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

Electronic Supplementary Information for

Alkylated Green Fluorescent Protein Chromophores: Dynamics in the Gas Phase and in Aqueous Solution

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1 Analysis of the *p*HBDI$^-$ molecular dynamics trajectory

The S_0, S_1, and T_1 TD-DFT energies along the trajectory are plotted in Fig. S1. The relative energies of the three states are shown in panel (a), while (b) shows the S_1/S_0 and S_1/T_1 energy difference. In the example, the trajectory was propagated for 3395 fs, and the T_1 single-point energies (SCF calculations with triplet multiplicity) were calculated every 10 fs. The trajectory enters the P-trap at ≈1330 fs, when the P-twist angle ϕ reaches 90°. The average S_1/T_1 energy difference during the remaining trajectory is 0.32±0.25 eV. The spin-orbit coupling (SOC) matrix element, and the S_1/T_1 energy difference at the MS-CASPT2 level, were calculated at 10 points with the smallest S_1/T_1 energy difference, and the results provided in Table S1.

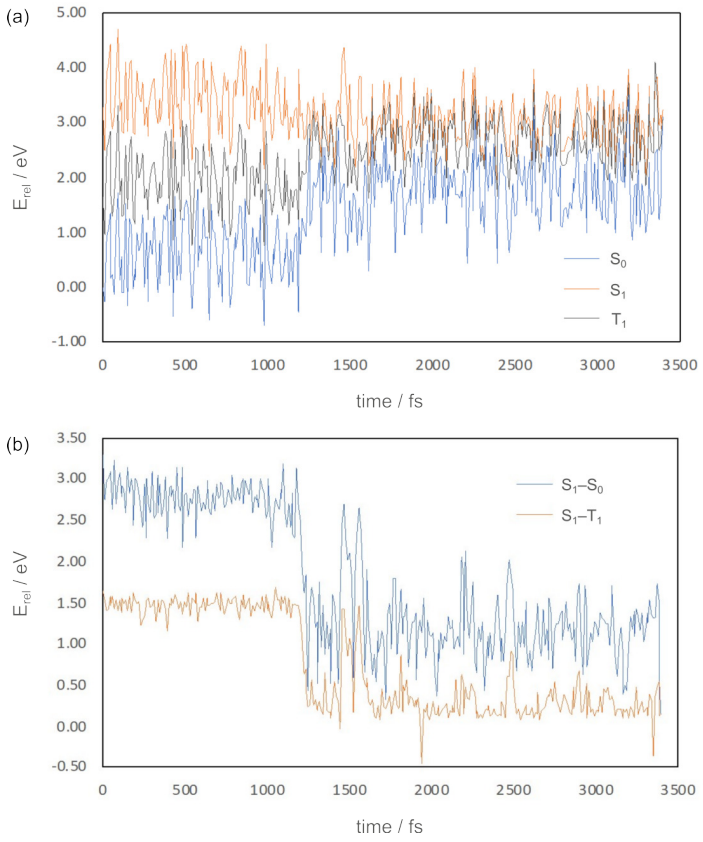

Fig. S1 TD-DFT molecular dynamics: (a) relative S_0, S_1, and T_1 energies along an example molecular dynamics trajectory for *p*HBDI$^-$, and (b) S_1/S_0 and S_1/T_1 energy differences along that same trajectory.

Time / fs	ϕ	ΔE_{TD-DFT} /eV	$\Delta E_{MS-CASPT2}$ / eV	SOC / cm^{-1}
1390	113°	0.09	0.02	0.17
1440	129°	-0.03	-0.18	0.11
1690	70°	0.09	0.01	0.13
1990	93°	0.08	0.01	0.15
2450	104°	0.10	0.00	0.18
2540	95°	0.08	0.00	0.10
2620	97°	0.09	-0.12	0.18
2660	85°	0.09	-0.01	0.14
3200	86°	0.09	-0.01	0.16
3230	85°	0.09	0.01	0.19

Table S1 MS-CASPT2 S_1/T_1 energy difference (in eV), spin-orbit coupling (SOC) elements (in cm^{-1}), and P-twist angle, ϕ, for 10 points along the trajectory with the lowest S_1/T_1 TD-DFT energy difference (in eV).

2 Fluorescence

Fluorescence excitation and emission spectra for *p*HBDI$^-$, 26Me$^-$, 35Me$^-$, and 35Bu$^-$ in ethanol were recorded at $T \approx 77$ K (samples immersed in a liquid nitrogen bath) using an Edinburgh Instruments FS5 spectrofluorometer. Time-resolved fluorescence measurements (time-correlated single-photon counting) at $T \approx 77$ K were performed using pulses of light from an EPL-485 module delivering a wavelength of 485 ± 8 nm with an instrument response function of ≈150 ps (FWHM).

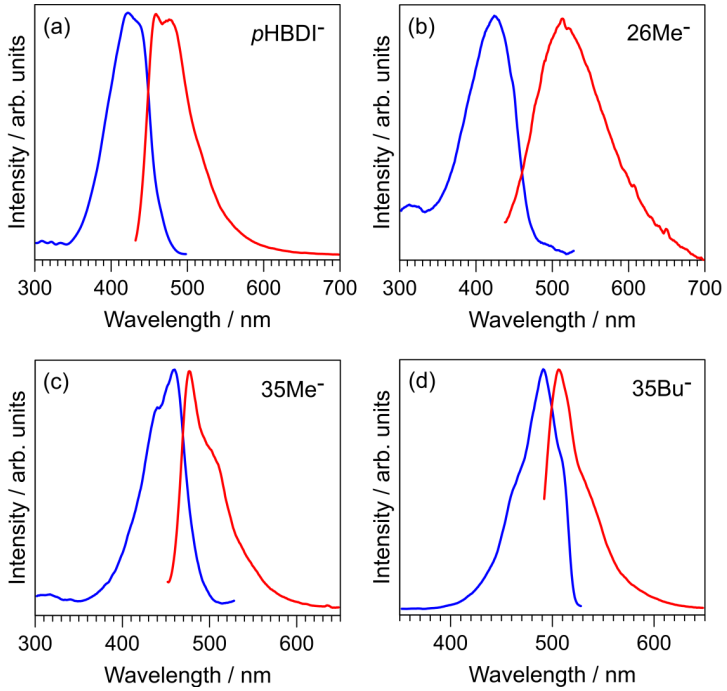

Fig. S2 Fluorescence excitation (blue) and emission (red) spectra recorded in ethanol at $T \approx 77$ K for: (a) *p*HBDI$^-$, (b) 26Me$^-$, (c) 35Me$^-$, and (d) 35Bu$^-$.

	Water	Ethanol			
	300 K	300 K	77 K	τ_1	τ_2
*p*HBDI$^-$	3108	2514	1919	0.36 ± 0.01	2.69 ± 0.01
26Me$^-$	4334	3548	4036	0.26 ± 0.01	3.07 ± 0.03
35Me$^-$	2614	1340	781	-	2.68 ± 0.02
35Bu$^-$	991	341	643	-	2.91 ± 0.01

Table S2 Stokes shifts (in cm^{-1}) for *p*HBDI$^-$, 26Me$^-$, 35Me$^-$, and 35Bu$^-$ in water ($T = 300$ K) and ethanol ($T = 300$ K and $T \approx 77$ K). Also included are the fitted excited-state lifetimes (in ns) from time-resolved fluorescence measurements in ethanol at $T \approx 77$ K. Suitability of single- or double-exponential fits was determined by examining the fit residuals. There was no evidence for phosphorescence or delayed fluorescence.

Species	τ_1^g	$\pm$	τ_2^g	$\pm$	τ_1^w	$\pm$	τ_2^w	$\pm$	τ_1^{eth}	τ_2^{eth}
*p*HBDI$^-$	0.46	0.07	4.64	0.39	0.29	0.04	1.19	0.18	0.25	0.87
26Me$^-$	0.07	0.02	1.58	0.41	0.06	-	-*	-	0.07	0.49
35Me$^-$	0.47	0.07	5.53	0.47	0.45	0.06	2.34	0.12	0.44	2.71
35Bu$^-$	1.28	0.16	9.72	1.11	0.61	0.17	3.19	0.30	0.59	2.97

Table S3 Fitted excited-state lifetimes and associated errors (in ps) from gas-phase time-resolved photoelectron imaging (g), and fluorescence upconversion in water (w) and ethanol (eth, taken from Conyard *et al.*[1], uncertainties not provided). *26Me$^-$ data could not be fit to a double exponential; τ_1^w is close to being limited by the laser cross-correlation (≈55 fs).

3 Modelling microsolvation

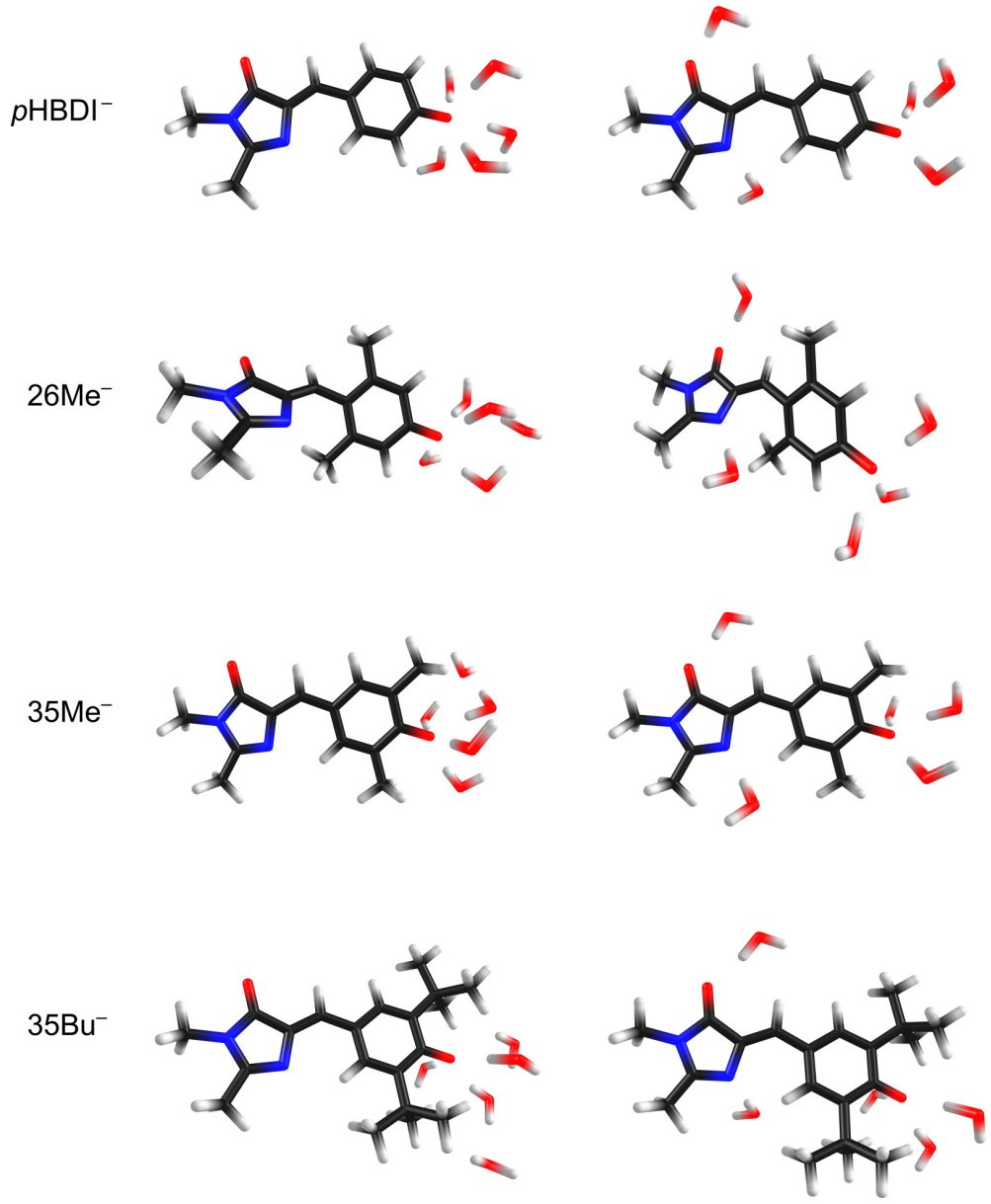

Fig. S3 Microsolvated structures for *p*HBDI$^-$, 26Me$^-$, 35Me$^-$, and 35Bu$^-$ with five explicit water molecules – (left, s1) five water molecules around the phenoxide deprotonation site, and (right, s2) three molecules around the phenoxide deprotonation site and two around the imidazolinone ring. Computed at the MP2/aug-cc-pVDZ level of theory (including the explicit waters) with the SMD implicit solvation model. Cartesian coordinates are given in Section 5.

An intriguing property of the aqueous absorption spectra of the alkylated *p*HBDI anions (Fig. S3a) is that, compared with *p*HBDI$^-$, they show substantial red shifts (ranging from 24 nm for 35Me$^-$ to 64 nm for 35Bu$^-$) with the degree of alkylation (excluding 26Me$^-$). On the other hand, gas-phase photodissociation spectra, which are proxies for the gas-phase absorption spectra, shown negligible differences.[2] We previously assumed this differing environmental behaviour arose because of changes in inductive effects with alkylation.[2] Here, microsolvation of the target anions was modelled using the SMD implicit solvation model combined with five explicit water molecules placed in two configurations (see Fig. S3): (a) with all water molecules surrounding the phenoxide deprotonation site (**1**), and (b) with three molecules surrounding the phenoxide deprotonation site and two coordinated to the imidazolinone ring (**2**). For microsolvated *p*HBDI$^-$ and 35Me$^-$, configuration **1** is more stable (0.06 eV and 0.07 eV lower in energy, respectively), while 26Me$^-$ and 35Bu$^-$ favour configuration **2** (0.03 eV and 0.05 eV lower in energy, respectively). The preference for configuration **2** is attributed

to the twisted ground-state geometry in 26Me$^-$, and the significant steric bulk around the phenoxide deprotonation site in 35Bu$^-$. Calculated vertical excitation wavelengths of the lower energy microsolvated structures (STEOM-DLPNO-CCSD/aug-cc-pVDZ level of theory) reproduced the trends in the absorption spectra in (Fig. S3a), with a mean difference of about 12 nm. This result supports our original hypothesis that the strong red shift in water is, in significant part, due to inductive effects.

4 Dihedral angles

Dihedral angles for single bond as part of the methine bridge for *p*HBDI$^-$ and 26Me$^-$ are given in Table S4. There is a clear twisting of the dihedral angle for 26Me$^-$ upon solvation of both ends of the chromophore (see φ_2).

	φ_g	φ_1	φ_2
*p*HBDI$^-$	0°	0.6°	6.7°
26Me$^-$	19.9°	19.4°	48.1°

Table S4 Computed equilibrium dihedral angles of the bridging single bond for *p*HBDI$^-$ and 26Me$^-$ in the gas phase (φ_g, computed at ωB97X-D/aug-cc-pVTZ level of theory) and aqueous solution (φ_1 and φ_2, computed at MP2/aug-cc-pVDZ level of theory, with the SMD implicit solvation model). The solvated structures have: (**1**) five water molecules around the phenoxide deprotonation site, and (**2**) three water molecules around the phenoxide deprotonation site and two around the imidazolinone ring. In terms of relative energies, *p*HBDI$^-$ favours solvation at site **1**, while 26Me$^-$ favours solvation site **2**. Structures are illustrated in Fig. S3.

5 Electronic structure geometries

Optimised structures (ωB97X-D/aug-cc-pVTZ), Å

Z-*p*HBDI$^-$ – S_0

C	4.271404	0.374736	0.000002
C	3.903653	-1.028333	0.000000
C	2.604634	-1.427705	0.000000
C	1.517043	-0.509509	0.000000
C	1.855403	0.875315	0.000000
C	3.147473	1.295141	0.000000
H	2.372429	-2.488749	-0.000001
H	1.047094	1.594007	-0.000001
C	0.206203	-1.007400	0.000000
H	0.117225	-2.091269	0.000000
O	5.453743	0.759860	-0.000001
C	-1.019844	-0.383970	0.000000
C	-2.268822	-1.118457	0.000000
C	-2.565719	1.115363	0.000000
N	-1.284135	0.993195	0.000000
N	-3.229300	-0.096087	0.000000
C	-3.306502	2.404853	0.000000
H	-3.946965	2.497066	0.880740
H	-2.586454	3.218717	0.000000
H	-3.946966	2.497065	-0.880739
O	-2.546447	-2.314686	0.000000
C	-4.643493	-0.330125	0.000000
H	-5.122252	0.089997	0.887608
H	-5.122253	0.090000	-0.887606
H	-4.784134	-1.410182	-0.000002
H	4.712182	-1.748964	-0.000001
H	3.387172	2.351713	-0.000001

Z-*p*HBDI$^-$ – D_0

C	4.224724	0.389961	0.000002
C	3.897855	-1.032508	-0.000002
C	2.613265	-1.450640	-0.000001
C	1.521037	-0.526773	0.000000
C	1.816102	0.873972	-0.000001
C	3.093897	1.313455	-0.000001
H	2.385989	-2.509549	-0.000002
H	0.990087	1.569140	-0.000001
C	0.209629	-1.048408	0.000000
H	0.114563	-2.128953	0.000000
O	5.387756	0.787458	0.000001
C	-0.989474	-0.388379	0.000000
C	-2.281032	-1.121640	0.000001
C	-2.532582	1.099808	0.000000
N	-1.239059	0.969498	0.000001
N	-3.218585	-0.090073	0.000000
C	-3.245346	2.398617	0.000000
H	-3.884839	2.486665	0.879770
H	-2.519300	3.205238	0.000000
H	-3.884838	2.486664	-0.879771
O	-2.526770	-2.304577	0.000001
C	-4.647098	-0.290122	-0.000001
H	-5.103562	0.144484	0.888740
H	-5.103562	0.144486	-0.888740
H	-4.822006	-1.363435	-0.000002
H	4.726813	-1.726481	-0.000003
H	3.330426	2.368658	-0.000002

Z-*p*HBDI$^-$ – triplet

C	4.245797	0.405079	-0.000007
C	3.925093	-1.002810	0.000000
C	2.640965	-1.452042	-0.000001
C	1.513807	-0.568369	-0.000004
C	1.817182	0.828372	-0.000002
C	3.105676	1.283084	-0.000001
H	2.444923	-2.518697	0.000001
H	0.992495	1.524789	-0.000001
C	0.211165	-1.111523	-0.000003
H	0.117650	-2.189806	-0.000002
O	5.431470	0.824617	0.000010
C	-1.018900	-0.419819	-0.000002
C	-2.305670	-1.110638	0.000000
C	-2.544777	1.114084	-0.000001
N	-1.237019	0.928358	-0.000003
N	-3.235899	-0.060266	0.000001
C	-3.212672	2.438493	-0.000001
H	-3.847779	2.572868	0.880777
H	-2.448002	3.210970	-0.000002
H	-3.847781	2.572867	-0.880777
O	-2.609516	-2.305832	0.000002
C	-4.656751	-0.252466	0.000004
H	-5.120080	0.183805	0.887630
H	-5.120083	0.183805	-0.887621
H	-4.831572	-1.327318	0.000004
H	4.757948	-1.696002	0.000004
H	3.311589	2.347137	0.000002

E-*p*HBDI$^-$ – S_0

C	-4.246612	0.270218	-0.000001
C	-3.869778	-1.131897	-0.000001
C	-2.569996	-1.521028	0.000000
C	-1.483437	-0.594952	0.000002
C	-1.832956	0.789324	0.000000
C	-3.128757	1.196562	-0.000001
H	-2.332162	-2.580907	0.000000
H	-1.031599	1.515842	0.000000
C	-0.184512	-1.115695	0.000002
H	-0.145947	-2.202734	0.000002
O	-5.431783	0.643879	-0.000002
C	1.091898	-0.582459	0.000003
C	1.583690	0.779932	0.000004
C	3.252142	-0.742171	-0.000001
N	2.190015	-1.466344	0.000005
N	2.975740	0.609765	0.000001
C	4.649279	-1.252793	-0.000005
H	5.200429	-0.913076	0.880681
H	4.621083	-2.339373	-0.000002
H	5.200421	-0.913082	-0.880698
O	1.053747	1.889519	0.000003
C	3.905512	1.700948	-0.000003
H	4.542220	1.687827	0.887752
H	4.542214	1.687827	-0.887762
H	3.316560	2.616885	-0.000001
H	-4.673572	-1.857914	-0.000003
H	-3.374482	2.251636	-0.000002

Z-26Me$^-$ – S_0

C	2.382208	-1.080471	-0.240663
C	2.963825	1.022083	0.305348
C	1.233401	-0.200224	-0.097524
C	3.862128	2.156387	0.649276
H	4.557922	2.375394	-0.164629
H	3.253094	3.036136	0.839127
H	4.458472	1.938439	1.538830
C	4.834799	-0.655851	0.000542
H	5.311469	-0.528199	0.975244
H	4.834380	-1.714158	-0.256675
H	5.414425	-0.108756	-0.746578
N	1.680251	1.083401	0.244933
N	3.465223	-0.233138	0.021606
C	-0.041636	-0.721497	-0.185107
H	0.044335	-1.797448	-0.294339
C	-1.369167	-0.258304	-0.124619
C	-1.811451	1.098858	-0.322516
C	-2.394865	-1.241976	0.137759
C	-3.127511	1.426357	-0.189482
C	-3.698497	-0.882686	0.288435
C	-4.159887	0.480128	0.160333
H	-3.453457	2.443221	-0.376649
H	-4.451614	-1.628585	0.515160
O	2.499739	-2.272151	-0.513073
C	-2.047621	-2.702892	0.296349
H	-1.577365	-3.107930	-0.602109
H	-1.355919	-2.871270	1.123240
H	-2.951547	-3.278954	0.488087
C	-0.865785	2.175441	-0.776727
H	-0.199200	2.489564	0.022171
H	-0.218622	1.817556	-1.578554
H	-1.430849	3.034584	-1.137970
O	-5.351426	0.804208	0.310753

Z-26Me$^-$ – D_0

C	2.451959	-1.005920	-0.429101
C	2.712406	0.986738	0.559498
C	1.162019	-0.296776	-0.180756
C	3.443862	2.118716	1.176987
H	4.140478	2.561617	0.463495
H	2.730657	2.870231	1.500128
H	4.025644	1.778755	2.035106
C	4.815258	-0.343945	0.066618
H	5.211798	-0.364315	1.081437
H	4.982985	-1.312601	-0.398503
H	5.336864	0.421036	-0.507844
N	1.428846	0.924410	0.435058
N	3.391907	-0.112071	0.068609
C	-0.022840	-0.868744	-0.458410
H	0.061878	-1.891117	-0.811946
C	-1.362362	-0.354814	-0.260026
C	-1.750689	0.967310	-0.640453
C	-2.325293	-1.259326	0.299954
C	-3.031329	1.372030	-0.398191
C	-3.588560	-0.825817	0.555583
C	-4.013125	0.519706	0.234458
H	-3.367690	2.357143	-0.693707
H	-4.324461	-1.473997	1.012676
O	2.683594	-2.080653	-0.926601
C	-1.928485	-2.667293	0.650786
H	-1.648926	-3.235464	-0.238437
H	-1.073930	-2.685228	1.327605
H	-2.755390	-3.186307	1.129908
C	-0.815463	1.894590	-1.364403
H	-0.108108	2.347751	-0.673269
H	-0.232649	1.361076	-2.115266
H	-1.380690	2.680207	-1.861487
O	-5.162080	0.913917	0.470248

Z-26Me$^-$ – triplet

C	2.464772	-1.015520	-0.390047
C	2.769362	0.997126	0.544643
C	1.204595	-0.326045	-0.149719
C	3.478744	2.172763	1.107856
H	4.136219	2.643009	0.369956
H	2.738422	2.901021	1.429346
H	4.099133	1.900304	1.966776
C	4.837580	-0.346059	0.039835
H	5.267384	-0.352400	1.044341
H	4.978864	-1.326978	-0.411943
H	5.361643	0.401705	-0.559830
N	1.462518	0.887857	0.433815
N	3.425815	-0.101523	0.070466
C	-0.042473	-0.927290	-0.402812
H	0.038482	-1.992418	-0.573311
C	-1.355812	-0.390068	-0.229525
C	-1.735628	0.943770	-0.608050
C	-2.392123	-1.248109	0.289253
C	-3.008066	1.390476	-0.375047
C	-3.655522	-0.777801	0.499115
C	-4.039247	0.577271	0.207496
H	-3.295403	2.393183	-0.670714
H	-4.421027	-1.421087	0.917989
O	2.735227	-2.122723	-0.865889
C	-2.065978	-2.671972	0.643013
H	-1.791892	-3.253338	-0.240959
H	-1.213369	-2.720314	1.323193
H	-2.922229	-3.155550	1.112773
C	-0.778463	1.830432	-1.351135
H	0.000794	2.213490	-0.694255
H	-0.269667	1.261756	-2.133103
H	-1.312645	2.663014	-1.809720
O	-5.198163	1.008526	0.422169

E-26Me$^-$ – S_0

C	1.797331	-0.707459	-0.423643
C	3.416610	0.698287	0.283300
C	1.261717	0.482976	0.206278
C	4.796096	1.196407	0.531869
H	5.364433	1.282261	-0.397716
H	4.732546	2.175990	0.998467
H	5.350568	0.524804	1.192254
C	4.148215	-1.438887	-0.850237
H	4.821202	-1.812370	-0.075147
H	3.588158	-2.273431	-1.269511
H	4.745840	-0.982138	-1.642958
N	2.331907	1.319850	0.584955
N	3.185557	-0.521006	-0.315412
C	-0.028483	0.978293	0.287656
H	0.000306	2.052726	0.441110
C	-1.317557	0.431263	0.191962
C	-1.685054	-0.919718	0.534350
C	-2.387165	1.318258	-0.205763
C	-2.973913	-1.341998	0.391762
C	-3.655070	0.860145	-0.372358
C	-4.039053	-0.510917	-0.110908
H	-3.250372	-2.344226	0.698630
H	-4.440699	1.524696	-0.713665
O	1.304476	-1.667403	-1.008971
C	-2.109403	2.770945	-0.504395
H	-1.719770	3.294923	0.371847
H	-1.374669	2.889556	-1.302386
H	-3.027856	3.270873	-0.808607
C	-0.703354	-1.855469	1.179752
H	-0.079792	-2.339313	0.429350
H	-0.032595	-1.321206	1.854459
H	-1.236886	-2.617128	1.748015
O	-5.202995	-0.918930	-0.272115

Z-35Me$^-$ – S_0

C	-2.796735	-1.190533	0.000005
C	-3.116488	1.040137	0.000001
C	-1.555437	-0.443684	0.000018
C	-3.869858	2.322341	-0.000009
H	-4.511239	2.408552	0.880721
H	-3.157648	3.143108	0.000004
H	-4.511211	2.408555	-0.880758
C	-5.179345	-0.426356	-0.000026
H	-5.662493	-0.011169	-0.887629
H	-5.308842	-1.507829	-0.000026
H	-5.662517	-0.011166	0.887562
N	-1.833655	0.930604	0.000016
N	-3.767712	-0.177888	-0.000007
C	-0.323262	-1.056345	0.000019
H	-0.403326	-2.140876	0.000015
C	0.983724	-0.548355	0.000018
C	1.306669	0.837185	0.000018
C	2.073929	-1.460642	0.000009
C	2.592492	1.283022	0.000006
C	3.376047	-1.065300	-0.000003
C	3.709308	0.349157	-0.000010
O	-3.062857	-2.389659	0.000003
O	4.892695	0.742852	-0.000021
H	1.844560	-2.523402	0.000010
C	4.516220	-2.037677	-0.000015
H	5.156817	-1.887625	-0.872146
H	5.156842	-1.887618	0.872096
H	4.155062	-3.067575	-0.000006
C	2.930735	2.743230	0.000003
H	2.026896	3.353763	0.000021
H	3.535596	3.002657	0.871988
H	3.535565	3.002661	-0.872002
H	0.488807	1.546308	0.000027

Z-35Me$^-$ – D_0

C	-2.804650	-1.198142	0.000004
C	-3.081756	1.021135	0.000002
C	-1.522050	-0.450728	0.000000
C	-3.811115	2.311168	0.000001
H	-4.451566	2.391871	0.879805
H	-3.094840	3.126551	0.000001
H	-4.451564	2.391871	-0.879805
C	-5.179692	-0.394710	-0.000001
H	-5.641937	0.034217	-0.888660
H	-5.341521	-1.470136	0.000001
H	-5.641939	0.034220	0.888656
N	-1.788226	0.906374	0.000001
N	-3.754117	-0.177699	0.000001
C	-0.317556	-1.097365	-0.000003
H	-0.402938	-2.178769	-0.000002
C	0.992755	-0.565614	-0.000005
C	1.271664	0.833506	-0.000003
C	2.084592	-1.483607	-0.000002
C	2.542522	1.304005	-0.000005
C	3.376445	-1.075802	-0.000004
C	3.673181	0.363846	-0.000023
O	-3.038573	-2.384134	0.000002
O	4.833595	0.768676	0.000012
H	1.857618	-2.543653	0.000003
C	4.533397	-2.017971	0.000007
H	5.165274	-1.846871	-0.872191
H	5.165276	-1.846850	0.872199
H	4.197986	-3.053423	0.000019
C	2.866324	2.761054	0.000004
H	1.959756	3.362889	0.000016
H	3.468177	3.019137	0.872142
H	3.468163	3.019150	-0.872139
H	0.435910	1.518084	0.000001

Z-35Me$^-$ – triplet

C	-2.828792	-1.190078	0.000001
C	-3.091596	1.032694	0.000001
C	-1.549988	-0.485694	0.000002
C	-3.775068	2.349390	0.000000
H	-4.411726	2.476580	0.880775
H	-3.019306	3.130648	0.000002
H	-4.411721	2.476581	-0.880780
C	-5.188777	-0.357536	-0.000004
H	-5.657295	0.073467	-0.887606
H	-5.351507	-1.434343	-0.000004
H	-5.657300	0.073467	0.887595
N	-1.783430	0.862032	0.000003
N	-3.770345	-0.149805	-0.000001
C	-0.314387	-1.164031	0.000003
H	-0.397751	-2.243219	0.000002
C	0.985055	-0.610320	0.000002
C	1.271086	0.786876	0.000003
C	2.114757	-1.486768	0.000002
C	2.551600	1.269996	0.000001
C	3.402727	-1.042256	0.000000
C	3.691097	0.379954	-0.000005
O	-3.120924	-2.388541	0.000000
O	4.874268	0.810322	0.000000
H	1.922119	-2.555078	0.000004
C	4.568326	-1.982121	-0.000003
H	5.202163	-1.809904	-0.872027
H	5.202168	-1.809901	0.872017
H	4.236187	-3.020754	0.000000
C	2.831120	2.741734	-0.000001
H	1.903939	3.314686	0.000003
H	3.425260	3.022297	0.872172
H	3.425252	3.022297	-0.872179
H	0.436222	1.472297	0.000005

E-35Me$^-$ – S_0

C	2.129678	0.715986	-0.000004
C	3.776553	-0.829630	0.000000
C	1.618434	-0.638912	-0.000002
C	5.166181	-1.360400	0.000003
H	5.722373	-1.028856	0.880692
H	5.122178	-2.446476	0.000004
H	5.722376	-1.028858	-0.880684
C	4.464406	1.603626	0.000002
H	5.100961	1.581587	-0.887739
H	3.888412	2.527792	0.000001
H	5.100957	1.581587	0.887746
N	2.703836	-1.538276	-0.000001
N	3.519333	0.525787	0.000000
C	0.334514	-1.156405	-0.000001
H	0.359724	-2.243807	0.000000
C	-0.957533	-0.619452	-0.000001
C	-1.282474	0.767694	0.000000
C	-2.052711	-1.532498	-0.000001
C	-2.569025	1.210446	0.000000
C	-3.352841	-1.138569	-0.000001
C	-3.686093	0.277934	-0.000002
O	1.616842	1.834073	-0.000003
O	-4.869593	0.667845	0.000004
H	-1.824934	-2.595697	0.000000
C	-4.493165	-2.110615	0.000000
H	-5.133561	-1.960037	0.872100
H	-5.133562	-1.960038	-0.872100
H	-4.132310	-3.140676	0.000001
C	-2.904407	2.671583	0.000001
H	-1.998625	3.278180	0.000002
H	-3.508587	2.932118	-0.872198
H	-3.508587	2.932116	0.872202
H	-0.466091	1.478416	0.000001

Z-35Bu$^-$ – S_0

C	-3.797305	-1.531565	-0.000002
C	-4.224008	0.681027	0.000001
C	-2.591575	-0.724038	-0.000002
C	-5.038306	1.925111	0.000003
H	-5.682844	1.979135	0.880753
H	-4.366590	2.779260	0.000005
H	-5.682843	1.979140	-0.880748
C	-6.214059	-0.883602	0.000004
H	-6.715950	-0.491889	-0.887630
H	-6.291953	-1.969912	-0.000009
H	-6.715942	-0.491910	0.887652
N	-2.937914	0.635331	-0.000001
N	-4.815529	-0.567523	0.000000
C	-1.332684	-1.271447	-0.000003
H	-1.352699	-2.358675	-0.000003
C	-0.053610	-0.687002	-0.000002
C	0.175658	0.710356	-0.000003
C	1.083259	-1.529519	0.000000
C	1.426255	1.253470	-0.000002
C	2.365958	-1.065077	0.000002
C	2.601373	0.378785	0.000001
O	-4.002177	-2.740974	-0.000003
O	3.761192	0.847600	0.000001
H	0.893538	-2.595807	0.000000
C	3.569126	-2.013134	0.000001
C	1.632868	2.771549	-0.000001
H	-0.699866	1.340100	-0.000005
C	3.147999	-3.486173	0.000000
H	2.562025	-3.742009	0.884781
H	2.562028	-3.742010	-0.884782
H	4.041629	-4.114442	0.000002
C	4.424921	-1.779313	-1.256702
H	4.773540	-0.750468	-1.293010
H	5.289566	-2.450088	-1.254597
H	3.838737	-1.983280	-2.155481
C	4.424924	-1.779316	1.256703
H	5.289565	-2.450096	1.254596
H	4.773547	-0.750473	1.293010
H	3.838741	-1.983281	2.155483
C	0.303813	3.534110	-0.000007
H	-0.296394	3.305875	0.882272
H	0.507583	4.607639	-0.000007
H	-0.296386	3.305873	-0.882290
C	2.410658	3.198356	1.256611
H	2.560703	4.282347	1.256175
H	1.848950	2.933866	2.155207
H	3.378992	2.705788	1.291470
C	2.410670	3.198361	-1.256603
H	3.379009	2.705799	-1.291449
H	1.848976	2.933866	-2.155206
H	2.560708	4.282353	-1.256166

Z-35Bu$^-$ – D_0

C	-3.786115	-1.558061	0.000004
C	-4.189446	0.642131	-0.000008
C	-2.548336	-0.739154	-0.000004
C	-4.989311	1.889572	-0.000014
H	-5.633214	1.934780	0.879806
H	-4.318767	2.743063	-0.000021
H	-5.633219	1.934769	-0.879832
C	-6.203173	-0.890857	0.000010
H	-6.689038	-0.488895	-0.888654
H	-6.303560	-1.973751	0.000013
H	-6.689028	-0.488892	0.888678
N	-2.891543	0.600571	-0.000012
N	-4.792239	-0.593037	0.000002
C	-1.307602	-1.314366	-0.000002
H	-1.328443	-2.398980	0.000002
C	-0.032293	-0.703463	-0.000003
C	0.151420	0.707175	-0.000003
C	1.111725	-1.549288	-0.000003
C	1.381991	1.276431	0.000001
C	2.381082	-1.072449	0.000000
C	2.575383	0.397268	0.000005
O	-3.952527	-2.755397	0.000014
O	3.707461	0.877036	0.000005
H	0.929198	-2.614447	-0.000005
C	3.599392	-1.991720	-0.000002
C	1.566903	2.791671	0.000004
H	-0.739400	1.312229	-0.000003
C	3.193642	-3.468965	-0.000006
H	2.615396	-3.735020	0.886253
H	2.615394	-3.735015	-0.886265
H	4.094259	-4.083163	-0.000008
C	4.445654	-1.740589	-1.260862
H	4.824143	-0.723158	-1.289087
H	5.293816	-2.427473	-1.271741
H	3.855734	-1.920927	-2.161272
C	4.445654	-1.740594	1.260858
H	5.293818	-2.427476	1.271731
H	4.824141	-0.723163	1.289089
H	3.855736	-1.920940	2.161268
C	0.220026	3.522375	0.000002
H	-0.373430	3.285831	0.884313
H	0.401584	4.597532	0.000003
H	-0.373428	3.285833	-0.884311
C	2.334815	3.227168	1.260721
H	2.426945	4.314749	1.272422
H	1.796029	2.926015	2.160884
H	3.330979	2.795584	1.288811
C	2.334820	3.227170	-1.260710
H	3.330977	2.795571	-1.288806
H	1.796028	2.926035	-2.160875
H	2.426967	4.314750	-1.272399

Z-35Bu$^-$ – triplet

C	-3.812787	-1.557181	0.000001
C	-4.200342	0.646362	-0.000001
C	-2.575143	-0.782005	0.000002
C	-4.952306	1.924667	-0.000004
H	-5.594630	2.017098	0.880764
H	-4.238925	2.744804	-0.000002
H	-5.594625	2.017097	-0.880776
C	-6.216558	-0.857323	-0.000002
H	-6.707391	-0.452626	-0.887654
H	-6.319713	-1.941339	-0.000006
H	-6.707390	-0.452633	0.887654
N	-2.882777	0.547546	0.000000
N	-4.811349	-0.570965	-0.000001
C	-1.299462	-1.389967	0.000003
H	-1.320067	-2.472124	0.000004
C	-0.040091	-0.757966	0.000002
C	0.148908	0.652290	0.000002
C	1.141064	-1.558081	0.000002
C	1.386798	1.235475	0.000000
C	2.402633	-1.041174	-0.000001
C	2.587054	0.410228	-0.000005
O	-4.035528	-2.769474	0.000002
O	3.740512	0.920280	-0.000004
H	0.990813	-2.628901	0.000004
C	3.637279	-1.946911	-0.000001
C	1.532108	2.760368	0.000001
H	-0.743434	1.253494	0.000004
C	3.270698	-3.434611	-0.000002
H	2.694795	-3.711834	0.884365
H	2.694798	-3.711833	-0.884372
H	4.187986	-4.027606	-0.000001
C	4.481867	-1.680101	-1.257901
H	4.806732	-0.643577	-1.287139
H	5.360643	-2.331668	-1.262751
H	3.898206	-1.890886	-2.156553
C	4.481866	-1.680104	1.257900
H	5.360641	-2.331672	1.262751
H	4.806733	-0.643580	1.287141
H	3.898204	-1.890889	2.156551
C	0.174598	3.471888	0.000004
H	-0.416482	3.220731	0.881714
H	0.339200	4.552091	0.000008
H	-0.416482	3.220737	-0.881707
C	2.292646	3.214897	1.257661
H	2.386991	4.304897	1.263403
H	1.747579	2.917226	2.155940
H	3.284719	2.772217	1.287685
C	2.292642	3.214899	-1.257660
H	3.284715	2.772218	-1.287689
H	1.747572	2.917231	-2.155938
H	2.386988	4.304900	-1.263400

E-35Bu$^-$ – S_0

C	-3.232192	0.414479	-0.000002
C	-4.781128	-1.227804	0.000001
C	-2.638585	-0.908856	0.000001
C	-6.136745	-1.839849	0.000003
H	-6.710812	-1.540952	-0.880673
H	-6.029074	-2.921361	0.000004
H	-6.710811	-1.540950	0.880679
C	-5.614370	1.161141	-0.000003
H	-6.247981	1.100771	0.887806
H	-5.094387	2.117921	0.000000
H	-6.247975	1.100774	-0.887817
N	-3.668885	-1.871624	0.000002
N	-4.606281	0.141297	-0.000001
C	-1.328332	-1.345199	0.000001
H	-1.285457	-2.431984	0.000002
C	-0.069038	-0.727084	0.000000
C	0.161892	0.672596	0.000000
C	1.073644	-1.569399	0.000000
C	1.413814	1.212521	0.000001
C	2.354295	-1.107275	0.000000
C	2.589246	0.338586	0.000003
O	-2.785919	1.559577	-0.000004
O	3.748986	0.803580	0.000001
H	0.885318	-2.635874	-0.000001
C	3.557219	-2.055480	-0.000001
C	1.621100	2.730965	0.000001
H	-0.711780	1.305931	0.000000
C	3.135975	-3.528548	0.000000
H	2.550066	-3.784238	0.884921
H	2.550064	-3.784238	-0.884921
H	4.029622	-4.156785	-0.000002
C	4.412925	-1.821863	-1.256788
H	4.762642	-0.793440	-1.292731
H	5.276819	-2.493588	-1.255099
H	3.826395	-2.024600	-2.155615
C	4.412926	-1.821862	1.256785
H	5.276822	-2.493584	1.255095
H	4.762639	-0.793437	1.292729
H	3.826397	-2.024601	2.155613
C	0.291553	3.491803	0.000003
H	-0.311913	3.262785	0.878961
H	0.495460	4.565505	0.000001
H	-0.311918	3.262783	-0.878951
C	2.399250	3.157576	1.256603
H	2.545111	4.242093	1.256838
H	1.837759	2.891562	2.154852
H	3.369806	2.669379	1.292481
C	2.399246	3.157575	-1.256604
H	3.369801	2.669375	-1.292488
H	1.837750	2.891564	-2.154851
H	2.545110	4.242092	-1.256838

*p*HBDI$^-$ P-twisted minimum (TD-CAM-B3LYP/6-311G(d,p))

C	3.436305	-0.265705	1.021087
C	2.200924	-0.782109	0.784572
C	1.489307	-0.533339	-0.42077
C	2.119514	0.313963	-1.37274
C	3.353573	0.847291	-1.169258
C	4.100735	0.584488	0.048483
H	3.977733	-0.46222	1.939066
H	1.718685	-1.41024	1.522939
H	1.574918	0.524171	-2.284609
H	3.832562	1.488583	-1.899843
C	0.177872	-1.139732	-0.67955
C	-2.422803	0.924175	0.465959
C	-1.025742	-0.53097	-0.325183
N	-1.147934	0.701838	0.305552
C	-2.331772	-1.090176	-0.560319
O	-2.732204	-2.143859	-1.080642
N	-3.193986	-0.105538	-0.027822
C	-4.620296	-0.24117	-0.045183
H	-4.822165	-1.201196	-0.523863
H	-5.049002	-0.248217	0.963131
H	-5.106076	0.553887	-0.621804
C	-3.008081	2.13416	1.102523
H	-3.663059	2.691823	0.421223
H	-3.603123	1.89403	1.9927
H	-2.187313	2.784432	1.40136
O	5.231114	1.055347	0.245106
H	0.132763	-2.103869	-1.167832

Initial conditions for the *p*HBDI$^-$ trajectory, a.u.

Initial geometry

C	-6.8554552	3.36651531	-0.0558245
C	-4.1850885	3.59913739	0.0938121
C	-2.547782	1.59201731	-0.065468
C	-3.6248638	-0.871747	-0.0897068
C	-6.268443	-1.2571249	0.0660379
C	-8.0229158	0.96776151	0.02409941
H	-7.9434199	5.08359109	0.37760848
H	-3.4656414	5.66205992	0.4745052
H	-2.8004976	-2.6921306	-0.2290899
H	-6.8709253	-2.9045082	0.00455078
C	-0.0470404	2.02109217	-0.1325689
C	4.28318783	-2.953226	-0.0222483
C	2.06071959	0.43294397	-0.0154507
N	1.93601987	-2.2887124	-0.0394873
C	4.51839212	1.21386888	-0.0443391
O	5.66562324	3.30061268	0.08553106
N	6.10481783	-1.0777859	0.00083484
C	8.78016351	-1.046758	0.02453483
H	9.20527452	1.02008525	-0.0222824
H	9.60114732	-1.8666526	1.80458411
H	9.29453925	-2.1455741	-1.7634763
C	4.88620855	-5.9008204	0.04520826
H	6.52299611	-6.3253257	-1.57246
H	6.44670215	-5.9163051	1.50729139
H	3.18013139	-6.9755803	0.52403356
O	-10.415903	0.46860554	0.02329024
H	0.58000516	3.63224764	-0.2325662

Initial velocity

0.00051765	0.0005276	-0.00020267
-0.00083514	-0.0005174	-0.00001454
-0.00029271	0.00010162	0.00003761
0.00031653	-0.00010989	-0.00011721
-0.00064499	-0.00035548	0.00004872
-0.00020974	-0.0000025	0.00030013
0.00002409	-0.00201294	-0.0001449
-0.00116742	-0.00201812	0.00049628
-0.00091149	0.001294	0.00070374
0.00251576	0.00071225	0.00079556
0.00035643	0.00059607	-0.00008579
0.00014629	-0.0000004	0.0000273
0.00039408	-0.00019282	-0.00011987
-0.00025945	0.00038031	-0.00001446
-0.00091889	-0.00038379	0.00029576
0.00031863	0.00023935	-0.00018191
-0.00017424	-0.00022793	0.00019037
0.00037398	-0.00003524	0.00021632
0.00152554	0.00215593	-0.00075256
-0.00050081	-0.0006291	-0.00137037
0.00254171	-0.00092875	-0.00058964
0.00014162	-0.00015791	-0.0004474
0.00101217	0.00076869	0.00364464
-0.0007202	0.00111514	-0.00311959
-0.00066943	0.00029492	0.00162438
0.00029975	0.00022042	-0.00010564
0.00020494	-0.00508433	0.0010969

Structures for SOC calculations, Å

$t = 1390$ fs

C	3.115724	0.468279	1.18341
C	2.112601	-0.253262	0.78772
C	1.455784	-0.402556	-0.5587
C	2.342547	-0.318223	-1.629595
C	3.541079	0.32326	-1.255954
C	3.992416	0.748413	0.030915
H	3.677352	0.669151	1.926719
H	1.47288	-0.495448	1.548568
H	2.253875	-0.794064	-2.614613
H	4.461278	0.377288	-1.893531
C	0.149873	-0.958298	-0.750652
C	-2.59965	0.98051	0.45464
C	-1.077805	-0.191778	-0.640095
N	-1.304081	0.930812	0.153907
C	-2.405798	-0.662336	-0.959053
O	-2.758971	-1.474313	-1.978172
N	-3.270034	-0.032135	-0.150278
C	-4.69165	-0.276359	-0.055557
H	-5.177759	0.70049	0.067627
H	-4.897791	-0.706626	-0.935534
H	-4.859672	-0.871528	0.796865
C	-3.035714	1.763745	1.585514
H	-3.628967	2.598238	1.1313
H	-3.567809	1.09802	2.285941
H	-2.002454	2.093455	1.972987
O	5.155236	0.979208	0.155645
H	-0.020041	-2.054094	-0.625742

$t = 1440$ fs

C	3.087084	0.463904	0.994472
C	1.966888	-0.074006	0.766416
C	1.381394	-0.44138	-0.478449
C	2.265148	-0.335125	-1.519759
C	3.642204	-0.021296	-1.213922
C	4.085929	0.546096	0.001551
H	3.538107	0.838565	2.104273
H	1.4992	-0.260186	1.731399
H	2.229653	-0.538689	-2.542839
H	4.391578	-0.228045	-1.926226
C	-0.010934	-0.94179	-0.979529
C	-2.43789	0.931049	0.539492
C	-1.148561	-0.250081	-0.631037
N	-1.208657	0.721819	0.373957
C	-2.417937	-0.370427	-1.236465
O	-2.895264	-1.095178	-2.063466
N	-3.284186	0.413188	-0.406265
C	-4.431943	-0.356856	0.104705
H	-5.226361	0.326182	0.33191
H	-4.654946	-0.888992	-0.947717
H	-3.86273	-0.989851	0.855691
C	-3.089355	1.850912	1.600836
H	-4.119704	2.050371	1.23962
H	-3.327759	1.104508	2.397224
H	-2.415968	2.629193	1.820069
O	5.124768	1.117898	0.291282
H	-0.247308	-1.961936	-1.172938

$t = 1690$ fs

C	3.717005	-0.452093	0.843979
C	2.556715	-1.102217	0.868232
C	1.447838	-0.725365	-0.143125
C	1.881746	0.316248	-0.892206
C	3.017762	1.067546	-0.738858
C	4.147405	0.712951	0.0544
H	4.554948	-0.777175	1.783617
H	2.326791	-1.803908	1.482295
H	1.148789	0.51992	-1.599339
H	3.075914	1.750996	-1.555503
C	0.166198	-1.320032	-0.526344
C	-2.500576	0.939078	0.364728
C	-0.976705	-0.63448	-0.145935
N	-1.181259	0.745813	0.213848
C	-2.216843	-1.275026	-0.422306
O	-2.519863	-2.289607	-0.884324
N	-3.176916	-0.224522	0.062149
C	-4.612568	-0.219366	-0.048557
H	-4.82573	0.270284	-0.940646
H	-5.173289	-1.186355	-0.0971
H	-4.986949	0.271176	0.743302
C	-3.132141	2.356356	0.72227
H	-3.998833	2.787904	0.112957
H	-3.28058	2.415289	1.805512
H	-2.324314	2.998427	0.704175
O	5.294248	1.080647	-0.235179
H	0.003657	-1.982639	-1.49776

$t = 1990$ fs

C	3.122394	-0.044075	1.119944
C	1.960699	-0.484014	0.838533
C	1.422361	-0.468943	-0.474244
C	2.306827	0.21405	-1.384038
C	3.530544	0.657005	-1.208393
C	4.209812	0.403569	0.095296
H	3.479113	-0.377672	2.112479
H	1.692965	-1.415371	1.327869
H	1.814694	0.575175	-2.248713
H	4.057743	1.009996	-2.038955
C	-0.010716	-0.939723	-0.904817
C	-2.527572	0.983917	0.564965
C	-1.105651	-0.104021	-0.687843
N	-1.239353	0.893994	0.288794
C	-2.398212	-0.610019	-1.025577
O	-2.616723	-1.451744	-1.891184
N	-3.294793	-0.246649	0.014644
C	-4.695771	-0.695415	0.22478
H	-4.699219	-1.43146	1.113692
H	-5.391713	0.199599	0.288005
H	-4.787468	-1.271717	-0.625987
C	-2.859807	2.165105	1.177852
H	-2.258439	2.352558	2.229973
H	-2.554915	3.104053	0.607478
H	-4.028787	2.199056	1.34729
O	5.354759	0.922926	0.414763
H	-0.050323	-1.900332	-1.242324

$t = 2450$ fs

C	3.112744	0.249467	1.092242
C	1.935951	-0.326232	0.62384
C	1.423214	-0.49516	-0.717381
C	2.346216	0.104534	-1.647381
C	3.576695	0.528147	-1.12724
C	4.122824	0.695303	0.265244
H	3.221982	0.110597	2.110055
H	1.16968	-0.429338	1.341509
H	2.563667	-0.050589	-2.703145
H	4.363766	0.474048	-1.863436
C	0.096127	-1.114418	-0.967465
C	-2.453951	1.047617	0.319676
C	-1.060943	-0.442188	-0.656714
N	-1.163677	0.854609	0.101316
C	-2.425912	-0.928158	-0.854012
O	-3.011003	-1.997098	-1.086071
N	-3.262117	0.12934	-0.264894
C	-4.704584	-0.381747	0.107676
H	-5.000234	-0.820600	-0.964944
H	-4.949712	-1.25543	0.684129
H	-5.417904	0.379064	0.307653
C	-2.727027	2.051311	1.339292
H	-3.826833	2.501462	1.339072
H	-2.645226	1.48243	2.452049
H	-2.119621	2.944646	1.258682
O	5.221636	1.146232	0.573377
H	0.046692	-2.21800	-1.028842

$t = 2540$ fs

C	3.245098	-0.160918	1.09062
C	2.059482	-0.623041	0.882423
C	1.585034	-0.604196	-0.573639
C	2.342347	0.206156	-1.423657
C	3.533826	0.804613	-1.146932
C	4.207103	0.437165	0.074683
H	3.635425	0.050998	2.105748
H	1.340654	-0.989466	1.653199
H	1.91667	0.191718	-2.390623
H	4.075486	1.165073	-2.147683
C	0.283583	-1.039568	-0.936537
C	-2.344617	0.912424	0.672854
C	-1.01592	-0.44907	-0.597878
N	-1.144687	0.906979	0.061636
C	-2.377756	-0.98421	-0.730577
O	-2.684433	-1.705587	-1.636188
N	-3.122503	-0.389476	0.33917
C	-4.581848	-0.253337	0.202314
H	-4.563297	-0.315245	-0.883447
H	-5.17193	-1.106998	0.636123
H	-4.95446	0.64156	0.833409
C	-3.164318	1.979621	1.077967
H	-3.494636	1.930816	2.147021
H	-2.705864	3.084262	1.120533
H	-4.135139	2.124442	0.405043
O	5.372254	0.600459	0.307294
H	0.296893	-2.175326	-1.108593

$t = 2620$ fs

C	3.616097	-0.628334	0.88801
C	2.286228	-0.685214	1.00389
C	1.5111	-0.381364	-0.187884
C	2.105444	0.518483	-1.102438
C	3.393183	0.857687	-1.103236
C	4.234331	0.277378	-0.038706
H	4.327105	-1.228791	1.466046
H	1.962357	-0.981977	1.999675
H	1.379751	0.861801	-1.889761
H	3.828672	1.514088	-1.697609
C	0.246052	-0.845297	-0.689888
C	-2.647856	0.896026	0.166988
C	-1.020204	-0.450512	-0.456514
N	-1.381622	0.734486	0.284037
C	-2.283239	-1.105217	-0.77227
O	-2.55692	-2.266667	-0.828483
N	-3.327767	-0.073044	-0.507548
C	-4.684427	-0.299955	0.070759
H	-5.662173	0.048216	-0.197791
H	-4.739558	-1.367815	-0.014553
H	-4.751837	-0.049233	1.080089
C	-3.141613	2.179694	0.780619
H	-3.241257	2.242296	1.861256
H	-2.425566	2.810344	0.506889
H	-4.202946	2.7045	0.273788
O	5.286989	0.746297	0.270214
H	0.322126	-1.788028	-1.131296

$t = 2660$ fs

C	3.540043	-0.466327	0.97205
C	2.311815	-0.947214	0.506262
C	1.452536	-0.416189	-0.502634
C	2.124196	0.675825	-1.16801
C	3.430296	0.870246	-0.997024
C	4.277778	0.381095	0.079905
H	4.093174	-1.165003	1.620727
H	1.897166	-1.777567	0.931656
H	1.57949	1.271336	-1.937131
H	3.96600	1.60606	-1.593546
C	0.122579	-1.039971	-0.542382
C	-2.408201	1.098563	0.442326
C	-0.855519	-0.466618	0.248484
N	-1.156772	0.912667	0.48638
C	-2.080506	-1.168108	0.087304
O	-2.445485	-2.159171	-0.505558
N	-3.119696	-0.00183	0.126494
C	-4.552539	-0.223974	0.00719
H	-5.136814	0.606677	-0.504576
H	-4.693054	-1.149595	-0.754382
H	-5.003538	-0.70495	1.076226
C	-3.384726	2.219383	0.762338
H	-4.307781	1.986655	1.328057
H	-2.827396	3.222147	0.945418
H	-3.827333	2.501657	-0.144958
O	5.442871	0.557426	0.086705
H	-0.006135	-1.983372	-1.023039

$t = 3200$ fs

C	3.607542	-0.251362	1.044998
C	2.386489	-0.925931	0.835893
C	1.443218	-0.571581	-0.19671
C	1.814873	0.375036	-1.136379
C	2.961131	1.105435	-1.14655
C	4.0514	0.628826	0.022593
H	4.402631	-0.56517	1.831277
H	2.050925	-1.723332	1.59812
H	1.057486	0.68784	-1.945505
H	3.373364	1.578149	-2.078745
C	0.183866	-1.407065	-0.484884
C	-2.220167	1.003168	0.440591
C	-1.002517	-0.738821	-0.037198
N	-1.028824	0.594744	0.296315
C	-2.377237	-1.190733	-0.249879
O	-2.905317	-2.279666	-0.429431
N	-3.123493	-0.073603	-0.094943
C	-4.490284	-0.110777	-0.253812
H	-4.909606	0.936051	-0.731915
H	-5.041189	-0.803881	-0.952959
H	-4.905504	-0.383394	0.69424
C	-2.880163	2.090901	0.991691
H	-3.223983	2.677057	0.16158
H	-3.709992	1.65621	1.522251
H	-2.138738	2.816606	1.442736
O	5.02464	1.29169	0.096527
H	0.031897	-2.176546	-1.205621

$t = 3230$ fs

C	3.368828	-0.293185	0.969912
C	2.163707	-0.759479	0.60059
C	1.508759	-0.580391	-0.531714
C	2.179191	0.349165	-1.396533
C	3.215817	1.206121	-1.040937
C	4.114682	0.645551	0.129474
H	4.082968	-0.711804	1.673227
H	1.762641	-1.515406	1.297857
H	1.387979	0.618592	-2.246296
H	3.297774	1.819824	-1.896898
C	0.285261	-1.320215	-0.499899
C	-2.356486	0.905594	0.469954
C	-0.951666	-0.817578	-0.017922
N	-1.181112	0.394187	0.622848
C	-2.420909	-1.332361	-0.270031
O	-2.775102	-2.474092	-0.662673
N	-3.115605	-0.099087	-0.104813
C	-4.547461	-0.072267	-0.168476
H	-5.019697	0.563134	-0.826496
H	-5.137668	-1.063809	-0.294479
H	-4.941038	0.348417	0.824083
C	-2.904866	2.173617	0.986685
H	-3.425259	2.678757	0.10940
H	-3.695189	1.794149	1.626691
H	-2.063833	2.98235	1.061427
O	5.277956	1.159746	0.368021
H	0.32278	-2.359679	-0.74872

Optimised microsolvated structures (MP2/aug-cc-pVDZ), Å

Five explicit water molecules and SMD implicit solvation:

s1: five waters around phenoxide

s2: three waters around phenoxide and two around imidazolinone

Structures shown in Fig. S3.

Z-*p*HBDI$^-$ – s1

C	2.225648	-0.210486	-0.01064
C	1.767766	-1.559203	-0.034138
C	0.399735	-1.852744	-0.034982
C	-0.578464	-0.819654	-0.013383
C	-0.126507	0.529852	0.00854
C	1.241362	0.822381	0.009886
H	0.067808	-2.897025	-0.052352
H	-0.855699	1.342029	0.024243
C	-1.974291	-1.211267	-0.014449
H	-2.167214	-2.292592	-0.0229
O	3.532529	0.08091	-0.007306
C	-3.109856	-0.436191	-0.007689
C	-4.468158	-1.035088	-0.010705
C	-4.510094	1.220172	-0.001919
N	-3.211528	0.970795	-0.001183
N	-5.303077	0.071845	-0.008008
C	-5.135186	2.569613	0.000794
H	-5.778744	2.690439	0.887719
H	-4.350278	3.336456	0.009307
H	-5.766867	2.698682	-0.89354
O	-4.834869	-2.229671	-0.014526
C	-6.761706	0.032453	-0.006001
H	-7.155778	0.503866	0.905147
H	-7.157762	0.547624	-0.892081
H	-7.064804	-1.021659	-0.031539
H	2.506738	-2.366979	-0.0514
H	1.578491	1.864005	0.02644
O	3.857288	2.055197	1.888813
H	3.73165	1.370958	1.188321
H	2.950513	2.288448	2.137101
O	4.734277	-1.59944	-1.833119
H	5.6446	-1.267514	-1.843754
H	4.292479	-1.019786	-1.167132
O	6.397368	0.785007	-0.018807
H	6.434335	1.395776	0.732674
H	5.467593	0.500589	-0.021137
O	4.581288	-1.578028	1.928647
H	4.430528	-2.471507	1.586311
H	4.22873	-0.998498	1.211546
O	3.771196	2.072248	-1.905926
H	4.722679	2.129392	-2.077681
H	3.709108	1.379992	-1.205043

Z-*p*HBDI$^-$ – s2

C	-3.134278	-0.281425	0.18122
C	-2.752775	1.017188	0.63914
C	-1.409437	1.399439	0.684666
C	-0.372399	0.509197	0.283359
C	-0.743814	-0.784187	-0.185346
C	-2.087261	-1.162697	-0.235932
H	-1.138504	2.401448	1.036909
H	0.025944	-1.480205	-0.522798
C	0.988453	0.984845	0.36343
H	1.110342	2.038866	0.646064
O	-4.408784	-0.654735	0.130636
C	2.175398	0.318835	0.149519
C	3.48484	0.996365	0.235396
C	3.686175	-1.199199	-0.226925
N	2.373557	-1.043627	-0.148818
N	4.392992	-0.017972	-0.018166
C	4.391951	-2.481292	-0.491018
H	5.0539	-2.732072	0.354285
H	3.654073	-3.281352	-0.631361
H	5.016281	-2.394234	-1.395115
O	3.773215	2.196065	0.463989
C	5.845169	0.130491	-0.040426
H	6.29947	-0.426102	0.791116
H	6.244766	-0.234734	-0.996028
H	6.070834	1.198699	0.066178
H	-3.536177	1.714112	0.954999
H	-2.362372	-2.158744	-0.59909
O	1.223667	-3.378433	1.039833
H	1.574976	-2.57455	0.593285
H	2.025531	-3.87037	1.271921
O	-5.776096	1.347861	-1.128435
H	-5.833249	2.068885	-0.484233
H	-5.290493	0.638573	-0.637446
O	2.224823	3.885304	-1.200548
H	1.318247	3.54454	-1.175143
H	2.706691	3.298883	-0.581262
O	-5.781344	0.257946	2.280711
H	-5.818995	1.218927	2.166045
H	-5.275003	-0.048876	1.484704
O	-4.943413	-1.852683	-2.240641
H	-5.402501	-1.146268	-2.718541
H	-4.738279	-1.440208	-1.362454

Z-26Me$^-$ – s1

C	4.584224	0.821855	0.309011
C	4.446034	-1.16067	-0.758619
C	3.182155	0.349987	0.142081
C	4.965734	-2.358557	-1.470356
H	5.614464	-2.946661	-0.800421
H	4.124344	-2.979198	-1.803335
H	5.568964	-2.053309	-2.340939
C	6.783187	-0.206758	-0.392602
H	7.080405	-0.056993	-1.440411
H	7.178836	0.613169	0.219975
H	7.183533	-1.161151	-0.025412
N	3.174148	-0.888094	-0.534689
N	5.329653	-0.193663	-0.263532
C	2.093536	1.084104	0.528446
H	2.319888	2.091623	0.903112
C	0.692252	0.671143	0.445888
C	0.236204	-0.589667	0.933676
C	-0.244189	1.603299	-0.097062
C	-1.131929	-0.904254	0.825259
C	-1.595673	1.243746	-0.209078
C	-2.071877	-0.018656	0.239054
H	-1.496867	-1.859367	1.221847
H	-2.309749	1.949485	-0.649565
O	5.032668	1.861651	0.832067
C	0.225454	2.954352	-0.593695
H	0.691669	3.538784	0.218302
H	0.978464	2.84778	-1.392491
H	-0.622362	3.533297	-0.990305
C	1.145336	-1.568036	1.649446
H	1.564224	-2.313549	0.955959
H	1.992162	-1.054516	2.130802
H	0.574033	-2.104542	2.42369
O	-3.369919	-0.347054	0.134117
O	-5.19599	1.578154	0.346944
H	-4.444277	0.924005	0.264061
H	-4.924682	2.316694	-0.219241
O	-5.236322	-2.336053	-0.318954
H	-4.446798	-1.790129	-0.112141
H	-5.855479	-1.661693	-0.663722
O	-6.772361	-0.090383	-1.259774
H	-7.701871	-0.025634	-0.994982
H	-6.306777	0.550261	-0.673926
O	-4.065388	-0.798017	2.733372
H	-3.850298	-0.658636	1.777023
H	-4.980544	-0.489766	2.80577
O	-3.97165	0.007799	-2.523471
H	-3.749031	-0.121349	-1.568403
H	-4.939847	-0.056411	-2.520801

Z-26Me$^-$ – s2

C	3.590506	0.559113	0.541768
C	3.348205	-1.537558	-0.249633
C	2.17299	0.210787	0.278543
C	3.787955	-2.874492	-0.728259
H	4.273543	-3.429284	0.091304
H	2.914637	-3.435609	-1.084981
H	4.520444	-2.76632	-1.544519
C	5.72196	-0.768403	0.266309
H	6.140903	-0.797163	-0.749514
H	6.138392	0.087908	0.811229
H	5.968952	-1.696416	0.798551
N	2.101879	-1.104581	-0.219839
N	4.272701	-0.597855	0.216788
C	1.120559	1.07313	0.436537
H	1.386772	2.107491	0.688943
C	-0.286097	0.728013	0.253644
C	-0.870412	-0.435065	0.839336
C	-1.09524	1.617836	-0.517834
C	-2.230838	-0.701879	0.602336
C	-2.44013	1.300557	-0.756218
C	-3.04259	0.129667	-0.215112
H	-2.693733	-1.575302	1.076289
H	-3.04869	1.966394	-1.379239
O	4.10065	1.621403	0.961243
C	-0.488332	2.86702	-1.121099
H	-0.071474	3.525549	-0.339909
H	0.33495	2.619817	-1.812048
H	-1.250671	3.433569	-1.677269
C	-0.118246	-1.342324	1.792608
H	0.316195	-2.209633	1.271428
H	0.705446	-0.810786	2.294096
H	-0.809442	-1.720657	2.562561
O	-4.331979	-0.161564	-0.444343
O	-5.756171	2.115364	-0.219254
H	-5.224838	1.281139	-0.329821
H	-5.079059	2.80587	-0.16434
O	-4.621012	-2.790407	-0.93025
H	-4.49288	-1.818008	-0.762024
H	-4.259013	-2.922497	-1.818411
O	3.102975	3.84905	-0.504065
H	3.416438	3.096626	0.037517
H	3.910601	4.357018	-0.670822
O	-5.417512	-0.73047	1.963875
H	-5.030623	-0.529474	1.070451
H	-6.176877	-0.132314	2.021755
O	0.063977	-2.571816	-1.540741
H	0.733825	-2.043575	-1.042182
H	0.604973	-3.088182	-2.156957

Z-35Me$^-$ – s1

C	-4.674504	-1.194446	-0.159748
C	-4.929518	0.990992	0.339199
C	-3.383316	-0.473598	-0.076674
C	-5.677525	2.236376	0.659147
H	-6.259566	2.105298	1.586312
H	-4.969675	3.065352	0.786077
H	-6.384963	2.477161	-0.151405
C	-7.05477	-0.396007	0.154343
H	-7.539488	0.195228	-0.635326
H	-7.254458	-1.461714	-0.013737
H	-7.451774	-0.100971	1.135487
N	-3.615153	0.882505	0.236351
N	-5.608708	-0.207165	0.117653
C	-2.179966	-1.110714	-0.288683
H	-2.27657	-2.180457	-0.520642
C	-0.828959	-0.599112	-0.25363
C	-0.494422	0.754779	0.031324
C	0.230684	-1.511662	-0.521241
C	0.838897	1.182863	0.049697
C	1.573116	-1.110993	-0.510668
C	1.89661	0.253642	-0.221599
O	-4.930541	-2.393666	-0.41198
O	3.16627	0.656801	-0.204288
H	-0.015458	-2.55791	-0.742758
C	2.692272	-2.081015	-0.798506
H	3.281276	-1.750189	-1.669957
H	3.385748	-2.145621	0.056166
H	2.290468	-3.084845	-1.00453
C	1.200782	2.615719	0.352943
H	0.294721	3.214407	0.53065
H	1.845218	2.675048	1.245983
H	1.76346	3.062874	-0.483669
H	-1.291873	1.472325	0.239427
O	3.840734	-0.21937	2.354685
H	4.438497	-0.966789	2.163209
H	3.627041	0.125403	1.458237
O	5.701843	-0.411453	-0.550146
H	4.76519	-0.11887	-0.474337
H	5.765888	-1.099966	0.137989
O	3.592418	1.195128	-2.857841
H	4.141033	0.454158	-3.155477
H	3.462582	1.007245	-1.897138
O	5.618889	-2.363123	1.583274
H	5.149777	-3.174478	1.336061
H	6.367916	-2.674977	2.113251
O	4.600695	2.883235	0.394097
H	5.472437	2.476234	0.282057
H	3.980837	2.137305	0.202215

Z-35Me$^-$ – s2

C	-3.832753	-0.915675	-0.099614
C	-3.950382	1.30548	0.26767
C	-2.498226	-0.2965	0.020169
C	-4.603646	2.629483	0.448769
H	-5.305126	2.597381	1.298215
H	-3.83662	3.392024	0.634634
H	-5.177753	2.897153	-0.453865
C	-6.159047	0.066911	0.05098
H	-6.568357	0.776646	-0.680515
H	-6.428299	-0.955515	-0.241542
H	-6.567087	0.282765	1.04845
N	-2.644731	1.085519	0.253656
N	-4.701971	0.152186	0.067691
C	-1.329182	-1.018426	-0.106292
H	-1.479557	-2.080486	-0.339099
C	0.043342	-0.594571	0.005065
C	0.452606	0.706445	0.413872
C	1.05395	-1.549767	-0.305106
C	1.806946	1.048766	0.492721
C	2.416048	-1.2324	-0.245079
C	2.819459	0.086294	0.151553
O	-4.180986	-2.104995	-0.297184
O	4.10305	0.416453	0.227782
H	0.749289	-2.560528	-0.605415
C	3.474459	-2.250194	-0.593015
H	4.055815	-1.925334	-1.471904
H	4.185532	-2.380867	0.239452
H	3.01358	-3.223569	-0.820153
C	2.235582	2.422129	0.947673
H	1.3577	3.031888	1.210032
H	2.89668	2.354023	1.827834
H	2.801325	2.942126	0.15737
H	-0.299454	1.447546	0.69218
O	4.932098	-0.769983	2.534197
H	5.20209	-1.664557	2.279073
H	4.660117	-0.358949	1.676038
O	6.434526	-0.551167	-0.783117
H	6.335161	-1.465429	-1.085745
H	5.531881	-0.314246	-0.454342
O	4.575602	2.243402	-1.736004
H	5.256763	1.802983	-2.264947
H	4.410794	1.605206	-0.997413
O	-1.334235	3.330344	-0.944369
H	-2.098807	3.839947	-1.251889
H	-1.744963	2.555251	-0.496781
O	-2.790364	-4.527792	-0.281677
H	-3.180697	-3.627868	-0.283591
H	-1.835565	-4.369489	-0.318728

Z-35Bu$^-$ – s1

C	-5.286963	-1.025513	-0.003568
C	-5.264283	1.231027	0.000765
C	-3.916534	-0.471246	-0.020031
C	-5.845334	2.600758	0.014168
H	-6.463084	2.746176	0.915797
H	-5.034908	3.340818	0.002972
H	-6.492979	2.751699	-0.865246
C	-7.548225	0.112455	0.027813
H	-7.940742	0.61303	-0.868394
H	-7.883946	-0.931989	0.038028
H	-7.916572	0.622615	0.928847
N	-3.973462	0.938321	-0.016831
N	-6.089463	0.107474	0.008887
C	-2.798776	-1.280865	-0.03152
H	-3.02349	-2.356851	-0.025594
C	-1.39917	-0.93357	-0.049443
C	-0.918098	0.399763	-0.077513
C	-0.44732	-1.985785	-0.05113
C	0.451298	0.702588	-0.085508
C	0.937363	-1.753527	-0.057731
C	1.425761	-0.380828	-0.047868
O	-5.696445	-2.210352	-0.00114
O	2.724132	-0.132474	0.016264
H	-0.833575	-3.00824	-0.046609
C	1.898269	-2.953839	-0.090879
C	0.870879	2.182364	-0.134626
H	-1.657815	1.197162	-0.096441
C	1.144937	-4.296914	-0.102921
H	0.535882	-4.436954	0.80541
H	0.490445	-4.394279	-0.984844
H	1.888871	-5.11023	-0.140746
C	2.742828	-2.906166	-1.378655
H	3.330758	-1.984333	-1.445092
H	3.432599	-3.767965	-1.407011
H	2.088278	-2.960203	-2.265561
C	2.811816	-2.973346	1.151085
H	3.464709	-3.862802	1.110975
H	3.445211	-2.081109	1.210875
H	2.206075	-3.034295	2.070723
C	-0.344691	3.119661	-0.281335
H	-1.029823	3.051091	0.579553
H	0.024576	4.157351	-0.335391
H	-0.914684	2.911227	-1.202406
C	1.590785	2.587691	1.167632
H	1.839795	3.662745	1.134162
H	0.933649	2.416592	2.037366
H	2.520786	2.026803	1.311554
C	1.782273	2.444164	-1.349625
H	2.745483	1.932607	-1.250768
H	1.296014	2.099765	-2.278431
H	1.959049	3.531166	-1.451404
O	4.933805	1.408958	0.60812
H	4.828576	2.365467	0.431904
H	4.054045	1.018573	0.407832
O	2.803081	-0.196541	2.852741
H	2.615238	0.720942	3.099518
H	2.814505	-0.1693	1.868953
O	4.081528	0.149606	-2.425466
H	4.965578	0.39987	-2.118202
H	3.577434	0.043254	-1.584891
O	5.825788	-1.228746	0.088447
H	4.901099	-1.410508	-0.143482
H	5.794621	-0.266652	0.251256
O	4.54425	4.194634	0.082521
H	3.699187	4.010069	-0.35636
H	5.129624	4.442212	-0.649804

Z-35Bu$^-$ – s2

C	4.520654	0.86237	-0.12156
C	4.51722	-1.392741	-0.136343
C	3.15675	0.306232	-0.141897
C	5.092213	-2.763875	-0.098368
H	5.695194	-2.899479	0.814836
H	4.277471	-3.499264	-0.112832
H	5.751966	-2.9286	-0.965949
C	6.790159	-0.260687	-0.104053
H	7.184782	-0.774968	-0.991159
H	7.119063	0.785659	-0.111248
H	7.157571	-0.754201	0.806427
N	3.225065	-1.100863	-0.157772
N	5.330625	-0.265629	-0.127483
C	2.021785	1.094066	-0.11789
H	2.218851	2.171636	-0.049311
C	0.635736	0.716153	-0.154606
C	0.177901	-0.610815	-0.365036
C	-0.333235	1.744944	-0.000895
C	-1.185322	-0.932227	-0.372166
C	-1.71059	1.486636	0.011939
C	-2.16857	0.110388	-0.112913
O	4.937306	2.048024	-0.108098
O	-3.446672	-0.18029	0.027557
H	0.040202	2.766016	0.115581
C	-2.704374	2.656914	0.099822
C	-1.608304	-2.388672	-0.616208
H	0.922825	-1.385927	-0.533951
C	-1.986929	4.005275	0.300235
H	-1.409976	4.026321	1.240069
H	-1.307901	4.242162	-0.535
H	-2.748784	4.80099	0.349972
C	-3.470075	2.744744	-1.236315
H	-4.006395	1.814132	-1.457042
H	-4.204508	3.5682	-1.195773
H	-2.768476	2.948761	-2.062952
C	-3.697795	2.506933	1.271392
H	-4.330386	3.410366	1.320808
H	-4.347291	1.631432	1.150059
H	-3.156488	2.41787	2.2278
C	-0.423307	-3.260904	-1.074532
H	0.358402	-3.342283	-0.302952
H	-0.798864	-4.277364	-1.280505
H	0.033457	-2.870471	-1.999733
C	-2.140239	-2.997992	0.696953
H	-2.467662	-4.038346	0.523099
H	-1.341761	-3.010009	1.458197
H	-2.988776	-2.428888	1.093891
C	-2.674714	-2.47447	-1.727497
H	-3.593282	-1.941187	-1.459857
H	-2.281082	-2.046836	-2.666035
H	-2.922602	-3.534002	-1.913891
O	-5.500559	-1.949047	0.640964
H	-5.203895	-2.869677	0.586682
H	-4.69167	-1.433348	0.426541
O	-3.283487	-0.330947	2.850951
H	-3.008887	-1.249872	2.986665
H	-3.382095	-0.265651	1.87403
O	-5.466931	-0.052402	-1.848901
H	-5.927069	-0.868244	-1.59975
H	-4.700697	-0.045223	-1.227367
O	1.913424	-2.604299	1.888093
H	2.298686	-2.120138	1.122382
H	2.694264	-2.971585	2.329616
O	3.644341	4.520133	-0.132743
H	2.712043	4.408751	-0.370066
H	4.000781	3.605703	-0.137442

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