Supporting Information for

Autocatalytic methylthiomethylation of carboxylic acid/phenol involving the formation of DMSO enolate: convenient synthesis of methylthiomethyl ester/ether

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1. General information

Reagents, catalysts and solvents were purchased from commercial suppliers and used without further purification unless otherwise noted. Column Chromatography was performed with silica gel (200-300 mesh). Melting points were determined using a X-4 melting point apparatus with microscope. The IR spectra were recorded with Mattson FTIR spectrometer 5000. Absorption maxima were measured in cm^{-1}. ^{1}H NMR (600 MHz) and ^{13}C NMR (151 MHz) spectra were achieved in $CDCl_3$, CD_3OD and DMSO-d_6 on a Bruker AVANCE 600 MHz spectrometer. High-resolution mass spectra were measured on a ThermoFish QE Focus facility.

2. Preparation of methylthiomethyl esters/ethers

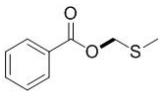
*General procedure for preparation of MTM esters (**2a-2aa**)*

To a solution of DMSO (1 mL) was added carboxylic acids **1** (0.3 mmol) in 5 mL round bottom flask. The reaction mixture was refluxed for 15 min. The solution was quenched with water and the organic layer was dried over Na_2SO_4 and evaporated. The resulting crude compound was purified by silica gel column chromatography using hexanes/ethyl acetate mixtures to afford corresponding products.

*General procedure for preparation of MTM ethers (**4a-4g**)*

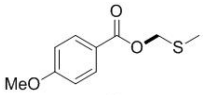
To a solution of DMSO (1 mL) was added phenols **3** (0.3 mmol) in 5 mL round bottom flask. The reaction mixture was refluxed for 60 min. The solution was quenched with water and the organic layer was dried over Na_2SO_4 and evaporated. The resulting crude compound was purified by silica gel column chromatography using hexanes/ethyl acetate mixtures to afford MTM phenyl ethers.

3. Analytical data of the products



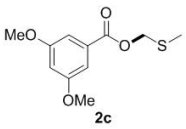
2a

methylthiomethyl benzoate (2a). Colorless oil; Yield: 85%; IR (cm^{-1}) 2923, 1721, 1601, 1412, 1332, 1260; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 – 8.09 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.62 – 7.59 (t, *J* = 7.5 Hz, 1H), 7.49 – 7.47 (t, *J* = 7.8 Hz, 2H), 5.42 (s, 2H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.27, 133.27, 129.84, 129.75, 128.45, 68.83, 15.51; HRMS Exact mass calcd. for $C_9H_{10}O_2NaS$ $[M+Na]^+$: 205.02937; found: 205.02905.



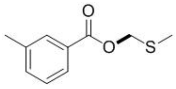
2b

methylthiomethyl 4-methoxybenzoate (2b). Colorless oil; Yield: 83%; IR (cm^{-1}) 2923, 1714, 1606, 1510, 1435, 1356, 1255, 1167; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 – 8.04 (d, *J* = 8.9 Hz, 2H), 6.96 – 6.94 (d, *J* = 8.9 Hz, 2H), 5.39 (s, 2H), 3.89 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.99, 163.63, 131.83, 122.22, 113.70, 68.48, 55.47, 15.47; HRMS Exact mass calcd. for $C_{10}H_{12}O_3NaS$ $[M+Na]^+$: 235.03994; found: 235.03928.



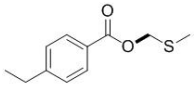
2c

methylthiomethyl 3,5-dimethoxybenzoate (2c). Colorless oil; Yield: 88%; IR (cm^{-1}) 2942, 1725, 1595, 1428, 1323, 1205, 1156; ^1H NMR (600 MHz, $CDCl_3$) δ 7.23 – 7.23 (d, *J* = 2.4 Hz, 2H), 6.69 – 6.69 (t, *J* = 2.4 Hz, 1H), 5.40 (s, 2H), 3.86 (s, 6H), 2.33 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.05, 160.69, 131.68, 107.35, 105.94, 69.01, 55.61, 15.55; HRMS Exact mass calcd. for $C_{11}H_{14}O_4NaS$ $[M+Na]^+$: 265.05050; found: 265.05020.



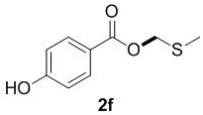
2d

methylthiomethyl 3-methylbenzoate (2d). Colorless oil; Yield: 85%; IR (cm^{-1}) 2922, 1720, 1589, 1414, 1344, 1268, 1189; ^1H NMR (600 MHz, CD_3OD) δ 7.87 (s, 1H), 7.85 – 7.84 (d, *J* = 7.8 Hz, 1H), 7.47 – 7.46 (d, *J* = 7.8 Hz, 1H),7.40 – 7.38 (t, *J* = 7.7 Hz, 1H), 5.43 (s, 2H), 2.42 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (151 MHz, CD_3OD) δ 166.34, 138.34, 133.78, 129.80, 129.62, 128.18, 126.38, 68.52, 19.90, 14.08; HRMS Exact mass calcd. for $C_{10}H_{10}O_2NaS$ $[M+Na]^+$: 219.04502; found: 219.04422.



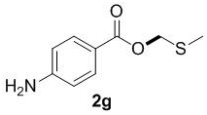
2e

methylthiomethyl 4-ethylbenzoate (2e). Colorless oil; Yield: 96%; IR (cm^{-1}) 2966, 1721, 1609, 1557, 1436, 1318, 1260, 1178; ^1H NMR (600 MHz, CD_3OD) δ 7.98 – 7.97 (d, *J* = 8.2 Hz, 2H), 7.36 – 7.35 (d, *J* = 7.7 Hz, 2H), 5.43 (s, 2H), 2.76 – 2.73 (q, *J* = 7.6 Hz, 2H), 2.33 (s, 3H), 1.30 – 1.27 (td, *J* = 7.6, 0.6 Hz, 3H). ^{13}C NMR (151 MHz, CD_3OD) δ 166.28, 150.39, 129.40, 127.77, 127.32, 68.39, 28.50, 14.34, 14.03; HRMS Exact mass calcd. for $C_{11}H_{14}O_2NaS$ $[M+Na]^+$: 233.06067; found: 233.06030.



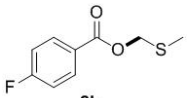
2f

methylthiomethyl 4-hydroxybenzoate (2f). White solid; Yield: 75%; Mp: 74.2-82.3 °C; IR (cm^{-1}) 3253, 2898, 1676, 1604, 1514, 1423, 1346, 1261, 1165; ^1H NMR (600 MHz, $CDCl_3$) δ 8.01 – 8.0 (d, *J* = 8.8 Hz, 2H), 6.91 – 6.89 (d, *J* = 8.8 Hz, 2H), 5.39 (s, 2H), 2.33 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.09, 160.17, 132.16, 122.31, 115.30, 68.62, 15.48; HRMS Exact mass calcd. for $C_9H_{10}O_3NaS$ $[M+Na]^+$: 221.02429; found: 221.02377.



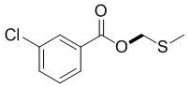
2g

methylthiomethyl 4-aminobenzoate (2g). White solid; Yield: 86%; Mp: 101.6-106.0 °C; IR (cm^{-1}) 3432, 3335, 2917, 1693, 1595, 1452, 1325, 1260, 1266, 1170; ^1H NMR (600 MHz, $CDCl_3$) δ 7.91 – 7.89 (d, *J* = 8.7 Hz, 1H), 6.67 – 6.66 (d, *J* = 8.7 Hz, 1H), 5.36 (s, 1H), 2.32 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.23, 151.14, 131.88, 119.27, 113.80, 68.11, 15.42; HRMS Exact mass calcd. for $C_9H_{11}O_2NNaS$ $[M+Na]^+$: 220.04027; found: 220.03987.



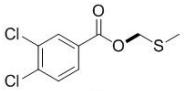
2h

methylthiomethyl 4-fluorobenzoate (2h). Colorless oil; Yield: 82%; IR (cm^{-1}) 3399, 2359, 1587, 1412, 1349; ^1H NMR (600 MHz, $CDCl_3$) δ 8.13 – 8.09 (m, 2H), 7.17 – 7.12 (m, 2H), 5.41 (s, 2H), 2.33 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.95(253.68), 165.30, 132.33(9.06), 126.08(3.02), 115.64(22.65), 69.02, 15.55. HRMS Exact mass calcd. for $C_9H_{10}O_2FS$ $[M+H]^+$: 201.03801; found: 201.03723.



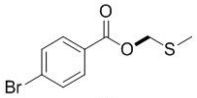
2i

methylthiomethyl 3-chlorobenzoate (2i). Colorless oil; Yield: 64%; IR (cm^{-1}) 2923, 1731, 1682, 1557, 1412, 1362, 1246, 1069; ^1H NMR (600 MHz, CD_3OD) δ 8.03 – 8.03 (t, J = 1.9 Hz, 1H), 8.01 – 7.99 (dt, J = 7.8, 1.4 Hz, 1H), 7.68 – 7.67 (ddd, J = 8.0, 2.3, 1.1 Hz, 1H), 7.55 – 7.52 (t, J = 7.9 Hz, 1H), 5.47 (s, 2H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, CD_3OD) δ 164.89, 134.35, 133.02, 131.82, 130.02, 128.99, 127.54, 69.14, 14.10. HRMS Exact mass calcd. for $C_9H_{10}O_2ClS$ $[M+H]^+$: 217.00845; found: 217.00789.



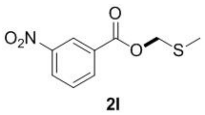
2j

methylthiomethyl 3,4-dichlorobenzoate (2j). Colorless oil; Yield: 65%; IR (cm^{-1}) 2924, 1729, 1603, 1534, 1429, 1361, 1237; ^1H NMR (600 MHz, CD_3OD) δ 8.17 – 8.17 (d, J = 2.0 Hz, 1H), 7.98 – 7.96 (dd, J = 8.4, 2.0 Hz, 1H), 7.72 – 7.71 (d, J = 8.4 Hz, 1H), 5.47 (s, 2H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, CD_3OD) δ 164.20, 137.37, 132.56, 131.02, 130.72, 130.16, 128.74, 69.40, 14.13. HRMS Exact mass calcd. for $C_9H_9O_2Cl_2S$ $[M+H]^+$: 250.96948; found: 250.96878.



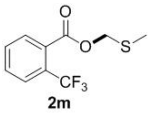
2k

methylthiomethyl 4-bromobenzoate (2k). Colorless oil; Yield: 83%; IR (cm^{-1}) 2921, 1720, 1589, 1442, 1366, 1258, 1081; ^1H NMR (600 MHz, $CDCl_3$) δ 7.95 – 7.94 (d, J = 8.5 Hz, 2H), 7.62 – 7.61 (d, J = 8.6 Hz, 2H), 5.41 (s, 2H), 2.33 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.57, 131.83, 131.26, 128.71, 128.47, 69.17, 15.59. HRMS Exact mass calcd. for $C_9H_9O_2BrNaS$ $[M+Na]^+$: 282.93988; found: 282.93884.



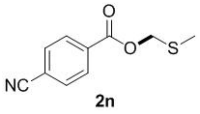
2l

methylthiomethyl 3-nitrobenzoate (2l). Colorless oil; Yield: 74%; IR (cm^{-1}) 3648, 2923, 1731, 1616, 1533, 1441, 1345, 1251, 1121; ^1H NMR (600 MHz, $CDCl_3$) δ 8.92 (s, 1H), 8.48 – 8.46 (d, J = 8.4 Hz, 1H), 8.43 – 8.42 (d, J = 7.8 Hz, 1H), 7.72 – 7.69 (t, J = 8.0 Hz, 1H), 5.48 (s, 2H), 2.37 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.23, 135.42, 131.63, 129.75, 127.71, 125.74, 124.73, 70.01, 15.76; HRMS Exact mass calcd. for $C_9H_9O_4NNaS$ $[M+Na]^+$: 250.01445; found: 250.01424.



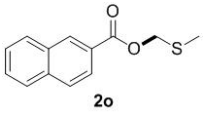
2m

methylthiomethyl 2-(trifluoromethyl) benzoate (2m). Colorless oil; Yield: 74%; IR (cm^{-1}) 2927, 1742, 1584, 1428, 1343, 1261, 1143; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.83 – 7.81 (m, 1H), 7.78 – 7.76 (m, 1H), 7.64 – 7.62 (dd, J = 6.2, 3.0 Hz, 2H), 5.40 (s, 2H), 2.32 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 161.66, 127.03, 126.68, 125.97(1.51), 125.64, 124.06(32.71), 122.01(5.03), 118.56(273.81), 65.32, 10.83; HRMS Exact mass calcd. for $C_{10}H_9O_2F_3NaS$ $[M+Na]^+$: 273.01676; found: 273.01590.



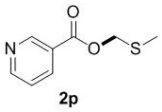
2n

methylthiomethyl 4-cyanobenzoate (2n). Colorless oil; Yield: 95%; IR (cm^{-1}) 2924, 2231, 1726, 1540, 1449, 1338, 1259, 1176 (m); ^{1}H NMR (600 MHz, CD_3OD) δ 8.22 – 8.21 (d, J = 8.6 Hz, 2H), 7.92 – 7.91 (d, J = 8.6 Hz, 2H), 5.49 (s, 2H), 2.35 (s, 3H). ^{13}C NMR (151 MHz, CD_3OD) δ 164.65, 133.79, 132.27, 129.84, 117.48, 116.38, 69.46, 14.11; HRMS Exact mass calcd. for $C_{10}H_9NO_2NaS$ $[M+Na]^+$: 230.02934; found: 230.02902.



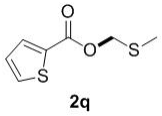
2o

methylthiomethyl 2-naphthoate (2o). White solid; Yield: 75%; Mp: 47.3-52.1 °C; IR (cm^{-1}) 2924, 1713, 1606, 1459, 1344, 1272, 1192; ^{1}H NMR (600 MHz, CD_3OD) δ 8.66 (s, 1H), 8.08 – 8.04 (m, 2H), 7.99 – 7.96 (m, 2H), 7.68 – 7.65 (t, J = 7.4 Hz, 1H), 7.62 – 7.60 (t, J = 7.5 Hz, 1H), 5.51 (s, 2H), 2.38 (s, 3H). ^{13}C NMR (151 MHz, CD_3OD) δ 166.34, 135.78, 132.57, 130.78, 129.05, 128.30, 128.06, 127.48, 127.07, 126.62, 124.58, 68.75, 14.12; HRMS Exact mass calcd. for $C_{13}H_{12}O_2NaS$ $[M+Na]^+$: 255.04502; found: 255.04469.



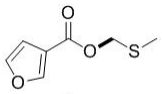
2p

methylthiomethyl nicotinate (2p). Colorless oil; Yield: 85%; IR (cm^{-1}) 3566, 2923, 1731, 1653, 1591, 1427, 1336, 1267, 1100; ^{1}H NMR (600 MHz, CD_3OD) δ 9.18 – 9.17 (m, 1H), 8.81 – 8.80 (d, J = 4.1 Hz, 1H), 8.47 – 8.45 (dt, J = 8.0, 2.0 Hz, 1H), 7.63 – 7.61 (m, 1H), 5.51 (s, 2H), 2.37 (s, 3H). ^{13}C NMR (151 MHz, CD_3OD) δ 165.96, 154.30, 151.17, 138.98, 127.86, 125.36, 70.71, 15.51; HRMS Exact mass calcd. for $C_8H_9NO_2NaS$ $[M+H]^+$: 184.04268; found: 184.04259.



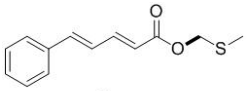
2q

(methylthio)methyl thiophene-2-carboxylate (2q). Colorless oil; Yield: 81%; IR (cm-1) 3383, 3108, 3098, 2945, 1708; 1H NMR (600 MHz, CDCl3) δ 7.87 – 7.86 (d, J = 3.8 Hz, 1H), 7.62 – 7.61 (d, J = 4.6 Hz, 1H), 7.15 – 7.13 (t, J = 4.4 Hz, 1H), 5.39 (s, 2H), 2.33 (s, 3H). 13C NMR (151 MHz, CDCl3) δ 161.83, 133.93, 133.30, 132.92, 127.87, 68.97, 15.51; HRMS Exact mass calcd for $C_7H_8O_2NaS_2$ $[M+Na]^+$: 210.98579; found: 210.98524.



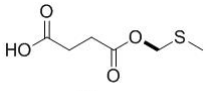
2r

(methylthio)methyl furan-2-carboxylate (2r). Colorless oil; Yield: 78%; IR (cm^{-1}) 3580, 3132, 3074, 1721; ^1H NMR (600 MHz, $CDCl_3$) δ 8.08 – 8.07 (dd, *J* = 1.6, 0.8 Hz, 1H), 7.46 – 7.45 (t, *J* = 1.7 Hz, 1H), 6.79 – 6.78 (dd, *J* = 1.9, 0.8 Hz, 1H), 5.33 (s, 2H), z2.30 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.69, 148.09, 143.87, 119.03, 109.81, 68.32, 15.49; HRMS Exact mass calcd for $C_7H_9O_3S$ $[M+H]^+$: 173.02669; found: 173.02620.



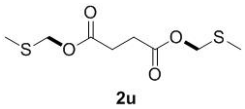
2s

methylthiomethyl (*2E*,*4E*)-5-phenylpenta-2,4-dienoate (2s). Yellow solid; Yield: 77%; Mp: 71.7-75.4 °C; IR (cm^{-1}) 2925, 1704, 1622, 1418, 1331, 1231, 1126; ^1H NMR (600 MHz, $CDCl_3$) δ 7.54 – 7.51 (m, 1H), 7.50 – 7.49 (m, 2H), 7.40 – 7.37 (m, 2H), 7.36 – 7.33 (m, 1H), 6.97 – 6.89 (m, 2H), 6.06 – 6.03 (d, *J* = 15.4 Hz, 1H), 5.27 (s, 2H), 2.30 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.63, 145.62, 141.14, 135.92, 129.23, 128.86, 127.29, 126.08, 120.45, 68.18, 15.47; HRMS Exact mass calcd. for $C_{13}H_{14}O_2NaS$ $[M+Na]^+$: 257.06067; found: 257.05981.



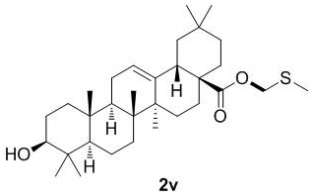
2t

4-(methylthiomethoxy)-4-oxobutanoic acid (2t). White solid; Yield: 91%; Mp: 62.9-75.3 °C; IR (cm^{-1}) 2956, 1727, 1421, 1375, 1251, 1165; ^1H NMR (600 MHz, $CDCl_3$) δ 5.18 (s, 2H), 2.74 – 2.68 (m, 4H), 2.25 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.94, 171.89, 68.65, 28.94, 28.78, 15.38; HRMS Exact mass calcd. for $C_6H_{10}O_4NaS$ $[M+Na]^+$: 201.01920; found: 201.01840.



2u

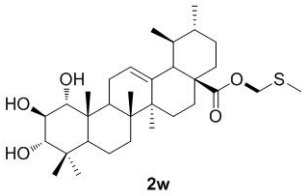
bis(methylthiomethyl) succinate (2u). Colorless oil; Yield: 78%; IR (cm^{-1}) 2924, 1737, 1419, 1364, 1142; ^1H NMR (600 MHz, $CDCl_3$) δ 5.18 (s, 4H), 2.72 (s, 4H), 2.26 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.87, 68.59, 29.09, 15.43; HRMS Exact mass calcd. for $C_8H_{14}O_4NaS_2$ $[M+Na]^+$: 261.02257; found: 261.02209.



2v

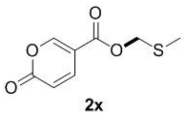
methylthiomethyl oleanolate (2v). White solid; Yield: 80%; Mp: 106.2-132.2 °C; IR (cm^{-1}) 3384, 2942, 1732, 1510, 1443, 1356, 1255, 1154; ^1H NMR (600 MHz, $CDCl_3$) δ 5.33 – 5.32 (t, *J* = 3.7 Hz, 1H), 5.18 – 5.16 (d, *J* = 11.6 Hz, 1H), 5.08 – 5.06 (d, *J* = 11.6 Hz, 1H), 3.24 – 3.22 (dd, *J* = 11.3, 4.3 Hz, 1H), 2.91 – 2.88 (dd, *J* = 14.1, 4.7 Hz, 1H), 2.25 (s, 3H), 2.04 – 1.98 (td, *J* = 14.7, 4.1 Hz, 1H), 1.93 – 1.86 (m, 2H), 1.76 – 1.70 (td, *J* = 13.9, 4.4 Hz, 1H), 1.68 – 1.62 (m, 6H), 1.60 – 1.58 (td, *J* = 4.8, 4.1, 2.7 Hz, 1H), 1.56 – 1.53 (m, 2H), 1.49 – 1.47 (dd, *J* = 12.6, 4.0 Hz, 1H), 1.45 – 1.42 (m, 1H), 1.40 – 1.38 (m, 1H), 1.36 – 1.33 (dd, *J* = 13.7, 4.2 Hz, 1H), 1.32 – 1.27 (m, 2H), 1.25 – 1.17 (m, 2H), 1.16 (s, 3H), 1.12 – 1.09 (dt, *J* = 13.5, 3.1 Hz, 1H), 1.00 (s, 3H), 0.95 (s,

3H), 0.92 (s, 6H), 0.80 (s, 3H), 0.78 (s, 3H), 0.76 – 0.74 (d, *J* = 9.7 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.28, 143.60, 122.52, 79.03, 67.95, 55.21, 47.62, 46.89, 45.90, 41.75, 41.23, 39.39, 38.76, 38.45, 37.03, 33.86, 33.09, 32.76, 32.27, 30.71, 28.11, 27.59, 27.20, 25.82, 23.61, 23.43, 23.06, 18.34, 17.13, 15.60, 15.46, 15.36; HRMS Exact mass calcd. for $C_{32}H_{52}O_3NaS$ $[M+Na]^+$: 539.35294; found: 539.35278.



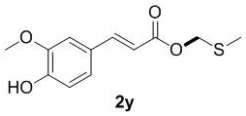
2w

methylthiomethyl 1,2-dihydroxyursolate (2w). White solid; Yield: 73%; Mp: 98.6-110.2 °C; IR (cm^{-1}) 3445, 2924, 1731, 1652, 1557, 1436, 1332, 1134; ^{1}H NMR (600 MHz, CD_3OD) δ 5.30 – 5.29 (t, *J* = 3.7 Hz, 1H), 5.15 – 5.09 (m, 2H), 4.62 (s, 1H), 3.97 – 3.96 (dd, *J* = 4.2, 2.9 Hz, 1H), 3.66 – 3.65 (d, *J* = 2.9 Hz, 1H), 3.50 – 3.49 (d, *J* = 4.2 Hz, 1H), 2.43 – 2.40 (dd, *J* = 10.4, 7.1 Hz, 1H), 2.28 – 2.27 (d, *J* = 1.8 Hz, 1H), 2.25 (s, 3H), 2.14 – 2.09 (td, *J* = 13.5, 4.5 Hz, 1H), 2.03 – 2.00 (m, 2H), 1.92 – 1.87 (td, *J* = 13.8, 4.8 Hz, 1H), 1.74 – 1.72 (dd, *J* = 5.7, 3.1 Hz, 1H), 1.72 – 1.69 (q, *J* = 4.8, 3.6 Hz, 1H), 1.67 – 1.62 (td, *J* = 13.4, 4.3 Hz, 2H), 1.60 – 1.58 (m, 1H), 1.56 – 1.53 (m, 2H), 1.40 – 1.39 (d, *J* = 3.7 Hz, 1H), 1.38 – 1.37 (t, *J* = 3.5 Hz, 1H), 1.35 (s, 1H), 1.27 (s, 3H), 1.25 – 1.22 (m, 2H), 1.18 (s, 3H), 1.15 – 1.12 (m, 2H), 1.03 (s, 3H), 1.00 (s, 3H), 0.99 (s, 1H), 0.93 (s, 3H), 0.92 (s, 3H), 0.88 (s, 3H). ^{13}C NMR (151 MHz, CD_3OD) δ 177.31, 137.90, 126.12, 76.12, 74.01, 73.54, 67.87, 52.94, 48.29, 48.24, 42.48, 40.15, 39.35, 39.06, 38.98, 38.07, 37.98, 36.48, 32.49, 30.31, 28.80, 27.68, 23.98, 22.82, 22.79, 20.13, 17.69, 17.13, 16.48, 16.21, 14.05, 13.63; HRMS Exact mass calcd. for $C_{32}H_{52}O_5NaS$ $[M+Na]^+$: 571.34277; found: 571.34271.



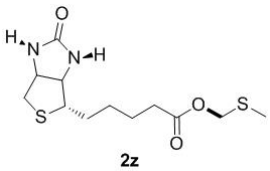
2x

methylthiomethyl 2-oxo-*2H*-pyran-5-carboxylate (2x). Yellow solid; Yield: 75%; Mp: 81.7-98.2 °C; IR (cm^{-1}) 2902, 1731, 1557, 1412, 1354, 1102; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.37 – 8.37 (dd, *J* = 2.6, 1.1 Hz, 1H), 7.83 – 7.81 (dd, *J* = 9.8, 2.6 Hz, 1H), 6.39 – 6.38 (dd, *J* = 9.8, 1.1 Hz, 1H), 5.37 (s, 2H), 2.32 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.73, 159.64, 158.52, 141.46, 115.42, 111.82, 69.76, 15.72; HRMS Exact mass calcd. for $C_8H_8O_4NaS$ $[M+Na]^+$: 223.00355; found: 223.00316.



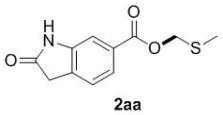
2y

methylthiomethyl (*E*)-3-(4-hydroxy-3-methoxyphenyl) acrylate (2y). White solid; Yield: 63%; Mp: 65.3-72.7 °C; IR (cm^{-1}) 3423, 2923, 1708, 1632, 1594, 1421, 1322, 1269, 1146; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 – 7.67 (d, *J* = 15.9 Hz, 1H), 7.12 – 7.10 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.06 – 7.06 (d, *J* = 1.9 Hz, 1H), 6.96 – 6.94 (d, *J* = 8.2 Hz, 1H), 6.35 – 6.33 (d, *J* = 15.9 Hz, 1H), 5.91 (s, 1H), 5.30 (s, 2H), 3.96 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.86, 148.19, 146.79, 145.77, 126.84, 123.29, 114.83, 114.77, 109.39, 68.20, 55.96, 15.47; HRMS Exact mass calcd. for $C_{12}H_{14}O_4NaS$ $[M+Na]^+$: 277.05050; found: 277.05020.



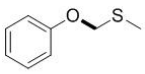
2z

methylthiomethyl 5-((*4S*)-2-oxohexahydro-*1H*-thieno[3,4-d]imidazole-4-yl)pentanoate (2z). Yellow solid; Yield: 62%; Mp: 98.7-112.4 ºC; IR (cm^{-1}) 3437, 3325, 2917, 1429, 1361, 1236, 1140; ^1H NMR (600 MHz, $CDCl_3$) δ 5.92 (s, 1H), 5.54 (s, 1H), 5.16 (s, 2H), 4.55 – 4.53 (t, *J* = 6.3 Hz, 1H), 4.36 – 4.34 (t, *J* = 6.0 Hz, 1H), 3.21 – 3.18 (dt, *J* = 10.9, 5.6 Hz, 1H), 2.96 – 2.93 (dd, *J* = 12.9, 5.0 Hz, 1H), 2.78 – 2.76 (d, *J* = 12.8 Hz, 1H), 2.42 – 2.39 (t, 2H), 2.27 (s, 3H), 2.07 (s, 1H), 1.76 – 1.70 (m, 5H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.24, 173.26, 68.15, 62.05, 60.20, 55.34, 40.56, 33.93, 28.31, 24.65, 21.00, 15.49; HRMS Exact mass calcd. for $C_{12}H_{20}O_3N_2NaS_2$ $[M+Na]^+$: 327.08076; found: 327.08072.



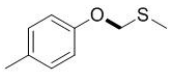
2aa

methylthiomethyl 2-oxoindoline-6-carboxylate (2aa). Yellow solid; Yield: 97%; Mp: 75.3-76.8 ºC; IR (cm^{-1}) 3209, 2903, 1715, 1596, 1421, 1363, 1262, 1199; ^1H NMR (600 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.81 – 7.80 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.59 (s, 1H), 7.34 – 7.33 (d, *J* = 7.7 Hz, 1H), 5.41 (s, 2H), 3.63 (s, 2H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.73, 165.83, 142.68, 130.89, 129.85, 124.60, 124.41, 110.33, 69.15, 36.23, 15.59; HRMS Exact mass calcd. for $C_{11}H_{11}O_3NNaS$ $[M+Na]^+$: 260.03519; found: 260.03458.



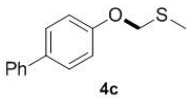
4a

methylthiomethyl phenyl ether (4a). Colorless oil; Yield: 62%; IR (cm^{-1}) 2923, 2893, 1601, 1497, 825, 613; ^1H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.33 (dd, *J* = 8.7, 7.3 Hz, 2H), 7.05 – 7.03 (tt, *J* = 7.3, 1.1 Hz, 1H), 7.01 – 6.99 (dd, *J* = 8.7, 1.1 Hz, 2H), 5.18 (s, 2H), 2.29 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.06, 129.49, 121.78, 115.98, 72.38, 14.62; HRMS Exact mass calcd. for C_8H_9OS $[M-H]^-$: 153.03686; found: 153.03661.



4b

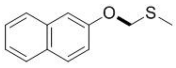
4-methyl-methylthiomethyl phenyl ether (4b). Colorless oil; Yield: 69%; IR (cm^{-1}) 2901, 2889, 1621, 1503, 824, 623; ^1H NMR (600 MHz, $CDCl_3$) δ 7.13 – 7.12 (d, *J* = 8.2 Hz, 2H), 6.89 – 6.88 (d, *J* = 8.6 Hz, 2H), 5.15 (s, 1H), 2.32 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.82, 131.21, 129.95, 116.01, 72.65, 20.55, 14.55; HRMS Exact mass calcd. for $C_9H_{12}ONaS$ $[M+Na]^+$: 191.03765; found: 191.03751.



4c

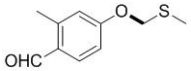
4-phenyl-methylthiomethyl phenyl ether (4c). Colorless oil; Yield: 72%; IR (cm^{-1}) 2923, 2837,1632, 1507, 835, 633; ^1H NMR (600 MHz, $CDCl_3$) δ 7.58 – 7.56 (td, *J* = 7.0, 1.8 Hz, 4H), 7.46 – 7.43 (t, *J* = 7.7 Hz, 2H), 7.35 – 7.32 (m, 1H), 7.07 – 7.05 (d, *J* = 8.7 Hz, 2H), 5.22 (s, 2H),

2.31(s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.51, 140.70, 134.90, 128.74, 128.19, 126.83, 116.22, 72.46, 14.63; HRMS Exact mass calcd. for $C_{14}H_{14}ONaS$ $[M+Na]^+$: 253.02937; found: 253.02905.



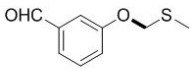
4d

methylthiomethyl naphthol ether (4d). Colorless oil; Yield: 70%; IR (cm^{-1}) 3010, 2918, 2899, 1609, 1554, 853, 642; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 – 7.79 (dd, *J* = 8.6, 2.4 Hz, 2H), 7.78 – 7.76 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.49 – 7.46 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.40 – 7.37 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.25 – 7.25 (d, *J* = 2.5 Hz, 1H), 7.22 – 7.21 (dd, *J* = 8.9, 2.5 Hz, 1H), 5.29 (s, 2H), 2.32 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.95, 134.25, 129.60, 129.41, 127.66, 126.98, 126.47, 124.08, 119.12, 109.03, 72.44, 14.76; HRMS Exact mass calcd. for $C_{12}H_{12}ONaS$ $[M+Na]^+$: 227.02765; found: 227.02745.



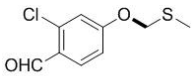
4e

3-methyl-4-formylmethylthiomethyl phenyl ether (4e). Colorless oil; Yield: 65%; IR (cm^{-1}) 2913, 2879, 1689, 1594, 873, 662; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.15 (s, 1H), 7.79 – 7.78 (d, *J* = 8.5 Hz, 1H), 6.92 – 6.90 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.82 – 6.81 (d, *J* = 1.6 Hz, 1H), 5.22 (s, 2H), 2.68 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.23, 161.07, 143.23, 134.52, 128.58, 118.63, 113.06, 72.19, 19.90, 14.69; HRMS Exact mass calcd. for $C_{10}H_{12}O_2NaS$ $[M+Na]^+$: 219.04938; found: 219.04912.



4f

3-formyl methylthiomethyl phenyl ether (4f). Colorless oil; Yield: 62%; IR (cm^{-1}) 2890, 2487, 1690, 1664, 846, 637; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.55 – 7.53 (dt, *J* = 7.5, 1.3 Hz, 1H), 7.51 – 7.48 (t, *J* = 7.8 Hz, 1H), 7.48 – 7.47 (dd, *J* = 2.7, 1.4 Hz, 1H), 7.26 – 7.25 (ddd, *J* = 8.1, 2.6, 1.2 Hz, 1H), 5.23 (s, 2H), 2.28 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.90, 157.57, 137.76, 130.17, 124.18, 122.91, 114.83, 72.51, 14.59; HRMS Exact mass calcd. for $C_9H_{10}O_2NaS$ $[M+Na]^+$: 205.02947; found: 205.02915.

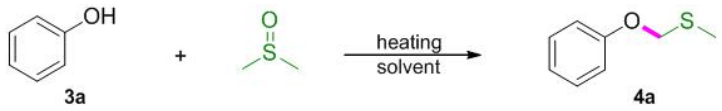


4g

3-chloro-4-formylmethylthiomethyl phenyl ether (4g). Colorless oil; Yield: 47%; IR (cm^{-1}) 2896, 2479, 1709, 1654, 859, 667; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.37 – 10.37 (d, *J* = 0.8 Hz, 1H), 7.94 – 7.92 (d, *J* = 8.7 Hz, 1H), 7.02 – 7.02 (d, *J* = 2.4 Hz, 1H), 6.97 – 6.95 (ddd, *J* = 8.7, 2.4, 0.9 Hz, 1H), 5.22 (s, 2H), 2.29 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 188.58, 162.04, 139.53, 130.94, 126.65, 117.09, 114.96, 72.72, 14.70; HRMS Exact mass calcd. for $C_9H_9ClO_2NaS$ $[M+Na]^+$: 239.04768; found: 239.04747.

4. Optimization of the reaction conditions

Table S1 Optimization of the reaction conditions: synthesis of MTM phenyl ethers*a*



Entry	*T* (°C)	t (min)	Solvent	Yield **4a** (%)[b]
1	reflux	15	/	11
2	180	15	/	/
3	reflux	30	/	30
4	reflux	60	/	62
5	reflux	90	/	59
6	reflux	60	DMF	6
7	reflux	60	DMA	/
8	reflux	60	1,4-dioxane	/
9	reflux	60	THF	/
10	reflux	60	DCE	/
11	reflux	60	CCl_4	/
12	reflux	60	EtOH	/
13[c]	reflux	60	/	24
14[d]	190	60	/	63

[a] Reaction conditions: **3a** (0.3 mmol), DMSO (1 mL), solvent (1 mL). [b] Isolated yield. [c] Under microwave irradiation. [d] Reaction carried out in a pressure-resistant reaction bottle.

5. HRMS of DMSO enolate 5

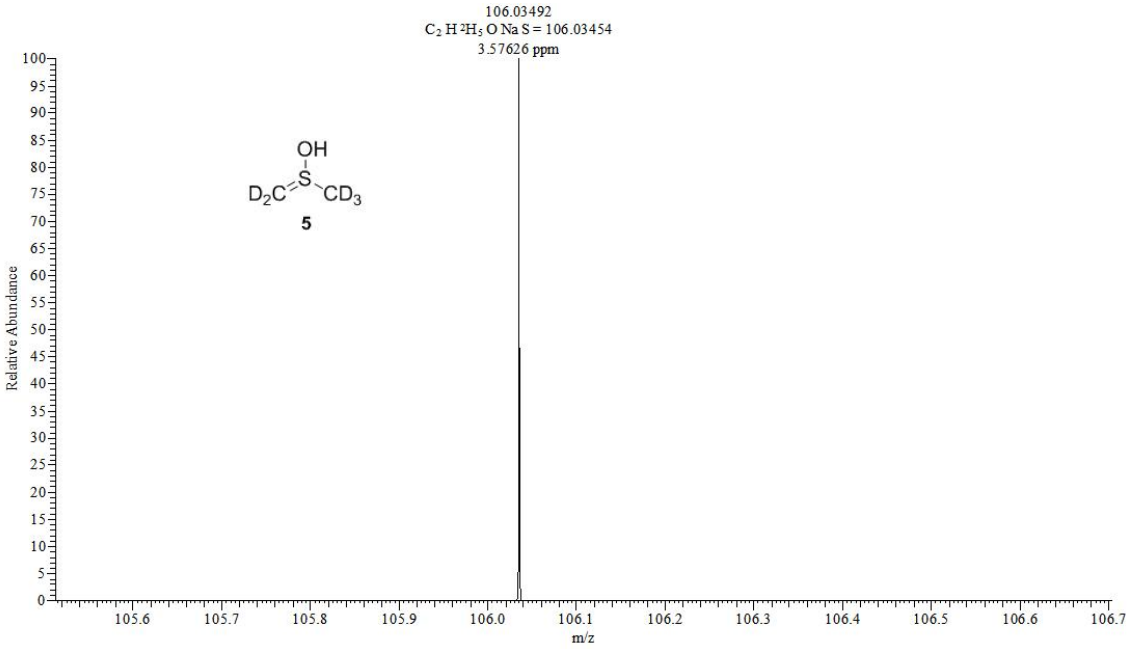
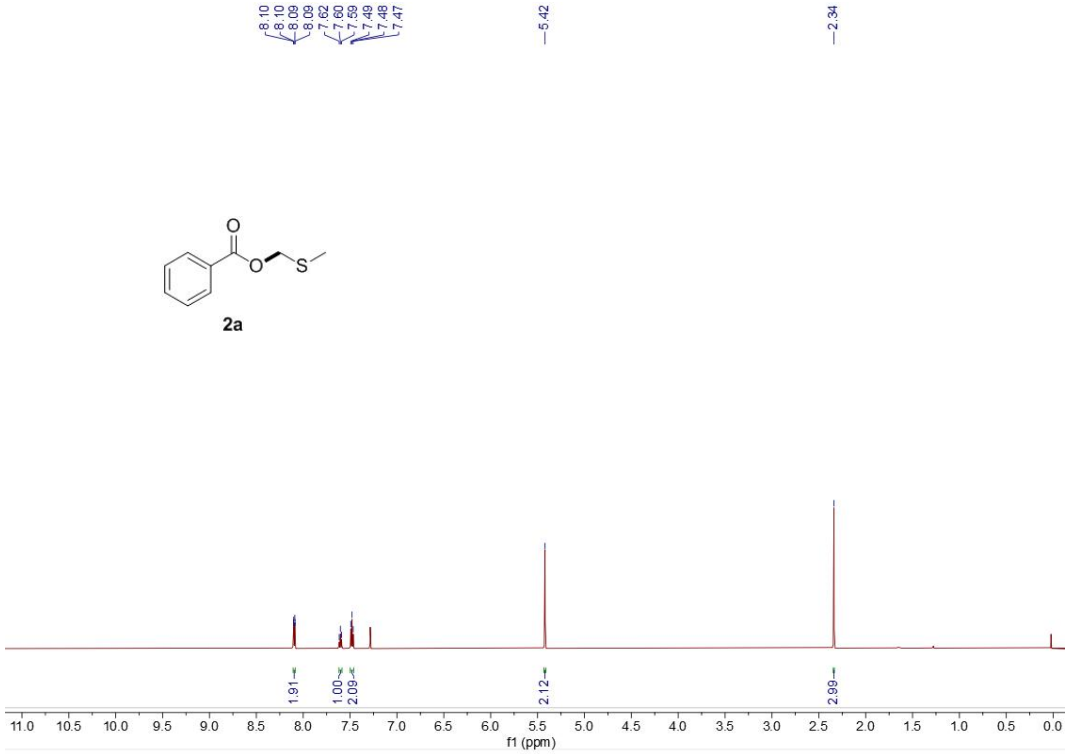
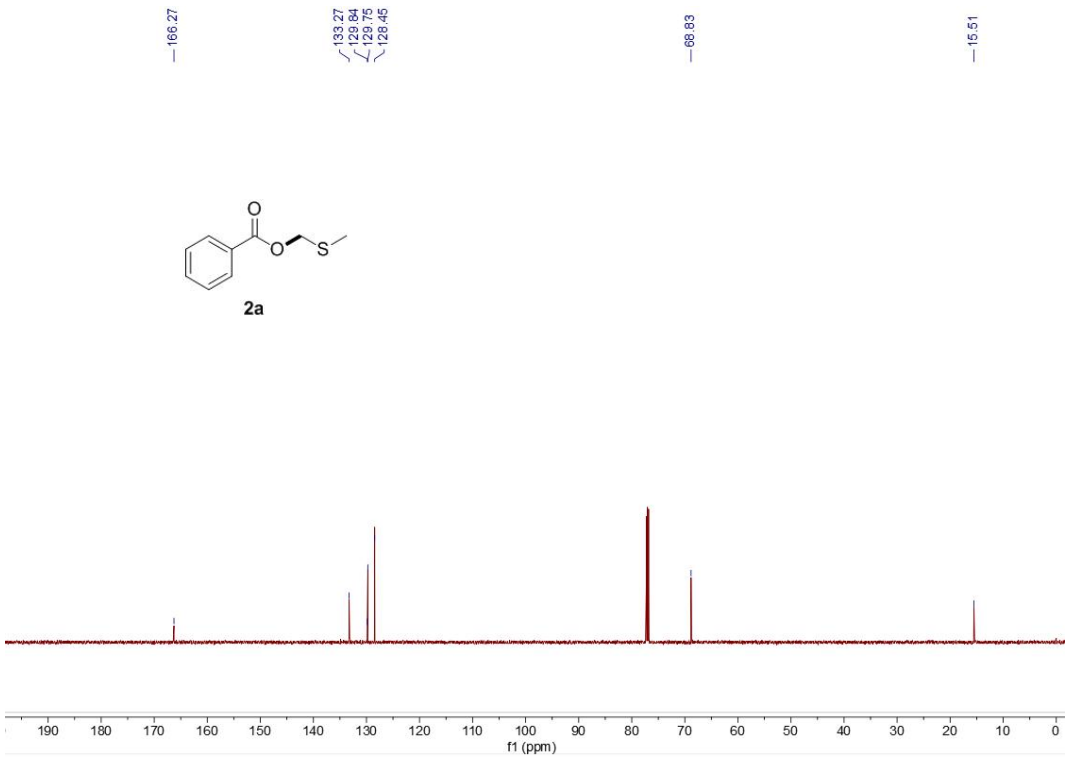
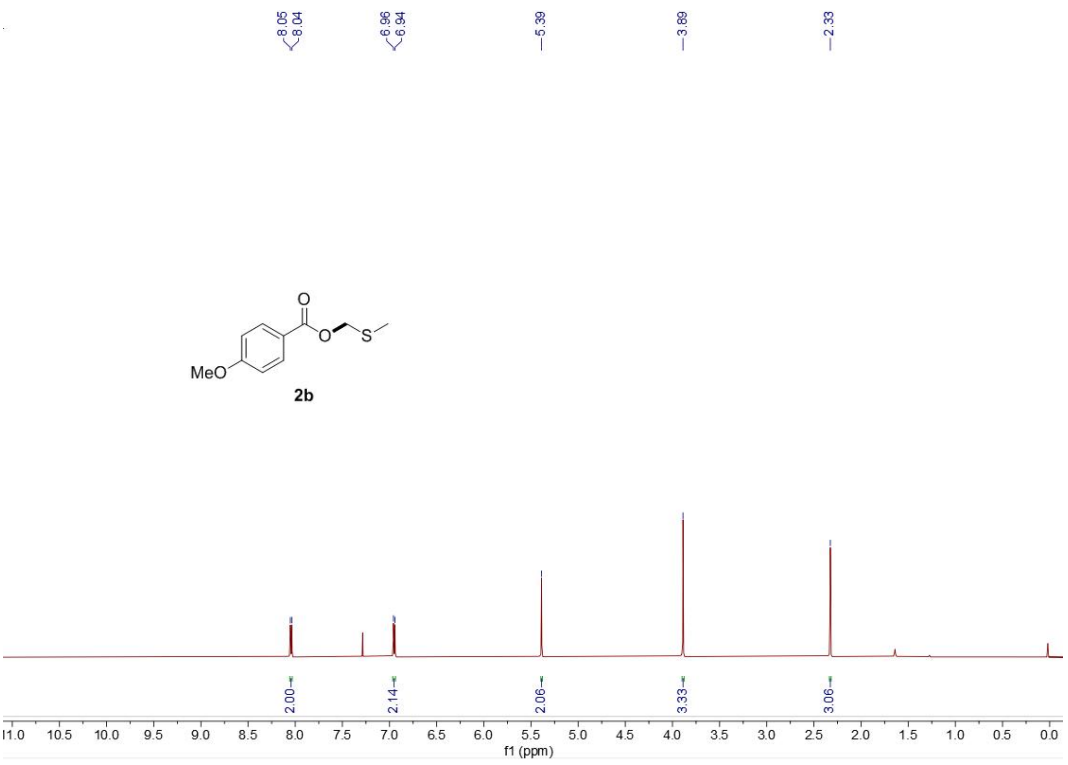


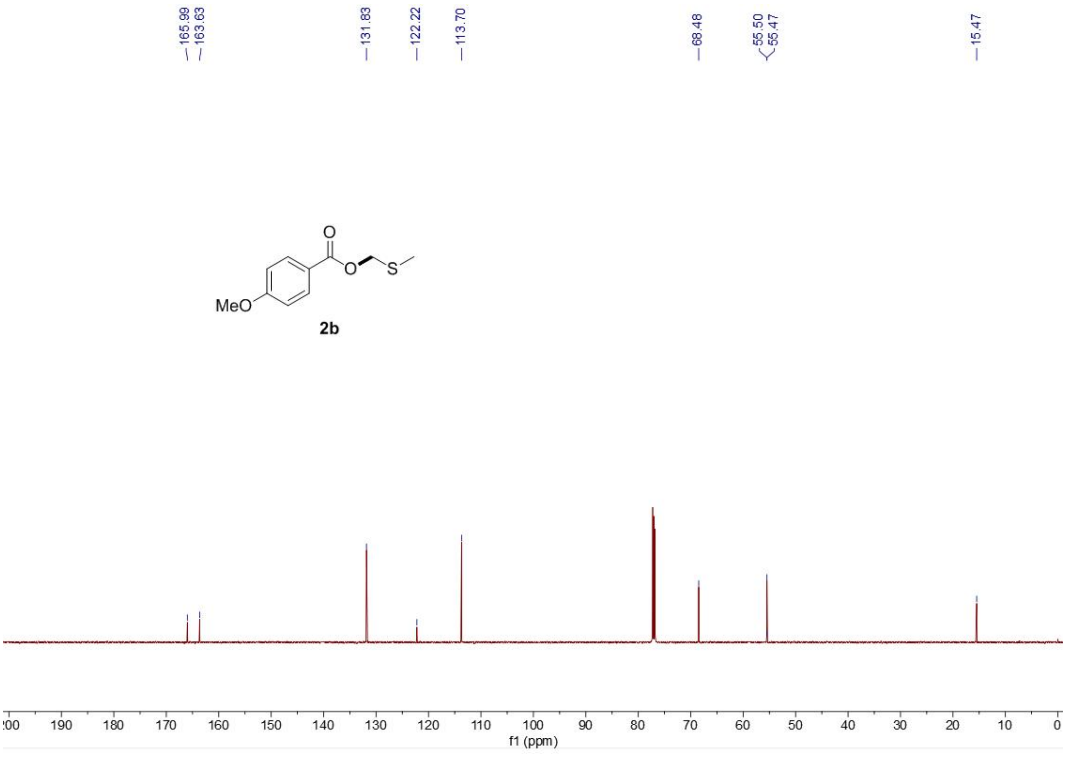
Fig. S1 HRMS of enolate **5**.

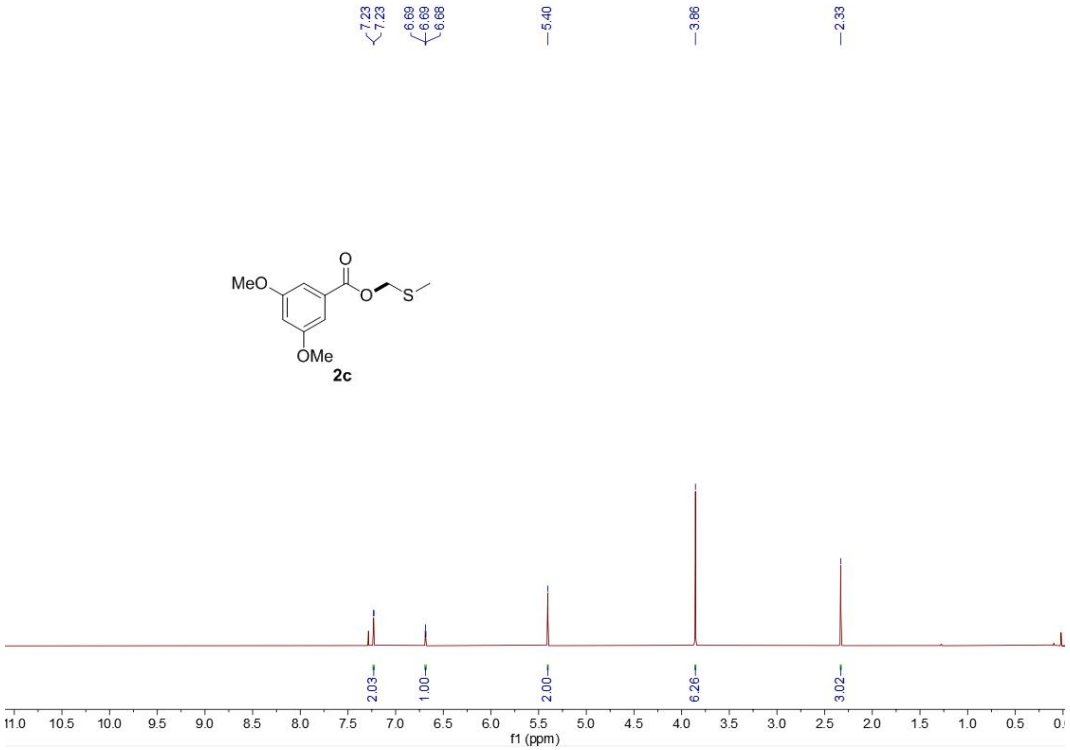
6. [1] H NMR & [13] C NMR spectra of the products

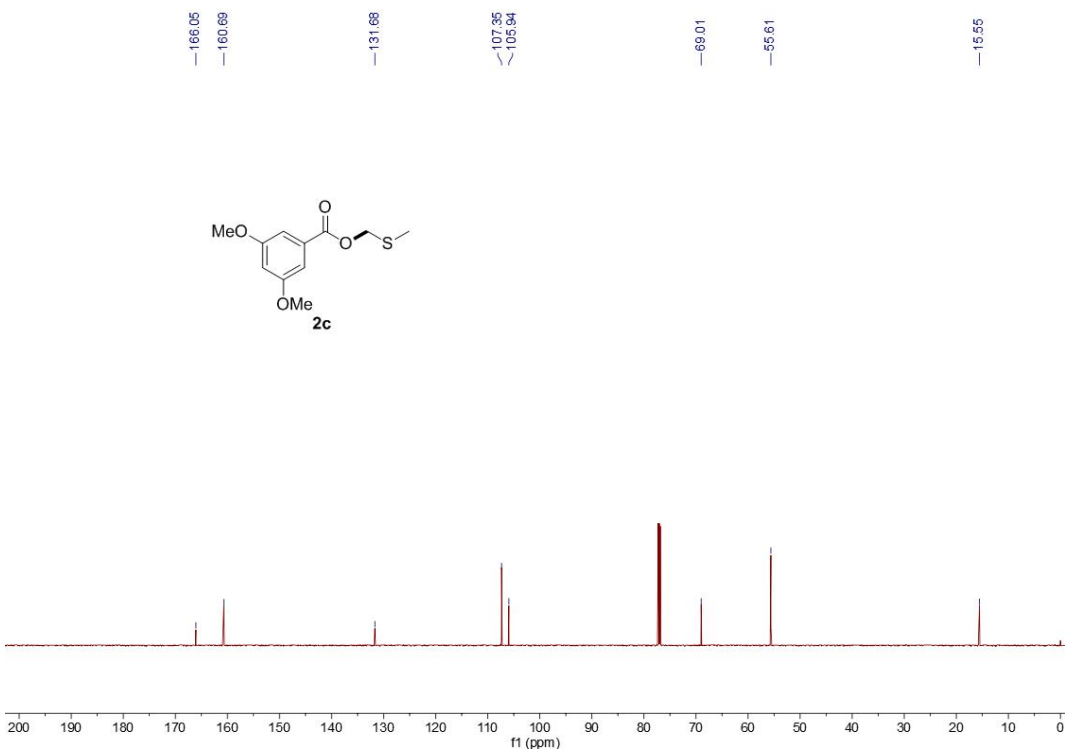


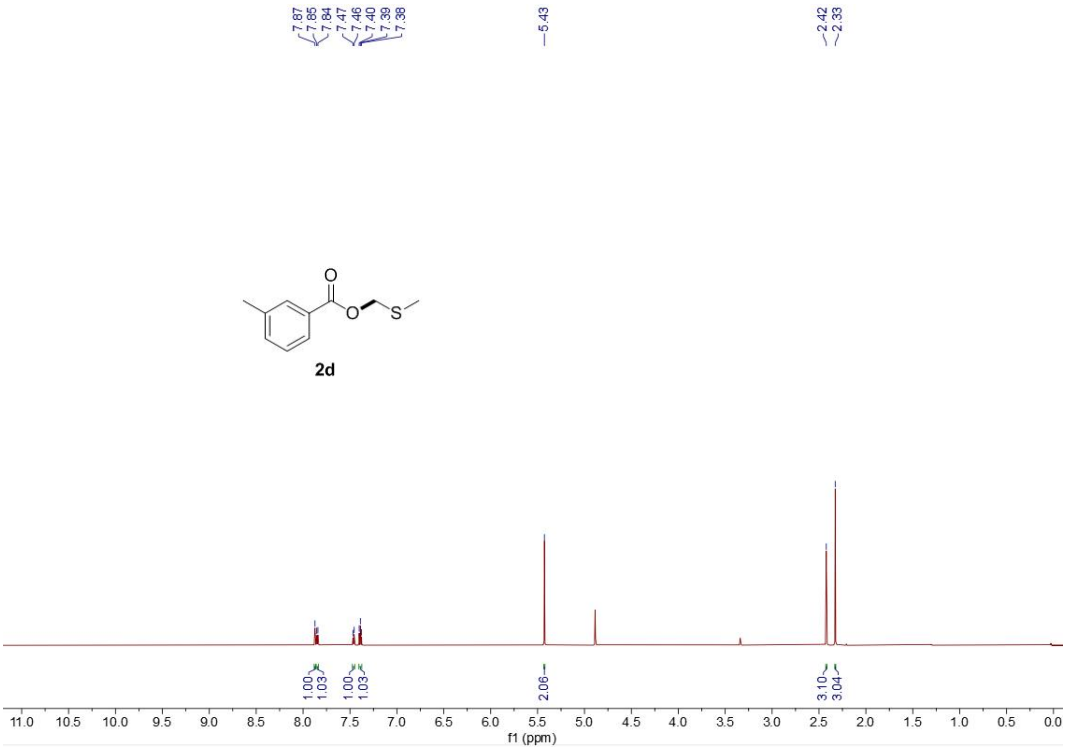


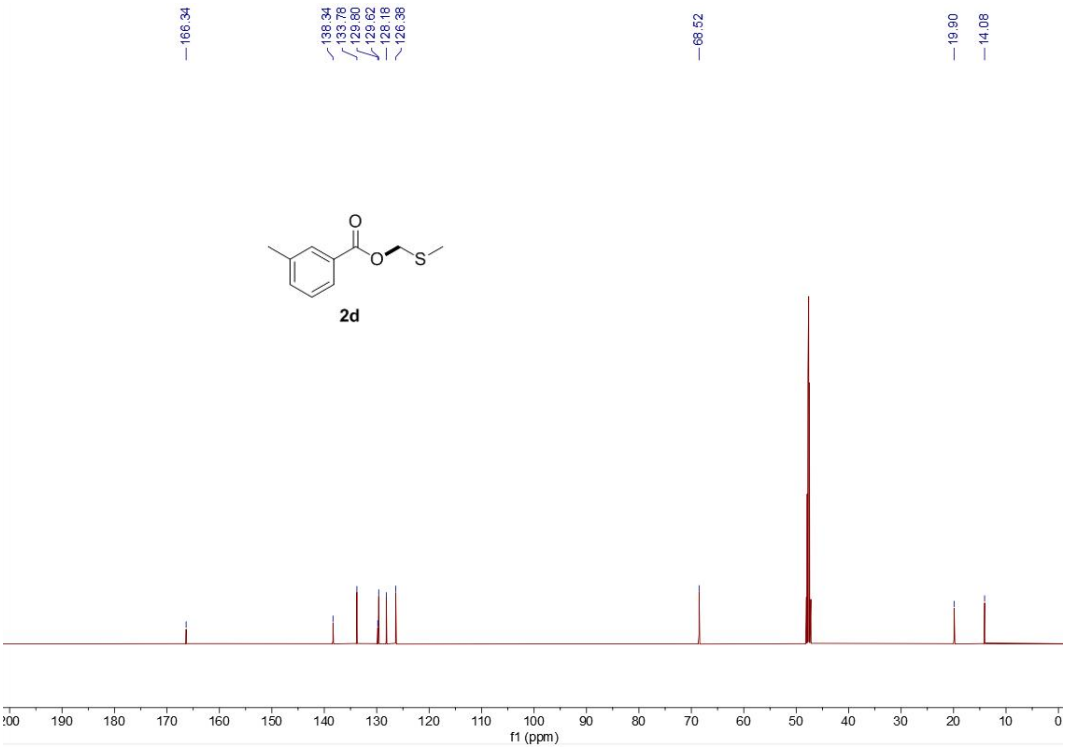

8.05
8.04
6.96
6.94
5.39
3.89
2.33
O
O
S
MeO
2b
2.00
2.14
2.06
3.33
3.06
f1 (ppm)


165.99
163.63
131.83
122.22
113.70
68.48
55.50
55.47
15.47
O
O
S
MeO
2b
f1 (ppm)


7.23
7.23
6.69
6.69
6.68
5.40
3.86
2.33
MeO
O
O
S
OMe
2c
2.03
1.00
2.00
6.26
3.02
f1 (ppm)


166.05
160.69
131.68
107.35
105.94
69.01
55.61
15.55
MeO
O
O
S
OMe
2c
f1 (ppm)


7.87
7.85
7.84
7.47
7.46
7.40
7.39
7.38
5.43
2.42
2.33
2d
1.00
1.03
1.00
1.03
2.06
3.10
3.04
f1 (ppm)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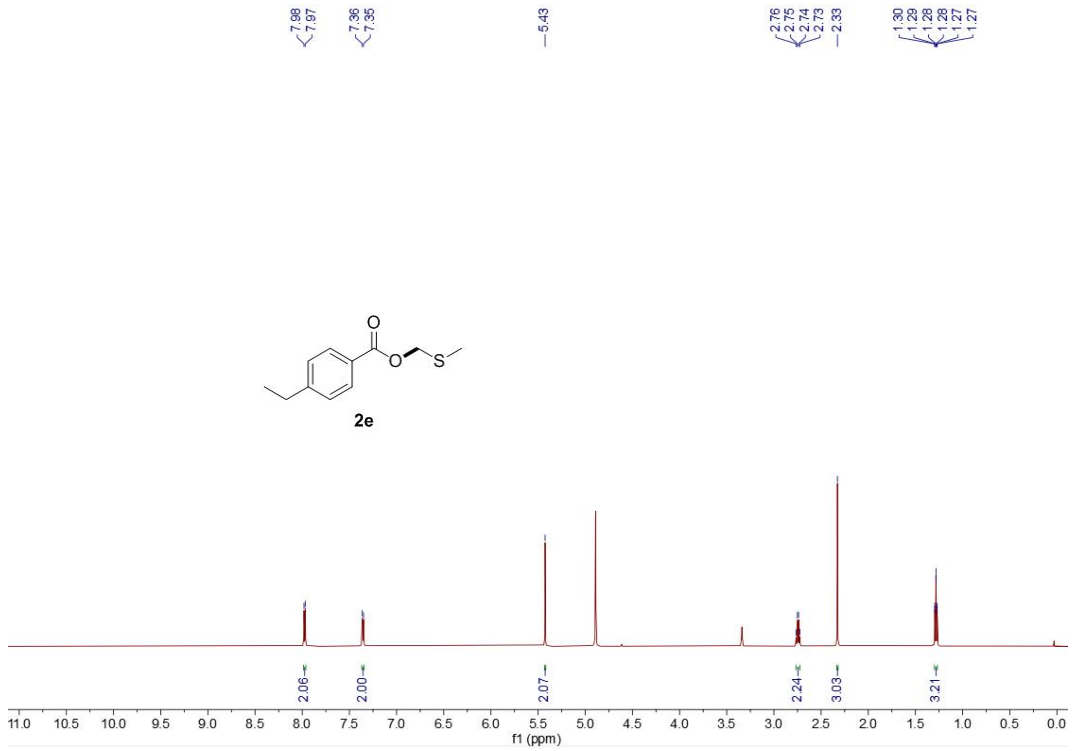
138.34
133.78
129.80
129.62
128.18
126.38
68.52
19.90
14.08
2d
f1 (ppm)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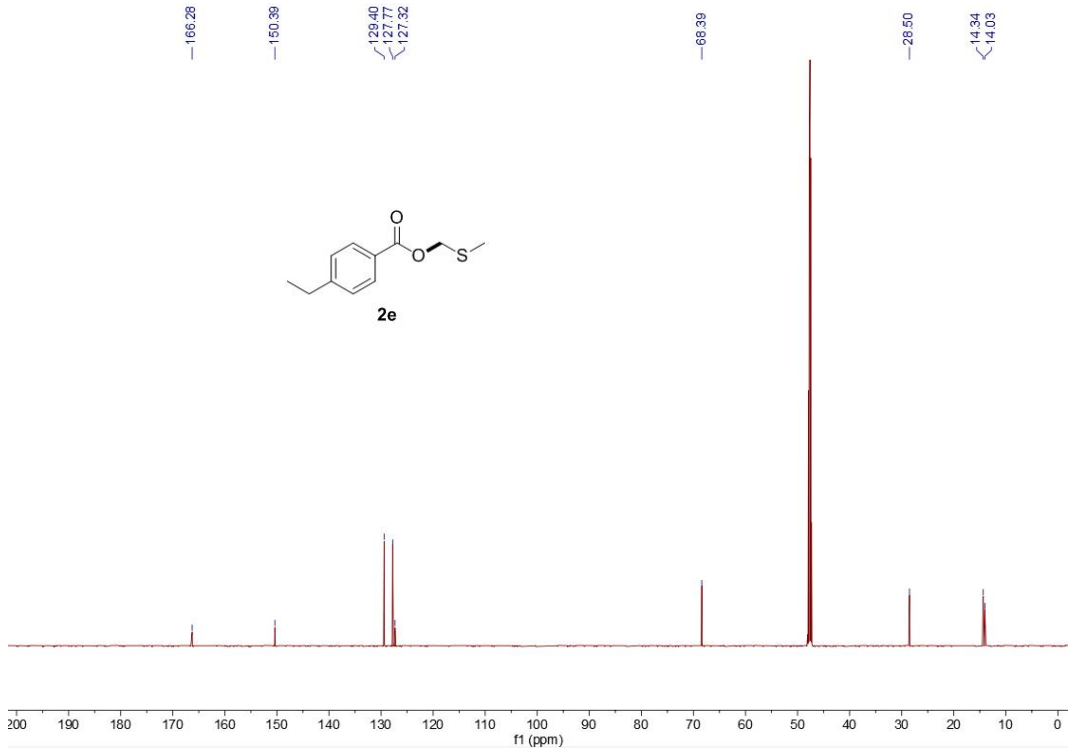
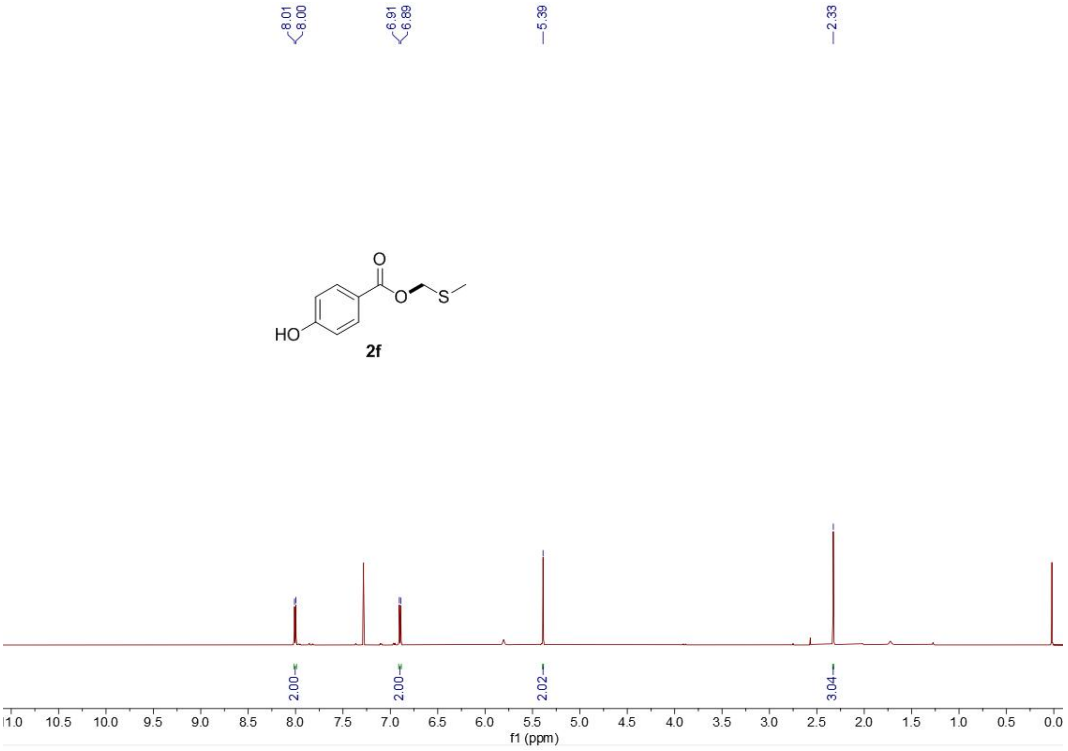
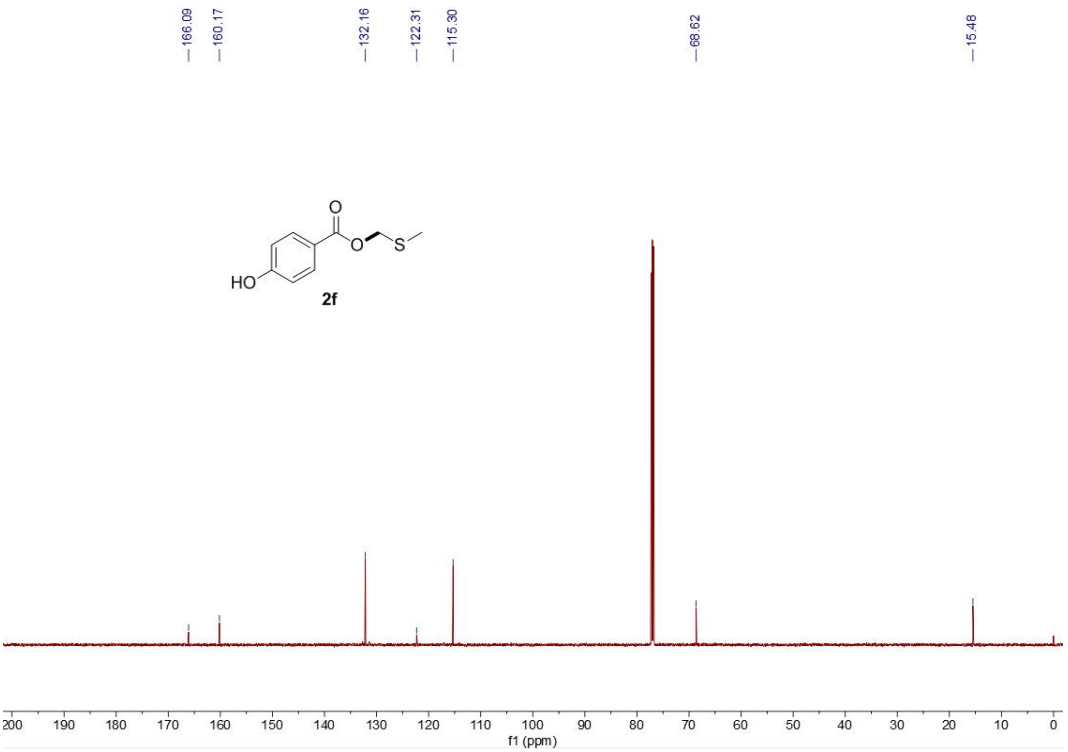
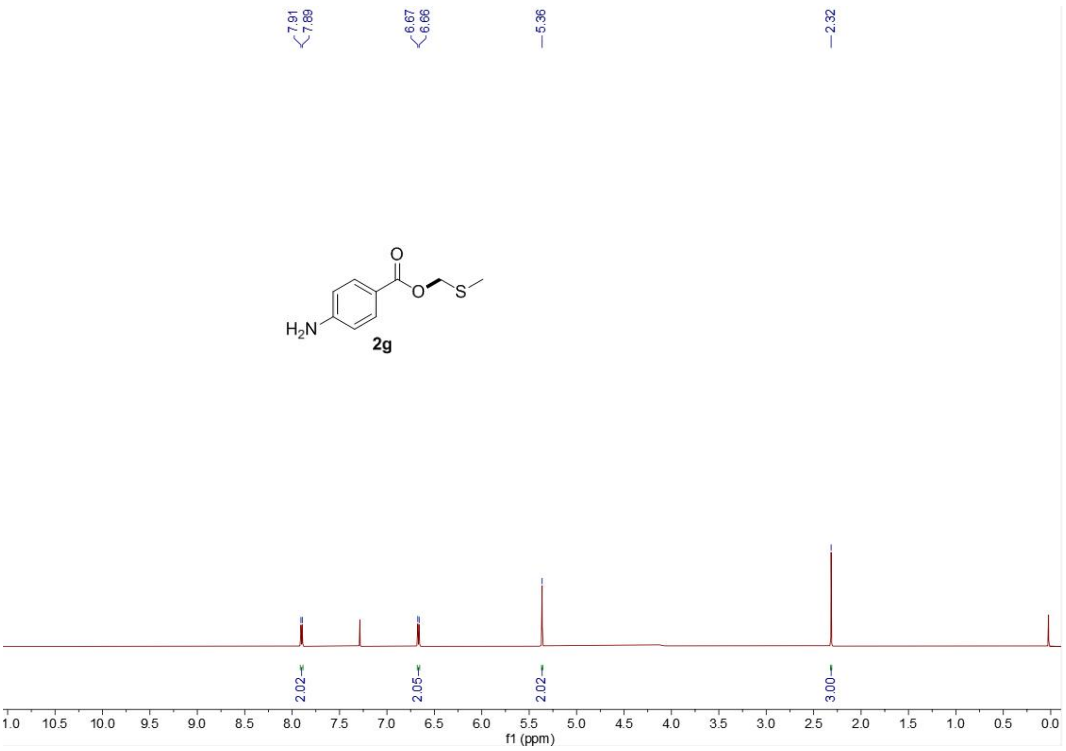
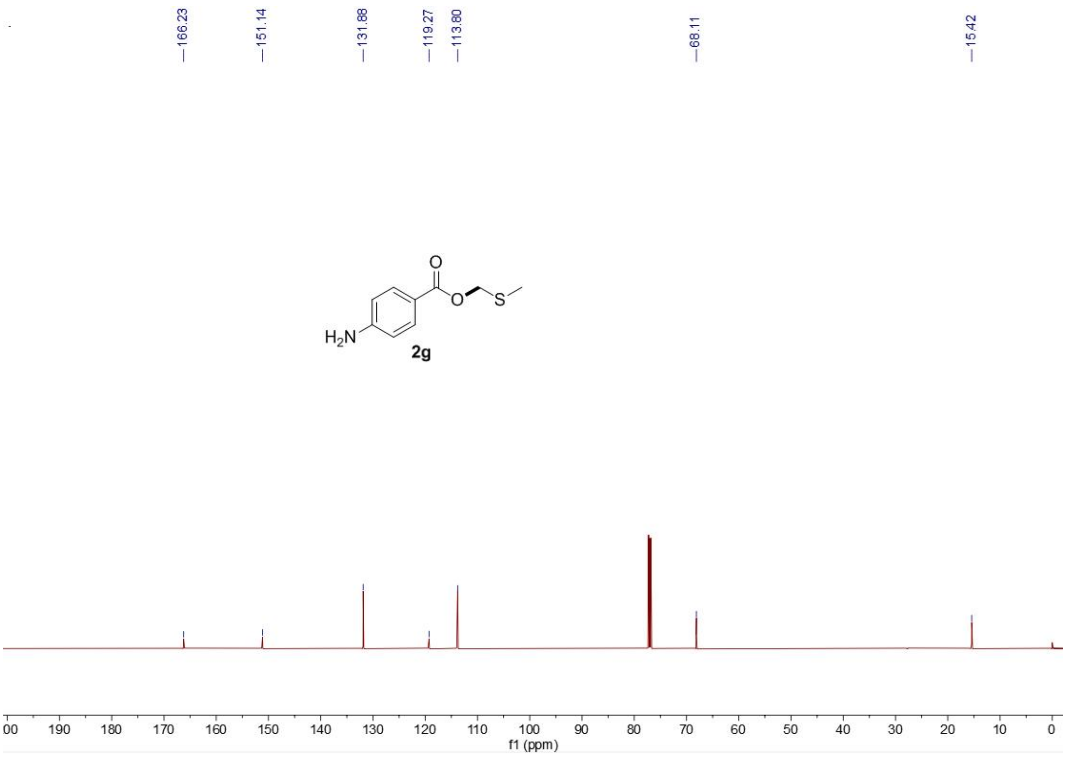
7.97
7.36
7.35
5.43
2.76
2.75
2.74
2.73
2.33
1.30
1.29
1.28
1.28
1.27
1.27
2e
2.06
2.00
2.07
2.24
3.03
3.21
f1 (ppm)

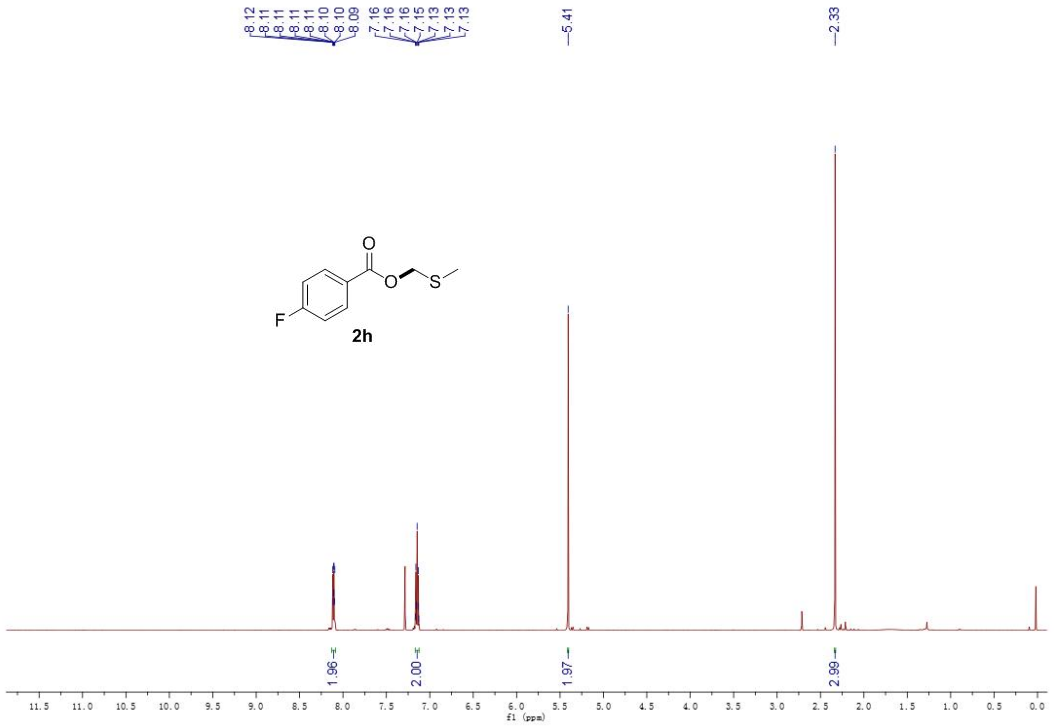

166.28
150.39
129.40
127.77
127.32
68.39
28.50
14.34
14.03
2e
f1 (ppm)

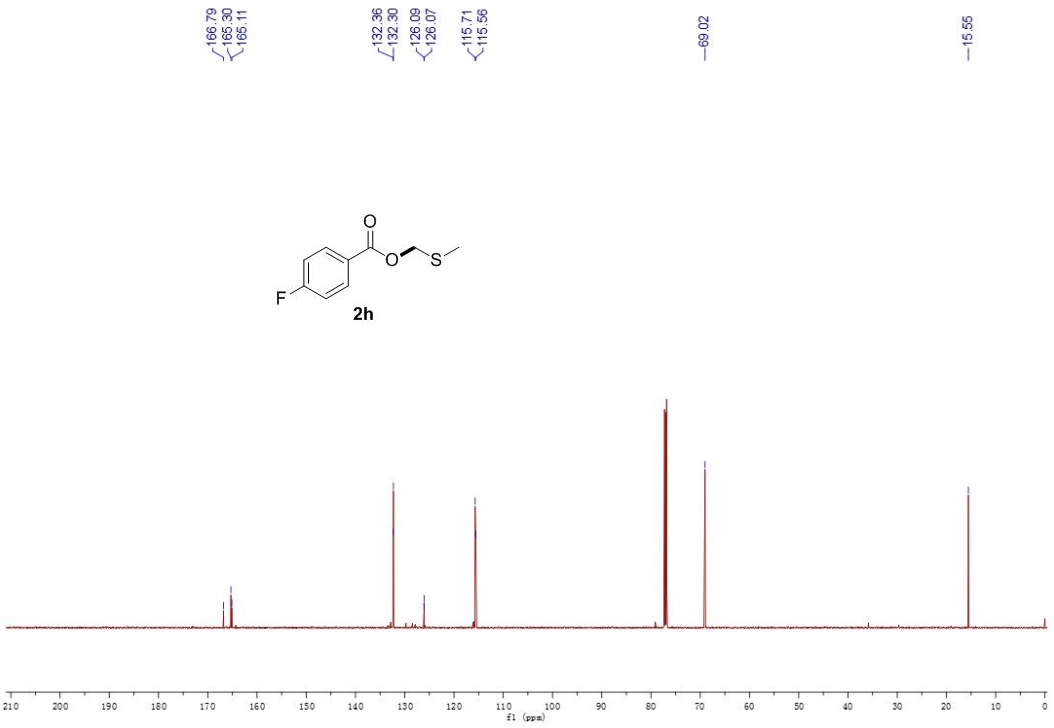

8.01
8.00
6.91
6.89
5.39
2.33
O
O
S
HO
2f
2.00
2.00
2.02
3.04
f1 (ppm)

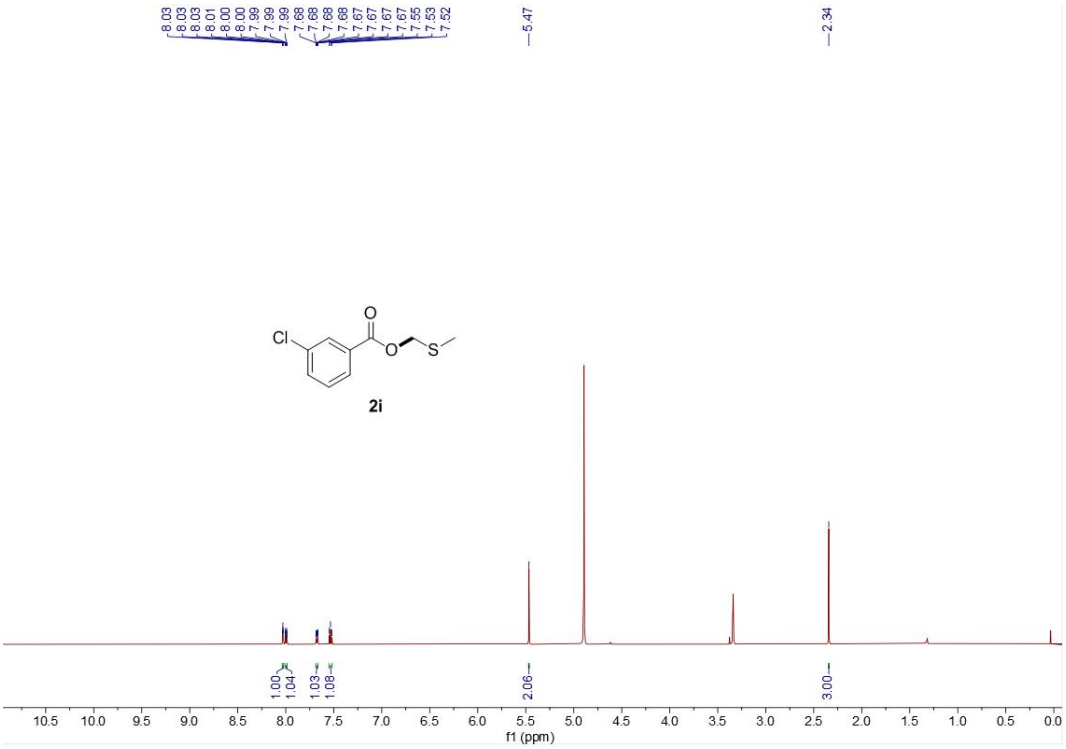

166.09
160.17
132.16
122.31
115.30
68.62
15.48
O
O
S
HO
2f
f1 (ppm)

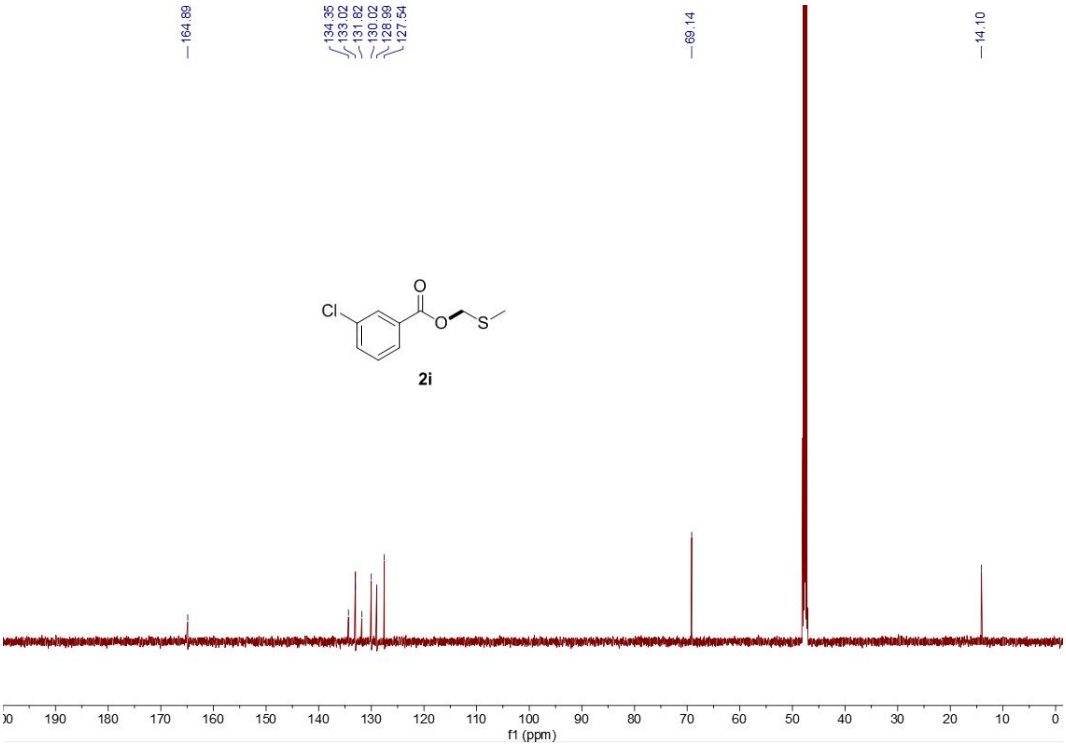

7.91
7.89
6.67
6.66
5.36
2.32
O
O
S
H_2N
2g
2.02
2.05
2.02
3.00
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

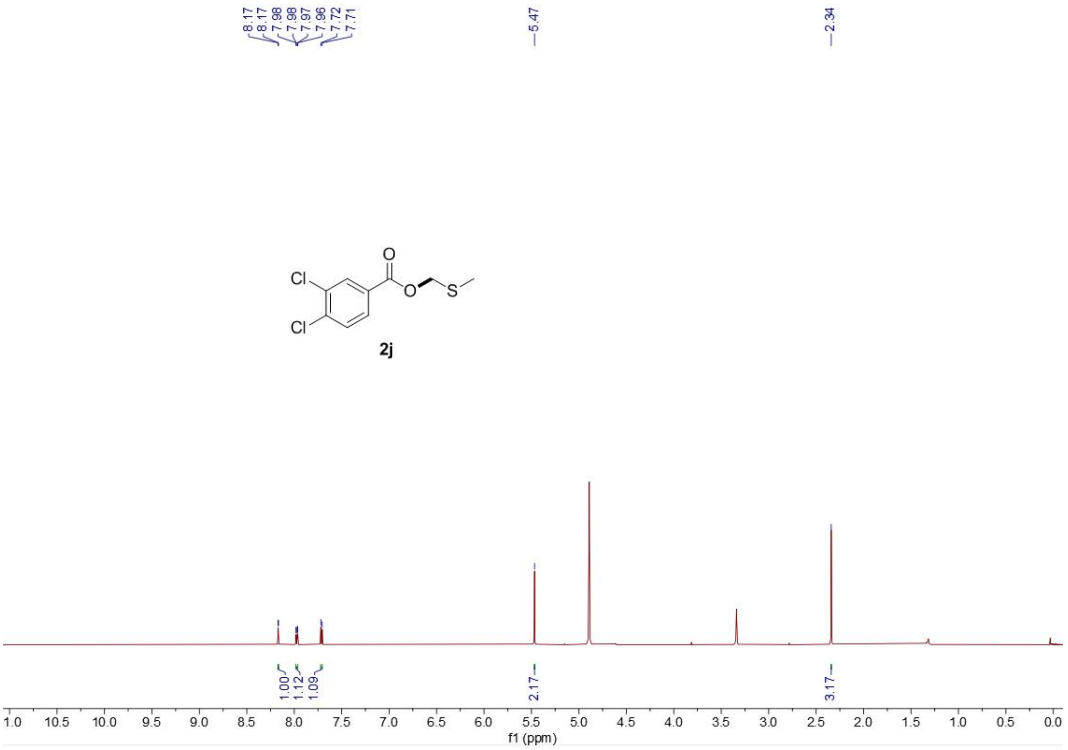

166.23
151.14
131.88
119.27
113.80
68.11
15.42
O
O
S
H_2N
2g
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

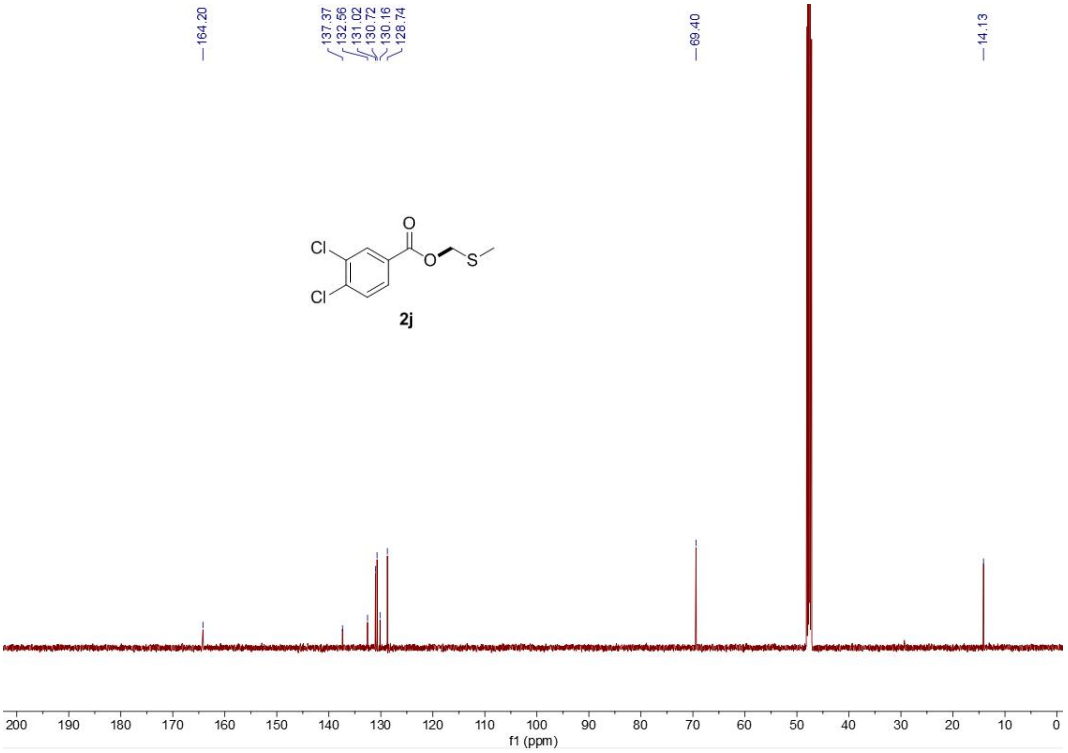

8.12
8.11
8.11
8.11
8.11
8.10
8.10
8.09
7.16
7.16
7.16
7.15
7.13
7.13
7.13
5.41
2.33
O
O
S
F
2h
1.96
2.00
1.97
2.99
f1 (ppm)

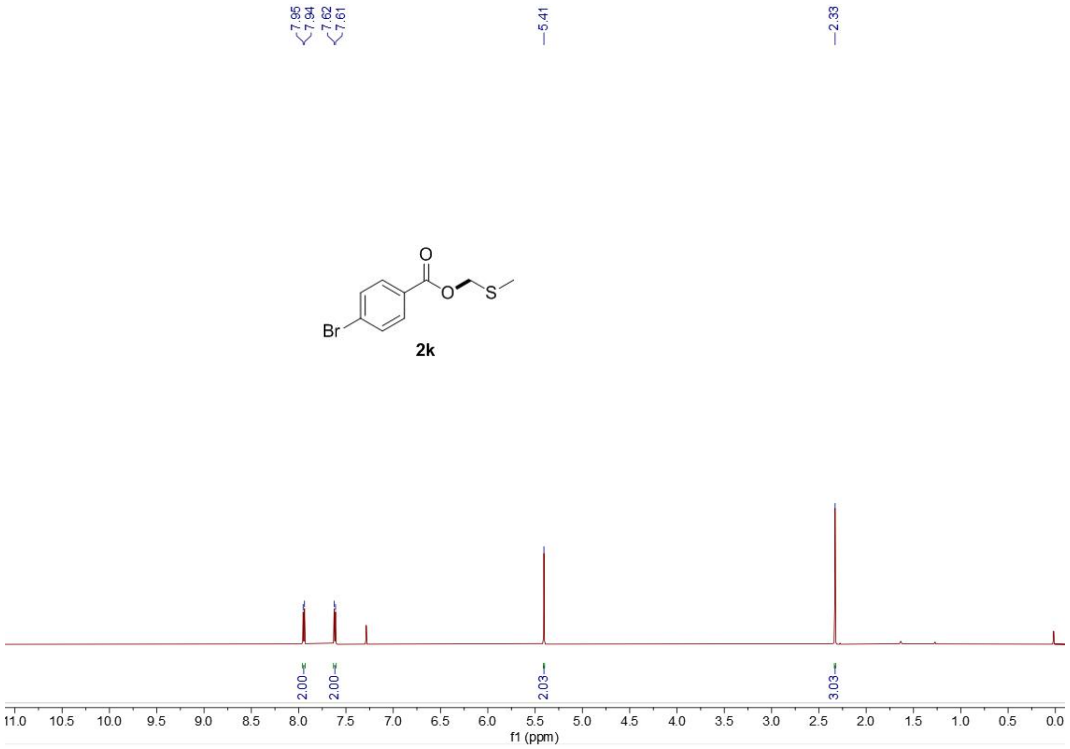

166.79
165.30
165.11
132.36
132.30
126.09
126.07
115.71
115.56
69.02
15.55
O
O
S
F
2h
f1 (ppm)

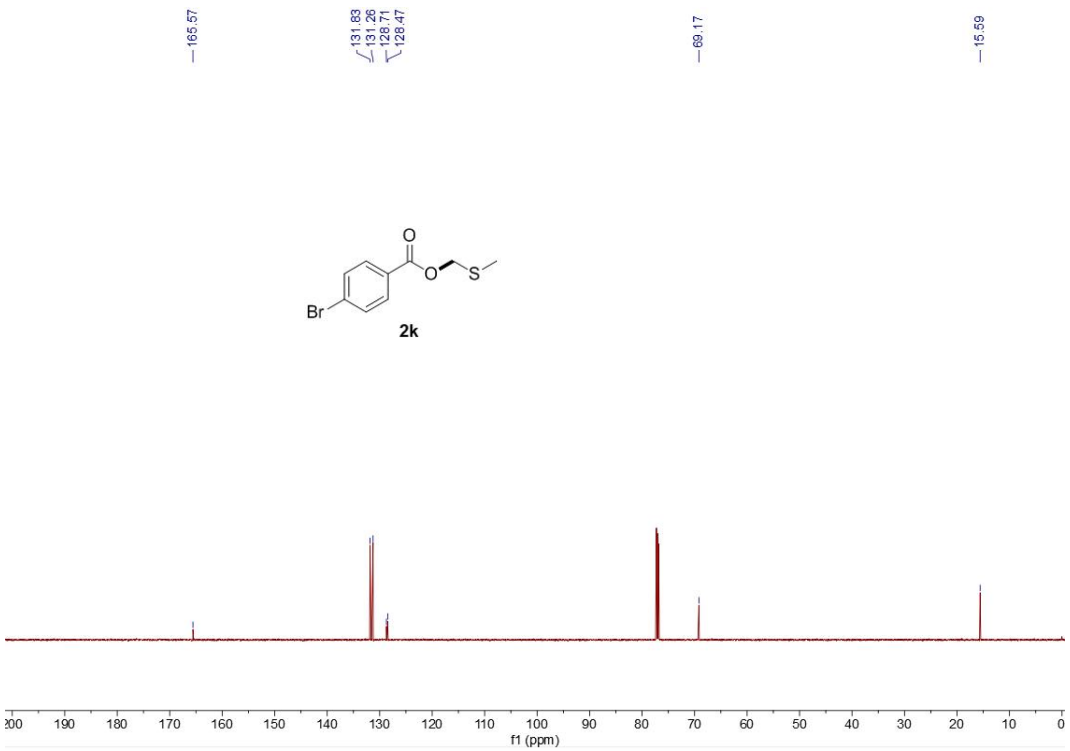

8.03
8.03
8.03
8.01
8.00
8.00
7.99
7.99
7.99
7.68
7.68
7.68
7.68
7.67
7.67
7.67
7.67
7.67
7.55
7.53
7.52
5.47
2.34
Cl
O
O
S
2i
1.00
1.04
1.03
1.08
2.06
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

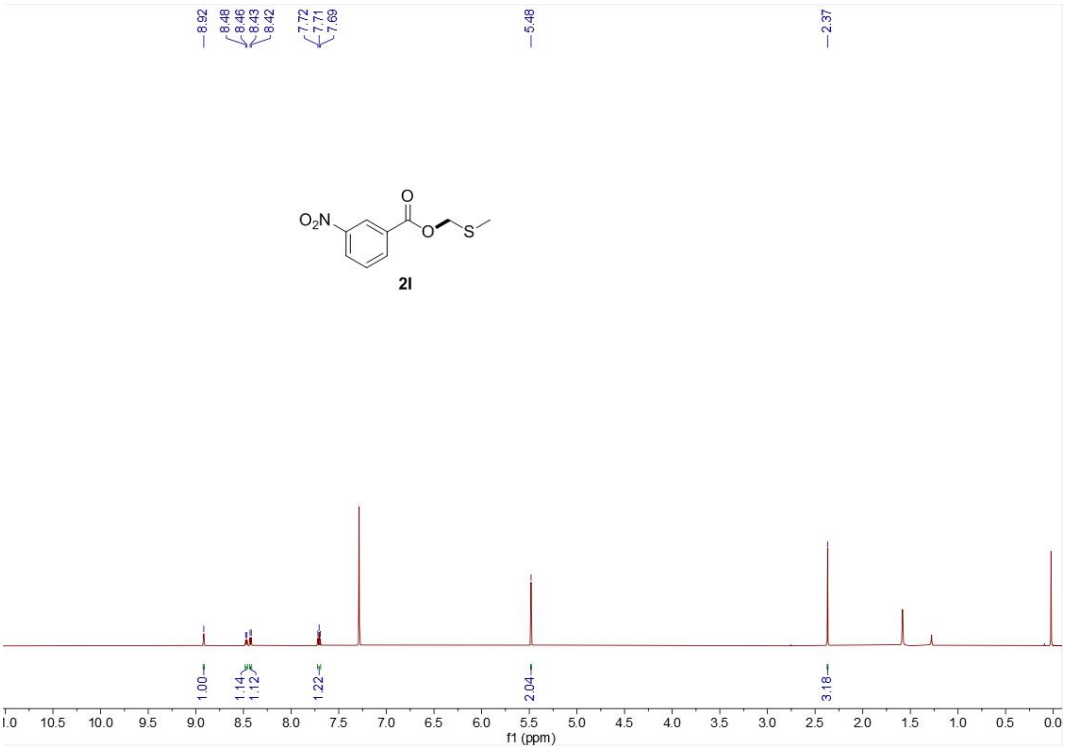

164.89
134.35
133.02
131.62
130.02
128.99
127.54
69.14
14.10
Cl
O
O
S
2i
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

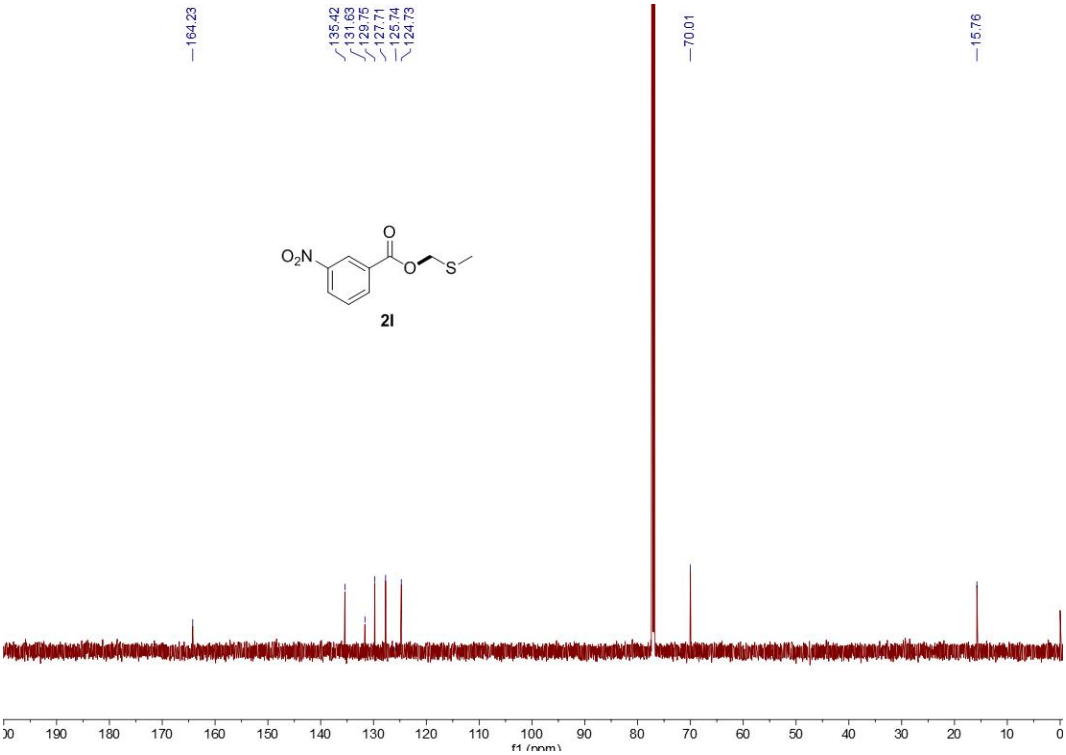

8.17
8.17
7.98
7.98
7.97
7.96
7.72
7.71
5.47
2.34
Cl
Cl
O
O
S
2j
1.00
1.12
1.09
2.17
3.17
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

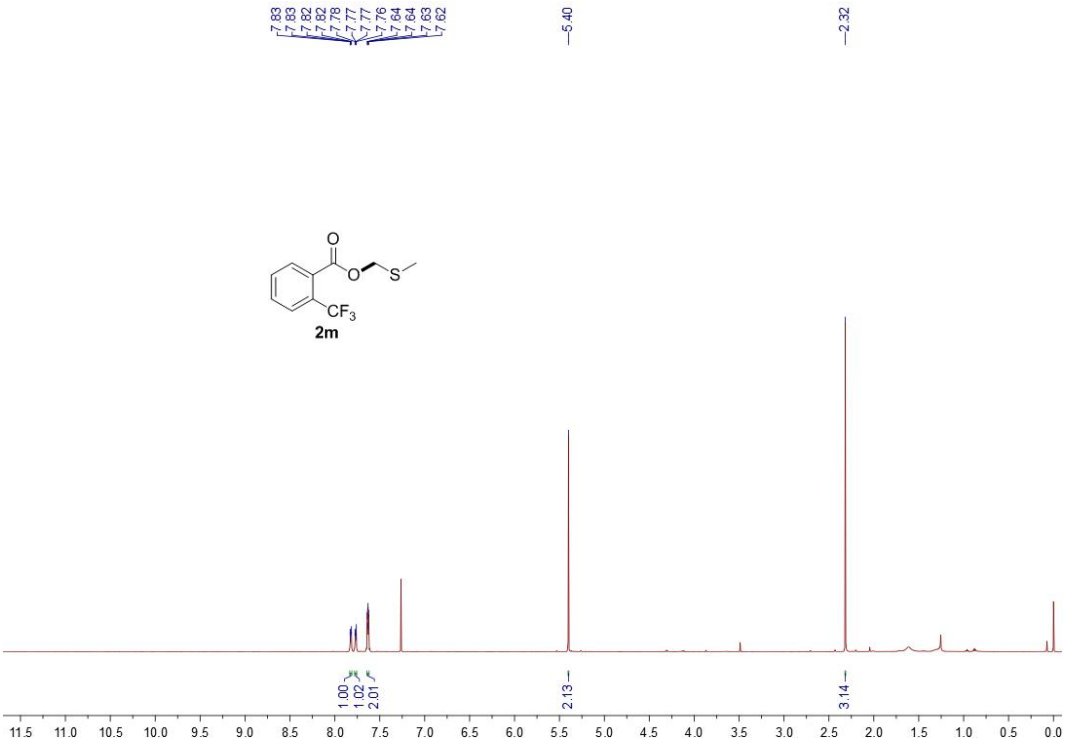

164.20
137.37
132.65
131.02
130.72
130.16
128.74
69.40
14.13
Cl
Cl
O
O
S
2j
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.95
7.94
7.62
7.61
5.41
2.33
O
O
S
Br
2k
2.00
2.00
2.03
3.03
f1 (ppm)


165.57
131.83
131.26
128.71
128.47
69.17
15.59
O
O
S
Br
2k
f1 (ppm)


8.92
8.48
8.46
8.43
8.42
7.72
7.71
7.69
5.48
2.37
O2N
O
O
S
2l
1.00
1.14
1.12
1.22
2.04
3.18
f1 (ppm)


164.23
135.42
131.63
129.75
127.71
125.74
124.73
70.01
15.76
O2N
O
O
S
2l
f1 (ppm)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7.83
7.82
7.82
7.78
7.77
7.77
7.76
7.64
7.64
7.63
7.62
5.40
2.32
O
O
S
CF3
2m
1.00
1.02
2.01
2.13
3.14
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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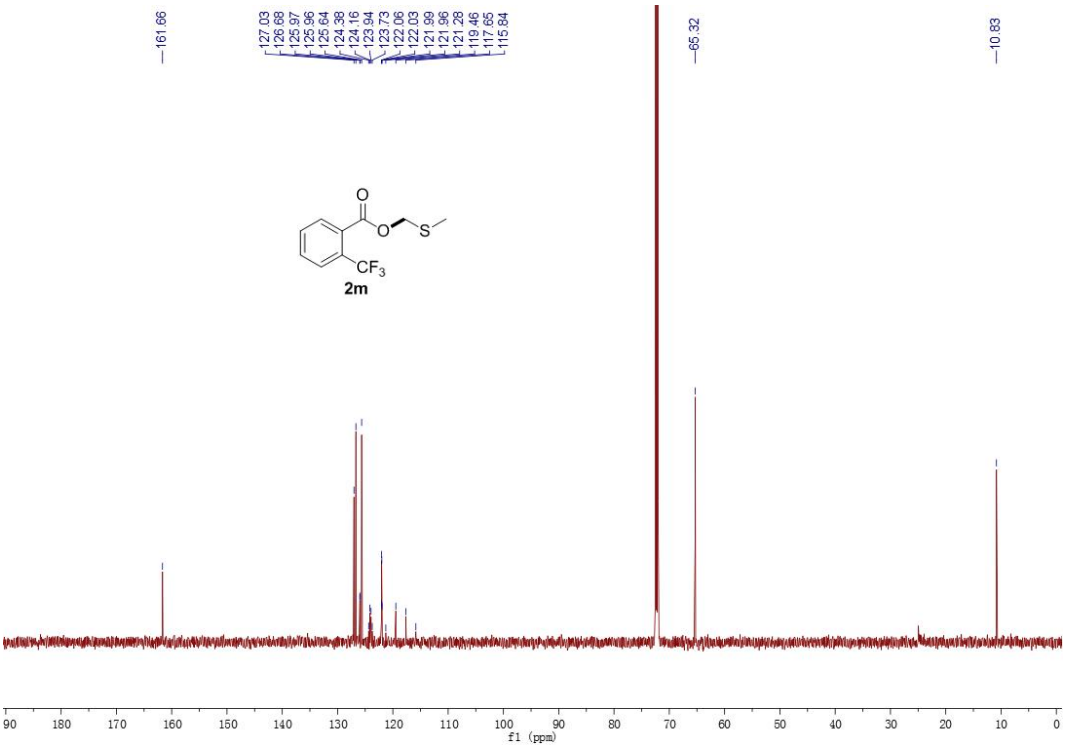
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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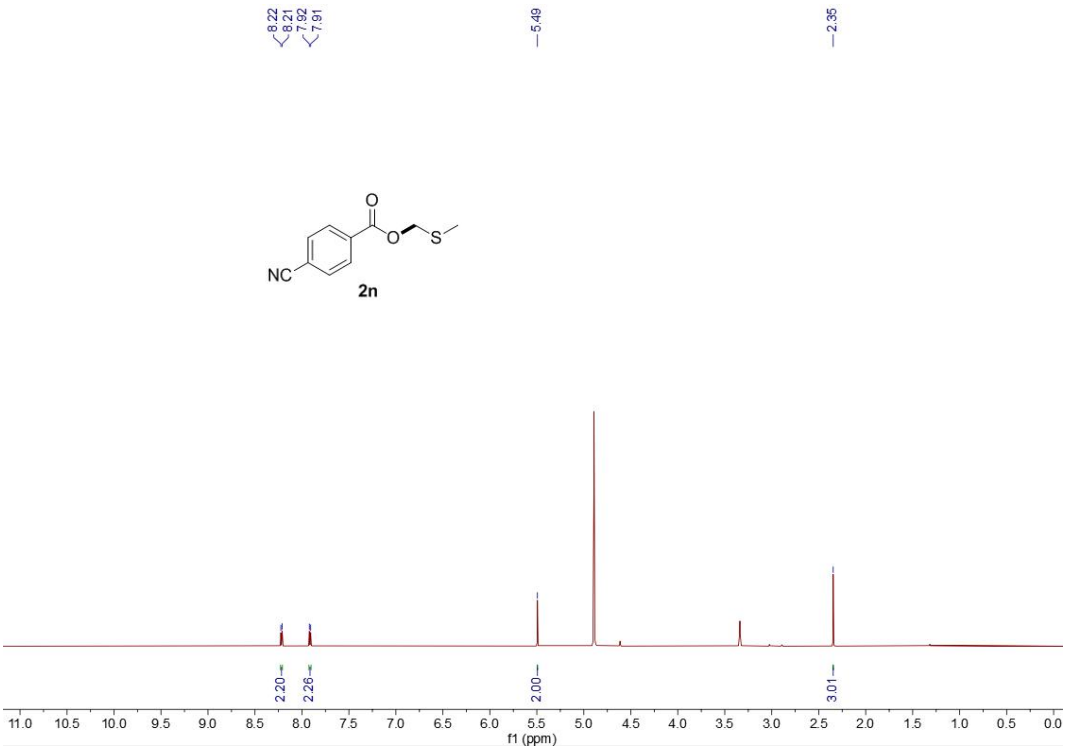
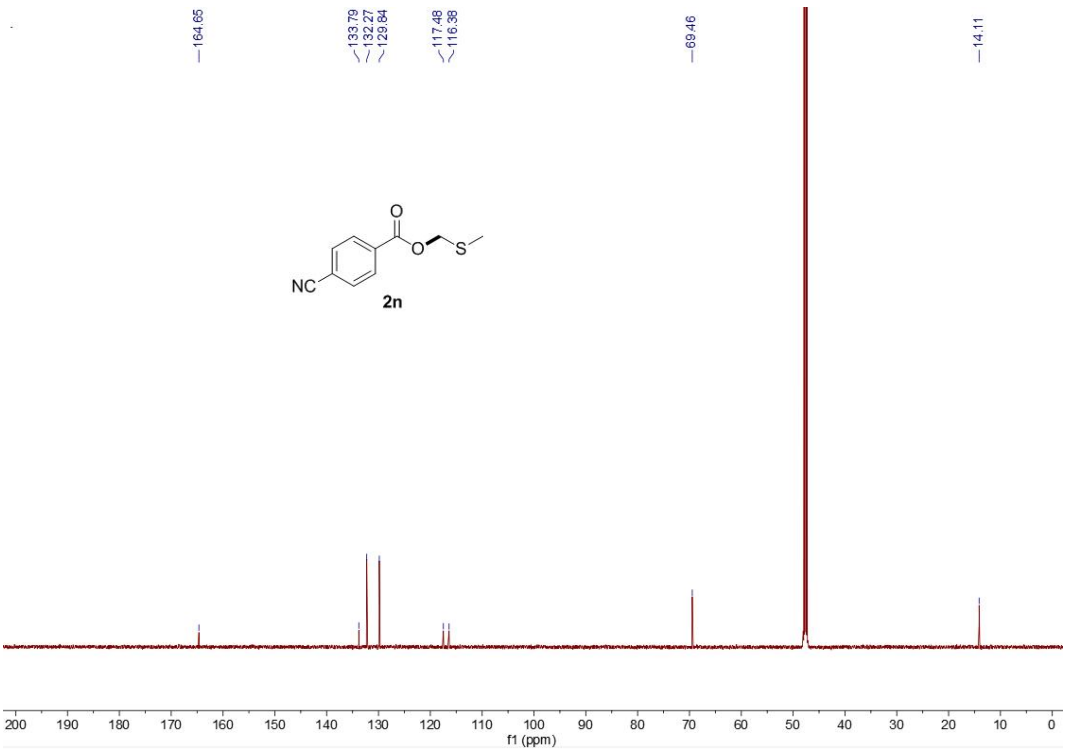
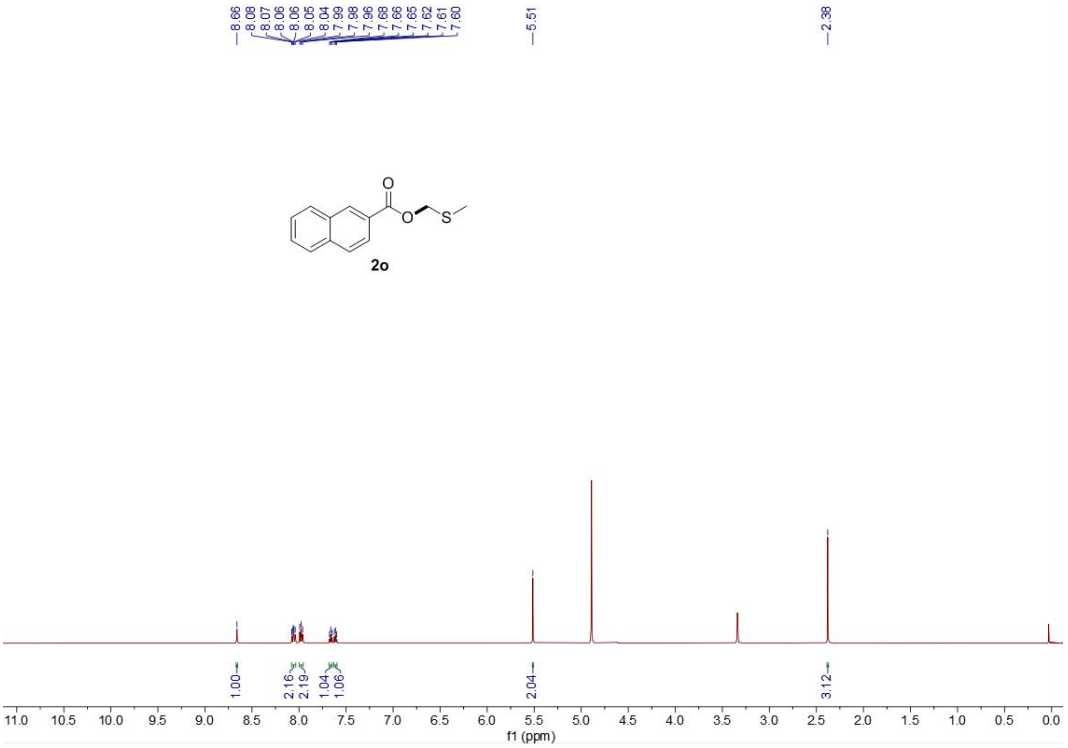
127.03
126.68
125.97
125.96
125.64
124.38
124.16
123.94
123.73
122.06
122.03
121.99
121.96
121.28
119.46
117.65
115.84
65.32
10.83
O
O
S
CF3
2m
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.22
8.21
7.92
7.91
5.49
2.35
O
O
S
NC
2n
2.20
2.26
2.00
3.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


164.65
133.79
132.27
129.64
117.48
116.38
69.46
14.11
O
O
S
NC
2n
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.08
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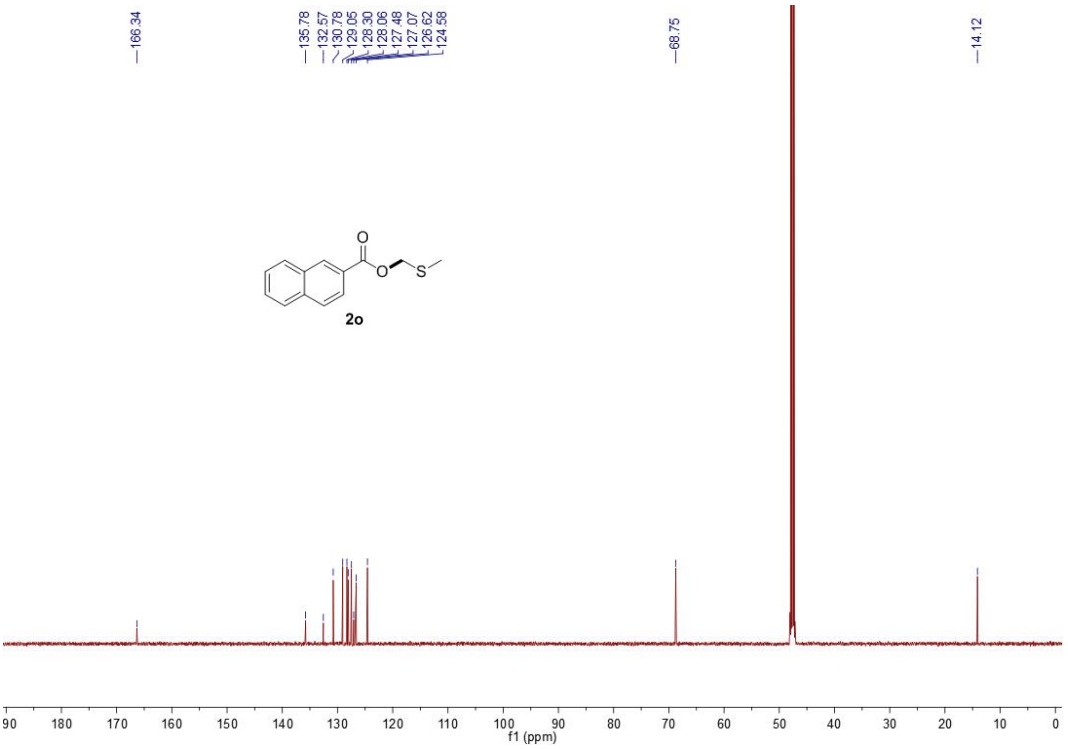
8.06
8.05
8.04
7.99
7.98
7.96
7.68
7.66
7.65
7.62
7.61
7.60
5.51
2.38
O
O
S
2o
1.00
2.16
2.19
1.04
1.06
2.04
3.12
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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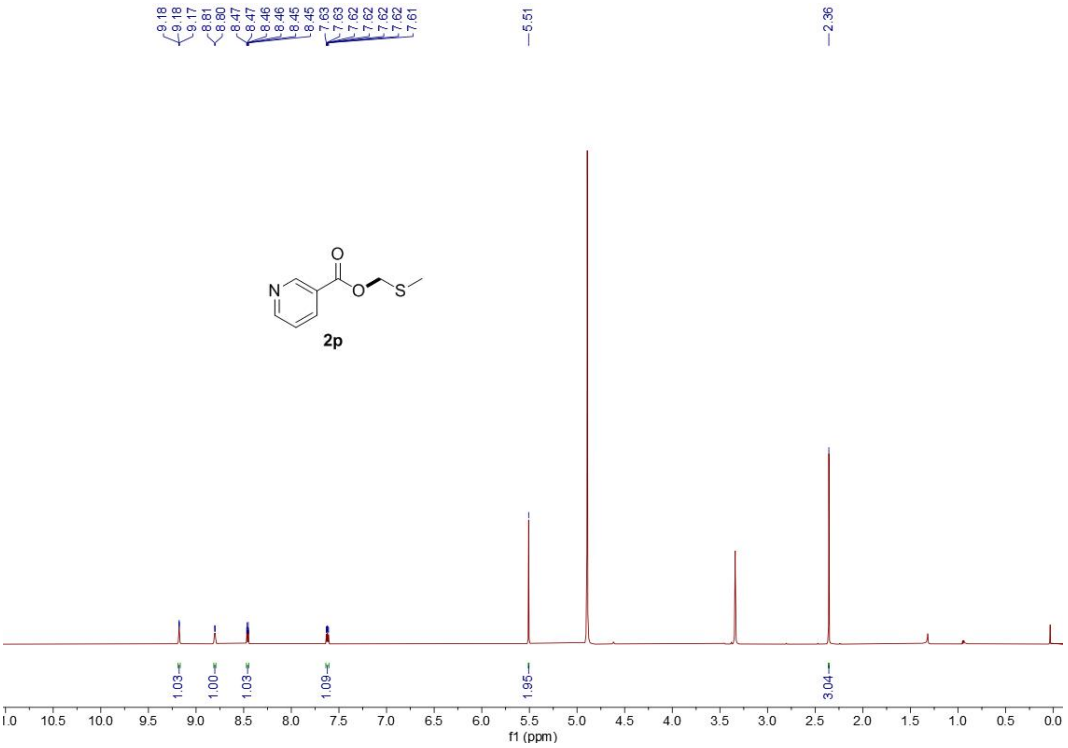
135.78
132.57
130.78
129.05
128.30
128.06
127.48
127.07
126.62
124.58
68.75
14.12
O
O
S
2o
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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9.18
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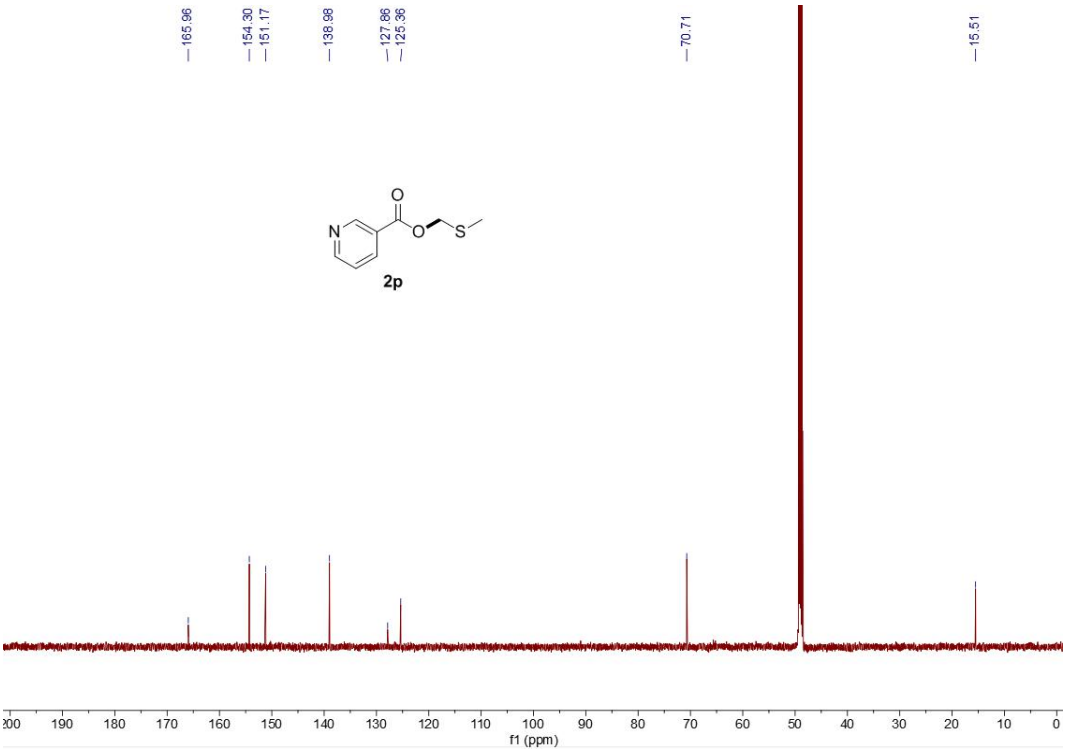
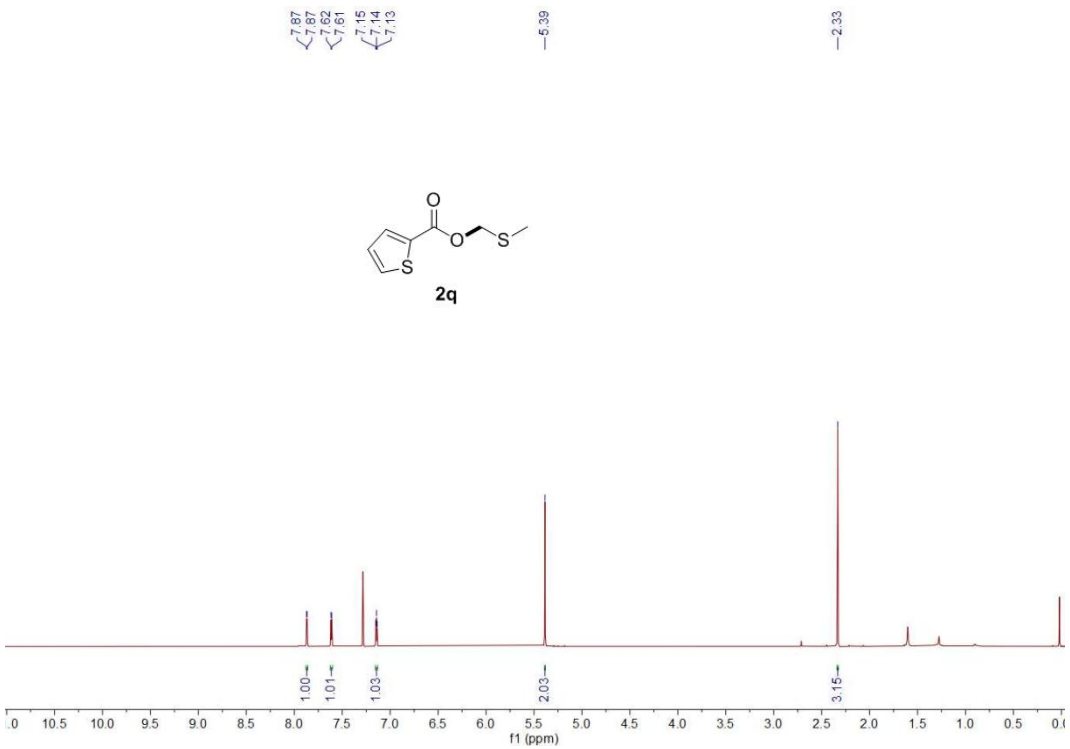
8.47
8.46
8.46
8.45
8.45
7.63
7.63
7.62
7.62
7.62
7.62
7.61
5.51
2.36
O
N
O
S
2p
1.03
1.00
1.03
1.09
1.95
3.04
f1 (ppm)


165.96
154.30
151.17
138.98
127.86
125.36
70.71
15.51
O
N
O
S
2p
f1 (ppm)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7.87
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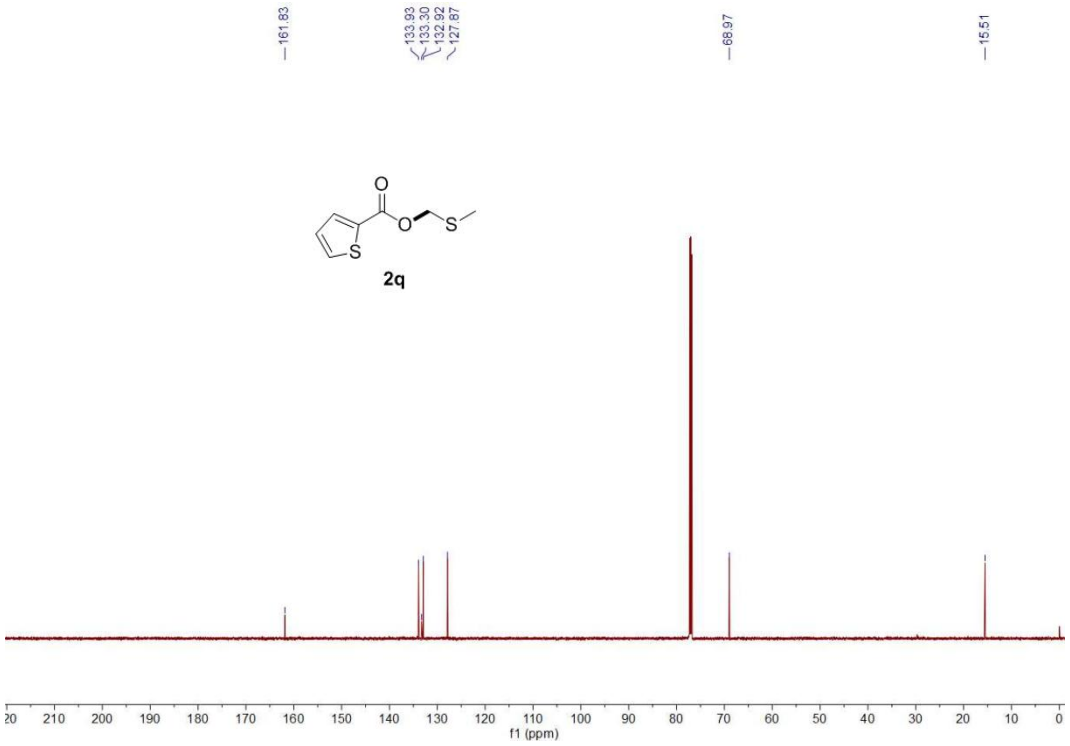
7.61
7.15
7.14
7.13
5.39
2.33
O
O
S
S
2q
1.00
1.01
1.03
2.03
3.15
f1 (ppm)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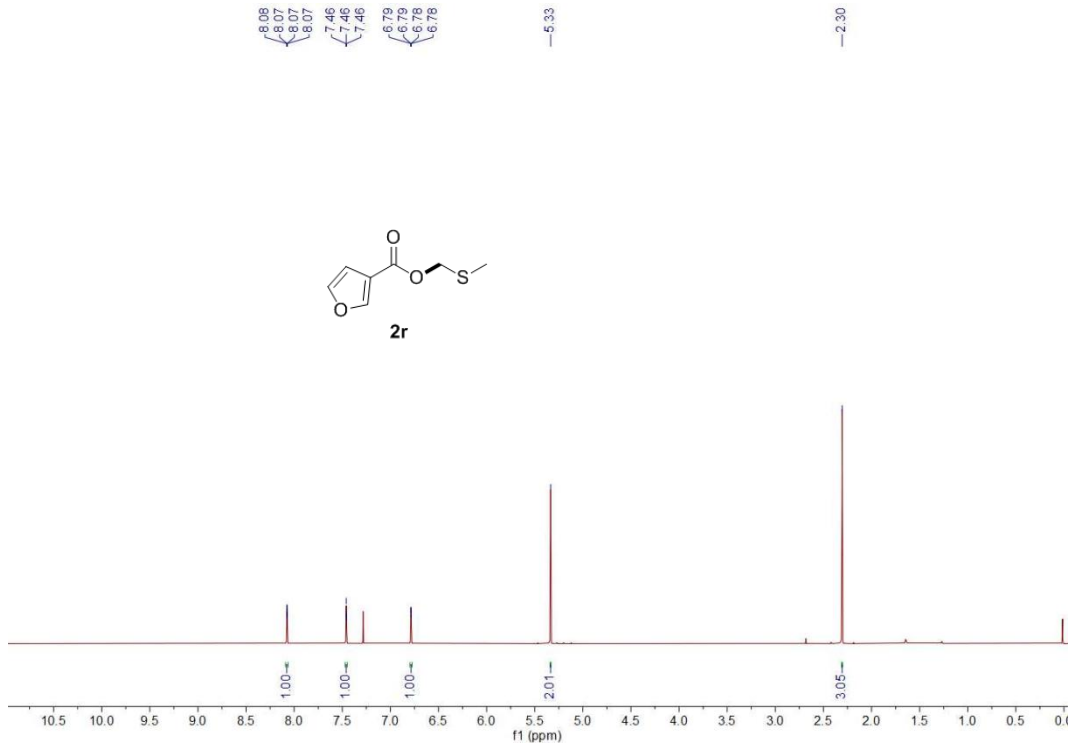
133.30
132.92
127.87
68.97
15.51
O
O
S
S
2q
f1 (ppm)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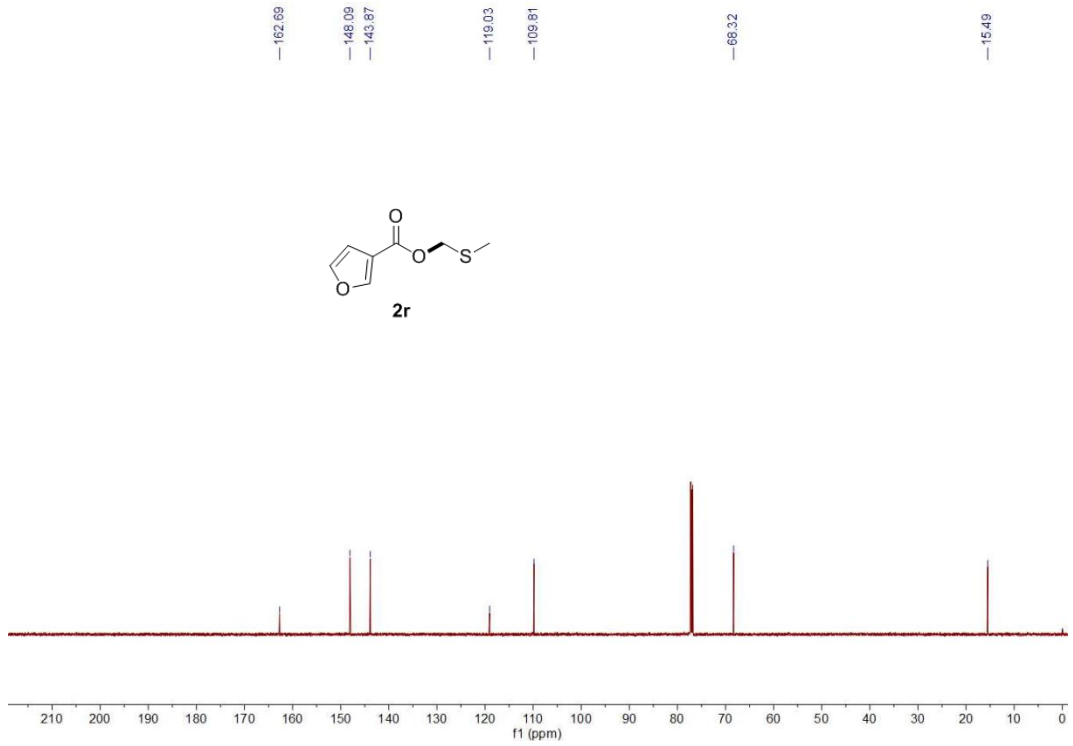
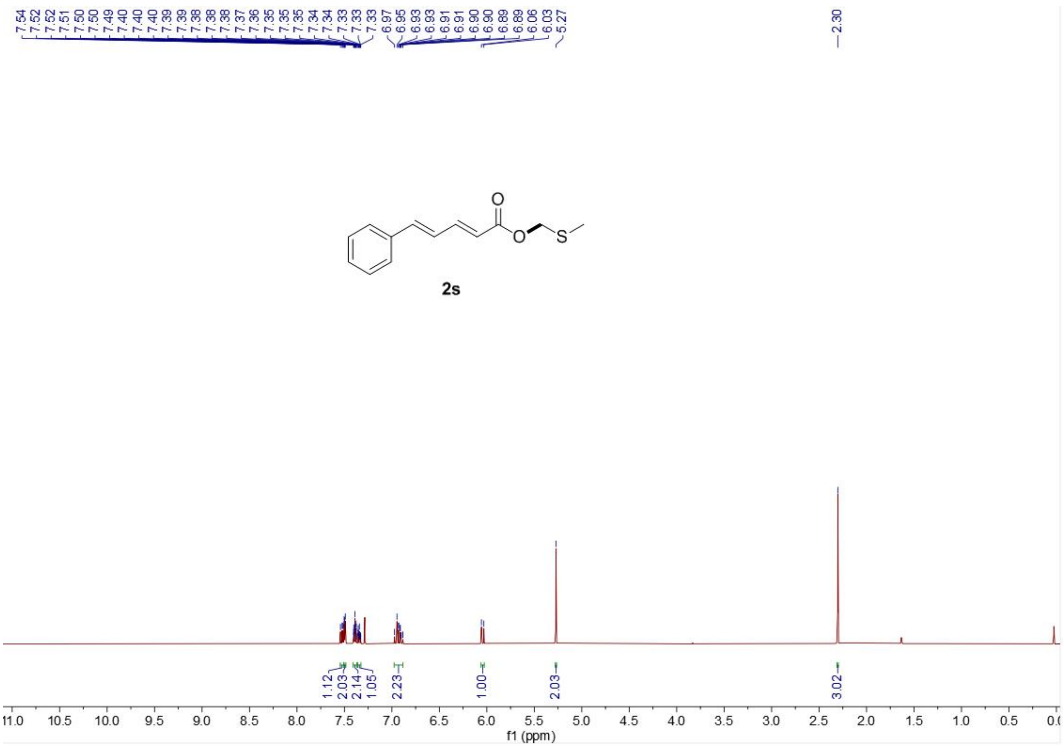
8.07
8.07
8.07
7.46
7.46
7.46
6.79
6.79
6.78
6.78
5.33
2.30
O
O
S
O
2r
1.00
1.00
1.00
2.01
3.05
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


162.69
148.09
143.87
119.03
109.81
68.32
15.49
O
O
S
O
2r
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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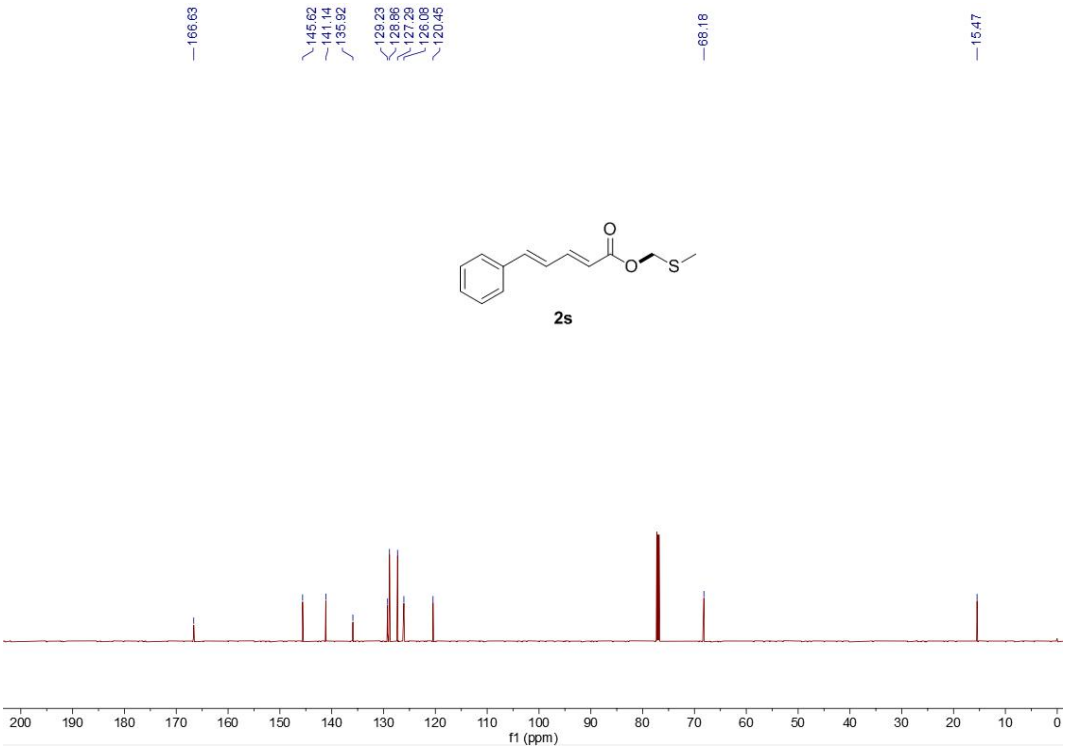
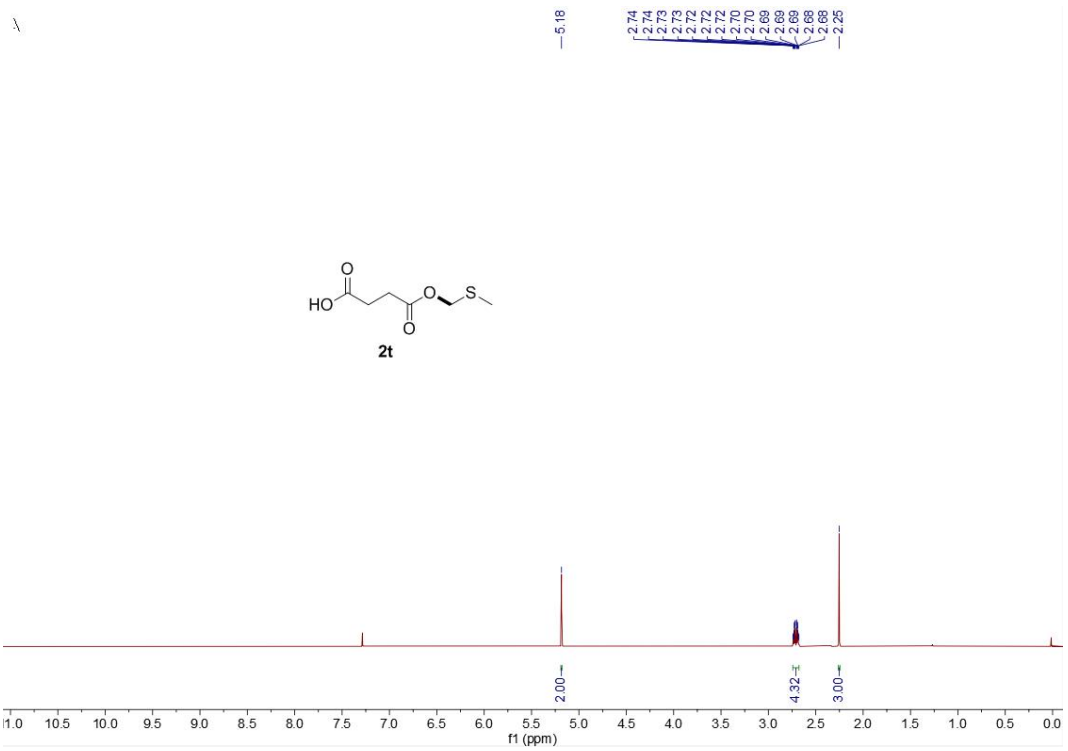
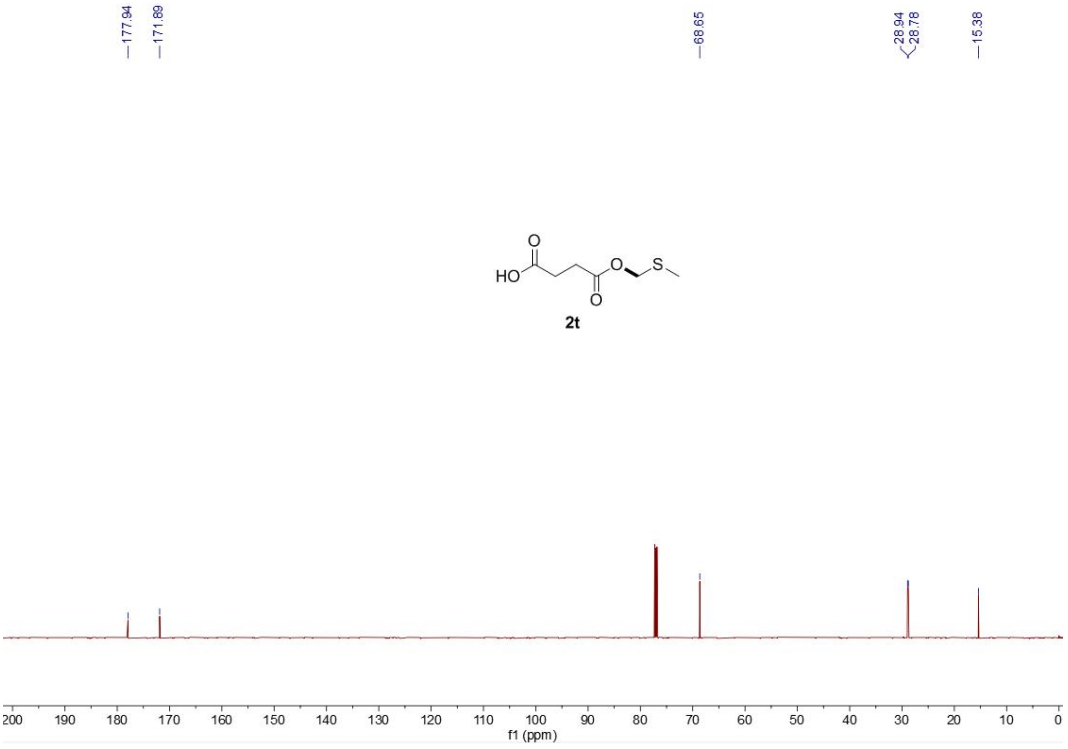
7.52
7.51
7.50
7.50
7.49
7.40
7.40
7.40
7.39
7.39
7.38
7.38
7.38
7.37
7.36
7.35
7.35
7.35
7.34
7.34
7.33
7.33
6.97
6.95
6.93
6.93
6.91
6.91
6.90
6.90
6.89
6.89
6.06
6.03
5.27
2.30
O
O
S
1.12
2.03
2.14
1.05
2.23
1.00
2.03
3.02
f1 (ppm)

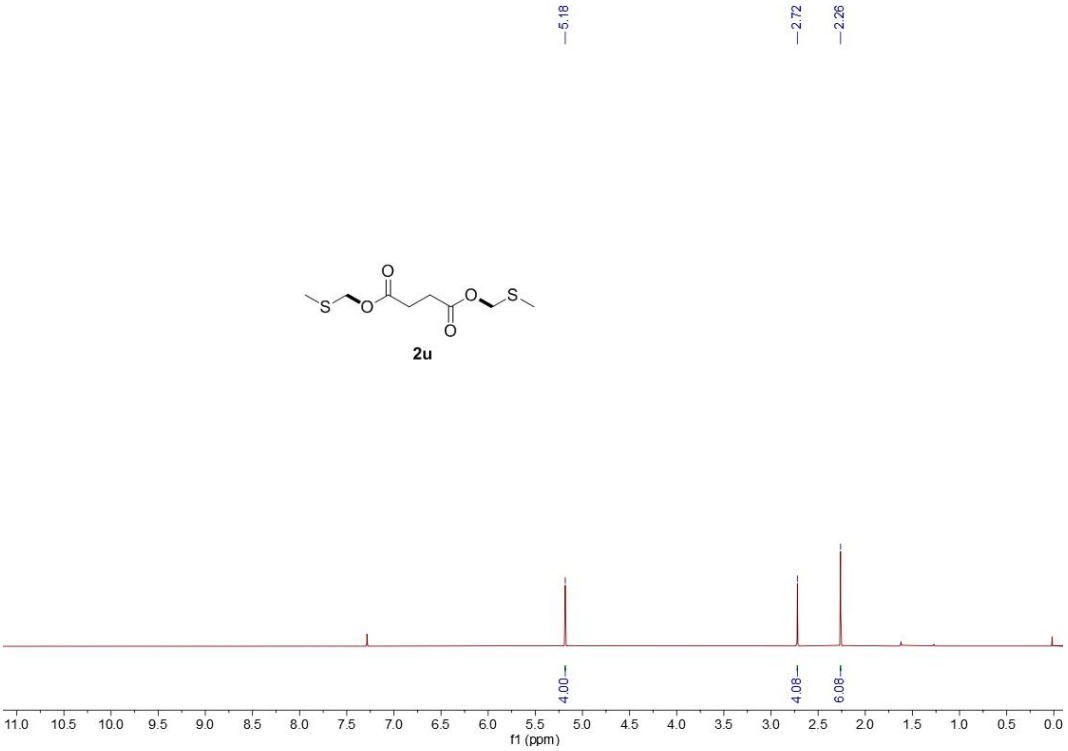
2s

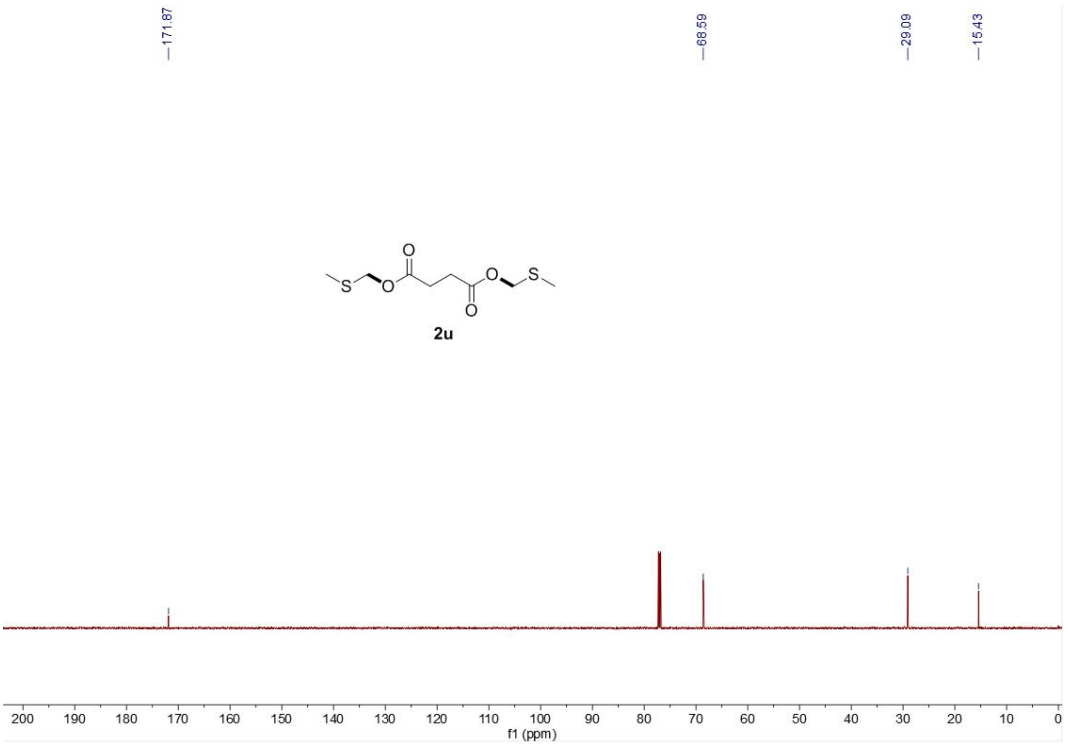

166.63
145.62
141.14
135.92
129.23
128.86
127.29
126.08
120.45
68.18
15.47
O
O
S
f1 (ppm)

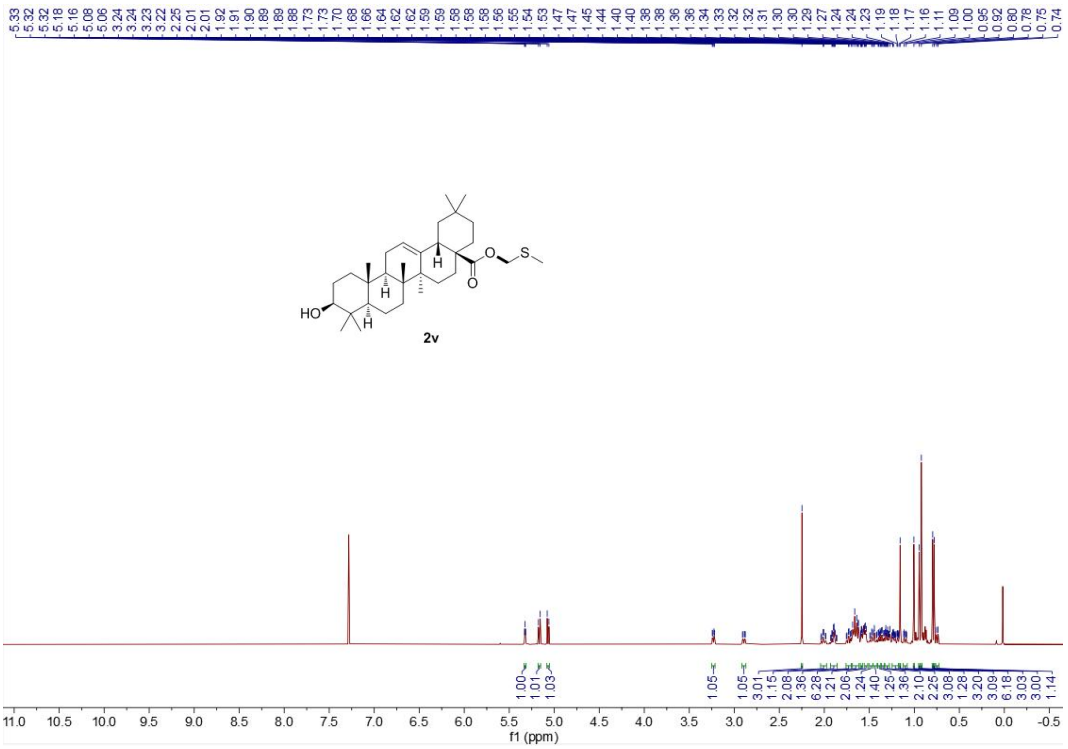
2s

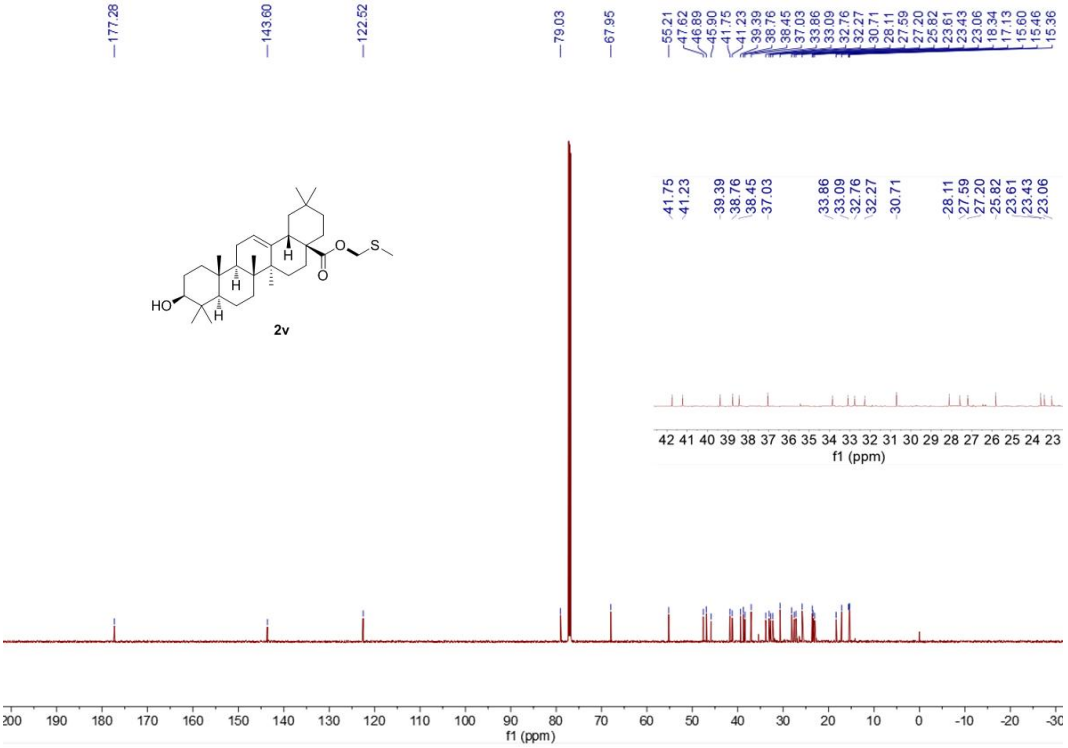

5.18
2.74
2.74
2.73
2.73
2.72
2.72
2.72
2.72
2.70
2.70
2.69
2.69
2.69
2.68
2.68
2.25
HO
O
O
O
S
2t
2.00
4.32
3.00
f1 (ppm)

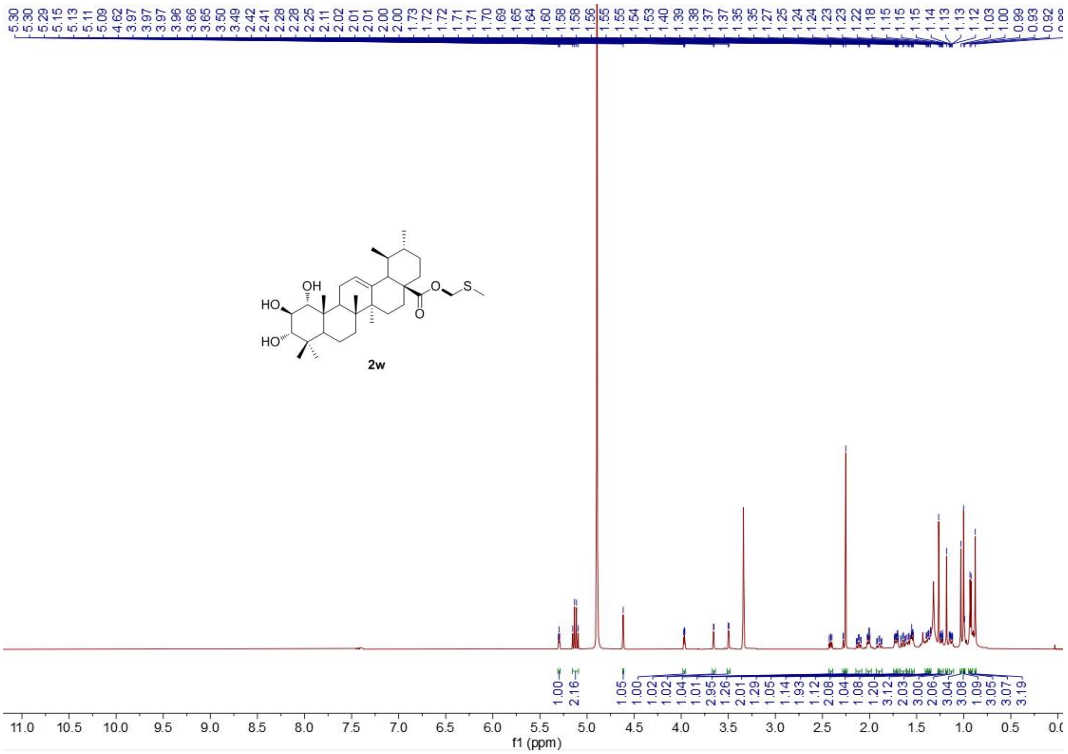

177.94
171.89
68.65
28.94
28.78
15.38
HO
O
O
O
S
2t
f1 (ppm)

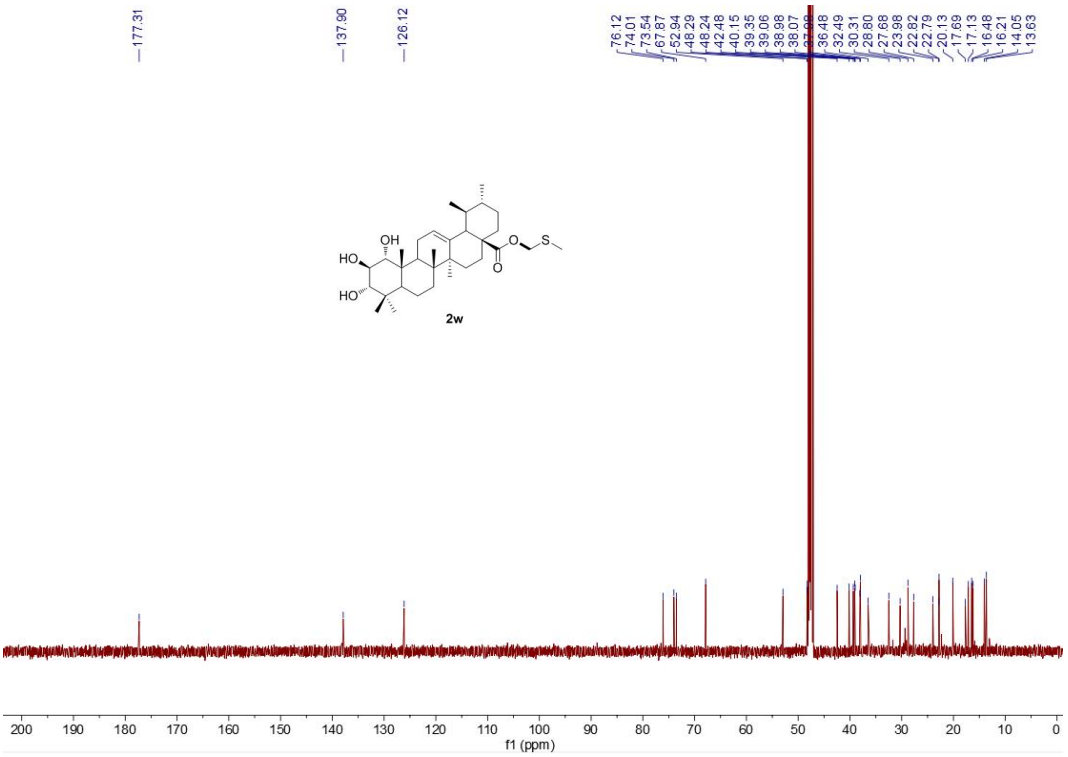

5.18
2.72
2.26
2u
4.00
4.08
6.08
f1 (ppm)

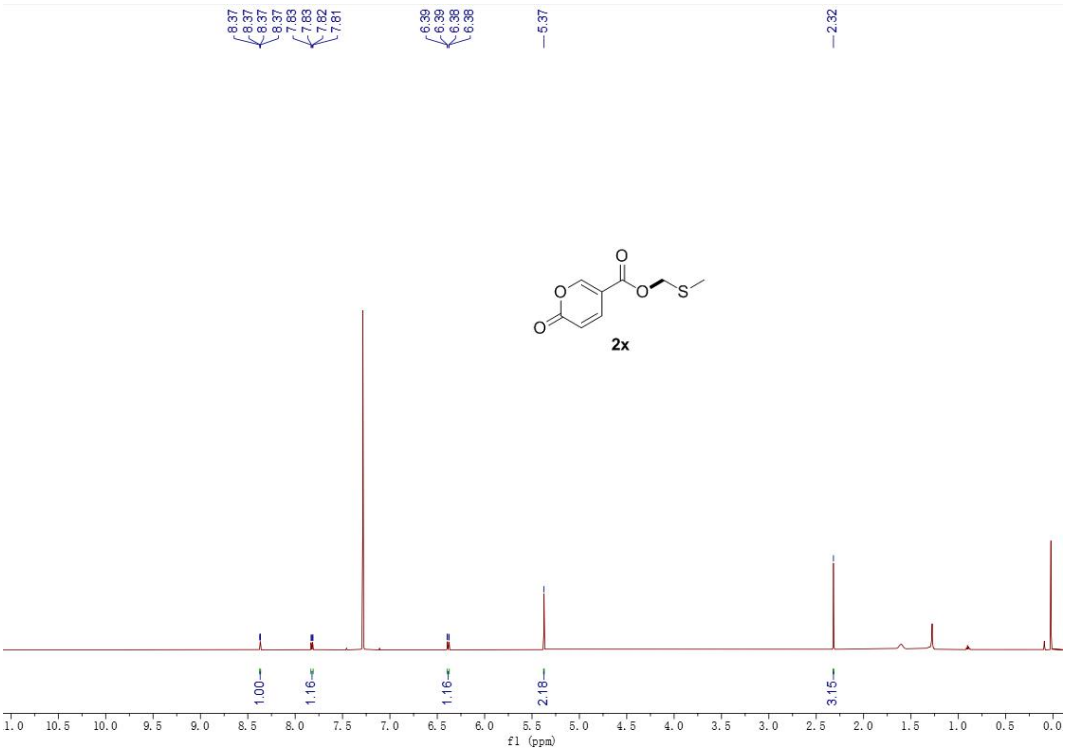

171.87
68.59
29.09
15.43
2u
f1 (ppm)

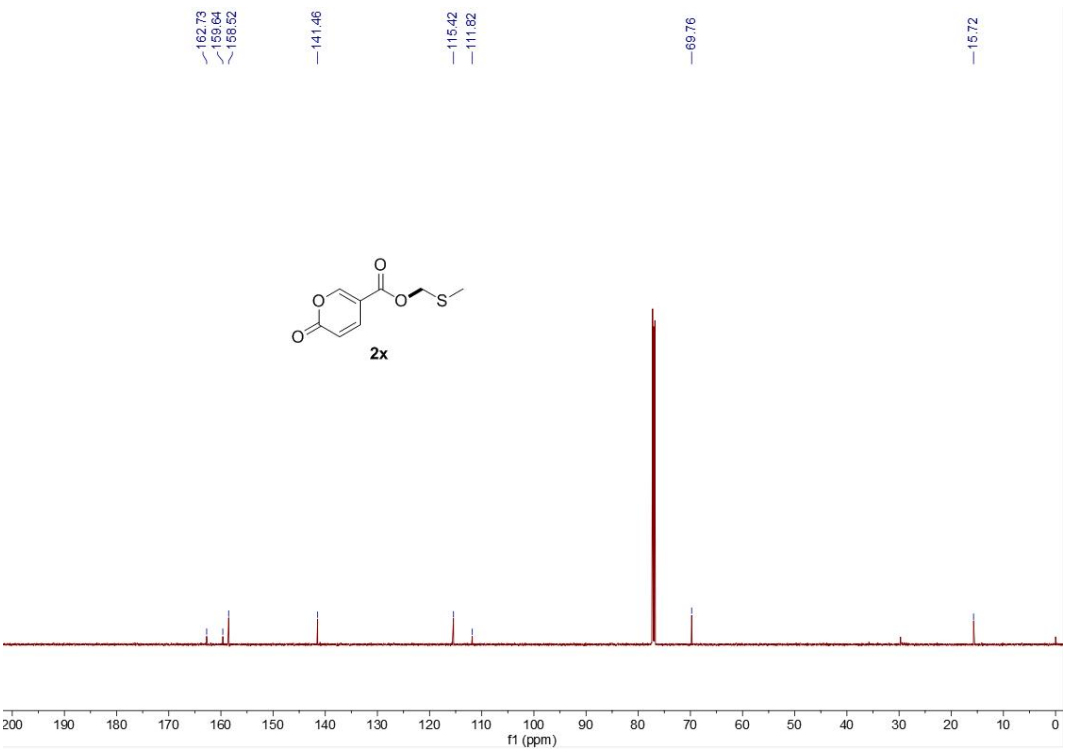

HO
O
O
S
H
H
H
2v
f1 (ppm)

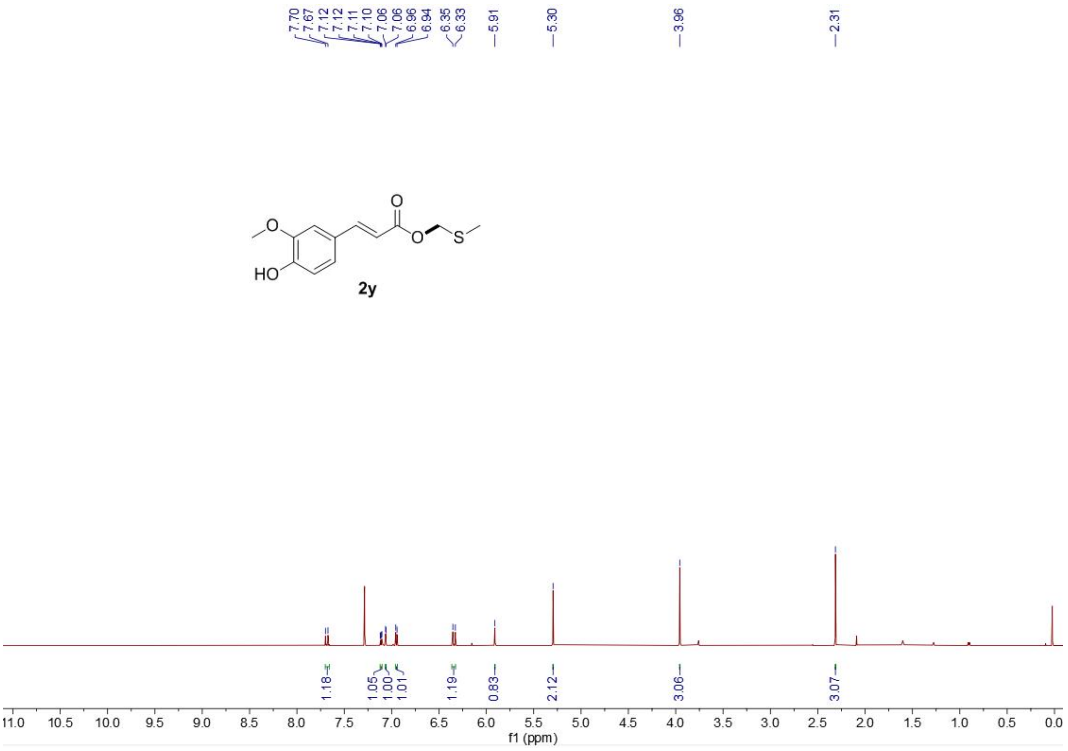

HO
O
O
S
H
H
H
2v
f1 (ppm)

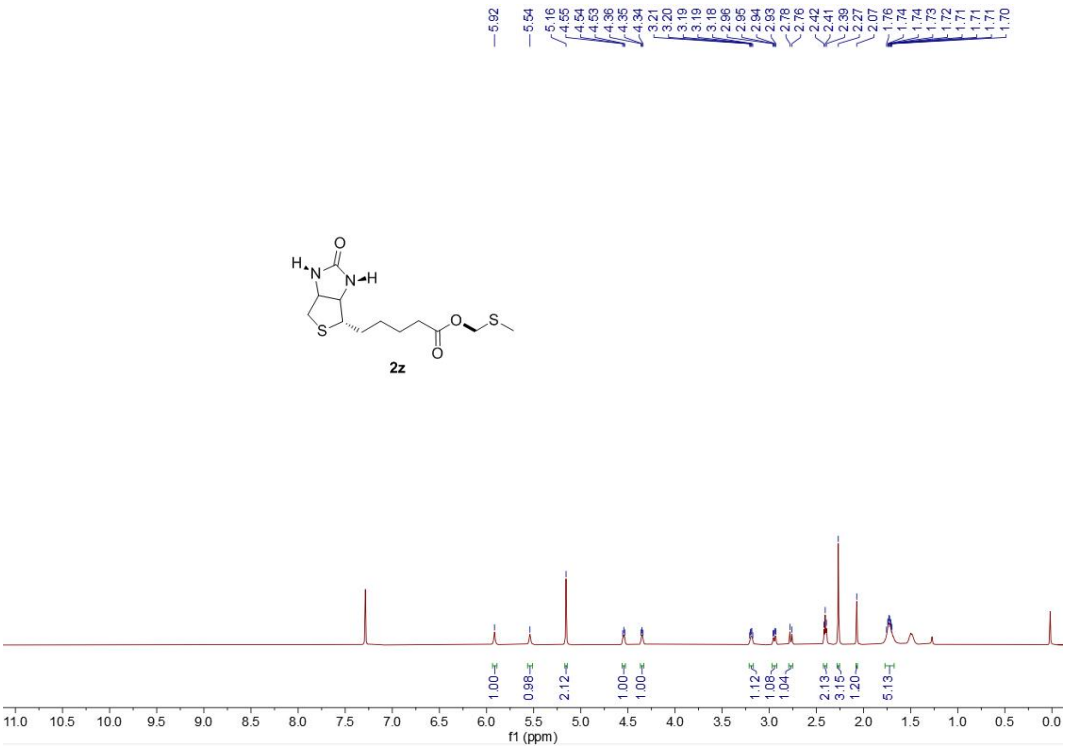

OH
HO
HO
O
O
S
2w
f1 (ppm)

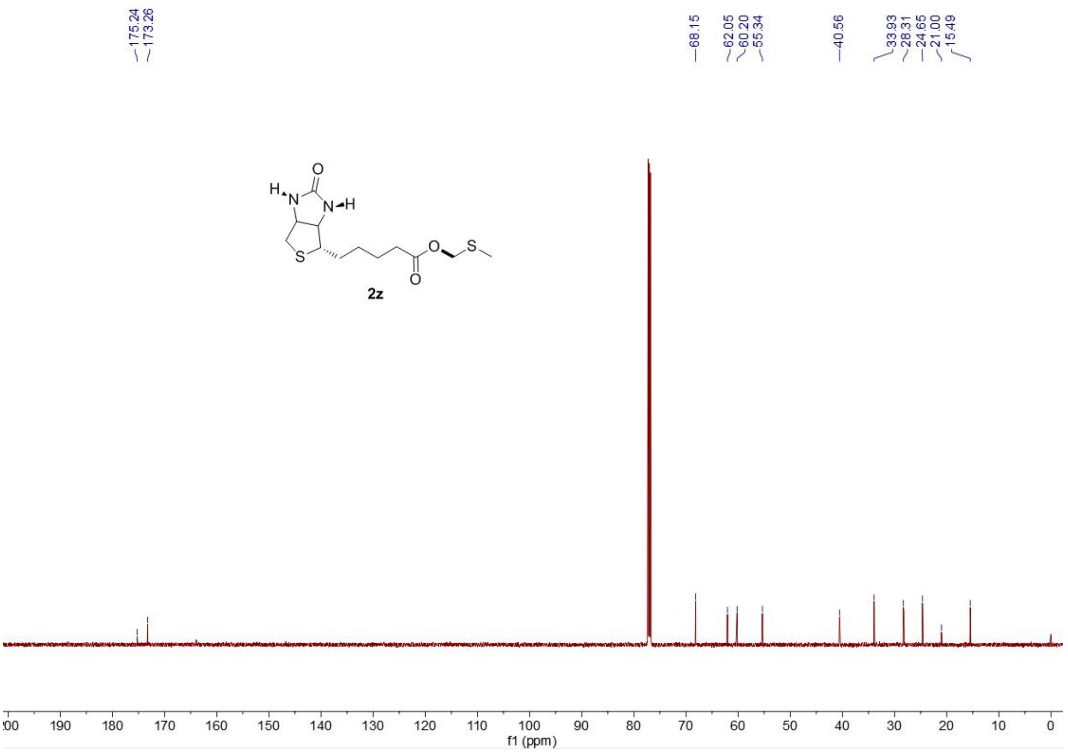

177.31
137.90
126.12
OH
HO
HO
O
O
S
2w
f1 (ppm)

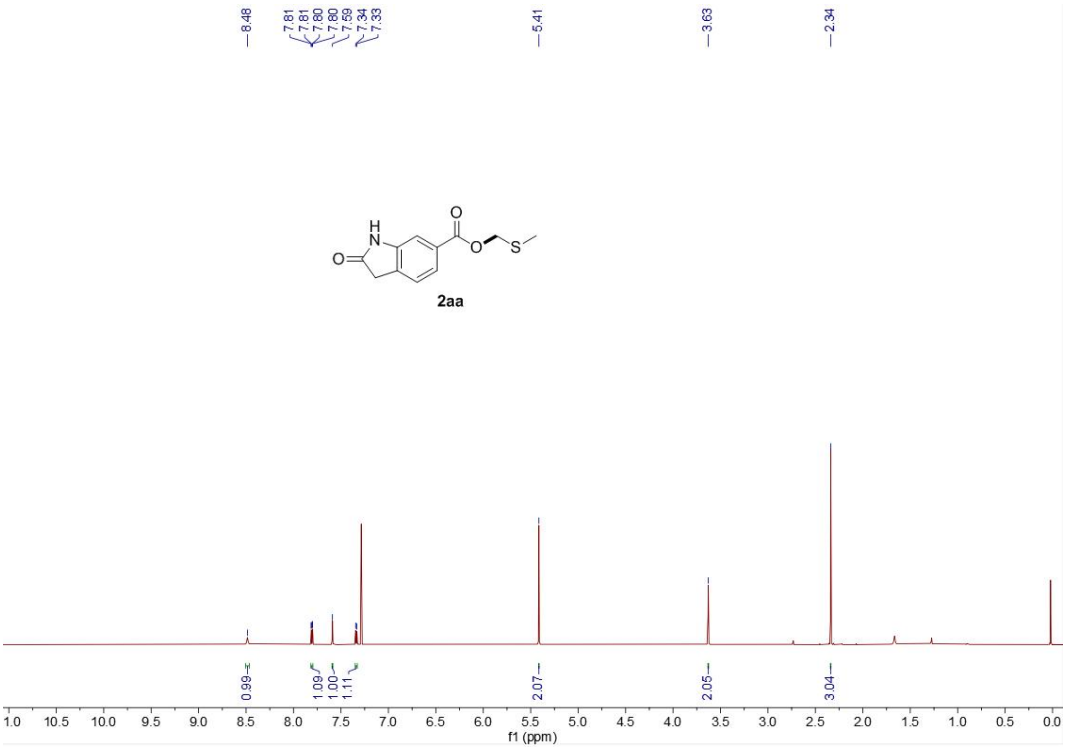

8.37
8.37
8.37
8.37
7.83
7.83
7.82
7.81
6.39
6.39
6.38
6.38
5.37
2.32
O
O
O
O
S
2x
1.00
1.16
1.16
2.18
3.15
f1 (ppm)

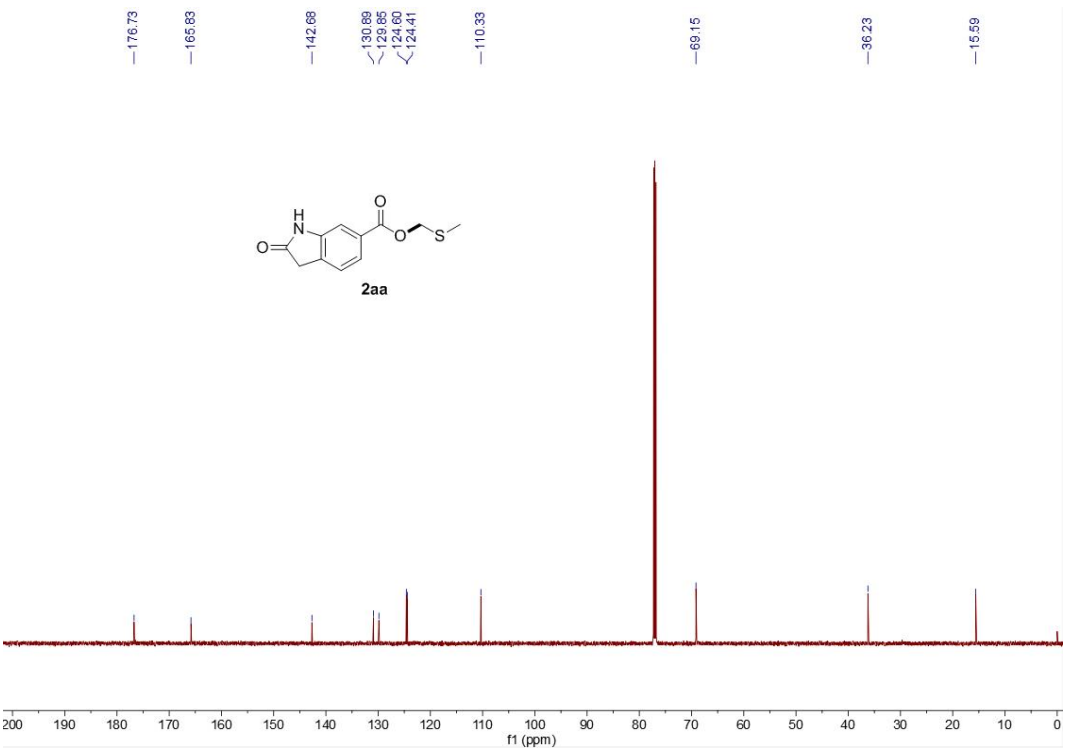

162.73
159.64
158.52
141.46
115.42
111.82
69.76
15.72
O
O
O
O
S
2x
f1 (ppm)


7.70
7.67
7.12
7.12
7.11
7.10
7.06
7.06
6.98
6.94
6.35
6.33
5.91
5.30
3.96
2.31
O
O
O
S
HO
2y
1.18
1.05
1.00
1.01
1.19
0.83
2.12
3.06
3.07
f1 (ppm)
166.86
148.19
146.79
145.77
126.84
123.29
114.83
114.77
109.39
68.20
55.96
15.47
O
O
O
S
HO
2y
f1 (ppm)

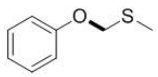

5.92
5.54
5.16
4.65
4.64
4.63
4.36
4.35
4.34
3.21
3.20
3.19
3.19
3.18
2.96
2.95
2.94
2.93
2.78
2.76
2.42
2.41
2.39
2.27
2.07
1.76
1.74
1.74
1.73
1.72
1.71
1.71
1.71
1.70
2z
1.00
0.98
2.12
1.00
1.00
1.12
1.08
1.04
2.13
3.15
1.20
5.13
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


175.24
173.26
68.15
62.05
60.20
55.34
40.56
33.93
28.31
24.65
21.00
15.49
2z
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

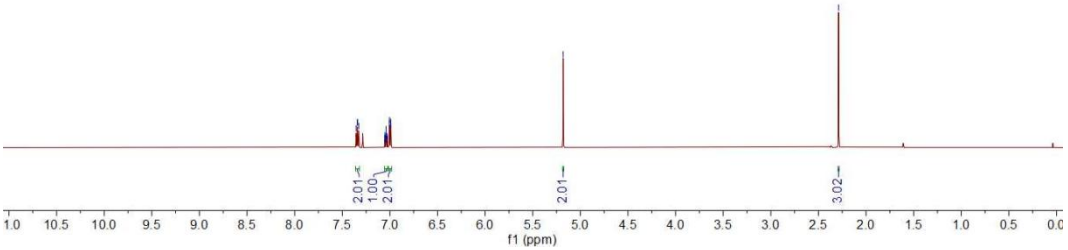

8.48
7.81
7.81
7.80
7.80
7.59
7.34
7.33
5.41
3.63
2.34
2aa
0.99
1.09
1.00
1.11
2.07
2.05
3.04
f1 (ppm)


176.73
165.83
142.68
130.89
129.85
124.60
124.41
110.33
69.15
36.23
15.59
2aa
f1 (ppm)

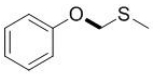

7.35
7.34
7.34
7.33
7.05
7.05
7.05
7.04
7.04
7.04
7.03
7.03
7.03
7.01
7.00
6.99
6.99
5.18
2.29



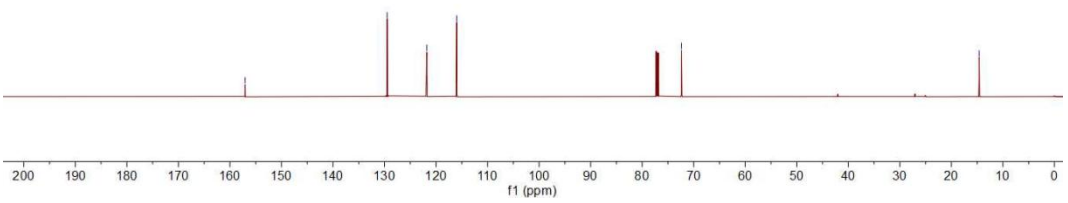
4a

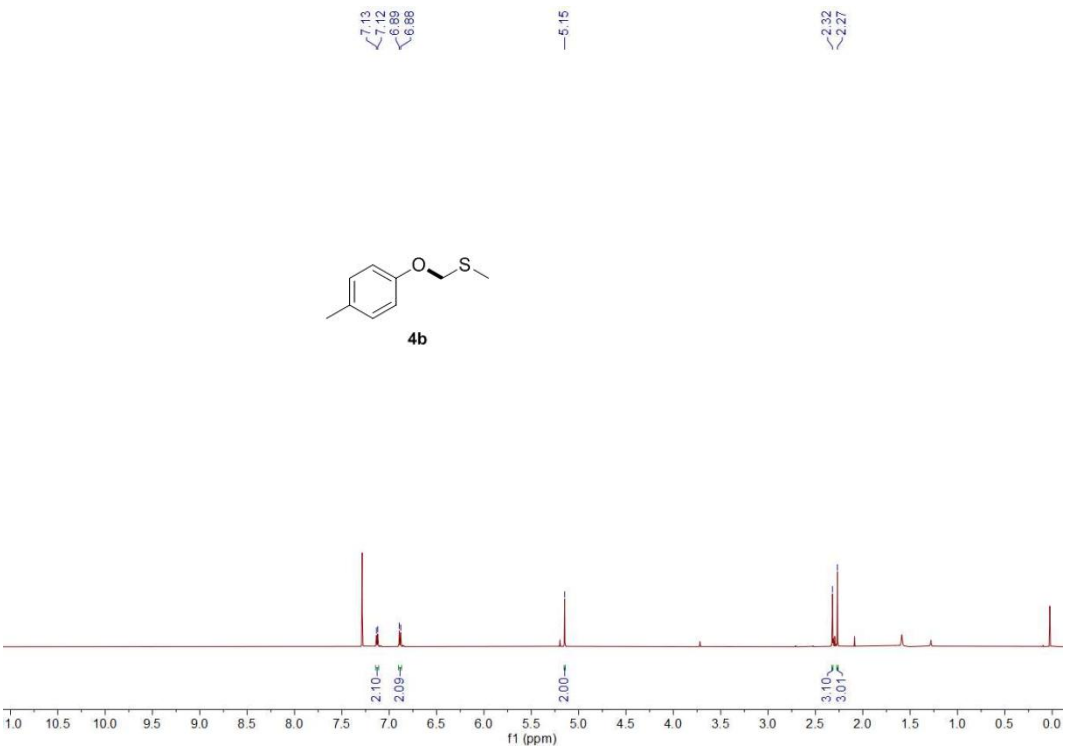

2.01
1.00
2.01
2.01
3.02
f1 (ppm)

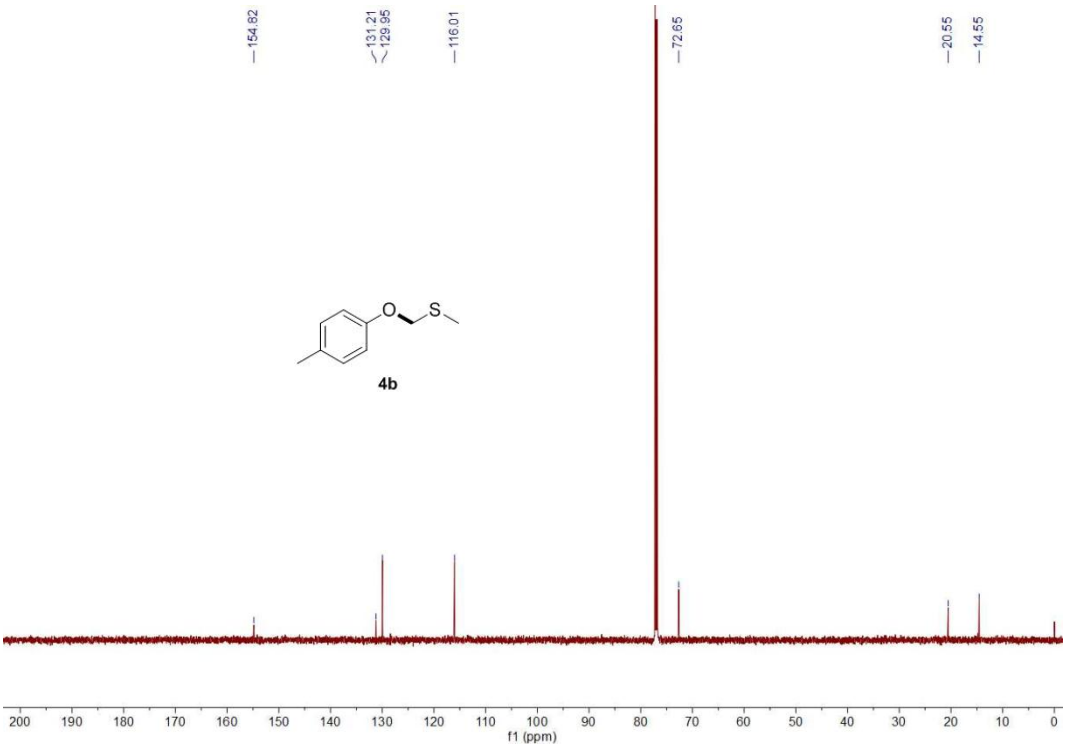

157.06
129.49
121.78
115.98
72.38
14.62



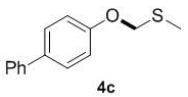
4a


f1 (ppm)

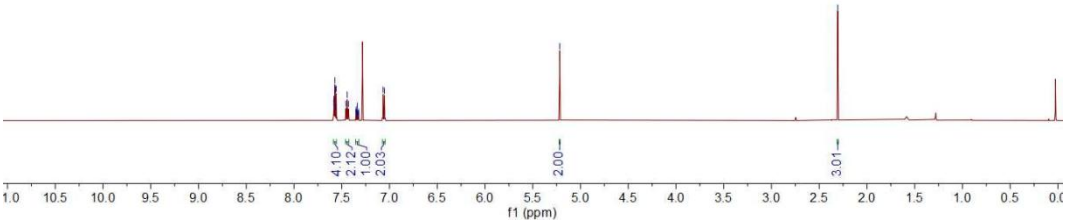

7.13
7.12
6.89
6.88
5.15
2.32
2.27
O
S
4b
2.10
2.09
2.00
3.10
3.01
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


154.82
131.21
129.95
116.01
72.65
20.55
14.55
O
S
4b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

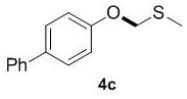

7.58
7.58
7.57
7.57
7.56
7.56
7.46
7.44
7.43
7.35
7.35
7.35
7.34
7.34
7.33
7.32
7.32
7.07
7.05
5.22
2.31


O
S
Ph

4c


4.10
2.12
1.00
2.03
2.00
3.01
f1 (ppm)

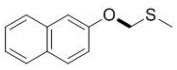

156.51
140.70
134.90
128.74
128.19
126.83
116.22
72.46
14.63


O
S
Ph

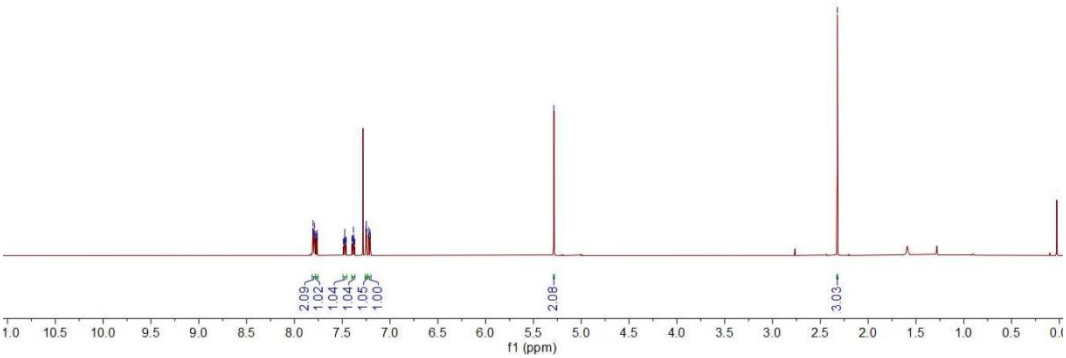
4c

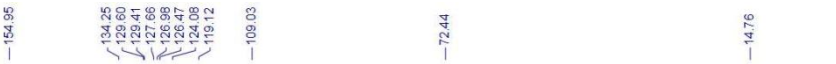
f1 (ppm)

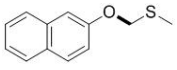

7.81
7.81
7.79
7.79
7.78
7.78
7.76
7.76
7.49
7.48
7.48
7.47
7.47
7.46
7.46
7.40
7.39
7.39
7.38
7.38
7.37
7.37
7.25
7.25
7.22
7.22
7.21
7.21
5.29
2.32



4d

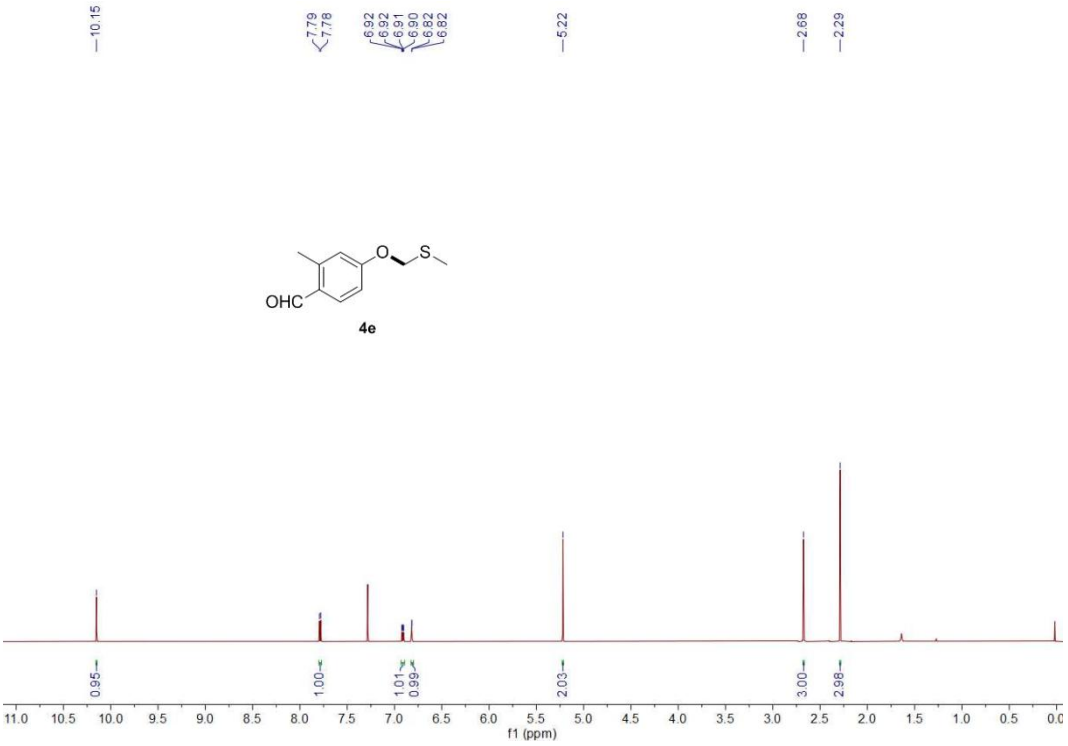

2.09
1.02
1.04
1.04
1.05
1.00
2.08
3.03
f1 (ppm)

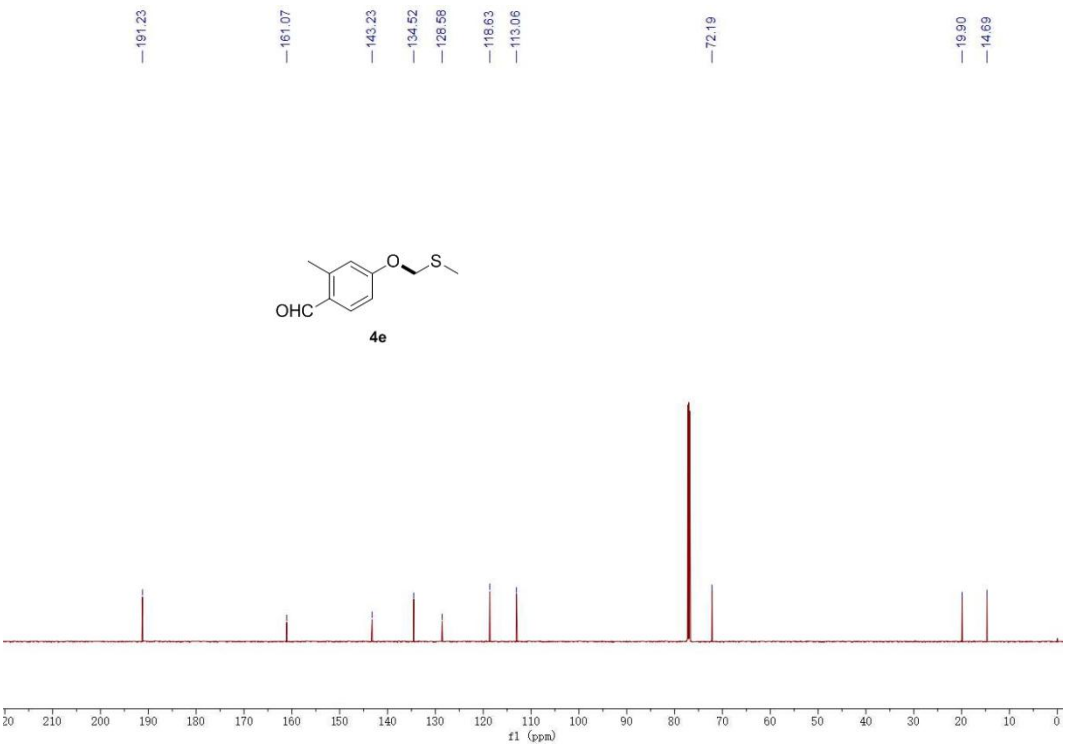

154.95
134.25
129.60
128.41
127.66
126.98
126.47
124.08
119.12
109.03
72.44
14.76



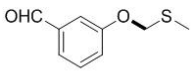
4d

f1 (ppm)

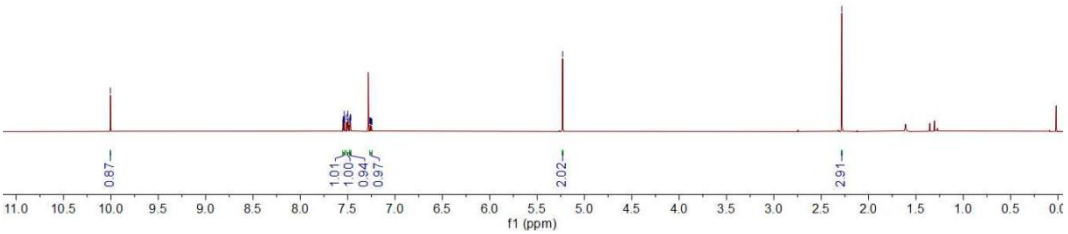

10.15
7.79
7.78
6.92
6.92
6.91
6.90
6.82
6.82
5.22
2.68
2.29
OHC
O
S
4e
0.95
1.00
1.01
0.99
2.03
3.00
2.98
f1 (ppm)

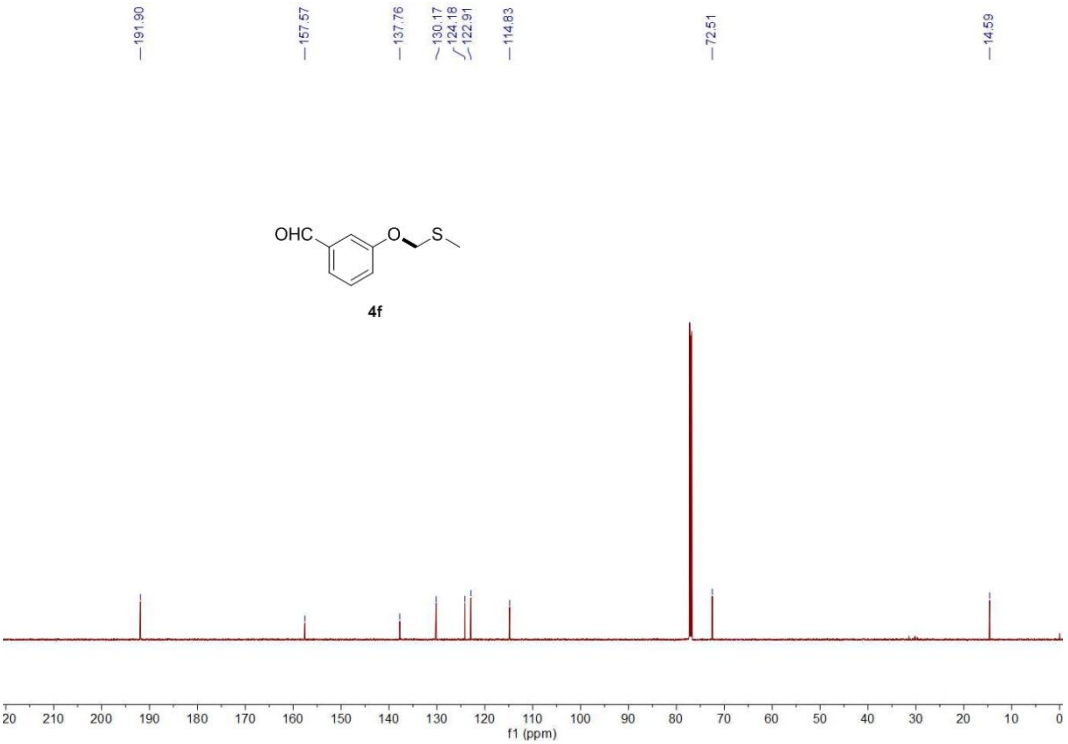

191.23
161.07
143.23
134.52
128.58
118.63
113.06
72.19
19.90
14.69
OHC
O
S
4e
f1 (ppm)

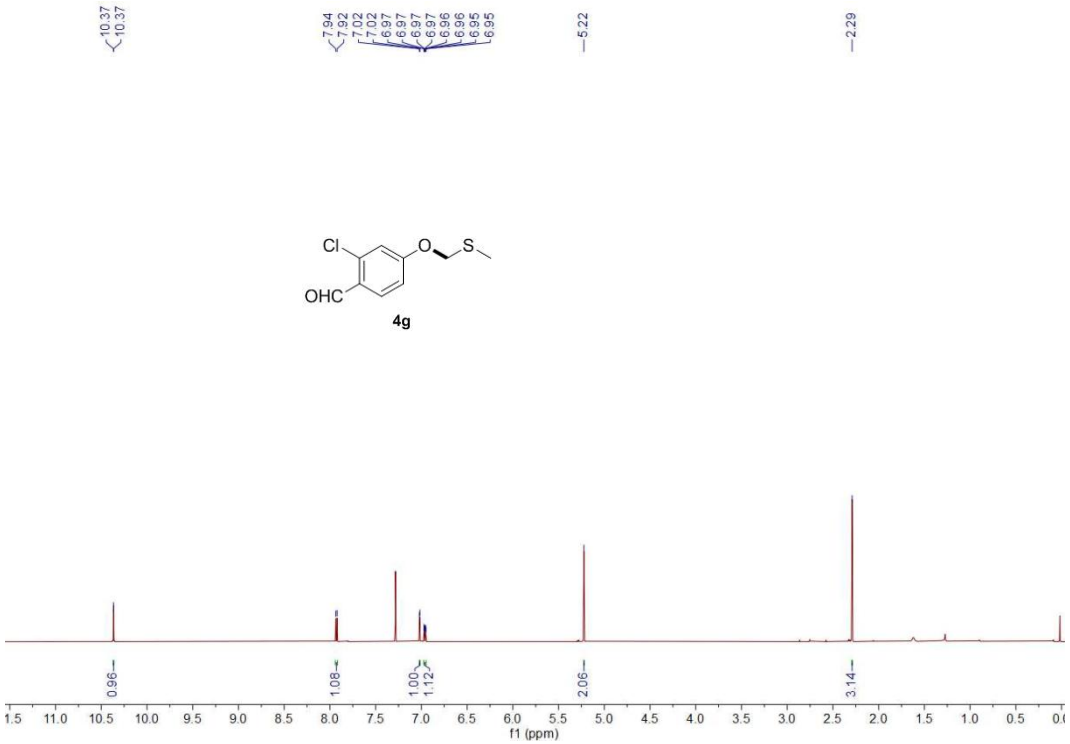

10.01
7.55
7.55
7.55
7.54
7.54
7.53
7.51
7.50
7.48
7.48
7.47
7.47
7.47
7.26
7.26
7.26
7.25
7.25
7.25
5.23
2.28

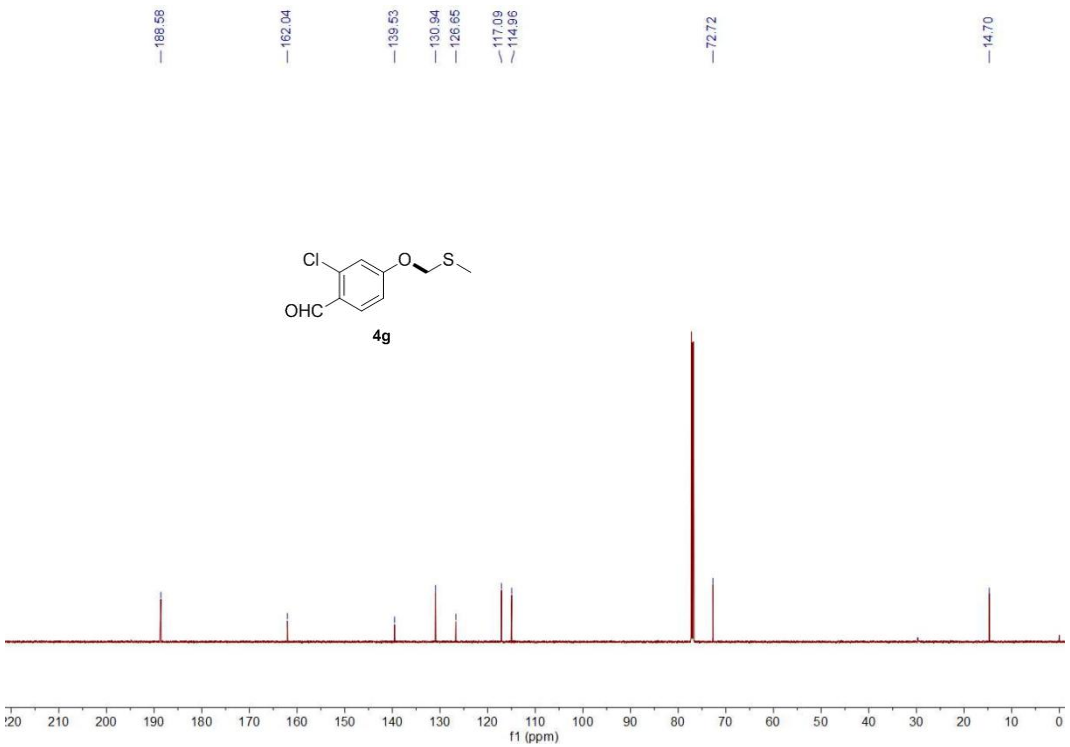

OHC
O
S

4f


0.87
1.01
1.00
0.94
0.97
2.02
2.91
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


191.90
157.57
137.76
130.17
124.18
122.91
114.83
72.51
14.59
OHC
O
S
4f
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


10.37
10.37
7.94
7.92
7.02
7.02
6.97
6.97
6.97
6.97
6.96
6.96
6.95
6.95
5.22
2.29
Cl
O
S
OHC
4g
0.96
1.08
1.00
1.12
2.06
3.14
f1 (ppm)


188.58
162.04
139.53
130.94
126.65
117.09
114.96
72.72
14.70
Cl
O
S
OHC
4g
f1 (ppm)