

The Highly Reactive Benzhydryl Cation Isolated and Stabilized in Water Ice

Supporting Information

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1. Experimental Details

Materials. Benzophenone (Sigma Aldrich 99 %), diphenylmethanol (Sigma Aldrich 99 %) and ^{13}C -benzophenone (Sigma Aldrich 99% ^{13}C) were used without further purification. p-Toluenesulfonyl hydrazide was purchased from ABCR and was used without further purification. Deuterated water (99% D) was purchased from Deutero GmbH.

Diphenyldiazomethane (DPDM). Benzophenone tosylhydrazone was synthesized according to a literature procedure¹. The sodium salt was prepared by treating the tosylhydrazone with 1.1 eq. of NaH (60 % dispersion in mineral oil) in dry CH_2Cl_2 . The NaH was washed three times with absolute pentane before using to remove the mineral oil. The slightly pink salt was stored under inert atmospheric conditions at $-40\text{ }^\circ\text{C}$. The diphenyldiazomethane was generated by sublimation of the pink salt at $45\text{ }^\circ\text{C}$ directly on the cold window. IR (Ar, 3 K): 3070 (m), 2046 (vs), 1598 (s), 1582 (m), 1502 (s), 1497 (s), 1457 (m), 1447 (m), 1320 (m), 1268 (m), 1262 (m), 1034 (m), 936 (m), 756 (s), 750 (s), 697 (s), 692 (s), 651 (s), 482 (m) cm^{-1} .

^{13}C -Diphenyldiazomethane was synthesized as described above by replacing benzophenone with ^{13}C -benzophenone. IR (Ar, 3 K): 3070 (m), 2046 (vs), 1598 (s), 1582 (m), 1502 (s), 1495 (s), 1455 (m), 1446 (m), 1316 (m), 1259 (m), 1034 (m), 927 (m), 755 (s), 750 (s), 697 (s), 692 (s), 650 (s), 482 (m) cm^{-1} .

α -deuterio-diphenylmethan(ol-d) (d₂-3) was synthesized according to a literature procedure². The product was washed several times with deuterated water to exchange the proton with a deuterium in the hydroxyl group.; ^1H NMR (200 MHz, DMSO) $\delta = 7.50 - 7.10$ (m), ^{13}C NMR (50 MHz, CD_2Cl_2) $\delta = 145.60, 128.03, 126.67, 126.20$; MS (EI) (m/z, %) 186 [M^+], 166, 105, 78, 51.

Simulations of EPR spectra. The simulations of EPR spectra were performed using Easyspin software – a MATLAB toolbox.³

2. Results from MD Simulations

a) QM/MM MD simulations of S-1...H₂O and T-1...H₂O in a box of Ar at 25 K:

The 1:1 water complexes of S-1 and T-1 were treated as QM region and placed in a box of Ar atoms (MM region). To ensure an adequate sampling of the different matrix sites, 10 ps QM/MM MD simulations (T = 25K) were carried out at the BLYP-D3/def2-SVP//CHARMM level of theory. Subsequently, 10 snapshots were taken from each MD run and re-optimized with the larger basis set def2-TZVP to evaluate the singlet-triplet gap in the presence of Ar. The QM/MM MD simulations did not show any reaction in the studied time scale, suggesting that the reaction does not proceed

thermally in argon at 25K. Cluster analysis performed on the trajectories revealed a single conformation throughout the simulations (RMSD cutoff: 0.02 Å) for both the singlet and triplet complexes. The results (Table S11) show an extra stabilization of the more polar singlet states in the Ar matrix, therefore reducing the DPC gap and enlarging the inverted gap in the H-bonded complexes (Figure 2). The variability in the predicted gaps (MAE = 0,1 kcal/mol) suggest that matrix effects are non-negligible for this system.

b) QM/MM MD simulations of S-1...H₂O and T-1...H₂O in a box of water at 3 K:

A 10 ps QM/MM MD simulation was run placing the 1:1 DPC-water complexes in a box of water at 3 K. The simulation for the singlet complex showed proton transfer followed by recombination with OH to yield 3; the process is over in less than 1 ps. In the case of the triplet complex, no reaction was observed. The predicted singlet-triplet gap for the system placed in a water box is also inverted. Its magnitude is -6.5 kcal/mol, which indicates that the solvent further stabilizes the singlet state.

c) QM MD simulations of S-1...5H₂O and T-1...5H₂O in the gas phase at 3 K:

Simulations with a QM region formed by DPC and 5 water molecules were performed. This amount of water molecules was chosen based on the distribution of water molecules around DPC in the previous QM/MM MD simulation of S-1...H₂O and T-1...H₂O (QM regions) in a box of water (MM region). During the gas phase MD simulation of S-1 and 5 water molecules, proton transfer was observed from the nearest water molecule after 0.5 ps, followed by recombination to yield alcohol 3 after 3.1 ps. No reaction was observed in the case of T-1. This recombination, which is not observed in the experiment, could be due to the restricted number of water molecules included in the QM region.

Cluster analysis of the trajectories revealed a single conformation throughout the simulations (RMSD cutoff: 0.02 Å) for the triplet complexes. In the case of the singlet system, two largely populated clusters were found, one cluster containing the structures of the initial complexes, and the other with the products of proton transfer.

Snapshots of the system, taken before proton transfer occurred, were re-optimized at the BLYP-D3/def2-TZVP level of theory in order to evaluate the effect of the additional water molecules on the singlet-triplet gap of 1. Again, a greater stabilization of the polar singlet states is observed, resulting in a greater inversion of the gap (ΔE (S-T) = -5.9 kcal/mol) (Table S12).

d) QM/MM MD simulations of S-1...5H₂O and T-1...5H₂O in a box of water at 3 K:

The MD simulations of S-1...5H₂O and T-1...5H₂O (QM regions) in a box of water showed no reaction. Cluster analysis performed on the trajectories revealed a single relevant conformation throughout the simulations (RMSD: 0.02 Å) for both the singlet and triplet systems. To assess the influence of this extended QM region (with respect to **b** where only a molecule of water was included in the QM region) on the singlet-triplet gap, 10 snapshots were taken from each trajectory and re-optimized at the BLYP-D3/def2-TZVP//CHARMM level of theory (Table S13). This shows a reduced gap with respect to the same system in the gas phase, close to that found in Ar.

e) QM/MM MD simulations of S-1...5H₂O in a box of water at 200 K:

S-1 and 5 water molecules were taken as QM region and placed in box of water. At early stages of this simulation proton transfer from the nearest water molecule to the carbene center was observed. This was rapidly followed by subsequent proton transfers between the water molecules that finally led to recombination to yield alcohol **3**. This recombination occurred with a water molecule different from the one that executed the initial proton transfer. The process is completed in about half a picosecond. This suggest that (at 200 K) with enough water molecules present, the chain of water-to-water proton transfers might move the OH away from the carbene center fast enough to prevent recombination and formation of **3**.

f) QM/MM MD simulations of benzhydryl cation-**2** in a box of water at 3 K:

To simulate the behavior of benzhydryl cation-**2**, this specie and 5 water molecules were taken as QM region and placed in a box of explicit water. No indication of reaction between the cation and the surrounding water molecules was found along the QM/MM MD simulations (Figure S13). This is in agreement with the experimental finding that **2** is kinetically stabilized in a water matrix at low temperatures.

3. Experiments in Argon Matrix

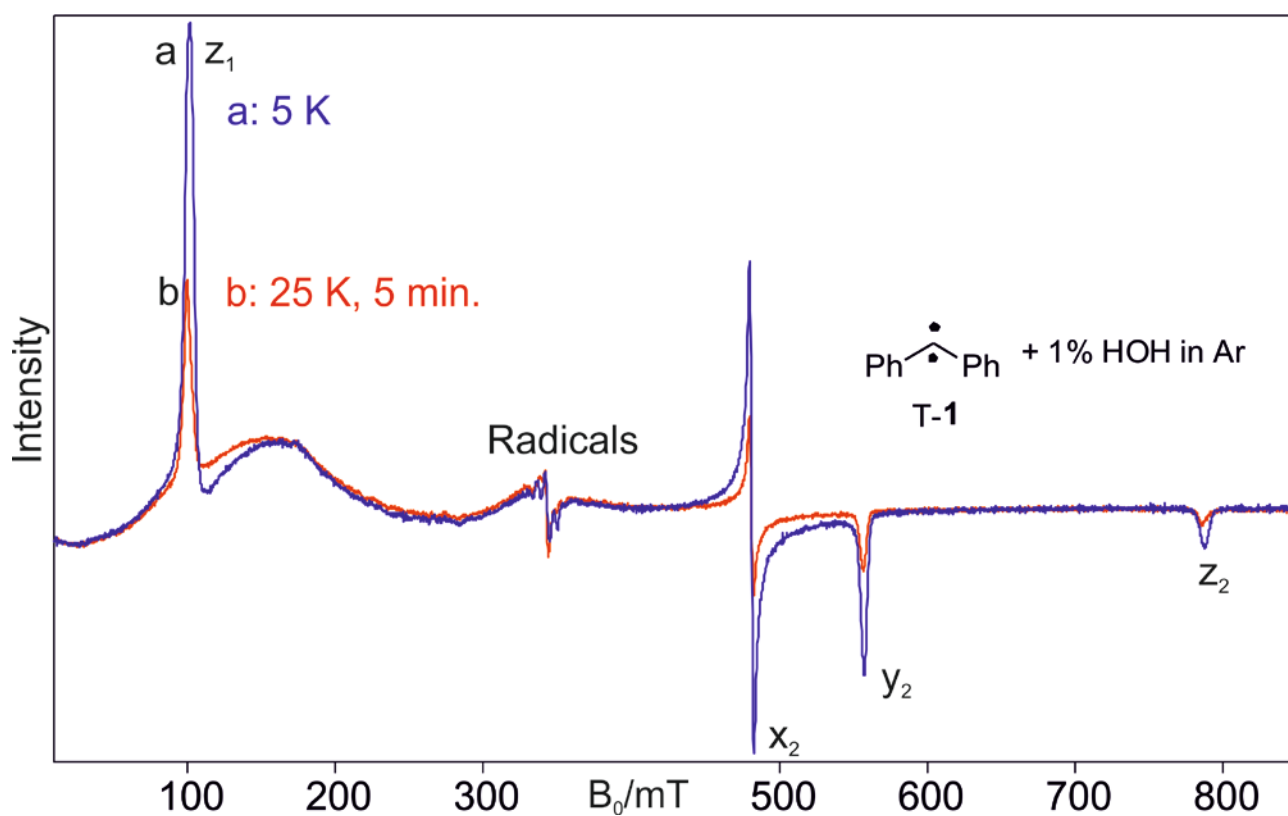


Figure S1. EPR spectra showing the reaction of T-1 in an argon matrix doped with 1% water. a) Matrix at 5 K showing the triplet spectrum of **1** with the zfs parameters $D = 0.417 \text{ cm}^{-1}$, $E = 0.019 \text{ cm}^{-1}$. b) After annealing for 5 min at 25 K 69% of the signal intensity of T-1 is lost. The signals of the radicals are formed during the initial photolysis of the precursor and do not change in intensity during annealing

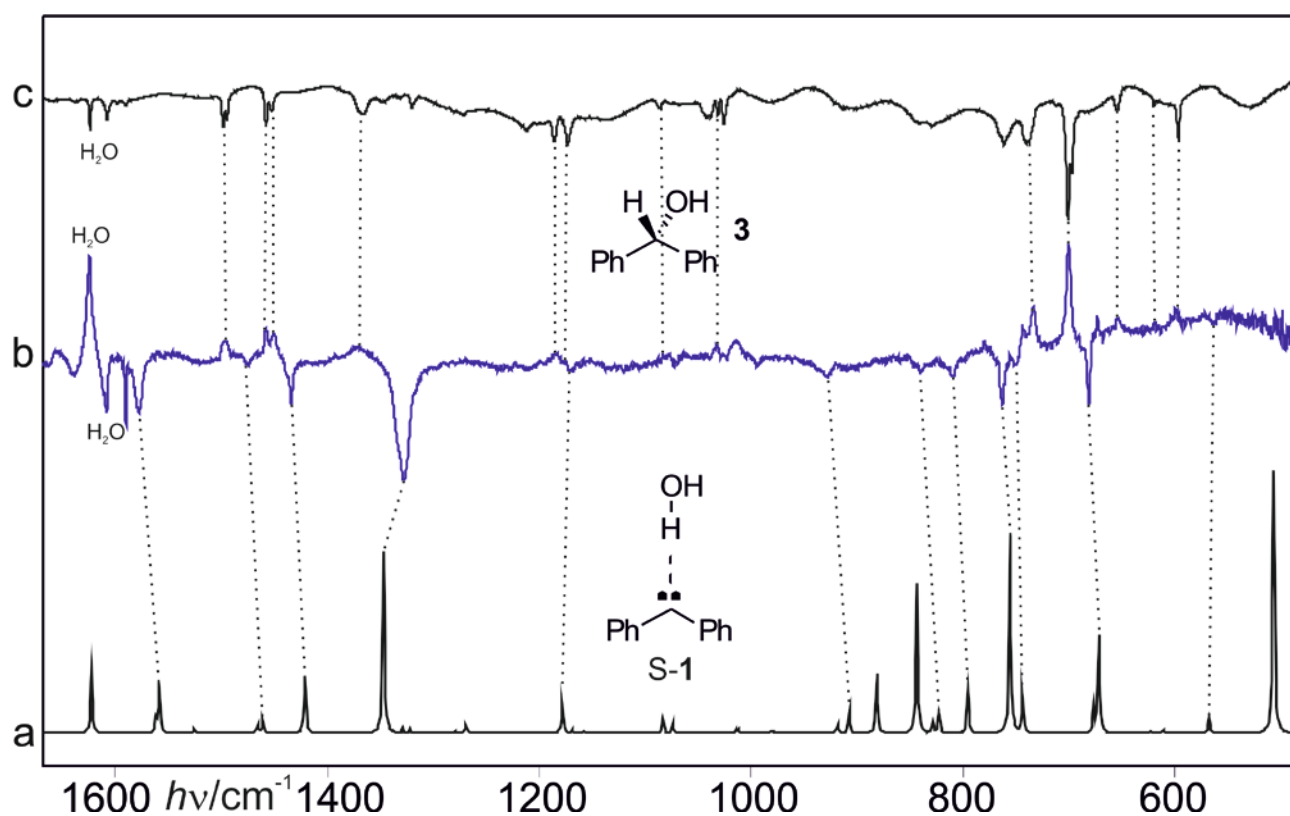


Figure S2. IR spectra showing the thermal rearrangement of the S-1...HOH complex. Difference IR spectra showing the disappearance of the complex between S-1 and HOH at 3 K after 17 hrs. to form **3**. a) IR spectrum of the complex between S-1 and HOH calculated at the BLYP-D3/def2-TZVP level of theory. b) Difference IR spectrum (Fig. 1-c). Bands pointing downwards are disappearing at 3 K and assigned to complex between S-1 and HOH. Bands pointing upwards are appearing and assigned to **3**. c) IR spectrum of **3** isolated in argon matrix at 3 K.

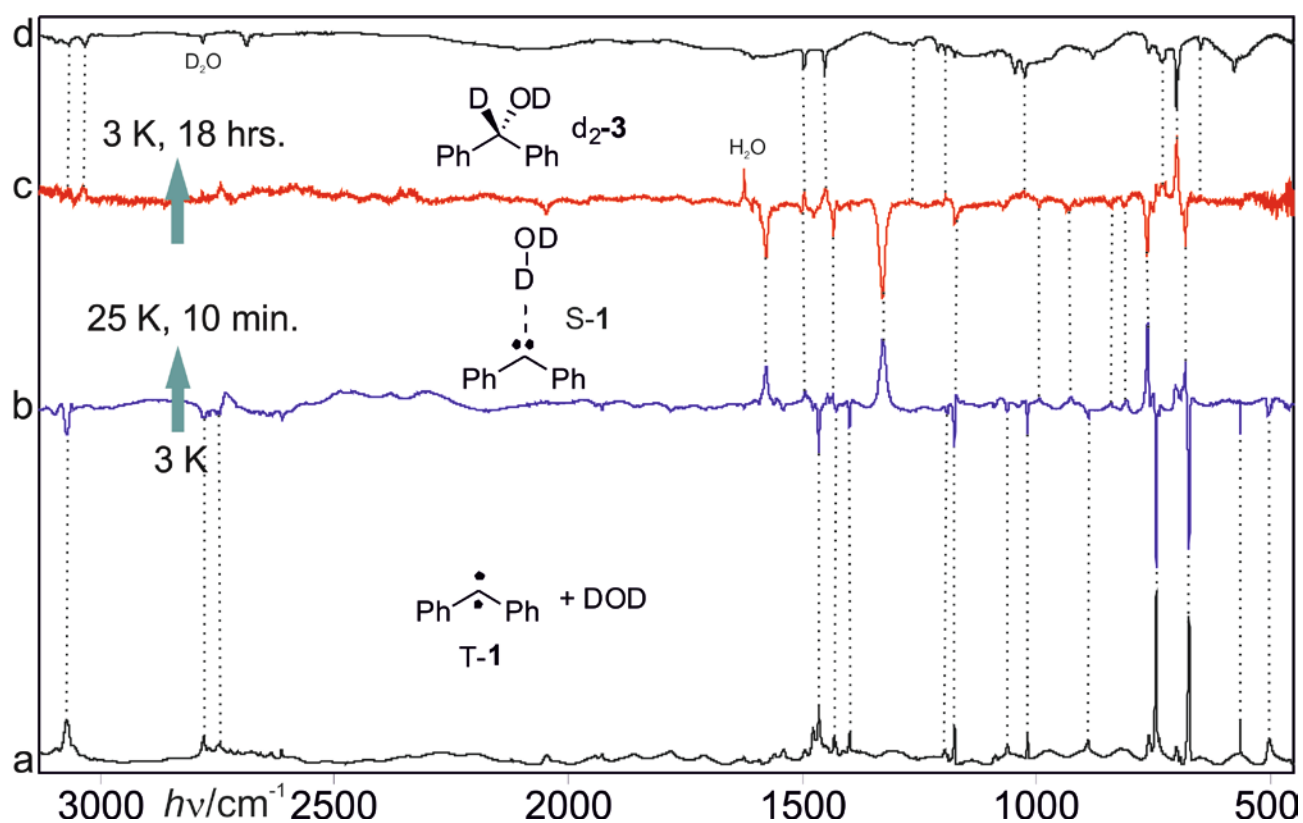


Figure S3. IR spectra showing the formation of the complex between S-1 and DOD. a) T-1 in Ar doped with 1% DOD at 3 K. b) Difference IR spectrum of the same matrix showing changes after annealing for 10 min at 25 K. Bands pointing downwards assigned to T-1 and DOD are disappearing, and bands pointing upwards assigned to the complex between S-1 and DOD are appearing. c) Difference IR spectrum of the same matrix showing changes after 17 hours at 3 K, and bands pointing downwards are assigned to the complex between S-1 and DOD. Bands pointing upwards are assigned to d₂-3. d) IR spectrum of d₂-3 matrix-isolated in argon at 3 K.

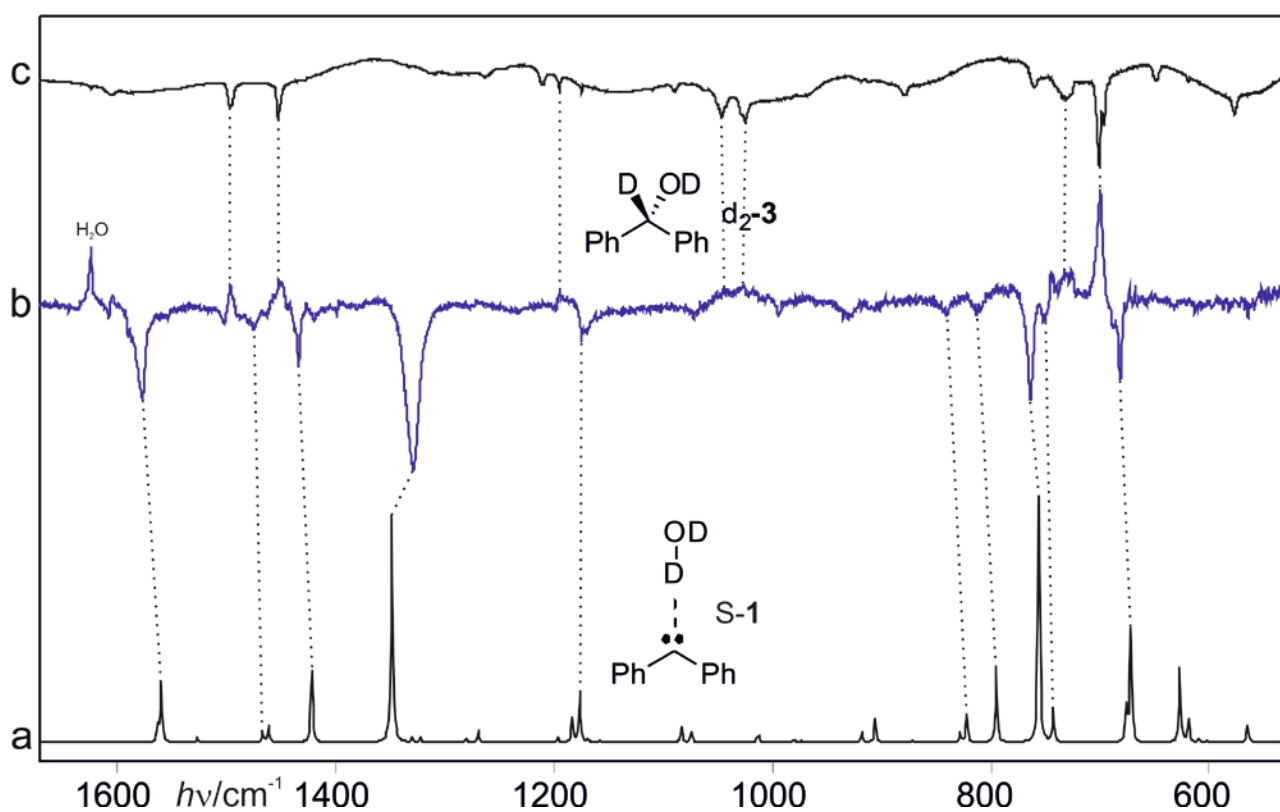


Figure S4. IR spectra showing the thermal rearrangement of the S-1...DOD complex. Difference IR spectra showing the disappearance of the complex between S-1 and DOD at 3 K after 17 hrs. to form d₂-3. a) IR spectrum of the complex between S-1 and DOD calculated at the BLYP-D3/def2-TZVP level of theory. b) Difference IR spectrum (Fig. 3-c). Bands pointing downwards are disappearing at 3 K and assigned to complex between S-1 and DOD. Bands pointing upwards are appearing and assigned to d₂-3. c) IR spectrum of d₂-3 isolated in argon matrix at 3 K.

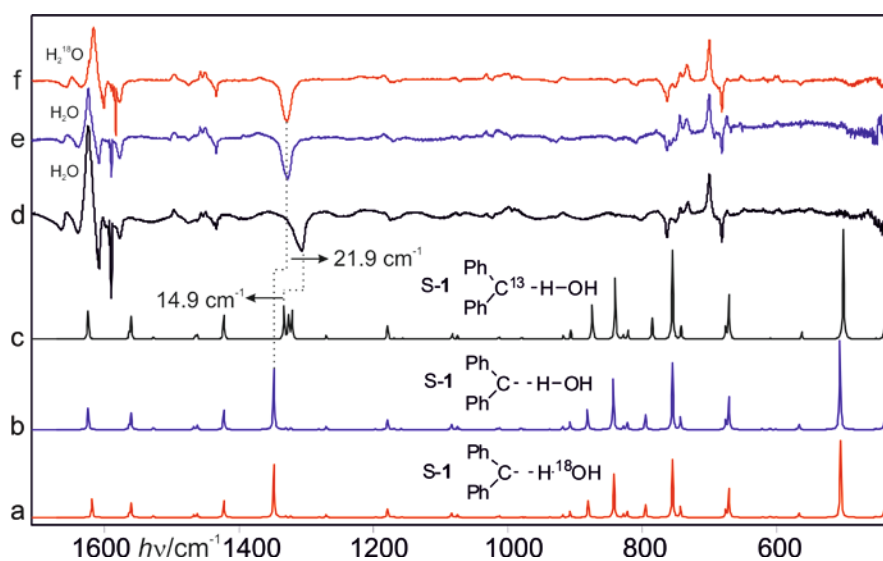


Figure S5a. IR spectra showing the isotopic shift of the C-C-C stretching of S-1 in its different isotopomers. a) IR spectrum of the complex between S-1 and H¹⁸OH calculated at the BLYP-D3/def2-TZVP level of theory. b) IR spectrum of the complex between S-1 and H¹⁸OH calculated at the BLYP-D3/def2-TZVP level of theory. c) IR spectrum of the complex between S-1 labeled with ¹³C and HOH calculated at the BLYP-D3/def2-TZVP level of theory. d) Difference IR spectrum showing the disappearance of the complex between S-1 labeled with ¹³C and HOH at 3 K. e) Difference IR spectrum showing the disappearance of the complex between S-1 and HOH at 3 K. f) Difference IR spectrum showing the disappearance of the complex between S-1 and H¹⁸OH at 3 K.

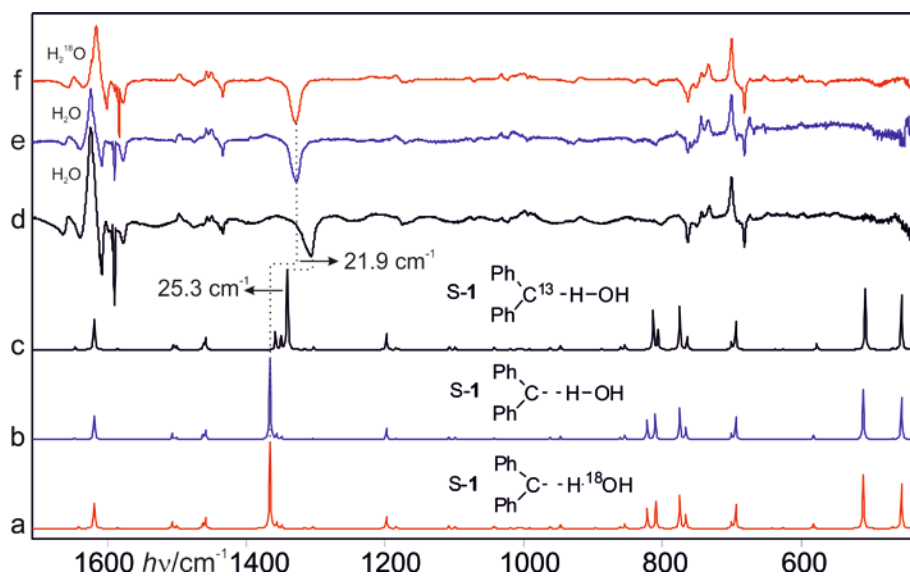


Figure S5b. Same experimental spectra as in Figure S5a, however, the IR spectra are now calculated at the B3LYP/6-311++G(d,p) level of theory.

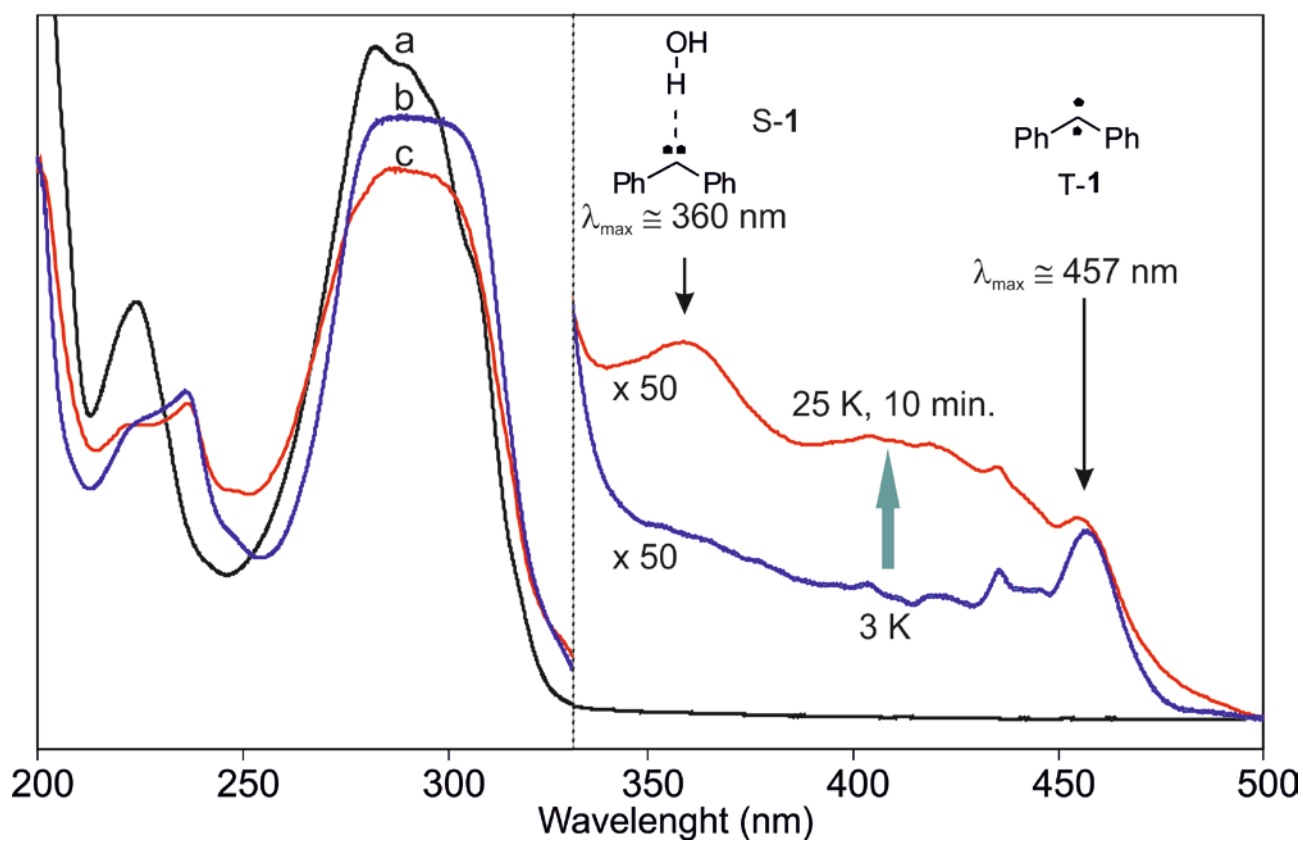


Figure S6. UV-vis spectra showing the disappearance of T-1 and the formation of the S-1 water complex. a) UV-vis spectrum of the diphenyldiazomethane in argon matrix doped with 1% of water at 8 K. b) UV-vis spectrum of T-1 generated upon irradiation of the same matrix at 8 K. c) UV-Vis spectrum of the same matrix after annealing up to 25 K and cooled back to 8K.

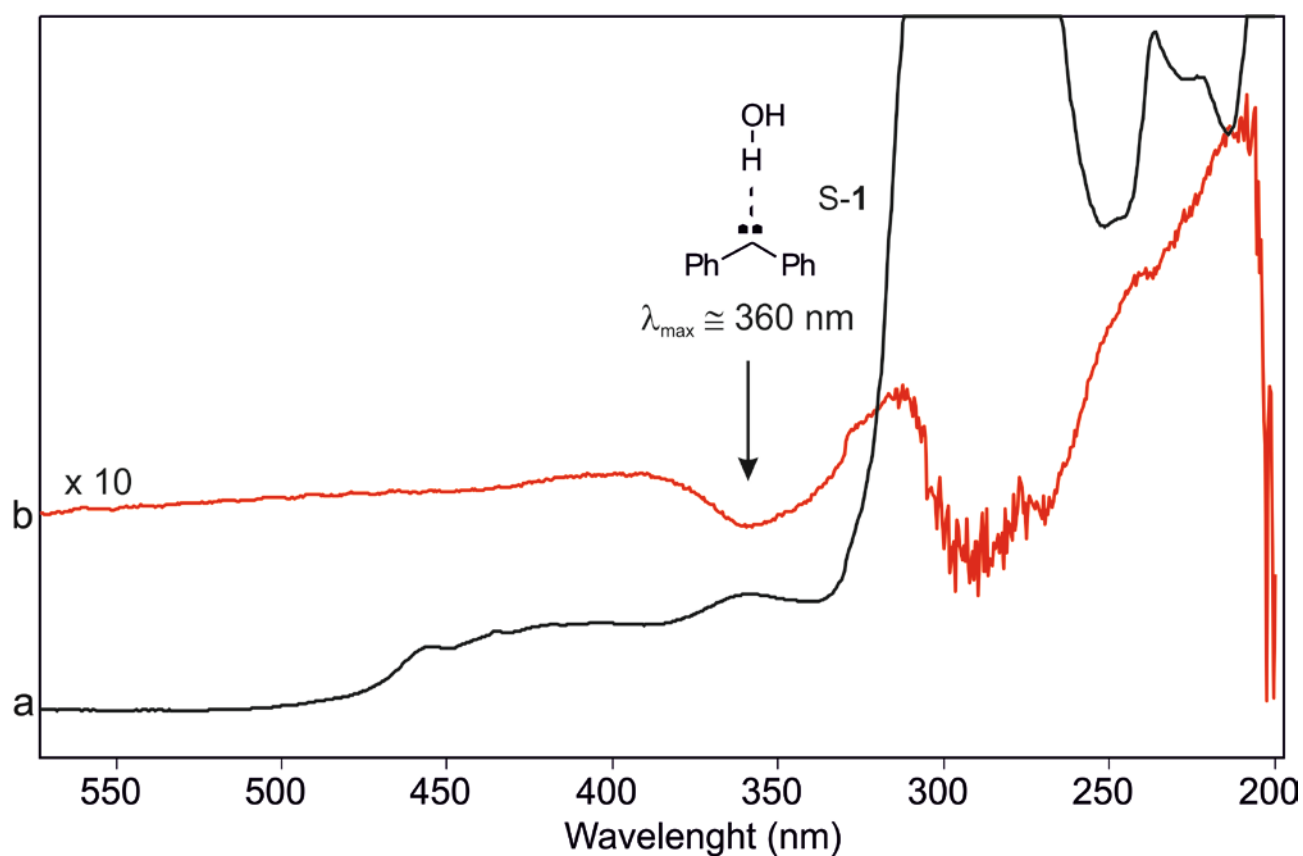


Figure S7. UV-vis spectra showing the disappearance of S-1 after 20 hrs. on the dark at 8 K in argon matrix doped with 1% of water. a) UV-vis spectrum (Fig. S6-c). b) difference UV-vis spectrum. Band pointing downwards is disappearing at 8 K and assigned to complex between S-1 and HOH.

Table S1. Reaction rate for the rearrangement of the complex between S-1 and HOH to **3** at various temperatures. Reaction rate k is obtained by fitting the decrease of the integrated intensities of the signal assigned to the asym. C-C-C str. vibration of the carbene center S-1 to the equation: $y = g + a \exp(-kt)^c$.

T (K)	Species	$g^{[a]}$	StdErr g	a	StdErr a	k (s^{-1})	StdErr k	$c^{[b]}$	StdErr c
	Complex								
3	S-1 + H ₂ O	1.48E-01	1.31E-01	8.53E-01	1.33E-01	5.79E-06	2.02E-06	6.55E-01	2.29E-02
	Complex								
12	S-1 + H ₂ O	3.55E-01	6.67E-02	6.46E-01	6.73E-02	5.66E-06	1.42E-06	5.86E-01	1.47E-02
	Complex								
3	¹³ C S-1 + H ₂ O	1.15E-01	1.74E-01	8.85E-01	1.75E-01	2.67E-06	1.23E-06	6.00E-01	1.76E-02
	Complex								
3	S-1 + D ₂ O	3.42E-01	2.35E-01	6.58E-01	2.36E-01	1.85E-06	1.56E-06	5.74E-01	2.47E-02
	Complex								
3	S-1 + H ₂ ¹⁸ O	3.36E-01	5.25E-02	6.64E-01	5.34E-02	9.79E-06	1.83E-06	6.27E-01	1.58E-02

^[a] g = y intercept. ^[b] c = parameter for superposition of exponential decays

Table S2. IR spectroscopic data of the complex between S-1 and HOH.

S-1...H-OH						
Mode	Sym	BLYP ^a [QM/MM] ^b		Argon ^c		Assignment
		ν/cm^{-1}	I_{rel}	ν/cm^{-1}	I_{rel}	
17	A	567.4 [570.1]	7.9	564.0	3.2	Skel. Vibr.
21	A	671.4 [689.2]	49.5	681.1	15.4	C-H def. (out-of-plane)
23	A	743.7 [748.9]	18.7	750.6	5.8	C-H def. (out-of-plane)
24	A	755.5 [760.0]	100	762.9	17.3	C-H def. (out-of-plane)
26	A	795.4 [799.1]	22.2	809.8	6.4	C-C-C def. carbene center
27	A	828.8 [837.6]	5.4	840.3	3.8	C-H def. (out-of-plane)
30	A	907 [926.2]	11.0	928.2	7.1	C-H def. (out-of-plane)
45	A	1178.9 [1158.6]	14.6	1169.6	3.2	C-H def. (in plane)
51	A	1347.9 [1332.6]	91.5	1327.5	100	C-C-C asym. str. Carbene center
52	A	1421.9 [1410.6]	25.0	1434.0	10.3	C=C str. Ring
55	A	1466.2 [1468.5]	4.4	1475.0	3.2	C=C str. Ring
58	A	1559.3 [1550.9]	24.9	1577.9	18.0	C=C str. Ring

^[a]Calculated at the BLYP-D3/ Def2-TZVP level of theory. ^[b]Calculated at the BLYP-D3/ def2-TZVP//CHARMM level of theory in an Ar matrix. ^[c]Argon matrix at 3 K.

Table S3. IR spectroscopic data of the complex between S-1 and DOD.

S-1...D-OD								
Mode	Sym	Calcd gas phase ^a		Shift ^b	Argon ^c		Shift ^b	Assignment
		ν/cm^{-1}	I_{rel}		ν/cm^{-1}	I_{rel}		
22	A	672.3	46.0	0.9	681.1	18.0	0.0	C-H def. (out-of-plane)
24	A	743.9	13.5	0.2	750.6	6.2	0.0	C-H def. (out-of-plane)
25	A	756.5	100	1.0	763.7	24.2	+0.8	C-H def. (out-of-plane)
26	A	795.7	30.2	0.3	810.3	6.2	+0.5	C-C-C def. carbene center
27	A	822.2	10.7	6.4	840.3	3.1	0.0	C-H def. (out-of-plane)
30	A	906.9	9.8	0.1	928.2	7.4	0.0	C-H def. (out-of-plane)
45	A	1176.8	20.5	/	1172.8	10.6	/	D ₂ O scissoring
52	A	1348.6	84.3	0.7	1329.0	100	+1.5	C-C-C asym. str. Carbene center
53	A	1421.8	25.8	0.1	1434.0	11.8	0.0	C=C str. Ring
56	A	1466.1	4.3	-0.1	1475.0	5.0	0.0	C=C str. Ring
59	A	1559.3	24.9	0.0	1577.9	24.8	0.0	C=C str. Ring

^[a]Calculated at the BLYP-D3/ def2-TZVP level of theory. ^[b]Frequency shift relative to S1...H2O ^[c]Argon matrix at 3 K.

Table S4. IR spectroscopic data of the complex between ¹³C-S-1 and HOH.

¹³ C-S-1...H-OH								
Mode	Sym	Calcd gas phase ^a		Shift ^b	Argon ^c		Shift ^b	Assignment
		ν/cm^{-1}	I_{rel}		ν/cm^{-1}	I_{rel}		
17	A	563.1	8.7	-4.3	560.0	1.8	-4.0	Skel. Vibr.
21	A	671.3	49.4	-0.1	681.1	14.8	0.0	C-H def. (out-of-plane)
23	A	742.5	15.0	1.3	750.6	4.4	0.0	C-H def. (out-of-plane)
24	A	755.1	100	0.4	762.9	15.1	0.0	C-H def. (out-of-plane)
26	A	786.0	24.0	-9.4	800.6	6.3	-9.3	C-C-C def. carbene center
27	A	828.7	5.2	0.1	840.3	2.8	0.0	C-H def. (out-of-plane)
30	A	906.7	10.1	0.3	928.2	6.5	0.0	C-H def. (out-of-plane)
45	A	1178.4	15.5	0.5	1169.6	3.2	0.0	C-H def. (in plane)
51	A	1333.0	36.0	-14.9	1306.7	100	-20.8	C-C-C asym. str. Carbene center
52	A	1421.7	22.9	0.2	1434.0	9.6	0.0	C=C str. Ring
55	A	1464.9	4.3	1.3	1475.0	3.7	0.0	C=C str. Ring
58	A	1559.3	25.2	0.0	1577.9	19.7	0.0	C=C str. Ring

^[a]Calculated at the BLYP-D3/ def2-TZVP level of theory. ^[b]Frequency shift relative to S1...H2O ^[c]Argon matrix at 3 K.

4. Experiments in Water Matrix

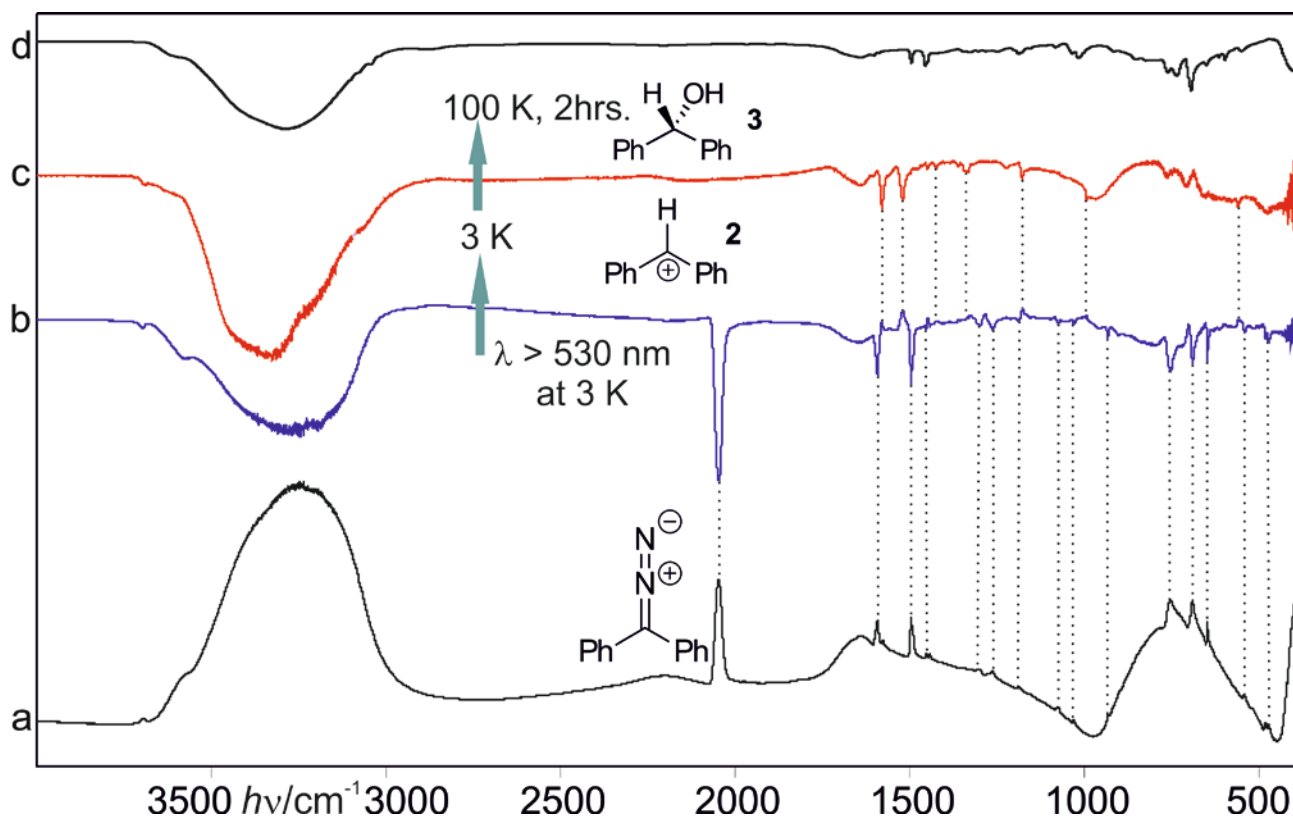


Figure S8. IR spectra showing the formation of **2**, upon photolysis of diphenyldiazomethane, and its disappearance after annealing for two hours from 3 K to 100 K. a) IR spectrum of diphenyldiazomethane in LDA ice matrix at 3 K. b) Difference IR spectrum of the same matrix showing changes after photolysis for 3 hrs. at 3 K. Bands pointing downwards assigned to diphenyldiazomethane are disappearing, and bands pointing upwards assigned to **2** are appearing. c) Difference IR spectrum of the same matrix showing changes after 2 hours of annealing from 3 K to 100 K, and bands pointing downwards are assigned to **2**. d) IR spectrum of **3** in LDA ice matrix at 3 K.

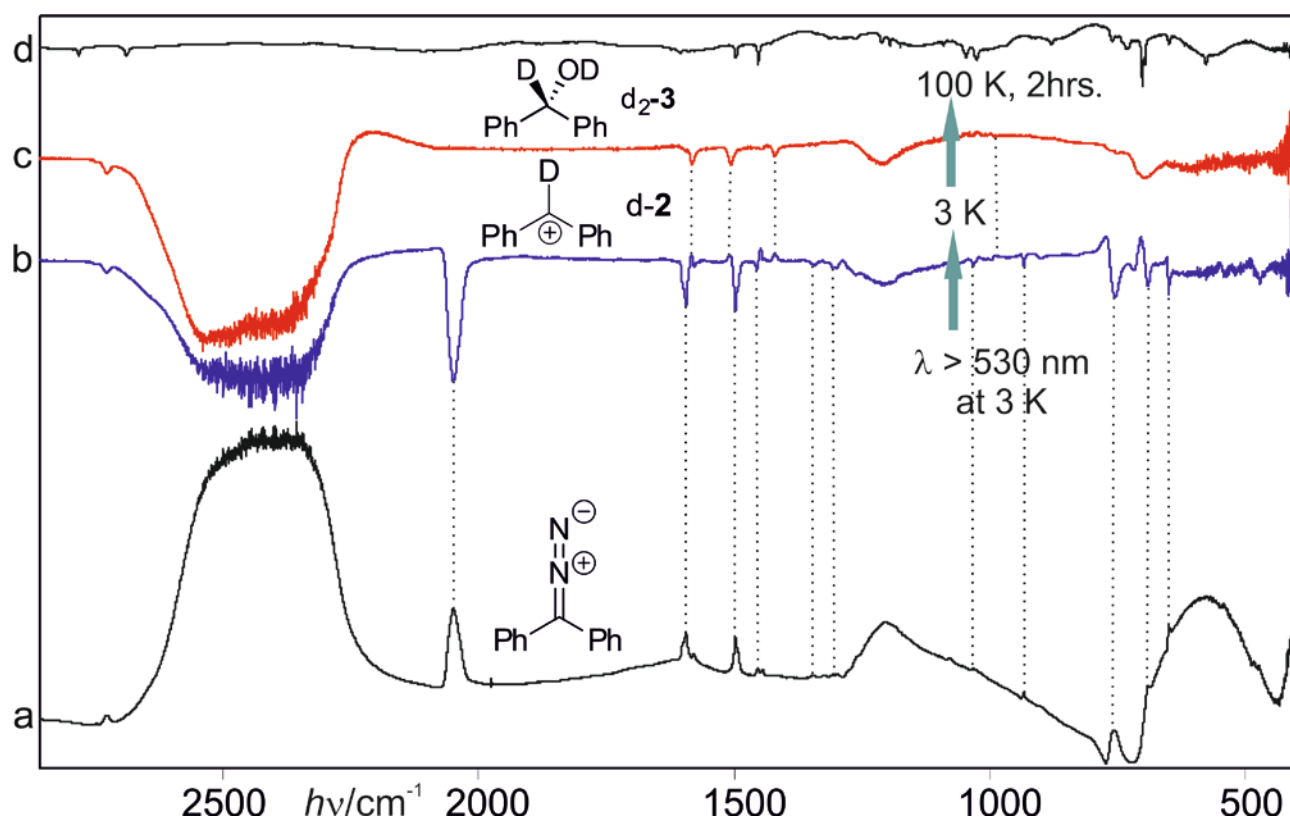


Figure S9. IR spectra showing the formation of d-2, upon photolysis of diphenyldiazomethane, and its disappearance after annealing for two hours from 3 K to 100 K. a) IR spectrum of diphenyldiazomethane in LDA ice matrix matrix at 3 K. b) Difference IR spectrum of the same matrix showing changes after photolysis for 3 hrs. at 3 K. Bands pointing downwards assigned to diphenyldiazomethane are disappearing, and bands pointing upwards assigned to d-2 are appearing. c) Difference IR spectrum of the same matrix showing changes after 2 hours of annealing from 3 K to 100 K, and bands pointing downwards are assigned to d-2. d) IR spectrum of d₂-3 matrix-isolated in argon at 3 K.

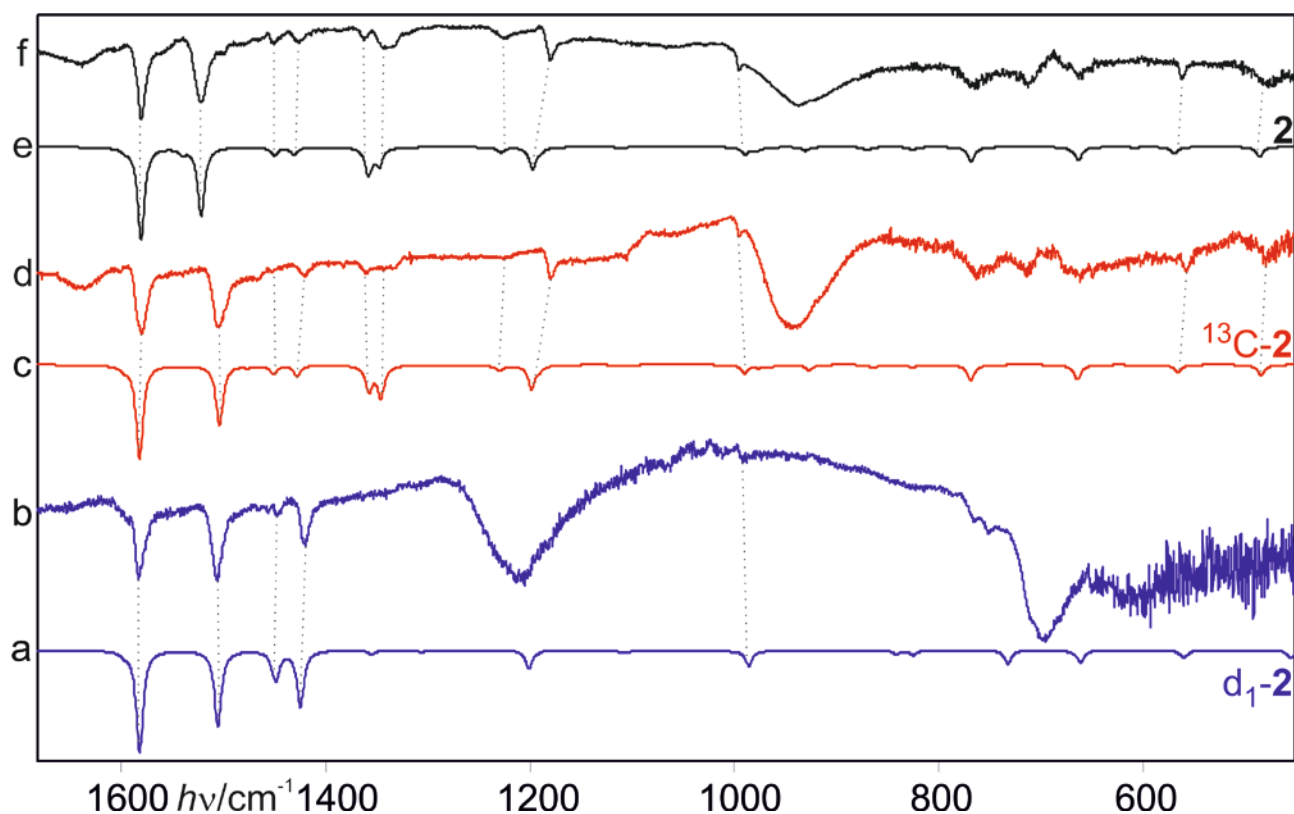


Figure S10. IR spectra in LDA ice showing the reaction of cation **2** (and corresponding isotopomers) at 100 K in 1700 – 500 cm^{-1} range. a) **d-2** calculated at the BLYP-D3/def2-TZVP level of theory. b) Difference IR spectrum: bands pointing downwards are disappearing upon warming from 3 K to 100 K and assigned to **d-2**. c) $^{13}\text{C-2}$ calculated at the BLYP-D3/def2-TZVP level of theory. d) Difference IR spectrum: bands pointing downwards are disappearing upon warming from 3 K to 100 K and assigned to $^{13}\text{C-2}$. e) **2** calculated at the BLYP-D3/def2-TZVP level of theory. f) Difference IR spectrum: bands pointing downwards are disappearing upon warming from 3 K to 100 K and assigned to **2**

Table S5. IR spectroscopic data of **2**

Benzhydryl cation - 2						
Mode	Sym	BLYP ^a [BLYP+water] ^b {QM/MM} ^c		LDA ice ^d		Assignment
		v/cm ⁻¹	I _{rel}	v/cm ⁻¹	I _{rel}	
11	B	482.8 [487.8] {606.6}	11 [11]	477.4	10.6	Skel. Vibr.
12	B	565.5 [570.2] {609.8}	8 [6]	561.0	10.4	Skel. Vibr.
29	B	983.4 [1001.2] {1000.1}	8 [7]	995.3	9.8	Skel. Vibr.
39	B	1190.2 [1184.1] {1185.9}	24 [21]	1180.0	37.7	C-H def. (in plane)
41	B	1220.9 [1226.7] {1240.2}	6 [10]	1223.7	17.1	C-H def. (in plane)
44	B	1339.0 [1338.7] {1340.5}	19 [12]	1338.8	25.4	C-H def. (in plane)
46	B	1349.9 [1349.8] {1373.2}	29 [39]	1362.0	22.6	C=C str. Ring
47	B	1422.3 [1421.6] {1408.6}	8 [8]	1426.0	8.8	C=C str. Ring
48	A	1441.4 [1440.7] {1424.1}	9 [9]	1451.0	9.3	C=C str. Ring
51	B	1512.5 [1516.4] {1519.6}	75 [65]	1521.6	100	C-C-C asym. str. Cationic center
54	B	1571.0 [1572.3] {1580.5}	100 [100]	1580.1	79.1	C=C str. Ring
56	A	3059.8 [3072.6] {3071.2}	1 [5]	/	/	C-H str. Cationic center

^[a]Calculated at the BLYP-D3/Def2-TZVP level of theory. ^[b]Calculated at the BLYP-D3/def2-TZVP level of theory, Benzhydryl cation - **2** and 5 water molecules. ^[c]Calculated at the BLYP-D3/def2-TZVP//CHARMM level of theory, Benzhydryl cation - **2** and 5 water molecules as QM region in a box of water. ^[d]LDA ice matrix at 3 K.

Table S6. IR spectroscopic data of ¹³C-**2**

¹³ C-Benzhydryl cation – ¹³ C- 2								
Mode	Sym	Calcd gas phase ^a		Shift ^b	LDA ice ^c		Shift ^b	Assignment
		v/cm ⁻¹	I _{rel}		v/cm ⁻¹	I _{rel}		
11	B	480.8	11	-2.0	476.8	10.4	-0.6	Skel. Vibr.
12	B	561.8	8	-3.7	558.5	10.2	-2.5	Skel. Vibr.
29	B	982.9	9	-0.5	995.3	10.8	0.0	Skel. Vibr.
39	B	1190.0	26	-0.2	1180.0	38.1	0.0	C-H def. (in plane)
41	B	1220.8	6	-0.1	1223.7	18.1	0.0	C-H def. (in plane)
44	B	1336.3	34	-2.7	1337.5	27.6	-1.3	C-H def. (in plane)
46	B	1348.2	24	-1.7	1360.3	22.6	-1.7	C=C str. Ring
47	B	1417.7	12	-4.6	1421.1	12.8	-4.9	C=C str. Ring
48	A	1440.7	9	-0.7	1451.0	9.8	0.0	C=C str. Ring
51	B	1493.2	65	-19.3	1504.1	89.3	-17.5	C-C-C asym. str. Cationic center
54	B	1570.9	100	0.1	1580.1	100	0.0	C=C str. Ring
56	A	3050.5	1	-9.3	/	/	/	C-H str. Cationic center

^[a]Calculated at the BLYP-D3/def2-TZVP level of theory. ^[b]Frequency shift relative to **2**. ^[c]LDA ice matrix at 3 K.

Table S7. IR spectroscopic data of **d-2**

d-Benzhydryl cation – d-2								
Mode	Sym	Calcd gas phase ^a		Shift ^b	LDA ice ^c		Shift ^b	Assignment
		ν/cm^{-1}	I_{rel}		ν/cm^{-1}	I_{rel}		
29	B	978.8	16	-4.6	991.8	7	-3.5	Skel. Vibr.
47	B	1414.6	55	-7.7	1419.8	52	-6.2	C=C str. Ring
48	B	1437.9	23	-3.5	1446.6	21	-4.4	C=C str. Ring
51	B	1494.7	75	-17.8	1506.4	100	-15.2	C-C-C asym. str. Cationic center
54	B	1570.8	100	-0.2	1583.0	92	+2.9	C=C str. Ring
56	A	2255.8	1	-804	/	/	/	C-H str. Cationic center

^[a]Calculated at the BLYP-D3/def2-TZVP level of theory. ^[b]Frequency shift relative to **2**. ^[c]LDA ice matrix at 3 K.

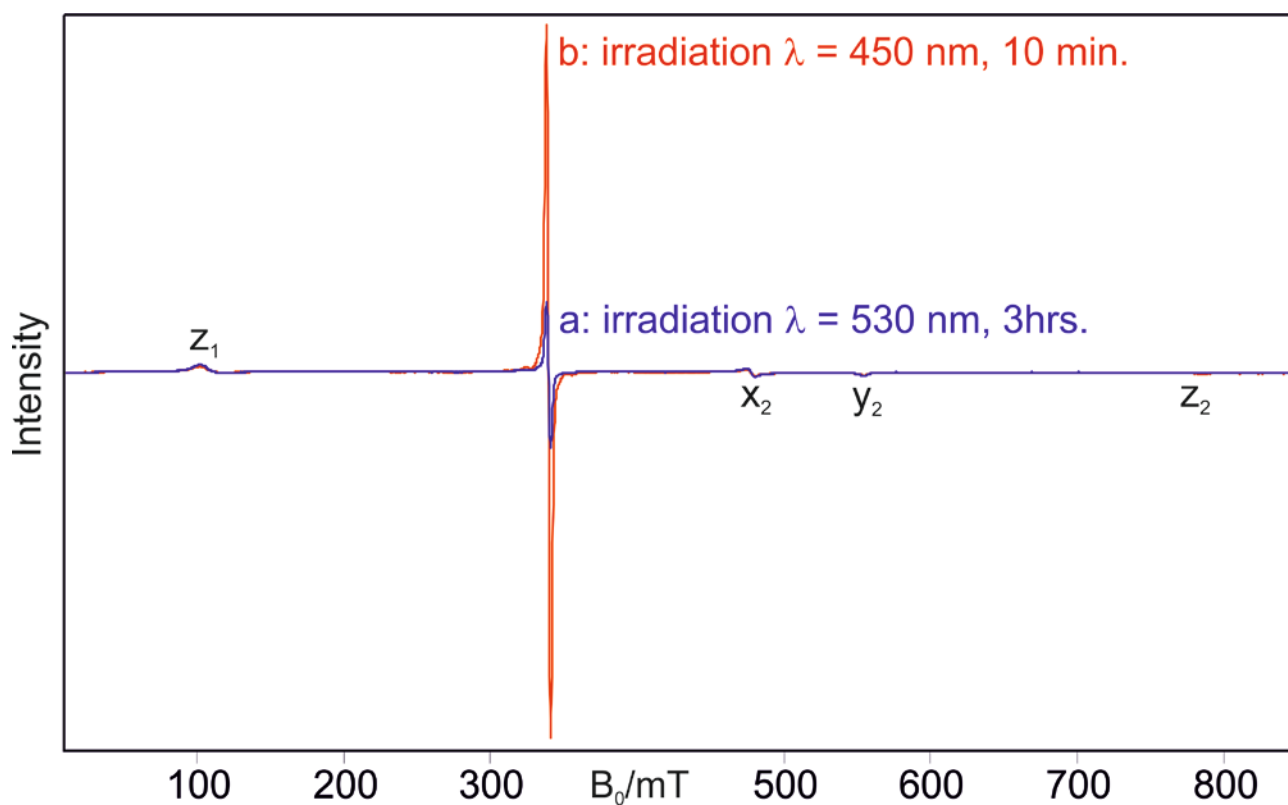


Figure S11. EPR spectra showing the formation of a strong radical signal after 10 minutes of irradiation with $\lambda = 450$ nm over a previous water matrix of diphenyldiazomethane irradiated for 3hrs. with $\lambda = 530$ nm. a) Water matrix at 5 K showing the triplet spectrum of **1** and a radical signal at about 340 mT. b) The same matrix after irradiation for 10 minutes with $\lambda = 450$ nm. The intensity of the radical signal strongly increases.

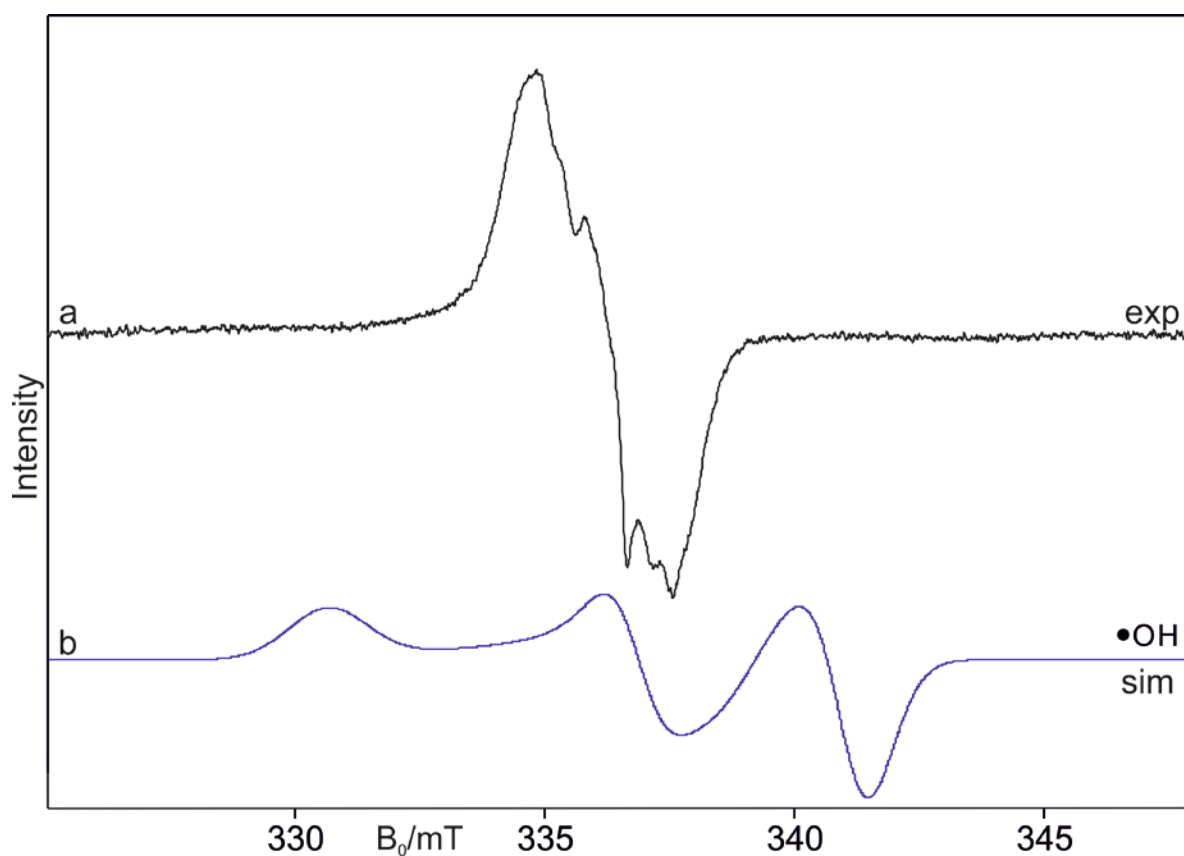


Figure S12. X-band EPR spectra showing the comparison among the experimental spectrum (Figure S11-b in the radical region 320- 350 mT) and the simulated spectra of OH radical. a) Experimental spectrum in the radical region recorded at 20 K to decrease the saturation of the signal. b) simulated spectrum of OH radical with parameters taken from literature⁴

5. Computational Results

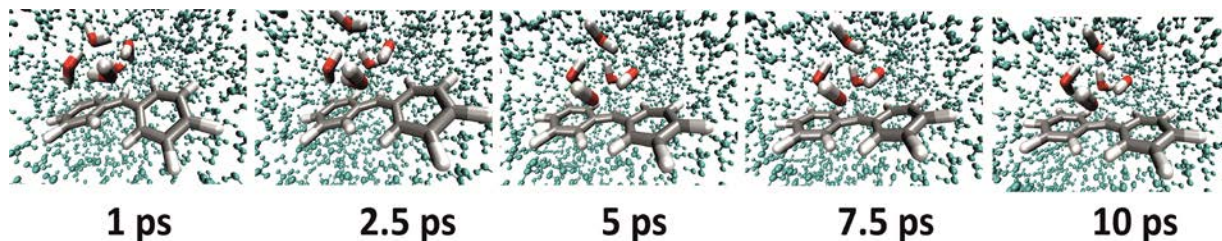


Figure S13. Selected snapshots from the QM/MM MD simulation of the cation **2** with 5 water molecules in a water box at 3 K. No evidence of thermal reaction was found.

Table S8. Adiabatical gap (ΔE_A) for **1**. All values are in kcal mol⁻¹.

(U)BLYP-D3/def2-TZVP	(U)BLYP-D3/def2-TZVP//CHARMM (in Ar)
ΔE_A	ΔE_A
3.33	1.5 ± 0.1

Table S9. Stabilization energies (ΔE) corrected with zero point vibrational energy (ΔE_{ZPVE}) for the complex of DPC with water. All values are in kcal mol⁻¹.

Complex	(U)BLYP-D3/Def2-TZVP	
	ΔE	ΔE_{ZPVE}
T- 1 ...H-OH	-6.32	-4.92
S- 1 ...H-OH	-11.79	-9.86

Table S10. Difference energies (ΔE) corrected with zero point vibrational energy (ΔE_{ZPVE}) between S-**1**...H-OH and T-**1**...H-OH. All values are in kcal mol⁻¹.

(U)BLYP-D3/def2-TZVP		(U)BLYP-D3/def2-TZVP//CHARMM (in Ar)	
ΔE	ΔE_{ZPVE}	ΔE	ΔE_{ZPVE}
-2.59	-1.62	-3.3 ± 0.1	-2.4 ± 0.1

Table S11. Energies (kcal/mol) and selected geometrical parameters of the 1:1 water complexes of DPC at different simulation times. QM/MM calculations in an Ar box at the BLYP-D3/def2-TZVP//CHARMM level of theory.

Time (ps)	ΔE (stabilization)		$\Theta(\text{C-C-C})$		$R(\text{C-H})$ (Å)		$\Theta(\text{C-H-O})$		ΔE (S-T)
	S-1	T-1	S-1	T-1	S-1	T-1	S-1	T-1	
1	-17.1	-13.5	121°	142°	1.82	1.86	166°	159°	-2.1
2	-16.8	-13.1	121°	143°	1.83	1.86	167°	161°	-2.2
2,5	-16.9	-13.2	121°	142°	1.83	1.86	167°	159°	-2.3
3	-16.8	-12.8	121°	143°	1.83	1.87	167°	160°	-2.5
4	-16.9	-12.9	121°	143°	1.82	1.86	167°	160°	-2.5
5	-16.9	-13.0	121°	142°	1.81	1.85	168°	159°	-2.4
6	-16.8	-12.7	121°	142°	1.81	1.86	168°	159°	-2.6
7	-16.9	-12.7	121°	143°	1.82	1.86	167°	160°	-2.6
7,5	-16.9	-13.0	121°	142°	1.81	1.85	167°	159°	-2.4
10	-16.7	-13.0	121°	141°	1.82	1.86	167°	157°	-2.3
Average	-16.9	-13.0	121.0°	142.3°	1.82	1.86	167.1°	159.3°	-2.4
MAE	0.08	0.2	0.004°	0.6°	0.006	0.004	0.4°	0.8°	0.1

Table S12. Singlet-triplet gaps (kcal/mol) and selected geometrical parameters of the DPC + 5 H₂O system at different simulation times. Gas phase calculations at the BLYP-D3/def2-TZVP level of theory.

	$\Theta(\text{C-C-C})$		$R(\text{C-H})$ (Å)		$\Theta(\text{C-H-O})$		ΔE (S-T)
	S-1	T-1	S-1	T-1	S-1	T-1	
1	122°	142°	1.78	1.99	175°	168°	-5.7
2	122°	142°	1.78	1.99	175°	167°	-5.7
3	122°	142°	1.78	1.99	175°	168°	-5.9
4	122°	142°	1.78	1.99	175°	168°	-5.9
5	122°	142°	1.78	1.99	175°	166°	-5.9
6	121°	142°	1.78	1.99	175°	168°	-5.8
7	121°	142°	1.78	1.99	175°	167°	-5.9
8	122°	142°	1.78	1.99	175°	167°	-5.9
9	122°	142°	1.78	1.99	175°	168°	-5.9
10	122°	142°	1.78	1.99	175°	167°	-6.0
Average	121.8°	142°	1.78	1.99	175°	167.4°	-5.9
MAE	0.3°	0.05°	0.0008	0.0007	0.08°	0.6°	0.08

Table S13. Singlet-triplet gaps (kcal/mol) and selected geometrical parameters of the DPC + 5 H₂O system at different simulation times. QM/MM simulations in a box of water at the BLYP-D3/def2-TZVP//CHARMM level of theory.

	$\Theta(\text{C-C-C})$		$R(\text{C-H}) (\text{\AA})$		$\Theta(\text{C-H-O})$		$\Delta E (\text{S-T})$
	S-1	T-1	S-1	T-1	S-1	T-1	
1	124°	141°	1.63	1.81	176°	152°	-2.8
2	124°	142°	1.64	1.81	175°	151°	-2.6
3	124°	142°	1.62	1.82	177°	150°	-2.9
4	124°	142°	1.63	1.82	177°	151°	-2.7
5	124°	142°	1.62	1.82	177°	150°	-2.9
6	124°	141°	1.63	1.81	176°	152°	-2.8
7	124°	142°	1.63	1.81	176°	152°	-2.0
8	124°	142°	1.63	1.82	176°	151°	-2.4
9	124°	142°	1.64	1.82	176°	150°	-3.3
5	124°	142°	1.62	1.82	177°	150°	-2.9
Average	124°	141.8°	1.63	1.82	176.2°	150.9°	-2.7
MAE	0.03	0.3°	0.006	0.005	0.5°	0.7°	0.2

6. Cartesian coordinates of optimized structures

Table S14. Cartesian coordinates of the optimized structure of S-1 calculated at the BLYP-D3/def2-TZVP level of theory

Atomic symbol	x	y	z
C	5.08921744084592	1.59163797114763	-2.14925895072264
C	2.71142946971402	1.44028826008904	-1.02991858589300
C	2.34084867194241	0.05492236203380	1.26656973465582
C	4.48775700564991	-1.19356610124858	2.32934394160924
C	6.81279499438952	-1.16586151437832	1.10715888609950
C	7.13595180106057	0.25881242437758	-1.11496037228900
H	5.35287503304017	2.71064916547541	-3.85755135883081
H	1.11442313045427	2.44435819536111	-1.84920961841611
H	4.23659640130325	-2.19731408985479	4.10745860506916
H	8.41050589590552	-2.18495074238102	1.91093837449387
H	8.98404822151584	0.35121914958324	-2.01621561140038
C	0.00000000000000	0.00000000000000	2.59128991124853
C	-2.34084867194241	-0.05492236203380	1.26656973465582
C	-4.48775700564991	1.19356610124858	2.32934394160924
C	-2.71142946971402	-1.44028826008904	-1.02991858589300
C	-6.81279499438952	1.16586151437832	1.10715888609950
H	-4.23659640130325	2.19731408985479	4.10745860506916
C	-5.08921744084592	-1.59163797114763	-2.14925895072264
H	-1.11442313045427	-2.44435819536111	-1.84920961841611
C	-7.13595180106057	-0.25881242437758	-1.11496037228900
H	-8.41050589590552	2.18495074238102	1.91093837449387
H	-5.35287503304017	-2.71064916547541	-3.85755135883081
H	-8.98404822151584	-0.35121914958324	-2.01621561140038

$$E = -501.2783144, ZPE = 0.1785712$$

$$E = -500.3381288 \text{ (CCSD(T)/cc-pVTZ//BLYP-D3/def2-TZVP)}$$

Table S15. Cartesian coordinates of the optimized structure of T-1 calculated at the BLYP-D3/def2-TZVP level of theory

Atomic symbol	x	y	z
C	-1.11580198116236	5.68785654367501	-2.28373519010501
C	-1.10542401438321	3.18853144758047	-1.47565751637579
C	0.00936696043120	2.50342972787344	0.90303297309632
C	1.06582616909098	4.49188552706009	2.40368039683735
C	1.02930952037562	6.98094104424083	1.56416774885216
C	-0.05336675530973	7.60351504397277	-0.78045264996354
H	-1.96656502822143	6.16297259018249	-4.09795161246007
H	-1.94990435832525	1.71383383387971	-2.63397235657638
H	1.90581749335167	4.01408082299232	4.21954296679009
H	1.85172389089379	8.45974641658891	2.73675354180398
H	-0.07599543635163	9.55686179107929	-1.42526853998592
C	0.00000000000000	0.00000000000000	1.73972047617365
C	-0.00936696043120	-2.50342972787344	0.90303297309632
C	-1.06582616909098	-4.49188552706009	2.40368039683735
C	1.10542401438321	-3.18853144758047	-1.47565751637579
C	-1.02930952037562	-6.98094104424083	1.56416774885216
H	-1.90581749335167	-4.01408082299232	4.21954296679009
C	1.11580198116236	-5.68785654367501	-2.28373519010501
H	1.94990435832525	-1.71383383387971	-2.63397235657638
C	0.05336675530973	-7.60351504397277	-0.78045264996354
H	-1.85172389089379	-8.45974641658891	2.73675354180398
H	1.96656502822143	-6.16297259018249	-4.09795161246007
H	0.07599543635163	-9.55686179107929	-1.42526853998592

$$E = -501.2829192, ZPE = 0.1779068$$

$$E = -500.3427498 \text{ (CCSD(T)/cc-pVTZ//BLYP-D3/def2-TZVP)}$$

Table S16. Cartesian coordinates of the optimized structure of S-1...HOH calculated at the BLYP-D3/def2-TZVP level of theory

Atomic symbol	x	y	z
C	-2.44437281789758	0.32927958534053	-0.03692084435794
C	-2.86634418597756	-1.95100187681785	1.35378828362926
C	-4.57914763013135	1.50421705941727	-1.19705994465032
C	-5.28011484159647	-2.97776210513017	1.55807109247712
H	-1.28271563266662	-2.83128308638205	2.32637234968576
C	-6.95634964143771	0.38864535573893	-1.10002246393771
H	-4.28179460085417	3.28851094756332	-2.17653807860575
C	-7.32036307743345	-1.83971303649068	0.30030803668287
H	-5.58538729753984	-4.67974164735786	2.67531277523581
H	-8.55366756065101	1.27889583918044	-2.04418940685815
H	-9.20069412758518	-2.66489678634770	0.44324402057520
C	2.26275811049519	0.19969771513356	-0.17953257635687
C	2.58343270995122	-2.23757982579981	-1.30608664715375
C	4.43827631014437	1.38592085774370	0.89793807509243
C	4.94197302367597	-3.40239127086596	-1.34775767166211
H	0.96990373729187	-3.13688745983687	-2.21051456176133
C	6.75236209622840	0.14159451427908	0.96829887416946
H	4.21591000428267	3.27611272626294	1.68194407107873
C	7.02027785134743	-2.24100578293758	-0.17549579189199
H	5.17227066756807	-5.23049041727394	-2.26629248661153
H	8.37755829587903	1.04227688776137	1.85383655294417
H	8.85449738604619	-3.17552844283484	-0.18331674707232
C	-0.05766054335469	1.57023985226685	-0.19853102966207
O	0.90569868608755	6.95002429527437	0.36682673835245
H	2.04087344253917	7.30722773714412	-1.03457990841175
H	0.38436850004108	5.14052411078413	0.07639661882662

$$E = -577.7423332, ZPE = 0.201979$$

$$E = -576.6854878 \text{ (CCSD(T)/cc-pVTZ//BLYP-D3/def2-TZVP)}$$

Table S17. Cartesian coordinates of the optimized structure of T-1...H2O calculated at the BLYP-D3/def2-TZVP level of theory

Atomic symbol	x	y	z
C	-2.47820195959465	0.06399206601682	-0.04410824872662
C	-3.12269255413792	-2.28759297754089	1.14978032191939
C	-4.49779396564732	1.53467406099769	-1.08607088053784
C	-5.61621710933164	-3.10707087072926	1.23560844367014
H	-1.62311742882041	-3.41672824431581	1.98966588571915
C	-6.98060634443963	0.68535329708142	-0.96413722847175
H	-4.05379618732897	3.33914750727254	-1.96819097571357
C	-7.56358787819470	-1.63749182043791	0.18419389952807
H	-6.06126365950680	-4.90281460711459	2.13964411472423
H	-8.48485763864565	1.83295929236656	-1.77494503369681
H	-9.51202532985587	-2.29149580703603	0.26774242912093
C	2.53124580297928	0.05899835473532	-0.08856036816171
C	3.18703611203029	-2.38871135632743	-1.06053304642200
C	4.53634522461109	1.61840839082586	0.84418059818235
C	5.68033181265232	-3.21324635957043	-1.03726849832803
H	1.69789666128283	-3.58687265823033	-1.81945061655418
C	7.01931286281145	0.76120477011918	0.83411617446839
H	4.08019138176075	3.49588508788102	1.55119327242285
C	7.61390010578880	-1.65503900891419	-0.09398671383582
H	6.13649056315041	-5.08170021873585	-1.77268795493560
H	8.51431725809170	1.97824802684114	1.55554993387200
H	9.56289632172549	-2.31288801199679	-0.09455248276568
C	0.02629664717859	0.90432672266988	-0.12031981631975
O	-0.22562491148841	6.60061283440562	0.04483101281750
H	0.06474752650474	4.80701946315676	-0.36375769929710
H	-1.39007035392746	6.52142245136389	1.46735113503815

$$E = -577.7383466, ZPE = 0.2004756$$

Table S18. Cartesian coordinates of the optimized structure of **TS** calculated at the BLYP-D3/def2-TZVP level of theory

Atomic symbol	x	y	z
C	-2.39531215658766	0.38248966841018	-0.28515330316641
C	-2.78403216287842	-1.69366099374181	1.38279687394106
C	-4.54021610104575	1.43019811309588	-1.52345535681523
C	-5.19305752309791	-2.69950903393351	1.74364648283687
H	-1.18283359413012	-2.45318030199174	2.42620565470634
C	-6.93707511269134	0.38470918785846	-1.19982694288299
H	-4.25438665229123	3.06082215577621	-2.74585827937277
C	-7.26691784951093	-1.67909926943412	0.43709051810283
H	-5.47252479681708	-4.26983736480898	3.04567136439578
H	-8.55678270270330	1.18302811257190	-2.18788097843684
H	-9.14601293184151	-2.47253892843758	0.72045812550962
C	2.37805573151854	0.28580334896365	-0.36308948504451
C	2.71335493082676	-2.31112713226624	-1.03153245132746
C	4.55131850274136	1.66902655621749	0.45453374170538
C	5.09511597869328	-3.43483925625259	-0.92737995583765
H	1.10910430783924	-3.38262377471946	-1.74519385943926
C	6.89107293134763	0.48975084357998	0.65358423609122
H	4.28820949370566	3.63790071400506	0.99460983424787
C	7.18578340925061	-2.05712401355149	-0.05450774407366
H	5.32523032082274	-5.39732056336514	-1.50814457622379
H	8.51478417227264	1.55746390425937	1.33424790224400
H	9.03575450999901	-2.95368909824792	0.06070124009796
C	0.02594053615509	1.57691058414473	-0.72173830685785
O	0.38690067674909	5.98923970428025	0.77305345152686
H	0.08753368001836	4.08264881850901	-0.52101560465080
H	-1.14232061589047	6.11524689336077	1.79766911946441

$$E = -577.7157166, ZPE = 0.1979$$

$$E = -576.6653447 \text{ (CCSD(T)/cc-pVTZ//BLYP-D3/def2-TZVP)}$$

Table S19. Cartesian coordinates of the optimized structure of **3** calculated at the BLYP-D3/def2-TZVP level of theory

Atomic symbol	x	y	z
C	2.43207753435665	-0.50455687775697	-0.41951920173051
C	2.24499464709844	-0.93541443629101	2.19397204148257
C	4.81502218923135	0.03779452267842	-1.45508912311936
C	4.39172353523298	-0.82392059438966	3.73598856676231
H	0.40629111879306	-1.32847747214664	3.02923099267576
C	6.96364080349981	0.15684726911546	0.08125822375861
H	4.98509754128426	0.35526851317719	-3.48465499095078
C	6.75577092876847	-0.27401028941858	2.68530083630209
H	4.21408927864439	-1.15462266782588	5.75988525619197
H	8.79667515340342	0.58770482764950	-0.75211100130065
H	8.42439910502094	-0.17196507818683	3.88527693134209
C	-2.34137067992843	0.23810549287407	-1.07525417020119
C	-2.40373164234783	2.62293987388269	0.09637603282998
C	-4.60904204063393	-1.11115896674569	-1.33792610281624
C	-4.67518245532117	3.62260499872703	1.00533430324610
H	-0.65951442073851	3.69252486568212	0.31936371663269
C	-6.88616203200904	-0.11149384190135	-0.43085755853404
H	-4.57880642249119	-2.94041386438146	-2.27334053910726
C	-6.92962573308923	2.25633300390197	0.74644182289889
H	-4.68463108599078	5.46886743156810	1.91618229979614
H	-8.62848952748443	-1.18485828596862	-0.65006579006891
H	-8.69840939443952	3.03301044494360	1.45508912311936
C	0.143619186178015	-0.80124388078261	-2.15050834040238
O	-0.06991986695508	-3.42229402853138	-2.94986249505107
H	0.527233591364029	0.20975960086525	-3.92496118015444
H	0.081258223758613	-4.46731258058983	-1.43808158791407

$$E = -577.815243, ZPE = 0.2071101$$

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