

Supporting Information
for
The Reactivity of Phthalimide *N*-Oxyl Radical (PINO) towards Phenolic O-H
Bond. A Kinetic Study

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Instrumentation

^1H NMR and ^{13}C NMR spectra were recorded with a 300 MHz NMR spectrometer in CDCl_3 .

UV-vis measurements were performed using a spectrophotometer equipped with a rapid kinetics accessory.

Materials

Solvents were of the highest grade commercially available and were used as received. NHPI, $\text{Pb}(\text{OAc})_4$ and all the phenols were commercial products and used without further purification.

Kinetic measurements

PINO was generated by the oxidation of NHPI (1 mM) with $\text{Pb}(\text{OAc})_4$ (0.15 mM) in CH_3CN containing 1 % AcOH, at 25 °C and under an argon atmosphere. A solution of the substrate was added into the PINO solution in the cuvette (substrate concentration in the range 0.6-5 mM) and the absorbance change was monitored at 380 nm. For the more reactive phenols (4-methylphenol and 4-phenylphenol) lower concentrations of substrates and reagents have been employed: phenol (0.1-0.6 mM), NHPI (0.4 mM) and $\text{Pb}(\text{OAc})_4$ (0.04 mM). For all the phenols investigated each kinetic trace obeyed a first-order kinetic.

The self decomposition of PINO, generated by the oxidation of NHPI (1 mM) with $\text{Pb}(\text{OAc})_4$ (0.5 mM) in CH_3CN , CCl_4 or HFP containing 1 % AcOH (at 25 °C under argon), followed a second-order kinetic and it was slow enough to allow the study the reaction of PINO with phenols.

The reaction of PINO with phenol was also studied in AcOH and in 1,1,1,3,3,3-hexafluoroisopropanol (HFP) and CCl_4 containing 1 % AcOH, using the following concentrations: phenol (0.1-0.6 mM), NHPI (0.4 mM) and $\text{Pb}(\text{OAc})_4$ (0.04 mM). Due to the high reactivity of PINO with phenol in HFP and CCl_4 only a lower limit value of k ($> 3 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$) could be given.

Reaction of PINO with 2-*tert*-butyl-4-methylphenol

An acetic acid solution of $\text{Pb}(\text{OAc})_4$ (0.1 mmol in 3 mL of AcOH) was added to 180 mL of CH_3CN . The mixture was degassed with argon then a solution of NHPI (0.4 mmol in 10 mL of CH_3CN) was added followed by a solution of 2-*tert*-butyl-4-methylphenol (0.4 mmol in 10 mL of CH_3CN). After the completion of the reaction, the solvent was removed under reduced pressure and the residue was purified by preparative TLC using hexane:ethyl acetate = 3:1 as eluent. The major product was identified by ^1H NMR, ^{13}C NMR and elemental analysis as the cross-coupling product **1** between PINO and the 2-*tert*-butyl-4-methylphenoxyl radical.

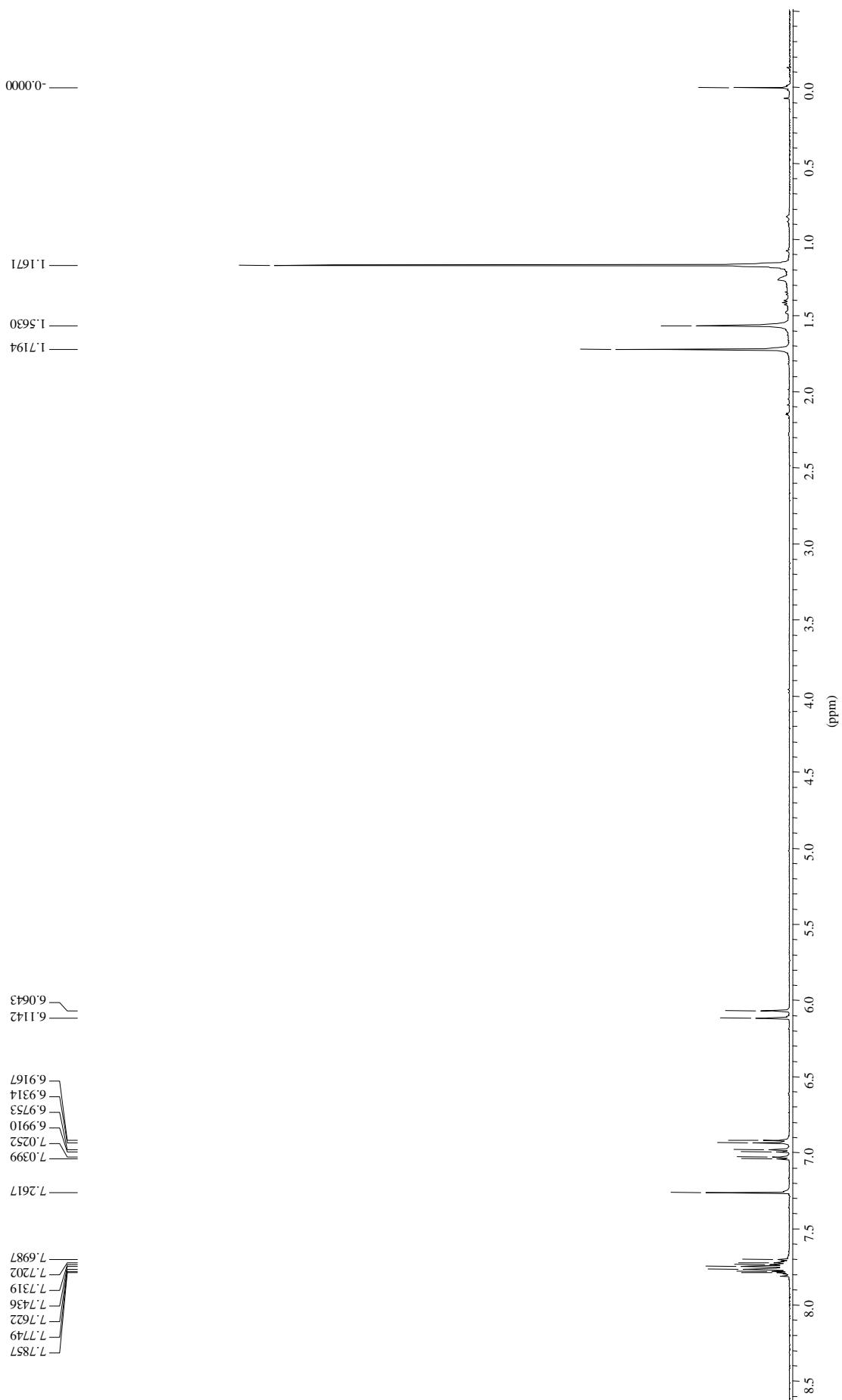
^1H NMR (CDCl_3 , 300 MHz) δ 1.17 (s, 9H), 1.72 (s, 3H), 6.10 (d, J = 10 Hz, 1H), 6.92 (s, J = 3 Hz, 1H), 7.01 (dd, J = 10 Hz and 3 Hz, 1H), 7.71-7.74 (m, 4H).

^{13}C NMR δ 23.9, 28.9, 34.6, 83.0, 123.6, 128.7, 132.3, 134.7, 141.3, 144.8, 147.3, 164.4, 185.4.

Anal. Calcd for $\text{C}_{19}\text{H}_{19}\text{NO}_4$: C, 70.14; H, 5.89; N, 4.31. Found: C, 70.01; H, 5.92; N, 4.21.

The ^1H NMR and ^{13}C NMR spectra of the isolated product are displayed in Page S4 and S5.

S4



S5

