Supporting Information

Silver(I)-catalyzed sequential hydroamination and Prins type cyclization for the synthesis of fused benzo-δ-sultams

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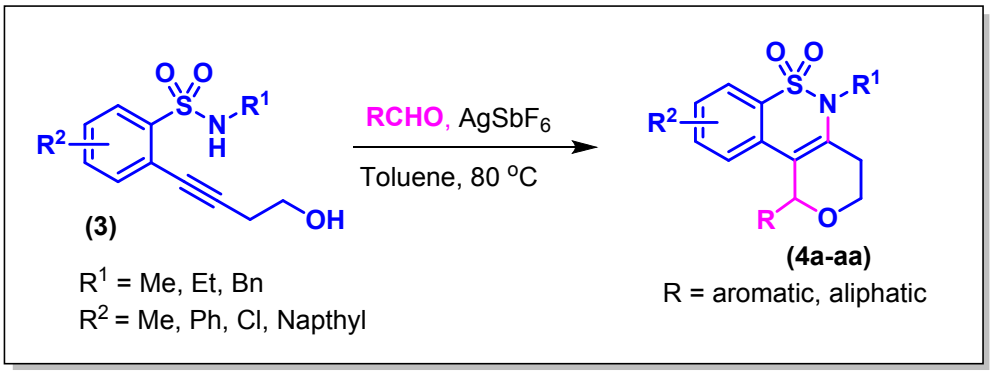

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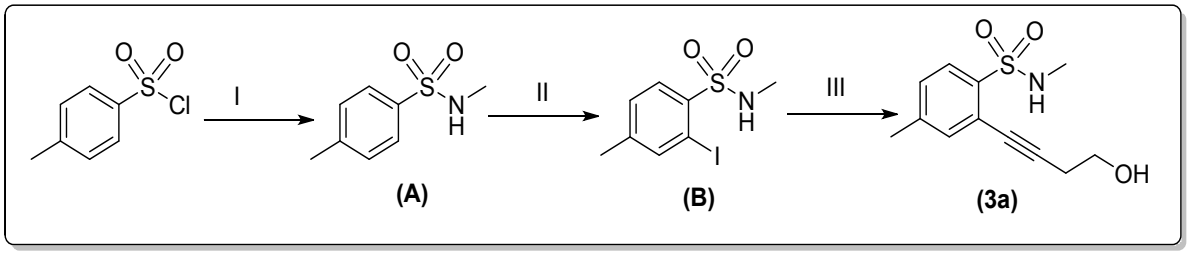
1. Experimental procedures



Reagents and conditions: (i) 40% Monomethylamine solution, $CHCl_3$, reflux (ii) *n*-BuLi, THF, I_2 (iii) $[PdCl_2(PPh_3)_2]$, CuI, CH_3CN, Et_3N

Synthesis of *N*,4-dimethylbenzenesulfonamide (A)

To a stirred solution of tosyl chloride (10g, 1 equiv, 0.052mmol) in chloroform (100 mL) at 0 ^oC was added 40% aqueous solution of monomethyl amine (4g, ~15ml, 0.12 mmol) drop wise. The resulting mixture was heated under reflux for about 4h. After completion, the solvent was removed under reduced pressure and the residue was dissolved in chloroform and washed with dil.HCl (1x50mL) followed by a brine solution. The organic layer was dried over Na_2SO_4 and concentrated under vacuum to obtain the desired compound **1a** (9.25g, 95% yield).

Synthesis of 2-iodo-*N*,4-dimethylbenzenesulfonamide (B)

To a solution of *N*,4-dimethylbenzenesulfonamide (5g, 0.027 mmol) in THF (50 mL) was cooled to 0 ^oC under nitrogen atmosphere and treated with a solution of *n*-BuLi in hexane (14 mL, 0.059 mmol) dropwise. The mixture was stirred at 0 ^oC for 15 min and then warmed to room temperature. After stirring for 1h at room temperature, the resulting bright yellow solution was cooled to -78 ^oC and stirred for 15 min. Then a solution of iodine (7.55g, 0.03 mmol) in THF (40mL) was added and the resulting mixture was stirred at -78 ^oC for 1h and then quenched with a sat. solution of NH_4Cl (40 mL) and washed with a sat. solution of $Na_2S_2O_3$ (100 mL) and then extracted with ethyl acetate. The organic layers were combined, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified using EtOAc/hexane to obtain the desired compound **2a** (7.1g, 85% yield).

Synthesis of 2-(4-hydroxybut-1-yn-1-yl)-*N*,4-dimethylbenzenesulfonamide by Sonogashira reaction (3a):

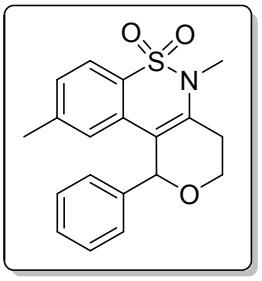
To a N_2-degassed solution of 2-iodo-*N*,4-dimethylbenzenesulfonamide (0.064 mmol), $Pd(PPh_3)_2Cl_2$ (2 mol%) and CuI (2 mol%), triethylamine (1.92 mmol, 3 equiv) was added 3-butyn-1-ol (1.92 mmol, 3 equiv) and the mixture was stirred at 80 °C for 10 h. After completion, as indicated by TLC, the mixture was diluted with EtOAc, filtered through celite and the filterate was collected and concentrated under vaccum. The resulting residue was purified by column chromatography on silica gel (60-120mesh) using a gradient mixture of ethyl acetate/hexane to give the compound **3a**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.0 Hz, 1H), 7.37 (s, 1H), 7.22 (d, *J* = 8.8 Hz, 1H), 6.22 (s, 1H), 3.89 (t, *J* = 5.4 Hz 2H), 2.73 (t, *J* = 5.6 Hz, 2H), 2.54 (d, *J* = 5.3 Hz, 3H), 2.38(s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 142.7, 138.1, 134.0, 129.4, 128.5, 120.9, 96.5, 78.6, 60.7, 29.3, 23.7, 21.0.

General procedure for the preparation of 4:

An oven dried RB flask was charged with compound **3** (50 mg, 1 equiv) and dissolved in toluene (3 mL) and then was added the respective aldehyde **2** (1.1 equiv) under inert atmosphere. The mixture was cooled to 0 °C and then $AgSbF_6$(5 mol%) was added. The resulting mixture was stirred at 25 °C and then heated to 80 °C. After completion, as monitored by TLC, the mixture was quenched with 5 mL of ice water and 5 mL of ethyl acetate. The organic layer was separated and dried over sodium sulfate. Removal of the solvent followed by purification on silica gel (60-120 mesh) using a gradient mixture of ethyl acetate/hexane afforded the corresponding product **4**.

2. Spectral data of products (4a-aa)

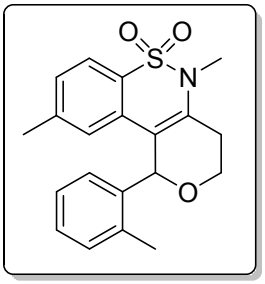
5,9-Dimethyl-1-phenyl-1,3,4,5-tetrahydrobenzo[e]pyrano[4,3-*c*][1,2]thiazine-6,6-dioxide (4a; Table 2):



Yield, 91%; Solid; mp 193-195 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.0 Hz, 1H), 7.39 – 7.34 (m, 2H), 7.33 – 7.24 (m, 3H), 7.17 (d, *J* = 7.5 Hz, 1H), 6.90 (s, 1H), 6.97 (s, 1H), 3.89 –

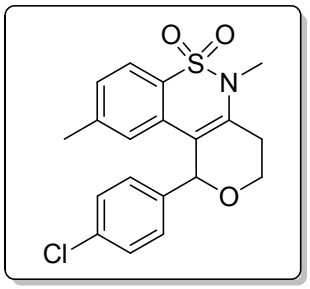
3.83 (m, 2H), 3.30(s, 3H), 2.81 – 2.72 (m, 1H), 2.64 – 2.56 (m, 1H), 2.25(s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 142.2, 139.5, 136.7, 131.7, 131.5, 129.1, 128.8, 128.5, 128.3, 128.0, 124.0, 121.6, 115.3, 74.6, 59.2, 30.4, 26.8, 21.8; IR (neat) ν_{max} 3422, 2928, 2873, 1609, 1465, 1370, 1321, 1250, 1174, 1126, 1027, 931, 895, 825, 762, 702, 579, 545, 508, 431 cm^{-1}; MS (ESI): *m/z* 342(M+H)$^+$. HRMS (ESI) calcd for $C_{19}H_{20}NO_3S$: 342.11584 (M+H)$^+$, found 342.11572.

5,9-Dimethyl-1-(o-tolyl)-1,3,4,5-tetrahydrobenzo[e]pyrano[4,3-*c*][1,2]thiazine-6,6-dioxide (4b; Table 2):



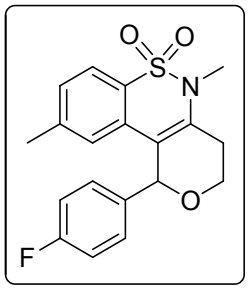
Yield, 90%; Solid; mp 155 - 158 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.22 (m, 1H), 7.20 – 7.15 (m, 2H), 7.10 – 7.01 (m, 2H), 6,75 (s, 1H), 6.17 (s, 1H), 3.85 – 3.81(dd, *J* = 4.0 Hz, *J* = 7.2 Hz, 2H), 3.31 (s, 3H), 2.84 – 2.24 (m, 1H), 2.62(s, 3H), 2.61 - 2.54(m, 1H), 2.25 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 142.2, 137.5, 137.0, 136.7, 131.5, 130.8, 129.6, 128.9, 128.3, 128.1, 125.8, 123.8, 121.8,115.8, 71.5, 58.9, 30.5, 27.0, 21.9, 19.1; IR (neat) ν_{max} 3450, 2924, 2876, 1617, 1475, 1359, 1323, 1250, 1174, 1119, 1087, 986, 923, 880, 827, 753, 719, 668, 625, 595, 548, 464 cm^{-1}; MS (ESI): *m/z* 356 (M+H)$^+$. HRMS (ESI) calcd for $C_{20}H_{22}O_3NS$: 356.13149 (M+H)$^+$, found 356.13155.

1-(4-Chlorophenyl)-5,9-dimethyl-1,3,4,5-tetrahydrobenzo[e]pyrano[4,3-*c*][1,2]thiazine-6,6-dioxide (4c; Table 2):



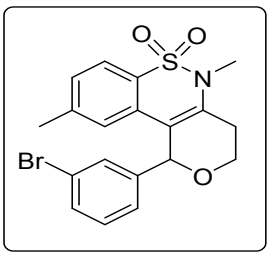
Yield, 95%; mp 198-200 ºC; Solid;^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75(d, *J* = 8.0 Hz, 1H), 7.32 – 7.27(m, 4H), 7.20(d, *J* = 8.0 Hz, 1H), 6.86(s, 1H), 5.94(s, 1H), 3.87 – 3.83(m, 2H), 3.30(s, 3H), 2.80 – 2.72(m, 1H), 2.64 – 2.57(m,1H), 2.28(s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.3, 138.2, 136.9, 134.2, 131.3, 130.5, 128.9, 128.7, 128.2, 123.8, 121.7, 114.9, 73.9, 59.3, 30.4, 26.7, 21.9; IR (neat) ν_{max} 3451, 2965, 2925, 1618, 1596, 1487, 1455, 1412, 1366, 1341, 1295, 1245, 1180, 1131, 1094, 1018, 987, 925, 896, 822, 792, 715, 698, 578, 552, 517, 446 cm^{-1}; MS (ESI): *m/z* 376 $(M+H)^+$. HRMS (ESI) calcd for $C_{19}H_{19}O_3N$ Cl S: 376.07687 $(M+H)^+$, found 376.07759.

1-(4-Fluorophenyl)-5,9-dimethyl-1,3,4,5-tetrahydrobenzo[*e*]pyrano[4,3-*c*][1,2]thiazine-6,6-dioxide (4d; Table 2):



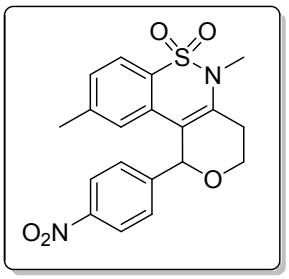
Yield, 90%; Solid; mp 194-195 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.0 Hz, 1H), 7.36 – 7.31 (m, 2H), 7.19 (d, *J* = 8.8 Hz , 1H), 7.01 – 6.96 (m, 2H), 6.87 (s, 1H), 5.95 (s, 1H), 3.88 – 3.83 (m, 2H), 3.30 (s, 3H), 2.80 – 2.27 (m, 1H), 2.65 – 2.58 (m, 1H), 2.27 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 142.2, 136.8, 135.6, 131.4, 130.9, 130.9, 128.9, 128.2, 123.9, 121.7, 115.6, 115.3, 115.2, 73.9, 59.3, 30.5, 26.8, 21.8; IR (neat) ν_{max} 3447, 3055, 2962, 2918, 2859, 1623, 1598, 1568, 1474, 1427, 1364, 1319, 1255, 1173, 1126, 1099, 1068, 1031, 992, 881, 820, 788, 694, 666, 585 cm^{-1}; MS (ESI): *m/z* 360 $(M+H)^+$. HRMS (ESI) calcd for $C_{19}H_{18}FNO_3S$: 360.10849 $(M+H)^+$, found 360.10642.

1-(3-Bromophenyl)-5,9-dimethyl-1,3,4,5-tetrahydrobenzo[e]pyrano[4,3-*c*][1,2]thiazine-6,6-dioxide (4e; Table 2):



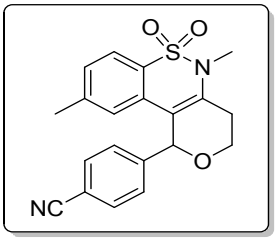
Yield, 88%; Solid; mp 196-198 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.1 Hz, 1H), 7.60 (s, 1H), 7.43 – 7.38 (m, 1H), 7.24 – 7.12 (m, 3H), 6.88 (m, 3H), 5.93 (s, 1H), 3.88 – 3.81 (m, 2H), 3.31 (s, 3H), 2.83 – 2.71 (m, 1H), 2.65 – 2.55 (m, 1H), 2.29 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 142.4, 141.9, 137.0, 132.3, 131.5, 131.3, 130.1, 128.8, 128.2, 127.7, 123.7, 122.6, 121.8, 114.5, 73.8, 59.2, 30.4, 26.7, 21.9; IR (neat) ν_{max} 3447, 3055, 2962, 2918, 2859, 1623, 1598, 1568, 1474, 1427, 1364, 1319, 1255, 1173, 1126, 1099, 1068, 1031, 992, 881, 820, 788, 694, 666, 585 cm^{-1}; MS (ESI): *m/z* 420 $(M+H)^+$. HRMS (ESI) calcd for $C_{19}H_{19}BrNO_3S$: 420.02818 $(M+H)^+$, found 420.02635.

5,9-Dimethyl-1-(4-nitrophenyl)-1,3,4,5-tetrahydrobenzo[e]pyrano[4,3-*c*][1,2]thiazine-6,6-dioxide (4f; Table 2):



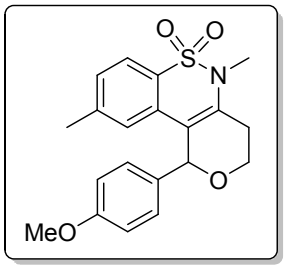
Yield, 78%; Solid; mp 202-204 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, J = 8.6 Hz, 2H), 7.77(d, J = 8.0 Hz, 1H), 7.54(d, J = 8.6 Hz, 2H), 7.22 (d, J = 8.6 Hz, 1H), 6.83(s, 1H), 6.04 (s,1H), 3.95 – 3.81 (m, 2H), 3.32 (s, 3H), 2.83 – 2.73 (m, 1H), 2.70 – 2.61 (m,1H), 2.28 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 147.8, 146.8, 142.5, 137.3, 131.1, 130.1, 129.0, 128.4, 123.8, 123.5, 121.9, 114.1, 73.7, 60.0, 30.0, 26.7, 21.8; IR (neat) ν_{max} 3448, 2921, 2858, 1614, 1524, 1481, 1349, 1327, 1248, 1175, 1128, 1104, 1065, 1035, 930, 898, 856, 826, 796, 751, 719, 684, 577, 548, 517, 442, 420 cm^{-1}; MS (ESI): *m/z* 409 $(M+Na)^+$. HRMS (ESI) calcd for $C_{19}H_{18}O_5N_2S$: 409.08465 $(M+Na)^+$, found 409.08286.

4-(5,9-Dimethyl-6,6-dioxido-1,3,4,5-tetrahydrobenzo[e]pyrano[4,3-*c*][1,2]thiazin-1-yl)benzonitrile (4g; Table 2):



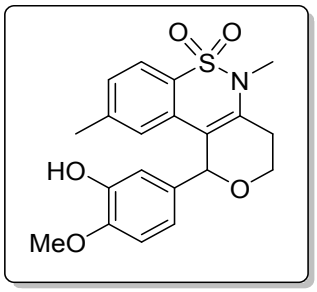
Yield, 81%; mp 180-182 ºC; Solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 1H), 6.82(s, 1H), 3.93 – 3.80(m, 2H), 3.32 (s, 3H), 2.80 – 2,73 (m, 1H), 2.28 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 144.9, 142.4, 137.3, 132.4, 131.2, 129.8, 128.9, 128.4, 123.5, 121.8, 118.4, 114.0, 112.2, 74.0, 55.9, 30.4, 26.6, 21.8; IR (neat) ν_{max} 3421, 3095, 2987, 2927, 2879, 2228, 1934, 1616, 1506, 1477, 1413, 1365, 1338, 1296, 1245, 1180, 1130, 1098, 1057, 1030, 990, 926, 895, 835, 792, 713, 681, 654, 574, 548, 514, 445 cm^{-1}; MS (ESI): *m/z* 367 $(M+H)^+$. HRMS (ESI) calcd for $C_{20}H_{19}O_3N_2S$: 367.11109 $(M+H)^+$, found 367.11133.

1-(4-Methoxyphenyl)-5,9-dimethyl-1,3,4,5-tetrahydrobenzo[e]pyrano[4,3-*c*][1,2]thiazine-6,6-dioxide (4h; Table 2):



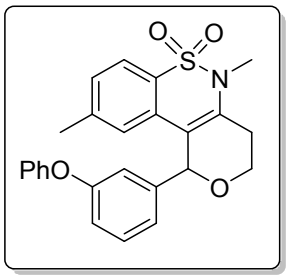
Yield 84%; Solid; mp 116-118 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71(d, *J* = 8.0 Hz ,1H), 7.24 (m, 1H), 7.16 (d, *J* = 7.9 Hz, 1H), 7.13 (dd, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.91 (s, 1H), 6.82 (t, *J* = 7.3 Hz, 1H), 6.47 (s, 1H), 4.00 (s, 3H), 3.96 – 3.84 (m, 2H), 3.29 (s, 3H), 2.80 – 2.72 (m, 1H), 2.66 – 2.59 (m, 1H), 2.26 (s, 1H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 157.4, 142.0, 136.4, 130.5, 130.2, 129.7, 128.9, 128.0, 127.4, 123.9, 121.6, 120.5, 116.0, 110.6, 68.0, 59.3, 55.8, 30.6, 26.8, 21.9; IR (neat) ν_{max} 3448, 2954, 2858, 2809, 1612, 1559, 1511, 1472, 1370, 1317, 1292, 1245, 1200, 1174, 1125, 1104, 1065, 1029, 990, 926, 896, 830, 796, 714, 686, 619, 575, 547, 511, 471 cm^{-1}; MS (ESI): *m/z* 372 $(M+H)^+$. HRMS (ESI) calcd for $C_{20}H_{22}NO_4S$: 372.12641 $(M+H)^+$, found 372.12795.

1-(3-Hydroxy-4-methoxyphenyl)-5,9-dimethyl-1,3,4,5-tetrahydrobenzo[e]pyrano[4,3-*c*][1,2]thiazine-6,6-dioxide (4i; Table 2):



Yield, 76%; Solid; mp 154-155 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 7.4 Hz, 1H), 7.02 (d, *J* = 1.9 Hz , 1H), 6.92 (s, 1H), 6.80 – 6.72 (m, 2H), 6.88 (s, 1H), 5.6 (s, 1H), 3.89 – 3.84 (m, 2H), 3.83 (s, 2H), 3.39 (s, 3H), 2.81 – 2.27 (m, 1H), 2.60 – 2.56 (m, 1H), 2.28 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 146.5, 145.5, 142.2, 136.5, 132.7, 131.6, 128.8, 128.0, 124.0, 121.6, 121.1, 115.5, 115.3, 110.3, 74.0, 58.7, 55.8, 30.5, 26.8, 21.9; IR (neat) ν_{max} 3615, 2937, 1622, 1595, 1509, 1444, 1329, 1271, 1233, 1200, 1175, 1126, 1095, 1020, 876, 816, 792, 762, 716, 661, 600, 550, 467 cm^{-1}; MS (ESI): *m/z* 388 $(M+H)^+$. HRMS (ESI) calcd for $C_{20}H_{22}NO_5S$: 388.12132 $(M+H)^+$, found 388.12322.

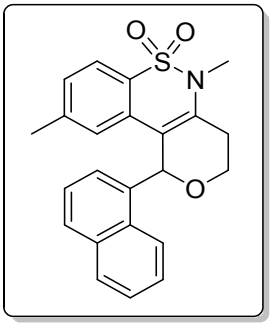
5,9-Dimethyl-1-(3-phenoxyphenyl)-1,3,4,5-tetrahydrobenzo[e]pyrano[4,3-*c*][1,2]thiazine 6,6-dioxide (4j; Table 2):



Yield, 85%; Solid; mp 177-179 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 7.9 Hz, 1H), 7.32 – 7.18 (m, 4H), 7.13 – 7.03 (m, 3H), 6.96 – 6.92 (d, *J* = 7.9 Hz, 2H), 6.92 – 6.88 (m, 2H), 5.90 (s, 1H), 3.95 – 3.83 (m, 2H), 3.29 (s, 3H), 2.79 – 2.71 (m, 1H), 2.65 – 2.57 (m, 1H), 2.30 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ157.3, 156.9, 142.1, 141.7, 136.8, 131.5, 129.9, 129.6, 128.9, 128.1, 124.0, 123.8, 123.2, 121.8, 119.7, 118.8, 118.7, 115.1, 74.5, 59.5, 30.4, 26.8, 21.9; IR (neat) ν_{max} 3448, 3054, 2967, 2864, 1590, 1483, 1449, 1374, 1315, 1247, 1208, 1183, 1128,

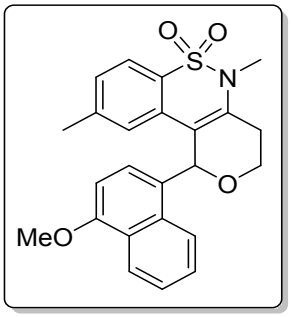
1104, 1067, 999, 934, 876, 826, 798, 756, 695, 551, 510, 462 cm^{-1}; MS (ESI): *m/z* 434 $(M+H)^+$. HRMS (ESI) calcd for $C_{25}H_{24}NO_4S$: 434.14206 $(M+H)^+$, found 434.14117.

1-(4-Methoxynaphthalen-2-yl)-5,9-dimethyl-1,3,4,5-tetrahydrobenzo[e]pyrano[4,3-*c*][1,2]thiazine 6,6-dioxide (4k; Table 2):



Yield, 87%; Solid; mp 218-220 ºC; ^1H NMR (400 MHz, $CDCl_3$): δ 8.52 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.78(d, *J* = 8.0 Hz, 2H), 7.68 – 7.63(m, 1H), 7.58 – 7.53(m, 1H), 7.33 – 7.25(m, 2H), 7.19 – 7.15 (d, *J* = 8.4 Hz, 2H), 6.81(d, *J* = 8.4 Hz, 2H), 3.90 – 3.83 (m, 1H), 3.80 – 3.72 (m, 1H), 3.34 (s, 3H), 2.94 – 2.83 (m, 1H), 2.56 – 2.49 (m, 1H), 2.15 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 142.3, 136.9, 134.1, 132.0, 131.5, 129.1, 128.7, 128.7, 128.4, 128.2, 126.5, 125.7, 125.0, 124.0, 123.5, 115.4, 70.4, 58.4, 30.4, 26.9, 21.8; IR (neat) ν_{max} 3424, 3056, 2917, 2888, 1937, 1610, 1599, 1507, 1472, 1399, 1365, 1327, 1294, 1249, 1205, 1179, 1124, 1091, 1045, 980, 927, 877, 829, 779, 736, 709, 682, 664, 637, 592, 553, 517, 466, 440 cm^{-1}; MS (ESI): *m/z* 392 $(M+H)^+$. HRMS (ESI) calcd for $C_{23}H_{22}NO_3S$ 392.13370 $(M+H)^+$, found 392.13149.

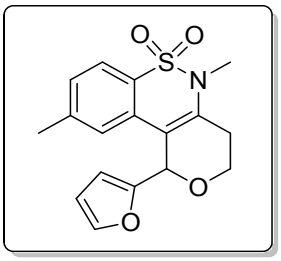
1-(4-Methoxynaphthalen-1-yl)-5,9-dimethyl-1,3,4,5-tetrahydrobenzo[e]pyrano[4,3-*c*][1,2]thiazine-6,6-dioxide (4l; Table 2):



Yield, 85%; Solid; mp 211-213 ºC; ^1H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, *J* = 8.5 Hz, 1H), 7.78 (d, *J* = 8.08 Hz, 1H), 7.69 – 7.65 (m, 1H), 7.57 – 7.53(m, 1H), 7.19 – 7.16 (m, 2H), 6.85 (s, 1H),

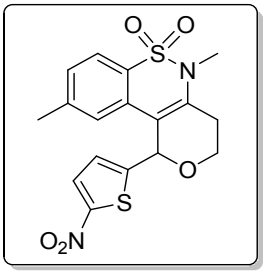
6.73 (s, 1H), 6.03 (d, J = 7.9 Hz, 1H), 3.93 (s, 3H), 3.87 – 3.82 (m, 1H), 3.81 – 3.74 (m, 1H), 3.33 (s, 1H), 2.92 – 2.84 (m, 1H), 2.53 – 2.47 (m, 1H), 2.71 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 155.7, 142.4, 136.7,132.9, 131.7, 129.0, 128.8, 128.2, 127.0, 126.1, 125.1, 123.6, 122.5, 121.6, 115.8, 102.7, 70.1, 58.0, 55.3, 30.5, 26.9, 21.8; IR (neat) ν_{max} 3445, 3046, 2971, 2938, 2859, 1596, 1510, 1479, 1461, 1422, 1386, 1318, 1296, 1265, 1210, 1174, 1155, 1123, 1091, 1062, 1043, 961, 929, 878, 840, 814, 757, 713, 660, 630, 597, 546, 508, 463, 417 cm^{-1}; MS (ESI): *m/z* 422 $(M+H)^+$. HRMS (ESI) calcd for $C_{24}H_{24}NO_4S$ 422.14206 $(M+H)^+$, found 422.14344.

1-(Furan-2-yl)-5,9-dimethyl-1,3,4,5-tetrahydrobenzo[e]pyrano[4,3-*c*][1,2]thiazine-6,6-dioxide (4m; Table 2):



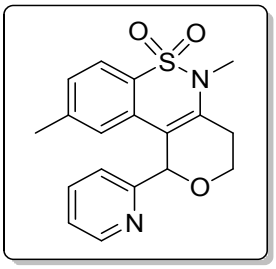
Yield, 84%; Solid; mp 162-163 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.0 Hz, 1H), 7.44 (s, 1H), 7.23 (d, J = 8.0 Hz, 1H), 6.97 (s, 1H), 6.25 (m, 1H), 6.17(d, J = 3.3 Hz, 1H), 6.05 (s, 1H), 3.96 – 3.91 (m, 1H), 3.89 – 3.83 (m, 1H), 3.28 (s, 3H), 2.87 – 2.79 (m, 1H), 2.47 – 2.41(m, 1H), 2.34 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ151.9, 143.1, 142.4, 136.6, 131.2, 128.9, 128.3, 123.2, 121.7, 113.6, 112.2, 110.4, 67.0, 58.2, 30.3, 26.3, 21.8; IR (neat) ν_{max} 3449, 3131, 3065, 2985, 2932, 1623, 1596, 1482, 1366, 1325, 1252, 1216, 1176, 1130, 1084, 1020, 929, 876, 822, 758, 712, 648, 596, 547, 430 cm^{-1}; MS (ESI): *m/z* 332 $(M+H)^+$. HRMS (ESI) calcd for $C_{17}H_{18}O_4NS$: 332.09511 $(M+H)^+$, found 332.09503.

5,9-Dimethyl-1-(5-nitrothiophen-2-yl)-1,3,4,5-tetrahydrobenzo[e]pyrano[4,3-*c*][1,2]thiazine-6,6-dioxide (4n; Table 2):



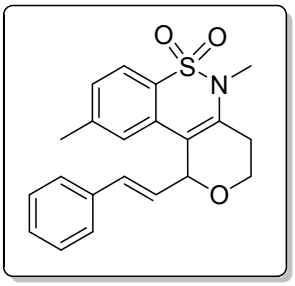
Yield, 80%; Solid; mp 160-161 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ7.80 (d, *J* = 7.9 Hz, 1H), 7.68 (d, *J* = 4.1 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.01 (s, 1H), 6.81 (d, *J* = 4.8 Hz, 1H), 6.16 (s, 1H), 4.04 – 3.97 (m, 1H), 3.92 – 3.84 (m, 1H), 3.31 (s, 3H), 2.90 – 2.79 (m, 1H), 2.48 – 2.45 (dt, *J* = 3.1 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ152.2, 151.4, 142.8, 137.3, 130.7, 128.7, 128.1, 122.9, 122.0, 113.1, 68.9, 59.0, 30.2, 26.2, 21.9; IR (neat) ν_{max} 3447, 3101, 2917, 1610, 1544, 1507, 1478, 1444, 1341, 1292, 1251, 1174, 1122, 1099, 1029, 991, 888, 816, 793, 730, 713, 598, 573, 547, 516, 469 cm^{-1}; MS (ESI): *m/z* 393 $(M+H)^+$. HRMS (ESI) calcd for $C_{17}H_{17}O_5N_2S_2$: 393.05734 $(M+H)^+$, found 393.05798.

5,9-Dimethyl-1-(pyridin-2-yl)-1,3,4,5-tetrahydrobenzo[e]pyrano[4,3-*c*][1,2]thiazine-6,6-dioxide (4o; Table 2):



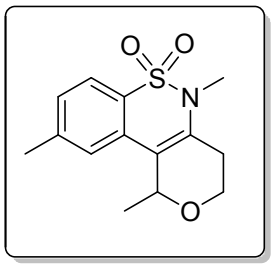
Yield, 79%; Solid; mp 190-192 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ8.75 (s, 1H), 8.52 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.56 (td, *J* = 9.6 Hz, 1H), 7.23 – 7.18 (m, 2H), 6.86 (s, 1H), 6.03 (s, 1H), 3.94 – 3.82 (m, 2H), 3.31 (s, 3H), 2.81-2.72 (m, 1H), 2.69 – 2.61 (m, 1H), 2.27 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 150.7, 149.5, 142.4, 137.3, 136.3, 135.4, 131.1, 129.0, 128.3, 123.7, 123.5, 121.8, 114.2, 72.6, 59.7, 30.5, 26.7, 21.8; IR (neat) ν_{max} 3448, 2919, 2870, 1600, 1478, 1426, 1370, 1312, 1251, 1180, 1129, 1104, 1063, 1025, 990, 930, 826, 796, 717, 689, 614, 551 cm^{-1}; MS (ESI): *m/z* 343 $(M+H)^+$. HRMS (ESI) calcd for $C_{18}H_{19}N_2O_3S$: 343.11109 $(M+H)^+$, found 343.11118.

(*E*)-5,9-Dimethyl-1-styryl-1,3,4,5-tetrahydrobenzo[e]pyrano[4,3-*c*][1,2]thiazine-6,6-dioxide (4p; Table 2):



Yield, 91%; Solid; mp 132-136 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.2 Hz, 1H), 7.73 – 7.18 (m, 6H), 7.15 (s, 1H), 6.58 – 6.49 (d, *J* = 16.2 Hz, 1H), 6.40 – 6.29 (dd, *J* = 5.2 Hz, 1H), 5.63 (d, *J* = 4.9 Hz, 1H), 4.13 – 4.03 (m, 1H), 3.98 – 3.90 (m, 1H), 3.27 (s, 3H), 2.84 – 2.71 (m, 1H), 2.54 – 2.44 (m, 1H), 2.39 (s, 1H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 142.3, 136.3, 136.1, 136.0, 131.4, 128.9, 128.4, 128.2, 128.0, 126.8, 126.7, 123.8, 121.8, 115.2, 71.5, 58.6, 30.3, 26.7, 21.9; IR (neat) ν_{max} 3749, 3449, 3026, 2977, 2917, 2865, 1603, 1482, 1452, 1368, 1319, 1247, 1176, 1124, 1086, 1065, 964, 883, 807, 753, 691, 589, 547, 461 cm^{-1}; MS (ESI): *m/z* 368 $(M+H)^+$. HRMS (ESI) calcd for $C_{21}H_{22}O_3NS$: 368.13149 $(M+H)^+$, found 368.13197.

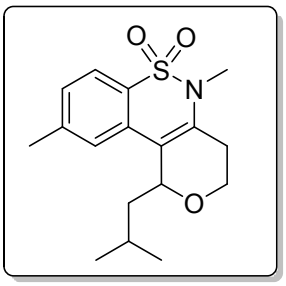
1,5,9-Trimethyl-1,3,4,5-tetrahydrobenzo[e]pyrano[4,3-*c*][1,2]thiazine-6,6-dioxide (4q; Table 2):



Yield, 75%; Solid; mp 138-139 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 7.9 Hz, 1H), 7.27 (d, *J* = 7.9 Hz, 1H), 7.13 (s, 1H), 5.14 – 5.08 (m, 1H), 4.15 – 4.05 (m, 1H), 3.85 – 3.79 (m, 1H), 3.20 (s, 3H), 2.68 – 2.60 (m, 1H), 2.56 – 2.50 (m, 1H), 2.45 (s, 3H), 1.44 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 142.2, 135.0, 131.8, 129.4, 128.0, 123.5, 122.0, 118.7, 69.1, 60.6, 30.6, 26.8, 21.9, 20.5; IR (neat) ν_{max} 3421, 2982, 2939, 2894, 2856, 2830, 1733, 1599, 1558, 1473, 1367, 1327, 1247, 1177, 116, 1112, 1075, 1036, 921, 865, 828, 781, 689, 548, 568, 491,

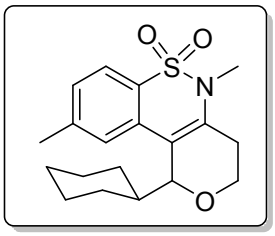
461, 421 cm^{-1}; MS (ESI): *m/z* 280 $(M+H)^+$. HRMS (ESI) calcd for $C_{14}H_{18}O_3NS$: 280.10019 $(M+H)^+$, found 280.09989.

1-Isobutyl-5,9-dimethyl-1,3,4,5-tetrahydrobenzo[e]pyrano[4,3-*c*][1,2]thiazine-6,6-dioxide (4r; Table 2):



Yield, 81%; Solid; mp 127-129 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76(d, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 7.9 Hz, 1H), 7.10 (s, 1H), 5.03 (d, *J* = 8.6 Hz, 1H), 4.11 – 4.05 (m, 1H), 3.84 -3.78 (m, – 1H), 3.20 (s, 3H), 2.59 – 2.55 (m, 2H), 2.45 (s, 3H), 2.00 – 1.92 (m, 1H), 1.73 – 1.66 (m, 1H), 1.49 – 1.43 (m, 1H), 1.07 (d, *J* = 6.5 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 142.1, 135.0, 131.7, 129.3, 127.9, 123.5, 122.0, 118.7, 70.7, 59.8, 42.4, 30.5, 26.7, 24.6, 23.7, 21.9, 21.3; IR (neat) ν_{max} 3448, 2951, 2869, 2838, 1616, 1597, 1462, 1365, 1317, 1247, 1174, 1113, 1073, 1036, 968, 895, 839, 807, 701, 630, 576, 547, 509, 468, 436, 407 cm^{-1}; MS (ESI): *m/z* 322 $(M+H)^+$. HRMS (ESI) calcd for $C_{17}H_{23}O_3NS$: 322.14695 $(M+H)^+$, found 322.14714.

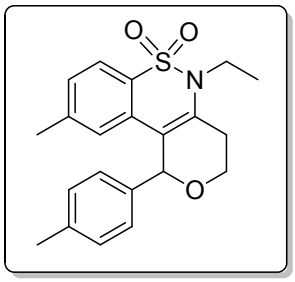
1-Cyclohexyl-5,9-dimethyl-1,3,4,5-tetrahydrobenzo[e]pyrano[4,3-*c*][1,2]thiazine-6,6-dioxide (4s; Table 2):



Yield, 77%; Solid; mp 158-160 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 7.8 Hz, 1H), 7.12 (s, 1H), 4.85 (d, *J* = 2.2 Hz, 1H), 4.14 (dd, *J* = 1.7 Hz , 1H), 3.66 (td, *J* = 3.0 Hz, *J* = 7.8 Hz, 1H), 3.18 (s, 3H), 2.77-2.66 (m, 1H), 2.46 (s, 3H), 2.40-2.33 (m, 1H), 1.80 – 1.68 (m, 3H), 1.64 – 1.39 (m, 5H), 1.26 – 1.01 (m, 2H), 1.00 – 0.88(m, 1H); ^{13}C NMR (400

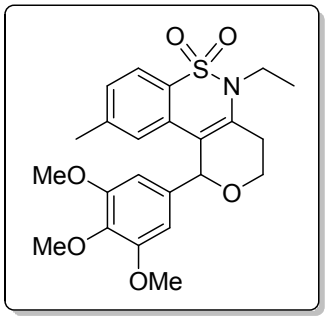
MHz, $CDCl_3$): δ141.8, 136.3, 132.3, 129.3, 127.8, 123.8, 122.0, 117.0, 62.1, 41.7, 30.8, 30.1, 26.8, 26.3, 26.1, 24.6, 22.0; IR (neat) ν_{max} 3450, 2926, 2856, 1609, 1453, 1332, 1247, 1174, 1125, 1032, 898, 866, 803, 696, 578, 551, 514, 445 cm^{-1}; MS (ESI): *m/z* 348 $(M+H)^+$. HRMS (ESI) calcd for $C_{19}H_{25}O_3NS$: 348.16299 $(M+H)^+$, found 348.16279.

5-Ethyl-9-methyl-1-(p-tolyl)-1,3,4,5-tetrahydrobenzo[e]pyrano[4,3-*c*][1,2]thiazine-6,6-dioxide (4t; Table 3):



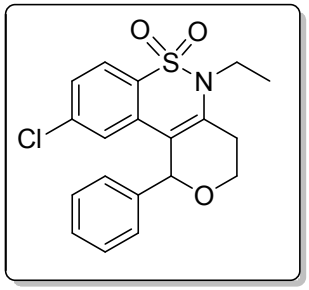
Yield, 92%; Solid; mp 172-174 ºC; ^1H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 7.9 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 7.9 Hz, 2H), 6.92(s, 1H), 5.96(s, 1H),3.96 – 3.81(m, 3H), 3.77 – 3.3.67(m, 1H), 2.81 – 2.72(m, 1H), 2.62 – 2.55(m, 1H), 2.29(s, 3H), 2.76(s, 3H), 1.12(t, *J* = 7.0 Hz, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 141.9, 138.1, 136.6, 133.4, 131.5, 130.2, 129.0, 128.2, 124.3, 117.8, 74.5, 59.1, 40.5, 26.8, 21.8, 21.1, 15.1; IR (neat) ν_{max} 3449, 2975, 2917, 2865, 1916, 1607, 1559, 1511, 1474, 1454, 1377, 1322, 1225, 1173, 1122, 1100, 991, 930, 904, 819, 769, 680, 658, 617, 577, 545, 510, 484 cm^{-1}; MS (ESI): *m/z* 370 $(M+H)^+$. HRMS (ESI) calcd for $C_{21}H_{24}NO_3S$ 370.14714 $(M+H)^+$, found 370.14778.

5-Ethyl-9-methyl-1-(3,4,5-trimethoxyphenyl)-1,3,4,5-tetrahydrobenzo[*e*]pyrano[4,3-*c*][1,2]thiazine-6,6-dioxide (4u; Table 3):



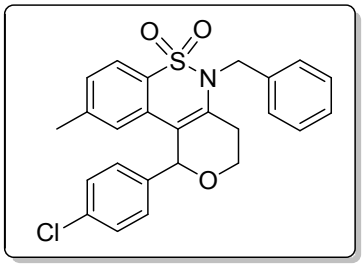
Yield, 88%; Solid; mp 149-151 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 7.9 Hz, 1H), 7.2 (d, *J* = 8.0 Hz, 1H), 6.97(s, 1H), 6.60 (s, 1H), 5.94(s, 1H), 4.02 – 3.86(m, 3H), 3.79 (s, 3H), 3.79 (s, 3H), 3.77 (s, 6H), 3.74 – 3.65 (s, 1H), 2.77 – 2.61 (m, 2H), 2.31 (s, 3H), 1.10 (t, *J* = 7.0 Hz 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 153.1, 142.0, 137.6, 135.6, 135.2, 131.71, 130.3, 128.3, 124.1, 121.1, 118.1, 106.0, 75.0, 60.6, 60.0, 56.0, 40.5, 26.7, 21.8, 15.0; IR (neat) ν_{max} 3447, 2981, 2939, 2885, 2835, 1614, 1592, 1504, 1462, 1423, 1314, 1228, 1203, 1173, 1122, 1057, 1011, 922, 885, 824, 779, 726, 691, 590, 548, 495 cm^{-1}; MS (ESI): *m/z* 446 $(M+H)^+$. HRMS (ESI) calcd for $C_{23}H_{28}NO_3S$: 446.16318 $(M+H)^+$, found 446.16423.

5-Ethyl-9-methyl-1-(p-tolyl)-1,3,4,5-tetrahydrobenzo[e]pyrano[4,3-*c*][1,2]thiazine-6,6-dioxide (4v; Table 3):



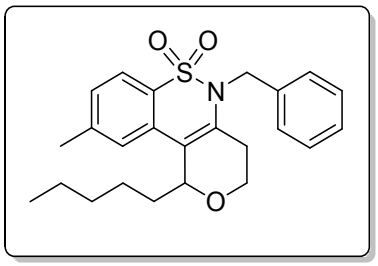
Yield, 94%; Solid; mp 182-184 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.3 Hz, 1H), 7.36 – 7.27(m, 6H), 7.09 (d, *J* = 1.83 Hz, 1H), 5.92(s,1H), 3.98 – 3.84(m, 3H), 3.81 – 3.71(m, 1H), 2.82 – 2.72(m, 1H), 2.69 – 2.61(m, 1H), 1.15(t, *J* = 7.0 Hz, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 139.0, 137.9, 137.1, 133.1, 130.7, 129.0, 128.7, 128.6, 127.4, 123.9, 122.9, 116.8, 74.9, 59.5, 40.6, 26.5, 15.3; IR (neat) ν_{max} 3059, 2976, 2930, 2869, 1901, 1611, 1583, 1546, 1493, 1459, 1397, 1371, 1351, 1328, 1279, 1228, 1209, 1174, 1125, 1093, 1063, 1037, 935, 874, 757, 701, 648, 598, 574, 517, 424 cm^{-1}; MS (ESI): *m/z* 376 $(M+H)^+$. HRMS (ESI) calcd for $C_{19}H_{18}ClNO_3S$ 376.07759 $(M+H)^+$, found 376.07687.

5-Benzyl-1-(4-chlorophenyl)-9-methyl-1,3,4,5-tetrahydrobenzo[e]pyrano[4,3-*c*][1,2]thiazine-6,6-dioxide (4w; Table 3):



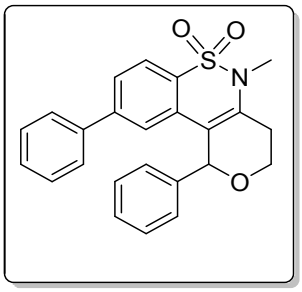
Yield, 93%; Solid; mp 156-158 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 7.9 Hz, 1H), 7.29 – 7.20 (m, 8H), 7.107 – 7.07(m, 2H), 6.81 (s, 1H), 5.86 (s, 1H), 5.08 (d, *J* = 16.7 Hz, 1H), 4.92 (d, *J* = 16.7 Hz, 1H), 3.76 – 3.67 (m, 2H), 2.62 – 2.50 (m, 2H), 2.27 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 142.2, 138.2, 136.2, 136.1, 134.2, 131.3, 130.4, 130.0, 128.7, 128.7, 128.4, 127.6, 126.7, 124.2, 128.6, 117.0, 74.1, 59.4, 48.5, 27.0, 21.9; IR (neat) ν_{max} 3058, 2960, 2890, 1618, 1597, 1486, 1449, 1412, 1359, 1327, 1221, 1176, 1142, 1086, 1059, 993, 904, 862, 828, 734, 690, 657, 595, 550, 471, 446 cm^{-1}; MS (ESI): *m/z* 452 $(M+H)^+$. HRMS (ESI) calcd for $C_{25}H_{22}ClNO_3S$: 452.10976 $(M+H)^+$, found 452.10817.

5-Benzyl-9-methyl-1-pentyl-1,3,4,5-tetrahydrobenzo[e]pyrano[4,3-*c*][1,2]thiazine-6,6-dioxide (4x; Table 3):



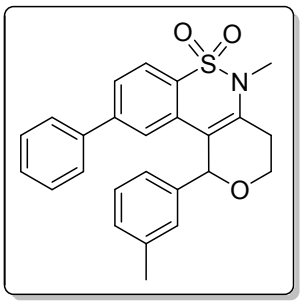
Yield, 78%; Solid; mp 122-124 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 8.08 Hz, 1H), 7.22 – 7.17 (m, 3H), 7.09(s, 1H), 7.04 – 7.01 (m, 2H), 5.02 (d, *J* = 16.8 Hz, 1H), 4.95 – 4.91 (m, 1H), 4.78 (d, *J* = 16.8 Hz, 1H), 4.01 – 3.95 (m, 1H), 3.62 – 3.55 (m, 1H), 2.60 – 2.51 (m, 1H), 2.46 (s, 1H), 2.36 – 2.28 (m, 1H), 1.77 – 1.64 (m, 2H), 1.46 – 1.37 (m, 2H), 1.30 – 1.19 (m, 4H), 0.84 (t, *J* = 6.96 Hz, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 142.0, 136.4, 134.6, 131.9, 130.4, 128.6, 128.1, 127.4, 126.5, 123.7, 121.9, 119.4, 72.8, 60.7, 48.4, 33.9, 31.5, 27.0, 24.4, 22.5, 22.0, 13.9; IR (neat) ν_{max} 3418, 3026, 2931, 2860, 1609, 1557, 1456, 1410, 1358, 1316, 1175, 1140, 1114, 1075, 1029, 913, 878, 795, 746, 693, 641, 593, 555, 512, 474 cm^{-1}; MS (ESI): *m/z* 412 $(M+H)^+$. HRMS (ESI) calcd for $C_{24}H_{30}O_3NS$: 412.19377 $(M+H)^+$, found 412.19409.

5-Methyl-1,9-diphenyl-1,3,4,5-tetrahydrobenzo[e]pyrano[4,3-*c*][1,2]thiazine-6,6-dioxide (4y Table 3):



Yield, 90%; Solid; mp 194-196 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.1 Hz, 1H), 7.55 (d, *J* = 8.1 Hz, 1H), 7.43 – 7.36 (m, 12H), 6.02 (s, 1H), 4.00 – 3.86 (m, 2H), 3.35 (s, 3H), 2.80 – 2.66 (m, 2H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 144.6, 139.6, 139.5, 137.1,131.9, 129.9, 129.8, 128.6, 128.5, 128.2, 127.2, 126.0, 122.8, 122.2, 115.6, 75.1, 59.7, 30.6, 26.9; IR (neat) ν_{max} 3447, 3030, 2970, 2925, 2881, 1612, 1594, 1550, 1474, 1453, 1400, 1375, 1314, 1289, 1258, 1232, 1170, 1123, 1097, 1027 995, 906, 872, 847, 825, 787, 767, 747, 710, 678, 625, 587, 547, 523, 480, 417 cm^{-1}; MS (ESI): *m/z* 404 $(M+H)^+$. HRMS (ESI) calcd for $C_{24}H_{22}NO_3S$: 404.13327 $(M+H)^+$, found 404.13149.

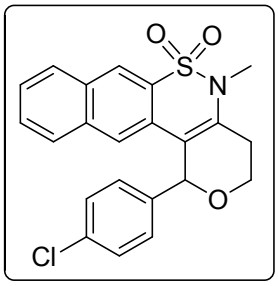
5-Methyl-9-phenyl-1-(*m*-tolyl)-1,3,4,5-tetrahydrobenzo[e]pyrano[4,3-*c*][1,2]thiazine-6,6-dioxide (4z; Table 3):



Yield, 91%; Solid; mp 174-176 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.2 Hz, 1H), 7.55 (dd, *J* = 8.19 Hz, 1H), 7.42 – 7.34 (m, 3H), 7.32 – 7.25(m, 5H), 7.12 (d, *J* = 7.94 Hz, 2H), 6.99 (s, 1H), 3.99 – 3.84 (m, 2H), 3.34 (s, 3H), 2.82 – 2.73 (m, 1H), 2.71 – 2.62 (m, 1H), 2.29 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 144.5, 139.6, 138.2, 136.9, 136.6, 132.0, 130.0, 129.3, 129.0, 128.8, 128.1, 127.2, 125.9, 122.8, 122.2, 115.8, 74.8, 59.4, 30.6, 26.8, 21.1; IR (neat) ν_{max}

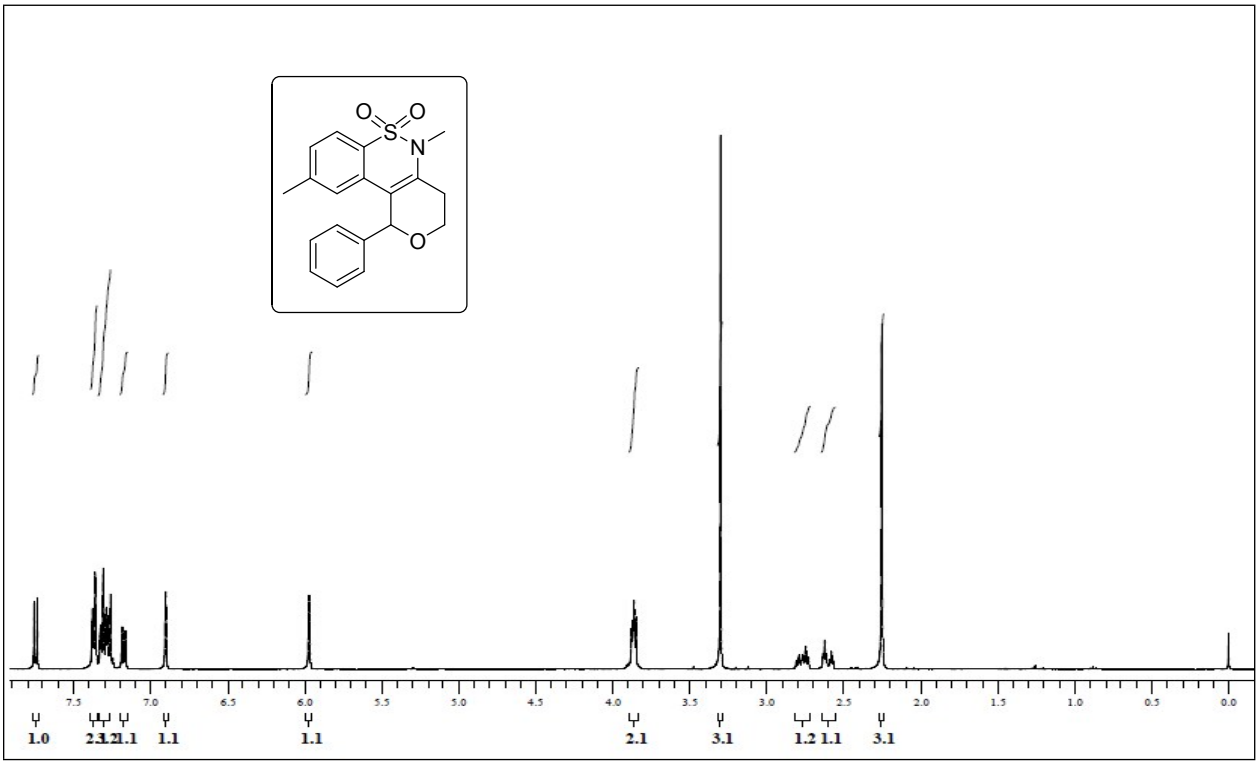
3419, 3030, 2967, 2922, 2873, 1716, 1616, 1595, 1553, 1507, 1471, 1400, 1317, 126,1230, 1173, 1124, 1093, 1063, 1024, 993, 871, 830, 766,705, 674, 578, 547, 519, 483, 421 cm^{-1}; MS (ESI): *m/z* 418 $(M+H)^+$. HRMS (ESI) calcd for $C_{25}H_{24}NO_3S$: 418.14614 $(M+H)^+$, found 418.14714.

1-(4-Chlorophenyl)-5-methyl-1,3,4,5-tetrahydronaphtho[2,3-*e*]pyrano[4,3-*c*][1,2]thiazine-6,6-dioxide (4aa; Table 3):

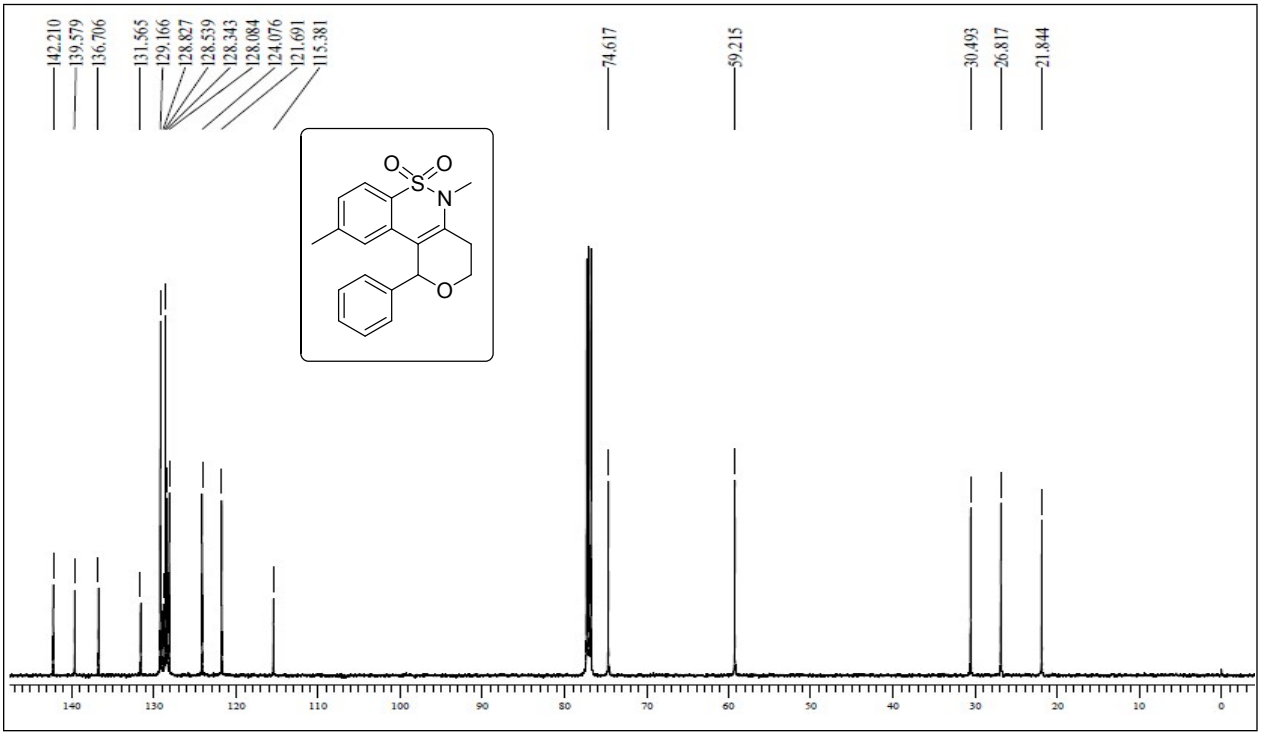


Yield, 85%; Solid; mp 250-252 ºC; ^1H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.86 (d, *J* = 8.5 Hz, 1H), 7.77(d, *J* = 8.2 Hz, 1H), 7.65 – 7.55 (m, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.29 (s, 1H), 4.68 – 4.54 (m, 2H), 3.62 – 3.52 (m, 1H), 3.42 – 3.32 (m, 1H), 2.93 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 138.1, 136.1, 135.6, 134.2, 133.8, 132.9, 132.5, 129.8, 129.5, 128.7, 128.3, 128.1, 127.2, 126.9, 124.5, 116.0, 100.2, 69.3, 31.3, 24.3; IR (neat) ν_{max} 3448, 3065, 2900, 1589, 1491, 1440, 1406, 194, 1248, 1203, 1170, 1135, 1089, 1027, 991, 954, 888, 860, 838, 810, 786, 748, 681, 637, 618, 552, 514, 457, 407 cm^{-1}; MS (ESI): *m/z* 412 $(M+H)^+$. HRMS (ESI) calcd for $C_{22}H_{19}O_3NClS$: 412.07854 $(M+H)^+$, found 412.07687.

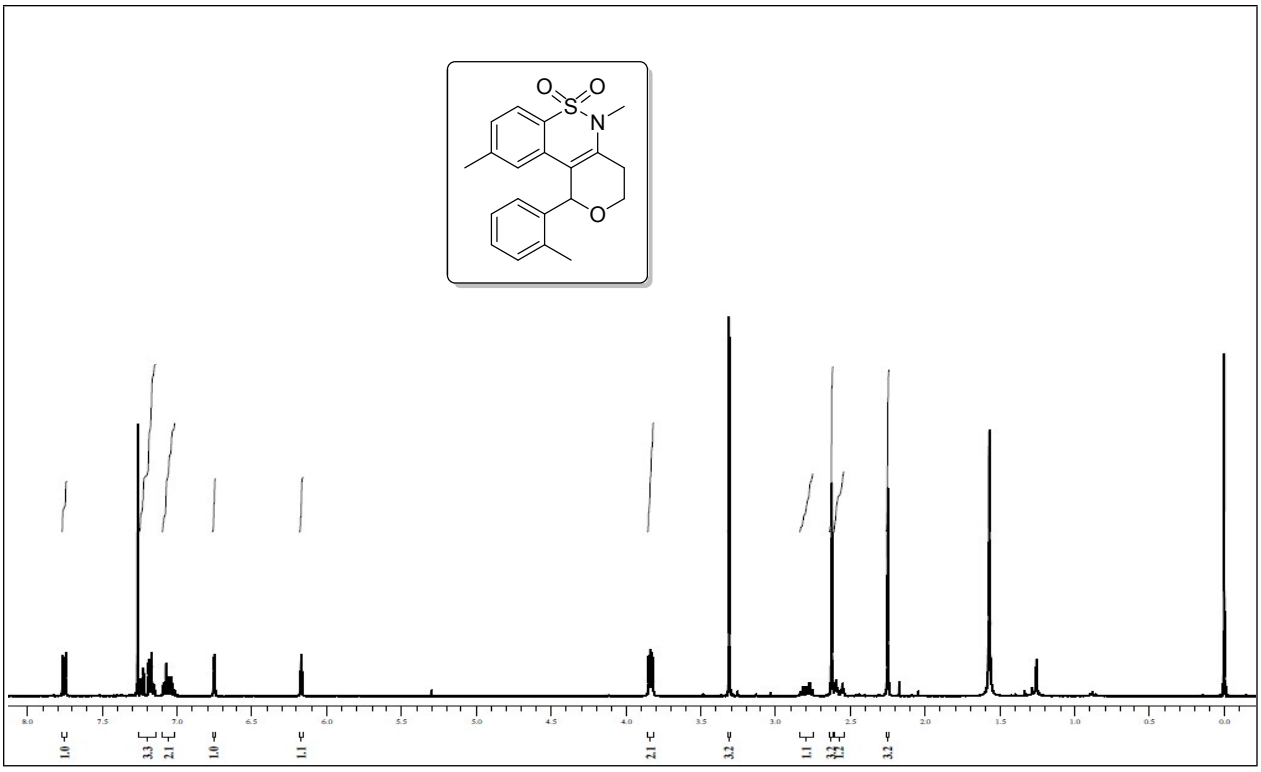
3. ^{1}H &^{13}C NMR spectra of products



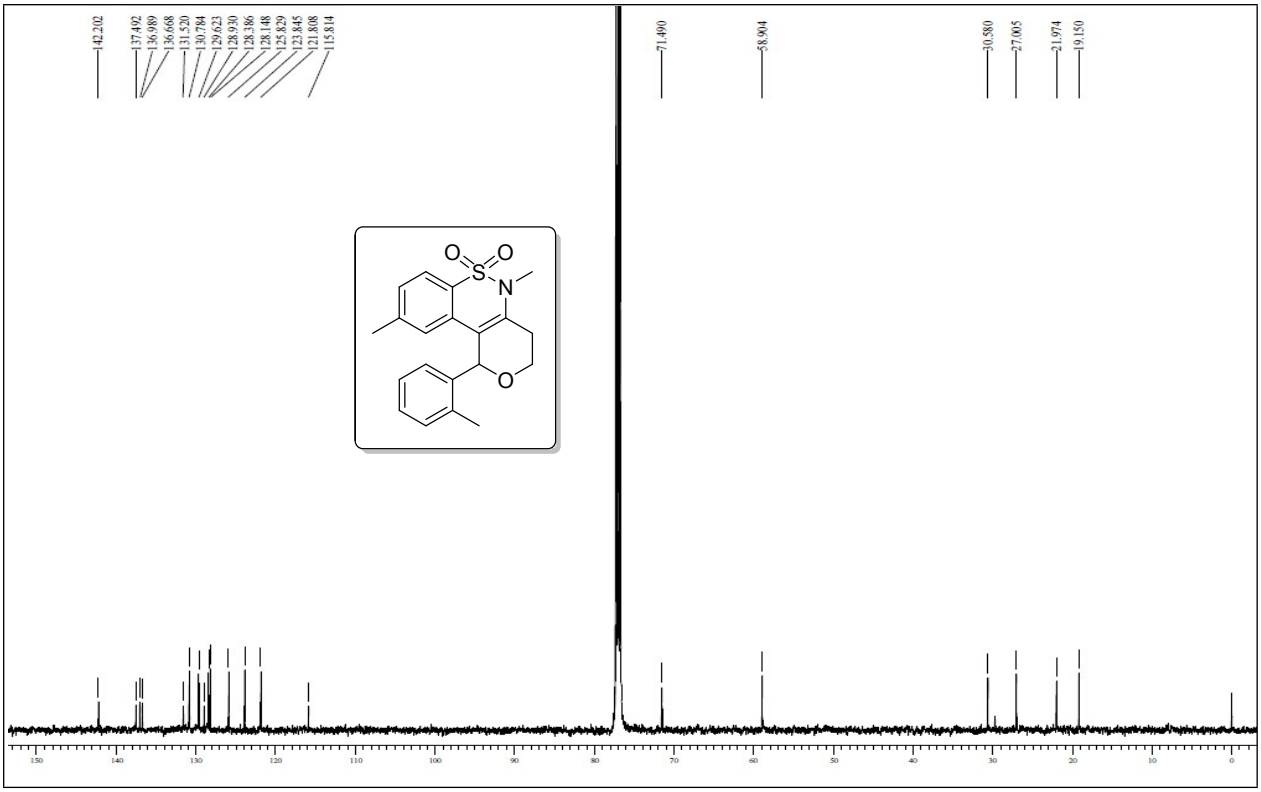
^{1}H NMR of Compound 4a



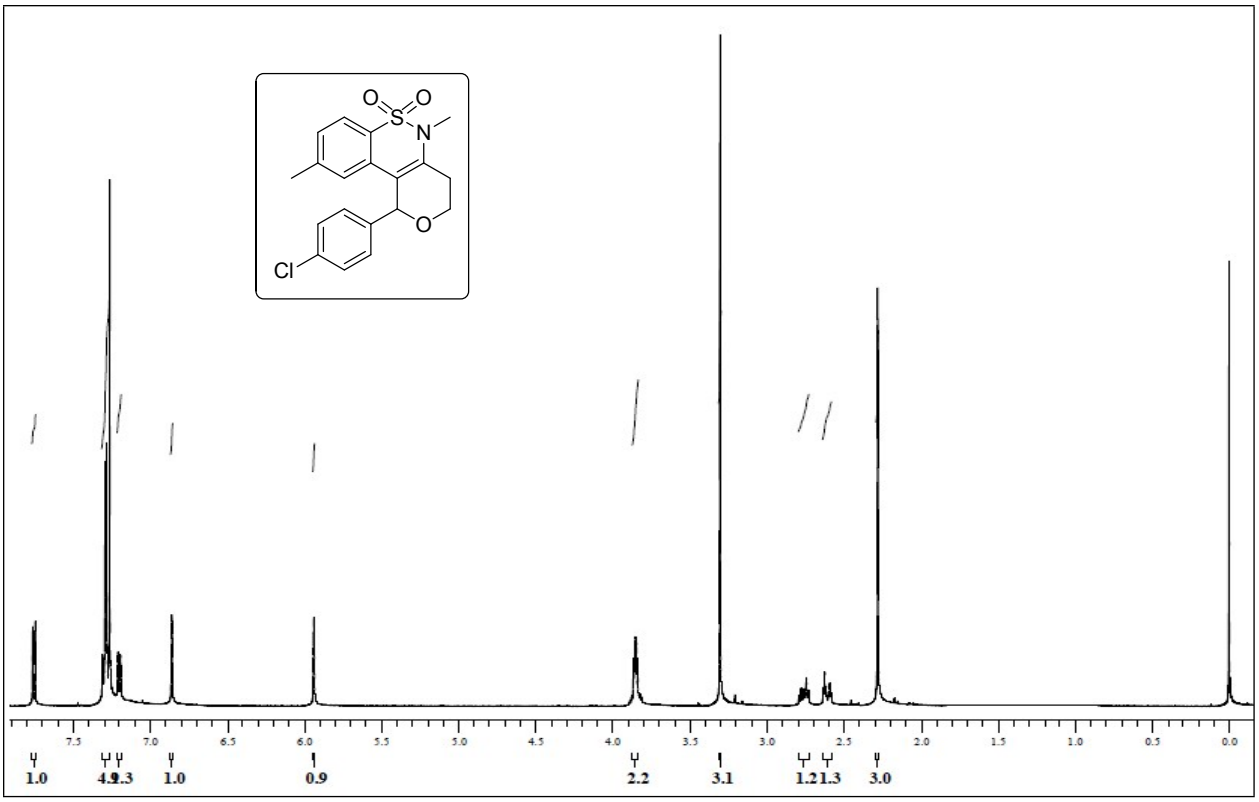
^{13}C NMR of Compound 4a



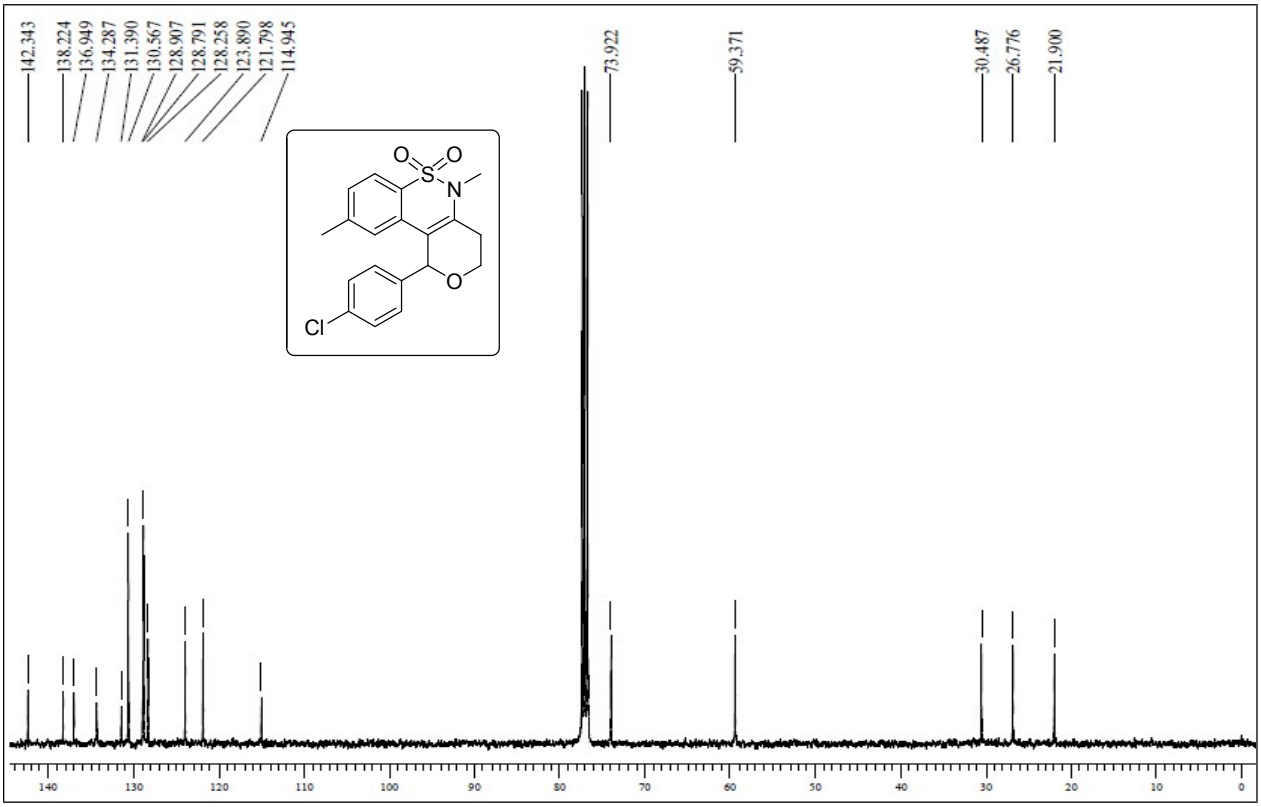
^{1}H NMR of Compound 4b



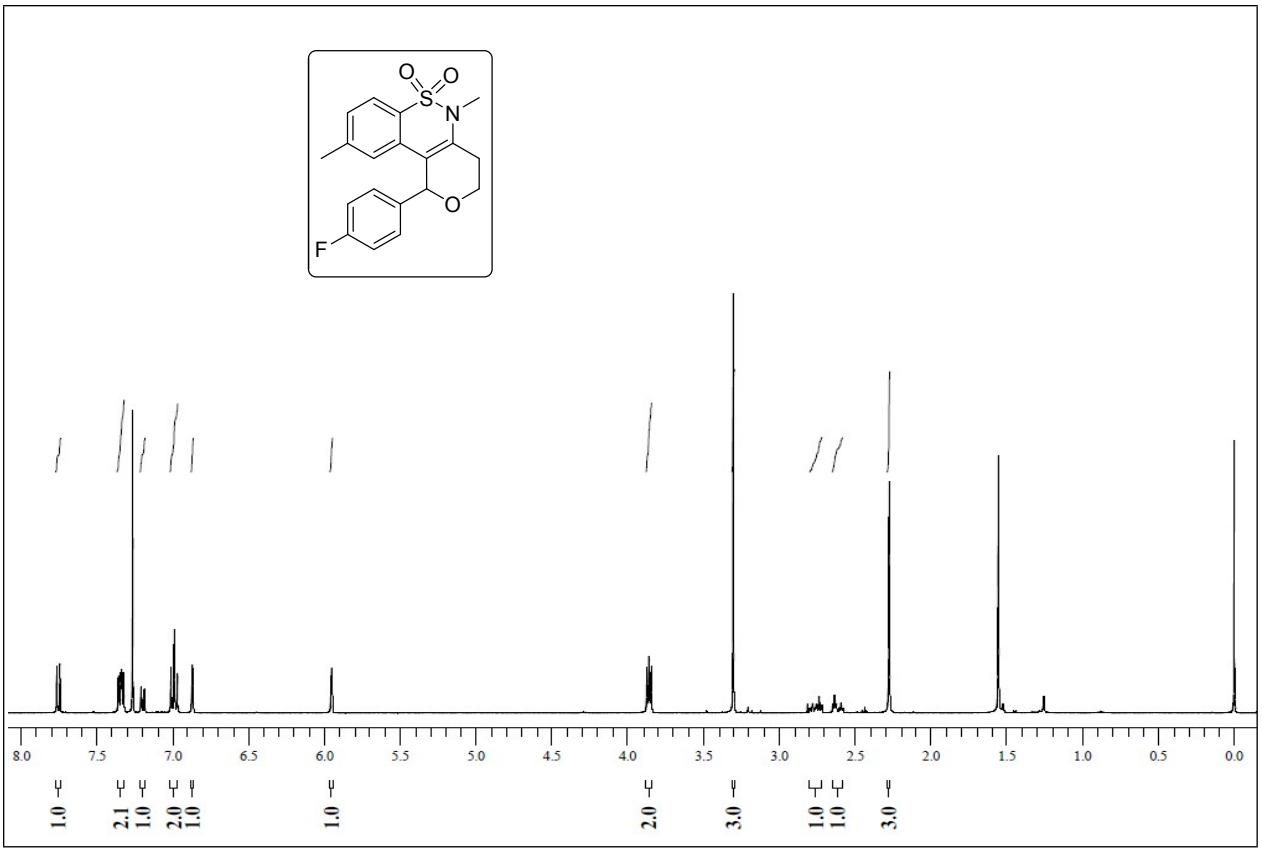
^{13}C NMR of Compound 4b



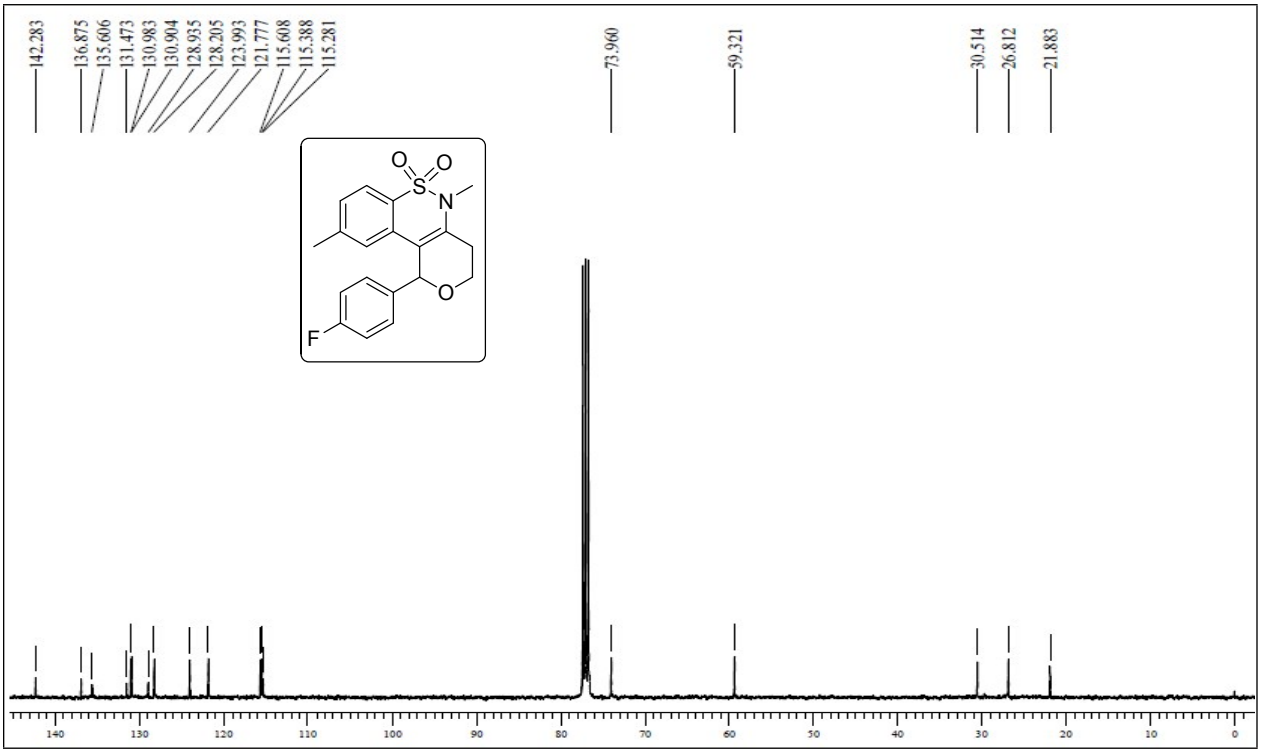
[1]H NMR of Compound 4c



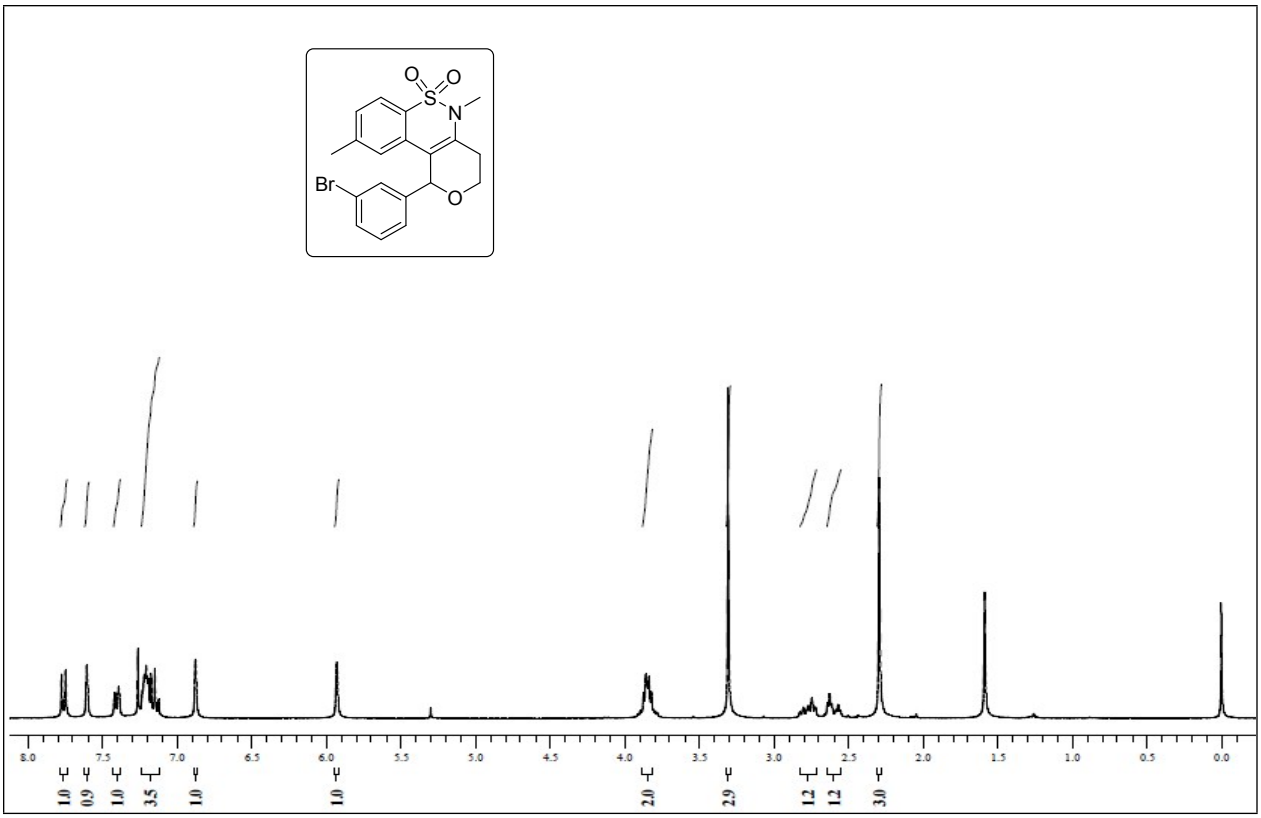
[13]C NMR of Compound 4c



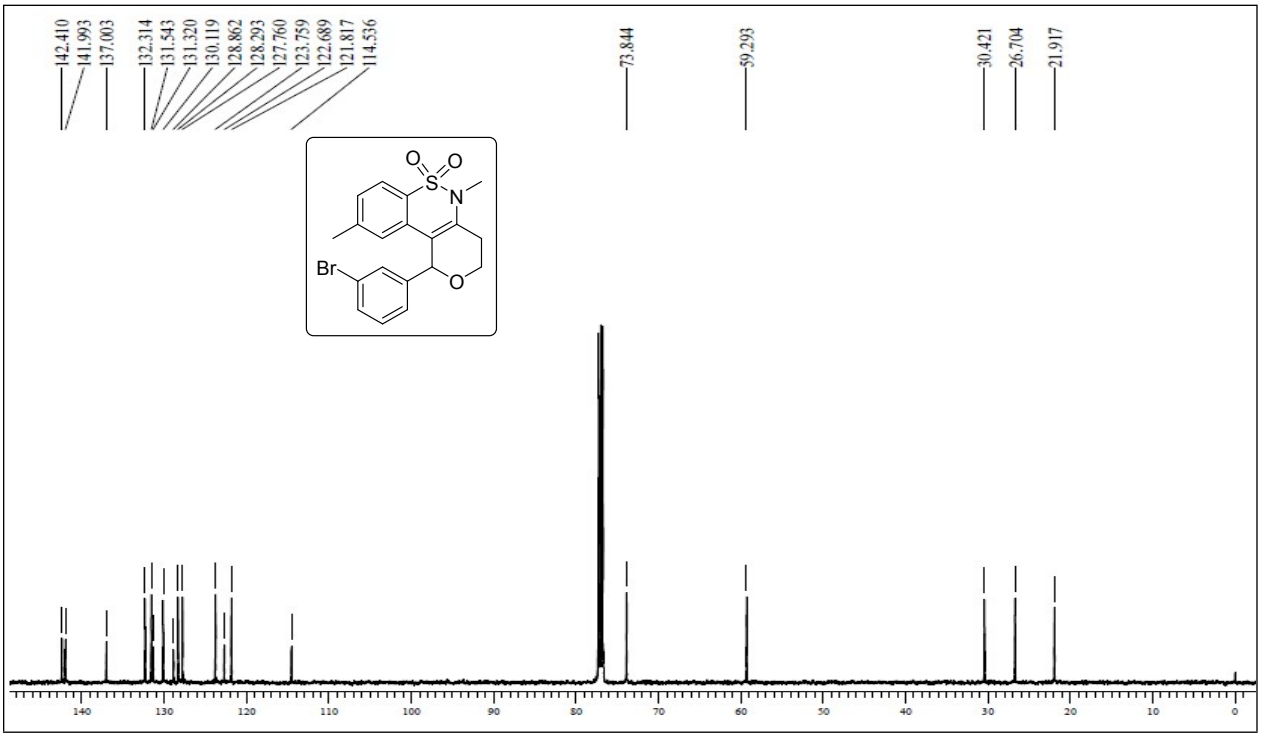
^{1}H NMR of Compound 4d



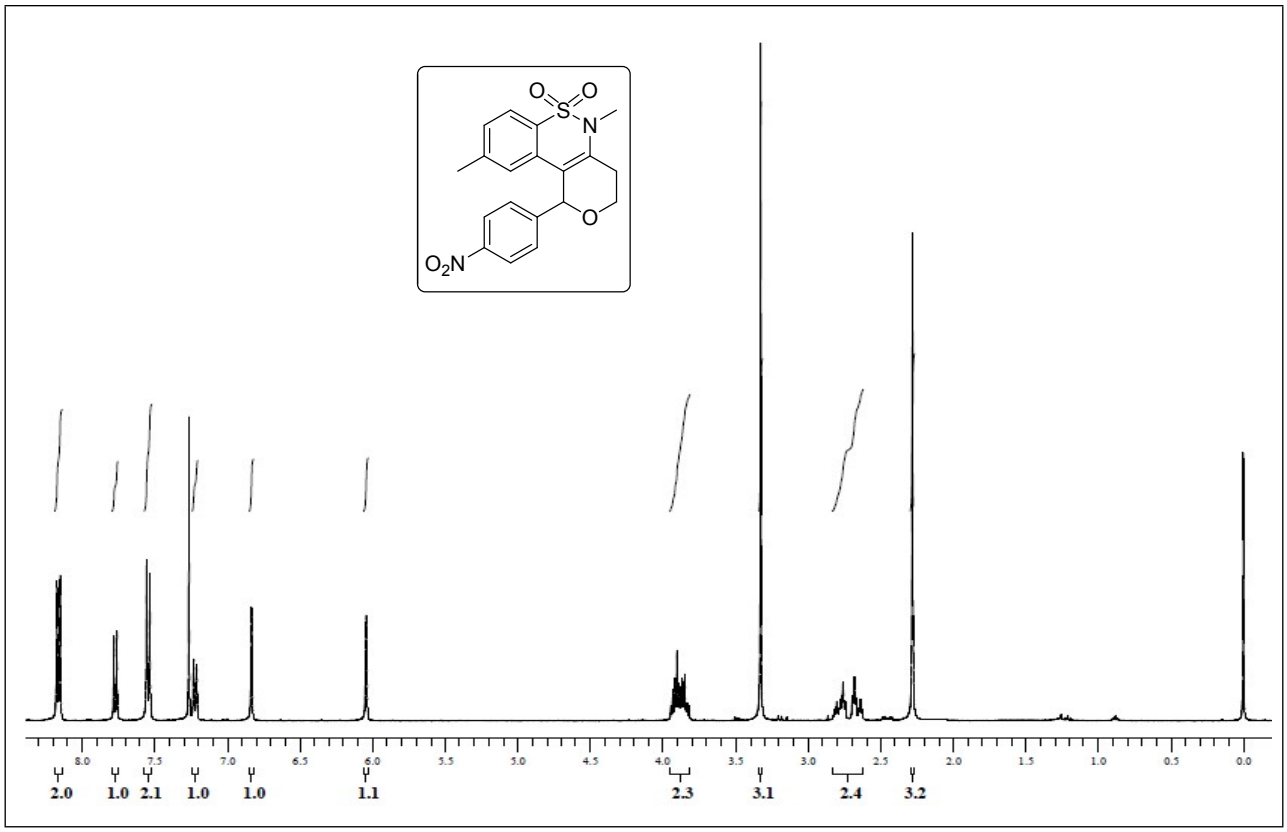
^{13}C NMR of Compound 4d



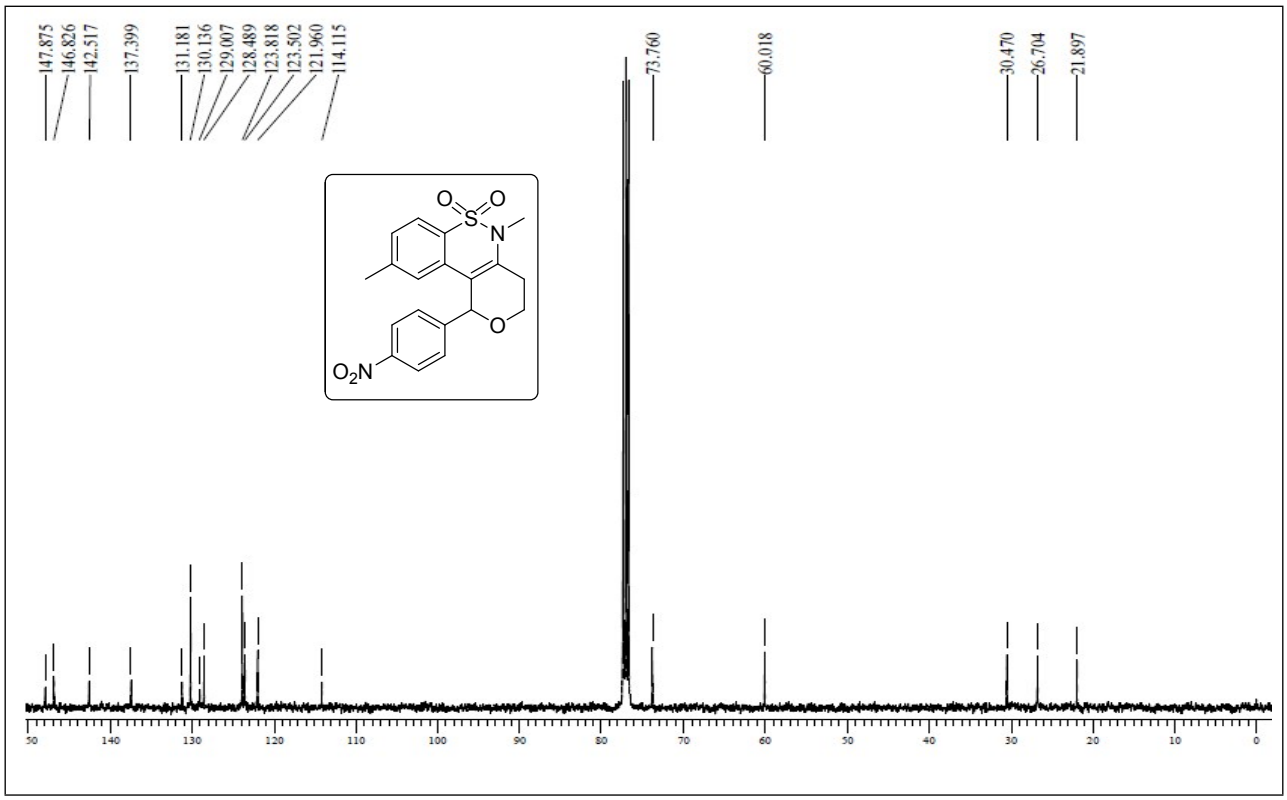
[1]H NMR of Compound 4e



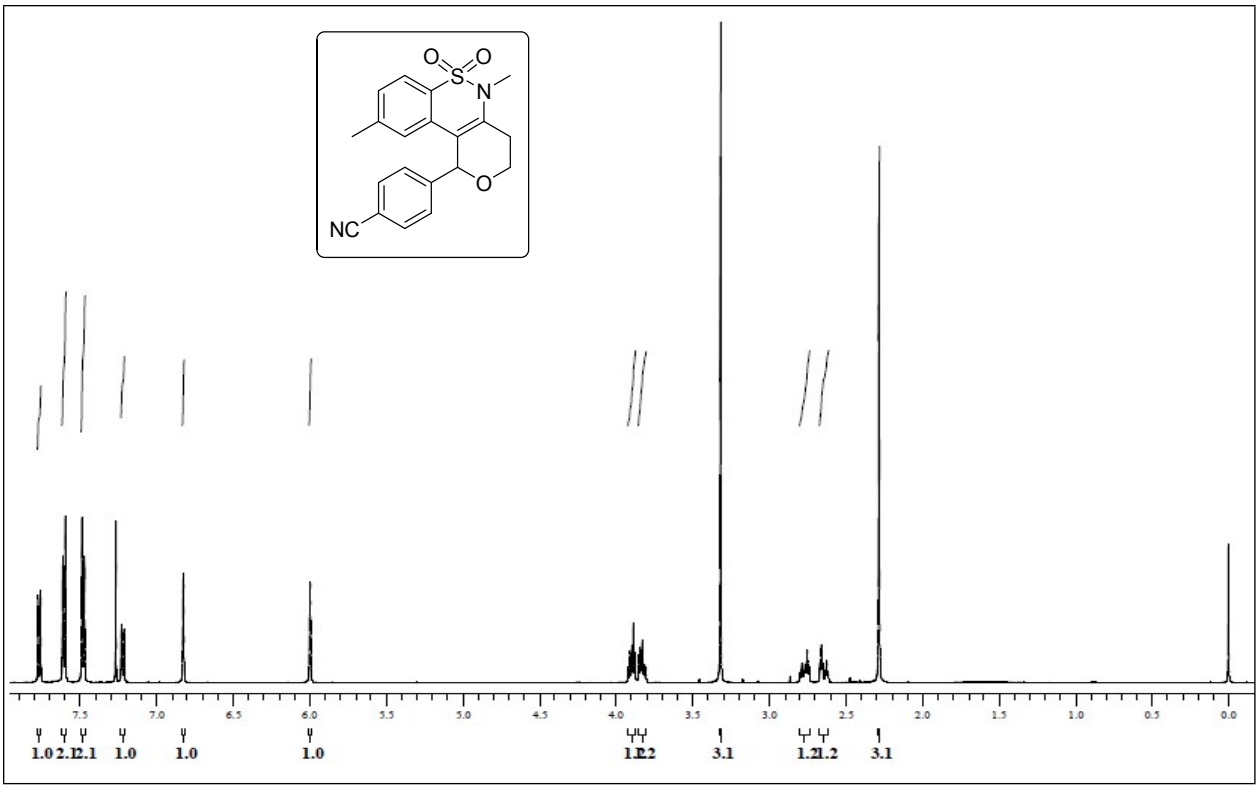
[13]C NMR of Compound 4e



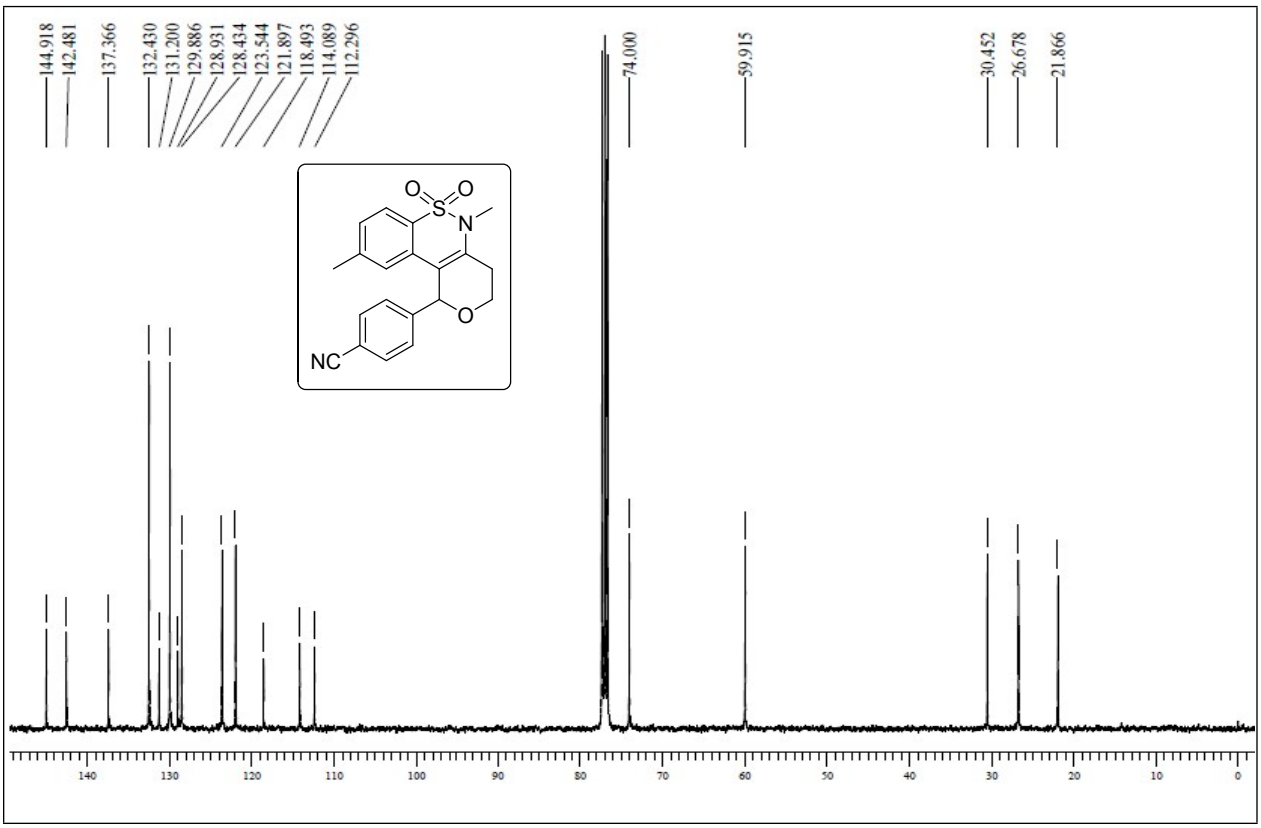
^{1}H NMR of Compound 4f



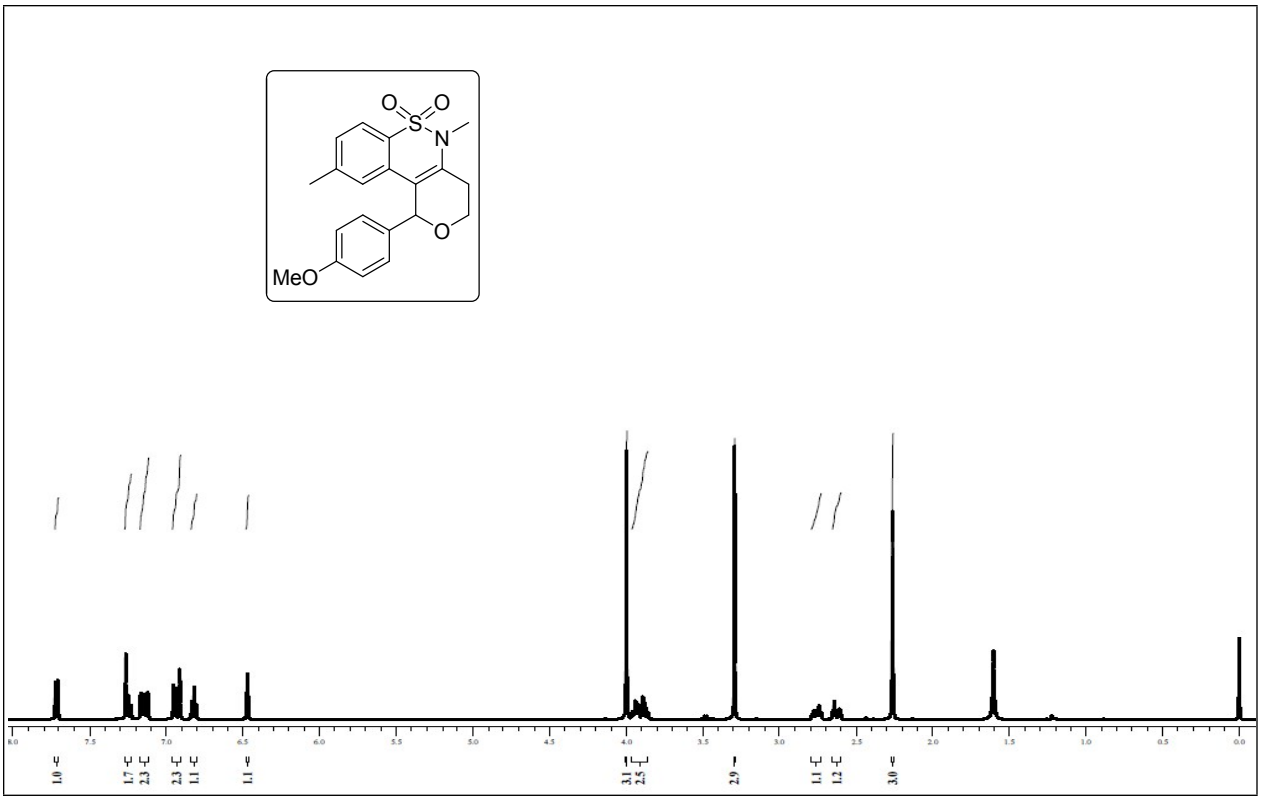
^{13}C NMR of Compound 4f



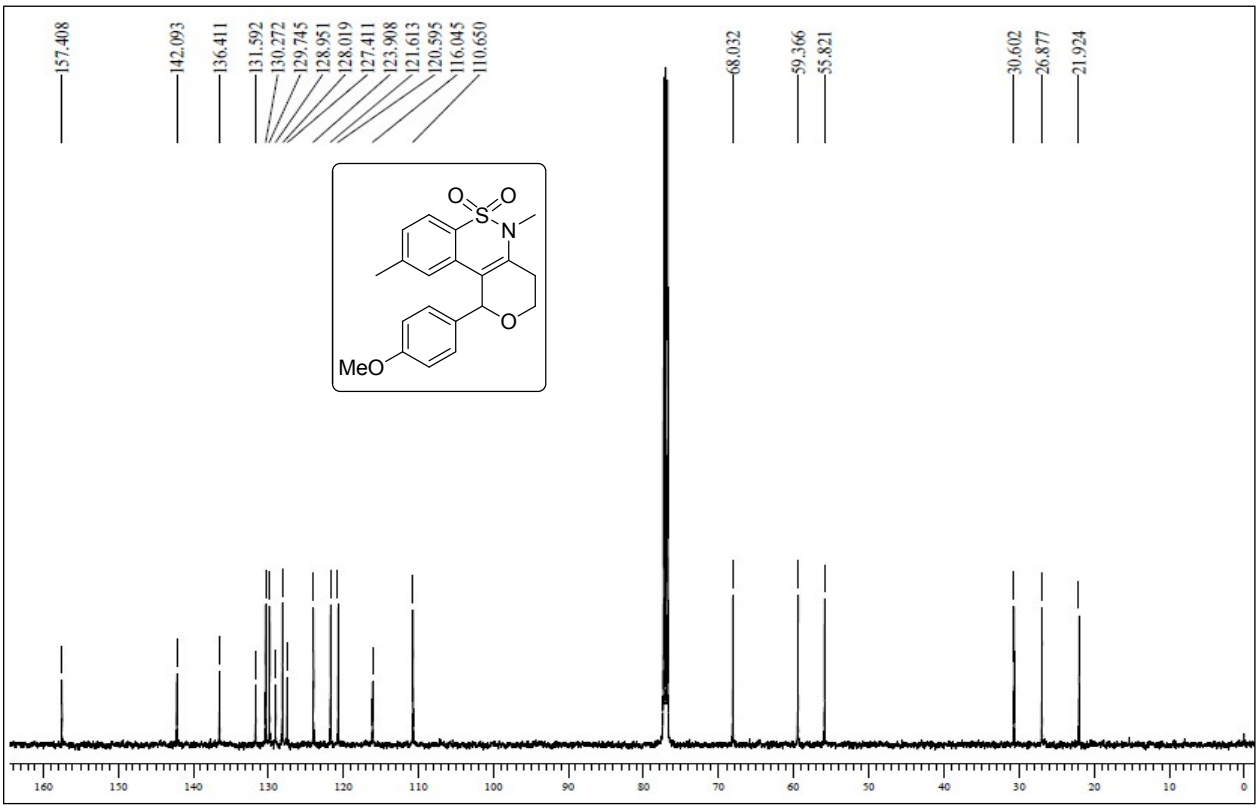
^{1}H NMR of Compound 4g



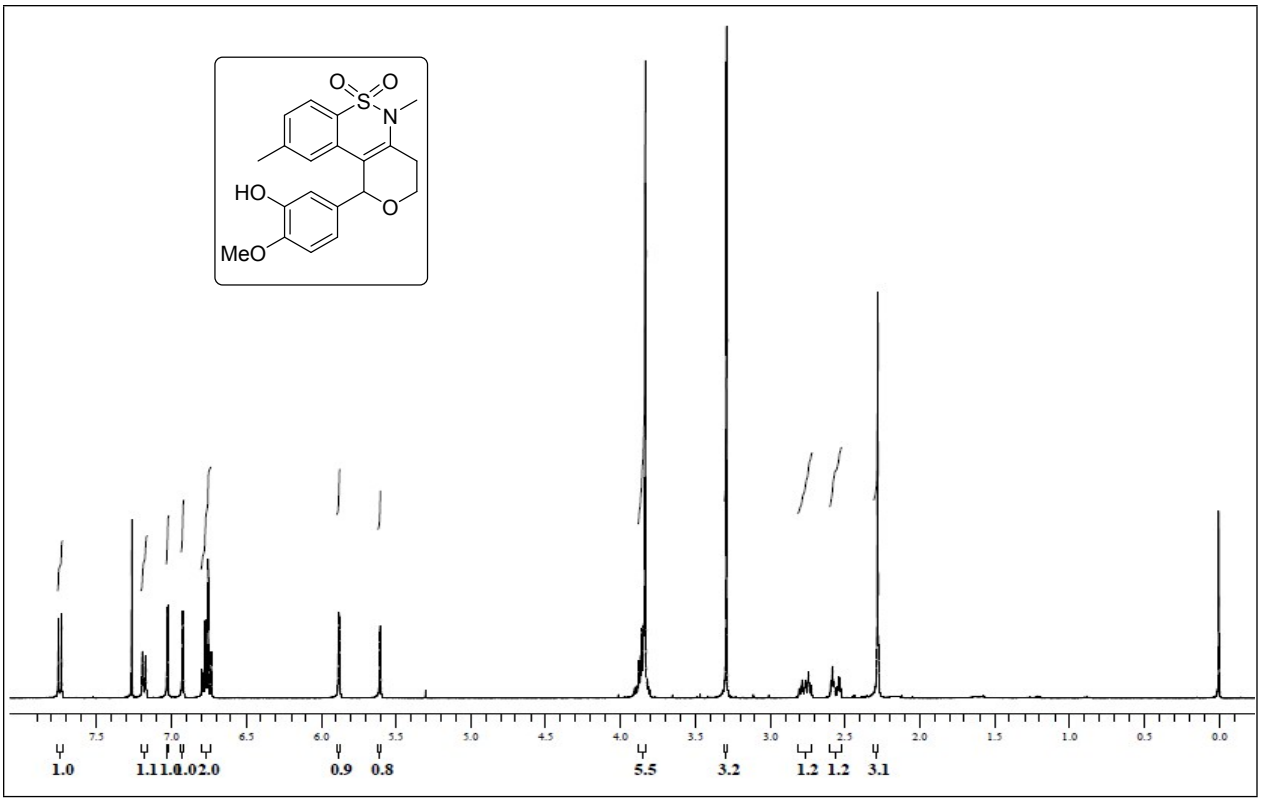
^{13}C NMR of Compound 4g



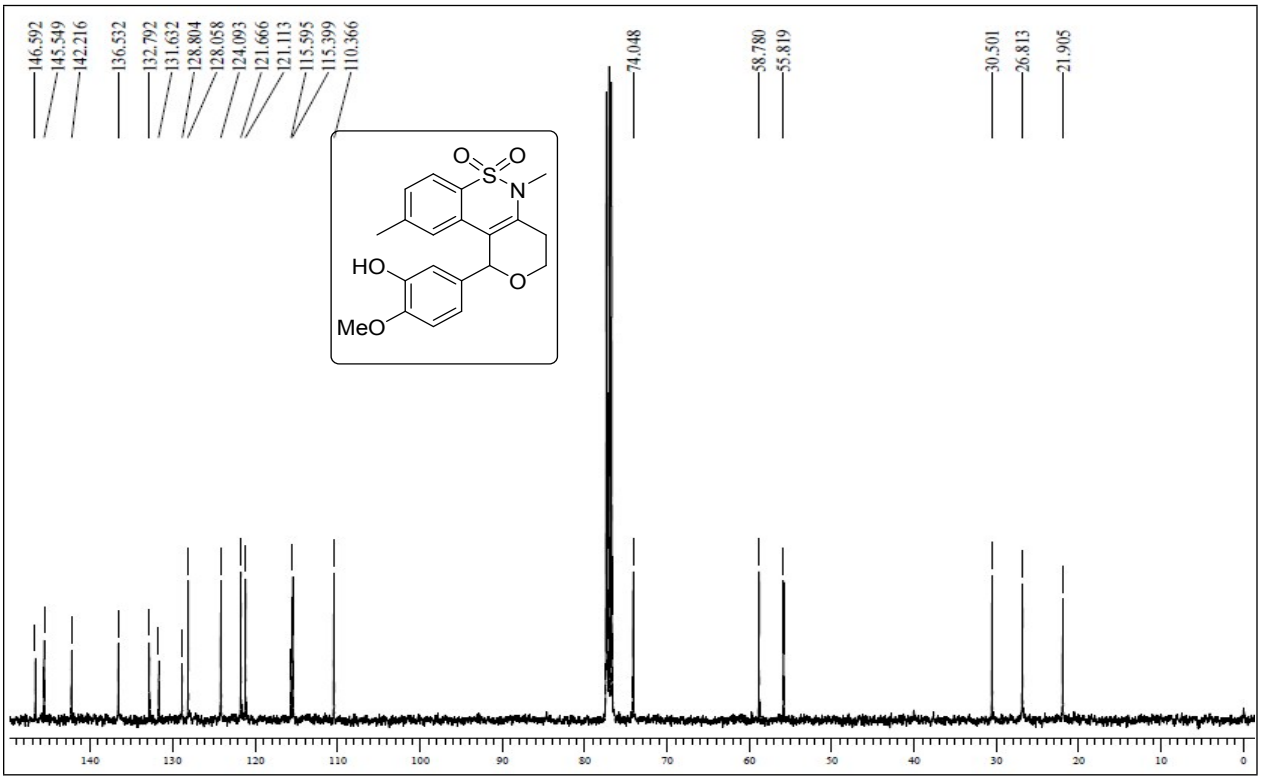
^{1}H NMR of Compound 4h



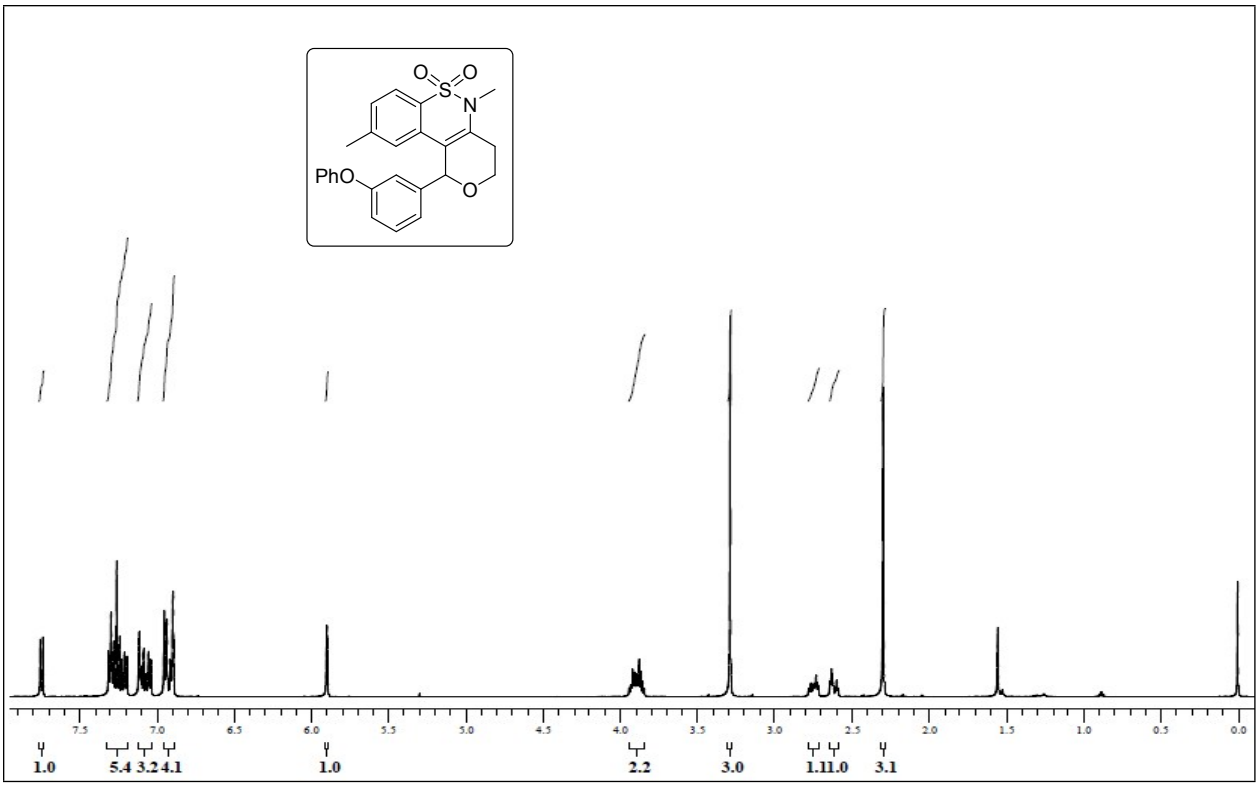
^{13}C NMR of Compound 4h



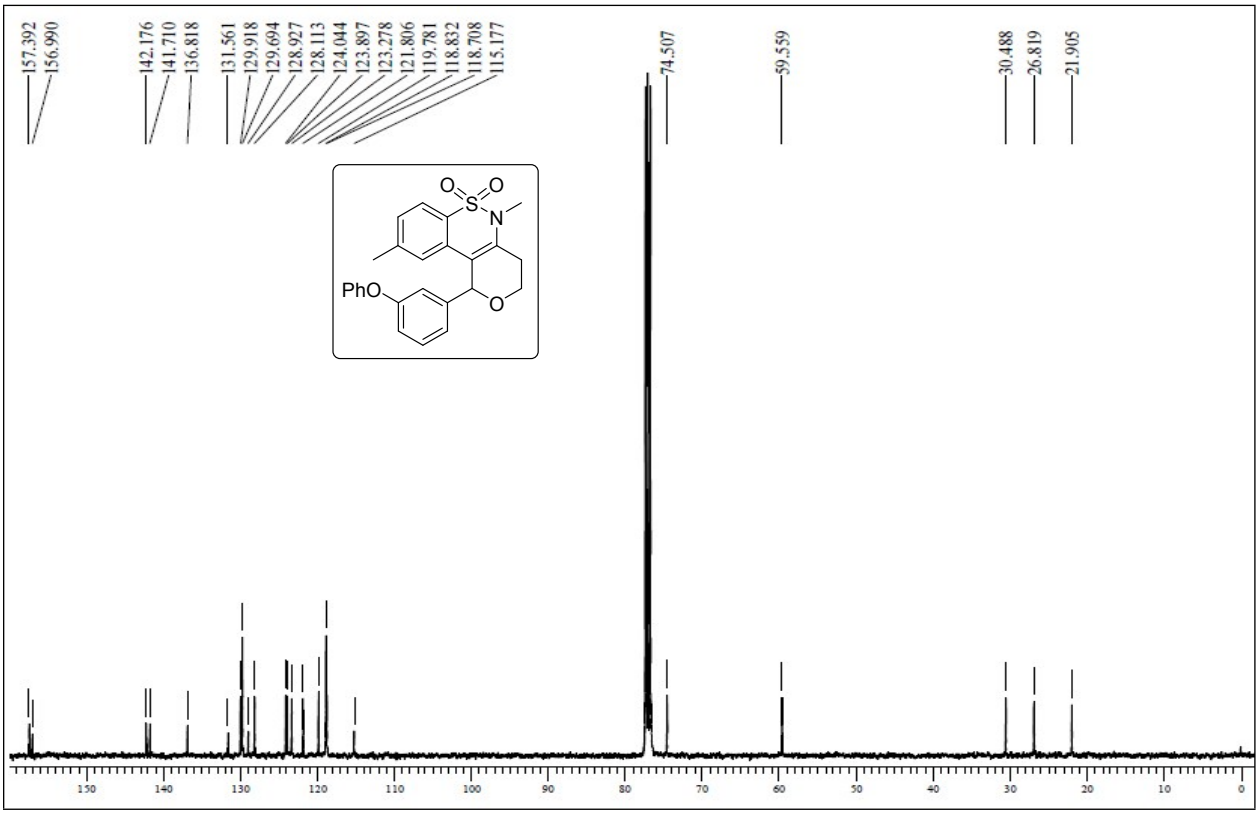
^{1}H NMR of Compound 4i



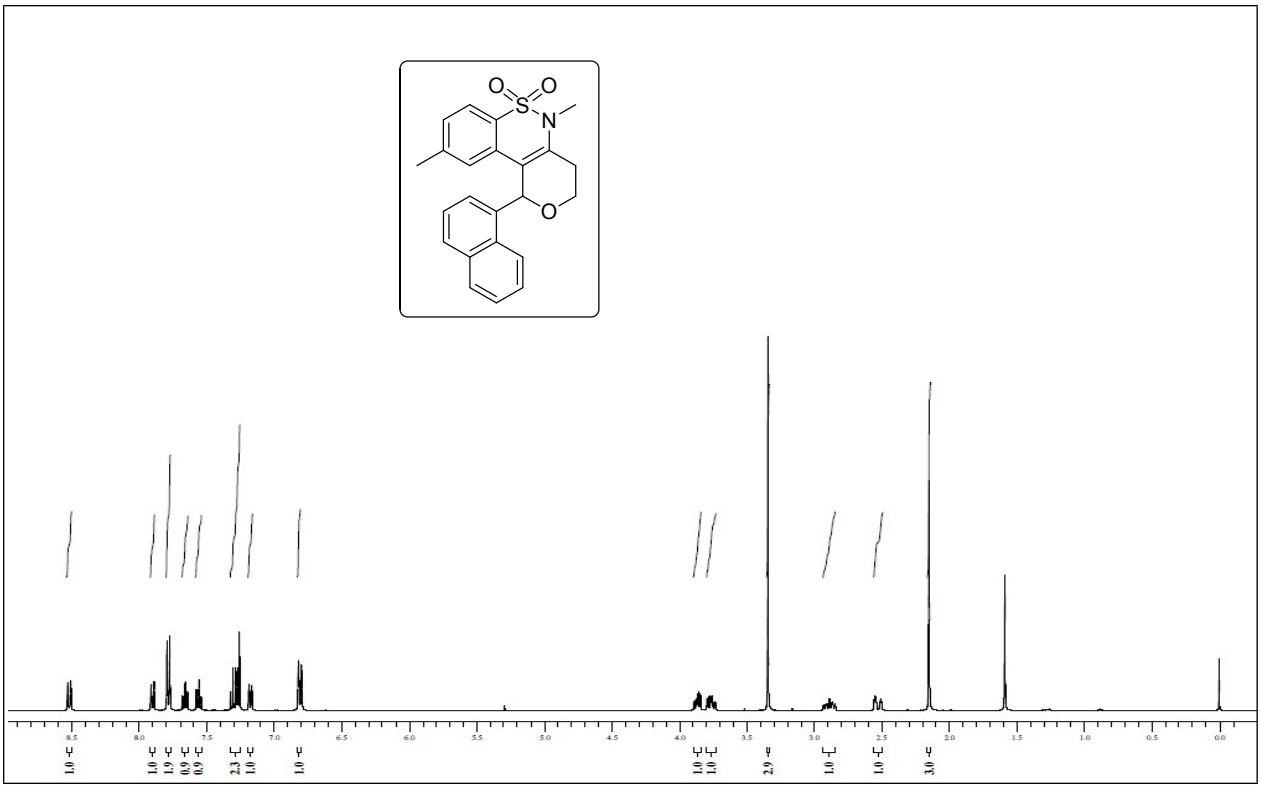
^{13}C NMR of Compound 4i



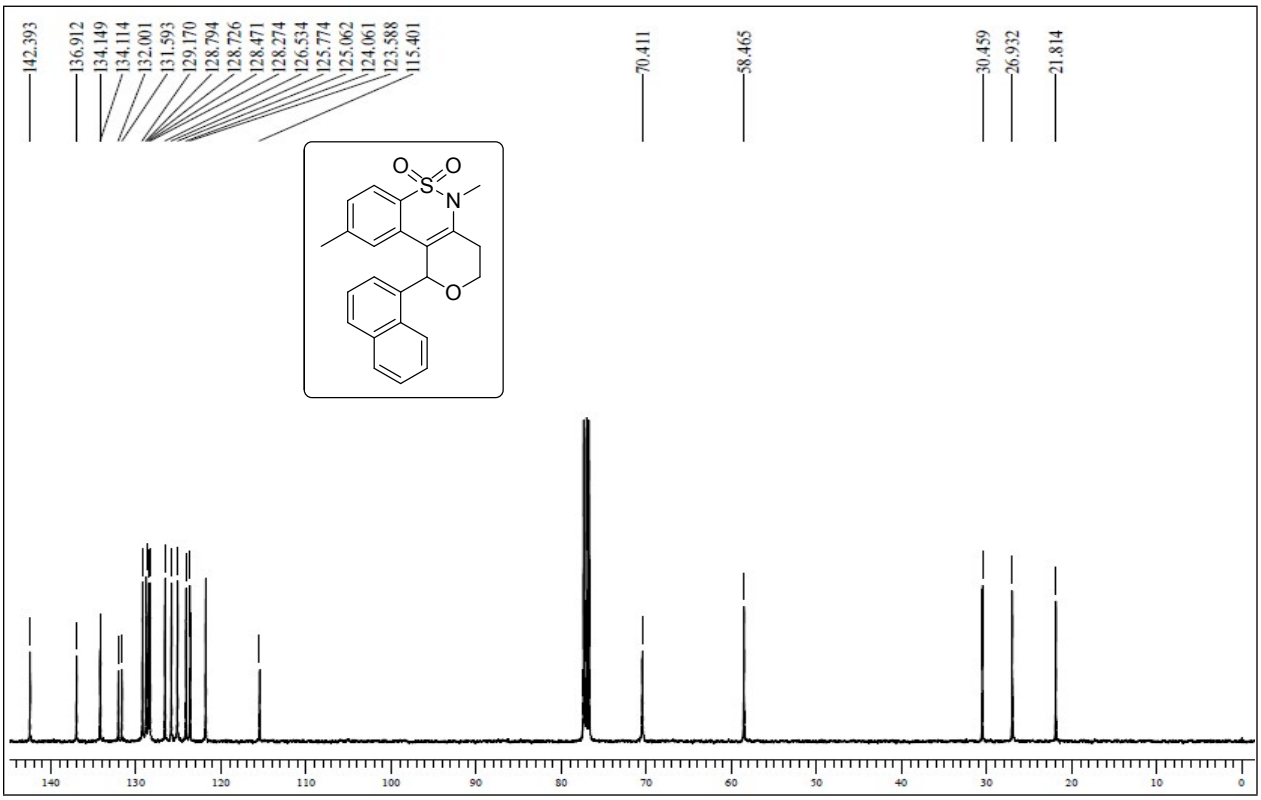
^{1}H NMR of Compound 4j



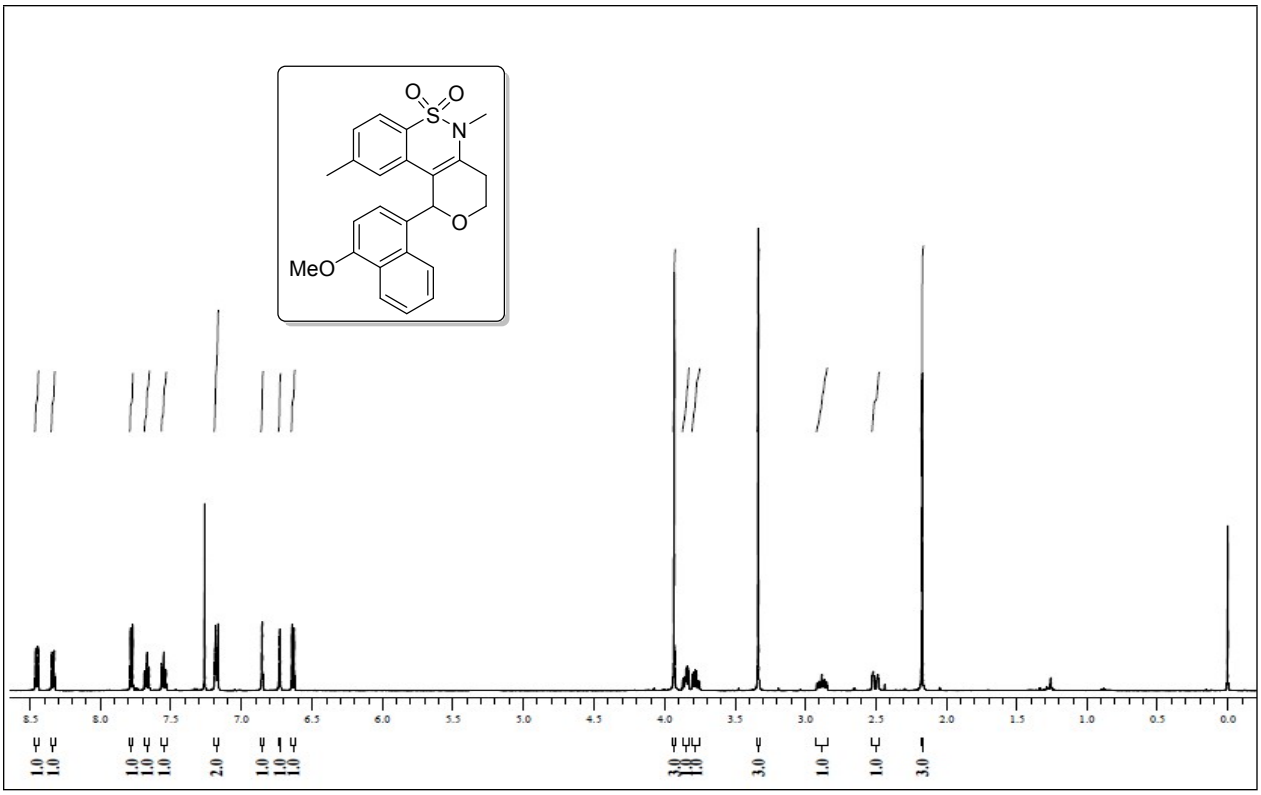
^{13}C NMR of Compound 4j



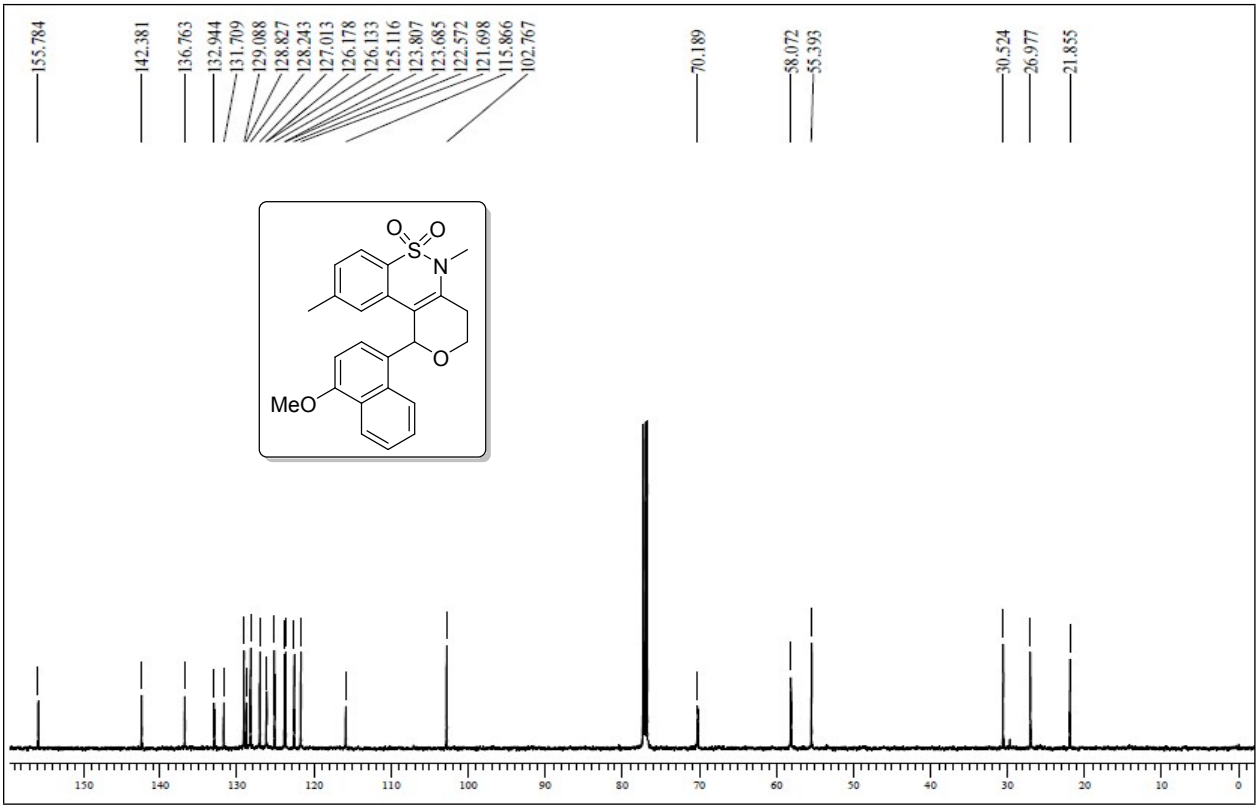
^{1}H NMR of Compound 4k



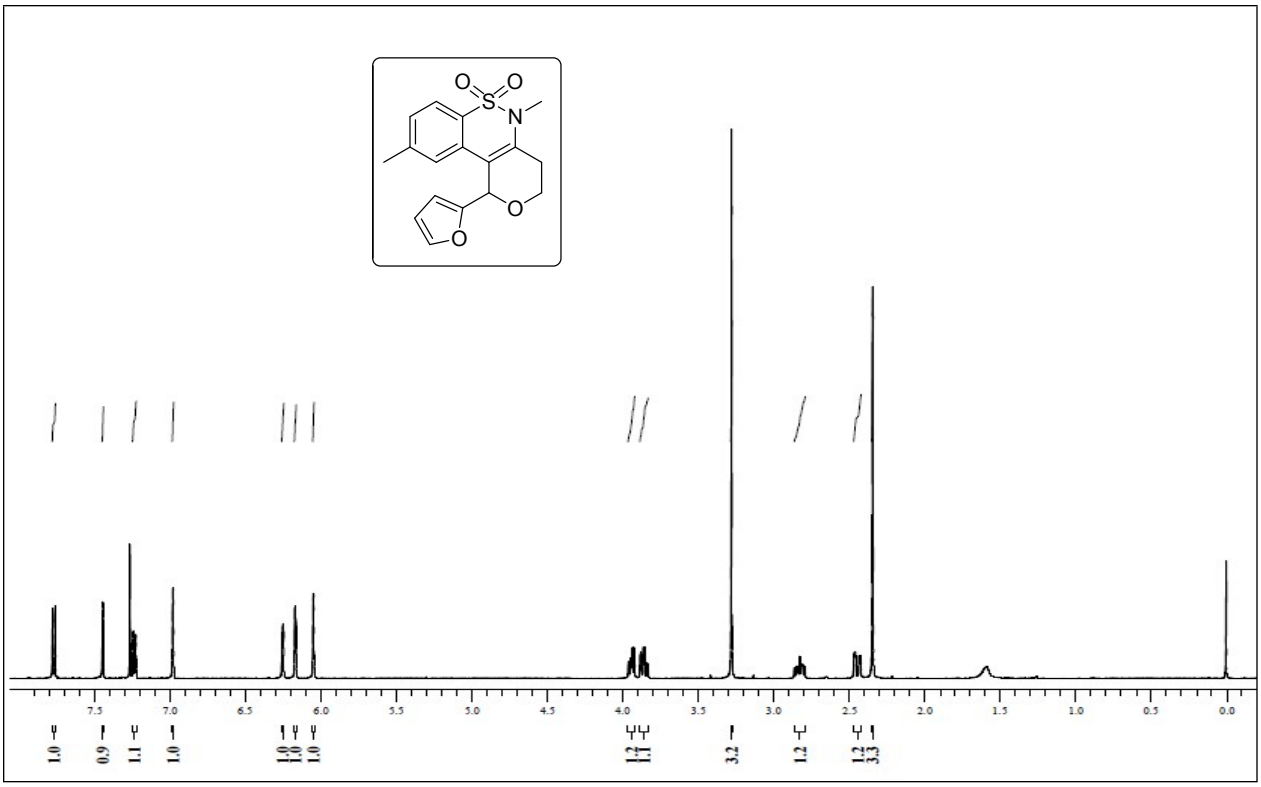
^{13}C NMR of Compound 4k



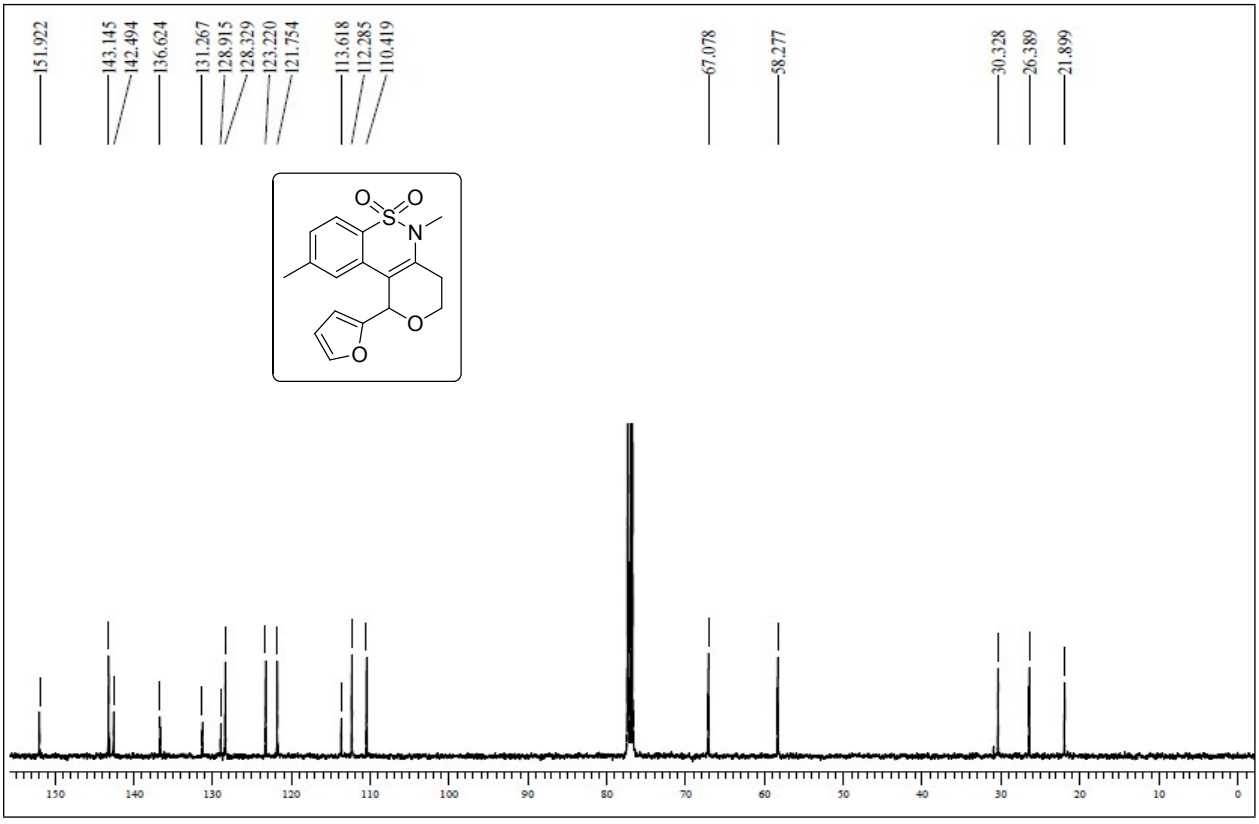
^{1}H NMR of Compound 4l



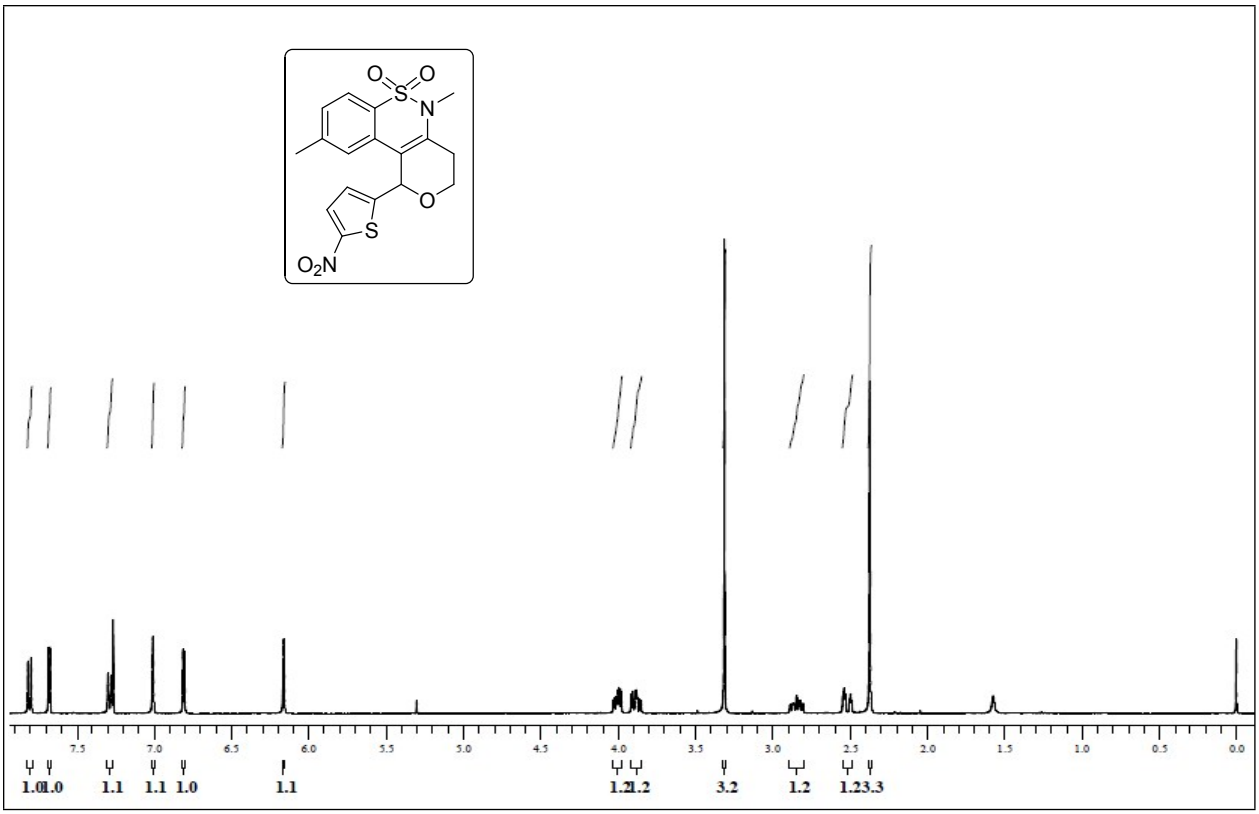
^{13}C NMR of Compound 4l



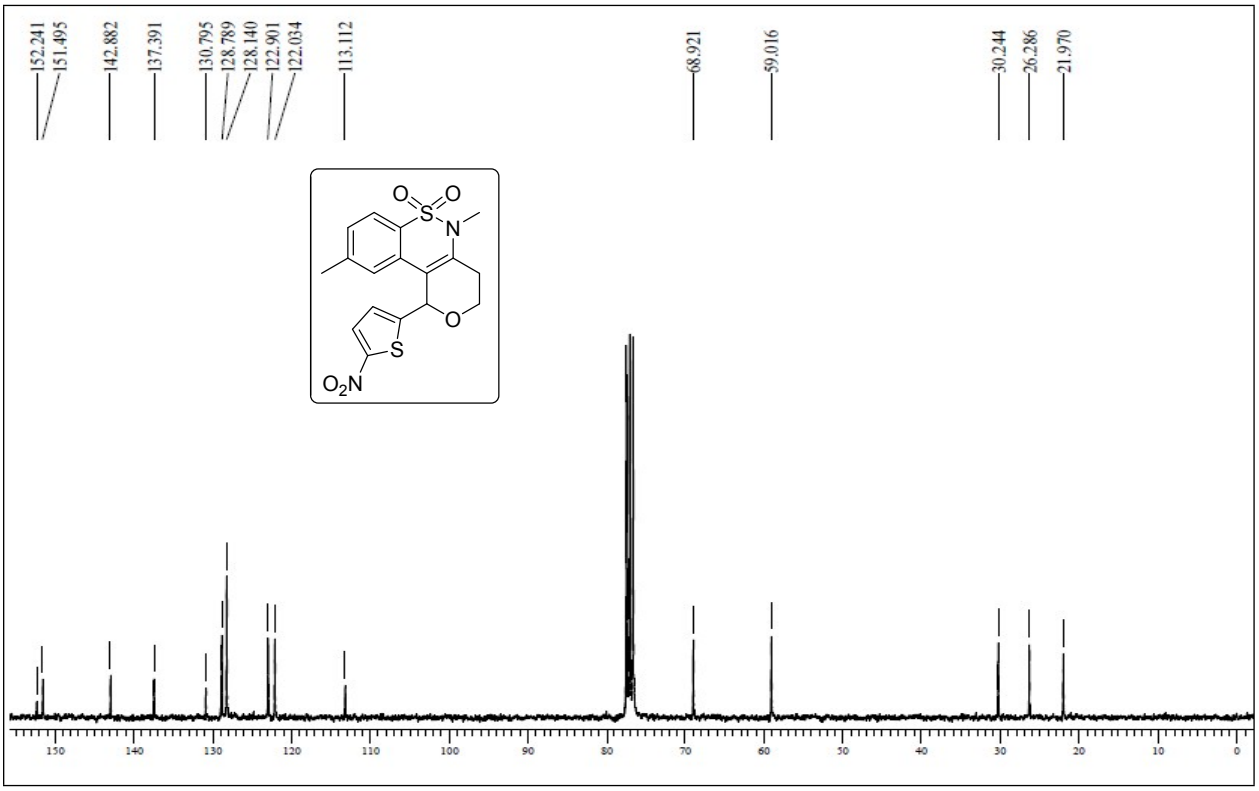
^{1}H NMR of Compound 4m



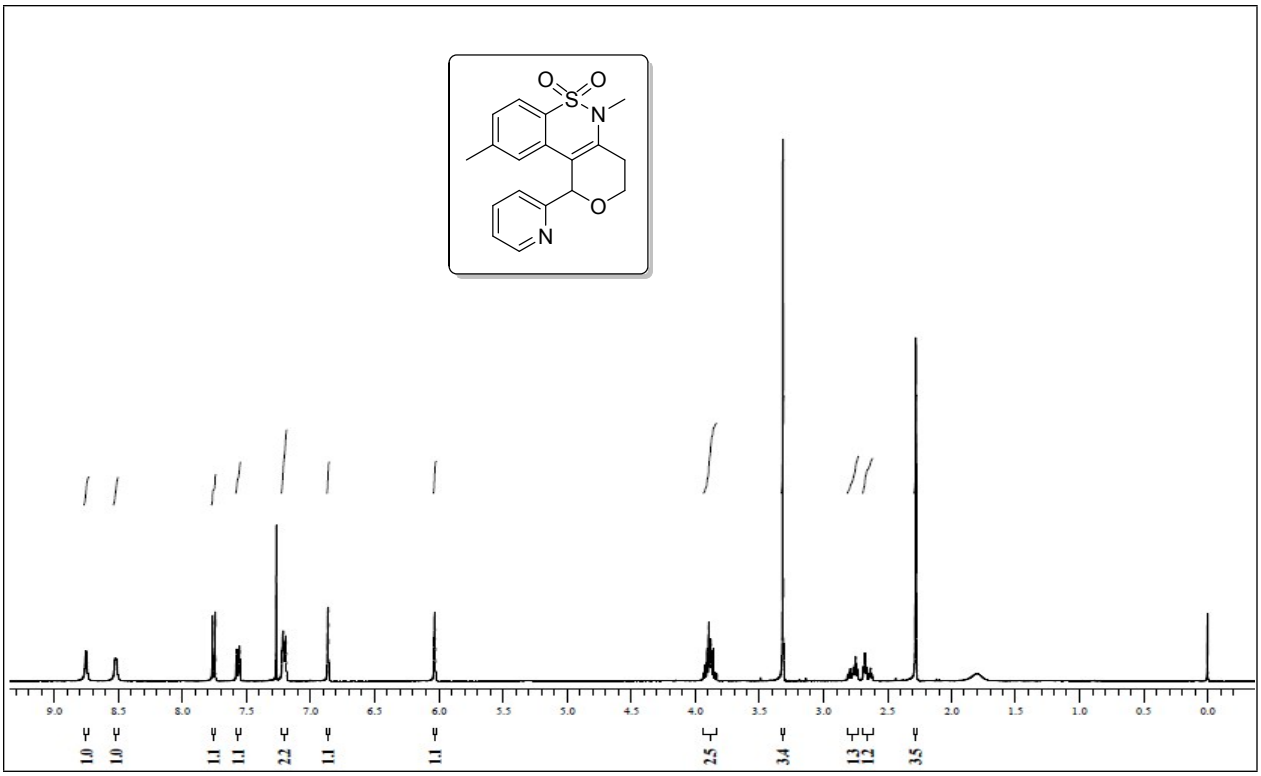
^{13}C NMR of Compound 4m



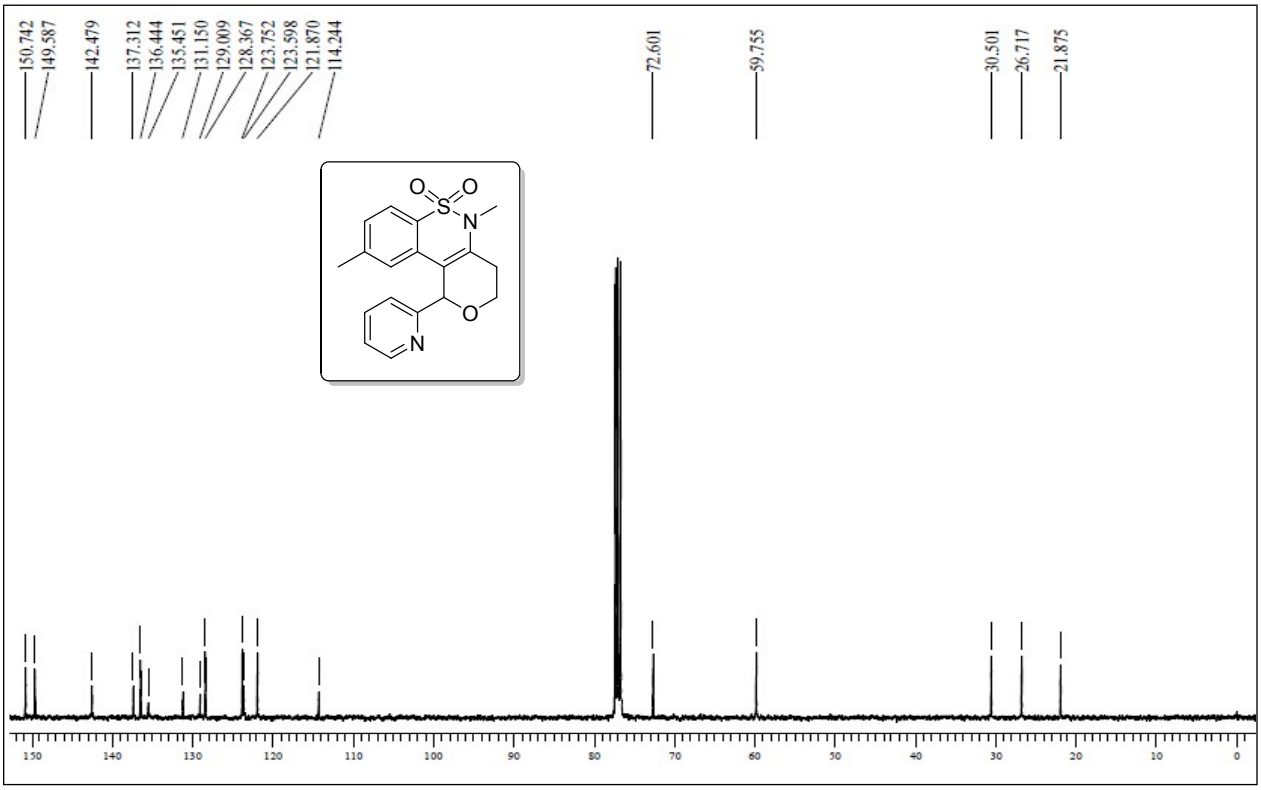
^{1}H NMR of Compound 4n



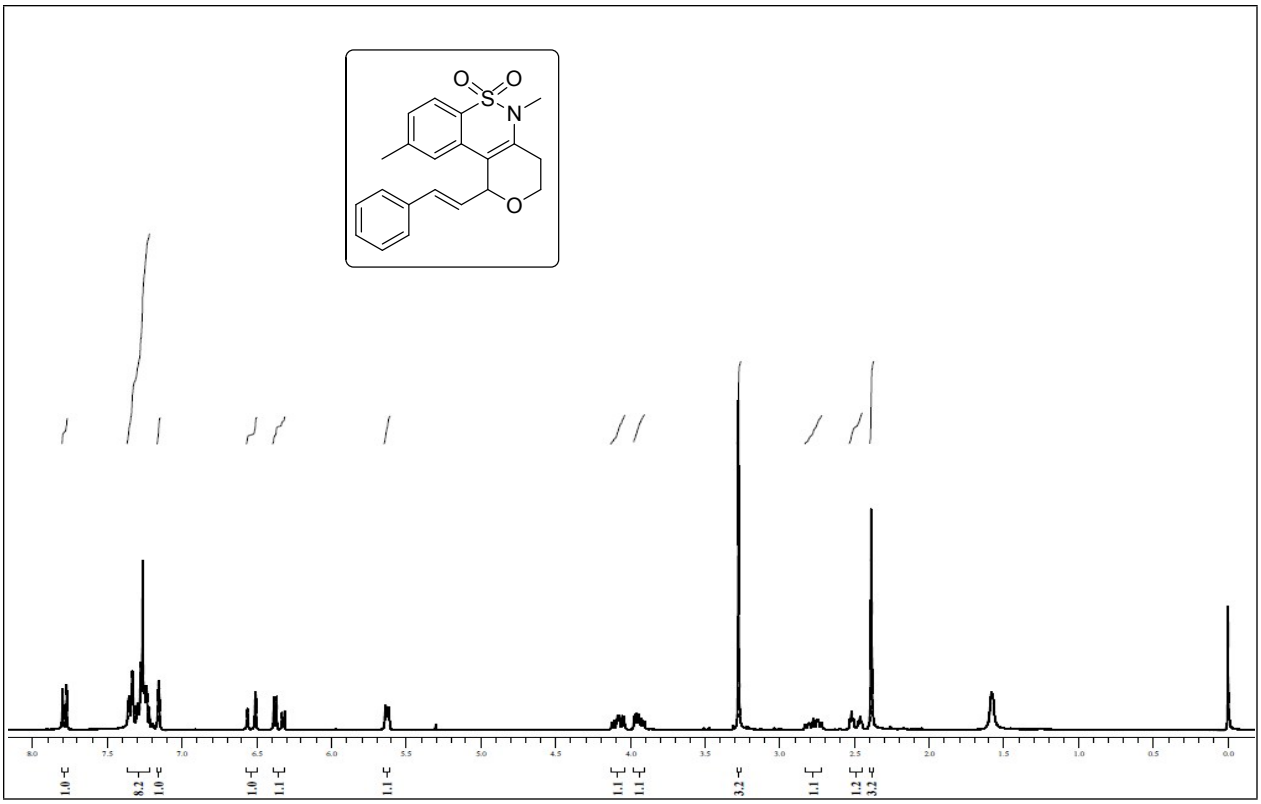
^{13}C NMR of Compound 4n



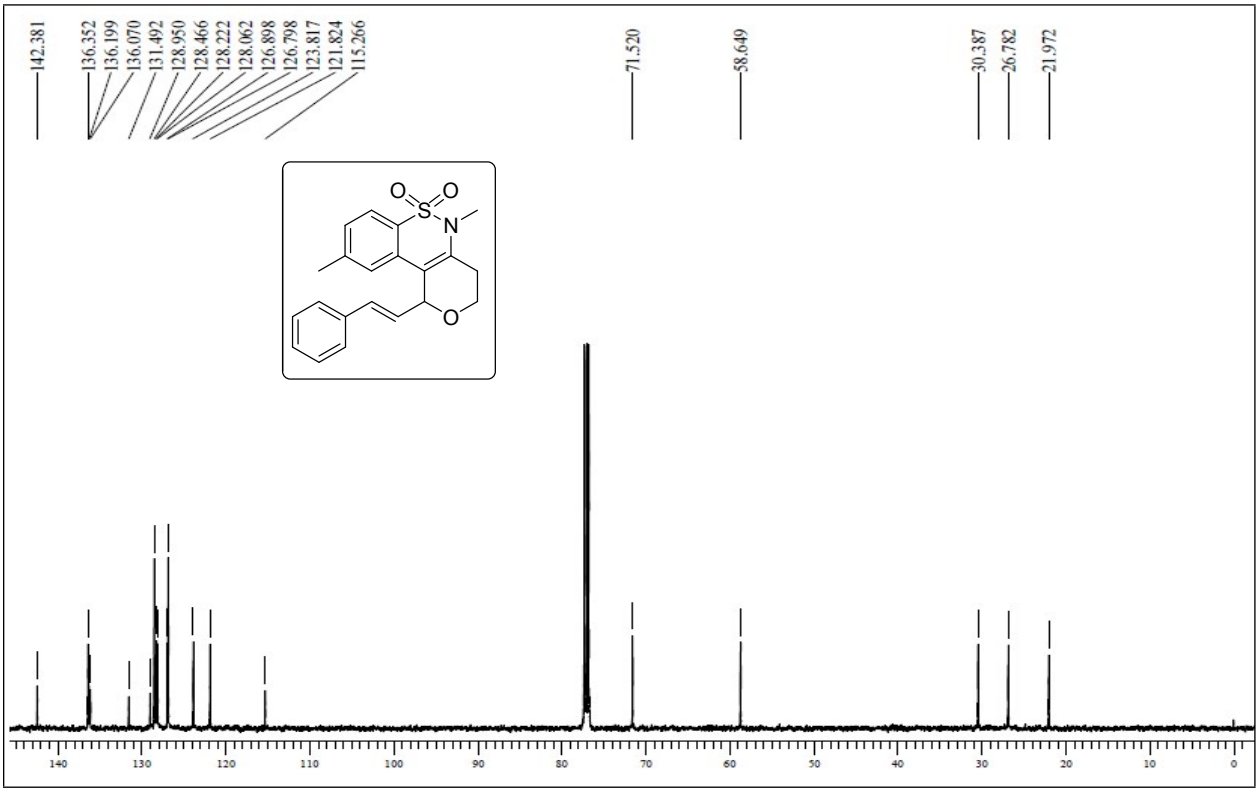
^{1}H NMR of Compound 4o



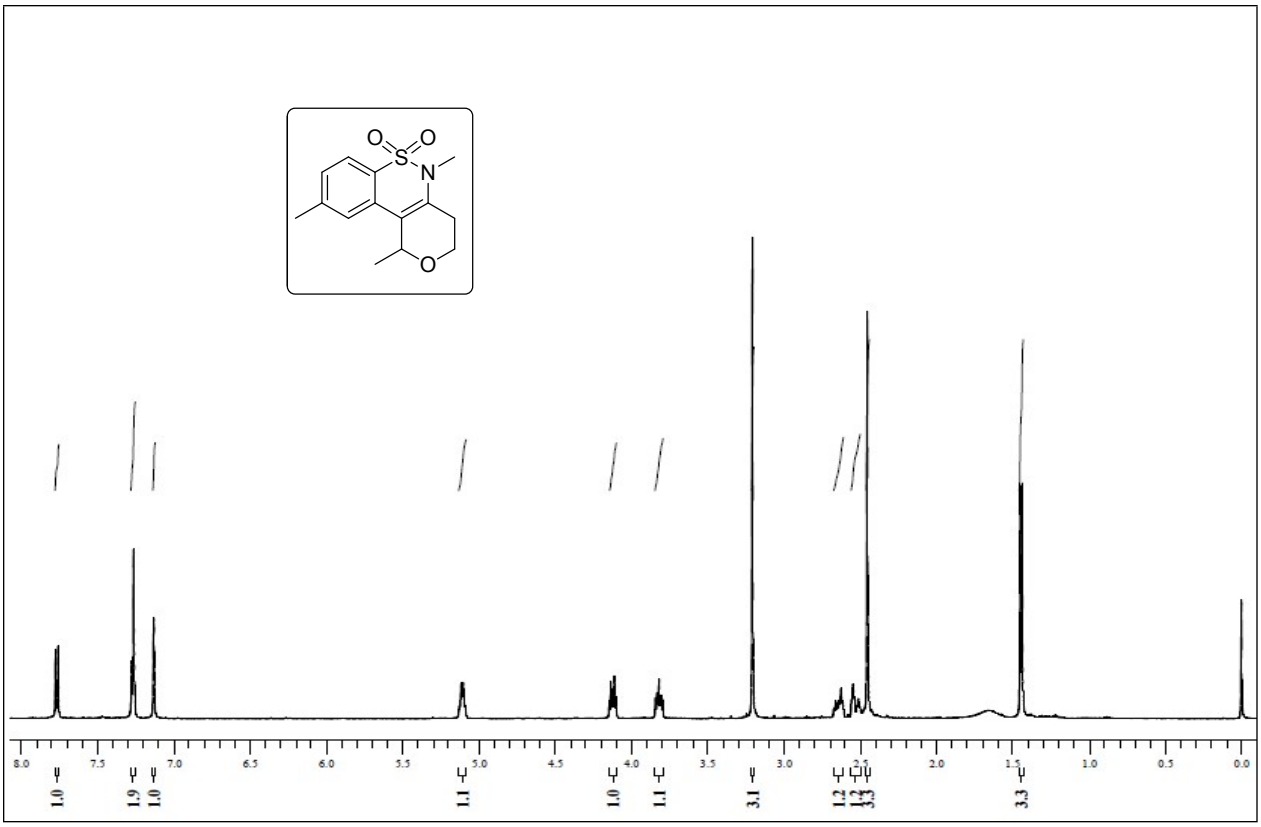
^{13}C NMR of Compound 4o



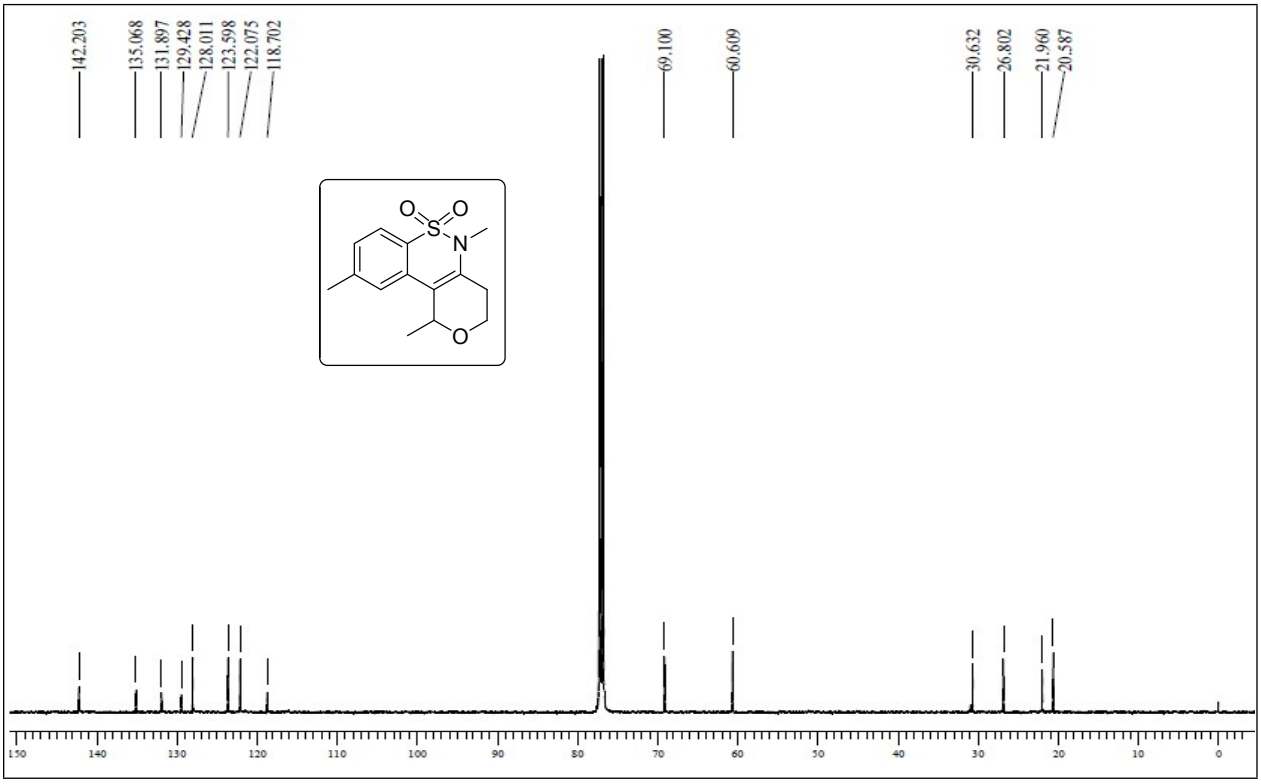
^{1}H NMR of Compound 4p



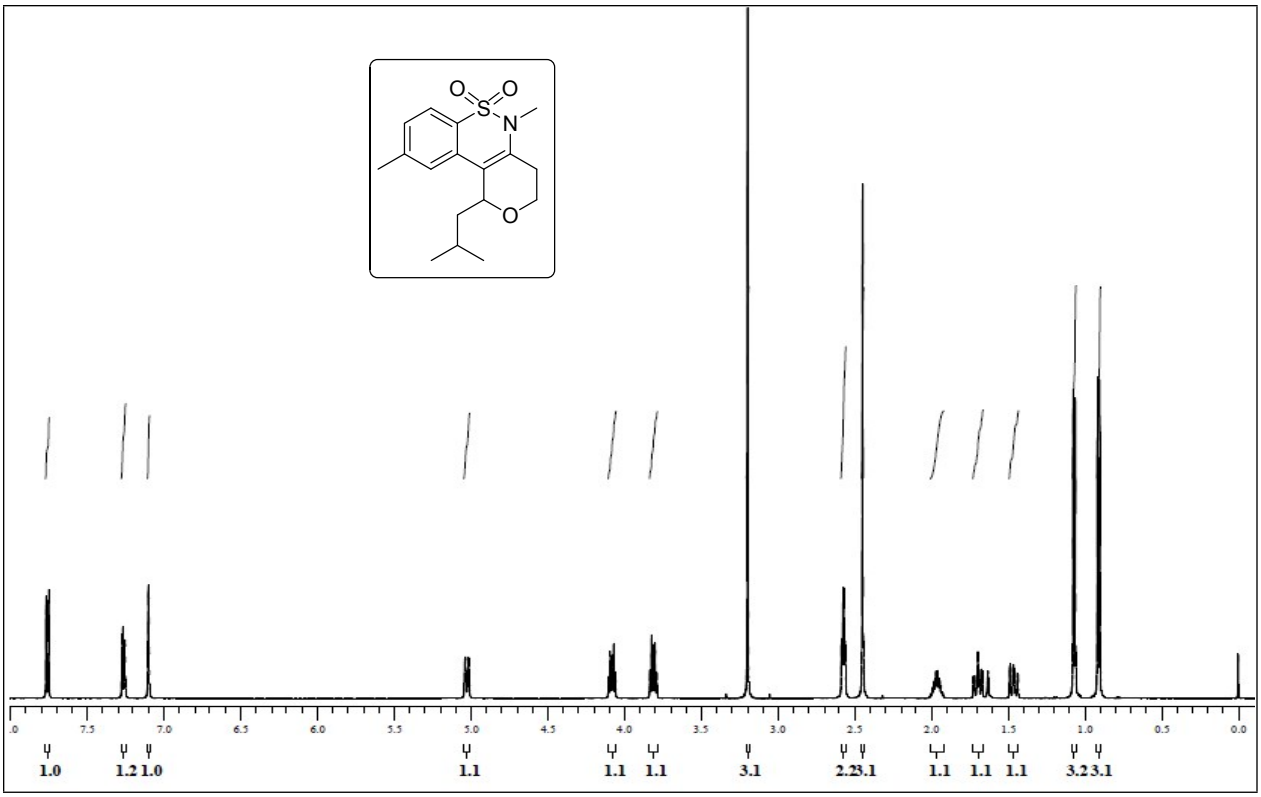
^{13}C NMR of Compound 4p



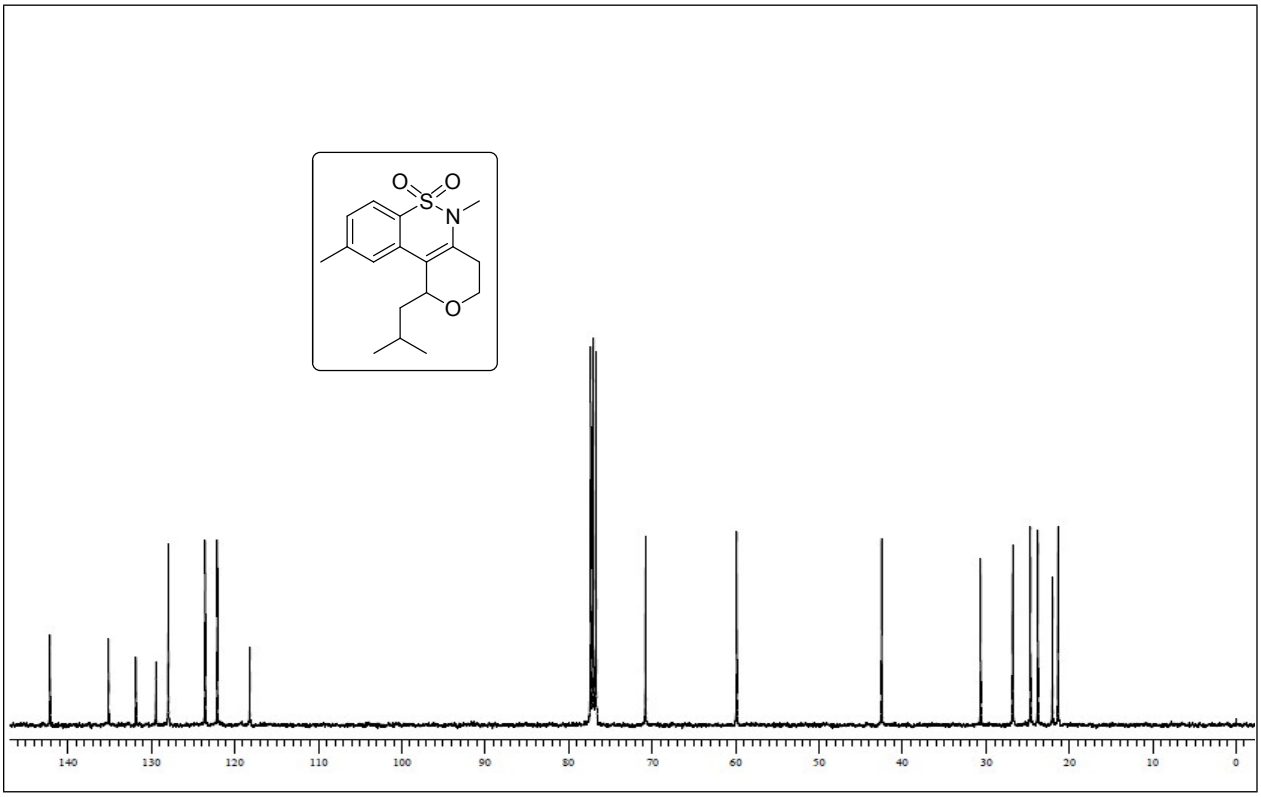
^{1}H NMR of Compound 4q



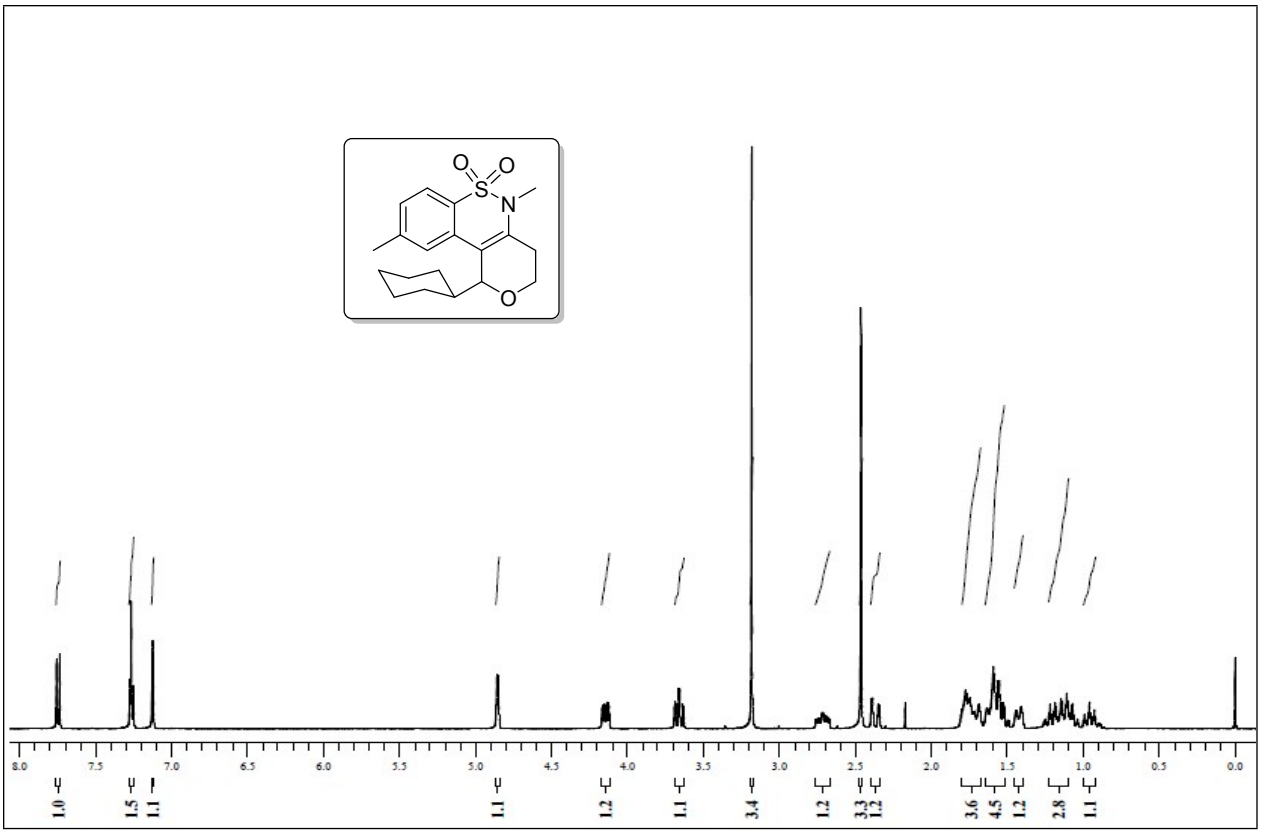
^{13}C NMR of Compound 4q



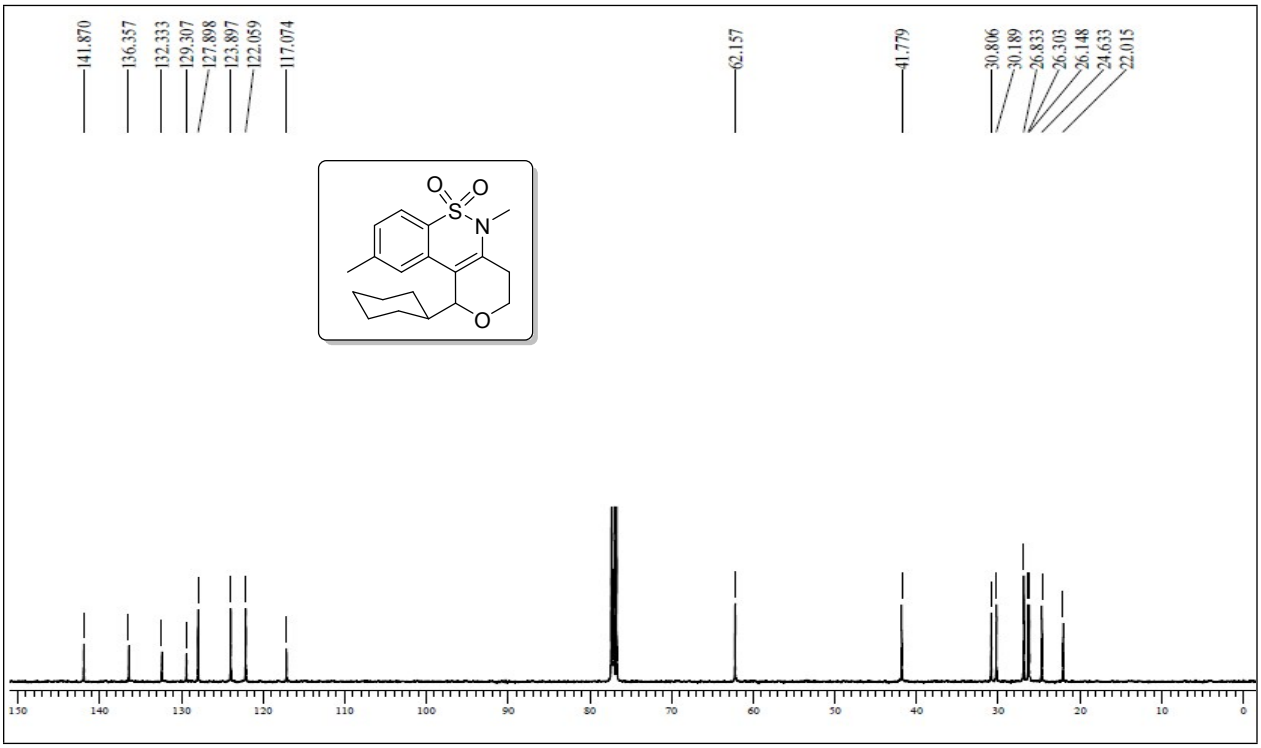
^{1}H NMR of Compound 4r



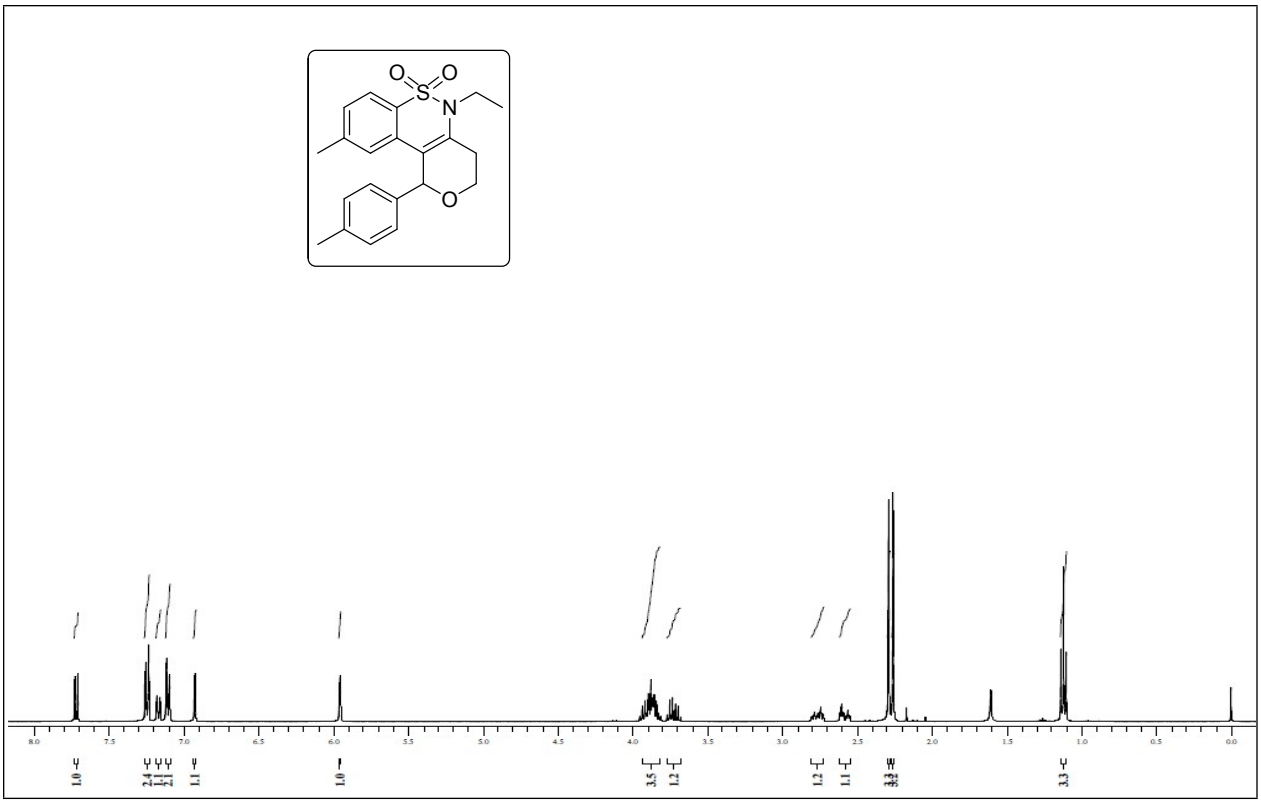
^{13}C NMR of Compound 4r



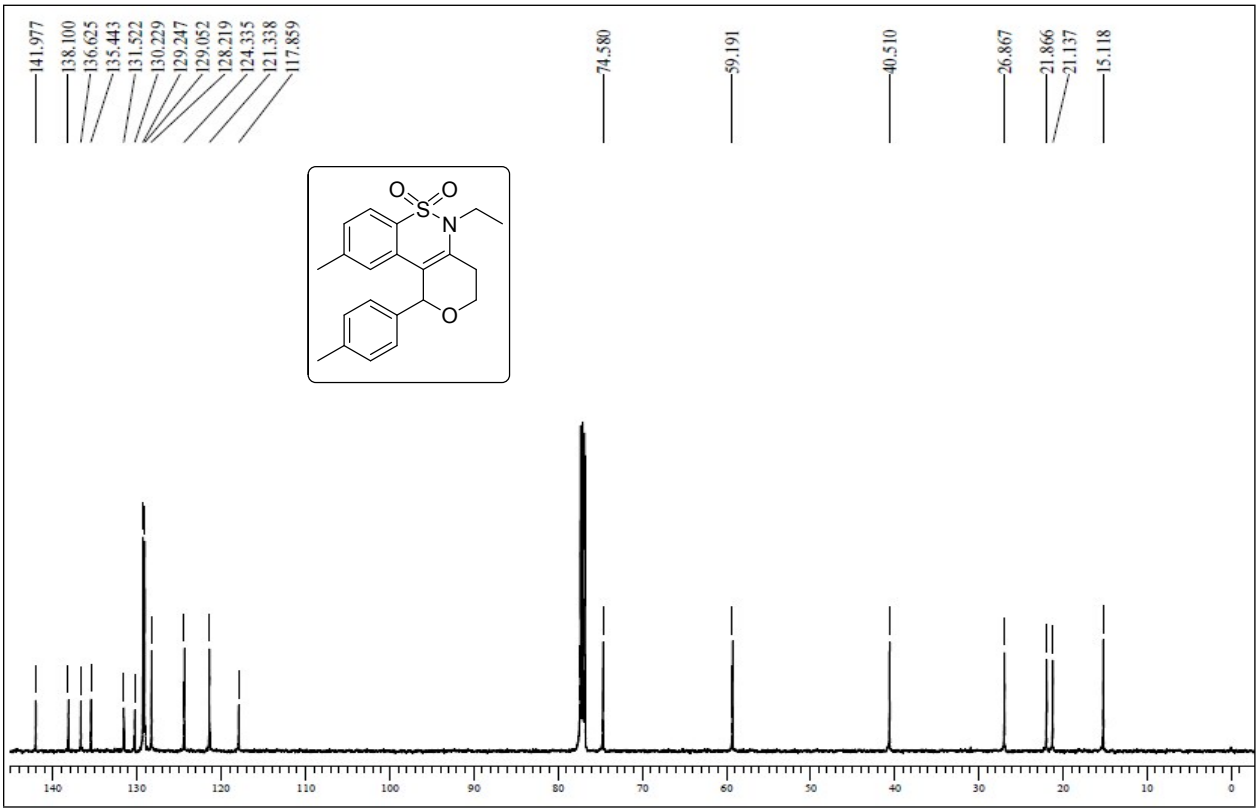
^{1}H NMR of Compound 4s



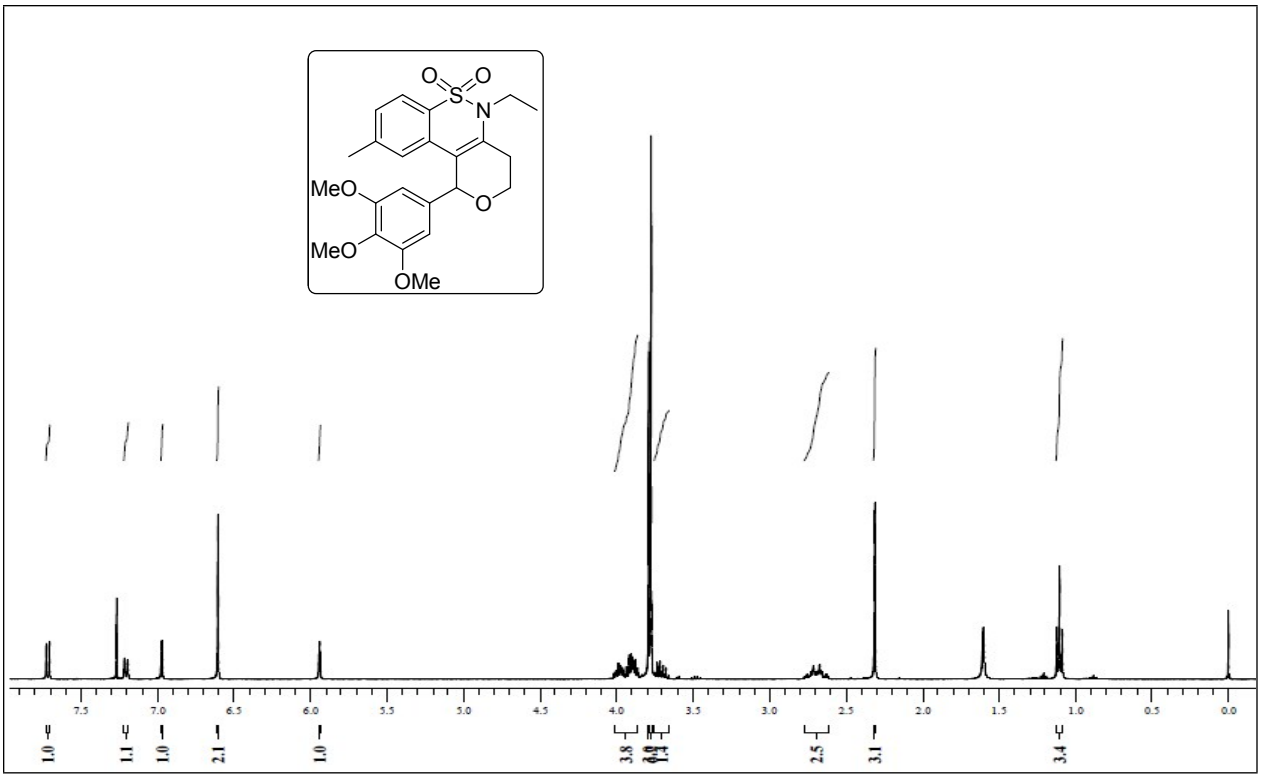
^{13}C NMR of Compound 4s



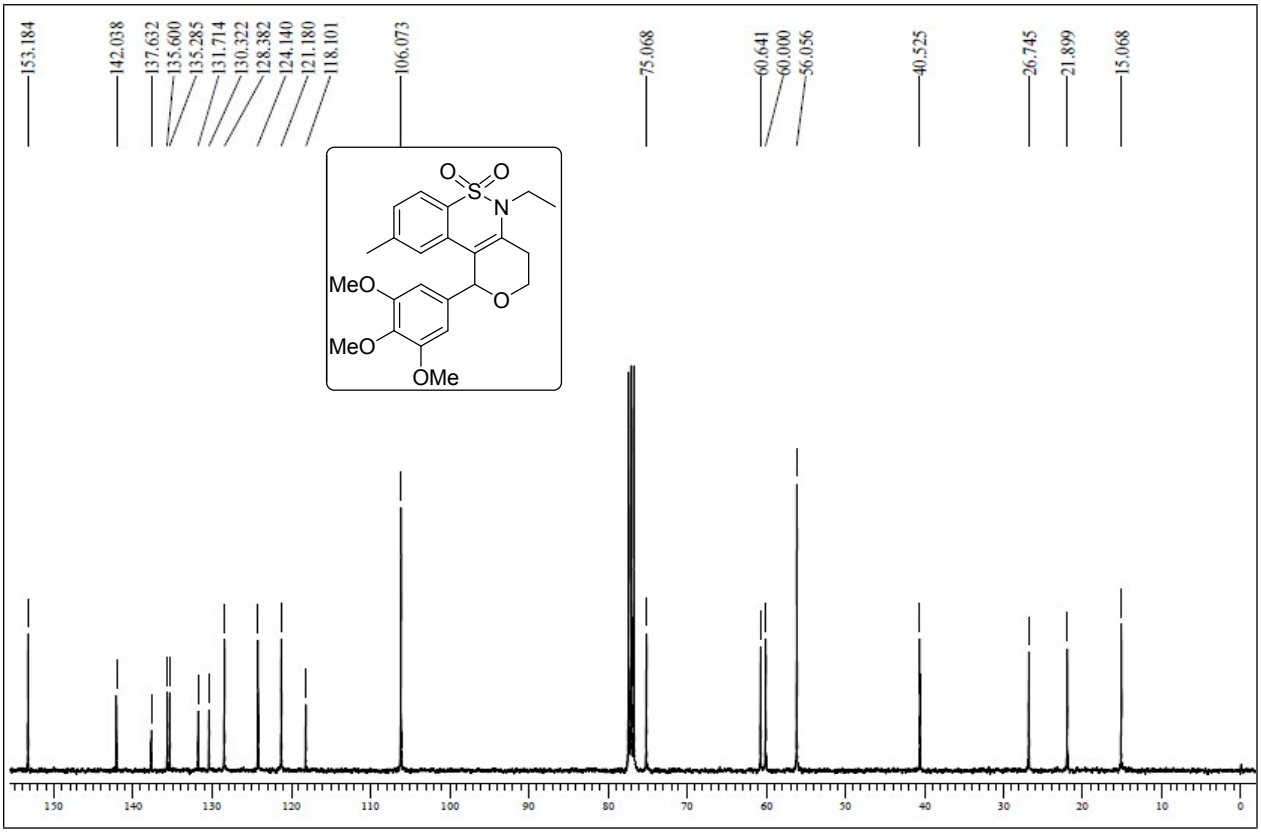
^{1}H NMR of Compound 4t



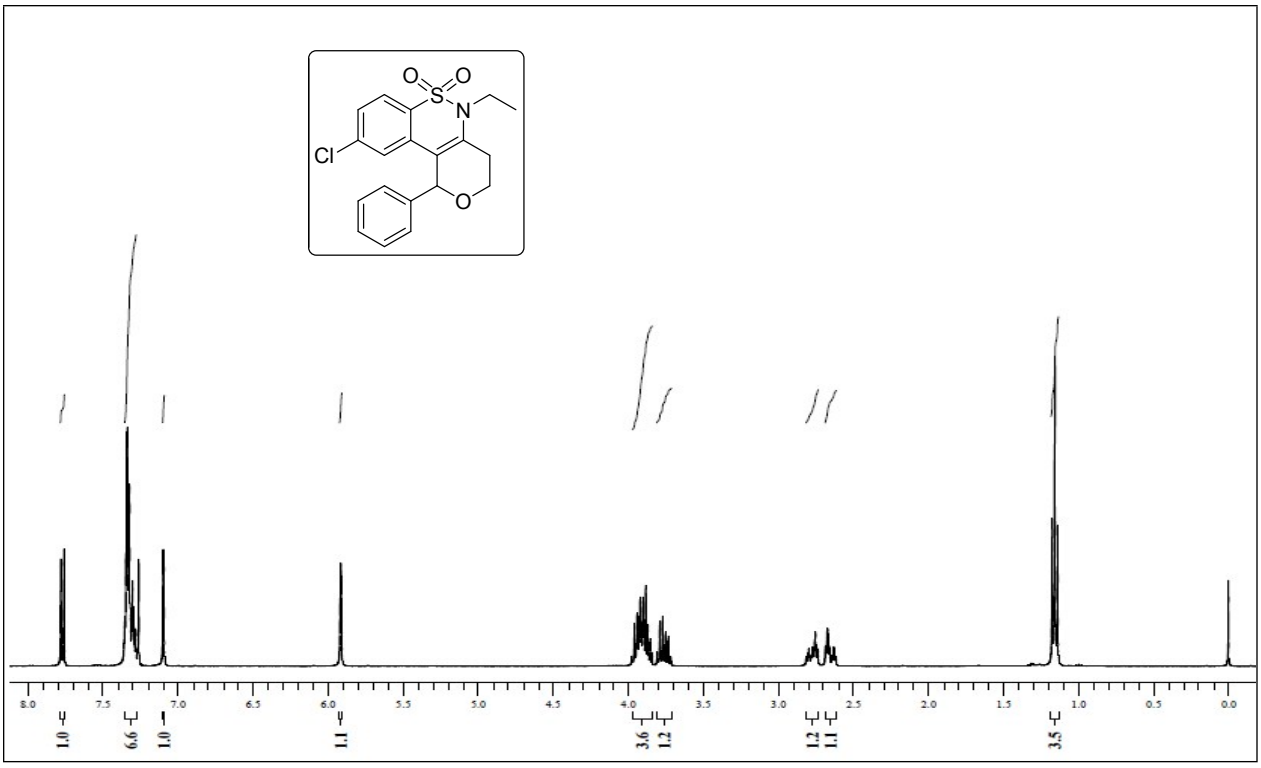
^{13}C NMR of Compound 4t



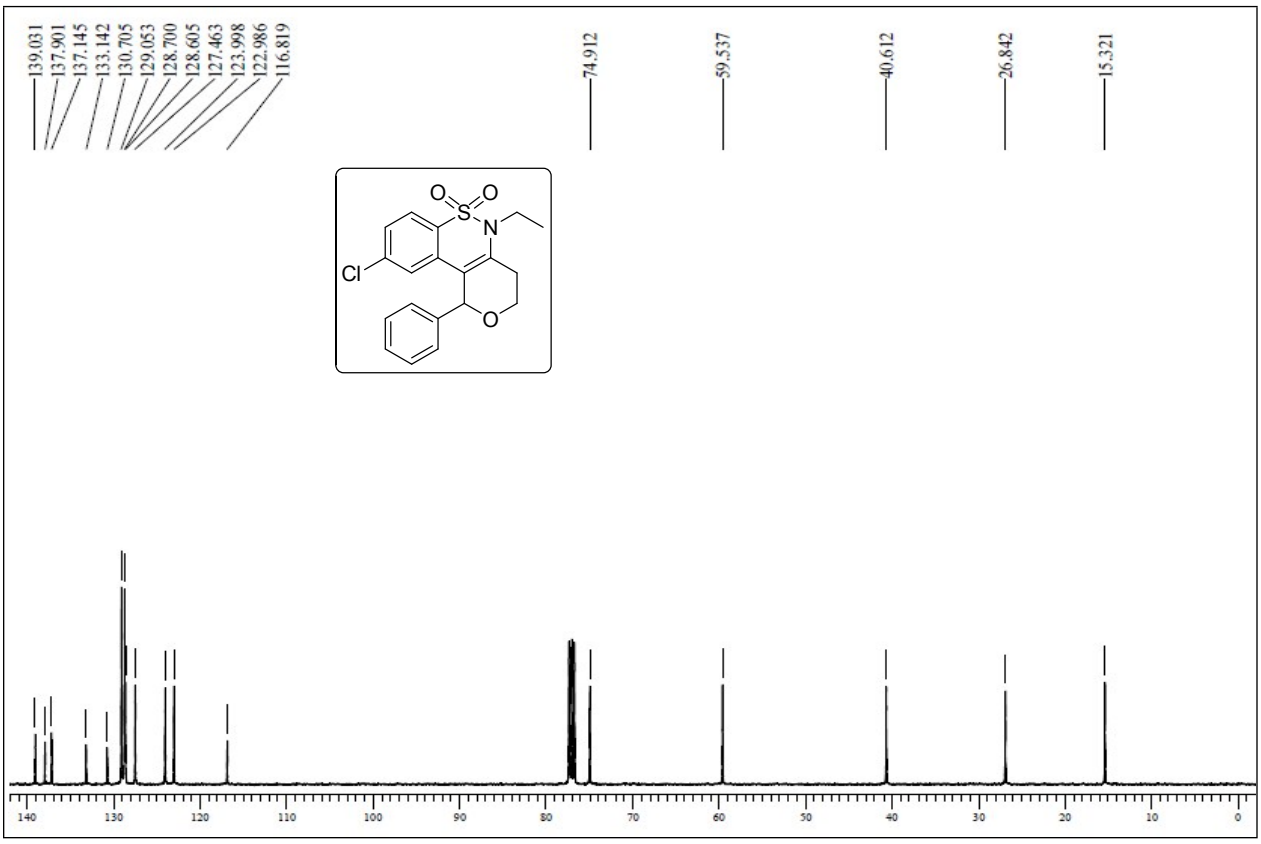
^{1}H NMR of Compound 4u



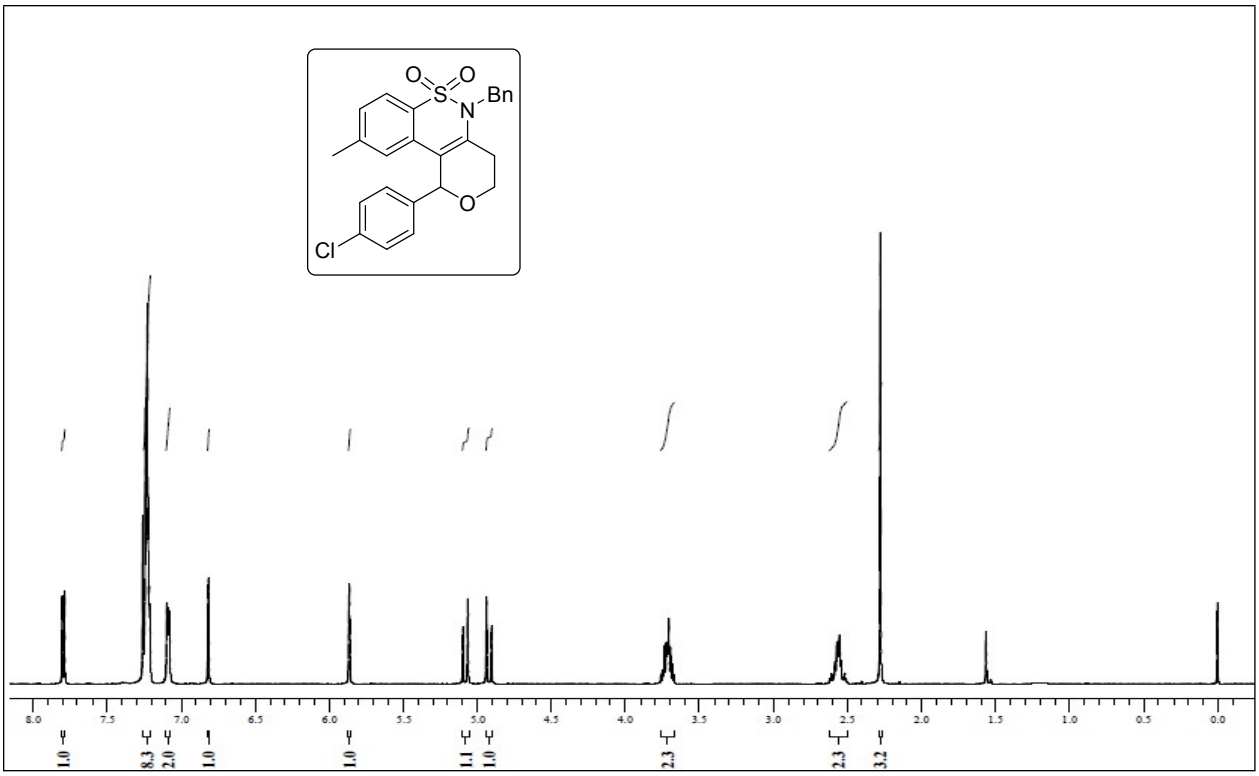
^{13}C NMR of Compound 4u



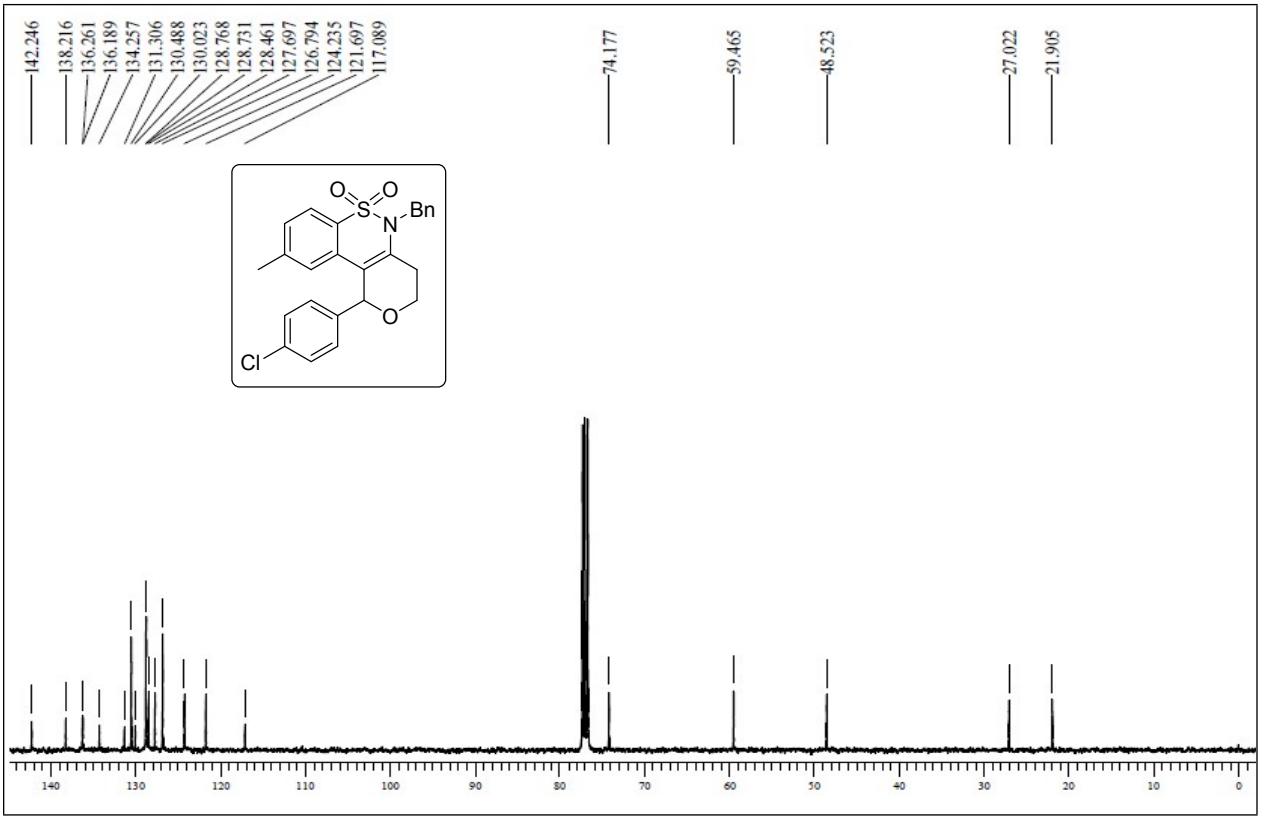
[1]H NMR of Compound 4v



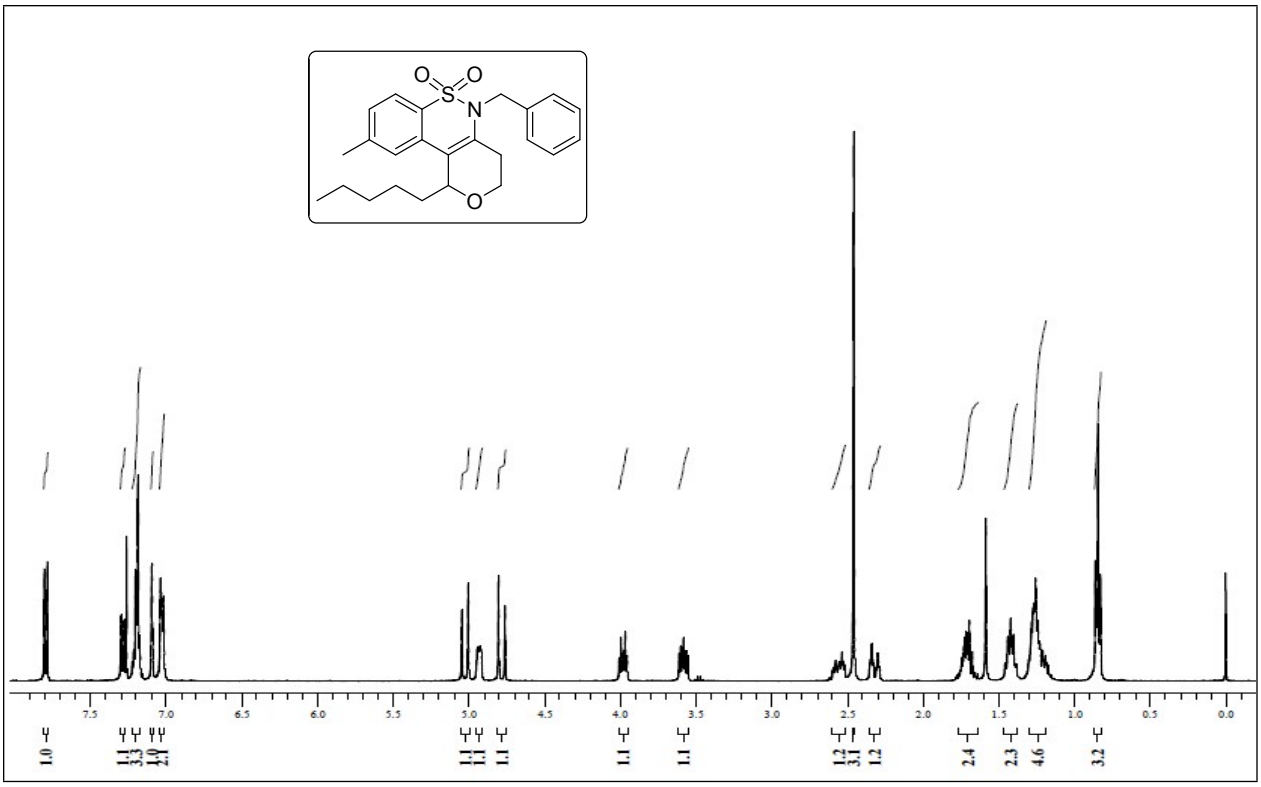
[13]C NMR of Compound 4v



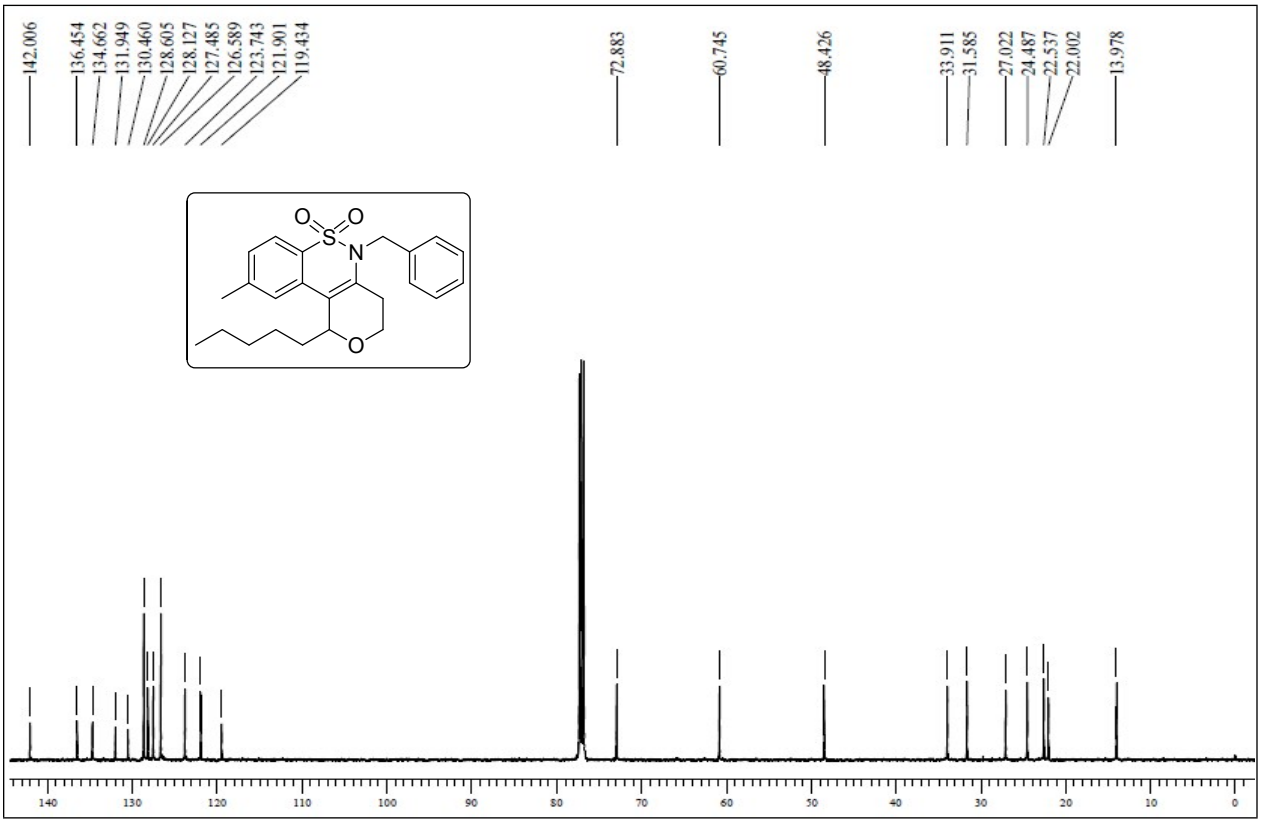
^{1}H NMR of Compound 4w



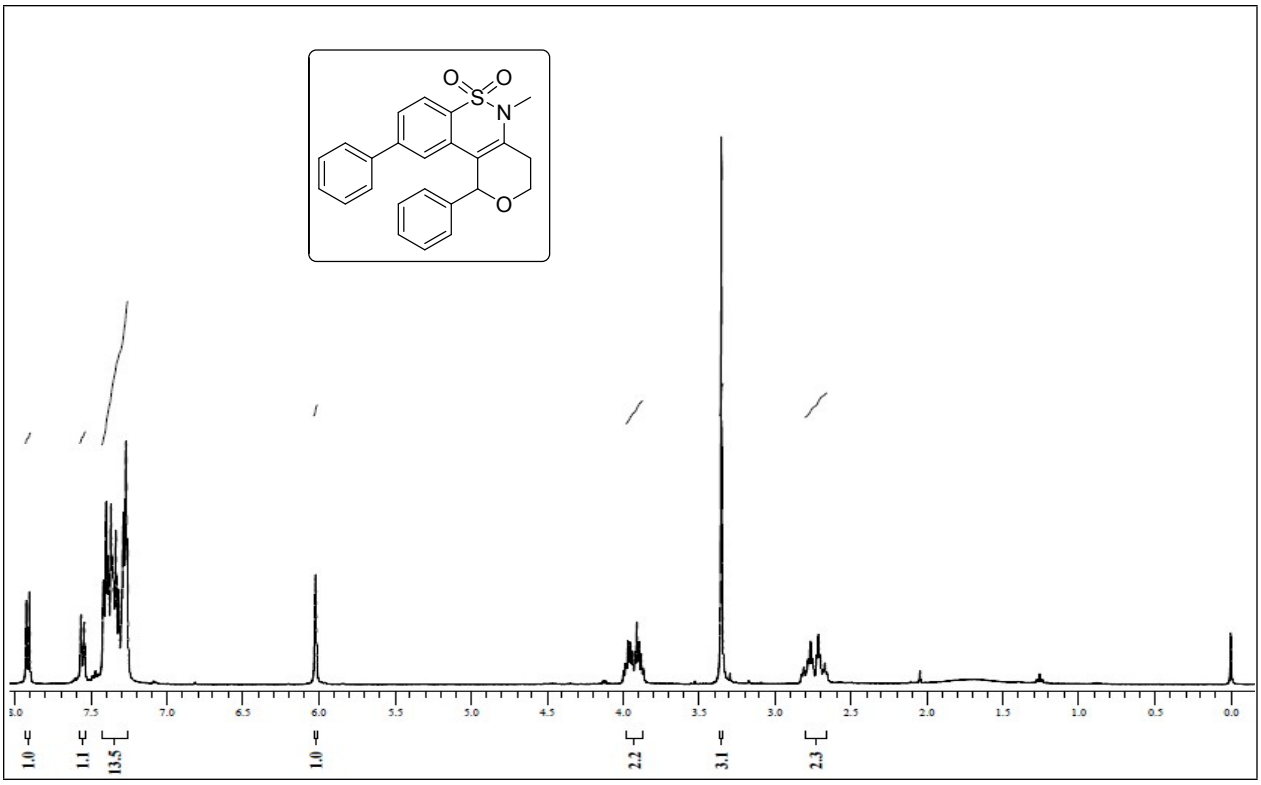
^{13}C NMR of Compound 4w



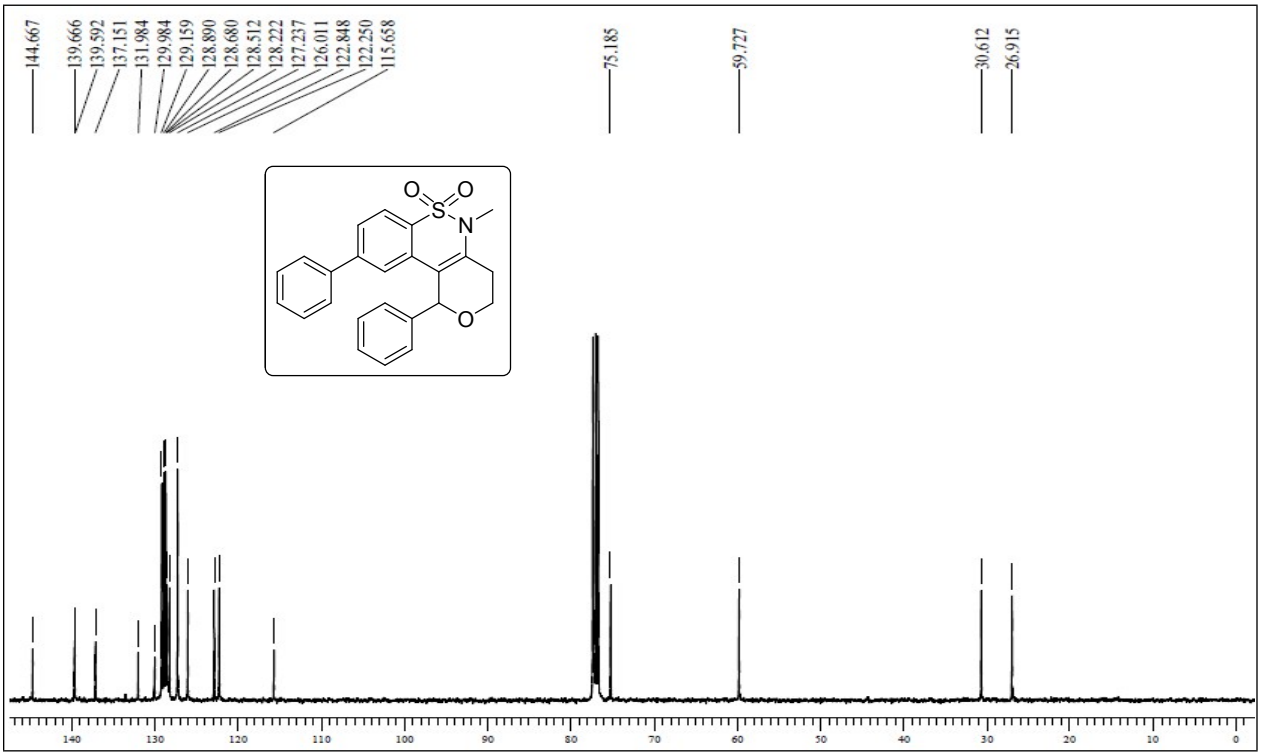
^{1}H NMR of Compound 4x



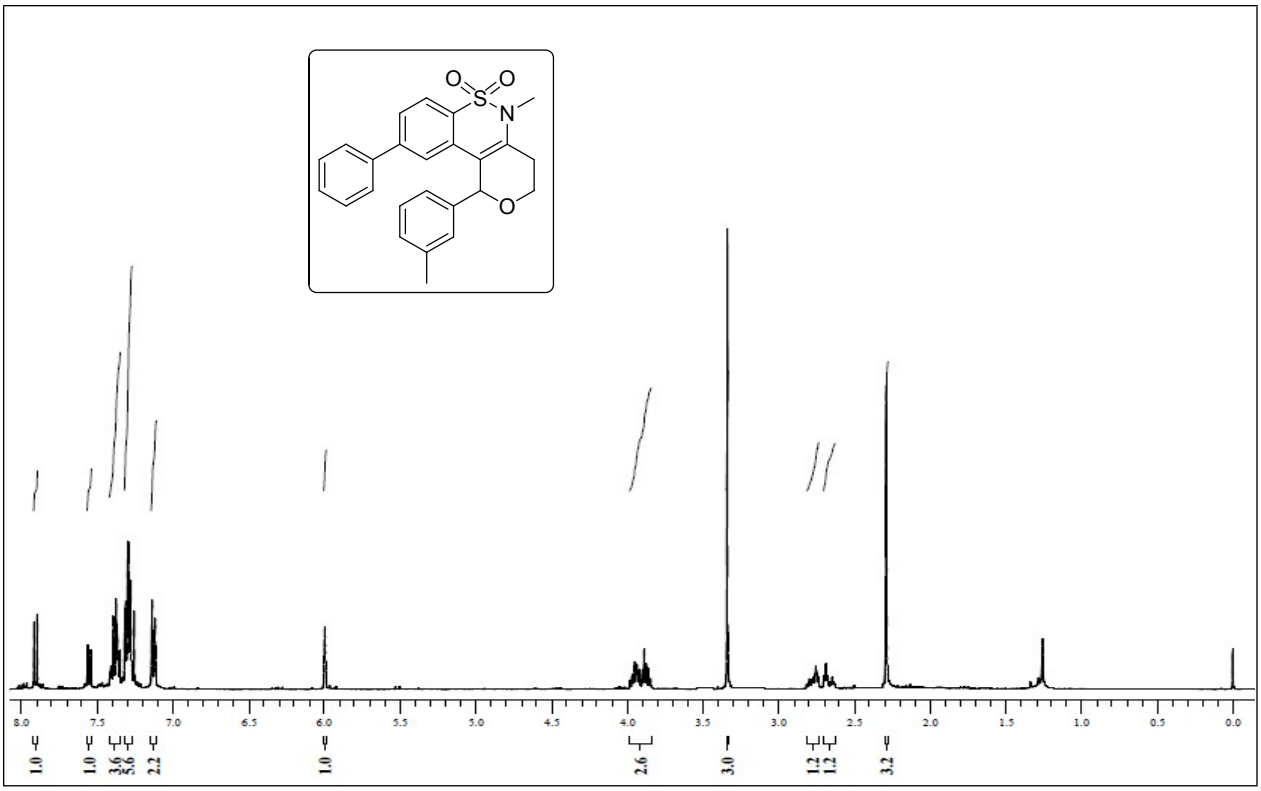
^{13}C NMR of Compound 4x



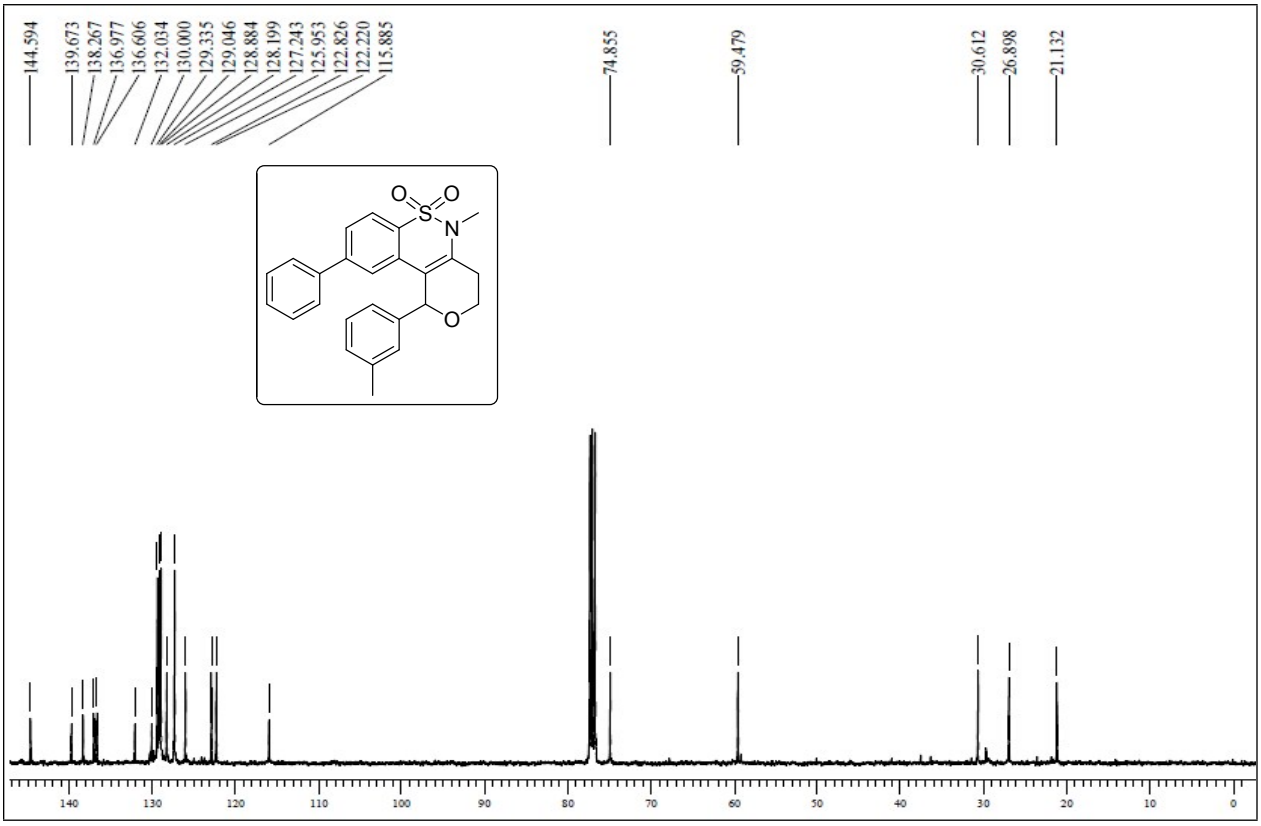
^{1}H NMR of Compound 4y



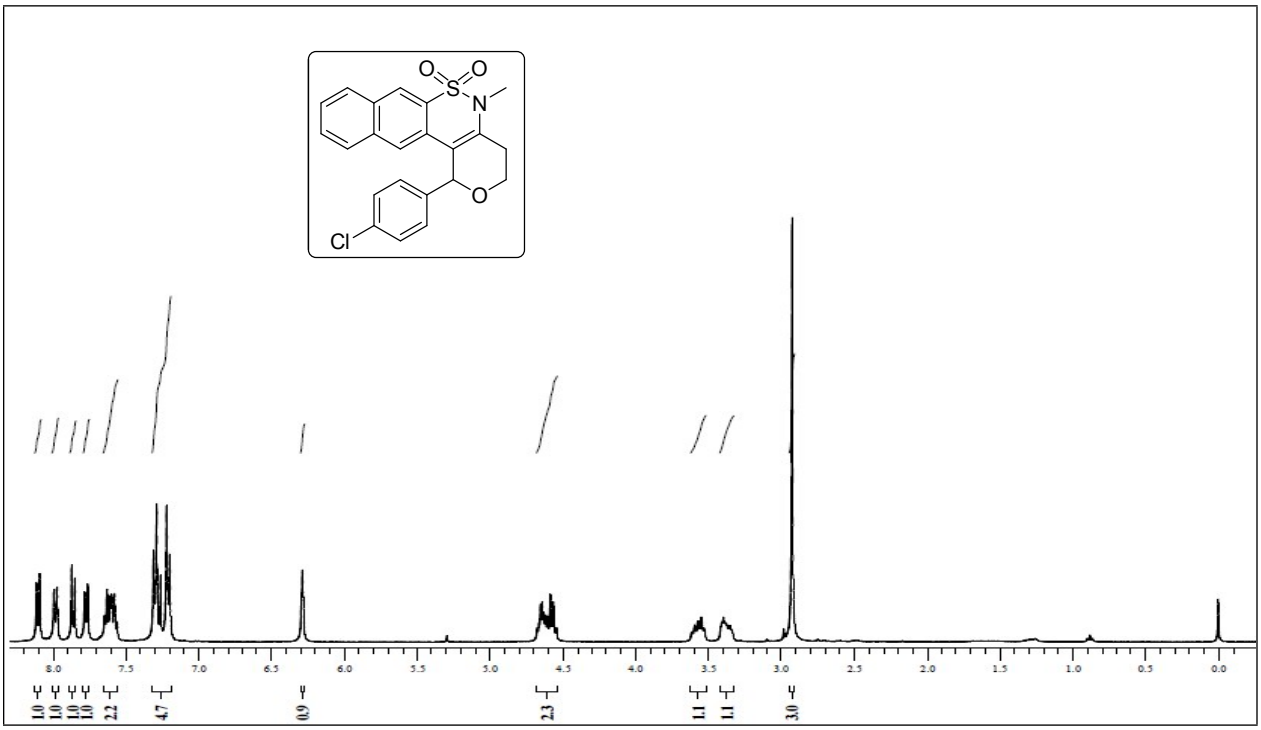
^{13}C NMR of Compound 4y



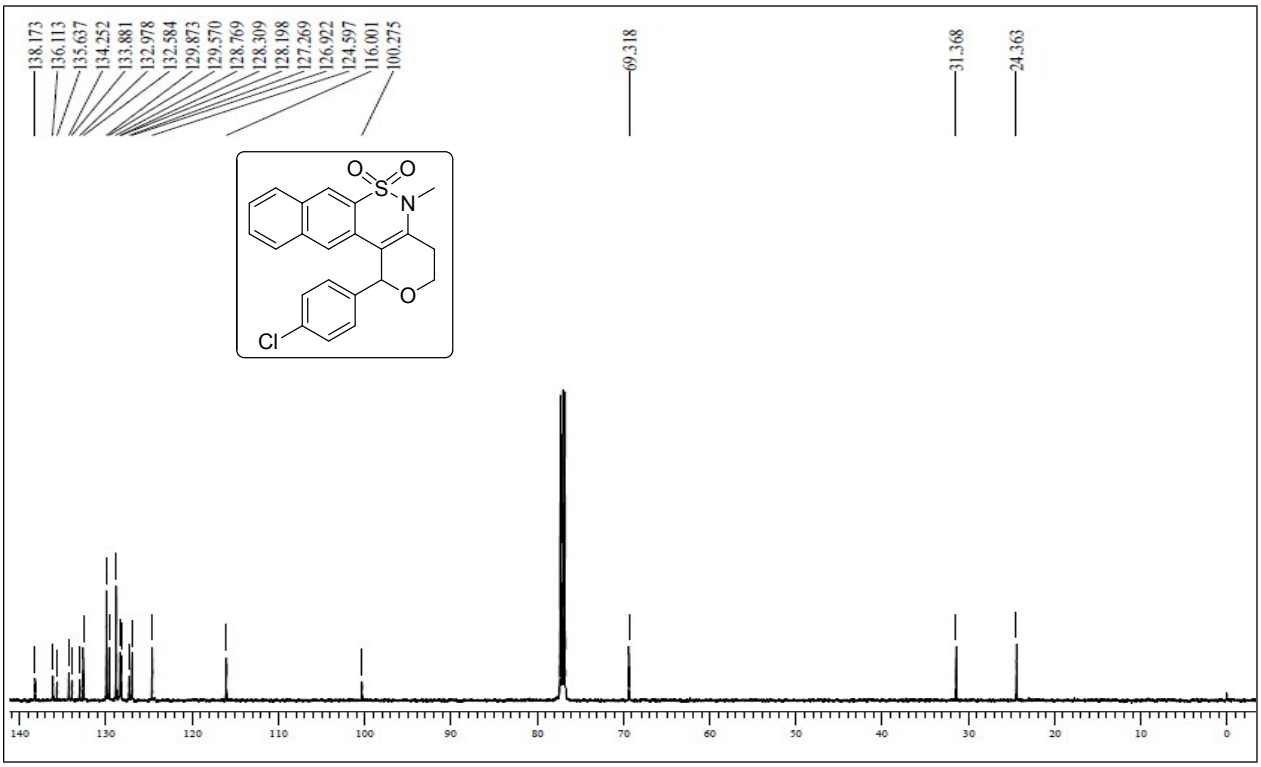
^{1}H NMR of Compound 4z



^{13}C NMR of Compound 4z



^{1}H NMR of Compound 4aa



^{13}C NMR of Compound 4aa

4. X-ray Crystallography of 4d

X-ray data for the compounds were collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated MoKα radiation (λ=0.71073Å) with ω-scan method [1]. Preliminary lattice parameters and orientation matrices were obtained from four sets of frames.

Integration and scaling of intensity data was accomplished using SAINT program [1]. The structure was solved by direct methods using SHELXS [2] and refinement was carried out by full-matrix least-squares technique using SHELXL [2]. Anisotropic displacement parameters were included for all non-hydrogen atoms. All other H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H or $1.2U_{eq}(c)$ for other H atoms]. The methyl groups were allowed to rotate but not to tip.

Crystal Data for 4d: $C_{17}H_{15}NO_3$ (M =281.31 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 6.0088(1) Å, b = 21.3777(5) Å, c = 10.8832(2) Å, β = 93.6225(7)°, V = 1395.20(5) Å^3, Z = 4, T = 294.15 K, μ(Mo Kα) = 0.092 mm^{-1}, $Dcalc$ = 1.3391 g/cm^3, 50265 reflections measured (5.34° ≤ 2Θ ≤ 61.42°), 4330 unique (R_{int} = 0.0856, R_{sigma} = 0.0516) which were used in all calculations. The final R_1 was 0.0686 (I>2σ(I)) and wR_2 was 0.1577 (all data). CCDC 1834668 contains supplementary Crystallographic data for the structure. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ccdc.cam.ac.uk].

1. Bruker (2001). SAINT (Version 6.28a) & SMART (Version 5.625). Bruker AXS Inc., Madison, Wisconsin, USA.
2. Sheldrick G. M. (2015**)** Acta Crystallogr C71: 3-8.