Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences

Supporting Information

Why is there no in-plane proton-coupled electron transfer from aryloxy radicals? A theoretical and experimental investigation

Yu-Zhe Chen, Yonghui Tian, Miklos Kertesz, Richard G. Weiss*

Department of Chemistry, Georgetown University, Washington, DC, 20057-1227, USA.

Email: weissr@georgetown.edu

This section contains:

-Synthetic scheme to **5**

-Representative HPLC chromatogram

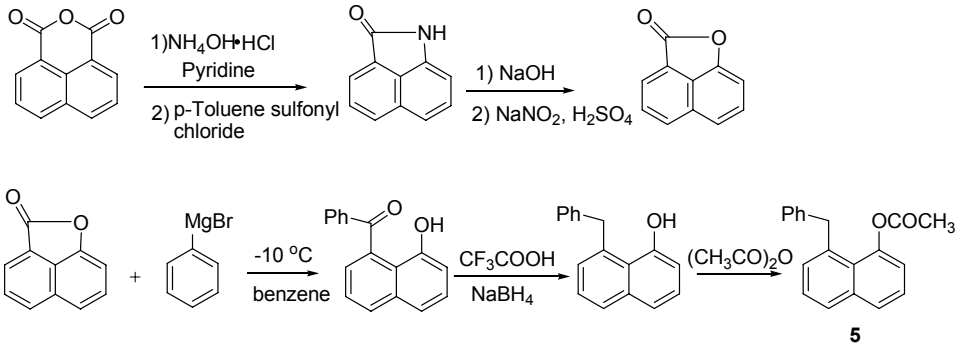
-Computed total energies and thermochemical parameters.

-Computed rate constants by Eyring's equation.

-Localized orbitals and SOMOs of the TSs for compounds **2,3,5 and 6**.

-Details of tunneling rate constant calculations.

-Complete list of authors for ref. 19.



Scheme S1. Synthetic scheme for **5**

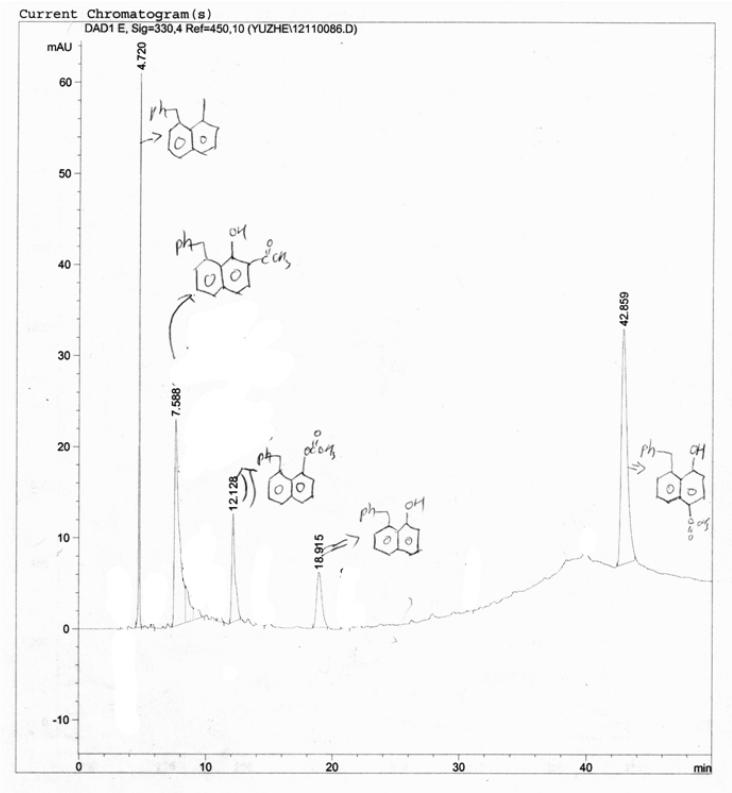


Figure S1. Representative HPLC chromatogram after irradiation of **5**. Detector wavelength = 330 nm. See text for details.

Table S1. Calculated thermochemistry values from Gaussian03 for the **IHT** process at the UB3LYP/6-31 G*// UB3LYP/6-31 G* level

	H_{sum}[a]	G_{sum}[a]	H_{corr}[a]	G_{corr}[a]	$H_{sum}+H_{corr}$[a]	$G_{sum}+G_{corr}$[a]	S[b]
1a	-346.021861	-346.061648	0.127582	0.087795	-345.894279	-345.973853	83.739
1b	-346.003773	-346.043261	0.126770	0.087282	-345.877003	-345.955979	83.109
TS_1	-345.964735	-346.002255	0.122180	0.084660	-345.842555	-345.917595	78.968
2a	-576.984489	-577.037558	0.213590	0.160522	-576.770899	-576.877036	111.692
2b	-576.981381	-577.031717	0.213737	0.163402	-576.767644	-576.868315	105.940
TS_2	-576.943015	-576.992550	0.208331	0.158796	-576.734684	-576.833754	104.254
3a	-807.943751	-808.006821	0.299463	0.236393	-807.644288	-807.770428	132.742
3b	-807.951919	-808.013180	0.299612	0.238352	-807.652307	-807.774828	128.934
TS_3	-807.906275	-807.966996	0.294026	0.233305	-807.612249	-807.733691	127.798
4a	-499.620294	-499.665470	0.177394	0.132217	-499.4429	-499.533253	95.081

4b	-499.595088	-499.639513	0.176831	0.132405	-499.418257	-499.507108	93.502
TS_4	-499.576273	-499.619507	0.171314	0.128080	-499.404959	-499.491427	90.994
5a	-730.581659	-730.639552	0.263285	0.205392	-730.318374	-730.43416	121.847
5b	-730.570874	-730.627050	0.263235	0.207060	-730.307639	-730.41999	118.232
TS_5	-730.552223	-730.607376	0.257526	0.202374	-730.294697	-730.40500	116.078
6a	-961.539875	-961.608404	0.349183	0.280654	-961.19069	-961.32775	144.231
6b	-961.533790	-961.601794	0.348683	0.280679	-961.18511	-961.32112	143.126
TS_6	-961.514200	-961.580599	0.343288	0.276889	-961.17091	-961.30371	139.748

a. Hartree/particle b. cal $mol^{-1}K^{-1}$

Table S2. Total energy parameters for the intramolecular hydrogen transfer within aryloxy radicals **1-6**.

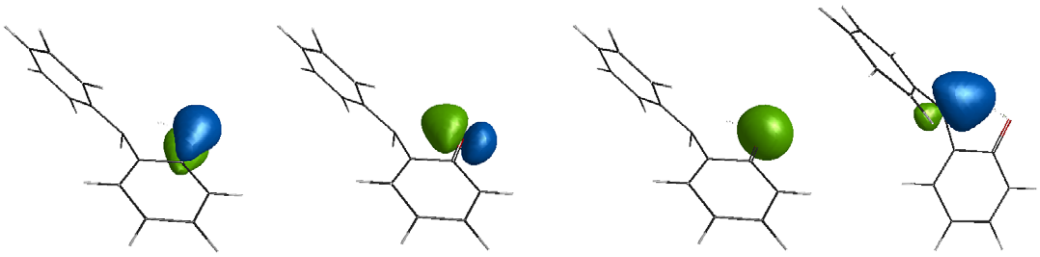
Radicals from	ΔH_{rxn} [a]	$\Delta H^{\ddagger}$ [a]	ΔS_{rxn} [b]	$\Delta S^{\ddagger}$ [b]	ΔG_{rxn} [a]	$\Delta G^{\ddagger}$ [a]
1	10.8	32.5	-0.6	-4.9	11.2	35.3
2	2.0	22.7	-5.8	-7.4	5.5	27.2
3	-5.03	20.1	-3.8	-4.9	-2.8	23.1
4	15.5	23.8	-1.6	-4.1	16.4	26.2
5	6.7	14.9	-3.6	-5.8	8.9	18.3
6	3.5	12.4	-1.1	-4.4	4.2	15.1

a. kcal mol^{-1}; b. cal $mol^{-1}K^{-1}$.

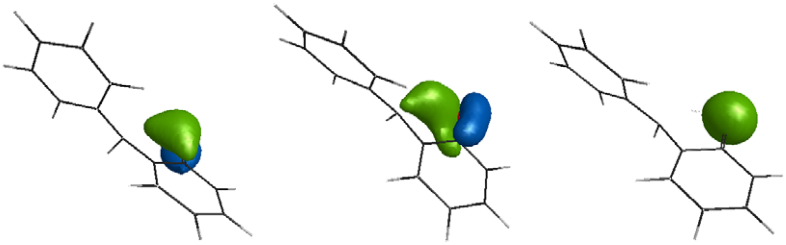
Table S3. Calculated **IHT** reaction rate constants (*k*) for **1a-6a** at 300K, 400K and 500K using eq 1 in the main text.

	k **(s^{-1})**					
Temperature	**1a**	**2a**	**3a**	**4a**	**5a**	**6a**
300K	1.17×10^{-13}	1.75×10^{-8}	9.11×10^{-5}	2.81×10^{-5}	2.97×10^{-1}	6.17
400K	4.21×10^{-7}	3.20×10^{-3}	1.96	8.14×10^{-1}	8.26×10^{2}	4.64×10^{4}
500K	3.81×10^{-3}	4.85	8.24×10^{2}	4.07×10^{2}	1.03×10^{5}	2.60×10^{6}

2:

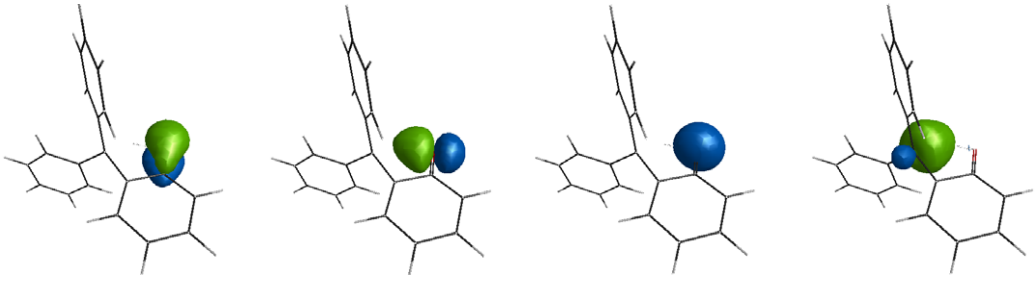


α-1 α-2 α-3 α-4

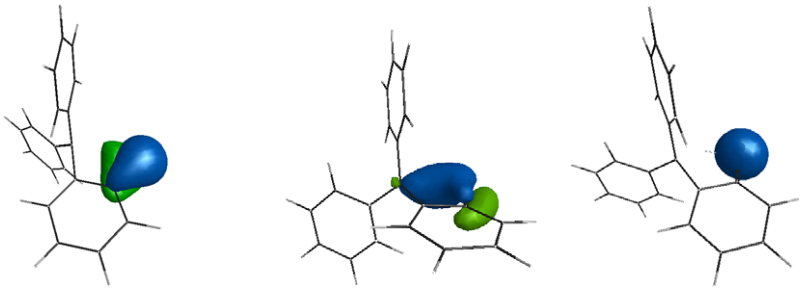


β-1 β-2 β-3

3:

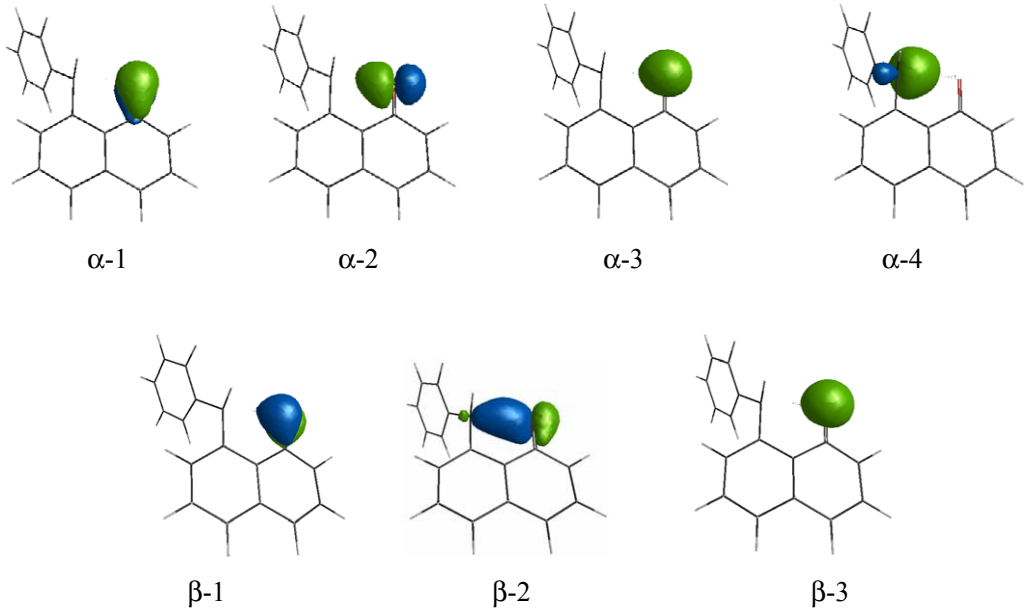


α-1 α-2 α-3 α-4



β-1 β-2 β-3

5:



6:

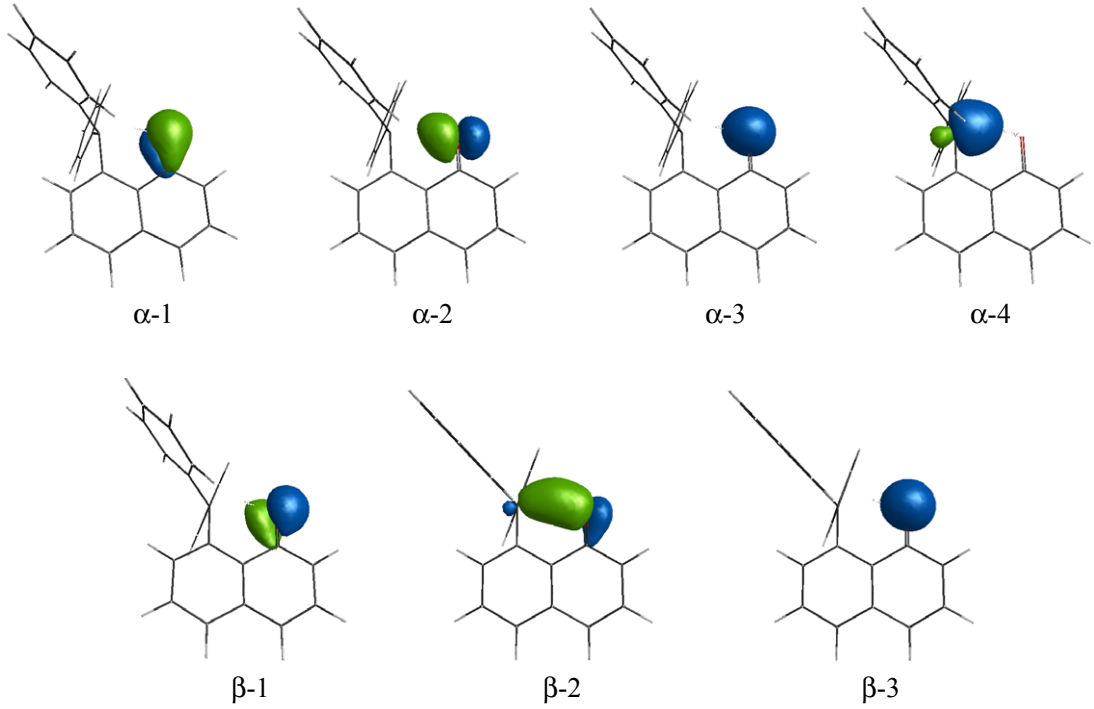
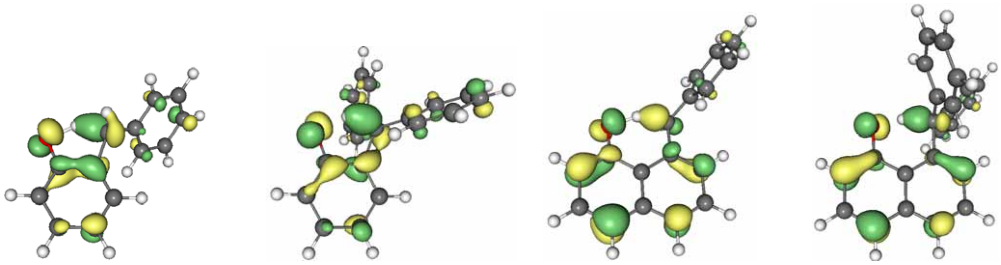


Figure S2. Pipek-Mezey localized orbitals of the transition state structures of **2, 3, 5** and **6**.



2 **3** **5** **6**

Figure S3. SOMOs of the transition state structures of **2, 3, 5, 6.**

Estimates of tunneling rate constants based on eq. (2) and (3) of Campos et al.[1] (eqs S1 and S2 below).

$$k_{ZPE} = c\nu_{C-H} P^G(E_{ZPE}) \qquad \text{(S1)}$$

$$P^G(E_{ZPE}) = 1/(1+\exp\{[1/\hbar c\,|\nu^*|]\Delta E^*\}) \qquad \text{(S2)}$$

The quantities are defined as:

c = speed of light; ν_{C-H} = frequency for a typical C-H vibration; k_{ZPE} = rate of tunneling from zero point energy (ZPE) levels; P^G = quantum mechanical permeability of the barrier (assumed to be quadratic with an imaginary frequency at the barrier top of ν^*). The barrier from the reactants, not including ZPE = ΔE^*. The assumed numerical value was $c\nu_{C-H} \approx 9.1\times10^{13}\,s^{-1}$.

Table S4. Calculated **IHT** tunneling reaction rate constants (k_{ZPE}) for **1a-6a** using eqs S1 and S2.

	ΔE^* [kcal/mol]	$\lvert\nu^*\rvert$ [cm^{-1}]	P^G	k_{ZPE} (s^{-1})
1a	39.2	2190	7.9E-18	7.2E-04
2a	27.5	2108	3.7E-13	3.3E+01
3a	26.9	2128	8.4E-13	7.6E+01
4a	31.4	2008	1.1E-15	1.0E-01
5a	22.1	1956	1.7E-11	1.5E+03
6a	19.8	1981	2.9E-10	2.6E+04

Complete list of authors for ref. 19 (main text).

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03, revision B.04; Gaussian, Inc.: Wallingford, CT, 2004.

[1] L. M. Campos, M. V. Warrier, K. Peterfy, K. N. Houk, M. A. Garcia-Garibay, Secondary Alpha Isotope Effects on Deuterium Tunneling in Triplet o-Methylanthrones: Extraordinary Sensitivity to Barrier Width. *J. Am. Chem. Soc.* 2005**, 127**, 10178-10179.