Matrix isolation, time-resolved IR, and computational study of the photochemistry of benzoyl azide

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Supporting Information, part 2

Figure S1-S6 and Table S1-S2

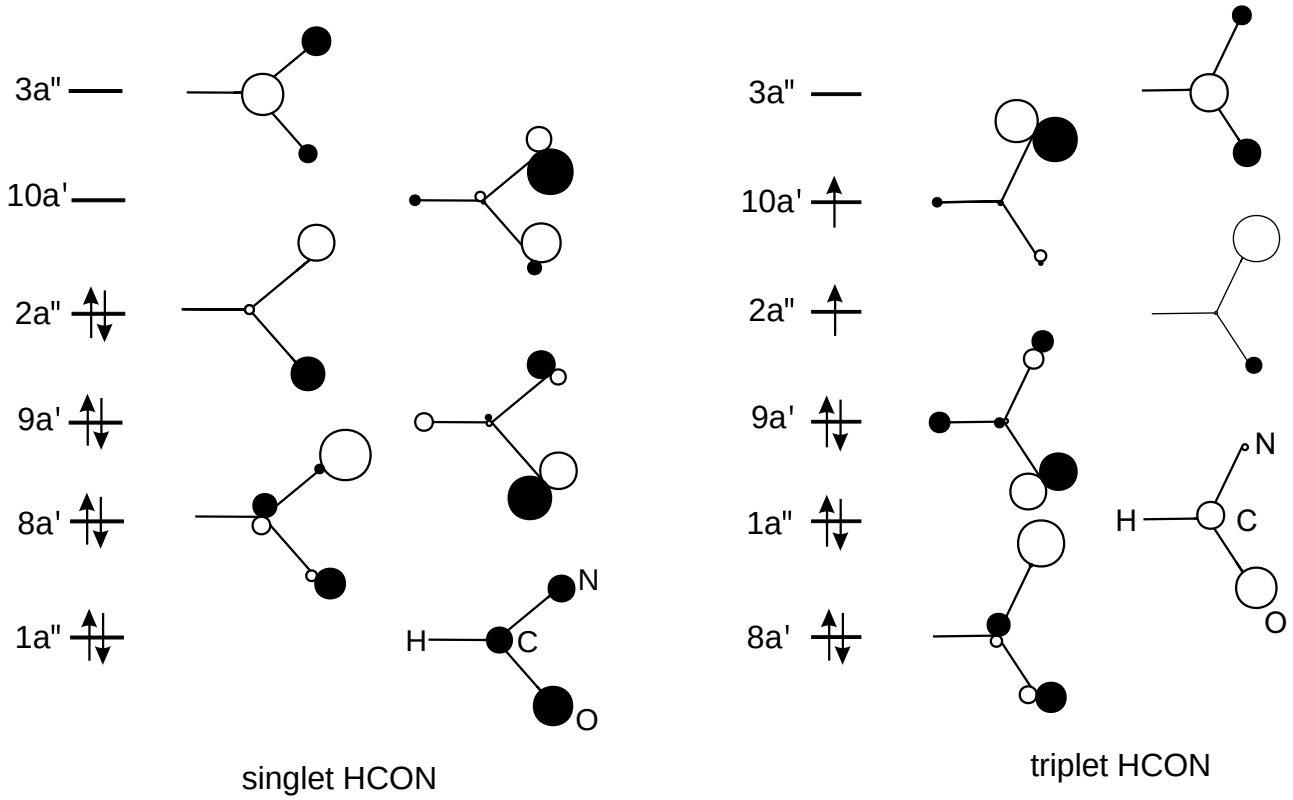

Figure S1: CASSCF orbitals of singlet and triplet HCON contained in the active space of the calculations whose results are listed in Table T1 and T2, respectively.

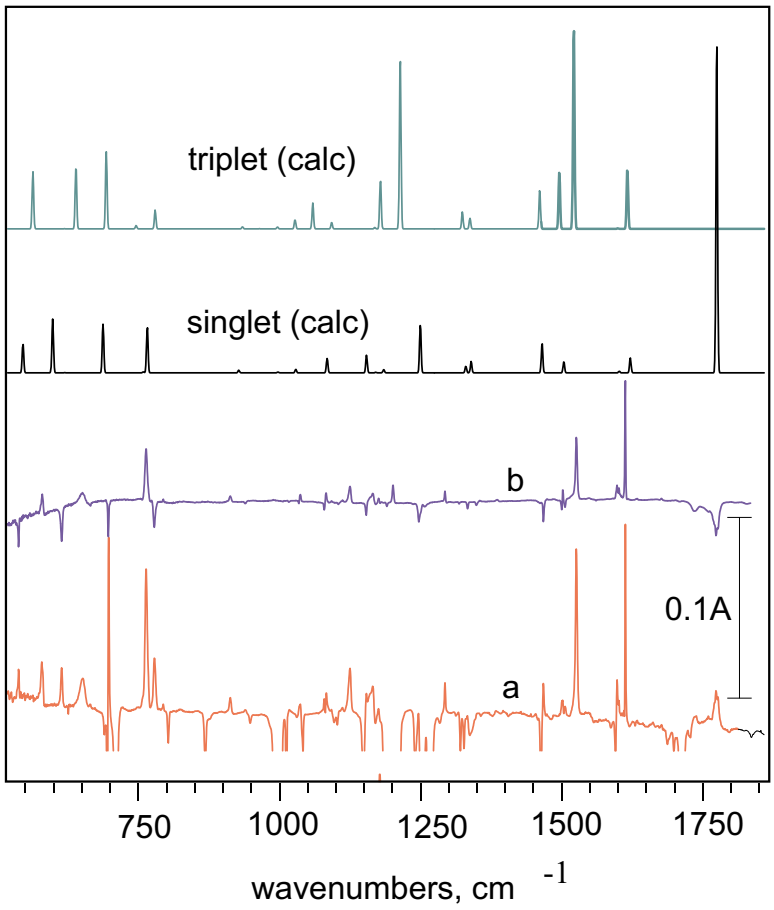

Figure S2:. Changes in IR spectra upon 254 nm irradiation of benzoyl azide (1b) in an Ar matrix at 12 K for 2 min (a) and subsequent 313 nm photolysis for 8 min (b).
The top two traces show the IR spectra of singlet and triplet benzoylnitrene calculated by the B3LYP/6-31G* and scaled by 0.97.

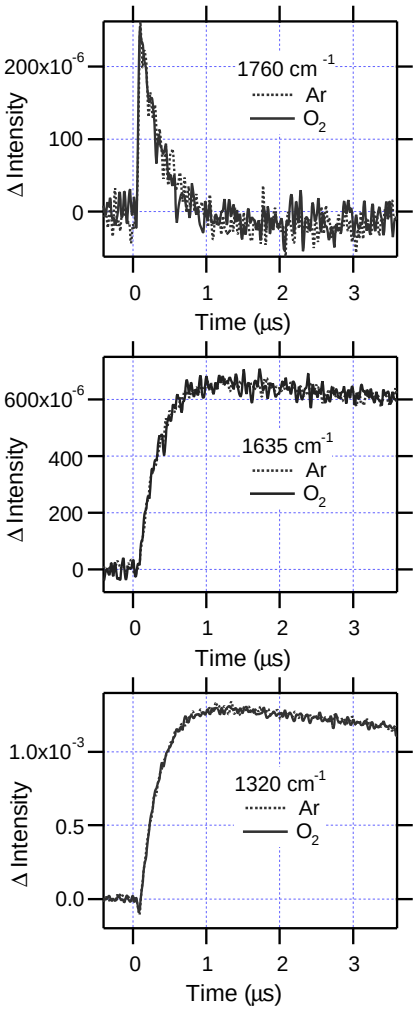

Figure S3. Kinetic traces observed at 1760, 1635, and 1320 cm^{-1} following 266 nm laser photolysis (5 ns, 2 mJ) of azide **1b** (3.3. mM) in argon- and oxygen-saturated acetonitrile-d_3.

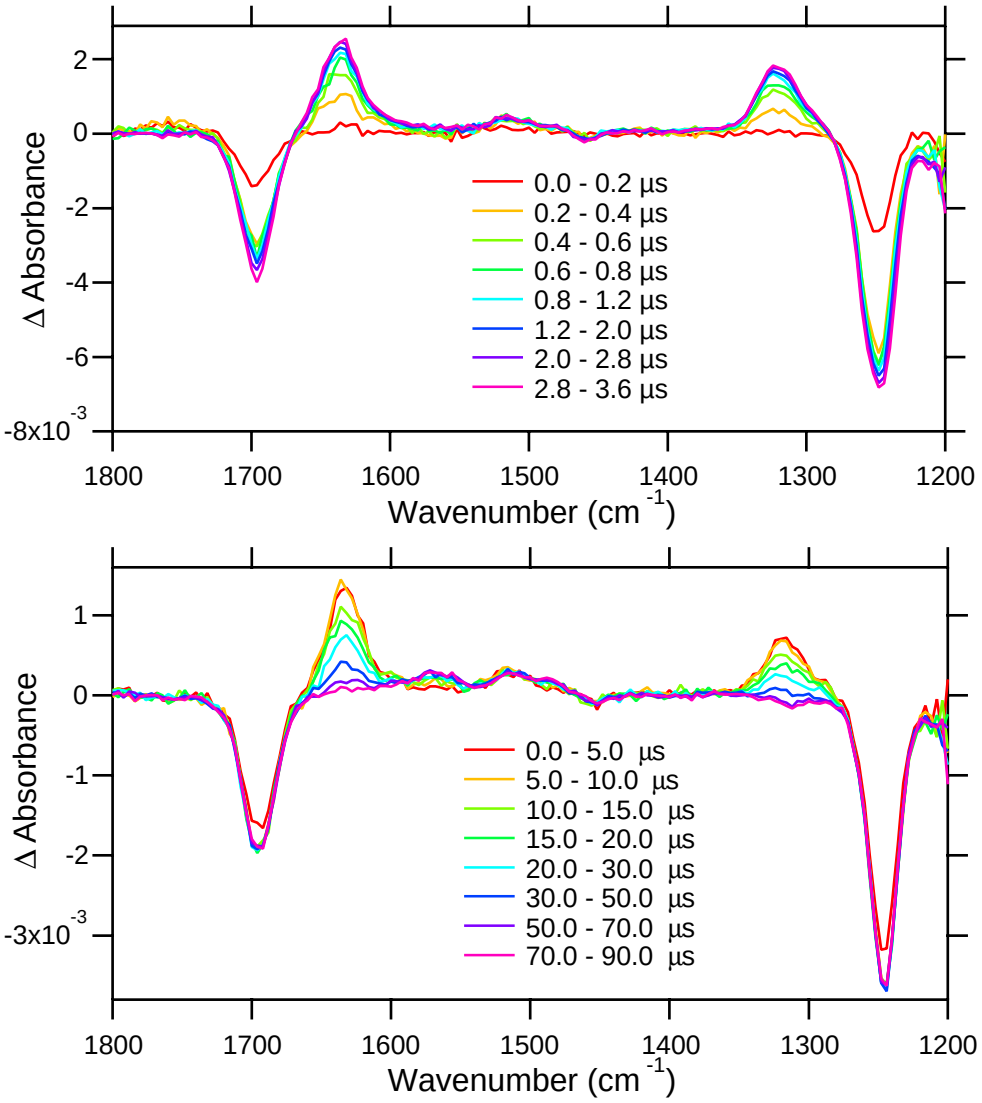

Figure S4. TRIR difference spectra averaged over the timescales indicated following 266 nm laser photolysis (5 ns, 2 mJ) of azide **1b** (3.3 mM) in argon-saturated acetonitrile-d_3.

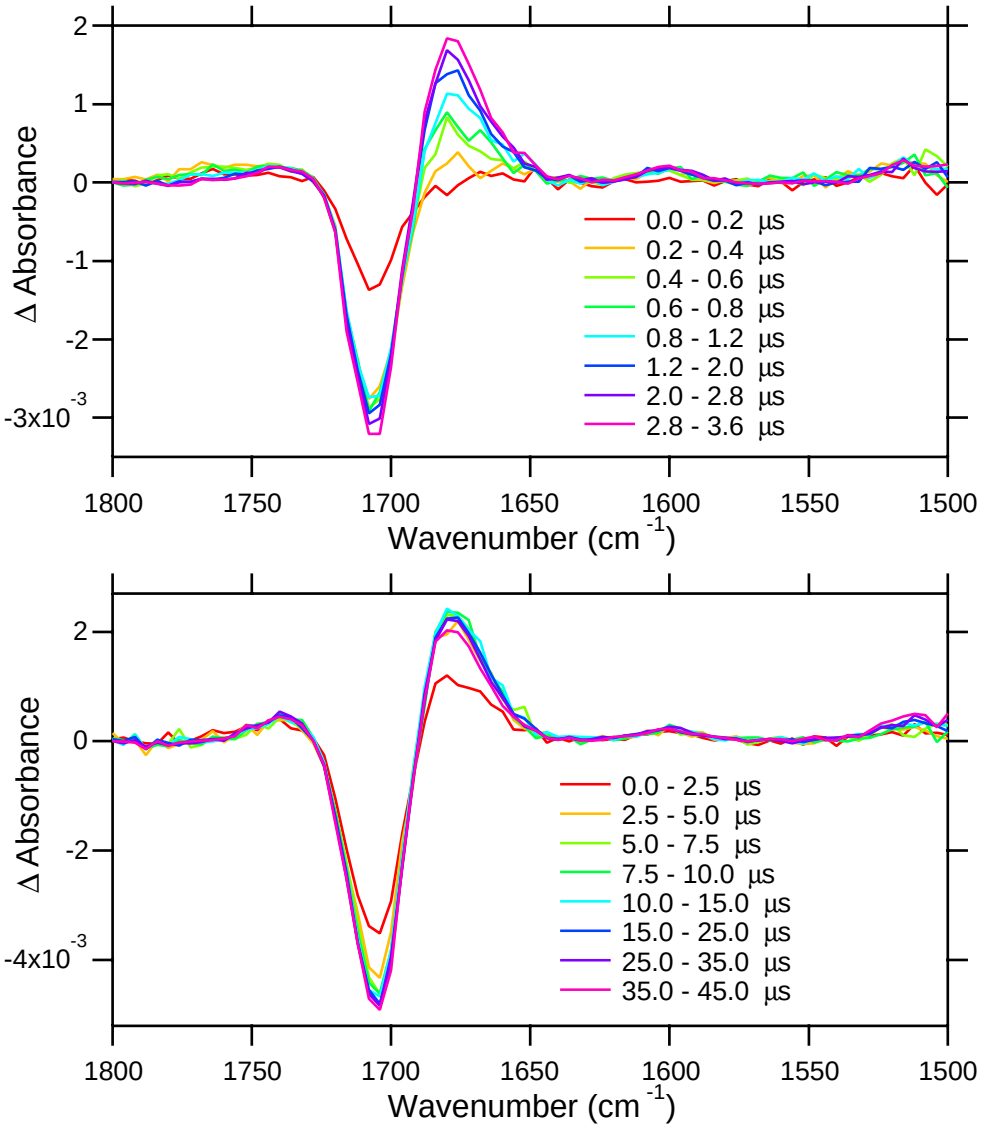

Figure S5. TRIR difference spectra averaged over the timescales indicated following 266 nm laser photolysis (5 ns, 2 mJ) of azide **1b** (3.3 mM) in argon-saturated cyclohexane.

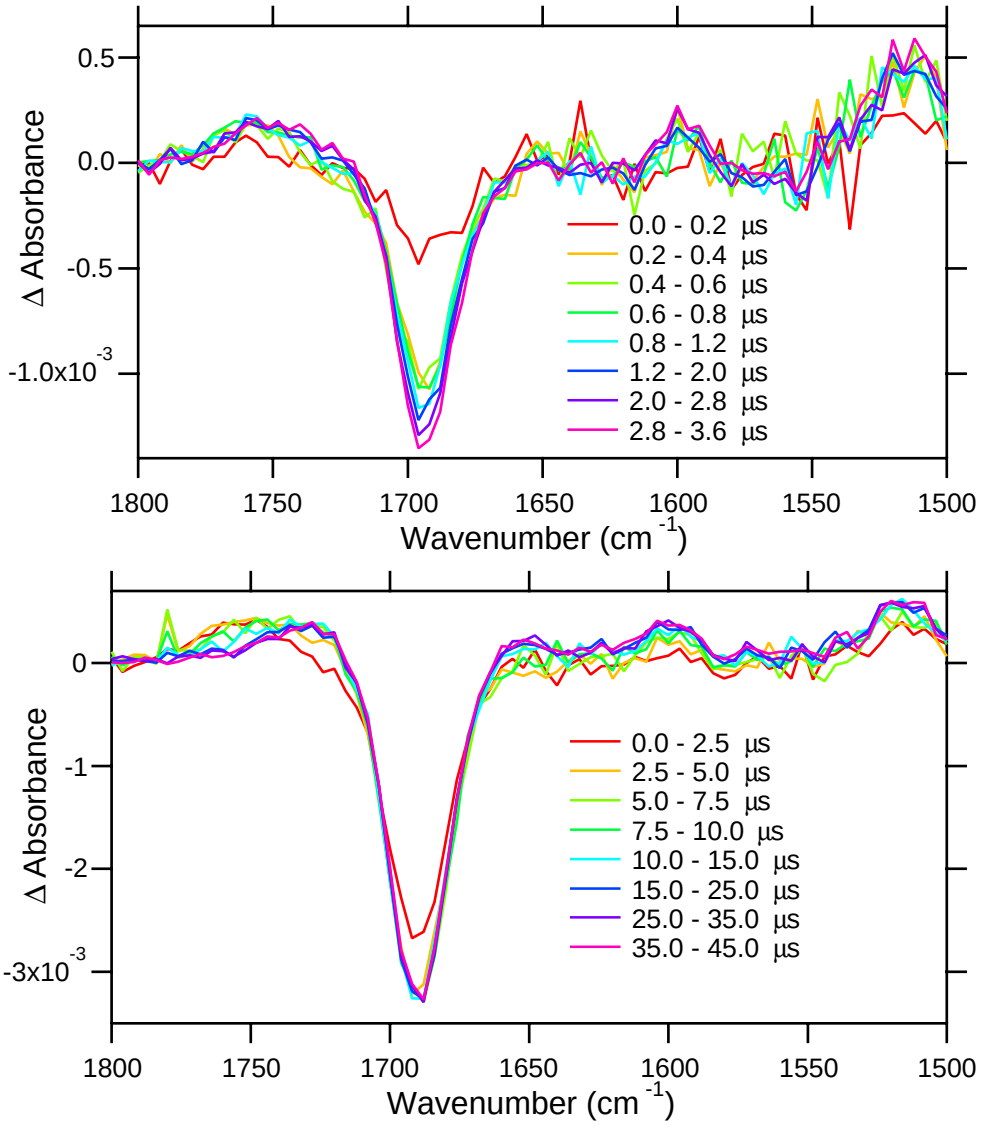

Figure S6. TRIR difference spectra averaged over the timescales indicated following 266 nm laser photolysis (5 ns, 2 mJ) of azide **1b** (3.3 mM) in argon-saturated dichloromethane.

Table T1. Vertical excitation energies of singlet formylnitrene calculated by the CASSCF(8,7)[a] / CASPT2 method at the B3LYP/6-31G* geometry.[b,c]

state	ΔE_{CASSCF}, eV	ΔE_{CASPT2} eV	ref. weight[d]	λ, nm	f[e]	Major configurations[f]
$1^1A'$	0.0	0.0	0.89			79% of ground configuration
$1^1A''$	2.51	2.32	0.88	534	2.1×10^{-4}	81%: 2a"→10a' 10%: 1a"→10a'
$2^1A'$	4.78	4.78	0.86	259	4.1×10^{-3}	42%: 2a"→3a" 20%: 9a'→10a' 19%: 2(2a"→10a')
$3^1A'$	5.81	5.77	0.88	215	3.0×10^{-3}	69%: 2(2a"→10a') 11%: 2a"→3a"
$2^1A''$	6.14	5.84	0.85	212	4.5×10^{-5}	43%: 1a"→10a' 17%: 2a"→10a' +9a'→ 10a' 17%: 2a"→ 3a" +2a"→10a'
$3^1A''$	7.14	7.06	0.86	176	7.4×10^{-5}	38%: 2a"→3a" + 2a"→10a' 26%: 9a'→3a" 18%: 2a"→10a' + 9a'→10a'

[a] Active space includes 4 a" and 3 a' orbitals shown in Figure S1; [b] Cartesian coordinates are given in Part 1 of the supporting information; [c] details of the calculation are given in Section B of Part 1 of the supporting information; [d]weight of the zero-order CASSCF wavefunction in the CASPT2 expansion;. [e] Oscillator strength for electronic transition, based on the CASSCF wave functions and the CASPT2 energy differences. [f] In a (8,7) CASSCF wavefunction; orbitals see Figure S1

Table T2. Vertical excitation energies of triplet formylnitrene calculated by the CASSCF(8,7)[a] / CASPT2 method at the B3LYP/6-31G* geometry. [b,c]

state	ΔE_{CASSCF}, eV	ΔE_{CASPT2},[d] eV	ref. weight[e]	λ, nm	f[f]	Major configurations[g]
$1^3A''$	0.0	0.0	0.88			88% of ground configuration
$1^3A'$	1.07	1.09	0.88	1137	3.3×10^{-4}	83%: 9a'→2a''
$2^3A''$	3.26	2.84	0.87	437	2.5×10^{-3}	85%: 9a'→ 10a'
$2^3A'$	4.18	3.84	0.87	323	7.2×10^{-3}	73%: 8a' → 2a''
$3^3A''$	4.09	4.23	0.88	293	1.8×10^{-2}	63%: 1a''→ 2a'' 20%: 2a''→ 3a''
$3^3A'$	5.20	5.61	0.88	221	8.0×10^{-6}	42%: 10a'→ 3a'' +9a'→ 10a' 18%: 10a'→ 3a'' 16%: 2a''→ 3a'' + 9a'→ 2a'' 11%: 9a'→3a''

[a] Active space includes 4 a'' and 3 a' orbitals shown in Figure S2; [b] Cartesian coordinates are given in Part 1 of the supporting information; [c] details of the calculation are given in Section B of Part 1 of the supporting information; [d] Calculated with a level shift of 0.25; [e] weight of the zero-order CASSCF wavefunction in the CASPT2 expansion;. [f] Oscillator strength for electronic transition, based on the CASSCF wave functions and the CASPT2 energy differences. e In a (8,7) CASSCF wavefunction; [g]orbitals see Figure S2

Table T3. Dependence of energy and reference weight of CASPT2 states on the level shift for singlet PhCON.[a]

CASPT2 states	$1^1A'$	$1^1A''$	$3^1A'$	$2^1A'$	$2^1A''$	$3^1A''$
level shift = 0.00 a.u.						
E_{CASPT2}, H	-398.439233	-398.286699	-398.285664	-398.257641	-398.439233	-398.249223
ΔE_{CASPT2}, eV	0.0	2.408	4.151	4.179	4.941	5.170
Ref. weight	0.728	0.722	**0.357**	**0.601**	**0.612**	**0.332**
level shift = 0.05 a.u.						
E_{CASPT2}, H	-398.438859	-398.350346	-398.296945	-398.285423	-398.259717	-398.260989
ΔE_{CASPT2}, eV	0.0	2.409	3.862	4.175	4.875	4.840
Ref. weight	0.736	0.730	**0.684**	0.703	0.703	**0.651**
level shift = 0.10 a.u.						
E_{CASPT2}, H	-398.437806	-398.349226	-398.292506	-398.285868	-398.288911	-398.279092
ΔE_{CASPT2}, eV	0.0	2.410	3.954	4.134	4.052	4.319
Ref. weight	0.744	0.738	0.716	0.713	**0.592**	**0.614**
level shift = 0.15 a.u.						
E_{CASPT2}, H	-398.436165	-398.347488	-398.289290	-398.280982	-398.255046	-398.278256
ΔE_{CASPT2}, eV	0.0	2.413	3.997	4.223	4.929	4.297
Ref. weight	0.751	0.746	0.730	0.734	0.735	**0.647**
level shift = 0.20 a.u.						
E_{CASPT2}, H	-398.434014	-398.345229	-398.285946	-398.277806	-398.252153	-398.248234
ΔE_{CASPT2}, eV	0.0	2.416	4.029	4.251	4.949	5.055
Ref. weight	0.758	0.753	0.740	0.744	0.744	0.739
level shift = 0.25 a.u.						
E_{CASPT2}, H	-398.431418	-398.342507	-398.282331	-398.274384	-398.248815	-398.244385
ΔE_{CASPT2}, eV	0.0	2.419	4.057	4.273	4.969	5.089
Ref. weight	0.765	0.760	0.749	0.753	0.753	0.749
level shift = 0.30 a.u.						
E_{CASPT2}, H	-398.428435	-398.339388	-398.278433	-398.270660	-398.245169	-398.240504
ΔE_{CASPT2}, eV	0.0	2.423	4.082	4.293	4.987	5.114
Ref. weight	0.771	0.767	0.757	0.761	0.760	0.757

[a] The results with level shift 0.25 a.u. are listed in Table 3 of the manuscript

Table T4. Dependence of energy and reference weight of CASPT2 states on the level shift for triplet PhCON[a]

CASPT2 states	1^3A" ground state	1^3A'	3^3A"	2^3A"	4^3A"	5^3A"	6^3A"	7^3A"	2^3A'	3^3A'
level shift = 0.00 a.u.										
E_{CASPT2}, H	-398.456137	-398.396656	-398.345397	-398.342861	-398.339915	-398.317860	-398.300386	-398.294458	-398.291843	-398.266949
ΔE_{CASPT2}, eV	0.0	1.619	3.013	3.082	3.163	3.763	4.238	4.400	4.471	5.148
Ref. weight	0.709	0.717	0.689	0.654	0.684	**0.201**	**0.591**	**0.616**	0.683	**0.594**
level shift = 0.05 a.u.										
E_{CASPT2}, H	-398.455669	-398.396151	-398.345069	-408.543683	-398.401763	-398.329051	-398.299337	-398.294969	-398.291811	-398.267337
ΔE_{CASPT2}, eV	0.0	1.620	3.010	-	1.467	3.445	4.254	4.373	4.459	5.125
Ref. weight	0.719	0.730	0.705	0.005	**0.373**	**0.576**	0.699	**0.672**	0.718	0.716
level shift = 0.10 a.u.										
E_{CASPT2}, H	-398.454394	-398.394971	-398.343531	-398.358915	-398.338882	-401.536226	-398.297824	-398.395801	-398.291455	-398.266900
ΔE_{CASPT2}, eV	0.0	1.617	3.017	2.598	3.143	-	4.260	1.594	4.434	5.102
Ref. weight	0.728	0.738	0.715	**0.675**	0.710	**0.029**	0.710	**0.391**	0.724	0.724
level shift = 0.15 a.u.										
E_{CASPT2}, H	-398.452453	-398.393193	-398.341299	-398.348611	-398.335460	-398.330181	-398.296679	-398.301511	-398.287970	-398.263563
ΔE_{CASPT2}, eV	0.0	1.613	3.025	2.826	3.184	3.327	4.239	4.107	4.476	5.140
Ref. weight	0.736	0.746	0.724	0.717	0.725	**0.678**	0.719	**0.689**	0.740	0.740
level shift = 0.20 a.u.										
E_{CASPT2}, H	-398.449950	-398.390893	-398.338462	-398.343686	-398.332487	-398.315235	-398.291879	-398.289739	-398.285390	-398.260777
ΔE_{CASPT2}, eV	0.0	1.607	3.034	2.892	3.196	3.666	4.301	4.360	4.478	5.148
Ref. weight	0.744	0.754	0.733	0.732	0.734	0.721	0.734	0.724	0.748	0.749
level shift = 0.25 a.u.										
E_{CASPT2}, H	-398.446967	-398.388141	-398.335108	-398.339439	-398.329060	-398.309074	-398.288207	-398.284384	-398.282307	-398.257706
ΔE_{CASPT2}, eV	0.0	1.601	3.044	2.926	3.208	3.752	4.320	4.424	4.481	5.150
Ref. weight	0.751	0.761	0.741	0.743	0.742	0.736	0.743	0.737	0.756	0.756
level shift = 0.30 a.u.										
E_{CASPT2}, H	-398.443572	-398.384995	-398.331316	-398.335192	-398.325222	-398.304014	-398.284260	-398.279649	-398.278867	-398.254247
ΔE_{CASPT2}, eV	0.0	1.594	3.055	2.949	3.220	3.798	4.335	4.461	4.482	5.152
Ref. weight	0.759	0.767	0.749	0.751	0.750	0.746	0.751	0.747	0.763	0.764