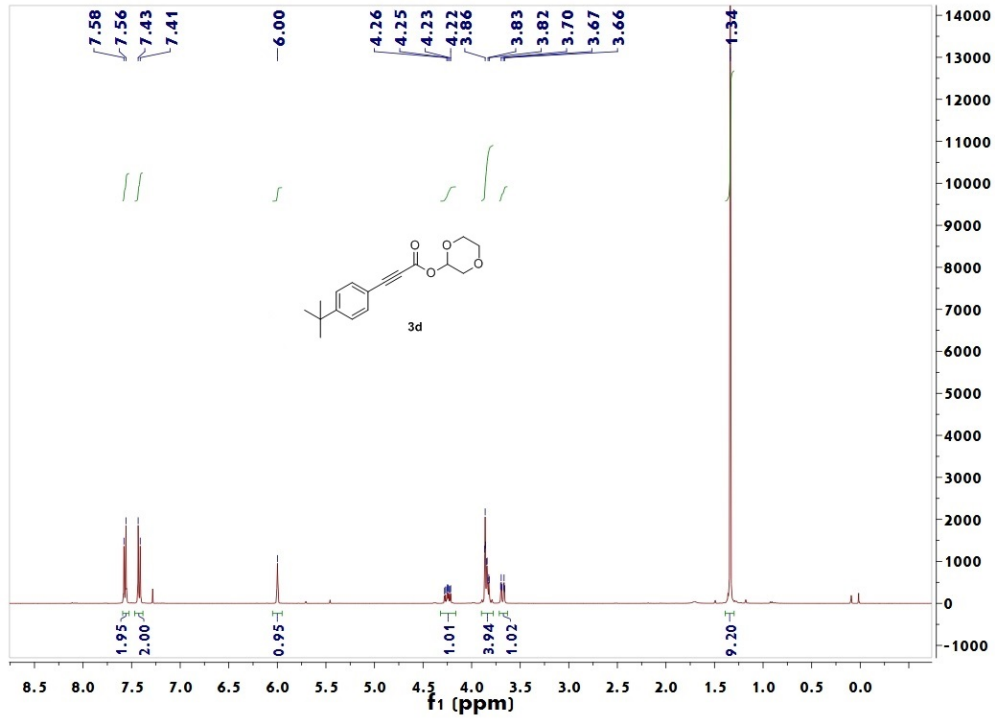


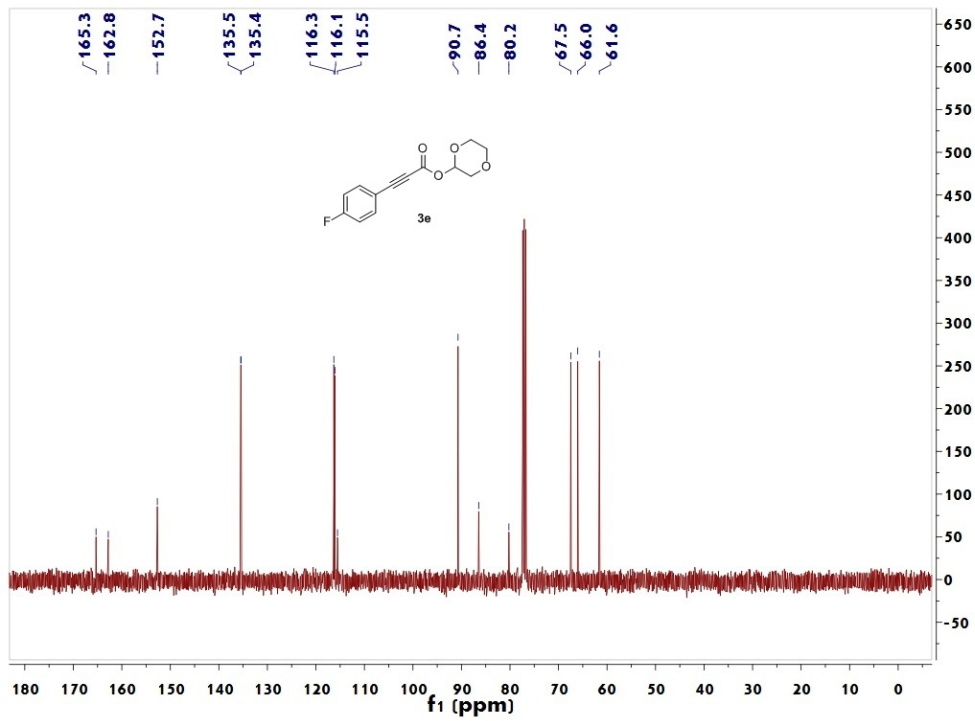
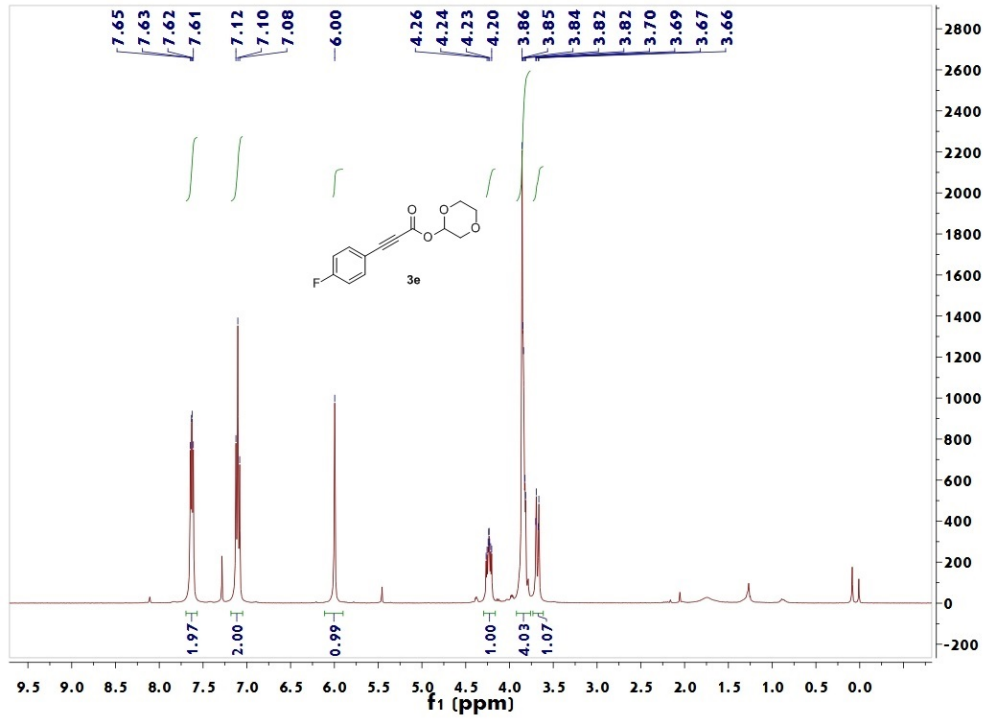
White oil; 24.7 mg; 35% yield; ^1H NMR (400 MHz, CDCl_3) (δ , ppm) 7.62-7.60 (m, 2H), 7.48 (ddd, $J = 6.6$ Hz, 3.9 Hz, 1.3 Hz, 1H), 7.40 (t, $J = 7.4$ Hz, 2H), 5.48 (s, 2H), 3.90-3.88 (m, 2H), 3.62-3.60 (m, 2H), 3.42 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) (δ , ppm) 153.4, 133.1, 130.8, 128.6, 119.4, 90.6, 87.2, 80.3, 71.4, 69.9, 59.1; HRMS (TOF MS Cl^+) calculated for $\text{C}_{13}\text{H}_{15}\text{O}_4$ $[\text{M}+\text{H}]^+$: 235.0970, found 235.0969.

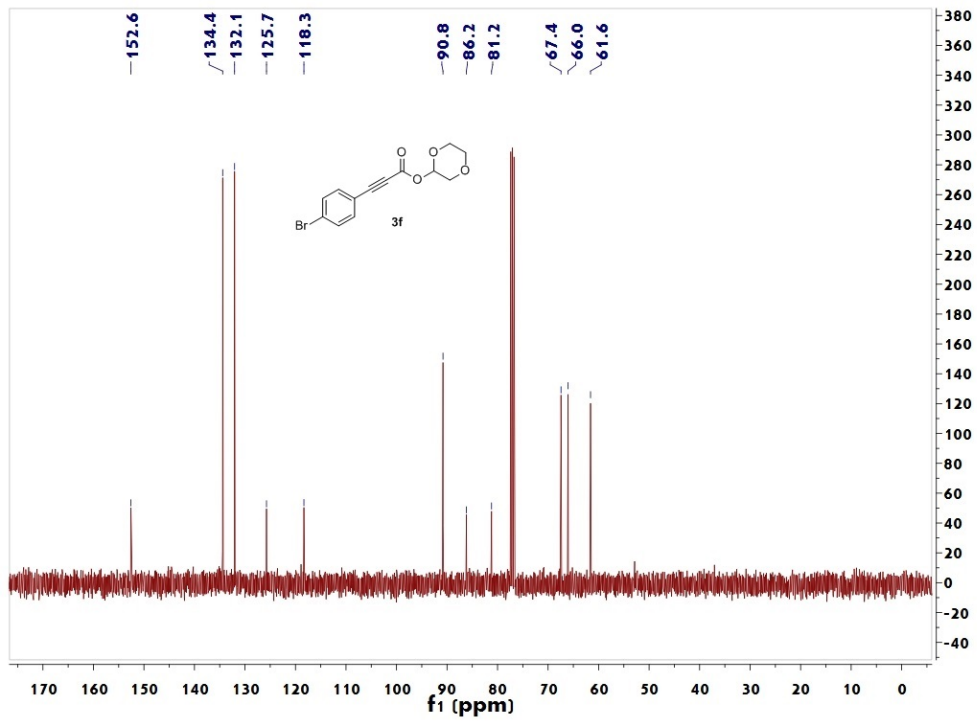
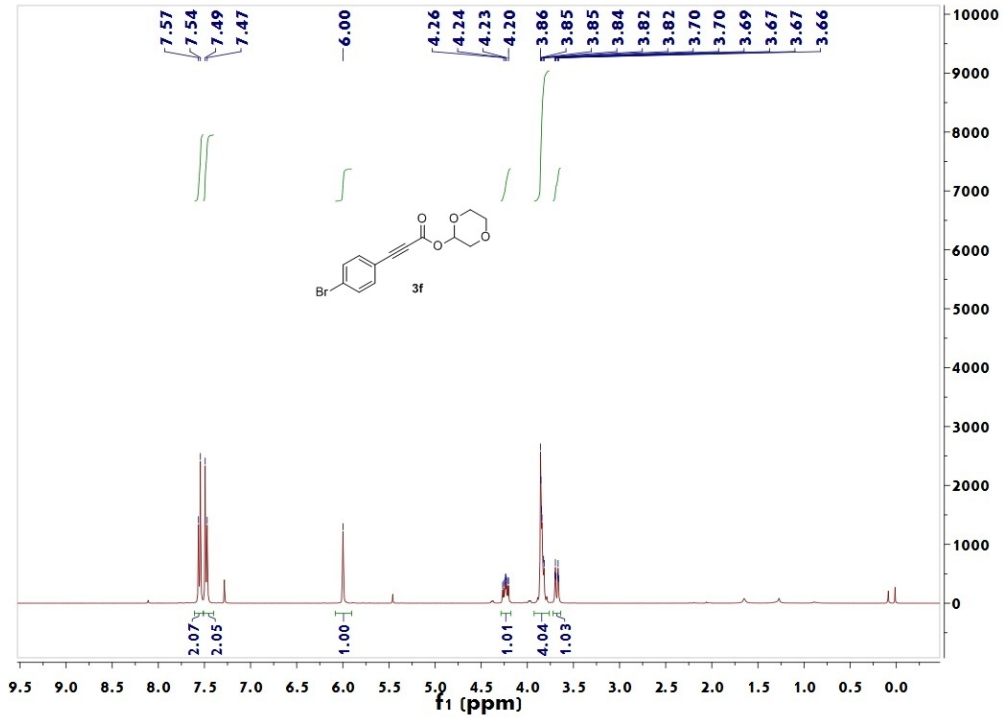


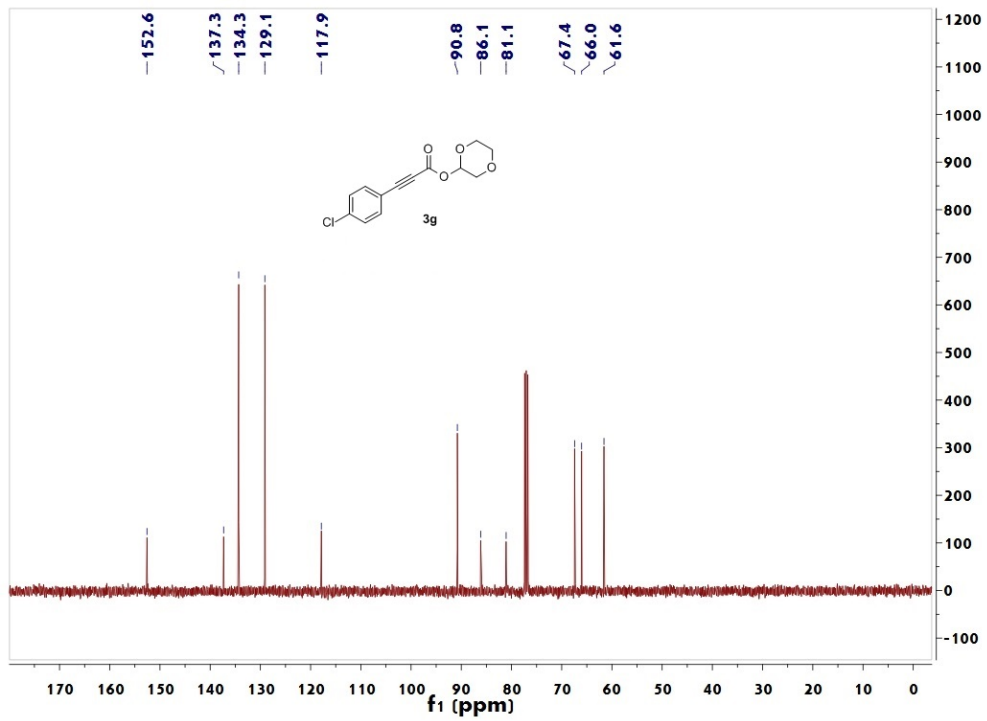
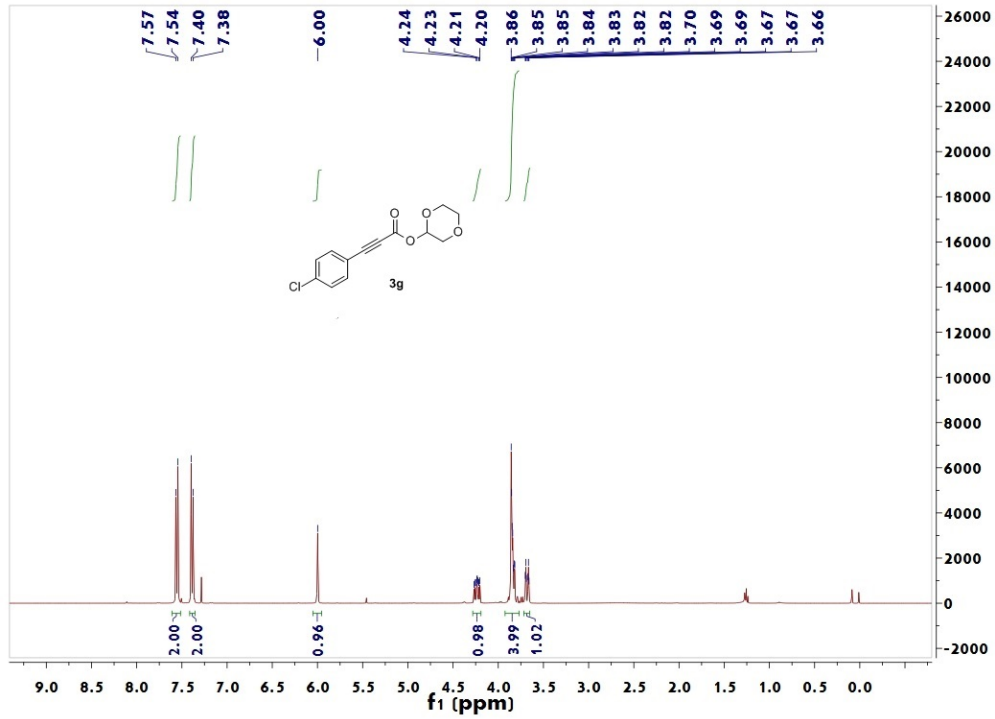


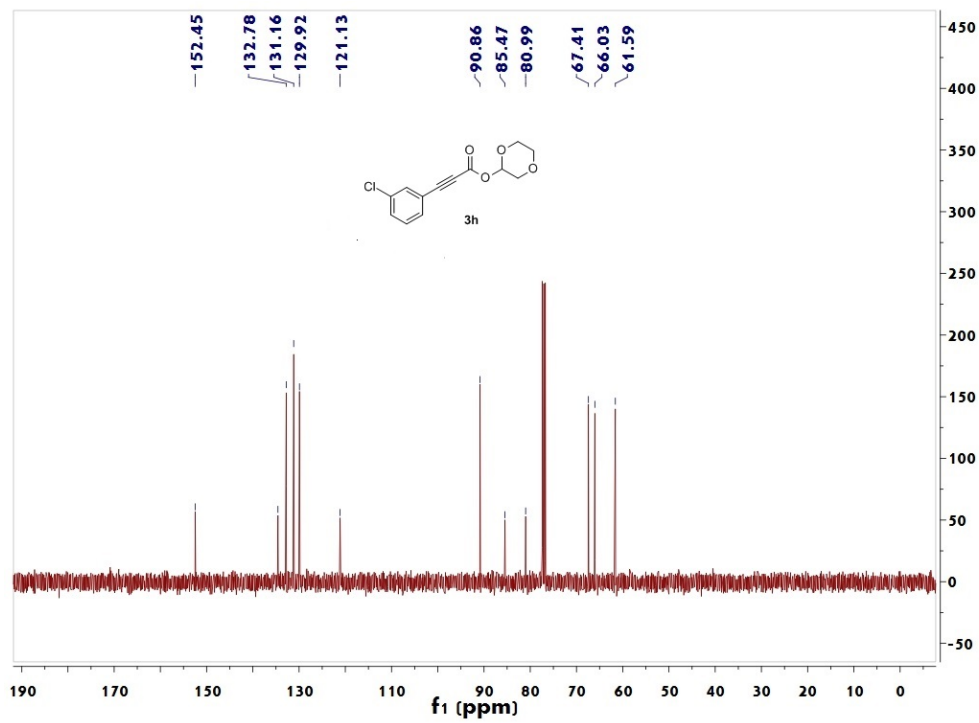
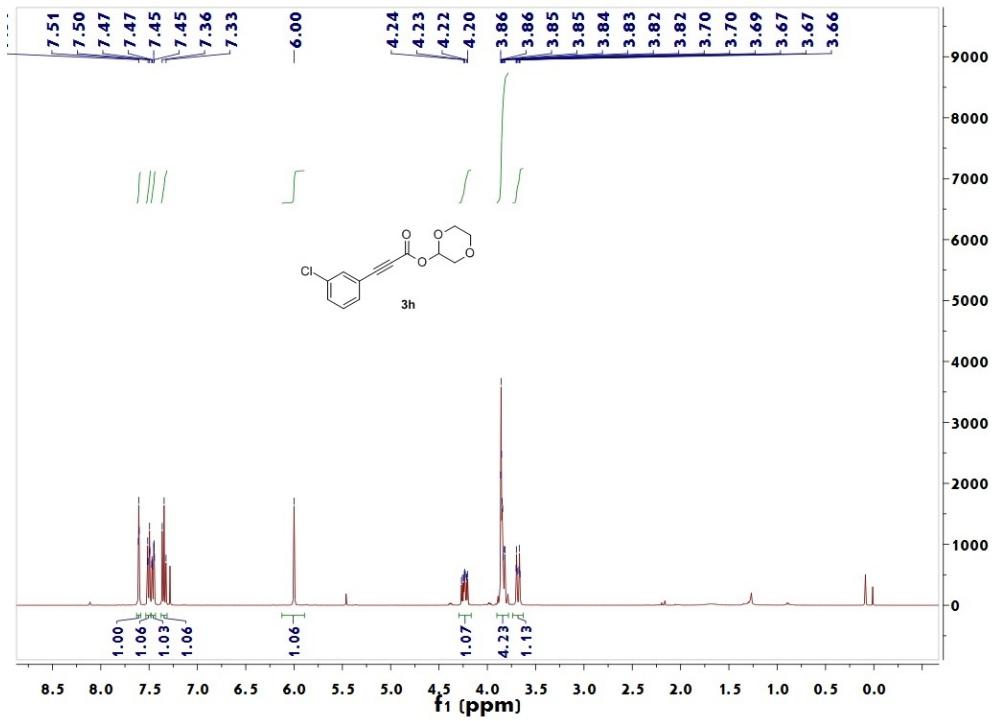


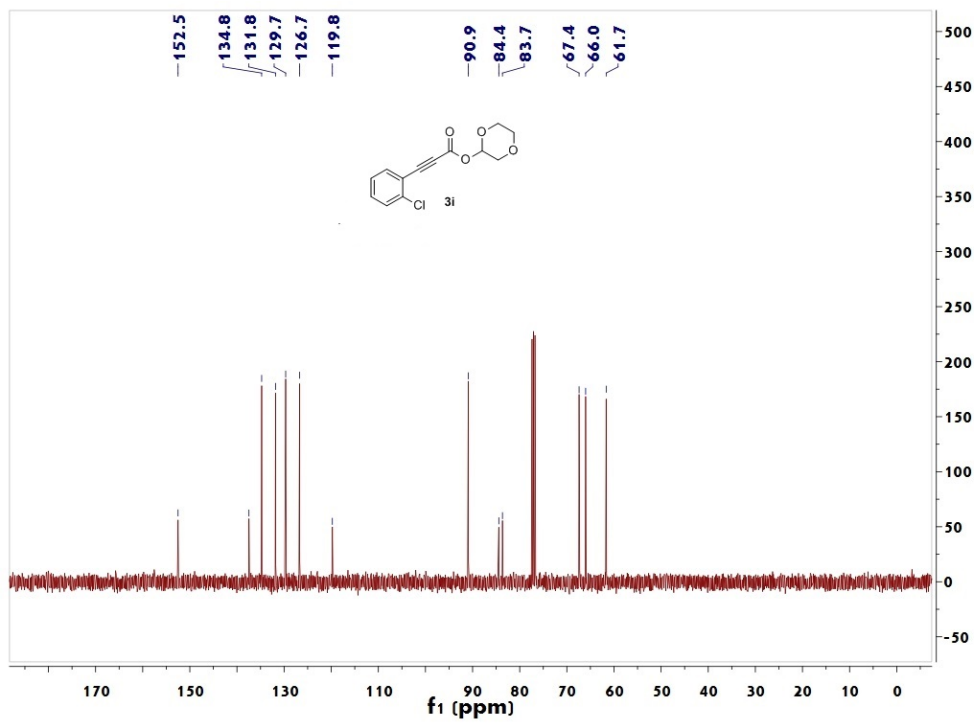
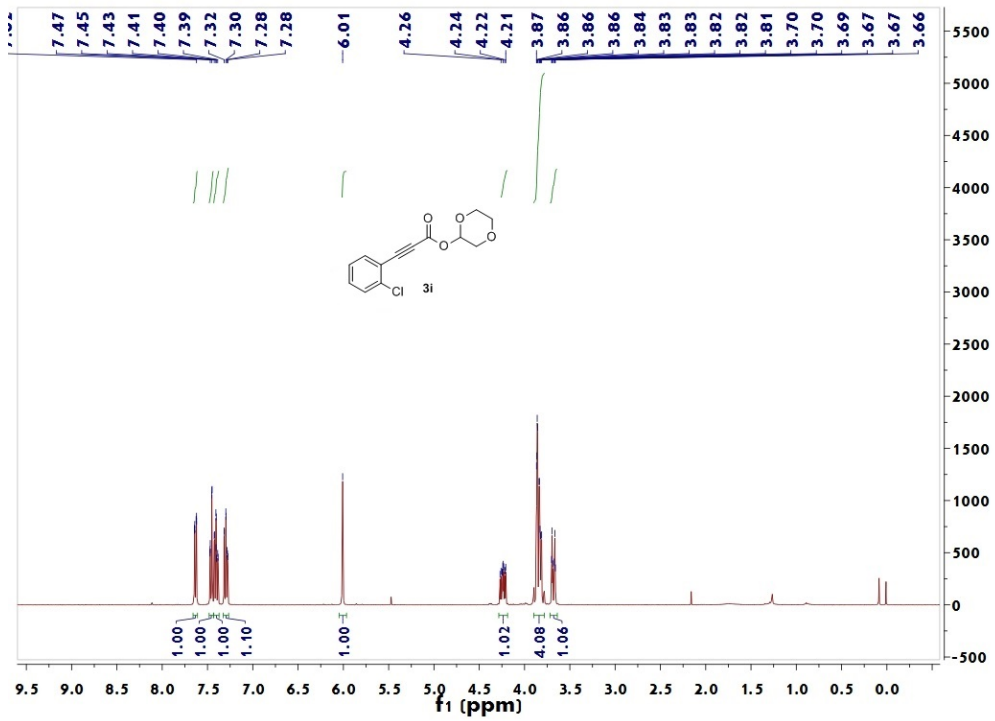


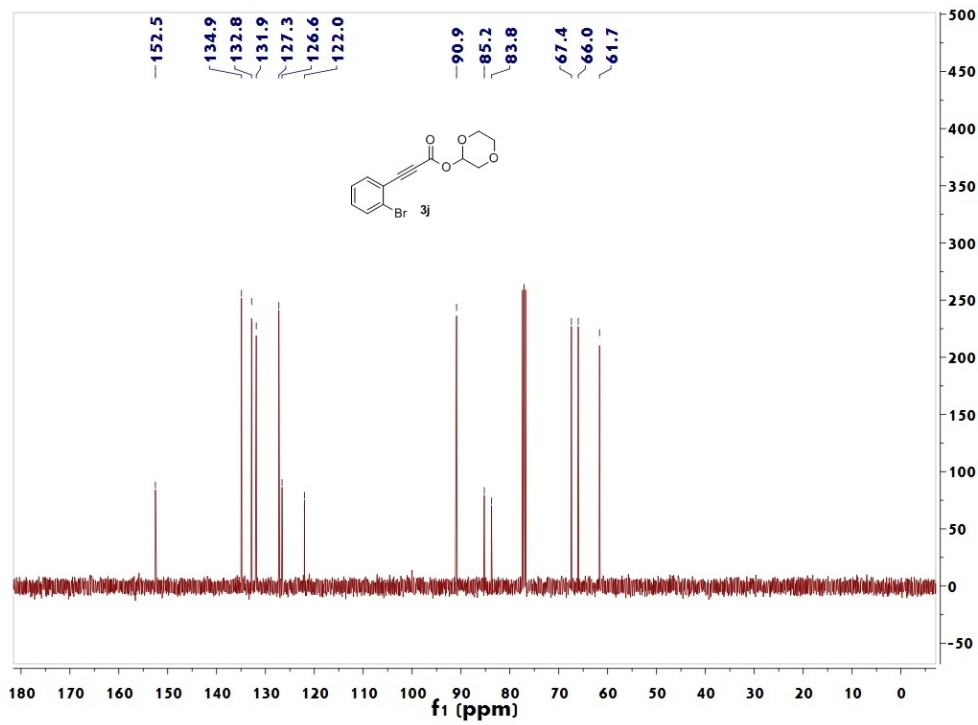
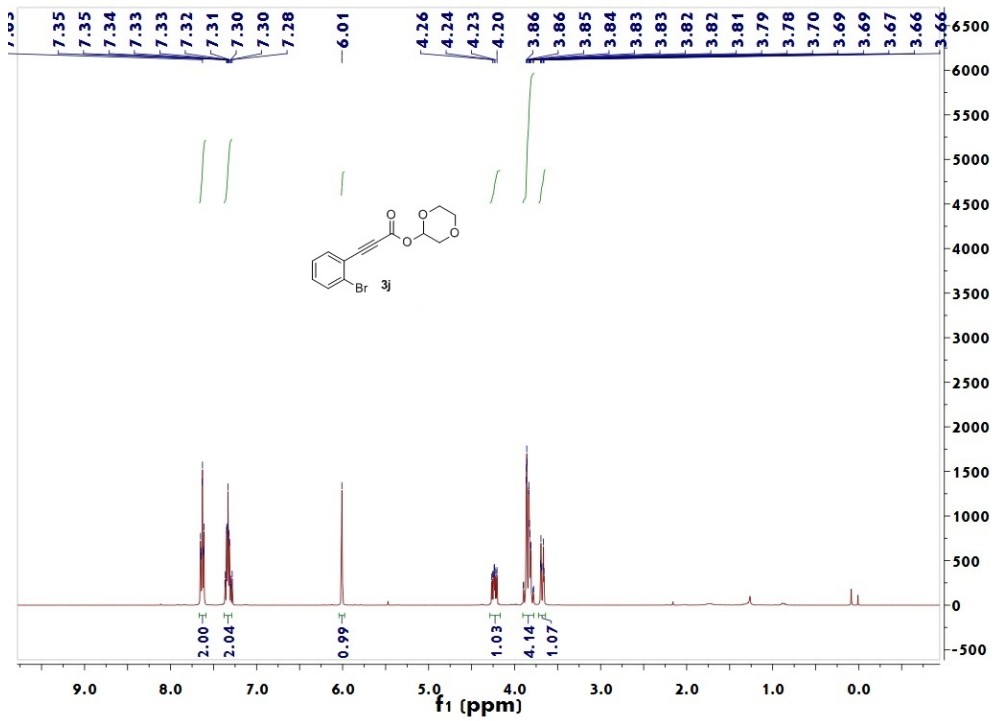


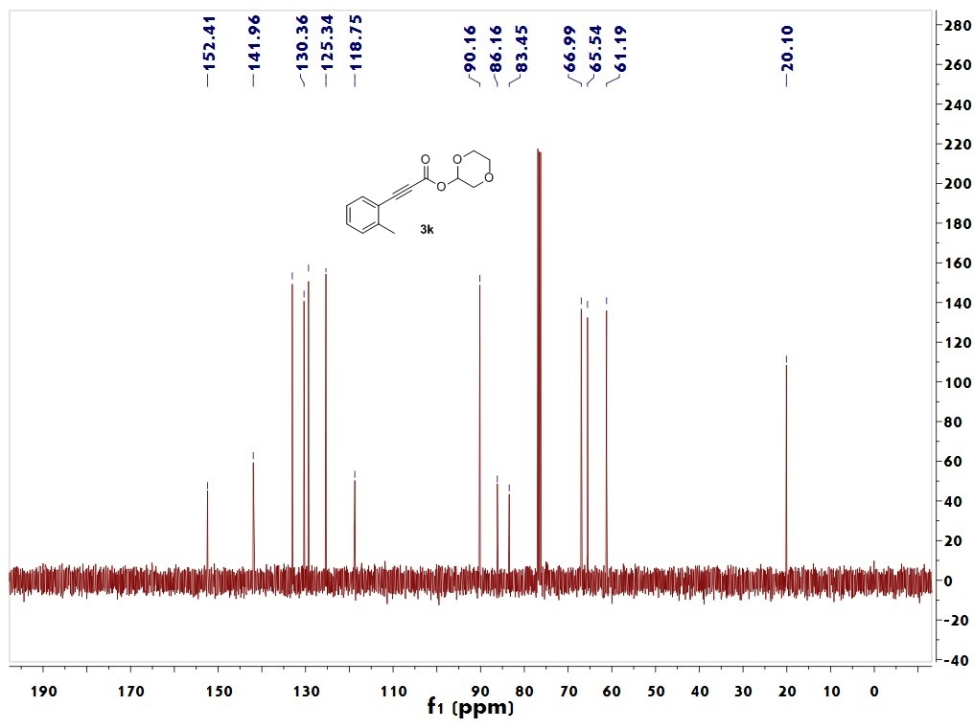
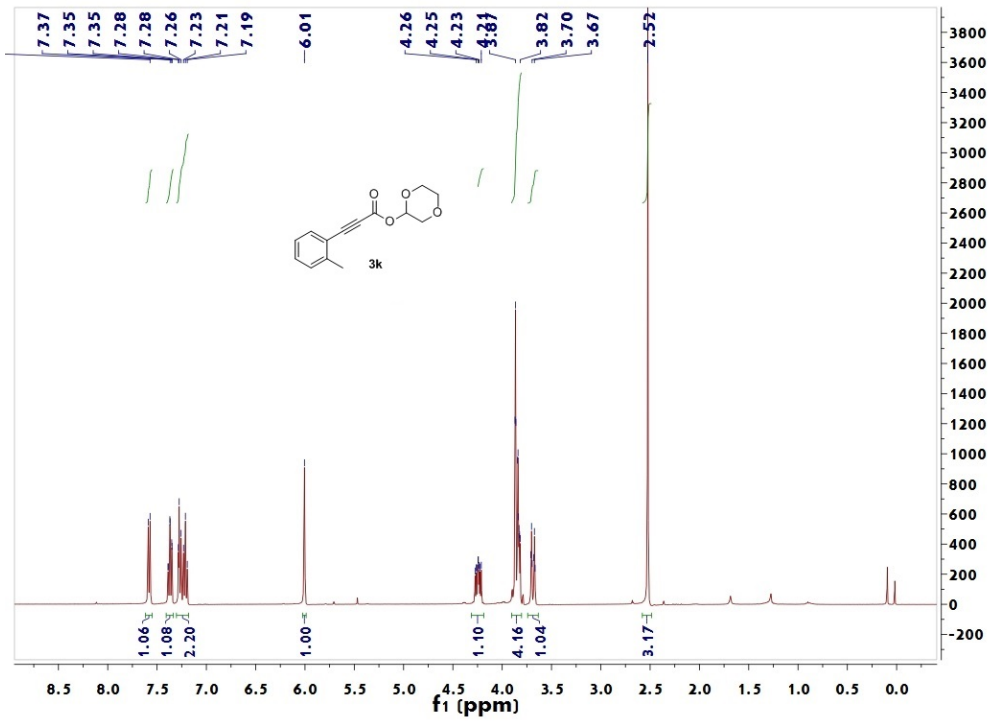


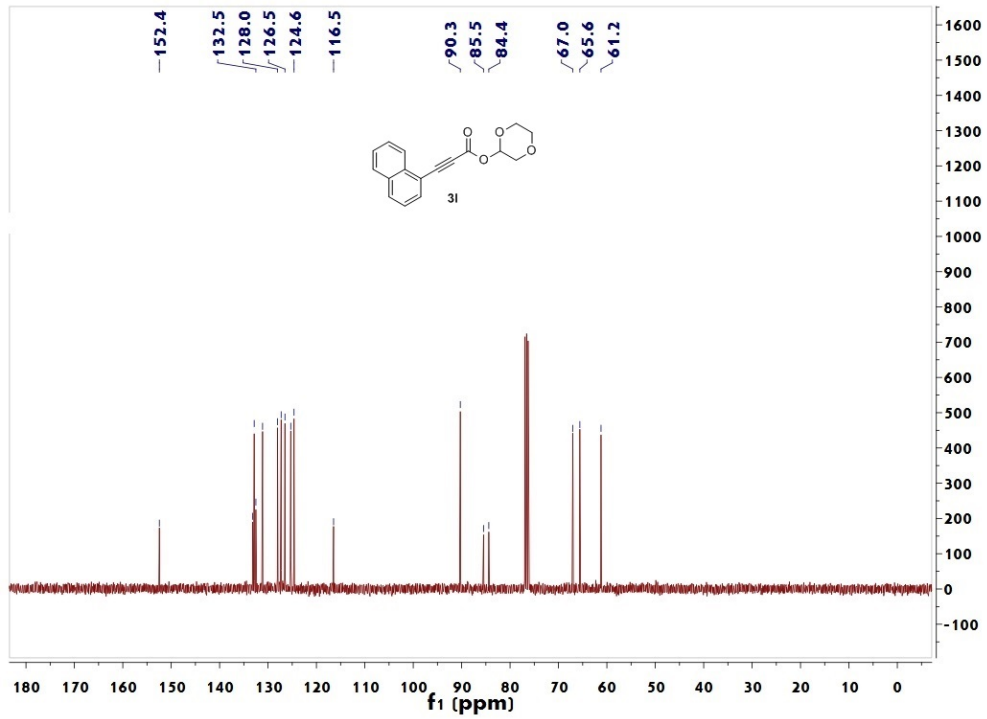
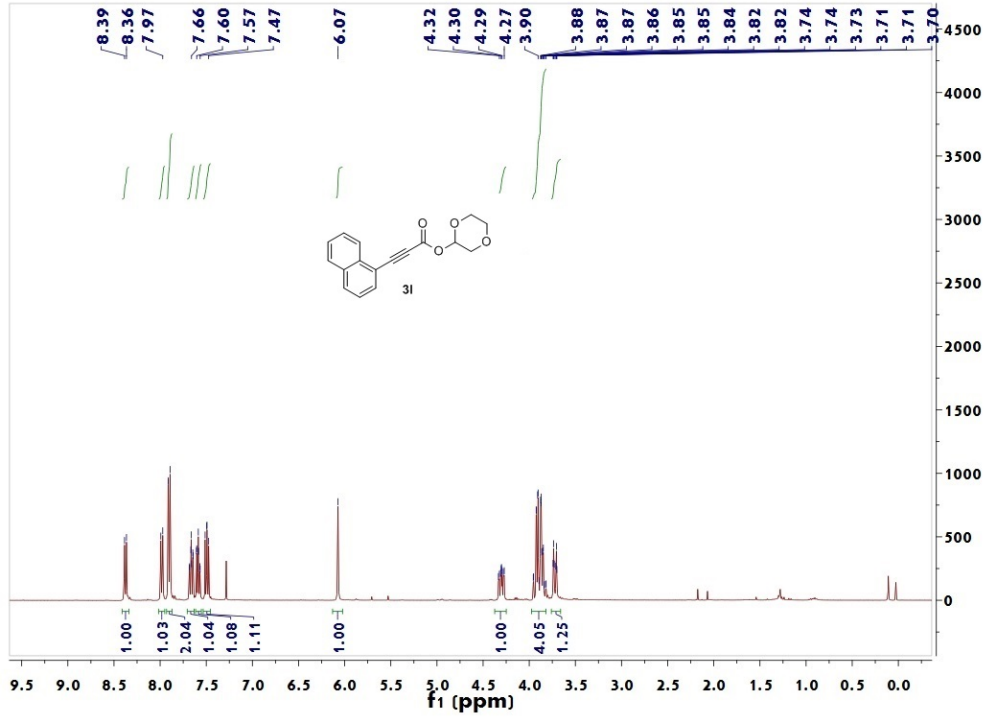


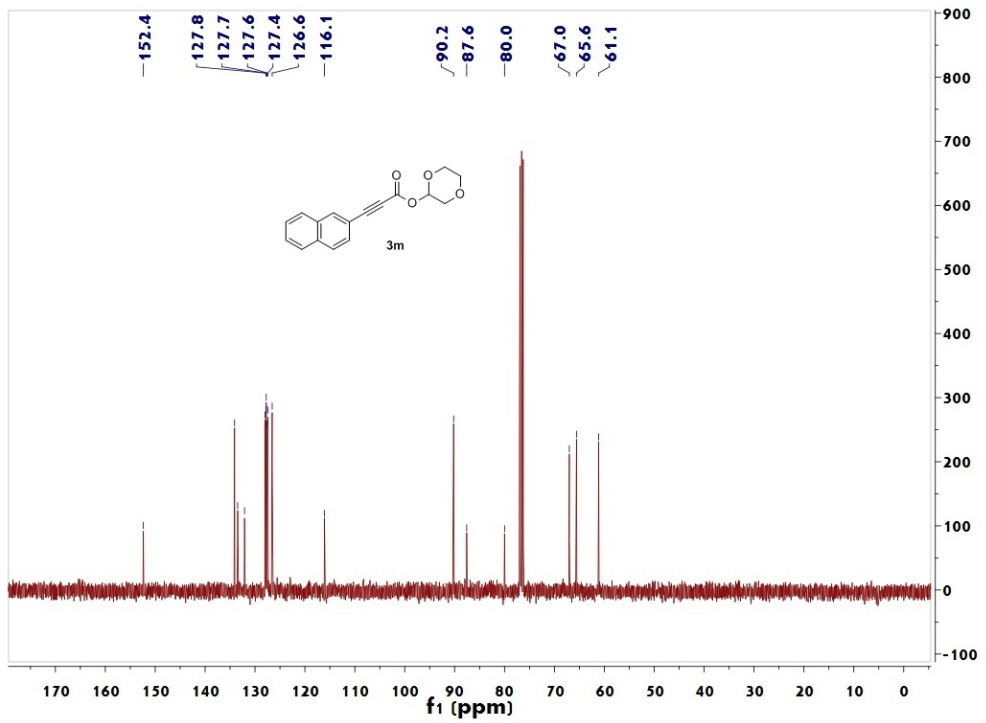
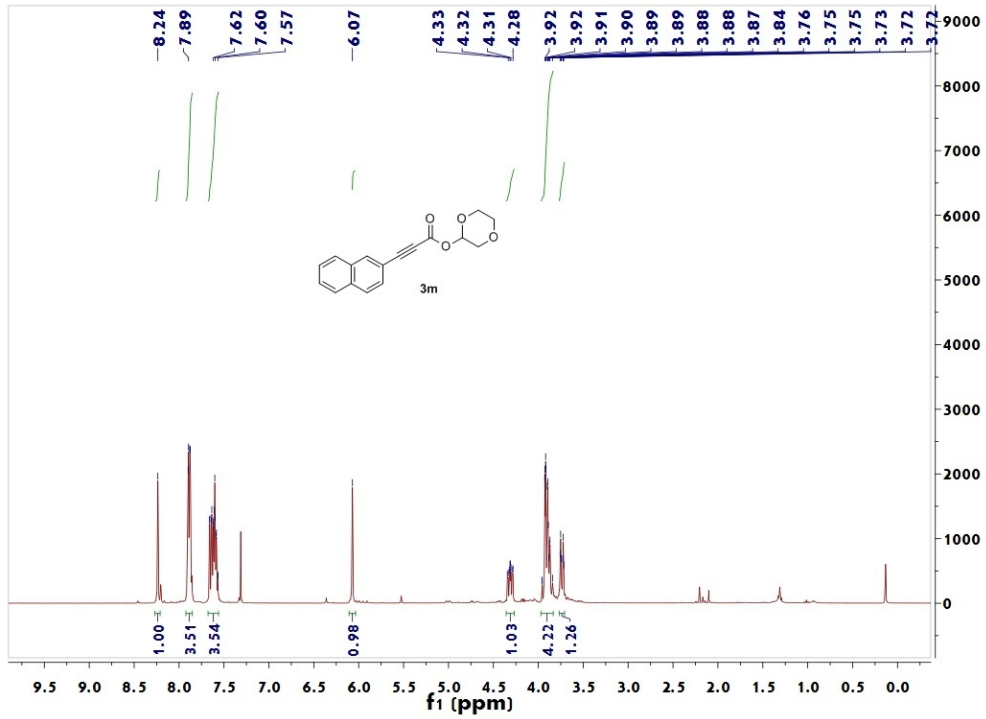


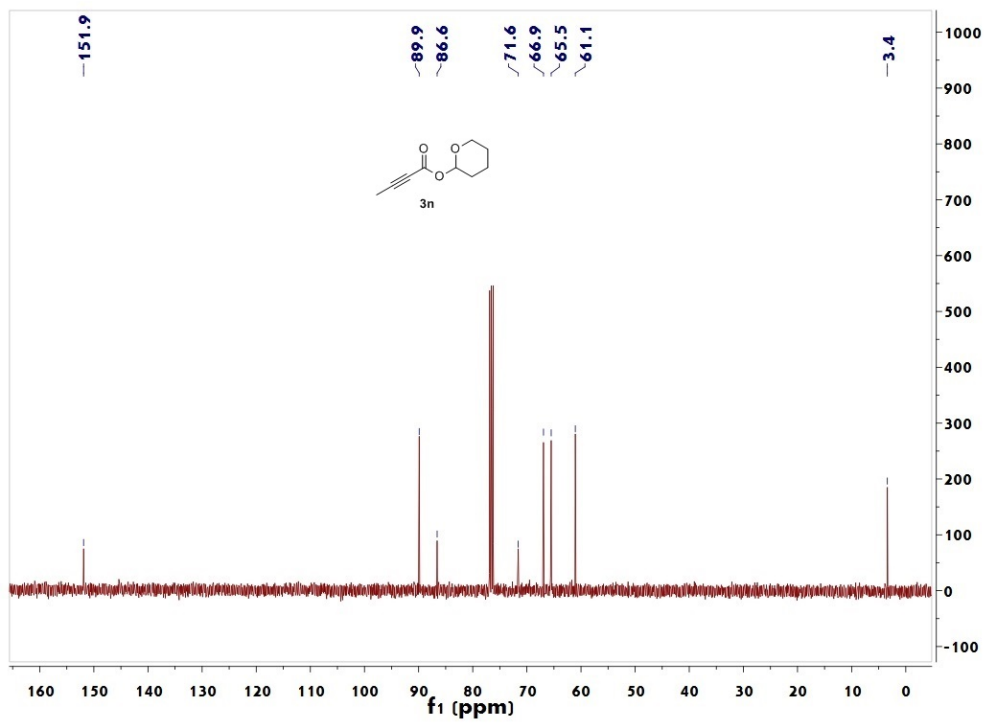
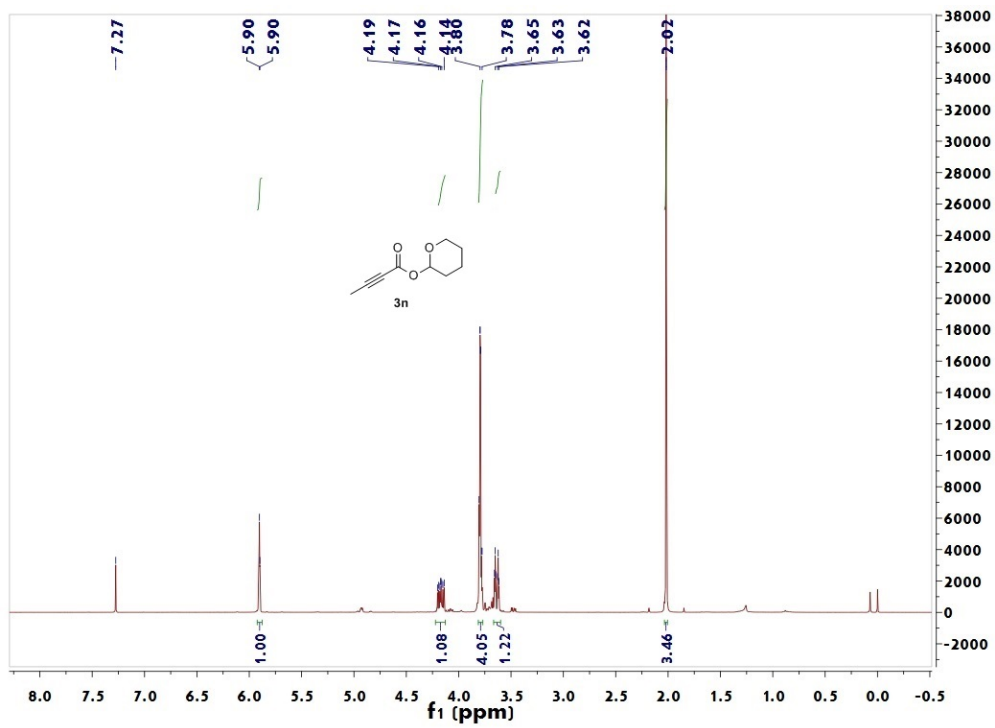


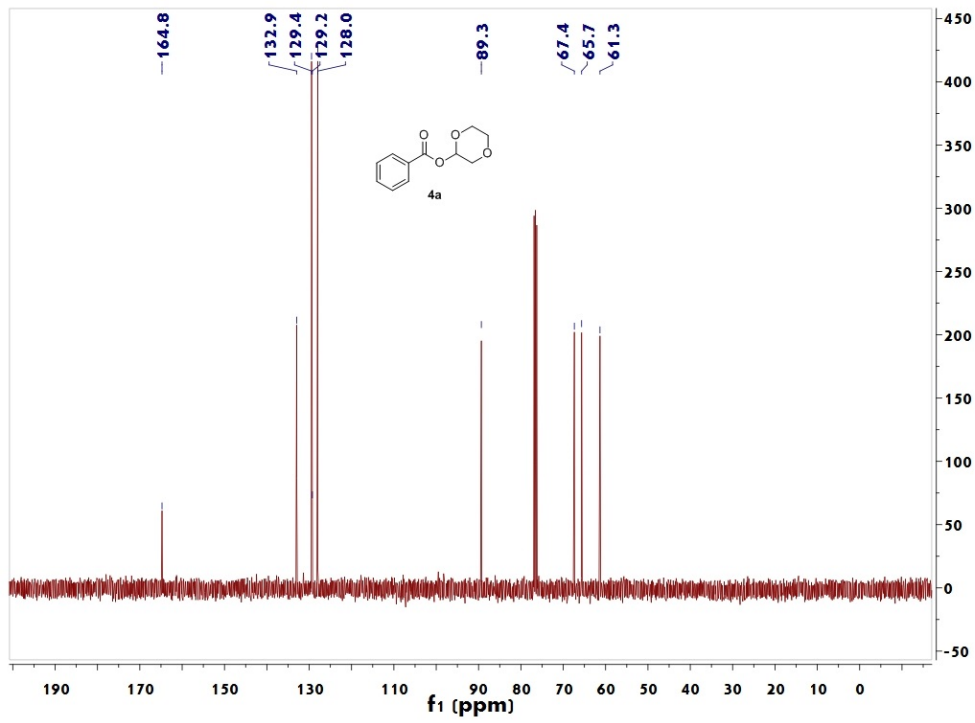
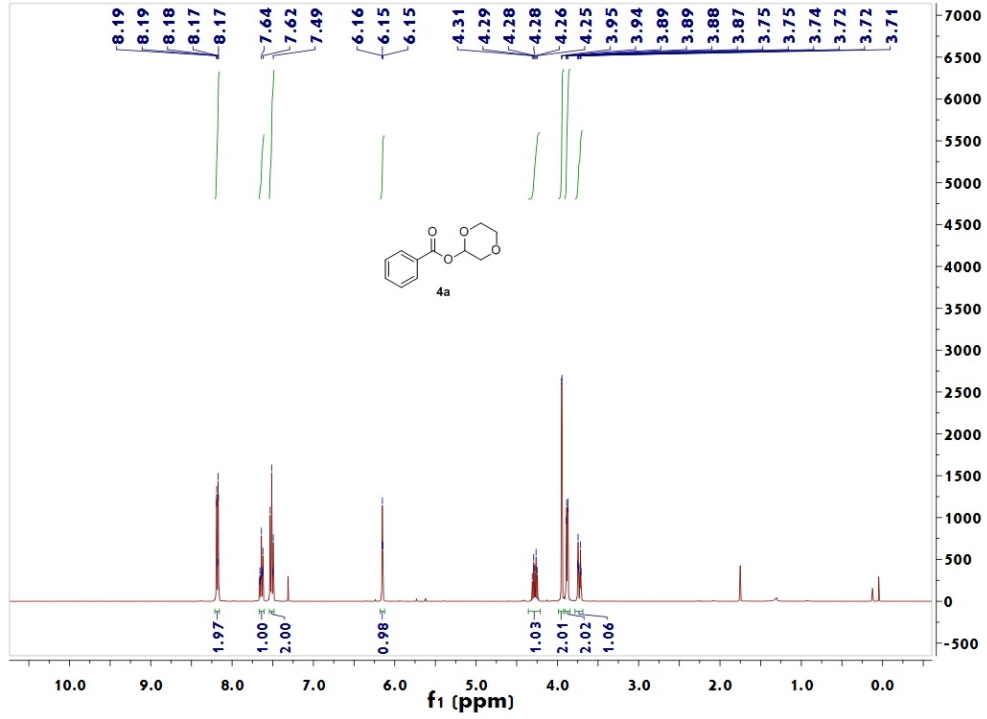


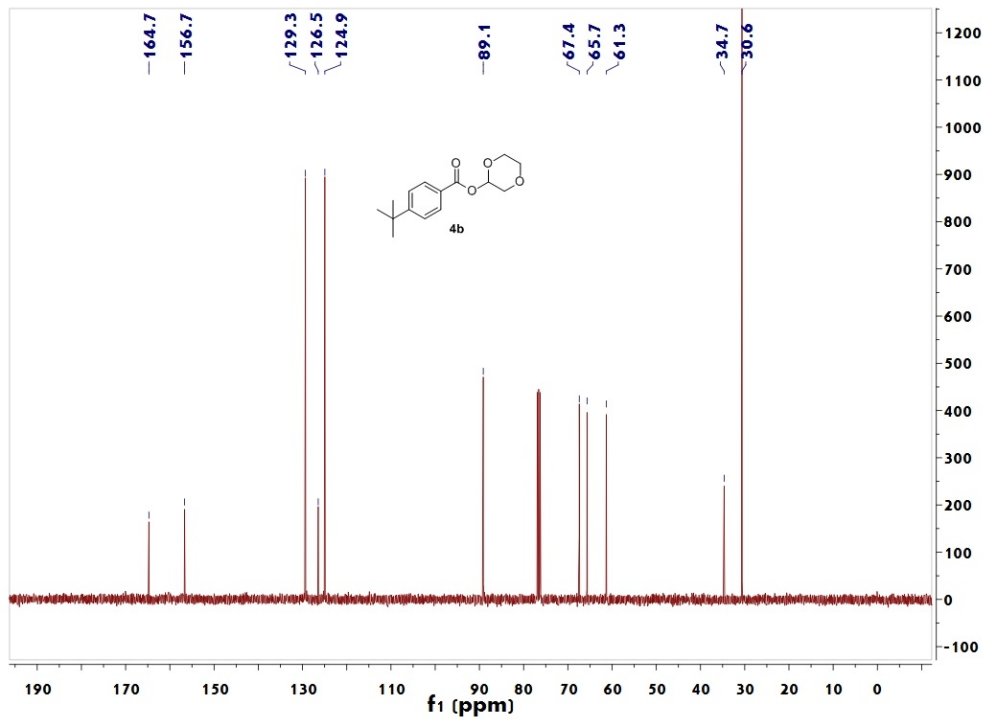
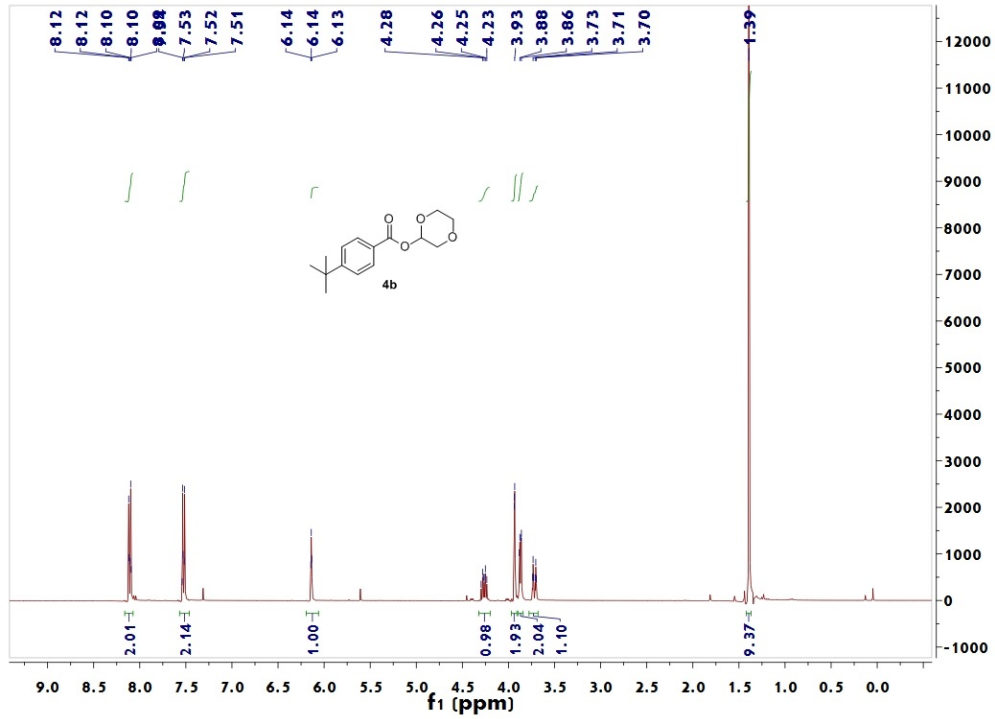


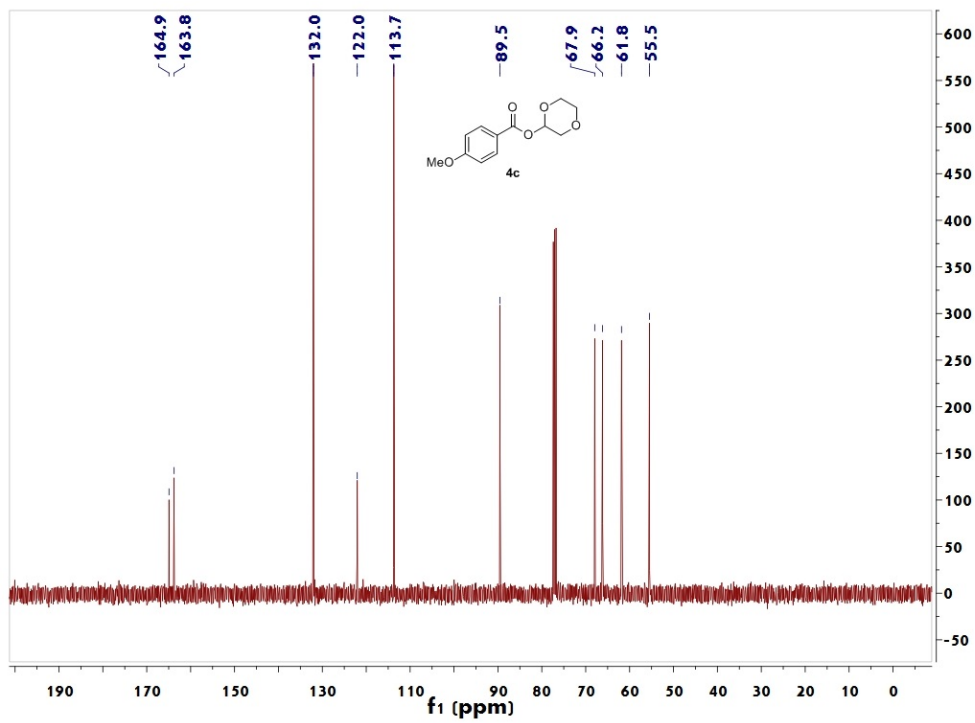
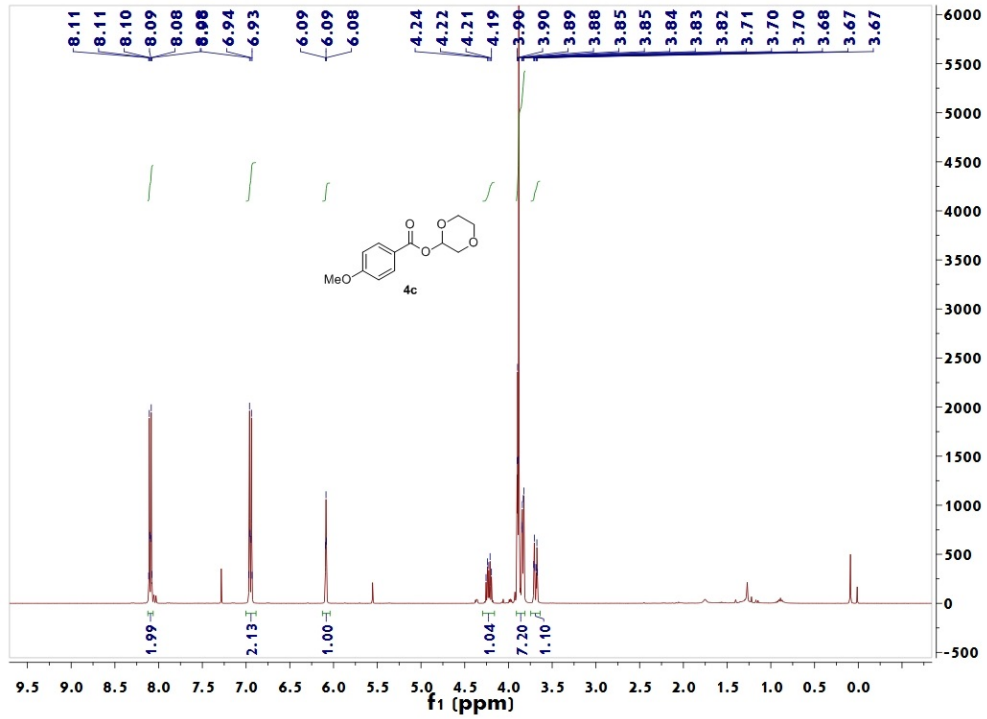


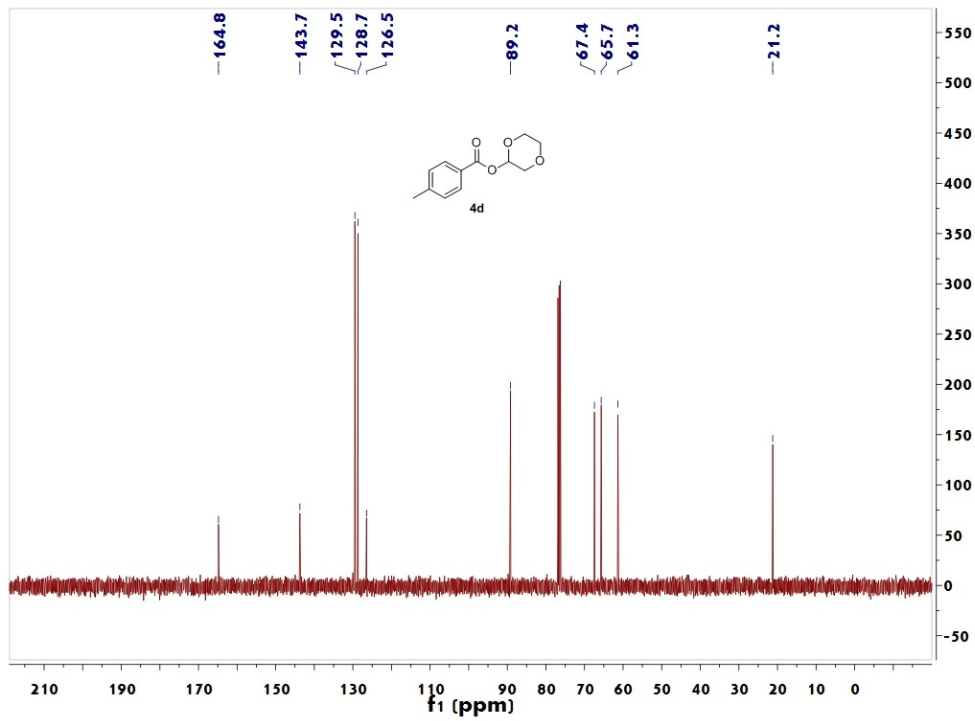
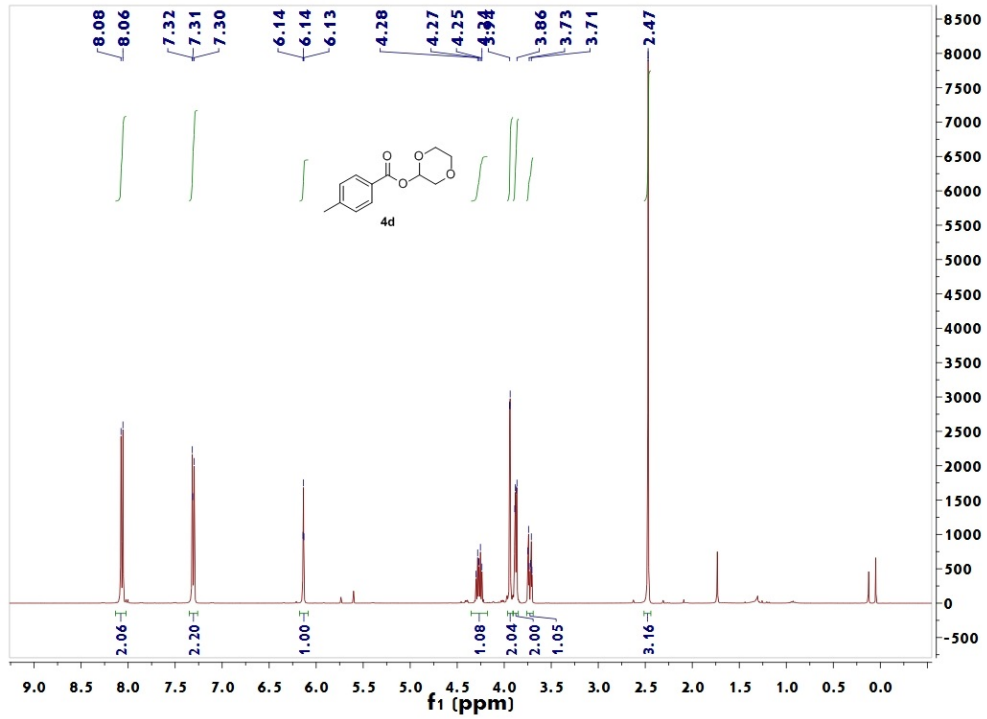


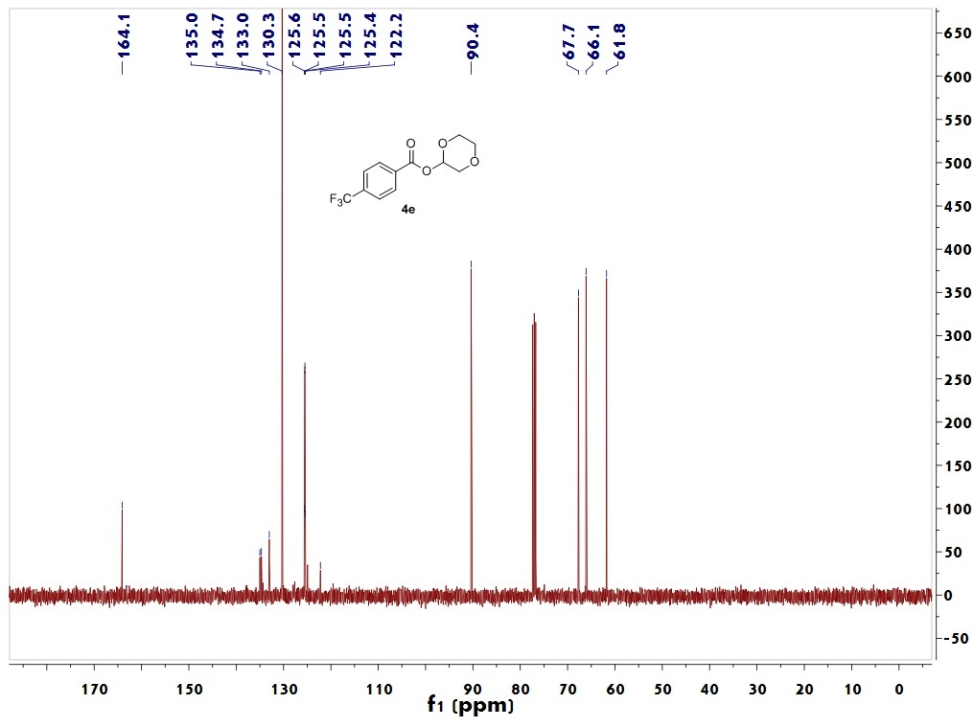
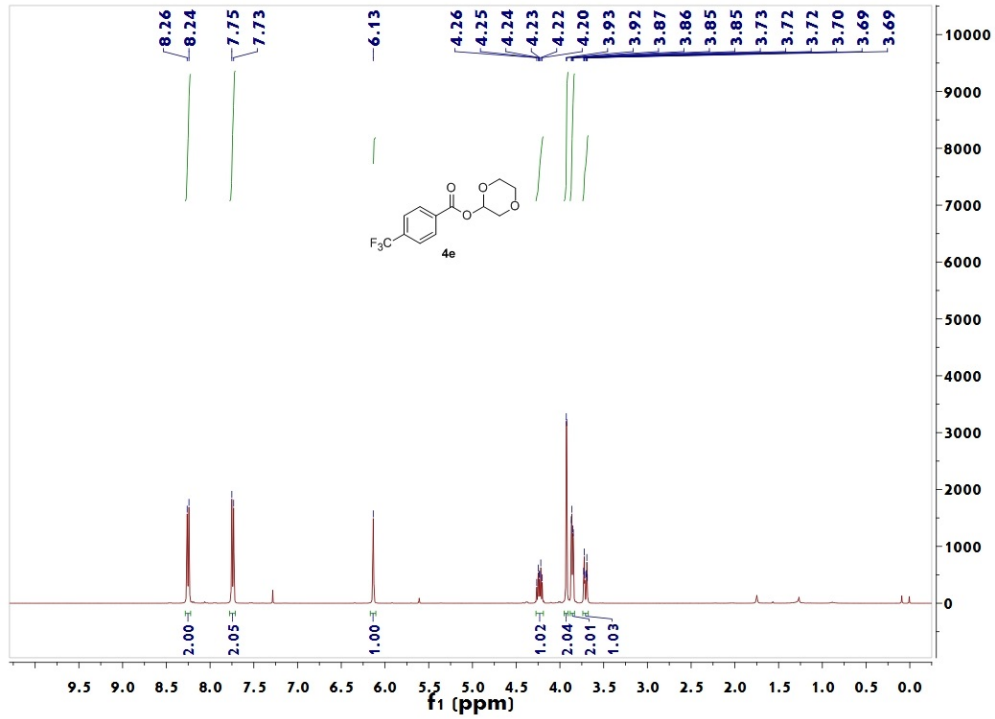


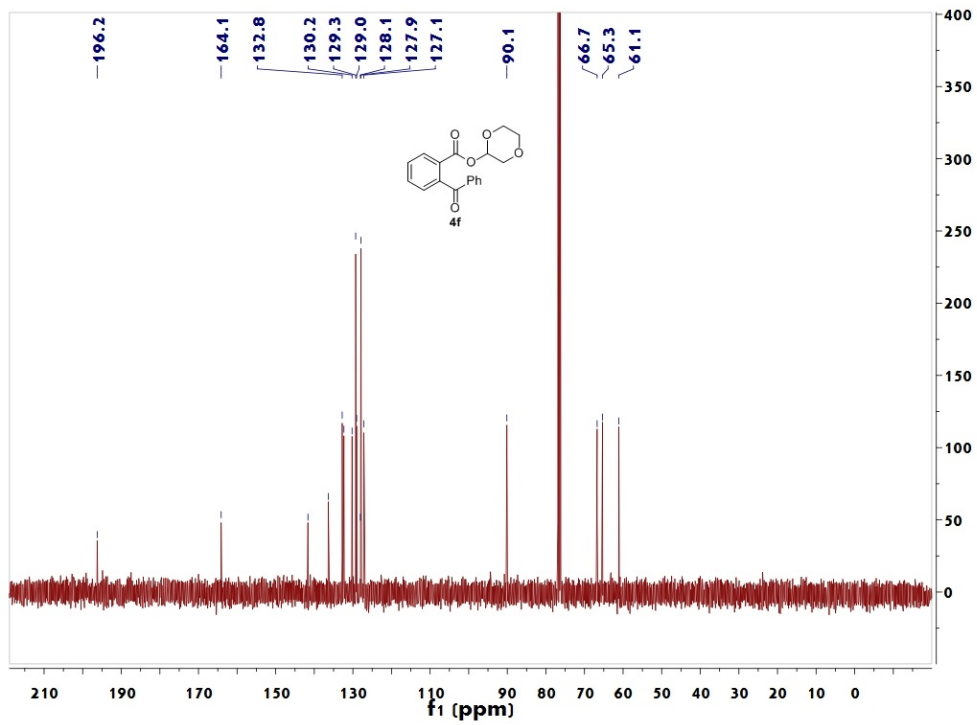
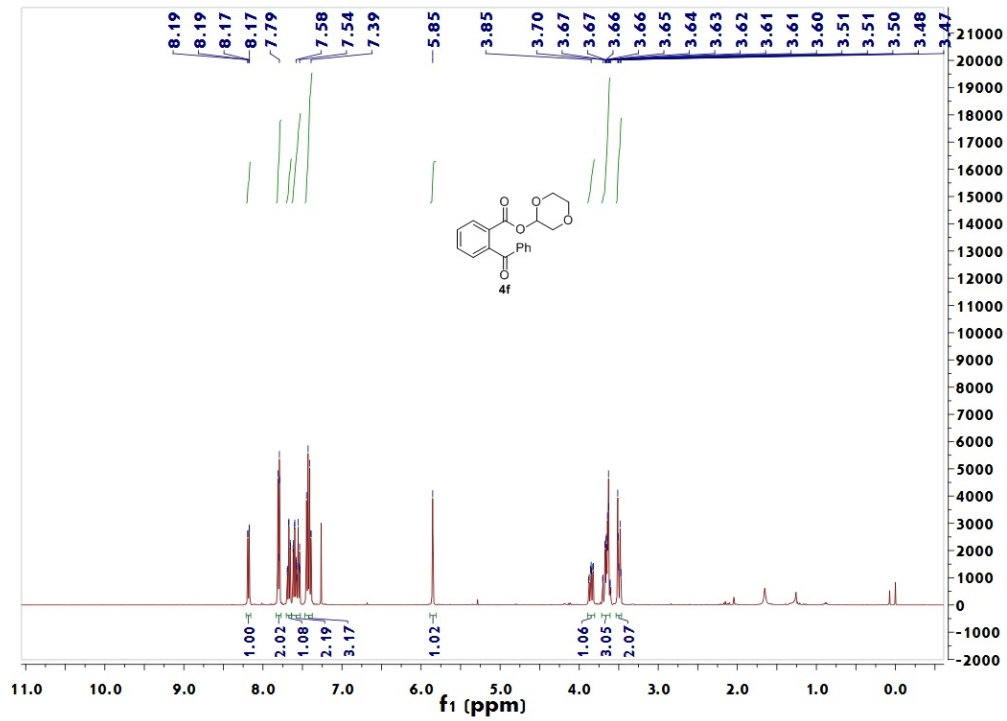


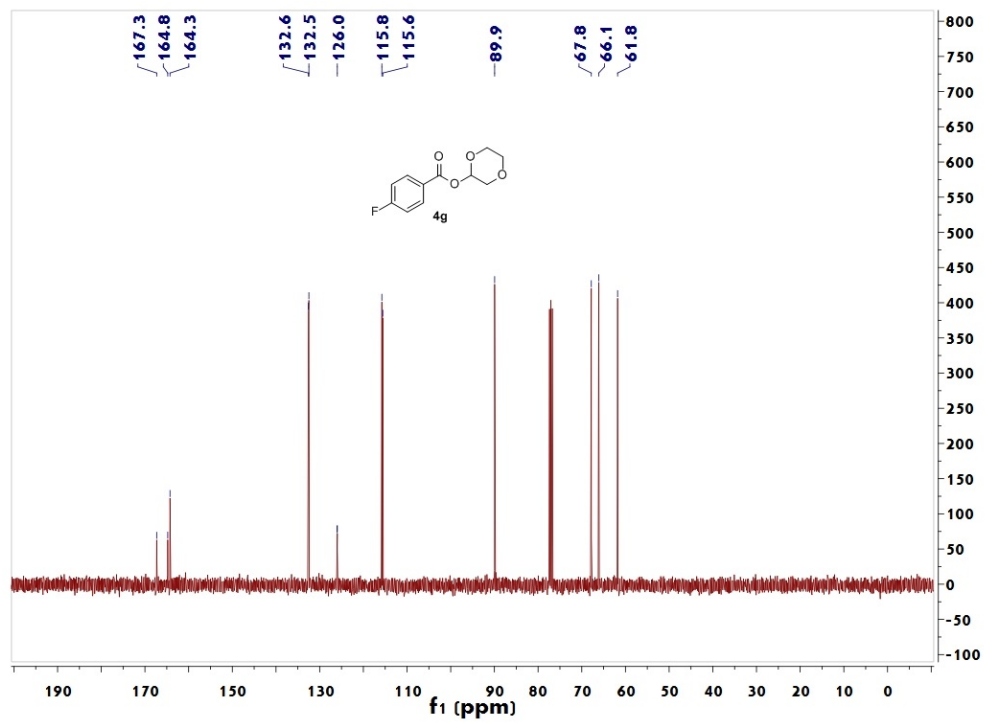
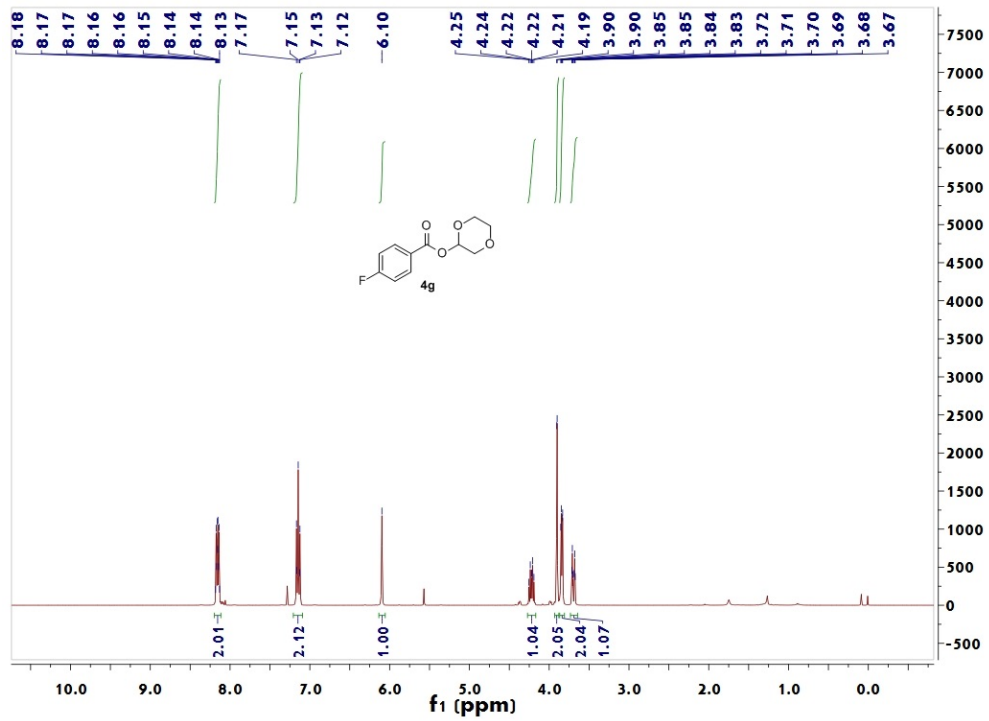


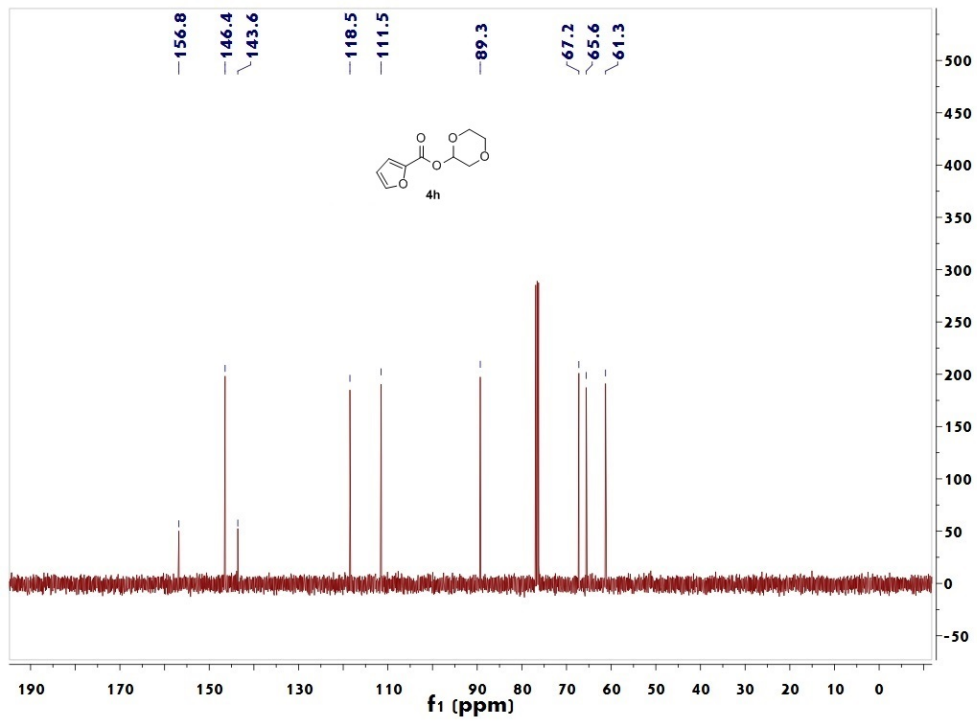
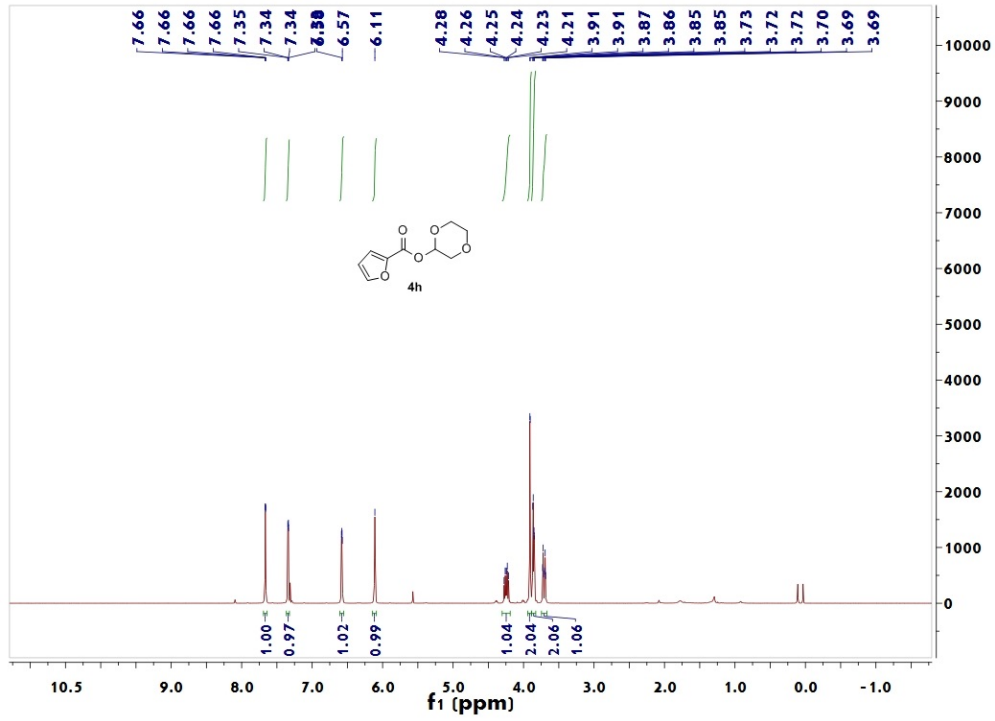


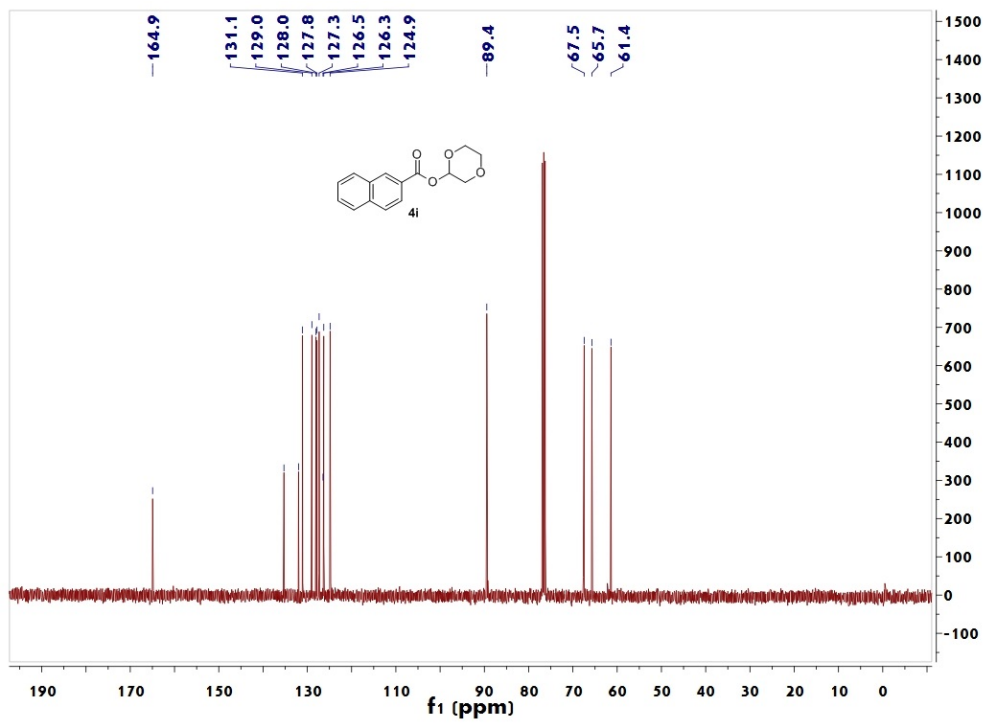
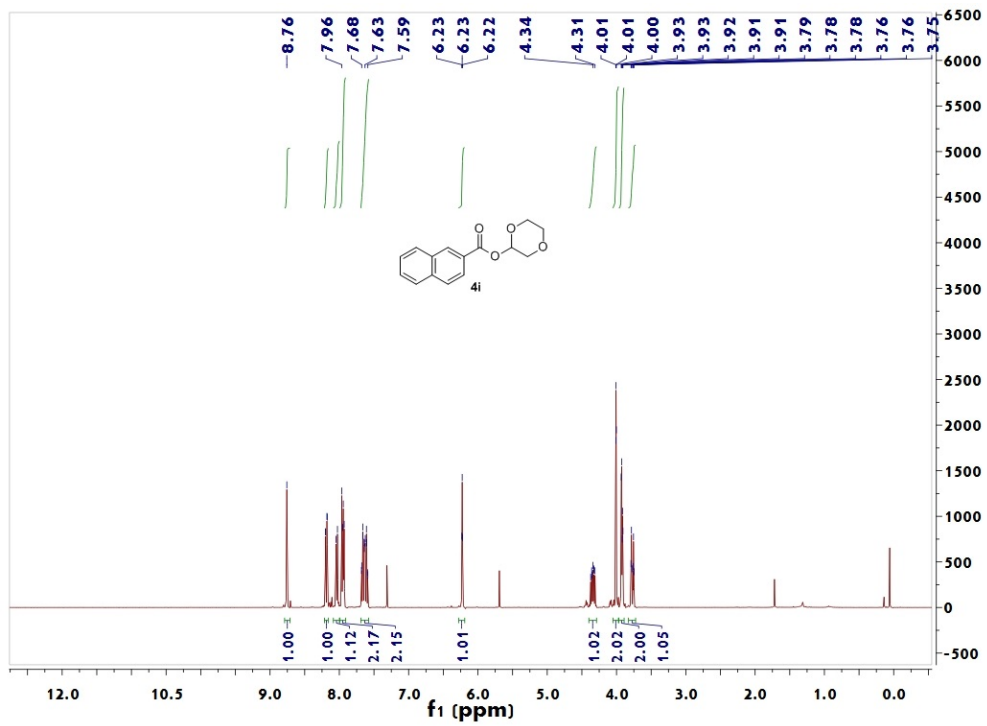


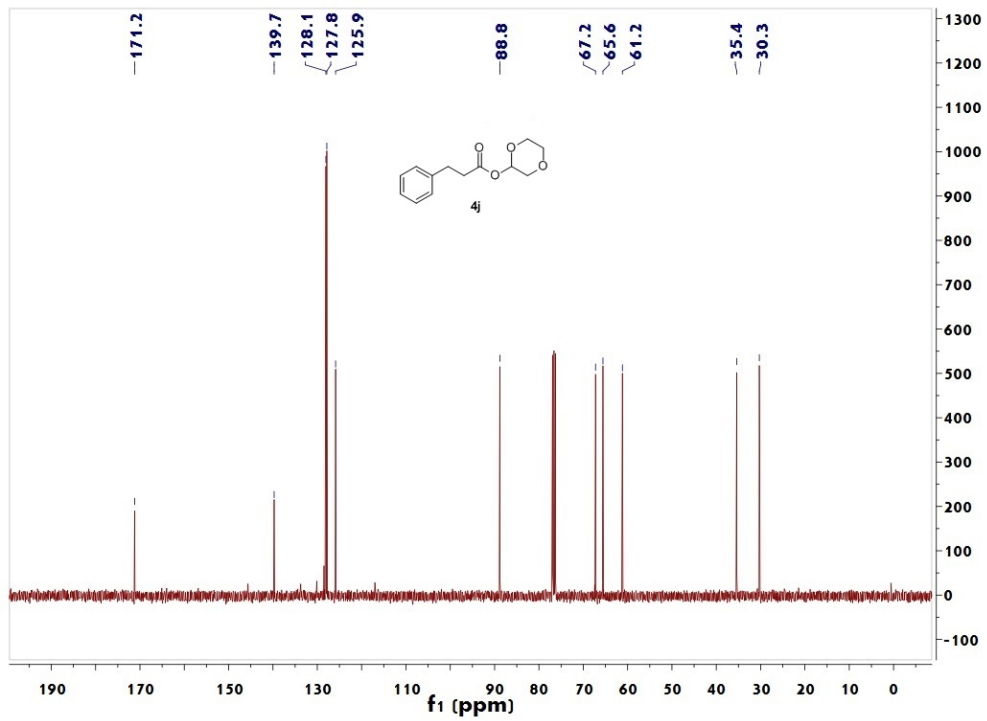
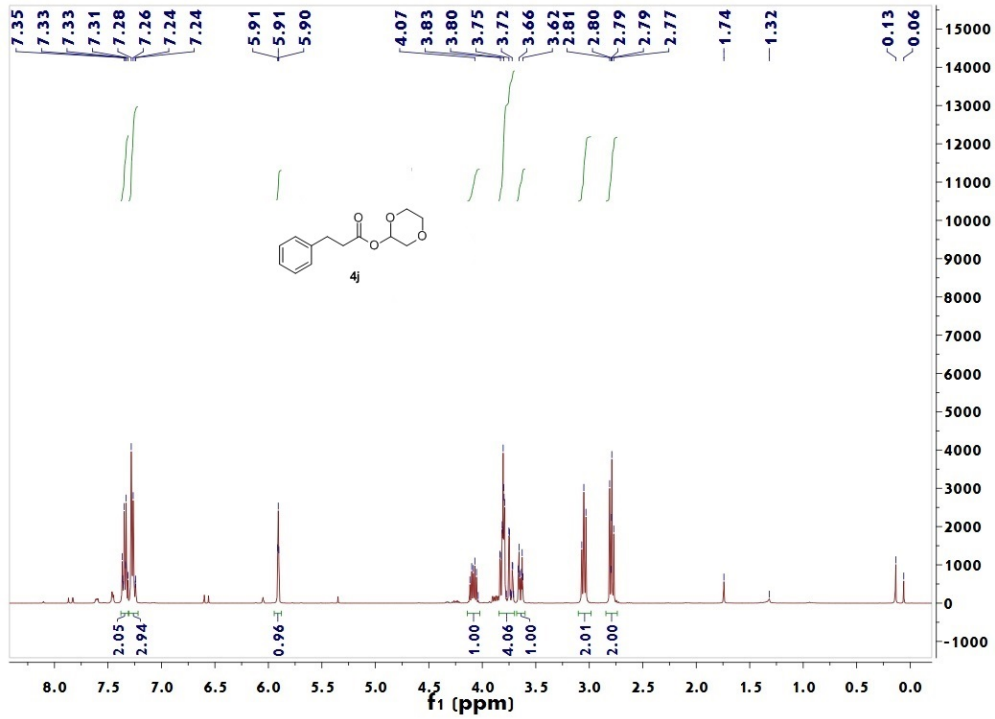


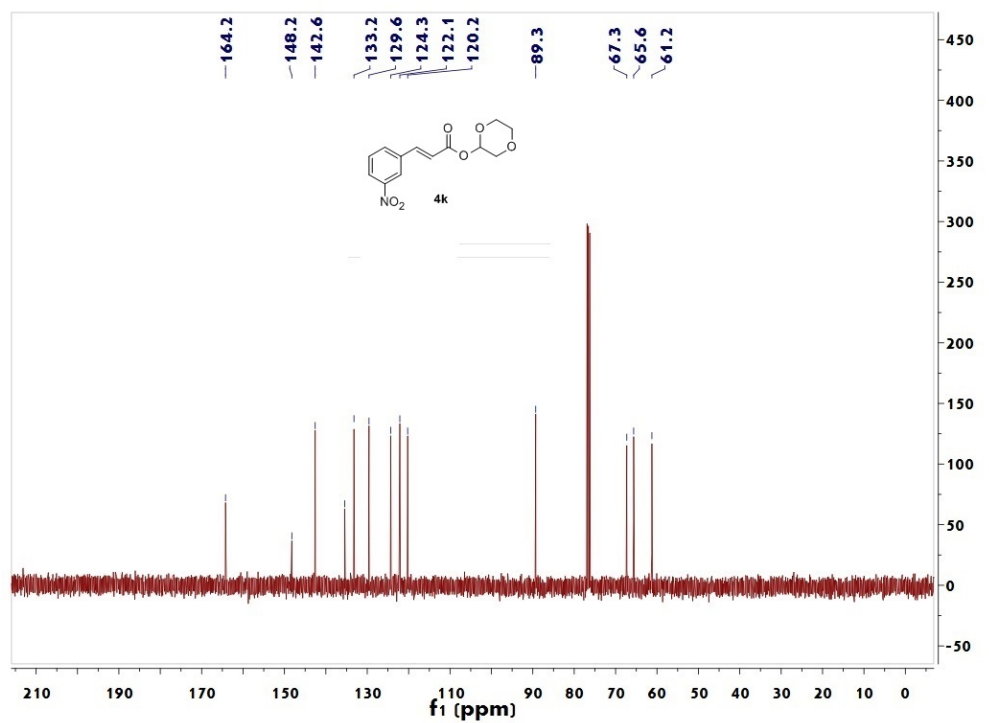
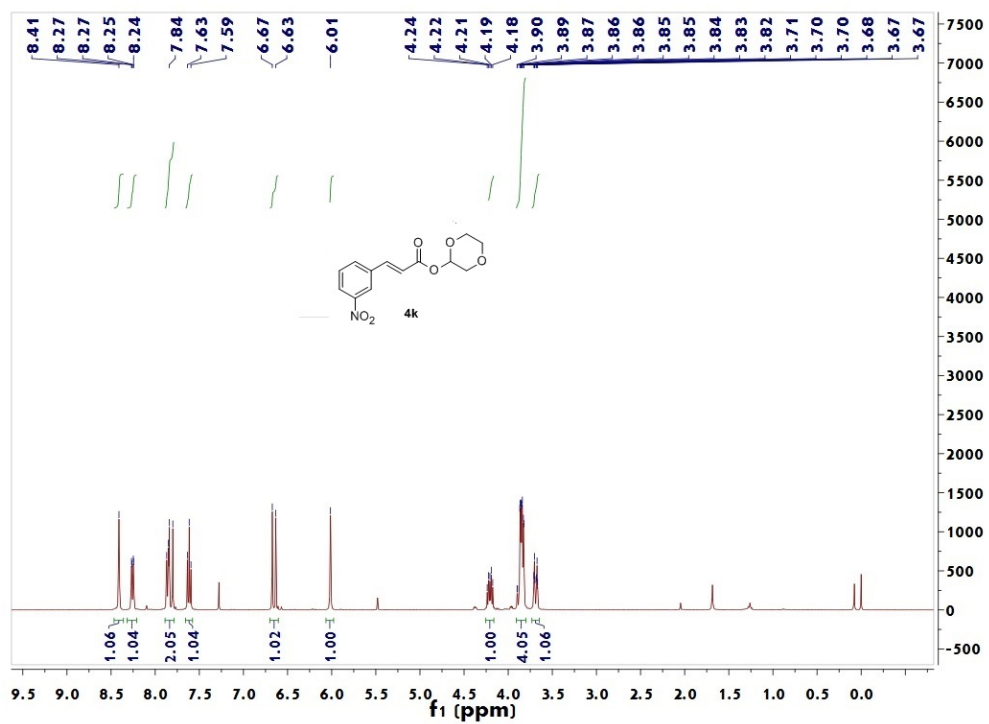


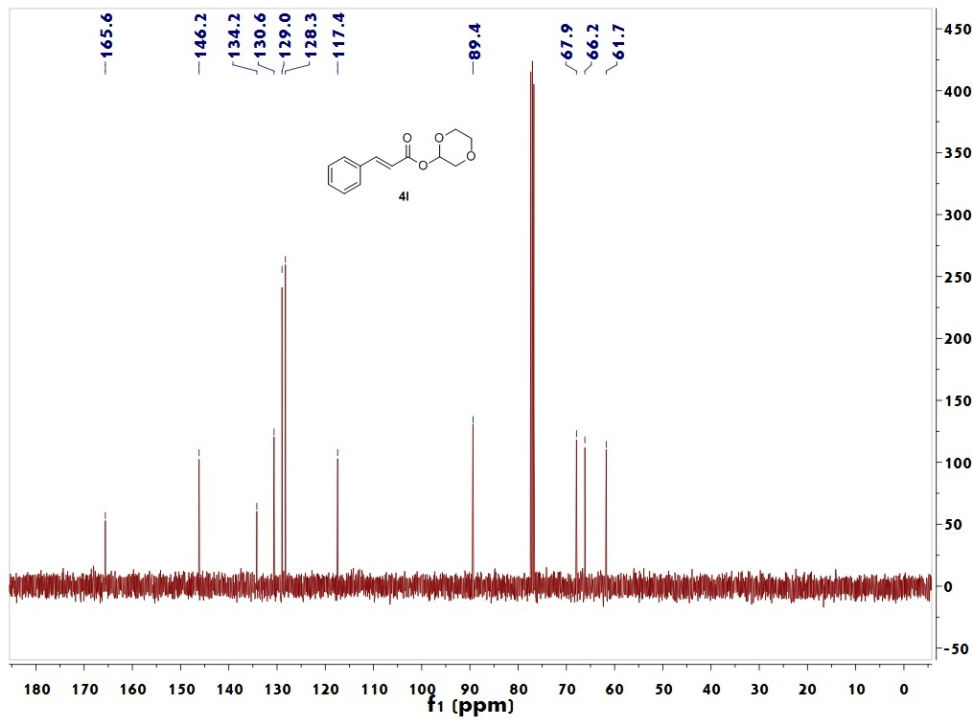
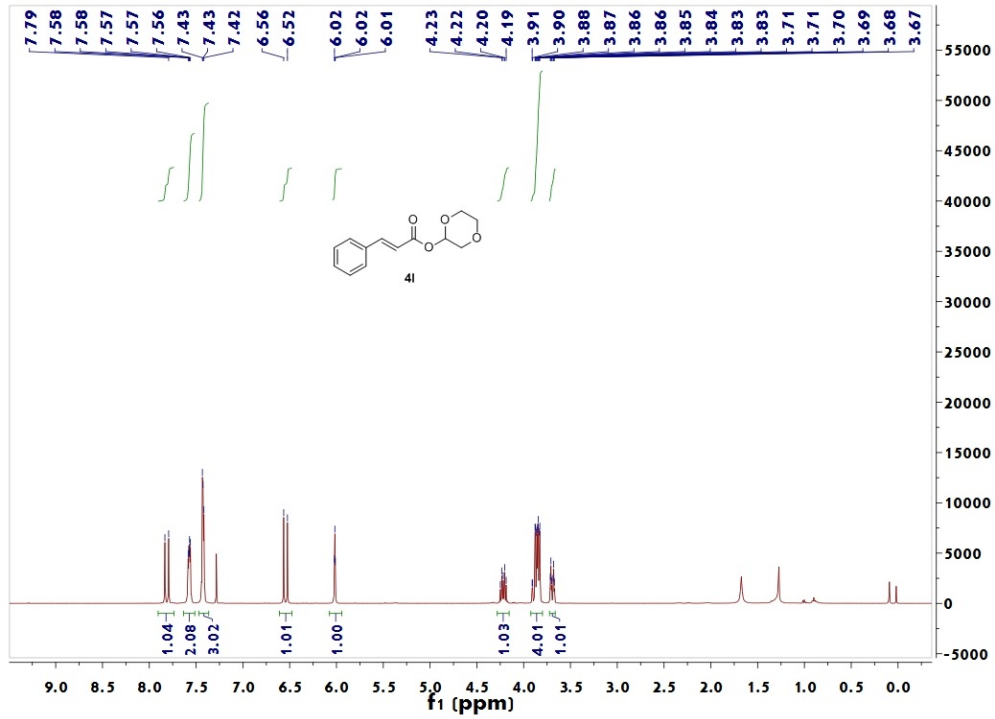


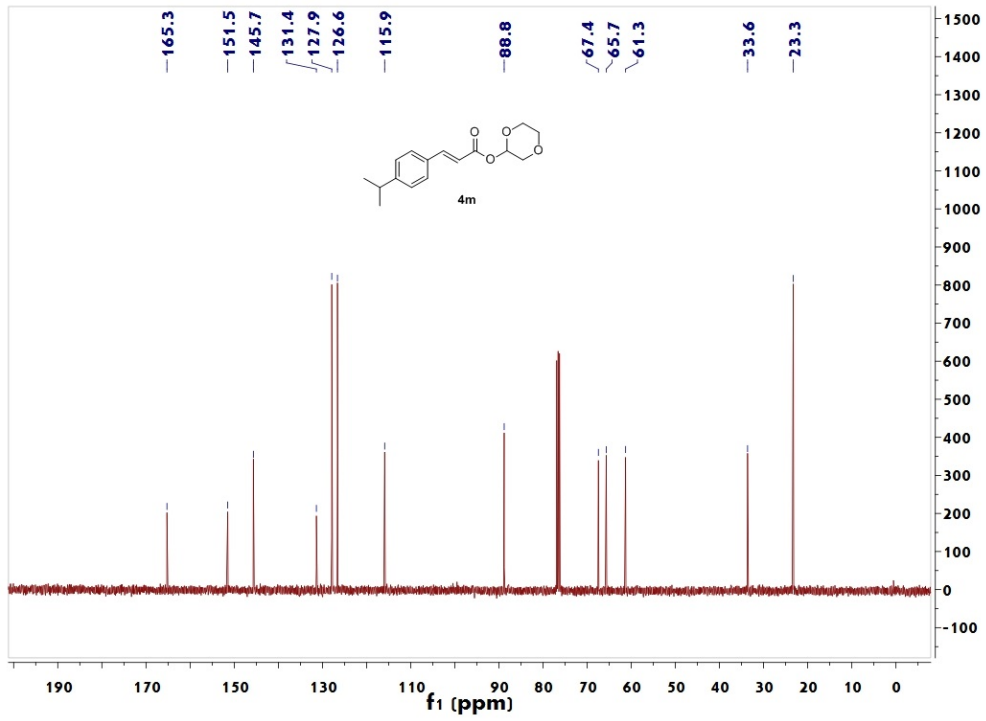
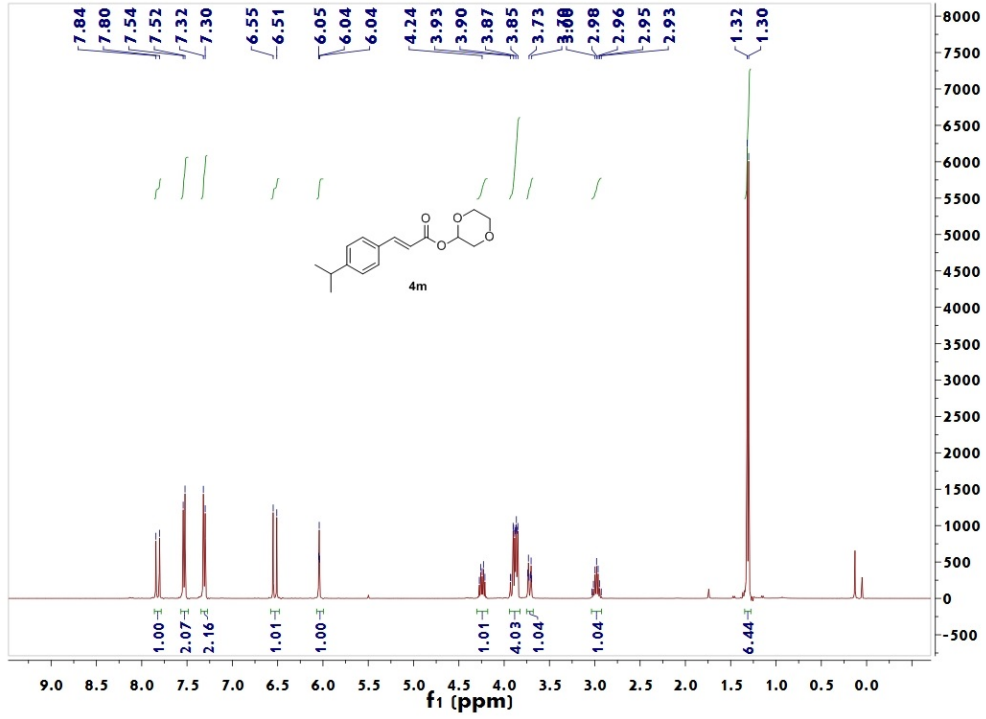


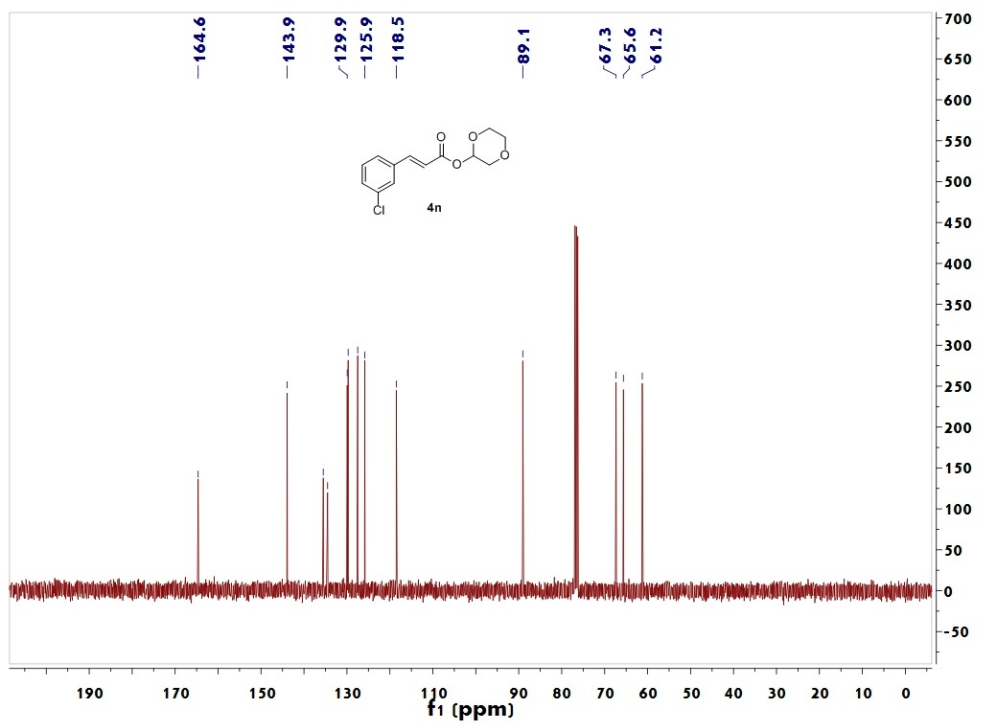
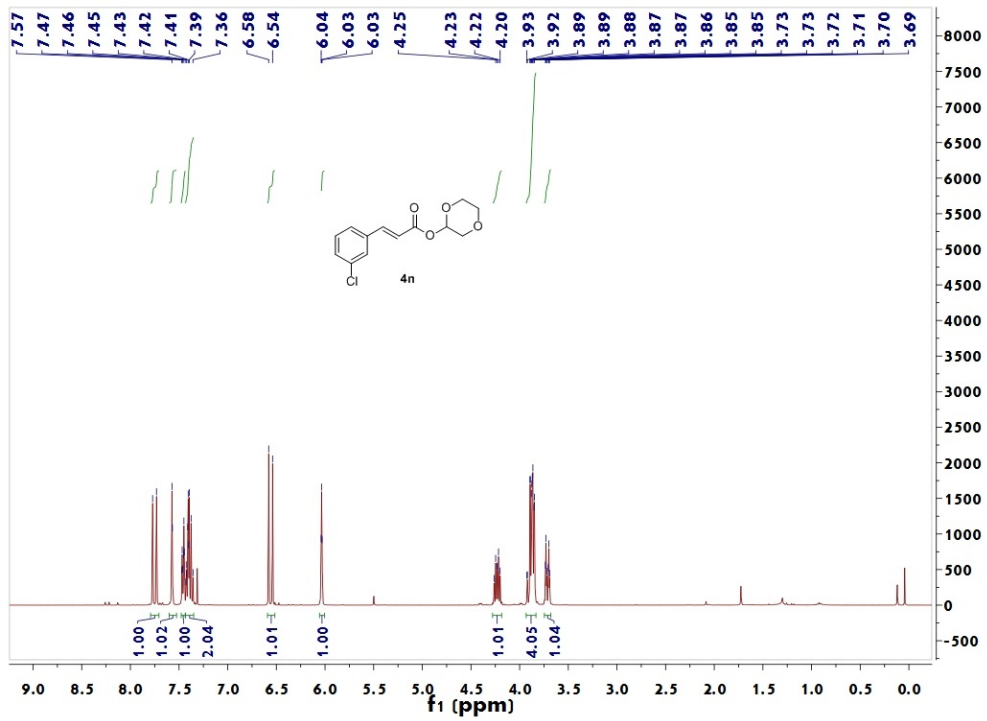


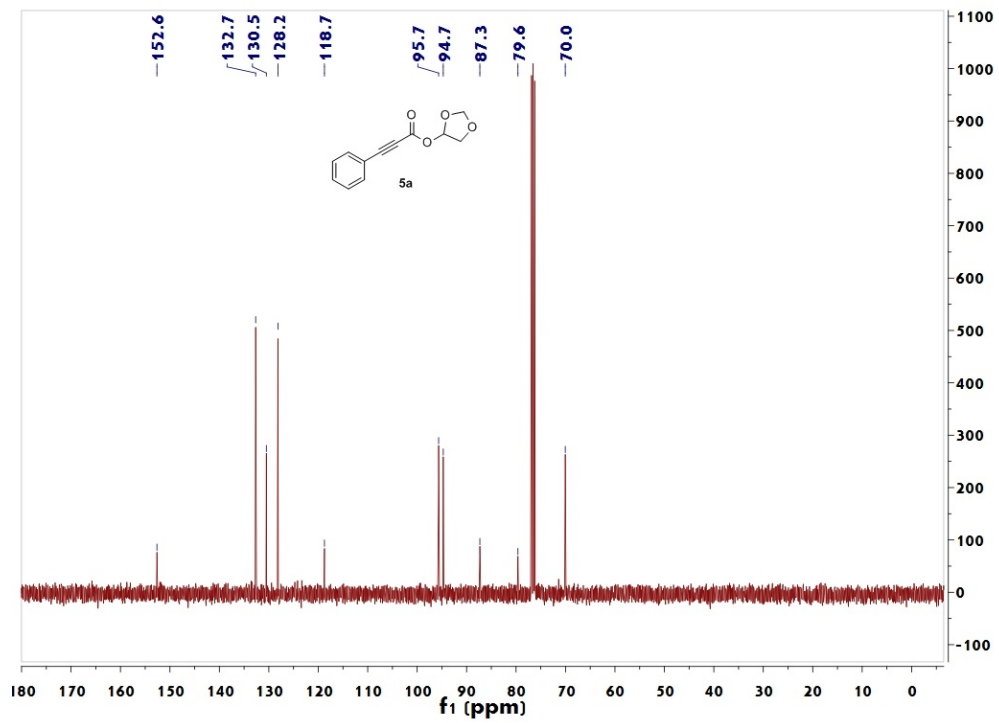
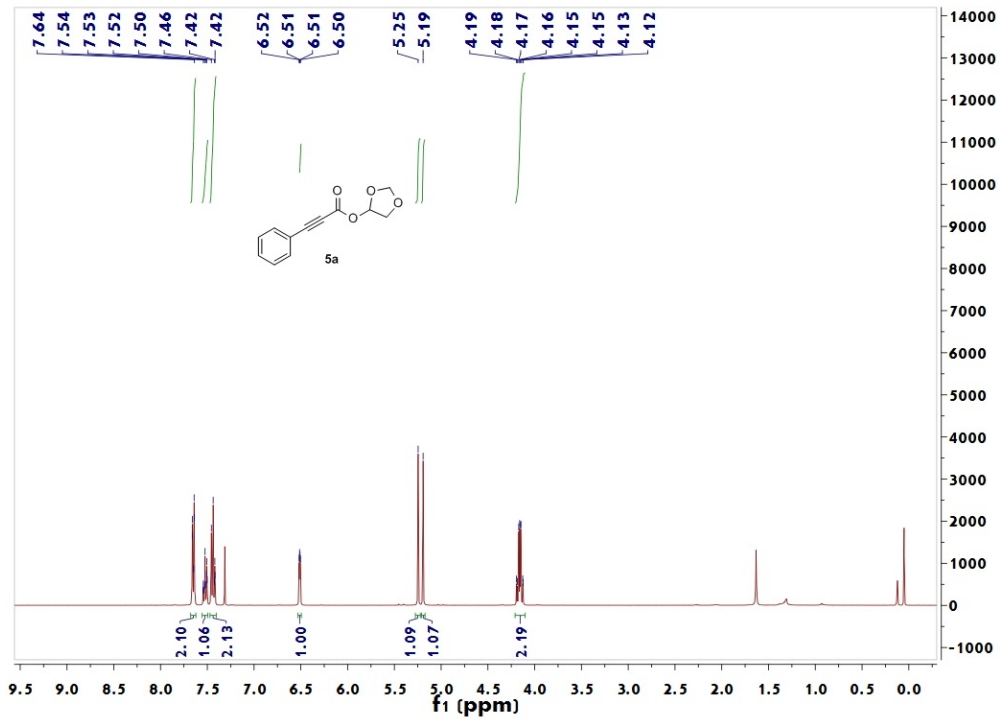


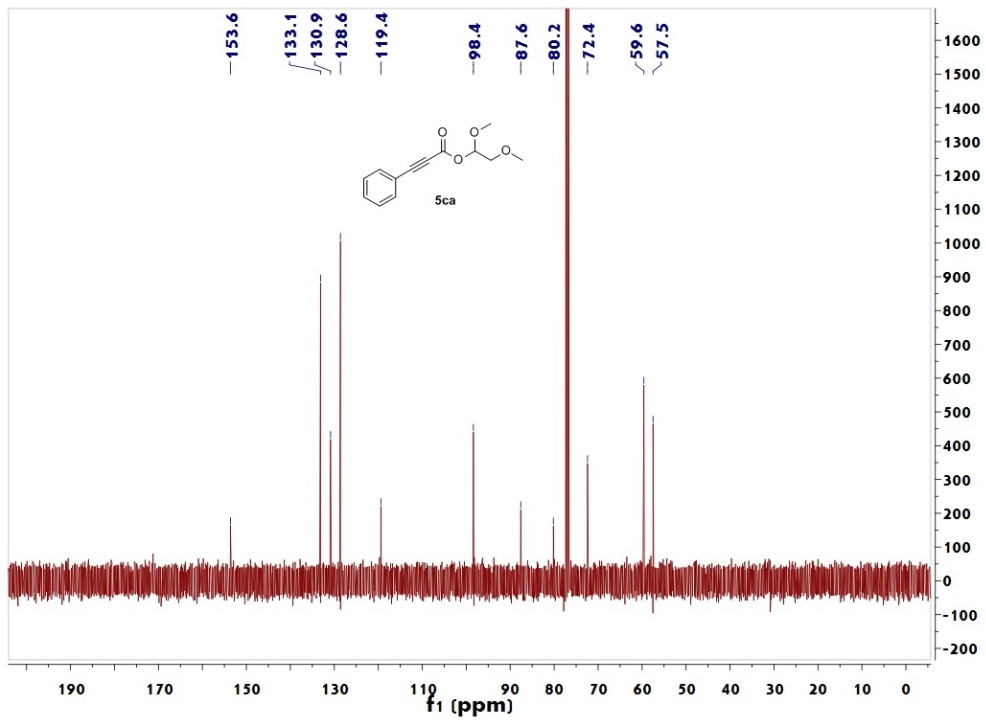
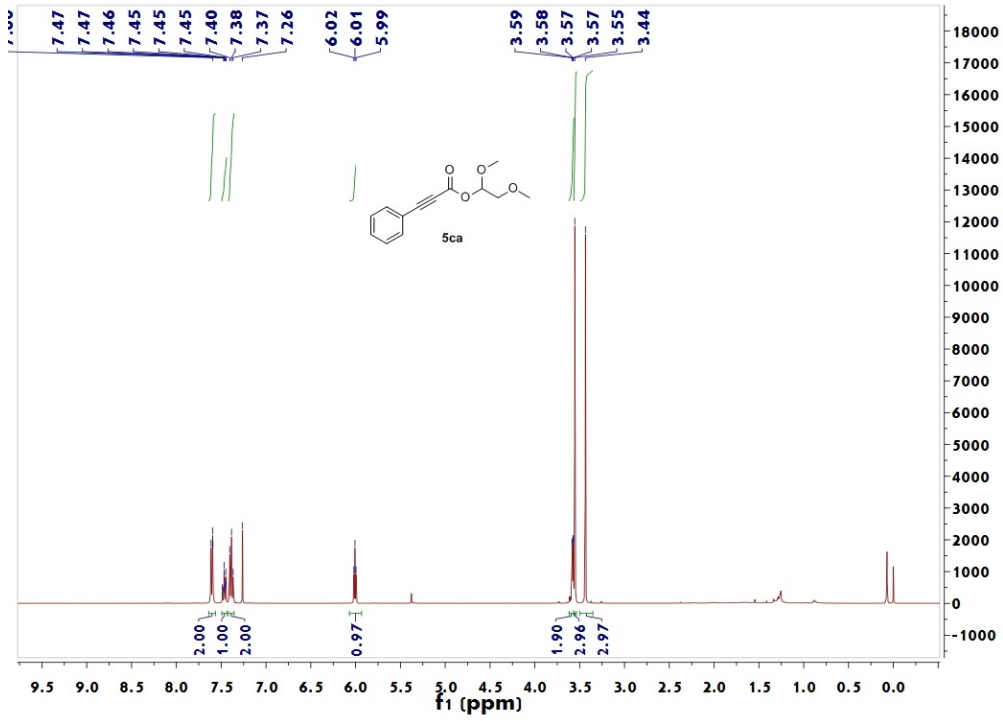


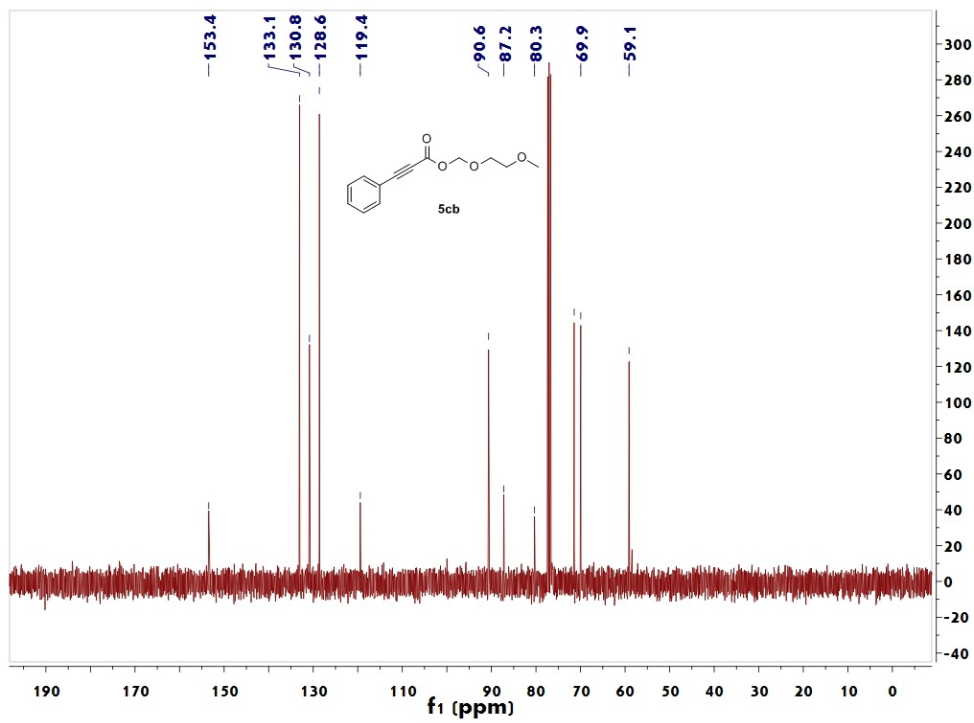
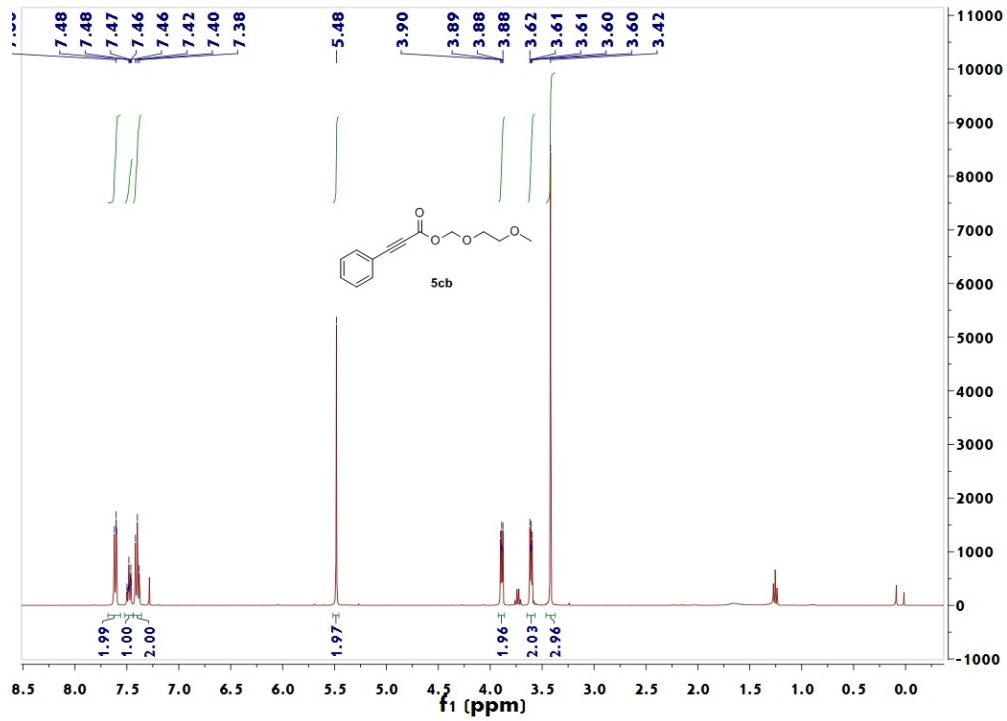




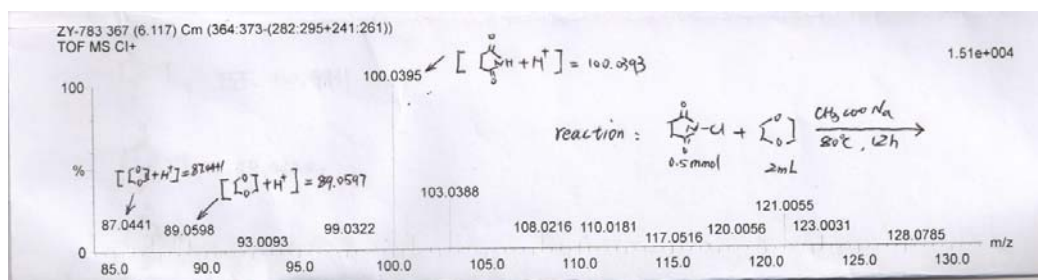








Copy of HR-MS Spectra:



Proton NMR Observation of Intermediates A and D:

