CHEMISTRY
A EUROPEAN JOURNAL

Supporting Information

Toluene Dioxygenase-Catalysed Synthesis of *cis*-Dihydrodiol Metabolites from 2-Substituted Naphthalene Substrates: Absolute Configurational and Conformational Assignments Based on Circular Dichroism and Optical Rotation Measurements

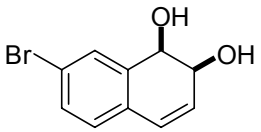
Marcin Kwit,[a] Jacek Gawronski,*[a] Derek R. Boyd,*[b] Narain D. Sharma,[b] Magdalena Kaik,[b] Rory More O'Ferrall[c] and Jaya S. Kudavalli[c]

[a] *Department of Chemistry*
A. Mickiewicz University
Grunwaldzka 6, 60 780 Poznan, Poland

[b] *School of Chemistry and Chemical Engineering*
The Queen's University of Belfast
Belfast BT9 5AG, UK

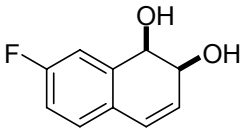
[c] *School of Chemistry & Chemical Biology, UCD*
Dublin 4, Ireland

Table A. Spectroscopic data for dihydrodiol **1a-1e**, **2a-2d**, **3a-3e**



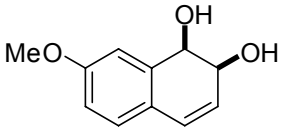
1a

Yield (0.09 g, 11.5%); m. p. 144-146 °C (lit.[a] 146 °C); R_f 0.47 (EtOAc:hexane 1:1); ^{1}H NMR δ 1.82 (d, 1H, $J_{OH,2}$ = 7.5 Hz, OH), 2.53 (d, 1H, $J_{OH,1}$ = 8.5 Hz, OH), 4.32-4.35 (m, 1H, 2-H), 4.65-4.69 (m, 1H, 1-H), 6.14 (dd, 1H, $J_{3,2}$ = 4.8, $J_{3,4}$ = 9.6 Hz, 3-H), 6.53 (d, 1H, $J_{4,3}$ = 9.6 Hz, 4-H), 6.99 (d,1H, $J_{5,6}$ = 8.0 Hz, 5-H), 7.41 (dd, 1H, $J_{6,8}$ = 1.5, $J_{6,5}$ = 8.0 Hz, 6-H), 7.70 (d, $J_{8,6}$ = 1.5 Hz, 8-H); ^{13}C NMR 67.3, 70.8, 122.7, 128.8, 129.7, 130.8, 131.8, 138.2; IR ν (cm^{-1}) 552, 832, 852, 932, 1012, 1042, 1100, 1190, 1267, 1333, 1477, 1636, 2361, 2853, 2923, 3326; $[\alpha]_D^{20}$ +240.1 (*c* = 0.5, MeOH), (lit.[a] $[\alpha]_D^{20}$ +255); CD (MeCN) Δε (nm) 1.8 (274); 15.6 (218); 4.5 (198); UV (MeCN) ε (nm): 17700 (265); 39400 (200); HR MS (EI): calcd for $[M-H]^+$ $C_{10}H_8O_2Br$: 238.9708; found: 238.9711.



1b

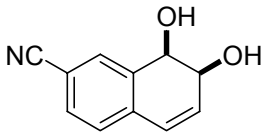
Yield (0.286 g, 13%); m. p. 138-140 °C; R_f 0.52 (EtOAc:hexane 1:1); ^{1}H NMR δ 1.89 (bs, 1H, OH), 2.71 (bs, 1H, OH), 4.30 (t, 1H, $J_{2,1}$ = $J_{2,3}$ = 4.8 Hz, 2-H), 4.69 (d, 1H, $J_{3,2}$ = 4.8 Hz, 1-H), 6.06 (dd, 1H, $J_{3,2}$ = 4.8, $J_{3,4}$ = 9.6 Hz, 3-H), 6.53 (d, 1H, $J_{4,3}$ = 9.6 Hz, 4-H), 6.93 (m, 1H, Aromatic), 7.02-7.11 (m, 1H, Aromatic), 7.32 (m, 1H, Aromatic); ^{13}C NMR 67.0, 71.0, 114.9 (m), 127.3, 128.1, 128.8, 129.4, 139.6, 162.3, 164.3; IR ν (cm^{-1}) 567, 827, 854, 1013, 1040, 1098, 1118, 1260, 1493, 1607, 2361, 3394; $[\alpha]_D^{20}$ +255.8 (*c* = 1.0, MeOH); CD (MeCN) Δε (nm) +3.7 (268), +15.3 (213); UV (MeCN) ε (nm) 12600 (258), 34500 (209); HR MS (EI): calcd for $C_{10}H_9FO_2$: 180.0587; found: 180.0582.



1c

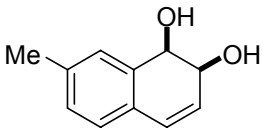
Yield (0.700 g, 8%)[b]; m. p. 108-110 °C (lit.,[c] 108-110 °C); R_f 0.20 (EtOAc:hexane 1:1); ^{1}H NMR δ 3.84 (s, 3H, OMe), 4.36 (dd, 1H, $J_{2,3}$ = 3.4, $J_{2,1}$ = 4.5 Hz, 2-H), 4.70 (d, 1H, $J_{1,2}$ = 4.5 Hz, 1-H), 5.99 (dd, 1H, $J_{3,2}$ = 3.4, $J_{3,4}$ 10.0 Hz, 3-H), 6.54 (d, $J_{4,3}$ = 10.0 Hz, 4-H), 6.80 (dd, 1H, $J_{6,8}$ = 2.7, $J_{6,5}$ = 8.6 Hz, 6-H), 7.06 (d, 1H, $J_{5,6}$ = 8.6 Hz, 5-H), 7.18 (d, 1H, $J_{8,6}$ = 2.7 Hz, 8-H); ^{13}C NMR 55.7, 67.7, 71.2., 113.3, 113.6, 125.1, 125.9, 128.6, 129.5, 138.2, 160.3; IR ν (cm^{-1}) 832, 940, 1036, 1220,

1498, 1575, 1607, 3560; $[\alpha]_D$ +276 (*c* = 1.0, MeOH). (lit.[c], $[\alpha]_D^{20}$ +247° in MeOH); CD (MeCN) Δε (nm) +1.2 (300), +11.1 (219); UV (MeCN) ε (nm) 14560 (270), 33235 (210); HR MS (EI): calcd for $[M-H]^+$ $C_{11}H_{11}O_3$: 191.0708; found: 191.0699.



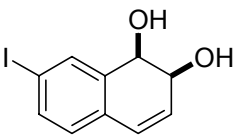
1d

Yield (0.038 g, 76%)[d]; m. p. 103-105 °C; R_f 0.49 (EtOAc:hexane 1:1); ^{1}H NMR δ 4.26 (m, 1H, $J_{2,1}$ = 5.0 Hz, 2-H), 4,56 (d, 1H, $J_{1,2}$ = 5.0 Hz, 1-H), 6.1 (dd, 1H, $J_{3,2}$ = 5.0, $J_{3,4}$ 9.7 Hz, 3-H), 6.46 (d, 1H, $J_{4,3}$ = 9.7 Hz, 4-H),.7.07 (d, 1H, $J_{5,6}$ = 8.2 Hz, 5-H), 7.54 (d, 1H, $J_{6,5}$ = 8.2 Hz, 6-H), 7.65 (s, 1H, 8-H); ^{13}C NMR 14.2, 21.0, 66.3, 69.9, 111.2, 119.0, 128.2, 128.8, 130.4, 132, 137.7; IR ν (cm^{-1}) 541, 594, 854, 1012, 1042, 1098, 1437, 1653, 2224, 2924, 3400; $[\alpha]_D^{20}$ +215.6 (*c* = 1.3, MeOH); CD (MeCN) Δε (nm) +0.72 (299), +13.2 (219); UV (MeCN) ε (nm): 14650 (282), 26850 (222); HR MS (EI): calcd for $C_{11}H_9NO_2$: 187.0633; found: 187.0619.



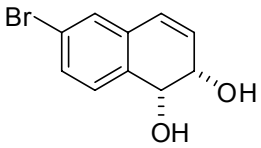
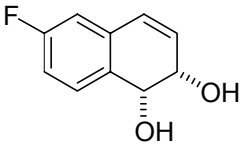
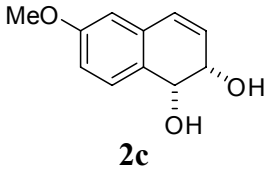
1e

Yield (0.08 g, 4.3%); m. p. 110-112 °C, (lit.[e] 104-105 °C); R_f 0.43 (EtOAc:hexane 1:1); ^{1}H NMR δ 1.58 (bs, 1H, OH) 1.98 (bs, 1H, OH), 2.38 (s, 3H, Me), 4.32-4.35 (m, 1H, $J_{2,3}$ = 4.2 Hz, 2-H) 4.65-4.69 (m, 1H, 1-H), 5.99 (dd, 1H, $J_{3,2}$ = 4.2, $J_{3,4}$ 9.7 Hz, 3-H), 6.51 (d, 1H, $J_{4,3}$ = 9.7 Hz, 4-H), 6.99 (d, 1H, $J_{6,5}$ = 7.6 Hz, 6-H), 7.12 (d, 1H, $J_{5,6}$ = 7.6 Hz, 5-H), 7.35 (s, 1H, 8-H); ^{13}C NMR 21.4, 68.0, 70.8, 126.9, 127.5, 129.0, 129.1, 135.5, 138.5; IR ν (cm^{-1}) 555, 694, 830, 1012, 1044, 1101, 1148, 1270, 1330, 1496, 2855, 2921, 3036, 3307; $[\alpha]_D^{20}$ +235.9 (*c* = 1.1, MeOH); CD (MeCN) Δε (nm) 2.6 (265); 15.6 (221); UV (MeCN) ε (nm) 9800 (266); 21500 (218); HR MS (EI): calcd for $[M-H]^+$ $C_{11}H_{11}O_2$: 175.0759; found: 175.0757.

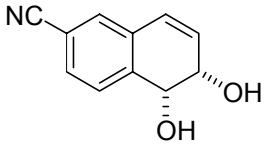


1g

Yield (0.09 g, 6.8%); m. p. 148-150 °C; R_f 0.48 (EtOAc:hexane 1:1); ^{1}H NMR (CD_3OD) δ 4.12 (t, 1H, $J_{2,1}$ = $J_{2,3}$ 4.7 Hz, 2-H) 4.49 (d, 1H, $J_{1,2}$ = 4.7, 1-H), 5.97 (dd, 1H, $J_{3,2}$ = 4.7, $J_{3,4}$ 9.7 Hz, 3-H), 6.43 (d, 1H, $J_{4,3}$ = 9.7 Hz, 4-H), 6.81 (d, 1H, $J_{5,6}$ = 7.8 Hz, 5-H), 7.51 (dd, 1H, $J_{6,8}$ = 0.7, $J_{6,5}$ = 7.8 Hz, 6-H), 7.74 (d, 1H, $J_{8,6}$ = 0.7 Hz, 8-H); ^{13}C NMR (CD_3OD)

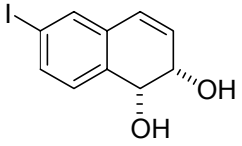
	68.5, 71.8, 94.0, 129.5, 129.9, 131.2, 133.8, 137.2, 138.3, 140.8; IR ν (cm^{-1}) 550, 830, 848, 1047, 1109, 1636, 2362, 2924, 3420; $[\alpha]_D^{20}$ +207.9 (*c* = 0.2, MeOH); CD (MeCN) Δε (nm) -0.5 (282); 15.4 (226), -0.6 (212); 8.8 (202); UV (MeCN) ε (nm) 14800 (272); 15900 (223); 17400 (203); HR MS (EI): calcd for $C_{10}H_9IO_2$: 287.9647; found: 287.9666.
 **2a**	Yield (0.13 g, 16.5%); m. p. 116-120°C; R_f 0.44 (EtOAc:hexane 1:1); ^{1}H NMR *δ* 1.99 (bs, 1H, OH), 2.42 (bs, 1H, OH), 4,35-4.38 (m, 1H, $J_{2,3}$ = 4.4 Hz, 2-H), 4.63-4.65 (m, 1H, 1-H), 6.11 (dd, 1H, $J_{3,2}$ = 4.4, $J_{3,4}$ = 9.6 Hz, 3-H), 6.50 (d, 1H, $J_{4,3}$ = 9.6 Hz, 4-H), 7.22-7.29 (m, 2H, 5-H and 6-H), 7.41 (d, 1H, $J_{8,6}$ = 1.1 Hz, 8-H); ^{13}C NMR 71.1, 74.0, 126.0, 131.7, 133.0, 133.5, 134.3, 134.9, 138.1, 138.9; IR ν (cm^{-1}) 668, 744, 785, 814, 866, 1035, 1083, 1190, 1266, 1358, 1387, 1576, 1627, 2342, 2361, 2918, 3272; $[\alpha]_D^{20}$ +140.8 (*c* = 0.4, MeOH); CD (MeCN) Δε (nm); 4.1 (263); 8.4 (227); -2.4 (202); UV (MeCN) ε (nm): 6800 (265); 26700 (222); HR MS (EI): calcd for $[M-H]^+$ $C_{10}H_8O_2Br$: 238.9708; found: 238.9710.
 **2b**	Yield (0.136 g, 6.1 %); m. p. 120-125 °C; R_f 0.51 (EtOAc:hexane 1:1); ^{1}H NMR *δ* 1.61 (bs, 1H, OH), 2.41 (bs, 1H, OH), 4.40-4.42 (m, 1H, $J_{2,3}$ = 3.8 Hz, 2-H), 4.65 (m, 1H, 1-H), 6.11 (dd, 1H, $J_{3,2}$ = 3.8, $J_{3,4}$ = 9.6 Hz, 3-H), 6.47 (d, $J_{4,3}$ = 9.6 Hz, 4-H), 6.85 (m, 1H, Aromatic), 6.98 (m, 1H, Aromatic), 7.45-7.48 (m, 1H, Aromatic); ^{13}C NMR 68.3, 70.7, 114.1 (d); 115.0 (d) , 128.3, 129.8, 130.8, 134.3, 162.1, 164.3; IR ν (cm^{-1}) 546, 673, 790, 819, 862, 943, 1014, 1043, 1097, 1255, 1333, 1408, 1492, 1582, 1610, 2361, 2670, 2859, 2926, 3040, 3306; $[\alpha]_D^{20}$ +202.0 (*c* = 1.2, MeOH); CD (MeCN) Δε (nm) +2.81 (258), +13.2 (213); UV (MeCN) ε (nm) 12 320 (258), 33 000 (207); HR MS (EI): calcd for $C_{10}H_9FO_2$ 180.0587; found: 180.0586.
 **2c**	Yield (2.3 g, 24%); m. p. 125-127 °C, (lit.[c] m. p. 109-111 °C); R_f 0.18 (EtOAc:hexane 1:1); ^{1}H NMR *δ* 1.67 (bs, 1H, OH), 2.30 (bs, 1H, OH), 3.82 (s, 3H, OMe), 4.39-4.42 (m, 1H, $J_{2,3}$ =

3.5 Hz, 2-H), 4.60-4,62 (m, 1H, 1-H), 6.01 (dd, 1H, $J_{3,2}$ = 3.5, $J_{3,4}$ = 9.8 Hz, 3-H), 6.47 (dd, 1H, $J_{4,2}$ = 1.42, $J_{4,3}$ = 9.8 Hz, 4-H), 6.64 (d, 1H, $J_{8,6}$ = 2.6 Hz, 8-H), 6.81 (dd, 1H, $J_{6,8}$ = 2.6, $J_{6,5}$ = 8.3 Hz, 6-H), 7.40 (d, 1H, $J_{5,6}$ = 8.3 Hz, 5-H); ^{13}C NMR 55.2, 68.6, 70.2, 113.0, 127.3, 128.8, 129.2, 130.3, 133.1, 160.1; IR ν (cm^{-1}) 604, 698, 800, 879, 984, 1034, 1064, 1163, 1262, 1298, 1451, 1497, 1571, 1609, 2959, 3015, 3258; $[\alpha]_D^{20}$ +189.7 (*c* = 1.1, MeOH), (lit.[c] $[\alpha]_D^{20}$ +165.5); CD (MeCN) Δε (nm) -0.4 (281); 1.2 (261); 17.4 (228); -13.6 (194), UV (MeCN) ε (nm): 1700 (298); 5300 (266); 27600 (228); HR MS (EI): calcd for $[M-H]^+$: $C_{11}H_{11}O_3$ 191.0708; found: 191.0699.



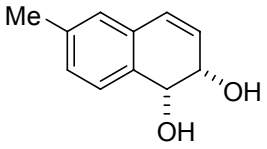
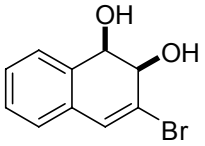
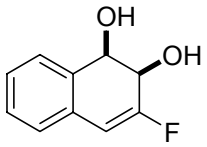
2d

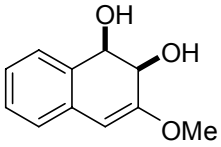
Yield (0.177 g, 14.5%); m. p. 132-134 °C; R_f 0.48 (EtOAc:hexane 1:1); ^{1}H NMR δ 1.89 (bs, 1H, OH), 2.65 (bs, 1H, OH), 4.34-4.36 (m, 1H, $J_{2,3}$ = 4.9 Hz, 2-H), 4.74-4.76 (m, 1H, 1-H), 6.27 (dd, 1H, $J_{3,4}$ = 9.7, $J_{3,2}$ = 4.9 Hz, 3-H), 6.59 (d, 1H, $J_{4,3}$= 9.7 Hz, 4-H), 7.39 (d, 1H, $J_{8,6}$ = 1.7 Hz, 8-H), 7.59 (dd, 1H, $J_{6,8}$ = 1.7, $J_{6,5}$ = 8.0 Hz, 6-H), 7.73 (d, 1H, $J_{5,6}$ = 8.0 Hz, 5-H); ^{13}C NMR 14.8, 21.6, 66.7, 70.7, 112.9, 119.0, 128.2, 129.2, 130.5, 132.8, 142.1; IR ν (cm^{-1}) 683, 800, 827, 1008, 1039, 1097, 1257, 1398, 1489, 1634, 1636, 2230, 2361, 2923, 3382; $[\alpha]_D^{20}$ +196.8 (*c* = 1.0, MeOH); CD (MeCN) Δε (nm) +5.48 (265), +4.51 (236), -3.06 (230), -3.41 (226), +3.44 (211); UV (MeCN) ε (nm): 73000 (265), 46800 (232), 46000 (226). HR MS (EI): calcd for $C_{11}H_9NO_2$ 187.0633; found: 187.0623.



2g

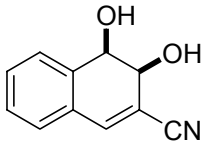
Yield (0.11 g, 8.3%), m. p. 138-140 °C; R_f 0.43 (EtOAc:hexane 1:1); ^{1}H NMR (CD_3OD) δ 4.15 (dd, 1H, $J_{2,3}$ = 4.3, $J_{2,1}$ = 4.8 Hz, 2-H), 4.46 (d, 1H, $J_{1,2}$ = 4.8 Hz, 1-H), 5.96 (dd, 1H, $J_{3,2}$ = 4.3, $J_{3,4}$ = 9.7 Hz, 3-H), 6.38 (d, $J_{4,3}$ = 9.7 Hz, 4-H), 7.15 (d, 1H, $J_{5,6}$ = 8.0 Hz, 5-H), 7.39 (d, $J_{8,6}$ = 1.7 Hz, 8-H), 7.48 (dd, 1H, $J_{6,8}$ = 1.7, $J_{6,5}$ = 8.0 Hz, 6-H); ^{13}C NMR (CD_3OD) 68.5, 71.9, 94.1, 129.1, 130.6, 131.8, 136.4, 136.5, 138.0, 138.2; IR ν (cm^{-1}) 528, 669, 696, 785, 806, 883, 1001, 1034, 1096, 1190, 1247, 1474, 1558, 1586, 2361, 2912, 3292;

	$[\alpha]_D^{20}$ +121.2 (*c* = 1.1, MeOH); CD (MeCN) Δε (nm) -0.6 (322); 2.7 (274), 5.1 (238); -0.3 (220), -2.9 (208); 7.9 (199); UV (MeCN) ε (nm) 6000 (266); 27100 (232); HR MS (EI): calcd for $C_{10}H_9IO_2$ 287.9647; found: 287.9668.
 **2e**	R_f 0.43 (EtOAc:hexane 1:1)[f]; ^{1}H NMR δ 2.1 (bs, 1H, OH), 2.32 (bs, 1H, OH), 4.32-4.34 (m, 1H, $J_{2,3}$ = 4.7 Hz, 2-H), 4.62-4.64 (m, 1H, 1-H), 6.01 (dd, 1H, $J_{3,2}$ = 4.7, $J_{3,4}$ = 8.7 Hz, 3-H), 6.46 (d, 1H, $J_{4,3}$ = 8.7 Hz, 4-H), 6.93 (s, 1H, 8-H), 7.11 (d, 1H, $J_{5,6}$ = 7.7 Hz, 5-H), 7.38 (d, $J_{6,5}$ = 7.7 Hz, 6-H).
 **3a**	Yield (0.11 g, 14%); m. p.152-154 °C; R_f 0.72 (EtOAc:hexane 1:1); ^{1}H NMR δ 1.67 (bs, 1H, OH), 2.57 (bs, 1H, OH), 4.42 (d, 1H, $J_{2,1}$ = 5.0 Hz, 2-H), 4.88 (d, 1H, $J_{1,2}$ = 5.0 Hz, 1-H), 6.92 (s, 1H, 4-H), 7.07 (d, 1H, $J_{8,7}$ = 7.2 Hz, 8-H), 7.28-7.34 (m, 2H, 6-H and 7-H), 7.56 (d, 1H, $J_{5,6}$ = 7.2 Hz, 5-H); ^{13}C NMR 30.3, 72.1, 74.3, 124.8, 126.8, 127.3, 129.1, 129.2, 131.7, 134.5; IR ν (cm^{-1}) 558, 599, 697, 757, 790, 879, 1020, 1050, 1093, 1120, 1213, 1274, 1324, 1420, 1483, 1624, 2342, 2361, 2926, 3324; $[\alpha]_D^{20}$ -156.2 (*c* = 1.0, MeOH); CD (MeCN) Δε (nm) 0.3 (308); -1.0 (277); -14.4 (225); -14.6 (207); UV (MeCN) ε (nm): 11800 (277); 19900 (220); HR MS (EI): calcd for $[M-H]^+$ $C_{10}H_8O_2Br$: 238.9708; found: 238.9705.
 **3b**	Yield (0.258 g, 11.7%); m. p. 168-169 °C; R_f 0.75 (EtOAc:hexane 1:1); ^{1}H NMR δ 1.58 (bs, 1H, OH), 2.60 (bs, 1H, OH), 4.46 (m, 1H, $J_{2,1}$ = 5.4 Hz, 2-H), 4.90 (d, 1H, $J_{1,2}$ = 5.4 Hz, 1-H), 6.18 (d, 1H, $J_{4,F}$ = 11.4 Hz, 4-H), 7.09-7.11 (m, 1H, Aromatic), 7.26-7.29 (m, 2H, Aromatic), 7.53-7.56 (m, 1H, Aromatic); ^{13}C NMR 68.3 (d), 71.9, 107.6 (d), 127.0 (d), 128.3, 129.0, 130.0, 133.9, 159.6, 161.7; IR ν (cm^{-1}) 531, 641, 705, 754, 852, 885, 963, 1052, 1099, 1142, 1216, 1314, 1428, 1455, 1485, 1678, 2361, 2859, 2923, 3071, 3339; $[\alpha]_D^{20}$ -188.1 (*c* = 0.8, MeOH); CD (MeCN) Δε (nm) -4.14 (257), -10.28 (205); UV (MeCN) ε (nm) 17720 (226), 34900 (221), 39400 (202); HR MS (EI): calcd for $C_{10}H_9FO_2$: 180.0587; found: 180.0585.



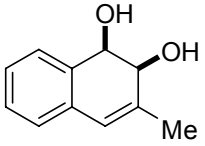
3c

Yield (1.36 g, 14%); m. p. 155-157 °C, (lit.[c] m. p. 154-156 °C); R_f 0.24 (EtOAc:hexane 1:1); ^{1}H NMR δ 1.69 (bs, 1H, OH), 2.58 (bs, 1H, OH), 3.77 (s, 3H, OMe), 4.34 (d, 1H, $J_{2,1}$ = 4.8 Hz, 2-H), 4.78 (d, 1H, $J_{1,2}$ = 4.8 Hz, 1-H), 5.57 (s, 1H, 4-H), 7.05 (d, 1H, $J_{8,7}$ = 7.5 Hz, 8-H), 7.17 (m, 1H, 6-H), 7.23 (m, 1H, 7-H), 7.48 (d, 1H, $J_{5,6}$ = 7.5 Hz, 5-H); ^{13}C NMR 55.6, 70.3, 71.3, 97.3, 125.6, 125.9, 127.3, 128.7, 132.1, 132.8, 156.9; IR ν (cm^{-1}) 538, 668, 707, 759, 822, 884, 948, 1030, 1115, 1167, 1194, 1639, 2342, 2361, 2930, 3368; $[\alpha]_D^{20}$ -183.0 (*c* = 1.1, MeOH) (lit.[c] $[\alpha]_D^{20}$-225); CD (MeCN) Δε (nm) -2.2 (292); -7.5 (231); -8.1 (205); UV (MeCN) ε (nm): 12200 (270); 20100 (216); HR MS (ES^-): calcd for [M-H_2O -H]$^-$: $C_{11}H_9O_2$ 173.0603; found: 173.0604.



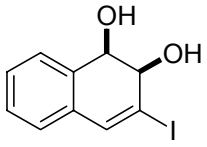
3d

Yield (0.088 g, 7.2%); m. p. 161-162°C; R_f 0.69 (EtOAc:hexane 1:1); ^{1}H NMR δ 2.47 (bs, 1H, OH), 2.59 (bs, 1H, OH), 4.52-4.56 (m, 1H, 2-H), 4.77-4.79 (m, 1H, 1-H), 7.25 (m, 1H, Aromatic), 7.28 (d, $J_{4,2}$ = 1.5 Hz, 4-H), 7.38 (m, 1H, Aromatic), 7.46 (m, 1H, Aromatic), 7.58 (d, 1H, $J_{5,6}$ = 7.4 Hz, 5-H); ^{13}C NMR (CD_3OD) 69.0, 71.5, 114.5, 120.0, 128.5, 130.0, 131.3, 132.5, 139.3, 143.9; IR ν (cm^{-1}) 536, 597, 704, 769, 805, 916, 949, 1050, 1106, 1140, 1290, 1332, 1416, 1453, 1572, 1626, 2211, 2363, 2663, 2869, 2919, 3234; $[\alpha]_D^{20}$ -114.7 (*c* = 1.1, MeOH); CD (MeCN) Δε (nm) -7.32 (222), -11.14 (203); UV (MeCN) ε (nm) 18200 (290), 31600 (224), 28400 (204), HR MS (EI): calcd for $C_{11}H_9NO_2$ 187.0633; found: 187.0622.



3e

Yield (0.15 g, 8%); m. p. 120-121 °C, (lit.[d] m. p. 115-116 °C); R_f 0.46 (EtOAc:hexane 1:1); ^{1}H NMR δ 1.59 (bs, 1H, OH), 1.95 (s, 3H, Me), 2.46 (bs, 1H, OH), 4.02 (d, 1H, $J_{2,1}$ = 4.5 Hz, 2-H), 4.64 (d, 1H, $J_{1,2}$ = 4.5 Hz, 1-H), 6.21 (s, 1H, 4-H), 6.95 (d, 1H, $J_{8,7}$ = 8.6 Hz, 8-H), 7.26-7.34 (m, 2H, 6-H and 7-H), 7.45 (d, 1H, $J_{5,6}$ = 8.6 Hz, 5-H); ^{13}C NMR 19.6, 70.1, 70.5, 123.3, 124.9, 125.7, 126.4, 127.3, 131.3 133.5, 136,2; IR ν (cm^{-1}) 566, 704, 757, 802, 888, 952, 1007, 1030, 1096, 1111,

	1279, 1446, 1653, 2361, 2917, 2967, 3024, 3368; $[\alpha]_D^{20}$ -192.4 (*c* = 0.7, MeOH); CD (MeCN) Δε (nm) -2.7 (260); -14.0 (213); UV (MeCN) ε (nm): 10000 (265); 20300 (219); 19800 (213); HR MS (EI): calcd for $[M-H]^+$ $C_{11}H_{11}O_2$: 175.0759; found: 175.0751.
 **3g**	Yield (0.20 g, 15%); m. p. 146-148 °C; R_f 0.7 (EtOAc : hexane 1:1); ^{1}H NMR δ 2.36-2.39 (m, 2H, 2xOH), 4.35-4,37 (m, 1H, 2-H), 4.79-4.81 (m, 1H, 1-H), 6.97 (d, 1H, $J_{8,7}$ = 7.4 Hz, 8-H), 7.19-7.27 (m, 2H, 6-H and 7-H), 7.47 (d, 1H, $J_{5,6}$ = 7.4 Hz, 5-H); ^{13}C NMR 71.1, 75.7, 101.1, 126.6, 127.8, 129.0, 129.5, 132.7, 135.2, 139.4; IR ν (cm^{-1}) 596, 694, 750, 1031, 1047, 1095, 1125, 1287, 1325, 1457, 1616, 2361, 2918, 3252; $[\alpha]_D^{20}$ -126.7 (*c* = 0.9, MeOH); CD (MeCN) Δε (nm) +1.36 (307), -15.80 (235), +1.41 (221), -17.82 (209); UV (MeCN) ε (nm) 17300 (275), 40700 (221), 416 (210), 46500 (198); HR MS (EI): calcd for $C_{10}H_9IO_2$ 287.9647; found: 287.9658.

[a] Reference 14; [b] Isolated using *S. yaniokuyae* B8/36; [c] Reference 15; [d] Not isolated from the isomeric mixture obtained when using *P. putida* UV4 but obtained by substitution of an I-atom in compound **1g**; [e] Reference 16.; [f] Isomer **2e** could not be separated from compound **1e.**

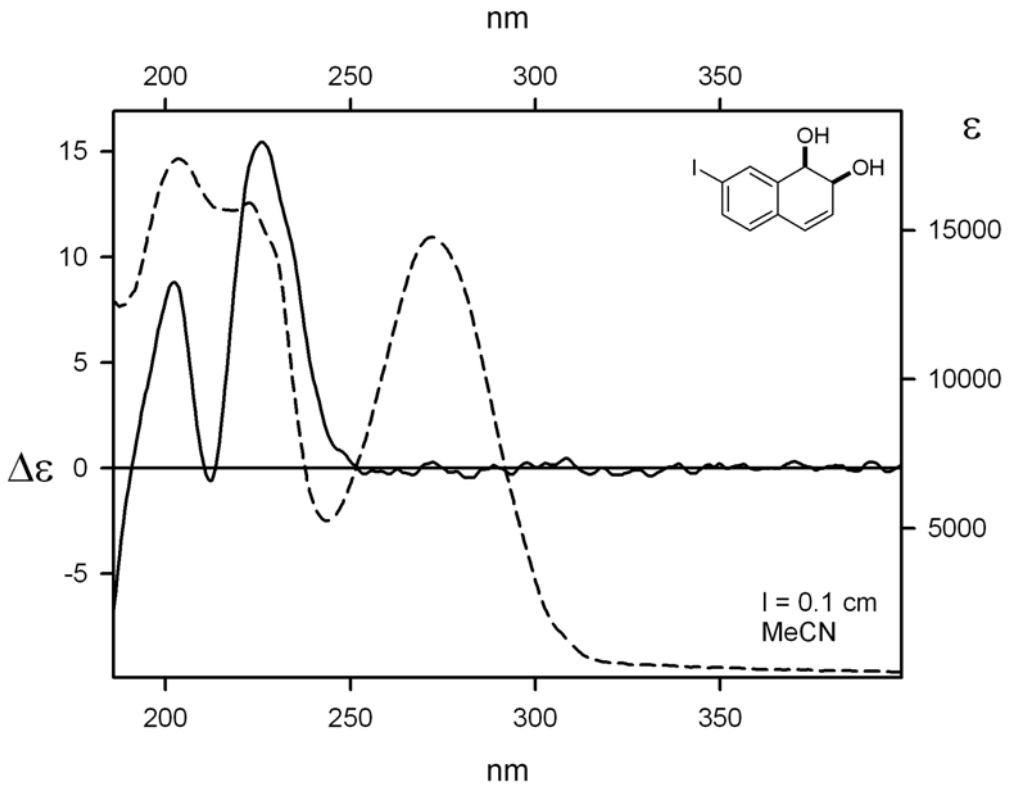


Figure A. Measured in acetonitrile solution CD (solid line) and UV (dashed line) spectra of **1g**.

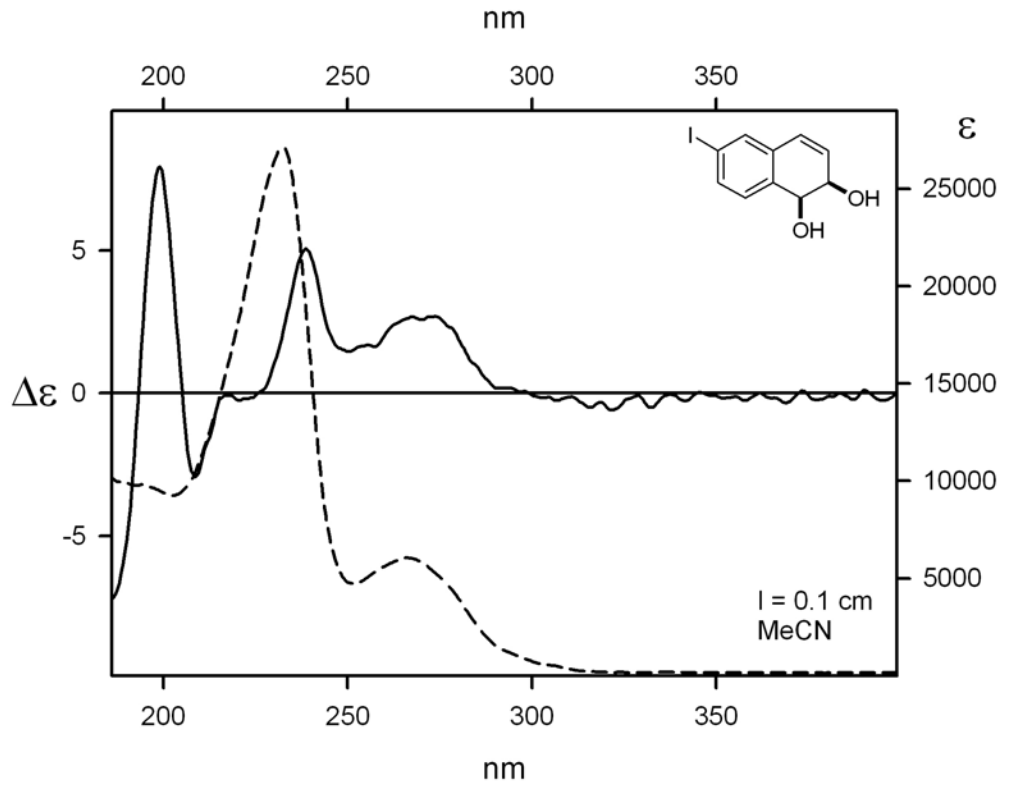


Figure B. Measured in acetonitrile solution CD (solid line) and UV (dashed line) spectra of **2g**.

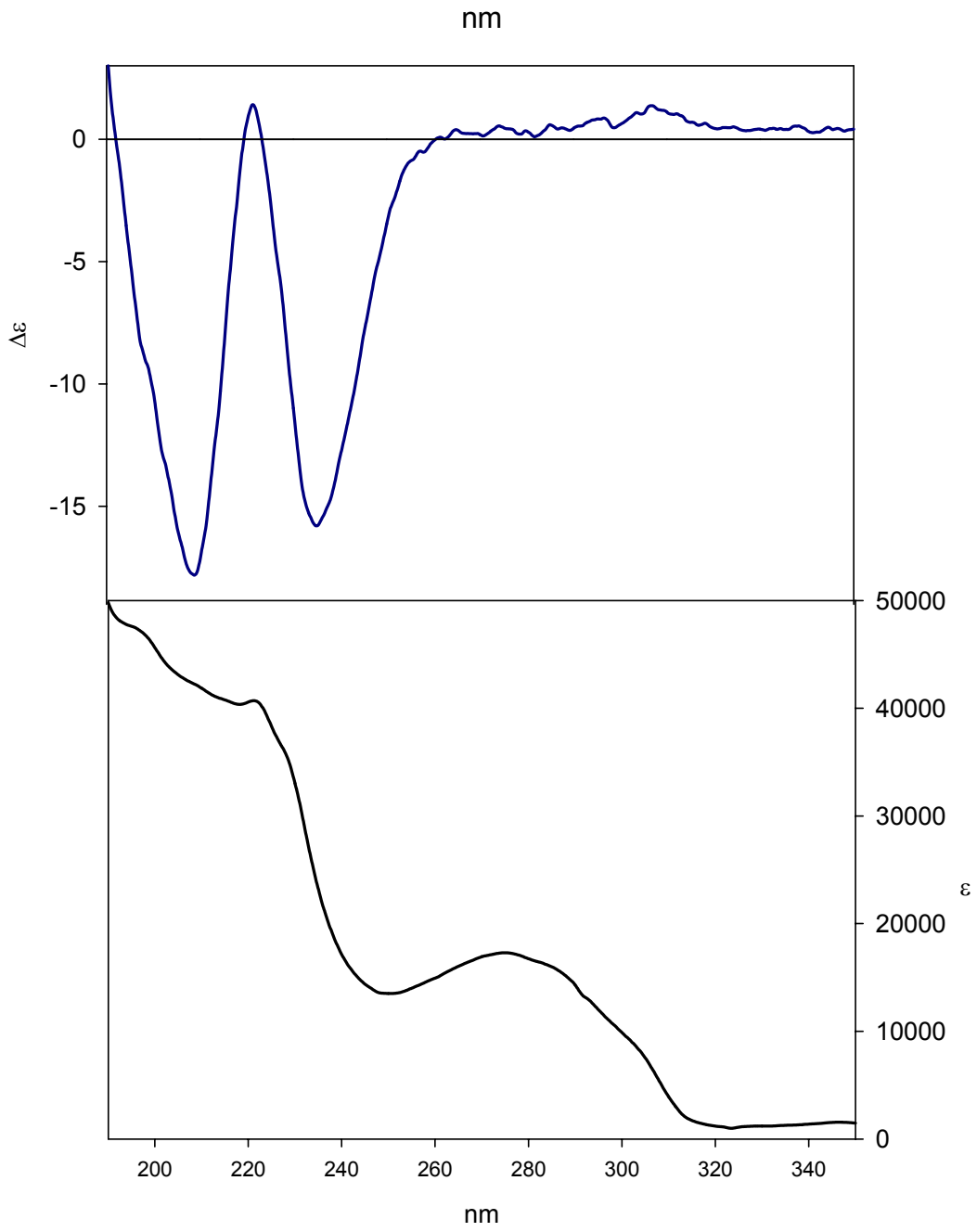
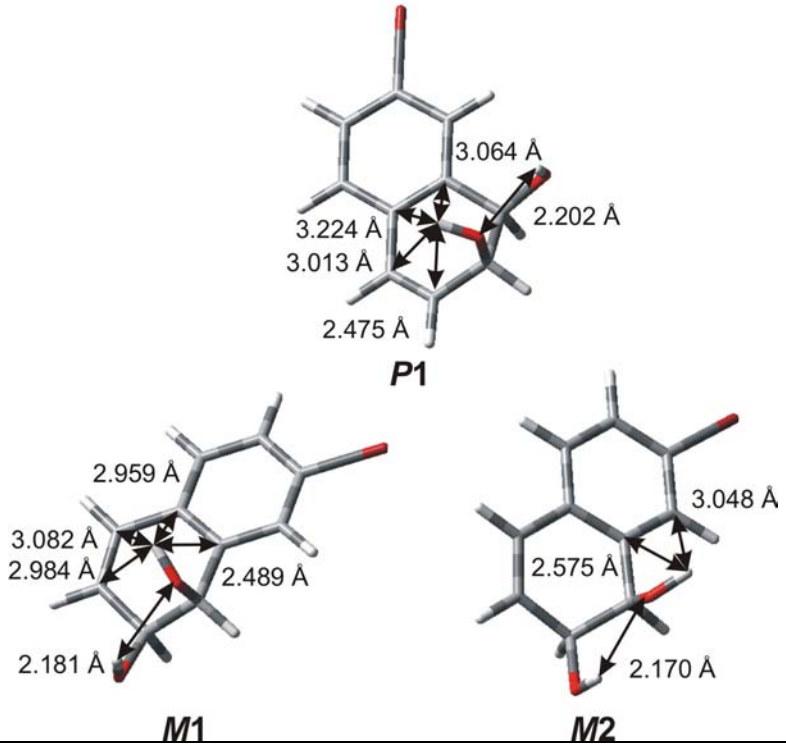


Figure C. Measured in acetonitrile solution CD (upper panel) and UV (lower panel) spectra of **3g**.



		1a(*P*1)	1a(*M*1)	1a(*M*2)
Energy[a] [Hartree]		-3111.209318 (-3109.593317)[b]	-3111.207817 (-3109.591921)[b]	-3111.206615 (-3109.591082)[b]
ΔE [kcal mol^{-1}][a]		0.00 (0.00)[b]	0.94 (0.88)[b]	1.70 (1.40)[b]
Population [%][a]		80 (76)[b]	16 (17)[b]	4 (10)[b]
ΔG [kcal mol^{-1}][a]		0.00	0.62	1.15
Population [%][a]		67	23	10
μ [D][a]		3.44	2.59	1.56
α [°][a]		-153.9 (-155.0)[b]	161.1 (160.2)[b]	66.8 (68.4)[b]
β [°][a]		-159.4 (-159.1)[b]	155.4 (156.6)[b]	162.6 (163.8)[b]
γ [°][a]		10.7 (11.7)[b]	-12.2 (-12.9)[b]	-11.2 (-11.9)[b]
[α] calcd.[c]	D	+197	+174	+93
	578 nm	+261	+233	+110
	546 nm	+302	+271	+125
	436 nm	+575	+521	+216

[α]$_D$ calcd. Boltzmann averaged

ΔE				ΔG			
D	578 nm	546 nm	436 nm	D	575 nm	546 nm	436 nm
+189 (+186)[b]	+250 (+246)[b]	+290 (+284)[b]	+552 (+541)[b]	+181	+239	+277	+527

[a] – B3LYP/6-311++G(D,P)
[b] – in parentheses results for geometries optimized at B2PLYP/6-311++G(D,P) level
[c] – B3LYP/6-311++G(2D,2P)

Figure 1A. Calculated at B3LYP/6-311++G(D,P) level structures of individual conformers of **1a**, their relative energies and some structural parameters.

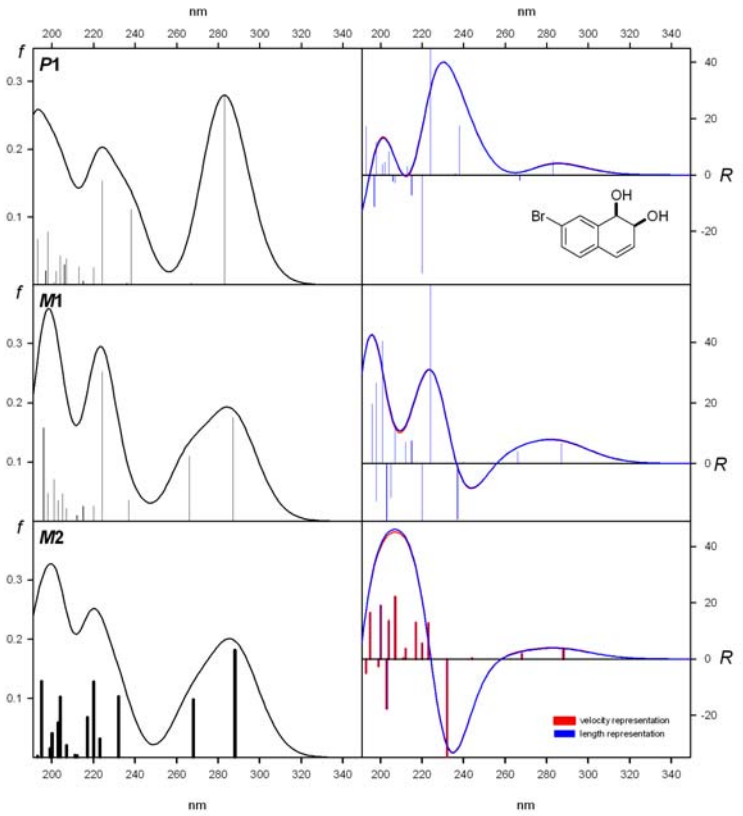


Figure 1B. Calculated at TDDFT/mPW1PW91/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **1a**.

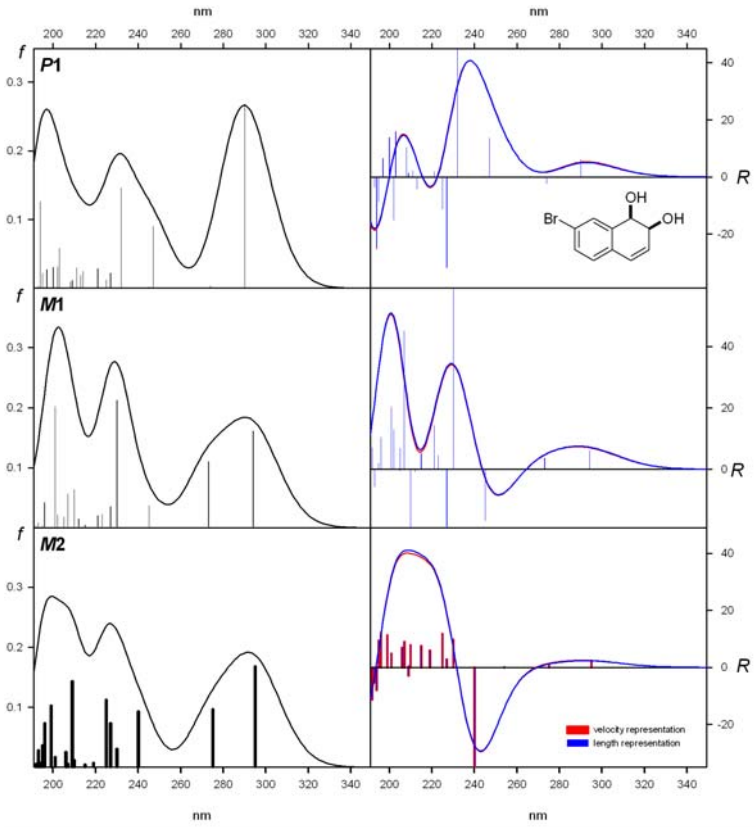


Figure 1C. Calculated at TDDFT/B3LYP/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **1a**.

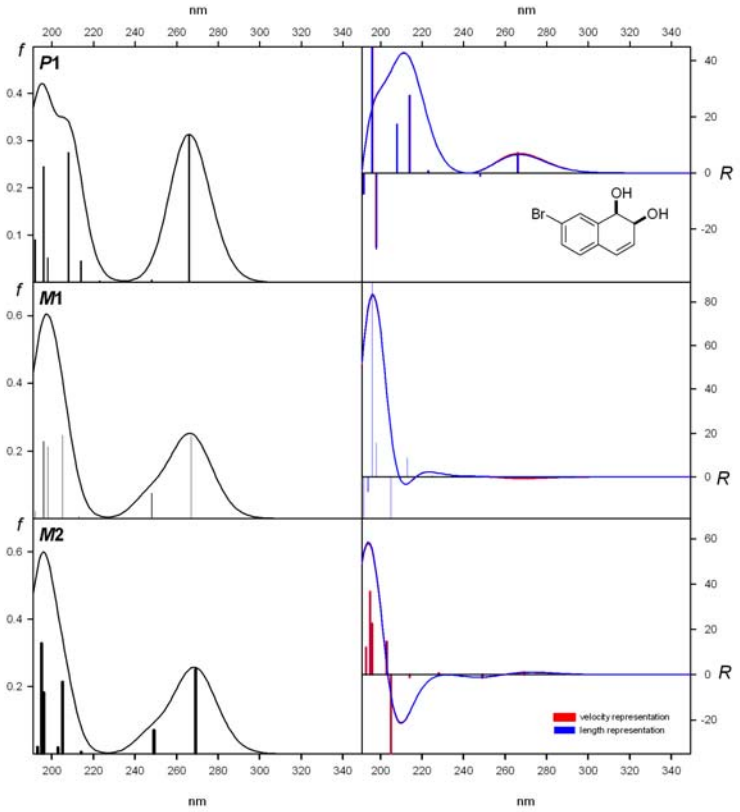


Figure 1D. Calculated at TDDFT/B2PLYP/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **1a**.

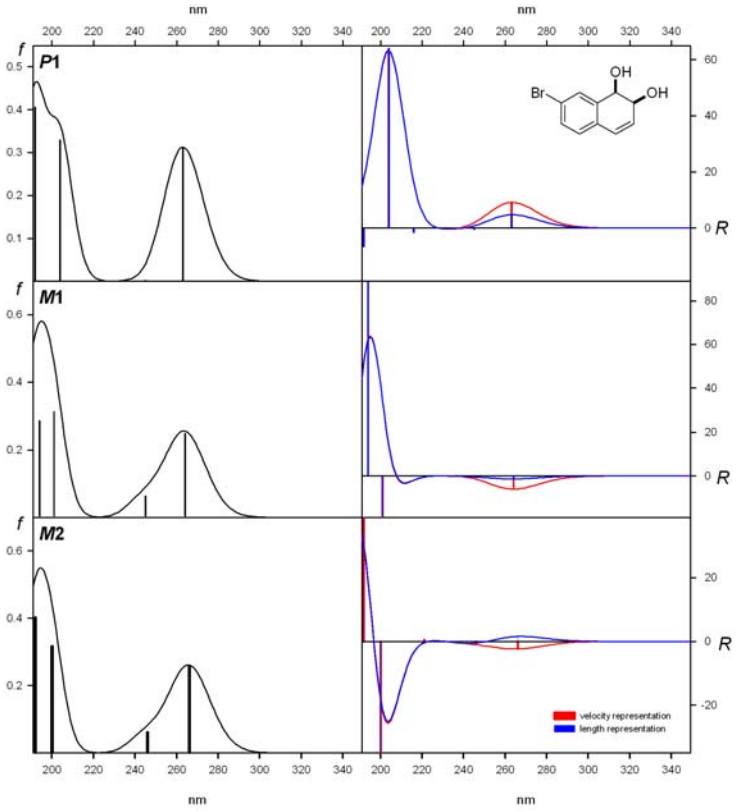
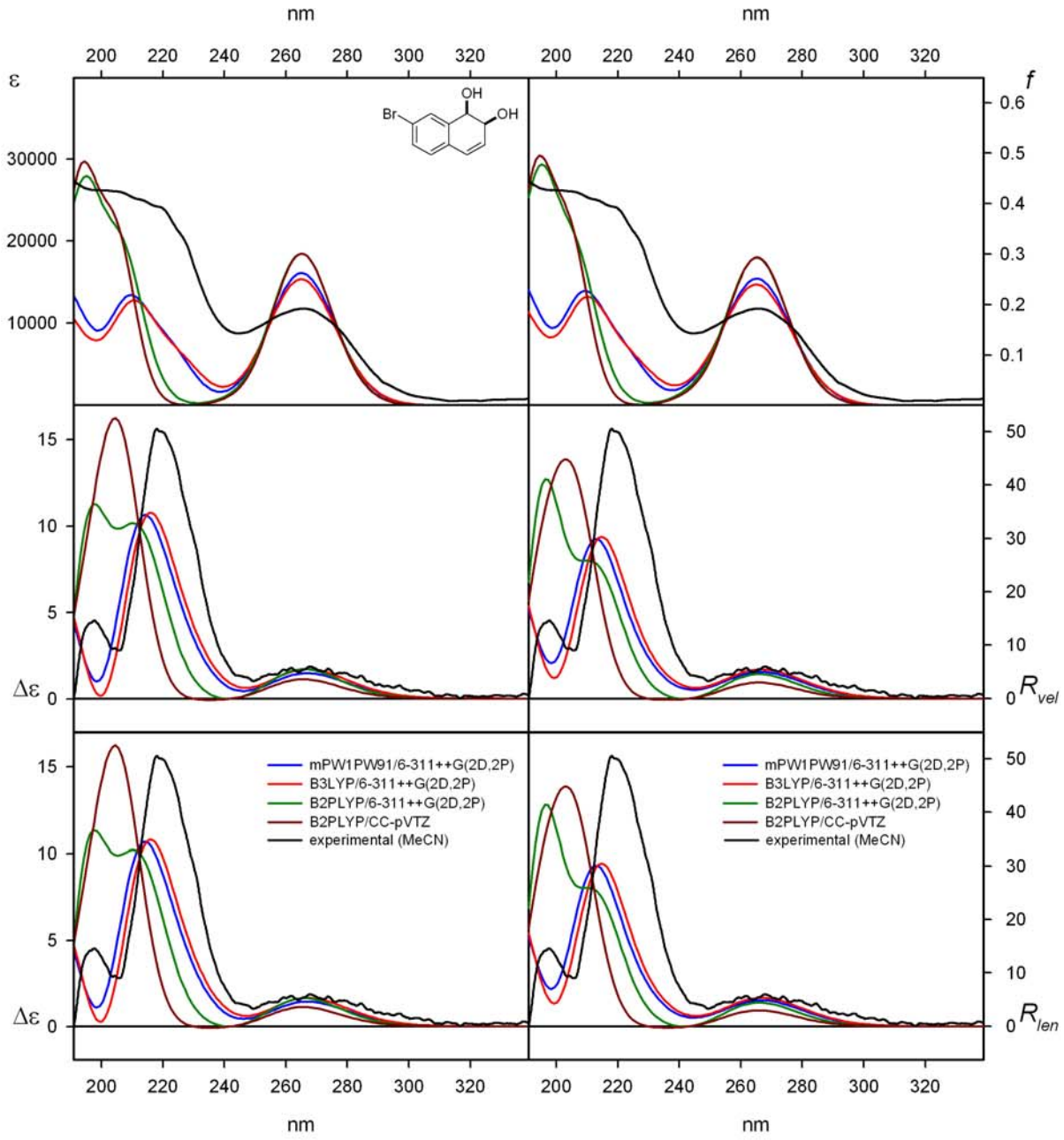
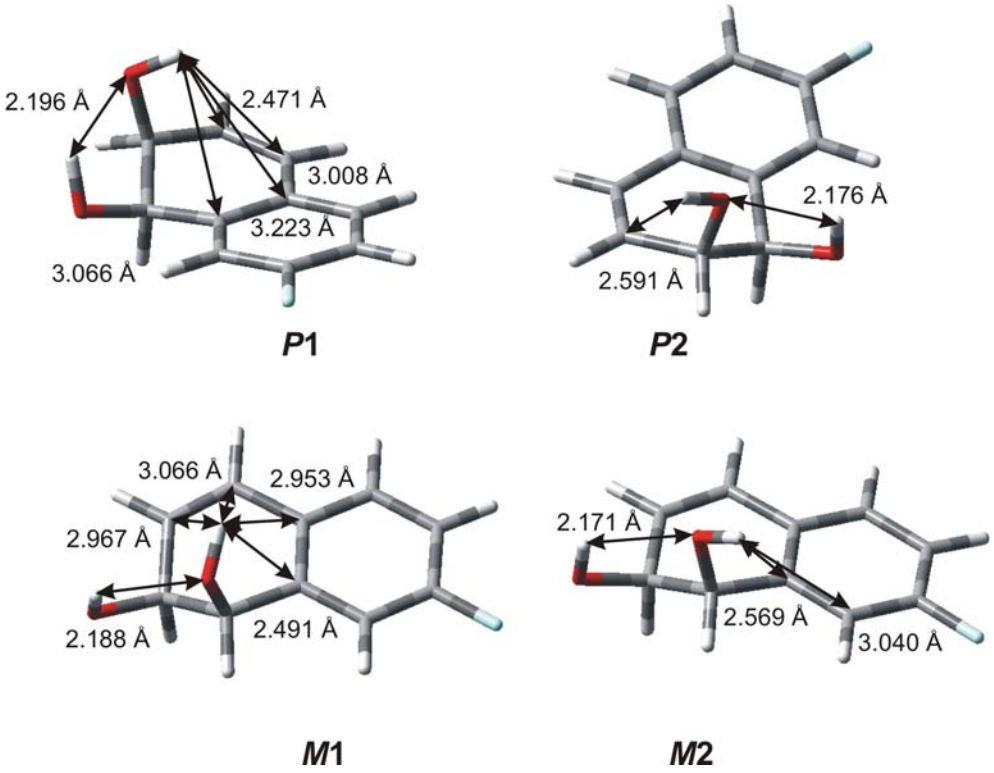


Figure 1E. Calculated at TDDFT/B2PLYP/CC-pVTZ level CD and UV spectra for individual conformers of **1a**.



Geometries were optimzed at B3LYP/6-311++G(D,P) level
Calculated energies were scaled by the factors of:
0.936 (mPW1PW91/6-311++G(2D,2P))
0.914 (B3LYP/6-311++G(2D,2P))
0.996 (B2PLYP/6-311++G(2D,2P))
1.008 (B2PLYP/CC-pVTZ)
σ = 0.5 eV

Figure 1F. Calculated Boltzmann averaged CD and UV spectra for *cis*-dihydrodiol **1a**. The rotational strenghts *R* were calculated at diferent levels of theory in both velocity and dipole length representations. The calculated CD and UV spectra were wavelength corrected to match the experimental long-wavelength λ_{max} values in the UV spectra.



		1b(*P*1)	**1b(*P*2)**	**1b(*M*1)**	**1b(*M*2)**
Energy[a] [Hartree]		-636.935709	-636.933205	-636.933817	-636.932420
ΔE [kcal mol^{-1}][a]		0.00	1.57	1.19	2.06
Population [%][a]		83	6	13	-
ΔG [kcal mol^{-1}][a]		0.00	0.76	0.93	1.51
Population [%][a]		65	17	13	5
μ [D][a]		3.40	4.08	2.62	1.67
α [°][a]		-154.0	-160.1	162.1	67.6
β [°][a]		-158.9	-69.1	155.8	163.0
γ [°][a]		10.8	11.2	-12.3	-11.3
[*α*] calcd.[b]	D	+242	+315	+134	+10
	575 nm	+349	+449	+163	-24
	546 nm	+410	+526	+185	-35
	436 nm	+848	+1083	+312	-149

$[\alpha]_D$ calcd. Boltzmann averaged

ΔE				*ΔG*			
D	578 nm	546 nm	436 nm	D	578 nm	546 nm	436 nm
+237	+337	+395	+809	+229	+323	+378	+768

[a] – B3LYP/6-311++G(D,P)
[b] – B3LYP/6-311++G(2D,2P)

Figure 2A. Calculated at B3LYP/6-311++G(D,P) level structures of individual conformers of **1b**, their relative energies and some structural parameters.

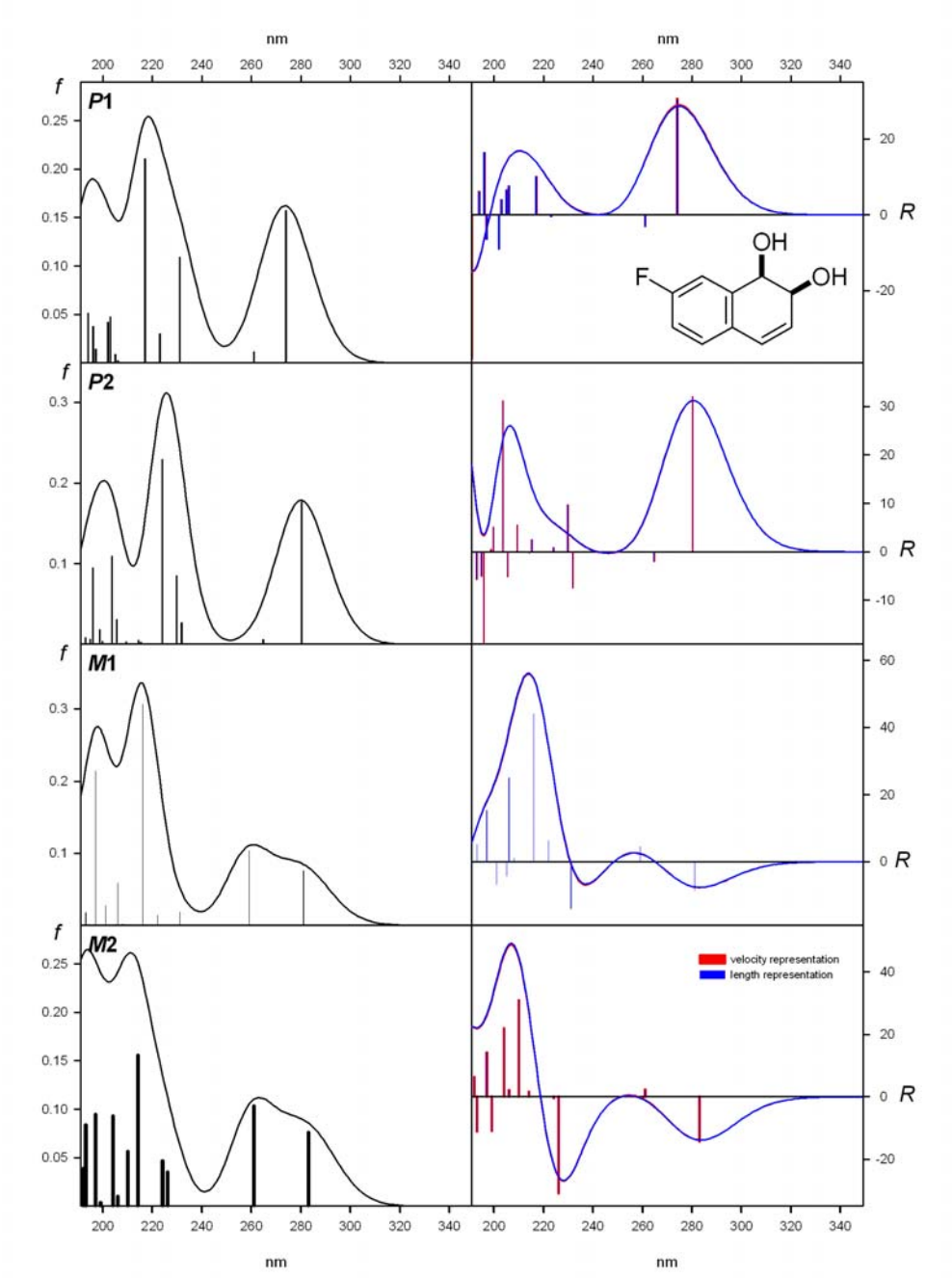


Figure 2B. Calculated at TDDFT/mPW1PW91/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **1b**.

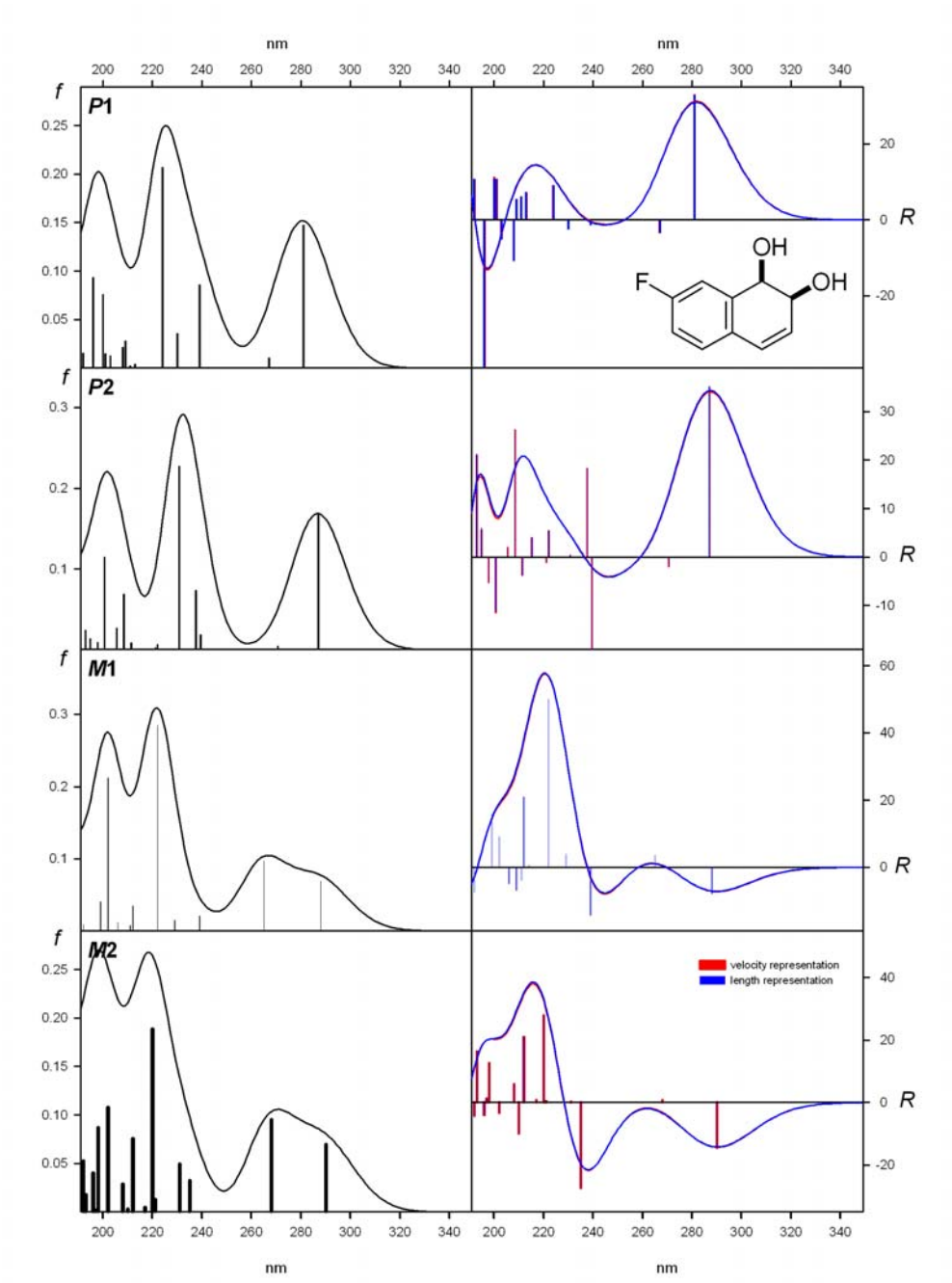


Figure 2C. Calculated at TDDFT/B3LYP/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **1b**.

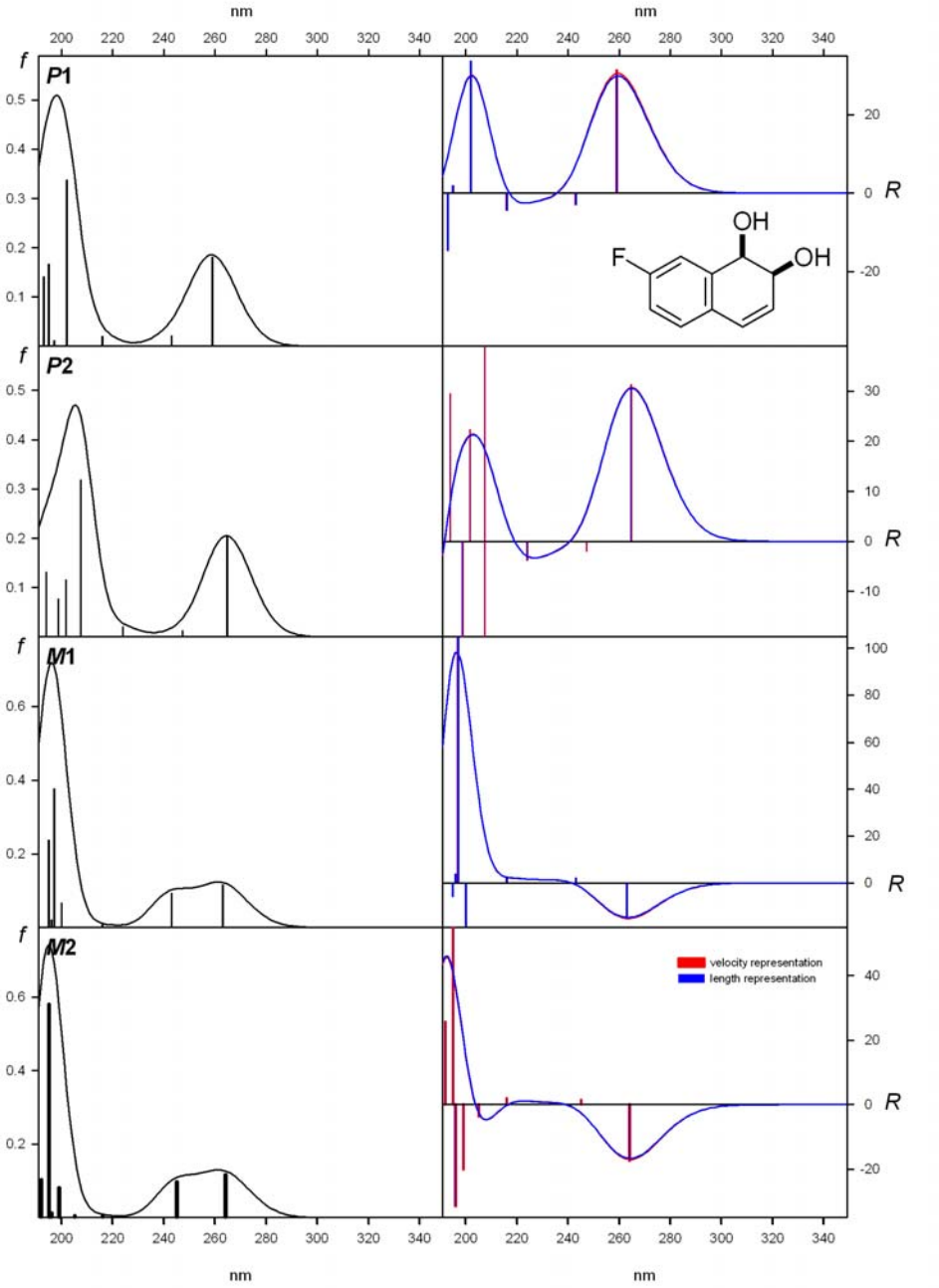


Figure 2D. Calculated at TDDFT/B2PLYP/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **1b**.

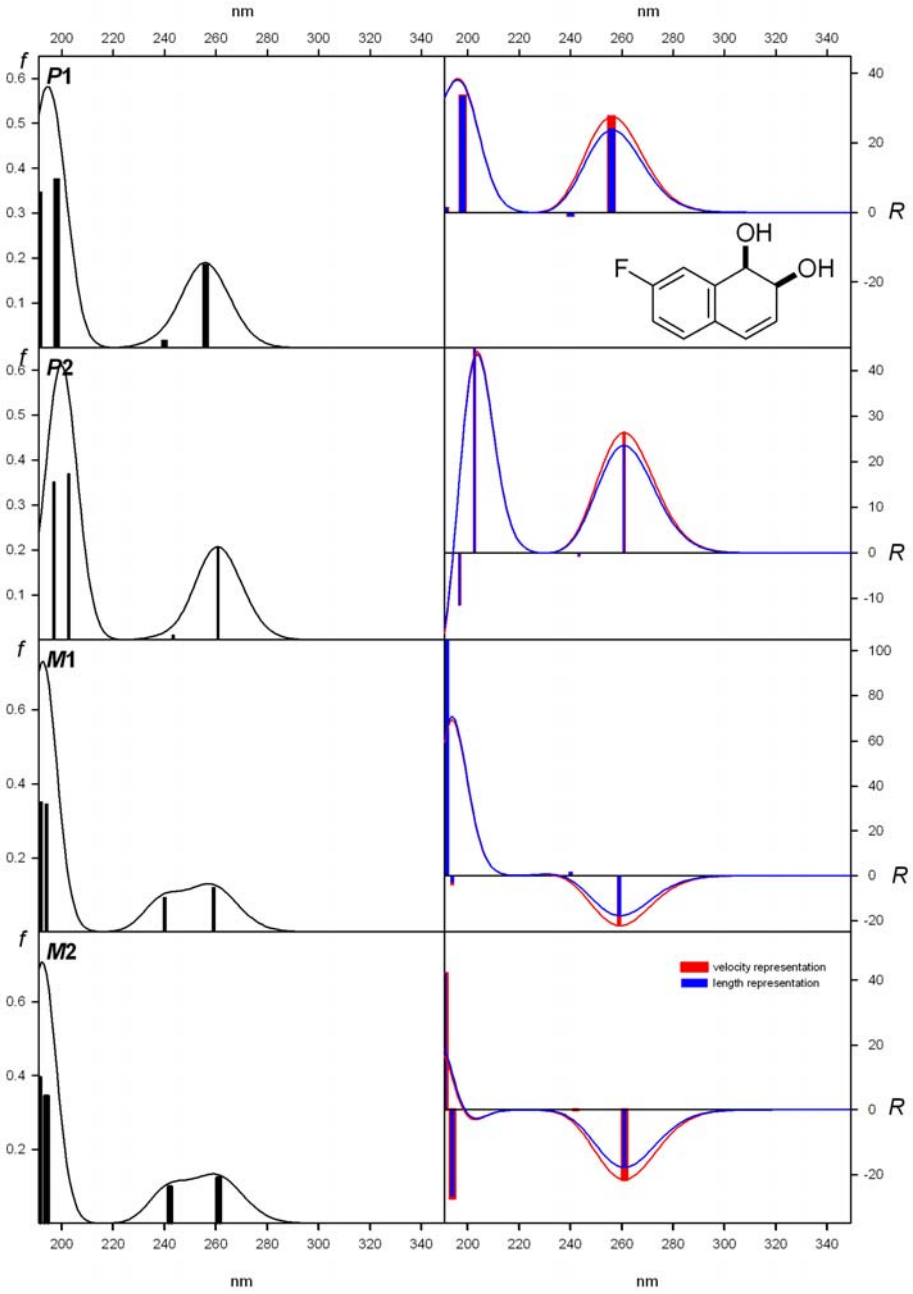
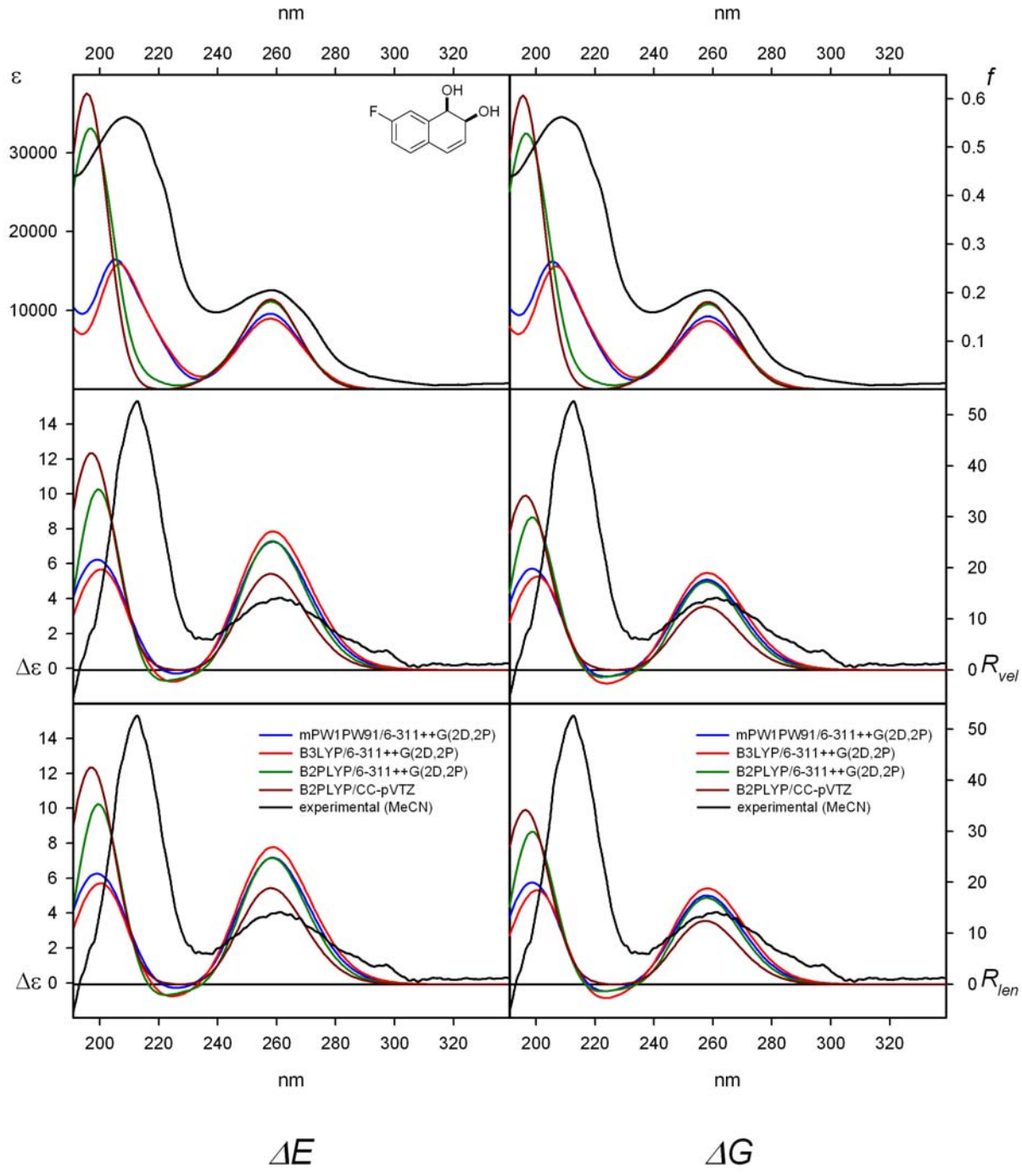
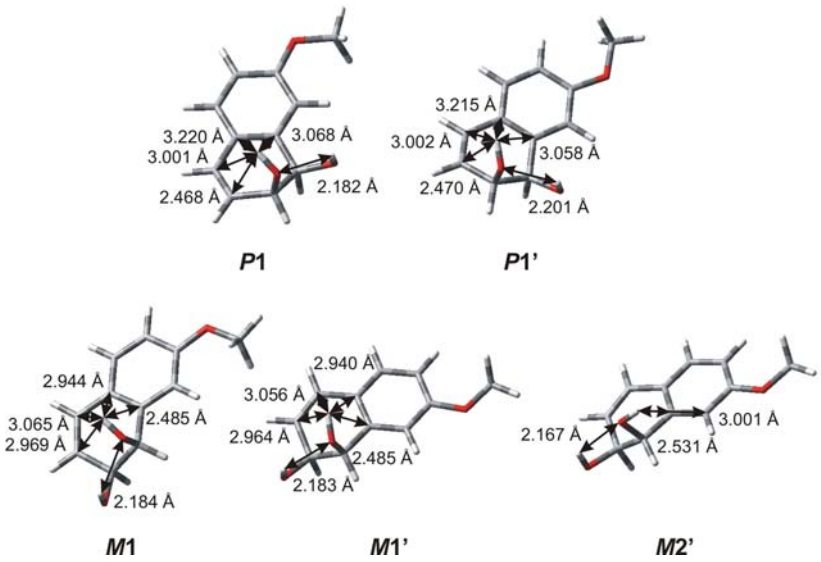


Figure 2E. Calculated at TDDFT/B2PLYP/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **1b**.



Geometries were optimzed at B3LYP/6-311++G(D,P) level
Calculated energies were scaled by the factors of:
0.942 (mPW1PW91/6-311++G(2D,2P))
0.918 (B3LYP/6-311++G(2D,2P))
0.996 (B2PLYP/6-311++G(2D,2P))
1.008 (B2PLYP/CC-pVTZ)
σ = 0.5 eV

Figure 2F. Calculated Boltzmann averaged CD and UV spectra for *cis*-dihydrodiol **1b**. The rotational strenghts *R* were calculated at diferent levels of theory in both velocity and dipole length representations. The calculated CD and UV spectra were wavelength corrected to match the experimental long-wavelength λ_{max} values in the UV spectra.



		1c(*P*1)	1c(*P*1')	1c(*M*1)	1c(*M*1')	1c(*M*2')
Energy[a] [Hartree]		-652.224551 (-650.887161)[b]	-652.223911 (-650.886567)[b]	-652.222448 (-650.885170)[b]	-652.222420 (-650.885164)[b]	-652.221014 (-650.884162)[b]
ΔE [kcal mol^{-1}][a]		0.00 (0.00)[b]	0.40 (0.37)[b]	1.32 (1.25)[b]	1.34 (1.25)[b]	2.22 (1.88)[b]
Population [%][a]		59 (56)[b]	29 (30)[b]	6 (6)[b]	6 (6)[b]	0 (2)[b]
ΔG [kcal mol^{-1}][a]		0.00	0.30	0.92	0.94	1.43
Population [%][a]		48	29	10	9	4
μ [D][a]		1.33	3.95	3.61	4.59	4.51
α [°][a]		-153.3 (-154.5)[b]	-155.0 (-156.3)[b]	161.8 (160.9)[b]	161.3 (160.4)[b]	72.2 (72.4)[b]
β [°][a]		-158.7 (-158.4)[b]	-159.0 (-158.8)[b]	156.0 (157.3)[b]	156.2 (157.3)[b]	163.2 (164.0)[b]
γ [°][a]		10.3 (11.3)[b]	10.3 (11.3/)[b]	-11.9 (-12.6)[b]	-12.1 (-12.7)[b]	-10.9 (-11.5)[b]
δ [°][a]		-179.3 (-179.2)[b]	-0.2 (-0.2)[b]	179.1 (179.2)[b]	-0.3 (-0.3)[b]	-0.8 (-0.8)[b]
[α] calcd.[c]	D	+319	+189	+178	+221	+118
	575 nm	+476	+261	+227	+307	+151
	546 nm	+562	+305	+261	+358	+174
	436 nm	+1229	+611	+472	+711	+323

[α]$_D$ calcd. Boltzmann averaged

ΔE				ΔG			
D	578 nm	546 nm	436 nm	D	578 nm	546 nm	436 nm
+267 (+261)[b]	+389 (+379)[b]	+457 (+447)[b]	+973 (+949)[b]	+251	+361	+424	+894

[a] – B3LYP/6-311++G(D,P)
[b] – in parentheses results for geometries optimized at B2PLYP/6-311++G(D,P) level
[c] – B3LYP/6-311++G(2D,2P)

Figure 3A. Calculated at B3LYP/6-311++G(D,P) level structures of individual conformers of **1c**, their relative energies and some structural parameters.

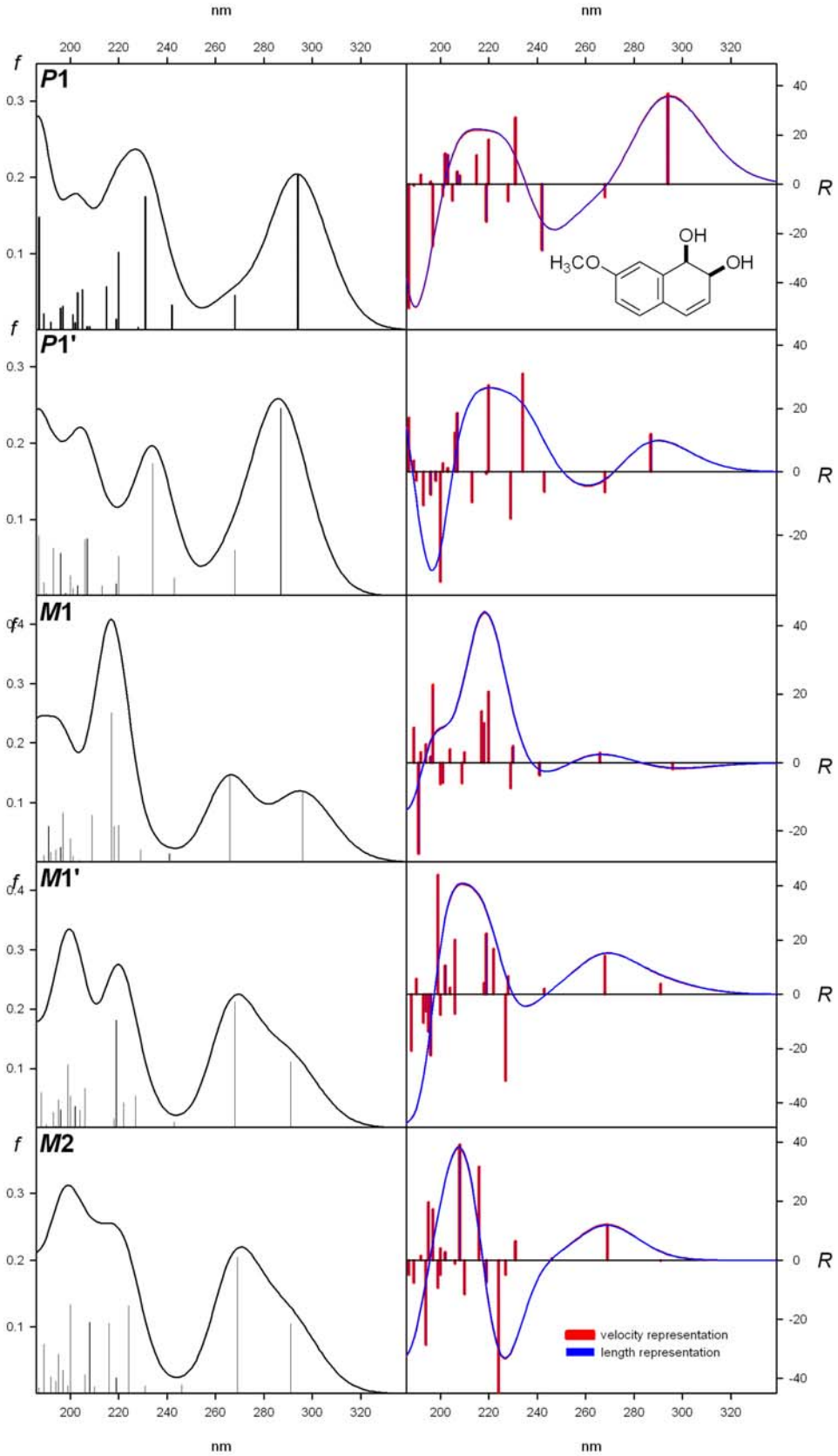


Figure 3B. Calculated at TDDFT/mPW1PW91/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **1c**.

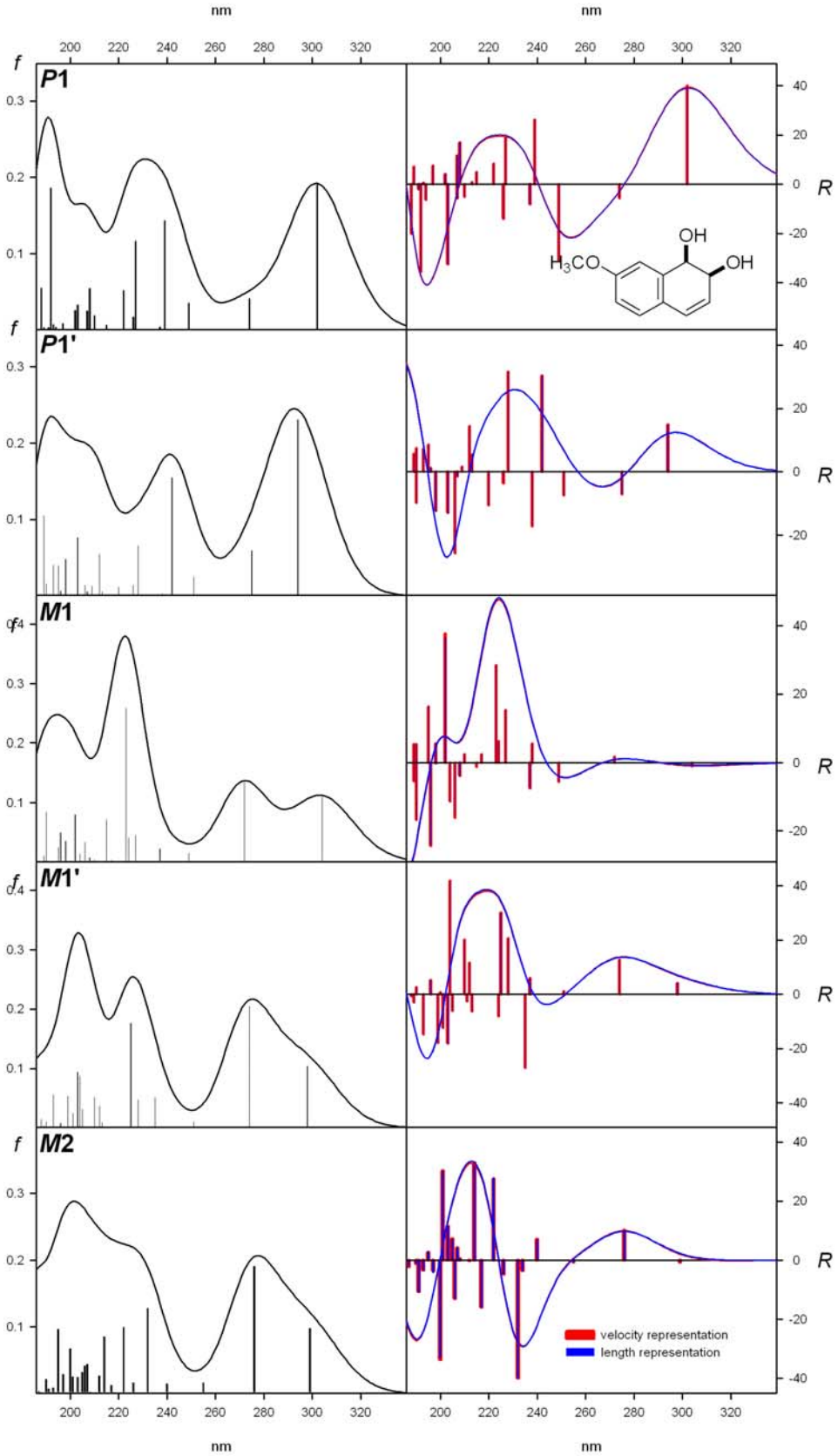


Figure 3C. Calculated at TDDFT/B3LYP/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **1c**.

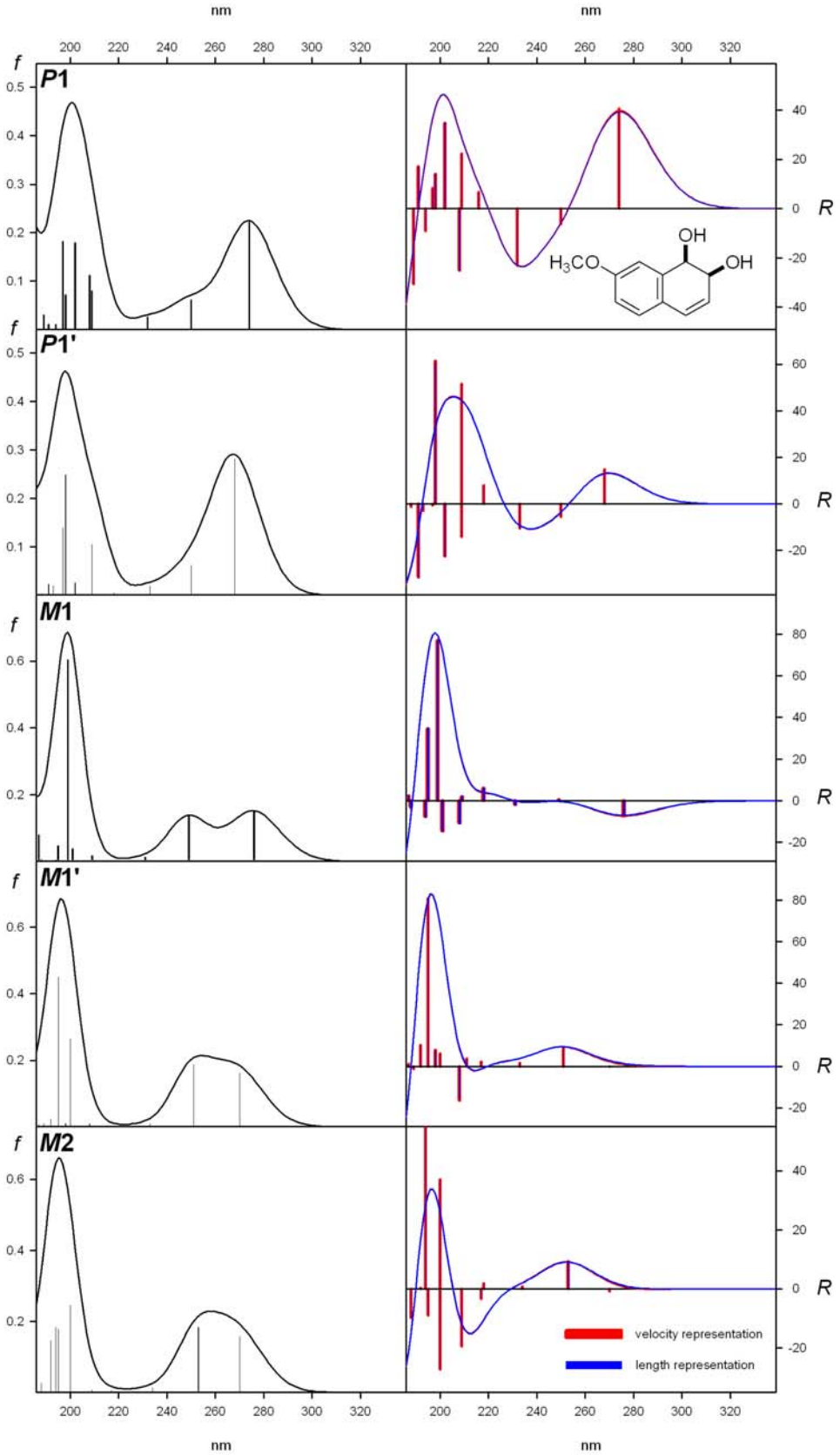


Figure 3D. Calculated at TDDFT/B2PLYP/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **1c**.

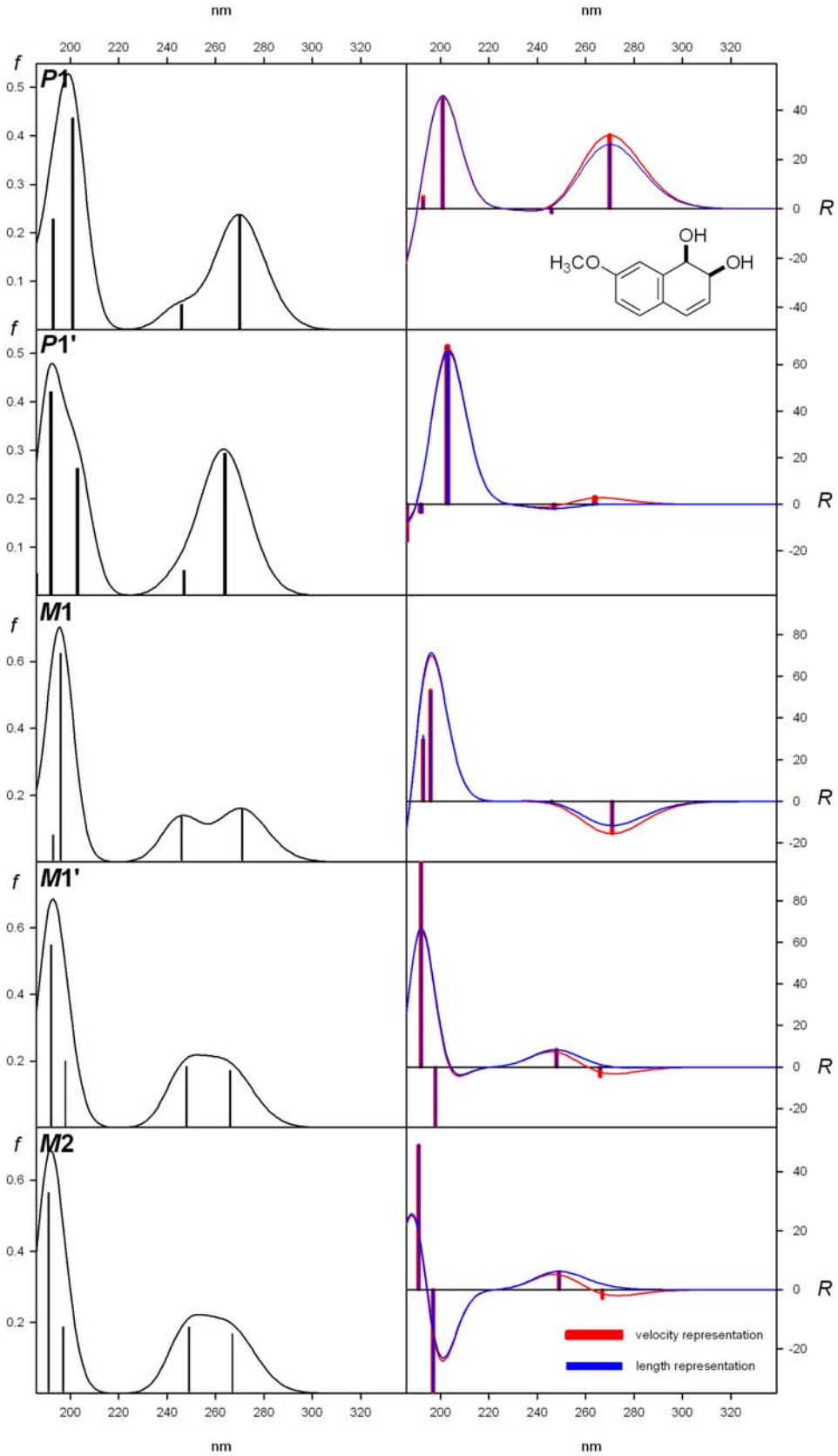
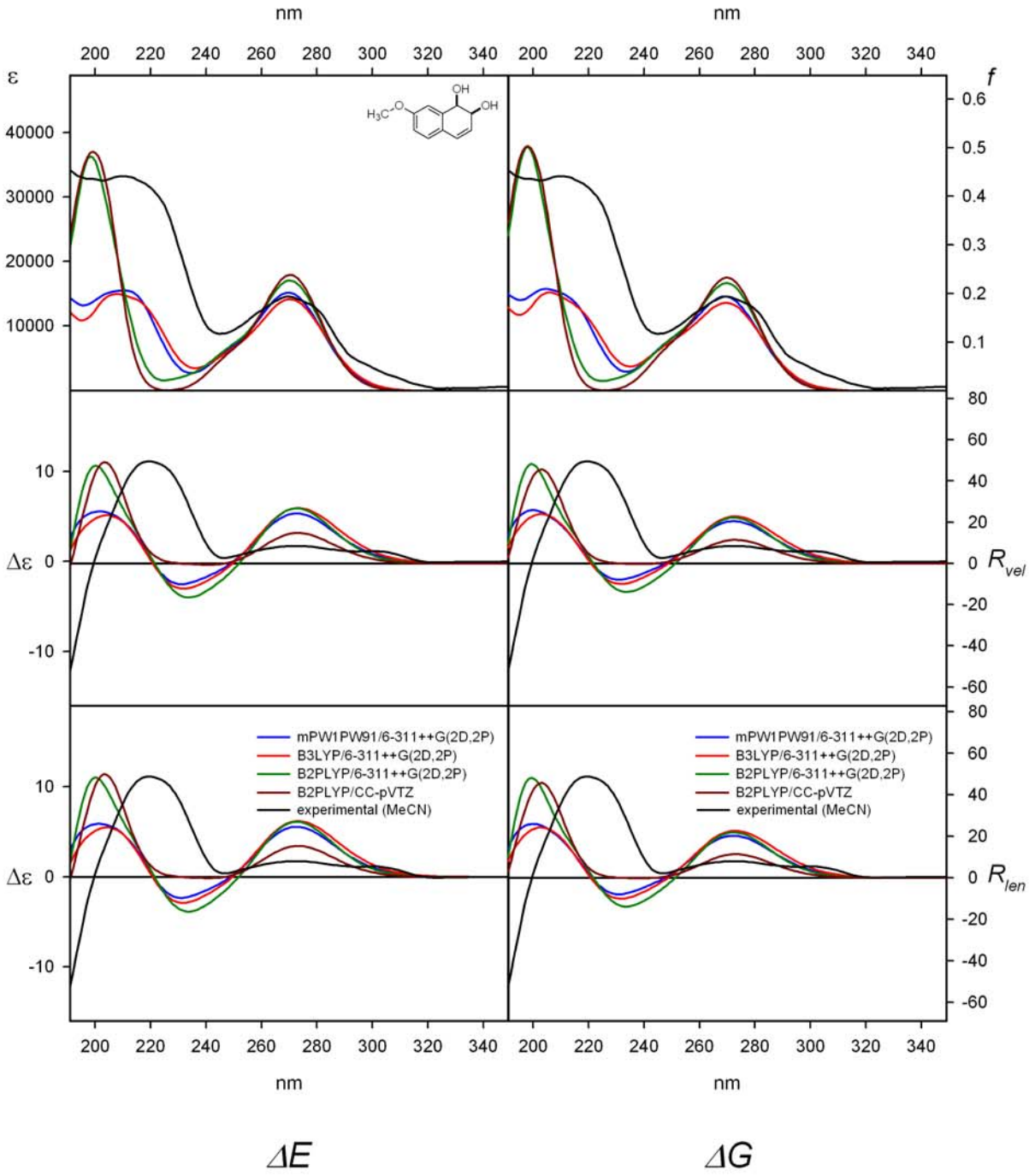
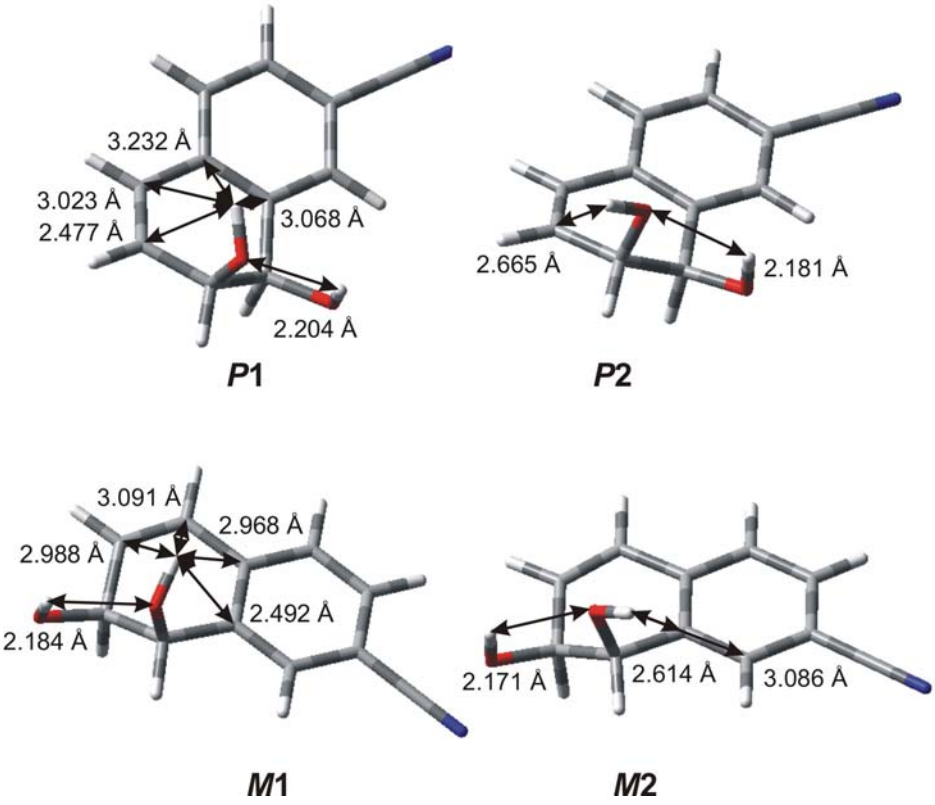


Figure 3E. Calculated at TDDFT/B2PLYP/CC-pVTZ level CD and UV spectra for individual conformers of **1c**.



Geometries were optimzed at B3LYP/6-311++G(D,P) level
Calculated energies were scaled by the factors of:
0.928 (mPW1PW91/6-311++G(2D,2P))
0.906 (B3LYP/6-311++G(2D,2P))
0.996 (B2PLYP/6-311++G(2D,2P))
1.011 (B2PLYP/CC-pVTZ)
σ = 0.5 eV

Figure 3F. Experimental CD and UV spectra in acetonitrile solution (black line) and calculated Boltzmann averaged CD and UV spectra for *cis*-dihydrodiol **1c**. The rotational strenghts *R* were calculated at diferent levels of theory in both velocity and dipole length representations.



		1d(*P*1)	1d(*P*2)	1d(*M*1)	1d(*M*2)
Energy[a] [Hartree]		-629.933082	-629.9309933	-629.931646	-629.930814
ΔE [kcal mol^{-1}][a]		0.00	1.31	0.90	1.42
Population [%][a]		71	7	15	7
ΔG [kcal mol^{-1}][a]		0.00	2.15	1.99	2.30
Population [%][a]		97	-	3	-
μ [D][a]		6.16	7.45	4.57	3.08
α [°][a]		-153.5	-159.4	161.2	61.7
β [°][a]		-159.6	-58.2	155.2	162.3
γ [°][a]		10.9	11.5	-12.4	-11.4
[α] calcd.[b]	D	+238	+310	+239	+138
	575 nm	+312	+406	+334	+184
	546 nm	+361	+469	+390	+214
	436 nm	+678	+890	+780	+424

[α]$_D$ calcd. Boltzmann averaged

ΔE				ΔG			
D	578 nm	546 nm	436 nm	D	578 nm	546 nm	436 nm
+215	+302	+353	+714	+239	+343	+403	+832

[a] – B3LYP/6-311++G(D,P)
[b] – B3LYP/6-311++G(2D,2P)

Figure 4A. Calculated at B3LYP/6-311++G(D,P) level structures of individual conformers of **1d**, their relative energies and some structural parameters.

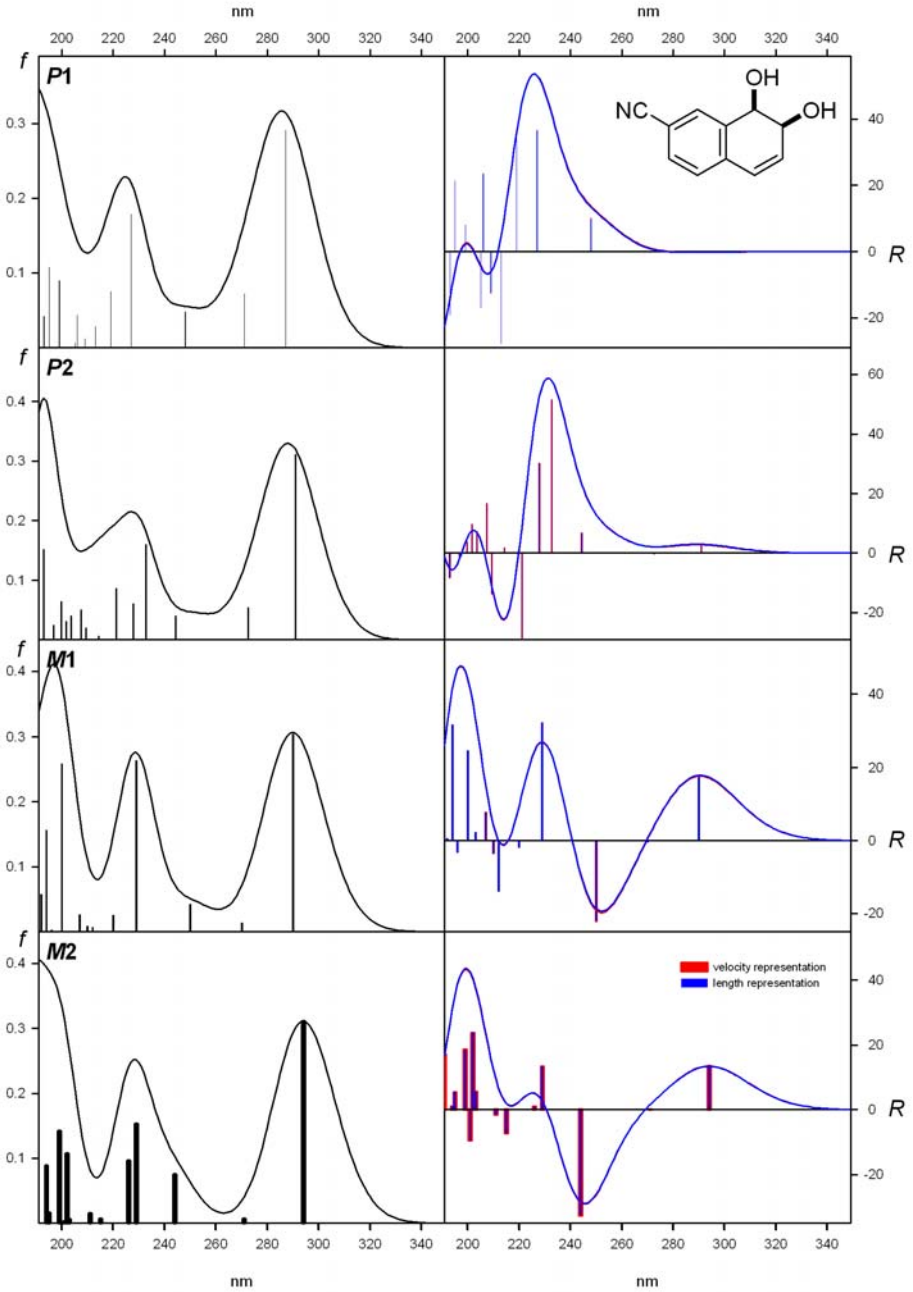


Figure 4B. Calculated at TDDFT/mPW1PW91/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **1d**.

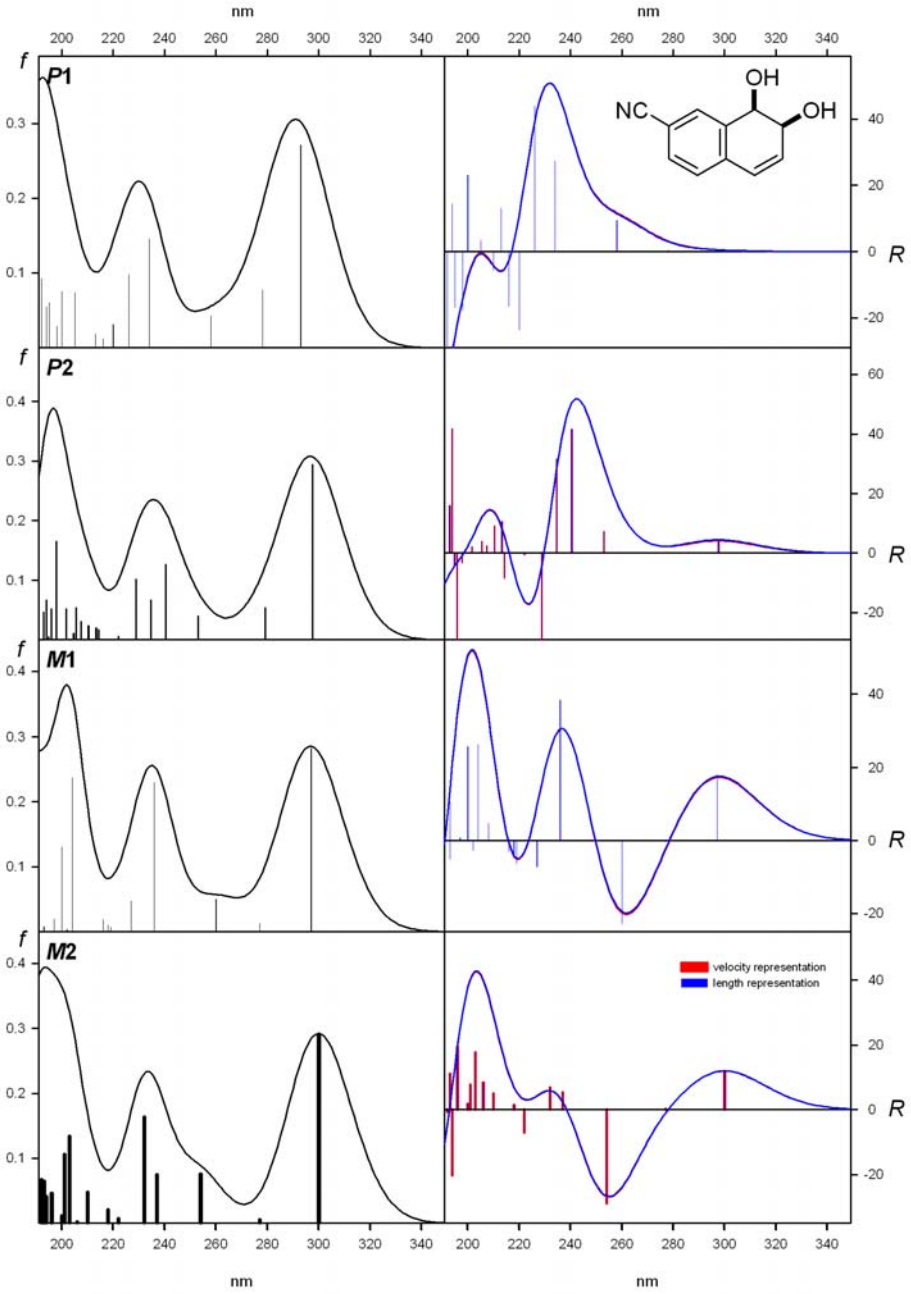


Figure 4C. Calculated at TDDFT/B3LYP/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **1d**.

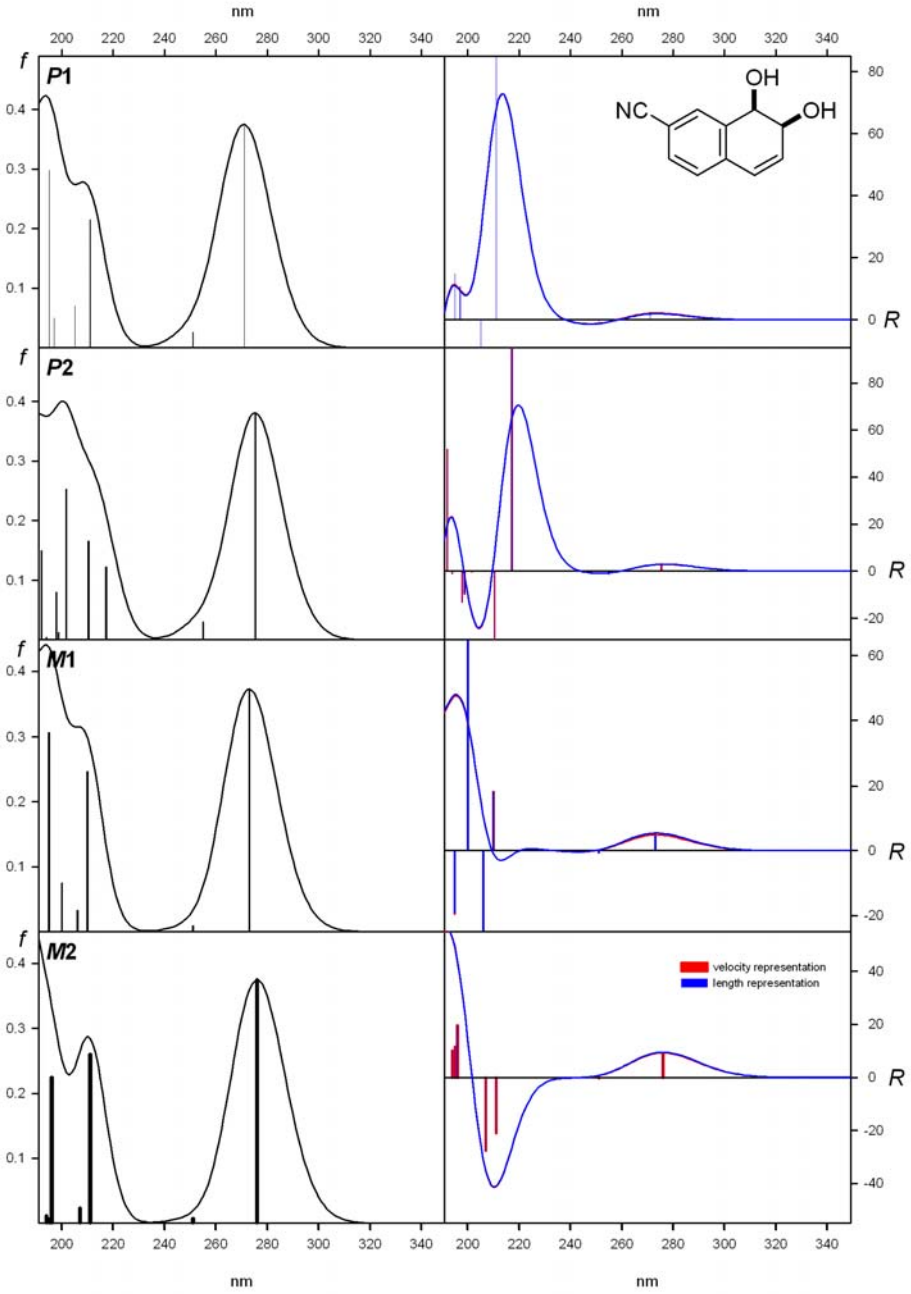


Figure 4D. Calculated at TDDFT/B2PLYP/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **1d**.

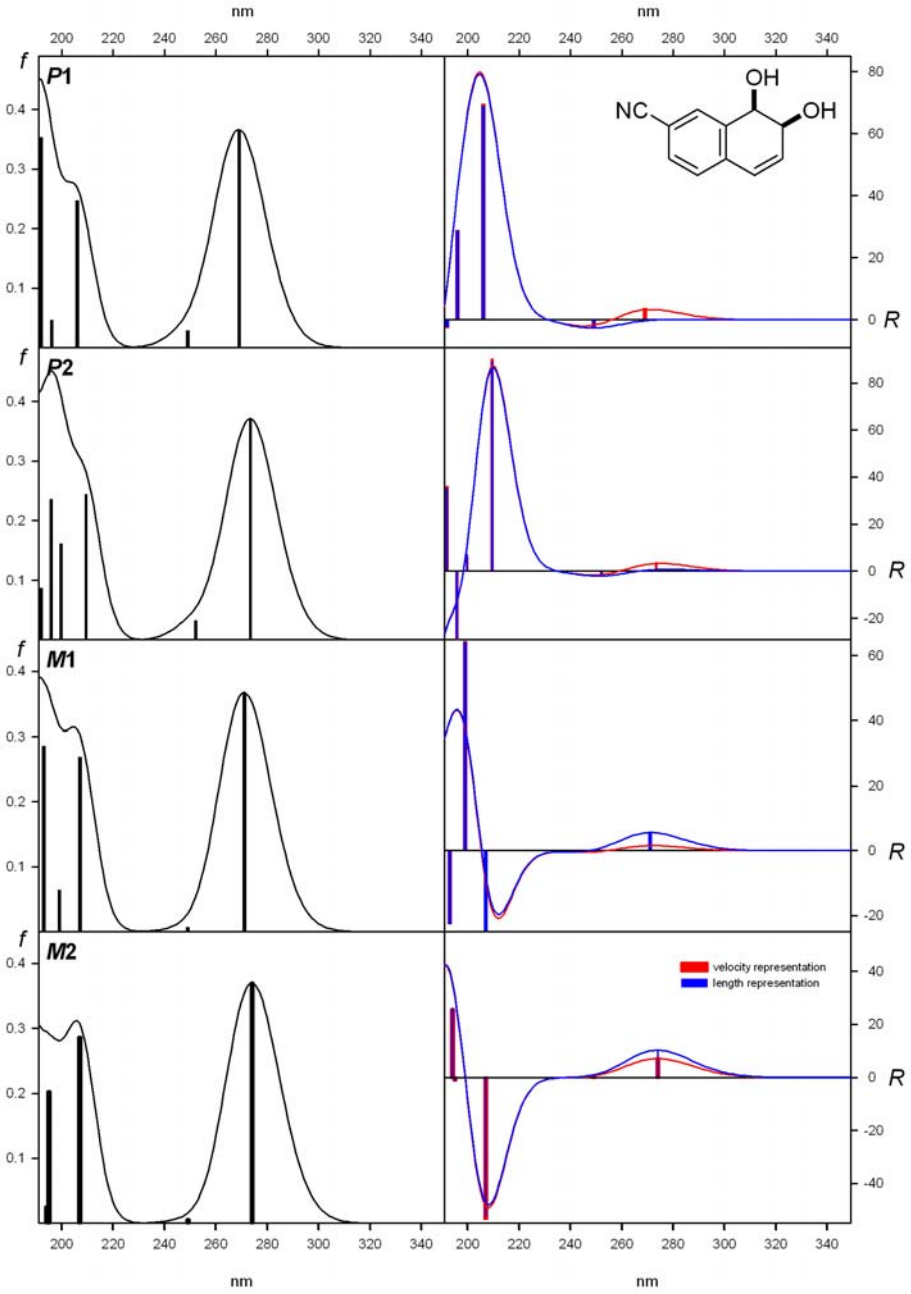
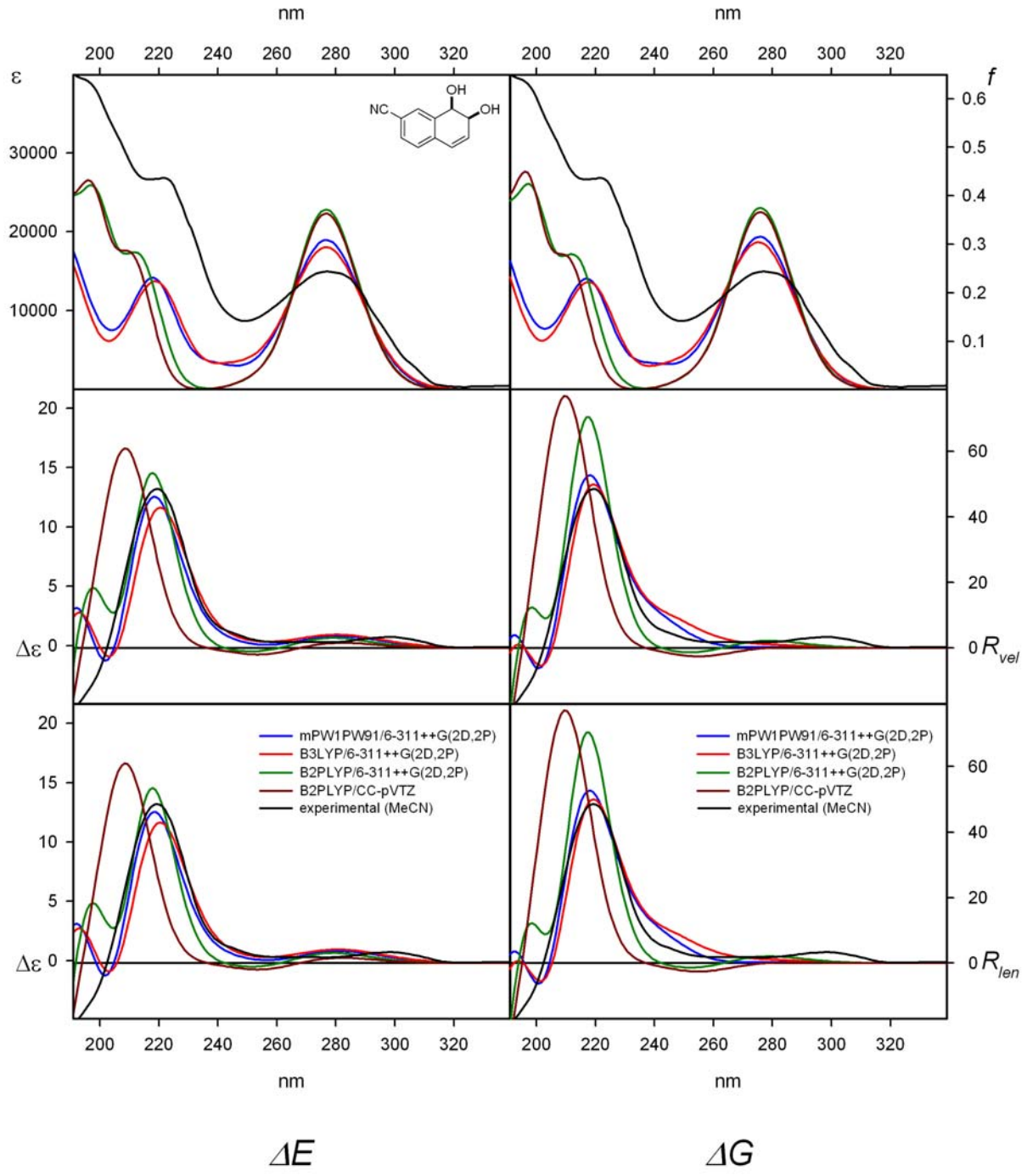
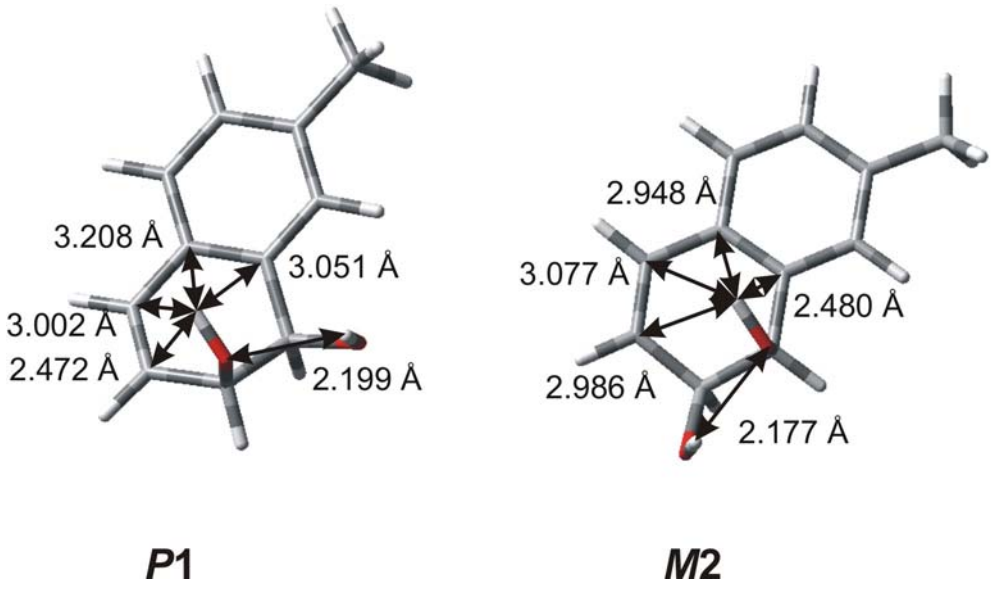


Figure 4E. Calculated at TDDFT/B2PLYP/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **1d**.



Geometries were optimzed at B3LYP/6-311++G(D,P) level
Calculated energies were scaled by the factors of:
0.965 (mPW1PW91/6-311++G(2D,2P))
0.945 (B3LYP/6-311++G(2D,2P))
1.018 (B2PLYP/6-311++G(2D,2P))
1.026 (B2PLYP/CC-pVTZ)
σ = 0.5 eV

Figure 4F. Experimental CD and UV spectra in acetonitrile solution (black line) and calculated Boltzmann averaged CD and UV spectra for *cis*-dihydrodiol **1d**. The rotational strenghts *R* were calculated at diferent levels of theory in both velocity and dipole length representations.



***P*1** ***M*2**

		1e(*P*1)	**1e(*M*1)**
Energy[a] [Hartree]		-576.994824 (-575.777828)[b]	-576.993771 (-575.776839)[b]
ΔE [kcal mol^{-1}][a]		0.00 (0.00)[b]	0.66 (0.62)[b]
Population [%][a]		76 (74)[b]	24 (26)[b]
ΔG [kcal mol^{-1}][a]		0.00	0.84
Population [%][a]		81	19
μ [D][a]		2.53	2.96
α [°][a]		-154.3 (-155.9)[b]	160.2 (159.2)[b]
β [°][a]		-159.6 (-159.4)[b]	155.8 (157.0)[b]
γ [°][a]		10.8 (11.6)[b]	-12.2 (-12.8)[b]
[α] calcd.[c]	D	+276	+205
	575 nm	+385	+274
	546 nm	+449	+318
	436 nm	+903	+603

[α]$_D$ calcd. Boltzmann averaged

ΔE				ΔG			
D	575 nm	546 nm	436 nm	D	575 nm	546 nm	436 nm
+259 (+257)[b]	+358 (+356)[b]	+417 (+415)[b]	+831 (+825)[b]	+262	+364	+424	+846

[a] – B3LYP/6-311++G(D,P)
[b] – in parentheses results for geometries optimized at B2PLYP/6-311++G(D,P) level
[c] – B3LYP/6-311++G(2D,2P)

Figure 5A. Calculated at B3LYP/6-311++G(D,P) level structures of individual conformers of **1e**, their relative energies and some structural parameters.

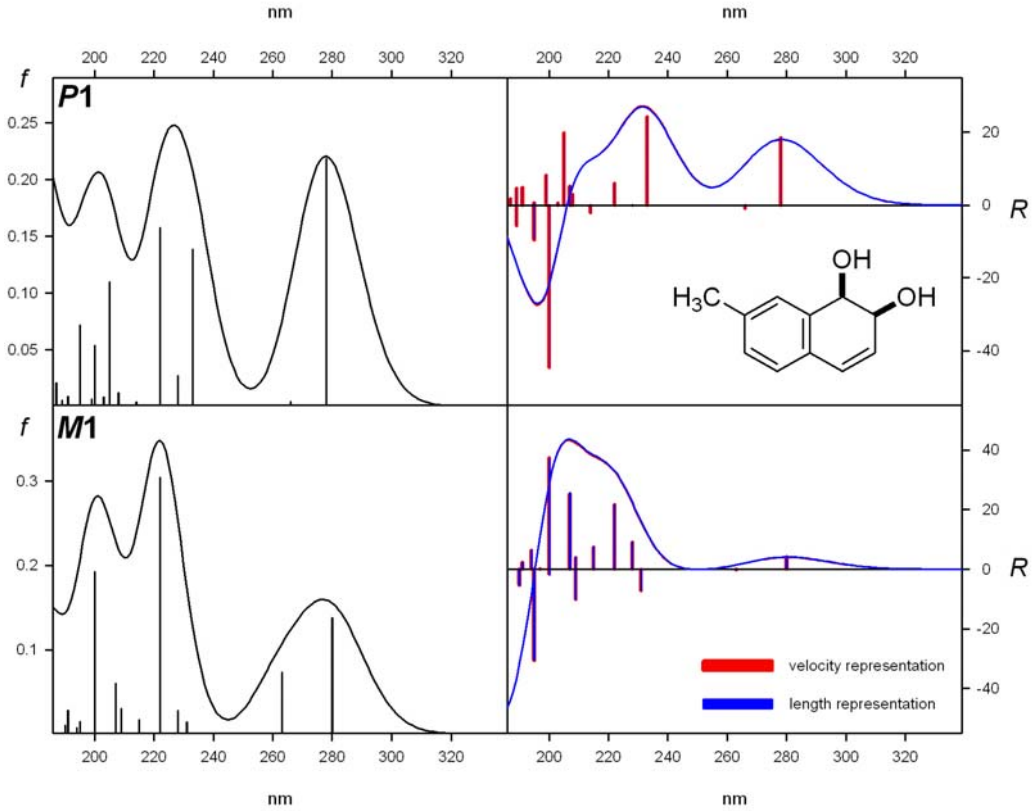


Figure 5B. Calculated at TDDFT/mPW1PW91/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **1e**.

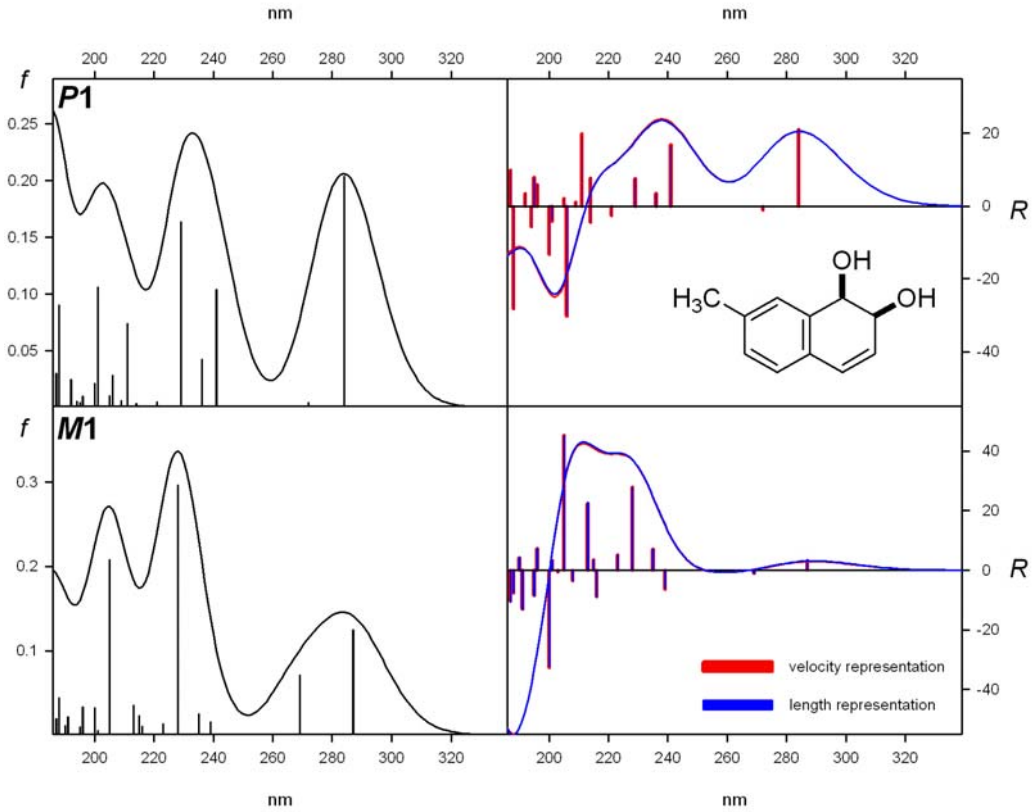


Figure 5C. Calculated at TDDFT/B3LYP/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **1e**.

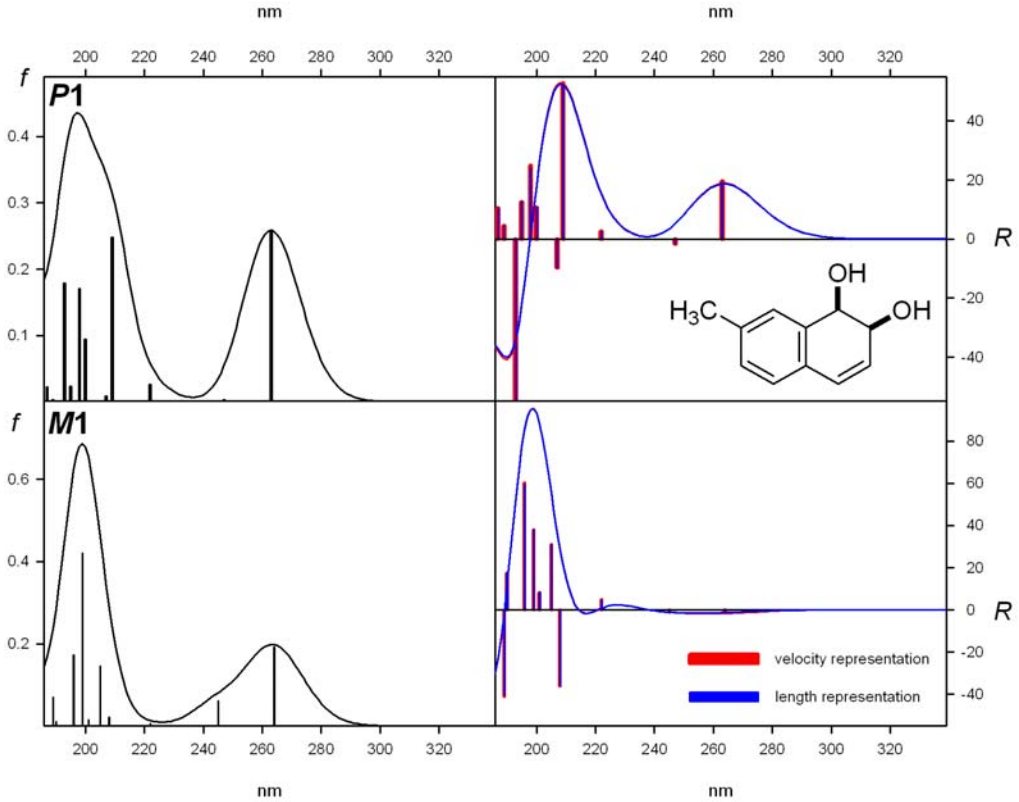


Figure 5D. Calculated at TDDFT/B2PLYP/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **1e**.

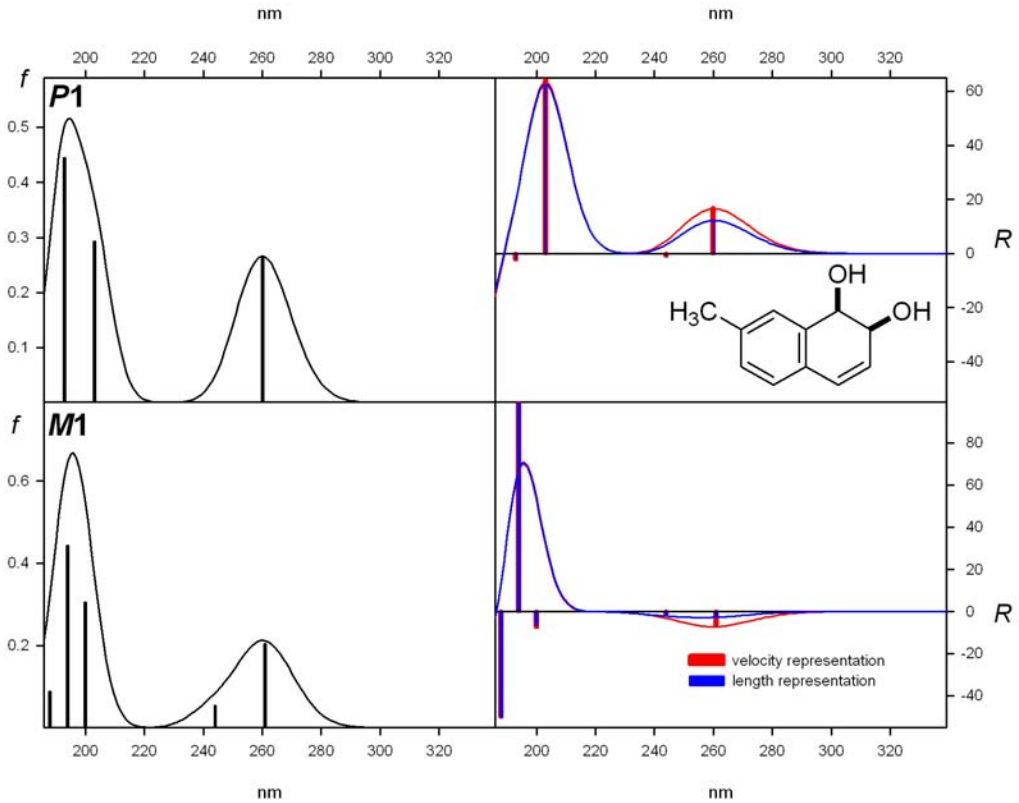
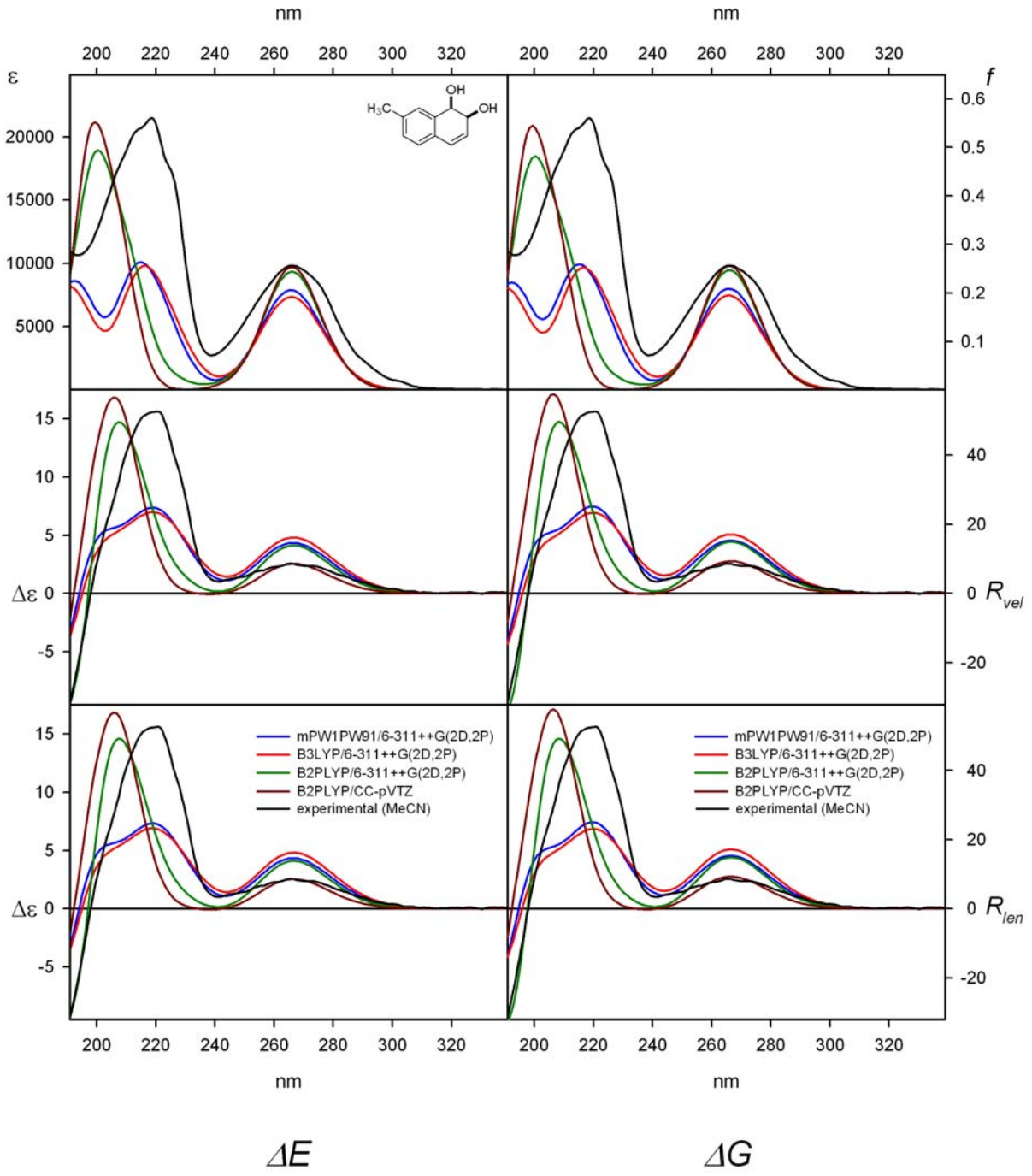


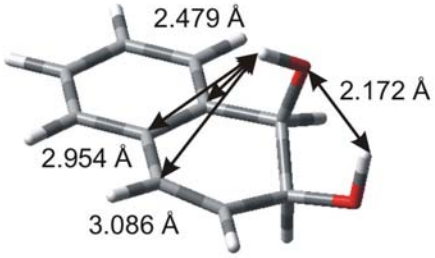
Figure 5E. Calculated at TDDFT/B2PLYP/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **1e.**

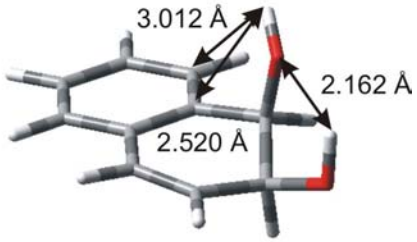


Geometries were optimzed at B3LYP/6-311++G(D,P) level
Calculated energies were scaled by the factors of:
0.957 (mPW1PW91/6-311++G(2D,2P))
0.937 (B3LYP/6-311++G(2D,2P))
1.011 (B2PLYP/6-311++G(2D,2P))
1.023 (B2PLYP/CC-pVTZ)
σ = 0.5 eV

Figure 5F. Calculated Boltzmann averaged CD and UV spectra for *cis*-dihydrodiol **1e**. The rotational strenghts *R* were calculated at diferent levels of theory in both velocity and dipole length representations. The calculated CD and UV spectra were wavelength corrected to match the experimental long-wavelength λ_{max} values in the UV spectra.

***P*1**





***M*1** ***M*2**

		1f(*P*1)	**1f(*M*1)**	**1f(*M*2)**
Energy[a] [Hartree]		-537.666903 (-537.547187)[b]	-537.665948 (-537.546346)[b]	-537.664496 (-537.545253)[b]
ΔE [kcal mol^{-1}] [a]		0.00 (0.00)[b]	0.60 (0.53)[b]	1.51 (1.21)[b]
Population [%][a]		70 (66)[b]	25 (26)[b]	5 (8)[b]
ΔG [kcal mol^{-1}] [a]		0.00	0.33	0.83
Population [%][a]		55	31	14
μ [D][a]		2.58	2.96	3.00
α [°][a]		-154.2 (-155.6)[b]	159.8 (158.6)[b]	74.9 (75.3)[b]
β [°][a]		-160.3 (-160.0)[b]	155.4 (156.7)[b]	162.6 (163.5)[b]
γ [°][a]		10.9 (11.9)[b]	-12.2 (-12.9)[b]	-11.2 (-11.8)[b]
[α] calcd.[c]	D	+290	+149	+7
	575 nm	+416	+182	-31
	546 nm	+488	+207	-42
	436 nm	+998	+355	-165

[α]$_D$ calcd. Boltzmann averaged

ΔE				ΔG			
D	575 nm	546 nm	436 nm	D	575 nm	546 nm	436 nm
241 (231)[b]	335 (319)[b]	391 (372)[b]	779 (738)[b]	207	281	327	636

[a] – B3LYP/6-311++G(D,P)
[b] – in parentheses results for geometries optimized at B2PLYP/6-311++G(D,P) level
[c] – B3LYP/6-311++G(2D,2P)

Figure 6A. Calculated at B3LYP/6-311++G(D,P) level structures of individual conformers of **1f**, their relative energies and some structural parameters.

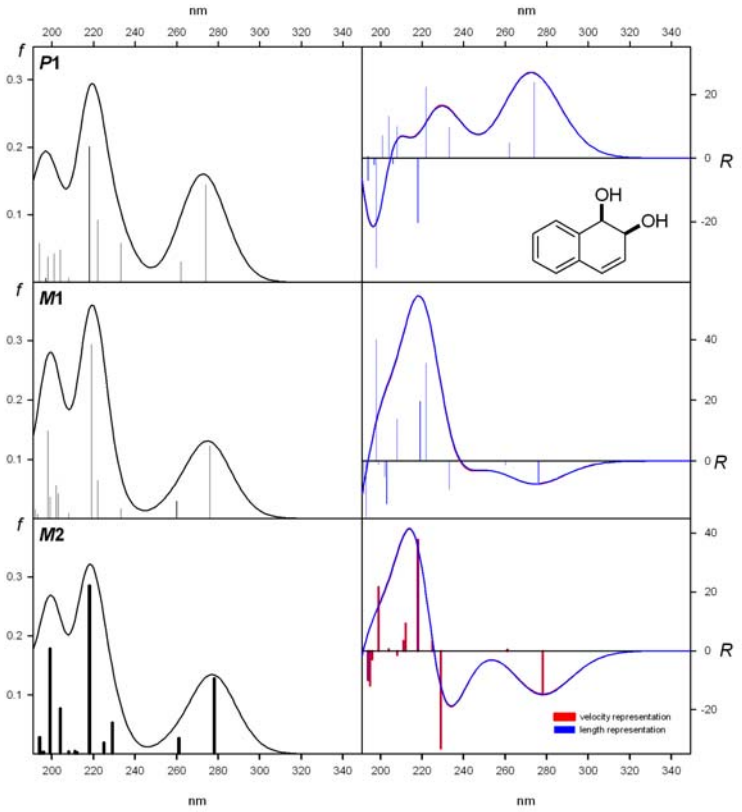


Figure 6B. Calculated at TDDFT/mPW1PW91/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **1f**.

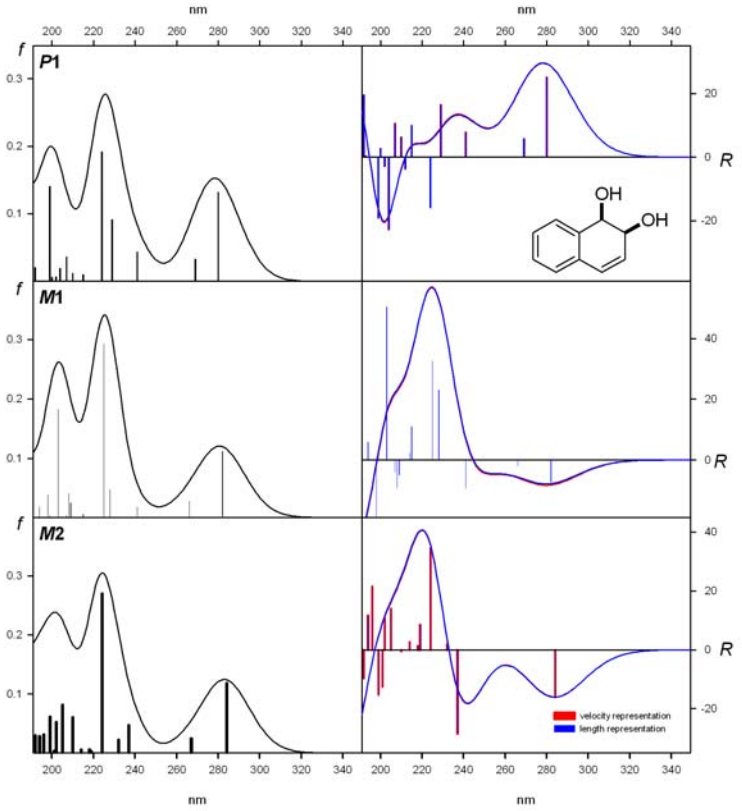


Figure 6C. Calculated at TDDFT/B3LYP/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **1f**.

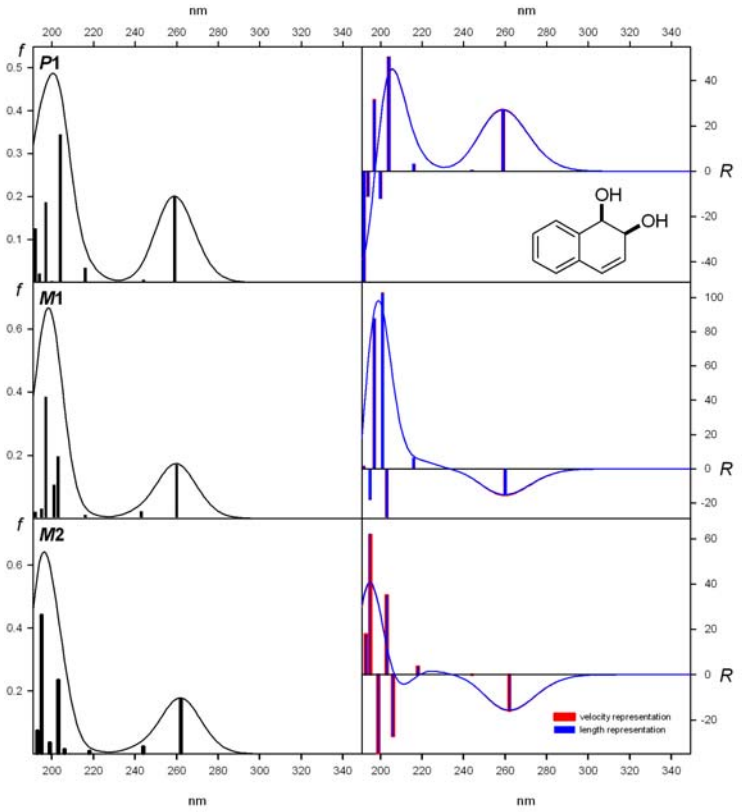


Figure 6D. Calculated at TDDFT/B2PLYP/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **1f**.

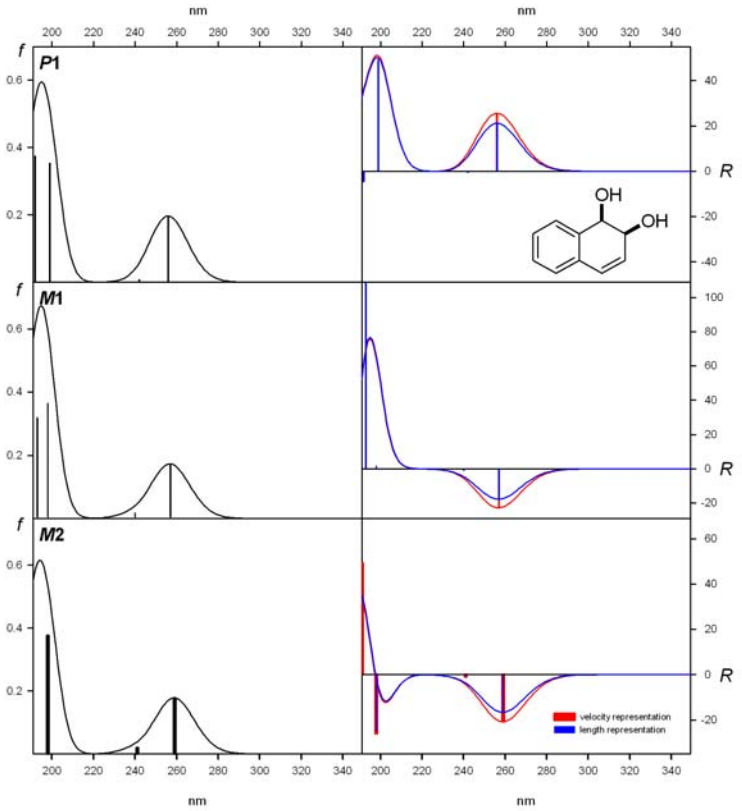


Figure 6E. Calculated at TDDFT/B2PLYP/CC-pVTZ level CD and UV spectra for individual conformers of **1f**.

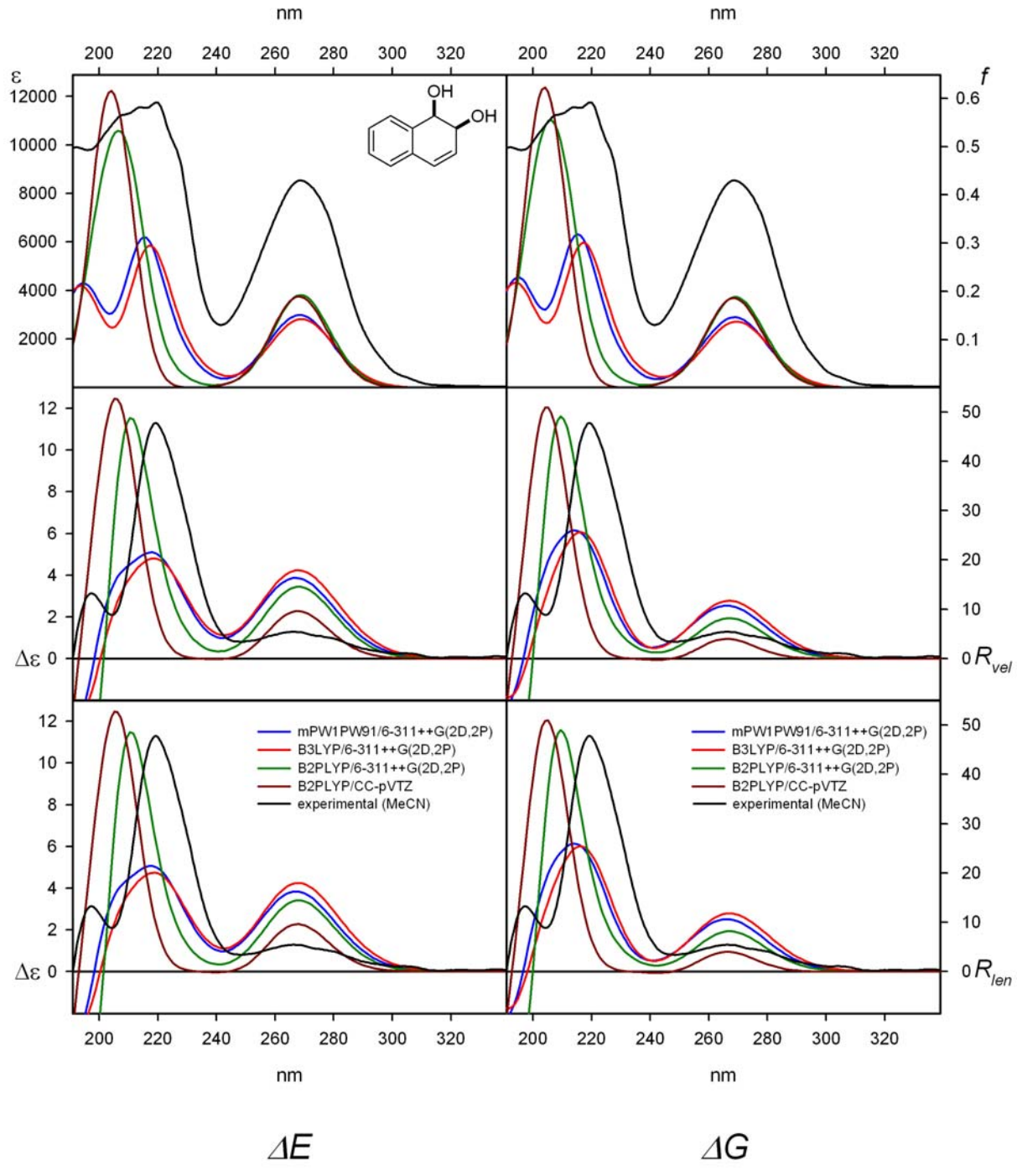
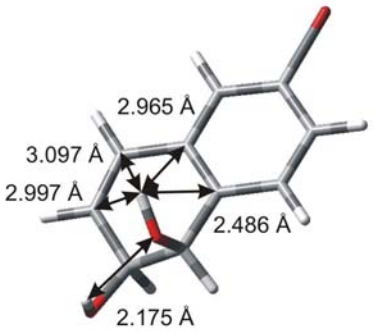


Figure 6F. Experimental CD and UV spectra in acetonitrile solution (black line) and calculated Boltzmann averaged CD and UV spectra for *cis*-dihydrodiol **1f**. The rotational strenghts *R* were calculated at diferent levels of theory in both velocity and dipole length representations. The calculated CD and UV spectra were wavelength corrected to match the experimental long-wavelength λ_{max} values in the UV spectra.

***P*1**



***M*1**

***M*2**

		2a(*P*1)	**2a(*M*1)**	**2a(*M*2)**
Energy[a] [Hartree]		-3111.209039 (-3111.593150)[b]	-3111.207930 (-3111.592041)[b]	-3111.206572 (-3111.591051)[b]
ΔE [kcal mol^{-1}][a]		0.00 (0.00)[b]	0.70 (0.43)[b]	1.55 (1.32)[b]
Population [%][a]		73 (71)[b]	22 (28)[b]	5 (8)[b]
ΔG [kcal mol^{-1}][a]		0.00	0.43	0.83
Population [%][a]		58	28	14
μ [D][a]		1.88	1.06	1.42
α [°][a]		-153.9 (-155.0)[b]	160.3 (159.5)[b]	71.4 (71.4)[b]
β [°][a]		-159.8 (-159.4)[b]	155.1 (156.4)[b]	162.7 (163.6)[b]
γ [°][a]		10.9 (11.8)[b]	-12.3 (-12.9)[b]	-11.3 (-12.0)[b]
[α] calcd.[c]	D	+134	+141	+50
	575 nm	+203	+178	+39
	546 nm	+240	+205	+40
	436 nm	+519	+362	+13

[α]$_D$ calcd. Boltzmann averaged

ΔE				ΔG			
D	575 nm	546 nm	436 nm	D	575 nm	546 nm	436 nm
+131 (+129)[b]	+189 (+185)[b]	+222 (+217)[b]	+459 (+445)[b]	+124	+173	+202	+404

[a] – B3LYP/6-311++G(D,P)
[b] – in parentheses results for geometries optimized at B2PLYP/6-311++G(D,P) level
[c] – B3LYP/6-311++G(2D,2P)

Figure 7A. Calculated at B3LYP/6-311++G(D,P) level structures of individual conformers of **2a**, their relative energies and some structural parameters.

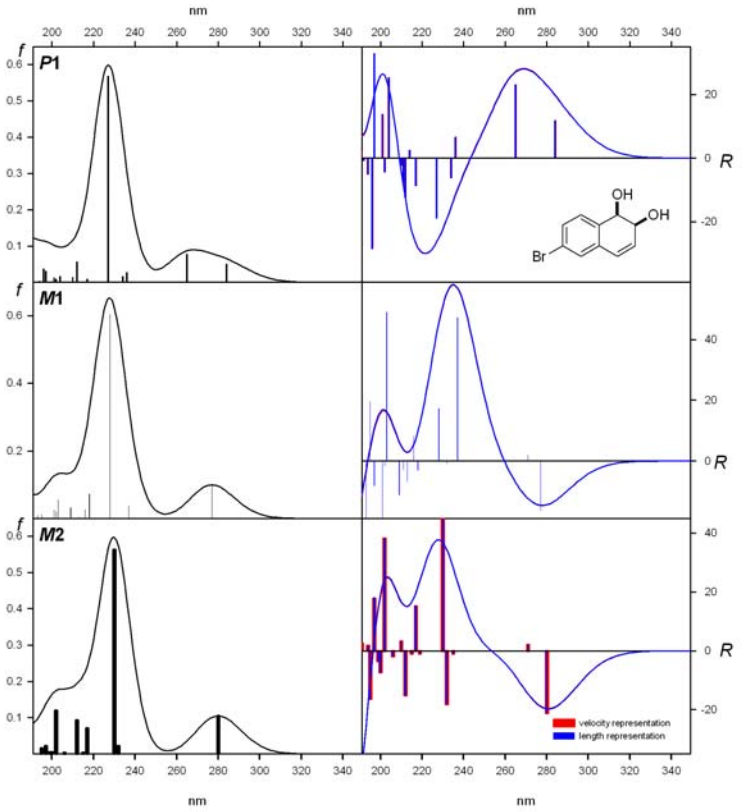


Figure 7B. Calculated at TDDFT/mPW1PW91/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **2a**.

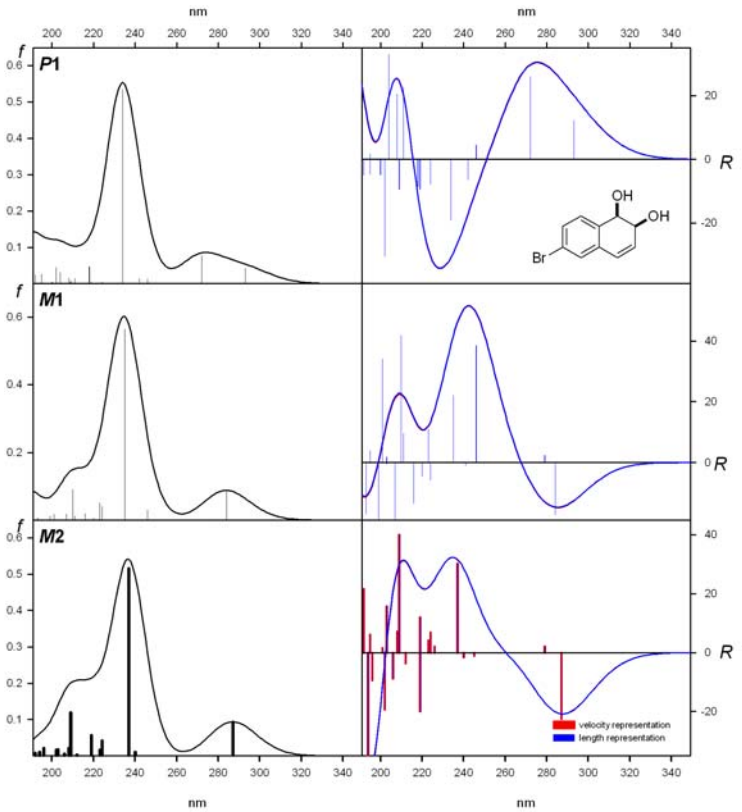


Figure 7C. Calculated at TDDFT/B3LYP/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **2a**.

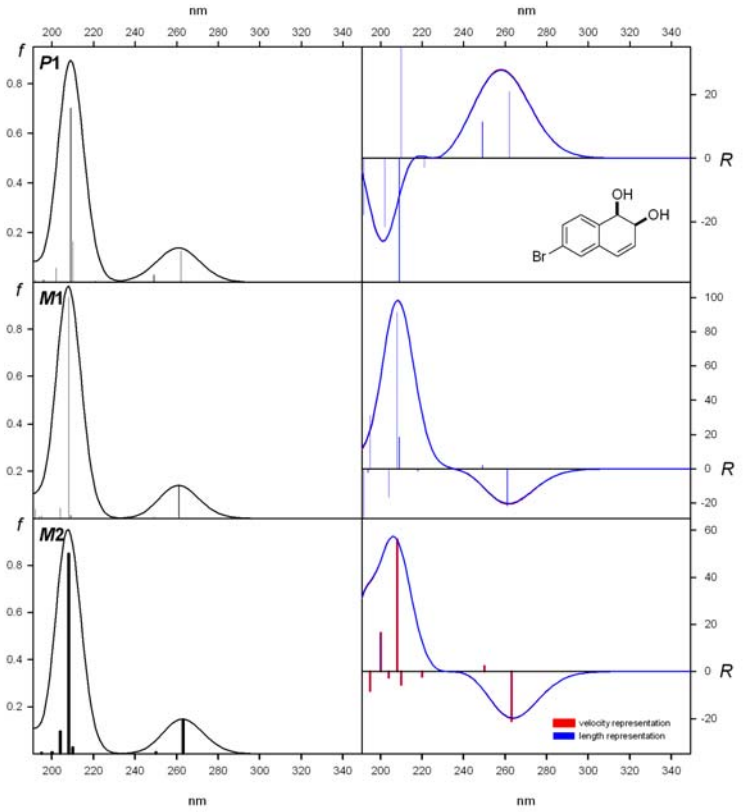


Figure 7C. Calculated at TDDFT/B2PLYP/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **2a**.

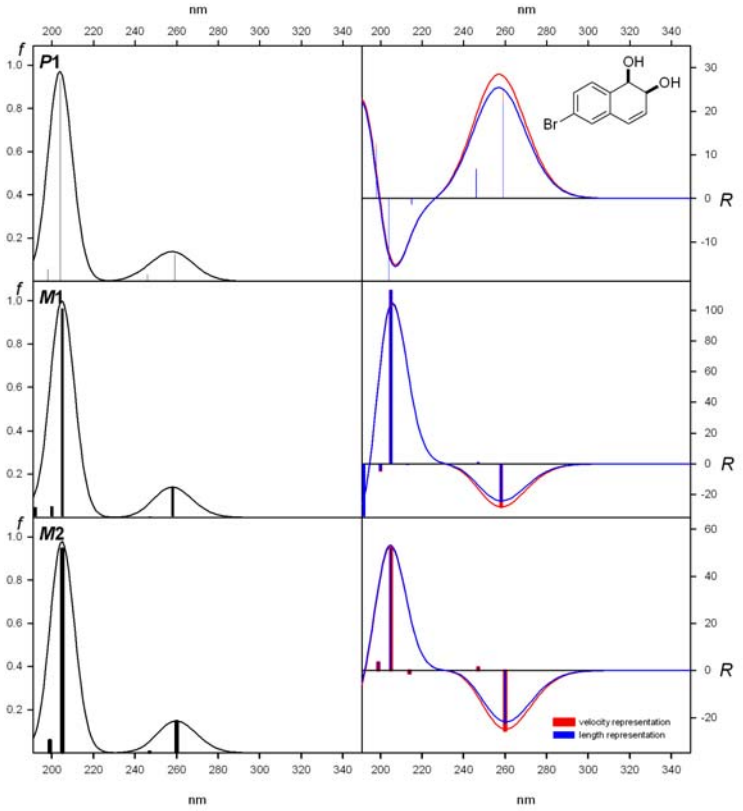


Figure 7D. Calculated at TDDFT/B2PLYP/CC-pVTZ level CD and UV spectra for individual conformers of **2a**.

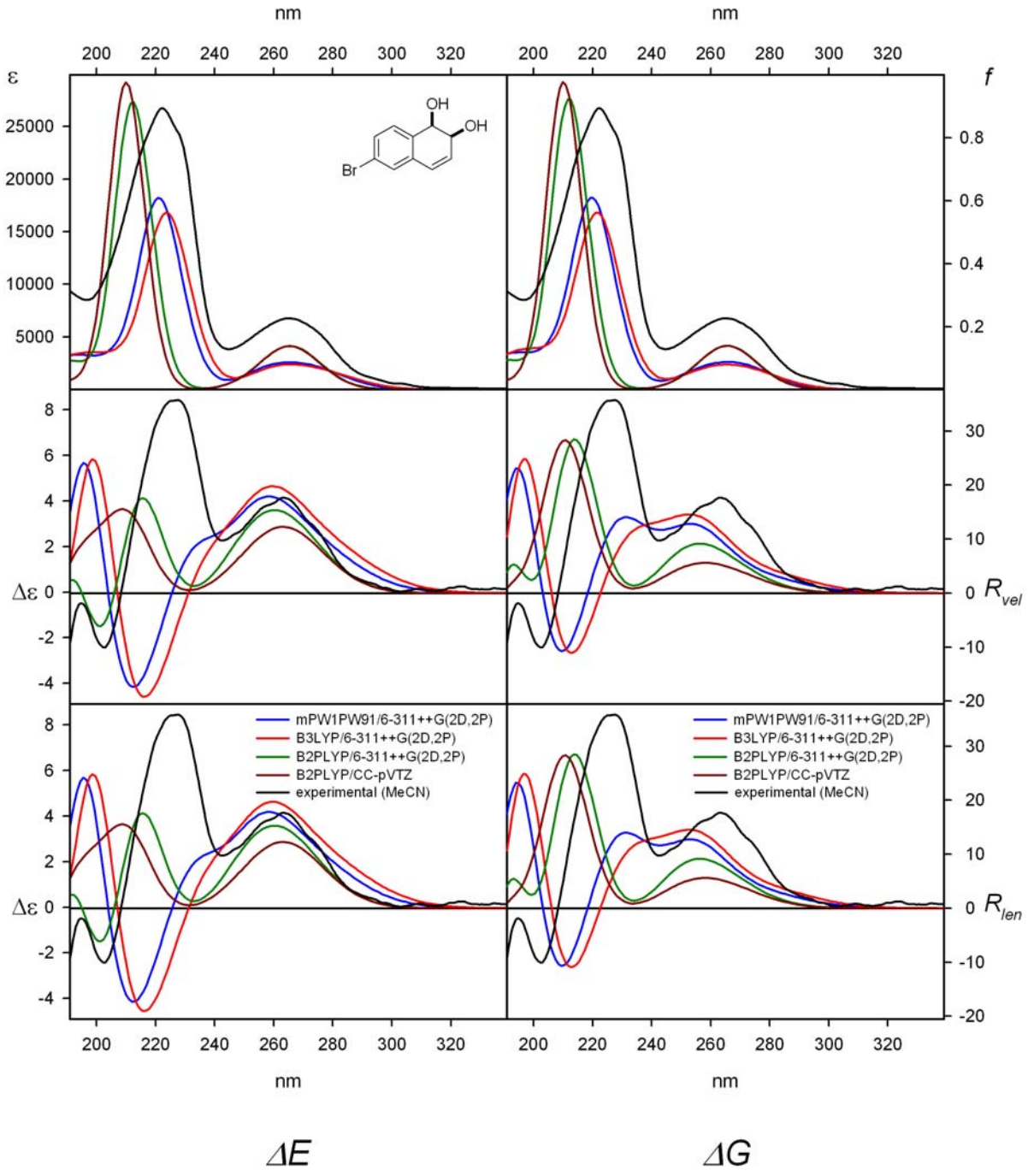
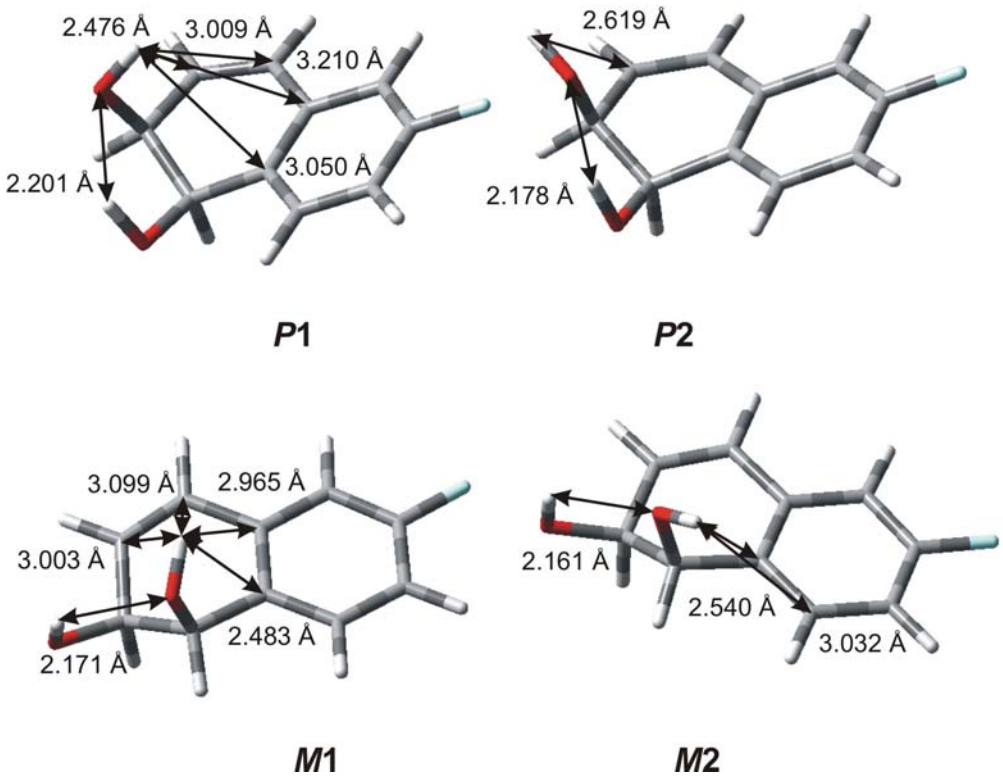


Figure 7F. Experimental CD and UV spectra in acetonitrile solution (black line) and calculated Boltzmann averaged CD and UV spectra for *cis*-dihydrodiol **2a**. The rotational strenghts *R* were calculated at diferent levels of theory in both velocity and dipole length representations. The calculated CD and UV spectra were wavelength corrected to match the experimental long-wavelength λ_{max} values in the UV spectra.



		2b(*P*1)	2b(*P*2)	2b(*M*1)	2b(*M*2)
Energy[a] [Hartree]		-636.935109	-636.932523	-636.934353	-636.932974
ΔE [kcal mol^{-1}][a]		0.00	1.62	0.47	1.34
Population [%][a]		62	4	28	6
ΔG [kcal mol^{-1}][a]		0.00	1.01	0.25	0.64
Population [%][a]		46	8	30	16
μ [D][a]		1.86	3.22	1.13	1.46
α [°][a]		-153.9	-160.1	159.7	72.8
β [°][a]		-160.2	-64.5	155.2	162.4
γ [°][a]		10.9	11.4	-12.4	-11.4
[α] calcd.[b]	D	+234	+295	+136	+14
	578 nm	+334	+422	+167	-16
	546 nm	+392	+495	+191	-25
	436 nm	+798	+1015	+329	-121

[α]$_D$ calcd. Boltzmann averaged

ΔE				ΔG			
D	578 nm	546 nm	436 nm	D	578 nm	546 nm	436 nm
+196	+270	+315	+620	+174	+235	+273	+528

[a] – B3LYP/6-311++G(D,P)
[b] – B3LYP/6-311++G(2D,2P)

Figure 8A. Calculated at B3LYP/6-311++G(D,P) level structures of individual conformers of **2b**, their relative energies and some structural parameters.

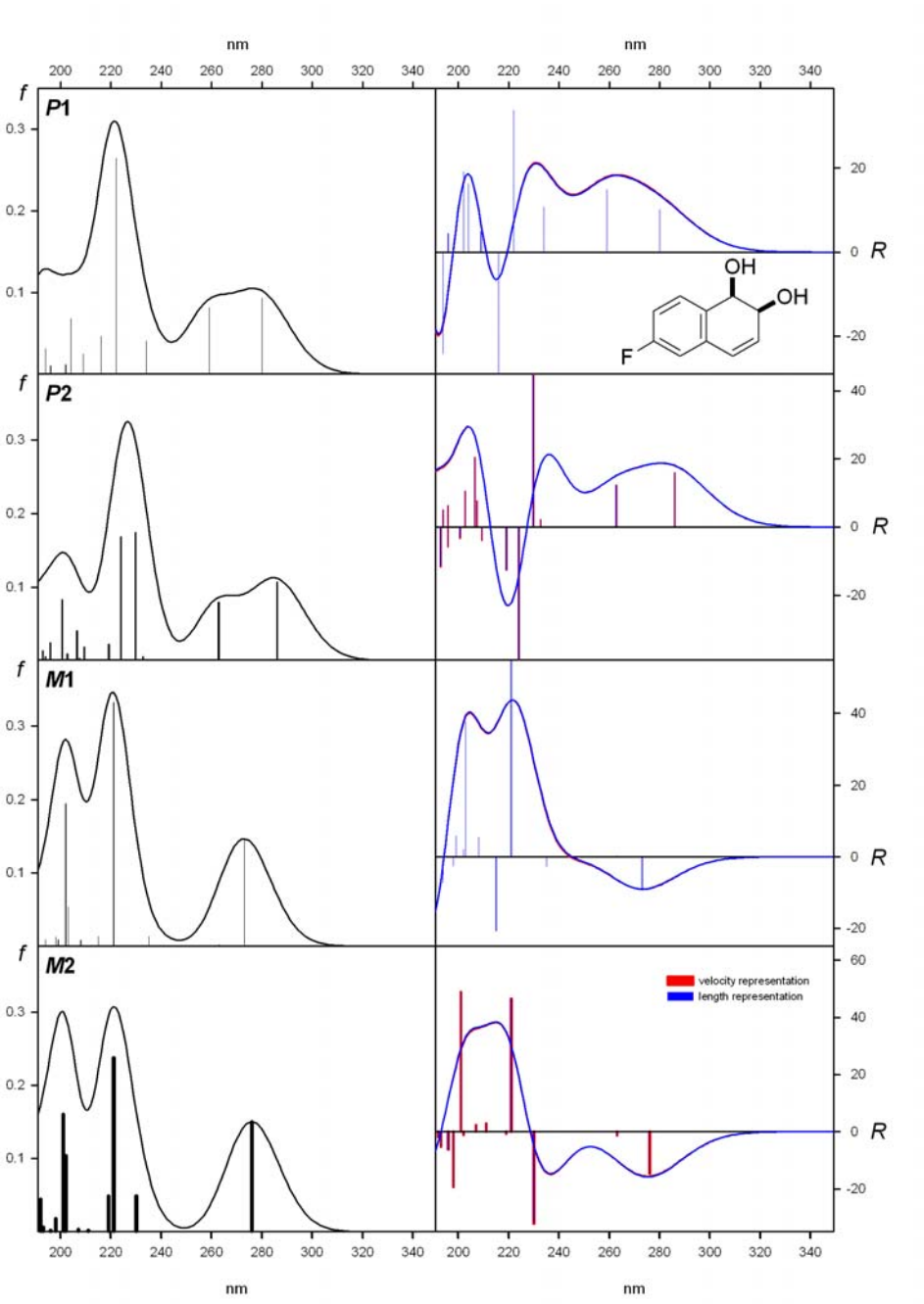


Figure 8B. Calculated at TDDFT/mPW1PW91/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **2b**.

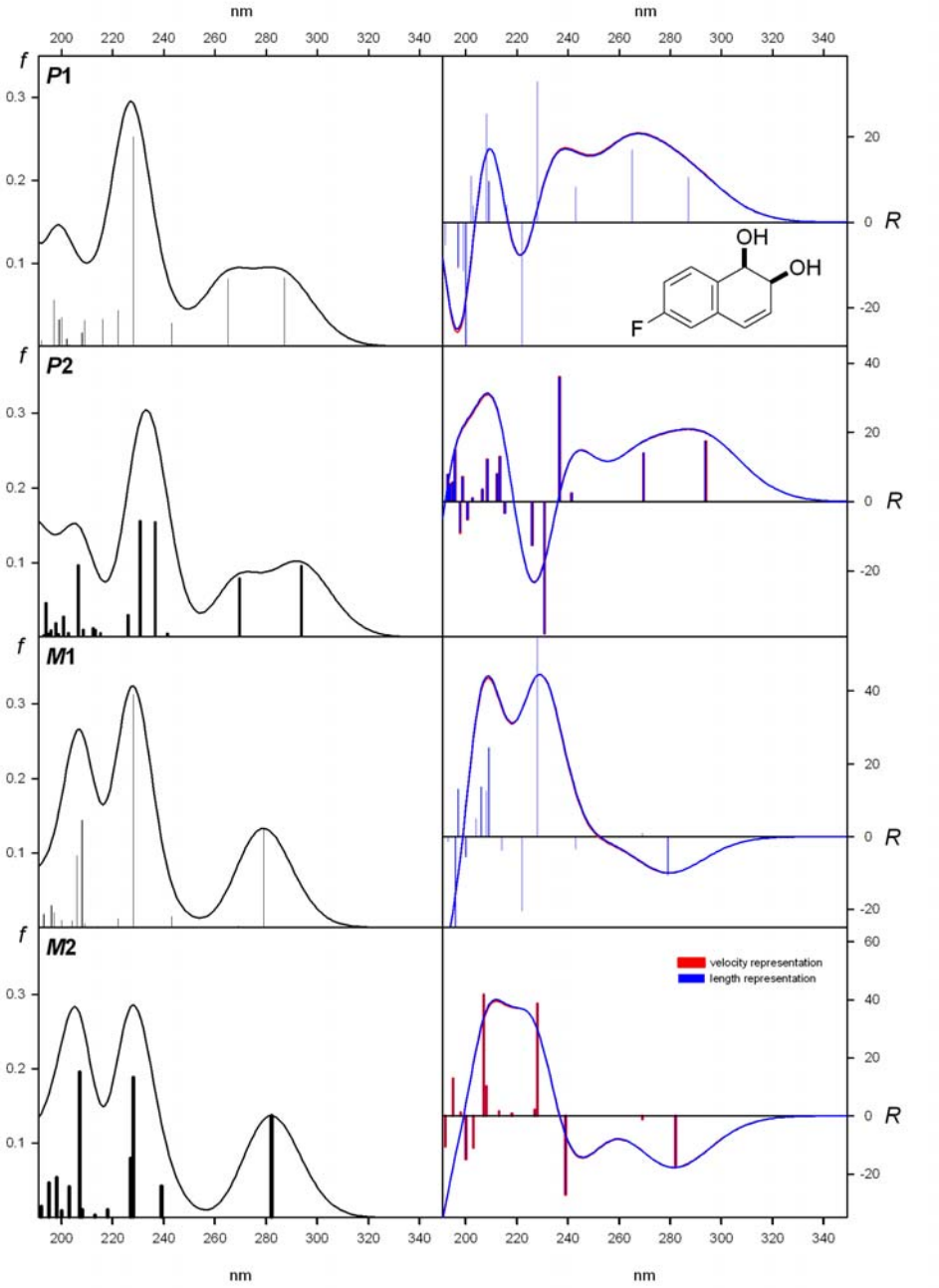


Figure 8C. Calculated at TDDFT/B3LYP/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **2b**.

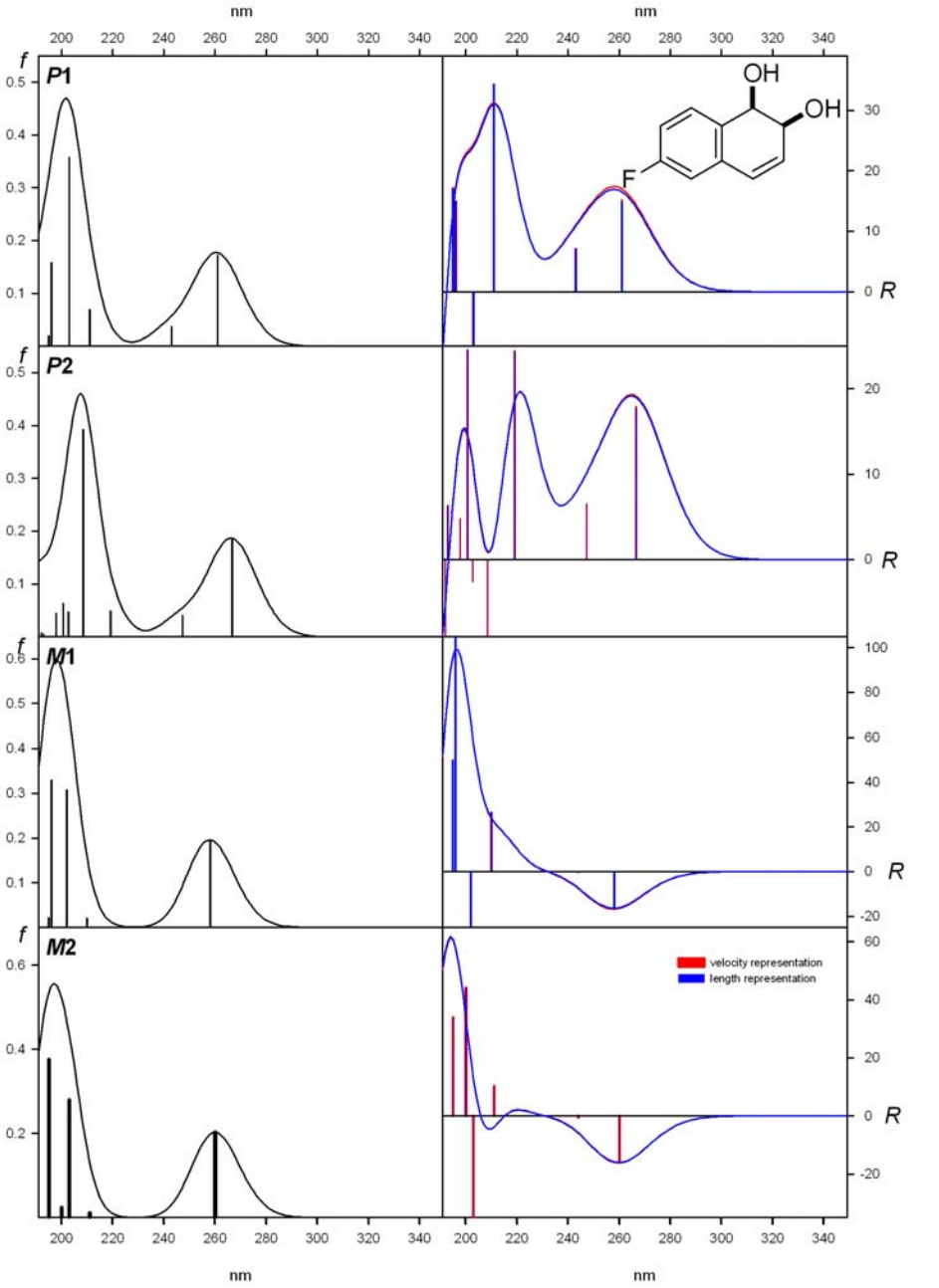


Figure 8D. Calculated at TDDFT/B2PLYP/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **2b**

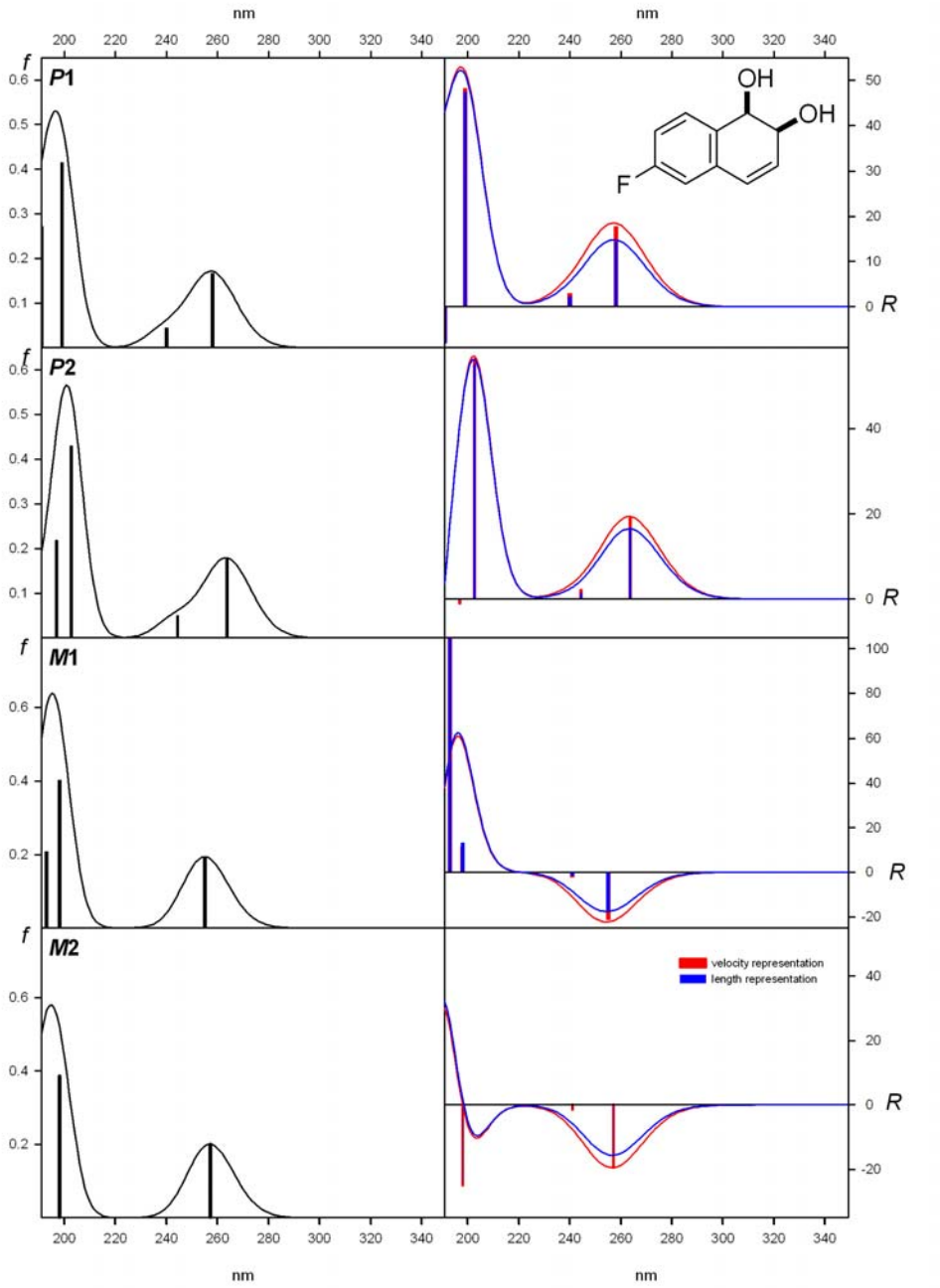


Figure 8E. Calculated at TDDFT/B2PLYP/CC-pVTZ level CD and UV spectra for individual conformers of **2b.**

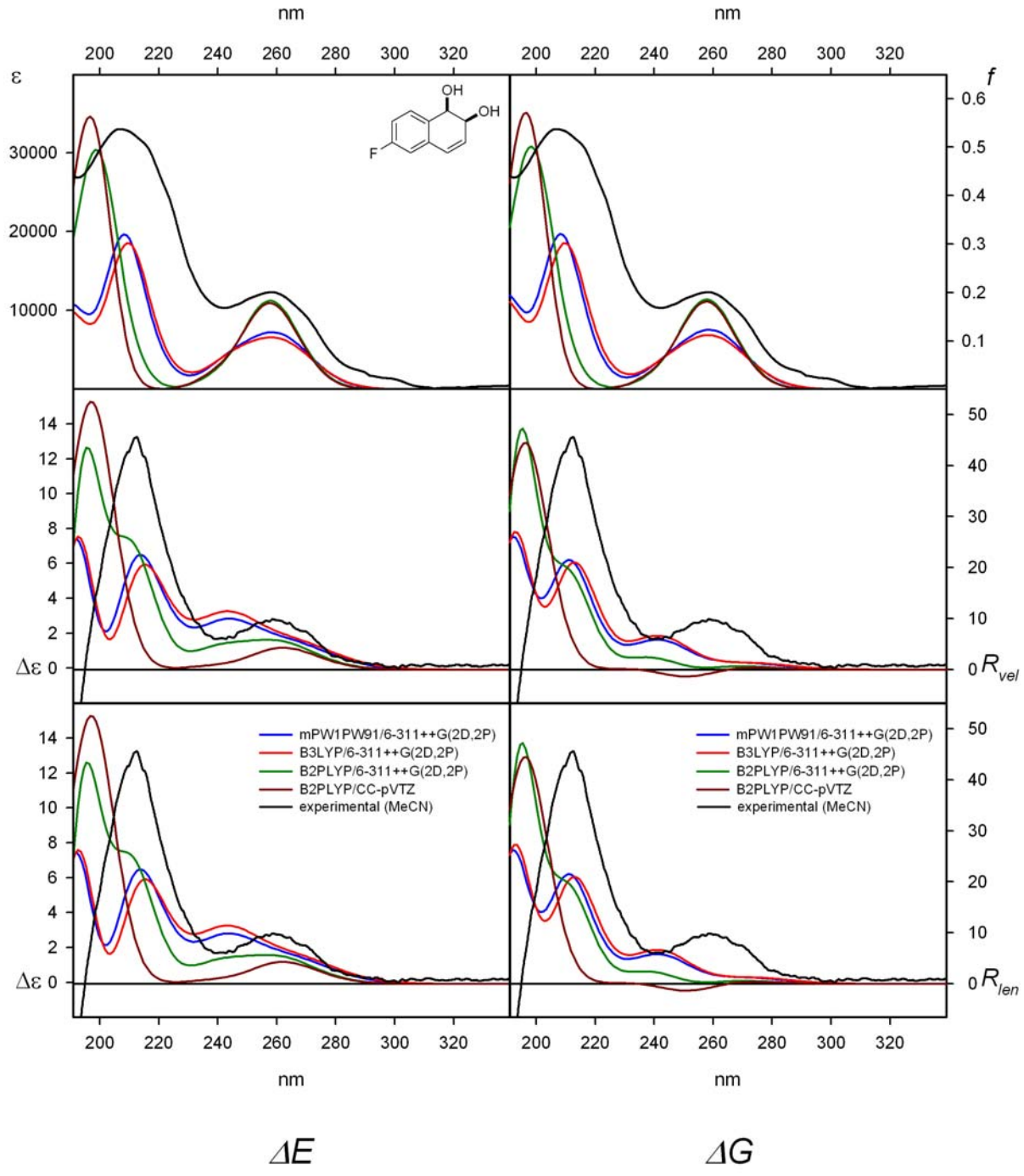
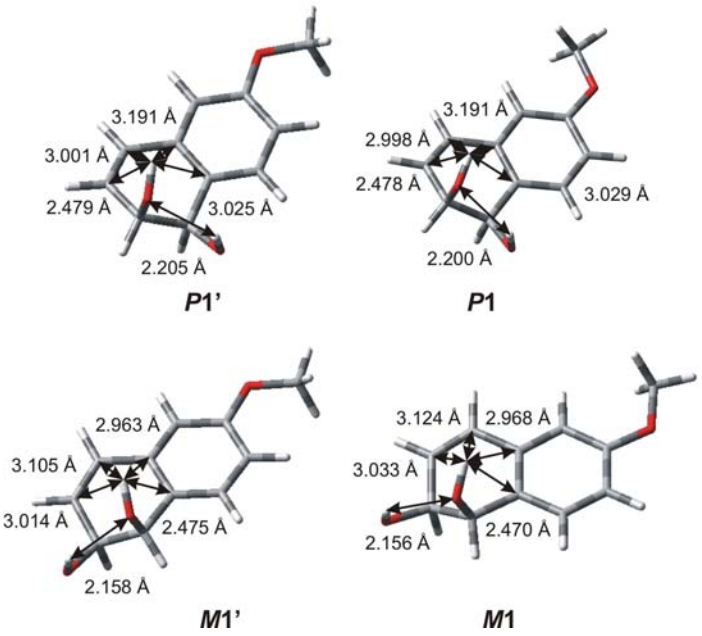


Figure 8F. Experimental CD and UV spectra in acetonitrile solution (black line) and calculated Boltzmann averaged CD and UV spectra for *cis*-dihydrodiol **2b**. The rotational strenghts *R* were calculated at diferent levels of theory in both velocity and dipole length representations. The calculated CD and UV spectra were wavelength corrected to match the experimental long-wavelength λ_{max} values in the UV spectra.



	2c(*P*1')	**2c(*P*1)**	**2c(*M*1')**	**2c(*M*1)**
Energy[a] [Hartree]	-652.223062 (-650.885911)[b]	-652.222672 (-650. 885408)[b]	-652.222869 (-650.885814)	-652.222642 (-650.885507)[b]
ΔE [kcal mol^{-1}] [a]	0.00 (0.00)[b]	0.25 (0.32)[b]	0.12 (0.06)	0.26 (0.25)[b]
Population [%][a]	32 (32)[b]	21 (18)[b]	26 (29)	21 (21)[b]
ΔG [kcal mol^{-1}] [a]	0.13	0.42	0.00	0.15
Population [%][a]	26	16	33	25
μ [D] [a]	2.59	3.89	2.77	1.19
α [°][a]	-154.7 (-155.2)[b]	-154.4 (-155.7)[b]	158.2 (156.7)[b]	157.5 (156.0)[b]
β [°][a]	-158.6 (-160.9)[b]	-161.4 (-161.4)[b]	155.1 (156.5)[b]	154.7 (156.1)[b]
γ [°][a]	10.9 (11.6)[b]	10.9 (11.9)[b]	-12.2 (-12.8)[b]	-12.1 (-12.8)[b]
δ [°][a]	0.5 (0.5)[b]	179.4 (179.4)[b]	0.0 (0.1)[b]	179.8 (179.8)[b]
$[\alpha]$ calcd.[c] D	+254	+167	+173	+148
575 nm	+374	+270	+216	+177
546 nm	+440	+322	+248	+201
436 nm	+930	+735	+428	+324

$[\alpha]_D$ calcd. Boltzmann averaged

ΔE				ΔG			
D	578 nm	546 nm	436 nm	D	578 nm	546 nm	436 nm
+192 (+193)[b]	+270 (+268)[b]	+315 (+313)[b]	+631 (+622)[b]	+187	+256	+298	+582

[a] – B3LYP/6-311++G(D,P)
[b] – in parentheses results for geometries optimized at B2PLYP/6-311++G(D,P) level
[c] – B3LYP/6-311++G(2D,2P)

Figure 9A. Calculated at B3LYP/6-311++G(D,P) level structures of individual conformers of **2c**, their relative energies and some structural parameters.

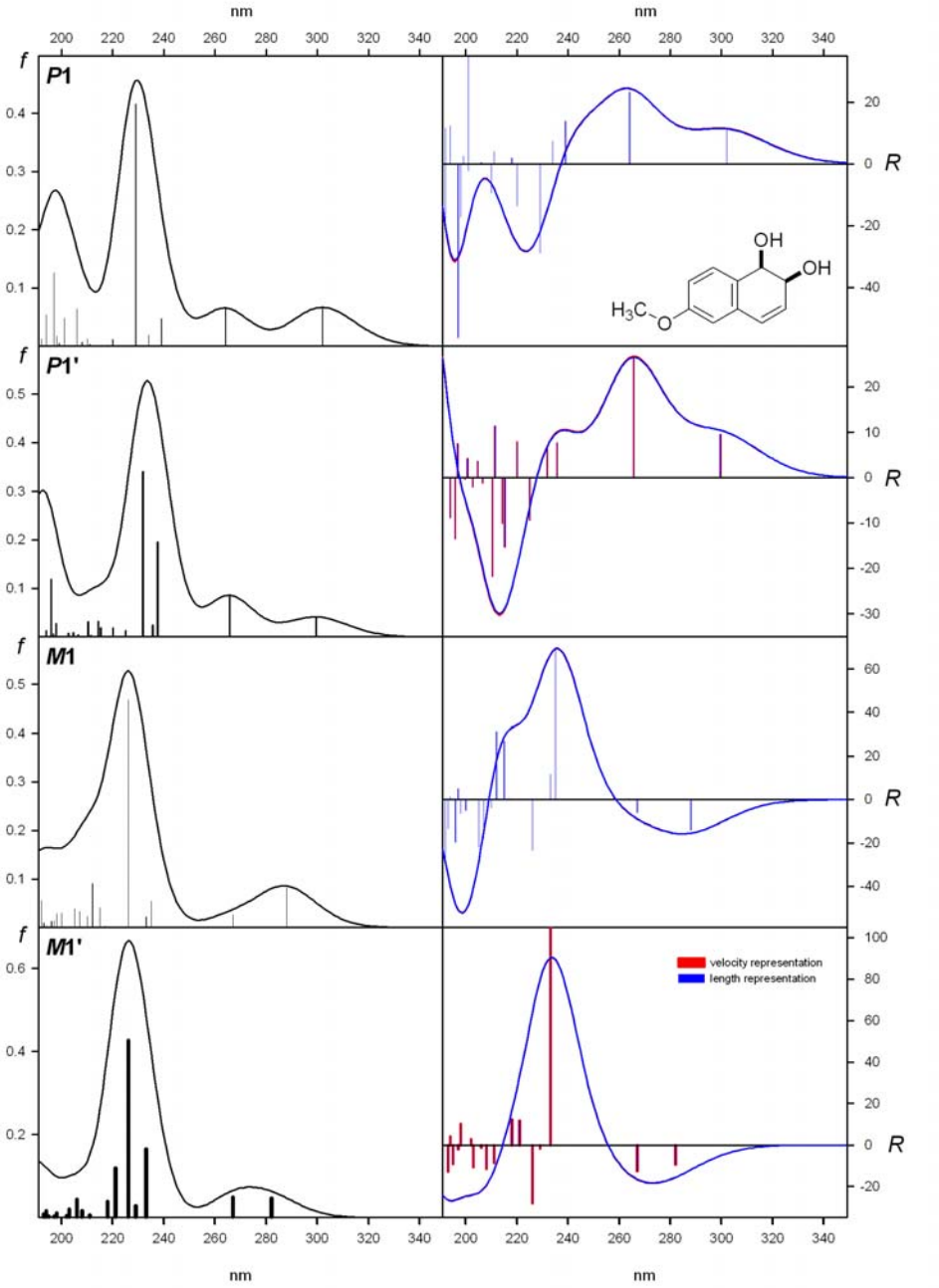


Figure 9B. Calculated at TDDFT/mPW1PW91/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **2c**.

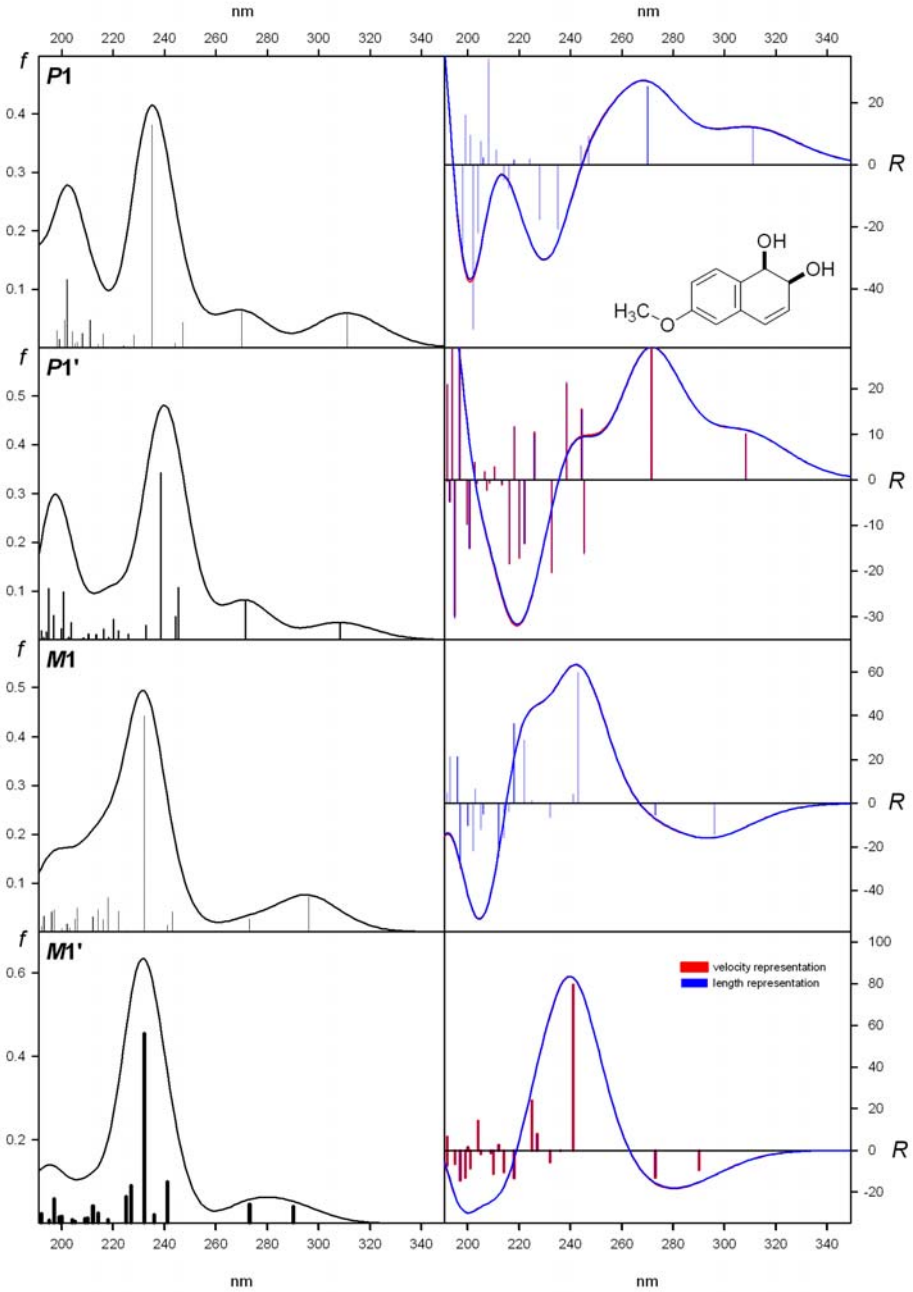


Figure 9C. Calculated at TDDFT/B3LYP/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **2c**.

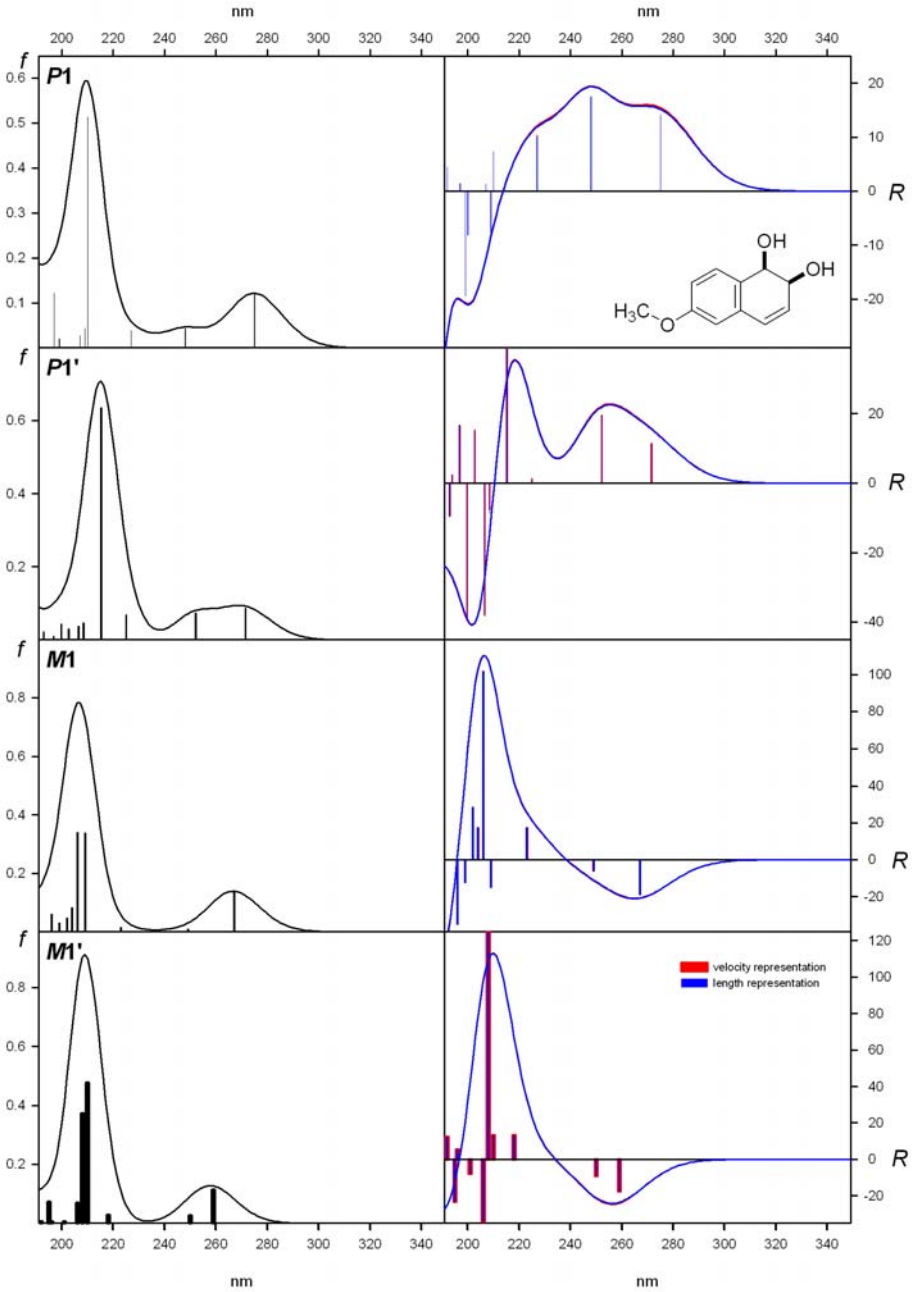


Figure 9D. Calculated at TDDFT/B2PLYP/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **2c**.

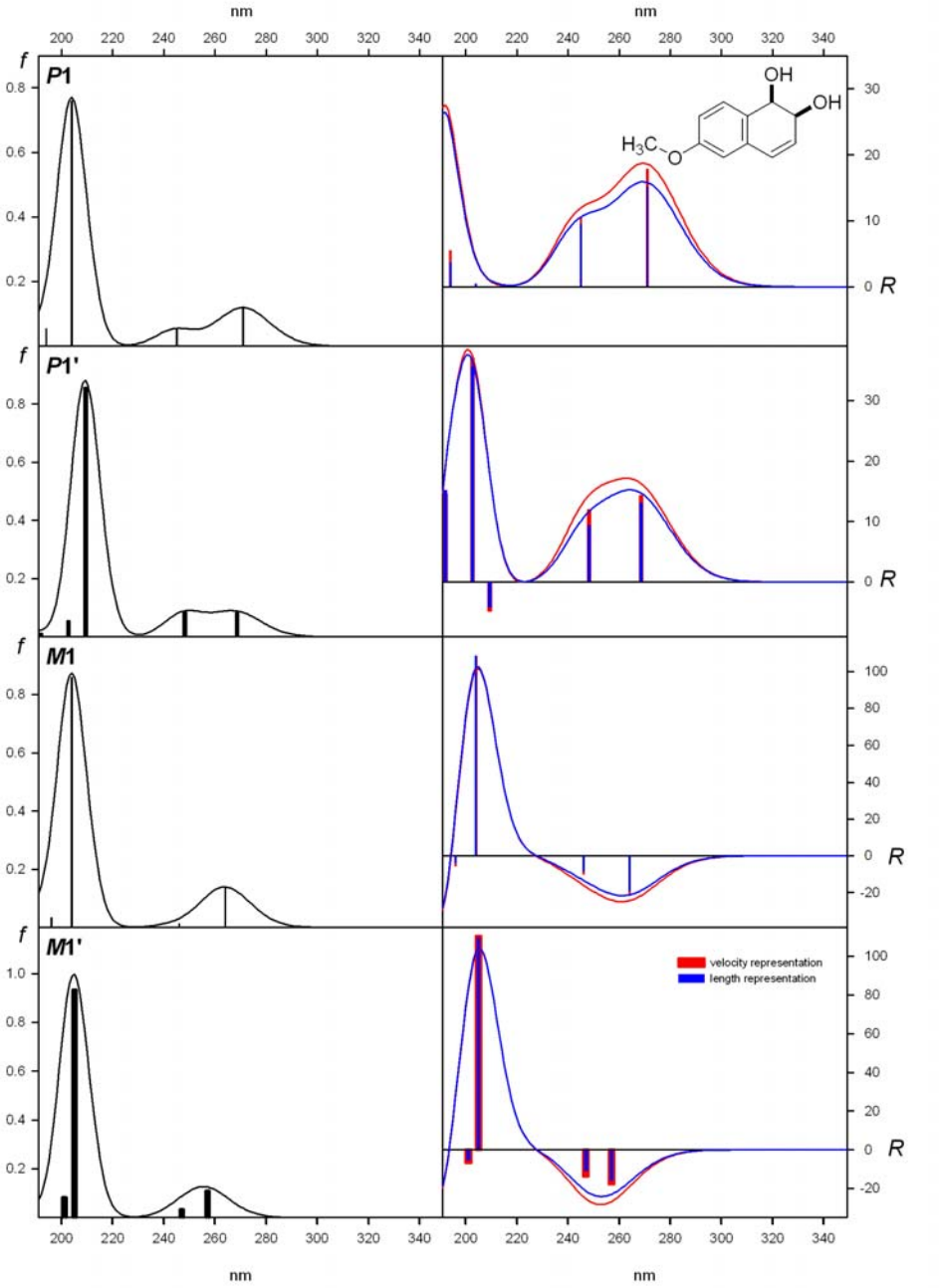
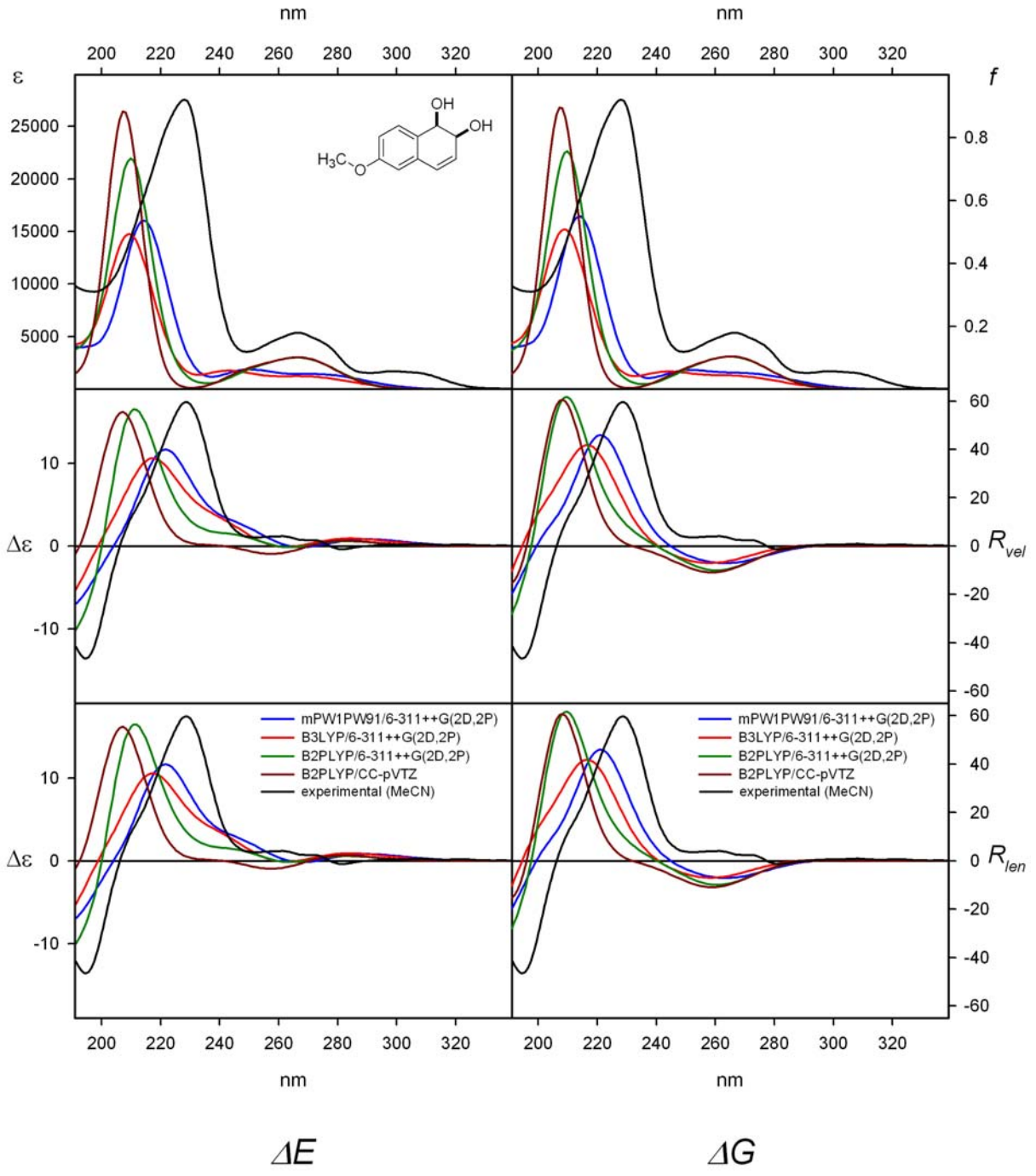
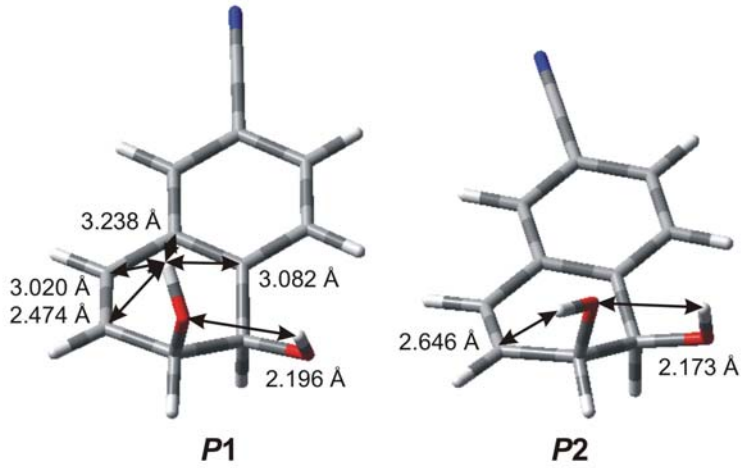


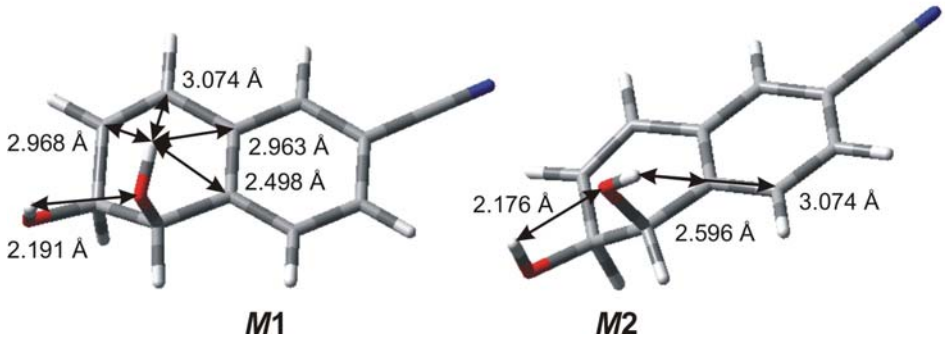
Figure 9E. Calculated at TDDFT/B2PLYP/CC-pVTZ level CD and UV spectra for individual conformers of **2c**.



Geometries were optimzed at B3LYP/6-311++G(D,P) level
Calculated energies were scaled by the factors of:
0.940 (mPW1PW91/6-311++G(2D,2P))
0.896 (B3LYP/6-311++G(2D,2P))
1.004 (B2PLYP/6-311++G(2D,2P))
1.015 (B2PLYP/CC-pVTZ)
σ = 0.5 eV

Figure 9F. Calculated Boltzmann averaged CD and UV spectra for *cis*-dihydrodiol **2c**. The rotational strenghts *R* were calculated at diferent levels of theory in both velocity and dipole length representations. The calculated CD and UV spectra were wavelength corrected to match the experimental long-wavelength λ_{max} values in the UV spectra.





		2d(*P*1)	**2d(*P*2)**	**2d(*M*1)**	**2d(*M*2)**
Energy[a] [Hartree]		-629.	-629.	-629.	-629.
ΔE [kcal mol^{-1}][a]		0.00	1.29	1.22	1.95
Population [%][a]		79	9	10	2
ΔG [kcal mol^{-1}][a]		0.00	0.79	0.97	1.39
Population [%][a]		65	17	12	6
μ [D][a]		3.89	5.95	2.33	3.01
α [°][a]		-153.2	-159.2	162.7	63.7
β [°][a]		-158.6	-61.2	155.4	163.0
γ [°][a]		10.9	11.5	-12.5	-11.5
[α] calcd.[b]	D	+192	+251	+168	+36
	578 nm	+296	+375	+208	+3
	546 nm	+351	+442	+237	-5
	436 nm	+773	+952	+400	-124

[α]$_D$ calcd. Boltzmann averaged

ΔE				ΔG			
D	578 nm	546 nm	436 nm	D	578 nm	546 nm	436 nm
+192	+288	+341	+734	+190	+281	+331	+705

[a] – B3LYP/6-311++G(D,P)
[b] – B3LYP/6-311++G(2D,2P)

Figure 10A. Calculated at B3LYP/6-311++G(D,P) level structures of individual conformers of **2d**, their relative energies and some structural parameters.

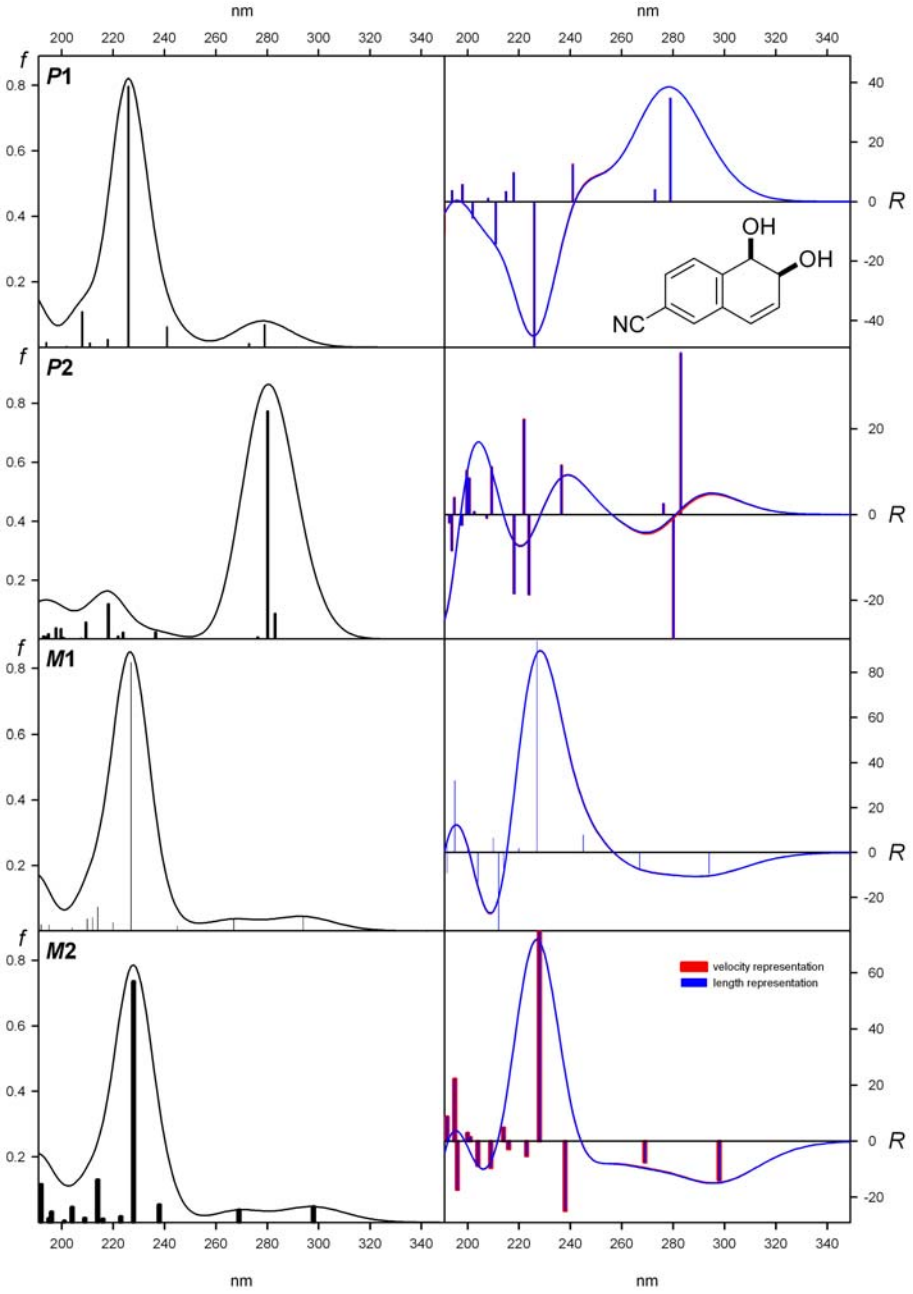


Figure 10B. Calculated at TDDFT/mPW1PW91/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **2d**.

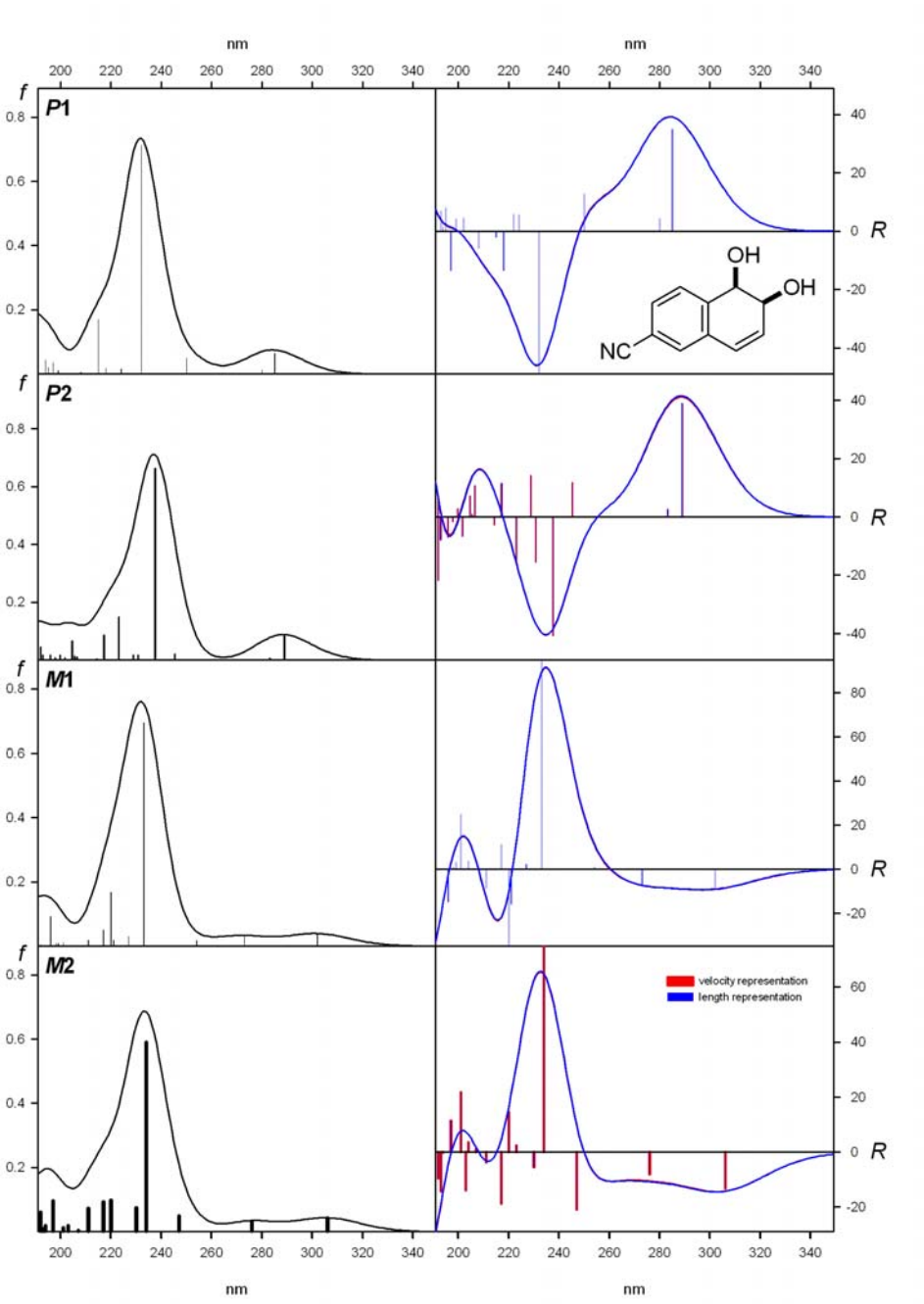


Figure 10C. Calculated at TDDFT/B3LYP/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **2d**.

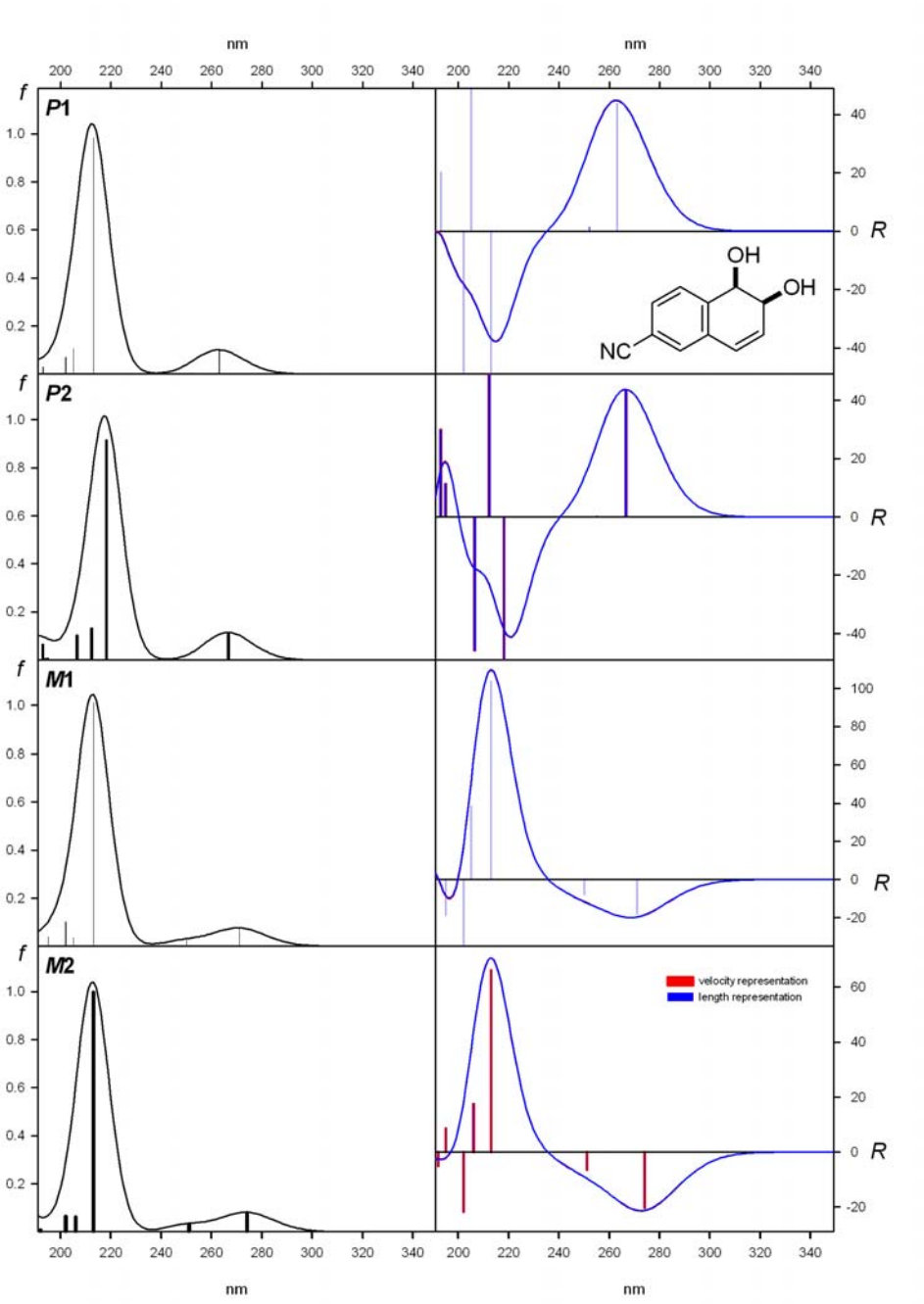


Figure 10D. Calculated at TDDFT/B2PLYP/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **2d**.

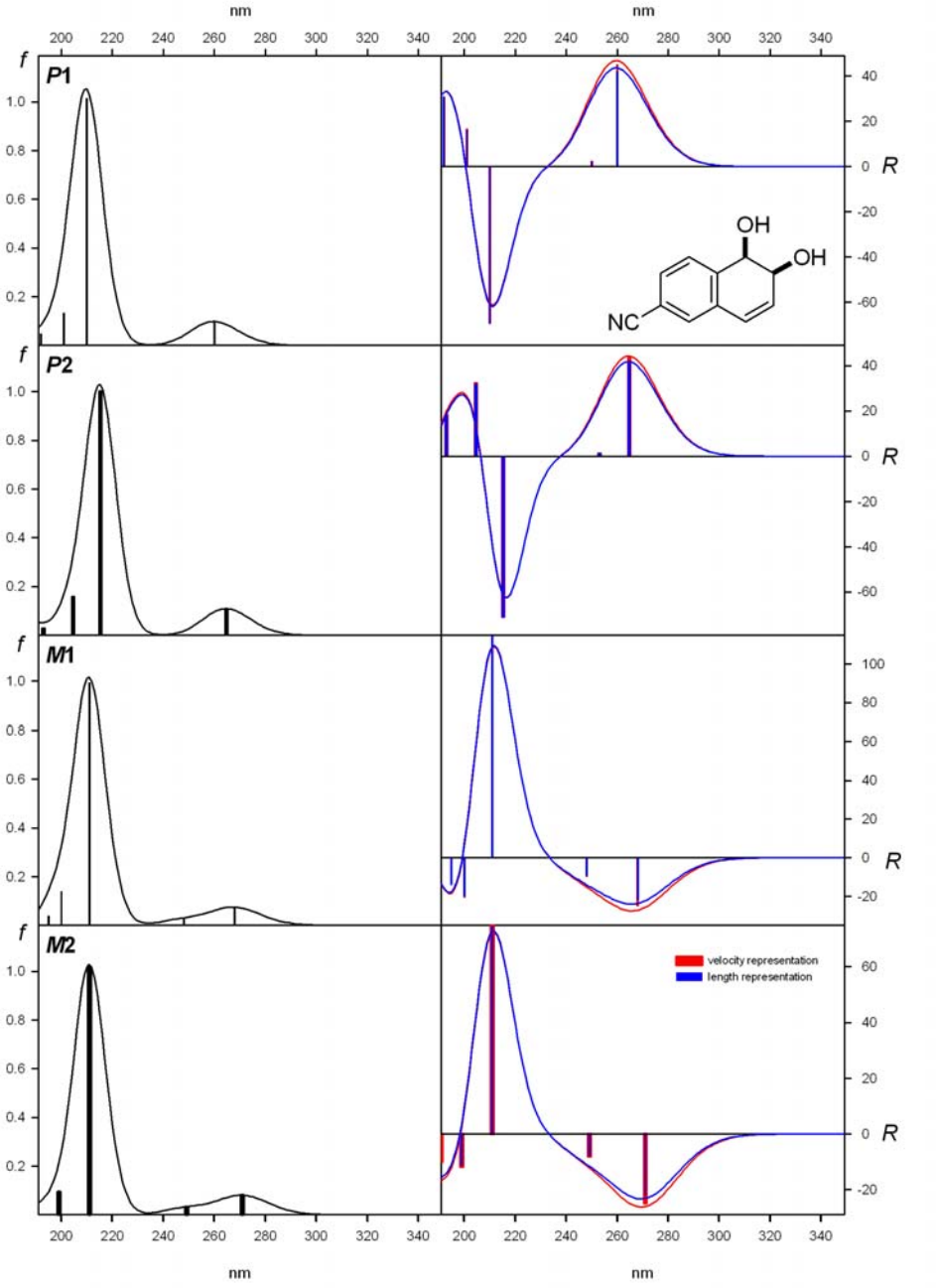
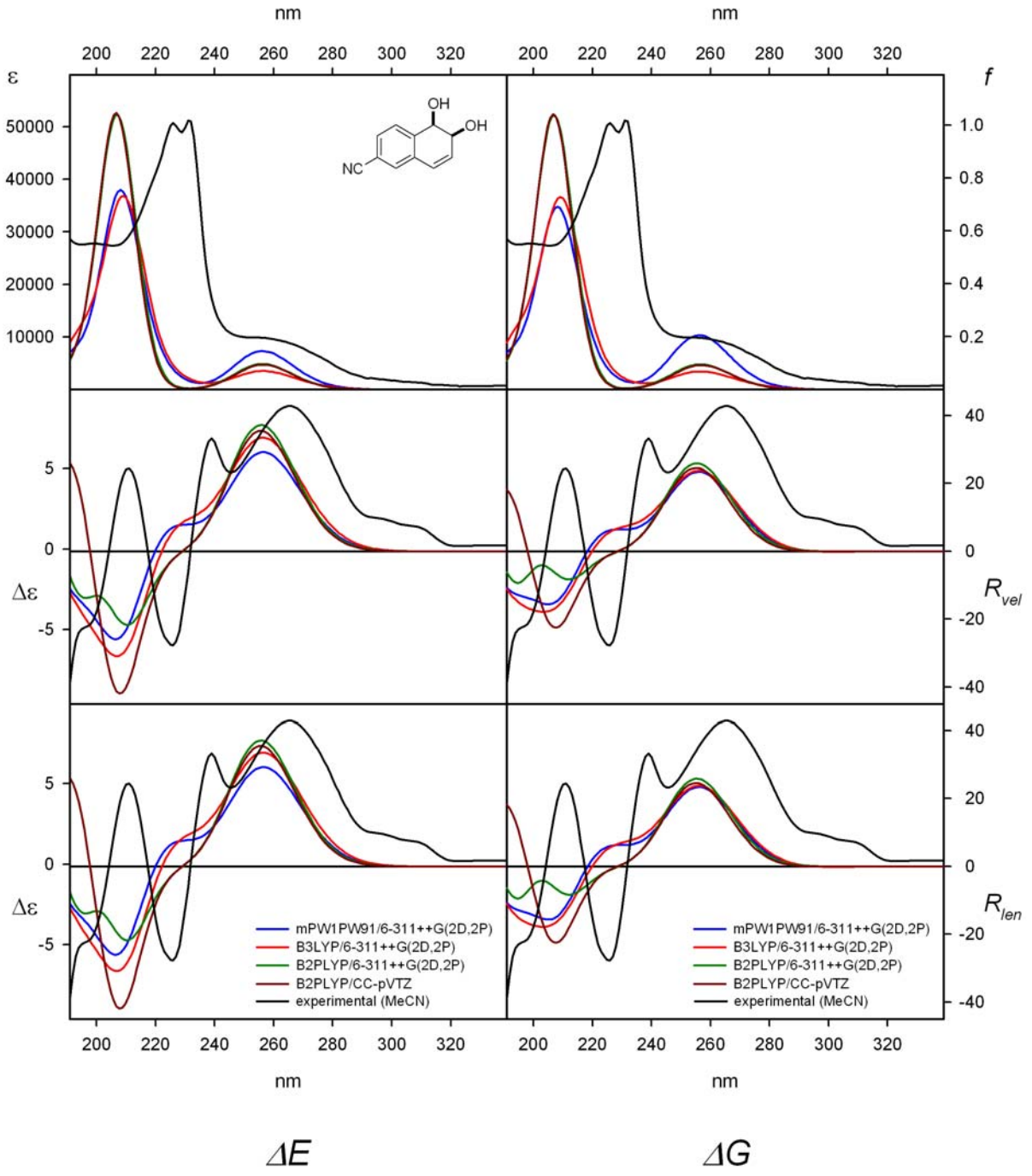
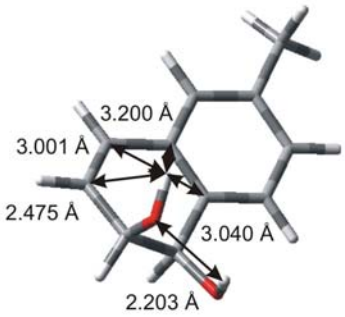


Figure 10E. Calculated at TDDFT/B2PLYP/CC-pVTZ level CD and UV spectra for individual conformers of **2d**.

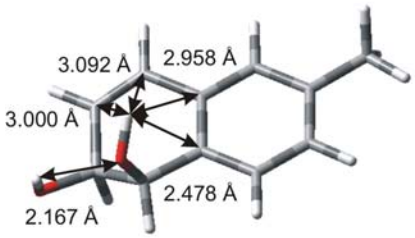


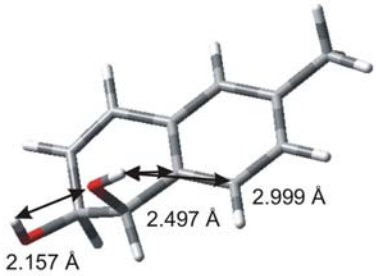
Geometries were optimzed at B3LYP/6-311++G(D,P) level
Calculated energies were scaled by the factors of:
0.921 (mPW1PW91/6-311++G(2D,2P))
0.901 (B3LYP/6-311++G(2D,2P))
0.973 (B2PLYP/6-311++G(2D,2P))
0.985 (B2PLYP/CC-pVTZ)
σ = 0.5 eV

Figure 10F. Experimental CD and UV spectra in acetonitrile solution (black line) and calculated Boltzmann averaged CD and UV spectra for *cis*-dihydrodiol **2d**. The rotational strenghts *R* were calculated at diferent levels of theory in both velocity and dipole length representations. The calculated CD and UV spectra were wavelength corrected to match the experimental long-wavelength λ_{max} values in the UV spectra.



***P*1**





***M*1** ***M*2**

		2e(*P*1)	**2e(*M*1)**	**2e(*M*2)**
Energy[a] [Hartree]		-576.994393 (-575.777438)[b]	-576.993745 (-575.776892)[b]	-576.992281 (-575.775789)[b]
ΔE [kcal mol^{-1}][a]		0.00 (0.00)[b]	0.41 (0.34)[b]	1.32 (1.03)[b]
Population [%][a]		63 (58)[b]	31 (32)[b]	6 (10)[b]
ΔG [kcal mol^{-1}][a]		0.00	1.42	0.32
Population [%][a]		60	5	35
μ [D][a]		2.94	3.50	1.42
α [°][a]		-154.6 (-155.9)[b]	159.3 (157.8)[b]	78.7 (78.4)[b]
β [°][a]		-160.5 (-160.3)[b]	155.2 (156.5)[b]	162.6 (163.5)[b]
γ [°][a]		10.9 (11.9)[b]	-12.3 (-12.9)[b]	-11.1 (-11.8)[b]
[α] calcd.[c]	D	+225	+170	+39
	575 nm	+330	+211	+14
	546 nm	+338	+241	+10
	436 nm	+813	+417	-65

$[\alpha]_D$ calcd. Boltzmann averaged

ΔE				ΔG			
D	575 nm	546 nm	436 nm	D	575 nm	546 nm	436 nm
+197 (+189)[b]	+274 (+260)[b]	+288 (+274)[b]	+638 (+598)[b]	+157	+213	+218	+486

[a] – B3LYP/6-311++G(D,P)
[b] – in parentheses results for geometries optimized at B2PLYP/6-311++G(D,P) level
[c] – B3LYP/6-311++G(2D,2P)

Figure 11A. Calculated at B3LYP/6-311++G(D,P) level structures of individual conformers of **2e**, their relative energies and some structural parameters.

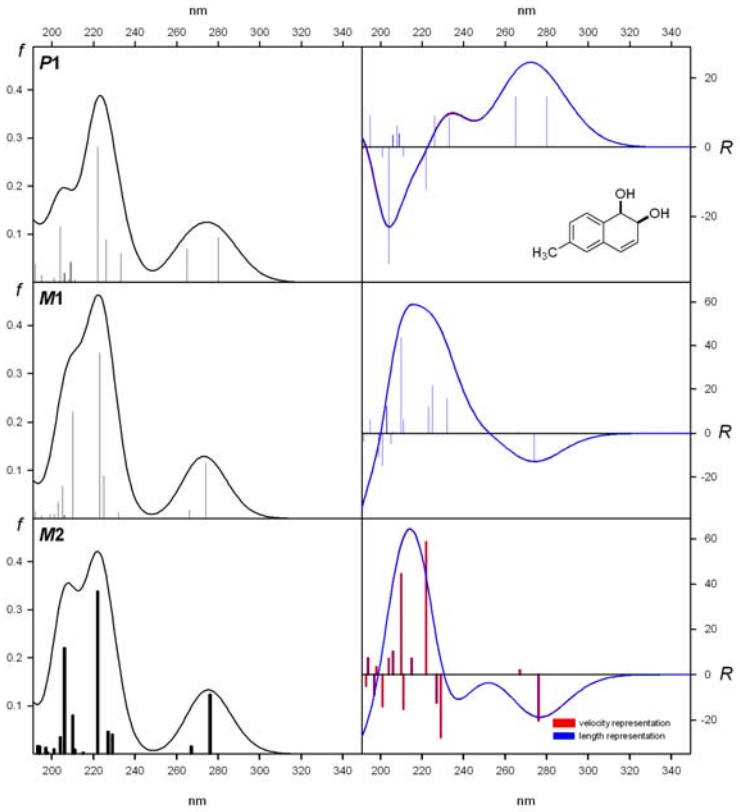


Figure 11B. Calculated at TDDFT/mPW1PW91/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **2e**.

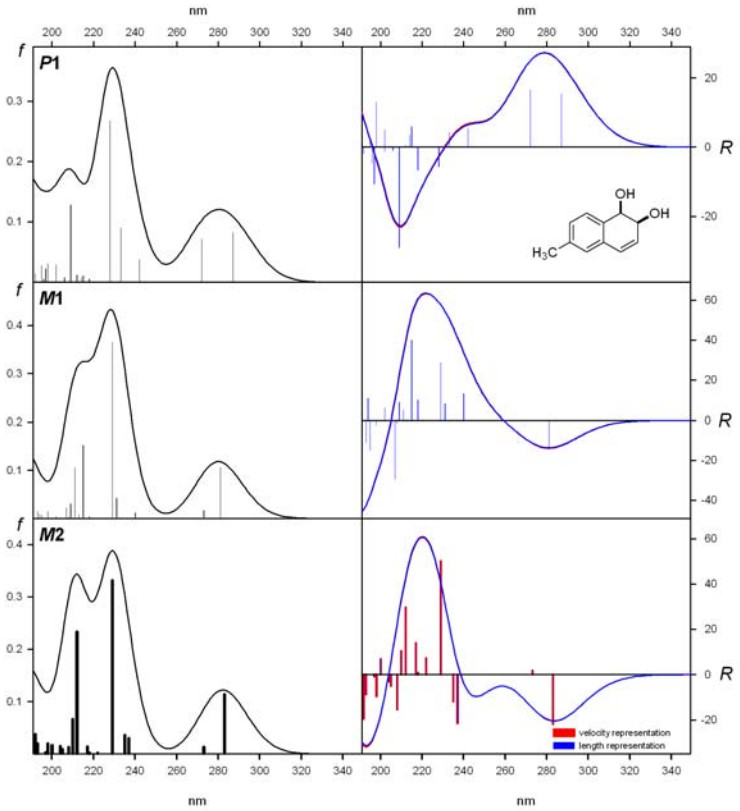


Figure 11C. Calculated at TDDFT/B3LYP/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **2e**.

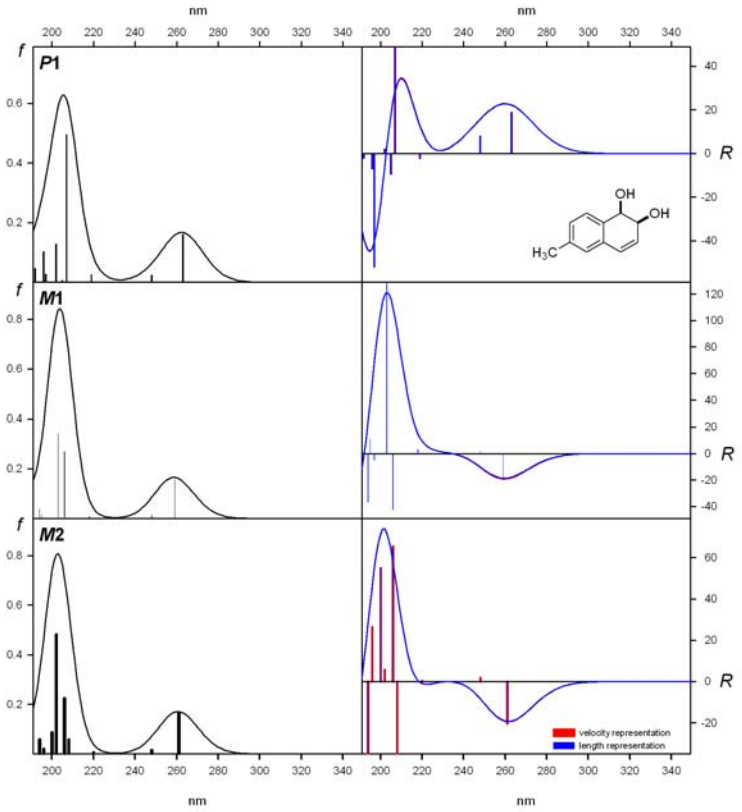


Figure 11D. Calculated at TDDFT/B2PLYP/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **2e**.

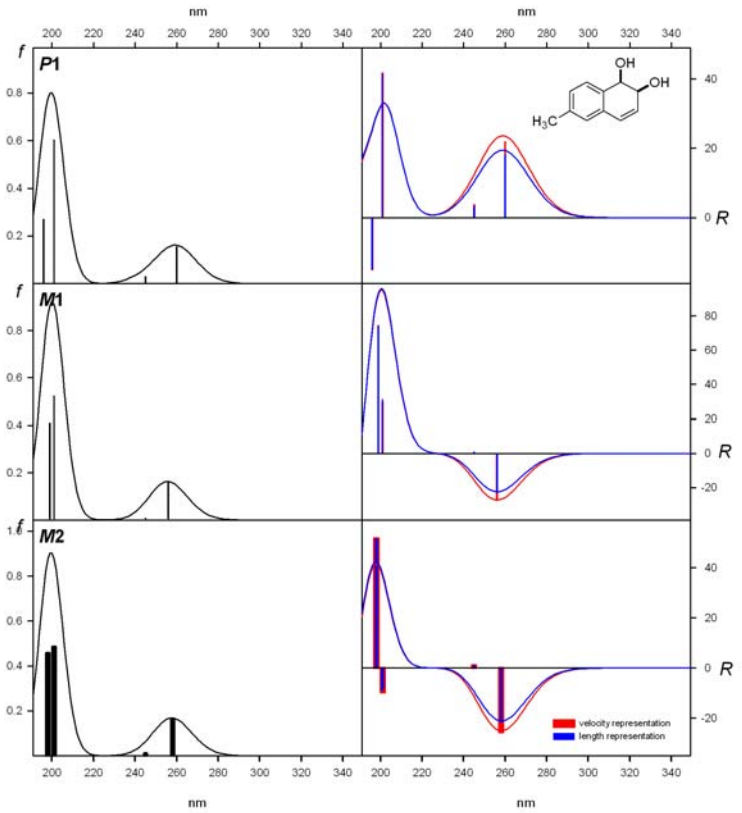


Figure 11E. Calculated at TDDFT/B2PLYP/CC-pVTZ level CD and UV spectra for individual conformers of **2e**.

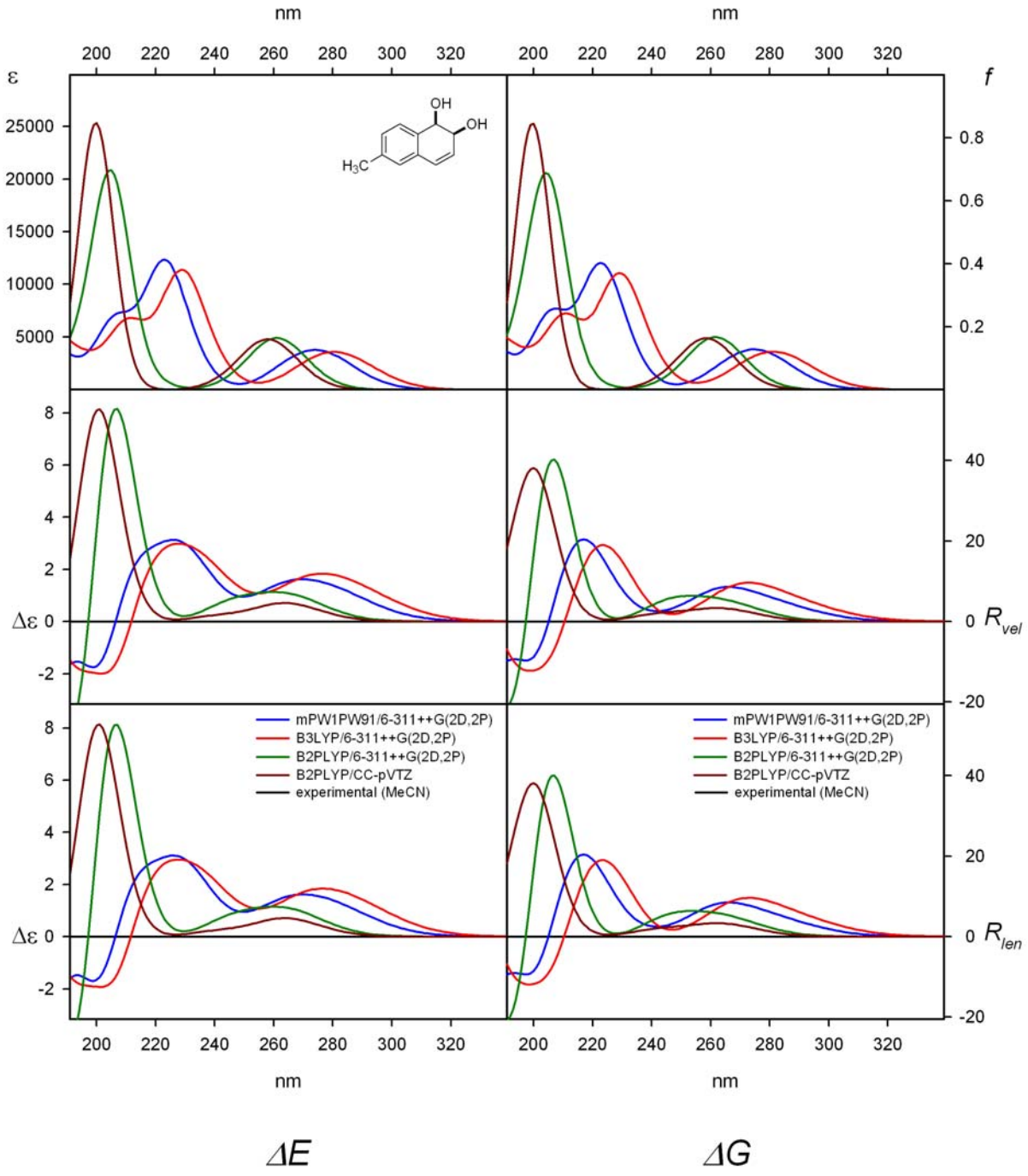
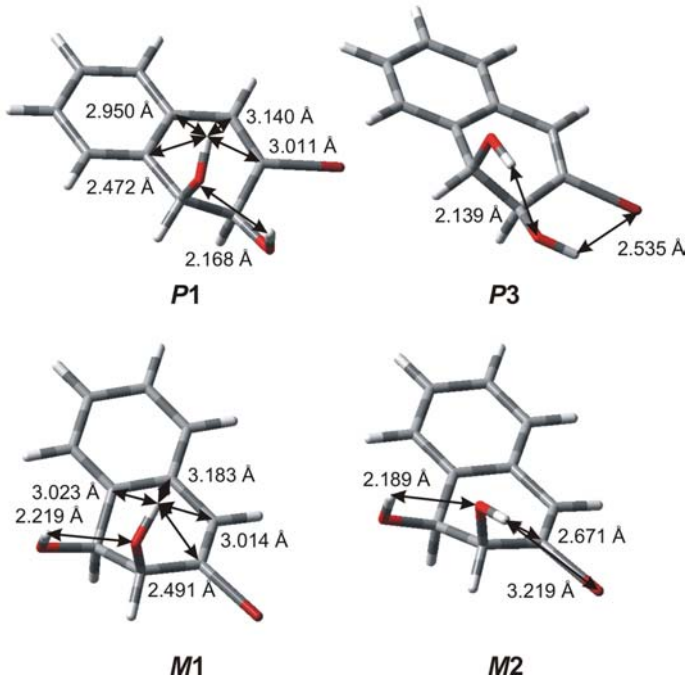


Figure 11F. Experimental CD and UV spectra in acetonitrile solution (black line) and calculated Boltzmann averaged CD and UV spectra for *cis*-dihydrodiol **2e**. The rotational strenghts *R* were calculated at diferent levels of theory in both velocity and dipole length representations.



		3a(*P*1)	**3a(*P*3)**	**3a(*M*1)**	**3a(*M*2)**
Energy[a] [Hartree]		-3111.207868 (-3111.591638)[b]	-3111.207703 (-3111.591665)[b]	-3111.209816 (-3111.593782)	-3111.209404 (-3111.593715)[b]
ΔE [kcal mol^{-1}] [a]		1.22 (1.35)[b]	1.32 (1.33	0.00 (0.00)	0.26 (0.04)[b]
Population [%][a]		7 (4)[b]	5 (5)[b]	54 (47)	34 (44)[b]
ΔG [kcal mol^{-1}] [a]		1.04	1.11	0.01	0.00
Population [%][a]		7	7	43	43
μ [D] [a]		3.78	1.97	2.77	1.19
α [°][a]		-158.1 (-157.0)[b]	75.2 (73.2	155.9 (156.7)[b]	160.8 (162.2)[b]
β [°][a]		-158.6 (-159.9)[b]	81.3 (75.2	161.3 (161.1)[b]	55.5 (56.7)[b]
γ [°][a]		11.5 (12.2)[b]	10.6 (11.2	-11.6 (-12.4)[b]	-10.6 (-11.3)[b]
[*α*] calcd.[c]	D	+9	+3	-126	-218
	575 nm	+25	+12	-184	-309
	546 nm	+33	+16	-216	-361
	436 nm	+112	+53	-440	-727

$[\alpha]_D$ calcd. Boltzmann averaged

ΔE				*ΔG*			
D	578 nm	546 nm	436 nm	D	578 nm	546 nm	436 nm
-141 (-154)[b]	-202 (-221)[b]	-236 (-258)[b]	-474 (-519) [b]	-147	-209	-245	-490

[a] – B3LYP/6-311++G(D,P)
[b] – in parentheses results for geometries optimized at B2PLYP/6-311++G(D,P) level
[c] – B3LYP/6-311++G(2D,2P)

Figure 12A. Calculated at B3LYP/6-311++G(D,P) level structures of individual conformers of **3a**, their relative energies and some structural parameters.

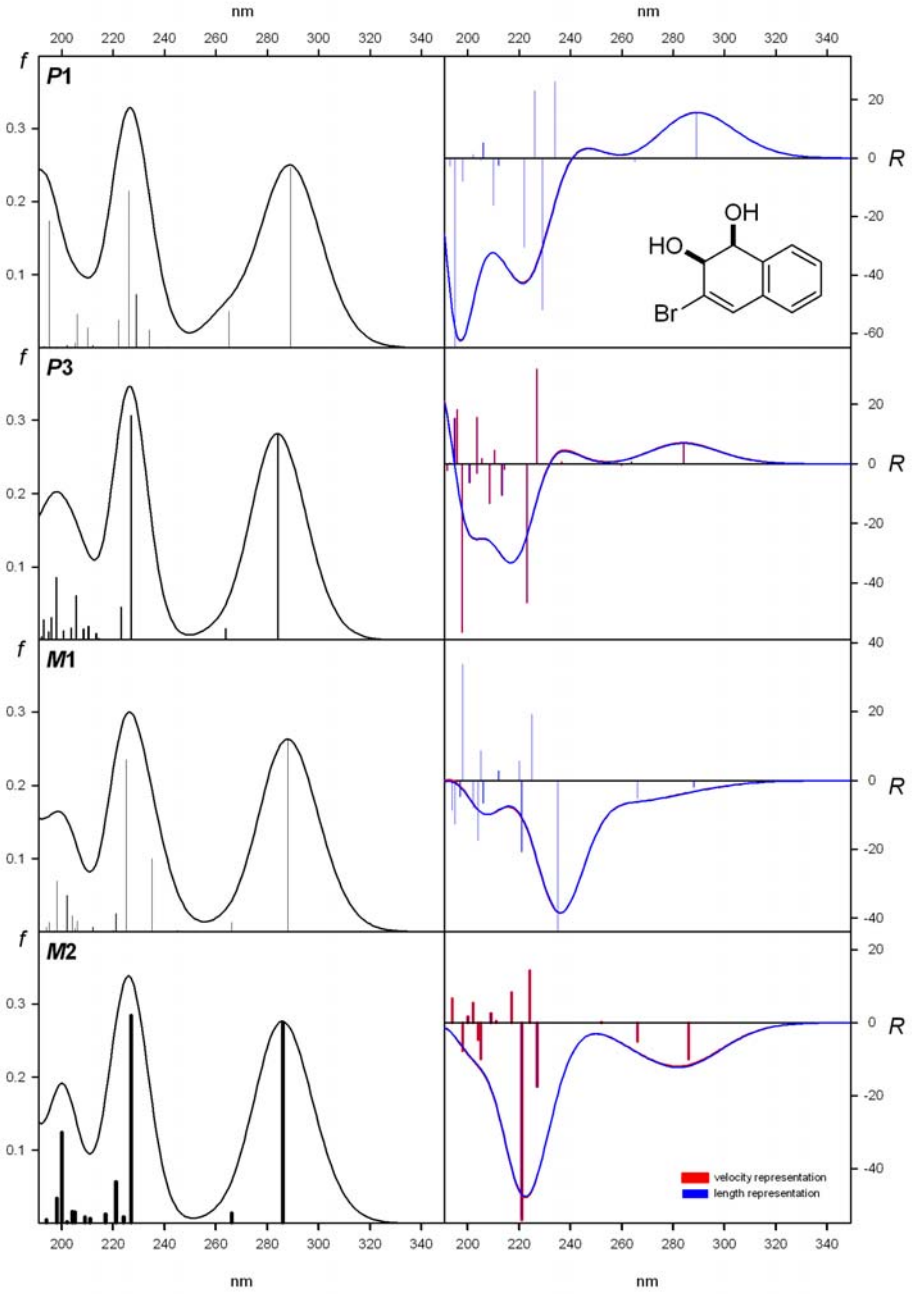


Figure 12B. Calculated at TDDFT/mPW1PW91/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **3a**.

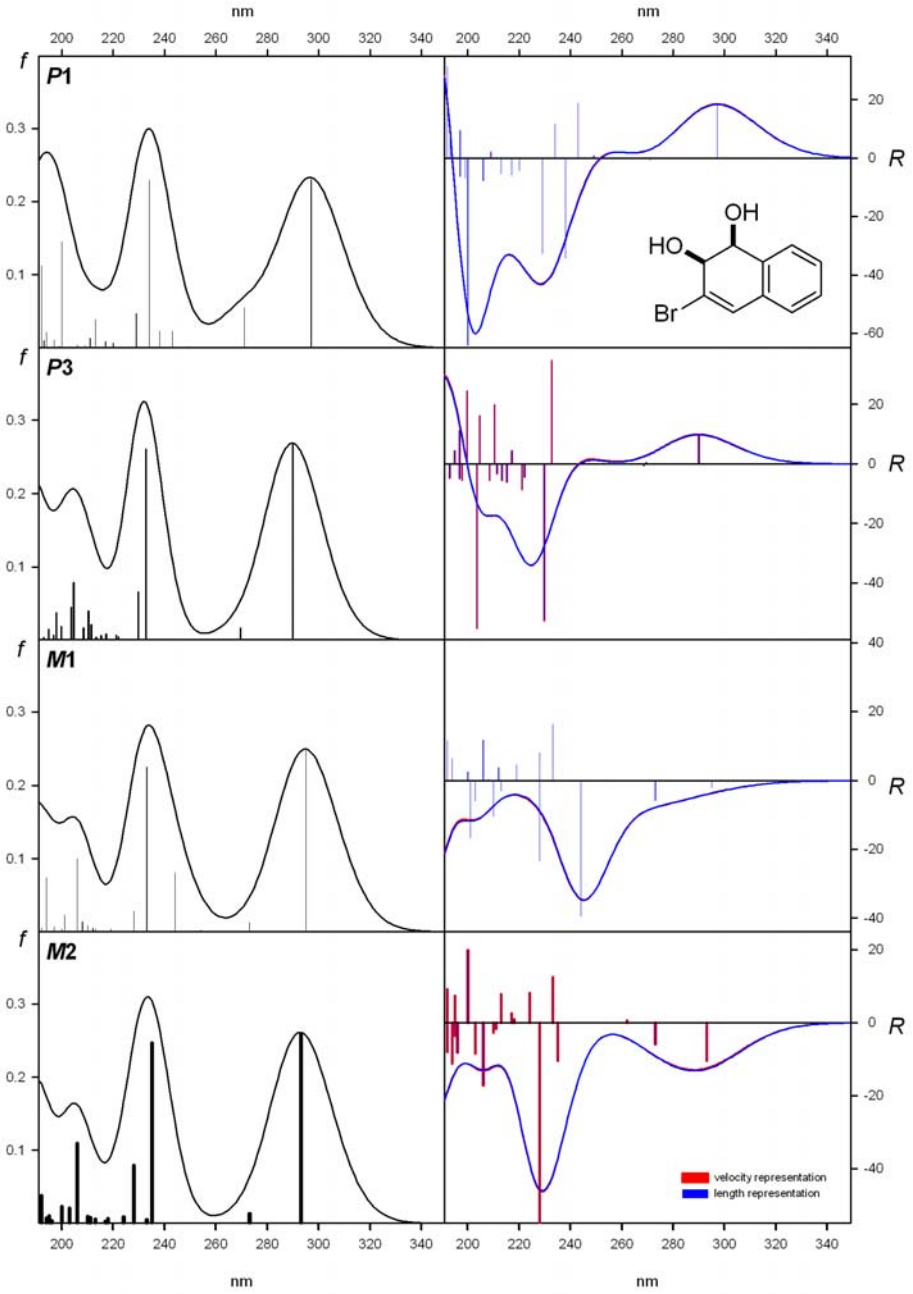


Figure 12C. Calculated at TDDFT/B3LYP/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **3a**.

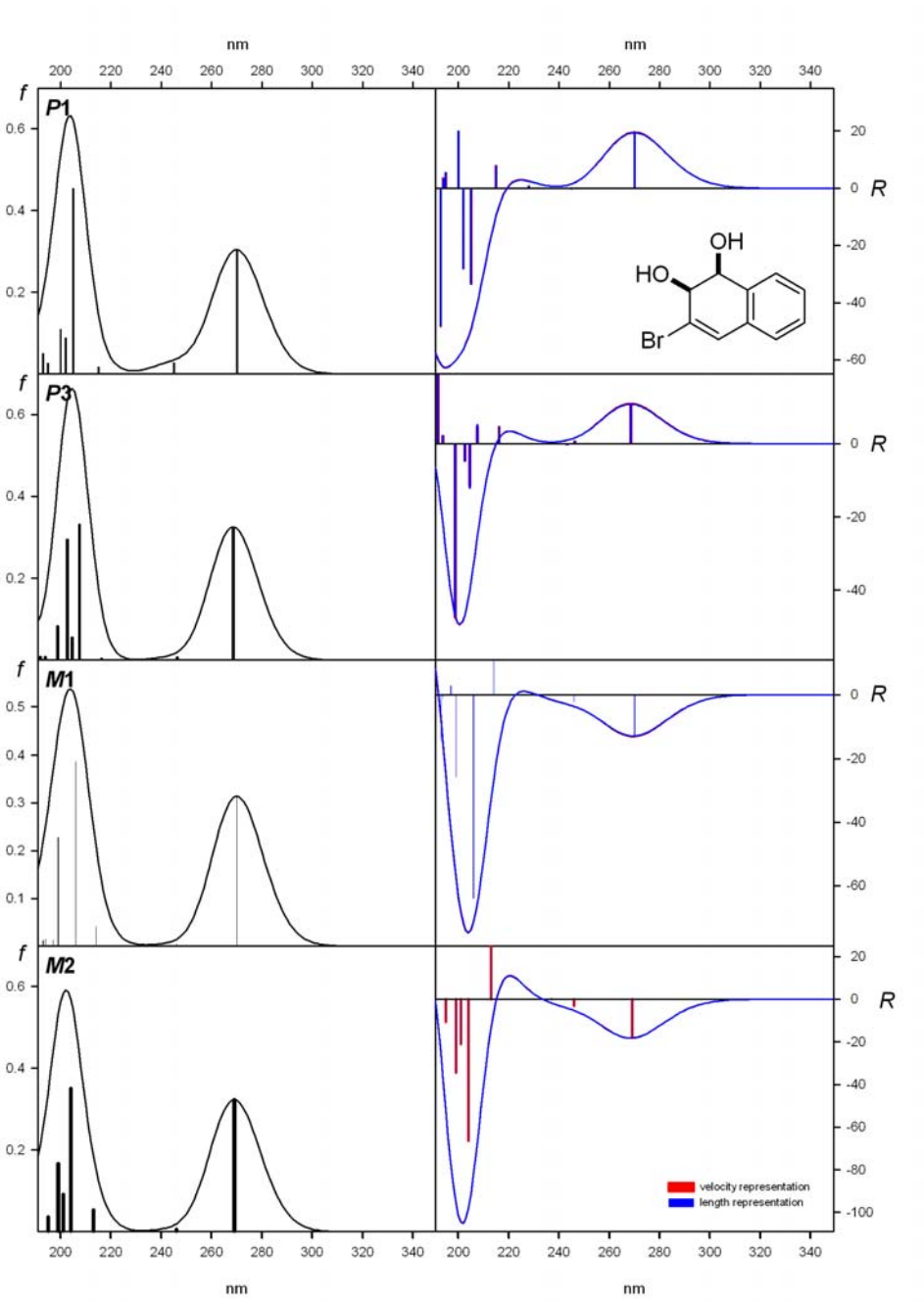


Figure 12D. Calculated at TDDFT/B2PLYP/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **3a**.

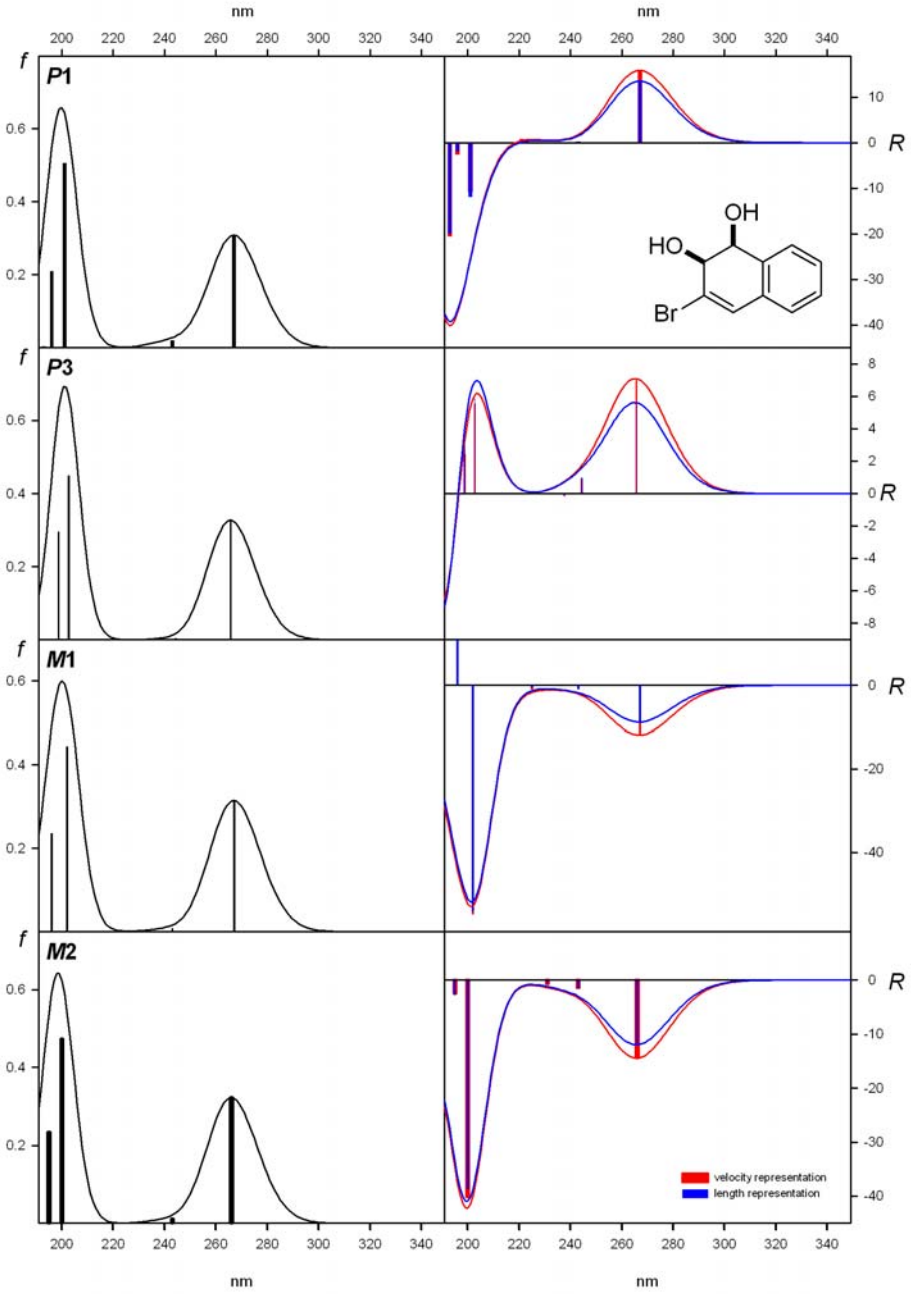


Figure 12E. Calculated at TDDFT/B2PLYP/CC-pVTZ level CD and UV spectra for individual conformers of **3a**.

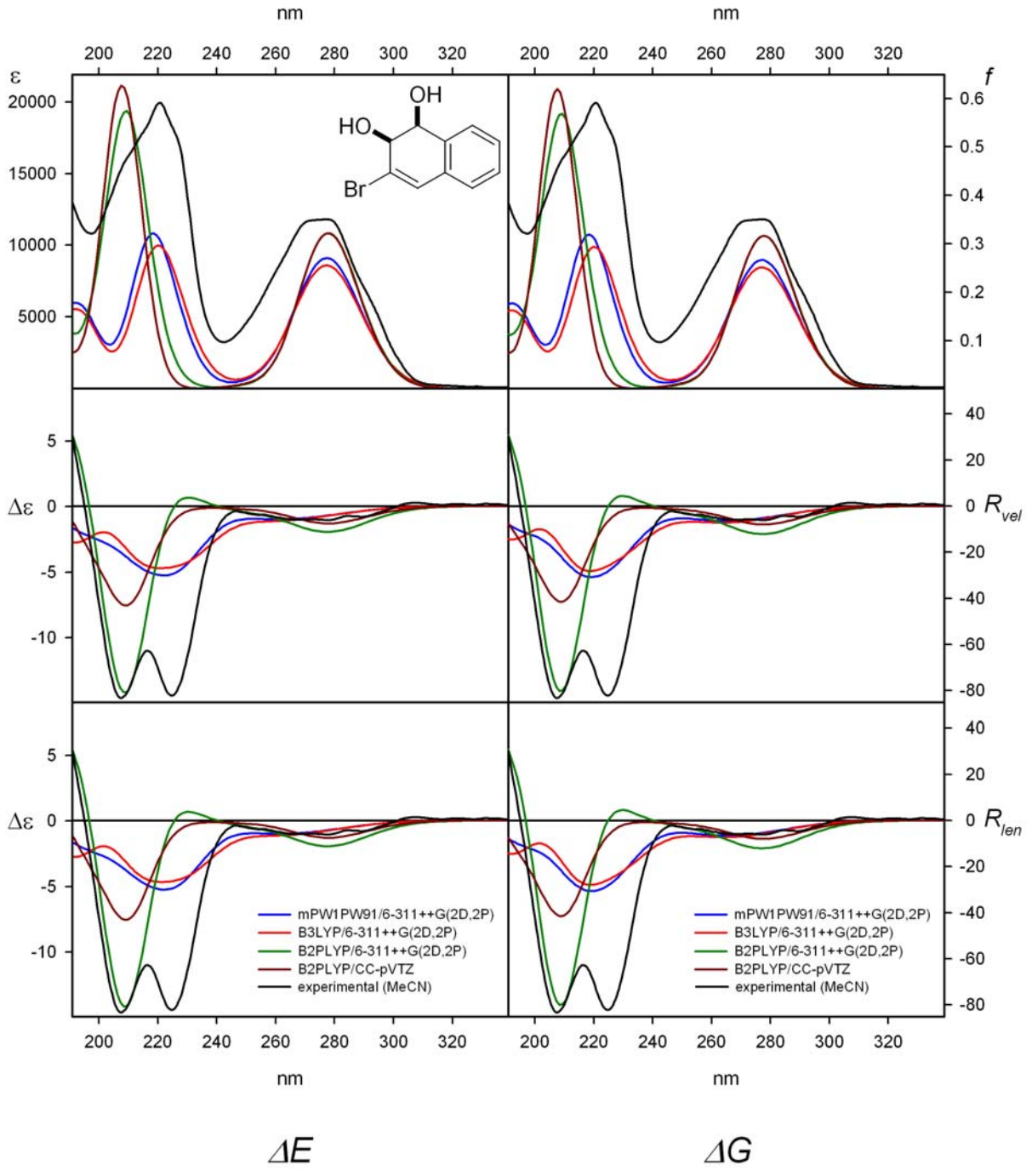
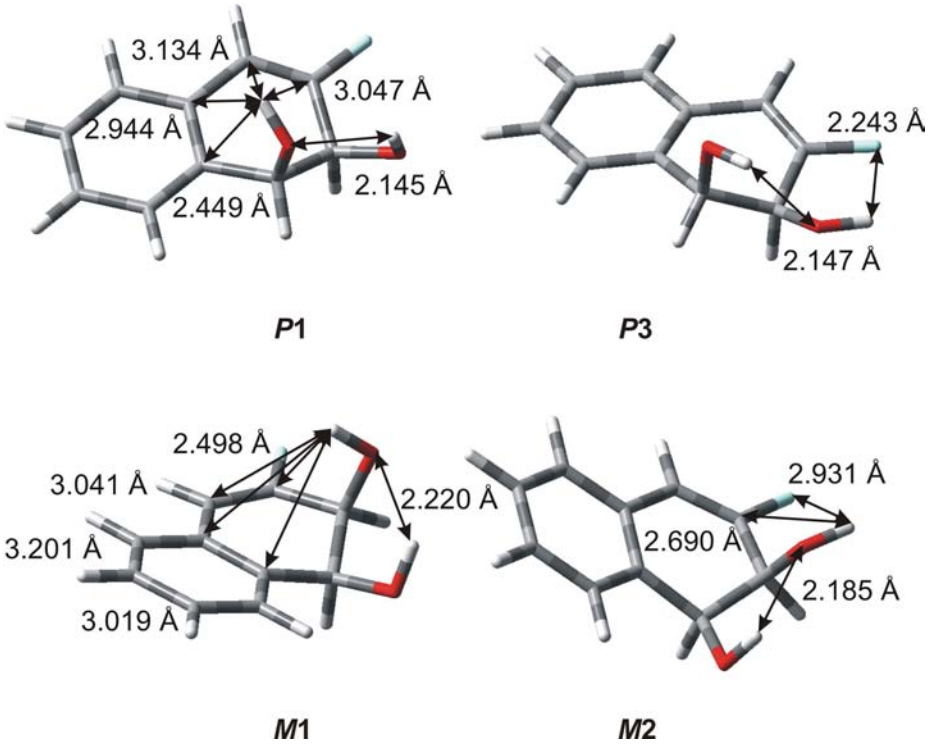


Figure 12F. Experimental CD and UV spectra in acetonitrile solution (black line) and calculated Boltzmann averaged CD and UV spectra for *cis*-dihydrodiol **3a**. The rotational strenghts *R* were calculated at diferent levels of theory in both velocity and dipole length representations. The calculated CD and UV spectra were wavelength corrected to match the experimental long-wavelength λ_{max} values in the UV spectra.



		3b(*P*1)	3b(*P*3)	3b(*M*1)	3b(*M*2)
Energy[a] [Hartree]		-636.932517	-636.932104	-636.934375	-636.933614
ΔE [kcal mol^{-1}][a]		1.17	1.42	0.00	0.48
Population [%][a]		8	6	60	26
ΔG [kcal mol^{-1}][a]		0.99	1.23	0.00	0.16
Population [%][a]		9	6	48	37
μ [D] [a]		3.80	1.87	2.59	1.03
α [°][a]		-154.3	75.5	155.4	160.5
β [°][a]		-157.2	83.1	162.2	52.3
γ [°][a]		11.2	10.9	-11.5	-10.6
[α] calcd.[b]	D	-37	-49	-256	-342
	575 nm	-15	-43	-379	-494
	546 nm	-11	-46	-447	-580
	436 nm	59	-40	-941	-1190

[α]$_D$ calcd. Boltzmann averaged

ΔE				ΔG			
D	578 nm	546 nm	436 nm	D	578 nm	546 nm	436 nm
-248	-360	-423	-872	-256	-369	-433	-889

[a] – B3LYP/6-311++G(D,P)
[b] – B3LYP/6-311++G(2D,2P)

Figure 13A. Calculated at B3LYP/6-311++G(D,P) level structures of individual conformers of **3b**, their relative energies and some structural parameters.

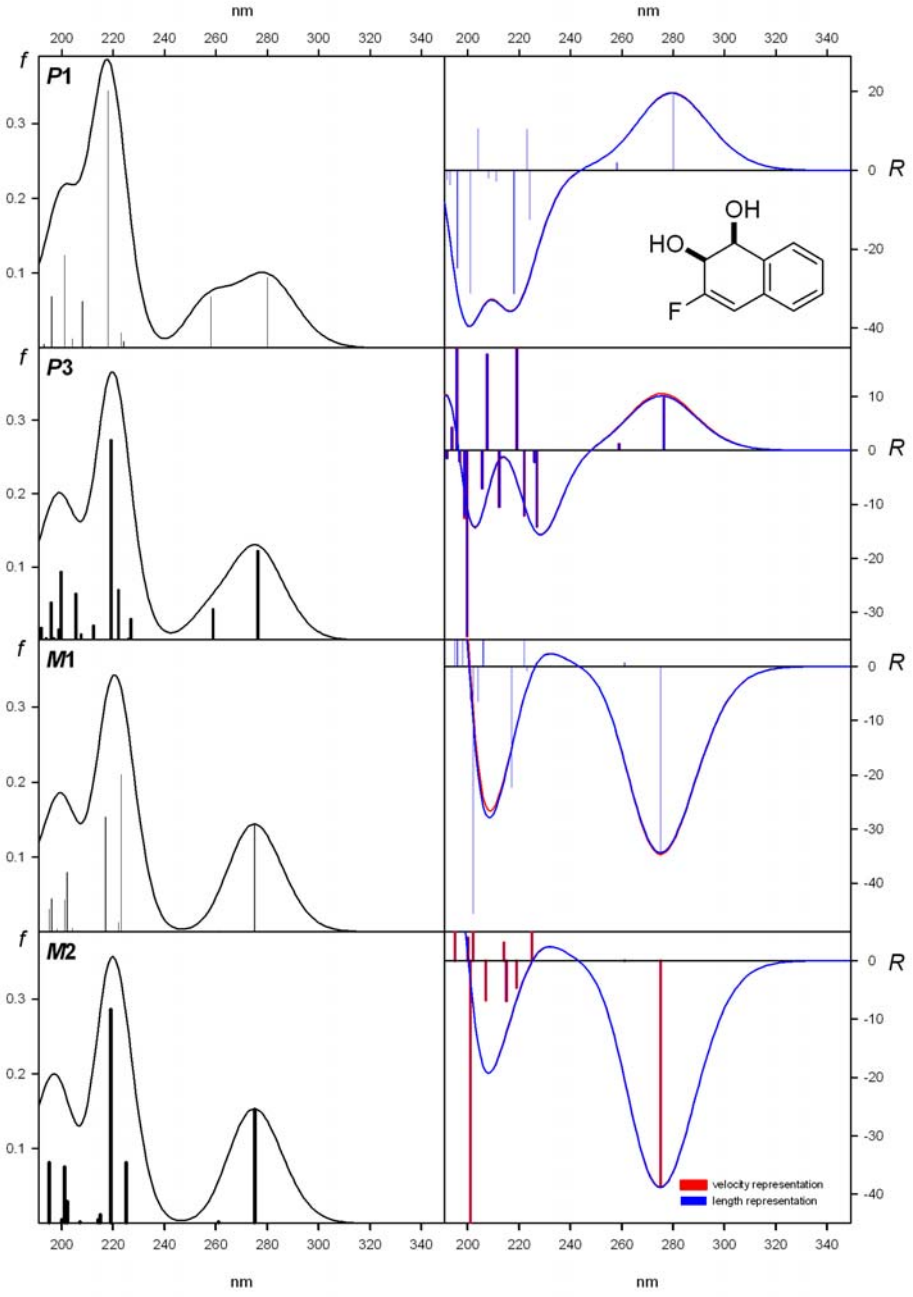


Figure 13B. Calculated at TDDFT/mPW1PW91/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **3b**.

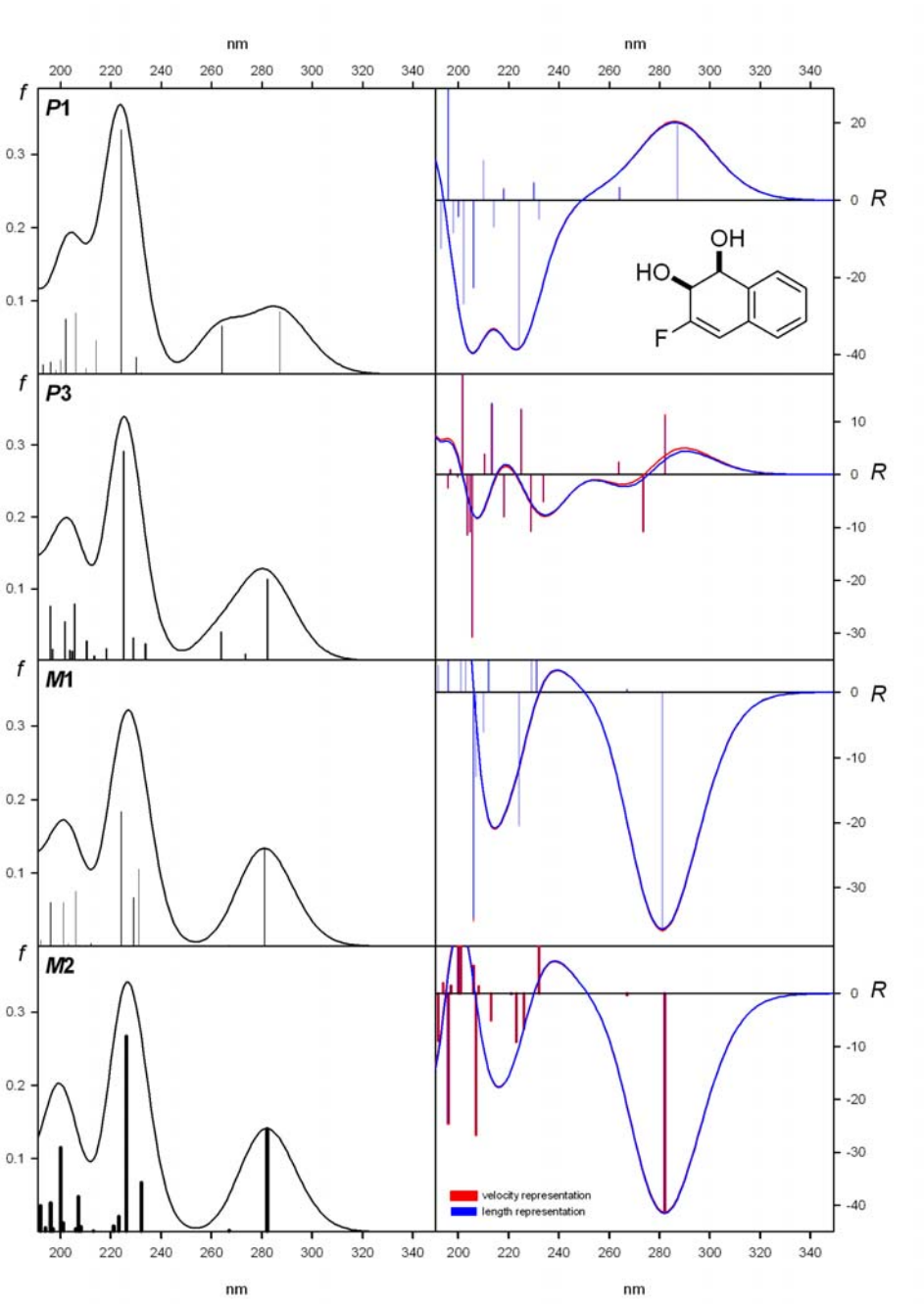


Figure 13C. Calculated at TDDFT/B3LYP/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **3b**.

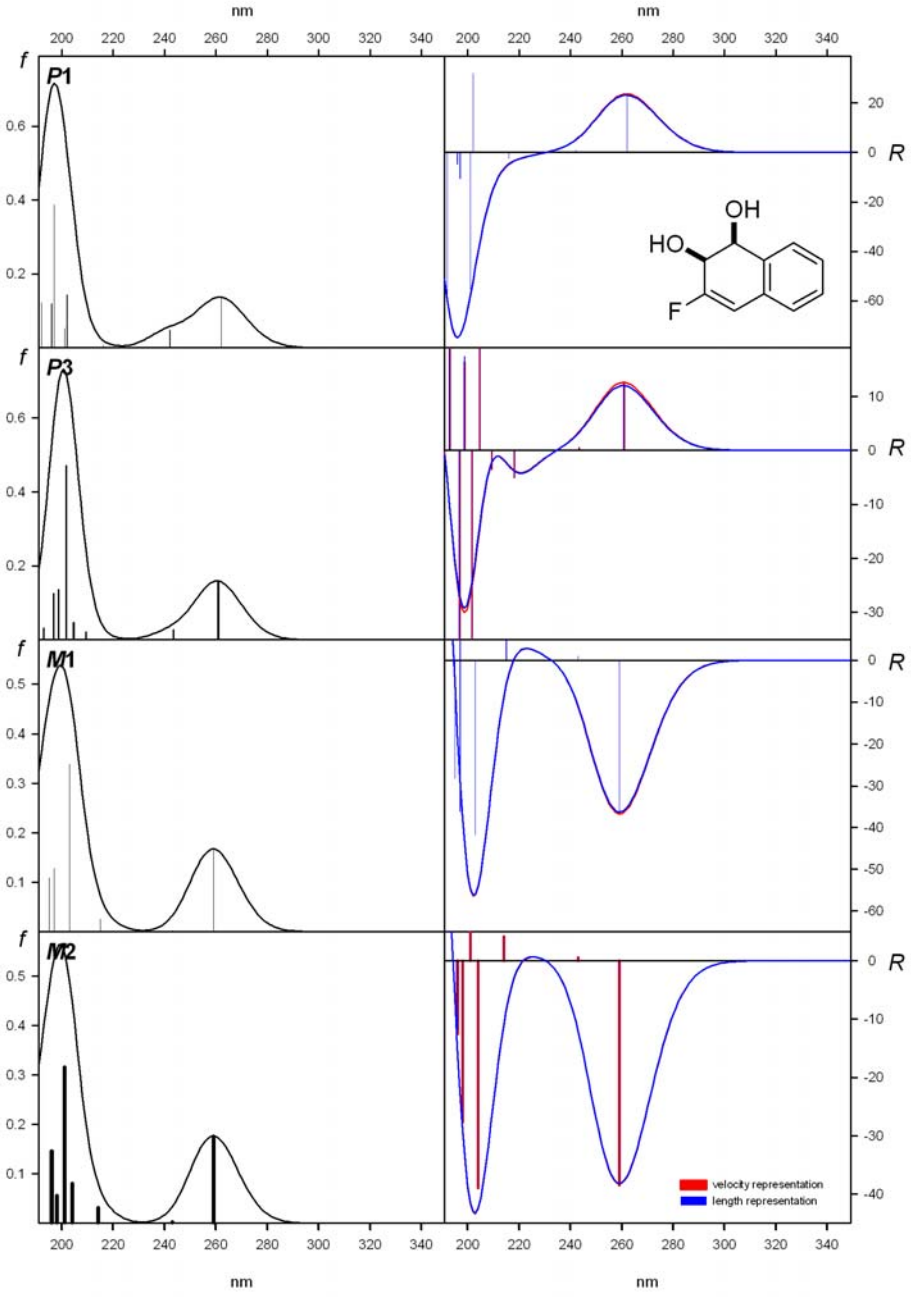


Figure 13D. Calculated at TDDFT/B2PLYP/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **3b**.

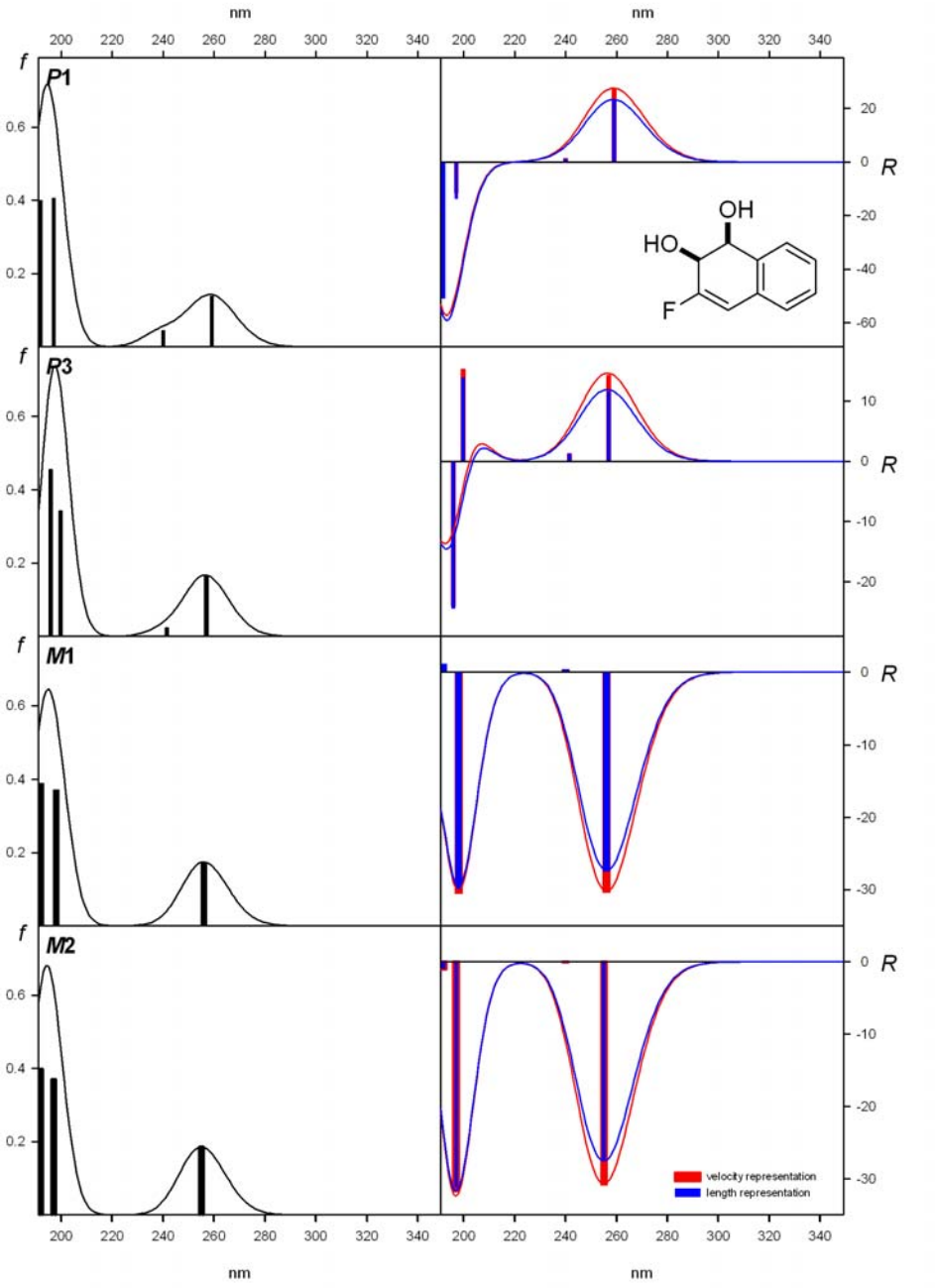
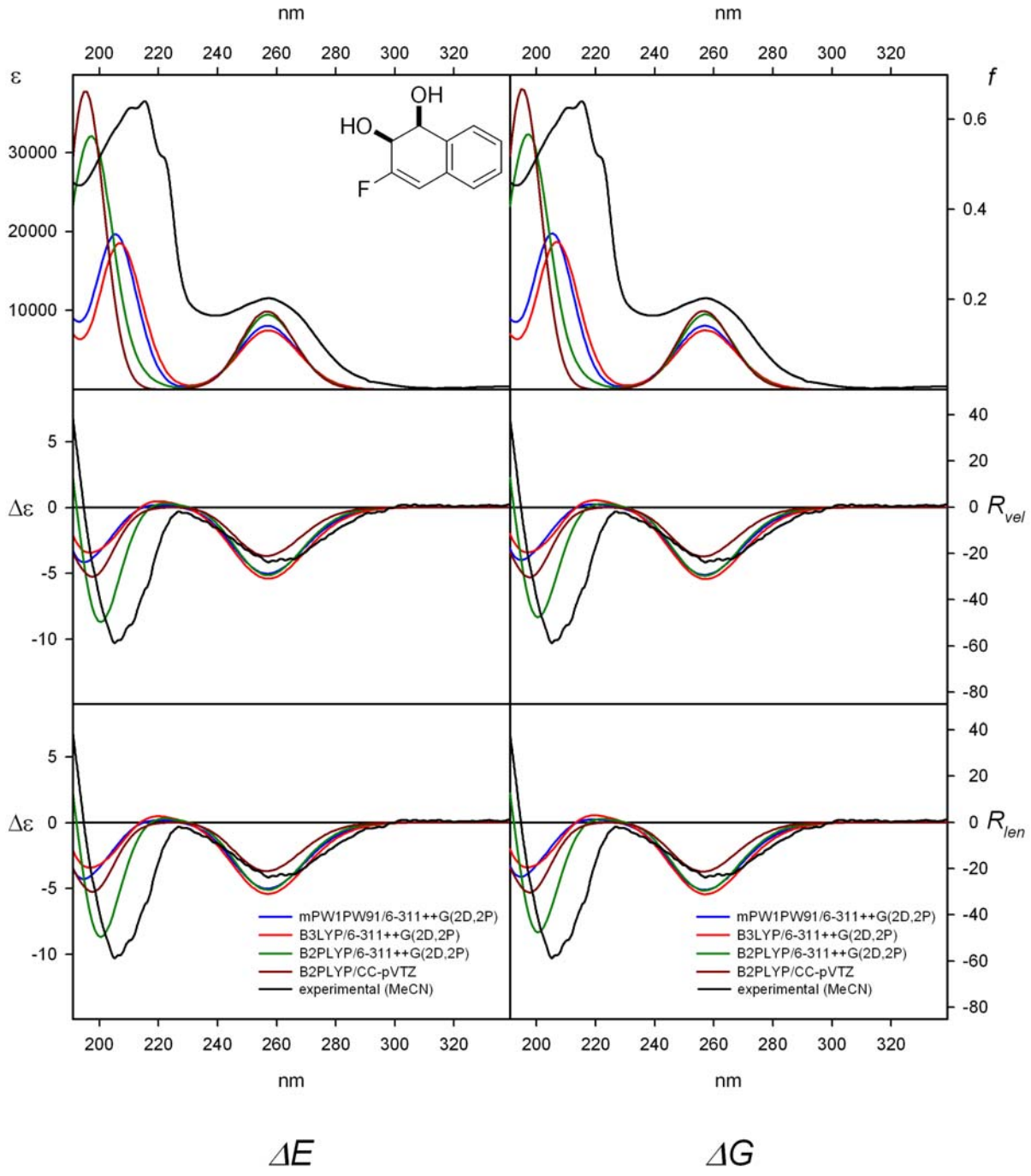
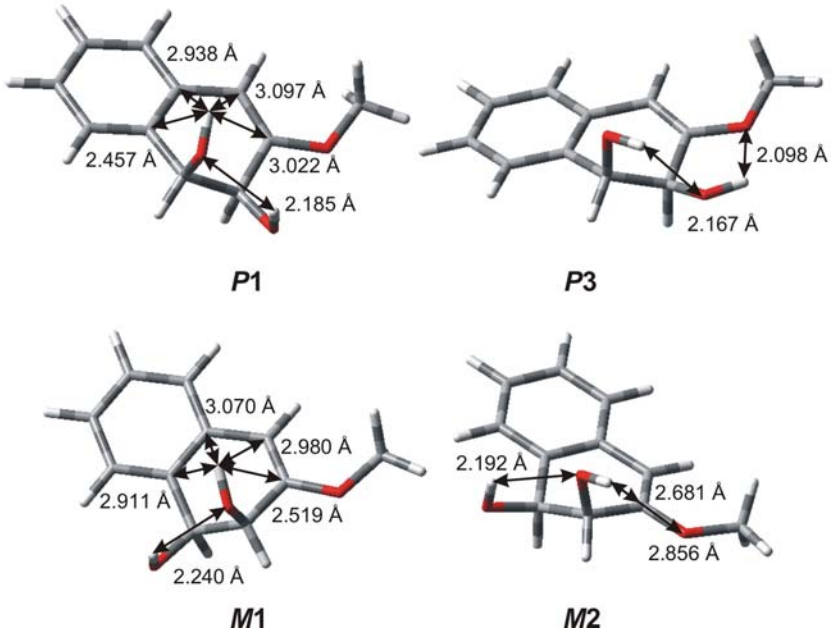


Figure 13E. Calculated at TDDFT/B2PLYP/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **3b**.



Geometries were optimzed at B3LYP/6-311++G(D,P) level
Calculated energies were scaled by the factors of:
0.934 (mPW1PW91/6-311++G(2D,2P))
0.915 (B3LYP/6-311++G(2D,2P))
0.992 (B2PLYP/6-311++G(2D,2P))
1.004 (B2PLYP/CC-pVTZ)
σ = 0.5 eV

Figure 13F. Experimental CD and UV spectra in acetonitrile solution (black line) and calculated Boltzmann averaged CD and UV spectra for *cis*-dihydrodiol **3b**. The rotational strenghts *R* were calculated at diferent levels of theory in both velocity and dipole length representations. The calculated CD and UV spectra were wavelength corrected to match the experimental long-wavelength λ_{max} values in the UV spectra.



	3c(*P*1)	**3c(*P*3)**	**3c(*M*1)**	**3c(*M*2)**
Energy[a] [Hartree]	-652.224035 (-652.886741)[b]	-652.226174 (-652.889476)[b]	-652.226711 (-652.889532)	-652.226018 (-652.889244)[b]
ΔE [kcal mol^{-1}] [a]	1.68 (1.75)[b]	0.34 (0.03)[b]	0.00 (0.00)[b]	0.43 (0.18)[b]
Population [%][a]	2 (1)[b]	27 (35)[b]	48 (37)[b]	23 (27)[b]
ΔG [kcal mol^{-1}] [a]	1.49	0.30	0.00	0.21
Population [%][a]	4	25	42	29
μ [D] [a]	3.39	3.47	3.61	1.19
α [°][a]	-155.7 (-154.1)[b]	774.9 (72.9)[b]	156.8 (157.7)[b]	161.1 (162.5)[b]
β [°][a]	-159.7 (-162.4)[b]	90.7 (88.2)[b]	165.4 (165.1)[b]	53.4 (54.7)[b]
γ [°][a]	12.5 (13.4)[b]	12.1 (12.7)[b]	-12.8 (-13.6)[b]	-11.6 (-12.2)[b]
δ [°][a]	1.1 (0.6)[b]	3.4 (3.1)[b]	0.8 (1.0)[b]	0.5 (0.3)[b]
[α] calcd.[c] D	-15	-42	-179	-309
575 nm	+7	-43	-257	-438
546 nm	+14	-48	-302	-513
436 nm	+111	-57	-627	-1049

[α]$_D$ calcd. Boltzmann averaged

ΔE				ΔG			
D	578 nm	546 nm	436 nm	D	578 nm	546 nm	436 nm
-169 (-164)[b]	-236 (-228)[b]	-276 (-267)[b]	-555 (-534)[b]	-176	-245	-287	-577

[a] – B3LYP/6-311++G(D,P)
[b] – in parentheses results for geometries optimized at B2PLYP/6-311++G(D,P) level
[c] – B3LYP/6-311++G(2D,2P)

Figure 14A. Calculated at B3LYP/6-311++G(D,P) level structures of individual conformers of **3c**, their relative energies and some structural parameters.

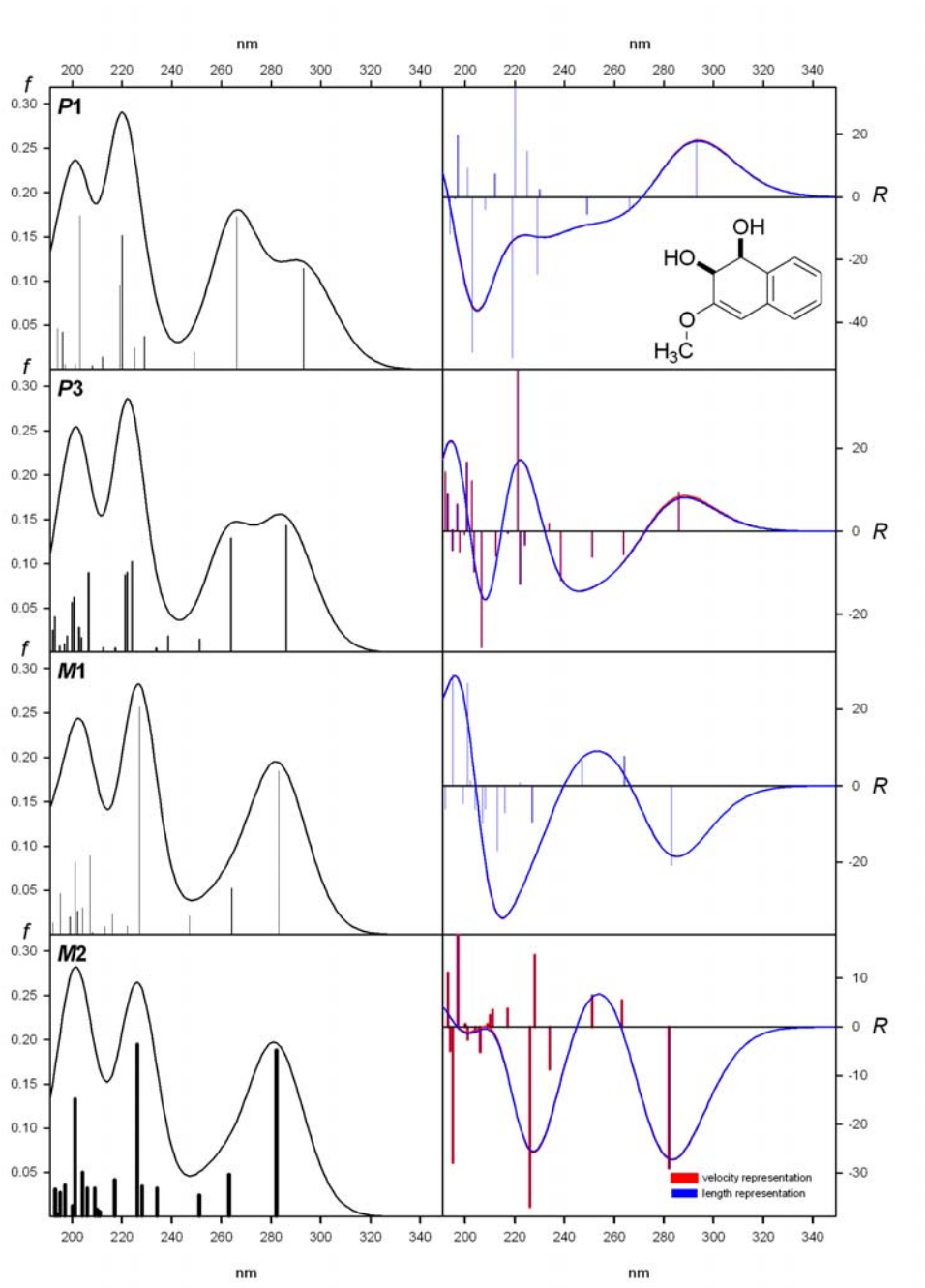


Figure 14B. Calculated at TDDFT/mPW1PW91/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **3c**.

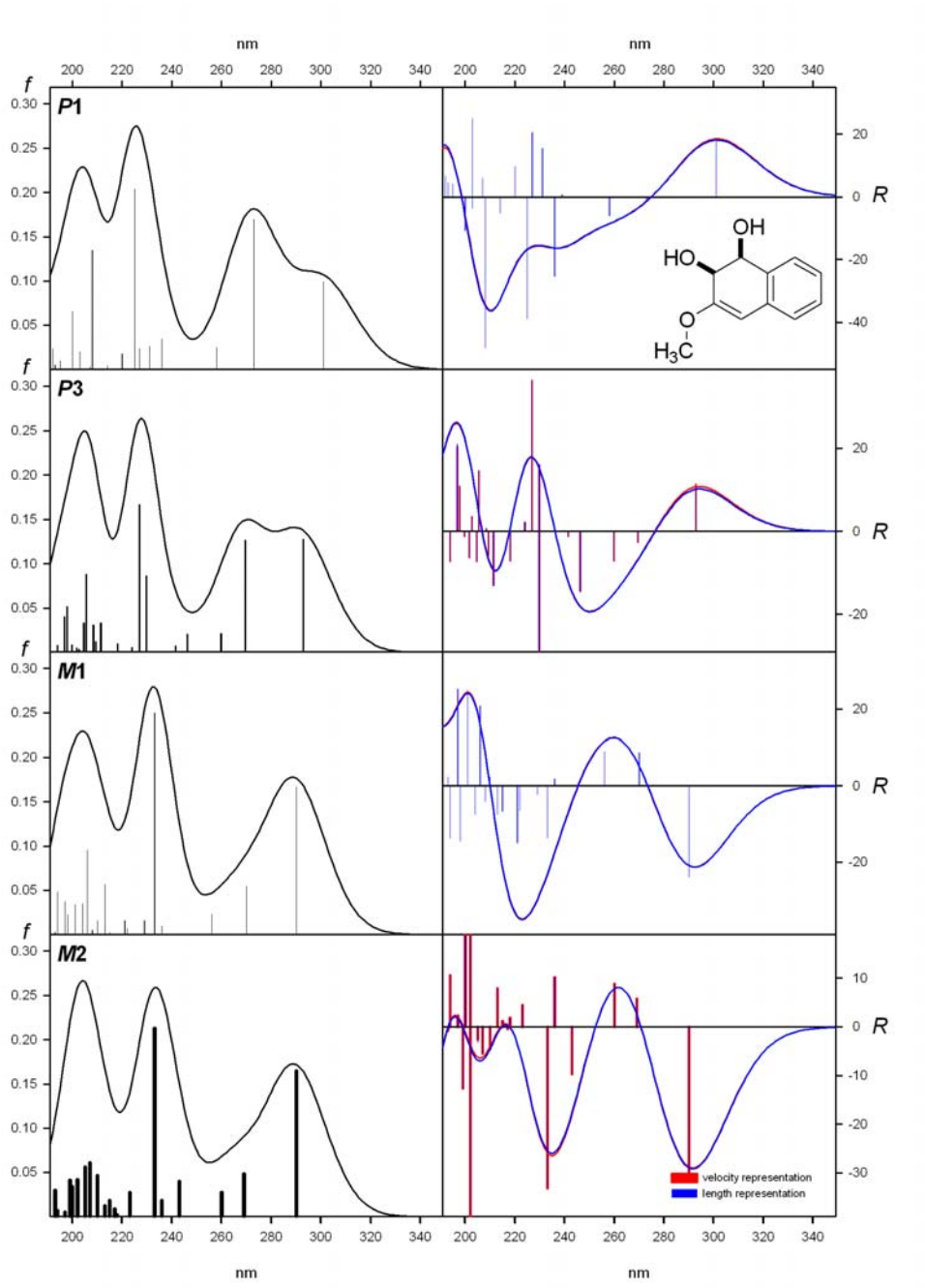


Figure 14C. Calculated at TDDFT/B3LYP/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **3c**.

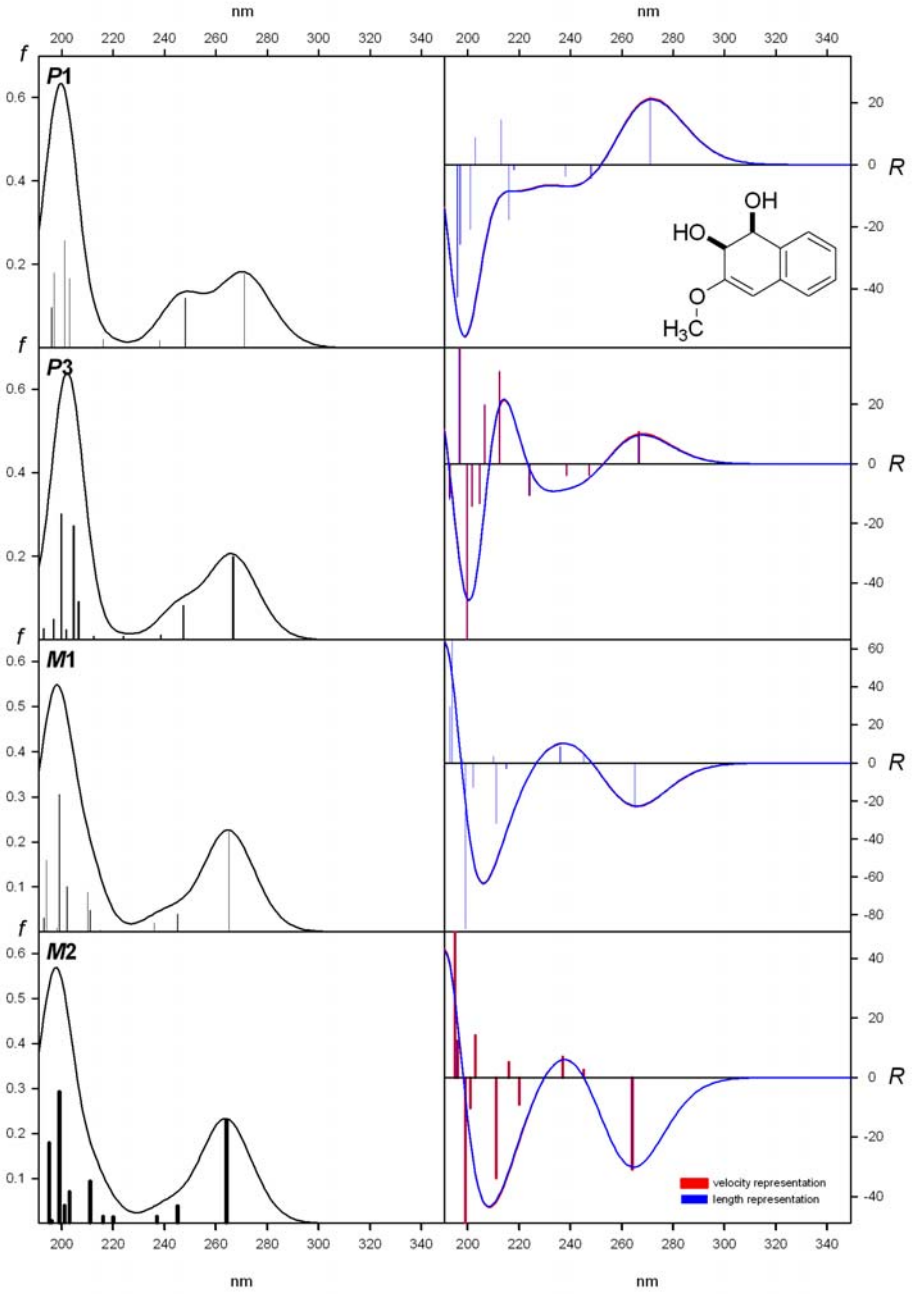


Figure 14D. Calculated at TDDFT/B2PLYP/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **3c**.

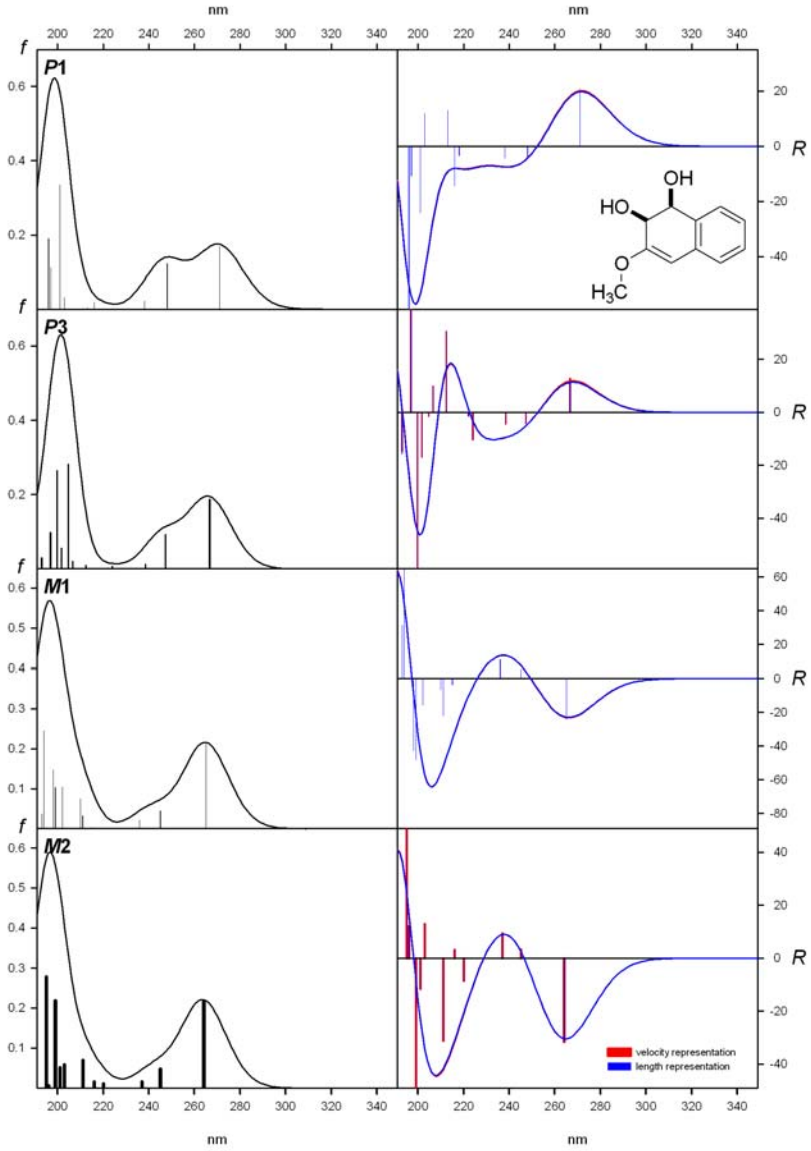
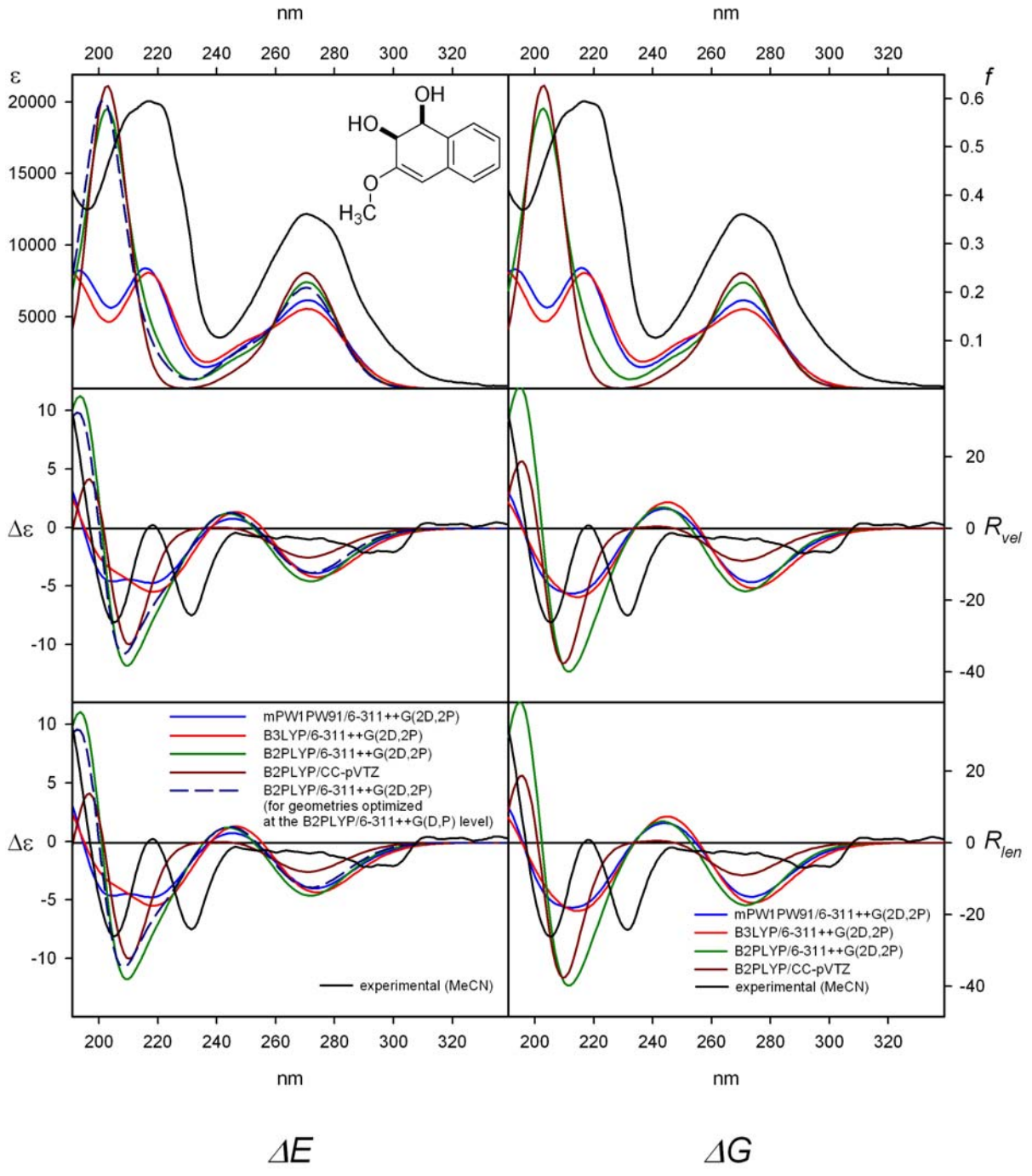
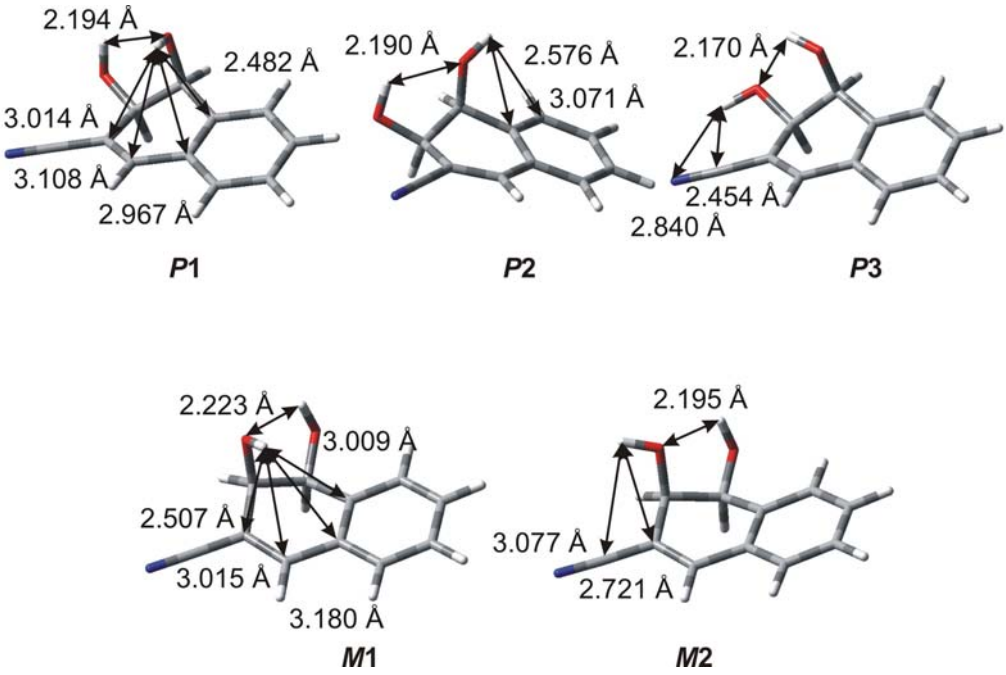


Figure 14E. Calculated at TDDFT/B2PLYP/CC-pVTZ level CD and UV spectra for individual conformers of **3c**.



Geometries were optimzed at B3LYP/6-311++G(D,P) level
Calculated energies were scaled by the factors of:
0.963 (mPW1PW91/6-311++G(2D,2P))
0.939 (B3LYP/6-311++G(2D,2P))
1.025 (B2PLYP/6-311++G(2D,2P))
1.036 (B2PLYP/CC-pVTZ)
σ = 0.5 eV

Figure 14F. Experimental CD and UV spectra in acetonitrile solution (black line) and calculated Boltzmann averaged CD and UV spectra for *cis*-dihydrodiol **3c**. The rotational strenghts *R* were calculated at diferent levels of theory in both velocity and dipole length representations. The calculated CD and UV spectra were wavelength corrected to match the experimental long-wavelength λ_{max} values in the UV spectra.



		3d(*P*1)	**3d(*P*2)**	**3d(*P*3)**	**3d(*M*1)**	**3d(*M*2)**
Energy[a] [Hartree]		-629.932034	-629.931226	-629.932146	-629.933738	-629.933760
ΔE [kcal mol^{-1}][a]		1.08	1.59	1.01	0.01	0.00
Population [%][a]		6	3	7	42	42
ΔG [kcal mol^{-1}][a]		1.11	1.37	0.94	0.27	0.00
Population [%][a]		7	5	10	30	48
μ [D][a]		6.84	7.60	4.27	5.41	3.44
α [°][a]		-158.7	-67.5	74.5	154.7	160.8
β [°][a]		-157.8	-164.5	73.8	162.4	-49.9
γ [°][a]		11.8	11.4	11.6	-11.3	-10.7
[α] calcd.[b]	D	-134	-25	-158	-81	-143
	575 nm	-212	-44	-249	-93	-174
	546 nm	-252	-53	-296	-104	-198
	436 nm	-557	-125	-661	-146	-329

$[\alpha]_D$ calcd. Boltzmann averaged

ΔE				ΔG			
D	578 nm	546 nm	436 nm	D	578 nm	546 nm	436 nm
-114	-144	-164	-283	-119	-153	-176	-313

[a] – B3LYP/6-311++G(D,P)
[b] – B3LYP/6-311++G(2D,2P)

Figure 15A. Calculated at B3LYP/6-311++G(D,P) level structures of individual conformers of **3d**, their relative energies and some structural parameters.

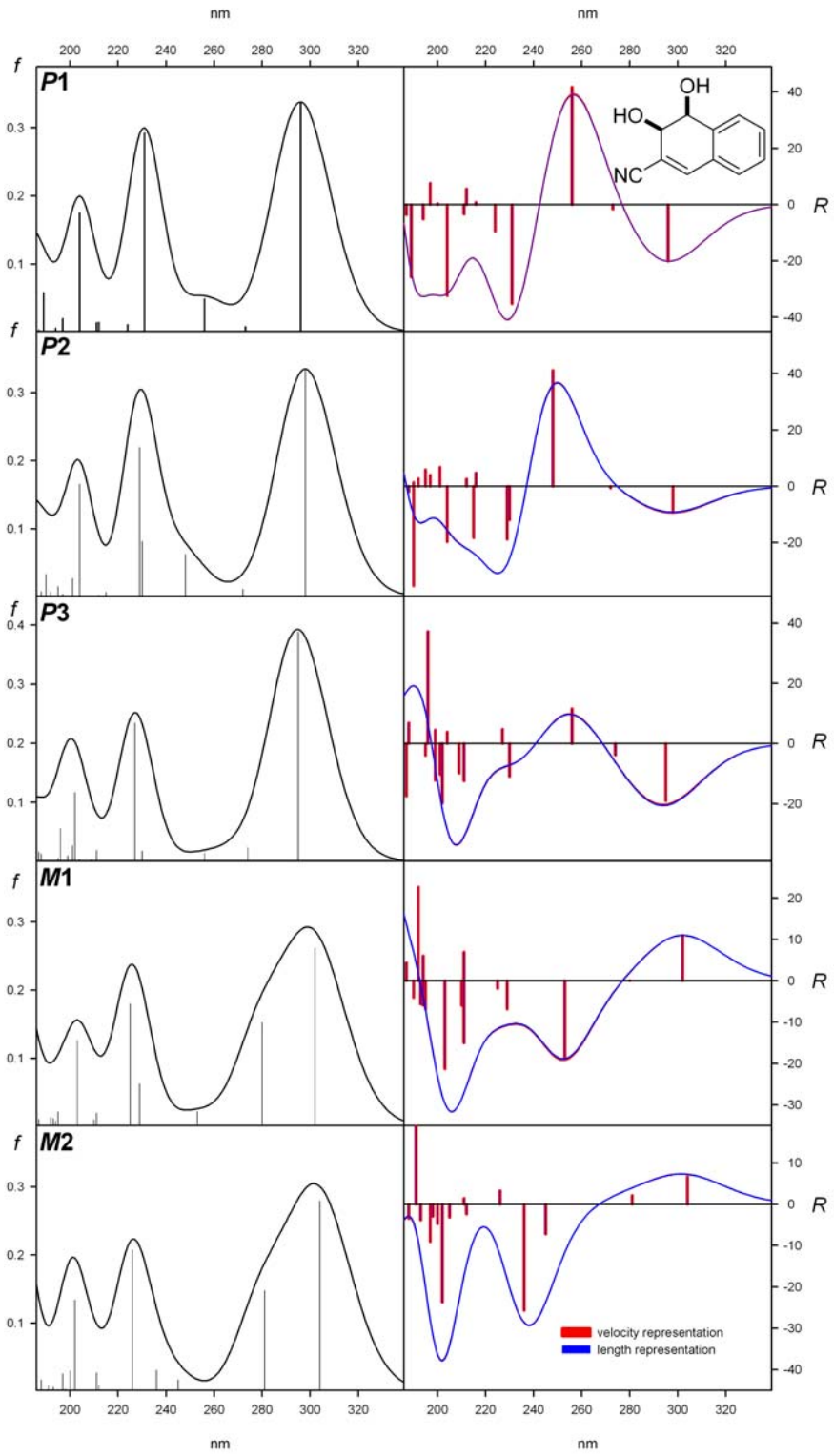


Figure 15B. Calculated at TDDFT/mPW1PW91/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **3d**.

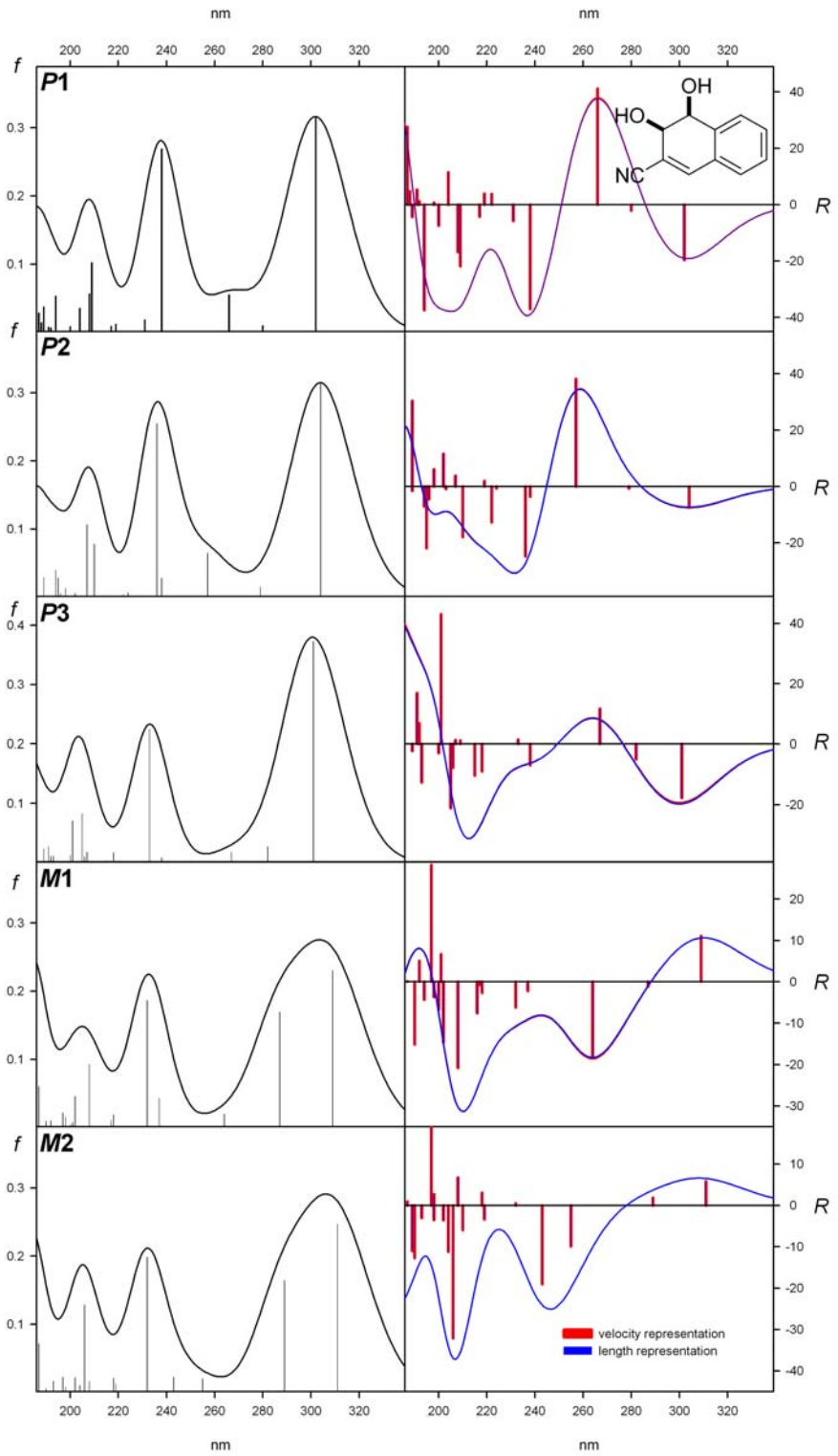


Figure 15C. Calculated at TDDFT/B3LYP/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **3d**.

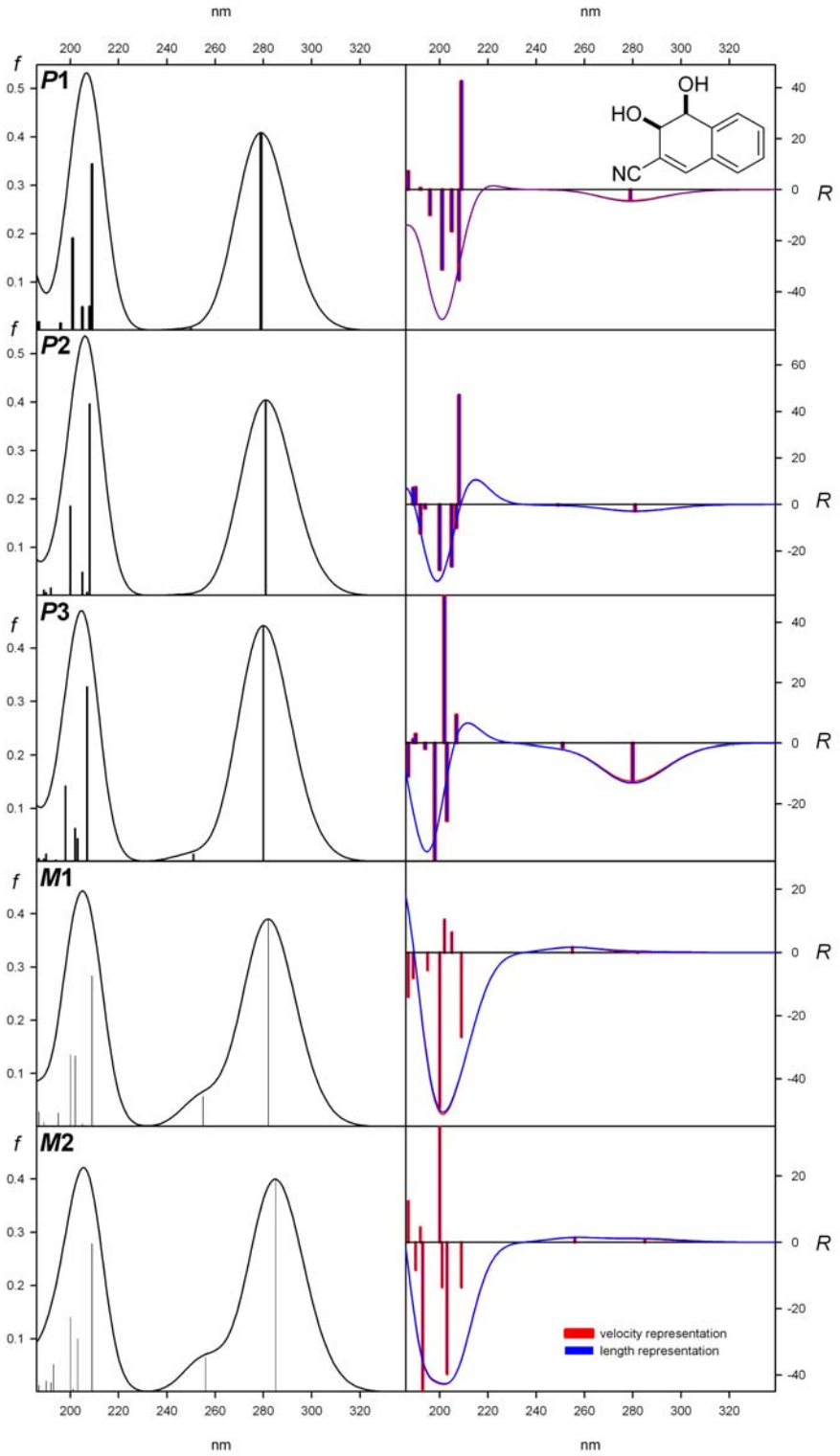


Figure 15D. Calculated at TDDFT/B2PLYP/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **3d**.

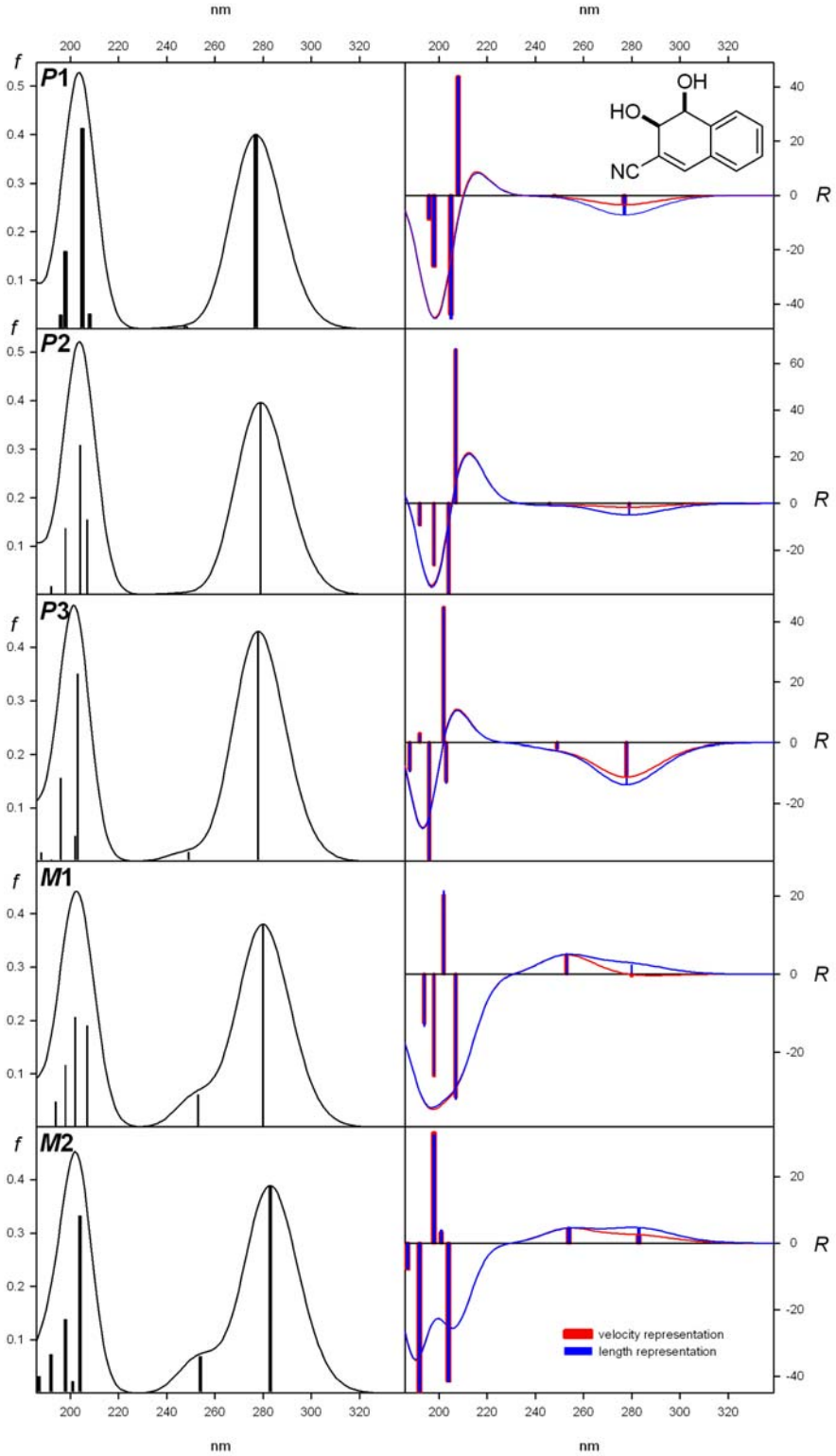


Figure 15E. Calculated at TDDFT/B2PLYP/CC-pVTZ level CD and UV spectra for individual conformers of **3d**.

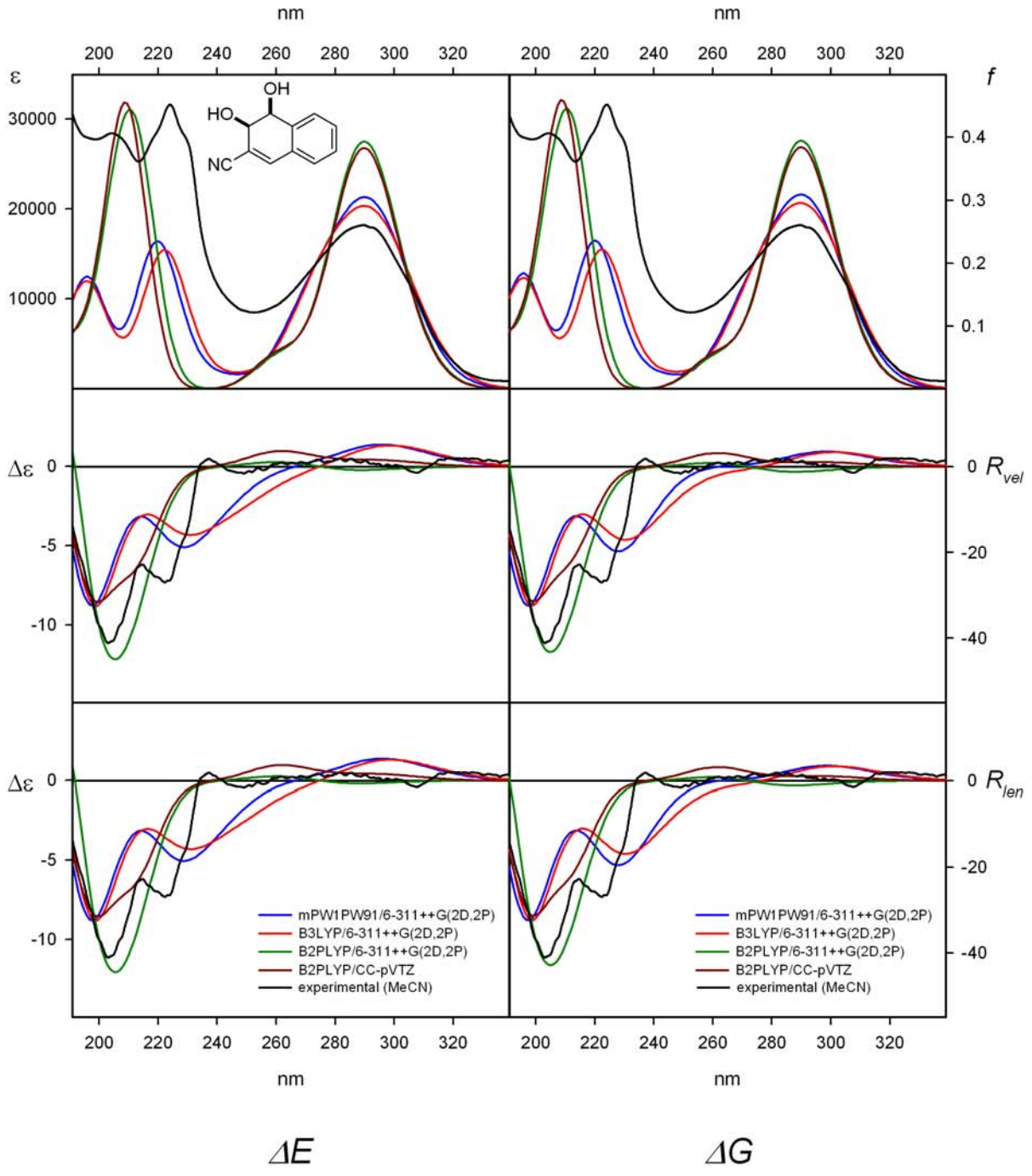
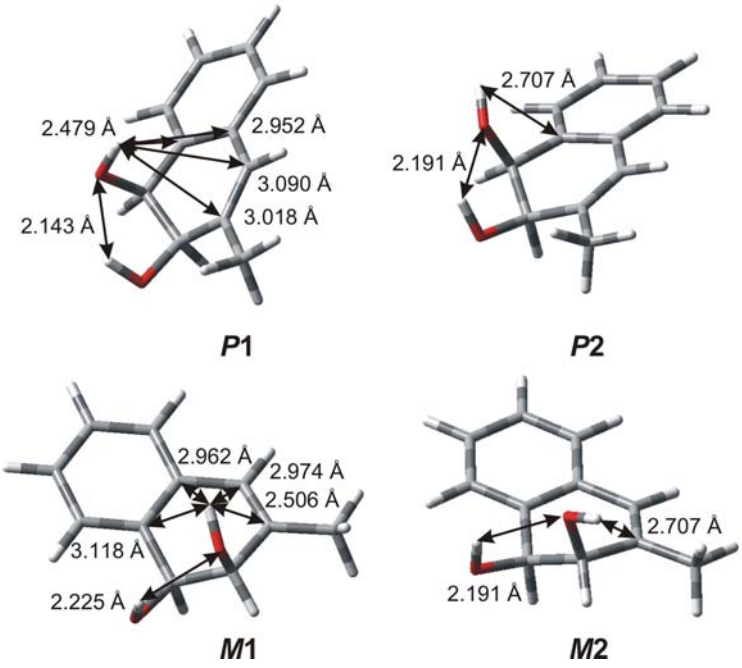


Figure 15F. Experimental CD and UV spectra in acetonitrile solution (black line) and calculated Boltzmann averaged CD and UV spectra for *cis*-dihydrodiol **3d**. The rotational strenghts *R* were calculated at diferent levels of theory in both velocity and dipole length representations. The calculated CD and UV spectra were wavelength corrected to match the experimental long-wavelength λ_{max} values in the UV spectra.



		3e(*P*1)	3e(*P*2)	3e(*M*1)	3e(*M*2)
Energy[a] [Hartree]		-576.995903 (-576.779043)[b]	-576.994320 (-576.77802)[b]	-576.996771 (-576.780009)	-576.993165 (-576.776571)[b]
ΔE [kcal mol^{-1}][a]		0.54 (0.61)[b]	1.54 (1.38)[b]	0.00 (0.00)[b]	2.26 (2.16)[b]
Population [%][a]		27 (24)[b]	5 (7)[b]	68 (69)[b]	0 (0)[b]
ΔG [kcal mol^{-1}][a]		0.32	0.75	0.00	1.64
Population [%][a]		30	14	52	3
μ [D][a]		2.40	2.30	2.51	2.85
α [°][a]		-159.7 (-158.4)[b]	-76.8 (-77.6)[b]	155.7 (156.7)[b]	161.2 (163.0)[b]
β [°][a]		-153.4 (-154.7)[b]	-159.4 (-160.6)[b]	164.9 (164.6)[b]	52.5 (58.8)[b]
γ [°][a]		11.9 (12.7)[b]	10.8 (11.5)[b]	-12.0 (-12.7)[b]	-12.1 (-12.7)[b]
[α] calcd.[c]	D	+5	+91	-223	-308
	575 nm	+44	+175	-327	-439
	546 nm	+58	+212	-384	-515
	436 nm	+207	+530	-800	-1052

[α]$_D$ calcd. Boltzmann averaged

ΔE				ΔG			
D	578 nm	546 nm	436 nm	D	578 nm	546 nm	436 nm
-146 (-146)[b]	-202 (-203)[b]	-235 (-236)[b]	-462 (-465)[b]	-111	-145	-168	-311

[a] – B3LYP/6-311++G(D,P)
[b] – in parentheses results for geometries optimized at B2PLYP/6-311++G(D,P) level
[c] – B3LYP/6-311++G(2D,2P)

Figure 16A. Calculated at B3LYP/6-311++G(D,P) level structures of individual conformers of **3e**, their relative energies and some structural parameters.

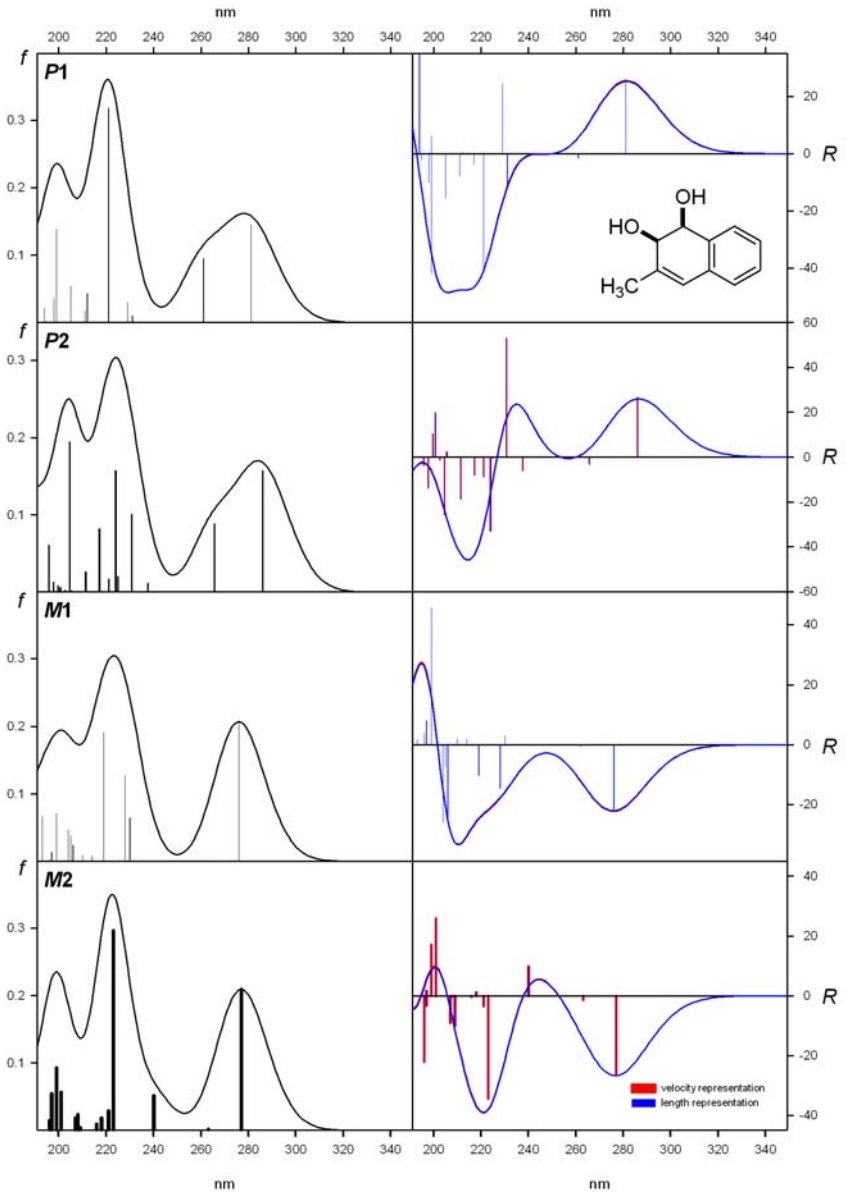


Figure 16B. Calculated at TDDFT/mPW1PW91/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **3e**.

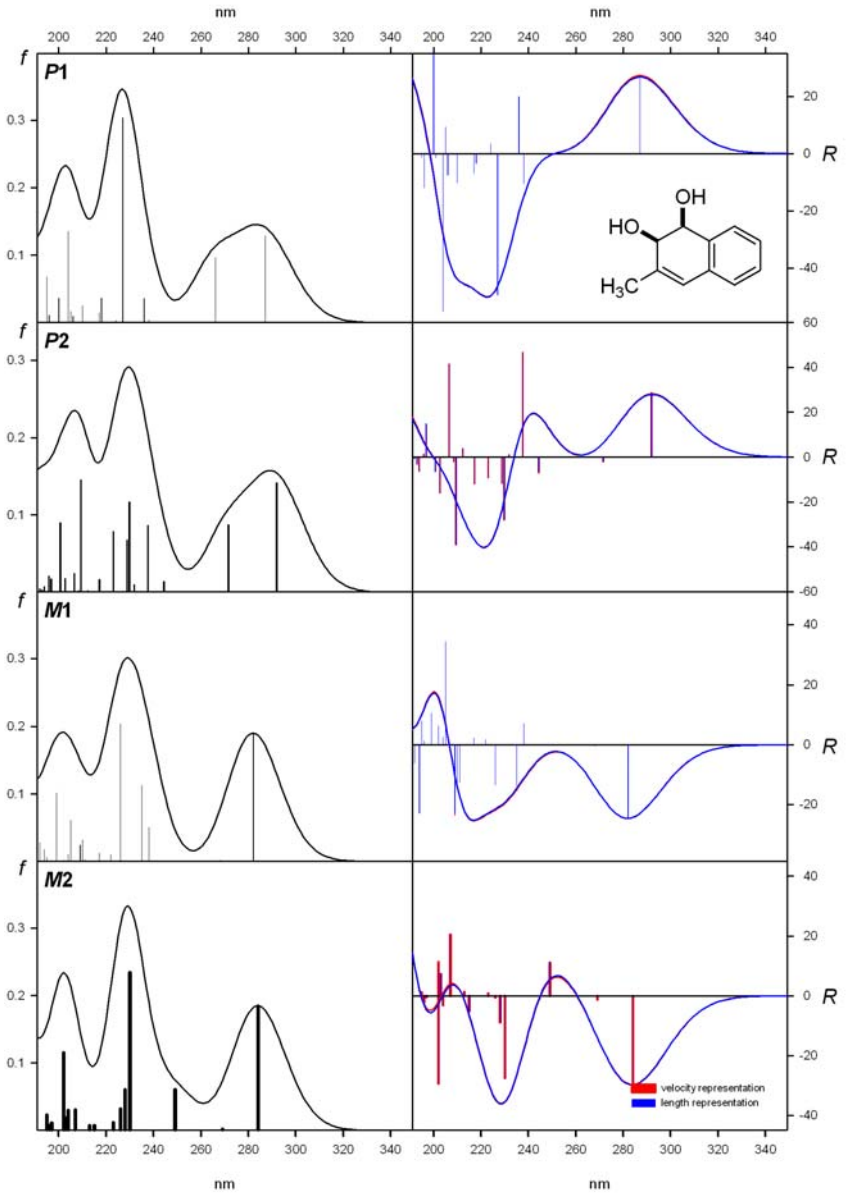


Figure 16C. Calculated at TDDFT/B3LYP/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **3e**.

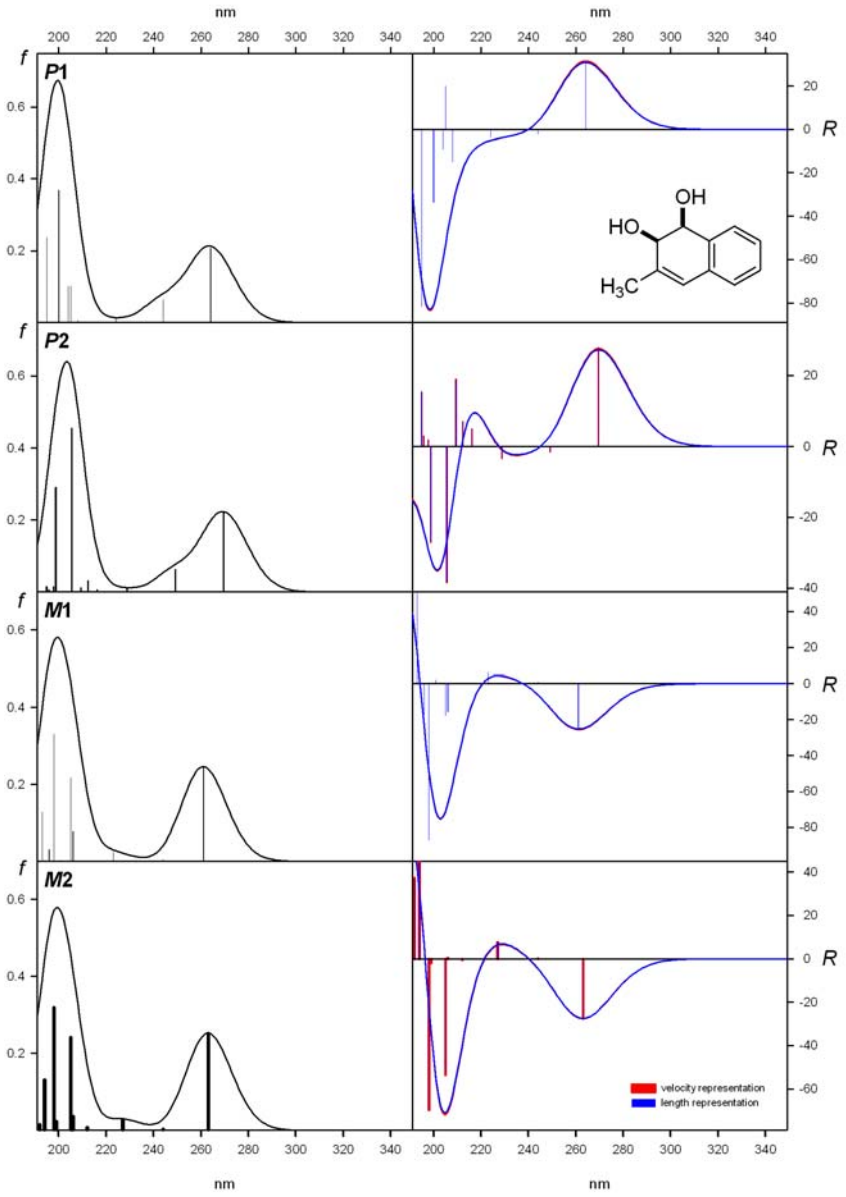


Figure 16D. Calculated at TDDFT/B2PLYP/6-311++G(2D,2P) level CD and UV spectra for individual conformers of **3e**.

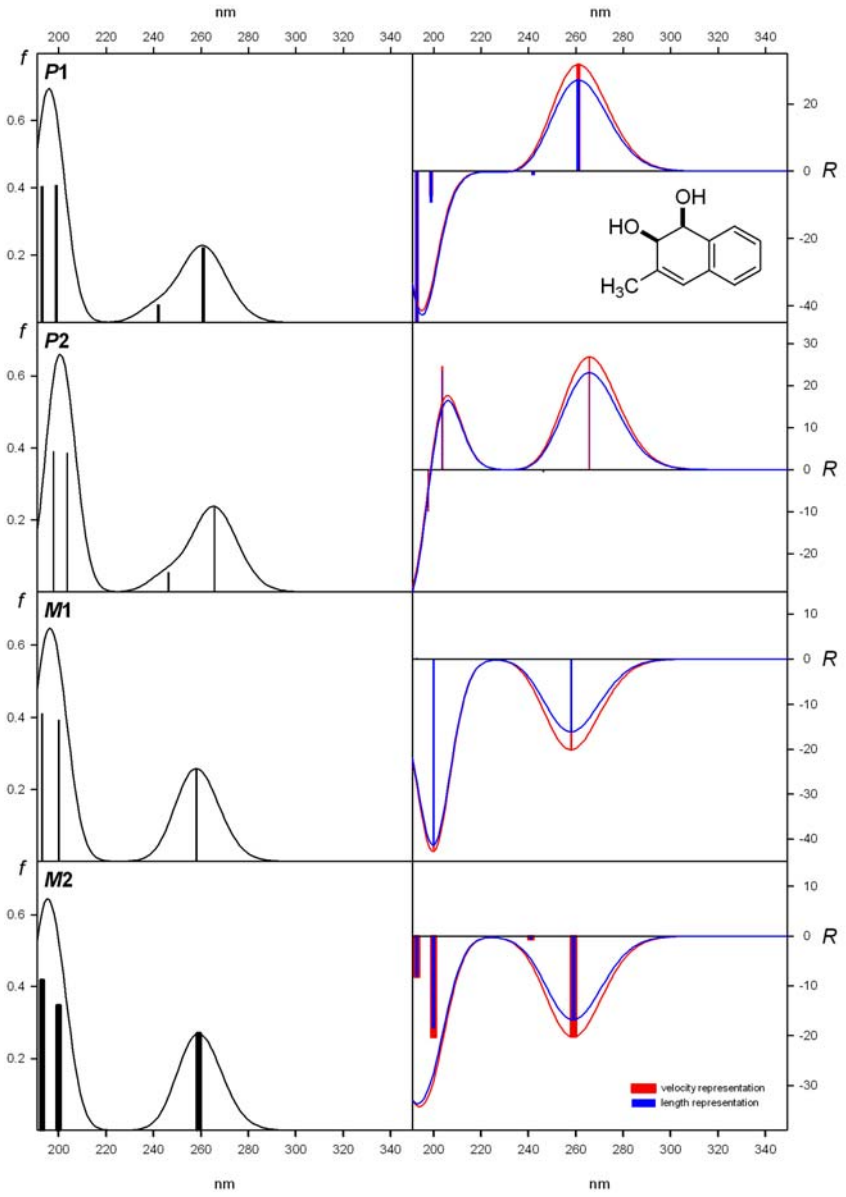
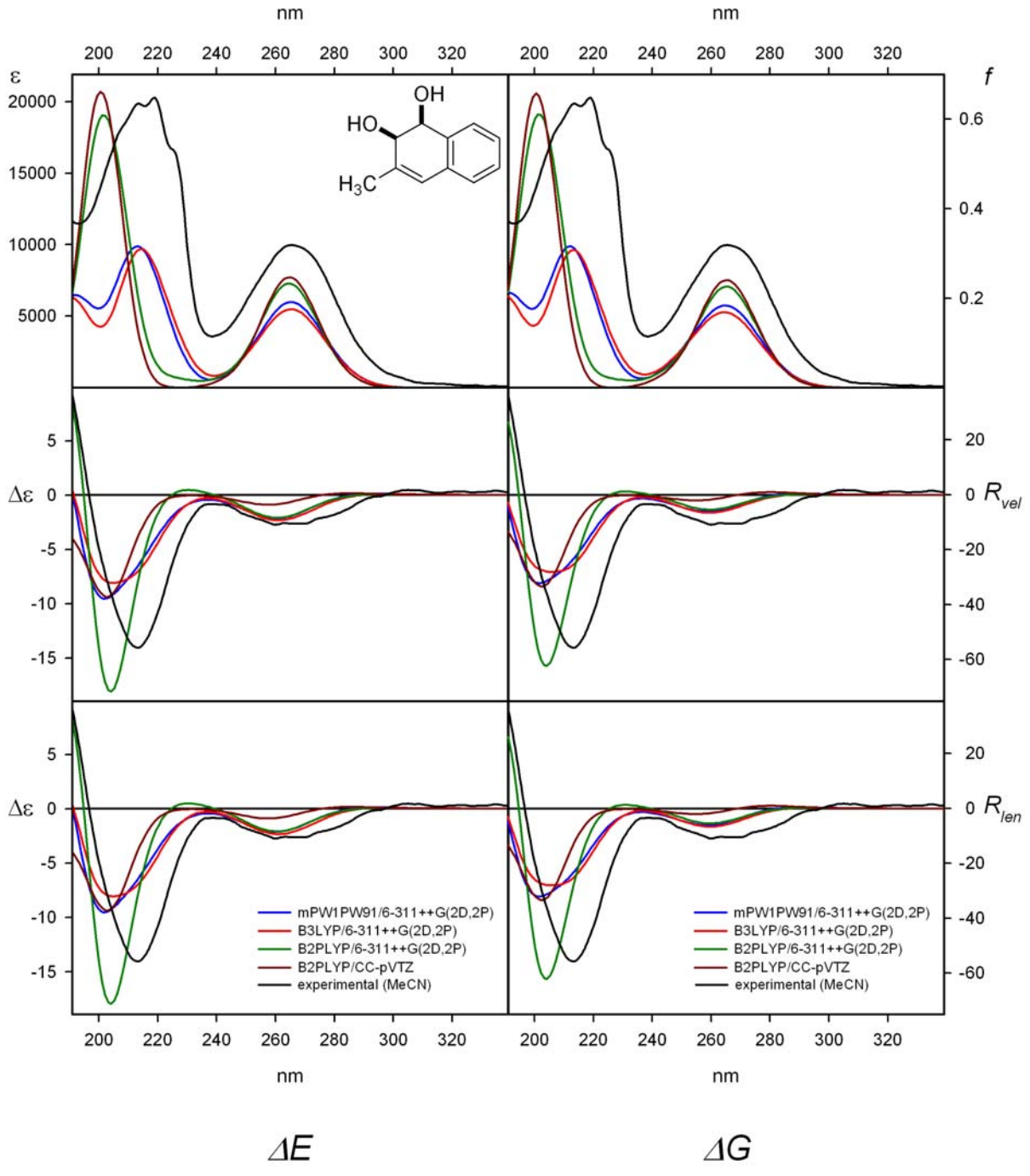


Figure 16E. Calculated at TDDFT/B2PLYP/CC-pVTZ level CD and UV spectra for individual conformers of **3e**.



Geometries were optimzed at B3LYP/6-311++G(D,P) level
Calculated energies were scaled by the factors of:
0.960 (mPW1PW91/6-311++G(2D,2P))
0.940 (B3LYP/6-311++G(2D,2P))
1.011 (B2PLYP/6-311++G(2D,2P))
1.023 (B2PLYP/CC-pVTZ)
σ = 0.5 eV

Figure 16F. Experimental CD and UV spectra in acetonitrile solution (black line) and calculated Boltzmann averaged CD and UV spectra for *cis*-dihydrodiol **3e**. The rotational strenghts *R* were calculated at diferent levels of theory in both velocity and dipole length representations. The calculated CD and UV spectra were wavelength corrected to match the experimental long-wavelength λ_{max} values in the UV spectra.