SUPPORTING INFORMATION

Masked Formylation of Activated Aromatics via Dithianes and a Mild, Sustainable Cleavage Protocol

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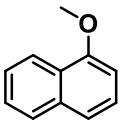
Experimental Procedures

General information

All reactions were performed under an atmosphere of nitrogen. Reactions that required heating were performed using a heating mantle or appropriate heating blocks depending on the reaction flask size. All solvents were distilled from appropriate drying agents prior to use. All reagents were used as received from commercial suppliers. Reaction progress was monitored by thin layer chromatography (TLC) performed on aluminum plates coated with silica gel F254 with 0.2 mm thickness TLC plates were visualized using ultraviolet (UV) light at 254 nm or stained with p-anisaldehyde, vanillin or KMnO4 solutions. Flash column chromatography was performed using silica gel 60 (230-400 mesh). All 1 H NMR, 13C and 19F NMR spectra were recorded using a BRUKER Avance III HD Ascend 400 spectrometer. Chemical shifts are given in parts per million (ppm, δ), referenced to the TMS (1 H and 13C) and trifluoracetic acid (19F), solvent peak of $CDCl_3$ defined at δ = 7.26 ppm (1 H NMR) and δ = 77.16 (13C NMR). Coupling constants are quoted in Hz (J). 1 H NMR splitting patterns were designated as singlet (s), doublet (d), triplet (t), quartet (q) and multiplet (m). Splitting patterns that could not be interpreted or easily visualized were designated as multiplet (m) or broad (br). Infrared (IR) spectra were collected on a SHIMADZU IR-TRACER-100, using a diamond ATR sensor or Thermo Nicolet-Nexus FTIR with Pike Miracle ATR cell spectrometers, and are reported in terms of absorption frequency (n, cm-1). High Resolution Mass spectrometric determinations were carried out on an Agilent 6520 or Agilent 5973 spectrometers, working with an electron spray ionization (ESI). GC-MS was recorded in a Thermo Scientific Trace 1300. All compounds were purified using Flash Chromatography (FC), the solvents used for purification are describes as follow: FC: (Solvent) or (Solvent 1 to Solvent 2) when a gradient of polarity was applied.

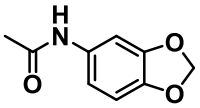
Synthesis of the Starting Materials

1-methoxynaphthalene (2k)



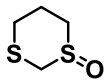
Naphthalen-1-ol (0.42 g, 2.95 mmol) and potassium carbonate (0.61 g, 4.42 mmol) were stirred in dry acetone for 1 hour. Lather dimethyl sulfate (0.37 g, 2.95 mmol) was added, and the mixture was stirred for 16 hours at room temperature. The solvent was evaporated, and the water and dichloromethane were added, and liquid-liquid extraction was performed. The product was purified by column chromatography (dichloromethane: cyclohexane 2:8) to afford the pure product as a white solid (0.341 g, 73%). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 8.34 – 8.24 (m, 1H), 7.89 – 7.77 (m, 1H), 7.53 – 7.36 (m, 4H), 6.83 (dd, J = 7.3, 1.3 Hz, 1H), 4.02 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) δ**: 155.6, 134.6, 127.6, 126.5, 126.0, 125.7, 125.3, 122.1, 120.4, 103.9, 55.6. **FT-IR (neat) υ (cm^{-1}):** 2935, 1577, 1508, 1462, 1392, 1265, 1099, 790, 767. The spectroscopic data is in accordance with the literature.[1]

N-(benzo[d][1,3]dioxol-5-yl)acetamide (2l)



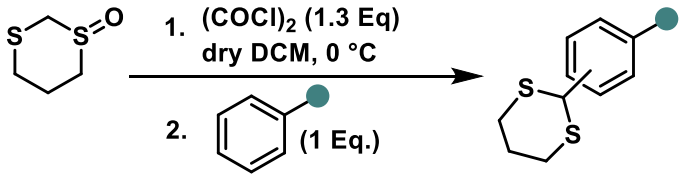
Benzo[d][1,3]dioxol-5-amine (1 g, 7.29 mmol) was dissolved in dichloromethane (10 mL) at 0°C. then, triethylamine (3,05 mL) and acetic anhydride (1,03 mL) were added and the reaction was left to stir for 3 hours at room temperature. The product was obtained as a brown solid (1. 1g, 6.1 mmol, 83%). **^{1}H NMR (400 MHz, $CDCl_3$) δ**: 7.20 (d, *J* = 1.7 Hz, 1H), 6.80 – 6.65 (m, 2H), 5.94 (s, 2H), 2.14 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) δ:** 168.3, 147.8, 144.4, 132.1, 113.3, 108.0, 103.1, 101.3, 24.4. **FT-IR (neat) υ (cm^{-1}):** 3305, 2908, 1658, 1543, 1477, 1234, 1180, 1037, 813. The spectroscopic data is in accordance with the literature.[3]

1,3-dithiane 1-oxide (1)



1,3-dithiane (3 g, 24.95 mmol) was dissolved in 70 mL of a solution methanol-water (85:15), then sodium periodate (5.87 g, 27.45 mmol) was added, and the mixture was left to stir for four hours. The solvent was evaporated, and ethyl acetate was added. Filtration was carried out and from the filtrate the pure product was obtained as a white solid (3 g, 88%, **m.p** 94°C).**^{1}H NMR (400 MHz, $CDCl_3$) δ:** 4.00 (dd, *J* = 12.6, 2.8 Hz, 1H), 3.64 (d, *J* = 12.7 Hz, 1H), 3.42 – 3.19 (m, 1H), 2.75 – 2.40 (m, 4H), 2.32 – 2.10 (m, 1H). **^{13}C NMR (100 MHz $CDCl_3$) δ:** 53.0, 50.5, 28.4, 27.3. **FT-IR (neat) υ (cm^{-1}):** 2954, 2900, 1431, 1168, 1006, 921. **HRMS (ESI):** Calcd. For $C_4H_8OS_2$ $(M+H)^+$: 137.0089; Found: 137.0092.

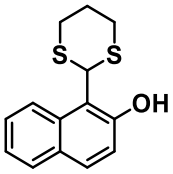
General procedure for masked formylation reaction.



In an oven-dried 2-neck round bottom flask, 1.35 eq. of 1,3-dithiane 1-oxide was dissolved in dry dichloromethane (0.15 M) and stirred over an ice bath for 10 minutes. In a separate oven-dried round bottom, 1.00 eq of the aromatic compound was dissolved in dry dichloromethane (0.33 M). After cooling, under a stream of nitrogen, 1.63 eq. of $(COCl)_2$ was added to the 2-neck flask using a micropipette and was left to stir over an ice bath for 30 min. Afterwards, the aromatic compound solution is injected into the 2-neck flask dropwise and then the progress of the reaction was tracked by thin layer chromatography until consumption of aromatic starting material. After completion, the reaction is quenched with a saturated $NaHCO_3$ solution. The phases are separated and then the aqueous phase is extracted

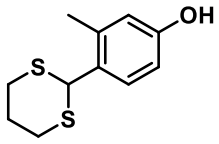
with ethyl acetate three times. The combined organic phases were subsequently washed with water and a saturated NaCl solution once.

1-(1,3-dithian-2-yl)naphthalen-2-ol (3a)



Following the general procedure, from naphthalen-2-ol (0.145 g, 1mmol), 1,3-dithiane 1-oxide (0.185 g, 1.35 mmol) and oxalyl chloride (0.206 g, 1.62 mmol), the compound was obtained as white solid (0.14 g, 85%). Column chromatography was carried out for purification (cyclohexane-dichloromethane 7:3). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 8.03 (bs, 1H), 7.76 (m, 2H), 7.45 (m, 3H), 7.15 (d, J = 8.9 Hz, 1H), 6.24 (s, 1H), 3.20 – 3.09 (m, 2H), 3.00 – 2.92 (m, 2H), 2.29 – 2.18 (m, 1H), 1.99 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$) δ:** 155.0, 131.2, 131.0, 129.1, 128.9, 127.2, 123.4, 121.7, 119.5, 113.9, 42.9, 32.0, 24.89. **FT-IR (neat) υ (cm^{-1}):** 3317, 3055, 2931, 2889, 1624, 1604, 1581, 1357, 1272, 1249, 1195, 956. **HRMS (ESI):** Calcd. for $(M+H)^+$: $C_{14}H_{15}OS_2$ 263.0558, found 263.0566.

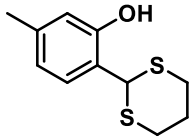
4-(1,3-dithian-2-yl)-3-methylphenol (3b)



General procedure was applied to *m*-cresol (1 mmol, 0.1081 g). The crude product was purified using flash column chromatography using 50% dichloromethane in cyclohexane as eluent to obtain the product as a white solid corresponding to a mixture of the two isomers (ortho and para) (0.0479 g, 21%, **m.p.** 159-161 °C).**^{1}H NMR (400 MHz, $CDCl_3$)** 7.45 (d, J = 8.3 Hz 1H), 6.65 (dd, J = 8.4, 2.8 Hz, 1H), 6.60 (d, J = 2.7 Hz, 1H), 5.25 (s, 1H), 4.94 (s, 1H), 3.07 (ddd, J = 14.9, 12.6, 2.5 Hz, 2H), 2.95 – 2.80 (m, 2H), 2.37 (s, 3H), 2.16 (ddt, J =

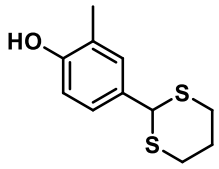
11.2, 4.3, 2.2 Hz, 1H), 1.99 – 1.83 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 155.1, 137.0, 129.6, 129.3, 117.2, 113.4, 47.63, 32.5 (2C), 25.2, 19.2. **FT-IR (neat) υ (cm^{-1}):** 3291, 2954, 2893, 1600, 1519, 1450, 1296, 1246, 1180. **HRMS (ESI)**: Calcd. for $C_{11}H_{15}OS_2$ $(M+H)^+$: 227.0559; Found: 227.0552.

2-(1,3-dithian-2-yl)-5-methylphenol (3b')



General procedure was applied to 3-cresol (1 mmol, 0.1081 g). The crude product was purified using flash column chromatography using 50% dichloromethane in cyclohexane as eluent to obtain 0.0311 g of a white solid (14% yield, **m.p.** 159-161 °C).**^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.21 (d, *J* = 6.4 Hz, 1H), 7.00 (s, 1H), 6.72 – 6.65 (m, 2H), 5.45 (s, 1H), 3.13 – 3.01 (m, 2H), 2.94 – 2.84 (m, 2H), 2.27 (s, 3H), 2.21 – 2.11 (m, 1H), 2.00 – 1.82 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 154.0, 140.1, 128.9, 128.6, 121.4, 117.5, 46.30, 31.8 (2C), 25.2, 21.2. **FT-IR (neat) υ (cm^{-1}):** 3205, 2941, 2897, 1612, 1501, 1415, 1283, 1265, 1180. **HRMS (ESI):** Calcd. for $C_{11}H_{15}OS_2$ $(M+H)^+$: 227.0559; Found: 227.0548.

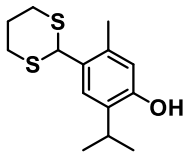
4-(1,3-dithian-2-yl)-2-methylphenol (3c)



General procedure was applied to o-cresol (1 mmol, 0.1081 g). The crude product was purified using flash column chromatography using 20% ethyl acetate in pentane as eluent to obtain 0.0697 g of a white solid (30% yield, **m.p.** 114-117 °C). **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.23 (d, *J* = 2.8 Hz, 1H), 7.14 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.68 (d, *J* = 8.1 Hz, 1H), 5.15 (s, 1H), 5.09 (s, 1H), 3.09 – 2.99 (m, 2H), 2.93 – 2.85 (m, 2H), 2.21 (s, 3H), 2.15 (dtt, *J* = 13.9, 4.5, 2.5 Hz, 1H), 1.96 – 1.82 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 154.0, 131.2, 130.4, 126.5, 124.3, 115.1, 50.9, 32.2 (2C), 25.1, 15.8. **FT-IR (neat) υ (cm^{-1}):** 3344, 2939, 2897,

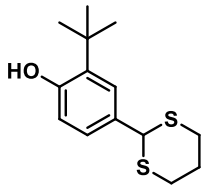
1604, 1504, 1419, 1338, 1265, 1192. **HRMS (ESI):** Calcd. for $C_{11}H_{15}OS_2$ $(M+H)^+$: 227.0559; Found: 227.0550.

4-(1,3-dithian-2-yl)-2-isopropyl-5-methylphenol (3d)



Following the general procedure, from 2-isopropyl-5-methylphenol (0. 1502 g,1 mmol), 1,3-dithiane 1-oxide (0. 184 g, 1.35 mmol) and oxalyl chloride (0.206 g, 1.62 mmol), the compound was obtained as a white solid (0.07 g, 34%, **m.p.** 135 °C). Column chromatography was carried out for purification (cyclohexane-dichloromethane 7:3). **^{1}H NMR (400 MHz, $CDCl_3$) δ**: 7.38 (s, 1H), 6.52 (s, 1H), 5.25 (s, 1H), 4.71 (s, 1H), 3.19 – 3.02 (m, 3H), 2.90 (m, 2H), 2.34 (s, 3H), 2.17 (m, 1H), 2.01 – 1.86 (m, 1H), 1.25 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$) δ:** 152.8, 134.2, 132.8, 130.0, 126.7, 117.6, 48.6, 33.0 (2C), 27.6, 25.7, 23.0 (2C), 19.1. **FT-IR (neat) υ (cm^{-1}):** 3285, 2958, 1666, 1512, 1458, 1338, 1273, 1168, 1037, 852, 771, 590, 466. **HRMS (ESI):** Calcd. for $C_{14}H_{21}OS_2^+$ $(M+H)^+$: 269.1028; Found: 269.1026.

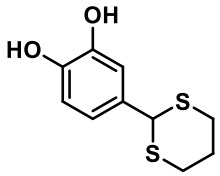
2-(tert-butyl)-4-(1,3-dithian-2-yl)phenol (3e)



General procedure was applied to 2-(tert-butyl)phenol (1 mmol, 0.1052 g). The crude product was purified using flash column chromatography using 20% ethyl acetate in pentane as eluent to obtain 0.2028 g of a white solid (76% yield, **m.p.** 116-118 °C).**^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.32 (d, *J* = 2.3 Hz, 1H), 7.16 (dd, *J* = 8.1, 2.3 Hz, 1H), 6.57 (d, *J* = 8.1 Hz, 1H), 5.18 (s, 1H), 5.12 (s, 1H), 3.04 (ddd, *J* = 14.8, 12.4, 2.5 Hz, 2H), 2.93 – 2.83 (m, 2H), 2.14 (dtt, *J* = 13.8, 4.6, 2.5 Hz, 1H), 1.97 – 1.83 (m, 1H), 1.39 (s, 9H). **^{13}C NMR (101 MHz,**

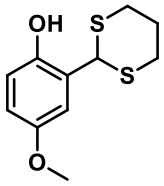
$CDCl_3$) δ: 154.4, 136.4, 130.9, 126.7, 126.2, 116.8, 51.41, 34.7, 32.3 (2C), 29.5 (3C), 25.0. **FT-IR (neat) υ (cm^{-1}):** 3309, 2943, 2924, 2843, 1666, 1600, 1500, 1419, 1265, 1265, 1195. **HRMS (ESI):** Calcd. for $C_{14}H_{21}OS_2$ $(M+H)^+$: 269.1028; Found: 269.1019.

4-(1,3-dithian-2-yl)benzene-1,2-diol (3f)



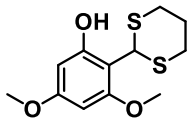
General procedure was applied to Catechol (1 mmol, 0.1101 g). The crude product was purified using flash column chromatography using 30% ethyl acetate in pentane as eluent to obtain 0.1235 g of a red-tan solid (54% yield, **m.p.** 156-157 °C). **^{1}H NMR (400 MHz, DMSO) δ:** 9.04 (s, 1H), 8.98 (s, 1H), 6.82 (s, 1H), 6.66 (s, 2H), 5.18 (s, 1H), 3.03 (t, J = 14.6 Hz, 2H), 2.82 (d, J = 14.1 Hz, 3H), 2.08 (d, J = 16.1 Hz, 1H), 1.74 – 1.59 (m, 1H). **^{13}C NMR (101 MHz, DMSO) δ:** 145.8, C2, 145.6 , C1, 130.8 , C4, 118.9 , C3, 115.8 , C5, 115.4 , C6, 50.31 , C7, 31.6 , C9-C11, 25.3 , C10.**FT-IR (neat) υ (cm-1):** 3402, 3290, 2893, 2924, 1603, 1519, 1450, 1296, 1246, 1180. **HRMS (ESI):** Calcd for $C_{10}H_{13}O_2S_2$ $(M+H)^+$: 229.0351; Found: 229.0348.

2-(1,3-dithian-2-yl)-4-methoxyphenol (3g)



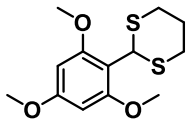
General procedure was applied to 4-methoxyphenol (0.4 mmol, 0.51 g). The crude product was purified using flash column chromatography using 10% dichloromethane in cyclohexane as eluent to obtain 0.054 g of a white solid (54 %, **m.p.** 119-120 °C). **^{1}H NMR (400 MHz, $CDCl_3$) δ**: 6.88 – 6.74 (m, 3H), 5.87 (s, 1H), 5.37 (s, 1H), 3.76 (s, 3H), 3.08 (m, 2H), 3.00 – 2.88 (m, 2H), 2.19 (m, 1H), 2.02 – 1.86 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$) δ:** 154.0, 148.5, 124.9, 118.6, 116.33, 114.3, 56.2, 47.9, 32.1 (2C), 25.4. **FT-IR (neat) υ (cm^{-1}):** 3398, 2889, 1504, 1334, 1265, 1215, 1157, 1033, 825. **HRMS (ESI):** Calcd. for $C_{11}H_{15}O_2S_2$ $(M+H)^+$: 243.0508; Found: 243.0491.

2-(1,3-dithian-2-yl)-3,5-dimethoxyphenol (3h)



Following the general procedure, from 3,5-dimethoxyphenol (0.051 g, 0.33 mmol), 1,3-dithiane 1-oxide (0,06 g, 0.44 mmol) and oxalyl chloride (0.067 g, 0.53 mmol), the compound was obtained as a white solid (0.08 g, 88%, **m.p.** 123-125 °C). Column chromatography was carried out for purification (cyclohexane-dichloromethane 9:1). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.06 (s, 1H), 6.11 (d, *J* = 2.4 Hz, 1H), 6.01 (d, *J* = 2.4 Hz, 1H), 5.95 (s, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 3.11 – 3.00 (m, 2H), 2.87 (m, 2H), 2.22 – 2.11 (m, 1H), 1.96 – 1.82 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$) δ:** 161.6, 158.5, 157.3, 104.1, 94.5, 91.4, 55.9, 55.4, 39.8, 31.8, 24.8. **FT-IR (neat) υ (cm^{-1}):** 3414, 2897, 1620, 1581, 1492, 1315, 1188, 1141, 1045, 983, 798, 705, 675. **HRMS (ESI):** Calcd. for $C_{12}H_{17}O_3S_2^+$ $(M+H)^+$: 273.0614, found 273.0606.

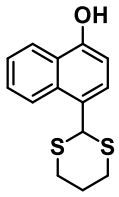
2-(2,4,6-trimethoxyphenyl)-1,3-dithiane (3i)



Following the general procedure, from 1,3,5-trimetoxybencene (0.08 g, 0.48 mmol), 1,3-dithiane 1-oxide (0,09 g, 0.65 mmol) and oxalyl chloride (0.1 g, 0.78 mmol), the compound was obtained as a white solid (0.13 g, 91%, **m.p.** 195 °C). Column chromatography was carried out for purification (cyclohexane-dichloromethane 9:1). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 6.11 (s, 2H), 5.82 (s, 1H), 3.86 (s, 6H), 3.79 (s, 3H), 3.19 – 3.01 (m, 2H), 2.87 (m, 2H), 2.19 – 2.07 (m, 1H), 1.97 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$) δ**: 161.1 (3C), 108.2, 91.3 (2C), 56.2, 55.4 (2C), 43.5, 33.4 (2C), 25.8. **FT-IR (neat) υ (cm^{-1}):** 3008, 2939, 2839,

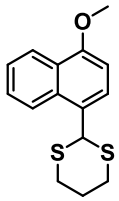
1585, 1465, 1415, 1334, 1219, 1184, 1149, 1107, 810, 529. **HRMS (ESI):** Calcd. for $C_{13}H_{19}O_3S_2^+$ $(M+H)^+$: 287.0770, found. 287.0774.

4-(1,3-dithian-2-yl)naphthalen-1-ol (3j)



Following the general procedure, from naphthalen-1-ol (0.083 g, 0.58 mmol), ,3-dithiane 1-oxide (0.11 g, 0,78 mmol) and oxalyl chloride (0,12 g, 0,93 mmol), the compound was obtained as a white solid (0.0417 g; 88%, **m.p.** 196°C). Column chromatography was carried out for purification (cyclohexane-dichloromethane 9:1). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 8.24 (m, 2H), 7.60 (m, 2H), 7.50 (m, 1H), 6.79 (d, *J* = 7.9 Hz, 1H), 5.84 (s, 1H), 5.37 (s, 1H), 3.25 – 3.13 (m, 2H), 2.98 (m, 2H), 2.29 – 2.20 (m, 1H), 2.06 – 1.92 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$) δ**: 151.8, 131.4, 127.6, 126.9, 126.5, 125.3, 124.6, 123.3, 122.5, 108.2, 48.0, 32.9, 25.5. **FT-IR (neat) υ (cm^{-1}):** 3317, 2897, 1585, 1350, 1253, 1226, 999, 821, 759, 601. **HRMS (ESI):** Calcd. for $C_{14}H_{15}OS_2$ $(M+H)^+$: 263.0559, found 263.0554.

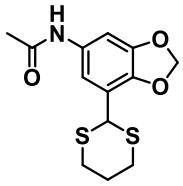
2-(4-methoxynaphthalen-1-yl)-1,3-dithiane (3k)



Following the general procedure, from 1-methoxynaphthalene (0.082 g, 0.52 mmol), 1,3-dithiane 1-oxide (0.10 g, 0.70 mmol) and oxalyl chloride (0.071 g, 0,84 mmol), the compound was obtained as a white solid (0.075 g, 71%, **m.p.** 126 °C). Column chromatography was carried out for purification (cyclohexane-dichloromethane 9:1). **^{1}H NMR (400 MHz,**

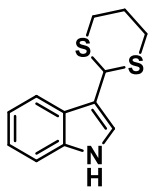
$CDCl_3$) δ: 8.31 (d, *J* = 8.3 Hz, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.64 – 7.54 (m, 1H), 7.49 (m, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 5.85 (s, 1H), 3.99 (s, 3H), 3.25 – 3.15 (m, 2H), 2.99 (m, 2H), 2.24 (m, 1H), 2.08 – 1.90 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$) δ:** 155.7, 131.1, 127.0, 126.9, 126.5, 125.9, 125.2, 123.1, 122.8, 103.5, 55.6, 48.05, 32.91, 25.55. **FT-IR (neat) υ (cm^{-1}):** 2935, 2893, 2831,1674, 1581, 1512, 1377, 1276, 1253, 1087,1022, 817, 756. **HRMS (ESI):** Calcd. for $C_{15}H_{17}OS_2$ $(M+H)^+$: 277.0715, found 277.0711.

N-(4-(1,3-dithian-2-yl)benzo[d][1,3]dioxol-5-yl)acetamide (3l)



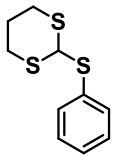
Following the general procedure, from N-(benzo[d][1,3]dioxol-5-yl)acetamide (0.18 g, 1.00 mmol), 1,3-dithiane 1-oxide (0.18 g, 1.35 mmol) and oxalyl chloride (0.21 g, 1.62 mmol), the compound was obtained as a gray solid (0.1579 g; 53%, **m.p.** 137 °C). Column chromatography was carried out for purification (dichloromethane- ethyl acetate 9:1). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 8.15 (bs, 1H), 7.43 (s, 1H), 6.84 (s, 1H), 5.95 (s, 2H), 5.19 (s, 1H), 3.06 (m, 2H), 2.92 (m, 2H), 2.28 – 2.14 (m, 4H), 1.89 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$) δ:** 168.5, 144.9, 130.5, 122.0, 108.2, 106.1, 101.7, 49.1, 32.0, 25.2, 24.6. **FT-IR (neat) υ (cm^{-1}):** 3248, 2900, 1654, 1531, 1504, 1481, 1423, 1273, 1176, 1037, 933, 771, 489. **HRMS (ESI):** Calcd. $C_{13}H_{16}NO_3S_2^+$ $(M+H)^+$: 298.0566, found 298.0569.

3-(1,3-dithian-2-yl)-1H-indole(3m)



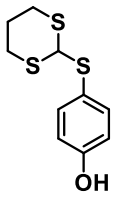
Following the general procedure, from indole (0.053 g, 0.45 mmol), 1,3-dithiane 1-oxide (0.083 g, 0.61 mmol), and oxalyl chloride (0.092 g, 0.73 mmol), the compound was obtained as a white solid (0.071 g, 64%, **m.p.** 134 °C), Column chromatography was carried out for purification (dichloromethane-cyclohexane 7:3). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 8.11 (bs, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.19 (m, 2H), 5.59 (s, 1H), 3.20 – 3.07 (m, 2H), 2.94 (m, 2H), 2.26 – 2.16 (m, 1H), 2.06 – 1.93 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$) δ**: 136.0, 125.6, 122.9, 122.6, 119.9, 119.7, 114.6, 111.3, 42.9, 32.2, 25.5. **FT-IR (neat) υ (cm^1):** 3667, 2924, 1454, 1419, 1176, 1076, 910, 748, 628, 590. **HRMS (ESI):** Calcd. for $C_{12}H_{14}NS_2^+$ $(M+H)^+$: 236.0562; found: 236.0558.

2-(phenylthio)-1,3-dithiane (3n)



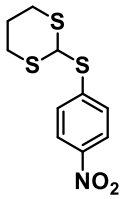
Following the general procedure, from thiophenol (0.06 g, 0.50 mmol), 1,3-dithiane 1-oxide (0.09 g, 0.67 mmol) and oxalyl chloride (0.10 g, 0.81 mmol), the compound was obtained as a white solid (0.07 g, 61%, **m.p.** 62 °C). It was crystalized from dichloromethane. **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.51 (m, 2H), 7.45 – 7.29 (m, 3H), 5.16 (s, 1H), 3.34 (m, 2H), 2.79 – 2.59 (m, 2H), 2.24 – 1.97 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$) δ:** 134.4, 133.5, 129.0, 128.5, 50.5, 26.7, 25.2. **FT-IR (neat) υ (cm^{-1}):** 2931, 1469, 1423, 1238, 1068, 1022, 906, 871, 767, 744, 690, 621, 489. **HRMS (ESI):** Calcd. For $C_{10}H_{13}S_3^+$ $(M+H)^+$: 229.0174; found 229.0197

4-((1,3-dithian-2-yl)thio)phenol (3o)



Following the general procedure, from 4-hidroythiophenol (0.063 g, 0.50 mmol), 1,3-dithiane 1-oxide (0.092 g, 0.67 mmol) and oxalyl chloride (0.103 g, 0.81 mmol), the compound was obtained as a white solid (0.081 g, 66 %, **m.p.** 105 °C). Column chromatography was carried out for purification (dichloromethane). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.43 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 8.5 Hz, 2H), 5.00 (s, 1H), 3.58 – 3.13 (m, 2H), 2.68 (m, 2H), 2.23 – 1.83 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$) δ:** 156.5, 136.9, 125.0, 116.0, 51.5, 26.7, 25.2. **FT-IR (neat) υ (cm^{-1}):** 2931, 1469, 1423, 1238, 1068, 1022, 906, 871, 767, 744, 690, 621, 489, 432. **HRMS (ESI):** Calcd. For $C_{10}H_{11}OS_3^-$: 242.9978, found 242.9954.

2-((4-nitrophenyl)thio)-1,3-dithiane (3p)

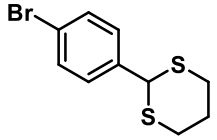


General procedure was applied to 4-nitrothiophenol (1 mmol, 0.155 g), 1,3-dithiane 1-oxide (0.183 g, 1.35 mmol) and oxalyl chloride (0.206 g, 1.63 mmol), the compound was obtained as a yellow crystalline solid (0.188 g, 69%, **m.p** 114-116 °C). Column chromatography was carried out for purification using 10% of ethyl acetate in pentane as eluent. **^{1}H NMR (400 MHz, CDCl3) δ:** 8.18 (d, *J* = 8.9 Hz, 3H), 7.52 (d, *J* = 8.8 Hz, 2H), 5.36 (s, 1H), 3.34 (ddd, J = 14.1, 10.8, 3.0 Hz, 2H), 2.71 (ddd, *J* = 14.2, 5.9, 3.1 Hz, 2H), 2.23 – 2.01 (m, 2H). **^{13}C NMR (101 MHz, CDCl3) δ:** 130.3, 126.4, 4, 124.5, 1, 124.0, 2, 6, 48.4, 8, 26.3, 10, 12, 25.0, 11. **FT-IR (neat) υ (cm^{-1}):** 3093, 2939, 2827, 2445, 1913, 1735, 1666, 1573, 1504, 1361, 1334, 1207, 1087, 833, 736, 532, 462**. HRMS (ESI):** Calcd for $C_{10}H_{12}NO_2S_3^+$ $(M+H)^+$: 274.0025; Found: 274.0876

General procedure for aromatic aldehyde protection into dithioacetals

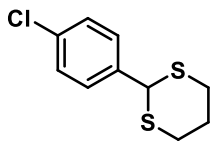
In a round bottom flask, 1 eq. of the aromatic aldehyde was dissolved in acetonitrile (0.07 M) and then the silica-supported sulfuric acid (SSA, 0.01 g per 1 eq of aldehyde) was suspended into the solution stirring at room temperature. With strong stirring, 1.1 eq. of 1,3-propanedithiol was added to the reaction mixture and was left to react for at least 1 hour before monitoring starting material consumption with TLC. The preparation of the SSA catalyst was carried out according to previous reports.[4]

2-(4-bromophenyl)-1,3-dithiane (3q)



General procedure was applied to 4-bromobenzaldehyde (1 mmol, 0.1850 g). The crude product was purified using flash column chromatography using 50% dichloromethane in cyclohexane as eluent to obtain 0.1105 g of a white solid (40% yield, **m.p.** 95-97°C).**^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.47 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 5.12 (s, 1H), 3.05 (t, *J* = 13.5 Hz, 2H), 2.91 (dt, *J* = 13.7, 3.3 Hz, 2H), 2.27 – 2.10 (m, 1H), 1.99 – 1.85 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 138.2, 131.9 (2C), 129.5 (2C), 122.4, 50.7, 32.0, 25.0. **FT-IR (neat) υ (cm^{-1}):** 2897, 1481, 1396, 1068, 1006, 883, 813, 756, 671, 462. **HRMS (ESI):** Calcd for $C_{10}H_{12}BrS_2^+$ $(M+H)^+$: 274.9558; Found: 274.9572

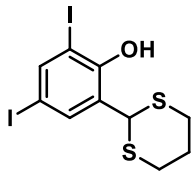
2-(4-chlorophenyl)-1,3-dithiane (3r)



General procedure was applied to 4-chlorobenzaldehyde (2.134 mmol, 0.3 g). The crude product was not purified. 0.5055 g of a white solid (Quantitative yield, **m.p.** 89-91°C). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.41 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 5.13 (s, 1H),

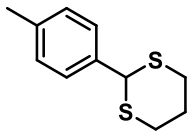
3.05 (ddd, J = 14.7, 12.3, 2.5 Hz, 2H), 2.91 (dt, J = 14.5, 4.3 Hz, 2H), 2.17 (dtt, J = 14.1, 4.8, 2.6 Hz, 1H), 1.99 – 1.85 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 137.7, 134.2, 129.2, 129.0, 50.6, 32.0, 25.0. **FT-IR (neat) υ (cm^{-1}):** 2927, 2893, 2276, 1489, 1404, 1273, 1083, 756. **HRMS (ESI):** Calcd. For $C_{10}H_{12}ClS_2^+$ $(M+H)^+$: 231.0063; Found: 231.0053.

2-(1,3-dithian-2-yl)-4,6-diiodophenol (3s)



General procedure was applied to 2-hydroxy-3,5-diiodobenzaldehyde (0.8023 mmol, 0.3 g). The crude product was purified using flash column chromatography using 10% ethyl acetate in pentane as eluent to obtain 0.2525 g of a white solid (68% yield, **m.p.** 131-133°C). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.91 (d, J = 2.1 Hz, 1H), 7.68 (d, J = 2.1 Hz, 1H), 6.26 (d, J = 2.5 Hz, 1H), 5.44 (s, 1H), 3.08 (t, J = 12.4 Hz, 2H), 2.92 (d, J = 13.6 Hz, 2H), 2.24 – 2.13 (m, 1H), 1.99 – 1.82 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 152.3, 145.9, 138.3, 126.9, 87.7, 83.2, 45.7, 31.9, 24.9. **FT-IR (neat) υ (cm^{-1}):** 3414, 2900, 1442, 1311, 1242, 1122, 1095. **HRMS (ESI):** Calcd for $C_{10}H_{11}I_2OS_2$ $(M+H)^+$: 464.8335; Found 464.8337.

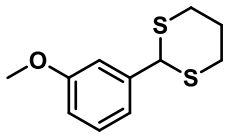
2-(p-tolyl)-1,3-dithiane (3t)



General procedure was applied to 4-methylbenzaldehyde (2.489 mmol, 0.3 g). The crude product was purified by recrystallization in hot methanol. 0.3228 g of a white solid (61% yield, **m.p.** 90-92°C). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.36 (d, J = 8.1 Hz, 2H), 7.15 (d, J = 7.8 Hz, 2H), 5.14 (s, 1H), 3.05 (ddd, J = 14.7, 12.4, 2.5 Hz, 2H), 2.94 – 2.85 (m, 2H), 2.33 (s, 3H), 2.16 (dtt, J = 14.0, 4.6, 2.5 Hz, 1H), 1.98 – 1.85 (m, 1H). **^{13}C NMR (101 MHz,**

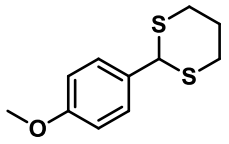
$CDCl_3$): δ 138.3, 136.2, 129.5(2C), 127.6 (2C), 51.2, 32.2 (2C), 25.2, 21.3. **FT-IR (neat) υ (cm^{-1}):** 3024, 2893, 1512, 1423, 1276, 1180, 756, 671, 509. Characterization data agreed with prior reports.[5]

2-(3-methoxyphenyl)-1,3-dithiane (3u)



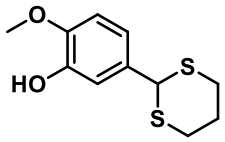
General procedure was applied to 3-methoxybenzaldehyde (1.47 mmol, 0.200 g). The crude product was purified using flash column chromatography using 40% dichloromethane in cyclohexane as eluent to obtain 0.200 g of a white solid (60% yield, **m.p.** 64-65 °C). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.24 (m, 1H), 7.08 – 6.99 (m, 2H), 6.87 – 6.80 (m, 1H), 5.14 (s, 1H), 3.79 (s, 3H), 3.04 (m, 2H), 2.94 – 2.84 (m, 2H), 2.15 (m, 1H), 1.99 – 1.82 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 160.2, 140.9, 130.1, 120.4, 114.7, 113.5, 55.6, 51.9, 32.5 (2C), 25.5. **HRMS (ESI):** Calcd for $C_{11}H_{15}OS_2^+(M+H)^+$: 227.0559, found 227.0562. Characterization data agreed with prior reports.[10]

2-(4-methoxyphenyl)-1,3-dithiane (3v)



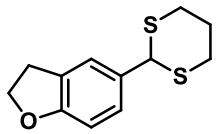
The product was obtain using 4-metoxy benzaldehyde (0.136 g, 1.0 mmol), 1,3-propanedithiol (0,162 g, 1.5 mmol) and $BF_3.OEt_2$ (0.014 g, 0.01 mmol). The crude product was purified using flash column chromatography using 10% ethyl acetate in pentane as eluent to obtain 0.177 g of a white solid (78% yield, **m.p.** 112-114 °C). **NMR (400 MHz, $CDCl_3$) δ:** 7.40 (d, *J*= 8.2 Hz, 2H), 6.88 (d, J= 7.9 Hz, 2H), 5.13 (s, 1H), 3.79 (s, 3H), 3.09 (m, 2H), 2.94 – 2.87 (m, 2H), 2.16 (m, 1H), 1.97 – 1.89 (m, 1H).**^{13}C NMR (101 MHz, $CDCl_3$) δ:** 159.6, 131.3, 128.9, 114.1, 55.3, 50.7, 32.2, 25.1. **FT-IR (neat) υ (cm^{-1}):** 3005, 2958, 2935, 2900, 1604, 1504, 1454, 1438, 1415, 1276, 1246, 1176, 1111, 1029, 883, 813, 775, 756, 551, 524. **HRMS (ESI):** Calcd for $C_{11}H_{15}OS_2^+(M+H)^+$: 227.0559, found 227.0559.

5-(1,3-dithian-2-yl)-2-methoxyphenol (3w)



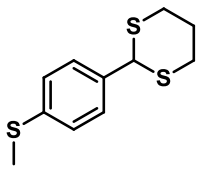
General procedure was applied to Isovanillin (1.972 mmol, 0.3 g). The crude product was not purified. 0.4782 g of a white solid (Quantitative yield, **m.p.** 90-91 °C**). ^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.05 (d, *J* = 2.3 Hz, 1H), 6.97 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.80 (d, *J* = 8.3 Hz, 1H), 5.63 (s, 1H), 5.08 (s, 1H), 3.87 (d, *J* = 1.8 Hz, 3H), 3.04 (ddd, *J* = 14.8, 12.4, 2.4 Hz, 2H), 2.89 (dt, *J* = 14.2, 3.8 Hz), 2.22 – 2.09 (m, 1H), 1.97 – 1.82 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 146.6, 145.6,132.4, 119.4,114.2, 110.6, 56.0, 50.9, 32.2 , 25.1. **FT-IR (neat) υ (cm^{-1}):** 3498, 2889, 1585, 1508, 1300, 1269, 1168. **HRMS (ESI):** Calcd. for $C_{11}H_{15}O_2S_2$ $(M+H)^+$: 243.0508; Found: 243.0509.

5-(1,3-dithian-2-yl)-2,3-dihydrobenzofuran (3x)



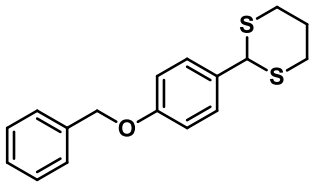
General procedure was applied to 2,3-dihydrobenzofuran-5-carbaldehyde (1.35 mmol, 0.200 g). The crude product was purified using flash column chromatography using 30% dichloromethane in cyclohexane as eluent to obtain 0.225 g of a white solid (70% yield, **m.p.** 89-91°C). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.32 (d, *J* = 1.9 Hz, 1H), 7.19 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.72 (d, *J* = 8.2 Hz, 1H), 5.11 (s, 1H), 4.56 (m, 2H), 3.19 (m, 2H), 3.04 (m, 2H), 2.94 – 2.84 (m, 2H), 2.21 – 2.09 (m, 1H), 1.89 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 160.6, 131.6, 128.2, 128.0, 124.8, 109.7, 71.9, 51.5, 32.7 (2C), 30.0, 25.5. **HRMS (ESI):** Calcd for $C_{12}H_{15}OS_2^+$ $(M+H)^+$: 239.0559; Found: 239.0557

2-(4-(methylthio)phenyl)-1,3-dithiane (3y)



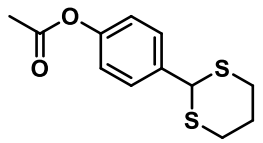
General procedure was applied to 4-(methylthio)benzaldehyde (1.31 mmol, 0.200 g). The crude product was purified using flash column chromatography using 30% dichloromethane in cyclohexane as eluent to obtain 0.200 g of colorless needles (63% yield, **m.p.** 165-167°C). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.38 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 5.13 (s, 1H), 3.04 (m, 2H), 2.89 (m, 2H), 2.46 (m, 1H), 2.15 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 139.3, 136.2, 128.6 (2C), 127.0 (2C), 51.3, 32.5 (2C), 25.0, 16.1. **HRMS (ESI):** Calcd for $C_{11}H_{15}S_3^+$ $(M+H)^+$: 243.0330, found 243.0331. Characterization data agreed with prior reports.[11]

2-(4-(benzyloxy)phenyl)-1,3-dithiane (3z)



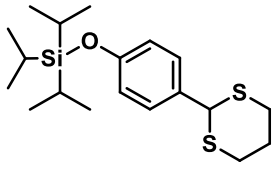
To a round bottom flask charged with a solution of 4-(1,3-dithian-2-yl)phenol in DCM (1 eq., 0.706 mmol, 0.150 g, 0.1 M), benzyl bromide (1.1 eq), tetrabutylammonium bromide (0.07 eq.), and 5 mL of a 10% w/w KOH aqueous solution were added. The reaction was left to stir at room temperature and was monitored with TLC until complete consumption of 4-(1,3-dithian-2-yl)phenol. Once finished, the organic phase was separated and washed with distilled water. Finally, it was dried over anhydrous sodium sulphate and the solvent was removed under reduced pressure. The crude product was purified using flash column chromatography using 30% dichloromethane in cyclohexane as eluent to obtain 0.1779 g of a white solid (83% yield, **m.p.** 118-120 °C). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.51 – 7.27 (m, 8H), 6.93 (d, *J* = 8.7 Hz, 2H), 5.13 (s, 1H), 5.04 (s, 2H), 3.05 (t, *J* = 12.2 Hz, 2H), 2.89 (dt, *J* = 14.1, 3.7 Hz, 2H), 2.22 – 2.09 (m, 1H), 2.00 – 1.83 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 158.8, 136.9, 131.6, 129.0 (2C), 128.7 (2C), 128.1, 127.5 (2C), 115.0 (2C), 70.1, 50.8, 32.2 (2C), 25.1.

4-(1,3-dithian-2-yl)phenyl acetate (3aa)



To a round bottom flask charged with a solution of 4-(1,3-dithian-2-yl)phenol in DCM (1 eq., 0.471 mmol, 0.100 g, 0.25 M), DMAP (0.05 eq.) and triethylamine (1.5 eq.) were added while stirring in an ice bath. After it has cooled down for 10 minutes, 1.5 eq. of acetyl chloride were added, and the reaction was left to stir further at that temperature for 1 h. Later, the reaction vessel was removed from the ice bath and was let to react overnight at room temperature. After that time, the reaction was monitored with TLC until complete consumption of 4-(1,3-dithian-2-yl)phenol. Once finished, the reaction is quenched with a saturated ammonium chloride solution and the organic phase was separated, then washed with distilled water. Finally, it was dried over anhydrous sodium sulphate and the solvent was removed under reduced pressure. No further purification was needed to afford the pure product. 0.1198 g of a light yellow solid (Quantitative yield, **m.p.** 100-102 °C). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.48 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 8.5 Hz, 2H), 5.16 (s, 1H), 3.05 (ddd, *J* = 14.7, 12.4, 2.5 Hz, 2H), 2.91 (dt, *J* = 14.1, 3.8 Hz, 2H), 2.29 (s, 3H), 2.17 (dtd, *J* = 14.2, 4.6, 2.3 Hz, 1H), 1.92 (dtt, *J* = 15.4, 12.4, 3.1 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 169.3, 150.5, 136.6, 129.0 (2C), 121.8 (2C), 50.7, 32.0, (2C), 25.0, 21.2. **HRMS (ESI): Calcd. for** $C_{12}H_{15}O_2S_2$ $(M+H)^+$: 255.0508; Found: 255.0514.

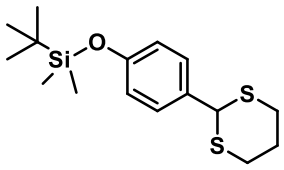
(4-(1,3-dithian-2-yl)phenoxy)triisopropylsilane (3ab)



In an oven-dried round bottom flask, 1 eq. of 4-(1,3-dithian-2-yl)phenol (0.706 mmol, 0.150 g) was dissolved in dry DCM (0.18 M) along with 3 eq. of Imidazole and 0.01 eq. of 4-Dimethylaminopyridine (DMAP). The solution was left to stir in an ice bath before adding

1.5 eq. of trisopropylsilyl chloride. After its addition, the reaction mixture is removed from the bath and left stirring at room temperature for 24 hours. After checking the complete consumption of the starting material using TLC, methanol is added to the reaction mixture and is left to stir for 30 additional minutes. Then, the reaction mixture was added to a separatory funnel with distilled water mixed. The organic phase is separated, and the aqueous phase is further extracted three times with dichloromethane. The combine organic phases are dried with anhydrous sodium sulphate and then the solvent was removed in vacuo to obtain the crude reaction mixture. The crude product was purified using flash column chromatography using 30% dichloromethane in cyclohexane as eluent to obtain 0.2129 g of a colorless oil (56% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.31 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 5.12 (s, 1H), 3.05 (td, *J* = 13.4, 2.4 Hz, 2H), 2.94 – 2.83 (m, 2H), 2.16 (ddt, *J* = 12.9, 4.5, 2.1 Hz, 1H), 1.98 – 1.81 (m, 1H), 1.30 – 1.17 (m, 3H), 1.08 (d, *J* = 7.4 Hz, 18H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 156.2, 131.5, 128.9 (2C), 120.0 (2C), 50.9, 32.2 (2C), 25.1, 17.9 (6C), 12.7 (3C). **FT-IR (neat) υ (cm^{-1}):** 2939, 2866, 1604, 1504, 1269, 1168 **HRMS (ESI):** Calcd. for $C_{19}H_{33}OS_2Si^+$ $(M+H)^+$: 369.1737 Found 369.1743.

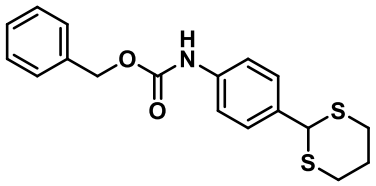
(4-(1,3-dithian-2-yl)phenoxy)(tert-butyl)dimethylsilane (3ac)



In an oven-dried round bottom flask, 1 eq. of 4-(1,3-dithian-2-yl)phenol (0.706 mmol, 0.150 g) was dissolved in dry DCM (0.18 M) along with 3 eq. of Imidazole and 0.01 eq. of 4-Dimethylaminopyridine (DMAP). The solution was left to stir in an ice bath before adding 1.5 eq. of Tert-Butyldimethylsilyl chloride. After its addition, the reaction mixture is removed from the bath and left stirring at room temperature for 24 hours. After checking the complete consumption of the starting material using TLC, methanol is added to the reaction mixture and is left to stir for 30 additional minutes. Then, the reaction mixture was added to a separatory funnel with distilled water mixed. The organic phase is separated, and the aqueous phase is further extracted three times with dichloromethane. The combine organic

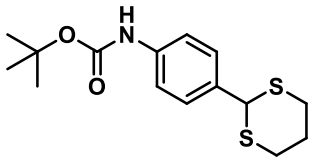
phases are dried with anhydrous sodium sulphate and then the solvent was removed in vacuo to obtain the crude reaction mixture. The crude product was purified using flash column chromatography using 30% dichloromethane in cyclohexane as eluent to obtain 0.1058 g of a white solid (46% yield, **m.p.** 84-85 °C). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.32 (d, *J* = 8.4 Hz, 2H, 3, 8), 6.78 (d, *J* = 8.5 Hz, 2H), 5.12 (s, 1H), 3.05 (ddd, *J* = 14.8, 12.5, 2.4 Hz, 2H), 2.90 (dt, *J* = 14.3, 3.7 Hz, 2H), 2.15 (ddq, *J* = 11.4, 4.6, 2.3 Hz, 1H), 1.99 – 1.83 (m, 1H), 0.97 (s, 9H), 0.19 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 155.8, 131.8, 128.9, 120.2 (2C), 50.9, 32.2 (2C), 25.7 (3C), 25.1, 18.2, -4.4 (2C). **FT-IR (neat) υ (cm^{-1}):** 2951, 2850, 1604, 1504, 1249, 1161. **HRMS (ESI):** Calcd. for $C_{16}H_{27}OS_2Si$ $(M+H)^+$: 327.1267; Found: 327.1269.

benzyl (4-(1,3-dithian-2-yl)phenyl)carbamate (3ad)



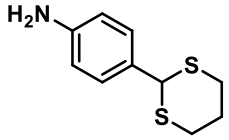
4-(1,3-dithian-2-yl)aniline (1 mmol, 0.2113 g) and $NaHCO_3$ (5 eq.) were added to 20 mL of 1,4-dioxane/H2O (1:1) and stirred at 0°C for 10 minutes. Later Benzyl chloroformate (1.1 eq) was added to the mixture which was left to stir for 18 hours. The precipitation of the product was observed, and the mixture was filtered through a Büchner funnel and the solid was washed with distilled water and dried in an oven until constant mass. 0.2591 g of a yellow solid (75% yield, **m.p.** 132-135 °C) were obtained as the final product. **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.45 – 7.26 (m, 9H), 6.75 (br, 1H), 5.19 (s, 2H), 5.13 (s, 1H), 3.04 (t, *J* = 13.5 Hz, 2H), 2.89 (d, *J* = 13.7 Hz, 2H), 2.22 – 2.08 (m, 1H), 1.99 – 1.82 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:**153.2, 137.9, 136.0, 134.2, 128.7 (2C), 128.6 (2C), 128.5 (2C), 128.4 (2C), 118.8, 67.2, 50.8, 32.1 (2C), 25.1. **FT-IR (neat) υ (cm^{-1}):** 3383, 2981, 2897, 1701, 1519, 1411, 1234, 1153. **HRMS (ESI):** Calcd. for $C_{18}H_{20}NO_2S_2$ $(M+H)^+$: 346.0930; Found: 346.0926.

***tert*-butyl (4-(1,3-dithian-2-yl)phenyl)carbamate (3ae)**



4-(1,3-dithian-2-yl)aniline (1 mmol, 0.2113 g) and di-tert-butyl dicarbonate (2 eq.) were refluxed in 20 mL of methanol for 24 h. Once cold the precipitation of the product was observed, and the mixture was filtered through a Büchner funnel and the solid was washed with distilled water and dried in an oven until constant mass. 0.2591 g of a light yellow solid (83% yield, **m.p.** 166-167 °C) were obtained as the final product. **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.39 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.52 (s, 1H), 5.13 (s, 1H), 3.05 (t, *J* = 14.7 Hz, 2H), 2.90 (d, *J* = 13.6 Hz, 2H), 2.22 – 2.09 (m, 1H), 1.98 – 1.84 (m, 1H), 1.51 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 152.6, 138.5, 133.6, 128.5 (2C), 118.6 (2C), 80.7, 50.9, 32.2 (2C), 28.4 (2C), 25.1. **FT-IR (neat) υ (cm^{-1}):** 3344, 2979, 2897, 1701, 1527, 1415, 1311, 1180. **HRMS (ESI):** Calcd. for C15H22NO2S2 $(M+H)^+$: 312.1087; Found: 312.1080.

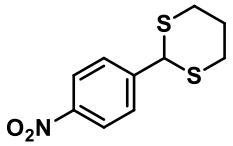
4-(1,3-dithian-2-yl)aniline



To mixture of iron powder (48 mmol, 6 eq.), HCl (5.6 mmol, 0.7 eq), 20 mL acetic acid, 20 mL ethanol and 10 mL water was added 1.2 g of 2-(4-nitrophenyl)-1,3-dithiane (8 mmol, 1 eq.). The mixture was refluxed for 1 hour while stirring. After observing complete consumption of 2-(4-nitrophenyl)-1,3-dithiane via TLC, the solution was let to cool down and the iron was removed by filtration. The filtrate was then alkalinized using solid NaOH until the solution was at a pH of 10. The aqueous phase was extracted with dichloromethane 3 times. The combined organic phases were dried over anhydrous sodium sulphate, and the solvent was removed under reduced pressure. No further purification was needed to afford a pure product. 1.082 g of a yellow solid (64% yield, **m.p.** 136-138°C). **^{1}H NMR (400 MHz,**

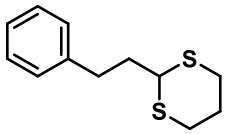
$CDCl_3$) δ: 7.25 (d, *J* = 8.6 Hz, 2H), 6.62 (d, *J* = 8.4 Hz, 2H), 5.08 (s, 1H), 3.70 (br, 2H), 3.04 (ddd, *J* = 14.7, 12.5, 2.5 Hz, 2H), 2.88 (dt, *J* = 14.2, 3.5 Hz, 2H), 2.14 – 2.07 (m, 1H), 1.98 – 1.81 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 146.6, 129.0, 128.8 (2C), 115.1, (2C), 51.0, 32.3 (2C), 25.1. Characterization data agreed with prior reports.[13]

2-(4-nitrophenyl)-1,3-dithiane



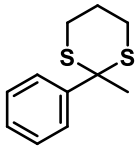
General procedure was applied to 4-nitrobenzaldehyde (1.99 mmol, 0.3 g). No further purification was needed to afford a pure product. 0.302 g of a white solid (63% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 8.20 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 5.24 (s, 1H), 3.08 (ddd, *J* = 14.7, 12.2, 2.5 Hz, 2H), 2.95 (dt, *J* = 14.2, 3.8 Hz, 2H), 2.28 – 2.15 (m, 1H), 2.03 – 1.89 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 147.7, 146.2, 129.0 (2C), 124.0 (2C), 50.5, 31.8 (2C), 24.8. Characterization data agreed with prior reports.[8]

2-phenethyl-1,3-dithiane



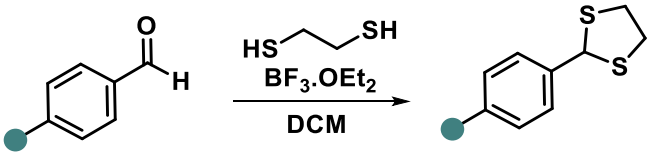
General procedure was applied to 3-phenylpropanal (2.23 mmol, 0.3 g). The crude product was purified using flash column chromatography using 50% dichloromethane in cyclohexane as eluent to obtain 0.0982 g of a colorless liquid (26% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.28 (t, *J* = 7.5 Hz, 2H), 7.20 (d, *J* = 7.6 Hz, 3H), 3.98 (t, *J* = 7.0 Hz, 1H), 2.89 – 2.79 (m, 6H), 2.15 – 2.01 (m, 3H), 1.93 – 1.79 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 141.0, 128.6 (2C), 128.5 (2C), 126.1, 46.6, 37.0, 32.6, 30.3 (2C), 26.1. [9]

2-methyl-2-phenyl-1,3-dithiane



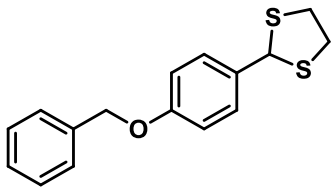
General procedure was applied to acetophenone (2.5 mmol, 0.3 g) with modifications to the solvent (0.5 M) and catalyst (0.1 eq). The crude product was purified using flash column chromatography using 10% dichloromethane in cyclohexane as eluent to obtain 0.3574 g of a white solid (68% yield, **m.p.** 39-42 °C). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.94 (d, *J* = 7.1 Hz, 2H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.26 (t, *J* = 7.1 Hz, 1H), 2.81 – 2.64 (m, 4H), 1.95 (d, *J* = 5.3 Hz, 2H), 1.80 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 143.8, 128.6 (2C), 127.8 (2C), 127.1, 54.1, 32.9, 28.1 (2C), 24.7. Characterization data agreed with prior reports.[12]

General procedure for 1,3-diothiolane derivates



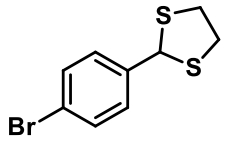
In an oven-dried round bottom flask was dissolved in dry dichloromethane the corresponding aldehyde (1.0 eq). Sequently 1,2-ethanedithiol (1.5 eq) and $BF_3.OEt_2$ (0.1 eq) were added slowly. The reaction mixture was allowed to stir at 25°C. Once the reaction is complete (monitored by TLC), a saturated solution of $NaHCO_3$ was added (10 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL). The organic extracts were combined, washed with NaCl (1 x 10 mL) and dried over Na_2SO_4 and then, the solvent was removed in vacuo to obtain the crude reaction mixture.

2-(4-(benzyloxy)phenyl)-1,3-dithiolane (5)



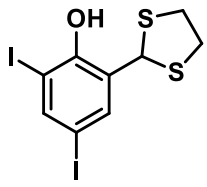
General procedure was applied. 4-(benzyloxy) benzaldehyde (1.0 mmol, 0.212 g), 1,3-ethanedithiol (0.12 mL) and $BF_3.OEt_2$ (12.3 μL). The crude product was purified using flash column chromatography using 15% ethyl acetate in pentane as eluent to obtain 0.254 g of a white solid (88% yield, **m.p.** 85-87 °C). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.48-7.30 (m, 7H), 6.92 (d, *J* = 8.6 Hz, 2H), 5.63 (s, 1H), 5.05 (s, 2H), 3.54-3.46 (m, 2H), 3.38-3.30 (m, 2H).**^{13}C NMR (101 MHz, $CDCl_3$) δ:**158.6, 136.9, 132.1, 129.2, 128.6, 128.0, 127.4, 114.8, 70.1, 56.0, 40.2. **FT-IR (neat) ν (cm^{-1}):** 3066, 3035, 2920, 1608, 1508, 1384, 1242, 1172, 1014, 914, 740, 609. **HRMS (ESI):** Calcd. for $C_{16}H_{17}OS_2^+(M+H)^+$: 289.0715 Found: 289.0717.

2-(4-bromophenyl)-1,3-dithiolane (5q)



General procedure was applied to 4-bromobenzaldehyde (1 mmol, 0.185 g). The crude product was purified using flash column chromatography using 10% ethyl acetate in pentane as eluent to obtain 0.240 g of a white solid (93% yield, **m.p.** 76-78 °C). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.45-7.39 (m, 4H), 5.58 (s, 1H), 3.54-3.32 (m, 4H).**^{13}C NMR (101 MHz, $CDCl_3$) δ:** 139.6, 131.6, 129.6, 121.8, 55.5, 40.3. **FT-IR (neat) υ (cm^{-1}):** 3043, 2916, 1585, 1489, 1404, 1276, 1068, 1010, 948, 856, 752, 686. **HRMS (ESI):** Calcd for $C_9H_{10}BrS_2^+$ $(M+H)^+$: 260.9402; Found: 260.9261

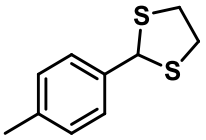
2-(1,3-dithiolan-2-yl)-4,6-diiodophenol (5s)



General procedure was applied to 2-hydroxy-3,5-diiodobenzaldehyde (1 mmol, 0.373 g). The crude product was purified using flash column chromatography using 10% ethyl acetate in

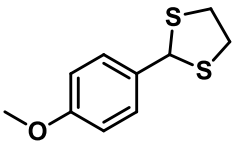
pentane as eluent to obtain 0.422 g of a pink solid (94% yield, **m.p.** 96-98 °C). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.89 (s, 1H), 7.76 (s, 1H), 6.37 (s, 1H), 5.80 (s, 1H), 3.51-3.32 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 152.8, 145.2, 138.1, 128.0, 87.7, 82.8, 51.4, 39.8. **FT-IR (neat) υ (cm^{-1}):** 3460, 2920, 1438, 1392, 1300, 1238, 1095, 856, 771, 732, 659, 536. **HRMS (ESI):** Calcd for $C_9H_9I_2OS_2^+$ $(M+H)^+$: 450.8179; Found: 450.8178.

2-(p-tolyl)-1,3-dithiolane (5t)



General procedure was applied to 4-Methylbenzaldehyde (1 mmol, 0.120 g). The crude product was purified using flash column chromatography using 10% ethyl acetate in pentane as eluent to obtain 0.192 g of a white solid (98% yield, **m.p.** 44-46 °C). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.42 (d, *J* = 7.9 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 5.63 (s, 1H), 3.76 – 3.12 (m, 4H), 2.33 (s, 3H).**^{13}C NMR (101 MHz, $CDCl_3$) δ:** 137.9, 137.1, 129.2, 127.8, 56.1, 40.2, 21.1.**FT-IR (neat) υ (cm^{-1}):** 2931, 1508, 1411, 1276, 1107, 968, 848, 829, 744. **HRMS (ESI):** Calcd for $C_{10}H_{13}S_2^+(M+H)^+$: 197.0453; Found: 197.0452.

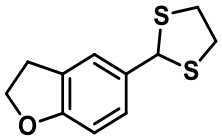
2-(4-methoxyphenyl) -1,3-dithiolane (5v)



General procedure was applied to 4-methoxybenzaldehyde (1 mmol, 0.136 g). The crude product was purified using flash column chromatography using 10% ethyl acetate in pentane as eluent to obtain 0.193 g of a white solid (91% yield, **m.p.** 63-65 °C). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.45 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 5.64 (s, 1H), 3.79 (s, 3H), 3.58 – 3.30 (m, 4H).**^{13}C NMR (101 MHz, $CDCl_3$) δ:** 159.4, 131.8, 129.1, 113.9, 56.1, 55.3, 40.2.

FT-IR (neat) υ (cm^{-1}): 2920, 2831, 1604, 1508, 1249, 1226, 1107, 837, 752, 690. **HRMS (ESI):** Calcd for $C_{10}H_{13}OS_2^+(M+H)^+$: 213.0402; Found 213.0401.

5-(1,3-dithiolan-2-yl)-2,3-dihydrobenzofuran (5z)

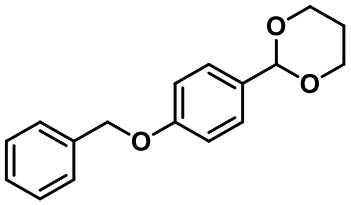


General procedure was applied to 2,3-Dihydrobenzo[b]furan-5-carbaldehyde (1 mmol, 0.148 g). The crude product was purified using flash column chromatography using 10% ethyl acetate in pentane as eluent to obtain 0.210 g of a white solid (93% yield, **m.p.** 69 °C). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 7.43 (s, 1H), 7.29 – 7.17 (m, 1H), 6.69 (d, *J* = 8.2 Hz, 1H), 5.64 (s, 1H), 4.57 (t, *J* = 8.7 Hz, 2H), 3.56 – 3.29 (m, 4H), 3.19 (t, *J* = 8.6 Hz, 2H).**^{13}C NMR (101 MHz, $CDCl_3$) δ:** 160.1, 131.5, 128.0, 127.6, 124.6, 108.9, 71.5, 56.5, 40.3, 29.6. **FT-IR (neat) υ (cm^{-1}):** 2889, 2854, 1604, 1485, 1323, 1249, 1091, 983, 883, 690, 536. **HRMS (ESI):** Calcd for $C_{11}H_{12}OS_2$ $(M+H)^+$: 225.0402; Found: 225.0401

General method for 1,3-dioxane

To a solution of 4-(benzyloxy) benzaldehyde (1.0 eq) in toluene (25 mL), the corresponding diol (10 eq), and p-toluenesulfonic acid (0.081 eq) were added into a round-bottomed flask equipped with a Dean-Stark trap with a condenser. The reaction mixture was heated at 145°C for 24 h. After cooling to room temperature, a solution of $NaHCO_3$ was added. The aqueous phase was extracted with ethyl acetate (3 x 20 mL). The organic layers were combined, washed with NaCl (1 x 10 mL) and dried over Na_2SO_4.[14]

2-(4-(benzyloxy)phenyl)-1,3-dioxane (6)

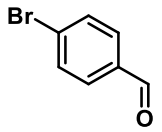


General procedure was applied. 4-(benzyloxy) benzaldehyde (1.0 mmol, 0.212 g), 1,3-propanediol (4.1 mL) and p-toluenesulfonic acid (0.020 g). The crude product was purified using flash column chromatography using 8% ethyl acetate in pentane as eluent to obtain 0.114 g of a white solid (42% yield, **m.p.** 88-90 °C). **^{1}H NMR (400 MHz, $CDCl_3$) δ: :** 7.48-7.30 (m, 7H), 6.96 (d, *J* = 8.7 Hz, 2H), 4.25-4.21 (m, 2H), 3.98-3.92 (m, 2H), 2.26-2.15 (m, 1H), 1.43-1.39 (m, 1H).**^{13}C NMR (101 MHz, $CDCl_3$) δ:** 159.1, 137.0, 131.6, 128.6, 127.9, 127.4, 127.3, 114.6, 101.5, 70.0, 67.4, 25.8. **FT-IR (neat) ν (cm^{-1}):** 2951, 2866, 1612, 1516, 1373, 1238, 1091, 987, 829, 752, 702, 509. **HRMS (ESI):** Calcd. for $C_{17}H_{19}O_3^+$ $(M+H)^+$: 271.1329; Found: 271.1323.

General procedure for 2-aryl-1,3-dithiane deprotection into their respective aromatic aldehyde.

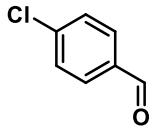
In an oven-dried 2-neck round bottom flask, 1 eq. of the 2-aryl-1,3-dithiane was dissolved in dry DCM (0.06 M). Under a stream of nitrogen, 2 eq. of $(COCl)_2$ were added to the 2-neck flask using a micropipette. The reaction mixture is left to stir for 24 h at room temperature (approximately 18 °C), tracking the consumption of the starting material using TLC. After complete consumption, the reaction is quenched with a saturated $NaHCO_3$ solution. The phases are separated and then the aqueous phase is extracted with dichloromethane or ethyl acetate (depending on the products solubility in water) three times. The combined organic phases were subsequently washed with water and a saturated NaCl solution once. The washed organic phase was finally dried with anhydrous sodium sulphate and then the solvent was removed in vacuo to obtain the crude reaction mixture. For aldehydes protected with 1,2-ethanedithiol the same procedure was applied to get the corresponding aldehyde. Therefore, for aldehydes protected with 1,3-dithiane and 1,3-dithiolane yield was reported separately.

4-bromobenzaldehyde (4q)



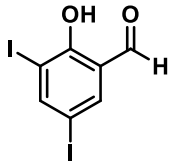
General procedure was applied to 3q (0.400 mmol, 0.110 g). The crude product was purified using flash column chromatography using 30% dichloromethane in cyclohexane as eluent to obtain 0.061 g of a white solid (83% yield, **m.p.** 54-57 °C). The same product is obtained by reaction of 5q (0.30 mmol, 77.9 mg) and $(COCl)_2$ (0.60 mmol, 76.1 mg) in 32% yield (18 mg, 0.097 mmol). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 9.98 (s, 1H), 7.76 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 8.1 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 191.1, 135.1, 132.5 (2C), 131.0 (2C), 129.8.

4-chlorobenzaldehyde (4r)



General procedure 8.4 was applied to 3r (0.650 mmol, 0.150 g). The crude product was purified using flash column chromatography using 10% dichloromethane in cyclohexane as eluent to obtain 0.0855 g of a yellow solid (93% yield, **m.p.** 45-47 °C). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 9.99 (s, 1H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 191.0, 141.0, 134.7, 131.0 (2C), 129.5 (2C).

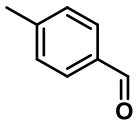
2-hydroxy-3,5-diiodobenzaldehyde (4s)



General procedure was applied to 3s (0.215 mmol, 0.100 g). The crude product was purified using flash column chromatography using 30% dichloromethane in cyclohexane as eluent to obtain 0.032 g of a brown solid (40% yield). The same product is obtained by reaction of 5s

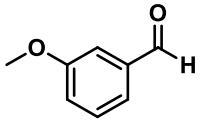
(0.20 mmol, 89.9 mg) and $(COCl)_2$ (0.40 mmol, 50.7 mg) in 35% yield (26.1 mg, 0.069 mmol). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 11.76 (s, 1H), 9.71 (s, 1H), 8.26 (s, 1H), 7.85 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 194.9, 160.2, 153.0, 142.1, 121.9, 87.2, 81.2.

4-methylbenzaldehyde (4t)



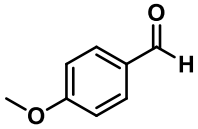
General procedure was applied to 3t (0.380 mmol, 0.080 g). The crude product was purified using flash column chromatography using 30% dichloromethane in cyclohexane as eluent to obtain 0.098 g of a colorless oil (64% yield). The same product is obtained by reaction of 5t (0.25 mmol, 49 mg) and $(COCl)_2$ (0.50 mmol, 63.4 mg) in 29% yield (9 mg, 0.074 mmol).**^{1}H NMR (400 MHz, $CDCl_3$) δ:** 9.96 (s, 1H), 7.78 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 7.8 Hz, 2H), 2.44 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 192.1, 145.6, 134.2, 129.9 (2C), 129.8 (2C), 21.9.

3-methoxybenzaldehyde (4u)



General procedure was applied to 3u (0.309 mmol, 0.070 g). The crude product was purified using flash column chromatography using 30% dichloromethane in cyclohexane as eluent to obtain 0.025 g of a colorless oil (83% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 9.98 (s, 1H), 7.56 – 7.30 (m, 3H), 7.19 (s, 1H), 3.87 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 192.2, 160.2, 137.8, 130.1, 123.6, 121.6, 112.1, 55.5.

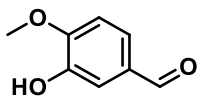
4- methoxybenzaldehyde (4v)



General procedure was applied to 3v (0.30 mmol, 67.8 mg), $(COCl)_2$ (0.60 mmol, 76.1 mg). to 5v (0.20 mmol, 45.4 mg). The crude product was purified using flash column

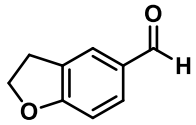
chromatography using 10% ethyl acetate in pentane as eluent to obtain 35 mg of a colorless oil (87% yield). The same product is obtained by reaction of 5v (0.20 mmol, 45 mg) and $(COCl)_2$ (0.40 mmol, 50.7 mg) in 67% yield (18 mg, 0.132 mmol). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 9.88 (s, 1H), 7.84 (d, *J* = *8.7* Hz, 2H), 7.00 (d, *J* = *8.6* Hz, 2H), 3.88 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 190.9, 164.6, 132.0, 129.9, 114.3, 55.6.

3-hydroxy-4-methoxybenzaldehyde (4w)



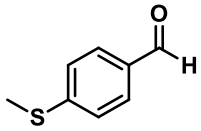
General procedure 8.4 was applied to 3w (0.618 mmol, 0.150 g), using $(COCl)_2$ (1.236 mmol, 156 mg). The crude product was purified using flash column chromatography using 50% dichloromethane in cyclohexane as eluent to obtain 0.0801 g of a yellow solid (85% yield, **m.p.** 54-57 °C). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 9.84 (s, 1H), 7.52 – 7.35 (m, 2H), 6.98 (d, *J* = 8.3 Hz, 1H), 5.88 (s, 1H), 3.99 (d, *J* = 1.6 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 191.2, 151.9, 146.2, 130.6, 124.7, 114.1, 110.2, 56.2.

2,3-dihydrobenzofuran-5-carbaldehyde (4x)



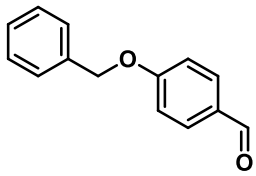
General procedure was applied to 3x (0.209 mmol, 0.050 g). The crude product was purified using flash column chromatography using 30% dichloromethane in cyclohexane as eluent to obtain 0.035g of a colorless oil (80% yield). The same product is obtained by reaction of 5z (0.25 mmol, 56 mg) and $(COCl)_2$ (0.50 mmol, 63.4 mg) in 80% yield (30 mg, 0.20 mmol). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 9.82 (s, 1H), 7.74 (s, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 1H), 4.68 (t, *J* = 8.8 Hz, 2H), 3.26 (t, *J* = 8.7 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 190.7, 165.7, 133.037, 130.4, 128.5, 126.0, 109.6, 72.5, 28.8.

4-(methylthio)benzaldehyde (4y)



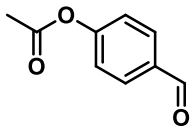
General procedure was applied to 3y (0.206 mmol, 0.050 g). The crude product was purified using flash column chromatography using 30% dichloromethane in cyclohexane as eluent to obtain 0.022 g of a colorless oil (70% yield).**^{1}H NMR (400 MHz, $CDCl_3$) δ:** δ 9.90 (s, 1H), 7.79 – 7.69 (m, 2H), 7.34 – 7.25 (m, 2H), 2.51 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 191.3, 148.0, 132.9, 130.0 (2C), 125.1 (2C), 14.6.

4-(benzyloxy)benzaldehyde (4z)



General procedure was applied to 3z (0.496 mmol, 0.150 g). The crude product was purified using flash column chromatography using 20% dichloromethane in cyclohexane as eluent to obtain 0.0935 g of a white solid (88% yield, **m.p.** 74-77 °C). The same product is obtained by reaction of 5 (0.20 mmol, 57.6 mg) and $(COCl)_2$ (0.40 mmol, 50.7 mg) in 87% yield (37 mg, 0.17 mmol). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 9.88 (s, 1H), 7.84 (d, J = 8.8 Hz, 2H), 7.40 (m, 5H), 7.08 (d, J = 8.7 Hz, 2H), 5.15 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 190.9, 163.8, 136.0, 132.1 (2C), 130.2, 128.8 (2C), 128.4, 127.6 (2C), 115.2 (2C), 70.3.

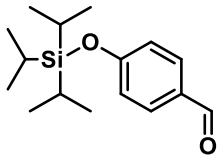
4-formylphenyl acetate (4aa)



General procedure was applied to 3aa (0.249 mmol, 0.063 g). The crude product was purified using flash column chromatography using 40% dichloromethane in cyclohexane as eluent to

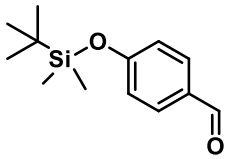
obtain 0.0293 g of a colorless oil (72% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 10.00 (s, 1H), 7.93 (d, *J* = 8.6 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 2.34 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 191.0, 168.8, 155.4, 134.0, 131.3 (2C), 122.4 (2C), 21.2.

4-((triisopropylsilyl)oxy)benzaldehyde (4ab)



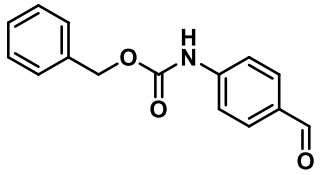
General procedure was applied to 3ab (0.407 mmol, 0.150 g). The crude product was purified using flash column chromatography using 3% dichloromethane in cyclohexane as eluent to obtain 0.0975 g of a yellow oil (86% yield).**^{1}H NMR (400 MHz, $CDCl_3$) δ:** 9.88 (s, 1H, 7), 7.79 (d, J = 8.8 Hz, 2H, 3, 5), 6.98 (d, J = 8.6 Hz, 2H), 1.35 – 1.24 (m, 3H), 1.11 (d, J = 7.5 Hz, 18H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 190.9, 162.0, 132.0 (2C), 130.2, 120.4 (2C), 17.9 (6C), 12.7 (3C).

4-((tert-butyldimethylsilyl)oxy)benzaldehyde (4ac)



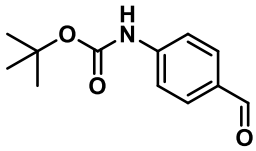
General procedure was applied to 3ac (0.233 mmol, 0.076 g). The crude product was purified using flash column chromatography using 5% dichloromethane in cyclohexane as eluent to obtain 0.0505 g of a colorless oil (92% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 9.89 (s, 1H, 7), 7.79 (d, *J* = 8.7 Hz, 2H), 6.95 (d, *J* = 8.6 Hz, 2H), 0.99 (s, 9H), 0.25 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 191.0, 161.5, 132.0 (2C), 130.4, 120.5 (2C), 25.6 (3C), 18.3, -4.3 (2C).

benzyl (4-formylphenyl)carbamate (4ad)



General procedure was applied to 3ad (0.585 mmol, 0.202 g). The crude product was purified using flash column chromatography using 50% ethyl acetate in pentane as eluent to obtain 0.123 g of a yellow solid (82% yield, **m.p.** 123-126 °C). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 9.89 (s, 1H), 7.83 (d, *J* = 8.7 Hz, 2H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.46 – 7.32 (m, 5H), 7.15 (br, 1H), 5.22 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 191.1, 152.8, 143.6, 135.6, 131.7, 131.4 (2C), 128.8 (2C), 128.7, 128.5 (2C), 118.1 (2C), 67.6.

tert-butyl (4-formylphenyl)carbamate (4ae)



General procedure was applied to 3ae (0.629 mmol, 0.196 g). The crude product was purified using flash column chromatography using 60% dichloromethane in cyclohexane as eluent to obtain 0.098 g of a white solid (70% yield, **m.p.** 136-138 °C). **^{1}H NMR (400 MHz, $CDCl_3$) δ:** 9.89 (s, 1H), 7.82 (d, *J* = 8.7 Hz, 2H), 7.55 (d, *J* = 8.6 Hz, 2H), 6.90 (br, 1H), 1.53 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 191.1, 152.1, 144.3, 135.9, 131.3 (2C), 117.8 (2C), 81.6, 28.3 (3C).

Crystal structure analysis of compounds 3n, 3o and 3p

X-ray crystallographic analysis was performed at ambient temperature (298 K) using CuKα radiation (λ = 1.54184 Å) and ω-scan measurements on an Agilent SuperNova diffractometer (Dual source, Cu at Zero configuration) equipped with an Atlas four-circle goniometer and CCD detector. Diffraction frames were processed and integrated with the CrysAlis PRO software suite[15], and empirical absorption corrections were applied using the SCALE3 ABSPACK scaling algorithm implemented in the same package. The molecular structures were solved using an iterative method and completed by Fourier difference mapping.[16] Subsequent refinements of the crystal structures were performed with SHELXL2018/3[17] and molecular as well as supramolecular graphics were generated with Mercury.[18] Electrostatic potentials mapped over Hirshfeld surfaces were performed using the CrystalExplorer program.[19] Crystallographic data for **3n**, **3o** and **3p** have been deposited at the Cambridge Crystallographic Data Center (CCDC) under deposition numbers 2486107, 2486109, and 2486108, respectively, and can be obtained from https://www.ccdc.cam.ac.uk/

The crystal structures of compounds **3n**, **3o** and **3p** were determined from single crystal X-ray diffraction experiments (Table 1). Figure 1a shows the molecular structures drawn in ORTEP style illustrating the observed conformations. The dithiane rings have chair conformations with puckering parameters values Q(Å)/θ(º)/φ(º) of 0.693(2)/180.00(17)/257(4), 0.693(5)/177.3(4)/237(6), and 0.690(2)/174.7(17)/313(2) for **3n**, **3o** and **3p**, respectively. Despite differences in their values, the dithiane rings adopt similar conformations in these examples. Figure 1b illustrates the molecular overlaps of compounds 3n-3o and 3n-3p, showing excellent structural similarity with RMS values of 0.00749 and 0.00725, respectively.

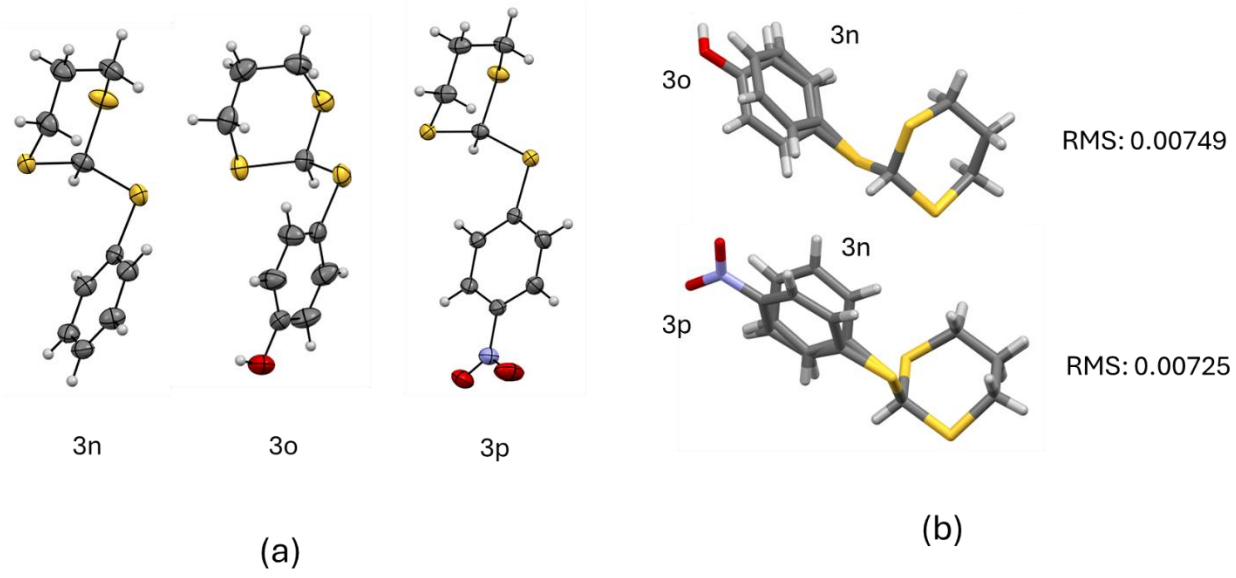


Figure 1. (a) ORTEP molecular structures with anisotropic thermal vibration ellipsoids drawn at 30% probability level. Hydrogen atoms are shown as spheres of arbitrary radius. (b) Molecular overlay showing similar conformations of dithiane rings.

Table 1. Crystallographic data and experimental details

	3n	**3o**	**3p**
Crystal data			
Chemical formula	$C_{10}H_{12}S_3$	$C_{20}H_{26}O_3S_6$	$C_{10}H_{11}NO_2S_3$
M_r	228.38	506.77	273.38
Crystal system, space group	Orthorhombic, *Pbca*	Monoclinic, $P2_1/c$	Triclinic, *P*-1
Temperature (K)	298	298	298
a, *b*, *c* (Å)	8.3092 (10), 13.1039 (11), 20.5375 (19)	22.657 (3), 5.3209 (6), 21.539 (2)	7.6276 (6), 9.1252 (9), 9.4474 (7)
α, *β*, *γ* (°)	90.0, 90.0, 90.0	90.0, 112.685 (13), 90.0	69.202 (8), 83.867 (7), 80.527 (7)

V (Å^3)	2236.2 (4)	2395.7 (5)	605.50 (9)
Z	8	4	2
Radiation type	Cu $K\alpha$	Cu $K\alpha$	Cu $K\alpha$
μ (mm^{-1})	5.66	5.43	5.48
Data collection			
Diffractometer	SuperNova, Dual, Cu at zero, Atlas	SuperNova, Dual, Cu at zero, Atlas	SuperNova, Dual, Cu at zero, Atlas
Absorption correction	Multi-scan *CrysAlis PRO* 1.171.41.119a (Rigaku Oxford Diffraction, 2021)	Multi-scan *CrysAlis PRO* 1.171.41.119a (Rigaku Oxford Diffraction, 2021)	Multi-scan *CrysAlis PRO* 1.171.41.119a (Rigaku Oxford Diffraction, 2021)
T_{min}, T_{max}	0.500, 1.000	0.422, 1.000	0.624, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7319, 2323, 2056	11360, 4976, 3708	8520, 2513, 2285
R_{int}	0.039	0.050	0.042
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.630	0.631	0.631
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.041, 0.114, 1.05	0.061, 0.214, 1.06	0.041, 0.112, 1.04
No. of reflections	2323	4976	2513
No. of parameters	119	269	145
No. of restraints	0	3	0
H-atom treatment	H-atom parameters constrained	H atoms treated by a mixture of	H-atom parameters constrained

		independent and constrained refinement	
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.35, −0.48	0.48, −0.53	0.27, −0.36

Electrostatic potentials (ESP) mapped over Hirshfeld surfaces and calculated using the B3LYP method with the 6-31G(d,p) basis set indicates that the most electronegative potentials are calculated over the sulfur atoms (acceptor) in compound **3n** (≈ –1.2 eV), while the most electropositive potentials are found over the phenyl ring (donor) (Figure 2a). These values make these groups more prone to form stronger non-classical C-H···S hydrogen bonds, thereby influencing the crystal packing (Table 2). Despite the long H···S distances compared to classical hydrogen bonds, and in the absence of additional functional groups, the crystal structure of compound **3n** can be described as a supramolecular assembly stabilized by exclusively weak interactions, and crystallizing in an Orthorhombic, *Pbca*, space group, forming an interesting molecular pattern (Figure 2a).

The supramolecular structure of **3o** is affected by the hydroxyl group. From ESP maps, the strongest electronegative and electropositive potentials are calculated over this -OH group which participates as acceptor (non-bonding electrons over the O atom) and hydrogen donor (Figure 2b). The electropositive potential over the hydrogen atom is higher (5.121 eV) than the values observed in compound **3n** (0.8–1.1 eV), due to its more acidic character. These features change the packing perspective, and the crystal structure is mainly controlled by O-H···O hydrogen bonds, including in this case crystallized water molecules (Table 3 and Figure 2b). In this case, the molecules are organized in chains along [010] direction in a Monoclinic, $P2_1/c$, space group. Inside the chains, weak C-H···S hydrogen bonds are also possible (Table 3). However, unlike in compound **3n**, the C–H···S interactions in this case are not primarily governed by electrostatic potentials, but rather by the molecular arrangement already established by the O–H···O hydrogen-bonding architecture.

The case of **3p** is similar to the observed in **3o**. The strongest electronegative potentials are calculated over the nitro group (Figure 2c), making it the most effective hydrogen bond acceptor and forming C-H···O hydrogen bonds to connect molecules in (010) sheets (Figure

2c and Table 4). Within the sheets, C–H···S hydrogen-bond interactions complement the prevailing supramolecular architecture in a Triclinic, *P*-1, space group.

Table 2. Hydrogen-bond geometry (Å, º) for **3n**

D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
C6—H6···S3^{i}	0.93	3.01	3.889 (2)	159
C3—H3···S1^{ii}	0.93	3.04	3.807 (2)	141

Symmetry code: (i) *x*−1/2, −*y*+3/2, −*z*, (ii) -x,1/2+y,1/2-z

Table 3. Hydrogen-bond geometry (Å, º) for **3o**

D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
O14—H14···O29	0.82	1.79	2.600 (8)	170
O28—H28···O14^{i}	0.82	1.88	2.687 (6)	170
C19—H19···S21^{ii}	0.93	2.98	3.712 (4)	136
C8—H8···S7^{iii}	0.98	2.95	3.590 (4)	124
O29—H29*A*···O28^{iv}	0.86 (2)	2.08 (6)	2.771 (7)	137 (8)
O29—H29*B*···S23^{v}	0.86 (2)	2.67 (2)	3.527 (5)	176 (9)
C2—H2···S9^{iii}	0.93	2.99	3.912 (5)	171
C10—H10*B*···S23^{iii}	0.97	3.02	3.701 (5)	128

Symmetry codes: (i) −*x*+1, −*y*, −*z*+1; (ii) −*x*+1, *y*+1/2, −*z*+1/2; (iii) −*x*, *y*−1/2, −*z*+1/2; (iv) −*x*+1, −*y*+1, −*z*+1; (v) *x*, −*y*+1/2, *z*+1/2.

Table 4. Hydrogen-bond geometry (Å, º) for **3p**

D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
C3—H3···S2	0.93	3.02	3.450 (2)	110
C5—H5···O2^{i}	0.93	2.54	3.285 (3)	137
C8—H8*B*···O1^{ii}	0.97	2.56	3.336 (3)	137

Symmetry codes: (i) *x*+1, *y*, *z*; (ii) *x*+1, *y*, *z*+1.

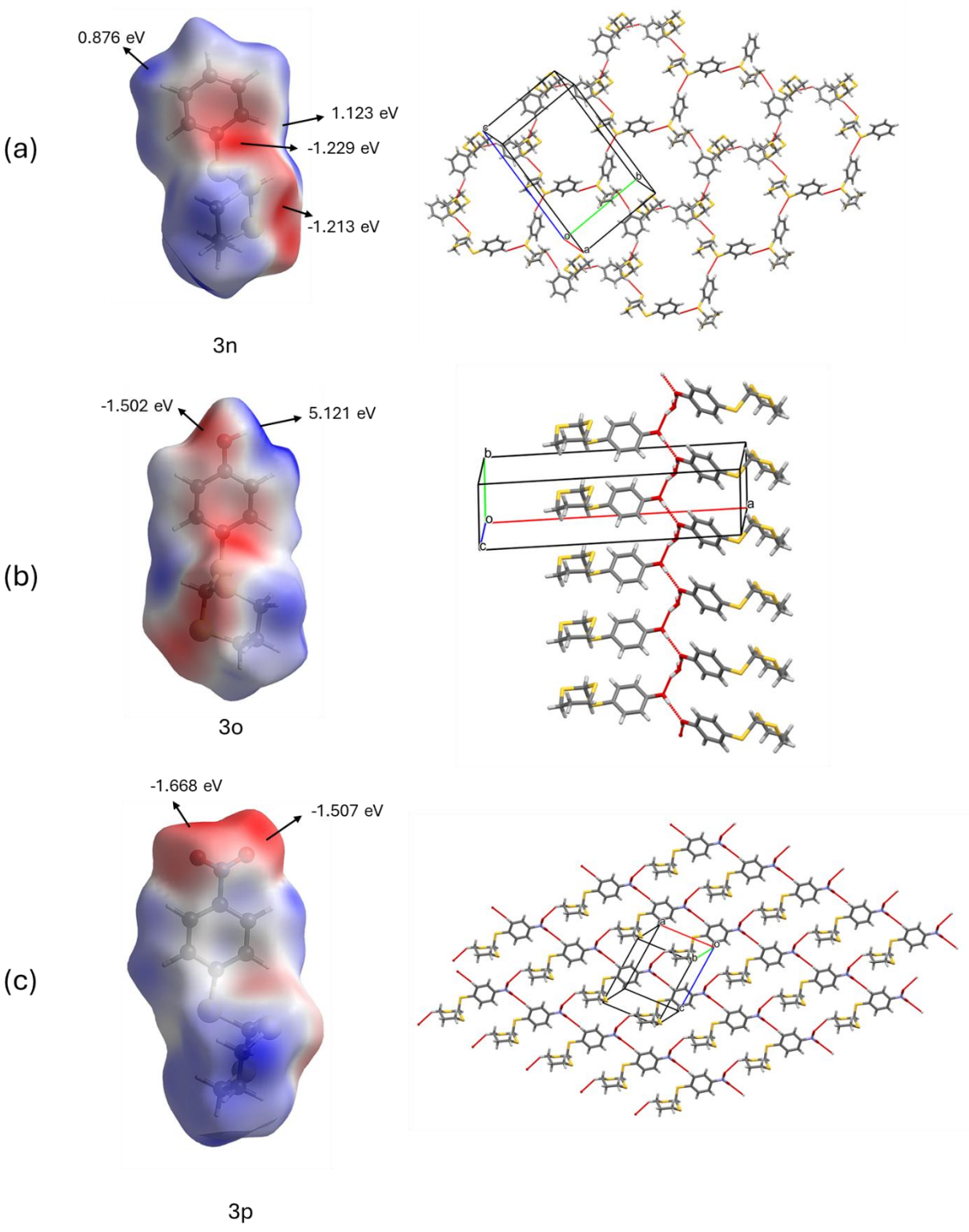


Figure 3. ESPs mapped on Hirshfeld surfaces mapped over the range −0.05 a.u. (red), through zero (white), to 0.05 a.u. (blue), and crystal packing for (a) **3n**, (b) **3o**, and (c) **3p**.

References

(1) Antoniak, D.; Barbasiewicz, M. Corey–Chaykovsky Cyclopropanation of Nitronaphthalenes: Access to Benzonorcaradienes and Related Systems. *Org. Lett.* **2019**, *21* (23), 9320-9325. DOI: 10.1021/acs.orglett.9b03375.

(2) Zhang, B.-S.; Jia, W.-Y.; Wang, Y.-M.; Oliveira, J. C. A.; Warratz, S.; Zhang, Z.-Q.; Gou, X.-Y.; Liang, Y.-M.; Wang, X.-C.; Quan, Z.-J.; et al. Template Synthesis to Solve the Unreachable Ortho C–H Functionalization Reaction of Aryl Iodide. *J. Org. Chem.* **2023**, *88* (23), 16539-16546. DOI: 10.1021/acs.joc.3c02014.

(3) Garay-Talero, A.; Acosta-Guzmán, P.; Gamba-Sánchez, D. Regioselective Organocatalyzed Monochlorination of Arenes with Electrophilic Chlorosulfoniums. *Adv. Synth. Catal.* **2023**, *365* (24), 4576-4582. DOI: 10.1002/adsc.202300971

(4) Shaterian, H. R.; Hosseinian, A.; Ghashang, M. Chemoselective Dithioacetalization and Oxathioacetalization of Carbonyl Compounds Using Alumina Sulfuric Acid as Catalyst. *Synth Commun.* **2008**, *38* (23), 4097-4106. DOI: 10.1080/00397910802272022.

(5) Arakawa, Y.; Mihara, T.; Fujii, H.; Minagawa, K.; Imada, Y. An uncommon use of irradiated flavins: Brønsted acid catalysis. *Chem Commun.* **2020**, *56* (42), 5661-5664, 10.1039/D0CC01960G. DOI: 10.1039/D0CC01960G.

(6) Xing, Z.; Yang, M.; Sun, H.; Wang, Z.; Chen, P.; Liu, L.; Wang, X.; Xie, X.; She, X. Visible-light promoted dithioacetalization of aldehydes with thiols under aerobic and photocatalyst-free conditions. *Green Chem.* **2018**, *20* (22), 5117-5122, 10.1039/C8GC02237B. DOI: 10.1039/C8GC02237B.

(7) Vale, J. R.; Rimpiläinen, T.; Sievänen, E.; Rissanen, K.; Afonso, C. A. M.; Candeias, N. R. Pot-Economy Autooxidative Condensation of 2-Aryl-2-lithio-1,3-dithianes. *J. Org. Chem.* **2018**, *83* (4), 1948-1958. DOI: 10.1021/acs.joc.7b02896.

(8) Lai, J.; Du, W.; Tian, L.; Zhao, C.; She, X.; Tang, S. Fe-Catalyzed Direct Dithioacetalization of Aldehydes with 2-Chloro-1,3-dithiane. *Org. Lett.* **2014**, *16* (17), 4396-4399. DOI: 10.1021/ol502276r.

(9) Arnodo, D.; Meazzo, C.; Baldino, S.; Blangetti, M.; Prandi, C. Efficient and Low-Impact Acetalization Reactions in Deep Eutectic Solvents. *Chemistry.* **2023**, *29* (36), e202300820. DOI: 10.1002/chem.202300820 From NLM.

(10) Jung, N.; Grässle, S.; Lütjohann, D. S.; Bräse, S. Solid-Supported Odorless Reagents for the Dithioacetalization of Aldehydes and Ketones. *Org. Lett.* **2014**, *16* (4), 1036-1039. DOI: 10.1021/ol403313h.

(11) Liu, L.; Wang, G.; Jiao, J.; Li, P. Sulfur-Directed Ligand-Free C–H Borylation by Iridium Catalysis. *Org. Lett.* **2017**, *19* (22), 6132-6135. DOI: 10.1021/acs.orglett.7b03008.

(12) Mohammadzadeh Dovvom, H.; Akhlaghinia, B. Facile chemoselective dithioacetalization of carbonyl compounds promoted by Fe3O4@MCM-41-GPTMS-Gu-CuIINPs as an efficient magnetic nanostructured catalyst. *Phosphorus Sulfur Silicon Relat. Elem*. **2023**, *198* (9), 752-764. DOI: 10.1080/10426507.2023.2194651.

(13) Haque, A.-M. J.; Kwon, S.-R.; Park, H.; Kim, T.-H.; Oh, Y.-S.; Choi, S.-Y.; Hong, J.-D.; Kim, K. Use of 1,3-dithiane combined with aryldiazonium cation for immobilization of biomolecules based on electrochemical addressing. *Chem. Commun.* **2009**, (32), 4865-4867, 10.1039/B909244G. DOI: 10.1039/B909244G.

(14) Abe, Y.; Yamada, T.; Yamamoto, T.; Esaka, Y.; Ikawa, T.; Sajiki, H. Electrochemically assisted deprotection of acetals, ketals, and dithioacetals under neutral conditions. *Green Chem.* **2025**, *27* (19), 5464-5470, 10.1039/D4GC06348A. DOI: 10.1039/D4GC06348A.

(15) CrysAlisPro 1.171.39.46e, Rigaku Oxford Diffraction, 2018.

(16) L. Palatinus and G. Chapuis, *J. Appl. Crystallogr*., 2007, **40**, 786–790.

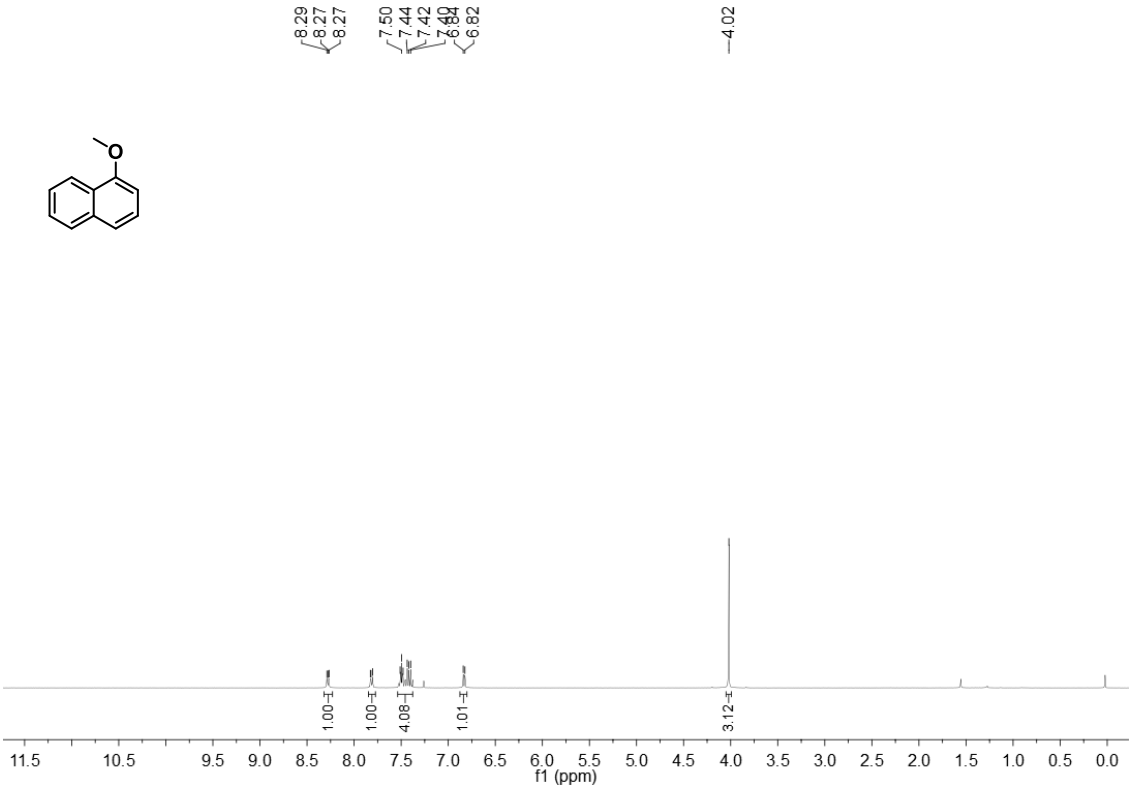
(17) G. M. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem*., 2015, **71**, 3–8.

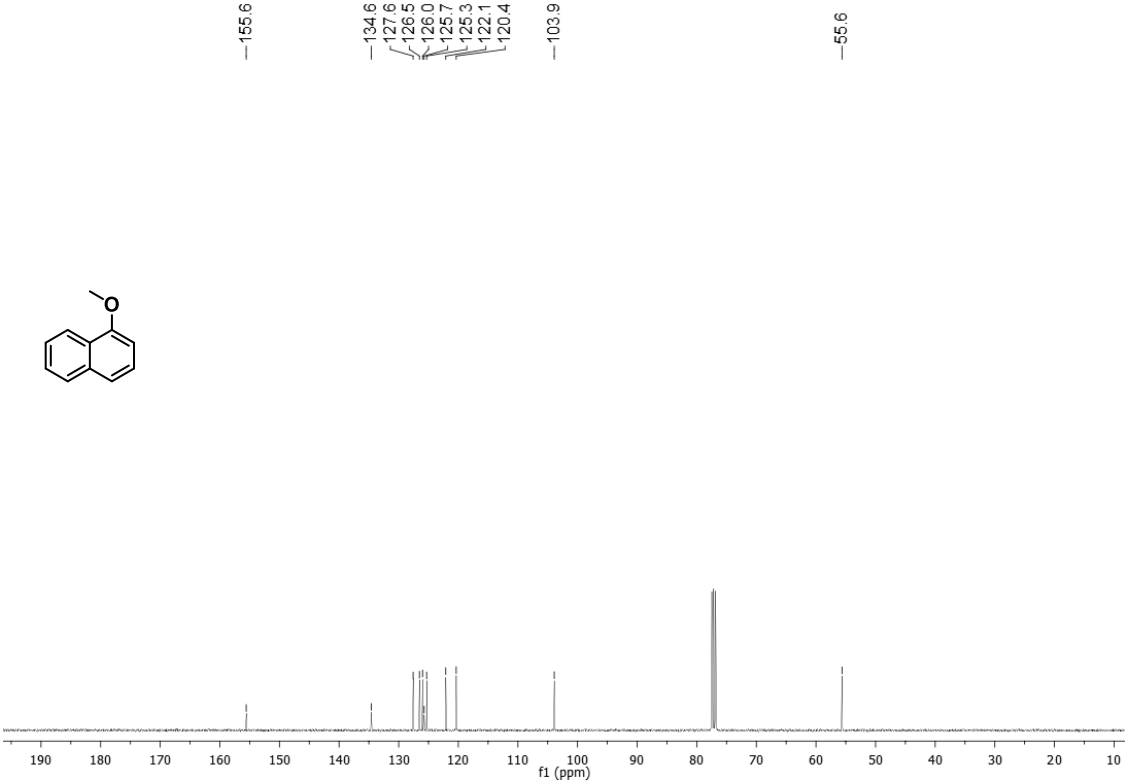
(18) C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *J. Appl. Crystallogr*., 2008, **41**, 466–470.

(19) M. J. Turner, J. J. McKinnon, S. K. Wolff, D. J. Grimwood, P. R. Spackman, D. Jayatilaka and M. A. Spackman, CrystalExplorer17, University of Western Australia, 2017.

NMR Spectra of all compounds

1-methoxynaphthalene (2k)





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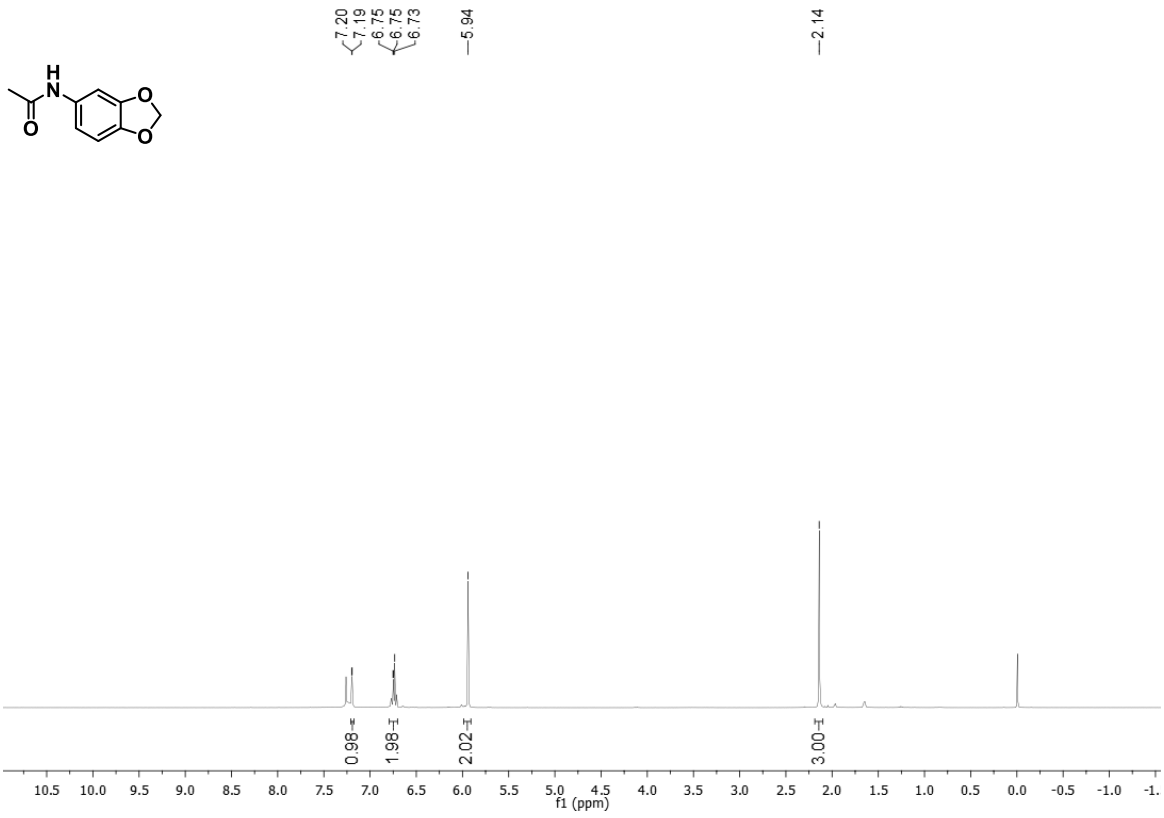

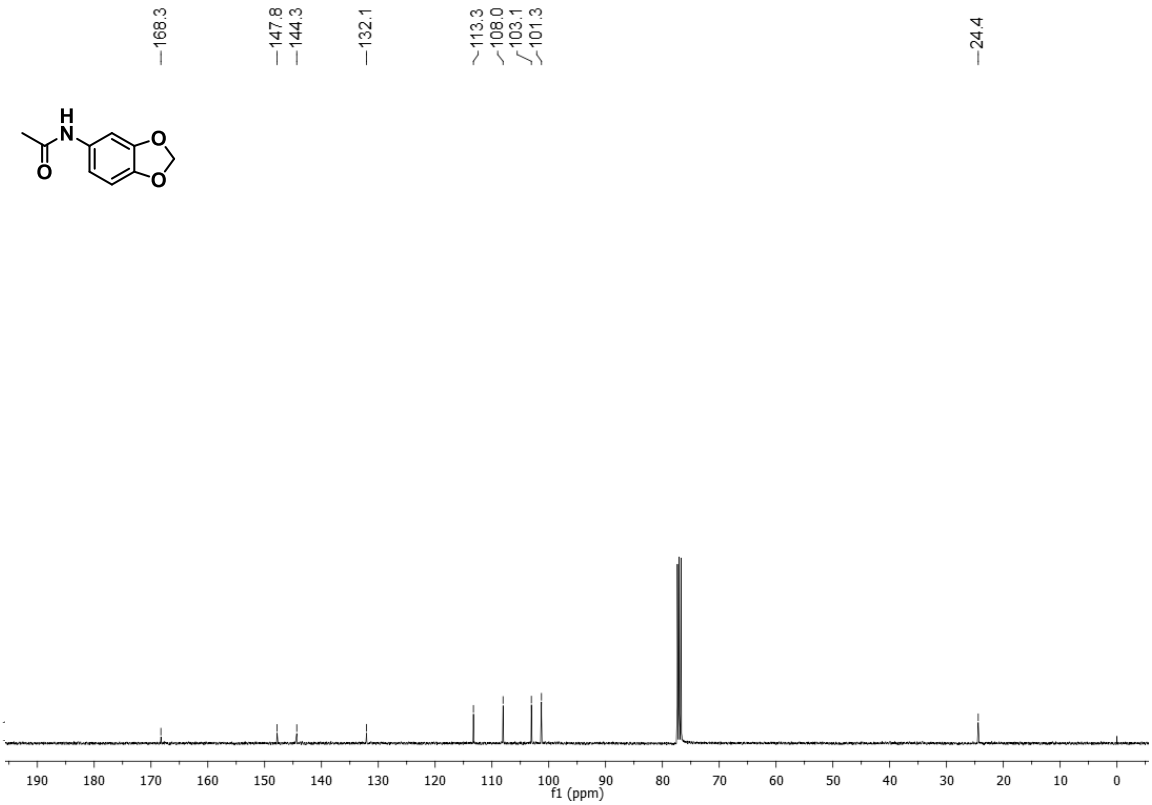

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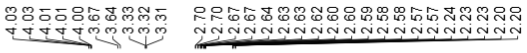
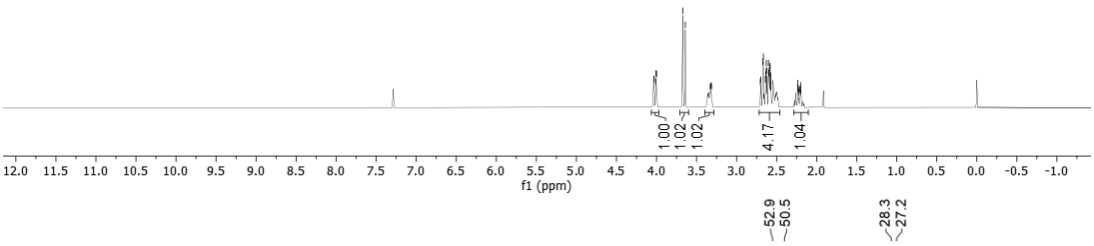
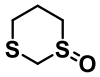
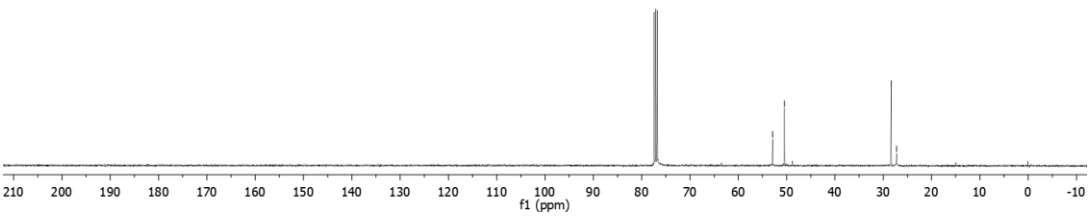
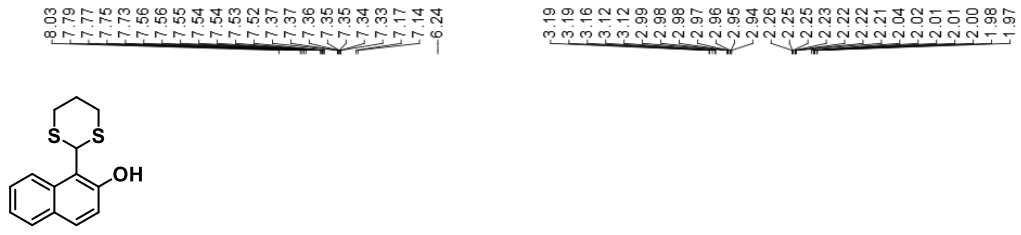


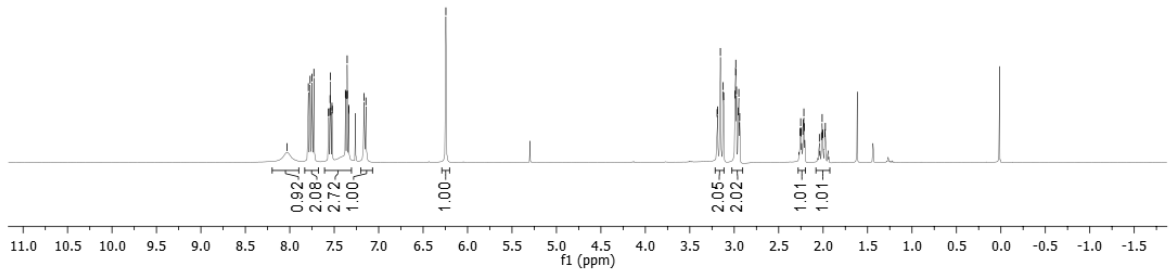


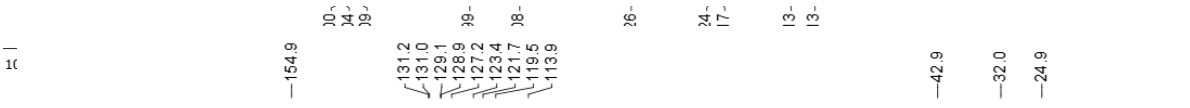


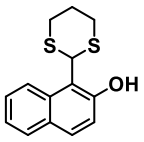


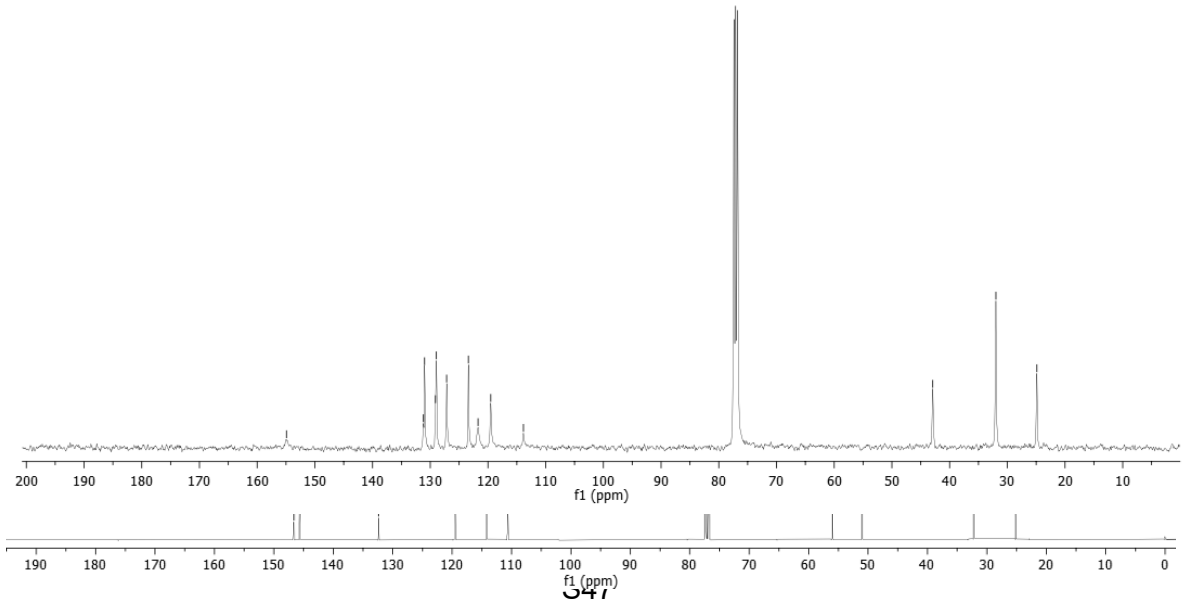
1-(1,3-dithian-2-yl)naphthalen-2-ol (3a)



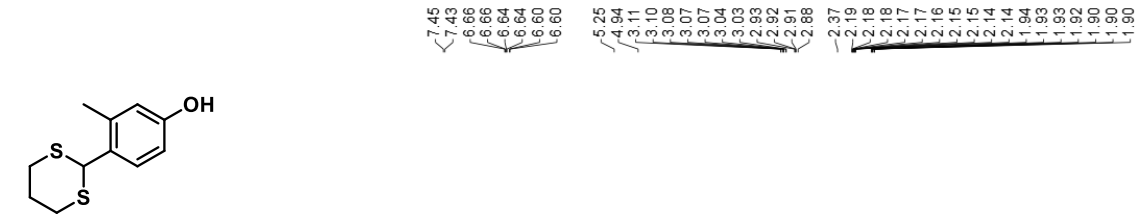


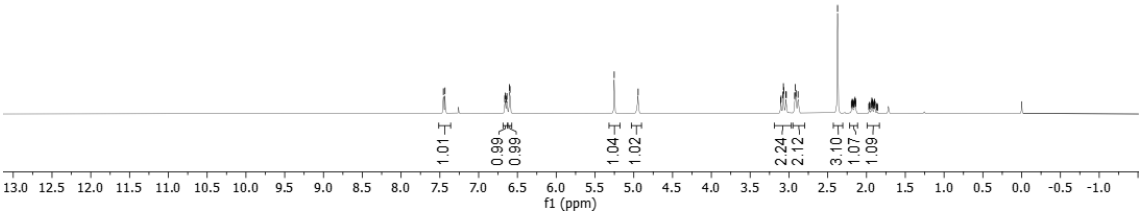


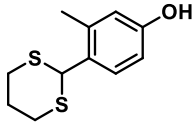


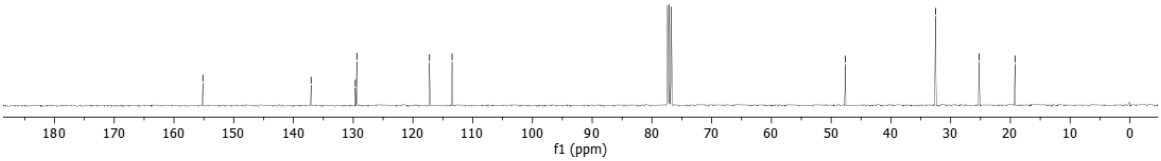


4-(1,3-dithian-2-yl)-3-methylphenol (3b)









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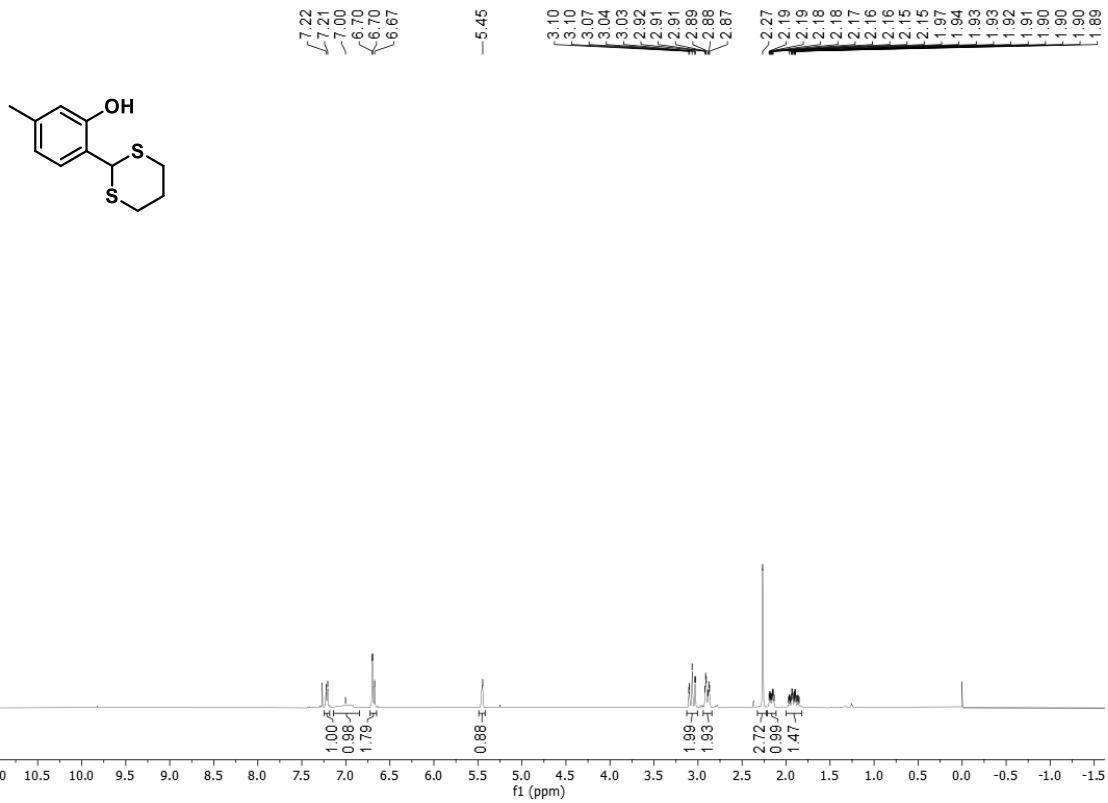

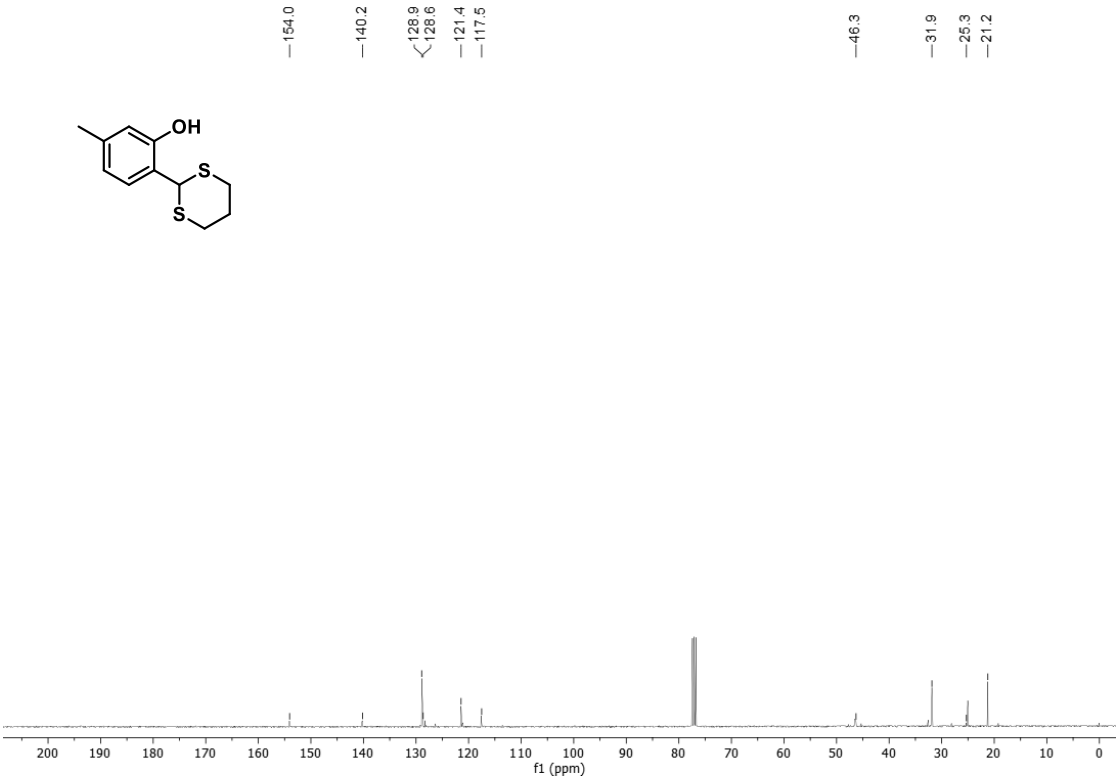

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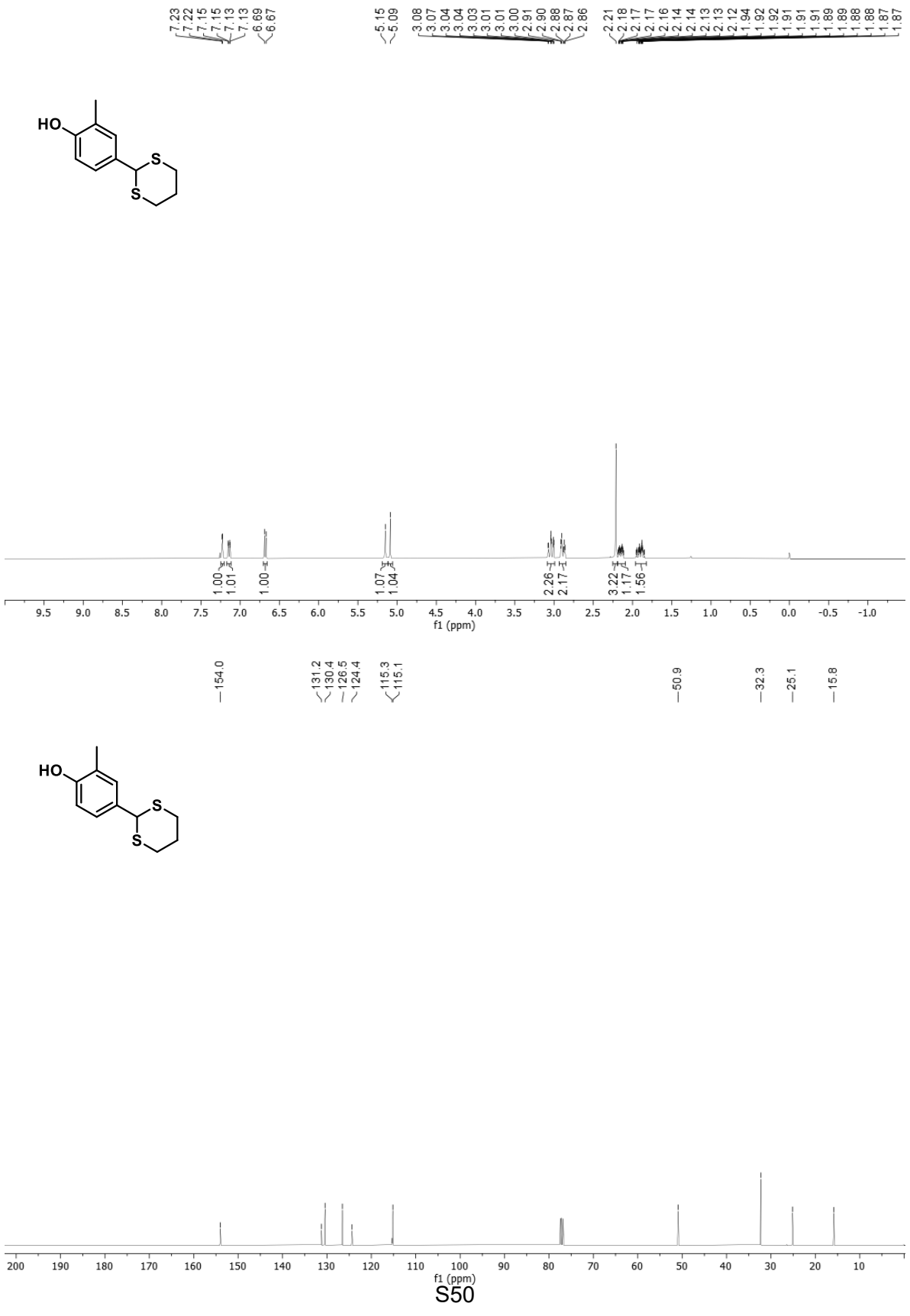

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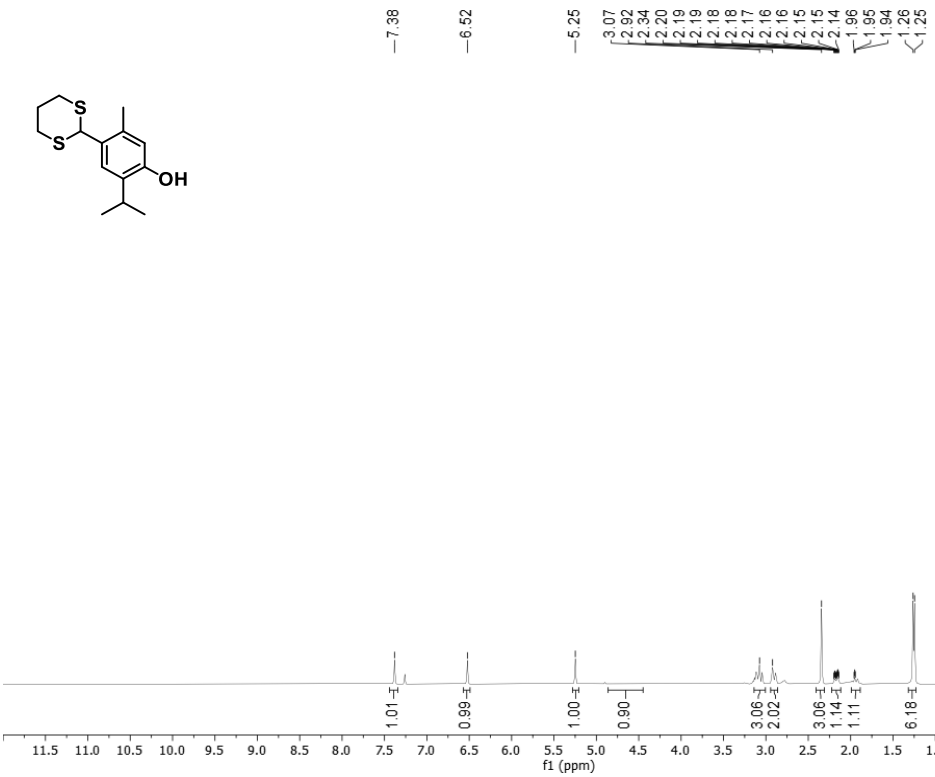

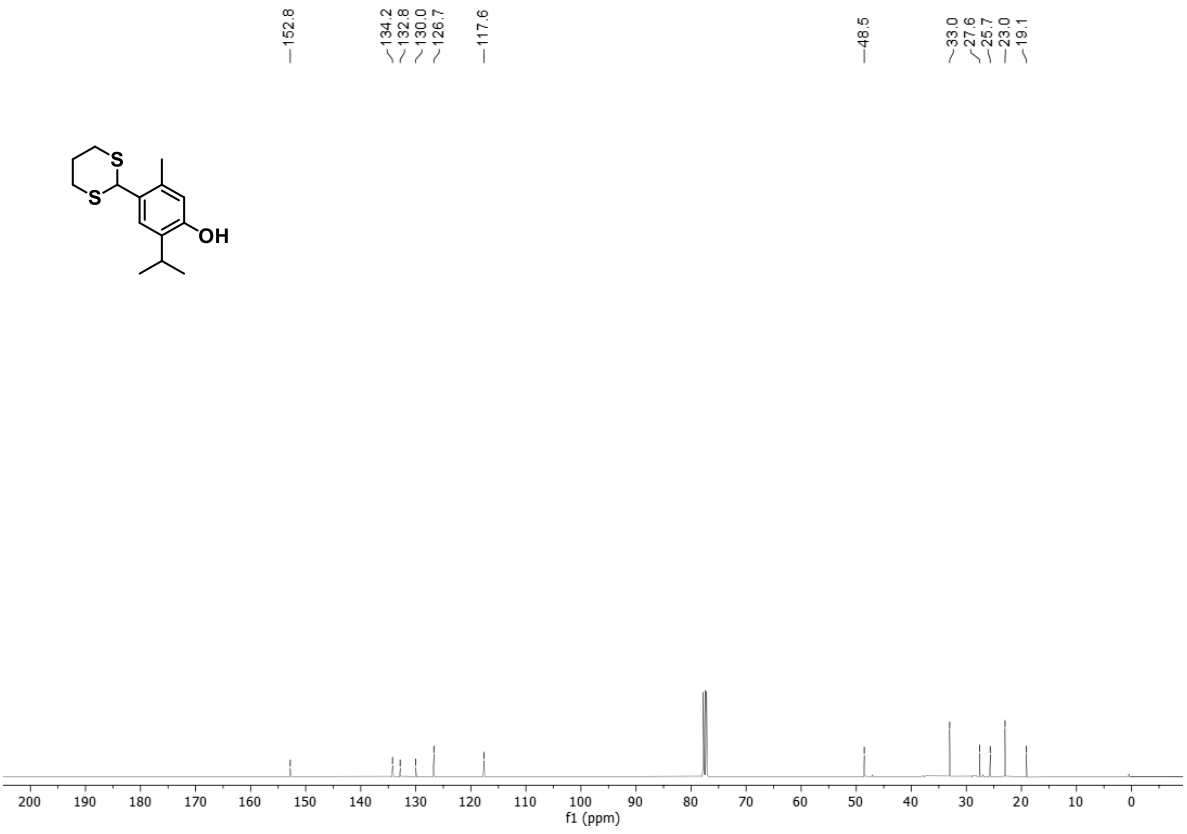

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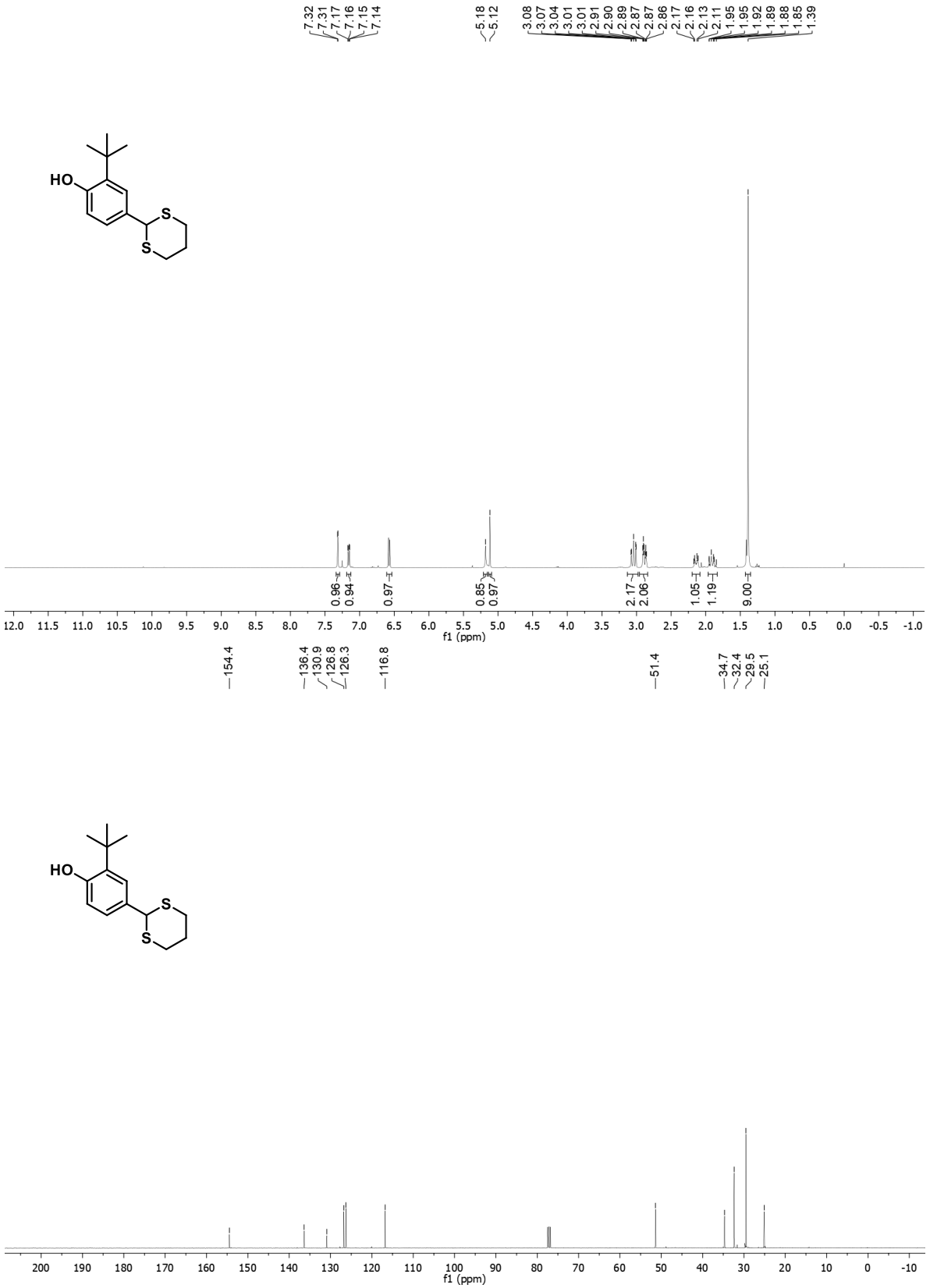
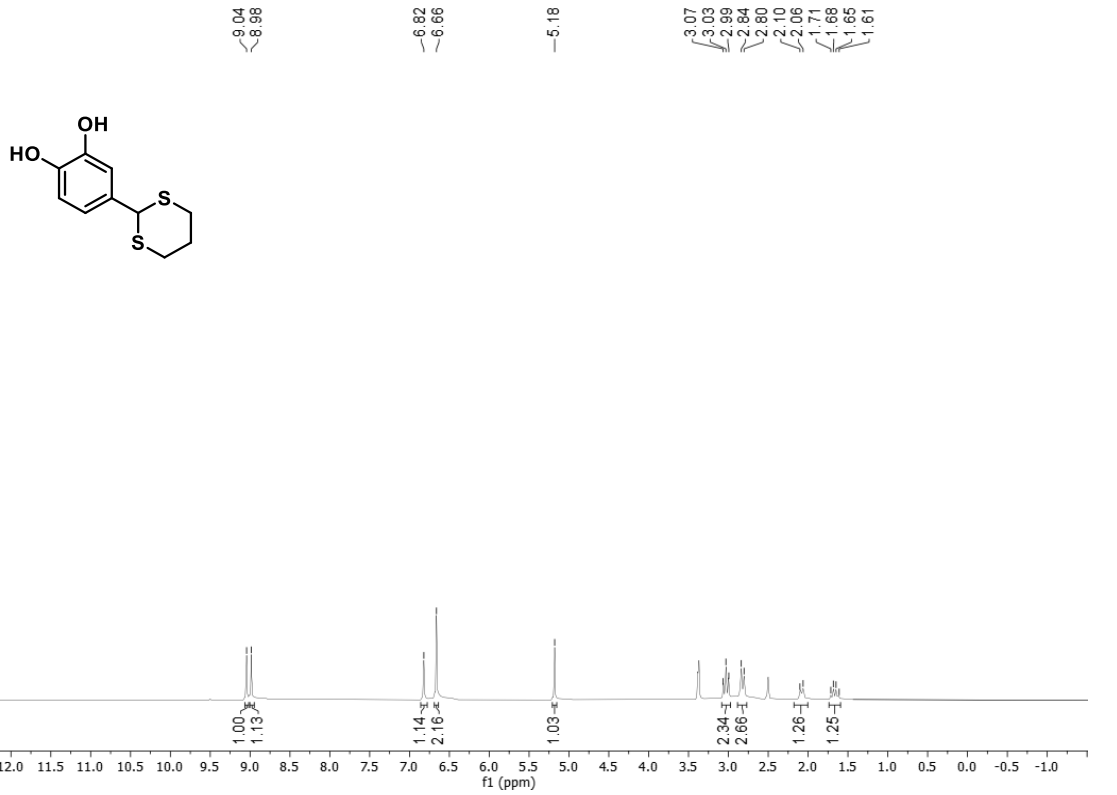
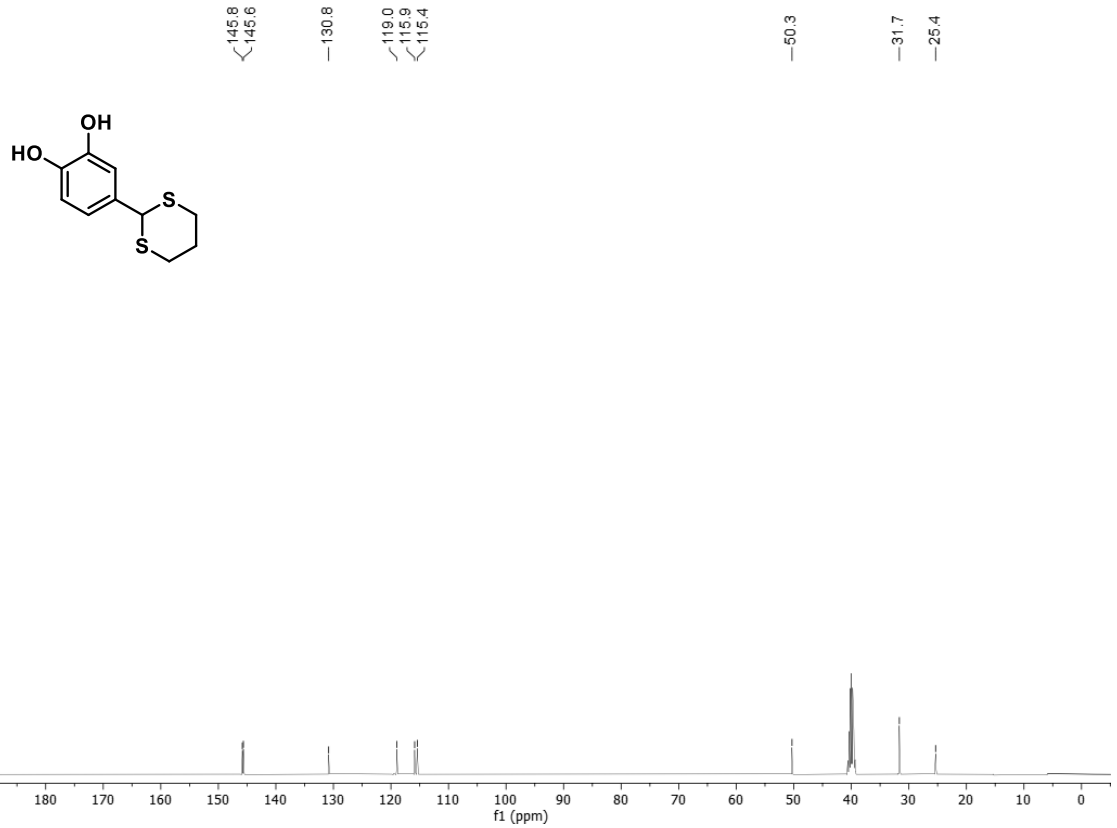
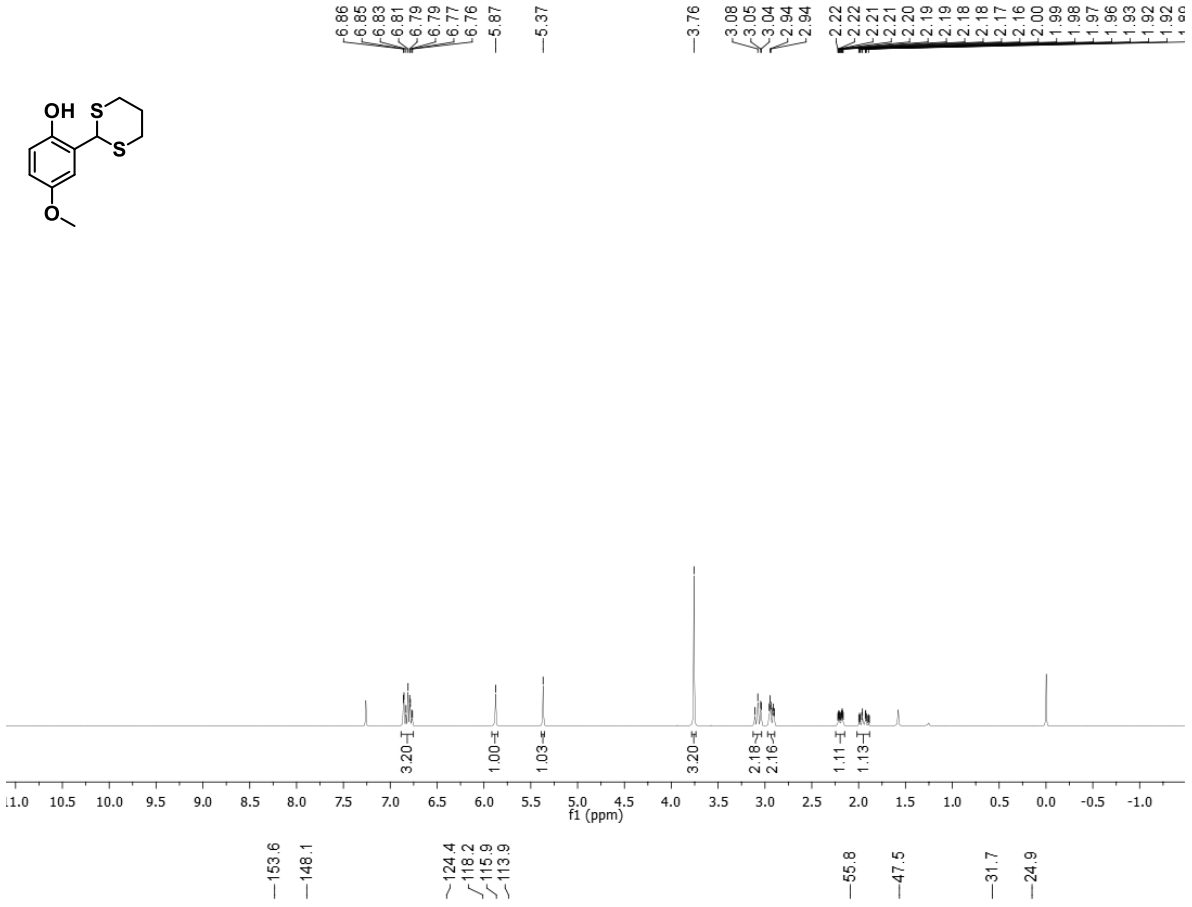


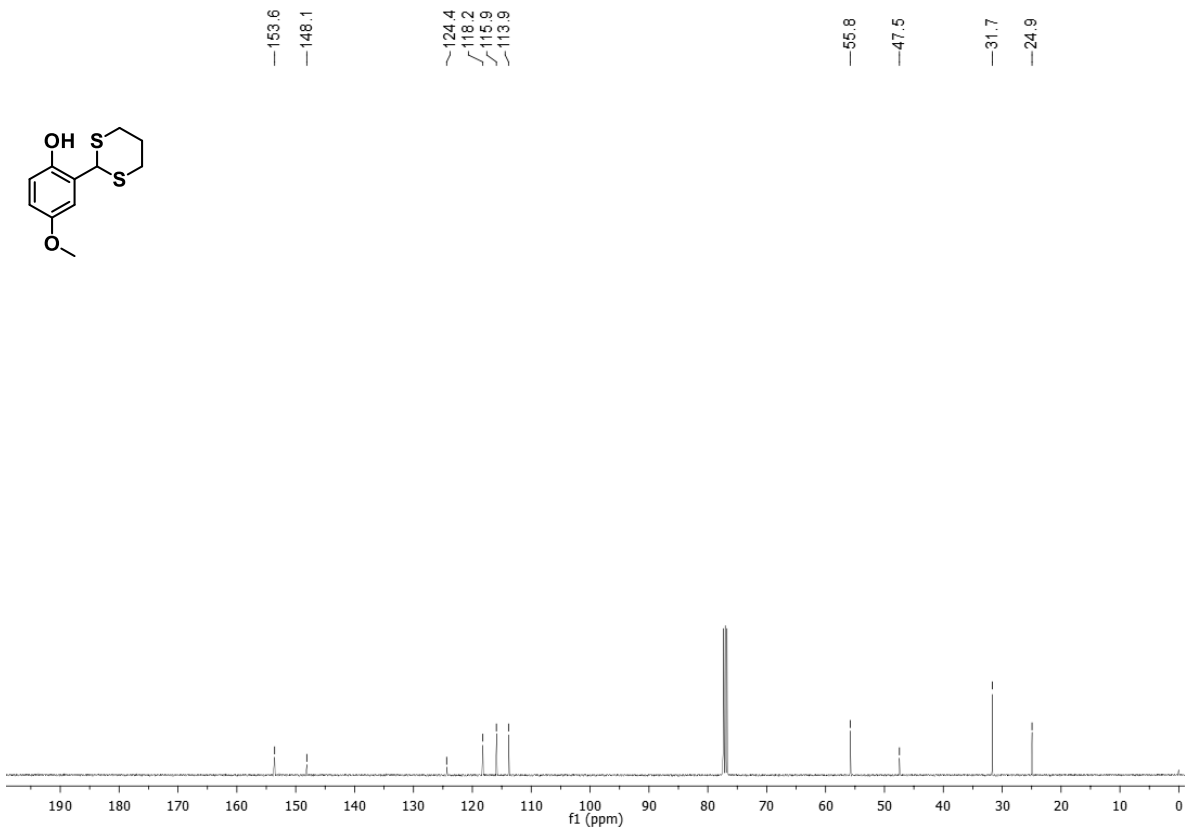
4-(1,3-dithian-2-yl)benzene-1,2-diol (3f)



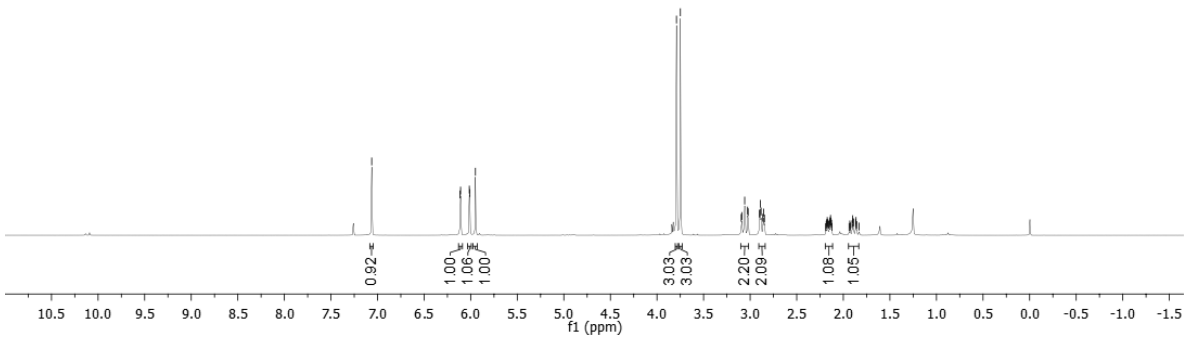


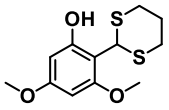
2-(1,3-dithian-2-yl)-4-methoxyphenol (3g)

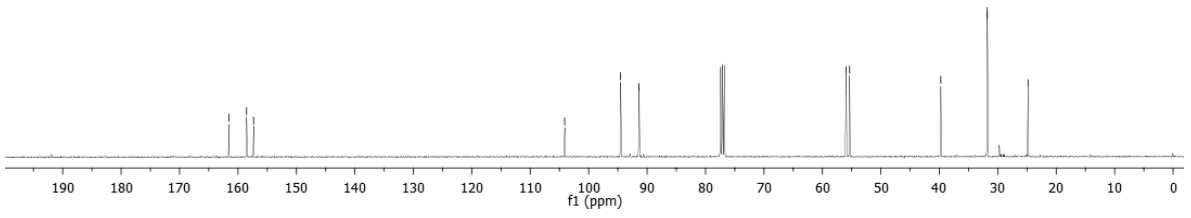




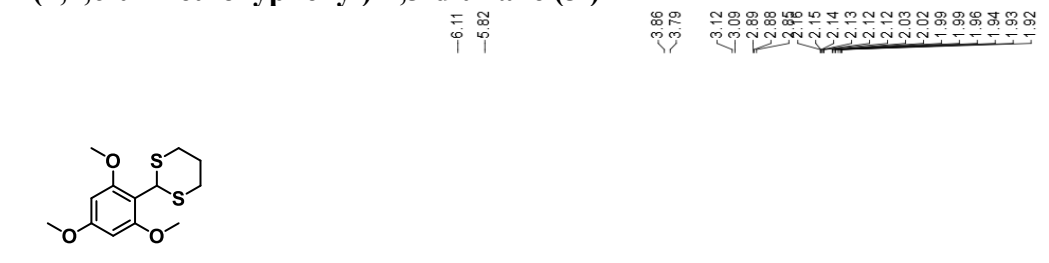
2-(1,3-dithian-2-yl)-3,5-dimethoxyphenol (3h)

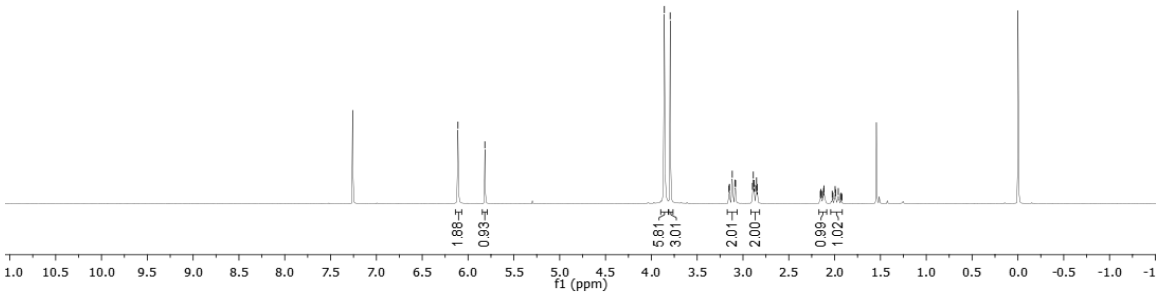


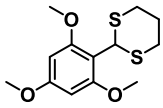


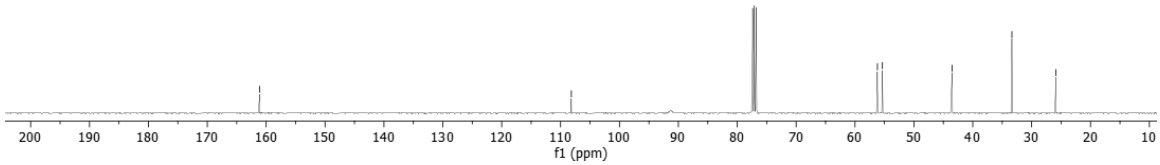


2-(2,4,6-trimethoxyphenyl)-1,3-dithiane (3i)

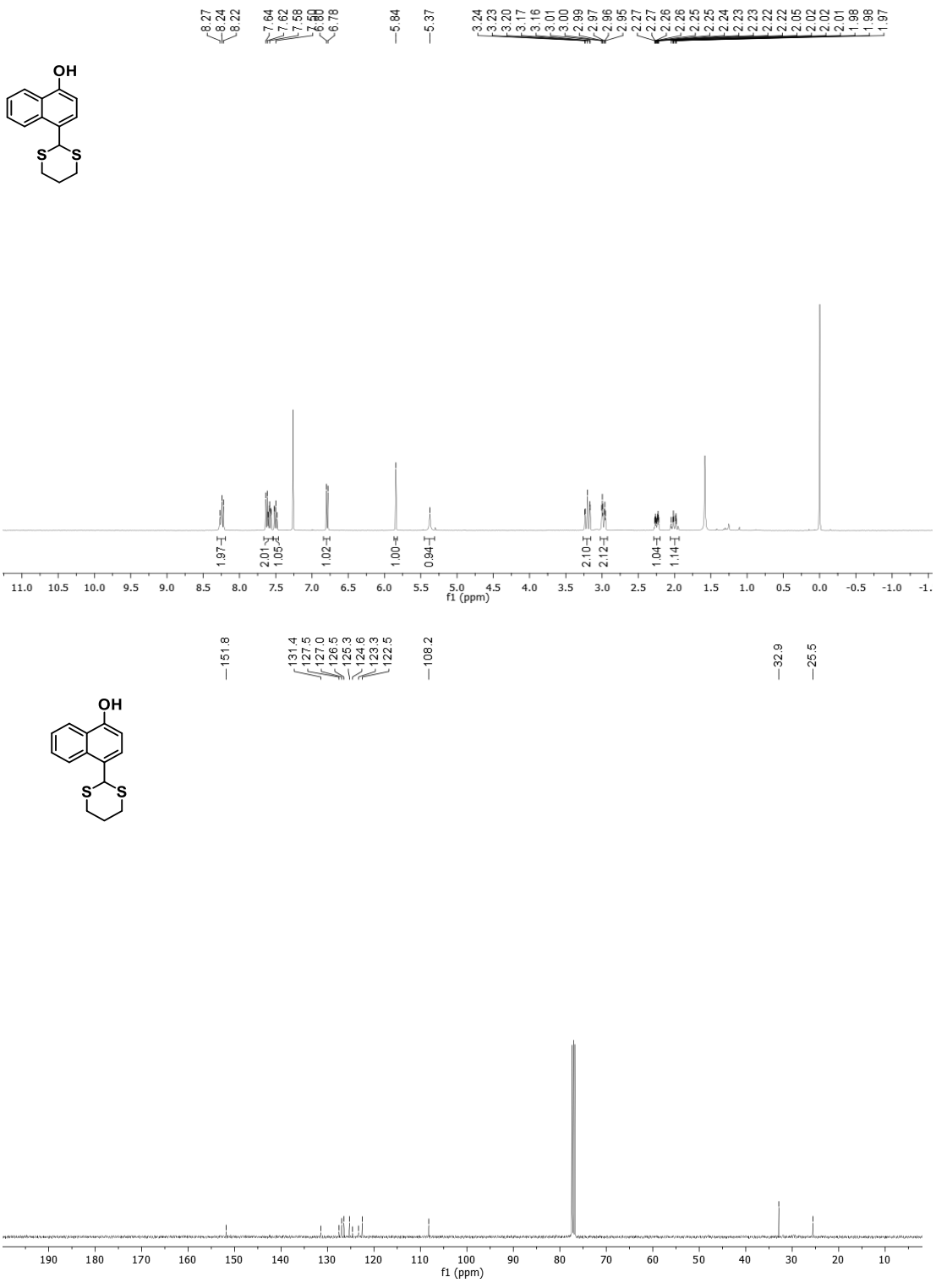




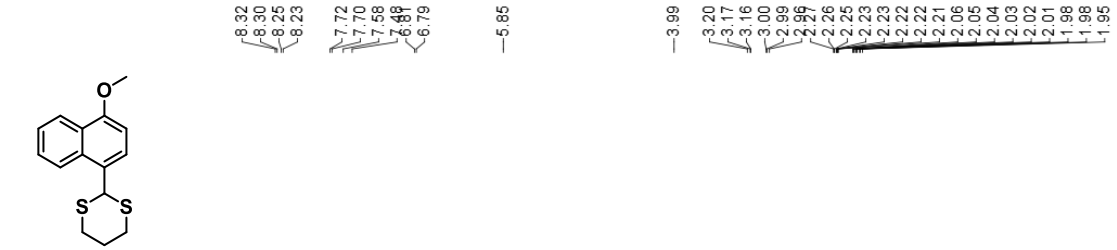


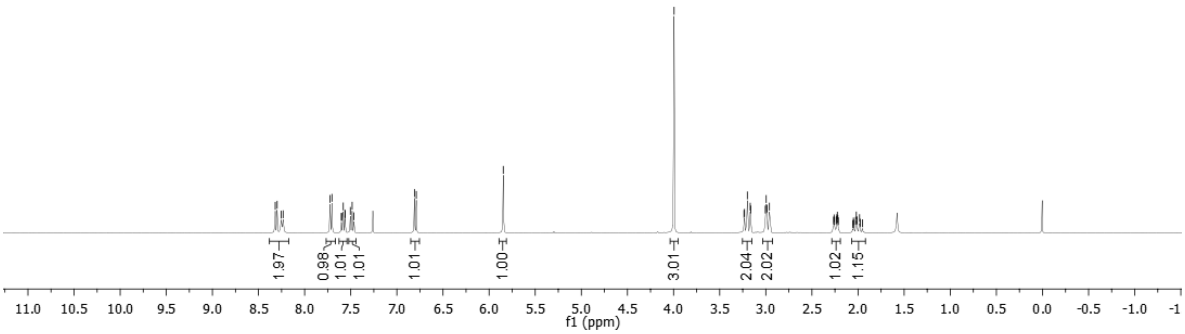


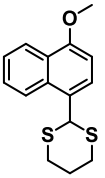
4-(1,3-dithian-2-yl)naphthalen-1-ol (3j)

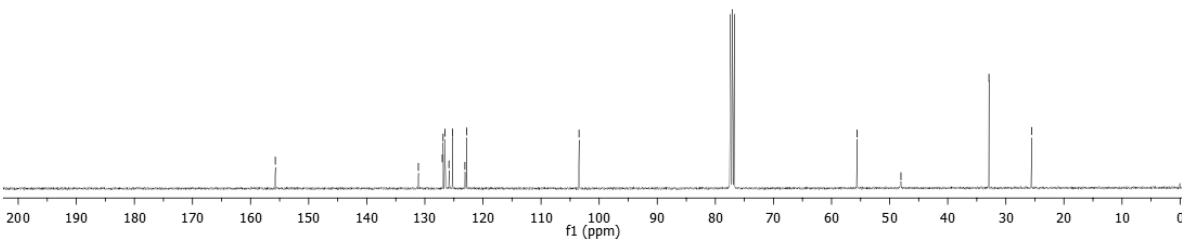


2-(4-methoxynaphthalen-1-yl)-1,3-dithiane (3k)

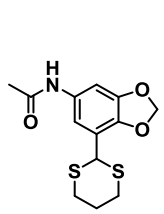


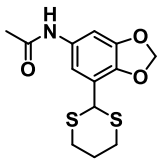


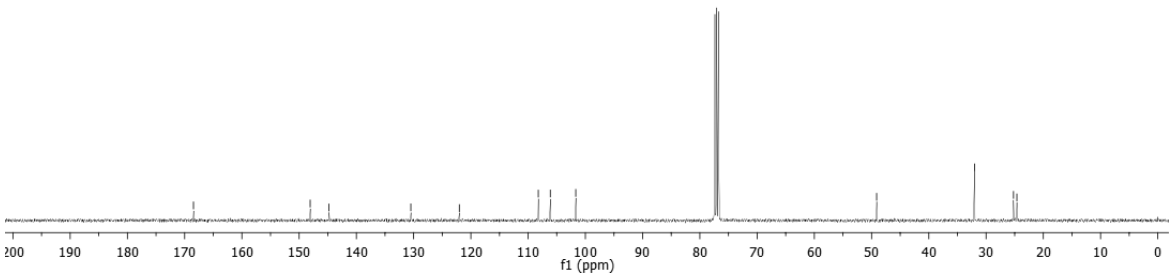




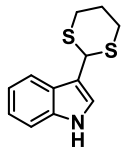
N-(4-(1,3-dithian-2-yl)benzo[d][1,3]dioxol-5-yl)acetamide (3l)

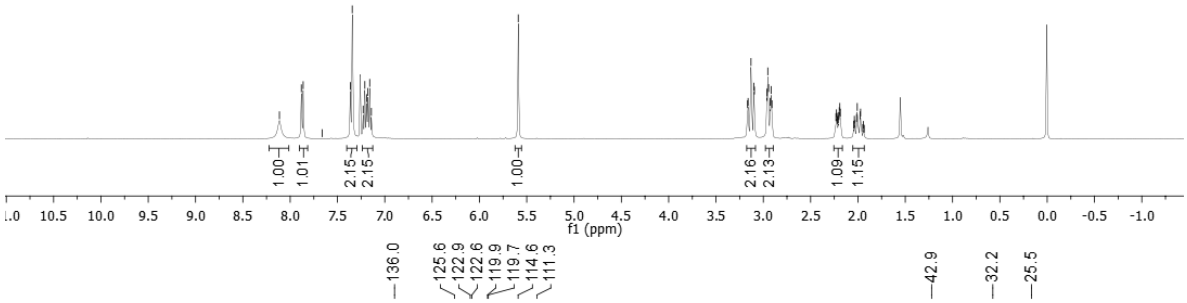


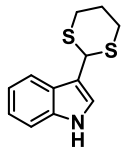


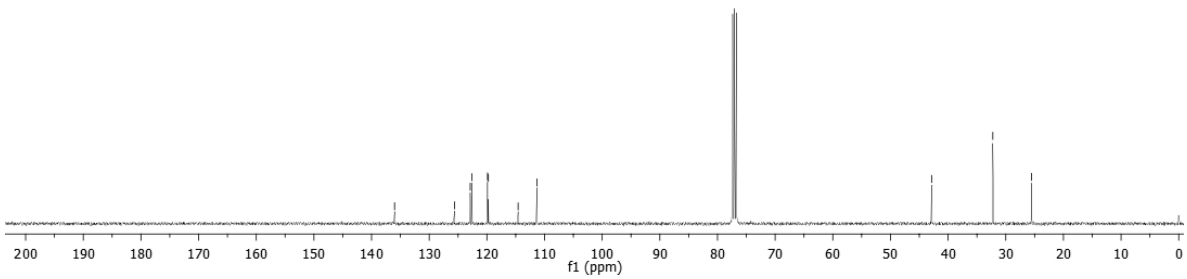


3-(1,3-dithian-2-yl)-1H-indole(3m)

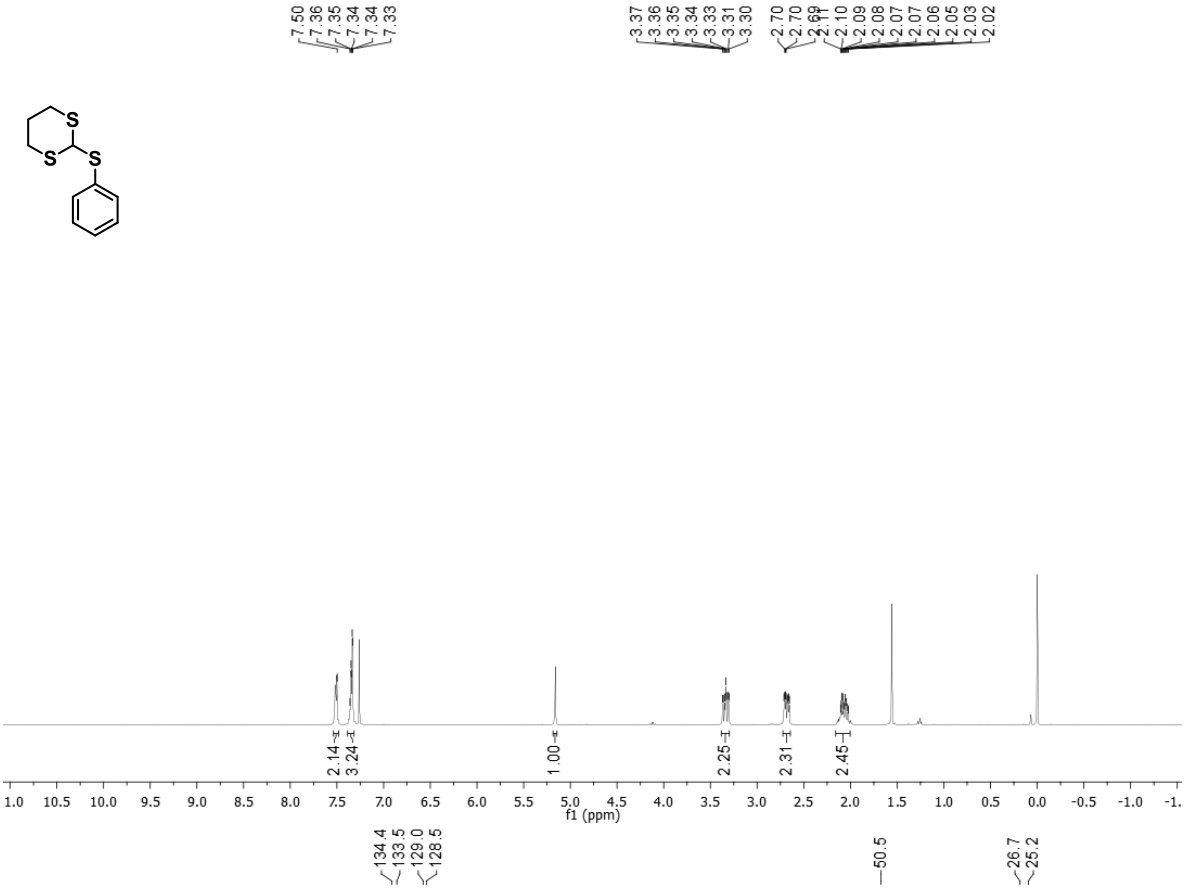




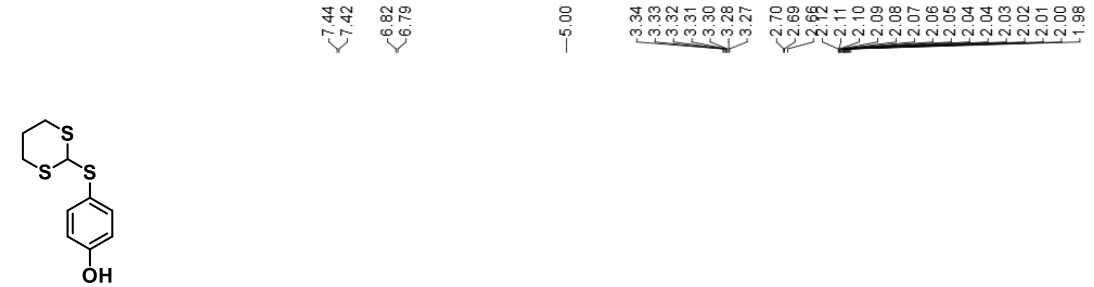


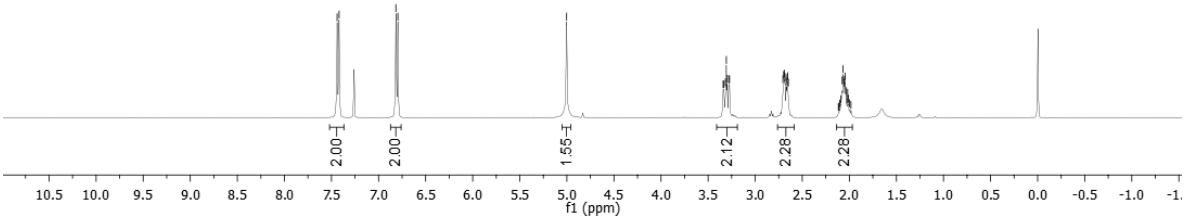


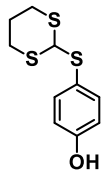
2-(phenylthio)-1,3-dithiane (3n)

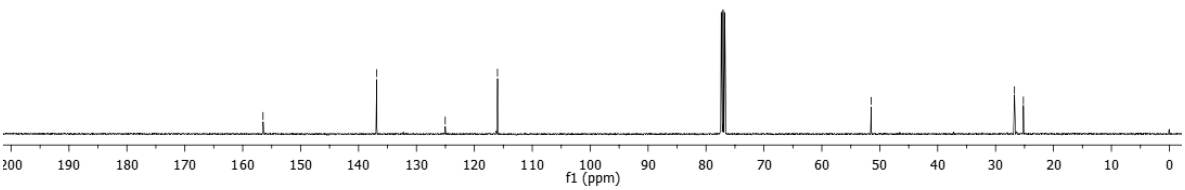


4-((1,3-dithian-2-yl)thio)phenol (3o)

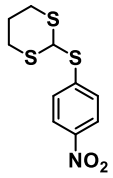


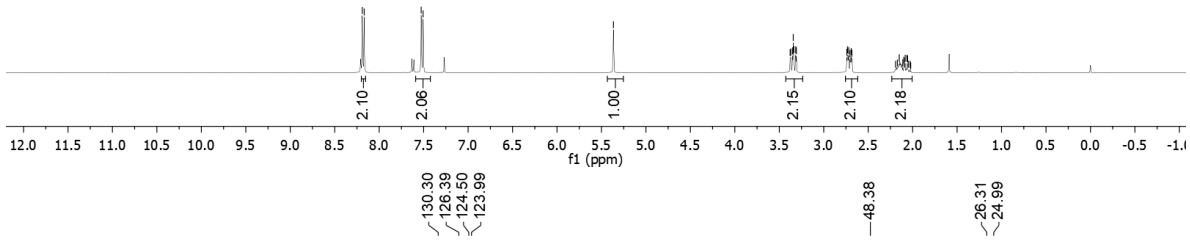


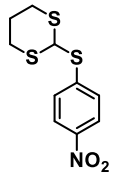


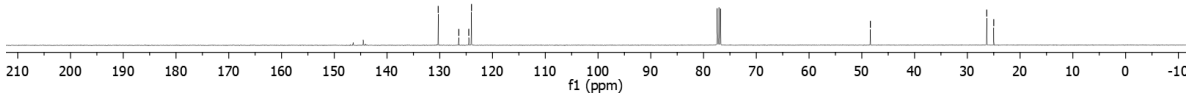


2-((4-nitrophenyl)thio)-1,3-dithiane (3p)

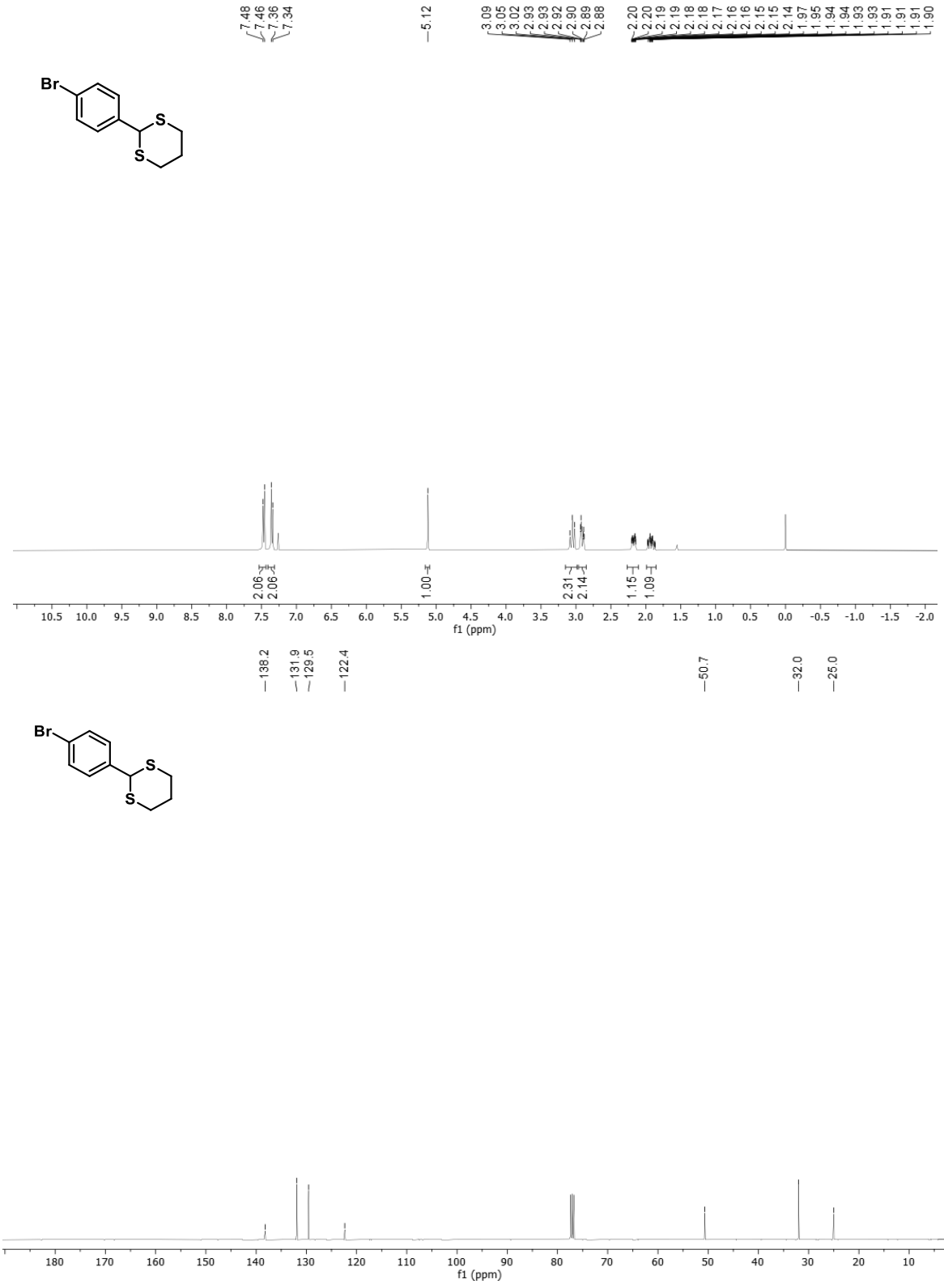




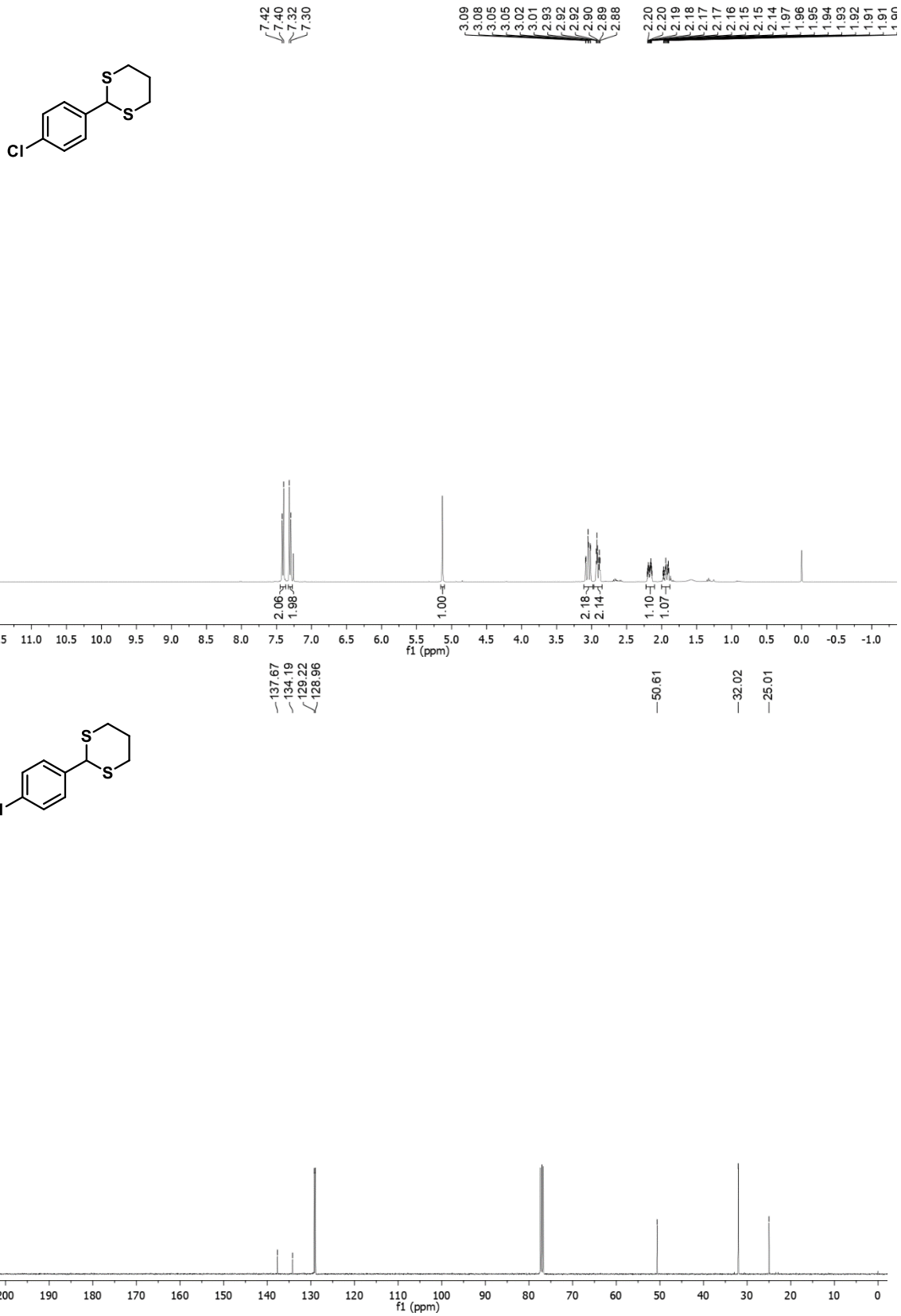




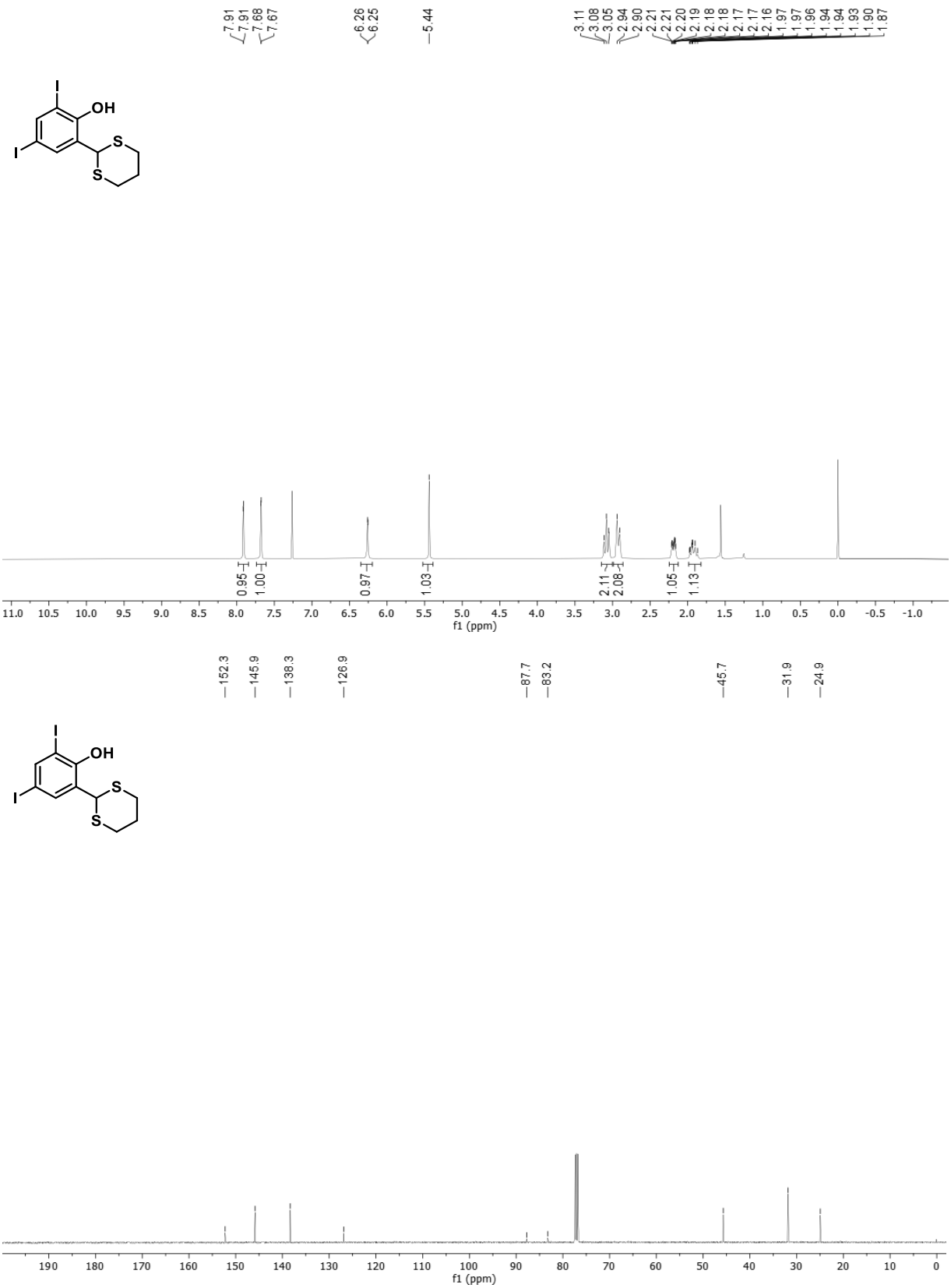
2-(4-bromophenyl)-1,3-dithiane (3q)



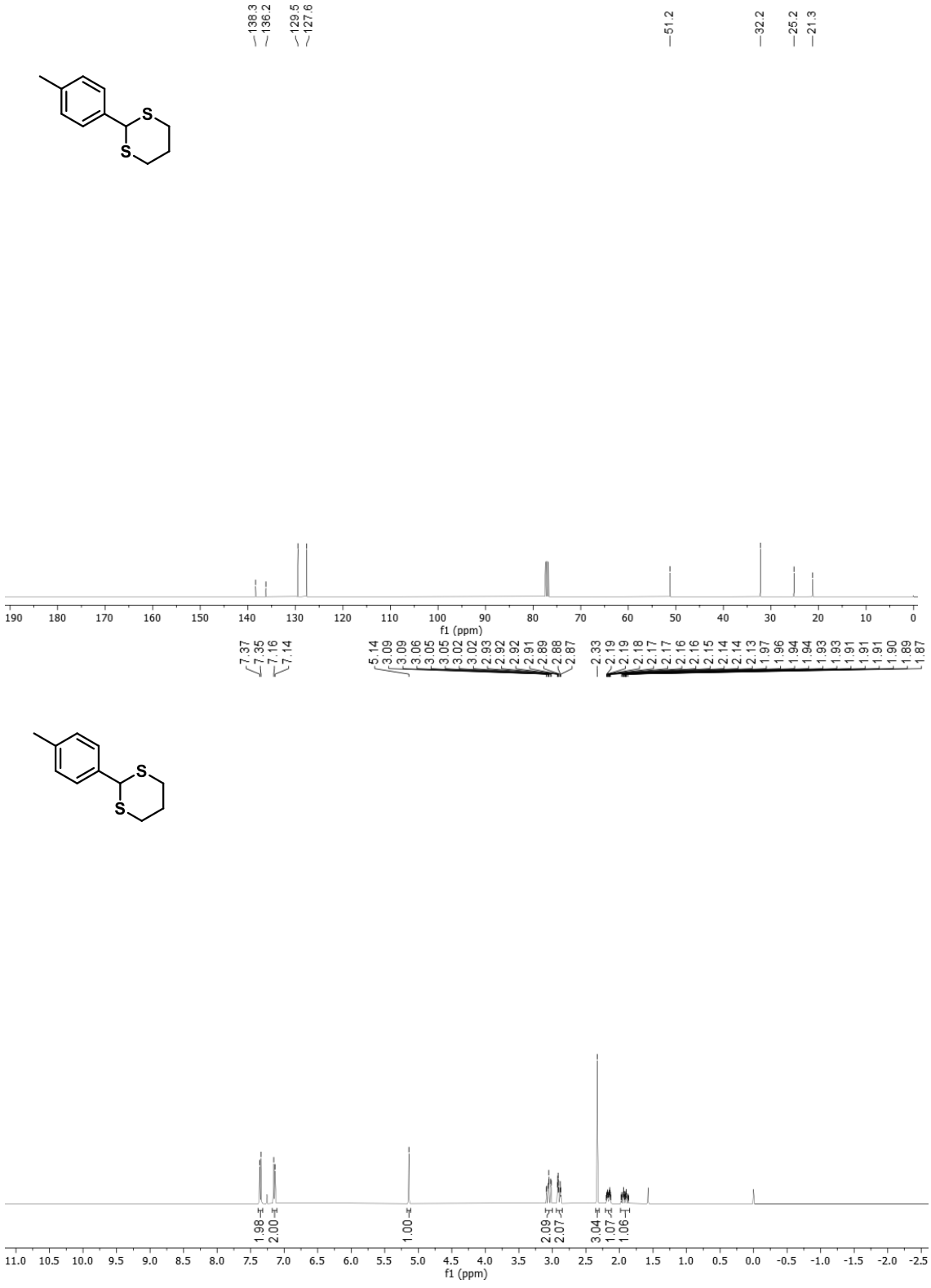
2-(4-chlorophenyl)-1,3-dithiane (3r)



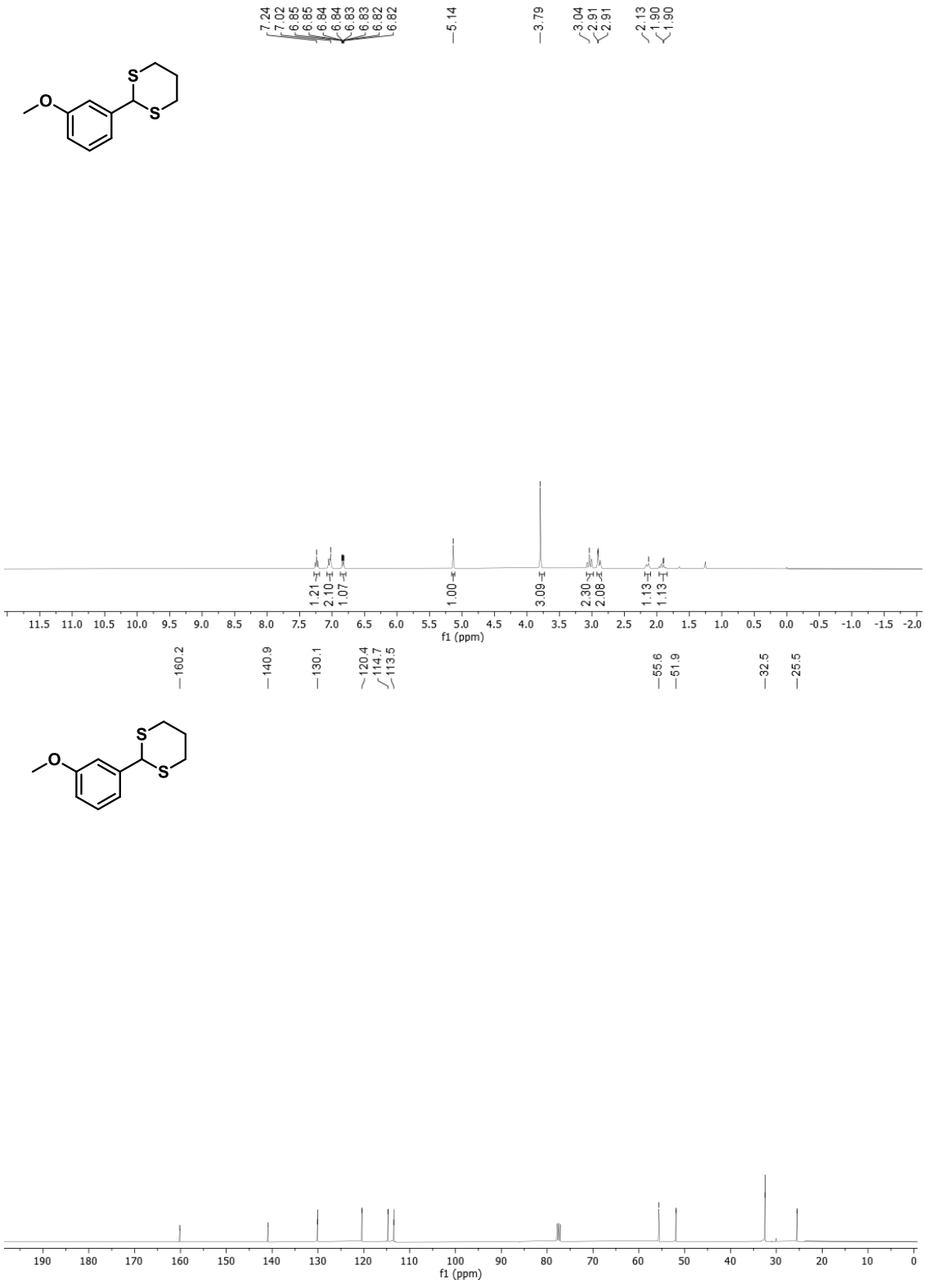
2-(1,3-dithian-2-yl)-4,6-diiodophenol (3s)



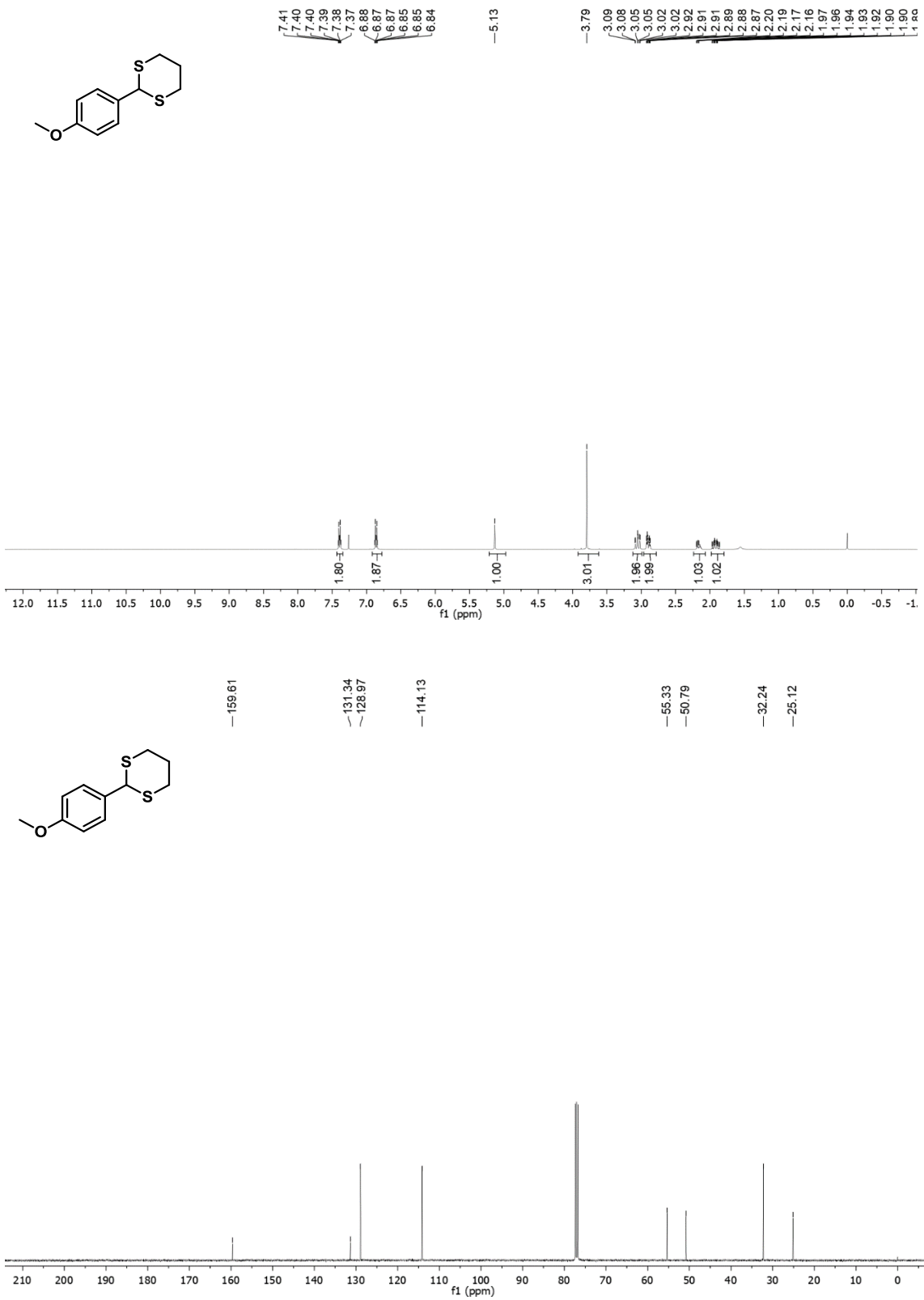
2-(p-tolyl)-1,3-dithiane (3t)



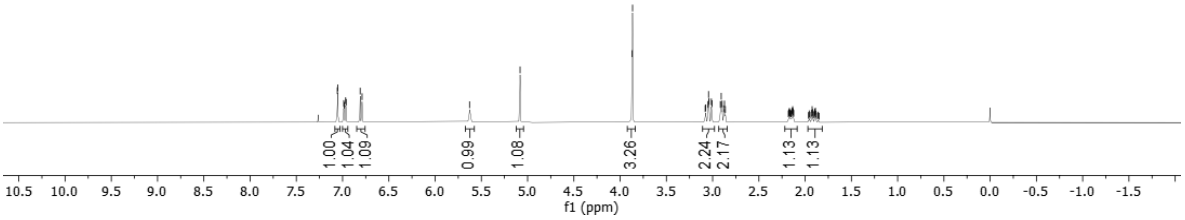
2-(3-methoxyphenyl)-1,3-dithiane (3u)

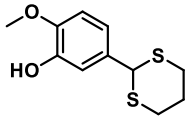


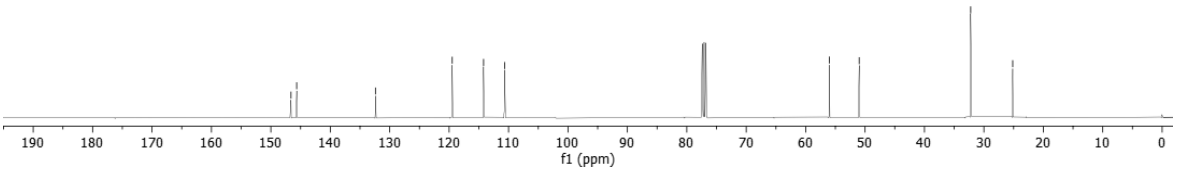
2-(4-methoxyphenyl)-1,3-dithiane (3v)



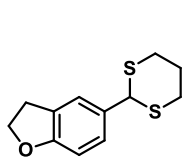
5-(1,3-dithian-2-yl)-2-methoxyphenol (3w)

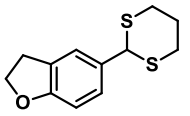




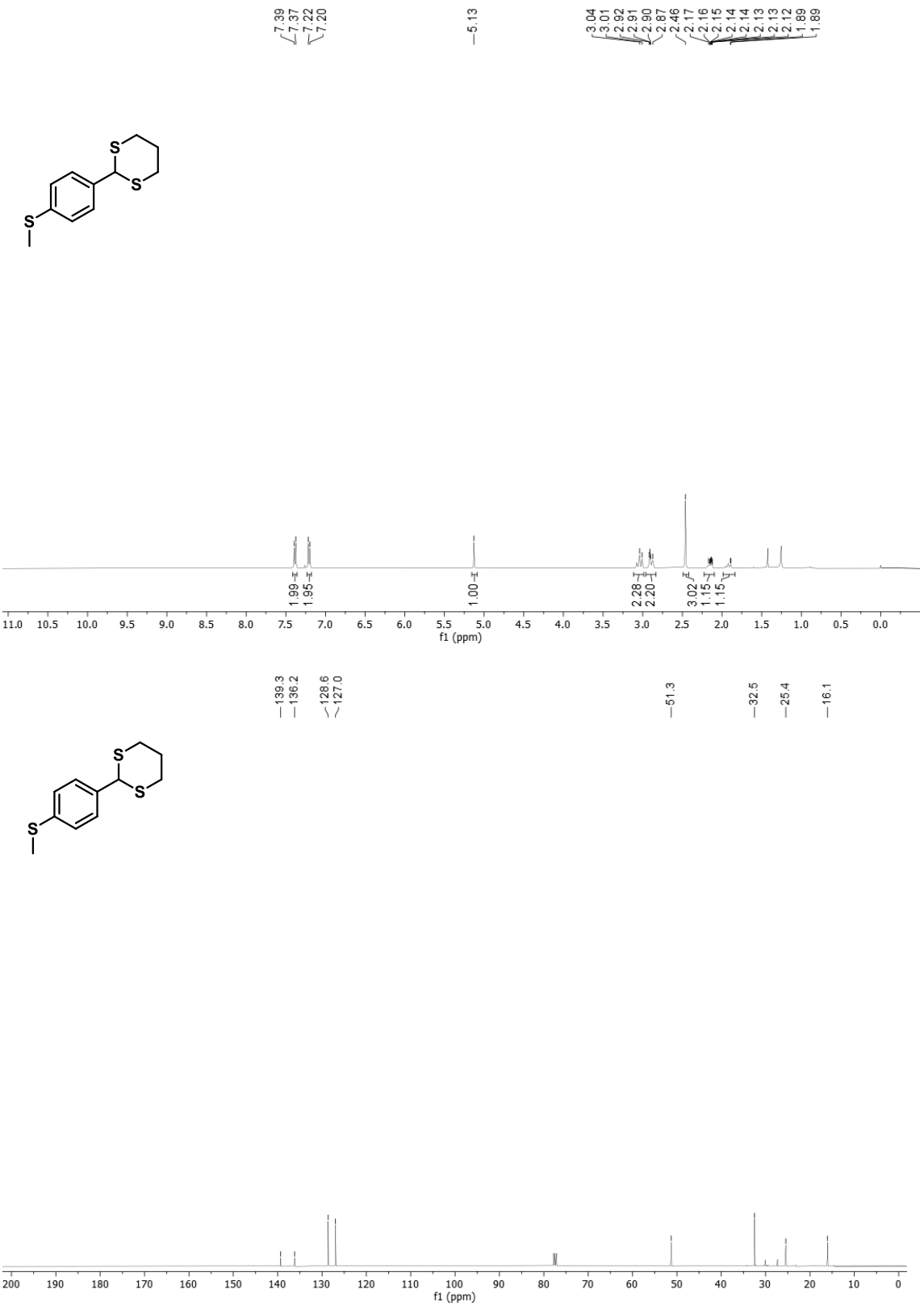


5-(1,3-dithian-2-yl)-2,3-dihydrobenzofuran (3x)

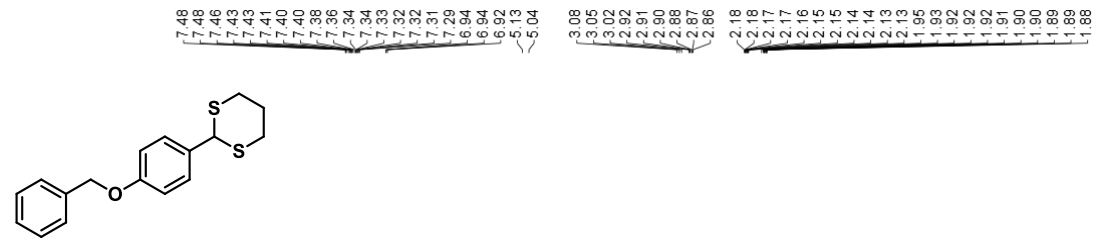


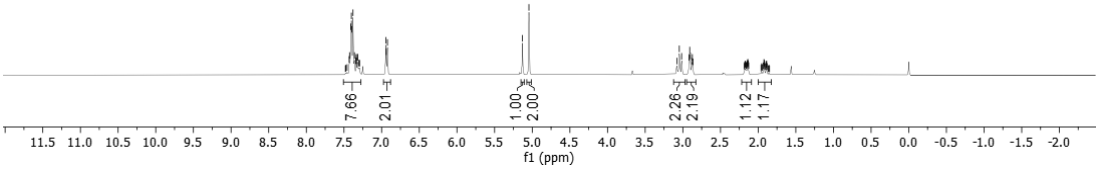


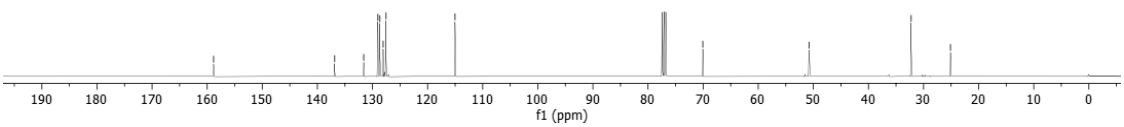
2-(4-(methylthio)phenyl)-1,3-dithiane (3y)



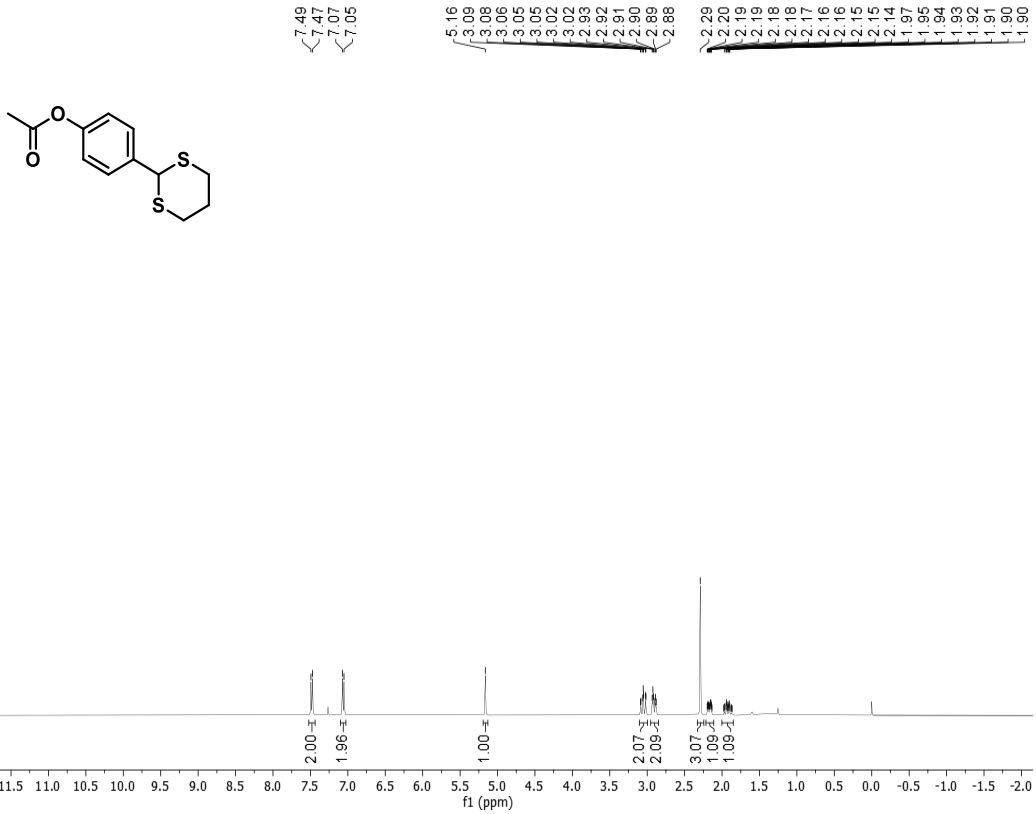
2-(4-(benzyloxy)phenyl)-1,3-dithiane (3z)

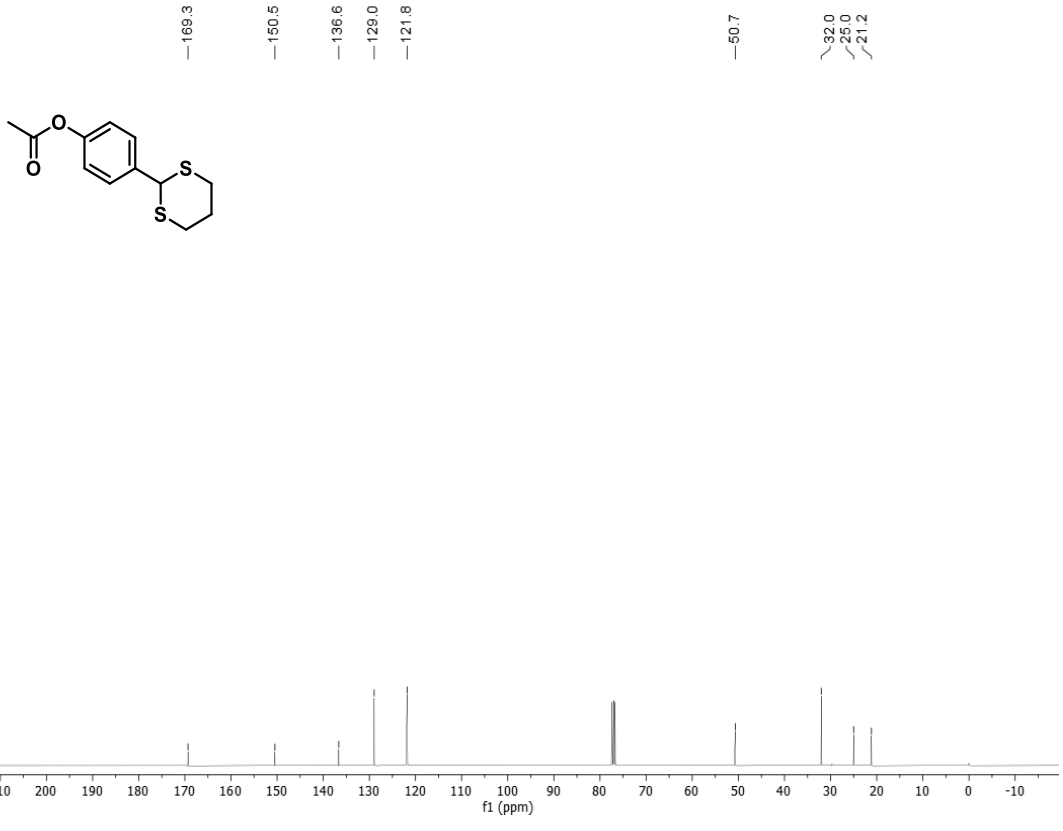




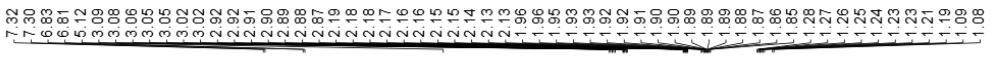


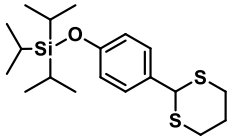
4-(1,3-dithian-2-yl)phenyl acetate (3aa)

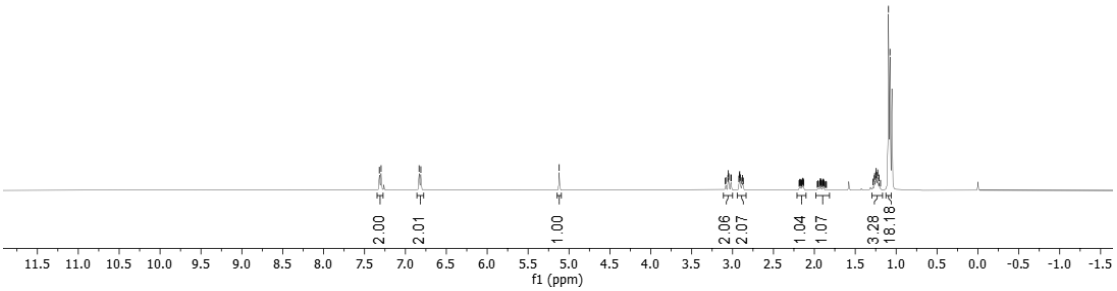


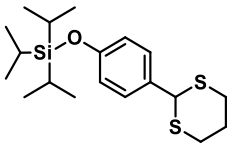


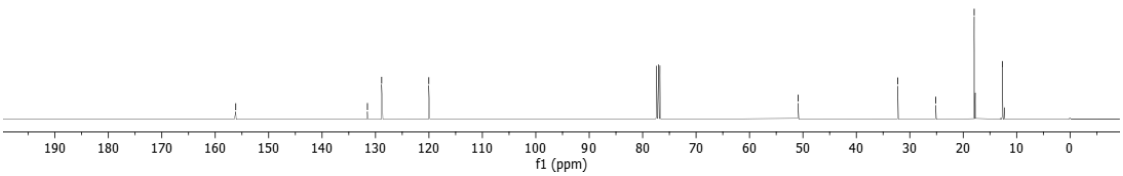
(4-(1,3-dithian-2-yl)phenoxy)triisopropylsilane (3ab)



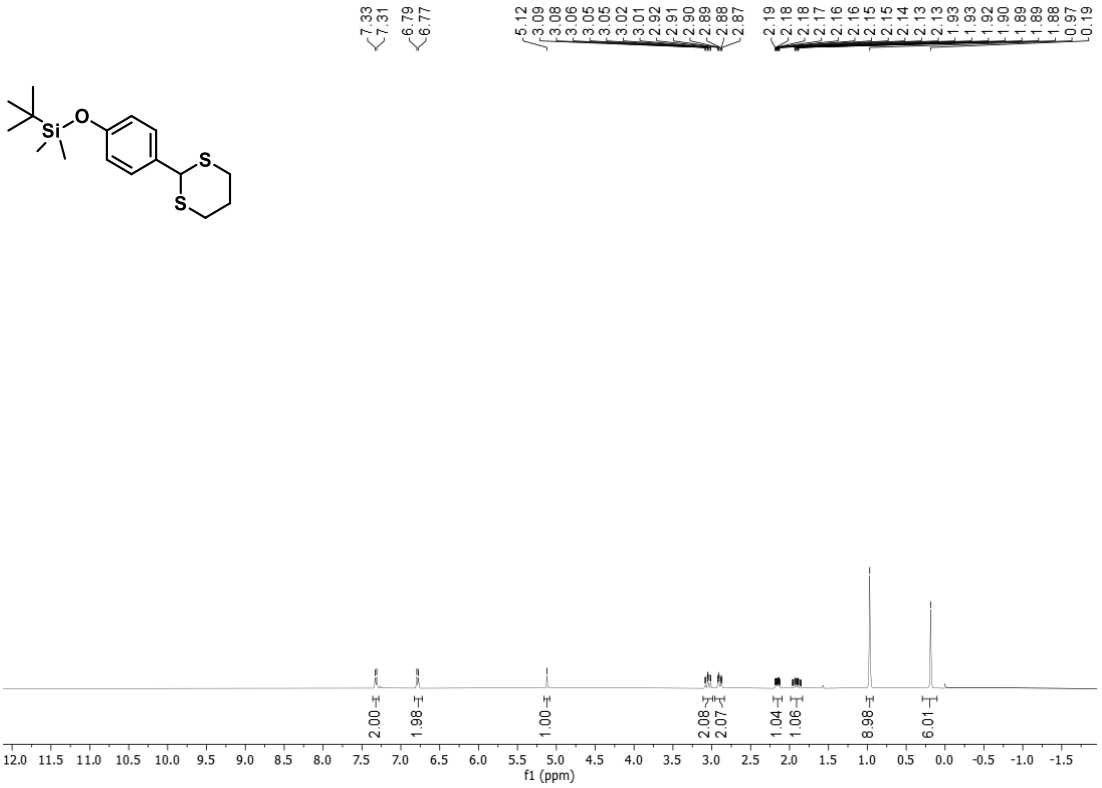


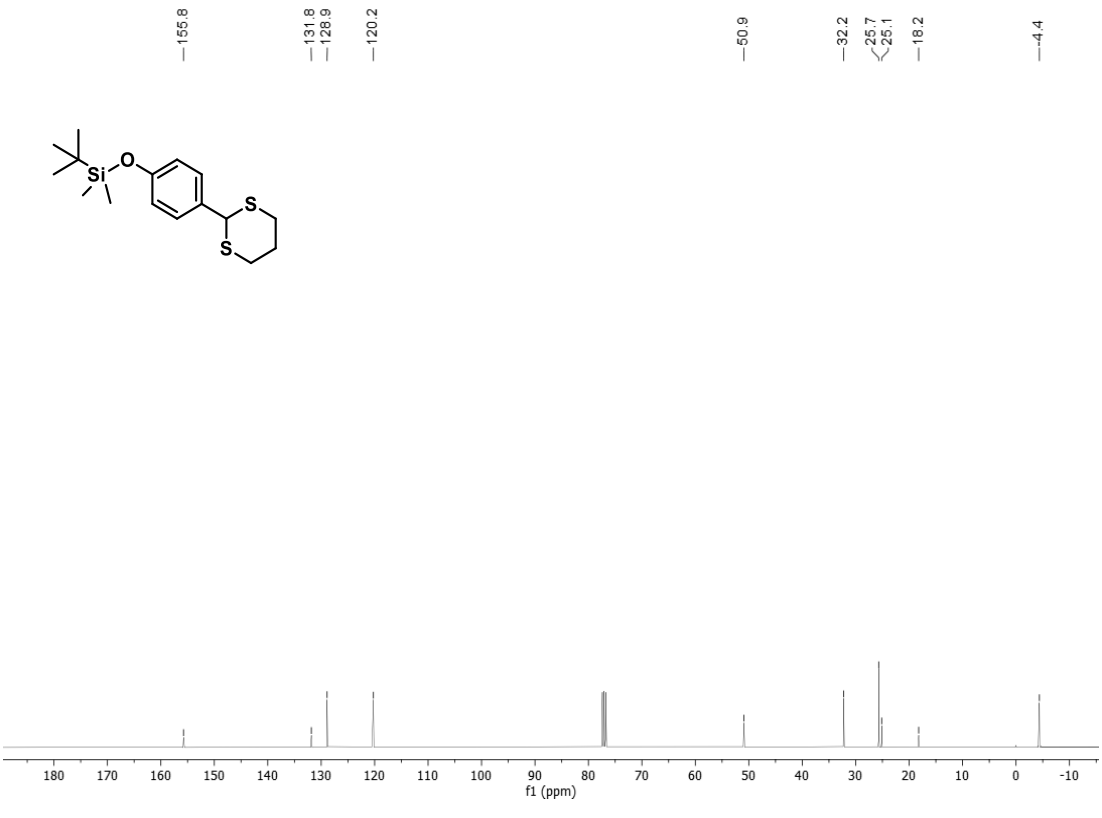




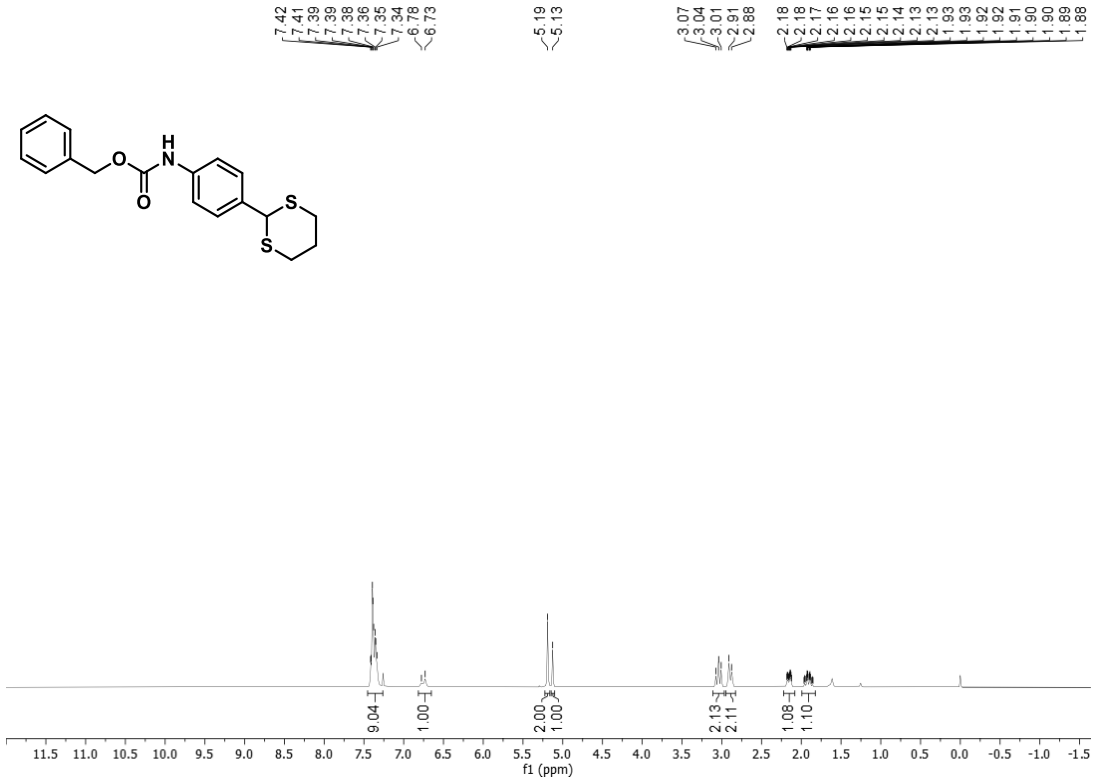


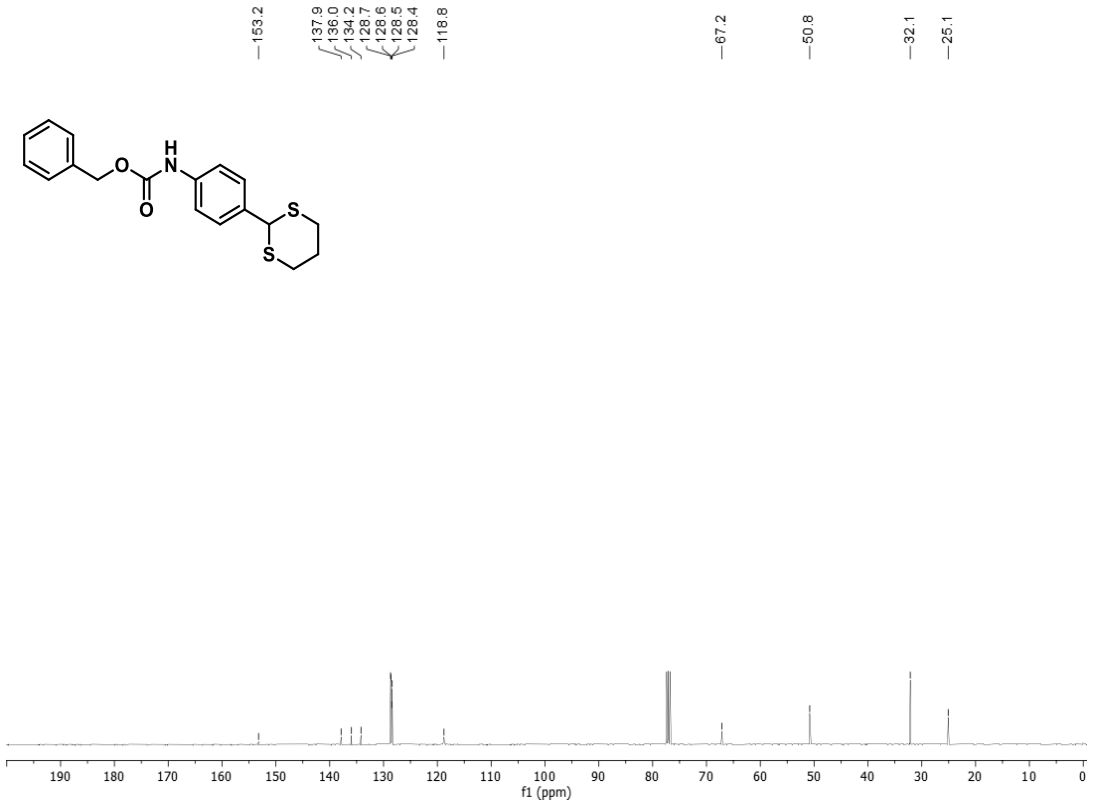
(4-(1,3-dithian-2-yl)phenoxy)(tert-butyl)dimethylsilane (3ac)



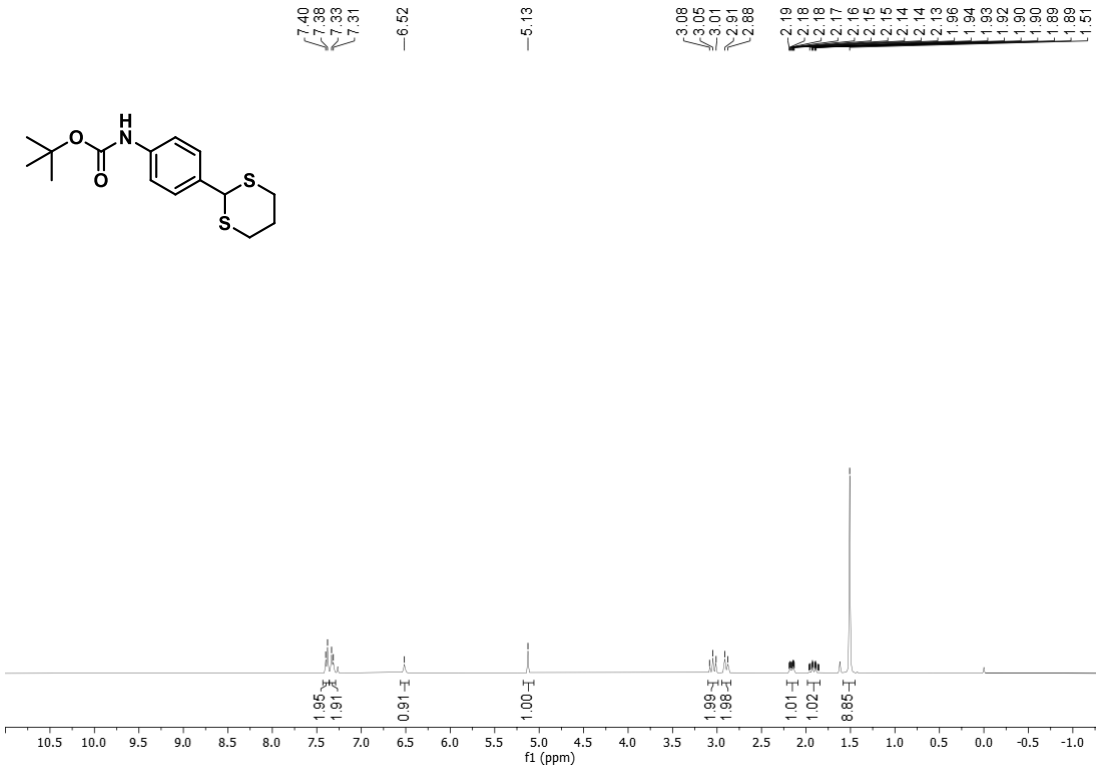


benzyl (4-(1,3-dithian-2-yl)phenyl)carbamate (3ad)

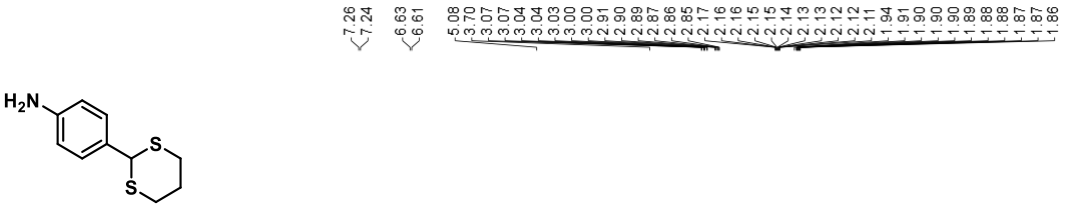


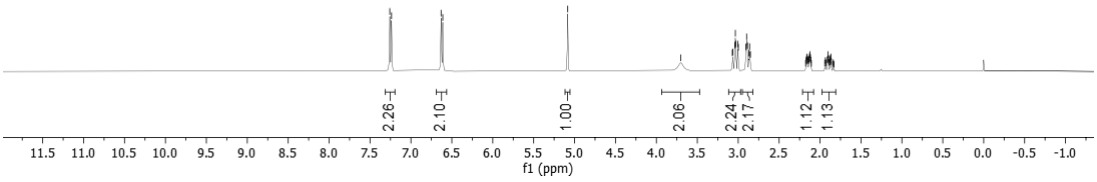


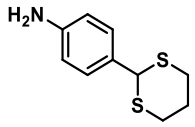
tert-butyl (4-(1,3-dithian-2-yl)phenyl)carbamate (3ae)

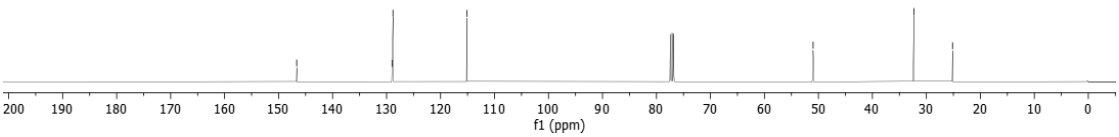


4-(1,3-dithian-2-yl)aniline

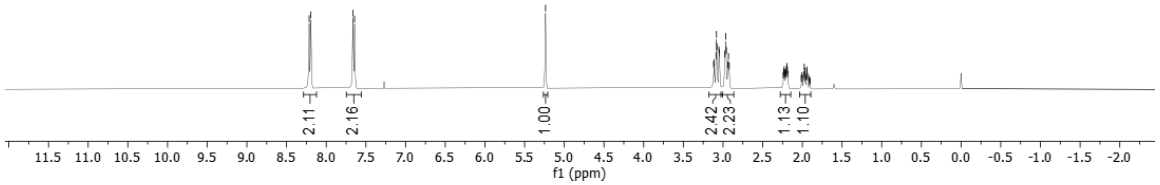


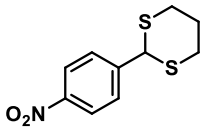


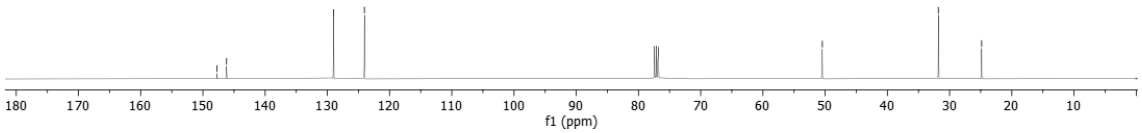




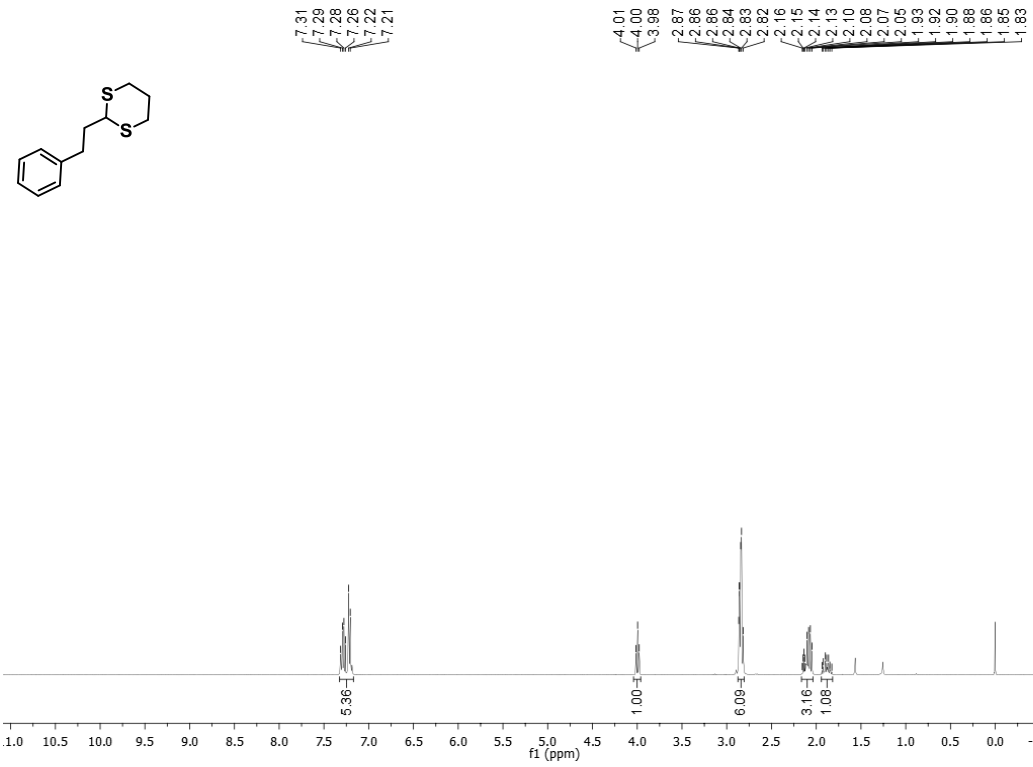
2-(4-nitrophenyl)-1,3-dithiane

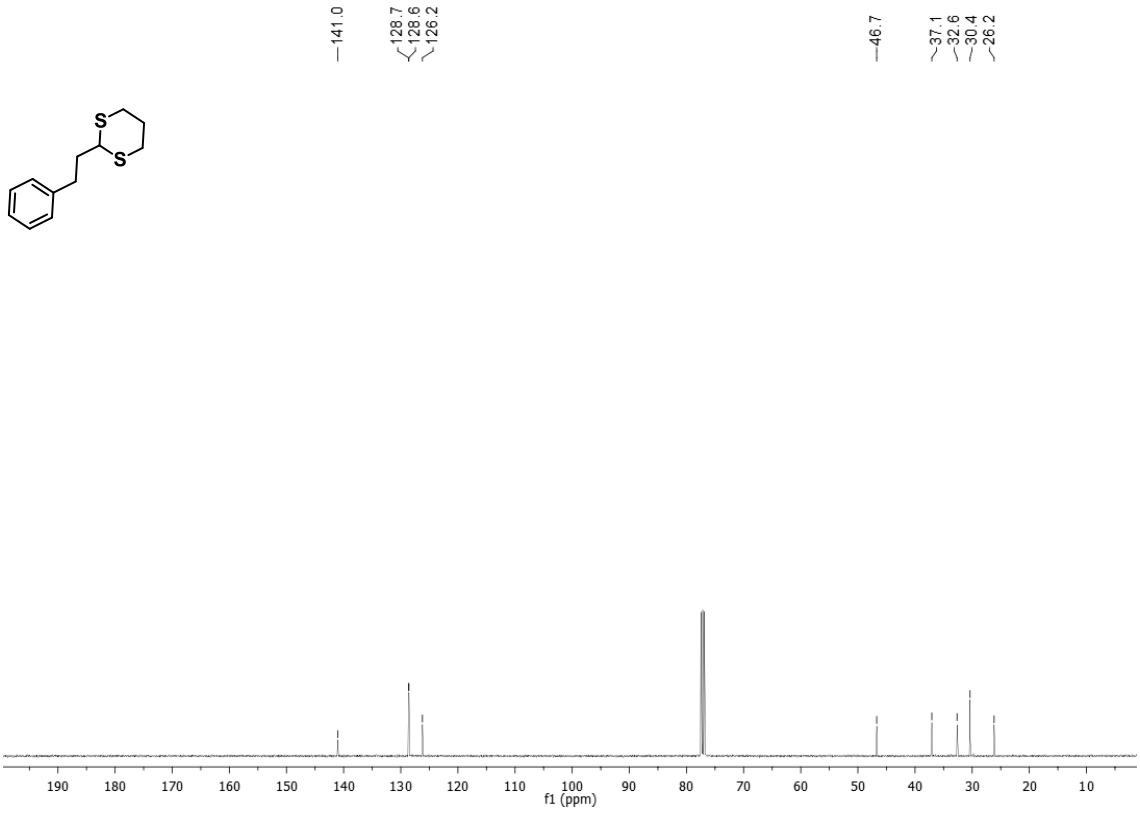




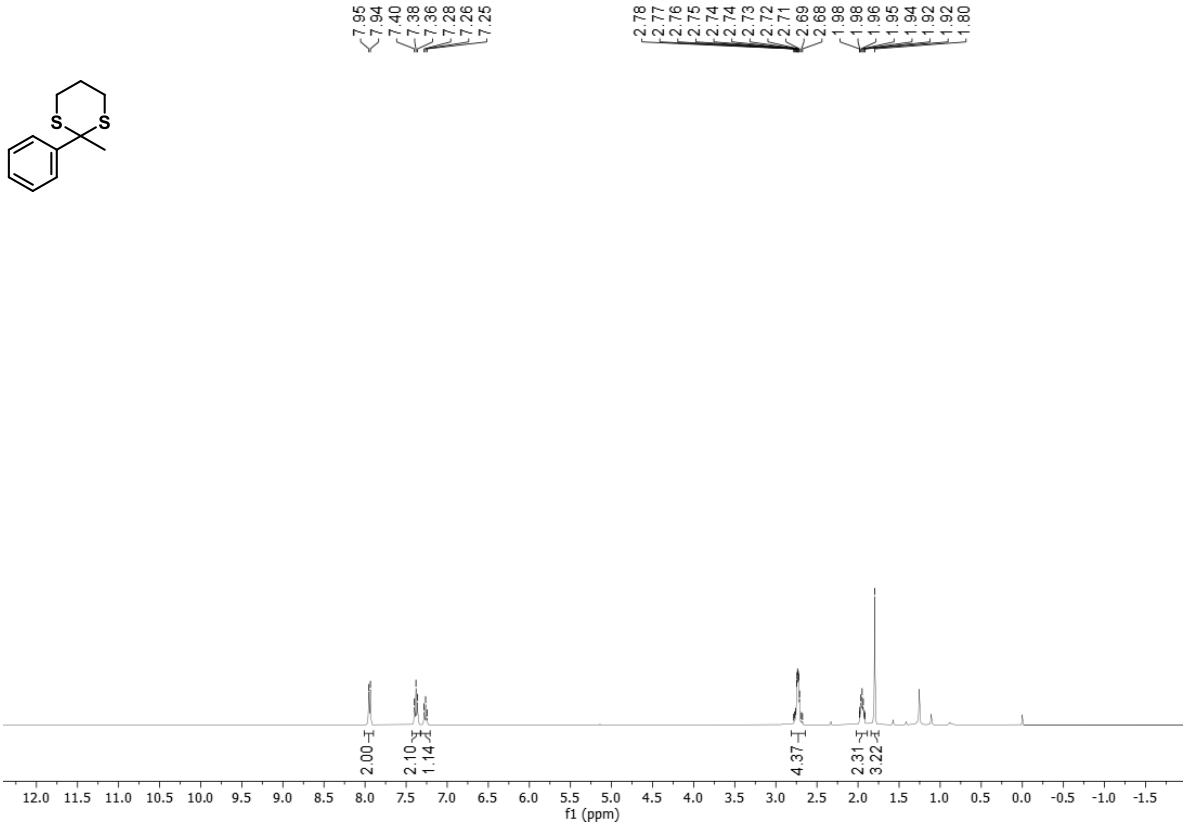


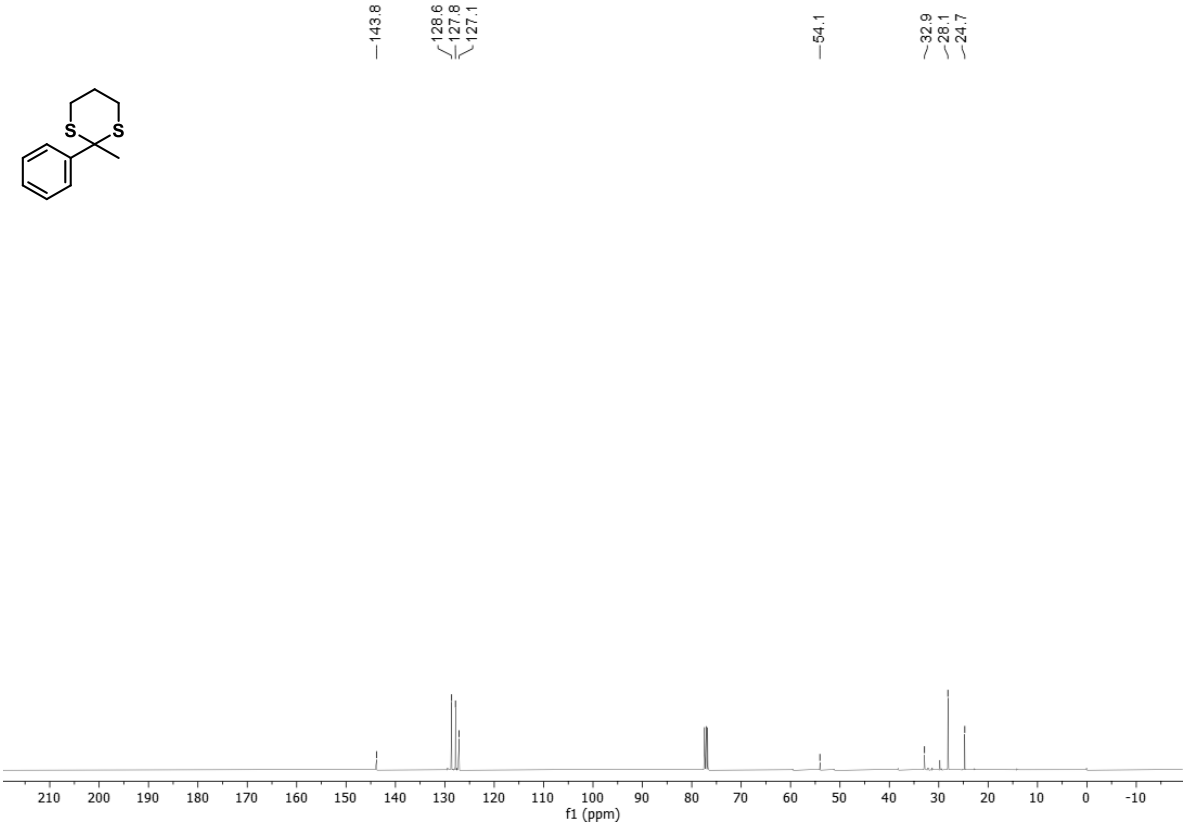
2-phenethyl-1,3-dithiane



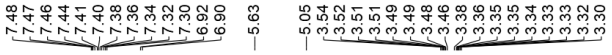


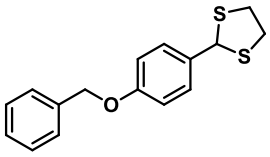
2-methyl-2-phenyl-1,3-dithiane

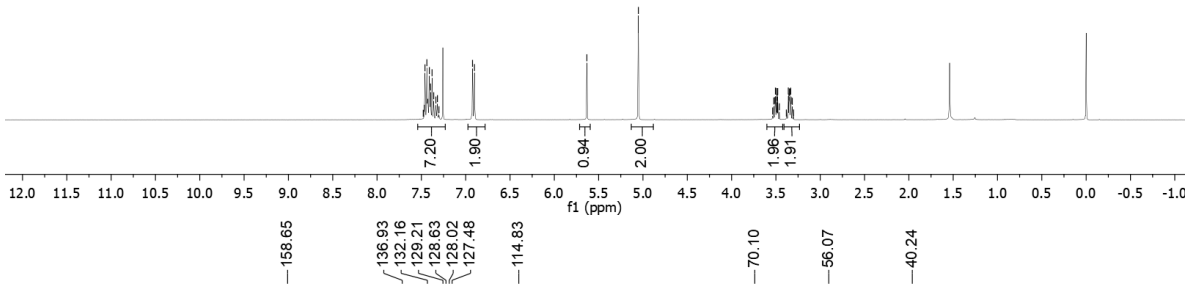


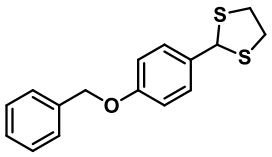


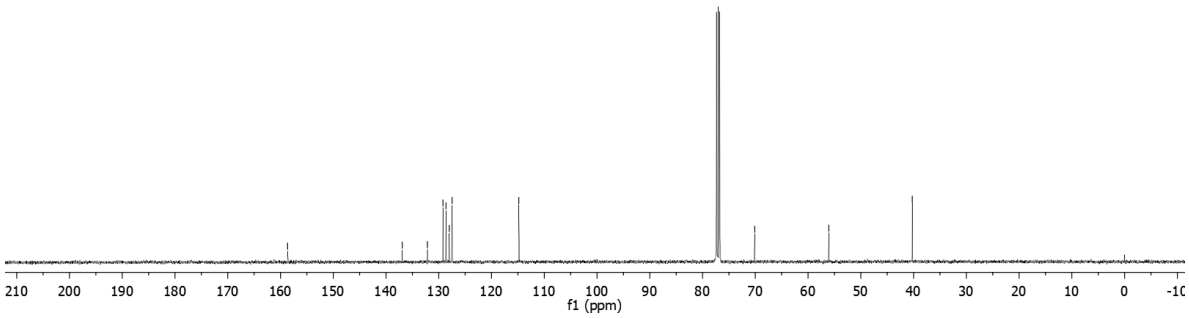
2-(4-(benzyloxy)phenyl)-1,3-dithiolane (5)



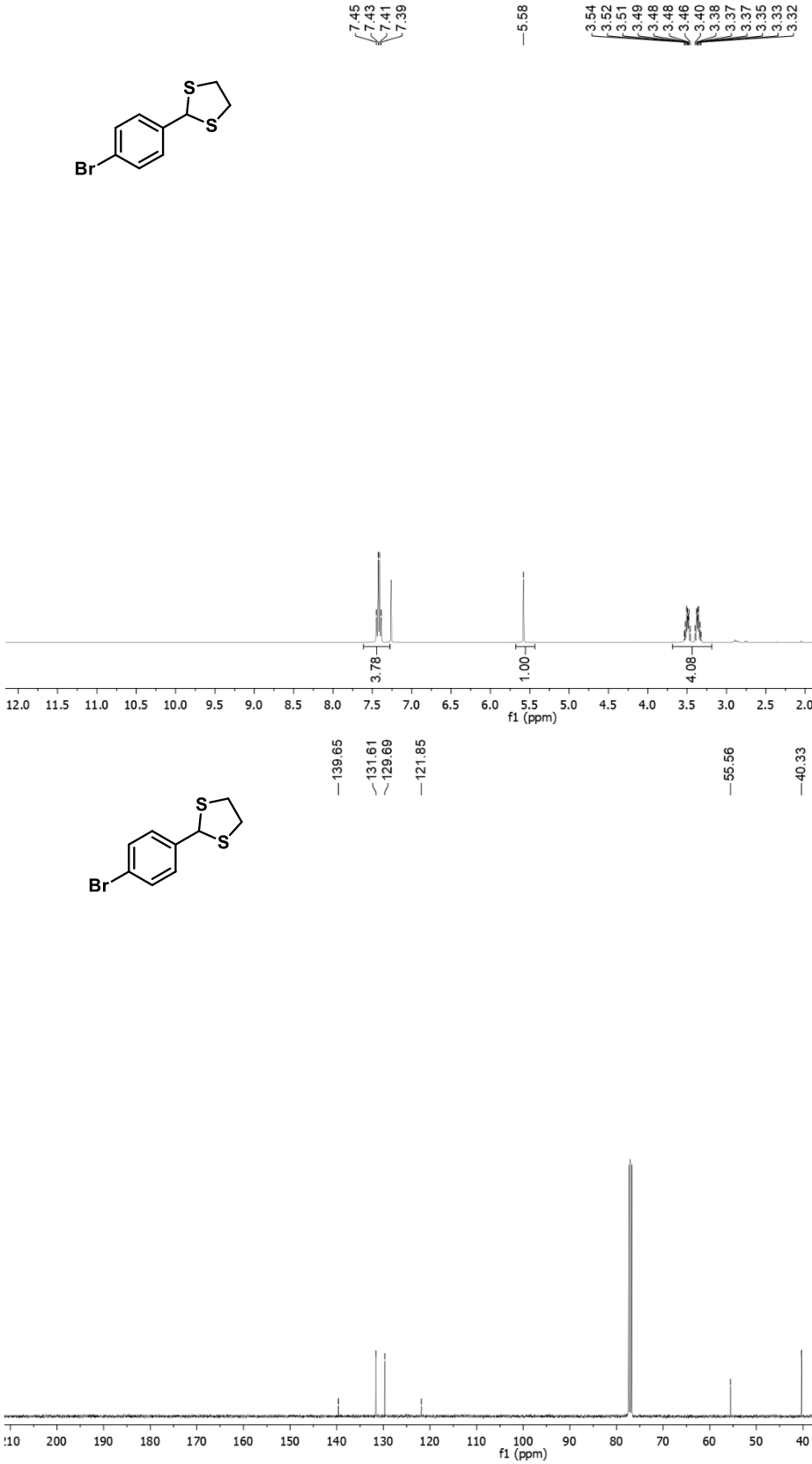




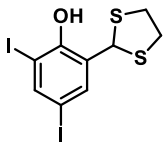


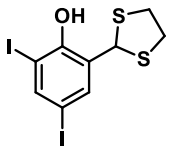


2-(4-bromophenyl)-1,3-dithiolane (5q)

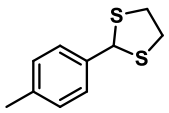


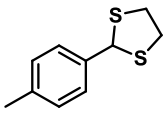
2-(1,3-dithiolan-2-yl)-4,6-diiodophenol (5s)



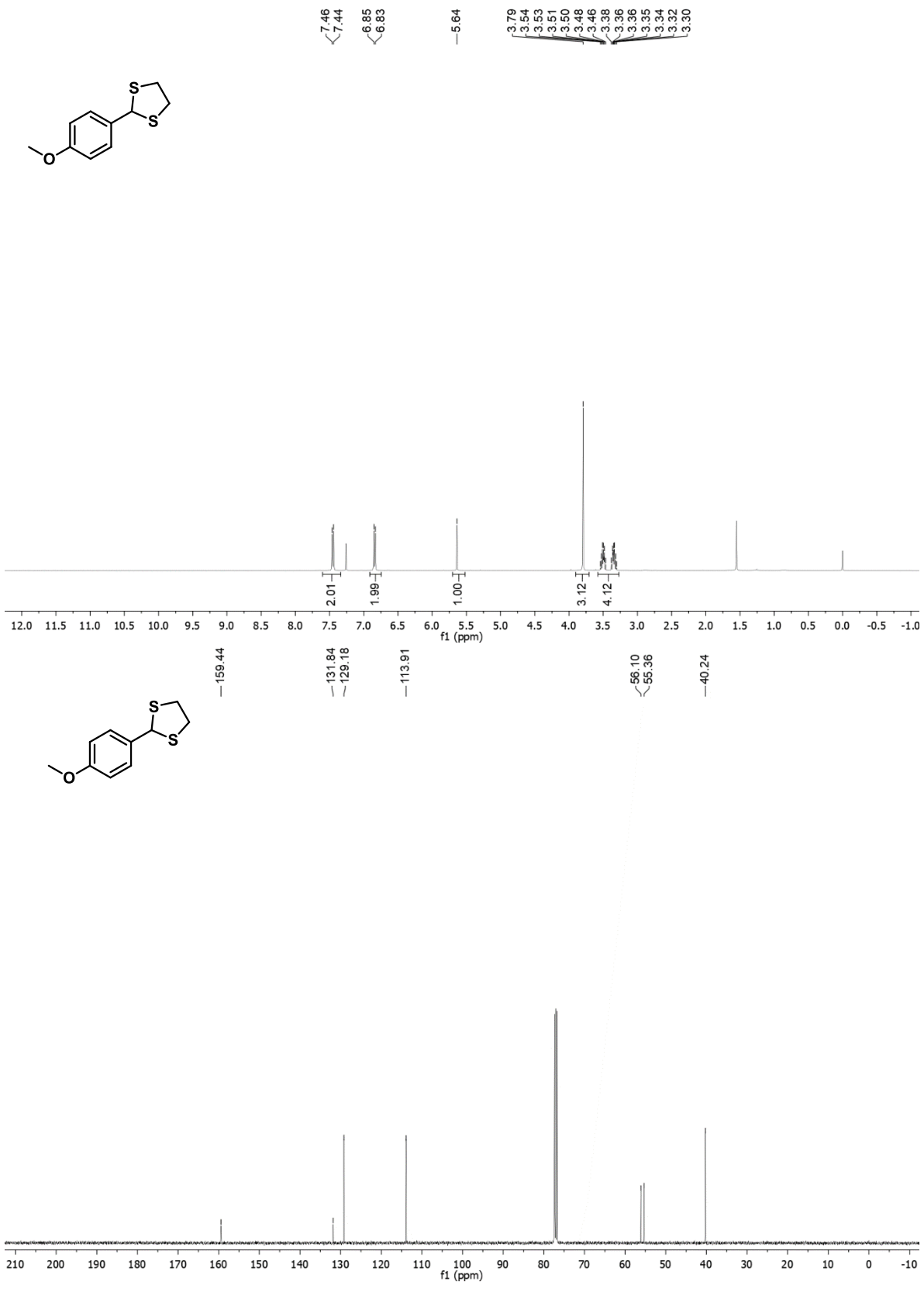


2-(p-tolyl)-1,3-dithiolane (5t)

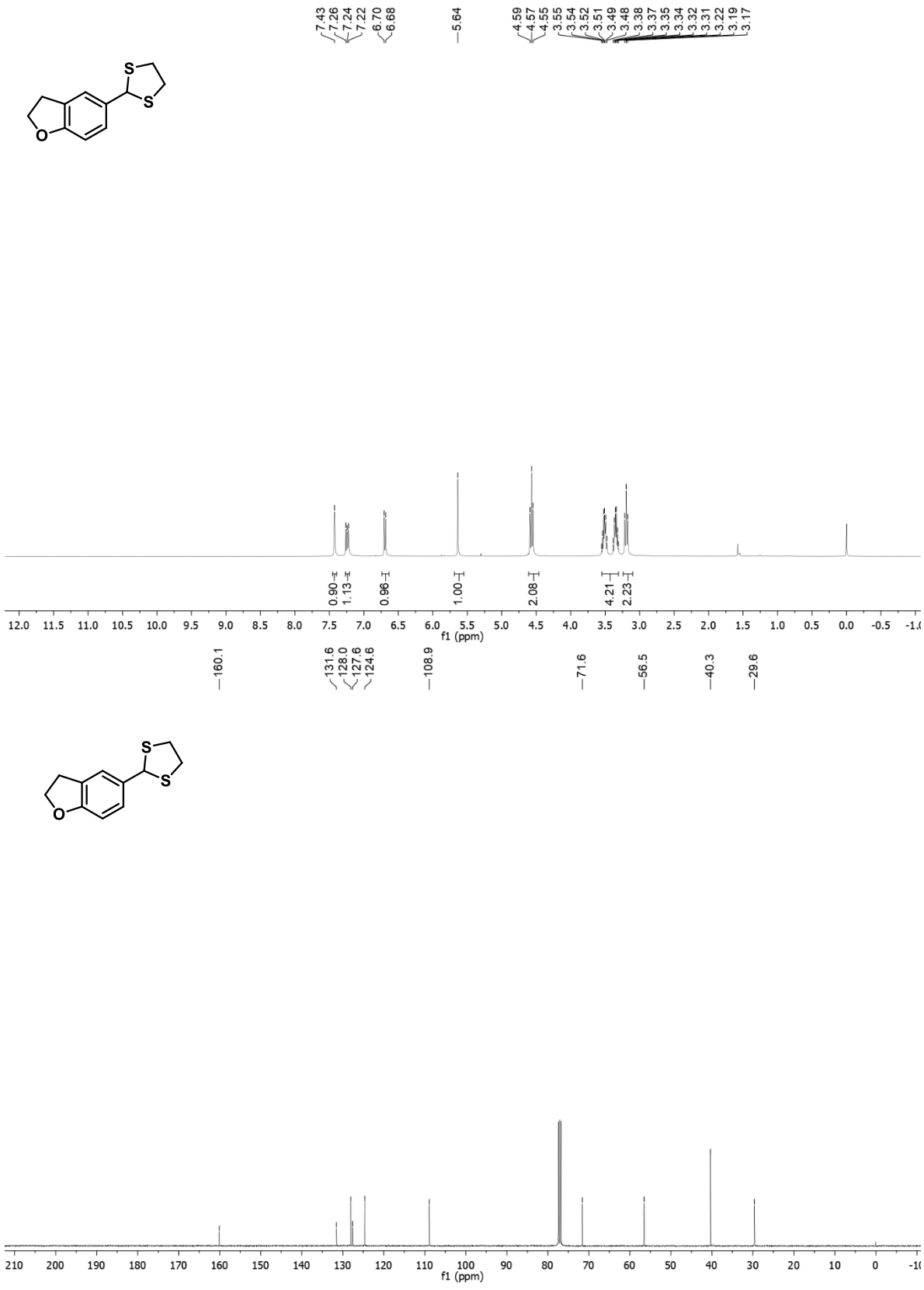




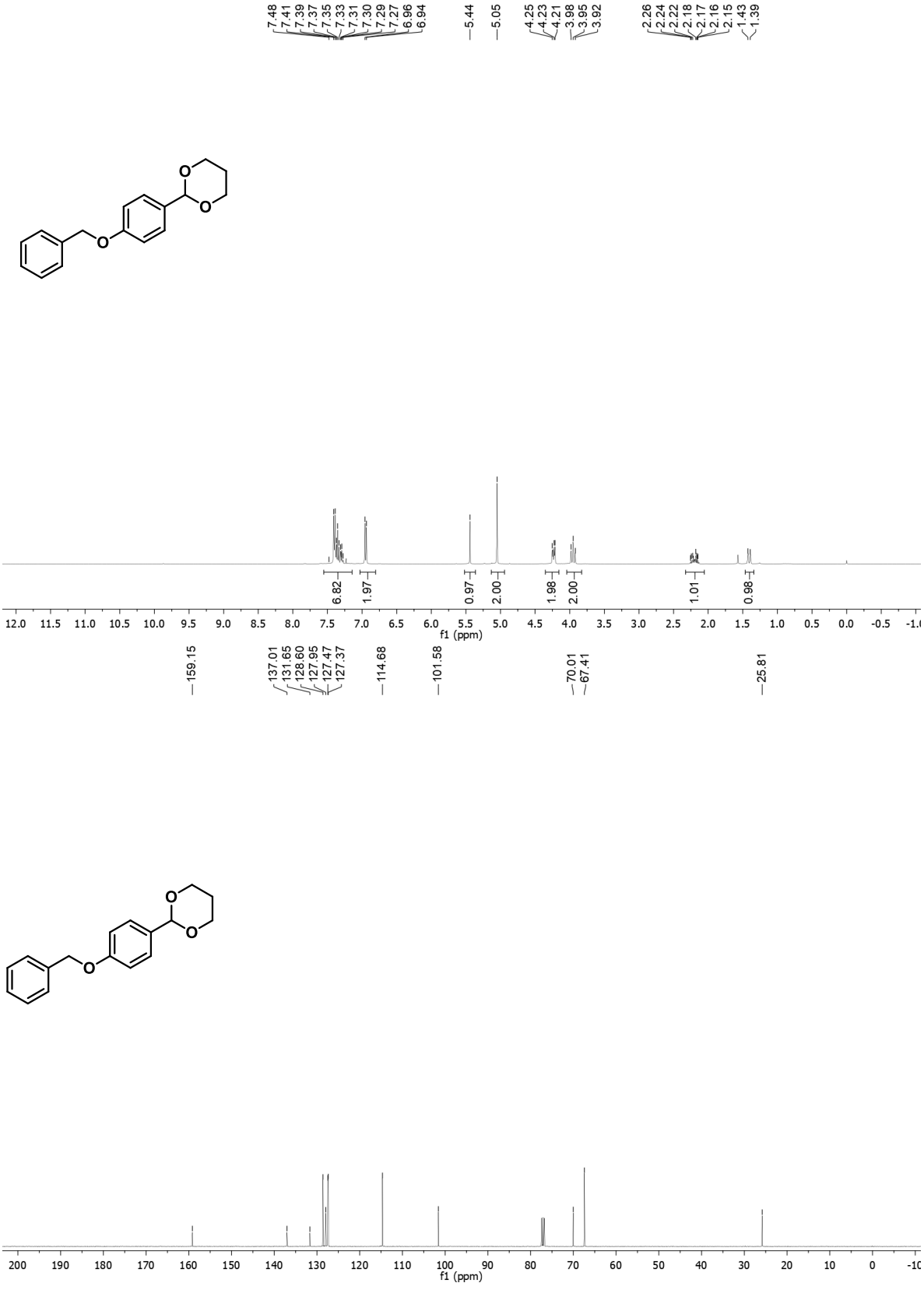
2-(4-methoxyphenyl) -1,3-dithiolane (5v)



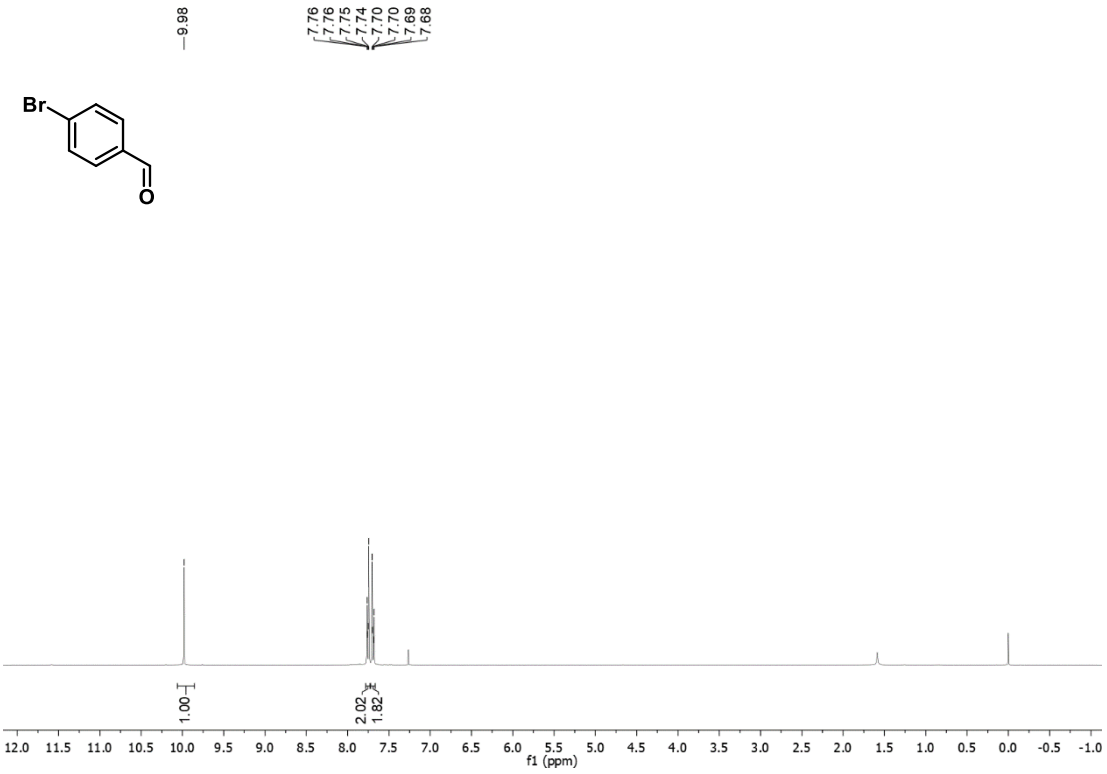
5-(1,3-dithiolan-2-yl)-2,3-dihydrobenzofuran (5z)

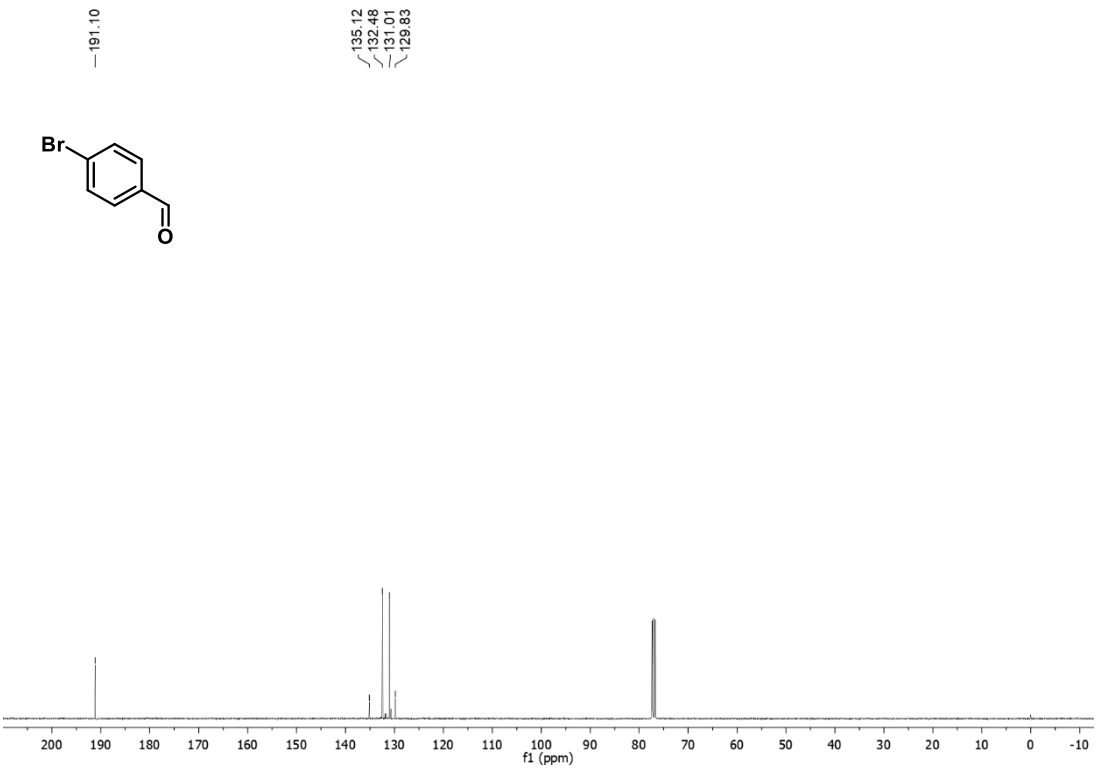


2-(4-(benzyloxy)phenyl)-1,3-dioxane (6)

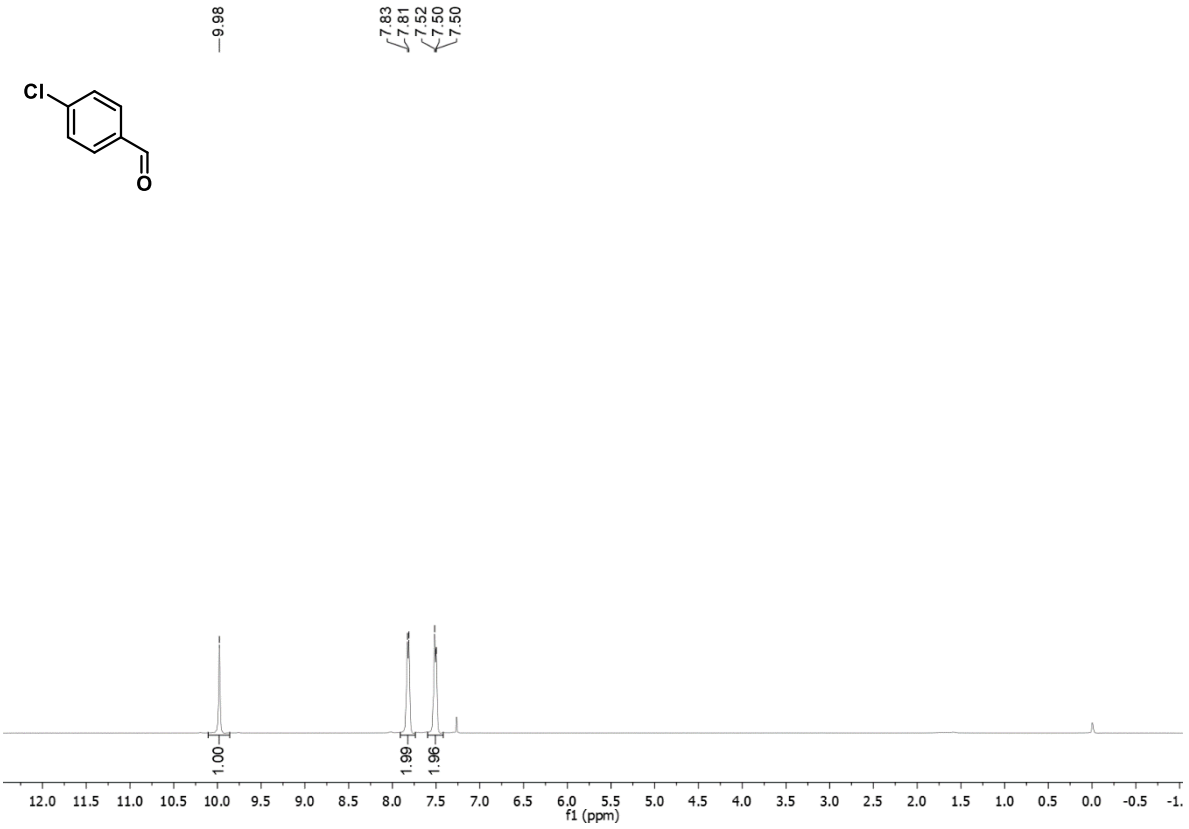


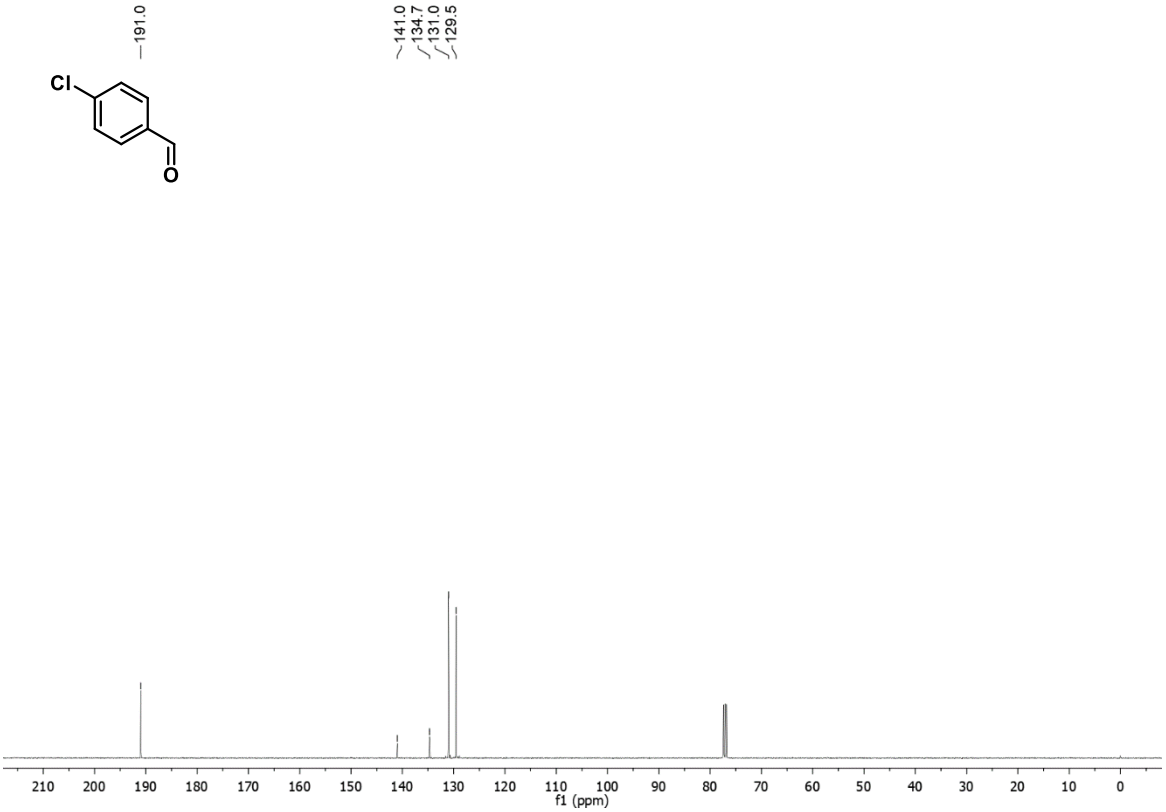
4-bromobenzaldehyde (4q)



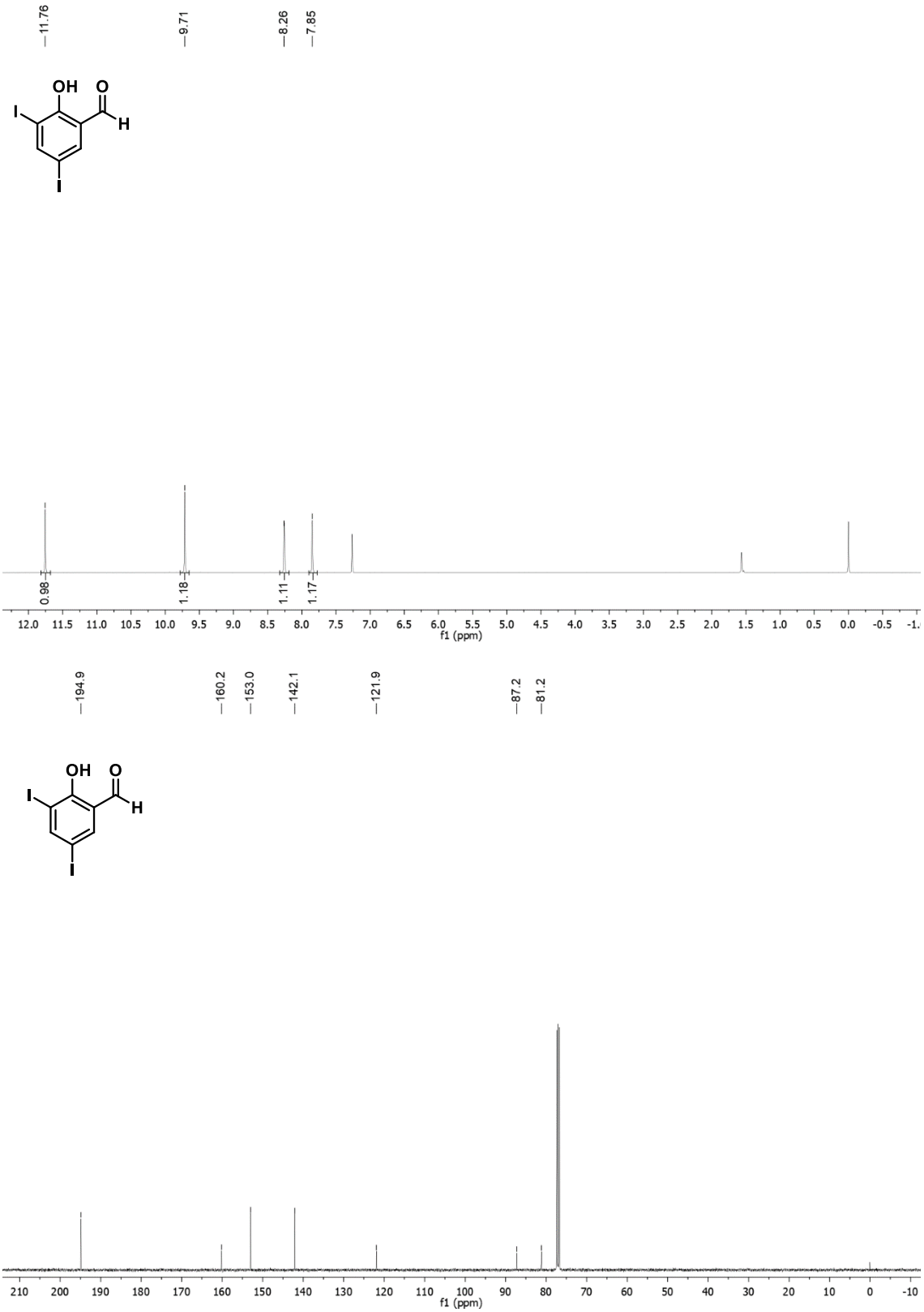


4-chlorobenzaldehyde (4r)

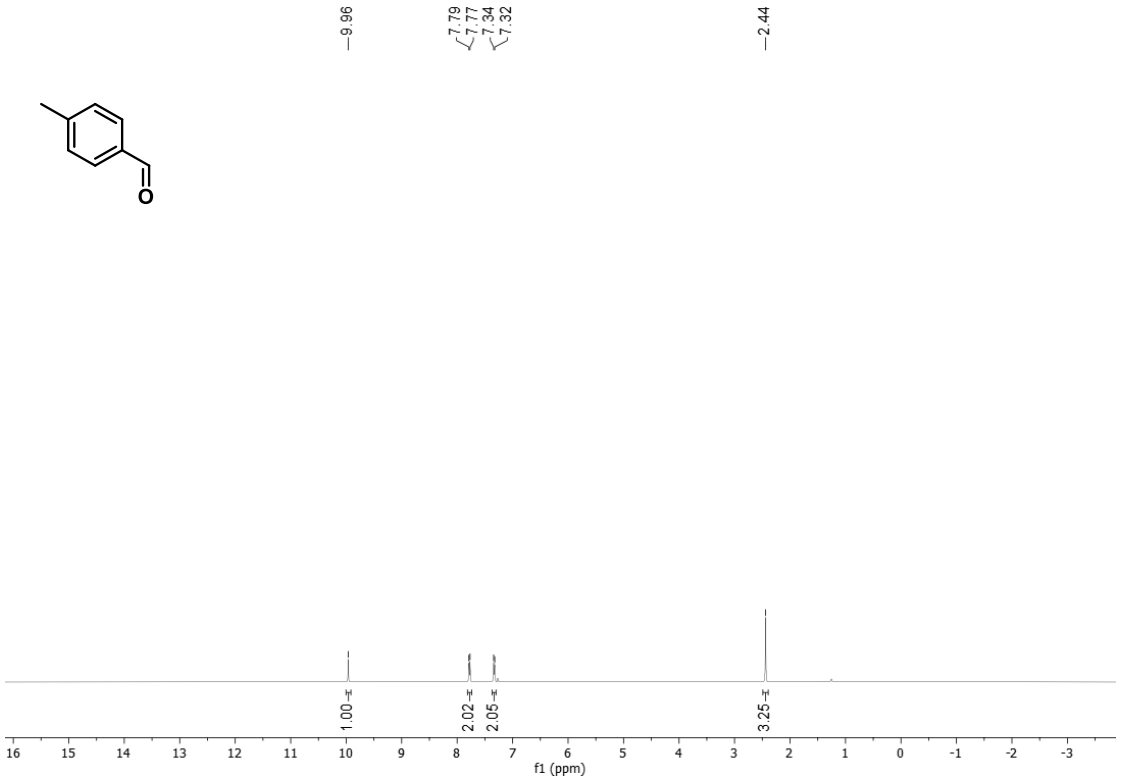


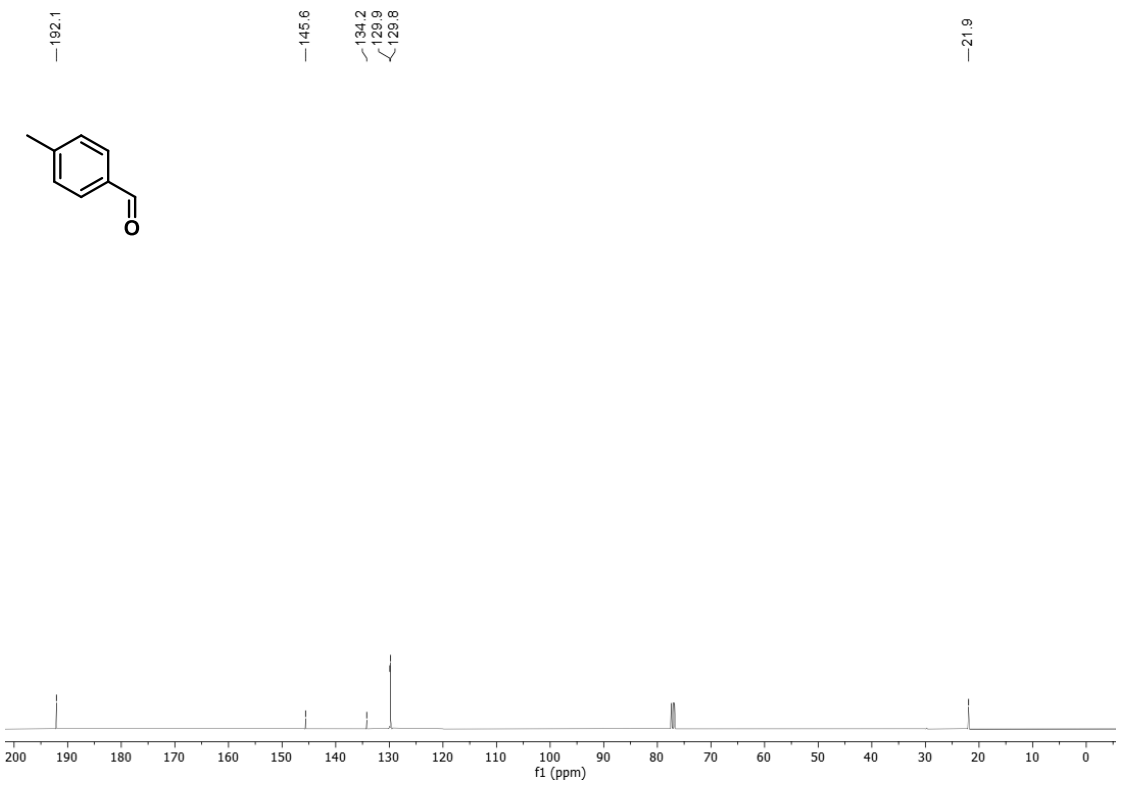


2-hydroxy-3,5-diiodobenzaldehyde (4s)

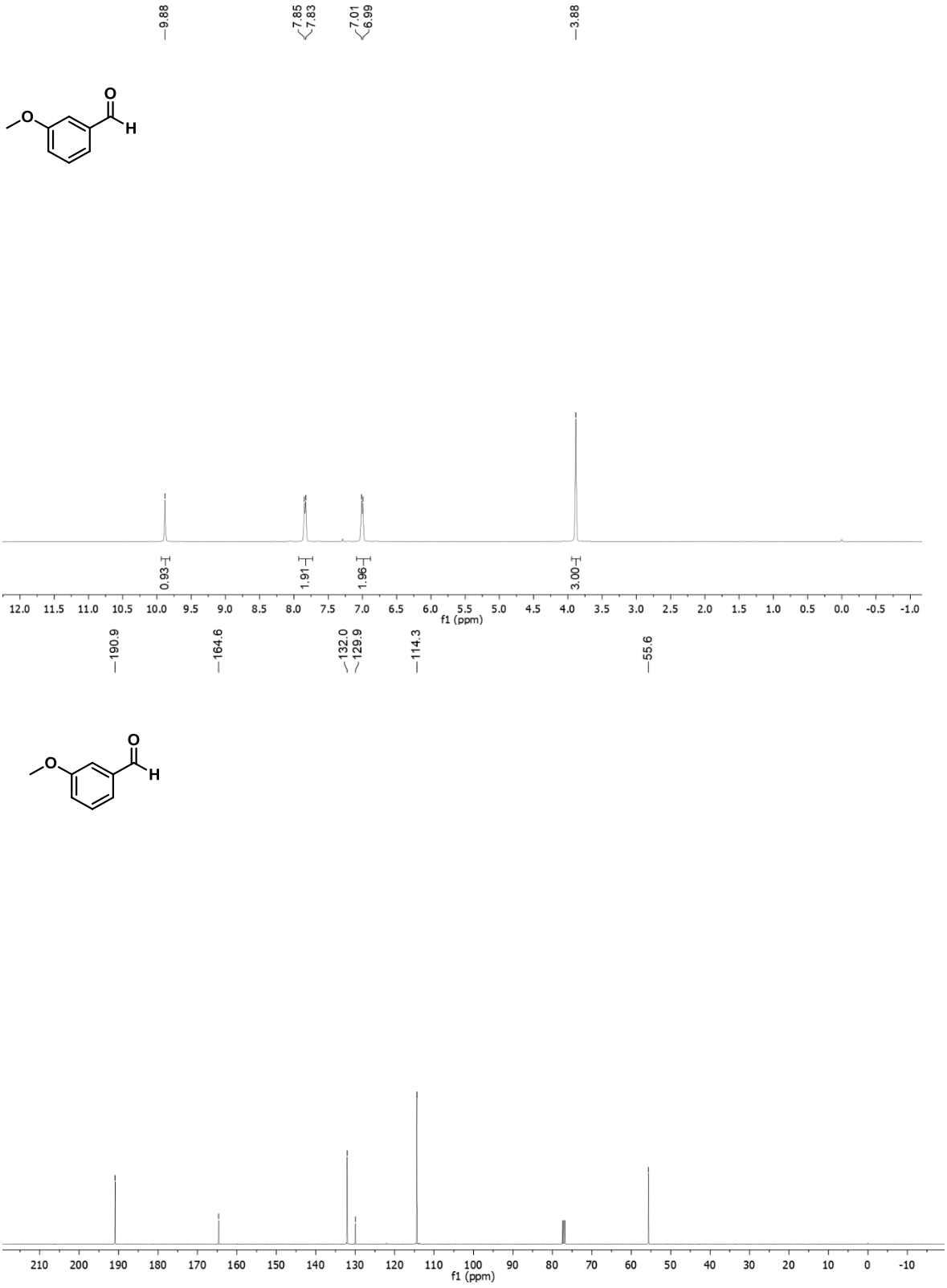


4-methylbenzaldehyde (4t)

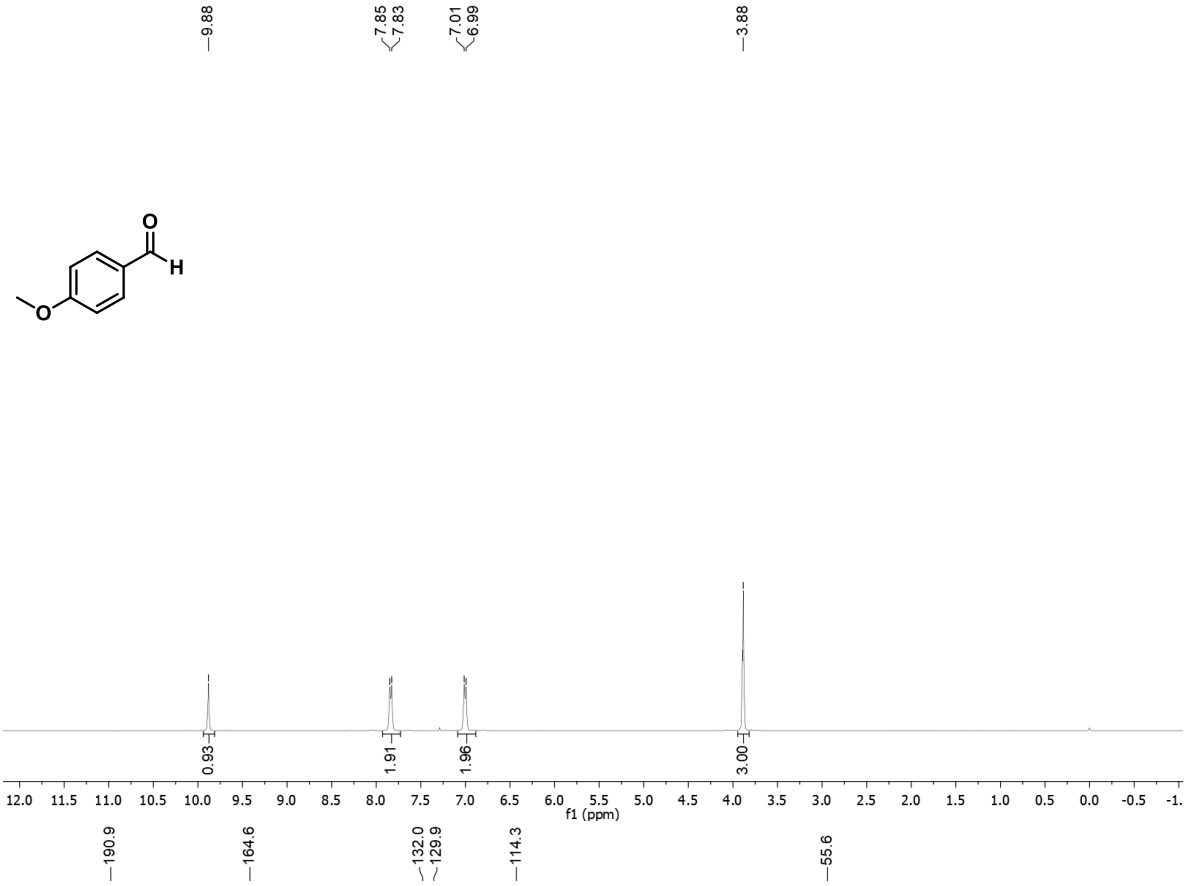


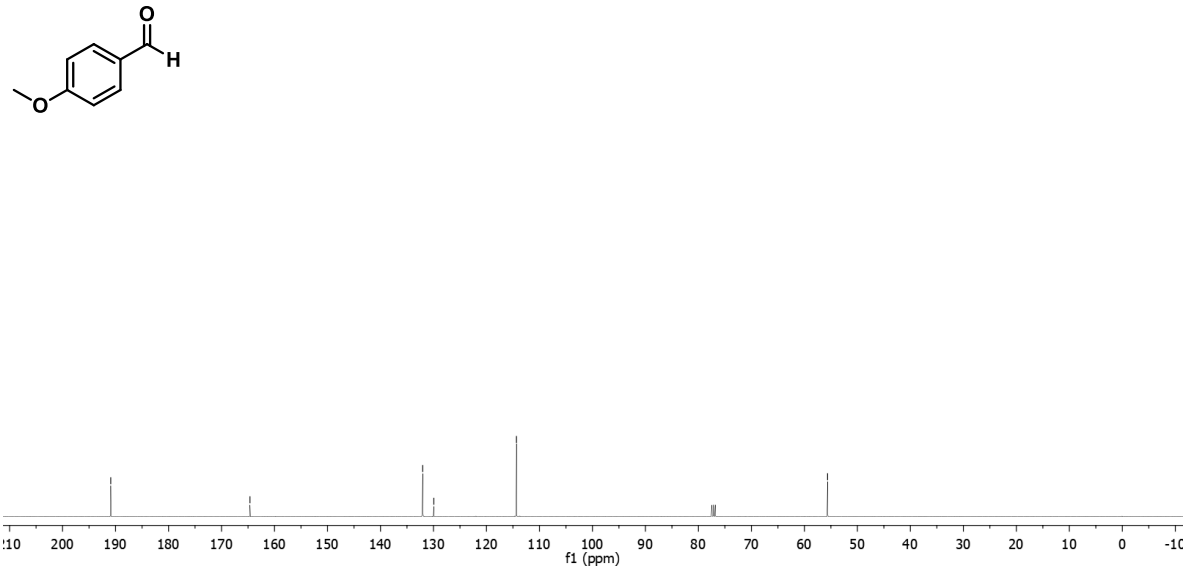


3-methoxybenzaldehyde (4u)

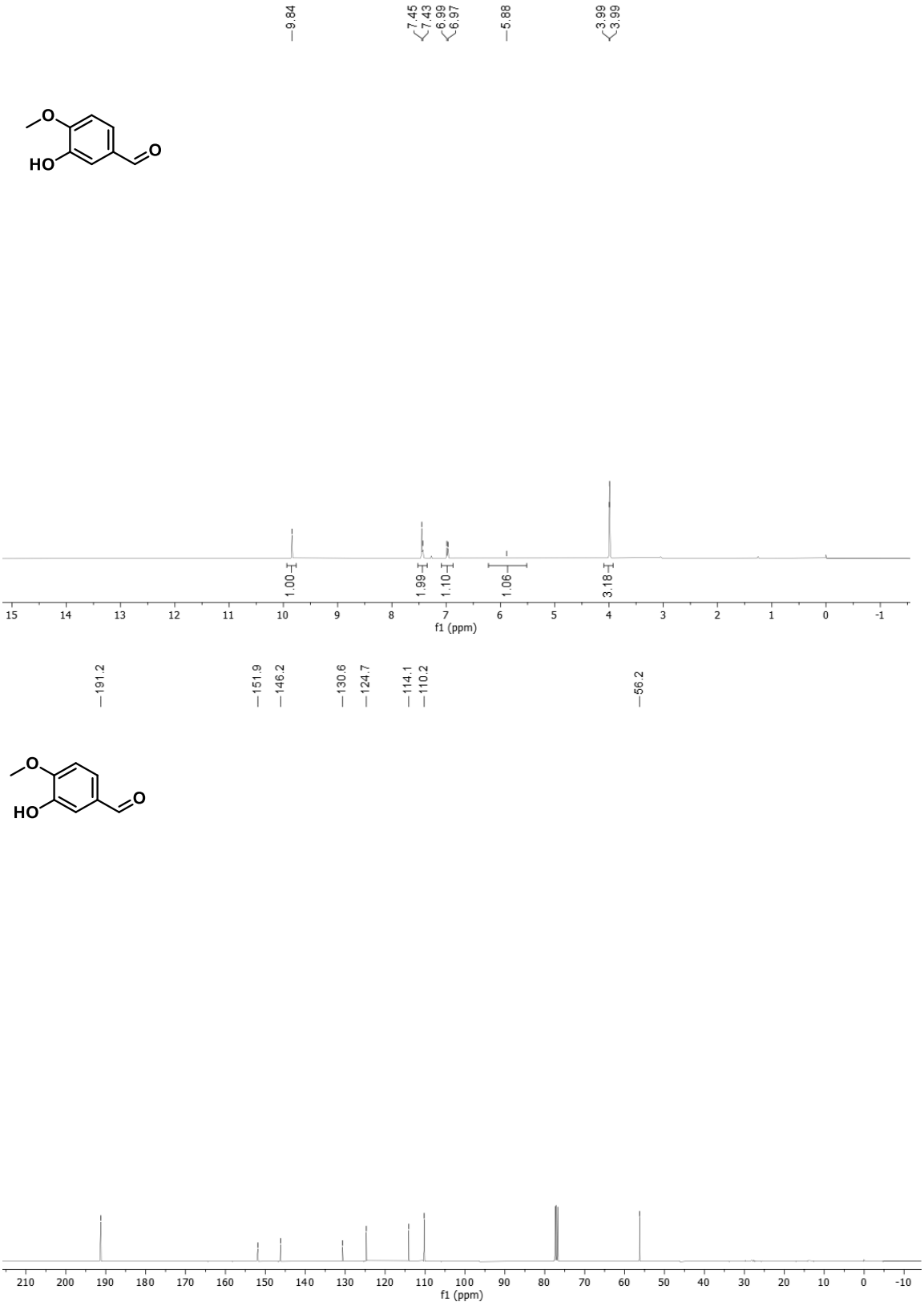


4- methoxybenzaldehyde (4v)

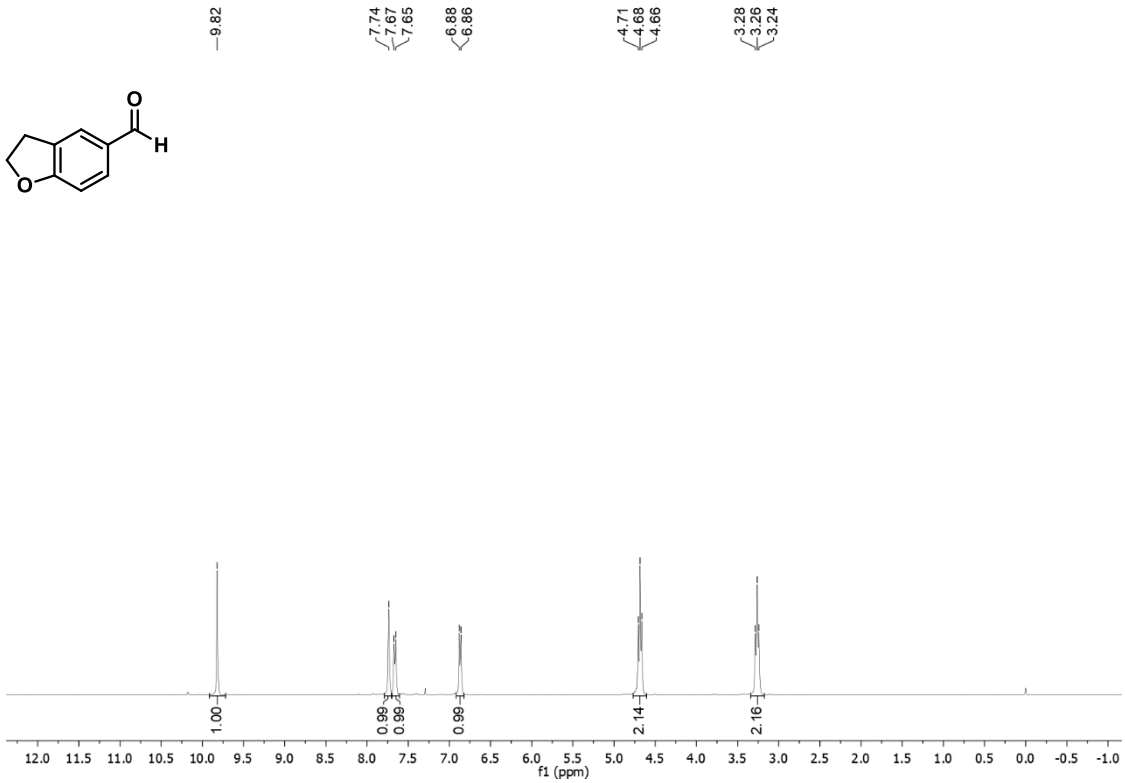


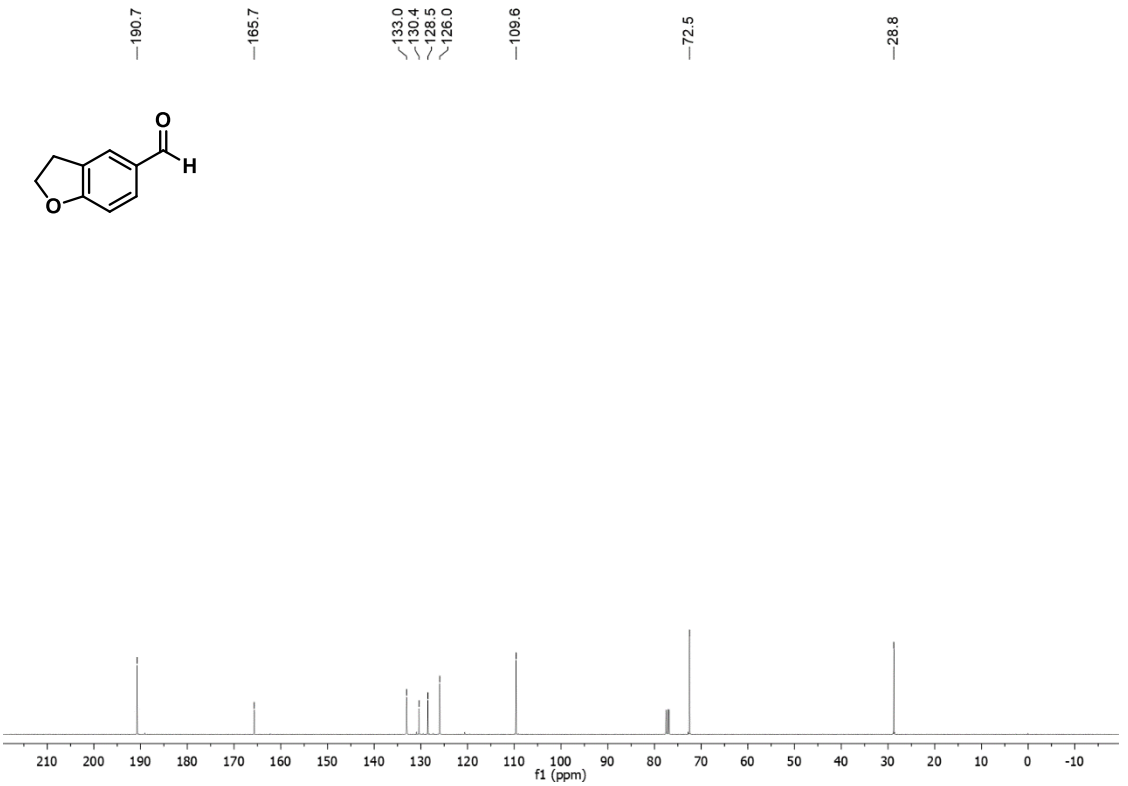


3-hydroxy-4-methoxybenzaldehyde (4w)

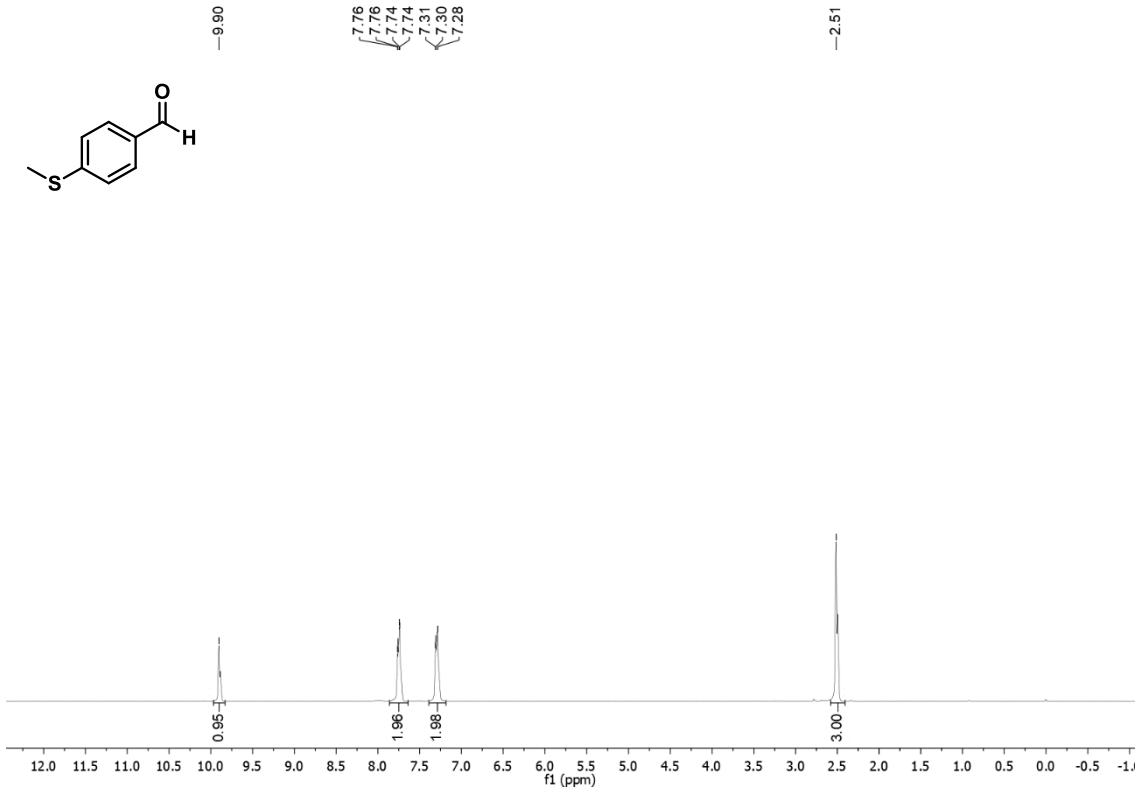


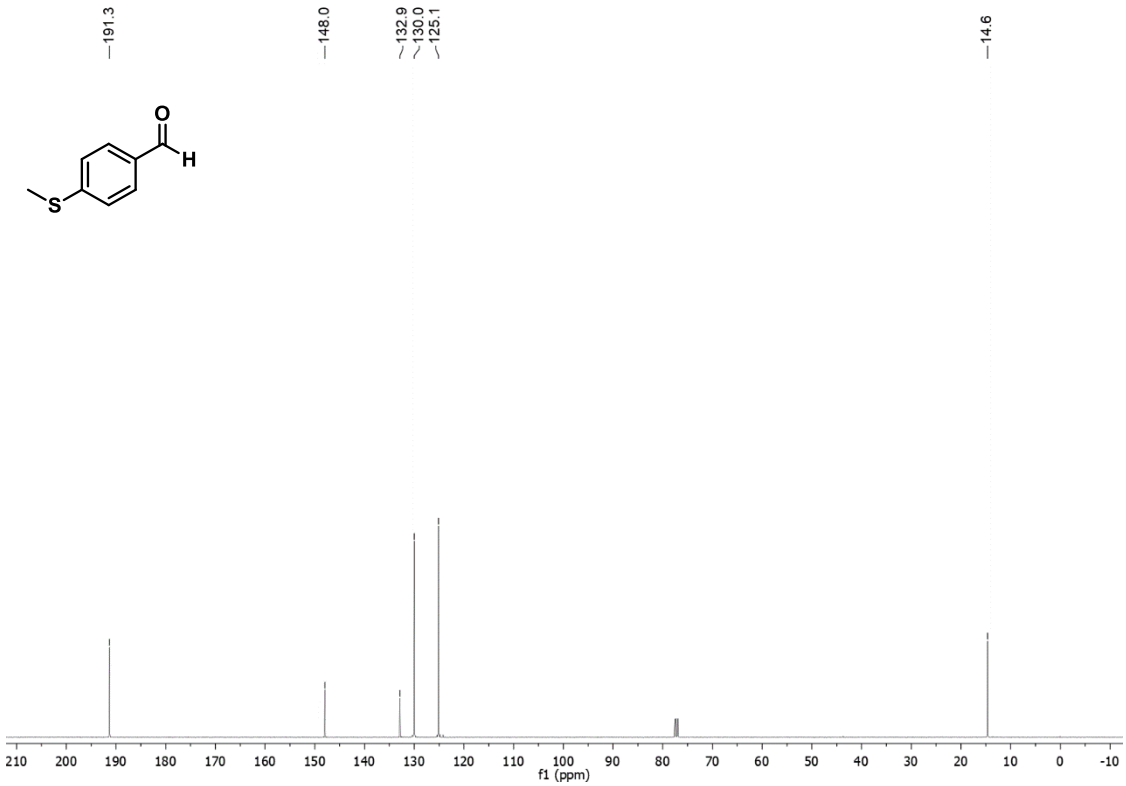
2,3-dihydrobenzofuran-5-carbaldehyde (4x)



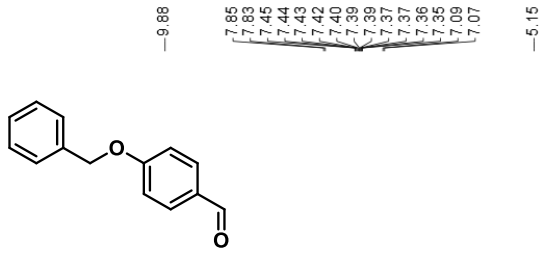


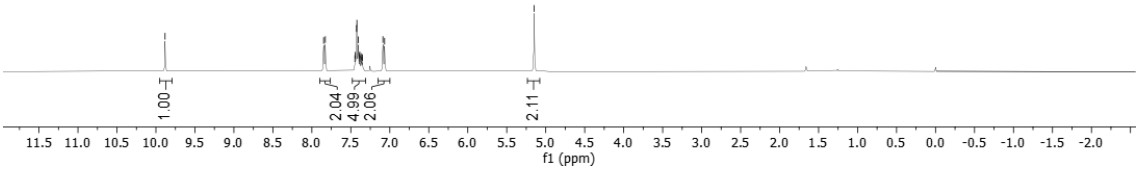
4-(methylthio)benzaldehyde (4y)

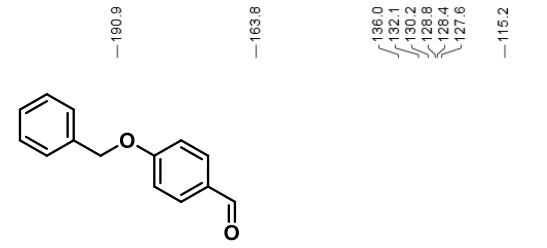


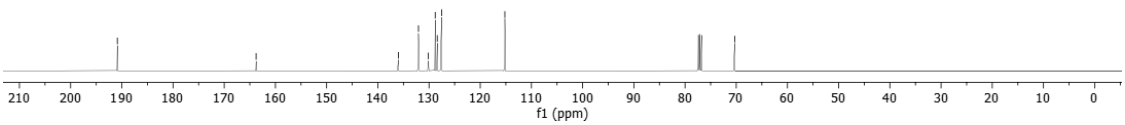


4-(benzyloxy)benzaldehyde (4z)

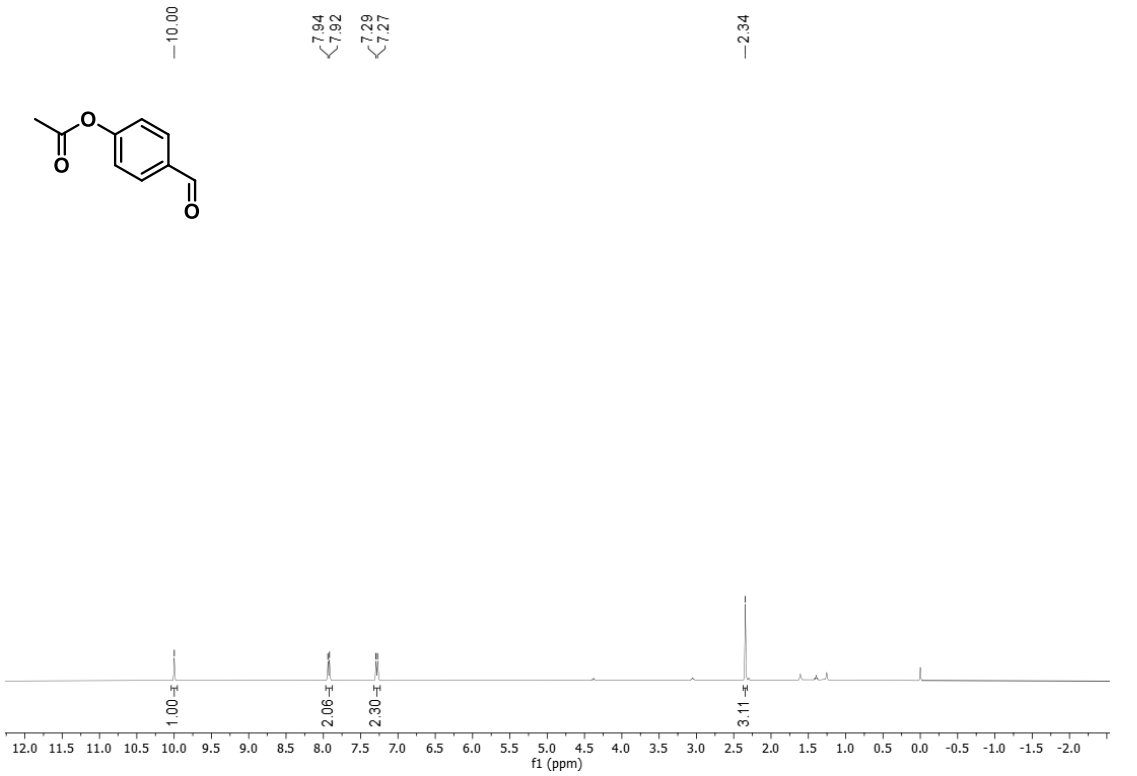


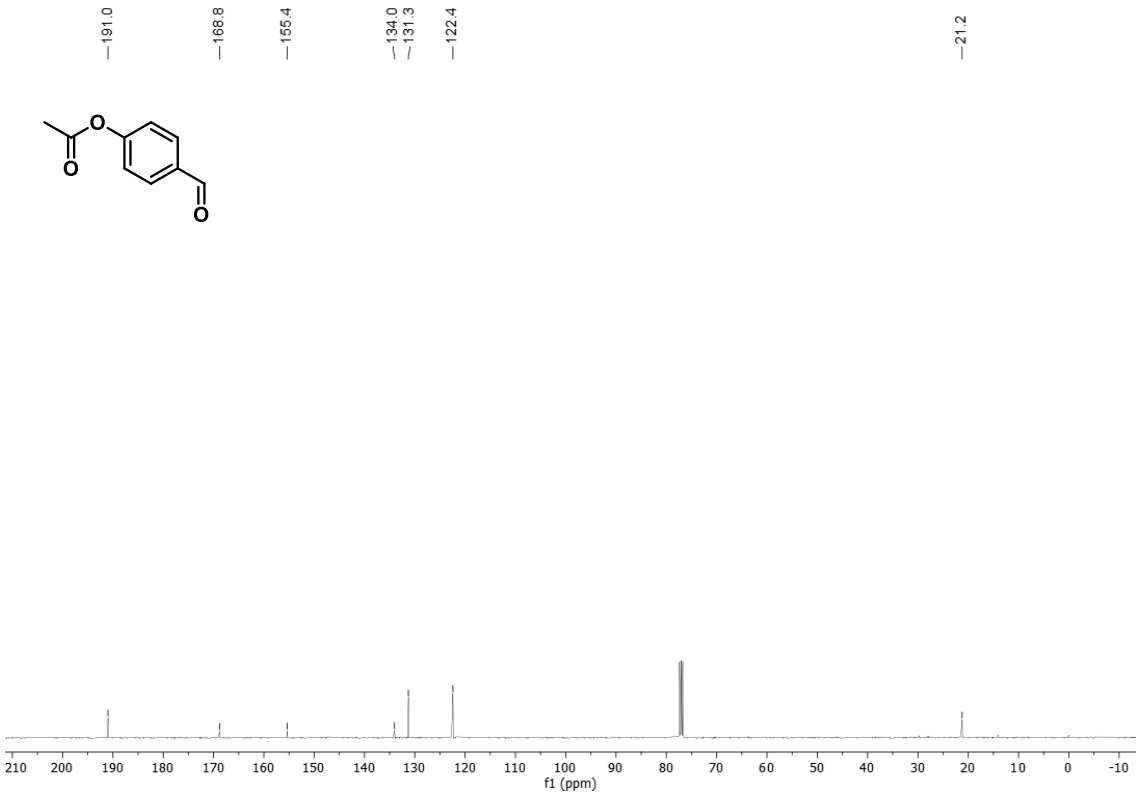




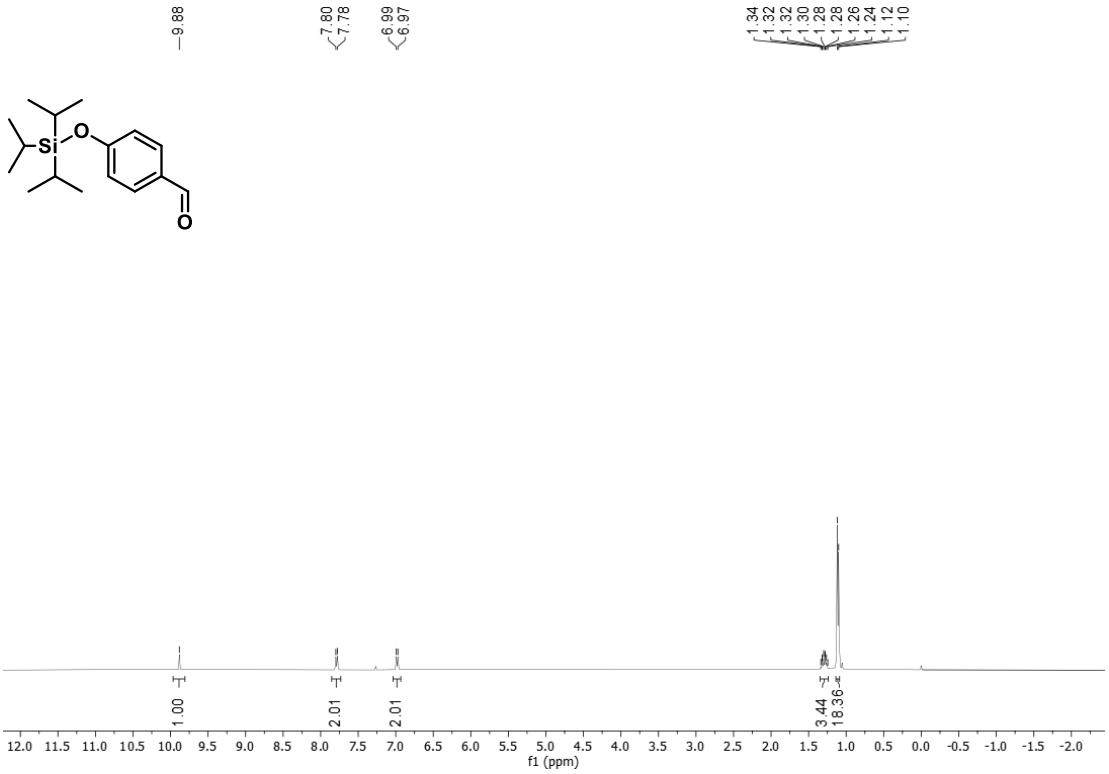


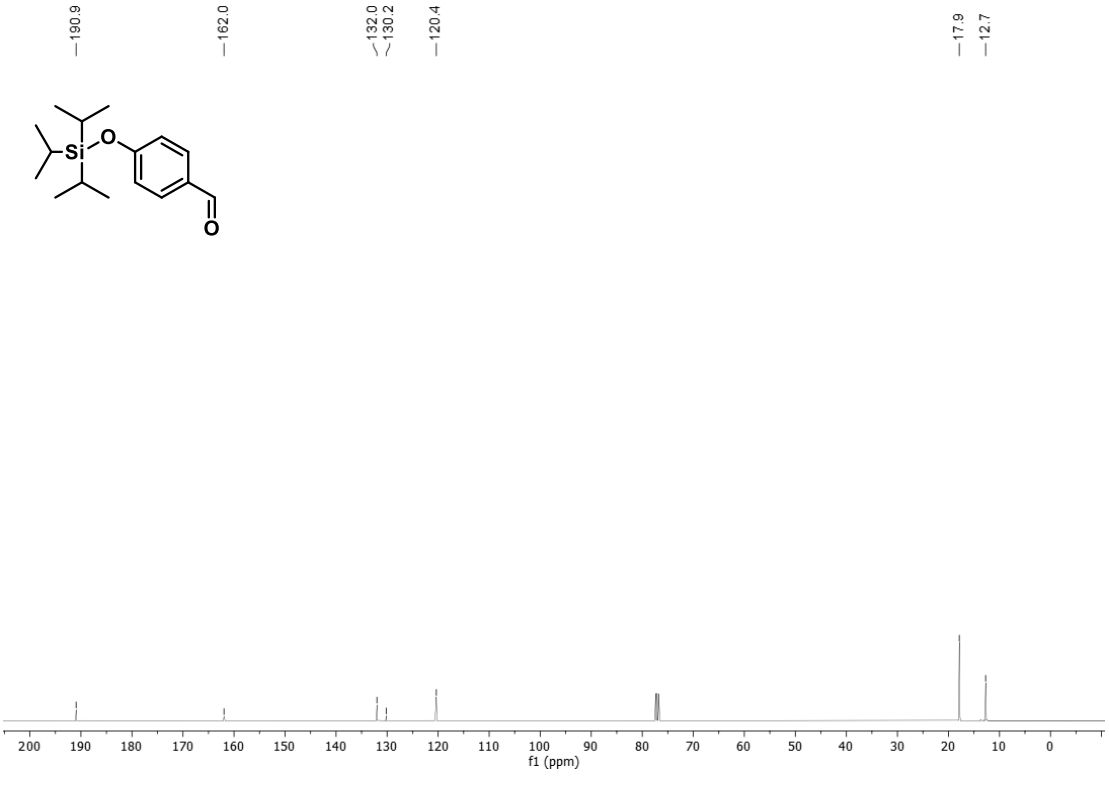
4-formylphenyl acetate (4aa)



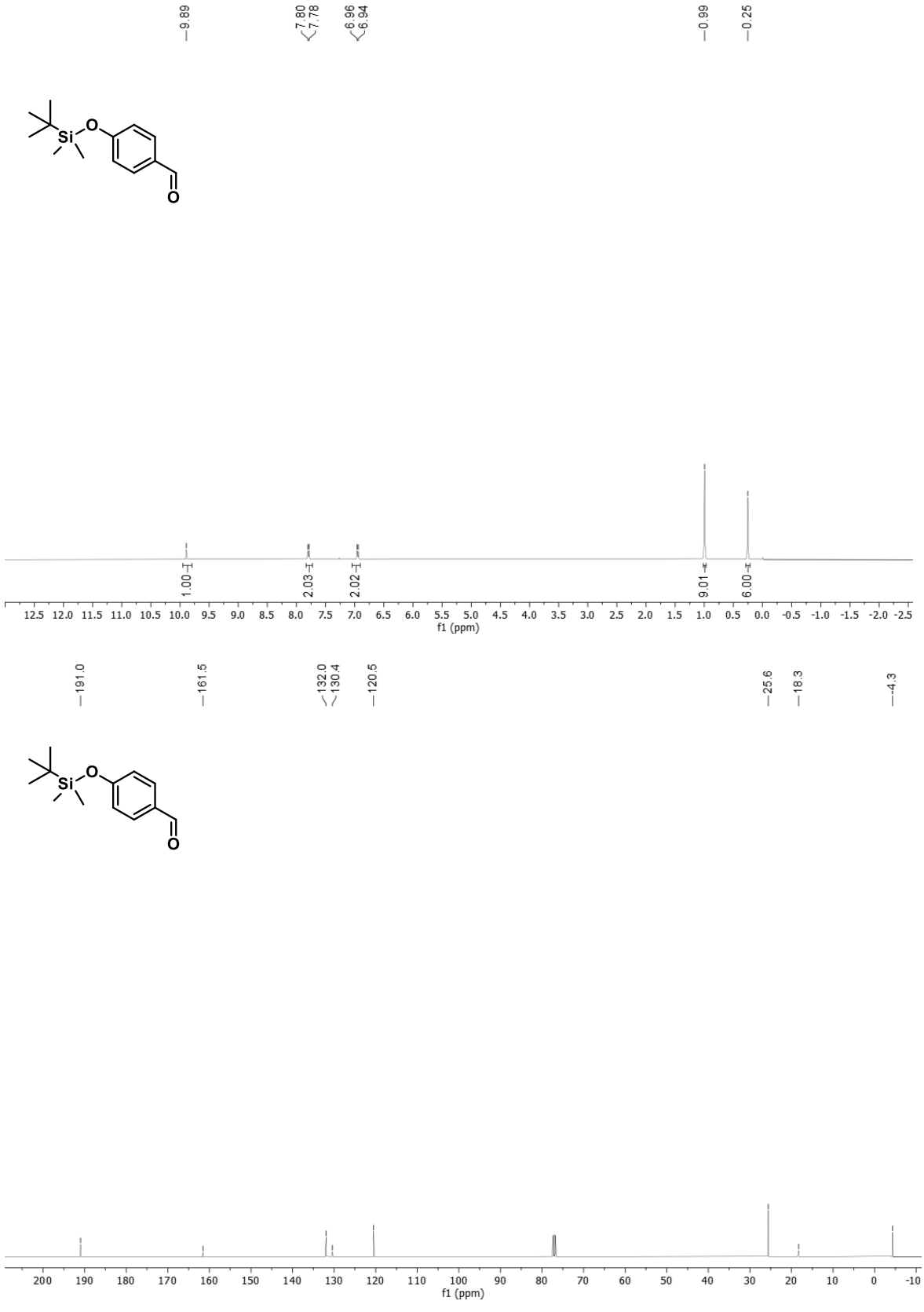


4-((triisopropylsilyl)oxy)benzaldehyde (4ab)

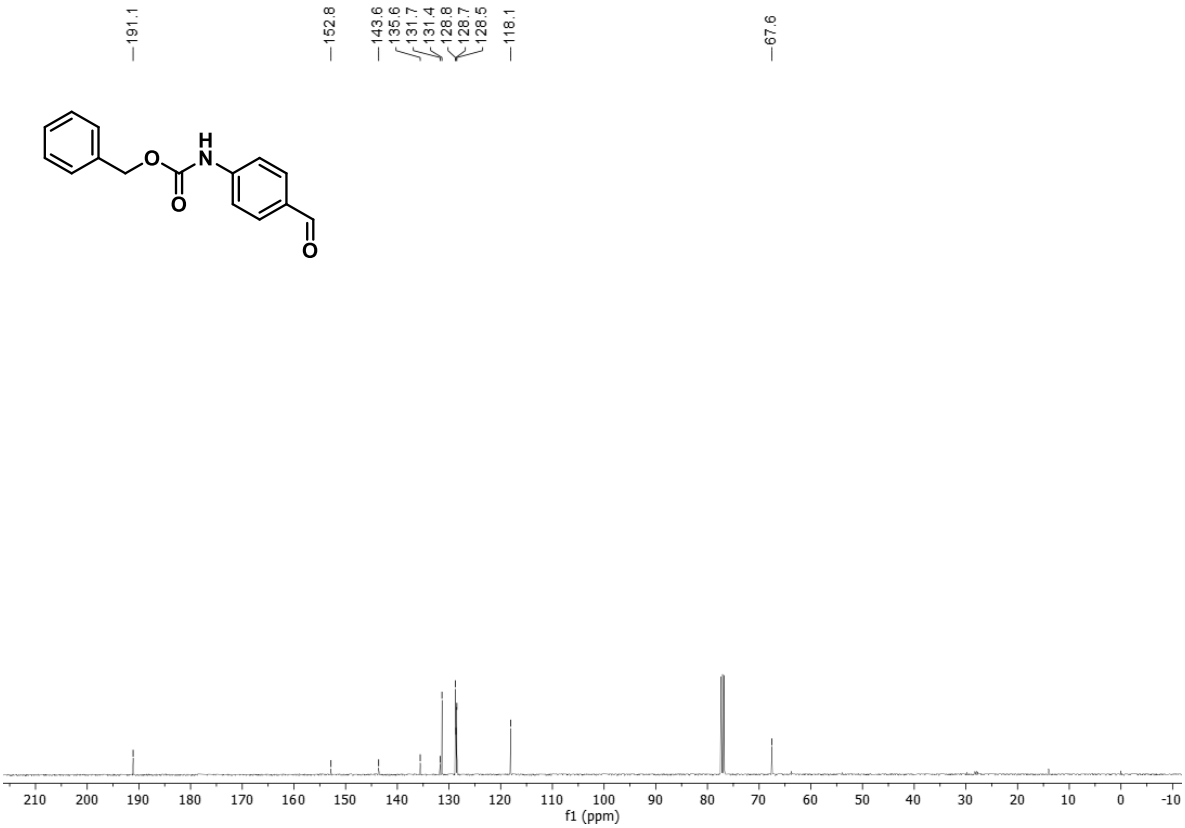




4-((tert-butyldimethylsilyl)oxy)benzaldehyde (4ac)



benzyl (4-formylphenyl)carbamate (4ad)



tert-butyl (4-formylphenyl)carbamate (4ae)