Supporting Information

Direct Synthesis of Methylene-1,2-dichalcogenolanes via Radical [3+2] Cycloaddition of Methylenecyclopropanes with Elemental Chalcogens

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Experimental Section

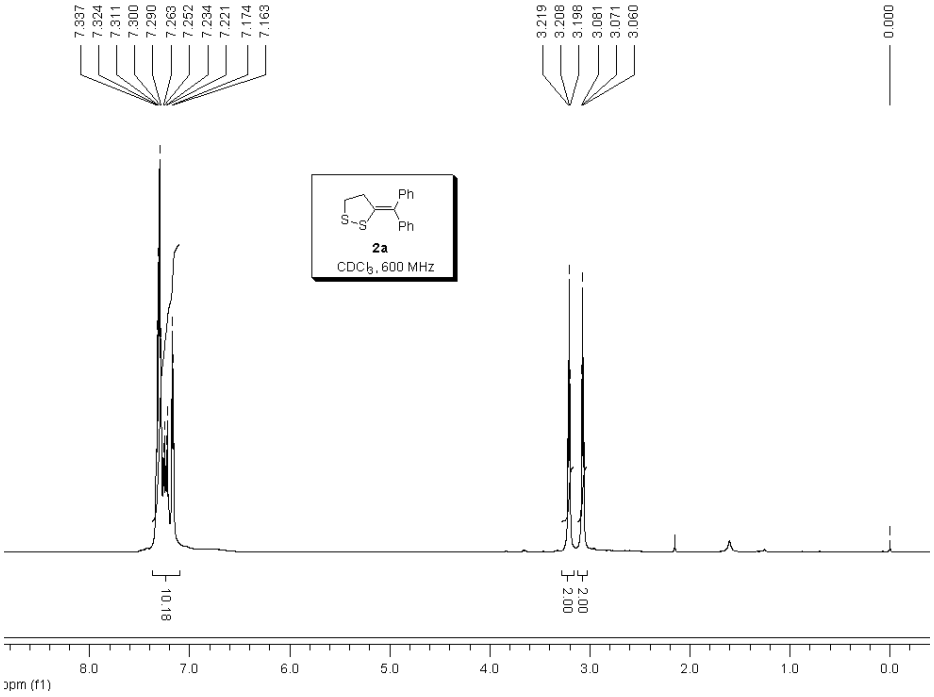
General. MCPs were prepared by literature methods (Brandi, A.; Goti, A. *Chem. Rev.* **1998**, *98*, 589). All solvents were dried by employing the standard methods. The reactions were performed under nitrogen atmosphere and then monitored by TLC. The products were purified by preparative TLC. Melting points were measured by a WRS-2A digital melting pointing instrument. ^{1}H and ^{13}C NMR (600 MHz for ^{1}H and 150 MHz for ^{13}C NMR spectroscopy) were recorded by using $CDCl_3$ as the solvent with TMS as the internal standard. *J*-values are shown in Hz.

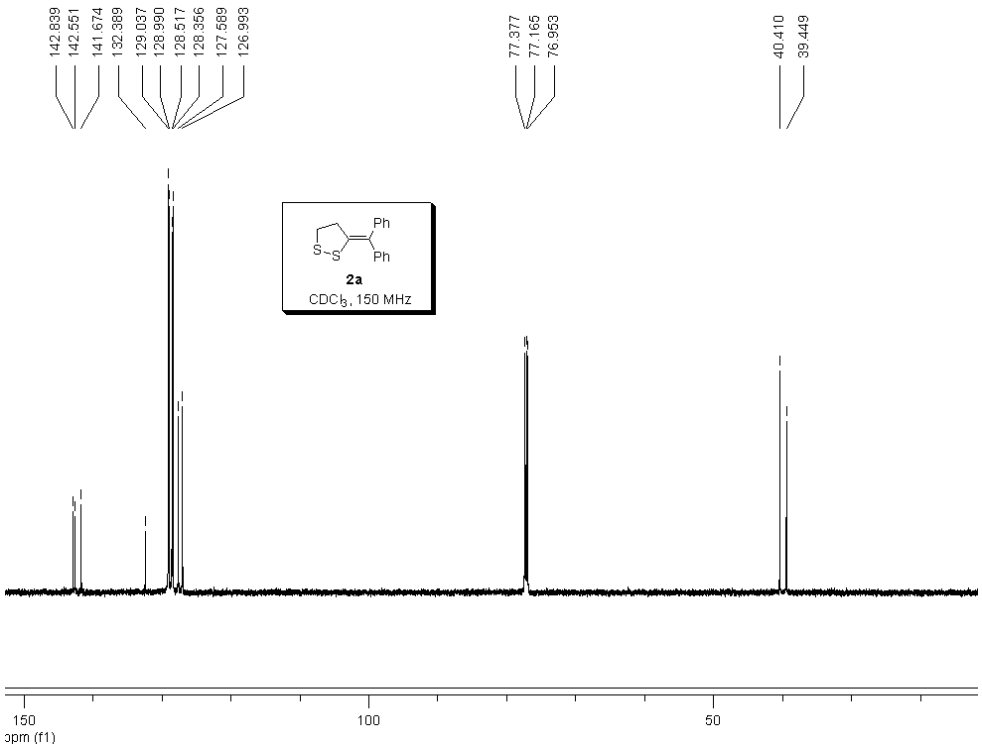
General procedure for reactions of MCPs with sulfur powder. A magnetic stirring bar and sulfur powder (0.66 mmol) were added to a Schlenk tube. The tube was then degassed and charged with nitrogen and a solution of a MCP (0.3 mmol) in DCE (1 mL) was injected under nitrogen. The mixture was then heated at 80 ^{o}C and monitored by TLC (eluent: petroleum ether). After completion of the reaction, the reaction mixture was transferred to a flask, the solvent evaporated, and the residue separated by preparative TLC (eluent: petroleum ether) to afford the corresponding methylene-1,2-dithiolanes **2**.

General procedure for reactions of MCPs with selenium or tellurium powder. A magnetic stirring bar, selenium (or tellurium) powder (0.66 mmol), and a MCP (0.3 mmol) were added to a Schlenk tube. The tube was then degassed and charged with nitrogen. The mixture was then heated at 220 ^{o}C for 3 h under nitrogen. After cooling to room temperature, the mixture was isolated by preparative TLC (eluent: petroleum ether) to afford the corresponding **3** or **4** (except compound **3n**, which was prepared in DCE at 80 ^{o}C as the method mentioned above).

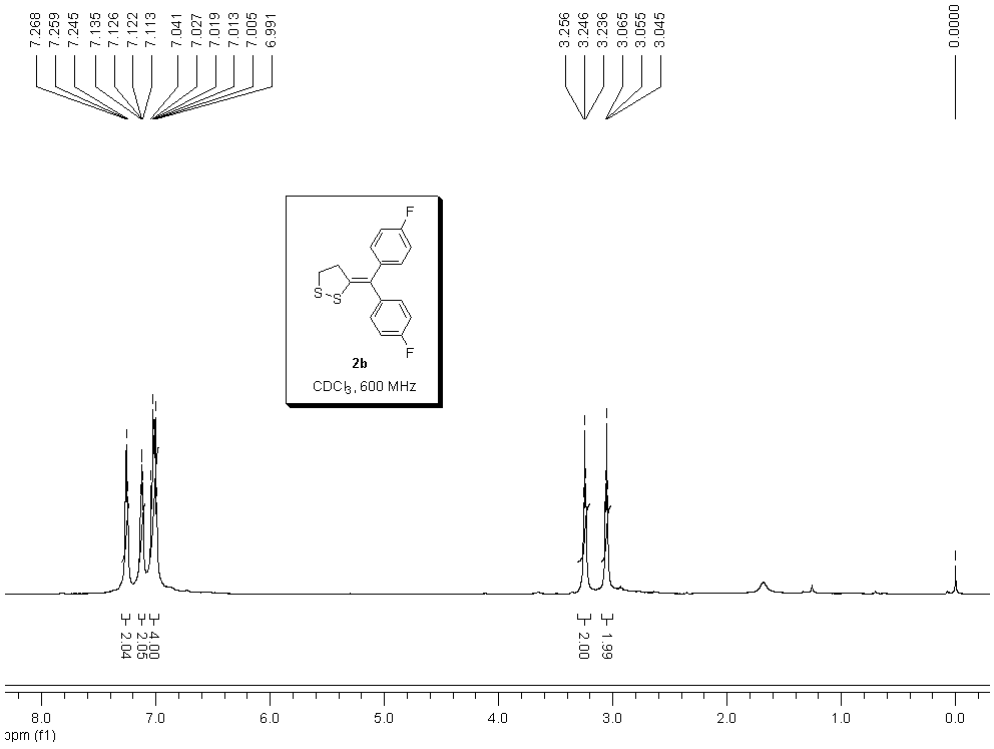
Characterization, ^{1}H and ^{13}C NMR Spectra of Products 2-4

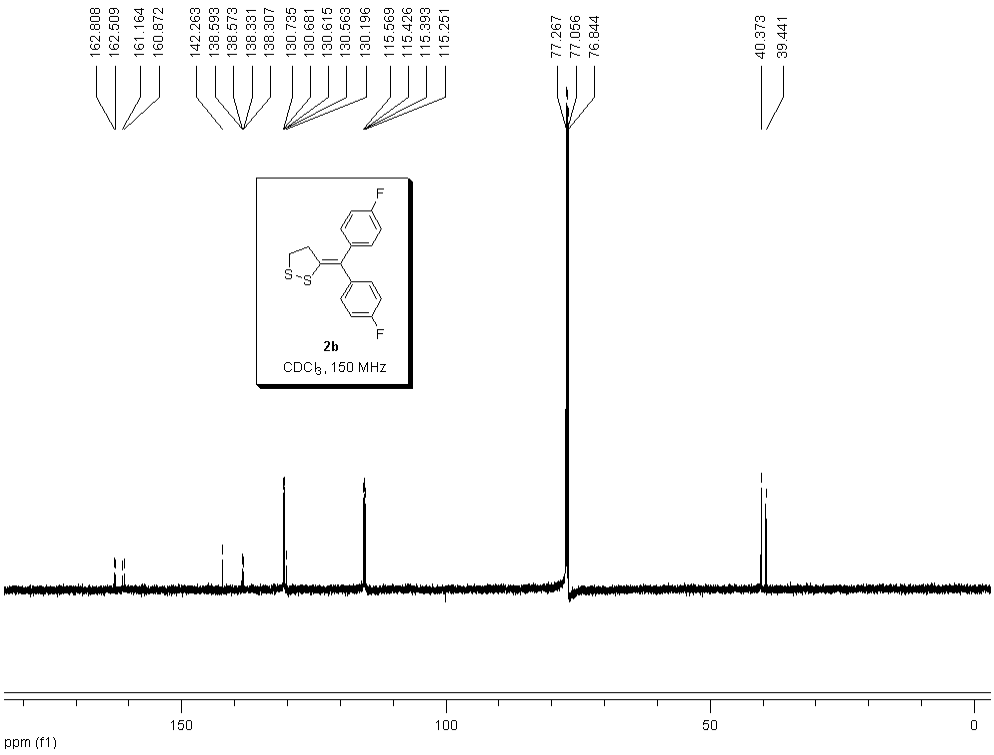
3-(Diphenylmethylene)-1,2-dithiolane (2a). Pale yellow crystal, m.p. 88.8-90.2 ^{o}C. IR (KBr): 2923, 2861, 1597, 1489, 1441, 1385, 1324, 1260, 1134, 1073, 755, 699 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, TMS, ppm): δ 7.16-7.34 (m, 10H), 3.21 (t, *J* = 6.3 Hz, 2H), 3.07 (t, *J* = 6.3 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 39.4, 40.4, 127.0, 127.6, 128.4, 128.5, 129.0 (d), 132.4, 141.7, 142.6, 142.8; MS (EI, 70 eV): *m/z* (%) 270 (100) [M^+], 237 (14), 223 (53); ***Anal. Calcd.*** for $C_{16}H_{14}S_2$: C, 71.07; H, 5.22. Found: 71.18; H, 5.35.



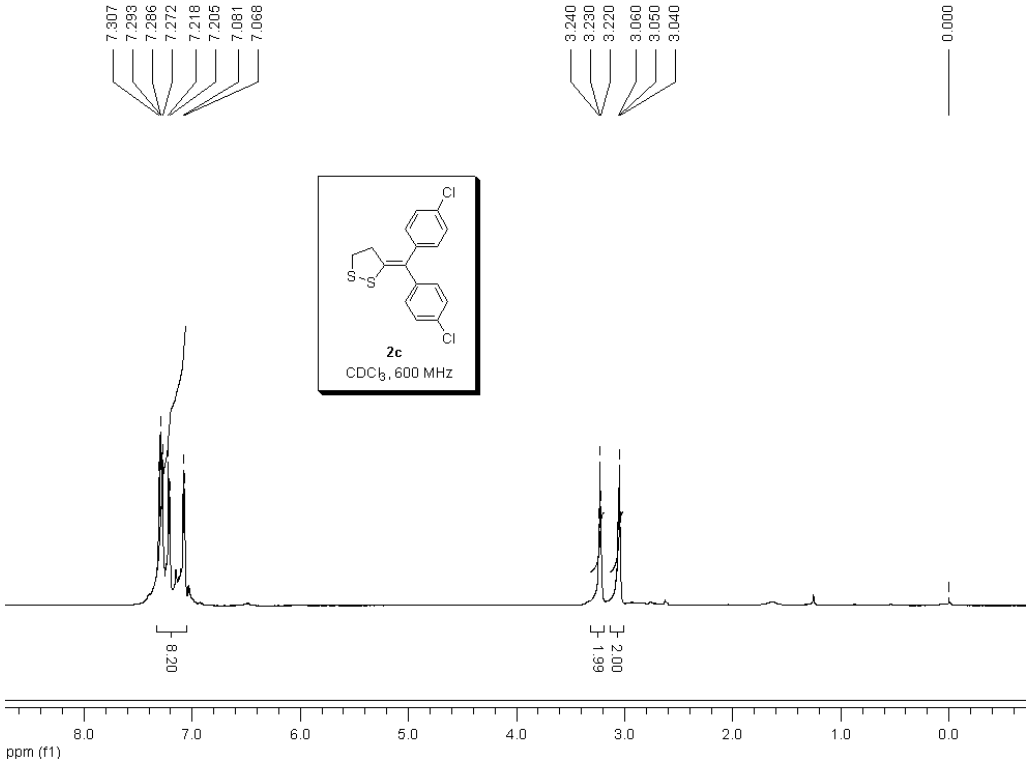


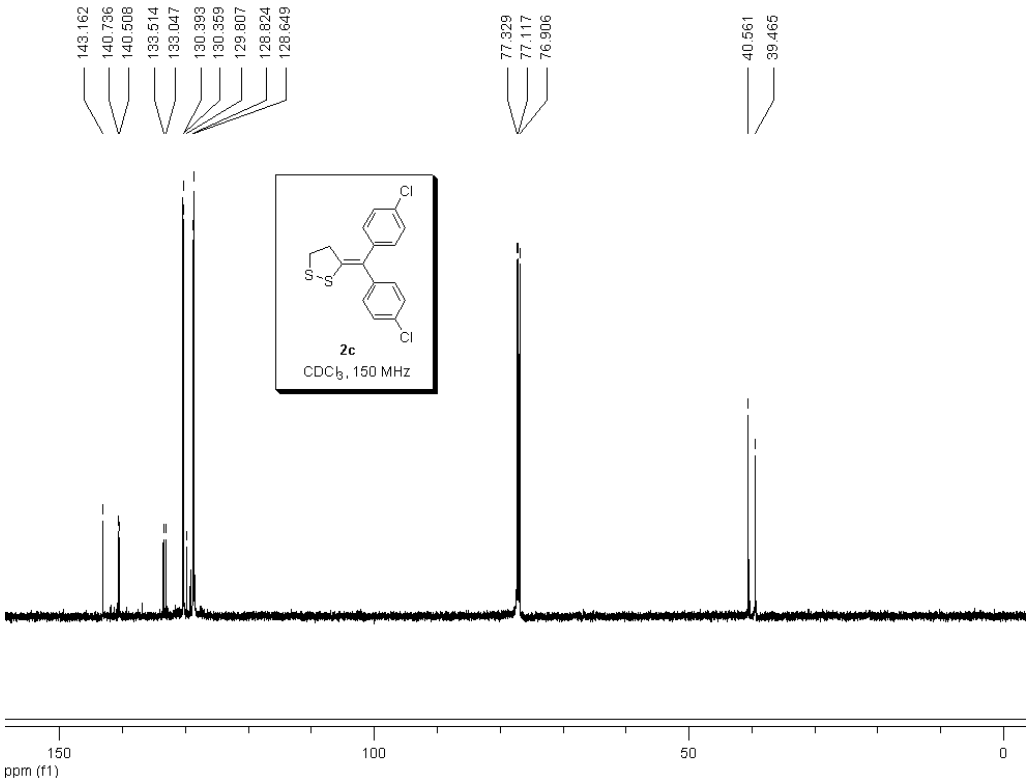
3-(Bis(4-fluorophenyl)methylene)-1,2-dithiolane (2b). Pale yellow oil. IR (film): 2977, 2871, 1706, 1591, 1503, 1383, 1222, 1153, 1126, 1067, 1013, 832 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, TMS, ppm): δ 6.99-7.27 (m, 8H), 3.25 (t, J = 6.0 Hz, 2H), 3.06 (t, J = 6.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 39.4, 40.4, 115.3 (d, J_{C-F} = 21.3 Hz), 115.5 (d, J_{C-F} = 21.5 Hz), 130.2, 130.6 (d, J_{C-F} = 7.8 Hz), 130.7 (d, J_{C-F} = 8.1 Hz), 138.3 (d, J_{C-F} = 3.6 Hz), 138.6 (d, J_{C-F} = 3.0 Hz), 142.3, 161.0 (d, J_{C-F} = 43.8 Hz), 162.7 (d, J_{C-F} = 44.9 Hz); MS (EI, 70 eV): *m/z* (%) 306 (100) [M^+], 273 (11), 259 (27); *Anal. Calcd.* for $C_{16}H_{12}F_2S_2$: C, 62.72; H, 3.95. Found: 62.84; H, 4.03.



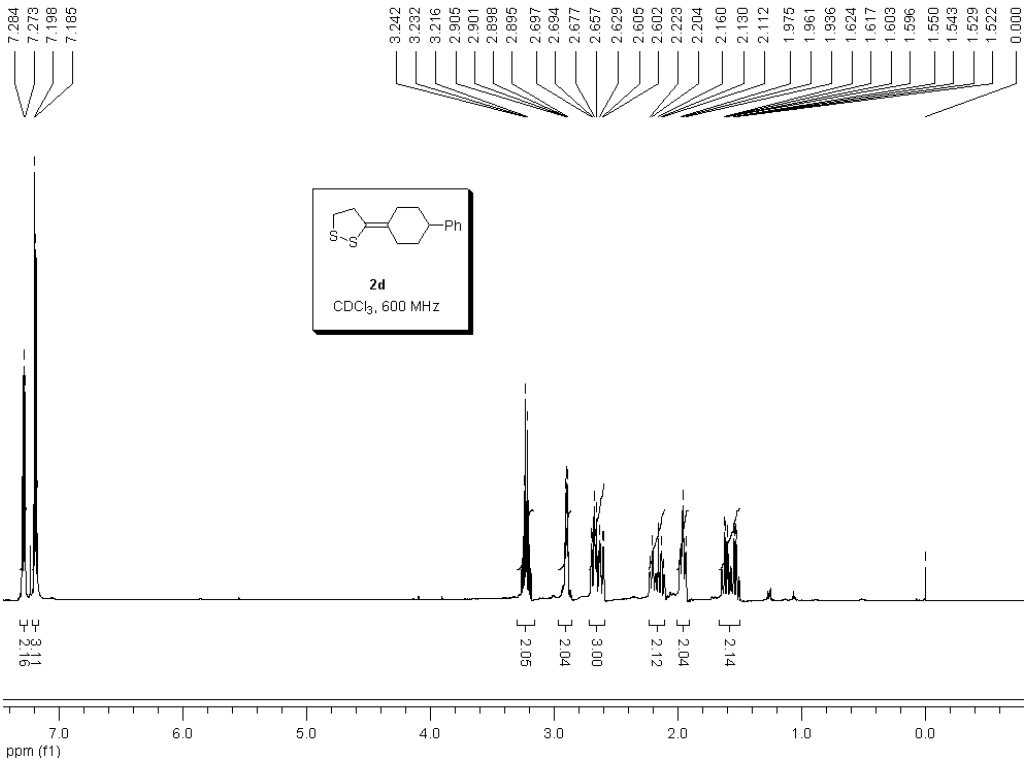


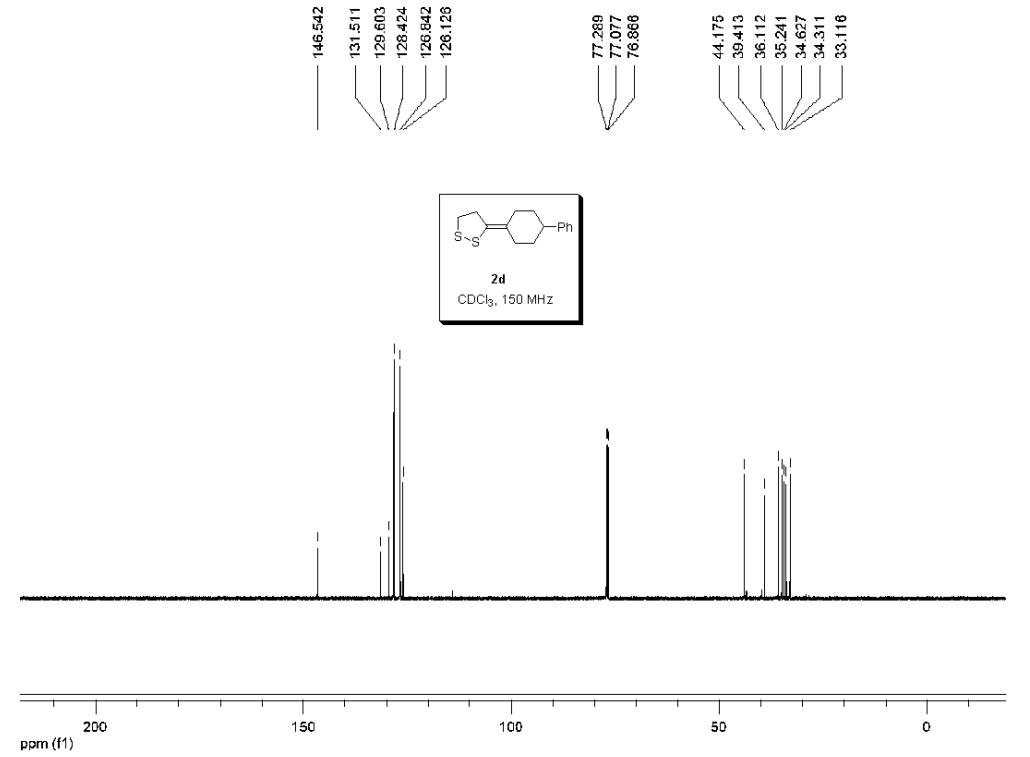
3-(Bis(4-chlorophenyl)methylene)-1,2-dithiolane (2c). Pale yellow oil. IR (film): 2984, 2871, 1486, 1392, 1137, 1090, 1014, 825, 786, 693 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, TMS, ppm): δ 7.07-7.31 (m, 8H), 3.23 (t, *J* = 6.0 Hz, 2H), 3.05 (t, *J* = 6.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 39.5, 40.6, 128.6, 128.8, 129.8, 130.4 (d), 133.0, 133.5, 140.5, 140.7, 143.2; MS (EI, 70 eV): *m/z* (%) 338 (34) [M^+], 318 (21), 84 (100); *Anal. Calcd.* for $C_{16}H_{12}Cl_2S_2$: C, 56.64; H, 3.56. Found: 56.77; H, 3.72.



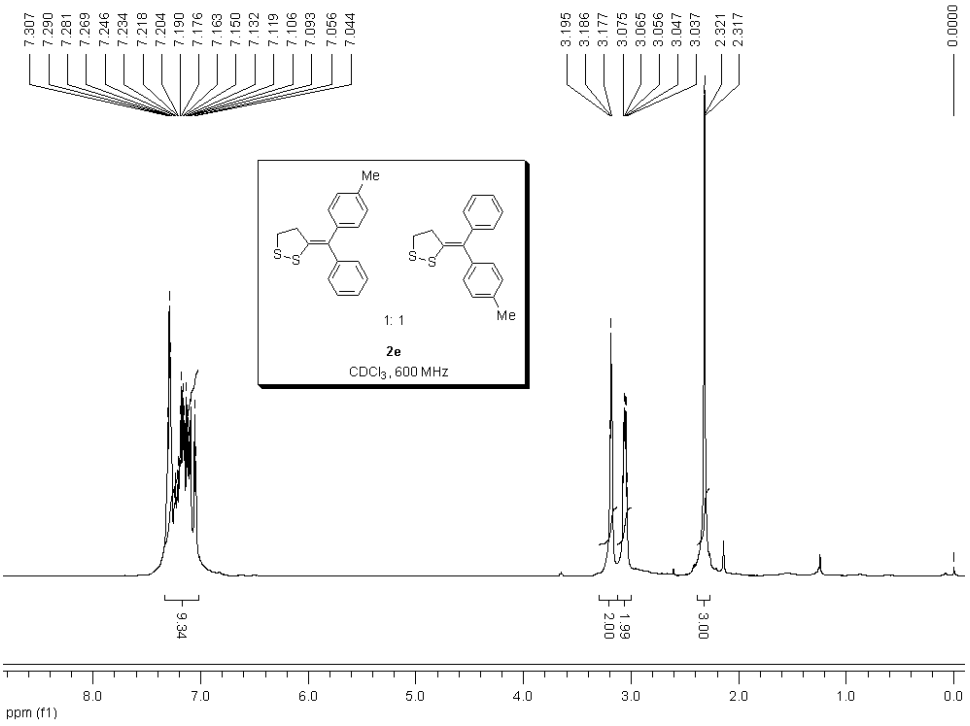


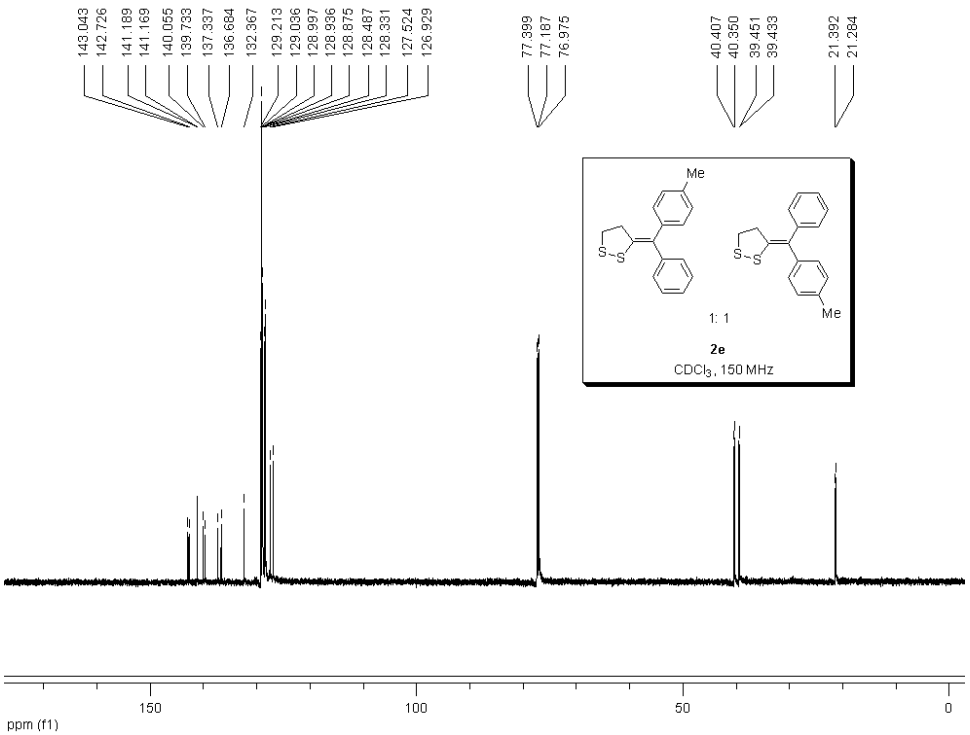
3-(4-Phenylcyclohexylidene)-1,2-dithiolane (2d). Pale yellow oil. IR (film): 2983, 2925, 2865, 1491, 1443, 1386, 1264, 1137, 1075, 976, 753, 698 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS, ppm): δ 7.28 (d, *J* = 6.6 Hz, 2H), 7.19-7.20 (m, 3H), 3.22-3.24 (m, 2H), 2.90-2.91 (m, 2H), 2.60-2.70 (m, 3H), 2.11-2.22 (m, 2H), 1.94-1.98 (m, 2H), 1.52-1.62 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 33.1, 34.3, 34.6, 35.2, 36.1, 39.4, 44.2, 126.1, 126.8, 128.4, 129.6, 131.5, 146.5; MS (EI, 70 eV): *m/z* (%) 262 (100) [M^+], 229 (6), 174 (43); *Anal. Calcd.* for $C_{15}H_{18}S_2$: C, 68.65; H, 6.91. Found: C, 68.83; H, 6.79.



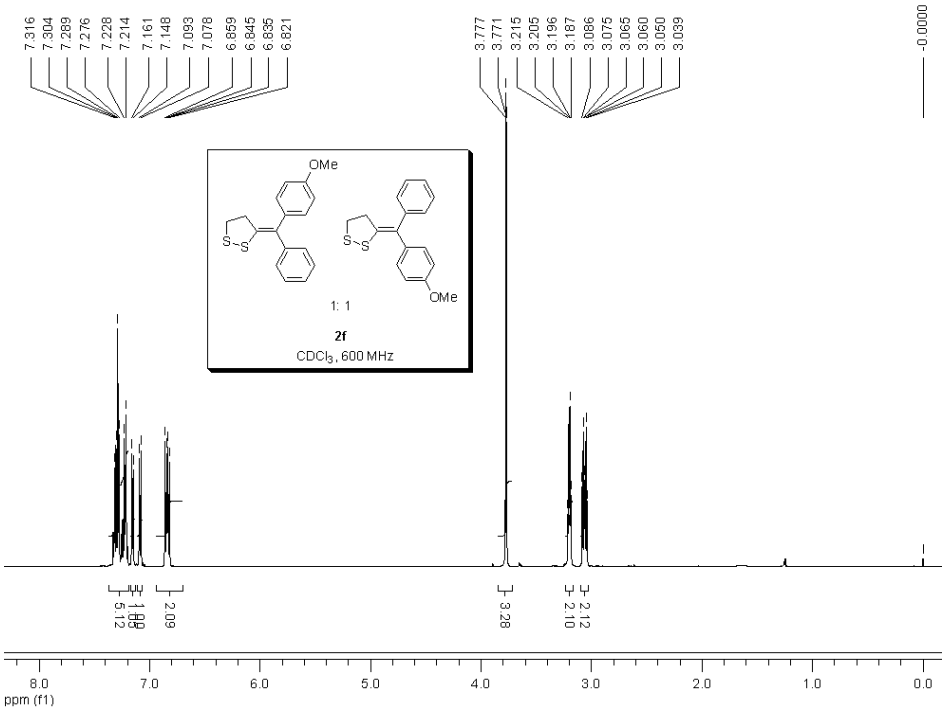


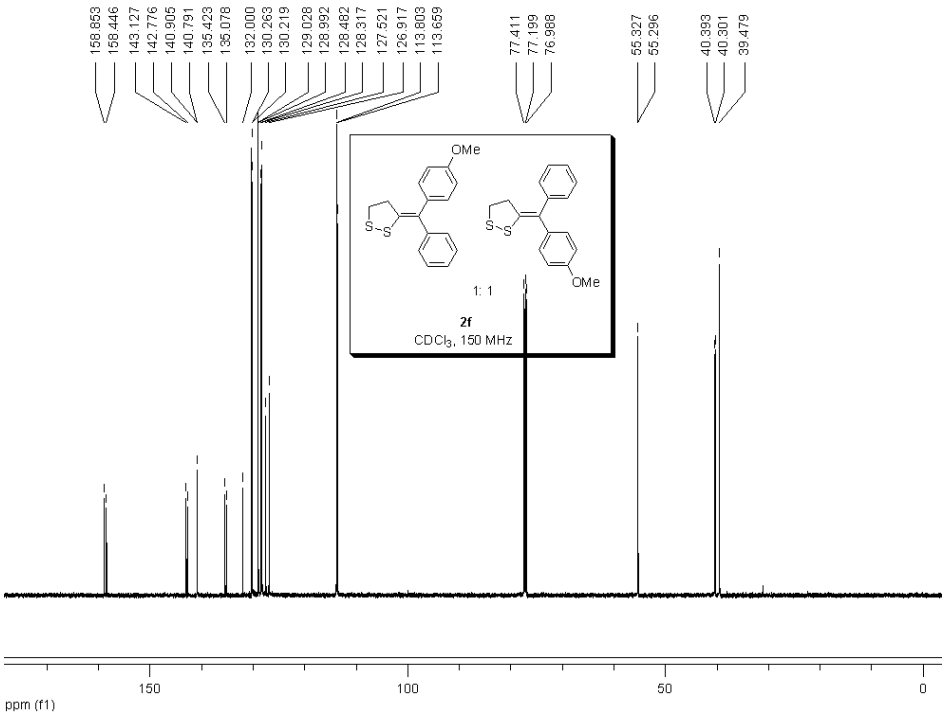
3-((4-Methylphenyl)(phenyl)methylene)-1,2-dithiolane (2e, *Z/E* 50/50). Pale yellow crystal, m.p. 72.4-74.1 ^{o}C. IR (KBr): 3050, 3022, 2979, 2920, 2868, 1596, 1506, 1442, 1261, 1179, 1131, 1073, 1029, 818, 741, 700 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, TMS, ppm): δ 7.04-7.31 (m, 9H), 3.18-3.20 (m, 2H), 3.04-3.08 (m, 2H), 2.32 [d(2 isomers' single peak), 3H); ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 21.3, 21.4, 39.4, 39.5, 40.4 (d), 126.9, 127.5, 128.3, 128.5, 128.9 (d), 129.0 (d), 129.2, 132.4, 136.7, 137.3, 139.7, 140.1, 141.2(d), 142.7, 143.0; MS (EI, 70 eV): *m/z* (%) 284 (100) [M^+], 251 (16), 237 (44), 221 (47); *Anal. Calcd.* for $C_{17}H_{16}S_2$: C, 71.78; H, 5.67. Found: 71.82; H, 5.75.



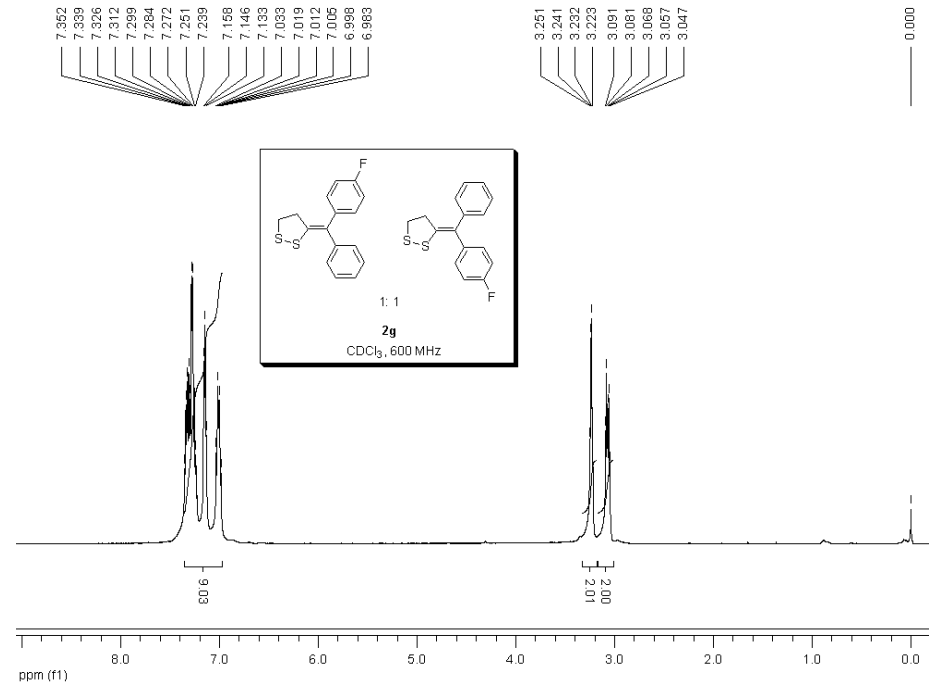


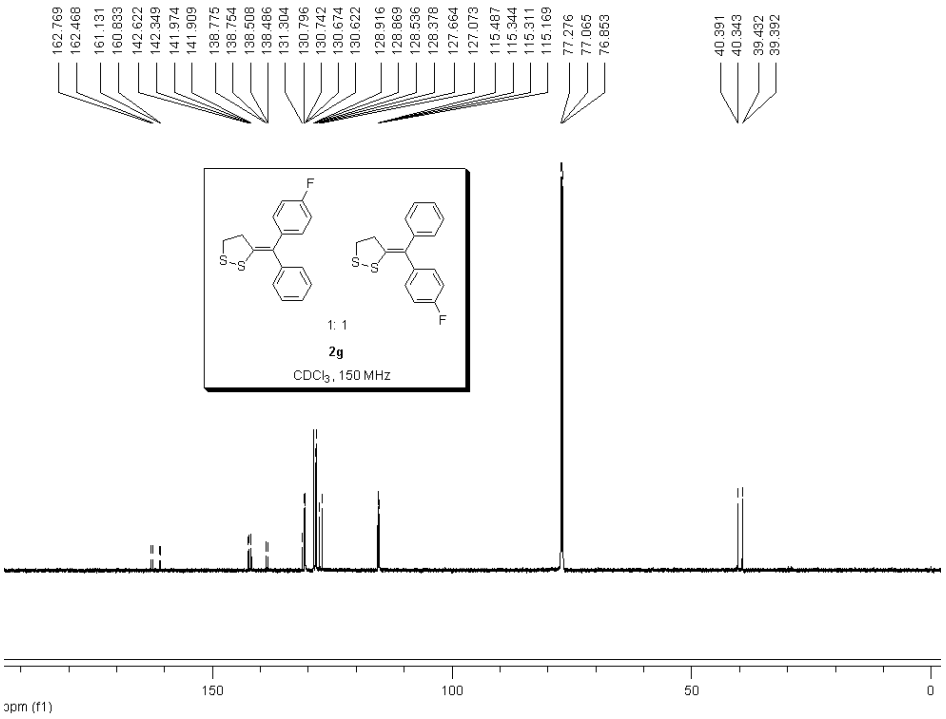
3-((4-Methoxyphenyl)(phenyl)methylene)-1,2-dithiolane (2f, *Z/E* 50/50). Pale yellow oil. IR (film): 2986, 2873, 1603, 1507, 1445, 1385, 1283, 1246, 1175, 1137, 1073, 1032, 830, 782, 743, 699 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS, ppm): δ 7.08-7.32 (m, 7H), 6.82-6.86 (m, 2H), 3.77[d(2 isomers' single peak), 3H], 3.19-3.22 (m, 2H), 3.04-3.09 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 39.5, 40.3, 40.4, 55.3 (d), 113.7, 113.8, 126.9, 127.5, 128.3, 128.5, 129.0 (d), 130.2, 130.3, 132.0, 135.1, 135.4, 140.8, 140.9, 142.8, 143.1, 158.4, 158.9; MS (EI, 70 eV): *m/z* (%) 300 (100) [M^+], 268 (16) [M^+-S], 236 (25) [M^+-2S]; HRMS (EI): *m/z* calcd for $C_{17}H_{16}OS_2$ 300.0643, Found 300.0646.



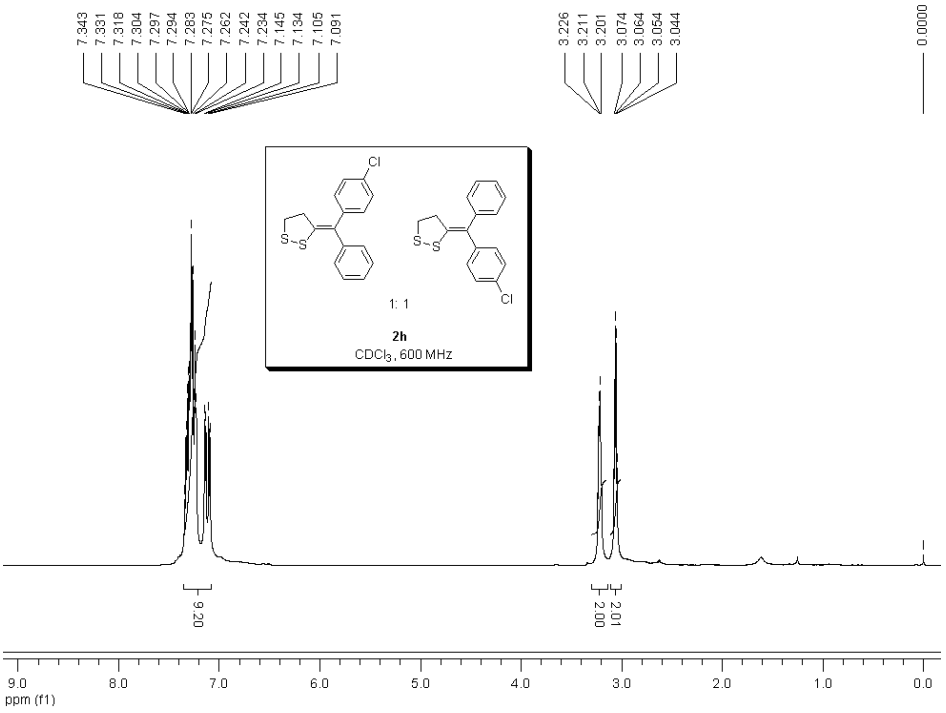


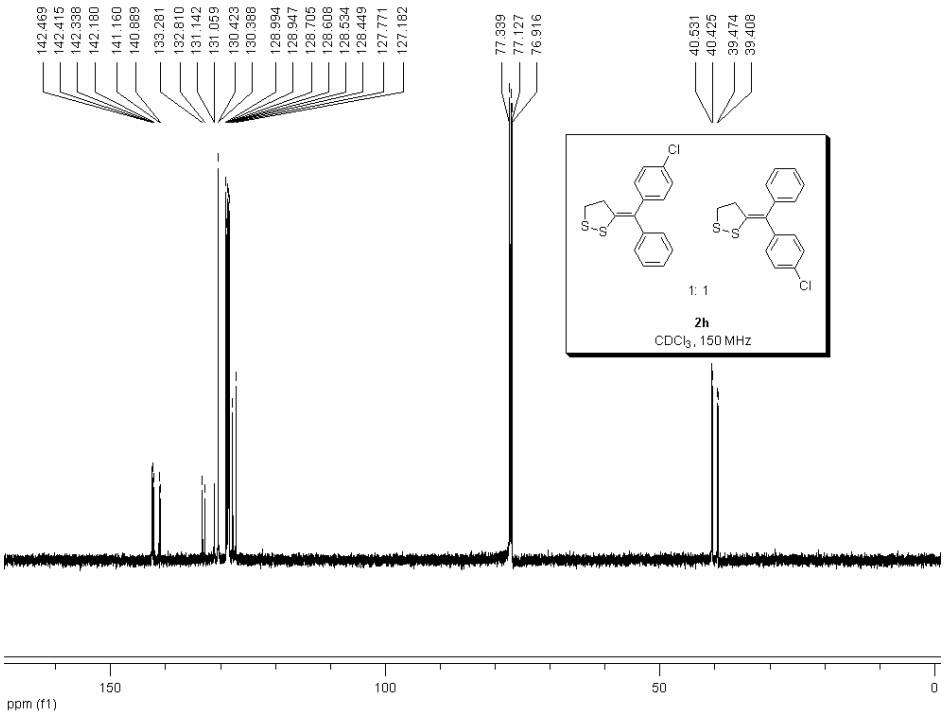
3-((4-Fluorophenyl)(phenyl)methylene)-1,2-dithiolane (2g, *Z/E* 50/50). Pale yellow oil. IR (film): 3054, 2983, 2926, 2871, 1597, 1502, 1440, 1225, 1150, 1075, 831, 745, 699 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS, ppm): δ 6.98-7.35 (m, 9H), 3.22-3.25 (m, 2H), 3.05-3.09 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 39.4 (d), 40.3, 40.4, 115.2 (d, J_{C-F} = 21.3 Hz), 115.4 (d, J_{C-F} = 21.5 Hz),127.1, 127.7, 128.4, 128.5, 128.9 (d, J_{C-F} = 7.1 Hz), 130.6 (d, J_{C-F} = 7.8 Hz), 130.7 (d, J_{C-F} = 8.1 Hz), 131.3, 138.5 (d, J_{C-F} = 3.3 Hz), 138.8 (d, J_{C-F} = 3.2 Hz), 141.9 (d, J_{C-F} = 9.8 Hz), 142.3, 142.6, 161.0 (d, J_{C-F} = 44.7 Hz), 162.6 (d, J_{C-F} = 45.2 Hz); MS (EI, 70 eV): *m/z* (%) 288 (100) [M^+], 255 (10), 241 (35); ***Anal. Calcd.*** for $C_{16}H_{13}FS_2$: C, 66.63; H, 4.54. Found: 66.80; H, 4.73.



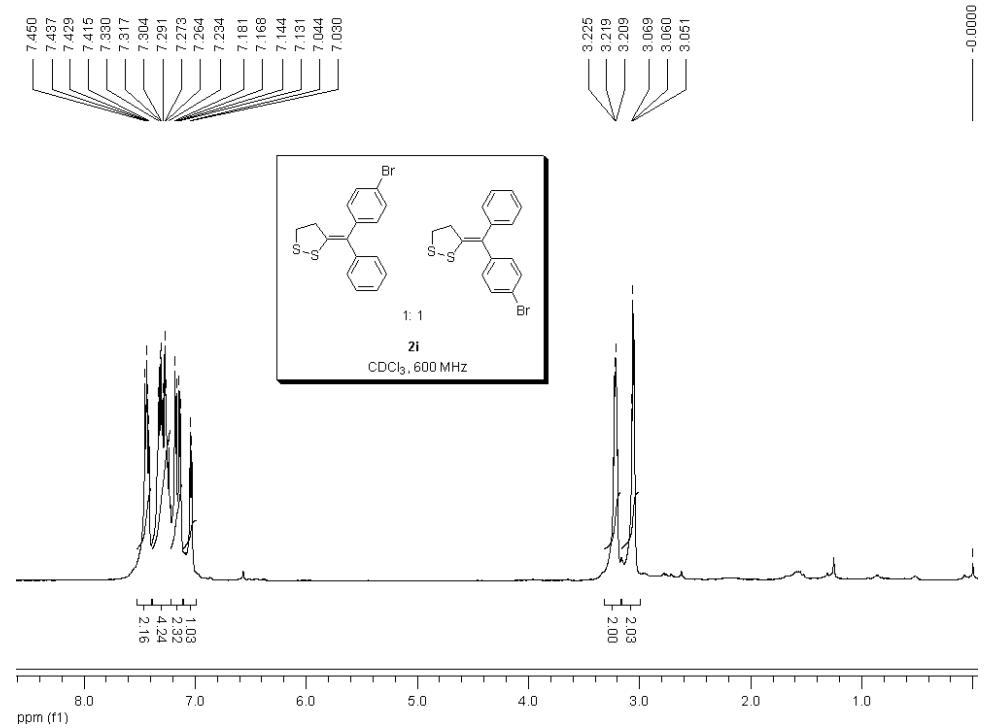


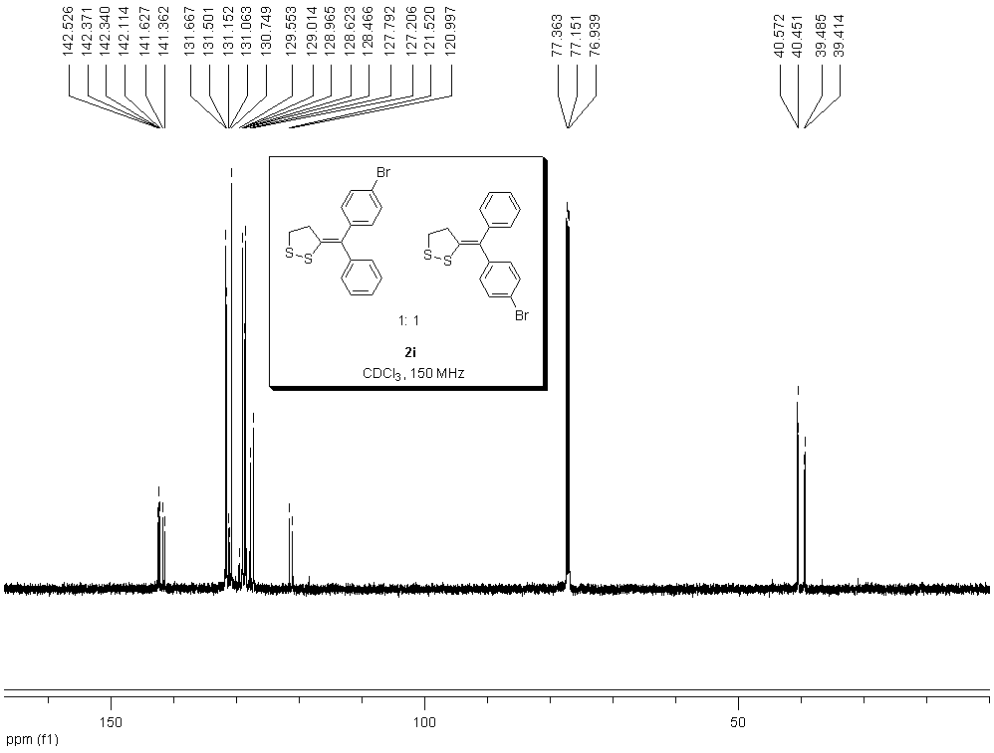
3-((4-Chlorophenyl)(phenyl)methylene)-1,2-dithiolane (2h, *Z/E* 50/50). Pale yellow oil. IR (film): 2984, 2872, 1486, 1440, 1389, 1260, 1137, 1086, 1014, 826, 759, 699 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, TMS, ppm): δ 7.09-7.34 (m, 9H), 3.20-3.23 (m, 2H), 3.04-3.07 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 39.4, 39.5, 40.4, 40.5, 127.2, 127.8, 128.4, 128.5, 128.6, 128.7, 128.9, 129.0, 130.4 (d), 131.1 (d), 132.8, 133.3, 140.9, 141.2, 142.2, 142.3, 142.4, 142.5; MS (EI, 70 eV): *m/z* (%) 304 (100) [M^+], 271 (8), 257 (12), 221 (26), 118 (47); *Anal. Calcd.* for $C_{16}H_{13}ClS_2$: C, 63.04; H, 4.30. Found: 63.26; H, 4.42.



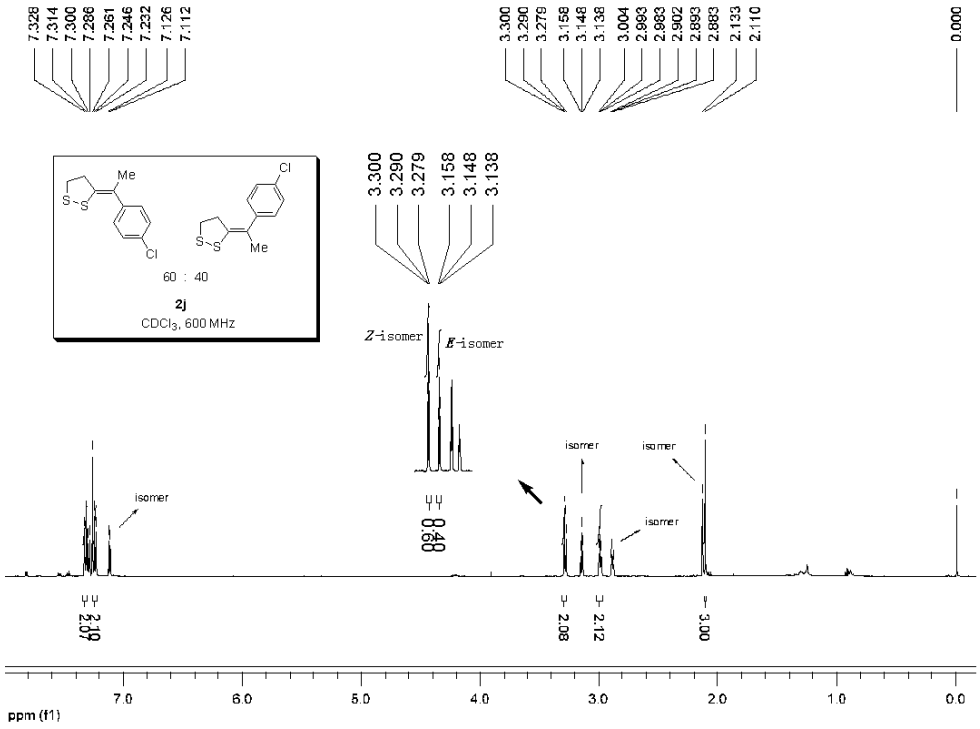


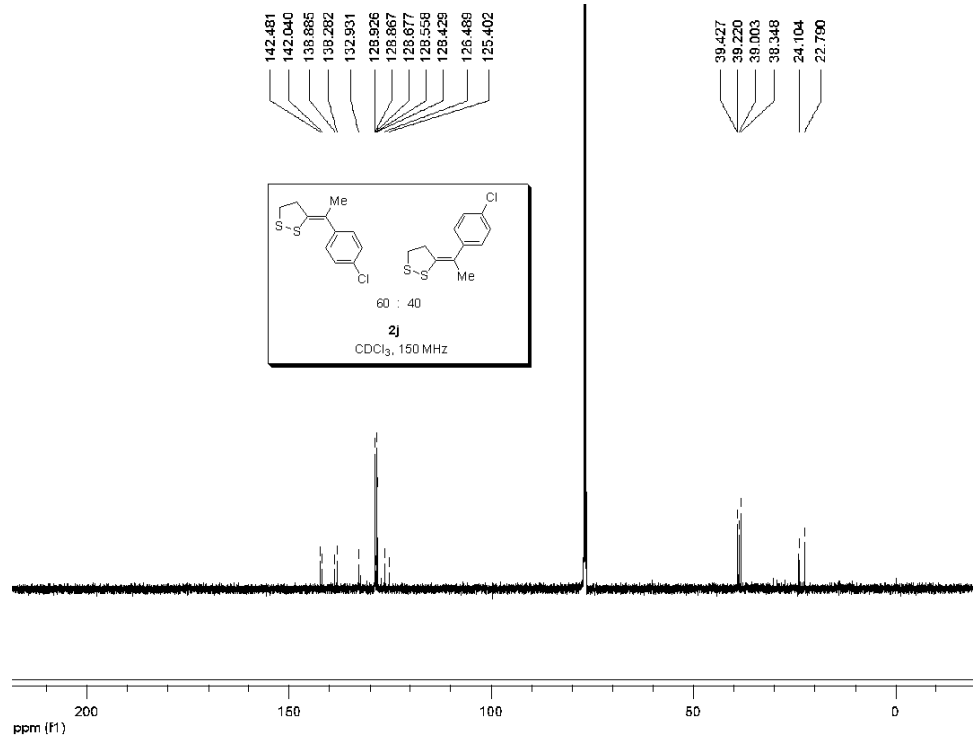
3-((4-Bromophenyl)(phenyl)methylene)-1,2-dithiolane (2i, *Z/E* 50/50). Pale yellow oil. IR (film): 3056, 3021, 2980, 2925, 2873, 1592, 1485, 1440, 1390, 1262, 1136, 1070, 1009, 824, 757, 700 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, TMS, ppm): δ 7.03-7.45 (m, 9H), 3.21-3.23 (m, 2H), 3.05-3.07 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 39.4, 39.5, 40.5, 40.6, 121.0, 121.5, 127.2, 127.8, 128.5, 128.6, 129.0 (d), 129.6, 130.7, 131.1, 131.2, 131.5, 131.7, 141.4, 141.6, 142.1, 142.3, 142.4, 142.5; MS (EI, 70 eV): *m/z* (%) 350 (100), 348 (90) [M^+], 221 (56); ***Anal. Calcd.*** for $C_{16}H_{13}BrS_2$: C, 55.01; H, 3.75. Found: 55.18; H, 3.96.



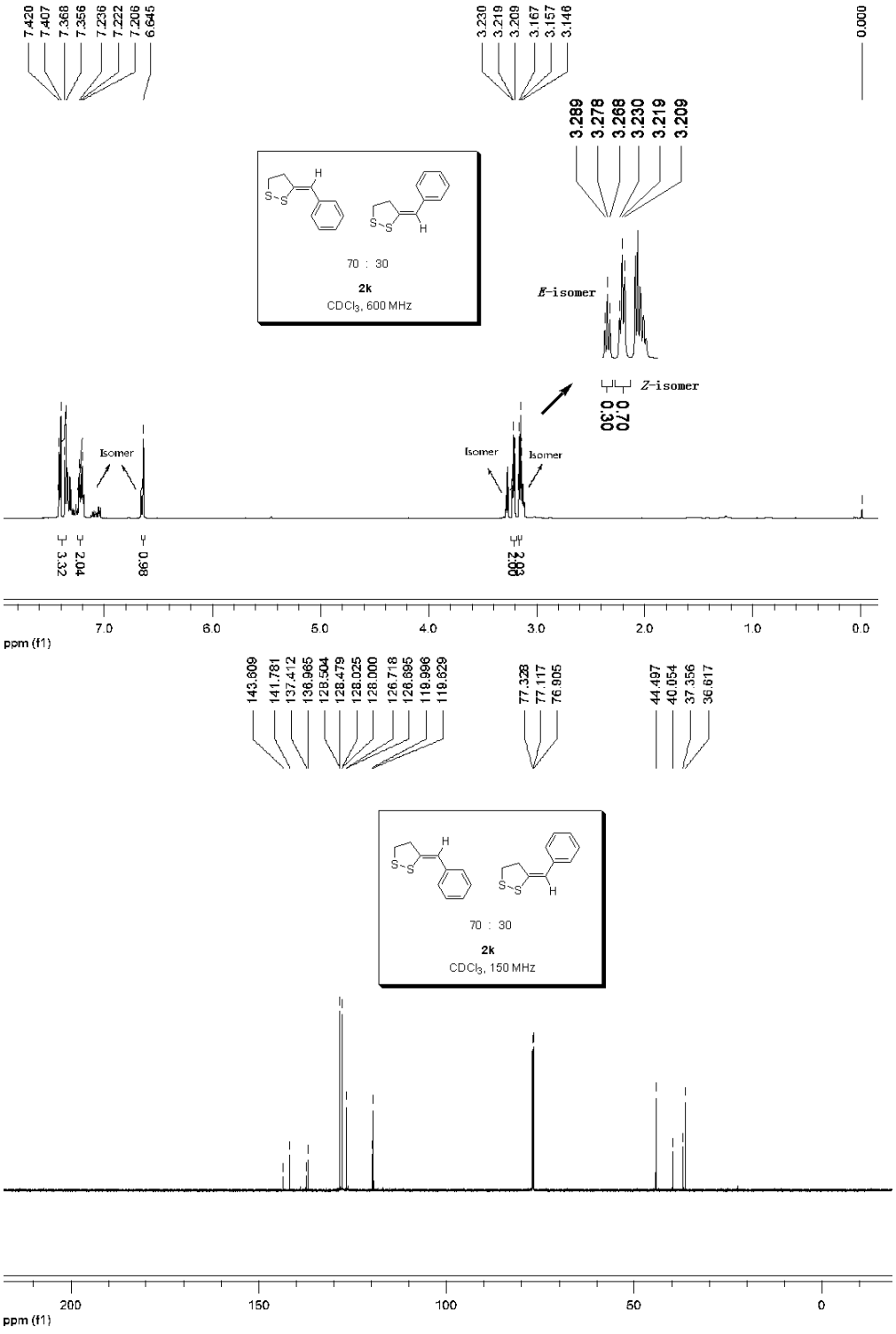


(*Z*)-3-(1-(4-Chlorophenyl)ethylidene)-1,2-dithiolane (2j, *Z/E* 60/40). Pale yellow oil. IR (film): 2925, 2868, 1655, 1601, 1485, 1389, 1248, 1136, 1091, 1012, 962, 827, 754, 689 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS, ppm): δ 7.23-7.33 (m, 4H), 3.29 (t, *J* = 6.3 Hz, 2H), 2.99 (t, *J* = 6.3 Hz, 2H), 2.11 (s, 3H); ^{13}C NMR (*Z, E* mixtures, 150 MHz, $CDCl_3$, ppm): δ 22.8, 24.1, 38.3, 39.0, 39.2, 39.4, 125.4, 126.5, 128.4, 128.6, 128.7, 128.9 (d), 132.9, 138.3, 138.9, 142.0, 142.5; MS (EI, 70 eV): *m/z* (%) 242 (56) [M^+], 162 (18) [M-Se], 84 (100); *Anal. Calcd.* for $C_{11}H_{11}ClS_2$: C, 54.42; H, 4.57. Found: C, 54.64; H, 4.70. For determination of the stereochemistry of the isomers, see NOESY spectra section in SI for detail. For determination of the ratio of the *Z/E* isomers, see focused ^1H NMR spectra below.

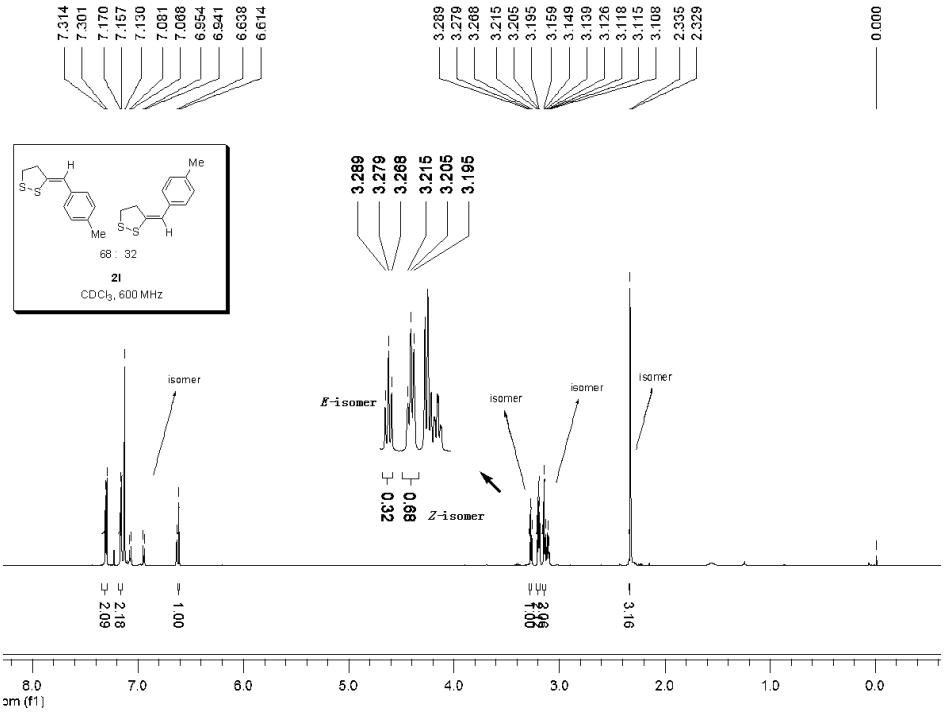


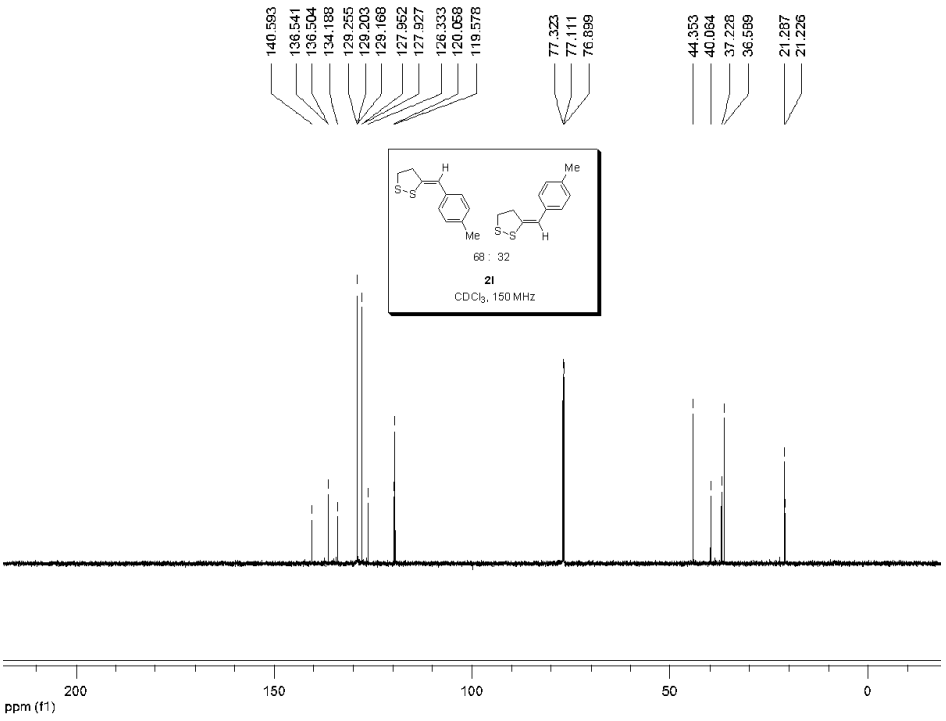


(*Z*)-3-Benzylidene-1,2-dithiolane (2k, *Z/E* 70/30). Pale yellow oil. IR (film): 3052, 3017, 2986, 2924, 1637, 1603, 1489, 1443, 1417, 1281, 1256, 1136, 1079, 1032, 962, 907, 841, 749, 691, 617 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS, ppm): δ 7.21-7.42 (m, 5H), 6.65 (s, 1H), 3.22 (t, *J* = 6.3 Hz, 2H), 3.16 (t, *J* = 6.3 Hz, 2H); ^{13}C NMR (*Z, E* mixtures, 150 MHz, $CDCl_3$, ppm): δ 36.6, 37.4, 40.1, 44.5, 119.6, 120.0, 126.7 (d), 128.0 (d), 128.5 (d), 137.0, 137.4, 141.8, 143.6; MS (EI, 70 eV): *m/z* (%) 194 (100) [M^+], 161 (27), 147 (68), 128 (40); *Anal. Calcd.* for $C_{10}H_{10}S_2$: C, 61.81; H, 5.19. Found: C, 61.88; H, 5.33. Stereochemistry of the isomers can be determined by analogy with those of **2o** or **2q** (see NOESY spectra section in the SI for detail). For determination of the ratio of the *Z/E* isomers, see focused ^1H NMR spectra below.

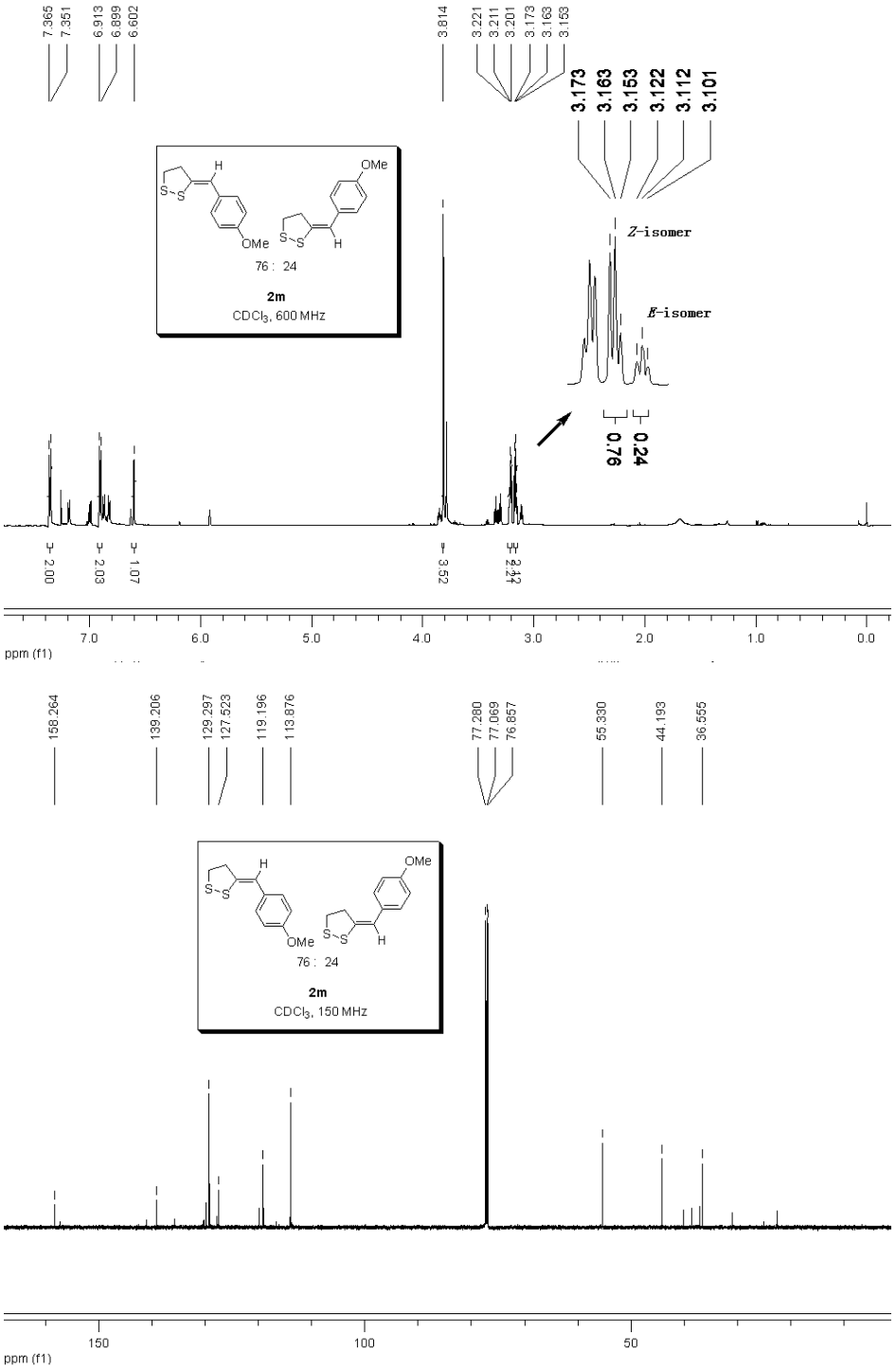


(*Z*)-3-(4-Methylbenzylidene)-1,2-dithiolane (2l, *Z/E* 68/32). Pale yellow oil. IR (film): 2989, 2917, 2870, 1639, 1611, 1510, 1414, 1384, 1130, 1068, 850, 798, 709 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS, ppm): δ 7.31 (d, *J* = 7.8 Hz, 2H), 7.16 (d, *J* = 7.8 Hz, 2H), 6.61 (s, 1H), 3.21 (t, *J* = 6.0 Hz, 2H), 3.15 (t, *J* = 6.0 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (*Z, E* mixtures, 150 MHz, $CDCl_3$, ppm): δ 21.2, 21.3, 36.6, 37.2, 40.1, 44.4, 119.6, 120.1, 126.3, 127.9, 128.0, 129.2 (d), 129.3, 134.2, 136.5 (d), 140.6; MS (EI, 70 eV): *m/z* (%) 208 (100) [M^+], 193 (64), 176 (100) [M^+-S]; *Anal. Calcd.* for $C_{11}H_{12}S_2$: C, 63.41; H, 5.81. Found: C, 63.67; H, 5.92. Stereochemistry of the isomers can be determined by analogy with those of **2o** or **2q** (see NOESY spectra section in the SI for detail). For determination of the ratio of the *Z/E* isomers, see focused ^1H NMR spectra below.

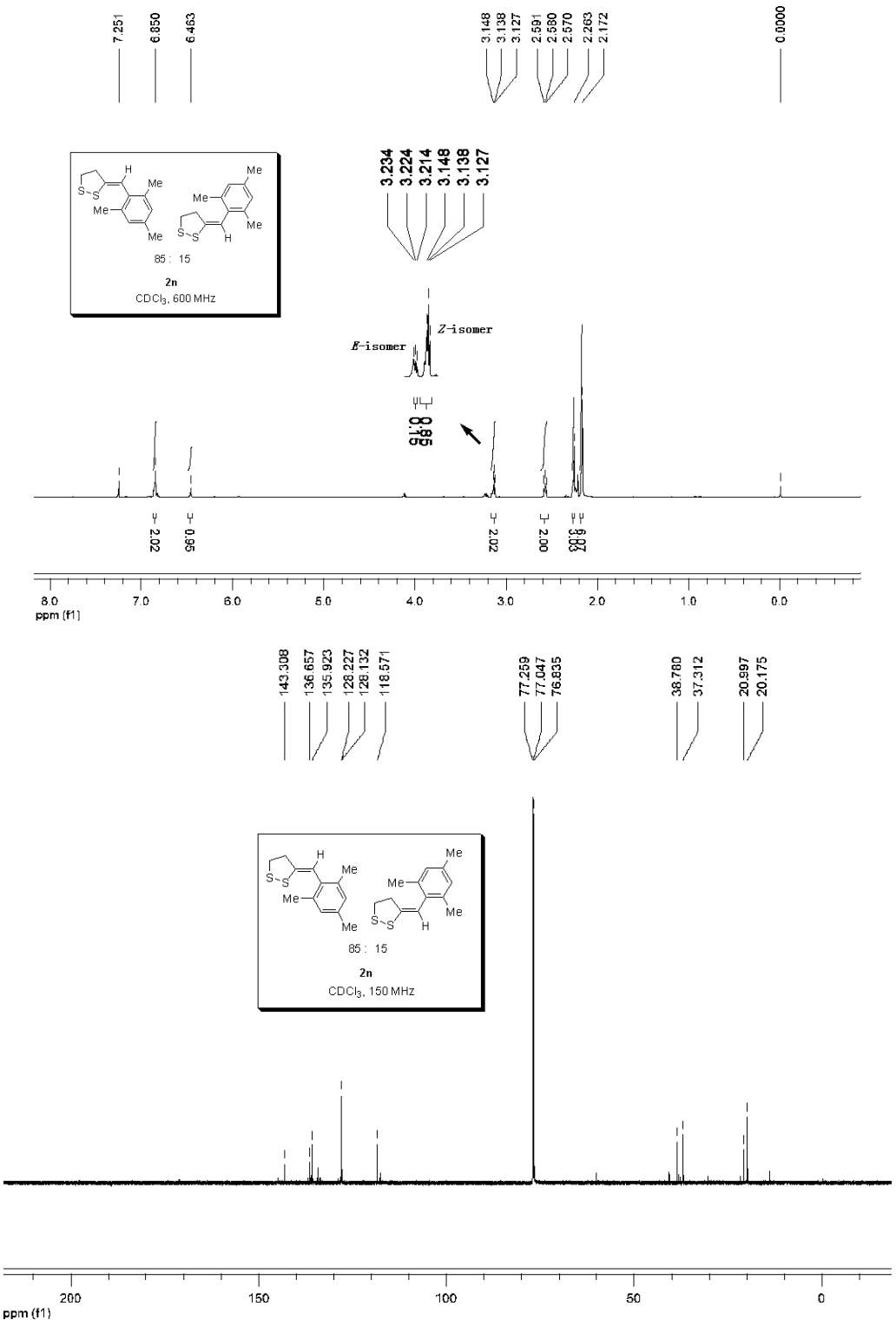




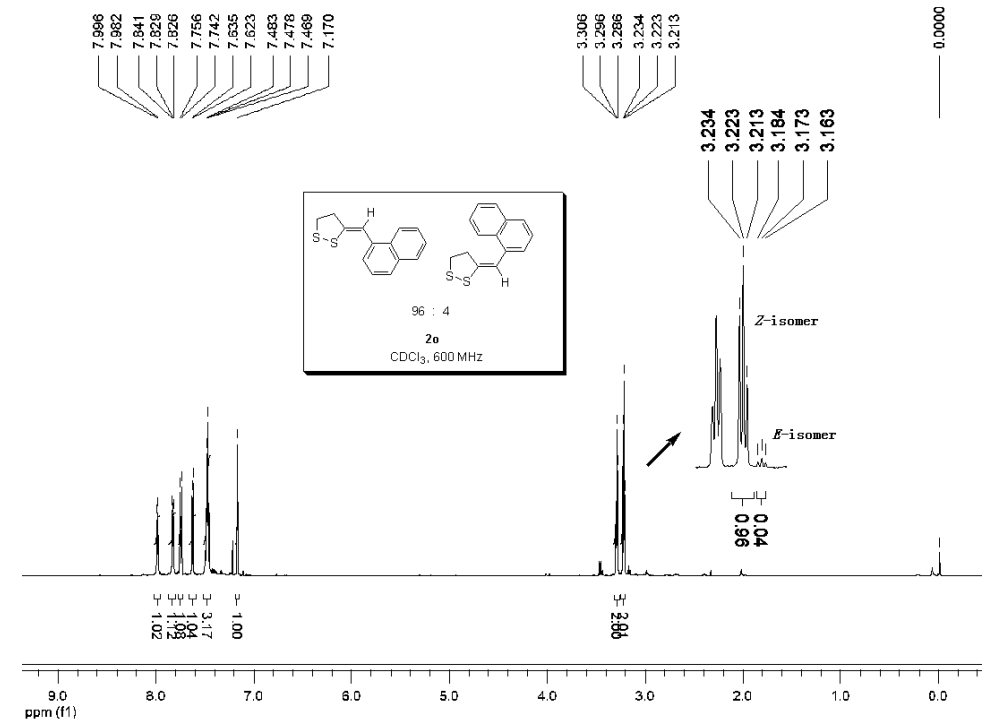
(*Z*)-3-(4-Methoxybenzylidene)-1,2-dithiolane (2m, *Z*/*E* 76/24). Pale yellow oil. IR (film): 2985, 2872, 1637, 1606, 1507, 1458, 1387, 1294, 1248, 1173, 1138, 1071, 1032, 845 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS, ppm): δ 7.36 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.60 (s, 1H), 3.81 (s, 3H), 3.21 (t, *J* = 6.0 Hz, 2H), 3.16 (t, *J* = 6.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 36.6, 44.2, 55.3, 113.9, 119.2, 127.5, 129.3, 139.2, 158.3; MS (EI, 70 eV): *m/z* (%) 224 (71) [M^+], 192 (100), 177 (38), 164 (62); *Anal. Calcd.* for $C_{11}H_{12}OS_2$: C, 58.89; H, 5.39. Found: C, 59.06; H, 5.24. Stereochemistry of the isomers can be determined by analogy with those of **2o** or **2q** (see NOESY spectra section in the SI for detail). For determination of the ratio of the *Z*/*E* isomers, see focused ^1H NMR spectra below.

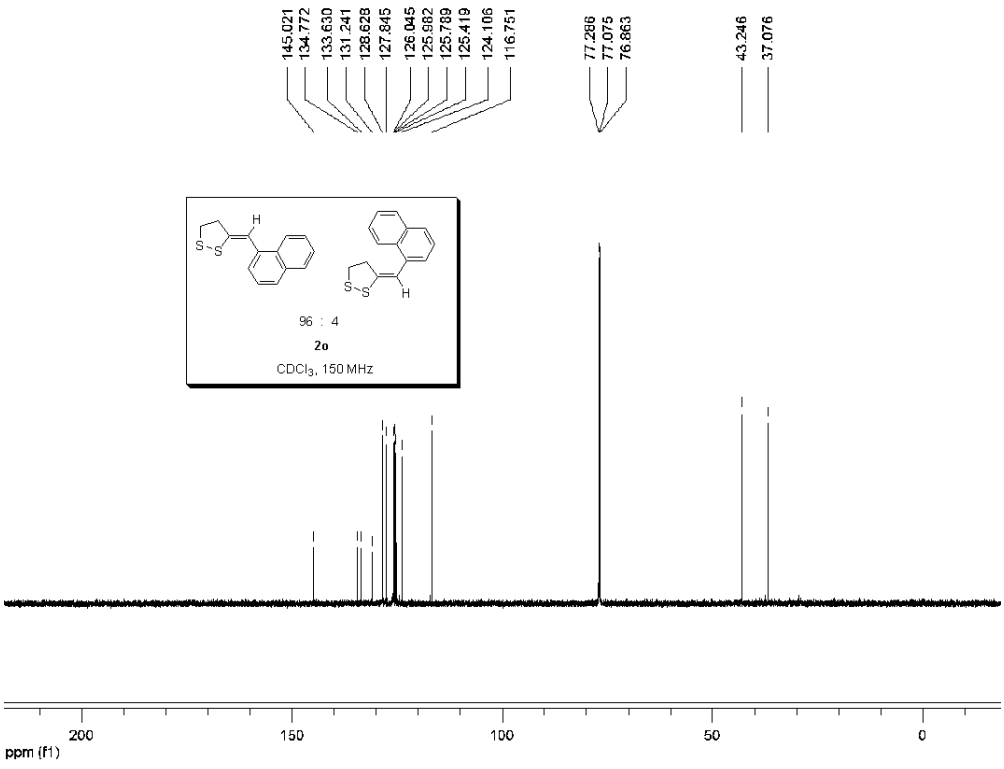


(*Z*)-3-(2,4,6-Trimethylobenzylidene)-1,2-dithiolane (2n, *Z*/*E* 85/15). Pale yellow oil. IR (film): 2983, 2915, 2869, 1612, 1441, 1381, 1323, 1136, 1071, 1037, 852, 682 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS, ppm): δ 6.85 (s, 2H), 6.46 (s, 1H), 3.14 (t, *J* = 6.3 Hz, 2H), 2.58 (t, *J* = 6.3 Hz, 2H), 2.26 (s, 3H), 2.17 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 20.2, 21.0, 37.3, 38.8, 118.6, 128.1, 128.2, 135.9, 136.7, 143.3; MS (EI, 70 eV): *m/z* (%) 236 (100) [M^+], 203 (14), 189 (34), 175 (36), 157 (70); *Anal. Calcd.* for $C_{13}H_{16}S_2$: C, 66.05; H, 6.82. Found: C, 65.83; H, 6.65. Stereochemistry of the isomers can be determined by analogy with those of **2o** or **2q** (see NOESY spectra section in the SI for detail). For determination of the ratio of the *Z*/*E* isomers, see focused ^1H NMR spectra below.

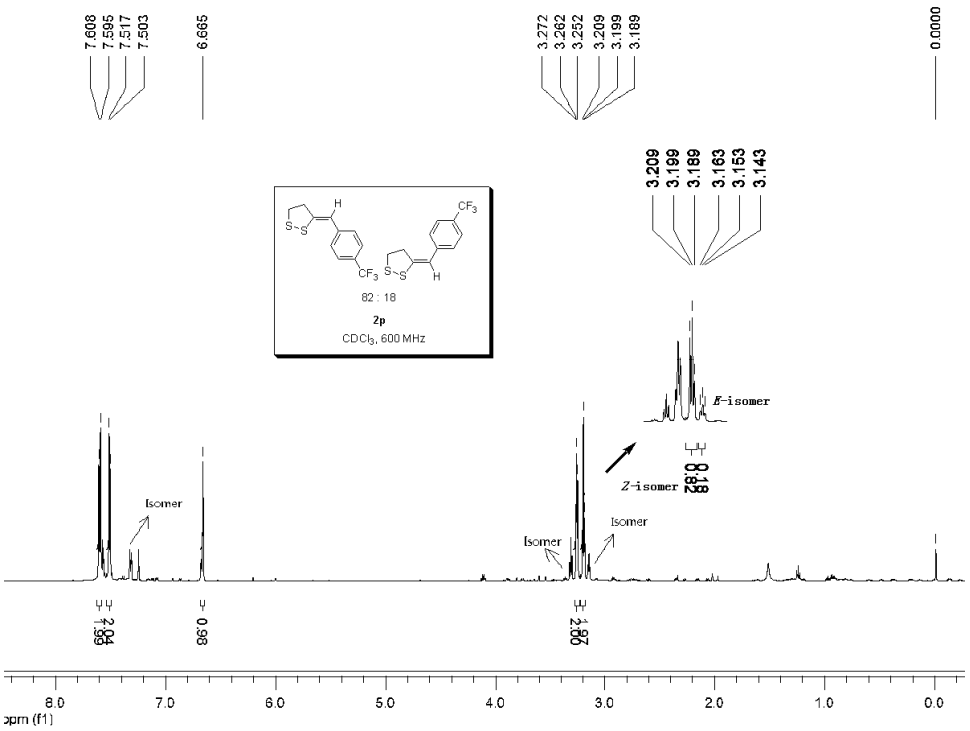


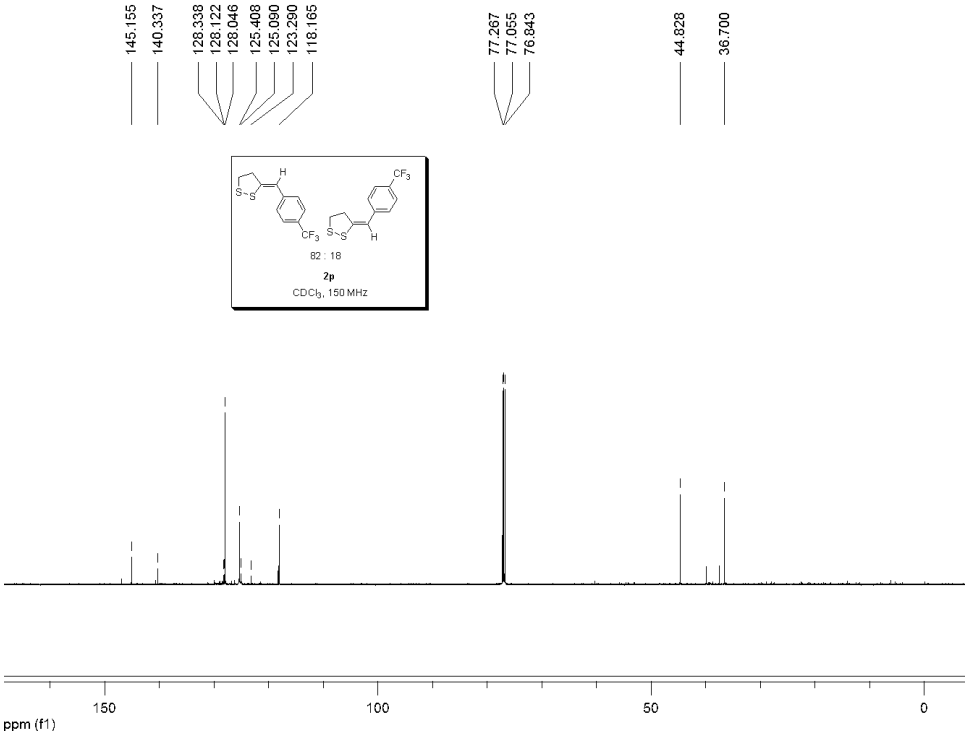
(*Z*)-3-(Naphthalen-1-ylmethylene)-1,2-dithiolane (2o, *Z/E* 96/4). Pale yellow oil. IR (film): 3050, 2923, 2856, 1595, 1505, 1418, 1389, 1287, 1208, 1137, 1076, 1033, 957, 774, 622 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS, ppm): δ 7.47-8.00 (m, 7H), 7.17 (s, 1H), 3.30 (t, *J* = 6.0 Hz, 2H), 3.22 (t, *J* = 6.3 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 37.1, 43.2, 116.8, 124.1, 125.4, 125.8, 126.0 (d), 127.8, 128.6, 131.2, 133.6, 134.8, 145.0; MS (EI, 70 eV): *m/z* (%) 244 (47) [M^+], 211 (12), 197 (100), 178 (32), 165 (61); *Anal. Calcd.* for $C_{14}H_{12}S_2$: C, 68.81; H, 4.95. Found: C, 68.93; H, 5.21. For determination of the stereochemistry of the isomers, see NOESY spectra section in SI for detail. For determination of the ratio of the *Z/E* isomers, see focused ^1H NMR spectra below.



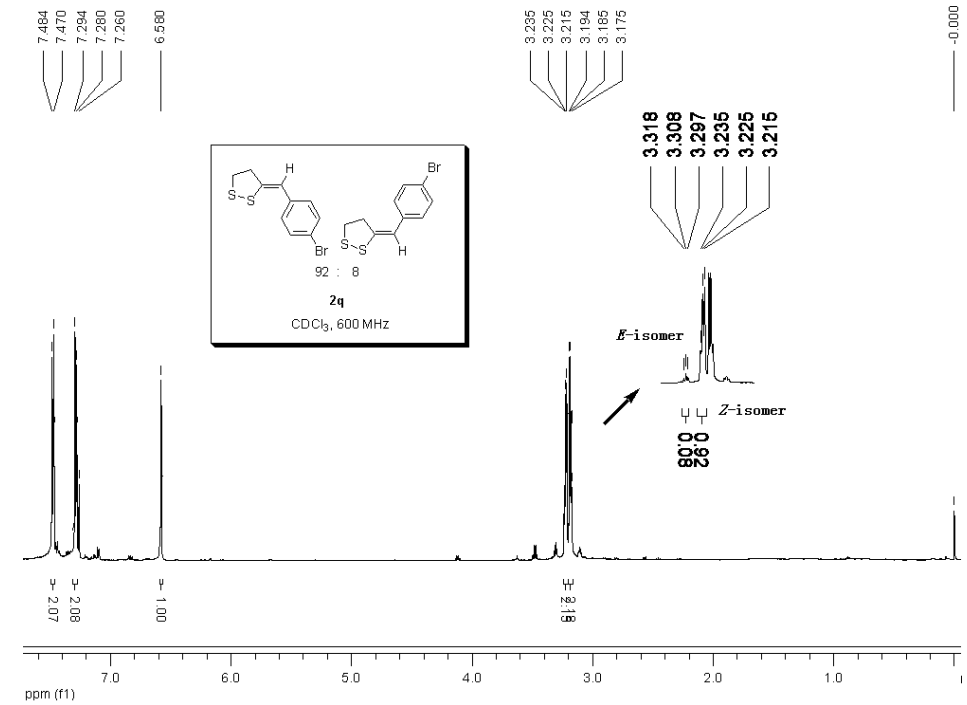


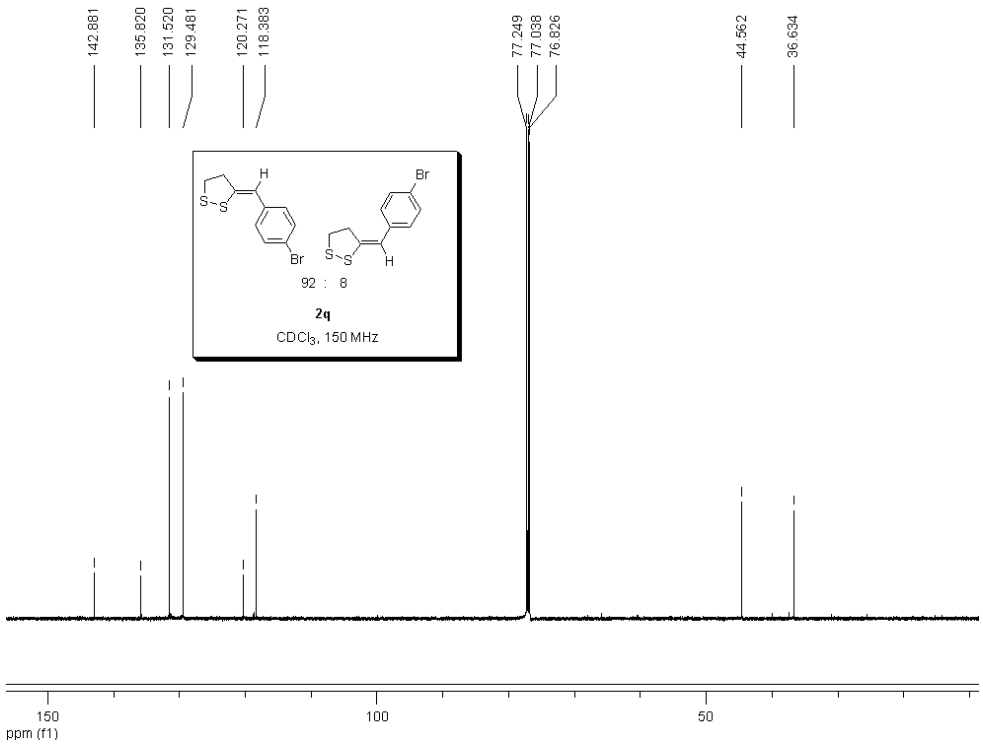
(*Z*)-3-(4-Trifluoromethylbenzylidene)-1,2-dithiolane (2p, *Z/E* 82/18). Pale yellow oil. IR (film): 2942, 1606, 1414, 1326, 1162, 1114, 1068, 1015, 861, 821 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS, ppm): δ 7.60 (d, *J* = 7.8 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 6.67 (s, 1H), 3.26 (t, *J* = 6.0 Hz, 2H), 3.20 (t, *J* = 6.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 36.7, 44.8, 118.2, 124.2 (d, J_{C-F} = 270.0 Hz), 125.4, 128.0, 128.2 (d, J_{C-F} = 32.4 Hz), 140.3, 145.2; MS (EI, 70 eV): *m/z* (%) 262 (100) [M^+], 229 (16), 215 (31), 183 (22); *Anal. Calcd.* for $C_{11}H_9F_3S_2$: C, 50.37; H, 3.46. Found: C, 50.14; H, 3.67. Stereochemistry of the isomers can be determined by analogy with those of **2o** or **2q** (see NOESY spectra section in the SI for detail). For determination of the ratio of the *Z/E* isomers, see focused ^1H NMR spectra below.



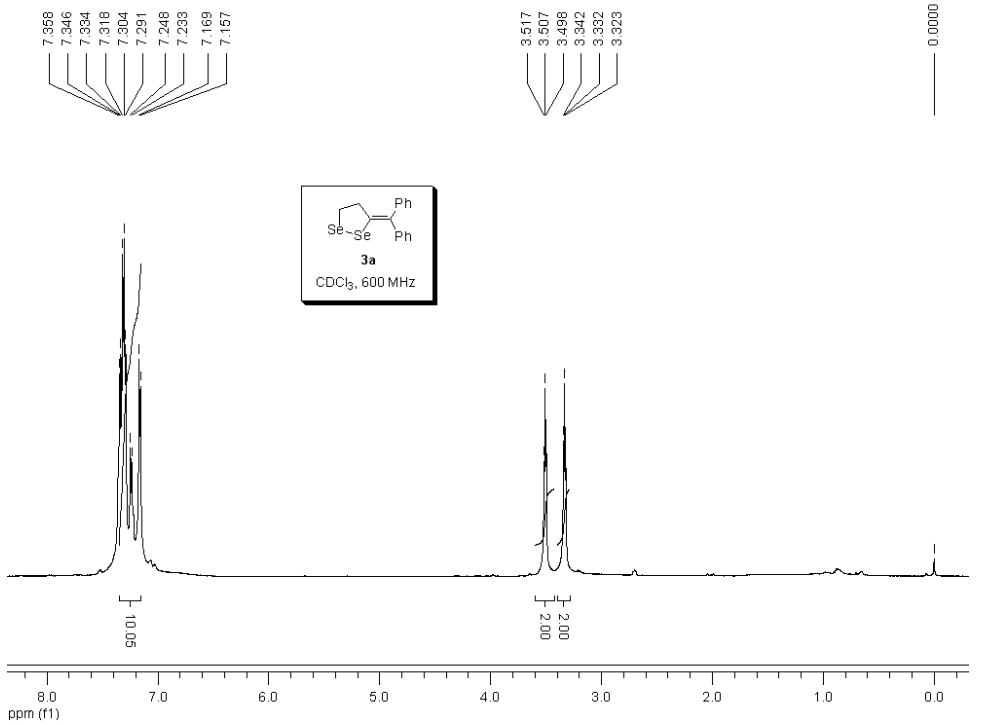


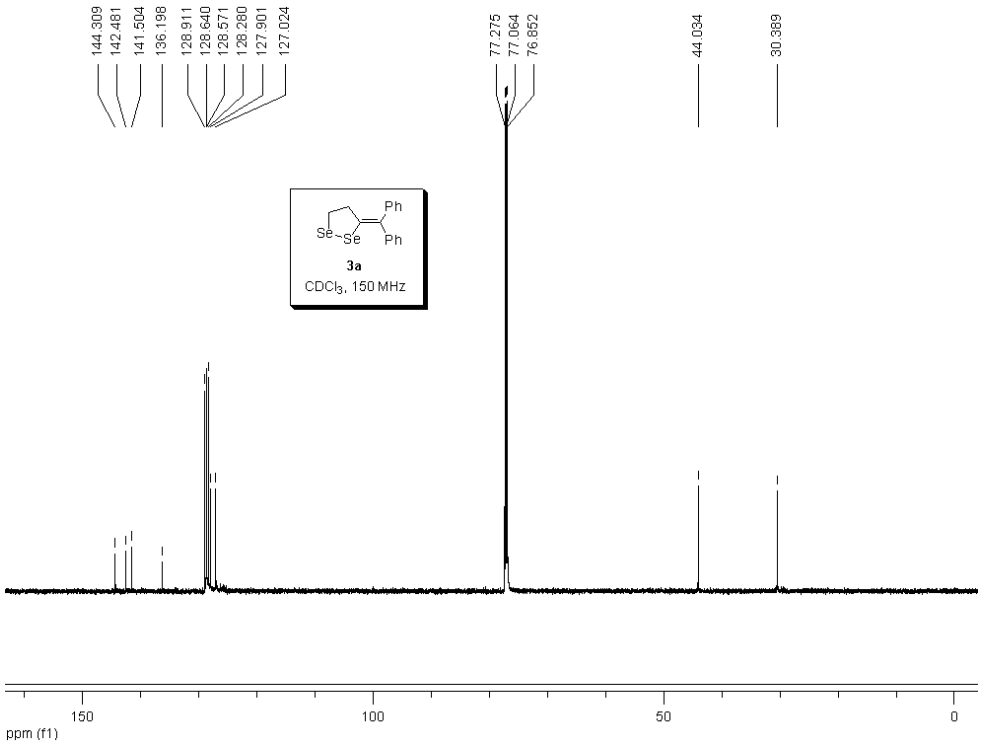
(*Z*)-3-(4-Bromobenzylidene)-1,2-dithiolane (2q, *Z/E* 92/8). Pale yellow crystal, m.p. 77.8-78.5 ^{o}C. IR (KBr): 2976, 2894, 1481, 1395, 1255, 1070, 1047, 1008, 960, 849, 801, 699 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, TMS, ppm): δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 6.58 (s, 1H), 3.23 (t, *J* = 6.0 Hz, 2H), 3.19 (t, *J* = 5.7 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 36.6, 44.6, 118.4, 120.3, 129.5, 131.5, 135.8, 142.9; MS (EI, 70 eV): *m/z* (%) 274 (100), 272 (98) [M^+], 227 (20), 193 (24); *Anal. Calcd.* for $C_{10}H_9BrS_2$: C, 43.96; H, 3.32. Found: C, 43.83; H, 3.17. For determination of the stereochemistry of the isomers, see NOESY spectra section in SI for detail. For determination of the ratio of the *Z/E* isomers, see focused ^{1}H NMR spectra below.



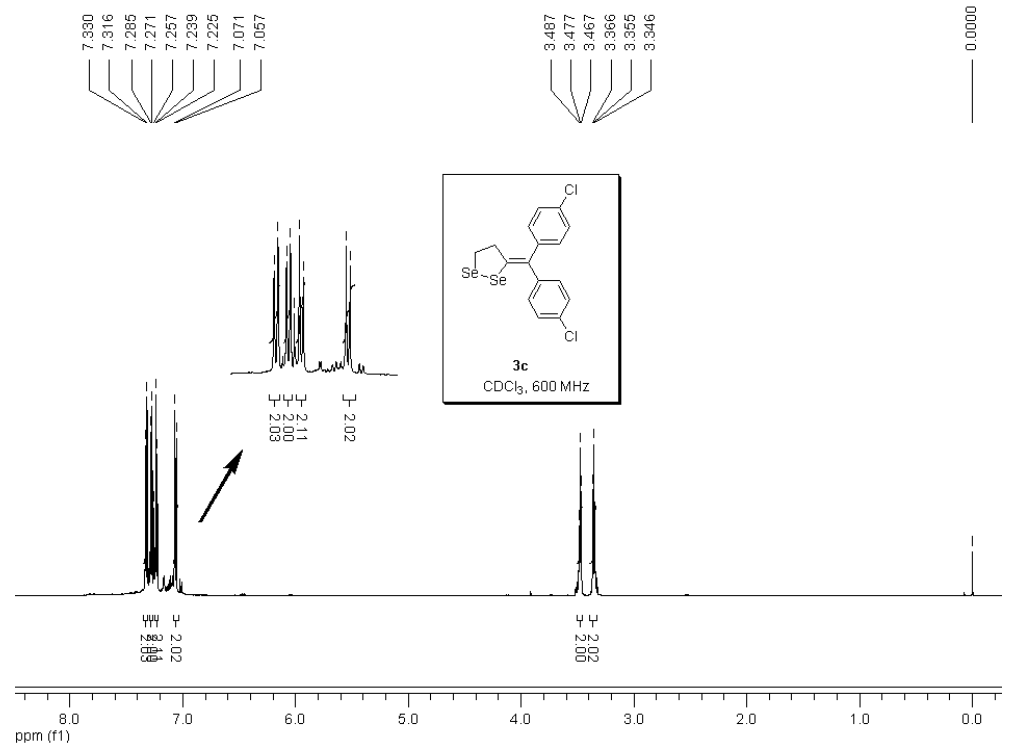


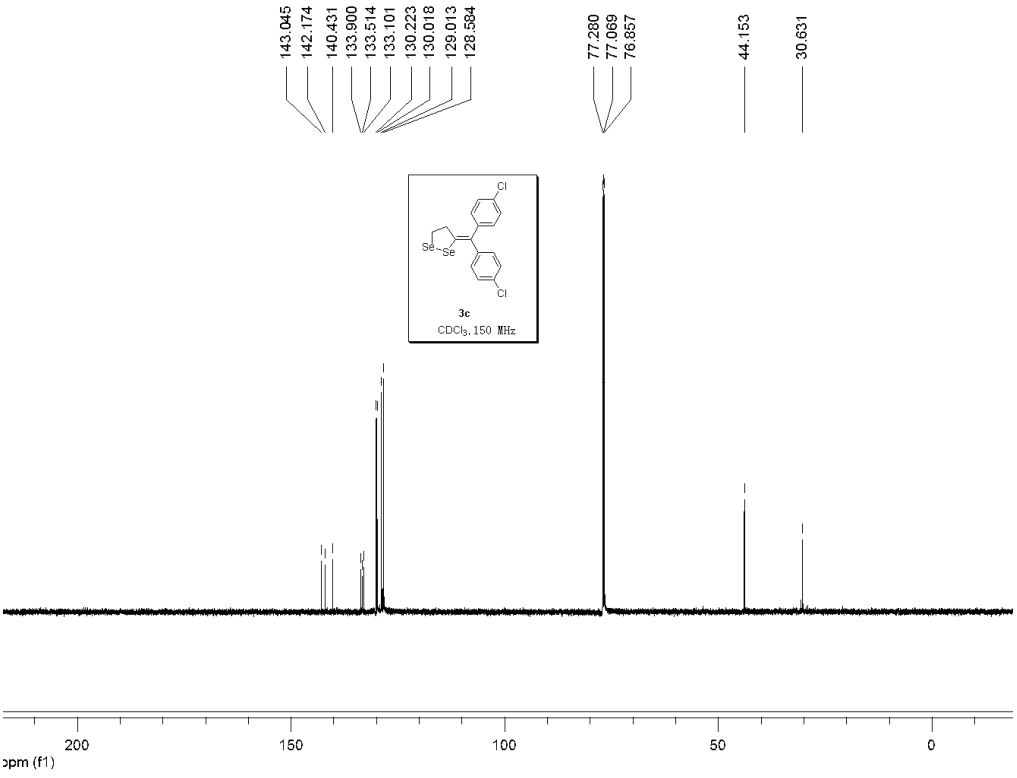
3-(Diphenylmethylene)-1,2-diselenolane (3a). Yellow oil. IR (film): 3053, 2984, 2931, 2872, 1595, 1488, 1440, 1386, 1249, 1138, 1072, 1029, 762, 699, 642 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, TMS, ppm): δ 7.16-7.36 (m, 10H), 3.51 (t, *J* = 5.7 Hz, 2H), 3.33 (t, *J* = 5.7 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 30.4, 44.0, 127.0, 127.9, 128.3, 128.6(d), 128.9, 136.2, 141.5, 142.5, 144.3; MS (EI, 70 eV): *m/z* (%) 366 (70) [M^{+}], 285 (24), 221 (39), 204 (67), 191 (100); *Anal. Calcd* for $C_{16}H_{14}Se_2$: C, 52.76; H, 3.87. Found: C, 52.91; H, 4.01.



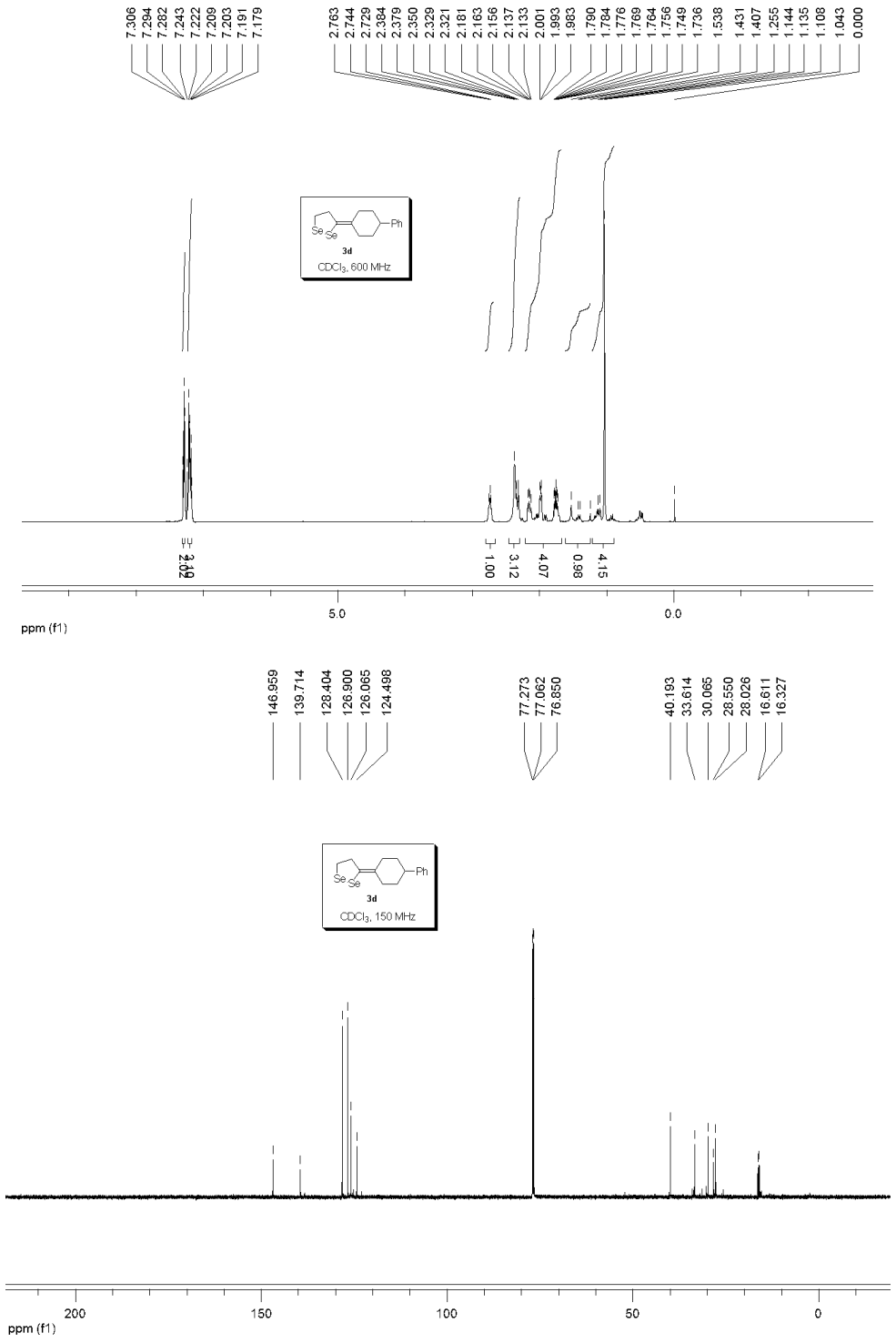


3-(Bis(4-chlorophenyl)methylene)-1,2-diselenolane (3c). Yellow oil. IR (film): 2982, 2933, 2872, 1487, 1393, 1137, 1090, 1013, 892, 820, 767, 728, 700 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, TMS, ppm): δ 7.06-7.33 (m, 8H), 3.48 (t, *J* = 6.0 Hz, 2H), 3.36 (t, *J* = 6.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 30.6, 44.2, 128.6, 129.0, 130.0, 130.2, 133.1, 133.5, 133.9, 140.4, 142.2, 143.0; MS (EI, 70 eV): *m/z* (%) 434 (67) [M^+], 354 (21) [M-Se], 202 (100); *Anal. Calcd.* for $C_{16}H_{12}Cl_2Se_2$: C, 44.37; H, 2.79. Found: C, 44.17; H, 3.04.

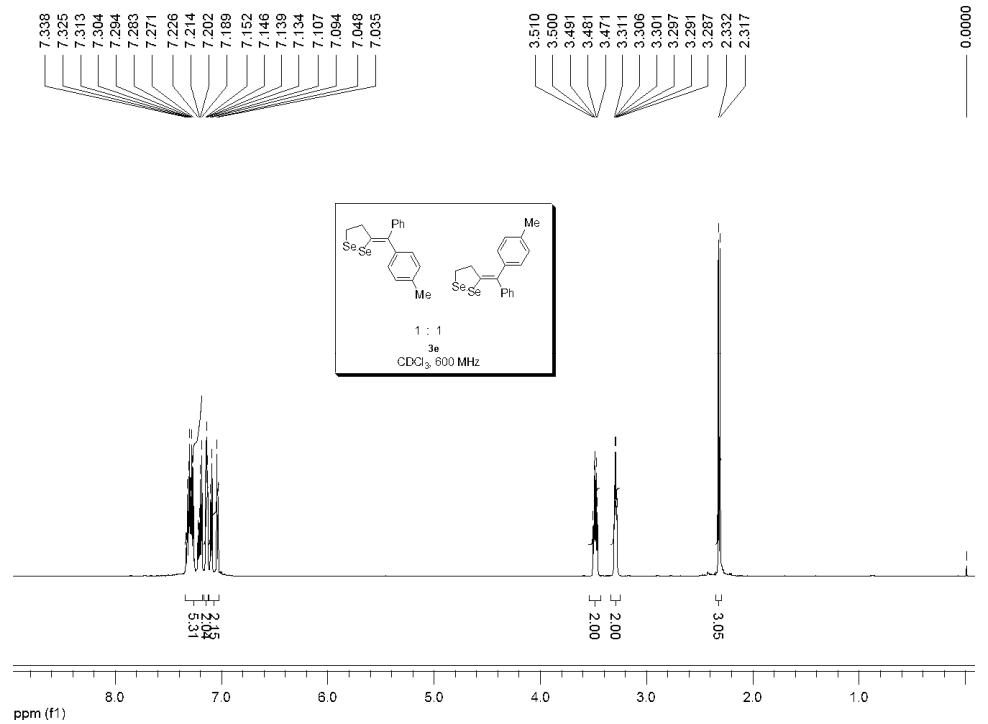


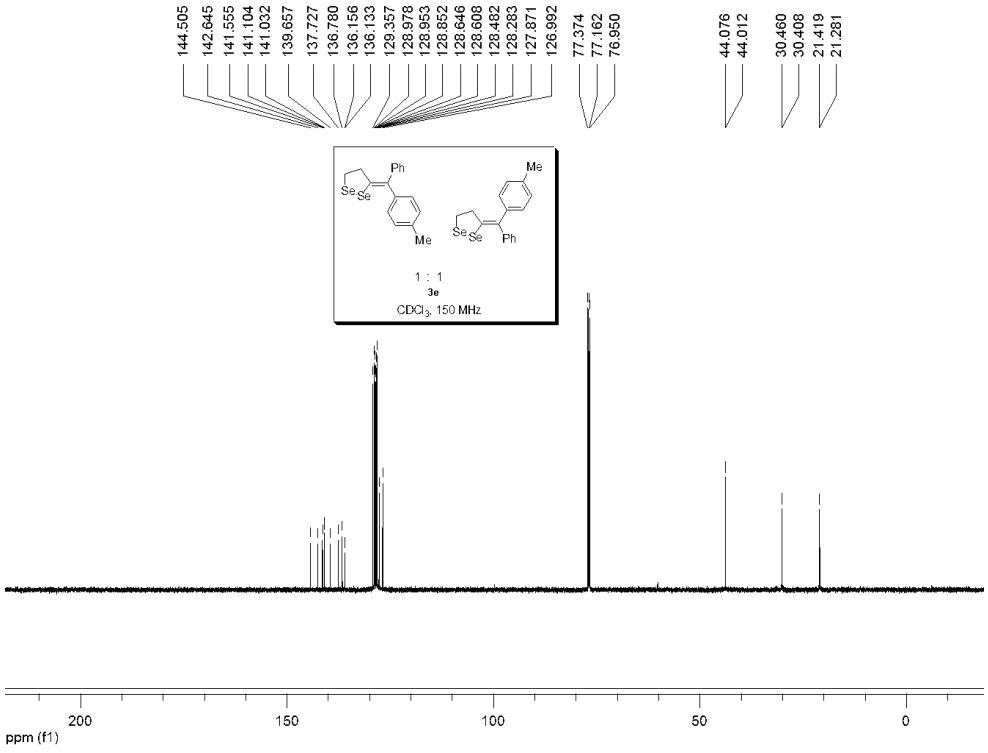


3-(4-Phenylcyclohexylidene)-1,2-diselenolane (3d). Yellow oil. IR (film): 2986, 2875, 1637, 1491, 1446, 1386, 1138, 1074, 1020, 753, 696 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS, ppm): δ 7.18-7.31 (m, 5H), 2.74 (t, J = 10.2 Hz, 1H), 2.32-2.38 (m, 3H), 1.74-2.18 (m, 4H), 1.26-1.54 (m, 1H), 1.04-1.14 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 16.3, 16.6, 28.0, 28.6, 30.1, 33.6, 40.2, 124.5, 126.1, 126.9, 128.4, 139.7, 147.0; MS (EI, 70 eV): *m/z* (%) 357 (16) [M^+-1], 277 (34), 199 (41), 91 (100). *Anal. Calcd*. for $C_{15}H_{18}Se_2$: C, 50.58; H, 5.09. Found: C, 50.80; H, 4.83.

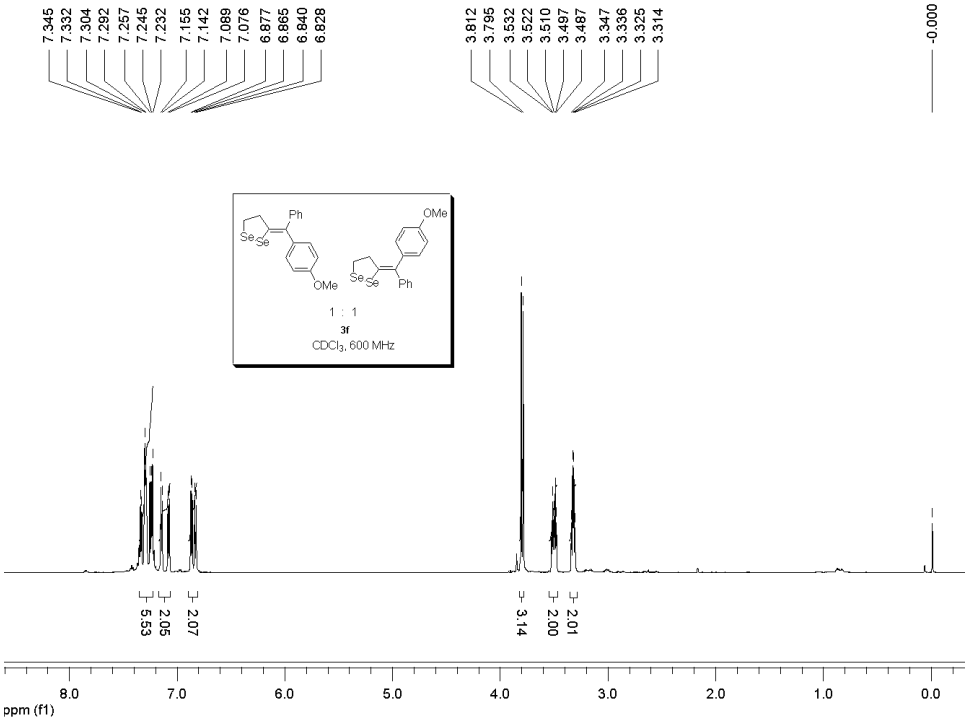


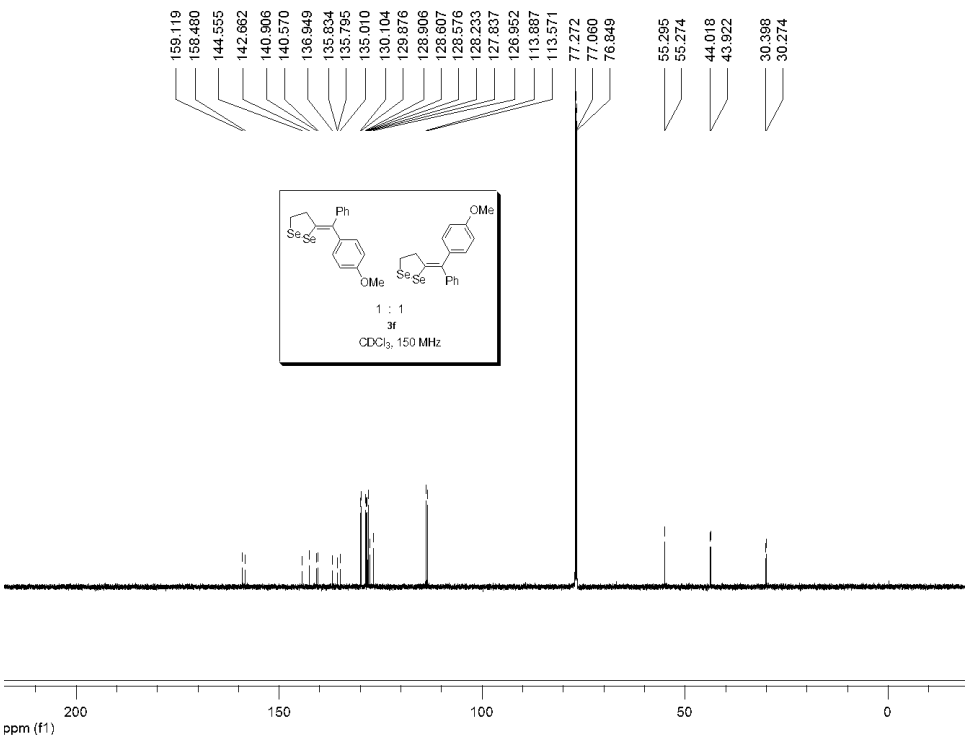
3-(Phenyl(p-tolyl)methylene)-1,2-diselenolane (3e, *Z/E* 50/50). Yellow oil. IR (film): 3020, 2982, 2928, 2872, 1597, 1504, 1442, 1413, 1249, 1138, 1070, 1027, 813, 768, 700 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, TMS, ppm): δ 7.04-7.34 (m, 9H), 3.47-3.51 (m, 2H), 3.29-3.31 (m, 2H); 2.32 and 2.33 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 21.3, 21.4, 30.4, 30.5, 44.0, 44.1, 127.0, 127.9, 128.3, 128.5, 128.6 (d), 128.9, 129.0 (d), 129.4, 136.1, 136.2, 136.8, 137.7, 139.7, 141.0, 141.1, 141.6, 142.6, 144.5; MS (EI, 70 eV): *m/z* (%) 380 (67) [M^+], 300 (24) [M-Se], 205 (100); HRMS (EI): *m/z* calcd for $C_{17}H_{16}Se_2$ 379.9582, Found 379.9578.



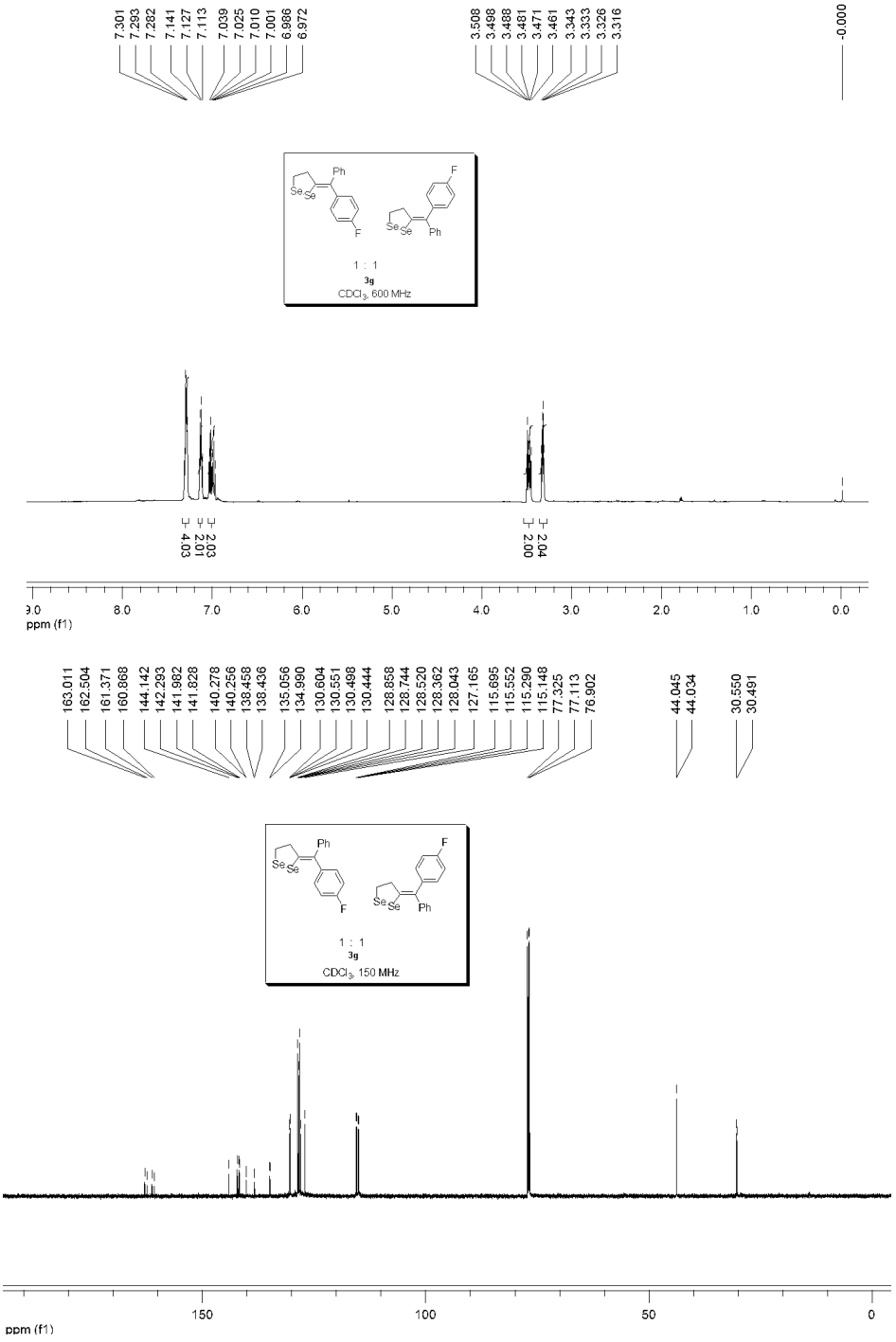


3-((4-Methoxyphenyl)(phenyl)methylene)-1,2-diselenolane (3f, *Z/E* 50/50). Yellow oil. IR (film): 2987, 2934, 2876, 1602, 1506, 1448, 1287, 1245, 1174, 1139, 1071, 1032, 826, 769, 733 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, TMS, ppm): δ 6.83-7.35 (m, 9H), 3.80 and 3.81 (s, 3H), 3.49-3.53 (m, 2H), 3.31-3.35 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 30.3, 30.4, 43.9, 44.0, 55.3 (d), 113.6, 113.9, 127.0, 127.8, 128.2, 128.6 (d), 128.9, 129.9, 130.1, 135.0, 135.8 (d), 136.9, 140.6, 140.9, 142.7, 144.6, 158.5, 159.1; MS (EI, 70 eV): *m/z* (%) 396 (71) [M^+], 316 (37) [M-Se], 236 (53) [M-2Se], 121 (100); *Anal. Calcd.* for $C_{17}H_{16}OSe_2$: C, 51.79; H, 4.09. Found: C, 52.04; H, 4.18.

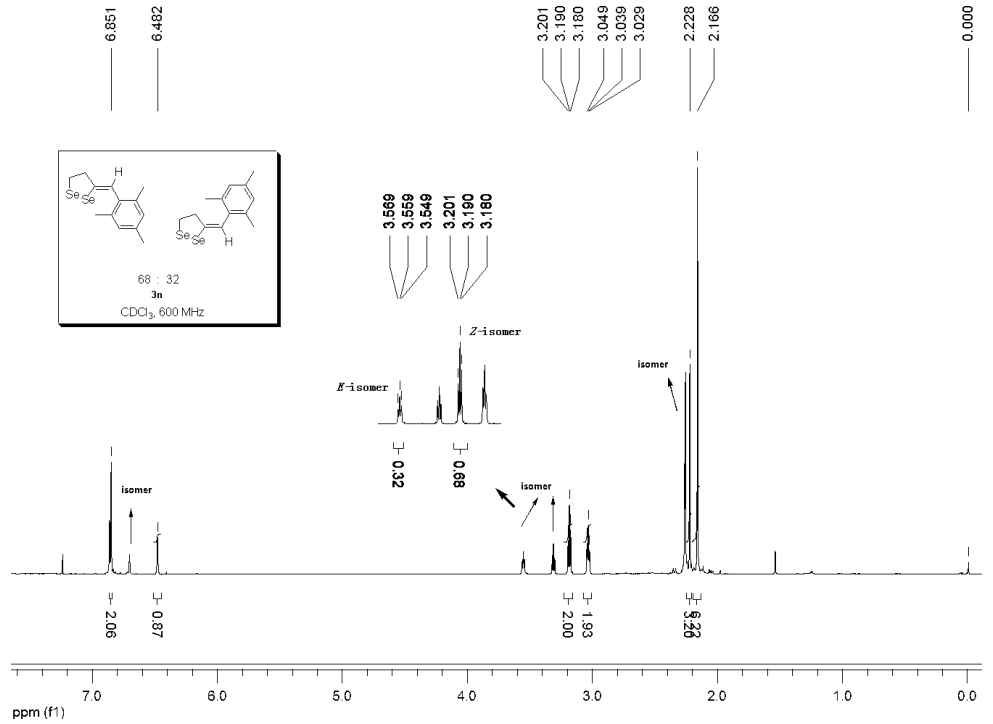


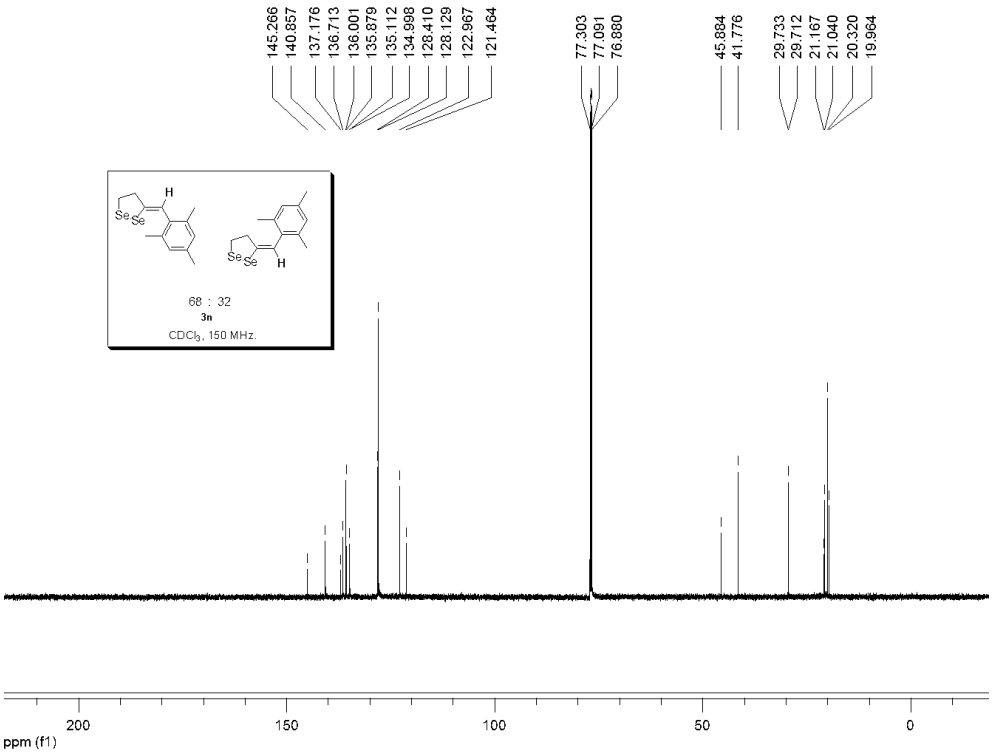


3-((4-Fluorophenyl)(phenyl)methylene)-1,2-diselenolane (3g, *Z/E* 50/50). Yellow oil. IR (film): 3053, 2980, 2933, 2872, 1597, 1502, 1443, 1411, 1297, 1225, 1152, 1072, 826, 768, 734, 700 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, TMS, ppm): δ 6.97-7.30 (m, 9H), 3.46-3.51 (m, 2H), 3.32-3.34 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 30.5, 30.6, 44.0(d), 115.2 (d, J_{C-F} = 21.3 Hz), 115.6 (d, J_{C-F} = 21.5 Hz), 127.2, 128.0, 128.4, 128.5, 128.7, 128.9, 130.5 (d, J_{C-F} = 8.1 Hz), 130.6 (d, J_{C-F} = 8.0 Hz), 135.0, 135.1, 138.4 (d, J_{C-F} = 3.3 Hz), 140.3 (d, J_{C-F} = 3.3 Hz), 141.8, 142.0, 142.3, 144.1, 161.1 (d, J_{C-F} = 75.5), 162.8 (d, J_{C-F} = 76.0 Hz); MS (EI, 70 eV): *m/z* (%) 384 (76) [M^+], 304 (24) [M-Se], 209 (100); *Anal. Calcd.* for $C_{16}H_{13}FSe_2$: C, 50.28; H, 3.43. Found: C, 50.10; H, 3.67.

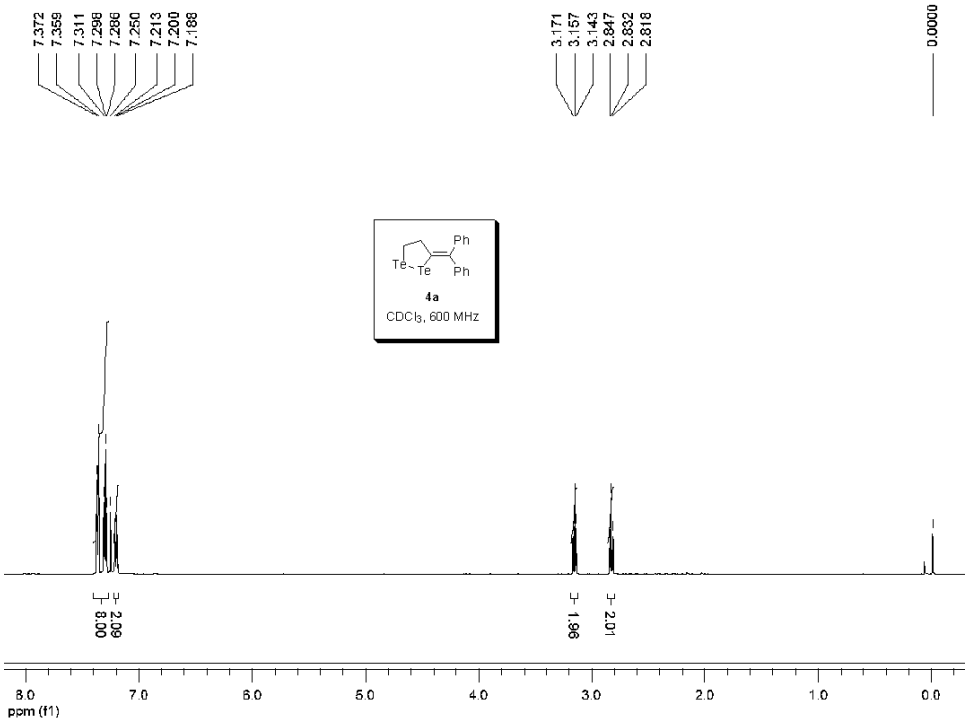


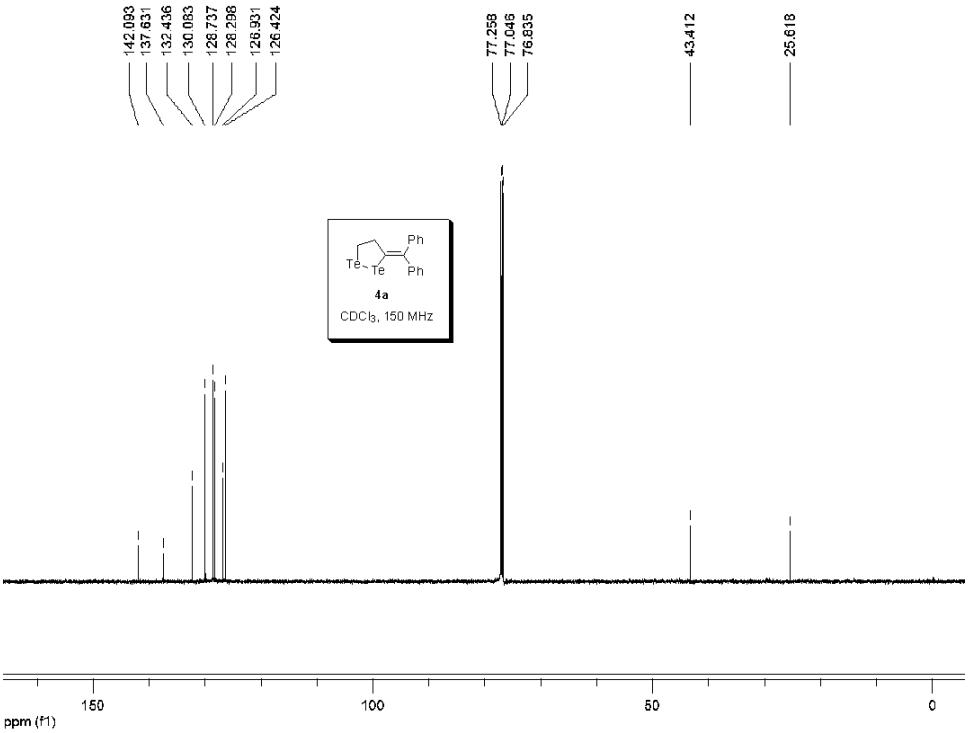
(*Z*)-3-(2, 4, 6-trimethylbenzylidene)-1,2-diselenolane (3n, *Z*/*E* 68/32). Yellow oil. IR (film): 2977, 2918, 2866, 1610, 1444, 1377, 1138, 1075, 1033, 947, 851, 810, 747 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS, ppm): δ 6.85 (s, 2H), 6.48 (s, 1H), 3.19 (t, *J* = 6.3 Hz, 2H), 3.04 (t, *J* = 6.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, ppm) (*Z*/*E* mixtures): δ 20.0, 20.3, 21.0, 21.2, 29.7 (d), 41.8, 45.9, 121.5, 123.0, 128.1, 128.4, 135.0, 135.1, 135.9, 136.0, 136.7, 137.2, 140.9, 145.3; MS (EI, 70 eV): *m/z* (%) 332 (44) [M^+], 252 (8) [M-Se], 157 (100); *Anal. Calcd.* for $C_{13}H_{16}Se_2$: C, 47.29; H, 4.88. Found: C, 47.55; H, 4.67. Stereochemistry of the isomers can be determined by analogy with those of **2o** or **2q** (see NOESY spectra section in the SI for detail). For determination of the ratio of the *Z*/*E* isomers, see focused ^1H NMR spectra below.



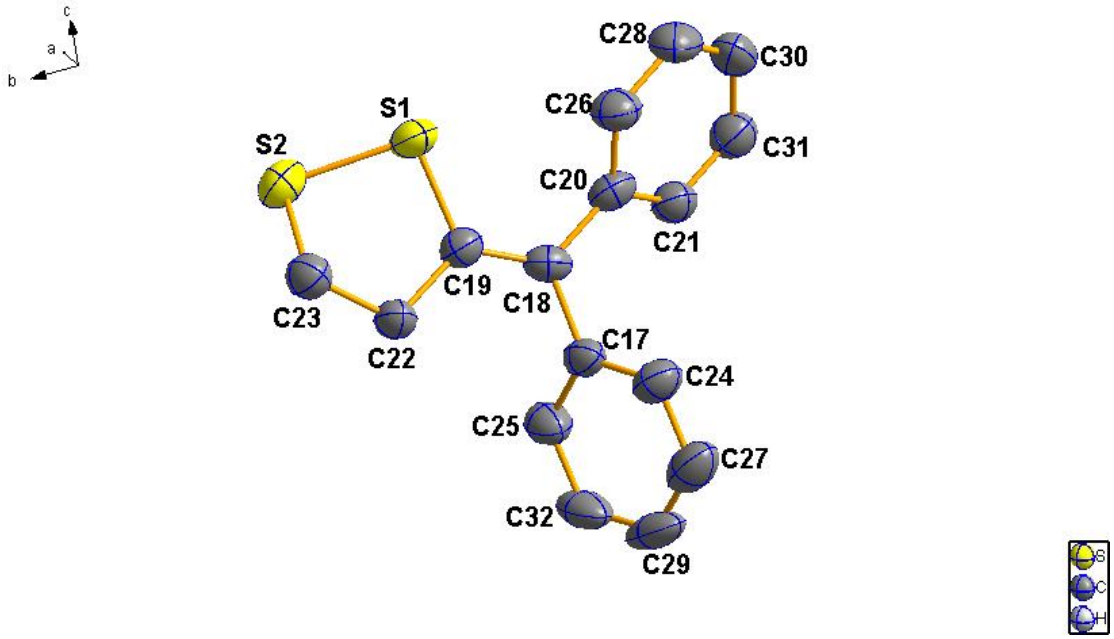


3-(Diphenylmethylene)-1,2-ditellurolane (4a). Red oil. IR (film): 3060, 2925, 2859, 1659, 1594, 1491, 1448, 1390, 1273, 1078, 1019, 805, 758, 700 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS, ppm): δ 7.19-7.37 (m, 10H), 3.16 (t, *J* = 8.4 Hz, 2H), 2.83 (t, *J* = 8.7 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 25.6, 43.4, 126.4, 126.9, 128.3, 128.7, 130.1, 132.4, 137.6, 142.1; MS (EI, 70 eV): *m/z* (%) 206 (17) [M^+-2Te], 180 (100), 165 (95). *Anal. Calcd* for $C_{16}H_{14}Te_2$: C, 41.64; H, 3.06. Found: C, 41.83; H, 3.18.





X-Ray Structure of 3-(diphenylmethylene)-1,2-dithiolane (2a).



Single-crystal X-ray diffraction data of **2a** have been deposited with the CCDC (deposition no. CCDC 906500).

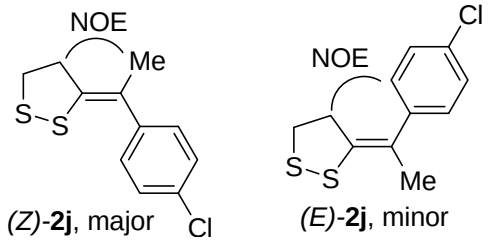
NOESY Spectra and Determination of the Products' Stereochemistry

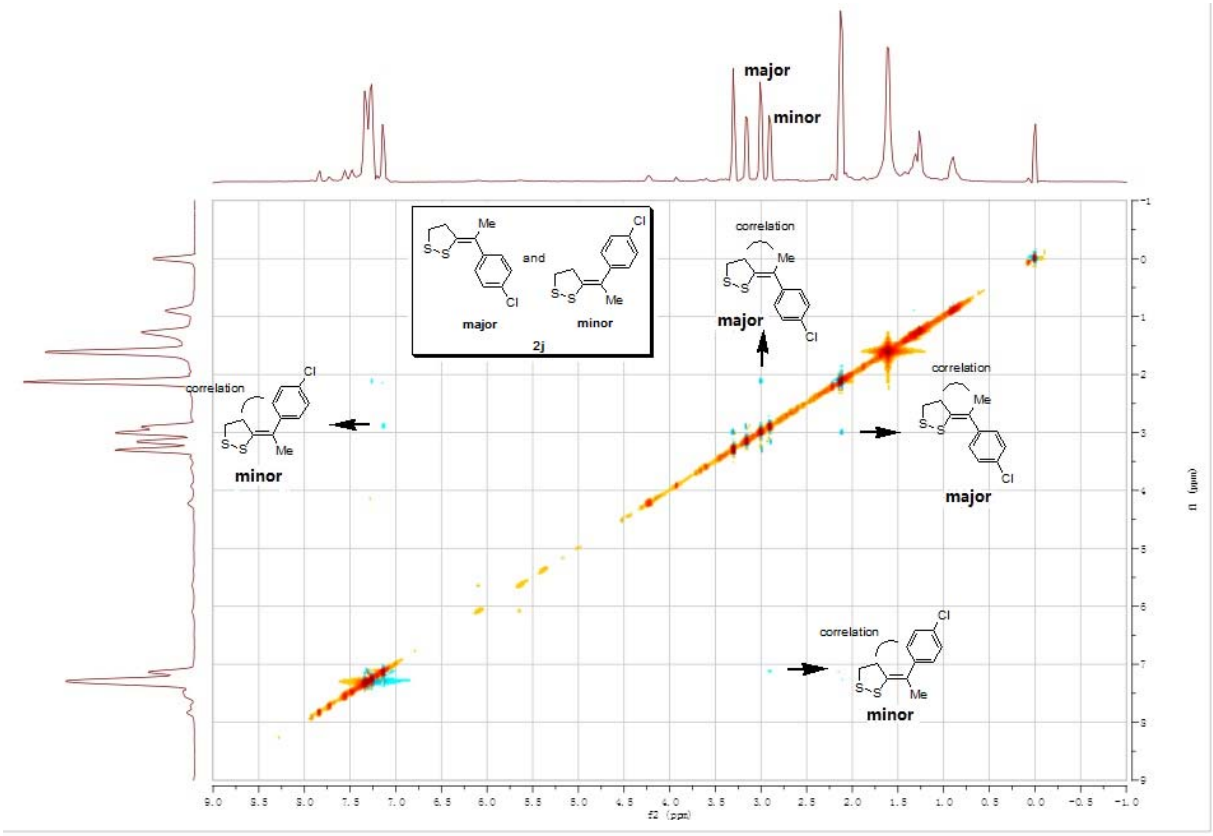
1. NOESY spectra of 2j

(1) As shown in the following NOESY spectra of **2j**, strong correlation can be observed between the protons of the allylic methyl (2.11 ppm) and the protons of the CH_2 (2.99 ppm) in 1,2-dithiolane ring, indicating that the stereomer correlates with the structure of (*Z*)-**2j**.

(2) Similarly, strong correlation can also be observed between the adjacent proton of the aryl group (7.11-7.33 ppm) and the protons of the CH_2 (2.89 ppm) in 1,2-dithiolane ring, indicating that the stereomer correlates with the structure of (*E*)-**2j**.

(3) The ratio of (*Z*)- and (*E*)-**2j** could be obtained by comparing the integration of the corresponding peaks in the ^{1}H NMR spectra (see product characterization and NMR spectra section in SI for detail).

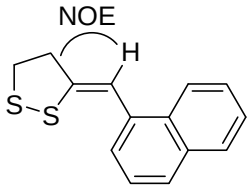




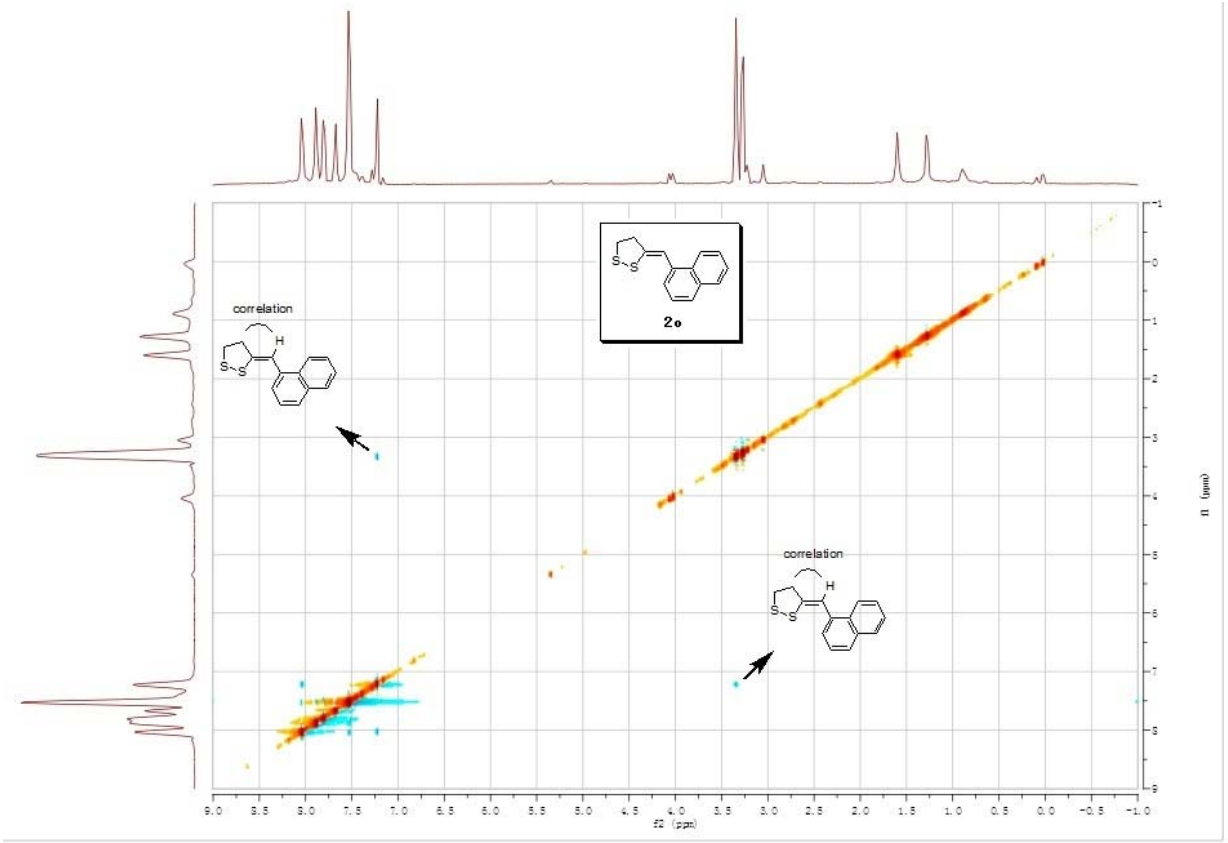
2. NOESY spectra of 2o

(1) As shown in the following NOESY spectra of **2o**, strong correlation can be observed between the vinylic proton (7.17 ppm) and the protons of CH_2 (3.22 ppm) in 1,2-dithiolane ring, indicating that the major stereomer correlates with the structure of (*Z*)-**2o**.

(2) The ratio of (*Z*)- and (*E*)-**2o** could be obtained by comparing the integration of the corresponding peaks in the ^{1}H NMR spectra (see product characterization and NMR spectra section in SI for detail).



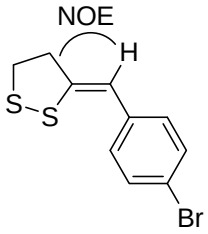
(Z)-**2o**



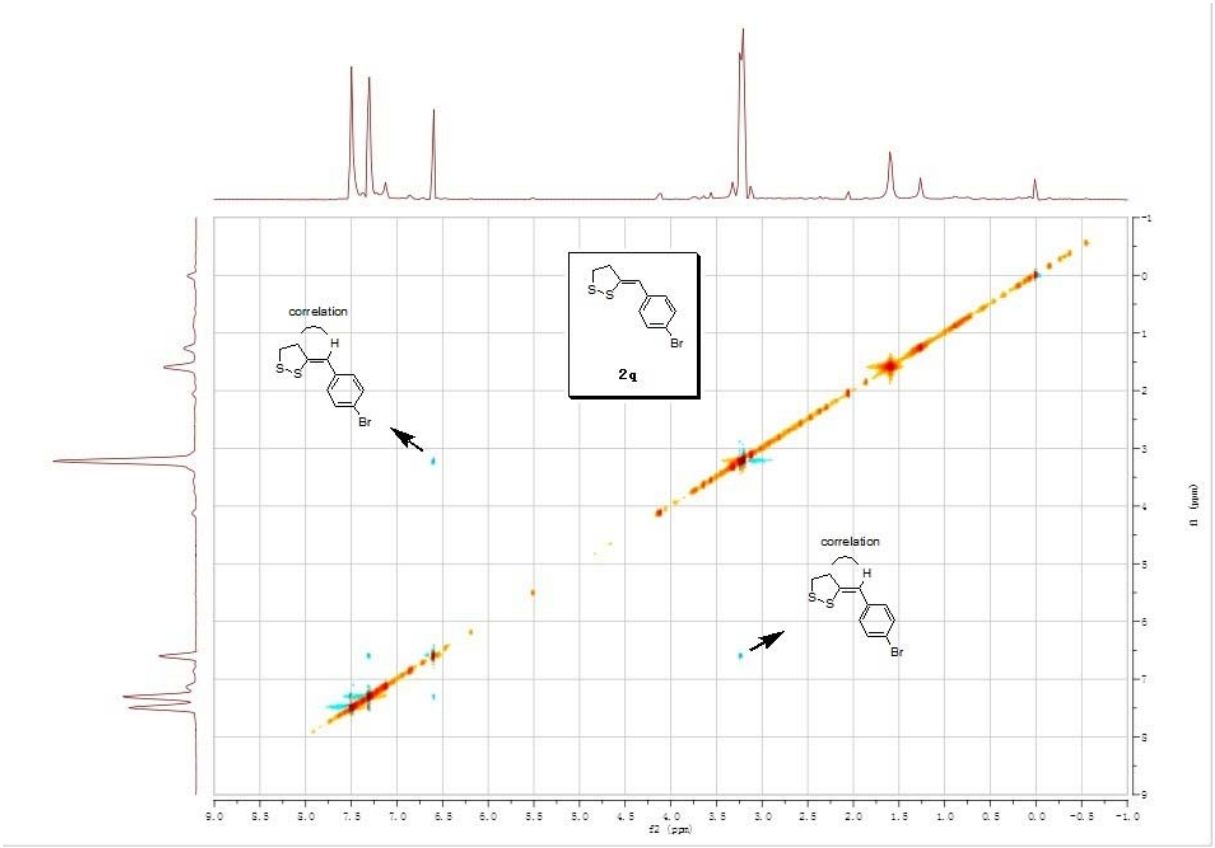
3. NOESY spectra of 2q

(1) As shown in the following NOESY spectra of **2q**, strong correlation can be observed between the vinylic proton (6.58 ppm) and the protons of CH_2 (3.18 ppm) in 1,2-dithiolane ring, indicating that the major stereomer correlates with the structure of (*Z*)-**2q**.

(2) The ratio of (*Z*)- and (*E*)-**2q** could be obtained by comparing the integration of the corresponding peaks in the ^{1}H NMR spectra (see product characterization and NMR spectra section in SI for detail).



(Z)-**2q**



4. Stereochemistry of Other Products

The stereochemistry of other unsymmetrical products **2** and **3**, mainly those derived from mono-substituted MCPs and containing a vinylic proton in the molecule, can be inferred analogously by comparing their NMR spectra and chemical shifts of the corresponding protons with those of **2o** and **2q**.