Supplementary Information

Natural Organic Acid as Green Catalyst for Xanthenones Synthesis: Methodology, Mechanism and Calcium Channel Blocking Activity

Bruna S. Terra,[a] Aura M. B. Osorio,[a] Aline de Oliveira,[a] Rebeca P. M. Santos,[b] Andressa P. Mouro,[b] Natália F. de Araújo,[b] Cameron C. da Silva,[c] Felipe T. Martins,[c] Luciene B. Vieira,[b] Daniella Bonaventura,[b] Heitor A. de Abreu,[a] Antonio F. C. Alcântara[a] and Ângelo de Fátima*[a]

[a]Departamento de Química and [b]Departamento de Farmacologia, Universidade Federal de Minas Gerais, Av. Pres. Antônio Carlos, 6627, 31270-901 Belo Horizonte-MG, Brazil

[c]Instituto de Química, Universidade Federal de Goiás, Campus Samambaia, CP 131, 74001-970 Goiânia-GO, Brazil

9,9-Dimethyl-12-phenyl-9,10-dihydro-8*H*-benzo[*a*]xanthen-11(12*H*)-one (**4a**)

mp 158-159 °C [Lit.[1] 155-156 °C]; IR (ATR) ν / cm^{-1} 2967, 1651, 1621, 1501, 1479, 1452, 1373, 1218, 1191, 1144, 1027, 933, 870, 837, 744; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, 1H, *J* 8.0 Hz), 7.67-7.64 (m, 2H), 7.35-7.30 (m, 3H), 7.28-7.23 (m, 2H), 7.12 (t, 2H, *J* 8.0 Hz), 6.98 (t, 1H, *J* 8.0 Hz), 5.70 (s, 1H), 2.44 (s, 2H), 2.21 (d, 2H, *J* 16.0 Hz), 2.15 (d, 2H, *J* 16.0 Hz), 1.00 (s, 3H), 0.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 164.3, 148.2, 145.3, 132.0, 131.9, 129.3, 128.9, 128.7, 127.5, 126.7, 125.3, 124.1, 118.2, 117.5, 114.7, 51.3, 41.8, 35.2, 32.6, 29.8, 27.5; HRMS (ESI) *m/z* $C_{25}H_{22}O_2$ $[M + Na]^+$ observed: 377.1425; $C_{25}H_{22}O_2$ $[M + Na]^+$ requires: 377.1518.

9,9-Dimethyl-12-(4-nitrophenyl)-9,10-dihydro-8*H*-benzo[*a*]xanthen-11(12*H*)-one (**4b**)

mp 172-174 °C; [Lit.[2] 177-179 °C]; IR (ATR) ν / cm^{-1} 2913, 1650, 1594, 1452, 1370, 1283, 1219, 1180, 1167, 1141, 1012, 974, 959, 836, 803, 766, 743, 729, 700, 656; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.03 (d, 2H, *J* 6.0 Hz), 7.82 (sl, 3H), 7.53-7.39 (m, 5H), 5.81 (s, 1H), 2.59 (s, 2H), 2.34 (d, 1H, *J* 16.0 Hz), 2.22 (d, 1H, *J* 16.0 Hz), 1.13 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 196.7, 164.6, 151.8, 147.7, 146.2, 131.5, 130.9, 129.6, 129.3 128.6, 127.3, 125.2, 123.5, 123.0, 117.0, 115.9, 112.9, 50.7, 41.3, 34.8, 32.2, 29.2, 27.0; HRMS (ESI) *m/z* $C_{25}H_{21}NO_4$ $[M + H]^+$ observed: 400.1488; $C_{25}H_{21}NO_4$ $[M + H]^+$ requires: 400.1549.

12-(4-Fluorophenyl)-9,9-dimethyl-9,10-dihydro-8*H*-benzo[*a*]xanthen-11(12*H*)-one (**4c**)

mp 165-167 °C; [Lit.[3] 185-186 °C]; IR (ATR) ν / cm^{-1} 2912, 1651, 1594, 1489, 1452, 1370, 1283, 1219, 1180, 1141, 1011, 975, 959, 836, 803, 766, 743, 729, 700, 657; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, 1H, *J* 12.0 Hz), 7.80-7.76 (m, 2H), 7.46-7.37 (m, 2H), 7.34-7.29 (m, 3H), 6.86 (t, 2H, *J* 8.0 Hz), 5.71 (s, 1H), 2.57 (s, 2H), 2.32 (d, 1H, *J* 16.0 Hz), 2.25 (d, 1H, *J* 16.0 Hz), 1.12 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 163.9, 161.2, 147.7, 140.5, 131.5, 131.2, 129.9, 129.8, 129.0, 128.4, 127.0, 124.9, 123.5, 117.3, 117.0, 115.1, 114.9, 114.0, 50.8, 41.3, 39.9, 32.2, 29.3, 27.0; HRMS (ESI) *m/z* $C_{25}H_{21}FO_2$ $[M + H]^+$ observed: 373.1589; $C_{25}H_{21}FO_2$ $[M + H]^+$ requires: 373.1604.

*e-mail: adefatima@qui.ufmg.br

12-(4-Chlorophenyl)-9,9-dimethyl-9,10-dihydro-8*H*-benzo[*a*]xanthen-11(12*H*)-one (**4d**)

mp 162-164 °C; [Lit.[1] 178-179 °C]; IR (ATR) ν / cm^{-1} 2951, 1659, 1647, 1597, 1488, 1368, 1224, 1198, 1184, 1166, 1141, 1087, 1027, 979, 937, 834, 812, 752, 728, 657; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.91 (d, 1H, *J* 8.0 Hz), 7.81-7.76 (m, 2H), 7.45-7.30 (m, 5H), 7.14 (d, 2H, *J* 8.0 Hz), 5.69 (s, 1H), 2.57 (s, 2H), 2.33 (d, 1H, *J* 16.0 Hz), 2.23 (d, 1H, *J* 16.0 Hz), 1.13 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 196.8, 164.0, 147.6, 143.2, 131.8, 131.4, 131.1, 129.7, 129.0, 128.4, 128.3, 127.1, 125.0, 123.4, 117.0, 113.7, 50.8, 41.3, 34.1, 32.2, 29.2, 27.0; HRMS (ESI) *m/z* $C_{25}H_{21}ClO_2$ $[M + Na]^+$ observed: 411.1120; $C_{25}H_{21}ClO_2$ $[M + Na]^+$ requires: 411.1128.

12-(2-Hydroxyphenyl)-9,9-dimethyl-9,10-dihydro-8*H*-benzo[*a*]xanthen-11(12*H*)-one (**4e**)

mp 224-227 °C; [Lit.[4] 229-230 °C]; IR (ATR) ν / cm^{-1} 3192, 2961, 1656, 1629, 1617, 1593, 1484, 1377, 1230, 1182, 1117, 1029, 810, 764; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (s, 1H, OH), 7.79-7.75 (m, 2H), 7.68 (d, 1H, *J* 8.0 Hz), 7.40-7.32 (m, 3H), 7.02-7.00 (m, 2H), 6.63-6.61 (m, 2H), 5.77 (s, 1H), 2.61 (s, 2H), 2.42 (d, 1H, *J* 16.0 Hz), 2.35 (d, 1H, *J* 16.0 Hz), 1.15 (s, 3H), 0.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.6, 166.8, 152.8, 147.8, 132.7, 131.5, 131.1, 129.1, 128.7, 128.2, 127.9, 127.5, 125.2, 123.4, 121.5, 118.8, 117.4, 116.5, 113.9, 50.2, 41.5, 32.3, 29.0, 28.0, 27.2; HRMS (ESI) *m/z* $C_{25}H_{22}O_3$ $[M + Na]^+$ observed: 393.1447; $C_{25}H_{22}O_3$ $[M + Na]^+$ requires: 393.1467.

12-(3-Hydroxyphenyl)-9,9-dimethyl-9,10-dihydro-8*H*-benzo[*a*]xanthen-11(12*H*)-one (**4f**)

mp 238-240 °C; [Lit.[5] 237-239 °C]; IR (ATR) ν / cm^{-1} 3407, 2964, 1638, 1615, 1585, 1478, 1466, 1369, 1348, 1275, 1223, 1175, 1145, 1113, 1025, 950, 820, 787, 751, 699; ^{1}H NMR (200 MHz, DMSO-d_6) δ 9.21 (s, 1H), 8.01 (d, 1H, *J* 8.0 Hz), 7.93-7.89 (m, 2H), 7.51-7.43 (m, 3H), 6.96 (t, 1H, *J* 8.0 Hz), 6.72 (d, 1H, *J* 8.0 Hz), 6.65 (s, 1H), 6.43 (d, 1H, *J* 8.0 Hz), 5.49 (s, 1H), 2.73-2.61 (m, 2H), 2.33 (d, 1H, *J* 16.0 Hz), 2.14 (d, 1H, *J* 16.0 Hz), 1.06 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (50 MHz, DMSO-d_6) δ 195.8, 163.6, 157.1, 147.1, 146.2, 131.0, 130.7, 128.9, 128.5, 127.0, 124.9, 123.2, 118.9, 117.3, 117.0, 115.1, 113.2, 50.1, 40.3, 33.9, 31.8, 28.7, 26.2; HRMS (ESI) *m/z* $C_{25}H_{22}O_3$ $[M + Na]^+$ observed: 393.1449; $C_{25}H_{22}O_3$ $[M + Na]^+$ requires: 393.1467.

12-(4-Hydroxyphenyl)-9,9-dimethyl-9,10-dihydro-8*H*-benzo[*a*]xanthen-11(12*H*)-one (**4g**)

mp 210-212 °C; [Lit.[2] 185-187 °C]; IR (ATR) ν / cm^{-1} 3161, 2966, 2871, 1651, 1628, 1617, 1588, 1510, 1450, 1369, 1221, 1184, 1169, 1026, 1012, 839, 825, 746, 653; ^{1}H NMR (200 MHz, DMSO-d_6) δ 9.21 (s, 1H), 8.03 (d, 1H, *J* 6.0 Hz), 7.89-7.86 (m, 2H), 7.48-7.39 (m, 3H), 7.08 (d, 2H, *J* 8.0 Hz), 6.58 (d, 2H, *J* 8.0 Hz), 5.47 (s, 1H), 2.59-2.56 (m, 2H), 2.31 (d, 1H, *J* 16.0 Hz), 2.11 (d, 1H, *J* 16.0 Hz), 1.03 (s, 3H), 0.88 (s, 3H); ^{13}C NMR (50 MHz, DMSO-d_6) δ 195.9, 164.3, 155.5, 147.0, 135.4, 131.0, 130.6, 129.0, 128.7, 128.4, 126.9, 124.8, 123.3, 117.7, 117.1, 114.8, 113.5, 50.1, 40.7, 33.1, 31.8, 28.8, 26.1; HRMS (ESI) *m/z* $C_{25}H_{22}O_3$ $[M + Na]^+$ observed: 393.1880; $C_{25}H_{22}O_3$ $[M + Na]^+$ requires: 393.1467.

9,9-Dimethyl-12-(4-(methylthio)phenyl)-9,10-dihydro-8*H*-benzo[*a*]xanthen-11(12*H*)-one (**4h**)

mp 171-173 °C; [Lit.[6] 209-211 °C]; IR (ATR) ν / cm^{-1} 2954, 1645, 1594, 1488, 1374, 1221, 1163, 1140, 1023, 976, 958, 933, 844, 820, 778, 747, 666; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.98 (d, 1H, *J* 6.0 Hz), 7.79-7.74 (m, 2H), 7.45-7.30 (m, 5H), 7.07 (d, 2H, *J* 8.0 Hz), 5.68 (s, 1H), 2.57 (s, 2H), 2.37 (s, 3H), 2.29-2.19 (m, 2H), 1.12, (s, 3H), 0.98 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 196.9, 163.8, 147.6, 141.7, 135.8, 131.4, 128.8, 128.3, 126.9, 126.4, 124.9, 123.5, 117.4, 117.0, 114.0, 50.8, 41.3, 34.1, 32.2, 29.2, 27.1, 15.6; HRMS (ESI) *m/z* $C_{26}H_{24}O_2S$ $[M + Na]^+$ observed: 423.1320; $C_{26}H_{24}O_2S$ $[M + Na]^+$ requires: 423.1395.

12-(4-Methoxyphenyl)-9,9-dimethyl-9,10-dihydro-8*H*-benzo[*a*]xanthen-11(12*H*)-one (**4i**)

mp 204-205 °C; [Lit.[6] 206-208 °C]; IR (ATR) ν / cm^{-1} 2956, 1645, 1594, 1509, 1378, 1259, 1224, 1026, 848, 799, 746; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.98 (d, 1H, *J* 8.0 Hz), 7.79-7.72 (m, 2H), 7.44-7.22 (m, 5H), 6.70 (d, 2H, *J* 8.0 Hz), 5.65 (s, 1H), 3.68 (s, 3H), 2.56 (s, 2H), 2.32 (d, 1H, *J* 16.0 Hz), 2.22 (d, 1H, *J* 16.0 Hz), 1.11 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 197.0, 163.6, 157.7, 147.6, 137.1, 131.4, 129.3, 128.7, 128.3, 126.9, 124.8, 123.6, 117.8, 117.0, 114.3, 113.5, 55.0, 50.8, 41.3, 33.8, 32.2, 29.2, 27.1; HRMS (ESI) *m/z* $C_{26}H_{24}O_3$ $[M + Na]^+$ observed: 407.1546; $C_{26}H_{24}O_3$ $[M + Na]^+$ requires: 407.1623.

4-(9,9-Dimethyl-11-oxo-9,10,11,12-tetrahydro-8*H*-benzo[*a*]xanthen-12-yl)benzonitrile (**4j**)

mp 206-208 °C; [Lit.[7] 203-204 °C]; IR (ATR) ν / cm^{-1} 2951, 2229, 1649, 1597, 1500, 1464, 1366, 1224, 1190, 1179, 1025, 1015, 978, 938, 845, 812, 752, 664; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.86-7.79 (m, 3H), 7.47-7.34 (m, 7H), 5.77 (s, 1H), 2.59 (s, 2H), 2.35 (d, 1H, *J* 16.0 Hz), 2.24 (d, 1H, *J* 16.0 Hz), 1.13 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 196.7, 164.5, 149.8, 147.7, 132.1, 131.5, 131.0, 129.5, 129.2, 128.6, 127.3, 125.1, 123.1, 118.8, 117.0, 116.0, 113.0, 110.0, 50.7, 41.3, 34.9, 32.2, 29.2, 27.0; HRMS (ESI) *m/z* $C_{26}H_{21}NO_2$ $[M + Na]^+$ observed: 402.1442; $C_{26}H_{21}NO_2$ $[M + Na]^+$ requires: 402.1470.

12-(4-Hydroxy-3-methoxyphenyl)-9,9-dimethyl-9,10-dihydro-8*H*-benzo[*a*]xanthen-11(12*H*)-one (**4k**)

mp 199-200 °C; [Lit.[1] 164-166 °C]; IR (ATR) ν / cm^{-1} 3549, 2969, 1644, 1619, 1597, 1510, 1372, 1267, 1200, 1184, 1169, 1121, 1038, 832, 757; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.00 (d, 1H, *J* 8.0 Hz), 7.80-7.74 (m, 2H), 7.48-7.30 (m, 3H), 7.02 (s, 1H), 6.71-6.63 (m, 2H), 5.65 (s, 1H), 3.81 (s, 3H), 2.54 (s, 2H), 2.29 (s, 2H), 1.12 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 197.1, 163.7, 147.7, 146.1, 143.8, 136.9, 131.4, 128.7, 128.3, 126.9, 124.8, 123.6, 121.0, 117.7, 117.0, 114.4, 114.1, 111.3, 55.8, 50.9, 41.4, 34.1, 32.2, 29.3, 27.1; HRMS (ESI) *m/z* $C_{26}H_{24}O_4$ $[M + Na]^+$ observed: 417.1300; $C_{26}H_{24}O_4$ $[M + Na]^+$ requires: 417.1314.

12-(4-Hydroxy-3,5-dimethoxyphenyl)-9,9-dimethyl-9,10-dihydro-8*H*-benzo[*a*]xanthen-11(12*H*)-one (**4l**)

mp 205-206 °C; [Lit.[8] 189-191 °C] IR (ATR) ν / cm^{-1} 3279, 2928, 2869, 1638, 1620, 1595, 1514, 1457, 1425, 1372, 1321, 1178, 1114, 807, 749, 664; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.97 (d, 1H, *J* 8.0 Hz), 7.76-7.70 (m, 2H), 7.44-7.30 (m, 3H), 6.52 (s, 2H), 5.61 (s, 1H), 5.36 (s, 1H), 3.71 (s, 6H), 2.52 (s, 2H), 2.25 (s, 2H), 1.07 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 196.9, 163.7, 147.7, 146.7, 136.0, 133.1, 131.4, 128.8, 128.3, 126.9, 124.9, 123.6, 117.5, 116.9, 114.3, 105.3, 56.2, 50.8, 41.3, 34.4, 32.2, 29.3, 26.9; HRMS (ESI) *m/z* $C_{27}H_{26}O_5$ $[M + Na]^+$ observed: 447.1404; $C_{27}H_{26}O_5$ $[M + Na]^+$ requires: 447.1420.

9,9-Dimethyl-12-(thiophen-2-yl)-9,10-dihydro-8*H*-benzo[*a*]xanthen-11(12*H*)-one (**4m**)

mp 174-176 °C; [Lit.[2] 163-164 °C]; IR (ATR) ν / cm^{-1} 2963, 1650, 1593, 1518, 1462, 1375, 1357, 1285, 1221, 1176, 1146, 1115, 1064, 1026, 1013, 975, 958, 834, 812, 744, 699, 663; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, 1H, *J* 8.4 Hz), 7.82-7.78 (m, 2H), 7,49 (ddd, 1H, ^{3}J 8.4 Hz, ^{3}J 7.4 Hz, ^{4}J 1.2 Hz), 7.42 (ddd, 1H, ^{3}J 7.4 Hz, ^{3}J 7.4 Hz, ^{4}J 1.2 Hz), 7.31 (d, 1H, *J* 8.4 Hz), 7.01 (dd, 1H, ^{3}J 5.2 Hz, ^{4}J 1.6 Hz), 6.78-6.74 (m, 2H), 6.05 (s, 1H), 2.57 (s, 2H), 2.35 (s, 2H), 1.14 (s, 3H), 1.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 164.5, 148.4, 131.3, 129.0, 128.3, 127.1, 126.2, 125.0, 124.9, 123.9, 123.4, 117.1, 117.0, 113.7, 50.7, 41.3, 32.2, 29.3, 29.2, 27.1; HRMS (ESI) *m/z* $C_{23}H_{20}O_2S$ $[M + Na]^+$ observed: 383.1001; $C_{23}H_{20}O_2S$ $[M + Na]^+$ requires: 383.1082.

9,9-Dimethyl-12-(pyridin-2-yl)-9,10-dihydro-8*H*-benzo[*a*]xanthen-11(12*H*)-one (**4n**)

mp 179-181 °C; [Lit.[9] 179-181 °C]; IR (ATR) ν / cm^{-1} 1645, 1428, 1377, 1222, 1176, 1144, 1014, 849, 803, 756, 742, 658; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (ddd, 1H, ^3J 4.8 Hz, ^4J 1.6 Hz, ^5J 1.2 Hz), 8.19 (d, 1H, *J* 8.0 Hz), 7.78-7.73 (m, 2H), 7.56-7.55 (m, 2H), 7.46 (ddd, 1H, ^3J 8.6 Hz, ^3J 7.0 Hz, ^4J 1.2 Hz), 7.39-7.33 (m, 2H), 6.97 (dd, 1H, *J* 8.4 Hz, ^3J 4.4 Hz), 5.88 (s, 1H), 2.66 (d, 1H, *J* 16.0 Hz), 2.61 (d, 1H, *J* 16.0 Hz), 2.34 (d, 1H, *J* 16.0 Hz), 2.24 (d, 1H, *J* 16.0 Hz), 1.13 (s, 3H), 1.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 165.1, 162.8, 147.7, 131.5, 131.4, 128.9, 128.4, 127.0, 124.8, 123.6, 121.4, 117.4, 112.6, 50.9, 41.4, 37.6, 32.3, 29.5, 27.1; HRMS (ESI) *m/z* $C_{24}H_{21}NO_2$ $[M + H]^+$ observed: 356.1629; $C_{24}H_{21}NO_2$ $[M + Na]^+$ requires: 356.1650.

9,9-Dimethyl-12-(5-nitrofuran-2-yl)-9,10-dihydro-8*H*-benzo[*a*]xanthen-11(12*H*)-one (**4o**)

mp 194-196 °C; IR (ATR) ν / cm^{-1} 2965, 1644, 1595, 1538, 1497, 1391, 1372, 1353, 1286, 1222, 1171, 1016, 975, 950, 812, 743, 735, 665; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, 1H, *J* 8.4 Hz), 7.85-7.81 (m, 2H), 7.58 (t, 1H, *J* 7.4 Hz), 7.47 (t, 1H, *J* 7.4 Hz), 7.32 (d, 1H, *J* 9.2 Hz), 7.12 (d, 1H, *J* 3.6 Hz), 6.46 (d, 1H, *J* 3.6 Hz), 5.92 (s, 1H), 2.68 (d, 1H, *J* 17.6 Hz), 2.62 (d, 1H, *J* 17.6 Hz), 2.41-2.33 (m, 2H), 1.17 (s, 3H), 1.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 166.4, 159.4, 147.9, 131.4, 131.0, 130.0, 128.8, 127.6, 125.4, 123.6, 117.4, 112.8, 112.6, 110.3, 109.1, 50.7, 41.4, 32.4, 29.4, 29.1, 27.2; HRMS (ESI) *m/z* $C_{23}H_{19}NO_5$ $[M + Na]^+$ observed: 412.1154; $C_{23}H_{19}NO_5$ $[M + Na]^+$ requires: 412.1161.

References

1. Li, J.; Lu, L.; Su, W.; *Tetrahedron Lett*. **2010**, *51*, 2434.
2. Rama, V.; Kanagara, K.; Pitchumani, K.; *Tetrahedron Lett.* **2012**, *53*, 1018.
3. Zhang, Z.-H.; Zhang, P.; Peng, Y.; Yang, S. H.; Wang, H. J.; Deng, J.; *J. Chem. Sci.* **2010**, *122*, 427.
4. Mo, L.-P.; Chen, H.-L.; *J. Chin. Chem. Soc*. **2010**, *57*, 157.
5. Khazaei, A.; Zolfigol, M. A.; Moosavi-Zare, A. R.; Zare, A.; Khojasteh, M.; Asgari, Z.; Khakyzadeh, V.; Khalafi-Nezhad, A.; *Catal. Commun.* **2012**, *20*, 54.
6. Tabatabaeian, K.; Khorshidi, A.; Mamaghani, M.; Dadashi, A.; Jalali, M. K.; *Can. J. Chem.* **2011**, *89*, 623.
7. Shirini, F.; Khaligh, N. G.; *Dyes Pigm.* **2012**, *95*, 789.
8. Iniyavan, P.; Sarveswari, S.; Vijayakumar, V.; *Res. Chem. Intermed.* **2015**, *41*, 7413.
9. Naidu, K. R. M.; Krishna, B. S.; Kumar, M. A.; Arulselvan, P.; Khalivulla, S. I.; Lasekan, O.; *Molecules* **2012**, *17*, 7543.

Table S1. Electronic nuclear energy, entropy, and total energy of reagents, intermediates, and products of the Scheme 1, for structures in the gaseous phase and without intermolecular interactions

Compound	E_{elect} / Hartree	S / (cal mol^{-1} K^{-1})	G_{total} / Hartree
1	–343.43350953	78.237	–343.345551
5	–343.77034961	78.577	–343.668383
2	–458.21069783	85.497	–458.080157
6(*RR*)/**6**(*SS*)	–802.00927345	119.064	–801.751280
6(*RS*)/**6**(*SR*)	–802.00608185	119.858	–801.748682
7(*RR*)/**7**(*SS*)	–802.19224398	122.395	–801.923617
7(*RS*)/**7**(*SR*)	–802.19600028	121.483	–801.927014
7(*RS*)/**7**(*SR*)	–802.18310871	123.758	–801.915177
8	–725.97601200	114.115	–725.747697
9	–725.97051987	113.723	–725.742029
3	–459.65702757	92.298	–459.488427
10(*RR*)/**10**(*SS*)	–1185.64222292	159.169	–1185.219512
10(*RS*)/**10**(*SR*)	–1185.64057052	159.534	–1185.217637
11(*RRR*)/**11**(*SSS*)	–1185.62683514	153.194	–1185.200008
11(*RRS*)/**11**(*SSR*)	–1185.63766615	159.205	–1185.214516
11(*RSR*)/**11**(*SRS*)	–1185.63038838	157.947	–1185.206107
11(*RSS*)/**11**(*SRR*)	–1185.62059066	159.179	–1185.219516
12(*RRR*)/**12**(*SSS*)	–1185.65473113	167.478	–1185.237566
12(*RRS*)/**12**(*SSR*)	–1185.61336051	153.972	–1185.187313
12(*RSR*)/**12**(*SRS*)	–1185.65037566	164.316	–1185.231176
12(*RSS*)/**12**(*SRR*)	–1185.65276349	165.508	–1185.234639
4(*R*)/**4**(*S*)	–1109.27718129	147.430	–1108.892093
H_2O	–76.01074652	44.987	–76.005366
H_3O^+	–76.28933842	48.251	–76.271703

Table S2. Electronic nuclear energy, entropy, and total energy of reagents, intermediates, and products of the Scheme 2, for structures in the gaseous phase and without intermolecular interactions

Compound	E_{elect} / Hartree	S / (cal mol^{-1} K^{-1})	G_{total} / Hartree
1	–343.43350953	78.237	–343.345551
5	–343.77034961	78.577	–343.668383
2	–458.21069783	85.497	–458.080157
13(*RR*)/**13**(*SS*)	–801.98843491	120.340	–801.731797
13(*RS*)/**13**(*SR*)	–801.99019428	121.009	–801.733947
14(*RR*)/**14**(*SS*)	–802.19164214	121.946	–801.923138
14(*RS*)/**14**(*SR*)	–802.19814540	122.692	–801.930406
15	–725.98218290	113.930	–725.754004
16	–725.97065189	115.240	–725.743349
3	–459.65702757	92.298	–459.488427
17(*RR*)/**17**(*SS*)	–1185.64723838	159.904	–1185.225088
17(*RS*)/**17**(*SR*)	–1185.64211859	159.600	–1185.219436
18(*RRR*)/**18**(*SSS*)	–1185.62990388	154.791	–1185.204187
18(*RRS*)/**18**(*SSR*)	–1185.64211857	159.598	–1185.219435
18(*RSR*)/**18**(*SRS*)	–1185.63641958	158.312	–1185.212540
18(*RSS*)/**18**(*SRR*)	–1185.63937867	161.594	–1185.217622
19(*RRR*)/**19**(*SSS*)	–1185.65552026	164.707	–1185.236694
19(*RSS*)/**19**(*SSR*)	–1185.65460163	165.579	–1185.236684
19(*RSR*)/**19**(*SRS*)	–1185.65648070	167.509	–1185.239495
19(*RSS*)/**19**(*SRR*)	–1185.64922236	168.478	–1185.232887
20(*R*)/**20**(*S*)	–1109.27716783	149.395	–1108.893327

Table S3. Changes in energy of each reaction step described on Scheme 1, based on data shown in Table S1, only one enantiomer is shown in each pair of ones

Step	Reaction	ΔE_{elect} / (kcal mol^{-1})	ΔS / (cal mol^{-1} K^{-1})	ΔG_{total} / (kcal mol^{-1})
1	**1** → **5**	–36.55	–2.92	–35.45
2	**5** + **2** → **6**(*RR*)	–17.71	–45.01	–1.72
2	**5** + **2** → **6**(*RS*)	–15.71	–44.22	–0.09
3	**6**(*RR*) → **7**(*RR*)	60.00	0.07	58.99
3	**6**(*RS*) → **7**(*RS*)	55.23	0.64	62.65
4	**7**(*RR*) → **8**	–45.87	39.97	–60.10
4	**7**(*RR*) → **9**	–42.43	39.58	–56.55
4	**7**(*RS*) → **8**	–51.61	38.61	–65.40
4	**7**(*RS*) → **9**	–48.16	38.22	–61.84
5	**8** + **3** → **10**(*RR*)	–5.76	–47.24	10.42
5	**8** + **3** → **10**(*RS*)	–4.73	–46.88	11.60
5	**9** + **3** → **10**(*RR*)	–9.21	–46.85	6.87
5	**9** + **3** → **10**(*RS*)	–8.17	–46.49	8.04
6	**10**(*RR*) → **11**(*RRR*)	9.66	–5.98	12.24
6	**10**(*RR*) → **11**(*RRS*)	2.86	0.04	3.13
6	**10**(*RS*) → **11**(*RSS*)	12.54	–0.36	–1.18
6	**10**(*RS*) → **11**(*RSR*)	6.39	–1.59	7.24
7	**11**(*RRR*) → **12**(*RRR*)	–17.50	14.28	–23.57
7	**11**(*RRS*) → **12**(*RRS*)	15.25	–5.23	17.07
7	**11**(*RSR*) → **12**(*RSR*)	–12.54	6.37	–15.73
7	**11**(*RSS*) → **12**(*RSS*)	–20.19	6.33	–9.49
8	**12**(*RRR*) → **4**(*R*)	55.35	28.20	46.29
8	**12**(*RRS*) → **4**(*R*)	29.39	41.71	14.76
8	**12**(*RSR*) → **4**(*R*)	52.62	31.37	42.28
8	**12**(*RSS*) → **4**(*R*)	54.12	30.17	44.45

Table S4. Changes in energy of each reaction step described on Scheme 2, based on data shown in Table S2

Step	Reaction	ΔE_{elect} / (kcal mol^{-1})	ΔS / (cal mol^{-1} K^{-1})	ΔG_{total} / (kcal mol^{-1})
1	**1** → **5**	–36.55	–2.92	–35.45
2	**2** + **3** → **13**(*RR*)	–4.64	–43.73	10.51
2	**2** + **3** → **13**(*RS*)	–5.74	–42.55	9.16
3	**13**(*RR*) → **14**(*RR*)	47.30	–1.66	47.06
3	**13**(*RS*) → **14**(*RS*)	44.33	–1.58	43.85
4	**14**(*RR*) → **15**	–50.12	40.24	–64.36
4	**14**(*RR*) → **16**	–42.89	41.55	–57.68
4	**14**(*RS*) → **15**	–46.04	39.49	–59.80
4	**14**(*RS*) → **16**	–38.81	40.80	–53.12
5	**15** + **3** → **17**(*RR*)	–5.04	–46.32	10.88
5	**15** + **3** → **17**(*RS*)	–1.82	–46.63	14.43
5	**16** + **3** → **17**(*RR*)	–12.27	–47.63	4.20
5	**16** + **3** → **17**(*RS*)	–9.06	–47.94	7.74
6	**17**(*RR*) → **18**(*RRR*)	10.88	–5.11	13.12
6	**17**(*RR*) → **18**(*RRS*)	3.21	–0.31	3.55
6	**17**(*RS*) → **18**(*RSS*)	1.72	1.99	1.14
6	**17**(*RS*) → **18**(*RSR*)	3.58	–1.29	4.33
7	**18**(*RRR*) → **19**(*RRR*)	–16.07	9.92	–20.40
7	**18**(*RRS*) → **19**(*RRS*)	–7.83	5.98	–10.82
7	**18**(*RSR*) → **19**(*RSR*)	–12.59	9.20	–16.91
7	**18**(*RSS*) → **19**(*RSS*)	–6.18	6.88	–9.58
8	**19**(*RRR*) → **20**(*R*)	55.86	32.94	44.97
8	**19**(*RRS*) → **20**(*R*)	55.28	32.07	44.96
8	**19**(*RSR*) → **20**(*R*)	56.46	30.14	46.73
8	**19**(*RSS*) → **20**(*R*)	51.90	29.17	42.58

Table S5. Electronic (E_{elect}), entropy (S) and Gibbs free energy (G_{total}) of the optimized compounds at LC-ωPBE/6-311++G(d,p) level of theory

Compound	E_{elect} / Hartree	S / (cal mol^{-1} K^{-1})	G_{total} / Hartree
25 °C			
5	–345.732635019	80.542	–345.638653019
2	–460.886681498	87.864	–460.765671498
6	–806.656781353	123.714	–806.416850353
13	–806.637386015	127.229	–806.400126015
TS-1	–806.640134897	123.978	–806.405818897
TS-2	–806.623670106	125.058	–806.386925106
130 °C			
5	–345.732635019	213.780	–345.638653
2	–460.886681498	263.830	–460.765671
6	–806.656781353	482.264	–806.400831
13	–806.637386015	483.614	–806.416850
TS-1	–806.640134897	479.662	–806.386925
TS-2	–806.623670106	480.059	–806.400126

Coordinates of chemical species calculated at LC-ωPBE/6-311++G(d,p) level of theory and energetic data

Cartesian coordinates of the structures calculated at LC-ωPBE/6-311++G(d,p) level of theory are given hereafter, and also the correspondent energetic data. The total Gibbs free energy (G_{total}) is the sum of the electronic energy (E_{elect}) with the thermal correction for the Gibbs free energy, which includes the zero point energy (ZPE) and depends on the temperature. This correction takes in account vibrational, translational and rotational motions in gas phase for the studied molecules.

Structure 5

E_{elect} = -345.732635019 Hartree

G_{total} at 25 °C = -345.638653019 Hartree

G_{total} at 130 °C = -345.638653 Hartree

Cartesian coordinate

C	0.098646	0.000000	-0.003574
C	0.072244	0.000000	1.383362
C	1.248104	0.000000	2.137998
C	2.460933	0.000000	1.503005
C	2.505542	0.000000	0.092977
C	1.312170	0.000000	-0.652918
C	3.702483	0.000000	-0.640319
O	4.893949	0.000000	-0.184525
H	3.678605	0.000000	-1.729241

H	3.364991	0.000000	2.105660
H	1.196985	0.000000	3.220001
H	-0.883646	0.000000	1.897043
H	-0.825478	0.000000	-0.568462
H	1.353156	0.000000	-1.737615
H	4.954698	0.000000	0.784449

Structure 2

E_{elect} = -460.886681498 Hartree

G_{total} at 25 °C = -460.765671498 Hartree

G_{total} at 130 °C = -460.765671Hartree

Cartesian coordinate

C	-1.203792	0.000000	-0.743898
C	0.010825	0.000000	-0.021622
C	1.236926	0.000000	-0.718828
C	1.209794	0.000000	-2.133446
C	0.031231	0.000000	-2.812827
C	-1.193407	0.000000	-2.106316
C	2.450691	0.000000	0.010479
C	2.445238	0.000000	1.371625
C	1.218172	0.000000	2.071799
C	0.036383	0.000000	1.396265
O	-2.381926	0.000000	-2.769078
H	0.023946	0.000000	-3.899447
H	2.148936	0.000000	-2.677591
H	3.388645	0.000000	-0.536376
H	3.379135	0.000000	1.922736
H	1.221768	0.000000	3.156573
H	-0.905425	0.000000	1.935620
H	-2.152456	0.000000	-0.219208
H	-2.226963	0.000000	-3.715971

Structure 6

E_{elect} = -806.637386015 Hartree

G_{total} at 25 °C = -806.400126015 Hartree

G_{total} at 130 °C = -806.416850 Hartree

Cartesian coordinate

C	-17.991785	-0.055460	7.880906
C	-17.211363	0.705758	8.738706
C	-15.839751	0.779388	8.552793
C	-15.245787	0.094479	7.506777
C	-16.023251	-0.661196	6.640896

C	-17.391961	-0.736467	6.826253
C	-19.482665	-0.123998	8.073136
O	-20.195238	0.148847	6.894082
C	-19.933264	-1.567874	8.544856
C	-19.453014	-1.765543	9.949409
C	-20.311428	-1.440711	11.009784
C	-21.670416	-1.098250	10.722593
C	-22.224666	-1.172639	9.478803
C	-21.404114	-1.580409	8.419120
C	-19.862138	-1.522103	12.332031
C	-18.575958	-1.937647	12.593966
C	-17.735686	-2.273210	11.539164
C	-18.163456	-2.179463	10.223432
O	-21.861793	-1.948603	7.271395
H	-23.285416	-1.007538	9.324658
H	-22.309250	-0.825406	11.558847
H	-20.535492	-1.268813	13.144391
H	-18.223121	-2.012382	13.615648
H	-16.728043	-2.616883	11.745773
H	-17.489531	-2.436276	9.413823
H	-19.503539	-2.285991	7.844896
H	-19.781930	0.570415	8.868330
H	-17.999389	-1.317322	6.137856
H	-15.559962	-1.189184	5.814960
H	-14.173468	0.155347	7.357972
H	-15.235267	1.380535	9.222632
H	-17.676016	1.249329	9.555922
H	-19.745384	0.846578	6.408347
H	-22.822229	-1.846648	7.195262

Structure 13

E_{elect} = -806.656781353 Hartree

G_{total} at 25 °C = -806.416850353 Hartree

G_{total} at 130 °C = -806.400831Hartree

Cartesian coordinate

C	-16.344571	1.086621	7.074601
C	-14.968462	1.344457	7.212257
C	-14.067873	1.168972	6.096266
C	-14.566064	0.735028	4.916666
C	-15.997072	0.466265	4.686818
C	-16.852448	0.655478	5.891837
C	-12.661363	1.436641	6.261933

C	-12.186484	1.851119	7.451471
C	-13.087194	2.021812	8.544420
C	-14.423676	1.781482	8.437013
O	-18.152750	0.439106	5.807138
H	-16.315520	1.219459	3.946432
H	-13.906014	0.577404	4.068031
H	-12.005243	1.296557	5.409753
H	-11.132491	2.056434	7.592357
H	-12.687825	2.356019	9.496768
H	-15.078702	1.920988	9.288793
H	-17.011527	1.220134	7.917514
H	-18.424687	0.108927	4.944314
C	-16.034188	-0.423942	1.566062
C	-15.386079	-0.491645	0.346055
C	-14.178143	-1.164289	0.240657
C	-13.624573	-1.767005	1.356767
C	-14.269409	-1.693053	2.582570
C	-15.476967	-1.018589	2.691865
C	-16.202320	-0.917719	4.016254
O	-15.786890	-1.845245	4.981409
H	-17.275496	-1.038212	3.806389
H	-13.833241	-2.168350	3.455230
H	-12.686035	-2.303819	1.275039
H	-13.673495	-1.226316	-0.716823
H	-15.830196	-0.030135	-0.528614
H	-16.992842	0.085335	1.632418
H	-15.937630	-2.740278	4.662051

Structure TS1

E_{elect} = -806.640134897 Hartree

G_{total} at 25 °C = -806.405818897 Hartree

G_{total} at 130 °C = -806.386925 Hartree

Cartesian coordinate

C	-0.658116	-0.403281	0.244671
C	-0.341069	-0.133524	1.586989
C	0.980655	0.211473	1.923999
C	1.958555	0.293892	0.912153
C	1.629356	0.028464	-0.387631
C	0.312416	-0.329351	-0.719429
C	1.301693	0.430764	3.295130
C	0.380924	0.289403	4.284512
C	-0.946781	-0.062947	3.946250

C	-1.333152	-0.162857	2.619478
C	-1.885849	2.065807	2.678076
O	-2.398547	2.291565	3.850656
O	-1.890408	-0.234239	4.871127
C	-2.679601	2.126208	1.468171
C	-2.042470	2.505674	0.288553
C	-2.781287	2.662391	-0.870868
C	-4.143271	2.418846	-0.857822
C	-4.780562	2.017123	0.312178
C	-4.054840	1.873511	1.473193
H	0.656917	0.426756	5.325079
H	2.322438	0.697187	3.551495
H	2.976575	0.557234	1.179894
H	2.384775	0.080465	-1.163109
H	0.065185	-0.556842	-1.750610
H	-1.671378	-0.689819	-0.016951
H	-2.326512	-0.540334	2.401676
H	-0.820310	2.273899	2.632256
H	-4.567335	1.534561	2.370776
H	-5.845620	1.817520	0.309855
H	-4.721187	2.539642	-1.767425
H	-2.291743	2.976329	-1.785163
H	-0.974562	2.696729	0.286262
H	-3.366246	2.290048	3.839235
H	-1.545004	-0.092664	5.759425

Structure TS2

E_{elect} = -806.623670106 Hartree

G_{total} at 25 °C = -806.386925106 Hartree

G_{total} at 130 °C = -806.400126 Hartree

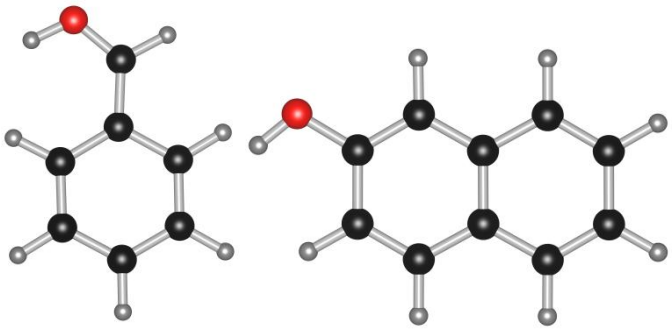
Cartesian coordinate

C	0.120259	0.115450	-0.185653
C	0.122762	-0.026765	1.197050
C	1.321235	-0.060092	1.888177
C	2.517124	0.048488	1.199682
C	2.519981	0.189634	-0.181876
C	1.326458	0.220145	-0.874297
C	-1.180440	0.208275	-0.869642
O	-1.318799	0.924069	-1.962830
C	-1.693687	-1.719846	-1.299623
C	-0.735651	-1.951158	-2.296503
C	-1.003878	-1.651198	-3.620088

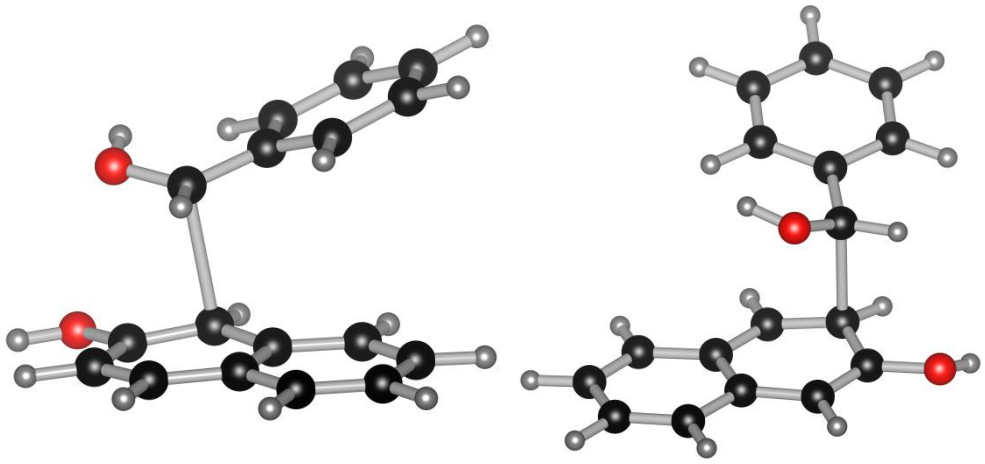
C	-2.322843	-1.230859	-3.970858
C	-3.336911	-1.171868	-2.992678
C	-3.048215	-1.453308	-1.694289
C	-0.003759	-1.764388	-4.635353
C	-0.297384	-1.456256	-5.919542
C	-1.607116	-1.023770	-6.261992
C	-2.587536	-0.915446	-5.326457
O	-4.010539	-1.338112	-0.762616
H	-1.513402	-2.122506	-0.305990
H	0.252401	-2.296403	-2.008536
H	0.987311	-2.107883	-4.356844
H	0.455425	-1.542834	-6.694088
H	-1.826489	-0.782703	-7.296594
H	-3.584029	-0.593318	-5.606509
H	-4.351169	-0.909790	-3.269342
H	-3.819281	-1.870358	0.015865
H	-2.053730	0.299414	-0.228079
H	1.355191	0.313377	-1.957851
H	3.458475	0.276308	-0.716965
H	3.456503	0.026520	1.740494
H	1.320183	-0.161170	2.967184
H	-0.815519	-0.092634	1.739857
H	-0.475955	1.075616	-2.409429

Table S6. Crystal data and refinement parameters of xanthenone **4e** derivatives reported in this study

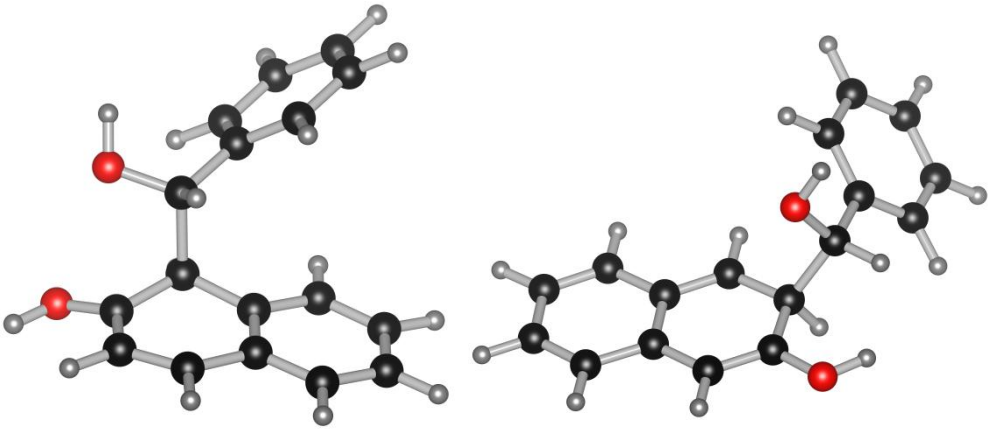
Structural formula		$C_{25}H_{22}O_3$
fw / (g mol^{-1})		370.43
Cryst. syst.		monoclinic
Space group		*C*2/c
Z / *Z'*		8/1
T / K		298(2)
Unit cell	*a* / Å	26.011(5)
	b / Å	6.8970(10)
	c / Å	21.557(5)
	β / degree	97.902(10)
V / $Å^3$		3830.6(13)
Calcd. density / (mg m^{-3})		1.285
Absorp. coeff. / mm^{-1}		0.083
θ-Range / degree		3.06 to 26.39
Index ranges	h	–31 to 32
	k	–8 to 8
	l	–26 to 26
Data collected		7430
Unique reflections		3918
Unique reflections with I > 2σ (I)		2820
Symmetry factor (R_{int})		0.0224
Completeness to θ_{max} / %		99.7
F (000)		1568
Parameters refined		256
Goodness-of-fit on F^2		1.050
R1 factor for I > 2σ (I)		0.0497
wR2 factor for all data		0.1355
Δρ max/min / (e$Å^{-3}$)		0.233/–0.231
CCDC deposit number		1002986



5 2



TS1 Imaginary wave number: 181*i* cm^{-1} TS2 Imaginary wave number: 321*i* cm^{-1}



6 13

Figure S1. Optimized structures at LC-ωPBE/6-311++G(d,p) level of theory. Legend atoms: C (black), O (red) and H (grey).

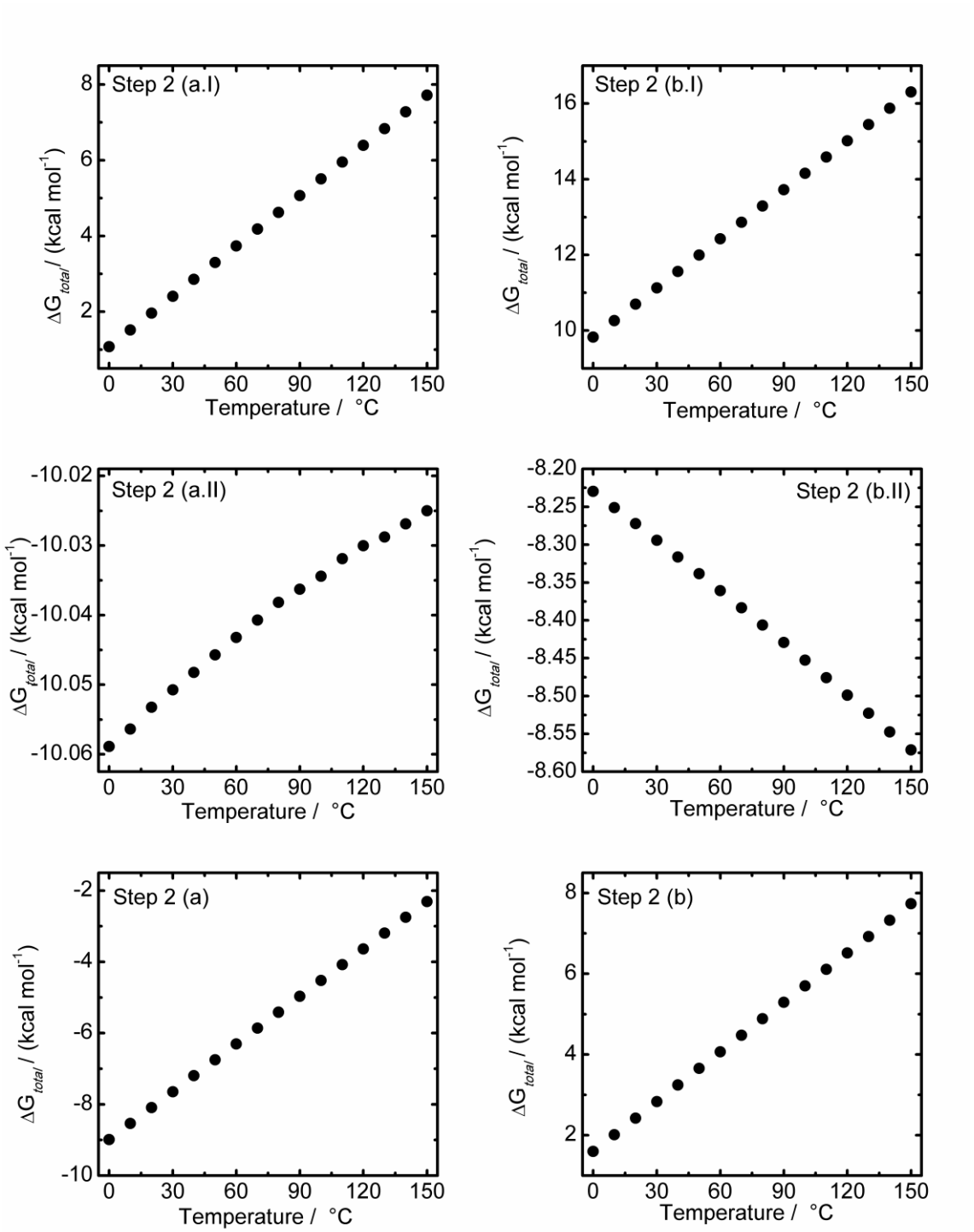
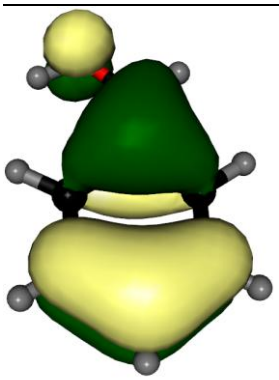


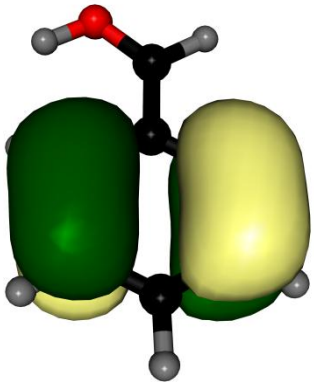
Figure S2. Variation of Gibbs free energy (ΔG_{total}) in function of temperature for the studied steps at LC-ωPBE/6-311++G(d,p) level of theory.

Compound: **5**



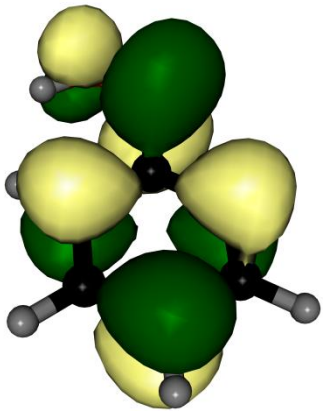
HOMO – 1

E = –0.56518 Hartree



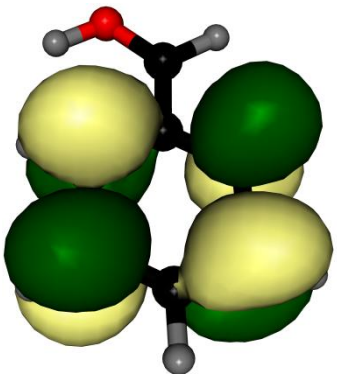
HOMO

E = –0.55492 Hartree



LUMO

E = –0.22307 Hartree

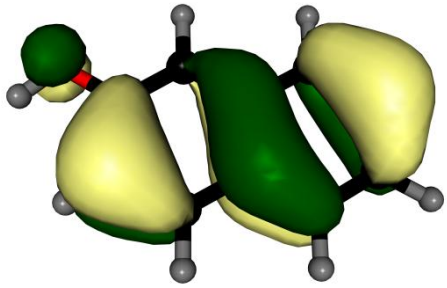


LUMO + 1

E = –0.11112 Hartree

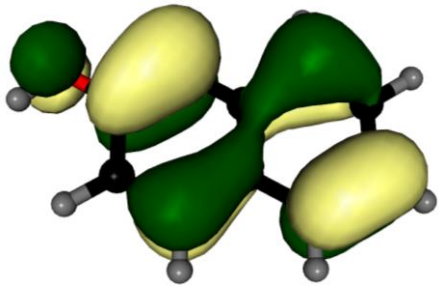
Figure S3. Frontier orbitals of all species sketched in Scheme 3.

Compound: **2**



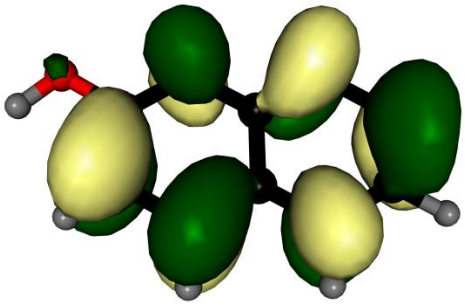
HOMO – 1

E = –0.34090 Hartree



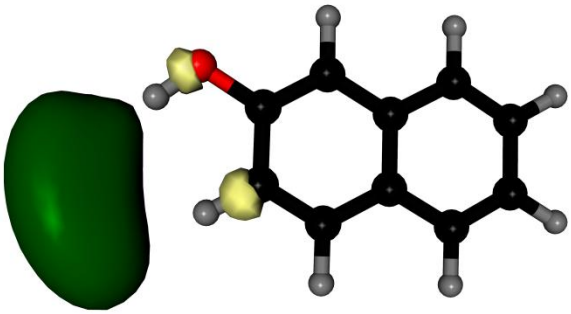
HOMO

E = –0.31031 Hartree



LUMO

E = 0.02934 Hartree

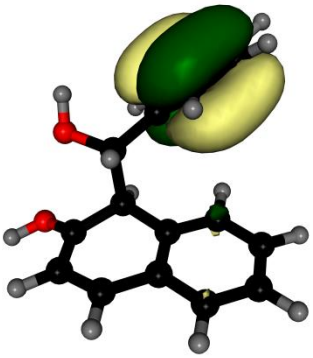


LUMO + 1

E = –0.03268 Hartree

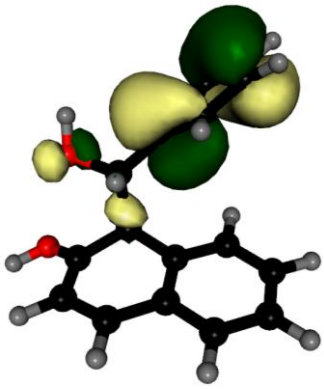
Figure S3. Frontier orbitals of all species sketched in Scheme 3 (cont.).

Compound: **6**



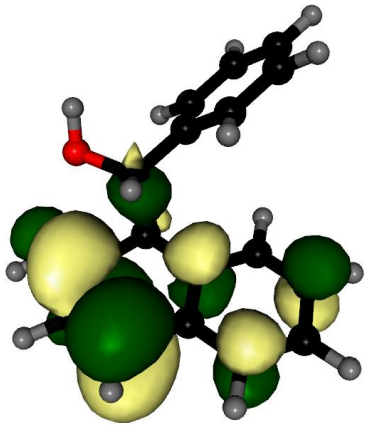
HOMO – 1

E = –0.47301 Hartree



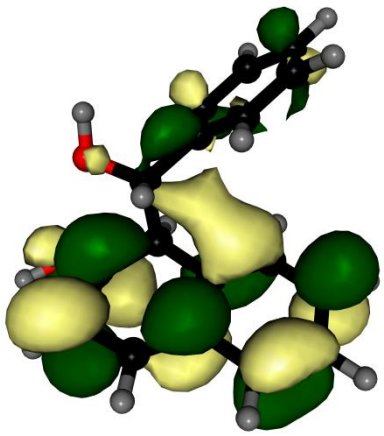
HOMO

E = –0.47075 Hartree



LUMO

E = –0.18861 Hartree

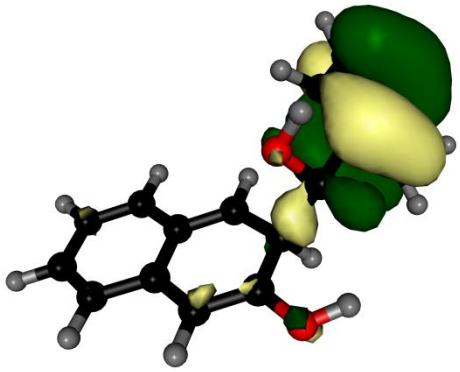


LUMO + 1

E = –0.08611 Hartree

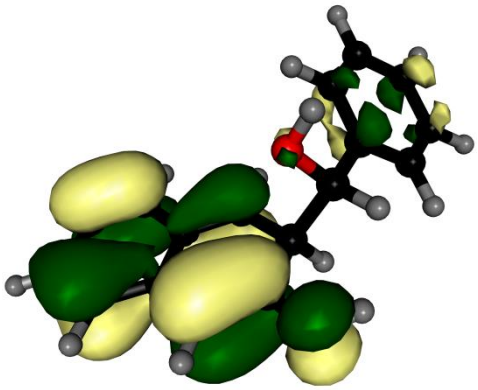
Figure S3. Frontier orbitals of all species sketched in Scheme 3 (cont.).

Compound: **13**



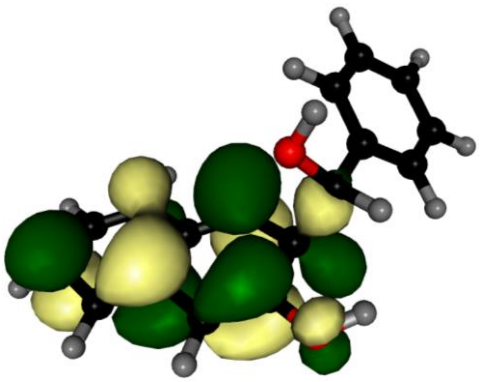
HOMO – 1

E = –0.47529 Hartree



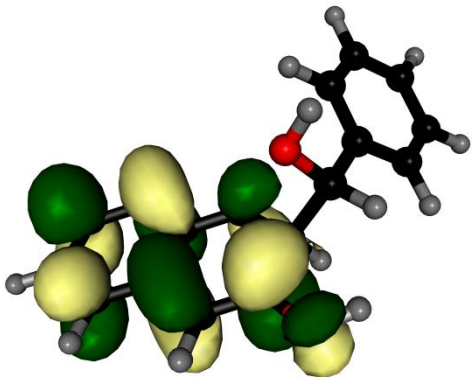
HOMO

E = –0.46650 Hartree



LUMO

E = –0.19926 Hartree

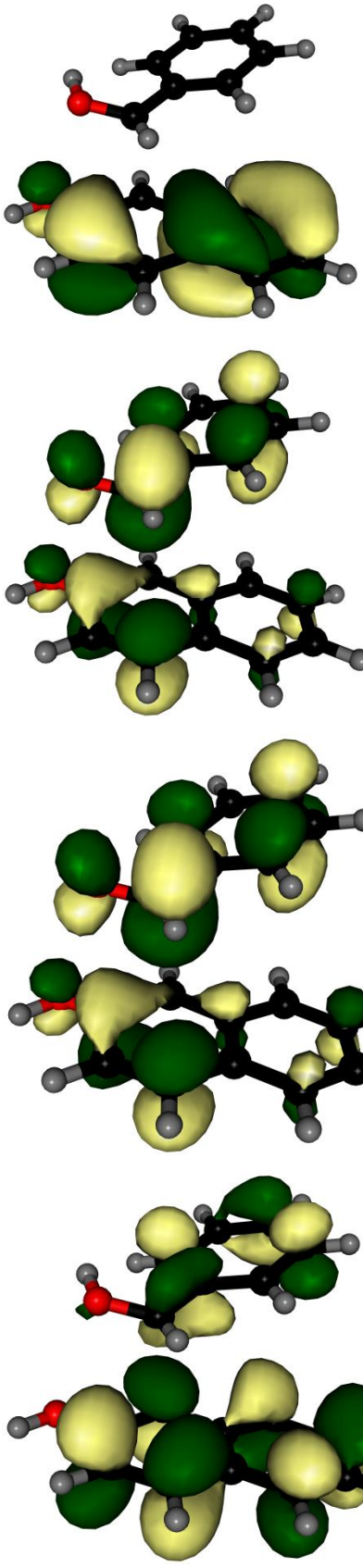


LUMO + 1

E = –0.09553 Hartree

Figure S3. Frontier orbitals of all species sketched in Scheme 3 (cont.).

Compound: **TS1**



HOMO – 1

E = –0.48191 Hartree

HOMO

E = –0.45144 Hartree

LUMO

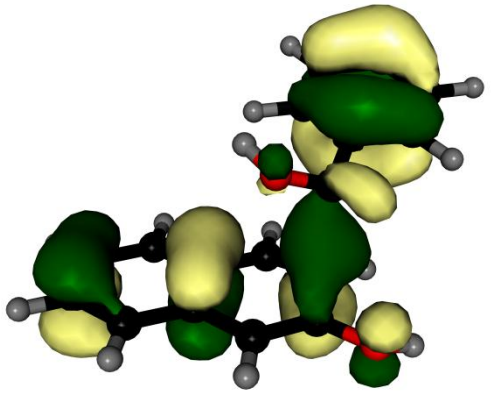
E = –0.18082 Hartree

LUMO + 1

E = –0.09809 Hartree

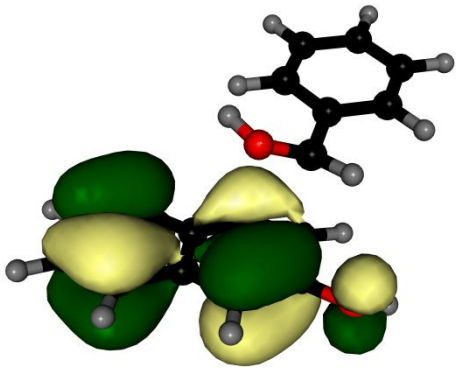
Figure S3. Frontier orbitals of all species sketched in Scheme 3 (cont.).

Compound: **TS2**



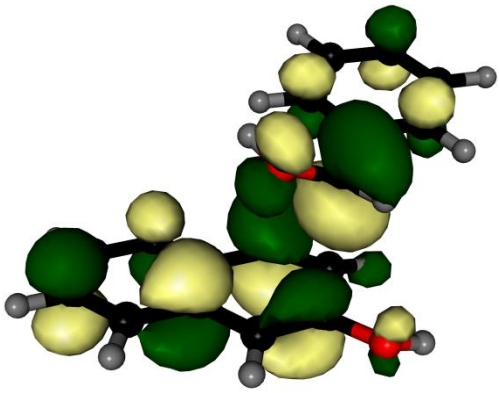
HOMO – 1

E = –0.48191 Hartree



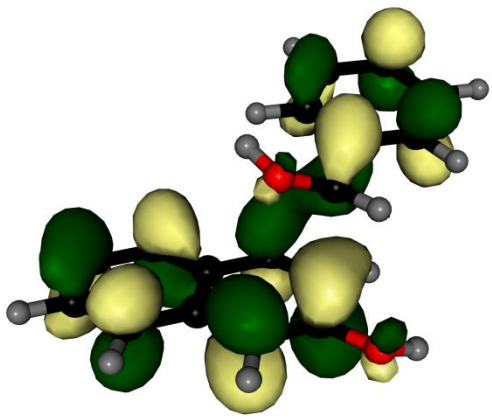
HOMO

E = –0.45144 Hartree



LUMO

E = –0.18082 Hartree



LUMO + 1

E = –0.09809 Hartree

Figure S3. Frontier orbitals of all species sketched in Scheme 3 (cont.).

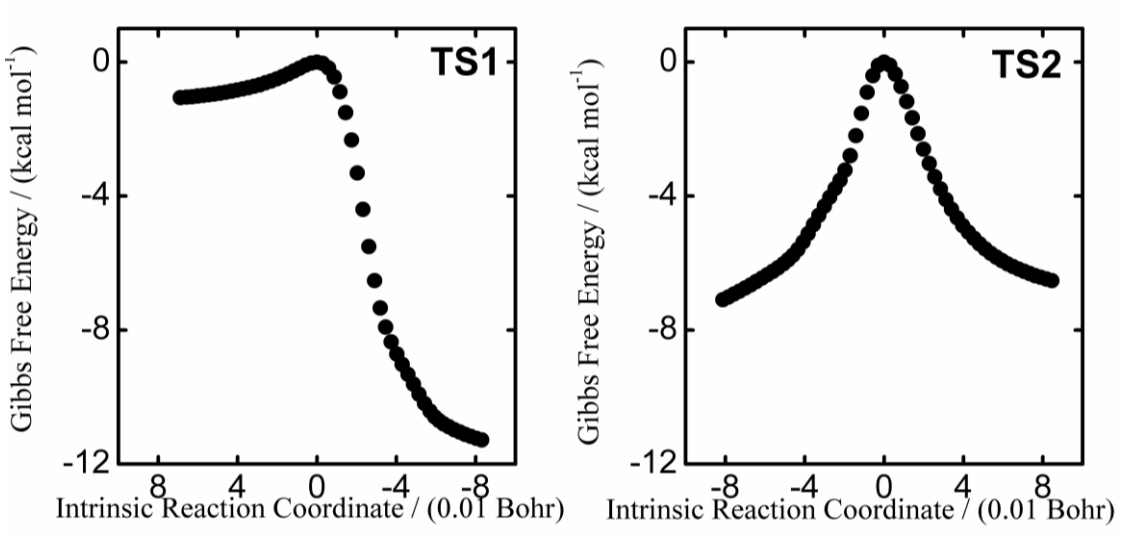


Figure S4. Gibbs free energy in function of intrinsic reaction coordinate for **TS1** and **TS2** at LC-ωPBE/6-311++G(d,p) level of theory.

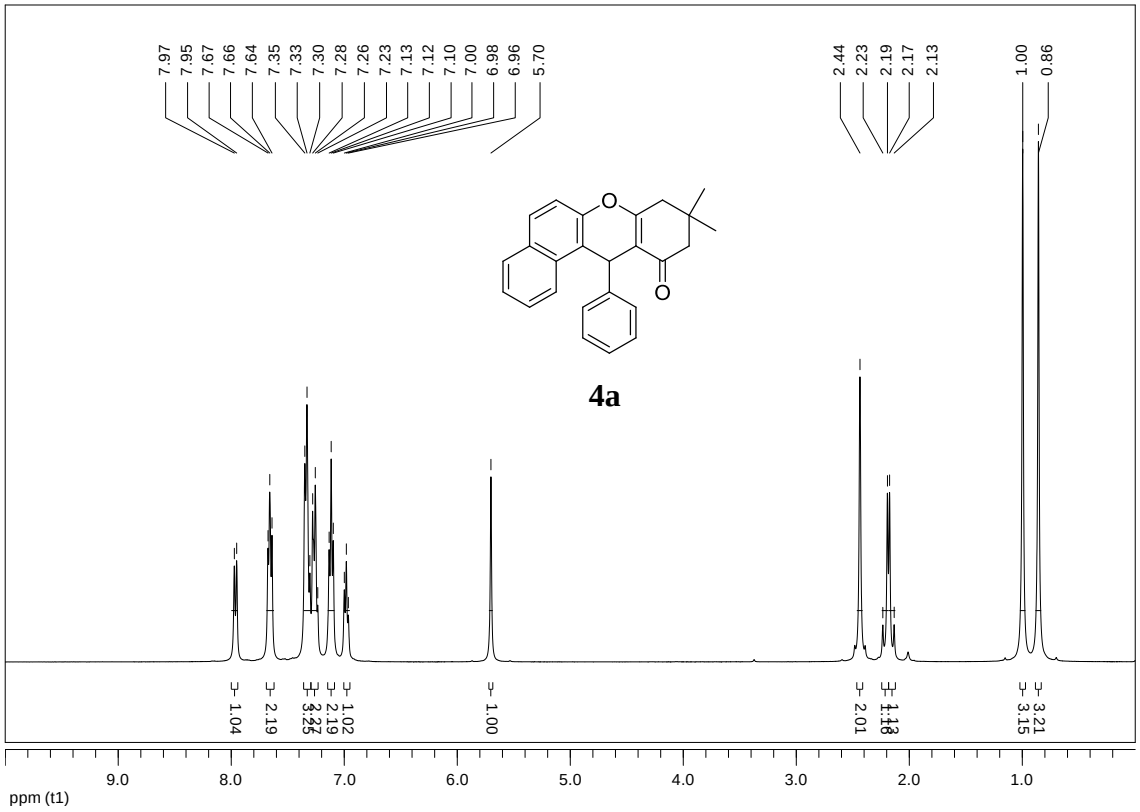


Figure S5. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4a**.

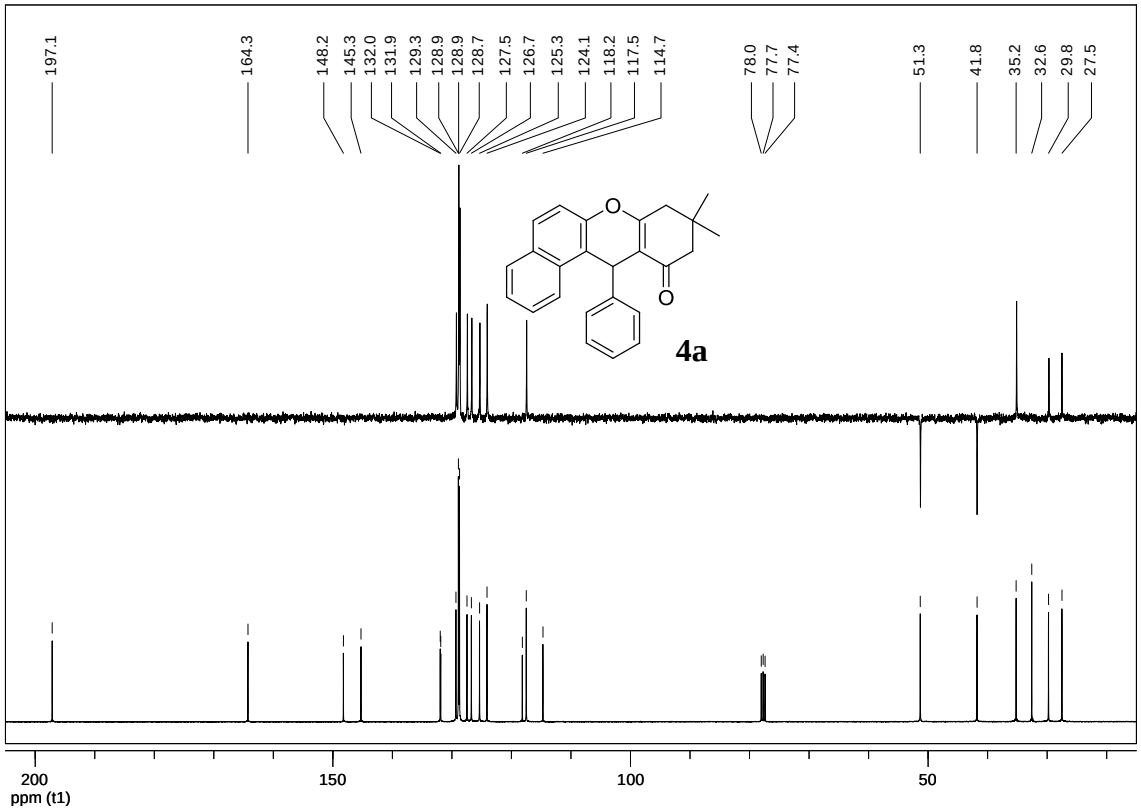


Figure S6. ^{13}C NMR spectrum (down) and DEPT 135 (up) (100 MHz, $CDCl_3$) of compound **4a**.

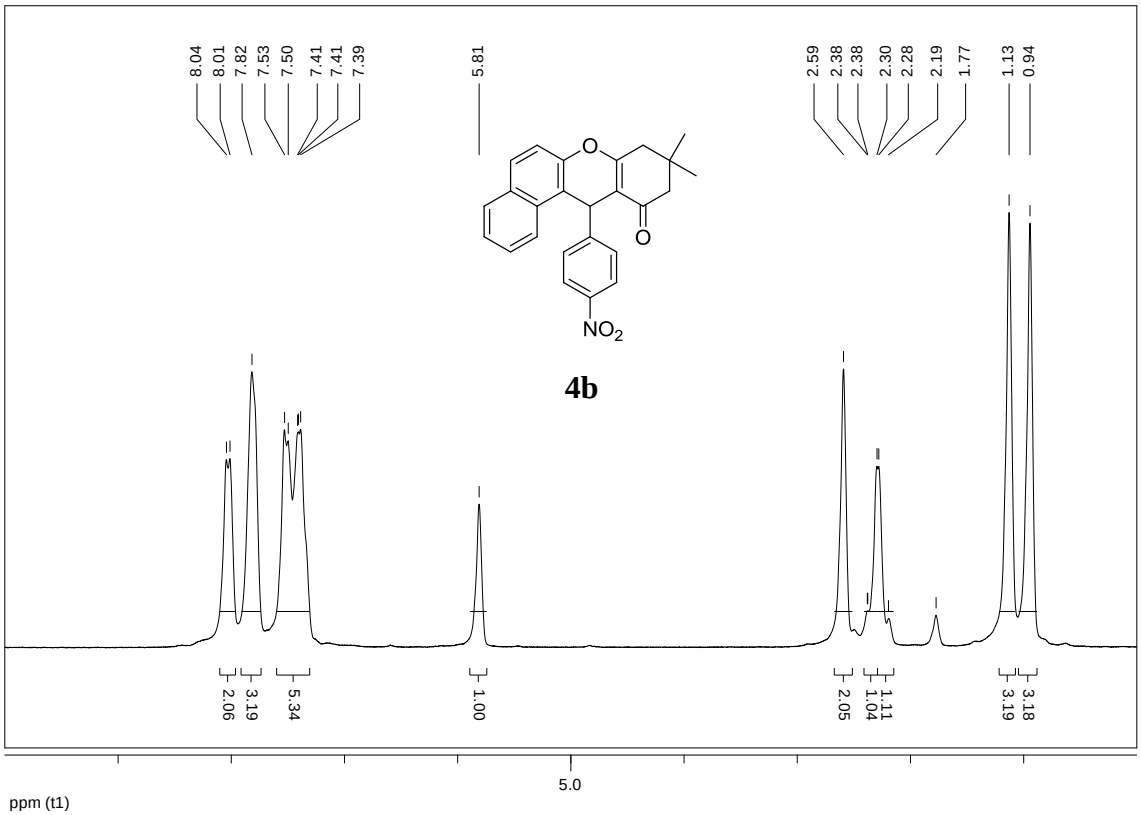


Figure S7. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of compound **4b**.

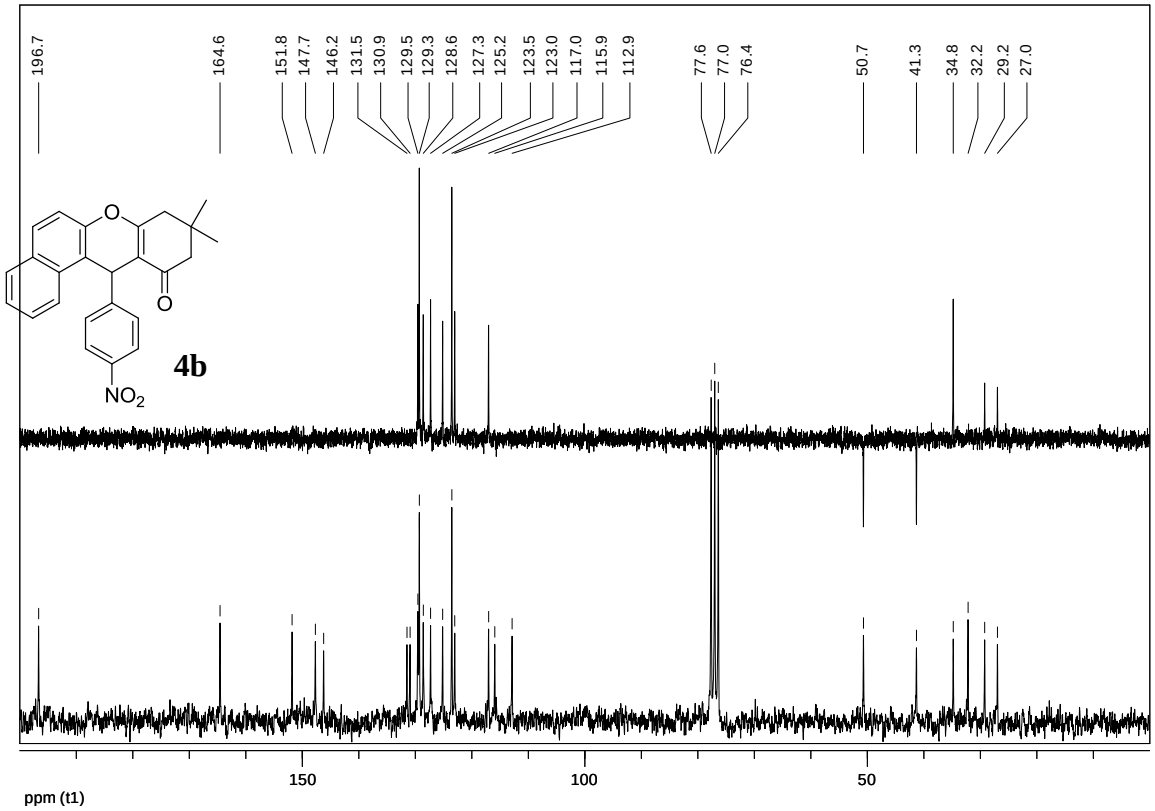


Figure S8. ^{13}C NMR spectrum (down) and DEPT 135 (up) (50 MHz, $CDCl_3$) of compound **4b**.

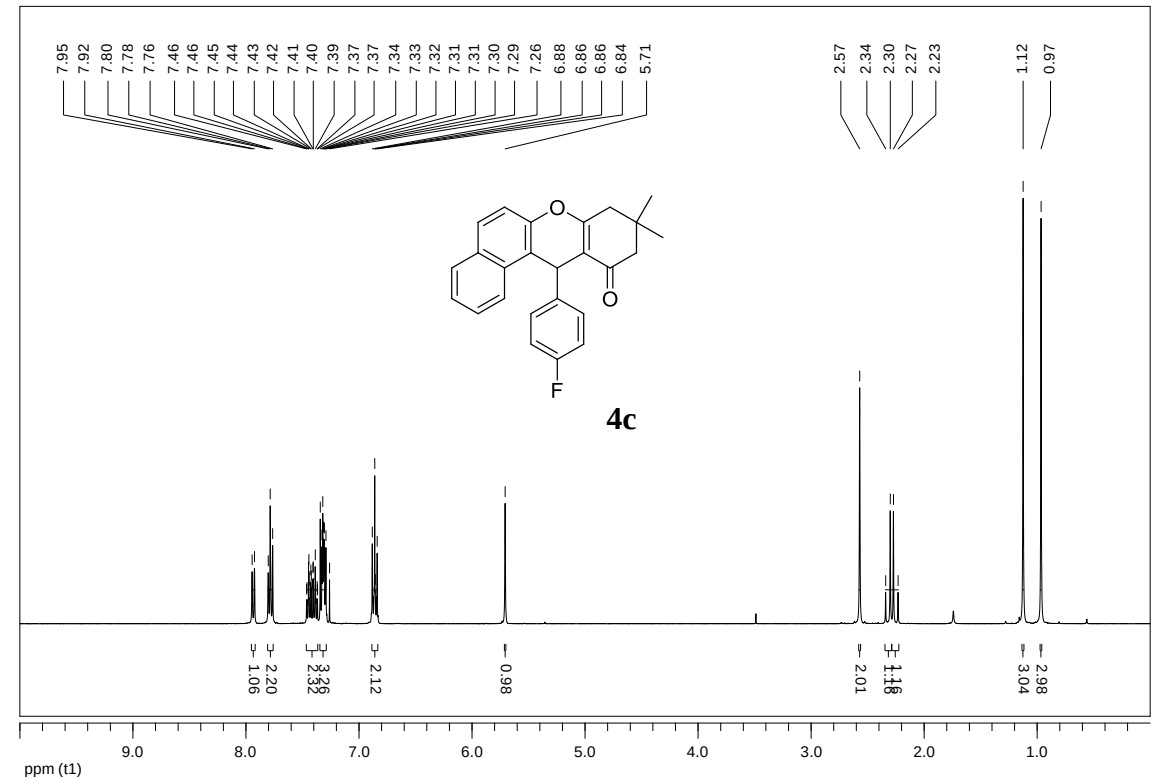


Figure S9. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4c**.

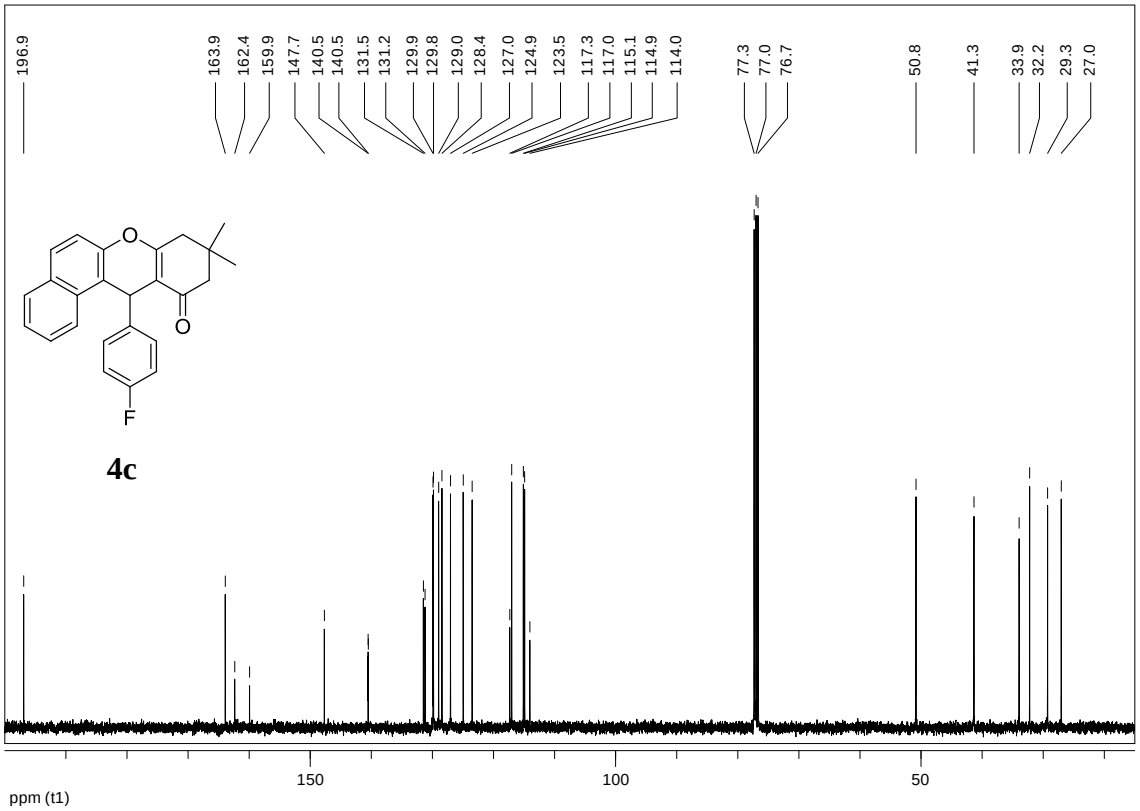


Figure S10. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4c**.

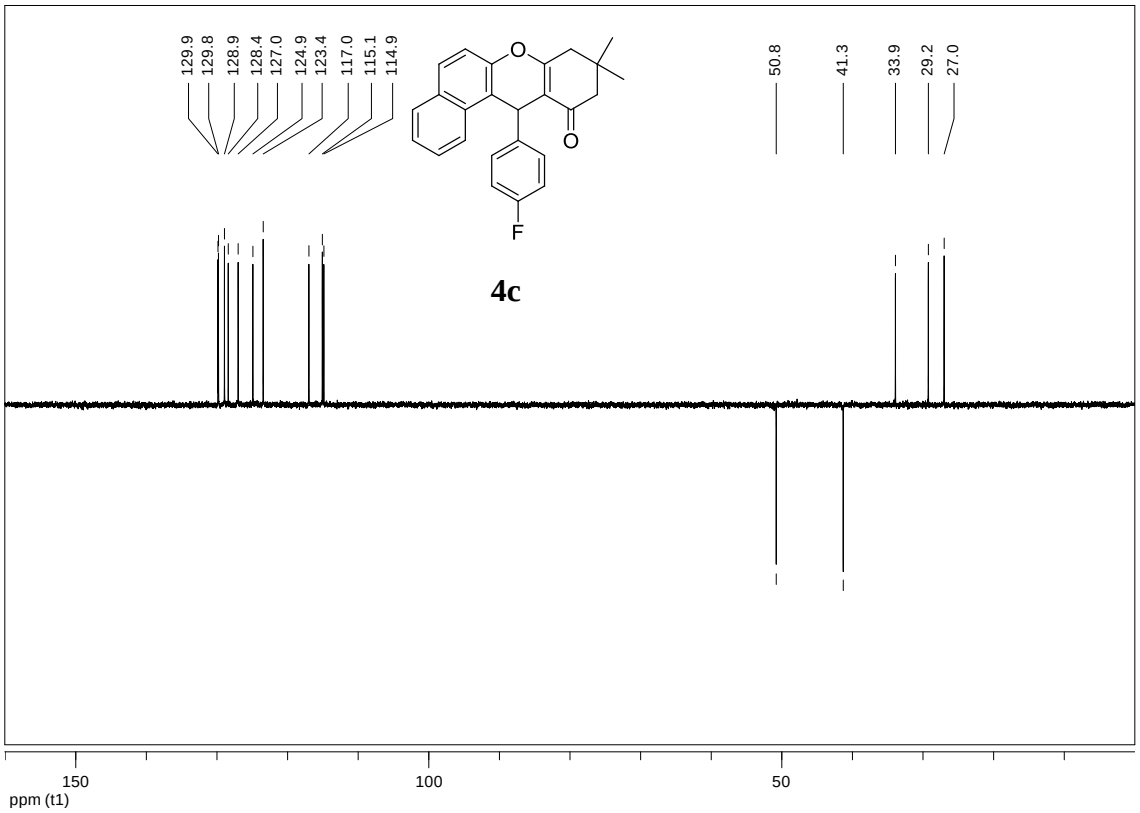


Figure S11. DEPT 135 spectrum (100 MHz, $CDCl_3$) of compound **4c**.

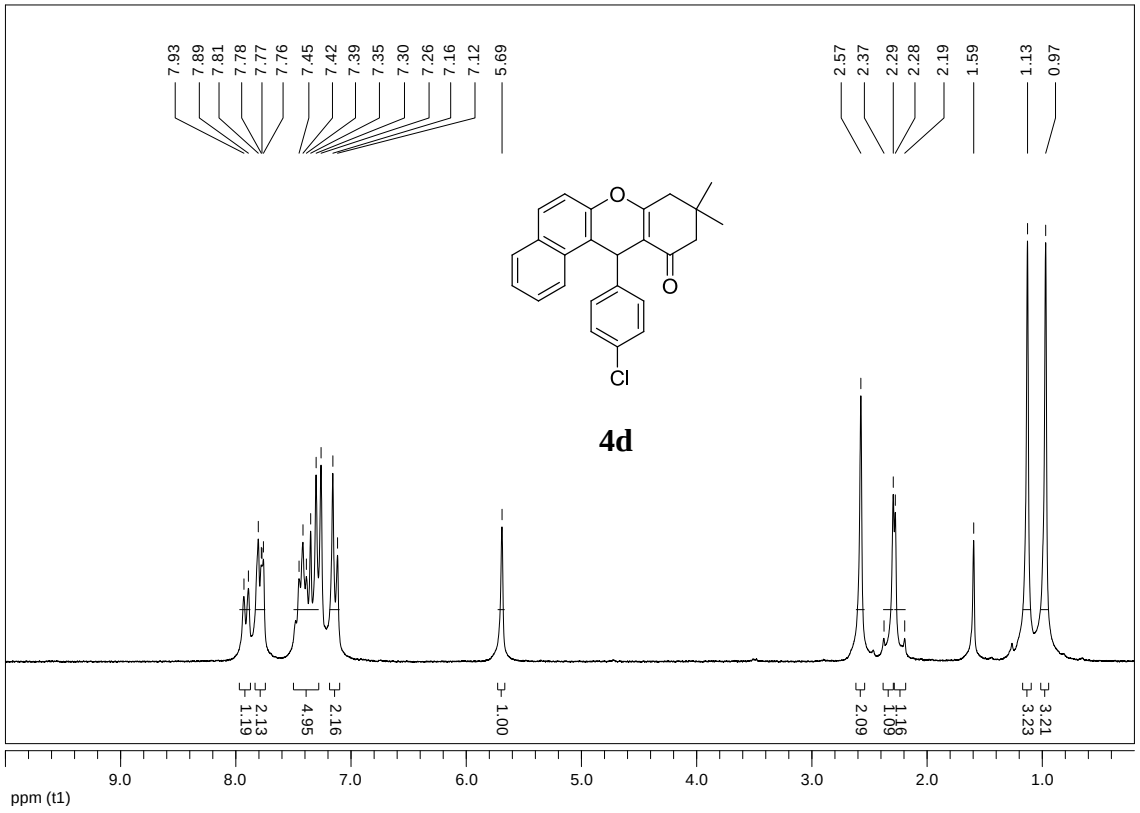


Figure S12. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of compound **4d**.

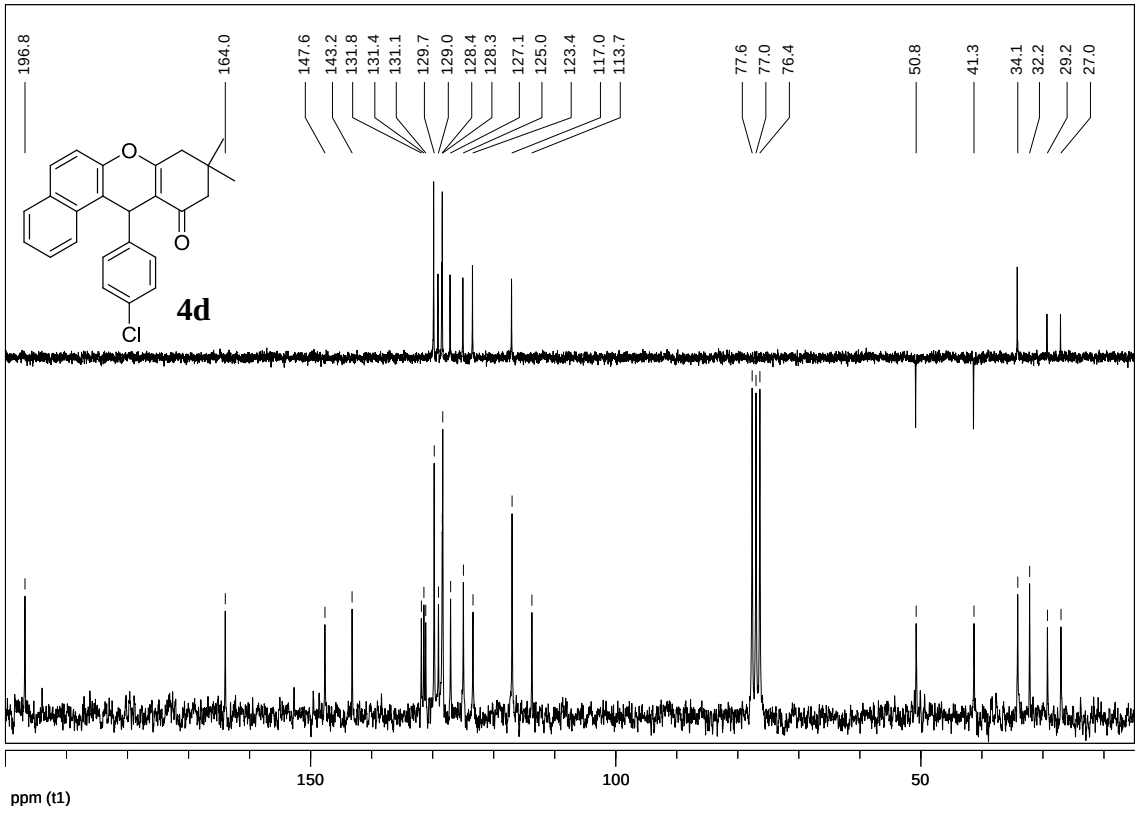


Figure S13. ^{13}C NMR spectrum (down) and DEPT 135 (up) (50 MHz, $CDCl_3$) of compound **4d**.

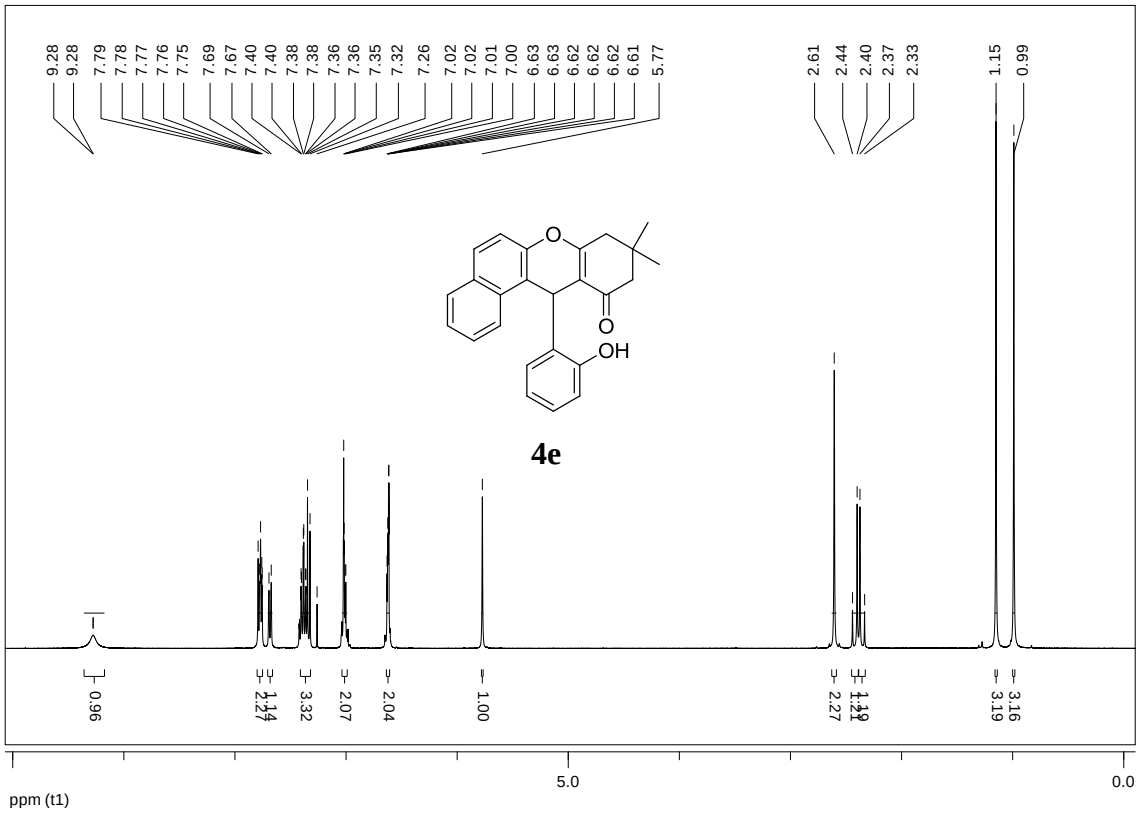


Figure S14. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4e**.

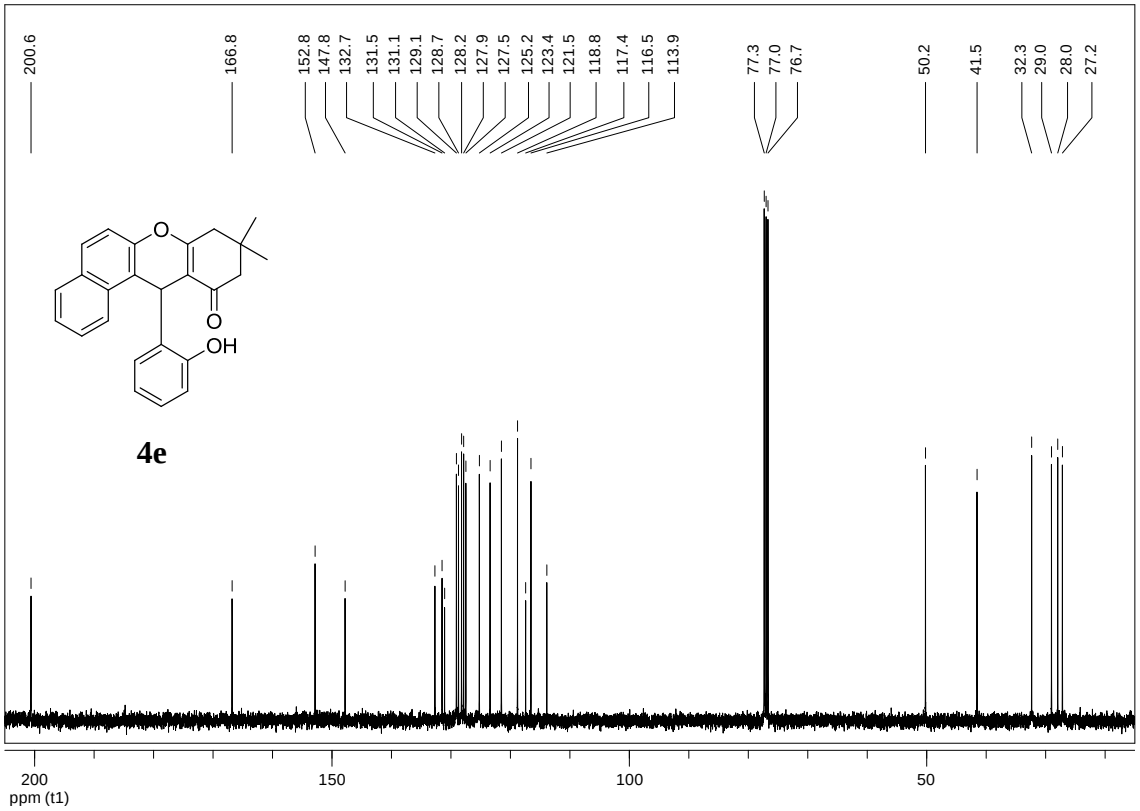


Figure S15. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4e**.

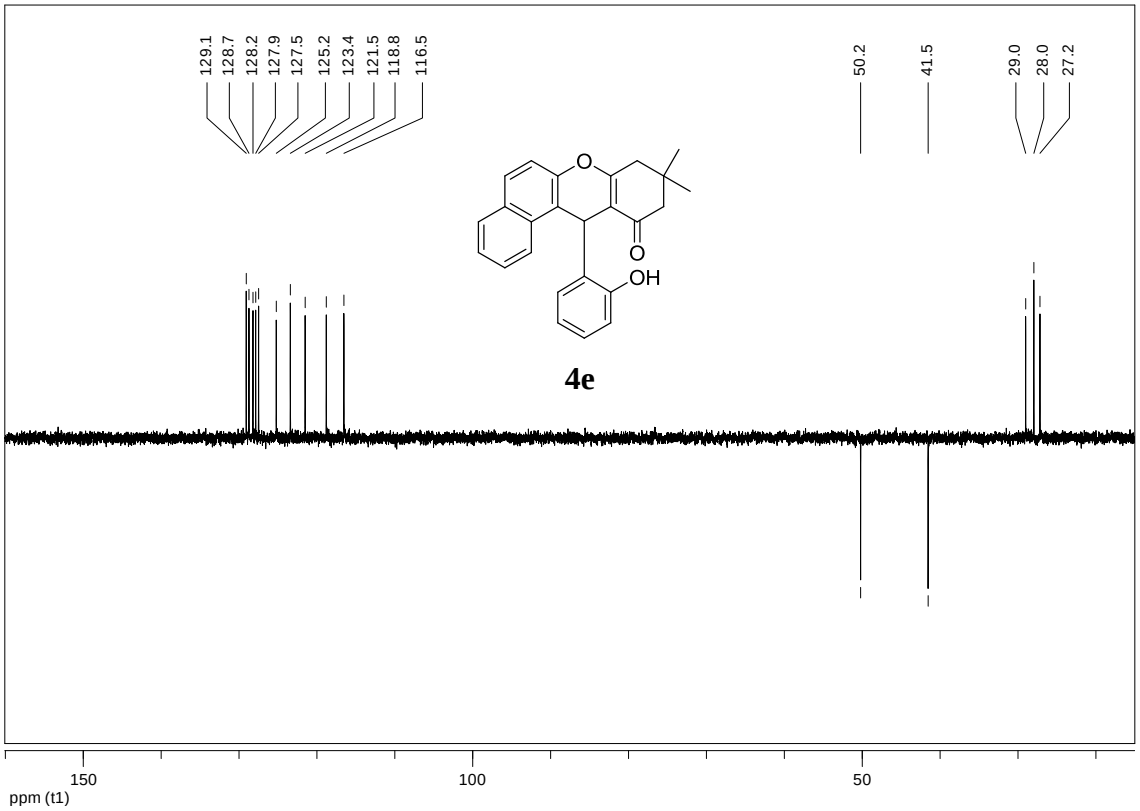


Figure S16. DEPT 135 spectrum (100 MHz, $CDCl_3$) of compound **4e**.

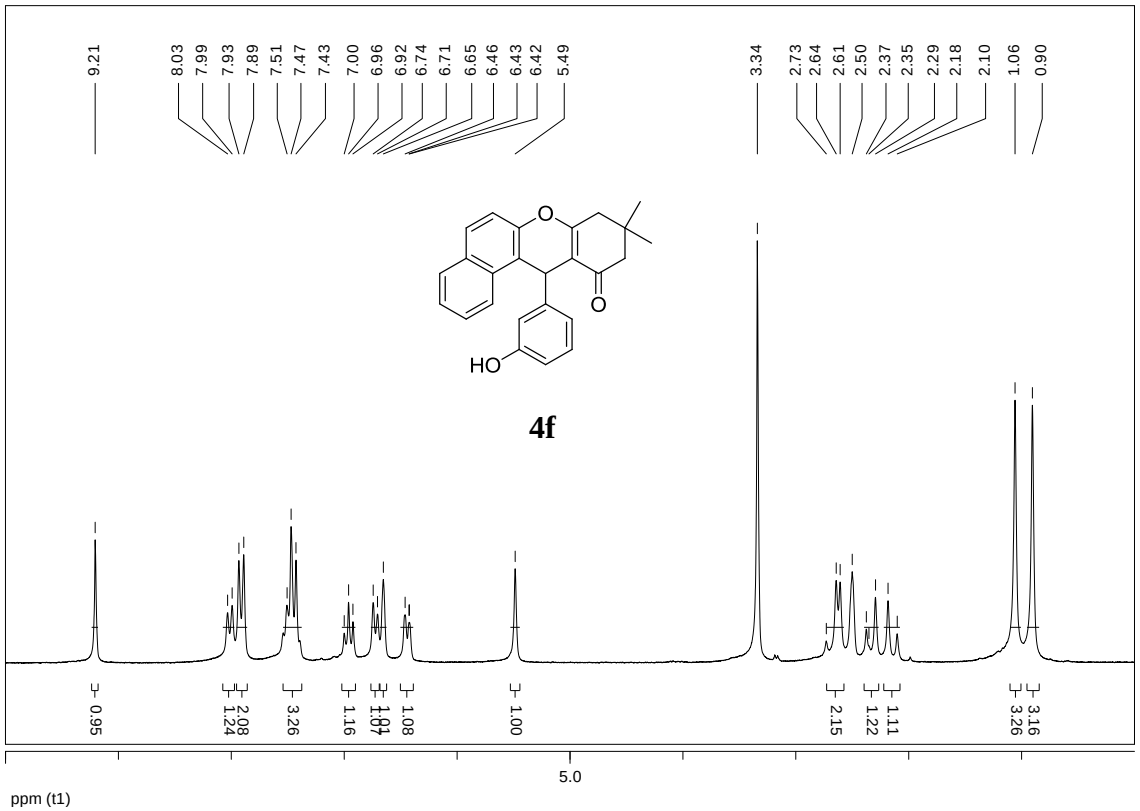


Figure S17. ^{1}H NMR spectrum (200 MHz, DMSO-d_6) of compound **4f**.

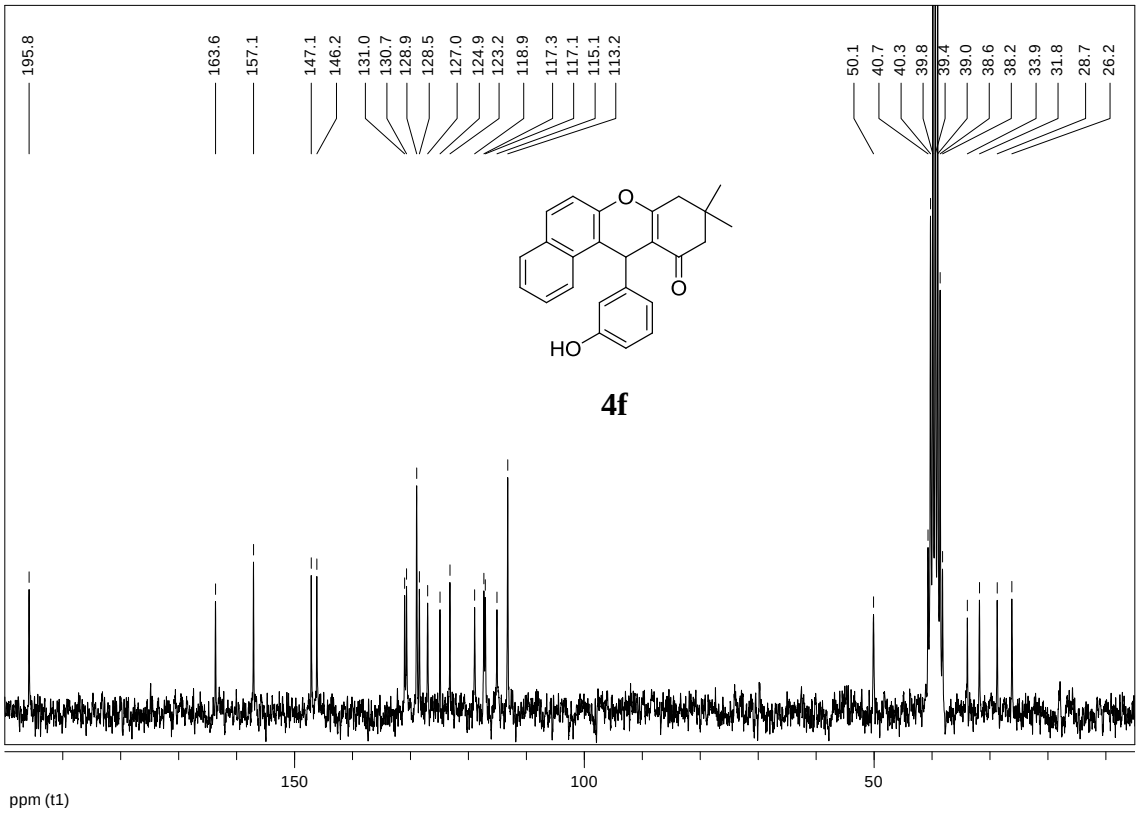


Figure S18. ^{13}C NMR spectrum (50 MHz, DMSO-d_6) of compound **4f**.

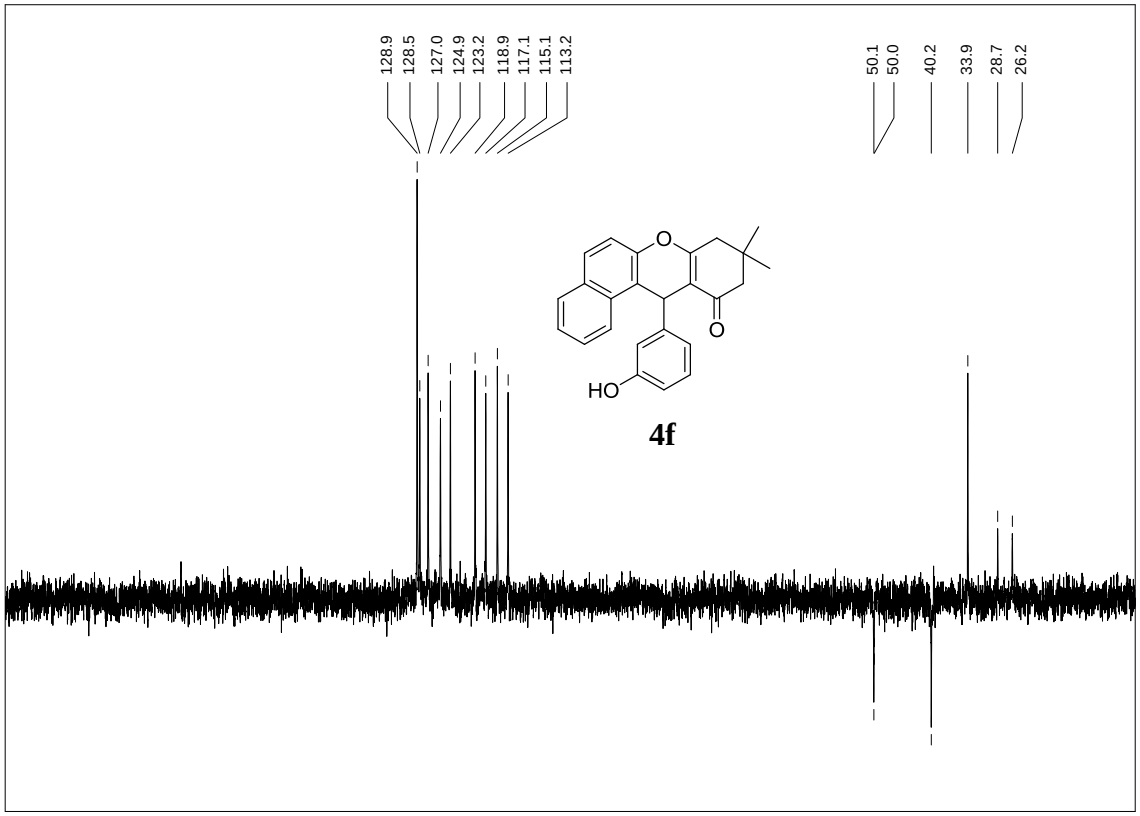


Figure S19. DEPT 135 spectrum (50 MHz, DMSO-d_6) of compound **4f**.

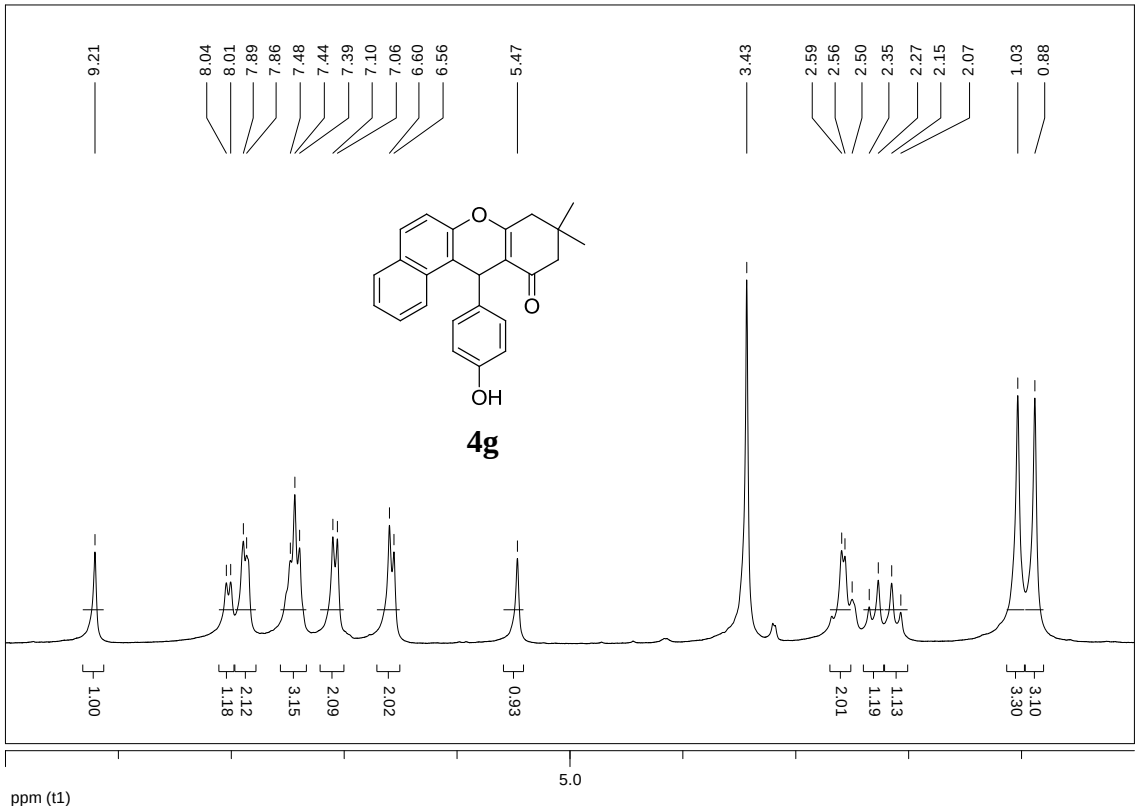


Figure S20. ^{1}H NMR spectrum (200 MHz, DMSO-d_6) of compound **4g**.

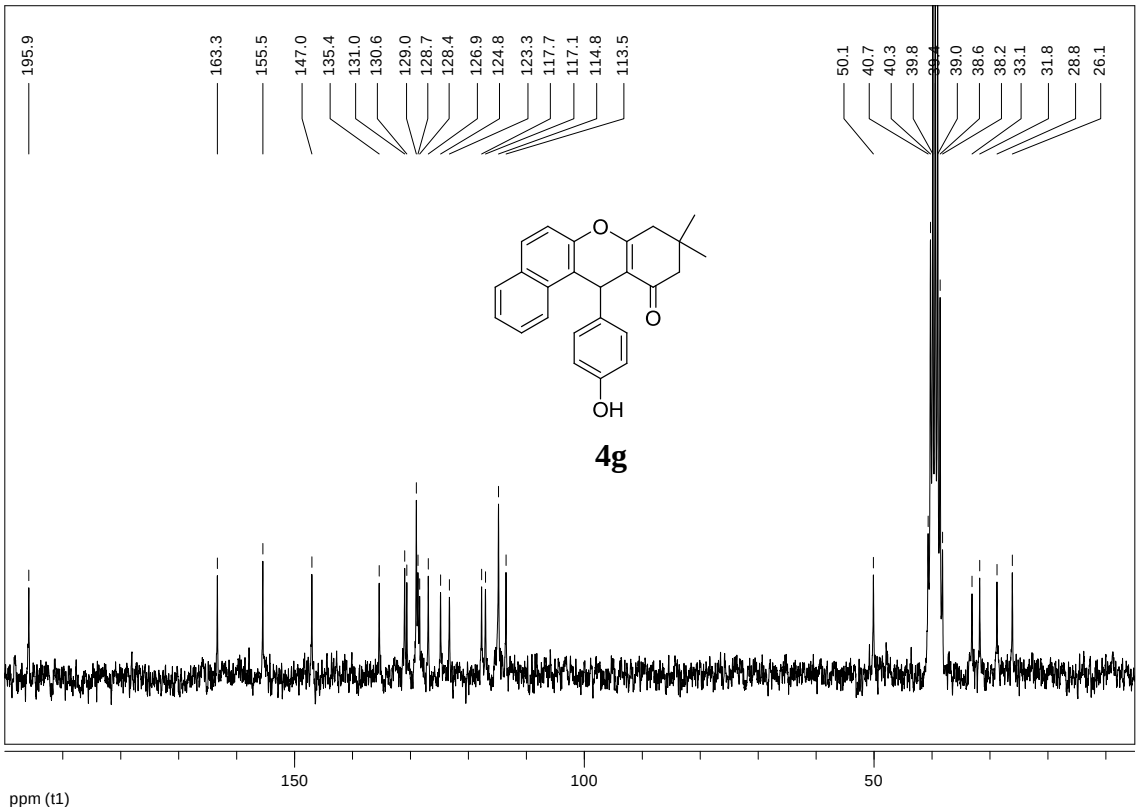


Figure S21. ^{13}C NMR spectrum (50 MHz, DMSO-d_6) of compound **4g**.

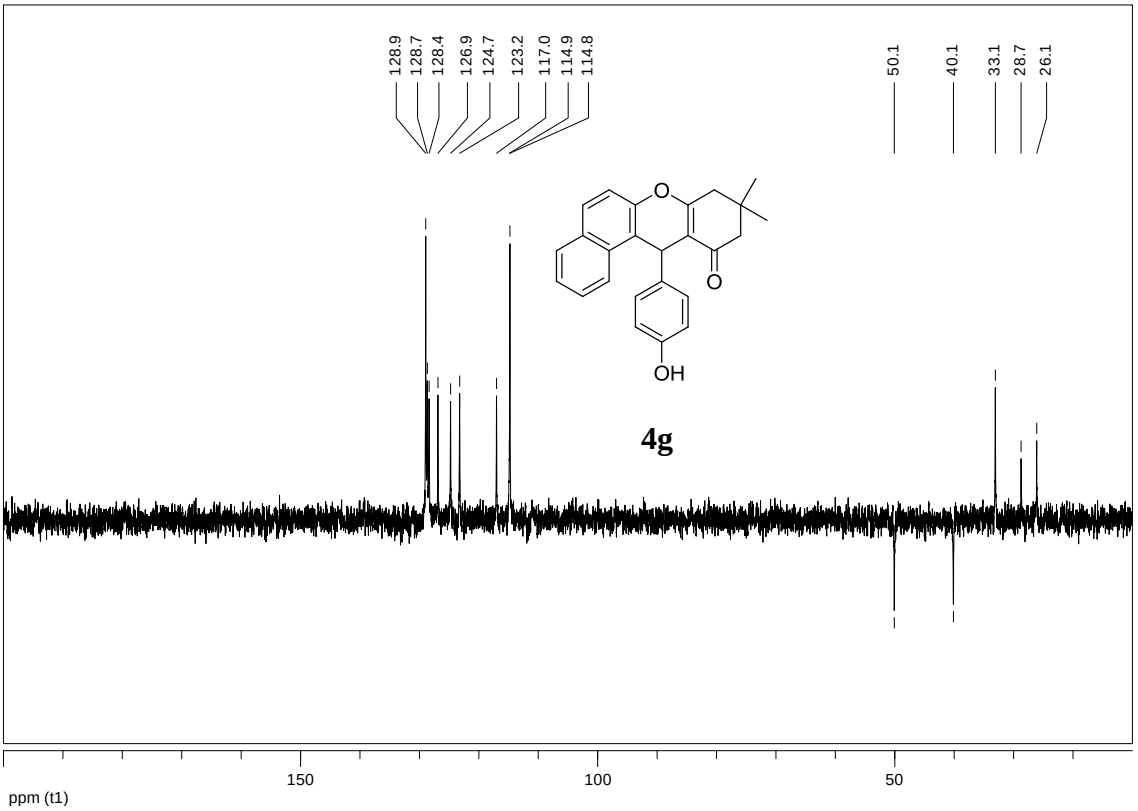


Figure S22. DEPT 135 spectrum (50 MHz, DMSO-d_6) of compound **4g**.

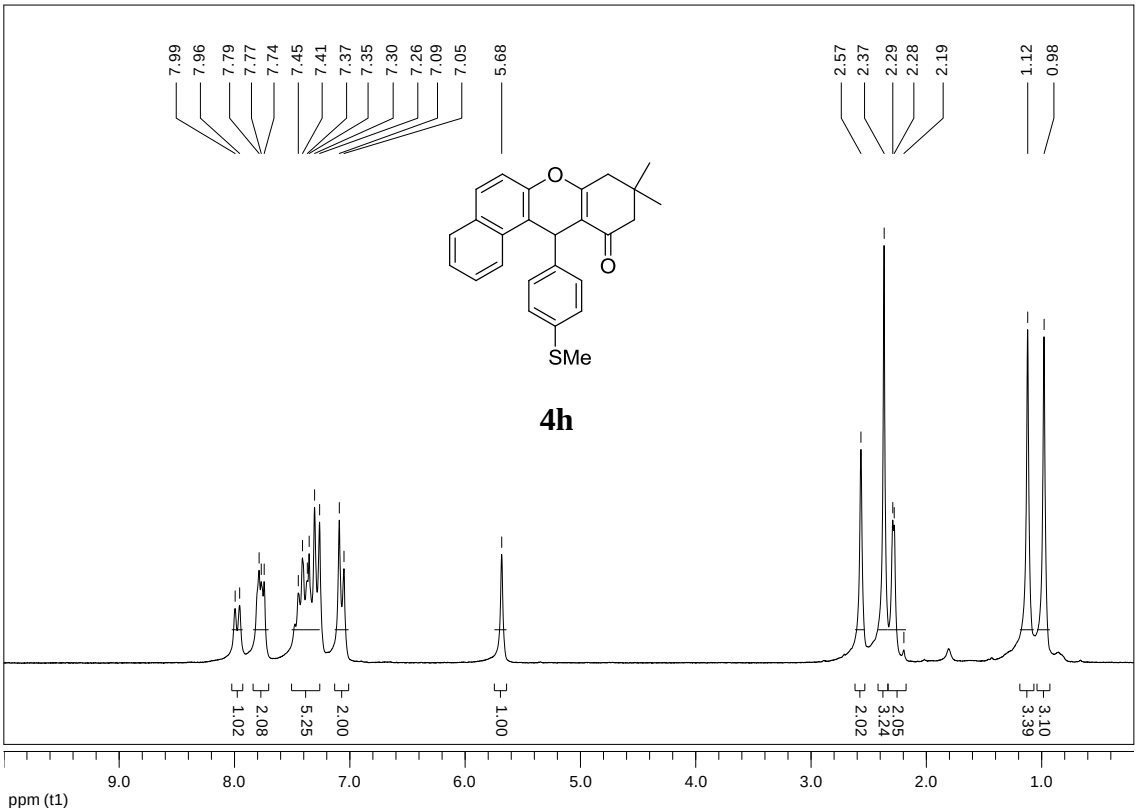


Figure S23. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of compound **4h**.

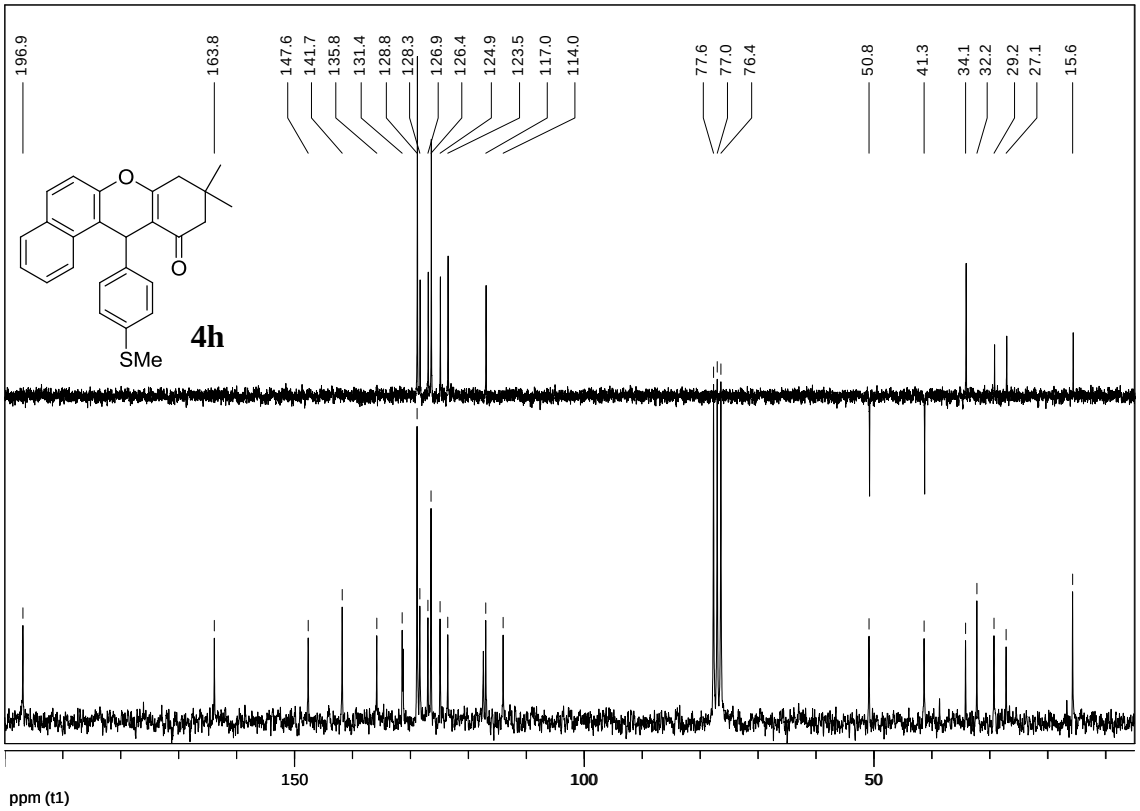


Figure S24. ^{13}C NMR spectrum (down) and DEPT 135 (up) (50 MHz, $CDCl_3$) of compound **4h**.

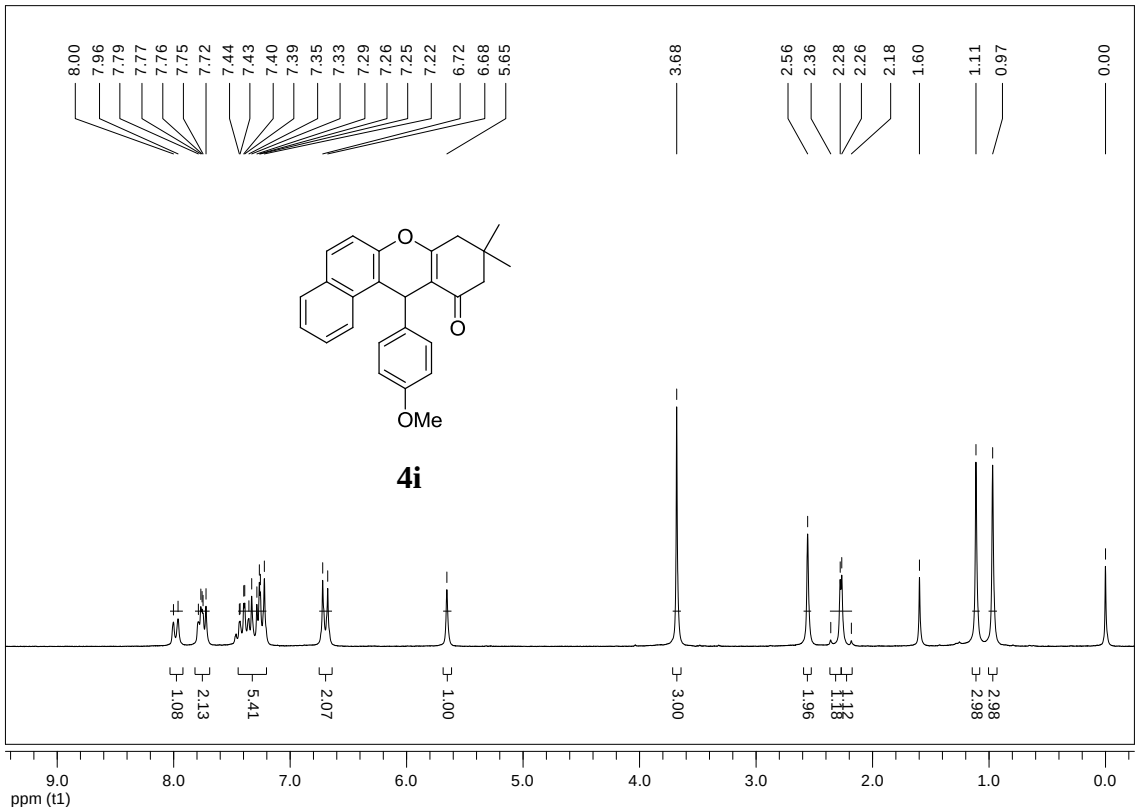


Figure S25. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of compound **4i**.

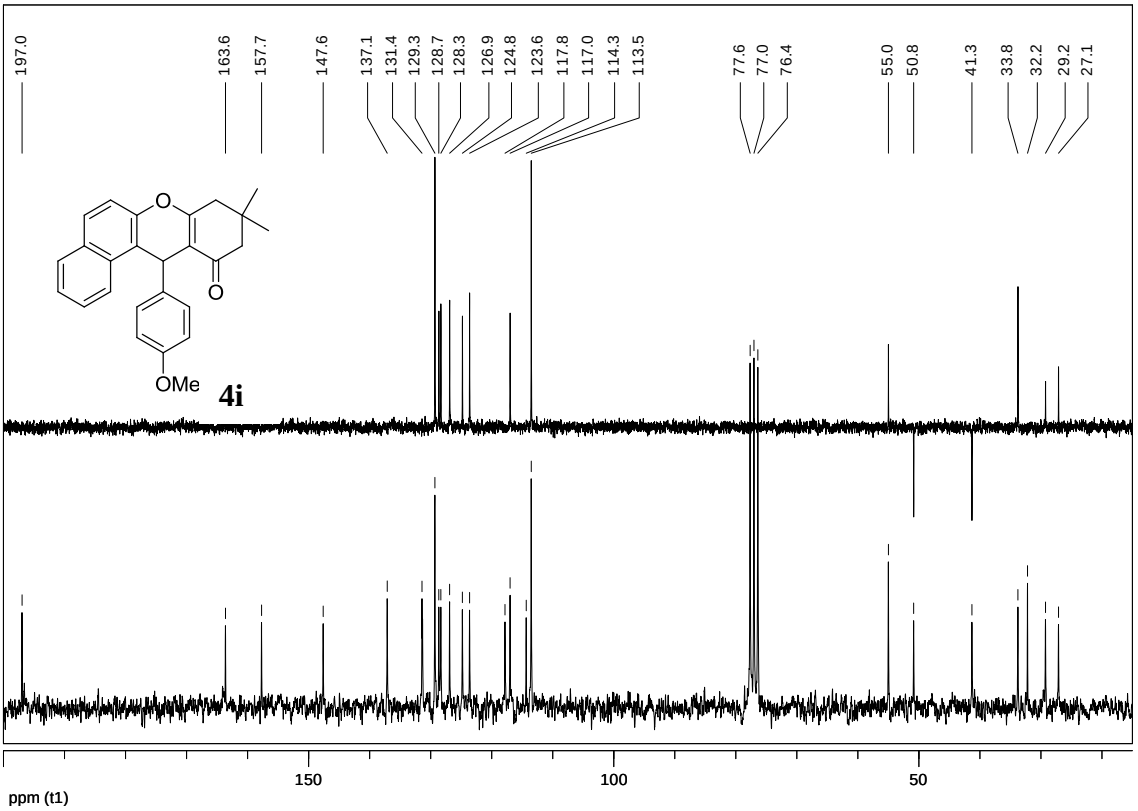


Figure S26. ^{13}C NMR spectrum (down) and DEPT 135 (up) (50 MHz, $CDCl_3$) of compound **4i**.

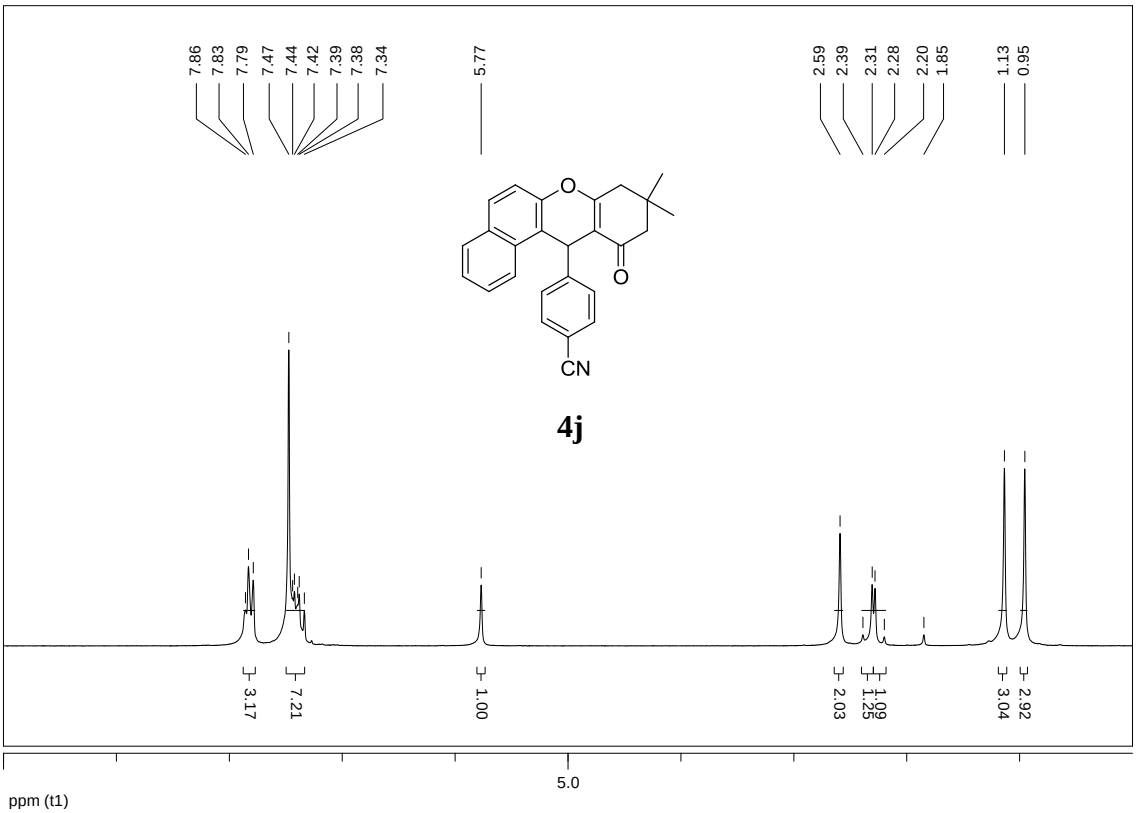


Figure S27. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of compound **4j**.

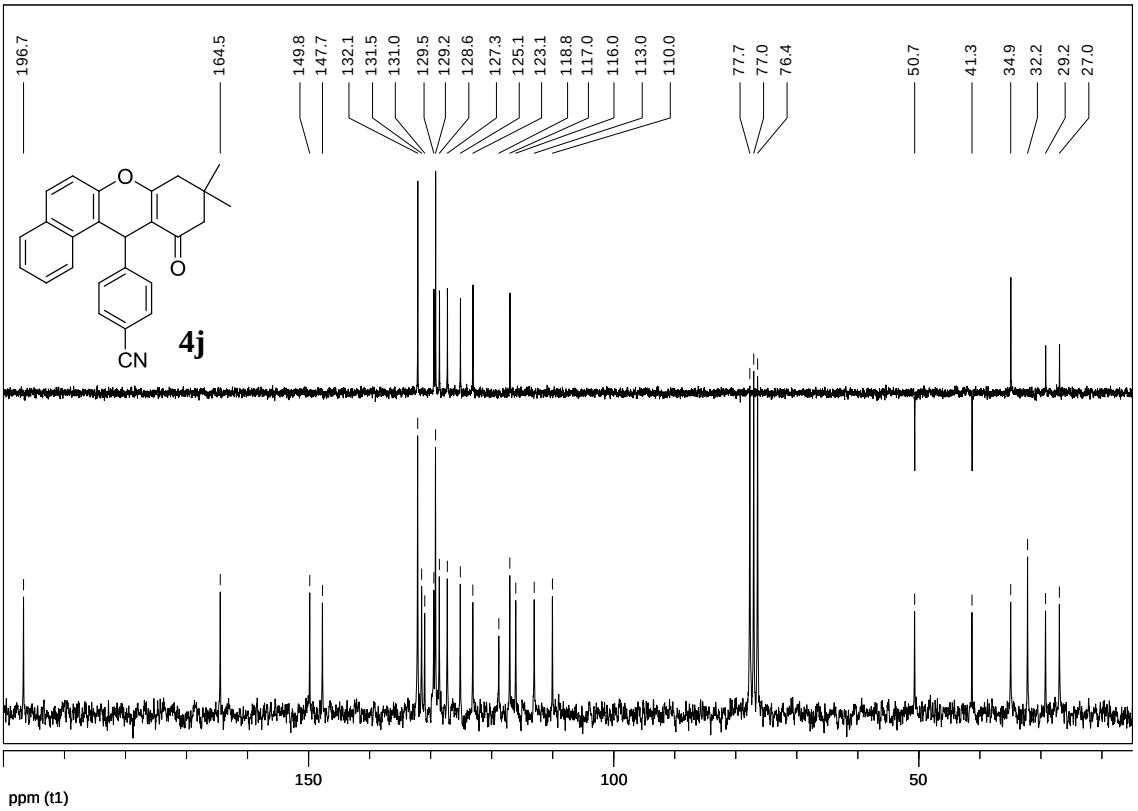


Figure S28. ^{13}C NMR spectrum (down) and DEPT 135 (up) (50 MHz, $CDCl_3$) of compound **4j**.

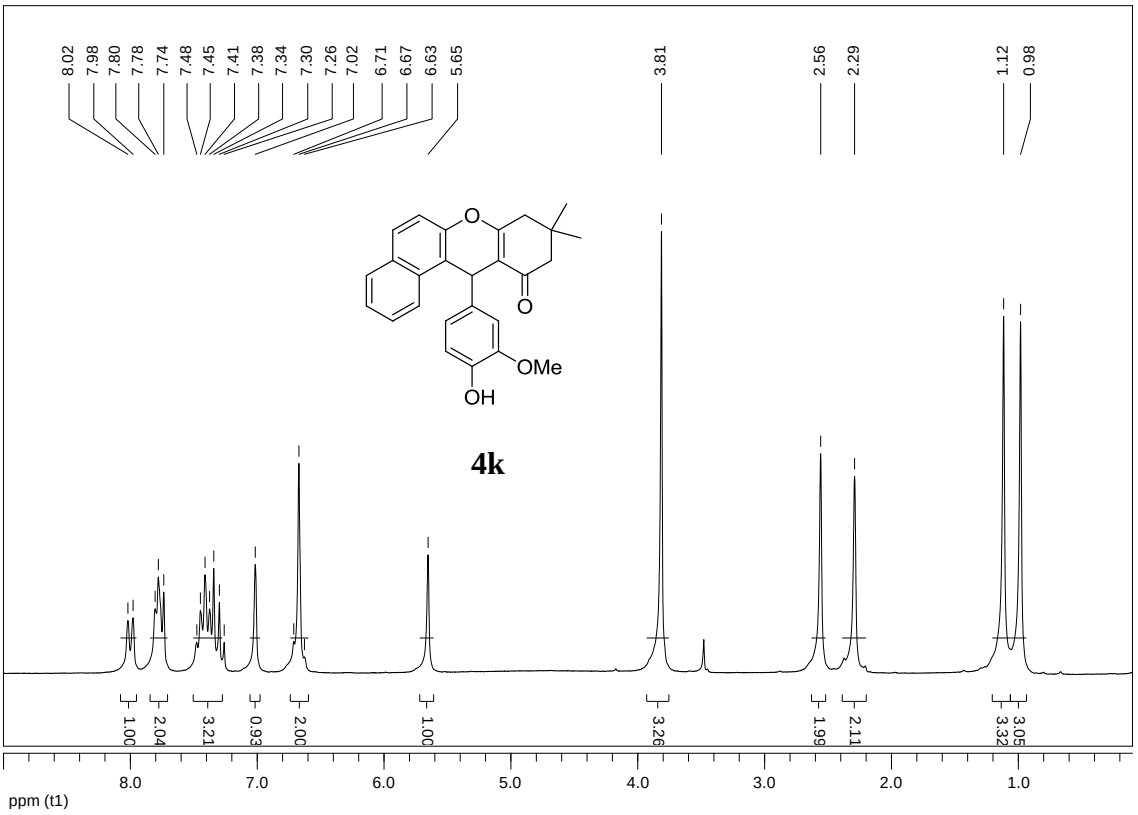


Figure S29. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of compound **4k**.

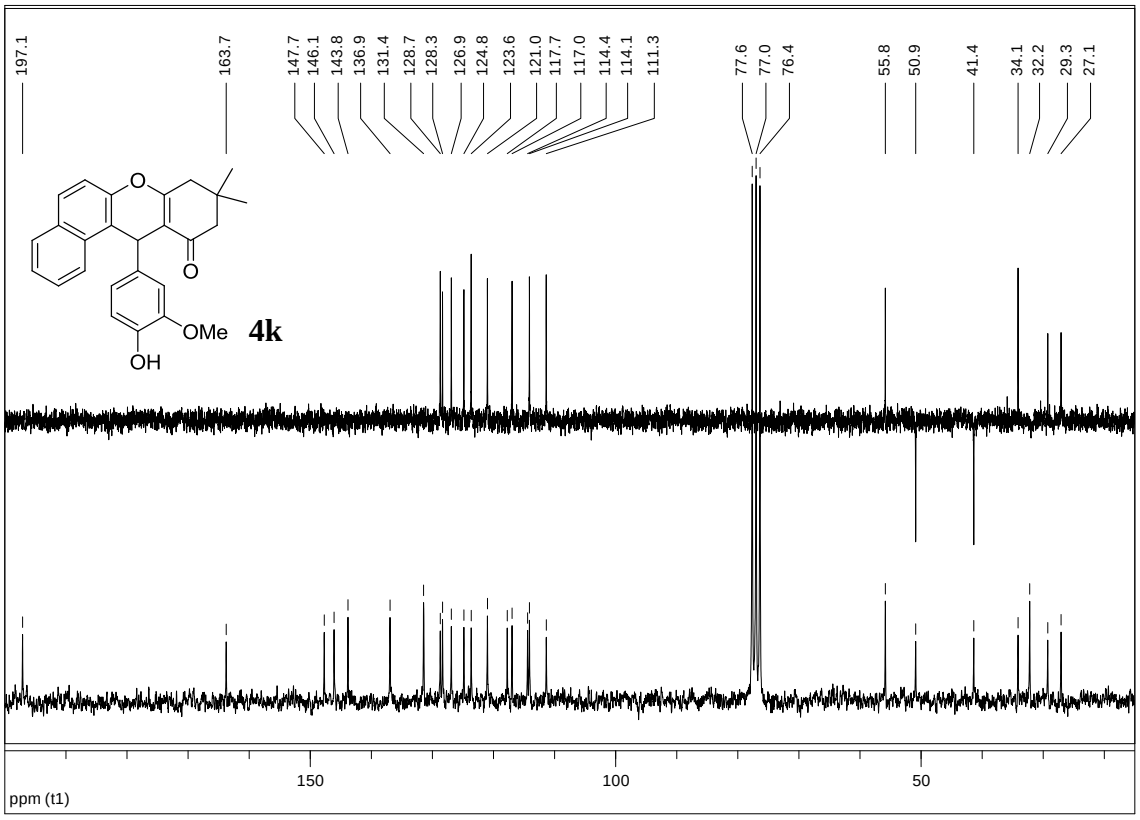


Figure S30. ^{13}C NMR spectrum (down) and DEPT 135 (up) (50 MHz, $CDCl_3$) of compound **4k**.

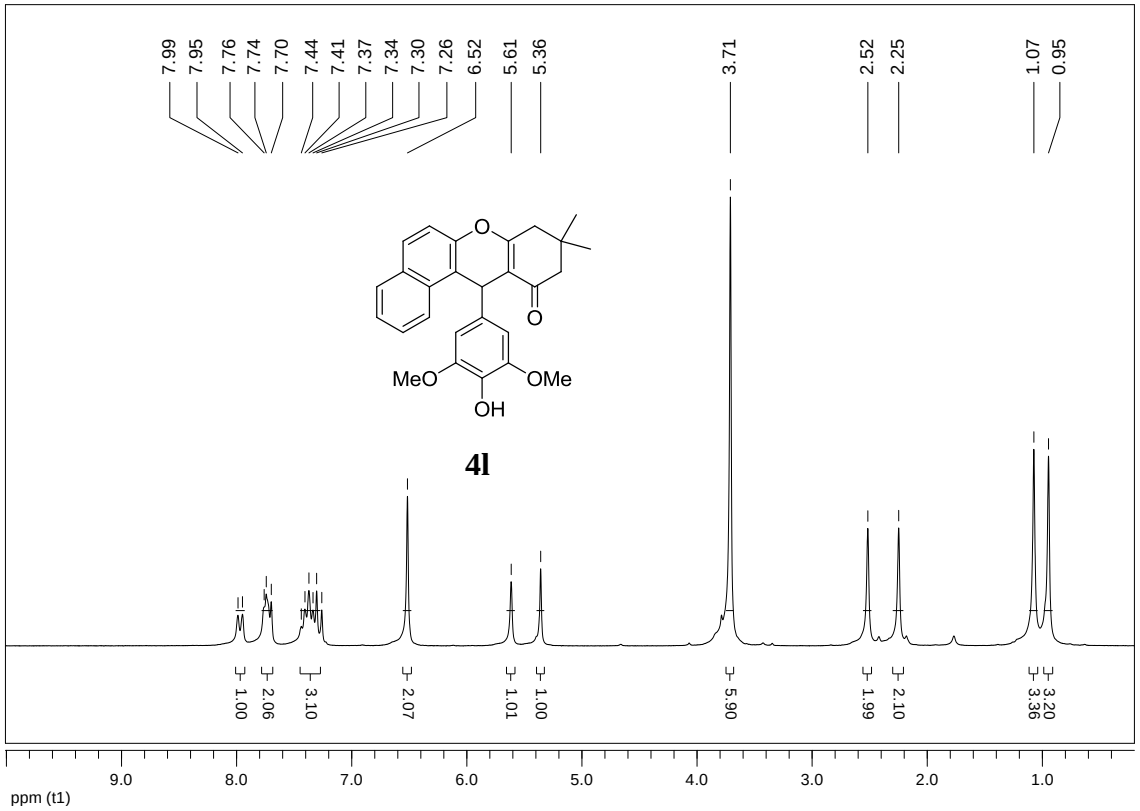


Figure S31. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of compound **4l**.

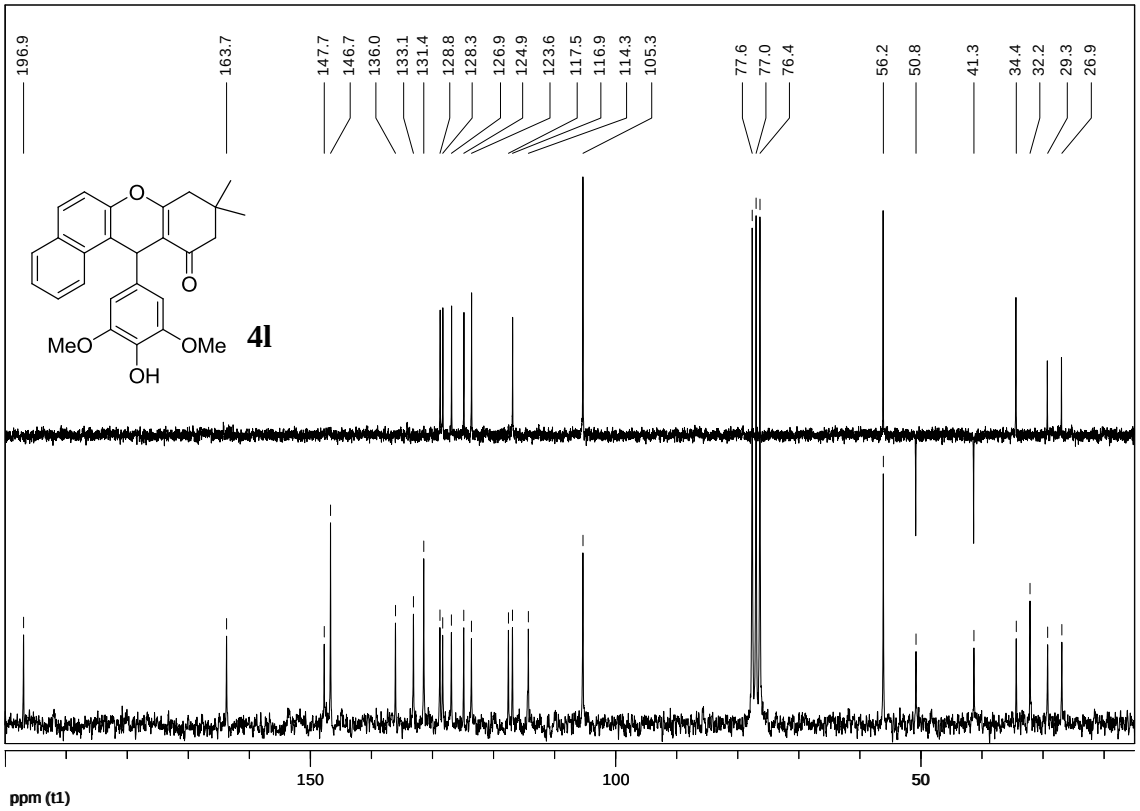


Figure S32. ^{13}C NMR spectrum (down) and DEPT 135 (up) (50 MHz, $CDCl_3$) of compound **4l**.

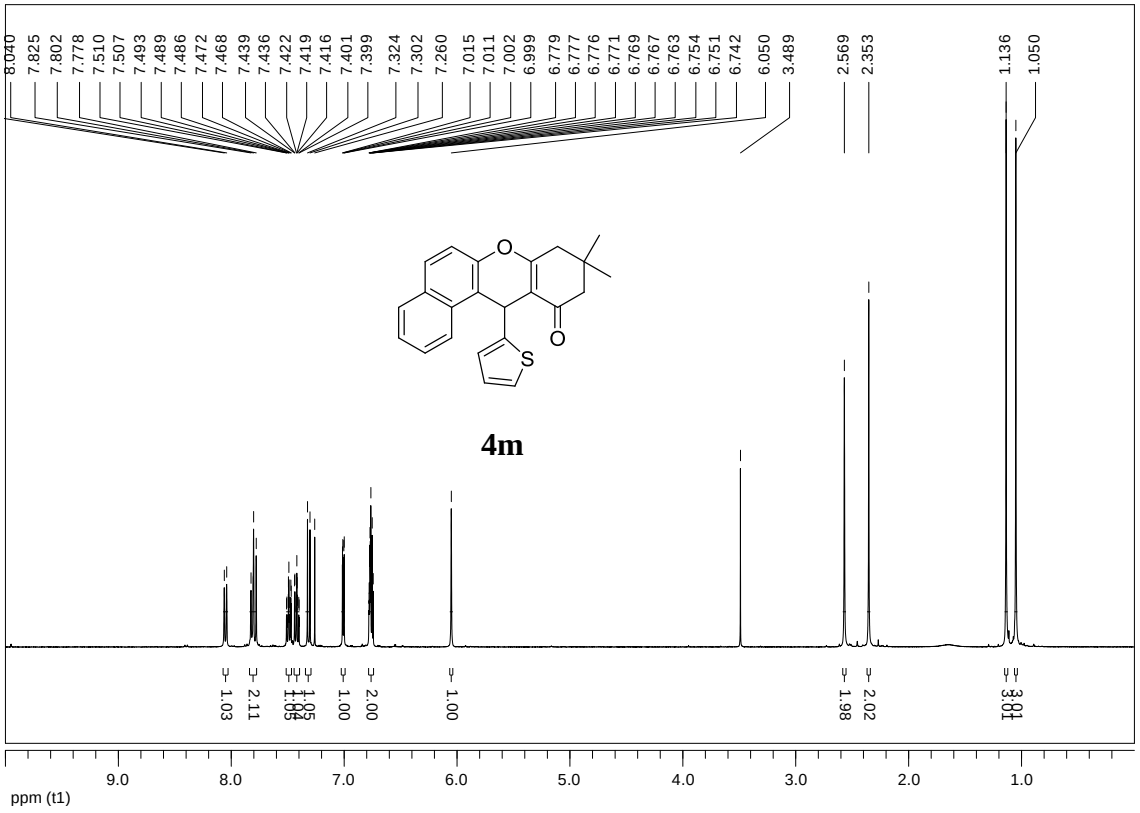


Figure S33. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4m**.

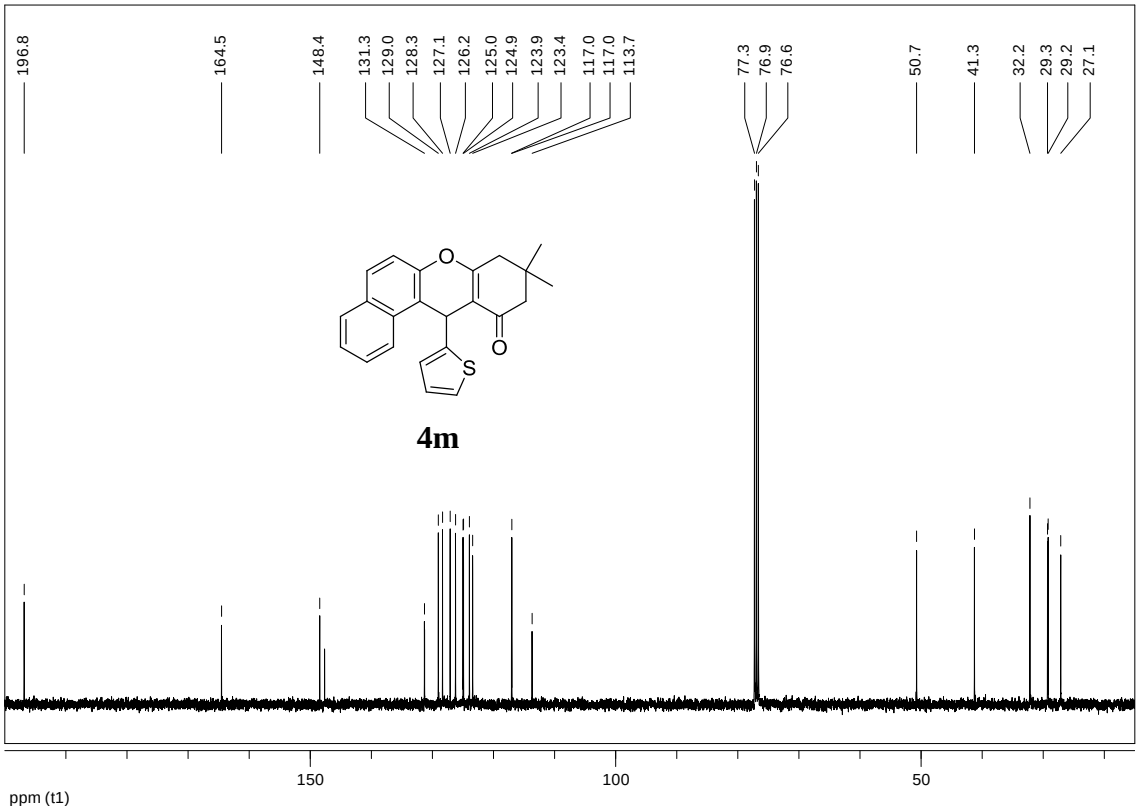


Figure S34. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4m**.

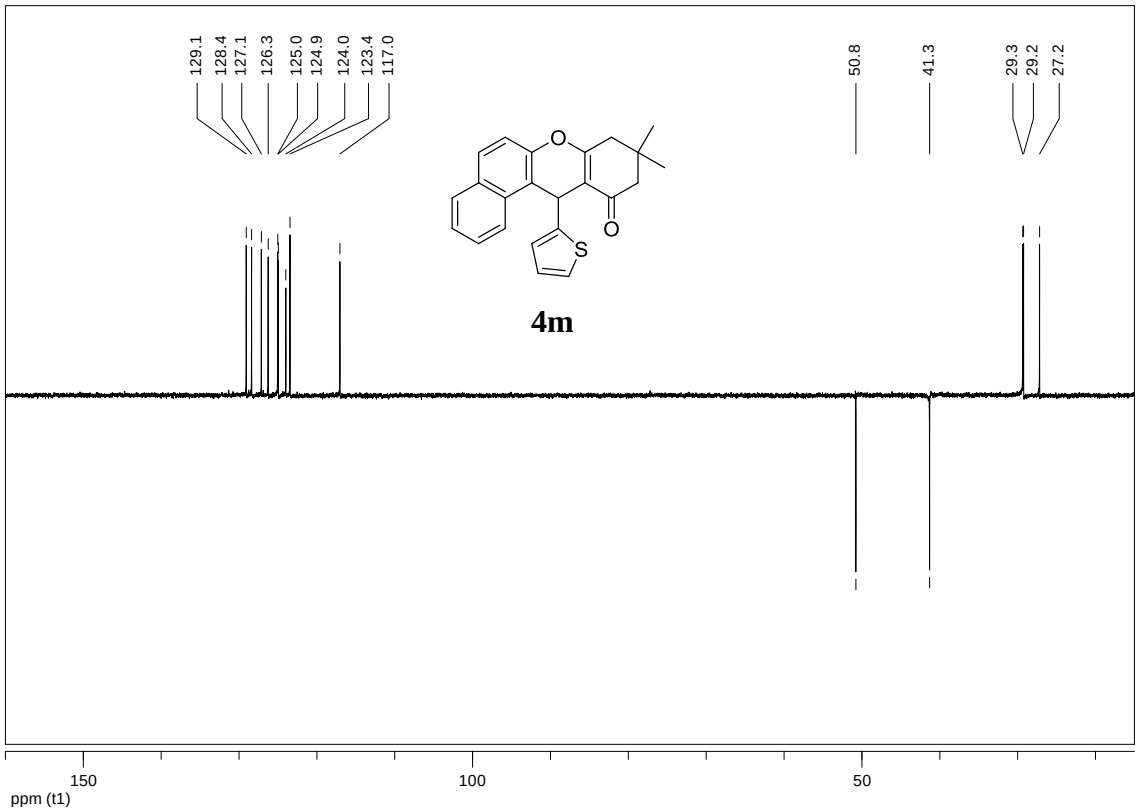


Figure S35. DEPT 135 spectrum (100 MHz, $CDCl_3$) of compound **4m**.

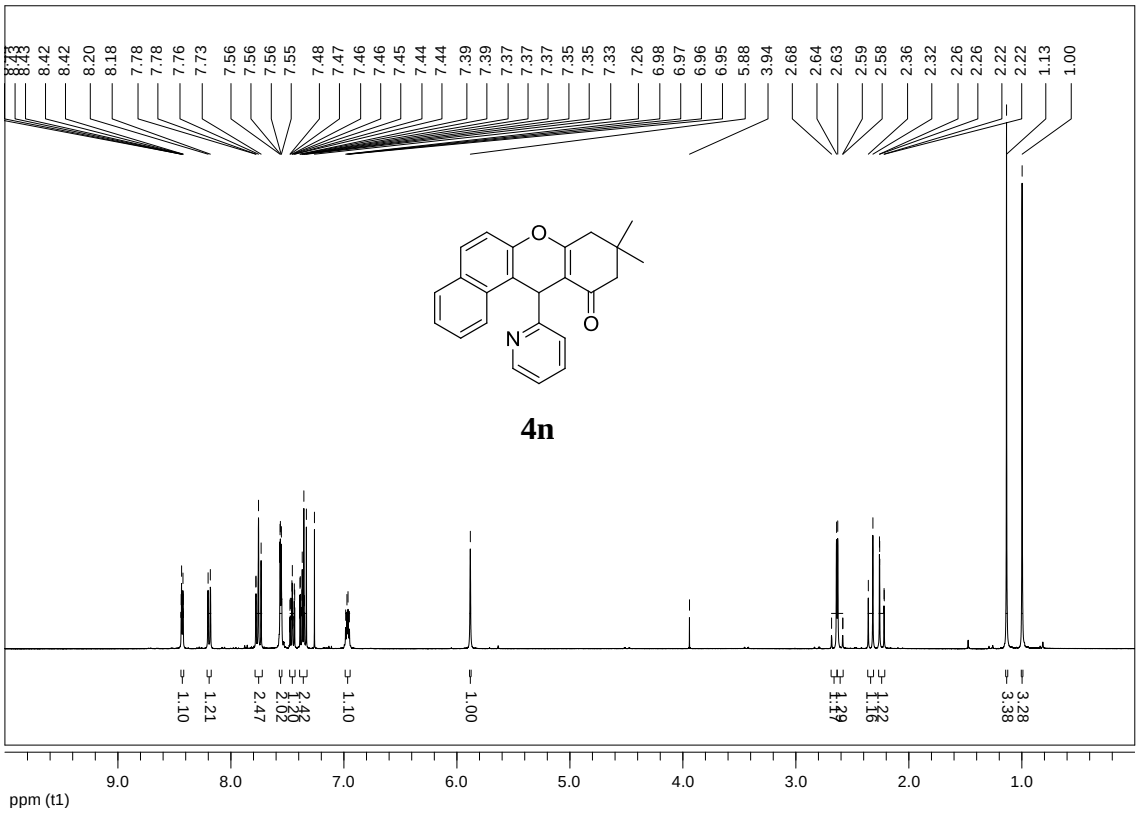


Figure S36. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4n**.

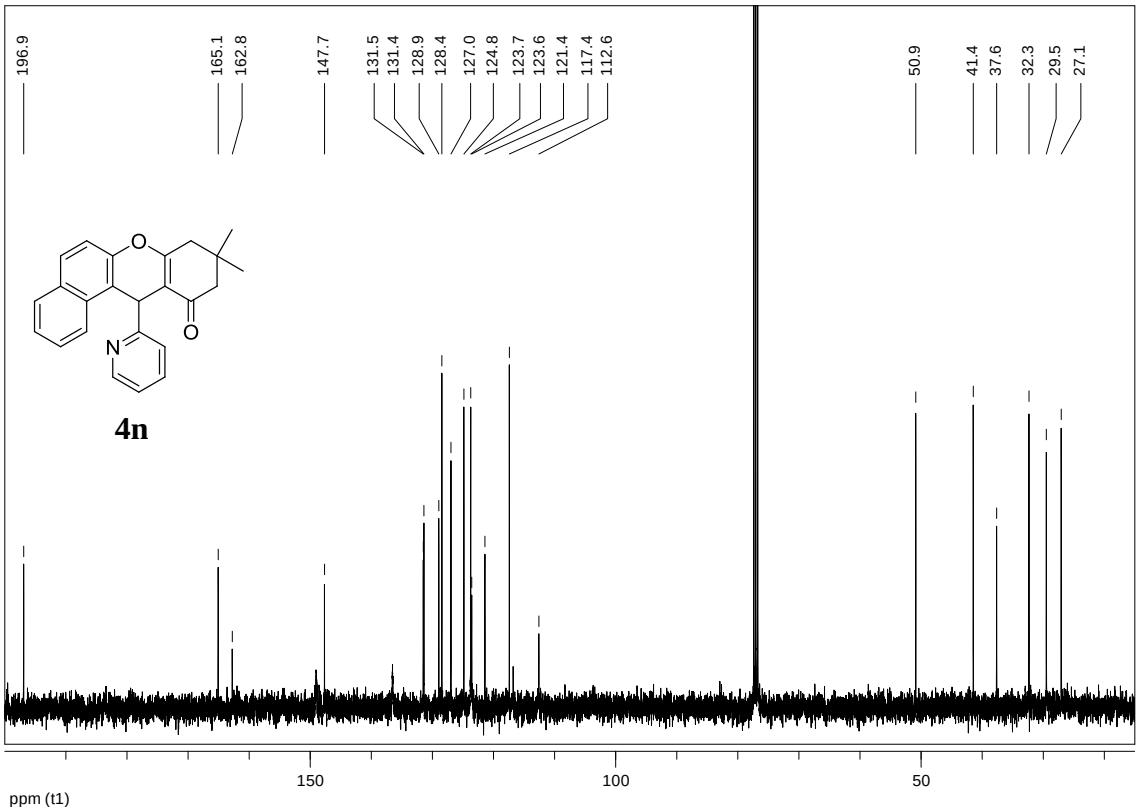


Figure S37. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4n**.

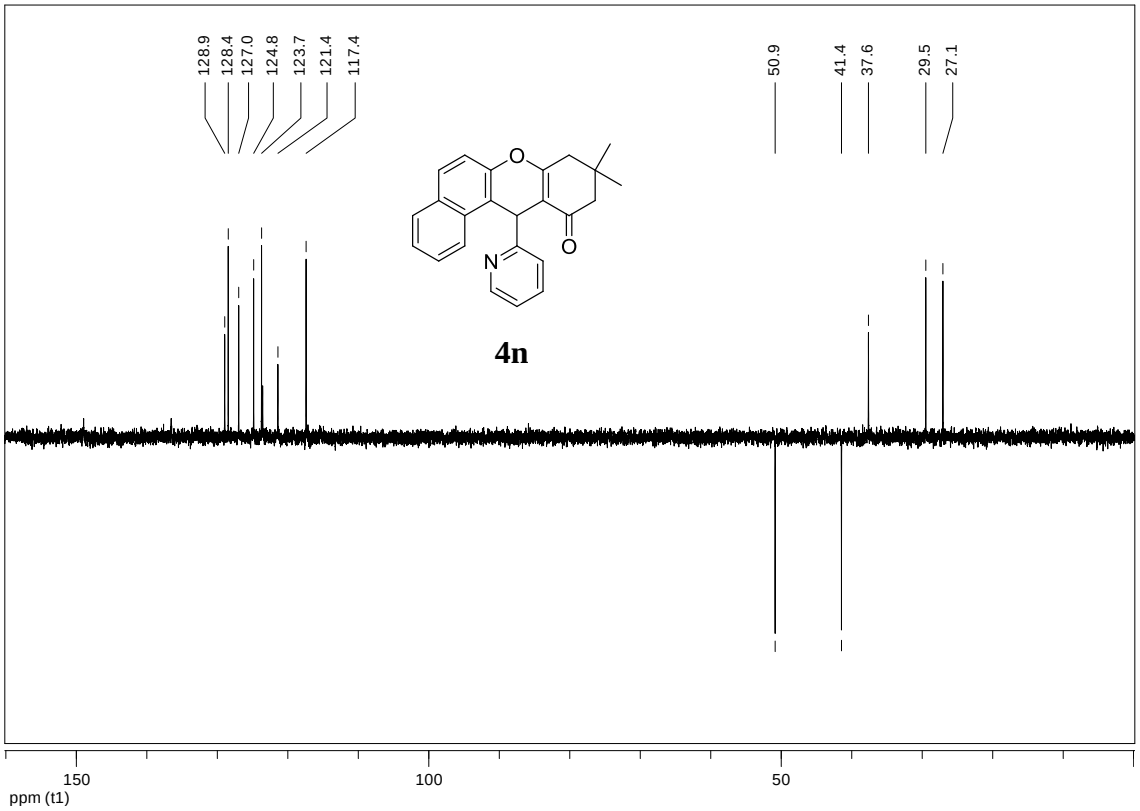


Figure S38. DEPT 135 spectrum (100 MHz, $CDCl_3$) of compound **4n**.

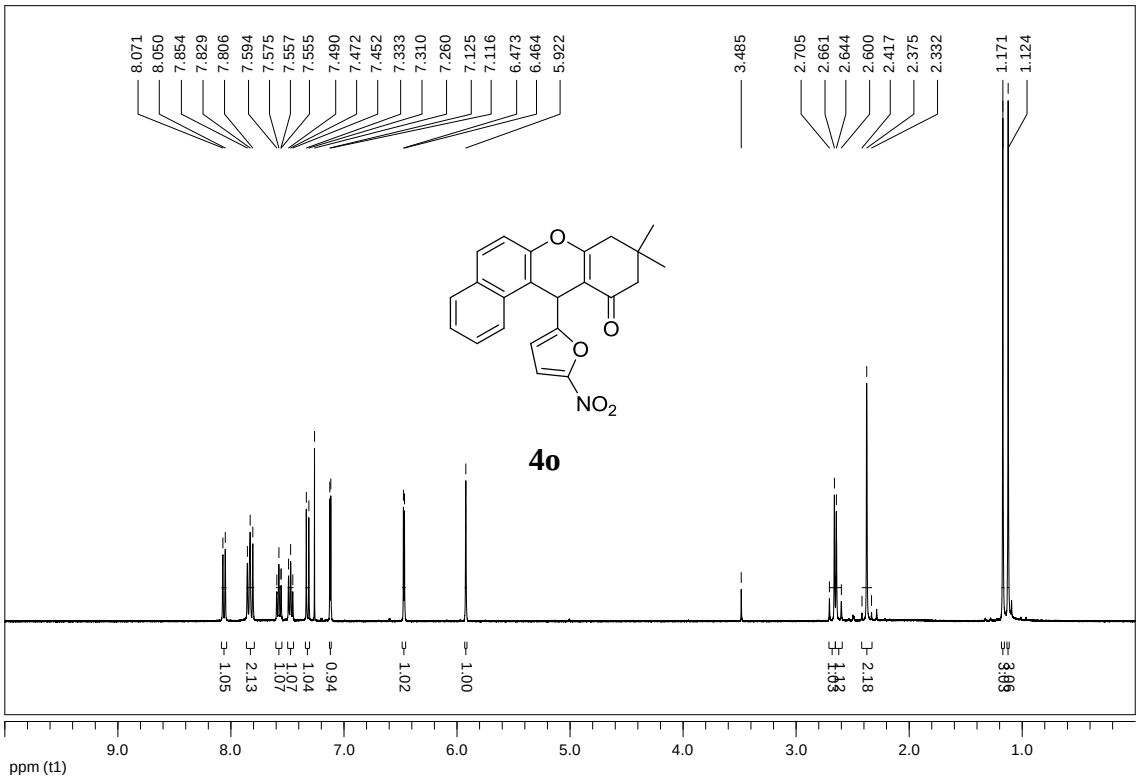


Figure S39. ^1H NMR spectrum (400 MHz, $CDCl_3$) of compound **4o**.

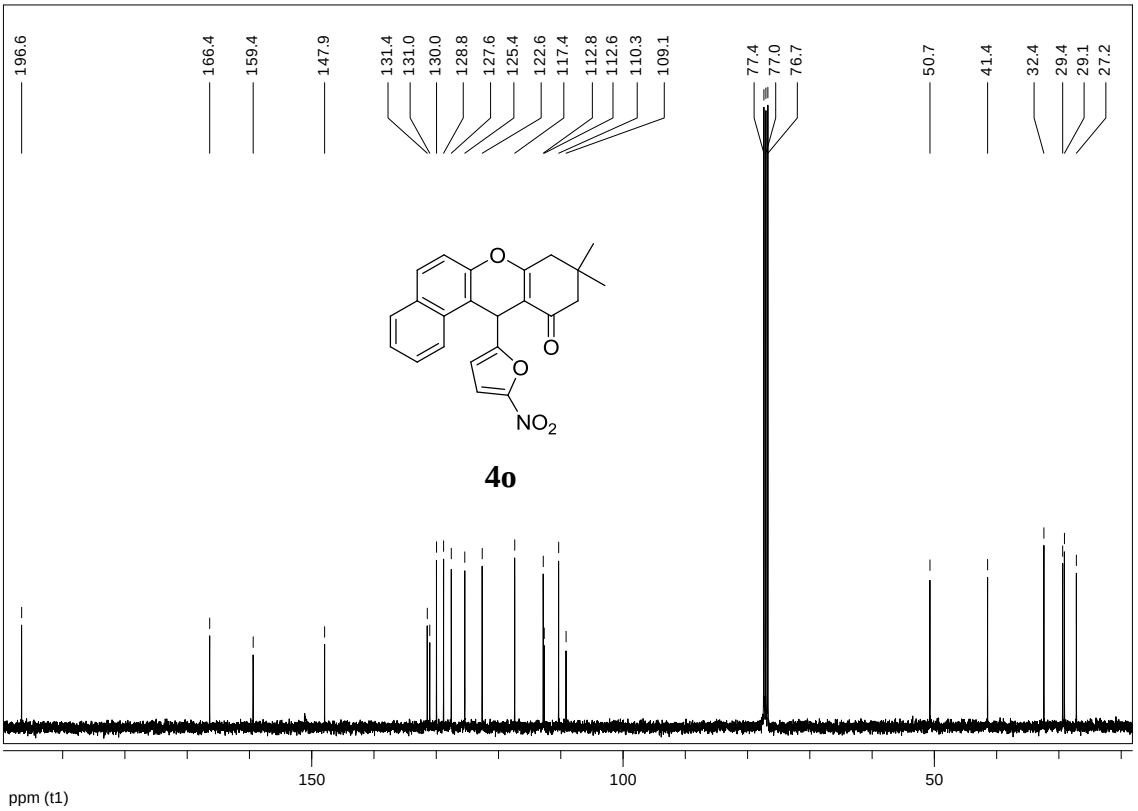


Figure S40. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4o**.

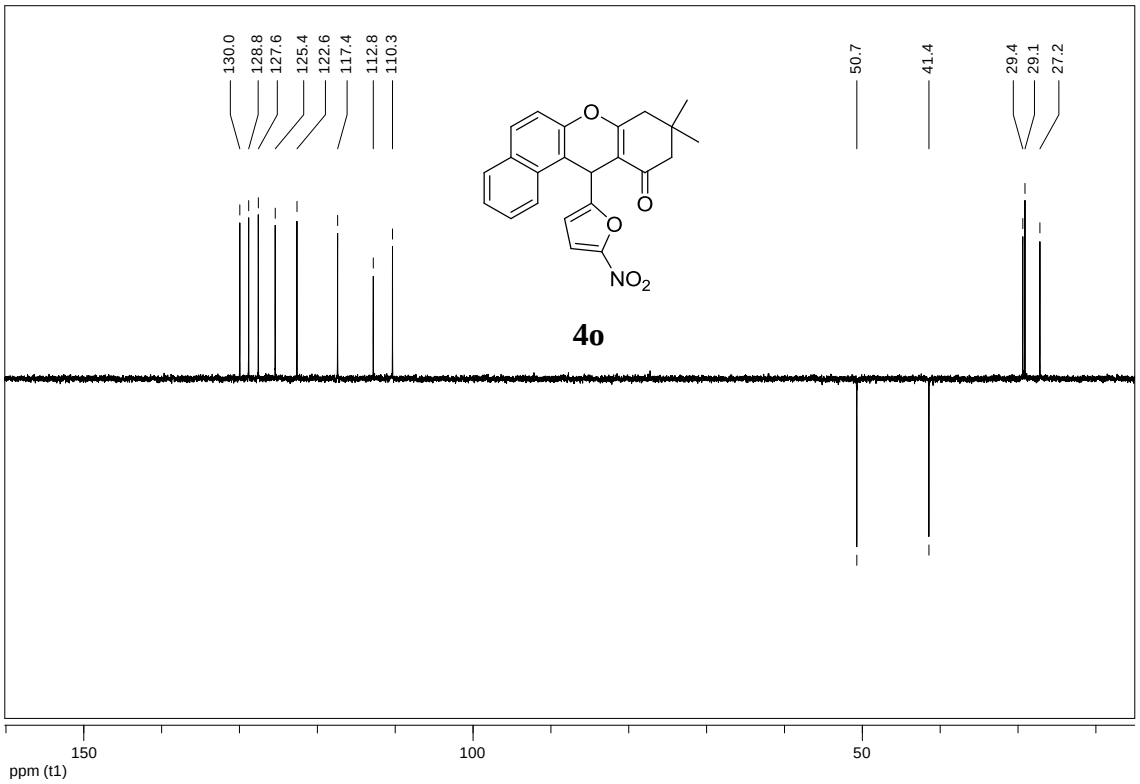


Figure S41. DEPT 135 spectrum (100 MHz, $CDCl_3$) of compound **4o**.