Supporting Information for

Non-Trivial Ground and Excited State Photophysics of a Substituted Phenol

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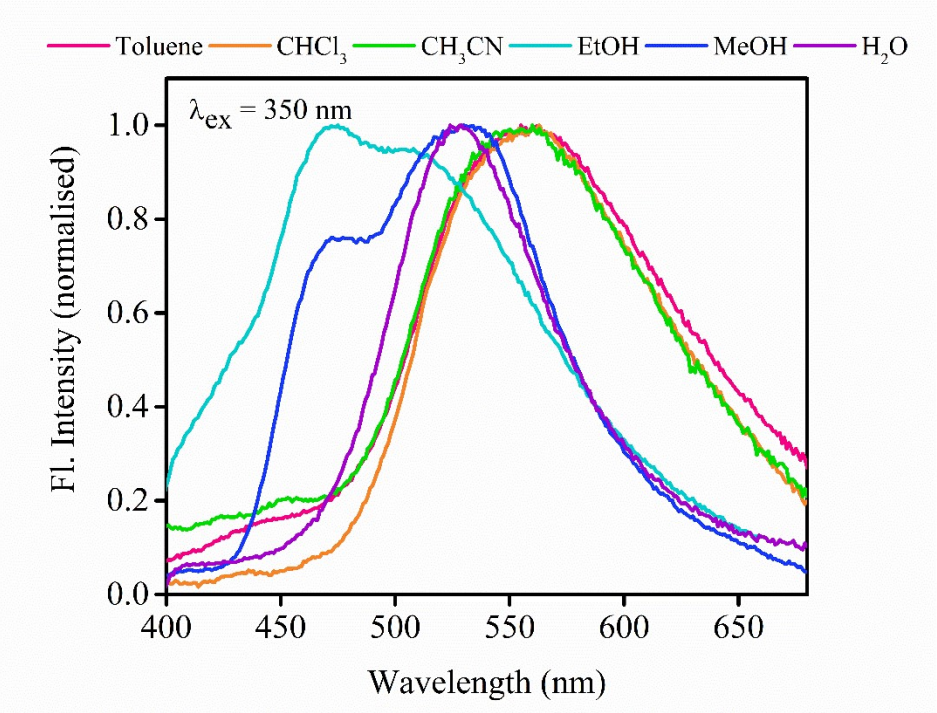


Figure S1: Normalised emission spectra of 5-tBHI in different solvent for λ_{ex} = 350 nm.

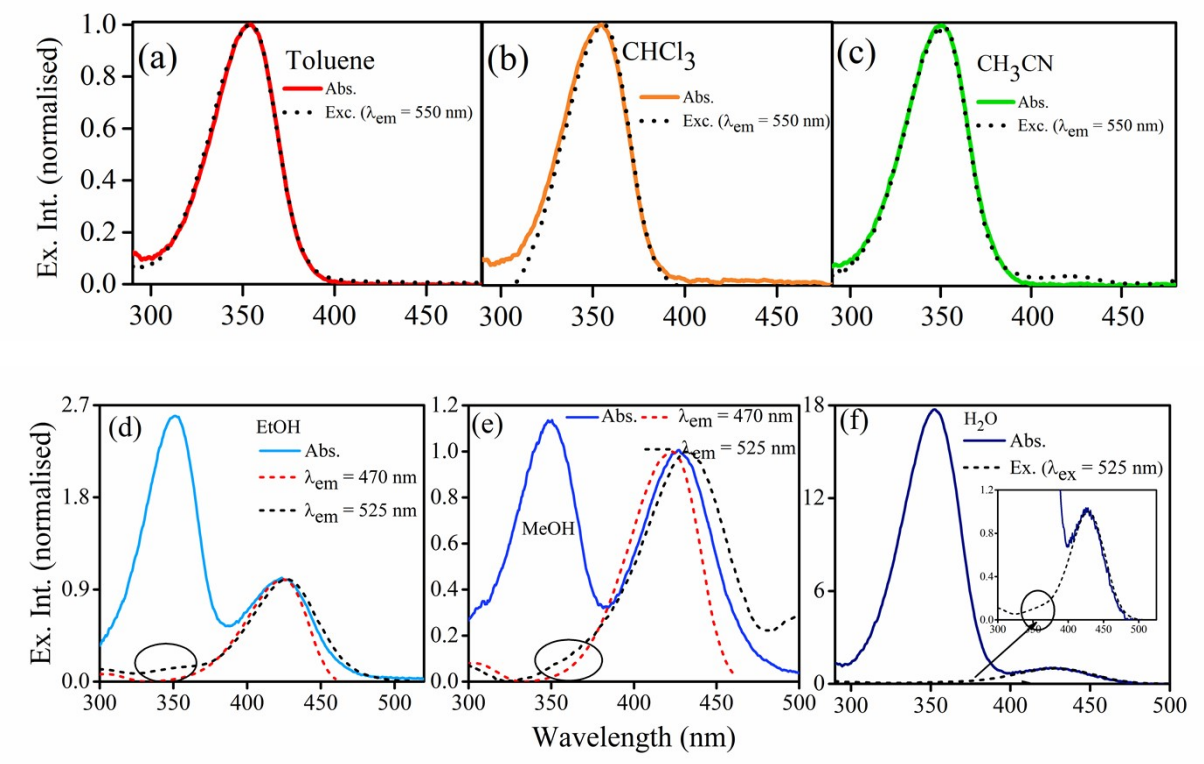


Figure S2: Peak normalized absorption (solid line) and excitation spectra (dash line) of 5-tBHI in neat solvents.

*Note that in toluene, Chloroform and acetonitrile, the absorption and excitation spectra are superimposable to each other.

Table S1: Spectral properties of 5-tBHI in neat solvents.

Solvent	ϕ_f (λ_{ex} = 350 nm)	ϕ_f (λ_{ex} = 425 nm)	dielectric constant of the solvent
Toluene	0.05		2.38
Chloroform	0.05		4.81
Acetonitrile	0.02		37.5
Ethanol	0.09	0.19	24.5
Methanol	0.11	0.23	32.7
Water	0.02	0.17	80.1

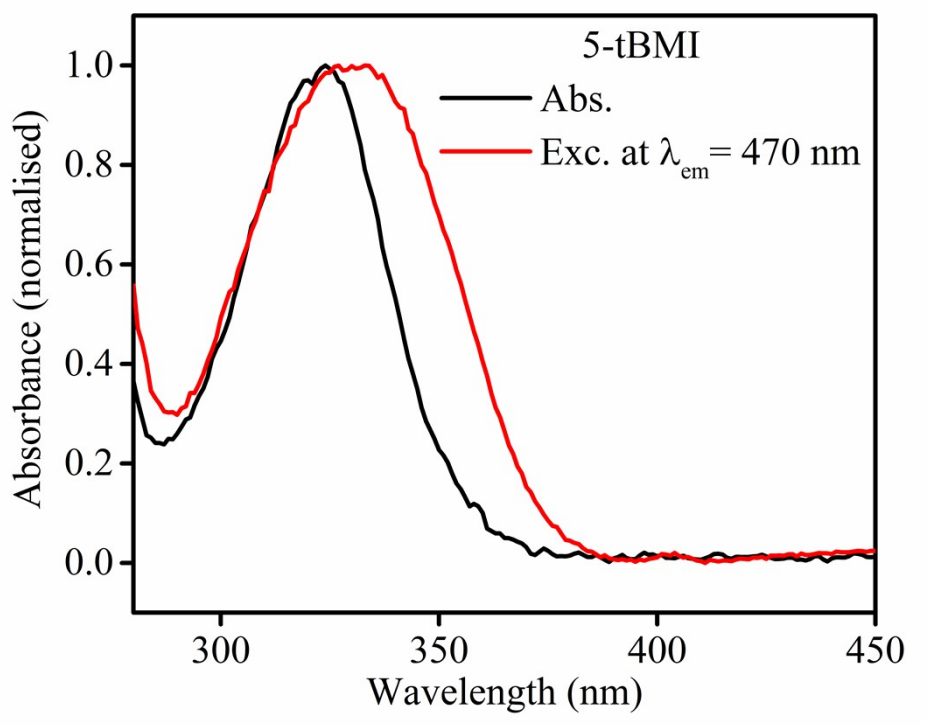


Figure S3: Normalized absorption and excitation spectra of 5-tBMI in water.

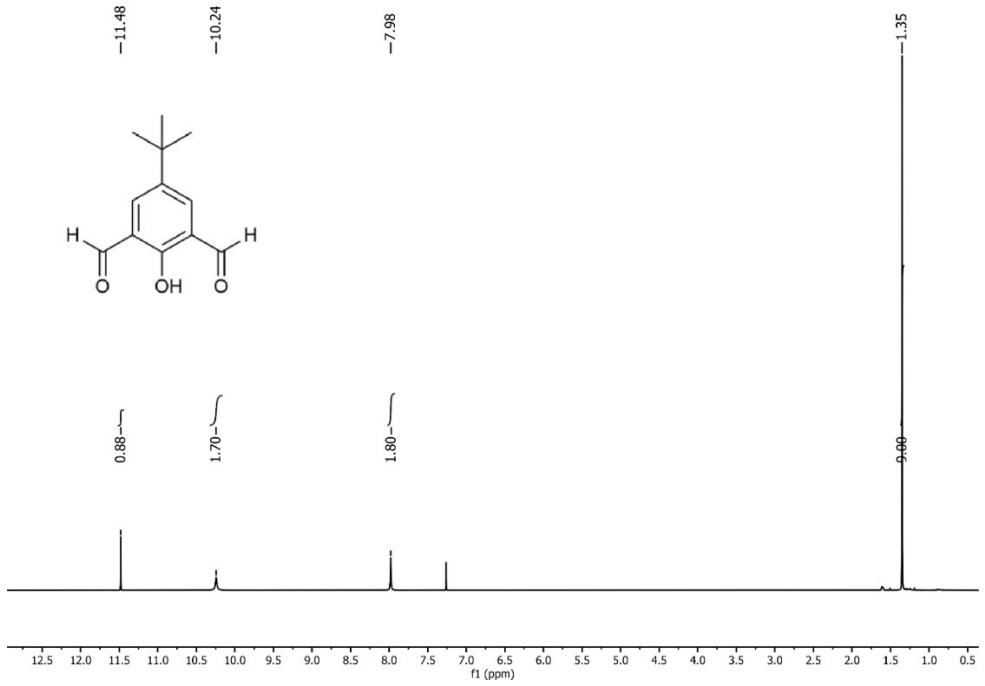


Figure S4: ^{1}H-NMR of 5-tBHI in $CDCl_3$.

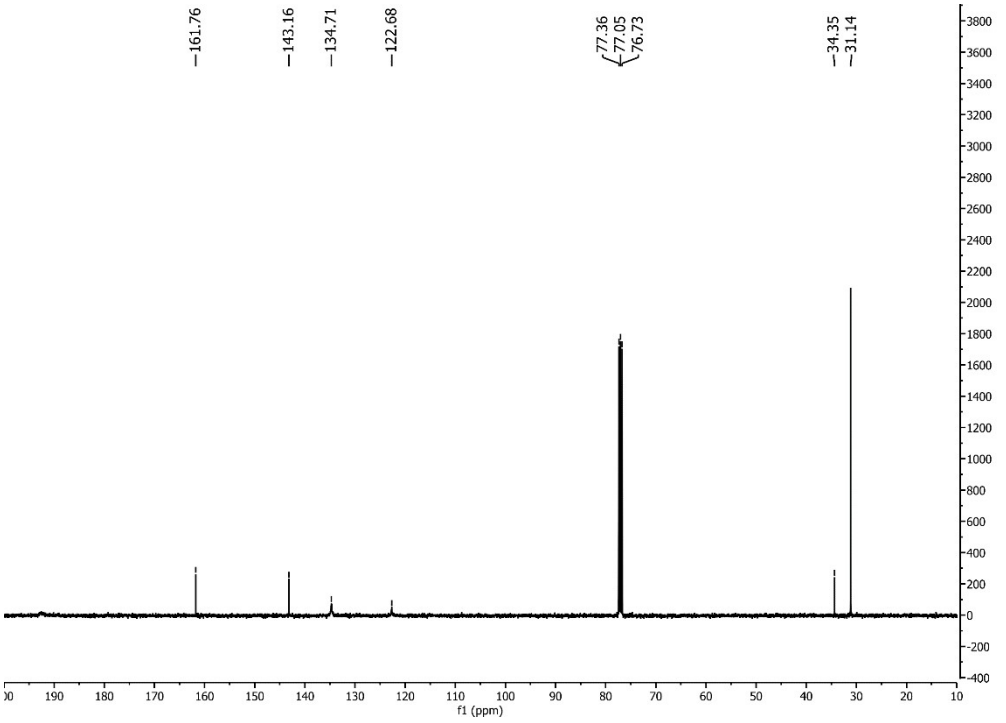


Figure S5: ^{13}C-NMR of 5-tBHI in $CDCl_3$.

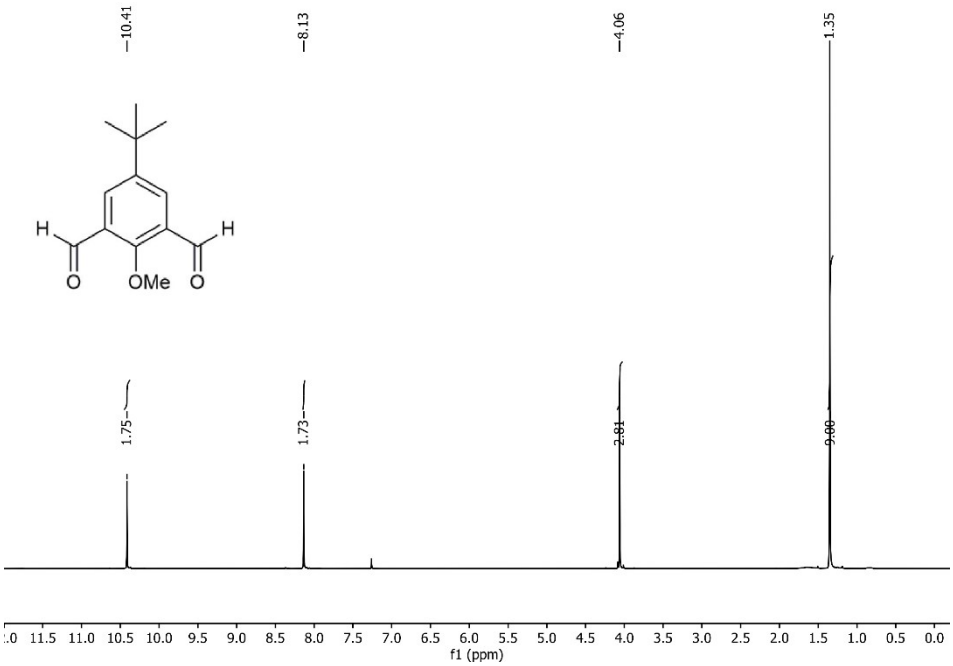


Figure S6: ^{1}H-NMR of 5-tBMI in $CDCl_3$.

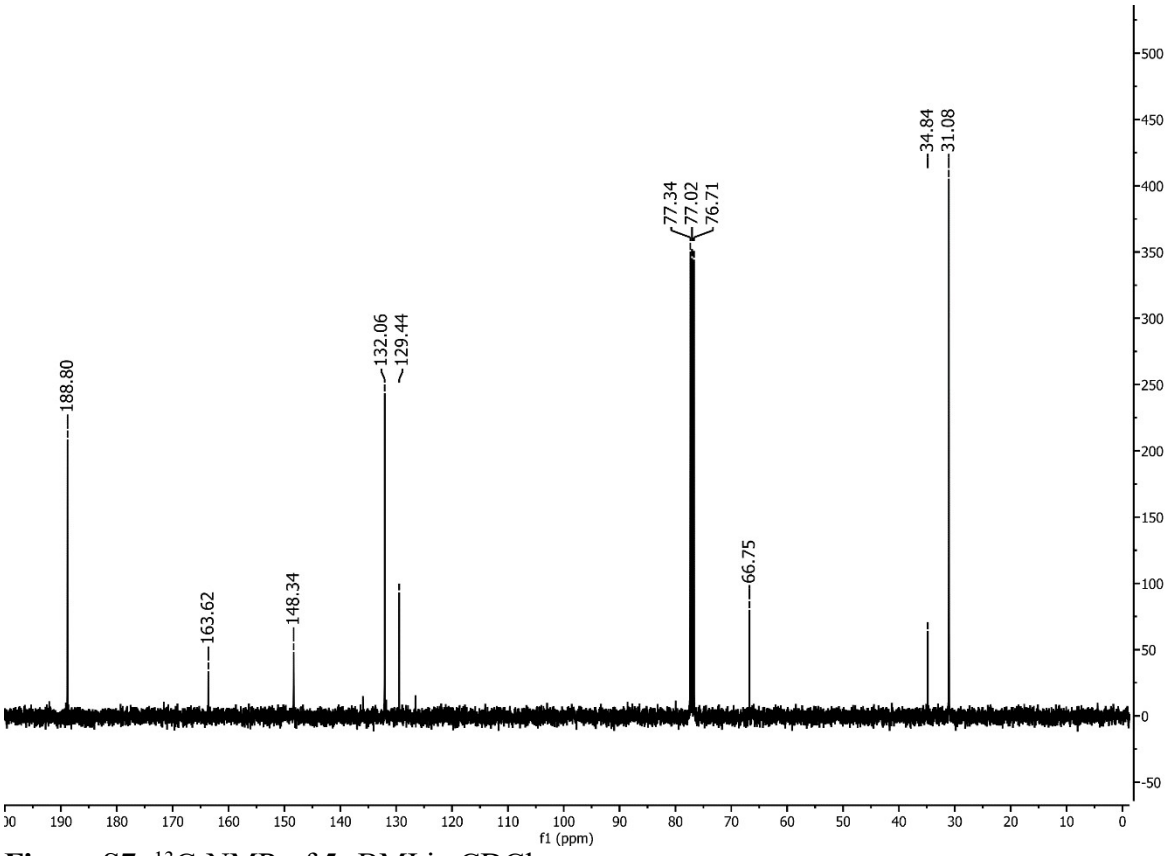


Figure S7: ^{13}C-NMR of 5-tBMI in $CDCl_3$.

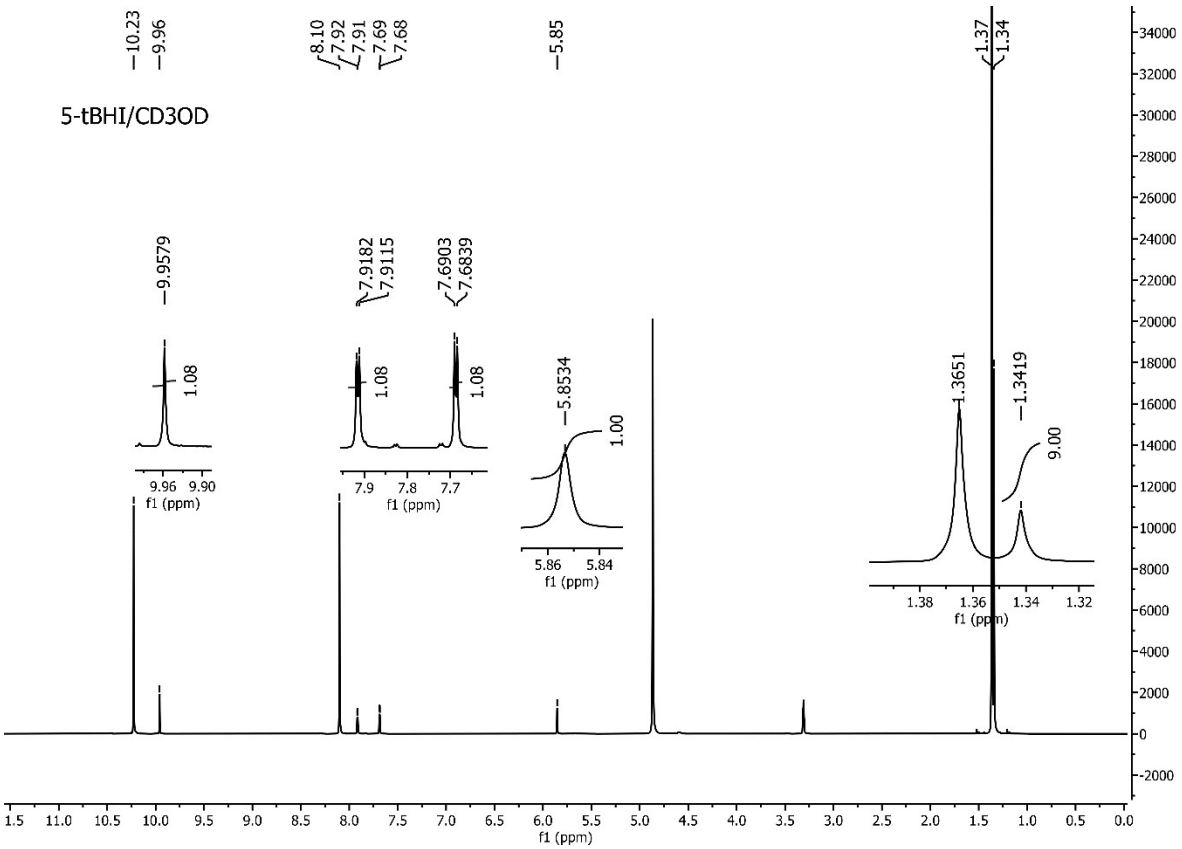


Figure S8: ^{1}H-NMR of 5-tBHI in CD_3OD.

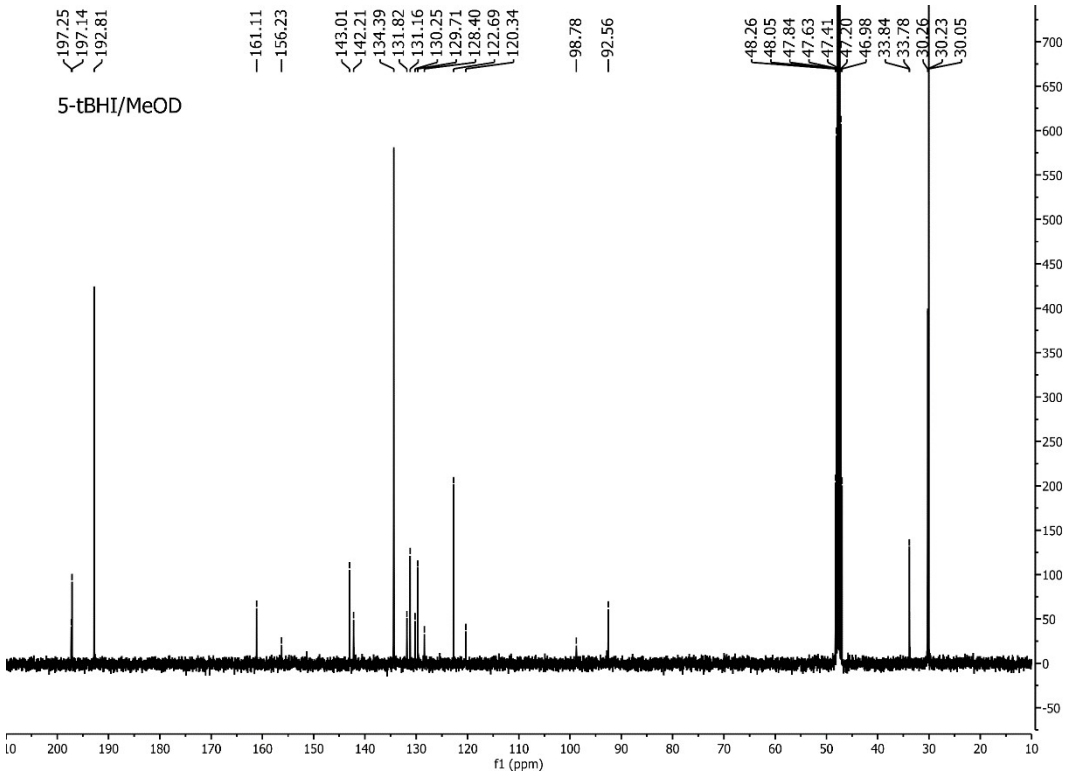


Figure S9: ^{13}C-NMR of 5-tBHI in CD_3OD.

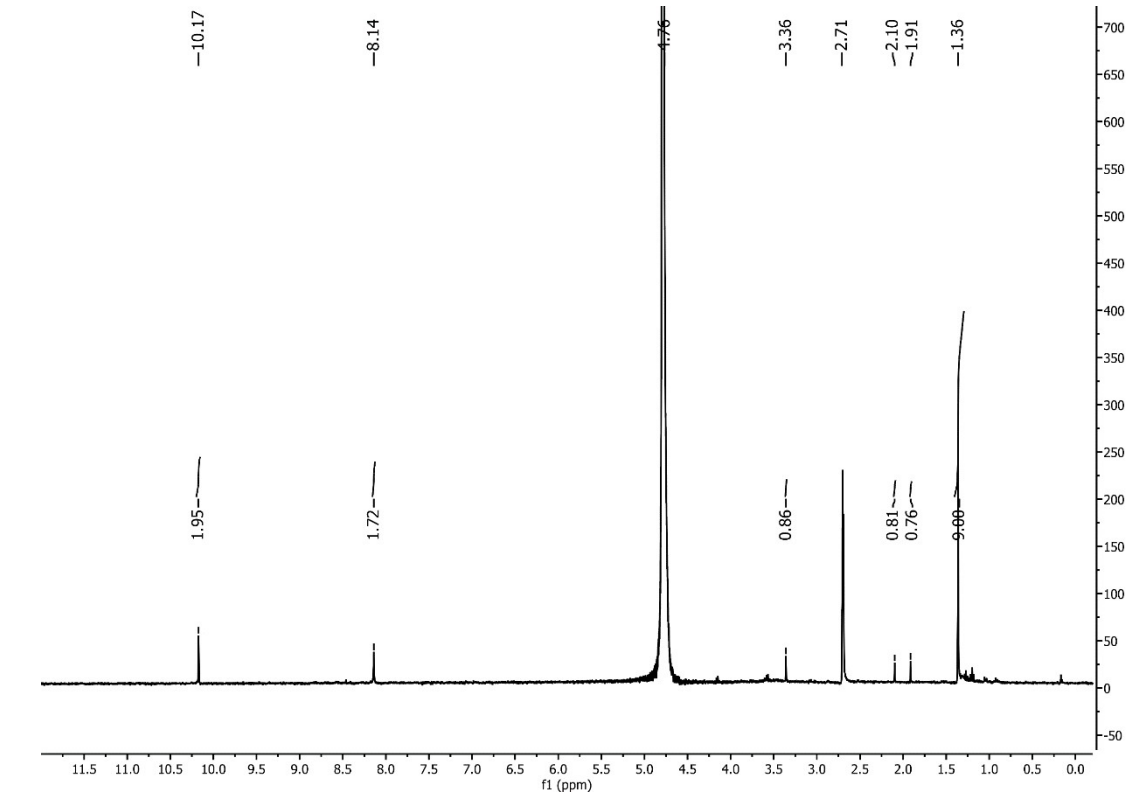


Figure S10: ^{1}H-NMR of 5-tBHI in D_2O.

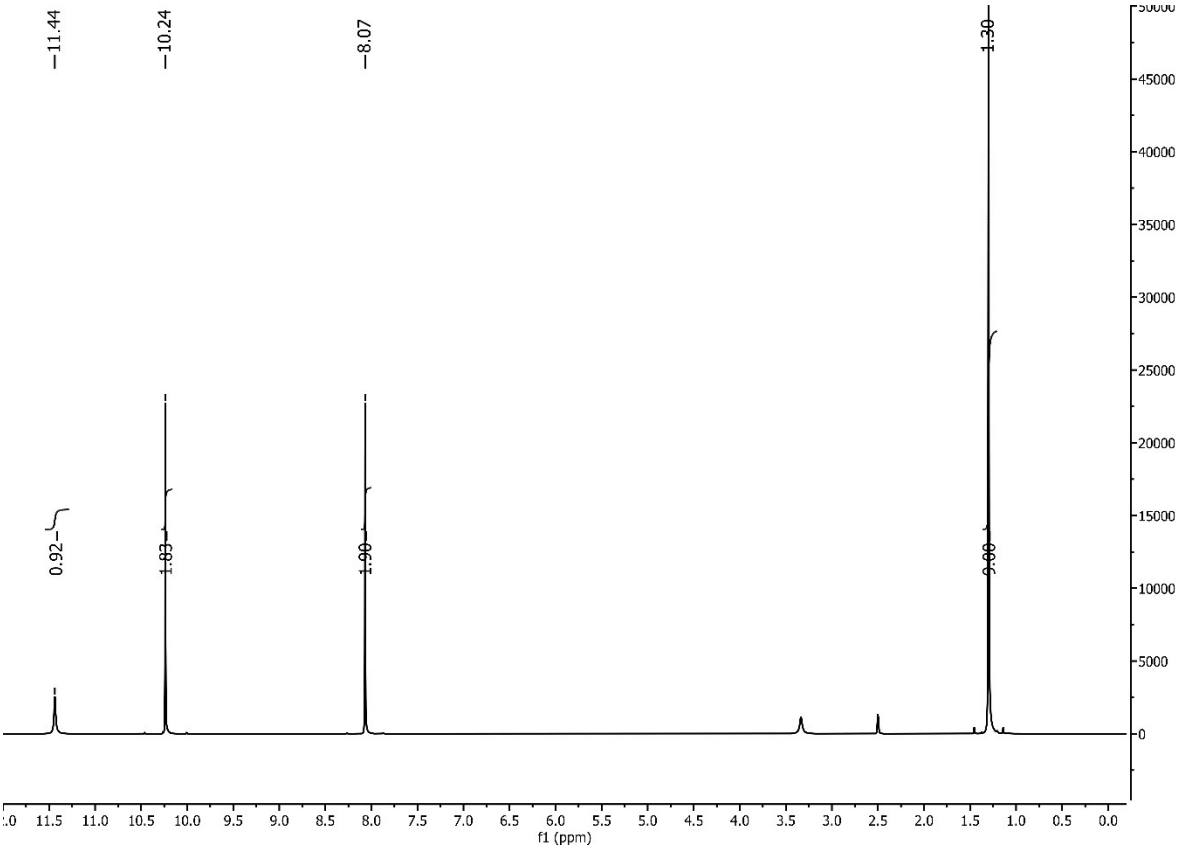


Figure S11: ^{1}H-NMR of 5-tBHI in DMSO-D_6.

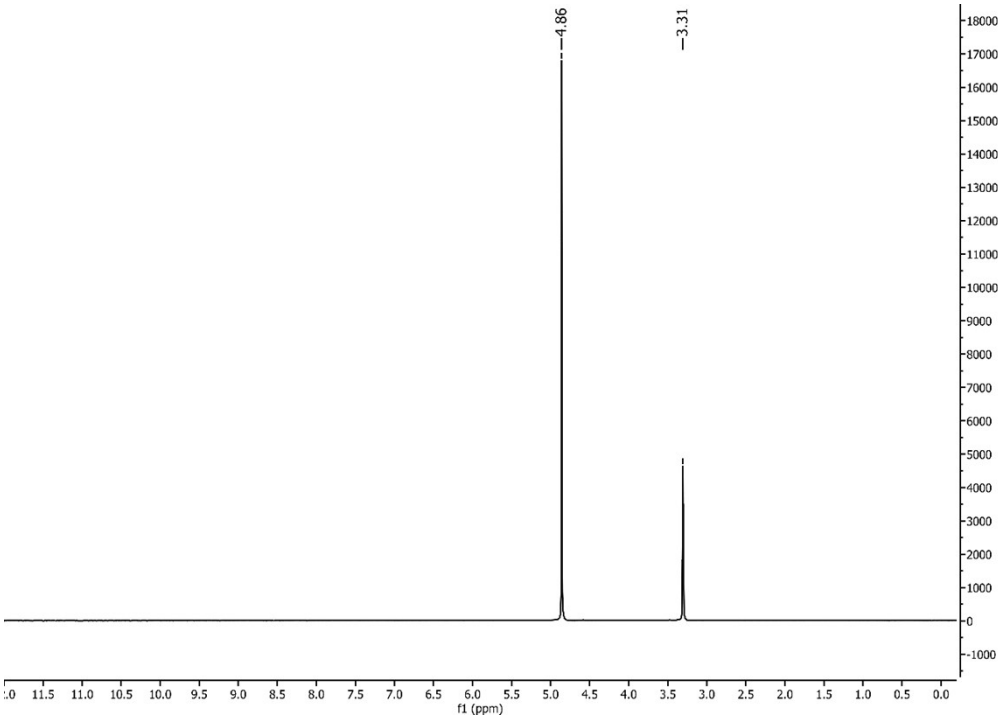


Figure S12: ^{1}H-NMR of CD_3OD.

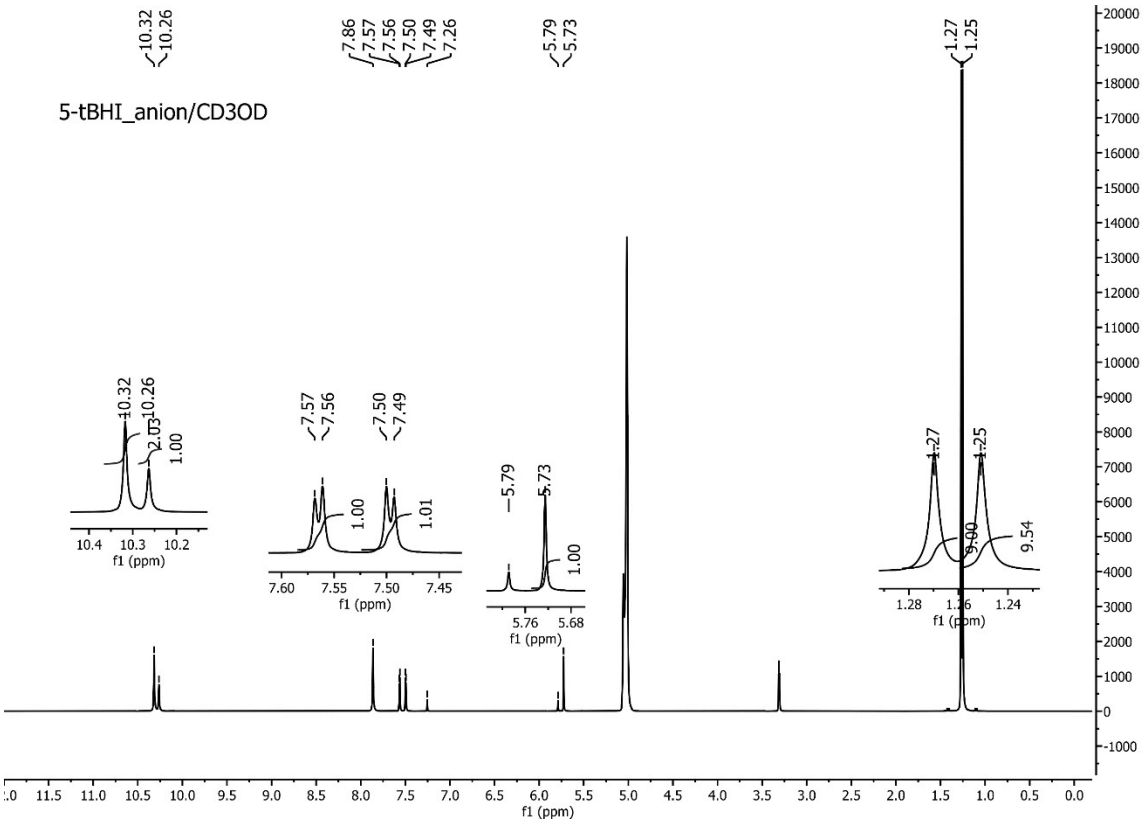


Figure S13: ^{1}H-NMR of 5-tBHI anion in CD_3OD.

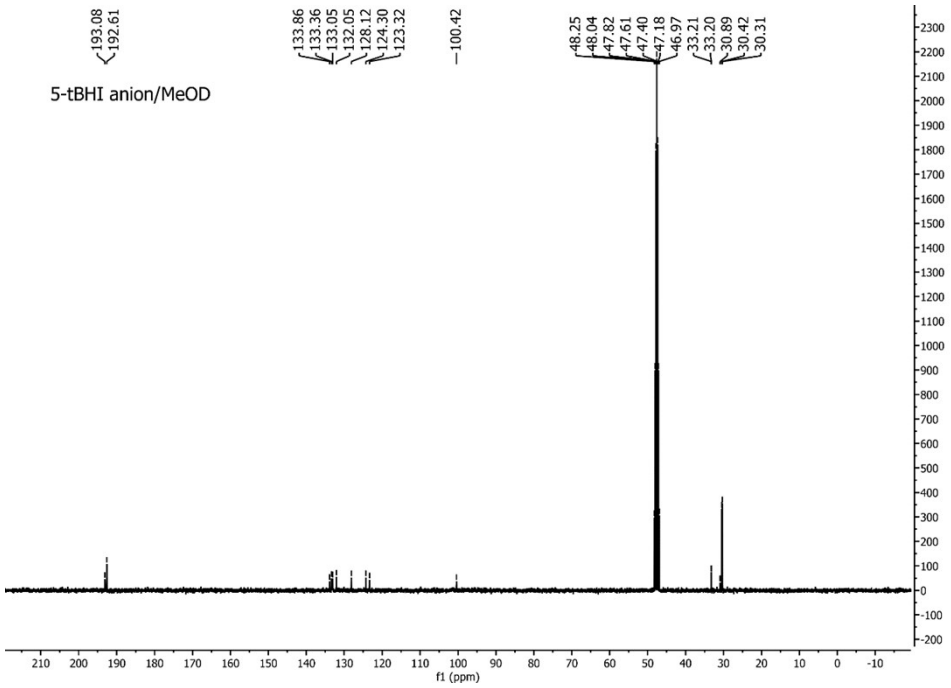


Figure S14: ^{13}C-NMR of 5-tBHI anion in CD_3OD.

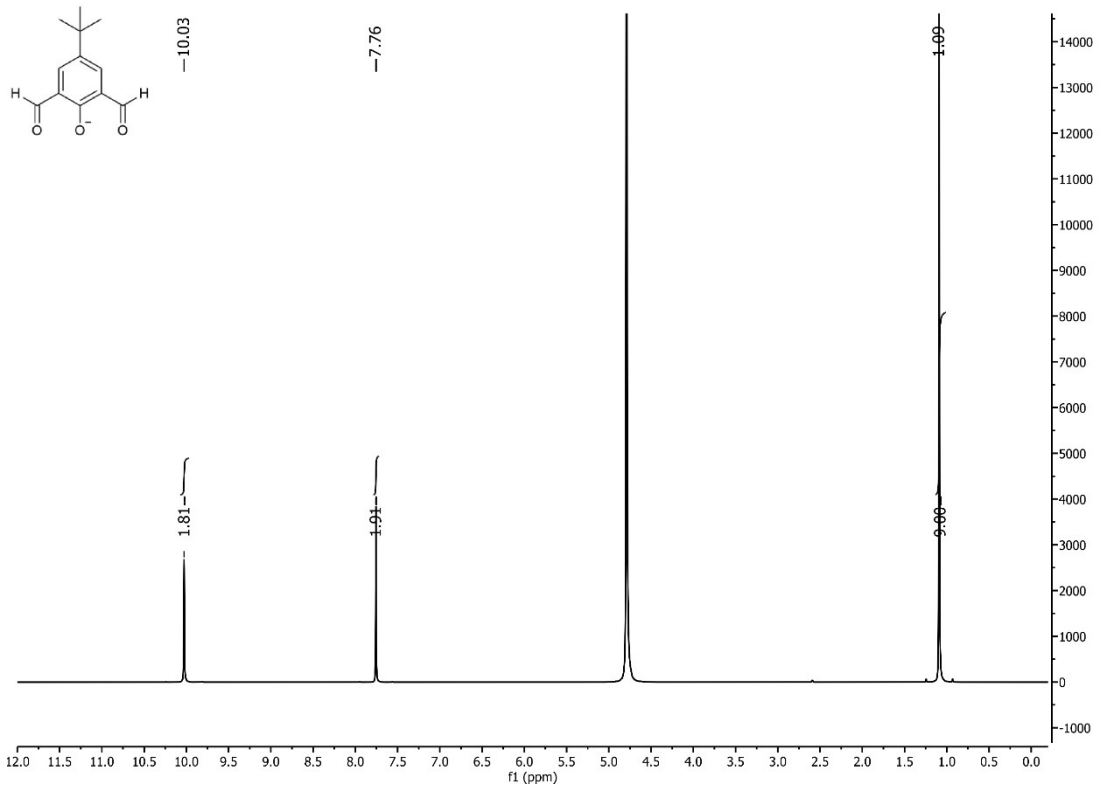


Figure S15: ^{1}H-NMR of 5-tBHI anion in D_2O.

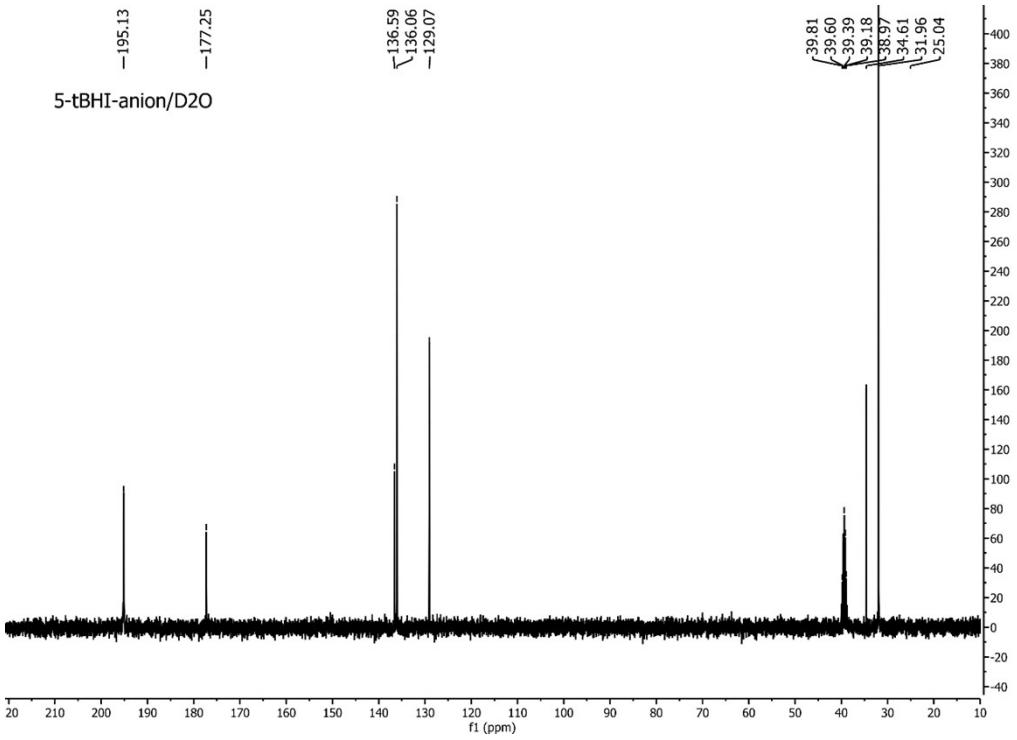


Figure S16: ^{13}C-NMR of 5-tBHI anion in D_2O.

Quantum Chemical (DFT) calculation

To have a theoretical basis of the results obtained from the experiments, Quantum chemical calculations were performed in the gas phase for 5-tBHI. In order to do so, the excited state highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), for the geometry optimized enol- and keto-form of 5-tBHI, were calculated under gas phase.

Figure S17 represents the frontier molecular orbitals of keto- and enol-form of 5-tBHI. The HOMOs of both enol and keto form were found to have an increased electron density on the aldehydic C=O, which enhances the intermolecular H-bonding in the molecule. However, energetically the HOMO of the enol form was found to be more stabilized than the keto form, On the other hand, the LUMOs of both keto and enol were found to have equally localised electron density, and energetically LUMO of both forms (Table S2) were equally placed. This difference between the HOMO and LUMO of the keto and enol form suggests the possibility of ground state heterogeneity, and is in line with our steady state results.

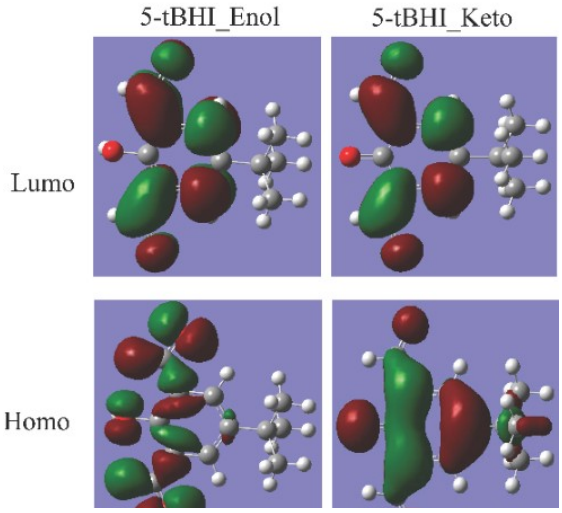


Figure S17. Frontier molecular orbitals of enol and keto form of 5-tBHI.

The calculation further showed a Δλ value of 361.5 nm between the LUMO and HOMO for the enol form, which matched pretty well with the experimental value of ~350 nm (Figure 7 in the main text). However, the energy gap for the keto form was found to be 483.4 nm, much red-shifted to the observed ~ 428 nm, but well within the approximation.

Table S2: Obtained energy and the energy gap of frontier molecular orbitals of keto- and enol-form of 5-tBHI

	ε_{HOMO} (Hartree)	ε_{LUMO} (Hartree)	$\Delta\varepsilon$ HOMO-LUMO (Hartree)	Δλ (nm)
5-tBHI_enol	-0.33427	-0.20808	0.12619	361.5
5-tBHI_keto	-0.30454	-0.21028	0.09426	483.4

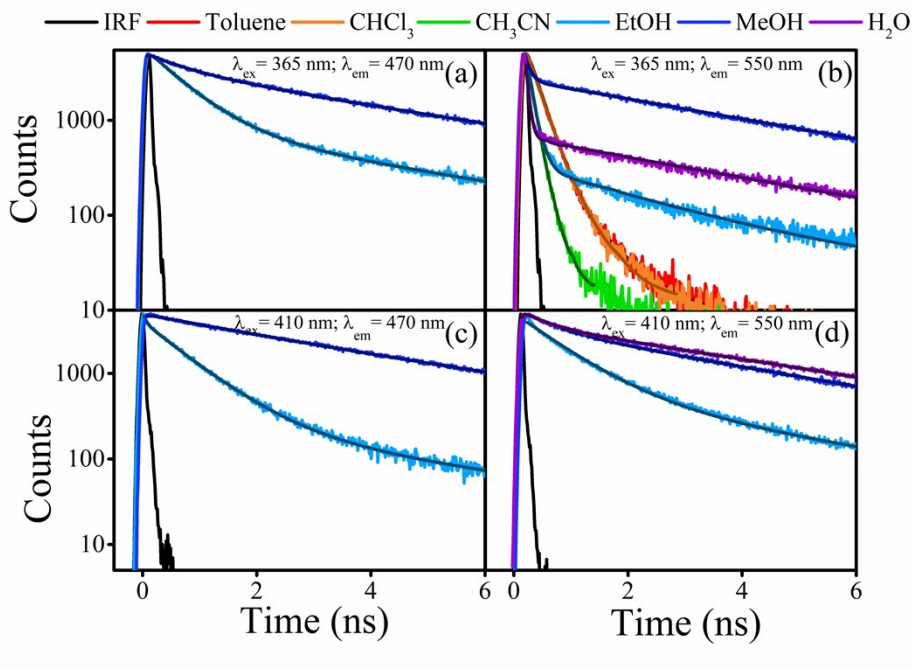


Figure S18: TCSPC decay profiles of 5-tBHI in neat solvents.

Table S3: Lifetime parameter from TCSPC decay of 5-tBHI at λ_{ex} = 365 nm in neat solvents.

λ_{ex} = 365 nm	λ_{em} = 470 nm					λ_{em} = 550 nm				
Solvent	τ_1 (ns)	a_1	τ_2 (ns)	a_2	χ^2	τ_1 (ns)	a_1	τ_2 (ns)	a_2	χ^2
Toluene						0.22	1			1.02
Chloroform						0.22	1			1.10
Acetonitrile						0.11	1			1.21
Ethanol	0.67	0.85	4.44	0.15	1.32	0.11	0.98	2.80	0.02	1.23
Methanol	0.77	0.36	4.55	0.64	1.24	0.08	0.71	4.11	0.29	1.24
Water* (*λ_{em} = 525 nm)						0.04	0.99	4.23	0.01	1.35

Table S4: Lifetime parameter from TCSPC decay of 5-tBHI at λ_{ex} = 410 nm in neat solvents.

λ_{ex} = 410 nm	λ_{em} = 470 nm							λ_{em} = 550 nm						
Solvent	τ_1 (ns)	a_1	τ_2 (ns)	a_2	τ_3 (ns)	a_3	χ^2	τ_1 (ns)	a_1	τ_2 (ns)	a_2	τ_3 (ns)	a_3	χ^2
Ethanol	0.03	0.86	0.77	0.13	4.36	0.01	1.14	0.10	0.71	0.79	0.21	3.78	0.07	1.05
Methanol					4.04	1.00	1.20			0.63	0.36	4.21	0.64	1.17
Water* (*λ_{em} = 525 nm)										0.43	0.32	4.62	0.68	1.38

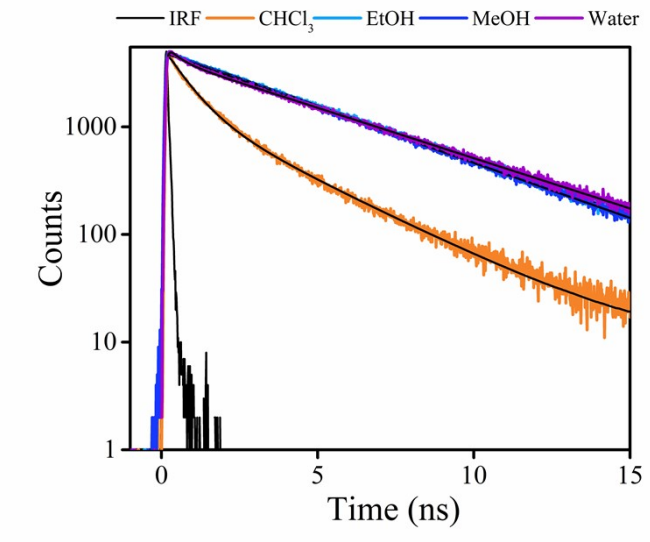


Figure S19: TCSPC decay profiles of 5-tBHI anion at λ_{ex} = 410 nm, λ_{em} = 530 nm in neat solvents.

Table S5: Lifetime parameter from TCSPC decay of 5-tBHI anion in neat solvents.

λ_{ex} = 410 nm	λ_{em} = 530 nm				
Solvent	τ_1 (ns)	a_1	τ_2 (ns)	a_2	χ^2
Chloroform	0.74	0.70	2.98	0.30	1.12
Ethanol			4.20		1.10
Methanol			4.22		1.01
Water	0.40	0.25	4.26	0.75	1.03

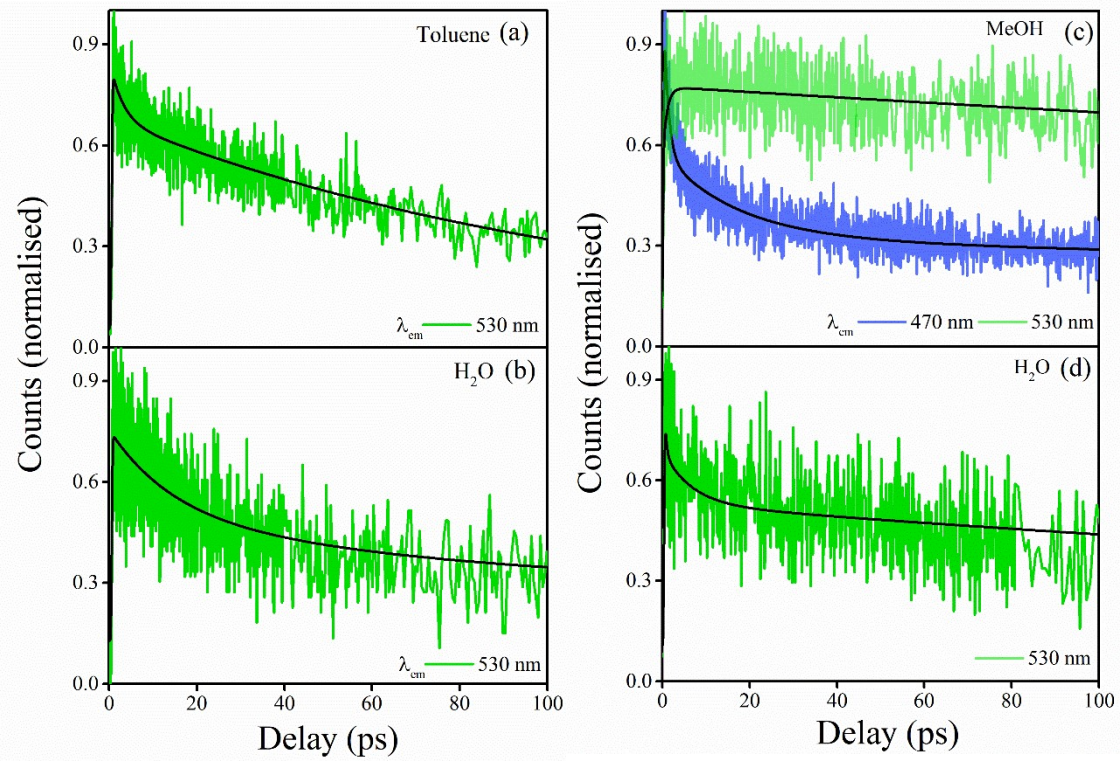
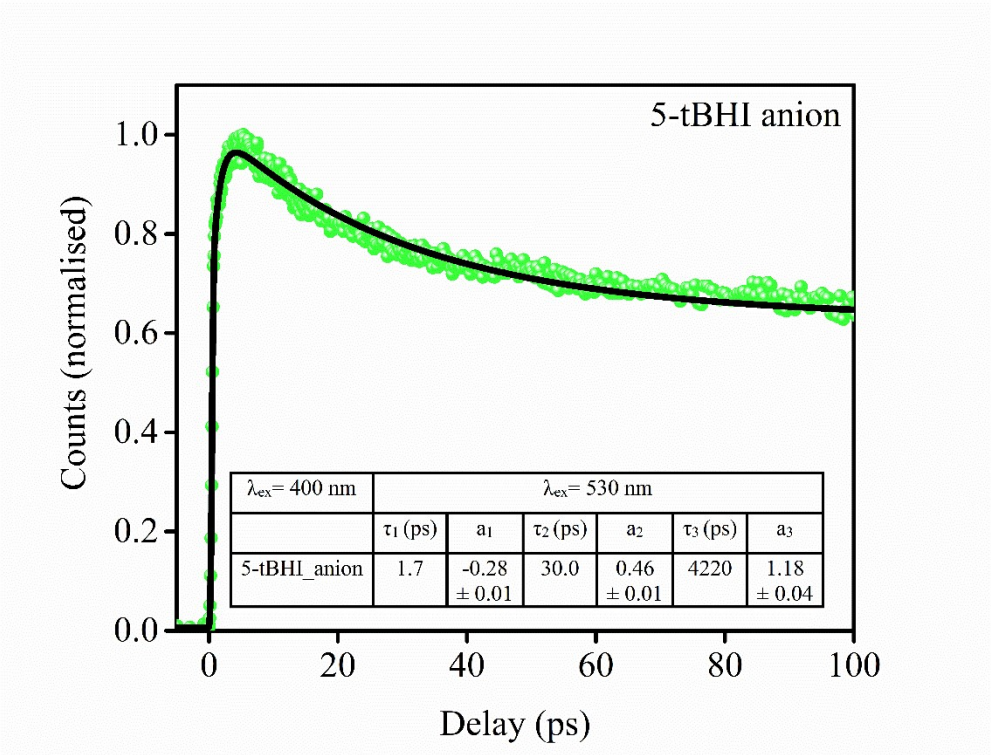


Figure S20: Femtosecond fluorescence transients of 5-tBHI in 100 ps range for λ_{ex} = 370 nm (a, b) and λ_{ex} = 400 nm (c, d).



λ_{ex}= 400 nm	λ_{ex}= 530 nm					
	τ_1 (ps)	a_1	τ_2 (ps)	a_2	τ_3 (ps)	a_3
5-tBHI_anion	1.7	-0.28 ± 0.01	30.0	0.46 ± 0.01	4220	1.18 ± 0.04

Figure S21: Femtosecond upconversion decay profile of 5-tBHI anion at λ_{ex} = 400 nm, λ_{em} = 530 nm in neat MeOH. The lifetime parameters are tabulated inside.

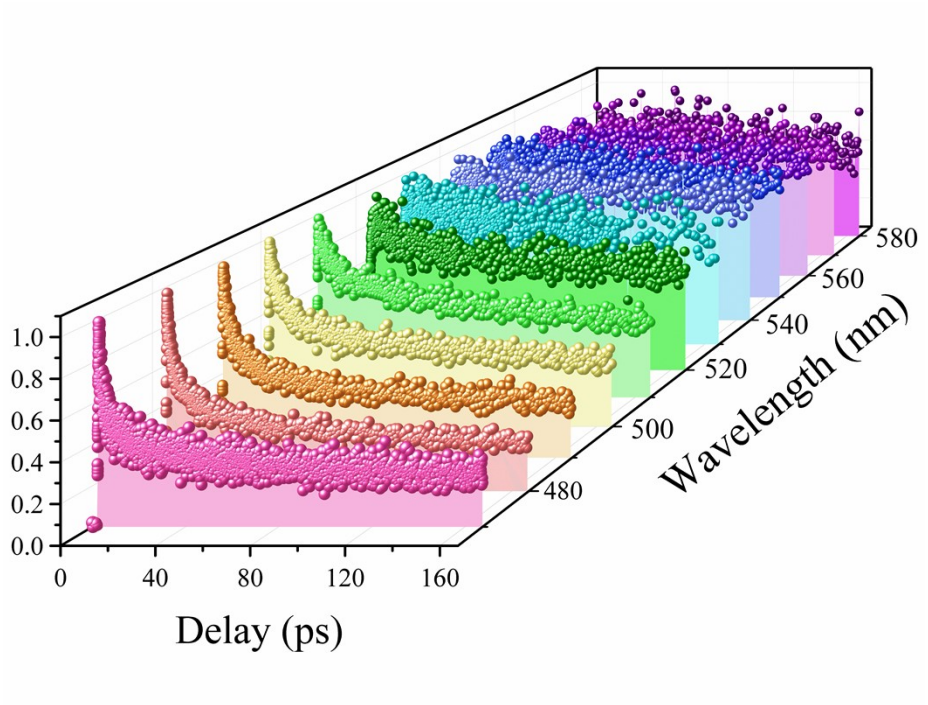


Figure S22: Wavelength dependent femtosecond upconversion decay profile of 5-tBHI in methanol. λ_{ex} = 400 nm.