Supplementary Material (ESI) for Org. Biomol. Chem.

A new domino autocatalytic reaction leading to polyfunctionalized spiro[5.5]undecanes and dispiro[4.2.5.2]pentadecanes

Bo Jiang,[a,b] Wen-Juan Hao,[a] Jin-Peng Zhang,[c] Shu-Jiang Tu*[a,b] and Feng Shi [a]

[a] School of Chemistry and Chemical Engineering, Xuzhou Normal University, Jiangsu, P. R. China, 221116.
[b] College of Chemistry and Chemical Engineering, Suzhou University, Suzhou, P. R. China
[c] Department of Public Health, Xuzhou Medical College, Xuzhou; P. R. China
E-mail: laotu@xznu.edu.cn

Supporting Information

1. General information

Melting points were determined in open capillaries and were uncorrected. IR spectra were taken on a FT-IR-Tensor 27 spectrometer in KBr pellets and reported in cm^{-1}. ^1H NMR spectra were measured on a Bruker DPX 400 MHz spectrometer in DMSO-d_6 with chemical shift (δ) given in ppm relative to TMS as internal standard. Element analysis was determined by using a Perkin-Elmer 240c elemental analysis instrument. X-ray crystallographic analysis was performed with a Siemens SMART CCD and a Semens P4 diffractometer.

2. General procedure for the synthesis of compounds 2a-2k

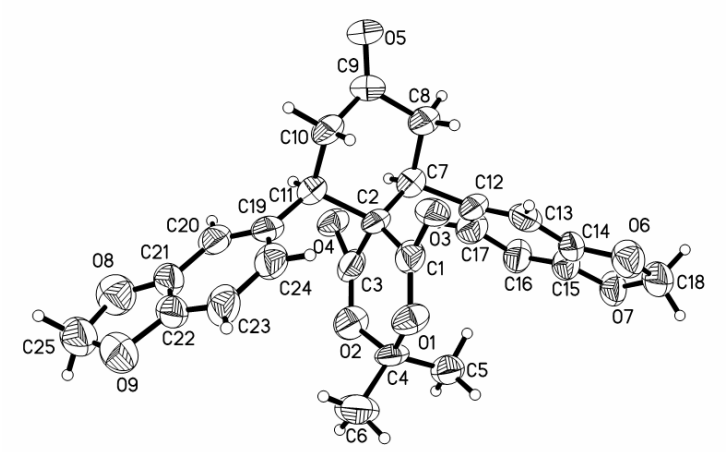
General procedure for the reaction of ethanamine 5' with Meldrum's acid 6: In a 25-mL flask, *N*-arylidene-1-phenylethanamine **5'** (2 mmol), Meldrum's acid **6** (5 mmol), and HOAc (4.0 mL) were mixed and stirred at 80 ^oC until the disappearance of starting material was confirmed by TLC. Upon completion, the reaction mixture was cooled to room temperature, and introduced into water. The resulting suspension was neutralized with 10% NaOH. The solid was collected by washing with water. The aqueous layers were then extracted thoroughly with ethylether (3 × 10 mL), and organic phases were evaporated under reduced pressure to give solid. The combined solid were purified by flash column chromatography (silica gel, mixtures of petroleum ether / acetic ester, 10:1, v/v) to afford the desired pure spirotriones **2a (2b, 2e,** and **2h)** and by-products acetamides.

General procedure for the reaction of diarylidenehydrazine 8 with Meldrum's acid 6: In a 25-mL flask, 1,2-diarylidenehydrazine **8** (2 mmol), Meldrum's acid **6** (5 mmol), and HOAc (4.0 mL) were mixed and stirred at 80 ^oC until the disappearance of starting material was confirmed by TLC. Upon completion, the reaction mixture was cooled to room temperature. The solid was collected by washing with water. The resulting suspension was neutralized with 10% NaOH. The aqueous layers were then extracted thoroughly with ethylether (3 × 10 mL), and organic phases were evaporated under reduced pressure to give solid. The combined solid were purified by flash column chromatography (silica gel, mixtures of petroleum ether / acetic ester, 10:1, v/v) to afford the desired pure spirotriones **2a-2k** and by-product acetohydrazide. All organic compounds except **2a-2e, 2g-2h,** and **2k** reported in literature[4,9] and are fully characterized by spectral analysis.

General procedure for investigation of autocatalyst: In a 25-mL flask, benzylidene-Meldrum's acid (2

mmol), 4-phenyl-but-3-en-2-one (2 mmol), acetohydrazide(1 mmol), and HOAc (4 mL) were mixed and than stirred at 80 ^{o}C until the disappearance of starting material was confirmed by TLC; Upon completion, the reaction mixture was cooled to room temperature. The subsequent work-up was the same as that of the above preparation of compounds **2a**.

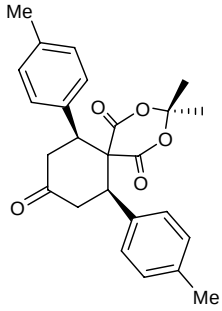
General procedure for investigation of reaction mechanism: In a 25-mL flask, benzylidene-Meldrum's acid (2 mmol), *N*′-benzylideneacetohydrazide (2 mmol), acetone (5 mmol) and HOAc (4 mL) were mixed and than stirred at 80 ^{o}C until the disappearance of starting material was confirmed by TLC; Upon completion, the reaction mixture was cooled to room temperature. The subsequent work-up was the same as that of the above preparation of compounds **2a**.



X-ray Crystallography Structure of Compound 2h

2h: The single-crystal growth was carried out in ethanol at room temperature. Crystal data for $C_{25}H_{22}O_9$, M = 466.43, Monoclinic, space group P2(1)/c, a = 6.8061(8) Å, b = 22.230(3) Å, c = 14.9656(16) Å, V = 2234.9(4) Å^3, Z = 4, T = 298(2) K, μ = 0.106 mm^{-1}, 10899 reflections measured, 3836 unique reflections, R = 0.0943, R_w = 0.1917. In the 1,3-dioxane ring, atoms C_7, C_8, C_{10}, and C_{11} are disordered over two positions. During the refinement process the disordered atoms C_7 and C_8 were both refined with occupancies of 0.58(2) and 0.42(2), respectively, and atoms C_{10} and C_{11} were both refined with occupancies of 0.56(2) and 0.44(2), respectively. In the cyclohexanone ring, atoms O_3 and O_4 are disordered over two positions, During the refinement process the disordered atom O_3 was refined with occupancies of 0.502(4) and 0.498(2) whereas atom O_4 was refined with occupancies of 0.414(4) and 0.586(2).

7,11-Di-*p*-tolyl-3,3-dimethyl-2,4-dioxaspiro[5.5]undecane-1,5,9-trione (2f)



White solid, mp: 180-182 ^{o}C

^{1}H NMR (400 MHz) (δ, ppm): 7.18 (d, J = 8.0 Hz, 4H, ArH), 7.03 (d, J = 8.4 Hz, 4H, ArH), 3.87 (dd, J_1 = 14.0 Hz, J_2 = 4.4 Hz, 2H, CH_2), 3.49 (t, J = 17.2 Hz, 2H, CH), 2.46 (dd, J_1 = 15.8 Hz, J_2 = 4.8 Hz, 2H, CH_2), 2.25 (s, 6H, CH_3), 0.55 (s, 6H, CH_3).

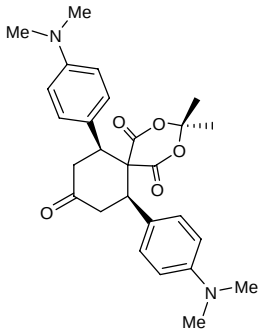
^{13}C NMR (100 MHz) (δ, ppm): 206.6, 167.6, 164.8, 137.8, 134.4, 129.5, 128.1, 105.9, 60.0, 48.4, 42.4, 27.8, 20.8.

IR (KBr, v, cm^{-1}): 2996, 2920, 1754, 1725, 1513, 1455, 1417, 1314, 1243, 1072, 893, 812, 742.

ESI-MS: m/z 429. 2 [M+Na] $^{+}$ (100%).

7,11-Bis-(4-dimethylaminophenyl)-3,3-dimethyl-2,4-dioxaspiro[5.5]undecane-1,5,9-trione (2i)

Pale yellow solid, mp: 229-231 ^{o}C



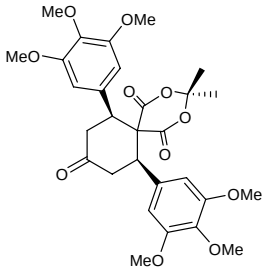
^{1}H NMR (400 MHz) (δ, ppm): 6.94 (d, J = 8.8 Hz, 4H, ArH), 6.99 (d, J = 8.8 Hz, 4H, ArH), 3.87 (dd, J_1 = 14.2 Hz, J_2 = 4.8 Hz, 2H, CH_2), 3.48-3.37 (m, 2H, CH), 2.84 (s, 12H, NCH_3), 2.39 (dd, J_1 = 15.4 Hz, J_2 = 4.8 Hz, 2H, CH_2), 0.61 (s, 6H, CH_3).

^{13}C NMR (100 MHz) (δ, ppm): 207.3, 168.0, 156.1, 150.3, 128.6, 124.5, 112.4, 105.8, 60.7, 48.1, 42.8, 27.9.

IR (KBr, v, cm^{-1}): 3044, 2992, 2892, 1754, 1726, 1613, 1523, 1450, 1358, 1195, 1167, 1046, 946, 813, 716.

ESI-MS: m/z 465.1 $[M+H]^+$ (100%), 497.2 $[M+Na]^+$

7,11-Bis-(3,4,5-trimethoxyphenyl)-3,3-dimethyl-2,4-dioxaspiro[5.5]undecane-1,5,9-trione (2j)



White solid, mp: 230-231 ^{o}C

^{1}H NMR (400 MHz) (δ, ppm): 6.43 (s, 4H, ArH), 3.99 (dd, J_1 = 14.0 Hz, J_2 = 4.4Hz, 2H, CH_2), 3.72 (s, 12H, OCH_3), 3.57 (s, 6H, OCH_3), 3.49 (t, J = 15.0 Hz, 2H, CH),.2.53-2.48 (m, 2H, CH_2), 0.71 (s, 6H, CH_3).

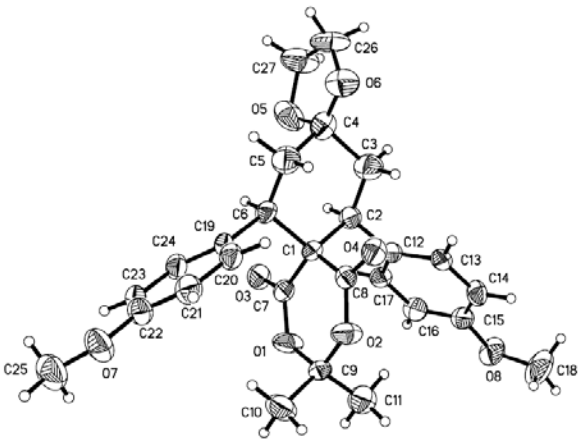
^{13}C NMR (100 MHz) (δ, ppm): 206.5, 167.9, 167.8, 165.1, 153.0, 137.7, 132.8, 106.0, 60.2, 60.0, 55.9, 49.0, 42.3, 27.7.

IR (KBr, v, cm^{-1}): 3006, 2940, 2841, 1763, 1729, 1589, 1509, 1427, 1350, 1246, 1130, 1001, 900.9, 839.5.

ESI-MS: m/z 557.8 $[M-H]^-$ (100%), 558.8 $[M]^-$

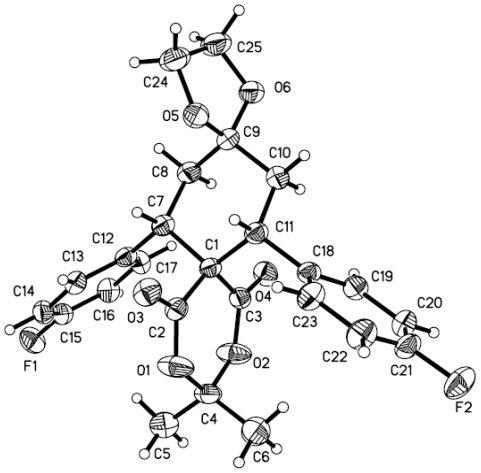
3. General procedure for the synthesis of compounds 3a-3j

In a 25-mL flask, 1,2-diarylidenehydrazine **8** (2 mmol), Meldrum's acid **6** (5 mmol), HOAc (4 mL) and ethane-1,2-diol (8 mL)were mixed and than stirred at 80 ^{o}C until the disappearance of starting material was confirmed by TLC. Upon completion, the reaction mixture was cooled to room temperature, and introduced into water. The solid was collected by washing with water. The aqueous layers were extracted thoroughly with ethylether (3 × 10 mL), and organic phases were evaporated under reduced pressure to give solid. The combined solid were purified by flash column chromatography (silica gel, mixtures of petroleum ether / acetic ester, 10:1, v/v) to afford the desired pure dispiro[4.2.5.2]pentadecane-9,13-diones **3**



X-ray Crystallography Structure of Compound 3e

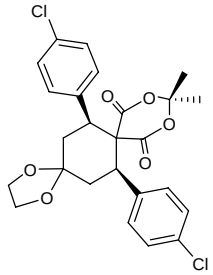
3e: The single-crystal growth was carried out in ethanol at room temperature. Crystal data for $C_{27}H_{30}O_8$, M = 482.51, Monoclinic, space group P2(1)/n, a = 9.977(5) Å, b = 20.162(9) Å, c = 12.508(6) Å, V = 2507(2) Å^3, Z = 4, T = 298(2) K, μ = 0.094 mm^{-1}, 11754 reflections measured, 4126 unique reflections, R = 0.0535, R_w = 0.1330. Atom O5 is restrained with effective standard deviation 0.01 so that their Uij components approximate to isotropic behavior



X-ray Crystallography Structure of Compound 3g

3g: The single-crystal growth was carried out in ethanol at room temperature. Crystal data for $C_{25}H_{24}F_2O_6$, M = 458.44, Triclinic, space group P-1, a = 8.146(4) Å, b = 10.714(5) Å, c = 13.580(7) Å, V = 1104.6(9) Å^3, Z = 2, T = 298(2) K, μ = 0.109 mm^{-1}, 5811 reflections measured, 3845 unique reflections, R = 0.0535, R_w = 0.1330.

7,14-Bis-(4-chlorophenyl)-11,11-dimethyl-1,4,10,12-tetraoxadispiro[4.2.5.2]pentadecane-9,13-dione (3a)



White solid, mp: 270-271 ^{o}C

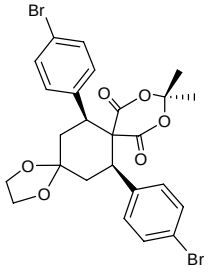
^{1}H NMR (400 MHz) (δ, ppm): 7.46 (d, J = 8.0 Hz, 4H, ArH), 7.13 (d, J = 8.0 Hz, 4H, ArH), 3.99-3.96 (m, 4H, CH_2), 3.86-3.81 (m, 2H, CH_2), 2.76 (t, J = 13.4 Hz, 2H, CH), 1.87-1.83 (m, 2H, CH_2), 0.56 (s, 6H, CH_3).

^{13}C NMR (100 MHz) (δ, ppm): 168.5, 164.3, 137.2, 133.2, 130.4, 129.2, 107.0, 105.9, 64.3, 60.2, 47.6, 35.5, 28.0.

IR (KBr, v, cm^{-1}): 3049, 2983, 1759, 1731, 1599, 1518, 1462, 1403, 1388, 1346, 1286, 1214, 1156, 1101, 1025, 968, 891, 769.

Anal. calcd. for $C_{25}H_{24}Cl_2O_6$, C, 61.11; H, 4.92; found C, 61.09; H, 4.84.

7,14-Bis-(4-bromophenyl)-11,11-dimethyl-1,4,10,12-tetraoxadispiro[4.2.5.2]pentadecane-9,13-dione (3b)



White solid, mp: 285-286 ^{o}C

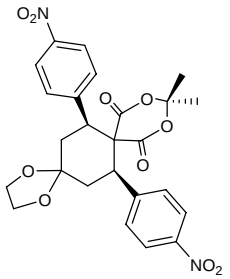
^{1}H NMR (400 MHz) (δ, ppm): 7.59 (d, J = 8.0 Hz, 4H, ArH), 7.06 (d, J = 8.0 Hz, 4H, ArH), 3.98-3.95 (m, 4H, CH_2), 3.81 (dd, J = 13.6 Hz, J = 2.8 Hz, 2H, CH_2), 2.75 (t, J = 13.6 Hz, 2H, CH), 1.86-1.83 (m, 2H, CH_2), 0.56 (s, 6H, CH_3).

^{13}C NMR (100 MHz) (δ, ppm): 168.5, 164.3, 137.6, 132.1, 130.7, 121.7, 107.0, 105.9, 64.3, 30.1, 47.6, 35.5, 27.9.

IR (KBr, v, cm^{-1}): 1758, 1724, 1487, 1392, 1377, 1287, 1254, 1233, 1153, 1093, 1068, 1010, 959, 896, 827.

Anal. calcd. for $C_{25}H_{24}Br_2O_6$, C, 51.75; H, 4.17; found C, 51.85; H, 4.11.

7,14-Bis-(4-nitrophenyl)-11,11-dimethyl-1,4,10,12-tetraoxadispiro[4.2.5.2]pentadecane-9,13-dione (3c)



White solid, mp: 290-291 ^{o}C

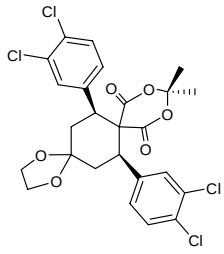
^{1}H NMR (400 MHz) (δ, ppm): 8.26 (d, J = 8.8 Hz, 4H, ArH), 7.42 (d, J = 8.8 Hz, 4H, ArH), 4.01-3.99 (m, 6H, CH_2), 2.91-2.84 (m, 2H, CH), 1.97-1.91 (m, 2H, CH_2), 0.51 (s, 6H, CH_3).

^{13}C NMR (100 MHz) (δ, ppm): 175.6, 163.9, 159.5, 149.8, 147.5, 132.4, 126.5, 108.9, 108.5, 66.6, 61.8, 59.1, 50.3, 38.3, 37.5, 30.3.

IR (KBr, v, cm^{-1}):1771, 1733, 1558, 1540, 1395, 1378, 1290, 1272, 1206, 1158, 1093, 1065, 1038, 998, 951, 899, 766.

Anal. calcd. for $C_{25}H_{24}N_2O_{10}$, C, 58.59; H, 4.72; N, 5.47; found C, 58.67; H, 4.79; N, 5.39.

7,14-Bis-(3,4-dichlorophenyl)-11,11-dimethyl-1,4,10,12-tetraoxadispiro[4.2.5.2]pentadecane-9,13-dione (3d)



White solid, mp: 267-268 ^{o}C

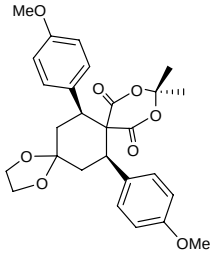
^{1}H NMR (400 MHz) (δ, ppm): 7.69 (d, J = 8.0 Hz, 2H, ArH), 7.30 (s, 2H, ArH), 7.15-7.11 (m, 2H, ArH), 3.98-3.97 (m, 4H, CH_2), 3.85 (dd, J = 13.4 Hz, J = 3.8 Hz, 2H, CH_2), 2.63 (t, J = 13.6 Hz, 2H, CH), 1.92-1.88 (m, 2H, CH_2), 0.64 (s, 6H, CH_3).

^{13}C NMR (100 MHz) (δ, ppm): 168.8, 164.6, 139.5, 132.2, 131.9, 131.8, 130.9, 129.3, 107.1, 106.6, 64.8, 60.4, 47.8, 40.8, 39.5, 35.7, 28.4.

IR (KBr, v, cm^{-1}): 2948, 2874, 1762, 1729, 1560, 1471, 1393, 1359, 1228, 1233, 1205, 1153, 1096, 1066, 1030, 1005, 964, 909, 823, 747, 715, 669.

Anal. calcd. for $C_{25}H_{22}Cl_4O_6$, C, 53.60; H, 3.96; found C, 53.54; H, 3.93.

7,14-Bis-(4-methoxyphenyl)-11,11-dimethyl-1,4,10,12-tetraoxadispiro[4.2.5.2]pentadecane-9,13-dione (3e)



White solid, mp: 206 ^{o}C;

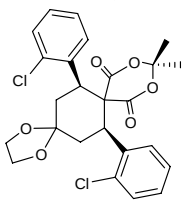
^{1}H NMR (400 MHz) (δ, ppm): 7.01 (d, J = 8.8 Hz, 4H, ArH), 6.91 (d, J = 8.8 Hz, 4H, ArH), 3.97-3.95 (m, 4H, CH_2), 3.76 (dd, J = 13.4 Hz, J = 3.2 Hz, 2H, CH_2), 3.70 (s, 6H, OCH_3), 2.75 (t, J = 13.4 Hz, 2H, CH), 1.79 (dd, J = 12.8 Hz, J = 3.4 Hz, 2H, CH_2), 0.53 (s, 6H, CH_3).

^{13}C NMR (100 MHz) (δ, ppm): 169.4, 165.1, 159.7, 130.9, 130.6, 114.9, 107.9, 106.0, 64.7, 64.6, 61.3, 55.8, 47.8, 36.4, 28.4.

IR (KBr, v, cm^{-1}): 2932, 1759, 1728, 1610, 1514, 1457, 1442, 1375, 1292, 1249, 1183, 1152, 1097, 1072, 1034, 999, 961, 900, 836.

Anal. calcd. for $C_{27}H_{30}O_8$, C, 67.21; H, 6.27; found $C_{27}H_{30}O_8$, C, 67.09; H, 6.35.

7,14-Bis-(2-chlorophenyl)-11,11-dimethyl-1,4,10,12-tetraoxadispiro[4.2.5.2]pentadecane-9,13-dione (3f)



White solid, mp: 221 ^{o}C

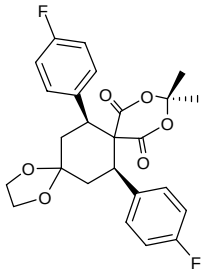
^{1}H NMR (400 MHz) (δ, ppm): 7.49 (d, J = 7.6 Hz, 2H, ArH), 7.39 (t, J = 7.4 Hz, 2H, ArH), 7.35–7.31 (m, 4H, ArH), 4.02-3.95 (m, 4H, CH_2), 3.84-3.81 (m, 2H, CH_2), 2.72 (t, J = 13.6 Hz, 2H, CH), 1.83-1.78 (m, 2H, CH_2), 0.51 (s, 6H, CH_3).

^{13}C NMR (100 MHz) (δ, ppm): 166.2, 165.8, 136.3, 133.6, 130.5, 129.9, 129.1, 128.1, 114.7, 106.6, 106.0, 64.3, 57.0, 43.7, 39.0, 37.3, 28.1.

IR (KBr, v, cm^{-1}): 1770, 1733, 1475, 1437, 1378, 1290, 1272, 1206, 1158, 1126, 1093, 1065, 1038, 998, 951, 766.

Anal. calcd. for $C_{25}H_{24}Cl_2O_6$, C, 61.11; H, 4.92; found C, 61.18; H, 4.86.

7,14-Bis-(4-fluorophenyl)-11,11-dimethyl-1,4,10,12-tetraoxadispiro[4.2.5.2]pentadecane-9,13-dione (3g)



White solid, mp: 259 ^oC

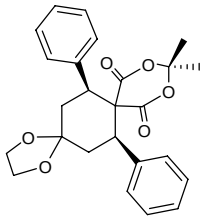
^1H NMR (400 MHz) (δ, ppm): 7.24-7.20 (m, 4H, ArH), 7.17-7.13 (m, 4H, ArH), 4.01-3.97 (m, 4H, CH_2), 3.84 (dd, J = 13.4 Hz, J = 3.8 Hz, 2H, CH_2), 2.77 (t, J = 13.4 Hz, 2H, CH), 1.84 (dd, J = 15.2 Hz, J = 3.0 Hz, 2H, CH_2), 0.55 (s, 6H, CH_3).

^{13}C NMR (100 MHz) (δ, ppm): 169.1, 164.9, 163.7, 161.2, 135.1, 131.0, 116.5, 107.6, 106.2, 64.7, 61.0, 47.9, 40.8, 39.5, 36.2, 28.4.

IR (KBr, v, cm^{-1}): 3054, 2971, 2934, 1761, 1728, 1605, 1508, 1422, 1393, 1379, 1366, 1300, 1226, 1160, 1143, 1092, 1064, 1014, 963, 898, 843, 763.

Anal. calcd. for $C_{25}H_{24}F_2O_6$, C, 65.50; H, 5.28; found C, 65.63; H, 5.21.

7,14-Diphenyl-11,11-dimethyl-1,4,10,12-tetraoxadispiro[4.2.5.2]pentadecane-9,13-dione (3h)



White solid, mp: 275-276 ^oC;

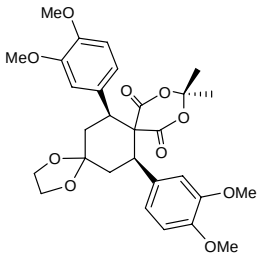
^1H NMR (400 MHz) (δ, ppm): 7.36-7.32 (m, 6H, ArH), 7.11 (d, J = 7.6 Hz, 4H, ArH), 3.99-3.97 (m, 4H, CH_2), 3.86-3.81 (m, 2H, CH_2), 2.82 (t, J = 13.6 Hz, 2H, CH), 1.88-1.83 (m, 2H, CH_2), 0.45 (s, 6H, CH_3).

^{13}C NMR (100 MHz) (δ, ppm): 168.7, 164.5, 138.4, 129.1, 128.5, 128.4, 107.3, 105.7, 64.3, 60.5, 48.2, 35.7, 27.9.

IR (KBr, v, cm^{-1}): 2932, 1761, 1730, 1558, 1493, 1455, 1379, 1281, 1153, 1091, 1060, 959, 896, 765, 703

Anal. calcd. for $C_{25}H_{26}O_6$, C, 71.07; H, 6.20; found $C_{25}H_{26}O_6$, C, 71.25; H, 6.26.

7,14-Bis-(3,4-dimethoxyphenyl)-11,11-dimethyl-1,4,10,12-tetraoxadispiro[4.2.5.2]pentadecane-9,13-dione (3i)



White solid, mp: 201 ^oC

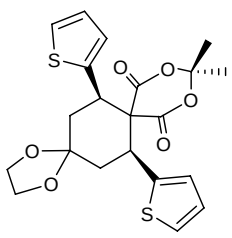
^1H NMR (400 MHz) (δ, ppm): 6.93 (d, J = 8.0 Hz, 2H, ArH), 6.65 (s, 2H, ArH), 6.62-6.61 (m, 2H, ArH), 3.99-3.96 (m, 4H, CH_2), 3.75 (dd, J = 13.8 Hz, J = 3.4 Hz, 2H, CH_2), 3.73 (s, 6H, OCH_3), 3.70 (s, 6H, OCH_3), 2.77 (t, J = 13.4 Hz, 2H, CH), 1.81 (dd, J = 13.6 Hz J = 3.4 Hz, 2H, CH_2), 0.57 (s, 6H, CH_3).

^{13}C NMR (100 MHz) (δ, ppm): 169.5, 165.4, 149.4, 149.3, 131.3, 121.1, 112.8, 112.7, 107.9, 106.0, 64.7, 61.3, 56.2, 56.1, 48.2, 40.8, 39.5, 36.5, 28.4.

IR (KBr, v, cm^{-1}):1761, 1730, 1590, 1519, 1466, 1449, 1377, 1271, 1245, 1166, 1144, 1095, 1068, 1025, 938, 767.

Anal. calcd. for $C_{29}H_{34}O_{10}$, C, 64.20; H, 6.32; found C, 64.34; H, 6.41.

7,14-Dithiophen-2-yl-11,11-dimethyl-1,4,10,12-tetraoxadispiro[4.2.5.2]pentadecane-9,13-dione (3j)



Pale yellow solid, mp: 250-252 ^oC

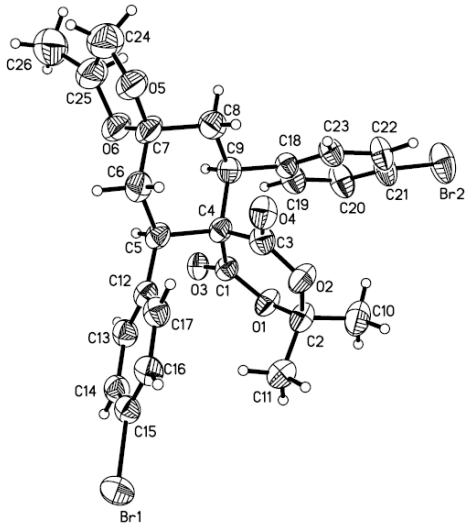
^1H NMR (400 MHz) (δ, ppm): 7.47 (d, J = 5.2 Hz, 2H, Thienyl-H), 7.01 (d, J = 3.6 Hz, 2H, Thienyl-H), 6.85 (d, J = 3.2 Hz, 2H, Thienyl-H), 4.06 (dd, J = 13.6 Hz, J = 4.0 Hz, 2H, CH_2), 3.98-3.97 (m, 4H, CH_2), 2.67 (t, J = 13.4 Hz, 2H, CH), 1.97 (dd, J = 12.8 Hz, J = 3.2 Hz, 2H, CH_2), 0.71 (s, 6H, CH_3).

IR (KBr, v, cm^{-1}): 3054, 2998, 2888, 1753, 1730, 1618, 1529, 1451, 1328, 1201, 1161, 1043, 927, 851, 774.

Anal. calcd. for $C_{21}H_{22}O_6S_2$, C, 58.05; H, 5.10; S, 14.76; found C, 58.05; H, 5.10; S, 14.76.

4. General procedure for the synthesis of compounds 4a-4b

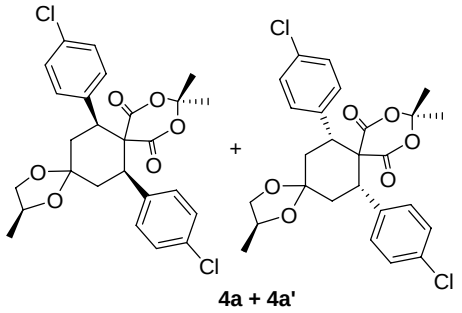
In a 25-mL flask, 1,2-diarylidenehydrazine **8** (2 mmol), Meldrum's acid **6** (5 mmol), HOAc (4 mL) and (*S*)-1,2-propanediol (8 mL)were mixed and than stirred at 80 ^{o}C until the disappearance of starting material was confirmed by TLC. Upon completion, the reaction mixture was cooled to room temperature, and introduced into water. The solid was collected by washing with water. The aqueous layers were extracted thoroughly with ethylether (3 × 10 mL), and organic phases were evaporated under reduced pressure to give solid. The combined solid were purified by flash column chromatography (silica gel, mixtures of petroleum ether / acetic ester, 10:1, v/v) to afford the desired pure dispiro[4.2.5.2]pentadecane-9,13-diones **4**.



X-ray Crystallography Structure of Compound 4b

4b The single-crystal growth was carried out in ethanol at room temperature. Crystal data for $C_{26}H_{26}Br_2O_6$, M = 594.29, Triclinic, space group P-1, a = 7.356(3) Å, b = 12.590(5) Å, c = 14.852(6) Å, V = 1267.8(8) Å^3, Z = 2, T = 193(2) K, μ = 3.236 mm^{-1}, 6454 reflections measured, 4330 unique reflections, R = 0.0728, R_w = 0.1245. In the bromophenyl ring (C_{18}-C_{23}), atom Br_2 was disordered over two positions. During the refinement process the disordered atom Br_2 was refined with occupancies of 0.51(4) and 0.49(4). In the 1,3-dioxolane ring, atoms C_{25} and C_{26} are disordered over two positions. During the refinement process the disordered atoms C_{25} and C_{26} were refined with occupancies of 0.320(18) and 0.680(18), 0.320(18) and 0.680(18), respectively. During refinement, atoms C_{25} and C_{25}' are constrained to have the same x, y and z parameters and anisotropic displacement parameters. All of the atoms of C, O, Br closer than 3.8 Å are restrained with an s. u. value of 0.02 Å^2 to have the same Uij components. If (according to the connectivity table, i.e. ignoring attached hydrogens) one or both of the two atoms involved is terminal (or not bonded at all), 0.04 is used instead as 0.02. The distance between C_{24}, C_{26} and C_{24}, C_{26}' is restrained to 2.54 Å with an estimated standard deviation 0.02. The distance of C_{25}-C_{26}, C_{24}-C_{25} and C_{25}-C_{26}' are restrained to 1.53 Å with an estimated standard deviation 0.02. The distance of O_5-C_7, O_5-C_{24}, O_6-C_7, O_6-C_{25} are restrained to 1.43 Å with an estimated standard deviation 0.02.

7,14-Bis-(4-chlorophenyl)-2,11,11-trimethyl-1,4,10,12-tetraoxa-dispiro[4.2.5.2]pentadecane-9,13-dione (4a and **4a')**



4a + 4a'

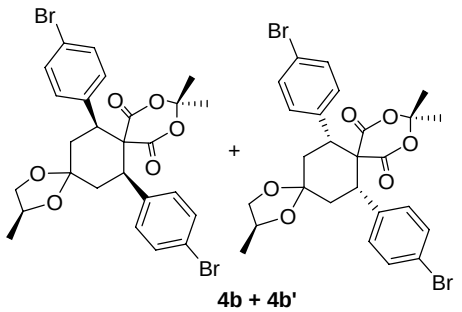
^{1}H NMR (400 MHz) (δ, ppm, mixture): 7.46-7.44 (m, 8H, ArH), 7.14-7.11 (m, 8H, ArH), 4.31-4.25 (m, 2H, CH), 4.15-4.10 (m, 2H, CH), 3.87-3.78 (m, 4H, CH_2), 3.49-3.47 (m, 2H, CH_2), 2.84 (q, J = 14.0 Hz, 2H, CH), 2.73-2.64 (m, 2H, CH), 1.92-1.89 (m, 2H, CH_2), 1.83-1.79 (m, 2H, CH_2), 1.25 (d, J = 6.0 Hz, 3H, CH_3), 1.21 (d, J = 6.0 Hz, 3H, CH_3), 0.56 (s, 12H, CH_3).

^{13}C NMR (100 MHz) (δ, ppm): 168.9, 164.6, 137.5, 133.5, 130.7, 130.6, 129.5, 129.4, 107.6, 107.5, 106.2, 72.5, 72.3, 70.6, 60.6, 60.5, 47.9, 47.8, 47.7, 37.6, 37.0, 36.2, 35.9, 38.3, 28.2, 18.9, 18.8.

IR (KBr, v, cm^{-1}): 3032, 1762, 1728, 1586, 1509, 1468, 1412, 1363, 1340, 1281, 1223, 1167, 1135, 1027, 969, 894, 771.

Anal. calcd. for $C_{26}H_{26}Cl_2O_6$; C, 61.79; H, 5.19; found C, 61.79; H, 5.19.

7,14-Bis-(4-bromophenyl)-2,11,11-trimethyl-1,4,10,12-tetraoxa-dispiro[4.2.5.2]pentadecane-9,13-dione (4b and **4b')**



4b + 4b'

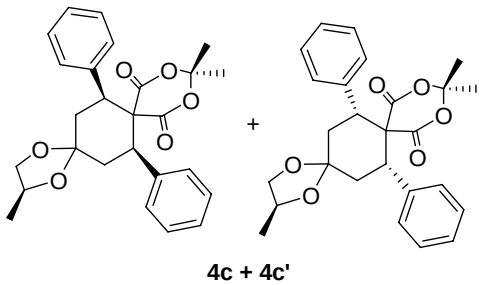
^{1}H NMR (400 MHz) (δ, ppm, mixture): 7.58-7.56 (m, 8H, ArH), 7.06-7.04 (m, 8H, ArH), 4.28-4.26 (m, 2H, CH), 4.25-4.10 (m, 2H, CH), 3.83-3.76 (m, 4H, CH and CH_2), 2.83 (q, J = 13.6 Hz, 2H, CH_2), 2.74-2.63 (m, 2H, CH_2), 1.91-1.87 (m, 2H, CH_2), 1.81-1.77 (m, 2H, CH_2), 1.24 (d, J = 6.4 Hz, 3H, CH_3), 1.19 (d, J = 6.0 Hz, 3H, CH_3), 0.55 (s, 12H, CH_3).

^{13}C NMR (100 MHz) (δ, ppm): 168.9, 164.6, 164.5, 137.9, 132.4, 131.0, 130.9, 122.0, 121.9, 107.6, 107.5, 106.2, 72.5, 72.3, 70.6, 60.0, 37.5, 36.9, 36.2, 35.8, 28.2, 18.9, 18.8.

IR (KBr, v, cm^{-1}): 1760, 1726, 1577, 1491, 1437, 1337, 1214, 1133, 1083, 1071, 1004, 956, 898, 824.

Anal. calcd. for $C_{26}H_{26}Br_2O_6$; C, 52.55; H, 4.41; found C, 52.68; H, 4.47.

7,14-Biphenyl-2,11,11-trimethyl-1,4,10,12-tetraoxa-dispiro[4.2.5.2]pentadecane-9,13-dione (4c and **4c')**


4c + 4c'

^{1}H NMR (400 MHz) (δ, ppm, mixture): 7.38-7.30 (m, 12H, ArH), 7.12-7.11 (m, 8H, ArH), 4.29-4.26 (m, 2H, CH), 4.14-4.11 (m, 2H, CH_2), 3.87-3.79 (m, 4H, CH_2), 3.50-3.48 (m, 2H, CH_2), 2.93-2.88 (m, 2H, CH), 2.78-2.74 (m, 2H, CH), 1.92-1.79 (m, 4H, CH_2), 1.26 (d, J = 6.0 Hz, 3H, CH_3), 1.21 (d, J = 6.4 Hz, 3H, CH_3), 0.44 (s, 12H, CH_3).

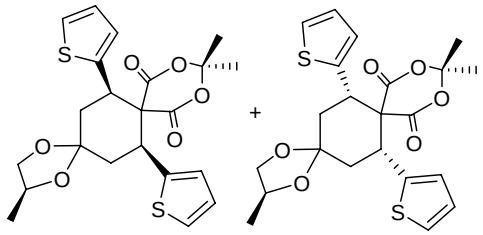
^{13}C NMR (100 MHz) (δ, ppm): 169.1, 169.0, 164.8, 164.7, 138.7, 129.5, 129.4, 128.8, 128.7, 107.9, 107.8, 106.0, 72.4, 72.2, 70.6, 60.8, 60.7, 48.5, 48.3, 37.7, 37.1, 36.4, 36.0, 28.1, 19.0, 18.8.

IR (KBr, v, cm^{-1}): 2952, 1760, 1732, 1561, 1501, 1467, 1323, 1279, 1151, 1103, 1015, 960, 897, 764.

Anal. calcd. for $C_{26}H_{28}O_6$; C, 71.54; H, 6.47; found C, 71.41; H, 6.54.

2,11,11-Trimethyl-7,14-dithiophen-2-yl-1,4,10,12-tetraoxa-dispiro[4.2.5.2]pentadecane-9,13-dione (4d and

4d')



4d + 4d'

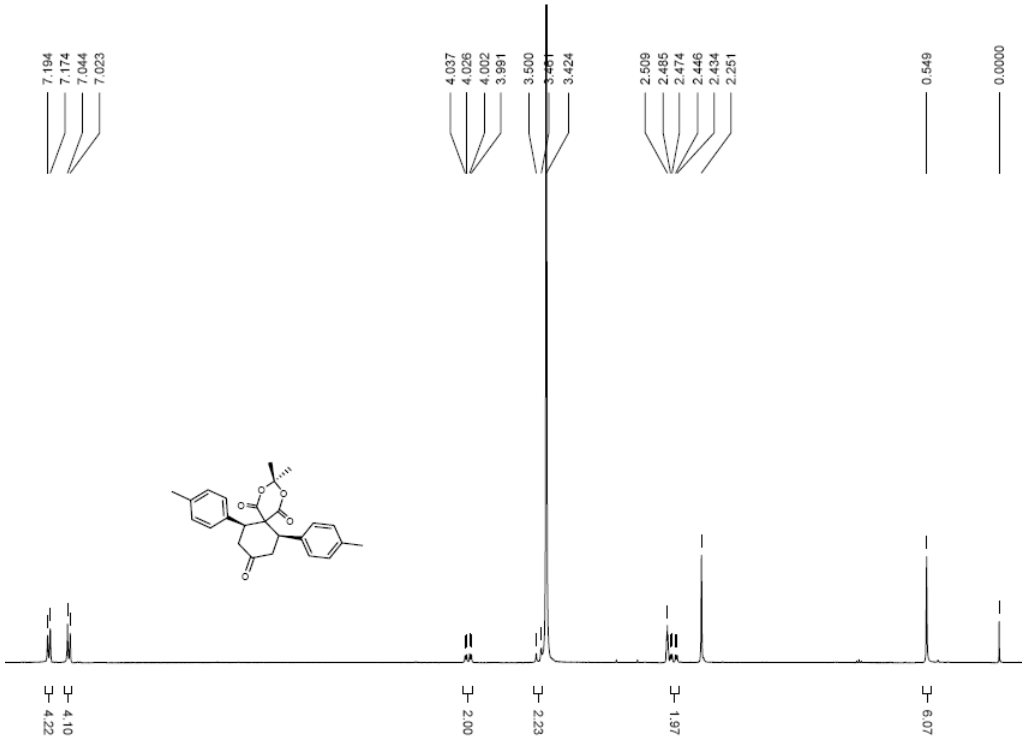
^{1}H NMR (400 MHz) (δ, ppm, mixture): 7.46 (d, J = 3.2 Hz, 4H, Thiophenyl-H), 7.01 (t, J = 4.2 Hz, 4H, Thiophenyl-H), 6.85-6.84 (m, 4H, Thiophenyl-H), 4.28-4.26 (m, 2H, CH), 4.15-4.03 (m, 6H, CH and CH_2), 2.75 (q, J = 13.2 Hz, 2H, CH_2), 2.61 (q, J = 14.0 Hz, 2H, CH_2), 2.05-1.92 (m, 4H, CH_2), 1.24 (d, J = 6.0 Hz, 3H, CH_3), 1.20 (d, J = 6.0 Hz, 3H, CH_3), 0.71 (s, 12H, CH_3).

^{13}C NMR (100 MHz) (δ, ppm): 171.3, 171.2, 166.6, 143.0, 129.6, 129.0, 128.9, 182.2, 108.8, 108.4, 74.4, 72.6, 72.5, 63.6, 63.5, 45.8, 45.7, 45.6, 40.7, 39.9, 39.6, 30.3, 20.8, 20.6.

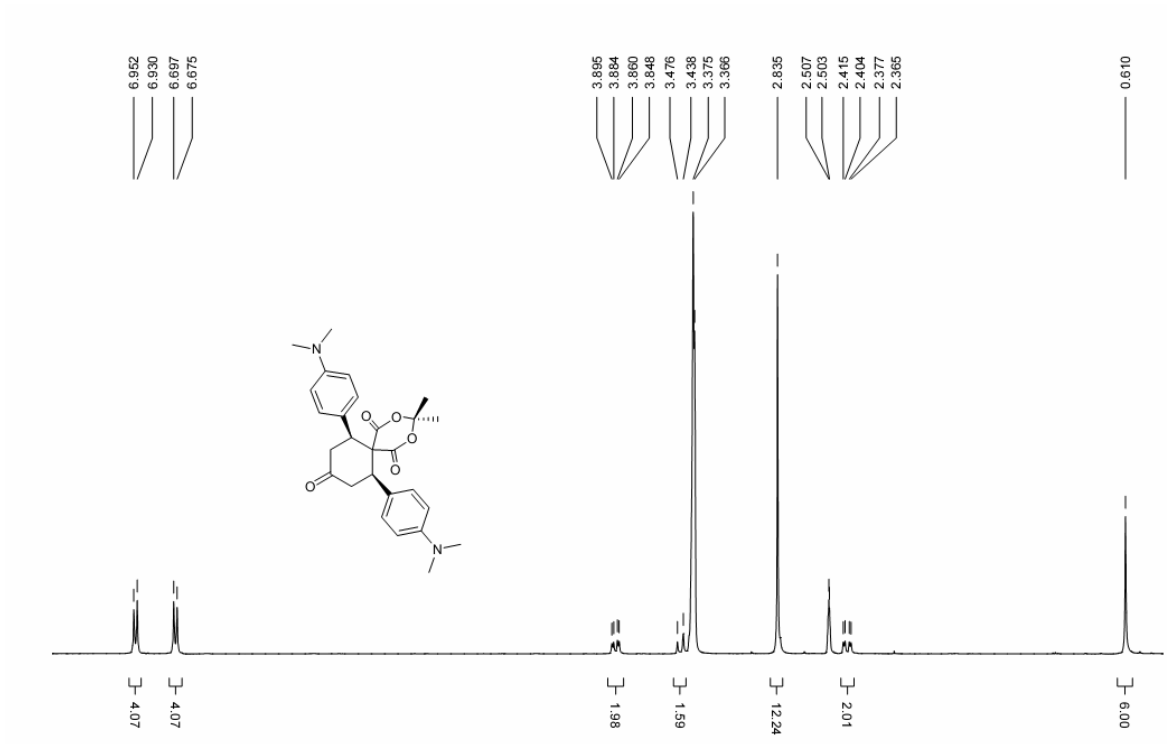
IR (KBr, v, cm^{-1}): 1763, 1735, 1588, 1543, 1471, 1354, 1280, 1125, 1104, 1072, 967, 881.

Anal. calcd. for $C_{22}H_{24}O_6S_2$; C, 58.91; H, 5.39; S, 14.30; found C, 58.74; H, 5.30; S, 14.43.

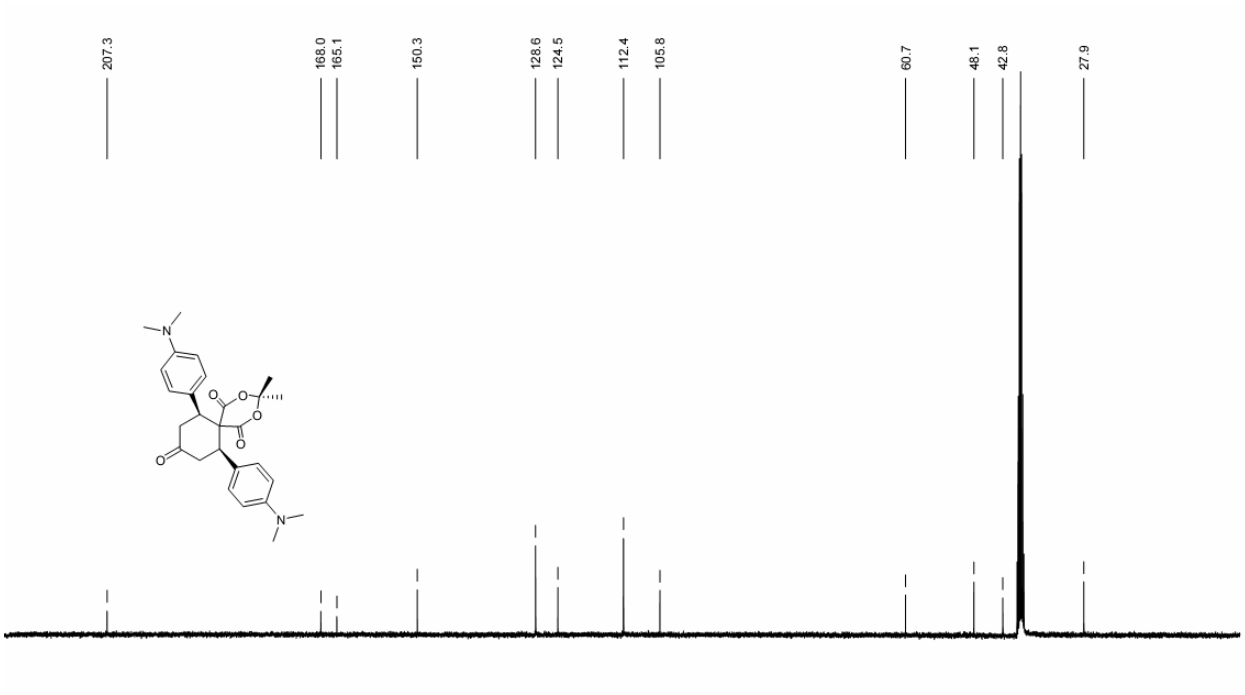
Appendix. NMR spectra of new compounds



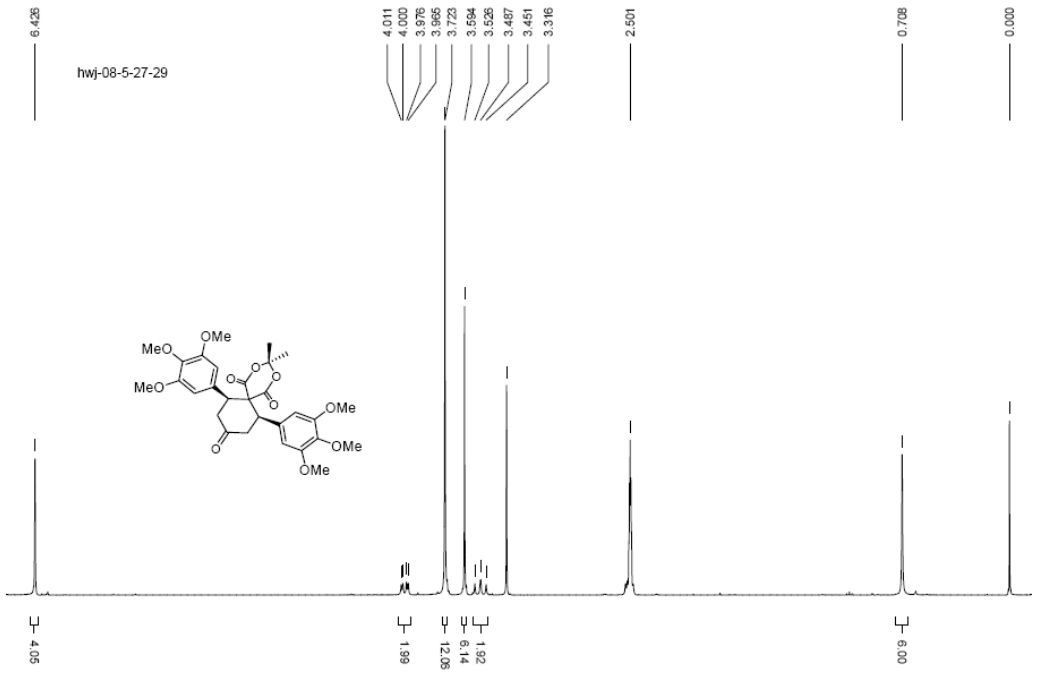
^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of Compound 2f



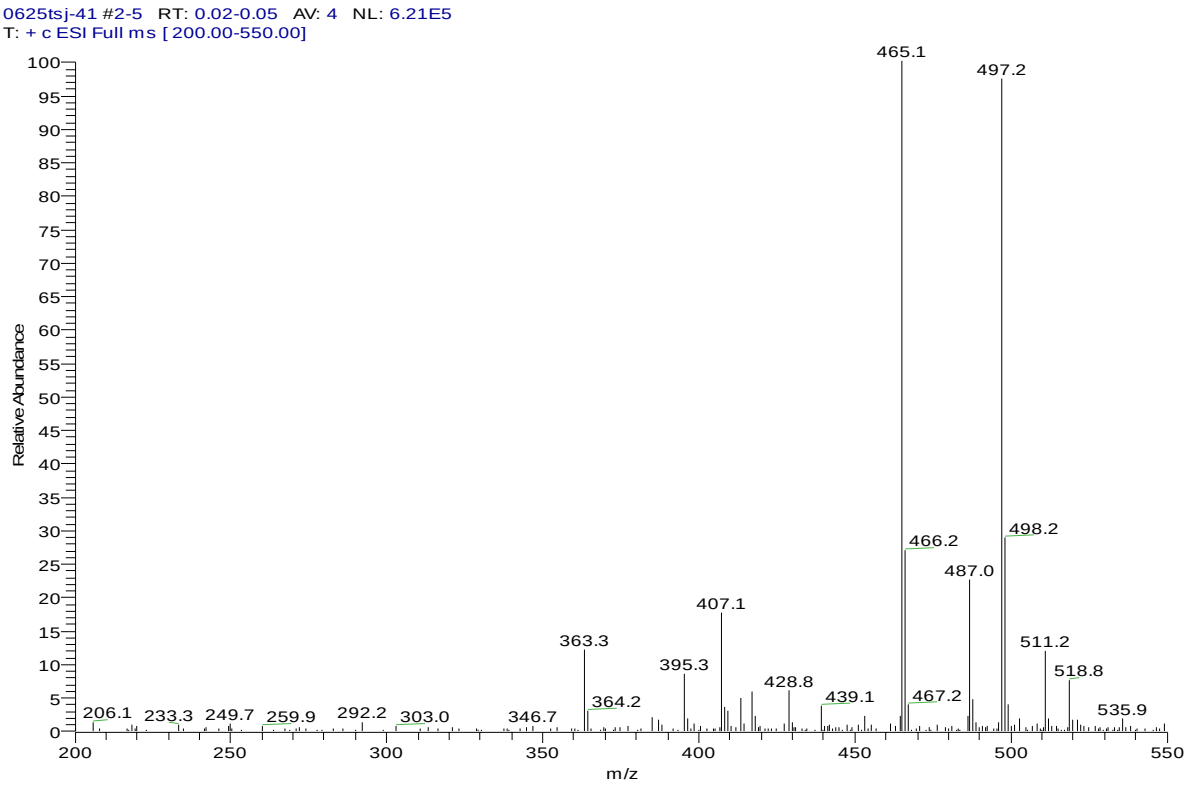
^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of Compound 2i



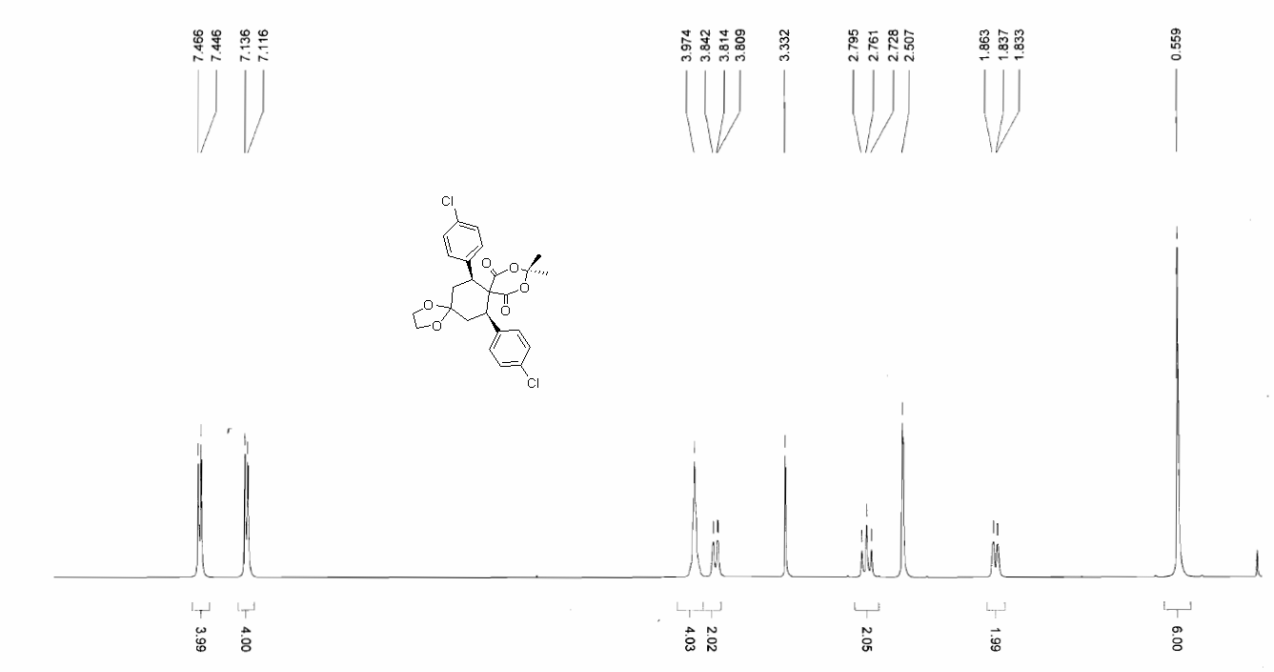
^{13}C NMR Spectrum (100 MHz, DMSO-d_6) of Compound 2i



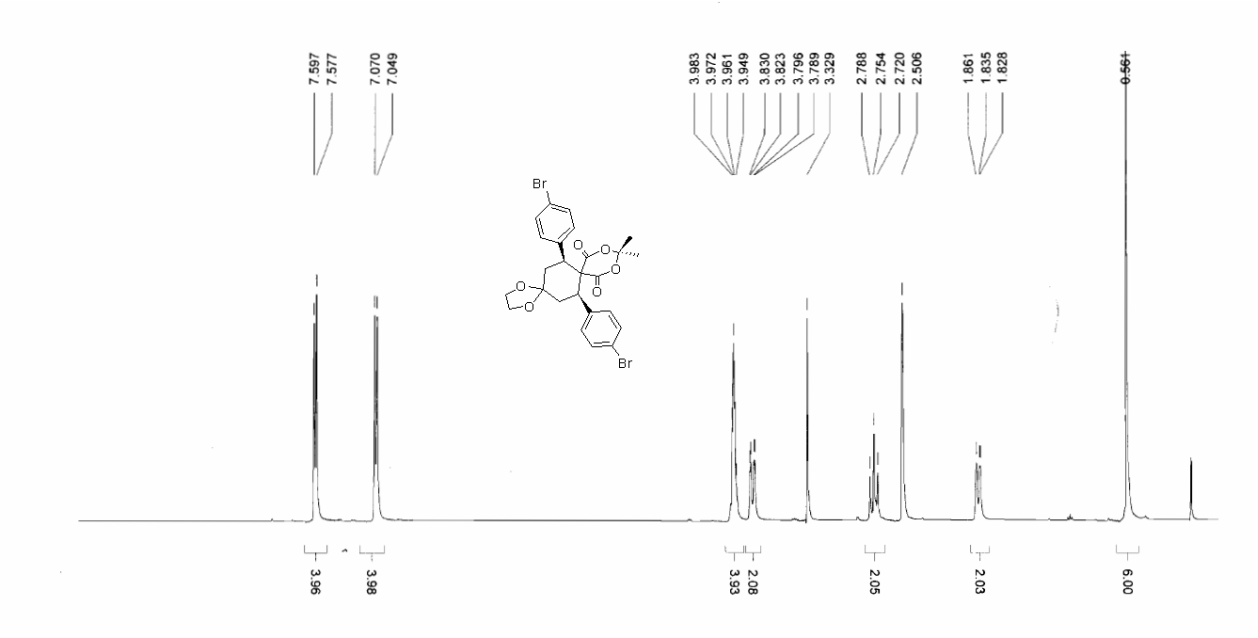
^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of Compound 2j



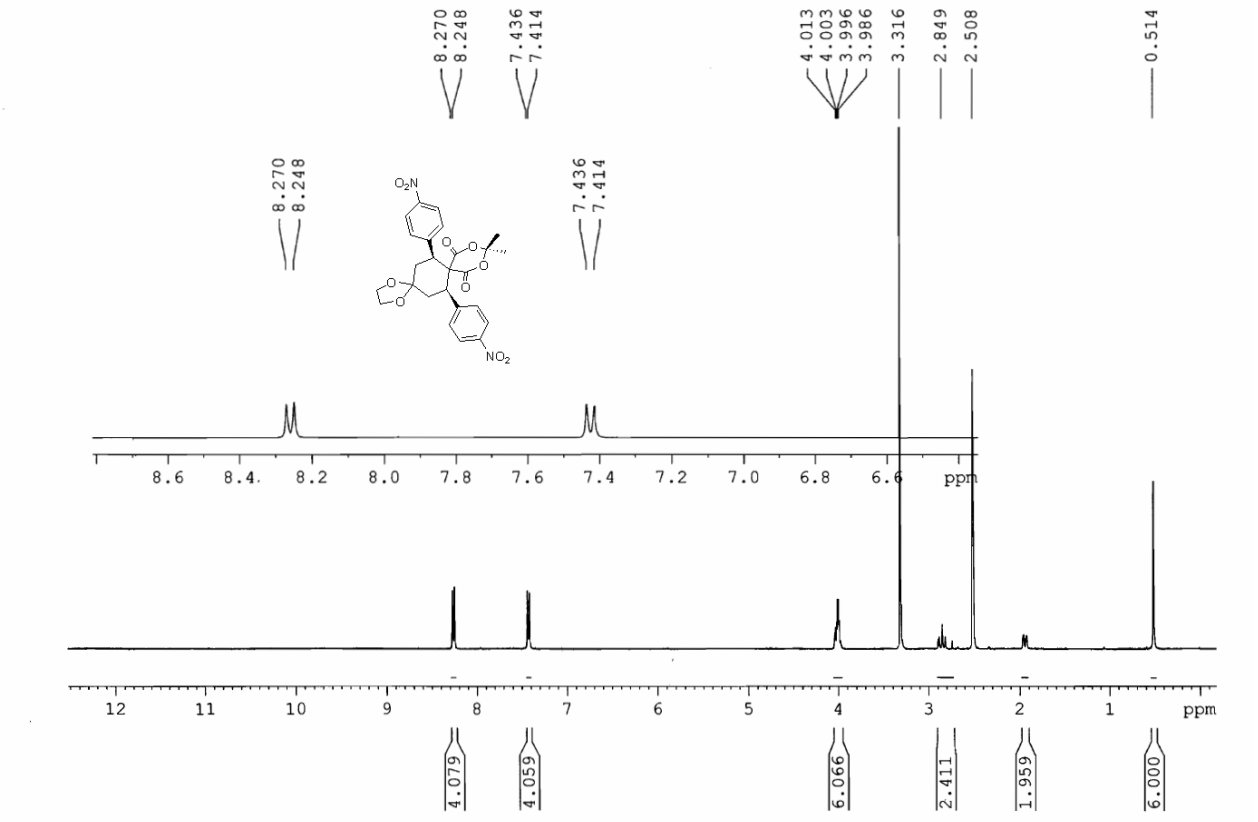
MS of Compound 2i



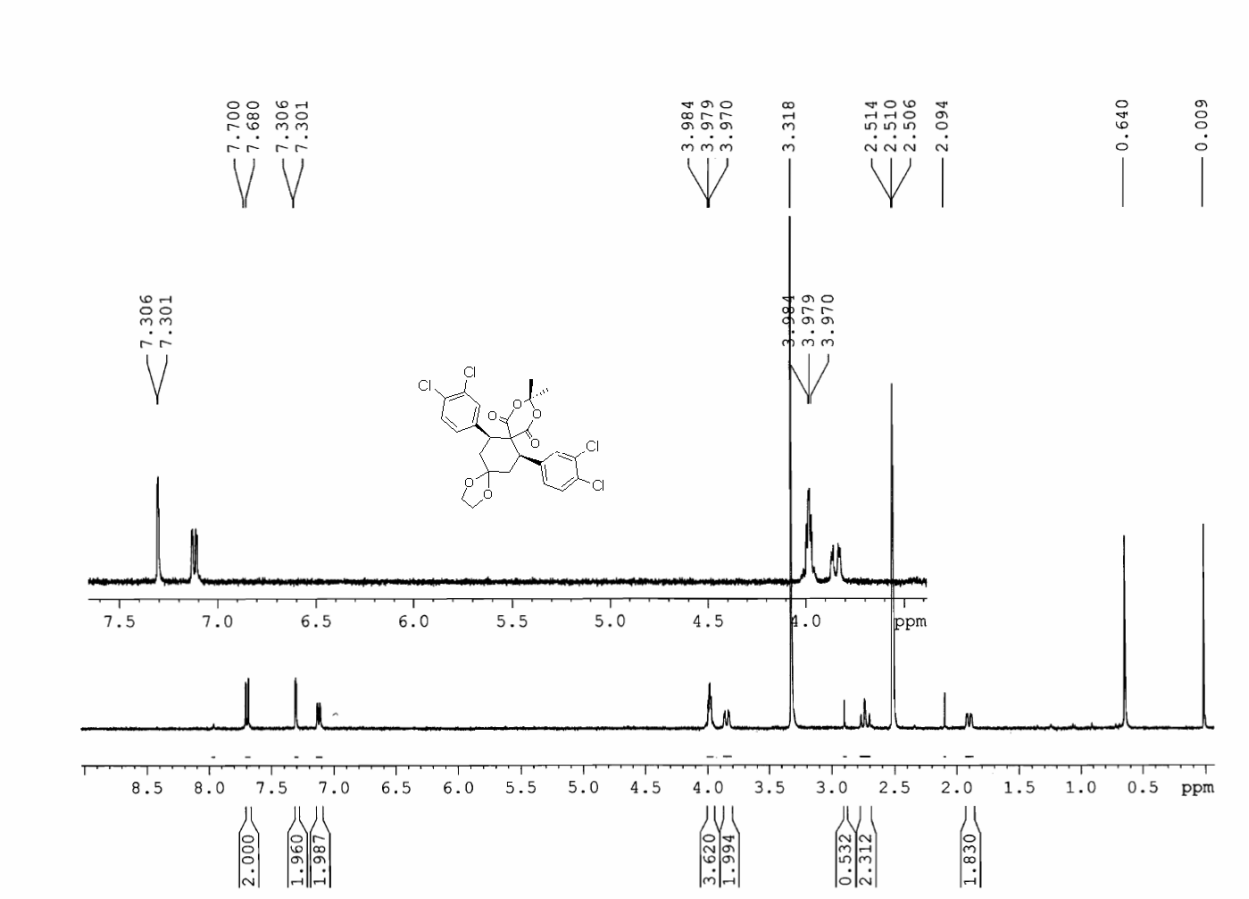
^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of Compound 3a



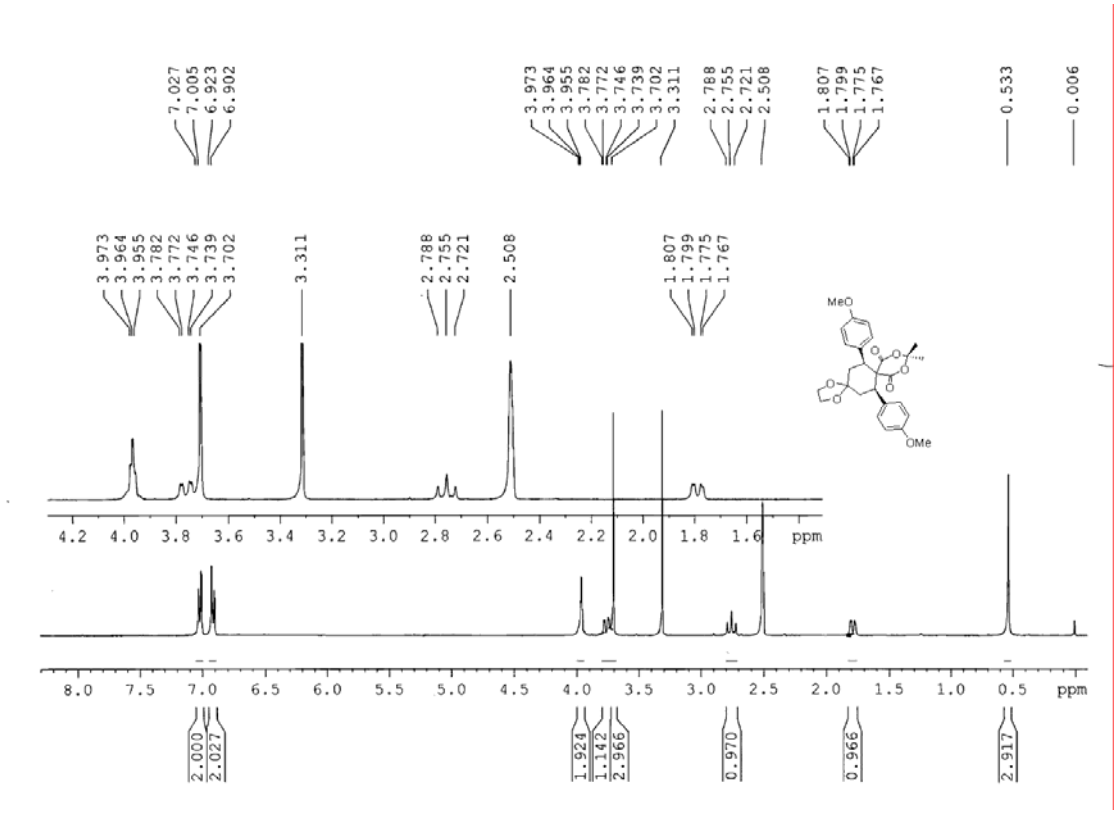
^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of Compound 3b



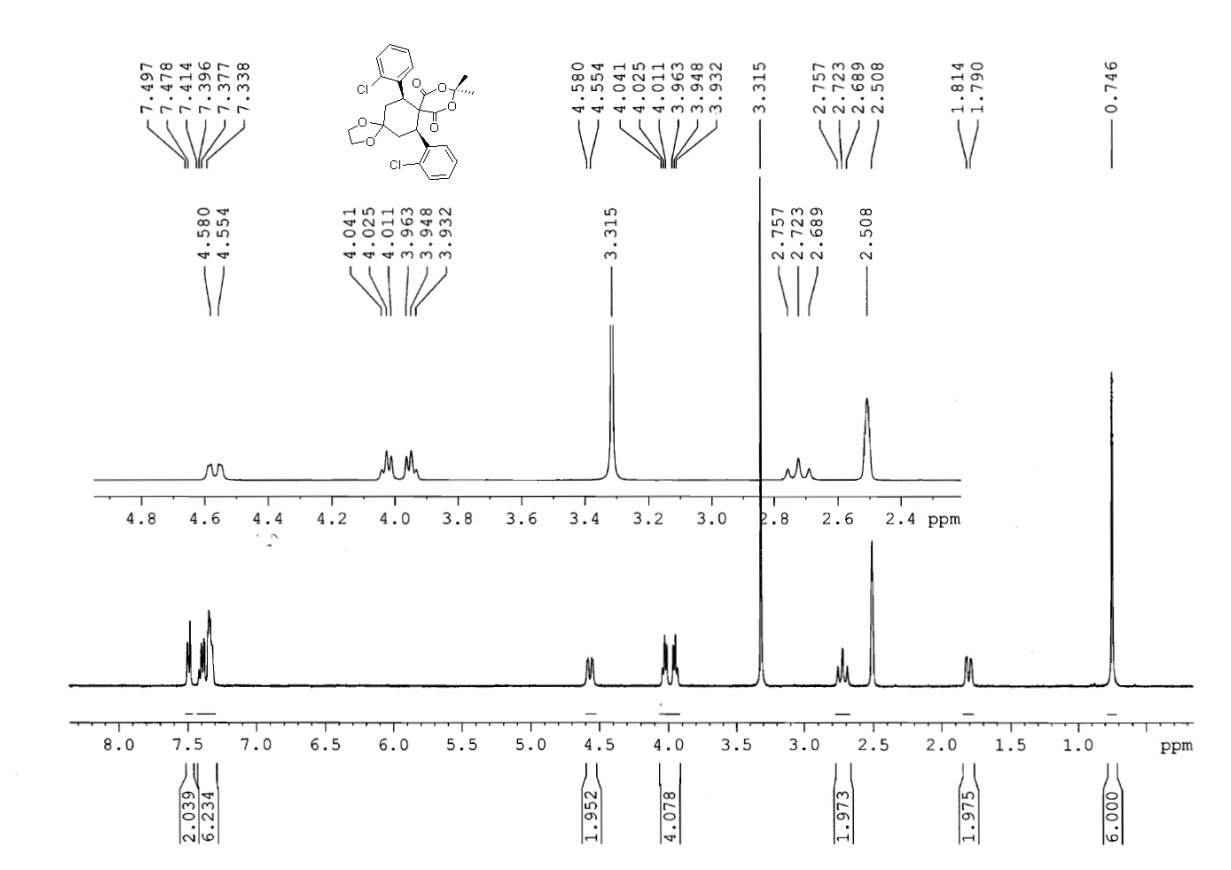
^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of Compound 3c



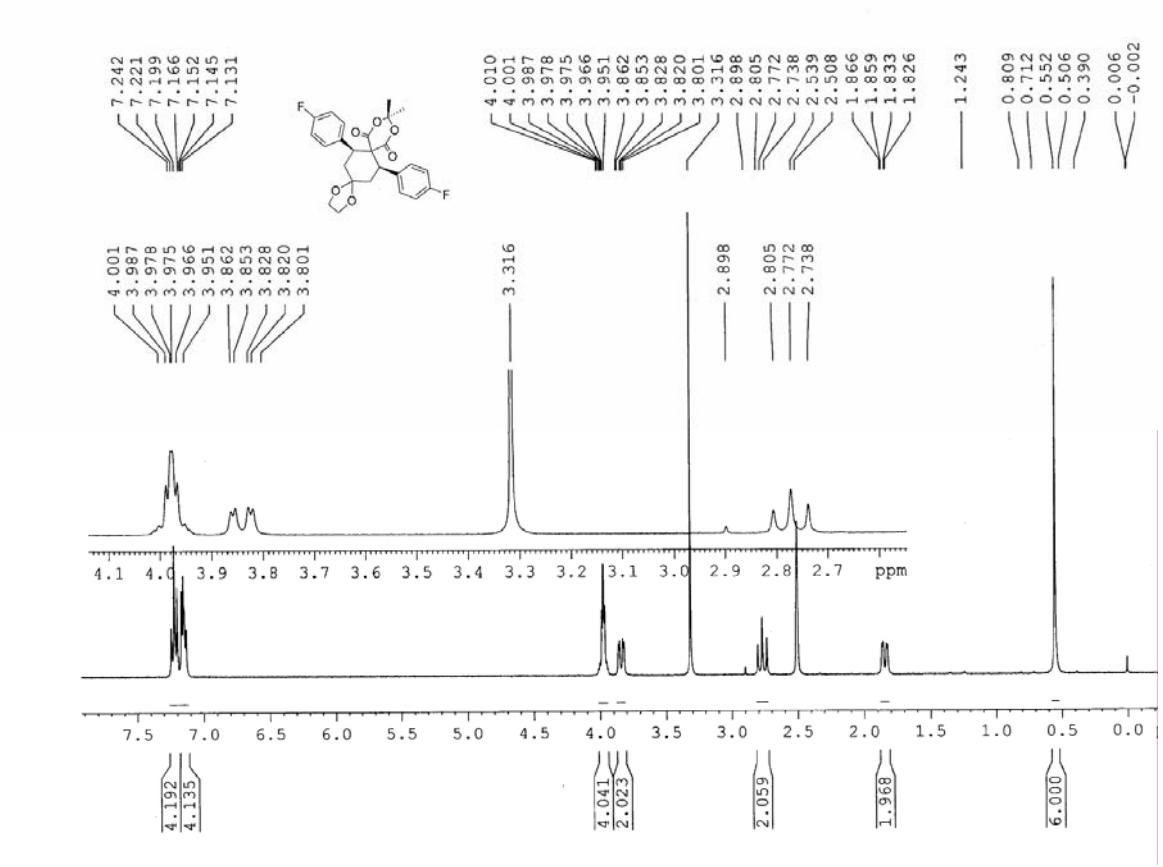
^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of Compound 3d



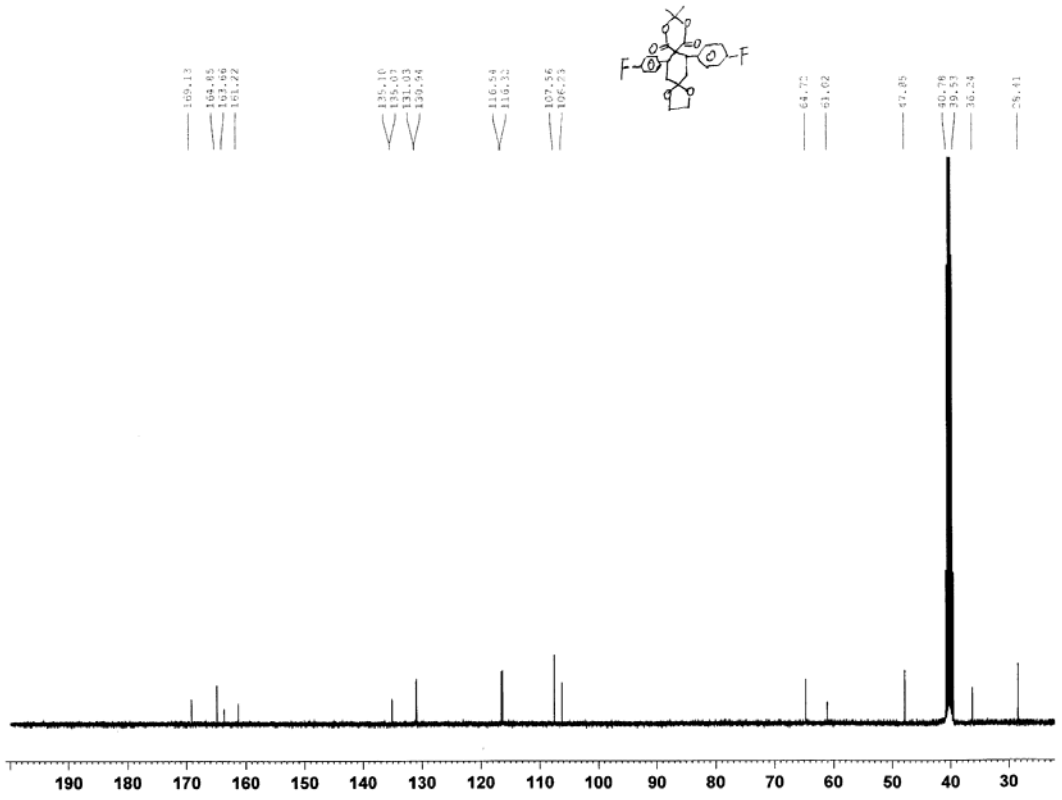
^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of Compound 3e



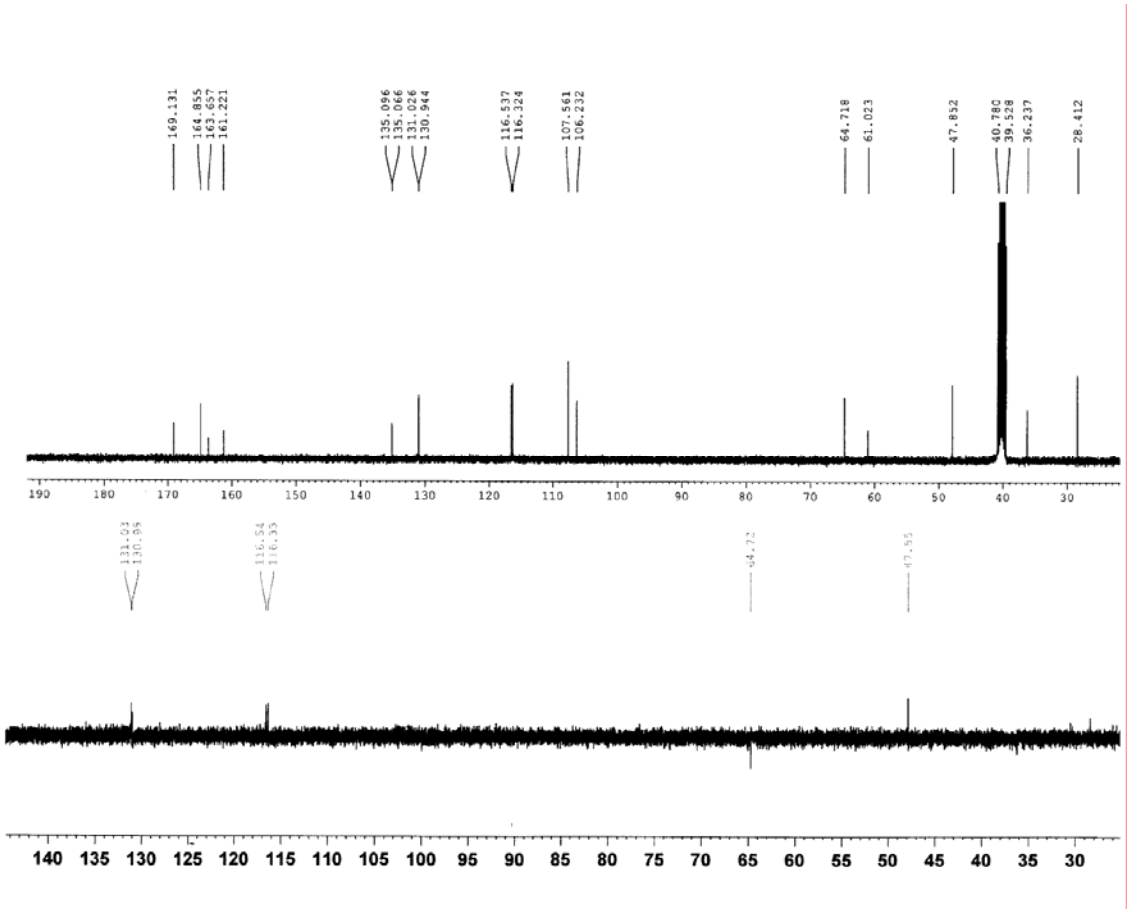
^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of Compound 3f



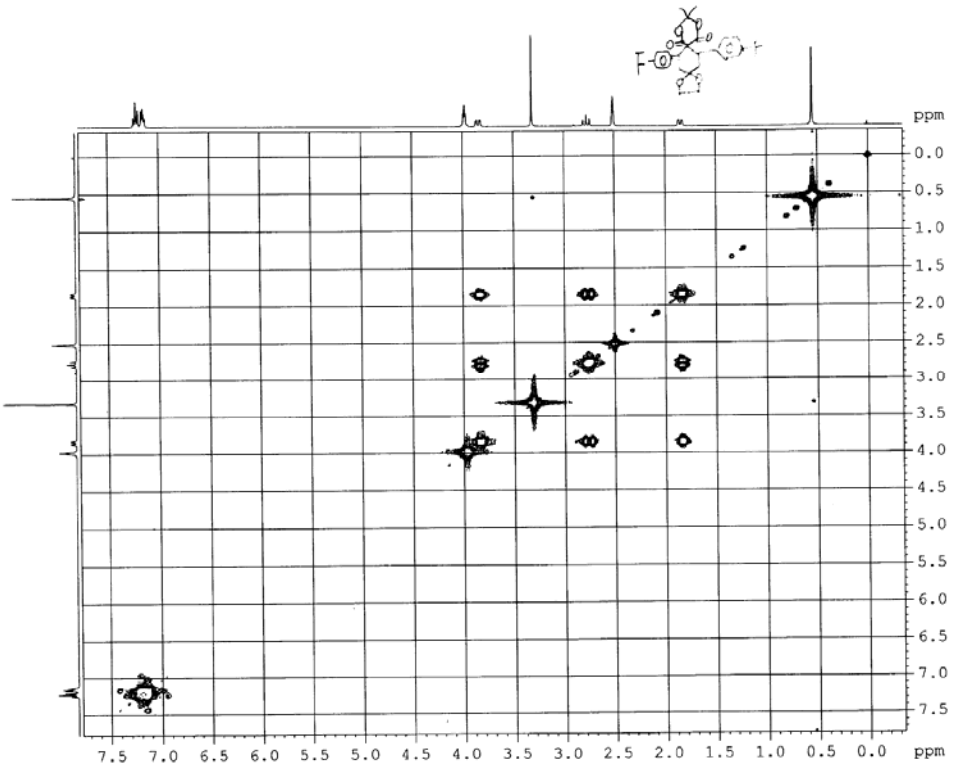
^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of Compound 3g



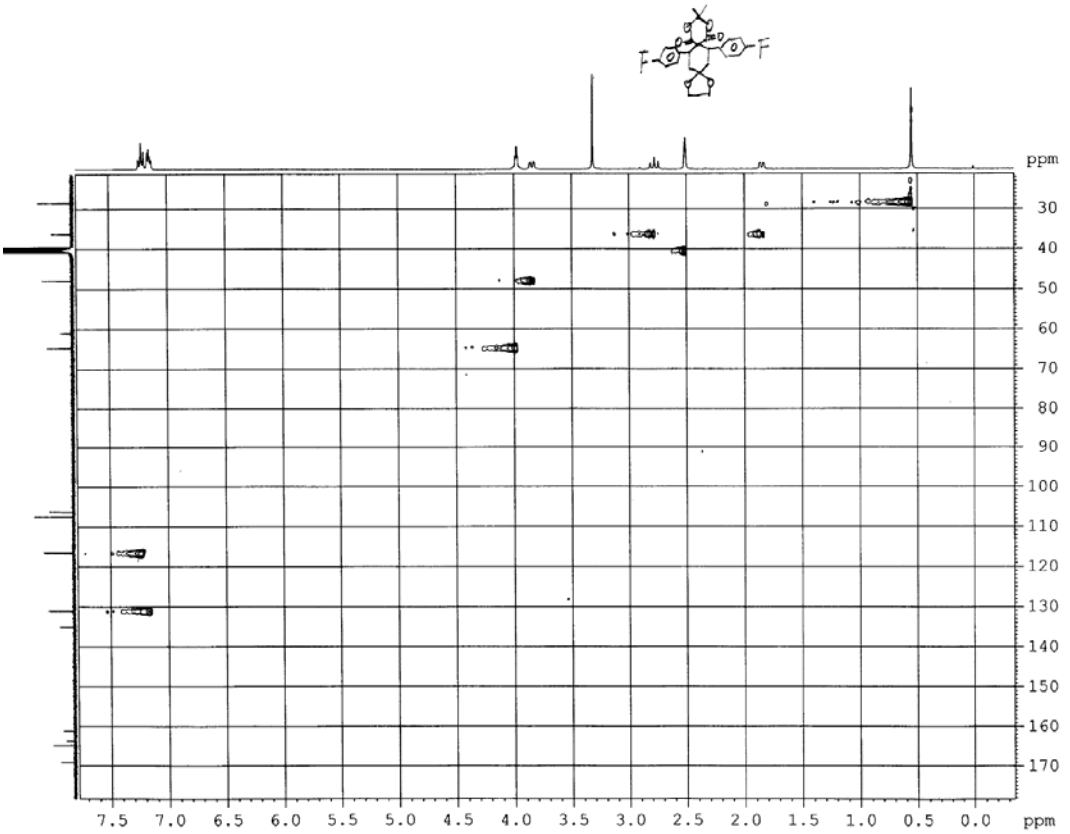
^{13}C NMR Spectrum (100 MHz, DMSO-d_6) of Compound 3g



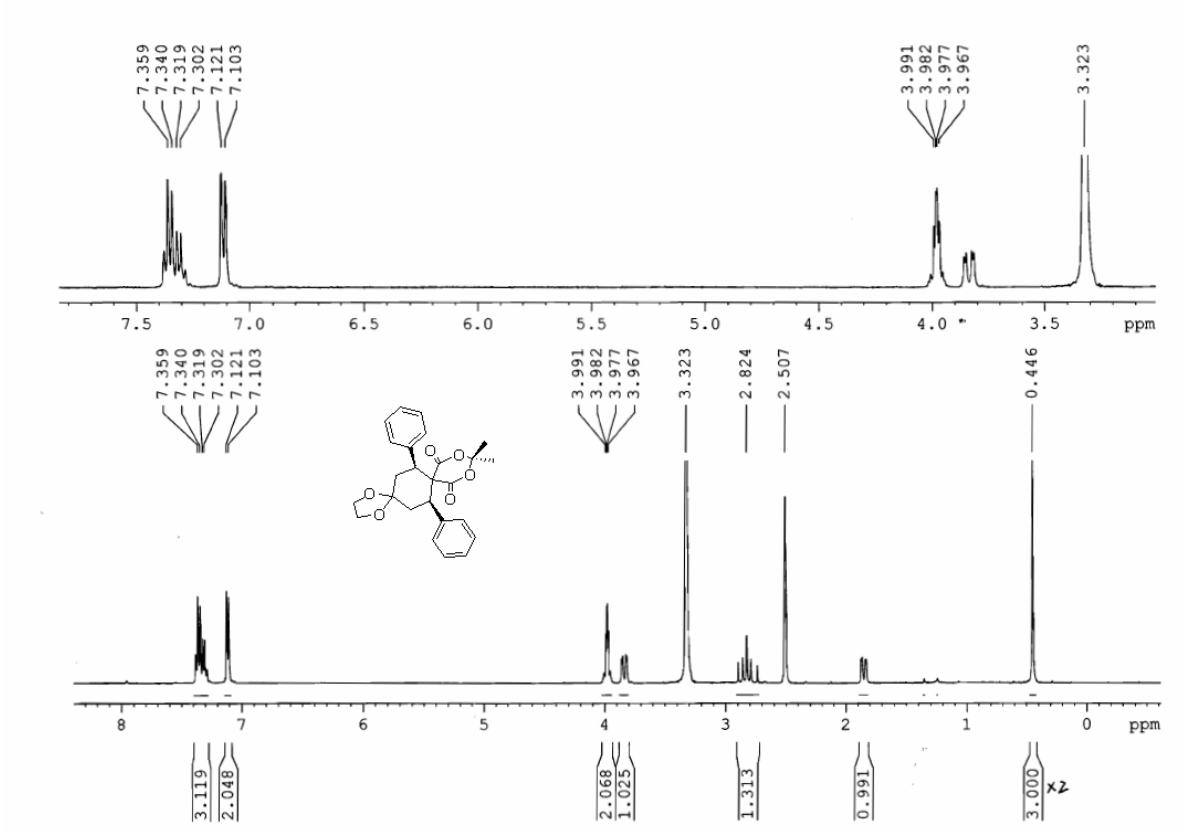
DEPT 135 Spectrum of Compound 3g



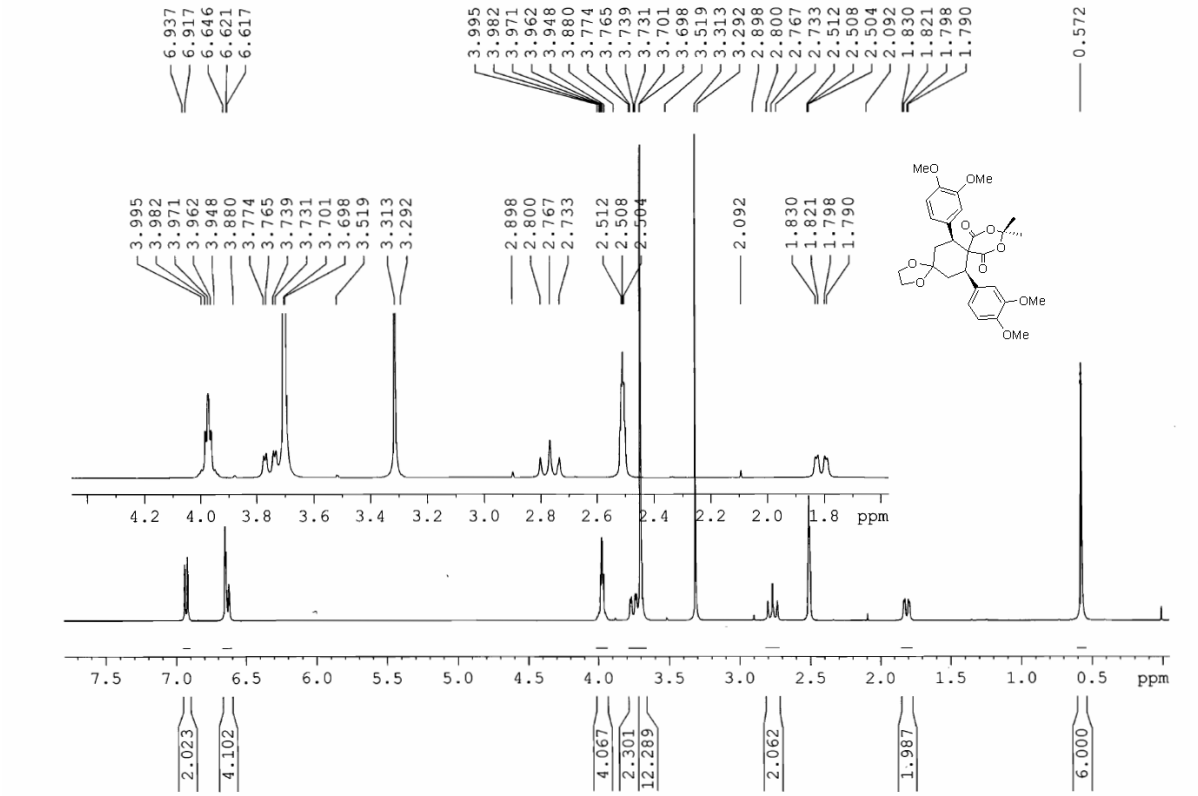
H-H COSY Spectrum of Compound 3g



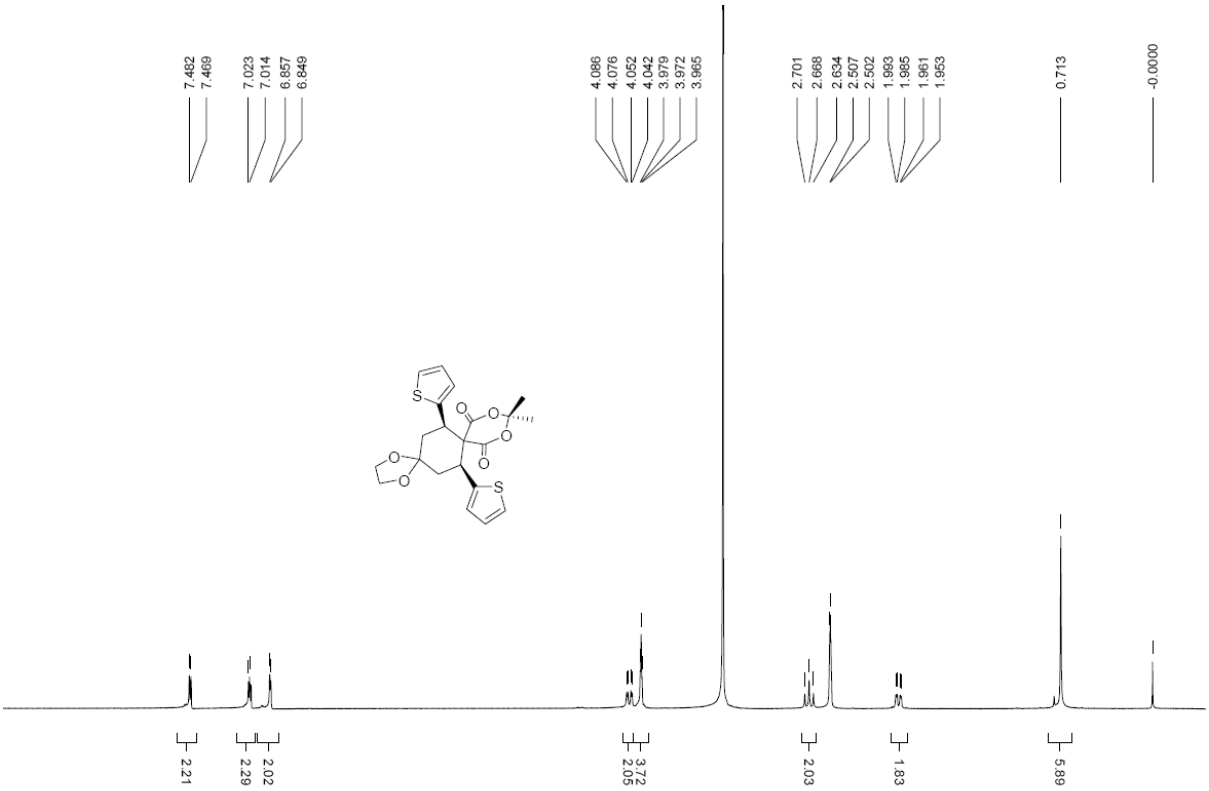
C-H COSY Spectrum of Compound 3g



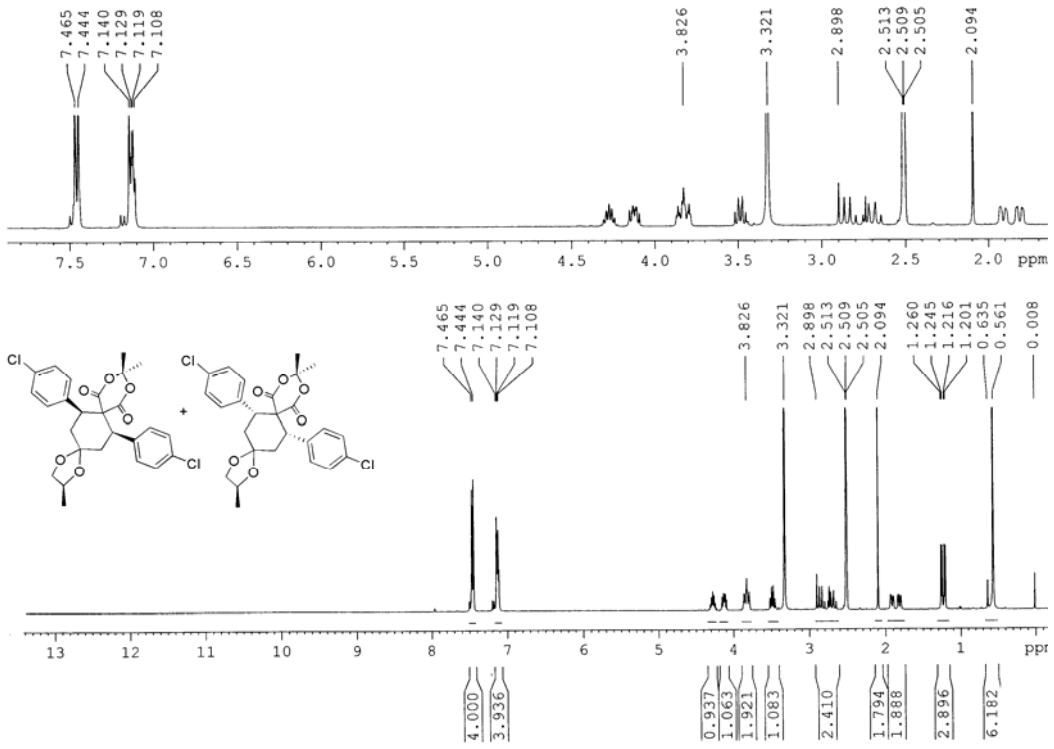
^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of Compound 3h



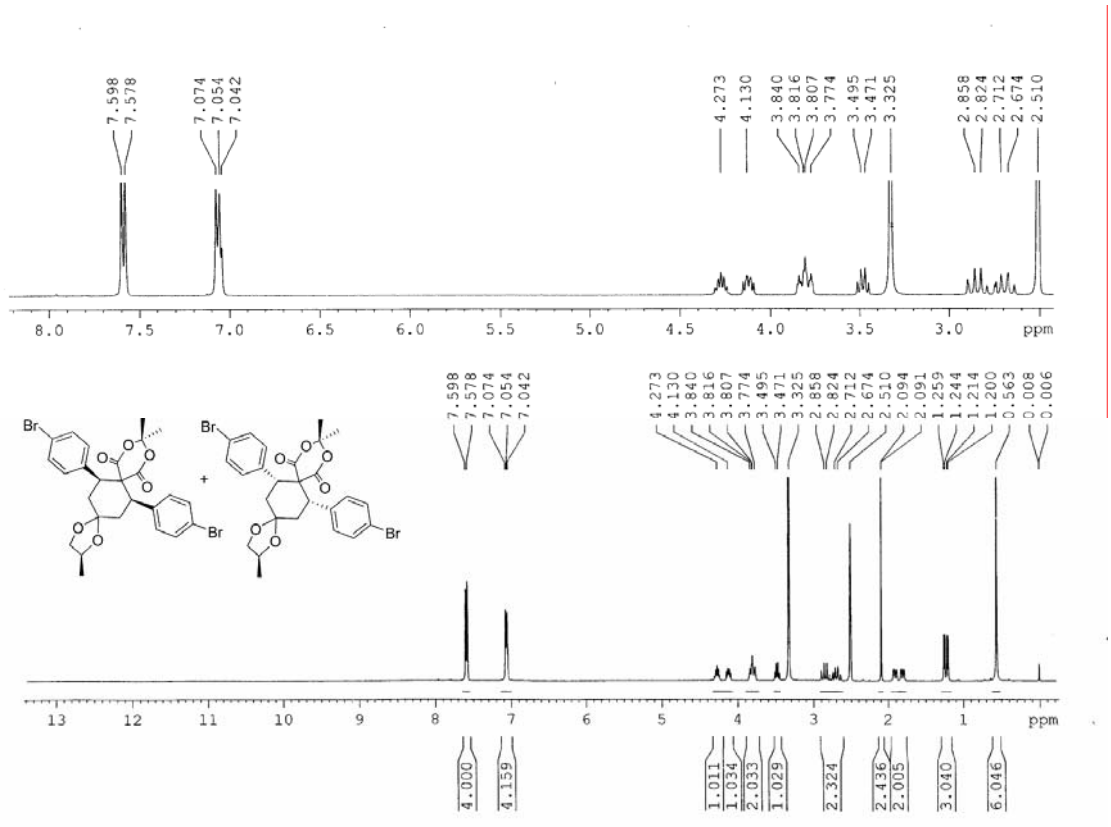
^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of Compound 3i



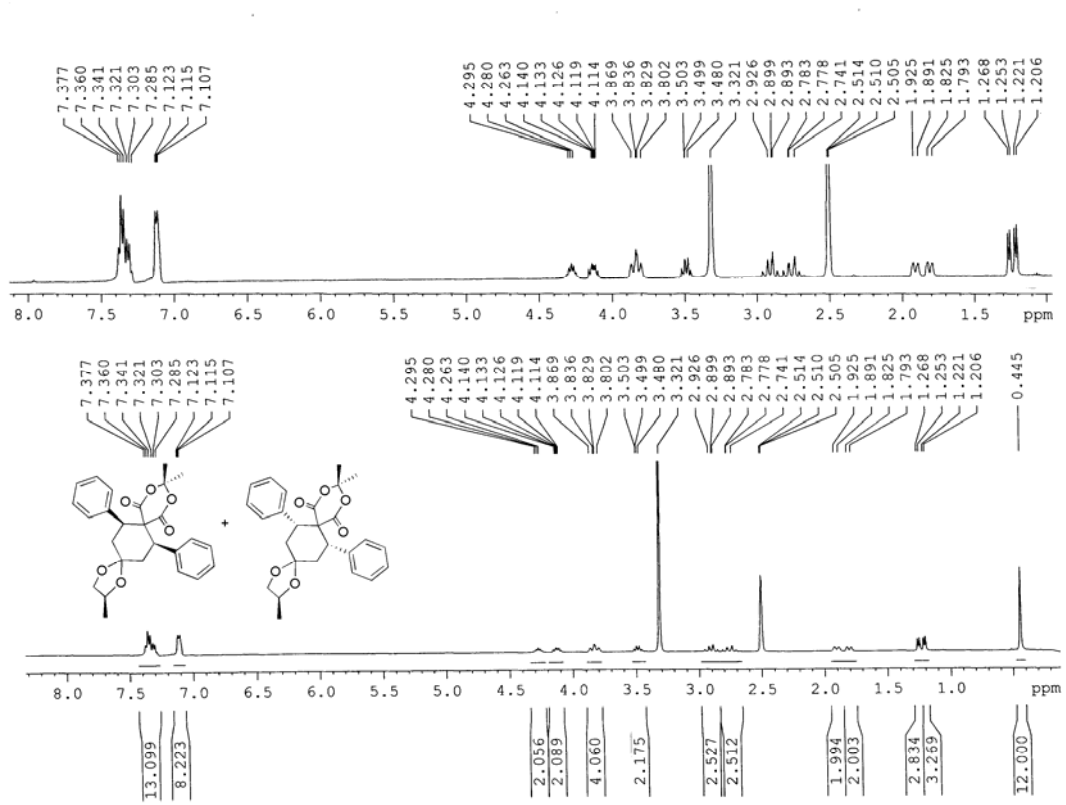
^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of Compound 3j



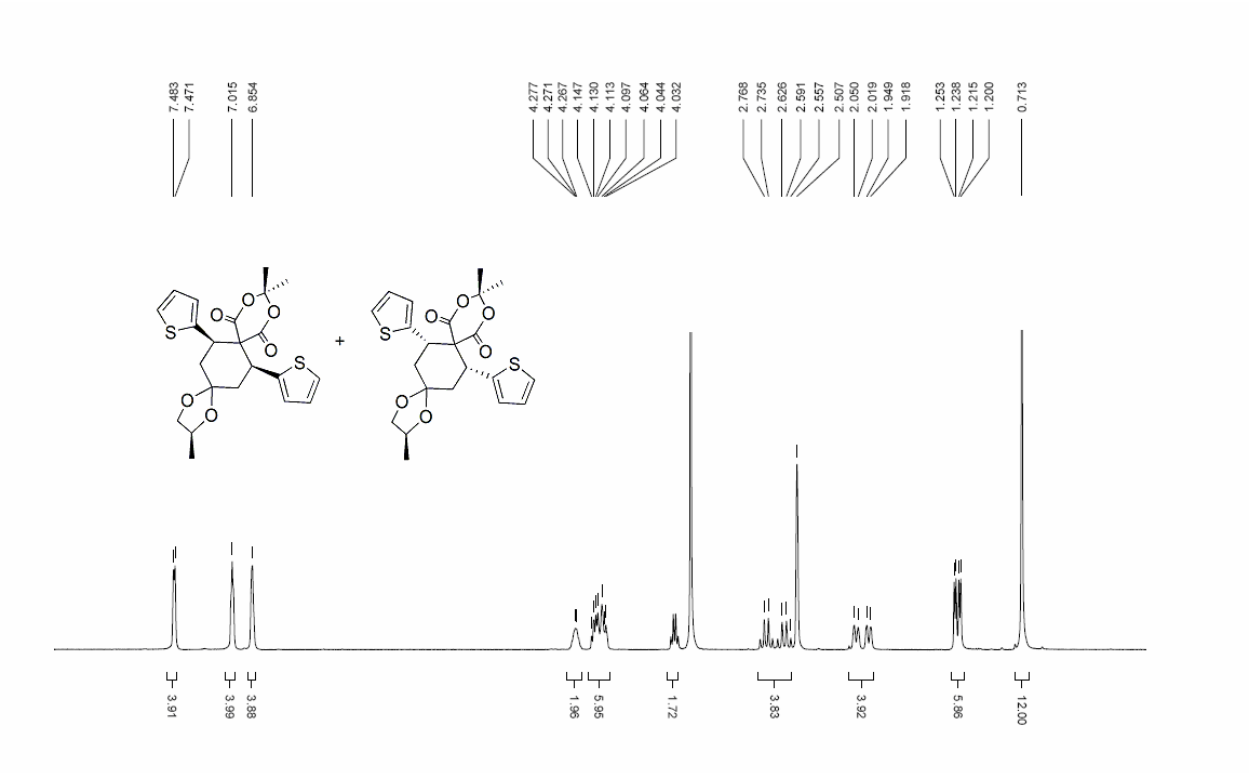
^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of Compounds 4a and 4a'



^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of Compounds 4b and 4b'



^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of Compounds 4c and 4c'



^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of Compounds 4d and 4d'