Supporting Information for

# The influence of reversible trianionic pincer $OCO^{3-}$ $\mu$-oxo $Cr^{IV}$ dimer formation ($[Cr^{IV}]_2(\mu$-O)) and donor ligands in oxygen-atom-transfer (OAT)†

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**Table S1.** Reduction of **2**. Variable Temperature vs. $k_{obs}$ (M/s)

| Temp. (K) | 1/T ($K^{-1}$) | k | k | k | Avg. k | ln(k/T) |
|---|---|---|---|---|---|---|
| 273.15 | 0.003661 | 14.2 | 15.5 | 13.0 | 14.2 | -2.95 |
| 283.15 | 0.003532 | 31.7 | 36.4 | 37.0 | 35.1 | -2.08 |
| 293.15 | 0.003411 | 59.2 | 55.4 | 49.6 | 54.7 | -1.68 |
| 313.15 | 0.003193 | 159 | 157 | 167 | 161 | -0.665 |

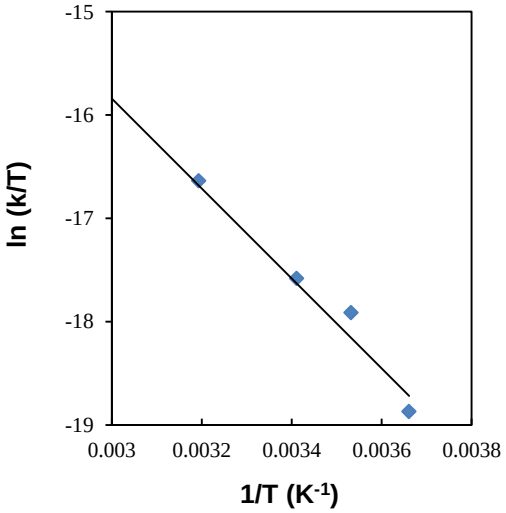



**Figure S1.** Eyring plot for the OAT from **2a** (0.186 mM**)** to $PPh_3$ (1.59 mM) in THF between 0 – 40 °C. Intercept (b) = -2(2); slope (m) = -4.6(5) x$10^3$. Calculated $\Delta S^{\ddagger}$ = -18(3) cal/mol; $\Delta H^{\ddagger}$ = 9.4(8) kcal/mol.

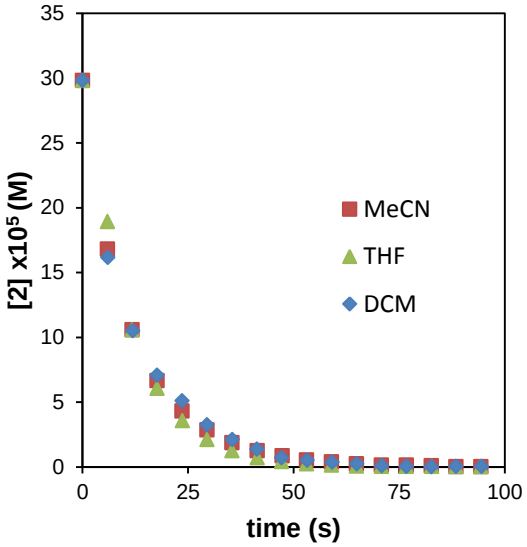
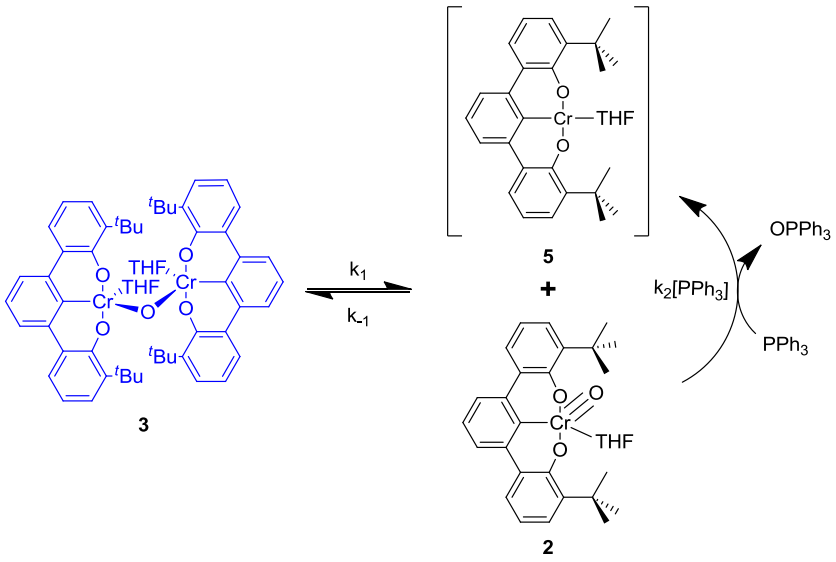



**Figure S2.** [**2**] vs time in MeCN, THF, and DCM/THF.




**Scheme S1.** Mechanism of OAT from **3**.

$$\frac{d[\mathbf{5}]}{dt} = k_2[PPh_3][\mathbf{2}]_{\mathbf{ss}} \quad (S1)$$

$$\Delta[\mathbf{2}]_{ss} = 0 = k_1[\mathbf{3}] - k_{-1}[\mathbf{5}][\mathbf{2}] - k_2[\mathbf{2}][PPh_3] \quad (S2)$$

$$[\mathbf{2}]_{ss} = \frac{k_1[\mathbf{3}]}{k_{-1}[\mathbf{5}] + k_2[PPh_3]} \quad (S3)$$

$$\frac{d[\mathbf{5}]}{dt} = \frac{k_1\, k_2[PPh_3][\mathbf{3}]}{k_{-1}[\mathbf{5}] + k_2[PPh_3]} \quad (S4)$$

*At late reaction times assume:* $k_{-1}[\mathbf{5}] >> k_2[PPh_3]$

$$\frac{d[\mathbf{5}]}{dt} = \frac{k_1\, k_2[\mathbf{3}][PPh_3]}{k_{-1}[\mathbf{5}]} \quad (S5)$$

*Mass-balance equation*

$$[\boldsymbol{Cr}]_{tot} = 2[\mathbf{3}] + [\mathbf{5}] + [\mathbf{2}] \quad (S6)$$

Since $[\mathbf{2}] = [\mathbf{2}]_{ss} \approx 0$

$$[\boldsymbol{Cr}]_{tot} = 2[\mathbf{3}] + [\mathbf{5}] \quad (S7)$$

$$\frac{d[\mathbf{5}]}{dt} = -\frac{d[\mathbf{3}]}{dt} = \frac{k_1\, k_2[\mathbf{3}][PPh_3]}{k_{-1}([\boldsymbol{Cr}]_{tot} - 2[\mathbf{3}])} \quad (S8)$$

$$\frac{-[\boldsymbol{Cr}]_{tot} + 2[\mathbf{3}]}{[\mathbf{3}]} d[\mathbf{3}] = \frac{k_1\, k_2[PPh_3]}{k_{-1}} dt \quad (S9)$$

*Integrated rate law*

$$-[\boldsymbol{Cr}]_{tot}\ln[\mathbf{3}] + 2[\mathbf{3}] = \frac{k_1\, k_2[PPh_3]}{k_{-1}}t \quad \text{(S10)}$$

*At early reaction times assume:* $k_2[PPh_3] >> k_{-1}[\mathbf{5}]$

$$\frac{d[\mathbf{5}]}{dt} = -\frac{d[\mathbf{3}]}{dt} = k_1[\mathbf{3}] \quad \text{(S11)}$$

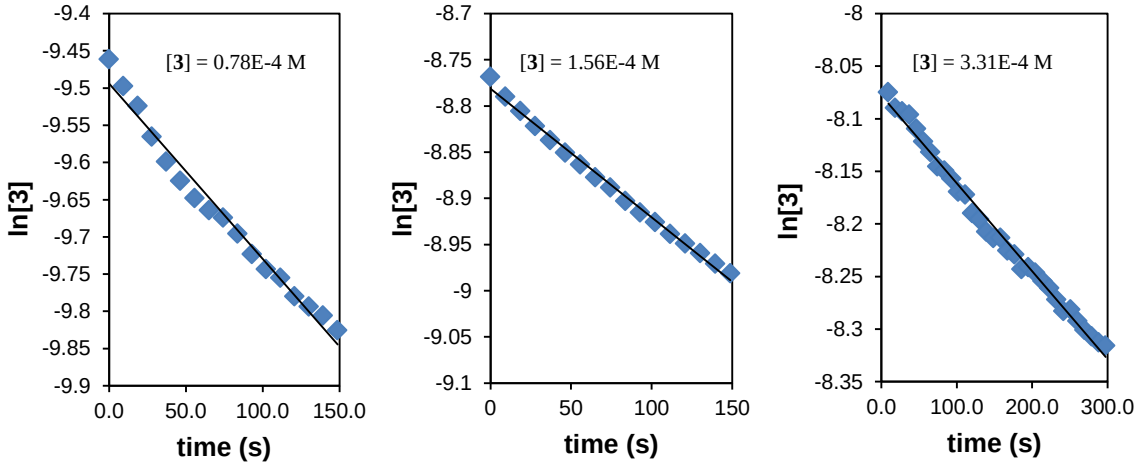



**Figure S2.** Averaged plots of ln[**3**] vs time between reaction times 0-150 s for [**3**] = 0.78 x$10^{-4}$ and 1.56 x$10^{-4}$ M and for 0-300 s for [**3**] = 3.31 x$10^{-4}$ M upon addition of $PPh_3$ (1.1 x$10^{-3}$ M).

**Table S2.** $k_1$ ($s^{-1}$) values obtained from the slope of the ln[**3**] vs time (0 - 150 s) plots for [**3**] (0.31, 0.16, and 0.08 mM); $PPh_3$ (1.10 mM) in $CH_2Cl_2$ (22°C).

| [**3**] x$10^4$ | $k_1$ x$10^4$ | $k_1$ x$10^4$ | $k_1$ x$10^4$ |
|---|---|---|---|
| 0.78 | 26.1 | 21.9 | 22.7 |
| 1.56 | 14.0 | 14.4 | 13.4 |
| 3.31 | 9.14 | 7.81 | 8.19 |

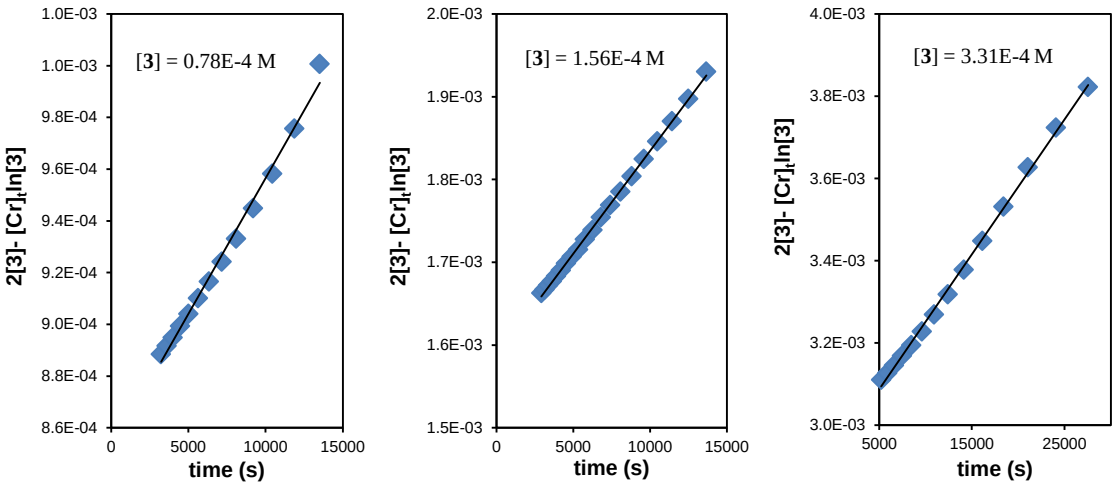



**Figure S3.** The average 2[**3**] – $[Cr]_{tot}$ln[**3**] vs time upon the addition of $PPh_3$ (1.1 x$10^{-3}$ M) into a solution of **3** (0.78, 1.56, and 3.31 (x$10^{-4}$) M) in $CH_2Cl_2$ .

**Table S3.** Slopes obtained from the plot of the $[Cr]_{tot}$ln[**3**] - 2[**3**] vs time for [**3**] (0.78, and 1.56, 3.11 (x$10^{-4}$) M); $PPh_3$ (1.10 x$10^{-3}$ M) in $CH_2Cl_2$ (22 °C).

| [**3**] x$10^4$ | m x$10^8$ | m x$10^8$ | m x$10^8$ |
|---|---|---|---|
| 0.78 | 3.10 | 3.51 | 3.59 |
| 1.56 | 3.14 | 2.42 | 2.29 |
| 3.31 | 9.14 | 7.81 | 8.19 |

# Supporting Information for [$^t$BuOCO]Cr$^V$O(CH$_2$PPh$_3$) (4).

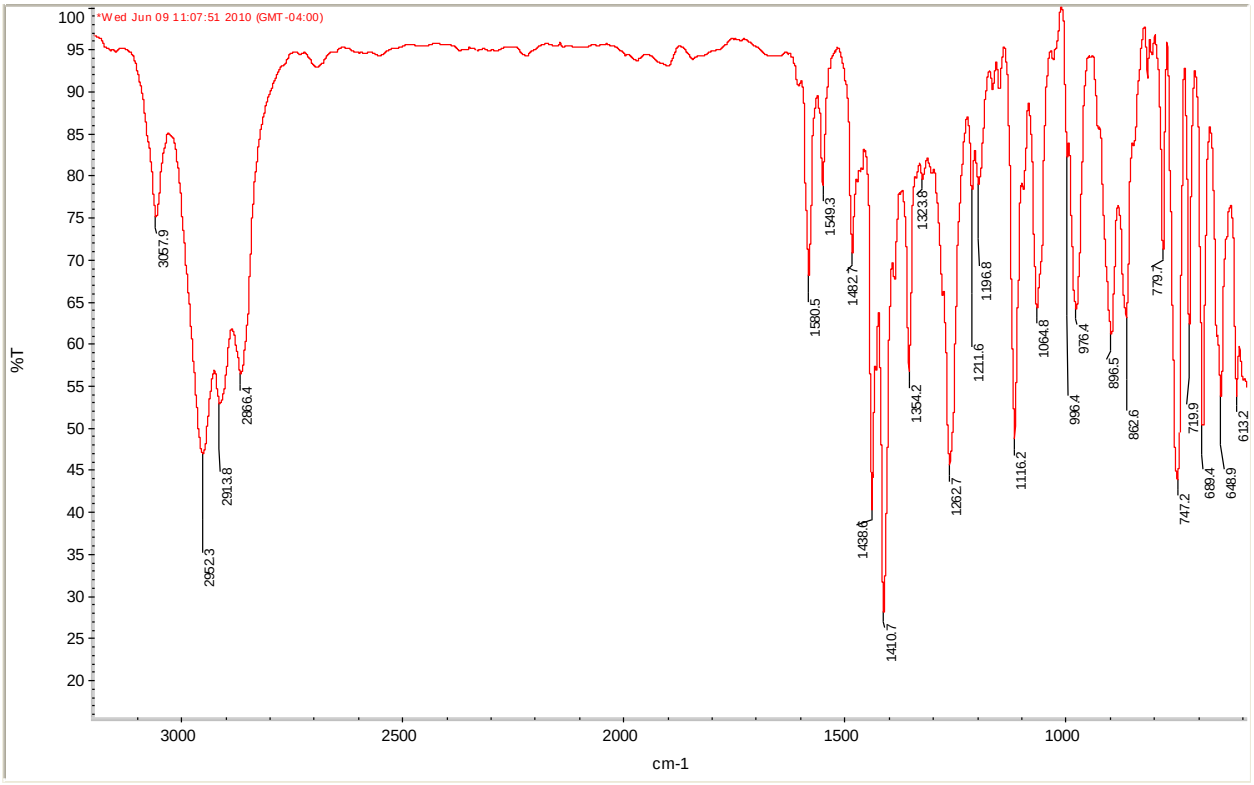



**Figure S4.** IR spectrum of [$^t$BuOCO]Cr$^V$O(CH$_2$PPh$_3$) (**4**) (thin-film).

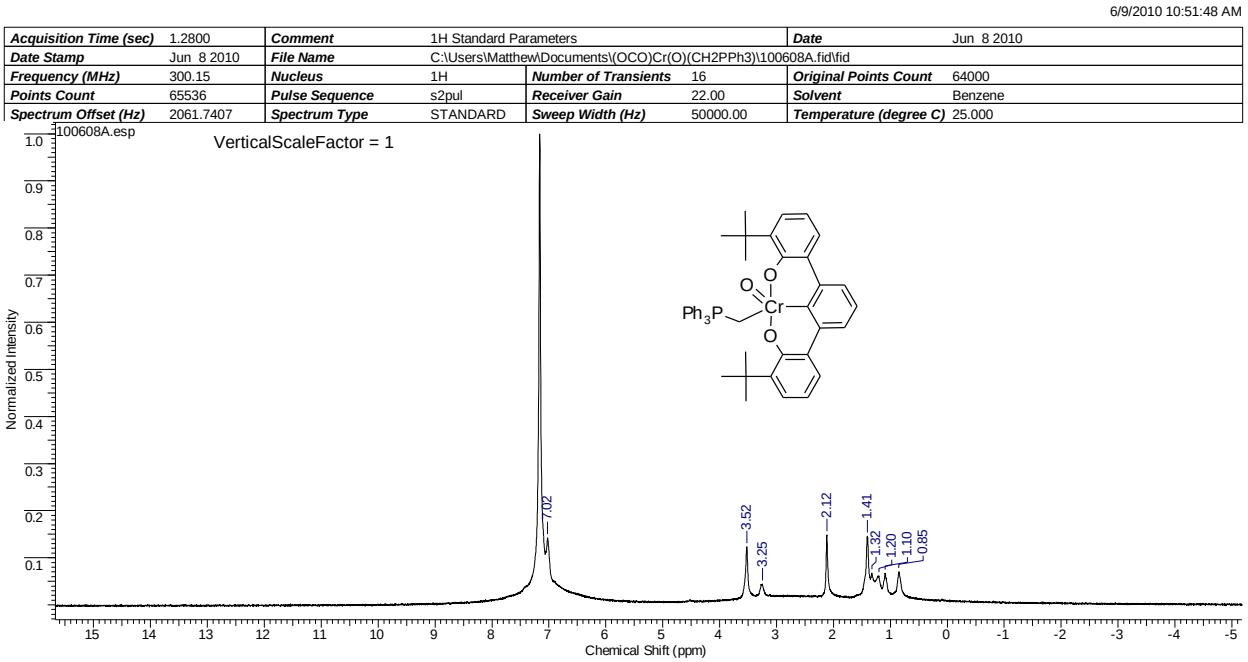



**Figure S5.** $^1$H NMR of [$^t$BuOCO]Cr$^V$O(CH$_2$PPh$_3$) (**4**) in C$_6$D$_6$ with 0.01 mL THF-$d_8$.

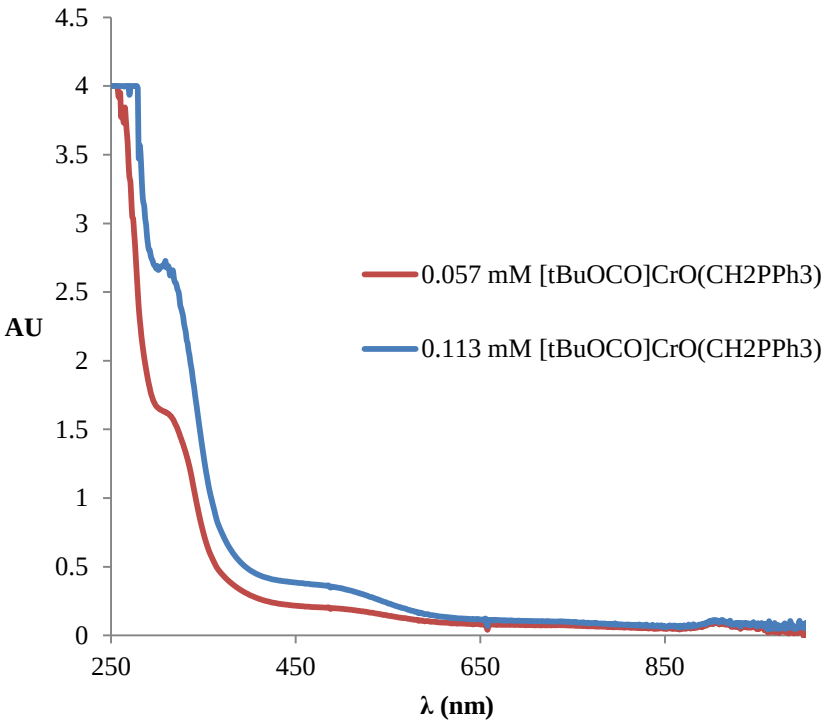



**Figure S6.** UV-vis of **4** in THF (0.057 mM, red; 0.113 mM, blue).

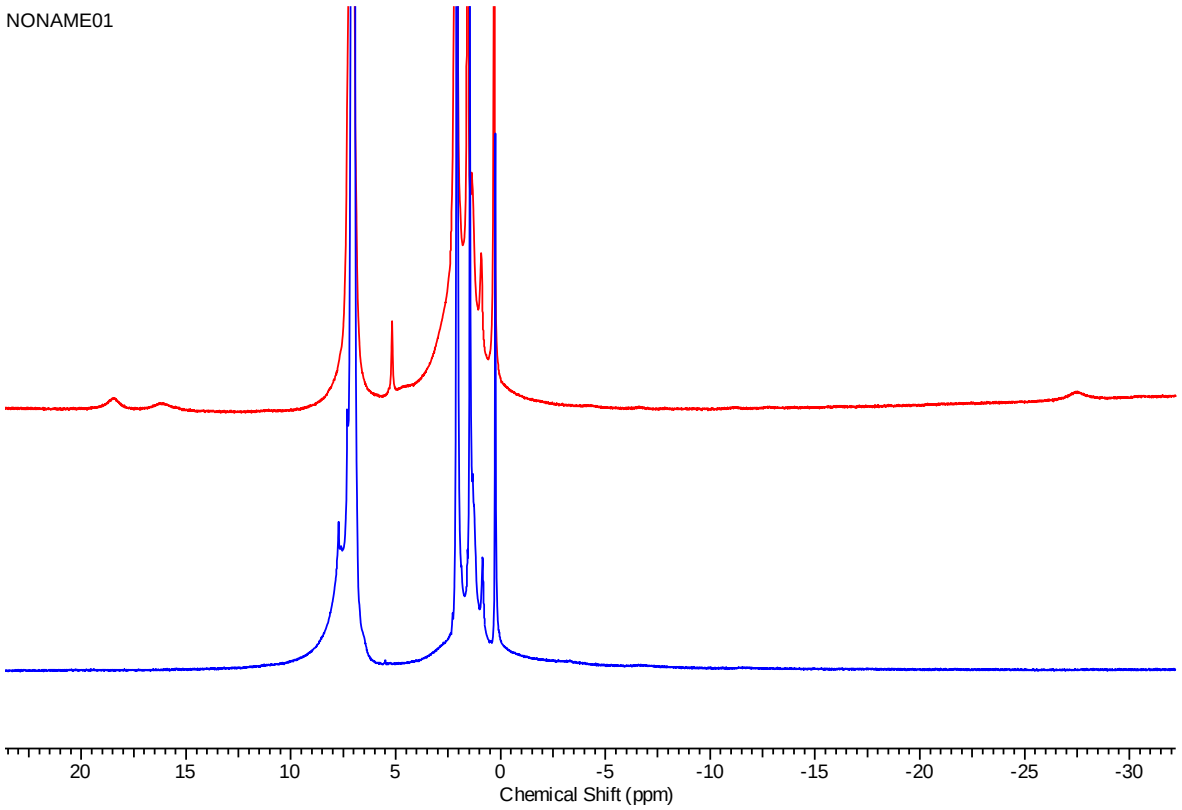



**Figure S7.** $^{1}$H NMR of **3** (2.43 x10$^{-5}$ mol) in $C_6D_6$ (red) and with $OPPh_3$ (5.82 x10$^{-5}$) in $C_6D_6$ (blue).

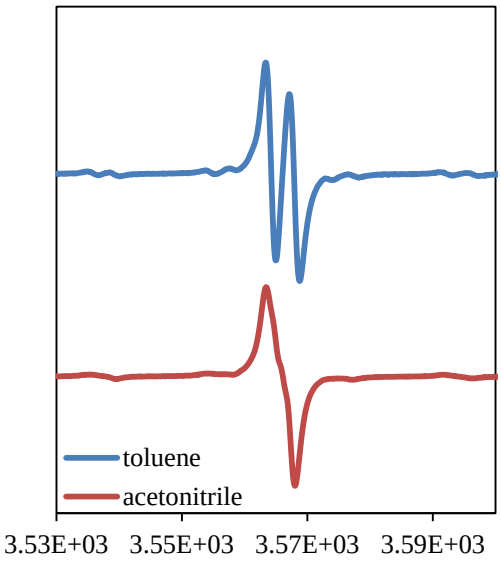



**Figure S8.** Solution EPR spectra of a mixture of **2** and **2a** (5.0 x10$^{-3}$ M) in toluene (blue) and a **2** and **2a** solution (1.6 x10$^{-3}$ M) in toluene (blue) after addition of 6 equivalents of MeCN (red)