

Supporting Information for:

Sterically directed Nitronate Complexes of 2,6-Di- *tert*-Butyl-4-Nitrophenoxide with Cu(II) and Zn(II) and Their H-Atom Transfer Reactivity

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Contents:

1. Crystallographic Data for (1) , (2) , (3) and Tp^{tBu}Cu^{II}-OAc	S2
2. Optical Spectra of (1) and (3)	S8
3. ¹ H NMR Spectra of (1) and (3)	S10
4. Cyclic Voltammetry of (1)	S12
5. ¹ H NMR of ½ [Tp ^{tBu} Cu ^I] ₂ + ^t Bu ₂ NPArO• (No Reaction).....	S13
6. ¹ H NMR of ½ [Tp ^{tBu} Cu ^I] ₂ + O ₂ N ^t Bu ₂ C ₆ H ₂ OH (No Reaction).....	S14
7. Optical and ¹ H NMR Data for the Completed Reaction Between ½ [Tp ^{tBu} Cu ^I] ₂ , O ₂ N ^t Bu ₂ C ₆ H ₂ OH and ^t Bu ₃ ArO•.....	S15
8. ¹ H NMR Data for the Completed Reaction Between (1) and TEMPOH.....	S17

1. Crystallographic Data for (1), (2), (3) and $Tp^{tBu}Cu^{II}-OAc$

1.A. Crystallographic Data for (1)

General Procedure

A green prism, measuring $0.18 \times 0.10 \times 0.05 \text{ mm}^3$ was mounted on a loop with oil. Data was collected at -173°C on a Bruker APEX II single crystal X-ray diffractometer, Mo-radiation.

Crystal-to-detector distance was 40 mm and exposure time was 10 seconds per frame for all sets. The scan width was 0.5° . Data collection was 97.7% complete to 25° in ϑ . A total of 51079 reflections were collected covering the indices, $h = -15$ to 15, $k = -13$ to 13, $l = -22$ to 22. 9047 reflections were symmetry independent and the $R_{\text{int}} = 0.0723$ indicated that the data was of average quality (0.07). Indexing and unit cell refinement indicated a primitive monoclinic lattice. The space group was found to be $P 2_1$ (No. 4).

The data was integrated and scaled using SAINT, SADABS within the APEX2 software package by Bruker.

Solution by direct methods (SHELXS, SIR97) produced a complete heavy atom phasing model consistent with the proposed structure. The structure was completed by difference Fourier synthesis with SHELXL97. Scattering factors are from Waasmaier and Kirfel.¹ Hydrogen atoms were placed in geometrically idealised positions and constrained to ride on their parent atoms with C---H distances in the range 0.95-1.00 Angstrom. Isotropic thermal parameters U_{eq} were fixed such that they were $1.2U_{\text{eq}}$ of their parent atom U_{eq} for CH's and $1.5U_{\text{eq}}$ of their parent atom U_{eq} in case of methyl groups. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares.

(1) Waasmaier, D.; Kirfel, A. *Acta. Cryst. A.* **1995**, 51, 416.

Table S1: Crystallographic data for **(1)** provided.

Empirical formula	$C_{35}H_{54}BCuN_7O_3$	
Formula weight	695.20	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2 ₁	
Unit cell dimensions	a = 11.3921(4) Å	$\alpha = 90^\circ$.
	b = 10.0553(4) Å	$\beta = 98.477(2)^\circ$.
	c = 16.8141(7) Å	$\gamma = 90^\circ$.
Volume	1905.03(13) Å ³	
Z	2	
Density (calculated)	1.212 Mg/m ³	
Absorption coefficient	0.615 mm ⁻¹	
F(000)	742	
Crystal size	0.18 x 0.10 x 0.05 mm ³	
Theta range for data collection	2.33 to 28.34°.	
Index ranges	-15 ≤ h ≤ 15, -12 ≤ k ≤ 13, -22 ≤ l ≤ 22	
Reflections collected	51079	
Independent reflections	9047 [R _{int} = 0.0723]	
Completeness to theta = 25.00°	97.7 %	
Max. and min. transmission	0.9699 and 0.8974	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	9047 / 115 / 439	
Goodness-of-fit on F ²	1.080	
Final R indices [I > 2σ(I)]	R1 = 0.0738, wR2 = 0.1592	
R indices (all data)	R1 = 0.0976, wR2 = 0.1712	
Absolute structure parameter	0.035(18)	
Largest diff. peak and hole	1.731 and -1.010 e.Å ⁻³	

1.B. Crystallographic Data For (2)

General Procedure

A yellow prism, measuring 0.15 x 0.15 x 0.10 mm³ was mounted on a loop with oil. Data was collected at -173°C on a Bruker APEX II single crystal X-ray diffractometer, Mo-radiation.

Crystal-to-detector distance was 40 mm and exposure time was 10 seconds per frame for all sets. The scan width was 0.5°. Data collection was 100% complete to 25° in θ . A total of 140212 reflections were collected covering the indices, $h = -18$ to 18, $k = -19$ to 19, $l = -26$ to 26. 9503 reflections were symmetry independent and the $R_{int} = 0.0442$ indicated that the data was of better than average quality (0.07). Indexing and unit cell refinement indicated a primitive monoclinic lattice. The space group was found to be $P 2_1/c$ (No. 14).

The data was integrated and scaled using SAINT, SADABS within the APEX2 software package by Bruker.

Solution by direct methods (SHELXS, SIR97) produced a complete heavy atom phasing model consistent with the proposed structure. The structure was completed by difference Fourier synthesis with SHELXL97. Scattering factors are from Waasmaier and Kirfel.¹ Hydrogen atoms were placed in geometrically idealised positions and constrained to ride on their parent atoms with C---H distances in the range 0.95-1.00 Angstrom. Isotropic thermal parameters U_{eq} were fixed such that they were $1.2U_{eq}$ of their parent atom U_{eq} for CH's and $1.5U_{eq}$ of their parent atom U_{eq} in case of methyl groups. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares.

(1) Waasmaier, D.; Kirfel, A. *Acta. Cryst. A.* **1995**, 51, 416.

Table S2: Crystallographic data for (2) provided.

Empirical formula	C ₃₅ H ₅₄ BN ₇ O ₃ Zn	
Formula weight	697.03	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2 ₁ /c	
Unit cell dimensions	a = 13.5042(10) Å	α = 90°.
	b = 14.5848(12) Å	β = 103.397(4)°.
	c = 19.8333(16) Å	γ = 90°.
Volume	3800.0(5) Å ³	
Z	4	
Density (calculated)	1.218 Mg/m ³	
Absorption coefficient	0.688 mm ⁻¹	
F(000)	1488	
Crystal size	0.15 x 0.15 x 0.10 mm ³	
Theta range for data collection	2.09 to 28.47°.	
Index ranges	-18 ≤ h ≤ 18, -19 ≤ k ≤ 19, -26 ≤ l ≤ 26	
Reflections collected	140212	
Independent reflections	9503 [R _{int} = 0.0442]	
Completeness to theta = 25.00°	100.0 %	
Max. and min. transmission	0.9344 and 0.9038	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	9503 / 0 / 439	
Goodness-of-fit on F ²	1.037	
Final R indices [I > 2σ(I)]	R1 = 0.0274, wR2 = 0.0651	
R indices (all data)	R1 = 0.0369, wR2 = 0.0696	
Largest diff. peak and hole	0.376 and -0.366 e.Å ⁻³	

1.C. Crystallographic Data For (3)

General Procedure

A dichroic brown/green needle, measuring 0.10 x 0.03 x 0.03 mm³ was mounted on a loop with oil. Data was collected at -173°C on a Bruker APEX II single crystal X-ray diffractometer, Mo-radiation.

Crystal-to-detector distance was 40 mm and exposure time was 10 seconds per frame for all sets. The scan width was 0.5°. Data collection was 100% complete to 25° in θ . A total of 41198 reflections were collected covering the indices, $h = -26$ to 26, $k = -10$ to 10, $l = -24$ to 24. 7126 reflections were symmetry independent and the $R_{int} = 0.0543$ indicated that the data was of good quality. Indexing and unit cell refinement indicated a C-centered monoclinic lattice. The space group was found to be C c (No. 9).

The data was integrated and scaled using SAINT, SADABS within the APEX2 software package by Bruker.

Solution by direct methods (SHELXS, SIR97) produced a complete heavy atom phasing model consistent with the proposed structure. The structure was completed by difference Fourier synthesis with SHELXL97. Scattering factors are from Waasmaier and Kirfel.¹ Hydrogen atoms were placed in geometrically idealised positions and constrained to ride on their parent atoms with C---H distances in the range 0.95-1.00 Angstrom. Isotropic thermal parameters U_{eq} were fixed such that they were 1.2 U_{eq} of their parent atom U_{eq} for CH's and 1.5 U_{eq} of their parent atom U_{eq} in case of methyl groups. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares.

(1) Waasmaier, D.; Kirfel, A. *Acta. Cryst. A.* **1995**, 51, 416.

Table S3: Crystallographic data for **(3)** provided.

Empirical formula	$C_{27}H_{38}BCuN_7O_3$	
Formula weight	582.99	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C c	
Unit cell dimensions	$a = 19.8577(9)$ Å	$\alpha = 90^\circ$.
	$b = 8.0385(3)$ Å	$\beta = 102.001(4)^\circ$.
	$c = 18.2723(9)$ Å	$\gamma = 90^\circ$.
Volume	$2853.0(2)$ Å ³	
Z	4	
Density (calculated)	1.357 Mg/m ³	
Absorption coefficient	0.807 mm ⁻¹	
F(000)	1228	
Crystal size	0.10 x 0.03 x 0.03 mm ³	
Theta range for data collection	2.10 to 28.38°.	
Index ranges	$-26 \leq h \leq 26$, $-10 \leq k \leq 10$, $-24 \leq l \leq 24$	
Reflections collected	41198	
Independent reflections	7126 [$R_{int} = 0.0543$]	
Completeness to theta = 25.00°	100.0 %	
Max. and min. transmission	0.9762 and 0.9237	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7126 / 2 / 361	
Goodness-of-fit on F^2	1.044	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0304$, $wR2 = 0.0615$	
R indices (all data)	$R1 = 0.0381$, $wR2 = 0.0641$	
Absolute structure parameter	0.010(7)	
Largest diff. peak and hole	0.272 and -0.346 e.Å ⁻³	

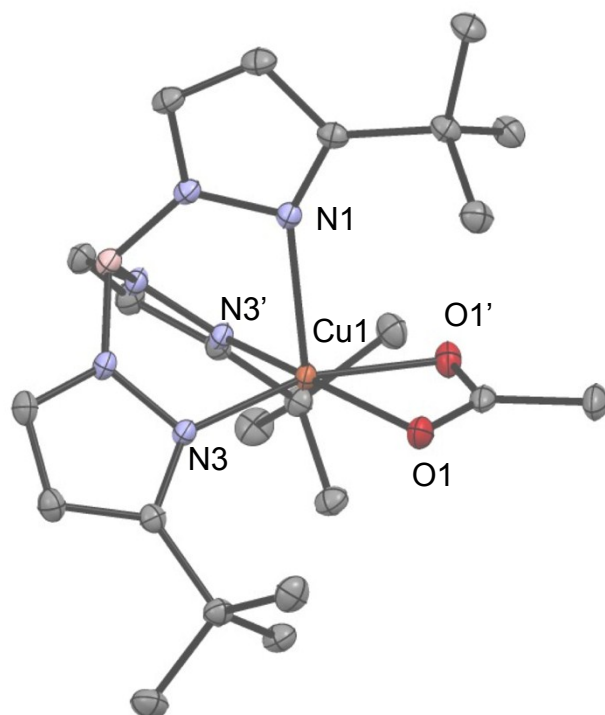
1.D. Crystallographic data for $Tp^{tBu}Cu^{II}-\kappa^2-OAc$ 

Figure S1. ORTEP of $Tp^{tBu}Cu^{II}-\kappa^2-OAc$ with select atom labels showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Table S4. Select bond lengths (Å) and angles (deg) of $Tp^{tBu}Cu^{II}-\kappa^2-OAc$

Primary Metal Coordination Sphere			
N1-Cu1	2.3580(15)	N3'-Cu1	1.9957(10)
N1'-Cu1	2.3580(15)	O1-Cu	2.0251(9)
N3-Cu1	1.9957(10)	O1'-Cu	2.0251(9)
N1-Cu-N3	92.75(4)	N1-Cu1-O1'	98.72(4)
N2-Zn1-N6	94.78(18)	N3-Cu1-N3'	91.94(6)
N1-Cu-N3'	92.75(4)	O1-Cu-O1'	64.81(5)
N1-Cu1-O1	98.72(4)		

General Procedure

A green prism, measuring 0.29 x 0.25 x 0.10 mm³ was mounted on a loop with oil. Data was collected at -173°C on a Bruker APEX II single crystal X-ray diffractometer, Mo-radiation.

Crystal-to-detector distance was 40 mm and exposure time was 10 seconds per frame for all sets. The scan width was 0.5°. Data collection was 100% complete to 25° in θ . A total of 83201 reflections were collected covering the indices, $h = -21$ to 21, $k = -20$ to 20, $l = -13$ to 13. 3313 reflections were symmetry independent and the $R_{int} = 0.0407$ indicated that the data was good (average quality 0.07). Indexing and unit cell refinement indicated a primitive orthorhombic lattice. The space group was found to be $Pnma$ (No.62).

The data was integrated and scaled using SAINT, SADABS within the APEX2 software package by Bruker.¹

Solution by direct methods (SHELXS, SIR97) produced a complete heavy atom phasing model consistent with the proposed structure. The structure was completed by difference Fourier synthesis with SHELXL97. Scattering factors are from Waasmaier and Kirfel.¹ Hydrogen atoms were placed in geometrically idealised positions and constrained to ride on their parent atoms with C---H distances in the range 0.95-1.00 Angstrom. Isotropic thermal parameters U_{eq} were fixed such that they were 1.2 U_{eq} of their parent atom U_{eq} for CH's and 1.5 U_{eq} of their parent atom U_{eq} in case of methyl groups. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares.

(1) Waasmaier, D.; Kirfel, A. *Acta. Cryst. A.* **1995**, 51, 416.

Table S5: Crystallographic data for Tp^tBuCu^{II}-OAc provided.

Empirical formula	C ₂₃ H ₃₇ BCuN ₆ O ₂	
Formula weight	503.94	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P n m a	
Unit cell dimensions	a = 15.964(3) Å	α = 90.000°.
	b = 15.477(3) Å	β = 90.000°.
	c = 10.284(2) Å	γ = 90.000°.
Volume	2540.9(8) Å ³	
Z	4	
Density (calculated)	1.317 Mg/m ³	
Absorption coefficient	0.891 mm ⁻¹	
F(000)	1068	
Crystal size	0.29 x 0.25 x 0.10 mm ³	
Theta range for data collection	2.36 to 28.49°.	
Index ranges	-21 ≤ h ≤ 21, -20 ≤ k ≤ 20, -13 ≤ l ≤ 13	
Reflections collected	83201	
Independent reflections	3313 [R(int) = 0.0407]	
Completeness to theta = 25.00°	100.0 %	
Max. and min. transmission	0.9162 and 0.7823	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3313 / 0 / 172	
Goodness-of-fit on F ²	1.048	
Final R indices [I > 2σ(I)]	R1 = 0.0232, wR2 = 0.0649	
R indices (all data)	R1 = 0.0248, wR2 = 0.0665	
Largest diff. peak and hole	0.400 and -0.413 e.Å ⁻³	

2. Optical Spectra of (1) and (3)

2.A. Optical Spectrum of (1)

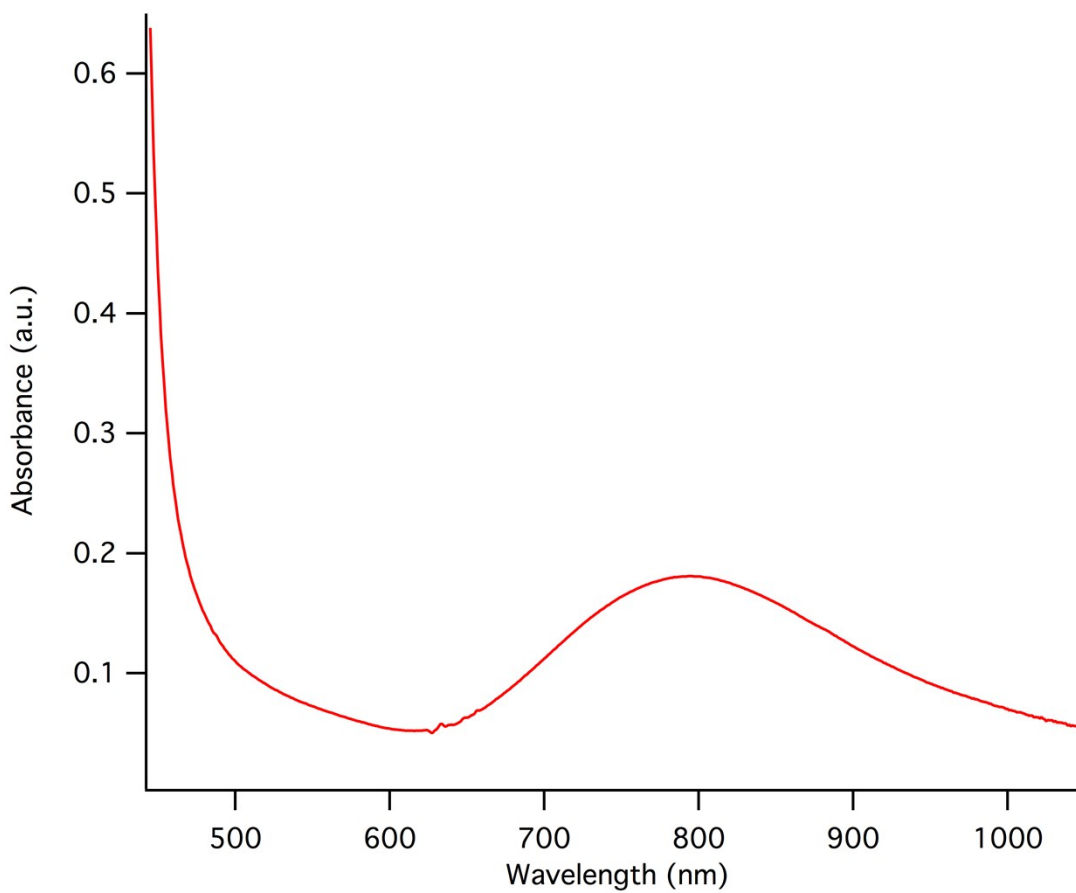


Figure S2. Optical spectrum of 1 mM (1) in benzene at room temperature. $\lambda_{\max} = 796$ nm (180 $M^{-1} \text{ cm}^{-1}$)

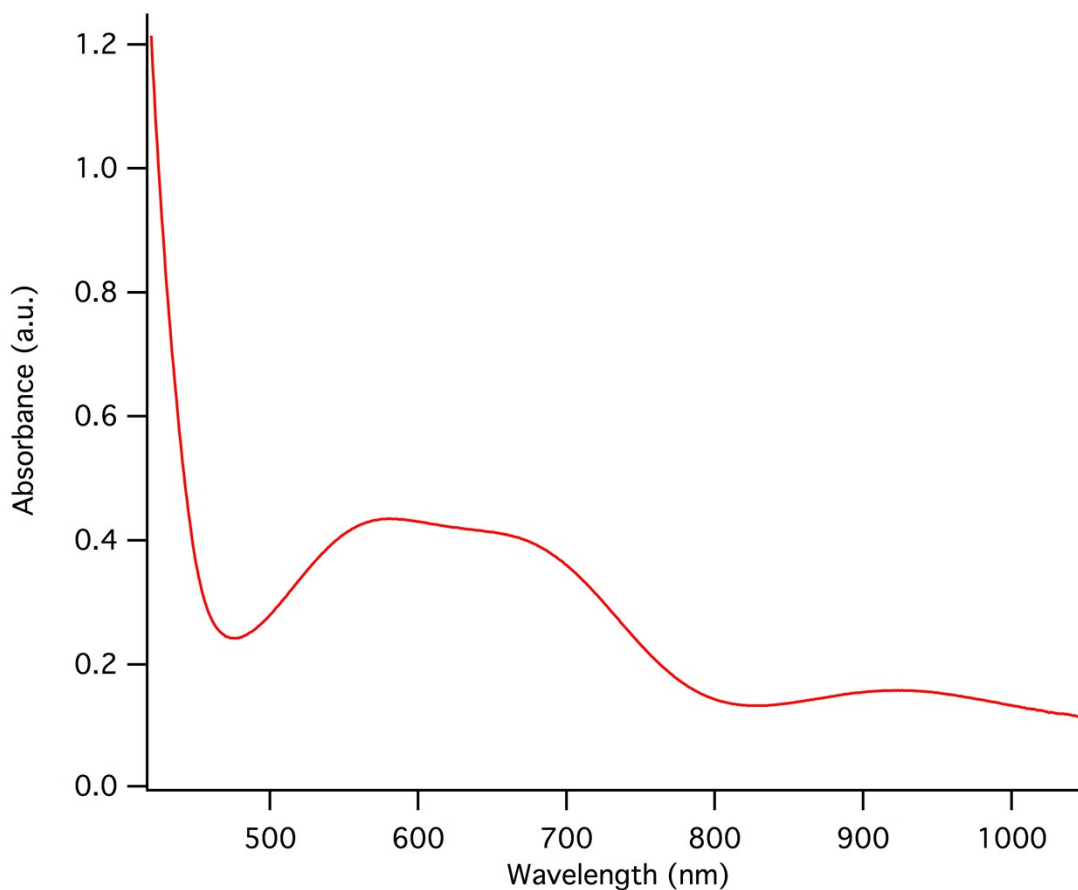
2.B. Optical Spectrum of (3)

Figure S3. Optical spectrum of 1 mM (3) in benzene at room temperature. $\lambda_{\max} = 583$ nm (430 $M^{-1} \text{ cm}^{-1}$), $\lambda_{\max} = 667$ nm (400 $M^{-1} \text{ cm}^{-1}$), $\lambda_{\max} = 830$ nm (130 $M^{-1} \text{ cm}^{-1}$).

3. 1H NMR Spectra of (1) and (3)

3.A. 1H NMR Spectrum of (1)

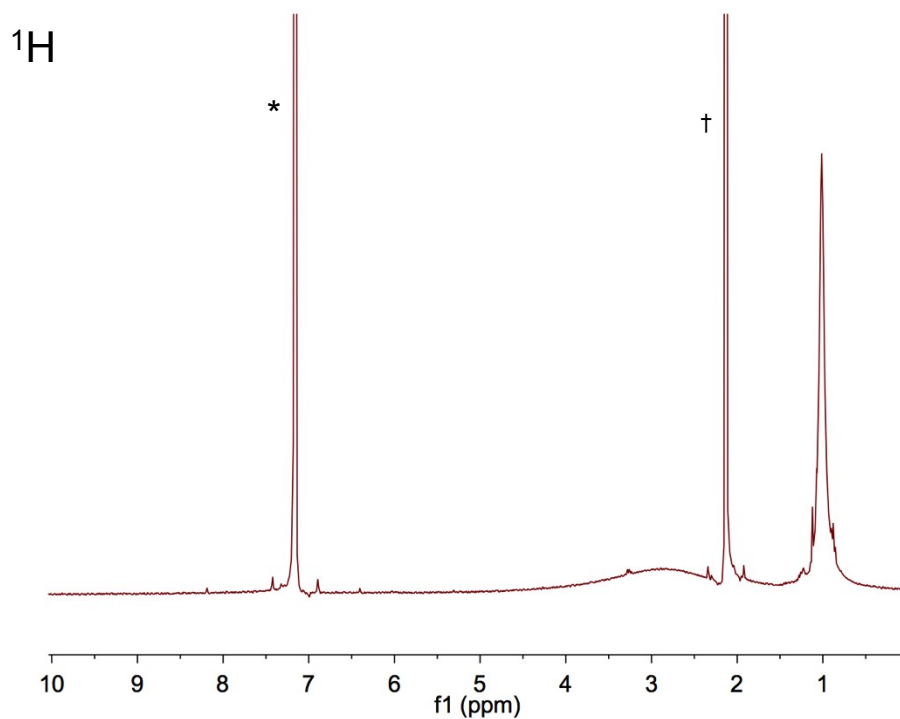


Figure S4. 1H NMR of (1) in benzene- d_6 . Signals for (1) are denoted with \dagger . Residual solvent signal and hexamethylbenzene internal standard are shown with * and \dagger , respectively.

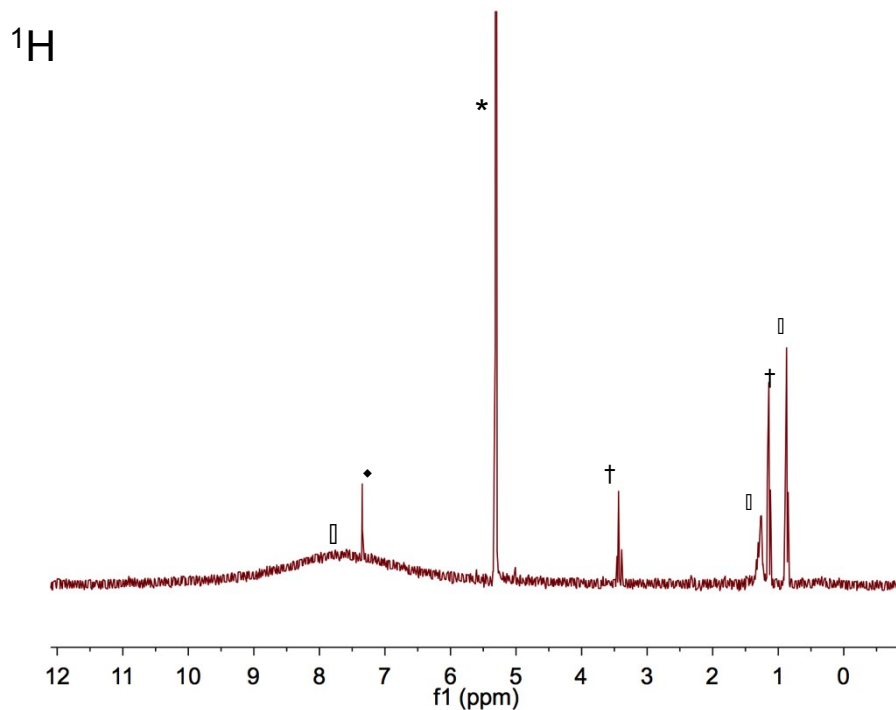
3.B. 1H NMR Spectrum of (3)

Figure S5. 1H NMR Spectrum of (3) in dichloromethane- d_2 . The broad feature of (3) is indicated by ✕. Residual solvent signal is shown by *. Signals from solvents used in synthesis and crystallizations are shown by ♦ (benzene), † (ether) and ★ (pentane).

4. Cyclic Voltammograms of (1) in Dichloromethane

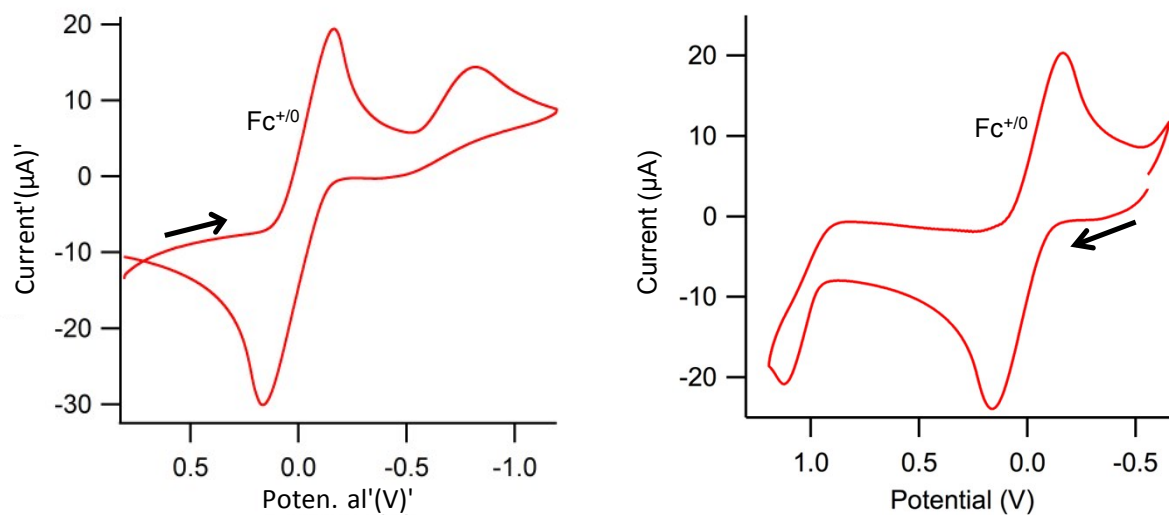


Figure S6. Cyclic Voltammograms of (1) (~1 mM) in dichloromethane with 0.1 mM $[nBu_4N][PF_6]$ with scan rate of 100 mV s^{-1} . Setup consisted of a 5 mm diameter glassy carbon working electrode and platinum auxiliary electrode. Potential is referenced to the ferrocene/ferrocenium internal standard. $E_{c,p} = -0.84 \pm 0.05\text{ V}$; $E_{a,p} = 1.10 \pm 0.05\text{ V}$; both vs. $Fc^{+/0}$.

5. 1H NMR of $\frac{1}{2} [Tp^{tBu}Cu^I]_2 + {}^tBu_2NParO^\bullet$ (No Reaction)

In a J. Young NMR tube, 14 mM $[Tp^{tBu}Cu^I]_2$ in benzene- d_6 was combined with 28 mM ${}^tBu_2NParO^\bullet$ (2,6-di-*tert*-butyl-4-(4'-nitrophenyl)phenoxy radical). After ~ 1 hour the 1H NMR spectrum of the reaction solution was collected. Overlay with the 1H NMR spectrum of untreated $[Tp^{tBu}Cu^I]_2$ shows no reaction occurs between $\frac{1}{2} [Tp^{tBu}Cu^I]_2$ and ${}^tBu_2NParO^\bullet$ under these conditions. It should be noted that the broad features arising from $[Tp^{tBu}Cu^I]_2$ are due to fluxional processes as previously reported.²

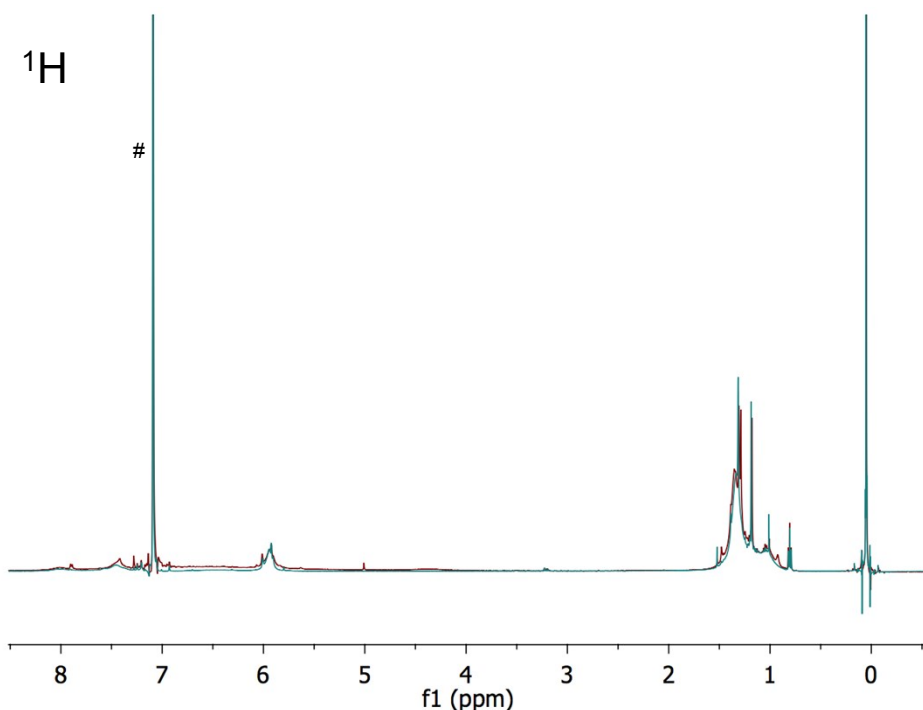
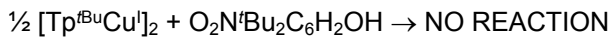


Figure S7. 1H NMR Spectrum of $\frac{1}{2} [Tp^{tBu}Cu^I]_2$ and ${}^tBu_2NParO^\bullet$ in benzene- d_6 (red) and 1H NMR spectrum of $[Tp^{tBu}Cu^I]_2$ in benzene- d_6 (turquoise). Additional sharp peaks observed in the spectrum of the former are due to diamagnetic impurities in ${}^tBu_2NParO^\bullet$ while the baseline discrepancy between ~ 8 and 5.5 ppm is due to the broad signal associated with ${}^tBu_2NParO^\bullet$. Residual solvent signal is denoted with #.

(2) Carrier, S. M.; Ruggiero, C. E.; Houser, R. P.; Tolman, W. B. *Inorg. Chem.* **1993**, 32, 4889.

6. 1H NMR of $\frac{1}{2} [Tp^{tBu}Cu^I]_2 + O_2N^tBu_2C_6H_2OH$ (No Reaction)

In a J. Young NMR tube, 2.5 mM $[Tp^{tBu}Cu^I]_2$ in toluene- d_8 was combined with 5 mM $O_2N^tBu_2C_6H_2OH$. After ~ 1 hour the 1H NMR spectrum of the reaction solution was collected. Overlay with the 1H NMR spectrum of untreated $[Tp^{tBu}Cu^I]_2$ shows no reaction occurs between $\frac{1}{2} [Tp^{tBu}Cu^I]_2$ and $O_2N^tBu_2C_6H_2OH$ under these conditions.

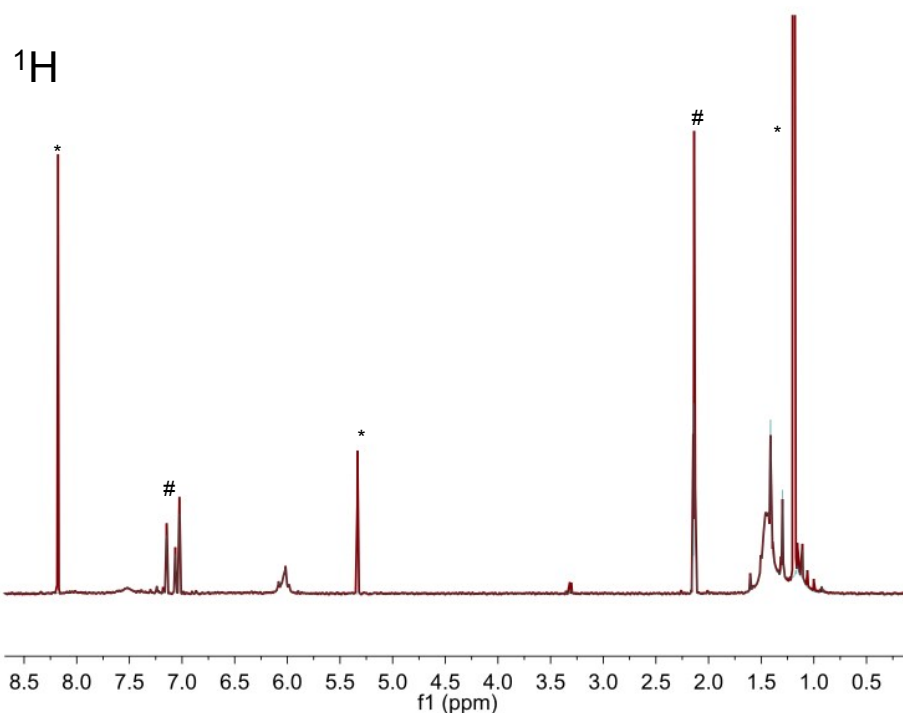
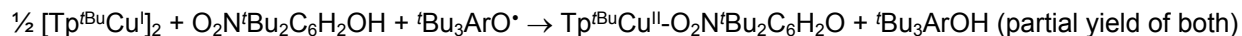


Figure S8. 1H NMR Spectrum of $\frac{1}{2} [Tp^{tBu}Cu^I]_2$ and $O_2N^tBu_2C_6H_2OH$ in toluene- d_8 (red) and 1H NMR spectrum of $[Tp^{tBu}Cu^I]_2$ in toluene- d_8 (turquoise). $O_2N^tBu_2C_6H_2OH$ is show with * and the residual solvent peaks are denoted with #.

7. Optical and ¹H NMR Data for the Completed Reaction Between ½ [Tp^tBuCu^I]₂, O₂N^tBu₂C₆H₂OH and ^tBu₃ArO[•]



In a J. Young NMR tube, 6 mM [Tp^tBuCu^I]₂ in benzene-*d*₆ containing hexamethylbenzene as an internal standard was combined with 12 mM O₂N^tBu₂C₆H₂OH followed by 12 mM ^tBu₃ArO[•]. After ~ 3 hours the ¹H NMR spectrum showed the appearance of Tp^tBuCu^{II}O₂N^tBu₂C₆H₂O and ^tBu₃ArO–H in ~50 and 80% respectively. Approximately 40% of O₂N^tBu₂C₆H₂O–H remained at the end of the reaction.

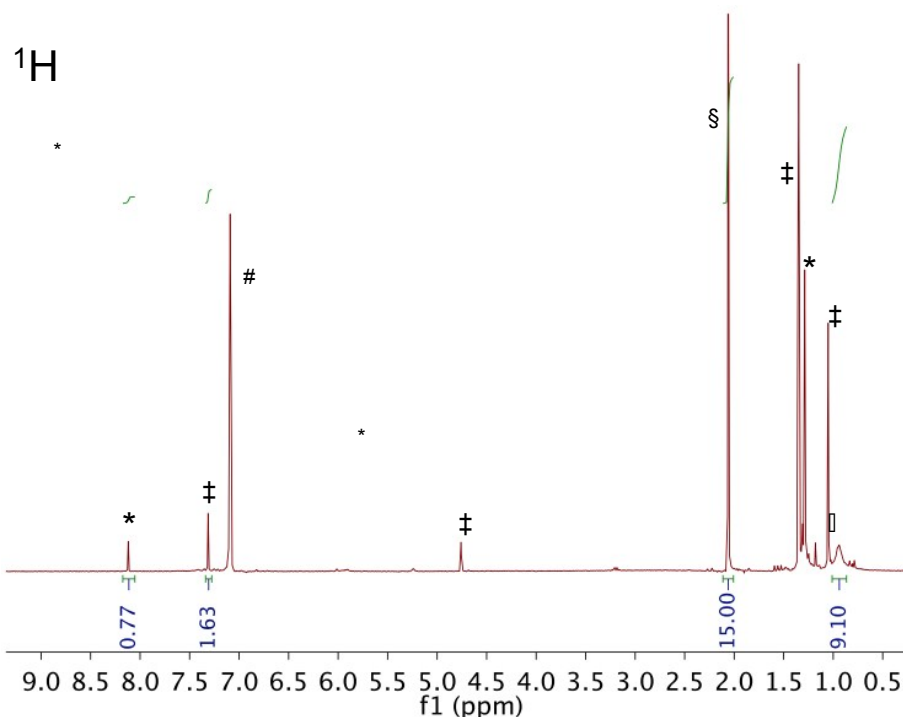


Figure S9. ¹H NMR Spectrum of the completed reaction between ½ [Tp^tBuCu^I]₂, O₂N^tBu₂C₆H₂OH and ^tBu₃ArO[•] in benzene-*d*₆. Tp^tBuCu^{II}-ON₂^tBu₃C₆H₂O is shown with ★, ^tBu₃ArO–H is shown with ‡, and O₂N^tBu₂C₆H₂OH is shown with *. The residual solvent peak and hexamethylbenzene are denoted by # and §, respectively.

To a 1 cm quartz cuvette containing $[\text{Tp}^{\text{tBu}}\text{Cu}^{\text{I}}]_2$ and $\text{O}_2\text{N}^{\text{tBu}}\text{C}_6\text{H}_2\text{OH}$ in benzene was added $^{\text{tBu}}\text{Bu}_3\text{ArO}^{\bullet}$ through a gastight septum via a gastight syringe (final concentration of all species was 2.5 mM, 5 mM and 5 mM, respectively). The reaction reached completion after ~ 1 hour as determined by UV/Vis spectroscopy (see main text Figure 2). Overlay of the spectrum of the completed reaction with a spectrum of independently prepared $\text{Tp}^{\text{tBu}}\text{Cu}^{\text{II}}\text{-O}_2\text{N}^{\text{tBu}}\text{C}_6\text{H}_2\text{O}$ (normalized at 800 nm) shows $\text{Tp}^{\text{tBu}}\text{Cu}^{\text{II}}\text{-O}_2\text{N}^{\text{tBu}}\text{C}_6\text{H}_2\text{O}$ was generated in roughly 60% yield.

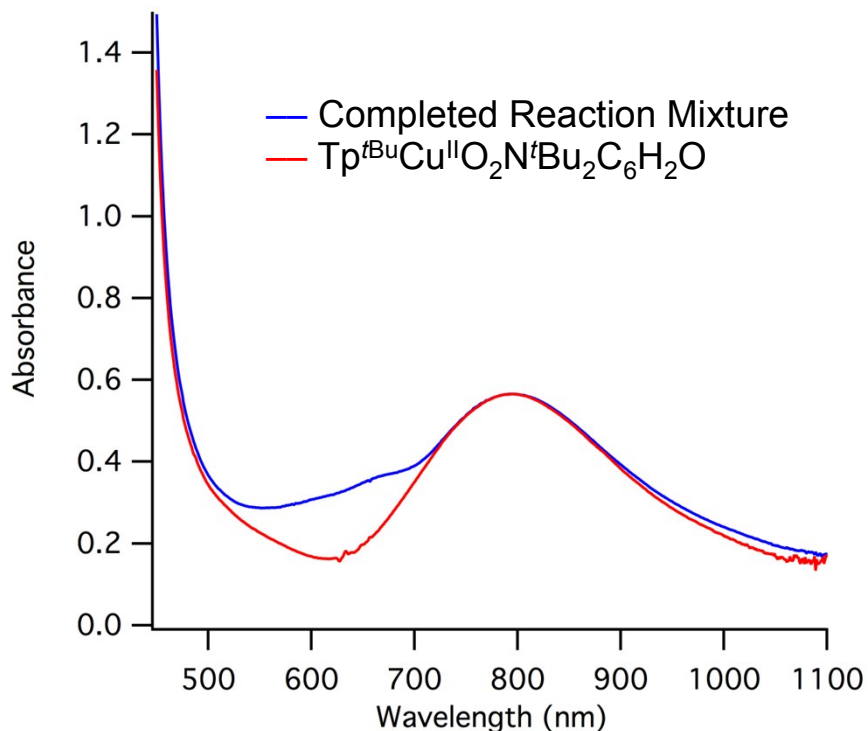
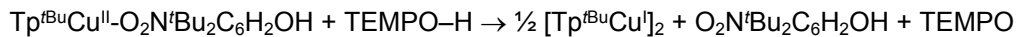


Figure S10. Optical spectrum of the completed reaction between 2.5 mM $[\text{Tp}^{\text{tBu}}\text{Cu}^{\text{I}}]_2$, 5 mM $\text{O}_2\text{N}^{\text{tBu}}\text{C}_6\text{H}_2\text{O-H}$ and 5 mM $^{\text{tBu}}\text{Bu}_3\text{ArO}^{\bullet}$ in benzene (blue). Overlay (red) shows the spectrum of independently prepared $\text{Tp}^{\text{tBu}}\text{Cu}^{\text{II}}\text{-O}_2\text{N}^{\text{tBu}}\text{C}_6\text{H}_2\text{O}$ in benzene normalized to match the intensity of the peak observed in the reaction mixture at 800 nm.

8. 1H NMR of $Tp^{tBu}Cu^{II}O_2N^tBu_2C_6H_2O + TEMPO-H$



In a J. Young NMR tube, 12 mM $Tp^{tBu}Cu^{II}-O_2N^tBu_2C_6H_2OH$ in benzene- d_6 was combined with 12 mM TEMPO-H. After ~ 1 hour, the solution had changed colors from dark blue-green to light pink. The 1H NMR spectrum displayed signals for $[Tp^{tBu}Cu^I]_2$ as well as $O_2N^tBu_2C_6H_2O-H$. Integration vs a hexamethylbenzene internal standard indicates the reactants were converted to products in quantitative yield.

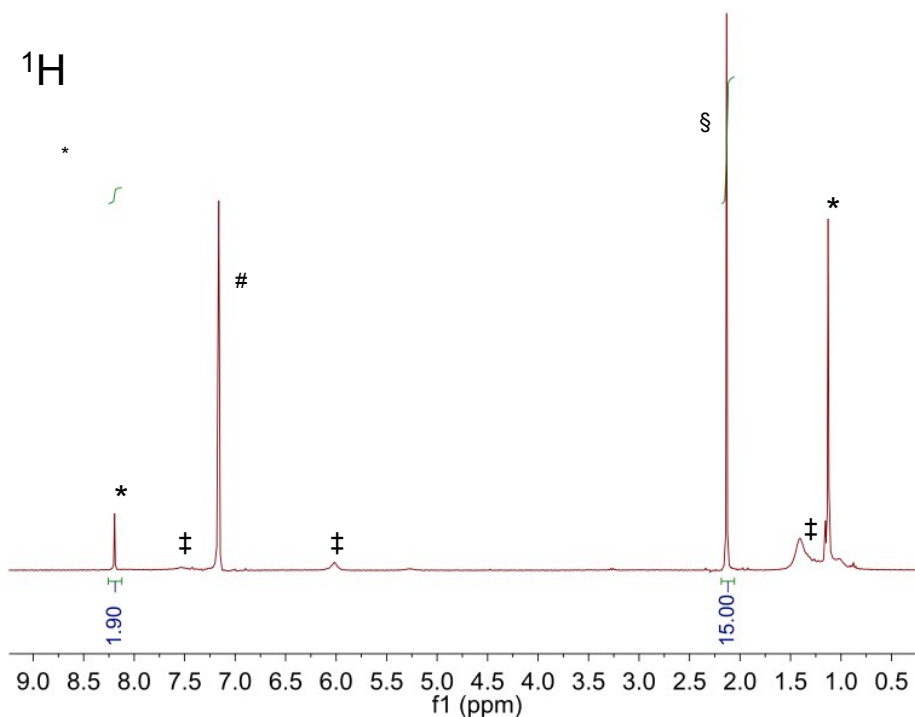


Figure S11. 1H NMR spectrum of the completed reaction between $Tp^{tBu}Cu^{II}-ON_2^tBu_3C_6H_2O$ and TEMPO-H generating $\frac{1}{2}[Tp^{tBu}Cu^I]_2$, $O_2N^tBu_2C_6H_2O-H$ and TEMPO. $[Tp^{tBu}Cu^I]_2$ is shown with ‡, and $O_2N^tBu_2C_6H_2OH$ is shown with *. The residual solvent peak and hexamethylbenzene are denoted by # and §, respectively.