Supplementary Material

Expedient nonclassical reaction of acetylenes with ketones: controlling the switch between bicyclic ketal and cyclopentenol formation

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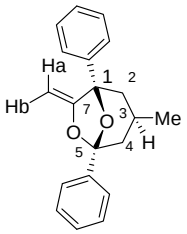
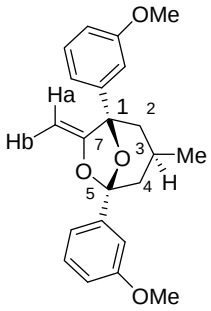
3-Methyl-7-methylene-1,5-diphenyl-6,8-dioxabicyclo[3.2.1]octane (3a).



^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.68-7.66 (m, 2H, H_{Ph}), 7.60-7.58 (m, 2H, H_{Ph}), 7.45-7.31 (m, 6H, H_{Ph}), 4.29 (d, 1H, ^2J = 2.3 Hz, H_b), 3.56 (d, 1H, ^2J = 2.3 Hz, H_a), 2.49 (m, 1H, H_4), 2.41 (m, 1H, C<u>H</u>-Me), 2.31 (m, 1H, H_2), 1.75 (m, 1H, $H_{4'}$), 1. 66 (m, 1H, $H_{2'}$), 1.11 (d, 3H, ^3J = 6.2 Hz, Me). ^{13}C NMR (101.6 MHz, $CDCl_3$): δ = 163.2 (C_7), 140.0 (C_i), 139.5 ($C_{i'}$), 128.9 (C_p), 128.3 (C_m, $C_{m'}$), 128.2 ($C_{p'}$), 126.0 (C_o), 125.4 ($C_{o'}$), 108.8 (C_5), 85.5 (C_1), 78.4 (=CH_2), 42.3, 40.9 (C_2, C_4), 25.4 (C_3), 21.4 (Me). IR (film) ν = 3289, 2956, 2970, 2808, 1729, 1682, 1381, 1337, 1275, 1146, 1129, 1114, 1061, 1026, 1012, 986, 827, 761, 698.

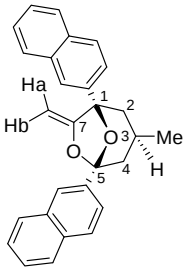
1**,5-Bis(3-methoxyphenyl)-3-methyl-7-methylene-6,8-dioxabicyclo[3.2.1]octane (3b).**



^{1}H NMR (400.1 MHz, C_6D_6): δ = 7.58-7.48 (m, 3H, H_{Ph}), 7.30-7.27 (m, 3H, H_{Ph}), 6.94-6.86 (m, 2H, H_{Ph}), 4.60 (d, 1H, ^2J = 2.2 Hz, H_b), 3.88 (d, 1H, ^2J = 2.2 Hz, H_a), 3.49 (s, 3H, MeO), 3.37 (s, 3H, MeO), 2.49-2.42 (m, 1H, C<u>H</u>-Me), 2.22 (dd, ^2J=12.8 Hz, ^3J=5.1 Hz, 1H, H_2), 2.14 (dd, ^2J=13.5 Hz, ^3J=5.5 Hz, 1H, H_4), 1.63 (dd, ^2J=12.8 Hz, ^3J=11.8 Hz, 1H, $H_{2'}$), 1.56 (dd, ^2J=13.5 Hz, ^3J=11.5 Hz, 1H, $H_{4'}$), 0.89 (d, ^3J=6.7 Hz, 3H, Me). ^{13}C NMR (101.6 MHz, C_6D_6): δ = 163.3 (C7), 160.0, 159.9 (2<u>C</u>-OMe), 142.0, 141.7 ($C_{i'}$, C_i), 129.4, 129.3, 118.3, 117.8, 114.4, 113.6, 112.1, 111.3 (8C_{aryl}), 109.0 (C5), 85.6 (C1), 78.3 (=CH_2), 54.6, 54.5 (2OMe), 42.9 (C4), 41.1 (C2), 25.4 (C3), 21.1 (Me). IR (film): ν=3285, 3078, 3000, 2955,

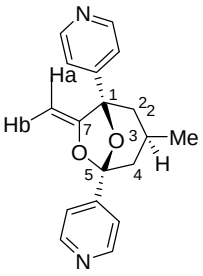
2917, 2871, 1835, 1681, 1604, 1491, 1454, 1434, 1365, 1338, 1264, 1213, 1179, 1130, 1105, 1080, 1047, 1022, 1010, 988, 956, 871, 782, 736, 660.

3-Methyl-7-methylene-1,5-di(naphthalen-2-yl)-6,8-dioxabicyclo[3.2.1]octane (3c).



^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 8.21 (s, 1H, H_{naphth}), 8.09 (s, 1H, H_{naphth}), 7.96-7.70 (m, 8H, H_{naphth}), 7.60-7.40 (m, 4H, H_{naphth}), 4.40 (d, 1H, ^2J = 2.4 Hz, H_b), 3.63 (d, 1H, ^2J = 2.4 Hz, H_a), 2.63 (m, 1H, H_2), 2.58 (m, 1H, C<u>H</u>-Me), 2.47 (m, 1H, H_4), 1.99 (m, 1H, $H_{2'}$), 1.86 (m, 1H, $H_{4'}$), 1.20 (d, 3H, ^3J = 6.4 Hz, Me). ^{13}C NMR (101.6 MHz, $CDCl_3$): δ = 163.3 (C_7), 137.3 ($C_{2'}$), 136.9 ($C_{2''}$), 133.5-123.3 (18 C_{naphth}), 109.3 (C_5), 85.8 (C_1), 78.9 (=CH_2), 42.5 (C_4), 40.8 (C_2), 25.6 (C_3), 21.5 (Me). IR (KBr): ν = 3058, 3024, 2956, 2925, 2870, 1771, 1716, 1681, 1601, 1507, 1456, 1371, 1356, 1330, 1278, 1223, 1194, 1166, 1126, 1093, 1069, 1030, 1021, 1008, 988, 954, 941, 907, 858, 818, 750, 733, 477.

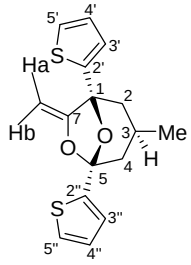
1,5-Di(pyrid-4-yl)-3-methyl-7-methylene-6,8-dioxabicyclo[3.2.1]octane (3d).



^{1}H NMR (400.1 MHz, C_6D_6): δ = 8.66-8.65 (m, 2H, H_{2pyr}), 8.60-8.59 (m, 2H, $H_{2'pyr}$), 7.27-7.26 (m, 2H, H_3), 7.08-7.07 (m, 2H, $H_{3'}$), 4.38 (d, ^2J=2.7 Hz, 1H, H_a), 3.53 (d, ^2J=2.7 Hz, 1H, H_b), 2.15-2.14 (m, 1H, C<u>H</u>-Me), 1.86 (dd, ^2J=13.0 Hz, ^3J=5.4 Hz, 1H, H_2), 1.75 (dd, ^2J=13.4 Hz, ^3J=5.4 Hz, 1H, H_4), 1.24 (dd, ^2J=13.0 Hz, ^3J=11.3 Hz, 1H, $H_{2'}$), 1.18 (dd, ^2J=13.4 Hz, ^3J=11.3 Hz, 1H, $H_{4'}$), 0.71 (d, ^3J=6.6 Hz, 3H, Me). ^{13}C NMR (101.6 MHz, C_6D_6): δ = 161.6 (C_7), 150.6 (C_{2pyr}, $C_{2'pyr}$), 147.8 ($C_{4'pyr}$), 147.0 (C_{4pyr}), 120.4 ($C_{3'pyr}$), 120.0 (C_{3pyr}), 108.2 (C_5),

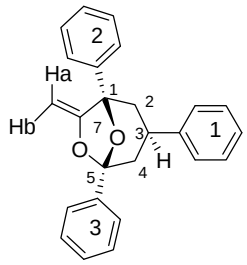
84.7 (C_1), 79.5 (=CH_2), 42.2 (C_4), 40.6 (C_2), 25.2 (C_3), 21.0 (Me). IR (film): ν = 3082, 3031, 2956, 2917, 2872, 1940, 1684, 1602, 1409, 1339, 1277, 1250, 1167, 1132, 1107, 1069, 1024, 1009, 990, 954, 852, 815, 752, 728, 685, 669, 646.

3-Methyl-7-methylene-1,5-di(thiophen-2-yl)-6,8-dioxabicyclo[3.2.1]octane (3e).



^{1}H NMR (400.1 MHz, C_6D_6): δ = 7.36 (d, ^3J=4.8 Hz, 1H, $H_{5''}$), 7.33 (d, ^3J=4.8 Hz, 1H; $H_{5'}$), 7.26 (d, ^3J=2.8 Hz, 1H; $H_{3''}$), 7.18 (d, ^3J=2.8 Hz, 1H; $H_{3'}$), 6.90-7.01 (m, 2H; $H_{4'}$, $H_{4''}$), 4.33 (d, ^2J=2.4 Hz, 1H; H_b), 3.74 (d, ^2J=2.4 Hz, 1H; H_a), 2.45-2.40 (m, 1H; C<u>H</u>-Me), 2.26 (dd, ^2J=13.5 Hz, ^3J=5.3 Hz, 1H, H_2), 2.14 (dd, ^2J=12.4 Hz, ^3J=4.7 Hz, 1H, H_4), 1.78 (dd, ^2J=12.4 Hz, ^3J=11.5 Hz, 1H, $H_{4'}$), 1.69 (dd, ^2J=13.5 Hz, ^3J=11.9 Hz, 1H, $H_{2'}$), 0.85 (d, ^3J=6.2 Hz, 3H, Me). ^{13}C NMR (101.6 MHz, C_6D_6): δ = 161.9 (C7), 143.1, 141.8 ($C_{2'}$, $C_{2''}$), 126.9, 126.7, 126.5, 126.2, 125.6, 125.2 (6C_{thioph}), 106.6 (C_5), 84.0 (C_1), 78.9 (=CH_2), 41.9, 41.2 (C_2, C_4), 25.1 (C_3), 21.1 (Me). IR (film): ν = 3107, 2955, 2924, 2870, 1684, 1541, 1441, 1357, 1323, 1267, 1240, 1218, 1166, 1129, 1090, 1044, 988, 960, 931, 856, 830, 811, 704.

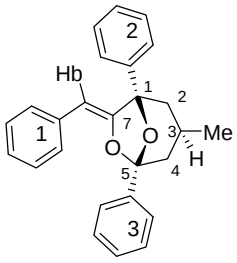
7-Methylene-1,3,5-triphenyl-6,8-dioxabicyclo[3.2.1]octane (3f).



^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.69 (m, 2H, H_{o3}), 7.59 (m, 2H, H_{o1}), 7.42 (m, 2H, H_{m3}), 7.38 (m, 2H, H_{m1}), 7.37 (m, 1H, H_{p3}), 7.32 (m, 5H, H_{p1}, H_{o2}, H_{m2}), 7.22 (m, 1H, H_{p2}), 4.39 (d, ^2J = 2.5 Hz, 1H, H_a), 3.65 (d, ^2J = 2.5 Hz, 1H, H_b), 3.60 (m, 1H, C<u>H</u>-Ph), 2.59 (dd, ^3J = 5.1 Hz, ^2J = 13.2 Hz, 1H, H_2), 2.51 (dd, ^3J = 5.6 Hz, ^2J = 12.0 Hz, 1H, H_4), 2.28 (dd, ^3J = 12.4

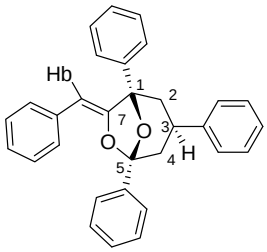
Hz, ^{2}J = 13.2 Hz, 1H, H_2), 2.18 (dd, ^{2}J = 12.0 Hz, ^{3}J = 13.5 Hz, 1H, H_4). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 162.8 (C_7), 143.8 (C_{i2}), 139.6 (C_{i3}), 139.3 (C_{i1}), 129.0 (C_{p3}), 128.9 (C_{p1}), 128.5 (C_{m3}), 128.4 (C_{m1}), 127.5 (C_{o2}), 127.0 (C_{p2}), 126.0 (C_{o3}), 125.5 (C_{o1}), 108.9 (C_5), 85.6 (C_1), 79.0 (=CH_2), 41.4 (C_4), 40.1 (C_2), 36.9 (C_3). IR (film): ν = 3088, 3062, 3030, 2956, 2923, 2849, 1953, 1884, 1808, 1744, 1683, 1638, 1603, 1496, 1450, 1378, 1348, 1309, 1272, 1249, 1142, 1115, 1095, 1062, 1014, 990, 956, 848, 813, 756, 723, 696.

3-Methyl-1,5-diphenyl-7-[(Z)-phenylmethylidene]-6,8-dioxabicyclo[3.2.1]octane (3g).



^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.71 (m, 2H, H_{o2}), 7.58 (m, 2H, H_{o1}), 7.48 (m, 2H, H_{o3}), 7.39 (m, 1H, H_{p2}), 7.36 (m, 2H, H_{m2}), 7.34 (m, 2H, H_{m1}), 7.29 (m, 2H, H_{p1}), 7.21 (m, 2H, H_{m3}), 7.04 (m, 2H, H_{p3}), 4.79 (s, 1H, H_b), 2.40 (dd, ^{3}J = 5.1 Hz, ^{2}J = 12.2 Hz, 1H, H_2), 2.34 (m, 1H, C<u>H</u>-Me), 2.30 (dd, ^{3}J = 5.1 Hz, ^{2}J = 13.2 Hz, 1H, H_4), 1.78 (dd, ^{3}J = 11.2 Hz, ^{2}J = 12.2 Hz, 1H, H_2), 1.69 (dd, ^{3}J = 10.5 Hz, ^{2}J = 13.2 Hz, 1H, H_4), 1.02 (m, 3H, ^{3}J = 6.4 Hz, C_3-Me). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 157.3 (C_7), 139.6 (C_{i1}), 139.6 (C_{i2}), 136.0 (C_{i3}), 128.3 (C_{m1}, C_{p1}, C_{m2}, C_{m3}), 127.6 (C_{o3}), 127.0 (C_{p2}), 126.5 (C_{o1}), 125.5 (C_{o2}), 125.4 (C_{p3}), 110.4 (C5), 95.9 (CH=Ph),, 86.7 (C_1), 42.2 (C_4), 40.7 (C_2), 25.3 (C_3), 21.4 (C_3-<u>Me</u>). IR (film): ν = 3060, 3031, 2954, 2917, 2872, 2841, 1684, 1599, 1493, 1450, 1355, 1310, 1273, 1243, 1190, 1144, 1095, 1062, 998, 945, 911, 817, 754, 696, 552, 494.

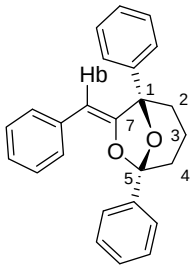
1,3,5-Triphenyl-7-[(Z)-phenylmethylidene]-6,8-dioxabicyclo[3.2.1]octane (3h).



^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.83 (m, 2H, H_{o3}), 7.68 (m, 2H, H_{o1}), 7.62 (m, 2H, H_{o4}), 7.50-7.35 (m, 15H, H_{Aryl}), 7.35 (m, 1H, H_{o2}), 7.33 (m, 2H, H_{m4}), 7.17 (m, 1H, H_{p4}), 4.94 (s,

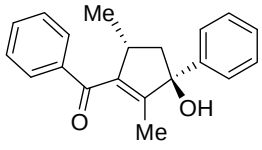
1H, H_b), 3.60 (m, 1H, H_3), 2.72 (dd, ^3J = 5.1 Hz, ^2J = 13.0 Hz, 1H, H_2), 2.61 (dd, ^3J = 5.6 Hz, ^2J = 13.6 Hz, 1H, H_4), 2.42 (dd, ^3J = 12.7 Hz, ^2J = 13.0 Hz, 1H, H_2), 2.32 (dd, ^3J = 11.7 Hz, ^2J = 13.6 Hz, 1H, H_4). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 156.9 (C_7), 143.8 (C_{i2}), 139.5 (C_{i3}) , 139.4 (C_{i1}), 135.9 (C_{i4}), 129.1-125.6 (C_{Aryl}), 110.5 (C_5), 96.5 (CH=Ph), 86.8 (C_1), 41.3 (C_4), 40.1 (C_2), 36.9 (C_3). IR (film): ν = 3082, 3059, 3028, 2954, 2920, 2850, 1684, 1597, 1493, 1449, 1356, 1311, 1272, 1234, 1181, 1154, 1092, 1058, 1029, 985, 942, 916, 891, 846, 819, 753, 697.

1,5-Diphenyl-7-[(Z)-phenylmethylidene]-6,8-dioxabicyclo[3.2.1]octane (3i).



^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.71 (m, 2H, H_{o2}), 7.58 (m, 2H, H_{o1}), 7.50 (m, 2H, H_{o3}), 7.44-7.05 (m, 9H, H_{Aryl}), 4.79 (s, 1H, H_b), 2.36-1.96 (m, 6H, $H_{2,3,4}$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 157.3 (C_7), 139.9 (C_{i1}), 139.7 (C_{i2}), 136.0(C_{i3}), 129.0 (C_{p2}), 128.3 (C_{m1}, C_{p1}, C_{m2}, C_{m3}), 127.4 (C_{o3}), 126.5 (C_{o1}), 125.5 (C_{o2}), 125.4 (C_{p3}), 110.9 (C_5), 96.0 (CH=Ph), 86.9 (C_1), 33.4 (C_4), 31.9 (C_2), 18.3 (C_3). IR (film): ν = 3086, 3061, 3030, 2954, 2934, 2921, 2875, 2847, 1683, 1599, 1495, 1449, 1360, 1313, 1294, 1265, 1222, 1197, 1181, 1146, 1133, 1109, 1091, 1062, 1040, 1030, 1014, 1002, 975, 942, 910, 899, 816, 756, 734, 694.

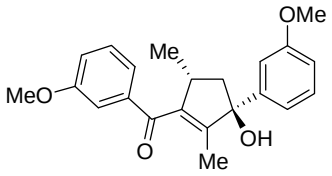
(3-Hydroxy-2,5-dimethyl-3-phenyl-1-cyclopentenyl)-(phenyl)methanone (4a).



^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.90-7.89 (m, 2H, H_{o1}), 7.59-7.55 (m, 1H, H_{p1}), 7.50-7.46 (m, 4H, H_{m1}), H_{o2}), 7.41-7.37 (m, 2H, H_{m2}), 7.29-7.25 (m, 1H, H_{p2}), 3.60-3.48 (m, 1H, H_5), 2.60 (dd, ^2J=14.2 Hz, ^3J=7.3 Hz, 1H, H_4), 2.33 (br. s, 1H, OH), 1.99 (dd, ^2J=14.2 Hz, ^3J=6.6 Hz, 1H, $H_{4'}$), 1.35 (d, ^5J=2.2 Hz, 3H, 2-Me), 1.10 (d, ^3J=6.9 Hz, 3H, 5-Me). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 198.1 (C=O), 146.5 (C_1), 145.3 (C_{i2}), 144.9 (C_2), 138.1 (C_{i1}), 133.4 (C_{p1}),

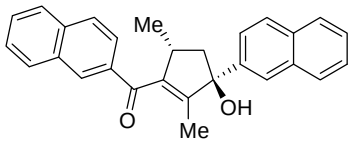
129.2 (C_{o1}), 128.9 (C_{m1}), 128.4 (C_{m2}), 127.0 (C_{p2}), 125.6 (C_{o2}), 88.7 (C_3), 51.0 (C_4), 39.9 (C_5), 19.4 (5-Me), 12.1 (2-Me). IR (film): ν = 3371, 3061, 3028, 2959, 2952, 2869, 1647, 1592, 1492, 1447, 1379, 1326, 1272, 1218, 1175, 1114, 1052, 1027, 999, 924, 866, 763, 728, 701.

[3-Hydroxy-3-(3-methoxyphenyl)-2,5-dimethyl-1-cyclopentenyl](3-methoxyphenyl)methanone (4b).



^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.49-7.47 (m, 1H, $H_6(Ar_1)$), 7.45-7.41 (m, 1H, $H_2(Ar_1)$), 7.38-7.34 (m, 1H, $H_5(Ar_1)$), 7.32-7.28 (m, 1H, $H_5(Ar_2)$), 7.13-7.12 (m, 1H, $H_4(Ar_1)$), 7.11-7.10 (m, 1H, $H_2(Ar_2)$), 7.04-7.02 (m, 1H, $H_6(Ar_2)$), 6.82-6.79 (m, 1H, $H_4(Ar_2)$), 3.84 (s, 3H, OMe_1), 3.82 (s, 3H, OMe_2), 3.56-3.51 (m, 1H, H_5), 2.71 (br. s, 1H, OH), 2.59 (dd, ^2J=14.3 Hz, ^3J=7.5 Hz, 1H, H_4), 1.98 (dd, ^2J=14.3 Hz, ^3J=6.7 Hz, 1H, $H_{4'}$), 1.37 (d, ^5J=2.1 Hz, 3H, 2-Me), 1.09 (d, ^3J=7.0 Hz, 3H, 5-Me). ^{13}C NMR: (100.6 MHz, $CDCl_3$): δ = 198.0 (C=O), 160.0 ($C_3(Ar_2)$), 159.7 ($C_3(Ar_1)$), 147.2 ($C_1(Ar_2)$), 146.4 (C_1), 144.7 (C_2), 139.3 ($C_1(Ar_1)$), 129.9 ($C_5(Ar_2)$), 129.4 ($C_5(Ar_1)$), 122.1-111.5 ($6C_{Aryl}$), 88.6 (C_3), 55.5 (OMe_2), 55.3 (OMe_1), 50.9 (C_4), 39.9 (C_5), 19.4 (5-Me), 12.1 (2-Me). IR (film): ν = 3460, 3075, 3054, 3001, 2959, 2940, 2870, 2836, 1647, 1596, 1582, 1486, 1453, 1432, 1376, 1320, 1287, 1204, 1158, 1132, 1112, 1085, 1045, 995, 974, 940, 910, 875, 835, 808, 788, 764, 733, 705, 688.

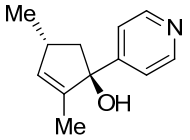
[3-Hydroxy-2,5-dimethyl-3-(2-naphthyl)-1-cyclopentenyl]-(2-naphthyl)methanone (4c).



^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 8.43-8.42 (m, 1H, $H_1(Naph_1)$), 8.08-8.09 (m, 1H, $H_1(Naph_2)$), 8.03-7.85, 7.63-7.47 (m, 12H, H_{Naph}), 3.69-3.64 (m, 1H, H_5), 2.70 (dd, ^2J=14.4 Hz, ^3J=7.5 Hz, 1H, H_4), 2.28 (s, 1H, OH), 2.15 (dd, ^2J=14.4 Hz, ^3J=6.7 Hz, 1H, $H_{4'}$), 1.41 (d, ^5J=1.8 Hz, 3H, 2-Me), 1.18 (d, ^3J=7.0 Hz, 3H, 5-Me). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 197.8 (C=O), 146.2 (C_1), 145.4-124.1 (C_2, $20C_{Naph}$), 89.1 (C_3), 50.9 (C_4), 40.3 (C_5), 19.5 (5-Me), 12.2 (2-Me). IR (film): ν = 3413, 3056, 3021, 2957, 2926, 2868, 2854, 1641, 1622,

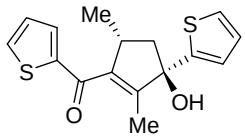
1597, 1506, 1465, 1437, 1376, 1354, 1311, 1275, 1223, 1189, 1126, 1106, 978, 907, 863, 820, 781, 763, 748, 733.

2,4-Dimethyl-1-(4-pyridinyl)-2-cyclopenten-1-ol (4d').



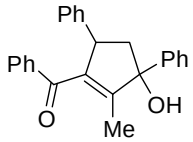
^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 8.54-8.52 (m, 2H, $H_{2,6}$(Pyr)), 7.33-7.32 (m, 2H, $H_{3,5}$(Pyr)), 5.64-5.63 (m, 1H, H_3), 3.01-2.92 (m, 1H, H_4), 2.64 (br. s, 1H, OH), 2.48 (dd, ^2J=14.4 Hz, ^3J=7.6 Hz, 1H, H_5), 1.78 (dd, ^2J=14.4 Hz, ^3J=6.0 Hz, 1H, $H_{5'}$), 1.46 (d, ^5J=1.6 Hz, 3H, 2-Me), 1.09 (d, ^3J=7.0 Hz, 3H, 4-Me). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 155.5 (C_4(Pyr)), 149.7 ($C_{2,6}$(Pyr)), 141.8 (C_2), 137.1 (C_3), 120.9 ($C_{3,5}$(Pyr)), 87.7 (C_1), 52.2 (C_5), 37.0 (C_4), 21.0 (4-Me), 11.9 (2-Me). IR (film): ν = 3199, 3083, 3060, 3029, 2956, 2925, 2868, 1600, 1553, 1437, 1412, 1373, 1353, 1225, 1122, 1102, 1067, 1034, 1001, 961, 930, 822, 662, 559.

[3-Hydroxy-2,5-dimethyl-3-(2-thienyl)-1-cyclopentenyl](2-thienyl)methanone (4e).



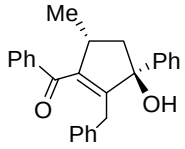
^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.69-7.68 (m, 1H, H_5(Thioph$_1$)), 7.67-7.66 (m, 1H, H_3(Thioph$_1$)), 7.24-7.23 (m, 1H, H_4(Thioph$_1$)), 7.13-7.11 (m, 1H, H_4(Thioph$_2$)), 7.01-6.99 (m, 2H, $H_{3,5}$(Thioph$_2$), 3.51-3.45 (m, 1H, H_5), 3.24 (br. s, 1H, OH), 2.70 (dd, ^2J=14.3 Hz, ^3J=7.6 Hz, 1H, H_4), 2.12 (dd, ^2J=14.3 Hz, ^3J=6.3 Hz, 1H, $H_{4'}$), 1.56 (d, ^5J=2.0 Hz, 3H, 2-Me), 1.10 (d, ^3J=7.0 Hz, 3H, 5-Me). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 189.8 (C=O), 150.6 (C_2(Thioph$_1$)), 145.0 (C_1), 144.6 (C_2), 144.0 (C_2(Thioph$_2$)), 135.2 (C_4(Thioph$_1$)), 134.5 (C_5(Thioph$_1$)), 128.5 (C_3(Thioph$_1$)), 127.1 (C_5(Thioph$_2$)), 124.5 (C_3(Thioph$_2$)), 123.3 (C_4(Thioph$_2$)), 87.0 (C_3), 51.0 (C_4), 39.5 (C_5), 19.4 (5-Me), 11.9 (2-Me). IR (film): ν = 3435, 3102, 3087, 3072, 2960, 2927, 2870, 1630, 1512, 1440, 1411, 1377, 1354, 1321, 1275, 1231, 1169, 1108, 1082, 1037, 987, 909, 846, 810, 730, 701.

(3-Hydroxy-2-methyl-3,5-diphenyl-1-cyclopentenyl)-(phenyl)methanone (4f).



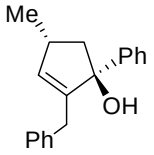
A mixture of two diastereomers in a 3:1 ratio. IR (film): ν = 3384, 3081, 3059, 3024, 3003, 2918, 2850, 1616, 1595, 1577, 1492, 1448, 1389, 1335, 1292, 1268, 1222, 1207, 1139, 1074, 1051, 1025, 969, 922, 875, 761, 737, 698. ^{1}H NMR (400.1 MHz, $CDCl_3$, major isomer): δ = 7.81-7.79 (m, 2H, H_{o1}), 7.52-7.50 (m, 1H, H_{p1}), 7.47-7.46 (m, 2H, H_{o2}), 7.42-7.40 (m, 4H, $H_{m1,2}$), 7.30-7.29 (m, 1H, H_{p2}), 7.25-7.23 (m, 2H, H_{o3}), 7.19-7.18 (m, 2H, H_{m3}), 7.09-7.07 (m, 1H, H_{p3}), 4.40-4.35 (m, 1H, H_5), 2.92 (dd, ^{2}J=13.6 Hz, ^{3}J=7.8 Hz, 1H, H_4), 2.31 (dd, ^{2}J=13.6 Hz, ^{3}J=7.9 Hz, 1H, $H_{4'}$), 2.27 (s, 1H, OH), 1.59 (d, ^{5}J=2.3 Hz, 3H, 2-Me). ^{13}C NMR (100.6 MHz, $CDCl_3$, major isomer): δ = 196.1 (C=O), 149.2 (C_1), 144.6 (C_{i2}), 142.3 (C_2), 142.8 (C_{i3}), 138.1 (C_{i1}), 132.8 (C_{p1}), 130.0 (C_{o1}), 128.7 (C_{m1}), 128.5 (C_{m3}), 128.3 (C_{m2}), 127.6 (C_{o3}), 127.4(C_{p2}), 126.5(C_{p3}), 124.7 (C_{o2}), 87.4 (C_3), 51.3 (C_4), 39.8 (C_5), 12.2 (2-Me). ^{1}H NMR (400.1 MHz, $CDCl_3$, minor isomer): δ = 4.75-4.70 (m, 1H, H_5), 2.84 (dd, ^{2}J = 14.7 Hz, ^{3}J=7.6 Hz, 1H, H_4), 2.31 (dd, ^{2}J=14.7 Hz, ^{3}J=8.1 Hz, 1H, $H_{4'}$), 2.14 (s, 1H, OH), 1.48 (d, ^{5}J=2.1 Hz, 3H, 2-Me).

(2-Benzyl-3-hydroxy-5-methyl-3-phenyl-1-cyclopentenyl)-(phenyl)methanone (4g).



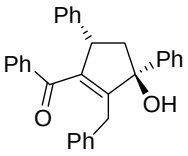
^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.93-7.91 (m, 2H, H_{o1}), 7.51-7.49 (m, 1H, H_{p1}), 7.41-6.70 (m, 12H, H_{Ph}), 3.59-3.54 (m, 1H, H_5), 3.42 (d, ^{2}J=14.9 Hz, 1H, Ph-C$\underline{H}_2$), 2.99 (d, ^{2}J=14.9 Hz, 1H, Ph-C$\underline{H}_2$), 2.52 (dd, ^{2}J=13.9 Hz, ^{3}J=7.0 Hz, 1H, H_4), 1.86 (dd, ^{2}J=13.9 Hz, ^{3}J=7.7 Hz, 1H, $H_{4'}$), 1.54 (s, 1H, OH), 1.06 (d, ^{3}J=7.0 Hz, 3H, 5-Me). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 198.2 (C=O), 147.5 (C_1), 146.9 (C_{i3}), 145.7 (C_2), 138.1 (C_{i2}), 137.7 (C_{i1}), 133.6 (C_{p1}), 129.2-128.4 ($C_{o1,2}$), $C_{m1,2,3}$), 127.1 (C_{p3}), 126.8 (C_{p2}), 125.9 (C_{o3}), 89.2 (C_3), 51.9 (C_4), 40.6 (Ph-$\underline{C}H_2$), 33.3 (C_5), 19.0 (5-Me). IR (film): ν = 3566, 3438, 3084, 3061, 3028, 2959, 2927, 2869, 1652, 1597, 1580, 1494, 1449, 1318, 1291, 1267, 1209, 1107, 1074, 1024, 1001, 992, 971, 946, 912,876, 762, 729, 701.

2-Benzyl-4-methyl-1-phenyl-2-cyclopenten-1-ol (4g').



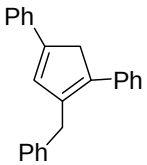
^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.42-7.40 (m, 2H, H_{o1}), 7.37-7.33 (m, 2H, H_{m1}), 7.24-7.23 (m, 2H, H_{m2}), 7.22-7.21 (m, 1H, H_{p1}), 7.17-7.16 (m, 1H, H_{p2}), 7.05-7.03 (m, 2H, H_{o2}), 5.41 (d, ^4J=1.6 Hz, 1H, H_3), 3.09-3.08 (m, 2H, Ph-C$\underline{H}_2$), 2.97-2.91 (m, 1H, H_4), 2.47 (dd, ^2J=14.3 Hz, ^3J=7.4 Hz, 1H, H_5), 1.82 (dd, ^2J=14.3 Hz, ^3J=6.2 Hz, 1H, $H_{5'}$), 1.71 (s, 1H, OH), 1.05 (d, ^3J=7.0 Hz, 3H, 4-Me). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 147.0 (C_2), 146.4 (C_{i1}), 139.8 (C_{i2}), 137.1 (C_3), 129.3 (C_{o2}), 128.5 (C_{m2}), 128.3 (C_{m1}), 126.6 (C_{p1}), 126.2 (C_{p2}), 125.7 (C_{o1}), 88.7 (C_1), 53.0 (C_5), 36.9 (Ph-$\underline{C}H_2$), 33.8 (C_4), 20.9 (4-Me). IR (film): ν = 3448, 3085, 3060, 3027, 2956, 2926, 2904, 2868, 1677, 1600, 1494, 1448, 1373, 1336, 1286, 1214, 1175, 1100, 1074, 1054, 1031, 982, 954, 858, 761, 701.

(2-Benzyl-3-hydroxy-3,5-diphenyl-1-cyclopentenyl)-(phenyl)methanone (4h).



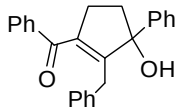
^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.67-7.65 (m, 2H, H_{o1}), 7.49-6.95 (m, 18H, H_{Ph}), 4.45-4.41 (m, 1H, H_5), 3.60 (d, ^2J=14.9 Hz, 1H, Ph-C$\underline{H}_2$), 3.23 (d, ^2J=14.9 Hz, 1H, Ph-C$\underline{H}_2$), 2.96 (dd, ^2J=13.9 Hz, ^3J=8.4 Hz, 1H, H_4), 2.34 (dd, ^2J=13.9 Hz, ^3J=6.42 Hz, 1H, $H_{4'}$), 1.93 (s, 1H, OH). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 196.6 (C=O), 150.2 (C_1), 145.4 (C_{i4}), 144.0 (C_{i3}), 142.3 (C_{i2}), 138.8 (C_{i1}), 133.0 (C_2), 129.3 (C_{p1}), 128.9-125.1 (19C_{Ph}), 88.8 (C_3), 52.5 (C_4), 52.0 (C_5), 33.0 (Ph-$\underline{C}H_2$). IR (film): ν = 3370, 3103, 3060, 3026, 2967, 2925, 1621, 1596, 1578, 1494, 1449, 1391, 1326, 1298, 1212, 1170, 1127, 1104, 1068, 982, 909, 760, 732, 701, 692.

1-(2-Benzyl-4-phenyl-1,3-cyclopentadienyl)benzene (4h'').



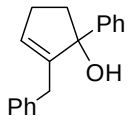
^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.46-7.12 (m, 15H, H_{Ph}), 6.70 (s, 1H, H_3), 3.91 (s, 2H, H_5), 3.82 (s, 2H, Ph-C$\underline{H}_2$). ^{13}C NMR(100.6 MHz, $CDCl_3$): δ = 144.9 (C_1), 140.6 (C_4), 140.3 (C_{i2}), 140.2 (C_3), 137.2 (C_{i3}), 135.9 (C_{i1}), 131.6-125.0 (15C_{Ph}, C_2), 44.1 (C_5), 34.5 (Ph-$\underline{C}H_2$). IR (film): ν = 3081, 3059, 3027, 2920, 2898, 2850, 1948, 1882, 1811, 1722, 1689, 1597, 1493, 1452, 1374, 1273, 1201, 1182, 1156, 1073, 1030, 914, 858, 751, 724, 696.

(2-Benzyl-3-hydroxy-3-phenyl-1-cyclopentenyl)(phenyl)-methanone (4i).

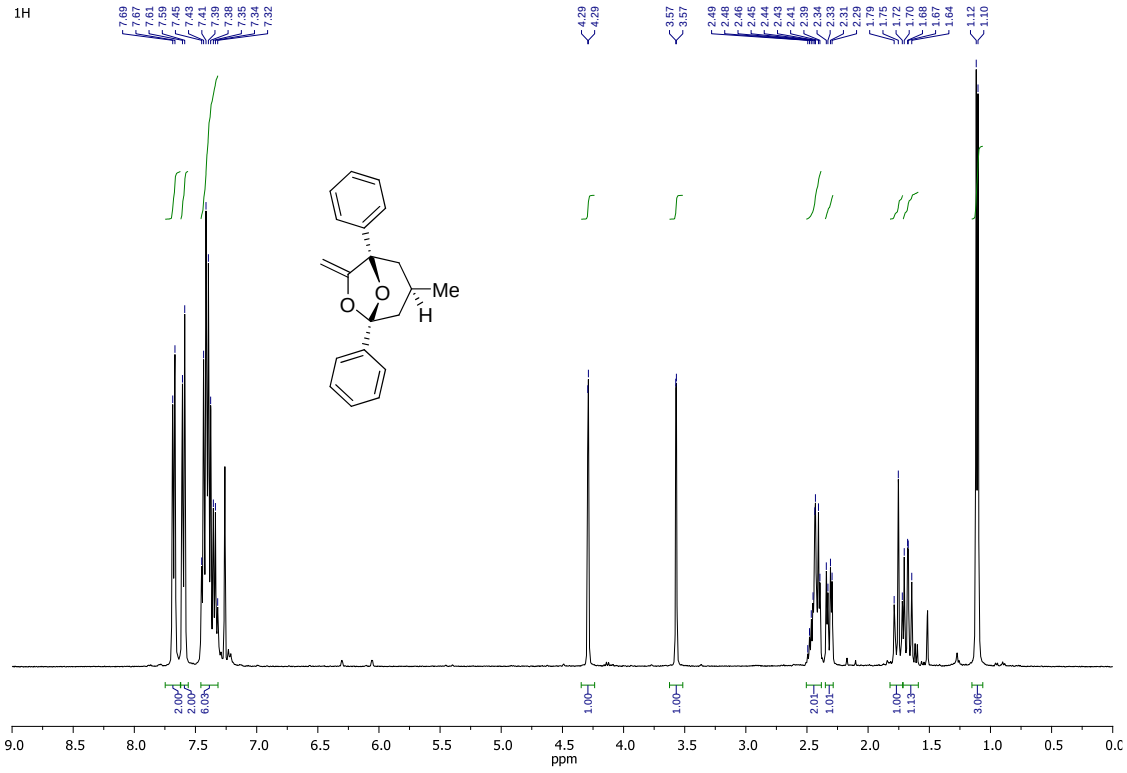


^{1}H NMR (400.1 MHz, C_6D_6): δ = 7.83-7.81 (m, 2H, H_{o1}), 7.41-7.39 (m, 2H, H_{o2}), 7.16-6.97, 6.87-6.78 (m, 11H, H_{Ph}), 3.49 (d, ^2J=14.8 Hz, 1H, Ph-C$\underline{H}_2$), 3.08 (d, ^2J=14.8 Hz, 1H, Ph-C$\underline{H}_2$), 2.78-2.73 (m, 1H, H_5), 2.48-2.43 (m, 1H, $H_{5'}$), 2.17-2.10 (m, 1H, H_4), 2.06-1.99 (m, 1H, $H_{4'}$), 1.53 (s, 1H, OH). ^{13}C NMR (100.6 MHz, C_6D_6): δ = 196.7 (C=O), 149.1 (C_1), 146.2 (C_{i3}), 141.3 (C_2), 139.0 (C_{i2}), 137.8 (C_{i1}), 133.0 (C_{p1}), 129.6 (C_{o2}), 129.2 (C_{o1}), 128.7 (C_{m1}), 128.5 ($C_{m2,3}$), 127.1 (C_{p3}), 126.4 (C_{p2}), 125.7 (C_{o3}), 89.7 (C_3), 42.8 (C_4), 33.5 (Ph-$\underline{C}H_2$), 33.0 (C_5). IR (film): ν = 3331, 3083, 3060, 3026, 2963, 2918, 2850, 1662, 1629, 1595, 1493, 1447, 1385, 1273, 1174, 1135, 1069, 1022, 923, 885, 770, 717, 703, 689.

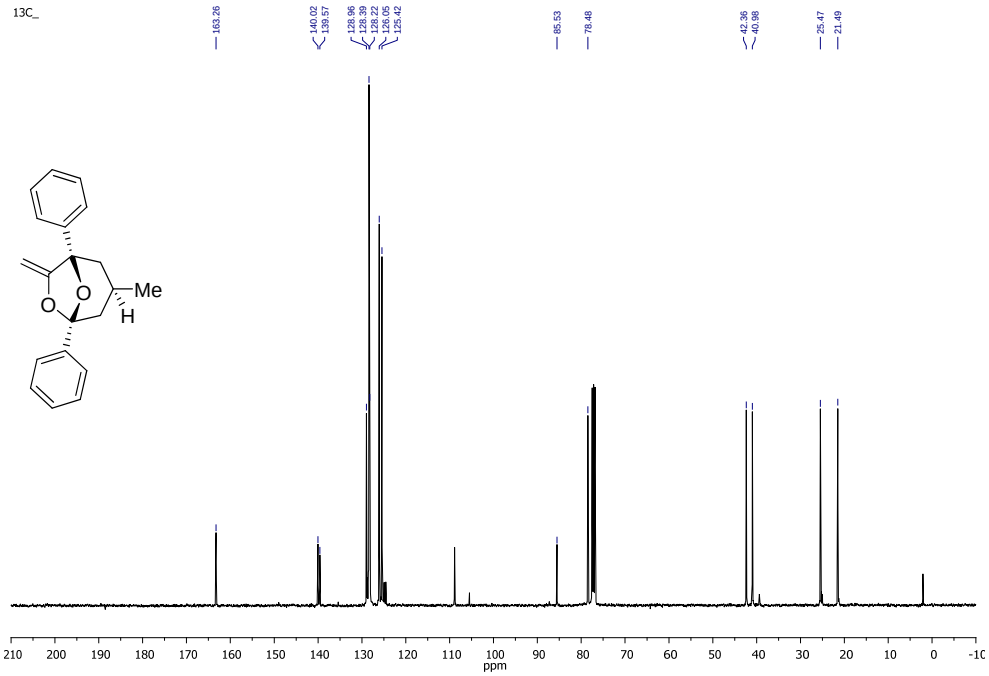
2-Benzyl-1-phenyl-2-cyclopenten-1-ol (4i').



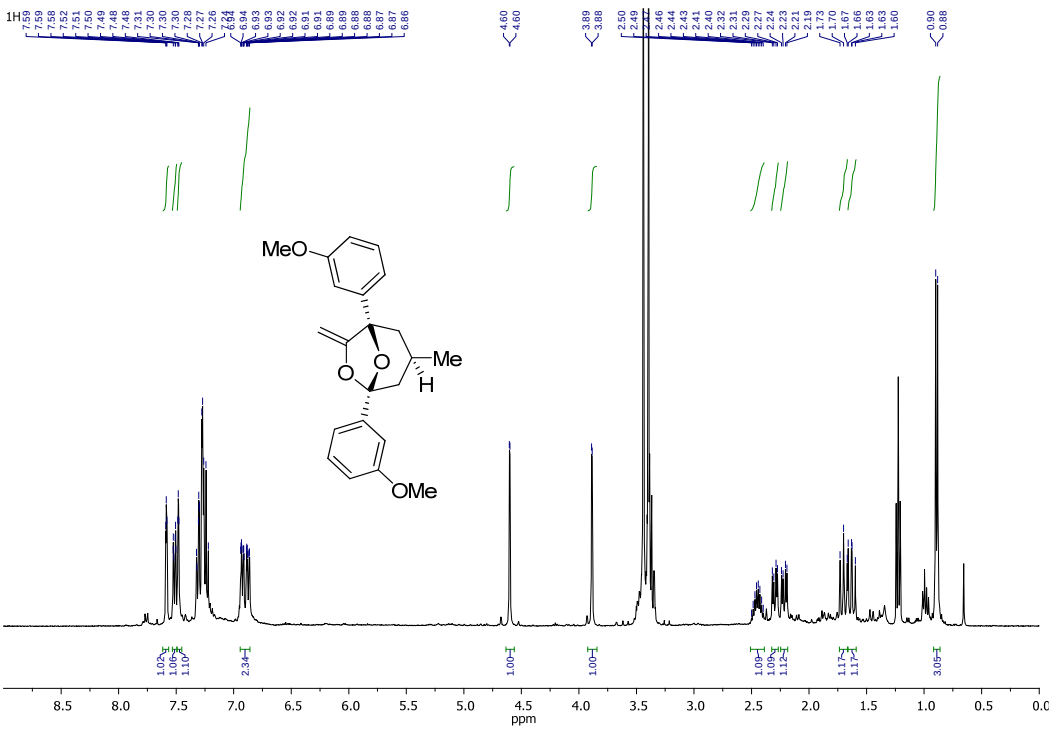
^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.40-7.38 (m, 2H, H_{o1}), 7.35-7.32 (m, 2H, H_{m1}), 7.25-7.24 (m, 2H, H_{m2}), 7.23-7.22 (m, 1H, H_{p1}), 7.19-7.17 (m, 1H, H_{p2}), 7.07-7.05 (m, 2H, H_{o2}), 5.45-5.44 (m, 1H, H_3), 3.19-3.15, 3.10-3.06 (m, 2H, Ph-C$\underline{H}_2$), 2.47-2.43 (m, 1H, H_4), 2.32-2.30 (m, 1H, H_5), 2.25-2.21 (m, 1H, $H_{4'}$), 2.20-2.19 (m, 1H, $H_{5'}$), 1.82 (s, 1H, OH). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 148.5 (C_2), 146.2 (C_{i1}), 139.9 (C_{i2}), 129.9 (C_3), 129.3 (C_{o2}), 128.5 (C_{m2}), 128.4 (C_{m1}), 126.7 (C_{p1}), 126.2 (C_{p2}), 125.2 (C_{o1}), 88.2 (C_1), 44.0 (C_5), 33.6 (Ph-$\underline{C}H_2$), 29.6 (C_4). IR (film): ν = 3566, 3448, 3084, 3059, 3027, 2964, 2930, 2905, 2853, 1951, 1881, 1811, 1751, 1681, 1600, 2581, 1497, 1448, 1361, 1334, 1298, 1281, 1222, 1176, 1089, 1059, 1028, 1002, 982, 942, 912, 846, 766, 701.



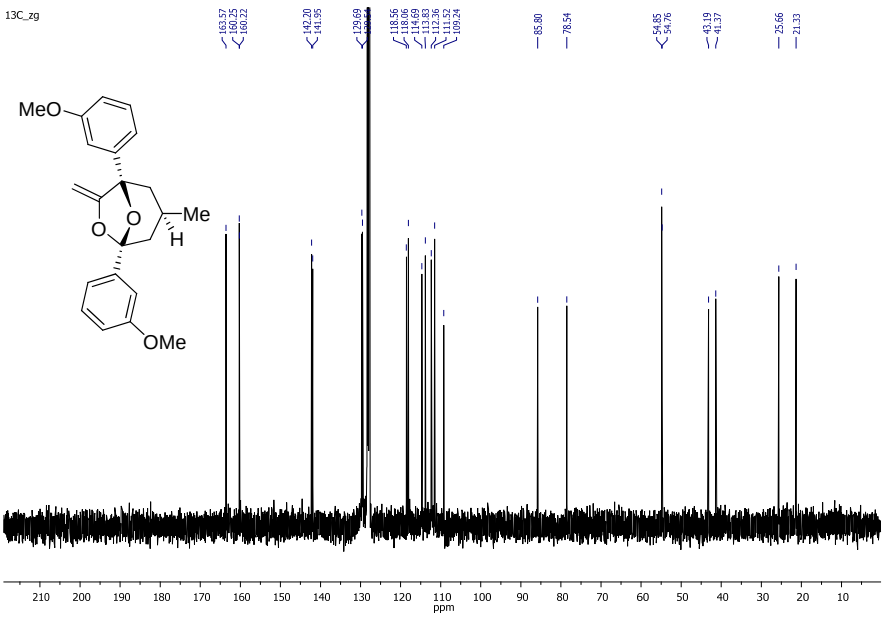
^{1}H NMR Spectrum of **3a** (400.1 MHz, $CDCl_3$)



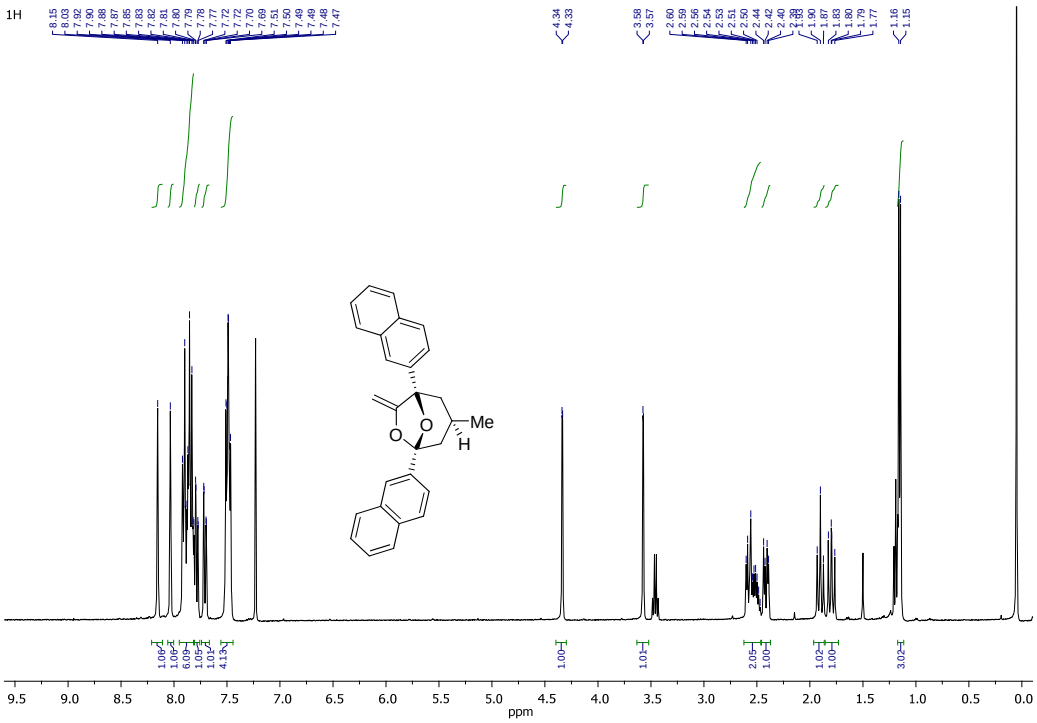
^{13}C NMR Spectrum of **3a** (100.6 MHz, $CDCl_3$)



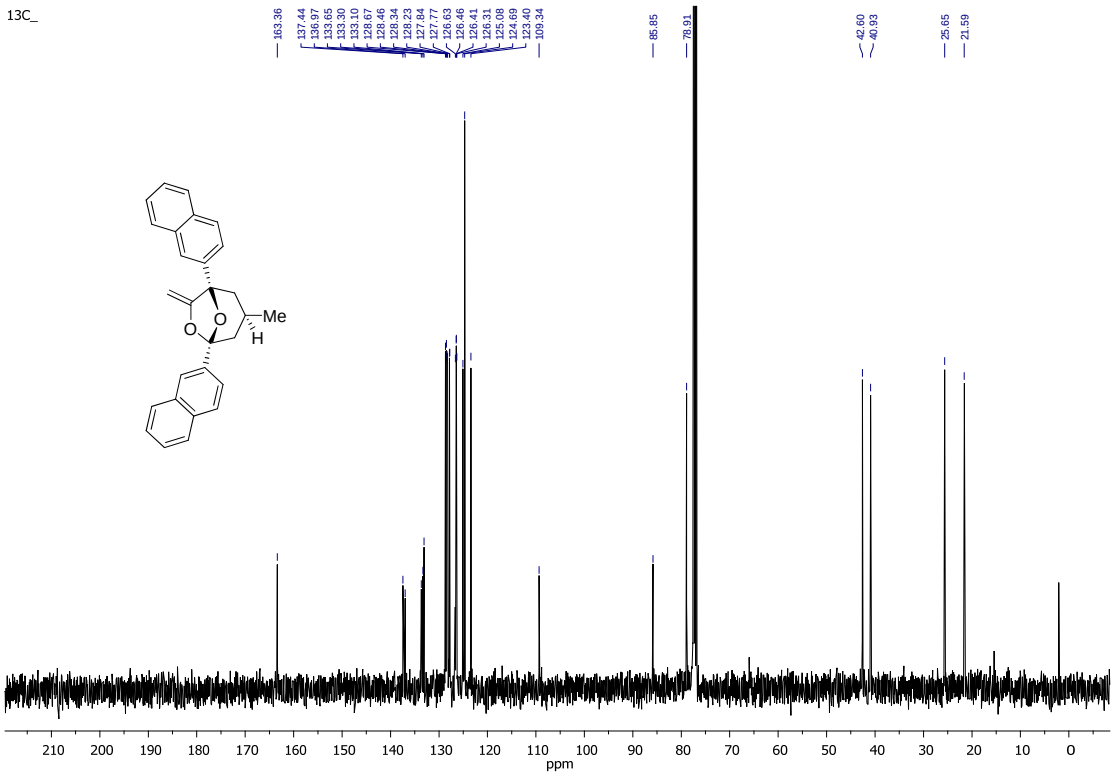
^{1}H NMR Spectrum of **3b** (400.1 MHz, C_6D_6)



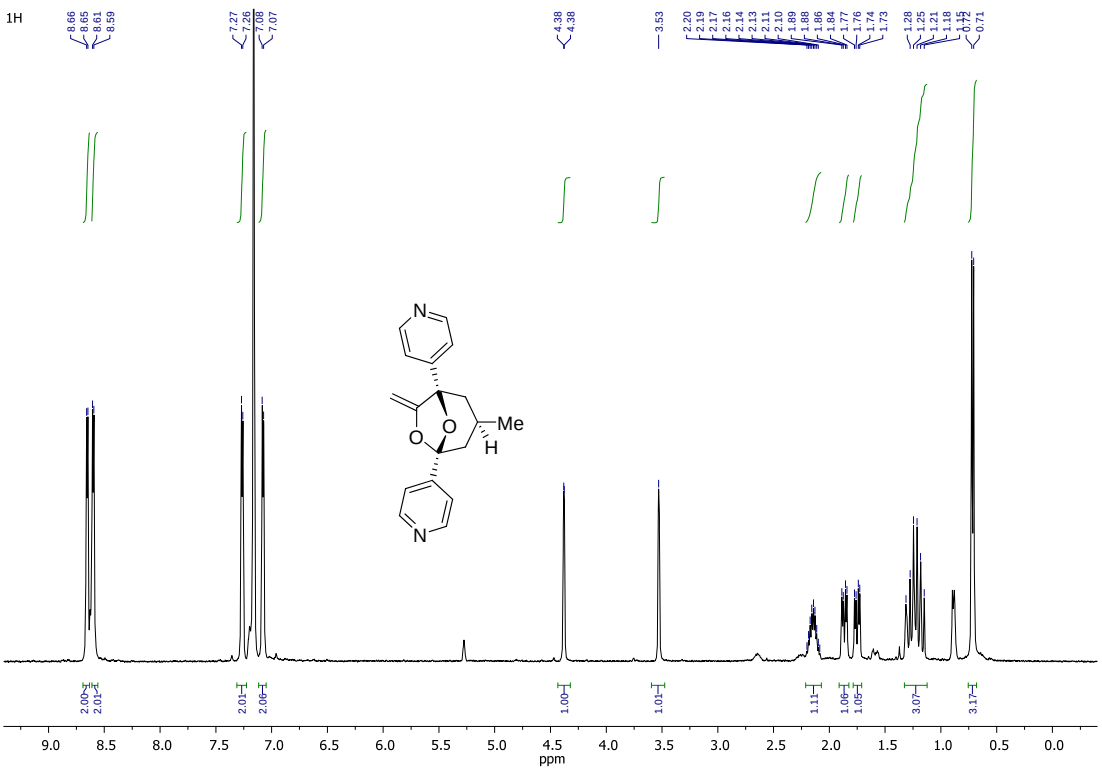
^{13}C NMR Spectrum of **3b** (100.6 MHz, C_6D_6)



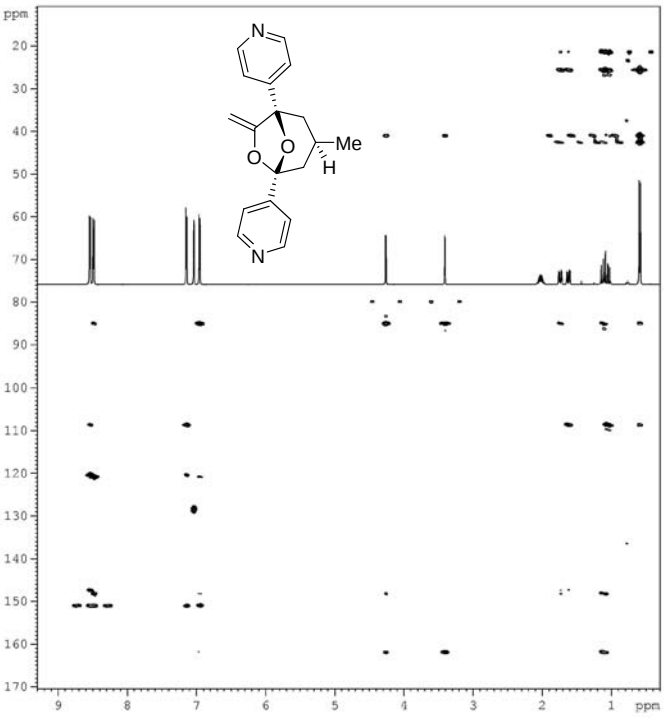
^{1}H NMR Spectrum of **3c** (400.1 MHz, $CDCl_3$)



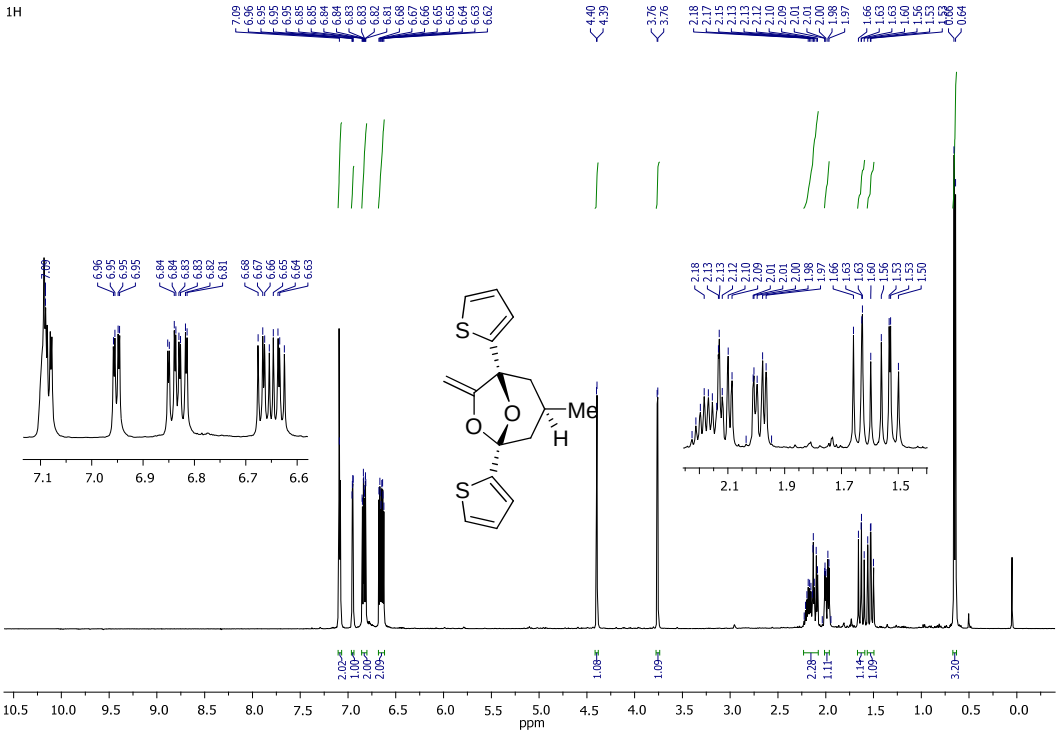
^{13}C NMR Spectrum of **3c** (100.6 MHz, $CDCl_3$)



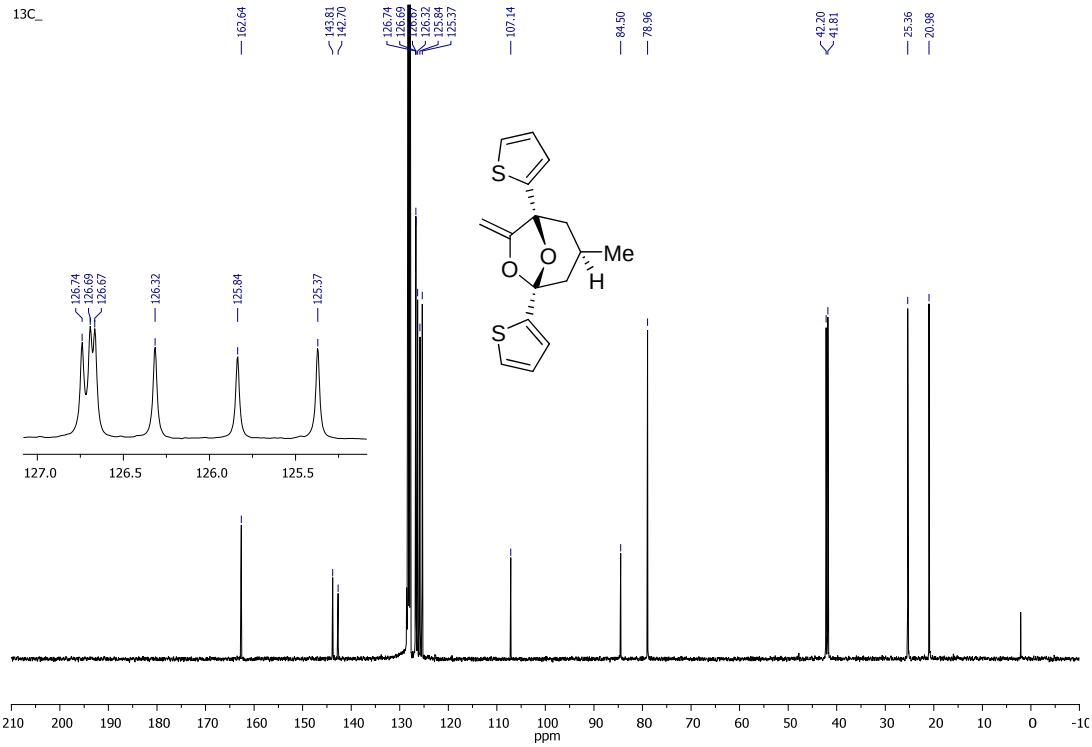
^{1}H NMR Spectrum of **3d** (400.1 MHz, C_6D_6)



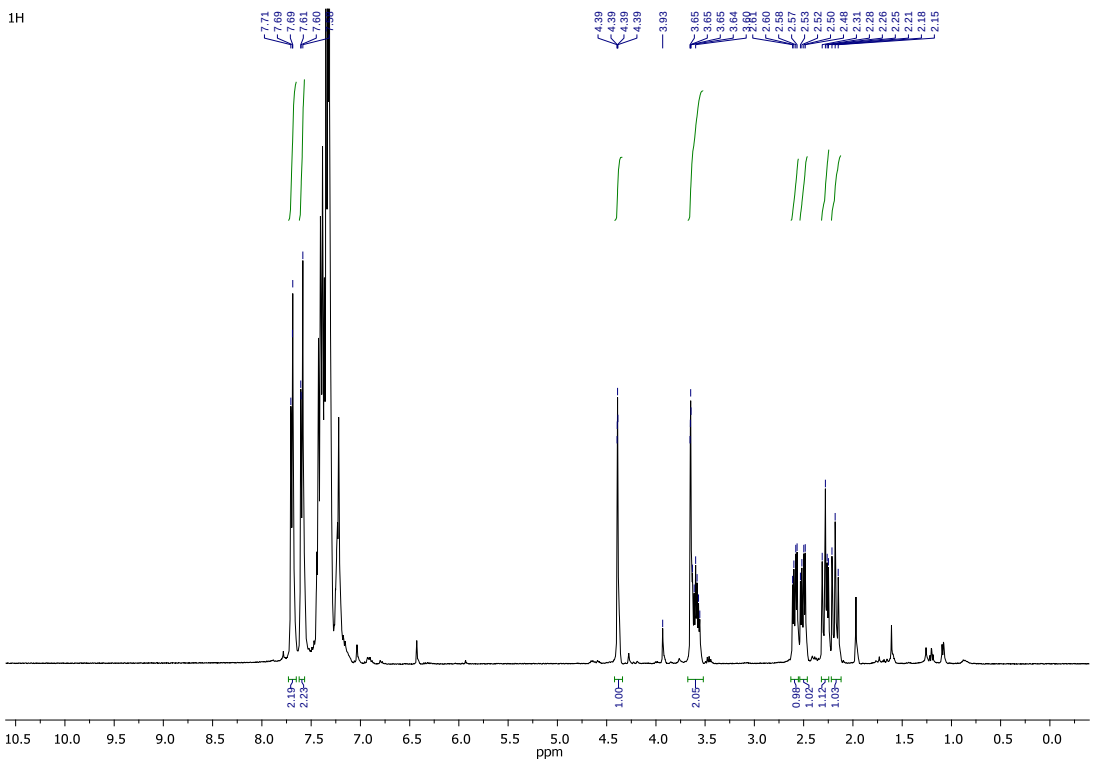
2D ^{1}H-^{13}C HMBC spectrum **3d**, C_6D_6



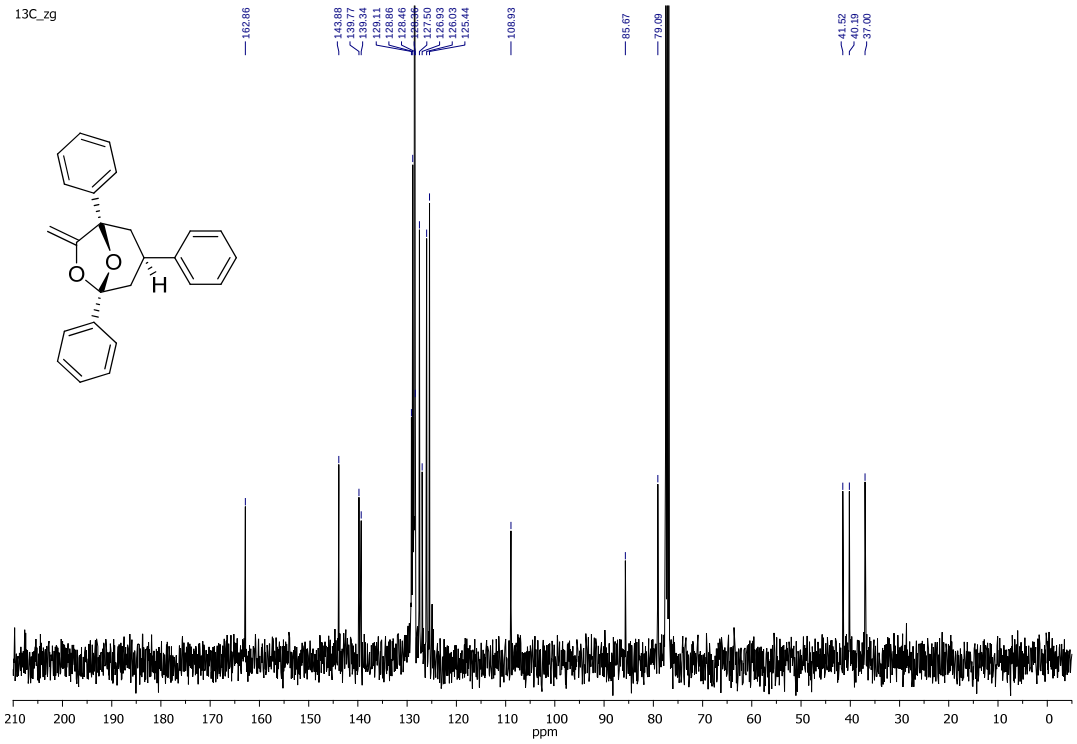
^{1}H NMR Spectrum of **3e** (400.1 MHz, C_6D_6)



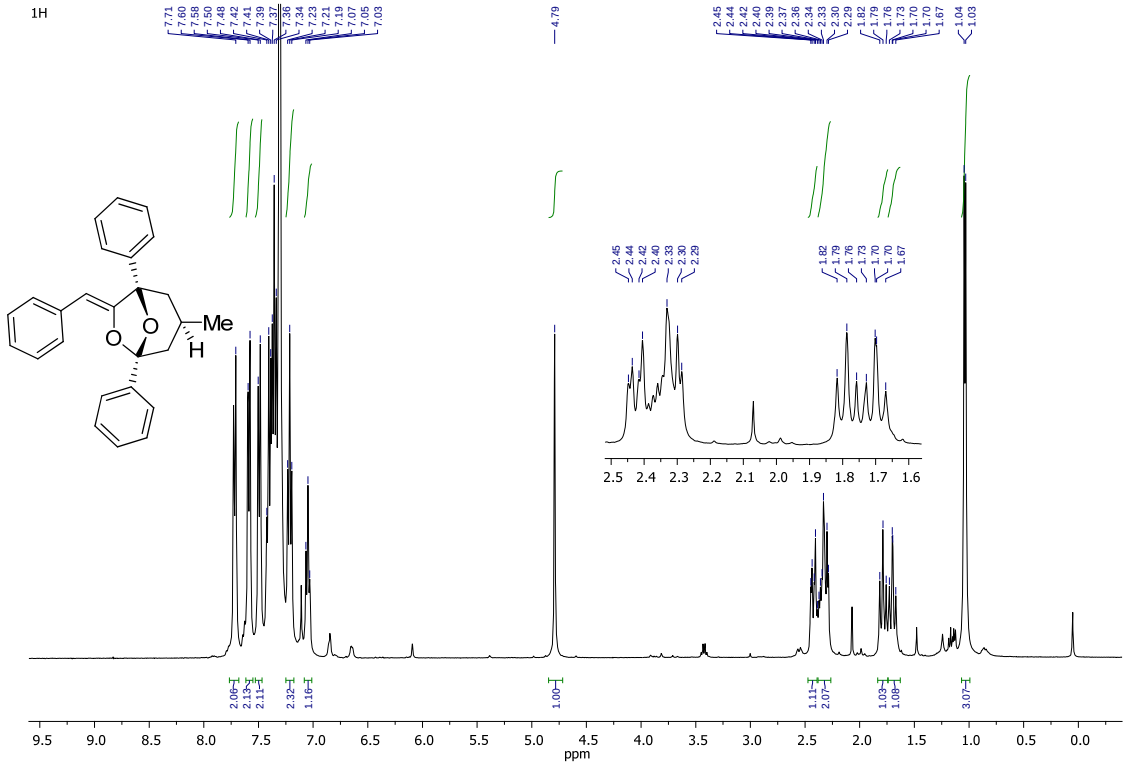
^{13}C NMR spectrum of **3e** (100.6 MHz, C_6D_6)



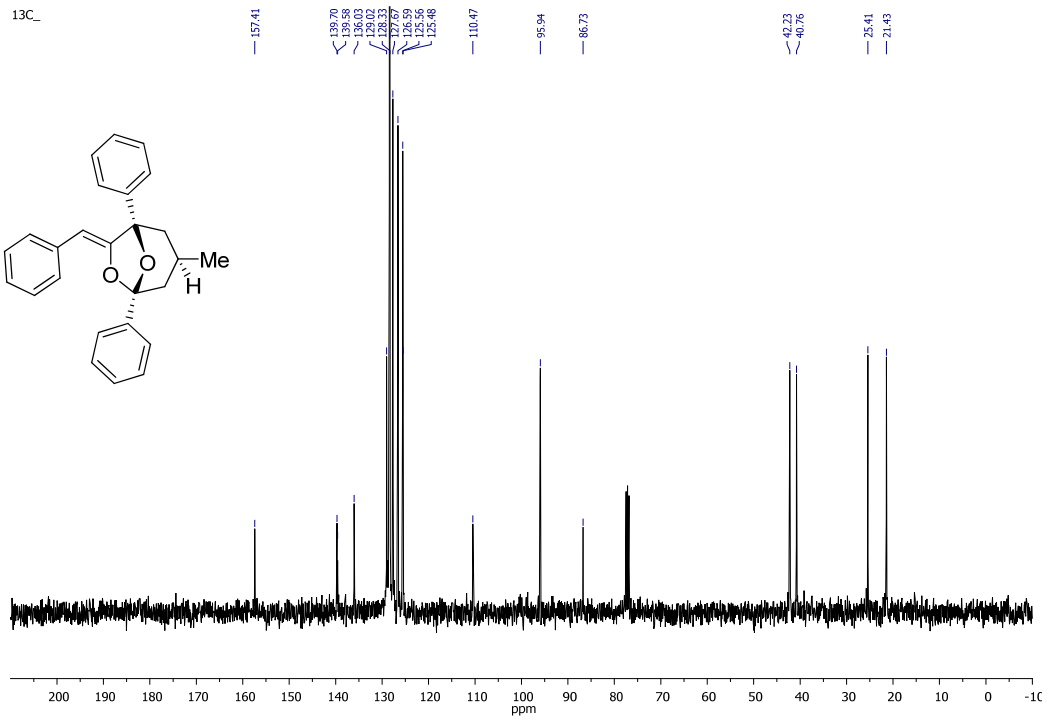
^{1}H NMR spectrum of **3f** (400.1 MHz, $CDCl_3$)



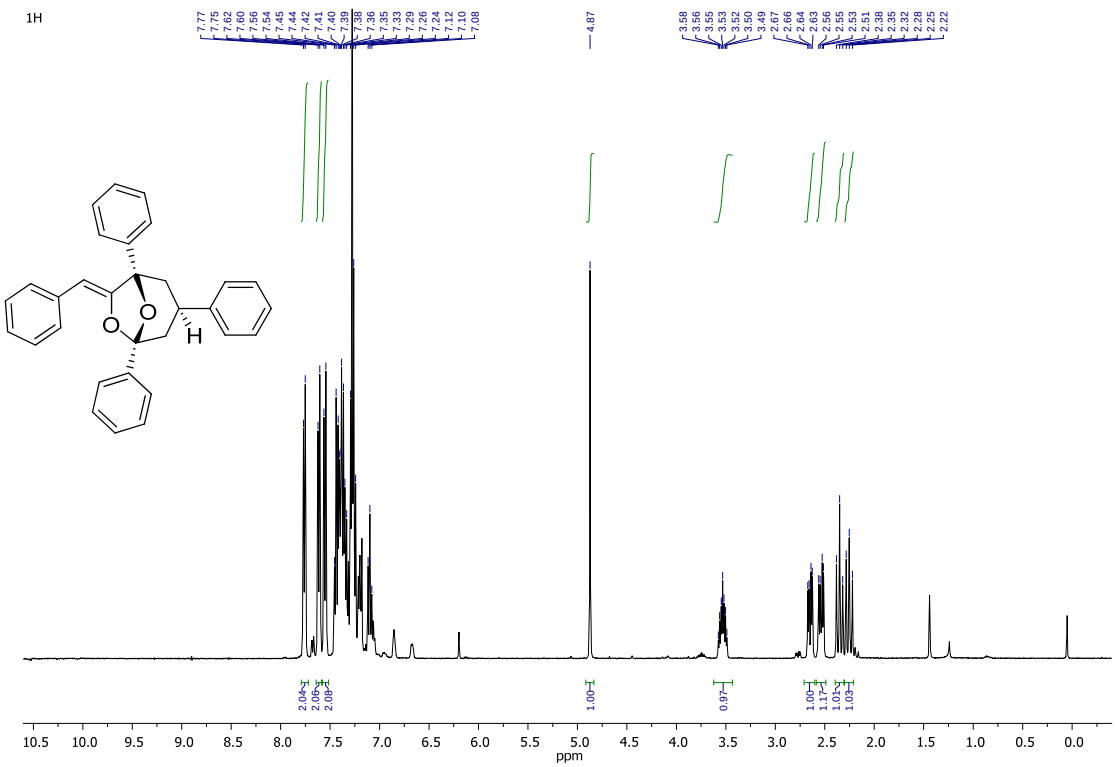
^{13}C NMR spectrum of **3f** (100.6 MHz, $CDCl_3$)



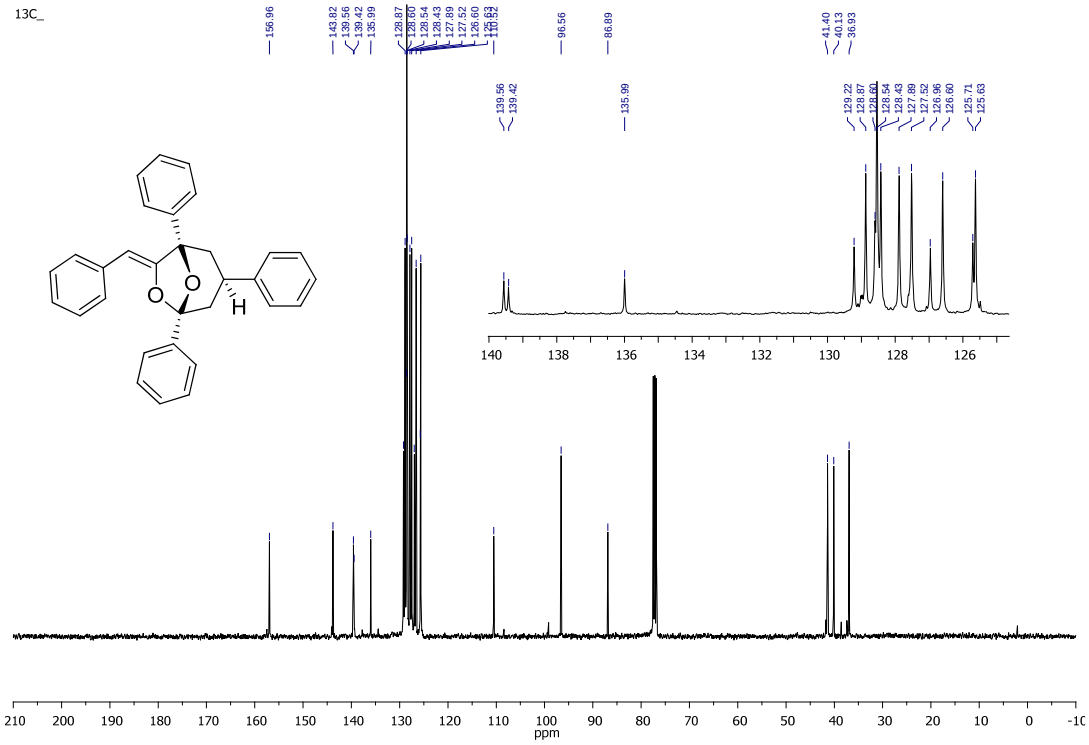
^{1}H NMR spectrum of **3g** (400.1 MHz, $CDCl_3$)



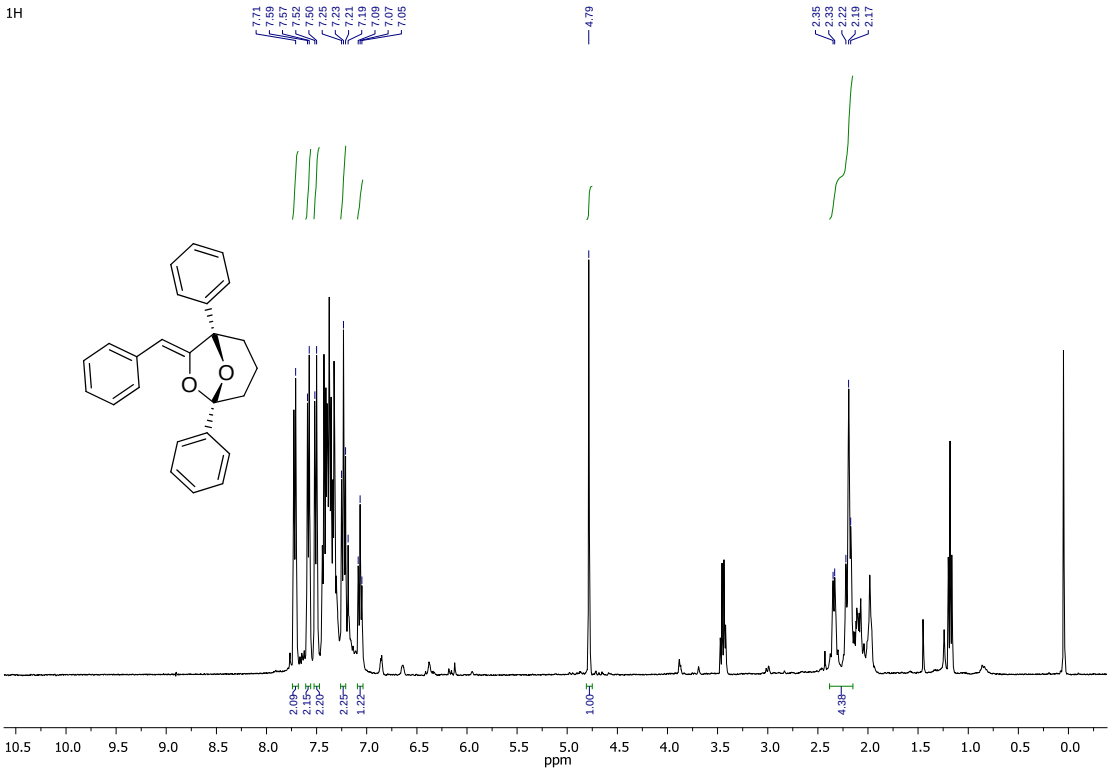
^{13}C NMR spectrum of **3g** (100.6 MHz, $CDCl_3$)



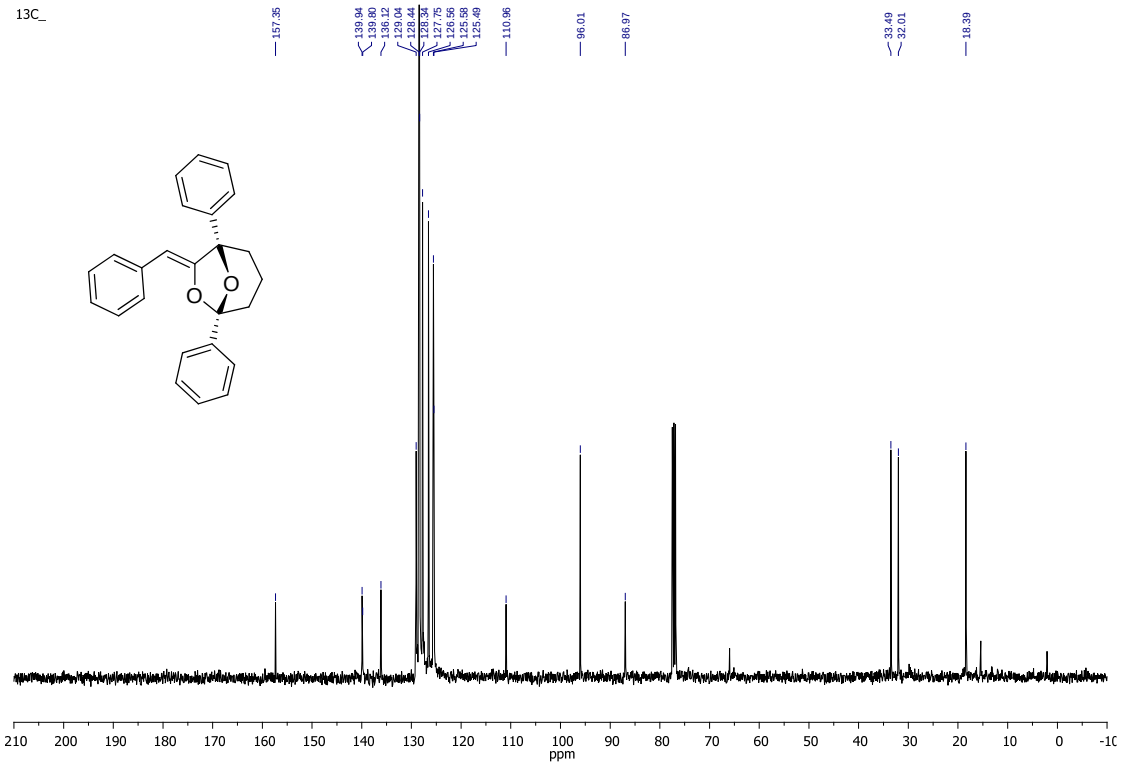
^{1}H NMR spectrum of **3h** (400.1 MHz, $CDCl_3$)



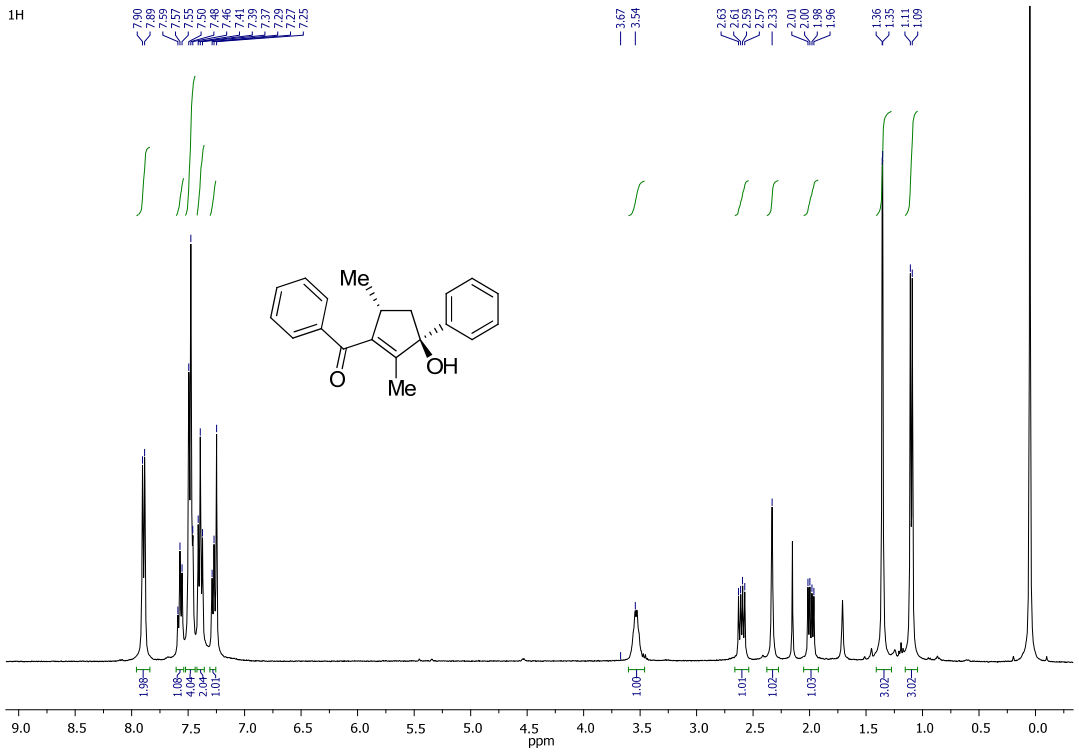
^{13}C NMR spectrum of **3h** (100.6 MHz, $CDCl_3$)



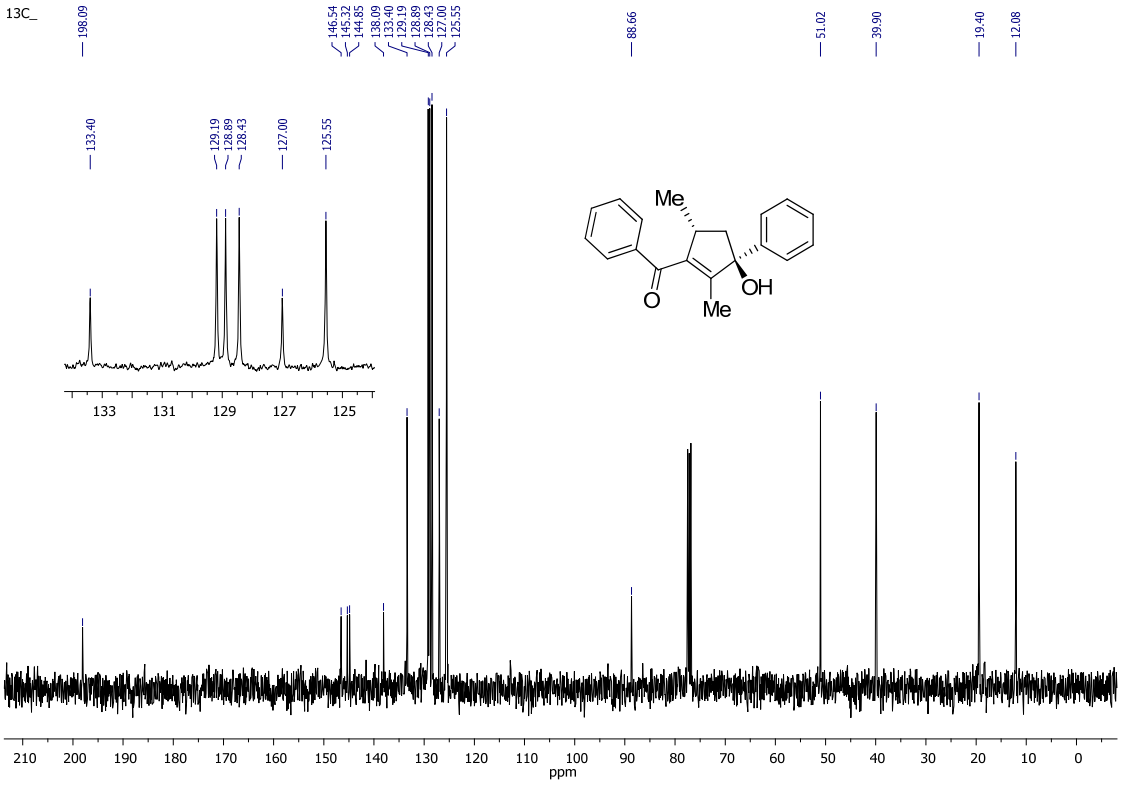
^{1}H NMR spectrum of **3i** (400.1 MHz, $CDCl_3$, ethyl ether)



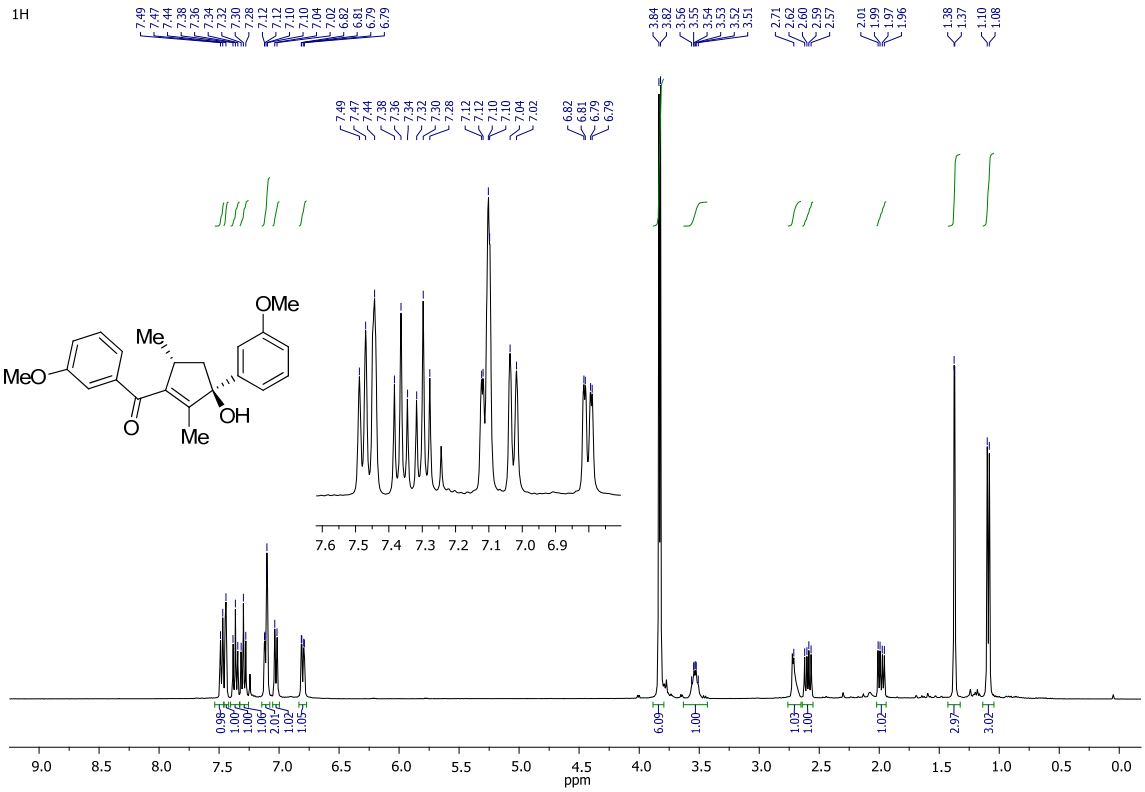
^{13}C NMR spectrum of **3i** (100.6 MHz, $CDCl_3$)



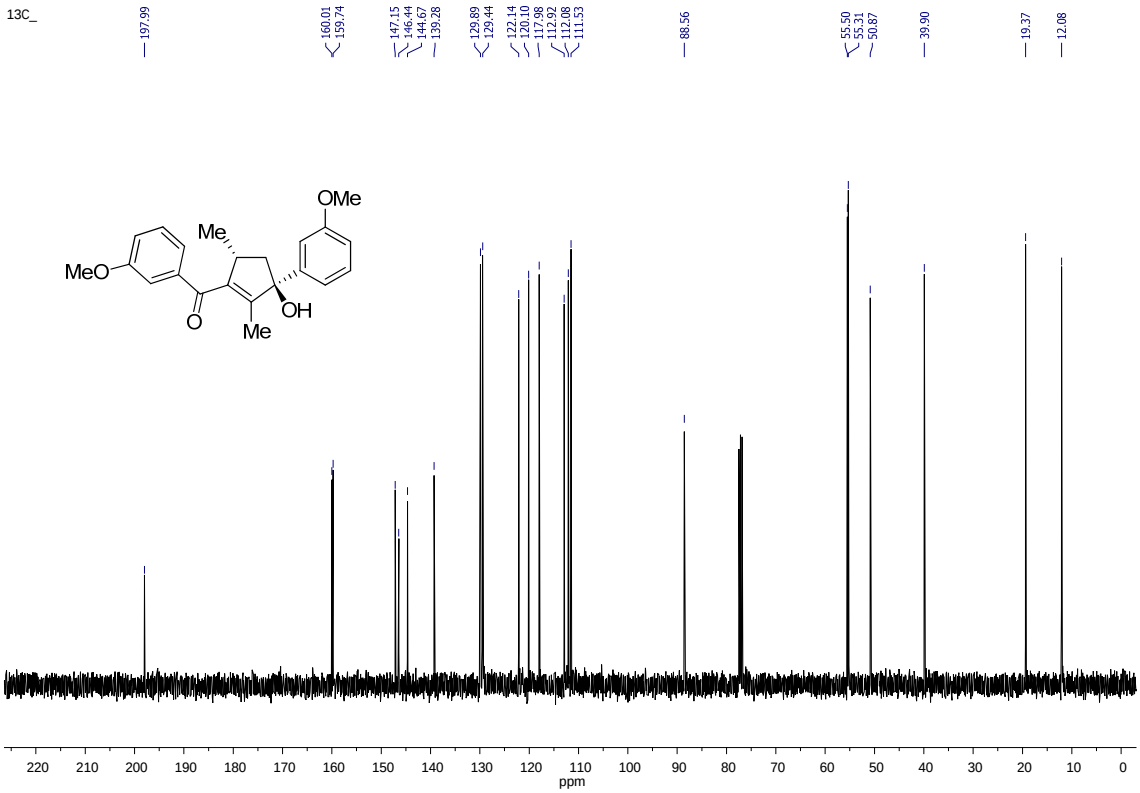
^{1}H NMR Spectrum of **4a** (400.1 MHz, $CDCl_3$)



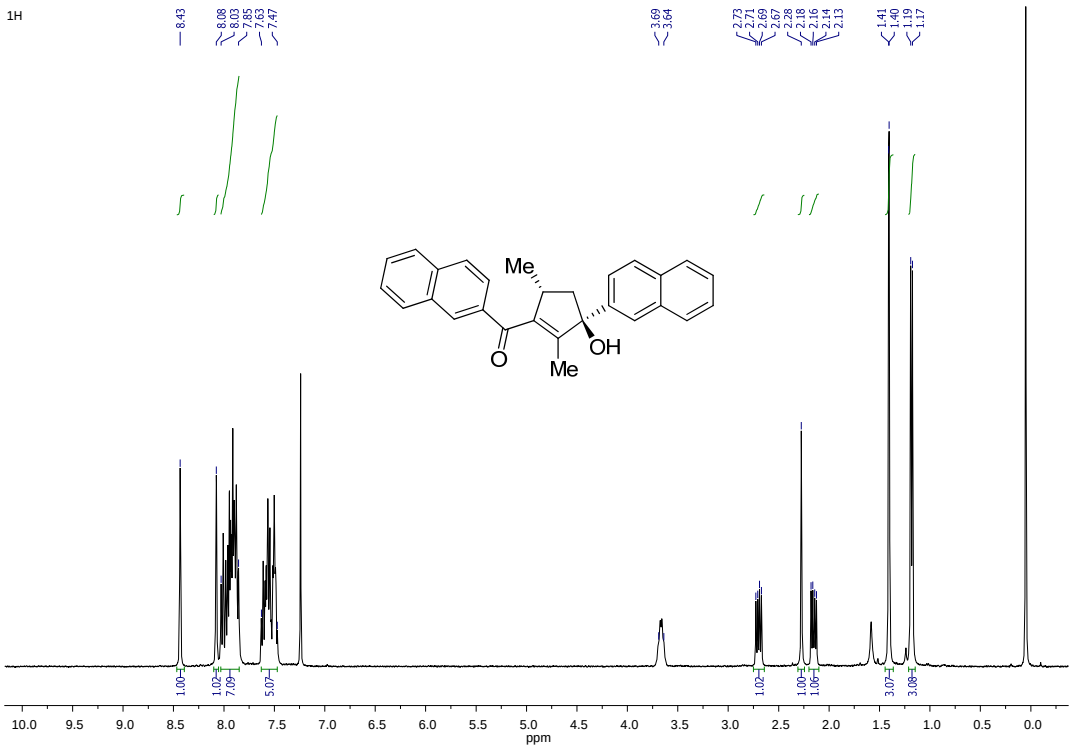
^{13}C NMR Spectrum of **4a** (100.6 MHz, $CDCl_3$)



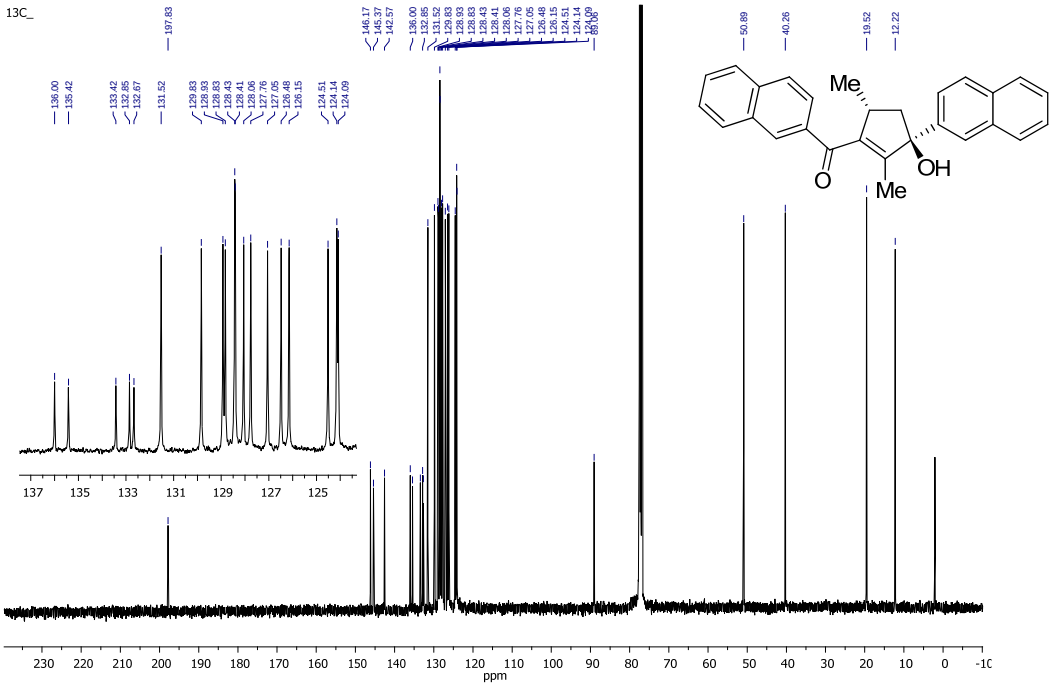
^{1}H NMR Spectrum of **4b** (400.1 MHz, $CDCl_3$)



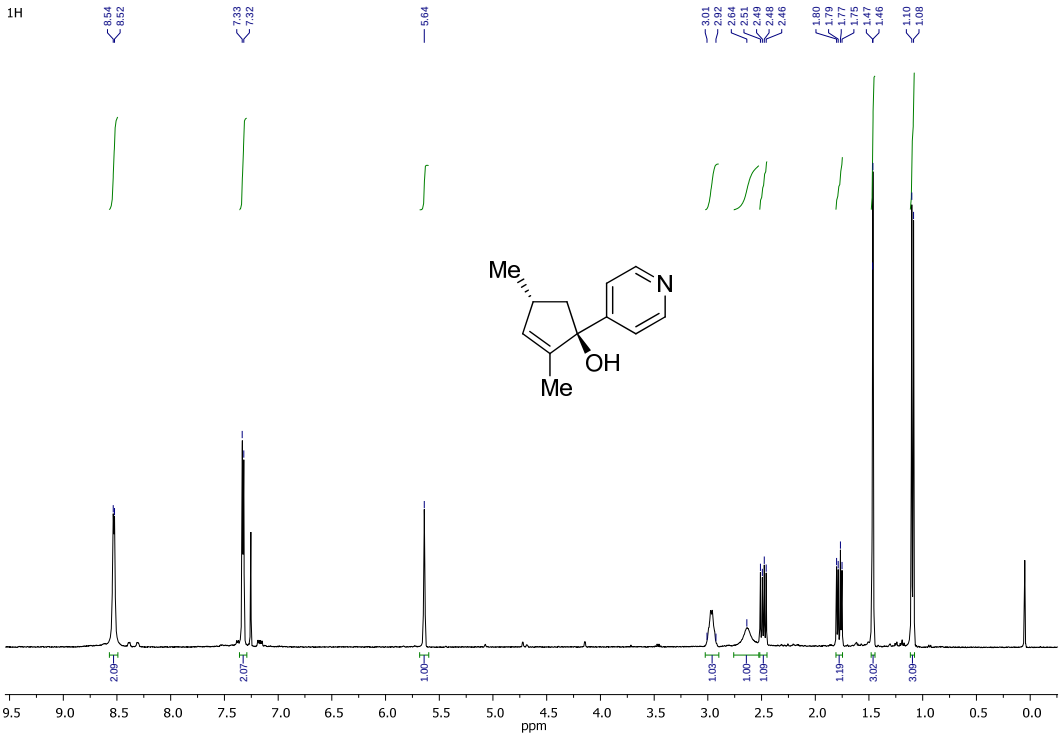
^{13}C NMR Spectrum of **4b** (100.6 MHz, $CDCl_3$)



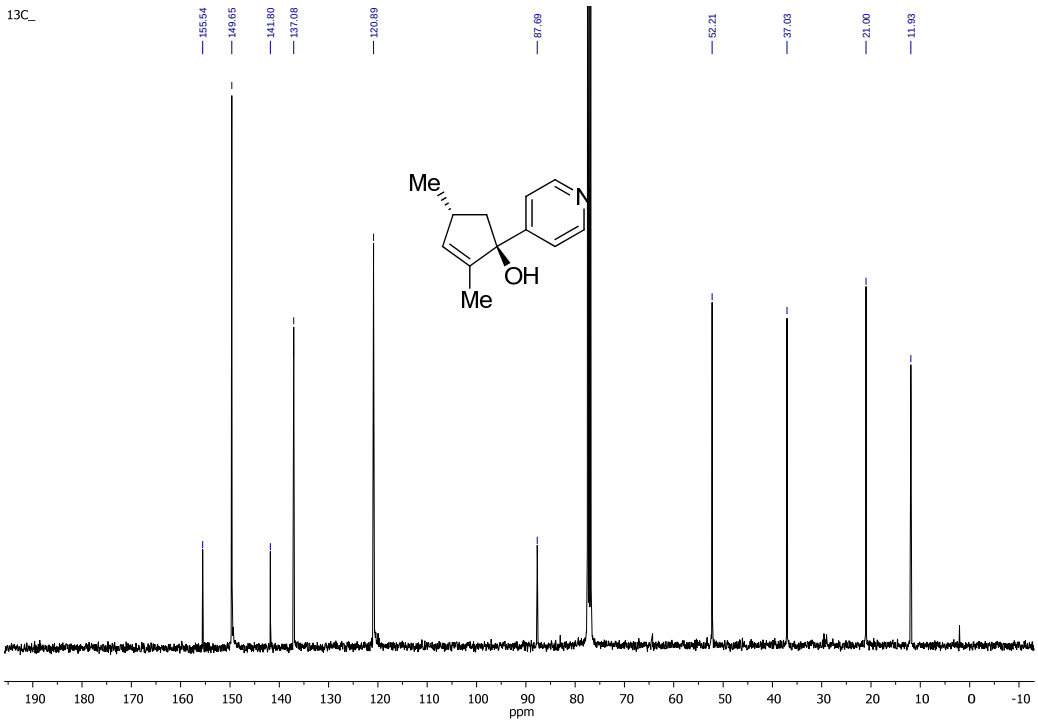
^{1}H NMR Spectrum of **4c** (400.1 MHz, $CDCl_3$)



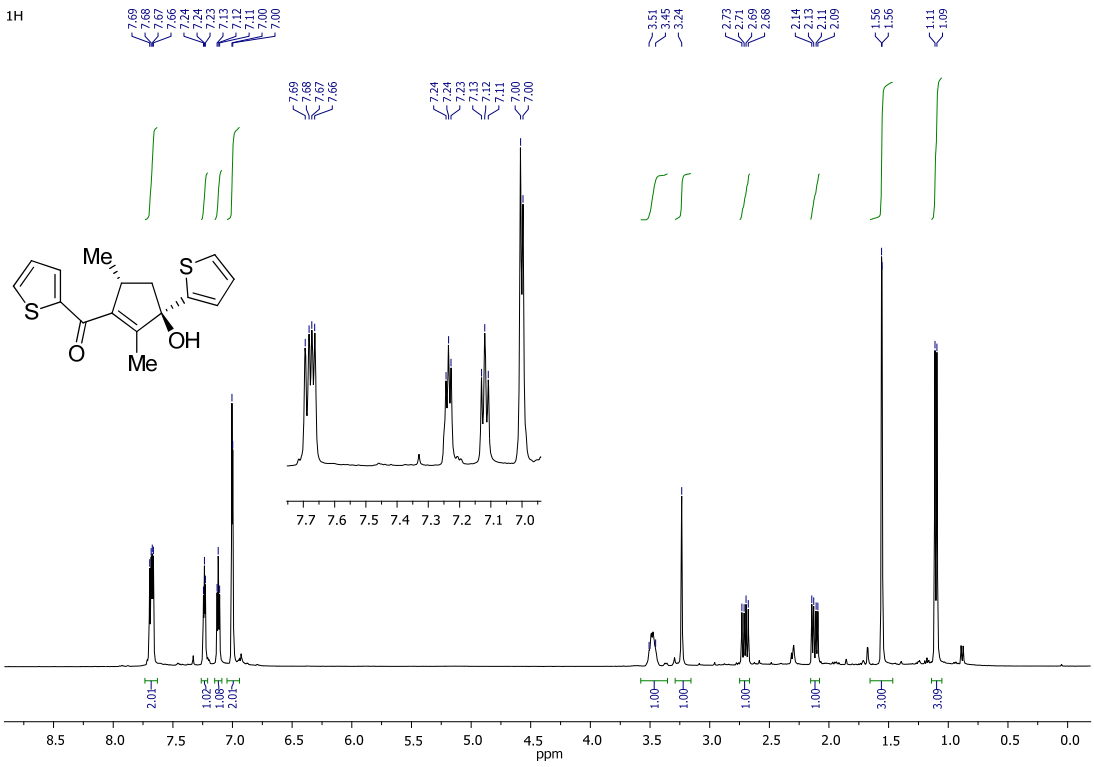
^{13}C NMR Spectrum of **4c** (100.6 MHz, $CDCl_3$)



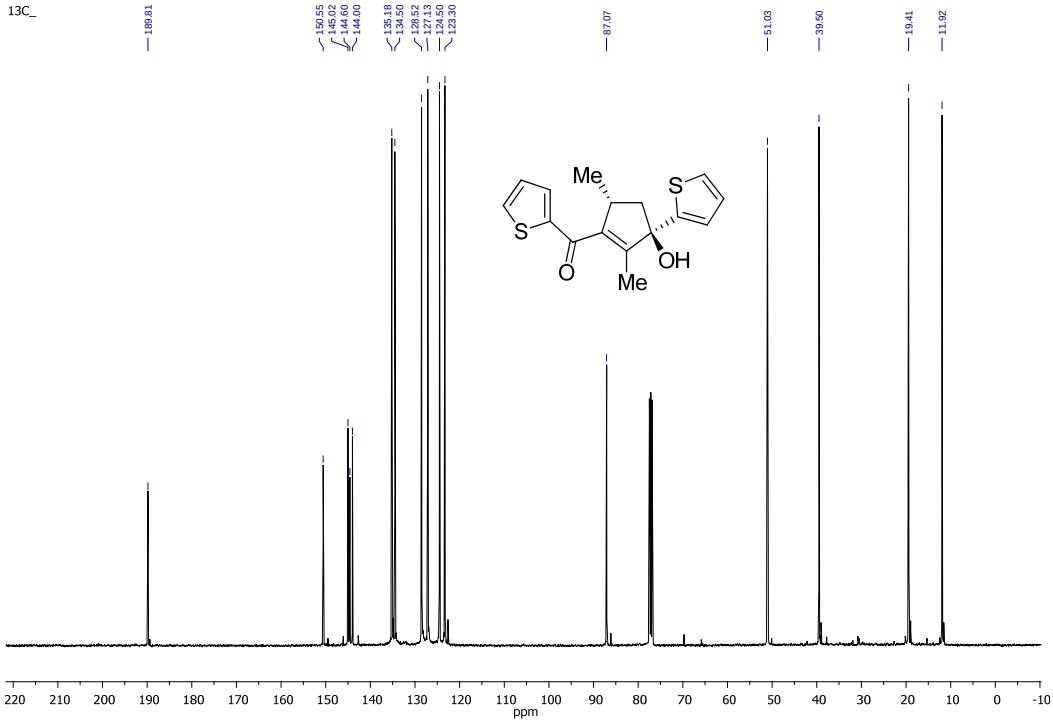
^{1}H NMR Spectrum of **4d'** (400.1 MHz, $CDCl_3$)



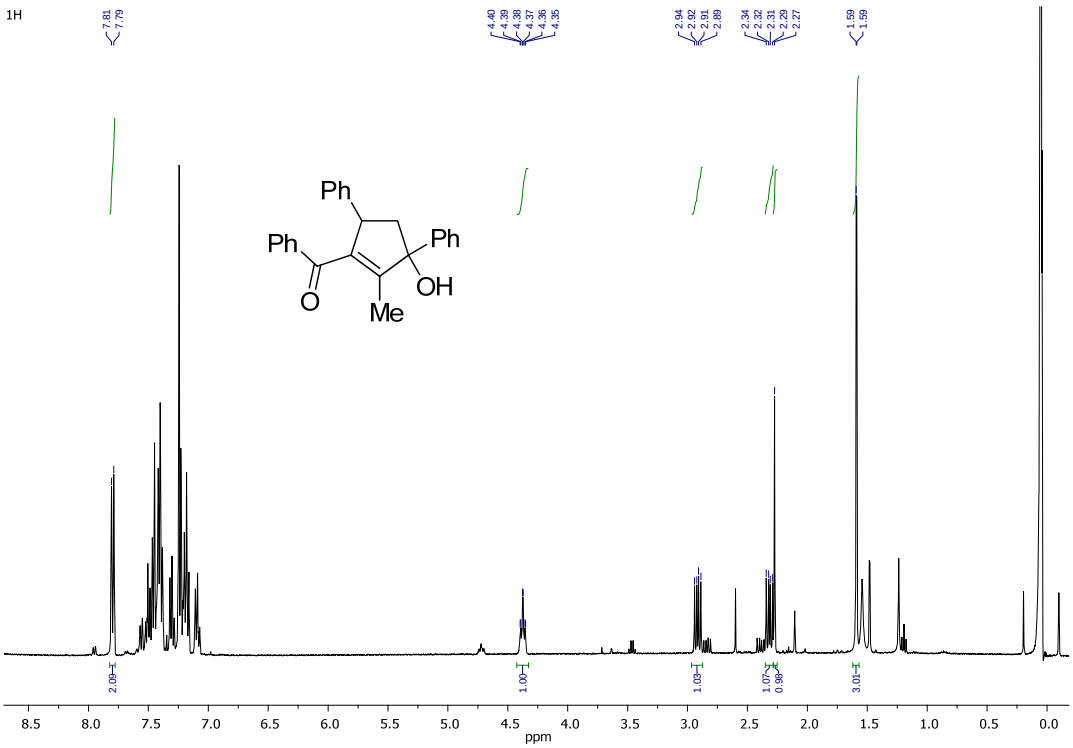
^{13}C NMR Spectrum of **4d'** (100.6 MHz, $CDCl_3$)



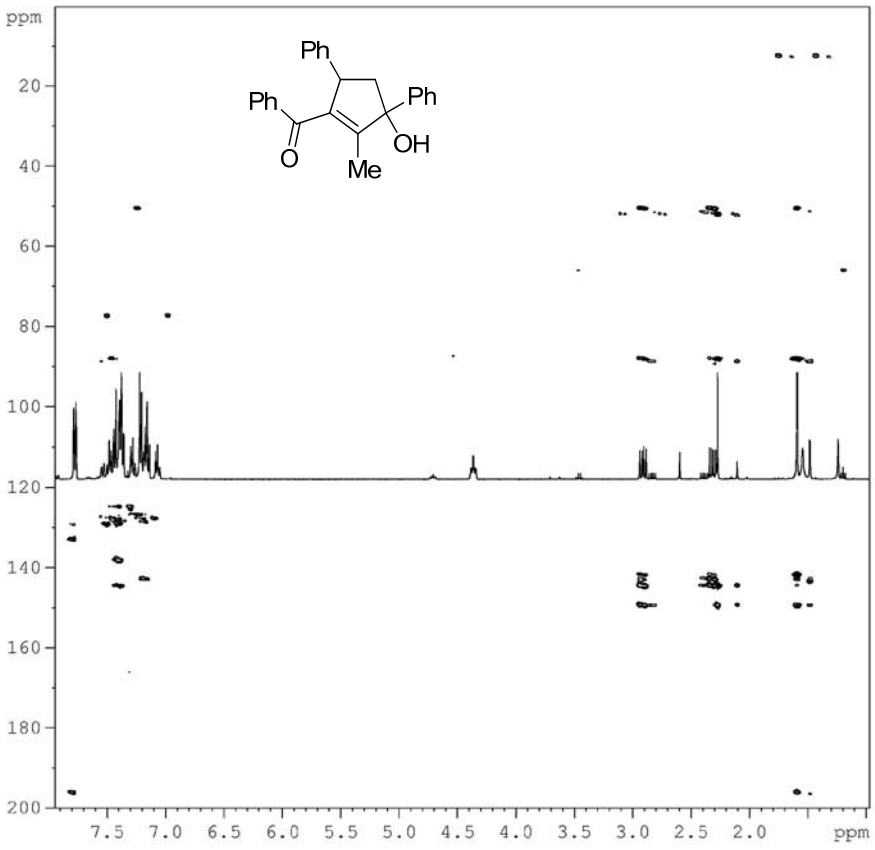
^{1}H NMR Spectrum of **4e** (400.1 MHz, $CDCl_3$)



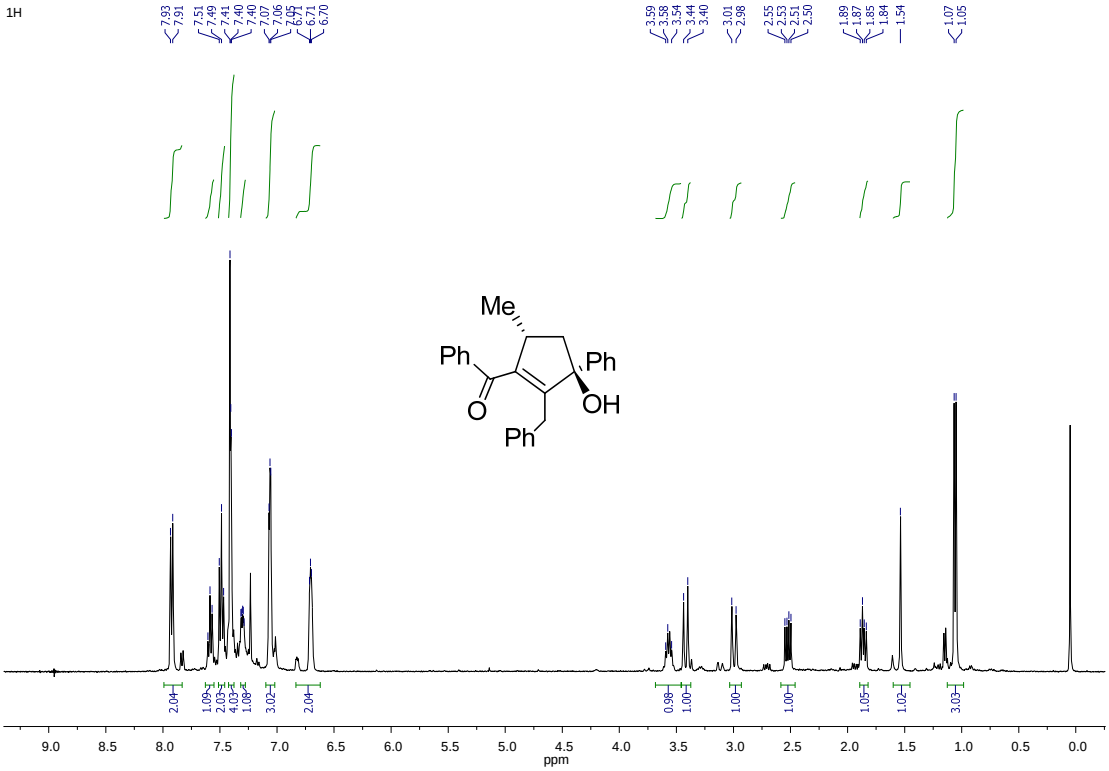
^{13}C NMR Spectrum of **4e** (100.6 MHz, $CDCl_3$)



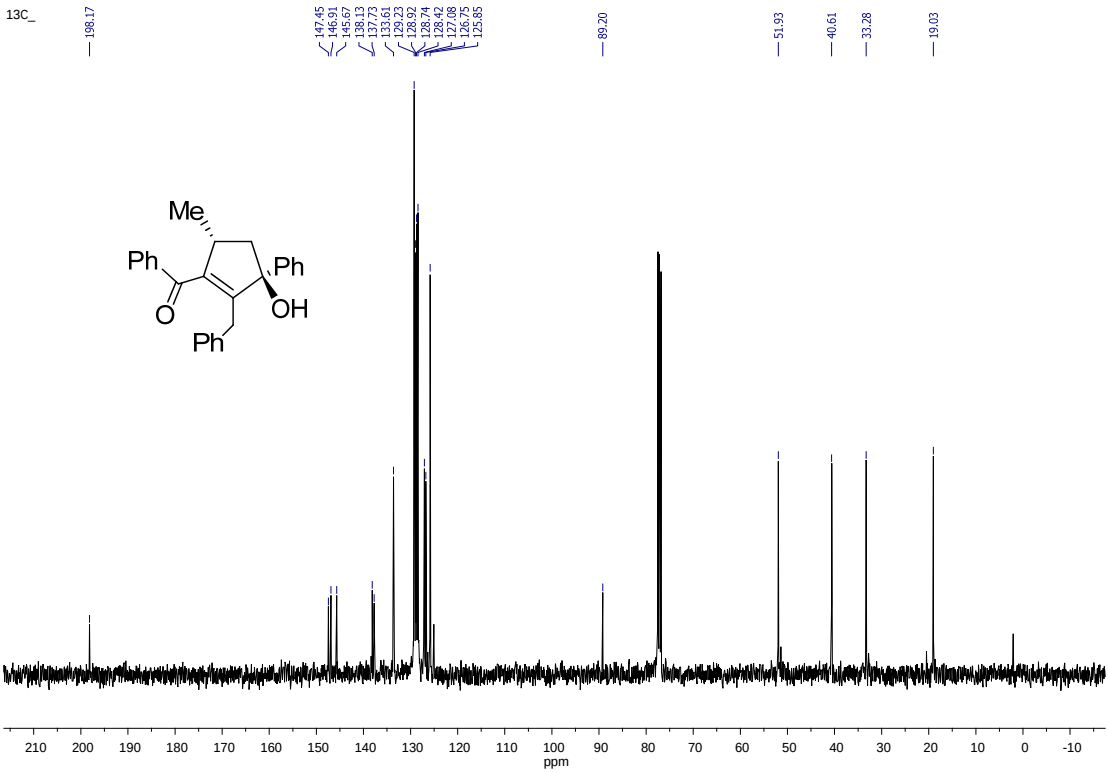
^{1}H NMR Spectrum of **4f** (a mixture of two diastereomers), 400.1 MHz, $CDCl_3$



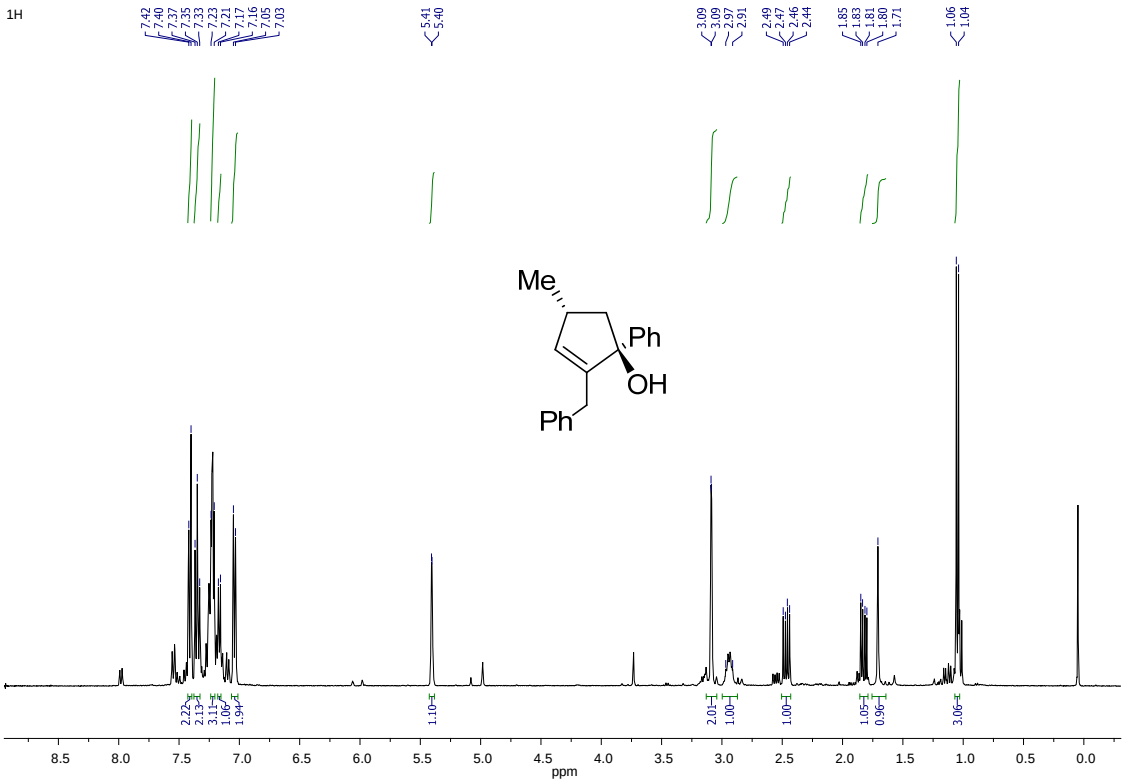
2D ^{1}H-^{13}C HMBC spectrum **4f** (a mixture of two diastereomers), $CDCl_3$



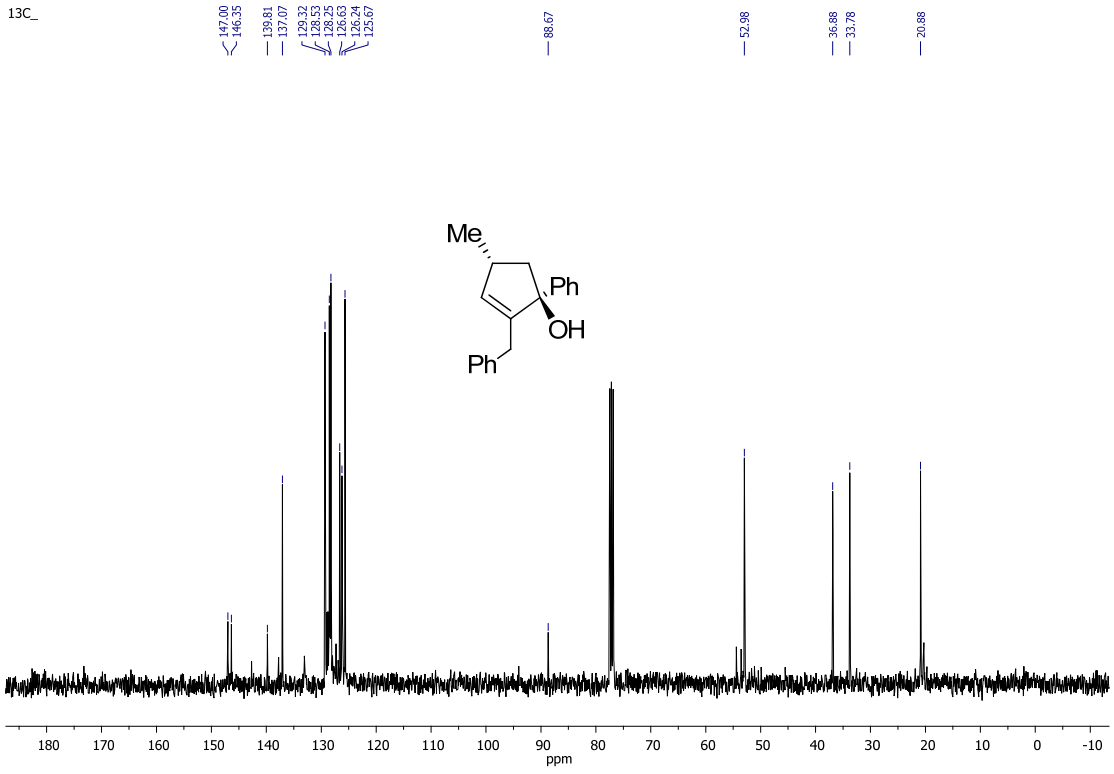
^{1}H NMR Spectrum of **4g** (400.1 MHz, $CDCl_3$)



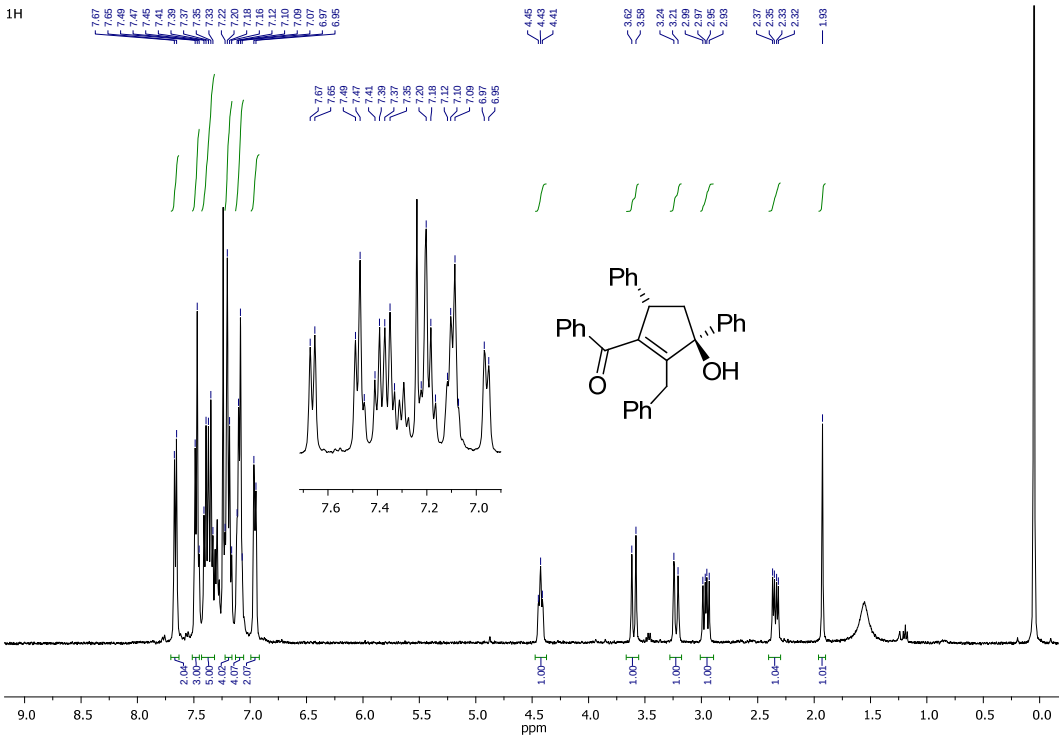
^{13}C NMR Spectrum of **4g** (100.6 MHz, $CDCl_3$)



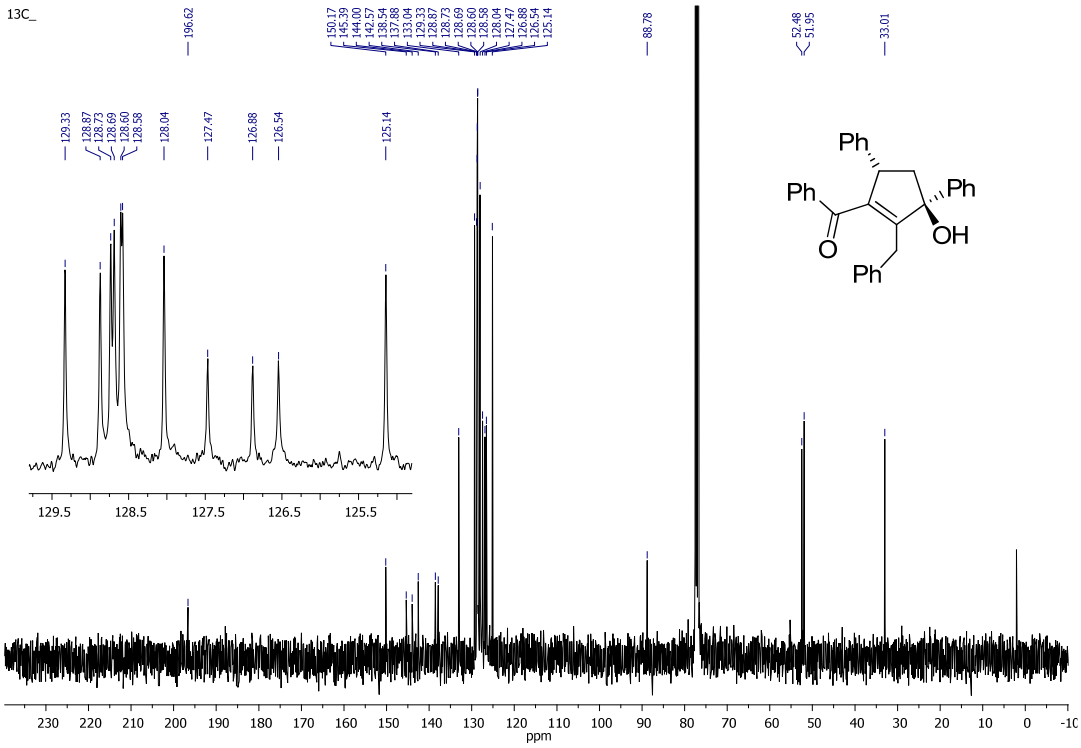
^{1}H NMR Spectrum of **4g'** (400.1 MHz, $CDCl_3$)



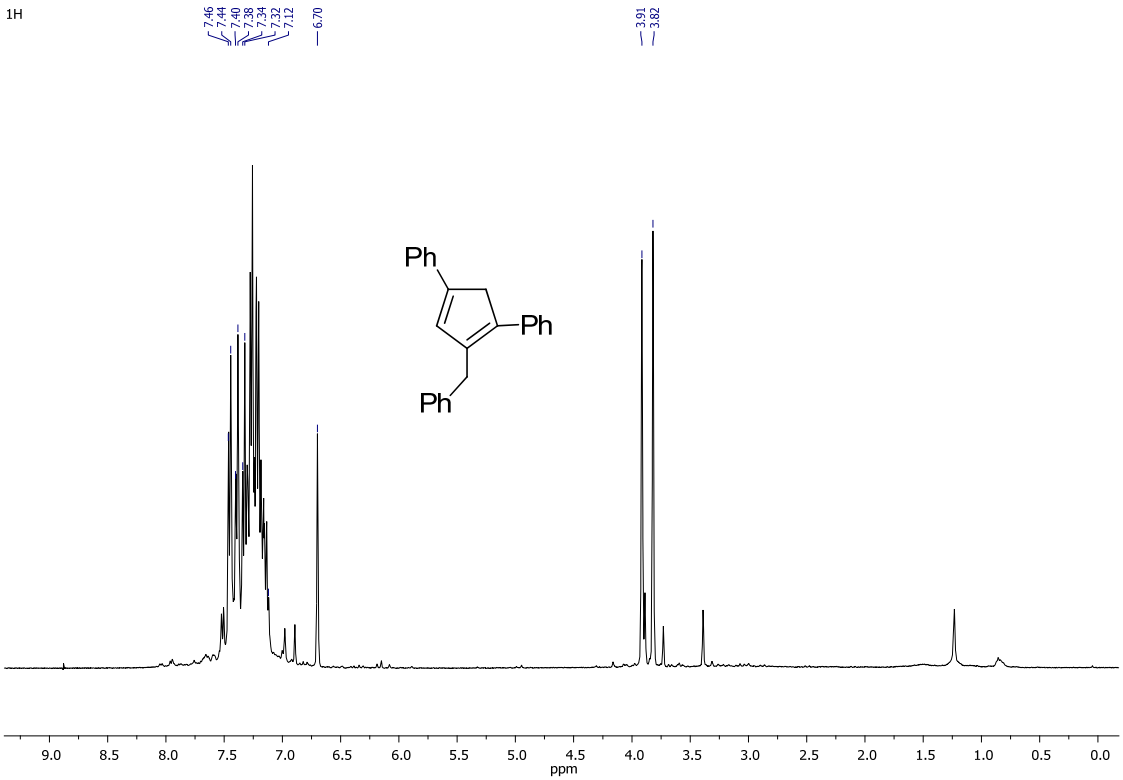
^{13}C NMR Spectrum of **4g'** (100.6 MHz, $CDCl_3$)



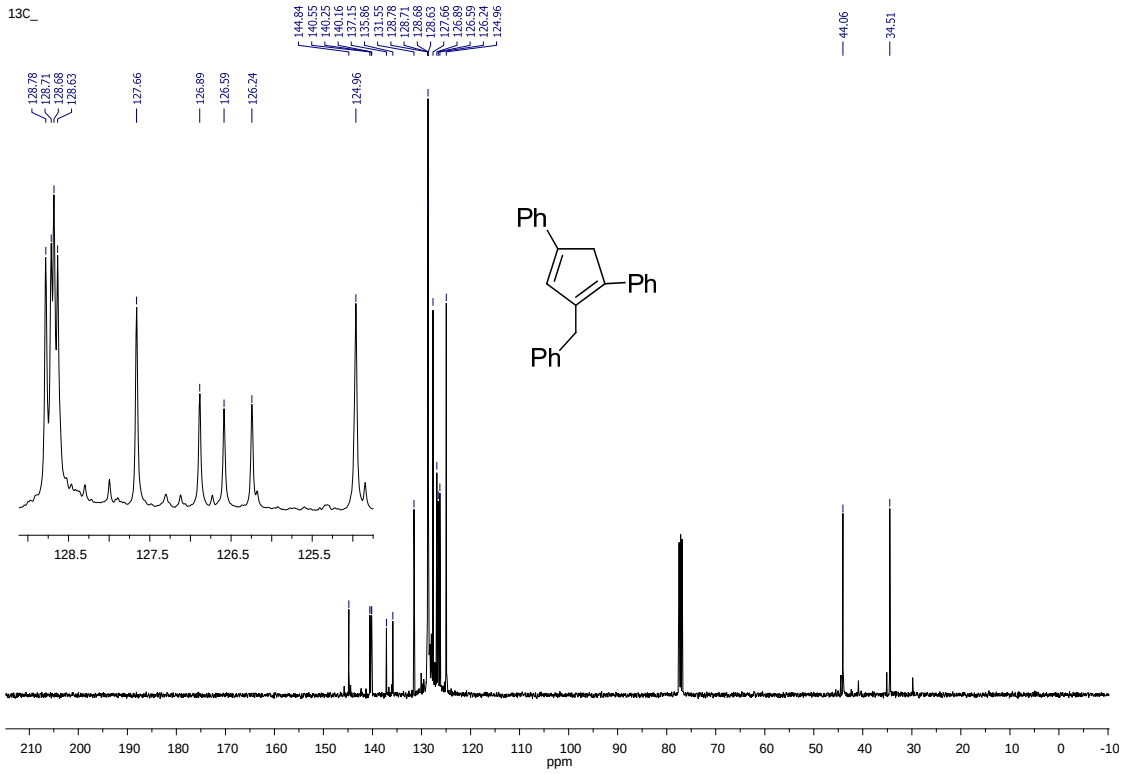
^{1}H NMR Spectrum of **4h** (400.1 MHz, $CDCl_3$)



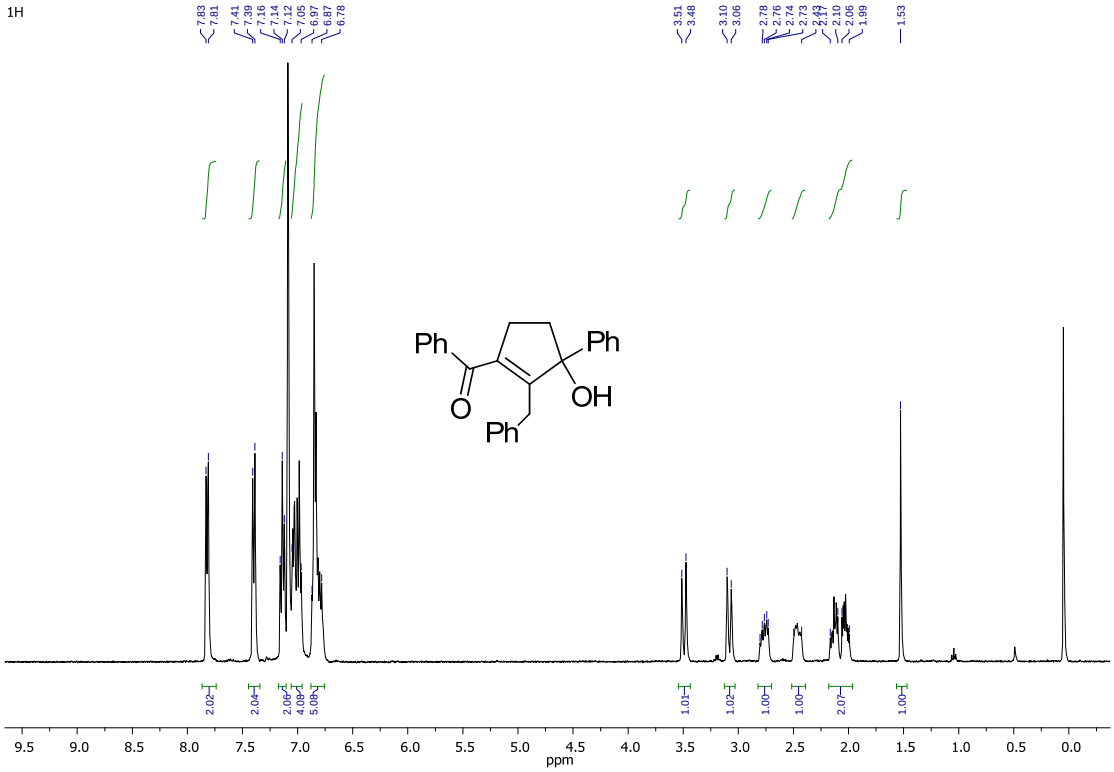
^{13}C NMR Spectrum of **4h** (100.6 MHz, $CDCl_3$)



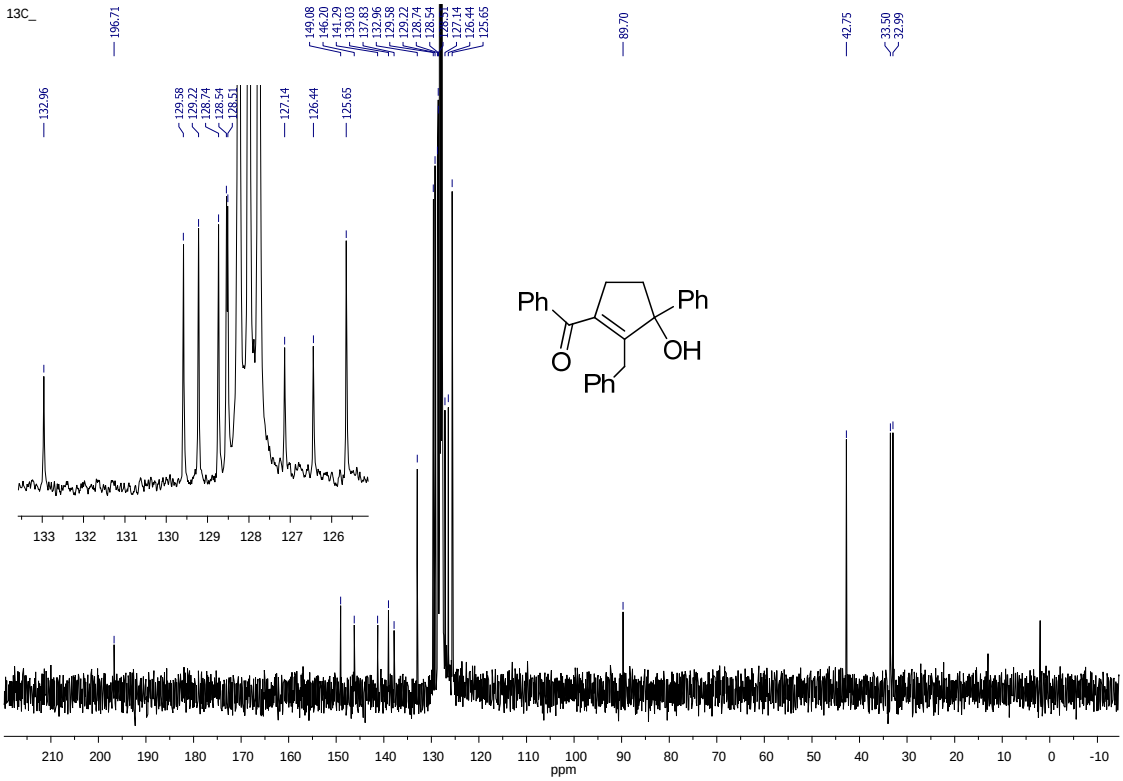
^{1}H NMR Spectrum of **4h''** (400.1 MHz, $CDCl_3$)



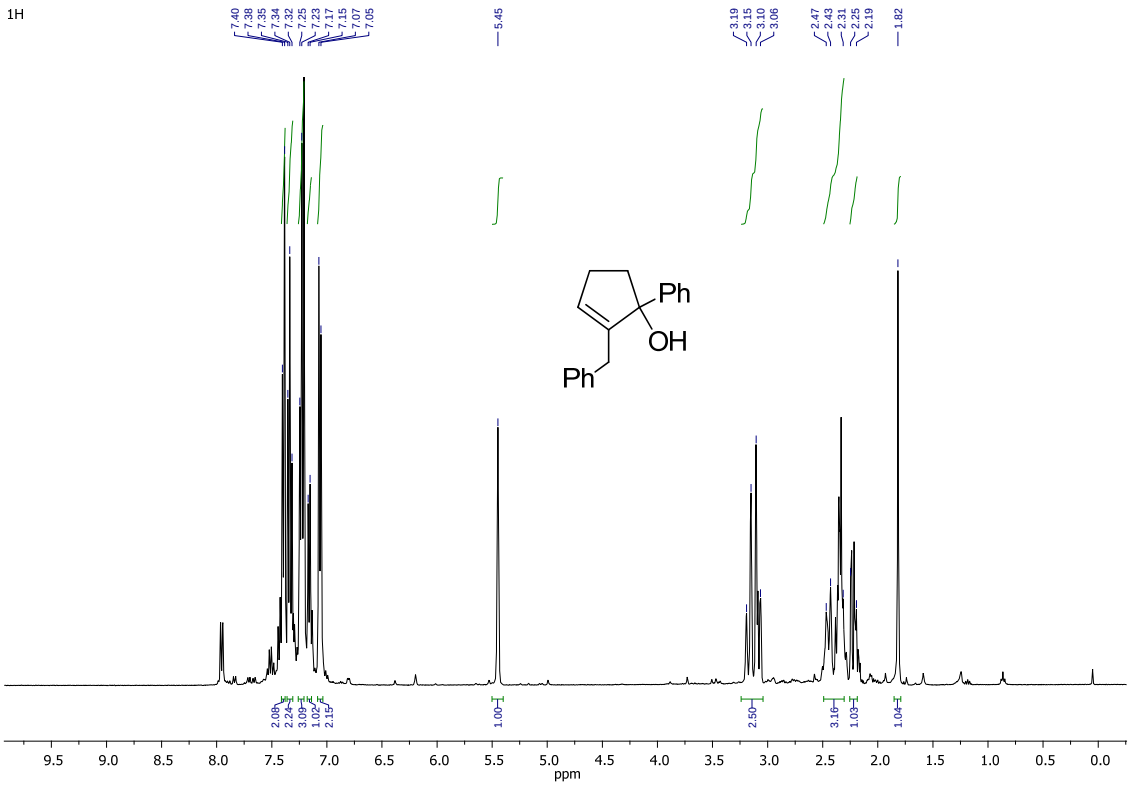
^{13}C NMR Spectrum of **4h''** (100.6 MHz, $CDCl_3$)



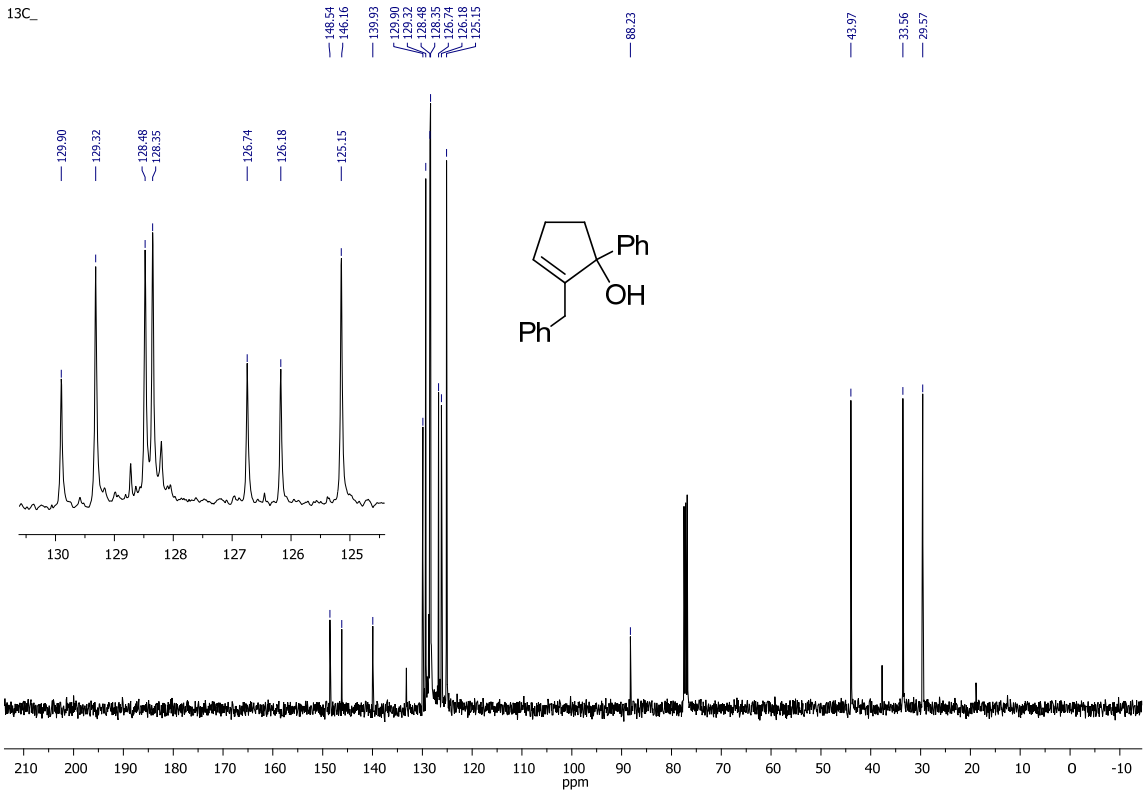
^{1}H NMR Spectrum of **4i** (400.1 MHz, C_6D_6)



^{13}C NMR Spectrum of **4i** (100.6 MHz, C_6D_6)



^{1}H NMR Spectrum of **4i'** (400.1 MHz, $CDCl_3$)



^{13}C NMR Spectrum of **4i'** (100.6 MHz, $CDCl_3$)