Synthesis of unsymmetrical ketones *via* C-H activation of aldehydes

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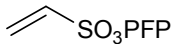
General Experimental

All reagents were purchased from Aldrich or AlfaAesar and were used as received without further purification. Where described below petrol refers to petroleum ether (40-60). All reactions were monitored by thin-layer chromatography (TLC) on pre-coated silica gel plates (254μm). Flash column chromatography was carried out with Kiesegel 60M 0.04/0.063mm (200-400 mesh) silica gel. ^{1}H NMR spectra were recorded at 300 MHz, 400 MHz and 500 MHz and ^{13}C NMR at 75 MHz, 101 MHz and 126 MHz on a Bruker AMX300, AMX400 and AMX500 at ambient temperature in $CDCl_3$ as described below. The chemical shifts (δ) for ^{1}H and ^{13}C are quoted relative to residual signals of the solvent on the ppm scale. Coupling constants (*J* values) are reported in Hertz (Hz). Mass spectra were obtained on a VG70-SE mass spectrometer or measured at EPSRC Mass Spectrometry Service, University of Swansea. Infrared spectra were obtained on a Perkin Elmer Spectrum 100 FTIR Spectrometer operating in ATR mode. Melting points were measured with a Gallenkamp apparatus and are uncorrected. Elemental analyses were carried out at the Department of Chemistry, University College London.

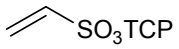
Ethenesulfonic acid pentafluorophenyl ester



Pentafluorophenol (11.5g, 62.5 mmol) and NEt_3 (19 ml, 137.5 mmol) in DCM (20 ml) dropwise over 1h to a solution at of 2-chloroethane sulfonyl chloride (10.13 g, 62.5 mmol) in DCM (100 ml) at -78°C. The mixture was allowed warm slowly to 21 °C and diluted with DCM (100 ml) and washed with water (x1), 2M HCl (x2) and sat. $NaHCO_3$ (x2), dried ($MgSO_4$) and the solvent removed *in vacuo*. Purification by column chromatography on silica gel (10% Et_2O/petrol) gave the product as a white solid (13.72g, 50mmol, 81%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.79 (dd, J =

9.8, 16.5 Hz, 1H), 6.53 (dd, J = 0.7, 16.5 Hz, 1H), 6.34 (dd, J = 0.7, 9.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.2 (s), 133.2 (d), 131.7 (d); IR (thin film) 2963, 1650, 1625 , 1520 cm^{-1}; LRMS (EI) 274 (46, $[M]^+$), 184 (47), 136 (17), 91 (100).

Ethenesulfonic acid 2,4,6-trichlorophenyl ester



2,4,6-Trichlorophenol (19.75 g, 0.1 mol) and NEt_3 (31.3 mL, 0.22 mol) in CH_2Cl_2 (50 mL) were added dropwise over 90 mins to a stirred solution of 2-chloroethane sulfonyl chloride (11.5 mL, 0.11 mol) in DCM (200 mL) at -10 °C. The mixture was allowed to warm slowly to 21 °C and filtered though a plug of 10% K_2CO_3/silica with CH_2Cl_2 (250 mL). The solvent was removed *in vacuo* and purification by recrystallization (CH_2Cl_2/petrol) and gave the product as a white solid (23.6 g, 82 mmol, 82 % yield): m.p. 53-55 °C; ^1H NMR (500 MHz, CDCl3) δ 7.39 (s, 2H), 6.93 (dd, 1H, J = 9.9, 16.6), 6.55 (dd, 1H, J = 0.9, 16.6), 6.26 (dd, 1H, J = 0.9, 9.9); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.05 (s), 133.96 (d), 133.18 (s), 131.52 (t), 130.84 (s), 129.27 (d); IR (thin film) 3081, 1561 cm^{-1}; LRMS (CI) 291 (34, $[M+H]^+$), 289 (96, $[M+H]^+$), 287 (100, $[M+H]^+$), 199 (16), 197 (14); HRMS (CI) calcd for $C_8H_6Cl_3O_3S$ $[M+H]^+$ 286.9103; observed 286.9107; *Anal*. calcd: C, 33.42; H, 1.75, found: C, 33.48; H, 1.70.

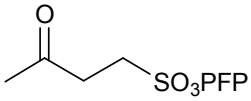
Typical procedure for the synthesis of ketone sulfonate esters – Method A

Aldehyde (5 mmol) was added to a stirred solution of ethenesulfonic acid ester (1 mmol) in dioxane (1 mL) and the reaction was stirred at 21 °C until complete by TLC. MePh (2 mL) was added and the solvent removed *in vacuo* and purification as appropriate afforded the desired ketone sulfonate ester.

Typical procedure for the synthesis of ketone sulfonate esters – Method B

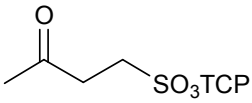
30% H_2O_2/H_20 (0.05mmol) was added to a stirred solution of aldehyde (2 mmol) and ethenesulfonic acid ester (1 mmol) in water (400 μL) and the reaction was stirred at 21 °C until complete by TLC. The solvent removed *in vacuo* and purification as appropriate afforded the desired ketone sulfonate ester.

3-Oxo-butane-1-sulfonic acid pentafluorophenyl ester



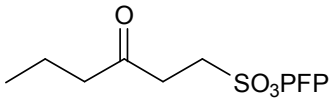
Using Method A. Reaction was complete after 3 h and column chromatography on silica gel (CH_2Cl_2/petrol) gave the product as a pale yellow oil (119 mg, 0.38 mmol, 38%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 – 3.75 (m, 2H), 3.21 – 3.17 (m, 2H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.4 (s), 46.9 (t), 36.8 (t), 29.8 (q); IR (neat) 1724 cm^{-1}; LRMS (ES) 336 (100%, $[M+NH_4]^+$); HRMS (ES) calcd for $C_{10}H_{11}F_5NO_4S$ $[M+NH_4]^+$ 336.0323; observed 336.0323.

3-Oxo-butane-1-sulfonic acid 2,4,6-trichlorophenyl ester



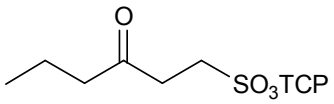
Using Method A. Reaction was complete after 20 h and column chromatography on silica gel (CH_2Cl_2/petrol) gave the product and 5-oxo-hexane-1,3-disulfonic acid bis-(2,4,6-trichlorophenyl) ester as a 30:1 mixture which was further purified by recrystallization (CH_2Cl_2/petrol) and gave the product as a white solid: m.p. 62-65 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (m, 2H), 3.84 (m, 2H), 3.22 (m, 2H), 2.27 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.99 (s),141.92, (s), 133.25 (s), 130.66 (s), 129.32 (d), 48.63 (t), 37.19 (t), 29.96 (q); IR (thin film) 3081, 2940, 1720, 1561 cm^{-1}; LRMS (CI) 335 (10, $[M+H]^+$), 333 (10, $[M+H]^+$), 135 (100); HRMS (CI) calcd for $C_{10}H_{10}Cl_3O_4S$ $[M+H]^+$ 330.9365; observed 330.9361.

3-Oxo-hexane-1-sulfonic acid pentafluorophenyl ester



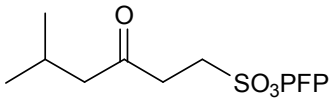
Using Method A. Reaction was complete after 1 h and column chromatography on silica gel (CH_2Cl_2/petrol) gave the product off-white crystalline solid (229 mg, 0.66 mmol, 66%). A small amount further purified by recrystallization (hexane) to give white crystals: m.p. 44-46 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.77 – 3.73 (m, 2H), 3.15 – 3.10 (m, 2H), 2.50 (t, J = 7.3, 2H), 1.71 – 1.59 (app sext, J = 7.3, 2H), 0.94 (t, J = 7.4, 3H): ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.9 (s), 47.0 (t), 44.6 (t), 35.9 (t), 17.2 (t), 13.6 (q), IR (neat) 2964, 1716 cm^{-1}; LRMS (CI) 364 (100%, $[M+NH_4]^+$); HRMS (ES) calcd for $C_{12}H_{15}F_5NO_4S$ $[M+NH_4]^+$ 364.0636; observed 364.0636.

3-Oxo-hexane-1-sulfonic acid 2,4,6-trichlorophenyl ester



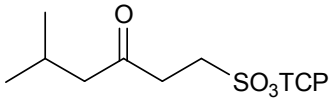
Using Method A. Reaction was complete after 20 h and column chromatography on silica gel (CH_2Cl_2/petrol) gave the product and 5-oxo-octane-1,3-disulfonic acid bis-(2,4,6-trichlorophenyl) ester as a 24:1 mixture which was further purified by recrystallization (CH_2Cl_2/petrol) and gave the product as a white solid: m.p. 62-64 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (s, 2H), 3.85 (m, 2H), 3.18 (m, 2H), 2.50 (t, 2H, J = 7.3), 1.66 (app sext., 1H, J = 7.4), 0.94 (t, 6H, J = 7.4), ^{13}C NMR (126 MHz, $CDCl_3$) δ 205.49 (s), 141.94 (s), 133.20 (s), 130.65 (s), 129.30 (d), 58.69 (t), 44.75 (t), 36.23 (t), 17.28 (t), 13.72 (q); IR (solid) 3066, 2968, 2939, 2879, 1713, 1561 cm^{-1}; LRMS (CI) 389 (12), 387 (33) 385 (35), 361 (11, $[M+H]^+$), 359 (10, $[M+H]^+$), 197 (100), 199 (96), 201 (29), 163 (32); HRMS (CI) calcd for $C_{12}H_{14}Cl_3O_4S$ $[M+H]^+$ 358.9678; observed 358.9681.

5-Methyl-3-oxo-hexane-1-sulfonic acid pentafluorophenyl ester



Using Method A. Reaction was complete after 3 h and column chromatography on silica gel (CH_2Cl_2/petrol) gave the product as an off-white crystalline solid (195 mg, 0.54 mmol, 54%). A small amount further purified by recrystallization (hexane) to give white crystals: m.p. 56-59 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.78 – 3.73 (m, 2H), 3.14 – 3.09 (m, 2H), 2.40 (d, J = 6.9, 2H), 2.18 (app sept, J = 6.7, 1H), 0.95 (d, J = 6.6, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.7 (s), 51.6 (t), 46.9 (t), 36.4 (t), 24.7 (d), 22.5 (q); IR (neat) 2964, 1720 cm^{-1}; LRMS (CI) 378 (100%, $[M+NH_4]^+$); HRMS (ES) calcd for $C_{13}H_{13}F_5O_4S$ $[M+NH_4]^+$. 378.0793; observed 378.0796.

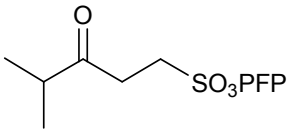
5-Methyl-3-oxo-hexane-1-sulfonic acid 2,4,6-trichlorophenyl ester



Using Method A. Reaction was complete after 20 h and column chromatography on silica gel (CH_2Cl_2/petrol) gave the product and 7-methyl-5-oxo-octane-1,3-disulfonic acid bis-(2,4,6-trichloro-phenyl) ester as a 21:1 mixture which was further purified by recrystallization

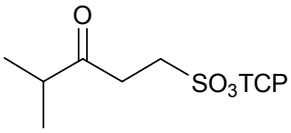
(CH_2Cl_2/petrol) and gave the product as a white solid. m.p. 59-62 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (s, 2H), 3.84 (m, 2H), 3.17 (m, 2H), 2.40 (d, 2H, J = 7.0), 2.18 (app sept, 1H, J = 6.7), 0.95 (d, 6H, J = 6.7); ^{13}C NMR (126 MHz, $CDCl_3$) δ 205.22 (s), 141.95 (s), 133.23 (s), 130.67 (s), 129.32 (d), 51.81 (t), 48.65 (t), 36.78 (t), 24.82 (d), 22.58 (q); IR (thin film) 3082, 2958, 2873, 1717, 1561 cm^{-1}; LRMS (CI) 401 (19), 399 (21), 375 (17, $[M+H]^+$), 373 (20, $[M+H]^+$), 201 (24), 199 (69), 197 (80), 177 (100), 139 (45), 113 (75); HRMS (CI) calcd for $C_{13}H_{16}Cl_3O_4S$ $[M+H]^+$ 372.9835; observed 372.9829.

4-Methyl-3-oxo-pentane-1-sulfonic acid pentafluorophenyl ester



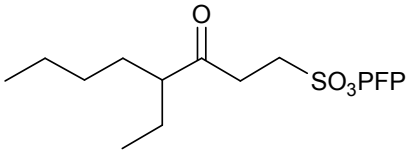
Using Method A. Reaction was complete after 3 h and column chromatography on silica gel (CH_2Cl_2/petrol) gave the product as a as a colourless oil (200 mg, 0.58 mmol, 58%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 – 3.74 (m, 2H), 3.21 – 3.18 (m, 2H), 2.74 – 2.67 (app. sept, *J* = 6.9, 1H), 1.18 (d, *J* = 6.9, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.7 (s), 47.2 (t), 41.0 (d), 33.7 (t), 18.1 (q); IR (neat) 2976, 1716 cm^{-1}; LRMS (CI) 364 (100%, $[M+NH_4]^+$); HRMS (ES) calcd for $C_{12}H_{15}F_5NO_4S$ $[M+NH_4]^+$. 364.0636; observed 364.0635.

4-Methyl-3-oxo-pentane-1-sulfonic acid 2,4,6-trichlorophenyl ester



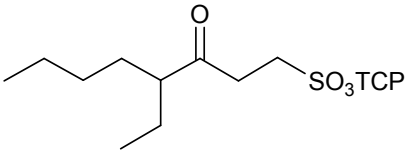
Using Method A. Reaction was complete after 42 h and column chromatography on silica gel (CH_2Cl_2/petrol) gave the product and 6-methyl-5-oxo-heptane-1,3-disulfonic acid bis-(2,4,6-trichlorophenyl) ester as a 10:1 mixture which was further purified by recrystallization (CH_2Cl_2/petrol) and gave the product as a white solid: m.p. 64-65 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (s, 2H), 3.84 (m, 2H), 3.23 (m, 2H), 2.69 (sept., 1H, J = 6.9), 1.16 (d, 6H, J = 6.9); ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.27 (s), 141.96 (s), 133.21 (s), 130.66 (s), 129.31 (d), 48.89 (t), 41.11 (s), 34.05 (t), 18.22 (q); IR (thin film) 3080, 2972, 1714, 1561 cm^{-1}; LRMS (CI) 433 (27), 431 (27), 361 (89, $[M+H]^+$) 359 (90, $[M+H]^+$), 163 (100), 99 (48); HRMS (CI) calcd for $C_{12}H_{14}Cl_3O_4S$ $[M+H]^+$ 358.9678; observed 358.9683.

4-Ethyl-3-oxo-octane-1-sulfonic acid pentafluorophenyl ester



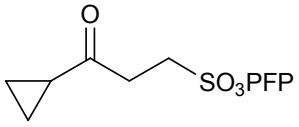
Using Method A. Reaction was complete after 1 h and column chromatography on silica gel (CH_2Cl_2/petrol) gave the product as a as a colourless oil (139 mg, 0.69 mmol, 69%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 – 3.83 (m, 2H), 3.23 – 3.19 (m, 2H), 2.49 (tt, *J* = 5.7, 8.0, 1H), 1.66 (m, 2H), 1.51 (m, 2H), 1.31 (m, 2H), 1.23 (m, 2H), 0.90 (t, *J* = 7.2, 3H), 0.89 (t, *J* = 7.4, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.9 (s), 54.0 (d), 47.1 (t), 35.6 (t), 31.0 (t), 29.8 (t), 24.7 (t), 22.8 (t), 14.0 (q), 11.8 (q); IR (neat) 2934, 2962, 2875, 1714 cm^{-1}; LRMS (CI) 420 (14, $[M+NH_4]^+$), 172 (100); HRMS (ES) calcd for $C_{16}H_{23}F_5NO_4S$ $[M+NH_4]^+$ 420.1262; observed 420.1265.

4-Ethyl-3-oxo-octane-1-sulfonic acid 2,4,6-trichlorophenyl ester



Using Method A. Reaction was complete after 48 h and column chromatography on silica gel (CH_2Cl_2/petrol) gave the product as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (s, 2H), 3.84 (m, 2H), 3.19 (m, 2H), 2.48 (tt, 1H, J = 5.7, 8.0), 1.55 (m, 4H), 1.25 (m, 4H), 0.88 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.45 (s), 141.99 (s), 133.23 (s), 130.66 (s), 129.32 (d), 54.07 (d), 48.76 (t), 35.89 (t), 31.05 (t), 29.70 (t), 24.73 (t), 22.85 (t), 13.98 (q), 11.89 (q); IR (thin film) 3082, 2959, 2932, 2874, 1713, 1561 cm^{-1}; LRMS (CI) 417 (18, $[M+H]^+$), 415 (19, $[M+H]^+$), 219 (49), 210 (19), 199 (55), 197 (61), 155 (100), 137 (29); HRMS (CI) calcd for $C_{16}H_{22}Cl_3O_4S$ $[M+H]^+$ 415.0304; observed 415.0307.

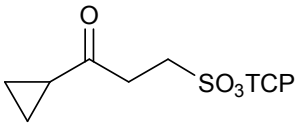
3-Cyclopropyl-3-oxo-propane-1-sulfonic acid pentafluorophenyl ester



Using Method A. Reaction was complete after 3 h and column chromatography on silica gel (CH_2Cl_2/petrol) gave the product as an off-white solid (213 mg, 0.62 mmol, 62%). A small

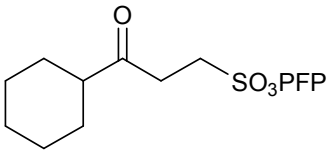
amount further purified by recrystallization (hexane) to give white crystals: m.p. 52-54 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 – 3.74 (m, 2H), 3.38 – 3.31 (m, 2H), 2.06 – 1.97 (tt, *J* = 4.5, 7.8, 1H), 1.18 – 1.12 (m, 2H), 1.06 – 0.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.9 (s), 47.1 (t), 36.5 (t), 20.7 (d), 11.8 (t); IR (neat) 1702 cm^{-1}; LRMS (CI) 362 (100%, $[M+NH_4]^+$); HRMS (ES) calcd for $C_{12}H_9F_5O_4S$ $[M+NH_4]^+$. 362.0480; observed 362.0484.

3-Cyclopropyl-3-oxo-propane-1-sulfonic acid 2,4,6-trichlorophenyl ester



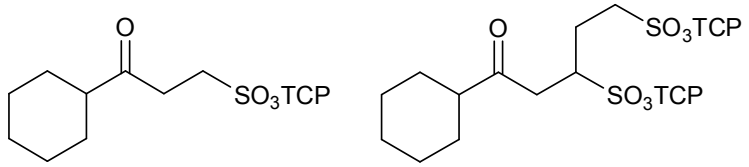
Using Method A. Reaction was complete after 96 h and column chromatography on silica gel (CH_2Cl_2/petrol) gave the product and 5-cyclopropyl-5-oxo-pentane-1,3-disulfonic acid bis-(2,4,6-trichlorophenyl) ester as a 18:1 mixture which was further purified by recrystallization (CH_2Cl_2/petrol) and gave the product as a white solid: m.p. 80-82 °C; ^{1}H NMR (500 MHz, CDCl3) δ 7.41 (s, 2H), 3.86 (m, 2H), 3.37 (m, 2H), 2.01 (tt, 1H, J = 4.5, 7.8), 1.13 (m, 2H), 1.00 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 205.37 (s), 141.97 (s), 133.22 (s), 130.69 (s), 129.32 (d), 48.77 (t), 36.87 (t), 20.85 (d), 11.72 (t); IR (thin film) 1702, 1562 cm^{-1}; LRMS (CI) 361 (13, $[M+H]^+$), 359, (37, $[M+H]^+$), 357 (39, $[M+H]^+$), 199 (30), 197 (32), 161 (100), 97 (48); HRMS (CI) calcd for $C_{12}H_{12}Cl_3O_4S$ $[M+H]^+$ 356.9522; observed 356.9515.

3-Cyclohexyl-3-oxo-propane-1-sulfonic acid pentafluorophenyl ester



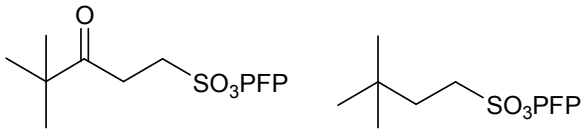
Using Method A. Reaction was complete after 3 h and column chromatography on silica gel (CH_2Cl_2/petrol) gave the product as an off-white solid (182 mg, 0.47 mmol, 47%): m.p. 62-64 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.79 – 3.72 (m, 2H), 3.22 – 3.16 (m, 2H), 2.49 – 2.40 (tt, *J* = 3.5, 11.2, 1H), 1.97 – 1.64 (m, 5H), 1.48 – 1.15 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.1 (s), 50.7 (d), 47.1 (t), 34.0 (t), 28.4 (t), 25.6 (t), 25.5 (t); IR (neat) 2934, 2855, 1706 cm^{-1}; LRMS (CI) 404 (100%, $[M+NH_4]^+$); HRMS (ES) calcd for $C_{15}H_{15}F_5O_4S$ $[M+NH_4]^+$. 404.0949; observed 404.0949.

3-Cyclohexyl-3-oxo-propane-1-sulfonic acid 2,4,6-trichlorophenyl ester and **5-cyclohexyl-5-oxo-pentane-1,3-disulfonic acid bis-(2,4,6-trichlorophenyl) ester**



Using Method A. Reaction was complete after 48 h and column chromatography on silica gel (CH_2Cl_2/petrol) gave 3-cyclohexyl-3-oxo-propane-1-sulfonic acid 2,4,6-trichlorophenyl ester and 5-cyclohexyl-5-oxo-pentane-1,3-disulfonic acid bis-(2,4,6-trichlorophenyl) ester as a 8:1 mixture: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (s, 2H, major), 4.43-4.38 (m, 1H, minor), 3.99-3.94 (m, 1H, minor), 3.90-3.71 (m, 2H, major), 3.52-3.47 (m, 1H, minor), 3.29-3.10 (m, 2H, major), 3.02 (ddd, *J* = 2.9, 9.4, 18.5, 1H, minor), 2.84 (br s, 1H , minor), 2.61 (br t, *J* = 13.1, 1H, minor), 2.43 (app t, *J* = 9.6, 1H, major), 2.30 (br s, 1H , minor), 1.89 (d, *J* = 12.3, 2H, major), 1.80 (d, *J* = 9.7, 2H, major), 1.69 (d, *J* = 10.8, 1H, major), 1.46 – 1.13 (m, 6H, major); ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.61 (s, major), 208.08 (s, minor), 141.97 (s, major), 141.55 (s, minor), 133.57, (s, minor), 133.29 (s, minor), 133.21 (s, major), 130.97 (d, minor), 130.68 (d, major), 130.63 (d, minor), 129.44 (s, minor), 129.31 (s, major), 129.28 (s, major), 128.18 (s, minor), 58.61, 51.60, 51.03, 50.86 (t, major), 40.78, 34.31 (t, major), 28.48 (t, major), 28.43, 28.42, 25.76 (t, major), 25.70, 25.57 (t, major), 25.53, 25.50, 25.42, 24.78; IR (thin film) 3080, 2930, 2854, 1710, 1561 cm^{-1}; LRMS (CI) 689 (3, $[M+H]^+$, minor), 687 (4, $[M+H]^+$, minor), 685 (2, $[M+H]^+$, minor), 403 (33, $[M+H]^+$, major), 401 (100, $[M+H]^+$, major), 399 (98, $[M+H]^+$, major); HRMS (CI) calcd for $C_{23}H_{23}Cl_6O_7S_2$ $[M+H]^+$(minor) 684.9016; observed 684.9021, calcd for $C_{15}H_{18}Cl_3O_4S$ $[M+H]^+$(major) 398.9991; observed 398.9988.

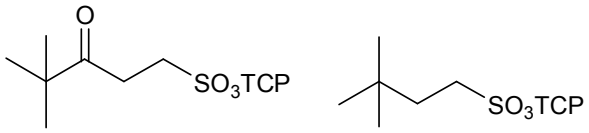
4,4-Dimethyl-3-oxo-pentane-1-sulfonic acid pentafluorophenyl ester and **3,3-dimethyl-butane-1-sulfonic acid pentafluorophenyl ester**



Using Method A. Reaction was complete after 3 h and column chromatography on silica gel (CH_2Cl_2/petrol) gave 3,3-dimethyl-butane-1-sulfonic acid pentafluorophenyl ester as an off-white solid (177 mg, 0.53 mmol, 53% yield) and 4,4-Dimethyl-3-oxo-pentane-1-sulfonic acid

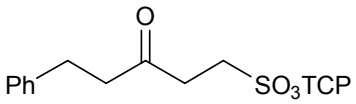
pentafluorophenyl ester (19 mg, 0.05 mmol, 5% yield). Data for 3,3-dimethyl-butane-1-sulfonic acid pentafluorophenyl ester: m.p. 40-43 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.51 – 3.33 (m, 2H), 2.02 – 1.85 (m, 2H), 1.00 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 49.7 (t), 36.5 (t), 31.0 (s), 28.8 (q); IR (neat) 2958, 1519 cm^{-1}; LRMS (CI) 361 (50, $[M+H]^+$), 177 (38), 113 (100), 95 (72); HRMS (ES) calcd for $C_{13}H_{14}F_5O_4S$ $[M+H]^+$ 361.0533; observed 361.0541. Data for 4,4-Dimethyl-3-oxo-pentane-1-sulfonic acid pentafluorophenyl ester: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.74 (m, 2H), 3.23 (m, 2H), 1.21 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.4 (s), 47.5 (t), 44.3 (s), 30.8 (t), 26.3 (q); IR (neat) 2971, 1710 cm^{-1}; LRMS (CI) 378 (65%, $[M+NH_4]^+$); HRMS (ES) calcd for $C_{13}H_{13}F_5O_4S$ $[M+NH_4]^+$. 378.0793; observed 378.0797.

4,4-Dimethyl-3-oxo-pentane-1-sulfonic acid 2,4,6-trichlorophenyl ester and **3,3-dimethyl-butane-1-sulfonic acid 2,4,6-trichlorophenyl ester**



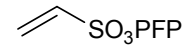
Using Method A. Reaction was complete after 48 h and column chromatography on silica gel (CH_2Cl_2/petrol) gave 3,3-dimethyl-butane-1-sulfonic acid 2,4,6-trichlorophenyl ester as a white solid, and 4,4-dimethyl-3-oxo-pentane-1-sulfonic acid 2,4,6-trichlorophenyl ester and 6,6-Dimethyl-5-oxo-heptane-1,3-disulfonic acid bis-(2,4,6-trichlorophenyl) ester as a 12:1 mixture which was further purified by column chromatography on silica gel (Et_2O/petrol) and gave 4,4-dimethyl-3-oxo-pentane-1-sulfonic acid 2,4,6-trichlorophenyl ester as a clear oil. Data for 4,4-dimethyl-3-oxo-pentane-1-sulfonic acid 2,4,6-trichlorophenyl ester: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (s, 2H), 3.83 (m, 2H), 3.28 (m, 2H), 1.21 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.91 (s), 141.98 (s), 133.22 (s), 130.67 (s), 129.32 (d), 49.28 (t), 44.37 (s), 31.07 (t), 26.47 (q); IR (thin film) 3082, 2969, 1708, 1561 cm^{-1}; LRMS (CI) 373 (6, $[M+H]^+$), 347 (97), 345 (100), 291 (39), 289 (38), 201 (10), 199 (34), 197 (53), 81 (75); HRMS (CI) calcd for $C_{13}H_{16}Cl_3O_4S$ $[M+H]^+$ 372.9835; observed 372.9839. Data for 3,3-dimethyl-butane-1-sulfonic acid 2,4,6-trichlorophenyl ester: m.p. 83-85 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (s, 2H), 3.53 (m, 2H), 1.99 (m, 2H), 0.99 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.17 (s), 133.00 (s), 130.73 (s), 129.28 (d), 51.29 (t), 36.69 (t), 29.02 (q); IR (thin film) 3082, 2958, 1561 cm^{-1}; LRMS (CI) 349 (39, $[M+H]^+$), 347 (96, $[M+H]^+$), 345 (100, $[M+H]^+$), 199 (13), 197 (16), 85 (20); HRMS (CI) calcd for $C_{12}H_{16}Cl_3O_3S$ $[M+H]^+$ 344.9886; observed 344. 9878.

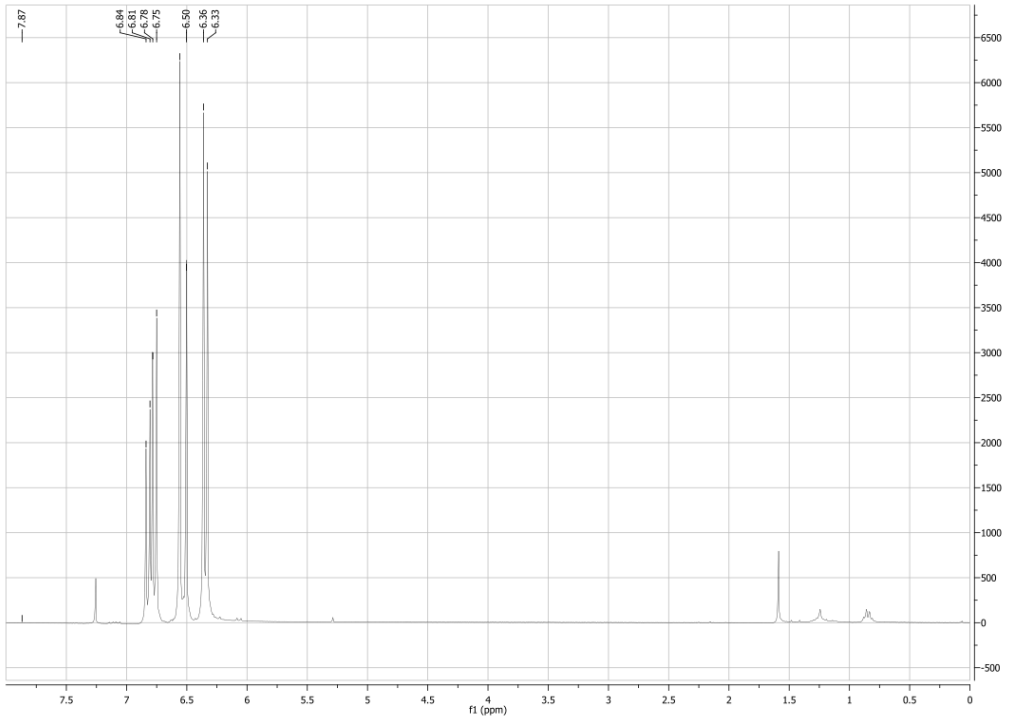
3-Oxo-5-phenyl-pentane-1-sulfonic acid 2,4,6-trichlorophenyl ester

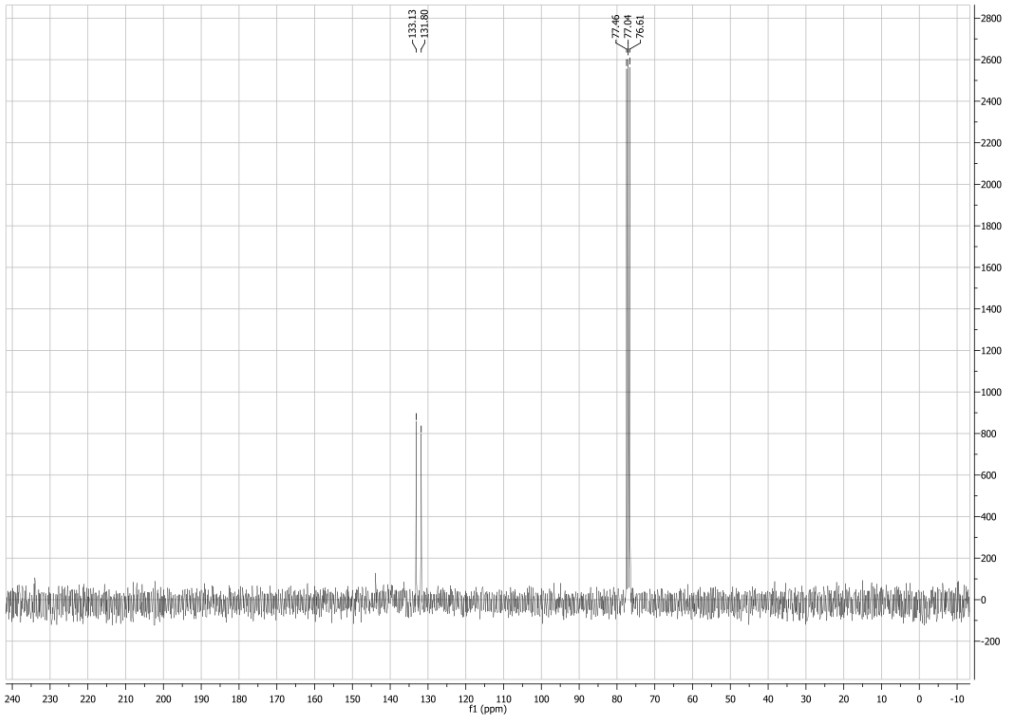


Using Method A. Reaction was complete after 48 h and column chromatography on silica gel (CH_2Cl_2/petrol) and recrystallization (CH_2Cl_2/petrol) gave the product as a white solid: m.p. 60-63 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (s, 2H), 7.29 (m, 2H), 7.20 (m, 3H), 3.84 (m, 2H), 3.16 (m, 2H), 2.96 (t, 2H, J = 7.4), 2.86 (t, 2H, J = 7.4); ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.57 (s), 141.92 (s), 140.34 (s), 133.25 (s), 130.66 (s), 129.33 (d), 128.73 (d), 128.36 (d), 126.50 (d), 48.61 (t), 44.32 (t), 36.57 (t), 29.72 (t); IR (thin film) 3082, 3028, 2944, 1719, 1604, 1562 cm^{-1}; LRMS (CI) 423 (23, $[M+H]^+$), 421 (22, $[M+H]^+$), 225 (15), 199 (22), 197 (24), 161 (100), 143 (21); HRMS (CI) calcd for $C_{17}H_{16}Cl_3O_4S$ $[M+H]^+$ 420.9835; observed 420.9828.

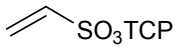
Ethenesulfonic acid pentafluorophenyl ester



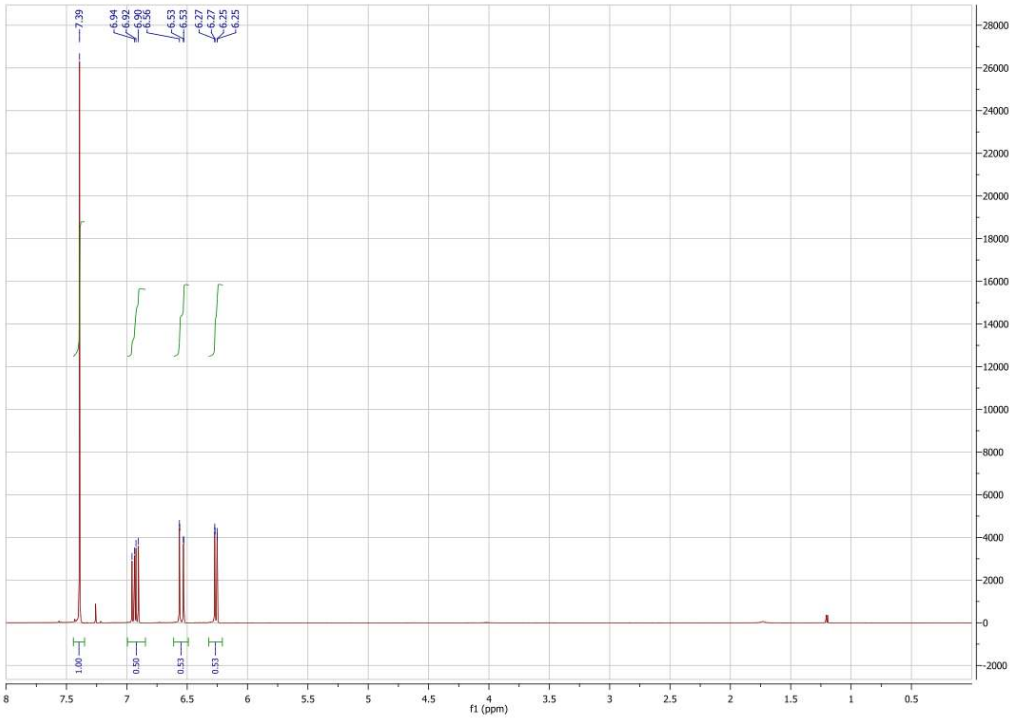


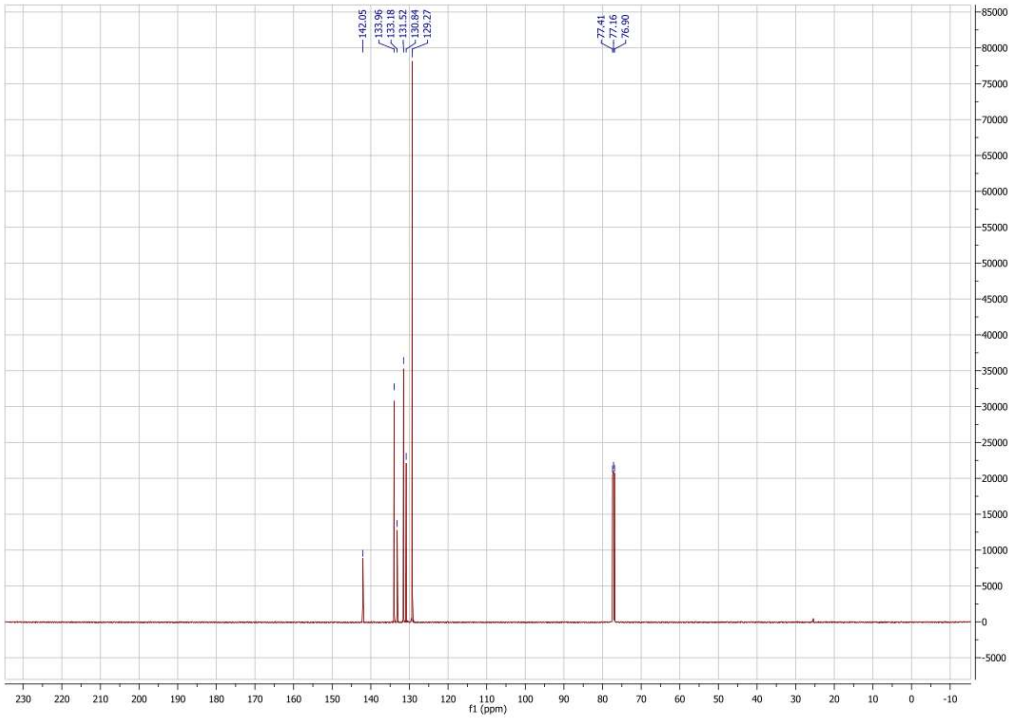


Ethenesulfonic acid 2,4,6-trichlorophenyl ester 2

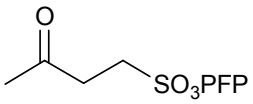


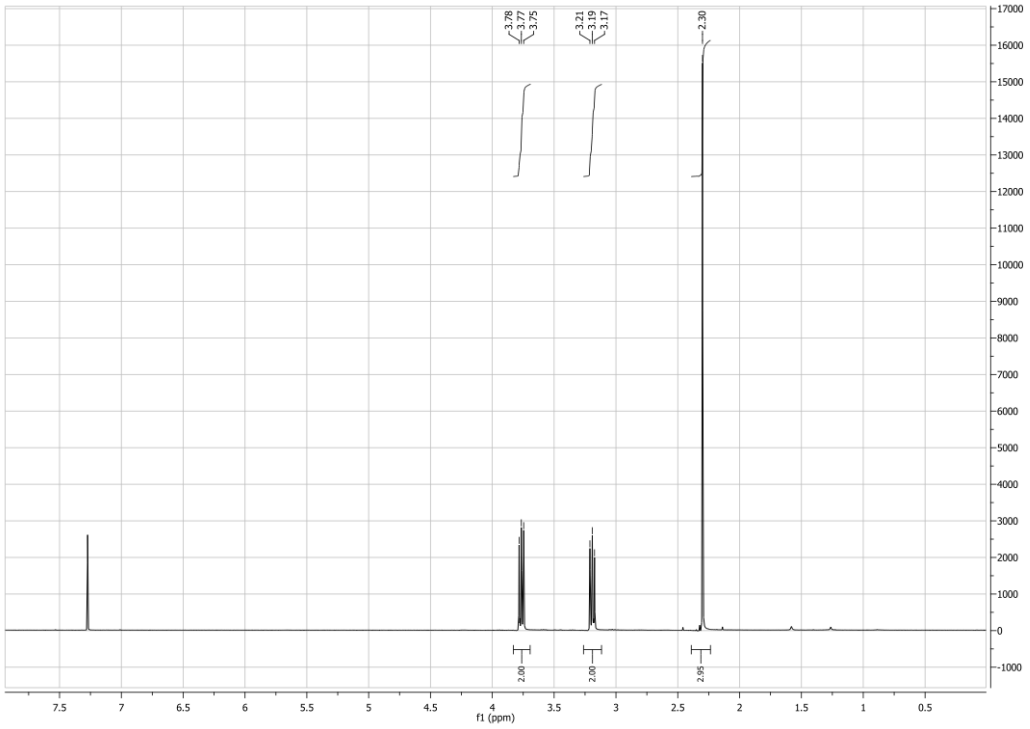
2

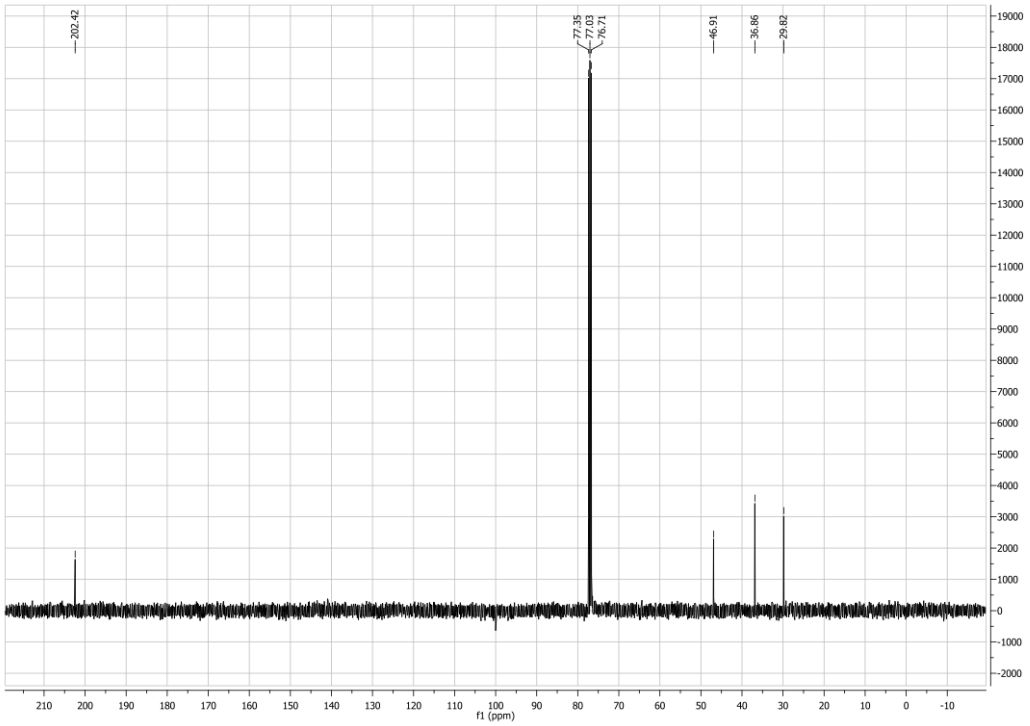




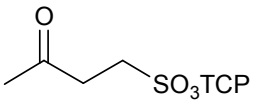
3-Oxo-butane-1-sulfonic acid pentafluorophenyl ester

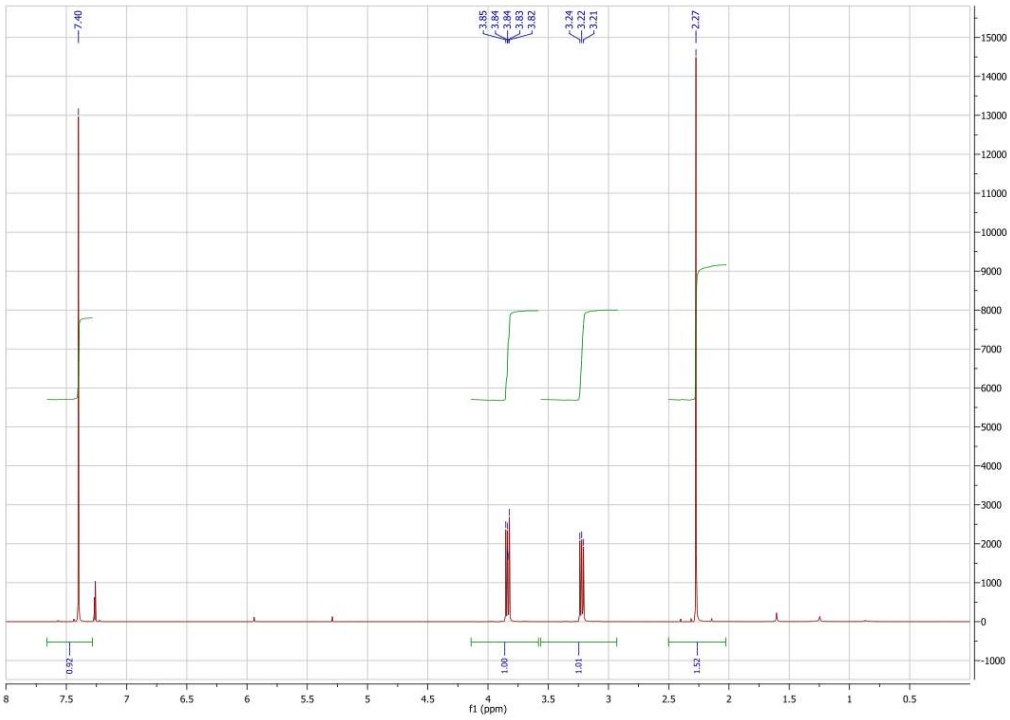


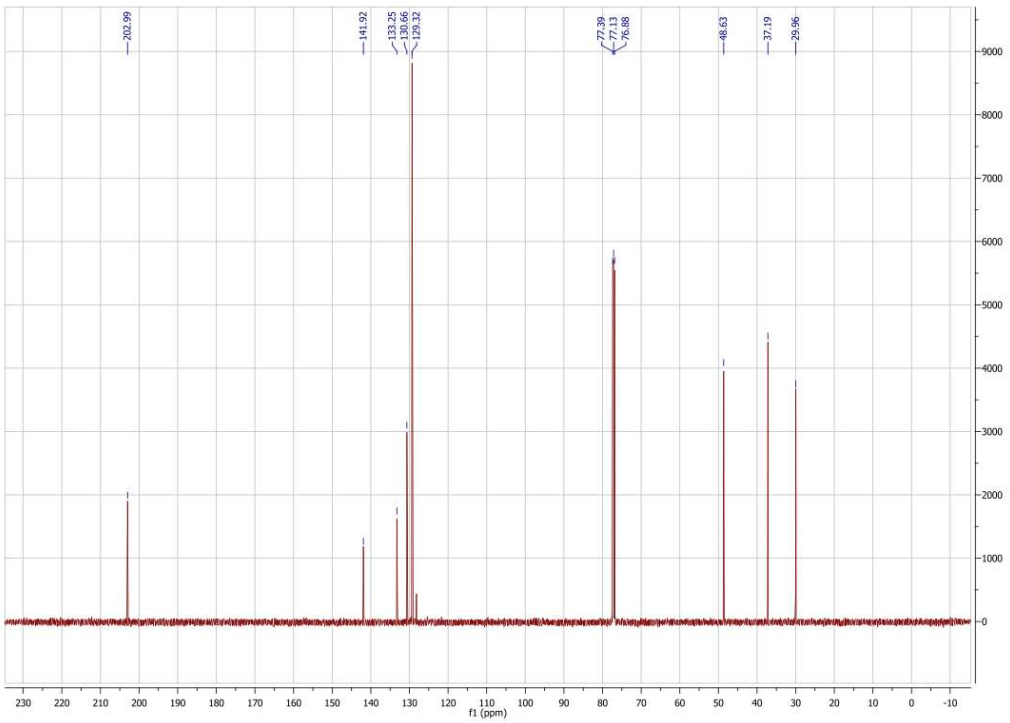




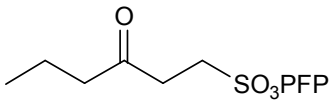
3-Oxo-butane-1-sulfonic acid 2,4,6-trichlorophenyl ester

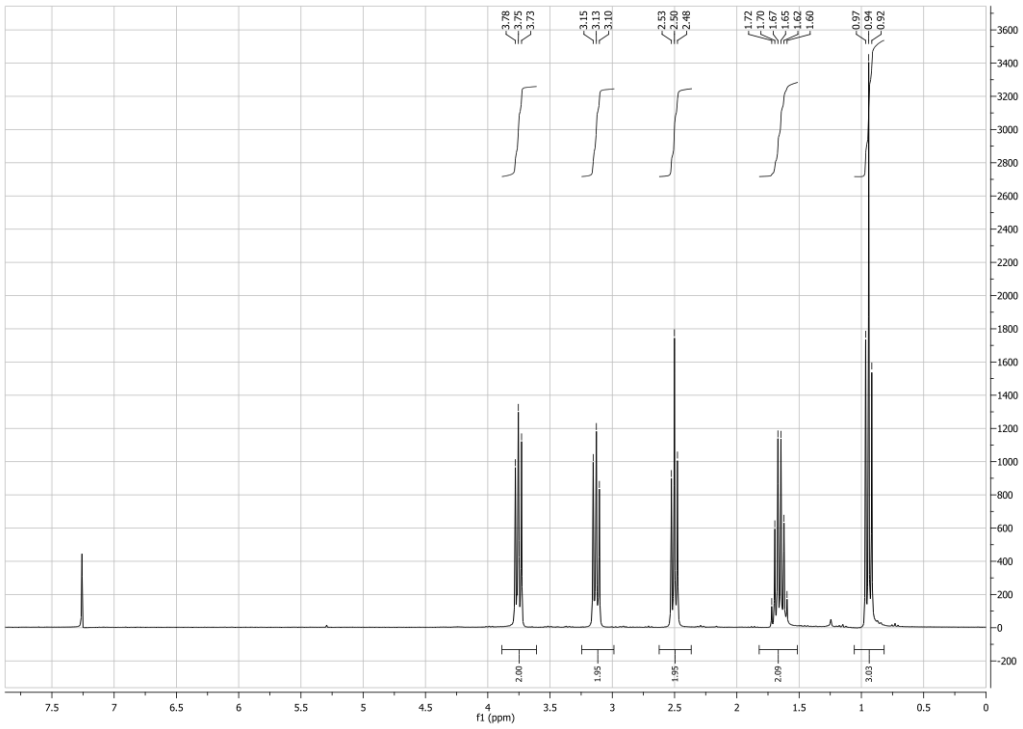


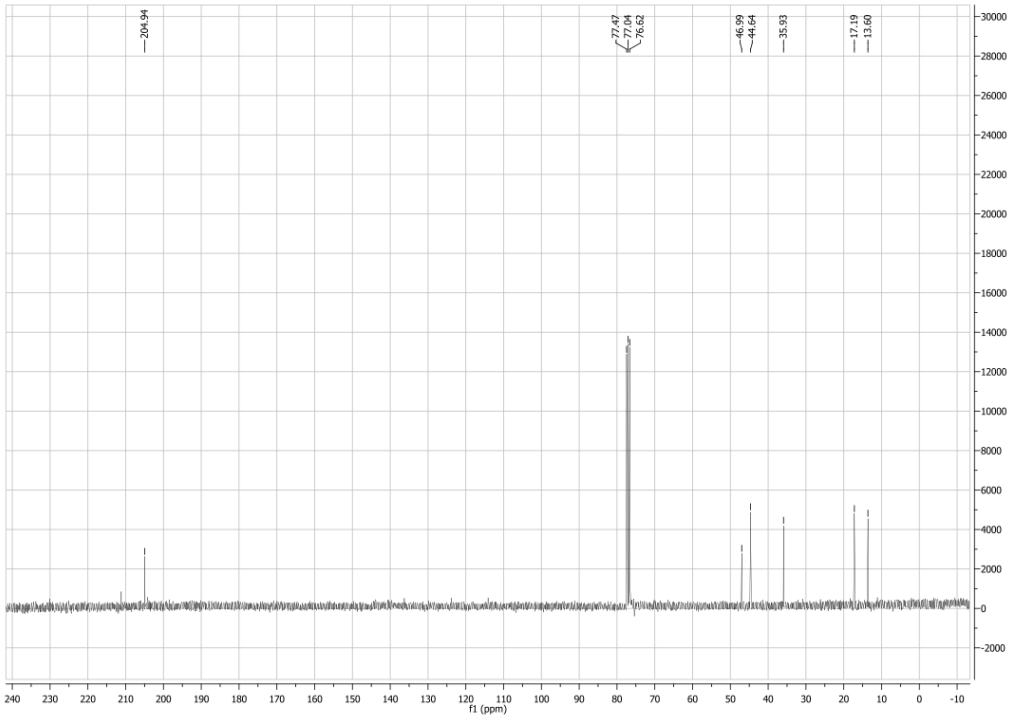




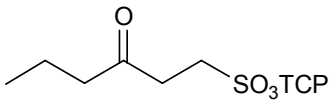
3-Oxo-hexane-1-sulfonic acid pentafluorophenyl ester

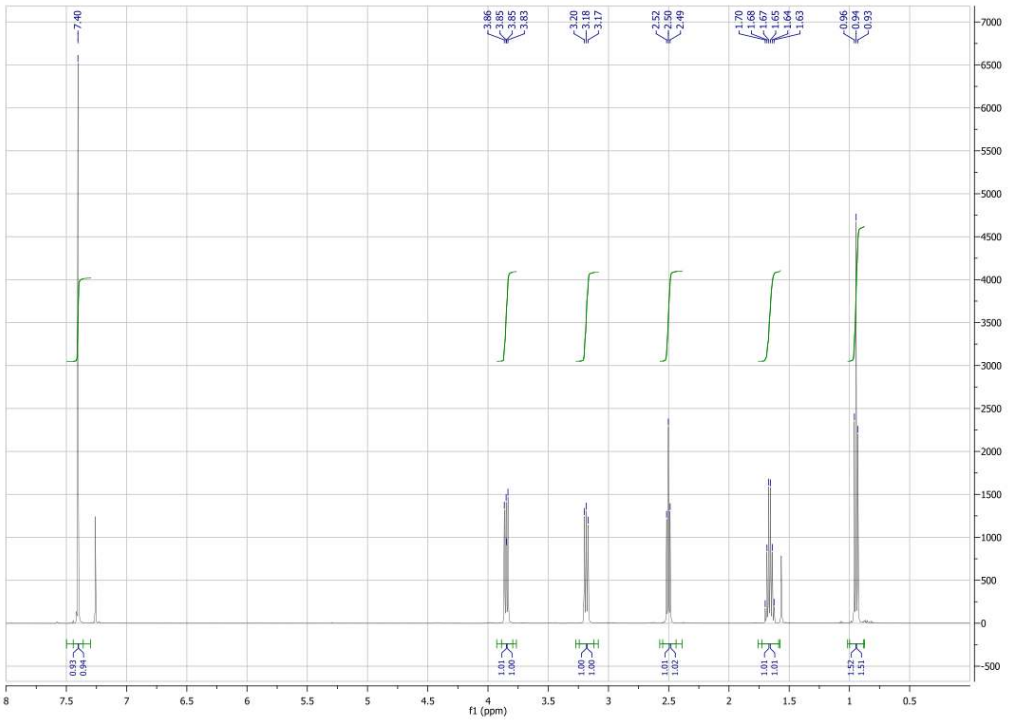


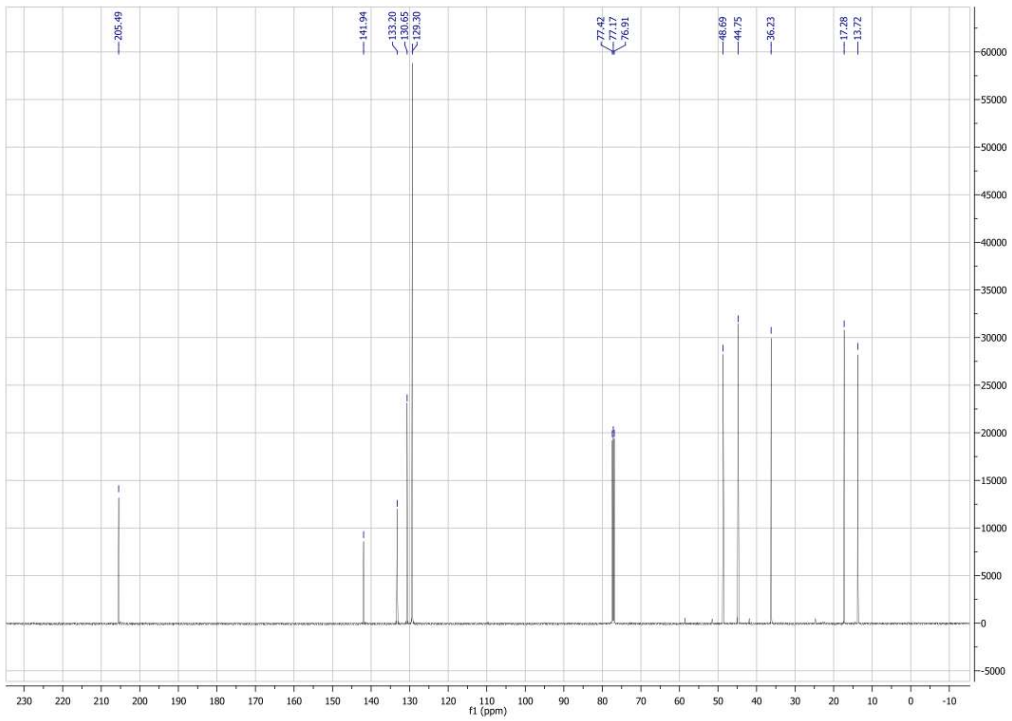




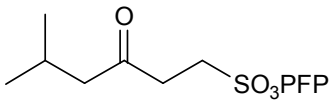
3-Oxo-hexane-1-sulfonic acid 2,4,6-trichlorophenyl ester

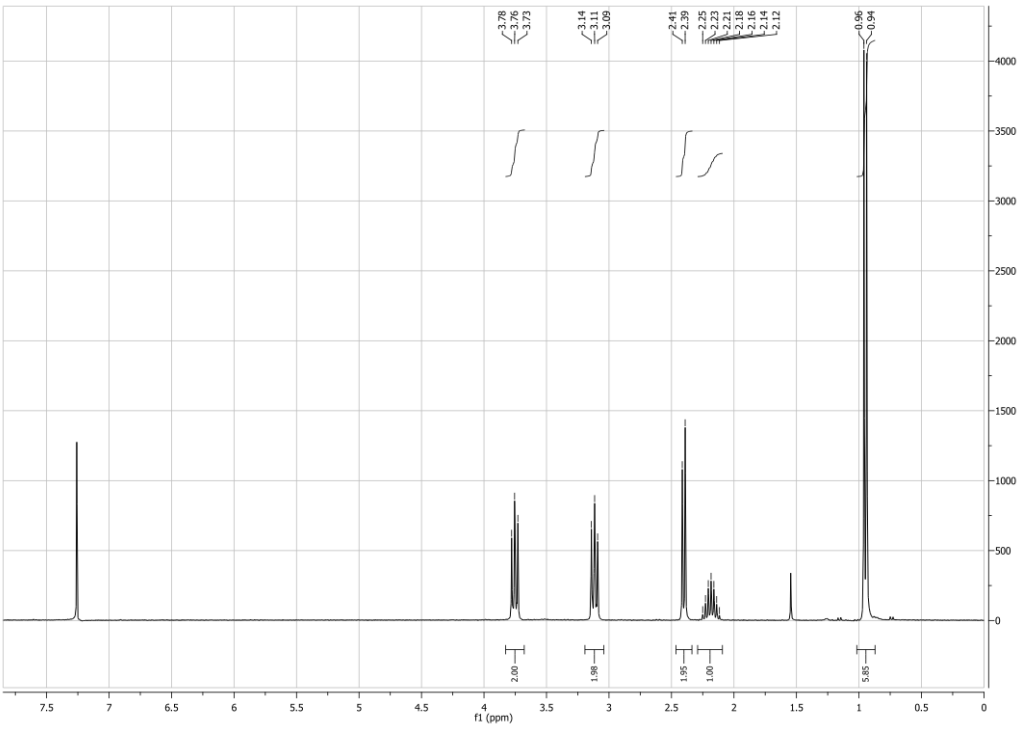


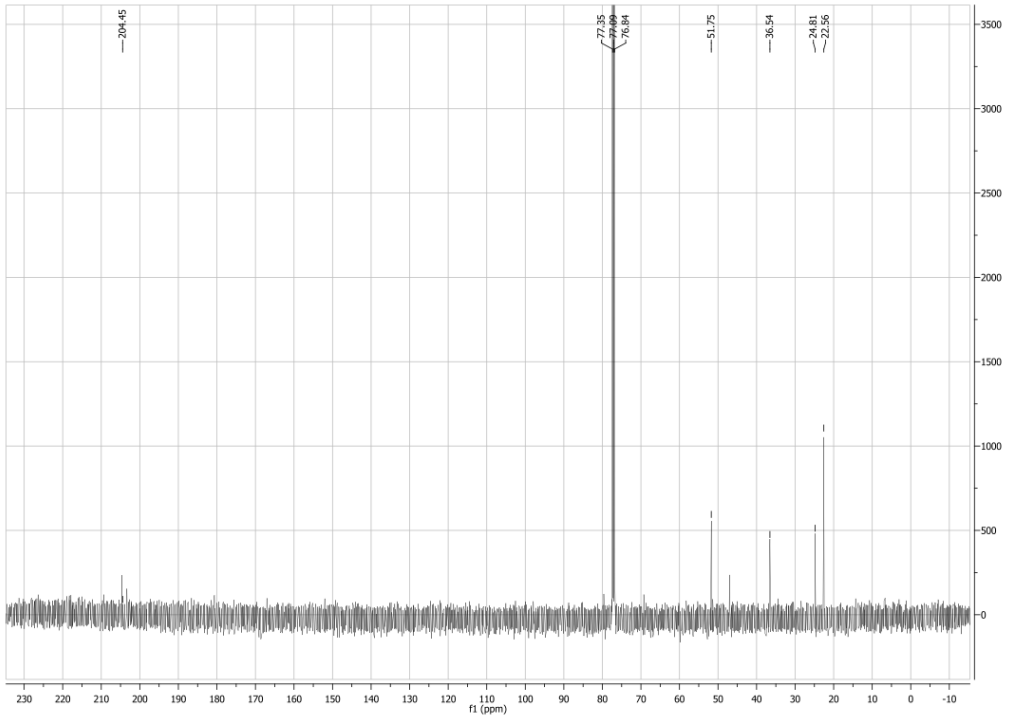




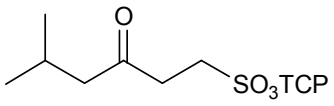
5-Methyl-3-oxo-hexane-1-sulfonic acid pentafluorophenyl ester

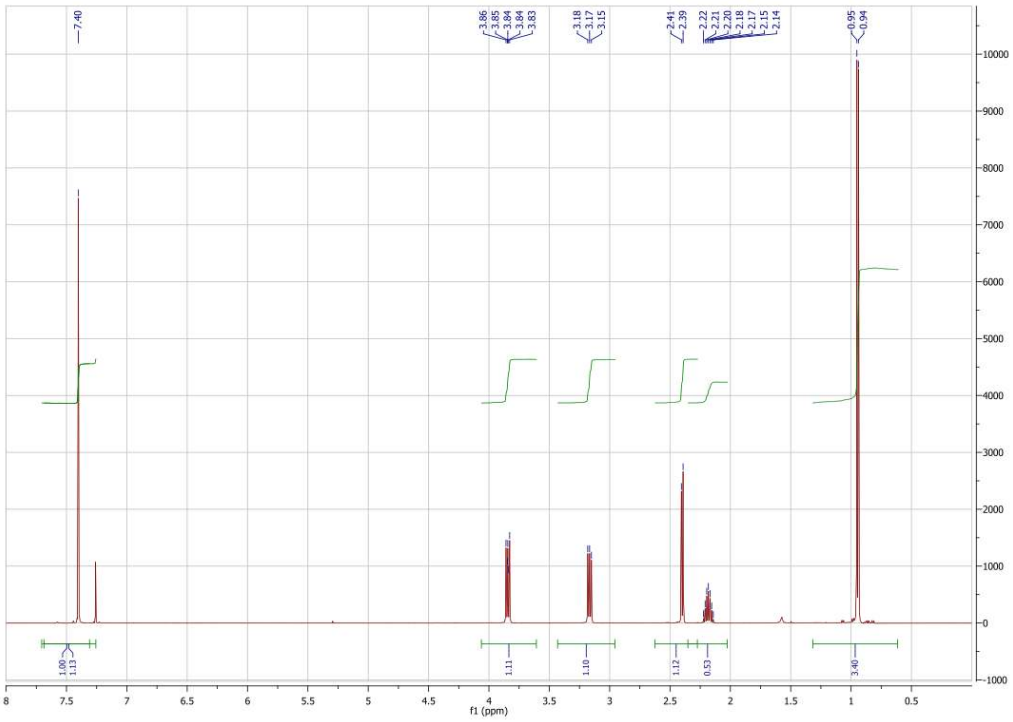


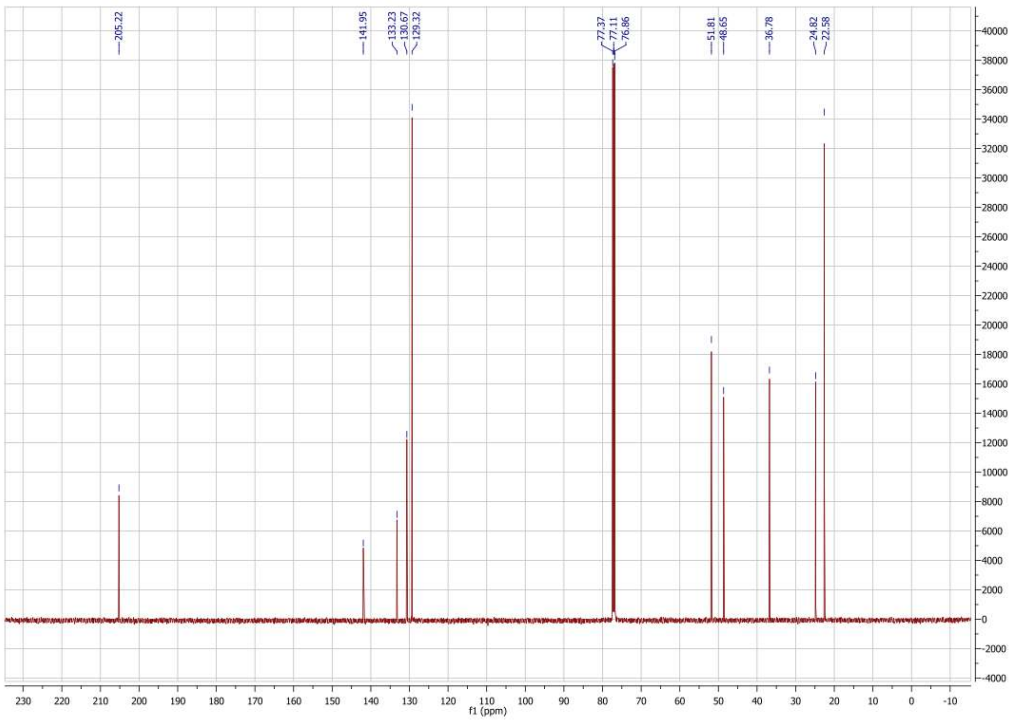




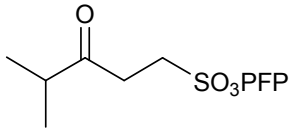
5-Methyl-3-oxo-hexane-1-sulfonic acid 2,4,6-trichlorophenyl ester 3

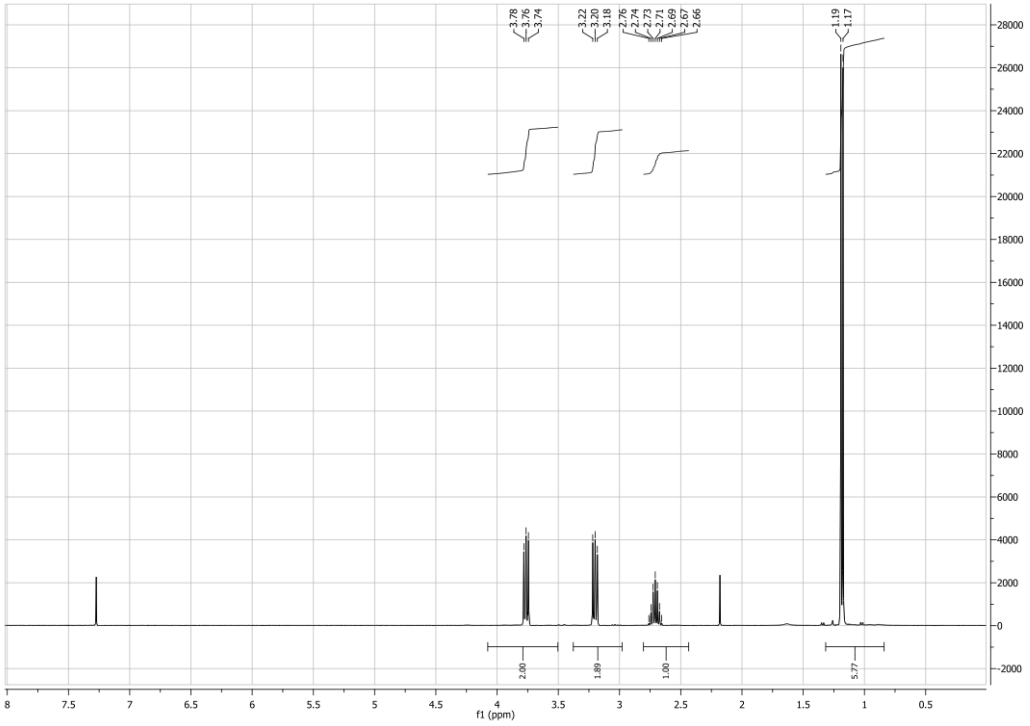


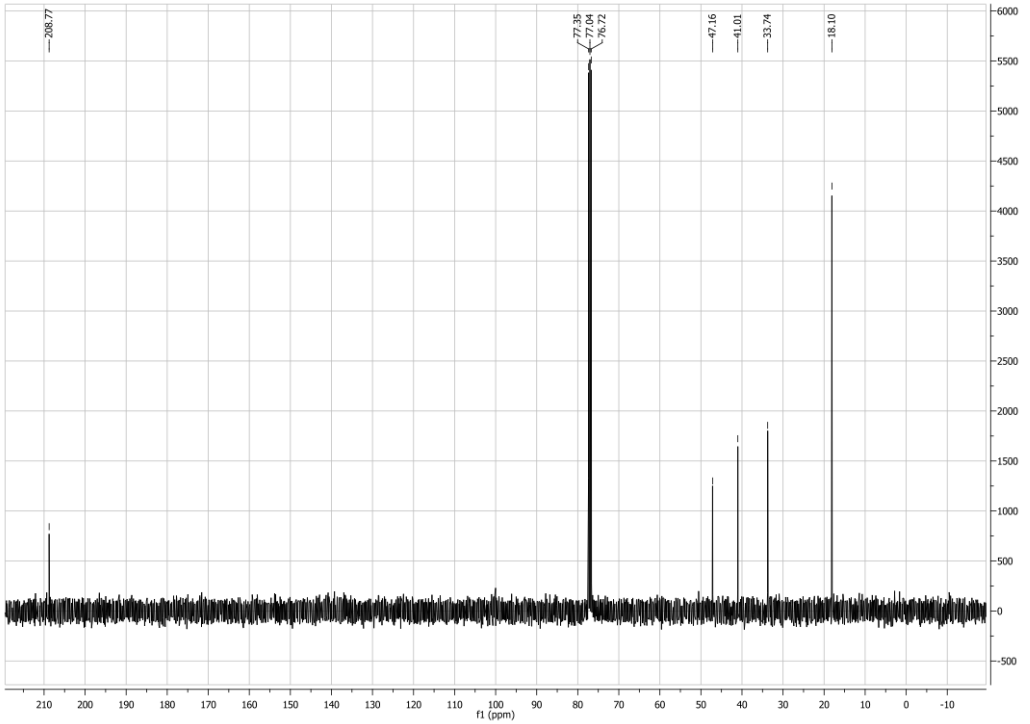




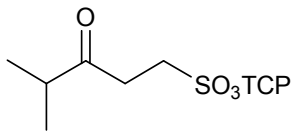
4-Methyl-3-oxo-pentane-1-sulfonic acid pentafluorophenyl ester

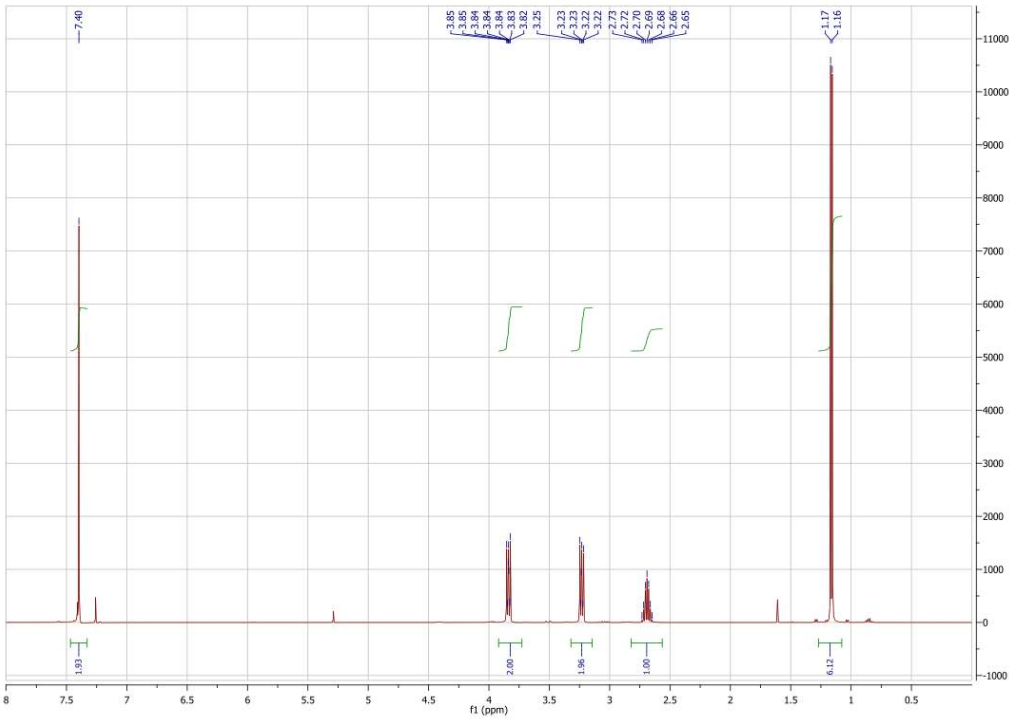


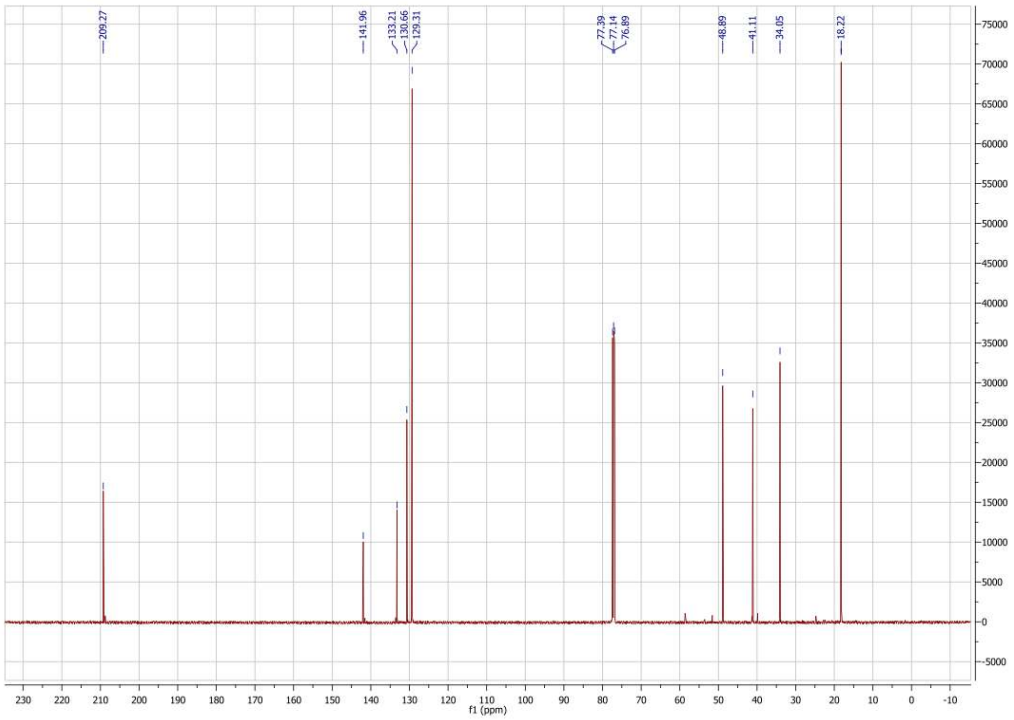




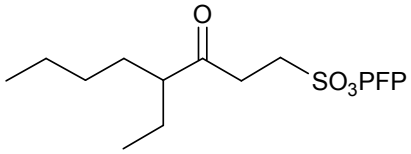
4-Methyl-3-oxo-pentane-1-sulfonic acid 2,4,6-trichlorophenyl ester

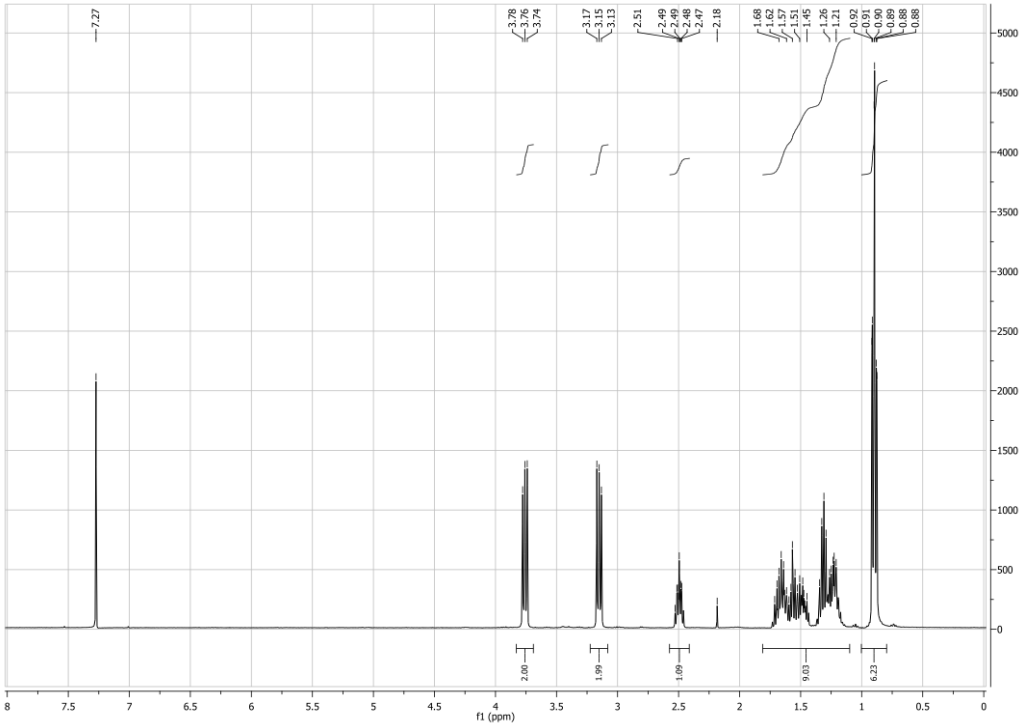


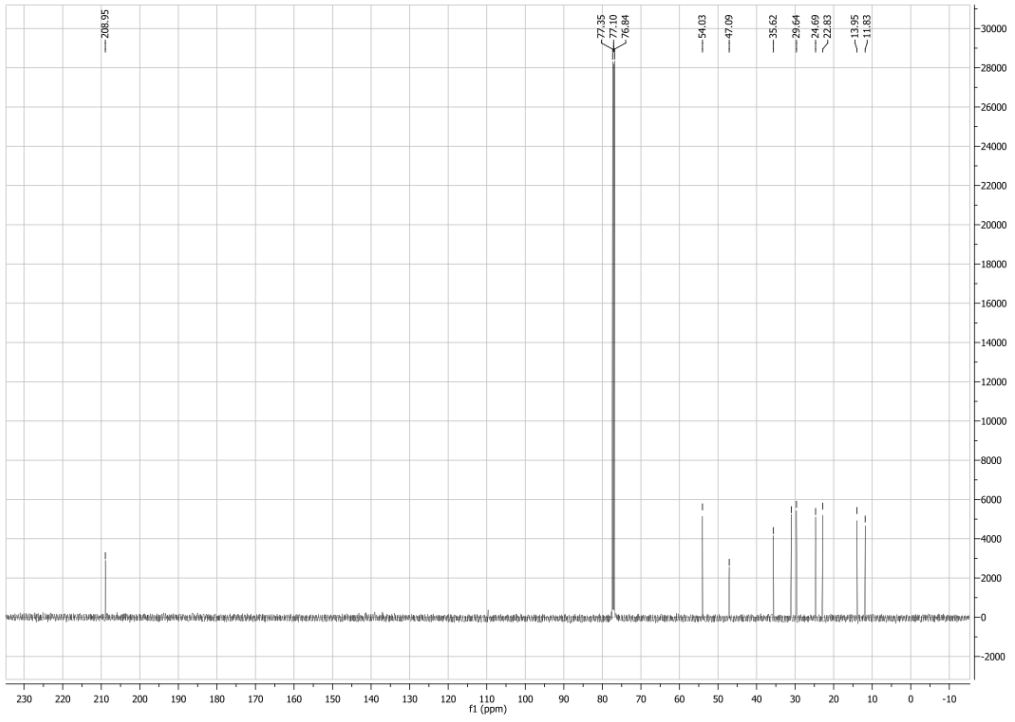




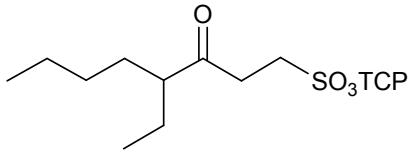
4-Ethyl-3-oxo-octane-1-sulfonic acid pentafluorophenyl ester

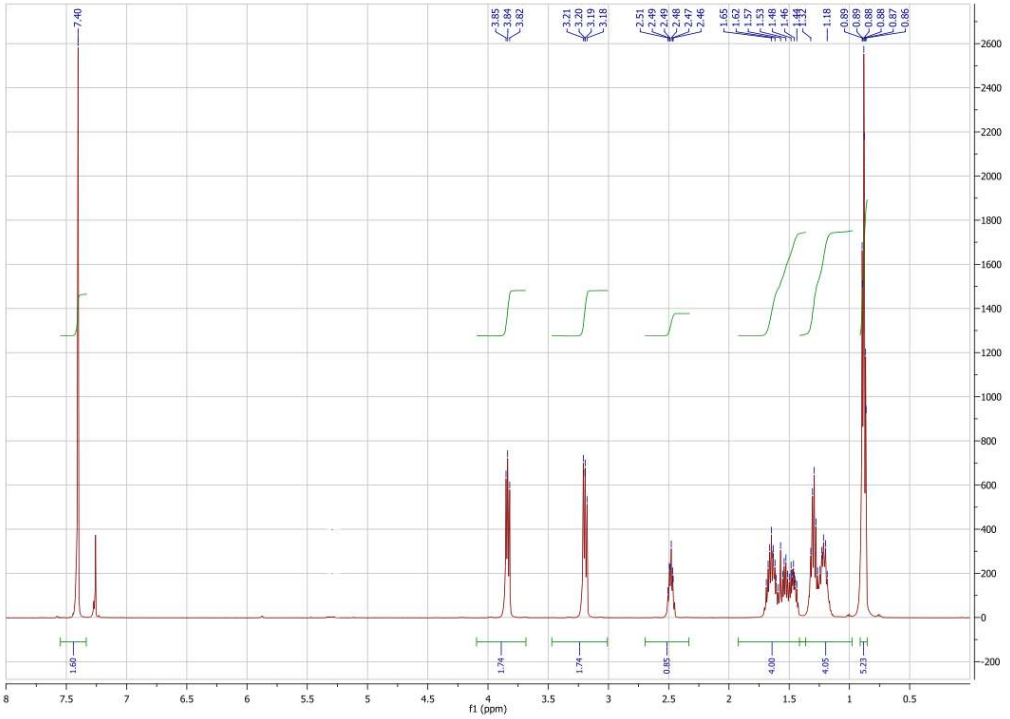


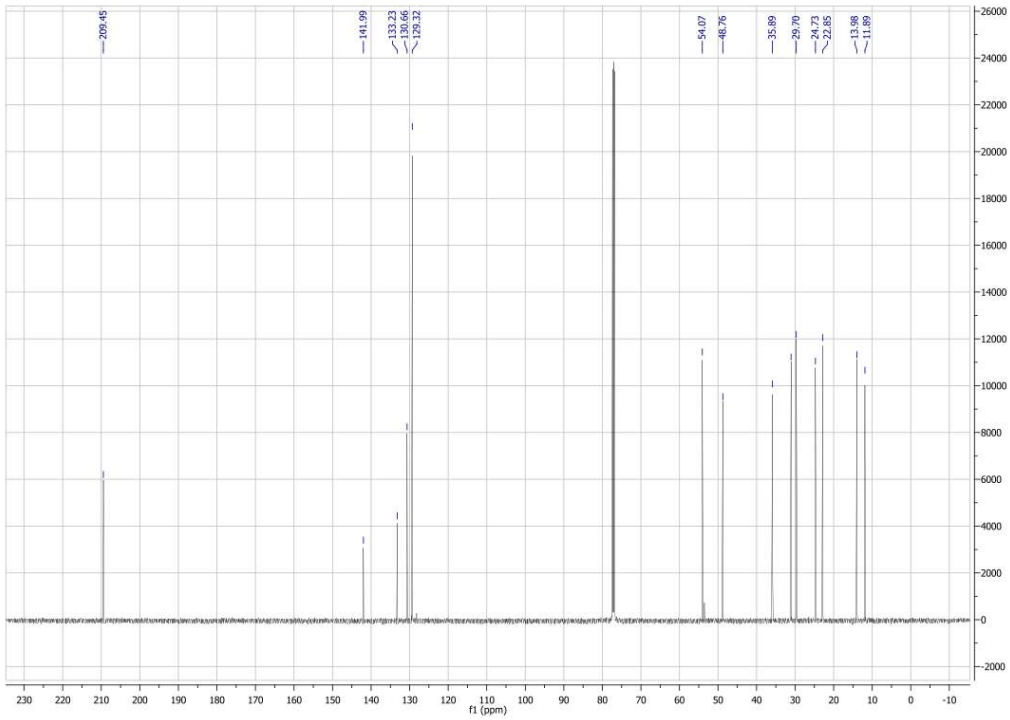




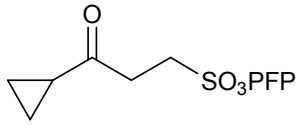
4-Ethyl-3-oxo-octane-1-sulfonic acid 2,4,6-trichlorophenyl ester

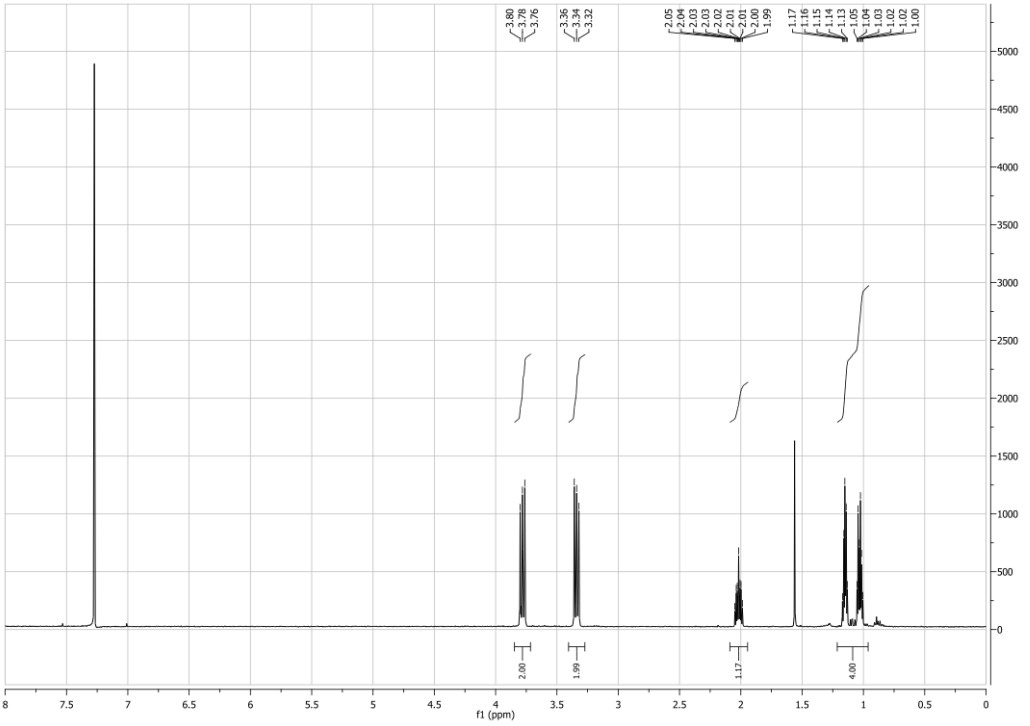


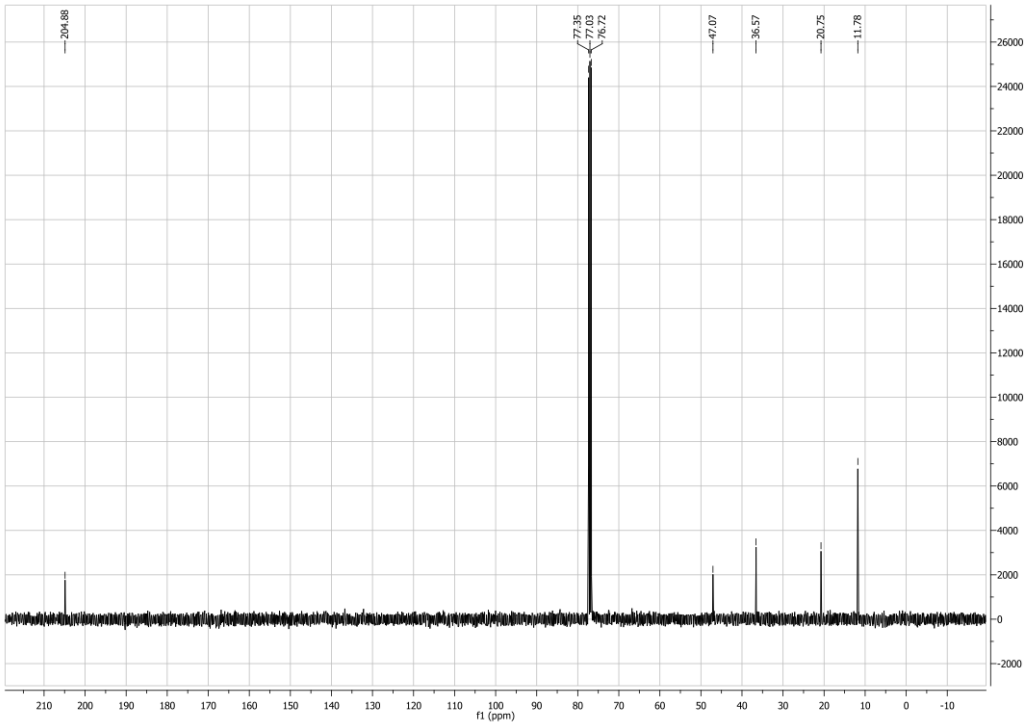




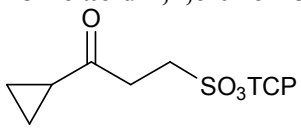
3-Cyclopropyl-3-oxo-propane-1-sulfonic acid pentafluorophenyl ester

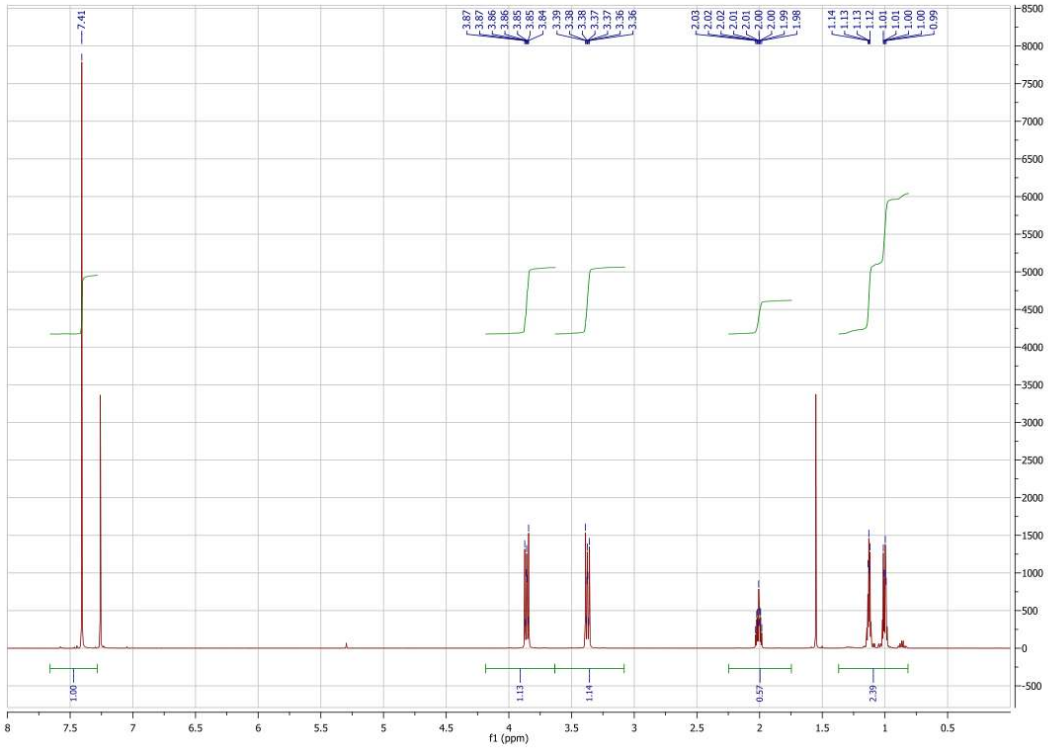


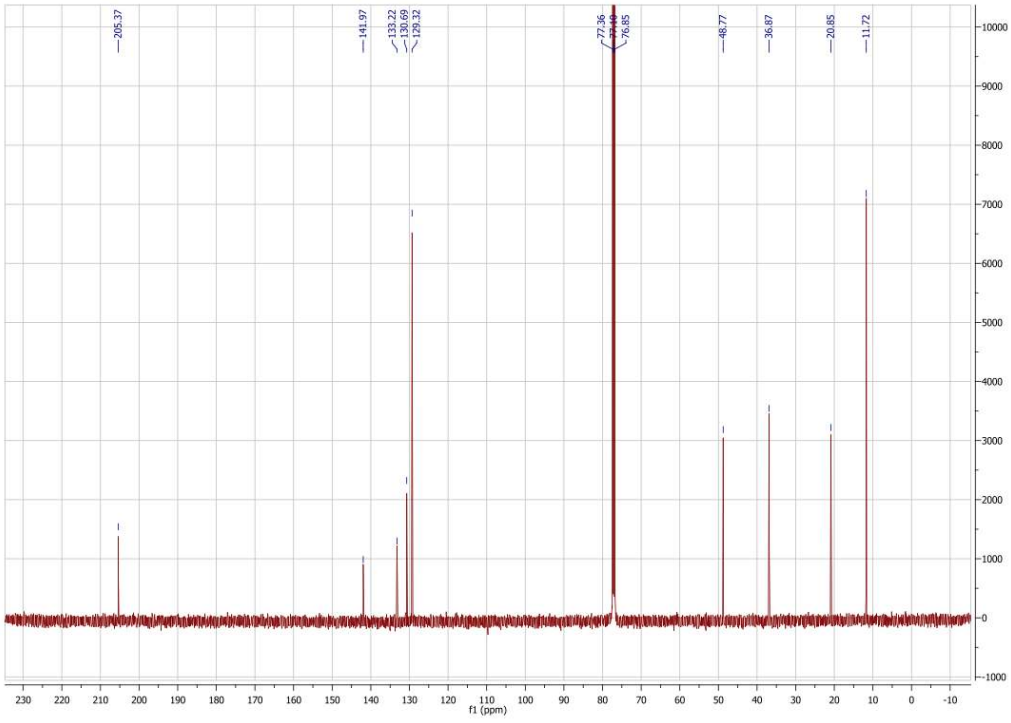




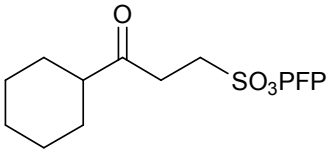
3-Cyclopropyl-3-oxo-propane-1-sulfonic acid 2,4,6-trichlorophenyl ester

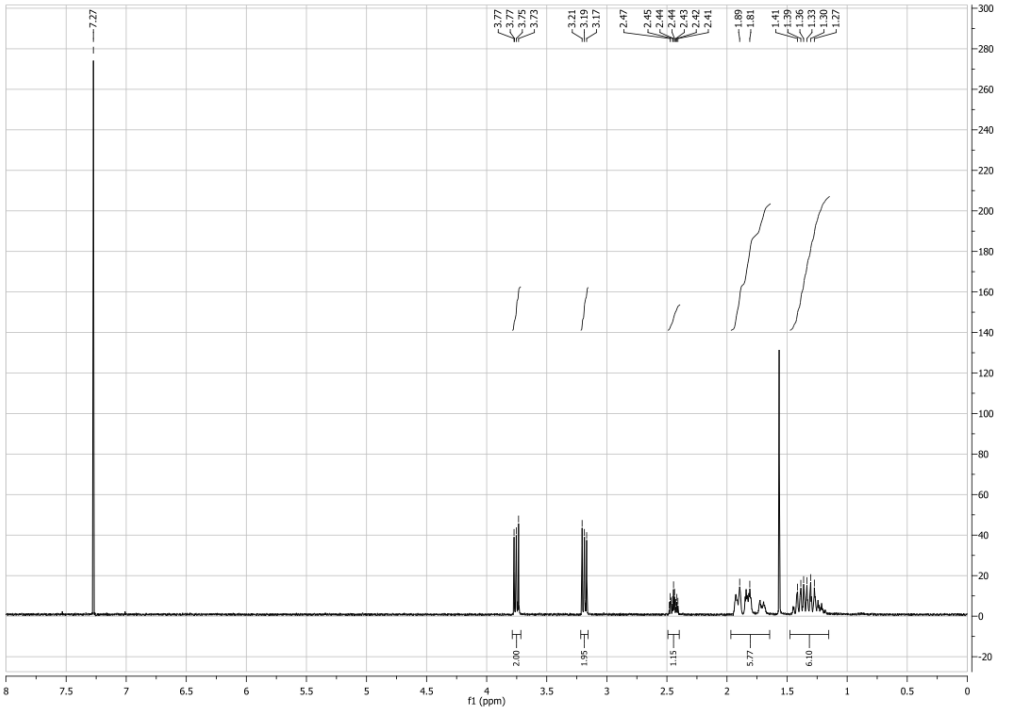


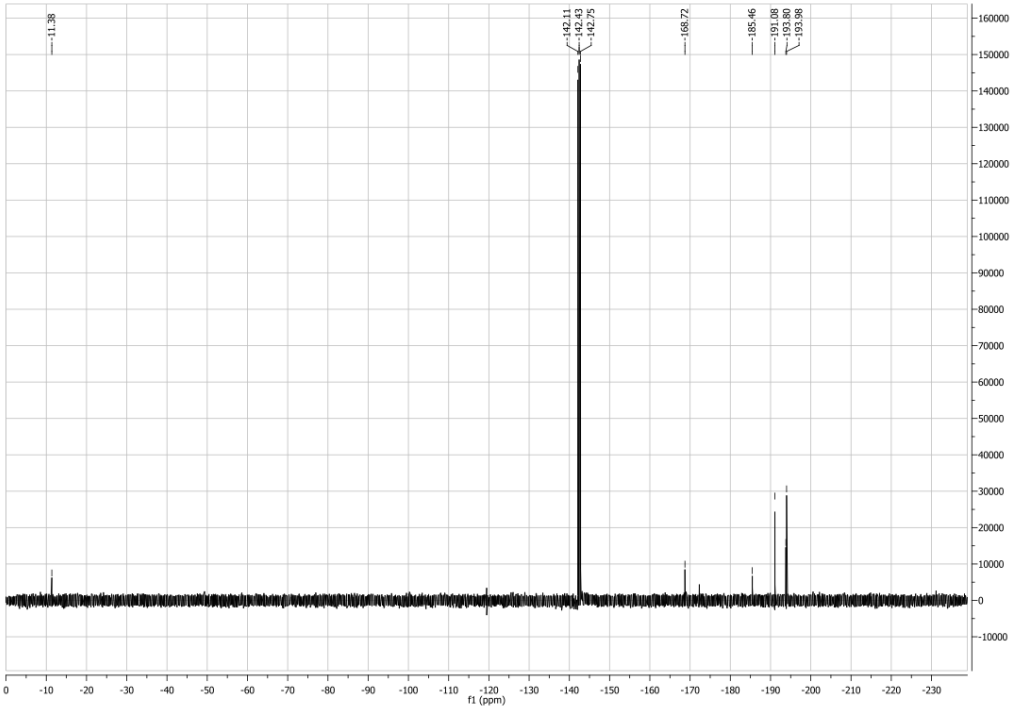




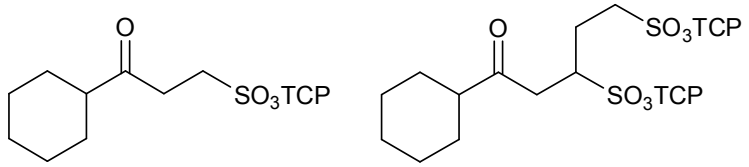
3-Cyclohexyl-3-oxo-propane-1-sulfonic acid pentafluorophenyl ester

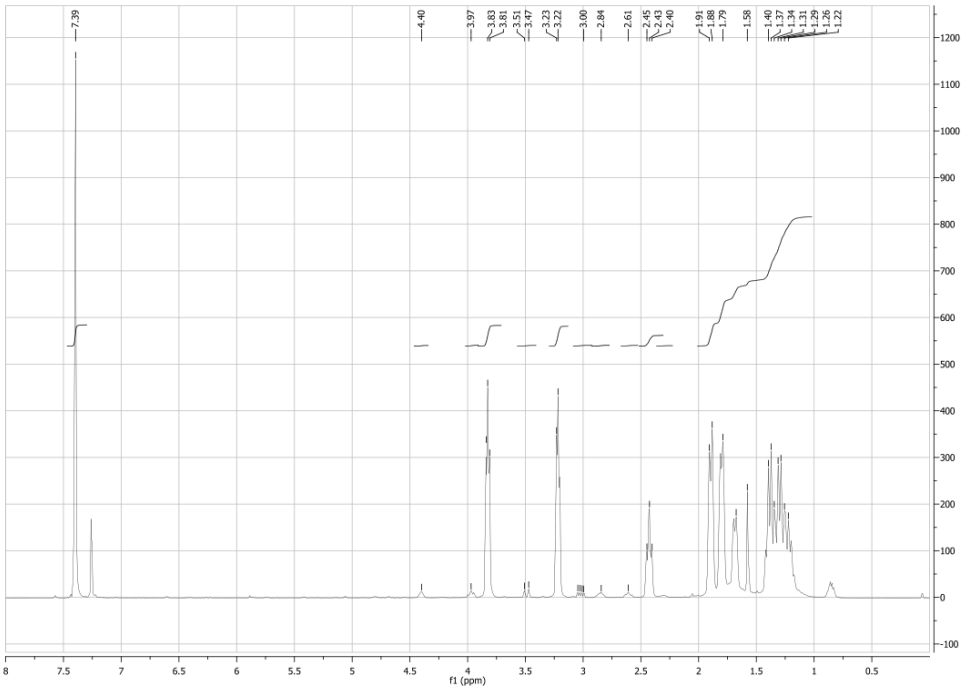


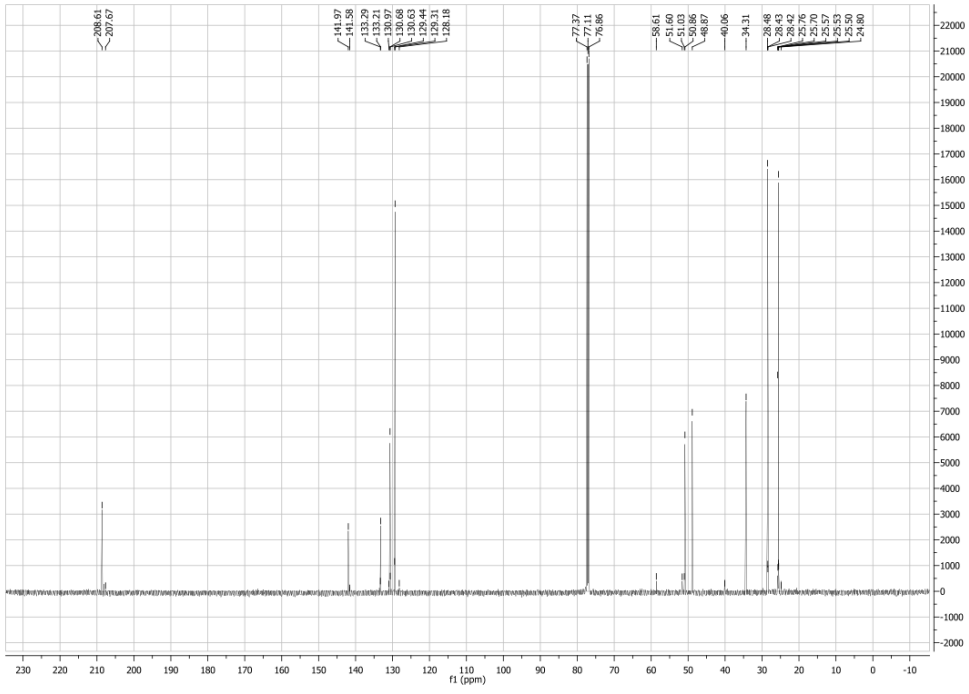




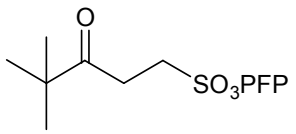
3-Cyclohexyl-3-oxo-propane-1-sulfonic acid 2,4,6-trichlorophenyl ester and **5-cyclohexyl-5-oxo-pentane-1,3-disulfonic acid bis-(2,4,6-trichlorophenyl) ester**

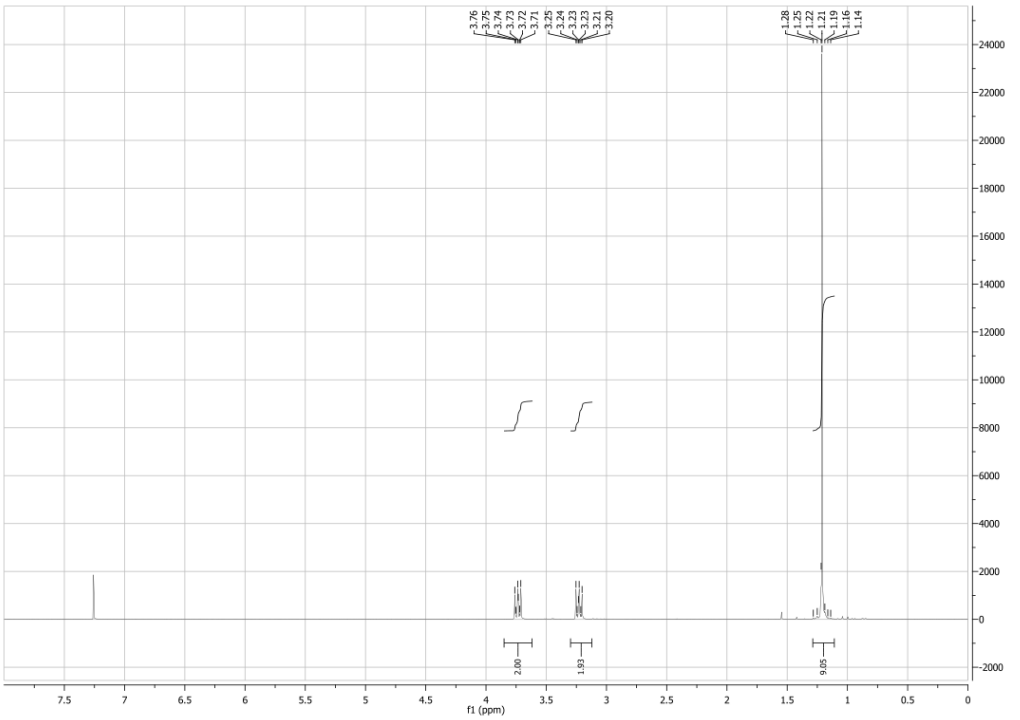


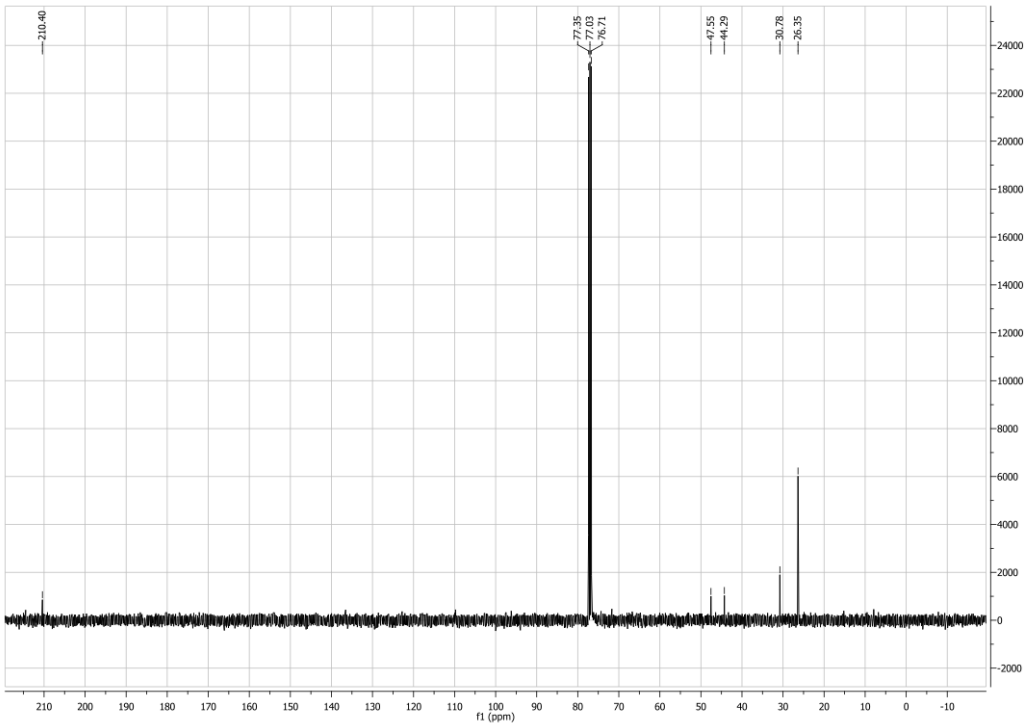




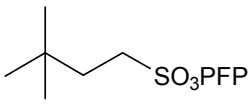
4,4-Dimethyl-3-oxo-pentane-1-sulfonic acid pentafluorophenyl ester

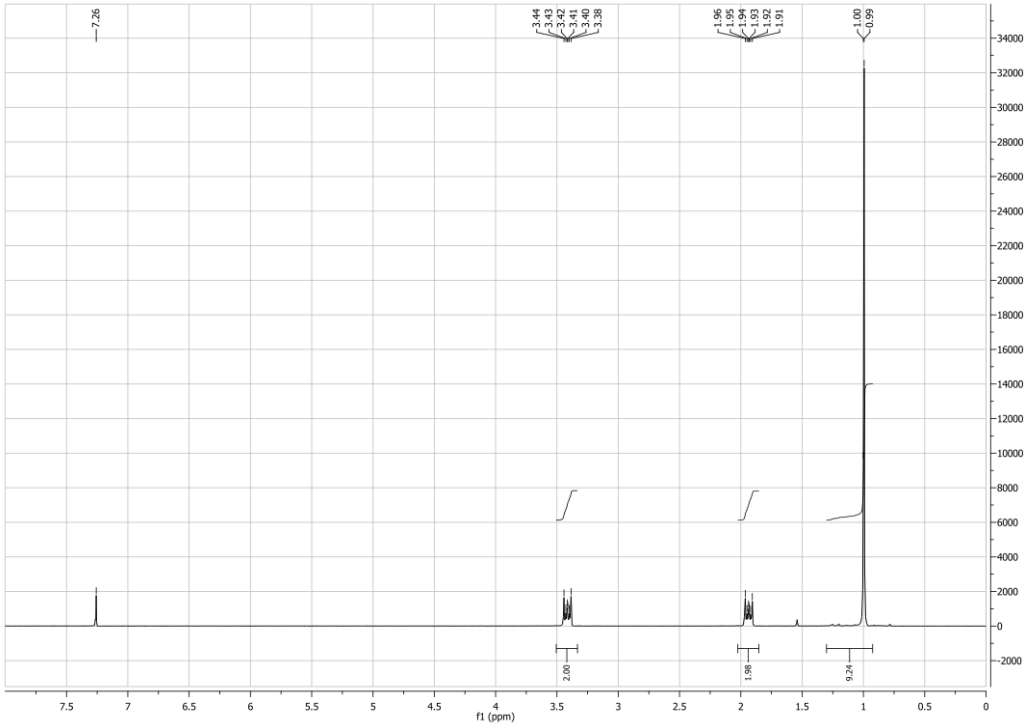


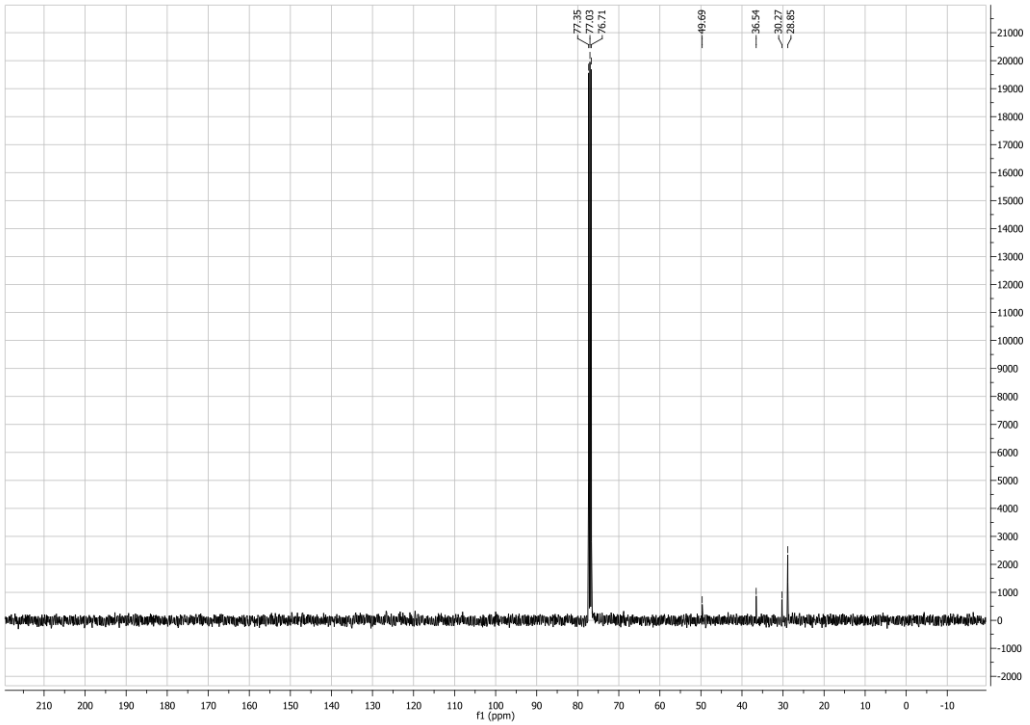




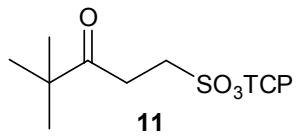
3,3-Dimethyl-butane-1-sulfonic acid pentafluorophenyl ester







4,4-Dimethyl-3-oxo-pentane-1-sulfonic acid 2,4,6-trichlorophenyl ester 11



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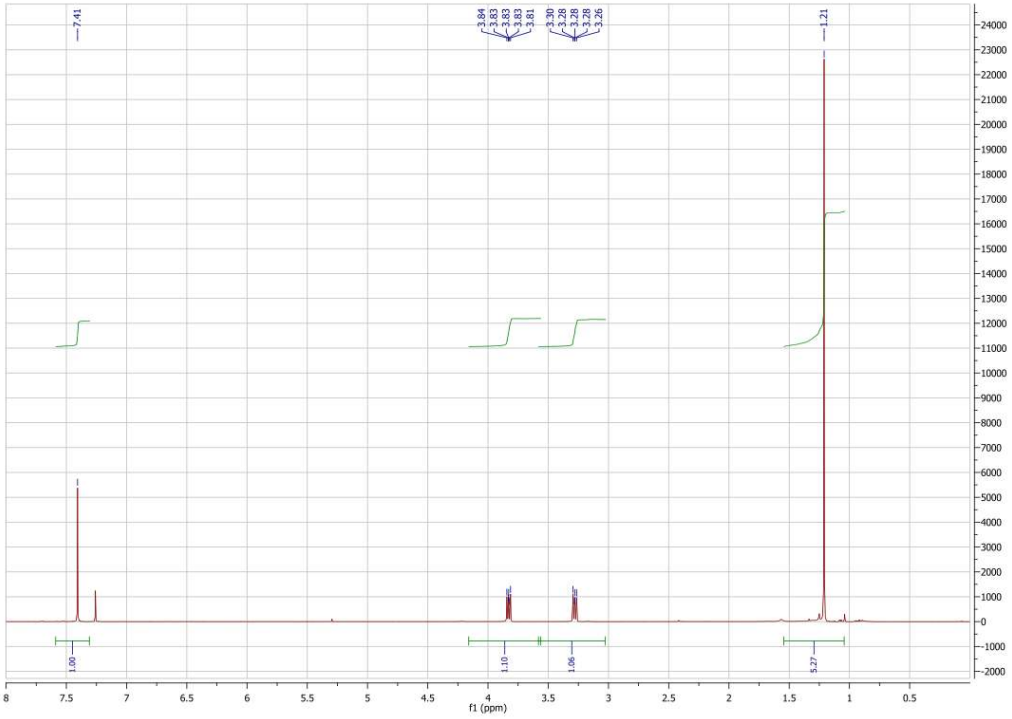
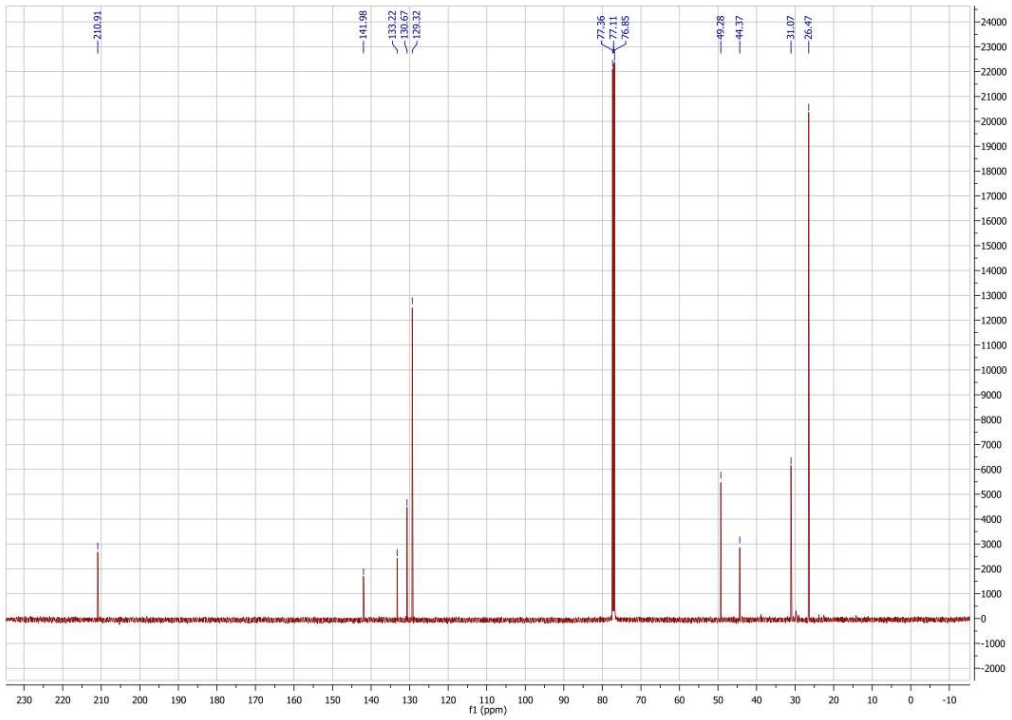
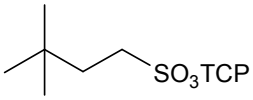




3,3-Dimethyl-butane-1-sulfonic acid 2,4,6-trichlorophenyl ester 12



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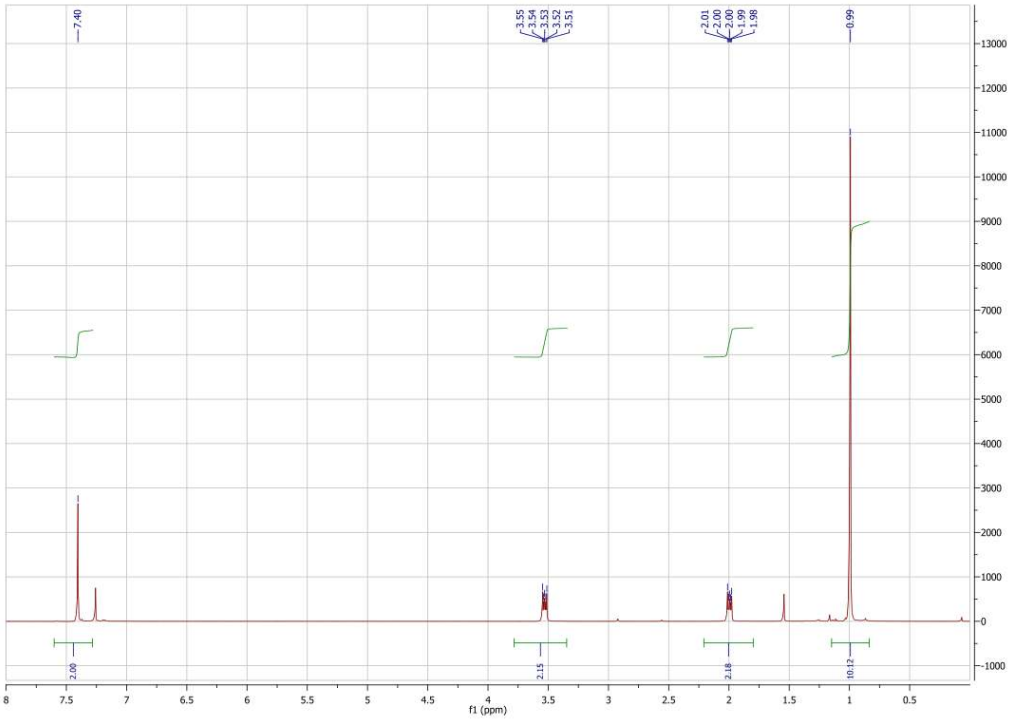

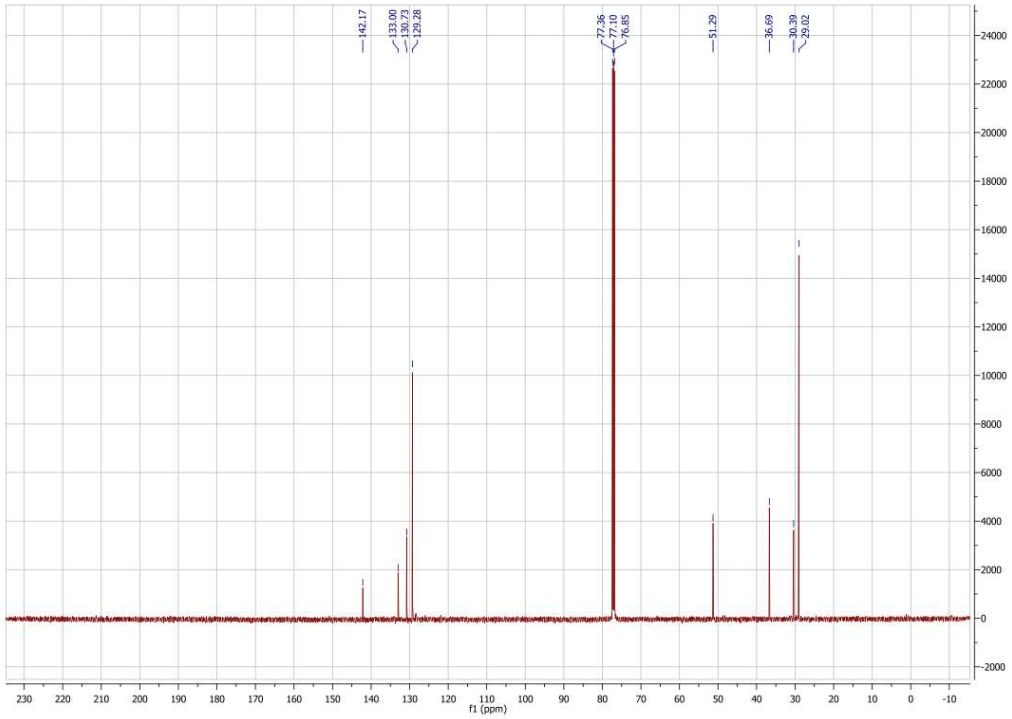

3-Oxo-5-phenyl-pentane-1-sulfonic acid 2,4,6-trichlorophenyl ester