Selective Metalations of 1,4-Dithiins and Condensed Analogs using TMP-Magnesium and -Zinc Bases

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Supporting Information

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A) General Information

All air and moisture sensitive reactions were carried out under argon atmosphere in flame-dried glassware. Syringes which were used to transfer anhydrous solvents or reagents were purged with argon prior to use. THF was continuously refluxed and freshly distilled from sodium benzophenone ketyl under nitrogen and stored over molecular sieves. Reactions were monitored by gas chromatography (GC and GC-MS) or thin layer chromatography (TLC). TLC was performed with aluminium plates covered with SiO_2 (Merck 60, F-254) and visualized by UV detection. Yields refer to isolated yields of compounds estimated to be > 95% pure as determined by ^{1}H-NMR (25 °C) and capillary GC. NMR spectra were recorded in solutions in $CDCl_3$ with residual solvent reference (δ = 7.26 ppm for ^{1}H-NMR and δ = 77.1 ppm for ^{13}C-NMR). Abbreviations for signal coupling are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. Purification by column chromatography was performed using SiO_2 (0.040 – 0.063 mm, 230 – 400 mesh ASTM) from Merck or using preparative high performance liquid chromatography (HPLC). All reagents were obtained from commercial sources. TMPH was distilled prior to use. CuCN, $ZnCl_2$ and LiCl were obtained from Merck.

B) Starting material synthesis

1. Preparation of Organometallic reagents:

***i*-PrMgCl·LiCl** was purchased as a solution in THF from Rockrood Lithium and titrated against iodine prior to use.[1]

Preparation of CuCN·2LiCl solution:

CuCN·2LiCl solution (1.0 M in THF) was prepared by drying CuCN (7.17 g, 80 mmol) and LiCl (6.77 g, 160 mmol) in a *Schlenk*-flask under vacuum at 140 °C for 5 h. After cooling, dry THF (80 mL) was added and stirring was continued until all salts were dissolved (24 h).

Preparation of $ZnCl_2$ solution:

$ZnCl_2$ solution (1.0 M in THF) was prepared by drying $ZnCl_2$ (136.3 g, 100 mmol) in a *Schlenk*-flask under vacuum at 140 °C for 5 h. After cooling, dry THF (100 mL) was added and stirring was continued until all salts were dissolved (12 h).

Preparation of TMPMgCl·LiCl (6):[2]

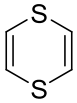
In a dry and argon flushed *Schlenk*-flask TMPH (2,2,6,6-tetramethylpiperidine, 14.8 g, 105 mmol) was added to *i*PrMgCl·LiCl (71.4 mL, 100 mmol, 1.40 M in THF) at 25 °C and the mixture was stirred for 3 days at 25 °C. The freshly prepared TMPMgCl·LiCl was titrated prior to use at 0 °C with benzoic acid using 4-(phenylazo)diphenylamine as indicator.

Preparation of TMPZn·LiCl (3):

[1] Krasovskiy, A.; Knochel, P. *Synthesis* **2006,** *2006*, 0890.
[2] Krasovskiy, A.; Krasovskaya, V.; Knochel, P. *Angew. Chem*. **2006**, *118*, 3024; *Angew. Chem., Int. Ed*. **2006**, *45*, 2958.

A flame-dried and argon flushed *Schlenk*-flask, equipped with a magnetic stirring bar and rubber septum, was charged with TMPH (2,2,6,6-tetramethylpiperidine, 10.2 mL, 60 mmol) dissolved in THF (60 mL). The solution was cooled to -40 °C and *n*BuLi (25 mL, 60 mmol, 2.4 M in hexane) was added dropwise and the mixture was allowed to warm up to -10 °C for 1 h. $ZnCl_2$ solution (66 mL, 66 mmol, 1.0 M in THF) was added dropwise and the resulting solution was stirred for 30 min at -10 °C and then 30 min at 25 °C. The solvents were removed under vacuum affording a yellowish solid. Freshly distilled THF was then slowly added and the solution was stirred until all salts were completely dissolved. The freshly prepared TMPZnCl·LiCl was titrated prior to use at 0 °C with benzoic acid using 4-(phenylazo)-diphenylamine as indicator.

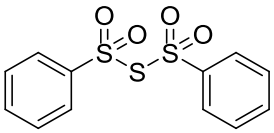
2. Preparation of 1,4-dithiine (**1**)[3]



According to the literature,[3] thionyl chloride (18.5 g, 11.3 mL, 156 mmol) was added to a solution of 1,4-dithiane-2,5-diol (6.77 g, 44.4 mmol) in dry DMF (250 mL) at 0 °C. After the addition, the reaction mixture was stirred at 25 °C for 2 h. The product which co-distills with DMF, was distilled under reduced pressure (100 °C, 270 mbar). After reducing half of the volume, another dry DMF (100 mL) was added to the reaction flask and the distillation was continued until a black residue was left. The distilled DMF was extracted with water (150 mL) and Et_2O (400 mL). The organic phase was washed with water (3 x 150 mL), sat. aq. $NaHCO_3$ solution (2 x 100 mL) and sat. aq. NaCl solution (100 mL). The organic phase was dried over anhydrous $MgSO_4$ and, after filtration, the solvent was evaporated *in vacuo*. 1,4-dithiine (**1**) was obtained as yellow liquid (4.18 g, 81%) and was used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 6.18 (s, 4H).

3. Preparation of bis(phenylsulfonyl)sulfide (**20**)[4]



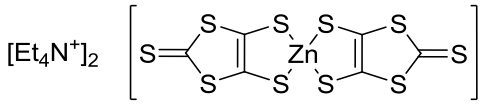
According to the literature,[4] sodium benzenesulfinate (41 g, 250 mmol) was suspended in dry Et_2O (300 mL) and a solution of sulfur dichloride (13 g, 125 mmol) in dry Et_2O (50 mL) was added dropwise. The mixture was stirred for 2 h at 40 °C. Afterwards water was added and the insoluble product was filtered off. After recrystallization from acetone, bis(phenylsulfonyl)sulfide was obtained as white crystals (24 g, 60%).

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 8.02 (d, *J*=7.6 Hz, 4 H), 7.71 (t, *J*=7.3 Hz, 2 H), 7.59 (t, *J*=7.8 Hz, 4 H).

[3] Grant, A. S.; Faraji-Dana, S.; Graham, E. *J. Sulfur Chem.* **2009**, *30*, 135.
[4] (a) Allared, F.; Hellberg, J.; Remonen, T. *Tetrahedron Lett.* 2002, **43**, 1553. (b) Dostert, C.; Wanstrath, C.; Frank, W.; Müller, T. J. J. *Chem. Commun.* **2012**, *48*, 7271.

4. Preparation of 1,4,5,8-tetrathianaphthalene (**4**)

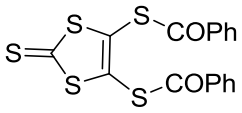
4.1. Synthesis of tetraethylammonium bis(1,3-dithiole-2-thione-4,5-dithiol) zincate (**21**)



According to the literature,[5] an oven-dried 1L round-bottomed flask, equipped with a mechanical stirrer, a 250-mL pressure-equalizing dropping funnel, and a gas inlet tube, was connected to nitrogen. The flask was charged with sodium (4.6 g, 200 mmol) and placed in an ice-water bath. Carbon disulfide (36 mL, 600 mmol) was introduced into the flask through the dropping funnel, after which 60 mL of DMF were added dropwise over 45 min. After the addition, the reaction mixture was allowed to warm to 25 °C and stir overnight. Methanol (20 mL) was added slowly through the dropping funnel to the reaction mixture in an ice bath. Afterwards, a mixture of methanol (80 mL) and deionized water (100 mL), was then added rapidly through the dropping funnel. A solution of $ZnCl_2$ (4.1 g, 30 mmol) in concentrated aqueous ammonium hydroxide (150 mL) and methanol (100 mL) was then added through the dropping funnel. A solution of tetraethylammonium bromide (10.5 g, 50 mmol) in water (50 mL) was added dropwise via the dropping funnel with vigorous stirring over at least 45 min, and the solution was stirred 12 h. The precipitated was collected by suction on a Büchner funnel and washed with water (100 mL), isopropanol (80 mL) and diethyl ether (40 mL). The product was then dried in a desiccator under vacuum affording **21** as a red powder (15 g, 84%).

^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 209.4, 135.1, 52.0, 7.1.

4.2. Synthesis of 4,5-dibenzoylthio-1,3-dithiole-1-thione (**22**).



According to the literature,[5] tetraethylammonium bis(1,3-dithiole-2-thione-4,5-dithio) zincate (**21**, 16 g, 223 mmol) was dissolved in acetone (400 mL) of benzoyl chloride (48.4 g, 345 mmol) was added dropwise. The reaction mixture was stirred for 12 h and the resulting yellow-light brown precipitate was collected by suction and washed with water (500 mL) and acetone (300 mL). This crude material was dissolved in chloroform (350 mL), Norit (0.5 g) was added and the mixture was heated under reflux for 10 min. The mixture was filtered while still hot, and washed with chloroform. The combined chloroform solutions were concentrated to 150 mL and the resulting mixture was warmed and methanol (50 mL) was added portionwise with stirring. The solution was then left overnight in the refrigerator. The resulting crystalline precipitate was collected by suction and air-dried, affording **22** (8.5 g, 43%).

^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 212.5, 185.6, 135.0, 134.9, 133.8, 129.3, 128.2.

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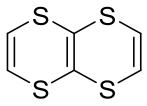
[5] Hansen, T. K.; Becher, J.; Joergensen, T.; Varma, K. S.; Khedekar, R.; Cava, M. P.*Organic Syntheses*, **1996**, *73*, 270.

4.3. Synthesis of 1,4,5,8-tetrathianaphthalene (**4**).



According to the literature,[6] sodium (3.0 g, 130 mmol) was dissolved in ethanol (50 mL) under N_2 in a 3-necked 1L round bottom flask equiped with a stir bar and two 250 mL addition funnels. Then, THF (165 mL) was added and the solution was refluxed. At that moment, 4,5-bis(benzoylthio)-1,3-dithiole-1-thione (**23**, 5.3 g, 13 mmol in 80 mL of THF) and *cis*-1,2-dichloroethylene (2.6 g, 27mmol in 80 mL of THF) were added simultaneously dropwise over 1 h to the sodium ethoxide solution. The reaction mixture was refluxed for 12 h. Water (130 mL) was added to dissolve the precipitate and then, the THF was removed under reduced pressure. The solid was collected and washed with water. The solid was purified by flash column chromatography on silica gel (*i*hexane) yielding **4** as yellow solid (1.6 g, 60%).

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 6.46 (s, 4 H).

C) General procedures

Typical Procedure 1 for the magnesiation of 1,4-dithiine (1) with TMPMgCl·LiCl (6) (TP1):

A dry and argon flushed *Schlenk*-flask was charged with a solution of 1,4-dithiine (**1**; 1.0 equiv) in dry THF (0.5 M). TMPMgCl·LiCl (**6**; 1.1 equiv) was added dropwise at -40 °C and the reaction mixture was stirred for 0.5 h. The completion of the reaction was checked by GC analysis of reaction aliquots quenched with iodine in dry THF.

Typical Procedure 2 for the magnesiation or zincation of monofunctionalized 1,4-dithiine derivatives (9) withTMPMgCl·LiCl (6) or TMPZnCl·LiCl (7) (TP2):

A dry and argon flushed *Schlenk*-flask was charged with a solution of the corresponding monofunctionalized 1,4-dithiine derivative (**9**; 1.0 equiv) in dry THF (0.5 M). TMPMgCl·LiCl (**6**; 1.05 - 1.1 equiv) or TMPZnCl·LiCl (**7**; 1.1 equiv) was added dropwise at the indicated temperature and the reaction mixture was stirred for 0.5 h. The completion of the reaction was checked by TLC analysis of reaction aliquots quenched with iodine in dry THF.

Typical Procedure 3 for the magnesiation of 1,4,5,8-tetrathianaphthalene (4) with TMPMgCl·LiCl (6) (TP3):

A dry and argon flushed *Schlenk*-flask was charged with a solution of 1,4,5,8-tetrathianaphthalene (**4**; 1.0 equiv) in dry THF (0.13 M). TMPMgCl·LiCl (**6**; 1.2 equiv) was added dropwise at -78 °C and the reaction mixture was stirred for 10 min. The completion of the reaction was checked by GC analysis of reaction aliquots quenched with iodine in dry THF.

[6] Meline, R. L.; Elsenbaumer, R. L. *Synthetic Metals*, **1997**, *86*, 1845.

Typical Procedure 4 for the zincation of monofunctionalized 1,4,5,8-tetrathianaphthalene derivatives (14) with TMPZnCl·LiCl (7) (TP4):

A dry and argon flushed *Schlenk*-flask was charged with a solution of the corresponding monofunctionalized 1,4,5,8-tetrathianaphthalene derivative (**14**; 1.0 equiv) in dry THF (0.13 M). TMPZnCl·LiCl (**7**; 1.1 equiv) was added dropwise at -40 °C and the reaction mixture was stirred for 0.5 h. The completion of the reaction was checked by TLC analysis of reaction aliquots quenched with iodine in dry THF.

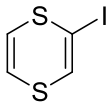
Typical Procedure 5 for the zincation of 1,4,5,6,9,10-hexathiaanthracene (5) with TMPZnCl·LiCl (7) (TP5):

A dry and argon flushed *Schlenk*-flask was charged with a solution of 1,4,5,6,9,10-hexathiaanthracene (**5**; 1.0 equiv) in dry THF (0.03 M). TMPZnCl·LiCl (**7**; 1.1 equiv) was added dropwise at -40 °C and the reaction mixture was stirred for 2 h. The completion of the reaction was checked by GC analysis of reaction aliquots quenched with iodine in dry THF.

D) Compounds synthesized according to the general procedures

1. Preparation of monofunctionalized 1,4-dithiine derivatives

1.1. Synthesis of 2-iodo-1,4-dithiine (**9a**)



According to **TP1**, 1,4-dithiine (**1**; 116 mg, 1.0 mmol) was dissolved in dry THF (2 mL). TMPMgCl·LiCl (0.99 mL, 1.1 mmol) was added dropwise at -40 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared magnesium reagent was added to a solution of iodine (177 mg, 0.7 mmol) in dry THF (1 mL) at -78 °C. The resulting solution was stirred at this temperature for 1 h and was then quenched with sat. aq. $Na_2S_2O_3$ solution (5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane) yielding **9a** as yellow liquid (127 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 6.52 - 6.46 (m, 2H), 6.24 (d, *J* = 6.6, 1H).

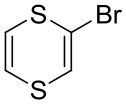
^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 125.9, 122.7, 121.7, 72.8.

IR (Diamond-ATR, neat) $\tilde{\nu}$ /cm^{-1}: 3025, 2921, 1678, 1598, 1554, 1534, 1513, 1469, 1273, 1217, 1134, 885, 839, 794, 768, 732, 668, 566.

MS (70 eV, EI) *m/z* (%): 242 (69), 115 (100), 89 (21), 71 (78), 57 (30), 45 (56).

HRMS (EI): *m/z* (M$^+$) for $C_4H_3IS_2$: calcd. 241.8721; found 241.8723.

1.2. Synthesis of 2-bromo-1,4-dithiine (**9b**)



According to **TP1**, 1,4-dithiine (**1**; 116 mg, 5.0 mmol) was dissolved in dry THF (10 mL). TMPMgCl·LiCl (4.95 mL, 5.5 mmol) was added dropwise at -40 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared magnesium reagent was added to a solution of 1,2-dibromotetrachloroethane (1.14 g, 3.5 mmol) in dry THF (5 mL) at -78 °C. The resulting solution was stirred at this temperature for 2 h and was then quenched with sat. aq. NH_4Cl solution (10 mL), extracted with Et_2O (3 x 80 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane) yielding **9b** as yellow liquid (529 mg, 78%).

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 6.40 (d, *J*=6.4 Hz, 1 H), 6.27 - 6.33 (m, 2 H).

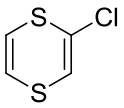
^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 126.0, 122.8, 121.9, 73.0.

IR (Diamond-ATR, neat) $\tilde{\nu}$ /cm^{-1}: 3031, 1563, 1555, 1524, 1503, 1493, 1468, 1446, 1413, 1322, 1275, 1218, 1188, 1135, 1091, 1070, 1031, 1011, 919, 886, 860, 827, 799, 773, 752, 701, 668.

MS (70 eV, EI) *m/z* (%): 196 (53), 194 (47), 115 (100), 71 (41), 57 (10), 45 (16).

HRMS (EI): *m/z* (M^+) for $C_4H_3BrS_2$: calcd. 193.8860; found 193.8840.

1.3. Synthesis of 2-chloro-1,4-dithiine (**9c**)



According to **TP1**, 1,4-dithiine (**1**; 813 mg, 7.0 mmol) was dissolved in dry THF (14 mL). TMPMgCl·LiCl (6.94 mL, 7.7 mmol) was added dropwise at -40 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared magnesium reagent was added to a solution of benzenesulfonyl chloride (865 mg, 4.9 mmol) in dry THF (5 mL) at -78 °C. The resulting solution was stirred at this temperature for 2 h and was then quenched with sat. aq. NH_4Cl solution (10 mL), extracted with Et_2O (3 x 80 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane) yielding **9c** as yellow liquid (413 mg, 56%).

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 6.37 (d, *J*=6.6 Hz, 1 H), 6.33 (d, *J*=6.6 Hz, 1 H), 6.16 (s, 1 H).

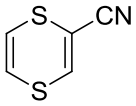
^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 123.0, 122.6, 122.3, 117.3.

IR (Diamond-ATR, neat) $\tilde{\nu}$ /cm^{-1}: 3035, 2922, 2179, 1601, 1579, 1548, 1528, 1455, 1402, 1278, 1206, 1136, 1065, 971, 928, 896, 818, 770, 668.

MS (70 eV, EI) *m/z* (%): 152 (21), 150 (52), 115 (87), 105 (13), 89 (14), 88 (17), 79 (12), 71 (45), 58 (23), 57 (52), 45 (100).

HRMS (EI): *m/z* (M^+) for $C_4H_3ClS_2$: calcd. 149.9365; found 149.9355.

1.4. Synthesis of 1,4-dithiine-2-carbonitrile (**9d**)



According to **TP1**, 1,4-dithiine (**1**; 116 mg, 1.0 mmol) was dissolved in dry THF (2 mL). TMPMgCl·LiCl (0.99 mL, 1.1 mmol) was added dropwise at -40 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared magnesium reagent was added to a solution of *p*-toluenesulfonyl cyanide (127 mg, 0.7 mmol) in dry THF (2 mL) at -60 °C. The resulting solution was stirred at this temperature for 2 h and was then quenched with sat. aq. NH_4Cl solution (5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/Et_2O, 95:5) yielding **9d** as orange oil (59 mg, 60%).

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 7.13 (s, 1 H), 6.32 (d, *J*=6.6 Hz, 1 H), 6.28 (d, *J*=6.6 Hz, 1 H).

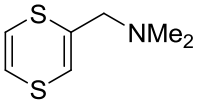
^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 140.1, 122.0, 121.1, 114.5, 105.3.

IR (Diamond-ATR, neat) $\tilde{\nu}$ /cm^{-1}: 3034, 2924, 2217, 1654, 1594, 1558, 1525, 1447, 1313, 1281, 1240, 1176, 1140, 1084, 1054, 999, 958, 932, 892, 851, 805, 785, 674, 661.

MS (70 eV, EI) *m/z* (%): 141 (100), 114 (19), 96 (13), 71 (27), 45 (33).

HRMS (EI): *m/z* (M^+) for $C_5H_3NS_2$: calcd. 140.9707; found 140.9694.

1.5. Synthesis of 1-(1,4-dithiin-2-yl)-*N*,*N*-dimethylmethanamine (**9e**)



A dry and argon-flushed *Schlenk*-flask was charged with *N,N,N',N'*-tetramethylmethanediamine (112 mg, 1.1 mmol) and anydrous CH_2Cl_2 (1.1 mL). Trifluoroacetic anhydride (231 mg, 1.1 mmol) was added dropwise and the solution was stirred for 15 min at 0 °C.[7] In a second dry and argon-flushed Schlenk flask, according to **TP1**, 1,4-dithiine (**1**; 116 mg, 1.0 mmol) was dissolved in dry THF (2 mL). TMPMgCl·LiCl (1.04 mL, 1.1 mmol) was added dropwise at -40 °C and the reaction mixture was stirred for 0.5 h. Then, the previously prepared methylene(dimethyl)iminium trifluoroacetate was added at -78 °C to the magnesiated 1,4-dithiin solution. The reaction mixture was stirred for 3 h warming to 25 ºC. The crude mixture was quenched with sat. aq. $NaHCO_3$ and extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with sat. aq. NaCl and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column

[7] V. Werner, M. Ellwart, A. J. Wagner, P. Knochel, *Org. Lett.* **2015**, *17*, 2026-2029.

chromatography on silica gel (*i*hexane/EtOAc, 8:2) yielding **9e** as orange oil (100 mg, 58%).

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 6.26 (d, *J*=7.0 Hz, 1 H), 6.24 (d, *J*=7.0 Hz, 1 H), 6.02 (s, 1 H), 3.10 (s, 2 H), 2.24 (s, 6 H).

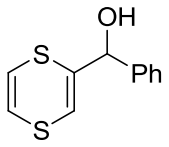
^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 135.5, 122.3, 121.9, 117.3, 64.5, 45.0.

IR (Diamond-ATR, neat) $\tilde{\nu}$ /cm^{-1}: 3025, 2973, 2942, 2853, 2817, 2771, 1538, 1464, 1450, 1351, 1262, 1225, 1174, 1147, 1091, 1042, 1023, 982, 890, 859, 834, 809, 782, 731, 668.

MS (70 eV, EI) *m/z* (%): 173 (23), 130 (6), 97 (8), 58 (100), 45 (11), 44 (6), 43 (18), 42 (11), 41 (7).

HRMS (EI): *m/z* (M^+) for $C_7H_{11}NS_2$: calcd. 173.0333; found 173.0322.

1.6. Synthesis of (1,4-dithiin-2-yl)(phenyl)methanol (**9f**)



According to **TP1**, 1,4-dithiine (**1**; 58 mg, 0.5 mmol) was dissolved in dry THF (1 mL). TMPMgCl·LiCl (0.50 mL, 0.55 mmol) was added dropwise at -40 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared magnesium reagent was added to a solution of benzaldehyde (37 mg, 0.35 mmol) in dry THF (1 mL) at -78 °C. The resulting solution was stirred at this temperature for 2 h and was then quenched with sat. aq. NH_4Cl solution (5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/EtOAc, 7:1) yielding **9f** as yellowish solid (75 mg, 97%).

m.p.: 64.9 - 68.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 7.31 - 7.42 (m, 6 H), 6.34 (d, *J*=6.8 Hz, 1 H), 6.28 (s, 1 H), 6.20 (d, *J*=6.8 Hz, 1 H), 5.36 (s, 1 H), 2.61 (br. s., 1 H).

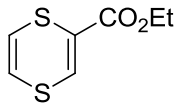
^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 140.3, 139.6, 128.5, 128.3, 126.6, 123.7, 121.9, 118.3, 75.7.

IR (Diamond-ATR, neat) $\tilde{\nu}$ /cm^{-1}: 3791, 3271, 3029, 3016, 2894, 2666, 1957, 1887, 1728, 1711, 1598, 1587, 1573, 1564, 1537, 1492, 1461, 1446, 1392, 1372, 1322, 1301, 1267, 1218, 1187, 1177, 1157, 1142, 1092, 1070, 1031, 1011, 919, 892, 859, 827, 794, 777, 748, 699, 687, 672.

MS (70 eV, EI) *m/z* (%): 223 (15), 222 (100), 116 (60), 107 (23), 105 (36), 103 (13), 79 (54), 77 (64), 71 (36), 58 (11), 45 (23).

HRMS (EI): *m/z* (M^+) for $C_{11}H_{10}OS_2$: calcd. 222.0173; found 222.0169.

1.7. Synthesis of ethyl 1,4-dithiine-2-carboxylate (**9g**)



According to **TP1**, 1,4-dithiine (**1**; 697 mg, 6.0 mmol) was dissolved in dry THF (12 mL). TMPMgCl·LiCl (5.95 mL, 6.6 mmol) was added dropwise at -40 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared magnesium reagent was added to a solution of ethyl cyanoformate (417 mg, 4.2 mmol) in dry THF (6 mL) at -60 °C. The resulting solution was stirred at this temperature for 2 h and was then quenched with sat. aq. NH_4Cl solution (10 mL), extracted with Et_2O (3 x 70 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/Et_2O, 95:5) yielding **9g** as red liquid (704 mg, 89%).

^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 7.29 (s, 1 H), 6.19 (d, *J*=7.1 Hz, 1 H), 6.03 (d, *J*=7.1 Hz, 1 H), 4.26 (q, *J*=7.1 Hz, 2 H), 1.32 (t, *J*=7.1 Hz, 4 H).

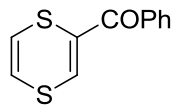
^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 161.1, 133.8, 125.6, 122.0, 119.6, 62.0, 14.1.

IR (Diamond-ATR, neat) $\tilde{\nu}$ /cm^{-1}: 3037, 2980, 2932, 2904, 1702, 1573, 1533, 1464, 1444, 1391, 1366, 1292, 1243, 1218, 1171, 1111, 1094, 1040, 994, 973, 889, 850, 830, 790, 731, 666.

MS (70 eV, EI) *m/z* (%): 190 (12), 189 (12), 188 (100), 162 (10), 160 (91), 143 (16), 142 (26), 115 (22), 114 (18), 111 (19).

HRMS (EI): *m/z* (M$^+$) for $C_7H_8O_2S_2$: calcd. 187.9966; found 187.9948.

1.8. Synthesis of (1,4-dithiin-2-yl)(phenyl)methanone (**9h**)



According to **TP1**, 1,4-dithiine (**1**; 1.16 g, 10.0 mmol) was dissolved in dry THF (20 mL). TMPMgCl·LiCl (9.91 mL, 11.0 mmol) was added dropwise at -40 °C and the reaction mixture was stirred for 0.5 h. $ZnCl_2$ solution (12.0 mL, 12.0 mmol, 1.0 M in THF) was added and the reaction mixture was allowed to stir for 15 min. CuCN.2LiCl solution (12.0 mL, 12.0 mmol, 1.0 M in THF) was added and the reaction mixture was allowed to stir for 15 min, before benzoyl chloride (984 mg, 7.0 mmol) was added. The reaction mixture was stirred at 25 °C for 12 h and was then quenched with sat. aq. NH_4Cl/NH_3 solution (8:1, 50 mL), extracted with Et_2O (3 x 100 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/Et_2O, 94:6) yielding **9h** as red liquid (1.20 g, 78%).

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 7.69 (d, *J*=7.6 Hz, 2 H), 7.56 (t, *J*=7.6 Hz, 1 H), 7.45 (t, *J*=7.6 Hz, 2 H), 6.96 (s, 1 H), 6.28 (d, *J*=7.6 Hz, 1 H), 6.10 (d, *J*=7.6 Hz, 1 H).

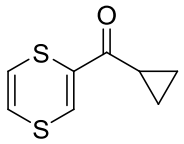
^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 188.6, 137.0, 136.8, 134.2, 132.5, 129.1, 128.4, 122.6, 119.7.

IR (Diamond-ATR, neat) $\tilde{\nu}$ /cm^{-1}: 3092, 3035, 2973, 2955, 2928, 2868, 2360, 1748, 1693, 1638, 1563, 1528, 1468, 1396, 1366, 1261, 1126, 1020, 938, 900, 872, 858, 770, 737, 666.

MS (70 eV, EI) *m/z* (%): 220 (40), 105 (100), 77 (63).

HRMS (EI): *m/z* (M$^+$) for $C_{11}H_8OS_2$: calcd. 220.0017; found 220.0014.

1.9. Synthesis of cyclopropyl(1,4-dithiin-2-yl)methanone (**9i**)



According to **TP1**, 1,4-dithiine (**1**; 232 mg, 2.0 mmol) was dissolved in dry THF (4 mL). TMPMgCl·LiCl (1.98 mL, 2.2 mmol) was added dropwise at -40 °C and the reaction mixture was stirred for 0.5 h. $ZnCl_2$ solution (2.4 mL, 2.4 mmol, 1.0 M in THF) was added and the reaction mixture was allowed to stir for 15 min. CuCN.2LiCl solution (2.4 mL, 2.4 mmol, 1.0 M in THF) was added and the reaction mixture was allowed to stir for 15 min, before cyclopropanecarbonyl chloride (146 mg, 1.4 mmol) was added. The reaction mixture was stirred at 25 °C for 20 h and was then quenched with sat. aq. NH_4Cl/NH_3 solution (8:1, 5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/Et_2O, 9:1) yielding **9i** as red oil (168 mg, 65%).

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 7.31 (s, 1 H), 6.20 (d, *J*=7.4 Hz, 1 H), 6.06 (d, *J*=7.4 Hz, 1 H), 2.29 - 2.39 (m, 1 H), 1.08 - 1.15 (m, 2 H), 0.92 - 1.00 (m, 2 H).

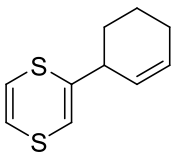
^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 192.6, 135.2, 133.2, 122.3, 119.7, 17.3, 11.8.

IR (Diamond-ATR, neat) $\tilde{\nu}$ /cm^{-1}: 3033, 2360, 2086, 1645, 1561, 1528, 1438, 1418, 1385, 1292, 1198, 1161, 1128, 1090, 1061, 1029, 984, 925, 878, 792, 718.

MS (70 eV, EI) *m/z* (%): 203 (98), 186 (12), 185 (13), 184 (100), 116 (51), 115 (20), 111 (10), 105 (12), 85 (11), 71 (30), 69 (88), 45 (32), 44 (13), 41 (61).

HRMS (EI): *m/z* (M$^+$) for $C_8H_8OS_2$: calcd. 184.0017; found 184.0014.

1.10. Synthesis of 2-(cyclohex-2-en-1-yl)-1,4-dithiine (**9j**)



According to **TP1**, 1,4-dithiine (**1**; 58 mg, 0.5 mmol) was dissolved in dry THF (1 mL). TMPMgCl·LiCl (0.50 mL, 0.55 mmol) was added dropwise at -40 °C and the reaction mixture was stirred for 0.5 h. $ZnCl_2$ solution (0.6 mL, 0.6 mmol, 1.0 M in THF) was added and the reaction mixture was allowed to stir for 15 min. CuCN.2LiCl solution (0.6 mL, 0.6 mmol, 1.0 M in THF) was added and the reaction mixture was allowed to stir for 15 min, and afterwards, 3-bromocyclohexene (56 mg, 0.35 mmol) was added. The reaction mixture was stirred at 25 °C for 12 h and was then quenched with sat. aq. NH_4Cl/NH_3 solution (8:1, 5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane) yielding **9j** as yellow oil (50 mg, 73%).

^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 6.35 (d, *J*=6.8 Hz, 1 H), 6.30 (d, *J*=6.8 Hz, 1 H), 5.92 (s, 1 H), 5.82 - 5.89 (m, 1 H), 5.56 - 5.63 (m, 1 H), 3.03 - 3.14 (m, 1 H), 1.96 - 2.08 (m, 2 H), 1.80 - 1.91 (m, 1 H), 1.62 - 1.74 (m, 2 H), 1.50 - 1.61 (m, 1 H).

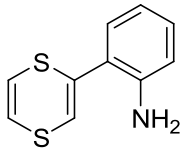
^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 142.4, 129.8, 127.7, 123.4, 122.6, 115.6, 42.4, 28.6, 24.9, 20.1.

IR (Diamond-ATR, neat) $\tilde{\nu}$ /cm^{-1}: 3019, 2926, 2856, 2831, 1720, 1647, 1584, 1535, 1444, 1429, 1343, 1212, 1159, 1134, 1086, 1045, 1019, 978, 964, 898, 887, 869, 805, 793, 784, 772, 734, 723, 708, 669, 652, 624, 612, 596, 587, 576, 571, 568, 564, 555.

MS (70 eV, EI) *m/z* (%): 196 (20), 79 (23), 77 (21), 53 (34), 52 (22), 45 (100).

HRMS (EI): *m/z* (M^+) for $C_{10}H_{12}S_2$: calcd. 196.0380; found 196.0386.

1.11. Synthesis of 2-(1,4-dithiin-2-yl)aniline (**9k**)



According to **TP1**, 1,4-dithiine (**1**; 1.16 g, 10.0 mmol) was dissolved in dry THF (20 mL). TMPMgCl·LiCl (9.91 mL, 11.0 mmol) was added dropwise at -40 °C and the reaction mixture was stirred for 0.5 h. $ZnCl_2$ solution (12.0 mL, 12.0 mmol, 1.0 M in THF) was added and the reaction mixture was allowed to stir for 15 min. The freshly prepared zinc reagent was added over 1 h to a solution of 2-iodoaniline (1.75 g, 8.0 mmol), $Pd(dba)_2$ (173 mg, 0.3 mmol) and P(2-furyl)$_3$ (139 mg, 0.6 mmol) in dry THF (7 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 6 h and was then quenched with sat. aq. NH_4Cl solution (50 mL), extracted with Et_2O (3 x 100 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/EtOAc, 14:1) yielding **9k** as yellow oil (1.56 g, 94%).

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 7.10 - 7.20 (m, 2 H), 6.66 - 6.78 (m, 2 H), 6.46 (d, *J*=6.8 Hz, 1 H), 6.39 (d, *J*=6.8 Hz, 1 H), 6.20 (s, 1 H), 3.93 (br. s., 2 H).

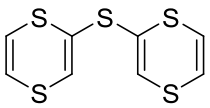
^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 143.9, 135.0, 130.7, 129.7, 123.0, 122.8, 122.8, 119.1, 118.5, 116.0.

IR (Diamond-ATR, neat) $\tilde{\nu}$ /cm^{-1}: 3435, 3352, 3204, 3024, 2923, 2853, 2620, 1936, 1669, 1611, 1575, 1533, 1486, 1450, 1365, 1302, 1281, 1256, 1211, 1157, 1138, 1054, 1032, 1007, 939, 910, 855, 792, 777, 746, 673, 655, 634, 577, 558.

MS (70 eV, EI) *m/z* (%): 207 (90), 190 (37), 174 (94), 173 (51), 130 (55), 117 (100), 90 (61), 89 (47), 77 (16), 63 (17), 58 (11), 57 (11), 45 (40), 43 (11).

HRMS (EI): *m/z* (M$^+$) for $C_{10}H_9NS_2$: calcd. 207.0176; found 207.0162.

1.12. Synthesis of di(1,4-dithiin-2-yl)sulfane (**9l**)



According to **TP1**, 1,4-dithiine (**1**; 348 mg, 2.0 mmol) was dissolved in dry THF (4 mL). TMPMgCl·LiCl (2.0 mL, 2.2 mmol) was added dropwise at -40 °C and the reaction mixture was stirred for 0.5 h. Bis(phenylsulfonyl)sulfide (**20**, 314 mg, 1.0 mmol) in dry THF (2 mL) was added at -78 °C and stirred for 12 h allowing to reach 23 °C. The resulting solution was then quenched with sat. aq. NH_4Cl solution (10 mL), extracted with EtOAc (3 x 20 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 9:1) yielding **9l** as brown solid (196 mg, 75%).

m.p.: 45.8 - 46.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 6.41 (s, 2 H), 6.28 - 6.36 (m, 4 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 126.9, 124.2, 122.8, 122.6.

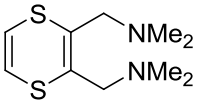
IR (Diamond-ATR, neat) $\tilde{\nu}$ /cm^{-1}: 3026, 2921, 2850, 1680, 1573, 1512, 1276, 1261, 1215, 1134, 1090, 1020, 883, 812, 769.

MS (70 eV, EI) *m/z* (%): 262 (32), 147 (14), 103 (100), 71 (30), 45 (34), 44 (53).

HRMS (EI): *m/z* (M$^+$) for $C_8H_6S_5$: calcd. 261.9073; found 261.9068.

2. Preparation of difunctionalized 1,4-dithiine derivatives

2.1. Synthesis of 1,1'-(1,4-dithiine-2,3-diyl)bis(*N*,*N*-dimethylmethanamine) (**11a**)



A dry and argon-flushed *Schlenk*-flask was charged with *N,N,N',N'*-tetramethylmethanediamine (45 mg, 0.44 mmol) and anydrous CH_2Cl_2 (0.44 mL). Trifluoroacetic anhydride (92 mg, 0.44 mmol) was added dropwise and the solution was

stirred for 15 min at 0 °C.[7] In a second dry and argon-flushed Schlenk flask, according to **TP2**, 1-(1,4-dithiin-2-yl)-N,N-dimethylmethanamine (**9e**; 69 mg, 0.4 mmol) was dissolved in dry THF (0.8 mL). TMPMgCl·LiCl (0.4 mL, 0.4 mmol) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. Then, the previously prepared methylene(dimethyl)iminium trifluoroacetate was added at -78 °C to the magnesiated 1-(1,4-dithiin-2-yl)-N,N-dimethylmethanamine solution. The reaction mixture was stirred for 1 h at -78 °C. The crude mixture was quenched with sat. aq. $NaHCO_3$ and extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with sat. aq. NaCl and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/EtOAc, 8:2) yielding **11a** as orange oil (59 mg, 64%).

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 6.43 (s, 2 H), 3.17 (s, 4 H), 2.27 (s, 12 H).

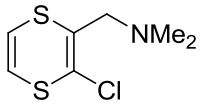
^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 131.7, 124.3, 61.7, 45.0.

IR (Diamond-ATR, neat) $\tilde{\nu}$ /cm^{-1}: 3388, 2973, 2941, 2853, 2817, 2767, 1609, 1536, 1453, 1344, 1260, 1175, 1135, 1096, 1041, 1029, 1007, 947, 911, 841, 804, 770, 731, 671.

MS (70 eV, EI) *m/z* (%): 230 (1), 185 (100), 141 (21), 140 (47), 129 (11), 94 (12), 58 (79), 42 (12).

HRMS (EI): *m/z* (M$^+$) for $C_{10}H_{18}N_2S_2$: calcd. 230.0911; found 230.0897.

2.2. Synthesis of 1-(3-chloro-1,4-dithiin-2-yl)-*N*,*N*-dimethylmethanamine (**11b**)



According to **TP2**, 1-(1,4-dithiin-2-yl)-N,N-dimethylmethanamine (**9e**; 74 mg, 0.43 mmol) was dissolved in dry THF (0.9 mL). TMPMgCl·LiCl (0.42 mL, 0.45 mmol) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. hexachloroethane (153 mg, 0.65 mmol) was added and the resulting solution was stirred for 12 h. Then, the reaction mixture was quenched with sat. aq. NH_4Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/EtOAc, 8:2) yielding **11b** as orange oil (38 mg, 43%).

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 6.46 (d, *J*=6.4 Hz, 1 H), 6.40 (d, *J*=6.4 Hz, 1 H), 3.26 (s, 2 H), 2.28 (s, 6 H).

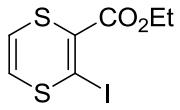
^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 129.9, 124.4, 122.7, 119.2, 62.0, 45.1.

IR (Diamond-ATR, neat) $\tilde{\nu}$ /cm^{-1}: 2974, 2943, 2856, 2820, 2772, 1587, 1562, 1535, 1453, 1348, 1262, 1174, 1156, 1095, 1042, 1027, 983, 888, 842, 801, 746, 673.

MS (70 eV, EI) *m/z* (%): 209 (9), 207 (23), 71 (4), 58 (100), 55 (5), 45 (5), 44 (7), 41 (5).

HRMS (EI): *m/z* (M$^+$) for $C_7H_{10}ClNS_2$: calcd. 206.9943; found 206.9941.

2.3. Synthesis of ethyl 3-iodo-1,4-dithiine-2-carboxylate (**11c**)



According to **TP2**, ethyl 1,4-dithiine-2-carboxylate (**9g**; 1.09 g, 5.81 mmol) was dissolved in dry THF (20 mL). TMPMgCl·LiCl (5.76 mL, 6.39 mmol) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared magnesium reagent was added to a solution of iodine (1.03 g, 4.07 mmol) in dry THF (6 mL) at -78 °C. The resulting solution was stirred at this temperature for 1 h and was then quenched with sat. aq. $Na_2S_2O_3$ solution (50 mL), extracted with Et_2O (3 x 100 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 2:1) yielding **11c** as orange liquid (793 mg, 62%).

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 6.61 (d, *J* = 6.2 Hz, 1H), 6.25 (d, *J* = 6.2 Hz, 1H), 4.31 (q, *J* = 7.2 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H).

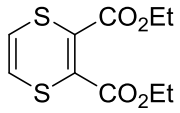
^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 162.2, 126.6, 124.4, 123.5, 83.2, 62.5, 14.0.

IR (Diamond-ATR, neat) $\tilde{\nu}$ /cm^{-1}: 3033, 2979, 2934, 1710, 1601, 1558, 1510, 1463, 1443, 1388, 1365, 1212, 1113, 1093, 1030, 889, 851, 795, 761, 676.

MS (70 eV, EI) *m/z* (%): 314 (100), 159 (69), 144 (10), 115 (16), 114 (20), 88 (21), 71 (13), 58 (10), 45 (14).

HRMS (EI): *m/z* (M^+) for $C_7H_7O_2IS_2$: calcd. 313.8932; found 313.8929.

2.4. Synthesis of diethyl 1,4-dithiine-2,3-dicarboxylate (**11d**)



According to **TP2**, ethyl 1,4-dithiine-2-carboxylate (**9g**; 188 mg, 1.0 mmol) was dissolved in dry THF (2 mL). TMPMgCl·LiCl (0.95 mL, 1.05 mmol) was added dropwise at -78 °C and the reaction mixture was stirred for 0.5 h. Ethyl cyanoformate (149 mg, 1.5 mmol) was added and the resulting solution was stirred at this temperature for 3 h. Then, the reaction mixture was quenched with sat. aq. NH_4Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/EtOAc, 8:2) yielding **11d** as orange oil (234 mg, 90%).

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 6.41 (s, 2 H), 4.28 (q, *J*=7.2 Hz, 4 H), 1.33 (t, *J*=7.1 Hz, 6 H).

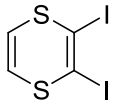
^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 162.3, 133.3, 123.8, 62.6, 13.9.

IR (Diamond-ATR, neat) $\tilde{\nu}$ /cm^{-1}: 3040, 2982, 2938, 2904, 1714, 1580, 1537, 1464, 1444, 1390, 1366, 1230, 1113, 1094, 1069, 1022, 965, 906, 853, 795, 765, 743, 680.

MS (70 eV, EI) *m/z* (%): 260 (100), 160 (36), 159 (25), 142 (34), 71 (19), 43 (35).

HRMS (EI): *m/z* (M^+) for $C_{10}H_{12}O_4S_2$: calcd. 260.0177; found 260.0174.

2.5. Synthesis of 2,3-diiodo-1,4-dithiine (**11e**)



According to **TP2**, 2-iodo-1,4-dithiine (**11a**; 242 mg, 1.0 mmol) was dissolved in dry THF (2 mL). TMPZnCl·LiCl (0.83 mL, 1.1 mmol) was added dropwise at -40 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared zinc reagent was added to a solution of iodine (177 mg, 0.7 mmol) in dry THF (1 mL) at -78 °C. The resulting solution was stirred at this temperature for 1 h and was then quenched with sat. aq. $Na_2S_2O_3$ solution (5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane) yielding **11e** as yellow solid (175 mg, 68%).

m.p.: 84.9 - 86.4 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 6.43 (s, 2H).

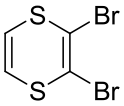
^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 123.4, 84.7.

IR (Diamond-ATR, neat) $\tilde{\nu}$ /cm^{-1}: 3024, 2962, 1592, 1544, 1485, 1260, 1092, 1020, 885, 872, 790, 757, 671.

MS (70 eV, EI) *m/z* (%): 368 (58), 241 (95), 127 (21), 114 (100), 88 (49), 61 (13), 45 (13), 43 (17).

HRMS (EI): *m/z* (M^+) for $C_4H_2I_2S_2$: calcd. 367.7687: found 367.7680.

2.6. Synthesis of 2,3-dibromo-1,4-dithiine (**11f**)



According to **TP2**, 2-bromo-1,4-dithiine (**9b**; 969 mg, 5.0 mmol) was dissolved in dry THF (10 mL). TMPZnCl·LiCl (6.4 mL, 5.5 mmol) was added dropwise at -40 °C and the mixture was stirred for 0.5 h. 1,2-Dibromotetrachloroethane (2.4 g, 7.5 mmol) in dry THF (4mL) was added and the resulting solution was stirred for 12 h and allowed to reach 23 °C. Then, the reaction mixture was quenched with sat. aq. NH_4Cl solution (20 mL), extracted with EtOAc (3 x 50 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by HPLC yielding **11f** as light brown oil (680 mg, 50%).

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 6.47 (s, 2 H).

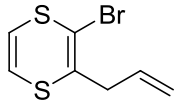
^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 123.6, 108.2.

IR (Diamond-ATR, neat) $\tilde{\nu}$ /cm^{-1}: 3032, 1594, 1548, 1523, 1275, 1258, 1128, 920, 883, 861, 803, 775, 754, 719, 669.

MS (70 eV, EI) *m/z* (%): 276 (23), 274 (33), 195 (78), 193 (64), 114 (38), 111 (29), 97 (33), 95 (63), 91 (58), 85 (39), 83 (47), 82 (29), 81 (27), 71 (67), 69 (57), 67 (28), 57 (100), 56 (27), 55 (64), 44 (55), 43 (62), 41 (51).

HRMS (EI): *m/z* (M$^+$) for $C_4H_2{}^{81}Br_2S_2$: calcd. 273.7965; found 273.7869.

2.7. Synthesis of 2-allyl-3-bromo-1,4-dithiine (**11g**)



According to **TP2**, 2-bromo-1,4-dithiine (**9b**; 316 mg, 1.6 mmol) was dissolved in dry THF (3 mL). TMPZnCl·LiCl (1.34 mL, 1.78 mmol) was added dropwise at -40 °C and the reaction mixture was stirred for 0.5 h. CuCN.2LiCl solution (1.94 mL, 1.94 mmol, 1.0 M in THF) was added and the reaction mixture was allowed to stir for 15 min, before allyl bromide (137 mg, 1.1 mmol) was added. The reaction mixture was stirred at -40 °C for 1 h and was then quenched with sat. aq. NH_4Cl/NH_3 solution (8:1, 5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane) yielding **11g** as yellow liquid (191 mg, 74%).

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 6.47 (d, *J*=6.6 Hz, 1 H), 6.38 (d, *J*=6.6 Hz, 1 H), 5.77 (ddt, *J*=16.7, 10.2, 6.3, 6.0 Hz, 1 H), 5.10 - 5.21 (m, 2 H), 3.23 (d, *J*=6.0 Hz, 2 H).

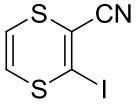
^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 132.0, 132.0, 123.7, 123.4, 117.7, 103.2, 41.5.

IR (Diamond-ATR, neat) $\tilde{\nu}$ /cm^{-1}: 3032, 3018, 2925, 2853, 2832, 1718, 1648, 1585, 1563, 1556, 1520, 1500, 1492, 1466, 1433, 1413, 1341, 1275, 1214, 1180, 1162, 1133, 1090, 1053, 1029, 1012, 979, 966, 915, 899, 885, 865, 822, 798, 780, 778, 741, 730, 705, 668, 654.

MS (70 eV, EI) *m/z* (%): 236 (78), 234 (75), 195 (16), 193 (16), 155 (28), 153 (11), 140 (14), 127 (13), 125 (10), 123 (19), 122 (100), 121 (38), 111 (23), 97 (20), 95 (11), 85 (14), 83 (14), 81 (10), 71 (22), 69 (32), 57 (28), 55 (16), 45 (27), 44 (14), 43 (28), 41 (21).

HRMS (EI): *m/z* (M$^+$) for $C_7H_7BrS_2$: calcd. 233.9171; found 233.9178.

2.8. Synthesis of 3-iodo-1,4-dithiine-2-carbonitrile (**11h**)



According to **TP2**, 1,4-dithiine-2-carbonitrile (**9d**; 93 mg, 0.66 mmol) was dissolved in dry THF (3 mL). TMPZnCl·LiCl (0.55 mL, 0.73 mmol) was added dropwise at 0 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared zinc reagent was added to a solution of iodine (117 mg, 0.46 mmol) in dry THF (1 mL) at -78 °C. The resulting solution was stirred at this temperature for 1 h and was then quenched with sat. aq. $Na_2S_2O_3$

solution (5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 2:1) yielding **11h** as orange liquid (106 mg, 86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 6.62 (d, *J*=6.2 Hz, 1 H), 6.31 (d, *J*=6.2 Hz, 1 H).

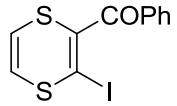
^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 124.3, 122.1, 116.0, 109.0, 96.6.

IR (Diamond-ATR, neat) $\tilde{\nu}$ /cm^{-1}: 3039, 3028, 2954, 2920, 2851, 2212, 1594, 1573, 1553, 1522, 1502, 1463, 1373, 1281, 1262, 1130, 1072, 1054, 1022, 892, 874, 841, 802, 791, 730, 679, 601, 557.

MS (70 eV, EI) *m/z* (%): 267 (84), 142 (10), 141 (14), 140 (100), 127 (13), 114 (10), 96 (61), 82 (10), 45 (15).

HRMS (EI): *m/z* (M$^+$) for $C_5H_2NIS_2$: calcd. 266.8673; found 266.8675.

2.9. Synthesis of (3-iodo-1,4-dithiin-2-yl)(phenyl)methanone (**11i**)



According to **TP2**, (1,4-dithiin-2-yl)(phenyl)methanone (**9h**; 220 mg, 1.0 mmol) was dissolved in dry THF (2 mL). TMPZnCl·LiCl (0.83 mL, 1.1 mmol) was added dropwise at 0 °C and the reaction mixture was stirred for 0.5 h. The freshly prepared zinc reagent was added to a solution of iodine (178 mg, 0.7 mmol) in dry THF (1 mL) at -78 °C. The resulting solution was stirred at this temperature for 1 h and was then quenched with sat. aq. $Na_2S_2O_3$ solution (5 mL), extracted with Et_2O (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 2:1) yielding **11i** as orange oil (189 mg, 78%).

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 7.88 (d, *J*=7.8 Hz, 2 H), 7.65 (t, *J*=7.3 Hz, 1 H), 7.51 (t, *J*=7.6 Hz, 2 H), 6.66 (d, *J*=6.4 Hz, 1 H), 6.55 (d, *J*=6.4 Hz, 1 H).

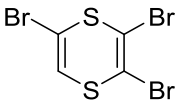
^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 191.2, 134.4, 133.4, 133.0, 130.0, 128.9, 125.9, 122.4, 75.8.

IR (Diamond-ATR, neat) $\tilde{\nu}$ /cm^{-1}: 3031, 2923, 1963, 1656, 1594, 1578, 1528, 1447, 1311, 1234, 1175, 1160, 1130, 1055, 1022, 999, 974, 935, 894, 806, 782, 727, 677.

MS (70 eV, EI) *m/z* (%): 348 (11), 347 (13), 346 (98), 220 (13), 219 (14), 191 (16), 190 (25), 147 (21), 105 (100), 77 (72), 51 (26), 43 (45).

HRMS (EI): *m/z* (M$^+$) for $C_{11}H_7OIS_2$: calcd. 345.8983; found 345.8976.

3. Preparation of 2,3,5-tribromo-1,4-dithiine (12)



2,3-dibromo-1,4-dithiine (**11g**; 213 mg, 0.78 mmol) was dissolved in dry CH_2Cl_2 (2 mL). Bromine (131 mg, 0.83 mmol) in dry CH_2Cl_2 (2 mL) and Et_3N (0.19 mL, 1.33 mmol) were added dropwise at 0 °C. The reaction was stirred for 24 h and allowed to reach 23 °C. Then, the reaction mixture was quenched with aq. HCl solution (5.0 mL, 2.0 M) and extracted with CH_2Cl_2 (3 x 10 mL) The combined organic phases were washed with water and brine and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane) yielding **12** as white solid (230 mg, 84%).

m.p.: 92.5 - 94.4 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 6.52 (s, 1 H).

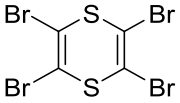
^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 122.0, 110.7, 110.2, 108.8.

IR (Diamond-ATR, neat) $\tilde{\nu}$ /cm^{-1}: 3035, 2358, 1553, 1532, 1519, 1222, 1206, 1194, 917, 860, 809, 776, 757, 720, 712.

MS (70 eV, EI) *m/z* (%): 356 (2), 354 (7), 352 (6), 350 (2), 275 (10), 273 (19), 271 (9), 194 (11), 192 (11), 61 (16), 45 (15), 44 (2), 43 (100), 41 (5).

HRMS (EI): *m/z* (M^+) for $C_4H^{79}Br_3S_2$: calcd. 349.7070; found 349.7066.

4. Preparation of perbromo-1,4-dithiine (13)



2,3,5-Tribromo-1,4-dithiine (**12**; 517 mg, 1.5 mmol) was dissolved in dry THF (9 mL). TMPZnCl·LiCl (1.81 mL, 1.6 mmol) was added dropwise at -78 °C and the mixture was stirred for 15 min. 1,2-Dibromotetrachloroethane (723 mg, 2.2 mmol) in dry THF (1 mL) was added and the resulting solution was allowed to reach 23 °C for 24 h, after which time it was warmed to 50 °C and stirred for further 12 h.. Then, the reaction mixture was quenched with sat. aq. NH_4Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane) yielding **13** as white solid (357 mg, 56%).

m.p.: 170.8 - 172.3

^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 110.5.

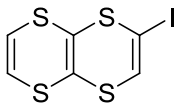
IR (Diamond-ATR, neat) $\tilde{\nu}$ /cm^{-1}: 3078, 3028, 2921, 2851, 1641, 1593, 1556, 1530, 1514, 1423, 1407, 1265, 1108, 1047, 985, 937, 914, 884, 848, 830, 798, 769, 676.

MS (70 eV, EI) *m/z* (%): 434 (18), 432 (25), 430 (18), 355 (35), 353 (100), 351 (94), 349 (29), 274 (36), 272 (69), 270 (32), 149 (24), 147 (23), 137 (31), 135 (29), 88 (39), 68 (30).

HRMS (EI): *m/z* (M^+) for $C_4{}^{79}Br_4S_2$: calcd. 427.6175; found 427.6178.

5. Preparation of monosubstituted 1,4,5,8-tetrathianaphthalene

5.1. Synthesis of 2-iodo-[1,4]dithiino[2,3-b][1,4]dithiine (**14a**)



According to **TP3**, 1,4,5,8-tetrathianaphthalene (**4**; 102 mg, 0.5 mmol) was dissolved in dry THF (4 mL). TMPMgCl·LiCl (0.51 mL, 0.6 mmol) was added dropwise at -78 °C and the mixture was stirred for 10 min. Iodine (191 mg, 0.75 mmol) in dry THF (1 mL) was added and the resulting solution was stirred at this temperature for 2 h. Then, the reaction mixture was quenched with sat. aq. $Na_2S_2O_3$ solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane) yielding **14a** as yellow solid (147 mg, 89%).

m.p.: 94.8 - 96.5 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 6.70 (s, 1 H), 6.47 (d, *J*=6.6 Hz, 1 H), 6.44 (d, *J*=6.6 Hz, 1 H).

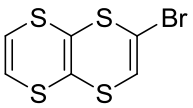
^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 129.4, 125.7, 125.6, 121.0, 120.1, 78.2.

IR (Diamond-ATR, neat) $\tilde{\nu}$ /cm^{-1}: 3025, 2926, 1607, 1568, 1533, 1510, 1470, 1366, 1260, 1213, 1128, 965, 906, 887, 864, 834, 801, 778, 759, 733.

MS (70 eV, EI) *m/z* (%): 330 (86), 285 (41), 203 (78), 159 (100), 146 (46), 127 (32), 88 (69), 69 (48), 57 (36), 45 (55).

HRMS (EI): *m/z* (M^+) for $C_6H_3IS_4$: calcd. 329.8162; found 329.8153.

5.2. Synthesis of 2-bromo-[1,4]dithiino[2,3-b][1,4]dithiine (**14b**)



According to **TP3**, 1,4,5,8-tetrathianaphthalene (**4**; 102 mg, 0.5 mmol) was dissolved in dry THF (4 mL). TMPMgCl·LiCl (0.51 mL, 0.6 mmol) was added dropwise at -78 °C and the mixture was stirred for 10 min. 1,2-Dibromotetrachloroethane (244 mg, 0.75 mmol) in dry THF (1 mL) was added and the resulting solution was stirred at this temperature for 2 h. Then, the reaction mixture was quenched with sat. aq. NH_4Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane) yielding **14b** as yellow solid (126 mg, 89%).

m.p.: 65.8 - 67.6 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 6.53 (s, 1 H), 6.43 - 6.48 (m, 2 H).

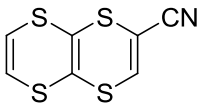
^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 125.9, 125.6, 123.8, 121.8, 119.6, 112.8.

IR (Diamond-ATR, neat) $\tilde{\nu}$ /cm^{-1}: 3032, 2923, 1551, 1538, 1517, 1280, 1263, 1208, 1135, 966, 904, 870, 850, 804, 782, 759, 701, 673.

MS (70 eV, EI) *m/z* (%): 284 (67), 282 (60), 239 (47), 237 (44), 203 (86), 159 (100), 127 (54), 88 (79), 69 (40), 45 (51).

HRMS (EI): *m/z* (M^+) for $C_6H_3{}^{81}BrS_4$: calcd. 283.8301; found 283.8278.

5.3. Synthesis of [1,4]dithiino[2,3-b][1,4]dithiine-2-carbonitrile (**14c**)



According to **TP3**, 1,4,5,8-tetrathianaphthalene (**4**; 102 mg, 0.5 mmol) was dissolved in dry THF (4 mL). TMPMgCl·LiCl (0.51 mL, 0.6 mmol) was added dropwise at -78 °C and the mixture was stirred for 10 min. 4-Tolylsulfonyl cyanide (136 mg, 0.75 mmol) in dry THF (1 mL) was added and the resulting solution was stirred for 12 h allowing to reach 23 °C. Then, the reaction mixture was quenched with sat. aq. NH_4Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/EtOAc, 96:4) yielding **14c** as orange solid (84 mg, 73%).

m.p.: 130.4 - 132.2 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 7.31 (s, 1 H), 6.49 (d, *J*=6.4 Hz, 1 H), 6.46 (d, *J*=6.4 Hz, 1 H).

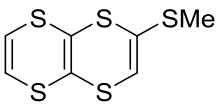
^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 143.3, 125.7, 125.2, 120.0, 118.6, 113.7, 109.9.

IR (Diamond-ATR, neat) $\tilde{\nu}$ /cm^{-1}: 3027, 2222, 1578, 1559, 1543, 1506, 1281, 1263, 1231, 1119, 1099, 1062, 966, 885, 862, 852, 803, 767, 678.

MS (70 eV, EI) *m/z* (%): 231 (4), 229 (20), 196 (4), 186 (4), 184 (29), 165 (8), 159 (8), 153 (6), 102 (6), 88 (10), 76 (7), 73 (4), 70 (8), 61 (14), 45 (13), 43 (100), 42 (5).

HRMS (EI): *m/z* (M^+) for $C_7H_3NS_4$: calcd. 228.9148; found 228.9144.

5.4. Synthesis of 2-(methylthio)-[1,4]dithiino[2,3-b][1,4]dithiine (**14d**)



According to **TP3**, 1,4,5,8-tetrathianaphthalene (**4**; 41 mg, 0.2 mmol) was dissolved in dry THF (1.6 mL). TMPMgCl·LiCl (0.21 mL, 0.24 mmol) was added dropwise at -78 °C

and the mixture was stirred for 10 min. *S*-Methyl thiomethanesulfonate (38 mg, 0.3 mmol) was added and the resulting solution was stirred for 12 h allowing to reach 23 °C. Then, the reaction mixture was quenched with sat. aq. NH_4Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane) yielding **14d** as light yellow solid (39 mg, 78%).

m.p.: 101.9 - 103.6 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 6.40 - 6.46 (m, 2 H), 6.08 (s, 1 H), 2.40 (s, 3 H).

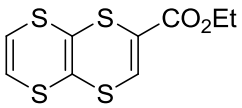
^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 139.0, 125.6, 125.6, 123.4, 119.9, 116.2, 18.1.

IR (Diamond-ATR, neat) $\tilde{\nu}$ /cm^{-1}: 3019, 2977, 2910, 2850, 1575, 1556, 1539, 1511, 1471, 1429, 1411, 1310, 1264, 1229, 1134, 968, 951, 904, 888, 857, 798, 766, 735.

MS (70 eV, EI) *m/z* (%): 250 (12), 159 (10), 70 (13), 61 (17), 45 (15), 43 (100).

HRMS (EI): *m/z* (M$^+$) for $C_7H_6S_5$: calcd. 249.9073; found 249.9068.

5.5. Synthesis of ethyl [1,4]dithiino[2,3-b][1,4]dithiine-2-carboxylate (**14e**)



According to **TP3**, 1,4,5,8-tetrathianaphthalene (**4**; 612 mg, 3.0 mmol) was dissolved in dry THF (24 mL). TMPMgCl·LiCl (3.3 mL, 3.6 mmol) was added dropwise at -78 °C and the mixture was stirred for 10 min. Ethyl cyanoformate (446 mg, 4.5 mmol) was added and the resulting solution was stirred for 12 h allowing to reach 23 °C. Then, the reaction mixture was quenched with sat. aq. NH_4Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 8:2 to 7:3) yielding **14e** as orange solid (600 mg, 72%).

m.p.: 99.3 - 101.2 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 7.45 (s, 1 H), 6.49 (d, *J*=6.6 Hz, 1 H), 6.44 (d, *J*=6.6 Hz, 1 H), 4.25 (q, *J*=7.1 Hz, 2 H), 1.32 (t, *J*=7.1 Hz, 3 H).

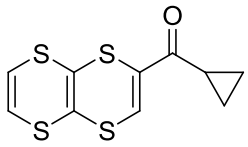
^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 160.8, 136.7, 130.4, 125.8, 125.0, 120.4, 116.8, 62.3, 14.1.

IR (Diamond-ATR, neat) $\tilde{\nu}$ /cm^{-1}: 3033, 2979, 1704, 1572, 1552, 1463, 1443, 1391, 1366, 1263, 1244, 1218, 1094, 1040, 997, 886, 856, 828, 805, 770, 731, 677.

MS (70 eV, EI) *m/z* (%): 295 (20), 276 (100), 231 (76), 221 (43), 207 (25), 203 (88), 159 (80), 147 (22), 146 (35), 103 (21), 91 (25), 88 (46), 85 (24), 81 (20), 76 (31), 71 (31), 70 (22), 69 (41), 69 (27), 57 (55), 55 (27), 44 (60), 43 (32), 40 (26).

HRMS (EI): *m/z* (M$^+$) for $C_9H_8O_2S_4$: calcd. 275.9407; found 275.9401.

5.6. Synthesis of [1,4]dithiino[2,3-b][1,4]dithiin-2-yl(cyclopropyl)methanone (**14f**)



According to **TP3**, 1,4,5,8-tetrathianaphthalene (**4**; 102 mg, 0.5 mmol) was dissolved in dry THF (4 mL). TMPMgCl·LiCl (0.51 mL, 0.6 mmol) was added dropwise at -78 °C and the mixture was stirred for 10 min. CuCN·2LiCl (0.6 mL, 0.6 mmol, 1.0 M in THF) was then introduced followed by cyclopropanecarbonyl chloride (78 mg, 0.75 mmol) and the reaction warmed to −40 ºC and stirring was continued for a further 18 h. Then, the reaction mixture was quenched with sat. aq. NH_4Cl/NH_3 solution (8:1, 5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/EtOAc, 96:4) yielding **14f** as dark red solid (89 mg, 65%).

m.p.: 90.3 - 91.6 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 7.48 (s, 1 H), 6.50 (d, *J*=6.4 Hz, 1 H), 6.44 (d, *J*=6.6 Hz, 1 H), 2.29 - 2.36 (m, 1 H), 1.11 - 1.21 (m, 2 H), 0.95 - 1.06 (m, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 192.5, 139.7, 135.6, 125.9, 124.8, 120.8, 116.8, 17.6, 12.3.

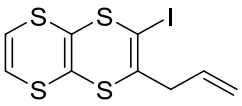
IR (Diamond-ATR, neat) $\tilde{\nu}$ /cm^{-1}: 3071, 3042, 3031, 3004, 2954, 2923, 2853, 1627, 1574, 1558, 1542, 1523, 1463, 1435, 1417, 1397, 1322, 1276, 1262, 1222, 1204, 1173, 1127, 1095, 1087, 1057, 1030, 959, 923, 890, 878, 847, 838, 827, 811, 800, 783, 769, 732, 719, 691, 674.

MS (70 eV, EI) *m/z* (%): 272 (100), 227 (63), 159 (59), 146 (19), 88 (21).

HRMS (EI): *m/z* (M^+) for $C_{10}H_8OS_4$: calcd. 271.9458; found 271.9452.

6. Preparation of disubstituted 1,4,5,8-tetrathianaphthalene

6.1. Synthesis of 2-iodo-3-allyl-[1,4]dithiino[2,3-b][1,4]dithiine (**15a**)



According to **TP4**, 2-iodo-[1,4]dithiino[2,3-b][1,4]dithiine (**14a**; 99 mg, 0.3 mmol) was dissolved in dry THF (2.4 mL). TMPZnCl·LiCl (0.41 mL, 0.33 mmol) was added dropwise at -40 °C and the mixture was stirred for 0.5 h. CuCN·2LiCl (0.06 mL, 0.06 mmol, 1.0 M in THF) was then introduced followed by allyl bromide (54 mg, 0.45 mmol) and the reaction was stirred for 12 h allowing to reach 23 °C. Then, the reaction mixture was quenched with sat. aq. NH_4Cl/NH_3 solution (8:1, 5 mL), extracted with EtOAc (3 x 15 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*.

The crude product was purified by flash column chromatography on silica gel (*i*hexane) yielding **15a** as yellow oil (75 mg, 68%).

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 6.43 (d, *J*=6.6 Hz, 1 H), 6.42 (d, *J*=6.6 Hz, 1 H), 5.67 - 5.82 (m, 1 H), 5.19 (dd, *J*=13.9, 2.3 Hz, 2 H), 3.26 (d, *J*=6.2 Hz, 2 H).

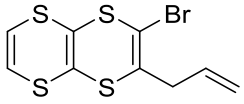
^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 139.6, 131.4, 125.7, 125.7, 121.3, 121.0, 118.5, 45.0.

IR (Diamond-ATR, neat) $\tilde{\nu}$ /cm^{-1}: 3078, 3028, 2977, 2905, 1636, 1580, 1549, 1516, 1419, 1279, 1262, 1093, 1037, 987, 969, 918, 887, 866, 821, 803, 768, 736, 671.

MS (70 eV, EI) *m/z* (%): 370 (100), 325 (67), 210 (49), 209 (31), 146 (47), 88 (31).

HRMS (EI): *m/z* (M$^+$) for $C_9H_7IS_4$: calcd. 369.8475; found 369.8464.

6.2. Synthesis of 2-bromo-3-allyl-[1,4]dithiino[2,3-b][1,4]dithiine (**15b**)



According to **TP4**, 2-bromo-[1,4]dithiino[2,3-b][1,4]dithiine (**14b**; 56 mg, 0.2 mmol) was dissolved in dry THF (1.6 mL). TMPZnCl·LiCl (0.28 mL, 0.22 mmol) was added dropwise at -40 °C and the mixture was stirred for 0.5 h. CuCN·2LiCl (0.04 mL, 0.04 mmol, 1.0 M in THF) was then introduced followed by allyl bromide (36 mg, 0.3 mmol) and the reaction was stirred for 2 h. Then, the reaction mixture was quenched with sat. aq. NH_4Cl/NH_3 solution (8:1, 5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane) yielding **15b** as yellow oil (46 mg, 71%).

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 6.37 - 6.48 (m, 2 H), 5.74 (ddt, *J*=17.5, 9.6, 6.4, 6.4 Hz, 1 H), 5.11 - 5.24 (m, 2 H), 3.23 (d, *J*=6.2 Hz, 2 H).

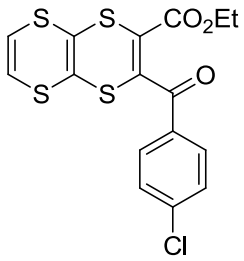
^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 136.1, 131.3, 125.9, 125.7, 122.1, 120.7, 118.4, 108.1, 41.2.

IR (Diamond-ATR, neat) $\tilde{\nu}$ /cm^{-1}: 3078, 3028, 2977, 2900, 1637, 1581, 1554, 1516, 1421, 1280, 1265, 987, 918, 887, 871, 841, 803, 769, 712.

MS (70 eV, EI) *m/z* (%): 324 (100), 322 (92), 279 (96), 277 (80), 210 (65), 167 (51), 146 (47), 88 (66), 69 (52), 57 (50), 45 (47).

HRMS (EI): *m/z* (M$^+$) for $C_9H_7BrS_4$: calcd. 321.8614; found 321.8610.

6.3. Synthesis of ethyl 3-(4-chlorobenzoyl)-[1,4]dithiino[2,3-b][1,4]dithiine-2-carboxylate (**15c**)



According to **TP4**, ethyl [1,4]dithiino[2,3-b][1,4]dithiine-2-carboxylate (**14d**; 83 mg, 0.3 mmol) was dissolved in dry THF (2.4 mL). TMPZnCl·LiCl (0.41 mL, 0.33 mmol) was added dropwise at -40 °C and the mixture was stirred for 0.5 h. CuCN·2LiCl (0.3 mL, 0.3 mmol, 1.0 M in THF) was then introduced followed by 4-chlorobenzoyl chloride (263 mg, 0.45 mmol) and the reaction was stirred for 2 h at the same temperature and further 12 h allowing to reach 23 °C. Then, the reaction mixture was quenched with sat. aq. NH_4Cl/NH_3 solution (8:1, 5 mL), extracted with EtOAc (3 x 15 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/EtOAc, 96:4) yielding **15c** as orange oil (68 mg, 55%).

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 7.79 (d, *J*=8.4 Hz, 2 H), 7.48 (d, *J*=8.4 Hz, 2 H), 6.50 (d, *J*=6.6 Hz, 1 H), 6.43 (d, *J*=6.6 Hz, 1 H), 4.06 (q, *J*=7.0 Hz, 2 H), 1.05 (t, *J*=7.0 Hz, 3 H).

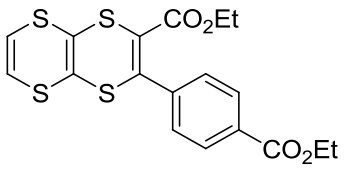
^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 187.9, 160.1, 147.5, 140.8, 132.6, 131.3, 130.3, 129.4, 125.6, 125.1, 124.8, 117.7, 62.9, 13.5.

IR (Diamond-ATR, neat) $\tilde{\nu}$ /cm^{-1}: 3036, 2958, 2925, 2854, 1714, 1672, 1585, 1572, 1552, 1485, 1463, 1444, 1399, 1366, 1297, 1243, 1172, 1092, 1023, 1011, 966, 907, 860, 837, 799, 769, 760, 739, 720, 678.

MS (70 eV, EI) *m/z* (%): 416 (15), 414 (34), 384 (13), 382 (44), 370 (11), 369 (15), 221 (9), 141 (23), 139 (100), 113 (10), 111 (48), 91 (15), 76 (9), 64 (13), 44 (76), 43 (18).

HRMS (EI): *m/z* (M$^+$) for $C_{16}H_{11}ClO_3S_4$: calcd. 413.9280; found 413.9269.

6.4. Synthesis of ethyl 3-(4-(ethoxycarbonyl)phenyl)-[1,4]dithiino[2,3-b][1,4]dithiine-2-carboxylate (**15d**)



According to **TP4**, ethyl [1,4]dithiino[2,3-b][1,4]dithiine-2-carboxylate (**14d**; 55 mg, 0.2 mmol) was dissolved in dry THF (1.6 mL). TMPZnCl·LiCl (0.41 mL, 0.33 mmol) was added dropwise at -40 °C and the mixture was stirred for 0.5 h. A solution of ethyl 4-iodobenzoate (72 mg, 0.26 mmol), $Pd(dba)_2$ (7 mg, 0.012 mmol) and P(2-furyl)$_3$ (6 mg, 0.024 mmol) in dry THF (1 mL) was added to the freshly prepared zinc reagent at -40 °C. Then, the reaction mixture was stirred at 25 °C for 12 h. The reaction was quenched with sat. aq. NH_4Cl solution (5 mL), extracted with EtOAc (3 x 15 mL) and dried over

anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/EtOAc, 96:4) yielding **15d** as orange solid (63 mg, 74%).

m.p.: 125.9 - 127.1 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 8.03 (d, *J*=8.2 Hz, 2 H), 7.41 (d, *J*=8.2 Hz, 2 H), 6.47 (d, *J*=6.6 Hz, 1 H), 6.44 (d, *J*=6.6 Hz, 1 H), 4.40 (q, *J*=7.0 Hz, 2 H), 4.03 (q, *J*=7.2 Hz, 2 H), 1.41 (t, *J*=7.1 Hz, 3 H), 1.00 (t, *J*=7.1 Hz, 3 H).

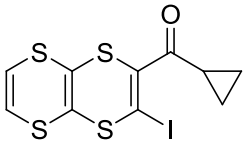
^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 165.8, 162.8, 150.8, 140.2, 131.4, 129.5, 129.0, 125.8, 125.1, 124.4, 122.5, 120.4, 62.0, 61.2, 14.3, 13.6.

IR (Diamond-ATR, neat) $\tilde{\nu}$ /cm^{-1}: 2980, 2934, 2902, 1709, 1606, 1573, 1499, 1463, 1444, 1403, 1365, 1269, 1202, 1177, 1102, 1045, 1018, 968, 917, 860, 805, 765, 733, 698, 678.

MS (70 eV, EI) *m/z* (%): 426 (12), 425 (11), 424 (57), 392 (14), 381 (16), 380 (22), 379 (100), 350 (20), 323 (16), 276 (10), 146 (10).

HRMS (EI): *m/z* (M$^+$) for $C_{18}H_{16}O_4S_4$: calcd. 423.9931; found 423.9916.

6.5. Synthesis of cyclopropyl(3-iodo-[1,4]dithiino[2,3-b][1,4]dithiin-2-yl)methanone (**15e**)



According to **TP4**, [1,4]dithiino[2,3-b][1,4]dithiin-2-yl(cyclopropyl)methanone (**14e**; 54 mg, 0.2 mmol) was dissolved in dry THF (1.6 mL). TMPZnCl·LiCl (0.27 mL, 0.22 mmol) was added dropwise at -40 °C and the mixture was stirred for 0.5 h. Iodine (76 mg, 0.3 mmol) in dry THF (1 mL) was added at -78 °C and stirred for 2 h. The reaction was quenched with sat. aq. $Na_2S_2O_3$ solution (5 mL), extracted with EtOAc (3 x 15 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/EtOAc, 96:4) yielding **15e** as orange solid (66 mg, 83%).

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 6.48 (d, *J*=6.7 Hz, 1 H), 6.43 (d, *J*=6.7 Hz, 1 H), 2.34 - 2.43 (m, 1 H), 1.27 (quin, *J*=3.8 Hz, 2 H), 1.12 (dq, *J*=7.5, 3.7 Hz, 2 H).

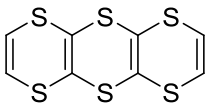
^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 197.5, 137.0, 125.9, 125.4, 122.6, 121.1, 83.0, 20.8, 14.1.

IR (Diamond-ATR, neat) $\tilde{\nu}$ /cm^{-1}: 3032, 2923, 1667, 1580, 1524, 1501, 1442, 1416, 1370, 1262, 1190, 1149, 1110, 1088, 1062, 1027, 976, 950, 925, 883, 864, 842, 803, 771, 734.

MS (70 eV, EI) *m/z* (%): 400 (20), 398 (100), 353 (50), 243 (19), 146 (52), 88 (35), 69 (80), 41 (58).

HRMS (EI): *m/z* (M$^+$) for $C_{10}H_7IOS_4$: calcd. 397.8424; found 397.8414.

7. Preparation of 1,4,5,6,9,10-hexathiaanthracene (5)



Di(1,4-dithiin-2-yl)sulfane (**9l**; 52 mg, 0.2 mmol) was dissolved in dry $CHCl_3$ (20 mL). Sulfur dichloride (41 mg, 0.4 mmol) in dry $CHCl_3$ (3 mL) was added dropwise at 0 °C over 15 min and the mixture was stirred for 3 h allowing to reach 23 °C. Then, the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 8:2) yielding **5** as light yellow solid (32 mg, 55%).

m.p.: 194.0 - 195.8 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 6.42 (s, 4 H).

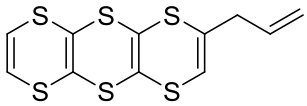
^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 125.6, 123.5.

IR (Diamond-ATR, neat) $\tilde{\nu}$ /cm^{-1}: 3029, 2916, 1583, 1552, 1514, 1278, 1264, 1132, 981, 882, 846, 806, 776, 672.

MS (70 eV, EI) *m/z* (%): 292 (100), 247 (42), 190 (55), 158 (39), 88 (61), 57 (36).

HRMS (EI): *m/z* (M^+) for $C_8H_4S_6$: calcd. 291.8637; found 291.8636.

6. Preparation of 2-allyl-1,4,5,6,9,10-hexathiaanthracene (16)



According to **TP5**, 1,4,5,6,9,10-hexathiaanthracene (**5**; 29 mg, 0.1 mmol) was dissolved in dry THF (3 mL). TMPZnCl·LiCl (0.14 mL, 0.11 mmol) was added dropwise at -40 °C and the mixture was stirred for 2 h. CuCN·2LiCl (0.02 mL, 0.02 mmol, 1.0 M in THF) was then introduced followed by allyl bromide (22 mg, 0.15 mmol) and the reaction was stirred for 12 h allowing to reach 23 °C. Then, the reaction mixture was quenched with sat. aq. NH_4Cl/NH_3 solution (8:1, 5 mL), extracted with EtOAc (3 x 15 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by HPLC yielding **16** as yellow solid (17 mg, 51%).

m.p.: 119.2 - 121.4 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 6.42 (s, 2 H), 6.07 (s, 1 H), 5.77 (ddt, *J*=16.6, 10.3, 6.7, 6.7 Hz, 1 H), 5.13 - 5.22 (m, 2 H), 3.07 (dd, *J*=6.4, 0.8 Hz, 2 H).

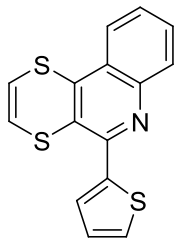
^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 141.5, 132.9, 125.7, 124.2, 123.5, 123.5, 119.2, 118.8, 40.3.

IR (Diamond-ATR, neat) $\tilde{\nu}$ /cm^{-1}: 3077, 3027, 2922, 2852, 1640, 1592, 1554, 1514, 1422, 1408, 1283, 1265, 1225, 1108, 1046, 985, 914, 883, 845, 805, 769, 732.

MS (70 eV, EI) *m/z* (%): 334 (24), 332 (100), 268 (17), 247 (24), 230 (20), 190 (25), 158 (21), 146 (22), 88 (37), 83 (20), 73 (22), 71 (25), 69 (30), 57 (42), 55 (33), 43 (37), 41 (29).

HRMS (EI): *m/z* (M^+) for $C_{11}H_8S_6$: calcd. 331.8950; found 331.8953.

7. Synthesis of 5-(thiophen-2-yl)-[1,4]dithiino[2,3-*c*]quinoline (17)



According to the literature,[8] thiophene-2-carbaldehyde (73 mg, 0.65 mmol) was added to a solution of 2-(1,4-dithiin-2-yl)aniline (**9k**; 104 mg, 0.5 mmol) and TFA (114 mg, 1.0 mmol) in EtOH (0.2 mL) at 25 °C. The reaction mixture was heated under microwave irradiation using a Biotage Initiator 2.5 system (130 °C, 100 W, 15 min). The reaction mixture was allowed to cool to 25 °C and was then quenched with sat. aq. NH_4Cl solution (5 mL), extracted with EtOAc (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/EtOAc/NEt_3, 98:2:0.05) yielding **17** as yellow solid (90 mg, 60%).

m.p.: 128.8 - 131.2 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 8.28 (d, *J*=8.4 Hz, 1 H), 8.09 (d, *J*=8.4 Hz, 1 H), 7.94 (d, *J*=3.1 Hz, 1 H), 7.68 - 7.74 (m, 1 H), 7.51 - 7.60 (m, 2 H), 7.20 (dd, *J*=4.8, 4.0 Hz, 1 H), 6.71 (d, *J*=6.6 Hz, 1 H), 6.60 (d, *J*=6.6 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 149.8, 146.3, 142.6, 142.5, 130.0, 130.0, 129.5, 128.8, 127.4, 127.2, 126.6, 126.3, 125.9, 124.1, 123.5.

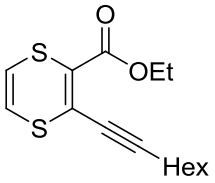
IR (Diamond-ATR, neat) $\tilde{\nu}$ /cm^{-1}: 3079, 3064, 3021, 2923, 2852, 1607, 1579, 1558, 1544, 1531, 1474, 1447, 1425, 1374, 1356, 1336, 1307, 1292, 1235, 1221, 1156, 1134, 1070, 1051, 971, 916, 894, 882, 858, 849, 836, 799, 774, 760, 743, 729, 706, 687, 656.

MS (70 eV, EI) *m/z* (%): 301 (14), 300 (25), 299 (100), 298 (46), 267 (14), 266 (45), 222 (10).

HRMS (EI): *m/z* (M^+) for $C_{15}H_9NS_3$: calcd. 298.9897; found 298.9889.

8. Synthesis of ethyl 3-(3-oxooct-1-yn-1-yl)-1,4-dithiine-2-carboxylate (18)

[8] Youn, S. W.; Bihn, J. H. *Tetrahedron Lett.* **2009**, *50*, 4598.



Ethyl 3-iodo-1,4-dithiine-2-carboxylate (**11c**; 1.13 g, 3.6 mmol) was added to a solution of 1-octyne (593 mg, 5.4 mmol), CuI (14 mg, 0.07 mmol) and $Pd(PPh_3)_2Cl_2$ (25 mg, 0.04 mmol) in NEt_3 (18 mL) at 25 °C. The reaction mixture was stirred at this temperature for 4 h and was then quenched with sat. aq. NH_4Cl solution (10 mL), extracted with EtOAc (3 x 70 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/EtOAc, 9:1) yielding **18** as orange oil (817 mg, 77%).

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 6.38 (s, 2 H), 4.28 (q, *J*=7.0 Hz, 2 H), 2.44 (t, *J*=7.1 Hz, 2 H), 1.59 (quin, *J*=7.3 Hz, 2 H), 1.38 - 1.47 (m, 2 H), 1.27 - 1.36 (m, 6 H), 0.86 - 0.94 (m, 3 H).

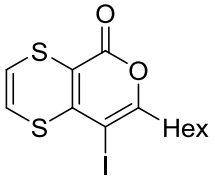
^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 161.7, 128.5, 128.2, 123.7, 123.6, 102.7, 61.9, 31.3, 28.6, 28.1, 22.5, 20.1, 14.1, 14.0. (One signal not observed; possible coincidental isochronicity).

IR (Diamond-ATR, neat) $\tilde{\nu}$ /cm^{-1}: 3035, 2954, 2929, 2857, 2208, 1701, 1562, 1530, 1464, 1444, 1426, 1389, 1365, 1325, 1260, 1233, 1181, 1110, 1094, 1044, 1016, 960, 898, 864, 830, 797, 760, 723, 676.

MS (70 eV, EI) *m/z* (%): 298 (11), 297 (19), 296 (100), 198 (13), 197 (25), 171 (10), 153 (50), 143 (15), 43 (36), 41 (10).

HRMS (EI): *m/z* (M^+) for $C_{15}H_{20}O_2S_2$: calcd. 296.0905; found 296.0900.

9. Synthesis of 7-hexanoyl-8-iodo-5*H*-[1,4]dithiino[2,3-*c*]pyran-5-one (19)



According to literature,[9] a solution of iodine (841 mg, 3.3 mmol) in dry CH_2Cl_2 (22 mL) was added dropwise to a solution of ethyl 3-(3-oxooct-1-yn-1-yl)-1,4-dithiine-2-carboxylate (**18**; 817 mg, 2.8 mmol) in dry CH_2Cl_2 (35 mL) at 25 °C. The reaction mixture was stirred at this temperature for 2 h and was then quenched with sat. aq. $Na_2S_2O_3$ solution (5 mL), extracted with CH_2Cl_2 (3 x 10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (*i*hexane/CH_2Cl_2, 2:1) yielding **19** as red oil (972 mg, 88%).

[9] Yao, T; Larock, R. C. *J. Org. Chem.* **2003**, *68*, 5936.

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 6.32 (d, *J*=7.1 Hz, 1 H), 6.11 (d, *J*=7.1 Hz, 1 H), 2.78 - 2.85 (m, 2 H), 1.66 (quin, *J*=7.6 Hz, 2 H), 1.36 (quin, *J*=7.0 Hz, 2 H), 1.26 - 1.33 (m, 4 H), 0.89 (t, *J*=6.7 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 163.0, 156.8, 153.3, 125.2, 121.4, 113.9, 74.1, 37.2, 31.3, 28.7, 27.0, 22.4, 14.0.

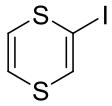
IR (Diamond-ATR, neat) $\tilde{\nu}$ /cm^{-1}: 3035, 2952, 2925, 2854, 1697, 1574, 1554, 1489, 1463, 1377, 1351, 1333, 1252, 1175, 1144, 1105, 1029, 977, 891, 858, 792, 745, 723, 673.

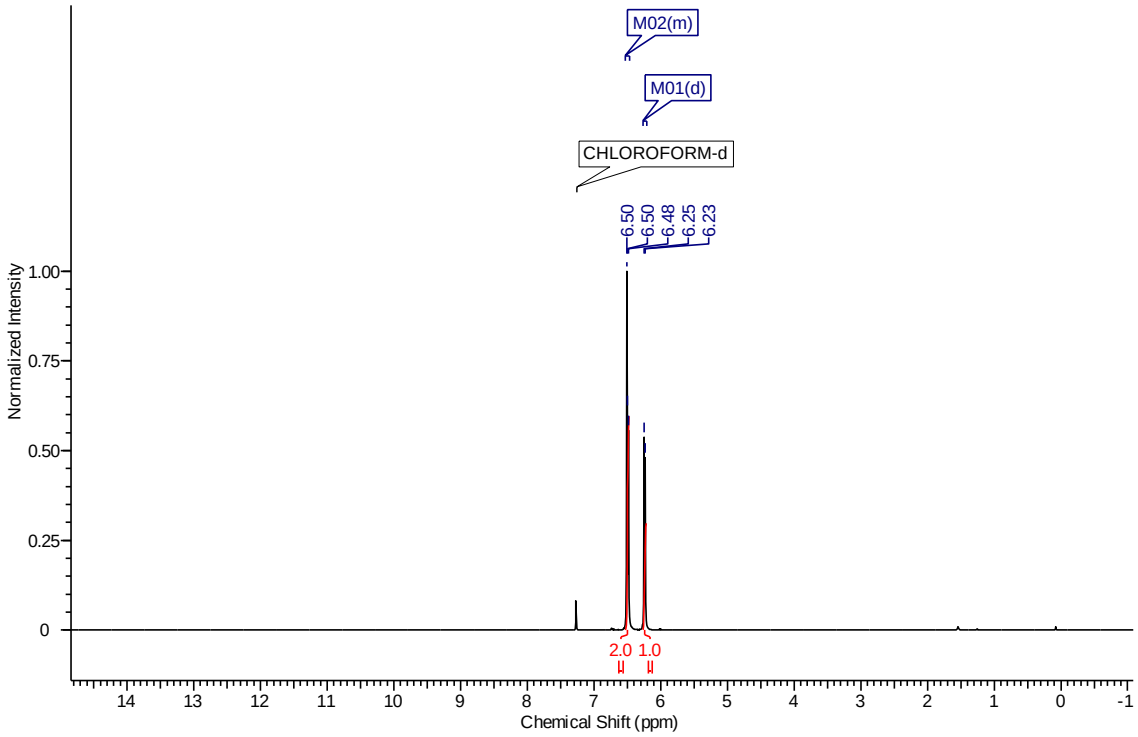
MS (70 eV, EI) *m/z* (%): 396 (10), 395 (17), 394 (100), 324 (34), 295 (10), 197 (24), 127 (23), 43 (23), 41 (10).

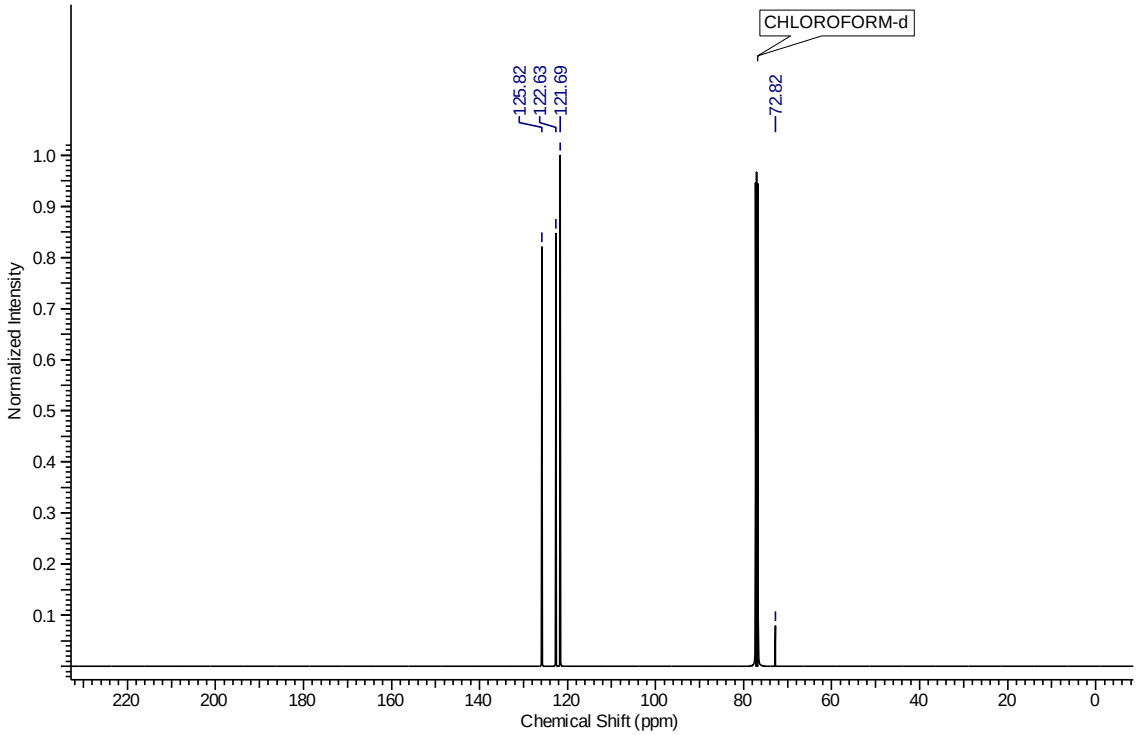
HRMS (EI): *m/z* (M^+) for $C_{13}H_{15}O_2IS_2$: calcd. 393.9558; found 393.9553.

E) NMR-Spectra

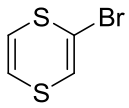
2-Iodo-1,4-dithiine (**9a**)

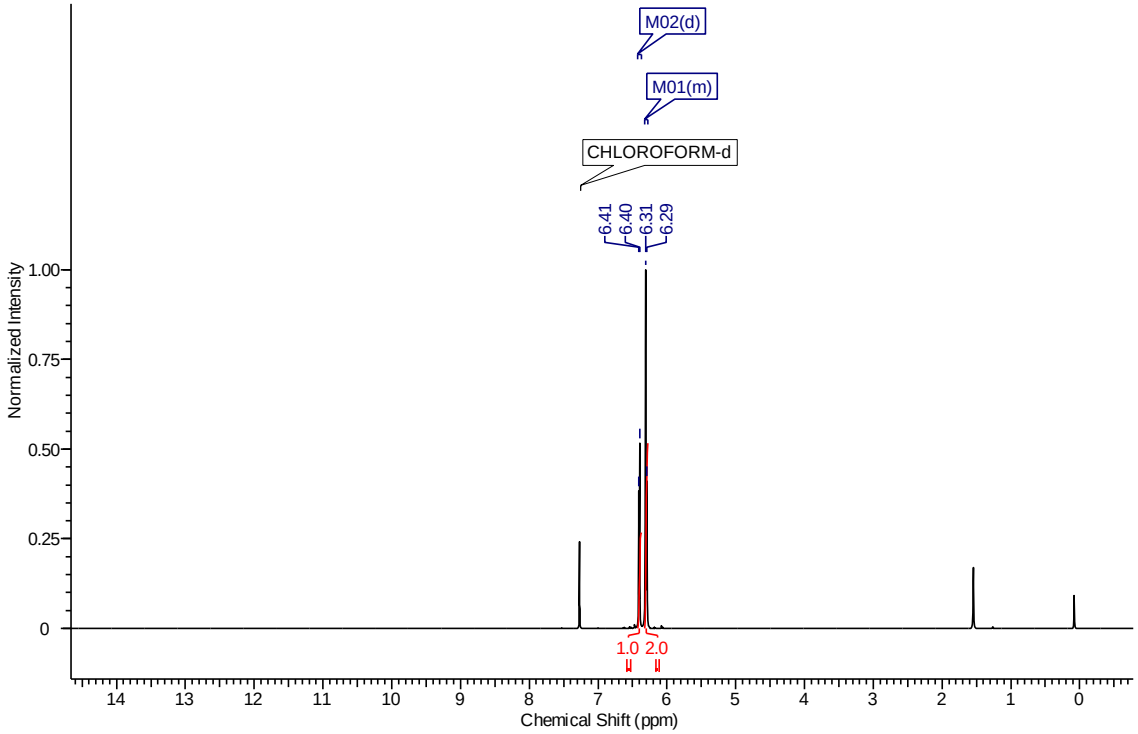


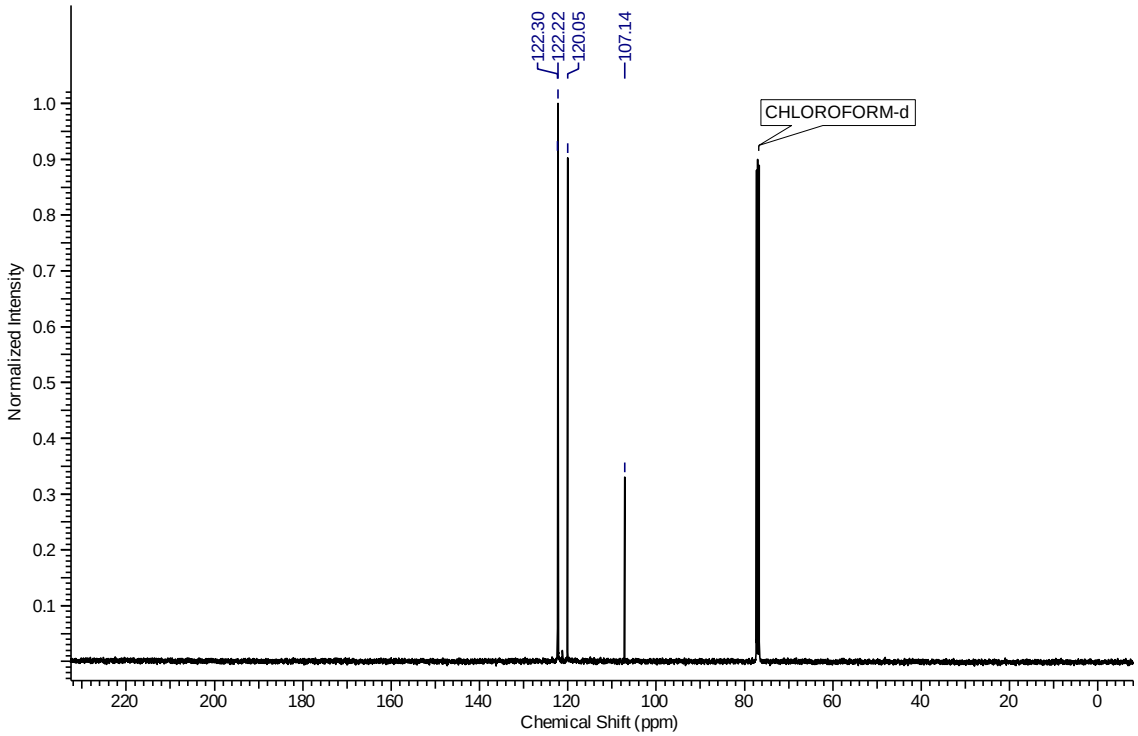




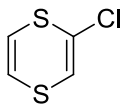
2-Bromo-1,4-dithiine (**9b**)

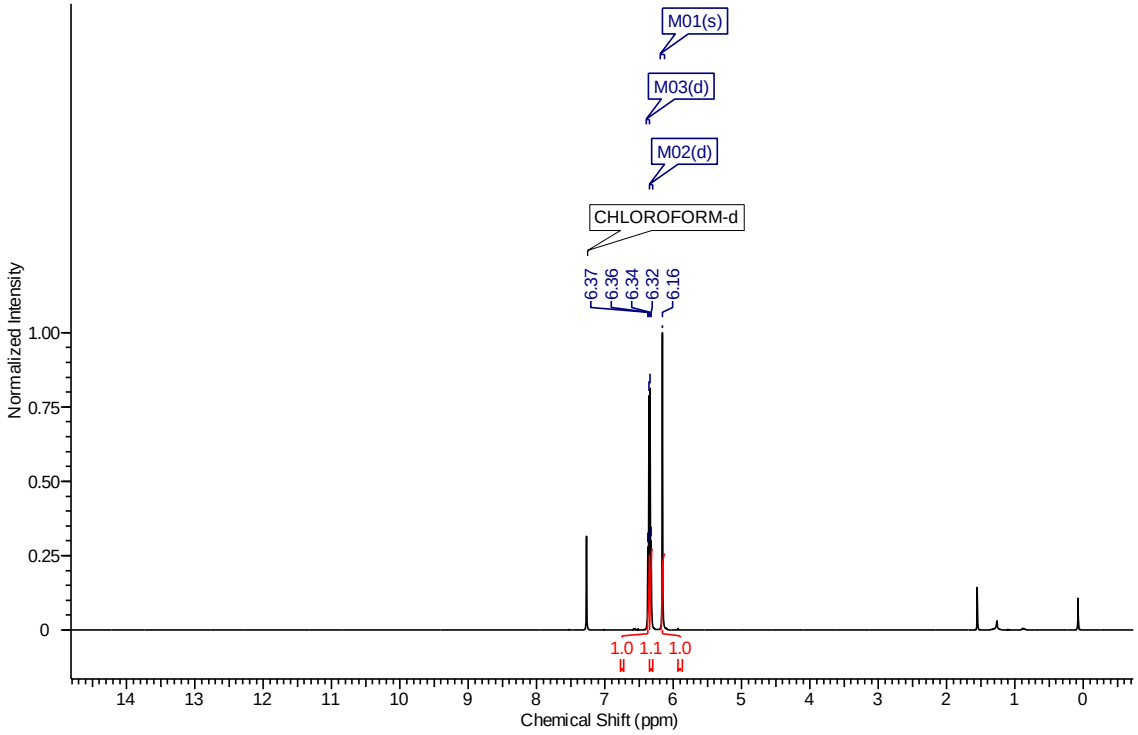


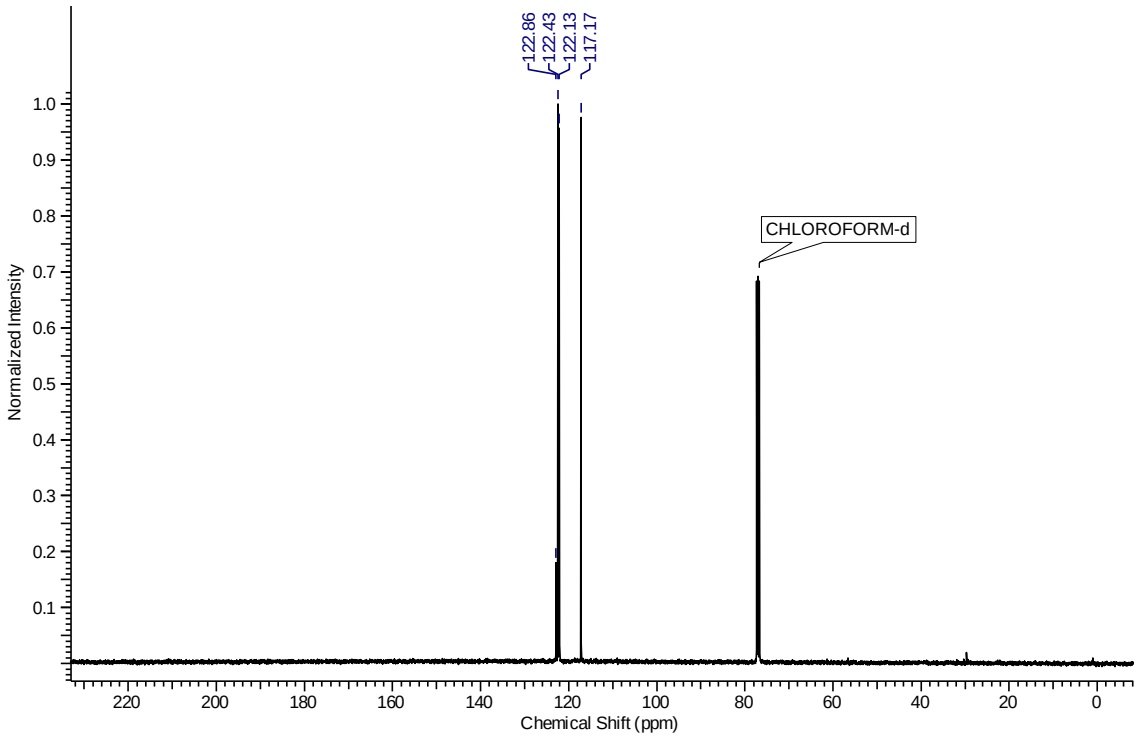




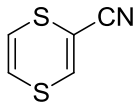
2-Chloro-1,4-dithiine (**9c**)

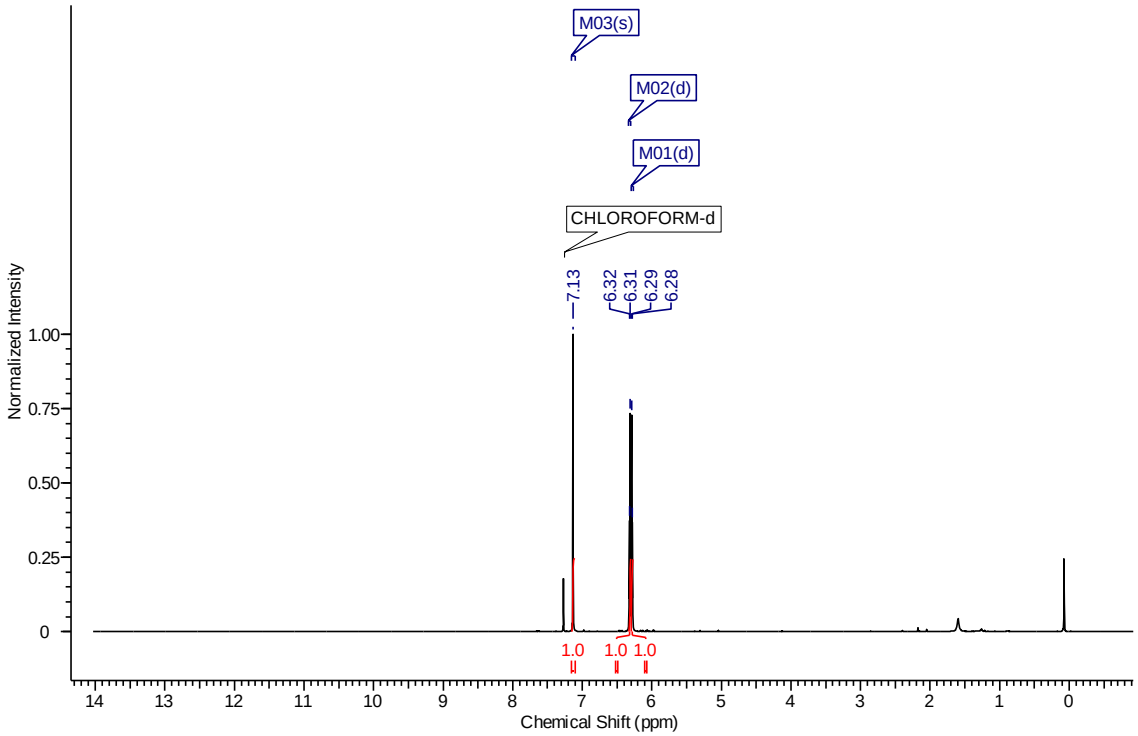


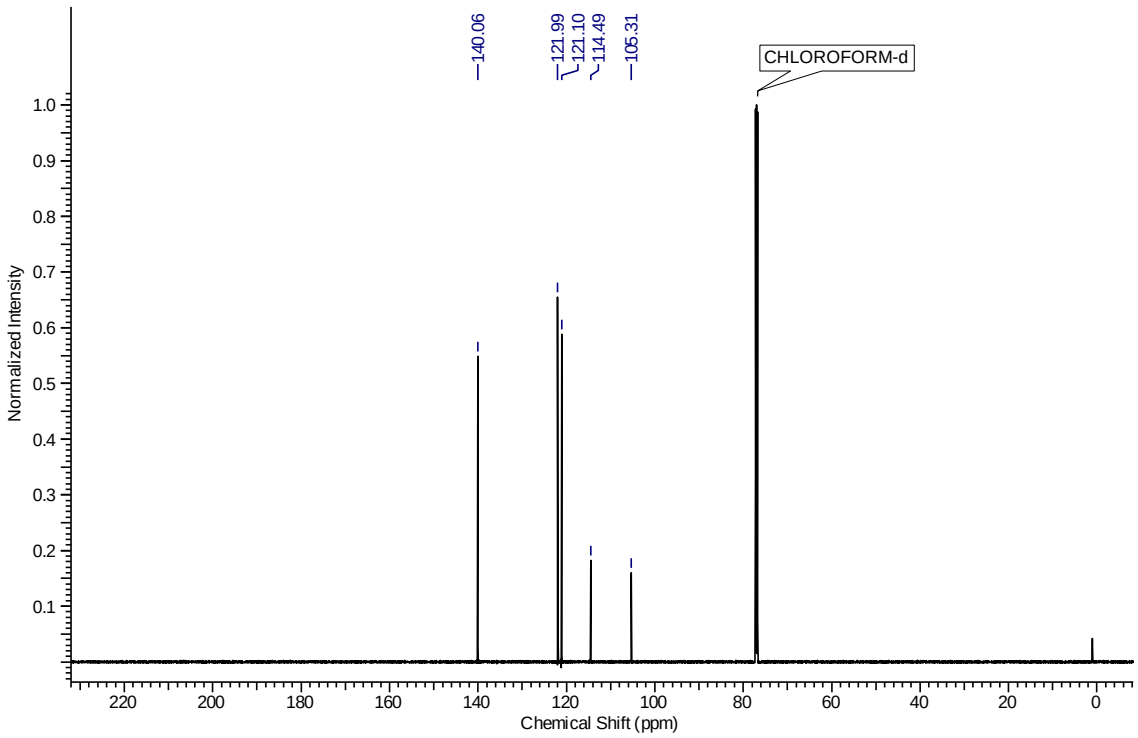




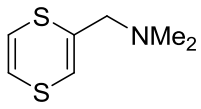
1,4-Dithiine-2-carbonitrile (**9d**)

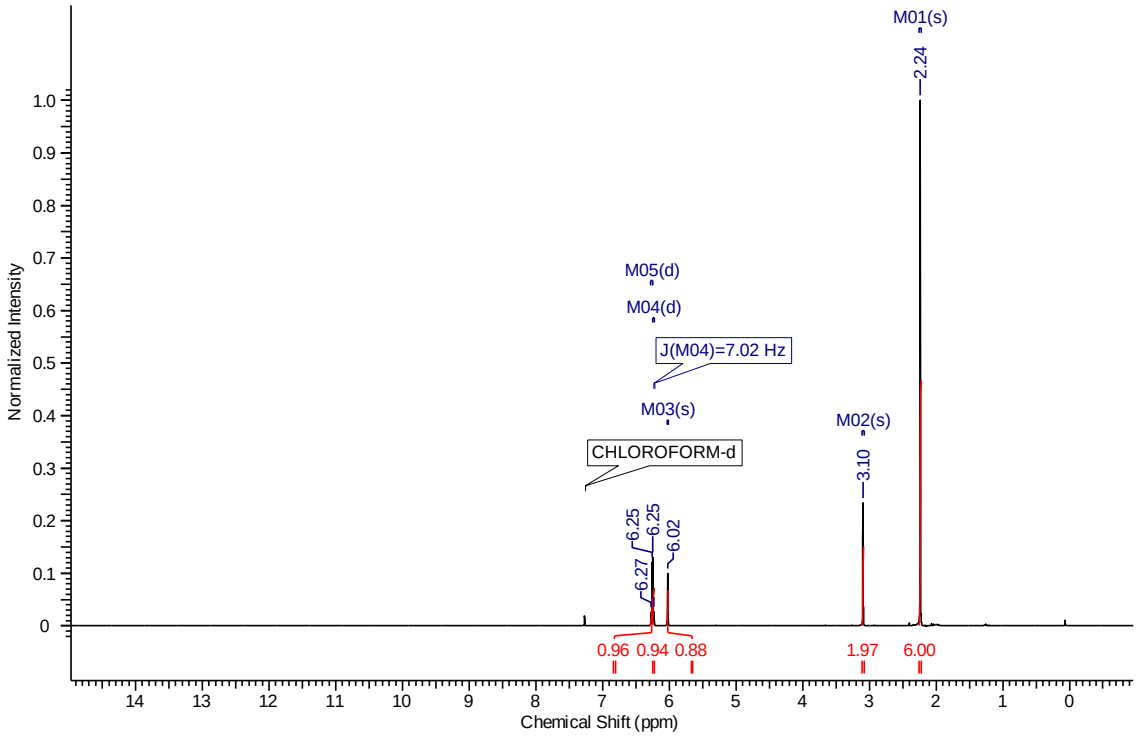


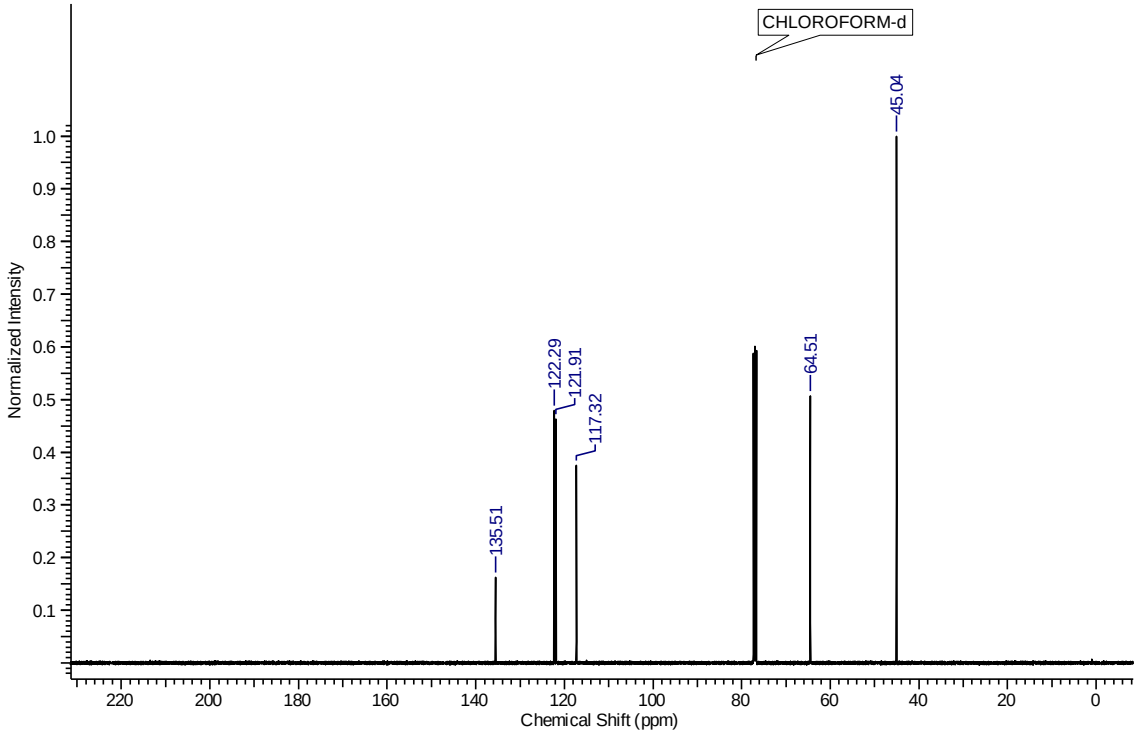




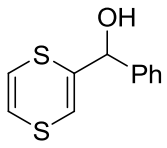
1-(1,4-Dithiin-2-yl)-*N*,*N*-dimethylmethanamine (**9e**)

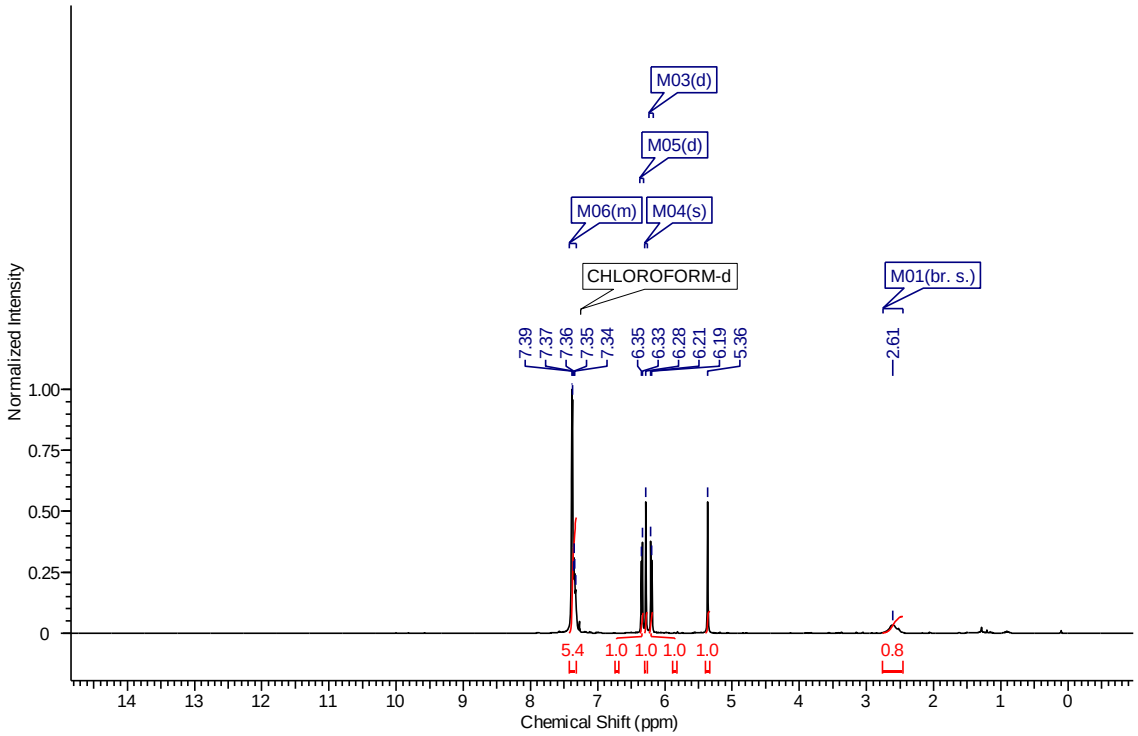


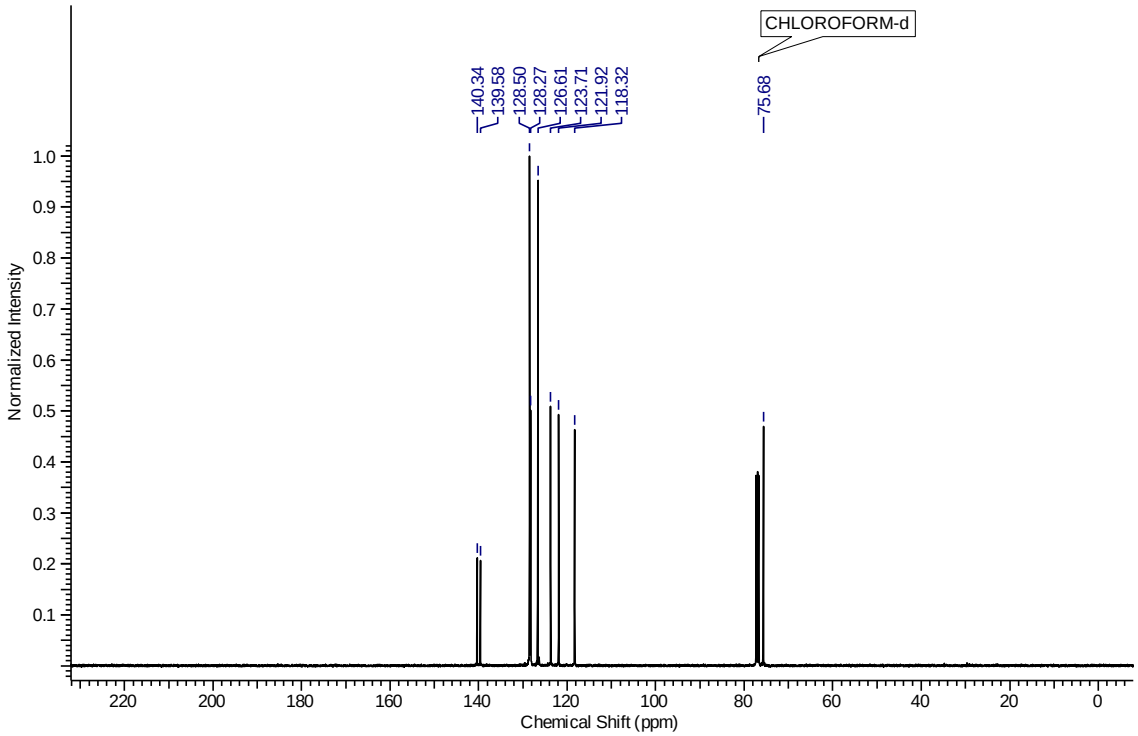




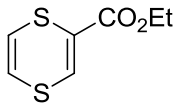
(1,4-Dithiin-2-yl)(phenyl)methanol (**9f**)

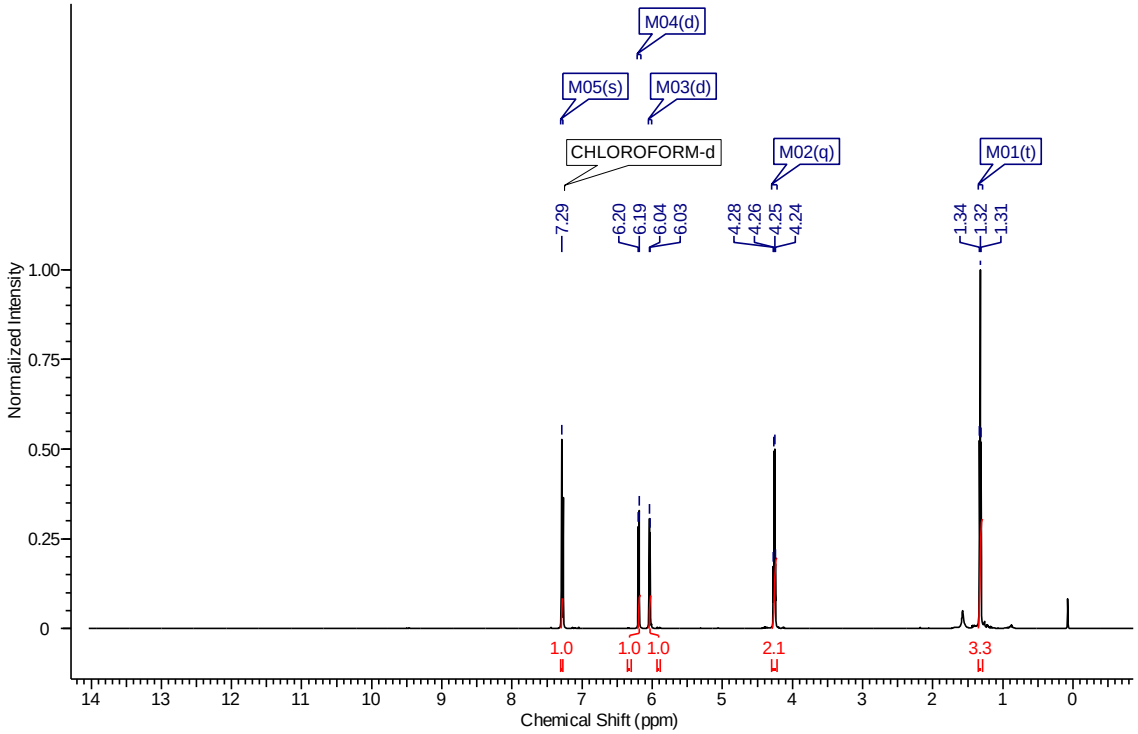


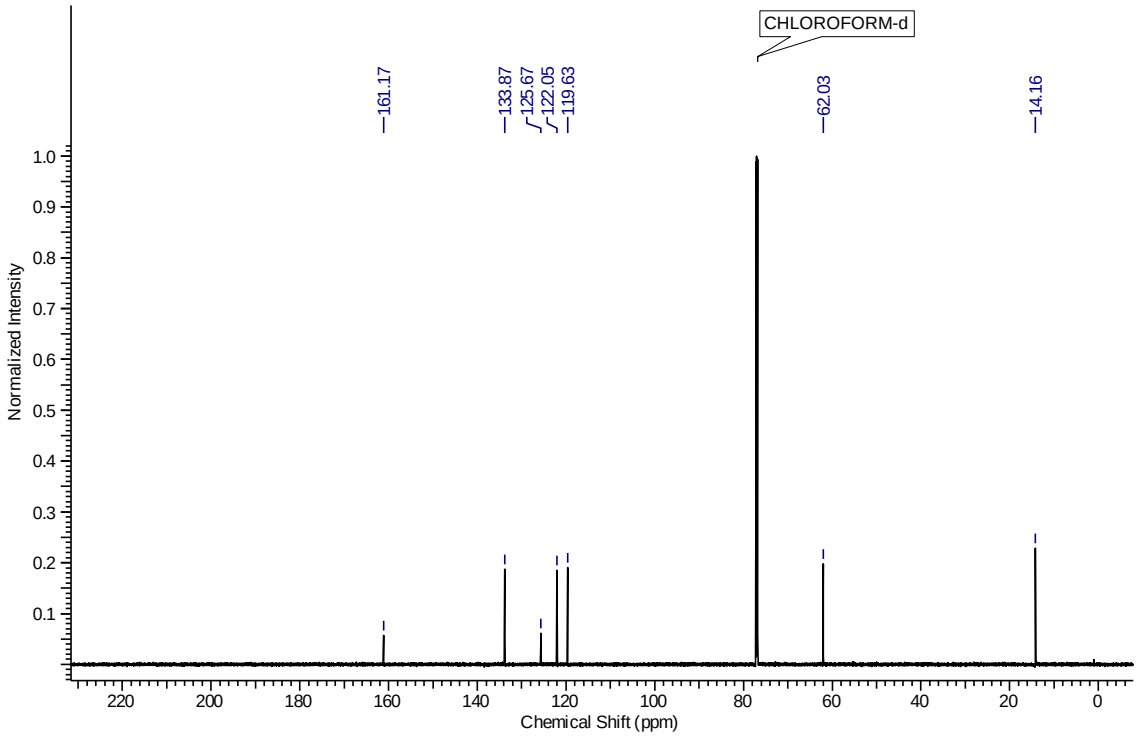




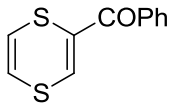
Ethyl 1,4-dithiine-2-carboxylate (**9g**)

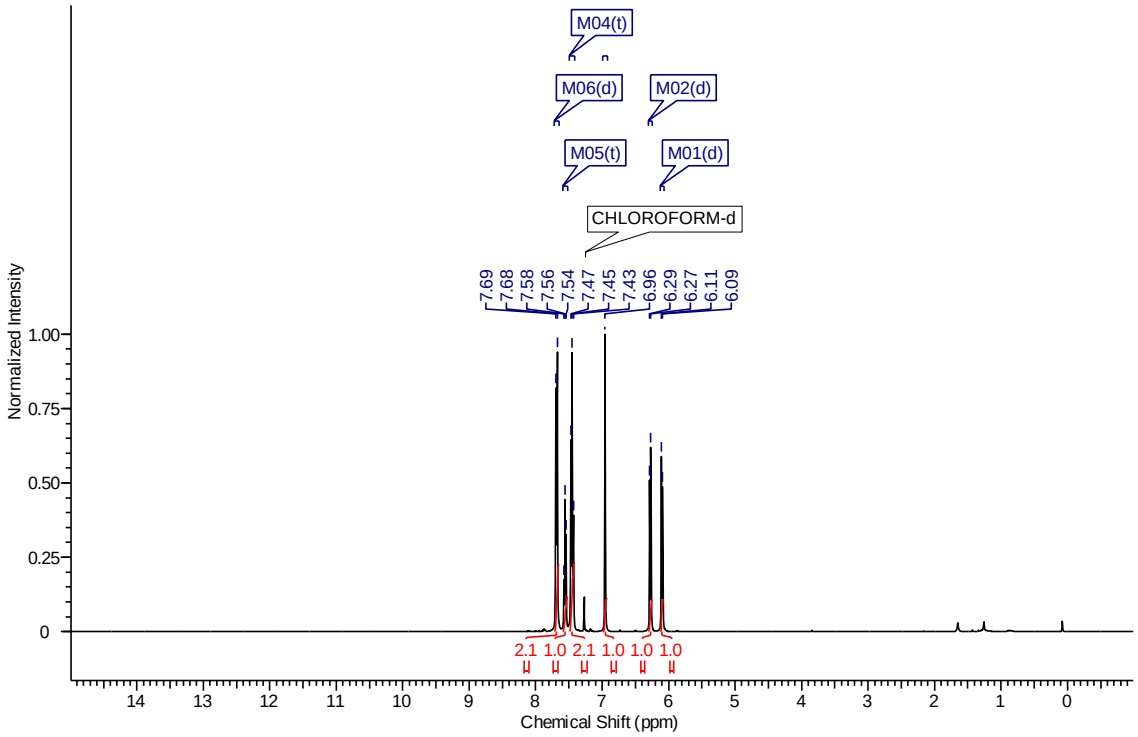


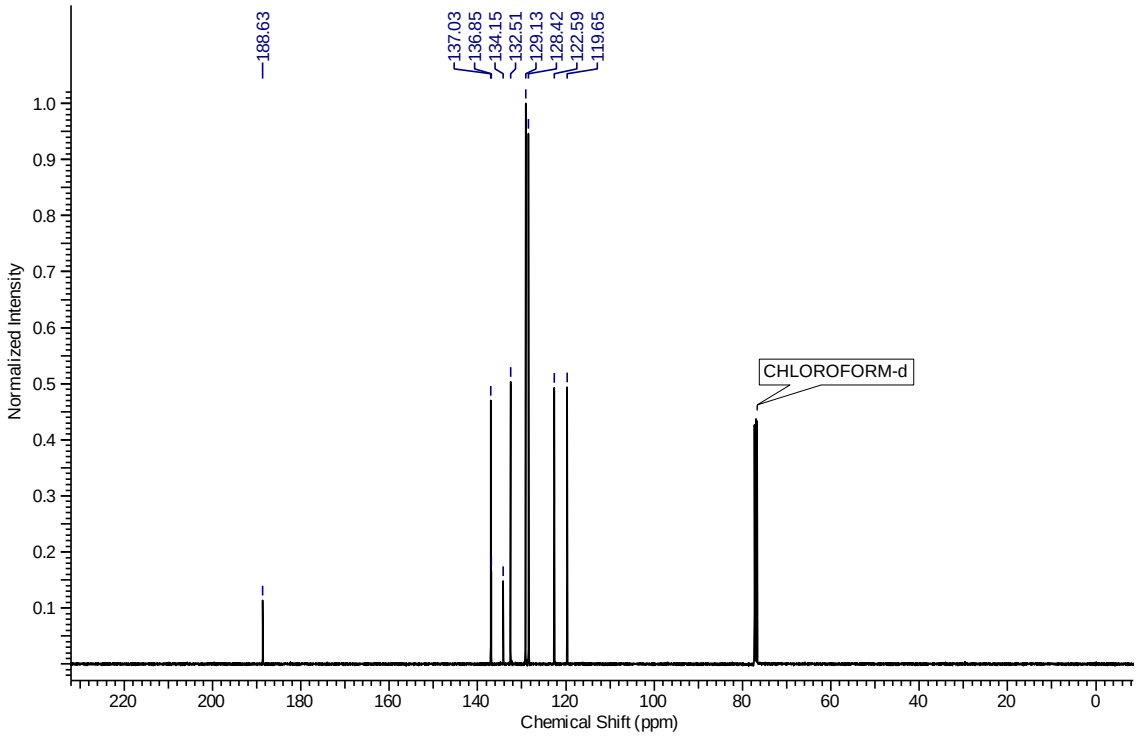




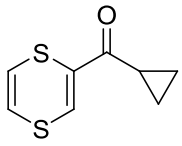
(1,4-Dithiin-2-yl)(phenyl)methanone (**9h**)

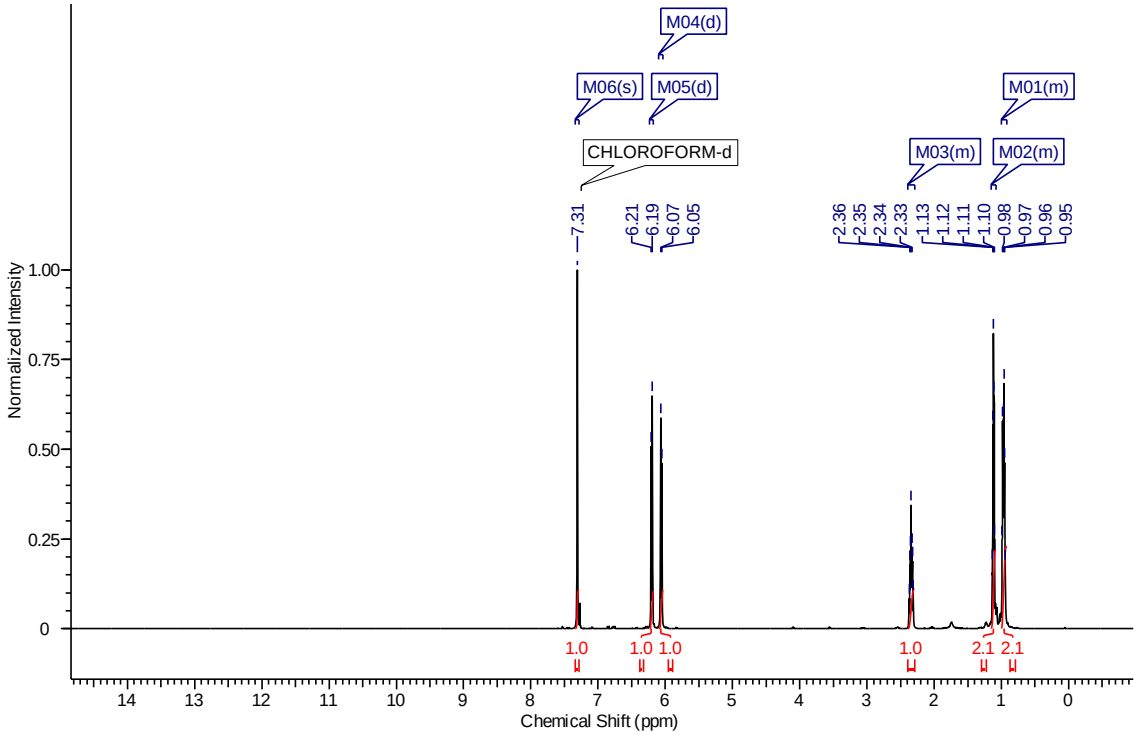


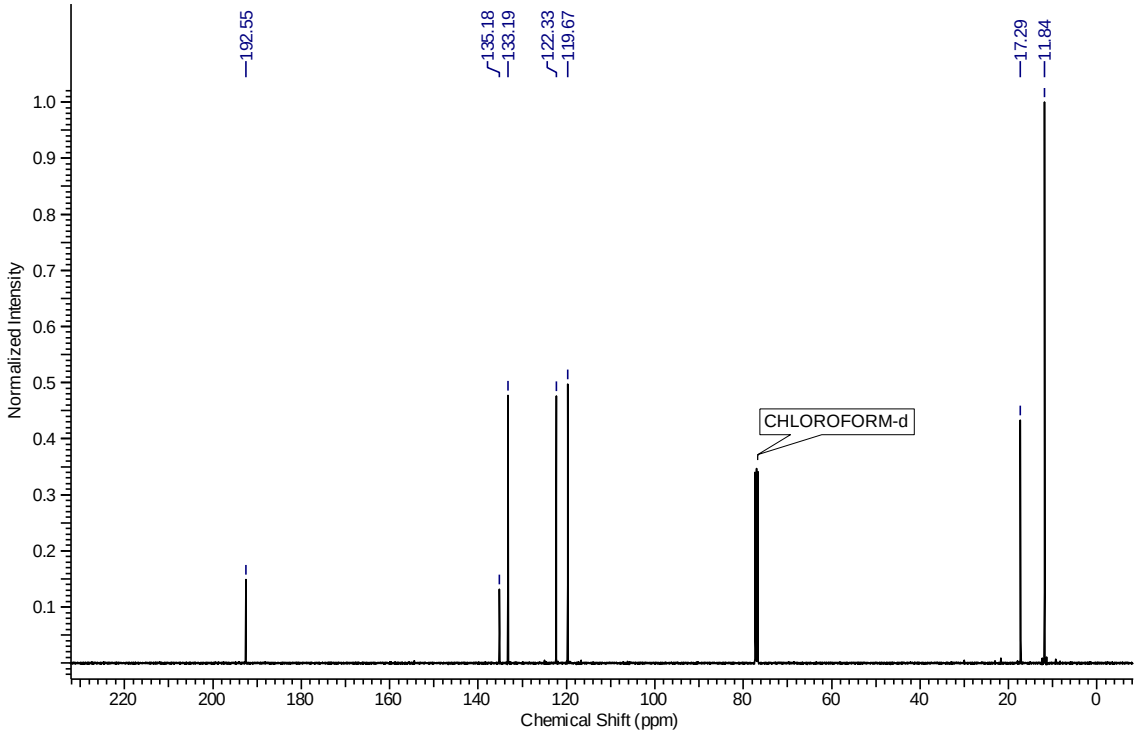




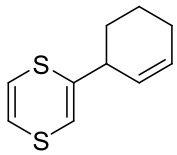
Cyclopropyl(1,4-dithiin-2-yl)methanone (**9i**)

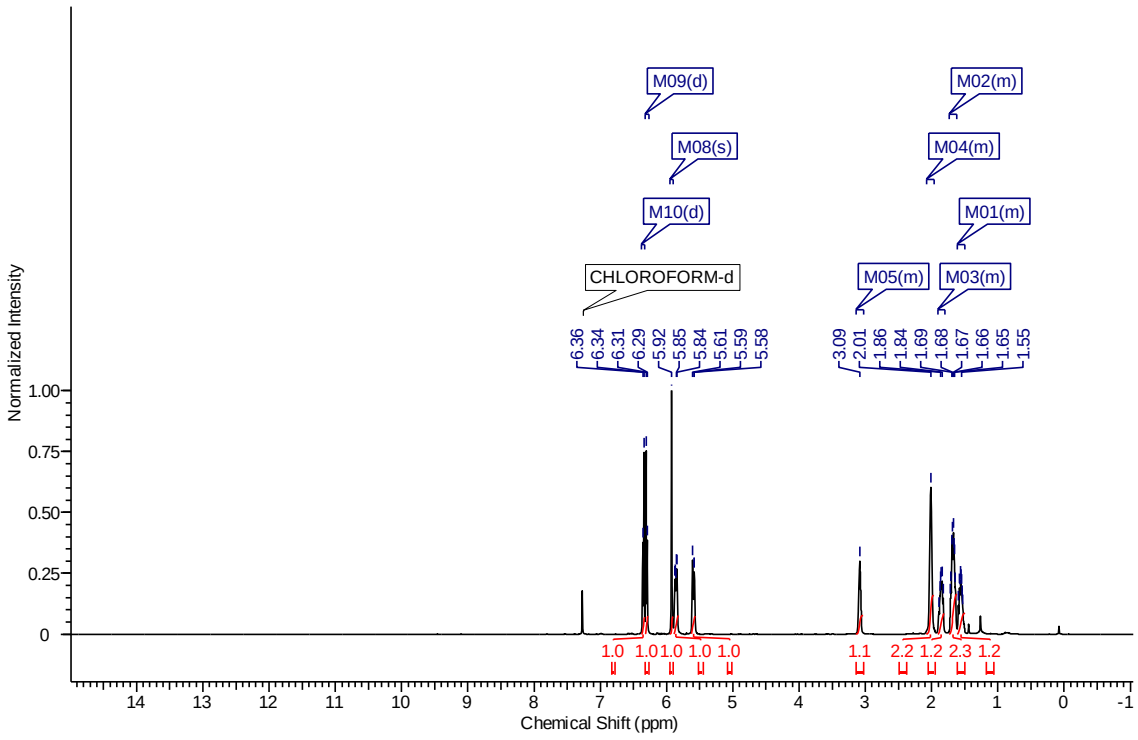


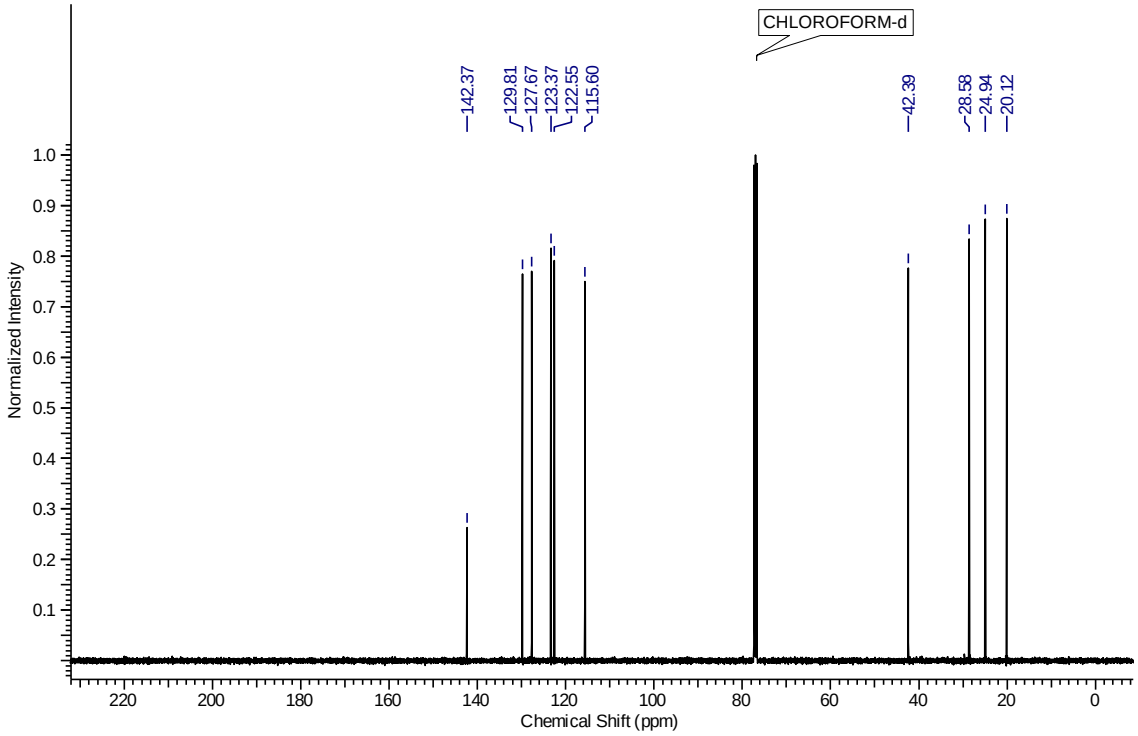




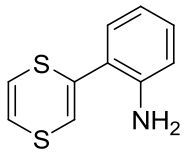
2-(Cyclohex-2-en-1-yl)-1,4-dithiine (**9j**)

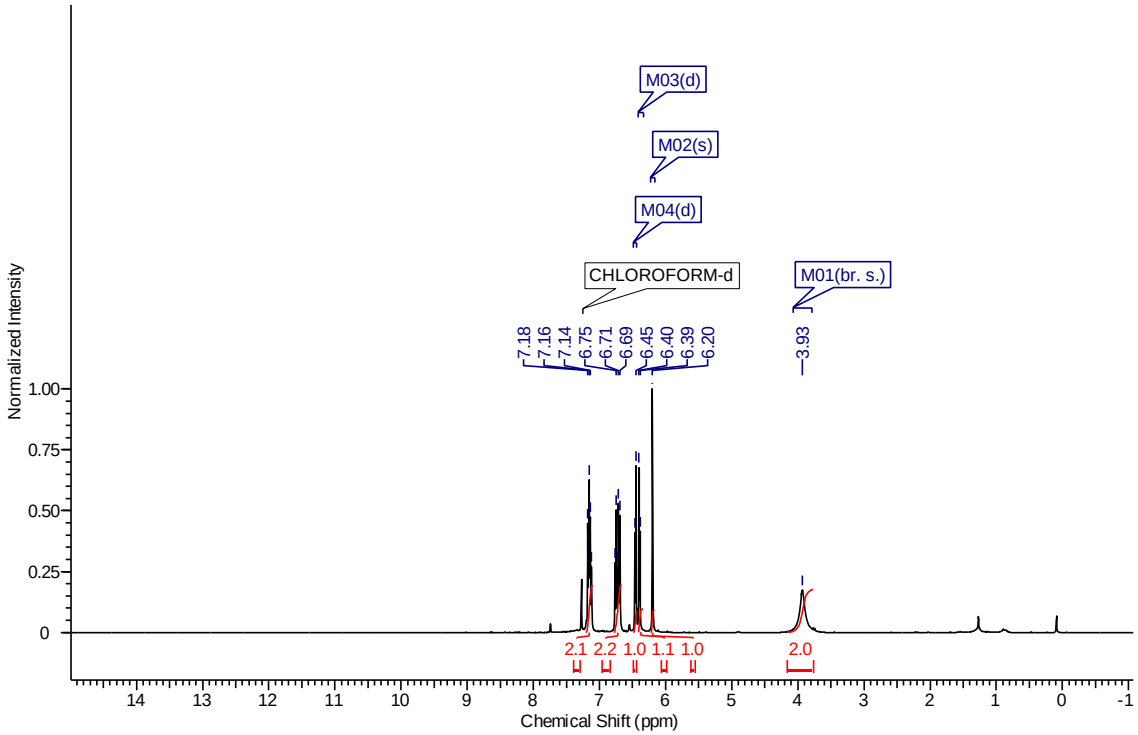


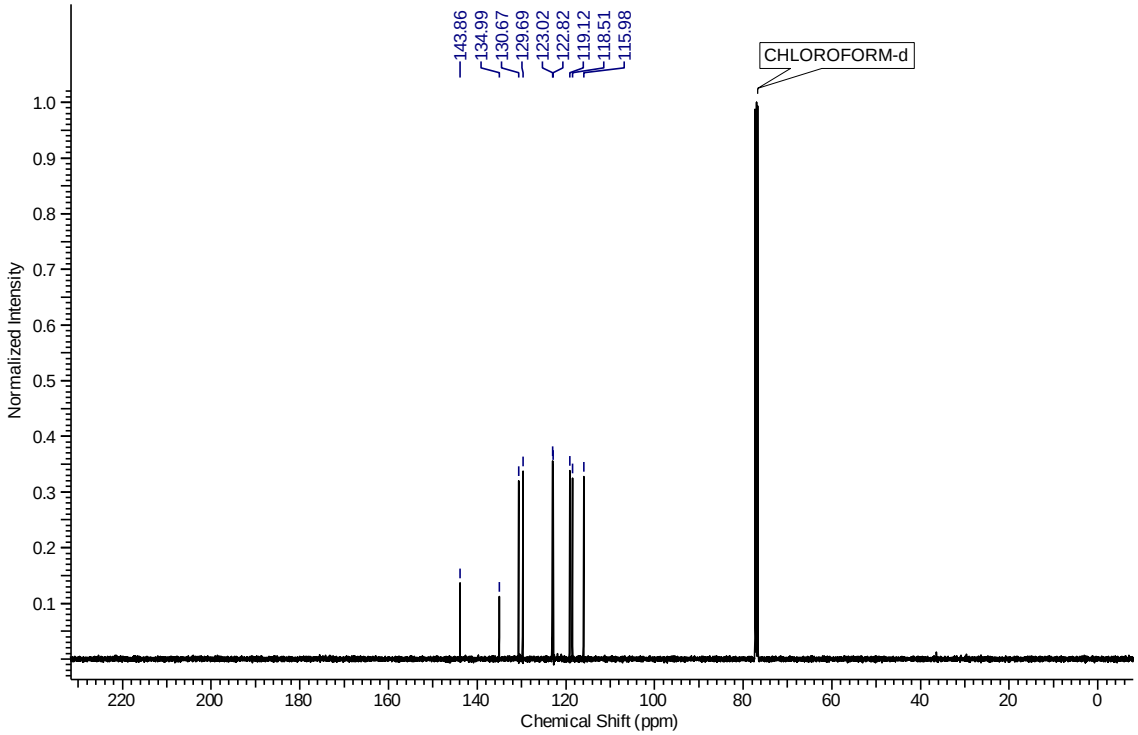




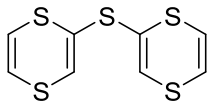
2-(1,4-Dithiin-2-yl)aniline (**9k**)

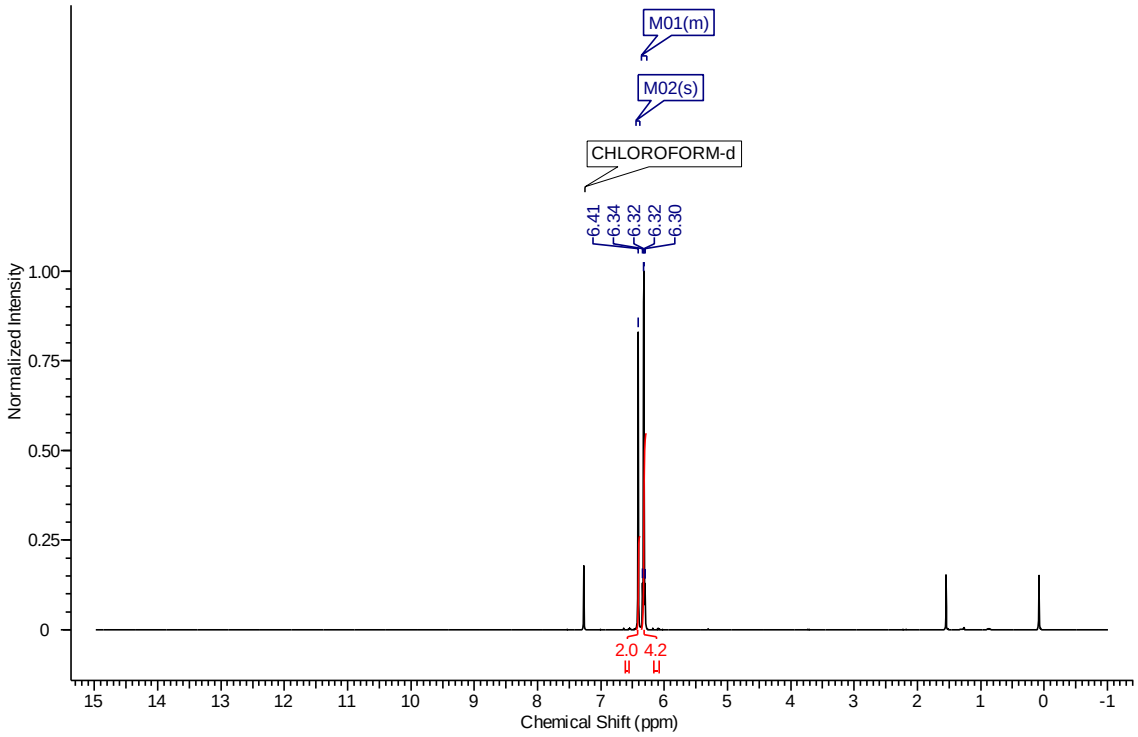


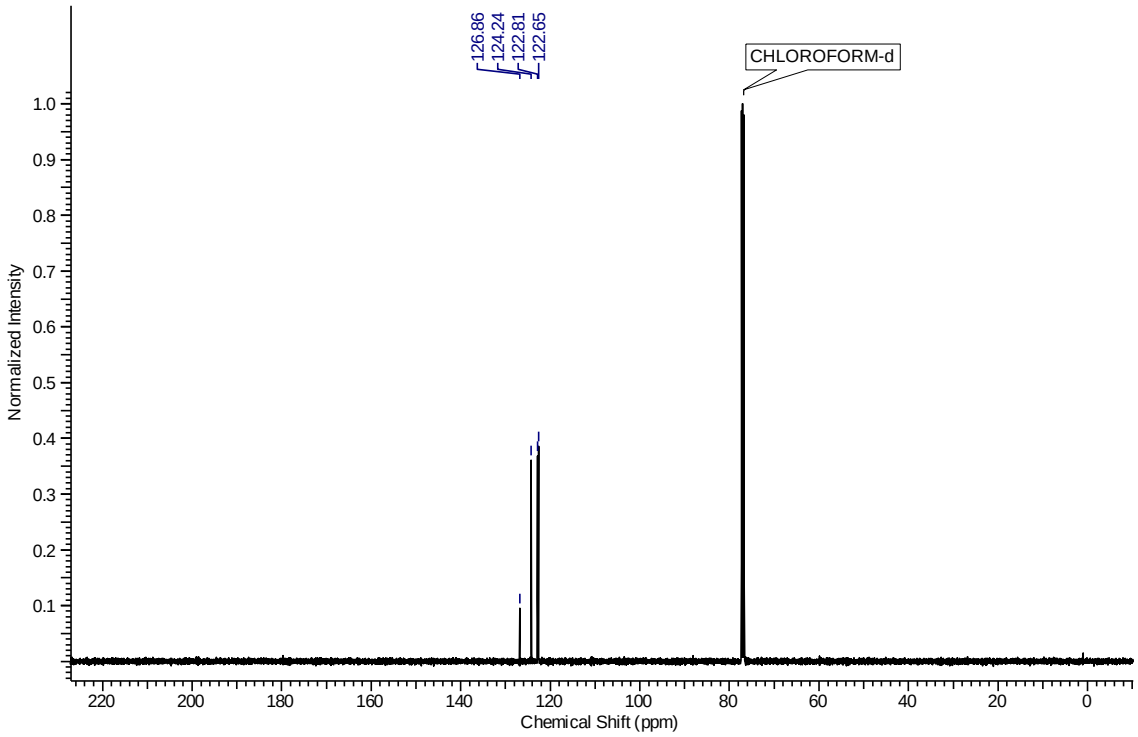




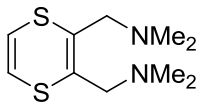
Di(1,4-dithiin-2-yl)sulfane (**9l**)

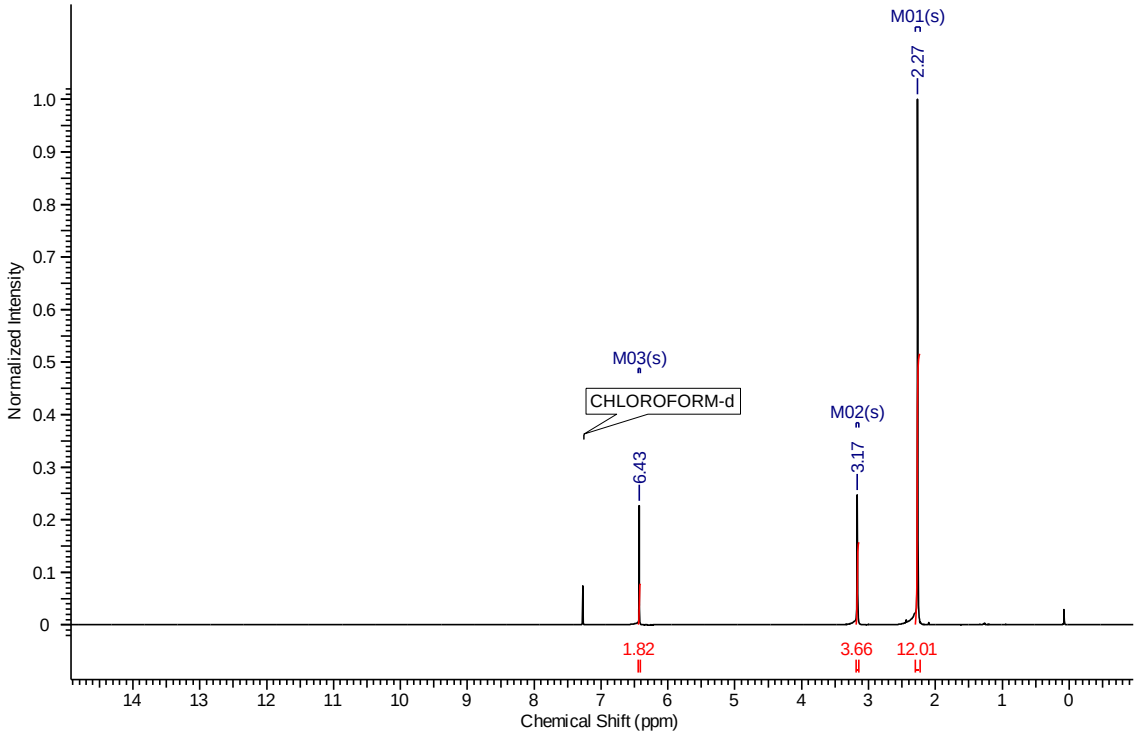


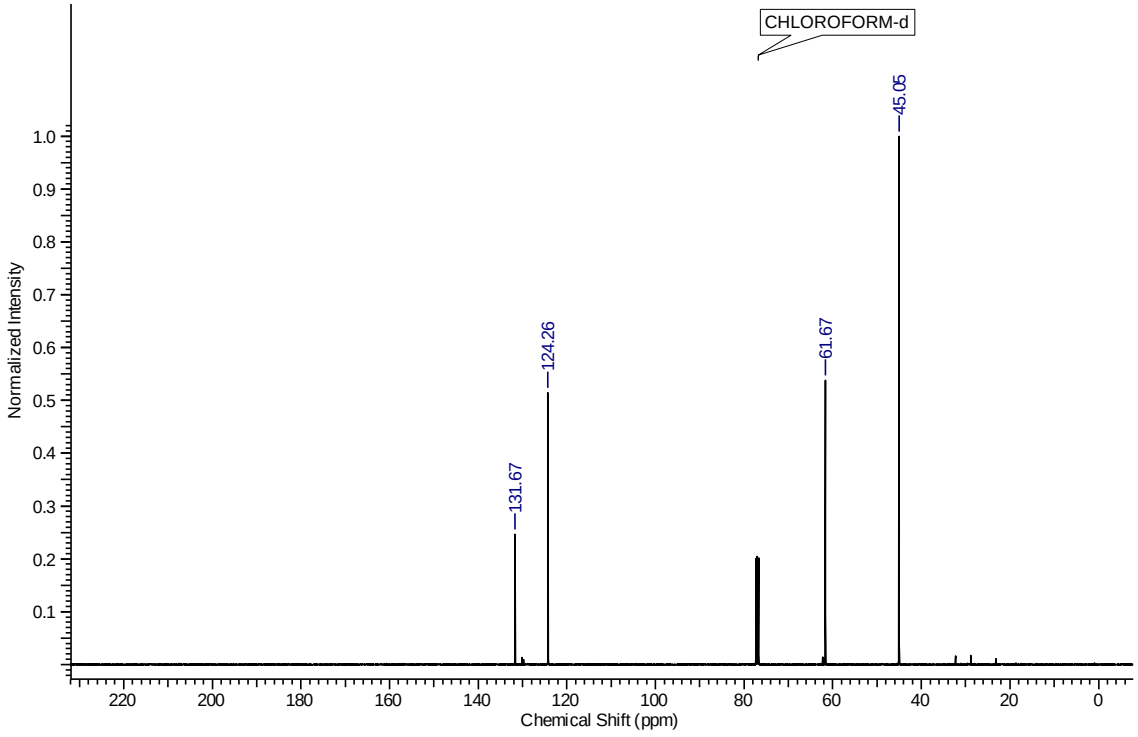




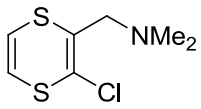
1,1'-(1,4-Dithiine-2,3-diyl)bis(*N*,*N*-dimethylmethanamine) (**11a**)

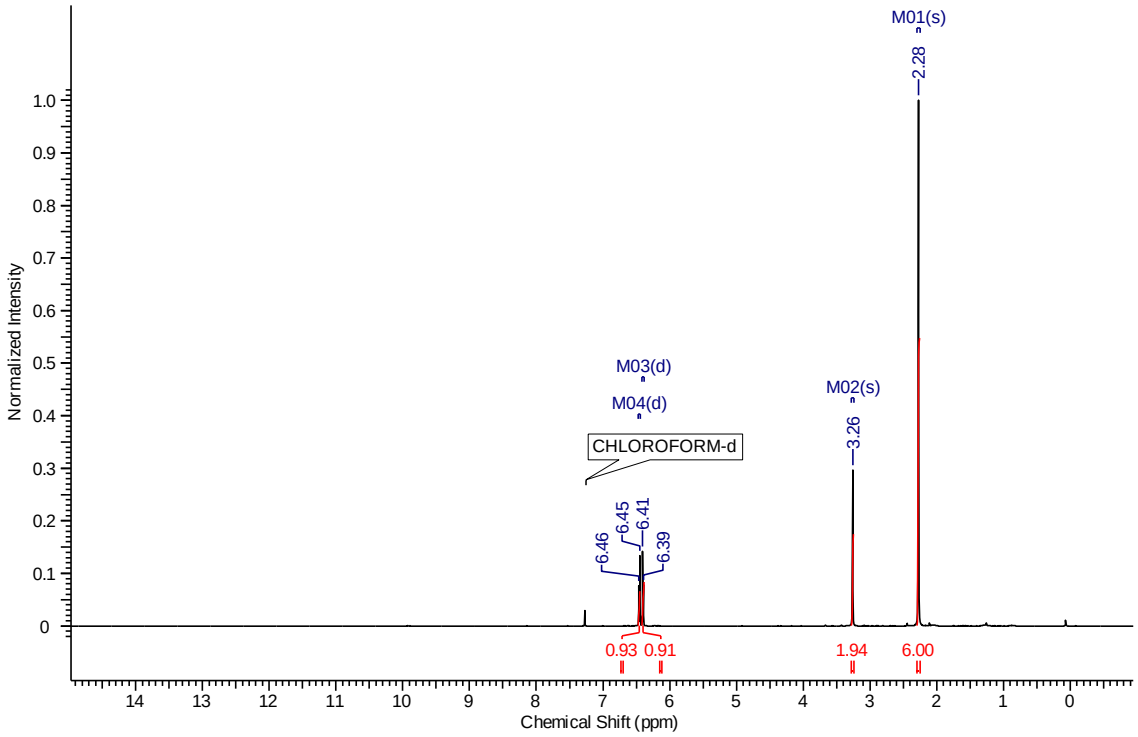


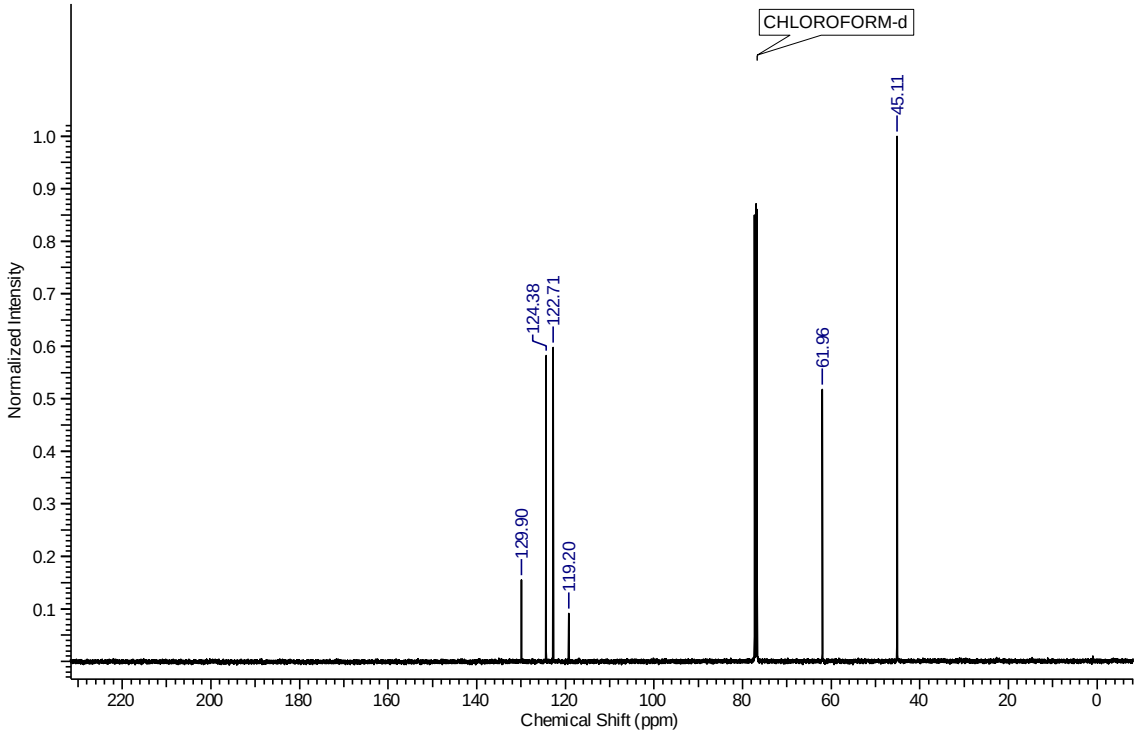




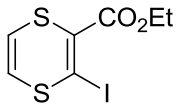
1-(3-Chloro-1,4-dithiin-2-yl)-*N*,*N*-dimethylmethanamine (**11b**)

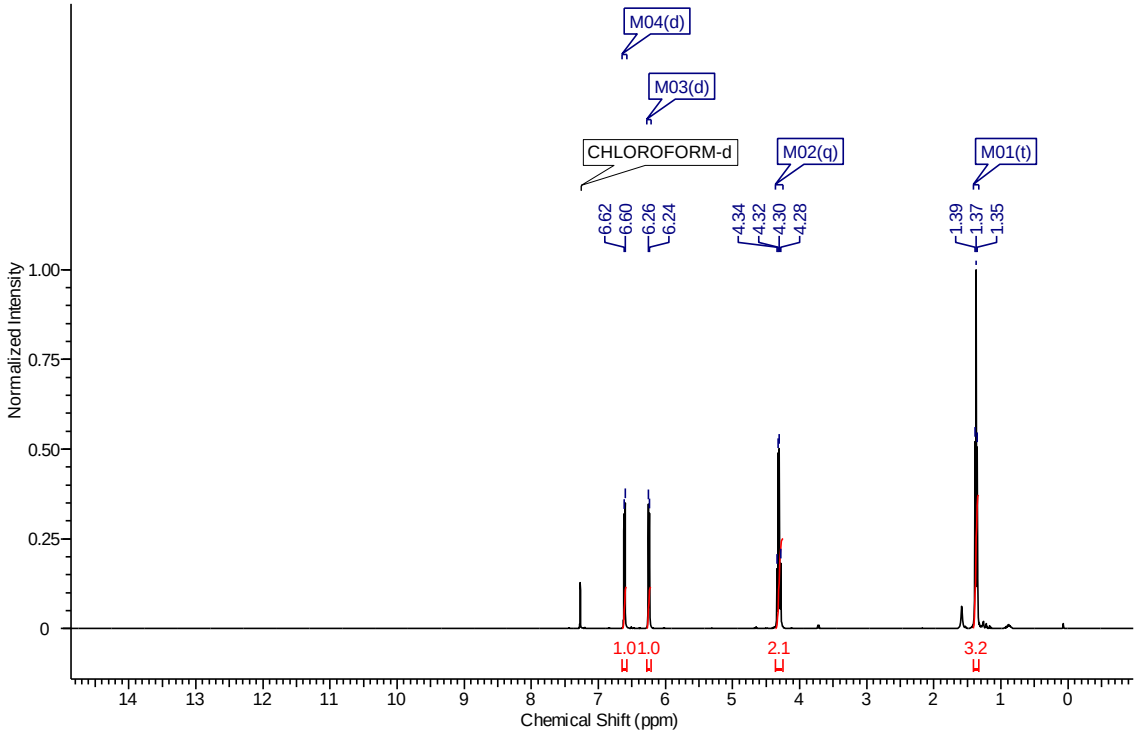


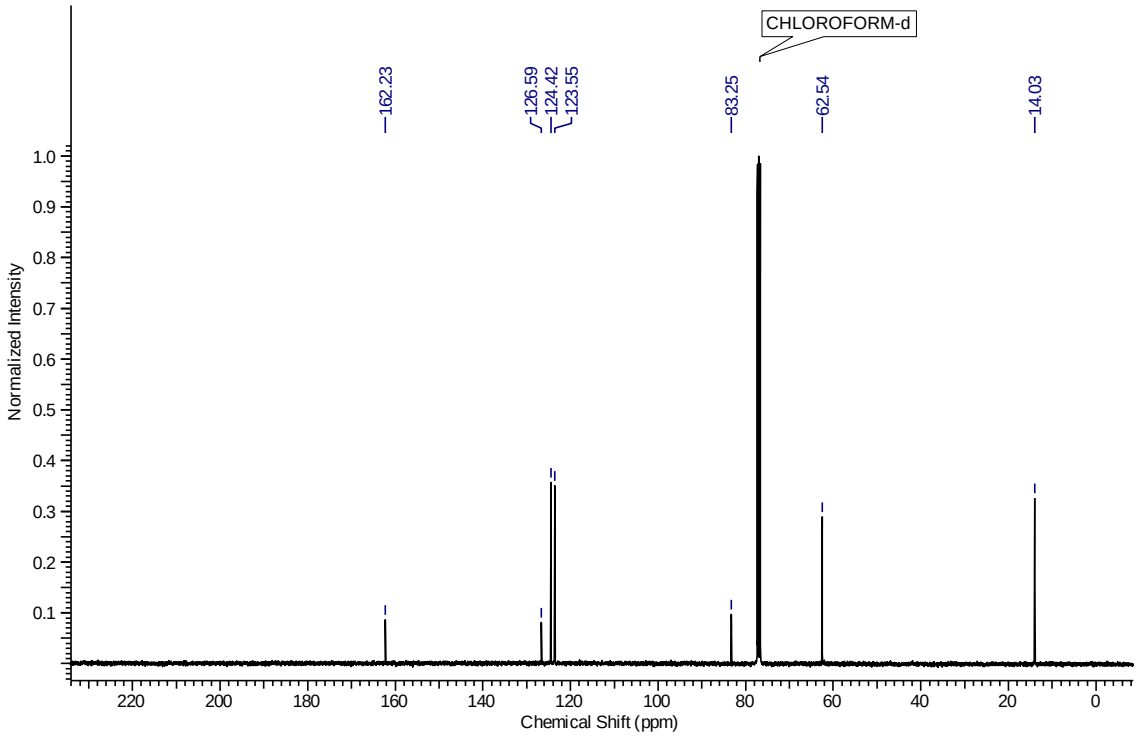




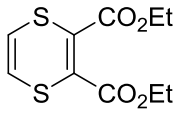
Ethyl 3-iodo-1,4-dithiine-2-carboxylate (**11c**)

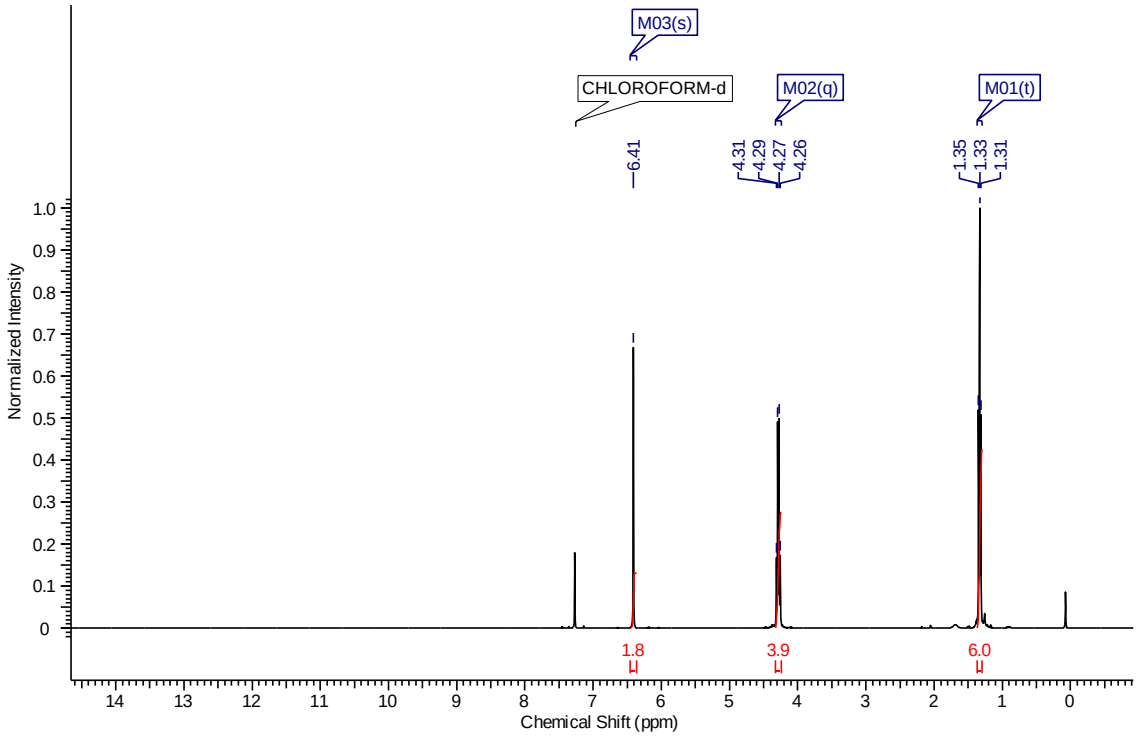


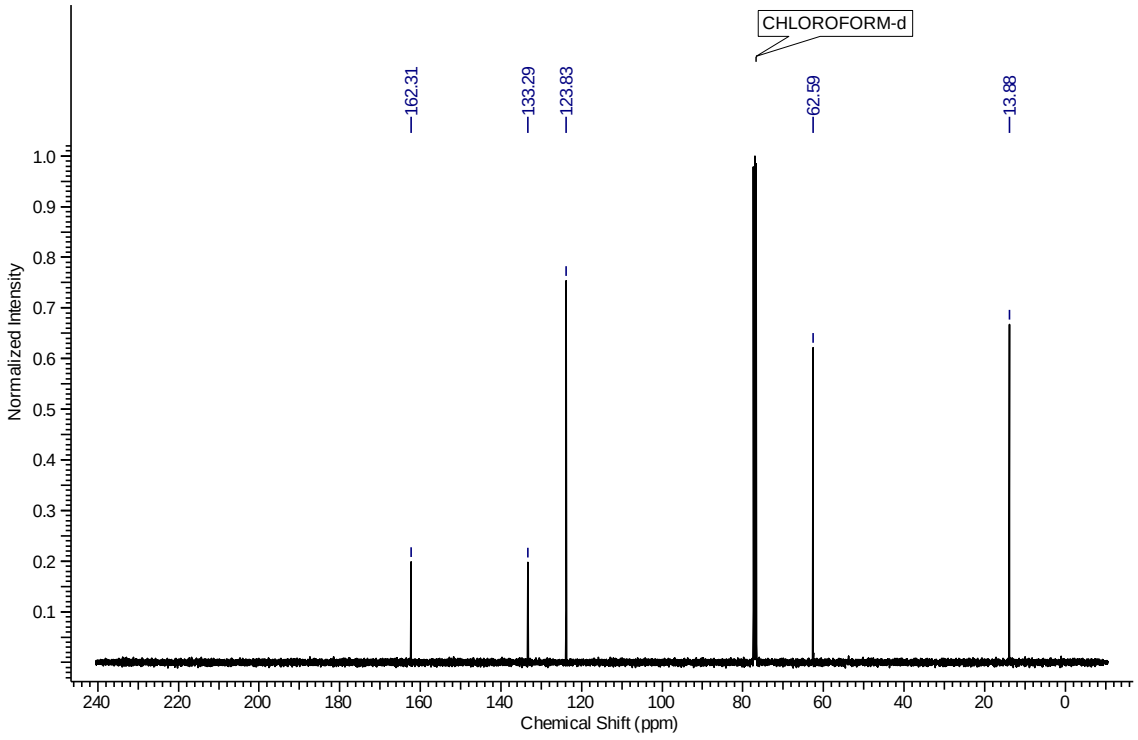




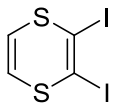
Diethyl 1,4-dithiine-2,3-dicarboxylate (**11d**)

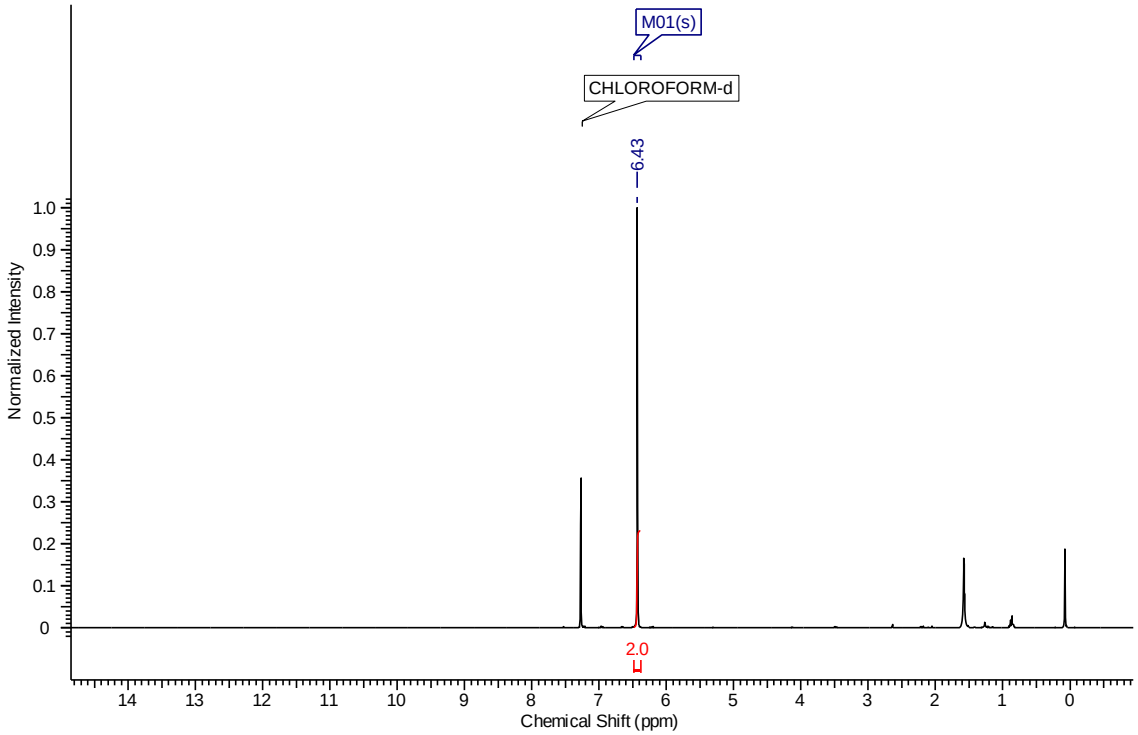


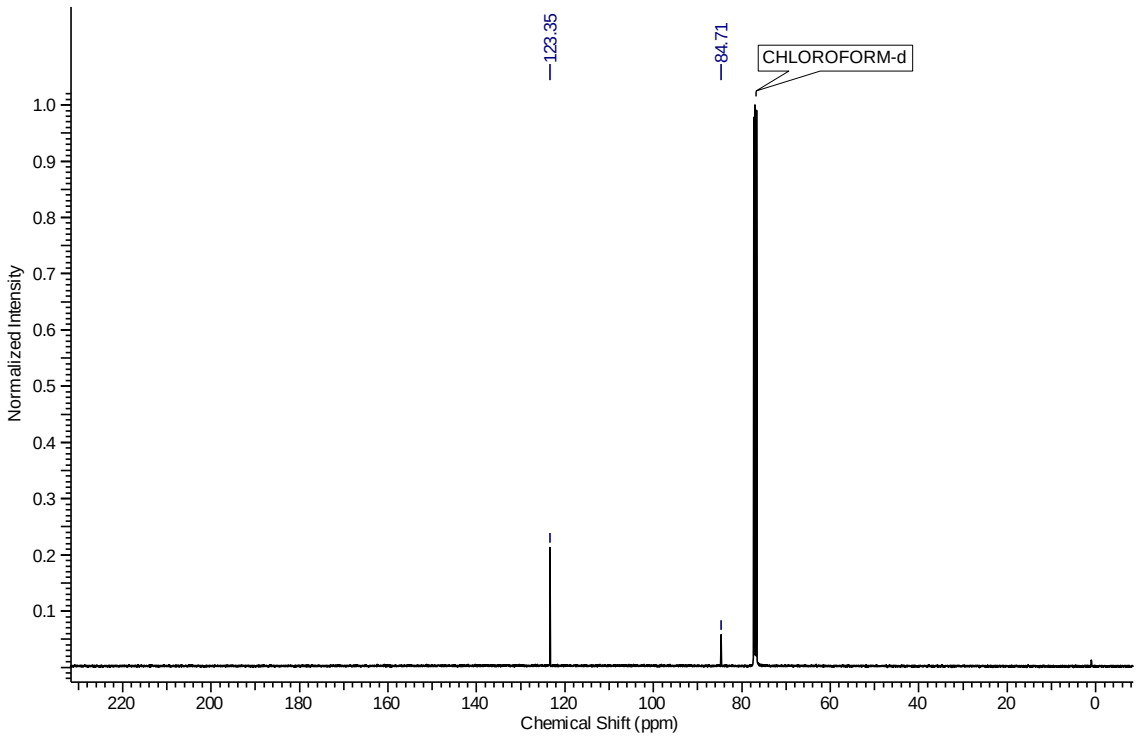




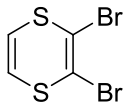
2,3-Diiodo-1,4-dithiine (**11e**)

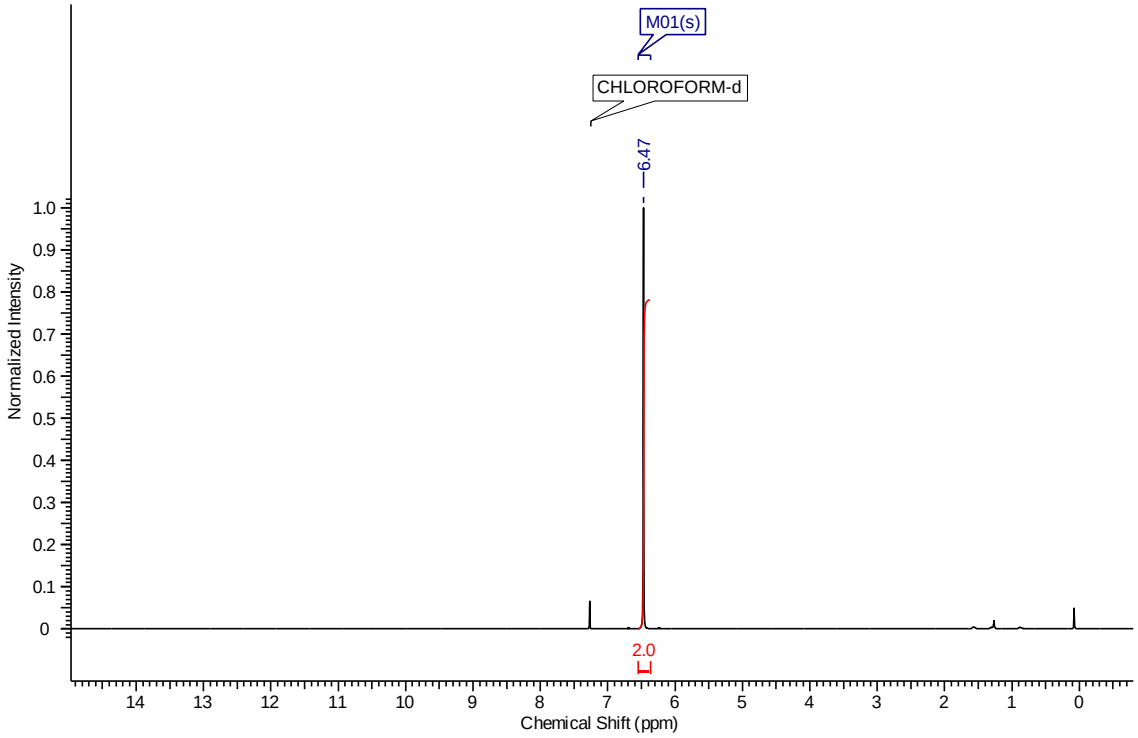


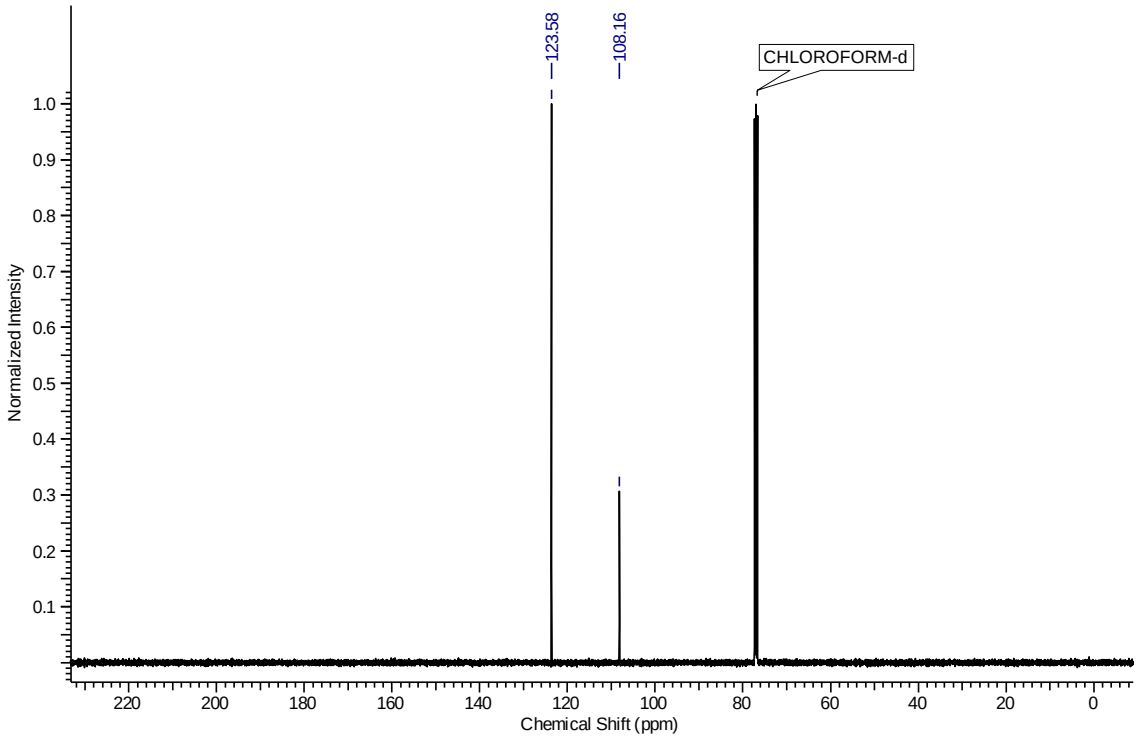




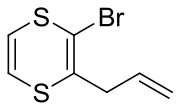
2,3-Dibromo-1,4-dithiine (**11f**)

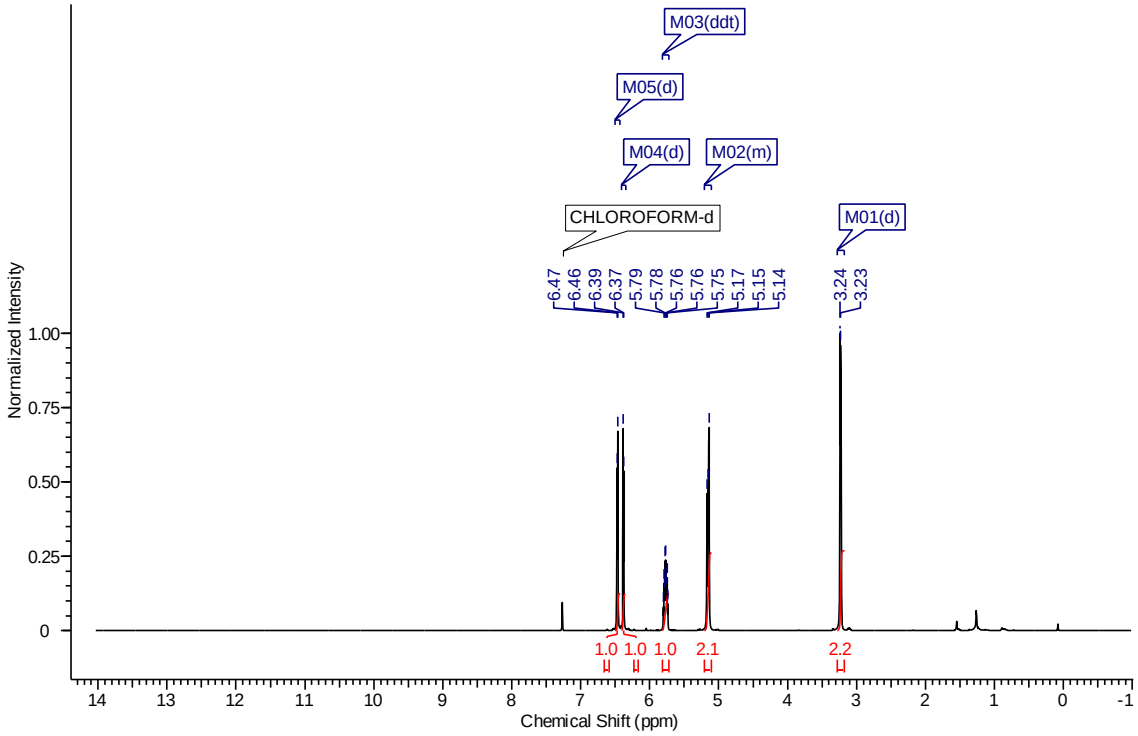


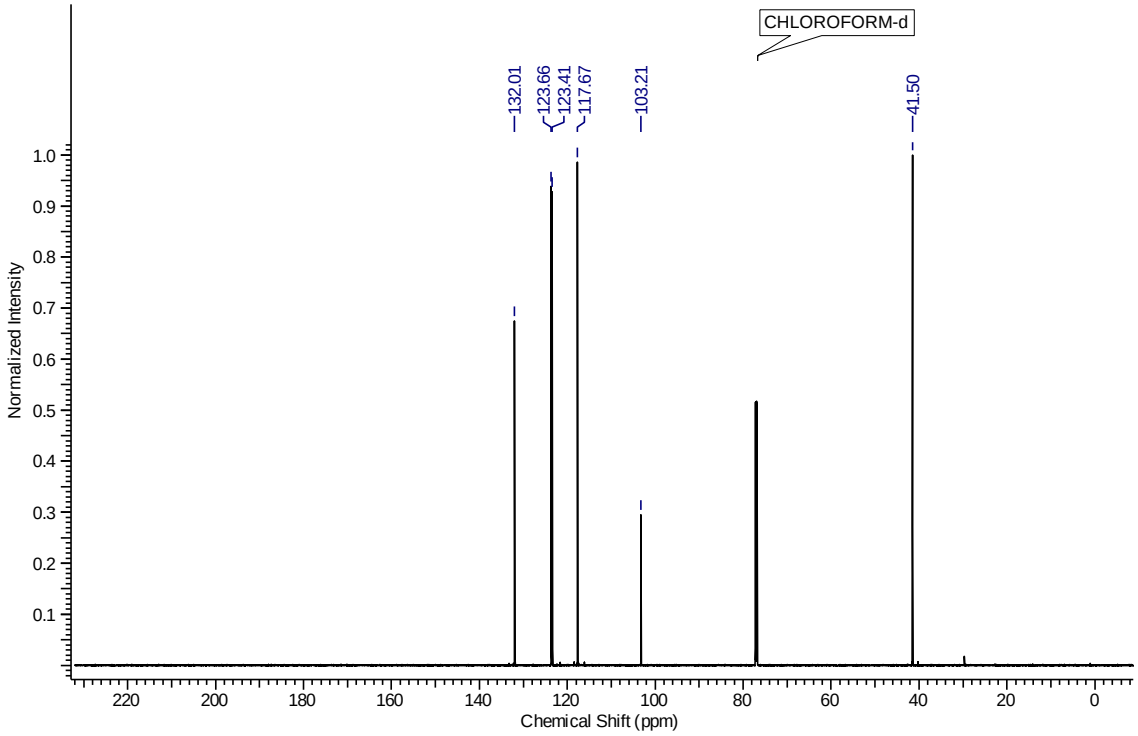




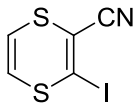
2-Allyl-3-bromo-1,4-dithiine (**11g**)

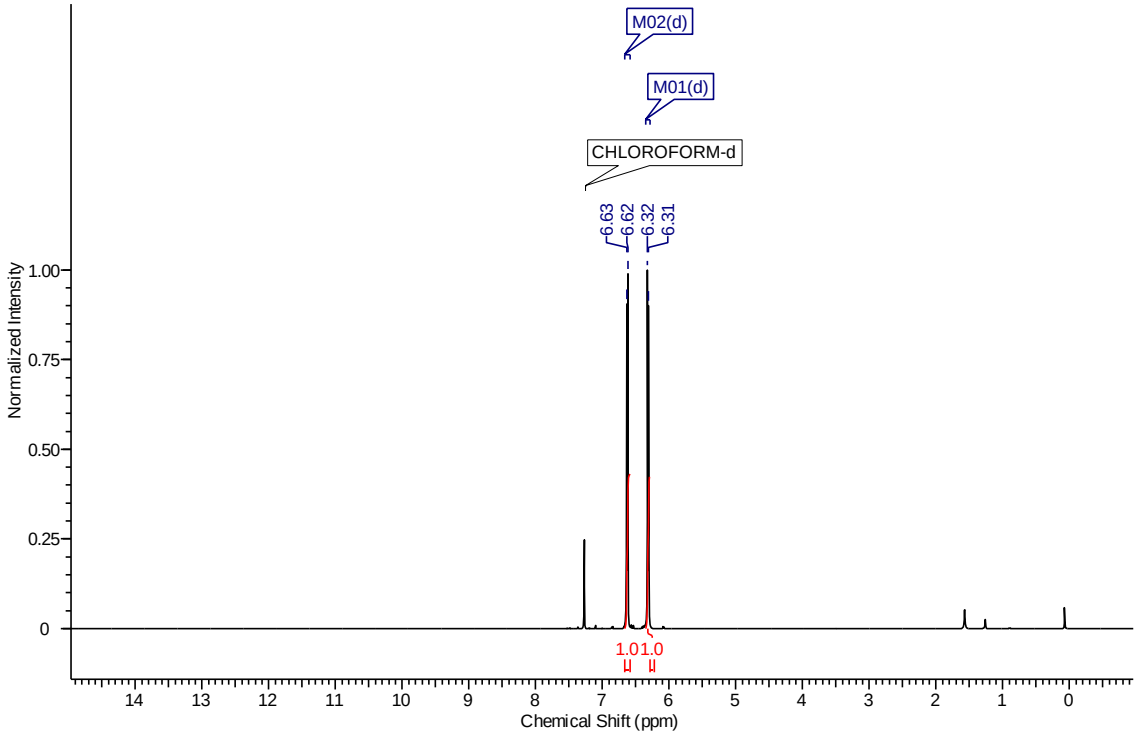


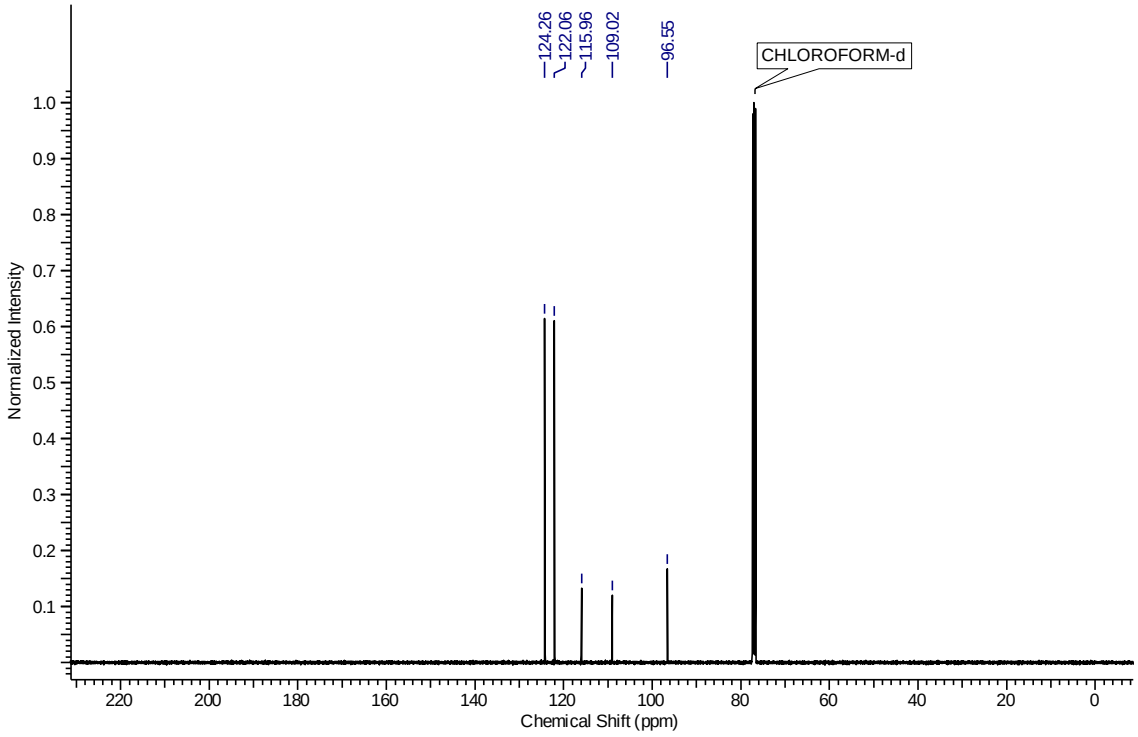




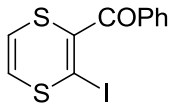
3-Iodo-1,4-dithiine-2-carbonitrile (**11h**)

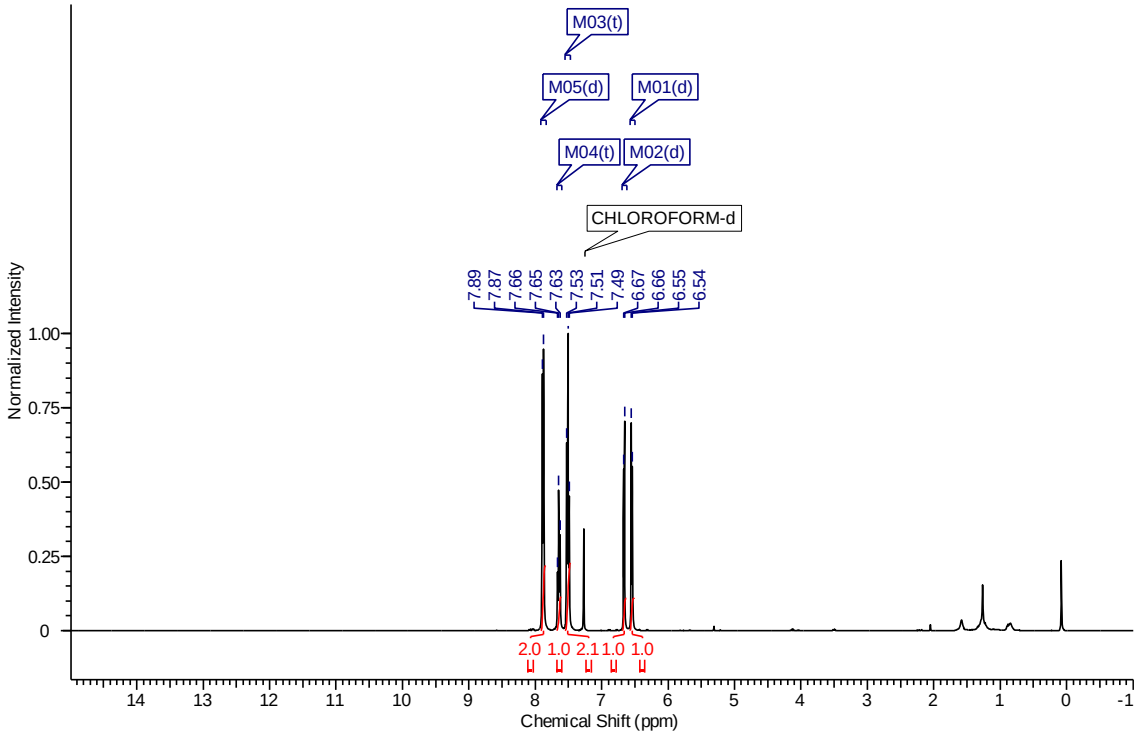


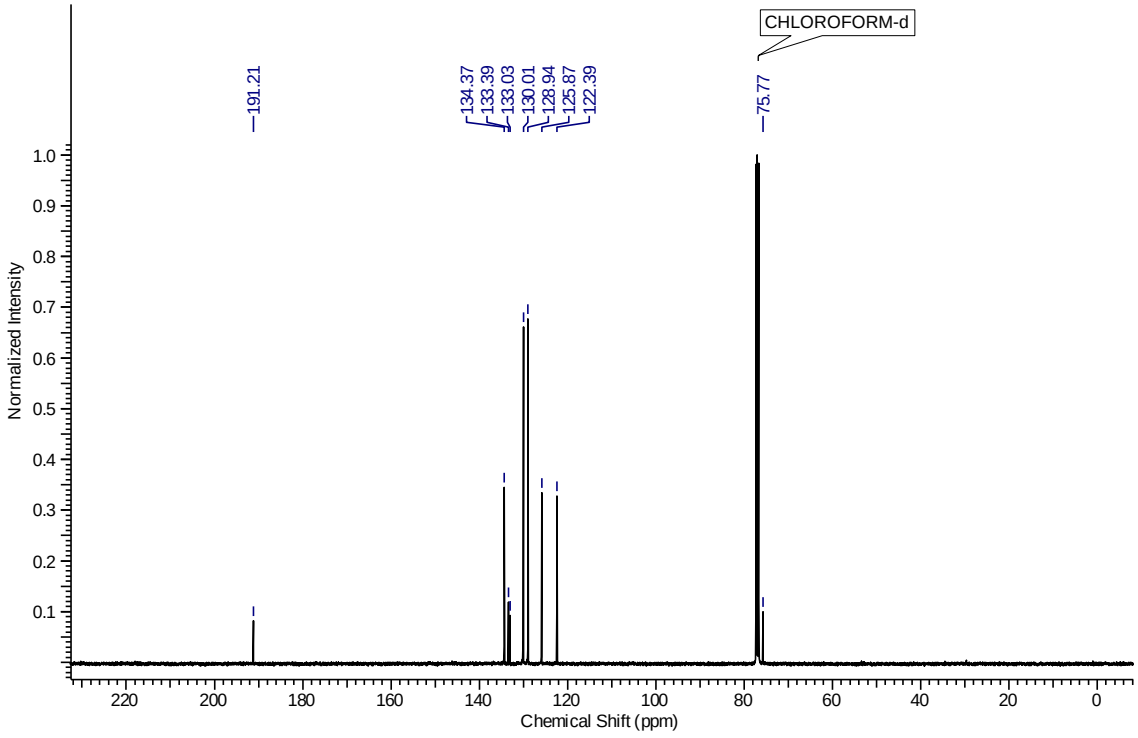




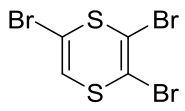
(3-Iodo-1,4-dithiin-2-yl)(phenyl)methanone (**11i**)

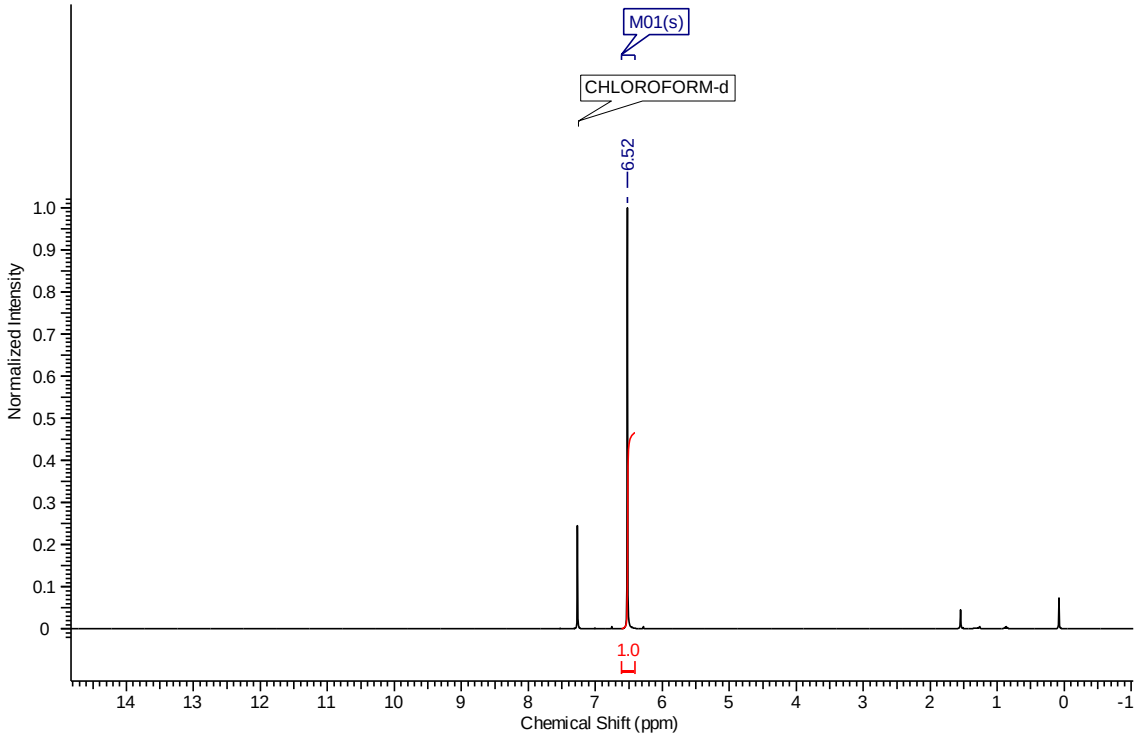


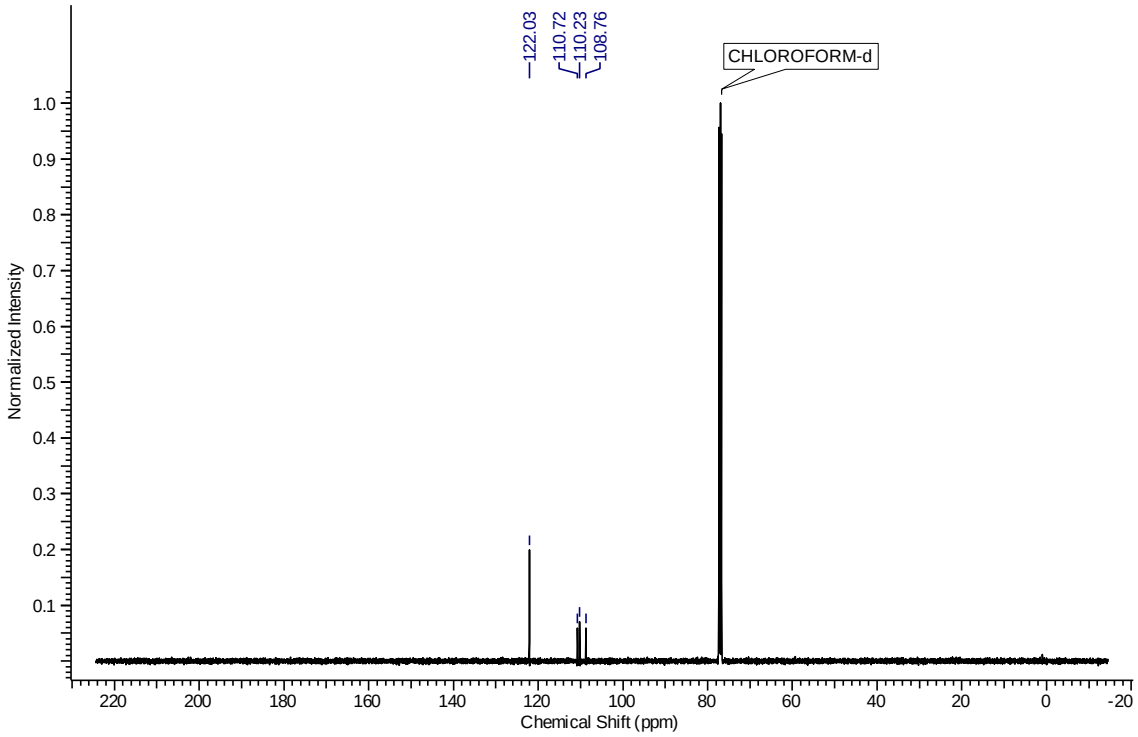




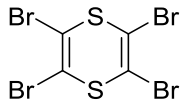
2,3,5-Tribromo-1,4-dithiine (**12**)

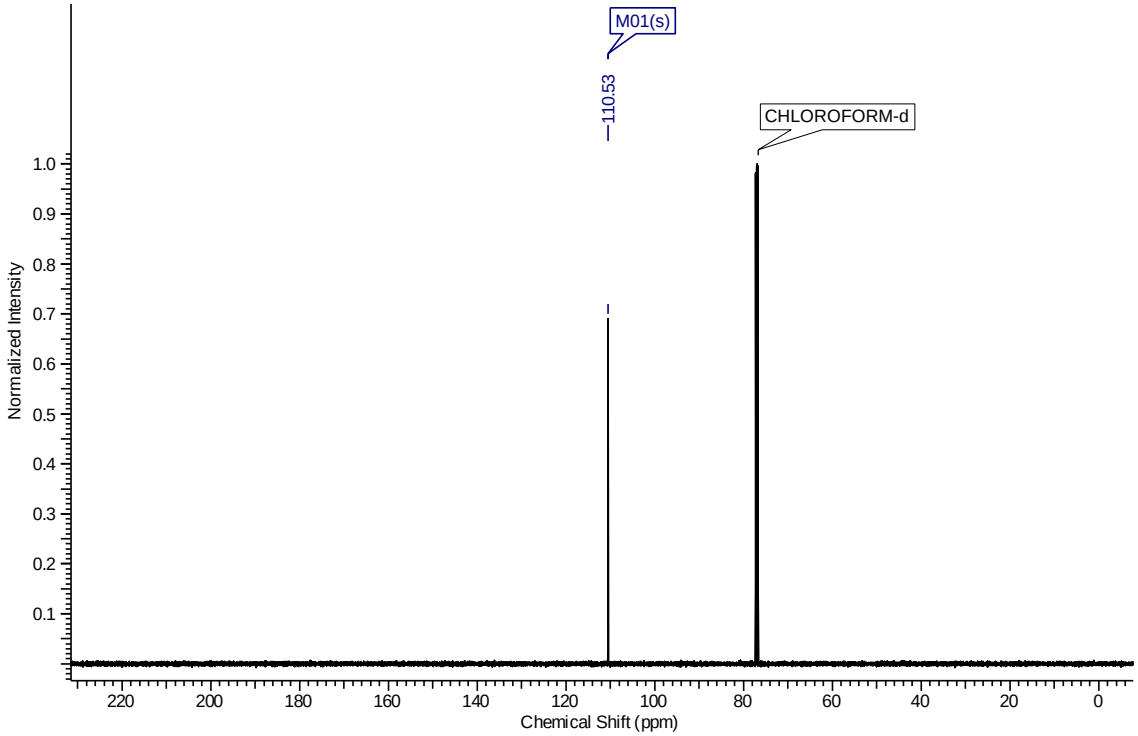




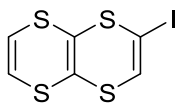


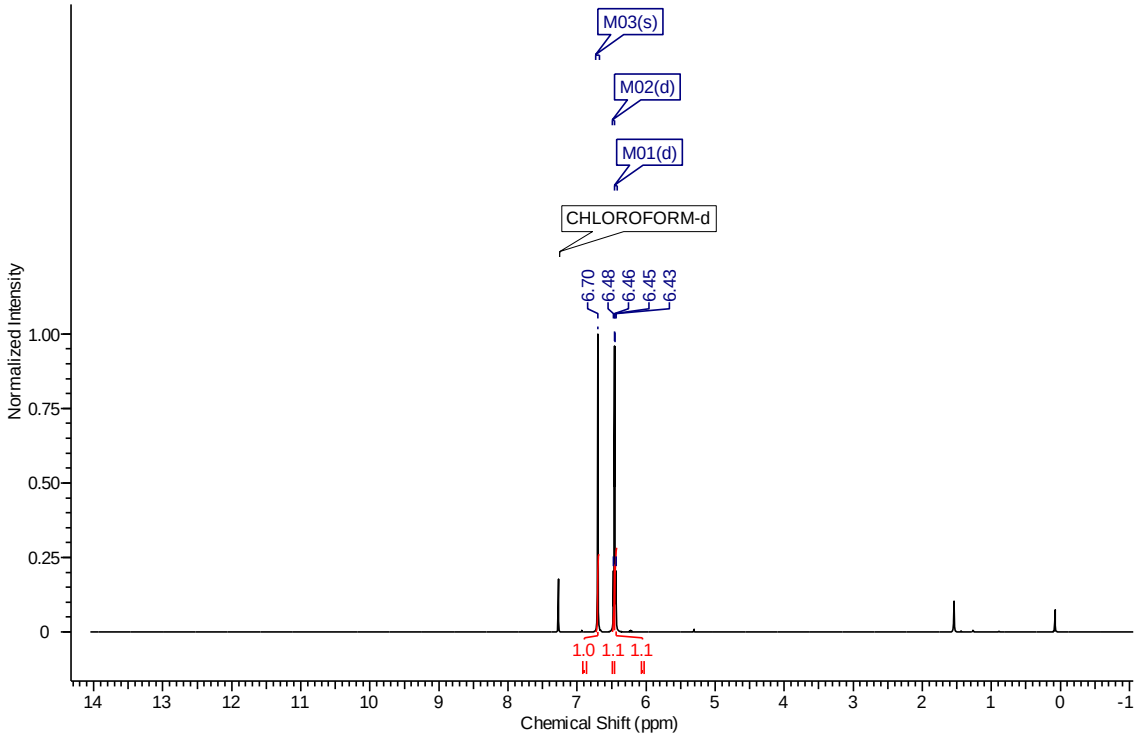
Perbromo-1,4-dithiine (**13**)

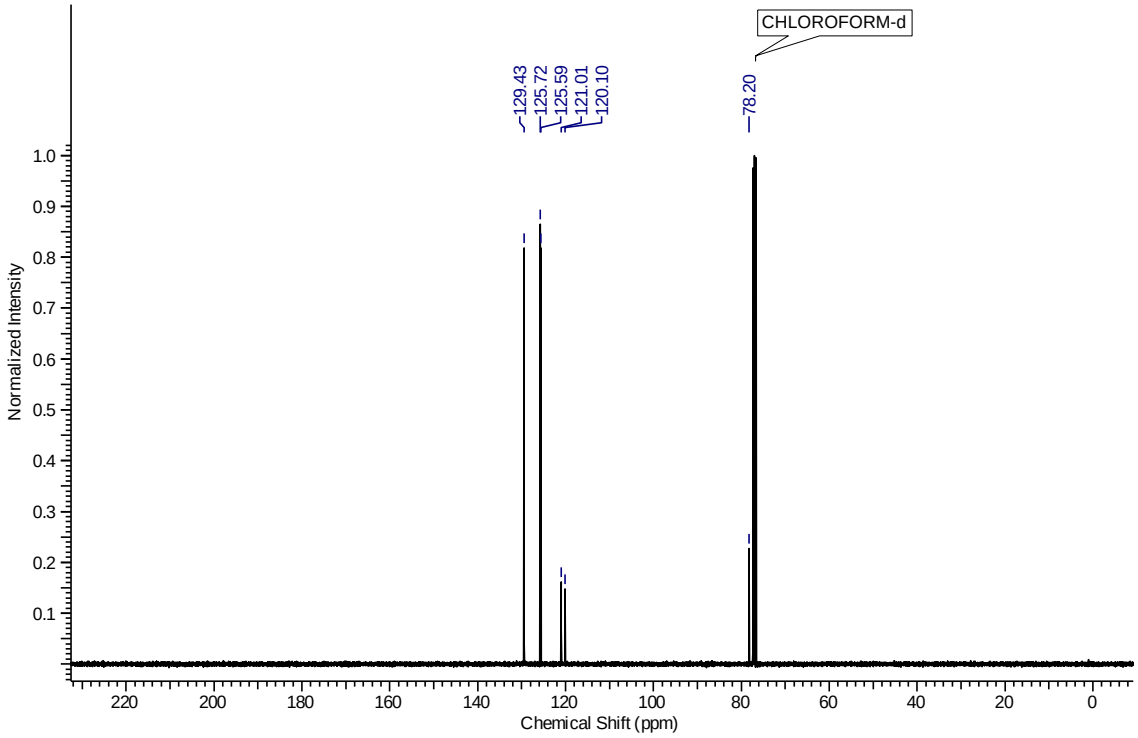




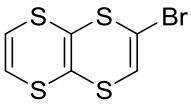
2-Iodo-[1,4]dithiino[2,3-b][1,4]dithiine (**14a**)

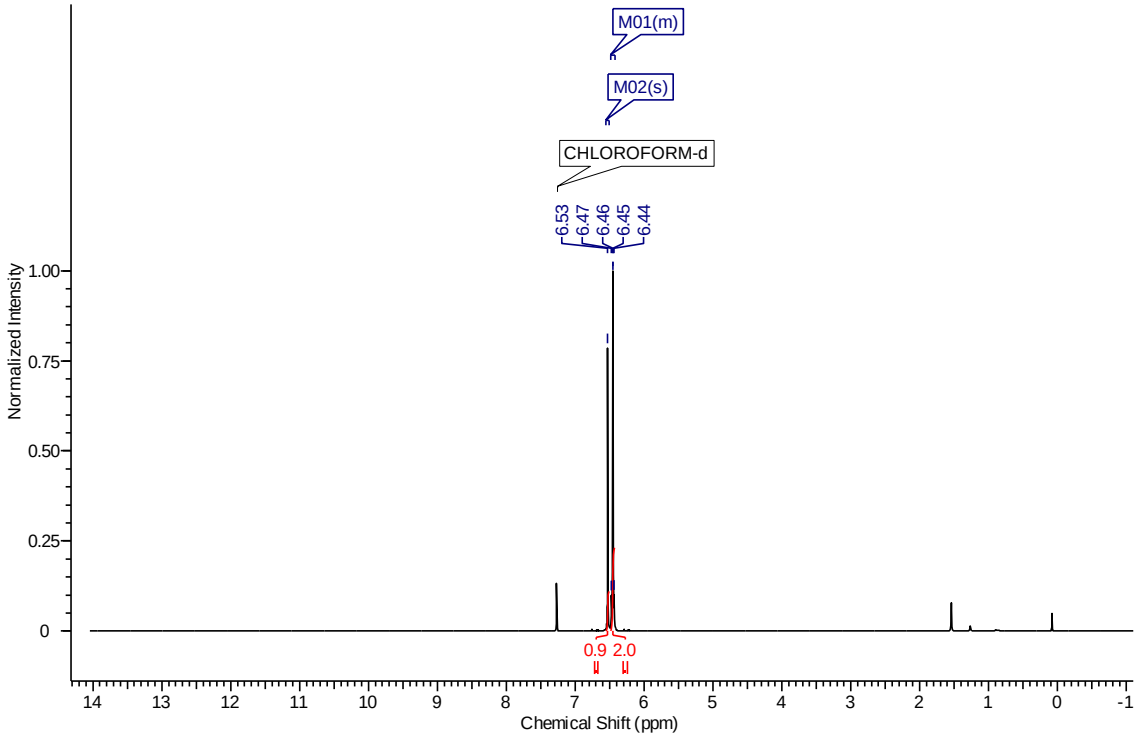


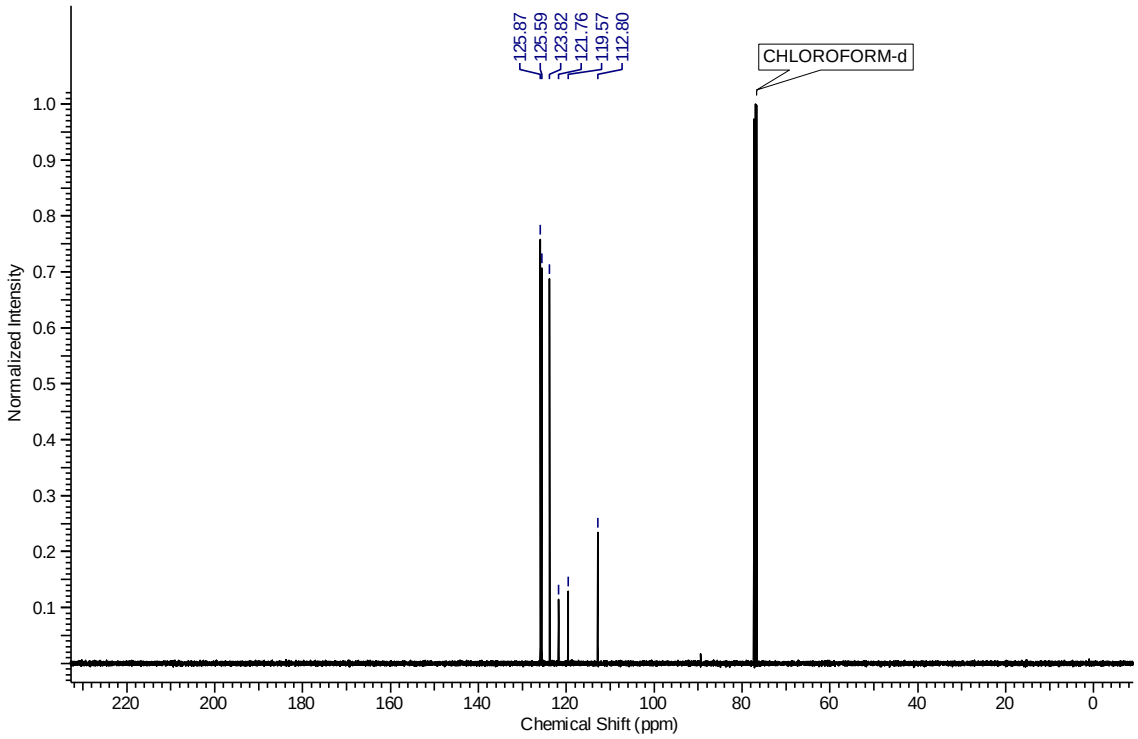




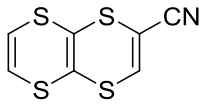
2-Bromo-[1,4]dithiino[2,3-b][1,4]dithiine (**14b**)

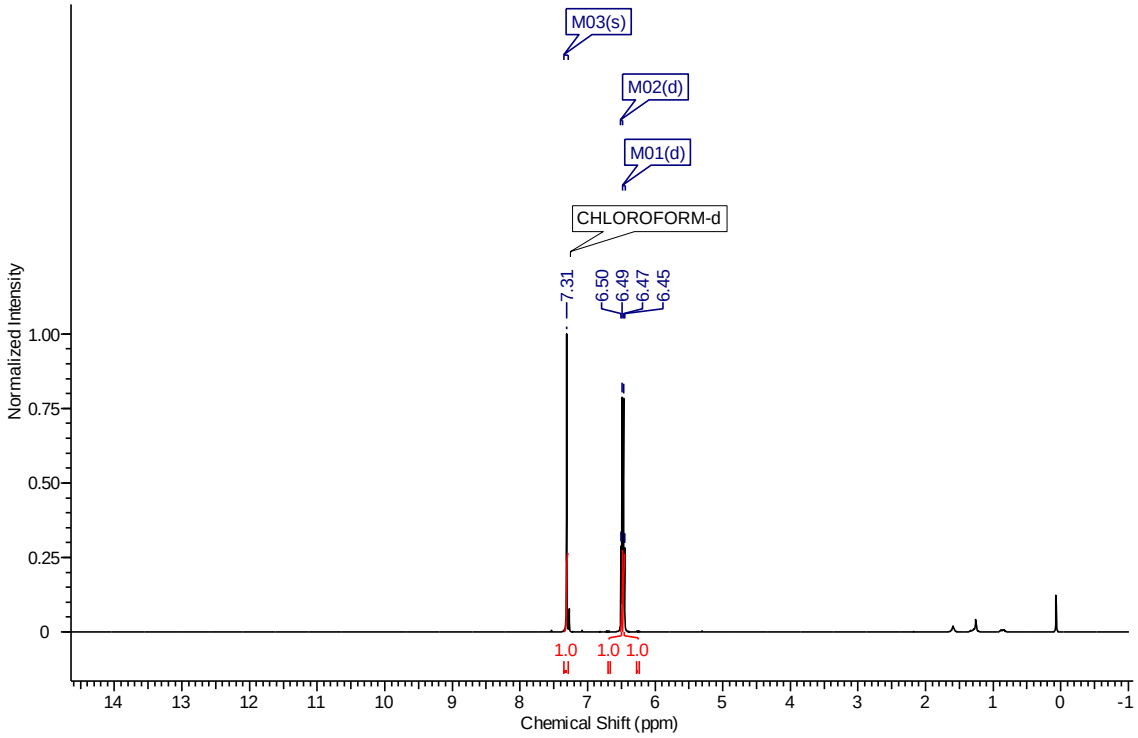


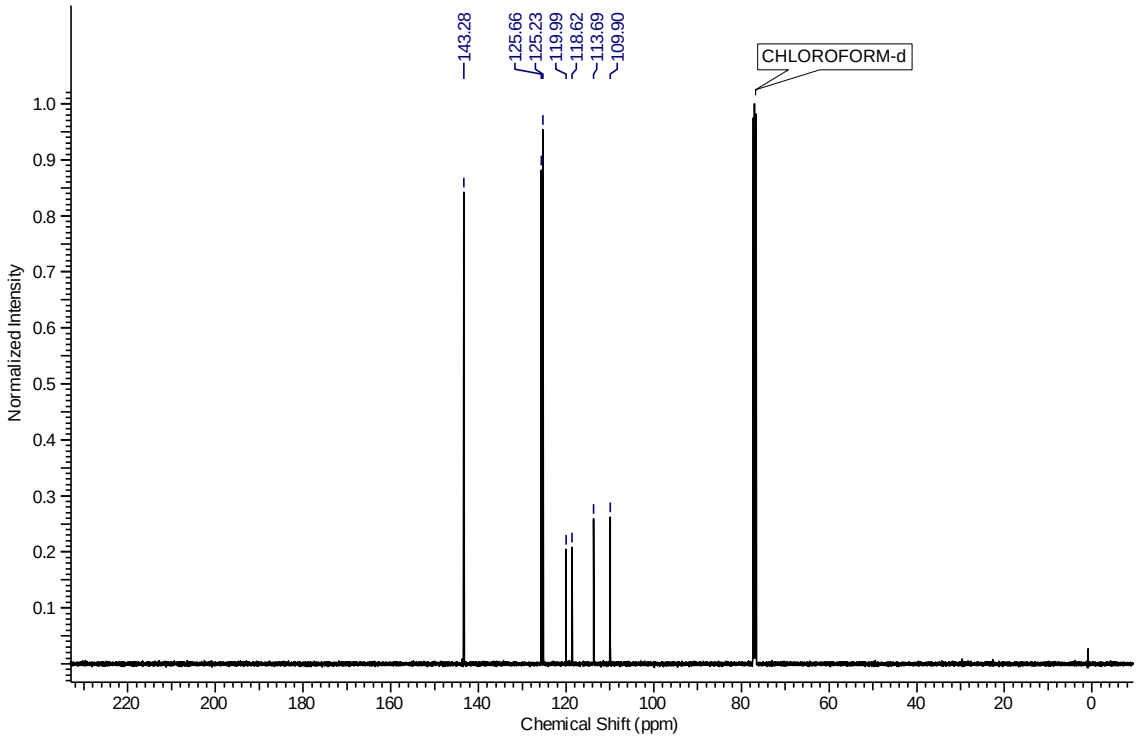




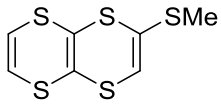
[1,4]Dithiino[2,3-b][1,4]dithiine-2-carbonitrile (**14c**)

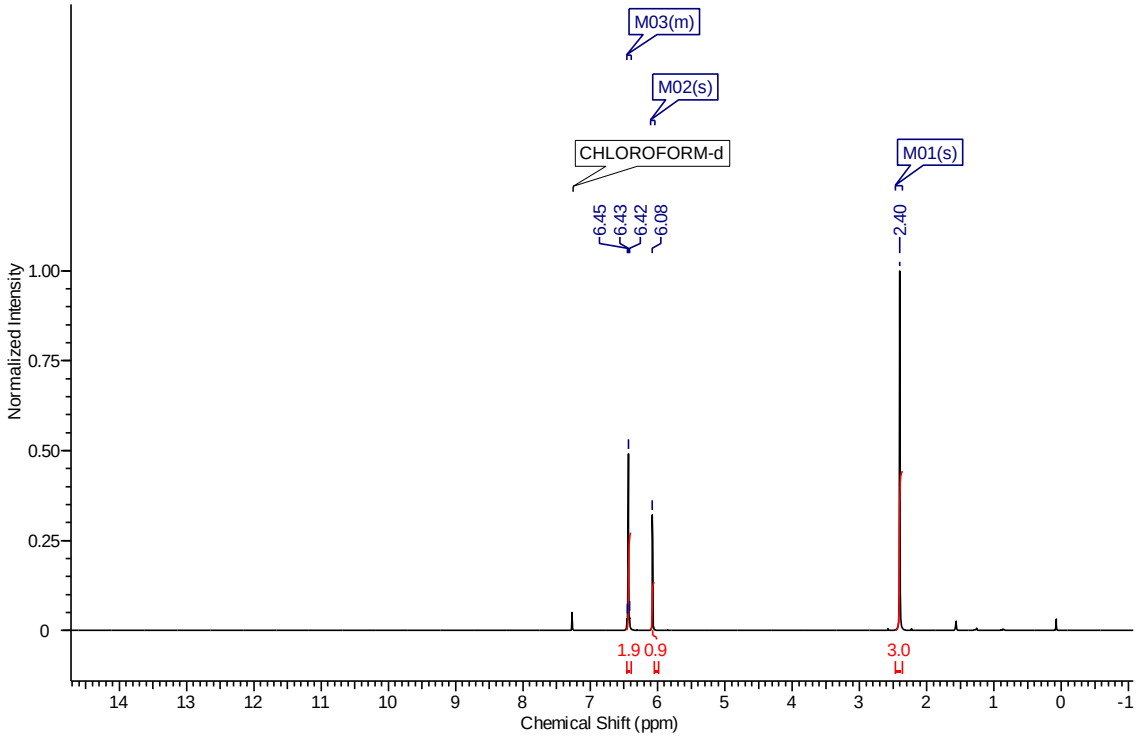


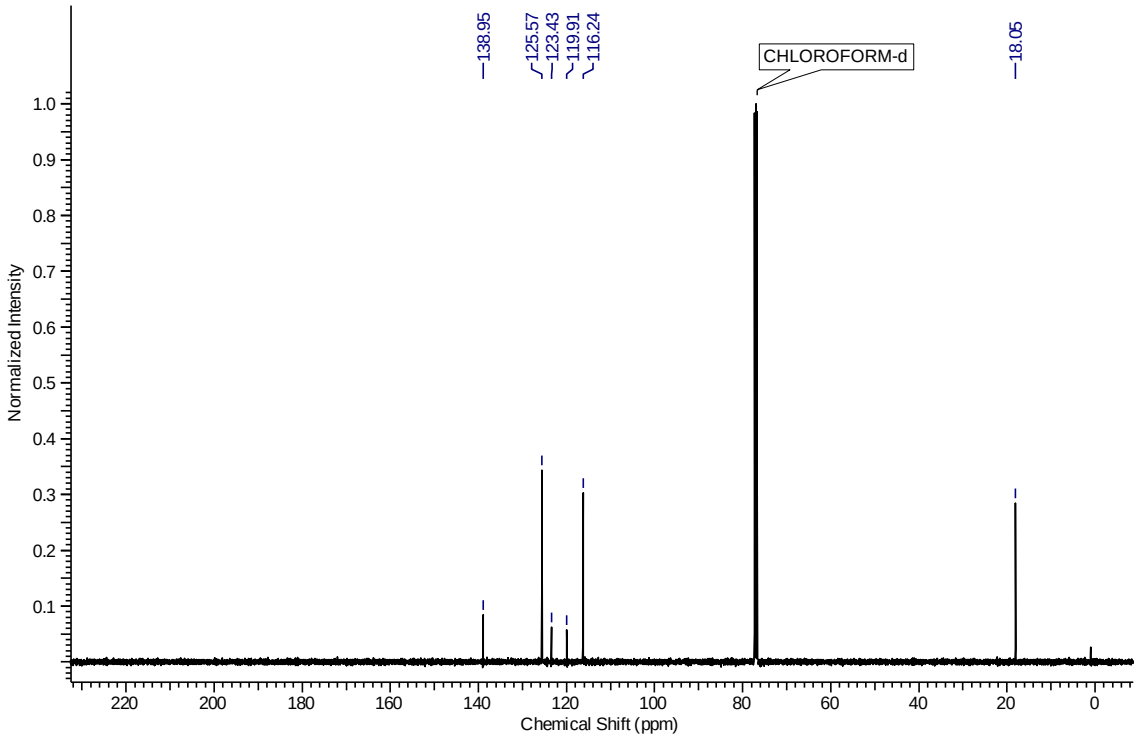




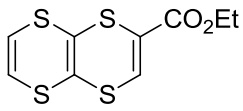
2-(Methylthio)-[1,4]dithiino[2,3-b][1,4]dithiine (**14d**)

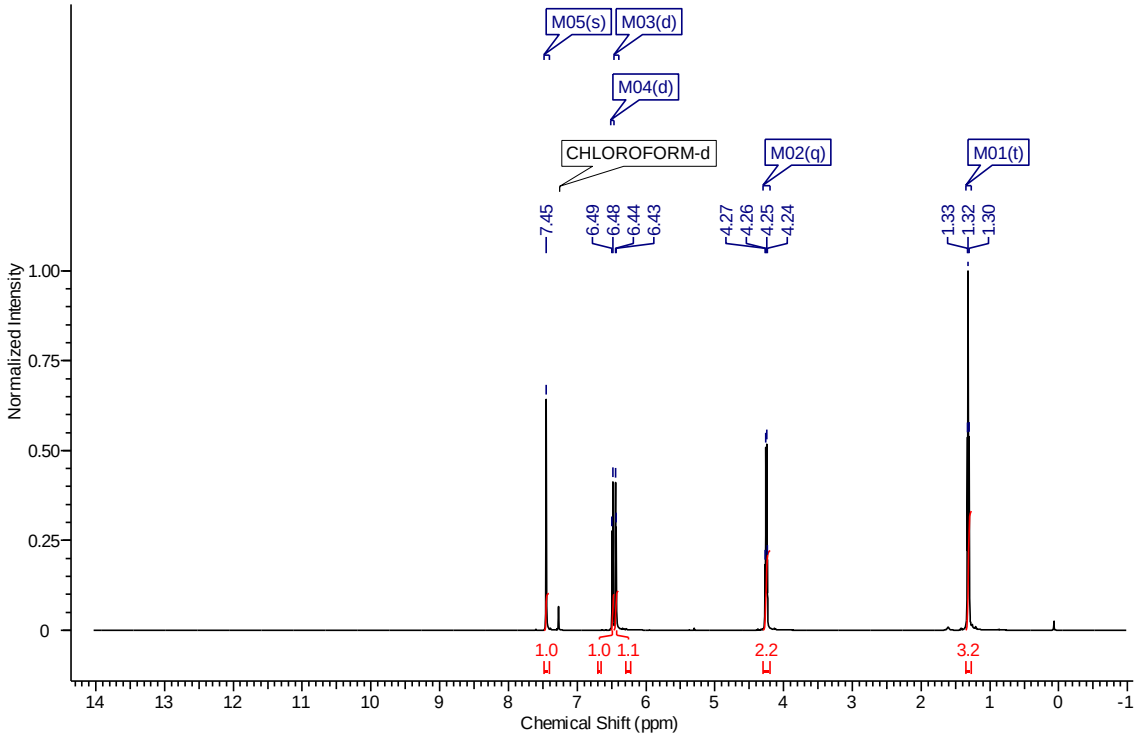


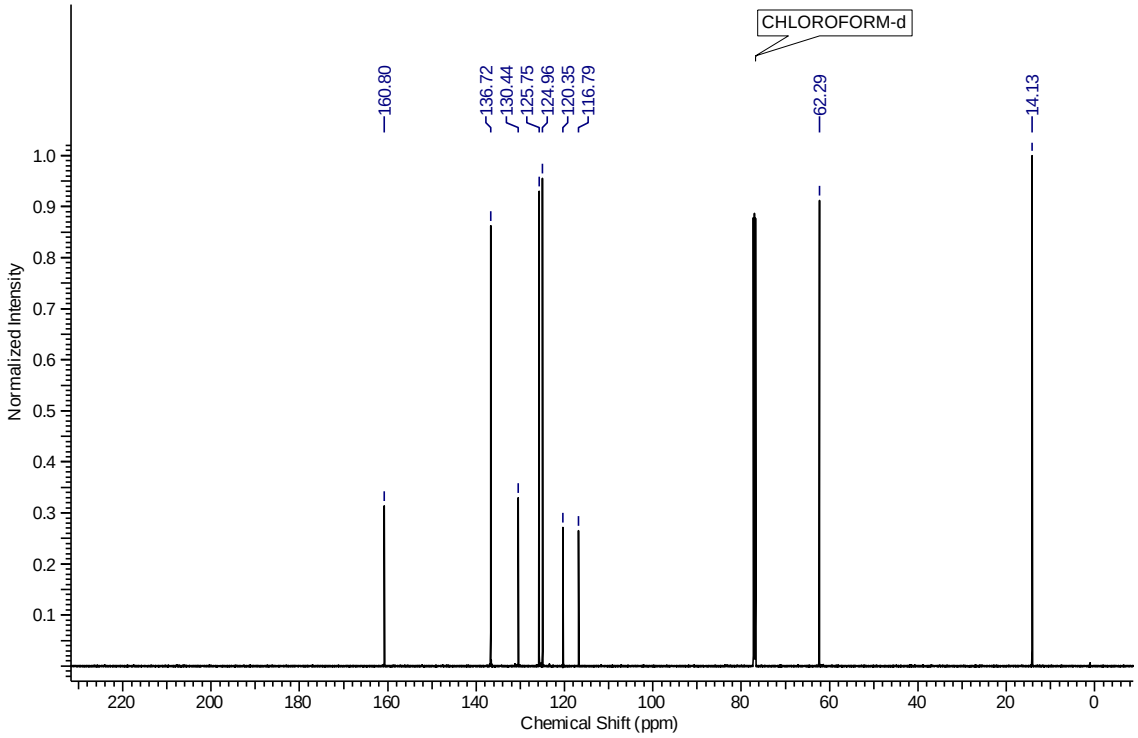




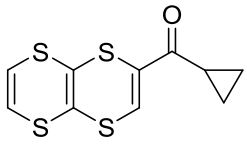
Ethyl [1,4]dithiino[2,3-b][1,4]dithiine-2-carboxylate (**14e**)

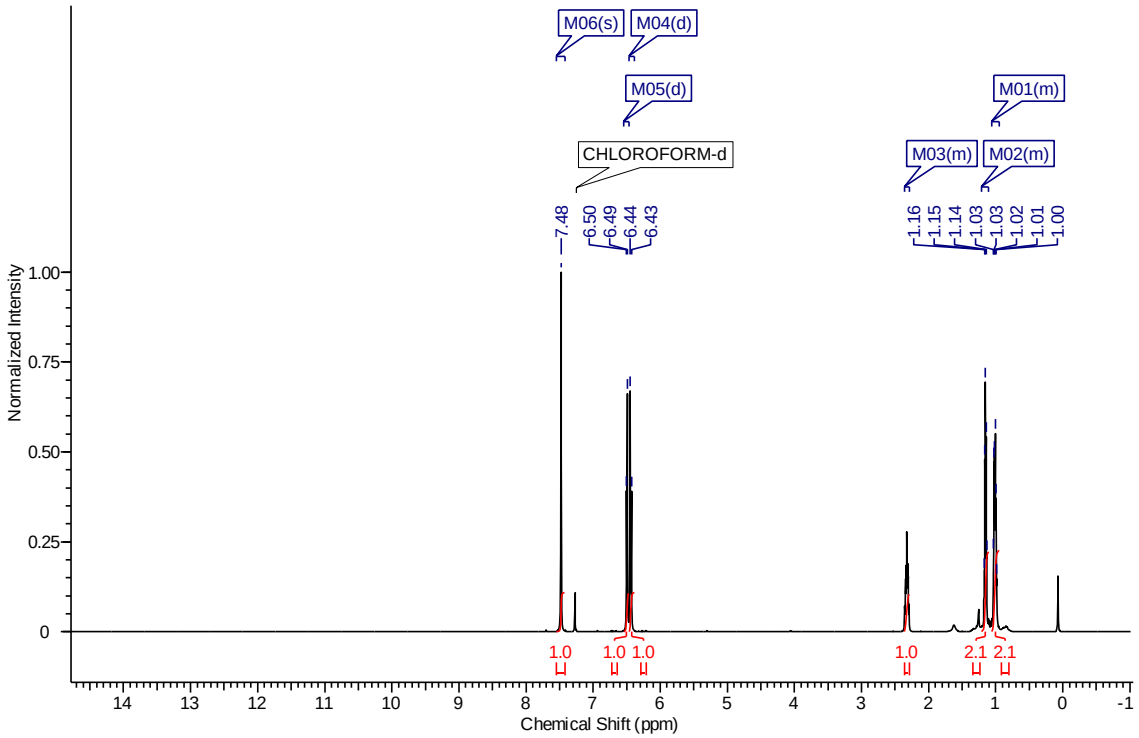


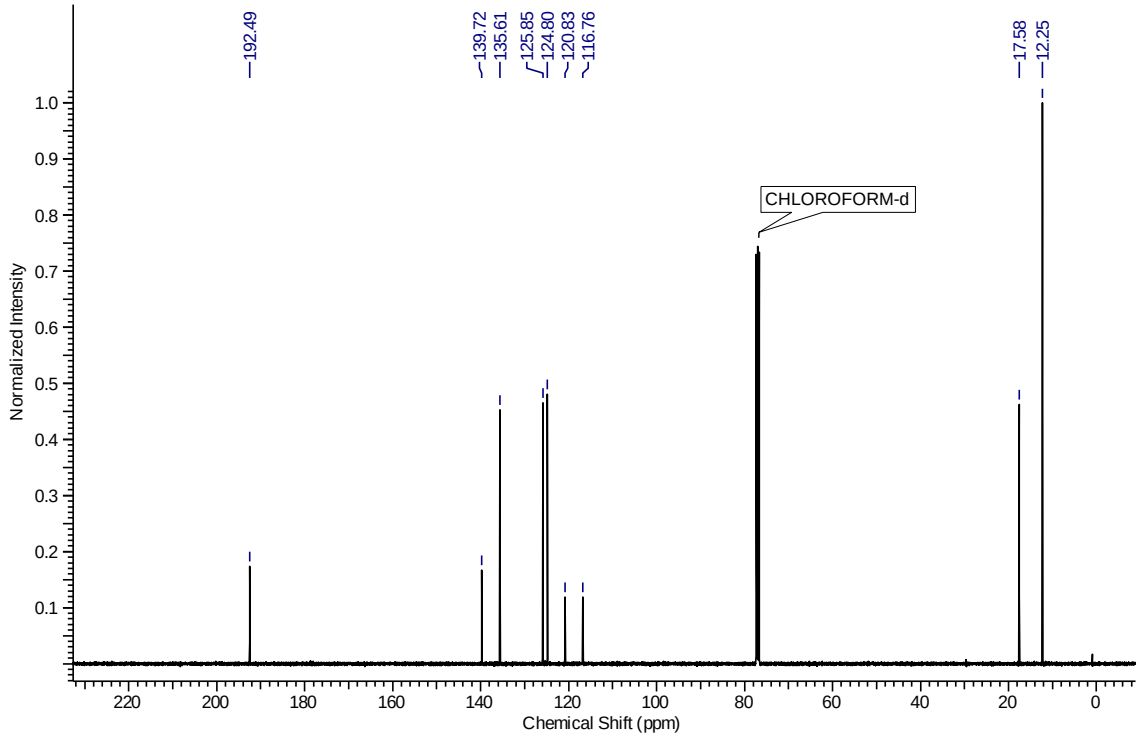




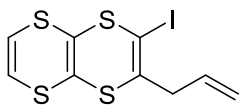
[1,4]Dithiino[2,3-b][1,4]dithiin-2-yl(cyclopropyl)methanone (**14f**)

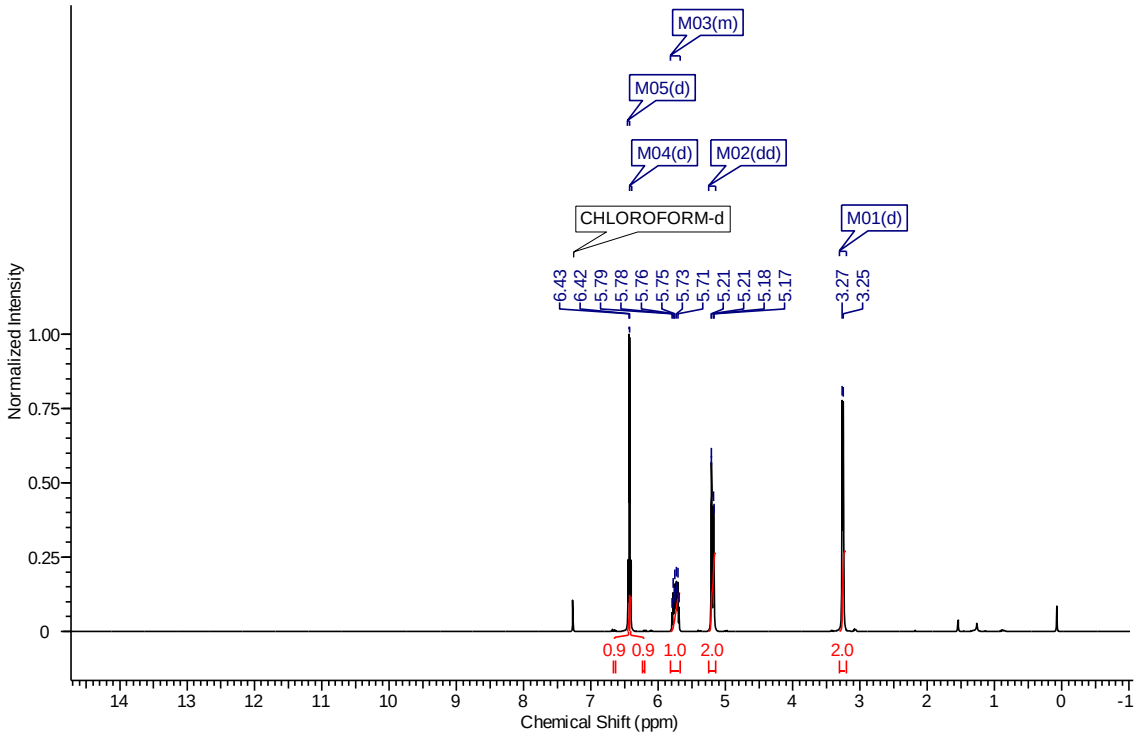


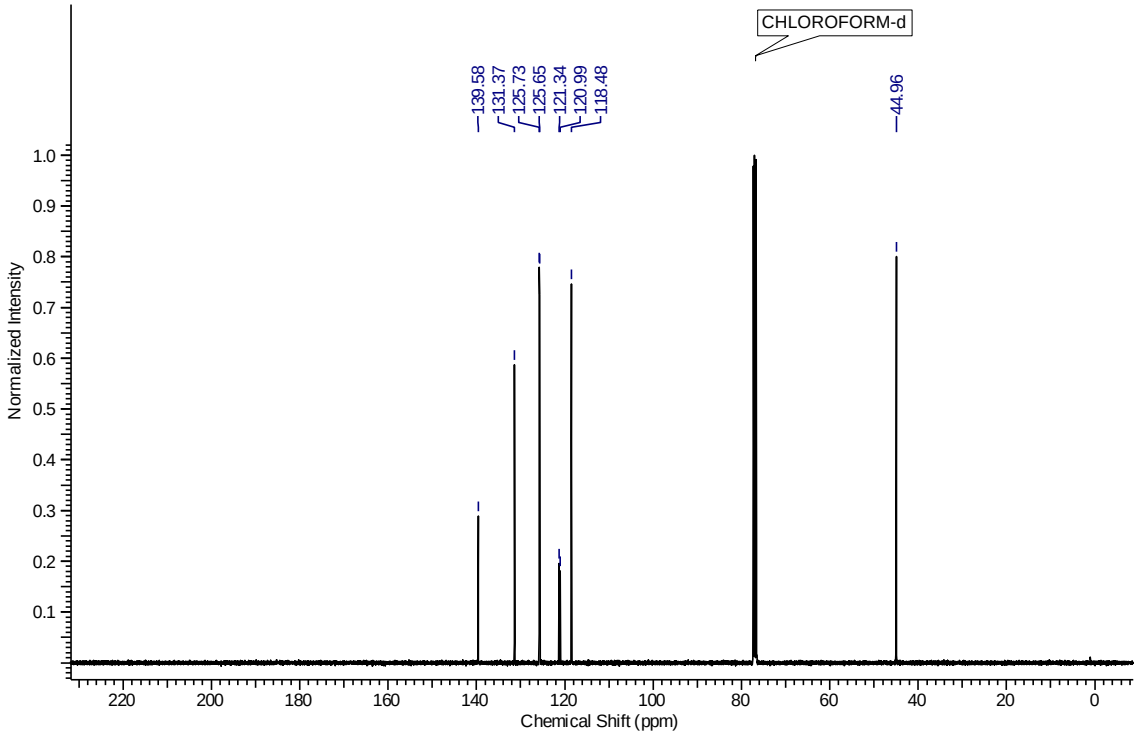




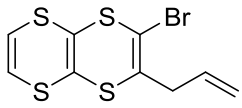
2-Iodo-3-allyl-[1,4]dithiino[2,3-b][1,4]dithiine (**15a**)

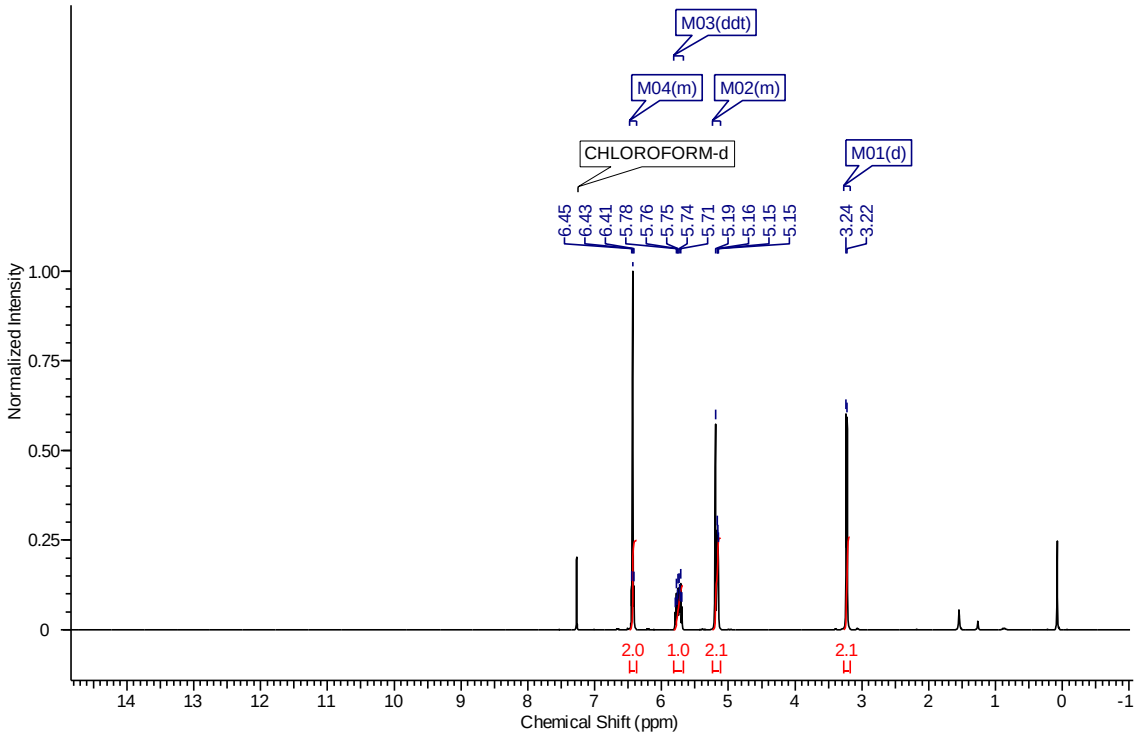


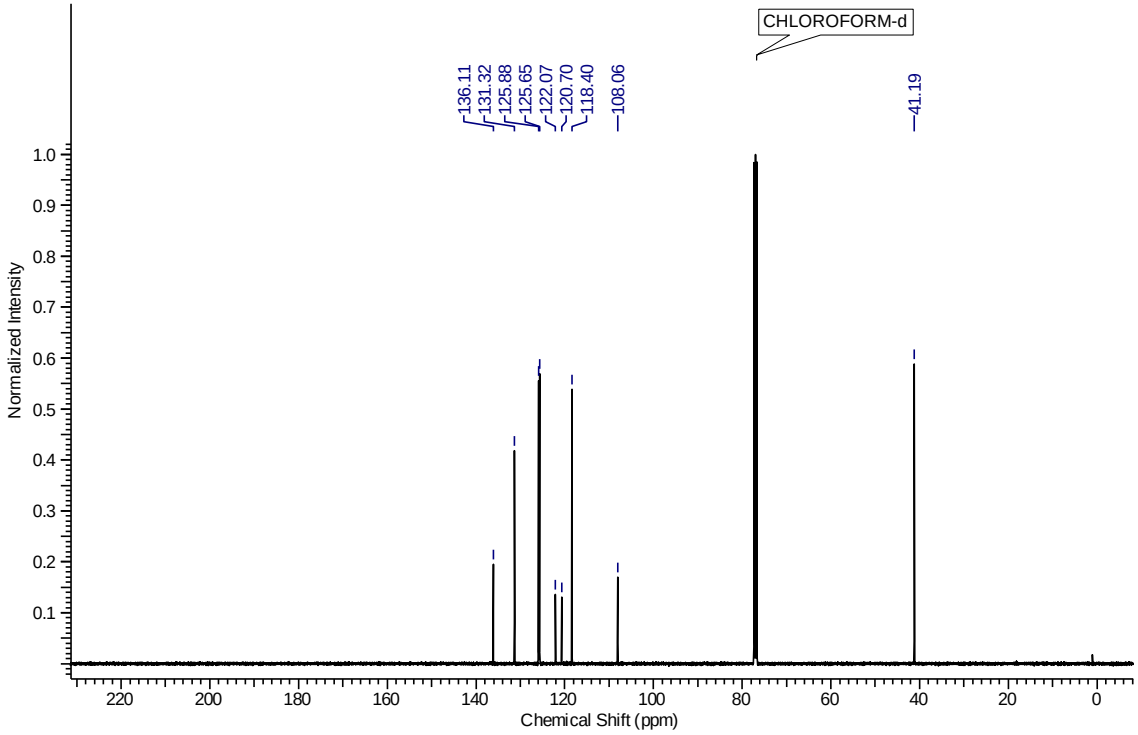




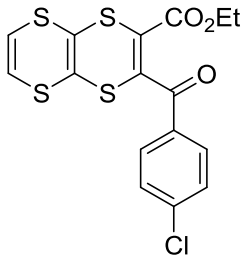
2-Bromo-3-allyl-[1,4]dithiino[2,3-b][1,4]dithiine (**15b**)

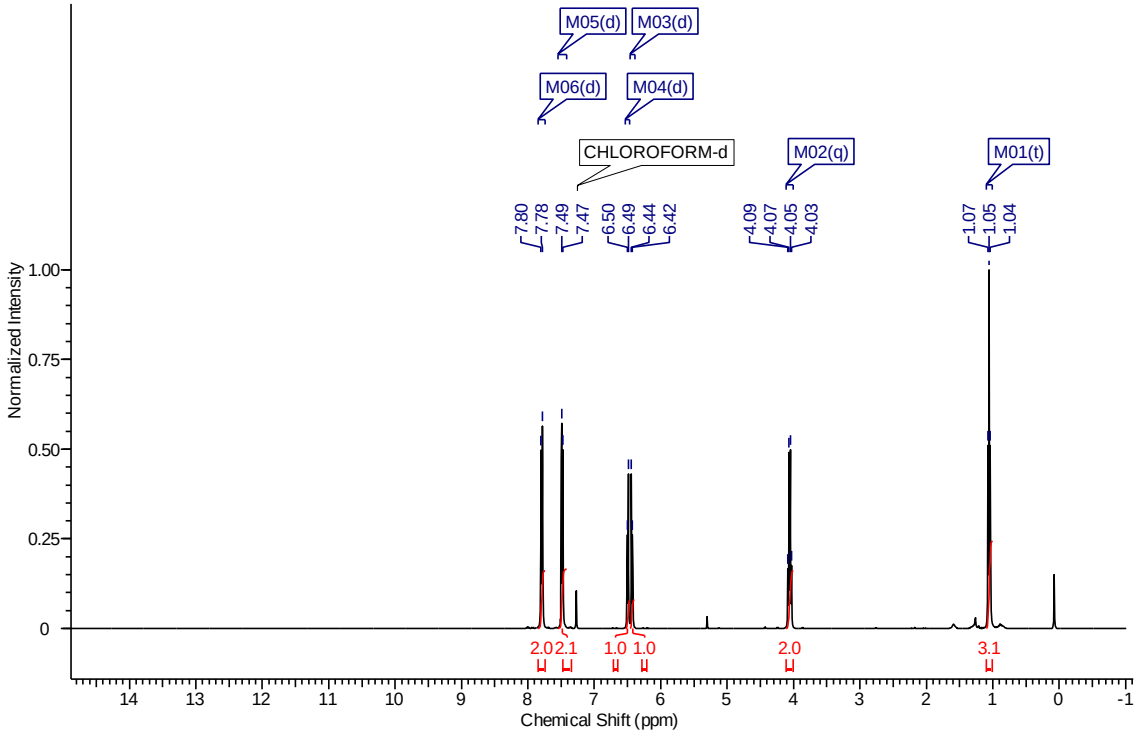


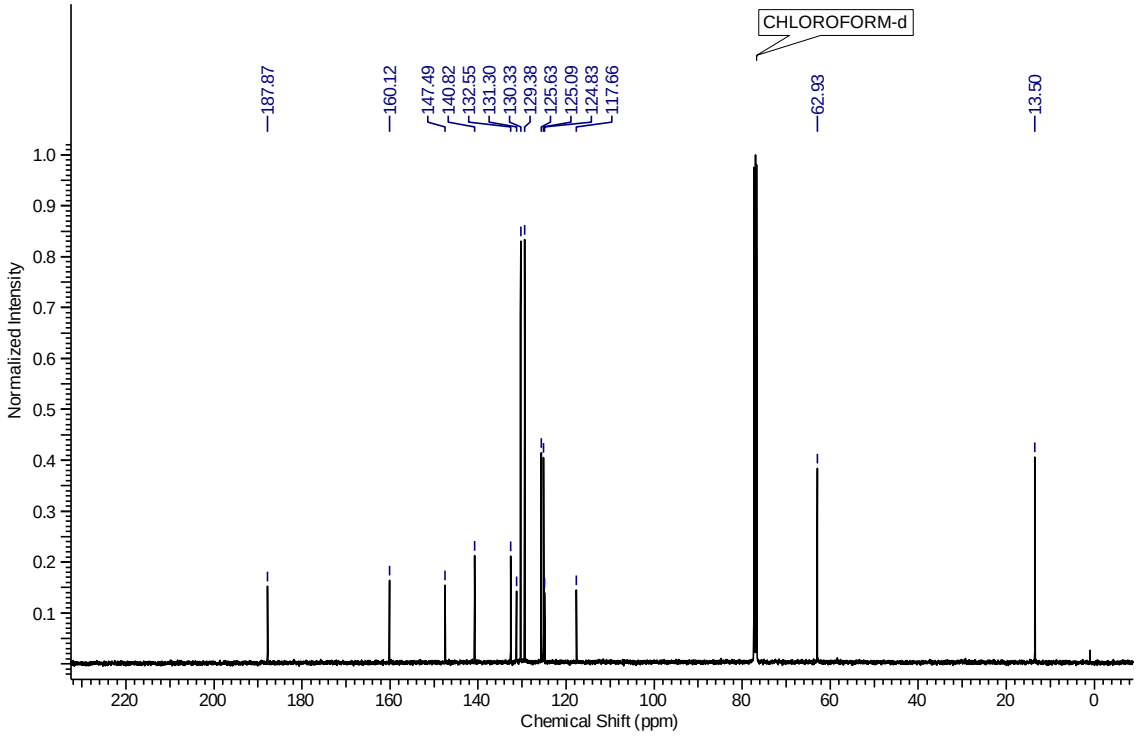




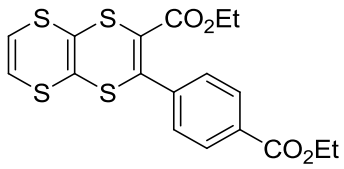
Ethyl 3-(4-chlorobenzoyl)-[1,4]dithiino[2,3-b][1,4]dithiine-2-carboxylate (**15c**)

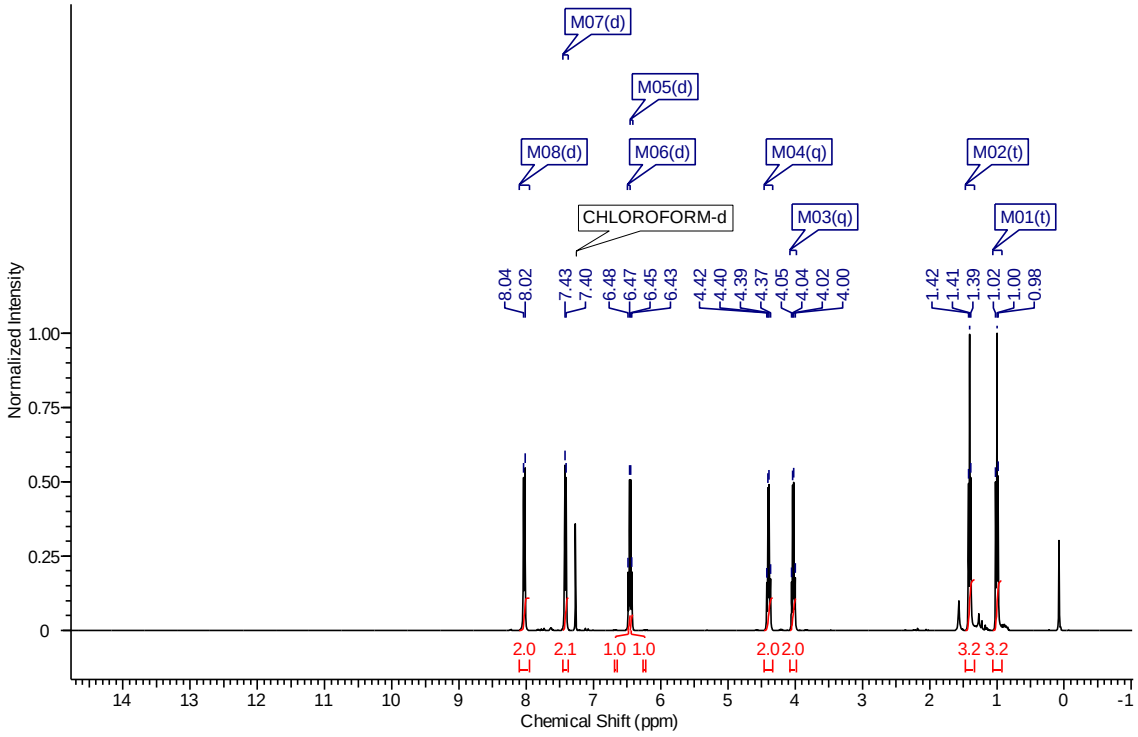


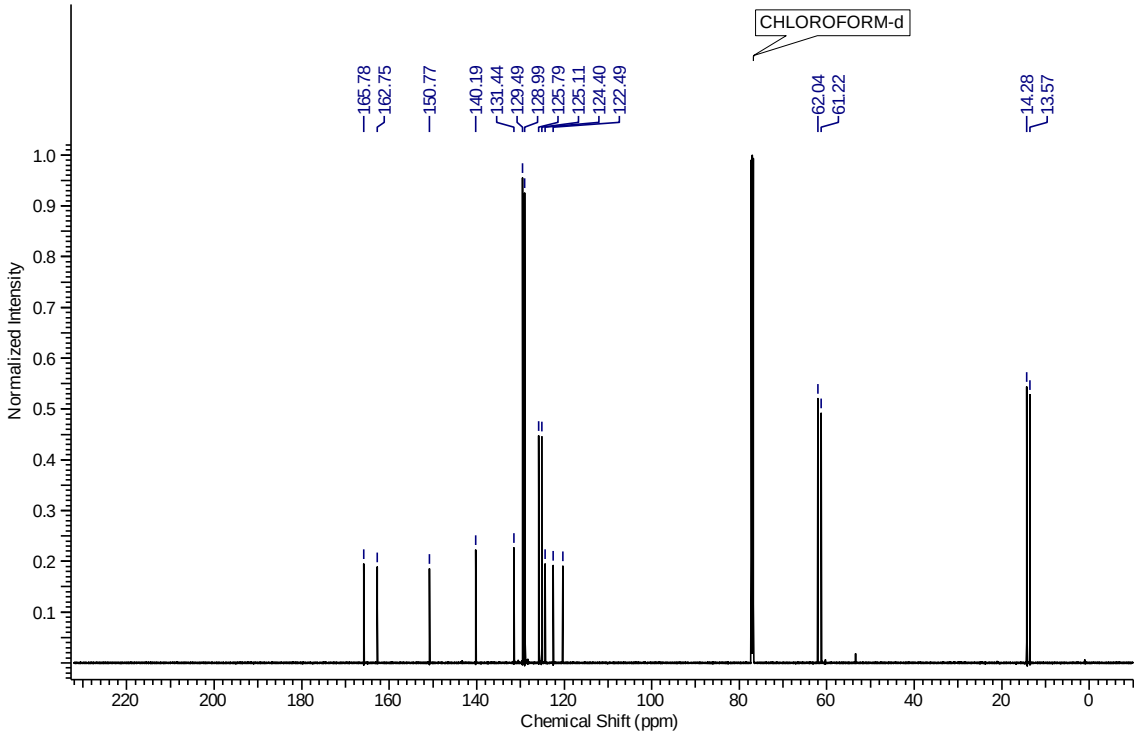




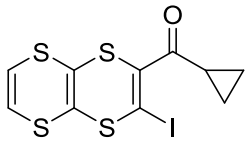
Ethyl 3-(4-(ethoxycarbonyl)phenyl)-[1,4]dithiino[2,3-b][1,4]dithiine-2-carboxylate (**15d**)

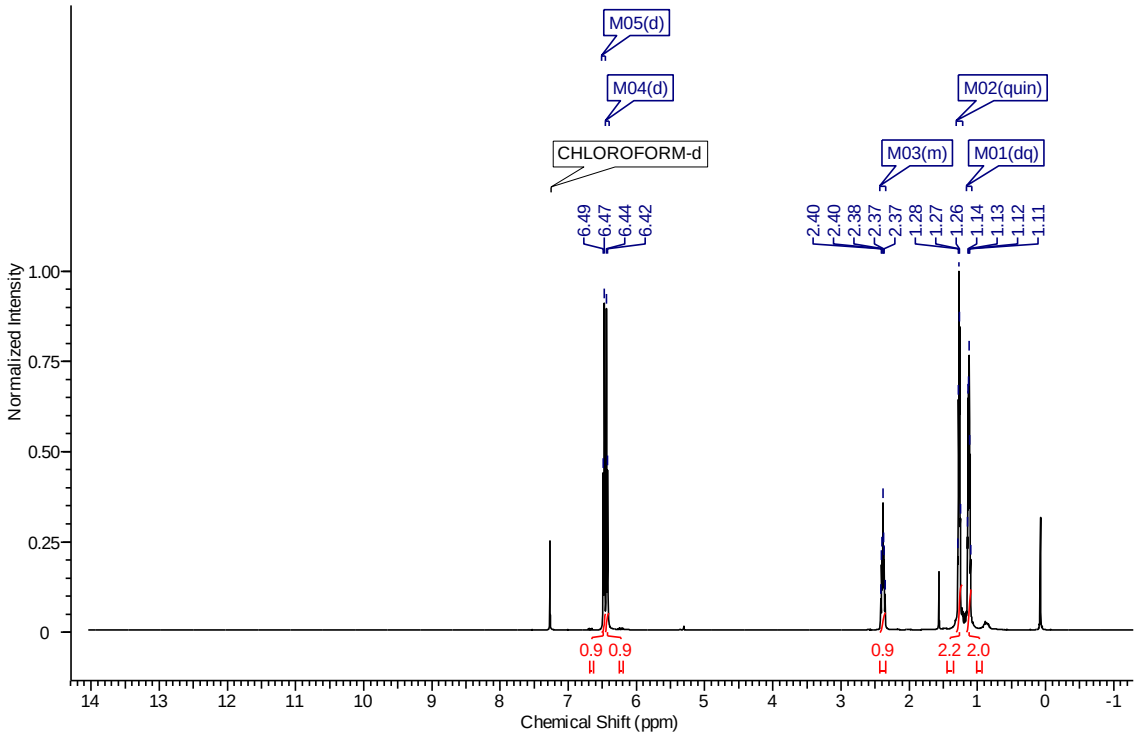


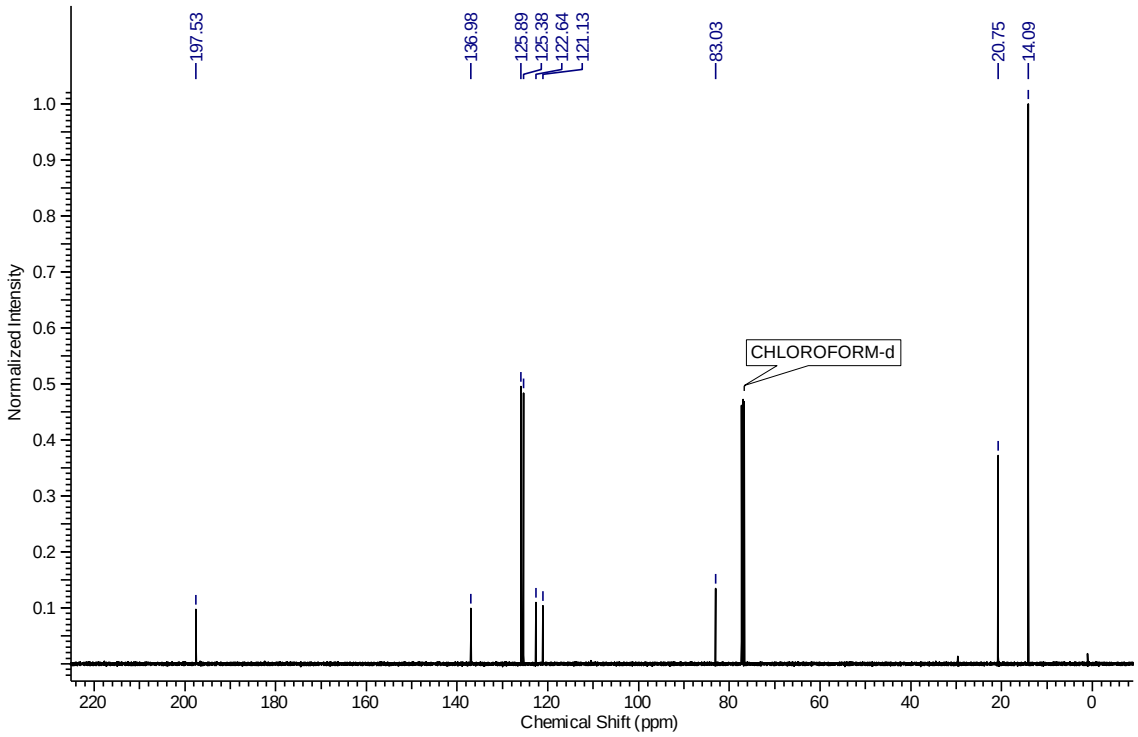




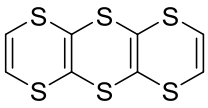
Cyclopropyl(3-iodo-[1,4]dithiino[2,3-b][1,4]dithiin-2-yl)methanone (**15e**)

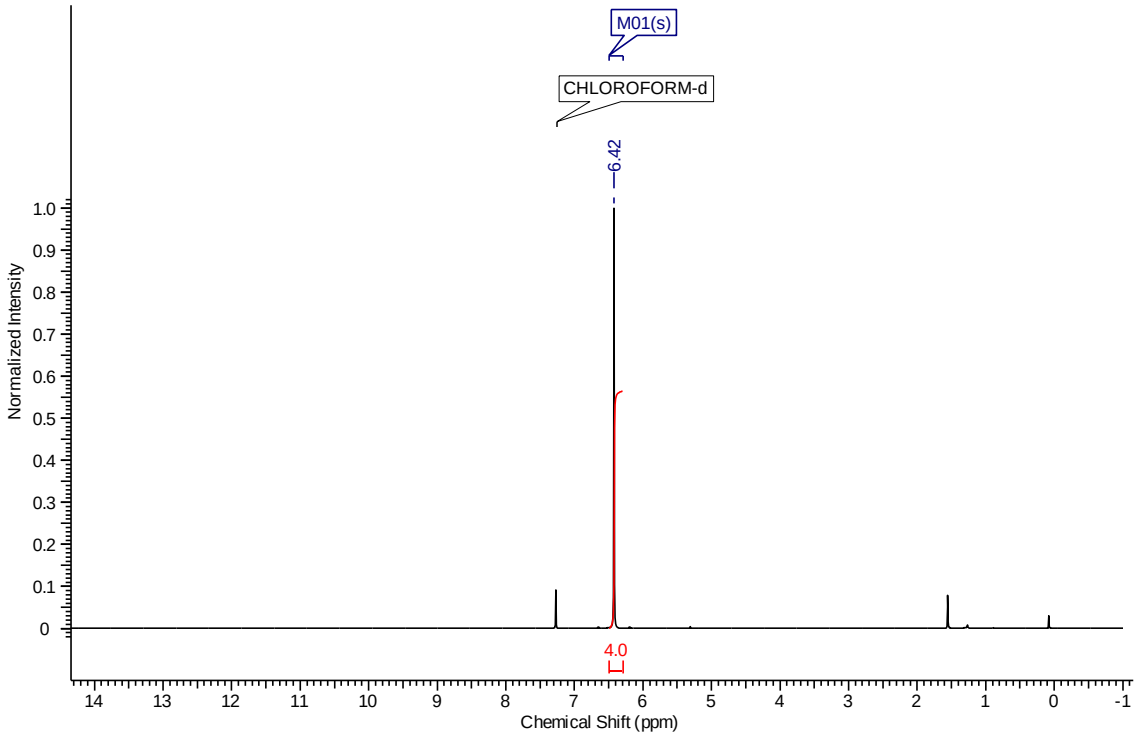


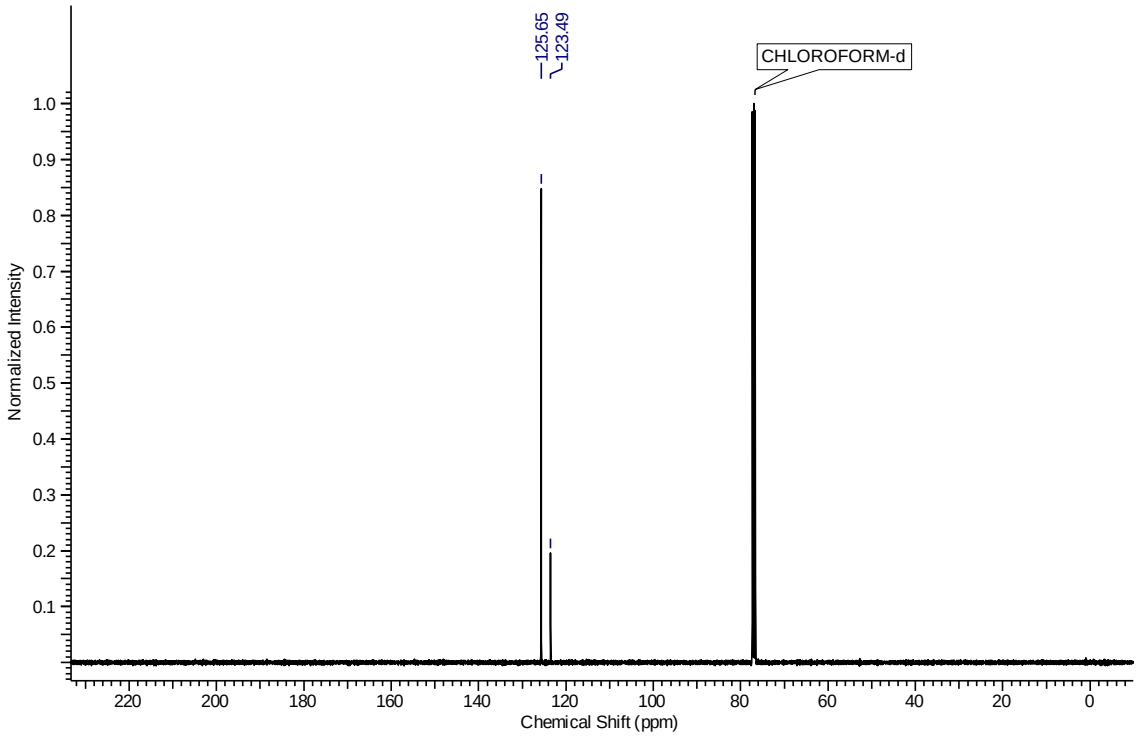




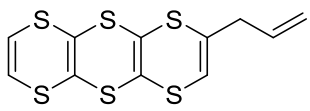
1,4,5,6,9,10-Hexathiaanthracene (**5**)

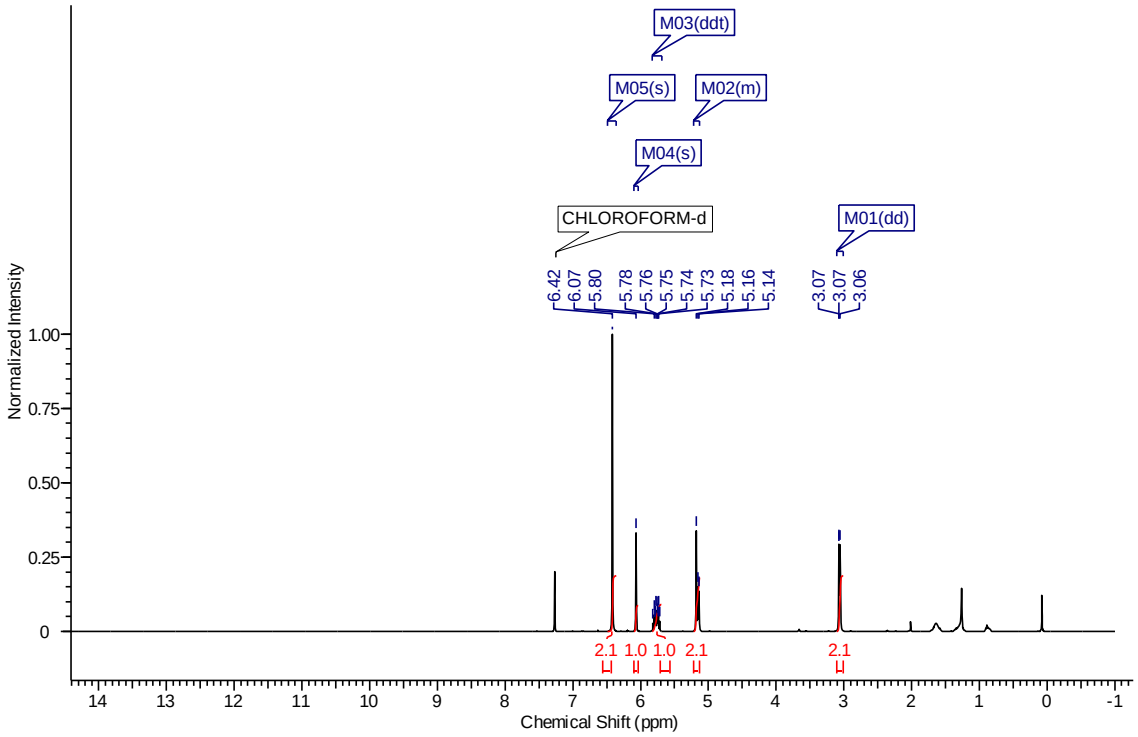


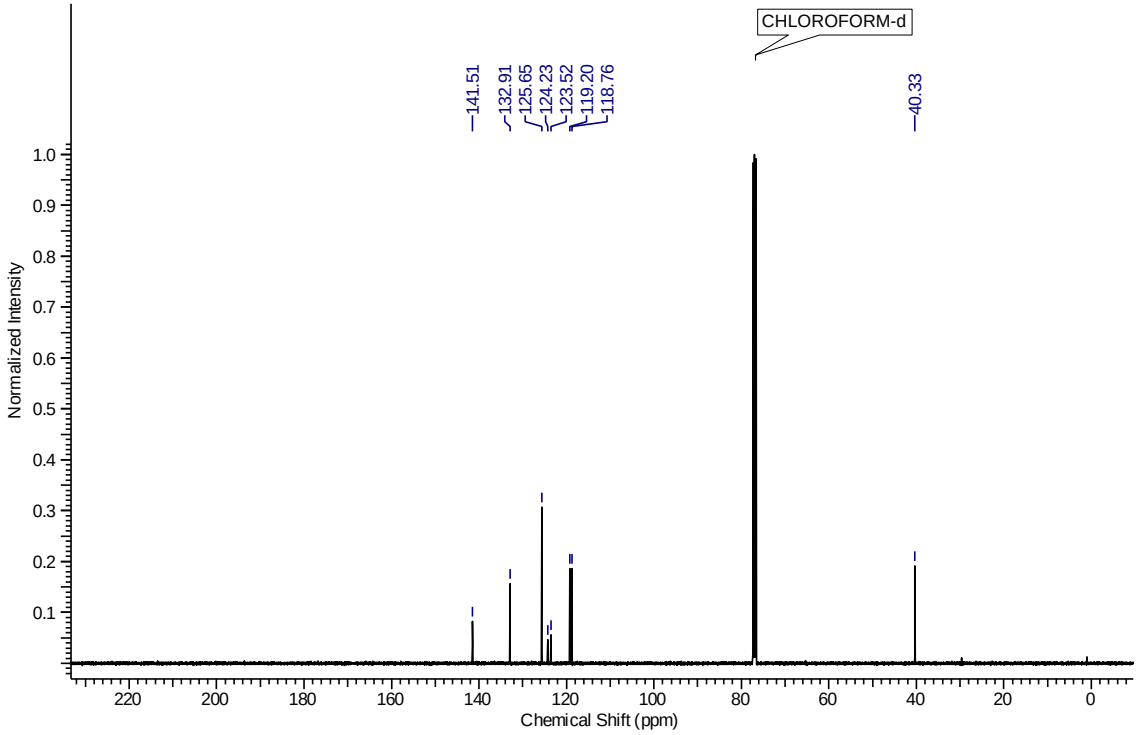




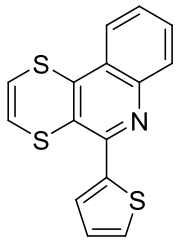
2-Allyl-1,4,5,6,9,10-hexathiaanthracene (**16**)

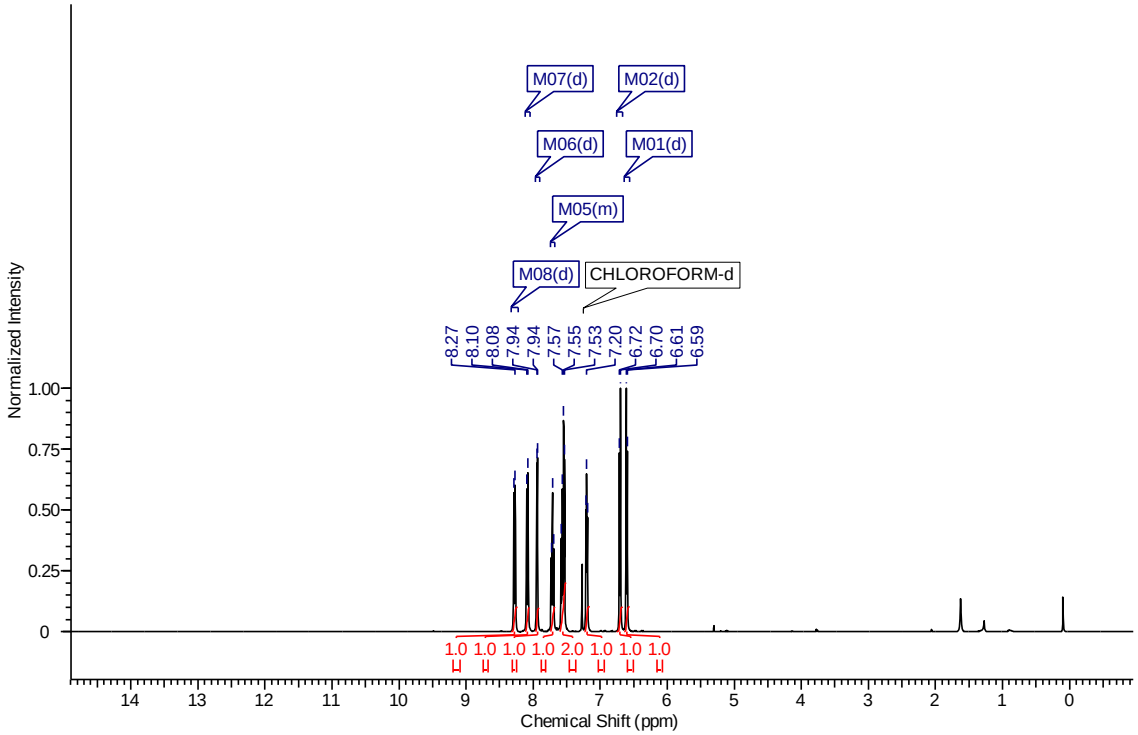


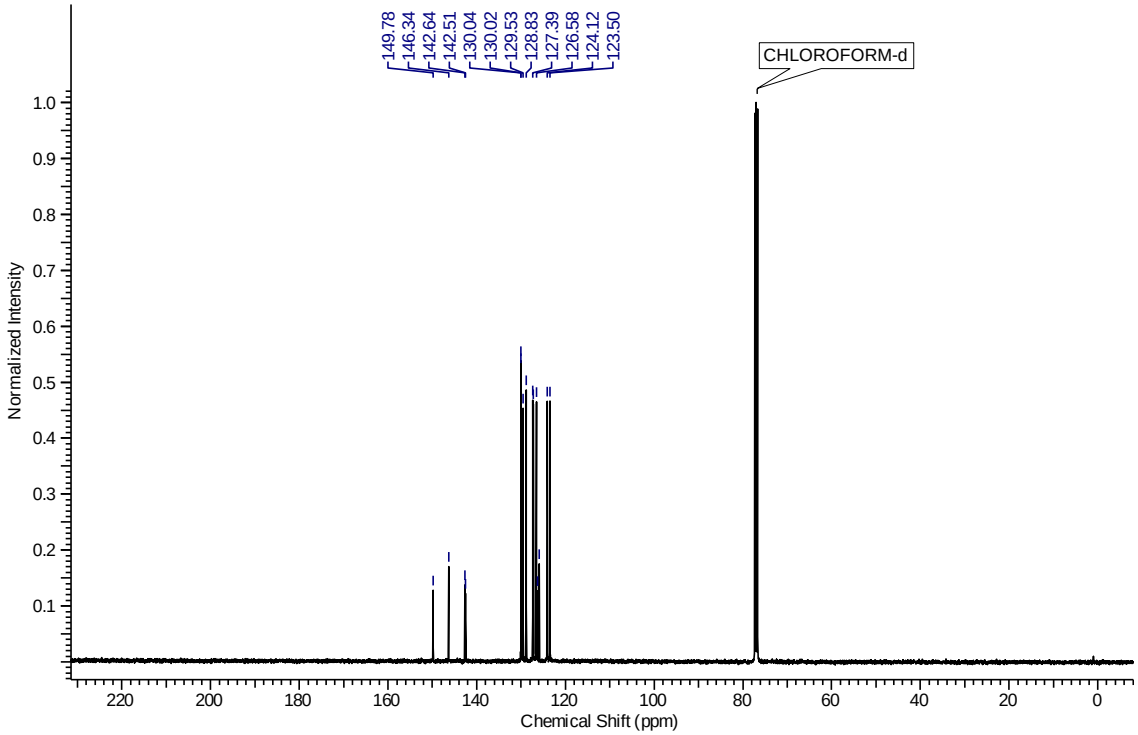




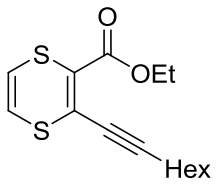
5-(Thiophen-2-yl)-[1,4]dithiino[2,3-*c*]quinoline (**17**)

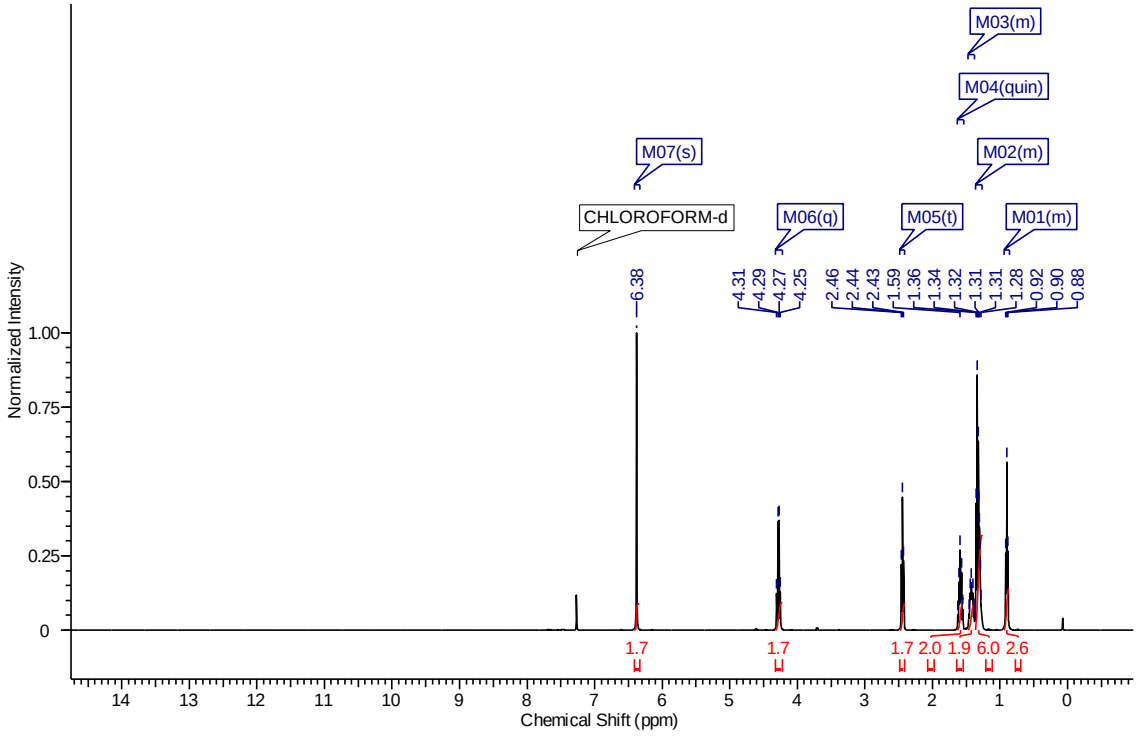


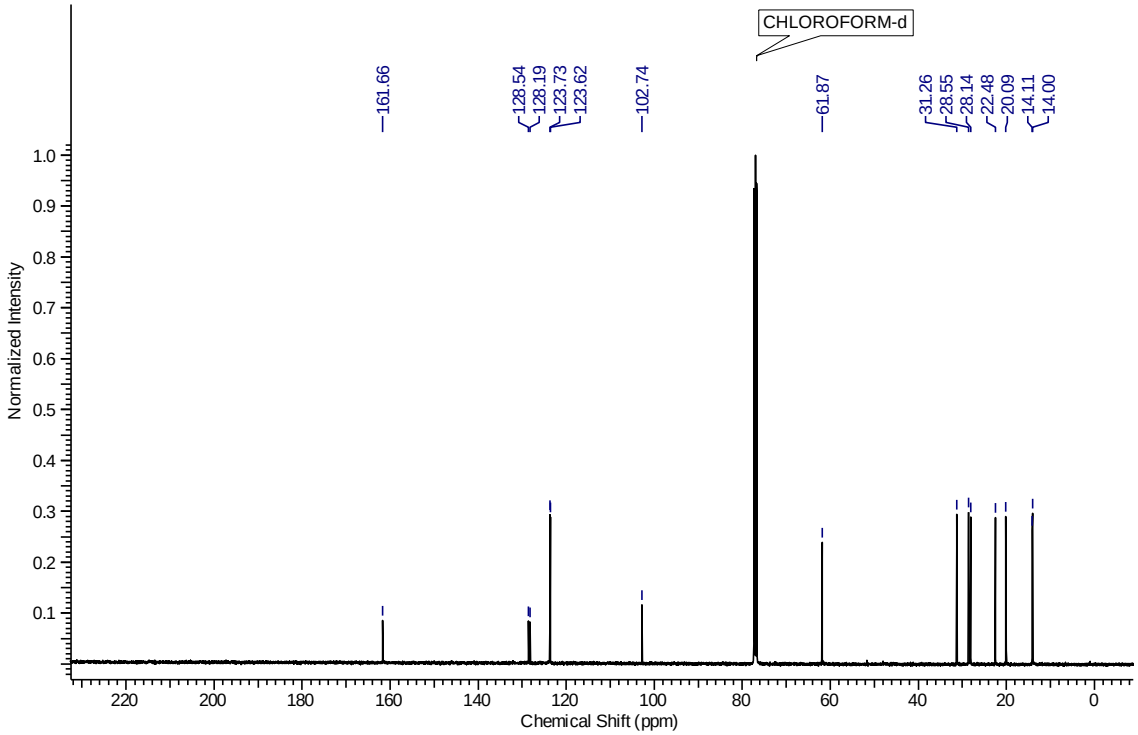




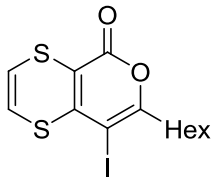
Ethyl 3-(3-oxooct-1-yn-1-yl)-1,4-dithiine-2-carboxylate (**18**)

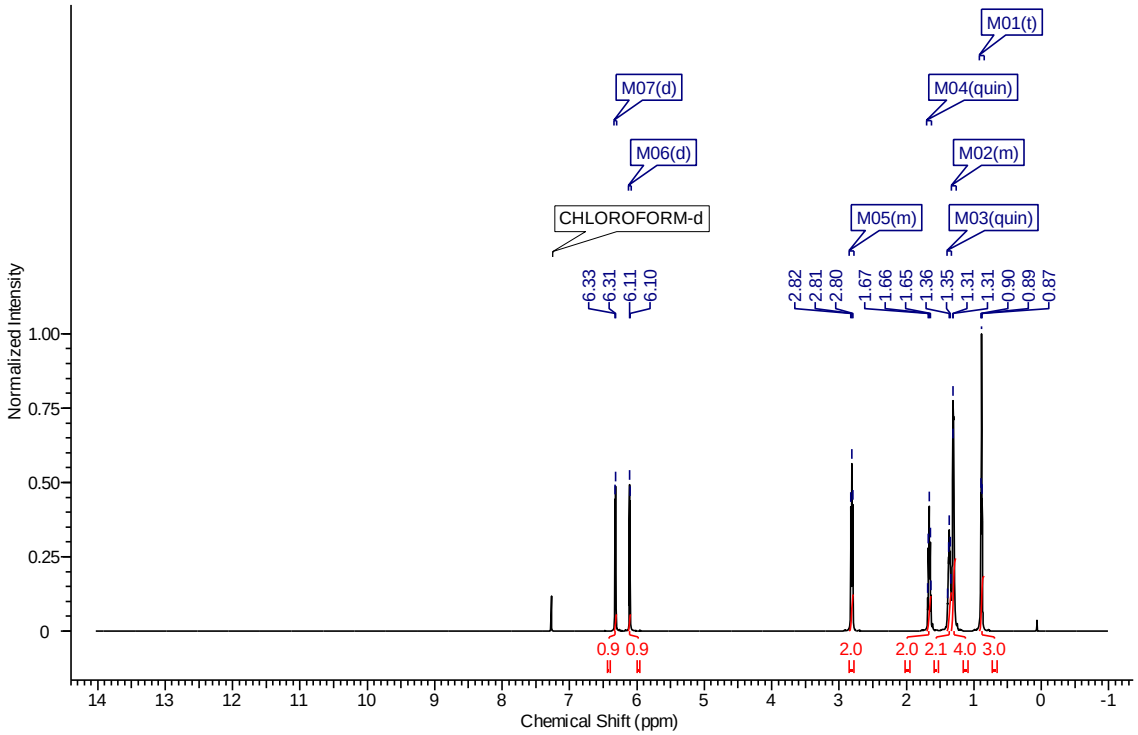


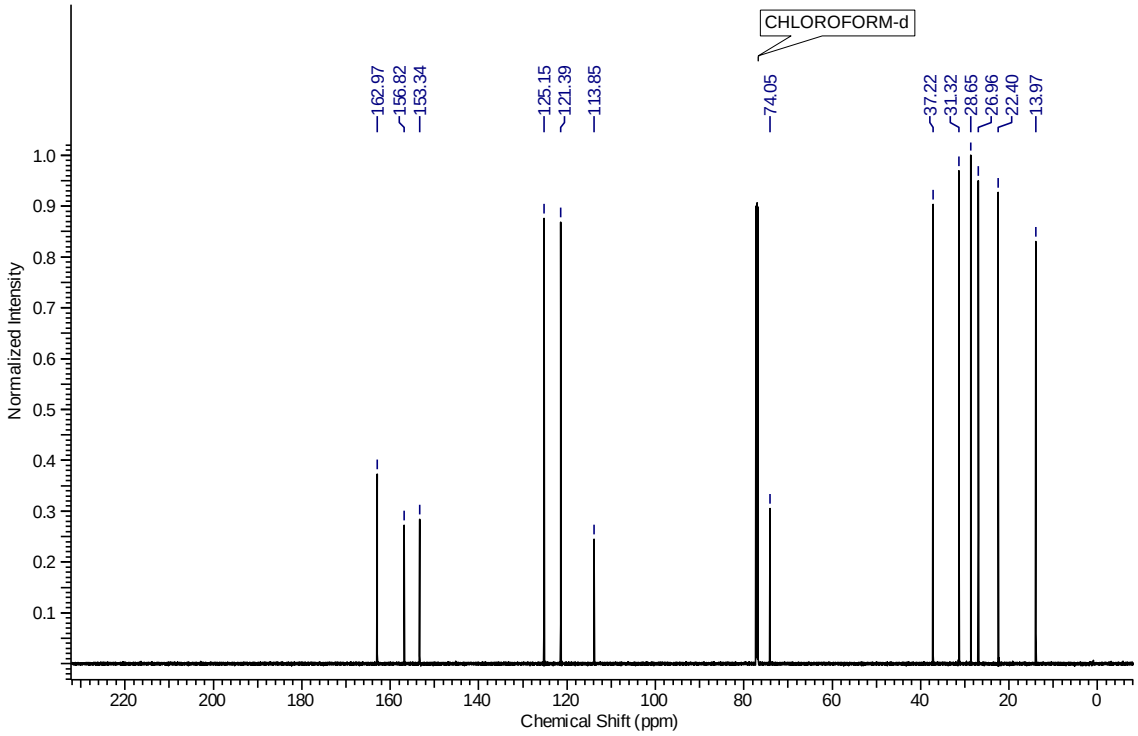




7-Hexanoyl-8-iodo-5*H*-[1,4]dithiino[2,3-*c*]pyran-5-one (**19**)







E) SINGLE CRYSTAL X-RAY DIFFRACTION STUDIES

Table 1. Details for X-ray data collection and structure refinement for compounds **11e**, **14c** and **14d**.

	11e	**14c**	**14d**
Empirical formula	$C_4H_2I_2S_2$	$C_7H_3NS_4$	$C_7H_6S_5$
Formula mass	367.98	229.34	250.42
T[K]	173(2)	173(2)	173(2)
Crystal size [mm]	0.15 × 0.10 × 0.02	0.35 × 0.10 × 0.01	0.25 × 0.15 × 0.02
Crystal description	yellow block	yellow platelet	yellow platelet
Crystal system	monoclinic	triclinic	Tetragonal
Space group	*P*21/*n*	*P*-1	*P*41212
a [Å]	12.9361(3)	3.9407(5)	7.89440(10)
b [Å]	7.6445(2)	7.3930(8)	7.89440(10)
c [Å]	16.4323(4)	15.5227(14)	31.4906(10)
α [°]	90	78.238(8)	90
β [°]	95.386(2)	87.991(8)	90
γ [°]	90	82.647(9)	90
V [Å^3]	1617.82(7)	439.08(8)	1962.54(8)
Z	8	2	8
$\rho_{calcd.}$ [g cm^{-3}]	3.022	1.735	1.695
μ [mm^{-1}]	8.194	1.016	1.119
F(000)	1312	232	1024
Θ range [°]	4.13 – 25.24	4.21 – 25.24	4.14 – 25.24
Index ranges	-18 ≤ *h* ≤ 18	-5 ≤ *h* ≤ 4	-10 ≤ *h* ≤ 10
	-10 ≤ *k* ≤ 10	-10 ≤ *k* ≤ 10	-10 ≤ *k* ≤ 11
	-23 ≤ *l* ≤ 23	-17 ≤ *l* ≤ 22	-36 ≤ *l* ≤ 43
Reflns. collected	31600	4284	18662
Reflns. obsd.	4117	1743	2257
Reflns. unique	4921 (R_{int} = 0.0344)	2689 (R_{int} = 0.0330)	2806 (R_{int} = 0.0652)
R_1, wR_2 (2σ data)	0.0241, 0.0480	0.0453, 0.0747	0.0367, 0.0654
R_1, wR_2 (all data)	0.0339, 0.0518	0.0841, 0.0914	0.0574, 0.0716
GOOF on F^2	1.057	1.031	1.036
Peak/hole [e Å^{-3}]	1.631 / -1.380	0.409 / -0.395	0.357 / -0.288

Table 2. Details for X-ray data collection and structure refinement for compounds **9l** and **5**.

	9l	**5**
Empirical formula	$C_8H_6S_5$	$C_8H_4S_6$
Formula mass	262.43	292.47
T[K]	173(2)	173(2)
Crystal size [mm]	0.40 × 0.35 × 0.04	0.15 × 0.01 × 0.01
Crystal description	yellow block	pale yellow rod
Crystal system	triclinic	orthorhombic
Space group	*P*-1	*Pna*21
a [Å]	6.1998(2)	19.0955(17)
b [Å]	9.3980(4)	3.9322(3)
c [Å]	10.0285(4)	14.6103(16)
α [°]	112.307(4)	90
β [°]	102.451(3)	90
γ [°]	90.518(3)	90
V [Å^3]	525.20(4)	1097.05(18)
Z	2	4
$\rho_{calcd.}$ [g cm^{-3}]	1.659	1.771
μ [mm^{-1}]	1.049	1.198
F(000)	268	592
Θ range [°]	4.20 – 25.24	4.30 – 25.24
Index ranges	-8 ≤ *h* ≤ 8	-21 ≤ *h* ≤ 23
	-13 ≤ *k* ≤ 13	-4 ≤ *k* ≤ 4
	-14 ≤ *l* ≤ 14	-17 ≤ *l* ≤ 18
Reflns. collected	10463	6517
Reflns. obsd.	2783	1560
Reflns. unique	3188 (R_{int} = 0.0222)	2186 (R_{int} = 0.0776)
R_1, wR_2 (2σ data)	0.0260, 0.0617	0.0715, 0.1640
R_1, wR_2 (all data)	0.0323, 0.0660	0.1037, 0.1908
GOOF on F^2	1.041	1.031
Peak/hole [e Å^{-3}]	0.358 / -0.344	2.244 / -0.652

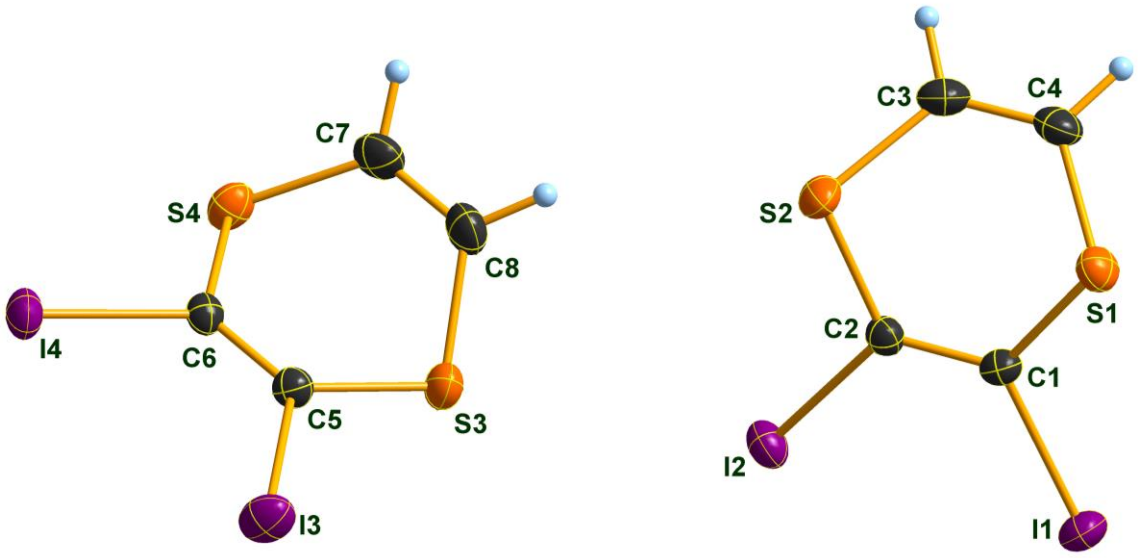


Figure S1. Molecular structure of compound **11e** in the crystal, DIAMOND[10] representation of the two crystallographically independent molecules; thermal ellipsoids are drawn at 50 % probability level.

Table 3. Selected bond lengths (Å) of compound **11e**.

I1 – C1	2.092(3)	S3 – C5	1.759(3)
I2 – C2	2.094(3)	S3 – C8	1.762(4)
I3 – C5	2.086(3)	C1 – C2	1.339(4)
I4 – C6	2.099(3)	C3 – C4	1.315(5)
S4 – C7	1.750(4)	C5 – C6	1.332(4)
S4 – C6	1.765(3)	C7 – C8	1.315(5)
S2 – C2	1.757(3)	S1 – C1	1.760(3)
S2 – C3	1.759(3)	S1 – C4	1.761(3)

Table 4. Selected bond angles (°) of compound **11e**.

C7 – S4 – C6	101.1(2)	C6 – C5 – S3	123.2(2)
C2 – S2 – C3	100.3(1)	C6 – C5 – I3	124.2(2)
C1 – S1 – C4	100.9(2)	S3 – C5 – I3	112.6(2)
C5 – S3 – C8	101.4(1)	C5 – C6 – S4	122.4(2)
C2 – C1 – S1	121.3(2)	C5 – C6 – I4	124.0(2)
C2 – C1 – I1	124.3(2)	S4 – C6 – I4	113.6(2)
S1 – C1 – I1	114.4(2)	C8 – C7 – S4	123.7(3)
C1 – C2 – S2	122.6(2)	C7 – C8 – S3	122.8(3)
C1 – C2 – I2	123.2(2)	C4 – C3 – S2	123.2(3)

[10] DIAMOND, Crystal Impact GbR., Version 3.2i.

S2 – C2 – I2	114.1(2)	C3 – C4 – S1	121.6(3)

Table 5. Selected torsion angles (°) of compound **11e**.

C4 – S1 – C1 – C2	-40.7(3)	C8 – S3 – C5 – C6	37.2(3)
C4 – S1 – C1 – I1	138.9(2)	C8 – S3 – C5 – I3	-143.7(2)
S1 – C1 – C2 – S2	-0.4(4)	S3 – C5 – C6 – S4	0.0(4)
I1 – C1 – C2 – S2	-179.9(2)	I3 – C5 – C6 – S4	-180.0(1)
S1 – C1 – C2 – I2	177.4(1)	S3 – C5 – C6 – I4	180.0(1)
I1 – C1 – C2 – I2	-2.1(4)	I3 – C5 – C6 – I4	1.0(4)
C3 – S2 – C2 – C1	40.4(3)	C7 – S4 – C6 – C5	-37.8(3)
C3 – S2 – C2 – I2	-137.5(2)	C7 – S4 – C6 – I4	142.3(2)
C2 – S2 – C3 – C4	-39.8(3)	C6 – S4 – C7 – C8	39.1(3)
S2 – C3 – C4 – S1	-1.2(5)	S4 – C7 – C8 – S3	-2.0(5)
C1 – S1 – C4 – C3	41.8(3)	C5 – S3 – C8 – C7	-36.3(3)

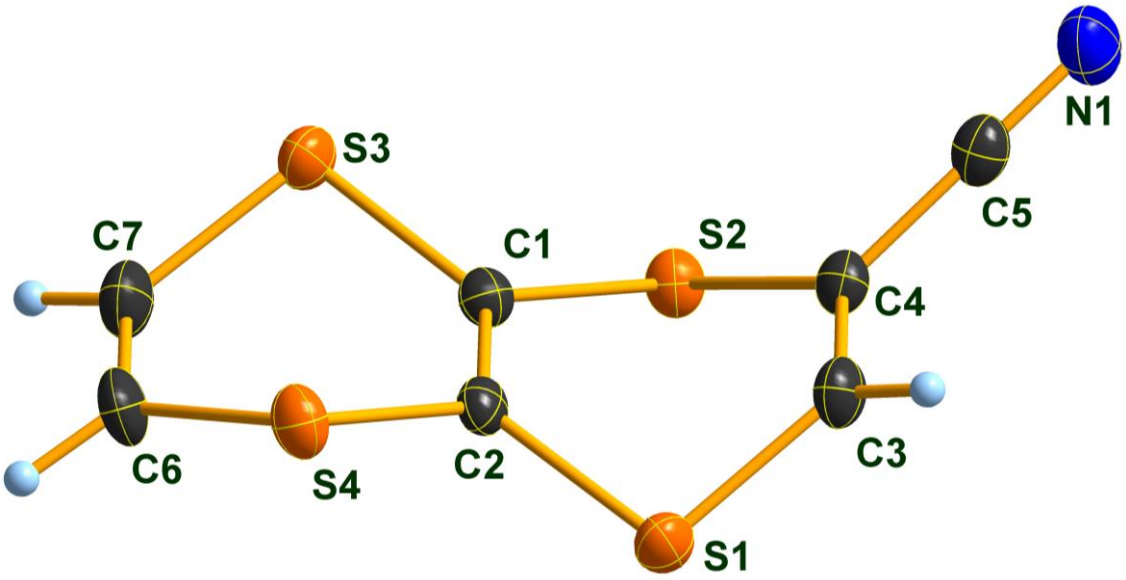


Figure S2. Molecular structure of compound **14c** in the crystal, DIAMOND[10] representation; thermal ellipsoids are drawn at 50 % probability level.

Table 6. Selected bond lengths (Å) of compound **14c**.

S3 – C1	1.759(3)	C4 – C3	1.333(3)
S3 – C7	1.765(3)	C4 – C5	1.440(3)
S1 – C3	1.750(3)	N1 – C5	1.139(3)
S1 – C2	1.765(3)	C2 – C1	1.331(3)
S4 – C2	1.760(3)	C6 – C7	1.319(4)
S4 – C6	1.761(3)	S2 – C4	1.777(3)
S2 – C1	1.767(3)		

Table 7. Selected bond angles (°) of compound **14c**.

C1 – S3 – C7	99.7(1)	C2 – C1 – S2	121.7(2)
C3 – S1 – C2	99.6(1)	S3 – C1 – S2	114.9(1)
C2 – S4 – C6	99.8(1)	C4 – C3 – S1	121.8(2)
C1 – S2 – C4	98.2(1)	C7 – C6 – S4	123.0(2)
C3 – C4 – C5	121.2(2)	C6 – C7 – S3	124.3(2)
C3 – C4 – S2	123.1(2)	S4 – C2 – S1	113.2(1)
C5 – C4 – S2	115.7(2)	N1 – C5 – C4	178.8(3)
C1 – C2 – S4	123.5(2)	C2 – C1 – S3	123.5(2)
C1 – C2 – S1	123.2(2)		

Table 8. Selected torsion angles (°) of compound **14c**.

C1 – S2 – C4 – C3	44.1(3)	C7 – S3 – C1 – C2	-36.8(2)
C1 – S2 – C4 – C5	-133.8(2)	C7 – S3 – C1 – S2	143.3(2)
C6 – S4 – C2 – C1	39.3(2)	C4 – S2 – C1 – C2	-42.6(2)
C6 – S4 – C2 – S1	-143.0(2)	C4 – S2 – C1 – S3	137.4(2)
C3 – S1 – C2 – C1	41.3(2)	C5 – C4 – C3 – S1	175.1(2)
C3 – S1 – C2 – S4	-136.4(2)	S2 – C4 – C3 – S1	-2.7(3)
S4 – C2 – C1 – S3	-1.4(3)	C2 – S1 – C3 – C4	-39.9(3)
S1 – C2 – C1 – S3	-178.9(1)	C2 – S4 – C6 – C7	-38.8(3)
S4 – C2 – C1 – S2	178.5(1)	S4 – C6 – C7 – S3	0.7(4)
S1 – C2 – C1 – S2	1.1(3)	C1 – S3 – C7 – C6	37.4(3)

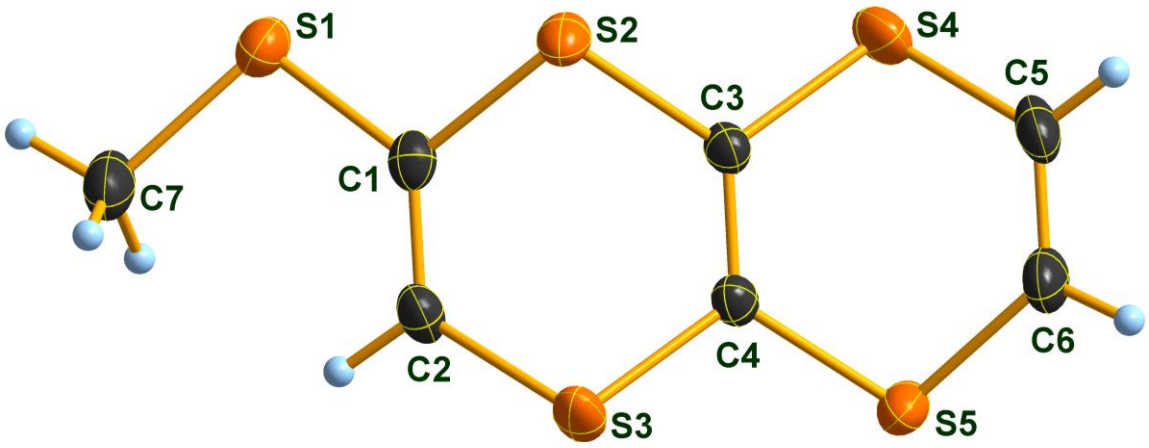


Figure S3. Molecular structure of compound **14d** in the crystal, DIAMOND[10] representation; thermal ellipsoids are drawn at 50 % probability level.

Table 9. Selected bond lengths (Å) of compound **14d**.

S2 – C3	1.766(3)	C4 – C3	1.321(4)
S2 – C1	1.776(3)	C2 – C1	1.324(5)
S5 – C6	1.763(3)	C5 – C6	1.309(5)
S5 – C4	1.767(3)	S4 – C3	1.762(3)
S1 – C1	1.749(3)	S3 – C4	1.763(3)
S1 – C7	1.799(4)	S3 – C2	1.764(3)
S4 – C5	1.757(4)		

Table 10. Selected bond angles (°) of compound **14d**.

C3 – S2 – C1	100.3(2)	C4 – C3 – S2	122.9(2)
C6 – S5 – C4	99.6(2)	S4 – C3 – S2	114.4(2)
C1 – S1 – C7	103.0(2)	C6 – C5 – S4	123.3(3)
C5 – S4 – C3	99.7(2)	C5 – C6 – S5	123.0(3)
C4 – S3 – C2	100.6(2)	C2 – C1 – S1	128.7(3)
C3 – C4 – S3	122.8(2)	C2 – C1 – S2	121.5(3)
C3 – C4 – S5	122.9(2)	S1 – C1 – S2	109.9(2)
S3 – C4 – S5	114.3(2)	C4 – C3 – S4	122.6(2)
C1 – C2 – S3	124.0(3)		

Table 11. Selected torsion angles (°) of compound **14d**.

C2 – S3 – C4 – C3	36.8(3)	S3 – C4 – C3 – S4	-179.4(2)
C2 – S3 – C4 – S5	-144.3(2)	S5 – C4 – C3 – S4	1.7(4)
C6 – S5 – C4 – C3	38.7(3)	S3 – C4 – C3 – S2	3.5(4)
C6 – S5 – C4 – S3	-140.3(2)	S5 – C4 – C3 – S2	-175.5(2)
C4 – S3 – C2 – C1	-38.9(3)	C5 – S4 – C3 – C4	-40.8(3)
S3 – C2 – C1 – S1	180.0(2)	C5 – S4 – C3 – S2	136.6(2)
S3 – C2 – C1 – S2	0.3(4)	C1 – S2 – C3 – C4	-41.8(3)
C7 – S1 – C1 – C2	10.5(4)	C1 – S2 – C3 – S4	140.9(2)
C7 – S1 – C1 – S2	-170.8(2)	C3 – S4 – C5 – C6	39.6(4)
C3 – S2 – C1 – C2	39.5(3)	S4 – C5 – C6 – S5	0.9(5)
C3 – S2 – C1 – S1	-140.3(2)	C4 – S5 – C6 – C5	-40.2(4)

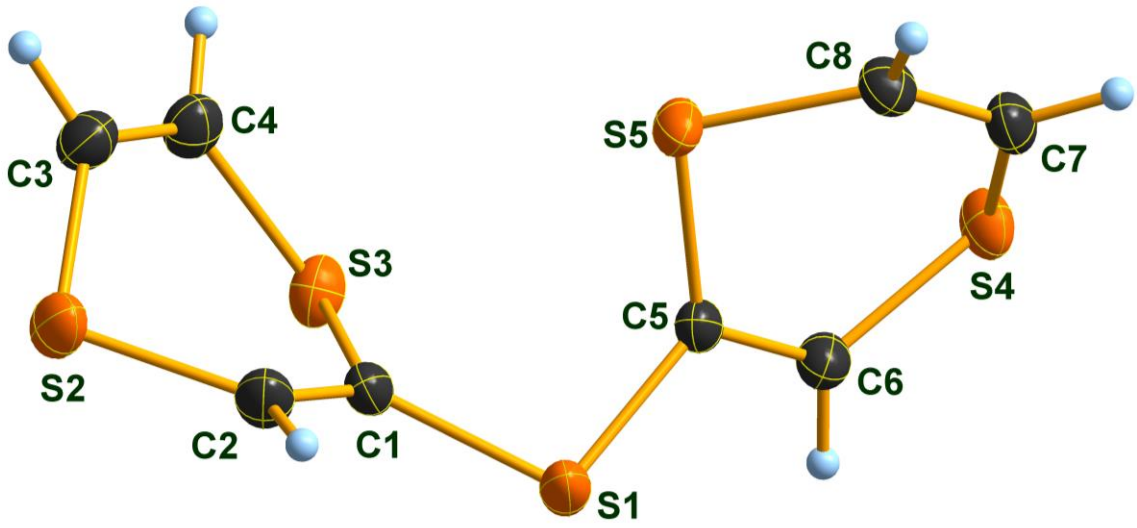


Figure S4. Molecular structure of compound **9l** in the crystal, DIAMOND[10] representation; thermal ellipsoids are drawn at 50 % probability level.

Table 12. Selected bond lengths (Å) of compound **9l**.

S4 – C6	1.747(1)	C5 – C6	1.336(2)
S4 – C7	1.752(1)	C1 – C2	1.332(2)
S5 – C8	1.761(1)	C8 – C7	1.318(2)
S5 – C5	1.773(1)	C4 – C3	1.324(2)
S2 – C3	1.756(2)	S3 – C1	1.764(1)
S2 – C2	1.759(2)	S1 – C5	1.764(1)
S3 – C4	1.754(2)	S1 – C1	1.767(1)

Table 13. Selected bond angles (°) of compound **9l**.

C6 – S4 – C7	101.2(1)	C3 – C4 – S3	123.3(1)
C8 – S5 – C5	99.9(1)	C5 – C6 – S4	123.9(1)
C3 – S2 – C2	100.0(1)	C8 – C7 – S4	124.2(1)
C4 – S3 – C1	100.8(1)	C4 – C3 – S2	123.8(1)
C5 – S1 – C1	101.8(1)	C2 – C1 – S1	120.9(1)
C6 – C5 – S1	119.2(1)	S3 – C1 – S1	115.7(1)
C6 – C5 – S5	122.1(1)	C1 – C2 – S2	123.2(1)
S1 – C5 – S5	118.3(1)	C7 – C8 – S5	122.7(1)
C2 – C1 – S3	123.2(1)		

Table 14. Selected torsion angles (°) of compound **9l**.

C1 – S1 – C5 – C6	-139.0(1)	C3 – S2 – C2 – C1	-40.0(1)
C1 – S1 – C5 – S5	48.3(1)	C5 – S5 – C8 – C7	40.5(1)
C8 – S5 – C5 – C6	-41.4(1)	C1 – S3 – C4 – C3	-37.6(1)
C8 – S5 – C5 – S1	131.2(1)	S1 – C5 – C6 – S4	-167.7(1)
C4 – S3 – C1 – C2	35.3(1)	S5 – C5 – C6 – S4	4.7(2)
C4 – S3 – C1 – S1	-149.0(1)	C7 – S4 – C6 – C5	34.0(1)
C5 – S1 – C1 – C2	-130.8(1)	S5 – C8 – C7 – S4	-2.8(2)
C5 – S1 – C1 – S3	53.3(1)	C6 – S4 – C7 – C8	-35.3(1)
S3 – C1 – C2 – S2	3.7(2)	S3 – C4 – C3 – S2	0.5(2)
S1 – C1 – C2 – S2	-171.8(1)	C2 – S2 – C3 – C4	38.0(2)

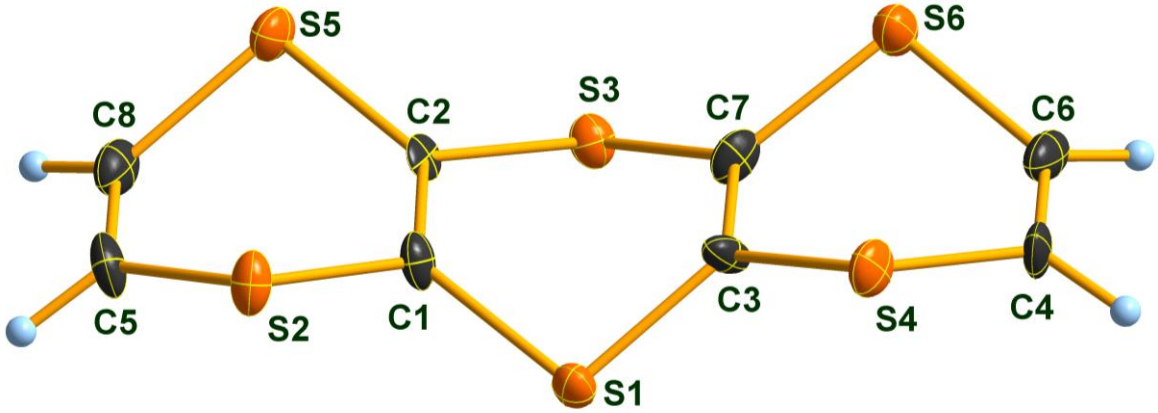


Figure S5. Molecular structure of compound **5** in the crystal, DIAMOND[10] representation; thermal ellipsoids are drawn at 50 % probability level.

Table 15. Selected bond lengths (Å) of compound **5**.

S1 – C3	1.748(14)	S6 – C6	1.765(13)
S1 – C1	1.774(14)	S6 – C7	1.781(15)
S2 – C1	1.753(13)	C1 – C2	1.365(19)
S2 – C5	1.763(13)	C3 – C7	1.314(18)
S3 – C7	1.746(13)	C4 – C6	1.32(2)
S3 – C2	1.782(14)	C5 – C8	1.27(2)
S4 – C4	1.758(14)	S5 – C2	1.741(12)
S4 – C3	1.775(12)	S5 – C8	1.791(16)

Table 15. Selected bond angles (°) of compound **5**.

C3 – S1 – C1	98.8(6)	C6 – C4 – S4	122.9(11)
C1 – S2 – C5	99.9(7)	C8 – C5 – S2	123.5(12)
C7 – S3 – C2	100.1(6)	C4 – C6 – S6	123.4(12)
C4 – S4 – C3	100.3(7)	C3 – C7 – S3	122.9(11)
C2 – S5 – C8	98.2(6)	C3 – C7 – S6	123.3(10)
C6 – S6 – C7	99.3(7)	S3 – C7 – S6	113.8(8)
C2 – C1 – S2	121.6(10)	C5 – C8 – S5	124.2(11)
C2 – C1 – S1	122.5(10)	S5 – C2 – S3	115.4(8)

S2 – C1 – S1	115.9(7)	C7 – C3 – S1	123.6(10)
C1 – C2 – S5	123.8(10)	C7 – C3 – S4	122.6(11)
C1 – C2 – S3	120.8(9)	S1 – C3 – S4	113.8(8)

Table 15. Selected torsion angles (°) of compound **5**.

C5 – S2 – C1 – C2	38.5(11)	C4 – S4 – C3 – S1	138.1(8)
C5 – S2 – C1 – S1	-139.2(8)	C3 – S4 – C4 – C6	38.0(14)
C3 – S1 – C1 – C2	41.4(12)	C1 – S2 – C5 – C8	-40.0(14)
C3 – S1 – C1 – S2	-140.9(8)	S4 – C4 – C6 – S6	2.6(19)
S2 – C1 – C2 – S5	1.9(15)	C7 – S6 – C6 – C4	-40.8(14)
S1 – C1 – C2 – S5	179.5(7)	S1 – C3 – C7 – S3	2.7(17)
S2 – C1 – C2 – S3	-178.1(7)	S4 – C3 – C7 – S3	-179.5(7)
S1 – C1 – C2 – S3	-0.5(14)	S1 – C3 – C7 – S6	-176.6(7)
C8 – S5 – C2 – C1	-40.3(11)	S4 – C3 – C7 – S6	1.2(17)
C8 – S5 – C2 – S3	139.6(7)	C2 – S3 – C7 – C3	40.1(13)
C7 – S3 – C2 – C1	-40.4(11)	C2 – S3 – C7 – S6	-140.6(7)
C7 – S3 – C2 – S5	139.7(7)	C6 – S6 – C7 – C3	38.6(13)
C1 – S1 – C3 – C7	-43.5(13)	C6 – S6 – C7 – S3	-140.7(8)
C1 – S1 – C3 – S4	138.5(7)	S2 – C5 – C8 – S5	-0.1(19)
C4 – S4 – C3 – C7	-39.9(13)	C2 – S5 – C8 – C5	40.1(14)

Single Crystal X-Ray Diffraction Studies

Single crystals of compounds **11e**, **14c**, **14d**, **9l** and **5**, suitable for X-ray diffraction, were obtained by slow evaporation of hexane- and THF-, as well as CH_2Cl_2-solutions solution. The crystals were introduced into perfluorinated oil and a suitable single crystal was carefully mounted on the top of a thin glass wire. Data collection was performed with an Oxford Xcalibur 3 diffractometer equipped with a Spellman generator (50 kV, 40 mA) and a Kappa CCD detector, operating with Mo-K_α radiation (λ = 0.71071 Å).

Data collection was performed with the CrysAlis CCD software;[11] CrysAlis RED software[12] was used for data reduction. Absorption correction using the SCALE3 ABSPACK multiscan method[13] was applied. The structures were solved with

[11] CrysAlis CCD, Oxford Diffraction Ltd., Version 1.171.27p5 beta (release 01-04-2005 CrysAlis171.NET) (compiled Apr 1 2005, 17:53:34).
[12] CrysAlis RED, Oxford Diffraction Ltd., Version 1.171.27p5 beta (release 01-04-2005 CrysAlis171.NET) (compiled Apr 1 2005, 17:53:34).
[13] SCALE3 ABSPACK – An Oxford Diffraction Program (1.0.4, gui:1.0.3) (C), Oxford Diffraction, Ltd., 2005.

SHELXS-97,[14] refined with SHELXL-97[15] and finally checked using PLATON.[16] Details for data collection and structure refinement are summarized in Table 1 and Table 2.

CCDC 1518630 (**11e**), CCDC 1518626 (**14c**), CCDC 1518629 (**14d**), CCDC 1518628 (**9l**) and CCDC 1518627 (**5**) contains supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

[14] Sheldrick, G. M. (1997) SHELXS-97: *Program for Crystal Structure Solution*, University of Göttingen, Germany.
[15] Sheldrick, G. M. (1997) SHELXL-97: *Program for the Refinement of Crystal Structures*, University of Göttingen, Germany.
[16] Spek, A. L. (1999) PLATON: *A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands.