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## Aerobic Oxidation of Olefins and Lignin Model Compounds Using Photogenerated Phthalimide-N-oxyl (PINO) Radical

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# oxyl (PINO) Radical

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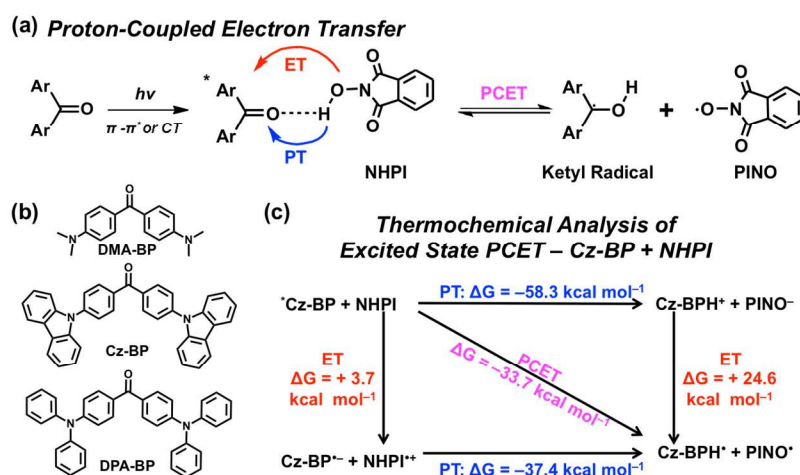
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3 ABSTRACT: A metal-free protocol to generate phthalimide-*N*-oxyl (PINO) radicals from *N*-  
4 hydroxyphthalimide (NHPI) via a photoinduced proton-coupled electron transfer (PCET) process  
5 is reported. Using donor-substituted aromatic ketones such as 4,4'-bis(diphenylamino)-  
6 benzophenone (DPA-BP), PINO radicals are efficiently produced and subsequently utilized to  
7 functionalize olefins to afford a new class of alkyl hydroperoxides. The DPA-BP/NHPI/O<sub>2</sub>  
8 photocatalytic system exhibits high efficiency toward the aerobic oxidation of  $\beta$ -O-4 lignin  
9 models.  
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## INTRODUCTION

One of the prominent challenges in organic synthesis is to develop efficient and inexpensive catalytic systems for selective oxidation of organic compounds under mild and environment-friendly conditions.<sup>1</sup> Using ubiquitous molecular oxygen in combination with organic nitroxyl radicals such as TEMPO (2,2,6,6-tetramethylpiperidine-*N*-oxyl)<sup>2</sup> or PINO (phthalimide-*N*-oxyl)<sup>3</sup> is a powerful catalytic approach toward sustainable aerobic oxidation.<sup>4</sup> However, the generation of short lived PINO radicals *in situ* from its parent hydroxylamine, *N*-hydroxyphthalimide (NHPI), often requires toxic metals such as Co<sup>II</sup>, Mn<sup>II</sup>, Pb<sup>IV</sup>, and V<sup>IV</sup>.<sup>5</sup> Although several metal-free processes have been reported,<sup>6</sup> using light as the clean and traceless reagent to photochemically activate NHPI has not been well studied and understood.<sup>7</sup> Herein, we report the use of donor-substituted aromatic ketones under the irradiation of a household fluorescent lamp to activate NHPI via a proton-coupled electron transfer (PCET) process. The resulting PINO radicals are further utilized for the aerobic oxidation of olefins and lignin model compounds.

Aromatic ketones such as benzophenone (BP) and its derivatives have been extensively studied for photochemical homolytic X-H (X = C, N, O) bond activation.<sup>8</sup> The underlining mechanism of this hydrogen abstraction reaction is highly dependent on the nature of the ketone's excited state ( $n,\pi^*$  or  $\pi,\pi^*/CT$ ; CT = charge transfer) and the hydrogen donor's ionization potential as well as the X-H bond dissociation energy (BDE). It was found that the rate of hydrogen abstraction of phenols, a popular hydrogen donor substrate due to its biological relevance,<sup>9</sup> is faster with ketones that exhibit the lowest  $\pi,\pi^*/CT$ . Leigh *et al.* attributed such favorable kinetics to a coupled electron/proton transfer that is facilitated by hydrogen-bonded exciplex formed between phenol and ketone.<sup>10</sup> Recently, Meyer, Wenger, and Dempsey, among others, further provided detailed kinetic parameters of this process using photoexcited *N*-containing

heterocyclic fluorophores as the hydrogen acceptor.<sup>11</sup> In view of the comparable thermochemical parameters of phenol ( $pK_a = 30.0$  in  $CH_3CN$  and  $E(PhOH^{+/0}) = 1.25$  V vs.  $Fc^{+/0}$ ,  $Fc$  = ferrocene) and NHPI ( $pK_a = 23.5$  in  $CH_3CN$  and  $E(NHPI^{+/0}) = 1.2$  V vs.  $Fc^{+/0}$ ),<sup>12</sup> we envisioned that the activation of NHPI may be facilitated by the photoexcited aromatic ketones with the lowest  $\pi,\pi^*/CT$  via PCET (Figure 1a). Figure 1b lists three donor-substituted benzophenones that exhibit lowest CT, namely, DMA-BP (4,4'-bis(dimethylamino)-benzophenone, also named as Michler's ketone), Cz-BP (4,4'-bis(9-carbazolyl)-benzophenone), and DPA-BP (4,4'-bis(diphenylamino)-benzophenone). A rough thermochemical analysis was performed for Cz-BP and provided supportive thermodynamic parameters for the hydrogen atom transfer (HAT) from NHPI (Figure 1c, see Supporting Information S-2 for details): electron transfer in both stepwise ET-PT (electron transfer-proton transfer) ( $\Delta G^\circ = +3.7$  kcal mol<sup>-1</sup>) and PT-ET ( $\Delta G^\circ = +24.6$  kcal mol<sup>-1</sup>) processes would likely encounter high-energy intermediates; in contrast, the PCET step ( $\Delta G^\circ = -33.7$  kcal mol<sup>-1</sup>) exhibits significantly more favorable thermochemical energetics to generate PINO radicals.



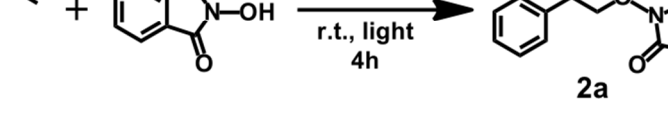
**Figure 1.** (a) Scheme of PCET from NHPI to an aromatic ketone. (b) Structures of DMA-BP, Cz-BP, and DPA-BP. (c) Thermochemical analysis of excited state PCET for Cz-BP and NHPI.

## RESULTS AND DISCUSSION

We first chose a stoichiometric addition reaction to test the feasibility and efficiency of photoinduced generation of PINO radicals.<sup>13</sup> It is known that in the presence of molecular oxygen PINO can be effectively trapped by olefins to form the 1,2-dioxygenated product<sup>13</sup> that can be potentially transformed into a variety of derivatives.<sup>14</sup> We examined the reaction of styrene (**1a**) with NHPI in MeCN in the presence of a ketone photocatalyst (2 mol %) and oxygen (1 atm) under the irradiation of a 26W white compact fluorescent lamp (CFL) for 4 h. To our delight, DPA-BP gave rise to the dioxygenated product hydroperoxide **2a** with an excellent yield (92%, Table 1, entry 1). Blue LED ( $\lambda_{\text{max}} = 465 \text{ nm}$ ) was also an effective light source for DPA-BP due to its considerable absorbance above 400 nm (Figure S1) albeit a longer reaction time (12 h) was required (Table 1, entry 2). Control experiments confirmed the essential role of light irradiation, oxygen, and the photocatalyst (entries 3-5). Cz-BP gave the essentially same yield as that of DPA-BP (90%, entry 6). Interestingly DMA-BP gave the lowest yield (12%, entry 7). <sup>1</sup>H NMR spectroscopy revealed a significant decomposition of DMA-BP (Supporting Information, Figure S9), possibly due to its reactive *N*-methyl C-H bond in the presence of PINO.<sup>15</sup>

Since hydrogen bonding (H-bond) between NHPI and the photo-excited ketone is essential for the proposed PCET process, solvents with strong hydrogen bonding ability (either as acceptors or donors) are expected to negatively affect the abstraction of hydrogen atom and subsequent reactions. Indeed, strong H-bond acceptors such as DMF and DMSO significantly compete with the ketone to form H-bond with NHPI and completely quenched the reaction (Supporting Information, Table S4, entry 2-3).<sup>16</sup> H-bond donors such as methanol also completely (in pure MeOH) or partially (in a solvent mixture of MeCN and MeOH, v:v=10:1) quenched the reaction

**Table 1.** Initial studies for the photo-induced dioxygenation of styrene.<sup>a</sup>



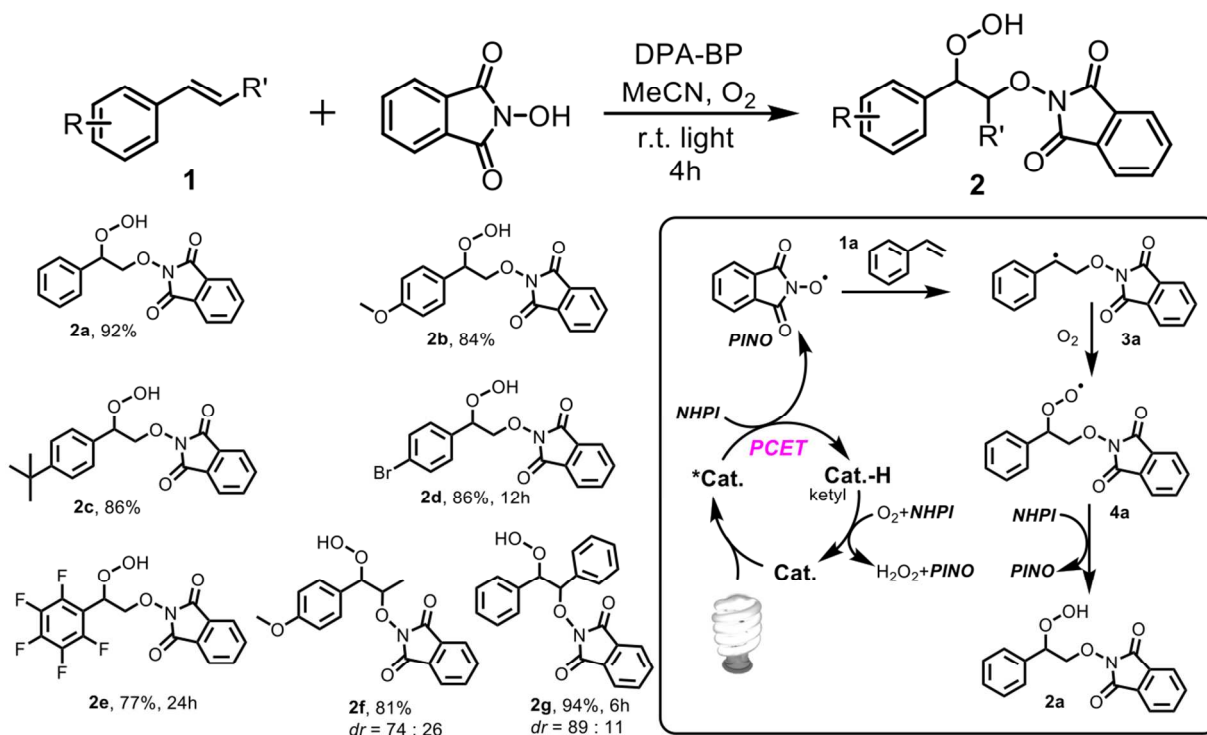
Reaction scheme showing the photo-induced dioxygenation of styrene (**1a**) with N-hydroxyphthalimide (NHPI) to form the cyclic peroxide product (**2a**). The reaction conditions are: Photocatalyst, MeCN, O<sub>2</sub>, r.t., light, 4h.

Entry	Photocatalyst	Yield (%) <sup>b</sup>
1	DPA-BP	92
2	DPA-BP	89 <sup>c</sup>
3	DPA-BP	No reaction <sup>d</sup>
4	DPA-BP	Trace <sup>e</sup>
5	None	Trace
6	Cz-BP	90
7	DMA-BP	12 <sup>f</sup>

<sup>a</sup>Reaction conditions: photocatalyst (2.0 mol %), styrene (52 mg, 0.5 mmol), NHPI (98 mg, 0.6 mmol), O<sub>2</sub> (1 atm), 5 mL MeCN, 26 W CFL, room temperature for 4h. <sup>b</sup>Isolated yield. <sup>c</sup>A blue LED was used as the light source and 12h reaction time. <sup>d</sup>Without light. <sup>e</sup>Without O<sub>2</sub>. <sup>f</sup>Decomposition of DMA-BP was observed.

(Table S4, entry 4-5), despite methanol's weaker Stern-Volmer quenching constant (20 M<sup>-1</sup>) for \*DPA-BP than that of NHPI (330 M<sup>-1</sup>) (Figures S6-8).<sup>17</sup> Lastly, additives acting as strong H-bond acceptors such as fluoride (as TBAF, tetra-*n*-butylammonium fluoride) also inhibited the reaction via the competitive binding with NHPI (Table S4, entry 6).<sup>18</sup> On the other hand, the reaction proceeded smoothly in MeCN and acetone (Table S4, entry 7), which are weaker H-bond acceptor compared with DMF and DMSO, and do not disrupt the H-bond interaction of the photo-excited ketone with NHPI.

On the basis of the thermochemical calculation and control experiments described above, a possible reaction pathway is outlined (Scheme 1, inset). First, the photoexcited ketone (\*Cat.)

**Scheme 1.** Photochemical aerobic oxidation of olefins.

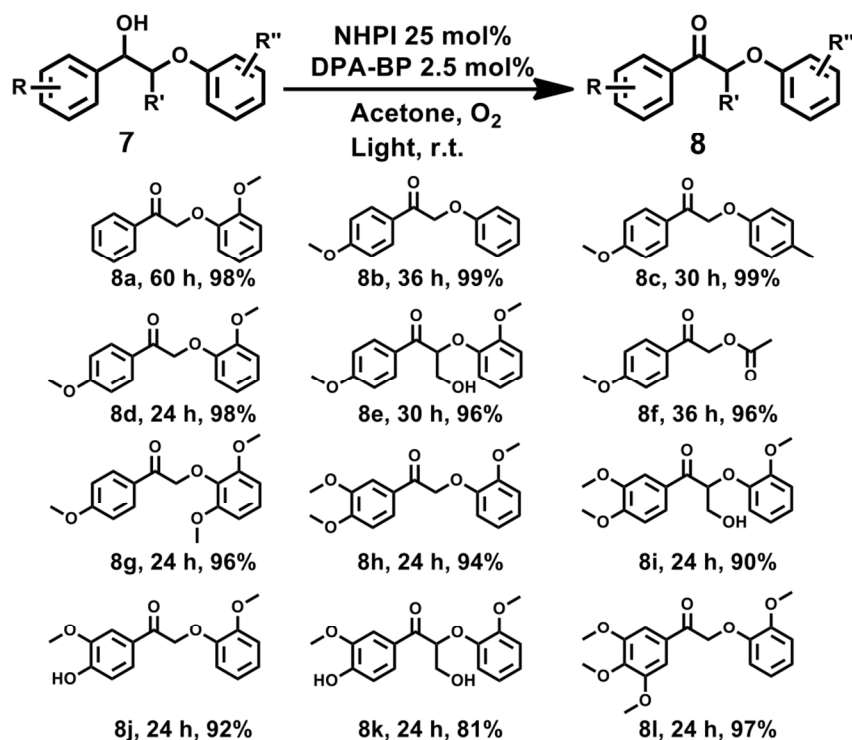
abstracts a hydrogen atom from NHPI via PCET, forming the ketyl (Cat.-H) and PINO radicals. The latter then quickly adds to styrene **1a** to give the benzyl radical **3a**, which further binds with O<sub>2</sub> and transforms into a peroxy radical **4a** that abstracts a hydrogen atom from another NHPI to afford the 1,2-dioxygenation product **2a**. This nearly thermoneutral reaction (BDE of ROO–H 88.5 kcal mol<sup>-1</sup> and O–H in NHPI: 88 kcal mol<sup>-1</sup>)<sup>19</sup> does proceed at an appreciable rate (e.g. 7.2 × 10<sup>3</sup> M<sup>-1</sup> s<sup>-1</sup>).<sup>19b</sup> The ketone photocatalyst Cat. is regenerated from the ketyl radical Cat.-H by coupling with O<sub>2</sub>, and the thus generated peroxy radical undergoes a similar hydrogen abstraction from NHPI and release the PINO radical and H<sub>2</sub>O<sub>2</sub>.<sup>20</sup>

A series of substituted styrenes were used to investigate the scope of this transformation under the optimized conditions (Scheme 1). Excellent to good yields of the dioxygenated product were obtained. No significant detrimental effect was observed for electron-donating substituents such as methoxyl (**2b**, 84% yield) or *tert*-butyl (**2c**, 86% yield). This is in contrast with the previous



observation of product decomposition when *p*-methoxy-styrene was used as the substrate.<sup>13b</sup> Interestingly, the reaction rate decreases as the electron-withdrawing capability of the substituent groups increases, possibly due to the slower addition of the electrophilic PINO radical to the C-C double bond. For example, *p*-bromo-styrene (**2d**, 86% yield) and 2,3,4,5,6-pentafluoro-styrene (**2e**, 77% yield) require a longer reaction time of 12 h and 24 h, respectively. *p*-Methoxyl-(*E*)- $\beta$ -methylstyrene **1f** was a compatible substrate and provided a mixture of diastereoisomers **2f** (*dr* = 74:26, determined by <sup>1</sup>H NMR). (*E*)-1,2-Diphenylethene **1g** gave a high yield (94%, *dr* = 89:11, determined by <sup>1</sup>H NMR) of the major diastereoisomer **2g** with a slightly longer reaction time (6 h), which can be attributed to the steric effect induced by the two bulky phenyl groups. However, when non-aromatic alkenes, such as cyclohexene, was used as substrate in the same reaction, no expected product was obtained possibly due to the unstable radical intermediate.

**Scheme 2.** Reactivity of DPA-BP/NHPI/O<sub>2</sub> photocatalytic system towards lignin  $\beta$ -O-4 models.

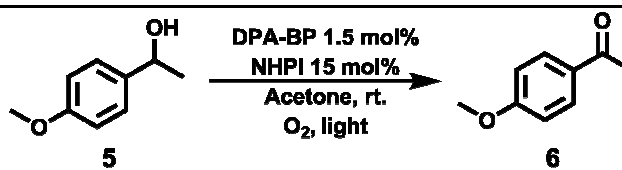


Encouraged by this result, we next tested the efficiency of the DPA-BP/NHPI/O<sub>2</sub> system toward the aerobic oxidation of secondary benzylic alcohols. This fundamental reaction has recently attracted much attention in the depolymerization of lignin, a biopolymer that can be potentially used to provide value-added monomers for biorefineries.<sup>21</sup> It is known that the oxidation of benzylic position of the most dominant  $\beta$ -O-4 linkage structure in lignin models facilitates the subsequent C-O bond cleavage ( $\sim 14$  kcal mol<sup>-1</sup> decrease of BDE<sup>22</sup>), to allow for the access to high-value aromatic products, including a recently reported photoredox approach.<sup>23</sup> To date, most methods for the oxidation of lignin and its related model compounds<sup>24</sup> employ transition-metal-based oxidants at elevated temperatures, affording products with low selectivity and poor yield.<sup>25</sup> Only a few metal-free approaches such as laccase enzymes<sup>26</sup> and TEMPO/HNO<sub>3</sub>/HCl<sup>27</sup> have been employed for aerobic alcohol oxidation in lignin models.

We first tested DPA-BP as the photocatalyst (1.5 mol %) and NHPI as the co-catalyst (15 mol %) for the aerobic oxidation of *p*-methoxyl- $\alpha$ -methylbenzyl alcohol **5** (Table 2). After irradiation of the reaction mixture with a 26 W CFL under 1 atm O<sub>2</sub> for 24 h in acetone, the ketone product **6** was obtained in an excellent yield (97%, Table 2, entry 1). Solvent screening revealed CH<sub>3</sub>CN is another effective solvent (93%, Supporting Information, Table S5). Similar to dioxygenation of styrene, polar solvents such as strong H-bond acceptor (DMF and DMSO) and H-bond donator (methanol) strongly quenched the reaction (Table S5). Light irradiation, photocatalyst, NHPI, and molecular oxygen are all essential to this reaction (Table S6). In the presence of less NHPI (5 mol% and 10 mol%), the reaction rate decreased (Table S6, entries 7-8); however, as the ratio of NHPI increased to 20 mol%, lower selectivity was observed (Table S6, entry 9). Our catalytic system also compares favorably to the metal-based Co(AcO)<sub>2</sub>/NHPI/O<sub>2</sub> catalytic system<sup>3a</sup> under the same reaction condition (48% yield, Table 2,

entry 3). Cz-BP gave a lower yield (42%, entry 4) and DMA-BP was ineffective (entry 5). The synergistic catalytic activity of photocatalyst and PINO is essential for this reaction. For instance, moderately oxidative photocatalyst such as  $[\text{Ru}(\text{bpy})_3]^{2+}$ , which does not have H-bond interaction with NHPI, exhibited a diminished activity (6% yield, entry 6). In the absence of NHPI, despite their higher reduction potentials ( $E^{M+/M} > +1.80 \text{ V}$ ) than that of the benzylic alcohol **5** ( $E^{+/0} > +1.67 \text{ V}$ ) (Supporting Information, Table S1 and Figure S13),  $[\text{Ru}(\text{bpz})_3]^{2+}$  (bpz = 2,2'-bipyrazine) and  $\text{Acr-Mes}^+$  (9-mesityl-10-methylacridinium) resulted in a poor yield of the

**Table 2.** Initial studies for the photo-induced oxidation of benzylic alcohol.<sup>a</sup>

			
Entry	Photocatalyst	Conversion (%)	Yield (%) <sup>b</sup>
1	DPA-BP	100	97
2	DPA-BP	89	84 <sup>c</sup>
3	None	50	48 <sup>d</sup>
4	Cz-BP	43	42
5	DMA-BP	7	6
6	$[\text{Ru}(\text{bpy})_3]^{2+}$	6	6
7	$[\text{Ru}(\text{bpz})_3]^{2+}$	15 <sup>e</sup>	15 <sup>e</sup>
8	$\text{Acr}^+-\text{Mes}$	41 <sup>e</sup>	39 <sup>e</sup>

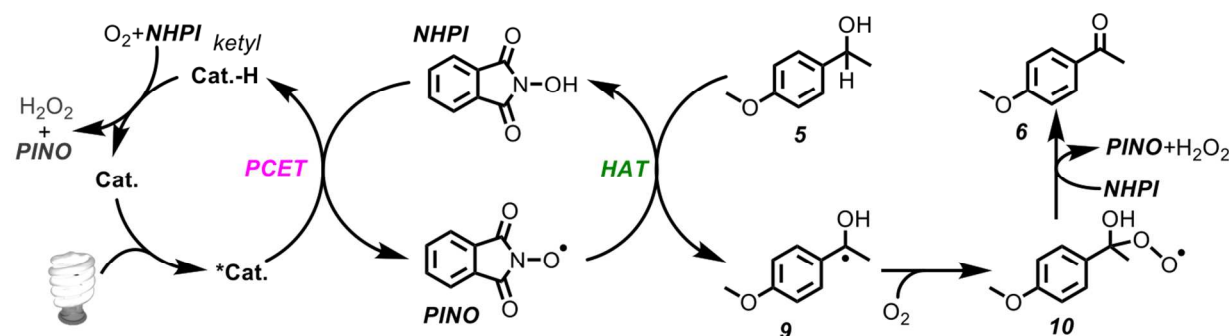
<sup>a</sup>Reaction condition: photocatalyst (1.5 mol %), **5** (50  $\mu\text{L}$ , 0.35 mmol), NHPI (7.5 mg, 15 mol %),  $\text{O}_2$  (1 atm), 5 mL acetone, 26 W CFL, room temperature for 24h. <sup>b</sup>Isolated yield. <sup>c</sup>A blue LED as the light source was used and 48h reaction time. <sup>d</sup>2 mol %  $\text{Co}(\text{AcO})_2$ , NHPI 15 mol %, benzoic acid 10 mol %, dark. <sup>e</sup>No NHPI.

ketone product (< 40% yield, Table 2, entry 7-8). Moreover, the formation of H<sub>2</sub>O<sub>2</sub> as the other reduction product of O<sub>2</sub> was confirmed by the standard iodide test (Figure S15).

Next, we sought to apply the DPA-BP/NHPI/O<sub>2</sub> photocatalytic system to a series of  $\beta$ -O-4 lignin models **7**, including several with an additional hydroxymethyl fragment that features in lignin (**7e**, **7i**, and **7k**), to determine its efficiency and selectivity (Scheme 2). Overall, the benzylic carbonyl compounds **8** were obtained in excellent isolated yields (81-99%). Except for substrate **7a**, which required 60 h to complete the conversion (98% yield), most lignin models with electron-donating substituents proceeded in a faster reaction rate (24-36 h). This oxidation protocol is also effective toward several  $\beta$ -O-4-linked diols (**7e**, **7i**, and **7k**) (> 81% yield). In particular, the yield for **8i** represents a two-fold increase comparing to that of a previously reported TEMPO/HNO<sub>3</sub>/HCl catalyst system.<sup>27</sup> Considerably more challenging lignin models (**7j** and **7k**), which contain free phenols and tend to undergo decomposition<sup>25b</sup> or inhibit catalysts,<sup>28</sup> exhibited good reactivity with excellent yields of corresponding ketone **8j** (92%) and **8k** (81%), respectively. Such high chemoselectivity is reasonable because the stronger O-H bond of phenols (BDE: 87.7 kcal mol<sup>-1</sup>)<sup>12</sup> cannot sufficiently compete with the C $\alpha$ -H in benzylic alcohol (BDE is 75~85 kcal mol<sup>-1</sup>)<sup>3d</sup> to react with PINO radical via hydrogen abstraction. Moreover, compared with NHPI (pK<sub>a</sub> = 23.5 in CH<sub>3</sub>CN), phenol (pK<sub>a</sub> = 30.0 in CH<sub>3</sub>CN) is a weaker H-bond donor so that the interaction between NHPI and DPA-BP will not be significantly weakened in the presence of the phenolic substrate (4 eq.) under the reaction condition.

Scheme 3 illustrates the proposed mechanism for benzylic alcohol oxidation. A photoinduced PCET between  $^*\text{Cat.}$  and NHPI generates the reactive PINO radical, which abstracts a hydrogen atom from the benzylic alcohol to afford the  $\alpha$ -hydroxybenzylic radical **9** and regenerate NHPI. This is a thermodynamically favorable step on the basis of the BDE of  $\text{C}_{\alpha}\text{-H}$  ( $75\sim 85\text{ kcal mol}^{-1}$ ) in benzylic alcohol<sup>3d</sup> and  $\text{O-H}$  ( $88\text{ kcal mol}^{-1}$ ) in NHPI.<sup>19b,29</sup> Radical **9** is intercepted by  $\text{O}_2$  to generate the peroxy radical **10**, which abstracts a hydrogen atom from NHPI and release the ketone and  $\text{H}_2\text{O}_2$  as the products. The regeneration of photocatalyst  $\text{Cat.}$  from ketyl  $\text{Cat.-H}$  follows a similar fashion as the transformation from ketyl **9** to ketone **6**.

**Scheme 3.** Proposed reaction mechanism for the oxidation of benzylic alcohols.



It is known that superoxide ( $\text{O}_2^{\bullet-}$ ), commonly formed by single electron reduction by excited photocatalysts, can undergo a hydrogen abstraction reaction.<sup>30</sup> However, it usually exhibits lower reactivities compared to peroxy radical.<sup>31</sup> We further ruled out the role of this mechanism in the generation of PINO radicals in our catalytic system: when a structural analogue of **5** that contains the active C-H bond, *p*-(1-ethoxyethyl)-anisole, was subjected to the DPA-BP/NHPI catalyst system in the absence of  $\text{O}_2$ , the ketone product **6** was successfully generated, presumably due to the decomposition of the  $\alpha$ -benzyl radical following the hydrogen abstraction by PINO (Supporting Information, Figure S14).

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3 In summary, we have demonstrated a new example of utilizing proton-coupled electron  
4 transfer in chemical photocatalysis. The hydrogen bond between DPA-BP and NHPI is used to  
5 facilitate the formation of synthetically useful PINO radicals via the photoinduced *unidirectional*  
6 PCET pathway where the electron and proton are simultaneously transferred in a single  
7 elementary step.<sup>11b-d</sup> This strategy serves as a useful addition to the photoinduced *bidirectional*  
8 PCET recently employed by Knowles et al. to generate ketyl and amidyl radicals.<sup>32</sup> Both PCET  
9 mechanisms allow for a rapid reaction rate due to the decreased activation barriers. The obtained  
10 PINO radicals can be used to access a new class of alkyl hydroperoxides. Furthermore, the DPA-  
11 BP/NHPI/O<sub>2</sub> photocatalytic system exhibits high efficiency and selectivity for the aerobic  
12 oxidation of benzylic alcohols including  $\beta$ -O-4 lignin models. Our metal-free catalytic system  
13 holds a great potential utility for the future development of green aerobic oxidation methods.  
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## EXPERIMENTAL SECTION

**General Information.** All solvents and reagents were purchased from commercial sources and, unless otherwise noted, used without further purification.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured in  $\text{CDCl}_3$  at 300 or 400 MHz and 100 MHz, respectively.  $^{19}\text{F}$  NMR spectra were measured in  $\text{CDCl}_3$  at 376 MHz. The chemical shift references were as follows: ( $^1\text{H}$ ), 7.26 ppm ( $\text{CDCl}_3$ ); ( $^{13}\text{C}$ ), 77.0 ppm ( $\text{CDCl}_3$ ). High resolution mass spectrometry was conducted on a Q-TOF mass spectrometer equipped with an ESI or EI mode. Thin-layer chromatography (TLC) was performed on 0.25 mm hard-layer silica G plates containing a fluorescent indicator. Developed TLC plates were visualized with a hand-held UV lamp. All the compounds were purified by flash column chromatography with silica gel with the product purity higher than 95% (calculated from  $^1\text{H}$ -NMR spectra). UV-vis, fluorescence excitation and emission spectra were measured in  $\text{CH}_3\text{CN}$ . Cyclic voltammetry (CV) was performed using an Epsilon electrochemical workstation: glassy carbon electrode as the working electrode, Pt wire as the counter electrode,  $\text{Ag}/\text{AgCl}$  ( $\text{KCl}$ , 3 M) electrode as the reference electrode, and ferrocenium-ferrocene ( $\text{Fc}^+/\text{Fc}$ ) as the internal standard. Scan rate:  $100 \text{ mV s}^{-1}$  (in the range  $-2.2$  to  $+1.8 \text{ V}$ ).  $\text{Bu}_4\text{NPF}_6$  (0.1 M in  $\text{MeCN}$ ) was used as the supporting electrolyte.

**Photocatalysts and Starting Materials Preparation.** The photocatalysts  $\text{Cz-BP}$ ,<sup>33</sup>  $\text{DPA-BP}$ ,<sup>34</sup> and  $[\text{Ru}(\text{bpz})_3](\text{PF}_6)_2$ <sup>35</sup> were synthesized using reported procedures. The lignin model compounds **7** were prepared via a literature procedure.<sup>23</sup>

**General Procedures.** *Dioxygenation of Styrenes.* The mixture of styrene (0.5 mmol),  $\text{NHPI}$  (98 mg, 0.6 mmol) and  $\text{DPA-BP}$  (5.0 mg,  $10 \mu\text{mol}$ , 2 mol%) in 5 mL  $\text{MeCN}$  was stirred under  $\text{O}_2$  atmosphere (1 atm) with irradiation of the light source (26 W CFL, distance app. 2 cm) at room temperature. The reaction was monitored via TLC (hexanes : ethyl acetate = 5 : 1 ~ 2 : 1). Upon

consumption of starting material, removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel using hexane/ethyl acetate (10 : 1 ~ 4 : 1) as the eluent to yield the products.

*2-(2-Hydroperoxy-2-phenylethoxy)isoindoline-1,3-dione (2a)*. Prepared from styrene (57  $\mu$ L, 52 mg, 0.5 mmol) and NHPI (98 mg, 0.6 mmol). White solid, 137 mg (92 %); mp 78-80 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz): 7.86–7.95 (2H, m), 7.74–7.86 (2H, m), 7.33–7.48 (5H, m), 5.38–5.51 (1H, m), 4.45–4.62 (2H, m).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz): 164.8, 135.7, 134.8, 128.9, 128.8, 128.7, 127.1, 124.9, 85.5. HRMS (ESI-MS)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{16}\text{H}_{13}\text{NO}_5\text{Na}^+$  322.0691; Found 322.0680.

*2-(2-Hydroperoxy-2-(4-methoxyphenyl)ethoxy)isoindoline-1,3-dione (2b)*. Prepared from *p*-methoxy-styrene (67 mg, 0.5 mmol) and NHPI (98 mg, 0.6 mmol). White solid, 144 mg (84 %); mp 87-89 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz): 9.42 (1H, brs), 7.84–7.92 (2H, m), 7.77–7.84 (2H, m), 7.37 (2H, d,  $J = 8.7$  Hz), 6.93 (2H, d,  $J = 8.7$  Hz), 5.34–5.42 (1H, m), 4.51–4.56 (m, 2H), 3.85 (3H, s).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz): 163.8, 134.8, 128.7, 128.6, 127.7, 123.8, 114.2, 84.9, 78.9, 55.3. HRMS (ESI-MS)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{17}\text{H}_{15}\text{NO}_6\text{Na}^+$  352.0797; Found 352.0788.

*2-(2-(4-(tert-Butyl)phenyl)-2-hydroperoxyethoxy)isoindoline-1,3-dione (2c)*. Prepared from *p*-(*tert*-butyl)-styrene (80 mg, 0.5 mmol) and NHPI (98 mg, 0.6 mmol). White solid, 152 mg (86 %); mp 86-88 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz): 7.85–7.92 (2H, m), 7.77–7.85 (2H, m), 7.43 (2H, d,  $J = 8.4$  Hz), 7.36 (2H, d,  $J = 8.4$  Hz), 5.44 (1H, dd,  $J_1 = 7.2$  Hz,  $J_2 = 4.2$  Hz), 4.49–4.59 (2H, m), 1.32 (9H, s).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz): 163.8, 134.8, 132.8, 128.8, 126.9, 125.7, 123.8, 85.3, 78.9, 34.5, 31.3. HRMS (ESI-MS)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{20}\text{H}_{21}\text{NO}_5\text{Na}^+$  378.1317; Found 378.1310.



2-(2-(4-Bromophenyl)-2-hydroperoxyethoxy)isoindoline-1,3-dione (**2d**). Prepared from *p*-bromo-styrene (91 mg, 0.5 mmol) and NHPI (98 mg, 0.6 mmol). White solid, 162 mg (86 %); mp 93-95 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): 7.85–7.92 (2H, m), 7.78–7.85 (2H, m), 7.55 (2H, *J* = 8.4 Hz, d), 7.33 (2H, *J* = 8.4 Hz, d), 5.40 (1H, *J*<sub>1</sub> = 7.8 Hz, *J*<sub>2</sub> = 3.6 Hz, dd), 4.44–4.56 (2H, m). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): 163.8, 134.9, 134.8, 131.9, 128.8, 128.7, 123.9, 123.0, 84.8, 78.5. HRMS (ESI-MS) *m/z*: [M+Na]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>12</sub>BrNO<sub>5</sub>Na<sup>+</sup> 399.9797; Found 399.9786.

2-(2-Hydroperoxy-2-(perfluorophenyl)ethoxy)isoindoline-1,3-dione (**2e**). Prepared from 2,3,4,5,6-pentafluoro-styrene (97 mg, 0.5 mmol) and NHPI (98 mg, 0.6 mmol). White solid, 149 mg (77 %); mp 93-95 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): 9.70 (1H, brs), 7.87–7.92 (2H, m), 7.80–7.87 (2H, m), 5.86 (1H, *J*<sub>1</sub> = 9.0 Hz, *J*<sub>2</sub> = 3.0 Hz, dd), 4.74–4.84 (1H, m), 4.50–4.59 (1H, m). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 282 MHz): 140.35 (2F, m), 151.75 (1F, m), 160.87 (2F, m). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): 136.8, 135.0, 128.6, 124.0, 77.8. HRMS (EI-MS) *m/z*: [M]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>8</sub>NF<sub>5</sub>O<sub>5</sub><sup>+</sup> 389.0323; Found 389.0315.

2-((1-Hydroperoxy-1-(4-methoxyphenyl)propan-2-yl)oxy)isoindoline-1,3-dione (**2f**). Prepared from *p*-methoxyl-(*E*)-β-methylstyrene (74 mg, 0.5 mmol) and NHPI (98 mg, 0.6 mmol). White solid, 140 mg (81 %); mp 103 °C (decomposition). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): 10.03 (1H, brs), 7.86–7.94 (2H, m), 7.77–7.86 (2H, m), 7.42 (1.4H, *J* = 8.0 Hz, d), 7.29 (0.6H, *J* = 8.0 Hz, d), 6.94 (2H, *J* = 8.0 Hz, d), 5.08 (1H, s), 4.78–4.95 (0.74H, m), 4.60–4.67 (0.26H, m), 3.83 (3H, s), 1.31 (3H, *J* = 8.0 Hz, d). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): 164.70, 159.95, 134.85, 130.00, 128.77, 123.84, 133.89, 87.89, 83.98, 55.28, 14.66. HRMS (ESI-MS) *m/z*: [M+Na]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>17</sub>NO<sub>6</sub>Na<sup>+</sup> 366.0954; Found 366.0951.

2-(2-Hydroperoxy-1,2-diphenylethoxy)isoindoline-1,3-dione (**2g**). Prepared from (*E*)-1,2-diphenylethene (90 mg, 0.5 mmol) and NHPI (98 mg, 0.6 mmol). White solid, 176 mg (94 %);

mp 136-137 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz): 10.24 (1H, brs), 7.67–7.81 (4H, m), 7.12–7.33 (10H, m), 5.94 (0.89 H,  $J = 4.2$  Hz, d), 5.61 (0.11H,  $J = 4.2$  Hz, d), 5.48 (0.11H,  $J = 4.2$  Hz, d), 5.26 (0.9H,  $J = 4.2$  Hz, d).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz): 164.1, 134.7, 133.9, 133.5, 128.9, 128.8, 128.6, 128.5, 128.0, 127.8, 123.7, 89.1, 87.9. HRMS (ESI-MS)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{22}\text{H}_{17}\text{NO}_5\text{Na}^+$  398.1004; Found 398.1016.

*Aerobic oxidation of benzyl alcohol 5.* The mixture of **5** (50  $\mu\text{L}$ , 0.3 mmol), NHPI (7.3 mg, 45  $\mu\text{mol}$ , 15 mol%) and DPA-BP (2.3 mg, 4.5  $\mu\text{mol}$ , 1.5 mol%) in 5 mL acetone was stirred under  $\text{O}_2$  atmosphere (1 atm) with the irradiation of light source (26 W CFL, distance app. 2 cm) at room temperature. The reaction was monitored via  $^1\text{H}$ -NMR or TLC (hexanes : ethyl acetate = 20 : 1). Upon consumption of starting material (24 h), removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel using hexane/ethyl acetate (20:1) as the eluent to yield the product **6**.<sup>36</sup>  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz): 7.32 (2H,  $J = 12.0$  Hz, d), 6.97 (2H,  $J = 12.0$  Hz, d), 3.90 (3H, s), 2.59 (3H, s). HRMS (ESI-MS)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_9\text{H}_{11}\text{O}_2^+$  151.0759; Found 151.0742.

*Aerobic oxidation of lignin model compounds 7.* The mixture of lignin model compound **7a-l** (0.2 mmol), NHPI (8.0 mg, 50  $\mu\text{mol}$ , 25 mol%) and DPA-BP (2.6 mg, 5.0  $\mu\text{mol}$ , 2.5 mol%) in 5 mL acetone was stirred under  $\text{O}_2$  atmosphere (1 atm) with irradiation of the light source (26 W CFL, distance app. 2 cm) at room temperature. The reaction was monitored via TLC (hexanes : ethyl acetate = 10 : 1 ~ 4 : 1). Upon consumption of starting material, removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel using hexane/ethyl acetate (50 : 1 ~ 10 : 1) as the eluent to yield the product **8a-l**.

*2-(2-Methoxyphenoxy)-1-phenylethan-1-one (8a).*<sup>37</sup> Prepared from **7a** (48.8 mg, 0.2 mmol). White solid, 47.4 mg (98 %).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz): 8.06 (2H,  $J = 9.0$  Hz, d), 7.63 (1H,  $J$

= 6.0 Hz, t), 7.52 (2H,  $J$  = 6.0 Hz, t), 6.93~7.00 (2H, m), 6.88 (2H,  $J$  = 3.0 Hz, d), 5.37 (2H, s), 3.91 (3H, s). HRMS (ESI-MS)  $m/z$ :  $[M+Na]^+$  Calcd for  $C_{15}H_{14}O_3Na^+$  265.0841; Found 265.0853.

*1-(4-Methoxyphenyl)-2-phenoxyethan-1-one (8b)*.<sup>37</sup> Prepared from **7b** (48.8 mg, 0.2 mmol). White solid, 48.2 mg (99 %).  $^1H$  NMR ( $CDCl_3$ , 400 MHz): 8.05 (2H,  $J$  = 12.0 Hz, d), 7.25~7.35 (2H, m), 6.90~7.07 (5H, m), 5.24 (2H, s), 3.91 (3H, s). HRMS (ESI-MS)  $m/z$ :  $[M+Na]^+$  Calcd for  $C_{15}H_{14}O_3Na^+$  265.0841; Found 265.0854.

*1-(4-Methoxyphenyl)-2-(p-tolyloxy)ethan-1-one (8c)*.<sup>23</sup> Prepared from **7c** (51.6 mg, 0.2 mmol). White solid, 50.7 mg (99 %).  $^1H$  NMR ( $CDCl_3$ , 400 MHz): 8.02 (2H,  $J$  = 8.0 Hz, d), 7.16 (1H,  $J$  = 8.0 Hz, t), 6.98 (2H,  $J$  = 8.0 Hz, d), 6.66~6.87 (3H, m), 5.19 (2H, s), 3.89 (3H, s), 2.32 (3H, s). HRMS (ESI-MS)  $m/z$ :  $[M+H]^+$  Calcd for  $C_{16}H_{17}O_3^+$  257.1178; Found 257.1183.

*2-(2-Methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one (8d)*.<sup>23</sup> Prepared from **7d** (54.8 mg, 0.2 mmol). White solid, 53.5 mg (98 %).  $^1H$  NMR ( $CDCl_3$ , 400 MHz): 8.06 (2H,  $J$  = 9.3 Hz, d), 6.92~7.01 (4H, m), 6.88 (2H, d,  $J$  = 3.9 Hz), 5.31 (2H, s), 3.91 (3H, s), 3.90 (3H, s). HRMS (ESI-MS)  $m/z$ :  $[M+Na]^+$  Calcd for  $C_{16}H_{16}O_4Na^+$  295.0946; Found 295.0948.

*3-Hydroxy-2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)propan-1-one (8e)*.<sup>23</sup> Prepared from **7e** (60.8 mg, 0.2 mmol). White solid, 58.2 mg (98 %).  $^1H$  NMR ( $CDCl_3$ , 400 MHz): 8.11 (2H,  $J$  = 9.0 Hz, d), 6.81~7.05 (6H, m), 5.40 (1H,  $J$  = 6.9 Hz, t), 4.02~4.15 (2H, m), 3.90 (3H, s), 3.88 (3H, s), 3.14 (1H,  $J$  = 6.9, t). HRMS (ESI-MS)  $m/z$ :  $[M+Na]^+$  Calcd for  $C_{17}H_{18}O_5Na^+$  325.1052; Found 325.1047.

*2-(4-Methoxyphenyl)-2-oxoethyl acetate (8f)*.<sup>23</sup> Prepared from **7f** (40.2 mg, 0.2 mmol). White solid, 38.6 mg (96 %).  $^1H$  NMR ( $CDCl_3$ , 400 MHz): 7.91 (2H,  $J$  = 8.0 Hz, d), 6.97 (2H,  $J$  =

8.0 Hz, d), 5.30 (2H, s), 3.88 (3H, s), 2.23 (3H, s). HRMS (ESI-MS)  $m/z$ :  $[M+H]^+$  Calcd for  $C_{11}H_{13}O_4^+$  209.0814; Found 209.0825.

*2-(2,6-Dimethoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one (8g)*.<sup>23</sup> Prepared from **7g** (60.8 mg, 0.2 mmol). White solid, 58.0 mg (96 %).  $^1H$  NMR ( $CDCl_3$ , 400 MHz): 8.11 (2H,  $J = 8.0$  Hz, d), 7.03 (1H,  $J = 8.0$  Hz, t), 6.98 (2H,  $J = 8.0$  Hz, d), 6.61 (2H,  $J = 8.0$  Hz, d), 5.16 (2H, s), 3.90 (3H, s), 3.83 (6H, s). HRMS (ESI-MS)  $m/z$ :  $[M+Na]^+$  Calcd for  $C_{17}H_{18}O_5Na^+$  325.1052; Found 325.1061.

*1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)ethan-1-one (8h)*.<sup>38</sup> Prepared from **7h** (60.8 mg, 0.2 mmol). White solid, 57.2 mg (94 %).  $^1H$  NMR ( $CDCl_3$ , 400 MHz): 7.73 (1H,  $J_1 = 9.0$  Hz,  $J_2 = 3.0$  Hz, dd), 7.63 (1H,  $J = 3.0$  Hz, d), 6.90–7.00 (3H, m), 6.88 (2H,  $J = 3.0$  Hz, d), 5.32 (2H, s), 3.98 (3H, s), 3.96 (3H, s), 3.91 (3H, s). HRMS (ESI-MS)  $m/z$ :  $[M+Na]^+$  Calcd for  $C_{17}H_{18}O_5Na^+$  325.1052; Found 325.1051.

*1-(3,4-Dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propan-1-one (8i)*.<sup>23</sup> Prepared from **7i** (66.8 mg, 0.2 mmol). White solid, 59.8 mg (90 %).  $^1H$  NMR ( $CDCl_3$ , 400 MHz): 7.80 (1H,  $J_1 = 9.0$  Hz,  $J_2 = 3.0$  Hz, dd), 7.64 (1H,  $J = 3.0$  Hz, d), 6.98–7.10 (1H, m), 6.77–6.98 (4H, m), 5.42 (1H,  $J = 3.0$  Hz, t), 4.09 (2H,  $J = 6.0$  Hz, t), 3.97 (3H, s), 3.94 (3H, s), 3.89 (3H, s), 3.01–3.19 (1H, m). HRMS (ESI-MS)  $m/z$ :  $[M+H]^+$  Calcd for  $C_{18}H_{21}O_6^+$  333.1338; Found 333.1346.

*1-(4-Hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)ethan-1-one (8j)*.<sup>38</sup> Prepared from **7j** (58.0 mg, 0.2 mmol). White solid, 53.0 mg (92 %).  $^1H$  NMR ( $CDCl_3$ , 400 MHz): 7.57–7.65 (2H, m), 6.90–7.00 (3H, m), 6.87 (2H,  $J = 3.0$  Hz, d), 6.39 (1H, brs), 5.30 (2H, s), 3.96 (3H, s), 3.90 (3H, s). HRMS (ESI-MS)  $m/z$ :  $[M+H]^+$  Calcd for  $C_{16}H_{17}O_5^+$  289.1076; Found 289.1081.

*3-Hydroxy-1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)propan-1-one (8k)*.<sup>38</sup> Prepared from **7k** (64.0 mg, 0.2 mmol). White solid, 51.5 mg (81 %).  $^1H$  NMR ( $CDCl_3$ , 400

MHz): 7.56–7.80 (2H, m), 6.81–7.05 (5H, m), 5.44 (1H,  $J = 6.3\text{Hz}$ , t), 4.05–4.12 (2H, m), 4.08 (3H, s), 3.89 (3H, s), 3.02 (1H, brs). HRMS (ESI-MS)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{19}\text{O}_6^+$  319.1182; Found 319.1191.

*2-(2-Methoxyphenoxy)-1-(3,4,5-trimethoxyphenyl)ethan-1-one (8I)*.<sup>39</sup> Prepared from **7I** (66.8 mg, 0.2 mmol). White solid, 64.4 mg (97 %).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz): 7.36 (2H, s), 6.89–7.05 (2H, m), 6.89 (2H,  $J = 6.0\text{Hz}$ , d), 5.29 (2H, s), 3.95 (3H, s), 3.94 (6H, s), 3.91 (3H, s). HRMS (ESI-MS)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{18}\text{H}_{20}\text{NaO}_6^+$  355.1158; Found 355.1167.

## ASSOCIATED CONTENT

**Supporting Information.** Physical measurements, spectroscopic characterizations, CV diagrams, and NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interests.

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## Table of Contents Graphic

## Photochemical Generation of PINO Radicals

