

# Predicting Electrocatalytic Properties: Modeling Structure-Activity Relationships of Nitroxyl Radicals.

## Supporting Information

David P. Hickey<sup>a†</sup>, David A. Schiedler<sup>a†</sup>, Ivana Matanovic<sup>b,c</sup>, Phuong Vy Doan<sup>a</sup>, Plamen Atanassov<sup>b</sup>, Shelley D. Minteer<sup>a\*</sup>, Matthew S. Sigman<sup>a\*</sup>

<sup>a</sup>Department of Chemistry, University of Utah, Salt Lake City, Utah, 84112

<sup>b</sup>Department of Chemical & Biological Engineering, University of New Mexico, Albuquerque, New Mexico, 87131

<sup>c</sup>Theoretical Division, Los Alamos National Laboratory, LosAlamos, NM, 87545

\*[sigman@chem.utah.edu](mailto:sigman@chem.utah.edu)

\*[minteer@chem.utah.edu](mailto:minteer@chem.utah.edu)

## 1 MATERIALS AND METHODS

### 1.1 Materials

All chemicals, including TEMPO, 4-oxo-TEMPO, 4-methoxy-TEMPO, 4-hydroxy-TEMPO, 4-carboxy-TEMPO, 4-acetamido-TEMPO, 4-amino-TEMPO, 4-amino-4-carboxy-TEMPO, ABNO, AZADO, and 2-methyl-AZADO were purchased from Sigma and used without further purification.

### 1.2 Synthesis and Characterization

All reactions were carried out under an inert N<sub>2</sub> atmosphere in oven-dried glassware. Flash column chromatography was carried out with SiliaFlash F60, 40-63 µm silica gel. Reactions and column chromatography were monitored with EMD-Millipore silica gel 60 F254 aluminum-backed plates and visualized with potassium permanganate, iodine, or vanillin stains. Toluene (PhMe) and methylene chloride (DCM), diethyl ether (Et<sub>2</sub>O), acetonitrile (MeCN), and tetrahydrofuran (THF) were dried by passage through activated alumina columns. All other reagents and solvents were used without further purification from commercial sources.

Instrumentation: Proton and carbon NMR spectra (<sup>1</sup>H NMR and <sup>13</sup>C NMR) were recorded in deuterated chloroform (CDCl<sub>3</sub>) unless otherwise specified using a Varian VXR 500 MHz, Varian Inova 400 MHz, or Varian Unity 300 MHz spectrometer and calibrated to residual solvent signals. Multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, spt = septet, br = broad, m = multiplet. Melting points were determined with a Thomas Hoover capillary melting point apparatus and are uncorrected. IR spectra were recorded

using a Thermo Nicolet FT-IR. High resolution mass spectrometry (HRMS) data were obtained on a Waters LCP Premier XE instrument by ESI/TOF.

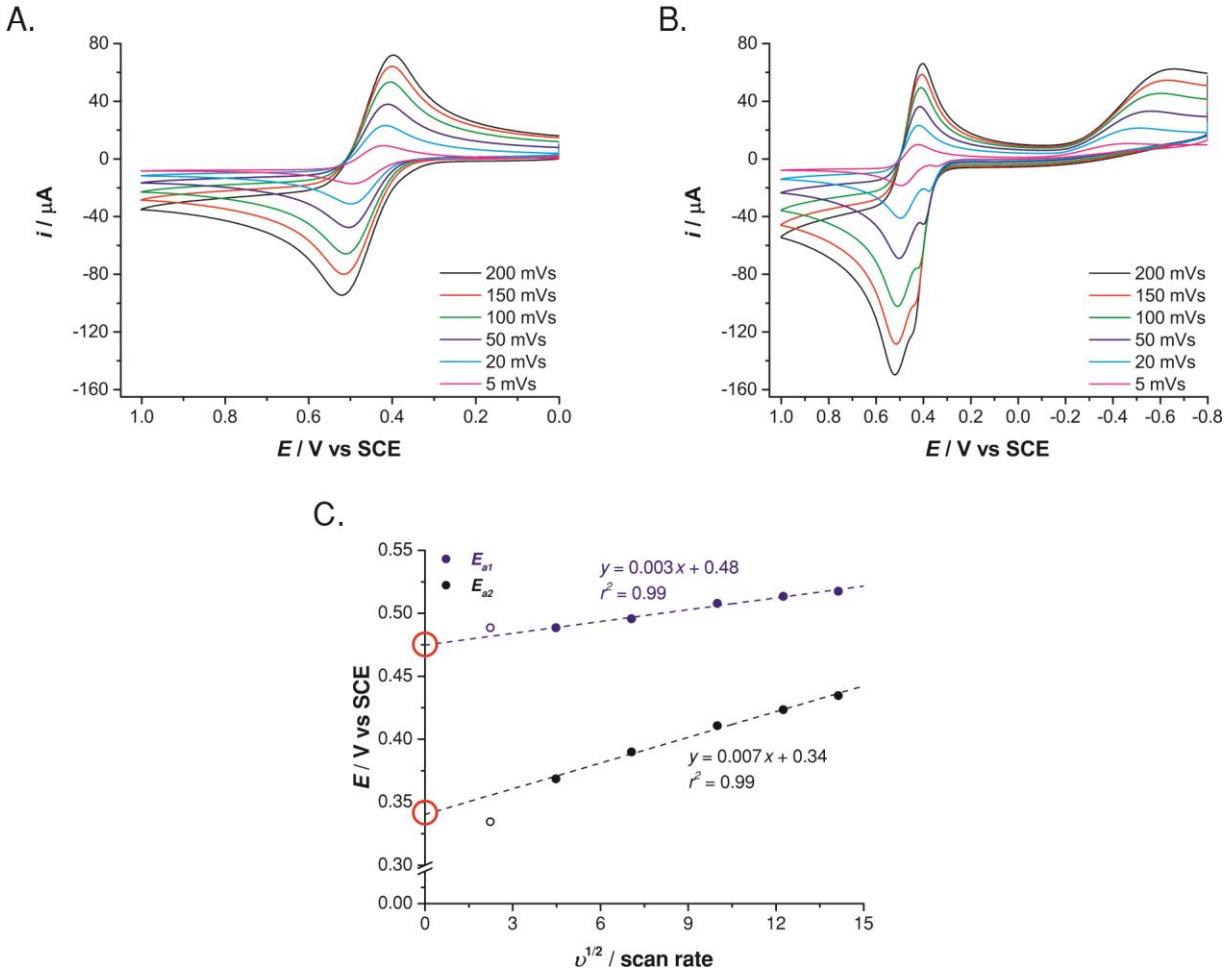
### 1.3 Electrochemical Characterization

All electrochemical experiments were performed using a Bio-Logic VSP potentiostat with a standard three-electrode cell including a 3 mm glassy carbon working electrode, a saturated calomel reference electrode, and a Pt mesh counter electrode. All electrochemical experiments were performed using quiescent solutions of 5 mM TEMPO derivative in 150 mM Robinson buffer consisting of equal parts phosphate, acetate, and borate at 25 °C. Concentrated NaOH was added to each buffer to result in the desired pH. Values for  $E_{a1}$  and  $E_{a2}$  were determined by measuring the peak oxidation at scan rates of 200 mV s<sup>-1</sup>, 150 mV s<sup>-1</sup>, 100 mV s<sup>-1</sup>, 50 mV s<sup>-1</sup>, 20 mV s<sup>-1</sup> and 5 mV s<sup>-1</sup>, and extrapolating to 0 mV s<sup>-1</sup> to determine the absolute thermodynamic potential. The catalytic activity of each nitroxyl radical species was determined by measuring their corresponding CVs in the presence of 0 mM, 50 mM, 100 mM, 300 mM, 500 mM, 750 mM, and 1000 mM glycerol at 10 mV s<sup>-1</sup>, from 0 V to 1 V vs SCE at 25 °C. The catalytic activity was measured either in terms of catalytic current density ( $j_{max}$ ), or the ratio of the peak oxidative catalytic current divided by the peak reductive catalytic current ( $i_{pa}/i_{pc}$ )<sub>cat</sub>. Catalytic current density,  $j_{max}$ , is defined as the difference in current density of the nitroxyl radical species in presence and absence of glycerol at 1 V, while ( $i_{pa}/i_{pc}$ )<sub>cat</sub> is defined as the difference in the peak current ratios of a nitroxyl radical species in the presence and absence of glycerol (i.e.  $(i_{pa}/i_{pc})_{with\ glycerol} - (i_{pa}/i_{pc})_{without\ glycerol}$ ).

## 2 EXPERIMENTAL TECHNIQUES AND EQUATIONS

### 2.1 Peak Assignments and Determination of $E_{a1}$ and $E_{a2}$

The peak assignments for  $E_{a1}$  and  $E_{a2}$  were determined by standard cyclic voltammetry (CV) with a delay at -0.8 V vs SCE. The resulting CVs were compared to CVs performed using a narrower potential window (from 0 V to 1.0 V vs. SCE). Example CVs of AZADO (Figure S2.1) with both potential ranges contain a reversible redox couple corresponding to the reversible oxidation/reduction of  $\mathbf{T^*/T^+}$ , while only the CV with an expanded window (-0.8 V to 1.0 V vs SCE) contains an irreversible oxidation peak and an irreversible reduction peak. These two electrochemically irreversible peaks are attributed to the reduction of  $\mathbf{T^*}$  to  $\mathbf{T^-}$ , which is immediately followed by a protonation step, and the oxidation of  $\mathbf{TH}$  to  $\mathbf{T^*}$ , which is coupled to a deprotonation step. The ground state of AZADO is the radical  $\mathbf{T^*}$  species, and thus the oxidation of  $\mathbf{TH}$  to  $\mathbf{T^*}$  is only observed for CVs in which the potential is sufficiently low to electrochemically generate the  $\mathbf{TH}$  species. Both  $E_{a1}$  and  $E_{a2}$  were observed to be linearly dependent on the square root of the scan rate; however,  $E_{a2}$  is lower than the expected value at slow scan rates (i.e. at 5 mV s<sup>-1</sup>) due to diffusion of the  $\mathbf{TH}$  species away from the electrode. In order to account for such diffusional effects and define consistent potentials for each nitroxyl radical analogue, all  $E_a$  values used throughout the manuscript were derived by extrapolating oxidation potentials to 0 mV s<sup>-1</sup>.<sup>1,2</sup>



**Figure S2.1.** Example of the procedure used to determine values of  $E_{a1}$  and  $E_{a2}$ . CVs of AZADO starting at (A) 0 V so that the reduced TH species does not build up and  $E_{a2}$  is not observed, and (B) starting at -0.8 V so that TH is produced near the electrode surface and subsequently  $E_{a2}$  is observed. (C) Extrapolations of both  $E_{a1}$  and  $E_{a2}$  as a function of the square root of the scan rate were used to determine the theoretical non-diffusion limited oxidation potentials.

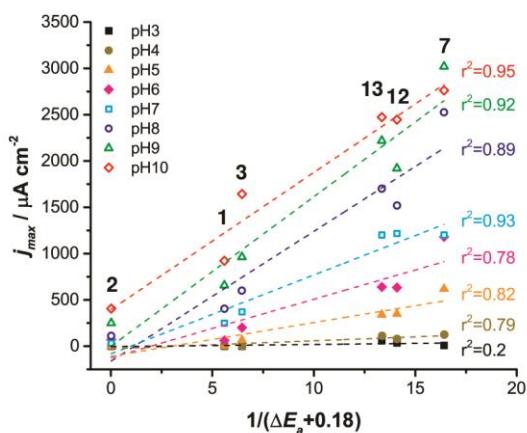
Additionally, CVs were performed at various scan rates to determine the nature of the electron transfer processes involved with each oxidation peak. The peak oxidative current ( $i_{pa}$ ) for both  $E_{a1}$  and  $E_{a2}$  exhibit a linear correlation with the square root of the scan rate, which is characteristic of diffusion-limited electron transfer (i.e. one involving a homogeneous redox species). This suggest that all of the species studied are both water soluble and homogeneously solvated.

## 2.2 Application of Activity Model at Various pH

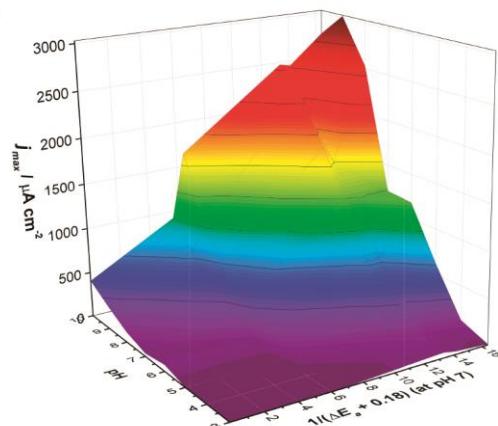
Stable nitroxyl radical catalysts are used under a variety of pH conditions, however the model described in this work was derived at pH 7. Therefore, as a preliminary effort, we tested the ability of the experimental model to predict the relative activity of a small subset of catalysts at a wide pH range. Using the relative activity of each nitroxyl radical catalyst at pH 7 (quantified by

the corresponding values of  $(\Delta E_a - 0.18)^{-1}$ ), the catalytic activity of structures **1**, **2**, **3**, **7**, **12**, and **13** were compared under pH conditions ranging from three to ten (Figure S2.2).

A.



B.

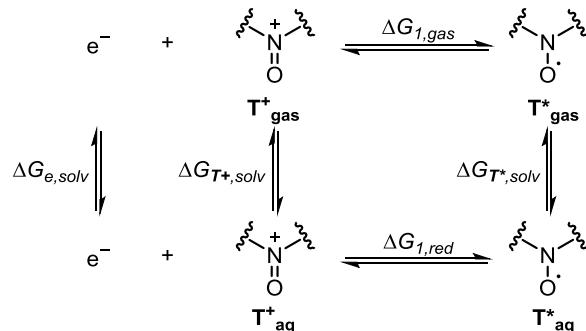


**Figure S2.2.** Activity-pH profiles for a small subset of nitroxyl radical catalysts in which each pH is represented by a different shape (A), and the corresponding three-dimensional representation of the same activity-pH profile (B).

The relative activity of each nitroxyl radical catalyst is demonstrated to scale with pH, thus indicating that the relative catalytic activity calculated at pH 7 should provide a good approximation of the activity under aqueous conditions at any pH. While the initial findings are compelling, further investigations are needed to confirm this trend across a wider range of nitroxyl radical catalysts.

### 2.3 Derivation of Modified Nernst Kinetics

Oxidation potentials for  $E_{a1}$  were computationally determined using the free energy cycle for the reduction of  $\mathbf{T}^+$  to  $\mathbf{T}^*$  as previously described.<sup>3</sup> As a general procedure, the geometries for  $\mathbf{T}^*$  and  $\mathbf{T}^+$  were optimized using an aqueous CPCM solvation model as described below; the corresponding free energies for each structure ( $G_{T^*}^o$  and  $G_{T^+}^o$ , respectively) were used to determine the change in free energy ( $\Delta G_{red}$ ) and reversible redox potential ( $E_{1/2}^o$ ) for the reduction reaction by;



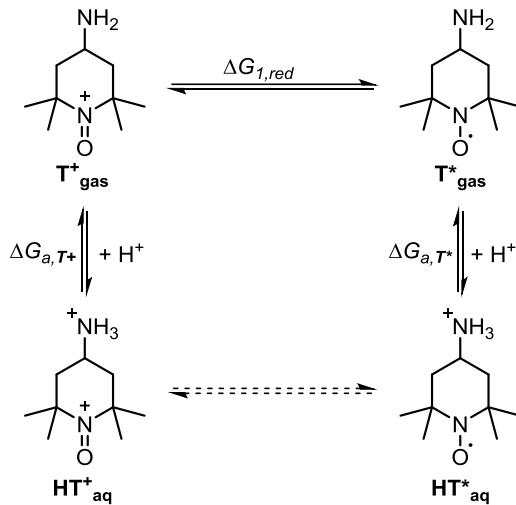
Where

$$(1) \quad \Delta G_{1,red} = \Delta G_{1,gas} + \Delta G_{T^*,solv} - \Delta G_{e,solv} - \Delta G_{T^+,solv}$$

$$(2) \quad E_{a1}^o = -\frac{\Delta G_{1,red}}{nF}$$

$$(3) \quad E_{a1} = E_{a1}^o - 4.684$$

And  $n$  is the number of electrons transferred,  $F$  is Faraday's constant, and the conversion factor (-4.684) is a reference term to set all potentials versus SCE. For species that contain an ionizable functional group (most commonly an amine), an additional equilibrium term was added to the standard Nernst equation to account for multiple protonation states. The resulting equation is described using 4-amino-TEMPO as an example;



$$(4) \quad K_{a,T^+} = \frac{[\text{T}^+][\text{H}^+]}{[\text{HT}^+]} = \exp\left(-\frac{\Delta G_{a,T^+}}{RT}\right)$$

$$(5) \quad K_{a,T^*} = \frac{[\text{T}^*][\text{H}^+]}{[\text{HT}^*]} = \exp\left(-\frac{\Delta G_{a,T^*}}{RT}\right)$$

Where  $R$  is the gas constant and  $T$  is the absolute temperature (for all calculations here,  $T$  is assumed to be 298.15 K). Assuming that the total concentration of  $\text{T}^*$  and  $\text{T}^+$  ( $[\text{T}^*]_{\text{tot}}$  and  $[\text{T}^+]_{\text{tot}}$ , respectively) can be described by;

$$(6) \quad [\text{T}^*]_{\text{tot}} = [\text{T}^*] + [\text{HT}^*]$$

$$(7) \quad [\text{T}^+]_{\text{tot}} = [\text{T}^+] + [\text{HT}^+]$$

Then the standard Nernst equation (8) can be rewritten as;

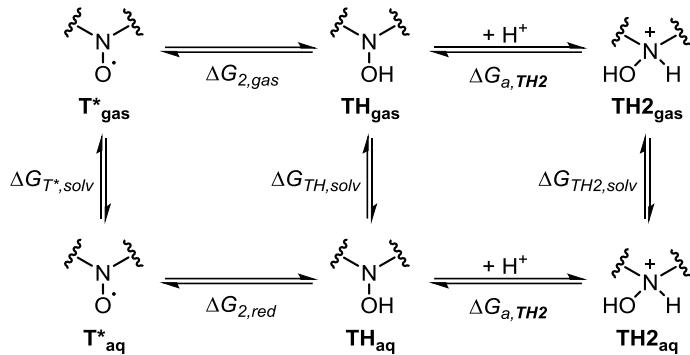
$$(8) \quad E_{a1} = E_{a1}^o + \frac{RT}{nF} \ln\left(\frac{[\text{T}^+]}{[\text{T}^*]}\right)$$

$$(9) \quad E_{a1} = E_{a1}^o + \frac{RT}{nF} \ln\left(1 + \frac{[\text{H}^+]}{K_{a,T^*}}\right) - \frac{RT}{nF} \ln\left(1 + \frac{[\text{H}^+]}{K_{a,T^+}}\right) + \frac{RT}{nF} \ln\left(\frac{[\text{T}^*]_{\text{tot}}}{[\text{T}^+]_{\text{tot}}}\right)$$

And if the diffusion constants for  $\text{T}^*$  and  $\text{T}^+$  are approximately equal, then equation 9 becomes;

$$(10) \quad E_{a1} = E_{a1}^o + \frac{RT}{nF} \ln \left( 1 + \frac{[H^+]}{K_{a,T^*}} \right) - \frac{RT}{nF} \ln \left( 1 + \frac{[H^+]}{K_{a,TH^+}} \right)$$

Values of  $E_{a2}$  were computed using a method similar to that for computing  $E_{a1}$  as previously reported.<sup>4</sup> However, here existing methods for predicting  $E_{a2}$  do not account for any protonation dynamics. To compensate for multiple protonation states of  $\mathbf{T}^*$ , we first assumed the protonation of  $\mathbf{T}^*$  to  $\mathbf{TH}$  to be rapid and therefore the effective concentration of  $\mathbf{T}^*$  at any point is effectively zero. The resulting equilibrium can then be described by the free energy cycle;



While  $E_{a1}$  is electrochemically reversible and is therefore analogous to the corresponding oxidation potential,  $E_{a2}$  is not electrochemically reversible. Therefore, the  $E_{a2}$  was calculated from the free energy cycle corresponding to the oxidation of  $\mathbf{TH}$  to  $\mathbf{T}^*$  by;

$$(11) \quad \Delta G_{2,ox} = -\Delta G_{2,gas} + \Delta G_{T^*,solv} - \Delta G_{TH,solv} - \Delta G_{H^+,solv}$$

$$(12) \quad E_{a2}^o = -\frac{\Delta G_{2,ox}}{nF}$$

And, as above, the acid dissociation equilibrium can be described by;

$$(13) \quad K_{a,TH2} = \exp \left( -\frac{\Delta G_{a,TH2} + \Delta G_{H^+}}{RT} \right)$$

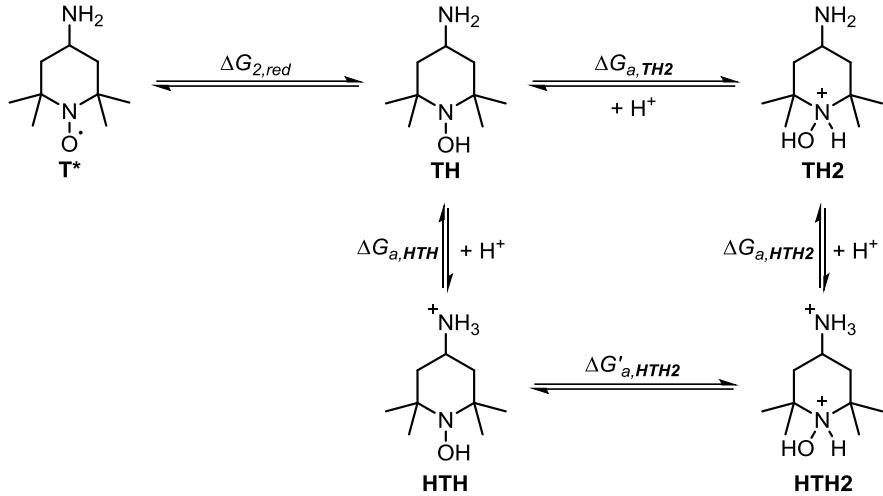
Incorporating the acid dissociation equilibrium into the standard Nernst equation;

$$(14) \quad E_{a2} = E_{a2}^o - \frac{RT}{nF} \ln \left( \frac{[T^*]}{[TH]} \right)$$

Becomes

$$(15) \quad E_{a2} = E_{a2}^o - \frac{RT}{nF} \ln \left( 1 + \frac{[H^+]}{K_{a,TH2}} \right)$$

Finally, values of  $E_{a2}$  for nitroxyl radical compounds containing an ionizable substituent were calculated using a similar treatment as described above, in which the following square mechanism is described (again using 4-amino-TEMPO as an example compound);



Where the corresponding acid dissociation constants can be described as;

$$(16) \quad K_{a,HTH} = \frac{[TH][H^+]}{[HTH]} = \exp\left(-\frac{\Delta G_{a,HTH} + \Delta G_{H^+}}{RT}\right)$$

$$(17) \quad K_{a,HTH2} = \frac{[TH2][H^+]}{[HTH2]} = \exp\left(-\frac{\Delta G_{a,HTH2} + \Delta G_{H^+}}{RT}\right)$$

Then, assuming that the total concentration of **TH** ( $[TH]_{tot}$ ) can be described as;

$$(18) \quad [TH]_{tot} = [TH] + [TH2] + [HTH] + [HTH2]$$

Equation 14 can be rewritten as;

$$(19) \quad E_{a2} = E_{a2}^o - \frac{RT}{nF} \ln \left( 1 + \frac{[H^+]}{K_{a,TH}} + [H^+] K_{a,HTH} + \frac{[H^+]^2}{K'_{a,HTH2} K_{a,HTH}} \right) + \frac{RT}{nF} \ln \left( 1 + \frac{[H^+]}{K_{a,HTH2}} \right) + \frac{RT}{nF} \ln \left( \frac{[T^*]_{tot}}{[TH]_{tot}} \right)$$

And when the diffusion constants for **T\*** and **TH** are approximately equivalent, equation 19 is condensed to;

$$(20) \quad E_{a2} = E_{a2}^o - \frac{RT}{nF} \ln \left( 1 + \frac{[H^+]}{K_{a,TH}} + [H^+] K_{a,HTH} + \frac{[H^+]^2}{K'_{a,HTH2} K_{a,HTH}} \right) + \frac{RT}{nF} \ln \left( 1 + \frac{[H^+]}{K_{a,HTH2}} \right)$$

## 2.4 Optimization of Computational Level of Theory and Basis Set

In order to identify optimal computational approach for the calculation of standard redox potentials of different TEMPOs we compared Density Functional Theory (DFT) with B3LYP functional<sup>5-8</sup> and second order Møller-Plesset perturbation theory (MP2)<sup>9-12</sup> in combination with different basis sets and solvation models (Table S2.1 – Table S2.4). Solvation models that were tested included Polarizable Continuum (PCM) model<sup>13-16</sup>, CPCM polarizable conductor calculation model<sup>14,17</sup> and Truhlar and coworkers' SMD solvation model<sup>18</sup> as implemented by Gaussian 09 code.<sup>19</sup> Calculated standard redox potentials were expressed relative to the saturated calomel electrode (SCE) by subtracting 4.684 V. The correction includes experimental value of the absolute standard hydrogen electrode potential of 4.44 V and the conversion between the standard hydrogen electrode and the saturated calomel electrode of 0.244 eV.<sup>20</sup> When calculated values in Tables S2.1-S2.4 were compared to the experimentally determined values, B3LYP functional with 6-31+G(d,p) basis set and CPCM solvation model was proven to provide the best tradeoff between the accuracy and the computational time.

**Table S2.1. Standard redox potentials of TEMPO vs SCE in V ( $E_{a1}$ ) calculated using different levels of theory, basis sets, and solvation models.**

Level of Theory	$E^{\circ} / V$
B3LYP/6-31G(d), PCM	0.379
B3LYP/6-31G(d), CPCM	0.380
B3LYP/6-31G(d), SMD	0.147
B3LYP/6-31+G(d,p), PCM	0.616
B3LYP/6-31+G(d,p), CPCM	0.618
B3LYP/6-31+G(d,p), SMD	0.383
MP2/6-31G(d), PCM	-0.182
MP2/6-31+G(d), PCM	0.113
MP2/6-31+G(d), CPCM	0.125
MP2/6-31+G(d), SMD	-0.140
MP2/6-31++G(d), PCM	0.098
MP2/6-31++G(d), SMD	-0.152
Experimental	0.499

**Table S2.2. Standard redox potentials of different TEMPOs vs SCE in V ( $E_{a1}$ ) calculated using different levels of theory – DFT and MP2 comparison. \*Computational analysis for TEMPO-COOH did not converge under these conditions.**

	B3LYP/6-31+G(d,p), CPCM	MP2/6-311++G(d,p), PCM
TEMPO	0.618	0.098
TEMPO-NH <sub>2</sub>	0.681	0.152
TEMPO-OH	0.701	0.181
TEMPO-COOH	0.734	DNC*
oxo-TEMPO	0.902	0.318
AZADO	0.517	0.010
ABNO	0.548	0.021

**Table S2.3.** Standard redox potentials of different TEMPO vs SCE in V ( $E_{a1}$ ) calculated using B3LYP/6-31G(d) level of theory and PCM, CPCM, and SMD solvation models.

	B3LYP/6-31G(d), CPCM	B3LYP/6-31G(d), CPCM	B3LYP/6-31G(d), CPCM
TEMPO	0.379	0.380	0.147
TEMPO-NH <sub>2</sub>	0.433	0.430	0.214
TEMPO-NH <sub>3</sub> <sup>+</sup>	0.772	0.768	0.409
TEMPO-OH	0.434	0.436	0.216
TEMPO-COOH	0.497	0.494	0.251
TEMPO-COO <sup>-</sup>	0.227	0.210	0.096
oxo-TEMPO	0.657	0.659	0.361
AZADO	0.249	0.250	0.055
ABNO	0.268	0.277	0.071

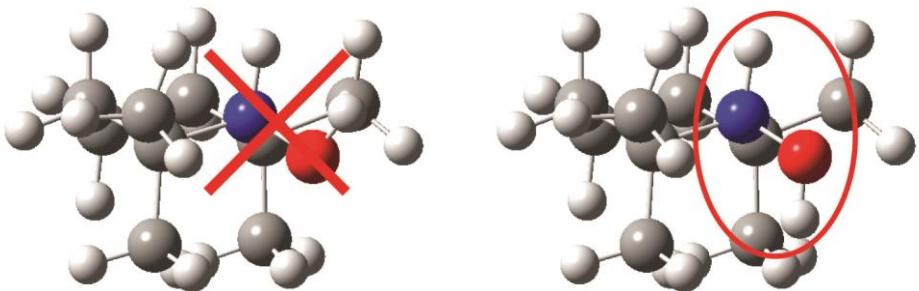
**Table S2.4.** Standard redox potentials of different TEMPO vs SCE in V ( $E_{a1}$ ) calculated using B3LYP/6-31+G(d,p) level of theory and PCM, CPCM, and SMD solvation models.

	B3LYP/6-31+G(d,p), CPCM	B3LYP/6-31+G(d,p), CPCM	B3LYP/6-31+G(d,p), CPCM
TEMPO	0.616	0.618	0.383
TEMPO-NH <sub>2</sub>	0.681	0.681	0.460
TEMPO-NH <sub>3</sub> <sup>+</sup>	0.976	0.971	0.610
TEMPO-OH	0.697	0.701	0.474
TEMPO-COOH	0.737	0.734	0.419
TEMPO-COO <sup>-</sup>	0.438	0.507	0.387
oxo-TEMPO	0.905	0.902	0.581
AZADO	0.515	0.517	0.307
ABNO	0.539	0.548	0.304

## 2.5 Computational Summary and Protocols

As a general procedure for the calculation of free energies (and the corresponding oxidation potentials), the geometry for each structure was optimized using B3LYP/6-31+G(d,p) CPCM level of theory, basis set and solvation model. The optimized geometry was subsequently used to compute both the free energy and the vibrational spectrum for each structure. While geometry optimization was performed in both the gas phase and with various solvation models, the relative energy differences ( $\Delta G_{a1}$ ,  $\Delta G_{a2}$ , etc.) were found to be negligible for all compounds containing either zero or a single charge. However, for compounds containing either a permanent or temporary cationic or anionic species (**5**, **7**, **10**, **25**, **26**, **27**, **28**, and **29**), solvated geometry optimization resulted in abnormal geometries. Therefore, the geometry optimization for such compounds was performed in the gas phase and the optimized structure was used to calculate the corresponding free energies and frequencies with a CPCM solvation model.

The initial configuration for all TEMPO derivatives was input with substituents in the axial position, and with all diastereomers in the *anti*-configuration. Additionally, the orientation of protons on nitrogen and oxygen atoms of the TH<sub>2</sub> species were placed in opposite sides of the plane of the compound about the N-O bond as shown below.



Finally, a compilation of the relevant predicted and experimental data ( $E_{a1}$ ,  $E_{a2}$ , and catalytic activity) are provided in Table S5 below. There are two anomalous points in the computational data set that presented problems for two separate reasons. The first, analogue **9**, contains two ionizable substituents (carboxyl and amine groups) whose protonation equilibrium is not accounted for in even the expanded kinetic model presented here. Due to uncertainty of the structure of **9** with respect to protonation state, the computational data was not included. The second, analogue 29, did not converge to a single geometry under the computational constraints described above (specifically geometry optimization in the gas phase). Therefore, the structure presented in the data below was optimized using a CPCM solvation model. It should be noted that 29 is the largest compound studied in this work both in terms of the number of atoms and the number of possible configurations. Therefore, it is somewhat expected that this compound would be computationally expensive to compute.

**Table S2.5. Compiled computational and experimental values of  $E_{a1}$ ,  $E_{a2}$  and catalytic activity (as represented by  $(i_{pa}/i_{pc})_{cat}$ ) for all compounds studied. The training set is compiled above the dashed line and the validation set is listed below the dashed line.**

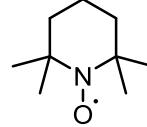
Catalyst		$E_{a1}$ / V vs SCE		$E_{a2}$ / V vs SCE		$(i_{pa}/i_{pc})_{cat}$	
Number	Abbreviation	Predicted	Experimental	Predicted	Experimental	Predicted	Experimental
1	TEMPO	0.543	0.529	0.496	0.528	43.4	13.1
2	TEMPO-oxo	0.669	0.582	0.713	0.701	22.6	0.1
3	TEMPO-OMe	0.544	0.615	0.456	0.590	61.0	28.3
7	TEMPO-NH <sub>2</sub>	0.679	0.661	0.709	0.542	24.6	42.4
8	TEMPO-ketal	0.581	0.627	0.611	0.578	24.9	37.1
12	ABNO	0.514	0.508	0.435	0.399	56.9	83.4
13	AZADO	0.500	0.491	0.385	0.386	80.3	75.4
14	nor-AZADO	0.519	0.504	0.343	0.348	197.9	197.7
4	TEMPO-OH	0.592	0.612	0.594	0.611	30.1	29.1
5	TEMPO-COOH	0.593	0.580	0.672	0.603	18.1	3.9
6	TEMPO-NHAc	0.593	0.635	0.550	0.641	41.9	28.5
9	TEMPO-NH <sub>2</sub> (-4-COOH)	-	0.427	-	0.511	-	0.7
10	TEMPO-NHBn(-3-Cl)	0.755	0.673	1.063	0.623	2.6	18.4
11	TEMPO-oxo(-3-Cl)	0.705	0.767	0.895	1.238	8.4	0.0
15	ABNO-oxo	0.582	0.696	0.481	0.581	68.7	83.0
16	ABNO-OAc	0.589	0.619	0.435	0.466	133.0	160.3
17	ABOO	0.491	0.442	0.877	0.845	0.1	9.0
18	ABNO-NHAc	0.571	0.608	0.461	0.470	76.3	131.5
19	Me-AZADO	0.472	0.433	0.382	0.330	63.0	53.7
20	Me <sub>2</sub> -nor-AZADO	0.423	0.370	0.793	0.749	0.6	18.9
21	Me <sub>2</sub> -ABNO-oxo	0.590	0.621	0.609	0.644	26.8	0.0
22	Me <sub>2</sub> -ABNO-OAc	0.532	0.512	0.716	0.727	8.9	19.1
23	ABOO-oxo	0.423	0.702	0.613	1.090	8.6	0.0
24	ABNO-OH	0.565	0.687	0.424	0.569	110.4	63.9
25	TEMPO-N-(Pyrrolidinone)	0.681	0.712	0.857	0.988	9.3	12.2
26	TEMPO-NHBn	0.696	0.798	1.210	1.160	3.0	0.0
27	TEMPO-NMe <sub>2</sub>	0.703	0.663	0.856	0.587	10.9	25.2
28	TEMPO-NMe <sub>2</sub> Pr	0.706	0.775	0.681	0.598	36.3	61.6
29	TEMPO-NMe <sub>2</sub> Bn	0.708	0.750	0.909	0.593	7.7	163.1

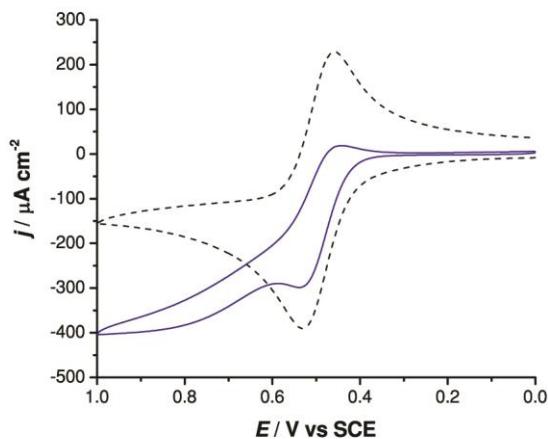
### 3 CHARACTERIZATION OF NITROXYL RADICAL COMPOUNDS

#### 3.1 TEMPO (1)

TEMPO was purchased from Sigma Aldrich and used without purification.

**Table S3.1. Summary table of electrocatalytic properties of TEMPO.**

	$E_{a1}$	0.529
	$E_{a2}$	0.528
	$j_{max}$	247.2
	$(i_{pa}/i_{pc})_{cat.}$	13.33



**Figure S3.1.** CV of 5 mM TEMPO in the absence (dashed) and presence (solid) of 1 M glycerol using 150 mM Robinson buffer at 25 °C.

#### Optimized Geometry Coordinates Using B3LYP/6-31+G(d,p) CPCM

TEMPO, T*				TEMPO, T+			
Symbol	X	Y	Z	Symbol	X	Y	Z
C	1.3354	-0.0742	-0.0234	C	1.3619	-0.0766	0.0231
C	1.2460	1.3919	-0.4977	C	1.2529	1.3165	-0.6432
C	0.0000	2.1263	-0.0016	C	0.0000	2.1015	-0.2596
C	-1.2460	1.3920	-0.4977	C	-1.2529	1.3165	-0.6432
C	-1.3354	-0.0741	-0.0234	C	-1.3619	-0.0766	0.0231
H	2.1603	1.9027	-0.1751	H	2.1616	1.8581	-0.3632
H	0.0000	2.2053	1.0921	H	0.0000	2.3578	0.8048

H	0.0000	3.1530	-0.3844	H	0.0000	3.0524	-0.8012
H	-2.1603	1.9027	-0.1751	H	-2.1616	1.8581	-0.3632
H	-1.2465	1.4072	-1.5955	H	-1.2818	1.1816	-1.7302
H	1.2465	1.4072	-1.5956	H	1.2818	1.1816	-1.7302
N	0.0000	-0.7525	-0.1926	C	2.4075	-0.9530	-0.6690
O	0.0000	-2.0366	-0.0752	H	3.3490	-0.3986	-0.6571
C	2.3563	-0.8259	-0.8940	H	2.5606	-1.9006	-0.1501
H	3.3152	-0.2997	-0.8516	H	2.1390	-1.1525	-1.7095
H	2.5047	-1.8485	-0.5424	C	1.6699	0.0164	1.5399
H	2.0281	-0.8589	-1.9377	H	1.5808	-0.9587	2.0237
C	1.7643	-0.1621	1.4579	H	2.7100	0.3433	1.6166
H	1.7287	-1.2004	1.7992	H	1.0487	0.7411	2.0625
H	2.7922	0.2005	1.5607	C	-2.4075	-0.9529	-0.6690
H	1.1288	0.4401	2.1116	H	-2.5607	-1.9006	-0.1501
C	-2.3563	-0.8259	-0.8940	H	-3.3490	-0.3986	-0.6571
H	-2.5047	-1.8485	-0.5424	H	-2.1390	-1.1525	-1.7095
H	-3.3152	-0.2997	-0.8516	C	-1.6699	0.0164	1.5399
H	-2.0281	-0.8589	-1.9377	H	-2.7100	0.3433	1.6166
C	-1.7643	-0.1621	1.4579	H	-1.5808	-0.9587	2.0237
H	-2.7922	0.2005	1.5607	H	-1.0486	0.7410	2.0625
H	-1.7287	-1.2004	1.7992	O	0.0000	-1.9524	-0.3547
H	-1.1288	0.4401	2.1116	N	0.0000	-0.7810	-0.1146

TH			
Symbol	X	Y	Z
C	1.2976	-0.0515	-0.0326
C	1.2518	1.4308	-0.4714
C	0.0000	2.1695	0.0089
C	-1.2518	1.4308	-0.4713
C	-1.2976	-0.0515	-0.0326
H	2.1616	1.9225	-0.1070
H	0.0000	2.2593	1.1018
H	0.0000	3.1938	-0.3822
H	-2.1616	1.9225	-0.1070
H	-1.2858	1.4694	-1.5682
H	1.2858	1.4693	-1.5682
N	0.0000	-0.6694	-0.4482
C	2.4067	-0.7632	-0.8325
H	3.3621	-0.2489	-0.6835
H	2.5272	-1.8008	-0.5084
H	2.1736	-0.7568	-1.9024
C	1.6323	-0.1765	1.4728

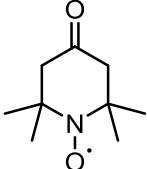
TH2			
Symbol	X	Y	Z
C	1.3608	-0.0270	-0.0193
C	1.2618	1.4483	-0.4569
C	0.0034	2.1707	0.0331
C	-1.2558	1.4536	-0.4623
C	-1.3589	-0.0183	-0.0138
H	2.1649	1.9438	-0.0872
H	0.0010	2.2555	1.1246
H	0.0065	3.1945	-0.3532
H	-2.1592	1.9542	-0.0997
H	-1.2938	1.5013	-1.5581
H	1.3059	1.5014	-1.5521
C	2.4315	-0.7596	-0.8409
H	3.3808	-0.2354	-0.7050
H	2.5581	-1.7924	-0.5118
H	2.2017	-0.7508	-1.9118
C	1.6417	-0.1912	1.4777
H	1.5232	-1.2279	1.7974

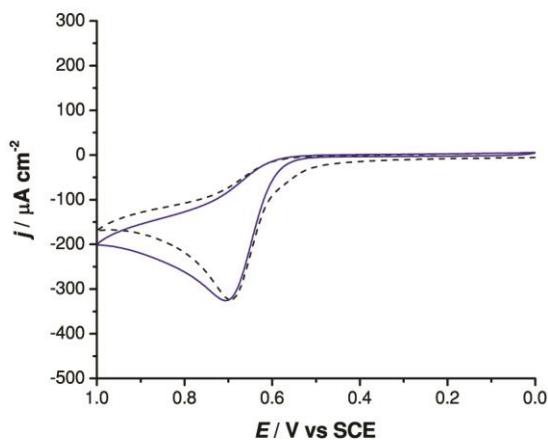
H	1.4813	-1.2039	1.8138	H	2.6840	0.0941	1.6424
H	2.6847	0.0827	1.6316	H	1.0244	0.4487	2.1062
H	1.0344	0.4868	2.1000	C	-2.4418	-0.7493	-0.8223
C	-2.4067	-0.7632	-0.8325	H	-2.6222	-1.7641	-0.4561
H	-2.5271	-1.8008	-0.5084	H	-3.3788	-0.1980	-0.7119
H	-3.3621	-0.2489	-0.6835	H	-2.2087	-0.7833	-1.8924
H	-2.1736	-0.7567	-1.9024	C	-1.6309	-0.1722	1.4852
C	-1.6323	-0.1765	1.4728	H	-2.6823	0.0752	1.6524
H	-2.6847	0.0827	1.6316	H	-1.4696	-1.1994	1.8172
H	-1.4813	-1.2039	1.8138	H	-1.0350	0.4987	2.1023
H	-1.0343	0.4868	2.1000	O	0.0583	-2.0437	0.0223
O	0.0000	-2.0510	0.0003	H	-0.5339	-2.5520	-0.5598
H	0.0001	-2.5523	-0.8268	H	0.0106	-0.7062	-1.4372
				N	-0.0020	-0.6913	-0.4097

### 3.2 4-Oxo-TEMPO (2)

4-Oxo-TEMPO was purchased from Sigma Aldrich and used without purification.

**Table S3.2. Summary table of electrocatalytic properties of TEMPO-oxo.**

	$E_{a1}$ $E_{a2}$ $j_{max}$ $(i_{pa}/i_{pc})_{cat.}$	0.628 0.701 32.1 0.08
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**Figure S3.2.** CV of 5 mM 4-oxo-TEMPO in the absence (dashed) and presence (solid) of 1 M glycerol using 150 mM Robinson buffer at 25 °C.

#### Optimized Geometry Coordinates Using B3LYP/6-31+G(d,p) CPCM

oxo-TEMPO, T*				oxo-TEMPO, T+			
Symbol	X	Y	Z	Symbol	X	Y	Z
C	1.3342	-0.2989	-0.0250	C	1.3528	-0.3478	0.0157
C	1.2630	1.1170	-0.6519	C	1.3104	1.0345	-0.6770
C	-1.2631	1.1169	-0.6519	C	-1.2370	1.1547	-0.6198
C	-1.3342	-0.2990	-0.0250	C	-1.3785	-0.2486	0.0162
H	2.1380	1.6950	-0.3456	H	2.2091	1.5827	-0.3876
H	-2.1380	1.6949	-0.3457	H	-2.0635	1.7718	-0.2625
H	-1.2824	1.0212	-1.7454	H	-1.3318	1.0642	-1.7094
H	1.2824	1.0212	-1.7454	H	1.3337	0.8938	-1.7651
N	0.0000	-0.9856	-0.1582	C	2.3714	-1.2770	-0.6447

O	0.0000	-2.2563	0.0476	H	3.3320	-0.7567	-0.6397
C	2.3743	-1.1313	-0.7911	H	2.4846	-2.2126	-0.0951
H	3.3266	-0.5927	-0.7954	H	2.1028	-1.4961	-1.6810
H	2.5258	-2.1027	-0.3179	C	1.6424	-0.2141	1.5335
H	2.0603	-1.2892	-1.8272	H	1.4997	-1.1636	2.0527
C	1.7315	-0.2155	1.4647	H	2.6954	0.0672	1.6149
H	1.6653	-1.2049	1.9249	H	1.0501	0.5630	2.0149
H	2.7652	0.1348	1.5446	C	-2.4480	-1.0802	-0.6950
H	1.1004	0.4762	2.0282	H	-2.6376	-2.0240	-0.1822
C	-2.3743	-1.1313	-0.7911	H	-3.3699	-0.4939	-0.6871
H	-2.5257	-2.1028	-0.3179	H	-2.1742	-1.2797	-1.7340
H	-3.3266	-0.5928	-0.7954	C	-1.6868	-0.1614	1.5342
H	-2.0603	-1.2893	-1.8272	H	-2.7154	0.2000	1.6101
C	-1.7315	-0.2155	1.4647	H	-1.6321	-1.1438	2.0071
H	-2.7652	0.1347	1.5446	H	-1.0436	0.5399	2.0638
H	-1.6653	-1.2049	1.9249	O	-0.0807	-2.1813	-0.2967
H	-1.1004	0.4762	2.0282	N	-0.0375	-1.0033	-0.1142
C	0.0000	1.8627	-0.2980	C	0.0793	1.8546	-0.3493
O	-0.0001	2.9804	0.2026	O	0.1415	3.0090	0.0339

TH			
Symbol	X	Y	Z
C	1.2975	-0.2782	-0.0414
C	1.2669	1.1630	-0.6169
C	-1.2669	1.1630	-0.6168
C	-1.2975	-0.2782	-0.0414
H	2.1371	1.7236	-0.2665
H	-2.1370	1.7236	-0.2665
H	-1.3143	1.1042	-1.7125
H	1.3143	1.1042	-1.7125
N	0.0000	-0.9230	-0.4101
C	2.4116	-1.0602	-0.7628
H	3.3630	-0.5274	-0.6664
H	2.5352	-2.0555	-0.3283
H	2.1784	-1.1673	-1.8269
C	1.6184	-0.2444	1.4711
H	1.4511	-1.2277	1.9170
H	2.6722	0.0178	1.6104
H	1.0261	0.4918	2.0180
C	-2.4116	-1.0601	-0.7628
H	-2.5352	-2.0555	-0.3283
H	-3.3630	-0.5274	-0.6664

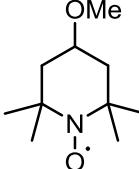
TH2			
Symbol	X	Y	Z
C	1.3725	-0.1907	-0.0336
C	1.2245	1.2527	-0.5687
C	-1.3284	1.1252	-0.6156
C	-1.3453	-0.3042	-0.0300
H	2.0474	1.8495	-0.1701
H	-2.2234	1.6472	-0.2710
H	-1.3732	1.0829	-1.7122
H	1.3195	1.2561	-1.6630
N	0.0410	-0.9427	-0.3748
C	2.4802	-0.9305	-0.7963
H	3.4040	-0.3549	-0.7002
H	2.6504	-1.9258	-0.3830
H	2.2549	-1.0178	-1.8642
C	1.6520	-0.2204	1.4725
H	1.5828	-1.2329	1.8724
H	2.6784	0.1270	1.6145
H	1.0037	0.4399	2.0471
C	-2.4012	-1.1605	-0.7428
H	-2.5241	-2.1367	-0.2665
H	-3.3616	-0.6442	-0.6747

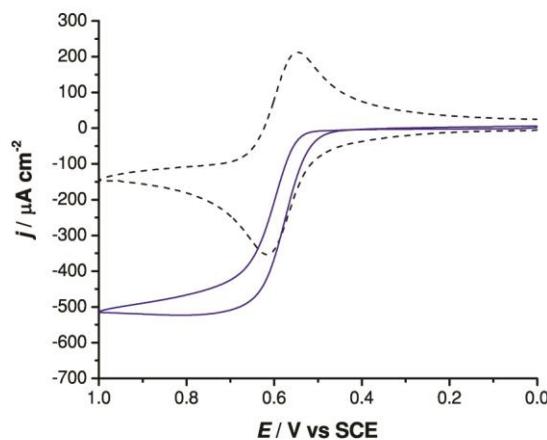
H	-2.1784	-1.1673	-1.8269	H	-2.1789	-1.2970	-1.8068
C	-1.6184	-0.2444	1.4711	C	-1.5910	-0.3021	1.4815
H	-2.6722	0.0179	1.6104	H	-2.6526	-0.0963	1.6387
H	-1.4512	-1.2277	1.9170	H	-1.3659	-1.2742	1.9226
H	-1.0261	0.4918	2.0180	H	-1.0307	0.4712	2.0067
O	0.0000	-2.2566	0.1510	O	0.1539	-2.2431	0.1795
H	0.0000	-2.8293	-0.6290	H	-0.3425	-2.8460	-0.4028
C	0.0000	1.9070	-0.2704	C	-0.0952	1.9246	-0.2412
O	0.0000	3.0275	0.2279	O	-0.1594	3.0472	0.2303
				H	0.0593	-1.0472	-1.3968

### 3.3 4-Methoxy-TEMPO (3)

4-Methoxy-TEMPO was purchased from Sigma Aldrich and used without purification.

**Table S3.3. Summary table of electrocatalytic properties of TEMPO-OMe.**

	$E_{a1}$ $E_{a2}$ $j_{max}$ $(i_{pa}/i_{pc})_{cat.}$	0.615 0.590 371.1 28.29
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**Figure S3.3.** CV of 5 mM 4-methoxy-TEMPO in the absence (dashed) and presence (solid) of 1 M glycerol using 150 mM Robinson buffer at 25 °C.

### Optimized Geometry Coordinates Using B3LYP/6-31+G(d,p) CPCM

T*				T+			
Symbol	X	Y	Z	Symbol	X	Y	Z
C	0.1654	1.3910	-0.0780	C	0.2078	1.4125	-0.0198
C	-0.9452	0.8982	-1.0311	C	-0.8869	0.9635	-1.0173
C	-1.3624	-0.5696	-0.8791	C	-1.3533	-0.4941	-0.9041
C	-0.1280	-1.4614	-0.9775	C	-0.1574	-1.4405	-0.9836
C	1.0390	-1.1251	-0.0231	C	0.9969	-1.1820	0.0143
H	-1.8076	1.5638	-0.9217	H	-1.7253	1.6535	-0.8885
H	-0.4127	-2.5066	-0.8176	H	-0.4884	-2.4702	-0.8229
H	0.2349	-1.3852	-2.0093	H	0.2487	-1.3857	-1.9985
H	-0.5985	1.0169	-2.0650	H	-0.5126	1.1165	-2.0351

N	1.2599	0.3626	0.0152	C	0.8812	2.7057	-0.4884
O	2.3643	0.7578	0.5506	H	0.0912	3.4476	-0.6278
C	0.7799	2.6741	-0.6662	H	1.5866	3.0914	0.2494
H	-0.0153	3.4086	-0.8277	H	1.3973	2.5686	-1.4422
H	1.5193	3.1055	0.0109	C	-0.3252	1.5930	1.4275
H	1.2619	2.4718	-1.6280	H	0.4947	1.7881	2.1224
C	-0.3749	1.6913	1.3381	H	-0.9714	2.4744	1.4000
H	0.4489	1.9790	1.9974	H	-0.9176	0.7465	1.7645
H	-1.0816	2.5262	1.2859	C	2.2778	-1.8900	-0.4368
H	-0.8942	0.8321	1.7639	H	3.0747	-1.8073	0.3041
C	2.3207	-1.7740	-0.5764	H	2.0341	-2.9478	-0.5614
H	3.1626	-1.6336	0.1039	H	2.6358	-1.5029	-1.3944
H	2.1498	-2.8478	-0.7019	C	0.6509	-1.5965	1.4704
H	2.5834	-1.3506	-1.5510	H	0.6301	-2.6894	1.4724
C	0.7889	-1.6426	1.4112	H	1.4268	-1.2657	2.1647
H	0.7491	-2.7369	1.3973	H	-0.3251	-1.2387	1.7866
H	1.6105	-1.3368	2.0653	O	2.4280	0.6720	0.1280
H	-0.1548	-1.2765	1.8162	N	1.2870	0.3239	0.0423
O	-2.0593	-0.8638	0.3395	O	-2.0916	-0.7741	0.2848
C	-3.4014	-0.3922	0.3769	C	-3.4519	-0.3402	0.2542
H	-3.4560	0.7040	0.3923	H	-3.5349	0.7522	0.1991
H	-3.9739	-0.7639	-0.4849	H	-3.9823	-0.7847	-0.5982
H	-3.8475	-0.7783	1.2961	H	-3.9092	-0.6826	1.1838
H	-2.0311	-0.8201	-1.7174	H	-1.9927	-0.7021	-1.7739

TH			
Symbol	X	Y	Z
C	-0.4505	-1.3302	-0.0411
C	1.0048	-1.0073	-0.4523
C	1.4989	0.3454	0.0664
C	0.5575	1.4436	-0.4135
C	-0.9159	1.2192	-0.0056
H	1.6442	-1.8235	-0.0998
H	1.5508	0.3397	1.1649
H	0.8850	2.4147	-0.0264
H	0.6236	1.4877	-1.5079
H	1.0711	-0.9878	-1.5474
N	-1.2870	-0.1597	-0.4467
C	-0.9317	-2.5334	-0.8765
H	-0.2552	-3.3824	-0.7331
H	-1.9354	-2.8463	-0.5756
H	-0.9494	-2.2795	-1.9413

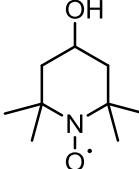
TH2			
Symbol	X	Y	Z
C	-0.4142	-1.3887	-0.0285
C	1.0218	-1.0203	-0.4480
C	1.5147	0.3382	0.0709
C	0.5847	1.4477	-0.4168
C	-0.8851	1.2845	0.0138
H	1.6647	-1.8305	-0.0928
H	1.5660	0.3362	1.1683
H	0.9269	2.4145	-0.0367
H	0.6514	1.4957	-1.5108
H	1.0979	-1.0124	-1.5425
N	-1.3079	-0.1610	-0.4070
C	-0.9314	-2.5579	-0.8797
H	-0.2497	-3.4017	-0.7479
H	-1.9302	-2.8697	-0.5698
H	-0.9478	-2.3099	-1.9463

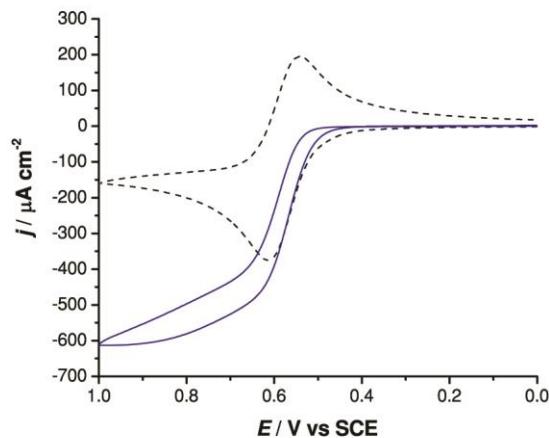
C	-0.5390	-1.7174	1.4548	C	-0.5443	-1.7266	1.4608
H	-1.5838	-1.7864	1.7682	H	-1.5899	-1.8152	1.7602
H	-0.0761	-2.6990	1.6018	H	-0.0690	-2.6992	1.6122
H	-0.0276	-1.0139	2.1138	H	-0.0454	-1.0143	2.1160
C	-1.7910	2.1981	-0.8142	C	-1.7772	2.2394	-0.7949
H	-2.8402	2.1297	-0.5140	H	-2.8134	2.2342	-0.4459
H	-1.4563	3.2266	-0.6436	H	-1.3993	3.2555	-0.6589
H	-1.7188	1.9830	-1.8852	H	-1.7522	2.0230	-1.8684
C	-1.1319	1.5125	1.4988	C	-1.1064	1.5097	1.5129
H	-1.0396	2.5899	1.6726	H	-1.0120	2.5829	1.6977
H	-2.1345	1.2053	1.8070	H	-2.1084	1.2031	1.8190
H	-0.4057	1.0151	2.1437	H	-0.3740	1.0052	2.1410
O	-2.6495	-0.4140	-0.0220	O	-2.6302	-0.4669	0.0065
H	-3.1327	-0.4907	-0.8564	H	-3.2295	0.0528	-0.5585
O	2.8062	0.6671	-0.4335	O	2.8087	0.6467	-0.4431
C	3.8720	-0.0288	0.2051	C	3.8881	-0.0093	0.2227
H	4.8017	0.3697	-0.2070	H	4.8074	0.3801	-0.2184
H	3.8595	0.1398	1.2914	H	3.8793	0.2138	1.2978
H	3.8357	-1.1089	0.0135	H	3.8599	-1.0966	0.0804
				H	-1.3091	-0.1605	-1.4339

### 3.4 4-Hydroxy-TEMPO (4)

4-Hydroxy-TEMPO was purchased from Sigma Aldrich and used without purification.

**Table S3.4. Summary table of electrocatalytic properties of TEMPO-OH.**

	$E_{a1}$	0.612
	$E_{a2}$	0.661
	$j_{max}$	515.1
	$(i_{pa}/i_{pc})_{cat.}$	29.14



**Figure S3.4.** CV of 5 mM 4-hydroxy-TEMPO in the absence (dashed) and presence (solid) of 1 M glycerol using 150 mM Robinson buffer at 25 °C.

#### Optimized Geometry Coordinates Using B3LYP/6-31+G(d,p) CPCM

T*				T+			
Symbol	X	Y	Z	Symbol	X	Y	Z
C	-0.1735	-1.3744	-0.0139	C	0.9090	-1.0827	0.0253
C	1.2951	-1.0569	-0.3648	C	1.6559	0.2055	-0.3794
C	1.7903	0.2734	0.1978	C	1.0326	1.4994	0.1534
C	0.9294	1.3966	-0.3603	C	-0.3961	1.6284	-0.3642
C	-0.5666	1.2654	-0.0098	C	-1.3314	0.4681	0.0299
H	1.9154	-1.8839	-0.0002	H	2.6830	0.0946	-0.0175
H	1.7492	0.2684	1.2948	H	1.0470	1.5124	1.2497
H	1.2844	2.3647	0.0088	H	-0.8532	2.5459	0.0171
H	1.0496	1.4007	-1.4509	H	-0.3628	1.7094	-1.4564

H	1.4103	-1.0207	-1.4551	H	1.7005	0.2694	-1.4720
N	-1.0265	-0.1523	-0.2355	C	1.3435	-2.2759	-0.8301
O	-2.3008	-0.3426	-0.2294	H	2.4283	-2.3634	-0.7345
C	-0.6849	-2.4801	-0.9528	H	0.8924	-3.2095	-0.4911
H	-0.0286	-3.3518	-0.8682	H	1.1025	-2.1200	-1.8847
H	-1.7007	-2.7820	-0.6912	C	1.0688	-1.4223	1.5314
H	-0.6764	-2.1413	-1.9934	H	0.4258	-2.2574	1.8171
C	-0.3201	-1.8419	1.4517	H	2.1102	-1.7262	1.6646
H	-1.3767	-1.9800	1.6962	H	0.8786	-0.5751	2.1881
H	0.1930	-2.8004	1.5795	C	-2.6001	0.4589	-0.8274
H	0.1105	-1.1336	2.1633	H	-3.3131	-0.2974	-0.4964
C	-1.3802	2.1764	-0.9444	H	-3.0664	1.4413	-0.7217
H	-2.4393	2.1682	-0.6807	H	-2.3683	0.3000	-1.8835
H	-1.0064	3.2012	-0.8576	C	-1.7115	0.4868	1.5350
H	-1.2756	1.8580	-1.9862	H	-2.3754	1.3447	1.6678
C	-0.8439	1.6630	1.4575	H	-2.2560	-0.4178	1.8132
H	-0.6321	2.7286	1.5907	H	-0.8563	0.6169	2.1962
H	-1.8955	1.4869	1.6997	O	-1.2455	-1.8004	-0.5787
H	-0.2265	1.1068	2.1670	N	-0.5981	-0.8671	-0.2100
O	3.1431	0.5405	-0.2090	O	1.7389	2.6395	-0.3379
H	3.7192	-0.1362	0.1739	H	2.5987	2.6911	0.1030

TH			
Symbol	X	Y	Z
C	-0.3033	-1.3081	-0.0208
C	1.2057	-1.1989	-0.3383
C	1.8517	0.0737	0.2068
C	1.1138	1.2914	-0.3327
C	-0.3989	1.2836	-0.0171
H	1.7086	-2.0875	0.0627
H	1.8284	0.0729	1.3040
H	1.5523	2.2096	0.0737
H	1.2538	1.3146	-1.4209
H	1.3456	-1.2057	-1.4265
N	-0.9353	-0.0331	-0.4815
C	-0.8973	-2.4383	-0.8848
H	-0.3597	-3.3737	-0.6972
H	-1.9526	-2.6015	-0.6492
H	-0.8101	-2.1954	-1.9487
C	-0.5420	-1.6636	1.4665
H	-1.6033	-1.5756	1.7122
H	-0.2379	-2.7009	1.6424

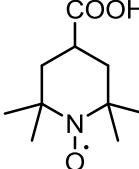
TH2			
Symbol	X	Y	Z
C	-0.2774	-1.3687	-0.0090
C	1.2200	-1.2099	-0.3347
C	1.8634	0.0657	0.2202
C	1.1402	1.2950	-0.3243
C	-0.3640	1.3457	0.0035
H	1.7253	-2.0963	0.0624
H	1.8362	0.0631	1.3161
H	1.5901	2.2050	0.0836
H	1.2891	1.3276	-1.4108
H	1.3683	-1.2206	-1.4215
N	-0.9603	-0.0302	-0.4463
C	-0.9007	-2.4639	-0.8868
H	-0.3568	-3.3942	-0.7056
H	-1.9514	-2.6258	-0.6405
H	-0.8146	-2.2336	-1.9538
C	-0.5483	-1.6678	1.4697
H	-1.6137	-1.6128	1.6992
H	-0.2171	-2.6929	1.6547

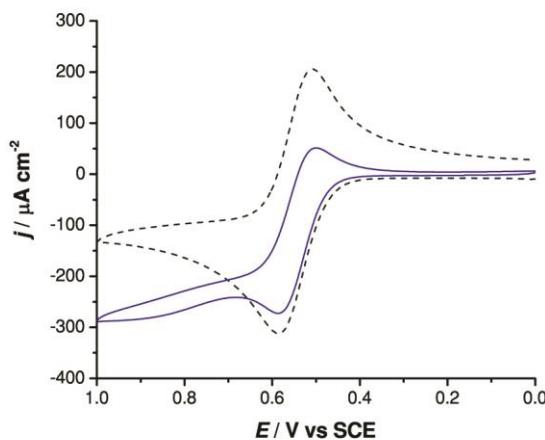
H	0.0242	-1.0363	2.1567	H	-0.0028	-1.0203	2.1541
C	-1.0749	2.3695	-0.8776	C	-1.0539	2.4081	-0.8664
H	-2.1388	2.4549	-0.6400	H	-2.1026	2.5536	-0.5922
H	-0.6065	3.3411	-0.6888	H	-0.5466	3.3623	-0.7048
H	-0.9719	2.1357	-1.9421	H	-0.9830	2.1783	-1.9349
C	-0.6651	1.6159	1.4711	C	-0.6547	1.6138	1.4838
H	-0.4326	2.6707	1.6522	H	-0.4365	2.6679	1.6723
H	-1.7188	1.4554	1.7131	H	-1.7060	1.4407	1.7207
H	-0.0598	1.0254	2.1607	H	-0.0375	1.0266	2.1621
O	-2.3440	-0.0857	-0.1448	O	-2.3353	-0.1430	-0.1157
H	-2.7797	-0.1020	-1.0083	H	-2.8213	0.4478	-0.7180
O	3.2242	0.1888	-0.2161	O	3.2231	0.1764	-0.2115
H	3.7248	-0.5468	0.1640	H	3.7497	-0.5031	0.2331
				H	-0.8962	-0.0361	-1.4718

### 3.5 4-Carboxy-TEMPO (5)

4-Carboxy-TEMPO was purchased from Sigma Aldrich and used without purification.

**Table S3.5. Summary table of electrocatalytic properties of TEMPO-COOH.**

	$E_{a1}$	0.580
	$E_{a2}$	0.603
	$j_{max}$	158.5
	$(i_{pa}/i_{pc})_{cat.}$	3.88



**Figure S3.5.** CV of 5 mM 4-carboxy-TEMPO in the absence (dashed) and presence (solid) of 1 M glycerol using 150 mM Robinson buffer at 25 °C.

#### Optimized Geometry Coordinates Using B3LYP/6-31+G(d,p) CPCM for TEMPO-COOH

T*				T+			
Symbol	X	Y	Z	Symbol	X	Y	Z
C	0.8285	1.3521	-0.1023	C	0.8327	1.3831	-0.0522
C	-0.6673	1.1557	-0.4246	C	-0.6636	1.1778	-0.3756
C	-1.2747	-0.0939	0.2454	C	-1.2752	-0.0873	0.2529
C	-0.5223	-1.3281	-0.2534	C	-0.5236	-1.3256	-0.2358
C	0.9826	-1.3043	0.0824	C	0.9794	-1.3297	0.1161
H	-1.1983	2.0610	-0.1156	H	-1.1801	2.0745	-0.0254
H	-1.1956	0.0026	1.3333	H	-1.2337	-0.0102	1.3453
H	-0.9471	-2.2418	0.1745	H	-0.9452	-2.2344	0.2013
H	-0.6497	-1.3974	-1.3391	H	-0.6347	-1.4142	-1.3208

H	-0.7905	1.0595	-1.5100	H	-0.7843	1.1365	-1.4632
N	1.5645	0.0466	-0.2435	C	1.4675	2.4034	-1.0013
O	2.8506	0.1221	-0.2506	H	0.8772	3.3200	-0.9306
C	1.4243	2.3392	-1.1208	H	2.4962	2.6358	-0.7230
H	0.8526	3.2719	-1.0921	H	1.4435	2.0566	-2.0373
H	2.4670	2.5625	-0.8886	C	1.0751	1.8080	1.4199
H	1.3705	1.9311	-2.1348	H	2.1400	1.7934	1.6611
C	1.0327	1.9038	1.3258	H	0.7160	2.8369	1.5026
H	2.1000	1.9528	1.5569	H	0.5317	1.2002	2.1411
H	0.6182	2.9149	1.3879	C	1.7373	-2.3819	-0.6978
H	0.5427	1.2923	2.0873	H	2.7820	-2.4608	-0.3940
C	1.7015	-2.3462	-0.7915	H	1.2525	-3.3436	-0.5144
H	2.7594	-2.4166	-0.5328	H	1.6882	-2.1699	-1.7689
H	1.2381	-3.3251	-0.6346	C	1.2388	-1.5430	1.6313
H	1.6161	-2.0899	-1.8520	H	0.9741	-2.5827	1.8391
C	1.2386	-1.6241	1.5721	H	2.2933	-1.4006	1.8767
H	0.9451	-2.6584	1.7769	H	0.6293	-0.9062	2.2701
H	2.3022	-1.5144	1.7996	O	2.6808	0.0805	-0.6820
H	0.6731	-0.9752	2.2453	N	1.5707	0.0462	-0.2430
C	-2.7556	-0.1710	-0.0706	C	-2.7564	-0.1831	-0.0892
O	-3.2682	-0.8684	-0.9281	O	-3.2711	-1.0665	-0.7469
O	-3.4791	0.6637	0.7074	O	-3.4504	0.8444	0.4345
H	-4.4130	0.6042	0.4382	H	-4.3872	0.7483	0.1863

TH

Symbol	X	Y	Z
C	0.8114	1.3096	-0.1060
C	-0.6994	1.1628	-0.3961
C	-1.3172	-0.0913	0.2612
C	-0.5608	-1.3334	-0.2171
C	0.9552	-1.2707	0.0760
H	-1.2059	2.0698	-0.0512
H	-1.2535	0.0079	1.3496
H	-0.9646	-2.2359	0.2547
H	-0.7118	-1.4408	-1.2967
H	-0.8455	1.0952	-1.4810
N	1.4592	0.0184	-0.4888
C	1.3697	2.3892	-1.0553
H	0.8183	3.3257	-0.9225
H	2.4251	2.5860	-0.8485
H	1.2709	2.0718	-2.0983
C	1.0609	1.7699	1.3493

TH2

Symbol	X	Y	Z
C	0.9321	-1.2732	0.1115
C	-0.1190	-1.2874	-1.0168
C	-1.1369	-0.1307	-1.0692
C	-0.4253	1.2366	-0.9407
C	0.5223	1.3937	0.2592
N	1.5188	0.1833	0.2137
C	2.0976	-2.2118	-0.2445
C	0.4095	-1.6873	1.4975
C	1.3568	2.6765	0.1110
C	-0.1848	1.4326	1.6221
C	-2.3666	-0.3446	-0.1815
O	-2.5793	-1.3445	0.4737
O	-3.3060	0.6280	-0.1966
O	2.3916	0.3349	-0.8987
H	0.4145	-1.2849	-1.9715
H	-0.6453	-2.2423	-0.9507

H	2.1249	1.7052	1.5896	H	-1.5614	-0.1473	-2.0827
H	0.7519	2.8150	1.4564	H	0.1527	1.3861	-1.8567
H	0.5065	1.1885	2.0879	H	-1.1312	2.0707	-0.8968
C	1.6399	-2.4028	-0.7156	H	2.0912	0.2039	1.0668
H	2.7087	-2.4503	-0.4903	H	2.8952	-2.1605	0.5034
H	1.1946	-3.3671	-0.4493	H	2.5176	-2.0049	-1.2274
H	1.5159	-2.2483	-1.7923	H	1.7050	-3.2318	-0.2436
C	1.2471	-1.4905	1.5795	H	-0.5101	-1.2005	1.8011
H	1.0409	-2.5344	1.8385	H	1.1735	-1.5401	2.2673
H	2.2996	-1.2903	1.7951	H	0.1986	-2.7579	1.4506
H	0.6381	-0.8657	2.2349	H	1.8166	2.7705	-0.8741
C	-2.7926	-0.1619	-0.0753	H	2.1246	2.7542	0.8880
O	-3.2947	-0.8239	-0.9674	H	0.6861	3.5296	0.2359
O	-3.5321	0.6390	0.7252	H	0.5276	1.3804	2.4508
H	-4.4608	0.5871	0.4373	H	-0.9343	0.6582	1.7609
O	2.8708	0.1204	-0.1767	H	-0.6969	2.3947	1.6945
H	3.2953	0.0837	-1.0452	H	-3.0767	1.3644	-0.7850
				H	3.0556	1.0008	-0.6469

#### Optimized Geometry Coordinates Using B3LYP/6-31+G(d,p) CPCM for TEMPO-COO-

Symbol	T*			T+			
	X	Y	Z	X	Y	Z	
C	0.8595	1.3354	-0.0163	C	-0.8818	-1.3509	0.0669
C	-0.6490	1.2283	-0.3225	C	0.6339	-1.2447	-0.2593
C	-1.3284	-0.0102	0.2768	C	1.3255	0.0000	0.2987
C	-0.6323	-1.2496	-0.2978	C	0.6338	1.2447	-0.2593
C	0.8775	-1.3296	0.0104	C	-0.8818	1.3509	0.0670
H	-1.1232	2.1480	0.0408	H	1.0850	-2.1607	0.1361
H	-1.2316	0.0031	1.3669	H	1.2944	0.0000	1.3908
H	-1.0937	-2.1685	0.0837	H	1.0849	2.1608	0.1362
H	-0.7780	-1.2487	-1.3841	H	0.7603	1.2633	-1.3464
H	-0.7927	1.2034	-1.4091	H	0.7603	-1.2633	-1.3464
N	1.5275	0.0051	-0.2409	C	-1.5637	-2.4134	-0.7967
O	2.8171	0.0138	-0.2641	H	-1.0383	-3.3560	-0.6254
C	1.4973	2.3481	-0.9830	H	-2.6127	-2.5518	-0.5272
H	0.9753	3.3057	-0.8912	H	-1.4986	-2.1707	-1.8602
H	2.5537	2.5043	-0.7565	C	-1.1426	-1.6459	1.5663
H	1.4082	2.0055	-2.0188	H	-2.2014	-1.5430	1.8150
C	1.1124	1.7906	1.4381	H	-0.8537	-2.6881	1.7237
H	2.1832	1.7696	1.6586	H	-0.5494	-1.0280	2.2368
H	0.7531	2.8172	1.5649	C	-1.5638	2.4134	-0.7967
H	0.5947	1.1616	2.1663	H	-2.6127	2.5517	-0.5271

C	1.5294	-2.3527	-0.9356	H	-1.0384	3.3560	-0.6253
H	2.5872	-2.4924	-0.7044	H	-1.4987	2.1707	-1.8602
H	1.0185	-3.3146	-0.8267	C	-1.1426	1.6458	1.5663
H	1.4383	-2.0310	-1.9779	H	-0.8538	2.6880	1.7238
C	1.1367	-1.7520	1.4736	H	-2.2014	1.5429	1.8150
H	0.7907	-2.7803	1.6209	H	-0.5494	1.0280	2.2368
H	2.2072	-1.7126	1.6930	O	-2.5630	0.0000	-0.8571
H	0.6110	-1.1153	2.1893	N	-1.5196	0.0000	-0.2666
C	-2.8497	-0.0132	-0.0314	C	2.8410	0.0000	-0.1015
O	-3.1961	-0.0950	-1.2464	O	3.6681	0.0000	0.8513
O	-3.6354	0.0736	0.9602	O	3.0966	0.0001	-1.3367

TH				TH2			
Symbol	X	Y	Z	Symbol	X	Y	Z
C	0.8373	1.2973	-0.0233	C	-0.6216	1.3747	0.2019
C	-0.6824	1.2333	-0.3003	C	0.3493	1.2610	-0.9847
C	-1.3702	-0.0100	0.2839	C	1.1543	-0.0489	-1.0791
C	-0.6661	-1.2552	-0.2725	C	0.2325	-1.2804	-0.9974
C	0.8547	-1.2924	0.0048	C	-0.7727	-1.3191	0.1671
H	-1.1356	2.1502	0.0971	N	-1.4992	0.0724	0.2167
H	-1.2857	0.0046	1.3748	C	-1.5801	2.5635	0.0216
H	-1.1062	-2.1692	0.1461	C	0.0685	1.5222	1.5674
H	-0.8297	-1.2870	-1.3558	C	-1.8555	-2.3824	-0.0890
H	-0.8430	1.2379	-1.3849	C	-0.1487	-1.5999	1.5448
N	1.4211	0.0012	-0.4848	C	2.4512	-0.1000	-0.2048
C	1.4441	2.4011	-0.9131	O	2.8445	-1.2370	0.1824
H	0.9383	3.3538	-0.7231	O	3.0489	0.9994	-0.0246
H	2.5096	2.5374	-0.7069	O	-2.3840	0.2047	-0.8894
H	1.3231	2.1505	-1.9721	H	-0.2289	1.3913	-1.9057
C	1.1240	1.6590	1.4537	H	1.0418	2.1029	-0.9124
H	2.1853	1.5284	1.6809	H	1.5651	-0.0625	-2.0985
H	0.8679	2.7103	1.6243	H	-0.3370	-1.3500	-1.9305
H	0.5435	1.0627	2.1595	H	0.8421	-2.1836	-0.9205
C	1.4766	-2.4070	-0.8608	H	-2.0710	0.1071	1.0706
H	2.5437	-2.5247	-0.6510	H	-2.3312	2.5995	0.8177
H	0.9832	-3.3620	-0.6505	H	-2.0856	2.5504	-0.9429
H	1.3533	-2.1809	-1.9251	H	-0.9835	3.4770	0.0861
C	1.1475	-1.6176	1.4891	H	0.9059	0.8480	1.7164
H	0.8963	-2.6656	1.6854	H	-0.6402	1.4113	2.3944
H	2.2090	-1.4776	1.7097	H	0.4668	2.5383	1.6147
H	0.5673	-1.0069	2.1827	H	-2.3055	-2.3068	-1.0814
C	-2.8885	-0.0129	-0.0339	H	-2.6370	-2.3673	0.6792

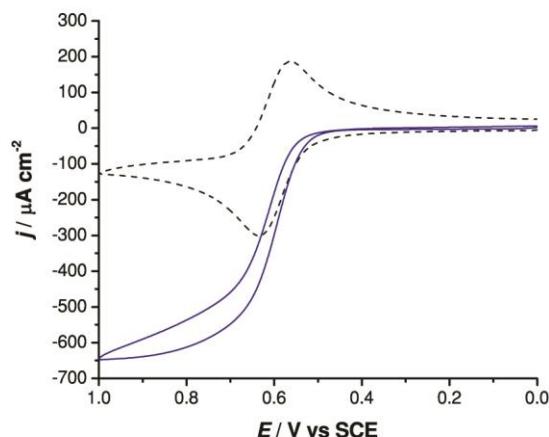
O	-3.2327	-0.0993	-1.2498	H	-1.3746	-3.3619	-0.0385
O	-3.6816	0.0788	0.9529	H	-0.8340	-1.3524	2.3620
O	2.8410	0.0141	-0.1793	H	0.8027	-1.1009	1.6982
H	3.2559	0.0079	-1.0529	H	0.0463	-2.6733	1.6002

### 3.6 4-Acetamido-TEMPO (6)

4-Acetamido-TEMPO was purchased from Sigma Aldrich and used without purification.

**Table S3.6. Summary table of electrocatalytic properties of TEMPO-NHAc.**

	$E_{a1}$	0.635
	$E_{a2}$	0.641
	$j_{max}$	518.3
	$(i_{pa}/i_{pc})_{cat.}$	28.51



**Figure S3.6.** CV of 5 mM 4-acetamido-TEMPO in the absence (dashed) and presence (solid) of 1 M glycerol using 150 mM Robinson buffer at 25 °C.

#### Optimized Geometry Coordinates Using B3LYP/6-31+G(d,p) CPCM

Symbol	T*			T+			
	X	Y	Z	X	Y	Z	
C	-1.3026	-1.3326	-0.0304	C	-1.2974	-1.3610	0.0116
C	0.1422	-1.2467	-0.5650	C	0.1404	-1.2550	-0.5417
C	0.9004	0.0000	-0.0980	C	0.9018	0.0000	-0.0954
C	0.1422	1.2467	-0.5650	C	0.1404	1.2550	-0.5417
C	-1.3026	1.3326	-0.0304	C	-1.2974	1.3610	0.0116
H	0.6747	-2.1517	-0.2547	H	0.6683	-2.1543	-0.2122
H	1.0060	0.0000	0.9889	H	1.0375	0.0000	0.9880
H	0.6747	2.1517	-0.2547	H	0.6684	2.1543	-0.2122
H	0.1177	1.2479	-1.6626	H	0.1002	1.2856	-1.6364

H	0.1177	-1.2479	-1.6626	H	0.1002	-1.2856	-1.6363
N	-1.9877	0.0000	-0.1809	C	-2.1165	-2.4030	-0.7547
O	-3.2665	0.0000	-0.0225	H	-1.5618	-3.3433	-0.7134
C	-2.0834	-2.3595	-0.8680	H	-3.0977	-2.5634	-0.3057
H	-1.5541	-3.3170	-0.8417	H	-2.2406	-2.1218	-1.8036
H	-3.0904	-2.5072	-0.4742	C	-1.3284	-1.6753	1.5308
H	-2.1587	-2.0351	-1.9104	H	-2.3413	-1.5914	1.9297
C	-1.3307	-1.7579	1.4547	H	-1.0027	-2.7137	1.6306
H	-2.3554	-1.7237	1.8343	H	-0.6534	-1.0526	2.1152
H	-0.9625	-2.7846	1.5454	C	-2.1165	2.4030	-0.7548
H	-0.7064	-1.1208	2.0856	H	-3.0977	2.5634	-0.3058
C	-2.0834	2.3595	-0.8679	H	-1.5618	3.3433	-0.7134
H	-3.0904	2.5072	-0.4742	H	-2.2406	2.1218	-1.8036
H	-1.5542	3.3170	-0.8416	C	-1.3284	1.6753	1.5308
H	-2.1587	2.0351	-1.9104	H	-1.0027	2.7137	1.6306
C	-1.3307	1.7579	1.4547	H	-2.3413	1.5915	1.9297
H	-0.9625	2.7846	1.5454	H	-0.6533	1.0527	2.1152
H	-2.3554	1.7237	1.8343	O	-3.1570	0.0000	-0.4425
H	-0.7064	1.1208	2.0856	N	-1.9949	0.0000	-0.1661
N	2.2665	0.0000	-0.6172	N	2.2497	0.0000	-0.6452
C	3.3801	0.0000	0.1583	C	3.3744	0.0000	0.1233
H	2.3870	0.0000	-1.6219	H	2.3553	0.0000	-1.6515
O	3.3359	0.0000	1.3988	O	3.3331	0.0000	1.3610
C	4.7051	0.0000	-0.5788	C	4.6900	0.0000	-0.6267
H	5.2759	0.8829	-0.2768	H	5.2630	0.8831	-0.3299
H	5.2759	-0.8829	-0.2768	H	5.2630	-0.8831	-0.3299
H	4.5991	0.0000	-1.6662	H	4.5722	0.0000	-1.7126

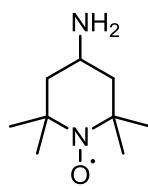
TH				TH2			
Symbol	X	Y	Z	Symbol	X	Y	Z
C	-1.2816	-1.2958	-0.0416	C	-1.2414	-1.3585	-0.0313
C	0.1825	-1.2522	-0.5352	C	0.2095	-1.2591	-0.5425
C	0.9408	0.0000	-0.0791	C	0.9605	0.0024	-0.0898
C	0.1824	1.2522	-0.5351	C	0.2076	1.2600	-0.5501
C	-1.2816	1.2958	-0.0416	C	-1.2388	1.3562	-0.0268
H	0.6973	-2.1529	-0.1834	H	0.7330	-2.1525	-0.1902
H	1.0523	0.0000	1.0067	H	1.0749	0.0058	0.9957
H	0.6972	2.1530	-0.1834	H	0.7316	2.1569	-0.2071
H	0.1863	1.2830	-1.6327	H	0.2047	1.2972	-1.6469
H	0.1864	-1.2829	-1.6327	H	0.2137	-1.3043	-1.6389
N	-1.9140	0.0000	-0.4363	N	-1.9292	0.0001	-0.3900
C	-2.0175	-2.4065	-0.8174	C	-2.0069	-2.4339	-0.8160

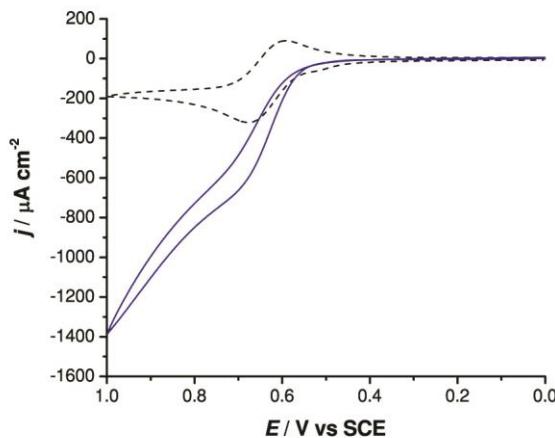
H	-1.4987	-3.3617	-0.6850	H	-1.4787	-3.3832	-0.6982
H	-3.0427	-2.5255	-0.4567	H	-3.0239	-2.5568	-0.4399
H	-2.0476	-2.1733	-1.8867	H	-2.0453	-2.2089	-1.8872
C	-1.3522	-1.6328	1.4671	C	-1.3308	-1.6419	1.4719
H	-2.3692	-1.4893	1.8404	H	-2.3545	-1.5435	1.8363
H	-1.0807	-2.6833	1.6152	H	-1.0186	-2.6785	1.6219
H	-0.6739	-1.0322	2.0754	H	-0.6759	-1.0143	2.0742
C	-2.0175	2.4065	-0.8174	C	-2.0092	2.4402	-0.7963
H	-3.0428	2.5254	-0.4567	H	-3.0031	2.6150	-0.3757
H	-1.4987	3.3617	-0.6850	H	-1.4537	3.3775	-0.7145
H	-2.0477	2.1733	-1.8867	H	-2.0995	2.2068	-1.8630
C	-1.3523	1.6328	1.4671	C	-1.3173	1.6291	1.4785
H	-1.0807	2.6833	1.6153	H	-1.0586	2.6797	1.6323
H	-2.3692	1.4892	1.8404	H	-2.3284	1.4719	1.8576
H	-0.6739	1.0322	2.0754	H	-0.6203	1.0332	2.0658
N	2.3062	0.0000	-0.6046	N	2.3194	0.0017	-0.6158
C	3.4256	0.0000	0.1604	C	3.4330	0.0012	0.1665
H	2.4199	0.0000	-1.6100	H	2.4408	0.0012	-1.6204
O	3.3944	0.0000	1.4021	O	3.3778	0.0010	1.4043
C	4.7445	0.0000	-0.5885	C	4.7589	0.0007	-0.5663
H	5.3181	0.8829	-0.2917	H	5.3261	-0.8848	-0.2655
H	5.3181	-0.8829	-0.2918	H	4.6558	0.0049	-1.6537
H	4.6288	0.0000	-1.6749	H	5.3303	0.8813	-0.2589
O	-3.2763	0.0000	0.0594	O	-3.2558	-0.0567	0.1132
H	-3.8079	0.0000	-0.7488	H	-3.8120	0.4636	-0.4936
				H	-1.9955	-0.0135	-1.4154

### 3.7 4-Amino-TEMPO (7)

4-Amino-TEMPO was purchased from Sigma Aldrich and used without purification.

**Table S3.7. Summary table of electrocatalytic properties of TEMPO-NH<sub>2</sub>.**

	$E_{a1}$	0.661
	$E_{a2}$	0.542
	$j_{max}$	1200.4
	$(i_{pa}/i_{pc})_{cat.}$	42.37



**Figure S3.7.** CV of 5 mM 4-amino-TEMPO in the absence (dashed) and presence (solid) of 1 M glycerol using 150 mM Robinson buffer at 25 °C.

#### Optimized Geometry Coordinates Using B3LYP/6-31+G(d,p) CPCM for TEMPO-NH<sub>2</sub>

T*				T+			
Symbol	X	Y	Z	Symbol	X	Y	Z
C	-0.3827	-1.3338	-0.0141	C	0.3956	1.3561	0.0314
C	1.1145	-1.2383	-0.3705	C	-1.0899	1.2563	-0.3745
C	1.8139	0.0000	0.1890	C	-1.8202	0.0164	0.1484
C	1.1145	1.2384	-0.3705	C	-1.1126	-1.2366	-0.3741
C	-0.3827	1.3338	-0.0141	C	0.3707	-1.3629	0.0314
H	1.6024	-2.1521	-0.0102	H	-1.5683	2.1703	-0.0073
H	1.7320	0.0000	1.2865	H	-1.8024	0.0163	1.2475
H	1.6023	2.1522	-0.0102	H	-1.6072	-2.1416	-0.0059
H	1.2288	1.2241	-1.4618	H	-1.1884	-1.2490	-1.4671

H	1.2288	-1.2240	-1.4618	H	-1.1646	1.2690	-1.4675
N	-1.0484	0.0000	-0.2289	C	1.1400	2.3902	-0.8179
O	-2.3373	0.0000	-0.2062	H	0.6033	3.3366	-0.7184
C	-1.0569	-2.3492	-0.9526	H	2.1658	2.5400	-0.4775
H	-0.5404	-3.3105	-0.8690	H	1.1485	2.1088	-1.8739
H	-2.1066	-2.4939	-0.6907	C	0.5909	1.6736	1.5384
H	-0.9980	-2.0156	-1.9933	H	1.6410	1.5870	1.8261
C	-0.5942	-1.7768	1.4511	H	0.2810	2.7134	1.6702
H	-1.6594	-1.7594	1.6973	H	-0.0194	1.0546	2.1932
H	-0.2264	-2.8001	1.5780	C	1.0966	-2.4102	-0.8177
H	-0.0634	-1.1385	2.1615	H	2.1191	-2.5792	-0.4766
C	-1.0569	2.3492	-0.9526	H	0.5421	-3.3464	-0.7191
H	-2.1066	2.4939	-0.6907	H	1.1112	-2.1286	-1.8736
H	-0.5405	3.3105	-0.8690	C	0.5600	-1.6834	1.5385
H	-0.9980	2.0156	-1.9933	H	0.2333	-2.7180	1.6702
C	-0.5942	1.7768	1.4511	H	1.6111	-1.6139	1.8268
H	-0.2265	2.8001	1.5780	H	-0.0404	-1.0545	2.1930
H	-1.6594	1.7594	1.6973	O	2.1880	-0.0198	-0.6075
H	-0.0635	1.1385	2.1615	N	1.0594	-0.0094	-0.2151
N	3.2252	0.0000	-0.2367	N	-3.1966	0.0285	-0.3667
H	3.7018	0.8137	0.1486	H	-3.7049	-0.7815	-0.0166
H	3.7018	-0.8136	0.1486	H	-3.6918	0.8455	-0.0142

TH				TH2			
Symbol	X	Y	Z	Symbol	X	Y	Z
C	-0.3600	-1.2963	-0.0203	C	-0.3160	-1.3611	-0.0061
C	1.1493	-1.2438	-0.3461	C	1.1824	-1.2376	-0.3389
C	1.8559	0.0000	0.1950	C	1.8645	0.0196	0.2118
C	1.1493	1.2438	-0.3461	C	1.1570	1.2636	-0.3374
C	-0.3600	1.2963	-0.0203	C	-0.3430	1.3524	0.0014
H	1.6170	-2.1541	0.0499	H	1.6646	-2.1385	0.0555
H	1.7913	0.0000	1.2934	H	1.7955	0.0181	1.3088
H	1.6170	2.1541	0.0499	H	1.6210	2.1741	0.0573
H	1.2811	1.2602	-1.4356	H	1.2964	1.2878	-1.4255
H	1.2811	-1.2601	-1.4356	H	1.3240	-1.2574	-1.4268
N	-0.9485	0.0000	-0.4781	N	-0.9702	-0.0097	-0.4441
C	-1.0008	-2.4046	-0.8797	C	-0.9670	-2.4435	-0.8803
H	-0.4970	-3.3591	-0.6947	H	-0.4418	-3.3851	-0.7019
H	-2.0602	-2.5290	-0.6385	H	-2.0198	-2.5838	-0.6297
H	-0.9108	-2.1660	-1.9444	H	-0.8809	-2.2150	-1.9478
C	-0.6058	-1.6419	1.4683	C	-0.5899	-1.6520	1.4737
H	-1.6624	-1.5161	1.7184	H	-1.6527	-1.5697	1.7071

H	-0.3383	-2.6893	1.6443	H	-0.2844	-2.6850	1.6590
H	-0.0144	-1.0340	2.1546	H	-0.0251	-1.0173	2.1543
C	-1.0008	2.4045	-0.8797	C	-1.0151	2.4285	-0.8664
H	-2.0602	2.5290	-0.6385	H	-2.0583	2.6009	-0.5854
H	-0.4970	3.3591	-0.6947	H	-0.4848	3.3711	-0.7112
H	-0.9108	2.1660	-1.9444	H	-0.9584	2.1949	-1.9350
C	-0.6059	1.6419	1.4683	C	-0.6204	1.6295	1.4825
H	-0.3384	2.6893	1.6443	H	-0.3863	2.6811	1.6662
H	-1.6624	1.5160	1.7184	H	-1.6724	1.4719	1.7278
H	-0.0144	1.0340	2.1546	H	-0.0062	1.0354	2.1573
N	3.2651	0.0000	-0.2457	N	3.2652	0.0342	-0.2364
H	3.7447	0.8131	0.1375	H	3.7415	0.8512	0.1417
H	3.7447	-0.8131	0.1375	H	3.7567	-0.7757	0.1375
O	-2.3570	0.0000	-0.1317	O	-2.3484	-0.0934	-0.1160
H	-2.7981	-0.0001	-0.9924	H	-2.8137	0.5410	-0.6897
				H	-0.9061	-0.0196	-1.4697

**Optimized Geometry Coordinates Using B3LYP/6-31+G(d,p) CPCM for TEMPO-NH<sub>3</sub><sup>+</sup>**

Symbol	T*			T+			
	X	Y	Z	X	Y	Z	
C	-0.4226	-1.3336	-0.0069	C	-0.4204	-1.3628	0.0282
C	1.0829	-1.2514	-0.3444	C	1.0744	-1.2594	-0.3433
C	1.7416	0.0000	0.2229	C	1.7528	0.0000	0.1941
C	1.0828	1.2514	-0.3444	C	1.0744	1.2594	-0.3433
C	-0.4226	1.3336	-0.0069	C	-0.4204	1.3628	0.0282
H	1.5641	-2.1565	0.0404	H	1.5511	-2.1608	0.0526
H	1.7299	0.0000	1.3143	H	1.7883	0.0000	1.2845
H	1.5641	2.1565	0.0404	H	1.5510	2.1608	0.0526
H	1.2058	1.2519	-1.4342	H	1.1693	1.2917	-1.4336
H	1.2058	-1.2519	-1.4342	H	1.1694	-1.2916	-1.4337
N	-1.0763	0.0000	-0.2559	C	-1.1291	-2.3997	-0.8483
O	-2.3630	0.0000	-0.2758	H	-0.5903	-3.3434	-0.7359
C	-1.0760	-2.3603	-0.9470	H	-2.1620	-2.5562	-0.5353
H	-0.5614	-3.3202	-0.8434	H	-1.1093	-2.1132	-1.9024
H	-2.1287	-2.5011	-0.6984	C	-0.6499	-1.6880	1.5284
H	-1.0015	-2.0366	-1.9894	H	-1.7083	-1.6125	1.7844
C	-0.6544	-1.7596	1.4595	H	-0.3332	-2.7248	1.6653
H	-1.7226	-1.7257	1.6883	H	-0.0679	-1.0652	2.2059
H	-0.3023	-2.7861	1.5998	C	-1.1292	2.3997	-0.8483
H	-0.1289	-1.1240	2.1762	H	-2.1621	2.5562	-0.5353
C	-1.0760	2.3603	-0.9470	H	-0.5904	3.3434	-0.7359
H	-2.1287	2.5011	-0.6984	H	-1.1094	2.1132	-1.9023

H	-0.5614	3.3202	-0.8434	C	-0.6500	1.6879	1.5284
H	-1.0015	2.0366	-1.9894	H	-0.3333	2.7248	1.6654
C	-0.6545	1.7596	1.4595	H	-1.7084	1.6124	1.7844
H	-0.3023	2.7861	1.5998	H	-0.0680	1.0652	2.2059
H	-1.7226	1.7257	1.6883	O	-2.2249	0.0000	-0.6014
H	-0.1289	1.1240	2.1762	N	-1.0932	0.0000	-0.2255
H	3.6941	0.8247	0.2347	H	3.7015	0.8229	0.1237
H	3.6941	-0.8246	0.2347	H	3.7015	-0.8228	0.1237
H	3.3568	0.0000	-1.1556	H	3.3119	0.0001	-1.2543
N	3.2152	0.0000	-0.1400	N	3.2049	0.0001	-0.2338

Symbol	TH			TH2			
	X	Y	Z	X	Y	Z	
C	-0.3990	-1.2964	-0.0134	C	-1.3440	-0.3772	0.1974
C	1.1172	-1.2565	-0.3188	C	-1.3036	0.7099	-0.8947
C	1.7819	0.0000	0.2335	C	-0.0487	1.5885	-0.9917
C	1.1172	1.2565	-0.3188	C	1.2567	0.7888	-0.8865
C	-0.3990	1.2964	-0.0134	C	1.3599	-0.2973	0.2033
H	1.5781	-2.1581	0.0989	N	0.0328	-1.1334	0.1515
H	1.7862	0.0000	1.3250	C	-2.4418	-1.4057	-0.1236
H	1.5781	2.1581	0.0989	C	-1.6034	0.1458	1.6190
H	1.2582	1.2834	-1.4063	C	2.5166	-1.2541	-0.1348
H	1.2582	-1.2834	-1.4063	C	1.5956	0.2265	1.6288
N	-0.9705	0.0000	-0.4906	N	-0.0864	2.7887	-0.0479
C	-1.0223	-2.4079	-0.8806	O	0.0065	-1.8861	-1.0540
H	-0.5192	-3.3606	-0.6871	H	-1.3891	0.2185	-1.8679
H	-2.0831	-2.5323	-0.6495	H	-2.2036	1.3230	-0.7905
H	-0.9209	-2.1691	-1.9439	H	-0.0600	2.0634	-1.9733
C	-0.6654	-1.6338	1.4728	H	1.3736	0.3036	-1.8592
H	-1.7231	-1.4902	1.7056	H	2.1177	1.4549	-0.7801
H	-0.4170	-2.6842	1.6551	H	0.0340	-1.7940	0.9394
H	-0.0774	-1.0341	2.1696	H	-2.4340	-2.2284	0.5974
C	-1.0223	2.4079	-0.8806	H	-2.3532	-1.8118	-1.1294
H	-2.0831	2.5323	-0.6496	H	-3.4053	-0.8979	-0.0369
H	-0.5192	3.3606	-0.6871	H	-0.9752	0.9734	1.9356
H	-0.9209	2.1691	-1.9439	H	-1.5133	-0.6498	2.3639
C	-0.6654	1.6338	1.4728	H	-2.6353	0.5022	1.6456
H	-0.4170	2.6842	1.6551	H	2.4806	-1.6158	-1.1632
H	-1.7231	1.4902	1.7056	H	2.5561	-2.1022	0.5565
H	-0.0775	1.0341	2.1696	H	3.4515	-0.7012	-0.0194
H	3.7373	0.8246	0.2189	H	1.5731	-0.5839	2.3630
H	3.7373	-0.8246	0.2189	H	0.9078	0.9977	1.9630

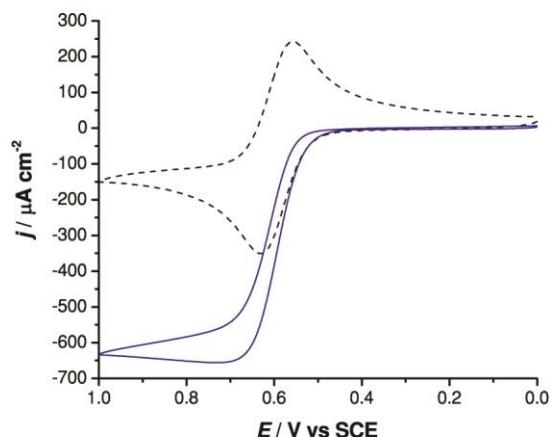
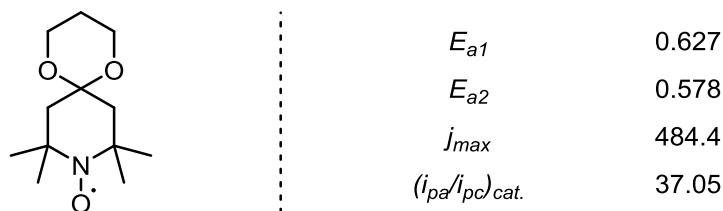
H	3.3785	0.0000	-1.1657	H	2.5972	0.6607	1.6530
N	3.2528	0.0000	-0.1484	H	-0.9305	3.3478	-0.2088
O	-2.3826	0.0000	-0.1843	H	-0.0714	2.5552	0.9468
H	-2.8032	0.0000	-1.0559	H	0.7135	3.4065	-0.2193
				H	0.5649	-2.6708	-0.9121

### 3.8 4,4-(1,3-Dioxane)-TEMPO (8)

**8** was prepared according to the procedure of Yamada *et al.*<sup>21</sup>

Data for **8**: Rf 0.27 (4:1 hexanes:EtOAc); IR (neat) 2965, 2934, 2876 cm<sup>-1</sup>; HRMS (TOF MS ES+) calcd for C<sub>12</sub>H<sub>22</sub>NO<sub>3</sub>Na [M+Na]<sup>+</sup>: 251.1497, found 251.1499.

**Table S3.8.** Summary table of electrocatalytic properties of TEMPO-ketal.



**Figure S3.8.** CV of 5 mM 4,4-(1,3-dioxane)-TEMPO in the absence (dashed) and presence (solid) of 1 M glycerol using 150 mM Robinson buffer at 25 °C.

## Optimized Geometry Coordinates Using B3LYP/6-31+G(d,p) CPCM

T*				T+			
Symbol	X	Y	Z	Symbol	X	Y	Z
C	0.9769	1.3845	-0.1185	C	0.9779	1.4120	-0.0689
C	-0.3713	0.9983	-0.7672	C	-0.3567	1.0266	-0.7429
C	0.1175	-1.4455	-0.6246	C	0.1144	-1.4391	-0.6246
C	1.5008	-1.2194	0.0206	C	1.4898	-1.2502	0.0466
H	-1.0793	1.8040	-0.5575	H	-1.0575	1.8305	-0.5085
H	-0.2739	-2.4103	-0.2884	H	-0.2850	-2.3972	-0.2831

H	0.2384	-1.5040	-1.7111	H	0.2566	-1.5084	-1.7065
H	-0.2442	0.9704	-1.8547	H	-0.2172	1.0376	-1.8278
N	1.9202	0.2145	-0.1477	C	1.6499	2.5667	-0.8211
O	3.1578	0.4766	0.0985	H	0.9303	3.3877	-0.8612
C	1.6054	2.5111	-0.9593	H	2.5452	2.9203	-0.3083
H	0.8998	3.3453	-1.0229	H	1.9080	2.2829	-1.8444
H	2.5301	2.8714	-0.5052	C	0.8368	1.7799	1.4333
H	1.8245	2.1659	-1.9744	H	1.8186	1.9261	1.8890
C	0.8131	1.8733	1.3376	H	0.2994	2.7314	1.4615
H	1.7960	2.0823	1.7686	H	0.2668	1.0434	1.9938
H	0.2303	2.8003	1.3460	C	2.5461	-2.1312	-0.6306
H	0.2988	1.1395	1.9590	H	3.5038	-2.0930	-0.1099
C	2.5248	-2.0952	-0.7251	H	2.1784	-3.1595	-0.5988
H	3.5103	-2.0281	-0.2611	H	2.6916	-1.8491	-1.6765
H	2.1941	-3.1380	-0.6926	C	1.4804	-1.5256	1.5759
H	2.6091	-1.7921	-1.7733	H	1.3385	-2.6041	1.6838
C	1.5229	-1.5883	1.5206	H	2.4397	-1.2558	2.0229
H	1.3395	-2.6623	1.6299	H	0.6639	-1.0223	2.0867
H	2.5068	-1.3615	1.9403	O	3.0984	0.4280	-0.2623
H	0.7565	-1.0557	2.0836	N	1.9322	0.2100	-0.1207
C	-0.9415	-0.3763	-0.3750	C	-0.9392	-0.3576	-0.3818
C	-3.2442	0.0119	-1.0254	C	-3.2268	0.0323	-1.0705
C	-2.5204	0.2950	1.3317	C	-2.5589	0.2748	1.3058
C	-3.6861	-0.0999	0.4308	C	-3.6948	-0.1251	0.3719
H	-3.9741	-0.4283	-1.7085	H	-3.9311	-0.4031	-1.7816
H	-3.1041	1.0632	-1.3125	H	-3.0922	1.0909	-1.3300
H	-2.7162	0.0624	2.3808	H	-2.7665	0.0151	2.3453
H	-2.3152	1.3714	1.2564	H	-2.3715	1.3556	1.2558
H	-3.9882	-1.1309	0.6473	H	-3.9798	-1.1663	0.5579
H	-4.5463	0.5532	0.6170	H	-4.5709	0.5066	0.5552
O	-2.0288	-0.7290	-1.2388	O	-1.9933	-0.6888	-1.2760
O	-1.3441	-0.4623	0.9890	O	-1.3560	-0.4542	0.9721

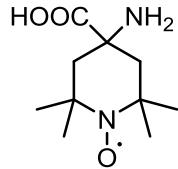
TH				TH2			
Symbol	X	Y	Z	Symbol	X	Y	Z
C	0.9806	1.3358	-0.1290	C	0.9418	1.3897	-0.1167
C	-0.4035	0.9992	-0.7339	C	-0.4188	1.0188	-0.7436
C	0.0695	-1.4590	-0.5869	C	0.0371	-1.4593	-0.6108
C	1.4719	-1.1984	0.0094	C	1.4299	-1.2676	0.0206
H	-1.0894	1.8103	-0.4761	H	-1.1068	1.8272	-0.4873
H	-0.3157	-2.4083	-0.2012	H	-0.3660	-2.4071	-0.2445
H	0.1661	-1.5599	-1.6728	H	0.1395	-1.5545	-1.6969

H	-0.3128	0.9965	-1.8255	H	-0.3311	1.0286	-1.8355
N	1.8749	0.1749	-0.4155	N	1.8884	0.1734	-0.3649
C	1.5456	2.5369	-0.9163	C	1.5630	2.5612	-0.8931
H	0.8447	3.3770	-0.8713	H	0.8660	3.4022	-0.8622
H	2.4981	2.8691	-0.4946	H	2.5038	2.8840	-0.4426
H	1.7019	2.2712	-1.9668	H	1.7350	2.3128	-1.9462
C	0.8819	1.7457	1.3593	C	0.8710	1.7359	1.3739
H	1.8823	1.8513	1.7869	H	1.8705	1.8318	1.8015
H	0.3802	2.7170	1.4318	H	0.3777	2.7081	1.4564
H	0.3130	1.0330	1.9544	H	0.2906	1.0189	1.9488
C	2.4503	-2.1796	-0.6707	C	2.4330	-2.2167	-0.6536
H	3.4512	-2.0966	-0.2387	H	3.4212	-2.1453	-0.1946
H	2.1054	-3.2094	-0.5300	H	2.0745	-3.2409	-0.5257
H	2.5150	-1.9784	-1.7449	H	2.5197	-2.0298	-1.7295
C	1.5197	-1.4619	1.5329	C	1.4677	-1.4732	1.5384
H	1.4012	-2.5360	1.7137	H	1.3491	-2.5450	1.7193
H	2.4891	-1.1577	1.9360	H	2.4317	-1.1692	1.9501
H	0.7276	-0.9480	2.0740	H	0.6612	-0.9621	2.0568
C	-0.9826	-0.3768	-0.3544	C	-1.0026	-0.3622	-0.3627
C	-3.2721	0.0390	-1.0340	C	-3.2958	0.0488	-1.0247
C	-2.5769	0.3098	1.3339	C	-2.5905	0.3044	1.3402
C	-3.7370	-0.0636	0.4161	C	-3.7468	-0.0839	0.4260
H	-4.0012	-0.3879	-1.7267	H	-4.0177	-0.3835	-1.7203
H	-3.1096	1.0879	-1.3189	H	-3.1502	1.1025	-1.2984
H	-2.7917	0.0770	2.3795	H	-2.7893	0.0572	2.3847
H	-2.3553	1.3837	1.2661	H	-2.3857	1.3817	1.2794
H	-4.0604	-1.0892	0.6281	H	-4.0474	-1.1180	0.6272
H	-4.5884	0.6045	0.5899	H	-4.6095	0.5648	0.6141
O	-2.0675	-0.7221	-1.2297	O	-2.0771	-0.6922	-1.2389
O	-1.4089	-0.4635	1.0050	O	-1.4065	-0.4471	0.9965
O	3.1753	0.4574	0.1590	O	3.1570	0.4409	0.2202
H	3.7500	0.5319	-0.6155	H	3.8065	0.4883	-0.5029
				H	2.0173	0.1459	-1.3825

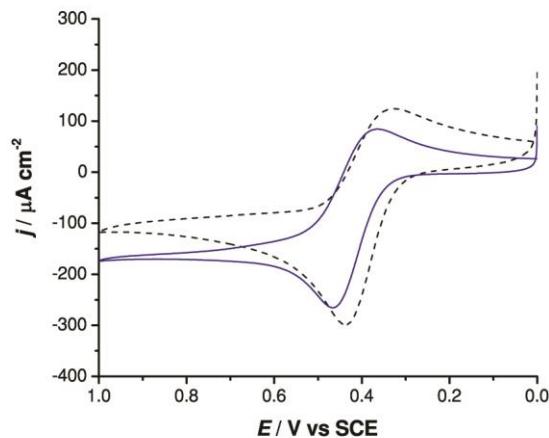
### 3.9 4-Amino-4-Carboxy-TEMPO (9)

4-Amino-4-carboxy-TEMPO (9) was purchased from Sigma and used without purification.

**Table S3.9. Summary table of electrocatalytic properties of TEMPO-NH<sub>2</sub>(-4-COOH).**



$E_{a1}$	0.427
$E_{a2}$	0.511
$j_{max}$	56.2
$(i_{pa}/i_{pc})_{cat.}$	0.74



**Figure S3.9.** CV of 5 mM 4-amino-4-carboxy-TEMPO in the absence (dashed) and presence (solid) of 1 M glycerol using 150 mM Robinson buffer at 25 °C.

#### Optimized Geometry Coordinates Using B3LYP/6-31+G(d,p) CPCM

T*				T+			
Symbol	X	Y	Z	Symbol	X	Y	Z
C	1.0024	1.3276	-0.0459	C	-1.0144	-1.3530	0.0160
C	-0.5201	1.2535	-0.3130	C	0.5110	-1.2602	-0.2601
C	-1.2678	0.0000	0.1543	C	1.2627	0.0000	0.1796
C	-0.5201	-1.2535	-0.3130	C	0.5110	1.2602	-0.2601
C	1.0024	-1.3276	-0.0459	C	-1.0144	1.3530	0.0160
H	-0.9873	2.1566	0.0953	H	0.9643	-2.1603	0.1660
H	-0.9873	-2.1566	0.0953	H	0.9643	2.1603	0.1660
H	-0.6813	-1.2855	-1.3938	H	0.6590	1.3225	-1.3413
H	-0.6813	1.2854	-1.3939	H	0.6590	-1.3225	-1.3413

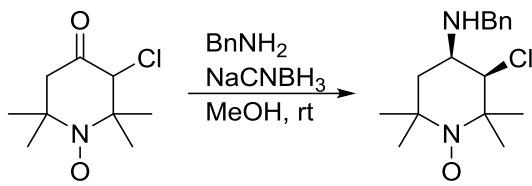
N	1.6428	0.0000	-0.3339	C	-1.6449	-2.4113	-0.8944
O	2.9269	0.0000	-0.4331	H	-1.1194	-3.3518	-0.7124
C	1.5944	2.3587	-1.0248	H	-2.7021	-2.5618	-0.6716
H	1.0852	3.3175	-0.8873	H	-1.5329	-2.1514	-1.9496
H	2.6608	2.5018	-0.8451	C	-1.3756	-1.6668	1.4906
H	1.4523	2.0367	-2.0607	H	-2.4569	-1.6424	1.6400
C	1.3461	1.7643	1.3960	H	-1.0241	-2.6836	1.6822
H	2.4312	1.8196	1.5137	H	-0.9107	-1.0039	2.2164
H	0.9261	2.7558	1.5911	C	-1.6449	2.4113	-0.8944
H	0.9719	1.0778	2.1585	H	-2.7021	2.5618	-0.6716
C	1.5943	-2.3587	-1.0248	H	-1.1194	3.3518	-0.7124
H	2.6607	-2.5018	-0.8451	H	-1.5329	2.1514	-1.9496
H	1.0852	-3.3175	-0.8873	C	-1.3756	1.6668	1.4906
H	1.4523	-2.0367	-2.0607	H	-1.0241	2.6836	1.6822
C	1.3461	-1.7643	1.3960	H	-2.4569	1.6424	1.6400
H	0.9261	-2.7558	1.5911	H	-0.9107	1.0039	2.2164
H	2.4312	-1.8196	1.5137	O	-2.6950	0.0000	-0.9059
H	0.9719	-1.0778	2.1585	N	-1.6482	0.0000	-0.3311
C	-2.7353	0.0000	-0.4604	C	2.7021	0.0000	-0.5388
O	-2.8287	0.0000	-1.7011	O	3.6723	0.0000	0.2758
O	-3.6663	0.0000	0.4049	O	2.7042	0.0000	-1.7786
H	-2.6026	0.0000	1.6441	H	2.7062	0.0000	1.5495
H	-1.1946	-0.8285	2.1441	H	1.3452	0.8295	2.1719
H	-1.1946	0.8285	2.1441	H	1.3452	-0.8295	2.1719
N	-1.5336	0.0000	1.6549	N	1.6332	0.0000	1.6522

TH			
Symbol	X	Y	Z
C	0.9798	1.2926	-0.0513
C	-0.5496	1.2575	-0.2975
C	-1.3036	0.0000	0.1553
C	-0.5496	-1.2575	-0.2975
C	0.9798	-1.2926	-0.0513
H	-1.0009	2.1556	0.1401
H	-1.0009	-2.1556	0.1401
H	-0.7217	-1.3160	-1.3755
H	-0.7217	1.3160	-1.3755
N	1.5315	0.0000	-0.5503
C	1.5512	2.4047	-0.9569
H	1.0589	3.3577	-0.7373
H	2.6237	2.5319	-0.7899
H	1.3866	2.1630	-2.0115

TH2			
Symbol	X	Y	Z
C	0.9523	1.3491	-0.0258
C	-0.5711	1.2677	-0.2778
C	-1.3172	0.0075	0.1849
C	-0.5781	-1.2612	-0.2685
C	0.9474	-1.3530	-0.0329
H	-1.0209	2.1674	0.1542
H	-1.0287	-2.1540	0.1764
H	-0.7723	-1.3338	-1.3430
H	-0.7565	1.3301	-1.3546
C	1.5462	2.4391	-0.9341
H	1.0225	3.3766	-0.7322
H	2.6059	2.6108	-0.7286
H	1.4115	2.2117	-1.9968
C	1.3492	1.6321	1.4257

C	1.3462	1.6534	1.4080	H	2.4298	1.5592	1.5574
H	2.4307	1.6247	1.5372	H	1.0506	2.6581	1.6541
H	1.0052	2.6702	1.6281	H	0.8759	0.9804	2.1567
H	0.9146	0.9892	2.1573	C	1.5285	-2.4339	-0.9593
C	1.5512	-2.4047	-0.9569	H	2.5998	-2.5613	-0.7982
H	2.6237	-2.5319	-0.7899	H	1.0317	-3.3809	-0.7344
H	1.0589	-3.3577	-0.7372	H	1.3481	-2.2083	-2.0154
H	1.3866	-2.1630	-2.0115	C	1.3548	-1.6547	1.4128
C	1.3462	-1.6534	1.4080	H	1.0189	-2.6697	1.6393
H	1.0052	-2.6702	1.6281	H	2.4389	-1.6261	1.5300
H	2.4307	-1.6247	1.5372	H	0.9172	-0.9887	2.1534
H	0.9146	-0.9892	2.1573	C	-2.7736	0.0035	-0.4788
C	-2.7666	0.0000	-0.4636	O	-2.8212	0.0176	-1.7195
O	-2.8573	0.0000	-1.7054	O	-3.7210	-0.0177	0.3639
O	-3.7044	0.0000	0.3956	O	2.9523	-0.0639	-0.2826
O	2.9582	0.0000	-0.3098	H	3.3848	0.4492	-0.9886
H	3.3370	0.0000	-1.2002	H	-2.7057	-0.0138	1.6149
H	-2.6415	0.0000	1.6472	H	-1.2959	-0.7992	2.1892
H	-1.2335	-0.8282	2.1448	H	-1.3441	0.8579	2.1669
H	-1.2335	0.8282	2.1448	N	-1.6326	0.0133	1.6720
N	-1.5749	0.0000	1.6569	H	1.4205	-0.0125	-1.5378
				N	1.5550	-0.0017	-0.5197

### 3.10 3-Chloro-4-(N-Benzylamino)-TEMPO (10)

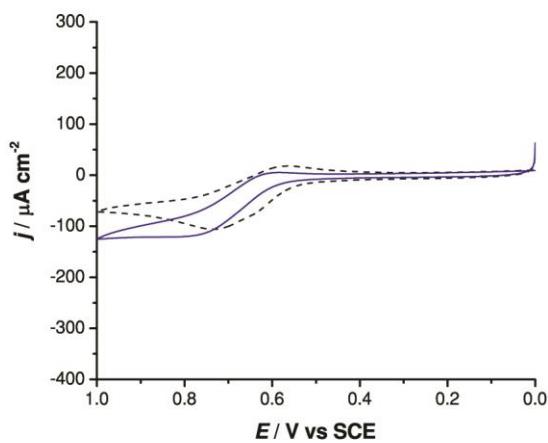


**( $\pm$ )-(3R,4R)-4-(benzylamino)-3-chloro-2,2,6,6-tetramethylpiperidin-1-oxyl (Syn1).** To a MeOH (2.3 mL, 0.3 M) solution of 2,2,6,6-tetramethyl-3-chloro-4-oxopiperidine-1-oxyl<sup>22</sup> (0.1441 g, 0.704 mmol) stirring at room temperature was added benzyl amine (0.15 mL, 1.37 mmol) followed by sodium cyanoborohydride (0.2210 g, 0.352 mmol). The reaction was stirred at room temperature for 48 h. The reaction was concentrated and the resulting oily mixture was extracted with EtOAc, filtered through celite, and concentrated again. Purification by FCC (3:1 hexanes:EtOAc) gave **Syn1** (0.0595 g, 0.202 mmol, 29%) as a red oil.

Data for **Syn1**:  $R_f$  0.82 (9:1 EtOAc:10% NH<sub>4</sub>OH in MeOH); IR (neat) 3329, 2978, 2939 cm<sup>-1</sup>; HRMS (TOF MS ES+) calcd for C<sub>16</sub>H<sub>25</sub>N<sub>2</sub>OCl [M+H]<sup>+</sup>: 296.1655, found 296.1663.

**Table S3.10. Summary table of electrocatalytic properties of TEMPO-NHBn(-Cl).**

	$E_{a1}$ $E_{a2}$ $j_{max}$ $(i_{pa}/i_{pc})_{cat.}$	0.673 0.623 53.6 18.40
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**Figure S3.10.** CV of 5 mM **10** in the absence (dashed) and presence (solid) of 1 M glycerol using 150 mM Robinson buffer at 25 °C.

**Optimized Geometry Coordinates Using B3LYP/6-31+G(d,p) CPCM for 3-Cl-TEMPO-NHBn**

T*				T+			
Symbol	X	Y	Z	Symbol	X	Y	Z
C	1.3210	1.8178	0.0616	C	1.2367	1.8437	0.1473
C	0.0868	1.1437	-0.5593	C	0.0355	1.1200	-0.4866
C	-0.1419	-0.3122	-0.1343	C	-0.1377	-0.3519	-0.0901
C	1.1044	-1.0908	-0.5591	C	1.1203	-1.1015	-0.5434
C	2.4297	-0.6079	0.0933	C	2.4597	-0.5881	0.0717
H	-0.7859	1.7424	-0.2874	H	-0.8489	1.6868	-0.1868
H	-0.2553	-0.3736	0.9586	H	-0.2454	-0.4403	1.0008
H	1.1966	-1.0421	-1.6464	H	1.1884	-1.0511	-1.6320
H	0.1657	1.1691	-1.6525	H	0.1058	1.1870	-1.5771
N	2.5005	0.8951	-0.0560	C	1.5120	3.1785	-0.5507
O	3.6580	1.4162	0.1478	H	0.5929	3.7665	-0.4976
C	1.6438	3.0918	-0.7380	H	2.3082	3.7395	-0.0594
H	0.7606	3.7375	-0.7503	H	1.7689	3.0337	-1.6029
H	2.4710	3.6416	-0.2861	C	1.0812	2.0677	1.6757
H	1.9076	2.8470	-1.7713	H	2.0081	2.4466	2.1110
C	1.0946	2.1903	1.5439	H	0.3078	2.8313	1.7906
H	2.0222	2.5726	1.9785	H	0.7605	1.1791	2.2156
H	0.3348	2.9755	1.6059	C	3.6719	-1.1058	-0.7084
H	0.7518	1.3448	2.1443	H	4.6065	-0.7991	-0.2383
C	3.6219	-1.1941	-0.6831	H	3.6287	-2.1957	-0.7030
H	4.5618	-0.8746	-0.2324	H	3.6594	-0.7615	-1.7457
H	3.5742	-2.2846	-0.6579	C	2.6266	-0.8863	1.5848
H	3.6055	-0.8655	-1.7267	H	2.8514	-1.9503	1.6736
C	2.5556	-0.9667	1.5902	H	3.4704	-0.3250	1.9905
H	2.7331	-2.0375	1.7078	H	1.7321	-0.6777	2.1684
H	3.4100	-0.4279	2.0068	O	3.5122	1.4784	-0.2952
H	1.6649	-0.7061	2.1653	N	2.4688	0.9546	-0.0503
N	-1.3366	-0.8731	-0.8082	N	-1.3101	-0.9227	-0.7829
H	-1.3165	-1.8799	-0.6648	H	-1.2914	-1.9293	-0.6379
C	-2.6109	-0.3845	-0.3647	C	-2.5975	-0.4290	-0.3685
C	-3.1746	0.7601	-0.9505	C	-3.1776	0.6586	-1.0377
C	-3.3400	-1.0692	0.6218	C	-3.3096	-1.0522	0.6681
C	-4.4287	1.2210	-0.5407	C	-4.4395	1.1273	-0.6616
H	-2.6382	1.2713	-1.7435	H	-2.6471	1.1186	-1.8656
C	-4.6037	-0.6186	1.0153	C	-4.5801	-0.5942	1.0295
H	-2.9143	-1.9588	1.0794	H	-2.8685	-1.8987	1.1882
C	-5.1496	0.5340	0.4421	C	-5.1460	0.5021	0.3712
H	-4.8500	2.1085	-1.0042	H	-4.8768	1.9704	-1.1885

H	-5.1562	-1.1655	1.7741	H	-5.1231	-1.0915	1.8279
H	-6.1287	0.8881	0.7506	H	-6.1311	0.8606	0.6543
Cl	0.8837	-2.8973	-0.2302	Cl	0.9823	-2.8873	-0.1823

TH				TH2			
Symbol	X	Y	Z	Symbol	X	Y	Z
C	1.3636	1.7535	0.0708	C	1.2323	1.7970	0.0932
C	0.0680	1.1502	-0.5043	C	-0.0037	1.1053	-0.5007
C	-0.1827	-0.3140	-0.1193	C	-0.1957	-0.3638	-0.0954
C	1.0458	-1.1152	-0.5575	C	1.0439	-1.1444	-0.5542
C	2.3928	-0.6235	0.0464	C	2.4002	-0.6475	0.0323
H	-0.7695	1.7641	-0.1629	H	-0.8698	1.6880	-0.1785
H	-0.2960	-0.3969	0.9719	H	-0.2909	-0.4410	0.9972
H	1.1121	-1.0963	-1.6474	H	1.0852	-1.1203	-1.6463
H	0.0948	1.2148	-1.5985	H	0.0216	1.1651	-1.5952
N	2.4650	0.8281	-0.3228	C	1.4752	3.1354	-0.6210
C	1.6247	3.0906	-0.6517	H	0.5725	3.7428	-0.5235
H	0.7583	3.7501	-0.5381	H	2.2973	3.6965	-0.1695
H	2.4958	3.6007	-0.2324	H	1.6676	3.0040	-1.6914
H	1.7967	2.9242	-1.7199	C	1.1531	2.0185	1.6065
C	1.2417	2.0405	1.5862	H	2.1215	2.3147	2.0136
H	2.2170	2.3071	2.0010	H	0.4518	2.8389	1.7778
H	0.5663	2.8888	1.7375	H	0.7845	1.1541	2.1561
H	0.8425	1.2001	2.1560	C	3.5794	-1.2495	-0.7467
C	3.5543	-1.3128	-0.6983	H	4.5289	-0.8999	-0.3399
H	4.5118	-0.9823	-0.2901	H	3.5442	-2.3355	-0.6524
H	3.4925	-2.3971	-0.5825	H	3.5333	-1.0032	-1.8126
H	3.5260	-1.0689	-1.7651	C	2.5729	-0.8930	1.5361
C	2.5303	-0.9179	1.5584	H	2.8398	-1.9412	1.6764
H	2.7879	-1.9683	1.7132	H	3.3893	-0.2875	1.9313
H	3.3379	-0.3082	1.9694	H	1.6712	-0.7020	2.1152
H	1.6200	-0.7156	2.1240	O	3.6545	1.3859	0.2576
O	3.7036	1.3496	0.2078	H	3.9831	2.0665	-0.3572
H	4.2104	1.5771	-0.5847	H	2.5220	0.9388	-1.3062
N	-1.3894	-0.8483	-0.7982	N	2.4414	0.8868	-0.2831
H	-1.3850	-1.8564	-0.6630	N	-1.3886	-0.9230	-0.7663
C	-2.6583	-0.3465	-0.3633	H	-1.3858	-1.9273	-0.6046
C	-3.1723	0.8498	-0.8911	C	-2.6625	-0.4028	-0.3471
C	-3.4405	-1.0700	0.5530	C	-3.2201	0.7034	-1.0059
C	-4.4253	1.3209	-0.4908	C	-3.3890	-1.0191	0.6839
H	-2.5992	1.3943	-1.6341	C	-4.4711	1.1963	-0.6246
C	-4.7038	-0.6081	0.9349	H	-2.6809	1.1597	-1.8300

H	-3.0559	-1.9993	0.9661	C	-4.6496	-0.5373	1.0497
C	-5.1984	0.5949	0.4221	H	-2.9664	-1.8795	1.1966
H	-4.8058	2.2484	-0.9092	C	-5.1916	0.5774	0.4025
H	-5.2959	-1.1861	1.6390	H	-4.8895	2.0537	-1.1436
H	-6.1767	0.9581	0.7223	H	-5.2032	-1.0305	1.8434
Cl	0.8010	-2.9095	-0.1682	H	-6.1684	0.9550	0.6892
				Cl	0.8701	-2.9234	-0.1596

**Optimized Geometry Coordinates Using B3LYP/6-31+G(d,p) CPCM for 3-Cl-TEMPO-NH<sub>2</sub>Bn<sup>+</sup>**

Symbol	T*			T+			
	X	Y	Z	X	Y	Z	
C	1.2639	1.8365	0.0028	C	1.1639	1.8644	0.0764
C	0.0607	1.1175	-0.6389	C	0.0013	1.0843	-0.5673
C	-0.0877	-0.3286	-0.1771	C	-0.0836	-0.3744	-0.1212
C	1.1684	-1.1067	-0.5642	C	1.1891	-1.1183	-0.5383
C	2.4484	-0.5578	0.1304	C	2.4897	-0.5319	0.0971
H	-0.8418	1.6826	-0.3921	H	-0.9134	1.6133	-0.2906
H	-0.2691	-0.3978	0.8963	H	-0.2479	-0.4579	0.9537
H	1.3118	-1.0698	-1.6463	H	1.2975	-1.0922	-1.6244
H	0.1739	1.1364	-1.7290	H	0.0946	1.1410	-1.6565
N	2.4712	0.9417	-0.0720	C	1.4065	3.1867	-0.6563
O	3.6058	1.5049	0.1371	H	0.4680	3.7452	-0.6394
C	1.5671	3.1004	-0.8189	H	2.1706	3.7861	-0.1606
H	0.6666	3.7194	-0.8675	H	1.6933	3.0232	-1.6976
H	2.3651	3.6819	-0.3555	C	0.9620	2.1230	1.5932
H	1.8672	2.8410	-1.8383	H	1.8581	2.5642	2.0330
C	0.9860	2.2308	1.4694	H	0.1457	2.8457	1.6710
H	1.8943	2.6399	1.9186	H	0.6822	1.2361	2.1588
H	0.2098	3.0012	1.4945	C	3.7338	-1.0211	-0.6504
H	0.6459	1.3930	2.0820	H	4.6449	-0.6703	-0.1662
C	3.6850	-1.1328	-0.5803	H	3.7316	-2.1118	-0.6211
H	4.5942	-0.7718	-0.0999	H	3.7306	-0.6997	-1.6950
H	3.6679	-2.2231	-0.5202	C	2.6329	-0.7891	1.6188
H	3.7036	-0.8369	-1.6331	H	2.9070	-1.8385	1.7389
C	2.5192	-0.8722	1.6398	H	3.4393	-0.1784	2.0281
H	2.7219	-1.9337	1.7943	H	1.7189	-0.6097	2.1822
H	3.3416	-0.2984	2.0729	O	3.4689	1.5715	-0.2664
H	1.6029	-0.6210	2.1777	N	2.4380	1.0120	-0.0633
C	-2.6309	-0.4410	-0.3438	C	-2.6227	-0.4995	-0.3328
C	-3.3780	0.3779	-1.1868	C	-3.3403	0.2839	-1.2332
C	-3.0699	-0.7953	0.9307	C	-3.0970	-0.7995	0.9424
C	-4.6066	0.8633	-0.7296	C	-4.5793	0.7911	-0.8315

H	-3.0237	0.6336	-2.1806	H	-2.9592	0.4954	-2.2274
C	-4.2990	-0.3019	1.3729	C	-4.3361	-0.2839	1.3274
H	-2.4809	-1.4465	1.5687	H	-2.5300	-1.4262	1.6232
C	-5.0648	0.5266	0.5465	C	-5.0743	0.5107	0.4445
H	-5.2006	1.5009	-1.3756	H	-5.1526	1.4012	-1.5211
H	-4.6563	-0.5716	2.3610	H	-4.7229	-0.5108	2.3150
H	-6.0200	0.9049	0.8958	H	-6.0376	0.9061	0.7496
H	-1.2748	-1.9762	-0.6390	H	-1.2588	-2.0460	-0.5052
H	-1.2756	-0.8657	-1.8376	H	-1.2368	-1.0177	-1.7715
N	-1.3258	-0.9630	-0.8170	N	-1.3037	-1.0464	-0.7473
Cl	0.9436	-2.8889	-0.1964	Cl	1.0654	-2.8816	-0.1226

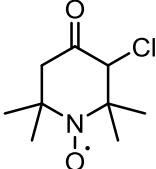
TH				TH2			
Symbol	X	Y	Z	Symbol	X	Y	Z
C	1.2593	1.7775	0.0146	C	1.1726	1.8189	-0.0099
C	0.0035	1.0969	-0.5737	C	-0.0234	1.0683	-0.6261
C	-0.1250	-0.3607	-0.1415	C	-0.1395	-0.3837	-0.1594
C	1.1252	-1.1349	-0.5549	C	1.1146	-1.1680	-0.5635
C	2.4230	-0.5451	0.0729	C	2.4185	-0.5996	0.0795
H	-0.8787	1.6592	-0.2568	H	-0.9212	1.6231	-0.3432
H	-0.2912	-0.4480	0.9330	H	-0.2966	-0.4455	0.9177
H	1.2302	-1.1274	-1.6417	H	1.2216	-1.1700	-1.6509
H	0.0568	1.1477	-1.6673	H	0.0417	1.1059	-1.7191
N	2.4131	0.8972	-0.3396	C	1.4123	3.1293	-0.7732
C	1.4617	3.1069	-0.7386	H	0.4985	3.7262	-0.7286
H	0.5569	3.7181	-0.6648	H	2.2175	3.7083	-0.3177
H	2.2899	3.6743	-0.3076	H	1.6439	2.9561	-1.8293
H	1.6742	2.9228	-1.7961	C	1.0115	2.1021	1.4865
C	1.0906	2.0910	1.5191	H	1.9366	2.4938	1.9112
H	2.0439	2.4171	1.9417	H	0.2419	2.8710	1.5894
H	0.3706	2.9065	1.6389	H	0.6921	1.2403	2.0699
H	0.7276	1.2462	2.1064	C	3.6538	-1.1941	-0.6101
C	3.6356	-1.1894	-0.6275	H	4.5678	-0.8089	-0.1555
H	4.5621	-0.8081	-0.1944	H	3.6449	-2.2769	-0.4777
H	3.6213	-2.2736	-0.4953	H	3.6678	-0.9865	-1.6849
H	3.6284	-0.9618	-1.6979	C	2.5098	-0.7935	1.5970
C	2.5340	-0.7965	1.5935	H	2.8043	-1.8263	1.7870
H	2.8397	-1.8284	1.7806	H	3.2829	-0.1465	2.0119
H	3.3010	-0.1373	2.0049	H	1.5744	-0.6155	2.1250
H	1.6046	-0.6253	2.1383	O	3.5555	1.5288	0.3328
O	3.6101	1.5012	0.1866	H	4.1767	1.7940	-0.3689
H	4.1153	1.7362	-0.6053	H	2.5718	0.9717	-1.3023

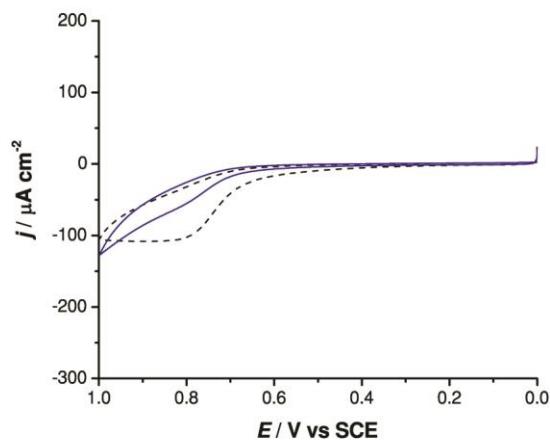
C	-2.6701	-0.4470	-0.3315	N	2.4297	0.9293	-0.2852
C	-3.3959	0.3566	-1.2071	C	-2.6823	-0.4685	-0.3187
C	-3.1276	-0.7532	0.9488	C	-3.4156	0.3117	-1.2091
C	-4.6207	0.8760	-0.7783	C	-3.1240	-0.7425	0.9742
H	-3.0274	0.5755	-2.2046	C	-4.6349	0.8431	-0.7794
C	-4.3527	-0.2261	1.3630	H	-3.0597	0.5031	-2.2168
H	-2.5549	-1.3930	1.6126	C	-4.3437	-0.2029	1.3876
C	-5.0968	0.5881	0.5033	H	-2.5466	-1.3670	1.6485
H	-5.1978	1.5023	-1.4503	C	-5.0960	0.5895	0.5148
H	-4.7238	-0.4583	2.3556	H	-5.2196	1.4516	-1.4609
H	-6.0487	0.9934	0.8308	H	-4.7040	-0.4089	2.3898
H	-1.3303	-2.0065	-0.5598	H	-6.0437	1.0045	0.8423
H	-1.3032	-0.9371	-1.7945	H	-1.3485	-2.0371	-0.5167
N	-1.3677	-0.9998	-0.7722	H	-1.3367	-1.0130	-1.7866
Cl	0.9217	-2.9075	-0.1229	N	-1.3829	-1.0376	-0.7612
				Cl	0.9365	-2.9224	-0.1184

### 3.11 3-Chloro-4-Oxo-TEMPO (11)

3-Chloro-4-oxo-TEMPO (**11**) was synthesized using a previously reported procedure.<sup>22</sup>

**Table S3.11.** Summary table of electrocatalytic properties of TEMPO-oxo(-3-Cl).

	$E_{a1}$ $E_{a2}$ $j_{max}$ $(i_{pa}/i_{pc})_{cat.}$	0.767 1.238 31.0 0.00
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**Figure S3.11.** CV of 5 mM **11** in the absence (dashed) and presence (solid) of 1 M glycerol using 150 mM Robinson buffer at 25 °C.

#### Optimized Geometry Coordinates Using B3LYP/6-31+G(d,p) CPCM

Symbol	T*			T+			
	X	Y	Z	X	Y	Z	
C	-0.4603	1.0132	0.0812	C	-0.4983	1.0147	0.1324
C	-1.1775	-0.2158	-0.5642	C	-1.1782	-0.2043	-0.5759
C	0.9235	-1.5905	-0.6359	C	0.9573	-1.5831	-0.5998
C	1.7916	-0.4325	-0.0849	C	1.8306	-0.4314	-0.0521
H	1.3560	-2.5468	-0.3346	H	1.3814	-2.5253	-0.2484
H	0.9202	-1.5470	-1.7321	H	1.0055	-1.5807	-1.6954
H	-1.1060	-0.1218	-1.6513	H	-1.0914	-0.0723	-1.6586
N	1.0232	0.8601	-0.1803	C	-0.9478	2.3502	-0.4587
O	1.7166	1.9334	-0.0477	H	-2.0296	2.4182	-0.3380

C	-0.9198	2.3004	-0.6205	H	-0.4926	3.1883	0.0703
H	-2.0028	2.3990	-0.5236	H	-0.7098	2.4224	-1.5225
H	-0.4477	3.1698	-0.1625	C	-0.6863	0.9966	1.6691
H	-0.6609	2.2801	-1.6831	H	-0.0283	1.7238	2.1477
C	-0.7116	1.1162	1.5990	H	-1.7191	1.2945	1.8593
H	-0.0360	1.8658	2.0181	H	-0.5324	0.0126	2.1100
H	-1.7391	1.4348	1.7863	C	3.0989	-0.2473	-0.8884
H	-0.5527	0.1694	2.1198	H	3.7785	0.4787	-0.4410
C	3.0505	-0.2960	-0.9550	H	3.6043	-1.2153	-0.9247
H	3.7329	0.4480	-0.5413	H	2.8628	0.0570	-1.9109
H	3.5645	-1.2611	-0.9893	C	2.1923	-0.6372	1.4426
H	2.7885	-0.0051	-1.9765	H	2.9082	-1.4625	1.4665
C	2.1962	-0.6984	1.3805	H	2.6745	0.2508	1.8558
H	2.8865	-1.5466	1.4150	H	1.3379	-0.9138	2.0584
H	2.7042	0.1780	1.7909	O	1.6239	1.8829	-0.3808
H	1.3407	-0.9383	2.0159	N	1.0265	0.8831	-0.1314
C	-0.5120	-1.5318	-0.1750	C	-0.5067	-1.5342	-0.2139
O	-1.0700	-2.4327	0.4228	O	-1.0952	-2.4718	0.2770
Cl	-2.9510	-0.2349	-0.2025	Cl	-2.9374	-0.2289	-0.2241

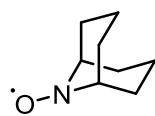
TH				TH2			
Symbol	X	Y	Z	Symbol	X	Y	Z
C	-0.4039	0.9980	0.0417	C	-0.4785	1.0139	0.0234
C	-1.2084	-0.1973	-0.5689	C	-1.2401	-0.2178	-0.5687
C	0.8430	-1.6548	-0.6241	C	0.8447	-1.6657	-0.6391
C	1.7257	-0.4997	-0.0849	C	1.7561	-0.5548	-0.0744
H	1.2417	-2.6167	-0.2943	H	1.2425	-2.6307	-0.3194
H	0.8589	-1.6315	-1.7211	H	0.8596	-1.6486	-1.7362
H	-1.1624	-0.1147	-1.6584	H	-1.2245	-0.1584	-1.6618
N	1.0089	0.7706	-0.4125	N	1.0298	0.8001	-0.3700
C	-0.8703	2.3058	-0.6247	C	-0.9032	2.3078	-0.6815
H	-1.9401	2.4537	-0.4626	H	-1.9726	2.4553	-0.5242
H	-0.3407	3.1570	-0.1918	H	-0.3752	3.1652	-0.2620
H	-0.6756	2.2805	-1.7015	H	-0.7255	2.2649	-1.7610
C	-0.5974	1.1082	1.5690	C	-0.6263	1.1429	1.5419
H	0.1821	1.7496	1.9857	H	0.1305	1.8164	1.9448
H	-1.5656	1.5633	1.7905	H	-1.6044	1.5798	1.7473
H	-0.5653	0.1429	2.0773	H	-0.5778	0.1881	2.0641
C	3.0432	-0.4922	-0.8824	C	3.0821	-0.5057	-0.8437
H	3.7381	0.2489	-0.4797	H	3.7745	0.2133	-0.4004
H	3.5206	-1.4750	-0.8196	H	3.5456	-1.4933	-0.7849
H	2.8543	-0.2623	-1.9356	H	2.9411	-0.2716	-1.9038

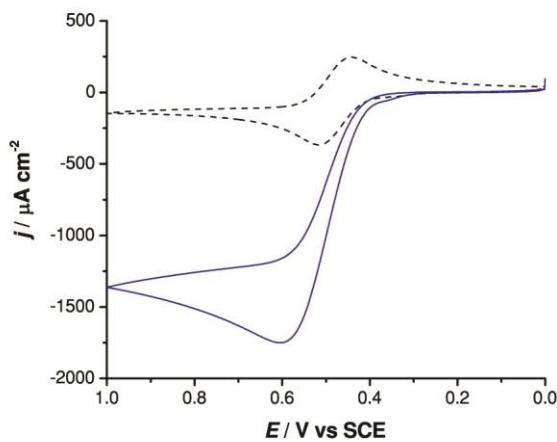
C	2.0522	-0.7186	1.4099	C	2.0162	-0.7257	1.4245
H	2.7663	-1.5428	1.5043	H	2.7174	-1.5563	1.5366
H	2.5119	0.1778	1.8328	H	2.4802	0.1651	1.8500
H	1.1769	-0.9773	2.0089	H	1.1229	-0.9770	1.9956
O	1.8017	1.8621	0.0976	O	1.7639	1.8720	0.1986
H	2.0775	2.3362	-0.7002	H	2.3080	2.2606	-0.5096
C	-0.5966	-1.5420	-0.1869	C	-0.5967	-1.5559	-0.1835
O	-1.1969	-2.4266	0.3970	O	-1.1862	-2.4462	0.3902
Cl	-2.9708	-0.1302	-0.1527	H	1.0571	0.9163	-1.3904
				Cl	-2.9798	-0.1606	-0.1176

### 3.12 ABNO (12)

ABNO was purchased from Sigma Aldrich and used without purification.

**Table S3.12. Summary table of electrocatalytic properties of ABNO.**

	$E_{a1}$	0.508
	$E_{a2}$	0.399
	$j_{max}$	859.2
	$(i_{pa}/i_{pc})_{cat.}$	83.44



**Figure S3.12.** CV of 5 mM ABNO in the absence (dashed) and presence (solid) of 1 M glycerol using 150 mM Robinson buffer at 25 °C.

#### Optimized Geometry Coordinates Using B3LYP/6-31+G(d,p) CPCM

T*				T+			
Symbol	X	Y	Z	Symbol	X	Y	Z
C	-0.0180	-1.2405	-0.3548	C	-0.0117	-1.2570	-0.3386
H	-0.3027	-2.0576	-1.0207	H	-0.0989	-2.0520	-1.0787
C	-0.0180	1.2405	-0.3548	C	-0.0117	1.2569	-0.3386
H	-0.3026	2.0576	-1.0208	H	-0.0989	2.0520	-1.0788
C	-0.8767	1.2749	0.9559	C	-1.1794	1.2687	0.7006
H	-1.5265	2.1554	0.9421	H	-1.7860	2.1543	0.4985
H	-0.2124	1.3887	1.8206	H	-0.7551	1.3834	1.7013
C	-0.8767	-1.2749	0.9559	C	-1.1794	-1.2687	0.7006
H	-0.2125	-1.3887	1.8206	H	-0.7551	-1.3834	1.7014

H	-1.5265	-2.1554	0.9421	H	-1.7861	-2.1543	0.4985
C	1.5021	-1.2710	-0.1001	C	1.4158	-1.2655	0.3063
H	2.0126	-1.3696	-1.0664	H	2.1506	-1.3737	-0.4979
H	1.7459	-2.1638	0.4871	H	1.4619	-2.1691	0.9209
C	1.5021	1.2710	-0.1001	C	1.4158	1.2655	0.3063
H	2.0126	1.3696	-1.0665	H	2.1506	1.3737	-0.4979
H	1.7459	2.1638	0.4871	H	1.4619	2.1691	0.9208
N	-0.3215	0.0000	-1.0955	C	1.6847	0.0000	1.1256
O	-1.2601	0.0000	-1.9836	H	2.7320	0.0000	1.4453
C	1.9916	0.0000	0.6148	H	1.0855	0.0000	2.0413
H	3.0859	0.0000	0.6626	C	-2.0394	0.0000	0.6301
H	1.6411	0.0000	1.6538	H	-2.6266	0.0000	-0.2962
C	-1.7227	0.0000	1.1204	H	-2.7546	0.0000	1.4567
H	-2.5224	0.0000	0.3706	O	-0.0621	0.0000	-2.3133
H	-2.2095	0.0000	2.1016	N	-0.0649	0.0000	-1.1118

TH				TH2			
Symbol	X	Y	Z	Symbol	X	Y	Z
C	-0.0038	-1.2179	-0.3636	C	0.0022	-1.2729	-0.2770
H	-0.3160	-2.0589	-0.9898	H	-0.3105	-2.1179	-0.8950
C	-0.0038	1.2179	-0.3636	C	0.0152	1.2477	-0.3738
H	-0.3160	2.0589	-0.9898	H	-0.3021	2.0366	-1.0572
C	-0.7519	1.2755	1.0074	C	-0.7583	1.3194	0.9689
H	-1.4183	2.1447	1.0248	H	-1.4243	2.1852	0.9424
H	-0.0212	1.4352	1.8104	H	-0.0309	1.5080	1.7647
C	-0.7519	-1.2755	1.0074	C	-0.7726	-1.2386	1.0648
H	-0.0212	-1.4352	1.8104	H	-0.0474	-1.3764	1.8728
H	-1.4183	-2.1447	1.0248	H	-1.4476	-2.0971	1.1020
C	1.5324	-1.2674	-0.2097	C	1.5369	-1.2807	-0.1347
H	1.9762	-1.3706	-1.2078	H	1.9909	-1.4309	-1.1227
H	1.8067	-2.1618	0.3621	H	1.8027	-2.1567	0.4643
C	1.5324	1.2674	-0.2098	C	1.5482	1.2560	-0.2286
H	1.9762	1.3705	-1.2078	H	2.0068	1.3303	-1.2231
H	1.8068	2.1618	0.3621	H	1.8189	2.1710	0.3065
N	-0.2810	0.0000	-1.1558	N	-0.3166	-0.0398	-1.1163
O	-1.6903	0.0000	-1.5372	O	-1.6650	0.0368	-1.5556
C	2.0795	0.0000	0.4677	C	2.0720	0.0106	0.5051
H	3.1752	0.0000	0.4360	H	3.1654	0.0043	0.4796
H	1.8055	0.0000	1.5299	H	1.7887	0.0510	1.5622
C	-1.5599	0.0000	1.3077	C	-1.5690	0.0559	1.3091
H	-2.4728	0.0000	0.7064	H	-2.4908	0.0400	0.7242
H	-1.8705	0.0000	2.3592	H	-1.8613	0.0962	2.3623

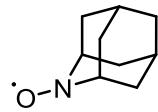
H		-1.6419	-0.0001	-2.5039
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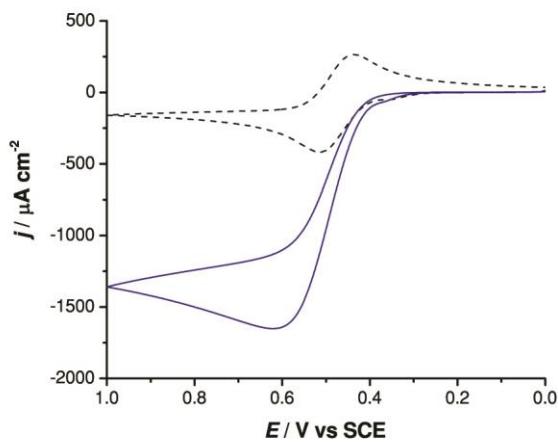
H		-1.8336	-0.7784	-2.0640
H		0.2643	-0.0644	-1.9630

### 3.13 AZADO (13)

AZADO was purchased from Sigma Aldrich and used without purification.

**Table S3.13. Summary table of electrocatalytic properties of AZADO.**

	$E_{a1}$	0.491
	$E_{a2}$	0.386
	$j_{max}$	802.8
	$(i_{pa}/i_{pc})_{cat.}$	75.41



**Figure S3.13.** CV of 5 mM AZADO in the absence (dashed) and presence (solid) of 1 M glycerol using 150 mM Robinson buffer at 25 °C.

#### Optimized Geometry Coordinates Using B3LYP/6-31+G(d,p) CPCM

T*				T+			
Symbol	X	Y	Z	Symbol	X	Y	Z
C	0.6210	1.2483	-0.2098	C	0.6557	0.0001	1.2614
H	1.3174	2.0732	-0.3769	H	1.3920	0.0002	2.0651
C	0.6210	-1.2483	-0.2097	C	0.6557	-0.0001	-1.2614
H	1.3174	-2.0732	-0.3768	H	1.3920	-0.0002	-2.0651
C	0.0603	-1.2561	1.2311	C	-0.2315	-1.2791	-1.2457
H	0.8893	-1.2749	1.9484	H	0.4056	-2.1683	-1.2727
H	-0.5277	-2.1695	1.3808	H	-0.8146	-1.2578	-2.1714
C	0.0603	1.2561	1.2311	C	-0.2315	-1.2789	1.2459
H	-0.5277	2.1696	1.3807	H	-0.8146	-1.2574	2.1716

H	0.8893	1.2749	1.9483	H	0.4056	-2.1681	1.2730
C	-0.8144	0.0000	1.4378	C	-1.1308	-1.2620	0.0001
H	-1.2185	0.0000	2.4569	H	-1.7567	-2.1609	0.0002
C	-1.9718	0.0000	0.4141	C	-2.0191	0.0000	0.0000
H	-2.6056	-0.8829	0.5669	H	-2.6696	-0.0001	-0.8818
H	-2.6056	0.8830	0.5668	H	-2.6696	0.0001	0.8818
C	-0.5283	1.2522	-1.2340	C	-0.2315	1.2791	1.2457
H	-0.1214	1.2716	-2.2518	H	0.4056	2.1683	1.2727
H	-1.1182	2.1661	-1.0976	H	-0.8146	1.2578	2.1714
C	-0.5283	-1.2523	-1.2340	C	-0.2315	1.2789	-1.2459
H	-0.1214	-1.2716	-2.2518	H	0.4056	2.1681	-1.2730
H	-1.1182	-2.1661	-1.0975	H	-0.8146	1.2574	-2.1716
C	-1.4050	0.0000	-1.0229	C	-1.1308	1.2620	-0.0001
H	-2.2265	0.0000	-1.7486	H	-1.7567	2.1609	-0.0002
N	1.4020	0.0000	-0.3882	O	2.6326	0.0000	0.0000
O	2.6593	0.0000	-0.0940	N	1.4309	0.0000	0.0000

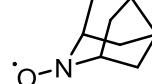
TH				TH2			
Symbol	X	Y	Z	Symbol	X	Y	Z
C	0.5562	0.3290	1.2251	C	0.5197	-0.3052	-1.2705
H	1.1957	0.5888	2.0750	H	1.1889	-0.5657	-2.0924
C	0.5558	0.3291	-1.2253	C	0.5193	-0.3053	1.2706
H	1.1952	0.5889	-2.0753	H	1.1883	-0.5658	2.0927
C	0.1974	-1.1714	-1.2479	C	0.1722	1.1874	1.2501
H	1.1106	-1.7764	-1.2647	H	1.0836	1.7918	1.2745
H	-0.3589	-1.3946	-2.1673	H	-0.3846	1.4033	2.1677
C	0.1978	-1.1715	1.2478	C	0.1725	1.1874	-1.2500
H	-0.3584	-1.3947	2.1673	H	-0.3840	1.4035	-2.1677
H	1.1109	-1.7765	1.2643	H	1.0839	1.7919	-1.2741
C	-0.6466	-1.5052	0.0000	C	-0.6737	1.5065	-0.0001
H	-0.9065	-2.5712	0.0000	H	-0.9324	2.5702	-0.0001
C	-1.9364	-0.6548	0.0002	C	-1.9569	0.6481	-0.0003
H	-2.5440	-0.8942	-0.8828	H	-2.5650	0.8821	0.8819
H	-2.5438	-0.8942	0.8834	H	-2.5647	0.8822	-0.8826
C	-0.7313	1.1758	1.2481	C	-0.7426	-1.1814	-1.2492
H	-0.4766	2.2421	1.2695	H	-0.4778	-2.2452	-1.2757
H	-1.2889	0.9512	2.1655	H	-1.2980	-0.9712	-2.1690
C	-0.7317	1.1759	-1.2478	C	-0.7430	-1.1814	1.2489
H	-0.4769	2.2422	-1.2693	H	-0.4782	-2.2453	1.2755
H	-1.2895	0.9513	-2.1652	H	-1.2987	-0.9713	2.1685
C	-1.5761	0.8476	0.0002	C	-1.5852	-0.8511	-0.0003
H	-2.4913	1.4524	0.0004	H	-2.4905	-1.4662	-0.0004

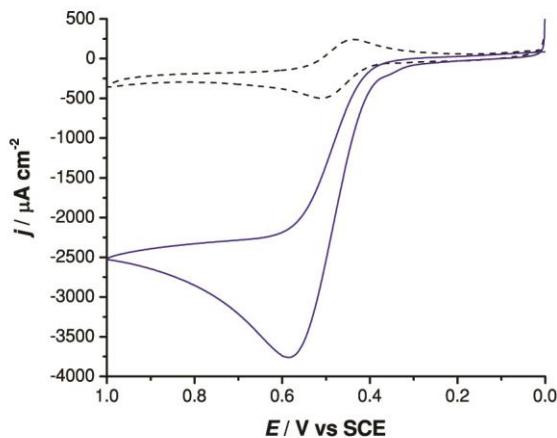
N	1.3024	0.7206	-0.0001	N	1.3092	-0.6337	0.0002
O	2.5594	-0.0214	-0.0003	O	2.5365	0.0896	0.0004
H	3.2201	0.6855	-0.0004	H	3.2536	-0.5684	0.0000
				H	1.5259	-1.6369	0.0002

### 3.14 nor-AZADO (14)

**14** was prepared according to the procedure of Iwabuchi *et al.*<sup>23</sup>

**Table S3.14.** Summary table of electrocatalytic properties of nor-AZADO.

	$E_{a1}$	0.504
	$E_{a2}$	0.348
	$j_{max}$	2169.0
	$(i_{pa}/i_{pc})_{cat.}$	197.71



**Figure S3.14.** CV of 5 mM nor-AZADO in the absence (dashed) and presence (solid) of 1 M glycerol using 150 mM Robinson buffer at 25 °C.

#### Optimized Geometry Coordinates Using B3LYP/6-31+G(d,p) CPCM

T*				T+			
Symbol	X	Y	Z	Symbol	X	Y	Z
C	-0.4613	-1.2736	-0.1918	C	-0.4964	-1.2911	0.0000
H	-1.1571	-2.0919	-0.3810	H	-1.2387	-2.0873	0.0000
C	-0.4613	1.2736	-0.1918	C	-0.4964	1.2911	0.0000
H	-1.1571	2.0919	-0.3810	H	-1.2387	2.0873	0.0000
C	0.1820	1.2416	1.2109	C	0.4964	1.2314	1.1862
H	-0.5450	1.1434	2.0225	H	0.0157	1.1412	2.1625
H	0.7475	2.1664	1.3668	H	1.0557	2.1705	1.1645
C	0.1820	-1.2416	1.2109	C	0.4964	-1.2314	1.1862
H	0.7475	-2.1664	1.3668	H	1.0557	-2.1705	1.1645

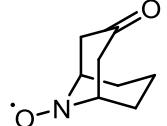
H	-0.5450	-1.1434	2.0225	H	0.0157	-1.1412	2.1625
C	1.5169	0.0000	-0.4774	C	1.3417	0.0000	-0.7967
H	1.9449	0.0000	1.7529	H	2.3335	0.0000	1.2499
C	0.7999	-1.2370	-1.0681	C	0.4965	-1.2314	-1.1862
H	0.5923	-1.1372	-2.1373	H	0.0157	-1.1412	-2.1625
H	1.3637	-2.1624	-0.9134	H	1.0557	-2.1705	-1.1645
C	0.7999	1.2370	-1.0681	C	0.4965	1.2314	-1.1862
H	0.5923	1.1372	-2.1373	H	0.0157	1.1412	-2.1625
H	1.3637	2.1624	-0.9134	H	1.0557	2.1705	-1.1645
C	1.0965	0.0000	1.0657	C	1.3417	0.0000	0.7967
H	2.5963	0.0000	-0.6417	H	2.3336	0.0000	-1.2499
N	-1.2211	0.0000	-0.3878	O	-2.4616	0.0000	0.0000
O	-2.4905	0.0000	-0.1568	N	-1.2630	0.0000	0.0000

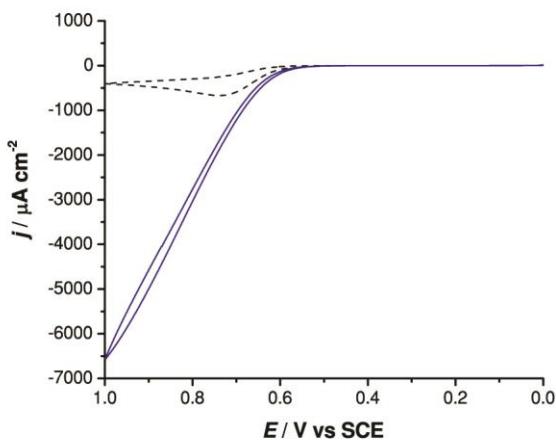
TH				TH2			
Symbol	X	Y	Z	Symbol	X	Y	Z
C	-0.3817	-1.2497	-0.3175	C	-0.3472	-1.3014	-0.2896
H	-1.0051	-2.0922	-0.6278	H	-1.0024	-2.1139	-0.6033
C	-0.3817	1.2497	-0.3175	C	-0.3472	1.3014	-0.2895
H	-1.0051	2.0922	-0.6278	H	-1.0024	2.1139	-0.6033
C	-0.0097	1.2338	1.1779	C	0.0167	1.2363	1.1927
H	-0.8690	1.1265	1.8455	H	-0.8418	1.1371	1.8603
H	0.5065	2.1655	1.4367	H	0.5361	2.1643	1.4474
C	-0.0097	-1.2338	1.1779	C	0.0167	-1.2363	1.1927
H	0.5065	-2.1655	1.4367	H	0.5361	-2.1643	1.4474
H	-0.8690	-1.1265	1.8455	H	-0.8418	-1.1371	1.8603
C	1.6261	0.0000	-0.2273	C	1.6360	0.0000	-0.2327
H	1.6312	0.0000	2.0434	H	1.6560	0.0000	2.0375
C	1.0239	-1.2332	-0.9396	C	1.0361	-1.2356	-0.9445
H	1.0248	-1.1357	-2.0294	H	1.0212	-1.1421	-2.0342
H	1.5396	-2.1637	-0.6800	H	1.5585	-2.1647	-0.6998
C	1.0239	1.2332	-0.9396	C	1.0361	1.2356	-0.9445
H	1.0248	1.1357	-2.0294	H	1.0212	1.1421	-2.0342
H	1.5396	2.1637	-0.6800	H	1.5584	2.1647	-0.6998
C	0.9253	0.0000	1.2093	C	0.9485	0.0000	1.2078
H	2.7181	0.0000	-0.1885	H	2.7260	0.0000	-0.2073
N	-1.0838	0.0000	-0.7465	O	-2.3659	0.0000	-0.0138
O	-2.3814	0.0000	-0.0799	H	-3.0414	0.0000	-0.7150
H	-3.0026	0.0000	-0.8220	H	-1.2521	0.0000	-1.6744
				N	-1.0969	0.0000	-0.6609

### 3.15 4-Oxo-ABNO (15)

**15** was prepared according to the procedure of Stahl *et al.*<sup>24</sup>

**Table S3.15. Summary table of electrocatalytic properties of oxo-ABNO.**

	$E_{a1}$	0.696
	$E_{a2}$	0.581
	$j_{max}$	2338.0
	$(i_{pa}/i_{pc})_{cat.}$	83.04



**Figure S3.15.** CV of 5 mM **15** in the absence (dashed) and presence (solid) of 1 M glycerol using 150 mM Robinson buffer at 25 °C.

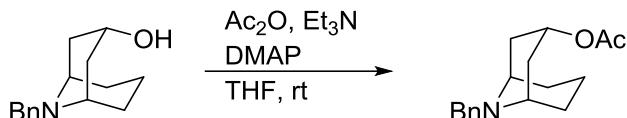
#### Optimized Geometry Coordinates Using B3LYP/6-31+G(d,p) CPCM

T*				T+			
Symbol	X	Y	Z	Symbol	X	Y	Z
C	-0.4985	0.3501	-1.2424	C	-0.5214	-0.3314	1.2623
H	-0.9770	0.8820	-2.0669	H	-1.0157	-0.8777	2.0655
C	-0.4982	0.3500	1.2425	C	-0.5211	-0.3313	-1.2625
H	-0.9764	0.8819	2.0672	H	-1.0152	-0.8775	-2.0659
C	-0.9035	-1.1417	1.2713	C	-0.9572	1.1675	-1.2614
H	-1.9951	-1.1868	1.3667	H	-2.0467	1.1989	-1.3596
H	-0.4813	-1.6103	2.1670	H	-0.5333	1.6046	-2.1701
C	-0.9039	-1.1416	-1.2712	C	-0.9576	1.1674	1.2613
H	-0.4819	-1.6102	-2.1670	H	-0.5340	1.6044	2.1701

H	-1.9954	-1.1867	-1.3662	H	-2.0471	1.1988	1.3591
C	1.0253	0.5891	-1.2941	C	1.0088	-0.5532	1.2958
H	1.2023	1.6554	-1.4919	H	1.2044	-1.6100	1.5191
H	1.4843	0.0269	-2.1117	H	1.4303	0.0355	2.1135
C	1.0257	0.5890	1.2939	C	1.0091	-0.5531	-1.2956
H	1.2026	1.6553	1.4917	H	1.2048	-1.6099	-1.5189
H	1.4848	0.0268	2.1113	H	1.4309	0.0356	-2.1131
N	-1.0213	0.9557	0.0002	C	-0.5062	1.9085	0.0000
O	-2.2020	1.4737	0.0003	H	-0.9483	2.9099	0.0000
C	-0.4646	-1.8888	0.0000	H	0.5783	2.0595	0.0002
H	-0.8961	-2.8954	0.0000	O	-1.9160	-1.7331	-0.0003
H	0.6229	-2.0331	-0.0002	N	-1.0495	-0.9070	-0.0002
C	1.7592	0.2791	-0.0002	C	1.7427	-0.2409	0.0002
O	2.9154	-0.1246	-0.0004	O	2.8981	0.1426	0.0004

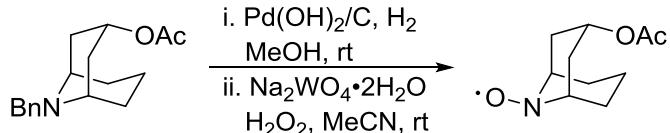
TH				TH2			
Symbol	X	Y	Z	Symbol	X	Y	Z
C	-0.4514	-1.2201	-0.3705	C	0.4200	1.2159	-0.4880
H	-0.9058	-2.0684	-0.8908	C	0.4256	-1.2953	-0.1983
C	-0.4514	1.2202	-0.3703	C	0.8596	-1.1280	1.2615
H	-0.9058	2.0686	-0.8904	C	0.8521	1.3876	0.9732
C	-0.8589	1.2633	1.1168	C	-1.1003	1.2161	-0.7264
H	-1.9493	1.3606	1.1678	C	-1.0946	-1.3526	-0.4362
H	-0.4373	2.1638	1.5786	N	0.9575	-0.1147	-1.0144
C	-0.8589	-1.2635	1.1165	O	2.3709	-0.0254	-0.9963
H	-0.4373	-2.1641	1.5782	C	0.4208	0.2144	1.8660
H	-1.9493	-1.3608	1.1676	C	-1.8307	-0.0329	-0.2539
C	1.0749	-1.2889	-0.5942	O	-2.9783	0.0105	0.1550
H	1.2597	-1.4871	-1.6592	H	0.8897	1.9726	-1.1184
H	1.5238	-2.1090	-0.0269	H	0.8856	-2.1850	-0.6346
C	1.0749	1.2890	-0.5940	H	1.9481	-1.2247	1.3153
H	1.2597	1.4874	-1.6589	H	0.4392	-1.9687	1.8212
H	1.5238	2.1090	-0.0265	H	1.9391	1.5055	1.0055
N	-0.9201	0.0001	-1.0709	H	0.4208	2.3290	1.3265
O	-2.3717	0.0001	-1.0297	H	-1.3049	1.3053	-1.8029
C	-0.4236	-0.0002	1.8768	H	-1.5370	2.0973	-0.2514
H	-0.8589	-0.0003	2.8825	H	-1.2916	-1.6756	-1.4685
H	0.6642	-0.0002	2.0248	H	-1.5320	-2.1099	0.2181
C	1.8118	0.0000	-0.2811	H	0.6714	-0.2156	-1.9957
O	2.9666	0.0000	0.1319	H	2.7067	-0.8193	-1.4536
H	-2.6109	0.0002	-1.9677	H	0.8696	0.3292	2.8567
				H	-0.6635	0.2297	2.0247

### 3.16 4-Acetyl-ABNO (16)



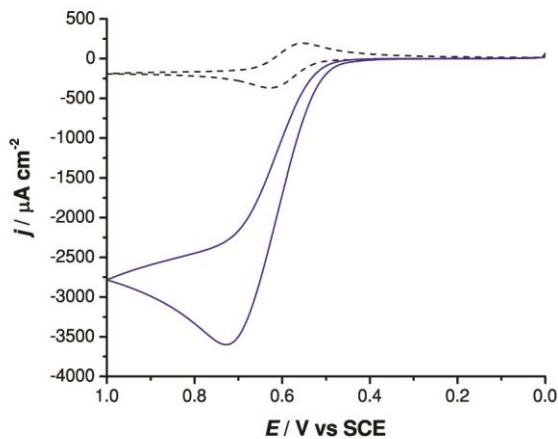
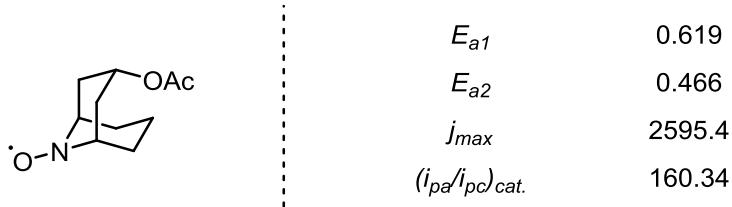
**(±)-(1*R*,3*r*,5*S*)-9-benzyl-9-azabicyclo[3.3.1]nonan-3-yl acetate (Syn2).** To a THF (3.7 mL, 0.3 M) solution of endo-9-benzyl-9-azabicyclo[3.3.1]nonan-3-one<sup>24</sup> (0.2579 g, 1.12 mmol) were added triethylamine (0.47 mL, 3.4 mmol), *N,N*-Dimethylpyridin-4-amine (0.0137 g, 0.112 mmol), and acetic anhydride (0.16 mL, 1.7 mmol). The mixture was stirred at room temperature for 1 h. The reaction mixture was then diluted with saturated aqueous sodium bicarbonate and extracted with EtOAc. The combined organic extracts were dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated. Purification by FCC (8:1 hexanes:EtOAc) gave **Syn2** (0.2699 g, 0.987 mmol, 89%) as a colorless oil.

Data for **Syn2**: R<sub>f</sub> 0.11 (3:2 hexanes:EtOAc); IR (neat) 2921, 1730 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.36–7.28 (m, 4 H), 7.22 (t, J = 7.8 Hz, 1 H), 5.23 (quin, J = 7.0 Hz, 1 H), 3.79 (s, 2 H), 3.02 (d, J = 9.0 Hz, 2 H), 2.39 (ddd, J = 14.8, 14.8, 7.4 Hz, 2 H), 2.26–2.13 (m, 1 H), 2.05 (s, 3 H), 1.95 (tt, J = 13.4, 5.0 Hz, 2 H), 1.57–1.50 (m, 1 H), 1.45 (ddd, J = 14.5, 7.0, 2.0 Hz, 2 H), 1.16 (dd, J = 13.7, 4.3 Hz, 2 H); <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) δ 170.6, 140.1, 128.3, 128.2, 126.7, 67.4, 56.1, 49.3, 31.6, 25.1, 21.6, 14.7; HRMS (TOF MS ES+) calcd for C<sub>17</sub>H<sub>24</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 274.1807, found 274.1806.



**(±)-(1*R*,3*r*,5*S*)-9-oxyl-9-azabicyclo[3.3.1]nonan-3-yl acetate (Syn3).** To a MeOH (10 mL, 0.1 M) solution of **Syn3** (0.2699 g, 0.987 mmol) was added 20% palladium hydroxide on activated charcoal (0.0353 g, 0.0503 mmol). The mixture was stirred at room temperature under an atmosphere of H<sub>2</sub> (balloon) for 15 h. The reaction mixture was then filtered through celite. To this solution were added sodium tungstate dihydrate (0.1667 g, 0.505 mmol) and 30% hydrogen peroxide (1.7 mL, 15 mmol). After stirring at room temperature for 22 h, the reaction was diluted with saturated aqueous sodium bicarbonate and extracted with EtOAc. The combined organic extracts were dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated. Purification by FCC (2:1 hexanes:EtOAc) gave **Syn3** (0.1352 g, 0.682 mmol, 69%) as a yellow solid which was in agreement with the previously reported characterization data.<sup>25</sup>

**Table S3.16.** Summary table of electrocatalytic properties of ABNO-OAc.



**Figure S3.16.** CV of 5 mM **16** in the absence (dashed) and presence (solid) of 1 M glycerol using 150 mM Robinson buffer at 25 °C.

## Optimized Geometry Coordinates Using B3LYP/6-31+G(d,p) CPCM

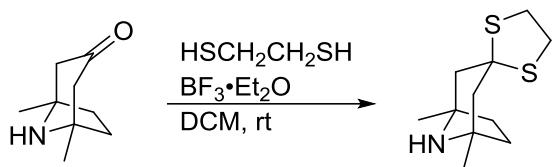
T*				T+			
Symbol	X	Y	Z	Symbol	X	Y	Z
C	1.4926	-0.3845	-1.2376	C	1.5149	-0.3616	-1.2561
H	1.9217	-0.9540	-2.0653	H	1.9673	-0.9402	-2.0619
C	1.4923	-0.3844	1.2380	C	1.5146	-0.3616	1.2565
H	1.9212	-0.9539	2.0659	H	1.9668	-0.9403	2.0623
C	2.0400	1.0632	1.2815	C	2.0716	1.0988	1.2715
H	3.1245	0.9878	1.4261	H	3.1540	1.0257	1.4177
H	1.6353	1.5756	2.1614	H	1.6544	1.5739	2.1641
C	2.0403	1.0631	-1.2811	C	2.0719	1.0988	-1.2710
H	1.6359	1.5754	-2.1612	H	1.6549	1.5740	-2.1637
H	3.1249	0.9876	-1.4254	H	3.1543	1.0257	-1.4169
C	-0.0415	-0.5423	-1.2766	C	-0.0244	-0.5296	-1.2741
H	-0.2674	-1.6068	-1.4079	H	-0.2460	-1.5924	-1.4152
H	-0.4412	-0.0128	-2.1476	H	-0.3969	0.0034	-2.1530
C	-0.0419	-0.5422	1.2766	C	-0.0247	-0.5296	1.2741

H	-0.2678	-1.6066	1.4078	H	-0.2464	-1.5924	1.4151
H	-0.4418	-0.0126	2.1474	H	-0.3974	0.0033	2.1529
N	1.9866	-1.0221	0.0003	C	-0.7291	-0.0441	-0.0001
O	3.1482	-1.5842	0.0005	H	-0.8488	1.0363	-0.0001
C	-0.7430	-0.0613	-0.0001	C	1.7590	1.8979	0.0002
H	-0.8620	1.0195	-0.0002	H	2.3772	2.8017	0.0003
C	1.7523	1.8709	0.0001	H	0.7238	2.2443	0.0001
H	2.3748	2.7727	0.0002	O	2.8387	-1.8379	0.0003
H	0.7179	2.2277	0.0000	N	2.0190	-0.9640	0.0002
O	-2.0866	-0.6336	-0.0003	O	-2.0548	-0.6261	-0.0003
C	-3.1571	0.1884	-0.0003	C	-3.1336	0.2011	-0.0003
O	-3.0824	1.4066	-0.0002	O	-3.0492	1.4152	-0.0003
C	-4.4428	-0.5968	-0.0005	C	-4.4135	-0.5884	-0.0006
H	-5.2921	0.0858	-0.0004	H	-5.2642	0.0920	-0.0005
H	-4.4852	-1.2420	-0.8831	H	-4.4521	-1.2334	-0.8832
H	-4.4852	-1.2425	0.8816	H	-4.4522	-1.2338	0.8819

TH				TH2			
Symbol	X	Y	Z	Symbol	X	Y	Z
C	1.3135	0.2192	-1.2582	C	-1.5237	-0.9882	0.8507
H	1.6221	0.1425	-2.3060	C	-1.2759	0.3739	-1.2487
C	1.5538	-0.9206	0.8749	C	-1.8577	1.6055	-0.5421
H	2.0340	-1.7956	1.3251	C	-2.1094	0.2232	1.5901
C	2.1220	0.3453	1.5537	C	-0.0008	-1.1965	0.9184
H	3.2137	0.2506	1.5566	C	0.2507	0.1747	-1.2116
H	1.8052	0.3643	2.6033	N	-1.8858	-0.8826	-0.6289
C	1.8714	1.5398	-0.6847	O	-3.2990	-0.9242	-0.7205
H	1.3808	2.3845	-1.1829	C	0.8161	-0.1265	0.1847
H	2.9326	1.5895	-0.9530	C	-1.7148	1.5849	0.9907
C	-0.2234	0.0700	-1.2270	O	2.1525	-0.6764	0.0479
H	-0.4882	-0.8148	-1.8171	C	3.1956	0.1875	0.0059
H	-0.6864	0.9389	-1.7054	O	3.0615	1.3978	0.0508
C	0.0286	-1.1258	1.0032	C	4.5063	-0.5448	-0.0879
H	-0.2072	-2.1324	0.6397	H	-2.0178	-1.9002	1.1910
H	-0.2622	-1.0794	2.0580	H	-1.5939	0.3660	-2.2944
N	1.8561	-0.9797	-0.5752	H	-2.9150	1.6815	-0.8134
O	3.3032	-0.9616	-0.7281	H	-1.3629	2.4843	-0.9662
C	-0.7882	-0.1221	0.1861	H	-3.1984	0.1213	1.5925
H	-0.8777	0.8318	0.7028	H	-1.7855	0.1501	2.6328
C	1.7337	1.6578	0.8454	H	0.2439	-2.1761	0.4907
H	2.3745	2.4703	1.2076	H	0.2827	-1.2359	1.9735
H	0.7123	1.9469	1.1135	H	0.5151	-0.6567	-1.8763

H	3.4750	-1.7916	-1.1952	H	0.7142	1.0723	-1.6287
O	-2.1414	-0.6732	0.0923	H	-1.5252	-1.7133	-1.1145
C	-3.1817	0.1791	0.0185	H	-3.5140	-0.9491	-1.6716
O	-3.0665	1.3950	0.0396	H	0.9018	0.7852	0.7728
C	-4.4897	-0.5582	-0.1097	H	-0.6966	1.8524	1.2845
H	-5.3185	0.1307	0.0528	H	-2.3613	2.3587	1.4153
H	-4.5662	-0.9801	-1.1176	H	4.6736	-1.1129	0.8327
H	-4.5394	-1.3866	0.6011	H	5.3169	0.1694	-0.2287
				H	4.4843	-1.2576	-0.9166

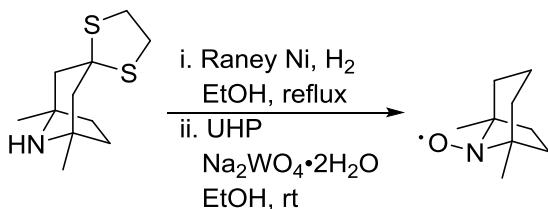
### 3.17 2,2,6,6-Dimethylazabicyclo[3.2.1]octan-N-oxy, ABOO (17)



#### (±)-(1R,5S)-1,5-dimethyl-8-azaspiro[bicyclo[3.2.1]octane-3,2'-[1,3]dithiolane]

**(Syn11).** To a DCM (3.0 mL, 0.3 M) solution of (1R,5S)-1,5-dimethyl-8-azabicyclo[3.2.1]octan-3-one<sup>26</sup> (0.1548 g, 1.01 mmol) were added 1,2-ethanedithiol (0.61 mL, 9.9 mmol) and borontrifluoride diethyl etherate (0.3 mL, 2.8 mmol). The mixture was stirred at room temperature for 19 h. The reaction mixture was then diluted with 1 M NaOH and extracted with DCM. The combined organic extracts were washed with additional 1 M NaOH, dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated. Purification by FCC (19:1 EtOAc:10% NH<sub>4</sub>OH in MeOH) gave **Syn11** (0.1994 g, 0.869 mmol, 86%) as a colorless oil.

Data for **Syn11**: R<sub>f</sub> 0.38 (1:9 EtOAc:10% NH<sub>4</sub>OH in MeOH); IR (neat) 2952, 2922, 2871 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 3.37 (t, J = 5.9 Hz, 2 H), 3.22 (t, J = 5.9 Hz, 2 H), 2.33–2.18 (m, 6 H), 1.53 (d, J = 7.8 Hz, 2 H), 1.20 (s, 6 H); <sup>13</sup>C (125 MHz, CDCl<sub>3</sub>) δ 64.2, 61.3, 55.0, 40.4, 37.2, 36.3, 27.6; HRMS (TOF MS ES+) calcd for C<sub>11</sub>H<sub>20</sub>NS<sub>2</sub> [M+H]<sup>+</sup>: 230.1037, found 230.1037.

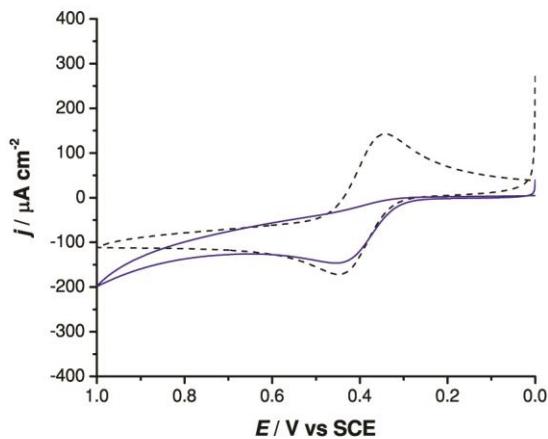


**(±)-(1R,5S)-1,5-dimethyl-8-azabicyclo[3.2.1]octan-8-oxyl (Syn12).** To a EtOH (8.0 mL, 0.1 M) solution of **Syn12** (0.1971 g, 0.859 mmol) was added Raney nickel (approx. 2 g). The mixture was heated to reflux with stirring under an atmosphere of H<sub>2</sub> (balloon) for 48 h. The reaction mixture was then filtered through celite. To the filtrate were added sodium tungstate dihydrate (0.2423 g, 2.58 mmol) and urea hydrogen peroxide (0.1422 g, 0.431 mmol). After stirring at room temperature for 24 h, the reaction mixture was concentrated. Purification by FCC (hexanes) gave **Syn12** (0.0317 g, 0.206 mmol, 24%) as a red oil.

Data for **Syn12**: R<sub>f</sub> 0.35 (9:1 hexanes:EtOAc); IR (neat) 2969, 2930 cm<sup>-1</sup>; HRMS (TOF MS ES+) calcd for C<sub>9</sub>H<sub>16</sub>NONa [M+Na]<sup>+</sup>: 177.1130, found 177.1127.

**Table S3.17. Summary table of electrocatalytic properties of ABOO.**

	$E_{a1}$	0.442
	$E_{a2}$	0.845
	$j_{max}$	115.8
	$(i_{pa}/i_{pc})_{cat.}$	9.79



**Figure S3.17.** CV of 5 mM **17** in the absence (dashed) and presence (solid) of 1 M glycerol using 150 mM Robinson buffer at 25 °C.

#### Optimized Geometry Coordinates Using B3LYP/6-31+G(d,p) CPCM

T*				T+			
Symbol	X	Y	Z	Symbol	X	Y	Z
C	-1.2031	-0.1498	0.1695	C	-1.2262	-0.1353	0.1532
C	1.2031	-0.1498	0.1695	C	1.2262	-0.1353	0.1532
C	1.2814	1.1596	-0.6587	C	1.2700	1.2123	-0.6680
H	1.4387	0.8741	-1.7057	H	1.4294	0.9601	-1.7224
H	2.1565	1.7406	-0.3420	H	2.1618	1.7445	-0.3215
C	-1.2814	1.1596	-0.6587	C	-1.2700	1.2123	-0.6680
H	-2.1565	1.7406	-0.3420	H	-2.1618	1.7445	-0.3215
H	-1.4387	0.8741	-1.7057	H	-1.4294	0.9601	-1.7224
C	-0.7800	0.1180	1.6320	C	-0.7813	0.0924	1.6166
H	-1.1620	-0.6782	2.2779	H	-1.1660	-0.7156	2.2436
H	-1.1978	1.0608	1.9976	H	-1.1987	1.0273	1.9953
C	0.7800	0.1180	1.6320	C	0.7813	0.0924	1.6166
H	1.1620	-0.6782	2.2779	H	1.1659	-0.7157	2.2436
H	1.1978	1.0608	1.9976	H	1.1987	1.0273	1.9953

C	-2.4591	-0.9980	0.0167	C	-2.4672	-0.9860	-0.0636
H	-2.3606	-1.9401	0.5654	H	-2.3599	-1.9687	0.4047
H	-3.3273	-0.4574	0.4083	H	-3.3178	-0.4795	0.3999
H	-2.6377	-1.2340	-1.0358	H	-2.6864	-1.1244	-1.1249
C	2.4591	-0.9980	0.0167	C	2.4672	-0.9860	-0.0636
H	3.3273	-0.4574	0.4083	H	3.3178	-0.4795	0.3999
H	2.3606	-1.9401	0.5654	H	2.3599	-1.9687	0.4047
H	2.6377	-1.2340	-1.0358	H	2.6864	-1.1244	-1.1249
C	0.0000	2.0070	-0.5248	C	0.0000	2.0506	-0.4797
H	0.0000	2.8005	-1.2809	H	0.0000	2.8721	-1.2043
H	0.0000	2.5174	0.4468	H	0.0000	2.5207	0.5088
O	0.0000	-1.4367	-1.4885	O	0.0000	-1.6557	-1.2276
N	0.0000	-0.8793	-0.3363	N	0.0000	-0.7912	-0.4022

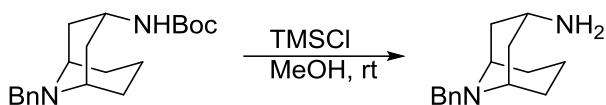
TH			
Symbol	X	Y	Z
C	-1.1746	-0.0689	-0.0085
C	1.1746	-0.0689	-0.0085
C	1.2616	1.4024	-0.4834
H	1.4131	1.3892	-1.5692
H	2.1477	1.8686	-0.0350
C	-1.2616	1.4024	-0.4834
H	-2.1477	1.8686	-0.0350
H	-1.4131	1.3892	-1.5692
C	-0.7765	-0.1446	1.5027
H	-1.1762	-1.0573	1.9602
H	-1.2003	0.6915	2.0677
C	0.7765	-0.1446	1.5027
H	1.1763	-1.0573	1.9602
H	1.2003	0.6915	2.0677
C	-2.4747	-0.7963	-0.3461
H	-2.4470	-1.8457	-0.0453
H	-3.3106	-0.3120	0.1707
H	-2.6667	-0.7604	-1.4230
C	2.4747	-0.7963	-0.3461
H	3.3106	-0.3120	0.1707
H	2.4470	-1.8457	-0.0453
H	2.6666	-0.7604	-1.4230
C	0.0000	2.2051	-0.1389
H	0.0000	3.1628	-0.6722
H	0.0000	2.4545	0.9300
N	0.0000	-0.6478	-0.7331

TH2			
Symbol	X	Y	Z
C	1.2329	0.1055	0.2159
C	-1.2329	0.1055	0.2159
C	-1.2782	-1.1341	-0.6968
H	-1.4878	-0.8221	-1.7292
H	-2.1495	-1.7252	-0.3976
C	1.2782	-1.1341	-0.6967
H	2.1495	-1.7252	-0.3975
H	1.4878	-0.8221	-1.7292
C	0.7805	-0.2347	1.6556
H	1.1663	0.5126	2.3548
H	1.1977	-1.1971	1.9591
C	-0.7805	-0.2347	1.6556
H	-1.1663	0.5126	2.3548
H	-1.1977	-1.1971	1.9591
C	2.4897	0.9603	0.1233
H	2.4007	1.8770	0.7168
H	3.3355	0.3934	0.5224
H	2.7214	1.2327	-0.9096
C	-2.4897	0.9603	0.1233
H	-3.3355	0.3934	0.5224
H	-2.4007	1.8770	0.7168
H	-2.7214	1.2327	-0.9096
C	0.0000	-1.9893	-0.6199
H	0.0000	-2.7294	-1.4249
H	0.0000	-2.5608	0.3141
H	0.0000	1.8152	0.3053

O	0.0000	-2.0823	-0.6077
H	0.0000	-2.3136	0.3401

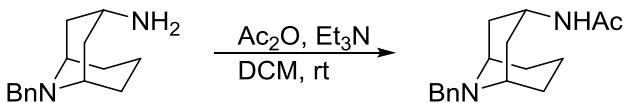
O	0.0000	1.4151	-1.5486
H	0.0001	0.6344	-2.1293
N	0.0000	0.9356	-0.2239

### 3.18 4-Acetamido-ABNO (18)



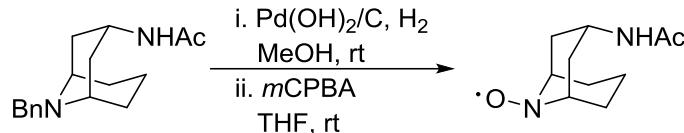
**( $\pm$ )-(1*R*,3*r*,5*S*)-9-benzyl-9-azabicyclo[3.3.1]nonan-3-amine (Syn4).** To a MeOH (0.3 mL, 0.5 M) solution of *tert*-butyl-9-benzyloxy-9-azabicyclo[3.3.1]nonan-3-yl carbamate<sup>27</sup> (0.0506 g, 0.153 mmol) was added chlorotrimethylsilane (0.1 mL, 0.78 mmol). The mixture was stirred at room temperature for 2 h. The reaction mixture was then concentrated to give a white foam. The foam was treated with 1 M NaOH solution and extracted with Et<sub>2</sub>O. The combined organic extracts were dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated to give **Syn4** (0.0297 g, 0.129 mmol, 84%) as a colorless oil.

Data for **Syn4**: R<sub>f</sub> 0.19 (9:1 EtOAc:10% NH<sub>4</sub>OH in MeOH); IR (neat) 2919, 2859 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.34–7.26 (m, 4 H), 7.22 (t, J = 7.0 Hz, 1 H), 3.81 (s, 2 H), 3.34 (spt, J = 11.5 Hz, 1 H), 3.04 (d, J = 10.5 Hz, 2 H), 2.25 (td, J = 11.7, 6.2 Hz, 2 H), 2.03–1.87 (m, 3 H), 1.52–1.46 (m, 1 H), 1.27 (br s, 2 H), 1.12 (td, J = 13.7, 2.7 Hz, 2 H), 0.99 (d, J = 11.7 Hz, 2 H); <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) δ 140.8, 128.11, 128.07, 126.5, 55.8, 49.4, 43.0, 37.4, 24.8, 14.3; HRMS (TOF MS ES+) calcd for C<sub>15</sub>H<sub>22</sub>N<sub>2</sub> [M+]: 287.1396, found 287.1392.



**( $\pm$ )-N-((1*R*,3*r*,5*S*)-9-benzyl-9-azabicyclo[3.3.1]nonan-3-yl)acetamide (Syn5).** To a DCM (1.4 mL, 0.3 M) solution of **Syn5** (0.0938 g, 0.407 mmol) were added triethylamine (170  $\mu$ L, 1.22 mmol), and acetic anhydride (60  $\mu$ L, 0.63 mmol). The mixture was stirred at room temperature for 38 h. The reaction mixture was then diluted with saturated aqueous sodium chloride and extracted with EtOAc. The combined organic extracts were dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated. Purification by FCC (9:1 hexanes:EtOAc) gave **Syn5** (0.0960 g, 0.352 mmol, 87%) as a white solid.

Data for **Syn5**: R<sub>f</sub> 0.17 (1:9 hexanes:EtOAc); mp = 159–161 °C; IR (neat) 3275, 2923, 2866, 1636 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.35 (d, J = 7.0 Hz, 2 H), 7.29 (t, J = 7.4 Hz, 2 H), 7.21 (t, J = 7.4 Hz, 1 H), 5.29 (d, J = 7.0 Hz, 1 H), 4.46–4.36 (m, 1 H), 3.81 (s, 2 H), 3.08 (d, J = 10.9 Hz, 2 H), 2.37 (td, J = 11.8, 6.4 Hz, 2 H), 1.97 (s, 3 H), 1.94 (d, J = 6.2 Hz, 3 H), 1.54 (d, J = 4.7 Hz, 1 H), 1.16 (ddd, J = 14.8, 1313, 3.1 Hz, 2 H), 0.99 (d, J = 6.6 Hz, 2 H); <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) δ 169.3, 140.3, 128.3, 128.2, 126.7, 55.7, 49.0, 41.7, 33.6, 24.5, 26.7, 14.3; HRMS (TOF MS ES+) calcd for C<sub>17</sub>H<sub>25</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 273.1967, found 273.1961.

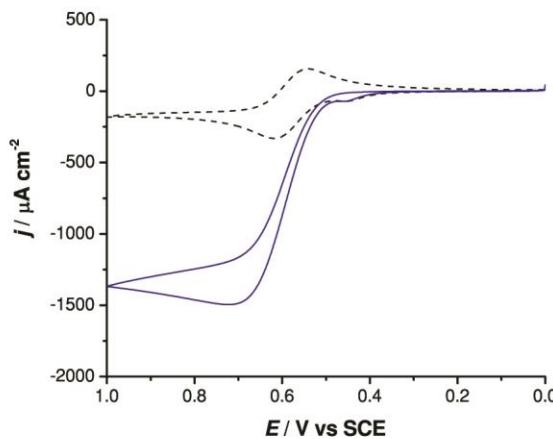


**( $\pm$ )-*N*-((1*R*,3*r*,5*S*)-9-oxyl-9-azabicyclo[3.3.1]nonan-3-yl)acetamide (Syn6).** To a MeOH (2.2 mL, 0.1 M) solution of **Syn6** (0.0612 g, 0.225 mmol) was added 20% palladium hydroxide on activated charcoal (0.0080 g, 0.011 mmol). The mixture was stirred at room temperature under an atmosphere of H<sub>2</sub> (balloon) for 18 h. The reaction mixture was then filtered through celite. The filtrate was concentrated and re-dissolved in THF (2.2 mL, 0.1 M). To this solution was added 3-chloroperoxybenzoic acid (0.1002 g, 0.406 mmol). After stirring at room temperature for 45 minutes, the reaction was diluted with saturated aqueous sodium bicarbonate and extracted with EtOAc. The combined organic extracts were dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated. Purification by FCC (9:1 EtOAc:10% NH<sub>4</sub>OH in MeOH) gave **Syn6** (0.0158 g, 0.080 mmol, 36%) as a yellow solid.

Data for **Syn6**: R<sub>f</sub> 0.18 (9:1 EtOAc:10% NH<sub>4</sub>OH in MeOH); decomposed 165–175 °C; IR (neat) 3290, 2936, 1652 cm<sup>-1</sup>; HRMS (TOF MS ES+) calcd for C<sub>10</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub>Na [M+Na]<sup>+</sup>: 220.1188, found 220.1190.

**Table S3.18. Summary table of electrocatalytic properties of ABNO-NHAc.**

	$E_{a1}$	0.608
	$E_{a2}$	0.470
	$j_{max}$	1402.8
	$(i_{pa}/i_{pc})_{cat.}$	131.49



**Figure S3.18.** CV of 5 mM **18** in the absence (dashed) and presence (solid) of 1 M glycerol using 150 mM Robinson buffer at 25 °C.

**Optimized Geometry Coordinates Using B3LYP/6-31+G(d,p) CPCM**

<b>T*</b>				<b>T+</b>			
<b>Symbol</b>	<b>X</b>	<b>Y</b>	<b>Z</b>	<b>Symbol</b>	<b>X</b>	<b>Y</b>	<b>Z</b>
C	1.5312	-0.3765	-1.2376	C	1.5577	-0.3467	-1.2555
H	1.9807	-0.9314	-2.0648	H	2.0338	-0.9078	-2.0602
C	1.5312	-0.3765	1.2376	C	1.5577	-0.3467	1.2555
H	1.9807	-0.9314	2.0648	H	2.0338	-0.9078	2.0602
C	2.0339	1.0877	1.2814	C	2.0572	1.1335	1.2711
H	3.1200	1.0459	1.4286	H	3.1415	1.1014	1.4189
H	1.6119	1.5872	2.1607	H	1.6216	1.5927	2.1631
C	2.0339	1.0877	-1.2814	C	2.0572	1.1335	-1.2711
H	1.6119	1.5872	-2.1607	H	1.6215	1.5927	-2.1631
H	3.1200	1.0458	-1.4286	H	3.1414	1.1014	-1.4189
C	0.0035	-0.5827	-1.2778	C	0.0244	-0.5753	-1.2757
H	-0.1806	-1.6548	-1.4222	H	-0.1434	-1.6462	-1.4339
H	-0.4112	-0.0653	-2.1493	H	-0.3663	-0.0531	-2.1533
C	0.0035	-0.5827	1.2778	C	0.0244	-0.5753	1.2756
H	-0.1806	-1.6548	1.4223	H	-0.1434	-1.6462	1.4339
H	-0.4112	-0.0652	2.1493	H	-0.3663	-0.0532	2.1533
N	2.0455	-0.9981	0.0000	C	-0.7134	-0.1182	0.0000
O	3.2241	-1.5245	0.0000	H	-0.8209	0.9648	0.0000
C	-0.7312	-0.1234	0.0000	C	1.7176	1.9218	0.0000
H	-0.8299	0.9608	0.0000	H	2.3049	2.8460	0.0000
C	1.7253	1.8877	0.0000	H	0.6714	2.2316	0.0000
H	2.3252	2.8049	0.0000	O	2.9145	-1.7917	0.0000
H	0.6825	2.2174	0.0000	N	2.0787	-0.9323	0.0000
C	-3.2071	0.1758	0.0000	C	-3.1774	0.1829	0.0000
O	-3.1424	1.4154	0.0000	O	-3.0948	1.4181	0.0000
C	-4.5443	-0.5391	0.0000	C	-4.5172	-0.5231	0.0000
H	-5.1099	-0.2275	-0.8830	H	-5.0798	-0.2074	0.8831
H	-4.4567	-1.6280	0.0000	H	-5.0799	-0.2073	-0.8831
H	-5.1099	-0.2275	0.8830	H	-4.4358	-1.6122	0.0000
N	-2.1067	-0.6188	0.0000	N	-2.0788	-0.6238	0.0000
H	-2.2462	-1.6211	0.0000	H	-2.2212	-1.6257	0.0000

<b>TH</b>			
<b>Symbol</b>	<b>X</b>	<b>Y</b>	<b>Z</b>
C	-1.4896	-0.3910	1.2152
H	-1.9155	-0.9316	2.0673
C	-1.4896	-0.3912	-1.2151
H	-1.9155	-0.9318	-2.0672
C	-1.9886	1.0697	-1.2741

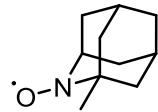
<b>TH2</b>			
<b>Symbol</b>	<b>X</b>	<b>Y</b>	<b>Z</b>
C	-1.4567	-0.3747	1.2504
H	-1.8954	-0.9398	2.0771
C	-1.4589	-0.3365	-1.2636
H	-1.9104	-0.8786	-2.0971
C	-1.9648	1.1130	-1.2588

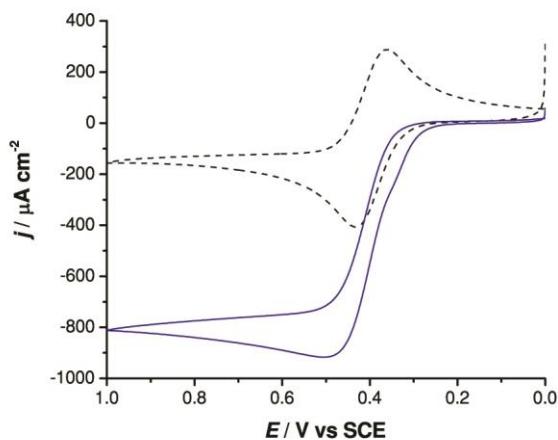
H	-3.0730	1.0382	-1.4290	H	-3.0464	1.0911	-1.4215
H	-1.5598	1.5607	-2.1560	H	-1.5271	1.6085	-2.1307
C	-1.9885	1.0698	1.2740	C	-1.9675	1.0719	1.2909
H	-1.5598	1.5610	2.1558	H	-1.5365	1.5412	2.1803
H	-3.0730	1.0384	1.4289	H	-3.0502	1.0428	1.4478
C	0.0408	-0.5821	1.2739	C	0.0657	-0.6049	1.2638
H	0.2346	-1.6520	1.4220	H	0.2499	-1.6775	1.4057
H	0.4439	-0.0567	2.1467	H	0.4710	-0.1026	2.1466
C	0.0408	-0.5823	-1.2738	C	0.0628	-0.5667	-1.2873
H	0.2346	-1.6522	-1.4219	H	0.2467	-1.6347	-1.4615
H	0.4438	-0.0570	-2.1467	H	0.4665	-0.0381	-2.1553
N	-1.9466	-1.1067	0.0001	N	-1.9788	-1.0469	-0.0177
O	-3.4026	-1.0995	0.0001	O	-3.3934	-1.0737	-0.0963
C	0.7793	-0.1220	0.0000	C	0.8037	-0.1269	-0.0057
H	0.8768	0.9624	-0.0001	H	0.9039	0.9569	0.0104
C	-1.6863	1.8816	-0.0001	C	-1.6499	1.8939	0.0293
H	-2.2893	2.7976	-0.0001	H	-2.2501	2.8086	0.0435
H	-0.6438	2.2148	-0.0001	H	-0.6071	2.2198	0.0362
H	-3.6165	-2.0432	0.0001	H	-3.7004	-1.5930	0.6707
C	3.2592	0.1717	0.0000	H	-1.6559	-2.0220	-0.0477
O	3.2022	1.4125	0.0000	C	3.2710	0.1770	0.0042
C	4.5940	-0.5490	0.0000	O	3.1930	1.4135	0.0226
H	5.1611	-0.2401	-0.8830	C	4.6106	-0.5306	-0.0012
H	5.1611	-0.2400	0.8829	H	5.1749	-0.2079	-0.8808
H	4.5018	-1.6376	0.0000	H	5.1731	-0.2237	0.8852
N	2.1565	-0.6173	0.0000	H	4.5282	-1.6197	-0.0111
H	2.2931	-1.6200	0.0000	N	2.1725	-0.6266	-0.0130
				H	2.3160	-1.6283	-0.0245

### 3.19 2-Methyl-AZADO (19)

2-Methyl-AZADO was purchased from Sigma Aldrich and used without purification.

**Table S3.19. Summary table of electrocatalytic properties of Me-AZADO.**

	$E_{a1}$	0.433
	$E_{a2}$	0.333
	$j_{max}$	656.5
	$(i_{pa}/i_{pc})_{cat.}$	53.66



**Figure S3.19.** CV of 5 mM **19** in the absence (dashed) and presence (solid) of 1 M glycerol using 150 mM Robinson buffer at 25 °C.

#### Optimized Geometry Coordinates Using B3LYP/6-31+G(d,p) CPCM

Symbol	T*			T+			
	X	Y	Z	X	Y	Z	
C	-1.0147	-0.5820	0.0123	C	-1.0379	-0.5753	0.0000
C	0.4396	1.4357	-0.4129	C	0.4475	1.5035	0.0000
H	0.3219	2.4796	-0.7125	H	0.3003	2.5835	0.0000
C	1.0492	1.3149	1.0010	C	1.1667	0.9892	1.2769
H	0.4567	1.9063	1.7090	H	0.6613	1.3765	2.1667
H	2.0641	1.7299	0.9906	H	2.1753	1.4132	1.2552
C	-0.3816	-0.7044	1.4239	C	-0.2631	-1.0495	1.2758
H	-0.4022	-1.7584	1.7274	H	-0.3089	-2.1429	1.2628
H	-0.9930	-0.1435	2.1415	H	-0.7971	-0.7056	2.1676

C	1.0668	-0.1724	1.4114	C	1.1872	-0.5455	1.2591
H	1.4972	-0.2703	2.4151	H	1.6948	-0.9074	2.1599
C	1.9082	-0.9792	0.3987	C	1.9160	-1.0566	0.0000
H	2.9439	-0.6158	0.3970	H	2.9548	-0.7080	0.0000
H	1.9377	-2.0363	0.6931	H	1.9409	-2.1521	0.0000
C	-0.1504	-1.3662	-1.0031	C	-0.2631	-1.0495	-1.2758
H	-0.5973	-1.2821	-2.0014	H	-0.7971	-0.7056	-2.1676
H	-0.1717	-2.4265	-0.7239	H	-0.3089	-2.1429	-1.2628
C	1.2757	0.6415	-1.4295	C	1.1667	0.9892	-1.2769
H	0.8501	0.7542	-2.4336	H	0.6613	1.3765	-2.1667
H	2.2905	1.0558	-1.4538	H	2.1753	1.4132	-1.2552
C	1.2980	-0.8419	-1.0123	C	1.1872	-0.5455	-1.2591
H	1.8892	-1.4189	-1.7331	H	1.6948	-0.9074	-2.1599
N	-0.9322	0.8678	-0.3726	O	-1.8859	1.6289	0.0000
O	-1.9045	1.6654	-0.0825	N	-0.9170	0.9182	0.0000
C	-2.4654	-1.0512	-0.0076	C	-2.4999	-0.9835	0.0000
H	-2.9133	-0.9037	-0.9956	H	-3.0197	-0.6167	0.8887
H	-2.4957	-2.1197	0.2276	H	-3.0197	-0.6167	-0.8887
H	-3.0690	-0.5165	0.7291	H	-2.5438	-2.0750	0.0000

TH			
Symbol	X	Y	Z
C	-0.9434	-0.6534	0.0257
C	0.3649	1.3311	-0.6617
H	0.2302	2.3020	-1.1493
C	0.9007	1.5122	0.7729
H	0.2341	2.1665	1.3452
H	1.8824	2.0013	0.7321
C	-0.4039	-0.5001	1.4687
H	-0.3776	-1.4882	1.9461
H	-1.0899	0.1246	2.0525
C	1.0051	0.1286	1.4445
H	1.3765	0.2382	2.4712
C	1.9648	-0.7706	0.6356
H	2.9716	-0.3320	0.6246
H	2.0477	-1.7569	1.1117
C	0.0324	-1.5452	-0.7807
H	-0.3501	-1.6717	-1.8012
H	0.0562	-2.5379	-0.3139
C	1.3345	0.4573	-1.4765
H	0.9735	0.3584	-2.5073
H	2.3133	0.9507	-1.5144

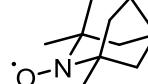
TH2			
Symbol	X	Y	Z
C	-0.9461	-0.7022	0.0405
C	0.4382	1.3653	-0.6177
H	0.2915	2.3427	-1.0845
C	0.9285	1.4799	0.8280
H	0.2671	2.1295	1.4087
H	1.9122	1.9598	0.8009
C	-0.3996	-0.5401	1.4698
H	-0.3831	-1.5384	1.9195
H	-1.0842	0.0711	2.0663
C	1.0149	0.0741	1.4534
H	1.3798	0.1574	2.4822
C	1.9664	-0.8123	0.6230
H	2.9751	-0.3823	0.6222
H	2.0396	-1.8096	1.0729
C	0.0282	-1.5393	-0.8174
H	-0.3563	-1.6434	-1.8398
H	0.0429	-2.5448	-0.3844
C	1.3551	0.4719	-1.4643
H	0.9931	0.4124	-2.4979
H	2.3371	0.9542	-1.5002

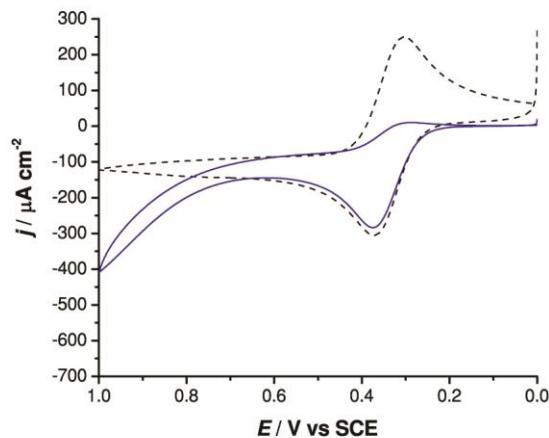
C	1.4408	-0.9260	-0.8079	C	1.4405	-0.9260	-0.8230
H	2.1169	-1.5696	-1.3843	H	2.1047	-1.5596	-1.4193
N	-0.9651	0.6646	-0.6924	N	-0.9473	0.7092	-0.6118
O	-1.8807	1.5575	0.0127	O	-1.9065	1.5069	0.0652
C	-2.3480	-1.2592	0.0074	C	-2.3689	-1.2530	-0.0023
H	-2.7260	-1.3244	-1.0193	H	-2.7621	-1.2818	-1.0241
H	-2.3220	-2.2701	0.4280	H	-2.3467	-2.2789	0.3748
H	-3.0477	-0.6620	0.5980	H	-3.0477	-0.6709	0.6231
H	-2.5750	1.7100	-0.6432	H	-1.9484	2.3514	-0.4203
				H	-1.2752	0.6016	-1.5797

### 3.20 2,6-Dimethyl-norAZADO (20)

**20** was prepared according to the procedure of Iwabuchi *et al.*<sup>28</sup>

**Table S3.20. Summary table of electrocatalytic properties of Me<sub>2</sub>-nor-AZADO.**

	$E_{a1}$	0.370
	$E_{a2}$	0.749
	$j_{max}$	303.3
	$(i_{pa}/i_{pc})_{cat.}$	18.93



**Figure S3.20.** CV of 5 mM **20** in the absence (dashed) and presence (solid) of 1 M glycerol using 150 mM Robinson buffer at 25 °C.

#### Optimized Geometry Coordinates Using B3LYP/6-31+G(d,p) CPCM

Symbol	T*			T+			
	X	Y	Z	X	Y	Z	
C	-1.3025	0.2175	-0.0819	C	-1.3295	0.2216	0.0000
C	1.3025	0.2175	-0.0819	C	1.3295	0.2216	0.0000
C	1.2422	-0.6083	1.2254	C	1.2328	-0.7788	1.1841
H	1.1466	0.0135	2.1212	H	1.1440	-0.2943	2.1596
H	2.1624	-1.1966	1.3151	H	2.1640	-1.3523	1.1720
C	-1.2422	-0.6083	1.2254	C	-1.2328	-0.7788	1.1841
H	-2.1624	-1.1966	1.3151	H	-2.1640	-1.3523	1.1720
H	-1.1466	0.0135	2.1212	H	-1.1440	-0.2943	2.1596
C	0.0000	-1.7113	-0.6161	C	0.0000	-1.6153	-0.7958

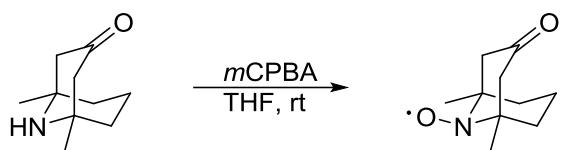
H	0.0000	-2.4193	1.5410	H	0.0000	-2.6083	1.2474
C	-1.2338	-0.9286	-1.1084	C	-1.2328	-0.7788	-1.1841
H	-1.1345	-0.5804	-2.1413	H	-1.1440	-0.2943	-2.1596
H	-2.1570	-1.5132	-1.0345	H	-2.1640	-1.3523	-1.1720
C	1.2338	-0.9286	-1.1084	C	1.2328	-0.7788	-1.1841
H	1.1345	-0.5804	-2.1413	H	1.1440	-0.2943	-2.1596
H	2.1570	-1.5132	-1.0345	H	2.1640	-1.3523	-1.1720
C	0.0000	-1.4904	0.9666	C	0.0000	-1.6153	0.7958
H	0.0000	-2.7615	-0.9164	H	0.0000	-2.6083	-1.2474
N	0.0000	0.9953	-0.1720	O	0.0000	2.1790	0.0000
O	0.0000	2.2174	0.2359	N	0.0000	0.9813	0.0000
C	-2.4924	1.1510	-0.2285	C	2.4855	1.1965	0.0000
H	-2.4564	1.6904	-1.1803	H	3.4104	0.6148	0.0000
H	-3.4104	0.5554	-0.2052	H	2.4772	1.8324	-0.8888
H	-2.5316	1.8839	0.5800	H	2.4772	1.8324	0.8888
C	2.4924	1.1510	-0.2285	C	-2.4855	1.1965	0.0000
H	3.4104	0.5554	-0.2052	H	-2.4772	1.8324	-0.8888
H	2.4564	1.6904	-1.1803	H	-3.4104	0.6148	0.0000
H	2.5316	1.8839	0.5800	H	-2.4772	1.8324	0.8888

TH			
Symbol	X	Y	Z
C	-1.2756	0.1905	-0.1521
C	1.2756	0.1905	-0.1521
C	1.2376	-0.4613	1.2485
H	1.1392	0.2637	2.0619
H	2.1625	-1.0274	1.4104
C	-1.2376	-0.4613	1.2485
H	-2.1625	-1.0274	1.4104
H	-1.1392	0.2637	2.0619
C	0.0000	-1.8029	-0.4296
H	0.0000	-2.2229	1.8011
C	-1.2265	-1.0825	-1.0191
H	-1.1274	-0.8769	-2.0898
H	-2.1575	-1.6395	-0.8663
C	1.2265	-1.0825	-1.0191
H	1.1274	-0.8769	-2.0898
H	2.1575	-1.6395	-0.8663
C	0.0000	-1.3764	1.1097
H	0.0000	-2.8839	-0.5913
N	0.0000	0.9600	-0.4220
O	0.0000	2.0868	0.5061

TH2			
Symbol	X	Y	Z
C	-1.3391	0.1513	-0.1336
C	1.3391	0.1513	-0.1336
C	1.2412	-0.4886	1.2555
H	1.1491	0.2361	2.0682
H	2.1597	-1.0600	1.4180
C	-1.2412	-0.4886	1.2555
H	-2.1597	-1.0600	1.4180
H	-1.1491	0.2361	2.0682
C	0.0000	-1.8048	-0.4432
H	0.0000	-2.2454	1.7811
C	-1.2337	-1.0910	-1.0301
H	-1.1397	-0.8677	-2.0973
H	-2.1569	-1.6617	-0.8941
C	1.2337	-1.0910	-1.0301
H	1.1397	-0.8677	-2.0973
H	2.1569	-1.6617	-0.8941
C	0.0000	-1.3952	1.0980
H	0.0000	-2.8814	-0.6177
O	0.0000	2.0768	0.5273
H	-0.0001	2.8765	-0.0269

H	0.0000	2.8538	-0.0828	H	0.0000	1.2968	-1.3139
C	-2.4820	1.0785	-0.4342	N	0.0000	0.9541	-0.3468
H	-2.4466	1.4664	-1.4585	C	2.5117	1.0785	-0.4014
H	-3.4014	0.4939	-0.3214	H	3.4309	0.4932	-0.3099
H	-2.5301	1.9260	0.2542	H	2.4794	1.4909	-1.4158
C	2.4820	1.0785	-0.4342	H	2.5570	1.8987	0.3176
H	3.4014	0.4939	-0.3214	C	-2.5117	1.0785	-0.4014
H	2.4466	1.4664	-1.4585	H	-2.4794	1.4908	-1.4158
H	2.5301	1.9260	0.2542	H	-3.4309	0.4932	-0.3099
				H	-2.5570	1.8986	0.3176

### 3.21 2,6-Dimethyl-4-Oxo-ABNO (21)

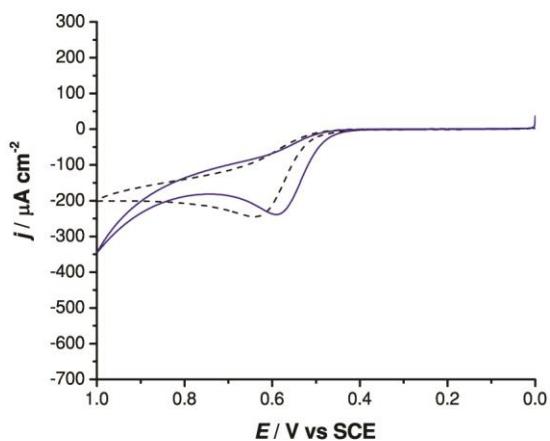


**( $\pm$ )-(1R,5S)-9-hydroxy-1,5-dimethyl-9-azabicyclo[3.3.1]nonan-3-one (Syn7).** To a THF (14.5 mL, 0.1 M) solution of (1R,5S)-1,5-dimethyl-9-azabicyclo[3.3.1]nonan-3-one<sup>28</sup> (0.2432 g, 1.45 mmol) To this solution was added 3-chloroperoxybenzoic acid (0.6456 g, 2.62 mmol). After stirring at room temperature for 30 minutes, the reaction was diluted with saturated aqueous sodium bicarbonate and extracted with EtOAc. The combined organic extracts were dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated. Purification by FCC (3:1 hexanes:EtOAc) gave **Syn7** (0.1571 g, 0.862 mmol, 59%) as a red oil.

Data for **Syn7**:  $R_f$  0.07 (4:1 hexanes:EtOAc); IR (neat) 2936, 1703  $\text{cm}^{-1}$ ; HRMS (TOF MS ES+) calcd for  $C_{10}H_{16}NO_2$  [M+]: 182.1181, found 182.1183.

**Table S3.21.** Summary table of electrocatalytic properties of Me<sub>2</sub>-ABNO-oxo.

	$E_{a1}$	0.621
	$E_{a2}$	0.644
	$j_{max}$	184.6
	$(i_{pa}/i_{pc})_{cat.}$	0.00



**Figure S3.21.** CV of 5 mM **21** in the absence (dashed) and presence (solid) of 1 M glycerol using 150 mM Robinson buffer at 25 °C.

**Optimized Geometry Coordinates Using B3LYP/6-31+G(d,p) CPCM**

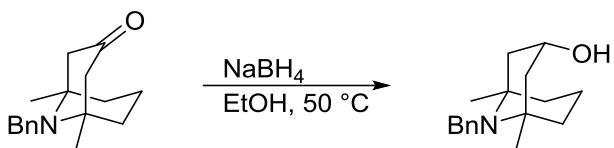
T*				T+			
Symbol	X	Y	Z	Symbol	X	Y	Z
C	1.2713	-0.3473	-0.1069	C	1.2993	-0.3622	-0.0686
C	-1.2712	-0.3477	-0.1068	C	-1.2993	-0.3622	-0.0686
C	-1.2693	-0.3660	1.4451	C	-1.2598	-0.3380	1.4993
H	-1.3594	-1.4132	1.7594	H	-1.3516	-1.3709	1.8500
H	-2.1627	0.1566	1.8050	H	-2.1644	0.1935	1.8091
C	1.2694	-0.3657	1.4451	C	1.2598	-0.3380	1.4993
H	2.1626	0.1573	1.8050	H	2.1644	0.1935	1.8091
H	1.3598	-1.4128	1.7594	H	1.3516	-1.3709	1.8500
C	1.2863	1.0945	-0.6729	C	1.2937	1.0650	-0.6800
H	1.4650	1.0348	-1.7560	H	1.5034	0.9858	-1.7551
H	2.1107	1.6680	-0.2401	H	2.1107	1.6357	-0.2329
C	-1.2866	1.0941	-0.6729	C	-1.2937	1.0650	-0.6800
H	-1.4653	1.0343	-1.7561	H	-1.5034	0.9858	-1.7551
H	-2.1112	1.6674	-0.2401	H	-2.1107	1.6357	-0.2329
N	0.0002	-0.9990	-0.5629	C	0.0000	0.3087	2.0724
O	0.0004	-2.2698	-0.7714	H	0.0000	0.1732	3.1590
C	0.0000	0.2431	2.0581	H	0.0000	1.3912	1.9097
H	0.0000	0.0673	3.1395	O	0.0000	-2.0814	-1.0213
H	-0.0002	1.3332	1.9387	N	0.0000	-1.0195	-0.4696
C	-0.0003	1.8762	-0.5134	C	0.0000	1.8498	-0.5581
O	-0.0005	3.0911	-0.3518	O	0.0000	3.0657	-0.4787
C	2.4769	-1.1142	-0.6521	C	-2.4713	-1.1867	-0.5829
H	2.4342	-1.1901	-1.7425	H	-2.4549	-1.2706	-1.6722
H	3.3906	-0.5779	-0.3783	H	-2.4771	-2.1895	-0.1506
H	2.5272	-2.1220	-0.2367	H	-3.3927	-0.6786	-0.2887
C	-2.4766	-1.1149	-0.6521	C	2.4713	-1.1867	-0.5829
H	-3.3904	-0.5789	-0.3783	H	2.4549	-1.2706	-1.6722
H	-2.4338	-1.1909	-1.7425	H	3.3927	-0.6786	-0.2887
H	-2.5266	-2.1228	-0.2367	H	2.4771	-2.1895	-0.1506

TH			
Symbol	X	Y	Z
C	-0.3120	-1.2469	-0.1511
C	-0.3120	1.2469	-0.1511
C	-0.4009	1.2662	1.3942
H	-1.4576	1.3652	1.6677
H	0.1102	2.1601	1.7706
C	-0.4009	-1.2662	1.3942
H	0.1102	-2.1601	1.7706

TH2			
Symbol	X	Y	Z
C	-0.2826	-1.3010	-0.1326
C	-0.2827	1.3010	-0.1326
C	-0.4028	1.2682	1.4017
H	-1.4598	1.3692	1.6664
H	0.1053	2.1594	1.7821
C	-0.4027	-1.2682	1.4017
H	0.1053	-2.1594	1.7821

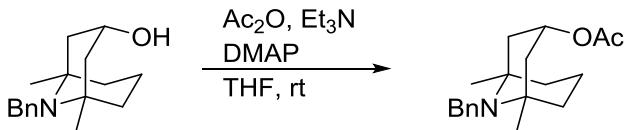
H	-1.4576	-1.3652	1.6677	H	-1.4598	-1.3692	1.6664
C	1.1576	-1.2787	-0.6428	C	1.1810	-1.2881	-0.6279
H	1.1496	-1.4487	-1.7290	H	1.2056	-1.4844	-1.7095
H	1.6993	-2.1120	-0.1863	H	1.7183	-2.1121	-0.1523
C	1.1576	1.2787	-0.6428	C	1.1810	1.2882	-0.6279
H	1.1496	1.4487	-1.7290	H	1.2055	1.4844	-1.7095
H	1.6993	2.1120	-0.1862	H	1.7183	2.1122	-0.1523
N	-0.9121	0.0000	-0.7247	C	0.1759	0.0000	2.0436
C	0.1747	0.0000	2.0461	H	-0.0627	0.0000	3.1112
H	-0.0549	0.0000	3.1178	H	1.2699	0.0000	1.9850
H	1.2699	0.0000	1.9799	C	1.9542	0.0000	-0.4185
C	1.9362	0.0000	-0.4374	O	3.1546	0.0000	-0.1991
O	3.1402	0.0000	-0.2005	C	-1.0268	-2.4956	-0.7316
C	-1.0327	-2.4672	-0.7392	H	-1.0362	-2.4621	-1.8259
H	-1.0543	-2.4109	-1.8329	H	-0.5049	-3.4082	-0.4321
H	-0.5046	-3.3824	-0.4522	H	-2.0527	-2.5534	-0.3648
H	-2.0592	-2.5352	-0.3727	C	-1.0269	2.4956	-0.7315
C	-1.0327	2.4672	-0.7392	H	-0.5050	3.4082	-0.4321
H	-0.5046	3.3824	-0.4522	H	-1.0363	2.4621	-1.8258
H	-1.0543	2.4109	-1.8329	H	-2.0527	2.5534	-0.3647
H	-2.0592	2.5352	-0.3727	O	-2.3168	-0.0001	-0.3210
O	-2.3204	0.0000	-0.3640	H	-2.8241	0.0007	-1.1514
H	-2.7645	0.0000	-1.2232	H	-0.8710	0.0000	-1.6941
				N	-0.9388	0.0000	-0.6691

### 3.22 2,6-Dimethyl-4-Acetyl-ABNO (22)



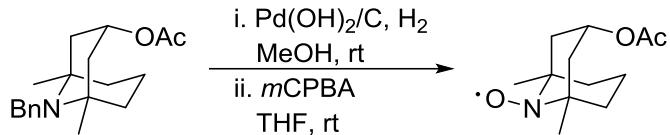
**(±)-(1*R*,3*r*,5*S*)-9-benzyl-1,5-dimethyl-9-azabicyclo[3.3.1]nonan-3-ol (Syn8).** To a EtOH (2.2 mL, 0.3 M) solution of (1*R*,5*S*)-9-benzyl-1,5-dimethyl-9-azabicyclo[3.3.1]nonan-3-one (0.1690 g, 0.657 mmol) was added sodium borohydride (0.1496 g, 3.95 mmol). The mixture was heated to 50 °C for 2.5 h. After cooling to room temperature, the reaction mixture was diluted with water and extracted with EtOAc. The combined organic extracts were dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated. Purification by FCC (2:1 hexanes:EtOAc) gave **Syn8** (0.1569 g, 0.605 mmol, 92%) as a white solid.

Data for **Syn8**: R<sub>f</sub> 0.42 (1:1 hexanes:EtOAc); mp = 127–128 °C; IR (neat) 3313, 2922 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.40 (d, J = 7.8 Hz, 2 H), 7.28 (t, J = 7.3 Hz, 2 H), 7.15 (t, J = 7.3 Hz, 1 H), 4.29 (ddd, J = 15, 10, 5 Hz, 1 H), 3.77 (s, 2 H), 2.17–2.07 (m, 1 H), 1.99 (dd, J = 14.1, 6.8 Hz, 2 H), 1.60–1.53 (m, 3 H), 1.50–1.45 (m, 3 H), 1.23–1.15 (m, 2 H), 1.03 (s, 6 H); <sup>13</sup>C (125 MHz, CDCl<sub>3</sub>) δ 145.8, 127.9, 126.7, 125.6, 64.4, 54.5, 46.7, 43.4, 32.2, 18.2; HRMS (TOF MS ES+) calcd for C<sub>17</sub>H<sub>26</sub>NO [M+H]<sup>+</sup>: 260.2009, found 260.2014.



**(±)-(1*R*,3*r*,5*S*)-9-benzyl-1,5-dimethyl-9-azabicyclo[3.3.1]nonan-3-yl acetate (Syn9).** To a THF (0.5 mL, 0.3 M) solution of **Syn9** (0.0410 g, 0.1581 mmol) were added triethylamine (65 μL, 0.47 mmol), *N,N*-Dimethylpyridin-4-amine (0.0025 g, 0.020 mmol), and acetic anhydride (25 μL, 0.26 mmol). The mixture was stirred at room temperature for 15 h. The reaction mixture was then diluted with saturated aqueous sodium bicarbonate and extracted with EtOAc. The combined organic extracts were dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated. Purification by FCC (19:1 hexanes:EtOAc) gave **Syn9** (0.0403 g, 0.134 mmol, 85%) as a colorless oil.

Data for **Syn9**: R<sub>f</sub> 0.33 (19:1 hexanes:EtOAc); IR (neat) 2920, 1731 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.43 (d, J = 7.4 Hz, 2 H), 7.28 (t, J = 7.3 Hz, 2 H), 7.16 (t, J = 7.0 Hz, 1 H), 5.25 (quin, J = 7.1 Hz, 1 H), 3.79 (s, 2 H), 2.22–2.11 (m, 1 H), 2.06 (s, 3 H), 2.04–2.01 (m, 2 H), 1.65–1.53 (m, 5 H), 1.26–1.23 (m, 2 H), 1.02 (s, 6 H); <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) δ 170.6, 145.4, 127.9, 126.7, 125.6, 67.8, 54.1, 46.8, 38.9, 34.4, 32.0, 21.6, 18.1; HRMS (TOF MS ES+) calcd for C<sub>19</sub>H<sub>28</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 302.2120, found 302.2120.

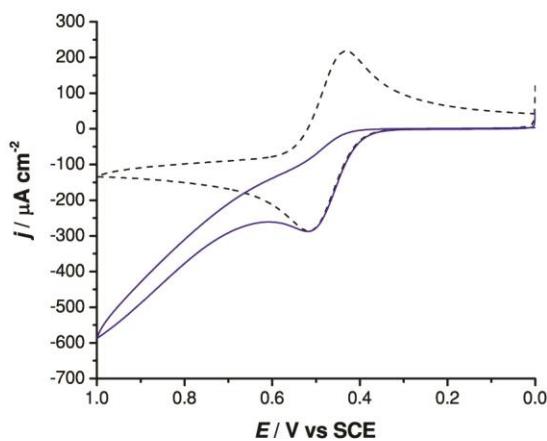


**( $\pm$ )-(1*R*,3*r*,5*S*)-9-oxyl-1,5-dimethyl-9-azabicyclo[3.3.1]nonan-3-yl acetate (Syn10).** To a MeOH (2.2 mL, 0.1 M) solution of **S10** (0.0649 g, 0.2153 mmol) was added 20% palladium hydroxide on activated charcoal (0.0084 g, 0.012 mmol). The mixture was stirred at room temperature under an atmosphere of  $\text{H}_2$  (balloon) for 23 h. The reaction mixture was then filtered through celite. The filtrate was concentrated and re-dissolved in THF (2.2 mL, 0.1 M). To this solution was added 3-chloroperoxybenzoic acid (0.0957 g, 0.388 mmol). After stirring at room temperature for 15 minutes, the reaction was diluted with saturated aqueous sodium bicarbonate and extracted with DCM. The combined organic extracts were dried over anhydrous  $\text{MgSO}_4$ , filtered, and concentrated. Purification by FCC (7:1 hexanes:EtOAc) gave **Syn10** (0.0296 g, 0.131 mmol, 61%) as a red oil.

Data for **Syn10**:  $R_f$  0.11 (4:1 hexanes:EtOAc); IR (neat) 2931, 1735  $\text{cm}^{-1}$ ; HRMS (TOF MS ES+) calcd for  $\text{C}_{12}\text{H}_{20}\text{NO}_3\text{Na} [\text{M}+\text{Na}]^+$ : 249.1341, found 249.1341.

**Table S3.22. Summary table of electrocatalytic properties of  $\text{Me}_2\text{-ABNO-OAc}$ .**

	$E_{a1}$	0.512
	$E_{a2}$	0.727
	$j_{max}$	32.5
	$(i_{pa}/i_{pc})_{cat.}$	19.08



**Figure S3.22.** CV of 5 mM **22** in the absence (dashed) and presence (solid) of 1 M glycerol using 150 mM Robinson buffer at 25 °C.

**Optimized Geometry Coordinates Using B3LYP/6-31+G(d,p) CPCM**

T*				T+			
Symbol	X	Y	Z	Symbol	X	Y	Z
C	1.0798	1.2641	-0.2840	C	-1.4113	-1.2498	0.0259
C	1.3758	-1.2385	-0.0276	C	-1.0734	1.2948	-0.2792
C	1.7954	-1.0491	1.4578	C	-1.5223	1.5113	1.2081
C	1.5032	1.4818	1.1958	H	-2.5822	1.7851	1.1828
C	-0.4418	1.0629	-0.4901	H	-0.9699	2.3870	1.5612
C	-0.1434	-1.4441	-0.2446	C	-1.8399	-0.9900	1.5134
N	1.7649	0.0153	-0.7515	H	-1.5039	-1.8649	2.0776
O	2.9608	0.1089	-1.2231	H	-2.9345	-0.9952	1.5313
C	-1.0088	-0.2329	0.0933	C	0.1155	-1.4600	-0.1878
C	1.3077	0.2579	2.1088	H	0.2725	-1.7328	-1.2366
O	-2.3145	-0.4897	-0.5147	H	0.4055	-2.3208	0.4206
C	-3.4163	-0.0068	0.0948	C	0.4507	1.0457	-0.4704
O	-3.3903	0.6315	1.1352	H	0.6556	1.0304	-1.5462
C	-4.6639	-0.3480	-0.6777	H	0.9670	1.9123	-0.0493
H	2.8920	-1.0680	1.4767	C	0.9977	-0.2531	0.1341
H	1.4525	-1.9151	2.0356	H	1.1704	-0.1500	1.2023
H	0.9620	2.3472	1.5951	C	-1.3156	0.3086	2.1322
H	2.5667	1.7498	1.1804	H	-1.8701	0.4918	3.0587
H	-0.6328	1.0506	-1.5697	H	-0.2702	0.2127	2.4284
H	-0.9723	1.9252	-0.0739	O	-2.6037	0.0326	-1.5532
H	-0.2985	-1.6835	-1.3032	N	-1.7635	0.0233	-0.7001
H	-0.4720	-2.3118	0.3369	O	2.2802	-0.5422	-0.4801
H	-1.1787	-0.1443	1.1635	C	3.3916	-0.0113	0.0903
H	0.2618	0.1697	2.4142	O	3.3569	0.6965	1.0806
H	1.8689	0.4186	3.0364	C	4.6307	-0.4050	-0.6653
H	-5.5438	-0.0748	-0.0957	H	5.5127	-0.0508	-0.1328
H	-4.6680	0.2044	-1.6230	H	4.6732	-1.4907	-0.7859
H	-4.6861	-1.4141	-0.9180	H	4.6037	0.0384	-1.6657
C	1.5337	2.4534	-1.1355	C	-1.5446	2.4494	-1.1560
H	1.3321	2.2766	-2.1963	H	-1.3159	2.2745	-2.2099
H	0.9805	3.3444	-0.8232	H	-2.6174	2.6242	-1.0514
H	2.6009	2.6455	-1.0137	H	-1.0157	3.3490	-0.8327
C	2.1189	-2.4357	-0.6279	C	-2.2015	-2.4110	-0.5662
H	1.7819	-3.3490	-0.1281	H	-3.2778	-2.2626	-0.4572
H	1.9107	-2.5315	-1.6978	H	-1.9703	-2.5572	-1.6240
H	3.1976	-2.3429	-0.4927	H	-1.9214	-3.3167	-0.0234

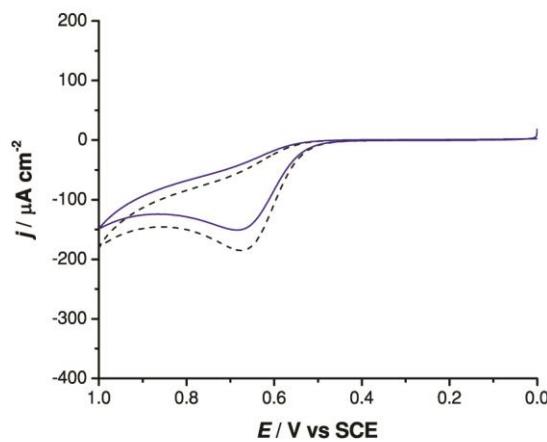
TH				TH2			
Symbol	X	Y	Z	Symbol	X	Y	Z
C	-1.0554	-1.2307	-0.3032	C	-1.3116	-1.2774	-0.0225
C	-1.3368	1.2250	-0.0538	C	-1.0180	1.2827	-0.2750
C	-1.7574	1.0613	1.4297	C	-1.4601	1.4618	1.1904
C	-1.4729	-1.4653	1.1717	C	-1.7488	-1.0673	1.4408
C	0.4716	-1.0540	-0.5016	C	0.2075	-1.4470	-0.2490
C	0.1842	1.4416	-0.2567	C	0.4953	1.0612	-0.4950
N	-1.6847	0.0101	-0.8570	N	-1.7113	0.0000	-0.8057
O	-3.1285	-0.1641	-0.7743	O	-3.1257	0.1040	-0.7537
C	1.0468	0.2327	0.0884	C	1.0679	-0.2315	0.0951
C	-1.2862	-0.2459	2.0933	C	-1.2633	0.2357	2.0976
O	2.3614	0.4852	-0.5092	O	2.3648	-0.4852	-0.5101
C	3.4559	-0.0034	0.1042	C	3.4656	0.0135	0.1022
O	3.4242	-0.6425	1.1448	O	3.4205	0.6720	1.1266
C	4.7100	0.3279	-0.6633	C	4.7175	-0.3507	-0.6486
H	-2.8521	1.0975	1.4593	H	-2.5179	1.7413	1.1843
H	-1.3995	1.9269	1.9998	H	-0.9110	2.3212	1.5868
H	-0.9212	-2.3271	1.5659	H	-2.8421	-1.1024	1.4681
H	-2.5319	-1.7461	1.1654	H	-1.3945	-1.9339	2.0071
H	0.6682	-1.0385	-1.5801	H	0.3796	-1.6999	-1.3028
H	0.9876	-1.9256	-0.0856	H	0.5293	-2.3130	0.3358
H	0.3483	1.6791	-1.3142	H	0.7003	1.0593	-1.5728
H	0.5029	2.3115	0.3276	H	1.0150	1.9283	-0.0786
H	-3.4052	-0.0967	-1.6984	H	-1.4463	-0.1447	-1.7889
H	1.2088	0.1423	1.1599	H	-3.4001	0.6253	-1.5289
H	-0.2423	-0.1612	2.4093	H	1.2283	-0.1386	1.1662
H	-1.8572	-0.4044	3.0160	H	-0.2207	0.1478	2.4095
H	5.5856	0.0906	-0.0593	H	-1.8334	0.3925	3.0184
H	4.7363	-0.2641	-1.5843	H	4.7809	-1.4357	-0.7704
H	4.7208	1.3830	-0.9480	H	5.5897	0.0161	-0.1086
C	-2.0564	2.4416	-0.6561	H	4.6894	0.0927	-1.6487
H	-1.7227	3.3555	-0.1535	C	-1.4812	2.4681	-1.1286
H	-1.8309	2.5345	-1.7238	H	-0.9142	3.3509	-0.8224
H	-3.1386	2.3605	-0.5345	H	-1.2882	2.3073	-2.1942
C	-1.4927	-2.4323	-1.1550	H	-2.5396	2.6935	-0.9792
H	-1.2782	-2.2534	-2.2140	C	-2.0463	-2.4670	-0.6494
H	-0.9465	-3.3276	-0.8398	H	-1.8398	-2.5468	-1.7215
H	-2.5615	-2.6272	-1.0442	H	-1.6859	-3.3812	-0.1707
				H	-3.1240	-2.4002	-0.4991

### 3.23 4-Oxo-2,2,6,6-Dimethylazabicyclo[3.2.1]octan-N-oxy, oxo-ABOO (23)

**23** was prepared according to the procedure of Keana *et al.*<sup>26</sup>

**Table S3.23. Summary table of electrocatalytic properties of ABOO-oxo.**

	$E_{a1}$ $E_{a2}$ $j_{max}$ $(i_{pa}/i_{pc})_{cat.}$	0.702 1.090 0 0
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**Figure S3.23.** CV of 5 mM **23** in the absence (dashed) and presence (solid) of 1 M glycerol using 150 mM Robinson buffer at 25 °C.

#### Optimized Geometry Coordinates Using B3LYP/6-31+G(d,p) CPCM

Symbol	T*			T+			
	X	Y	Z	X	Y	Z	
C	1.2048	0.4047	0.1597	C	1.2670	0.2534	0.1417
C	-1.2048	0.4046	0.1597	C	-1.1958	0.4871	0.1421
C	-1.2946	-1.0198	-0.4572	C	-1.3928	-0.9385	-0.4619
H	-1.4955	-0.9182	-1.5329	H	-1.6247	-0.8595	-1.5318
H	-2.1145	-1.5915	-0.0139	H	-2.2547	-1.3946	0.0303
C	1.2946	-1.0198	-0.4572	C	1.1904	-1.1852	-0.4603
H	2.1146	-1.5915	-0.0140	H	1.9490	-1.7959	0.0352
H	1.4955	-0.9181	-1.5329	H	1.4356	-1.1516	-1.5296
C	0.7799	0.3434	1.6444	C	0.8116	0.2722	1.6205

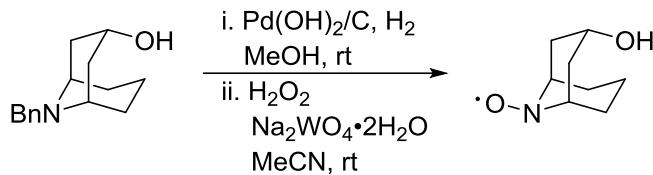
H	1.1605	1.2211	2.1730	H	1.2694	1.1218	2.1296
H	1.1986	-0.5397	2.1339	H	1.1456	-0.6387	2.1194
C	-0.7800	0.3434	1.6444	C	-0.7456	0.4139	1.6220
H	-1.1605	1.2211	2.1730	H	-1.0420	1.3308	2.1344
H	-1.1985	-0.5397	2.1339	H	-1.2402	-0.4221	2.1184
C	0.0000	-1.8053	-0.3131	O	0.1673	1.7743	-1.3564
O	0.0000	-3.0149	-0.1218	N	0.0912	0.9601	-0.4936
O	0.0000	1.4472	-1.6683	C	-0.1758	-1.8443	-0.3192
N	0.0000	1.0400	-0.4535	O	-0.2906	-3.0463	-0.1681
C	-2.4675	1.2119	-0.1078	C	2.5767	0.9514	-0.1769
H	-2.6730	1.2753	-1.1797	H	3.3773	0.4259	0.3483
H	-3.3210	0.7325	0.3808	H	2.7975	0.9336	-1.2463
H	-2.3669	2.2258	0.2913	H	2.5609	1.9868	0.1715
C	2.4674	1.2120	-0.1078	C	-2.3499	1.4209	-0.1755
H	3.3210	0.7326	0.3808	H	-2.5546	1.4597	-1.2482
H	2.6730	1.2754	-1.1797	H	-3.2398	1.0433	0.3340
H	2.3668	2.2258	0.2913	H	-2.1468	2.4305	0.1908

TH			
Symbol	X	Y	Z
C	0.3065	-1.1778	0.0040
C	0.3065	1.1778	0.0040
C	-1.1690	1.2816	-0.4533
H	-1.1888	1.5026	-1.5295
H	-1.6800	2.0987	0.0638
C	-1.1690	-1.2816	-0.4533
H	-1.6800	-2.0986	0.0638
H	-1.1889	-1.5026	-1.5295
C	0.3827	-0.7764	1.5116
H	1.2960	-1.1720	1.9676
H	-0.4532	-1.2008	2.0750
C	0.3827	0.7764	1.5116
H	1.2960	1.1719	1.9677
H	-0.4532	1.2008	2.0750
C	-1.9502	0.0000	-0.2545
O	-3.1450	0.0000	0.0177
N	0.8670	0.0000	-0.7365
O	2.3044	0.0000	-0.6507
H	2.5698	0.0000	0.2881
C	1.0307	2.4797	-0.3308
H	1.0057	2.6741	-1.4079
H	0.5349	3.3118	0.1793

TH2			
Symbol	X	Y	Z
C	-1.2300	-0.3777	0.2029
C	1.2299	-0.3779	0.2029
C	1.2934	1.0358	-0.4042
H	1.5555	0.9931	-1.4712
H	2.1017	1.5885	0.0802
C	-1.2932	1.0361	-0.4041
H	-2.1013	1.5890	0.0804
H	-1.5555	0.9936	-1.4710
C	-0.7804	-0.3429	1.6825
H	-1.1630	-1.2205	2.2081
H	-1.1977	0.5372	2.1747
C	0.7803	-0.3429	1.6825
H	1.1629	-1.2205	2.2082
H	1.1977	0.5372	2.1746
N	-0.0001	-1.0933	-0.4039
O	-0.0001	-1.2951	-1.7975
H	-0.0005	-0.4212	-2.2263
H	-0.0002	-2.0608	-0.0601
C	0.0002	1.8298	-0.2727
O	0.0003	3.0385	-0.1234
C	-2.4943	-1.1787	-0.0719
H	-2.4174	-2.1955	0.3248

H	2.0733	2.4571	-0.0074	H	-3.3339	-0.6877	0.4268
C	1.0307	-2.4797	-0.3308	H	-2.7123	-1.2279	-1.1417
H	0.5349	-3.3118	0.1793	C	2.4941	-1.1792	-0.0719
H	1.0057	-2.6741	-1.4079	H	3.3338	-0.6883	0.4268
H	2.0733	-2.4571	-0.0074	H	2.4170	-2.1960	0.3250
				H	2.7120	-1.2286	-1.1416

### 3.24 4-Hydroxy-ABNO (24)

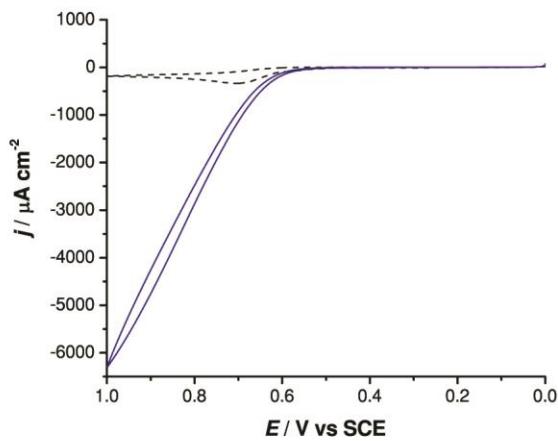


**( $\pm$ )-(1*R*,3*R*,5*S*)-9-azabicyclo[3.3.1]nonane-3,9-oxyl (24).** To a MeOH (13 mL, 0.1 M) solution of endo-9-benzyl-9-azabicyclo[3.3.1]nonan-3-one<sup>24</sup> (0.3025 g, 1.31 mmol) was added 20% palladium hydroxide on activated charcoal (0.0476 g, 0.0678 mmol). The mixture was stirred at room temperature under an atmosphere of  $\text{H}_2$  (balloon) for 16 h. The reaction mixture was then filtered through celite. The filtrate was concentrated and re-dissolved in MeCN (13 mL, 0.1 M). To this solution were added sodium tungstate dihydrate (0.2157 g, 0.654 mmol) and 30% hydrogen peroxide (2.2 mL, 19.4 mmol). After stirring at room temperature for 19 h, the reaction was diluted with saturated aqueous sodium bicarbonate and extracted with EtOAc. The combined organic extracts were dried over anhydrous  $\text{MgSO}_4$ , filtered, and concentrated. Purification by FCC (2:3 hexanes:EtOAc) gave **24** (0.0761 g, 0.487 mmol, 37%) as a yellow solid.

Data for **24**: Rf 0.52 (1:3 hexanes:EtOAc); mp = 107–109 °C; IR (neat) 2926, 2883, 1702  $\text{cm}^{-1}$ ; HRMS (TOF MS ES+): calcd for  $\text{C}_8\text{H}_{14}\text{NO}_2$  [M+]: 156.1025, found 156.1030.

**Table S3.24. Summary table of electrocatalytic properties of ABNO-OH.**

	$E_{a1}$	0.687
	$E_{a2}$	0.59
	$j_{max}$	6373.2
	$(i_{pa}/i_{pc})_{cat.}$	63.88



**Figure S3.24.** CV of 5 mM **24** in the absence (dashed) and presence (solid) of 1 M glycerol using 150 mM Robinson buffer at 25 °C.

#### Optimized Geometry Coordinates Using B3LYP/6-31+G(d,p) CPCM

T*				T+			
Symbol	X	Y	Z	Symbol	X	Y	Z
C	-0.4769	-0.6378	1.1275	C	-0.4972	-0.4257	1.2406
H	-0.8167	-1.4250	1.8050	H	-0.8307	-1.1073	2.0236
C	-0.4706	-0.1221	-1.2932	C	-0.4986	-0.3440	-1.2696
H	-0.8046	-0.5647	-2.2348	H	-0.8312	-0.9731	-2.0960
C	-1.2365	1.2033	-1.0592	C	-1.3254	0.9812	-1.2425
H	-2.2953	0.9980	-1.2589	H	-2.3734	0.7071	-1.3991
H	-0.9102	1.9436	-1.7983	H	-1.0061	1.5573	-2.1159
C	-1.2443	0.6689	1.4490	C	-1.3242	0.8985	1.2998
H	-0.9240	1.0434	2.4278	H	-1.0028	1.4162	2.2082
H	-2.3039	0.4006	1.5404	H	-2.3724	0.6159	1.4398
C	1.0619	-0.5659	1.1860	C	1.0445	-0.2909	1.2645
H	1.4517	-1.5876	1.0997	H	1.4712	-1.2938	1.3731
H	1.3717	-0.1818	2.1636	H	1.3032	0.2732	2.1645
C	1.0698	-0.0384	-1.3024	C	1.0453	-0.2119	-1.2756
H	1.4581	-1.0089	-1.6341	H	1.4686	-1.2079	-1.4423
H	1.3857	0.7084	-2.0399	H	1.3075	0.4047	-2.1405
N	-0.8673	-1.0690	-0.2307	C	1.6601	0.3579	0.0180
O	-1.9303	-1.7846	-0.3855	H	1.5331	1.4422	0.0542
C	1.6999	0.2676	0.0686	C	-1.1746	1.7844	0.0559
H	1.6013	1.3331	0.2965	H	-1.9565	2.5506	0.0818
C	-1.0877	1.7605	0.3710	H	-0.2249	2.3217	0.0727
H	-1.8482	2.5329	0.5331	O	-1.4923	-2.0991	-0.0692

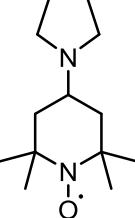
H	-0.1241	2.2662	0.4814	N	-0.8731	-1.0734	-0.0371
O	3.1022	-0.0585	0.0696	O	3.0571	0.0578	0.0727
H	3.5613	0.5525	-0.5239	H	3.5286	0.6411	-0.5388

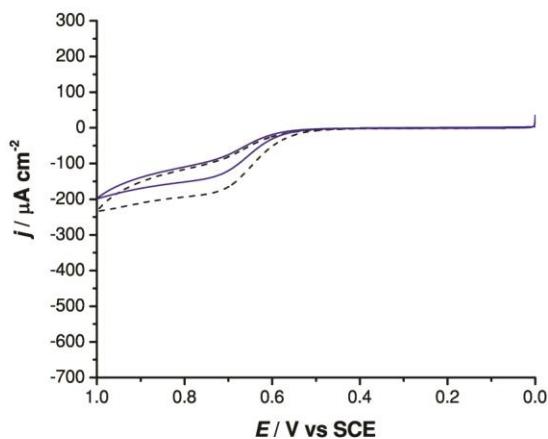
<b>TH</b>				<b>TH2</b>			
<b>Symbol</b>	<b>X</b>	<b>Y</b>	<b>Z</b>	<b>Symbol</b>	<b>X</b>	<b>Y</b>	<b>Z</b>
C	-0.4404	-1.2718	-0.0692	C	0.4158	1.2486	-0.3766
H	-0.7763	-2.2473	-0.4369	C	0.4210	-1.2649	-0.3267
C	-0.4349	1.0804	-0.6802	C	1.1638	-1.2583	1.0158
H	-0.7641	1.7555	-1.4774	C	1.1536	1.2955	0.9693
C	-1.1614	1.4830	0.6222	C	-1.1215	1.2641	-0.3486
H	-2.2262	1.5847	0.3836	C	-1.1186	-1.2727	-0.3007
H	-0.8140	2.4744	0.9373	N	0.8251	-0.0213	-1.1170
C	-1.1656	-0.9854	1.2641	O	2.2191	0.0609	-1.3611
H	-0.8192	-1.6981	2.0223	C	-1.7698	0.0102	0.2519
H	-2.2310	-1.1877	1.1064	C	0.9841	0.0328	1.8346
C	1.1006	-1.3165	-0.0013	O	-3.1538	0.0659	-0.1111
H	1.4708	-1.7006	-0.9598	H	0.7661	2.0630	-1.0139
H	1.4137	-2.0219	0.7763	H	0.7590	-2.1129	-0.9282
C	1.1077	1.1373	-0.6398	H	2.2268	-1.4219	0.8145
H	1.4765	1.0019	-1.6637	H	0.8156	-2.1282	1.5811
H	1.4265	2.1318	-0.3052	H	2.2151	1.4631	0.7653
N	-0.7797	-0.2904	-1.1279	H	0.7926	2.1806	1.5018
O	-2.2202	-0.3415	-1.3371	H	-1.4959	1.3783	-1.3738
C	1.7561	0.0480	0.2307	H	-1.4364	2.1561	0.2000
H	1.6836	0.3214	1.2881	H	-1.4890	-1.4226	-1.3226
C	-0.9985	0.4627	1.7655	H	-1.4344	-2.1462	0.2780
H	-1.7428	0.6663	2.5448	H	0.3557	-0.0278	-2.0318
H	-0.0235	0.5868	2.2476	H	2.4513	-0.7133	-1.9075
H	-2.2872	-0.5870	-2.2706	H	-1.6932	0.0331	1.3421
O	3.1543	-0.1060	-0.0890	H	0.0103	0.0370	2.3299
H	3.6170	0.7068	0.1589	H	1.7298	0.0505	2.6351

### 3.25 4-(N-Pyrrolidinyl)-TEMPO (25)

**25** was prepared according to the procedure of Anzai *et al.*<sup>29</sup>

**Table S3.25. Summary table of electrocatalytic properties of 4-oxo-TEMPO.**

		$E_{a1}$	0.712
		$E_{a2}$	0.988
		$j_{max}$	6.6
		$(i_{pa}/i_{pc})_{cat.}$	0.00



**Figure S3.25.** CV of 5 mM **25** in the absence (dashed) and presence (solid) of 1 M glycerol using 150 mM Robinson buffer at 25 °C.

#### Optimized Geometry Coordinates Using B3LYP/6-31+G(d,p) CPCM for TEMPO-NPyr

Symbol	T*			T+			
	X	Y	Z	X	Y	Z	
C	-1.5529	-1.3270	-0.0238	C	-1.5525	-1.3516	0.0215
C	-0.0656	-1.2357	-0.4230	C	-0.0621	-1.2444	-0.3668
C	0.6680	0.0000	0.1127	C	0.6687	0.0000	0.1579
C	-0.0656	1.2357	-0.4230	C	-0.0621	1.2444	-0.3668
C	-1.5529	1.3270	-0.0237	C	-1.5525	1.3516	0.0215
H	0.4085	-2.1586	-0.0780	H	0.3977	-2.1609	0.0094
H	0.6324	0.0000	1.2196	H	0.6534	0.0000	1.2638

H	0.4085	2.1586	-0.0780	H	0.3977	2.1609	0.0094
H	0.0155	1.2242	-1.5174	H	0.0243	1.2635	-1.4590
H	0.0155	-1.2243	-1.5174	H	0.0243	-1.2635	-1.4590
N	-2.2280	0.0000	-0.2223	C	-2.2741	-2.3997	-0.8311
O	-3.5157	0.0000	-0.1619	H	-1.7308	-3.3406	-0.7170
C	-2.2497	-2.3485	-0.9397	H	-3.3034	-2.5561	-0.5043
H	-1.7274	-3.3076	-0.8693	H	-2.2707	-2.1256	-1.8890
H	-3.2905	-2.4965	-0.6461	C	-1.7603	-1.6683	1.5278
H	-2.2238	-2.0173	-1.9826	H	-2.8129	-1.5844	1.8067
C	-1.7210	-1.7687	1.4481	H	-1.4490	-2.7072	1.6629
H	-2.7787	-1.7519	1.7249	H	-1.1567	-1.0474	2.1868
H	-1.3490	-2.7916	1.5655	C	-2.2741	2.3997	-0.8311
H	-1.1702	-1.1294	2.1418	H	-3.3034	2.5561	-0.5043
C	-2.2497	2.3485	-0.9397	H	-1.7308	3.3406	-0.7170
H	-3.2905	2.4965	-0.6460	H	-2.2707	2.1256	-1.8890
H	-1.7274	3.3076	-0.8693	C	-1.7603	1.6683	1.5278
H	-2.2238	2.0173	-1.9825	H	-1.4490	2.7071	1.6629
C	-1.7210	1.7687	1.4481	H	-2.8129	1.5844	1.8067
H	-1.3490	2.7915	1.5655	H	-1.1568	1.0474	2.1868
H	-2.7787	1.7519	1.7249	O	-3.3448	0.0000	-0.6607
H	-1.1702	1.1293	2.1418	N	-2.2261	0.0000	-0.2393
C	2.8535	1.1601	0.1653	C	2.8512	1.1634	0.1486
C	2.8535	-1.1601	0.1653	C	2.8512	-1.1634	0.1486
C	4.3197	0.7768	-0.1009	C	4.3079	0.7768	-0.1595
H	2.6873	1.3191	1.2489	H	2.7154	1.3259	1.2348
H	2.5619	2.0757	-0.3542	H	2.5469	2.0761	-0.3687
C	4.3197	-0.7768	-0.1009	C	4.3079	-0.7768	-0.1595
H	2.5619	-2.0757	-0.3542	H	2.5469	-2.0761	-0.3687
H	2.6873	-1.3191	1.2489	H	2.7154	-1.3259	1.2348
H	4.6474	1.1639	-1.0705	H	4.6075	1.1634	-1.1379
H	4.9828	1.1980	0.6602	H	4.9917	1.1976	0.5827
H	4.6475	-1.1639	-1.0704	H	4.6075	-1.1634	-1.1379
H	4.9828	-1.1980	0.6602	H	4.9917	-1.1976	0.5827
N	2.0779	0.0000	-0.3148	N	2.0620	0.0000	-0.3073

TH			
Symbol	X	Y	Z
C	-1.5304	-1.2903	-0.0309
C	-0.0280	-1.2426	-0.3893
C	0.7084	0.0000	0.1297
C	-0.0280	1.2426	-0.3893
C	-1.5304	1.2903	-0.0309

TH2			
Symbol	X	Y	Z
C	-1.4923	-1.3506	-0.0168
C	0.0017	-1.2483	-0.3775
C	0.7260	0.0010	0.1507
C	0.0012	1.2497	-0.3782
C	-1.4916	1.3477	-0.0097

H	0.4254	-2.1595	-0.0009	H	0.4590	-2.1600	0.0137
H	0.6871	0.0000	1.2369	H	0.6974	0.0013	1.2562
H	0.4254	2.1595	-0.0009	H	0.4587	2.1624	0.0108
H	0.0789	1.2657	-1.4815	H	0.1184	1.2801	-1.4688
H	0.0789	-1.2658	-1.4815	H	0.1220	-1.2796	-1.4677
N	-2.1317	0.0000	-0.4786	N	-2.1440	-0.0004	-0.4449
C	-2.1868	-2.4038	-0.8723	C	-2.1676	-2.4316	-0.8752
H	-1.6773	-3.3568	-0.6955	H	-1.6468	-3.3771	-0.7049
H	-3.2402	-2.5293	-0.6066	H	-3.2163	-2.5629	-0.6036
H	-2.1218	-2.1686	-1.9396	H	-2.1007	-2.2060	-1.9448
C	-1.7420	-1.6337	1.4640	C	-1.7394	-1.6377	1.4690
H	-2.7915	-1.5025	1.7395	H	-2.7951	-1.5353	1.7259
H	-1.4753	-2.6822	1.6343	H	-1.4498	-2.6764	1.6474
H	-1.1308	-1.0286	2.1351	H	-1.1475	-1.0146	2.1372
C	-2.1868	2.4038	-0.8723	C	-2.1680	2.4361	-0.8596
H	-3.2402	2.5293	-0.6066	H	-3.2032	2.6181	-0.5561
H	-1.6773	3.3568	-0.6955	H	-1.6245	3.3724	-0.7118
H	-2.1218	2.1685	-1.9396	H	-2.1365	2.2060	-1.9300
C	-1.7420	1.6337	1.4640	C	-1.7340	1.6258	1.4778
H	-1.4754	2.6822	1.6343	H	-1.4912	2.6764	1.6558
H	-2.7915	1.5025	1.7395	H	-2.7808	1.4726	1.7468
H	-1.1308	1.0286	2.1351	H	-1.1067	1.0294	2.1381
O	-3.5325	0.0000	-0.1008	O	-3.5167	-0.0691	-0.0893
H	-3.9922	0.0000	-0.9519	H	-3.9873	0.5619	-0.6626
C	2.8946	1.1594	0.1666	H	-2.1008	-0.0113	-1.4715
C	2.8946	-1.1594	0.1666	C	2.9098	1.1634	0.1729
C	4.3594	0.7769	-0.1092	C	2.9098	-1.1611	0.1728
H	2.7358	1.3174	1.2519	C	4.3708	0.7779	-0.1161
H	2.5978	2.0754	-0.3494	H	2.7598	1.3240	1.2578
C	4.3594	-0.7769	-0.1092	H	2.6120	2.0775	-0.3459
H	2.5977	-2.0754	-0.3494	C	4.3710	-0.7755	-0.1153
H	2.7358	-1.3174	1.2519	H	2.6122	-2.0750	-0.3464
H	4.6809	1.1641	-1.0809	H	2.7592	-1.3221	1.2576
H	5.0278	1.1980	0.6474	H	4.6830	1.1643	-1.0909
H	4.6808	-1.1640	-1.0810	H	5.0451	1.1995	0.6345
H	5.0278	-1.1980	0.6474	H	4.6843	-1.1629	-1.0893
N	2.1165	0.0000	-0.3087	H	5.0446	-1.1961	0.6364
				N	2.1270	0.0012	-0.2949

**Optimized Geometry Coordinates Using B3LYP/6-31+G(d,p) CPCM for TEMPO-NHPyr<sup>+</sup>**

T*				T <sup>+</sup>			
Symbol	X	Y	Z	Symbol	X	Y	Z
C	-1.5851	-1.3240	-0.0445	C	-1.5828	-1.3536	-0.0105
C	-0.1154	-1.2317	-0.5115	C	-0.1162	-1.2409	-0.4817
C	0.6151	-0.0090	0.0444	C	0.6191	-0.0118	0.0629
C	-0.0973	1.2575	-0.4290	C	-0.0964	1.2628	-0.3949
C	-1.5705	1.3318	0.0354	C	-1.5664	1.3589	0.0726
H	0.3761	-2.1624	-0.2172	H	0.3661	-2.1693	-0.1684
H	0.6807	-0.0421	1.1351	H	0.7004	-0.0466	1.1515
H	0.3986	2.1577	-0.0589	H	0.3917	2.1570	-0.0030
H	-0.0670	1.2933	-1.5248	H	-0.0721	1.3282	-1.4877
H	-0.0928	-1.1841	-1.6074	H	-0.1006	-1.2205	-1.5770
N	-2.2540	0.0130	-0.1931	C	-2.3523	-2.3676	-0.8624
O	-3.5375	0.0176	-0.0966	H	-1.8017	-3.3102	-0.8234
C	-2.3210	-2.3234	-0.9531	H	-3.3566	-2.5417	-0.4746
H	-1.7994	-3.2847	-0.9263	H	-2.4172	-2.0479	-1.9050
H	-3.3469	-2.4743	-0.6142	C	-1.7099	-1.7202	1.4921
H	-2.3419	-1.9681	-1.9877	H	-2.7496	-1.6566	1.8187
C	-1.6876	-1.7966	1.4228	H	-1.3811	-2.7584	1.5816
H	-2.7326	-1.7798	1.7427	H	-1.0878	-1.1115	2.1456
H	-1.3180	-2.8234	1.5016	C	-2.3209	2.4275	-0.7253
H	-1.1080	-1.1773	2.1112	H	-3.3261	2.5885	-0.3347
C	-2.2928	2.3897	-0.8164	H	-1.7615	3.3610	-0.6308
H	-3.3181	2.5325	-0.4725	H	-2.3820	2.1668	-1.7848
H	-1.7610	3.3422	-0.7337	C	-1.6967	1.6405	1.5938
H	-2.3138	2.0941	-1.8696	H	-1.3721	2.6736	1.7396
C	-1.6749	1.7177	1.5276	H	-2.7355	1.5549	1.9181
H	-1.3028	2.7371	1.6670	H	-1.0703	0.9997	2.2122
H	-2.7204	1.6844	1.8442	O	-3.4157	0.0297	-0.4933
H	-1.0974	1.0572	2.1785	N	-2.2645	0.0129	-0.1808
C	2.8849	1.2044	-0.0303	C	2.8822	1.2070	-0.0413
C	2.8747	-1.2346	0.0693	C	2.8762	-1.2357	0.0605
C	4.3229	0.7253	-0.1753	C	4.3161	0.7283	-0.2205
H	2.6338	1.4411	1.0062	H	2.6526	1.4364	1.0018
H	2.6144	2.0378	-0.6767	H	2.5984	2.0420	-0.6800
C	4.2850	-0.7041	0.3945	C	4.2943	-0.7033	0.3452
H	2.8611	-1.9786	-0.7257	H	2.8411	-1.9866	-0.7273
H	2.3664	-1.6368	0.9450	H	2.3898	-1.6252	0.9544
H	4.6177	0.7238	-1.2298	H	4.5874	0.7328	-1.2811
H	5.0115	1.3781	0.3650	H	5.0144	1.3803	0.3078
H	5.0559	-1.3444	-0.0382	H	5.0517	-1.3410	-0.1138

H	4.4313	-0.6851	1.4775	H	4.4719	-0.6891	1.4232
H	2.0572	-0.0544	-1.4426	H	2.0429	-0.0555	-1.4458
N	2.0665	-0.0192	-0.4182	N	2.0580	-0.0200	-0.4211

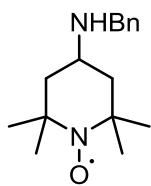
<b>TH</b>				<b>TH2</b>			
<b>Symbol</b>	<b>X</b>	<b>Y</b>	<b>Z</b>	<b>Symbol</b>	<b>X</b>	<b>Y</b>	<b>Z</b>
C	-1.5632	-1.2883	-0.0529	C	-1.5258	-1.3488	-0.0460
C	-0.0748	-1.2411	-0.4729	C	-0.0492	-1.2453	-0.4825
C	0.6530	-0.0100	0.0708	C	0.6748	-0.0089	0.0650
C	-0.0589	1.2605	-0.3957	C	-0.0319	1.2688	-0.4028
C	-1.5489	1.2952	0.0229	C	-1.5103	1.3540	0.0349
H	0.3966	-2.1667	-0.1315	H	0.4280	-2.1676	-0.1443
H	0.7245	-0.0411	1.1610	H	0.7396	-0.0408	1.1547
H	0.4176	2.1552	0.0127	H	0.4485	2.1590	0.0082
H	-0.0003	1.3219	-1.4895	H	0.0320	1.3469	-1.4944
H	-0.0203	-1.2269	-1.5690	H	0.0079	-1.2428	-1.5779
N	-2.1660	0.0193	-0.4460	N	-2.1918	0.0176	-0.4021
C	-2.2544	-2.3744	-0.9010	C	-2.2456	-2.4022	-0.9001
H	-1.7438	-3.3340	-0.7713	H	-1.7293	-3.3572	-0.7773
H	-3.2958	-2.5012	-0.5949	H	-3.2810	-2.5287	-0.5798
H	-2.2315	-2.1075	-1.9622	H	-2.2273	-2.1505	-1.9654
C	-1.7158	-1.6707	1.4386	C	-1.6956	-1.6769	1.4412
H	-2.7525	-1.5347	1.7550	H	-2.7386	-1.5857	1.7471
H	-1.4557	-2.7259	1.5703	H	-1.3950	-2.7184	1.5783
H	-1.0758	-1.0918	2.1061	H	-1.0785	-1.0699	2.1012
C	-2.2275	2.4360	-0.7615	C	-2.2173	2.4659	-0.7545
H	-3.2677	2.5565	-0.4489	H	-3.2416	2.6170	-0.4063
H	-1.7065	3.3808	-0.5766	H	-1.6748	3.4005	-0.5943
H	-2.2064	2.2300	-1.8362	H	-2.2237	2.2697	-1.8321
C	-1.6998	1.5922	1.5343	C	-1.6786	1.5949	1.5392
H	-1.4304	2.6358	1.7258	H	-1.4119	2.6367	1.7321
H	-2.7377	1.4478	1.8429	H	-2.7154	1.4504	1.8459
H	-1.0651	0.9704	2.1680	H	-1.0355	0.9744	2.1616
O	-3.5503	0.0147	-0.0292	O	-3.5361	-0.0294	0.0506
H	-4.0373	0.0419	-0.8650	H	-4.0937	0.3421	-0.6562
C	2.9237	1.2033	-0.0090	H	-2.2138	0.0351	-1.4292
C	2.9156	-1.2313	0.0807	C	2.9429	1.2060	-0.0027
C	4.3607	0.7312	-0.1871	C	2.9329	-1.2337	0.0863
H	2.6902	1.4259	1.0349	C	4.3783	0.7300	-0.1795
H	2.6383	2.0443	-0.6390	H	2.7071	1.4254	1.0411
C	4.3393	-0.7083	0.3601	H	2.6626	2.0477	-0.6340
H	2.8725	-1.9874	-0.7018	C	4.3552	-0.7093	0.3675

H	2.4294	-1.6158	0.9769	H	2.8919	-1.9894	-0.6966
H	4.6355	0.7479	-1.2470	H	2.4449	-1.6151	0.9829
H	5.0577	1.3776	0.3502	H	4.6549	0.7479	-1.2386
H	5.0924	-1.3417	-0.1122	H	5.0739	1.3756	0.3600
H	4.5265	-0.7085	1.4368	H	5.1078	-1.3426	-0.1054
H	2.0883	-0.0482	-1.4216	H	4.5407	-0.7107	1.4442
N	2.1040	-0.0175	-0.3972	H	2.1188	-0.0468	-1.4232
				N	2.1220	-0.0167	-0.3983

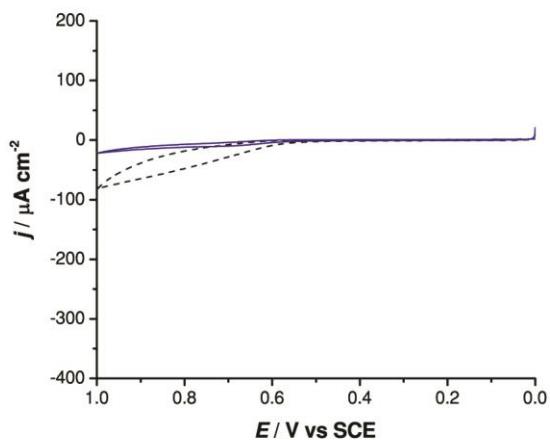
### 3.26 4-(*N*-Benzylamino)-TEMPO (26)

**26** was prepared according to the procedure of Ishikawa *et al.*<sup>30</sup>

**Table S3.26.** Summary table of electrocatalytic properties of TEMPO-NHBn.



$E_{a1}$	0.798
$E_{a2}$	1.160
$j_{max}$	0
$(i_{pa}/i_{pc})_{cat.}$	0.00



**Figure S3.26.** CV of 5 mM **26** in the absence (dashed) and presence (solid) of 1 M glycerol using 150 mM Robinson buffer at 25 °C.

## Optimized Geometry Coordinates Using B3LYP/6-31+G(d,p) CPCM for TEMPO-NHBn

T*				T+			
Symbol	X	Y	Z	Symbol	X	Y	Z
C	1.6204	1.3913	0.0946	C	1.5551	1.4128	0.1724
C	0.3101	0.9122	-0.5660	C	0.2665	0.8934	-0.5004
C	-0.0782	-0.5230	-0.2081	C	-0.0773	-0.5657	-0.1864
C	1.0571	-1.4451	-0.6577	C	1.0804	-1.4543	-0.6511
C	2.4216	-1.1431	-0.0082	C	2.4454	-1.1453	-0.0042
H	-0.4704	1.6173	-0.2694	H	-0.5289	1.5642	-0.1675
H	-0.2169	-0.6065	0.8809	H	-0.2290	-0.6846	0.8966
H	0.8124	-2.4913	-0.4373	H	0.8734	-2.5061	-0.4275
H	1.1479	-1.3598	-1.7478	H	1.1726	-1.3674	-1.7392

H	0.4065	0.9746	-1.6574	H	0.3569	1.0074	-1.5863
N	2.6857	0.3375	-0.0380	C	2.0258	2.7231	-0.4662
O	3.8895	0.7056	0.2380	H	1.1925	3.4275	-0.4118
C	2.1126	2.6498	-0.6406	H	2.8757	3.1551	0.0641
H	1.3214	3.4057	-0.6234	H	2.2896	2.5823	-1.5174
H	3.0015	3.0652	-0.1622	C	1.4009	1.5989	1.7066
H	2.3502	2.4229	-1.6845	H	2.3602	1.8383	2.1703
C	1.4159	1.7242	1.5902	H	0.7283	2.4497	1.8420
H	2.3735	1.9858	2.0486	H	0.9598	0.7379	2.2054
H	0.7425	2.5822	1.6822	C	3.5912	-1.7912	-0.7894
H	0.9791	0.8935	2.1495	H	4.5519	-1.6696	-0.2874
C	3.5262	-1.8326	-0.8275	H	3.3730	-2.8593	-0.8602
H	4.5039	-1.6993	-0.3612	H	3.6588	-1.3859	-1.8021
H	3.3112	-2.9039	-0.8880	C	2.5159	-1.5770	1.4853
H	3.5647	-1.4300	-1.8444	H	2.5254	-2.6699	1.4837
C	2.4824	-1.6451	1.4519	H	3.4372	-1.2233	1.9528
H	2.4255	-2.7382	1.4628	H	1.6595	-1.2476	2.0705
H	3.4277	-1.3431	1.9106	O	3.7855	0.7737	-0.1854
H	1.6617	-1.2600	2.0613	N	2.6703	0.3759	-0.0251
N	-1.3195	-0.9653	-0.8978	N	-1.2917	-1.0008	-0.9145
H	-1.3328	-1.9819	-0.8754	H	-1.3109	-2.0176	-0.8998
C	-2.5737	-0.4890	-0.4142	C	-2.5532	-0.5168	-0.4378
C	-3.0160	0.8133	-0.7082	C	-3.0192	0.7513	-0.8213
C	-3.4267	-1.3375	0.3145	C	-3.3694	-1.3215	0.3746
C	-4.2628	1.2575	-0.2610	C	-4.2616	1.2120	-0.3777
H	-2.3979	1.4661	-1.3145	H	-2.4222	1.3621	-1.4905
C	-4.6836	-0.8975	0.7395	C	-4.6222	-0.8674	0.7967
H	-3.1008	-2.3487	0.5465	H	-3.0205	-2.3069	0.6735
C	-5.1051	0.4068	0.4634	C	-5.0699	0.4057	0.4310
H	-4.5848	2.2674	-0.4995	H	-4.6063	2.1958	-0.6829
H	-5.3277	-1.5737	1.2947	H	-5.2427	-1.5071	1.4178
H	-6.0783	0.7526	0.7987	H	-6.0402	0.7620	0.7636

TH			
Symbol	X	Y	Z
C	1.6334	1.3082	-0.3280
C	0.2619	0.7216	-0.7310
C	-0.1104	-0.5629	0.0261
C	0.9969	-1.5988	-0.1821
C	2.3977	-1.1023	0.2403
H	-0.5019	1.4924	-0.5809
H	-0.1990	-0.3526	1.0961

TH2			
Symbol	X	Y	Z
C	1.5225	1.3894	0.1108
C	0.2129	0.8840	-0.5249
C	-0.1415	-0.5688	-0.1852
C	1.0003	-1.4850	-0.6430
C	2.3781	-1.1742	-0.0292
H	-0.5691	1.5657	-0.1820
H	-0.2819	-0.6667	0.9012

H	0.7670	-2.5131	0.3760	H	0.7795	-2.5271	-0.3878
H	1.0261	-1.8666	-1.2473	H	1.0632	-1.4364	-1.7375
H	0.2784	0.4864	-1.8034	H	0.2647	0.9830	-1.6163
N	2.6308	0.2019	-0.4521	C	1.9478	2.7083	-0.5541
C	2.0228	2.3800	-1.3658	H	1.1222	3.4183	-0.4659
H	1.2407	3.1442	-1.4248	H	2.8134	3.1617	-0.0627
H	2.9588	2.8746	-1.0914	H	2.1578	2.5825	-1.6216
H	2.1430	1.9297	-2.3564	C	1.4320	1.5754	1.6291
C	1.5687	1.9849	1.0623	H	2.4184	1.7296	2.0704
H	2.5718	2.2583	1.3998	H	0.8369	2.4737	1.8117
H	0.9743	2.9020	0.9904	H	0.9399	0.7491	2.1395
H	1.1088	1.3568	1.8272	C	3.4805	-1.9049	-0.8115
C	3.4435	-2.0926	-0.3106	H	4.4623	-1.7466	-0.3626
H	4.4503	-1.8295	0.0248	H	3.2603	-2.9751	-0.7914
H	3.2223	-3.1052	0.0427	H	3.5123	-1.5944	-1.8612
H	3.4294	-2.0957	-1.4053	C	2.4753	-1.5266	1.4592
C	2.5350	-1.0660	1.7817	H	2.4858	-2.6172	1.5311
H	2.5796	-2.0911	2.1645	H	3.4027	-1.1537	1.8968
H	3.4587	-0.5576	2.0693	H	1.6333	-1.1685	2.0489
H	1.6997	-0.5693	2.2782	O	3.8764	0.6640	0.3277
O	3.9199	0.7100	-0.0258	H	4.2056	1.4637	-0.1205
H	4.4482	0.6862	-0.8357	H	2.7498	0.4319	-1.2817
N	-1.3873	-1.1363	-0.4091	N	2.6260	0.3494	-0.2649
H	-1.3350	-1.5772	-1.3206	N	-1.3712	-1.0060	-0.8896
C	-2.6226	-0.5429	-0.1543	H	-1.3964	-2.0224	-0.8593
C	-2.8350	0.3522	0.9155	C	-2.6246	-0.5091	-0.4097
C	-3.7320	-0.8890	-0.9592	C	-3.0780	0.7669	-0.7840
C	-4.1107	0.8654	1.1679	C	-3.4517	-1.3103	0.3957
H	-2.0115	0.6494	1.5551	C	-4.3162	1.2371	-0.3388
C	-4.9983	-0.3709	-0.6962	H	-2.4751	1.3771	-1.4483
H	-3.5890	-1.5729	-1.7927	C	-4.7005	-0.8464	0.8193
C	-5.2042	0.5128	0.3716	H	-3.1139	-2.3016	0.6881
H	-4.2436	1.5525	1.9994	C	-5.1347	0.4339	0.4627
H	-5.8301	-0.6575	-1.3344	H	-4.6498	2.2267	-0.6377
H	-6.1908	0.9180	0.5734	H	-5.3285	-1.4844	1.4347
				H	-6.1017	0.7980	0.7964

Optimized Geometry Coordinates Using B3LYP/6-31+G(d,p) CPCM for TEMPO-NH<sub>2</sub>Bn<sup>+</sup>

Symbol	T*			T+			
	X	Y	Z	X	Y	Z	
C	1.4206	1.4113	0.0498	C	1.3832	1.4313	0.1045
C	0.1655	0.7584	-0.5735	C	0.1477	0.7516	-0.5250

C	0.0029	-0.6931	-0.1453	C	0.0030	-0.7114	-0.1181
C	1.2010	-1.5128	-0.6100	C	1.2124	-1.5195	-0.5870
C	2.5287	-1.0150	0.0049	C	2.5478	-1.0324	0.0171
H	-0.7012	1.3580	-0.2828	H	-0.7188	1.3388	-0.2118
H	-0.1486	-0.7780	0.9323	H	-0.1521	-0.8095	0.9570
H	1.0871	-2.5688	-0.3442	H	1.1193	-2.5731	-0.3085
H	1.2674	-1.4533	-1.7030	H	1.2817	-1.4733	-1.6788
H	0.2466	0.8025	-1.6663	H	0.2208	0.8296	-1.6151
N	2.6013	0.4859	-0.0809	C	1.6984	2.7500	-0.6077
O	3.7541	1.0066	0.1547	H	0.7962	3.3648	-0.5667
C	1.7410	2.6946	-0.7349	H	2.5063	3.2925	-0.1159
H	0.8640	3.3485	-0.7274	H	1.9574	2.5860	-1.6565
H	2.5776	3.2284	-0.2819	C	1.2349	1.6700	1.6311
H	1.9933	2.4634	-1.7741	H	2.1748	2.0190	2.0628
C	1.1991	1.7616	1.5380	H	0.4879	2.4593	1.7462
H	2.1291	2.1405	1.9692	H	0.8889	0.7957	2.1802
H	0.4365	2.5421	1.6185	C	3.7385	-1.5840	-0.7726
H	0.8680	0.9064	2.1321	H	4.6872	-1.3403	-0.2936
C	3.6926	-1.5904	-0.8192	H	3.6374	-2.6713	-0.8004
H	4.6525	-1.3242	-0.3744	H	3.7447	-1.2115	-1.7999
H	3.6102	-2.6810	-0.8459	C	2.6907	-1.3863	1.5210
H	3.6656	-1.2146	-1.8463	H	2.7868	-2.4738	1.5707
C	2.6722	-1.4579	1.4776	H	3.5936	-0.9386	1.9405
H	2.7463	-2.5485	1.5244	H	1.8308	-1.0959	2.1220
H	3.5833	-1.0304	1.9034	O	3.6690	1.0142	-0.2409
H	1.8268	-1.1516	2.0983	N	2.6045	0.5054	-0.0689
C	-2.5527	-0.6776	-0.3296	C	-2.5446	-0.6858	-0.3325
C	-3.2569	0.1023	-1.2429	C	-3.2344	0.0823	-1.2663
C	-3.0078	-0.8938	0.9697	C	-3.0150	-0.8882	0.9634
C	-4.4566	0.6918	-0.8341	C	-4.4388	0.6773	-0.8800
H	-2.8890	0.2496	-2.2538	H	-2.8547	0.2159	-2.2747
C	-4.2079	-0.2986	1.3638	C	-4.2195	-0.2867	1.3335
H	-2.4499	-1.5154	1.6630	H	-2.4685	-1.5032	1.6714
C	-4.9299	0.4941	0.4656	C	-4.9283	0.4955	0.4158
H	-5.0167	1.3015	-1.5351	H	-4.9894	1.2781	-1.5959
H	-4.5772	-0.4600	2.3710	H	-4.6027	-0.4360	2.3372
H	-5.8624	0.9530	0.7778	H	-5.8645	0.9585	0.7101
H	-1.2937	-2.2968	-0.5036	H	-1.2887	-2.3132	-0.4777
H	-1.2055	-1.2756	-1.7707	H	-1.1860	-1.3061	-1.7550
N	-1.2747	-1.2998	-0.7474	N	-1.2610	-1.3181	-0.7315

TH				TH2			
Symbol	X	Y	Z	Symbol	X	Y	Z
C	1.4231	1.3578	0.0359	C	1.3507	1.3997	0.0353
C	0.1229	0.7385	-0.5332	C	0.0868	0.7227	-0.5375
C	-0.0406	-0.7140	-0.1063	C	-0.0604	-0.7318	-0.0966
C	1.1517	-1.5478	-0.5647	C	1.1346	-1.5682	-0.5589
C	2.4905	-1.0026	-0.0100	C	2.4812	-1.0645	0.0053
H	-0.7222	1.3471	-0.1997	H	-0.7648	1.3230	-0.2079
H	-0.1934	-0.7955	0.9713	H	-0.2012	-0.8035	0.9826
H	1.0485	-2.5911	-0.2477	H	1.0346	-2.6099	-0.2399
H	1.1935	-1.5341	-1.6607	H	1.1743	-1.5718	-1.6548
H	0.1616	0.7905	-1.6282	H	0.1120	0.7771	-1.6321
N	2.5439	0.4499	-0.3572	C	1.6129	2.7167	-0.7093
C	1.6566	2.6983	-0.6884	H	0.7298	3.3515	-0.6053
H	0.7828	3.3464	-0.5674	H	2.4682	3.2453	-0.2859
H	2.5234	3.2184	-0.2731	H	1.7827	2.5566	-1.7791
H	1.8249	2.5347	-1.7573	C	1.2730	1.6541	1.5443
C	1.2968	1.6424	1.5515	H	2.2393	1.9694	1.9405
H	2.2699	1.9230	1.9613	H	0.5650	2.4718	1.6989
H	0.6092	2.4799	1.7062	H	0.9161	0.8009	2.1191
H	0.9151	0.7971	2.1266	C	3.6395	-1.7161	-0.7636
C	3.6326	-1.6922	-0.7818	H	4.6071	-1.4570	-0.3280
H	4.6053	-1.3956	-0.3816	H	3.5292	-2.8012	-0.6990
H	3.5450	-2.7795	-0.6894	H	3.6342	-1.4473	-1.8250
H	3.5947	-1.4273	-1.8430	C	2.6411	-1.3185	1.5077
C	2.6506	-1.3339	1.4926	H	2.8173	-2.3885	1.6405
H	2.8151	-2.4097	1.6102	H	3.5049	-0.7833	1.9044
H	3.5186	-0.8112	1.9009	H	1.7631	-1.0572	2.0961
H	1.7792	-1.0693	2.0934	O	3.7229	1.0381	0.2416
O	3.7663	0.9896	0.1926	H	4.4249	0.9791	-0.4311
H	4.2752	1.2408	-0.5913	H	2.6376	0.5285	-1.3399
C	-2.5969	-0.6764	-0.3116	N	2.5534	0.4635	-0.3183
C	-3.2823	0.0969	-1.2447	C	-2.6132	-0.6856	-0.2948
C	-3.0682	-0.8639	0.9866	C	-3.2985	0.0638	-1.2472
C	-4.4783	0.7089	-0.8588	C	-3.0818	-0.8457	1.0077
H	-2.9016	0.2229	-2.2538	C	-4.4950	0.6826	-0.8745
C	-4.2645	-0.2464	1.3580	H	-2.9200	0.1656	-2.2598
H	-2.5250	-1.4802	1.6960	C	-4.2787	-0.2211	1.3644
C	-4.9671	0.5399	0.4392	H	-2.5392	-1.4466	1.7308
H	-5.0231	1.3139	-1.5759	C	-4.9823	0.5425	0.4274
H	-4.6459	-0.3853	2.3641	H	-5.0414	1.2691	-1.6053
H	-5.8965	1.0164	0.7341	H	-4.6601	-0.3377	2.3732
H	-1.3518	-2.3113	-0.4475	H	-5.9125	1.0237	0.7114

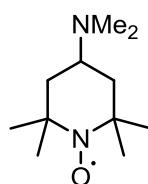
H	-1.2436	-1.3111	-1.7290
N	-1.3225	-1.3185	-0.7064

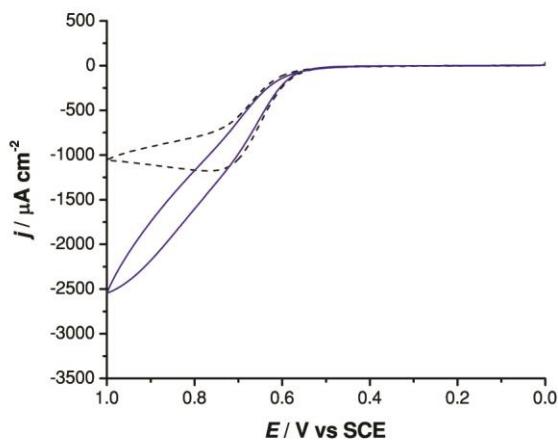
H	-1.3746	-2.3294	-0.3984
H	-1.2702	-1.3629	-1.7045
N	-1.3390	-1.3426	-0.6808

### 3.27 4-(*N,N*-Dimethylamino)-TEMPO (27)

**25** was prepared according to the procedure of Anzai *et al.*<sup>29</sup>

**Table S3.27.** Summary table of electrocatalytic properties of TEMPO-NMe<sub>2</sub>.

	$E_{a1}$	0.663
	$E_{a2}$	0.587
	$j_{max}$	1487.0
	$(i_{pa}/i_{pc})_{cat.}$	25.17



**Figure S3.27.** CV of 5 mM **27** in the absence (dashed) and presence (solid) of 1 M glycerol using 150 mM Robinson buffer at 25 °C.

#### Optimized Geometry Coordinates Using B3LYP/6-31+G(d,p) CPCM for TEMPO-NMe<sub>2</sub>

Symbol	T*			T+			
	X	Y	Z	X	Y	Z	
C	-0.9794	-1.3241	-0.0176	C	-0.9783	-1.3484	0.0287
C	0.4995	-1.2329	-0.4486	C	0.4992	-1.2419	-0.4058
C	1.2507	0.0000	0.0736	C	1.2528	0.0000	0.0962
C	0.4995	1.2329	-0.4486	C	0.4992	1.2419	-0.4058
C	-0.9794	1.3241	-0.0176	C	-0.9783	1.3484	0.0287
H	0.9695	-2.1611	-0.1158	H	0.9602	-2.1627	-0.0443
H	1.2369	0.0000	1.1805	H	1.2716	0.0000	1.2017
H	0.9695	2.1611	-0.1158	H	0.9603	2.1627	-0.0443
H	0.5573	1.2196	-1.5445	H	0.5517	1.2611	-1.5002

H	0.5573	-1.2196	-1.5445	H	0.5517	-1.2611	-1.5002
N	-1.6602	0.0000	-0.2020	C	-1.7251	-2.3959	-0.8039
O	-2.9464	0.0000	-0.1141	H	-1.1723	-3.3342	-0.7173
C	-1.6931	-2.3475	-0.9186	H	-2.7402	-2.5605	-0.4396
H	-1.1679	-3.3057	-0.8590	H	-1.7628	-2.1142	-1.8592
H	-2.7272	-2.4971	-0.6028	C	-1.1384	-1.6695	1.5402
H	-1.6899	-2.0166	-1.9619	H	-2.1820	-1.5870	1.8513
C	-1.1153	-1.7667	1.4574	H	-0.8219	-2.7083	1.6634
H	-2.1670	-1.7526	1.7562	H	-0.5152	-1.0488	2.1810
H	-0.7383	-2.7885	1.5669	C	-1.7250	2.3959	-0.8039
H	-0.5520	-1.1259	2.1396	H	-2.7402	2.5606	-0.4395
C	-1.6931	2.3475	-0.9186	H	-1.1723	3.3342	-0.7172
H	-2.7272	2.4971	-0.6028	H	-1.7628	2.1143	-1.8592
H	-1.1679	3.3057	-0.8590	C	-1.1383	1.6695	1.5402
H	-1.6899	2.0166	-1.9619	H	-0.8219	2.7082	1.6635
C	-1.1153	1.7667	1.4574	H	-2.1820	1.5870	1.8513
H	-0.7383	2.7885	1.5669	H	-0.5152	1.0488	2.1810
H	-2.1670	1.7526	1.7562	O	-2.8007	0.0000	-0.5722
H	-0.5520	1.1259	2.1396	N	-1.6634	0.0000	-0.2037
N	2.6621	0.0000	-0.3834	N	2.6408	0.0000	-0.4142
C	3.3923	-1.1934	0.0610	C	3.3876	-1.1971	-0.0026
H	2.9869	-2.0991	-0.3923	H	2.9695	-2.0998	-0.4506
H	4.4356	-1.1087	-0.2544	H	4.4170	-1.1063	-0.3572
H	3.3773	-1.3168	1.1608	H	3.4131	-1.3275	1.0949
C	3.3923	1.1934	0.0610	C	3.3876	1.1971	-0.0027
H	4.4356	1.1087	-0.2544	H	4.4170	1.1063	-0.3572
H	2.9869	2.0991	-0.3923	H	2.9695	2.0998	-0.4507
H	3.3773	1.3168	1.1608	H	3.4131	1.3276	1.0948

TH			
Symbol	X	Y	Z
C	-0.9572	-1.2875	-0.0250
C	0.5384	-1.2407	-0.4122
C	1.2921	0.0000	0.0911
C	0.5384	1.2407	-0.4122
C	-0.9572	1.2875	-0.0250
H	0.9878	-2.1616	-0.0315
H	1.2955	0.0000	1.1981
H	0.9879	2.1616	-0.0314
H	0.6244	1.2657	-1.5063
H	0.6244	-1.2657	-1.5063
N	-1.5685	0.0000	-0.4622

TH2			
Symbol	X	Y	Z
C	-0.9223	-1.3464	-0.0131
C	0.5632	-1.2457	-0.4082
C	1.3066	0.0005	0.1042
C	0.5642	1.2464	-0.4105
C	-0.9194	1.3466	-0.0066
H	1.0182	-2.1624	-0.0286
H	1.3017	0.0017	1.2097
H	1.0213	2.1638	-0.0348
H	0.6556	1.2743	-1.5037
H	0.6588	-1.2762	-1.5010
N	-1.5882	0.0016	-0.4215

C	-1.6277	-2.4033	-0.8524	C	-1.6177	-2.4264	-0.8565
H	-1.1147	-3.3558	-0.6834	H	-1.0991	-3.3745	-0.6946
H	-2.6760	-2.5286	-0.5671	H	-2.6616	-2.5521	-0.5635
H	-1.5825	-2.1698	-1.9211	H	-1.5704	-2.2035	-1.9277
C	-1.1395	-1.6304	1.4741	C	-1.1342	-1.6371	1.4776
H	-2.1831	-1.4972	1.7702	H	-2.1836	-1.5346	1.7588
H	-0.8714	-2.6794	1.6393	H	-0.8416	-2.6764	1.6471
H	-0.5139	-1.0264	2.1329	H	-0.5262	-1.0161	2.1332
C	-1.6277	2.4033	-0.8524	C	-1.6151	2.4366	-0.8374
H	-2.6760	2.5286	-0.5670	H	-2.6492	2.5950	-0.5202
H	-1.1147	3.3558	-0.6834	H	-1.0797	3.3770	-0.6873
H	-1.5825	2.1698	-1.9211	H	-1.5936	2.2156	-1.9101
C	-1.1395	1.6304	1.4741	C	-1.1238	1.6273	1.4864
H	-0.8714	2.6794	1.6393	H	-0.8619	2.6744	1.6582
H	-2.1831	1.4972	1.7702	H	-2.1669	1.4894	1.7762
H	-0.5139	1.0264	2.1329	H	-0.4906	1.0227	2.1333
N	2.7000	0.0000	-0.3819	N	2.7078	-0.0016	-0.3731
O	-2.9618	0.0000	-0.0575	O	-2.9487	-0.0474	-0.0117
H	-3.4374	0.0000	-0.8997	H	-3.4770	0.3600	-0.7202
C	3.4337	-1.1931	0.0550	H	-1.5781	-0.0080	-1.4488
H	3.0187	-2.0984	-0.3906	C	3.4442	-1.1960	0.0625
H	4.4735	-1.1120	-0.2735	H	3.0359	-2.1016	-0.3887
H	3.4326	-1.3147	1.1555	H	4.4822	-1.1086	-0.2676
C	3.4337	1.1931	0.0550	H	3.4435	-1.3199	1.1614
H	4.4735	1.1119	-0.2736	C	3.4456	1.1955	0.0528
H	3.0187	2.0984	-0.3906	H	4.4835	1.1038	-0.2762
H	3.4326	1.3148	1.1555	H	3.0387	2.0977	-0.4065
				H	3.4448	1.3288	1.1506

**Optimized Geometry Coordinates Using B3LYP/6-31+G(d,p) CPCM for TEMPO-NHMe<sub>2</sub><sup>+</sup>**

T*				T+			
Symbol	X	Y	Z	Symbol	X	Y	Z
C	-1.0299	-1.3209	-0.0311	C	-1.0266	-1.3492	0.0053
C	0.4607	-1.2484	-0.4461	C	0.4534	-1.2576	-0.4302
C	1.1839	-0.0181	0.1055	C	1.1918	-0.0211	0.0964
C	0.4873	1.2456	-0.3997	C	0.4820	1.2470	-0.3912
C	-1.0034	1.3266	0.0164	C	-0.9951	1.3554	0.0502
H	0.9206	-2.1818	-0.1120	H	0.9073	-2.1833	-0.0741
H	1.2377	-0.0349	1.1982	H	1.2652	-0.0354	1.1859
H	0.9629	2.1526	-0.0190	H	0.9560	2.1481	-0.0006
H	0.5500	1.2703	-1.4967	H	0.5253	1.2982	-1.4842
H	0.5184	-1.2238	-1.5436	H	0.4965	-1.2707	-1.5247

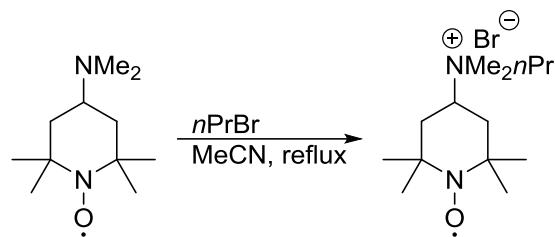
N	-1.6795	0.0139	-0.2488	C	-1.7801	-2.3721	-0.8513
O	-2.9797	0.0271	-0.1899	H	-1.2382	-3.3181	-0.7835
C	-1.7386	-2.3369	-0.9432	H	-2.7955	-2.5328	-0.4874
H	-1.2666	-3.3190	-0.8414	H	-1.8154	-2.0677	-1.8999
H	-2.7896	-2.4233	-0.6663	C	-1.1927	-1.6955	1.5099
H	-1.6875	-2.0271	-1.9913	H	-2.2376	-1.6100	1.8136
C	-1.1871	-1.7607	1.4417	H	-0.8843	-2.7382	1.6180
H	-2.2394	-1.6924	1.7274	H	-0.5728	-1.0902	2.1687
H	-0.8690	-2.8018	1.5571	C	-1.7273	2.4220	-0.7712
H	-0.6075	-1.1500	2.1398	H	-2.7385	2.5926	-0.4004
C	-1.6920	2.3883	-0.8588	H	-1.1644	3.3531	-0.6744
H	-2.7282	2.5231	-0.5476	H	-1.7709	2.1520	-1.8291
H	-1.1693	3.3449	-0.7608	C	-1.1487	1.6558	1.5662
H	-1.6895	2.0903	-1.9114	H	-0.8224	2.6893	1.7050
C	-1.1541	1.7161	1.5039	H	-2.1929	1.5784	1.8743
H	-0.8180	2.7467	1.6558	H	-0.5353	1.0202	2.2026
H	-2.2077	1.6559	1.7865	O	-2.8411	0.0335	-0.5365
H	-0.5859	1.0710	2.1800	N	-1.6966	0.0147	-0.2001
C	3.4305	-1.2208	0.2125	C	3.4212	-1.2220	0.1660
H	2.9595	-2.1472	-0.1054	H	2.9651	-2.1487	-0.1701
H	4.4533	-1.1830	-0.1629	H	4.4374	-1.1610	-0.2191
H	3.4308	-1.1506	1.3011	H	3.4238	-1.1621	1.2536
C	3.4189	1.2310	-0.0251	C	3.3968	1.2325	-0.0520
H	4.4658	1.0918	-0.2950	H	4.4379	1.0875	-0.3344
H	3.002157	2.05651	-0.59671	H	2.9817	2.0580	-0.6240
H	3.334242	1.428382	1.044364	H	3.3193	1.4179	1.0189
H	2.659965	-0.138464	-1.360584	H	2.6487	-0.1324	-1.3981
N	2.671301	-0.040335	-0.339436	N	2.6514	-0.0409	-0.3761

TH			
Symbol	X	Y	Z
C	-0.9946	-1.2885	-0.0159
C	0.5099	-1.2527	-0.3880
C	1.2211	0.0000	0.1274
C	0.5099	1.2527	-0.3879
C	-0.9946	1.2885	-0.0159
H	0.9559	-2.1666	0.0125
H	1.2893	0.0000	1.2194
H	0.9558	2.1666	0.0125
H	0.5958	1.2837	-1.4833
H	0.5958	-1.2837	-1.4833
N	-1.5836	0.0000	-0.4769

TH2			
Symbol	X	Y	Z
C	-0.9714	-1.3539	-0.0304
C	0.5182	-1.2615	-0.4290
C	1.2389	-0.0169	0.1074
C	0.5411	1.2523	-0.3993
C	-0.9459	1.3576	0.0051
H	0.9706	-2.1807	-0.0547
H	1.2853	-0.0278	1.1984
H	1.0084	2.1521	0.0026
H	0.6251	1.3075	-1.4906
H	0.6023	-1.2871	-1.5219
N	-1.6238	0.0133	-0.4155

C	-1.6496	-2.4072	-0.8502	C	-1.6710	-2.4130	-0.8945
H	-1.1393	-3.3607	-0.6801	H	-1.1706	-3.3716	-0.7390
H	-2.6955	-2.5354	-0.5632	H	-2.7192	-2.5240	-0.6126
H	-1.6061	-2.1706	-1.9177	H	-1.6116	-2.1758	-1.9612
C	-1.1953	-1.6213	1.4820	C	-1.1692	-1.6792	1.4544
H	-2.2389	-1.4584	1.7591	H	-2.2252	-1.7047	1.7336
H	-0.9619	-2.6760	1.6592	H	-0.7828	-2.6884	1.6157
H	-0.5722	-1.0285	2.1549	H	-0.6370	-1.0168	2.1345
C	-1.6496	2.4072	-0.8502	C	-1.6305	2.4519	-0.8272
H	-2.6955	2.5353	-0.5632	H	-2.6723	2.5830	-0.5308
H	-1.1393	3.3607	-0.6801	H	-1.1044	3.3943	-0.6578
H	-1.6061	2.1706	-1.9178	H	-1.5900	2.2366	-1.8996
C	-1.1954	1.6213	1.4820	C	-1.1281	1.6465	1.5004
H	-0.9619	2.6760	1.6592	H	-0.7682	2.6632	1.6747
H	-2.2389	1.4584	1.7590	H	-2.1779	1.6373	1.8040
H	-0.5722	1.0285	2.1549	H	-0.5636	0.9874	2.1576
O	-2.9735	0.0000	-0.1066	O	-3.0154	0.0220	-0.1566
H	-3.4418	0.0000	-0.9537	H	-3.1168	0.0476	0.8116
C	3.4598	-1.2323	0.0908	H	-1.6202	0.0271	-1.4422
H	3.0139	-2.1141	-0.3620	C	3.4656	-1.2244	0.2097
H	4.4950	-1.1361	-0.2373	H	3.0299	-2.1441	-0.1702
H	3.4194	-1.3039	1.1785	H	4.4967	-1.1478	-0.1300
C	3.4598	1.2323	0.0908	H	3.4226	-1.1951	1.2979
H	4.4950	1.1361	-0.2372	C	3.4529	1.2323	0.0222
H	3.0139	2.1141	-0.3620	H	4.4962	1.0935	-0.2556
H	3.4194	1.3039	1.1786	H	3.0415	2.0688	-0.5361
H	2.6781	0.0000	-1.3604	H	3.3676	1.3981	1.0958
N	2.703797	0.000005	-0.33486	H	2.7269	-0.1125	-1.3544
				N	2.7105	-0.0342	-0.3315

### 3.28 4-(*N,N*-Dimethyl-*N-n*-Propylammonium)-TEMPO Bromide (28)



#### *N-n*-propyl-1-oxyl-*N,N,2,2,6,6*-hexamethylpiperidin-4-ammonium bromide (Syn13).

To a MeCN (1.1 mL, 0.3 M) solution of 4-(dimethylamino)-2,2,6,6-tetramethylpiperidin-1-oxyl<sup>29</sup> (0.0682 g, 0.344 mmol) stirring at room temperature was added *n*-propyl bromide (35  $\mu$ L, 0.385 mmol). The reaction was heated to reflux for 18 h. After cooling to room temperature, the reaction was concentrated and the resulting solids were triturated with EtO<sub>2</sub>, and isolated by vacuum filtration to give Syn3 (0.1064 g, 0.330 mmol, 96%) as red crystals.

Data for Syn13:  $R_f$  0.04 (10% NH<sub>4</sub>OH in MeOH); decomp. 201–202 °C; IR (neat) 2978 cm<sup>-1</sup>; HRMS (TOF MS ES+) calcd for C<sub>14</sub>H<sub>30</sub>N<sub>2</sub>O [M]<sup>+</sup>: 242.2358, found 242.2356.

Table S3.28. Summary table of electrocatalytic properties of TEMPO-NMe<sub>2</sub>Pr.

	$E_{a1}$	0.755
	$E_{a2}$	0.598
	$j_{max}$	2767.0
	$(i_{pa}/i_{pc})_{cat.}$	156.61

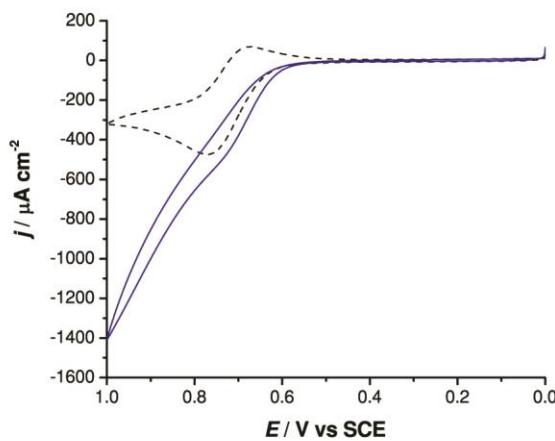


Figure S3.28. CV of 5 mM 28 in the absence (dashed) and presence (solid) of 1 M glycerol using 150 mM Robinson buffer at 25 °C.

**Optimized Geometry Coordinates Using B3LYP/6-31+G(d,p) CPCM**

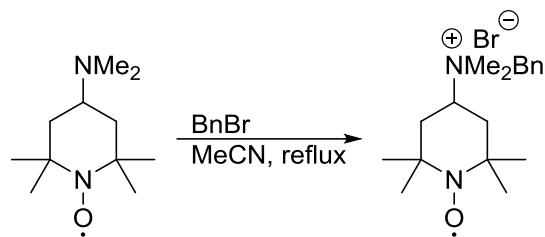
<b>T*</b>				<b>T+</b>			
<b>Symbol</b>	<b>X</b>	<b>Y</b>	<b>Z</b>	<b>Symbol</b>	<b>X</b>	<b>Y</b>	<b>Z</b>
C	-1.7823	-1.3152	-0.1853	C	1.7826	-1.3439	0.1571
C	-0.2349	-1.2441	-0.1908	C	0.2375	-1.2547	0.1418
C	0.2891	-0.0318	0.5808	C	-0.2929	-0.0324	-0.6161
C	-0.2092	1.2326	-0.1207	C	0.2109	1.2379	0.0778
C	-1.7537	1.3395	-0.1055	C	1.7519	1.3668	0.0751
H	0.1166	-2.1879	0.2291	H	-0.0916	-2.1921	-0.3081
H	-0.0781	-0.0596	1.6087	H	0.0570	-0.0577	-1.6494
H	0.1690	2.1442	0.3457	H	-0.1481	2.1443	-0.4116
H	0.1225	1.2307	-1.1631	H	-0.1292	1.2679	1.1155
H	0.1023	-1.1967	-1.2306	H	-0.1111	-1.2454	1.1775
N	-2.3626	0.0298	-0.5183	C	2.2515	-2.3368	1.2268
O	-3.6171	0.0520	-0.8041	H	1.7554	-3.2890	1.0261
C	-2.2199	-2.3010	-1.2823	H	3.3293	-2.4962	1.1844
H	-1.7437	-3.2701	-1.1063	H	1.9727	-2.0058	2.2302
H	-3.3023	-2.4377	-1.2713	C	2.3845	-1.7298	-1.2211
H	-1.9216	-1.9415	-2.2716	H	3.4747	-1.6759	-1.1956
C	-2.3300	-1.7944	1.1774	H	2.0922	-2.7673	-1.4010
H	-3.4225	-1.7731	1.1609	H	2.0141	-1.1242	-2.0468
H	-2.0063	-2.8238	1.3582	C	2.2031	2.4331	1.0791
H	-1.9888	-1.1821	2.0154	H	3.2772	2.6115	1.0229
C	-2.1713	2.3990	-1.1397	H	1.6861	3.3607	0.8232
H	-3.2509	2.5552	-1.1200	H	1.9343	2.1568	2.1015
H	-1.6767	3.3461	-0.9046	C	2.3338	1.6805	-1.3292
H	-1.8791	2.0952	-2.1493	H	2.0139	2.6971	-1.5709
C	-2.2885	1.7472	1.2851	H	3.4251	1.6556	-1.3101
H	-1.9468	2.7589	1.5238	H	1.9729	1.0153	-2.1121
H	-3.3813	1.7449	1.2722	O	3.3911	0.0603	1.1273
H	-1.9547	1.0816	2.0846	N	2.3706	0.0305	0.5103
C	2.2168	-1.3273	1.5060	C	-2.2311	-1.3252	-1.5090
H	2.1448	-2.1685	0.8210	H	-2.1516	-2.1692	-0.8281
H	3.2383	-1.2390	1.8678	H	-3.2589	-1.2308	-1.8497
H	1.5425	-1.4662	2.3506	H	-1.5747	-1.4609	-2.3678
C	2.2164	1.1039	1.6917	C	-2.2332	1.1119	-1.6841
H	3.2549	0.9900	1.9927	H	-3.2734	0.9896	-1.9743
H	2.0943	2.0432	1.1582	H	-2.1172	2.0479	-1.1430
H	1.5775	1.0828	2.5741	H	-1.6040	1.1025	-2.5735
C	2.5844	0.0550	-0.5408	C	-2.5675	0.0515	0.5529
H	2.2074	-0.7540	-1.1674	H	-2.1849	-0.7607	1.1716
H	2.2838	1.0052	-0.9826	H	-2.2635	1.0010	0.9935

N	1.8384	-0.0504	0.7913	N	-1.8391	-0.0491	-0.7939
C	4.1103	-0.0207	-0.4616	C	-4.0941	-0.0228	0.4925
H	4.5073	0.7711	0.1804	H	-4.4985	0.7716	-0.1413
H	4.429439	-0.978672	-0.04116	H	-4.419694	-0.979677	0.075232
C	4.703906	0.131962	-1.870179	C	-4.666037	0.127917	1.910542
H	5.795066	0.075872	-1.825116	H	-5.757597	0.073256	1.879741
H	4.353363	-0.661334	-2.538928	H	-4.307395	-0.66733	2.572413
H	4.433978	1.095986	-2.313999	H	-4.388917	1.090894	2.351906

TH				TH2			
Symbol	X	Y	Z	Symbol	X	Y	Z
C	-1.7510	-1.2855	-0.1599	C	-1.7206	-1.3436	-0.1532
C	-0.2002	-1.2486	-0.1330	C	-0.1760	-1.2536	-0.1566
C	0.3266	-0.0155	0.6044	C	0.3492	-0.0237	0.5953
C	-0.1889	1.2434	-0.0965	C	-0.1590	1.2448	-0.1022
C	-1.7392	1.2970	-0.1194	C	-1.7017	1.3590	-0.0933
H	0.1307	-2.1791	0.3322	H	0.1643	-2.1874	0.2926
H	-0.0205	-0.0301	1.6393	H	-0.0075	-0.0457	1.6258
H	0.1550	2.1571	0.3926	H	0.1997	2.1536	0.3832
H	0.1616	1.2635	-1.1328	H	0.1896	1.2738	-1.1388
H	0.1531	-1.2450	-1.1686	H	0.1753	-1.2473	-1.1931
N	-2.2083	0.0168	-0.7245	N	-2.2541	0.0234	-0.6850
C	-2.1670	-2.3802	-1.1631	C	-2.1724	-2.3978	-1.1739
H	-1.7217	-3.3392	-0.8795	H	-1.7239	-3.3560	-0.9021
H	-3.2530	-2.5023	-1.1752	H	-3.2574	-2.5189	-1.1636
H	-1.8320	-2.1244	-2.1731	H	-1.8452	-2.1549	-2.1902
C	-2.3361	-1.6562	1.2234	C	-2.3110	-1.6696	1.2222
H	-3.4221	-1.5377	1.2121	H	-3.3988	-1.5903	1.2067
H	-2.1119	-2.7052	1.4421	H	-2.0522	-2.7068	1.4488
H	-1.9373	-1.0592	2.0449	H	-1.9250	-1.0519	2.0310
C	-2.1466	2.4254	-1.0881	C	-2.1404	2.4596	-1.0702
H	-3.2316	2.5562	-1.0956	H	-3.2231	2.5972	-1.0485
H	-1.6935	3.3716	-0.7759	H	-1.6734	3.3990	-0.7655
H	-1.8144	2.1974	-2.1057	H	-1.8242	2.2494	-2.0974
C	-2.3194	1.6287	1.2755	C	-2.2871	1.6343	1.2954
H	-2.0870	2.6686	1.5265	H	-2.0332	2.6648	1.5557
H	-3.4063	1.5188	1.2625	H	-3.3745	1.5497	1.2830
H	-1.9239	1.0034	2.0775	H	-1.8925	0.9928	2.0818
O	-3.6534	0.0231	-0.7223	O	-3.6717	0.0377	-0.6097
H	-3.8803	0.0376	-1.6629	H	-4.0169	0.0184	-1.5196
C	2.2696	-1.2767	1.5452	H	-1.9929	0.0462	-1.6777
H	2.1835	-2.1390	0.8885	C	2.2792	-1.3021	1.5253

H	3.2970	-1.1802	1.8879	H	2.2077	-2.1546	0.8542
H	1.6079	-1.3865	2.4039	H	3.3024	-1.2039	1.8784
C	2.2694	1.1607	1.6491	H	1.6113	-1.4279	2.3768
H	3.3055	1.0492	1.9596	C	2.2791	1.1366	1.6669
H	2.1579	2.0780	1.0761	H	3.3140	1.0164	1.9766
H	1.6263	1.1825	2.5286	H	2.1744	2.0640	1.1090
C	2.6121	0.0360	-0.5474	H	1.6352	1.1438	2.5459
H	2.2416	-0.8050	-1.1342	C	2.6374	0.0450	-0.5493
H	2.2912	0.9612	-1.0265	H	2.2691	-0.7829	-1.1561
N	1.8821	-0.0241	0.7949	H	2.3293	0.9826	-1.0124
C	4.1399	-0.0117	-0.4819	N	1.8949	-0.0363	0.7895
H	4.5304	0.8222	0.1090	C	4.1638	-0.0146	-0.4680
H	4.479551	-0.938343	-0.010188	H	4.5529	0.8010	0.1482
C	4.716855	0.067834	-1.903224	H	4.491535	-0.95605	-0.018232
H	5.809342	0.034776	-1.867117	C	4.755342	0.098963	-1.881107
H	4.374998	-0.770343	-2.519784	H	5.846854	0.056014	-1.832758
H	4.424352	0.998405	-2.401042	H	4.414215	-0.719594	-2.523598
				H	4.475896	1.045312	-2.355751

### 3.29 4-(*N,N*-Dimethyl-*N*-Benzylammonium)-TEMPO Bromide (29)

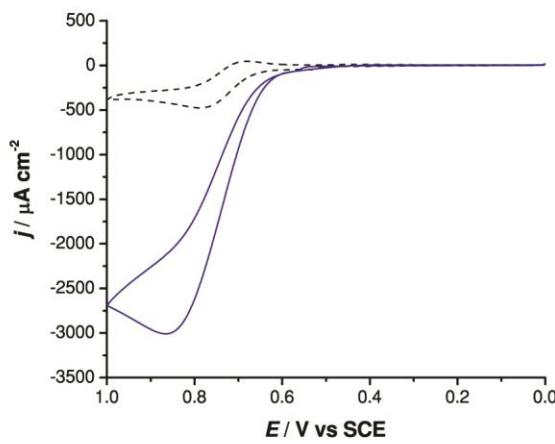


***N*-benzyl-1-oxyl-*N,N,2,2,6,6*-hexamethylpiperidin-4-ammonium bromide (Syn14).** To a MeCN (1.0 mL, 0.3 M) solution of 4-(dimethylamino)-2,2,6,6-tetramethylpiperidin-1-oxyl<sup>29</sup> (0.0598 g, 0.302 mmol) stirring at room temperature was added benzyl bromide (40  $\mu$ L, 0.336 mmol). The reaction was heated to reflux for 13 h. After cooling to room temperature, the reaction was concentrated and the resulting solids were triturated with EtO<sub>2</sub>, and isolated by vacuum filtration to give **Syn14** (0.1091 g, 0.295 mmol, 98%) as red crystals.

Data for **Syn14**: R<sub>f</sub> 0.13 (10% NH<sub>4</sub>OH in MeOH); decomp. 175–178 °C; IR (neat) 2977, 2932 cm<sup>-1</sup>; HRMS (TOF MS ES+) calcd for C<sub>18</sub>H<sub>30</sub>N<sub>2</sub>O [M]<sup>+</sup>: 290.2358, found 290.2354.

**Table S3.29. Summary table of electrocatalytic properties of TEMPO-NMe<sub>2</sub>Bn.**

	<i>E<sub>a1</sub></i>	0.750
	<i>E<sub>a2</sub></i>	0.593
	<i>j<sub>max</sub></i>	2308.9
	<i>(i<sub>pa</sub>/i<sub>pc</sub>)<sub>cat.</sub></i>	163.13



**Figure S3.29.** CV of 5 mM 29 in the absence (dashed) and presence (solid) of 1 M glycerol using 150 mM Robinson buffer at 25 °C.

**Optimized Geometry Coordinates Using B3LYP/6-31+G(d,p) CPCM**

<b>T*</b>				<b>T+</b>			
<b>Symbol</b>	<b>X</b>	<b>Y</b>	<b>Z</b>	<b>Symbol</b>	<b>X</b>	<b>Y</b>	<b>Z</b>
C	-2.7258	-1.3261	-0.1456	C	-2.7082	-1.3641	-0.0836
C	-1.1787	-1.2483	-0.1547	C	-1.1652	-1.2503	-0.0644
C	-0.6621	0.0016	0.5598	C	-0.6607	0.0316	0.6089
C	-1.1644	1.2279	-0.2044	C	-1.1754	1.2419	-0.1795
C	-2.7096	1.3288	-0.1974	C	-2.7191	1.3440	-0.2132
H	-0.8243	-2.1702	0.3086	H	-0.8283	-2.1478	0.4545
H	-1.0330	0.0228	1.5865	H	-1.0218	0.0775	1.6375
H	-0.7920	2.1638	0.2161	H	-0.8407	2.1867	0.2513
H	-0.8312	1.1757	-1.2452	H	-0.8180	1.2054	-1.2114
H	-0.8414	-1.2477	-1.1956	H	-0.8069	-1.3128	-1.0946
N	-3.3120	-0.0025	-0.5456	C	-3.1546	-2.4498	-1.0683
O	-4.5662	-0.0006	-0.8338	H	-2.6505	-3.3758	-0.7824
C	-3.1592	-2.3686	-1.1905	H	-4.2311	-2.6171	-1.0236
H	-2.6807	-3.3260	-0.9634	H	-2.8686	-2.2016	-2.0931
H	-4.2412	-2.5072	-1.1735	C	-3.3142	-1.6407	1.3188
H	-2.8604	-2.0604	-2.1968	H	-4.4045	-1.6014	1.2819
C	-3.2707	-1.7383	1.2401	H	-3.0123	-2.6560	1.5877
H	-4.3632	-1.7188	1.2239	H	-2.9565	-0.9634	2.0925
H	-2.9456	-2.7572	1.4707	C	-3.1682	2.3222	-1.3049
H	-2.9294	-1.0851	2.0466	H	-4.2455	2.4885	-1.2783
C	-3.1290	2.3327	-1.2851	H	-2.6690	3.2748	-1.1140
H	-4.2090	2.4867	-1.2740	H	-2.8800	1.9736	-2.2996
H	-2.6372	3.2920	-1.0992	C	-3.3344	1.7569	1.1507
H	-2.8355	1.9778	-2.2775	H	-3.0387	2.7961	1.3151
C	-3.2490	1.8038	1.1698	H	-4.4245	1.7085	1.1140
H	-2.9090	2.8264	1.3594	H	-2.9763	1.1652	1.9917
H	-4.3417	1.7998	1.1538	O	-4.3172	-0.0676	-1.1919
H	-2.9170	1.1789	2.0022	N	-3.3095	-0.0333	-0.5544
C	1.2741	-1.2409	1.5467	C	1.2976	-1.1887	1.5690
H	1.1649	-2.1176	0.9138	H	1.2027	-2.0672	0.9361
H	2.3114	-1.1452	1.8592	H	2.3353	-1.0719	1.8714
H	0.6293	-1.3230	2.4211	H	0.6634	-1.2818	2.4500
C	1.2562	1.1867	1.6380	C	1.2514	1.2411	1.6603
H	2.3105	1.1130	1.8949	H	2.3148	1.1871	1.8805
H	1.0783	2.1095	1.0922	H	1.0376	2.1638	1.1272
H	0.6523	1.1613	2.5446	H	0.6801	1.1950	2.5869
C	1.6423	0.0595	-0.5652	C	1.6289	0.1208	-0.5532
H	1.2797	-0.7877	-1.1458	H	1.2396	-0.7023	-1.1502
H	1.3167	0.9804	-1.0461	H	1.3238	1.0618	-1.0077

N	0.8858	0.0005	0.7801	N	0.8829	0.0491	0.8047
C	3.1492	0.0249	-0.4673	C	3.1343	0.0436	-0.4706
C	3.8852	1.2186	-0.3947	C	3.9028	1.2148	-0.3709
C	3.8413	-1.1952	-0.5296	C	3.7913	-1.1929	-0.5783
C	5.2809	1.1918	-0.3512	C	5.2975	1.1482	-0.3436
H	3.3694	2.1746	-0.3831	H	3.4145	2.1840	-0.3276
C	5.2369	-1.2234	-0.4858	C	5.1857	-1.2601	-0.5508
H	3.2917	-2.1273	-0.6236	H	3.2166	-2.1071	-0.6955
C	5.9593	-0.0300	-0.3913	C	5.9412	-0.0900	-0.4275
H	5.8356	2.1234	-0.2951	H	5.8783	2.0620	-0.2664
H	5.7576	-2.1748	-0.5349	H	5.6795	-2.2232	-0.6347
H	7.0445	-0.0515	-0.3614	H	7.0256	-0.1419	-0.4101

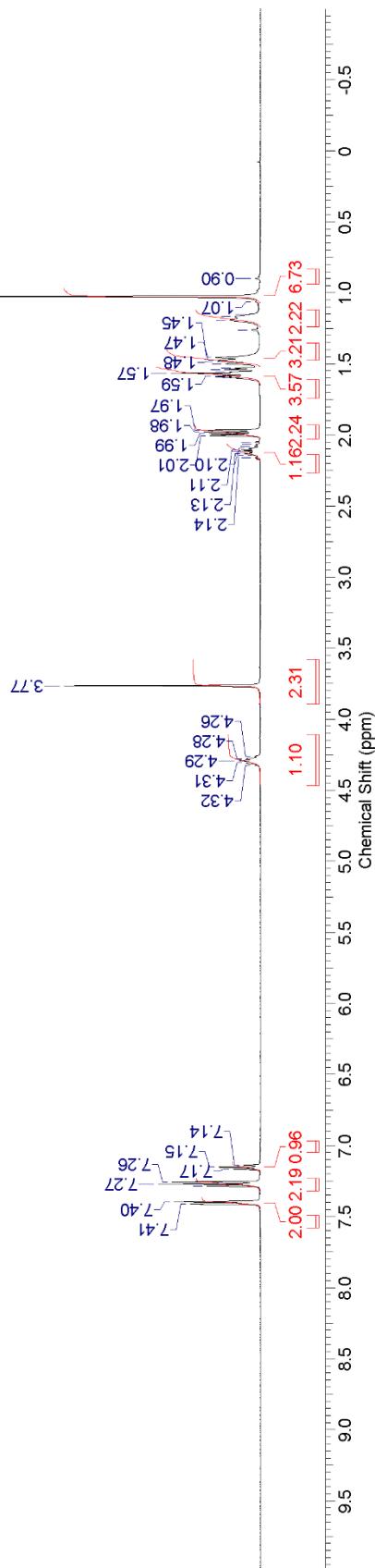
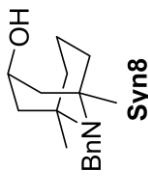
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C	-2.6982	-1.2943	-0.1108
C	-1.1471	-1.2591	-0.0670
C	-0.6271	0.0176	0.5981
C	-1.1351	1.2306	-0.1854
C	-2.6843	1.2845	-0.2306
H	-0.8279	-2.1582	0.4626
H	-0.9855	0.0653	1.6282
H	-0.7955	2.1742	0.2472
H	-0.7755	1.1841	-1.2175
H	-0.7777	-1.3257	-1.0951
N	-3.1467	-0.0297	-0.7622
C	-3.1060	-2.4500	-1.0463
H	-2.6670	-3.3899	-0.6968
H	-4.1922	-2.5695	-1.0628
H	-2.7590	-2.2598	-2.0667
C	-3.2988	-1.5726	1.2874
H	-4.3836	-1.4476	1.2579
H	-3.0843	-2.6070	1.5749
H	-2.9036	-0.9270	2.0732
C	-3.0759	2.3520	-1.2724
H	-4.1604	2.4827	-1.3039
H	-2.6262	3.3152	-1.0113
H	-2.7288	2.0628	-2.2692
C	-3.2821	1.7040	1.1332
H	-3.0525	2.7580	1.3194
H	-4.3688	1.5928	1.1136
H	-2.8965	1.1322	1.9785

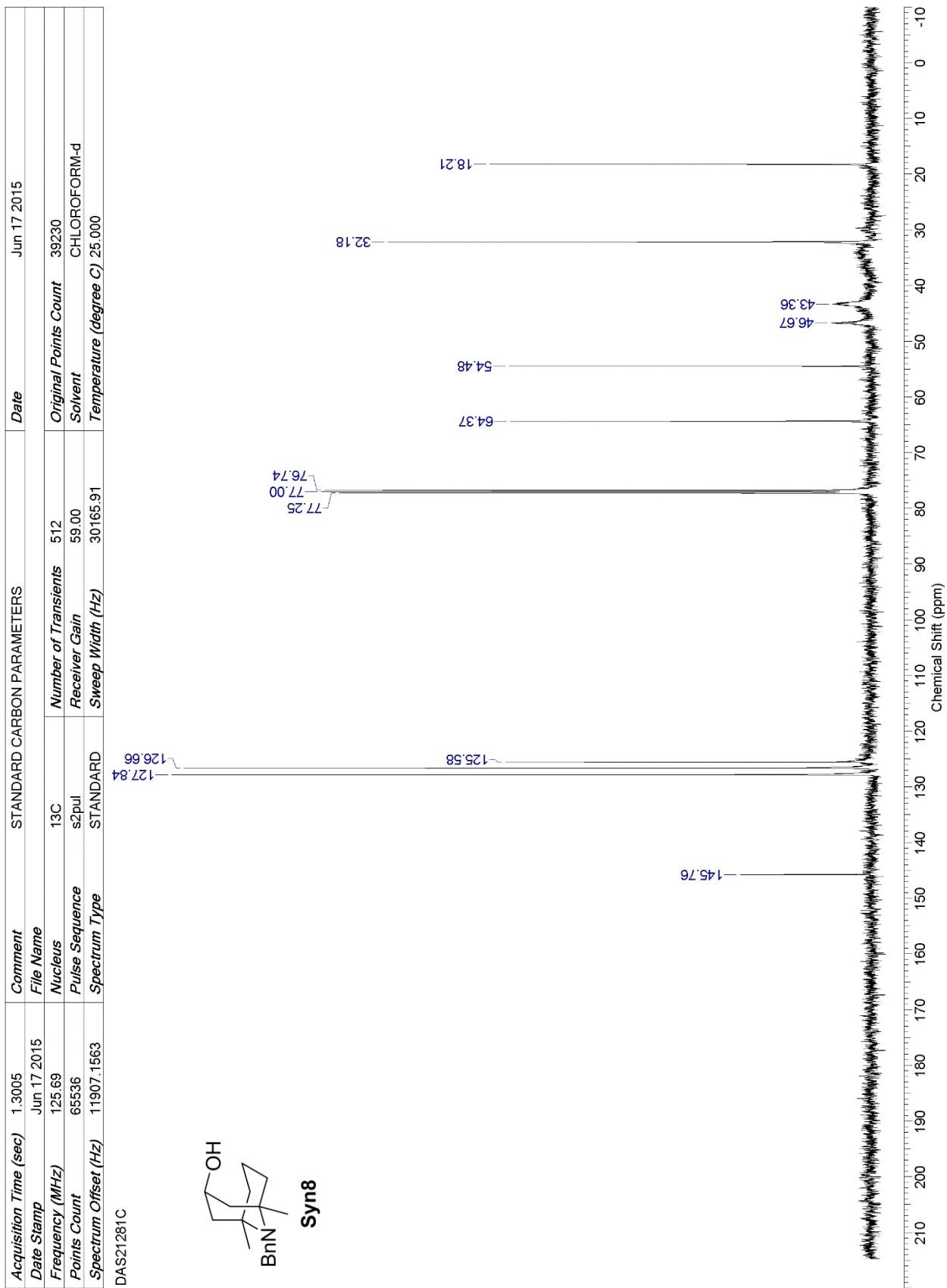
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C	-1.1256	1.2611	-0.1323
C	-2.6707	1.3478	-0.1206
H	-0.7434	-2.1638	0.2712
H	-0.9596	-0.0154	1.6018
H	-0.7866	2.1787	0.3494
H	-0.7774	1.2932	-1.1693
H	-0.7503	-1.2221	-1.2132
N	-3.2020	0.0030	-0.7088
C	-3.0731	-2.4136	-1.2035
H	-2.6143	-3.3663	-0.9293
H	-4.1565	-2.5480	-1.2026
H	-2.7401	-2.1647	-2.2166
C	-3.2302	-1.6954	1.1959
H	-4.3192	-1.6363	1.1803
H	-2.9521	-2.7283	1.4194
H	-2.8555	-1.0733	2.0069
C	-3.1300	2.4410	-1.0963
H	-4.2147	2.5625	-1.0703
H	-2.6772	3.3878	-0.7931
H	-2.8143	2.2362	-2.1246
C	-3.2575	1.6136	1.2693
H	-3.0143	2.6458	1.5330
H	-4.3439	1.5174	1.2566
H	-2.8571	0.9735	2.0538

O	-4.5917	-0.0225	-0.7788	O	-4.6193	-0.0157	-0.6294
H	-4.8067	-0.0632	-1.7216	H	-4.9674	0.0198	-1.5378
C	1.3343	-1.2223	1.5484	H	-2.9446	0.0278	-1.7024
H	1.2297	-2.0901	0.9026	C	1.3238	-1.1638	1.6513
H	2.3726	-1.1199	1.8558	H	1.1435	-2.0956	1.1216
H	0.6965	-1.3253	2.4258	H	2.3803	-1.0843	1.8956
C	1.2936	1.2014	1.6776	H	0.7298	-1.1239	2.5638
H	2.3571	1.1500	1.9007	C	1.3391	1.2646	1.5247
H	1.0726	2.1316	1.1605	H	2.3773	1.1693	1.8331
H	0.7204	1.1388	2.6022	H	1.2322	2.1323	0.8789
C	1.6693	0.1149	-0.5454	H	0.6995	1.3609	2.4014
H	1.2806	-0.7024	-1.1513	C	1.7009	-0.0677	-0.5732
H	1.3584	1.0583	-0.9906	H	1.3783	-0.9975	-1.0386
N	0.9265	0.0258	0.8049	H	1.3368	0.7699	-1.1667
C	3.1765	0.0445	-0.4679	N	0.9461	0.0108	0.7768
C	3.9399	1.2170	-0.3471	C	3.2071	-0.0300	-0.4744
C	3.8412	-1.1857	-0.5965	C	3.8983	1.1898	-0.5520
C	5.3351	1.1581	-0.3209	C	3.942709	-1.222786	-0.38343
H	3.4458	2.1824	-0.2850	C	5.293643	1.218768	-0.503936
C	5.2363	-1.2461	-0.5710	H	3.349039	2.1205	-0.660737
H	3.2703	-2.1005	-0.7278	C	5.338089	-1.194655	-0.33569
C	5.9860	-0.0747	-0.4272	H	3.427369	-2.178774	-0.360284
H	5.9108	2.0737	-0.2264	C	6.015825	0.026971	-0.389985
H	5.7353	-2.2051	-0.6718	H	5.814288	2.169428	-0.564282
H	7.0707	-0.1209	-0.4107	H	5.892892	-2.125028	-0.264586
				H	7.100837	0.049309	-0.356099

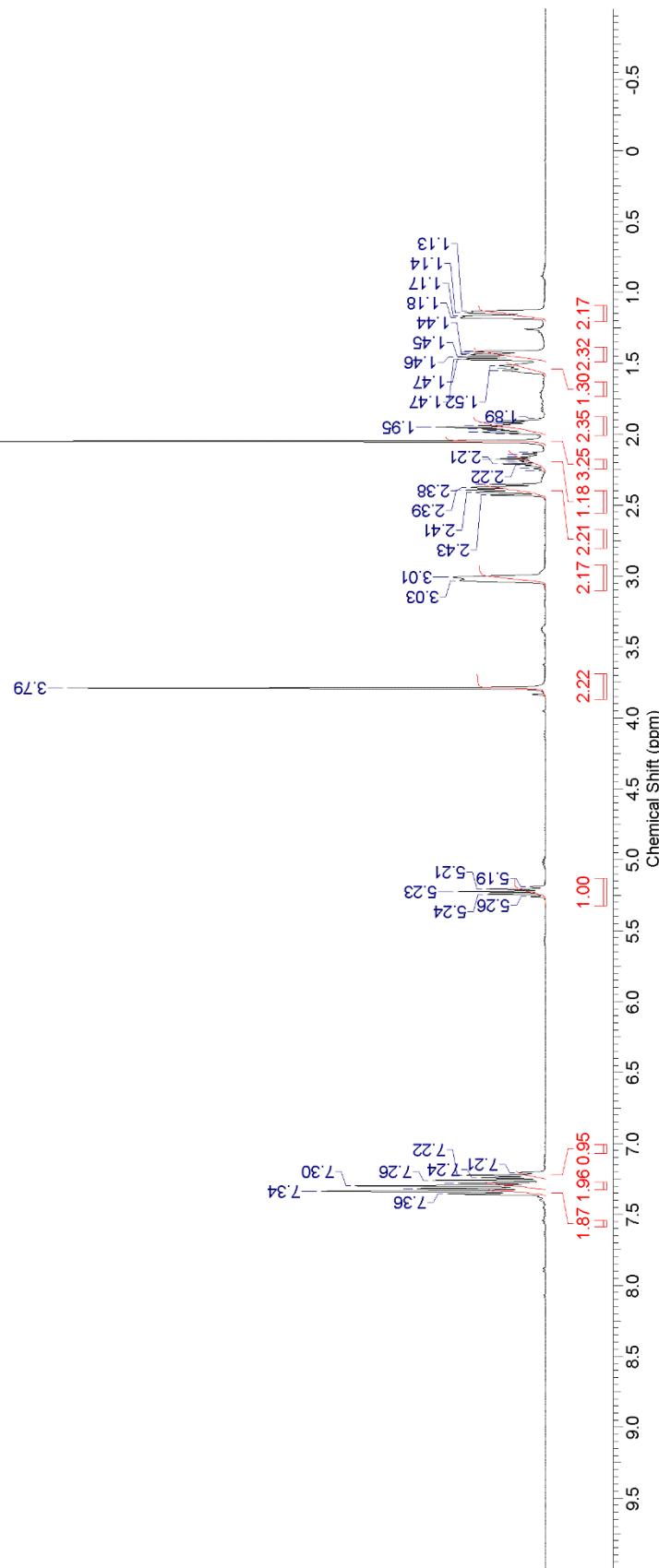
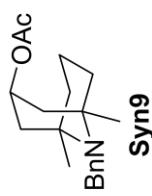
#### **4 NMR DATA FOR SYNTHESIZED COMPOUNDS**

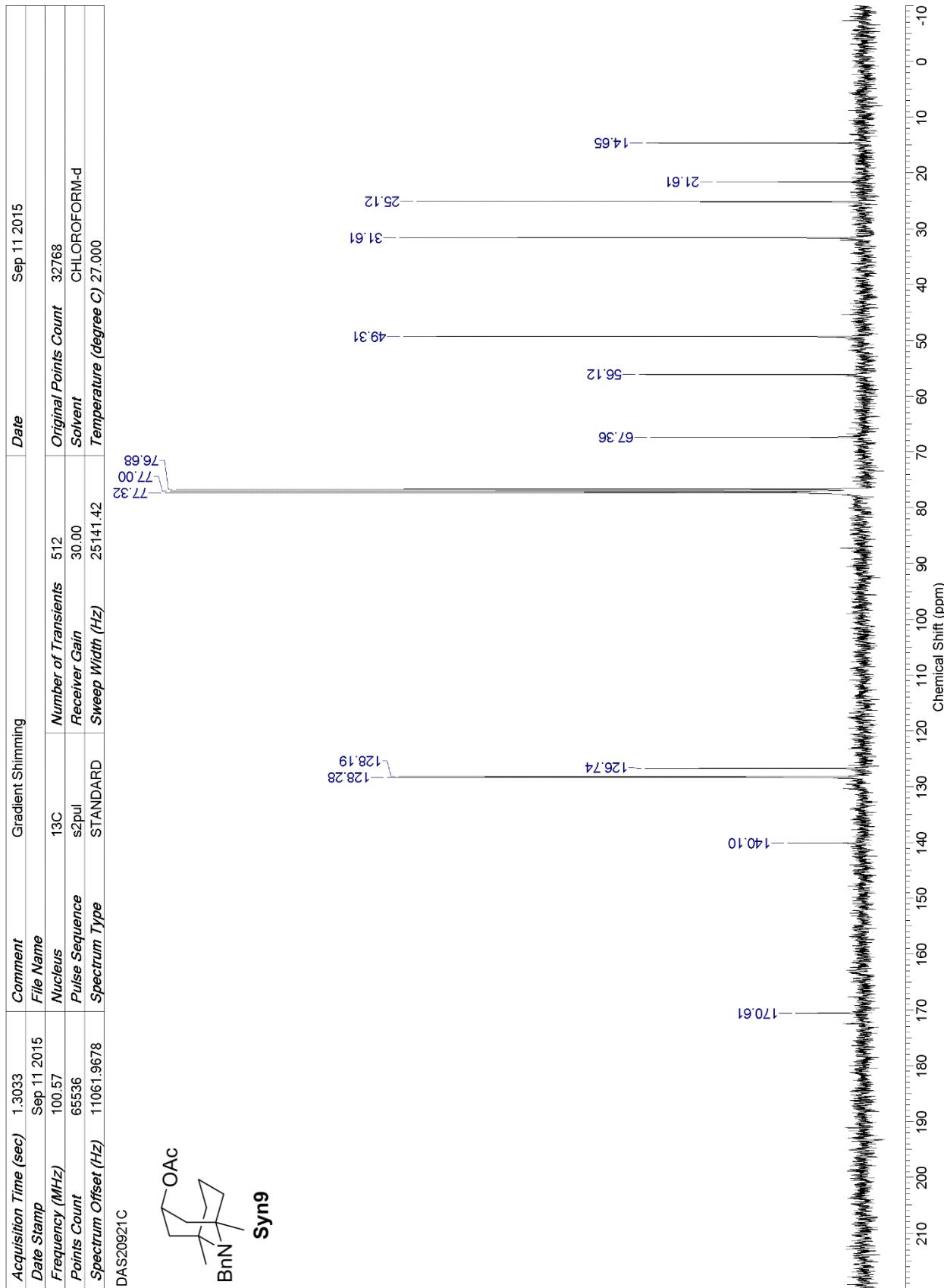
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Points Count	16384	Pulse Sequence	s2pul	Receiver Gain	27.00	Solvent	CHLOROFORM-d
Spectrum Offset (Hz)	2494.5852	Spectrum Type	STANDARD	Sweep Width (Hz)	8000.00	Temperature (degree C)	25.000





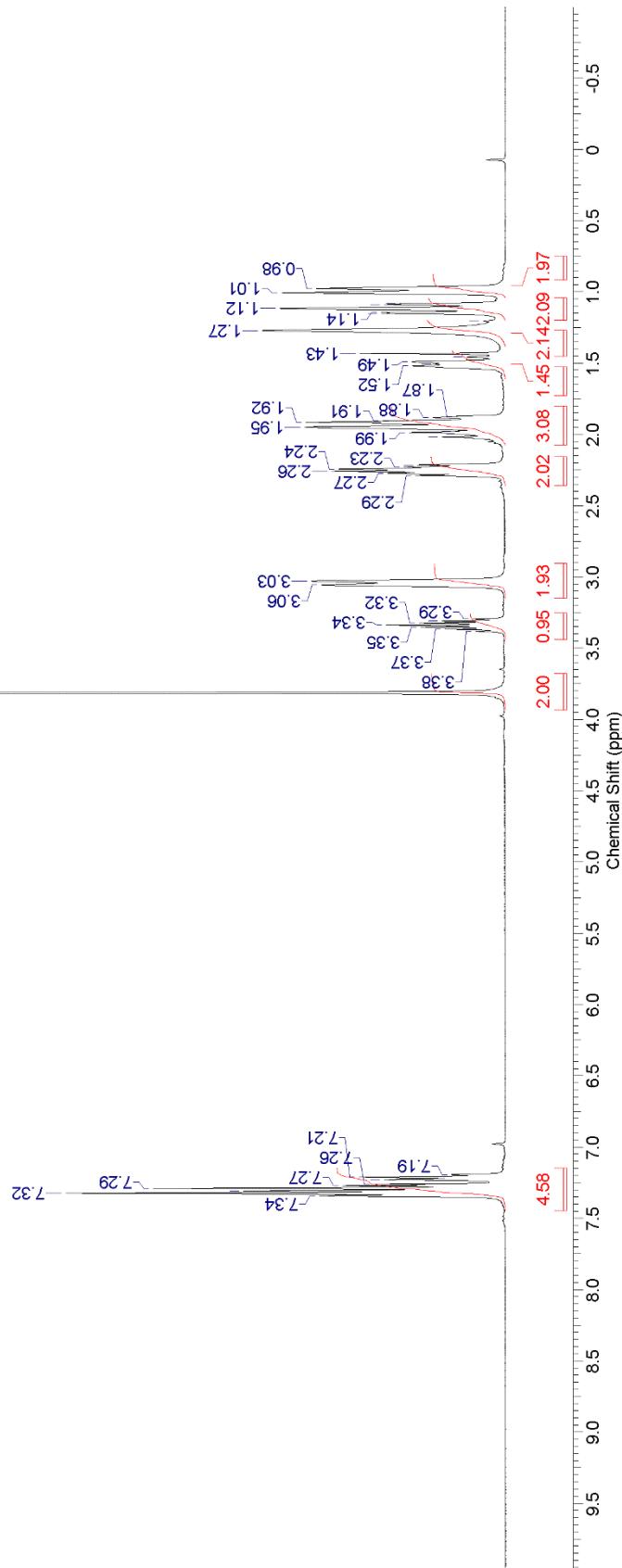
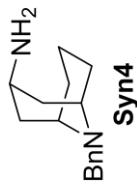
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<i>Date Stamp</i>	Sep 11 2015	<i>File Name</i>				<i>Date</i>	
<i>Frequency (MHz)</i>	399.91	<i>Nucleus</i>	1H	<i>Number of Transients</i>	32	<i>Original Points Count</i>	16384
<i>Points Count</i>	16384	<i>Pulse Sequence</i>	s2pul	<i>Receiver Gain</i>	46.00	<i>Solvent</i>	CHLOROFORM-d
<i>Spectrum Offset (Hz)</i>	2399.4604	<i>Spectrum Type</i>	STANDARD	<i>Sweep Width (Hz)</i>	6398.46	<i>Temperature (degree C)</i>	27.000

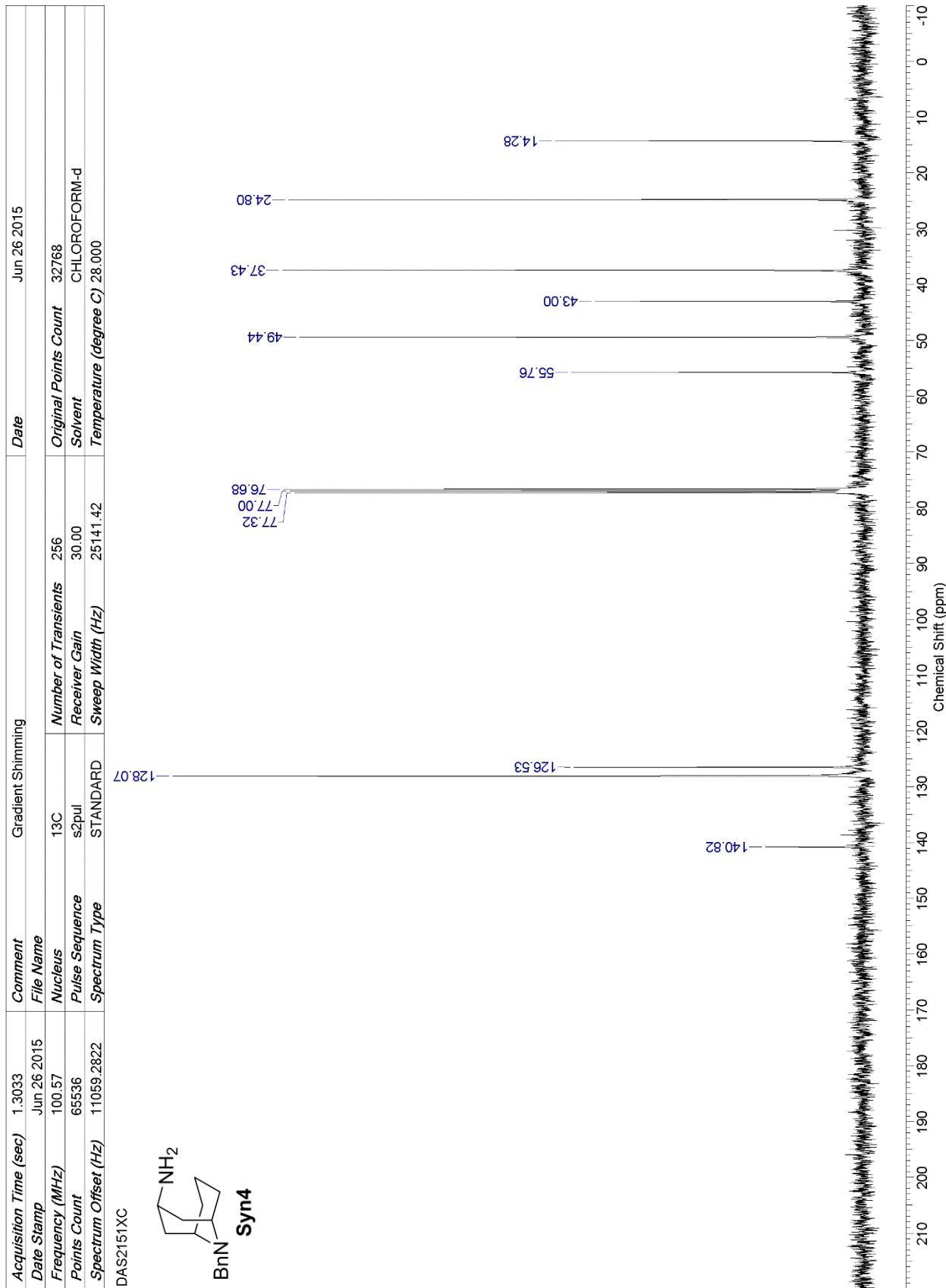




			<i>Comment</i>	Gradient Shimming			<i>Date</i>	
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<i>Points Count</i>	16384	<i>Pulse Sequence</i>	2D�	<i>Receiver Gain</i>	40.00		<i>Solvent</i>	CHLOROFORM-d
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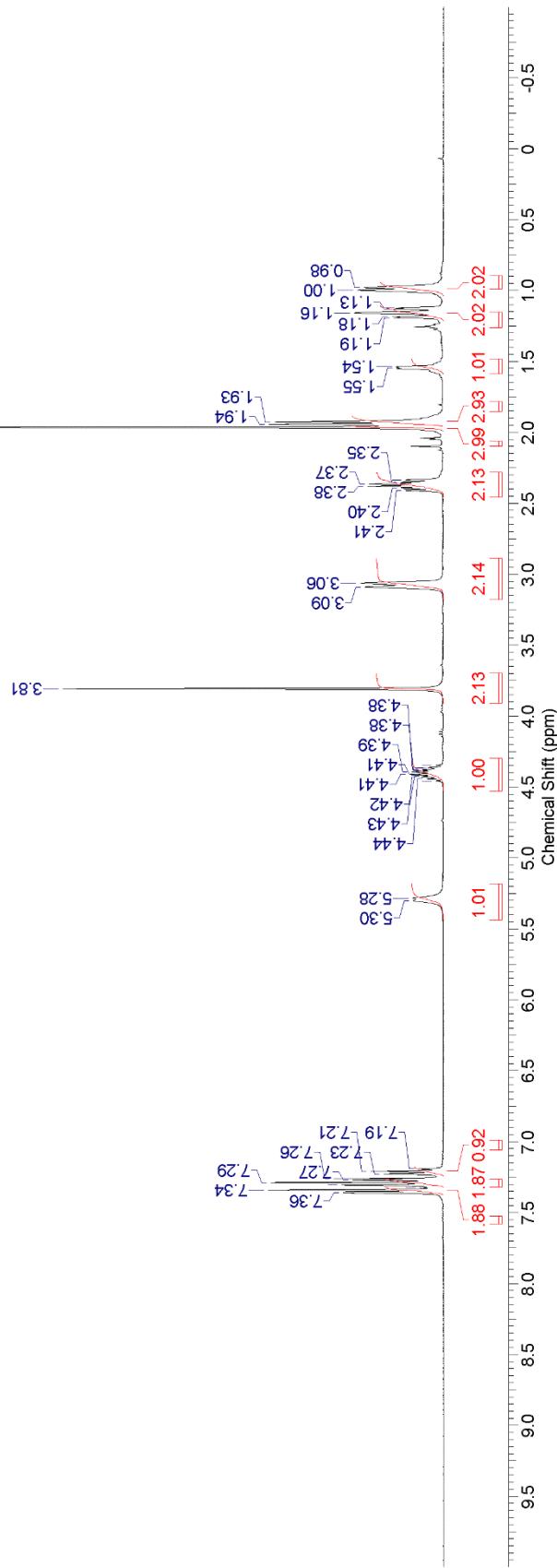
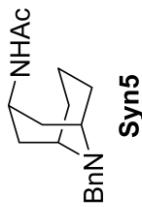
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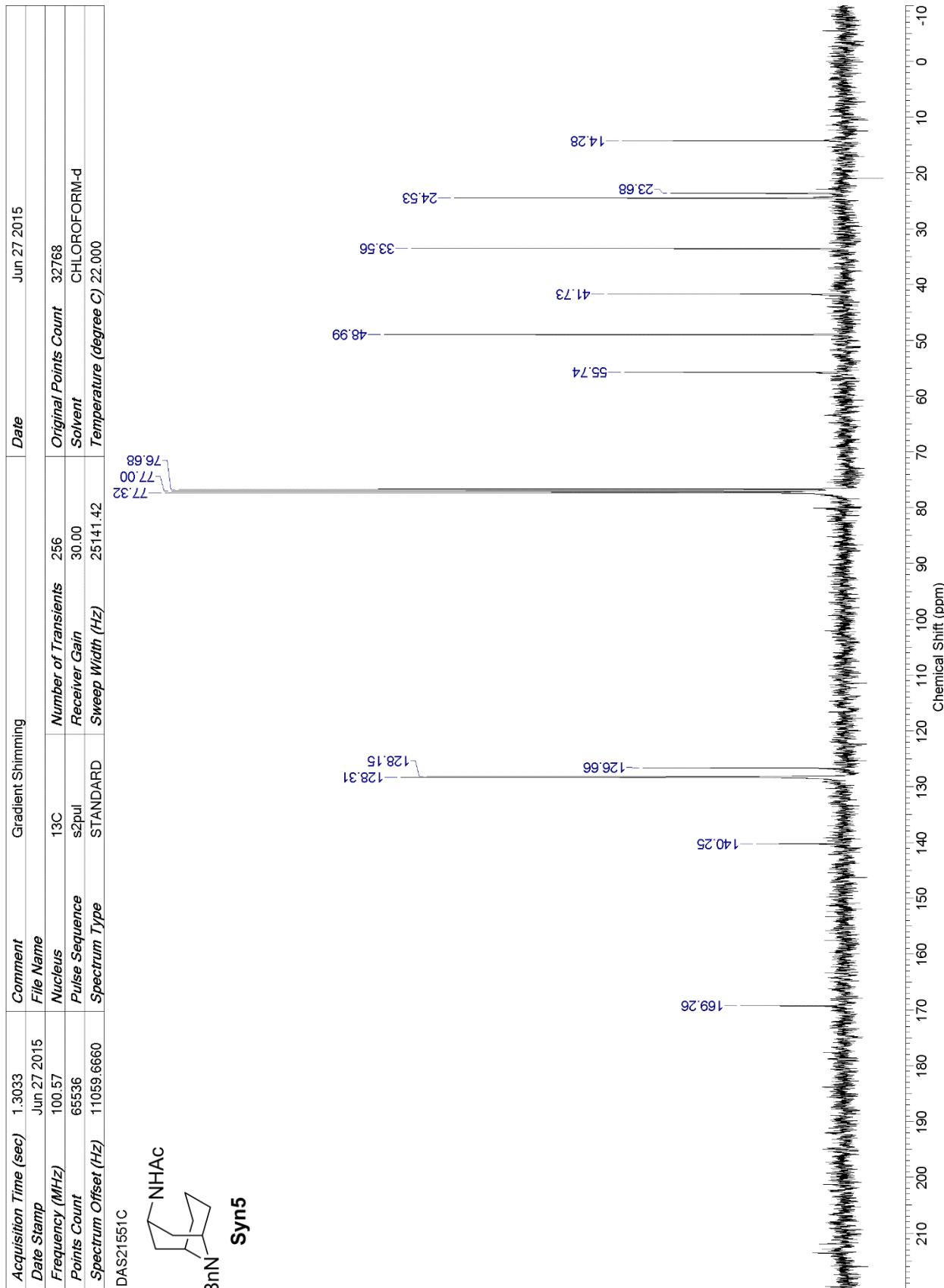




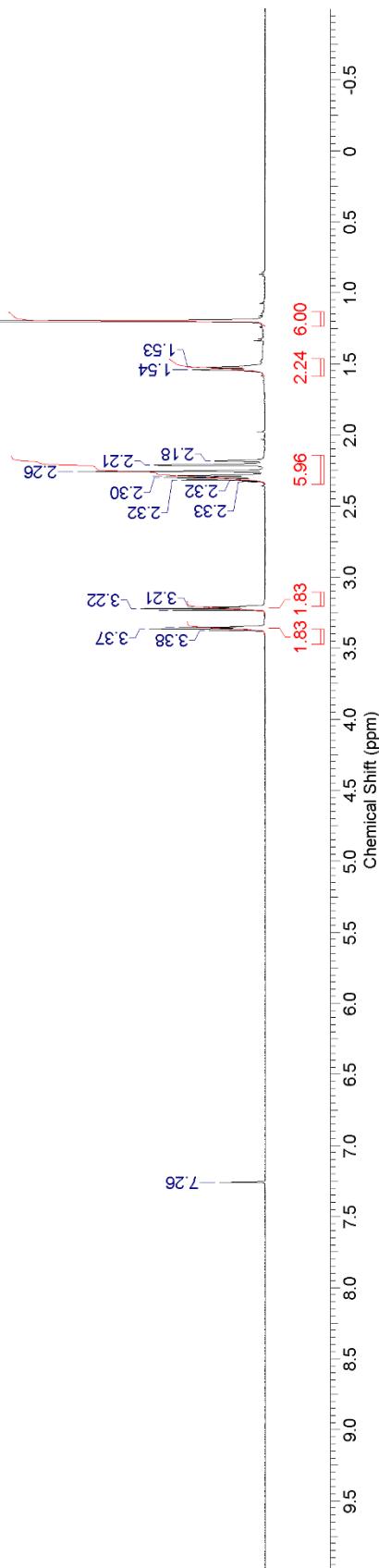
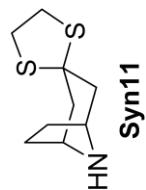
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<i>Points Count</i>	16384	<i>Pulse Sequence</i>	sc-pul	<i>Sweep Width (Hz)</i>	6398.46	<i>Temperature (degree C)</i>	22.000
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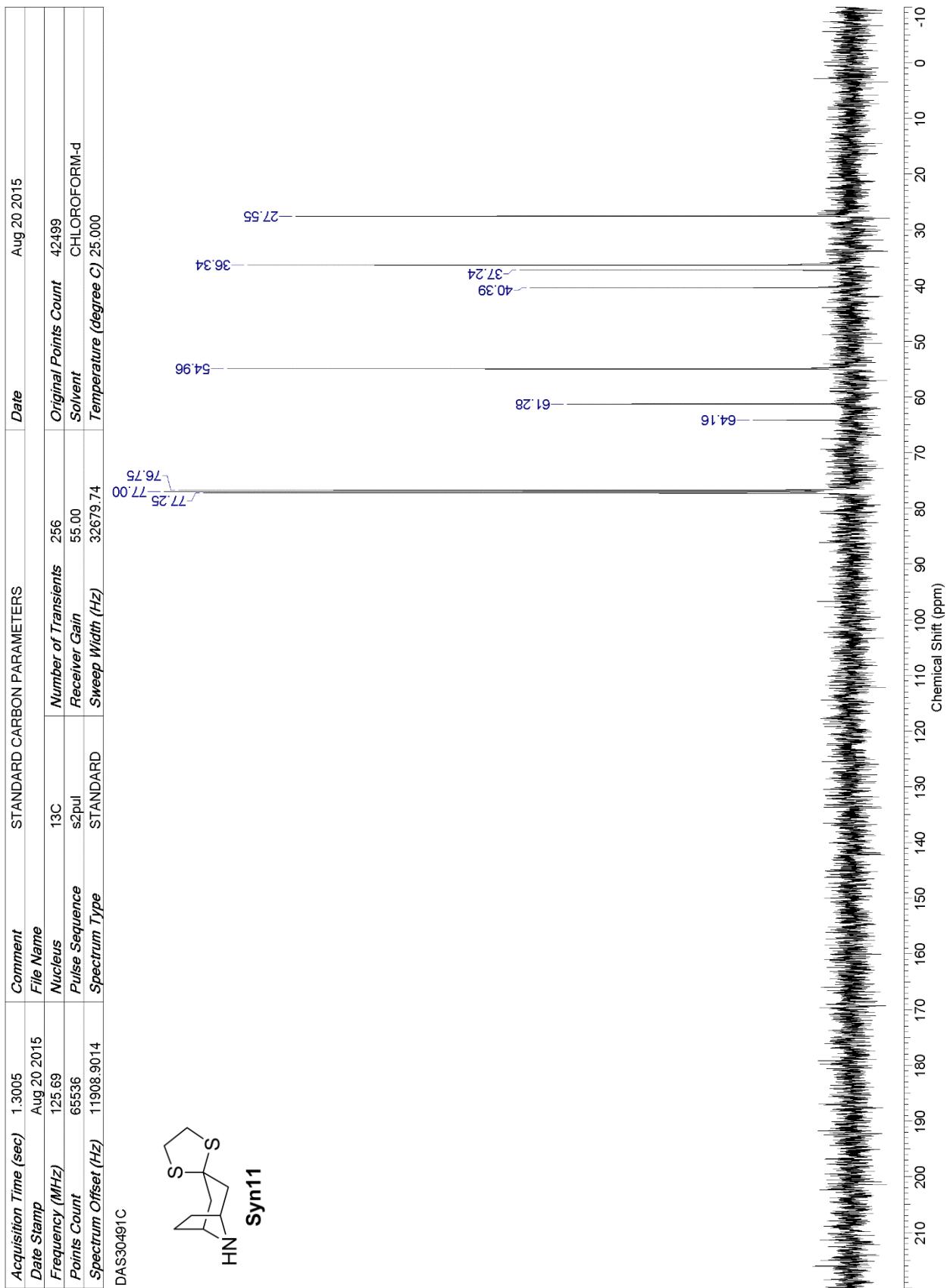
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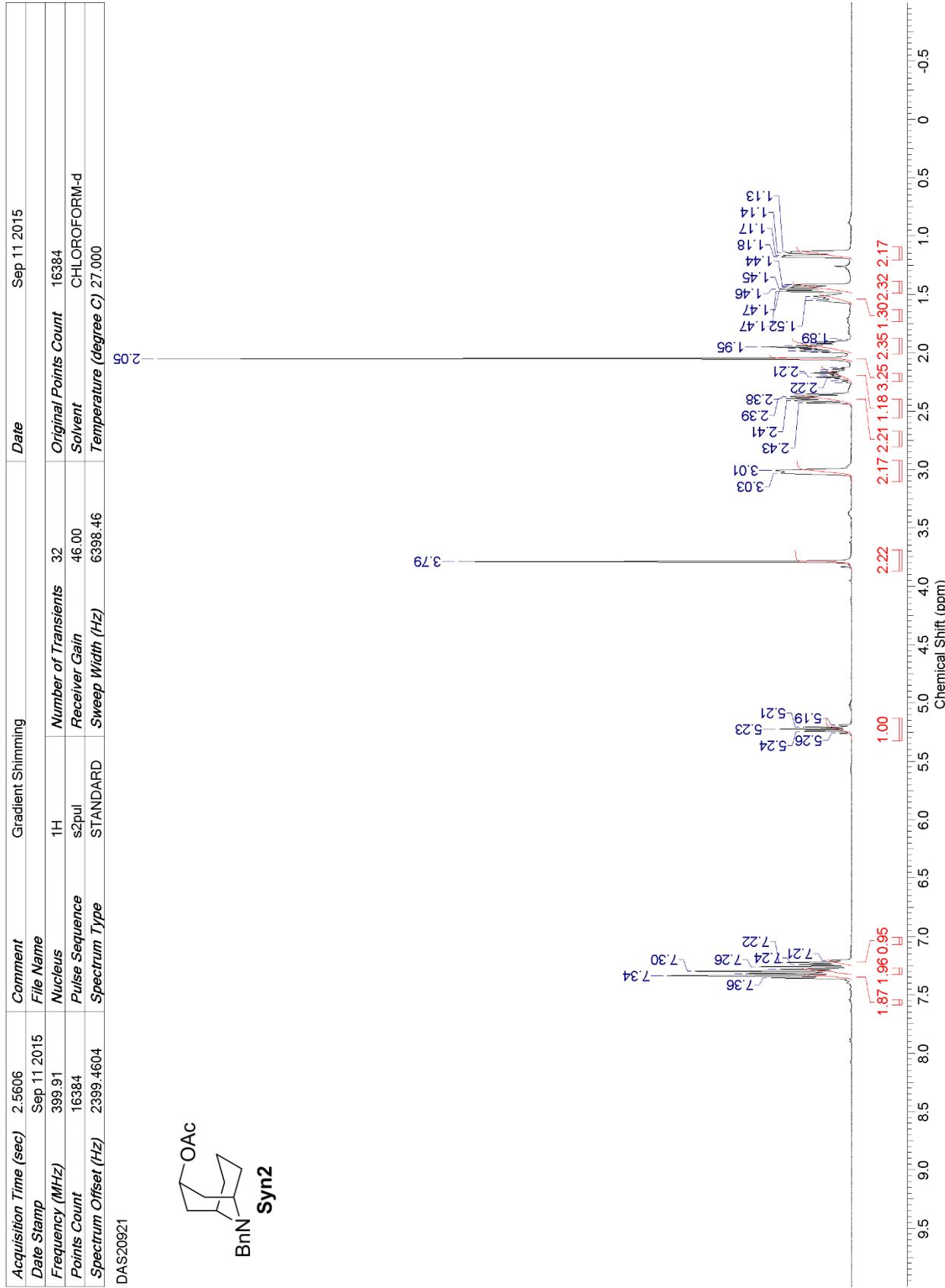


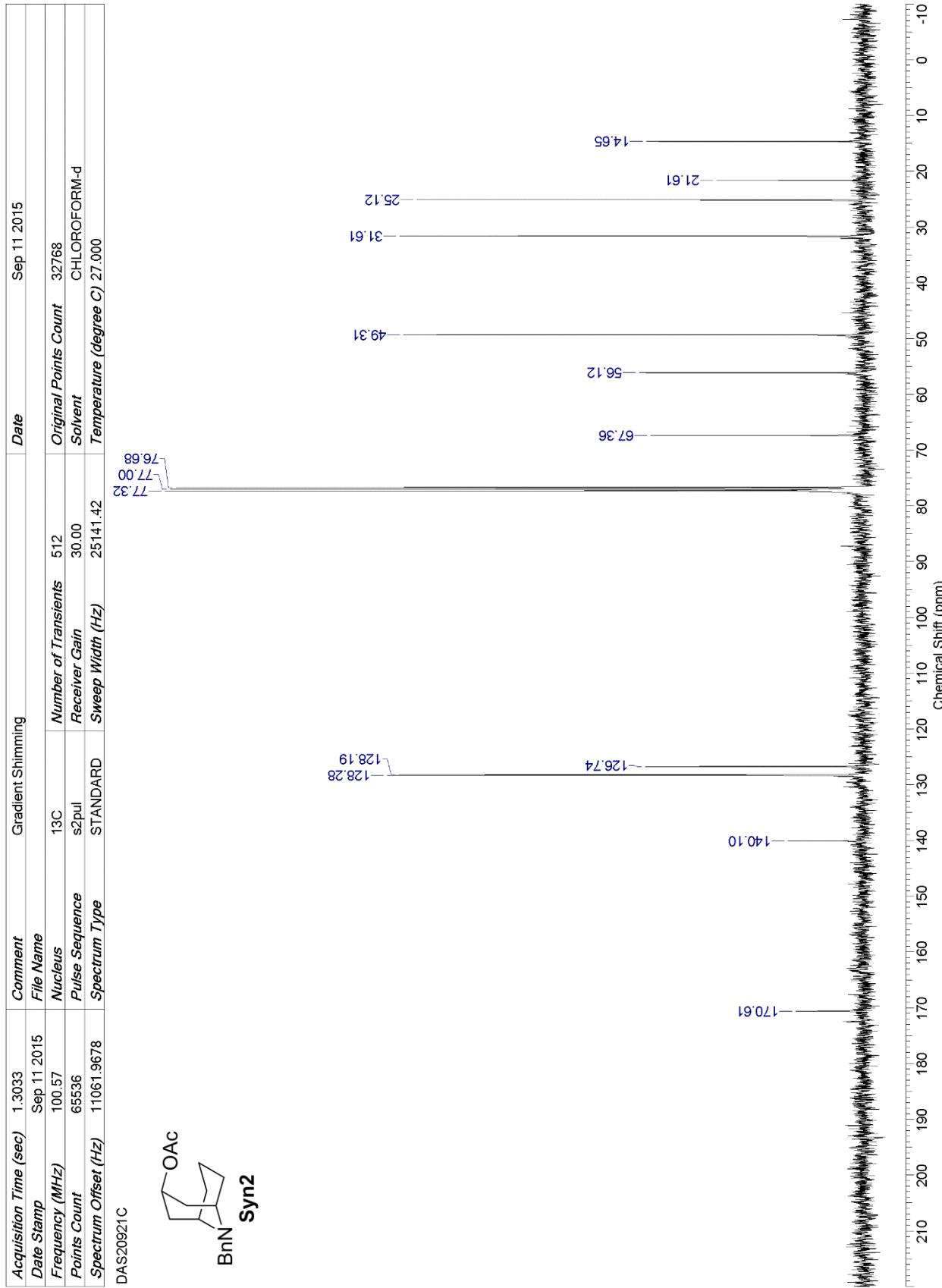


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DASS30491	20						









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