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Supplemental Material for JA974197F

Dissociative Electron Transfer to Biologically Relevant Bicyclic Endoperoxides.
Determination of Thermochemical Parameters.

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Table 1. Rate constants for electron transfer ($\log(k_{ET})$) from electrochemically generated donors (D^+) with varying standard potentials (E°) to ASC and DASC in 0.1M TEAP/DMF and MeCN solutions at 25°C.

Donor	E° (MeCN)	E° (DMF)	ASC		DASC	
	vs. SCE ^a	vs. SCE ^a	$\log(k_{ET})^b$ MeCN	$\log(k_{ET})^b$ DMF	$\log(k_{ET})^b$ MeCN	$\log(k_{ET})^b$ DMF
fluoranthene	d	-1.738	d	3.89	d	3.91
perylene	-1.690	-1.640	4.00	3.86	3.96	3.78
acenaphthylene	-1.651	-1.629	3.64	3.42	3.45	3.45
1,4-dicyanobenzene	-1.573	d	3.44	d	3.22	d
tetracene	c	-1.544	d	3.44	d	3.20
4,4'-dimethoxyazobenzene	-1.526	-1.531	2.91	3.08	2.80	2.78
4-methyl-4'methoxyazobenzene	-1.478	-1.478	2.75	2.97	2.54	2.49
4-methoxyazobenzene	-1.438	-1.424	2.47	2.60	2.10	2.17
azobenzene	-1.335	-1.315	1.75	1.94	1.81	1.47
3,3'-dimethoxyazobenzene	-1.278	-1.285	1.39	1.62	1.38	1.29
2-nitrobiphenyl	-1.157	-1.188	0.157	0.822	0.230	0.214
nitrobenzene	-1.100	-1.100	-0.477 ^c	-0.767 ^c	-0.647 ^c	-1.030 ^c
4-nitrobiphenyl	d	-1.078	d	d	d	-0.976 ^c
1-nitronaphthalene	-1.041	-1.040	-0.602 ^c	-1.230 ^c	d	-0.899 ^c

^a E° measured versus an internal standard (ferrocene) and corrected: $Fc/Fc^+ = 0.449$ V vs SCE in MeCN and 0.470 V vs. SCE in DMF. ^b Measured by homogeneous redox catalysis (ref. 22). ^c not soluble ^d not measured. ^e Measured using methods outlined in reference 23.