Supplementary Material (ESI) for *PCCP*

Electronic supplementary information

Supporting Information

A Time-Resolved Spectroscopy and Density Functional Theory Study of the Solvent Dependent Photochemistry of Fenofibric Acid

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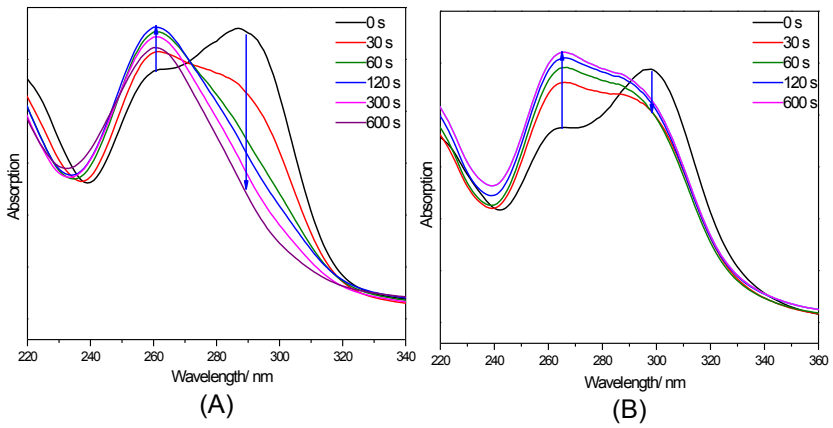

Figure 1S. UV/vis absorption spectra for the photolysis of FA in the MeCN/H_2O (9:1) and MeCN/H_2O (3:7) mixed solvents. The time periods the sample solution is exposed to the 299 nm excitation laser

pulse are labeled for each of the spectra traces.

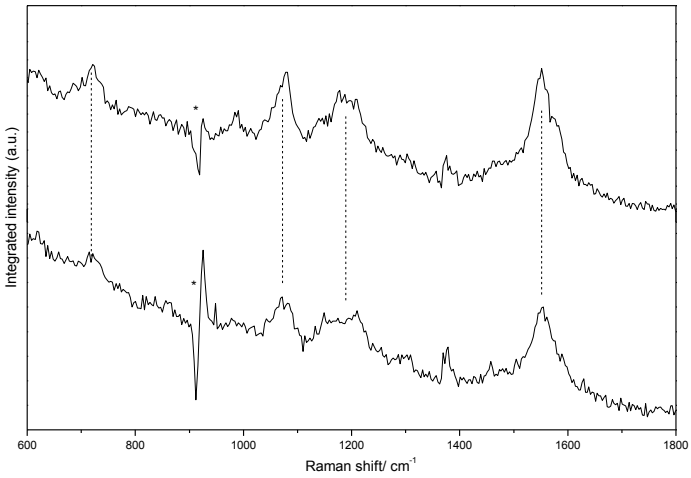

Figure 2S. Comparison of the subtracted resonance Raman spectrum of FA (top) obtained in MeCN/H_2O(9:1) at 10 ns with the one obtained in acetonitrile at 0 ns. The asterisk (*) marks subtraction artifacts.

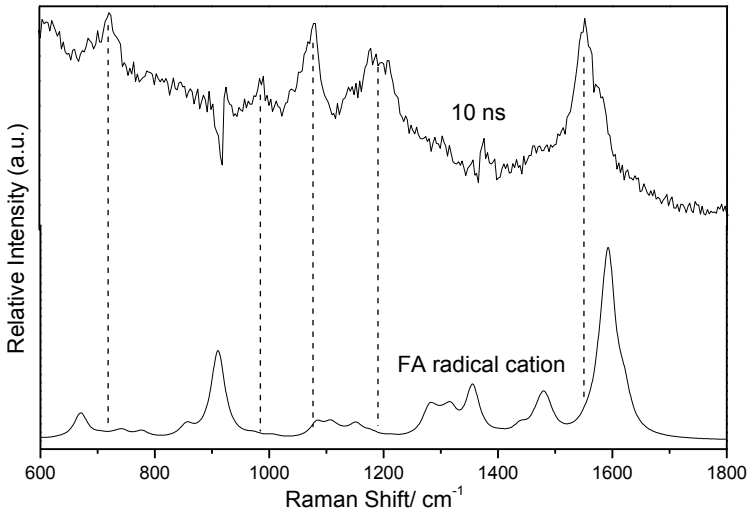

Figure 3S. Comparison of the subtracted resonance Raman spectrum of FA (top) obtained in MeCN/H_2O(9:1) at 10 ns with the DFT calculation predicted Raman spectrum of the FA radical cation.

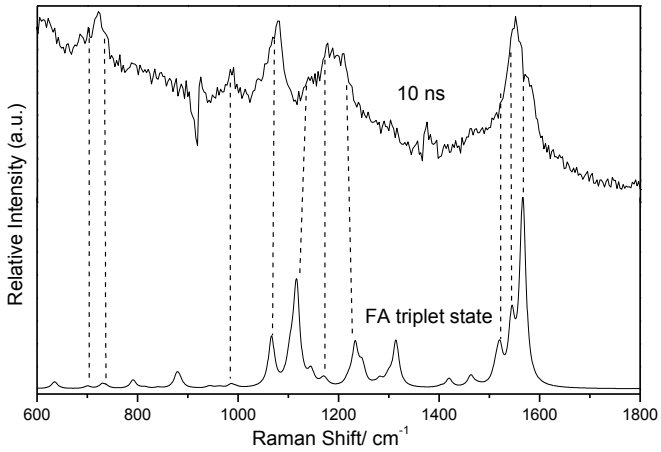

Figure 4S. Comparison of the subtracted resonance Raman spectrum of FA (top) obtained in MeCN/H_2O(9:1) at 10 ns with the DFT calculation predicted Raman spectrum of the FA triplet state.

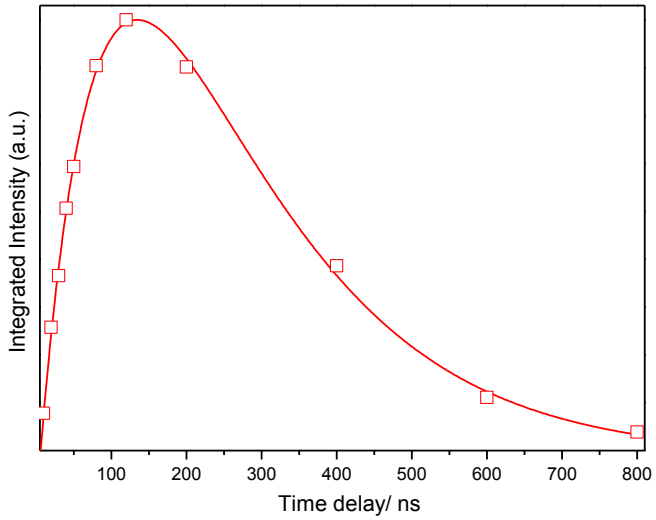

Figure 5S. The time-dependence of the resonance Raman band 1583 cm^{-1} for FA ((closed squares) in MeCN/H_2O(9:1) was fit by a two-exponential function with a 98 ns growth time constant and a 174 ns decay time constant for FA. The solid lines indicate the kinetics fitting to the experimental data points.

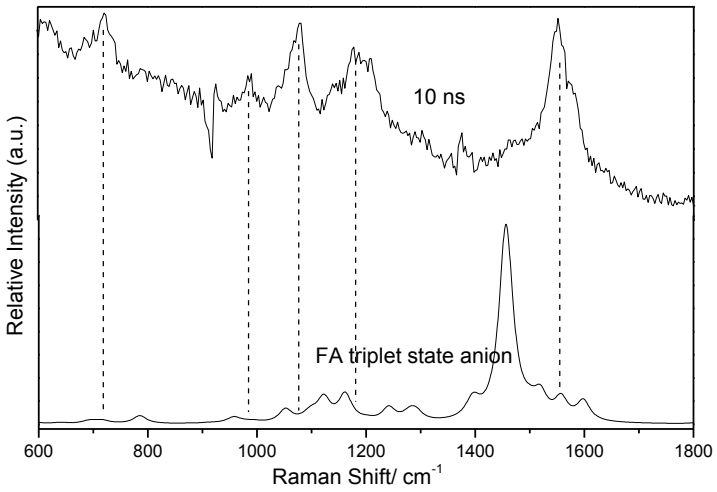

Figure 6S. Comparison of the subtracted resonance Raman spectrum of FA (top) obtained in MeCN/H_2O(9:1) at 10 ns with the DFT calculation predicted Raman spectrum of the FA benzophenone like anion.

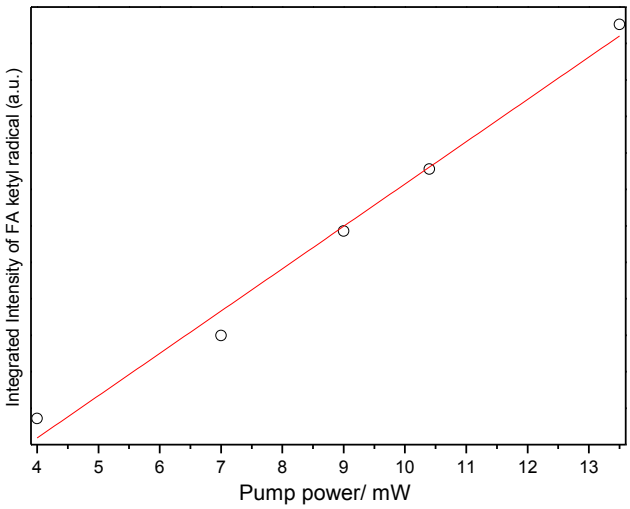

Figure 7S. Power dependence of 1.5 mM FA in 1:9 H_2O:MeCN neutral solution obtained by 299 nm pump laser and 341.5 nm probe laser.

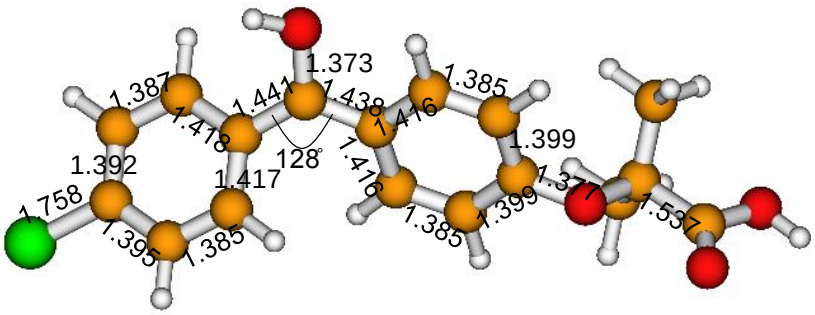

Figure 8S. Optimized structure of the FA ketyl radical by the UB3LPY/6-311G**. Selected bond

lengths and angles are displayed in the structure.

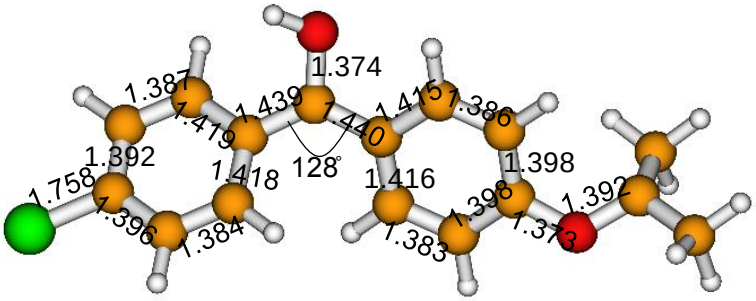

Figure 9S. Optimized structure of the FA biradical by the UB3LPY/6-311G**. Selected bond lengths and angles are displayed in the structure.

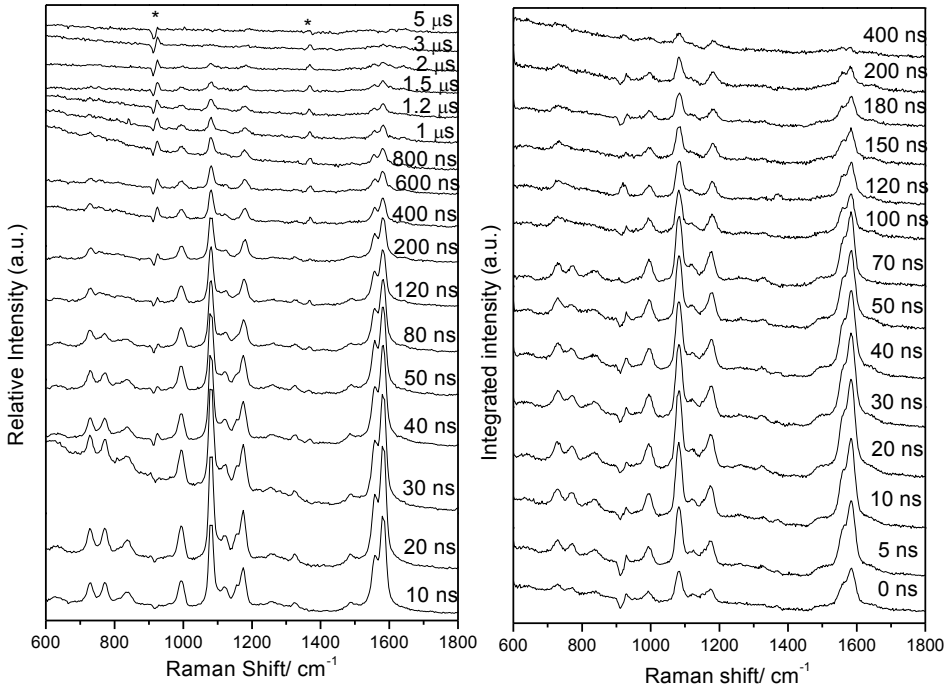

Figure 10S. Shown are the ns-TR^3 spectra of intermediates obtained after 299 nm photolysis of 1.5 mM FA in MeCN/H_2O (3:7) mixtures in open air (left) and oxygen purging conditions (right) obtained using a 341.5 nm probe wavelength at various time delays indicated next to the spectra. The asterisks (*) marks regions affected by solvent subtraction artifacts and/or stray light.

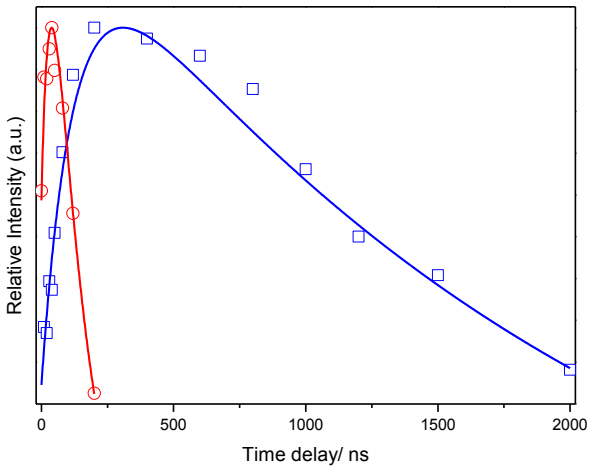

Figure 11S. The time-dependence of the resonance Raman band 1583 cm^{-1} for the triplet state FA anion ((closed circles) in the MeCN/PB (1:1) was fit by a two-exponential function with a ~37 ns growth time constant and a ~105 ns decay time constant; The time-dependence of the resonance Raman band 1585 cm^{-1} for the FA carbanion ((closed squares) in the MeCN/PB (1:1) was fit by a two-exponential function with a ~107 ns growth time constant and a ~1950 ns decay time constant. The solid lines indicate the kinetics fitting to the experimental data points.

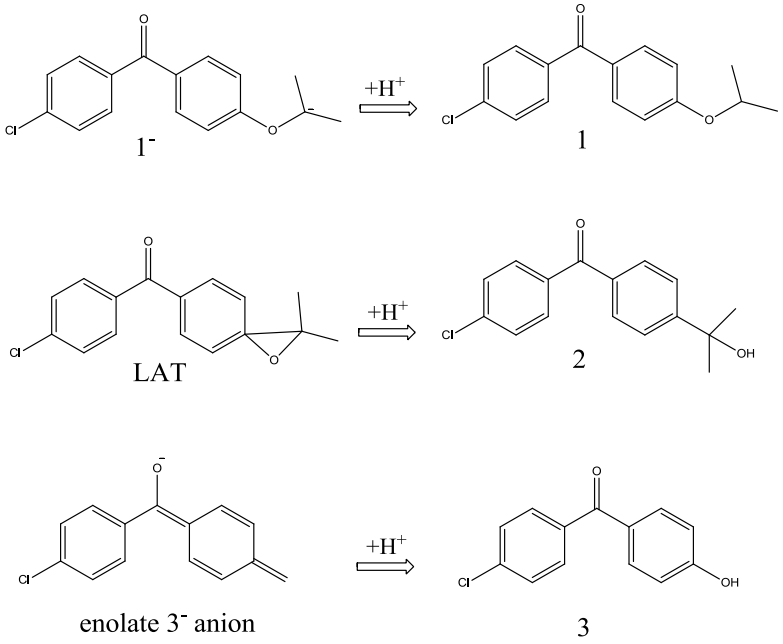

Figure 12S. The proposed three intermediates by Miranda and coworkers after the photodecarboxylation from anionic form and its corresponding photoproducts.

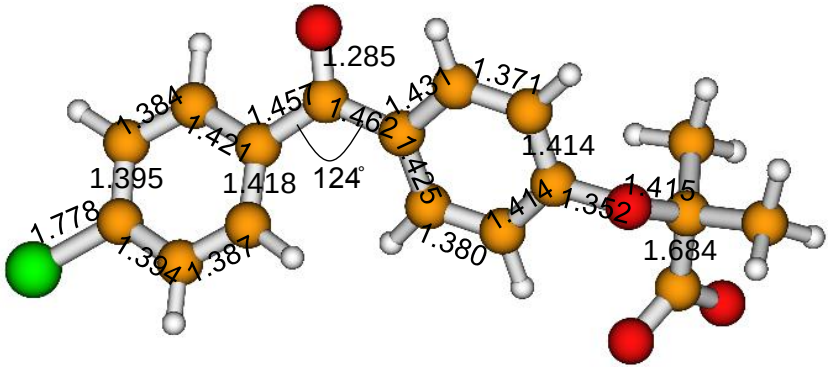

Figure 13S. Optimized structure of $^{3}FA^{-}$ anion calculated from the B3LYP/6-311G** DFT calculations. Selected bond lengths (in Å) and bond angles (in deg) are labeled.

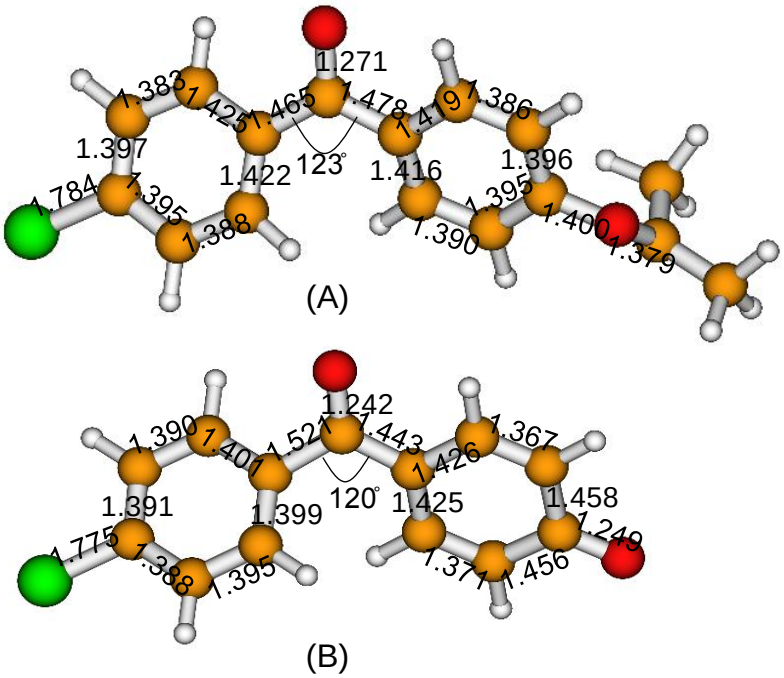

Figure 14S. Optimized structures of FA carbanion (A) and enolate 3^{-} anion (B) calculated from the B3LYP/6-311G** DFT calculations. Selected bond lengths (in Å) and bond angles (in deg) are labeled.

Table 1S. Raman frequencies (cm^{-1}) and vibrational assignments for the FA Ketyl radical, the FA biradical, the FA carbanion and the enolate 3^{-} anion for which the structures are displayed in Figure 5S,

Figure 6S and Figure 10S.

Calc. Raman Shifts (cm^{-1}) FA ketyl radical	Expt. Raman Shifts (cm^{-1})	Vibrational mode
706	**728**	O-H bend, C-C stretch, C-O stretch, ring breath stretch
731	**758**	O-H bend, C-C stretch, ring breath stretch
795	**806**	C-H bend, C-C stretch, C-O stretch,ring breath stretch
992	**995**	C=C stretch
1082	**1082**	C-Cl stretch, C-O stretch
1121	**1121**	C-H bend
1152		C-H bend
1175	**1177**	C-H bend, C-O stretch
1234		C-H bend, C-O stretch
1326	**1326**	C=C stretch, C-O stretch
1377		C-C stretch, O-H bend
1572	**1558**	C=C stretch
1589	**1583**	C=C stretch
FA biradical		
716	**728**	Ring breath stretch
760	**772**	Ring breath stretch, C-O stretch
819	**836**	Ring breath stretch, C-H bend, C-O stretch
978	**994**	Ring breath stretch
1063		C-Cl stretch
1081	**1082**	C-O stretch, C-H bend
1110	**1121**	C-H bend
1140		C-H bend
1168	**1174**	C-H bend

1195		O-H bend
1250	**1258**	C=C stretch
1315	**1324**	C-O stretch, C-H bend
1367		O-H stretch, C-C stretch, C-H bend
1475	**1488**	C=C stretch, C-H bend
1558	**1560**	C=C stretch
1580	**1582**	C=C stretch
FA carbanion		
700	**728**	C-H bend
778	**784**	Ring breath stretch
838		C-C stretch, C-O stretch
996	**993**	Ring breath stretch
1072	**1081**	C-Cl stretch
1144		C-H stretch
1185	**1179**	C-H stretch
1265	**1275**	C-C stretch, C-H bend
1318	**1328**	C=C stretch, C-H bend
1424		C=O stretch, C=C stretch, C-H bend
1487	**1490**	C=O stretch, C=C stretch, C-H bend
1526		C=C stretch
1559	**1558**	C=C stretch
1590	**1585**	C=C stretch
1630	**1640**	C=C stretch
Enolate 3^- anion		
728	**728**	Ring breath stretch
799	**784**	Ring breath stretch
908		Ring breath stretch

1006	**993**	Ring breath stretch
1070	**1081**	C-Cl stretch
1153	**1179**	C-C stretch, C-H stretch
1280	**1275**	C-C stretch, C=C stretch, C-H bend
1300	**1318**	C=C stretch, C-C stretch, C-H bend
1409		C-C stretch, C-H bend
1476	**1490**	C=C stretch, C-H bend
1565	**1558**	C=C stretch, C=O stretch,
1589	**1585**	C=C stretch, C=O stretch,
1632	**1640**	C=C stretch, C=O stretch,

Figure 15S. The Cartesian coordinates, total energies, and vibrational zero-point energies for the optimized geometry from the (U)B3LYP/6-311G** calculations for the species of interest in the paper are given.

FA radical cation

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	-0.000008604	-0.000008285	-0.000003798
2	6	-0.000004296	-0.000002713	0.000004637
3	6	-0.000004318	0.000005397	-0.000003076
4	6	-0.000005705	0.000005882	-0.000009484
5	6	0.000013862	-0.000011451	-0.000019142
6	1	0.000001826	-0.000011964	0.000012466
7	1	0.000001754	-0.000012308	0.000006000
8	1	0.000002105	0.000004159	-0.000009417
9	1	-0.000001312	0.000013522	-0.000004920
10	6	0.000008469	0.000002478	-0.000017525
11	6	-0.000000220	0.000001888	-0.000003068
12	6	-0.000001135	-0.000000208	-0.000003713
13	6	-0.000000886	0.000000643	-0.000000099
14	6	0.000003785	0.000001872	-0.000004437
15	1	0.000000895	-0.000003095	-0.000011430
16	6	0.000003248	0.000003693	0.000009991
17	1	-0.000001009	0.000004486	0.000007411
18	1	-0.000001751	0.000005126	0.000011011
19	1	0.000000108	-0.000001453	-0.000004195
20	6	0.000006479	0.000004436	0.000028795
21	6	-0.000006769	-0.000001316	0.000004233
22	8	0.000001390	-0.000012998	-0.000006985
23	17	0.000004341	0.000005817	0.000008286
24	8	-0.000033301	0.000001340	-0.000051386
25	6	0.000046022	0.000027004	0.000043769
26	6	-0.000000275	0.000007574	0.000001198
27	1	-0.000012553	0.000000275	0.000002531
28	1	0.000002274	0.000002368	0.000008237
29	1	-0.000005630	0.000016741	0.000003760
30	6	0.000011958	-0.000022408	0.000005354
31	1	-0.000015889	0.000002906	-0.000007274
32	1	-0.000001380	0.000000616	-0.000008785
33	1	0.000007144	-0.000009960	-0.000017358

34	6	-0.000031945	-0.000017594	-0.000001125
35	8	0.000003570	-0.000015844	0.000019836
36	8	0.000017658	0.000027452	-0.000012636
37	1	0.000000090	-0.000014077	0.000022341

Sum of electronic and thermal Free Energies= -1417.701618(a.u.)
Zero-point correction= 0.282756 (Hartree/Particle)

FA benzophenone like anion

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	-0.000016304	-0.000000476	-0.000004648
2	6	0.000007443	0.000010857	-0.000002249
3	6	0.000008412	-0.000015749	0.000005979
4	6	-0.000012421	0.000003521	-0.000002407
5	6	0.000013628	0.000009885	-0.000000772
6	1	0.000003709	0.000000619	0.000000811
7	1	-0.000000243	-0.000001240	0.000001605
8	1	0.000000778	-0.000000457	0.000001525
9	1	-0.000003585	-0.000001390	-0.000000164
10	6	-0.000002420	0.000024295	-0.000000605
11	6	0.000000532	-0.000006531	-0.000000772
12	6	-0.000004770	0.000000152	0.000000000
13	6	0.000000949	0.000002989	0.000001504
14	6	0.000003780	-0.000001610	0.000000782
15	1	-0.000000130	0.000000442	0.000001341
16	6	-0.000000972	-0.000001501	-0.000000887
17	1	0.000000466	-0.000000060	0.000001079
18	1	0.000000924	0.000001171	0.000000978
19	1	-0.000000677	0.000000506	0.000001386
20	6	-0.000001411	-0.000012871	0.000000646
21	6	-0.000003502	0.000006167	0.000002374
22	8	-0.000000324	-0.000012985	0.000000244
23	17	0.000002300	-0.000000723	0.000000833
24	8	0.000006216	0.000003810	-0.000000368
25	6	0.000009200	0.000005190	0.000006055
26	6	0.000005325	-0.000003518	-0.000011741
27	1	-0.000003435	-0.000002451	0.000002245
28	1	-0.000002017	-0.000000492	-0.000002563
29	1	-0.000003530	-0.000001495	0.000003677
30	6	0.000000377	-0.000007717	-0.000003410
31	1	-0.000000383	0.000000878	-0.000003674
32	1	0.000000476	0.000000878	0.000002712
33	1	-0.000000633	0.000000976	0.000002185

34	6	-0.000004430	0.000004040	0.000007029
35	8	-0.000000897	-0.000002684	-0.000006709
36	8	-0.000000873	-0.000000401	-0.000000121
37	1	-0.000001559	-0.000002026	-0.000003899

Sum of electronic and thermal Free Energies= -1418.021774 (a.u.)
Zero-point correction= 0.279921 (Hartree/Particle)

FA-ketyl-radical

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	-0.000003172	0.000000813	0.000004359
2	6	-0.000005348	-0.000001155	-0.000012110
3	6	0.000003066	-0.000000245	0.000004117
4	6	0.000001755	0.000000294	0.000003831
5	6	-0.000004857	-0.000001292	-0.000008257
6	6	0.000002147	-0.000000178	0.000002016
7	6	0.000011281	0.000004851	-0.000001851
8	8	0.000006027	0.000001441	0.000011669
9	6	0.000004723	-0.000003175	0.000008286
10	6	-0.000004444	0.000003982	-0.000006018
11	6	-0.000020746	-0.000007736	0.000008581
12	6	0.000010881	-0.000000558	-0.000020293
13	6	-0.000000885	0.000005895	0.000009469
14	6	-0.000005774	-0.000003078	0.000002613
15	6	0.000001591	0.000002152	-0.000001975
16	6	0.000006750	0.000003043	-0.000003760
17	17	0.000000387	0.000000182	-0.000004710
18	6	-0.000002967	-0.000000757	-0.000004302
19	8	0.000000355	0.000000563	0.000000938
20	6	-0.000000956	-0.000005321	-0.000004537
21	8	0.000000466	-0.000001918	0.000002822
22	1	0.000002381	-0.000000095	-0.000003139
23	1	-0.000001931	0.000001030	-0.000000855
24	1	0.000001281	0.000000873	0.000000457
25	1	0.000000370	0.000001781	0.000000150
26	1	-0.000000233	0.000002108	0.000001458
27	1	-0.000001696	-0.000001760	0.000000179
28	1	-0.000000918	-0.000000184	0.000001936
29	1	-0.000000390	0.000000557	0.000000159
30	1	0.000001738	0.000000041	0.000000003

31	1	0.000001627	0.000000243	-0.000000021
32	1	0.000000301	-0.000000468	-0.000000087
33	1	-0.000000408	-0.000000726	0.000001186
34	1	-0.000000189	-0.000000429	0.000001344
35	1	0.000000765	-0.000000631	0.000000843
36	1	-0.000000297	-0.000000635	0.000001012
37	8	0.000003040	-0.000001688	0.000003673
38	1	-0.000005721	0.000002182	0.000000816

Sum of electronic and thermal Free Energies=-1418.548137(a.u.)
Zero-point correction=0.293739 (Hartree/Particle)

FA-biradical

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	0.000001345	-0.000002276	-0.000000913
2	6	-0.000000738	0.000000248	0.000002367
3	6	0.000000178	0.000001957	-0.000000984
4	6	-0.000000224	0.000002660	-0.000002409
5	6	0.000000254	-0.000000258	0.000000451
6	6	-0.000001918	-0.000001529	0.000001131
7	6	0.000003126	-0.000003047	0.000000294
8	8	-0.000008302	0.000002005	-0.000002969
9	6	0.000000241	-0.000000526	-0.000008679
10	6	0.000003613	0.000001494	0.000006493
11	6	-0.000000423	-0.000001243	0.000000751
12	6	0.000000974	-0.000001536	0.000001135
13	6	0.000000927	-0.000000570	0.000001237
14	6	-0.000001146	-0.000000482	-0.000000498
15	6	-0.000001501	0.000000767	-0.000002042
16	6	-0.000001125	0.000000089	-0.000000533
17	17	-0.000001312	0.000000838	-0.000001297
18	6	0.000002406	0.000000396	0.000000844
19	1	-0.000000849	0.000003948	-0.000001612
20	1	0.000000341	0.000002129	-0.000000775
21	1	0.000000531	-0.000003978	0.000001900
22	1	0.000000389	-0.000002850	0.000000775
23	1	0.000002654	-0.000002281	0.000002675
24	1	-0.000002555	0.000000509	-0.000002000
25	1	-0.000003131	0.000001378	-0.000002864
26	1	0.000001670	-0.000001431	0.000001770
27	1	-0.000000973	0.000002280	0.000000766
28	1	-0.000000567	0.000000952	-0.000002935
29	1	-0.000003919	0.000003075	-0.000002675
30	1	0.000005268	0.000002311	-0.000002562
31	1	0.000005739	0.000003039	0.000004550
32	1	-0.000001501	0.000000983	0.000001993
33	8	0.000000587	-0.000004352	0.000004874
34	1	-0.000000058	-0.000004699	0.000001741

Sum of electronic and thermal Free Energies=-1229.301508(a.u.)
Zero-point correction=0.265362 (Hartree/Particle)

FA-carbanion

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	-0.000005948	0.000004141	0.000005976
2	6	0.000026203	0.000009025	-0.000021128
3	6	-0.000011313	-0.000006995	0.000005619
4	6	-0.000008547	0.000001285	-0.000002306
5	6	0.000020280	0.000010977	-0.000016739
6	6	-0.000004250	-0.000000974	0.000000562
7	6	-0.000022529	0.000000928	0.000031705
8	8	0.000006164	-0.000007558	-0.000005116
9	8	-0.000022297	-0.000005366	0.000017979
10	6	0.000013573	0.000011275	-0.000001282
11	6	0.000006743	0.000003763	-0.000006202
12	6	0.000010807	0.000006205	-0.000015747
13	6	-0.000006188	-0.000003520	0.000000550
14	6	-0.000003581	-0.000001327	0.000003337
15	6	-0.000001213	-0.000003156	0.000007471
16	6	0.000000756	-0.000004164	-0.000004032
17	6	0.000004403	-0.000003920	0.000001839
18	17	0.000002240	-0.000003205	-0.000001543
19	6	-0.000002267	-0.000000955	0.000006045
20	1	0.000000302	0.000000223	-0.000000672
21	1	0.000000885	-0.000000119	0.000001950
22	1	0.000001358	-0.000001145	-0.000001078
23	1	-0.000001021	0.000004166	0.000000309
24	1	0.000000078	-0.000001036	0.000001709
25	1	0.000001501	0.000000160	0.000001135
26	1	0.000000288	-0.000002710	0.000002052
27	1	0.000002088	-0.000002696	-0.000000487
28	1	0.000007289	0.000001759	-0.000005482
29	1	-0.000005621	0.000003136	0.000001066
30	1	-0.000001244	-0.000002362	-0.000004923
31	1	-0.000004538	-0.000004197	-0.000002109
32	1	-0.000004136	-0.000003504	0.000005883
33	1	-0.000000264	0.000001864	-0.000006339

Sum of electronic and thermal Free Energies=-1228.772942(a.u.)
Zero-point correction=0.251430 (Hartree/Particle)

enolate 3^- anion

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	0.000037593	0.000015217	0.000027115
2	6	-0.000091565	-0.000006524	-0.000020097
3	6	0.000007233	-0.000023352	0.000008847
4	6	0.000051718	0.000003411	-0.000002011
5	6	-0.000077529	0.000024329	-0.000007630
6	6	0.000008519	-0.000016131	-0.000000226
7	6	0.000115862	-0.000012433	-0.000028648
8	8	0.000040170	-0.000008009	0.000003689
9	6	-0.000012970	0.000045164	0.000031692
10	6	-0.000028910	-0.000022264	-0.000016499
11	6	0.000004092	-0.000014974	-0.000005109
12	6	0.000061634	-0.000010022	0.000018410
13	6	-0.000038288	0.000016777	-0.000006666
14	6	0.000029890	-0.000032747	-0.000001371
15	17	-0.000029112	0.000008518	-0.000000195
16	1	-0.000020206	0.000002618	0.000000212
17	1	-0.000021850	0.000019837	-0.000003163
18	1	-0.000000516	-0.000018183	0.000000360
19	1	0.000003934	0.000003424	-0.000011324
20	1	0.000005365	0.000012903	0.000006250
21	1	-0.000006383	-0.000000684	-0.000002198
22	1	-0.000002819	0.000001121	-0.000000037
23	1	-0.000008091	0.000005690	0.000002966
24	8	-0.000027771	0.000006311	0.000005632

Sum of electronic and thermal Free Energies=-1110.968978 (a.u.)
Zero-point correction= 0.171848 (Hartree/Particle)