Supporting Information

To Photodeprotection or Not: Effect of the Oxidation State of Sulfur Atom of Thiochromone Derivatives

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S1. Expermental and computational methods

Compounds TC and TS-PPG were synthesized using previously reported methods,[1] and the relative synthesis routes were shown in Scheme S2 and S3, and ^{1}H NMR and ^{13}C NMR were used to characterize the prepared sample (Figure S21−S24).

Steady-state photolysis experiments were performed in a photochemical reactor PRP-100 (Rayonet, 254 nm). Samples were prepared in the dark and degassed by purifying Ar 30 min. UV−vis spectra were recorded on a UV−1700 spectrophotometer (Shimadzu) after different irradiate time.

The apparatus and methods of fs-TA measurements[2] has been detailed previously. Here is a simple description, a commercial regenerative amplified Ti:Sapphire laser system was employed to carry out the fs-TA measurements with an automated data acquisition system. a white continuum light (330–800 nm) was selected as the probe pulse, which was generated in a CaF_2 crystal by a about 5% of the amplified 800 nm output obtained from the laser system. The probe pulse was divided into two beams, one beam would pass the sample solution sealed in a 2 mm path-length cuvette, and the other was used as a reference to monitor the stability of probe pulse. And a 267 nm laser beam was employed to excite sample. At the experiments, the absorbance of samples at 267 nm was around 1.

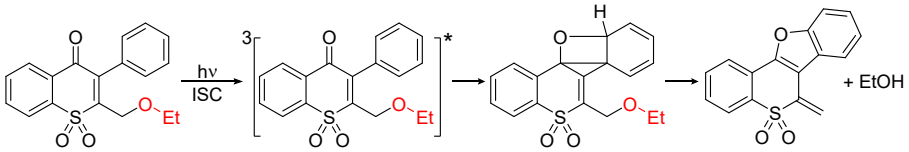
The ns-TA experiments[3] were conducted on a commercial flash photolysis spectrometer (LP-980, Edinburgh Instruments). The 266 nm laser beam, generated from an Nd:YAG Q-switched laser's forth harmonic output, was selected as the pump pulse. And a pulse Xe lamp (150 W) was used as probe light. The sample solution used in fs-TA or ns-TA were degassed by purifying Ar for 30 min before measurements.

The ns-TR[2] measurements were done using a home-made apparatus. The 266 nm laser, yielded from the fourth harmonic of Nd:YAG Q-switched laser, used as light source. First, two Raman spectrum were obtained with a low-power laser beam and a high-power laser beam respectively. Then, A difference Raman spectrum was produced by subtracting the low-power Raman spectrum from high-power Raman spectrum with an appropriately coefficient to remove the signals of precursor and solvent Raman bands, which contained the signals of species generated during the time of laser pulse (10 ns) mainly. A backscattering geometry was used to acquire the Raman scattered, and the signal was detected with a liquid nitrogen-cooled charge-coupled device (CCD). The sample concentration was 4×10^{-4} M approximately.

DFT computation, employing (U)ωB97X-D[4] method with a 6-311G** set basis, were performed to search the optimized structures of triplet state and possible intermediates existed in reactions, while the frequency computations also conducted to verify the obtained structure located at the minima point. Several key processes were studied by gaining the optimized structures of the reactant complexes (RC), transition states (TS) and product complexes (PC),[5] and the intrinsic reaction coordinates (IRC)[6] calculation were performed to confirm that the obtained TS connect the minima of RC and PC respectively. The calculation of UV−vis spectrum and excited singlet state was performed at TD-ωB97X-D /6-311G** level,[7] the Gibbs free energies of all species involved in the reaction paths, were obtained with the addition of electronic energy (ωB97X-D /6-311+G**) and thermal free energy correction (ωB97X-D /6-311G**). The broken symmetry methodology was employed to gain the open-shell singlet

(OSS) configuration.[8] The solvent effect was considered with the solvation model based on density (SMD).[9] The Gaussian 16 software was used in all of computation.[10]

S2. Figures and Tables



Scheme S1. The possible photodeprotection reaction mechanism of TS-PPG.[11]

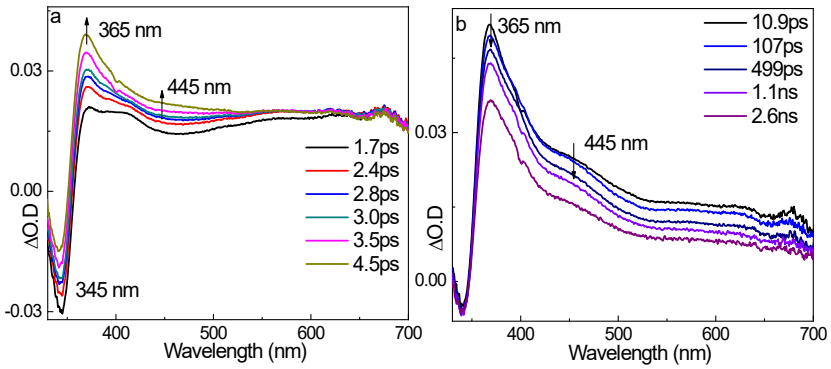


Fig. S1. The fs-TA results of TC in MeOH (λ_{ex} = 266 nm).

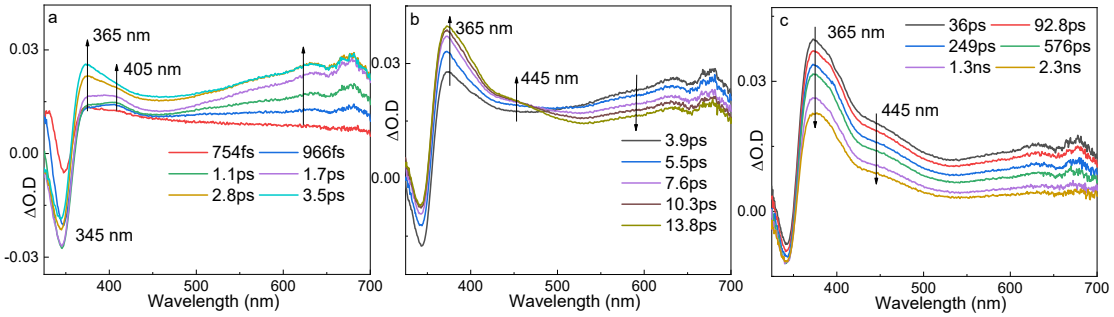


Fig. S2. The fs-TA results of TC in MeCN-H_2O (λ_{ex} = 266 nm).

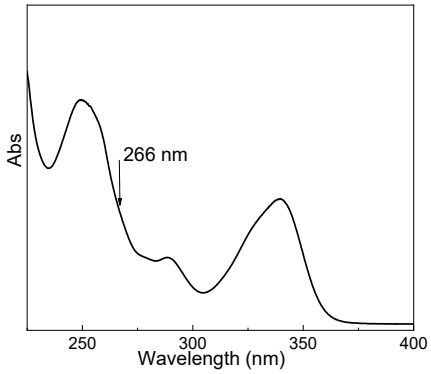


Fig. S3. The UV−vis spectra of TC in MeCN.

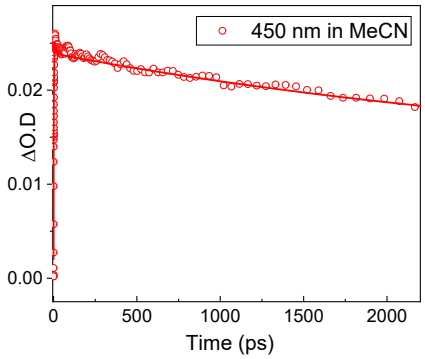


Fig. S4. Kinetics fitting of the absorption bands at 450 nm detected by fs-TA experiments of TC in MeCN (the solid lines depict the best fit to the data).

Table S1. The absorption and kinetic information of intermediate involved in the photochemical reaction of TC.

Intermediate	Absorption band (nm)	τ (ps)
TC(S_n)	405	nd
TC(S_1)	365, 500-700	4.1
TC(T)	365, 445	nd

τ: lifetime of intermediates; nd: not determined

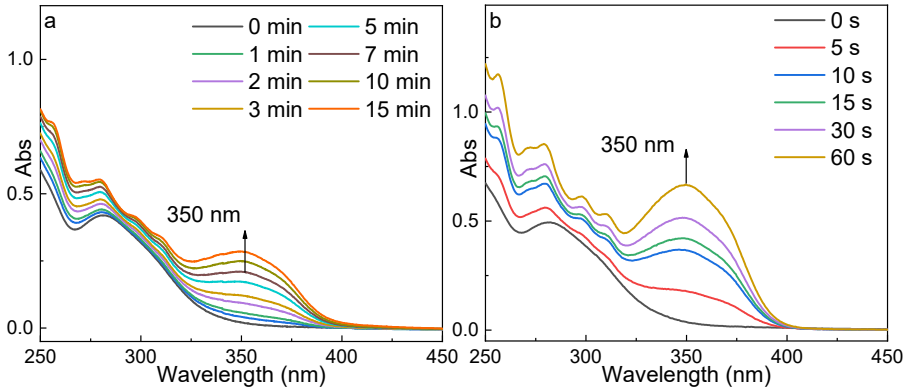


Fig. S5. Steady state absorption spectra of TS-PPG in (a) MeCN and (b) MeOH recorded at different irradiation times upon 266 nm light.

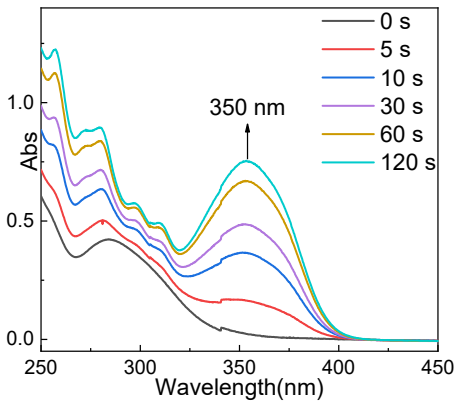


Fig. S6. Steady state absorption spectra of TS-PPG in MeCN-H_2O recorded at different irradiation times upon 266 nm light.

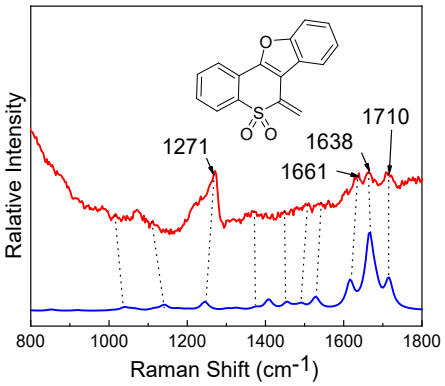


Fig. S7. (Red line) the ns-TR^2 spectra of TS-PPG in MeOH under 266 nm irradiation. (Blue line) the calculated normal Raman spectrum of the photodeprotection reaction product (TD-ωB97X-D /6-311G** (MeOH) with a scale factor of 1.00 and a half-width of 2000 cm^{-1}).

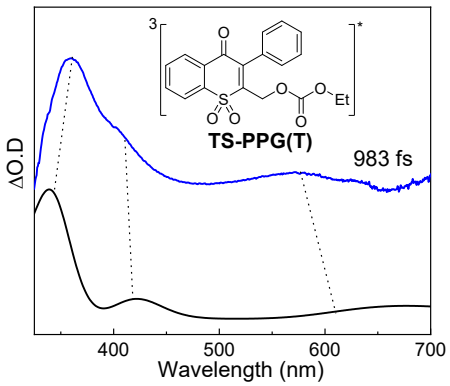


Fig. S8. Comparison of the 983 fs fs-TA spectrum of TS-PPG in MeCN with the calculated UV−vis spectra of TS-PPG(T). (TD-ωB97X-D /6-311G** (MeCN) with a scale factor of 1.00 and a half-width of 2000 cm^{-1}).

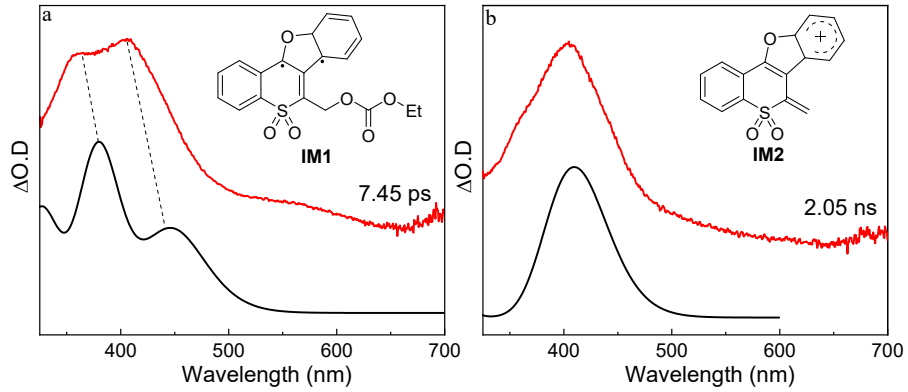


Fig. S9. Comparison of the fs-TA spectrum of TS-PPG in MeCN with the calculated UV−vis spectra of (a) IM1 and (b) IM2. (TD-ωB97X-D /6-311G** (MeCN) with a scale factor of 1.00 and a half-width of 2000 cm^{-1}).

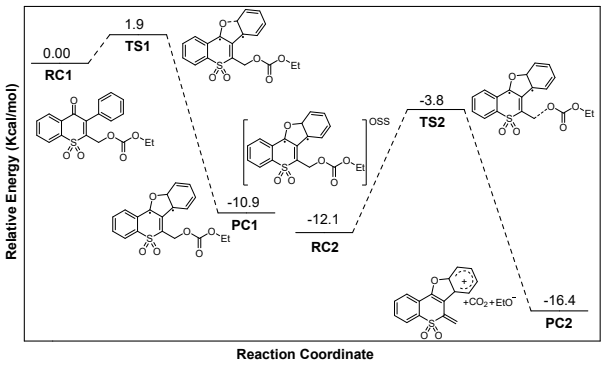


Fig. S10. Reactive energy profile obtained from (U)ωB97X-D /6-311+G** calculation for the photodeprotection of TS-PPG in MeCN.

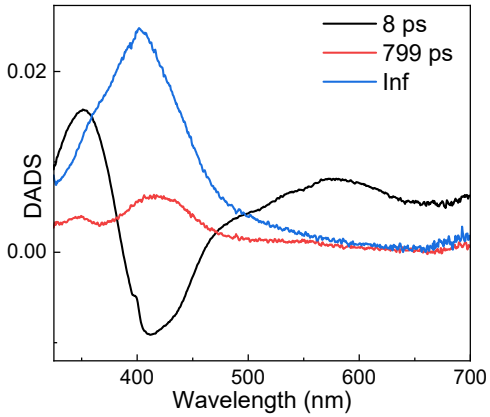


Fig. S11. Decay-associated difference spectra (DADS) of the fs-TA signals of TS-PPG in MeCN.

Table S2. The absorption and kinetic information of the intermediates involved in the photochemical reaction of TS-PPG.

Intermediate	Absorption band (nm)	τ (ps)
TS-PPG(T)	360, 575	7.0 (in MeCN)
		8.0 (in MeCN-H_2O)
IM1	360, 405	799.0 (in MeCN)
		451.0 (in MeCN-H_2O)
IM2	400	nd
IM3(S_1)	510	nd
IM3	505	nd

τ: lifetime of intermediates; nd: not determined

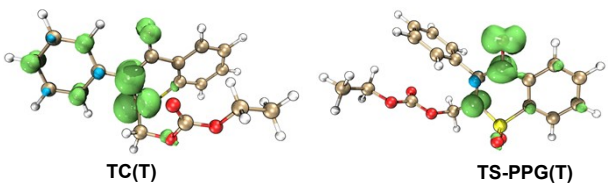


Fig. S12. The spin distributions for (left) TC(T) and (right) TS-PPG(T).

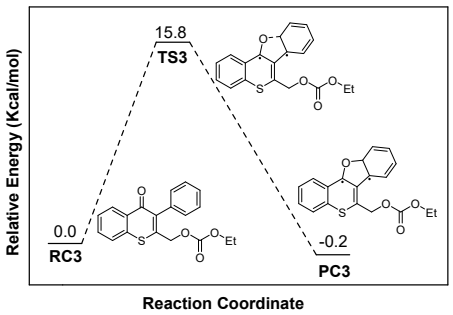


Fig. S13. Reactive energy profile obtained from (U)ωB97X-D /6-311+G** calculation for the cyclization reaction of TC in MeCN.

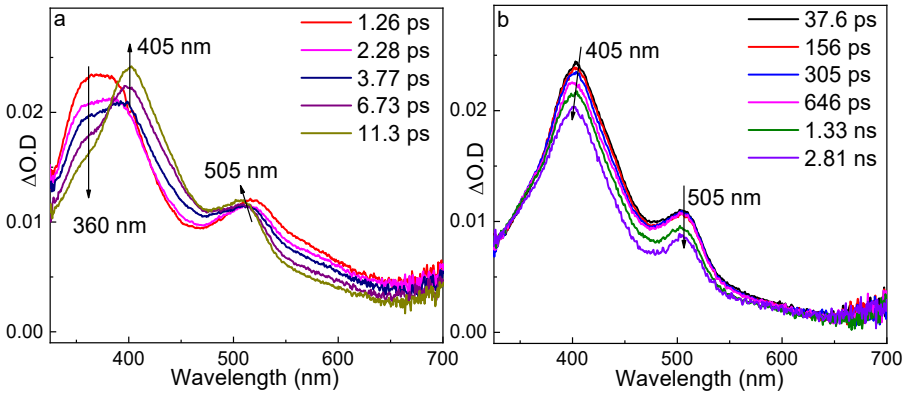


Fig. S14. The fs-TA results of TS-PPG in MeOH (λ_{ex} = 266 nm).

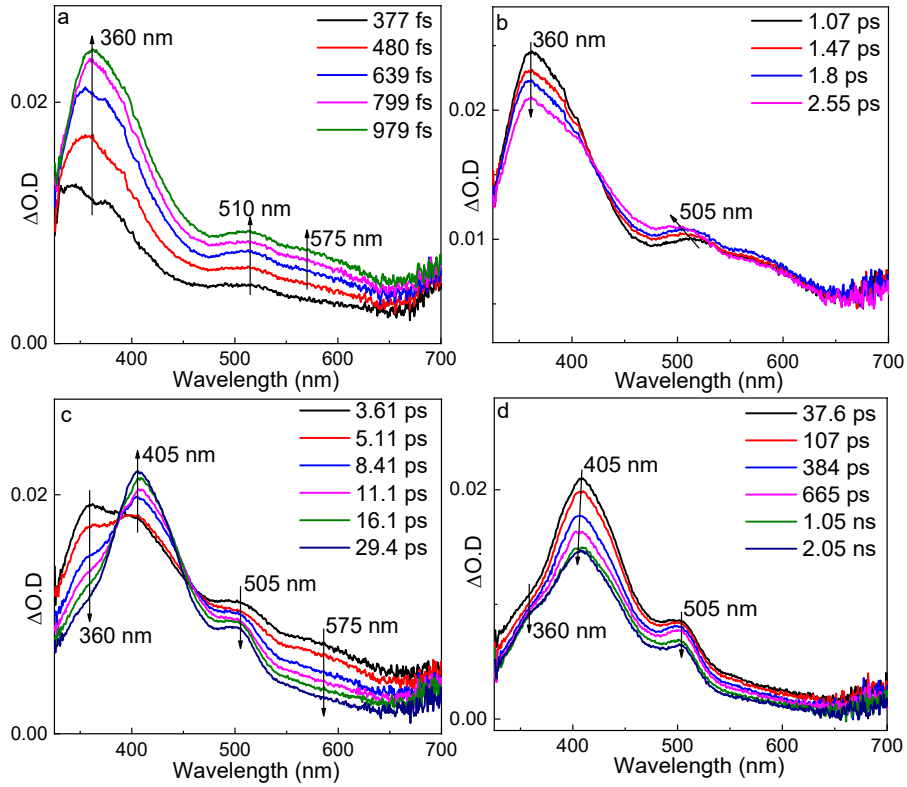


Fig. S15. fs-TA of TS-PPG in MeCN-H_2O (v: v= 1:1) (λ_{ex} = 266 nm).

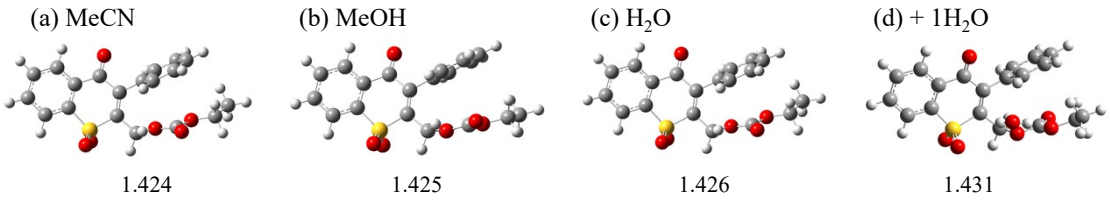


Fig. S16. The C−O bond distances of TS-PPG(S_0) in different solvents and with 1H_2O.

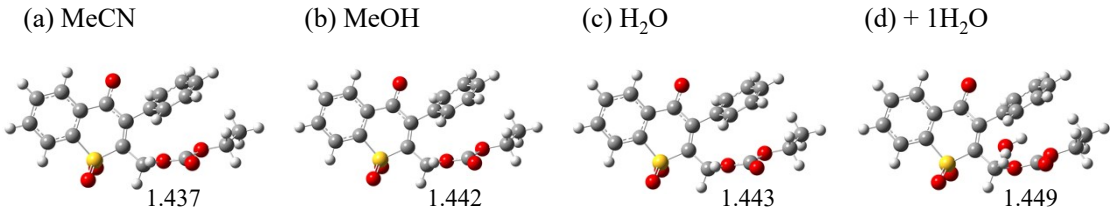


Fig. S17. The C−O bond distances of TS-PPG(S_1) in different solvents and with 1H_2O.

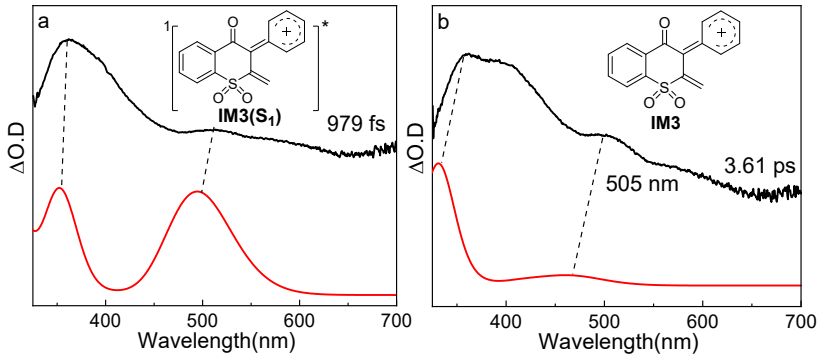


Fig. S18. Comparison of the fs-TA spectrum of TS-PPG in MeCN-H_2O with the calculated UV−vis spectra of (a) IM3(S_1) and (b) IM3 (TD-ωB97X-D /6-311G** (H_2O) with a scale factor of 1.00 and a half-width of 2000 cm^{-1}).

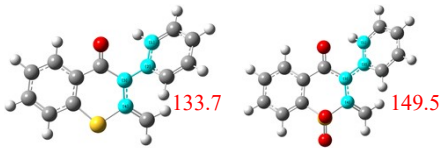


Fig. S19. The dihedral angle of cation intermediates produced from the heterolytic cleavage of (left) TC(S_1) and (right) TS-PPG(S_1).

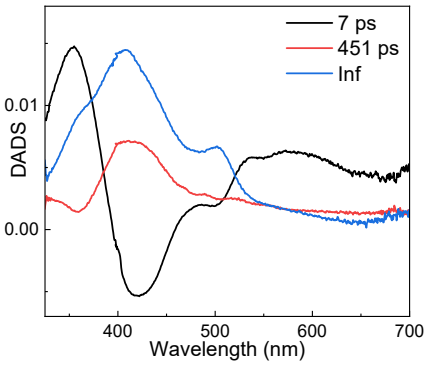
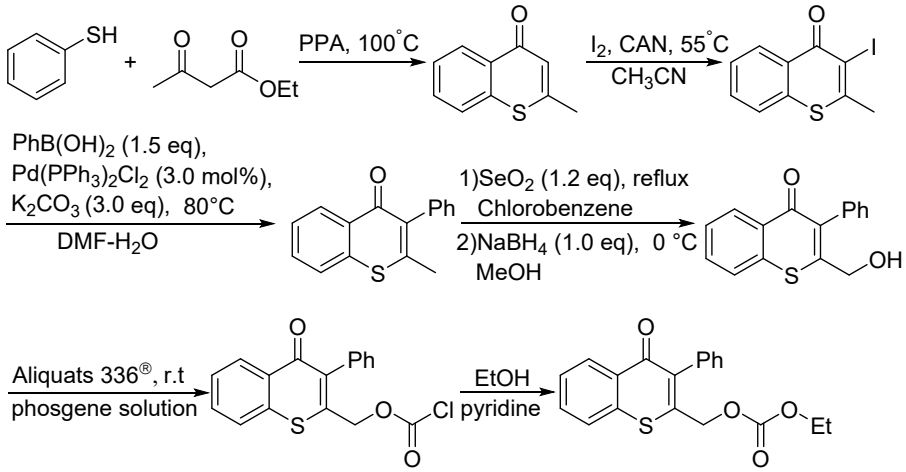


Fig. S20. DADS of the fs-TA signals of TS-PPG in MeCN-H_2O.



Scheme S2. The synthetic route of TC.

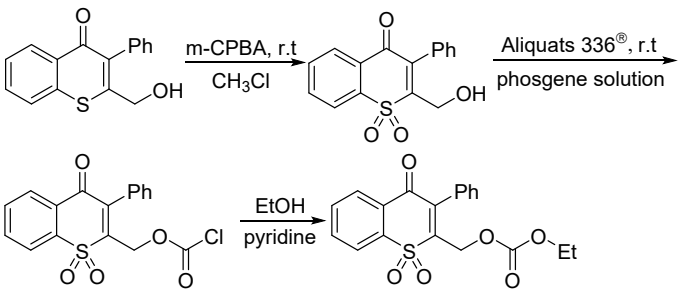
TC

mp: 72-73 ℃

^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ (ppm): 8.51 (d, *J = 7.7 Hz*, 1H), 7.66–7.61 (m, 2H), 7.54 (m, 1H), 7.46 (t, *J = 7.3 Hz*, 2H), 7.42–7.39 (m, 1H), 7.25–7.21 (m, 2H), 5.00 (s, 2H), 4.24 (m, 2H), 1.33 (t, *J = 7.1 Hz*, 3H).

^{13}C NMR (101 MHz, $CDCl_3$/TMS): δ (ppm): 178.6, 154.2, 144.9, 144.2, 140.6, 134.9, 133.4, 130.8, 129.8, 129.2, 129.1, 129.0, 128.6, 123.3, 65.0, 60.6, 14.3.

HRMS (ESI): m/z calculated for $[C_{19}H_{17}O_4S]^+$: 341.0842, found: 341.0843.



Scheme S3. The synthetic route of TS-PPG.

TS-PPG

mp: 83-84 ℃

^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ (ppm): (d, *J = 6.6 Hz,* 1H), 8.12 (d, *J = 6.7 Hz*, 1H), 7.94–7.86 (m, 1H), 7.77 (d, *J = 7.8 Hz*, 1H), 7.51–7.45 (m, 3H), 7.33–7.28 (m, 2H), 5.10 (s, 2H), 4.19–4.24 (m, 2H), 1.31 (t, *J = 14.3 Hz*, 3H).

^{13}C NMR (101 MHz, $CDCl_3$/TMS): δ (ppm): 178.6, 154.2, 144.9, 144.2, 140.6, 134.9, 133.4, 130.8, 129.8, 129.2, 129.1, 129.0, 128.6, 123.3, 65.0, 60.6, 14.3.

HRMS (ESI): m/z calculated for $[C_{19}H_{16}O_6SNa]^+$: 395.0560, found: 395.0564.

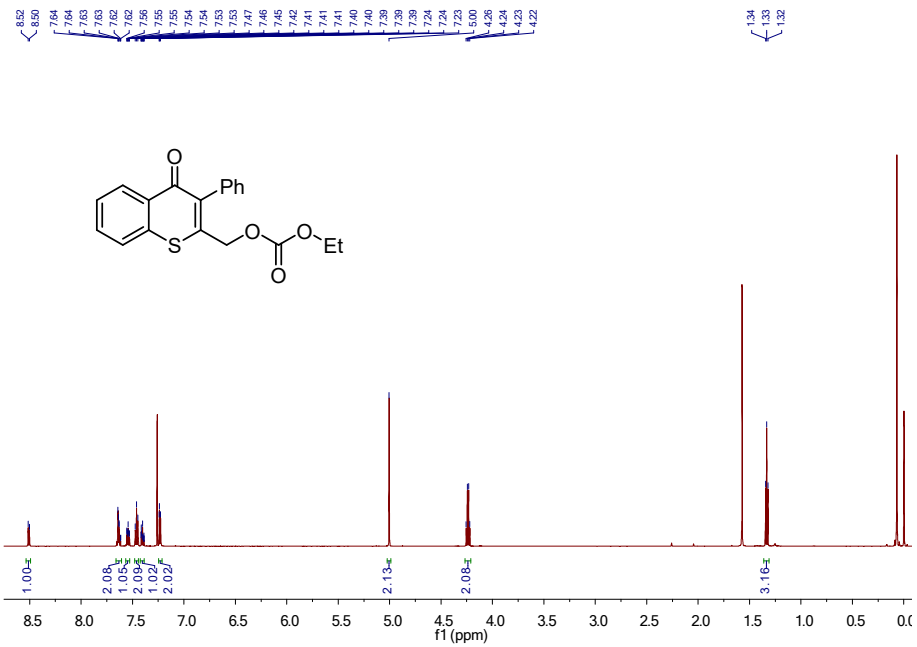


Fig. S21. The ^{1}H NMR spectra of TC in $CDCl_3$.

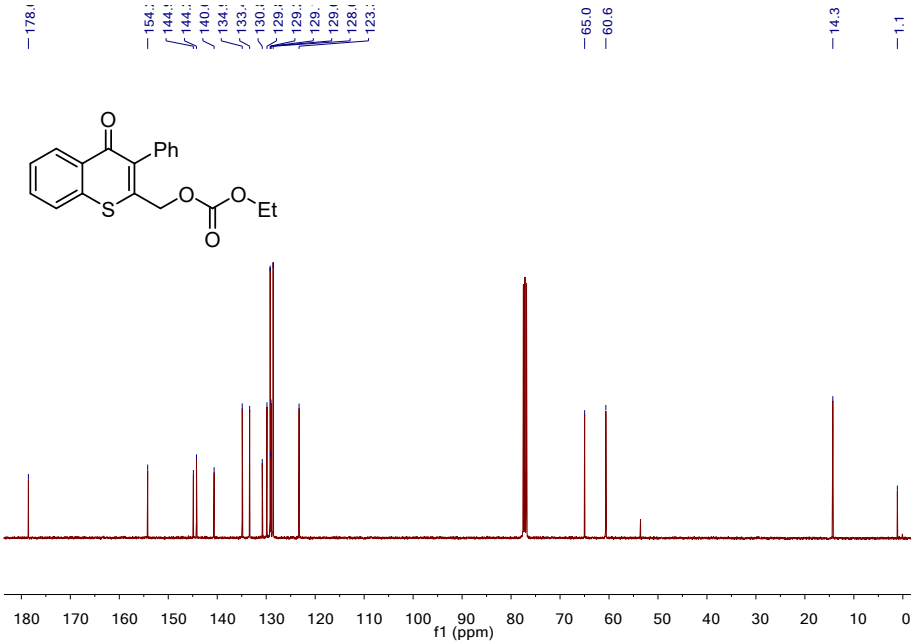


Fig. S22. The ^{13}C NMR spectra of TC in $CDCl_3$.

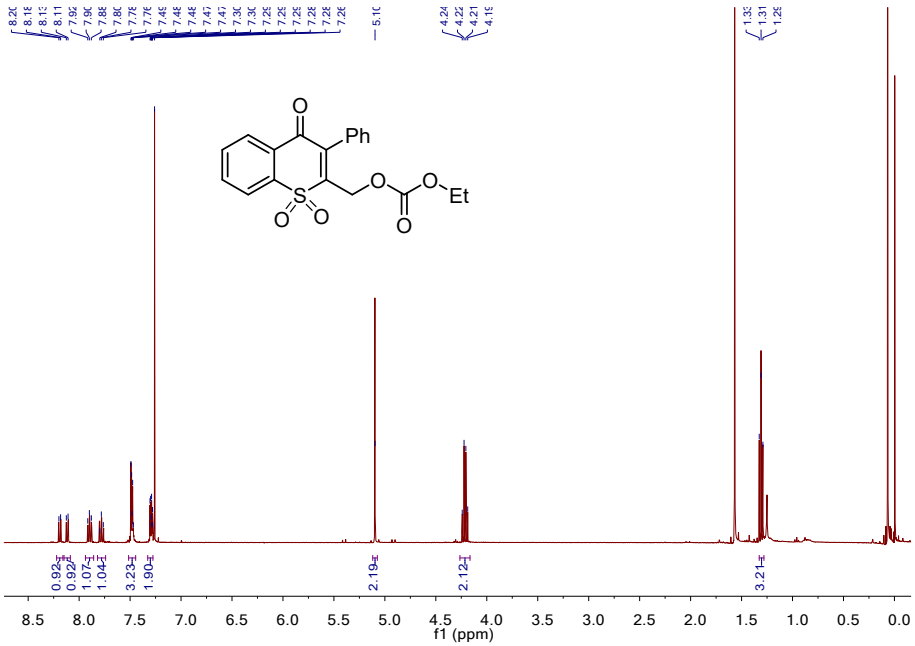


Fig. S23. The ^{1}H NMR spectra of TS-PPG in $CDCl_3$.

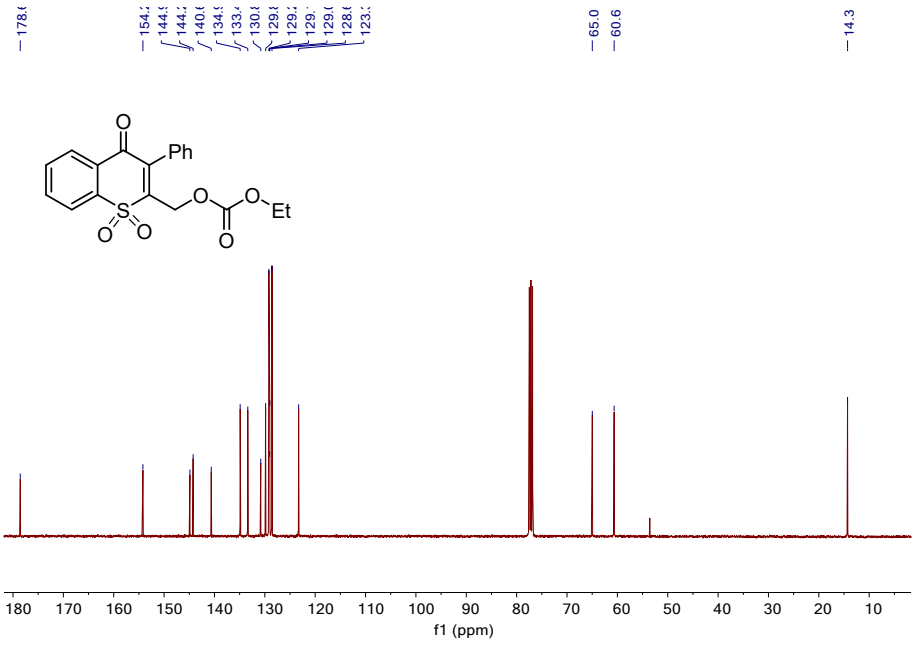


Fig. S24. The ^{13}C NMR spectra of TS-PPG in $CDCl_3$.

Cartesian coordinates and total energies for the optimized geometry for the compounds and intermediates considered in this paper are given.

TC(T)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.059475	-2.322439	-0.503611
2	6	0	3.335848	-2.179985	0.855625
3	6	0	2.388507	-1.623825	1.708563
4	6	0	1.154054	-1.213813	1.205292
5	6	0	0.850947	-1.374707	-0.155994
6	6	0	1.823393	-1.928348	-0.996319
7	6	0	-0.467298	2.010132	1.065632
8	6	0	-0.805112	0.551724	1.136869
9	6	0	-1.402593	-0.200620	0.018413
10	6	0	-0.483351	-1.038999	-0.763635
11	1	0	3.803466	-2.741998	-1.173225
12	1	0	4.297193	-2.489468	1.254355
13	1	0	1.583905	-2.046562	-2.047956
14	8	0	-0.770324	-1.501608	-1.866835
15	16	0	0.003183	-0.437664	2.338916
16	6	0	-2.822888	-0.127870	-0.199592
17	6	0	-3.501682	-0.874856	-1.196660
18	6	0	-3.604004	0.717422	0.631085
19	6	0	-4.873996	-0.763295	-1.351842
20	1	0	-2.936978	-1.533649	-1.841692
21	6	0	-4.975420	0.817764	0.468779
22	1	0	-3.120168	1.295735	1.412855
23	6	0	-5.620174	0.080814	-0.526484
24	1	0	-5.371112	-1.344050	-2.123228
25	1	0	-5.546558	1.473720	1.118763
26	1	0	-6.695186	0.161785	-0.656428
27	8	0	0.951569	2.201144	0.869767
28	6	0	1.407136	1.893901	-0.350127
29	8	0	0.721346	1.696929	-1.329213
30	8	0	2.728640	1.846354	-0.295608
31	6	0	3.396080	1.483682	-1.524197
32	1	0	3.309556	2.318074	-2.226633
33	1	0	2.893221	0.612949	-1.952118
34	6	0	4.835268	1.181648	-1.179859
35	1	0	5.373074	0.906162	-2.092486
36	1	0	5.327324	2.053753	-0.738153

37	1	0	4.896657	0.345630	-0.475873
38	1	0	2.616441	-1.491716	2.762088
39	1	0	-1.025646	2.500160	0.265215
40	1	0	-0.671101	2.509572	2.015349

Sum of electronic and zero-point Energies= -1432.310775
Sum of electronic and thermal Free Energies= -1432.363753
The number of imaginary frequencies: 0

TS-PPG(T)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.301939	1.438546	-0.377541
2	6	0	-5.604283	0.112892	-0.071971
3	6	0	-4.581954	-0.809329	0.094997
4	6	0	-3.264243	-0.400518	-0.044627
5	6	0	-2.940313	0.933087	-0.326887
6	6	0	-3.987822	1.852198	-0.495369
7	6	0	0.553901	-1.558529	1.013567
8	6	0	-0.569953	-0.740839	0.447671
9	6	0	-0.462647	0.587796	0.114636
10	6	0	-1.553009	1.357383	-0.338628
11	1	0	-6.100921	2.158211	-0.510335
12	1	0	-6.635320	-0.200996	0.034567
13	1	0	-3.760260	2.891300	-0.701208
14	8	0	-1.316270	2.595362	-0.718094
15	6	0	0.844011	1.306602	0.240144
16	6	0	1.683639	1.409228	-0.868514
17	6	0	1.231021	1.864558	1.456333
18	6	0	2.900396	2.067969	-0.756912
19	1	0	1.389750	0.950573	-1.805291
20	6	0	2.450792	2.517014	1.564838
21	1	0	0.578571	1.776068	2.317819
22	6	0	3.285348	2.620593	0.458948
23	1	0	3.551858	2.141347	-1.620223
24	1	0	2.753036	2.938194	2.516087
25	1	0	4.238739	3.129188	0.545929
26	8	0	1.602858	-1.681745	0.044429
27	6	0	2.819508	-1.294291	0.438629
28	8	0	3.138230	-0.971197	1.550802
29	8	0	3.615624	-1.329734	-0.621323
30	6	0	4.964942	-0.896280	-0.386959

31	1	0	5.453466	-1.606732	0.284674
32	1	0	4.938339	0.076490	0.109375
33	6	0	5.650440	-0.826620	-1.730903
34	1	0	6.686804	-0.506392	-1.600907
35	1	0	5.647602	-1.802192	-2.220496
36	1	0	5.145197	-0.111613	-2.383711
37	1	0	-4.792226	-1.845107	0.333926
38	1	0	0.957589	-1.091748	1.913333
39	1	0	0.202494	-2.559691	1.264122
40	16	0	-2.004838	-1.655196	-0.020577
41	8	0	-2.320352	-2.609832	1.031560
42	8	0	-1.830629	-2.140670	-1.379520

Sum of electronic and zero-point Energies= -1582.618746
Sum of electronic and thermal Free Energies= -1582.674650
The number of imaginary frequencies: 0

IM1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.474816	-2.103848	-0.912507
2	6	0	-3.768762	-3.254587	-0.562492
3	6	0	-2.461327	-3.154113	-0.108056
4	6	0	-1.868400	-1.904995	-0.010418
5	6	0	-2.569696	-0.732095	-0.335962
6	6	0	-3.892419	-0.856253	-0.793938
7	6	0	1.313174	-0.021959	1.848545
8	6	0	0.145714	-0.190541	0.926888
9	6	0	-0.705508	0.800247	0.474181
10	6	0	-1.963257	0.542291	-0.123614
11	1	0	-5.494393	-2.185646	-1.270573
12	1	0	-4.236261	-4.228195	-0.644001
13	1	0	-4.444243	0.041365	-1.041625
14	8	0	-2.642952	1.663297	-0.437154
15	6	0	-0.582594	2.244223	0.493666
16	6	0	0.502088	3.090142	0.484305
17	6	0	-1.961112	2.764412	0.208362
18	6	0	0.331743	4.409267	0.051843
19	1	0	1.497366	2.708859	0.669532
20	6	0	-1.993877	4.040523	-0.552179
21	6	0	-0.901234	4.838760	-0.528460
22	1	0	1.184755	5.075980	0.031030

23	1	0	-2.924310	4.341542	-1.017669
24	1	0	-0.940474	5.815437	-0.997692
25	8	0	2.503183	-0.640183	1.356087
26	6	0	3.087430	-0.041757	0.315172
27	8	0	2.777871	1.029700	-0.137922
28	8	0	4.067864	-0.815230	-0.108699
29	6	0	4.770665	-0.344075	-1.271864
30	1	0	5.235138	0.617441	-1.039040
31	1	0	4.047821	-0.187622	-2.075335
32	6	0	5.793463	-1.395690	-1.630091
33	1	0	6.350184	-1.080082	-2.515516
34	1	0	6.499656	-1.545457	-0.811136
35	1	0	5.304754	-2.347067	-1.846780
36	1	0	-1.899193	-4.036895	0.172764
37	1	0	1.479747	1.033214	2.064138
38	1	0	1.116293	-0.556897	2.778781
39	16	0	-0.139256	-1.869313	0.426219
40	8	0	0.055228	-2.737673	1.577095
41	8	0	0.631534	-2.105918	-0.784702
42	1	0	-2.498207	2.911389	1.165697

Sum of electronic and zero-point Energies = -1582.636189
Sum of electronic and thermal Energies= -1582.690571
The number of imaginary frequencies: 0

IM2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.046949	2.703985	-0.236965
2	6	0	3.932392	1.635881	-0.095362
3	6	0	3.462367	0.325860	0.055100
4	6	0	2.098332	0.100733	0.052054
5	6	0	1.190031	1.170535	-0.109218
6	6	0	1.674141	2.477835	-0.247142
7	6	0	-0.176498	-2.679584	-1.323470
8	6	0	0.043202	-1.610050	-0.562808
9	6	0	-0.793312	-0.409359	-0.426653
10	6	0	-0.221136	0.874472	-0.202982
11	1	0	3.428646	3.715864	-0.348076
12	1	0	5.004716	1.820217	-0.098542
13	1	0	0.974487	3.300683	-0.378742
14	8	0	-1.113513	1.834214	-0.117437

15	6	0	-2.155522	-0.220699	-0.426842
16	6	0	-3.279567	-1.107724	-0.346721
17	6	0	-2.407468	1.246600	-0.375138
18	6	0	-4.414533	-0.604110	0.204908
19	1	0	-3.172663	-2.166015	-0.567129
20	6	0	-3.547414	1.672044	0.491911
21	6	0	-4.531743	0.779562	0.680046
22	1	0	-5.260542	-1.268469	0.373368
23	1	0	-3.609762	2.708500	0.814313
24	1	0	-5.436758	1.064501	1.210534
25	1	0	4.145642	-0.512878	0.174464
26	1	0	-1.066855	-2.769043	-1.943670
27	1	0	0.554006	-3.486746	-1.345711
28	16	0	1.507659	-1.540798	0.449200
29	8	0	2.475093	-2.513007	-0.027070
30	8	0	1.070276	-1.504046	1.837033
31	1	0	-2.659630	1.572969	-1.402511

Sum of electronic and zero-point Energies= -1239.424269
Sum of electronic and thermal Energies= -1239.466336
The number of imaginary frequencies: 0

IM3(S_1)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.461789	-2.481188	-0.160508
2	6	0	-4.204493	-1.317133	-0.332269
3	6	0	-3.580905	-0.073293	-0.278593
4	6	0	-2.211472	-0.019386	-0.055454
5	6	0	-1.444621	-1.180328	0.112666
6	6	0	-2.088897	-2.414438	0.053438
7	6	0	0.917462	2.430712	-0.692895
8	6	0	0.229450	1.346061	-0.264907
9	6	0	0.777179	0.066069	-0.007290
10	6	0	0.032715	-1.150606	0.256902
11	1	0	-3.951055	-3.448151	-0.203033
12	1	0	-5.272735	-1.371224	-0.511186
13	1	0	-1.501676	-3.319235	0.164324
14	8	0	0.686797	-2.165035	0.526872
15	6	0	2.226054	-0.123300	-0.042835
16	6	0	2.982239	0.009864	1.174393
17	6	0	2.880909	-0.446575	-1.280935

18	6	0	4.333549	-0.190286	1.145661
19	1	0	2.458898	0.264629	2.088511
20	6	0	4.232248	-0.643820	-1.286370
21	1	0	2.284158	-0.532041	-2.181230
22	6	0	4.957661	-0.512836	-0.079118
23	1	0	4.929247	-0.102344	2.045531
24	1	0	4.755153	-0.896275	-2.200389
25	1	0	6.030891	-0.665477	-0.095664
26	1	0	-4.155480	0.837315	-0.410983
27	1	0	1.982929	2.382596	-0.889856
28	1	0	0.418889	3.377657	-0.869475
29	16	0	-1.494094	1.586707	0.168193
30	8	0	-2.096797	2.530691	-0.773179
31	8	0	-1.532181	1.920360	1.596439

Sum of electronic and zero-point Energies= -1239.498061

Sum of electronic and thermal Free Energies= -1,239.542564

The number of imaginary frequencies: 0

IM3.3H_2O

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.838513	1.925190	-0.237317
2	6	0	-4.394570	0.778450	0.321215
3	6	0	-3.629911	-0.377945	0.451905
4	6	0	-2.308963	-0.360785	0.027078
5	6	0	-1.732329	0.780289	-0.549308
6	6	0	-2.519969	1.924284	-0.677522
7	6	0	0.219239	-2.563350	-1.802949
8	6	0	-0.036314	-1.607100	-0.909895
9	6	0	0.616676	-0.305071	-0.807429
10	6	0	-0.332771	0.855462	-1.049254
11	1	0	-4.435096	2.825366	-0.336134
12	1	0	-5.426306	0.776922	0.654901
13	1	0	-2.085514	2.815138	-1.116242
14	8	0	0.050083	1.773298	-1.748332
15	6	0	1.974724	-0.143634	-0.588182
16	6	0	2.565338	1.163985	-0.475854
17	6	0	2.815206	-1.297985	-0.413718
18	6	0	3.916584	1.287458	-0.275199
19	1	0	1.944910	2.048905	-0.517702
20	6	0	4.166309	-1.148372	-0.225707

21	1	0	2.378887	-2.289108	-0.410596
22	6	0	4.716516	0.139489	-0.165087
23	1	0	4.366257	2.269220	-0.186736
24	1	0	4.800936	-2.017322	-0.100123
25	1	0	5.783361	0.252277	0.000393
26	1	0	-4.062646	-1.278459	0.874682
27	1	0	-0.382426	-3.466372	-1.837595
28	16	0	-1.350039	-1.829301	0.284389
29	8	0	-0.733615	-1.786325	1.613960
30	8	0	-2.137790	-3.005784	-0.074244
31	8	0	2.106602	-0.196547	2.761115
32	1	0	2.918045	0.026621	2.282438
33	1	0	1.838460	-1.042115	2.373589
34	8	0	0.422824	3.856689	0.404189
35	1	0	0.335684	3.000452	0.873010
36	1	0	0.095773	3.650060	-0.481735
37	8	0	0.177011	1.334564	1.553179
38	1	0	-0.627025	1.187578	2.068924
39	1	0	0.883439	0.838869	2.029850
40	1	0	1.009439	-2.438569	-2.536749

Sum of electronic and zero-point Energies= -1,468.74751
Sum of electronic and thermal Free Energies= -1,468.80013
The number of imaginary frequencies: 0

TS1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.224615	1.340757	-0.156354
2	6	0	-5.525063	-0.008098	0.050506
3	6	0	-4.499682	-0.943118	0.115000
4	6	0	-3.180154	-0.520828	-0.024168
5	6	0	-2.855476	0.833899	-0.214530
6	6	0	-3.909310	1.759747	-0.283168
7	6	0	0.676361	-1.809400	0.754908
8	6	0	-0.470943	-0.930386	0.355967
9	6	0	-0.389002	0.428707	0.103345
10	6	0	-1.470292	1.271873	-0.257575
11	1	0	-6.026263	2.070848	-0.209607
12	1	0	-6.555648	-0.329423	0.159714
13	1	0	-3.677256	2.810079	-0.423296
14	8	0	-1.203112	2.522851	-0.527250

15	6	0	0.804046	1.279648	0.233345
16	6	0	0.810490	2.345355	-0.729554
17	6	0	1.673099	1.320851	1.312674
18	6	0	1.626859	3.487735	-0.506564
19	1	0	0.534724	2.120660	-1.755387
20	6	0	2.509960	2.426096	1.476775
21	1	0	1.654970	0.548687	2.073133
22	6	0	2.465565	3.516769	0.583178
23	1	0	1.627290	4.290235	-1.236358
24	1	0	3.172116	2.466863	2.335761
25	1	0	3.120361	4.366542	0.746397
26	8	0	1.745928	-1.635343	-0.190993
27	6	0	2.976408	-1.489517	0.310287
28	8	0	3.289431	-1.590996	1.475764
29	8	0	3.790696	-1.213967	-0.697528
30	6	0	5.171483	-0.988417	-0.339697
31	1	0	5.563092	-1.890390	0.138712
32	1	0	5.214867	-0.165082	0.379015
33	6	0	5.916258	-0.659317	-1.612091
34	1	0	6.969607	-0.479633	-1.375318
35	1	0	5.858670	-1.487332	-2.325384
36	1	0	5.508692	0.241339	-2.081629
37	1	0	-4.719323	-1.994681	0.271524
38	1	0	1.038180	-1.572876	1.757724
39	1	0	0.384491	-2.862167	0.750615
40	16	0	-1.933204	-1.777222	-0.109479
41	8	0	-2.225049	-2.817429	0.885499
42	8	0	-1.819551	-2.224149	-1.506449

Sum of electronic and zero-point Energies= -1582.667015
Sum of electronic and thermal Free Energies= -1582.721437
The number of imaginary frequencies: 1
The imaginary frequency= -115.57

RC2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.357115	-0.714942	0.235496
2	6	0	4.981785	-2.057284	0.137813
3	6	0	3.637482	-2.406790	0.058870
4	6	0	2.670931	-1.408800	0.076822
5	6	0	3.034018	-0.050194	0.155747

6	6	0	4.396793	0.283648	0.238162
7	6	0	-1.216225	-0.809619	-1.116715
8	6	0	0.110844	-0.549465	-0.510269
9	6	0	0.655311	0.709808	-0.314742
10	6	0	2.014225	0.951060	0.041390
11	1	0	6.407364	-0.449635	0.298934
12	1	0	5.739273	-2.834277	0.124811
13	1	0	4.687390	1.327412	0.287579
14	8	0	2.329765	2.236909	0.145921
15	6	0	0.076969	2.021451	-0.417659
16	6	0	-1.238243	2.470209	-0.351222
17	6	0	1.203229	2.999250	-0.372447
18	6	0	-1.477627	3.795777	-0.008330
19	1	0	-2.068967	1.779896	-0.450249
20	6	0	0.892591	4.277809	0.320739
21	6	0	-0.403996	4.664625	0.388763
22	1	0	-2.499051	4.151862	0.073510
23	1	0	1.711442	4.922588	0.622329
24	1	0	-0.652971	5.644751	0.784271
25	8	0	-2.246065	-0.767893	-0.090203
26	6	0	-3.491537	-0.922702	-0.540054
27	8	0	-3.809716	-1.094735	-1.696469
28	8	0	-4.317974	-0.852683	0.497282
29	6	0	-5.719846	-0.995341	0.188068
30	1	0	-5.877280	-1.962260	-0.298246
31	1	0	-6.008544	-0.204602	-0.510401
32	6	0	-6.480301	-0.894920	1.489934
33	1	0	-7.551359	-0.999028	1.289814
34	1	0	-6.179105	-1.688138	2.181212
35	1	0	-6.310790	0.074441	1.968968
36	1	0	3.341296	-3.448397	-0.014581
37	1	0	-1.445099	-0.051827	-1.871285
38	1	0	-1.244631	-1.793108	-1.591952
39	16	0	0.961632	-1.911464	0.154324
40	8	0	0.768824	-3.085684	-0.708890
41	8	0	0.652678	-2.100727	1.581615
42	1	0	1.523720	3.250752	-1.400140

Sum of electronic and zero-point Energies= -1582.68988

Sum of electronic and thermal Free Energies= -1582.74376

The number of imaginary frequencies: 0

TS2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.498300	-0.022572	-0.021647
2	6	0	5.337125	-1.407795	-0.018431
3	6	0	4.064468	-1.973830	0.027802
4	6	0	2.955335	-1.143677	0.063239
5	6	0	3.103387	0.256468	0.041731
6	6	0	4.389230	0.811154	0.004588
7	6	0	-0.767622	-1.273171	-1.238396
8	6	0	0.305855	-0.769034	-0.557861
9	6	0	0.619706	0.629403	-0.344242
10	6	0	1.921437	1.080150	-0.035997
11	1	0	6.493299	0.408084	-0.054277
12	1	0	6.208053	-2.054410	-0.048387
13	1	0	4.510283	1.888640	-0.023006
14	8	0	2.021023	2.385410	0.117709
15	6	0	-0.157467	1.781172	-0.395561
16	6	0	-1.557045	2.020550	-0.453890
17	6	0	0.751633	2.942414	-0.249769
18	6	0	-1.996514	3.218628	0.029538
19	1	0	-2.253086	1.243768	-0.762751
20	6	0	0.226582	4.090204	0.534962
21	6	0	-1.110860	4.230615	0.578946
22	1	0	-3.065005	3.407576	0.072050
23	1	0	0.918545	4.839828	0.902584
24	1	0	-1.554223	5.107368	1.038388
25	8	0	-2.368094	-1.580702	-0.017242
26	6	0	-3.434997	-1.027284	-0.422352
27	8	0	-3.593665	-0.277036	-1.398276
28	8	0	-4.505731	-1.339651	0.373412
29	6	0	-5.750671	-0.739063	0.020858
30	1	0	-6.035042	-1.039268	-0.993925
31	1	0	-5.651248	0.352386	0.025869
32	6	0	-6.782628	-1.195771	1.031536
33	1	0	-7.756231	-0.753683	0.794568
34	1	0	-6.886762	-2.285854	1.017846
35	1	0	-6.501099	-0.887067	2.043858
36	1	0	3.936742	-3.051299	0.038693
37	1	0	-1.363946	-0.625960	-1.871625
38	1	0	-0.789712	-2.331017	-1.467762
39	16	0	1.339238	-1.875613	0.308262

40	8	0	1.317314	-3.197126	-0.326167
41	8	0	1.097748	-1.816772	1.757199
42	1	0	0.921351	3.346348	-1.267734

Sum of electronic and zero-point Energies= -1582.677683
Sum of electronic and thermal Free Energies= -1582.730591
The number of imaginary frequencies: 1
The imaginary frequency= -203.00

PC2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.979211	2.759445	-0.235455
2	6	0	3.899809	1.721366	-0.124478
3	6	0	3.469082	0.401064	0.016375
4	6	0	2.110946	0.137018	0.035924
5	6	0	1.167888	1.175818	-0.087861
6	6	0	1.614824	2.493187	-0.220915
7	6	0	-0.245356	-2.728547	-1.189352
8	6	0	0.037771	-1.622533	-0.505351
9	6	0	-0.787814	-0.426660	-0.357732
10	6	0	-0.238829	0.846718	-0.149071
11	1	0	3.323830	3.782143	-0.342430
12	1	0	4.963312	1.934293	-0.146532
13	1	0	0.896317	3.298302	-0.330167
14	8	0	-1.138900	1.802219	-0.046600
15	6	0	-2.167731	-0.251831	-0.363183
16	6	0	-3.274844	-1.126302	-0.295773
17	6	0	-2.412775	1.208227	-0.324729
18	6	0	-4.448174	-0.601392	0.175132
19	1	0	-3.159907	-2.189546	-0.468652
20	6	0	-3.600702	1.668884	0.434067
21	6	0	-4.602774	0.780229	0.580009
22	1	0	-5.295038	-1.265005	0.320220
23	1	0	-3.684946	2.716475	0.700908
24	1	0	-5.543898	1.083225	1.024765
25	1	0	4.186752	-0.407401	0.108726
26	1	0	-1.187331	-2.831553	-1.719480
27	1	0	0.459906	-3.552349	-1.240245
28	16	0	1.578152	-1.532558	0.393310
29	8	0	2.542171	-2.471691	-0.171461

30	8	0	1.274607	-1.599902	1.824022
31	1	0	-2.635638	1.499183	-1.373402

Sum of electronic and zero-point Energies= -1239.600553
Sum of electronic and thermal Free Energies= -1239.642401
The number of imaginary frequencies: 0

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.186013	-0.019479	-0.000414
2	8	0	1.323416	1.218744	0.000121
3	8	0	2.028414	-0.932140	0.000355
4	8	0	-0.144466	-0.511604	-0.000324
5	6	0	-1.172374	0.455438	-0.000229
6	6	0	-2.503908	-0.274944	0.000338
7	1	0	-1.093636	1.107560	-0.881140
8	1	0	-1.093105	1.108003	0.880298
9	1	0	-3.334142	0.440447	0.000381
10	1	0	-2.598455	-0.911289	-0.886789
11	1	0	-2.597951	-0.910821	0.887855

Sum of electronic and zero-point Energies= -343.077643
Sum of electronic and thermal Free Energies= -343.108321
The number of imaginary frequencies: 0

RC3

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.670858	0.612068	0.019248
2	6	0	-5.714288	-0.711488	-0.412851
3	6	0	-4.534743	-1.428915	-0.592354
4	6	0	-3.310622	-0.813237	-0.339367
5	6	0	-3.249327	0.522493	0.076414
6	6	0	-4.444552	1.221784	0.256477
7	6	0	0.429690	-1.792516	0.953509
8	6	0	-0.739754	-0.993304	0.502703
9	6	0	-0.730346	0.496073	0.397156
10	6	0	-1.952561	1.245299	0.261623
11	1	0	-6.590729	1.169508	0.164929
12	1	0	-6.667347	-1.193776	-0.607014

13	1	0	-4.393103	2.257509	0.575822
14	8	0	-1.942162	2.488465	0.277383
15	16	0	-1.832037	-1.778946	-0.581347
16	6	0	0.549655	1.216277	0.261387
17	6	0	0.837266	1.909179	-0.924774
18	6	0	1.499953	1.212532	1.292253
19	6	0	2.059530	2.550553	-1.087266
20	1	0	0.106263	1.919953	-1.727374
21	6	0	2.713783	1.873687	1.133485
22	1	0	1.280260	0.714252	2.230815
23	6	0	3.002029	2.533346	-0.059427
24	1	0	2.276599	3.067004	-2.017595
25	1	0	3.435731	1.869552	1.944534
26	1	0	3.955648	3.037314	-0.186450
27	8	0	1.487663	-1.696867	-0.036492
28	6	0	2.726916	-1.520463	0.425987
29	8	0	3.084459	-1.650011	1.575909
30	8	0	3.498334	-1.187269	-0.600687
31	6	0	4.874635	-0.900254	-0.283065
32	1	0	5.360714	-1.823464	0.046738
33	1	0	4.903081	-0.179634	0.538666
34	6	0	5.514541	-0.342631	-1.533004
35	1	0	6.564924	-0.112027	-1.329346
36	1	0	5.471877	-1.065687	-2.353538
37	1	0	5.011694	0.577609	-1.847111
38	1	0	-4.571289	-2.464154	-0.918896
39	1	0	0.811849	-1.440435	1.913355
40	1	0	0.164386	-2.847833	1.056326

Sum of electronic and zero-point Energies= -1432.316977

Sum of electronic and thermal Free Energies= -1432.369815

The number of imaginary frequencies: 0

TS3

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.488476	0.627937	0.450332
2	6	0	5.673072	-0.740310	0.266860
3	6	0	4.570852	-1.567949	0.065120
4	6	0	3.284449	-1.033076	0.052807
5	6	0	3.082102	0.349640	0.231536
6	6	0	4.207485	1.164720	0.427845

7	6	0	-0.694175	-1.921659	-0.774600
8	6	0	0.546419	-1.167849	-0.416090
9	6	0	0.594990	0.213548	-0.167052
10	6	0	1.748572	0.935907	0.187170
11	1	0	6.343002	1.278798	0.608460
12	1	0	6.670457	-1.168635	0.278179
13	1	0	4.057148	2.230573	0.562941
14	8	0	1.631424	2.235102	0.400441
15	16	0	1.944341	-2.186388	-0.122873
16	6	0	-0.513390	1.156716	-0.271099
17	6	0	-0.353165	2.272696	0.620660
18	6	0	-1.478360	1.220546	-1.279745
19	6	0	-1.071004	3.475581	0.377122
20	1	0	-0.063418	2.071284	1.648078
21	6	0	-2.205944	2.388492	-1.462587
22	1	0	-1.609831	0.400580	-1.975964
23	6	0	-1.980063	3.524280	-0.652405
24	1	0	-0.941151	4.317114	1.049598
25	1	0	-2.929851	2.444507	-2.269639
26	1	0	-2.558282	4.426355	-0.827438
27	8	0	-1.707538	-1.666470	0.221696
28	6	0	-2.956934	-1.509176	-0.219356
29	8	0	-3.335746	-1.650763	-1.361656
30	8	0	-3.712295	-1.169437	0.816525
31	6	0	-5.104520	-0.930147	0.520586
32	1	0	-5.537602	-1.842390	0.100659
33	1	0	-5.171114	-0.136216	-0.228820
34	6	0	-5.777183	-0.534664	1.814322
35	1	0	-6.838119	-0.344386	1.624233
36	1	0	-5.697173	-1.333728	2.557912
37	1	0	-5.330712	0.376321	2.224887
38	1	0	4.715617	-2.635112	-0.080764
39	1	0	-1.085127	-1.641609	-1.755854
40	1	0	-0.510117	-3.000092	-0.795090

Sum of electronic and zero-point Energies= -1432.291033
Sum of electronic and thermal Free Energies= -1432.344645
The number of imaginary frequencies: 1
The imaginary frequency= -271.21

PC3

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	5.422788	-0.177121	0.741565
2	6	0	5.403702	-1.526424	0.389585
3	6	0	4.208866	-2.125251	-0.005314
4	6	0	3.032214	-1.383162	-0.047087
5	6	0	3.037048	-0.013995	0.305847
6	6	0	4.255435	0.570847	0.699381
7	6	0	-1.006615	-1.483414	-1.116222
8	6	0	0.323556	-1.007419	-0.637651
9	6	0	0.572168	0.297679	-0.213217
10	6	0	1.827373	0.743716	0.246418
11	1	0	6.351764	0.293271	1.049022
12	1	0	6.314375	-2.116152	0.419108
13	1	0	4.266669	1.621210	0.970488
14	8	0	1.844949	2.066502	0.566623
15	16	0	1.556739	-2.253198	-0.527410
16	6	0	-0.283596	1.456061	-0.197592
17	6	0	0.471962	2.501845	0.577282
18	6	0	-1.488278	1.790073	-0.800818
19	6	0	0.247727	3.895268	0.097563
20	1	0	0.154820	2.448617	1.638540
21	6	0	-1.836842	3.136605	-0.913261
22	1	0	-2.123710	1.044341	-1.266809
23	6	0	-0.916625	4.173479	-0.538998
24	1	0	0.959186	4.666099	0.376672
25	1	0	-2.768934	3.408235	-1.398077
26	1	0	-1.157535	5.199025	-0.804466
27	8	0	-1.938769	-1.418976	-0.014132
28	6	0	-3.223235	-1.268994	-0.341992
29	8	0	-3.663310	-1.184651	-1.468403
30	8	0	-3.928860	-1.222009	0.779197
31	6	0	-5.352523	-1.044819	0.614403
32	1	0	-5.742493	-1.873144	0.016316
33	1	0	-5.529169	-0.111016	0.073269
34	6	0	-5.964333	-1.014764	1.995413
35	1	0	-7.046805	-0.880351	1.905339
36	1	0	-5.775435	-1.951868	2.528199
37	1	0	-5.560933	-0.185342	2.584546
38	1	0	4.197308	-3.176202	-0.281675
39	1	0	-1.377031	-0.866190	-1.938452
40	1	0	-0.966735	-2.517558	-1.471563

Sum of electronic and zero-point Energies= -1432.370107

Sum of electronic and thermal Free Energies= -1432.316729

The number of imaginary frequencies: 0

TS-PPG(S_0) in MeCN

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.320533	1.584642	-0.241996
2	6	0	-5.661444	0.242803	-0.083710
3	6	0	-4.666040	-0.724279	0.008719
4	6	0	-3.334884	-0.327619	-0.059573
5	6	0	-2.969859	1.011369	-0.212091
6	6	0	-3.986214	1.965885	-0.301546
7	6	0	0.542664	-1.772510	0.483947
8	6	0	-0.569390	-0.781092	0.211058
9	6	0	-0.425814	0.548764	0.104954
10	6	0	-1.555299	1.483862	-0.234466
11	1	0	-6.098658	2.337542	-0.313055
12	1	0	-6.703419	-0.054549	-0.029309
13	1	0	-3.712072	3.009252	-0.410628
14	8	0	-1.306041	2.647951	-0.487530
15	6	0	0.898096	1.198630	0.323595
16	6	0	1.576905	1.799586	-0.740781
17	6	0	1.467868	1.202973	1.597598
18	6	0	2.820575	2.383546	-0.531727
19	1	0	1.136866	1.793642	-1.732895
20	6	0	2.712063	1.795288	1.805008
21	1	0	0.939066	0.740187	2.426056
22	6	0	3.391225	2.382751	0.741431
23	1	0	3.346627	2.841095	-1.364394
24	1	0	3.149422	1.792102	2.798842
25	1	0	4.363008	2.840595	0.901801
26	8	0	1.621070	-1.516552	-0.409793
27	6	0	2.842305	-1.432666	0.138924
28	8	0	3.121815	-1.693863	1.286209
29	8	0	3.676678	-1.032785	-0.805359
30	6	0	5.040551	-0.819343	-0.383292
31	1	0	5.474783	-1.783100	-0.101611
32	1	0	5.036413	-0.167379	0.494113
33	6	0	5.773887	-0.188130	-1.542897
34	1	0	6.816605	-0.016051	-1.258232
35	1	0	5.758299	-0.841093	-2.421038
36	1	0	5.323914	0.773521	-1.808962
37	1	0	-4.925828	-1.770653	0.134286

38	1	0	0.878255	-1.687236	1.519741
39	1	0	0.208388	-2.800270	0.323101
40	16	0	-2.120561	-1.614012	-0.035935
41	8	0	-2.356647	-2.463012	1.132905
42	8	0	-2.072210	-2.255510	-1.351655

Sum of electronic and zero-point Energies= -1582.436956
Sum of electronic and thermal Free Energies= -1582.491683
The number of imaginary frequencies: 0

TS-PPG(S_0) in MeOH

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.319626	1.604307	-0.199347
2	6	0	-5.665080	0.261054	-0.071086
3	6	0	-4.673396	-0.712074	-0.000627
4	6	0	-3.342412	-0.316376	-0.061160
5	6	0	-2.971146	1.024510	-0.184300
6	6	0	-3.984240	1.983668	-0.251520
7	6	0	0.529106	-1.798058	0.427009
8	6	0	-0.574647	-0.790111	0.183015
9	6	0	-0.427228	0.540877	0.102887
10	6	0	-1.556672	1.487847	-0.197818
11	1	0	-6.095286	2.361254	-0.252551
12	1	0	-6.708005	-0.033954	-0.022416
13	1	0	-3.709835	3.029288	-0.336419
14	8	0	-1.300659	2.660078	-0.414046
15	6	0	0.903660	1.178604	0.310925
16	6	0	1.569082	1.785360	-0.758768
17	6	0	1.495304	1.157369	1.574746
18	6	0	2.824305	2.349604	-0.564724
19	1	0	1.110703	1.797357	-1.742851
20	6	0	2.751840	1.728720	1.765549
21	1	0	0.975955	0.689409	2.406313
22	6	0	3.418508	2.321896	0.697099
23	1	0	3.340899	2.811873	-1.400661
24	1	0	3.208640	1.704843	2.750344
25	1	0	4.400079	2.762766	0.845054
26	8	0	1.627089	-1.501560	-0.431615
27	6	0	2.836493	-1.421340	0.137352
28	8	0	3.102808	-1.717815	1.282289
29	8	0	3.678888	-0.973503	-0.774471

30	6	0	5.048310	-0.793682	-0.339546
31	1	0	5.460988	-1.774746	-0.088657
32	1	0	5.046507	-0.168184	0.556805
33	6	0	5.791774	-0.139279	-1.478388
34	1	0	6.835958	0.009002	-1.185832
35	1	0	5.769161	-0.766593	-2.374946
36	1	0	5.356776	0.836438	-1.717011
37	1	0	-4.937298	-1.760011	0.102863
38	1	0	0.841163	-1.767198	1.473122
39	1	0	0.199620	-2.814770	0.201725
40	16	0	-2.134178	-1.603963	-0.056476
41	8	0	-2.366402	-2.467782	1.105398
42	8	0	-2.100821	-2.245763	-1.374937

Sum of electronic and zero-point Energies= -1582.435916
Sum of electronic and thermal Free Energies= -1582.490095
The number of imaginary frequencies: 0

TS-PPG(S_0) in H_2O

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.307609	1.621125	-0.234238
2	6	0	-5.659713	0.279124	-0.112599
3	6	0	-4.672640	-0.697427	-0.027820
4	6	0	-3.339445	-0.306766	-0.067546
5	6	0	-2.961519	1.032946	-0.184171
6	6	0	-3.970273	1.995472	-0.265793
7	6	0	0.525608	-1.800569	0.451916
8	6	0	-0.576426	-0.791678	0.204458
9	6	0	-0.422666	0.538586	0.123965
10	6	0	-1.545996	1.491676	-0.178193
11	1	0	-6.079237	2.380652	-0.298789
12	1	0	-6.703827	-0.012268	-0.080452
13	1	0	-3.691218	3.039782	-0.346001
14	8	0	-1.283616	2.665866	-0.381461
15	6	0	0.912160	1.167678	0.332144
16	6	0	1.580605	1.769286	-0.738533
17	6	0	1.505239	1.142237	1.595167
18	6	0	2.840286	2.324215	-0.546539
19	1	0	1.120498	1.784368	-1.721444
20	6	0	2.766287	1.704147	1.783918
21	1	0	0.983568	0.677078	2.426450

22	6	0	3.436150	2.291691	0.714336
23	1	0	3.360033	2.780688	-1.383223
24	1	0	3.224282	1.676966	2.767604
25	1	0	4.421544	2.723476	0.860323
26	8	0	1.610978	-1.525784	-0.431166
27	6	0	2.830159	-1.437325	0.120205
28	8	0	3.114769	-1.729690	1.262357
29	8	0	3.656922	-0.987073	-0.806081
30	6	0	5.028147	-0.781280	-0.385672
31	1	0	5.468415	-1.756572	-0.162885
32	1	0	5.022007	-0.175804	0.523767
33	6	0	5.738624	-0.081133	-1.518071
34	1	0	6.782352	0.085318	-1.235664
35	1	0	5.718754	-0.686134	-2.429336
36	1	0	5.276174	0.888984	-1.724829
37	1	0	-4.942147	-1.744048	0.070310
38	1	0	0.855282	-1.747247	1.491223
39	1	0	0.188323	-2.820034	0.255288
40	16	0	-2.137405	-1.599737	-0.042707
41	8	0	-2.384926	-2.456302	1.122069
42	8	0	-2.095148	-2.250945	-1.357047

Sum of electronic and zero-point Energies= -1582.431269
Sum of electronic and thermal Free Energies= -1582.484885
The number of imaginary frequencies: 0

TS-PPG(S_0) with 1H_2O

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.223177	1.433381	0.956783
2	6	0	5.590382	0.169904	0.500889
3	6	0	4.624112	-0.708577	0.020478
4	6	0	3.295982	-0.300515	0.005738
5	6	0	2.904338	0.964543	0.453055
6	6	0	3.891739	1.829364	0.929144
7	6	0	-0.487804	-1.415924	-1.398164
8	6	0	0.607539	-0.576164	-0.778275
9	6	0	0.440607	0.674928	-0.326625
10	6	0	1.501160	1.453566	0.400199
11	1	0	5.978615	2.116536	1.329537
12	1	0	6.630651	-0.136222	0.515158
13	1	0	3.602332	2.817742	1.267432

14	8	0	1.195860	2.513760	0.920940
15	6	0	-0.863204	1.374335	-0.503168
16	6	0	-1.738514	1.500461	0.578871
17	6	0	-1.215464	1.890201	-1.751184
18	6	0	-2.966748	2.130511	0.404679
19	1	0	-1.470434	1.074242	1.540265
20	6	0	-2.444577	2.522610	-1.918359
21	1	0	-0.530840	1.789895	-2.588287
22	6	0	-3.321649	2.641004	-0.842987
23	1	0	-3.650179	2.215463	1.244276
24	1	0	-2.717025	2.918925	-2.891479
25	1	0	-4.282011	3.129448	-0.976438
26	8	0	-1.443511	-1.711658	-0.375204
27	6	0	-2.699572	-1.285045	-0.559996
28	8	0	-3.172245	-0.879047	-1.598157
29	8	0	-3.329083	-1.407284	0.598671
30	6	0	-4.702662	-0.946818	0.648069
31	1	0	-5.326732	-1.700133	0.161252
32	1	0	-4.773368	-0.008763	0.094028
33	6	0	-5.049122	-0.764896	2.105468
34	1	0	-6.084431	-0.421472	2.188182
35	1	0	-4.950763	-1.706301	2.653994
36	1	0	-4.395975	-0.015916	2.564455
37	1	0	4.906472	-1.693027	-0.337837
38	1	0	-0.962595	-0.879026	-2.219931
39	1	0	-0.106898	-2.364258	-1.778554
40	16	0	2.104625	-1.493828	-0.523566
41	8	0	2.530627	-2.046986	-1.812957
42	8	0	1.844599	-2.446234	0.563613
43	8	0	-1.194095	-1.081994	2.689061
44	1	0	-2.015890	-1.163317	2.179669
45	1	0	-0.520456	-1.118222	1.995919

Sum of electronic and zero-point Energies= -1658.818992
Sum of electronic and thermal Free Energies= -1658.876247
The number of imaginary frequencies: 0

TS-PPG(S_1) in MeCN

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.210632	1.683896	-0.068381
2	6	0	-5.589205	0.345365	0.046003

3	6	0	-4.620679	-0.652102	0.060532
4	6	0	-3.277810	-0.304400	-0.042460
5	6	0	-2.879560	1.039819	-0.136137
6	6	0	-3.871425	2.034119	-0.152640
7	6	0	0.505590	-1.859523	0.628130
8	6	0	-0.592742	-0.889328	0.291596
9	6	0	-0.426622	0.462284	0.159597
10	6	0	-1.467355	1.387661	-0.128752
11	1	0	-5.967261	2.461963	-0.079037
12	1	0	-6.637639	0.077817	0.124083
13	1	0	-3.581741	3.077949	-0.213441
14	8	0	-1.127594	2.625209	-0.309856
15	6	0	0.892841	1.139659	0.312192
16	6	0	1.400553	1.865078	-0.781796
17	6	0	1.604068	1.108602	1.516196
18	6	0	2.604085	2.561424	-0.660274
19	1	0	0.882504	1.837775	-1.734661
20	6	0	2.802345	1.799051	1.624933
21	1	0	1.208535	0.559107	2.364260
22	6	0	3.305871	2.524475	0.536373
23	1	0	2.995335	3.110415	-1.510744
24	1	0	3.349653	1.781477	2.562052
25	1	0	4.249213	3.053106	0.631603
26	8	0	1.587873	-1.669073	-0.297939
27	6	0	2.809069	-1.526406	0.230834
28	8	0	3.125070	-1.779973	1.371258
29	8	0	3.606414	-1.064782	-0.720794
30	6	0	4.967637	-0.799403	-0.323014
31	1	0	5.452691	-1.747967	-0.074085
32	1	0	4.954595	-0.169203	0.570313
33	6	0	5.645020	-0.107397	-1.482303
34	1	0	6.684089	0.109290	-1.215283
35	1	0	5.641986	-0.740510	-2.375004
36	1	0	5.143151	0.836728	-1.716876
37	1	0	-4.904788	-1.696297	0.147130
38	1	0	0.873186	-1.716577	1.646383
39	1	0	0.157632	-2.891502	0.542385
40	16	0	-2.108103	-1.628241	-0.191413
41	8	0	-2.458258	-2.685998	0.763898
42	8	0	-2.030728	-2.021503	-1.605346

Sum of electronic and zero-point Energies= -1582.320886

Sum of electronic and thermal Free Energies= -1582.375097

The number of imaginary frequencies: 0

TS-PPG(S_1) in MeOH

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.158315	1.746845	-0.078995
2	6	0	-5.564799	0.415107	0.018847
3	6	0	-4.618140	-0.602383	0.035998
4	6	0	-3.267467	-0.277514	-0.046660
5	6	0	-2.840955	1.058857	-0.125646
6	6	0	-3.811490	2.071176	-0.145412
7	6	0	0.487798	-1.914496	0.631213
8	6	0	-0.599547	-0.929248	0.314286
9	6	0	-0.415213	0.423434	0.184327
10	6	0	-1.421132	1.378422	-0.103896
11	1	0	-5.899983	2.539323	-0.091662
12	1	0	-6.619378	0.168150	0.081881
13	1	0	-3.494553	3.107782	-0.196032
14	8	0	-1.035568	2.603317	-0.273669
15	6	0	0.904915	1.088295	0.334832
16	6	0	1.387602	1.841704	-0.760616
17	6	0	1.633646	1.047828	1.529846
18	6	0	2.578060	2.564781	-0.640903
19	1	0	0.872674	1.794826	-1.713690
20	6	0	2.815484	1.760881	1.631126
21	1	0	1.257747	0.480394	2.374839
22	6	0	3.291104	2.518843	0.544453
23	1	0	2.949551	3.131778	-1.487928
24	1	0	3.376970	1.743318	2.559611
25	1	0	4.226998	3.060225	0.639396
26	8	0	1.570363	-1.704456	-0.298601
27	6	0	2.792532	-1.544460	0.215187
28	8	0	3.131972	-1.816470	1.347864
29	8	0	3.563615	-1.033364	-0.729872
30	6	0	4.934127	-0.761390	-0.354463
31	1	0	5.427458	-1.711629	-0.131561
32	1	0	4.929765	-0.144048	0.547976
33	6	0	5.577730	-0.046878	-1.518112
34	1	0	6.619565	0.177834	-1.269137
35	1	0	5.563344	-0.669307	-2.418255
36	1	0	5.060853	0.894662	-1.729818
37	1	0	-4.926226	-1.640955	0.109188
38	1	0	0.862283	-1.795595	1.650004

39	1	0	0.141460	-2.944044	0.519562
40	16	0	-2.122473	-1.621215	-0.186816
41	8	0	-2.509874	-2.686809	0.751711
42	8	0	-2.048583	-2.023728	-1.603404

Sum of electronic and zero-point Energies= -1582.318801
Sum of electronic and thermal Free Energies= -1582.372043
The number of imaginary frequencies: 0

TS-PPG(S_1) in H_2O

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.144877	1.768924	-0.083222
2	6	0	-5.559177	0.439275	0.008080
3	6	0	-4.618224	-0.583322	0.026707
4	6	0	-3.265268	-0.265919	-0.047739
5	6	0	-2.831030	1.068258	-0.121143
6	6	0	-3.795990	2.085702	-0.142242
7	6	0	0.480806	-1.925087	0.630692
8	6	0	-0.601485	-0.933142	0.317861
9	6	0	-0.409736	0.419161	0.191338
10	6	0	-1.409882	1.380423	-0.094318
11	1	0	-5.881619	2.565355	-0.096859
12	1	0	-6.614942	0.197901	0.064942
13	1	0	-3.473257	3.120282	-0.188324
14	8	0	-1.017137	2.605915	-0.258183
15	6	0	0.914075	1.075141	0.343373
16	6	0	1.399674	1.830783	-0.749452
17	6	0	1.644700	1.023671	1.536761
18	6	0	2.595400	2.544762	-0.628780
19	1	0	0.882479	1.791581	-1.701237
20	6	0	2.831339	1.728339	1.639082
21	1	0	1.266461	0.454039	2.378866
22	6	0	3.310270	2.487931	0.554922
23	1	0	2.969881	3.112058	-1.473723
24	1	0	3.394480	1.702635	2.565848
25	1	0	4.250345	3.021007	0.650243
26	8	0	1.558690	-1.729464	-0.309015
27	6	0	2.784566	-1.561923	0.199652
28	8	0	3.131713	-1.837094	1.329755
29	8	0	3.547530	-1.041286	-0.748175
30	6	0	4.911815	-0.739548	-0.369533

31	1	0	5.428990	-1.679847	-0.161555
32	1	0	4.890821	-0.136010	0.541568
33	6	0	5.535781	0.010430	-1.521183
34	1	0	6.571275	0.256529	-1.268211
35	1	0	5.536427	-0.596229	-2.431588
36	1	0	4.995265	0.942156	-1.715158
37	1	0	-4.932917	-1.619804	0.094711
38	1	0	0.864185	-1.803097	1.645350
39	1	0	0.125194	-2.951782	0.527701
40	16	0	-2.127910	-1.616319	-0.183715
41	8	0	-2.523718	-2.679036	0.755683
42	8	0	-2.054958	-2.023889	-1.599849

Sum of electronic and zero-point Energies= -1582.314540
Sum of electronic and thermal Free Energies= -1582.367641
The number of imaginary frequencies: 0

TS-PPG(S_1) with $1H_2O$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.135188	1.793227	0.325652
2	6	0	5.565176	0.478971	0.138005
3	6	0	4.635641	-0.539902	-0.034211
4	6	0	3.278360	-0.233924	-0.016310
5	6	0	2.829496	1.086630	0.152666
6	6	0	3.782427	2.099687	0.328708
7	6	0	-0.412998	-1.827040	-1.059067
8	6	0	0.654979	-0.866806	-0.632635
9	6	0	0.440816	0.466368	-0.382452
10	6	0	1.409193	1.397291	0.064909
11	1	0	5.863050	2.586646	0.458993
12	1	0	6.624359	0.246394	0.125585
13	1	0	3.448996	3.124806	0.449531
14	8	0	0.995514	2.596842	0.328318
15	6	0	-0.875416	1.130933	-0.554040
16	6	0	-1.425890	1.787070	0.573386
17	6	0	-1.532112	1.194639	-1.788449
18	6	0	-2.606993	2.524459	0.445862
19	1	0	-0.979002	1.635235	1.548265
20	6	0	-2.706030	1.919648	-1.897137
21	1	0	-1.103961	0.704644	-2.656182
22	6	0	-3.246289	2.584652	-0.779591

23	1	0	-3.029883	3.015068	1.315528
24	1	0	-3.210127	1.986331	-2.855295
25	1	0	-4.174714	3.136057	-0.884028
26	8	0	-1.452142	-1.820665	-0.048942
27	6	0	-2.697751	-1.525281	-0.445949
28	8	0	-3.114716	-1.594505	-1.582341
29	8	0	-3.379887	-1.147244	0.620861
30	6	0	-4.738474	-0.700489	0.393861
31	1	0	-5.343973	-1.566943	0.116177
32	1	0	-4.732576	0.012383	-0.434566
33	6	0	-5.206689	-0.061878	1.678701
34	1	0	-6.232927	0.294378	1.549524
35	1	0	-5.190223	-0.780292	2.503620
36	1	0	-4.572796	0.792226	1.937821
37	1	0	4.962366	-1.564887	-0.177592
38	1	0	-0.854045	-1.555443	-2.019215
39	1	0	-0.032118	-2.846178	-1.135346
40	16	0	2.143197	-1.591904	-0.078322
41	8	0	2.614746	-2.573145	-1.069729
42	8	0	1.965925	-2.115221	1.289974
43	8	0	-0.958544	-0.679648	2.686885
44	1	0	-1.822263	-0.248256	2.734065
45	1	0	-0.974286	-1.082554	1.804617

Sum of electronic and zero-point Energies= -1658.701441

Sum of electronic and thermal Free Energies= -1658.758507

The number of imaginary frequencies: 0

Notes and references

1 S. Kitani, K. Sugawara, K. Tsutsumi, T. Morimoto and K. Kakiuchi, *Chem. Commun.* 2008, **336**, 2103–2105.
2 J. Ma, X. Zhang, N. Basarić and D. L. Phillips, *J. Am. Chem. Soc.,* 2017, **139**, 18349–18357.
3 Y. Hu, F. Zhan, Q. Wang, Y. Sun, C. Yu, X. Zhao, H. Wang, R. Long, G. Zhang, C. Gao, W. Zhang, J. Jiang, Y. Tao and Y. Xiong, *J. Am. Chem. Soc.,* 2020, **142**, 5618–5626.
4 J. Da Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.,* 2008, **10**, 6615–6620.
5 H. B. Schlegel, *J. Comput. Chem.,* 1982, **3**, 214–218.
6 E. Cancès, B. Mennucci, J. Tomasi, *J. Chem. Phys.,* 1997, **107**, 3032–3041.
7 M. E. Casida and M. Huix-Rotllant, *Annu. Rev. Phys. Chem.,* 2012, **63**, 287–323.
8 L. Noodleman, T. Lovell, W. G. Han, J. Li and F. Himo, *Chem. Rev.,* 2004, **104**, 459–508.
9 A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B,* 2009, **113**, 6378–6396.
10 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Jr. Montgomery, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, *Gaussian 16, rev. A*., **03**, Gaussian, Inc.: Wallingford, CT, 2016.
11 Y. Zhang, H. Zhang, C. Ma, J. Li, Y. Nishiyama, H. Tanimoto, T. Morimoto and K. Kakiuchi, *Tetrahedron Lett.,* 2016, **57**, 5179–5184.