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## Supplementary Material

### A Novel Synthesis of 3,6-Disubstituted 1,2-Dithiin Molecules Involving A Direct Oxidative Deprotection-Cyclization Sequence from (Z,Z)-1,4-Bis(*tert*-butyl)thio-1,3-butadiene Precursors

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#### Experimental

**General Methods.** Both proton (360 MHz) and C-13 (90.6 MHz) NMR spectra were recorded on a Bruker WM-360 FT NMR spectrometer. The solvent used for NMR spectroscopy was chloroform-d<sub>1</sub> (CDCl<sub>3</sub>) as indicated. Chemical shifts are reported in  $\delta$  units with respect to tetramethylsilane ( $\delta$  0.00) as internal standard. Coupling constants ( $J$  values) are given in hertz or cycles/sec (Hz). The following abbreviations are used to describe peak patterns: “s” for singlet, “d” for doublet, “t” for triplet, “q” for quartet, “m” for multiplet, “br” for broadened. Data are presented as follows: chemical shift (multiplicity, integrated intensity, and coupling constant). Infrared (IR) spectra were recorded on a Nicolet Model 5-DX FT-IR spectrometer using sodium chloride plates (liquid) or potassium bromide pellets (solid). Data are reported in wavenumbers (cm<sup>-1</sup>). High resolution mass spectroscopic (HRMS) data were obtained using a VG Analitica 170-250S mass spectrometer. Flash column chromatography was performed by the method of Still using Merck 230-400 mesh silica gel. Analytical thin layer chromatography (TLC) was performed using Merck 60-F-254 0.2 mm precoated silica gel plates. Compounds were visualized using ultraviolet light, iodine vapor, or ceric ammonium sulfate/sulfuric acid. Solvents were freshly distilled prior to use. Diethyl ether (Et<sub>2</sub>O) and tetrahydrofuran (THF) were distilled from sodium/benzophenone ketyl. Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) and triethylamine (Et<sub>3</sub>N) were distilled from calcium hydride. Benzene and toluene were distilled from sodium metal. All other reagents were used as received, or distilled as necessary. All air- or moisture-sensitive reactions were conducted in oven- or flame-dried

glassware, and under an atmosphere of house nitrogen. Moisture-sensitive reagents were transferred through septa using syringes or cannulas.

**(Z,Z)-2,5-Bis(*t*-butylthio)-2,4-hexadiene-1,6-diol (7a).** To a suspension of sodium hydride (0.200 g, 5.00 mmol) in dry DMF (80 mL) at room temperature was added dropwise 2-methylpropanethiol (2.71 g, 30.0 mmol). The mixture turned clear and yellowish after 5 min, to which was added 2,4-hexadiyne-1,6-diol (**3a**; R = CH<sub>2</sub>OH) (1.32 g, 12.0 mmol). The mixture turned immediately dark brown. The reaction mixture was stirred for 10 h at room temperature, upon which time it was poured into a mixture of ethyl acetate (80 mL) and water (80 mL). The resulting aqueous layer was extracted with ethyl acetate (2 x 70 mL) and the combined organic layers were washed with brine (150 mL) and dried (Na<sub>2</sub>SO<sub>4</sub>). Removal of the solvent by rotary evaporation gave a brown solid, which was purified by recrystallization from hexanes/ethyl acetate to afford the bis-(*t*-BuSH) adduct **7a** (R = CH<sub>2</sub>OH) as a white solid (2.71 g, 78%): mp 119.0-120.0 °C; R<sub>f</sub>(1/1 ethyl acetate/hexanes) 0.51; <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 1.36 (s, 18H), 2.15 (t, 2H, J = 6.2 Hz), 4.29 (d, 4H, J = 6.2 Hz), 7.54 (s, 2H); <sup>13</sup>C NMR (90.6 MHz, CDCl<sub>3</sub>) δ 32.08, 48.58, 68.32, 135.42, 138.36; IR (KBr) 3208, 2962, 1363, 1165, 1148, 1083, 989, 901, 776 cm<sup>-1</sup>. Anal. Calcd for C<sub>14</sub>H<sub>26</sub>O<sub>2</sub>S<sub>2</sub>: C, 57.89, H, 9.02. Found: C, 57.96, H, 9.01.

**(Z,Z)-1,4-Bis(*t*-butylthio)-1,3-butadiene (7b).** To a suspension of sodium hydride (0.16 g, 4.0 mmol) in dry DMF (40 mL) was added dropwise 2-methyl-2-propanethiol (1.91 g, 21.0 mmol) at room temperature. The mixture became clear and yellowish after 5 min, to which was then added 1,4-ditrimethylsilyl-1,3-butadiyne (**3b**; R = TMS) (1.95 g, 10.0 mmol). The reaction mixture was stirred at room temperature for 8 h and then was poured into water (40 mL). The resulting mixture was extracted with diethyl ether (4 x 80 mL) and the combined organic layers were washed first with water (2 x 300 mL) and then with brine (300 mL) and dried (Na<sub>2</sub>SO<sub>4</sub>). Removal of the solvent by rotary evaporation gave a brown residue, which was purified by recrystallization from methanol at -78 °C to afford the bis-(*t*-BuSH)-adduct **7b** (R = H) as a white solid (1.52 g, 66%): mp 56.0-58.0 °C; R<sub>f</sub> (hexanes) 0.10; <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 1.38 (s, 18H), 6.24 and 6.48 (AA'BB' spin

system, 4H,  $J_{AB} = 8.8$  Hz);  $^{13}\text{C}$  NMR (90.6 MHz,  $\text{CDCl}_3$ )  $\delta$  30.95, 44.11, 124.01, 124.14; IR (KBr) 2966, 1459, 1368, 1311, 1153, 776, 690  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{12}\text{H}_{22}\text{S}_2$ : C, 62.55, H, 9.62. Found: C, 62.13, H, 9.45.

**(Z,Z)-1,4-Diphenyl-1,4-bis-(*t*-butylthio)-1,3-butadiene (7c; R = Ph).** To a suspension of sodium hydride (40 mg, 1.00 mmol) in dry DMF (15 mL) was added dropwise 2-methyl-2-propanethiol (596 mg, 6.60 mmol) at room temperature. The mixture became clear and yellowish after 5 min, to which was then added 1,4-diphenyl-1,3-butadiyne (3c; R = Ph) (607 mg, 3.00 mmol). The reaction mixture was stirred at room temperature for 12 h, upon which time water (10 mL) was added. The resulting precipitates were washed with 2 mL of methanol (primarily for the purpose of removing the residual DMF) and recrystallized from chloroform to afford bis(*t*-BuSH) adduct 7c (R = Ph) as white crystals (643 mg, 56%): mp 238.0-239.0  $^{\circ}\text{C}$ ;  $R_f$  (2/1 hexanes/dichloromethane) 0.53;  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.15 (s, 18H), 7.26-7.37 (m, 6H), 7.68-7.71 (m, 4H), 7.79 (s, 2H);  $^{13}\text{C}$  NMR (90.6 MHz,  $\text{CDCl}_3$ )  $\delta$  31.76, 48.16, 127.79, 128.05, 128.13, 138.02, 138.87, 143.95; IR (KBr) 2961, 1592, 1484, 1458, 1442, 1364, 1155, 906, 764, 696  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{24}\text{H}_{30}\text{S}_2$ : C, 75.34, H, 7.90. Found: C, 75.17, H, 8.02.

**(Z,Z)-1,6-Diacetoxy-2,5-bis(*t*-butylthio)-2,4-hexadiene (9).** To a solution of diol 7a (1.45 g, 5.0 mmol) and pyridine (4.04 mL, 50.0 mmol) in dry dichloromethane (50 mL) was added dropwise acetic anhydride (2.83 mL, 30.0 mmol) at 0  $^{\circ}\text{C}$ . The reaction mixture was stirred at room temperature for 3 h, upon which time it was diluted with dichloromethane (30 mL) and the resulting solution was washed successively with saturated aqueous copper sulfate (60 mL), saturated aqueous sodium bicarbonate (2 x 60 mL), and brine (60 mL) and dried ( $\text{Na}_2\text{SO}_4$ ). Removal of the solvent by rotary evaporation provided a yellowish solid, which was recrystallized from with to afford diacetate 9 as white crystals (1.78g, 95%): mp 84.0-85.0  $^{\circ}\text{C}$ ;  $R_f$  (2/1 hexanes/ethyl acetate) 0.64;  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  1.35 (s, 18H), 2.15 (s, 6H), 4.75 (s, 4H), 7.49 (s, 2H);  $^{13}\text{C}$  NMR (90.6 MHz,  $\text{CDCl}_3$ )  $\delta$  20.89, 31.95, 48.75, 68.86, 133.29, 136.65, 170.29; IR (KBr) 2966, 1743, 1377, 1272,

1216, 1159, 1061, 899  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{18}\text{H}_{30}\text{O}_4\text{S}_2$ : C, 57.72, H, 8.07. Found: C, 57.60, H, 8.25.

**(Z,Z)-2,5-Bis(*t*-butylthio)-2,4-hexadiene-1,6-dial (10).** A 250-mL, three-necked, round-bottomed flask was charged with a solution of oxalyl chloride (3.39 mL, 38.9 mmol) in dry dichloromethane (80 mL). The solution was cooled to -78 °C and to that solution was added dropwise DMSO (5.52 mL, 77.8 mmol). After 10 min, diol **7a** (2.82 g, 9.72 mmol) in THF (10 mL) was added with stirring at -78 °C. A white precipitate formed immediately. After another 15 min at that temperature, triethylamine (13.5 mL, 97.0 mmol) was added dropwise. The reaction mixture turned bright yellow and was allowed to gradually warm up to room temperature during the period of 12 h. The reaction mixture was then poured into saturated aqueous ammonium chloride (80 mL) and the resulting aqueous layer extracted with dichloromethane (2 x 80 mL). The combined organic layers were washed first with water (2 x 200 mL) and then with brine (200 mL) and dried over  $\text{Na}_2\text{SO}_4$ . The crude reaction mixture obtained upon removal of the solvent by rotary evaporation was recrystallized from hexanes/ethyl acetate to give the bis-aldehyde **10** (2.53 g, 90%) as yellow crystals: mp 152.0 °C (color change observed at 130.0 °C);  $R_f$ (2/1 hexanes/ethyl acetate) 0.66;  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  1.35 (s, 18H), 8.42 (s, 2H), 9.76 (s, 2H);  $^{13}\text{C}$  NMR (90.6 MHz,  $\text{CDCl}_3$ )  $\delta$  31.72, 50.09, 143.96, 148.84, 192.16; IR (KBr) 2966, 1680, 1462, 1363, 1166, 1075, 660  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{14}\text{H}_{22}\text{O}_2\text{S}_2$ : C, 58.70, H, 7.74. Found: C, 58.52, H, 7.89.

**(Z,Z)-2,5-Bis(*t*-butylthio)-1,3-butadiene-1,4-dioic Acid Dimethyl Ester (11).** A 50-mL round-bottomed flask was charged with manganese dioxide (870 mg, 10.0 mmol), sodium cyanide (167 mg, 3.4 mmol), acetic acid (61 mg, 1.0 mmol), and methanol (10 mL). To this mixture was added dialdehyde **10** (143 mg, 0.5 mmol) was added at room temperature. The reaction mixture was kept stirring at that temperature for 1.5 h, upon which time it was filtered. The filtrate thus obtained was then poured into water (10 mL) and the resulting mixture extracted with ethyl acetate (2 x 25 mL). The combined organic layers were washed first with water (50 mL) and then with brine (50 mL) and dried ( $\text{Na}_2\text{SO}_4$ ). Removal of the solvent by rotary evaporation afforded a brown residue,

which was recrystallized from hexanes/ethyl acetate to provide dimethyl ester **11** (147 mg, 85%) as bright yellow crystals: mp 96.0-98.0 °C;  $R_f$ (2/1 hexanes/ethyl acetate) 0.70;  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  1.32 (s, 18H), 3.86 (s, 6H), 8.44 (s, 2H);  $^{13}\text{C}$  NMR (90.6 MHz,  $\text{CDCl}_3$ )  $\delta$  31.22, 49.45, 52.94, 134.67, 145.68, 167.72; IR (KBr) 2952, 1694, 1532, 1454, 1433, 1363, 1230, 1159, 1089, 770  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{16}\text{H}_{26}\text{O}_4\text{S}_2$ : C, 55.46, H, 7.56. Found: C, 55.34, H, 7.57.

**(Z,Z)-3,6-Bis(*t*-butylthio)-1,1,8,8-tetrabromo-1,3,5,7-octatetraene (12).** To a solution of triphenylphosphine (6.29 g, 24.0 mmol) in dry dichloromethane (80 mL) was added carbon tetrabromide (3.98 g, 12.0 mmol) at 0 °C. The solution turned orange immediately. After 20 min at that temperature, dialdehyde **10** (0.86 g, 3.0 mmol) was added in one portion. The solution first turned dark green and then dark brown. The reaction mixture was stirred at 0 °C for 0.5 h, upon which time it was poured into hexanes (400 mL). The resulting mixture was then filtered through silica gel in a short-stem glass funnel. The filtrate thus obtained was concentrated by rotary evaporation to give a yellow solid, which was then recrystallized from dichloromethane/hexanes to afford tetrabromide **12** (1.57 g, 87%) as yellow crystals: mp 169.0-170.0 °C;  $R_f$ (9/1 hexanes/ether) 0.61;  $^1\text{H}$  NMR (360 Hz,  $\text{CDCl}_3$ )  $\delta$  1.36 (s, 18H), 7.07 (s, 2H), 7.68 (s, 2H);  $^{13}\text{C}$  NMR (90.6 MHz,  $\text{CDCl}_3$ )  $\delta$  31.73, 47.68, 90.55, 134.69, 138.93, 141.19; IR (KBr) 2958, 1579, 1452, 1366, 1152, 918, 867, 717, 561  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{16}\text{H}_{22}\text{Br}_4\text{S}_2$ : C, 32.13, H, 3.71. Found: C, 32.28, H, 3.69.

**(Z,Z)-4,7-Bis(*t*-butylthio)-4,6-decadiene-2,8-diyne (13).** To a cooled solution (-78 °C) of tetrabromide **12** (2.56 g, 4.72 mmol) in dry THF (25 mL) was added 1.4 M *n*-BuLi in hexanes (14.9 mL, 20.8 mmol). The solution turned dark green. It was kept stirring for 1 h at -78 °C and then gradually warmed to room temperature and was kept at that temperature for 1 h. The solution was then cooled down to -78 °C and methyl iodide (1.50 mL, 24.0 mmol) was added dropwise at that temperature. It was gradually warmed to room temperature and a mixture of water (30 mL) and ether (20 mL) was added. The aqueous layer was extracted with ether (50 mL). The combined organic layers were washed first with water (80 mL) and then with brine (80 mL) and dried ( $\text{Na}_2\text{SO}_4$ ). Removal of the solvent by rotary evaporation afforded a red oil, which was purified by

silica gel flash column chromatography using hexanes/ether (10/1) as the eluent to provide **13** (856 mg, 73%) as a light yellowish solid: mp 130.5-132.0 °C;  $R_f$  (9/1 hexanes/ether) 0.50;  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  1.42 (s, 18H), 2.03 (s, 6H), 7.42 (s, 2H);  $^{13}\text{C}$  NMR (90.6 MHz,  $\text{CDCl}_3$ )  $\delta$  4.75, 31.33, 47.89, 82.98, 90.00, 119.10, 139.45; IR (KBr) 2957, 2207, 1470, 1364, 1163, 1148, 904, 868  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{18}\text{H}_{26}\text{S}_2$ : C, 70.53, H, 8.55. Found: C, 70.58, H, 8.44.

**(Z,Z)-1,4-Diido-bis(*t*-butylthio)-1,3-butadiene (15).** A 250-mL round-bottomed flask at -78 was charged with (Z,Z)-1,4-bis(*t*-butylthio)-1,3-butadiene (**7b**) (1.11 g, 4.84 mmol), potassium *t*-butoxide (2.29 g mg, 19.4 mmol) and THF (100 mL) and the solution was cooled to -78 °C. To this solution was added dropwise 1,4 M *n*-BuLi in hexanes (13.9 mL, 19.4 mmol) at -78 °C. The resulting solution was kept stirring at that temperature for 6 h, upon which time precooled (-78 °C) iodine (4.92 g, 19.40 mmol) in 20 mL THF was added through a cannula. The reaction mixture was kept stirring at -78 °C and then saturated aqueous ammonium chloride (30 mL) was added at that temperature which was followed immediately by the addition of 0.1 M aqueous sodium thiosulfate (100 mL). The resulting mixture was warmed to room temperature and extracted with diethyl ether (2 x 150 mL). The combined organic layers were washed successively with 0.1 M aqueous sodium thiosulfate (300 mL), water (300 mL), and brine (300 mL) and dried ( $\text{Na}_2\text{SO}_4$ ). Removal of the solvent by rotary evaporation afforded a yellow oil, which was purified by silica gel flash column chromatography by using hexanes as the eluent to provide the diiodide **15** (1.12 g, 48%) as a slightly pic-colored solid: mp 107.0-108.0 °C;  $R_f$  (hexanes) 0.31;  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  1.42 (s, 18H), 7.90 (s, 2H);  $^{13}\text{C}$  NMR (90.6 MHz,  $\text{CDCl}_3$ )  $\delta$  30.86, 51.55, 90.75, 151.14; IR (KBr) 2956, 1469, 1453, 1367, 1251, 1157, 908, 788  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{12}\text{H}_{20}\text{I}_2\text{S}_2$ : C, 29.89, H, 4.18. Found: C, 29.92, H, 4.19.

**3,6-Diacetoxymethyl-1,2-dithiin (8; R =  $\text{CH}_2\text{OAc}$ ).** To a solution of diacetate **9** (94 mg, 0.25 mmol) in dry acetonitrile (2 mL) at room temperature was added in one portion *N*-iodosuccinimide (124 mg, 0.55 mmol) at room temperature. The solution immediately turned red. The reaction mixture was then purged with nitrogen for 5 min, and was heated to refluxre for 1.5 h, upon which

time it was poured onto a mixture of 0.1 M aqueous sodium thiosulfate (10 mL) and ethyl ether (10 mL). The resulting aqueous layer was extracted with ether (2 x 10 mL) and the combined organic layers were washed with saturated successieli with saturated aqueous sodium bicarbonate (20 mL), water (20 mL), and brine (20 mL) and dried ( $\text{Na}_2\text{SO}_4$ ). Removal of the solvent by rotary evaporation gave a red oil, which was purified by silica gel flash chromatography by using hexanes/ethyl acetate (2/1) as the eluent to afford dithiin **8** ( $\text{R} = \text{CH}_2\text{OAc}$ ; 54 mg, 83%).<sup>11</sup>

**3,6-Diformyl-1,2-dithiin (10).** A 5-mL round-bottomed flask at room temperature was charged with **10** (143 mg, 0.5 mmol), *N*-bromosuccinimide (197 mg, 1.1 mmol) and acetonitrile (3 mL). The mixture was stirred at room temperature for 40 min, upon which time it was poured onto a mixture of diethyl ether (20 mL) and water (20 mL). The organic layer was washed first with water (20 mL) and then with brine (20 mL) and dried ( $\text{Na}_2\text{SO}_4$ ). Removal of the solvent by rotary evaporation gave a purple solid, which was purified by silica gel flash column chromatography using hexanes/ethyl acetate (3/1) as the eluent to afford dithiin **8** ( $\text{R} = \text{CHO}$ ; 59 mg, 69%) as a purple solid.<sup>11</sup>

**3,6-Dicarbomethoxy-1,2-dithiin (8;  $\text{R} = \text{COOMe}$ ).** In a 5-mL round-bottomed flask, **11** (104 mg, 0.30 mmol) and *N*-bromosuccinimide (119 mg, 0.66 mmol) were dissolved in dry acetonitrile (2 mL) at 0 °C. The reaction mixture immediately turned deep red. The reaction mixture was kept stirring for 20 min at that temperature and then poured onto a mixture of diethyl ether (15 mL) and 0.1 M aqueous sodium thiosulfate (15 mL). The aqueous layer was extracted with diethyl ether (15 mL) and the combined organic layers were washed first with water (2 x 30 mL) and then with brine (30 mL), and dried ( $\text{Na}_2\text{SO}_4$ ). Removal of the solvent by rotary evaporation provided a dark-red solid, which was purified by silica gel flash column chromatography using hexanes/ethyl acetate (5/1) as the eluent to afford dithiin **8** ( $\text{R} = \text{COOMe}$ ; 64 mg, 91%) as a red solid: mp 96.0-98.0 °C;  $\text{R}_f$  (2/1 hexanes/ethyl acetate) 0.54;  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  3.87 (s, 6H), 7.41 (s, 2H);  $^{13}\text{C}$  NMR (90.6 MHz,  $\text{CDCl}_3$ )  $\delta$  53.06, 130.51, 136.50, 162,48; IR (KBr) 2957, 1722, 1706, 1437, 1273,

1255, 1242, 1060, 727  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_8\text{H}_8\text{O}_4\text{S}_2$ : C, 41.37, H, 3.47. Found: C, 41.32, H, 3.63.

**3,6-Diphenyl-1,2-dithiin (8; R = Ph).** In a 10-mL round-bottomed flask, **7c** (77 mg, 0.20 mmol) and iodine (112 mg, 0.44 mmol) were dissolved in a mixture of THF (1 mL) and acetonitrile (2 mL) at room temperature. The resulting mixture was heated to reflux for 10 h, upon which time it was cooled to room temperature and was diluted with a mixture of diethyl ether (10 mL) and 0.1 M aqueous sodium thiosulfate (10 mL). The aqueous layer was extracted with diethyl ether (10 mL) and the combined organic layers were washed first with water (20 mL) and then with brine (20 mL) and dried ( $\text{Na}_2\text{SO}_4$ ). Removal of the solvent by rotary evaporation provided a red residue, which was purified by silica gel flash column chromatography using hexanes as the eluent to give the dithiin **8** (R = Ph;<sup>11</sup> 30 mg, 56% or 80% based on recovered starting material) as a red solid together with recovered starting material **7c** (23 mg, 30%).

**3,6-Diiodo-1,2-dithiin (8; R = I).** In a 5-mL round-bottomed flask, **15** (48 mg, 0.10 mmol) and *N*-bromosuccinimide (20 mg, 0.11 mmol) were dissolved acetone (1 mL) at room temperature. The reaction mixture was stirred at room temperature for 0.5 hr, upon which time it was diluted with diethyl ether (10 mL). The resulting mixture was washed first with water (2 x 10 mL) and then with brine (10 mL) and dried ( $\text{Na}_2\text{SO}_4$ ). Evaporation of the solvent by rotary evaporation provided a red solid, which was purified by silica gel flash column chromatography using hexanes as the eluent to provide dithiin (**8**, R = I; 35 mg, 95%) as a red solid: mp: 65.0-67.0 °C (decompose);  $R_f$  (hexanes) 0.52;  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  6.73 (s, 2H);  $^{13}\text{C}$  NMR (90.6 MHz,  $\text{CDCl}_3$ )  $\delta$  76.24, 140.02; IR (KBr) 2953, 1722, 900, 886, 798, 789, 677  $\text{cm}^{-1}$ . High resolution MS (EI 70 ev). Calcd for  $\text{C}_4\text{H}_2\text{I}_2\text{S}_2$ : m/z 367.7687. Found: m/z 367.7683.

**(Z,Z)-2,5-Di-2'-(trimethylsilyl)-ethylthio-2,4-hexadiene-1,6-dioic Acid Dimethyl Ester** In a 50-mL round-bottomed flask, manganese dioxide (1.24 g, 14.20 mmol) was suspended in a solution of sodium cyanide (245 mg, 4.98 mmol) in a mixture of acetic acid (87 mg, 1.42 mmol) and

methanol (10 mL) at room temperature. The solution was then treated with (*Z,Z*)-2,5-di-2'-(trimethylsilyl)ethylthio-2,4-hexadien-1,6-dial (266 mg, 0.71 mmol). The resulting mixture was kept stirring at room temperature for 0.5 h, upon which time it was filtered and the filtrate was poured into water (10 mL). The resulting mixture was extracted with ether (2 x 25 mL). The combined organic layers were washed first with water (50 mL) and then with brine (50 mL) and dried ( $\text{Na}_2\text{SO}_4$ ). Evaporation of the solvent by rotary evaporation afforded a brown residue, which was purified by silica gel flash column chromatography using hexanes/ethyl acetate (9/1) as the eluent to provide the titled dimethyl ester as a yellow solid (223 mg, 72%): mp 51-52 °C;  $R_f$  (hexanes/ethyl acetate, 9/1) 0.35;  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  0.03 (s, 18H), 0.85 (4H) and 2.91 (4H) (two sets of AA'XX'), 3.89 (s, 6H), 8.04 (s, 2H);  $^{13}\text{C}$  NMR (90.6 MHz,  $\text{CDCl}_3$ )  $\delta$  -1.85, 18.08, 30.27, 52.75, 135.27, 138.49, 165.69; IR (KBr) 2952, 1716, 1431, 1249, 1220, 1040, 861, 841  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{18}\text{H}_{34}\text{O}_4\text{S}_2\text{Si}_2$ : C, 49.73, H, 7.88. Found: C, 49.40, H, 8.16.

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SF 360.134  
SY 79.0  
O1 5800.000  
S1 32768  
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HZ/PT .244

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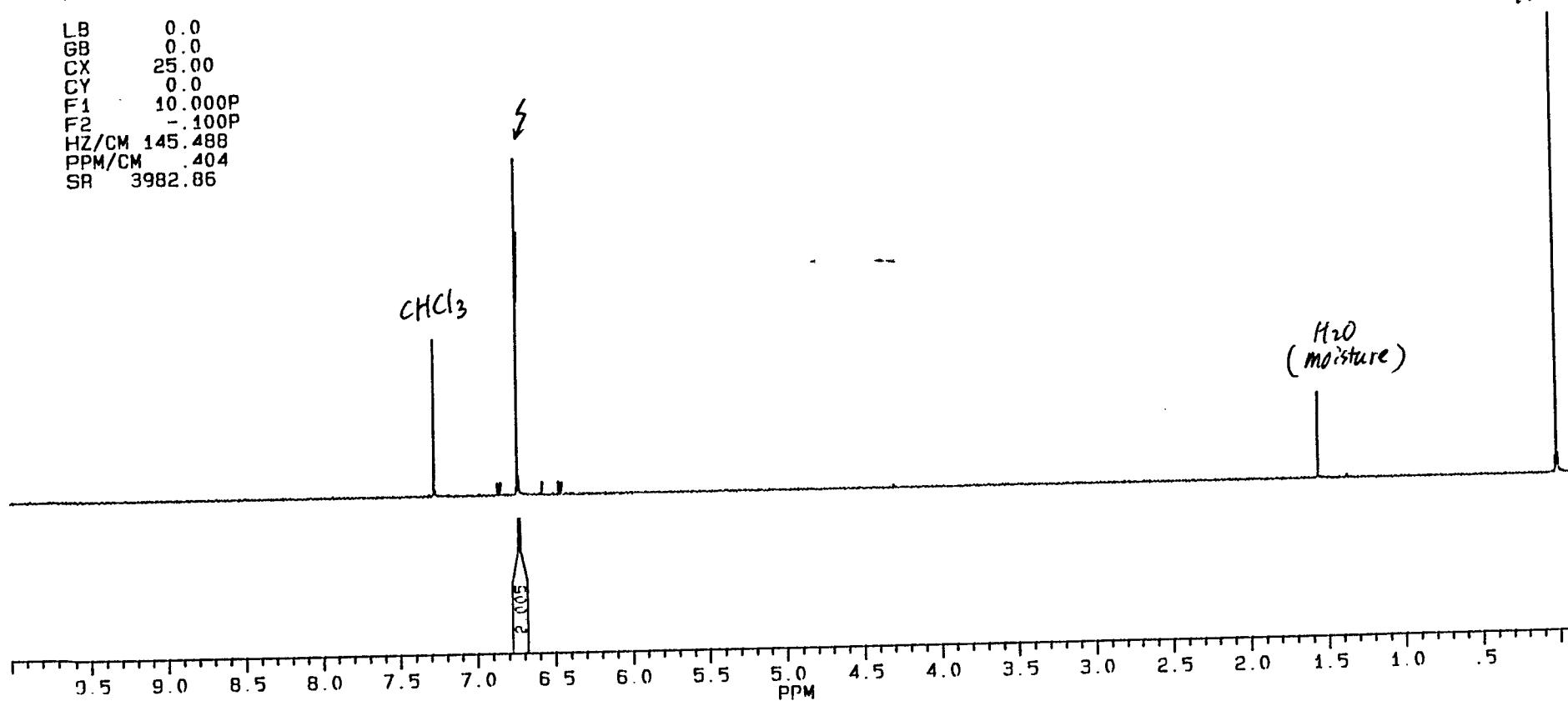
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PPM/CM .404  
SR 3982.86

360 MHz  $^1\text{H}$  NMR spectrum of 3,6-diiodo-1,2-dithiin (8; R = I) in  $\text{CDCl}_3$

#	CURSOR	FREQUENCY	PPM	INTENSITY
1	5714	2422.009	6.07254	5.492
2	15635	.069	.0002	7.669

10



90.6 MHz  $^{13}\text{C}$  NMR spectrum of 3,6-diiodo-1,2-dithiin (**8**; R = I) in  $\text{CDCl}_3$ 

	#	CURSOR	FREQUENCY	PPM	INTENSITY
<del>BRUKER</del>	1	5555	12679.459	140.0162 -	24.756
JDP19527	2	4072	12040.414	133.0477	1.558
DATE 20-3-96	3	10203	7005.663	77.3650	40.378
	4	10229	6970.823	77.0114	43.369
SF 90.556	5	10255	6941.976	76.6577	41.428
SY 174.0	6	10286	6904.010	76.2441 -	4.053
01 5220.000					
SI 32768	7	15942	.073	.0008	5.988
TD 32768					
SW 20000.000					
Hz/PT 1.221					

PW 4.1  
 RD .500  
 AQ .819

RG 8192  
 NS 4357  
 TE 297

FW 25000  
 Q2 6000.000  
 DP 14H CPD

LB -.600  
 GB .200  
 CX 25.00  
 CY 0.0  
 F1 200.005P  
 F2 -.998P  
 HZ/CM 728.076  
 PPM/CM 8.040  
 SR -4240.45

II

