Electronic Supplementary Material (ESI) for Organic and Biomolecular Chemistry
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# Supporting Information

# for

# One-Electron Oxidation of Ferrocenes by Short-Lived *N*-oxyl Radicals. Structural Effects on the Intrinsic Electron Transfer Reactivities of *N*-oxyl Radicals

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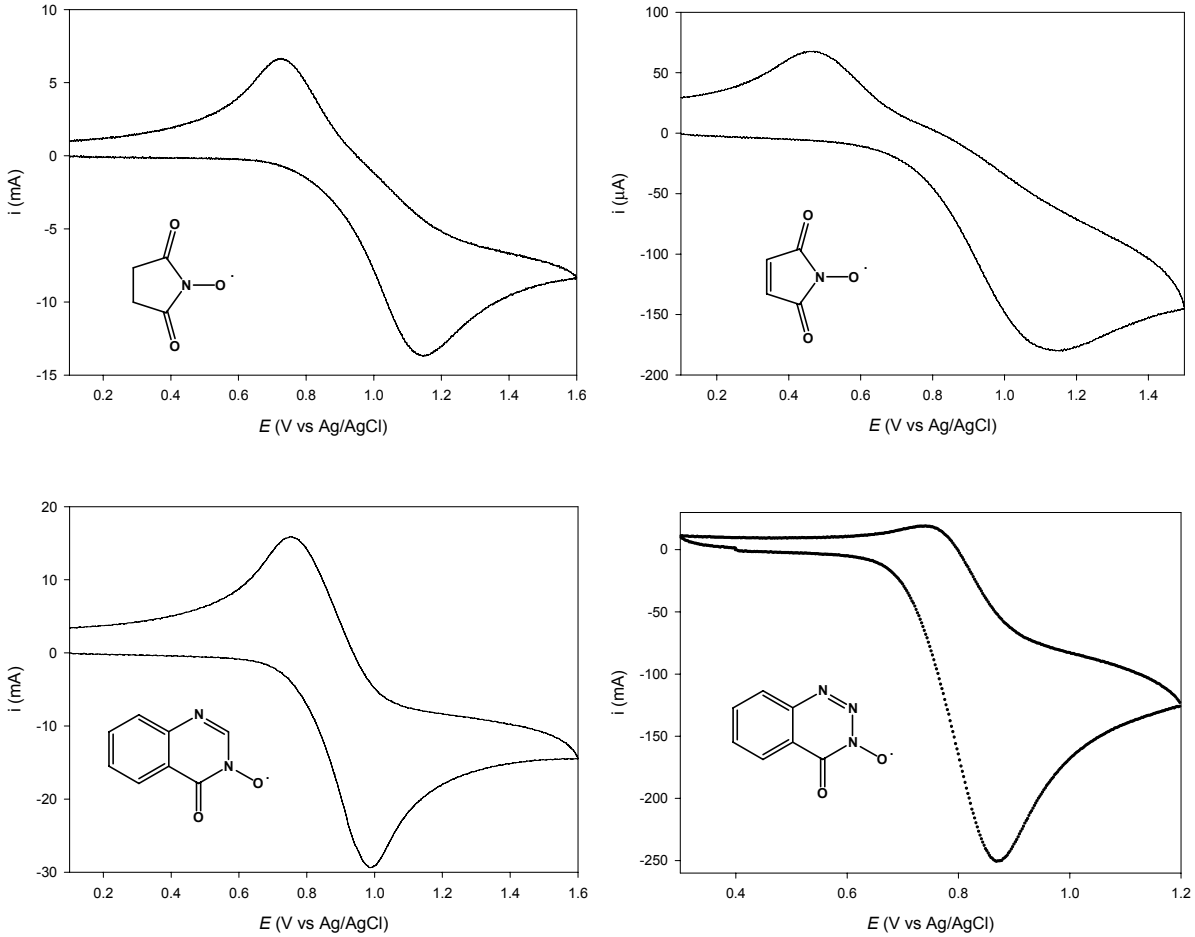


**Figure S1.** Cyclic voltammogram of 2 mM solutions of *N*-hydroxyderivatives **1H-4H** (2 mM) in MeCN at 25 °C in the presence of collidine (4 mM), containing $Bu_4NBF_4$ (0.1 M) as the supporting electrolyte. Voltage sweep rate 500 $mV/s^{-1}$

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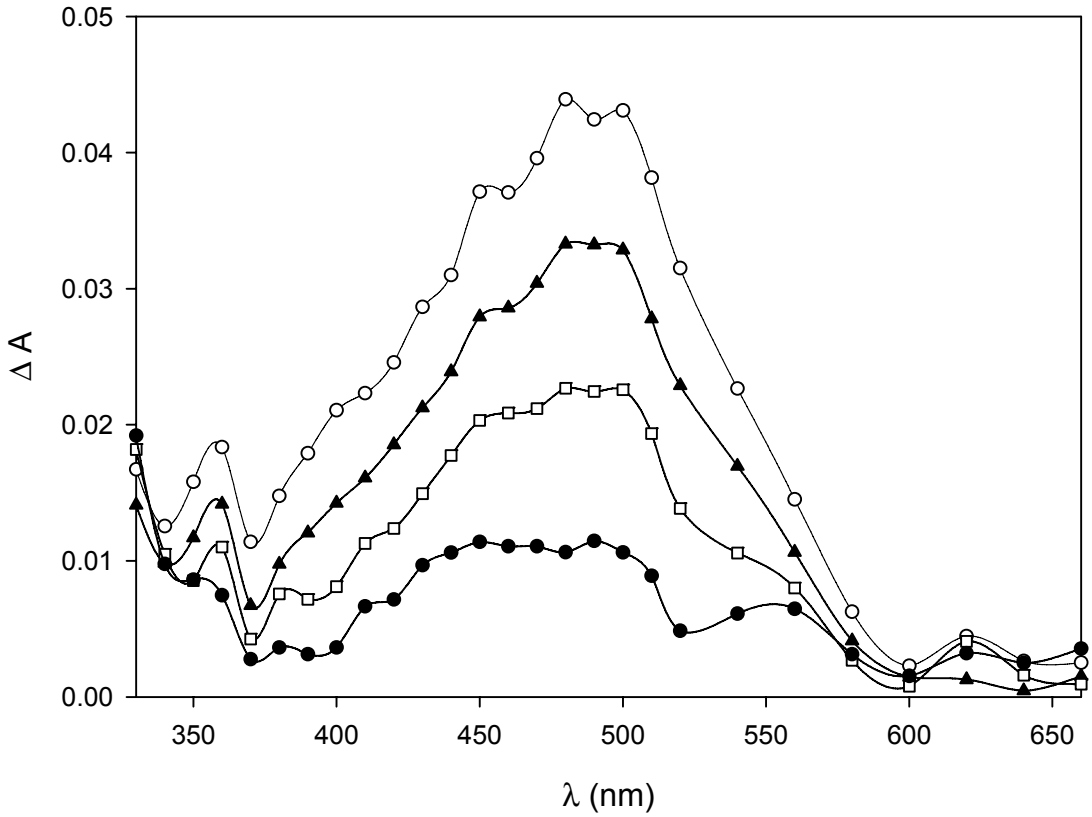


**Figure S2**. Transient absorption spectra measured 96 ns (empty circles), 416 ns (filled triangles), 1.0 μs (empty squares) and 3.0 μs (filled circles) after 355 nm laser excitation of a solution of dicumyl peroxide (0.9 M) and NHQO (2.5 mM) in $CH_3CN$ at 25 °C under $N_2$

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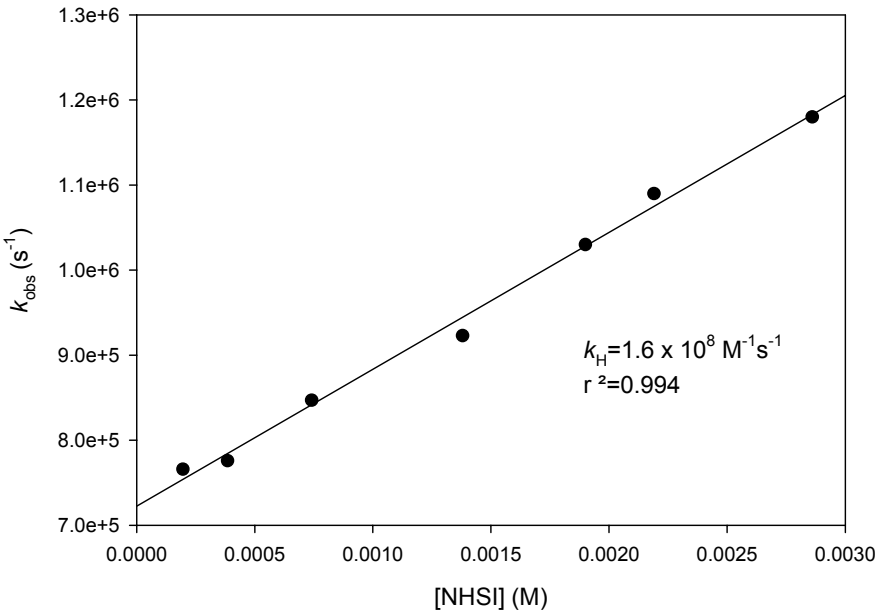


**Figure S3**. Dependence of $k_{obs}$ on the concentrations of NHSI for the hydrogen atom abstraction from NHSI by the cumyloxyl radical in $CH_3CN$ at 25 °C.

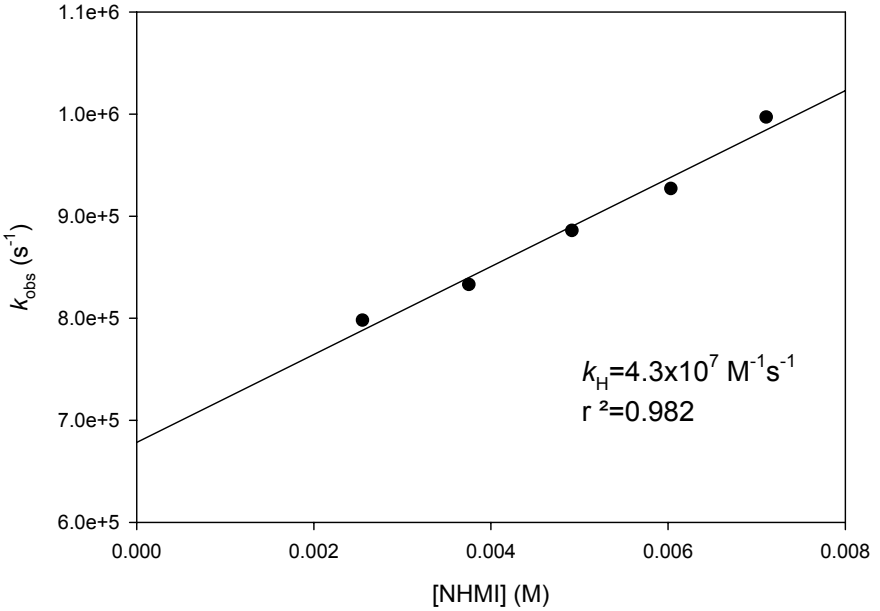


**Figure S4**. Dependence of $k_{obs}$ on the concentrations of NHMI for the hydrogen atom abstraction from NHMI by the cumyloxyl radical in $CH_3CN$ at 25 °C.

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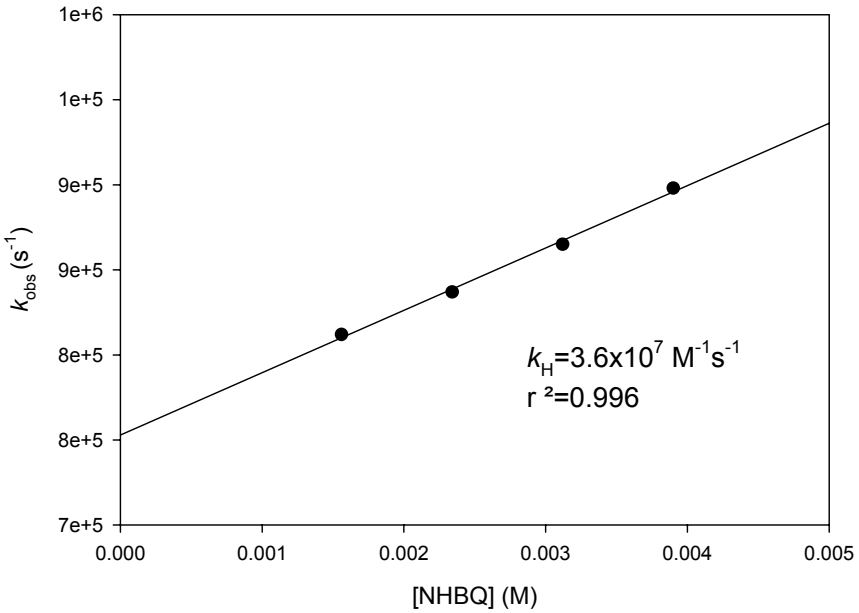


**Figure S5**. Dependence of $k_{obs}$ on the concentrations of NHBQ for the hydrogen atom abstraction from NHBQ by the cumyloxyl radical in $CH_3CN$ at 25 °C.

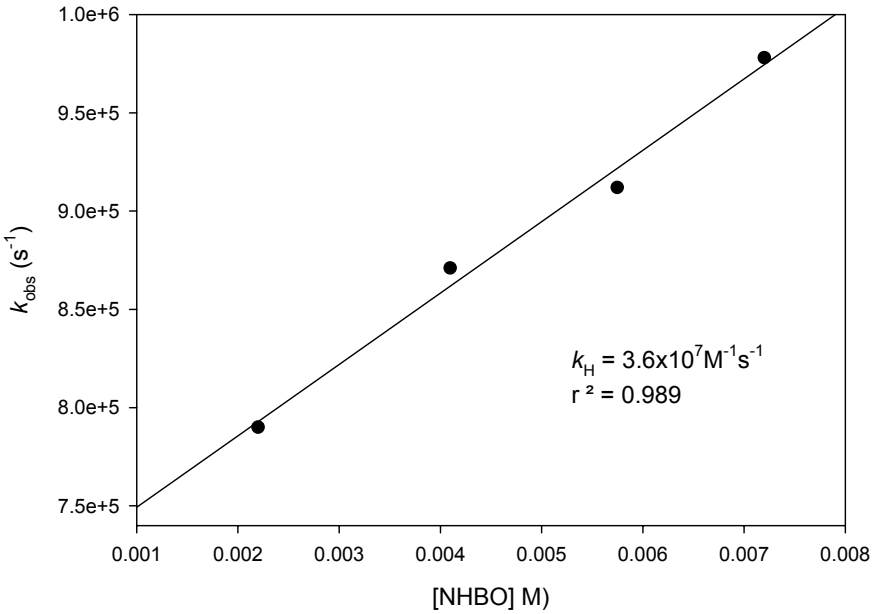


**Figure S6**. Dependence of $k_{obs}$ on the concentrations of NHBO for the hydrogen atom abstraction from NHBO by the cumyloxyl radical in $CH_3CN$ at 25 °C.

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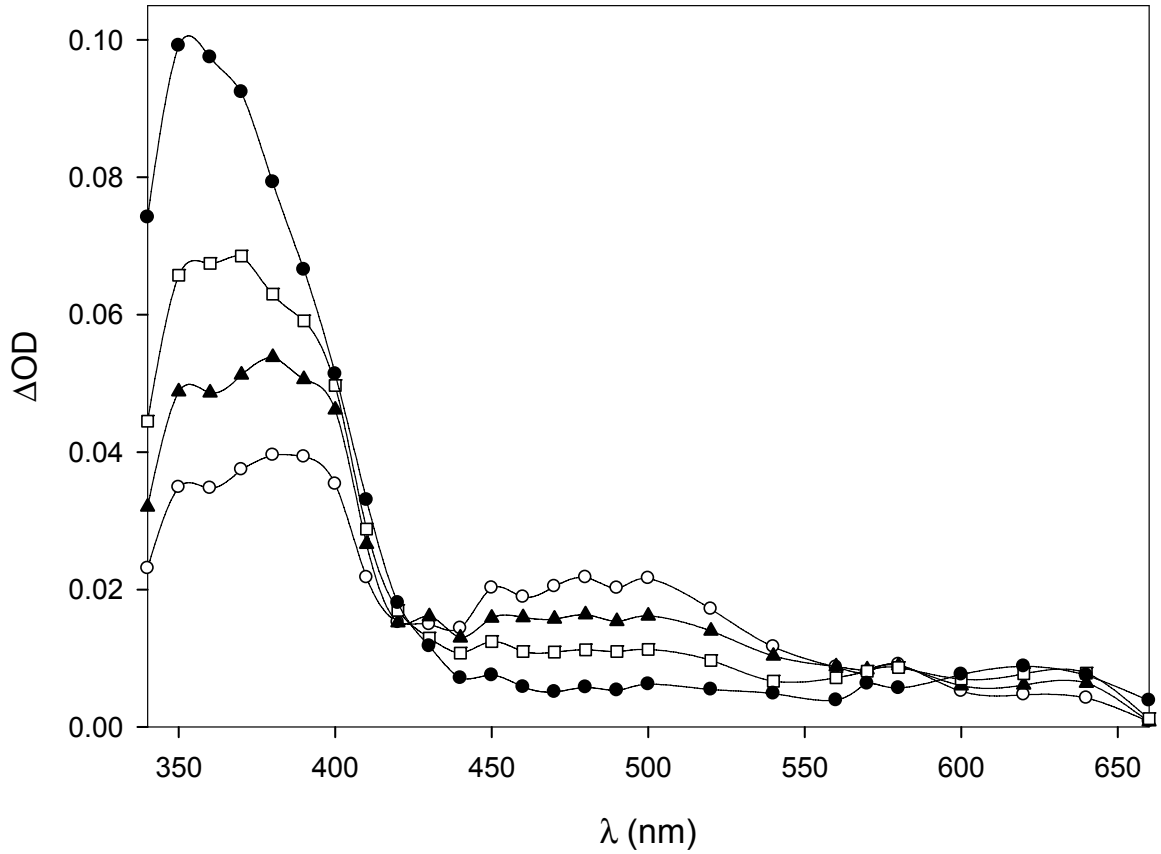


**Figure S7.** Time-resolved absorption spectra observed after 355 nm LFP of an $N_2$-saturated $CH_3CN$ solution (T = 25 °C) containing dicumyl peroxide (1 M), NHBO (5.0 mM) and ethylferrocene carboxylate (0.1 mM), at 1.4 μs (empty circles), 4.0 μs (filled triangles), 31 μs (empty squares) and 300 μs (filled circles).

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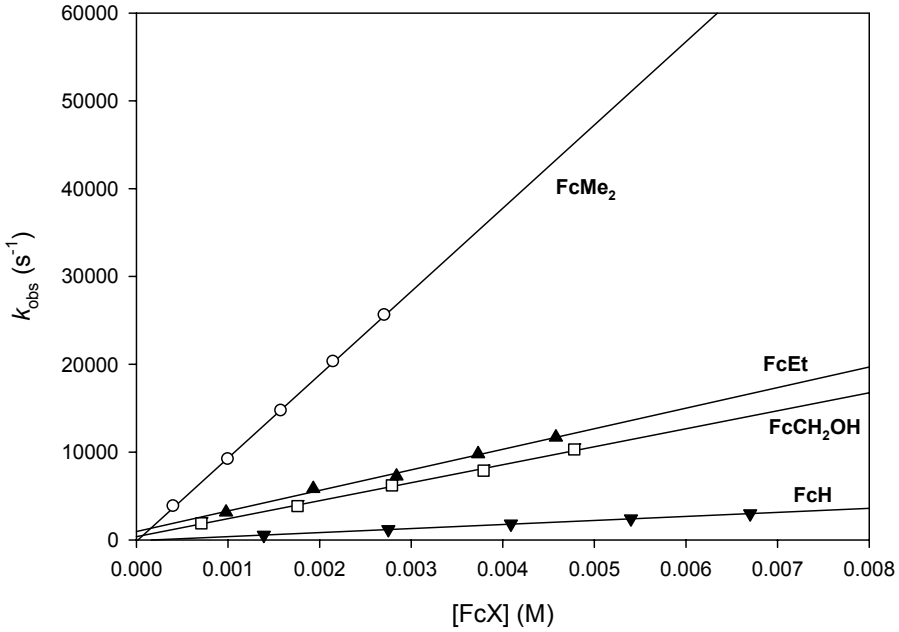


**Figure S8.** Plots of the observed rate constant ($k_{obs}$) against [FcX] for the reactions of the MINO radical measured in argon-saturated MeCN solution at $T$ = 25 °C, following the buildup of the ferrocenium ions.

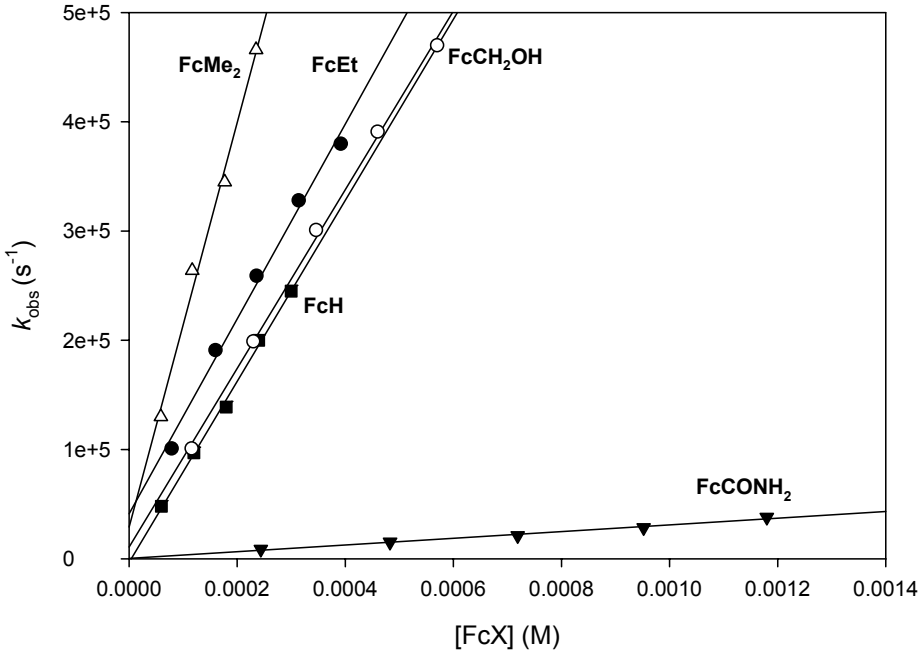


**Figure S9.** Plots of the observed rate constant ($k_{obs}$) against [FcX] for the reactions of the BQNO radical measured in argon-saturated MeCN solution at $T$ = 25 °C, following the buildup of the ferrocenium ions.

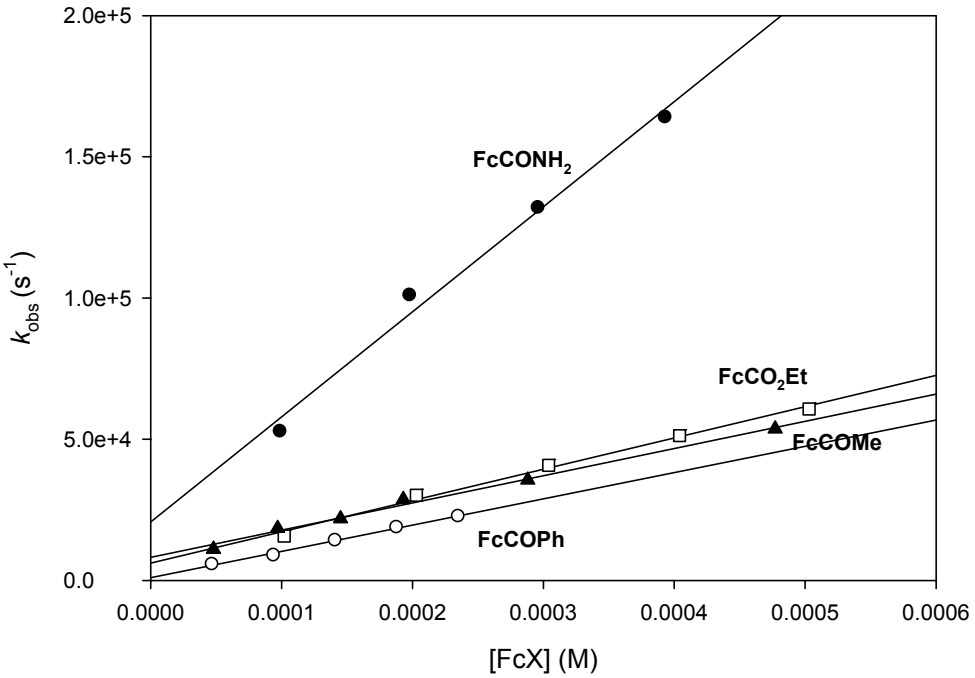


**Figure S10.** Plots of the observed rate constant ($k_{obs}$) against [FcX] for the reactions of the BONO radical measured in argon-saturated MeCN solution at $T$ = 25 °C, following the decay of the BONO radical.

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**Determination of the reorganization energies**

The second-order rate constants ($k_{et}$) for the electron transfer process from the substitued ferrocenes FcX to *N*-oxyl radicals **1-4** were treated according to eq 1, which combines the Eyring and Marcus equation.[S1]

$$k_{et} = Ze^{-\frac{(\lambda+\Delta G^{\circ\prime})^2}{4\lambda RT}} \qquad (1)$$

Z is taken as $6\times10^{11}$, λ is the reorganization energy representing the energy associated with adjustments in the nuclear geometries and solvent shells of the interacting species which are required to make possible the transfer of the electron from the ferrocene donors to the acceptor *N*-oxyl radicals **1-4** and $\Delta G^{\circ\prime}$ is the standard free energy for the same step corrected for the electrostatic interaction arising from the charge variation in the reactants upon electron transfer. Δ $G^{\circ\prime}$ values are calculated from the $\Delta G^{\circ}$ values reported in Table S1. The $\Delta G^{\circ}$ values have then be corrected for the electrostatic free energy change due to the change in $Z_1$ and $Z_2$ upon electron transfer on the basis of eq 2 to give the $\Delta G^{\circ\prime}$ value to introduce in the eq 1.

$$\Delta G^{\circ\prime} = \Delta G^{\circ} + (Z_1\text{-}Z_2\text{-}1)(e^2f/Dr_{12}) \qquad (2)$$

In eq 2, e is the electron charge, $Z_1$ and $Z_2$ are the charge numbers of the reactants**,** $r_{12}$ is the distance between *N*-oxyl radicals **1-4** and the ferrocenes in the encounter complex (taken as 7.0 Å for SINO and MINO radicals and 7.4 Å for QONO and BONO radicals),[S2] D is the dielectric constant of the solvent (35 for $CH_3CN$), and f is a factor depending upon the ionic strength ($f \cong 1$ for $\mu \rightarrow 0$). The values of $\Delta G^{\circ\prime}$ evaluated as described above are listed in Table S1. These values refer to reactions carried out at 25 °C.

Nonlinear least squares curve fitting of the experimental data has been carried out using the reorganization energy λ as adjustable parameter. The best fit of the experimental data with the curve

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calculated by eq 1 (Figure 7 and Figures S10-S12) are obtained for λ values of 43.6 kcal $mol^{-1}$ (**1**), 49.3 kcal $mol^{-1}$ (**2**), 36.0 kcal $mol^{-1}$ (**3**) and 28.4 kcal $mol^{-1}$ (**4**).

**Table S1.** Standard free energy ($\Delta G°$) and standard free energy corrected for the electrostatic contribution ($\Delta G°'$) for the electron transfer from ferrocenes (FcX) to *N*-oxyl radicals **1-4** at 25 °C in $CH_3CN$.

| FcX | SINO (1) | | MINO (2) | | QONO (3) | | BONO (4) | |
|---|---|---|---|---|---|---|---|---|
| | $\Delta G°$ | $\Delta G°'$ | $\Delta G°$ | $\Delta G°'$ | $\Delta G°$ | $\Delta G°'$ | $\Delta G°$ | $\Delta G°'$ |
| **FcH** | -11.7 | -13.1 | -8.2 | -9.6 | -9.9 | -11.2 | | |
| **$FcMe_2$** | -14.4 | -15.8 | -11.0 | -12.4 | -12.7 | -14.0 | | |
| **FcEt** | -13.3 | -14.7 | -9.8 | -11.2 | -11.5 | -12.8 | | |
| **$FcCH_2OH$** | -11.9 | -13.3 | -8.4 | -9.8 | -10.1 | -11.4 | | |
| **$FcCONH_2$** | -7.7 | -9.1 | | | -6.0 | -7.3 | -4.4 | -5.7 |
| **$FcCO_2Et$** | -6.1 | -7.5 | | | | | -2.8 | -4.1 |
| **FcCOMe** | | | | | | | -2.5 | -3.8 |
| **FcCOPh** | | | | | | | -1.9 | -3.2 |

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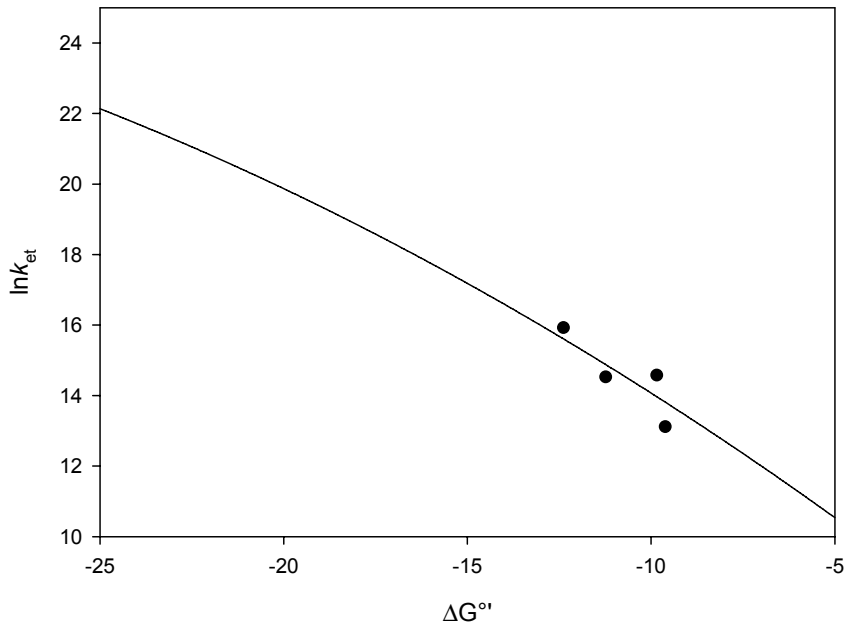


**Figure S11**. Diagram of ln$k_{et}$ vs $\Delta G^{\circ\prime}$ for the reactions of substituted ferrocenes with MINO. The solid circles correspond to the experimental values; the curve is calculated by nonlinear least-squares fit to eq 1.

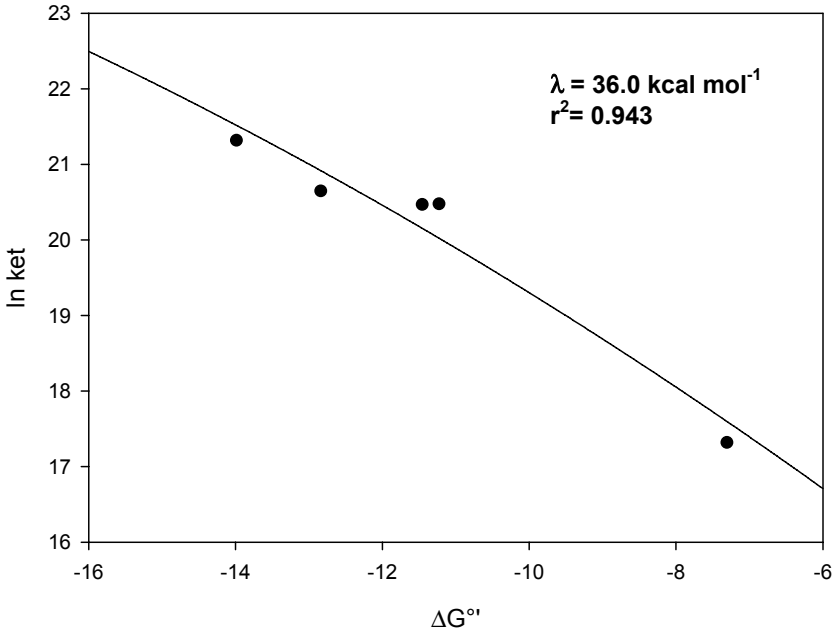


**Figure S12**. Diagram of ln$k_{et}$ vs $\Delta G^{\circ\prime}$ for the reactions of substituted ferrocenes with QONO. The solid circles correspond to the experimental values; the curve is calculated by nonlinear least-squares fit to eq 1.

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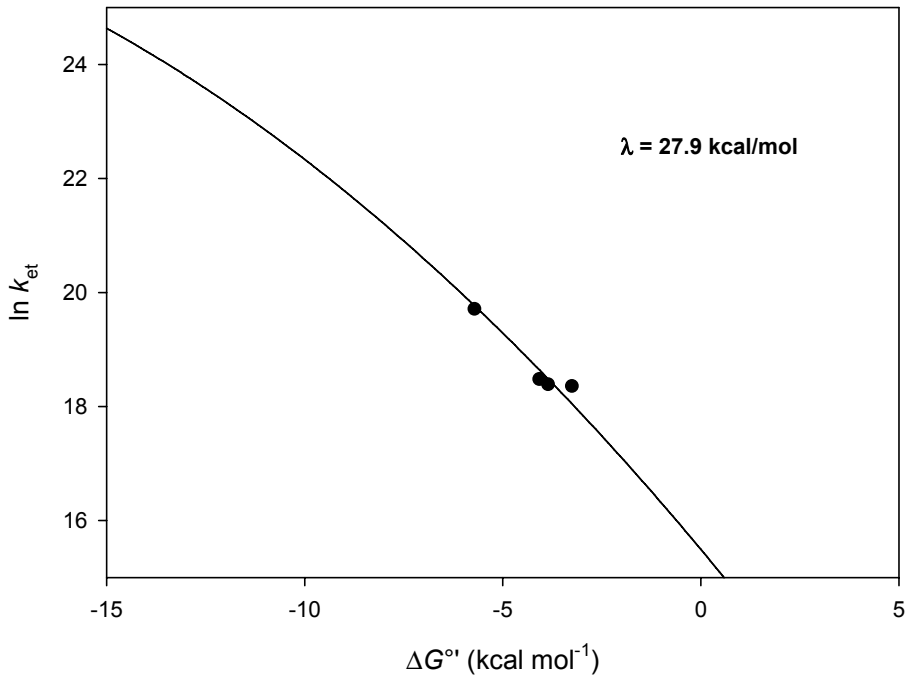


**Figure S13**. Diagram of ln $k_{et}$ vs $\Delta G^{\circ\prime}$ for the reactions of substituted ferrocenes with BONO. The solid circles correspond to the experimental values; the curve is calculated by nonlinear least-squares fit to eq 1.

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**References for Supporting Information**

S1. Eberson, L. *Electron Transfer Reactions in Organic Chemistry*; Springler Verlag: Berlin Heidelberg, 1986; Chapter 3.

S2. The radius of ferrocene (2.6 Å) is taken from ref. S3. The radii of SINO and MINO (4.4 Å) and QONO and BONO (4.8 Å) were calculated from the volume of the *N*-oxyl radicals given by the Hyperchem program.

S3. Carlson, B. W.; Miller, L. L.; Neta, P.; Grodkowski, J. *J. Am. Chem. Soc.*, **1984**, *103,* 7233.

S4. Baciocchi, E.; Bietti, M.; Gerini, M. F.; Lanzalunga O. *J. Org. Chem.* **2005**, *70*, 5144-5149.