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SUPPORTING INFORMATION

Copper–Catalyzed Oxidative Acyloxylation of C(sp^3)–H bond Adjacent to Oxygen by Cross–Dehydrogenative Coupling Approach.

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1. General Information:

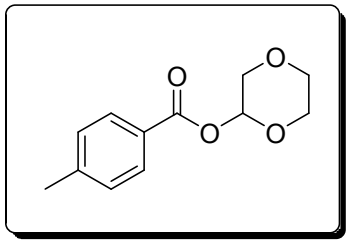
All solvents and reagents were used, as received from the suppliers. TLC was performed on Merck Kiesel gel 60, F_{254} plates with the layer thickness of 0.25 mm. Column chromatography was performed on silica gel (100-200 mesh) using a gradient of ethyl acetate and hexane as mobile phase. Melting points were determined on a Fisher John's melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin–Elmer RX-1 FT-IR system. ^{1}H NMR spectral data were collected at 300, 400 & 500 MHz, while ^{13}C NMR were recorded at 75, 100, 150 MHz. ^{1}H NMR spectral data are given as chemical shifts in ppm followed by multiplicity (s- singlet; d- doublet; t- triplet; q- quartet; m- multiplet), number of protons and coupling constants. ^{13}C NMR chemical shifts are expressed in ppm. HRMS (ESI) spectral data were collected using ORBITRAP High Resolution Mass Spectrometer.

2. General procedure for the synthesis of Acyloxylated products:

A solution of benzyl alcohol 1 (1.0 mmol) $Cu(OAc)_2$ (9 mg, 5 mol%) in 2 mL of the respective ether 2 was stirred at room temperature. To the same solution, a (5–6 M) TBHP solution in decane (4 equiv) was added dropwise before the mixture was heated at 100 ^{0}C (oil bath) for 8 h, under air. After cooling to room temperature, the reaction mixture was extracted with ethyl acetate and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure and was purified by column chromatography (gradient eluent of 5% EtOAc in hexane v/v) to give the desired product

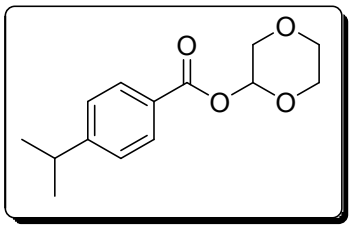
3. Analytical Data for the Products

1,4-Dioxan-2-yl 4-methylbenzoate (3a):



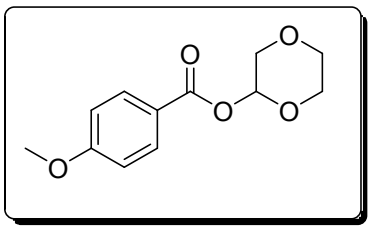
Colorless liquid (182 mg, 82%); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.02 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.8 Hz, 2H), 6.09 (t, *J* = 1.9 Hz, 1H), 3.90 – 3.88 (m, 2H), 3.83 (dd, *J* = 6.8, 2.6 Hz, 2H), 3.68 (dt, *J* = 11.8, 2.6 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 165.2, 144.2, 129.9, 129.1, 126.9, 89.6, 67.8, 66.1, 61.7, 21.7. IR (Neat): 2924, 1722, 1611, 1275, 1257, 1153, 1085, 1065, 1014, 911, 880, 754, 576 cm^{-1}. ESI-MS: m/z = 223 $[M+H]^+$, 240 $[M+NH_4]^+$. HRMS (ESI) calcd for $C_{12}H_{14}O_4Na$ $[M+Na]^+$ 245.07856, found 245.07843.

1,4-Dioxan-2-yl 4-isopropylbenzoate (3b):



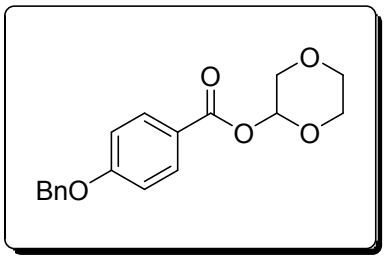
Colorless liquid (187 mg, 75%); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.07 – 8.04 (m, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 6.09 (t, *J* = 1.9 Hz, 1H), 4.26 – 4.18 (m, 1H), 3.89 (t, *J* = 3.7 Hz, 2H), 3.85 – 3.81 (m, 2H), 3.67 (dt, *J* = 11.8, 2.6 Hz, 1H), 3.01 – 2.93 (m, 1H), 1.27 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 165.3, 154.9, 130.1, 127.2, 126.5, 89.6, 67.8, 66.1, 61.7, 33.2, 23.6. IR (Neat): 2962, 1722, 1609, 1274, 1257, 1153, 1084, 1065, 1012, 910, 879, 854, 773, 706, 606, 577 cm^{-1}. ESI-MS: m/z = 251 $[M+H]^+$, 268 $[M+NH_4]^+$. HRMS (ESI) calcd for $C_{14}H_{18}O_4K$ $[M+K]^+$ 289.10599, found 289.10417.

1,4-Dioxan-2-yl 4-methoxybenzoate (3c):



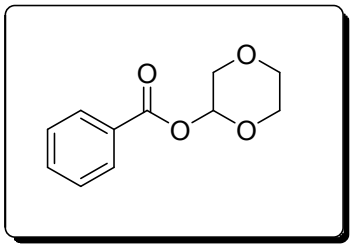
Colorless liquid (188 mg, 79%); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.08 (dd, *J* = 7.0, 1.6 Hz, 2H), 6.97 – 6.90 (m, 2H), 6.07 (t, *J* = 1.9 Hz, 1H), 4.25 – 4.16 (m, 1H), 3.87 (dd, *J* = 9.0, 1.8 Hz, 5H), 3.84 – 3.76 (m, 2H), 3.72 – 3.60 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 163.7, 159.7, 131.9, 122.0, 113.7, 89.5, 67.9, 66.1, 61.8, 55.4. IR (Neat): 2924, 1717, 1605, 1511, 1316, 1252, 1167, 1150, 909, 877, 848, 770, 609, 576 cm^{-1}. ESI-MS: m/z = 239 $[M+H]^+$, 261 $[M+Na]^+$. HRMS (ESI) calcd for $C_{12}H_{14}O_5Na$ $[M+Na]^+$ 261.07302, found 261.07334.

1,4-Dioxan-2-yl 4-(benzyloxy)benzoate (3d):



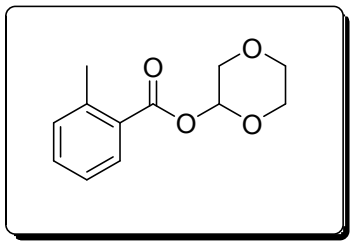
Colorless solid (216 mg, 69%), M.p. 65-68 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.07 (t, *J* = 13.4 Hz, 2H), 7.46 – 7.23 (m, 5H), 7.01 (d, *J* = 8.8 Hz, 2H), 6.07 (t, *J* = 1.9 Hz, 1H), 5.12 (s, 2H), 4.24 – 4.16 (m, 1H), 3.86 (d, *J* = 10.8 Hz, 2H), 3.79 (dd, *J* = 25.2, 6.7 Hz, 2H), 3.71 – 3.59 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 164.9, 162.9, 136.1, 132.1, 128.7, 128.2, 127.5, 122.2, 114.6, 89.5, 70.1, 67.9, 66.1, 61.8. IR (Neat): 3032, 2924, 1718, 1604, 1582, 1510, 1250, 1231, 1168, 1017, 911, 880, 850, 769, 740, 579 cm^{-1}. ESI-MS: m/z = 315 $[M+H]^+$, 332 $[M+NH_4]^+$. HRMS (ESI) calcd for $C_{18}H_{18}O_5Na$ $[M+Na]^+$ 337.10534, found 337.10464.

1,4-Dioxan-2-yl benzoate (3e)[1]:



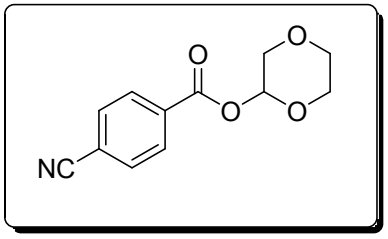
Colorless liquid (156 mg, 75%); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.13 (d, *J* = 7.3 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 6.10 (t, *J* = 2.0 Hz, 1H), 4.28 – 4.17 (m, 1H), 3.90 (d, *J* = 1.7 Hz, 2H), 3.83 (dd, *J* = 6.6, 2.3 Hz, 2H), 3.73 – 3.64 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 165.2, 133.4, 129.8, 128.4, 89.8, 67.8, 66.1, 61.7. IR (Neat): 2922, 1723, 1452, 1256, 1063, 1015, 909, 878,743, 710 cm^{-1}. ESI-MS: m/z = 209 $[M+H]^+$, 226 $[M+NH_4]^+$. HRMS (ESI) calcd for $C_{11}H_{12}O_4Na$ $[M+Na]^+$ 231.06324, found 231.06728.

1,4-Dioxan-2-yl 2-methylbenzoate (3f):



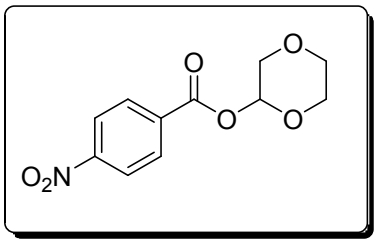
Colorless liquid (162 mg, 73%); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.08 (dd, *J* = 9.4, 8.2 Hz, 1H), 7.43 (dd, *J* = 11.2, 3.7 Hz, 1H), 7.28 (t, *J* = 6.9 Hz, 2H), 6.10 (t, *J* = 1.9 Hz, 1H), 4.28 – 4.16 (m, 1H), 3.90 (d, *J* = 1.7 Hz, 2H), 3.83 (dd, *J* = 6.6, 2.4 Hz, 2H), 3.69 (dt, *J* = 11.8, 2.5 Hz, 1H), 2.66 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 165.9, 140.9, 132.5, 131.8, 131.1, 125.8, 89.6, 67.9, 66.1, 61.8, 21.9. IR (Neat): 2926, 1720, 1247, 1230, 1053, 1013, 909, 878, 736, 581 cm^{-1}. ESI-MS: m/z = 223 $[M+H]^+$, 240 $[M+NH_4]^+$. HRMS (ESI) calcd for $C_{12}H_{15}O_4$ $[M+H]^+$ 223. 08084, found 223. 08109.

1,4-Dioxan-2-yl 4-cyanobenzoate (3g)[1]**:**



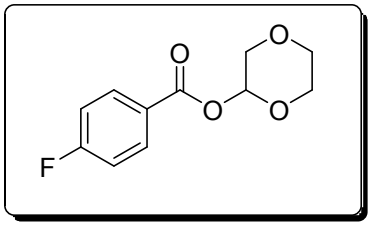
Colorless solid (160 mg, 69%), M.p. 130-132 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.22 (d, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 8.5 Hz, 2H), 6.11 (t, *J* = 1.9 Hz, 1H), 4.21 (dt, *J* = 11.9, 6.7 Hz, 1H), 3.91 (d, *J* = 1.7 Hz, 2H), 3.85 (dd, *J* = 6.9, 2.0 Hz, 2H), 3.69 (dt, *J* = 11.7, 2.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 163.7, 133.5, 132.3, 130.4, 117.9, 116.8, 90.6, 67.6, 66.1, 61.7. IR (Neat): 2958, 2231, 1728, 1277, 1259, 1090, 880, 771, 667 cm^{-1}. ESI-MS: m/z = 234 $[M+H]^+$, 272 $[M+K]^+$. HRMS (ESI) calcd for $C_{12}H_{12}NO_4$ $[M+H]^+$ 234.16417, found 234.16400.

1,4-Dioxan-2-yl 4-nitrobenzoate (3h)[1]**:**



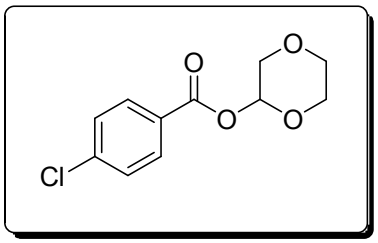
Pale yellow solid (169 mg, 67%), M.p. 120-125 °C; ^{1}HNMR (500 MHz, $CDCl_3$) δ 8.31 (m, 4H), 6.14 (t, *J* = 1.9 Hz, 1H), 4.27–4.19 (m, 1H), 3.93 (s, 2H), 3.86 (t, *J* = 9.6 Hz, 2H), 3.75–3.68 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 163.4, 150.7, 135.1, 130.9, 123.6, 90.7, 67.5, 66.1, 61.7. IR (Neat): 2975, 1724, 1526, 1347, 1318, 1275, 1258, 1114, 1091, 1009, 981, 909, 874, 848, 746, 714, 640, 578 cm^{-1}. ESI-MS: m/z = 254 $[M+H]^+$, 292 $[M+K]^+$. HRMS (ESI) calcd for $C_{11}H_{12}NO_6$ $[M+H]^+$ 254.13047, found 254.12958.

1,4-Dioxan-2-yl 4-fluorobenzoate (3i)[1]**:**



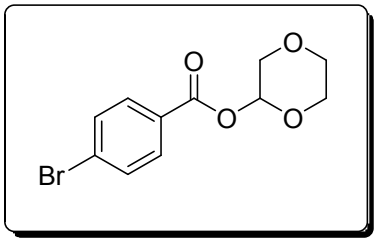
Colorless liquid (138 mg, 61%); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.18 – 8.13 (m, 2H), 7.17 – 7.11 (m, 2H), 6.09 (t, *J* = 1.9 Hz, 1H), 4.25 – 4.18 (m, 1H), 3.91 – 3.89 (m, 2H), 3.84 (dd, *J* = 6.7, 2.4 Hz, 2H), 3.69 (dt, *J* = 11.8, 2.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 167.7, 164.3, 132.4, 125.9, 115.8, 89.9, 67.8, 66.1, 61.7. IR (Neat): 2925, 1725, 1603, 1507, 1412, 1275, 1257, 1153, 1083, 1064, 1013, 910, 880, 854, 687, 605 cm^{-1}. ESI-MS: m/z = 227 $[M+H]^+$, 249 $[M+Na]^+$. HRMS (ESI) calcd for $C_{11}H_{11}FO_4Na$ $[M+Na]^+$ 289.05354, found 289.06414.

1,4-Dioxan-2-yl 4-chlorobenzoate (3j)[1]**:**



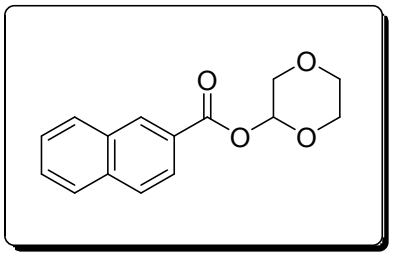
Colorless solid (158 mg, 65%), M.p. 76-80 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.06 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 6.09 (t, *J* = 1.9 Hz, 1H), 4.24 – 4.18 (m, 1H), 3.90 (s, 2H), 3.86–3.83 (m, 2H), 3.69 (d, *J* = 11.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 164.4, 139.9, 131.3, 128.8, 128.1, 90.0, 67.7, 66.1, 61.7. IR (Neat): 2923, 1723, 1593, 1453, 1257, 1154, 1114, 1087, 1065, 1009, 879, 851, 760, 580 cm^{-1}. ESI-MS: m/z = 243 $[M+H]^+$, 281 $[M+K]^+$. HRMS (ESI) calcd for $C_{11}H_{11}ClO_4K$ $[M+K]^+$ 281.01914, found 281.01908.

1,4-Dioxan-2-yl 4-bromobenzoate (3k)[1]**:**



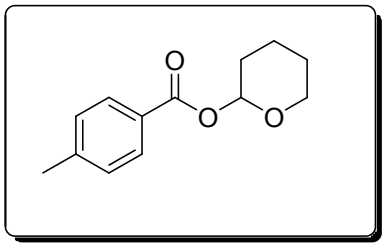
Colorless solid (192 mg, 67%), M.p. 68-75 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 6.01 (t, *J* = 1.9 Hz, 1H), 4.19 – 4.07 (m, 1H), 3.82 (d, *J* = 1.7 Hz, 2H), 3.76 (dd, *J* = 6.7, 2.3 Hz, 2H), 3.61 (dt, *J* = 11.7, 2.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 164.5, 131.8, 131.4, 129.6, 128.6, 90.0, 67.7, 66.1, 61.7. IR (Neat): 2925, 1727, 1589, 1397, 1357, 1274, 1258, 1232, 1214, 1086, 1067, 1009, 911, 880, 753, 667, 579 cm^{-1}. ESI-MS: m/z = 286 $[M+H]^+$, 308 $[M+Na]^+$. HRMS (ESI) calcd for $C_{11}H_{11}BrO_4Na$ $[M+Na]^+$ 308.14344, found 308.14323.

1,4-Dioxan-2-yl 2-naphthoate (3l)[2]**:**



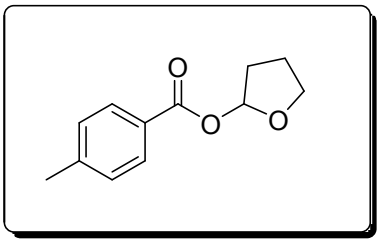
Colorless liquid (175 mg, 68%);^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.01 (d, *J* = 8.7 Hz, 1H), 8.35 (dd, *J* = 7.3, 1.2 Hz, 1H), 8.04 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.63 (ddd, *J* = 8.5, 6.8, 1.4 Hz, 1H), 7.56 – 7.47 (m, 2H), 6.21 (t, *J* = 1.9 Hz, 1H), 4.30 – 4.22 (m, 1H), 3.95 (dd, *J* = 3.1, 2.0 Hz, 2H), 3.86 – 3.82 (m, 2H), 3.73 – 3.68 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 165.9, 134.1, 130.9, 128.6, 128.1, 126.3, 125.7, 124.5, 89.8, 67.9, 66.2, 61.9. IR (Neat): 2923, 1718, 1510, 1265, 1233, 1193, 1128, 1109, 1066, 1018, 992, 909, 879, 782, 746, 655, 584 cm^{-1}. ESI-MS: m/z = 259 $[M+H]^+$, 276 $[M+NH_4]^+$. HRMS (ESI) calcd for $C_{15}H_{14}O_4Na$ $[M+Na]^+$ 281.07721, found 281.07757.

Tetrahydro-2H-pyran-2-yl 4-methylbenzoate (4b):



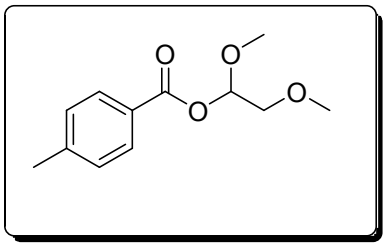
Colorless solid (150 mg, 68%), M.p. 185-190 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.98 (d, *J* = 8.2 Hz, 2H), 7.27 (d, 7.5 Hz, 2H), 6.24 (d, *J* = 1.9 Hz, 1H), 4.06 – 3.87 (m, 1H), 3.82 – 3.69 (m, 1H), 2.41 (s, 3H), 2.00 – 1.82 (m, 2H), 1.79 – 1.58 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 171.8, 144.5, 130.2, 129.2, 126.7, 94.6, 62.9, 30.7, 25.4, 21.7, 19.7. IR (Neat): 2925, 1717, 1611, 1269, 1217, 1175, 1069, 1019, 959, 908, 837, 771, 752, 667, 606 cm^{-1}. ESI-MS: m/z = 221 $[M+H]^+$, 244 $[M+Na]^+$. HRMS (ESI) calcd for $C_{13}H_{17}O_3$ $[M+H]^+$ 221.10186, found 221.10157.

Tetrahydrofuran-2-yl 4-methylbenzoate (4c):



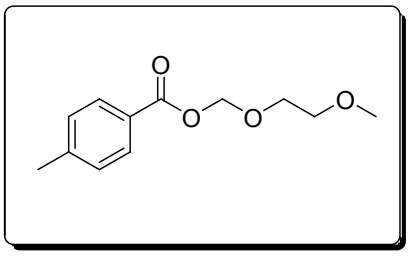
Colorless liquid (128 mg, 63%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.23 – 7.21 (m, 2H), 6.54 (dd, *J* = 13.8, 6.6 Hz, 1H), 4.05 – 3.88 (m, 2H), 2.40 (s, 3H), 2.23 – 2.10 (m, 2H), 2.04 – 1.90 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 166.0, 143.7, 129.7, 129.0, 127.6, 99.5, 68.9, 32.3, 22.9, 21.6. IR (Neat): 2948, 1710, 1692, 1611, 1550, 1514, 1216, 1034, 967, 907, 771, 746, 667, 625, cm^{-1}. ESI-MS: m/z = 207 $[M+H]^+$, 229 $[M+Na]^+$. HRMS (ESI) calcd for $C_{12}H_{15}O_3$ $[M+H]^+$ 207.08622, found 207.08592.

1,2-Dimethoxyethyl 4-methylbenzoate (4fa):



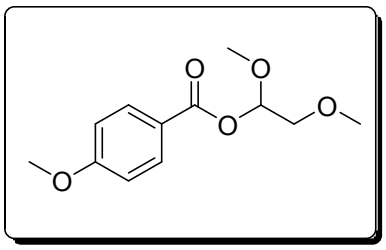
Colorless liquid (103 mg, 46%); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.99 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 6.14 (t, *J* = 4.9 Hz, 1H), 3.64 (dd, *J* = 4.9, 2.8 Hz, 1H), 3.55 (s, 3H), 3.45 (s, 3H), 3.41 (d, *J* = 4.7 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 166.2, 144.2, 129.9, 129.1, 126.7, 97.2, 72.8, 59.5, 57.1, 21.7. IR (Neat):2925, 1722, 1611, 1577, 1550, 1452, 1372, 1313, 1271, 1218, 1087, 1031, 1016, 986, 925, 841, 772, 669 cm^{-1}. ESI-MS: m/z = 225 $[M+H]^+$, 242 $[M+NH_4]^+$. HRMS (ESI) calcd for $C_{12}H_{20}NO_4$ $[M+NH_4]^+$ 242.28403, found 242.28466.

(2-Methoxyethoxy)methyl 4-methylbenzoate (4fa'):



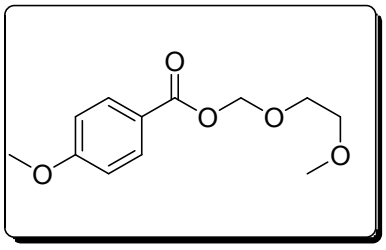
Colorless liquid (69 mg, 31%); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.98 – 7.94 (m, 2H), 7.26 – 7.22 (m, 2H), 5.56 (s, 2H), 3.89 – 3.85 (m, 2H), 3.59 – 3.56 (m, 2H), 3.38 – 3.37 (m, 3H), 2.34 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 166.0, 144.1, 129.8, 129.2, 127.1, 89.8, 71.5, 69.5, 59.1, 21.1. IR (Neat): 2925, 1723, 1612, 1272, 1168, 1118, 1059, 1017, 929, 803, 772, 754 cm^{-1}. ESI-MS: m/z = 225 $[M+H]^+$, 247 $[M+Na]^+$. HRMS (ESI) calcd for $C_{12}H_{17}O_4$ $[M+H]^+$ 225.14400, found 225.14377.

1,2-Dimethoxyethyl 4-methoxybenzoate (4fb):



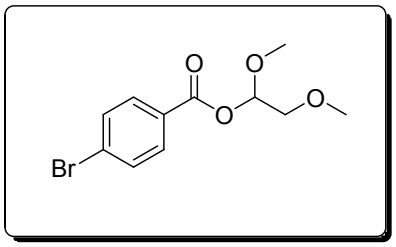
Colorless liquid (103 mg, 43%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 – 8.01 (m, 2H), 6.96 – 6.91 (m, 2H), 6.12 (dd, *J* = 5.1, 4.7 Hz, 1H), 3.87 (s, 3H), 3.66 – 3.58 (m, 2H), 3.53 (d, *J* = 3.5 Hz, 3H), 3.43 (d, *J* = 3.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 165.8, 163.7, 131.9, 121.9, 113.7, 97.1, 72.9, 59.5, 57.2, 55.5. IR (Neat): 2930, 1712, 1606, 1582, 1511, 1420, 1318, 1256, 1215, 1168, 1089, 1027, 928, 847, 745, 667 cm^{-1}. ESI-MS: m/z = 241 $[M+H]^+$, 263 $[M+Na]^+$. HRMS (ESI) calcd for $C_{12}H_{16}O_5Na$ $[M+Na]^+$ 263.08911, found 263.08899.

(2-Methoxyethoxy)methyl 4-methoxybenzoate (4fb'):



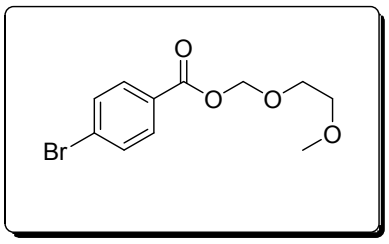
Colorless liquid (72 mg, 30%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 – 7.94 (m, 2H), 7.35 – 7.23 (m, 2H), 5.55 (s, 2H), 3.86 (s, 3H), 3.60 – 3.53 (m, 4H), 3.38 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 165.8, 163.6, 131.9, 122.2, 113.9, 113.7, 89.7, 71.6, 69.5, 59.1, 55.5. IR (Neat): 2924, 1708, 1630, 1550, 1487, 1453, 1423, 1389, 1242, 1220, 1173, 1030, 990, 929, 772, 690 cm^{-1}. ESI-MS: m/z = 241 $[M+H]^+$, 263 $[M+Na]^+$. HRMS (ESI) calcd for $C_{12}H_{20}NO_5$ $[M+NH_4]^+$ 240.14530, found 240.14816.

1,2-Dimethoxyethyl 4-bromobenzoate (4fc):



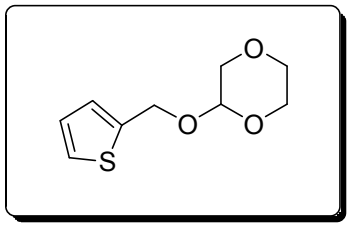
Colorless liquid (103 mg, 36%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 – 7.93 (m, 2H), 7.62 – 7.59 (m, 2H), 6.12 (t, *J* = 4.9 Hz, 1H), 3.66 – 3.59 (m, 2H), 3.54 (s, 3H), 3.43 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 165.5, 131.8, 131.4, 128.6, 128.5, 97.8, 72.7, 59.6, 57.4. IR (Neat):2923, 1727, 1678, 1644, 1590, 1498, 1397, 1269, 1219, 1126, 1090, 1028, 924, 848, 772, 671 cm^{-1}. ESI-MS: m/z = 288 $[M+H]^+$, 310 $[M+Na]^+$. (ESI) calcd for $C_{11}H_{14}BrO_4$ $[M+H]^+$ 288.18062, found 288.18055

(2-Methoxyethoxy)methyl 4-bromobenzoate (4fc'):



Colorless liquid (86 mg, 30%); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.94 (d, *J* = 6.8 Hz, 2H), 7.61 (d, *J* = 11.5 Hz, 2H), 5.58 (s, 2H), 3.88 (dd, *J* = 9.2, 4.4 Hz, 2H), 3.59 (dd, *J* = 8.8, 4.1 Hz, 2H), 3.38 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 165.4, 131.8, 131.6, 131.5, 131.3, 128.6, 128.5, 90.2, 71.5, 69.8, 59.1. IR (Neat): 2924, 1727, 1679, 1590, 1514, 1397, , 1219, 1169, 1067, 925, 849, 7726, 685, 671 cm^{-1}. ESI-MS: m/z = 288 $[M+H]^+$, 306 $[M+NH_4]^+$. HRMS (ESI) calcd for $C_{11}H_{17}NBrO_4$ $[M+NH_4]^+$ 306.03326, found 306.03355.

2-(thiophen-2-ylmethoxy)-1,4-dioxane (3n):

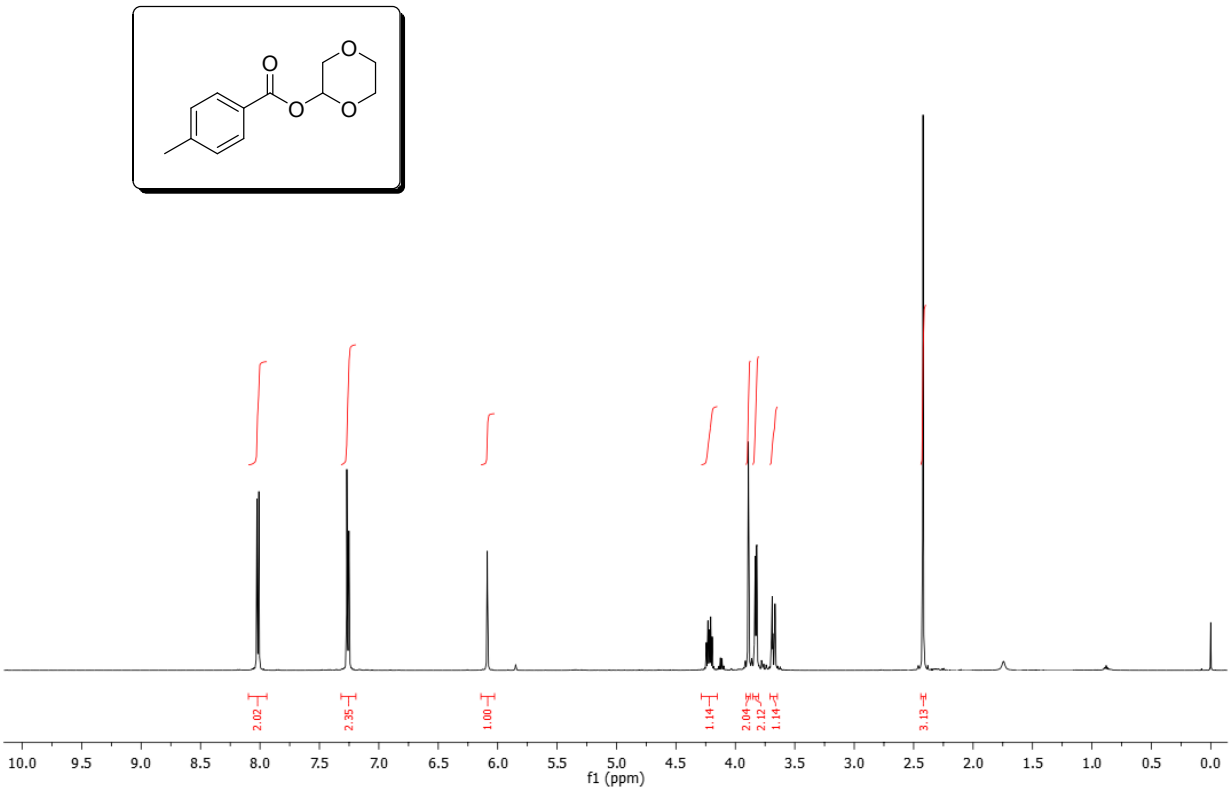


Colorless liquid (130 mg, 65%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 5.1, 1.0 Hz, 1H), 7.04 (d, *J* = 3.1 Hz, 1H), 6.98 (dd, *J* = 5.0, 3.5 Hz, 1H), 4.84 (dt, *J* = 22.0, 8.8 Hz, 2H), 4.66 – 4.65 (m, 1H), 4.13 – 4.06 (m, 1H), 3.74 – 3.68 (m, 3H), 3.62 – 3.55 (m, 2H).

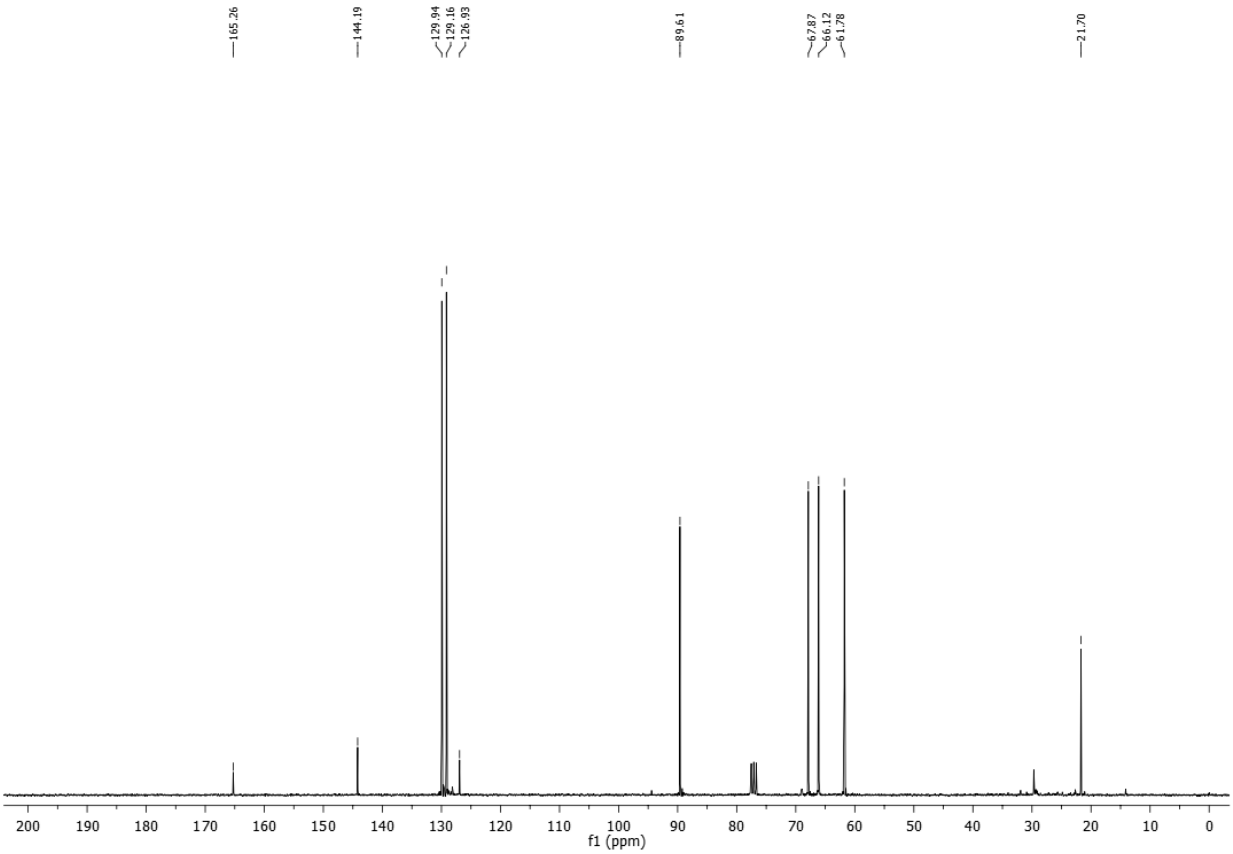
4. References:

[1] X. Wan, L. Chen, E. Shi, Z. Liu, S. Chen, W. Wei, H. Li, K. Xu, *Chem. Eur. J*. **2011**, *17*, 4085–4089.

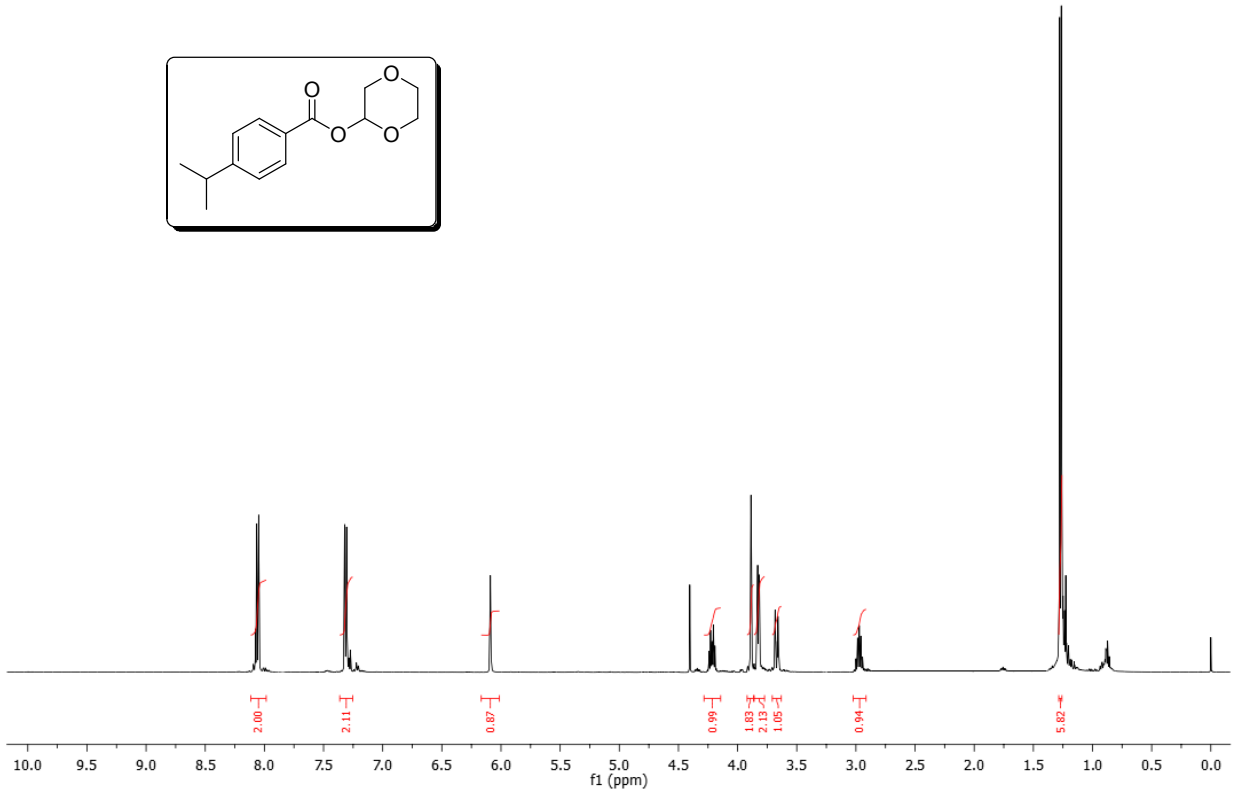
[2] S. zhang, L. N. Guo, H. Wang, X. H. Duan, *Org. Biomol. Chem,* **2013**, *11*, 4308–4311.



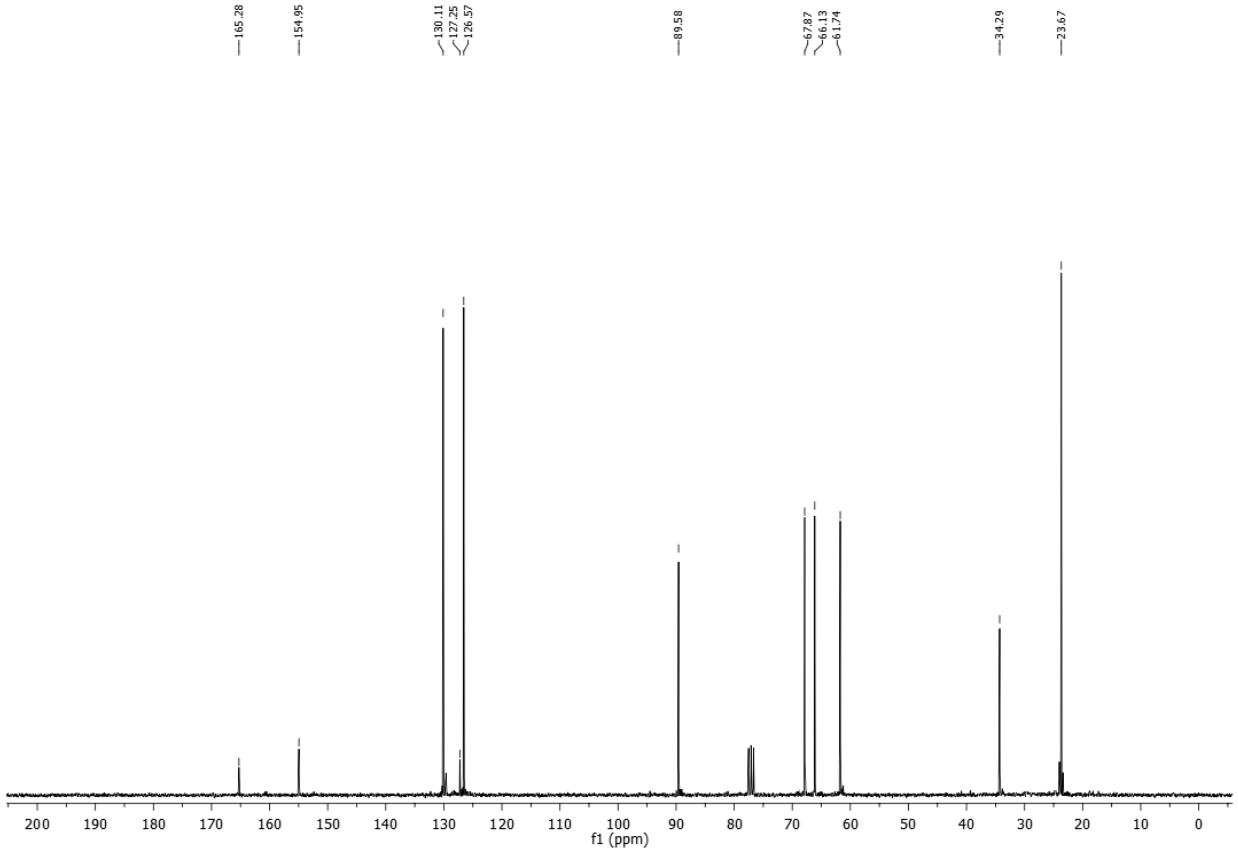
^{1}H NMR of Compound **3a**



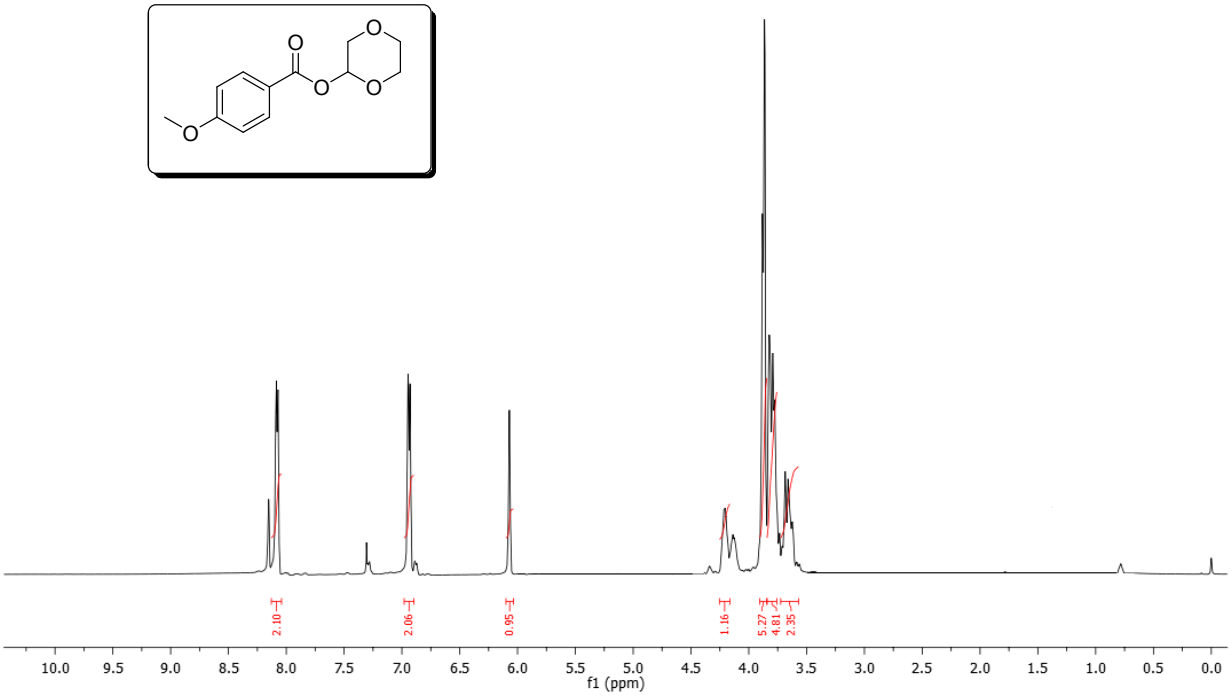
^{13} NMR of Compound **3a**



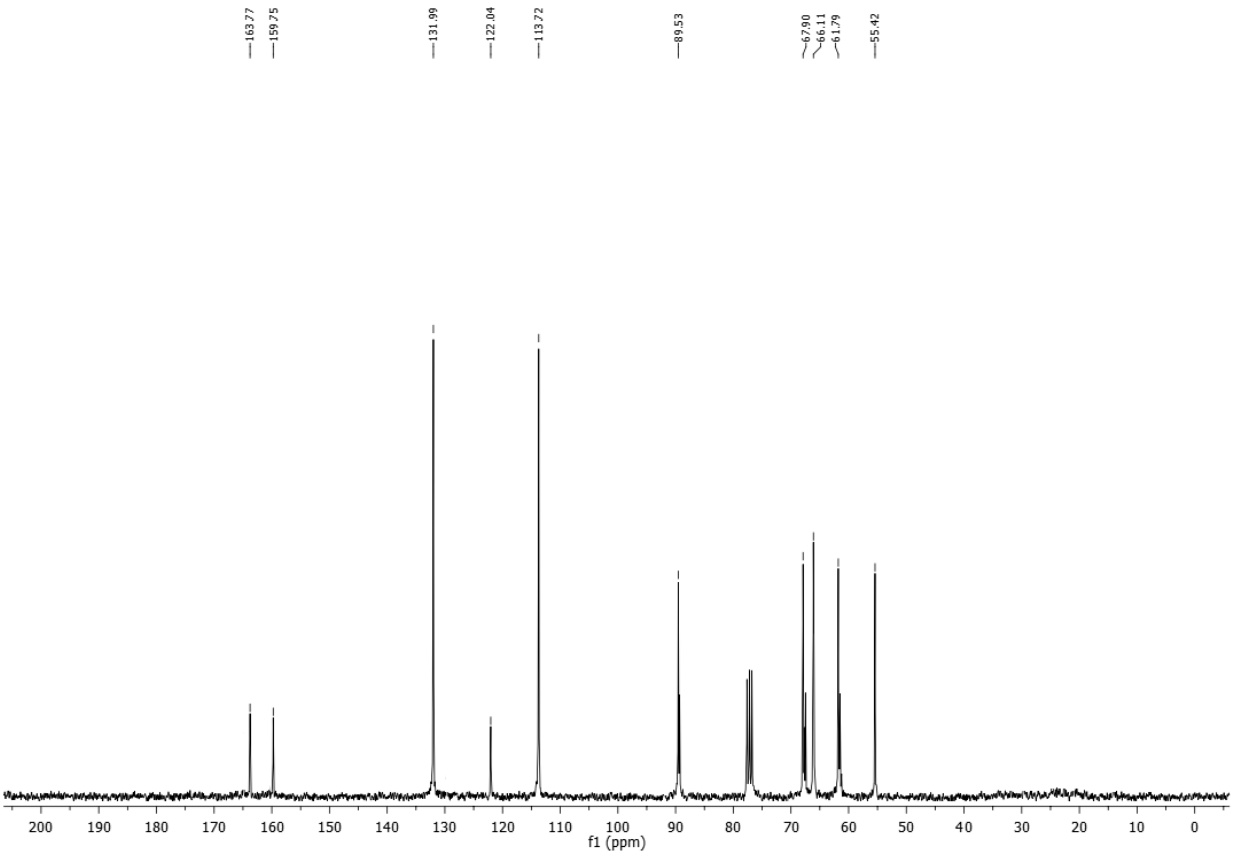
^{1}H NMR of Compound **3b**



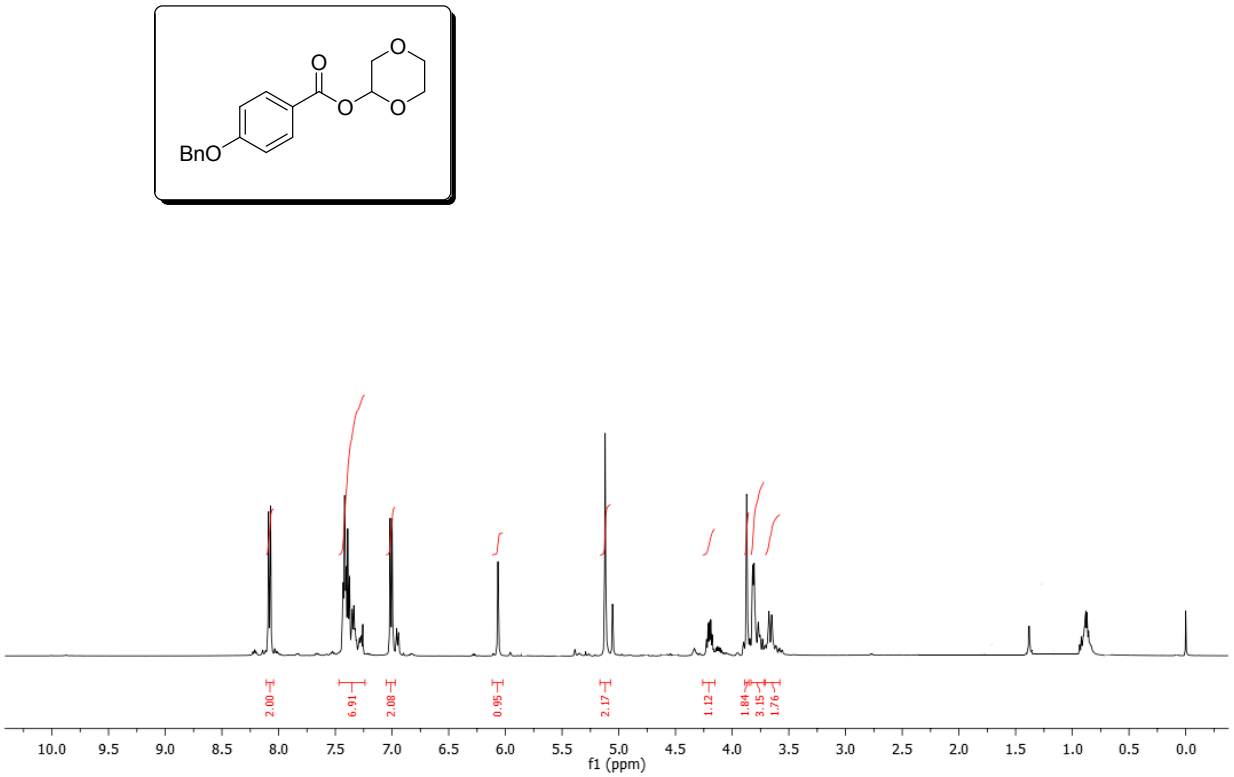
^{13}C NMR of Compound **3b**



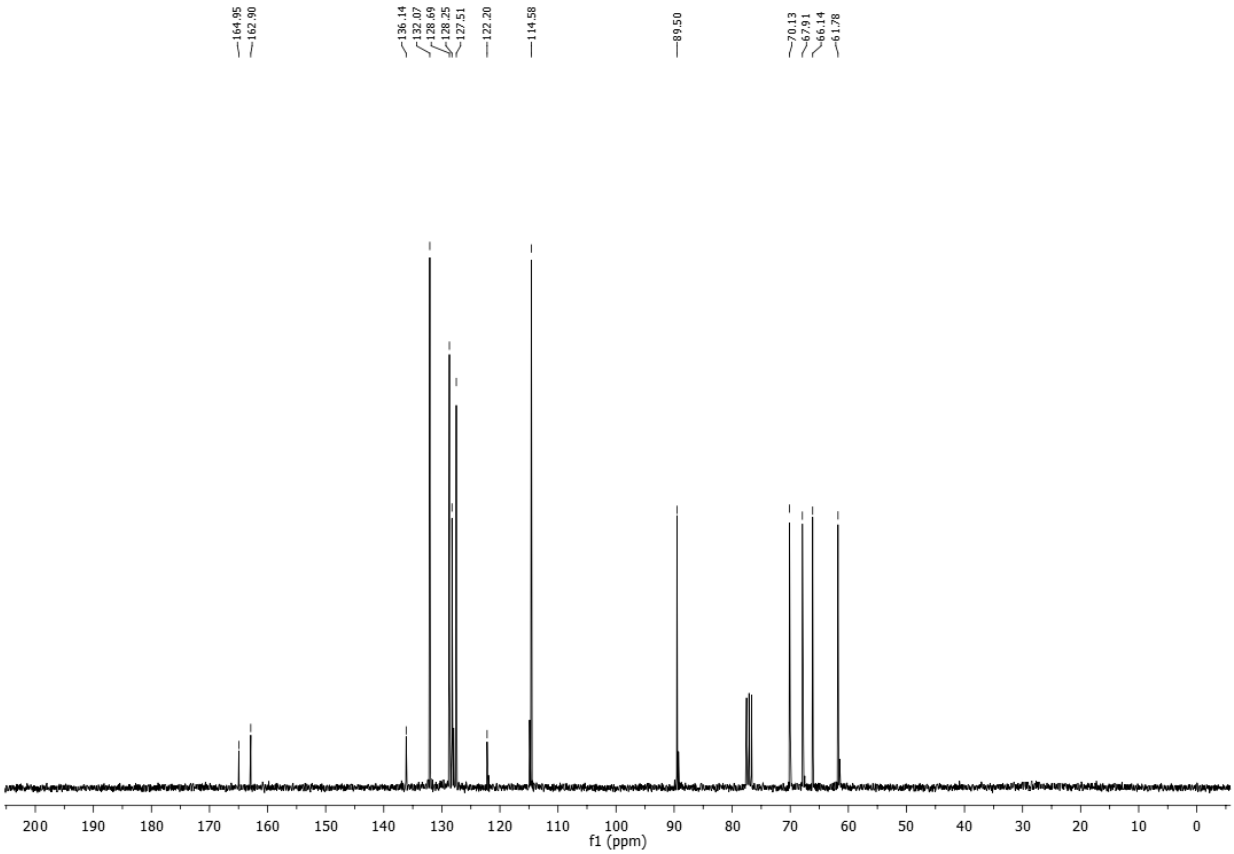
^{1}H NMR of Compound **3c**



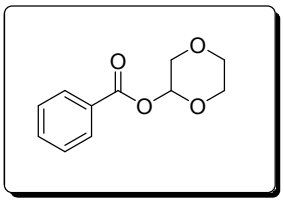
^{13}C NMR of Compound **3c**

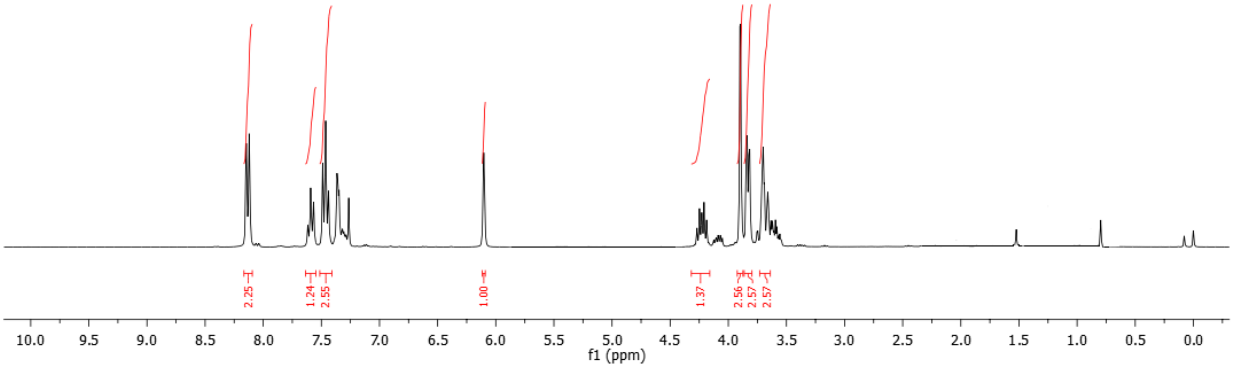


^{1}H NMR of Compound **3d**

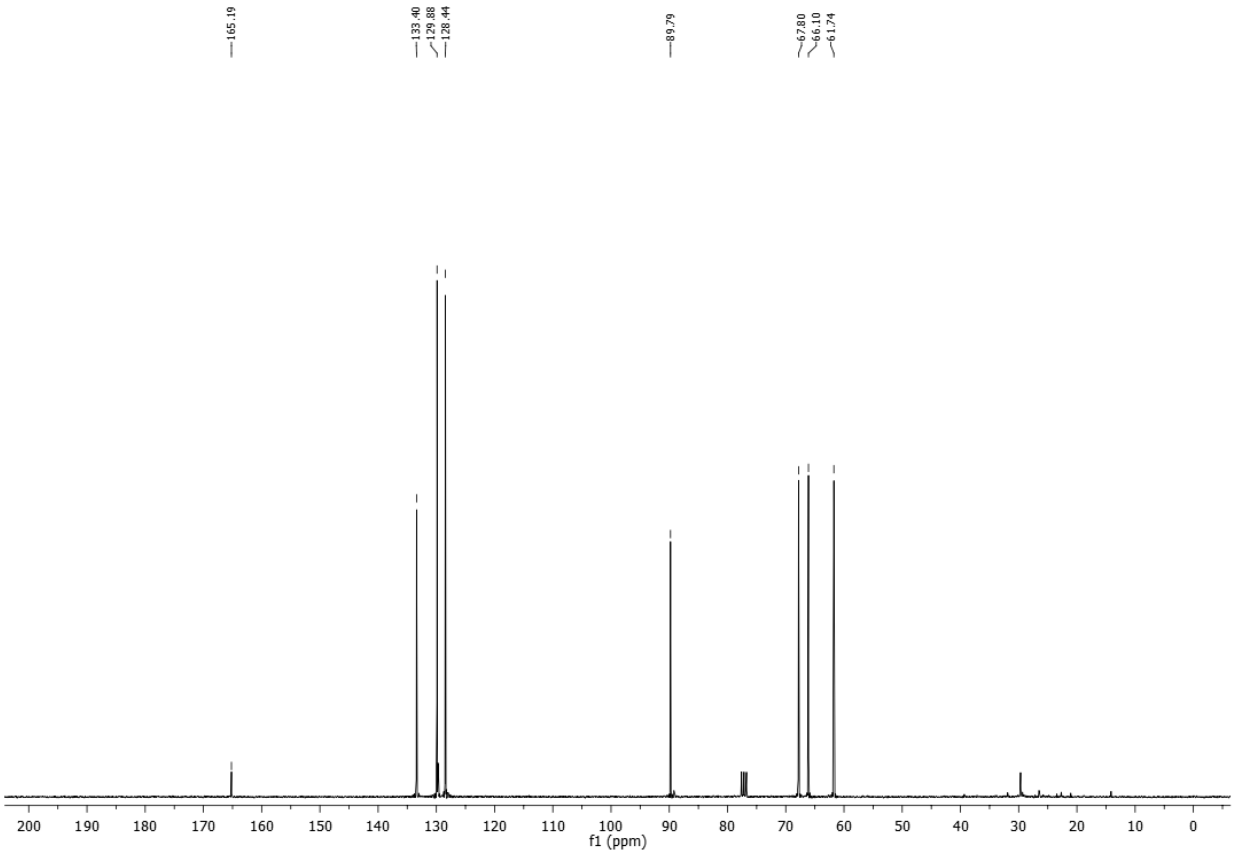


^{13}C NMR of Compound **3d**

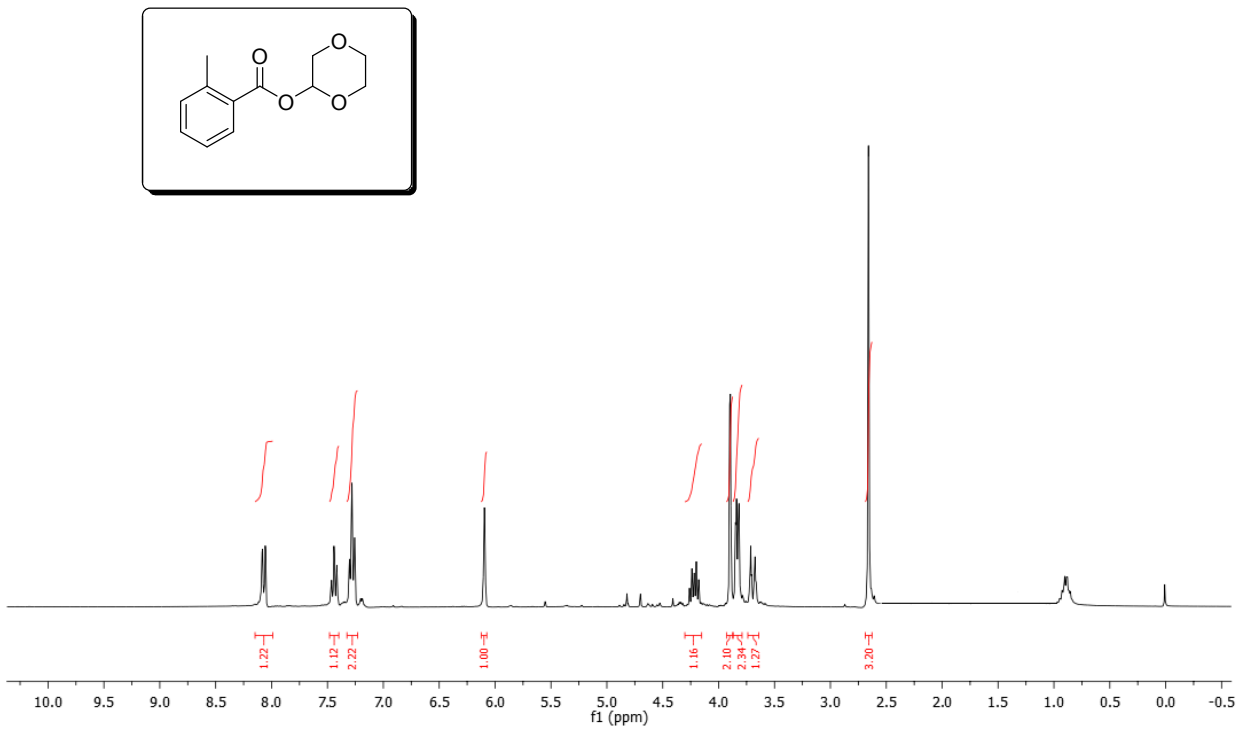




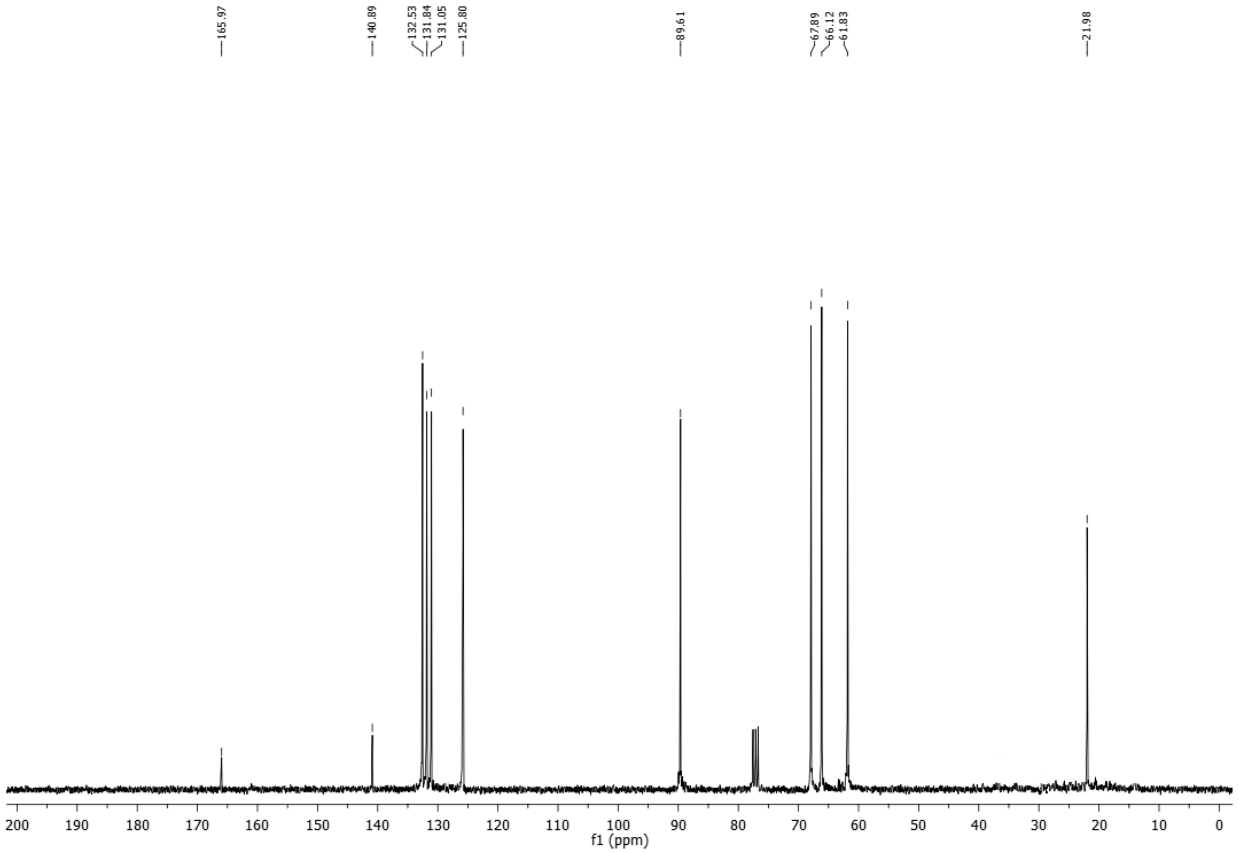
^{1}H NMR of Compound **3e**



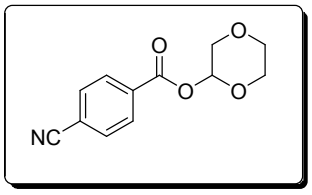
^{13}C NMR of Compound **3e**

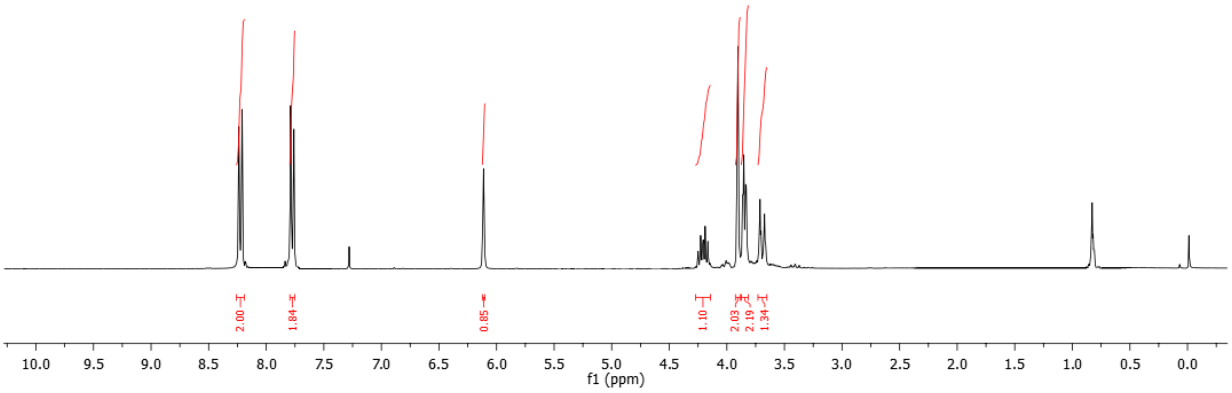


^{1}H NMR of Compound **3f**

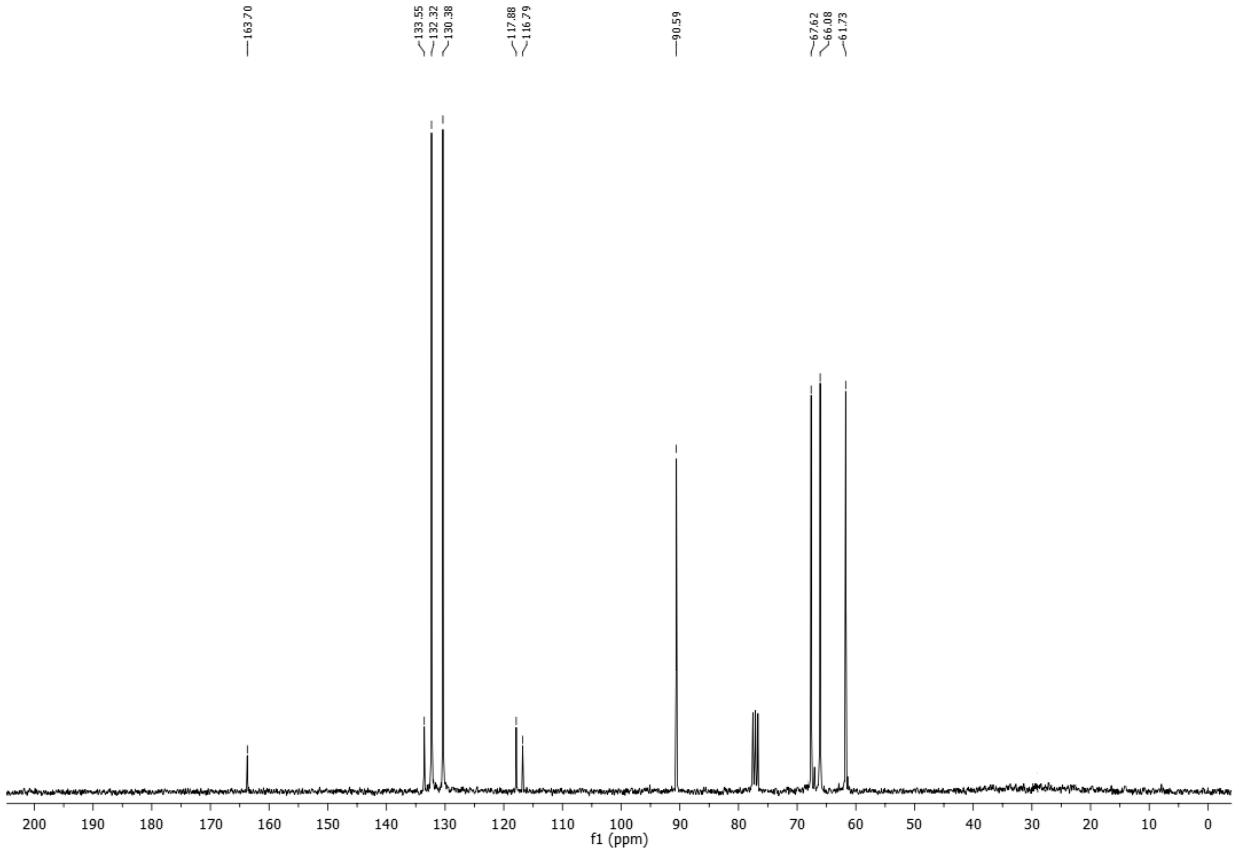


^{13}C NMR of Compound **3f**

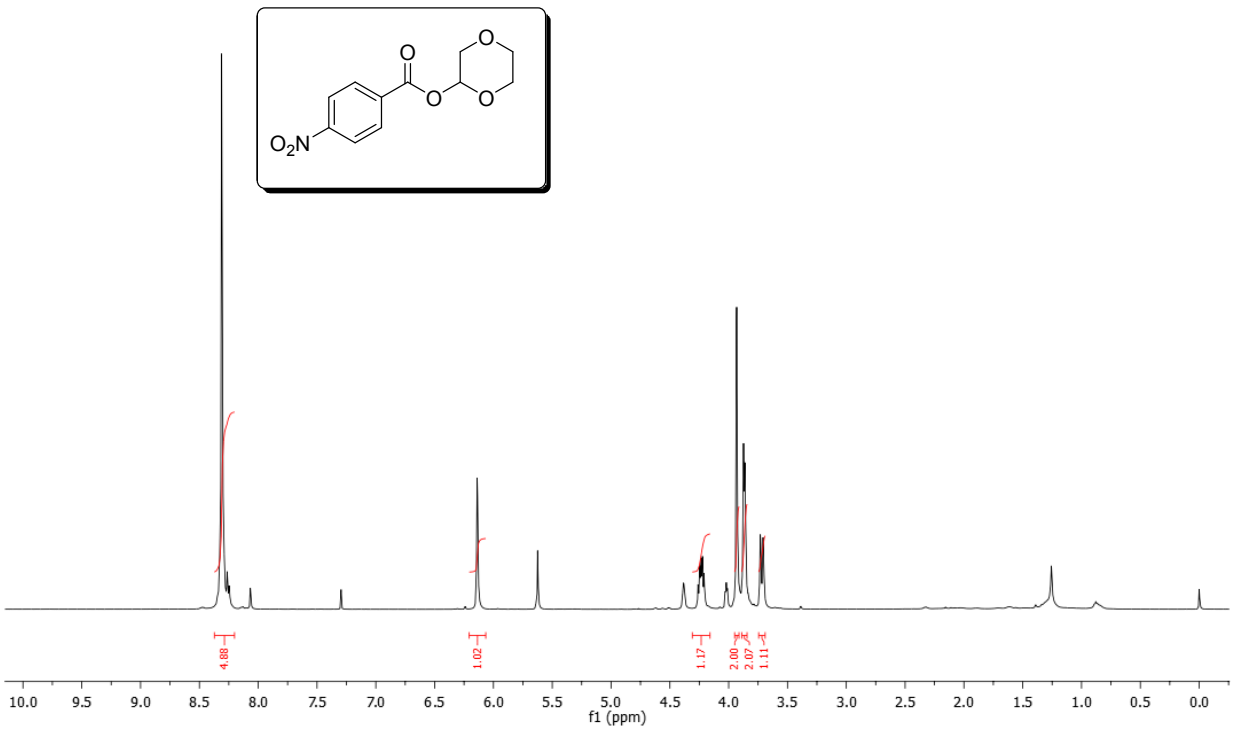




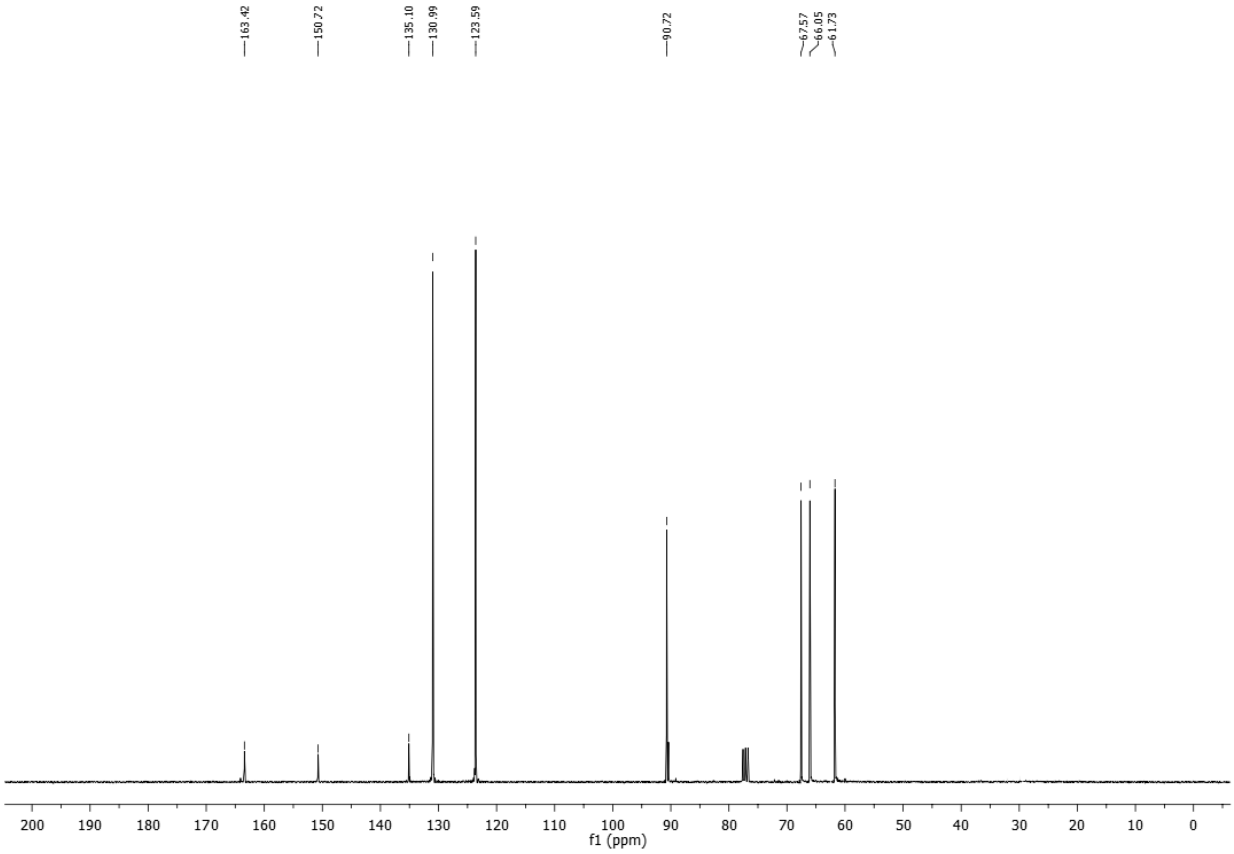
^{1}H NMR of Compound **3g**



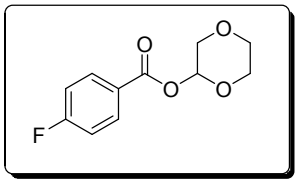
^{13}C NMR of Compound **3g**

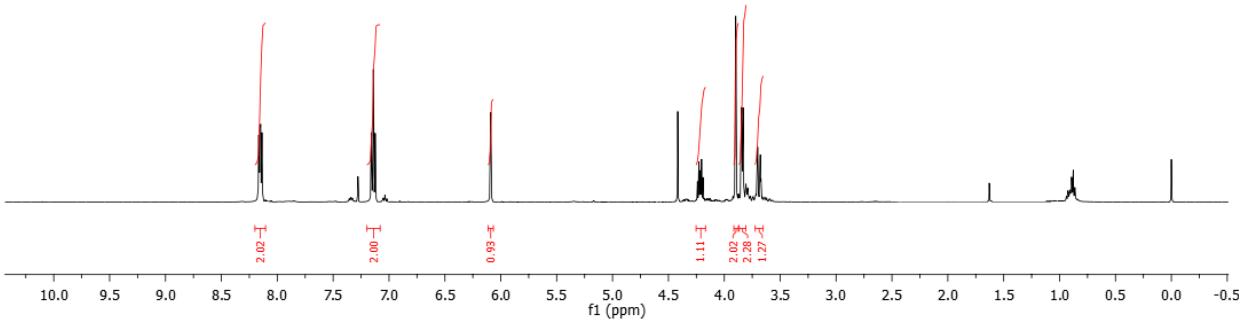


^{1}H NMR of Compound **3h**

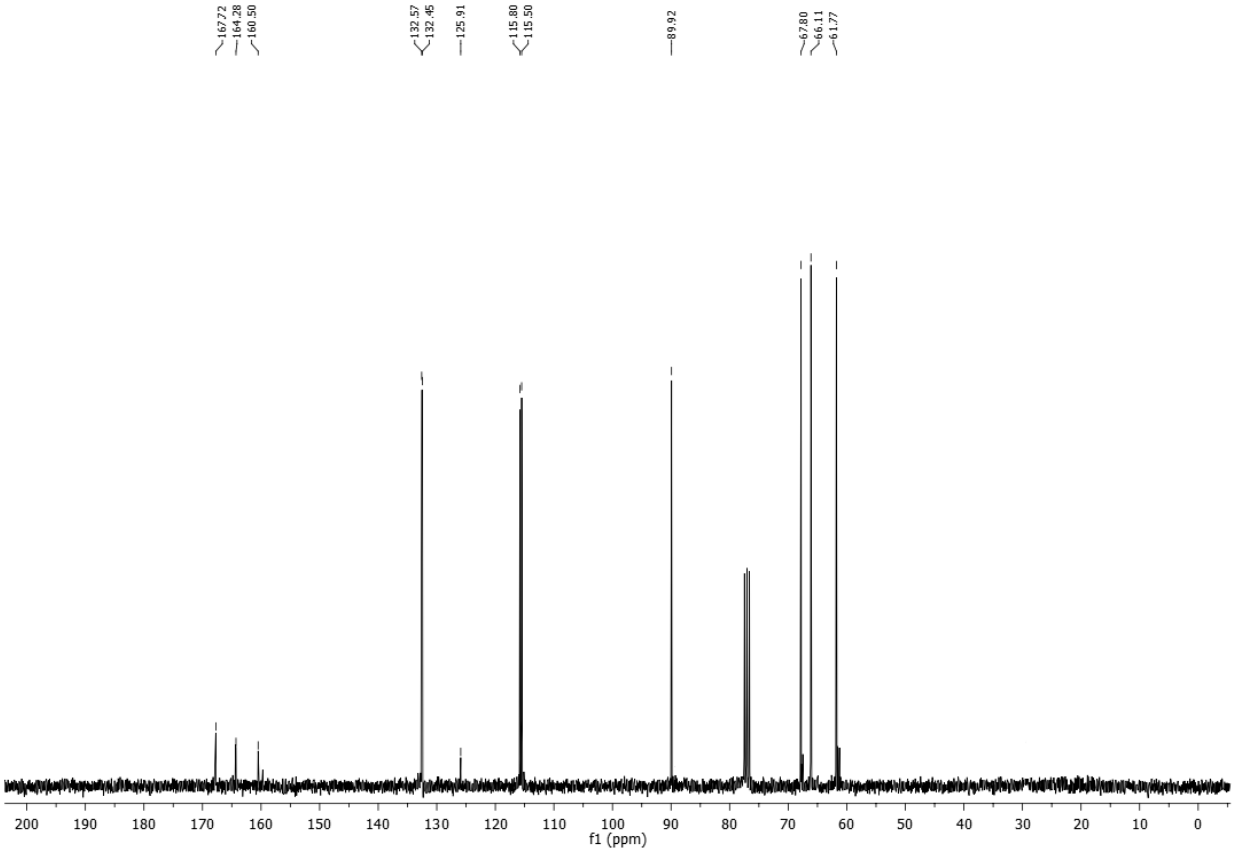


^{13}C NMR of Compound **3h**

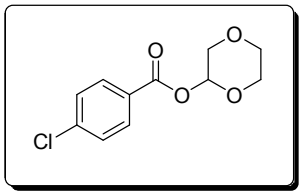


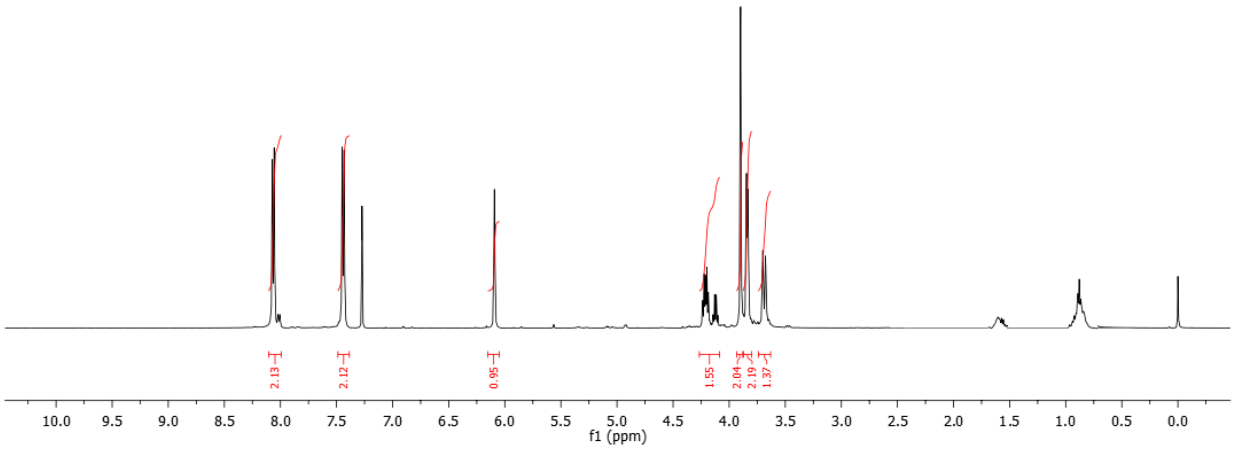


^{1}H NMR of Compound **3i**

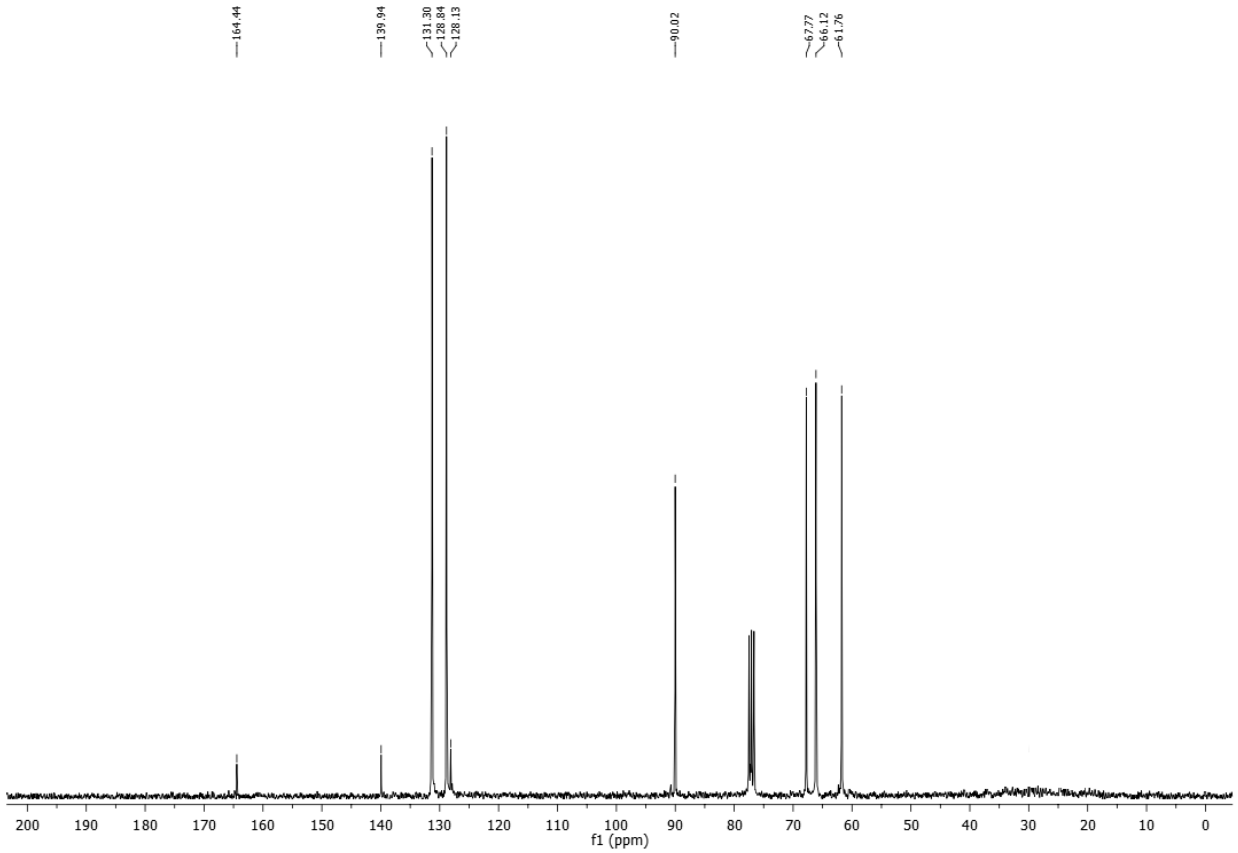


^{13}C NMR of Compound **3i**

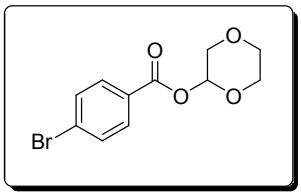


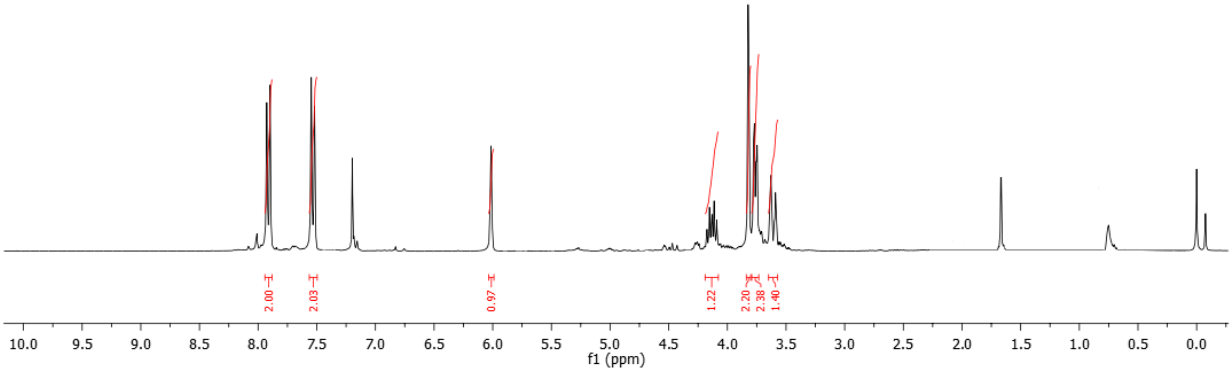


^{1}H NMR of Compound **3j**

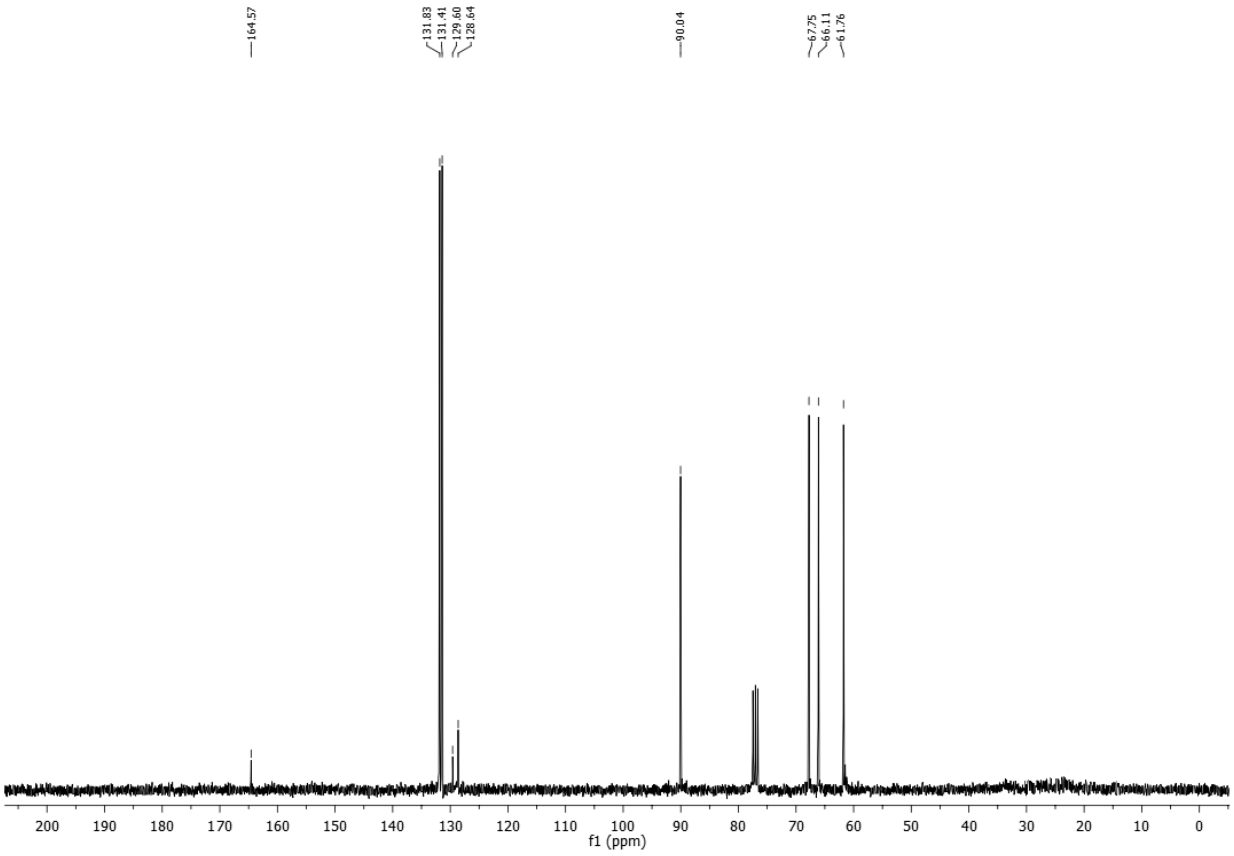


^{13}C NMR of Compound **3j**

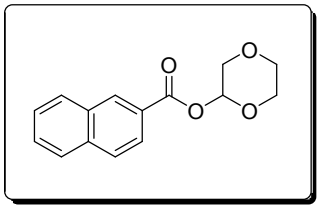


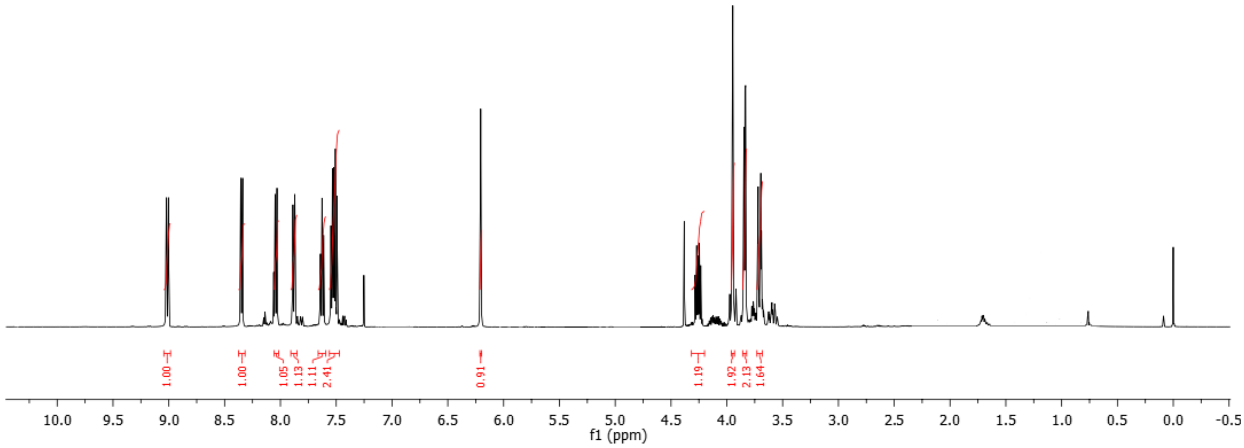


^{1}H NMR of Compound **3k**

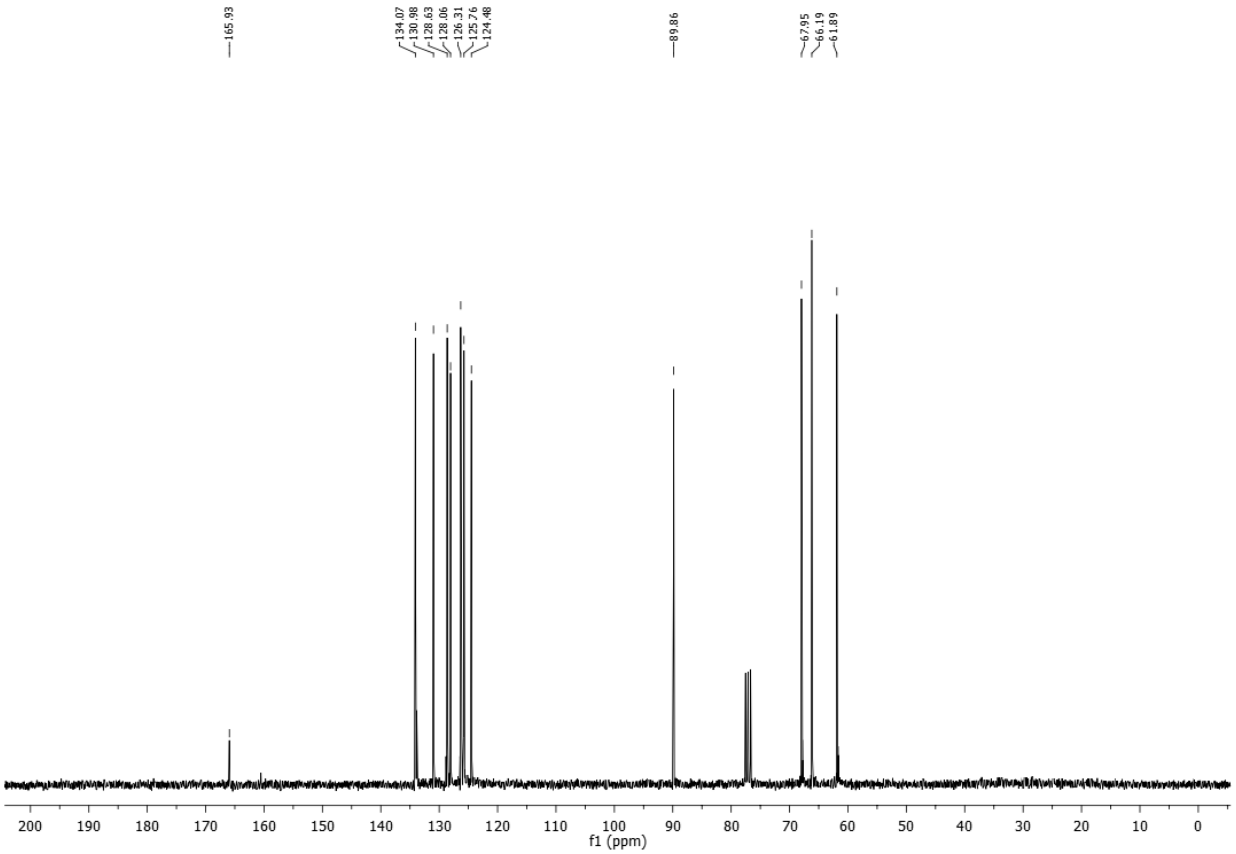


^{13}C NMR of Compound **3k**

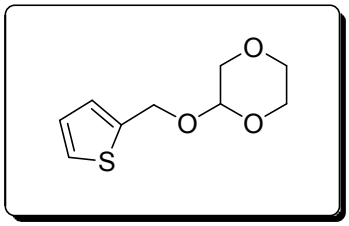


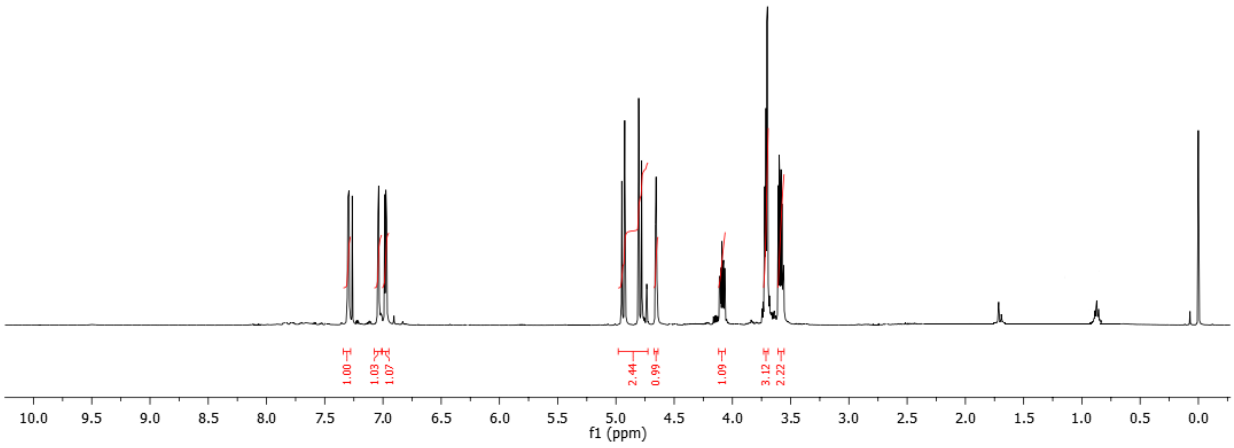


^{1}H NMR of Compound **3l**

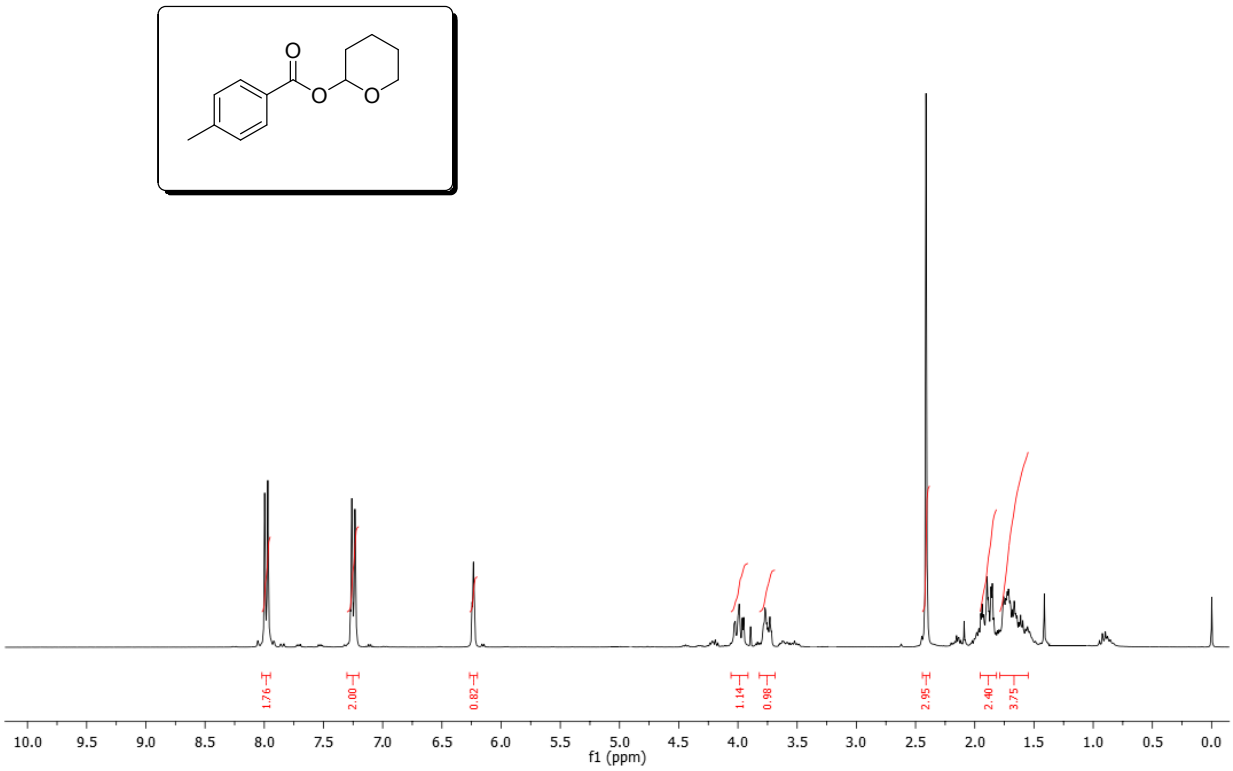


^{13}C NMR of Compound **3l**

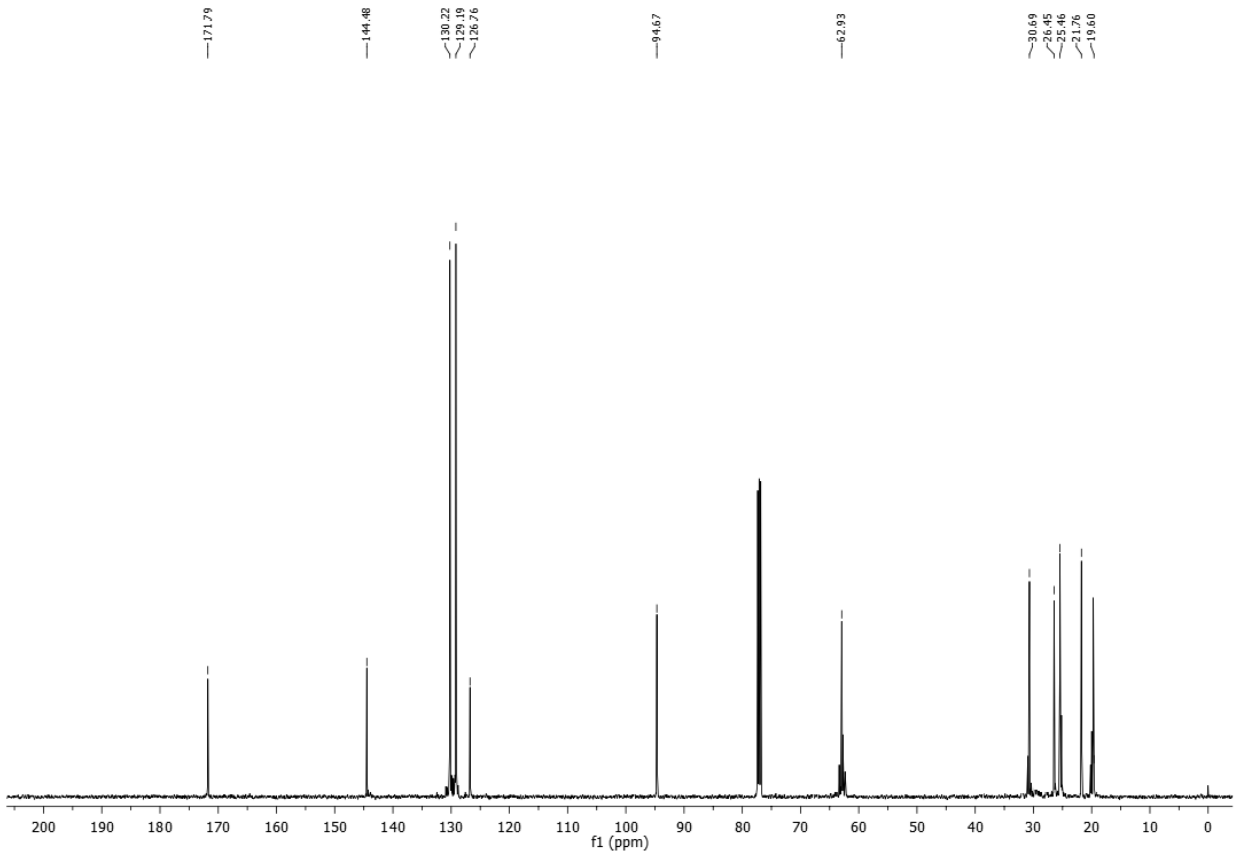




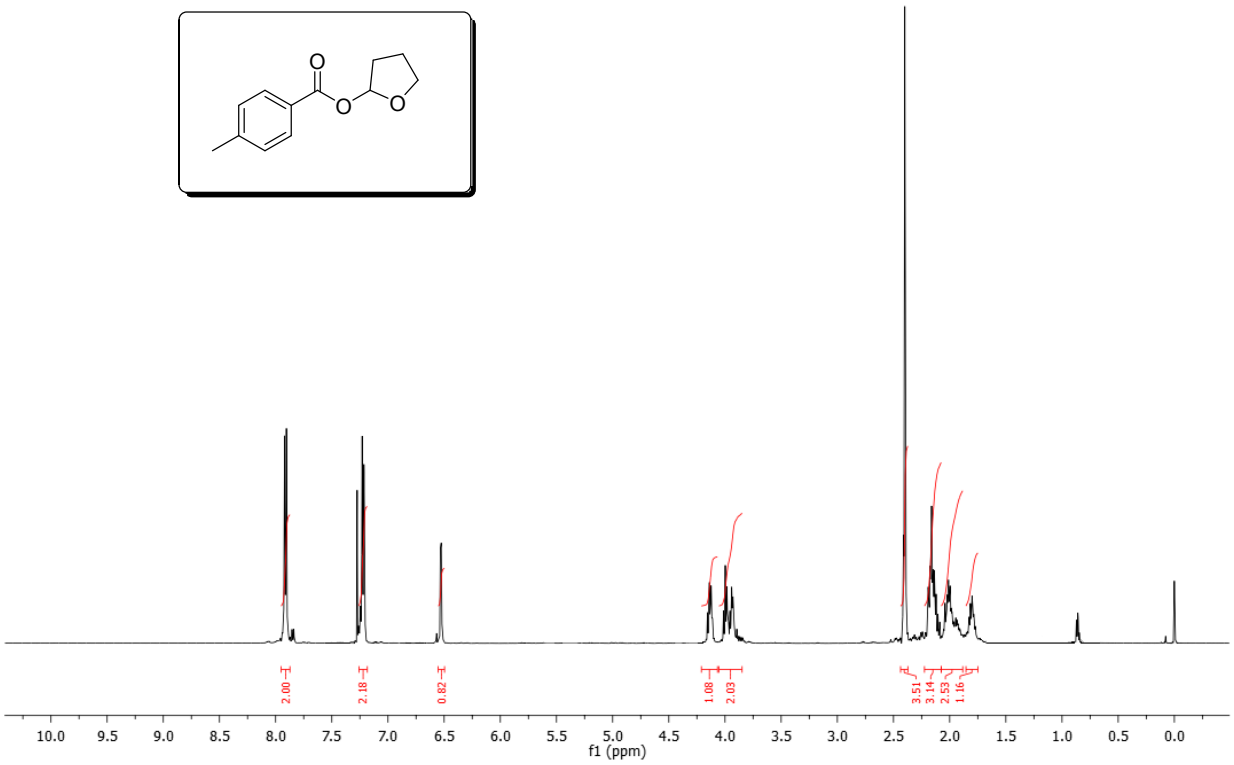
^{1}H NMR of Compound **3n**



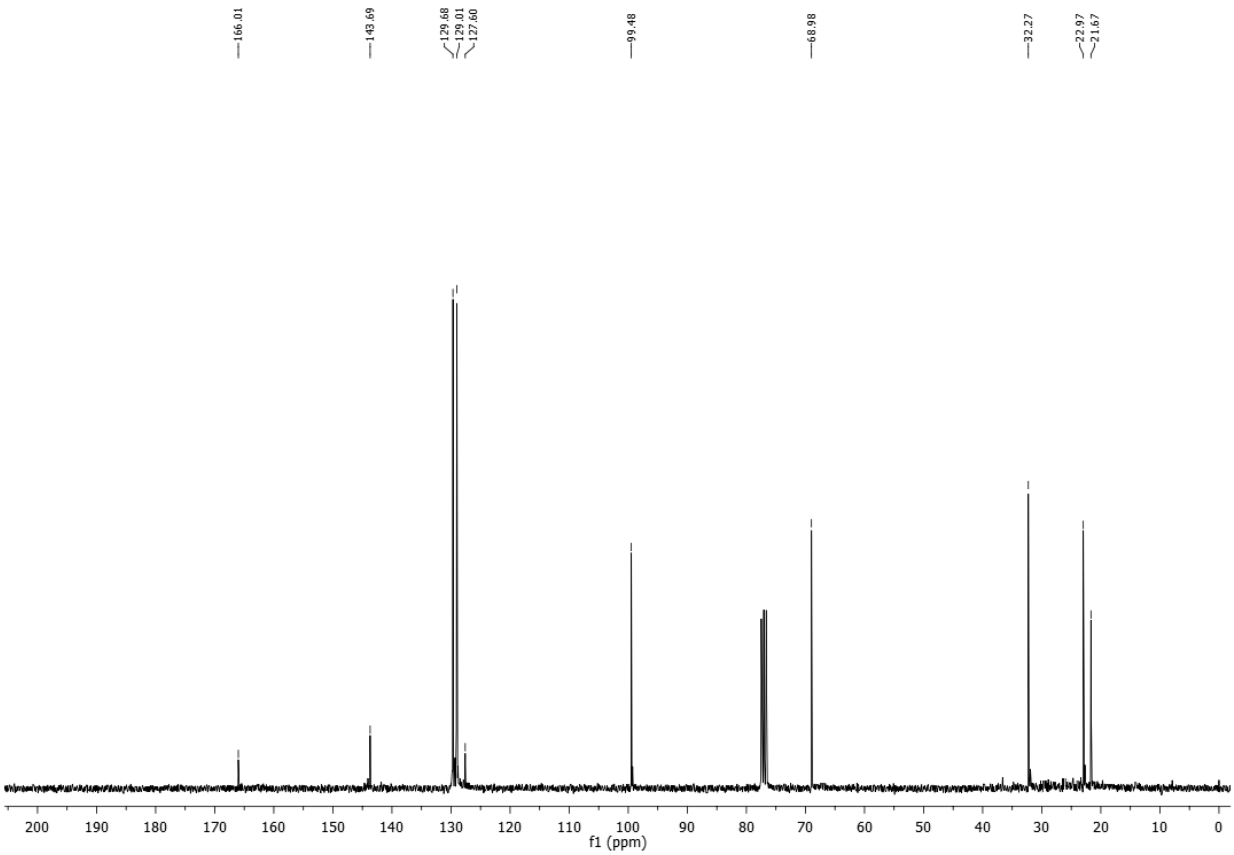
^{1}H NMR of Compound **4b**



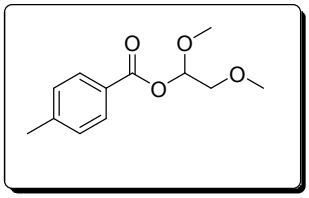
^{13}C NMR of Compound **4b**

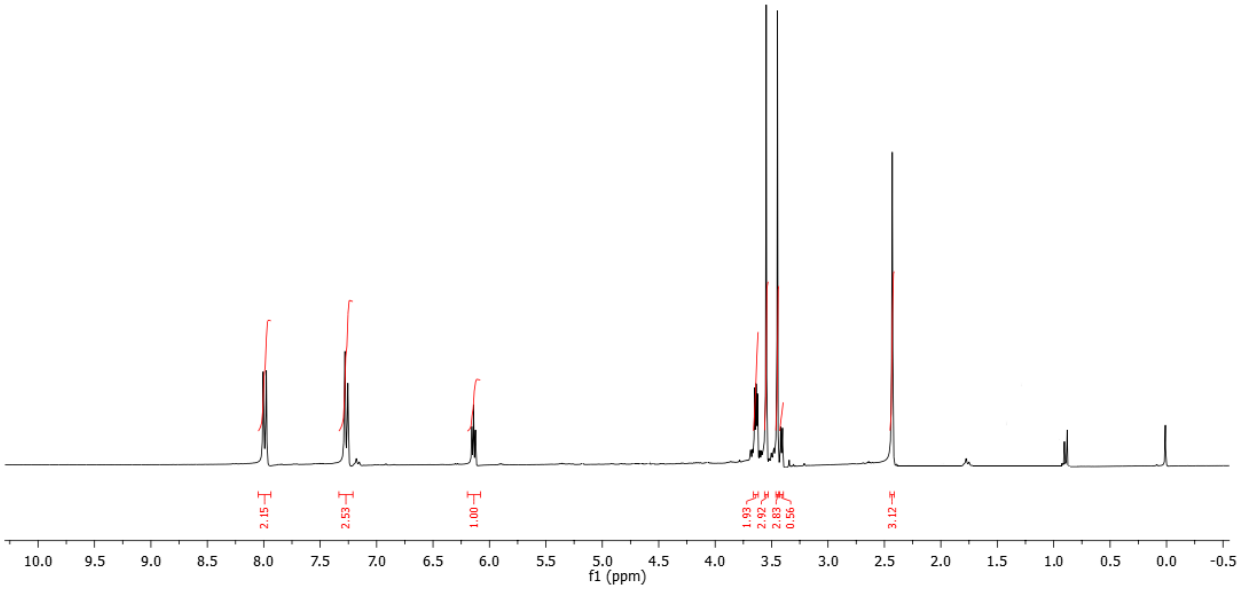


^{1}H NMR of Compound **4c**

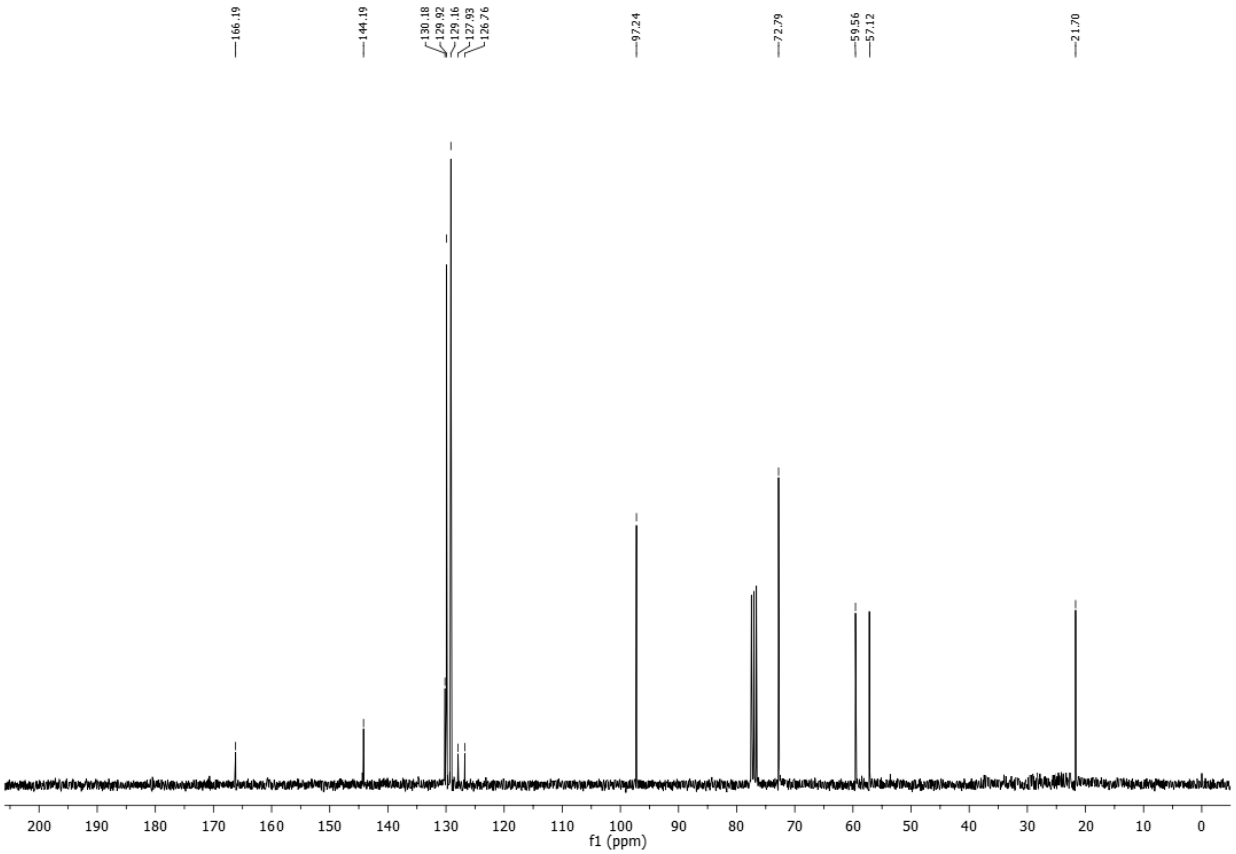


^{13}C NMR of Compound **4c**

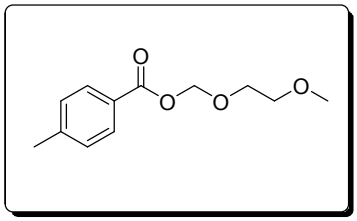


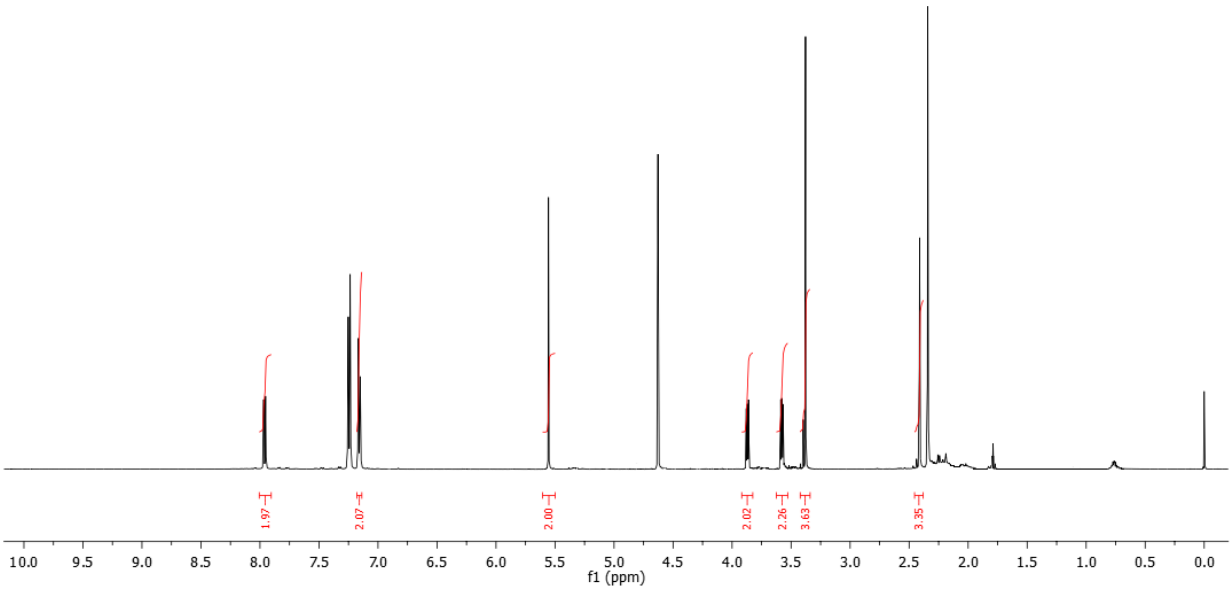


^{1}H NMR of Compound **4fa**

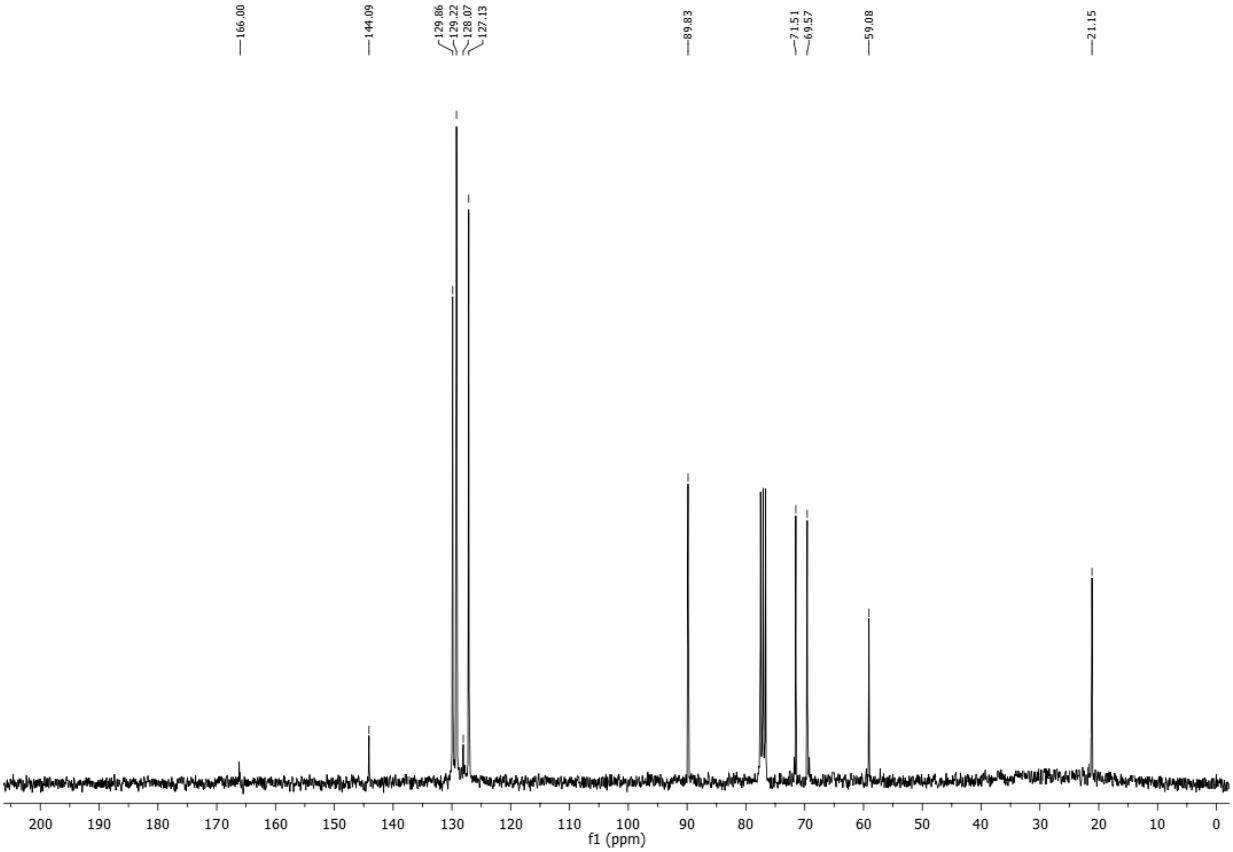


^{13}C NMR of Compound **4fa**

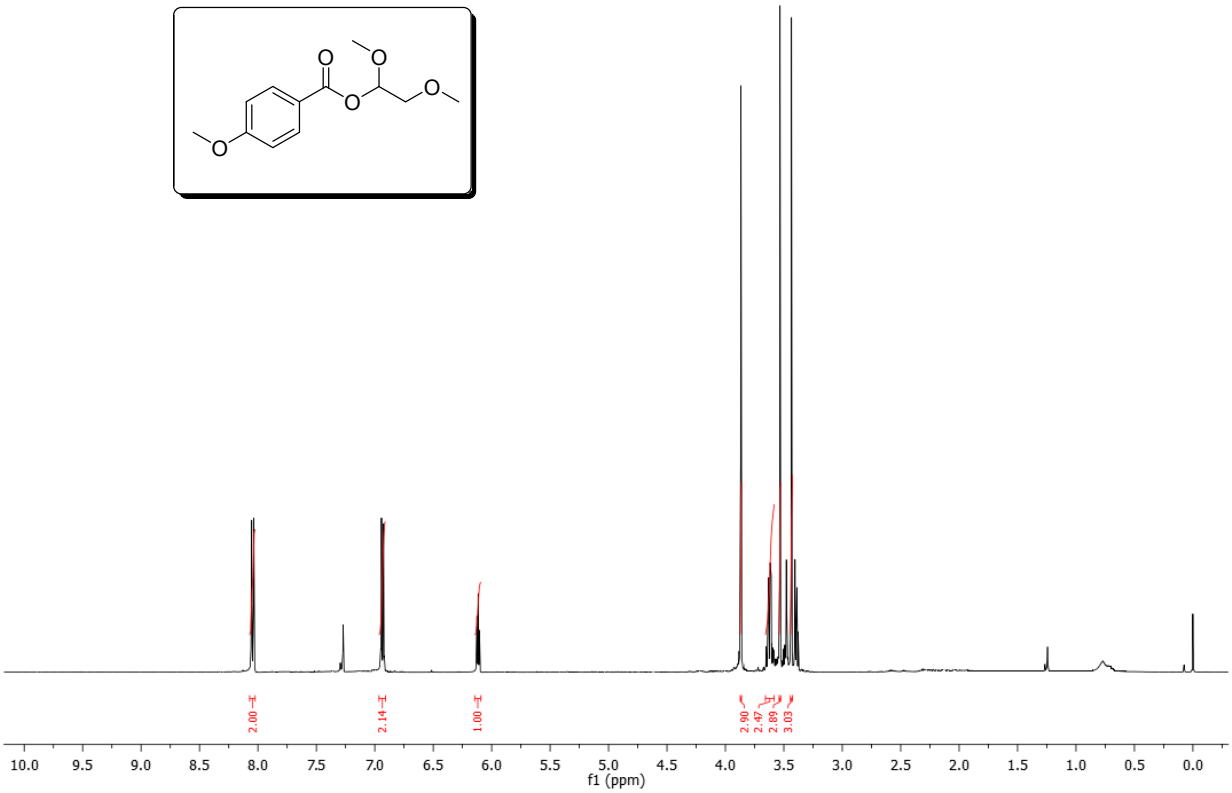




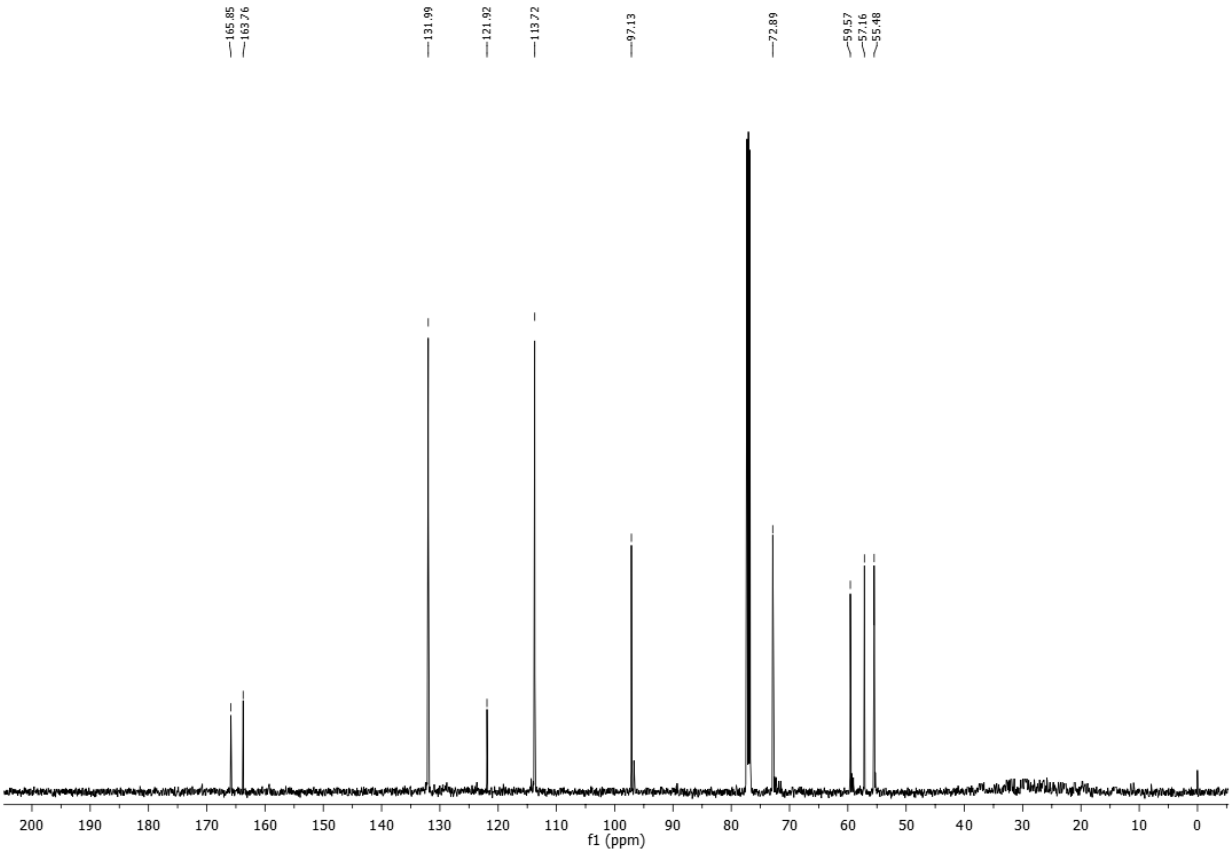
^{1}H NMR of Compound **4fa'**



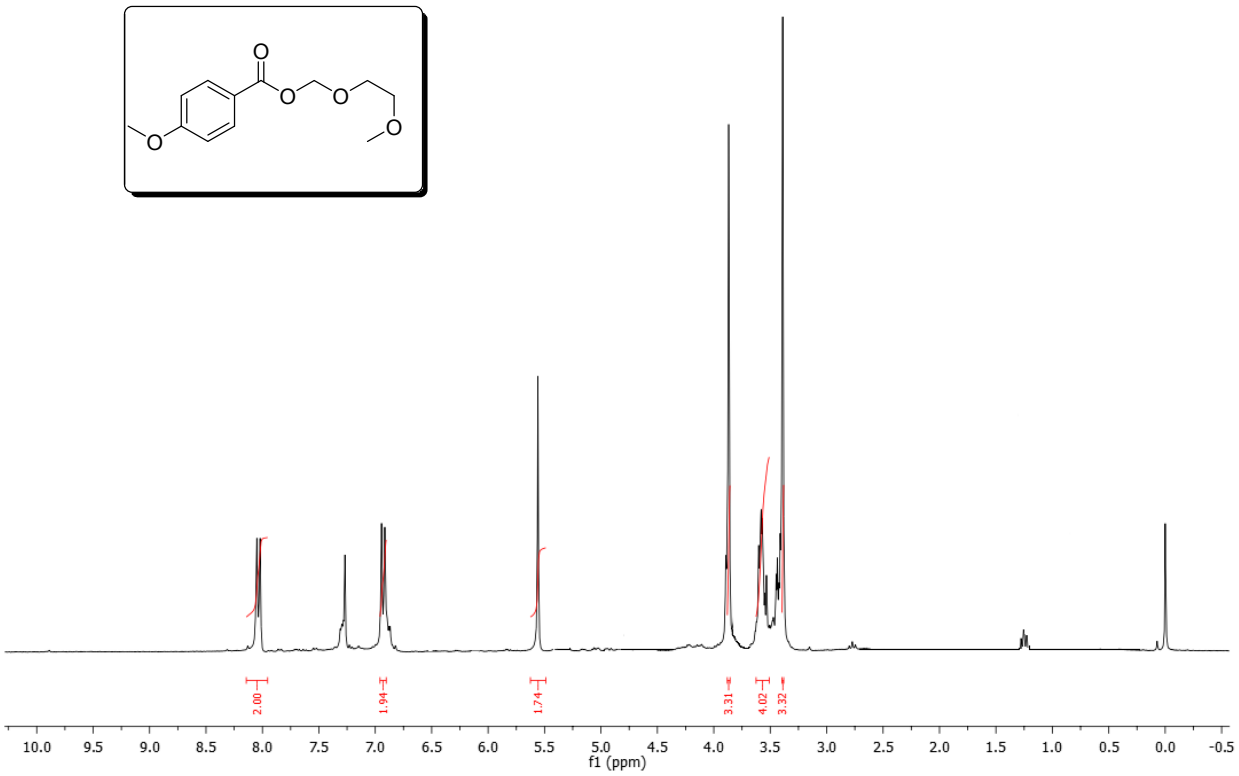
^{13}C NMR of Compound **4fa'**



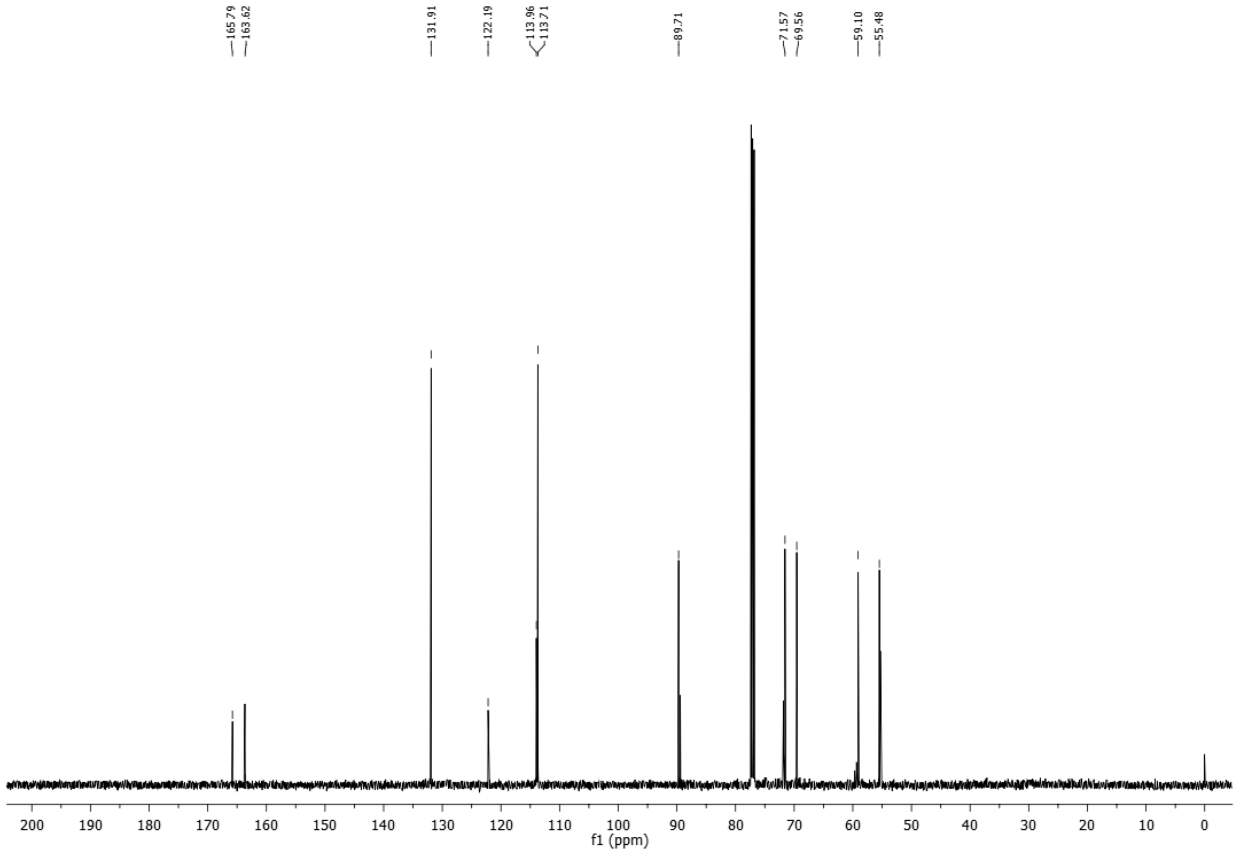
^{1}H NMR of Compound **4fb**



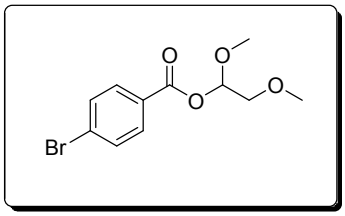
^{13}C NMR of Compound **4fb**

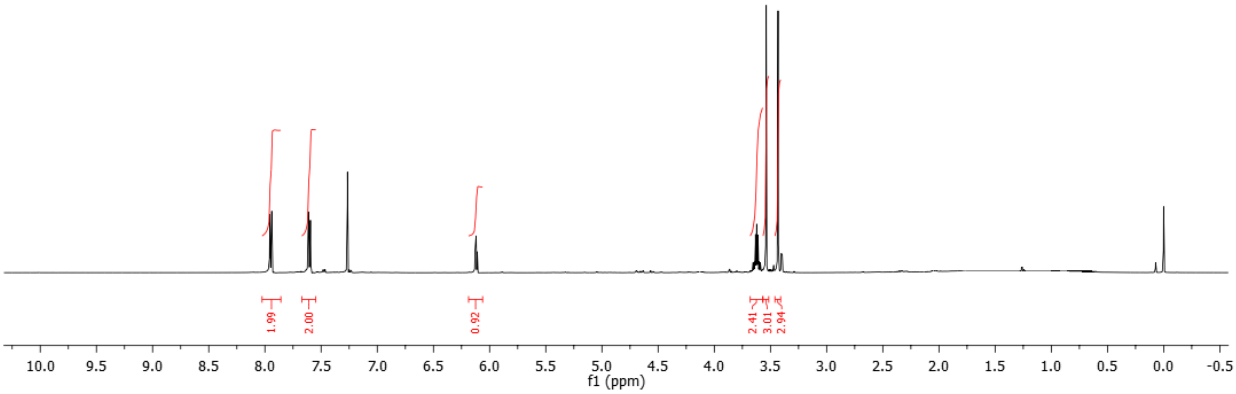


^{1}H NMR of Compound **4fb'**



^{13}C NMR of Compound **4fb'**





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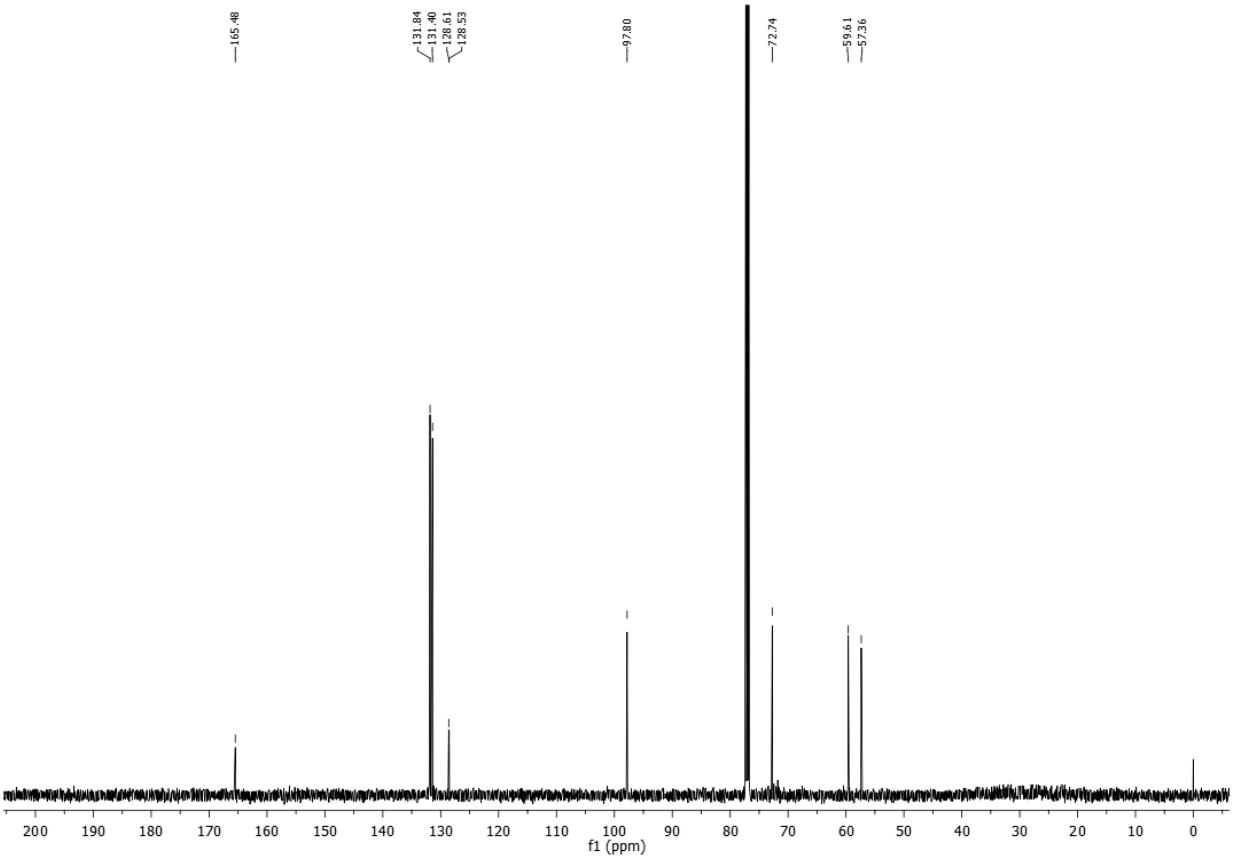

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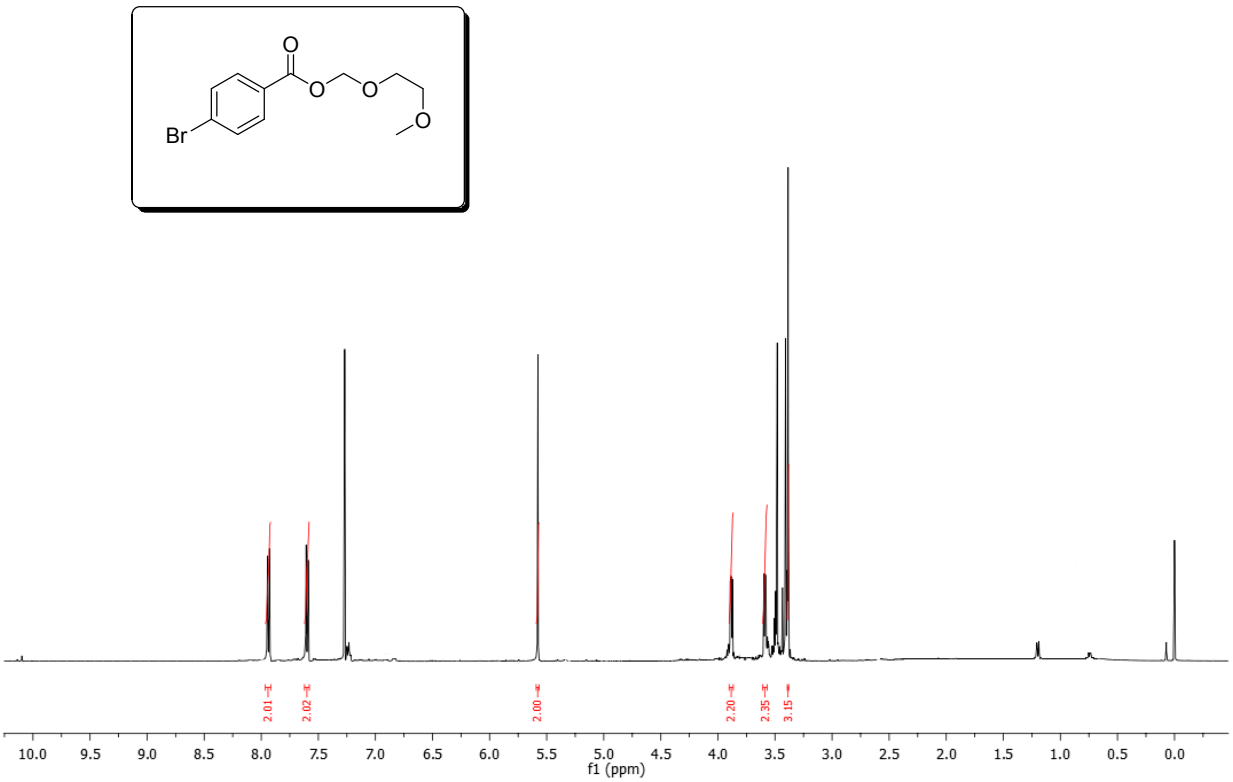
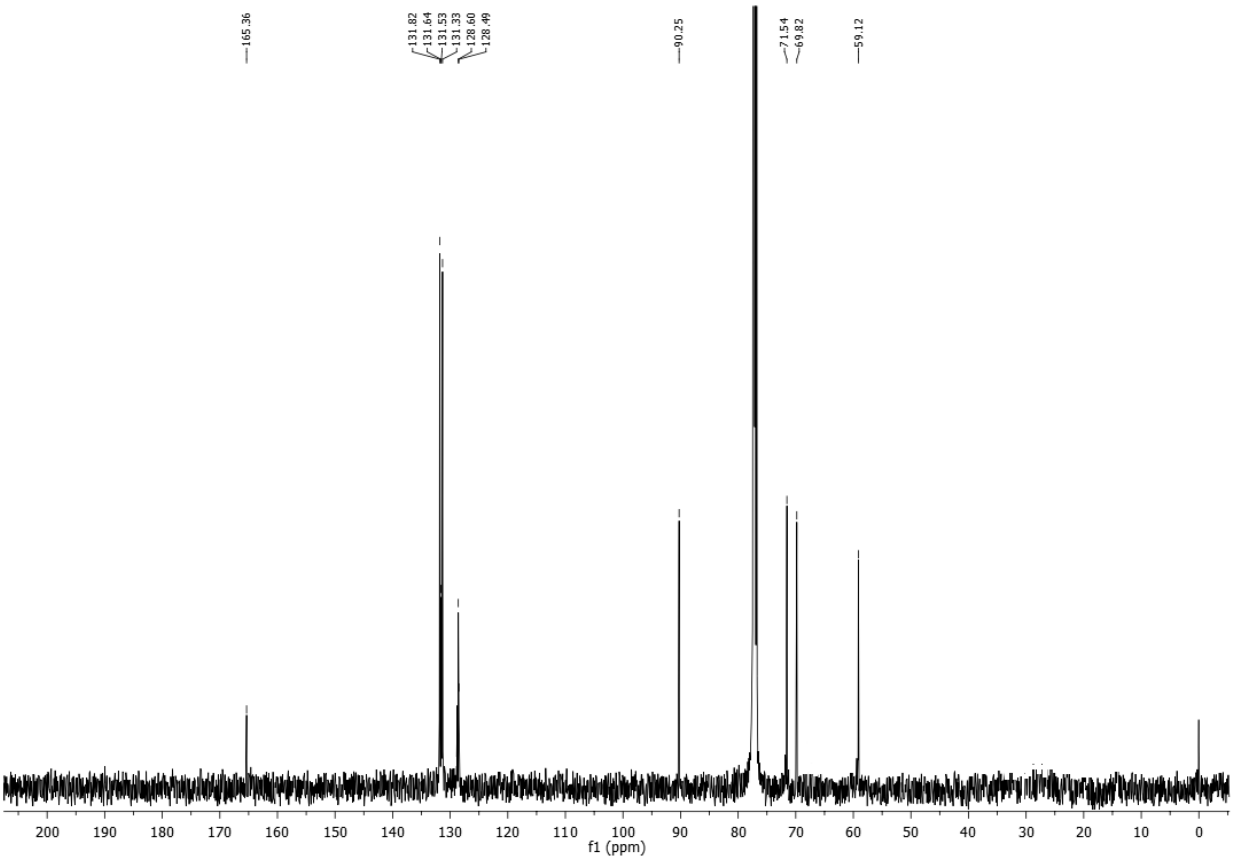


^{1} H NMR of Compound **4fc'**



^{13}C NMR of Compound **4fc'**