Supplementary Information for

Mechanism of phenol oxidation by heterodinuclear Ni Cu bis(μ-oxo) complexes involving nucleophilic oxo groups

Subrata Kundu,[§a] Enrico Miceli,[§a] Erik R. Farquhar,[b] and Kallol Ray*[a]

[a]Humboldt–Universität zu Berlin, Institut für Chemie, Brook–Taylor–Straße 2, D–12489 Berlin, Germany;

[b]Case Western Reserve University Center for Synchrotron Biosciences and Center for Proteomics and Bioinformatics, National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY–11973, USA.

§ These two authors contributed equally to the work.

* kallol.ray@chemie.hu-berlin.de

Experimental Section

1. Materials

All chemicals were purchased from Sigma-Aldrich, Acros, ABCR, TCI and used without further purification unless otherwise mentioned. $^{18}O_2$ (97 atom %) was purchased from Sigma-Aldrich. ^{16}O-^{18}O was generated by following previously reported procedure.[1] Anhydrous solvents (dichloromethane, acetone, *n*-hexane) were purchased from Carl-Roth GmbH ($\geq$ 99.5%, < 50 ppm H_2O) and degassed by freeze-pump-thaw method prior to use. $[(MeAN)Cu^{I}]BF_4$,[2] $[L(Ni)O_2]$[2,3] , and $[(AN)Cu^{I}]BF_4$[4] complexes were prepared by following the previously published procedures.

2. Instrumentation and Physical methods

Preparation and handling of air sensitive materials were performed in a N_2 glove box OMNI-Lab 2 (VAC) with O_2 and moisture concentrations less than 1 ppm. ^1H NMR spectra were recorded either on a Bruker AV 400 NMR spectrometer or on a Bruker DPX 300 spectrometer. Elemental analyses were performed with a Leco CHNS-932 elemental analyser. UV-Vis spectra were recorded by Agilent 8453 diode array spectrometer connected with a cryostat from Unisoku Scientific Instruments, Japan. IR spectra were measured by preparation of KBr pellet of solid sample with Shimadzu FTIR-8400S spectrometer. rRaman spectra were measured at -92 °C (Bruker cryostat) with 413-nm excitation, by using a Horiba Jobin-Yvon LabRAM HR800 confocal Raman spectrometer.

E^{ox} values *vs* standard calomel electrode (SCE) were obtained from the literature,[5] except for 4-bromo-2,6-di-tert-butylphenol, whose potential was measured by cyclic voltammetry in dry CH_3CN using Bu_4NPF_6 as supporting electrolyte and ferrocene as an internal standard. The measurement was repeated three times and the results were averaged to get the E^{ox} value. The potential against ferrocene was then corrected to the value against SCE by adding +0.40 V (standard potential of the Fc/Fc^+ couple against SCE).[6]

X-band EPR derivative spectra at 10 K were recorded on a Bruker ELEXSYS E500 spectrometer equipped with the Bruker dual-mode cavity (ER4116DM) and a Helium flow cryostat (Oxford Instrument ESR 910). Microwave frequencies were calibrated with a Hewlett-Packard frequency counter(HP5352B), and field control was calibrated with a Bruker NMR field probe (ER035M). X-band EPR spectra at 77 K were routinely measured on a spectrometer *ERS-300* (ZWG, Magnettech Berlin/Adlershof), which was equipped with a fused quartz Dewar for the measurements at liquid nitrogen temperature. The *g*-factors for the second derivative spectra were calculated with respect to an external reference of Cr^{3+}/MgO with *g*-factor of 1.9796. For spin quantification, the EPR spectra of complex **2**, and phenoxyl radical were integrated twice to obtain the area under the signal. A strong pitch (0.11% pitch in KCl) external standard was used to quantify the $S = 1/2$ signals.

XANES data at the Cu- and Ni-*K* edges were collected at beamline X3B of the National Synchrotron Lightsource (Brookhaven National Laboratory, Upton, NY, USA). A sagitally focusing Si(111) monochromator was used for energy selection, while a cylindrically-bent nickel-coated mirror located downstream of the monochromator provided vertical focusing and harmonic rejection. Sample temperatures were maintained at approximately 20 K using a He Displex cryostat. For Cu data, a Ni and Cu metal foils were used for internal energy calibration, with the first inflection point of the reference foil edge set to 8331.6 eV for Ni and 8979.0 eV for Cu. The Ni datasets have been referenced to a Ni metal foil energy of 8331.6 eV. XANES data were collected as fluorescence spectra using a 31 element solid state germanium detector (Canberra), over an energy range of 8779 – 9540 eV for Cu and 8133 – 9090 eV for Ni. Co (for Ni *K*-edge) or Ni (for Cu *K*-edge) filters of 3 absorption lengths were used to reduce scatter and maintain detector linearity. Samples were monitored for photoreduction during data collection (based upon red-shifts in the absorption edge), and typically only two scans were collected at a given position on the sample. Tandem Mossbauer/XAS cups with a sample window of ~6 mm x 10 mm were used to provide at least 5 independent beam spots on each sample. No significant photoreduction was observed at either edge, so all scans were included in the averaged data. Averaging and normalization of the XAS data was performed using Athena, a graphical implementation of the IFEFFIT package.[7]

3. Synthesis, Reactivity, and Spectroscopy

Synthesis of 2: The colorless solution of $[(AN)Cu^I]BF_4$ in anhydrous CH_2Cl_2 (2 mL; 0.2 mM) was cooled to -90 ^oC. Then one equivalent of $[L(Ni)O_2]$ in anhydrous CH_2Cl_2 (0.2 mL) was added, to yield deep orange-brown intermediate **2**. The generation of the deep orange-brown species **2** was monitored by the growth of 895 nm band in the UV-Vis spectrum.

In case of second order rate constant (k_2) determinations, the concentration of **2** starting solutions were in between 0.1 mM to 0.2 mM. The concentration of rRaman and XAS samples were in between 8 mM to 10 mM.

Synthesis of 2-$^{18}O_2$: 2-$^{18}O_2$ was synthesized by exposing the solution of ß-diketiminato-(toluene)nickel(I) complex in toluene to $^{18}O_2$ as mentioned in literature.[2,3] Then one equivalent of $[L(Ni)(^{18}O)_2]$ in anhydrous CH_2Cl_2 was added to the pre-cooled solution of $[(AN)Cu^I]BF_4$ in anhydrous CH_2Cl_2 at -90 ^oC, to yield deep orange-brown intermediate **2-$^{18}O_2$**.

Synthesis of 2-$^{16}O^{18}O$: After exposing the solution of the ß-diketiminato-(toluene)nickel(I) complex in toluene to the dry gas mixture containing $^{16}O_2$,$^{16}O^{18}O$,$^{18}O_2$ (1:2:1) lead to the change of the color from red to green. Then the reaction mixture was dried under vacuum to yield $[L(Ni)(^{18}O^{16}O)]$ as greenish powder. Then one equivalent of $[L(Ni)(^{18}O^{16}O)]$ in anhydrous CH_2Cl_2 was added to the pre-cooled solution of $[(AN)Cu^I]BF_4$ in anhydrous CH_2Cl_2 at -90 ^oC, to yield deep orange-brown intermediate **2-$^{16}O^{18}O$**.

Synthesis of mono-deuterated 2,4-di-tert-butylphenol: 150 mg of recrystallized 2,4-di-tert-butylphenol was dissolved in 1 mL CH_3CH_2OD under inert atmosphere. 1 h stirring and vacuum drying of the solution affords a white powder. Formation of the mono-deuterated product was evidenced by the absence of the characteristic O-H peak at $\delta = 4.58$ ppm in the ^1H-NMR spectrum. The whole procedure was repeated twice, to give a final deuteration of > 90%.

Mono-deuterated 4-Phenoxyphenol was synthesized similarly.

Determination of k_2: The reactivity studies of **1** and **2** were done at -50 – -90 °C, under inert atmosphere, by injecting the CH_2Cl_2 solution of the substrate (10-200 equivalents) to the preformed solution of **1** or **2** in CH_2Cl_2. 4-phenylphenol and 4-phenoxyphenol were dissolved in acetone. The pseudo-first order decay of 895 nm band was monitored by acquiring an UV-Vis spectrum in every 0.5-10 seconds. The pseudo-first order fitting of the decay curves yielded the rate constants (k_{obs}) which were found to be linearly increasing with the increment of substrate concentrations. The slope of the rate constant (k_{obs}) *vs* substrate concentration fitting plot provided the second order rate constants (k_2).

Product analysis: 2,4,6-tri-*tert*-butyl-phenol was added to the preformed solution of **1** or **2** at -50 – -90 °C, under inert atmosphere. Then the progress of the reaction was followed by a time-resolved UV-Vis spectrometer and after the completion of reaction, the resultant reaction mixture was analyzed by

EPR (77 K). The EPR signal at *g* ≈ 2 for 2,4,6-tri-*tert*-butyl-phenoxyl radical was quantified by using pitch (0.11% pitch in KCl) as an external standard.

After the phenol oxidation, the reaction mixtures were analyzed by GC-MS, ^{1}H-NMR. Before the product analysis, to remove the metal complex, the solution at the end of each reaction was filtered over silica gel and eluted with ethyl acetate. The ethyl acetate solution was then analyzed by GC-MS.

The final decay solutions of **1** or **2**, in presence of phenols, are found to exhibit *S=1/2* signal with typical Cu^{II} hyperfines.

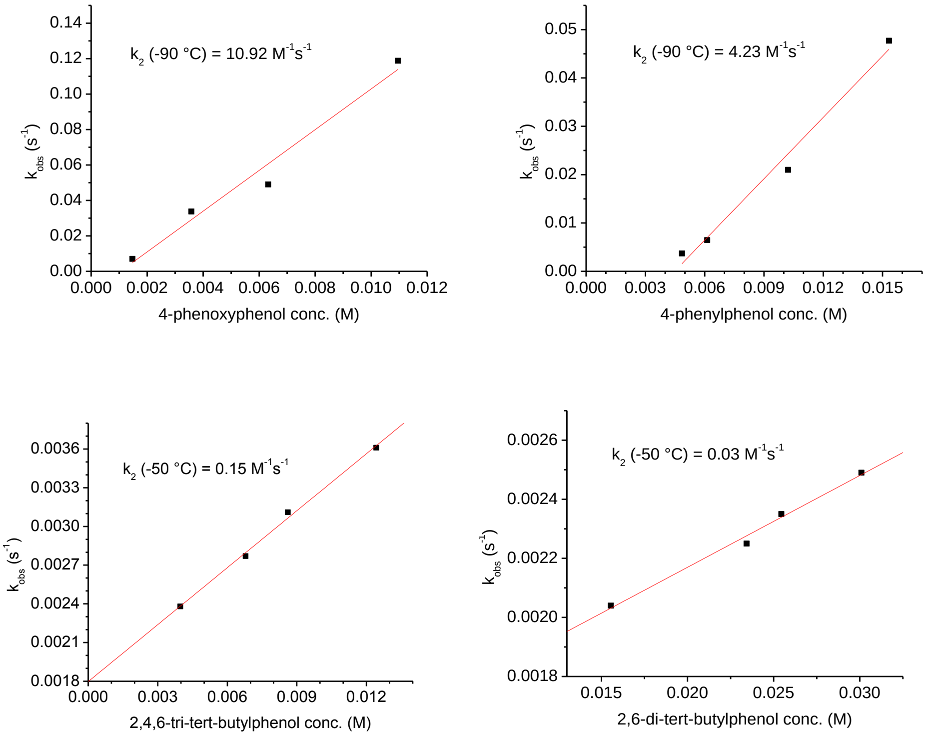

Figure S1: Linear dependence of k_{obs} on the concentration of substituted phenols reacting with **1** (0.2 mM in CH_2Cl_2) at the temperature specified in the plots. The slope of the linear fit corresponds to the k_2 value.

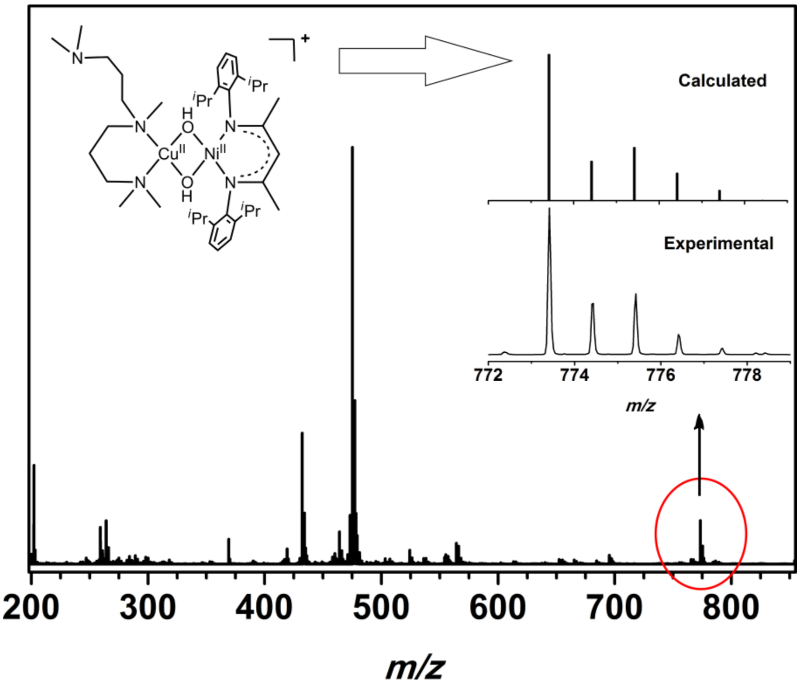

Figure S2: ESI-MS spectra of the resultant solution obtained after the reaction of **1** (in CH_2Cl_2) with 2,4-di-*tert*-butylphenol at -90 °C. Insets show the experimental and calculated mass and isotope distribution pattern of 773.414 peak, which is consistent with the formulation of $[(MeAN)Cu^{III}(\mu\text{-}OH)_2Ni^{III}L]^+$ (calculated $m/z = 773.418$).

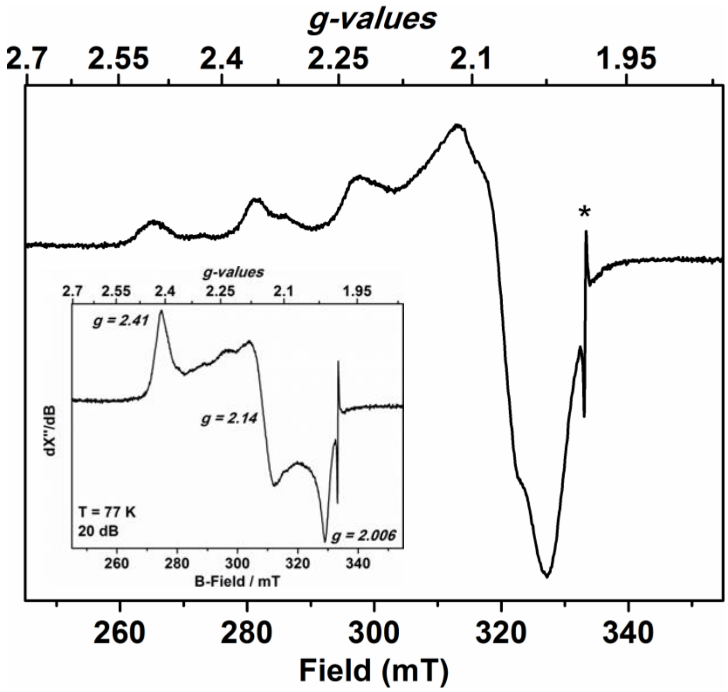

Figure S3: X-band EPR spectra (at 77 K) of the resultant solution obtained after the reaction of **1** (in CH_2Cl_2) with 2,4-di-*tert*-butylphenol at -90 °C. The signal marked by asterisks (*) comes from the MgO/Cr^{3+} reference with $g = 1.9796$. In the inset is given the EPR spectrum of **1**.

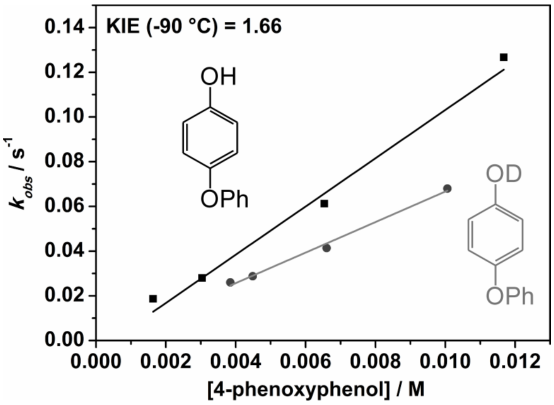

Figure S4: Determination of the k_2(O-H)/k_2(O-D) kinetic isotope effect for the reaction of **1** with 4-phenoxyphenol at -90 °C.

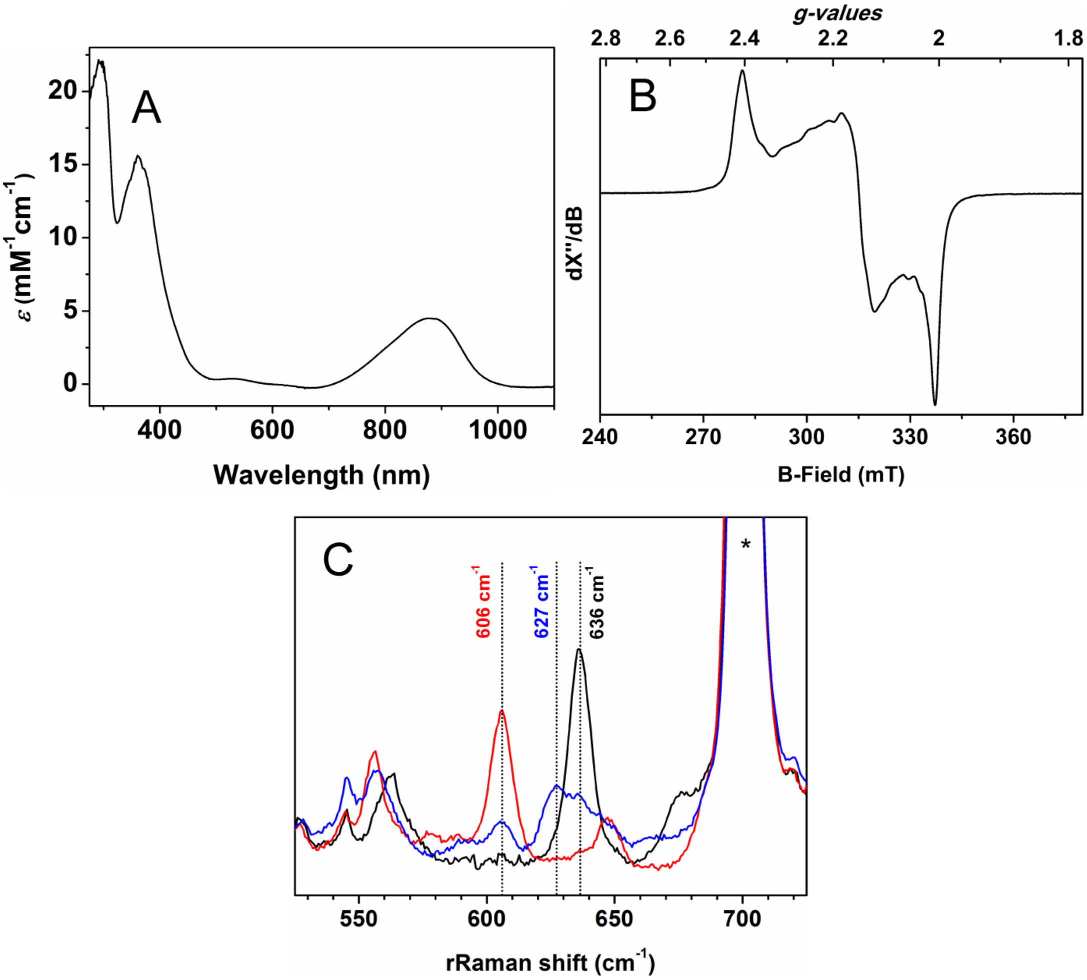

Figure S5: Spectroscopic characterization of **2**. (A) UV-Vis spectra in CH_2Cl_2 at -90 °C, (B) X-band EPR spectra in CH_2Cl_2 at 10 K, and (C) rRaman spectra (413 nm laser excitation) in CH_2Cl_2 at -90 °C [**2**-$^{16}O^{16}O$ (black trace), **2**-$^{18}O^{18}O$ (red trace), and **2**-$^{16}O^{18}O$ (blue trace). Bands originating from the solvent are marked by asterisks]. The spectroscopic features of **2** are near-identical to that of what we reported previously[2] for **1**; hence we avoid a detailed description in this manuscript.

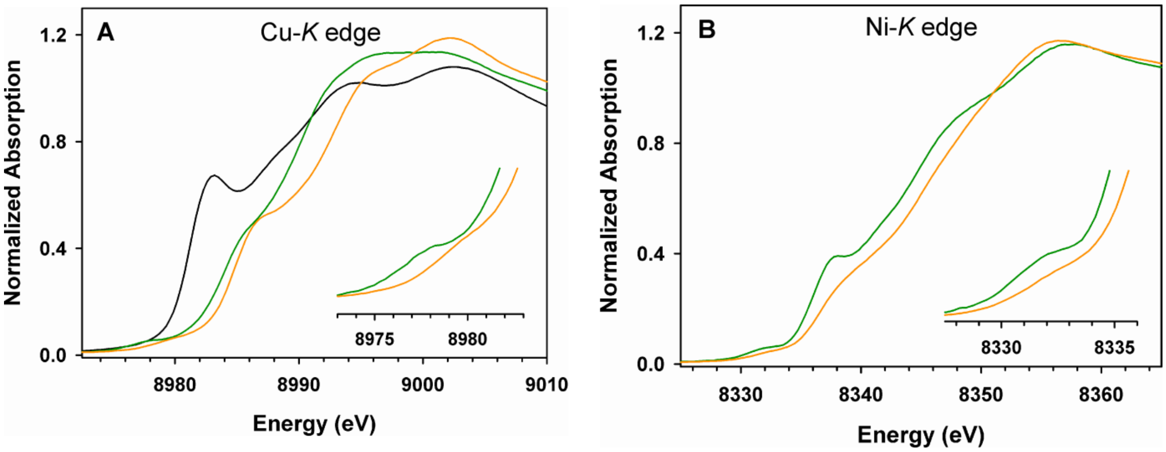

Figure S6: XAS spectra of **2**. (A) Cu-*K* edge spectra of $[(AN)Cu^{I}](BF_4)$ (black trace), $[(AN)Cu^{II}NTs](BF_4)$[4] (green trace), and **2** (orange trace); (B) Ni-*K* edge spectra of $LNi^{II}O_2$ (green trace), and **2** (orange trace). The spectroscopic features of **2** are near-identical to that of what we reported previously[2] for **1**; hence we avoid a detailed description in this manuscript.

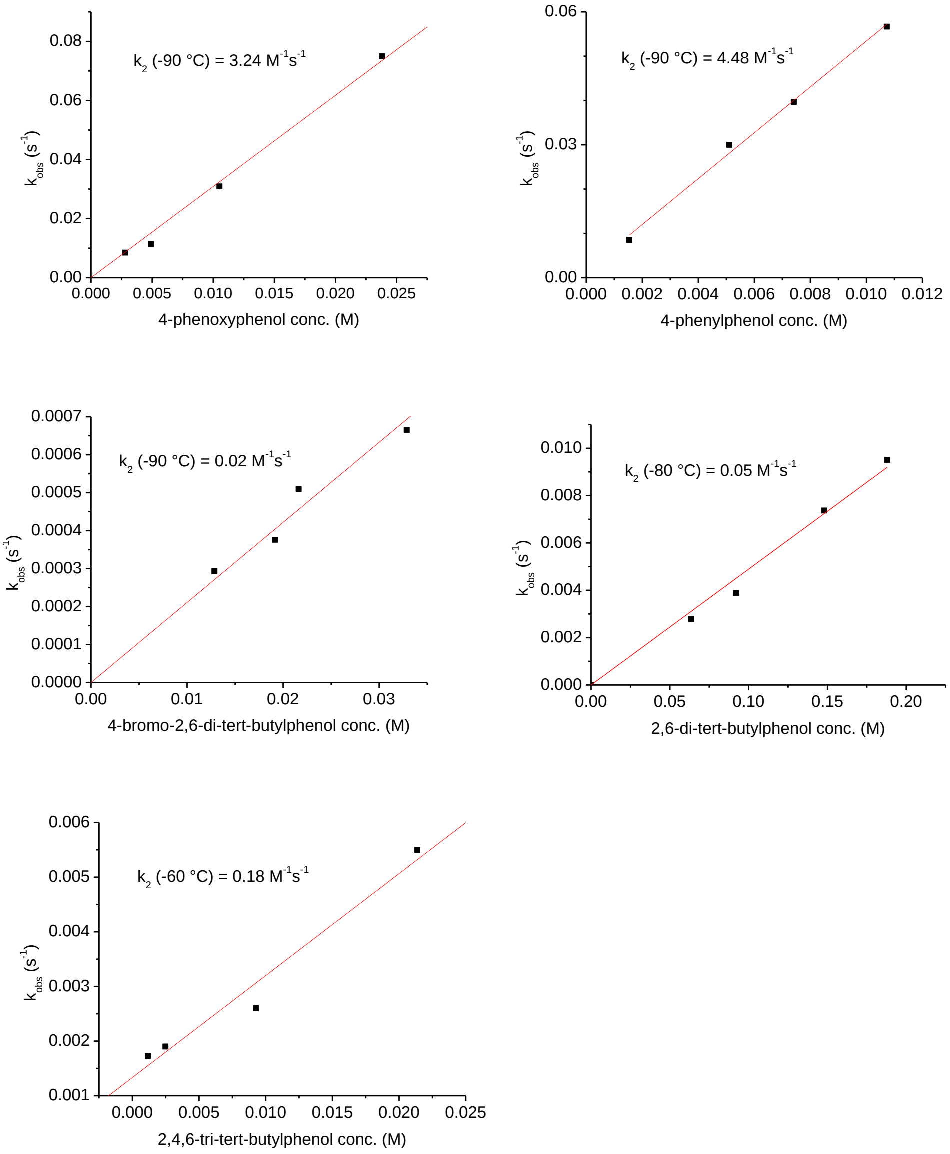

Figure S7: Linear dependence of k_{obs} on the concentration of substituted phenols reacting with **2** (0.2 mM in CH_2Cl_2) at the temperature specified in the plots. The slope of the linear fit corresponds to the k_2 value.

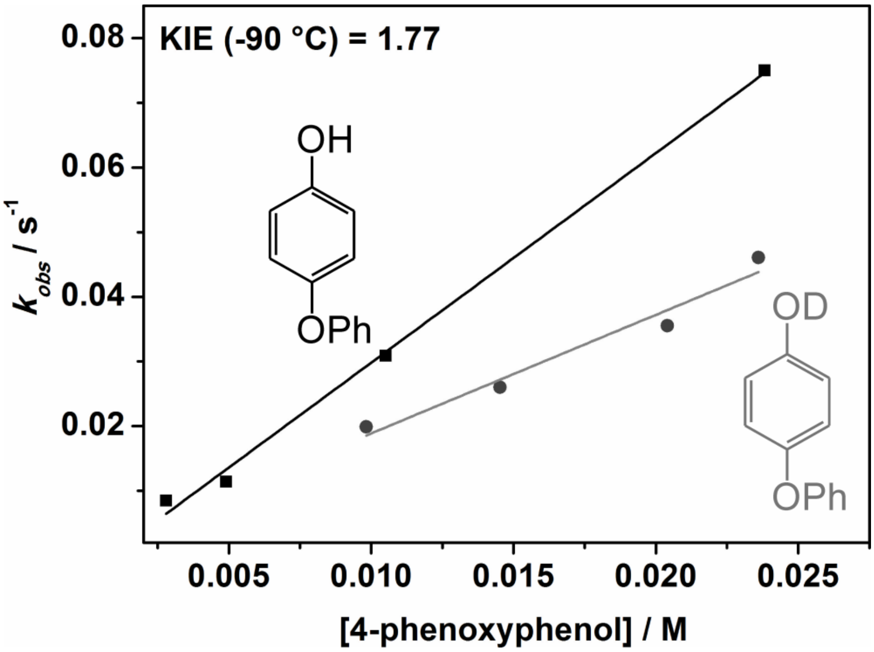

Figure S8: Determination of the k_2(O-H)/k_2(O-D) kinetic isotope effect for the reaction of **2** with 4-phenoxyphenol at -90 °C.

References for supplementary information:

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