Concerning the Mechanism of $FeCl_3$-Catalyzed α-Oxyamination of Aldehydes. Evidence for a Non-SOMO Activation Pathway

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# Supporting Information

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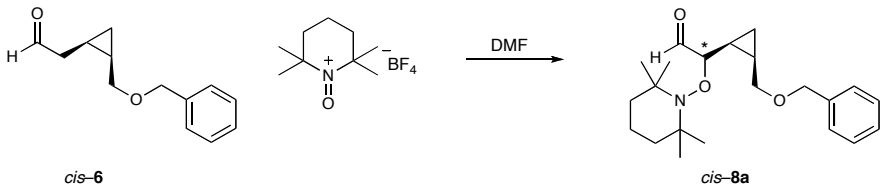
**I. General Information.** Commercial reagents were purified prior to use following the guidelines of Perrin and Armarego[1]. All solvents were purified according to the method of Grubbs[2], unless otherwise noted. $[Fe(dmf)_3Cl_2][FeCl_4]$ was prepared according to the procedure of Tobinaga and Kotani.[3] Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Chromatographic purification of products was accomplished using force-flow chromatography on Silicycle Siliflash® F60 230-400

mesh silica gel according to the method of Still.[4] Thin-layer chromatography (TLC) was performed on Silicycle 250 μm silica gel plates. TLC visualization was performed by ultraviolet light, $KMnO_4$, or CAM stain. $^1$H NMR spectra were recorded on a Bruker UltraShield 500 (500 MHz) outfitted with a cryoprobe and are referenced relative to residual $CDCl_3$ proton signals at δ 7.27 ppm or residual $C_6D_6$ at δ 7.16 ppm. Data for $^1$H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, ap = apparent), integration, coupling constant (Hz) and assignment. $^{13}$C NMR spectra were recorded on a Bruker UltraShield 500 (125 MHz) outfitted with a cryoprobe and are referenced relative to $CDCl_3$ at δ 77.2 ppm or $C_6D_6$ at δ 128.6 ppm. Data for $^{13}$C NMR are reported in terms of chemical shift. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in terms of frequency of absorption ($cm^{-1}$). High Resolution Mass spectra were obtained from the Princeton University Mass Spectral Facility on an Agilent 1200 ESI-TOF instrument. UV/Vis measurements were taken on a Thermo Genesys 6 single-beam spectrophotometer in a 10.0 mm path-length quartz cell. ReactIR experiments were performed using a Mettler-Toledo React-iC10 system fitted with a 6.3 mm AgX Dicomp Fiber Conduit probe.

## II. Synthesis and Characterization of *trans*-6, *cis*- and *trans*-8




*cis*–**6** *cis*–**8a**

Mixture of epimers at * position

**(±)-*cis*-2-(2-(Benzyloxymethyl)cyclopropyl)-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)acetaldehyde (*cis*–8a):** (±)-*cis*-2-(2-(benzyloxymethyl)cyclopropyl)acetaldehyde[5] (206 mg, 1.01 mmol) was dissolved in DMF (1.0 mL) at room temperature. Oxoammonium tetrafluoroborate[6] (245mg, 1.01 mmol) was added in one portion, and the solution was left to stir overnight (12 h). The reaction was diluted with EtOAc (15 mL) and was washed with saturated aqueous $NaHCO_3$ (10 mL). The organic layer was dried over anhydrous magnesium sulfate, then concentrated *in vacuo*, and the resulting residue was purified using flash column chromatography (silica gel, 10 : 1 hexanes : ethyl

acetate) to deliver the title compound as a clear oil (92 mg, 0.26 mmol, 26%). The product was isolated as an inseparable 3:1 mixture of stereoisomers at the α–position, and contained >95% *cis*–fused cyclopropane. 2D-NMR allowed for the assignment of all well resolved $^{1}$H NMR resonances to the respective isomers, as well as a large number, though not all $^{13}$C resonances.

**Major isomer:** $^{1}$H NMR (500 MHz, $CDCl_3$) δ9.78 (d, 1H, *J* = 4.5 Hz, C**H**O), 7.39–7.31 (m, 4H, Ar**H**), 7.30–7.26 (m, 1H, Ar**H**), 4.49 (s, 2H, OC**H**$_2$Ph), 3.89 (dd, 1H, *J* = 9.5 Hz, 4.5 Hz, OHC–C**H**), 3.53 (dd, 1H, *J* = 10.0 Hz, 6.5 Hz, *c*Pr–C**H**$_2$O), 3.40 (dd, 1H, *J* = 10.5 Hz, 7.5 Hz, *c*Pr–C**H**$_2$O), 1.52–1.10 (m, 20H), 1.02 (td, 1H, *J* = 8.5 Hz, 5.0 Hz, *c*Pr C**H**$_2$) 0.66 (dd, 1H, *J* = 11 Hz, 5.5 Hz, *c*Pr C**H**$_2$)

**Minor isomer:** $^{1}$H NMR (500 MHz, $CDCl_3$) δ9.82 (d, 1H *J* = 5.0 Hz, C**H**O), 7.39–7.31 (m, 4H, Ar**H**), δ7.30–7.26 (m, 1H, Ar**H**), 4.60 (d, 1H, *J* = 12.0 Hz, OC**H**$_2$Ph), 4.54 (d, 1H, *J* = 12.0 Hz, OC**H**$_2$Ph), 3.86 (dd, 1H, *J* = 9.0 Hz, 5.5 Hz, OHC-C**H**), 3.74 (dd, 1H, *J* = 10.0 Hz, 6.0 Hz, *c*Pr–C**H**$_2$O), 3.44 (dd, 1H, *J* = 10.0 Hz, 7.5 Hz, *c*Pr–C**H**$_2$O), δ1.52–1.10 (m, 20H), 0.86 (td, 1H, *J* = 8.5 Hz, 5.0 Hz, *c*Pr–C**H**$_2$), 0.41 (q, 1H, *J* = 5.5 Hz, *c*Pr–C**H**$_2$).

$^{13}$C NMR (125 MHz, $CDCl_3$) δ202.1 (min), 201.6 (maj), 138.3 (x2, maj and min), 128.5 (x2, maj and min), 128.0 (x2, maj and min), 127.8 (min), 127.7 (maj), 88.3 (maj), 87.9 (min), 73.1 (min), 72.9 (maj), 70.5 (min), 70.2 (maj), 40.1 (maj), 39.9 (min), 34.5, 34.4, 34.1, 33.7, 20.5, 17.2, 16.0, 15.7, 15.1, 9.8, 7.2.

IR (film) 2972, 2932, 2870, 1729, 1455, 1374, 1362, 1259, 1208, 1183, 1133, 1091, 1044, 957 cm $^{-1}$. HRMS exact mass calculated for $[M+H]^+$ ($C_{22}H_{34}NO_3$) requires *m/z* 359.2460 found 359.2458.

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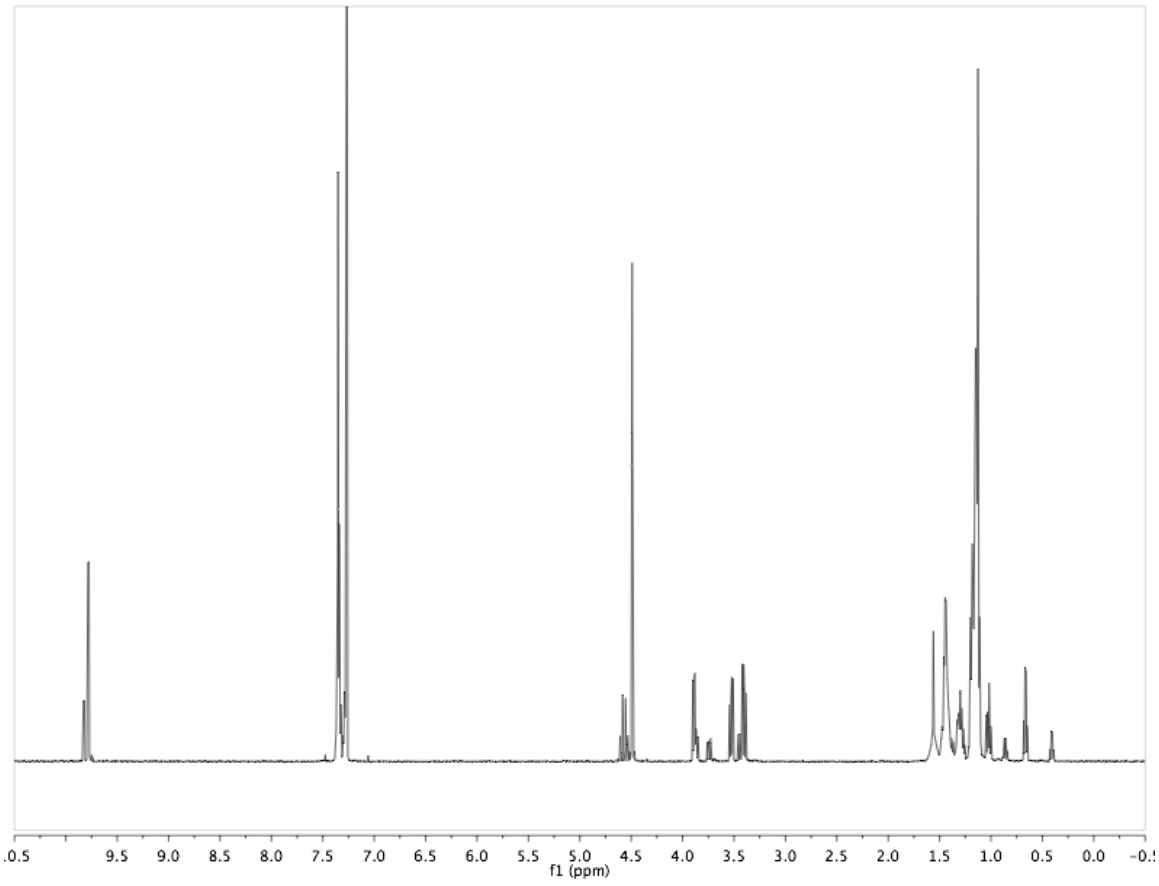

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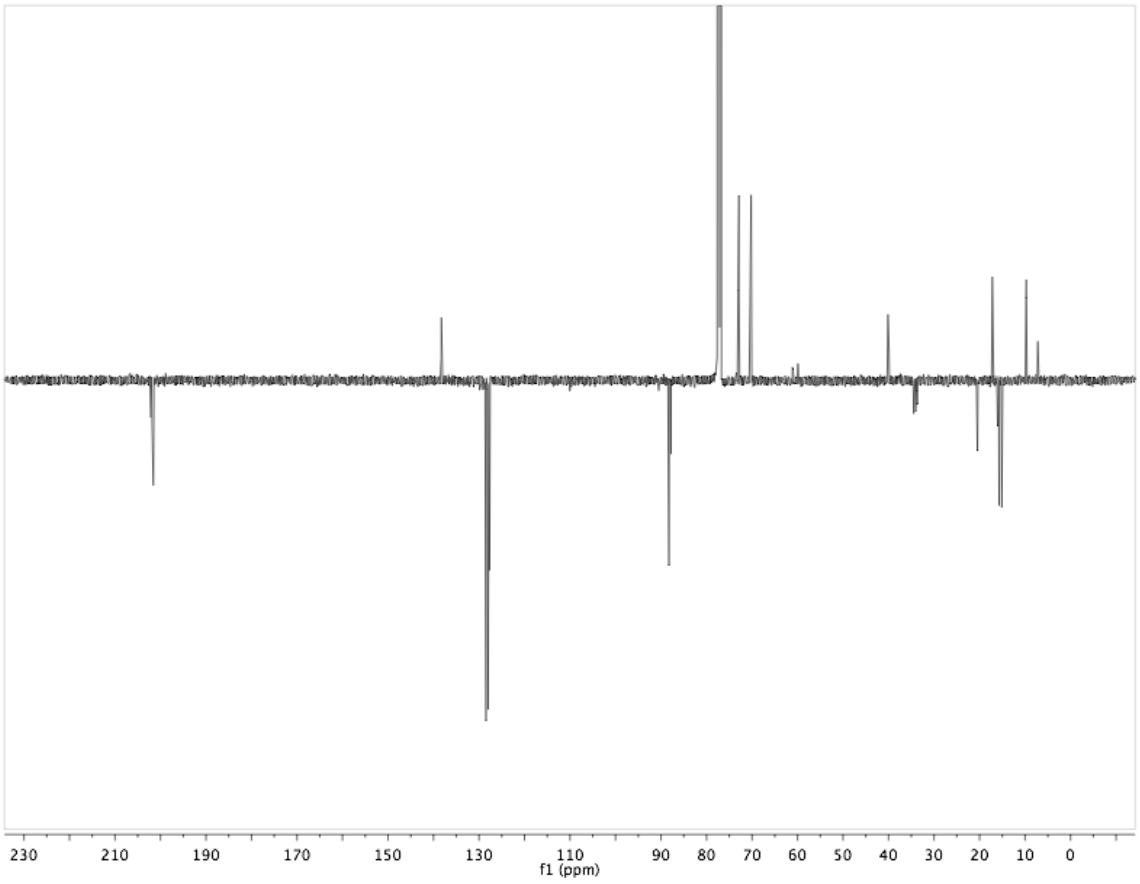
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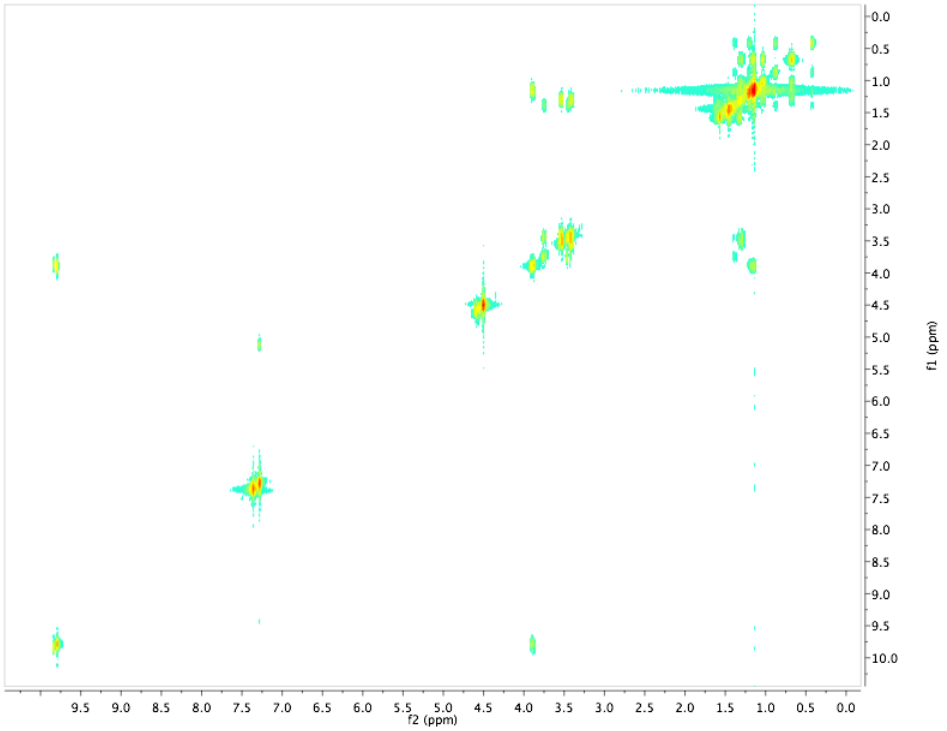
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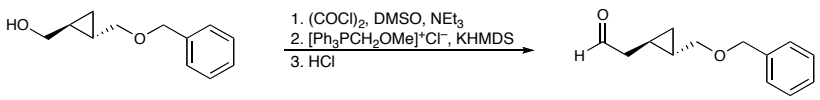


**(±)-*trans*-2-(2-(Benzyloxymethyl)cyclopropyl)acetaldehyde:** Oxalyl chloride (400 μL, 4.73 mmol) was dissolved in dry dichloromethane (10 mL) and cooled to –78 ºC under argon. Dimethylsulfoxide (600 μL, 8.45 mmol) was dissolved in dry dichloromethane (3 mL), and then added dropwise to the oxalyl chloride. The resulting solution was allowed to stir for 15 minutes at –78 ºC. *trans*-2-(Benzyloxymethyl)cyclopropyl)methanol[7] (600 mg, 3.12 mmol) was dissolved in dry dichloromethane (3 mL), and was added dropwise. The solution was left to stir at –78 ºC under argon for 30 minutes. Triethylamine (2.2 mL, 15.9 mmol) was added, and the solution was allowed to stir at –78 ºC for a further 90 minutes. At that point, the cooling bath was removed and the solution was allowed to warm to room temperature. TLC analysis after 15 minutes of warming indicated complete conversion. The reaction was quenched with saturated aqueous $NH_4Cl$ (30 mL) and was extracted with EtOAc (3 x 25 mL). The combined organic extracts were washed with water (2 x 25 mL) and brine (25 mL), then dried over anhydrous magnesium sulfate and concentrated *in vacuo*. The resulting oil was used immediately. (Methoxymethyl)triphenylphosphonium chloride (1.60 g, 4.67 mmol) was suspended in dry THF (7 mL) and was cooled to –78 ºC under argon. Potassium bis(trimethylsilyl)amide (850 mg, 4.26 mmol) was dissolved in dry THF (4.5 mL) and was added dropwise. The resulting solution was left to stir at –78 ºC for 20 minutes. The crude product from the previous operation was dissolved in dry THF (4 mL) and was added in one portion. The resulting solution was left to stir at –78 ºC for 10 minutes, then was warmed to 0 ºC with an ice water bath, and left to stir for 1h at 0 ºC. The reaction was quenched with saturated aqueous $NH_4Cl$ (25 mL), which was extracted with EtOAc (3 x 25 mL). The combined organic extracts were washed with water (2 x 25 mL) and brine (25 mL), then dried over anhydrous magnesium sulfate and concentrated *in vacuo*. The resulting clear oil was immediately dissolved in acetone (13 mL) to which water (1.5 mL) and concentrated HCl (3 drops) were added. The solution was heated to 65 ºC for 1h. After cooling to room temperature, the reaction was quenched with saturated aqueous

$NaHCO_3$, (25 mL) which was extracted with EtOAc (3 x 25 mL). The combined organic extracts were washed with water (2 x 25 mL) and brine (25 mL), dried over anhydrous magnesium sulfate and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (silica gel, gradient elution from 5 : 1 to 3 : 1 hexanes : EtOAc) to yield a clear oil (371 mg, 1.82 mmol, 58%).

$^1$H NMR (500 MHz, $CDCl_3$) δ9.80 (m, 1H, C**H**O), 7.40–7.32 (m, 4H, Ar**H**), 4.54 (s, 2H, OC**H**$_2$Ph), 3.38 (d, 2H, *J* = 7.0 Hz, *c*Pr–C**H**$_2$O), 2.45 (dd, 1H, *J* = 17.0 Hz, 6.5 Hz, OHC–C**H**$_2$), 2.30 (dd, 1H, *J* = 17.0 Hz, 7.5 Hz, OHC–C**H**$_2$), 1.03–0.91 (m, 2H, *c*Pr C**H**), 0.60 (dt, 1H, *J* = 8.5 Hz, 5.0 Hz, *c*Pr C**H**$_2$), 0.48 (dt, *J* = 8.0 Hz, 5.0 Hz, *c*Pr C**H**$_2$).

$^{13}$C NMR (125 MHz, $CDCl_3$) δ202.3, 138.5, 128.6, 127.8, 127.8, 73.7, 72.8, 47.8, 18.1, 10.6, 10.1. IR (film) 2861, 1725, 1454, 1362, 1096, 1027 cm$^{-1}$. HRMS exact mass calculated for $[M+H]^+$ ($C_{13}H_{17}O_2$) requires *m/z* 204.1150, found 204.1150.

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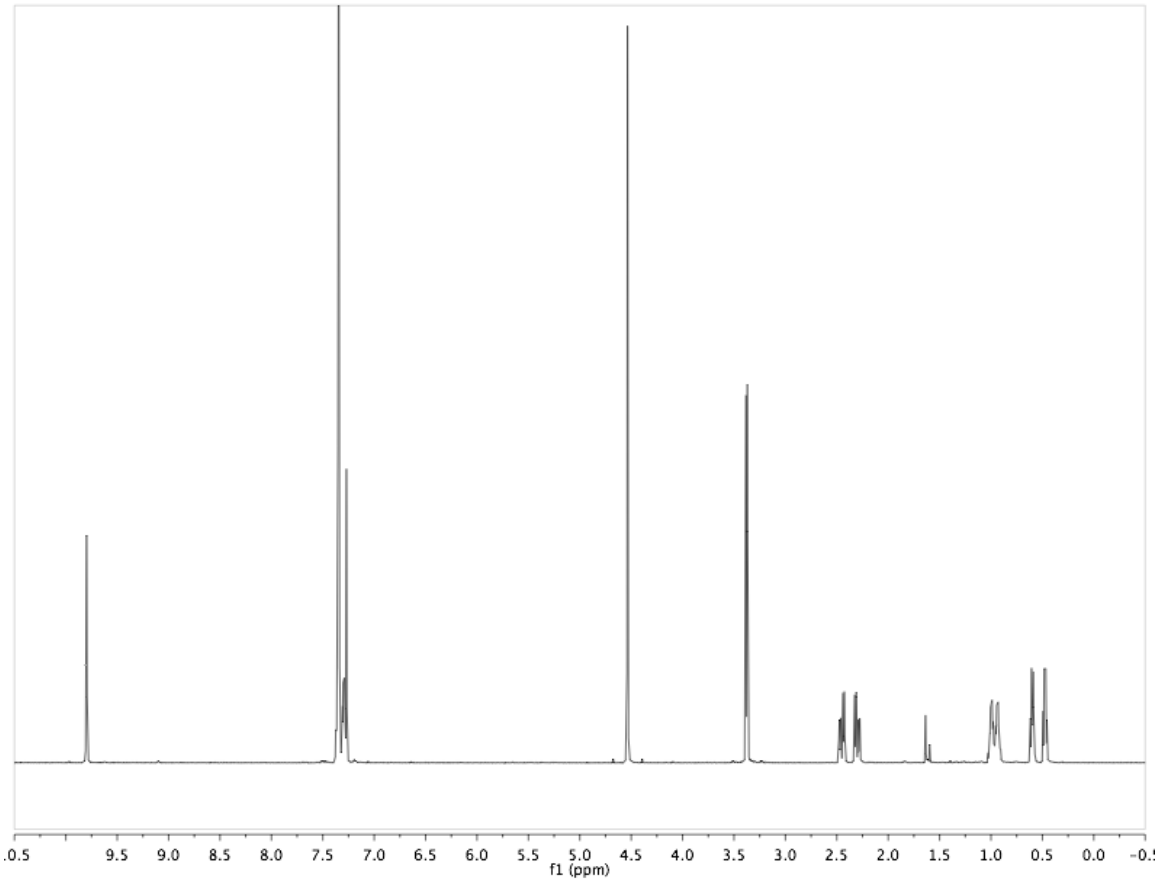

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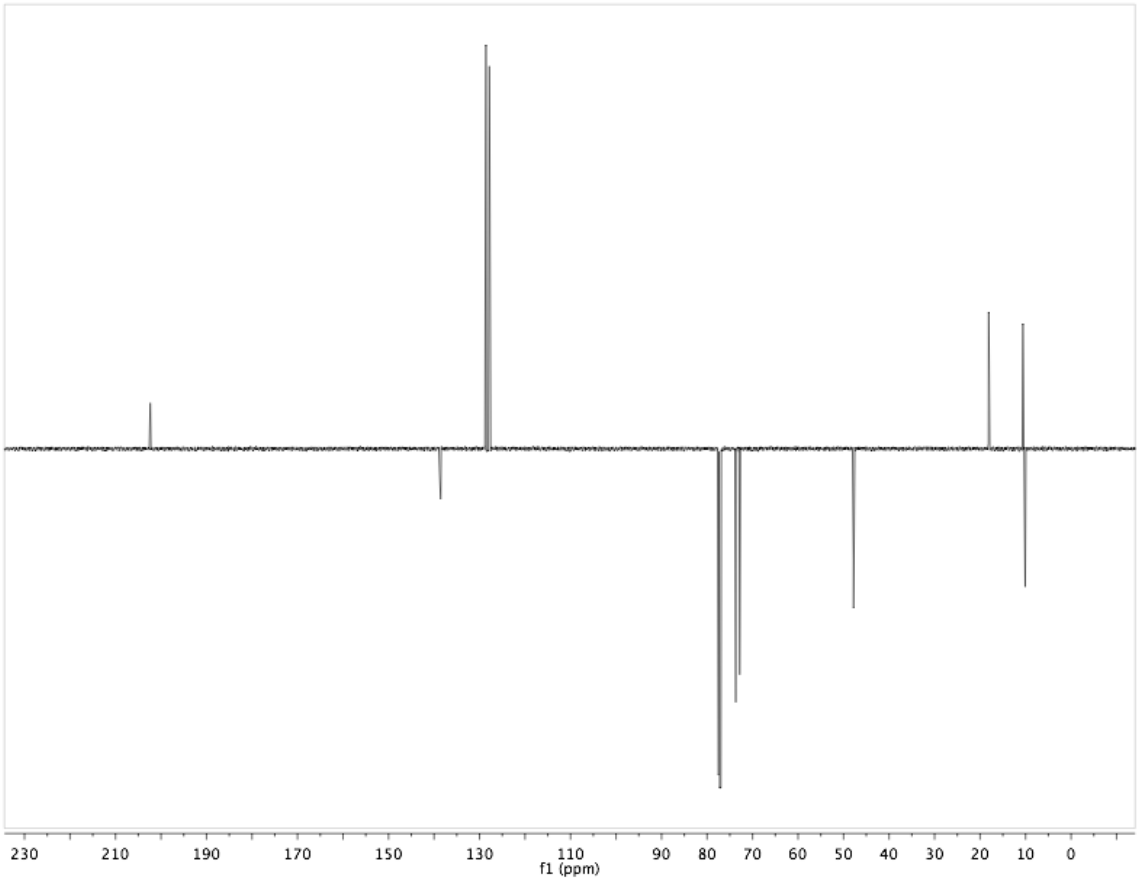
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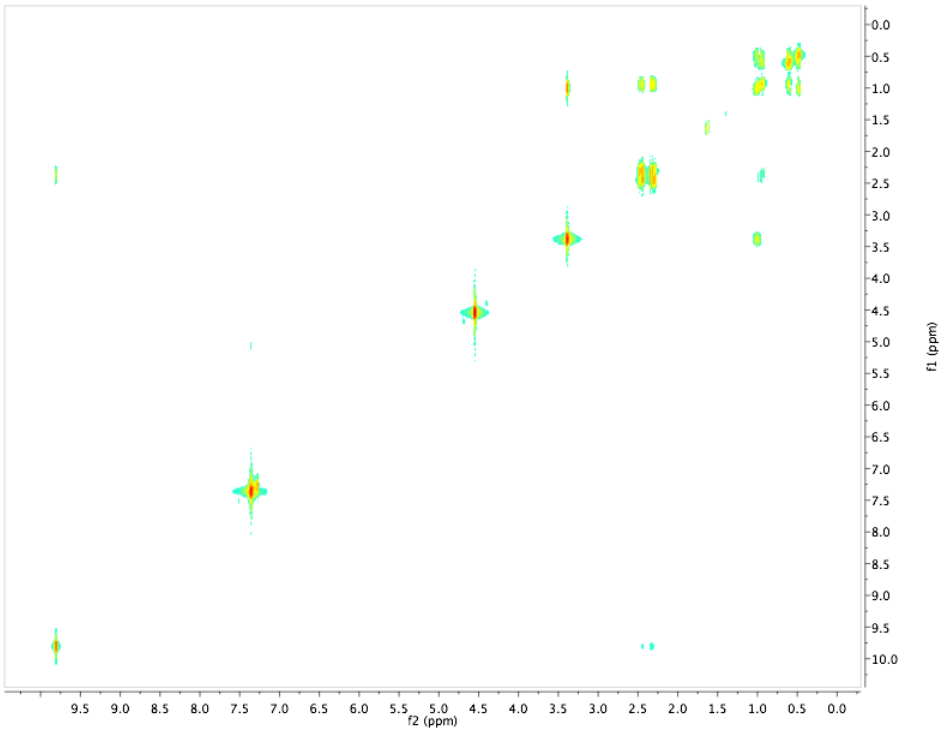
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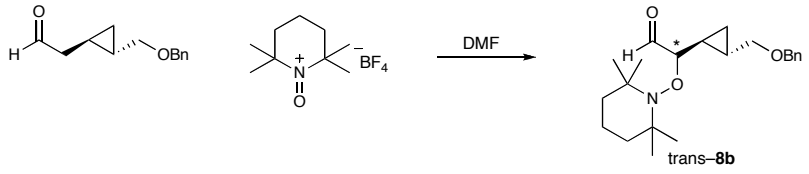



Mixture of isomers at * position

**(±)-*trans*-2-(2-(Benzyloxymethyl)cyclopropyl)-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)acetaldehyde (*trans*–8b):** (±)-*trans*-2-(2-(Benzyloxymethyl)cyclopropyl)acetaldehyde (206 mg, 1.01 mmol) was dissolved in DMF (1.0 mL) at room temperature. Oxoammonium tetrafluoroborate[6] (250 mg, 1.03 mmol) was added in one portion, and the solution was left to stir overnight (12 h). The reaction was diluted with EtOAc (15 mL), and was washed with saturated aqueous $NaHCO_3$ (10 mL). The organic layer was dried over anhydrous magnesium sulfate, then was concentrated *in vacuo*, and the resulting residue was purified using flash column chromatography (silica gel, 10 : 1 hexanes : ethyl acetate) to deliver the title compound as a clear oil (102 mg, 0.26 mmol, 26%). The product was isolated as an inseparable 1.6:1 mixture of epimers at the α–position, and contained >95% *trans*–fused cyclopropane. 2D-NMR allowed for the assignment of all well resolved $^1$H NMR resonances to the respective isomers, as well as a large number of $^{13}$C resonances.

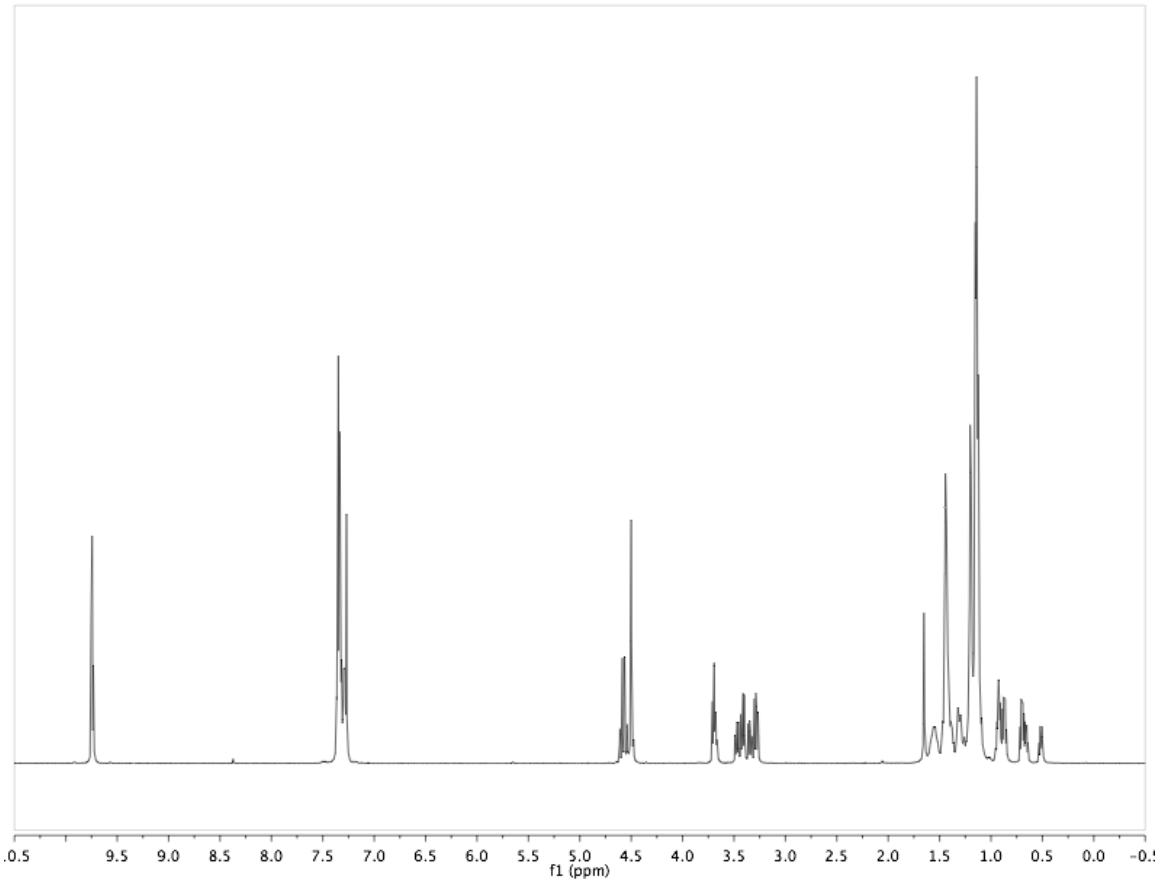
**Major isomer:** $^1$H NMR (500 MHz, $CDCl_3$) δ9.75 (d, 1H, *J* = 5.0 Hz, C**H**O), 7.37–7.30 (m, 4H, Ar**H**), 7.30–7.27 (m, 1H, Ar**H**), 4.50 (s, 2H, OC**H**$_2$Ph), 3.69 (m, 1H, OHC–C**H**), 3.42 (dd, 1H, *J* = 10.5 Hz, 6.5 Hz, *c*Pr–C**H**$_2$O), 3.28 (dd, 1H, *J* = 10.5 Hz, 7.0 Hz, *c*Pr–C**H**$_2$O), 1.60–1.08 (m, 19H), 0.98–0.90 (m, 1H, *c*PrC**H**), 0.87 (dt, 1H, *J* = 8.0 Hz, 5.5 Hz, *c*PrC**H**$_2$), 0.70 (dt, 1H, *J* = 8.5 Hz, 5.0 Hz, *c*PrC**H**$_2$).

**Minor isomer:** $^1$H NMR (500 MHz, $CDCl_3$) δ9.74 (δ, 1H, *J* = 5.0 Hz, C**H**O), 7.37–7.30 (m, 4H, Ar**H**) 7.30–7.27 (m, 1H, Ar**H**), 4.60 (d, 1H, *J* = 12.0 Hz, OC**H**$_2$Ph), 4.55 (d, 1H = 12.0 Hz, OC**H**$_2$Ph), 3.69 (m, 1H, OHC–C**H**), 3.47 (dd, 1H, *J* = 10.5 Hz, 6.5 Hz, *c*Pr–C**H**$_2$O), 3.34 (dd, 1H, *J* = 10.5 Hz, 7.0 Hz, *c*Pr–C**H**$_2$O), 1.60–1.08 (m, 19H), 0.98–0.90 (m, 1H, *c*PrC**H**), 0.66 (dt, 1H, *J* = 8.5 Hz, 5.0 Hz, *c*PrC**H**$_2$), 0.51 (dt, 1H, *J* = 8.5 Hz, 5.5 Hz, *c*PrC**H**$_2$).

$^{13}$C (125 MHz, $CDCl_3$) δ202.1 (maj), 202.0 (min), 138.5 (min), 138.5 (maj), 128.5 (x2, maj and min), 127.8 (x2, maj and min), 127.7 (x2, maj and min), 90.6 (min), 90.6 (maj),

73.1 (min), 73.1 (maj), 72.6 (maj), 72.5 (min), 61.1 (min), 61.0 (maj), 60.0 (maj), 59.9 (min), 40.2 (x2, maj and min), 34.5 (x2, maj and min), 34.0 (maj), 33.9 (min), 20.5, 17.8, 17.2, 16.8, 16.7, 14.6, 10.3, 6.6. IR (film) 2973, 2933, 2870, 1729, 1496, 1454, 1375, 1361, 1259, 1208, 1183, 1095, 1045, 1029, 989, 957, 922, 877 $cm^{-1}$. HRMS exact mass calculated for $[M + H]^+$ ($C_{22}H_{34}NO_3$) requires *m/z* 359.2460 found 359.2465.

**$^1$H NMR:**



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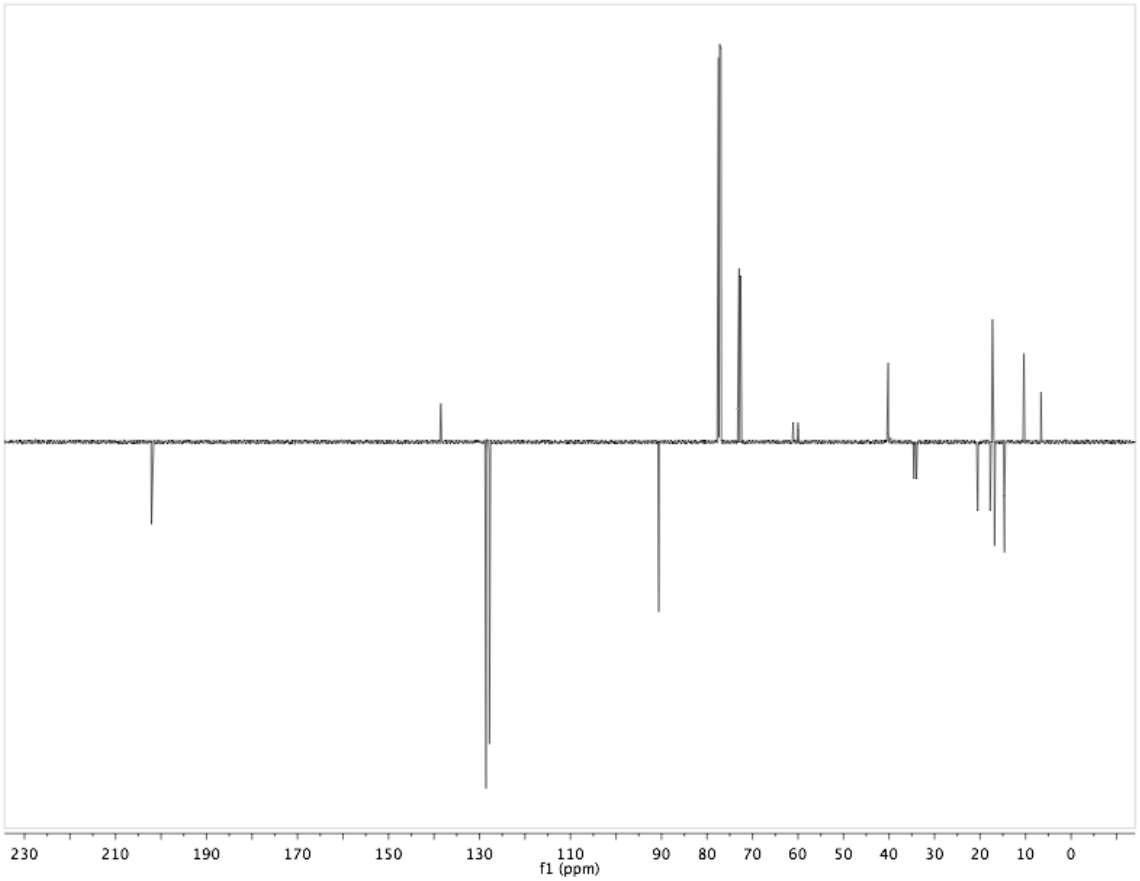
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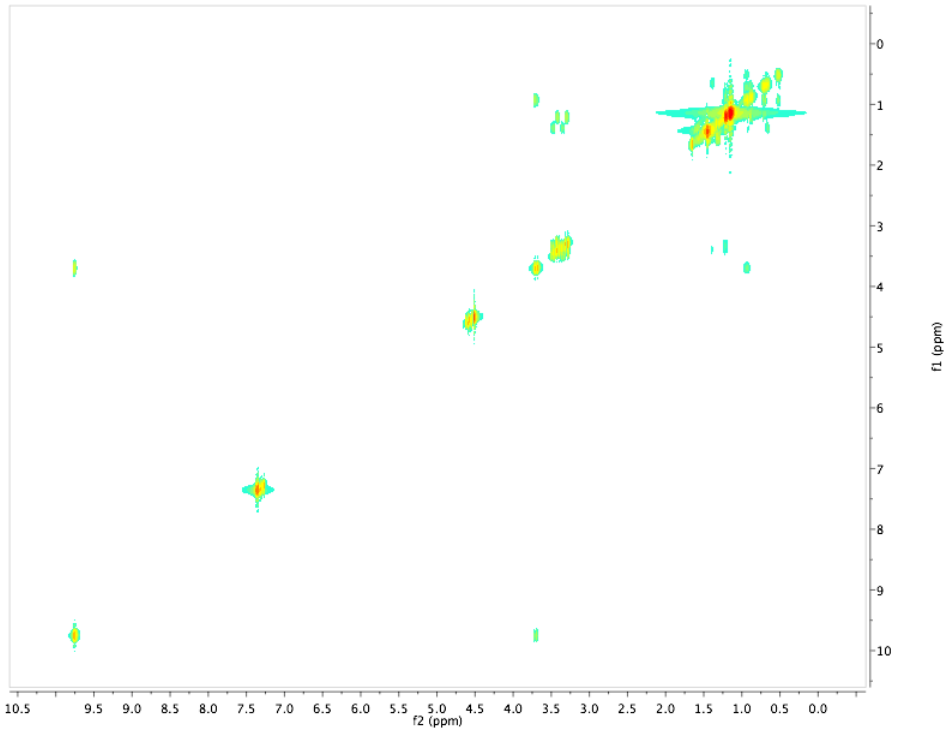
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## III. Radical Clock Investigations

### $^1$H NMR Spectra in $C_6D_6$

Although $CDCl_3$ was preferred for characterization, as the use of $C_6D_6$ obscured a number of signals in the $^{13}$C NMR, $C_6D_6$ allowed for resolution of the *cis* and *trans* isomers of both starting material and products by $^1$H NMR, allowing for easy analysis of crude reaction mixtures (See Figure S1).

***cis*-6**

$^1$H NMR (500 MHz, $C_6D_6$) δ9.49 (t, 1H, *J* = 2.0 Hz, C**H**O), 7.28 (d, 2H, *J* = 7.5 Hz, Ar**H**), 7.18 (t, 2H, *J* = 7.5 Hz, Ar**H**), 7.10 (t, 1H, *J* = 7.5 Hz, Ar**H**), 4.27 (d, 1H, *J* = 12.0 Hz, OC**H$_2$**Ph), 4.21 (d, 1H, *J* = 12.0 Hz, OC**H$_2$**Ph), 3.34 (dd, 1H, *J* = 10.0 Hz, 5.5 Hz, OC**H$_2$***c*Pr), 2.85 (dd, 1H, *J* = 10.0 Hz, 9.0 Hz, OC**H$_2$***c*Pr), 2.00 (ddd, 1H, *J* = 17.5 Hz, 7.5 Hz, 2.0 Hz, CHOC**H$_2$**), 1.84 (ddd, 1H, *J* = 17.5 Hz, 7.5 Hz, 2.0 Hz, CHOC**H$_2$**), δ1.03-0.95 (m, 1H, *c*PrC**H**), 0.83-0.76 (m, 1H *c*PrC**H**), 0.45 (td, 1H, *J* = 8.5 Hz, 4.5 Hz, *c*PrC**H$_2$**), –0.28 (q, 1H, *J* = 5.0 Hz, *c*PrC**H$_2$**).

***trans*-6**

δ9.35 (t, 1H, *J* = 2.0 Hz, C**H**O), 7.31 (d, 2H, *J* = 7.0 Hz, Ar**H**), 7.19 (t, 2H, *J* = 7.5 Hz, Ar**H**), 7.10 (t, 2H, *J* = 7.0 Hz, Ar**H**), 4.32 (s, 2H, OC**H$_2$**Ph), 3.14 (dd, 1H, *J* = 10.0 Hz, 6.5Hz, OC**H$_2$***c*Pr), 3.07 (dd, 1H, *J* = 10.5 Hz, 6.5 Hz, OC**H$_2$***c*Pr), 1.71 (ddd, 1H, *J* = 17.0 Hz, 7.0 Hz, 2.0 Hz, CHOC**H$_2$**), 1.64 (ddd, 1H, *J* = 17.0 Hz, 7.0 Hz, 2.0 Hz, CHOC**H$_2$**), 0.65-0.53 (m, 2H, *c*PrC**H**), 0.27 (dt, 1H, *J* = 8.5 Hz, 5.0 Hz, *c*PrC**H$_2$**), 0.02 (dt, 1H, *J* = 8.5 Hz, 5.0 Hz, *c*PrC**H$_2$**).

***cis*-8a Minor Isomer (resolved resonances)**

δ9.89 (d, 1H, *J* = 5.0 Hz, C**H**O), 7.35 (d, 2H, *J* = 7.0 Hz, Ar**H**), 7.18 (t, 2H, *J* = 7.5 Hz, Ar**H**), 7.09 (t, 1H, *J* = 7.5 Hz, Ar**H**), 4.38 (d, 1H, *J* = 12.0 Hz, OC**H$_2$**Ph), 4.34 (d, 1H, *J* = 12.0 Hz, OC**H$_2$**Ph), 4.02 (dd, 1H, *J* = 8.5 Hz, 5.0 Hz, CHOC**H**), 3.55 (dd, 1H, *J* = 10.5 Hz, 6.5 Hz, OC**H$_2$***c*Pr), 3.39 (dd, 1H, *J* = 10.5 Hz, 6.5 Hz, OC**H$_2$***c*Pr).

***cis*-8a Major Isomer (resolved resonances)**

δ9.81 (d, 1H, *J* = 4.5 Hz, C**H**O), 7.35 (d, 2H, *J* = 7.0 Hz, Ar**H**), 7.18 (t, 2H, *J* = 7.5 Hz, Ar**H**), 7.09 (t, 1H, *J* = 7.5 Hz, Ar**H**), 4.06 (dd, 1H, *J* = 9.5 Hz, 4.5 Hz, CHOC**H**), 3.44 (dd, 1H, *J* = 10.0 Hz, 6.5 Hz, OC**H$_2$***c*Pr), 3.39 (dd, 1H, *J* = 10.0 Hz, 6.0 Hz, OC**H$_2$***c*Pr).

***trans*-8b Isomer mix**

δ9.78 (d, 1H, *J* = 4.5 Hz, C**H**O), 9.76 (d, 1H, *J* = 5.0 Hz), 7.32 (d, 2H, *J* = 7.5 Hz, Ar**H**), 7.30 (d, 2H, *J* = 7.5 Hz, Ar**H**), 7.22-7.15 (m, 4H, Ar**H**), 7.12-7.08 (m, 2H, Ar**H**), 4.37 (d, 1H, *J* = 12.0 Hz, OC**H**$_2$Ph), 4.33 (d, 1H, *J* = 12.0 Hz, OC**H**$_2$Ph), δ3.78-3.74 (m, 1H, CHOC**H**), 3.21 (dd, 1H, *J* = 10.5 Hz, 6.0 Hz, OC**H**$_2$*c*Pr), 3.14 (dd, 1H, *J* = 10.0 Hz, 6.5 Hz, OC**H**$_2$*c*Pr), 3.09-3.04 (m, 2H, OC**H**$_2$*c*Pr)

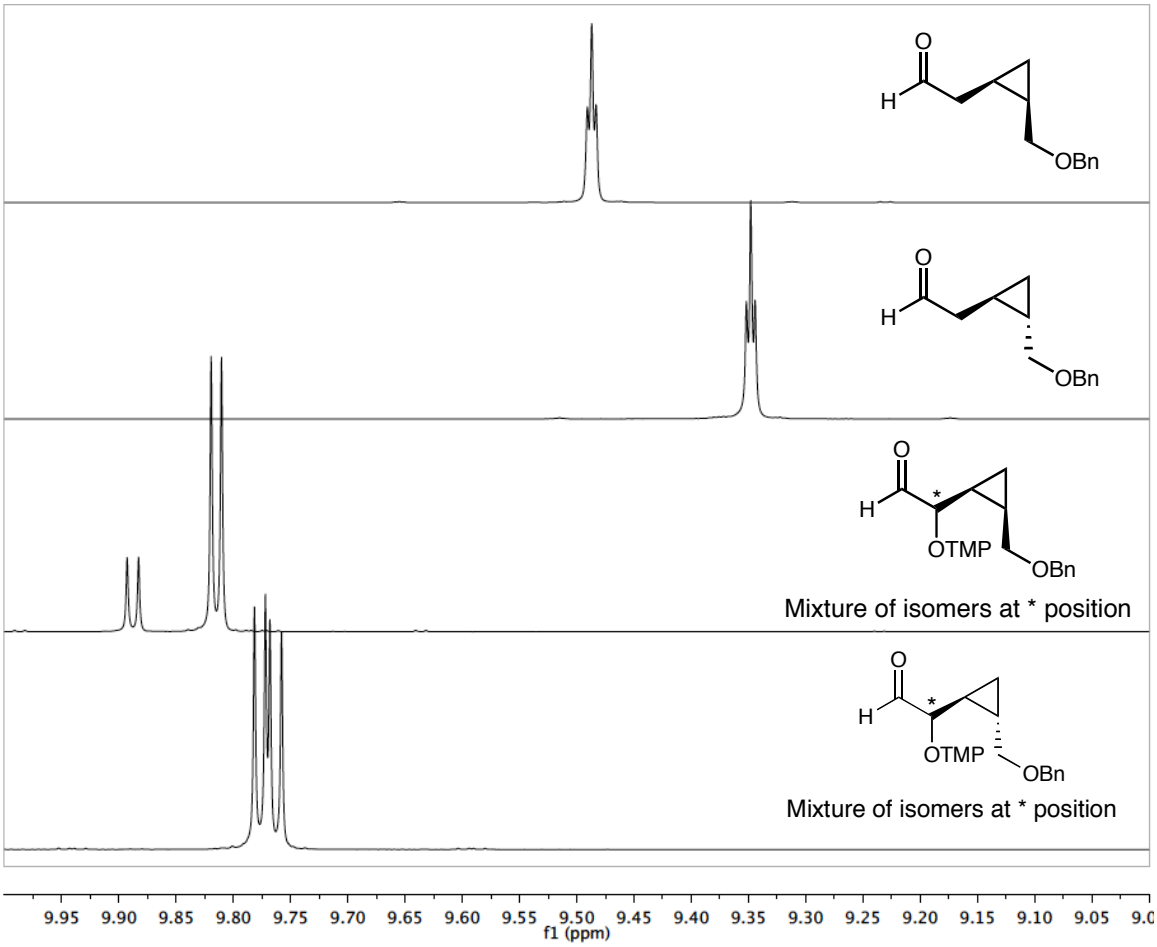
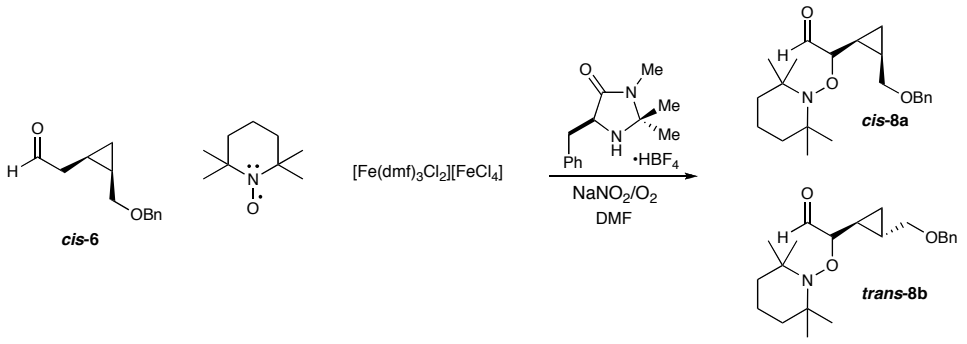
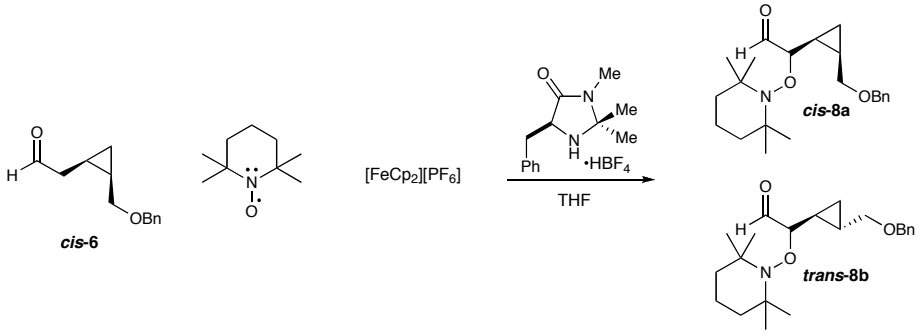



**Figure S1.** Aldehydic $^1$H NMR signals in $C_6D_6$ for all isomers of **6** and **8**.



Into each of six 8 mL vials having Teflon septa (labeled A-F), which were flame dried and allowed to cool while being purged with a pure $O_2$ atmosphere, was added $[Fe(dmf)_3Cl_2][FeCl_4]$ (3.8 mg, .007 mmol) and $NaNO_2$ (2.9 mg, 0.042 mmol). To vials 'E 1.0 M' and 'F 0.75 M' was added imidazolidinone catalyst **1**•$HBF_4$ (10.7 mg, 0.035 mmol). To vial 'A 4.0 M' was added TEMPO (43.8 mg, 0.28 mmol). To vial 'B 3.0 M' was added TEMPO (21.9 mg, 0.14 mmol). To vial 'D 1.5 M' was added DMF (47 μL). To vial 'E 1.0 M' was added DMF (140 μL). To vial 'F 0.75 M' was added DMF (233 μL). To an oven dried 16mL scintillation vial was added aldehyde ***cis*-6** (200 mg, 0.98 mmol), DMF (980 μL), TEMPO (360 mg, 1.18 mmol), and imidazolidinone catalyst **1**•$HBF_4$ (74.7 mg, 0.245 mmol). This stock solution was delivered to each of the six vials (140 μL), under a balloon-pressure atmosphere of oxygen. The reactions were held in a Chemglass PIE-BLOCK vial holder, which was maintained at 27 ºC (block temperature). The reactions were monitored by TLC analysis; when product formation appeared complete, each reaction mixture was poured into 3 mL of a mixture of diethyl ether and 1 M sodium ascorbate (2:1). The mixture was vigorously shaken for 30 seconds, and left to settle for 5 minutes. 1 mL of the ether layer was removed and concentrated *in vacuo*. The crude product was dissolved in benzene-$d_6$ and analyzed via $^1H$ NMR ($t_1$ delay = 10.0 s) (see Figure S2).




Into each of six flame-dried 8 mL vials having Teflon septa (labeled A-F) was added imidazolidinone catalyst **1**•$HBF_4$ (10.7 mg, 0.035 mmol). To vial 'A 4.0 M' was added TEMPO (43.8 mg, 0.28 mmol). To vial 'B 3.0 M' was added TEMPO (21.9 mg, 0.14 mmol). To vial 'D 1.5 M' was added THF (47 μL). To vial 'E 1.0 M' was added THF (140 μL). To vial 'F 0.75 M' was added THF (233 μL). To an oven dried 16mL scintillation vial was added aldehyde ***cis*-6a** (200 mg, 0.98 mmol), THF (980 μL) and

TEMPO (360 mg, 1.18 mmol). This stock solution was delivered to each of the six vials (140 μL), followed by ferrocenium hexafluorophosphate (47.0 mg, 0.142 mmol). The reactions were held in a Chemglass PIE-BLOCK vial holder, which was maintained at 27 ºC (block temperature). The reactions were monitored by TLC analysis; when product formation appeared complete, each reaction mixture was poured into 3 mL of a mixture of diethyl ether and 1 M sodium ascorbate (2:1). The mixture was vigorously shaken for 30 seconds, and left to settle for 5 minutes. 1mL of the ether layer was removed and concentrated *in vacuo*. The crude product was dissolved in benzene-$d_6$ and analyzed via $^1$H NMR ($t_1$ delay = 10.0 s) (see Figure S2).

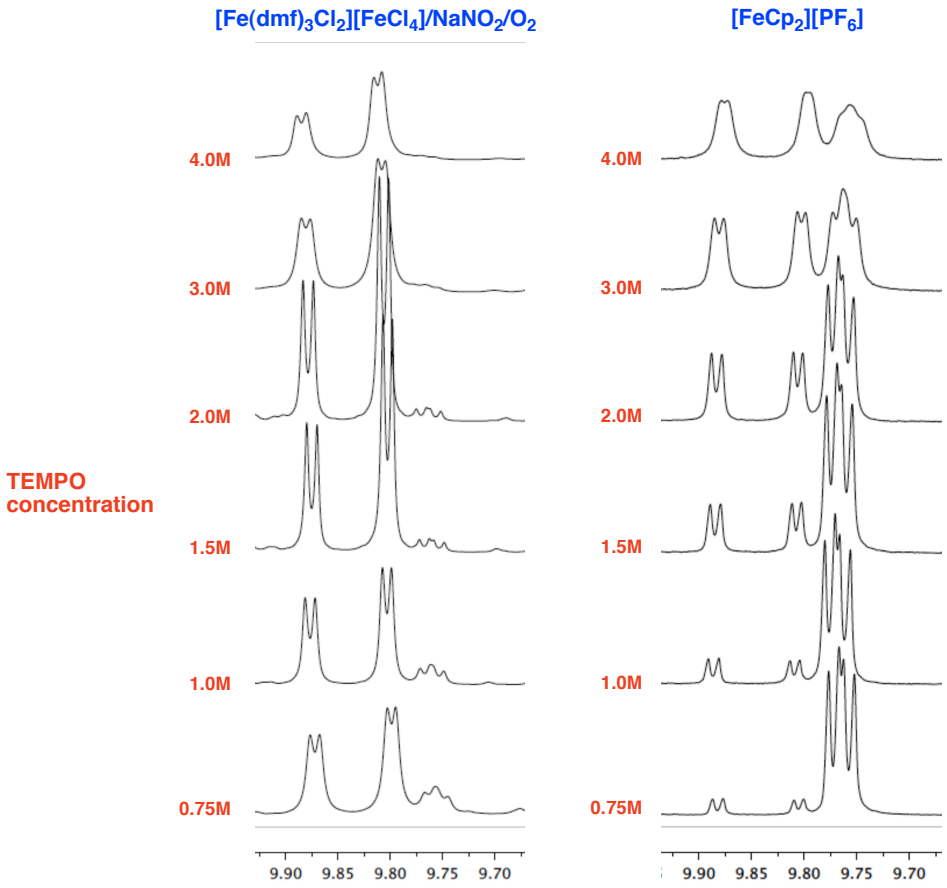
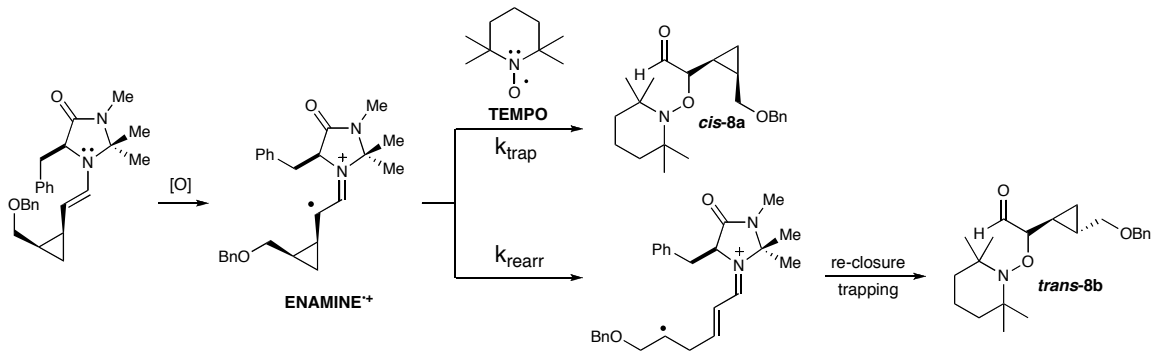



**Figure S2.** Effect of TEMPO concentration on cyclopropane isomer distribution.

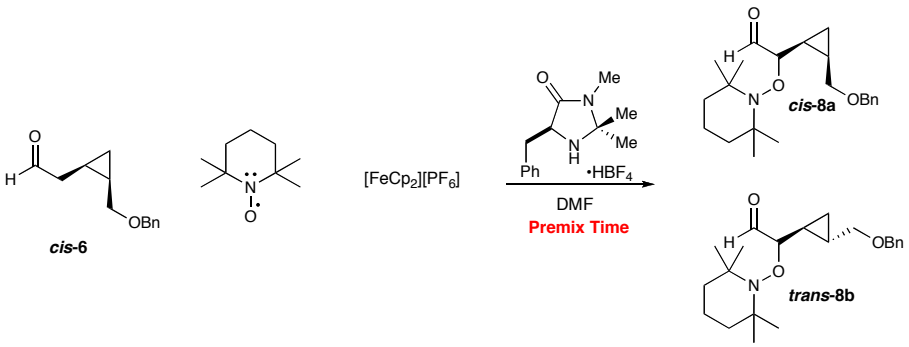
Importantly, the rate of radical cation formation (which is likely different for each oxidant) will not affect the distribution of products in this competition experiment, as it will impact the rate of each pathway equally. This inherent advantage to the use of a radical-clock competition experiment has been outlined in detail by Newcomb,[8] and the

pertinent equations are shown below (Figure S3). At the selectivity-determining step, the crucial competition is between a bimolecular trapping with TEMPO, or a unimolecular rearrangement that leads to the diastereomeric product. The selectivity between these species will depend on the inherent rate constant for each process and the concentration of TEMPO, but will not depend on the manner in which the radical cation is generated.




$$\frac{[\textit{cis}\text{-8a}]}{[\textit{trans}\text{-8b}]} = \frac{k_{trap}[\text{ENAMINE}^{\bullet+}][\text{TEMPO}]}{k_{rearr}[\text{ENAMINE}^{\bullet+}]} = \frac{k_{trap}[\text{TEMPO}]}{k_{rearr}}$$

**Figure S3.** Kinetic expression for product distribution using cyclopropane radical clock




To each of 7 flame dried vials (labeled A-G) was added imidazolidinone catalyst **1**•$HBF_4$ (21.7 mg, 0.071 mmol). To vials B-G was added $[FeCp_2][PF_6]$ (43.6 mg, 0.132 mmol). In an oven-dried scintillation vial, a stock solution was prepared from aldehyde ***cis*-6** (175 mg, 0.857 mmol), DMF (858 μL), and TEMPO (268 mg, 1.72 mmol). DMF (140 μL) was added to every vial, and a stopwatch was started. At the appropriate time, the stock solution (140 μL) was added: vial B (5 minutes), C (10 minutes), D (15 minutes), E (30

minutes), F (60 minutes), G (120 minutes). The stock solution (140 μL) was added to reaction vial 'A', which ***did not*** have ferrocenium hexafluorophosphate charged in it initially. The appropriate amount of $[FeCp_2][PF_6]$ (43.6 mg, 0.132 mmol) was added last, as this experiment was representative of zero minutes premixing time. The reactions were monitored by TLC analysis; when product formation had ceased, each reaction mixture was poured into 3 mL of a mixture of diethyl ether and 1 M sodium ascorbate (2:1). The mixture was vigorously shaken for 30 seconds, and left to settle for 5 minutes. 1 mL of the ether layer was removed and concentrated *in vacuo*. The crude product was dissolved in benzene-$d_6$ and analyzed via $^1$H NMR ($t_1$ delay = 10.0 s) (see Figure S4).

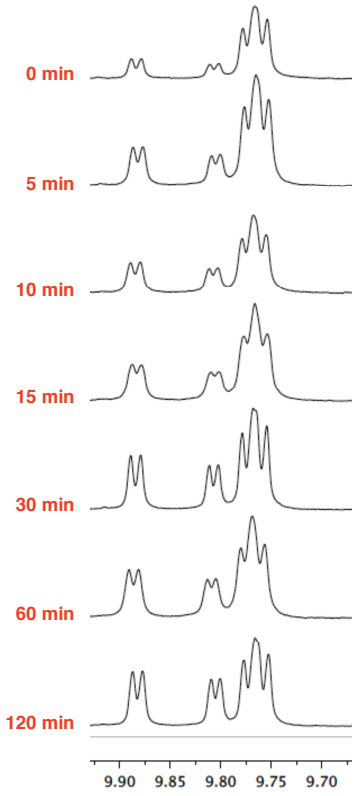
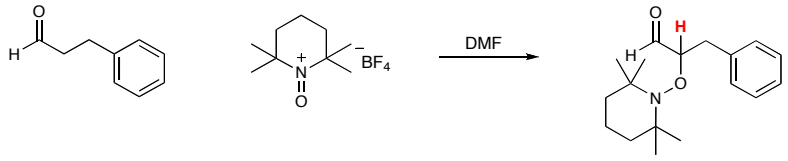



**Figure S4.** Effect of premixing time on cyclopropane isomer distribution

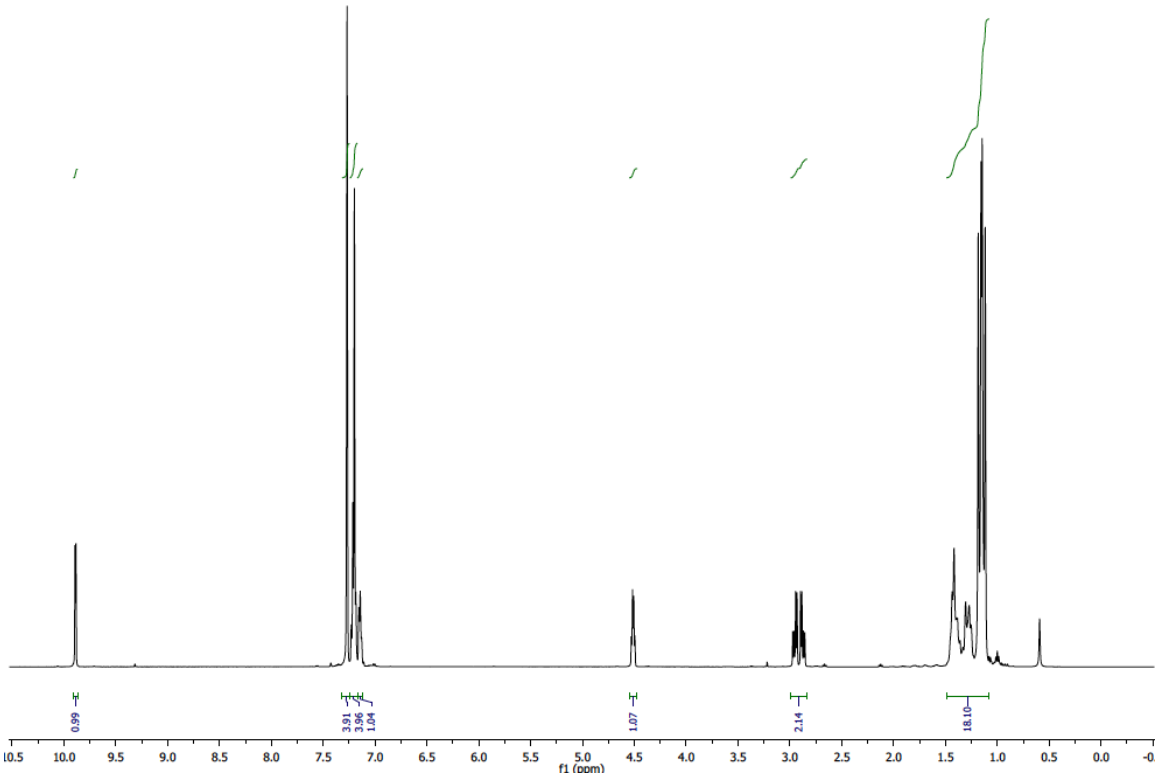
## IV. Determination of Rate Equation



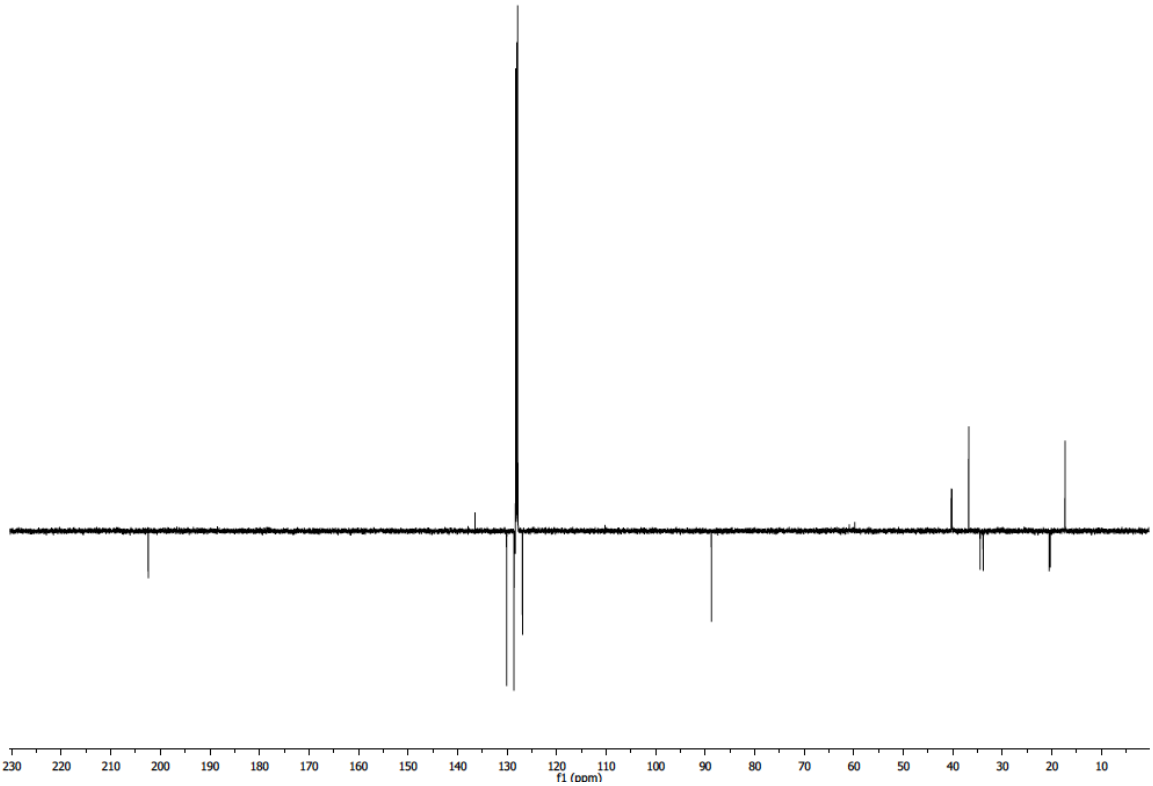
**Synthesis of authentic product (3-phenyl-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)propanal:** Hydrocinnamaldehyde (134 mg, 1.00 mmol) was dissolved in DMF (1.0 mL) at room temperature. Oxoammonium tetrafluoroborate[6] (245 mg, 1.01 mmol) was added in one portion, and the solution was left to stir overnight (12 h). The reaction was diluted with EtOAc (15 mL), and was washed with saturated aqueous $NaHCO_3$ (10 mL). The organic layer dried over anhydrous magnesium sulfate, then was concentrated *in vacuo*, and the resulting residue was purified using flash column chromatography (silica gel, 10 : 1 hexanes : ethyl acetate) to deliver the title compound as a clear oil (81 mg, 0.28 mmol, 28%).

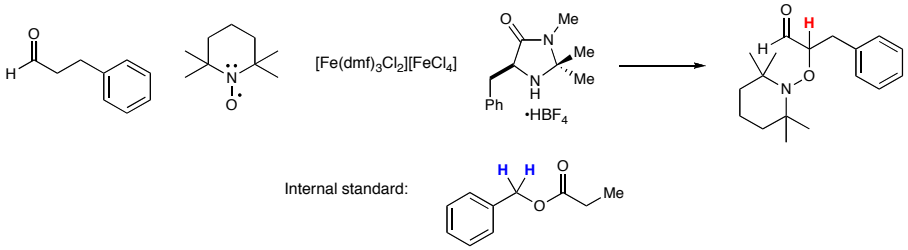
$^1$H NMR (500 MHz, $C_6D_6$) δ: 9.89 (d, 2H, $J$ = 5.0 Hz, C**H**O), 7.17-7.24 (m, 4H, Ar**H**), 7.12-7.17 (m, 1H, Ar**H**), 4.52 (dd, 1H, $J$ = 5.0, 10.0 Hz,CHO–C**H**), 2.92 (m, 2H, C**H**Ph), 1.34 (m, 6H, $C(CH_3)_2C\mathbf{H_2}C\mathbf{H_2}C\mathbf{H_2}$), 1.18 (s, 3H, $NC(C\mathbf{H_3})_2$), 1.16 (s, 3H, $NC(C\mathbf{H_3})_2$), 1.15 (s, 3H, $NC(C\mathbf{H_3})_2$), 1.12 (s, 3H, $NC(C\mathbf{H_3})_2$); $^{13}$C NMR (125 MHz, $C_6D_6$) δ: 202.5, 136.5, 130.1, 128.6, 126.9, 88.7, 40.3, 40.2, 36.8, 34.5, 33.9, 20.5, 20.3, 17.3. IR (thin film) 2973.8, 2931.6, 1731.7, 1603.8, 1496.5, 1455.0, 1375.2, 1361.8, 1259.2, 1241.8, 1208.2, 1182.6, 1132.9, 1074.0, 1044.6, 957.5, 749.1, 699.0 $cm^{-1}$. HRMS (ESI-TOF) calculated for $C_{18}H_{27}O_2N$ $[M+H]^+$ m/z 289.2042, found 289.2042.

**$^1$H NMR:**



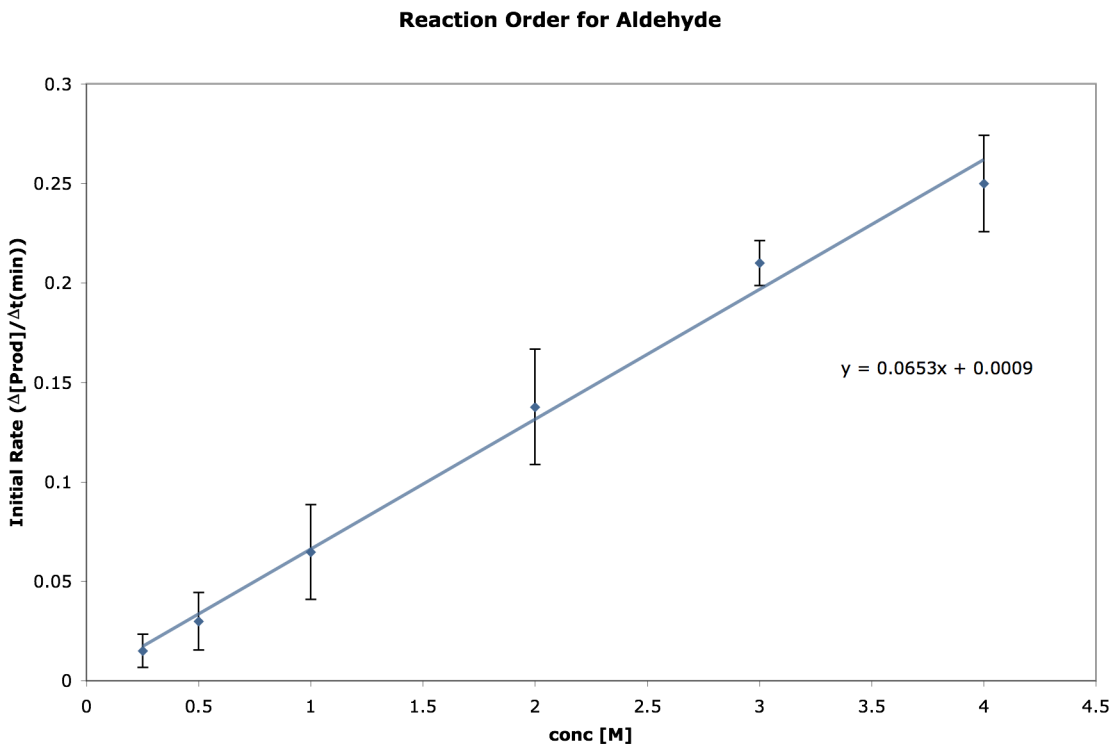
**$^{13}$C NMR:**



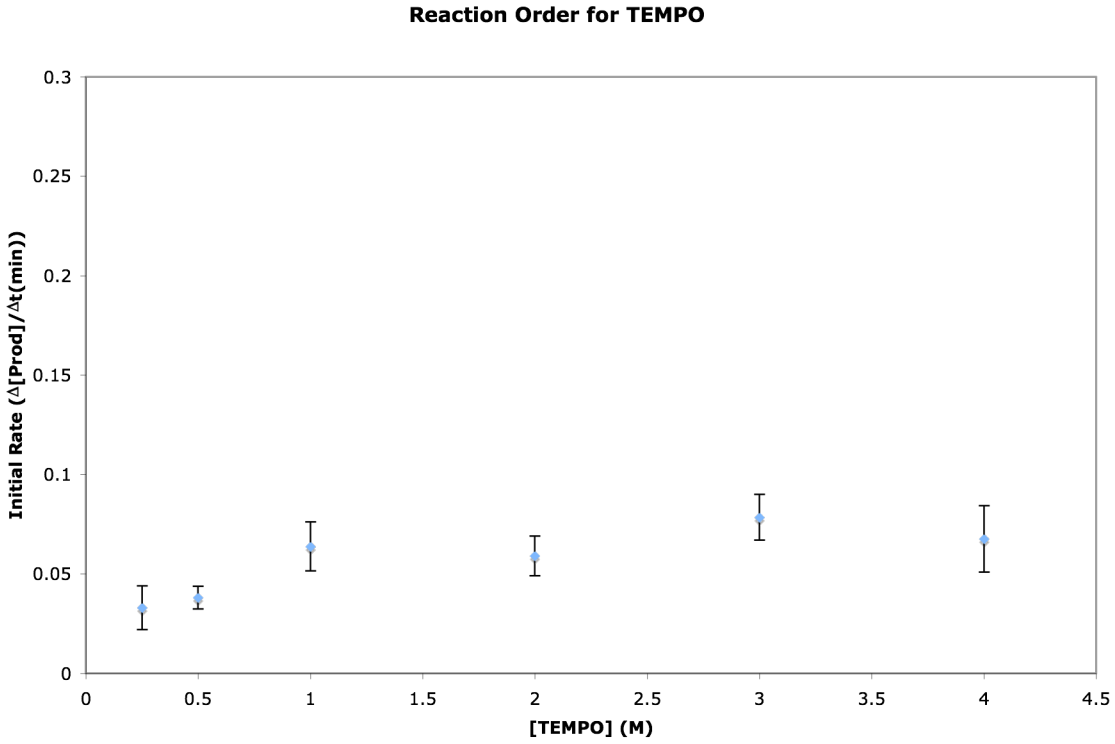

**Determination of reaction order for aldehyde:** Hydrocinnamaldehyde (4.62 mL, 35.1 mmol) was dissolved in 14 mL anhydrous diethyl ether. To 18 oven-dried 8 mL vials was added one of 100 μL (x3), 200 μL (x3), 400 μL (x3), 800 μL (x3), 1200 μL (x3) or 1600 μL (x3) of this stock solution. Each vial was concentrated *in vacuo* and stored at –40 ºC until required. Stock solution '**A**' was made by dissolving imidazolidinone catalyst **1**•$HBF_4$ (460 mg, 1.51 mmol) and benzyl propionate (240 μL, 1.51 mmol) in dry *N,N*–dimethylformamide (2.0 mL). Stock solution '**B**' was made by dissolving TEMPO (1.874

g, 11.99 mmol) in DMF (2.0 mL). Stock solution '**C**' was made by dissolving [Fe(dmf)-$_3$Cl$_2$][FeCl$_4$] (1.631 g, 30.00 mmol, 60.00 mmol total Fe) in DMF (2.0 mL). For each trial, a vial was warmed to room temperature under vacuum, and backfilled with argon once thawed. To the vial was added 333 μL of solution **A**, followed by 333 μL of solution **B**, and the resulting mixture was thoroughly mixed. 333 μL of solution **C** was added, and a stopwatch was simultaneously started. The solution was mixed vigorously for 15 seconds, and was then left to stir with a magnetic stirbar. At 0.5, 1, 1.5, 2, 3, 4, 6, 8, 15, 30, 60 and 120 minutes an aliquot (75 μL) was injected into a quenching solution made from 1M Na-ascorbate (0.75 mL) and diethyl ether (1.5 mL), and was mixed vigorously for one minute, then left to settle for five minutes. Sodium ascorbate was required to sequester iron from the organic phase, as well as to reduce TEMPO to the corresponding hydroxylamine (TEMPOH), so as to minimize interference in $^1$H NMR spectra. 1.0 mL of the organic layer was removed to a fresh vial, and was concentrated *in vacuo*, then analyzed by $^1$H NMR ($t_1$ delay = 10.0 s). The highlighted product resonance (red proton) was compared to the internal benzyl propionate standard (blue protons). The initial rate of product formation showed a first–order dependence on aldehyde concentration.



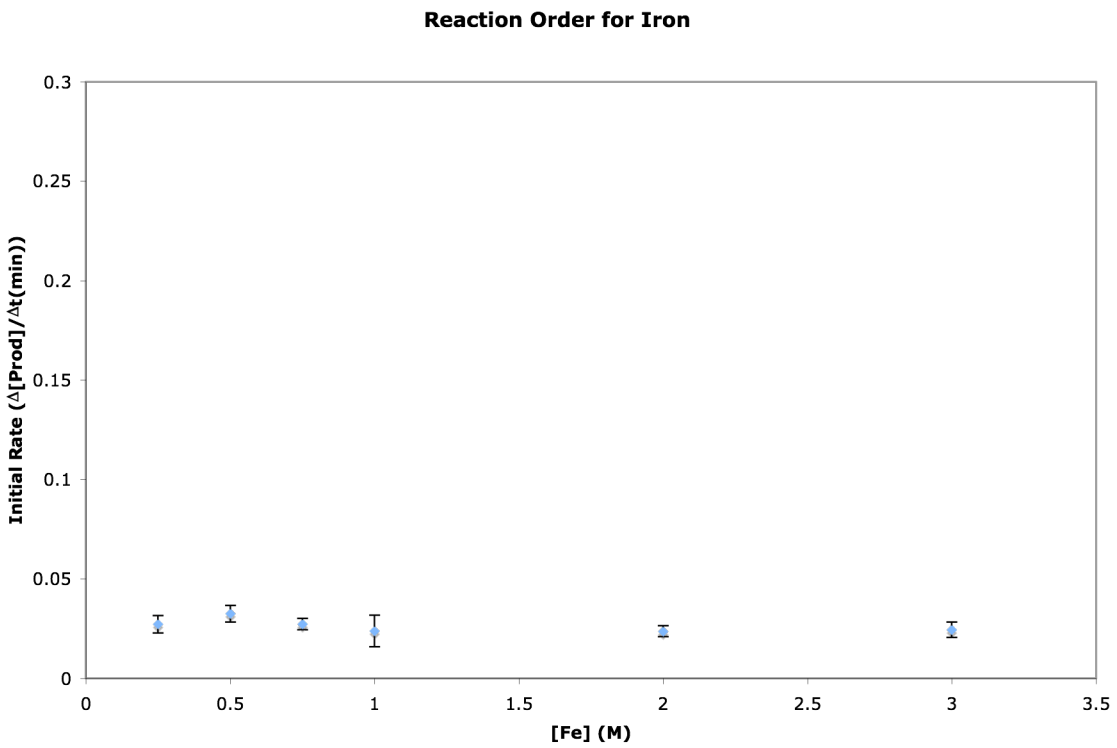

**Determination of reaction order for TEMPO**: Solution '**A**' was made by dissolving hydrocinnamaldehyde (790 μL, 6.00 mmol) and benzyl propionate (240 μL, 1.51 mmol) in dry DMF (2.0 mL). Solution '**B**' was made by dissolving $[Fe(dmf)_3Cl_2][FeCl_4]$ (1.631 g, 30.00 mmol, 60.00 mmol total Fe) in DMF (2.0 mL). TEMPO (3.748 g, 23.99 mmol) was dissolved in DMF (2.0 mL). 333 μL of this solution was used for trials at 4.0 M. 250 μL of this solution was mixed with 83 μL fresh DMF for trials at 3.0 M. 167 μL of this solution was mixed with 167 μL of fresh DMF for trials at 2.0 M. 250 μL of this solution was diluted with 750 μL of fresh DMF to generate a second stock solution. 333 μL of this second stock solution was used for trials requiring 1.0 M concentration. 167 μL of this second stock solution was mixed with 167 μL fresh DMF for trials requiring 0.5 M. 250 μL of this second stock solution was further diluted with 750 μL fresh DMF to make a final TEMPO solution. 333 μL of this final diluted TEMPO solution was used for trials requiring 0.25 M concentration. The proper amount (in all cases, 333 μL) of the desired TEMPO solution was charged into an oven dried vial, followed by imidazolidinone catalyst **1**•$HBF_4$ (76.2 mg, 0.25 mmol). 333 μL of solution **A** was added, and the resulting solution was thoroughly mixed. 333 μL of solution **B** was added, and a stopwatch was simultaneously started. The solution was mixed vigorously for 15

seconds, and was then left to stir with a magnetic stirbar. At 0.5, 1, 1.5, 2, 3, 4, 6, 8, 15, 30, 60 and 120 minutes an aliquot (75 μL) was injected into a quenching solution made from 1M Na-ascorbate (0.75 mL) and diethyl ether (1.5 mL), and was mixed vigorously for one minute, then left to settle for five minutes. Sodium ascorbate was required to sequester iron from the organic phase, as well as to reduce TEMPO to the corresponding hydroxylamine (TEMPOH), so as to minimize interference in $^1$H NMR spectra. 1.0 mL of the organic layer was removed to a fresh vial, and concentrated *in vacuo*, then analyzed by $^1$H NMR ($t_1$ delay = 10.0 s). The highlighted product resonance (red proton) was compared to the internal benzyl propionate standard (blue protons). The dependence of the initial rate of product formation on TEMPO concentration showed no significant dependence around the concentration where the typical reaction is performed.



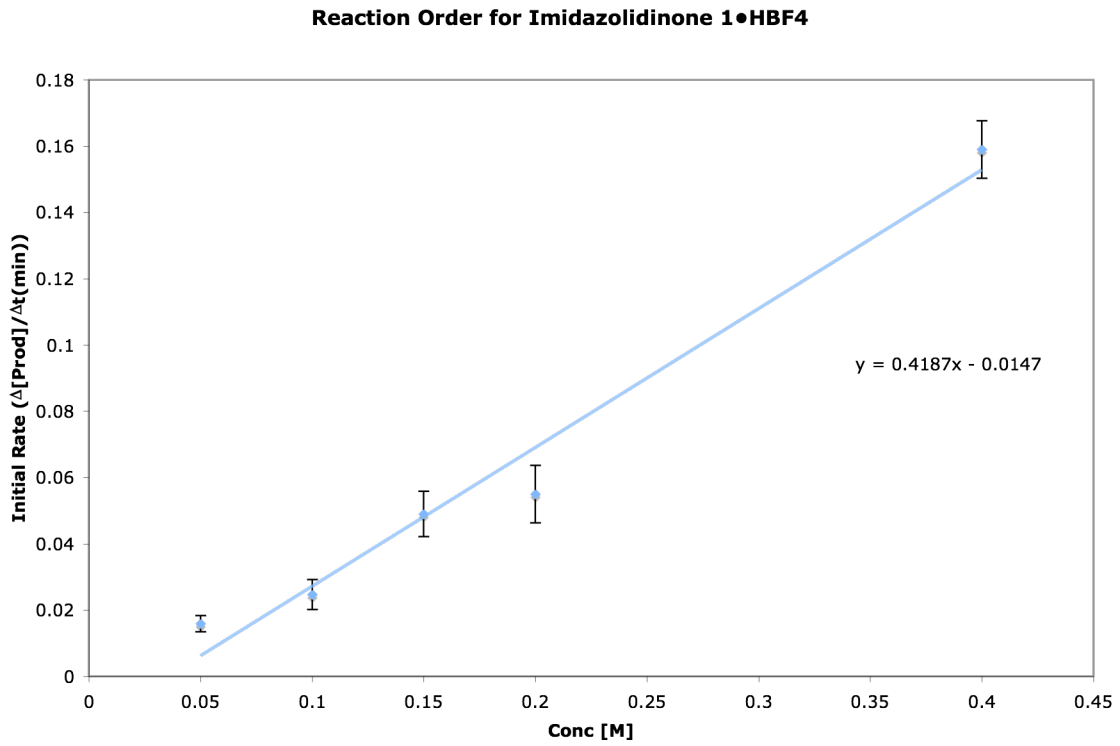

**Determination of reaction order for iron:** $[Fe(dmf)_3Cl_2][FeCl_4]$ was weighed out into an oven dried vial at one of six appropriate masses: 816 mg, 544 mg, 272 mg, 204 mg, 136 mg or 68 mg for reactions requiring 3.0 M, 2.0 M, 1.0 M, 0.75 M, 0.5 M and 0.25 M concentrations of iron, respectively. Stock solution '**A**' was made by dissolving hydrocinnamaldehyde (790 μL, 6.00 mmol) and benzyl propionate (240 μL, 1.51 mmol)

in DMF (2.0 mL). Stock solution '**B**' was made by dissolving imidazolidinone catalyst (460mg, 1.51 mmol) in DMF (2.0 mL). Stock solution '**C**' was made by dissolving TEMPO (1.874 g, 11.99 mmol) in DMF (2.0 mL). For each trial to a vial containing the appropriate amount of $[Fe(dmf)_3Cl_2][FeCl_4]$ was added 333 μL of solution **A**, followed by 333 μL of solution **B**, and the resulting mixture was thoroughly mixed. 333 μL of solution **C** was added, and a stopwatch was simultaneously started. The solution was mixed vigorously for 15 seconds, and was then left to stir with a magnetic stirbar. At 0.5, 1, 1.5, 2, 3, 4, 6, 8, 15, 30, 60 and 120 minutes an aliquot (75 μL) was injected into a quenching solution made from 1M Na-ascorbate (0.75 mL) and diethyl ether (1.5 mL), and was mixed vigorously for one minute, then left to settle for five minutes.. Sodium ascorbate was required to sequester iron from the organic phase, as well as to reduce TEMPO to the corresponding hydroxylamine (TEMPOH), so as to minimize interference in $^1$H NMR spectra. 1.0 mL of the organic layer was removed to a fresh vial, and concentrated *in vacuo*, then analyzed by $^1$H NMR ($t_1$ delay = 10.0 s). The highlighted product resonance (red proton) was compared to the internal benzyl propionate standard (blue protons). The dependence of the initial rate of product formation on iron concentration showed no significant dependence around the concentration where the typical reaction is performed.




**Determination of reaction order for catalyst 1•HBF$_4$:** Imidazolidinone catalyst **1**•HBF$_4$ (1.526 g, 5.00 mmol) was dissolved in 10.00 mL acetonitrile in a volumetric flask. To 15 oven dried vials one of 100 μL (x3), 200 μL (x3), 300 μL (x3), 400 μL (x3) or 800 μL (x3) was added. Each vial was concentrated *in vacuo* and stored at –40 ºC until required. Stock solution '**A**' was made by dissolving TEMPO (1.874 g, 11.99 mmol) in DMF (2.0 mL). Stock solution '**B**' was made by dissolving hydrocinnamaldehyde (790 μL, 6.00 mmol) and benzyl propionate (240 μL, 1.51 mmol) in dry DMF (2.0 mL). Stock solution '**C**' was made by dissolving [Fe(dmf)$_3$Cl$_2$][FeCl$_4$] (1.631 g, 30.00 mmol, 60.00 mmol total Fe) in DMF (2.0 mL). For each trial, a vial was warmed to room temperature under vacuum, and backfilled with argon once thawed. For each trial to a vial containing the appropriate amount of imidazolidinone catalyst was added 333 μL of solution **A**, followed by 333 μL of solution **B**, and the resulting mixture was thoroughly mixed. 333 μL of solution **C** was added, and a stopwatch was simultaneously started. The solution was mixed vigorously for 15 seconds, and was then left to stir with a magnetic stirbar. At 0.5, 1, 1.5, 2, 3, 4, 6, 8, 15, 30, 60 and 120 minutes an aliquot (75 μL) was injected into a quenching solution made from 1M Na-ascorbate (0.75 mL) and diethyl ether (1.5 mL), and was mixed vigorously for one minute, then left to settle for five minutes.. The sodium

ascorbate was required to sequester iron from the organic phase, as well as to reduce TEMPO to the corresponding hydroxylamine (TEMPOH), so as to minimize interference in $^1$H NMR spectra. 1.0 mL of the organic layer was removed to a fresh vial, and concentrated *in vacuo*, then analyzed by $^1$H NMR ($t_1$ delay = 10.0 s). The highlighted product resonance was compared to the internal benzyl propionate standard. The dependence of the initial rate of product formation on catalyst concentration showed a first–order dependence around the concentration where the typical reaction is performed.

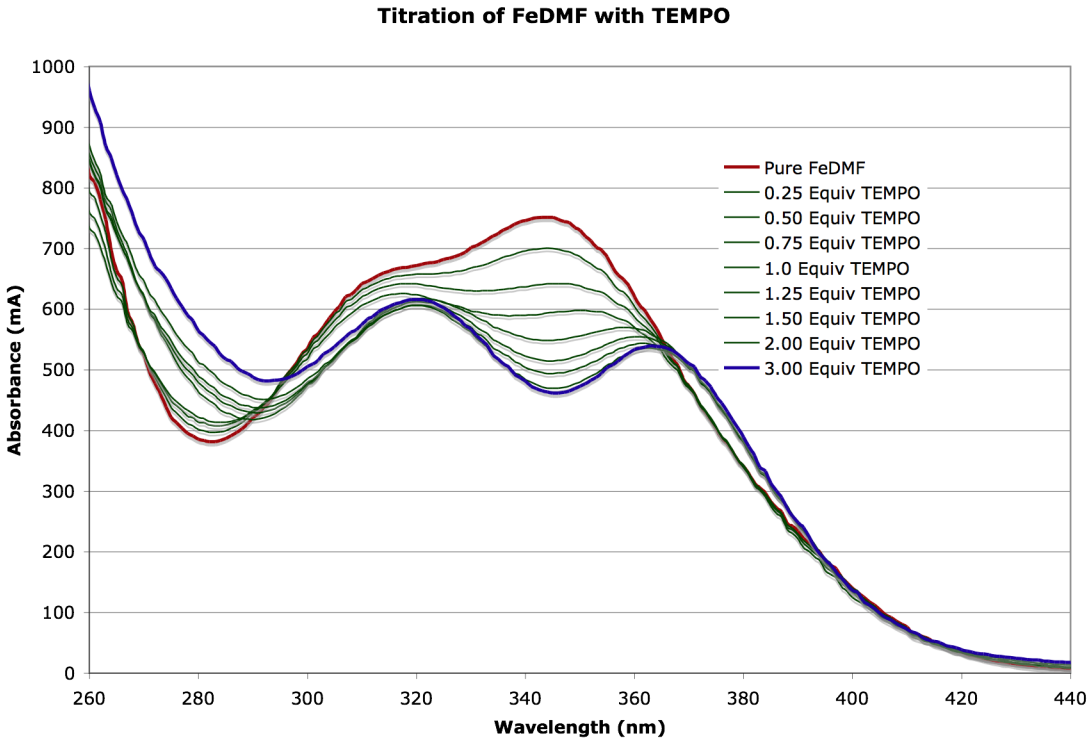



**V. UV/Vis investigations of $[Fe(dmf)_3Cl_2]$•TEMPO complex formation.**

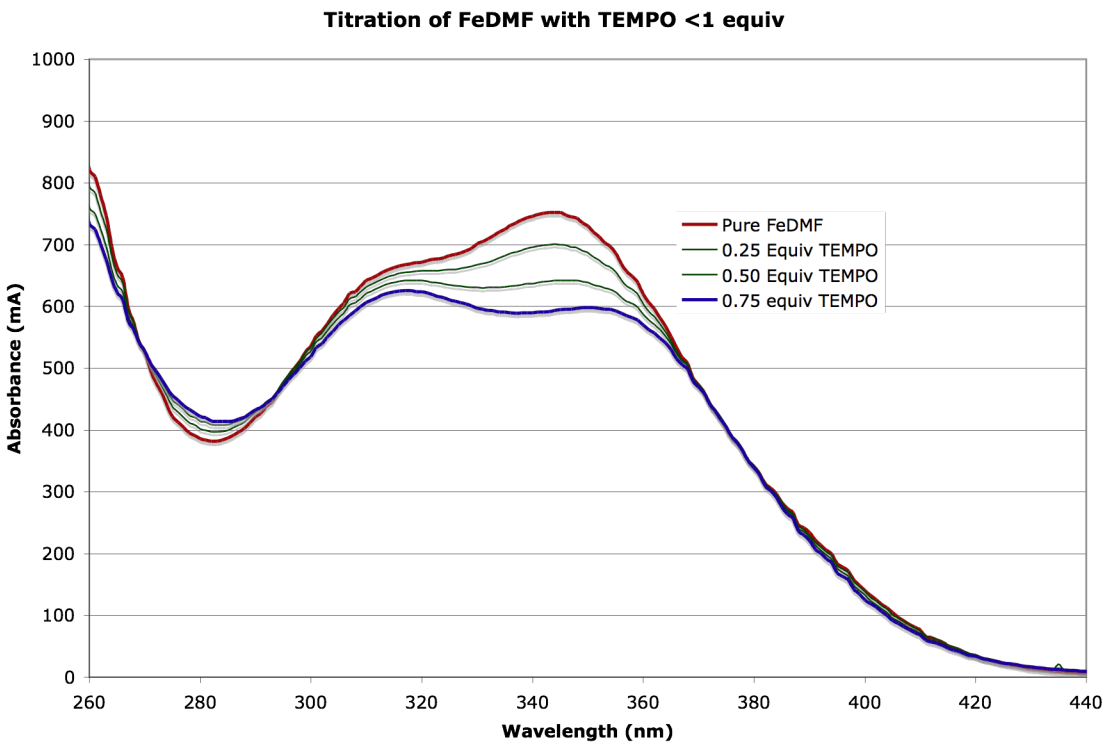
All $CH_2Cl_2$ used during UV/Vis investigations was FisherChemical Optima® grade solvent, which was further dried by the addition of activated (130 ºC, 24 h) 4Å molecular sieves.

The interaction between TEMPO and $[Fe(dmf)_3Cl_2][FeCl_4]$ was measured using the following titration experiment. Into a 100 mL A-grade volumetric flask was added precisely 54.4 mg $[Fe(dmf)_3Cl_2][FeCl_4]$ (0.100 mmol). TEMPO was added (precisely 46.9 mg; 31.3 mg; 23.4 mg; 19.5 mg; 15.6 mg; 11.7 mg; 7.8 mg; 3.9 mg, 3.00 equiv.;

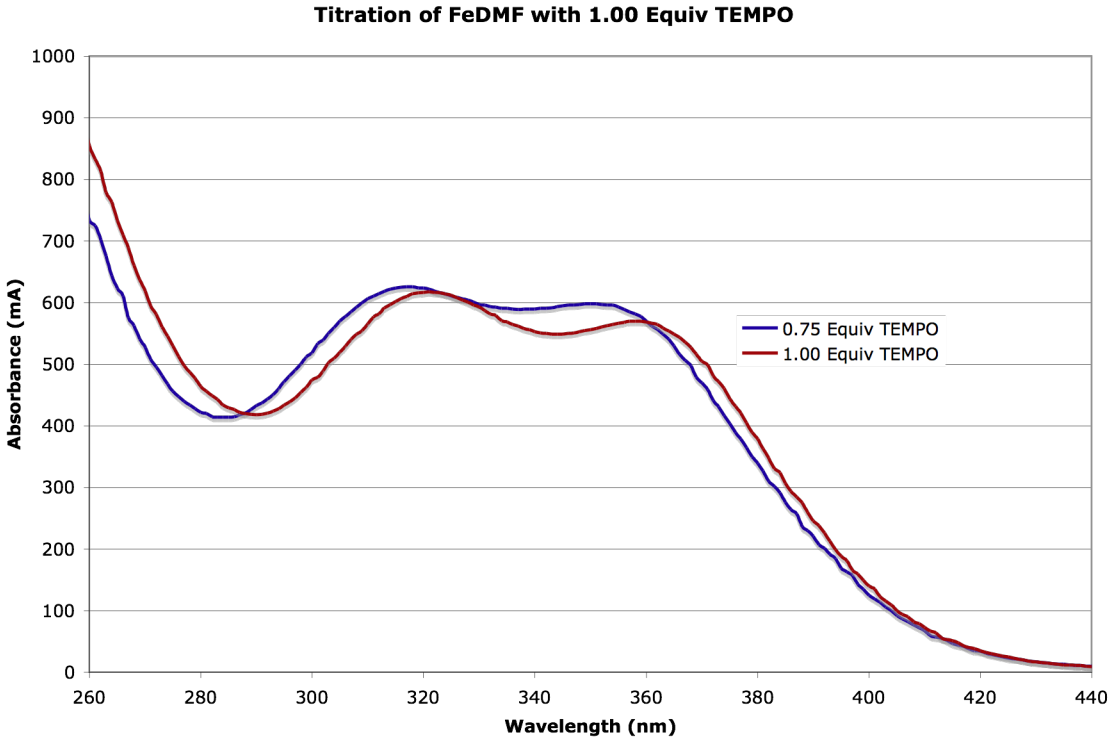
2.00 equiv.; 1.50 equiv.; 1.25 equiv.; 0.998 equiv.; 0.749 equiv.; 0.50 equiv.; 0.25 equiv.), followed by ~2 mL of $CH_2Cl_2$. The reaction was swirled vigorously for approximately two minutes to allow for complex formation to occur. The solution was then diluted to volume and mixed thoroughly. A 5 mL A-grade volumetric flask was filled with this solution, which was then quantitatively transferred (5 rinses of 1 mL $CH_2Cl_2$ was sufficient to give highly repeatable results) to a fresh 100 mL A-grade volumetric flask and diluted to volume. This final solution was then immediately analyzed.



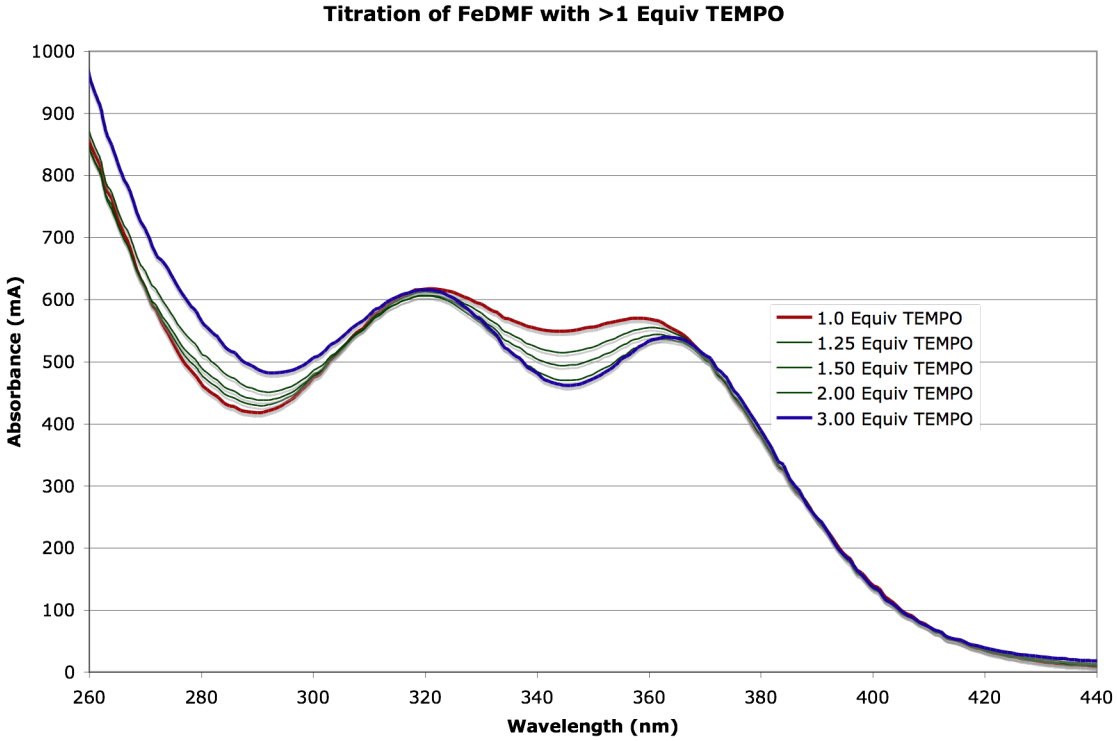

The interaction between $[Fe(dmf)_3Cl_2][FeCl_4]$ and TEMPO, up to 3.00 added equivalents displays the clear formation of a new species, which appears to occur through a stepwise, rather than continuous, association of TEMPO. Separating the above figure into three demonstrates this point more clearly. During the initial additions of TEMPO (0.25, 0.5, 0.75 equivalents), the maximum at 344 nm begins to disappear, while two new maxima at 317 nm and 352 nm begin to emerge.




Upon the further increase in TEMPO to 1.00 equivalents, the two emerging maxima are both shifted to longer wavelengths, 321 nm and 358 nm respectively.

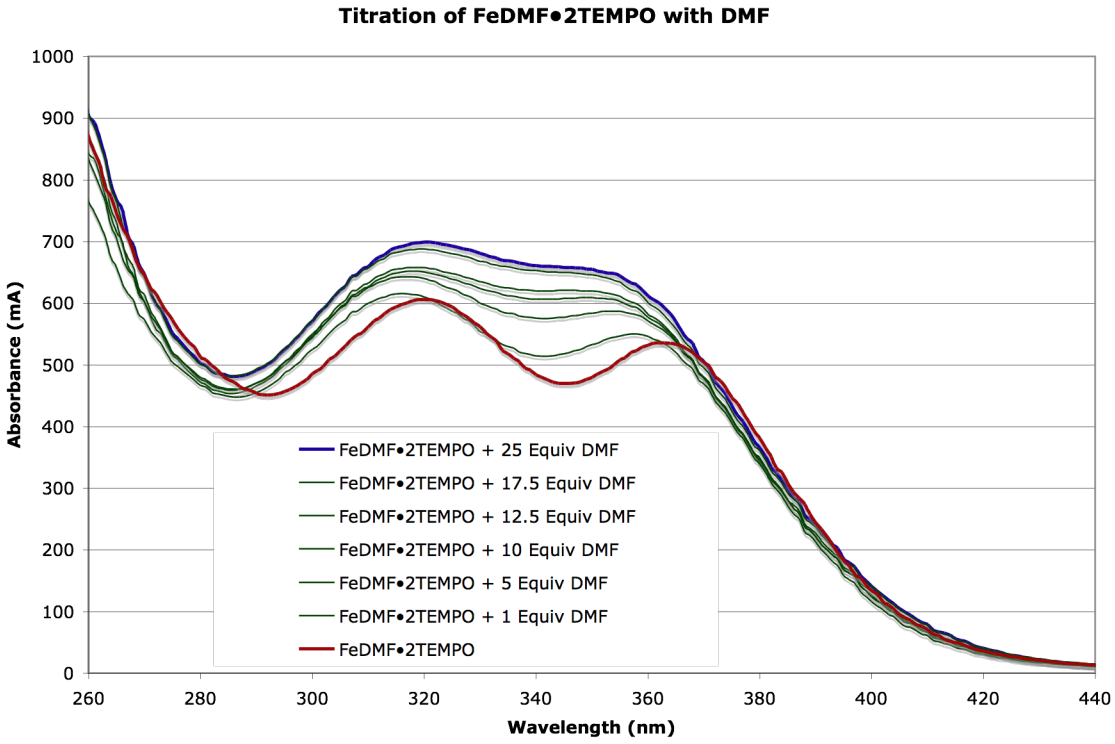


As the amount of TEMPO is further increased to 3.00 equiv, a smooth trend is again observed as the maximum at 321 nm and minimum at 346 nm become well defined. The longest wavelength maxmimum is further shifted to 363 nm. In the visible region of the spectrum, the results with 2.00 or 3.00 equivalents of TEMPO become essentially identical, within experimental error. The difference between these two trials in the UV region of the spectrum is likely due to the absorbance of an additional equivalent of free (unbound) TEMPO, which does weakly absorb in the UV region. Given that there appears to be two distinct processes involved in TEMPO complexation with $[Fe(dmf)_3Cl_2][FeCl_4]$, one occurring from 0-1 equivalents, and another that occurs between 1-2 equivalents, in addition to the fact that the addition of a third equivalent of TEMPO does not significantly perturb the visible region of the UV spectrum, we strongly believe that a 1:2 complex ($[Fe(dmf)_3Cl_2][FeCl_4]$•2TEMPO) is formed.

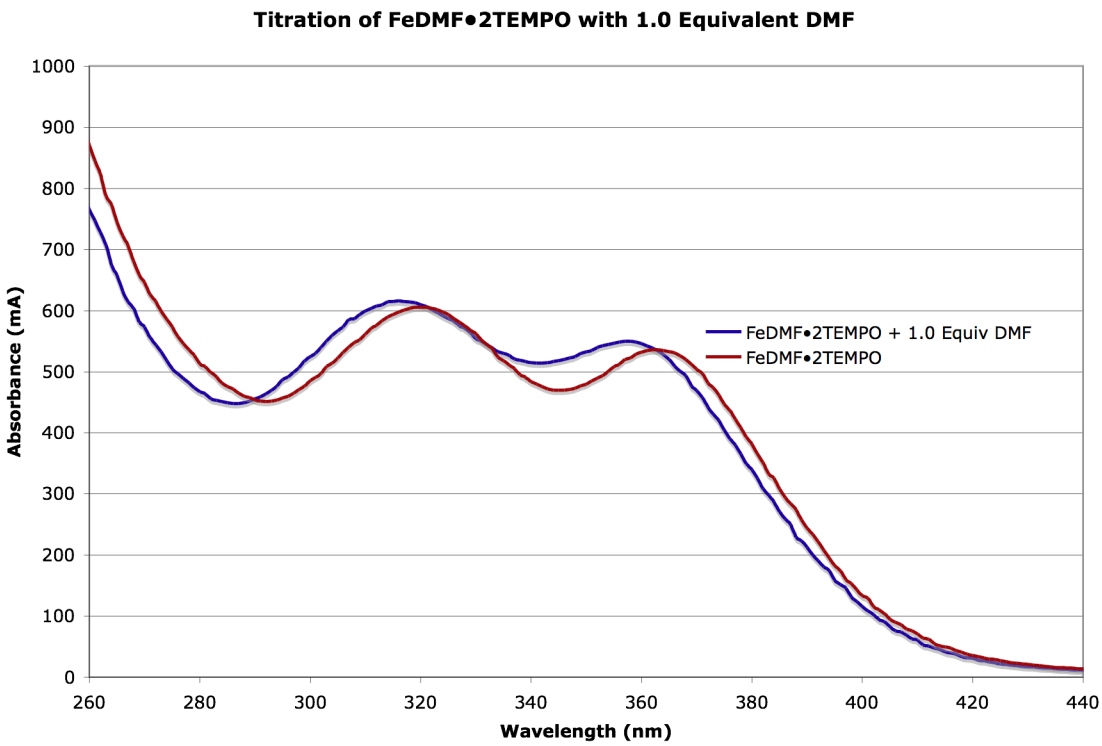



As the reaction described by Sibi is performed in DMF, we wanted to further investigate whether TEMPO or DMF would competitively form a complex with $[Fe(dmf)_3Cl_2][FeCl_4]$ when both species were present in varying stoichiometry. $[Fe(dmf)_3Cl_2][FeCl_4]$•2TEMPO was formed by charging precisely 54.4 mg $[Fe(dmf)_3Cl_2][FeCl_4]$ (0.100 mmol, 1.00 equiv) in a 100 mL A-grade volumetric flask, to which precisely 31.3 mg TEMPO was added (0.200 mmol, 2.00 equiv) and

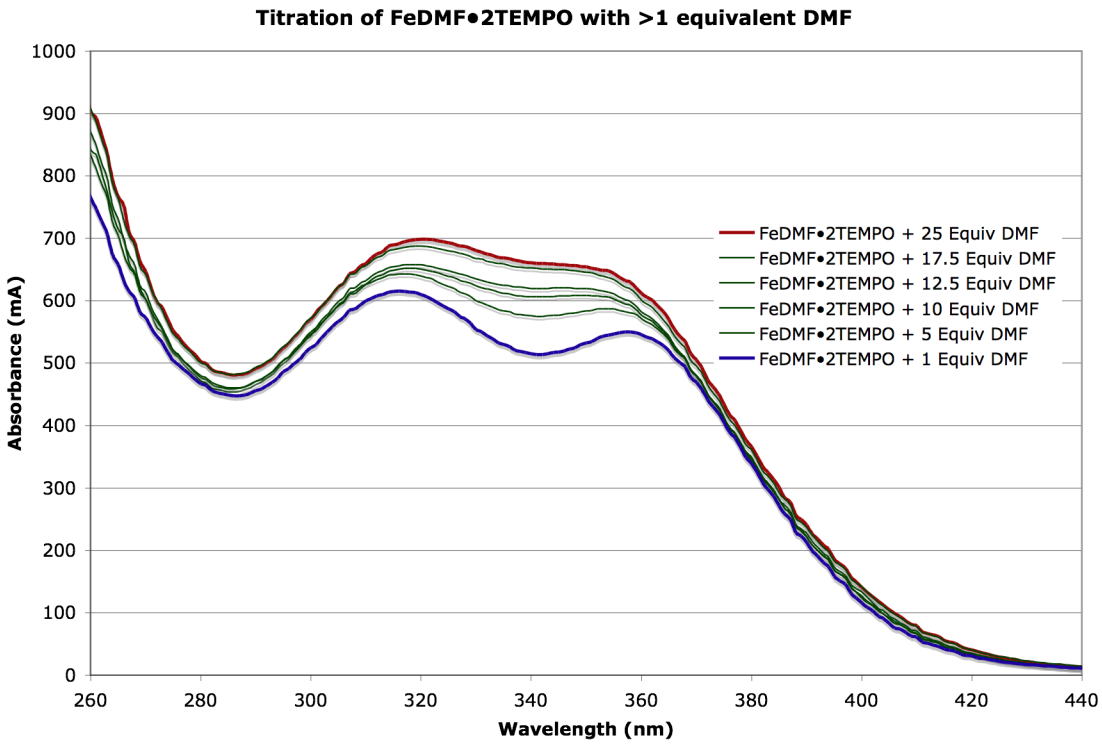
approximately 2 mL $CH_2Cl_2$. The flask was swirled vigorously until a homogeneous solution was obtained. Next, DMF (7.7 μL; 39 μL; 78 μL; 96 μL; 135 μL; 194 μL, 1.0 equiv.; 5.0 equiv.; 10.0 equiv.; 12.5 equiv.; 17.5 equiv.; 25.0 equiv.) was added to the volumetric flask, which was swirled vigorously for approximately one minute. The flask was diluted to volume with $CH_2Cl_2$. A 5 mL A-grade volumetric flask was filled with this solution, which was then quantitatively transferred (5 rinses of 1 mL $CH_2Cl_2$ was sufficient to give highly repeatable results) to a fresh 100 mL A-grade volumetric flask and diluted to volume. This final solution was then immediately analyzed.




Again, these results are most easily understood by breaking down the change between $[Fe(dmf)_3Cl_2][FeCl_4]$•2TEMPO and $[Fe(dmf)_3Cl_2][FeCl_4]$•2TEMPO + 25 equivalents DMF into two distinct steps. First, upon the addition of a single equivalent of DMF, there is a shifting of the maxima back to 317 nm and 358 nm.




Beyond the addition of the first equivalent of TEMPO, a smooth transition to a new product is observed, which appears to approach complete formation as the amount of added DMF approaches ~20 equivalents.




The displacement of TEMPO from $[Fe(dmf)_3Cl_2][FeCl_4]$•2TEMPO by DMF may be crucial in determining the reactivity of this system. Clearly, one equivalent of TEMPO is very weakly bound, and is displaced by the first equivalent of added DMF. At 2.0 M TEMPO concentration, which represents a 7:1 DMF:TEMPO ratio, the titration experiment above would suggest that significant amounts of TEMPO are still bound to iron, as complete formation of a new species does not occur until ~20 equivalents of DMF have been added. When 2.0 M TEMPO concentration was employed with radical clock substrate ***cis*-6a**, enamine addition predominated (95% ***cis*-8a** is delivered). However, when the concentration of TEMPO is lowered to 0.75 M, representing an 18:1 DMF:TEMPO ratio, most of the iron will be present as the fully DMF ligated complex, rather than the DMF/TEMPO complex. As such, some amount of a less favored SOMO-activation pathway is observed (15% ***trans*-8b** is delivered).

**VI. ReactIR Investigation of the Interaction Between Ferrocenium and TEMPO**

We were initially concerned that $[FeCp_2][PF_6]$ may reversibly form a complex with TEMPO, as such an interaction would alter the concentration of free TEMPO in solution, possibly inducing error into our radical clock investigations. ReactIR allowed for the direct observation of TEMPO in solution at the concentration the reaction is performed (2.0 M). A ReactIR probe was immersed in 1 mL pure THF to allow for the collection of a solvent background spectrum, and a 1 h experiment was initiated, with data points collected every 30 seconds (Figure S5). After three minutes and thirty seconds, the experiment was paused, TEMPO (315 mg, 2.02 mmol) was added to the THF solution, and the experiment was resumed. Of all the new peaks observed, the maxima found at 1471 $cm^{-1}$ and 1363 $cm^{-1}$ were both the most intense, and occurred at the position further away from significant THF absorbances, and were therefore used for analysis. After six minutes and thirty seconds (total experiment time), the experiment was paused and $[FeCp_2][PF_6]$ (327 mg, 0.99 mmol) was added to the solution. The experiment was then resumed, and continued undisturbed until one hour had elapsed. The addition of $[FeCp_2][PF_6]$ caused no change in either the position or intensity of the maxima at 1471 $cm^{-1}$ and 1363 $cm^{-1}$. A very slight increase in these peaks is seen over the course of the entire experiment due to the slow evaporation of THF, and is seen even before the addition of $[FeCp_2][PF_6]$.

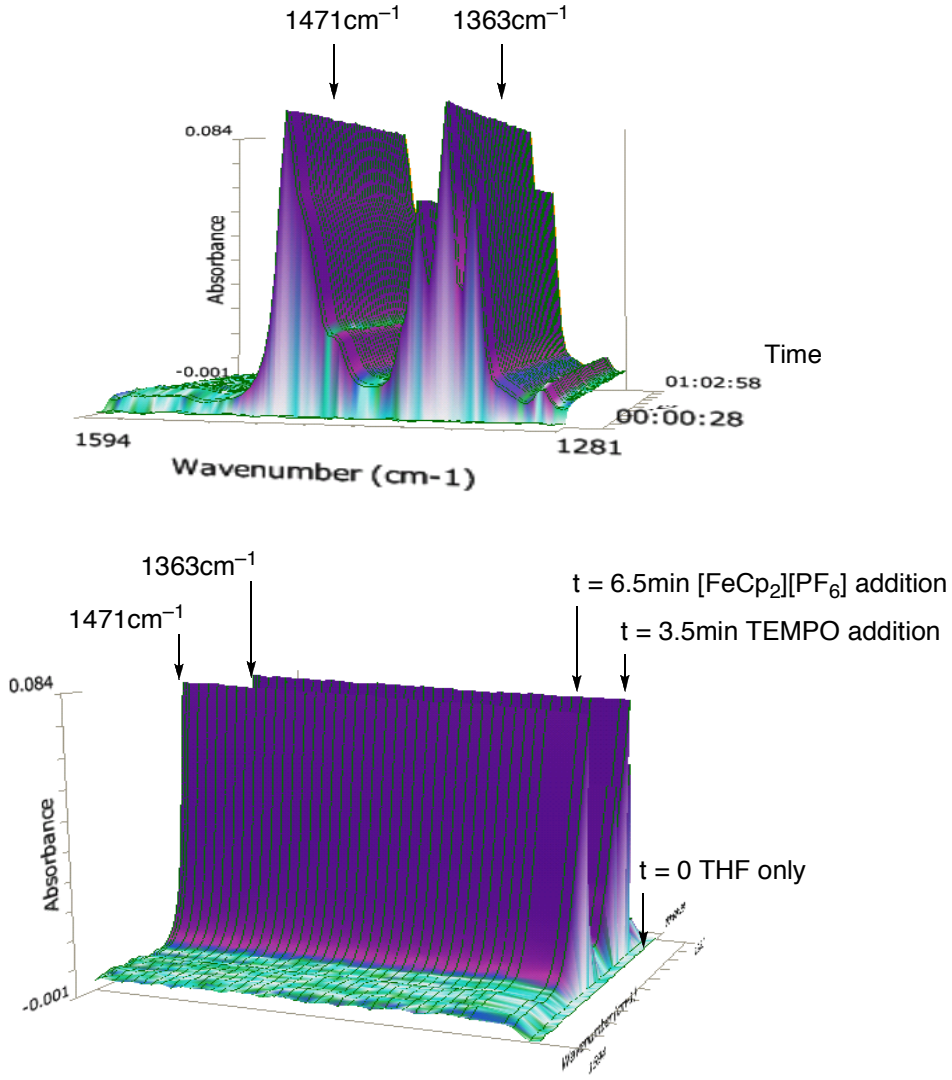
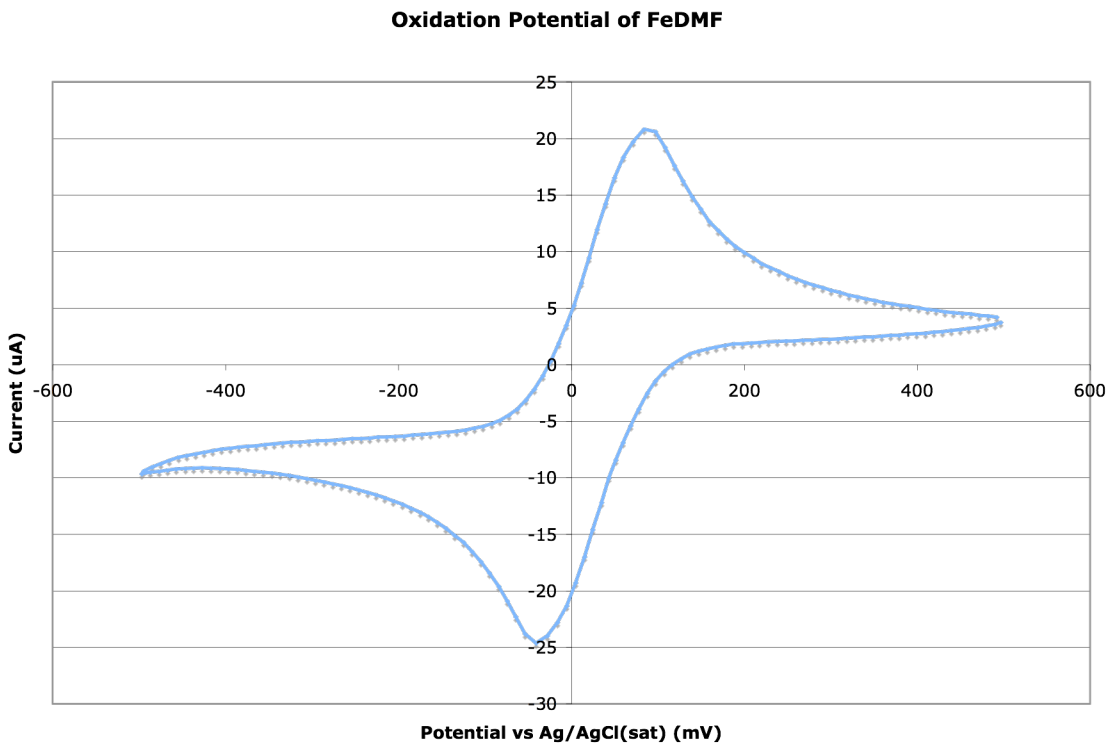


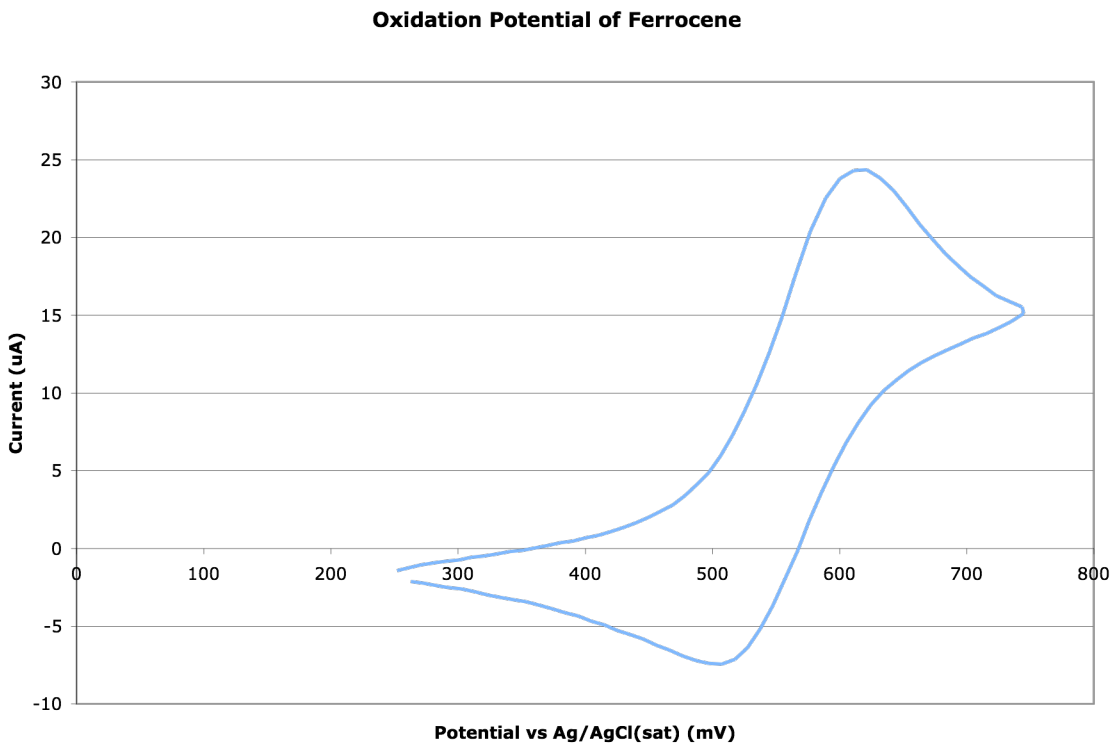

**Figure S5.** ReactIR investigation of the interaction between $[FeCp_2][PF_6]$ and TEMPO

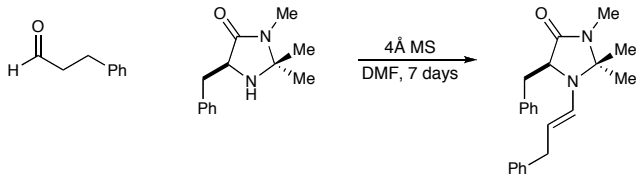
**VII. Cyclic Voltammetry Experiments Performed in DMF**

The oxidation potential of $[Fe(dmf)_3Cl_2][FeCl_4]$ in DMF was measured using the procedure of Safavi,[9] with the results in complete agreement.

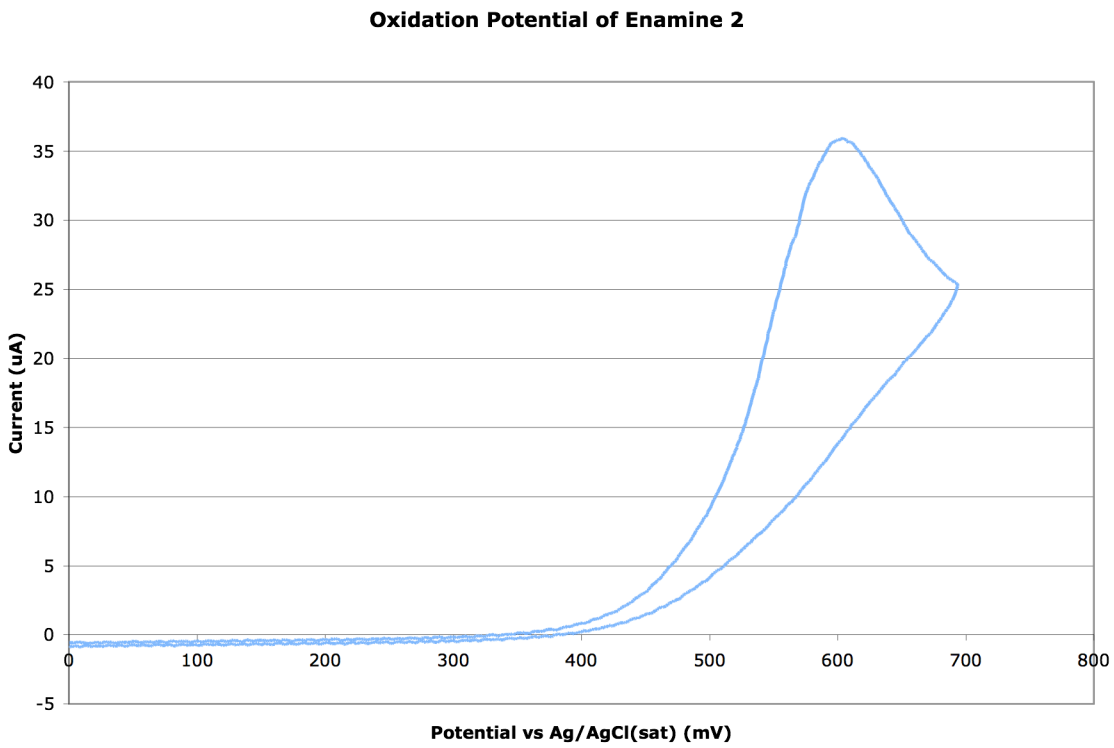



Ferrocene (4.7 mg, 0.025 mmol) and tetrabutylammonium hexafluorophosphate (194 mg, 0.500 mmol) were dissolved in DMF (5 mL) that had been purified according to IUPAC recommendations for electrochemistry.[10] The oxidation potential was measured using a platinum disk working electrode (2 mm), a platinum wire counter electrode, and a saturated Ag/AgCl reference electrode at 100 mV/s scan rate.



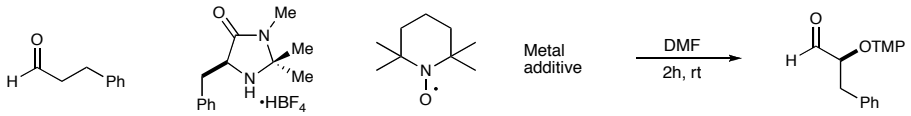




The procedure of Gellman was used to synthesis a 0.25 M solution of the enamine derived from imidazolidinone catalyst **1** in DMF.[11] Tetrabutylammonium hexafluorophosphate (194 mg, 0.500 mmol) was dissolved in DMF that had been purified according to the IUPAC recommendations for electrochemistry,[10] to which 0.5 mL of the enamine solution was added. The oxidation potential was measured using a platinum disk working electrode (2 mm), a platinum wire counter electrode, and a saturated Ag/AgCl reference electrode at 5 mV/s scan rate.



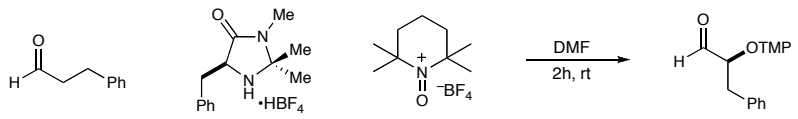

Solutions of imidazolidinone enamines prepared by the method of Gellman are invariably contaminated with some amount of free amine. Tetrabutylammonium hexafluorophosphate (194 mg, 0.500 mmol) and imidazolidinone catalyst **1** (11.0 mg, 0.050 mmol) were dissolved in DMF that had been purified according to the IUPAC recommendations for electrochemistry.[10] The oxidation potential was measured using a platinum disk working electrode (2 mm), a platinum wire counter electrode, and a saturated Ag/AgCl reference electrode at 5 mV/s scan rate. The irreversible oxidation feature observed for enamine was not seen with a solution of free catalyst **1**.

## VIII. Investigation of Other Oxidation Systems




Into one of six flame-dried 8mL vials fitted with a Teflon septum was charged 5 mol% of the appropriate metal additive (Vial A: $[Fe(dmf)_3Cl_2][FeCl_4]$ 5.4 mg, 0.01mmol, Vial B: $CuCl_2$ 2.7 mg, 0.02 mmol, Vial C: Co(salen) 6.5 mg, 0.02 mmol, Vial D: $Sc(OTf)_3$ 9.5

mg, 0.02 mmol, Vial E: $Zn(NTf_2)_2$ 12.1 mg, 0.02 mmol, Vial F: No metal additive). A stock solution was prepared by dissolving TEMPO (942 mg, 6.03 mmol), imidazolidinone catalyst **1**•$HBF_4$ (183 mg, 0.60 mmol), hydrocinnamaldehyde (396 μL, 3.01 mmol) and benzyl propionate (Internal Standard, 120 μL, 0.75 mmol) in DMF (3 mL). This stock solution was then delivered to each vial (0.4 mL), and the reaction was allowed to proceed for two hours at room temperature. An aliquot (100 μL) was injected into a quenching solution made from 1M Na-ascorbate (0.75 mL) and diethyl ether (1.5 mL). The sodium ascorbate was required to sequester metal ions from the organic phase, as well as to reduce TEMPO to the corresponding hydroxylamine (TEMPOH), so as to minimize interference in $^1$H NMR spectra. 1.0 mL of the organic layer was removed to a fresh vial, and concentrated *in vacuo*, then analyzed by $^1$H NMR ($t_1$ delay = 10.0 s). (Yield: Vial A: 72%. Vial B: 82%. Vial C: 75%. Vial D: 17%. Vial E: 12 %. Vial F: 11%.)




Hydrocinnamaldehyde (132 μL, 1.00 mmol) and imidazolidinone catalyst **1**•$HBF_4$ (61 mg, 0.2 mmol) were dissolved in DMF (0.5 mL) under argon. Oxoammonium tetrafluoroborate[6] (243 mg, 1.00 mmol) was dissolved in DMF (0.5 mL), which was drawn up into a syringe and attached to a syringe pump. The pump was activated at such a rate that complete addition of the oxoammonium solution took approximately one hour. The solution was left to further react for another hour after addition was complete at room temperature. An aliquot (100 μL) was injected into a quenching solution made from 1M Na-ascorbate (0.75 mL) and diethyl ether (1.5 mL). The sodium ascorbate was required to sequester metal ions from the organic phase, as well as to reduce TEMPO to the corresponding hydroxylamine (TEMPOH), so as to minimize interference in $^1$H NMR spectra. 1.0 mL of the organic layer was removed to a fresh vial, and concentrated *in vacuo*, then analyzed by $^1$H NMR ($t_1$ delay = 10.0 s). The yield was observed to be 19%.

## IX. Supporting Information References

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