Supporting Information for:

Preparation, Structural Characterization and Thermochemistry of an Isolable 4-Aryl Phenoxyl Radical

Thomas R. Porter,[†] *Werner Kaminsky,*[†] *James M. Mayer*[*,†,§]

[†] Department of Chemistry, University of Washington, Box 351700, Seattle, WA, 98195-1700, United States.

[§] Department of Chemistry, Yale University, 225 Prospect St., New Haven, CT, 06520-8107, United States.

[*] james.mayer@yale.edu

Contents:

1. ^{1}H NMR of ^{t}Bu$_2$NPArO$^\bullet$ in Acetonitrile-d_3

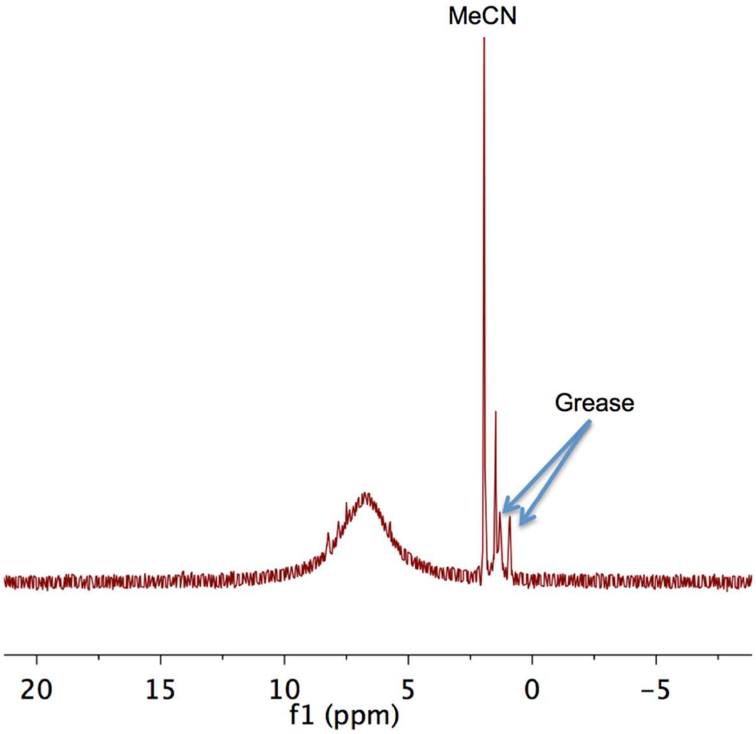
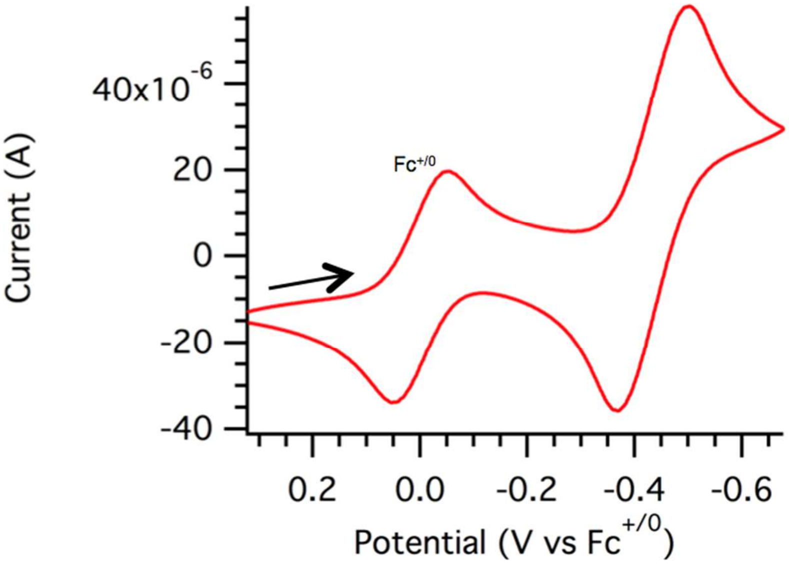


Figure S1. The ^{1}H NMR spectrum of ^{t}Bu$_2$NPArO$^\bullet$ in MeCN-d_3 shows the presence of only minor diamagnetic impurities.

2. Cyclic Voltammograms of ^{t}Bu$_2$NPArO$^\bullet$ and ^{t}Bu$_2$NPArOH in MeCN

Cyclic voltammetry of both ^{t}Bu$_2$NPArO$^\bullet$ and ^{t}Bu$_2$NPArOH (~2-3 mM) was preformed in MeCN with 0.1 M [^{n}Bu$_4$N][PF$_6$] supporting electrolyte and a ferrocene internal standard (~1 mM). Scan rates used were 100 mV/s. Data was collected in a N_2 filled glovebox. The electrochemical setup consisted of a glassy carbon working electrode, silver pseudo-reference electrode and a platinum auxiliary electrode. Values reported are referenced to the ferrocene/ferrocenium couple.



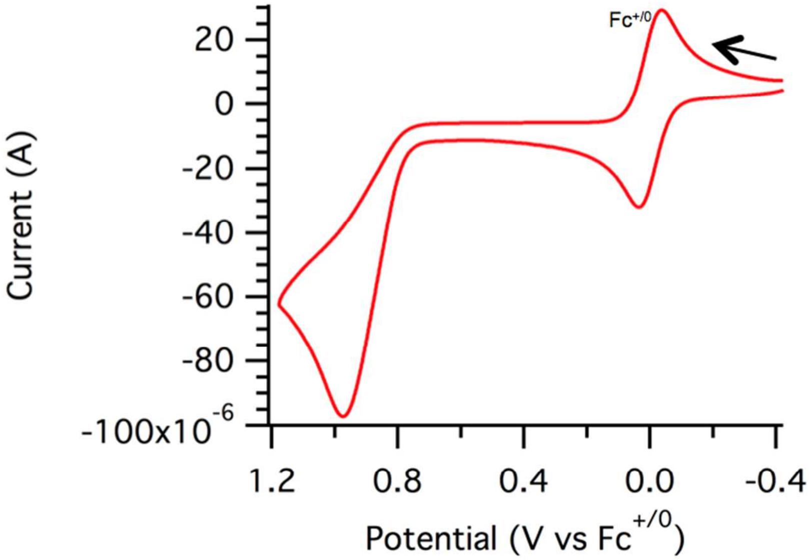


Figure S2. Cyclic voltammogram of ^{t}Bu$_2$NPArO$^\bullet$ (top) and ^{t}Bu$_2$NPArOH (bottom) in MeCN.

3. ^{1}H NMR equilibrium studies to determine ^{t}Bu$_2$NPArO-H BDFE

NMR tubes were prepared containing 5.1 mM ^{t}Bu$_2$NPArOH and various concentrations of ^{t}Bu$_3$ArO$^\bullet$ radical (1.3-20.4 mM). Equilibrium was reached rapidly as was evident by a rapid color change in the solution. Concentrations were determined by ^{1}H NMR integrations assuming mass balance in diamagnetic products ([^{t}Bu$_3$ArOH] + [^{t}Bu$_2$NPArOH] = 5.1 mM). The concentration of ^{t}Bu$_3$ArO$^\bullet$ was calculated using mass balance assumptions: $[{}^t\text{Bu}_3\text{ArO}^\bullet]_{eq} = [{}^t\text{Bu}_3\text{ArO}^\bullet]_0 - [{}^t\text{Bu}_3\text{ArOH}]_0$. Concentrations of ^{t}Bu$_2$NPArO$^\bullet$ were also calculated using mass balance assumptions: $[{}^t\text{Bu}_2\text{NPArO}^\bullet]_{eq} = 5.1\text{ mM} - [{}^t\text{Bu}_3\text{ArOH}]_{eq}$. This procedure was preformed in both toluene-d_8 and acetonitrile-d_3.

Equilibrium concentrations are possible to measure by ^{1}H NMR because the ArO$^\bullet$ + ArOH exchange rates are quite slow. Reported self exchange rates of ^{t}Bu$_3$ArO($^\bullet$/H) are slow in both acetonitrile ($k_{XH/X^\bullet} = 20 \pm 3$ M^{-1} s^{-1})[1] and benzene ($k_{XH/X^\bullet} = 95 \pm 14$ M^{-1} s^{-1}).[1] For the reactions discussed here, the chemical shift difference in toluene between the O–H resonances of ^{t}Bu$_2$NPArO–H and ^{t}Bu$_3$ArO–H is δ 0.27, which is 135 Hz on the 500 MHz instrument used here. Peak coalescence for these resonances would be expected to occur when the exchange rate is equal to roughly 300 M^{-1} s^{-1} from $k = \Delta\nu(\pi/\sqrt{2})$.[2] In this system, it is apparent the exchange rate must be slower than this because distinct O–H peaks are observed.

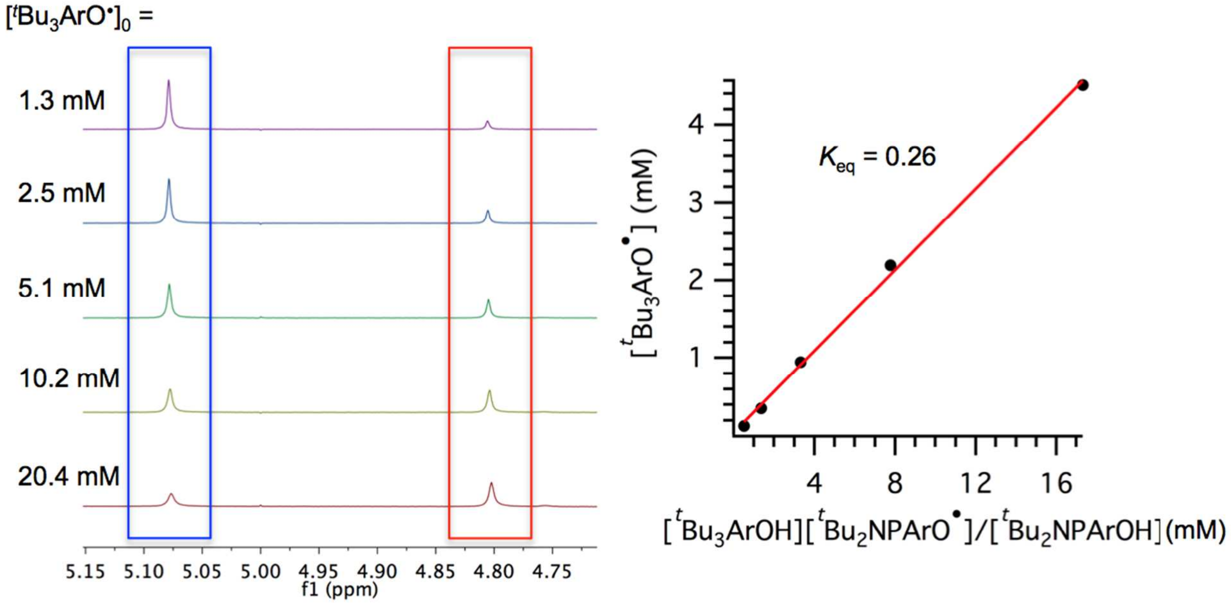


Figure S3. ^{1}H NMR spectra of equilibrium studies between ^{t}Bu$_2$NPArOH and ^{t}Bu$_3$ArO$^\bullet$. The blue box surrounds the phenolic O-H signals of ^{t}Bu$_2$NPArOH and the red box the phenolic O-H signal of ^{t}Bu$_3$ArOH. The plotted equilibrium data is shown in the graph on the right.

(1) Warren, J. J.; Mayer, J. M. *Proc. Natl. Acad. Sci.* **2010**, 107, 5282.
(2) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, NY, 1982.

4. Phenolic O-H BDFE vs. EPR $a_{3,5}$ correlation details

Pedulli and co-workers have reported an empirical correlation between substituted 2,6-^{t}Bu-4-X-phenol BDFEs and the hyperfine coupling constants of the corresponding radical arising from the 3,5 aromatic protons ($a_{3,5}$).[3] The correlation holds for nearly all phenols examined with the exception of X= -OMe -SMe, and –CH=CHPh.[4] The table below provides the numerical data (taken from reference 3) for the graph provided in the main text. Pedulli reports O-H bond strengths as bond dissociation enthalpies (BDEs) that are obtained from equilibrium EPR measurements with ^{t}Bu$_3$ArO$^•$ radical. Since these equilibrium measurements are free energies, it is it is at least as appropriate to use then to derive relative BDFEs. The absolute BDFEs are then derived using the reported solution phase BDFE of ^{t}Bu$_3$ArO-H in benzene, 76.7 kcal mol^{-1} [5] (taken to be the same as in toluene).

-X substituent	$a_{3,5}$	BDFE (C_6H_6) (kcal mol^{-1})
-NO_2	2.23	80.40
-COOH	2.16	79.73
-COOMe	2.14	79.56
-CHO	2.10	79.69
-CN	2.17	79.70
-H	1.95	78.06
-Cl	1.87	77.87
-Ph	1.73	76.70
-^{t}Bu	1.71	76.70
-Me	1.67	76.48
-SMe	1.39	76.49
-CH=CHPh[4]	1.55	74.36
-OMe	0.93	73.77

(3) Brigati, G.; Lucarini, M.; Mugnaini, V.; Pedulli, G. F. *J. Org. Chem.* **2002**, *67*, 4828.

(4) The $a_{3,5}$ and BDE/BDFE values reported for –CH=CHPh are somewhat ambiguous since in ref. 3 these values do not match between the text and figures.

(5) Warren, J. J.; Tronic, T. T.; Mayer, J. M. *Chem. Rev.* **2010**, *110*, 6961.

5. Determination of the molar extinction coefficient of $^{t}\mathrm{Bu_2NPArO^{\bullet}}$

The molar extinction coefficient (ε) of $^{t}\mathrm{Bu_2NPArO^{\bullet}}$ at 625 and 480 nm was determined in both MeCN and toluene using Beer's law plots with 4 different concentrations of $^{t}\mathrm{Bu_2NPArO^{\bullet}}$: ε_{625}(MeCN) = 495 ± 25 $\mathrm{M^{-1}\ cm^{-1}}$, ε_{480}(MeCN) = 510 ± 25 $\mathrm{M^{-1}\ cm^{-1}}$; ε_{625}(toluene) = 520 ± 25 $\mathrm{M^{-1}\ cm^{-1}}$, ε_{480}(MeCN) = 505± 25 $\mathrm{M^{-1}\ cm^{-1}}$.

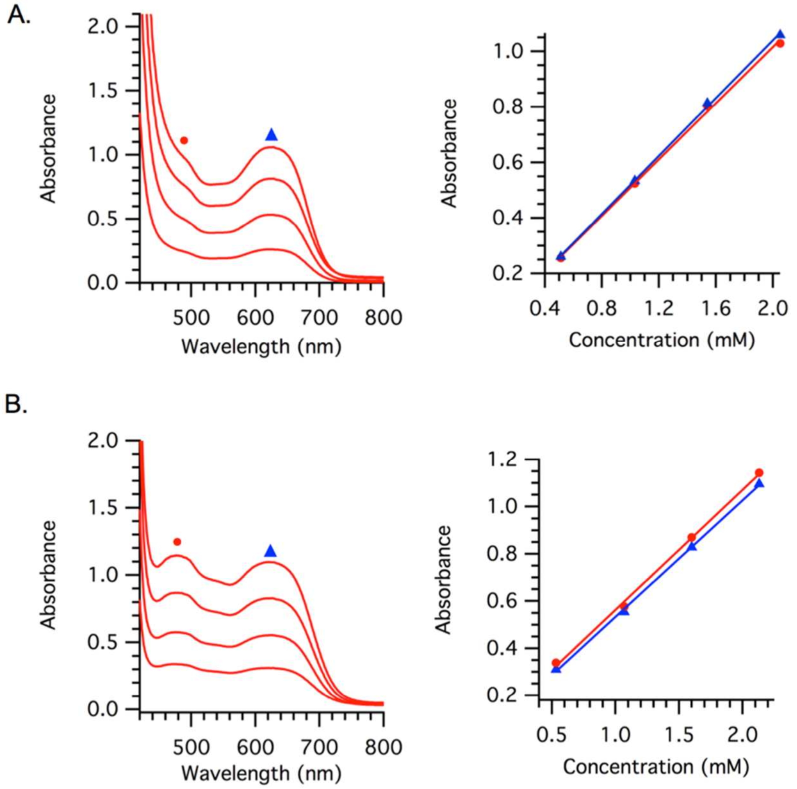


Figure S4. Spectra of $^{t}\mathrm{Bu_2NPArO^{\bullet}}$ at multiple concentrations and corresponding Beer's Law plots in (A) toluene and (B) MeCN.

While the ε values at both 625 and 480 nm were similar in MeCN and toluene, there is a higher energy absorbance band (*ca.* 400 nm) that displays solvatochromatic behavior. This band is observed at a lower energy in toluene than in MeCN. To confirm this difference in optical spectra was solvent related and not related to decomposition, a cuvette with a 180° Schlenk adapter was filled with $^{t}\mathrm{Bu_2NPArO^{\bullet}}$, ~2 mM in toluene and the optical spectrum was collected. The solvent was then removed *in vacuo* and the residual solid was redissolved in MeCN and the optical spectrum was collected and in agreement with previous MeCN spectra collected. Removal of the MeCN *in vacuo* and redissolution in toluene yielded the same spectrum initially observed.

6. Crystallographic details for $^{t}Bu_2NPArO^{\bullet}$

General Procedure

A black piece, measuring 0.40 x 0.10 x 0.01 mm^3 was mounted on a loop with oil. Data was collected at -173°C on a Bruker APEX II single crystal X-ray diffractometer, Mo-radiation.

Crystal-to-detector distance was 40 mm and exposure time was 60 seconds per frame for all sets. The scan width was 0.5°. Data collection was 100% complete to 25° in ϑ. A total of 116007 reflections were collected covering the indices, h = -16 to 16, k = -17 to 17, l = -29 to 29. 4383 reflections were symmetry independent and the R_{int} = 0.0472 indicated that the data was of good quality. Indexing and unit cell refinement indicated a primitive orthorhombic lattice. The space group was found to be P b c a (No. 61).

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

Solution by direct methods (SHELXS, SIR97) produced a complete heavy atom phasing model consistent with the proposed structure. The structure was completed by difference Fourier synthesis with SHELXL97. Scattering factors are from Waasmair and Kirfel.[6] Hydrogen atoms were placed in geometrically idealised positions and constrained to ride on their parent atoms with C---H distances in the range 0.95-1.00 Angstrom. Isotropic thermal parameters U_{eq} were fixed such that they were 1.2U_{eq} of their parent atom Ueq for CH's and 1.5U_{eq} of their parent atom U_{eq} in case of methyl groups. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares.

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

Table S1: Crystallographic data for ^{t}Bu$_2$NPArO$^{\bullet}$.

Empirical formula	C20 H24 N O3	
Formula weight	326.40	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 12.0741(8) Å	□= 90°.
	b = 13.1671(8) Å	□= 90°.
	c = 22.1093(14) Å	□ = 90°.
Volume	3515.0(4) Å^3	
Z	8	
Density (calculated)	1.234 Mg/m^3	
Absorption coefficient	0.082 mm^{-1}	
F(000)	1400	
Crystal size	0.40 x 0.10 x 0.01 mm^3	
Theta range for data collection	2.47 to 28.37°.	
Index ranges	-16<=h<=16, -17<=k<=17, -29<=l<=29	
Reflections collected	116007	
Independent reflections	4383 [R(int) = 0.0472]	
Completeness to theta = 25.00°	100.0 %	
Max. and min. transmission	0.9992 and 0.9678	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4383 / 0 / 223	
Goodness-of-fit on F^2	1.008	
Final R indices [I>2sigma(I)]	R1 = 0.0398, wR2 = 0.1022	
R indices (all data)	R1 = 0.0571, wR2 = 0.1124	
Largest diff. peak and hole	0.366 and -0.191 e.Å^{-3}	

7. Crystallographic details for ^{t}Bu$_2$NPArOH

General Procedure

A yellow piece, measuring 0.60 x 0.20 x 0.10 mm^3 was mounted on a loop with oil. Data was collected at -173^{o}C on a Bruker APEX II single crystal X-ray diffractometer, Mo-radiation.

Crystal-to-detector distance was 40 mm and exposure time was 10 seconds per frame for all sets. The scan width was 0.5^o. Data collection was 100% complete to 25^o in ϑ. A total of 59096 reflections were collected covering the indices, h = -15 to 15, k = -13 to 13, l = -20 to 20. 4313 reflections were symmetry independent and the R_{int} = 0.0297 indicated that the data was of good quality. Indexing and unit cell refinement indicated a primitive monoclinic lattice. The space group was found to be P 2_1/n (No. 14).

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

Solution by direct methods (SHELXS, SIR97) produced a complete heavy atom phasing model consistent with the proposed structure. The structure was completed by difference Fourier synthesis with SHELXL97. Scattering factors are from Waasmair and Kirfel.[6] Hydrogen atoms were placed in geometrically idealised positions and constrained to ride on their parent atoms with C---H distances in the range 0.95-1.00 Angstrom. Isotropic thermal parameters U_{eq} were fixed such that they were 1.2U_{eq} of their parent atom Ueq for CH's and 1.5U_{eq} of their parent atom U_{eq} in case of methyl groups. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares.

The hydroxyl-hydrogen seems to be disordered, with the dominating geometry refined.

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

Table S2: Crystallographic data for ^{t}Bu$_2$NPArOH.

Empirical formula	C20 H25 N O3	
Formula weight	327.41	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2_1/n	
Unit cell dimensions	a = 11.2752(4) Å	α= 90°.
	b = 10.1733(4) Å	β= 94.113(2)°.
	c = 15.1181(5) Å	γ = 90°.
Volume	1729.67(11) Å^3	
Z	4	
Density (calculated)	1.257 Mg/m^3	
Absorption coefficient	0.084 mm^{-1}	
F(000)	704	
Crystal size	0.60 x 0.20 x 0.10 mm^3	
Theta range for data collection	2.18 to 28.38°.	
Index ranges	-15<=h<=15, -13<=k<=13, -20<=l<=20	
Reflections collected	59096	
Independent reflections	4313 [R(int) = 0.0297]	
Completeness to theta = 25.00°	100.0 %	
Max. and min. transmission	0.9917 and 0.9514	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4313 / 1 / 227	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0364, wR2 = 0.0970	
R indices (all data)	R1 = 0.0454, wR2 = 0.1040	
Largest diff. peak and hole	0.362 and -0.233 e.Å^{-3}	

8. ORTEP of ^{t}Bu$_2$NPArOH

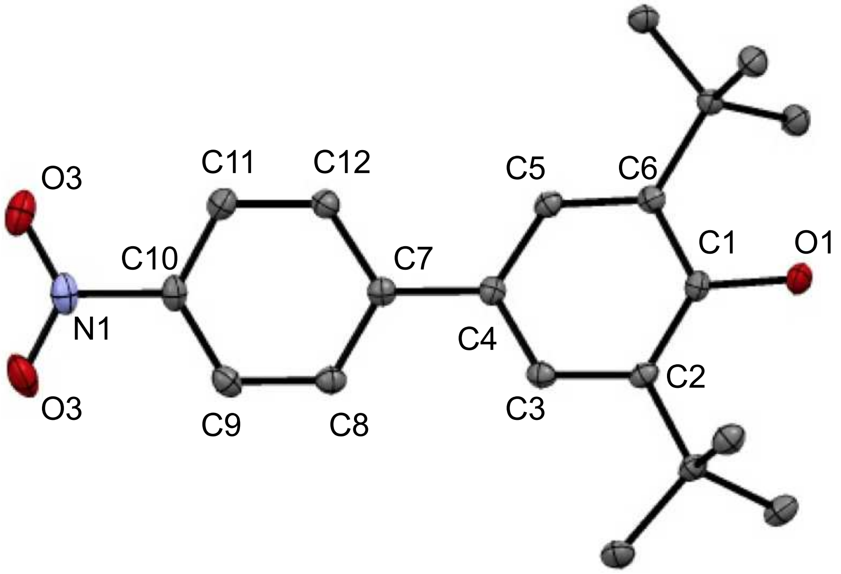


Figure S5. ORTEP of ^{t}Bu$_2$NPArOH showing 50% probability thermal ellipsoids and labels for select atoms. Hydrogen atoms are omitted for clarity.