

**Supporting Information for Rearrangements of Radical Ions: What it Means to be Both
a Radical and an Ion**

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Table S1. Rate constants for homogeneous electron transfer (k_1) between the reduced form of the mediator ($M^{\bullet-}$) and substrate **1** (0.5 M n Bu₄NClO₄ supporting electrolyte; DMF solvent)

Mediator	$E^{\circ}_{M/M^{\bullet-}}$ (V) ^a	1a	ρ^b	1b	ρ^b
		k_1 (M ⁻¹ s ⁻¹)		k_1 (M ⁻¹ s ⁻¹)	
naphthalene	-2.901	$4.2 (\pm 0.2) \times 10^2$	0.60	$5.9 (\pm 0.2) \times 10^2$	0.45
3,6-dimethylphenanthrene	-2.937	$1.3 (\pm 0.1) \times 10^3$	1.00	$8.1 (\pm 0.6) \times 10^2$	0.90
1,3-dimethylnaphthalene	-2.971	$3.5 (\pm 0.2) \times 10^3$	0.95	$2.2 (\pm 0.1) \times 10^3$	0.55
biphenyl	-2.977	$2.1 (\pm 0.1) \times 10^3$	0.95	$2.4 (\pm 0.2) \times 10^3$	0.65
methoxynaphthalene	-2.988	$5.2 (\pm 0.2) \times 10^3$	1.00	$2.8 (\pm 0.2) \times 10^3$	0.80
2,7-dimethoxynaphthalene	-3.027	$9.6 (\pm 0.3) \times 10^3$	1.00	$8.0 (\pm 0.3) \times 10^3$	0.30
o-methoxybiphenyl	-3.086	$3.4 (\pm 0.1) \times 10^4$	0.95	$3.6 (\pm 0.1) \times 10^4$	0.50

^avs. 0.1 M AgNO₃/Ag. ^b(± 0.05) for all ρ