SUPPORTING INFORMATION

Imido Transfer from Bis(imido)ruthenium(VI) Porphyrins to Hydrocarbons: Effect of Imido Substituents, C–H Bond Dissociation Energies, and $Ru^{VI/V}$ Reduction Potentials

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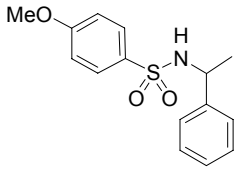
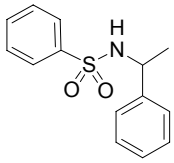
General. Ethylbenzene-d_{10} (Aldrich) was used as received. Pyrazole was recrystallized from petroleum ether. Dihydroanthracene, fluorene, and xanthene were recrystallized from EtOH. *p*-Nitrostyrene, indene, *p*-nitroethylbenzene, and toluene were purified by passing through a column of activated alumina. Other hydrocarbons and CH_2Cl_2 were purified as described previously.[1] The purity of all the hydrocarbons was checked by GC or ^{1}H NMR analysis. PhI=NSO_2R (SO_2R = Ms, Ts, Bs, Cs, Ns),[2,3] [Ru^{II}(Por)(CO)] (Por = TPP,[4] TMP,[5] 2,6-Cl_2TPP,[6] F_{20}-TPP[7]), and [Ru^{VI}(TPP)$(NTs)_2$] [1] were prepared by literature methods. UV-vis spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer interfaced with IBM compatible PC or a Perkin-Elmer Lambda 19 spectrophotometer. ^{1}H NMR spectra were measured on Brucker DPX 300 and 400 spectrometers. Chemical shifts (δ ppm) are relative to tetramethylsilane. IR spectra were obtained on a Bio-Rad FT-IR spectrometer. FAB mass spectra were recorded on a Finnigan MAT 95 mass spectrometer using 3-nitrobenzyl alcohol as matrix. Electrospray mass spectra (ESMS) were measured on a Finnigan LCQ quadrupole ion trap mass spectrometer (samples were dissolved in HPLC CH_2Cl_2). Cyclic voltammograms were recorded on a Princeton Applied Research Model 273A potentiostat/galvanostat coulometer and Model 270/250 universal programmer using a three-electrode cell system (working electrode: glassy carbon, counter electrode: platinum wire, reference electrode: 0.1 M Ag/$AgNO_3$ in MeCN). The electrolyte, [NBu^n_4]PF_6 (Avocado), was recrystallized three times from hot EtOH and dried in vacuo at 80 ^{o}C for 12 h before use. Ferrocene was used as an internal standard. Elemental analyses were performed by Institute of Chemistry, the Chinese Academy of Sciences.

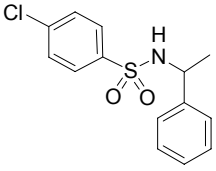
Characterization of Aziridination/Amidation Products.



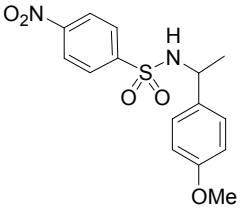
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.65 (d, J = 8.3 Hz, 2H), 7.18 (m, 5H), 7.00 (m, 2H), 4.61 (bd, J = 6.5 Hz, 1H), 4.46 (q, J = 6.8 Hz, 1H), 3.28 (s, 3H), 1.44 (d, J = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 126.0, 125.4, 124.4, 123.0, 111.5, 111.4, 111.1, 110.8, 52.4, 50.4, 26.5. HRMS (M^+): m/z calcd for $C_{15}H_{17}NO_3S$: 291.0929, found: 291.0931.



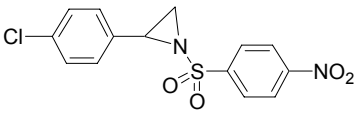
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.72 (d, J = 8.3 Hz, 2H), 7.5 (t, J = 8.3 Hz, 1H), 7.38 (d, J = 8.3 Hz, 2H), 7.16 (m, 3H), 7.09 (m, 2H), 5.04 (bd, J = 6.5 Hz, 1H), 4.49 (q, J = 6.8 Hz, 1H), 1.43 (d, J = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 134.03, 130.52, 130.26, 129.24, 128.73, 127.79, 55.43, 25.26. HRMS (M^+): m/z calcd for $C_{14}H_{15}NO_2S$: 261.0824, found: 261.0819.



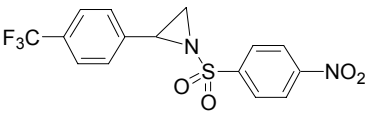
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.60 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.3 Hz, 2H), 7.19 (m, 3H), 7.07 (m, 2H), 4.69 (bd, J = 6.5 Hz, 1H), 4.52 (q, J = 6.8 Hz, 1H), 1.46 (d, J = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 131.8, 131.0, 130.9, 129.4, 129.0, 128.5, 127.7, 126.2, 53.9, 31.6. HRMS (M^+): m/z calcd for $C_{14}H_{14}ClNO_2S$: 295.0434, found: 295.0427.



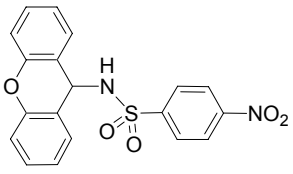
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.16 (d, J = 8.9 Hz, 2H), 7.79 (d, J = 8.9 Hz, 2H), 6.96 (d, J = 8.7 Hz, 2H), 6.67 (d, J = 8.7 Hz, 2H), 4.87 (bd, J = 6.5 Hz, 1H), 4.56 (q, J = 6.8 Hz, 1H), 3.81 (s, 3H), 1.46 (d, J = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 177.56, 161.81, 161.0, 129.95, 129.13, 127.87, 125.56, 115.66, 55.41, 31.40, 25.25. HRMS (M^+): m/z calcd for $C_{15}H_{16}N_2O_5S$: 336.0780, found: 336.0782.



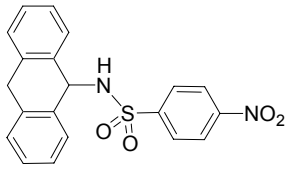
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.40 (d, J = 8.9 Hz, 2H), 8.20 (d, J = 8.9 Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 7.18 (d, J = 8.5 Hz, 2H), 3.89 (dd, J = 7.2 Hz, 1H), 3.12 (d, J = 7.2 Hz, 1H), 2.48 (d, J = 4.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 150.75, 143.79, 134.73, 132.73, 129.17, 128.83, 127.85, 124.48, 41.00, 36.65. HRMS (M^+): m/z calcd for $C_{14}H_{11}ClN_2O_4S$: 338.0128, found: 338.0123.



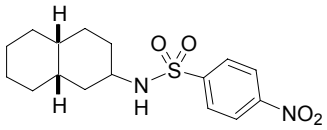
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.39 (d, J = 8.9 Hz, 2H), 8.20 (d, J = 8.9 Hz, 2H), 7.58 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 3.97 (dd, J = 7.2 Hz, 1H), 3.15 (d, J = 7.2 Hz, 1H), 2.50 (d, J = 4.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 150.78, 143.56, 138.33, 131.01, 129.27, 127.81, 126.83, 125.70, 124.39, 40.78, 36.80. HRMS (M^+): m/z calcd for $C_{15}H_{11}F_3N_2O_4S$: 372.0392, found: 372.0381.



^{1}H NMR (acetone-d_6, 400 MHz): δ = 8.41 (d, J = 8.8 Hz, 2H), 8.14 (d, J = 8.8 Hz, 2H), 7.78 (m, 1H), 7.30 (d, J = 8.1 Hz, 2H), 7.23 (d, J = 7.7 Hz, 2H), 7.13 (d, J = 8.2 Hz, 2H), 7.02 (m, 2H), 5.92 (d, J = 6.7 Hz, 1H). ^{13}C NMR (acetone-d_6, 100 MHz): δ = 151.7, 129.6, 129.4, 128.2, 127.9, 127.7, 127.5, 124.3, 123.4, 116.5, 49.4. HRMS (EI) calcd for $C_{19}H_{14}N_2O_5S$: 382.0623, found: 382.0628.



^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.14 (d, J = 8.7 Hz, 2H), 7.73 (d, J = 8.7 Hz, 2H), 7.36 (d, J = 7.1 Hz, 2H), 7.18 (m, 6H), 5.65 (d, J = 5.1 Hz, 1H), 4.95 (d, J = 5.1 Hz, 1H), 3.91 (d, J = 18.2 Hz, 1H), 3.79 (d, J = 18.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 149.9, 147.1, 137.6, 135.2, 128.9, 128.6, 128.3, 128.2, 127.0, 124.2, 57.6, 35.4. HRMS (EI) calcd for $C_{20}H_{16}N_2O_4S$: 380.0831, found: 380.0826.



^{1}H NMR ($CDCl_3$, 400 MHz) (major product): δ = 8.36 (d, J = 8.8 Hz, 2H), 8.06 (d, 2H), 4.55 (d, J = 7.8 Hz, 1H), 3.20 (m, 1H), 1.76 (m, 2H), 1.71–1.32 (m, 14H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 147.9, 128.5, 124.7, 124.6, 54.7, 35.5, 34.7, 34.2, 31.8, 31.0, 29.3, 26.9, 25.8, 21.1. HRMS (EI) calcd for $C_{16}H_{22}N_2O_4S$: 338.1300, found: 338.1296.

For characterization of the other aziridination/amidation products, see refs 1, 3a, 8–11.

References

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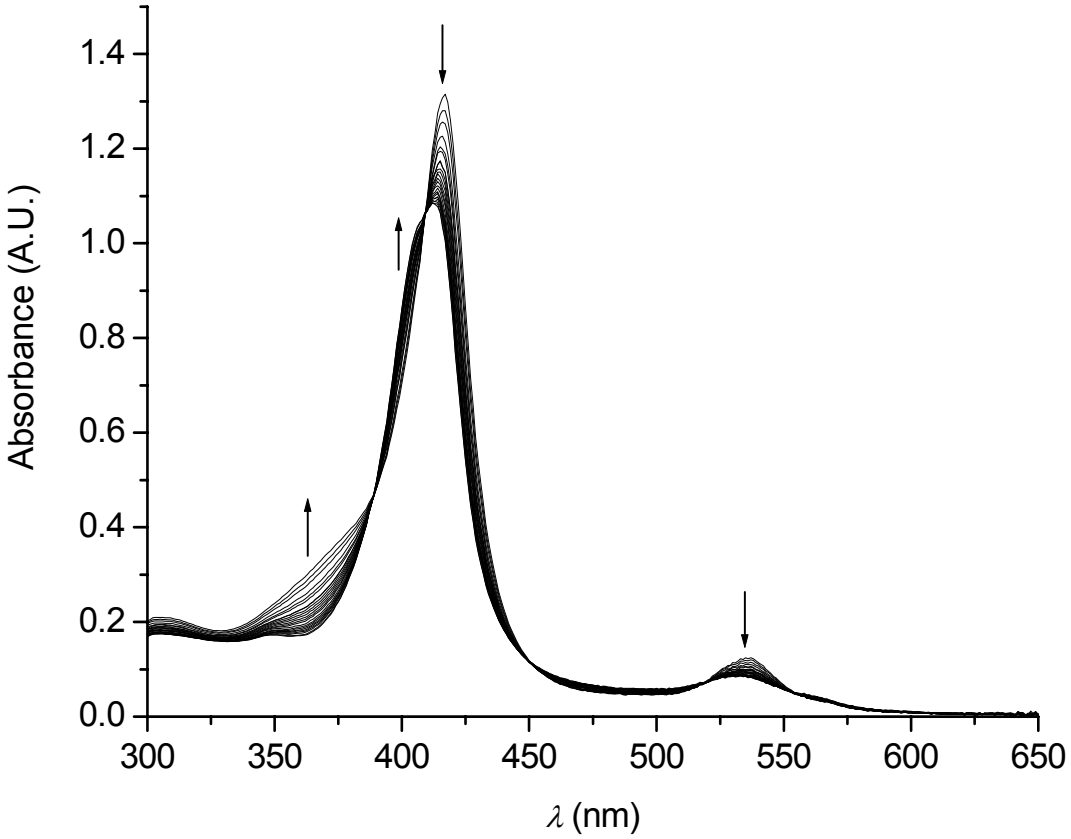

Figure S1. UV-vis spectral changes for reaction of $[Ru^{VI}(TMP)(NNs)_2]$ with styrene in CH_2Cl_2 containing pyrazole (2% w/w) at 298 K.

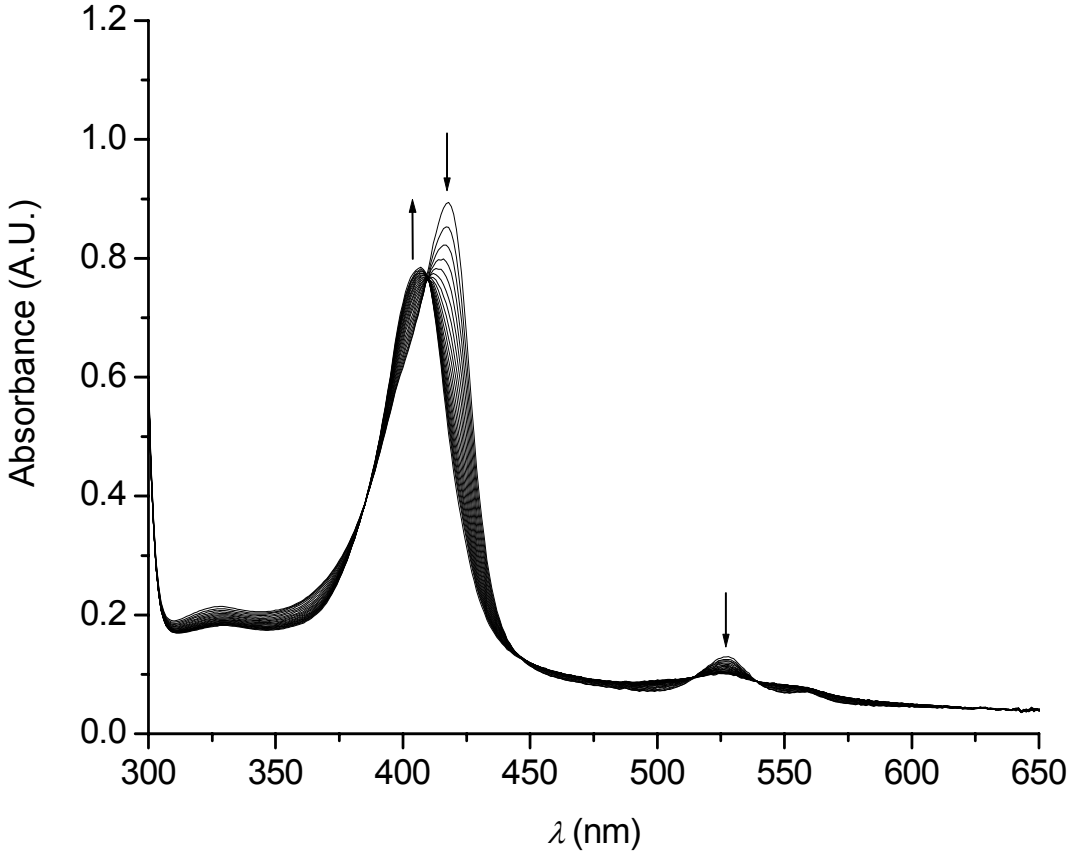

Figure S2. UV-vis spectral changes for reaction of $[Ru^{VI}(F_{20}\text{-TPP})(NTs)_2]$ with styrene in CH_2Cl_2 containing pyrazole (2% w/w) at 298 K.

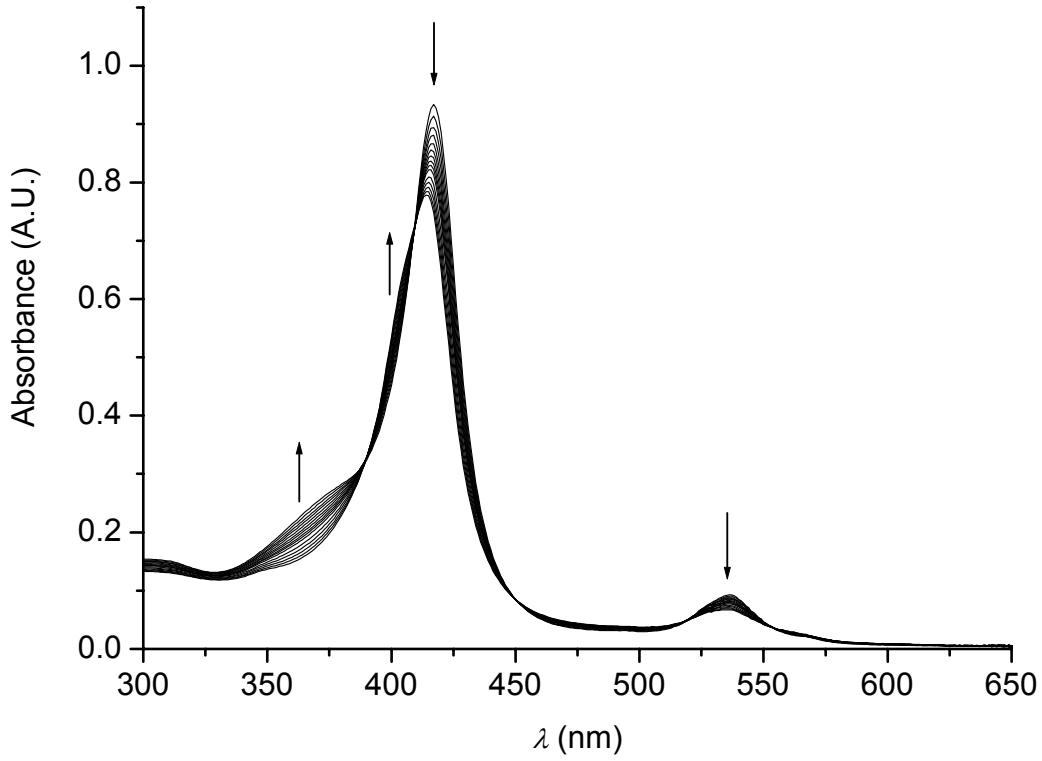

Figure S3. UV-vis spectral changes for reaction of $[Ru^{VI}(TMP)(NNs)_2]$ with cumene in CH_2Cl_2 containing pyrazole (2% w/w) at 298 K.

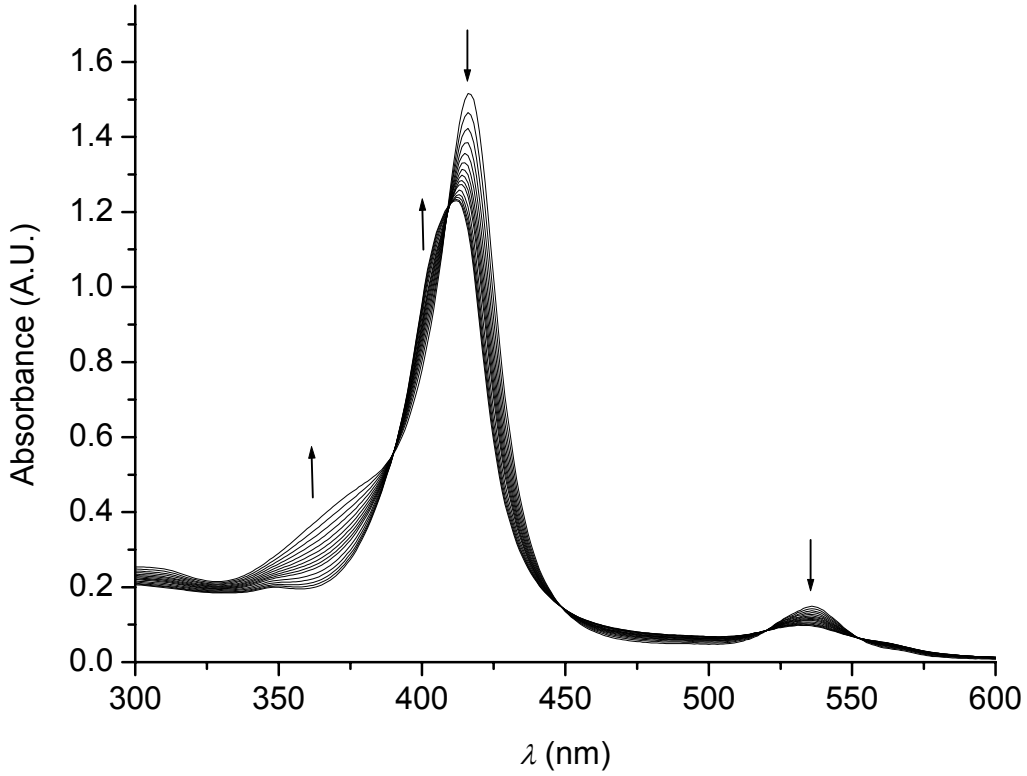

Figure S4. UV-vis spectral changes for reaction of $[Ru^{VI}(TMP)(NNs)_2]$ with tetrahydrofuran in CH_2Cl_2 containing pyrazole (2% w/w) at 298 K.

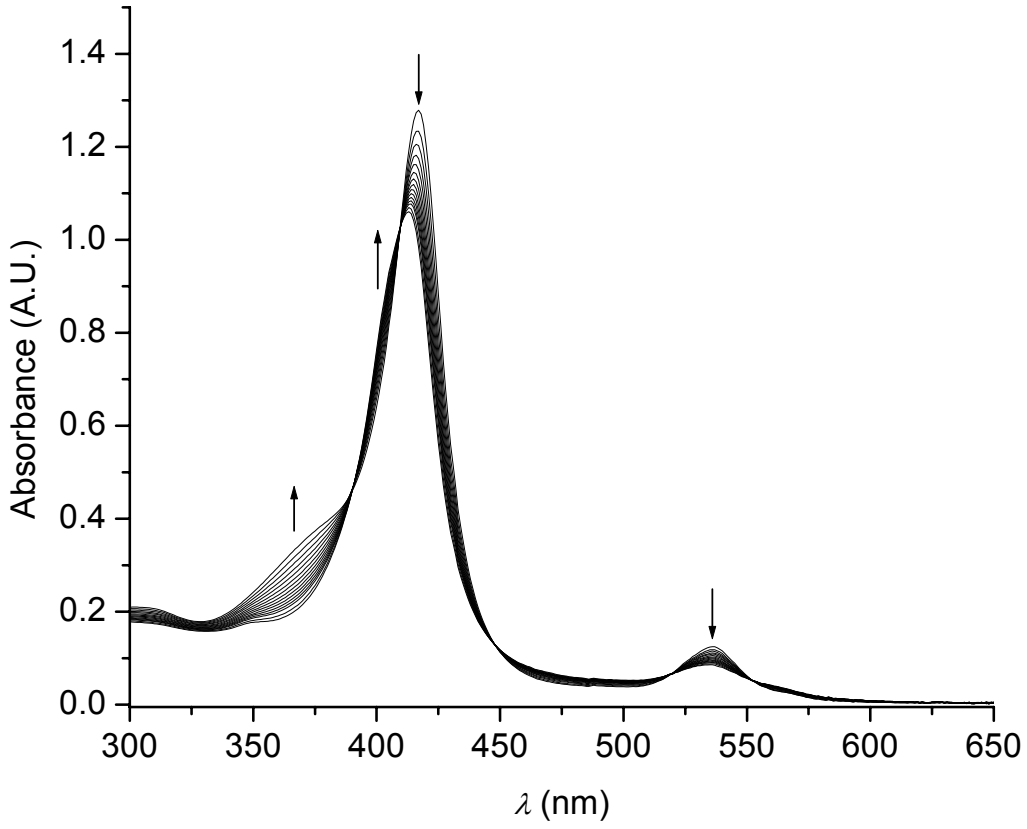

Figure S5. UV-vis spectral changes for reaction of $[Ru^{VI}(TMP)(NNs)_2]$ with toluene in CH_2Cl_2 containing pyrazole (2% w/w) at 298 K.

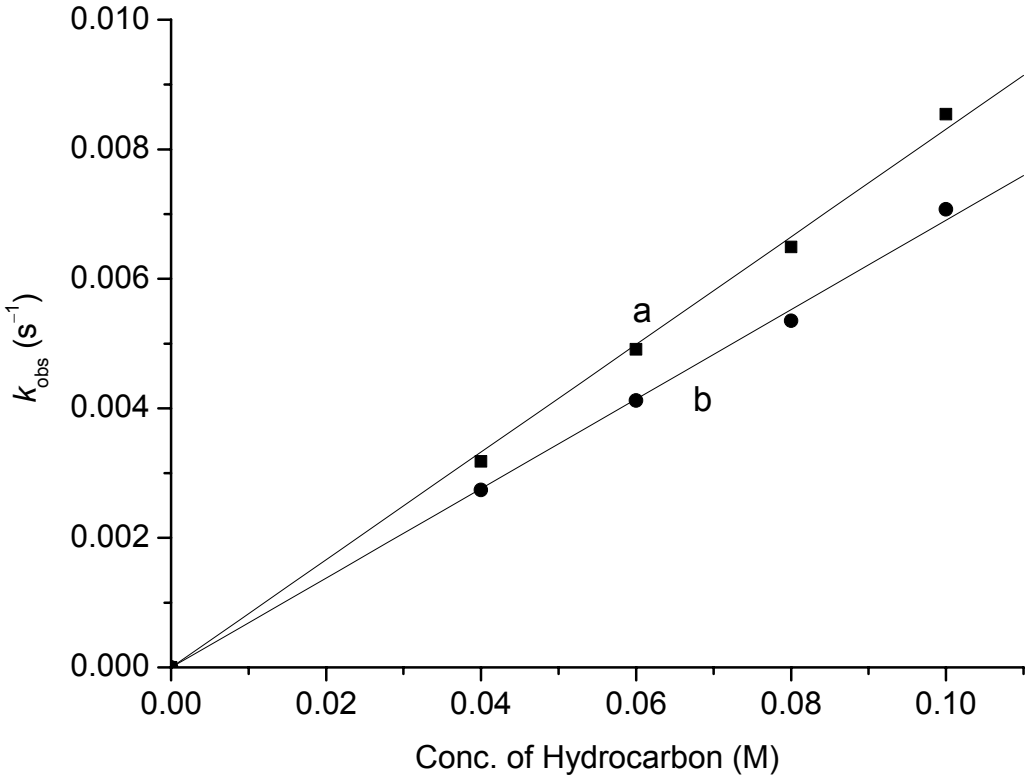

Figure S6. Plots of k_{obs} vs [hydrocarbon] for reaction of $[Ru^{VI}(TMP)(NNs)_2]$ with (a) styrene and (b) *p*-chlorostyrene in CH_2Cl_2 containing pyrazole (2% w/w) at 298 K.

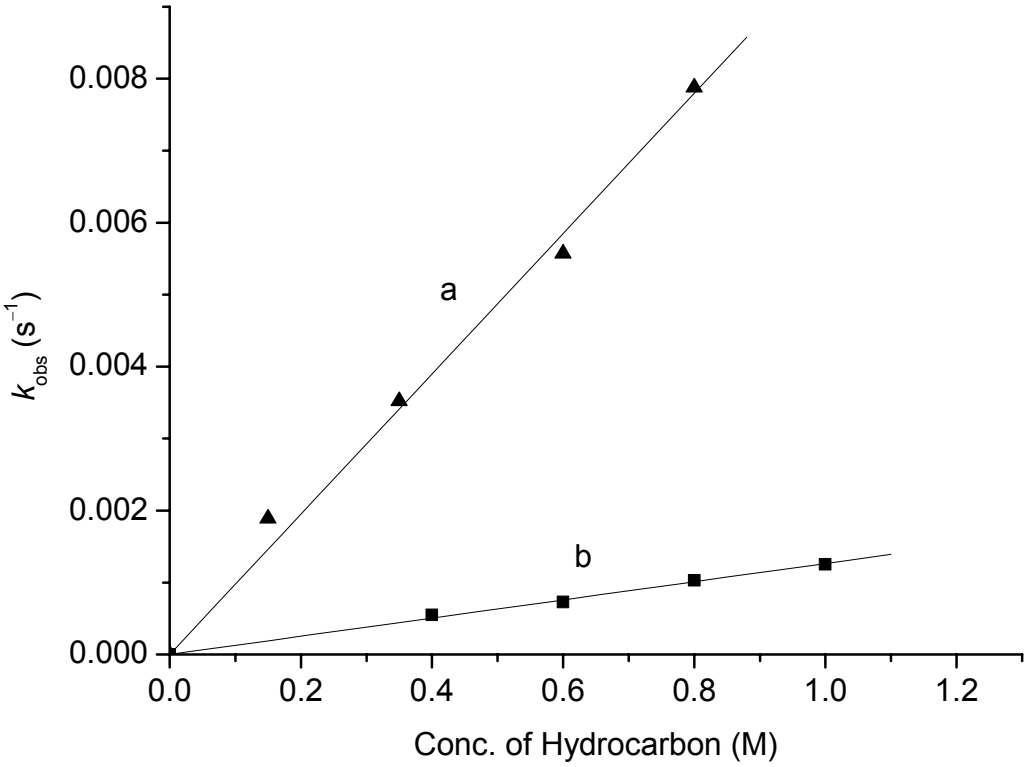

Figure S7. Plots of k_{obs} vs [hydrocarbon] for reaction of [Ru^{VI}(TMP)$(NNs)_2$] with (a) *p*-trifluorostyrene and (b) norbornene in CH_2Cl_2 containing pyrazole (2% w/w) at 298 K.

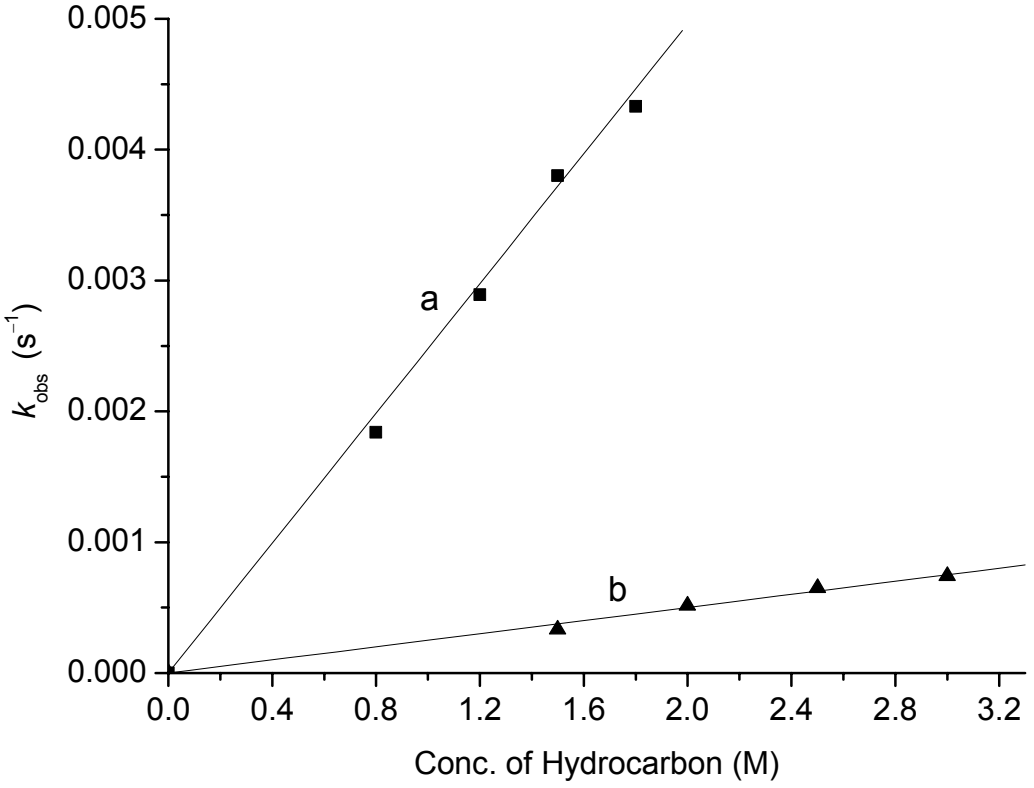

Figure S8. Plots of k_{obs} vs [hydrocarbon] for reaction of $[Ru^{VI}(TMP)(NNs)_2]$ with (a) ethylbenzene and (b) cumene in CH_2Cl_2 containing pyrazole (2% w/w) at 298 K.

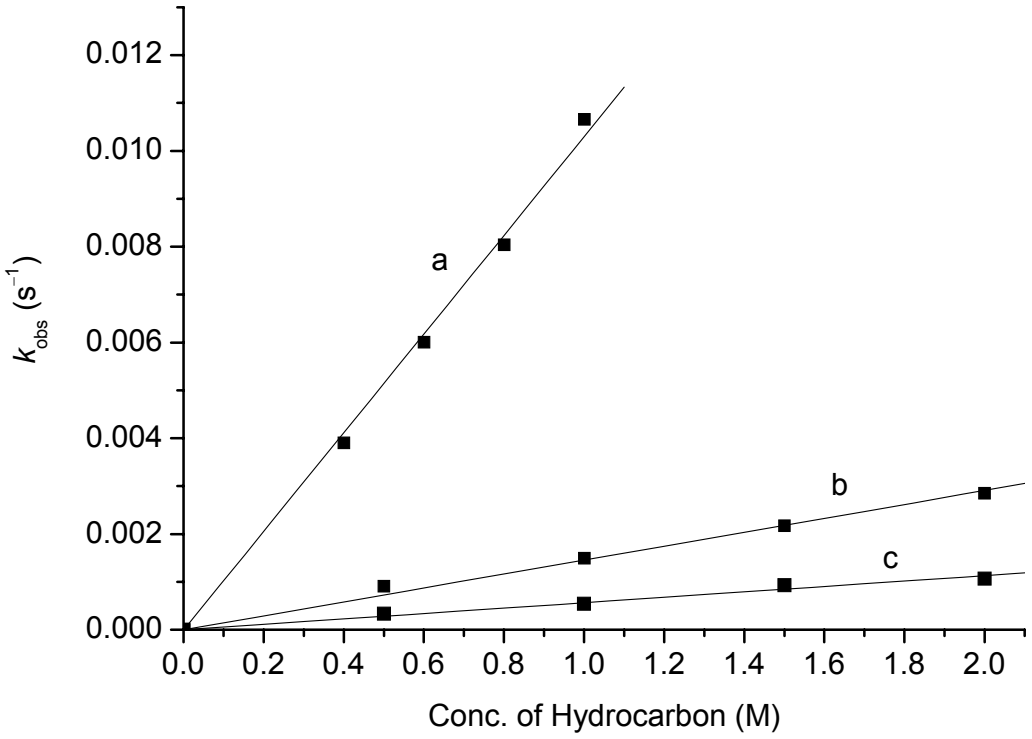

Figure S9. Plots of k_{obs} vs [hydrocarbon] for reaction of (a) [Ru^{VI}(TMP)$(NNs)_2$], (b) [Ru^{VI}(TMP)$(NBs)_2$], and (c) [Ru^{VI}(TMP)$(NMs)_2$] with tetrahydrofuran in CH_2Cl_2 containing pyrazole (2% w/w) at 298 K.

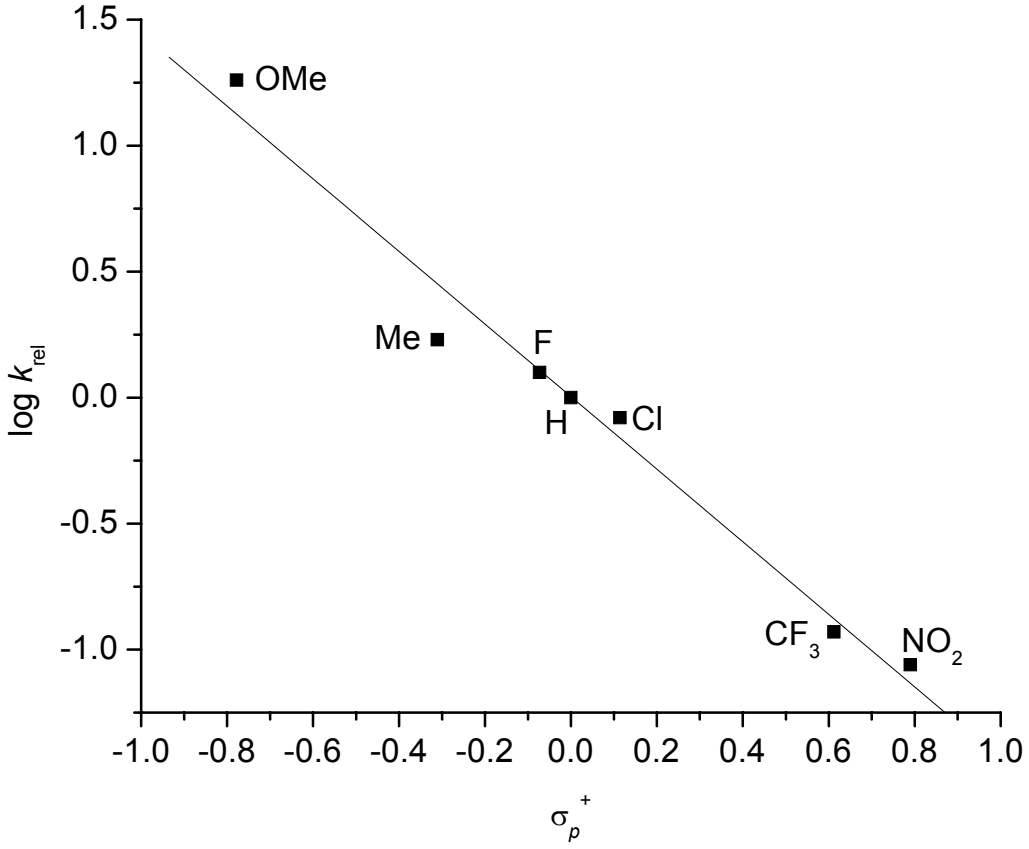

Figure S10. Plot of log k_{rel} vs σ_p^+ for reaction of $[Ru^{VI}(TMP)(NNs)_2]$ with *p*-$XC_6H_4CH{=}CH_2$ (X = OMe, Me, H, F, Cl, CF_3, NO_2) in CH_2Cl_2 containing pyrazole (2% w/w) at 298 K.

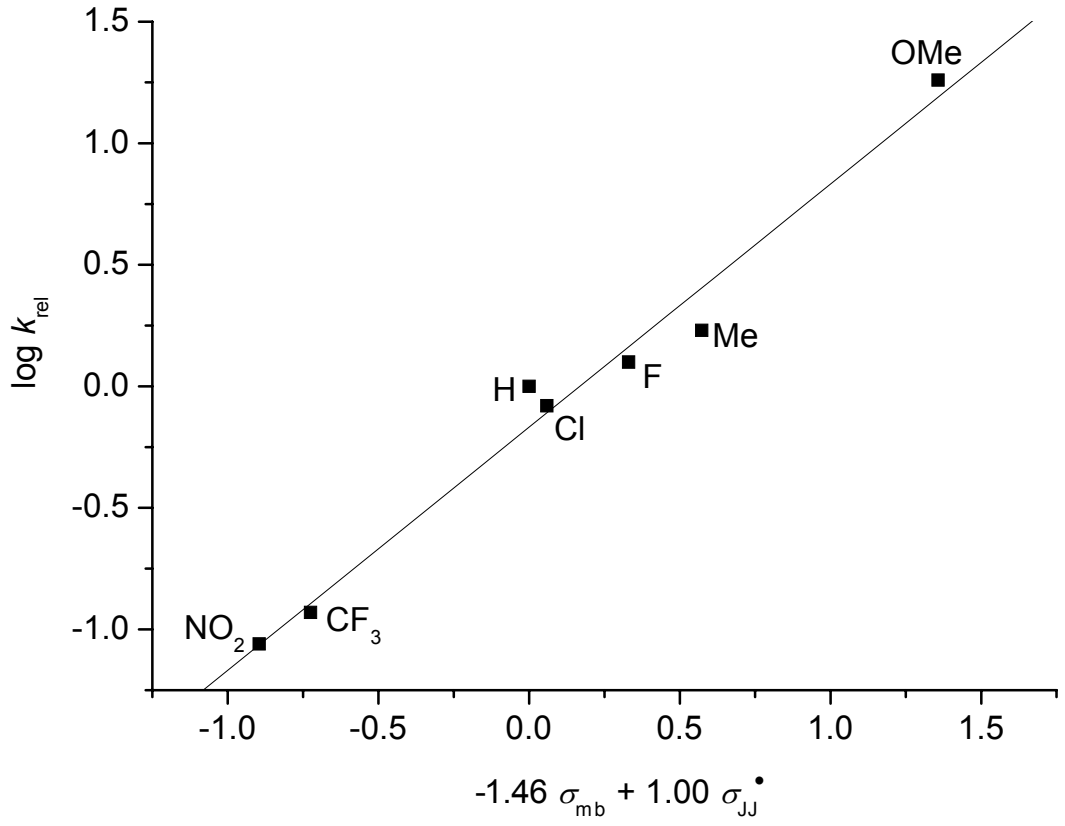

Figure S11. Plot of log k_{rel} vs (σ_{mb}, $\sigma_{JJ}^{\bullet}$) for reaction of [Ru^{VI}(TMP)$(NNs)_2$] with *p*-$XC_6H_4CH{=}CH_2$ (X = OMe, Me, H, F, Cl, CF_3, NO_2) in CH_2Cl_2 containing pyrazole (2% w/w) at 298 K.

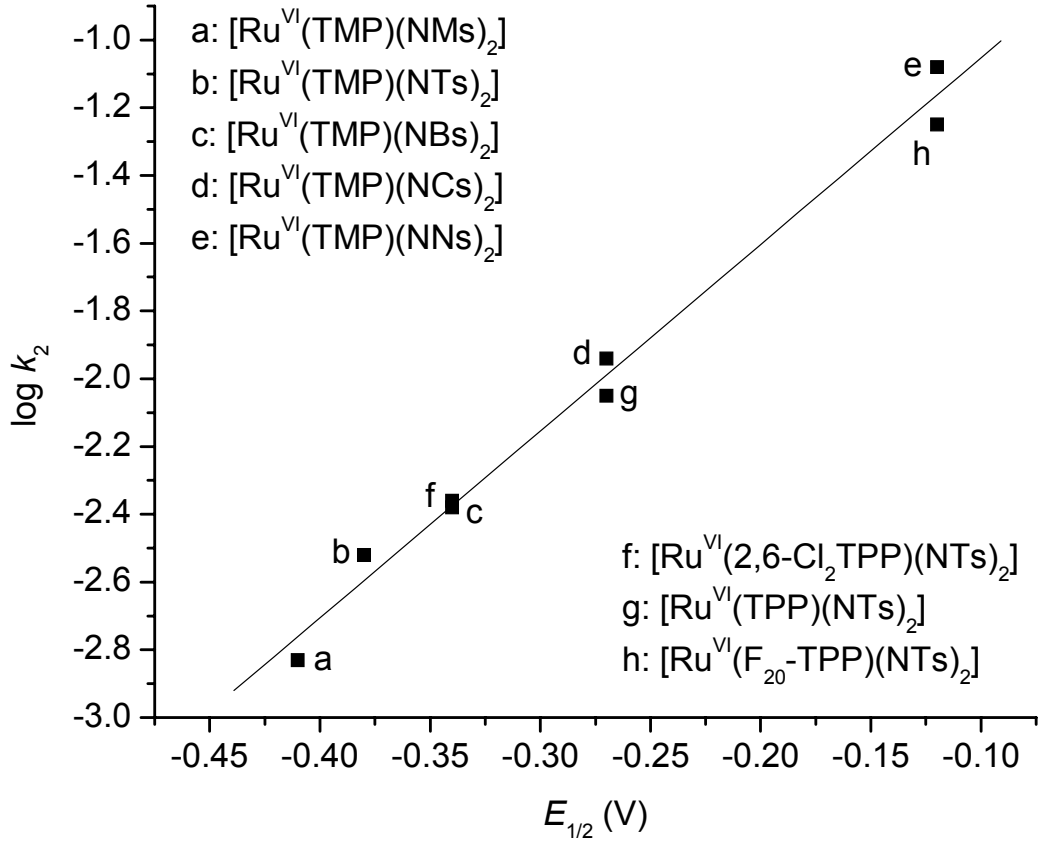

Figure S12. Plot of log k_2 vs $E_{½}(Ru^{VI/V})$ for reaction of $[Ru^{VI}(Por)(NSO_2R)_2]$ with styrene in CH_2Cl_2 containing pyrazole (2% w/w) at 298 K.