Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Characterisation of the electronic structure of galvinoxyl free radical by variable energy UPS, XPS and NEXAFS spectroscopy

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Table S1. Cartesian coordinates of galvinoxyl optimized at the M06-2X(D3)/6-31+G(d,p) level (C_2 symmetry).

H	2.655302	4.873852	1.639729
C	1.816619	5.578061	1.613300
H	2.063586	6.423011	2.265537
H	1.696483	5.946670	0.594460
C	0.527394	4.902911	2.122840
C	0.751826	4.504361	3.587220
H	1.605607	3.827706	3.701076
H	0.964578	5.404387	4.171541
H	-0.134483	4.028463	4.021034
C	-0.642842	5.906009	2.081623
H	-0.416600	6.752358	2.739244
H	-0.808009	6.285025	1.072797
H	-1.565501	5.436678	2.440250
H	-0.834226	0.621136	-0.994255
C	-0.488519	1.481529	-0.435619
C	-0.082799	1.268074	0.926847
C	0.175847	2.418930	1.748201
H	0.401645	2.229317	2.792869
C	0.199607	3.687412	1.258556
C	-0.094221	3.888153	-0.186974
C	-0.530719	2.718364	-1.000111
O	0.000000	5.006051	-0.698057
H	0.520872	4.436370	-2.916593
C	0.153875	3.480145	-3.290076
H	-0.188929	3.613889	-4.322032
H	0.980375	2.760795	-3.298413
C	-1.012292	2.952028	-2.430509
C	-2.175595	3.963911	-2.440815
H	-1.860451	4.940710	-2.073777
H	-2.543557	4.079092	-3.466026
H	-3.005510	3.602898	-1.823382
C	-1.520164	1.653296	-3.070291
H	-1.868542	1.868852	-4.084585
H	-0.730020	0.898961	-3.148948
H	-2.359343	1.223298	-2.512751
C	0.000000	0.000000	1.524679
H	0.000000	0.000000	2.615009
H	-2.655302	-4.873852	1.639729
C	-1.816619	-5.578061	1.613300
H	-2.063586	-6.423011	2.265537
H	-1.696483	-5.946670	0.594460
C	-0.527394	-4.902911	2.122840
C	-0.751826	-4.504361	3.587220
H	-1.605607	-3.827706	3.701076

H	-0.964578	-5.404387	4.171541
H	0.134483	-4.028463	4.021034
C	0.642842	-5.906009	2.081623
H	0.416600	-6.752358	2.739244
H	0.808009	-6.285025	1.072797
H	1.565501	-5.436678	2.440250
H	0.834226	-0.621136	-0.994255
C	0.488519	-1.481529	-0.435619
C	0.082799	-1.268074	0.926847
C	-0.175847	-2.418930	1.748201
H	-0.401645	-2.229317	2.792869
C	-0.199607	-3.687412	1.258556
C	0.094221	-3.888153	-0.186974
C	0.530719	-2.718364	-1.000111
O	0.000000	-5.006051	-0.698057
H	-0.520872	-4.436370	-2.916593
C	-0.153875	-3.480145	-3.290076
H	0.188929	-3.613889	-4.322032
H	-0.980375	-2.760795	-3.298413
C	1.012292	-2.952028	-2.430509
C	2.175595	-3.963911	-2.440815
H	1.860451	-4.940710	-2.073777
H	2.543557	-4.079092	-3.466026
H	3.005510	-3.602898	-1.823382
C	1.520164	-1.653296	-3.070291
H	1.868542	-1.868852	-4.084585
H	0.730020	-0.898961	-3.148948
H	2.359343	-1.223298	-2.512751

Table S2. Harmonic vibrational frequencies (cm^{-1}) of galvinoxyl calculated at the M06-2X(D3)/6-31+G(d,p) level (C_2 symmetry).

15.8204	21.1373	24.9242
38.2581	51.7949	66.1104
68.8226	76.6751	88.6480
126.1512	131.2673	142.8133
148.9246	161.7568	171.6979
187.0626	193.7913	216.6728
217.3925	235.2667	242.2436
254.7992	255.0314	256.0042
257.1285	269.1051	270.3288
286.1720	286.4325	299.7768
301.0440	315.0669	319.0523
329.7819	336.8563	348.9017
350.8881	356.3513	360.0072
362.4646	366.4396	381.1094
385.2363	385.8795	397.4866
400.9211	403.8413	410.1967
415.5822	442.2872	443.7297
457.9440	463.3739	500.0008
518.0179	522.6496	542.2613
588.2364	590.7852	600.0897
611.7131	615.9335	633.1695
661.9476	723.9057	764.0132
765.0409	813.6163	821.8004
824.3184	826.6508	832.7935

843.5950	864.5651	912.5389
915.2400	921.8275	930.0443
946.3187	949.1030	951.1303
952.2111	953.7772	956.9584
956.9959	958.0920	958.2192
964.6770	965.2468	965.4903
965.7968	965.9574	977.4121
995.4742	1044.8337	1047.7930
1050.0709	1050.9719	1053.1995
1054.1067	1054.5848	1054.8434
1110.8110	1116.9579	1169.3383
1211.0412	1215.2578	1240.0200
1240.9873	1241.8744	1242.0006
1248.8262	1250.0082	1253.3089
1253.6426	1269.0306	1295.5942
1302.1005	1309.8695	1313.0832
1333.0716	1383.1526	1391.5871
1394.3230	1394.4076	1394.4401
1394.8391	1395.3749	1397.3518
1398.3152	1414.7865	1425.7569
1426.1646	1428.9603	1429.1208
1429.7508	1443.7122	1479.2171
1482.6718	1483.0648	1483.4166
1483.5360	1483.8778	1497.7632
1498.5758	1500.3502	1501.4323
1501.4453	1501.9628	1503.1416
1503.7566	1507.7290	1507.9416
1508.3183	1508.5295	1517.0178
1519.0013	1519.8327	1519.9248
1535.1710	1535.2320	1537.6362
1538.1204	1595.6090	1598.0934
1658.5504	1673.1374	1690.5173
1700.5471	3057.1566	3057.1912
3057.8081	3059.5316	3061.5007
3061.6173	3061.8246	3061.8328
3065.5576	3065.6895	3065.8541
3066.4588	3128.6164	3128.8160
3129.4041	3129.4054	3130.8606
3130.8911	3131.3492	3131.4181
3134.0628	3134.4490	3134.5155
3138.1479	3143.6875	3143.7911
3144.3085	3145.2956	3169.0567
3186.5825	3186.5875	3187.5928
3187.5937	3190.3673	3190.4196
3192.1999	3192.2031	3226.0876
3226.6130	3254.4080	3267.6504

Table S3. Cartesian coordinates of galvinol optimized at the M06-2X(D3)/6-31+G(d,p) level.

H	-5.122192	-1.210104	2.708696
C	-5.769916	-1.222127	1.825141
H	-6.674676	-1.787286	2.076232
H	-6.054179	-0.198115	1.581980
C	-5.054026	-1.902064	0.641637
C	-4.773324	-3.357456	1.036971
H	-4.159097	-3.423786	1.941583
H	-5.722956	-3.859629	1.245131
H	-4.273767	-3.908864	0.232770
C	-5.979027	-1.920169	-0.590877
H	-6.884407	-2.491772	-0.358172
H	-6.271837	-0.911546	-0.884040
H	-5.481101	-2.405222	-1.437762
H	-0.498065	0.793790	-0.761797
C	-1.415710	0.329555	-0.420720
C	-1.303126	-1.003629	0.146981
C	-2.537716	-1.718719	0.424643
H	-2.429580	-2.742391	0.771570
C	-3.760628	-1.156115	0.312053
C	-3.848964	0.266630	-0.138922
C	-2.600125	0.957066	-0.588060
O	-4.928947	0.850910	-0.164337
H	-4.250405	3.064392	0.161826
C	-3.254980	3.347285	-0.181997
H	-3.308370	4.345439	-0.631415
H	-2.583247	3.399891	0.682515
C	-2.716315	2.344167	-1.220903
C	-3.655997	2.296066	-2.441424
H	-4.668889	2.013059	-2.154078
H	-3.691020	3.284672	-2.912540
H	-3.285024	1.580787	-3.183814
C	-1.352238	2.853711	-1.704870
H	-1.480762	3.840698	-2.159540
H	-0.639309	2.961237	-0.879426
H	-0.912714	2.191126	-2.458429
C	-0.110859	-1.612553	0.395801
H	-0.143462	-2.664958	0.680640
H	4.532874	-1.430172	-2.837185
C	5.316045	-1.498843	-2.074641
H	6.114741	-2.138869	-2.465755
H	5.725405	-0.502903	-1.905212
C	4.751158	-2.116188	-0.780544
C	4.291054	-3.541310	-1.120538
H	3.526293	-3.549327	-1.904151
H	5.149442	-4.109907	-1.490487
H	3.900041	-4.066001	-0.242430
C	5.859519	-2.237631	0.283325
H	6.661339	-2.880189	-0.096995
H	6.287906	-1.268190	0.537949
H	5.462830	-2.695289	1.195908
H	0.644782	0.853089	1.172371
C	1.468597	0.295512	0.745417
C	1.222857	-1.015533	0.326883
C	2.303209	-1.781977	-0.127141

H	2.108613	-2.808405	-0.416870
C	3.589152	-1.263481	-0.246094
C	3.777669	0.082379	0.145169
C	2.734256	0.875747	0.672155
O	5.043089	0.574656	0.002562
H	4.282150	2.924885	-0.553615
C	3.369095	3.228033	-0.031618
H	3.520945	4.253366	0.321278
H	2.570684	3.238271	-0.780181
C	2.963074	2.321656	1.151946
C	4.006832	2.370663	2.290299
H	4.995355	1.982891	2.029438
H	4.139328	3.405037	2.623906
H	3.653162	1.780494	3.140995
C	1.678747	2.933449	1.734628
H	1.889946	3.954605	2.065741
H	0.876116	2.986041	0.992505
H	1.316511	2.369423	2.599368
H	5.073586	1.500469	0.257500

Table S4. Harmonic vibrational frequencies (cm^{-1}) of galvinol calculated at the M06-2X(D3)/6-31+G(d,p) level.

17.2911	18.6735	28.1903
38.9200	52.2267	67.8898
70.0223	79.9079	88.2733
124.8041	133.8355	147.5173
149.6712	161.0678	163.9215
169.9495	190.9864	200.6257
206.9181	218.3288	225.7608
244.3392	250.8928	254.3850
258.3705	271.0025	273.7206
281.9068	286.0774	295.0182
306.8635	319.6546	323.9422
326.3351	341.0190	349.7177
353.7385	357.0235	361.5814
371.3392	376.9594	378.2305
383.0687	389.5814	399.1968
402.7536	408.0298	415.2642
433.6810	441.1807	442.1127
450.5647	458.6455	469.9754
505.6054	519.2520	529.8948
547.0505	584.2887	592.3780
600.6002	620.0416	634.2851
640.6453	650.8923	713.6335
764.6539	773.9237	797.5112
819.0015	822.1389	827.8958
837.0471	842.3709	887.3976
914.4138	919.9864	927.2666
934.3041	942.8206	948.3944
949.5016	951.0012	955.7328
956.8578	956.9643	959.3857
960.5533	963.3035	964.5818
965.1953	966.3673	969.9522
971.5932	1016.8400	1045.0532
1047.6903	1049.7857	1051.8787

1053.8062	1054.5706	1057.0121
1057.6988	1112.7355	1152.7890
1180.1043	1209.9376	1229.3904
1239.6296	1243.3256	1243.6292
1244.4376	1245.7534	1247.7507
1251.2454	1254.9380	1268.9730
1290.0704	1299.6960	1305.2156
1308.0025	1319.5573	1352.7490
1358.3683	1374.8250	1392.8257
1393.1922	1393.7067	1398.6330
1398.8522	1401.5158	1408.5013
1413.9093	1418.3603	1427.0163
1427.8757	1432.2036	1446.4841
1460.9392	1479.8742	1481.6593
1482.2627	1484.4739	1484.7625
1490.9476	1494.3170	1497.7388
1500.3131	1500.4146	1501.3384
1502.2475	1502.6353	1503.4806
1506.8260	1507.1420	1510.7056
1516.8925	1518.3508	1520.5557
1520.9275	1528.9509	1534.8656
1535.5487	1537.3009	1538.0575
1652.1526	1668.9631	1672.7981
1681.8404	1731.4338	1750.4898
3053.8518	3056.2038	3056.7132
3059.0339	3059.3556	3062.9253
3063.0511	3063.7629	3064.7608
3066.8090	3067.6610	3072.5321
3122.8038	3126.2774	3127.7862
3128.1509	3129.9109	3130.0201
3131.4234	3133.8739	3137.5536
3138.7120	3140.4867	3141.0008
3142.3772	3143.5442	3143.9292
3147.9887	3149.2033	3151.5092
3166.8104	3181.5773	3183.5758
3186.0411	3186.3988	3186.9724
3189.9102	3218.4615	3242.2891
3248.5433	3261.6857	3940.7844

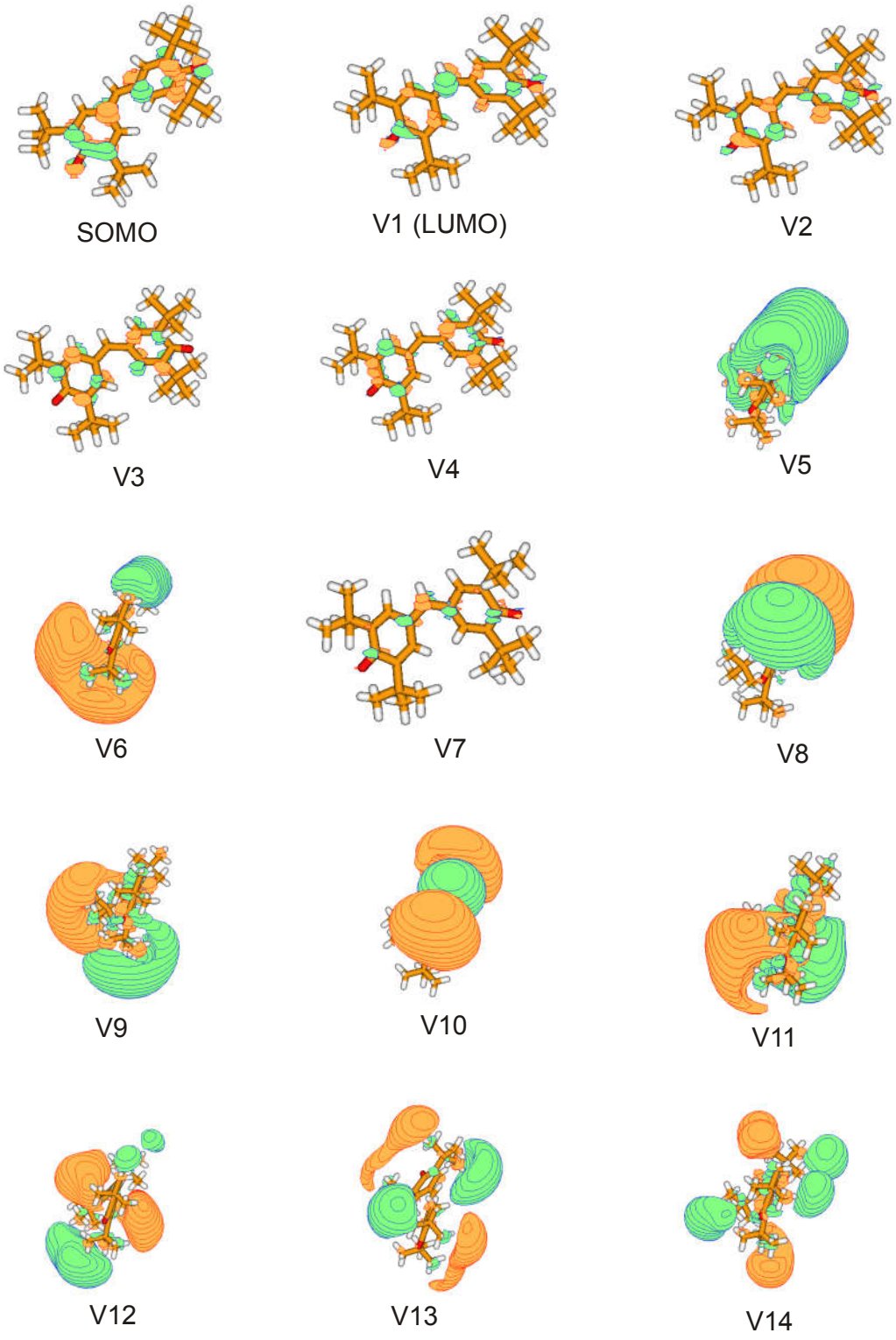


Figure S1. SOMO and low-lying virtual orbitals (V) of galvinoxyl at the SRC2-BLYP/6-311(2+)G* level (α-spin set).

Table S4. Shake-up spectrum and the corresponding monopole intensities of galvinoxyl (relative to the O 1s CEBE) at the TD-CAM-B3LYP//mixed basis set level (cc-pwCVTZ on O; Miyoshi mcp-dzp on C; STO-3G on H atoms).

state	E/eV	Mon. Int.	Relative
1	1.100	7.89E-05	0.001
2	1.869	1.69E-02	0.221
3	1.941	7.67E-02	1.000
4	2.170	4.27E-04	0.006
5	2.495	5.12E-02	0.667
6	3.080	1.51E-03	0.020
7	3.129	3.78E-04	0.005
8	3.201	1.17E-02	0.152
9	3.639	3.50E-04	0.005
10	3.673	8.07E-05	0.001

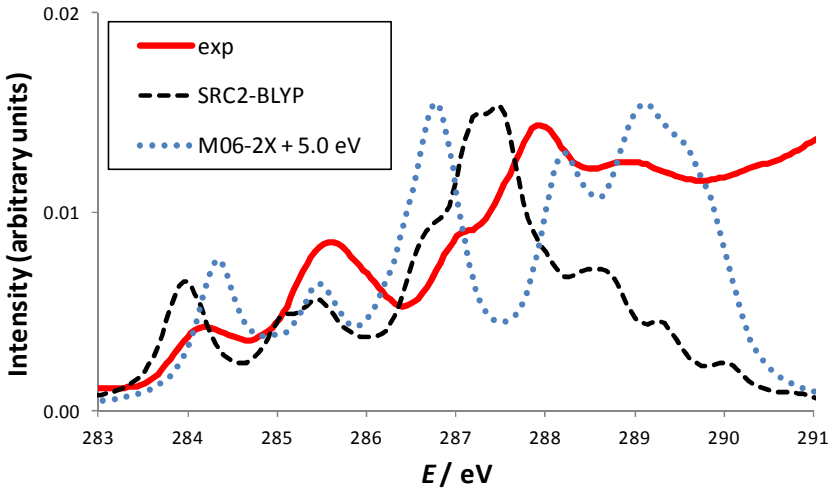


Figure S2. The RSES TDDFT modelled C 1s NEXAFS spectra of galvinoxyl at the SRC2-BLYP/6-311(2+)G* and M06-2X/Def2-TZVPD[1] (upshifted by 5.0 eV).

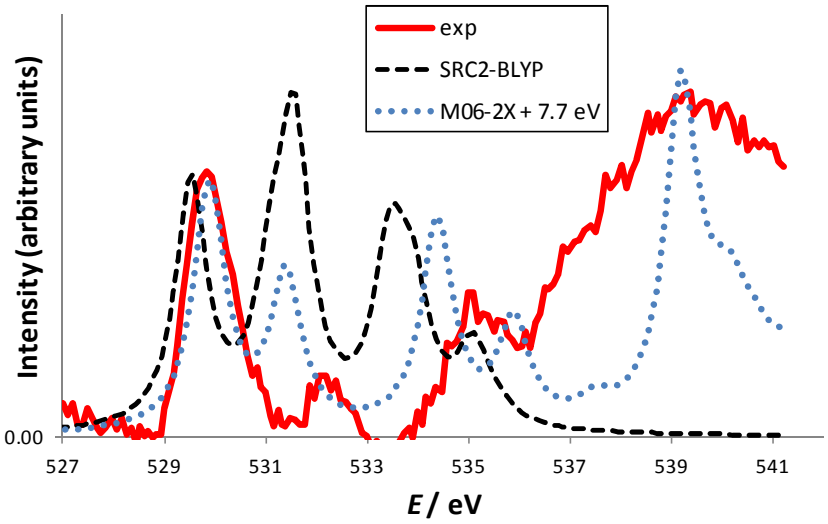
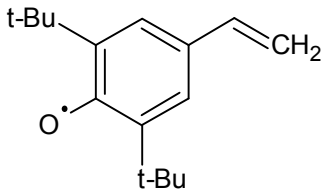


Figure S3. The RSES TDDFT modelled O 1s NEXAFS spectra of galvinoxyl at the SRC2-BLYP/6-311(2+)G* and M06-2X/Def2-TZVPD[1] (upshifted by 7.7 eV).

Table S5. C 1s core-electron binding energies (eV) of the half-fragment of galvinoxyl at the B3LYP//mixed basis set level (cc-pwCVTZ on C whose CEBE is calculated; Miyoshi mcp-dzp on O and remaining Cs; STO-3G on H atoms) (q = quaternary C atom)

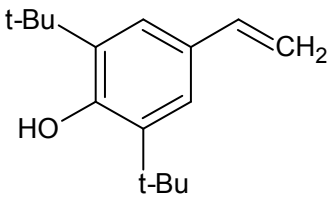


C1(end)	C2 (bridge)	C3(CH_3)	C4(q)	C5(CH_3)	C6(CH_3)
289.59	290.26	289.67	290.19	290.05	289.69

C7 (benzene)	C8 (benzene)	C9 (benzene)	C10 (benzene)	C11 to •O	C12 (benzene)
289.71	290.15	289.70	289.47	291.22	289.51

C13(CH_3)	C14(q)	C15(CH_3)	C16(CH_3)
289.69	290.21	289.70	290.07

Table S6. C 1s core-electron binding energies (eV) of the phenolic fragment of galvinol at the B3LYP//mixed basis set level (cc-pwCVTZ on C whose CEBE is calculated; Miyoshi mcp-dzp on O and remaining Cs; STO-3G on H atoms) (q = quaternary C atom)

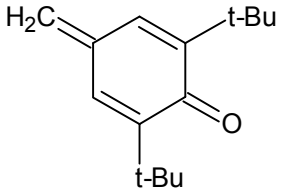


C1(end)	C2 (bridge)	C3(CH_3)	C4(q)	C5(CH_3)	C6(CH_3)
289.18	289.85	289.64	290.06	289.87	289.64

C7 (benzene)	C8 (benzene)	C9 (benzene)	C10 (benzene)	C11 to OH	C12 (benzene)
289.14	289.34	289.10	289.27	290.78	289.41

C13(CH_3)	C14(q)	C15(CH_3)	C16(CH_3)
290.35	290.60	290.31	290.24

Table S7. C 1s core-electron binding energies (eV) of the quinonic fragment of galvinol at the B3LYP//mixed basis set level (cc-pwCVTZ on C whose CEBE is calculated; Miyoshi mcp-dzp on O and remaining Cs; STO-3G on H atoms) (q = quaternary C atom)



C1(CH_3)	C2 (q)	C3(CH_3)	C4(CH_3)	C5(ring)	C6(ring)
289.70	290.23	290.08	289.72	289.89	290.54

C7 (ring)	C8 (ring)	C9 to O	C10 (ring)	C11 (CH_3)	C12 (q)
289.87	289.69	291.85	289.74	289.72	290.25

C13(CH_3)	C14(CH_3)	C15(end)
289.73	290.10	289.57

(1) For the TD-M06-2X calculations we use the property-optimized Def2-TZVPD basis set, which is a triple-ζ-valence polarized diffuse set contracted to

6s3p3d1f on the C and O atoms and to 3s2p on the H atoms.[2] To speed up the calculations, the resolution of identity approximation was adopted employing the Def2-TZVPP/J auxiliary basis set for fitting the Coulomb term[3] and the RIJCOSX integration scheme for the HF exchange term.[4] The final M06-2X energies are converged with respect to the 302 points Lebedev angular grid, which on average amounted to 3877 grid points per atom. The calculations are done with the Orca 3.0.3 package[5]

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