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Esterification via Iron-Catalyzed Activation of Triphenylphosphine with Air

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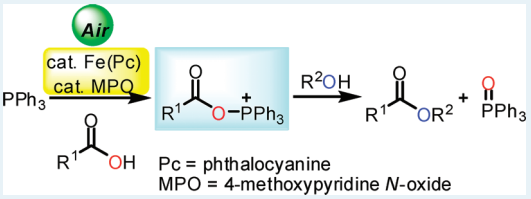
Supporting Information

ABSTRACT: Iron phthalocyanine-catalyzed oxidative activation of triphenylphosphine by molecular oxygen of air occurs, and esters and triphenylphosphine oxide are obtained in the presence of alcohols and carboxylic acids. Experimental results indicate that reactivity of esterification is dependent on acidity of the carboxylic acids and that an acyloxyphosphonium ion intermediate participates in the reaction mechanism. Addition of pyridine *N*-oxide derivatives accelerated the reaction, and a wide range of alcohols and carboxylic acids can be employed in this reaction.



KEYWORDS: esterification, iron, oxygen, phthalocyanines, triphenylphosphine

INTRODUCTION

Phosphines' potential as reducing agents and affinity with an oxygen atom have produced numerous useful reactions over the past century.[1] Generally, tertiary organophosphines such as triphenylphosphine are activated by electrophiles, which are potential oxidants, to generate highly reactive phosphonium ion intermediates (Scheme 1). Appel reaction, which is a method for direct transformation of alcohols into corresponding alkyl halides, is a typical example.[2,3] In this reaction, triphenylphosphine is activated by molecular halogens or tetrahalocarbons to generate a triphenylphosphonium halide, followed by reaction with alcohols to give corresponding alkyl halides via alkoxyphosphonium ion. Mukaiyama and co-workers reported oxidation−reduction condensation for the synthesis of esters or amides, which is mechanistically quite different from simple dehydrated condensations.[4] Oxidative activation of triphenylphosphine by di(2-pyridyl)disulfide causes generation of acyloxyphosphonium ion intermediates from carboxylic acids, and the reaction with alcohols or amines gives corresponding esters and amides.[4]

Recently, various reaction systems of the oxidation−reduction condensation have been reported.[5−8] Mitsunobu reaction is a similar method using diethyl azodicarboxylate as an oxidant, but stereochemical inversion of secondary alcohols occurs via alkoxyphosphonium ion intermediates.[9−12] The above examples demonstrate that highly reactive electrophiles (oxidants) are commonly required for the activation of alcohols or carboxylic acids using triphenylphosphine. On the other hand, molecular oxygen is an ideal oxidant from an economical viewpoint, but it is used in only special cases because of the inefficient oxidation activity. Therefore, efficient catalysts or devices are necessary to incorporate molecular oxygen into a practical oxidation process.[13,14] Among studies on aerobic oxidation, results of numerous investigations into structures and functions of heme-type or nonheme-type enzymatic models, such as cytochrome P450, that activate molecular oxygen have been reported.[15−17] Biomimetic high-valent oxoiron complexes generated by activation of molecular oxygen have been shown to have interesting functions, such as direct oxygenation of hydrocarbons.[18−25] Commonly, organophosphines are easily oxidized into corresponding phosphine oxides by these biomimetic complexes.[15,26] However, we found a rare example that triphenylphosphine was catalytically activated into triphenylphosphonium ion by molecular oxygen of air with the aid of iron phthalocyanine (Scheme 1).[27,28] Herein, we report a novel esterification reaction[29] that strongly suggests iron-catalyzed aerobic activation of triphenylphosphine.[30,31]

RESULTS AND DISCUSSIONS

To optimize reaction conditions, 3-phenylpropanol (**1a**) and 4-nitrobenzoic acid (**2a**) were chosen as model substrates (Table 1). Treatment of a mixture of these starting materials in heating THF with triphenylphosphine (2 equiv) and a catalytic amount of iron phthalocyanine (5 mol %) under air gave corresponding ester **3a** in 30% yield along with triphenylphosphine oxide (entry 1). Results of screening of several solvents indicated that the use of MeCN was suitable in this reaction (entries 2−4). Since the reaction was not completed even when the reaction time was prolonged, the use of additives was tested with intent to promote the reaction. Addition of a catalytic amount of pyridine or 4-(dimethylamino)-pyridine (DMAP) to the reaction mixture caused a decline in yield (entries 5 and 6).[32,33] When a catalytic amount of pyridine *N*-oxide was employed, clear acceleration of the reaction was observed by TLC or GC analysis, but the reaction was not completed yet (entry 7).[34] 4-(Dimethylamino)pyridine *N*-oxide (DMAPO)[35] was ineffective in this reaction (entry 8), whereas

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Scheme 1. Activation of Triphenylphosphine

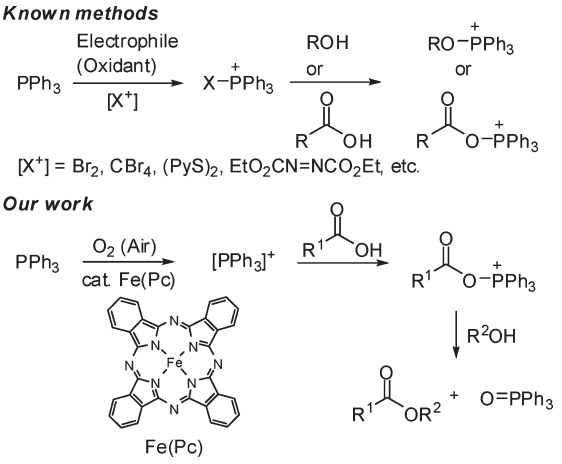
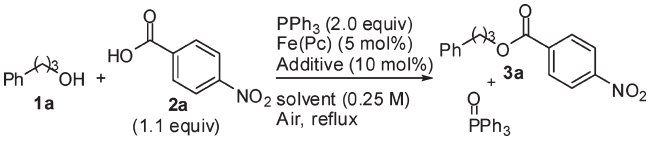


Table 1. Optimizations of Esterification

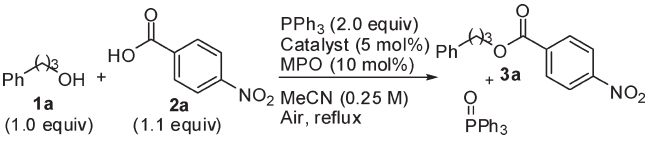


entry	solvent	additive	time (h)	yield (%)[a]	conv (%)[b]
1	THF		24	30	34
2	benzene		24	43	49
3	$(CH_2Cl)_2$		24	42	55
4	MeCN		24	52	56
5	MeCN	Py	24	10	21
6	MeCN	DMAP	24	28	35
7	MeCN	Py *N*-oxide	24	63	66
8	MeCN	DMAPO	24	35	35
9	MeCN	MPO	10	94	96
10	MeCN	DMPO	24	70	75
11[c]	MeCN	MPO	9	86	92
12[d]	MeCN	MPO	92	53	65
13[e]	MeCN	MPO	24	n.r.[f]	
14[g]	MeCN	MPO	24	3	8

[a] Isolated yield of **3a**. [b] Conversion yield was determined by GC analysis with dodecane as an internal standard. [c] Under O_2 atmosphere. [d] At room temperature. [e] In the absence of PPh_3. [f] No reaction. [g] Under argon atmosphere. Py = pyridine. DMAP = 4-(dimethylamino)pyridine. DMAPO = 4-(dimethylamino)pyridine *N*-oxide. MPO = 4-methoxypyridine *N*-oxide. DMPO = 2,4-dimethoxypyridine *N*-oxide.

the use of 4-methoxypyridine *N*-oxide (MPO) enabled completion of the reaction in a short time with an excellent yield of **3a** (entry 9). In reactions using pyridine, DMAP, and DMAPO, the basicity or nucleophilicity of the nitrogen atom might interrupt the work of an iron catalyst. Electronically richer 2,4-dimethoxypyridine *N*-oxides (DMPO) did not give improved results, probably due to the bulky 2-methoxy group (entry 10). The reaction under pure oxygen atmosphere gave unchanged results (entry 11). The reaction was sluggish at room temperature (entry 12). It was found that both triphenylphosphine and molecular oxygen are indispensable for the present

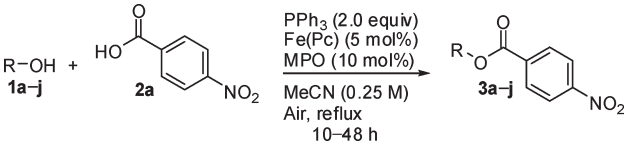
Table 2. Effects of Catalysts

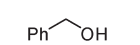
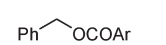
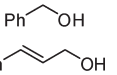
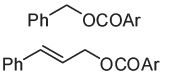
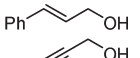
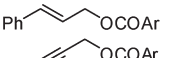
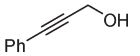
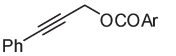
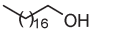
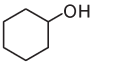
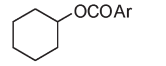
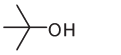
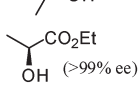
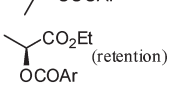
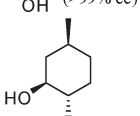
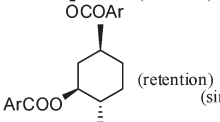
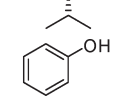
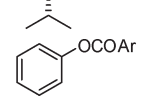


entry	catalyst	time (h)	yield (%)[a]	conv (%)[b]
1	Fe(*Pc*)	10	94	96
2	FeCl(*Pc*)	8	89	96
3	FeCl(TPP)	22	2	15
4	Co(*Pc*)	30	5	11
5	Cu(*Pc*)	24	n.r.	
6	InCl(*Pc*)	24	n.r.	
7	Mn(*Pc*)	24	n.r.	
8	Ni(*Pc*)	24	n.r.	
9	TiO(*Pc*)	24	n.r.	
10	Zn(*Pc*)	24	n.r.	
11	$ZrCl_2$(*Pc*)	24	n.r.	
12	H_2(*Pc*)	24	n.r.	
13	none	24	n.r.	

[a] Isolated yield. [b] Conversion yield was determined by GC analysis with dodecane as an internal standard.

Table 3. Scope of Alcohols



Entry	Alcohol (**1**)		Ester (**3**)	Yield [%][a]
1		a		94
2		b		77
3		c		87
4		d		68
5		e		71
6		f		64
7		g		4
8	 (>99% ee)	h	 (retention)	72 (>99% ee)
9		i	 (retention)	56 (single diastereomer)
10		j		82

[a] Isolated yield. Ar = 4-nitrophenyl.

reaction (entries 13 and 14), and these results ruled out the possibility of simple dehydrated condensation by an iron catalyst.[36]

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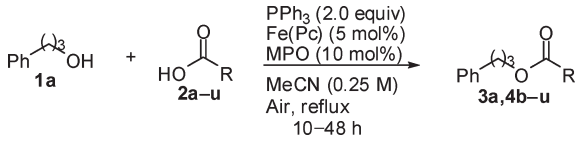
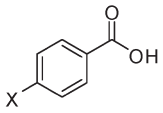
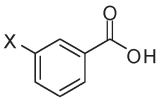
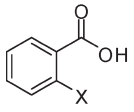
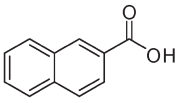
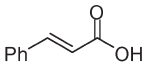
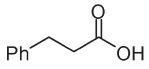
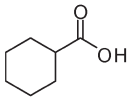
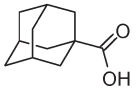
Table 4. Scope of Carboxylic Acids and Effects of Acidity

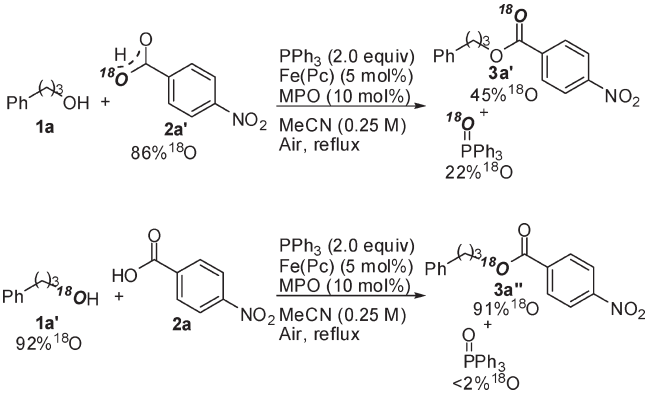


Entry	Carboxylic acid (**2**)		*p*Ka	Yield [%][a]
				
1	X = NO_2	**a**	3.41	94
2	X = CN	**b**	3.55	87
3	X = CF_3	**c**	3.69	86
4	X = CO_2Me	**d**	3.77	85
5	X = Cl	**e**	3.99	79
6	X = F	**f**	4.14	69
7	X = H	**g**	4.19	57 (74)[b]
8	X = Me	**h**	4.37	52
9	X = OMe	**i**	4.50	35 (43)[b]
				
10	X = NO_2	**j**	3.47	81
11	X = Cl	**k**	3.83	88
12	X = F	**l**	3.87	76 (88)[c]
13	X = Me	**m**	4.27	64
				
14	X = NO_2	**n**	2.16	55 (74)[d]
15	X = Br	**o**	2.86	50
16	X = Me	**p**	3.91	68
17		**q**	4.17	77
18		**r**	4.44	47 (55)[b]
19		**s**	4.65	53 (63)[b]
20		**t**	4.90	40
21		**u**	4.86	23

[a] Isolated yield. [b] Concentration is 0.50 M. [c] Concentration is 0.15 M. [d] Concentration is 0.05 M.

Next, the effects of catalysts were examined (Table 2). The reaction was independent of the oxidation state [Fe(II) of Fe(III)] of the iron phthalocyanine (entries 1 and 2). Interestingly, iron(III) tetraphenylporphyrin chloride [FeCl(TPP)] was an ineffective catalyst (entry 3). The reason is unclear, but it is known that the catalytic activity of metal phthalocyanines is different from metal porphyrins.[37−39] Other metal phthalocyanine compounds did not work as catalysts (entries 4−12). Cobalt and manganese phthalocyanines, which resemble iron phthalocyanine in behavior, were included in the above ineffective catalysts (entries 4 and 7).[40−42] No reaction was observed without a catalyst (entry 13).

Scheme 2. ^{18}O-Labeling Experiments



The scope of alcohols in the present reaction is shown in Table 3. Several primary alcohols, **1a**−**e**, afforded corresponding esters **3a**−**e** in moderate to good yields (entries 1−5). The reaction of secondary alcohol **1f** also readily took place (entry 6), whereas a tertiary alcohol **1g** gave ester **3g** in very low yield (entry 7). When optically active secondary alcohols **1h** and **1i** were used, retention of the stereochemistry of products was observed (entries 8 and 9). The reaction of phenol (**1j**) smoothly underwent esterification to give phenyl ester **3j** in good yield (entry 10).

Results of reactions and known pK_a values (**2a,g-i,n,p,q,r,t**,[43] **2c,d,s,u**,[44] **2b,e,f,k**−**m**,[45] **2j**,[46] **2o**[47]) of various carboxylic acids **2a**−**u** are summarized in Table 4. A positive relationship between the reactivity and acidity of 4- or 3-substituted carboxylic acids **2a**−**m** was observed in this esterification reaction (entries 1−13).[48,49] Reactivity of 2-substituted carboxylic acids **2n**−**p** was moderate, probably due to the steric effect (entries 14−16). The reaction of naphthalene-2-carboxylic acid **2q** readily proceeded to give ester **4q** in good yield (entry 17). Reactions of cinnamic acid (**2r**) and aliphatic carboxylic acid **2s** afforded the corresponding esters **4r** and **4s** in moderate yields, respectively (entries 18 and 19). Reactions of secondary or tertiary carboxylic acids **2t** and **2u** were sluggish due to their bulkiness and low acidity (entries 20 and 21). In the case of several carboxylic acids **2**, it was found that the change of concentration improved the yield of products (entries 7, 9, 12, 14, 18 and 19).[50]

To obtain support of the reaction path, examinations using ^{18}O-labeled starting materials were employed (Scheme 2). When ^{18}O-labeled 4-nitrobenzoic acid (**2a′**, 86% ^{18}O incorporation), in which one oxygen atom was replaced with an ^{18}O atom, was used with normal alcohol **1a**, ^{18}O-labeled ester **3a′** (45% ^{18}O incorporation), in which an ^{18}O atom was incorporated into a carbonyl oxygen atom, and ^{18}O-labeled triphenylphosphine oxide (22% ^{18}O incorporation) were obtained, respectively. On the other hand, the reaction of ^{18}O-labeled 3-phenylpropanol **1a′** (92% ^{18}O incorporation) with normal carboxylic acid **2a** gave ^{18}O-labeled ester **3a″** (91% ^{18}O incorporation), in which one ^{18}O was incorporated along with normal triphenylphosphine oxide. The production of stereochemically retentive esters **3h** and **3i** (Table 3, entries 8 and 9) and results of ^{18}O-labeled examinations strongly indicate that the present esterification passes through not an alkoxyphosphonium ion (Mitsunobu reaction intermediate), but an acyloxyphosphonium ion intermediate.[51]

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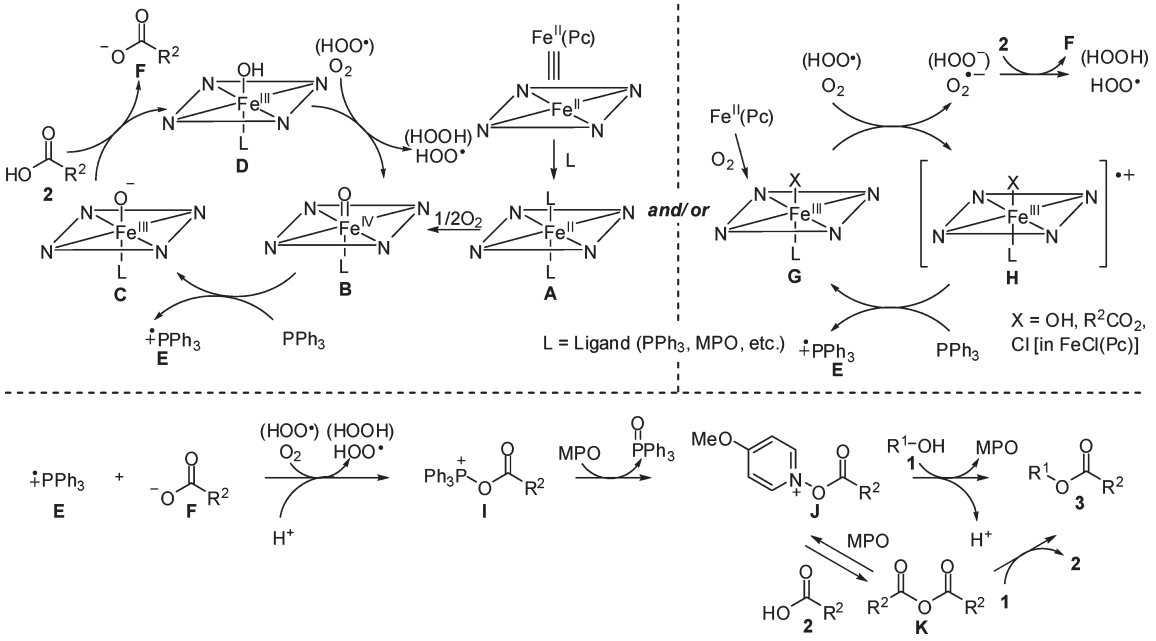
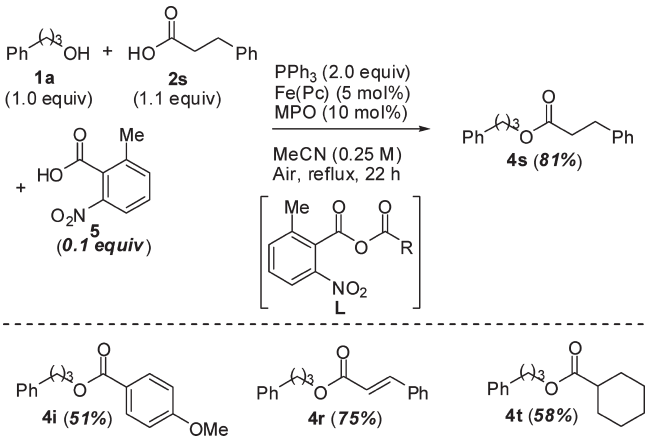
Scheme 3. Proposed Mechanism



On the basis of these results, a proposed reaction mechanism is shown in Scheme 3. Iron(II) phthalocyanine complex **A** having axial ligands such as triphenylphosphine or 4-methoxypyridine *N*-oxide might be oxidized into high-valent oxoiron(IV) complex **B** in the presence of oxygen.[27,52−54] Single electron oxidation of triphenylphosphine by complex **B** might take place to give triphenylphophine cation radical **E** along with basic iron(III) oxide complex **C**.[55−59] Complex **C** would abstract a proton from carboxylic acid **2** to give carboxylate **F** and iron(III) hydroxide complex **D**, which could be reoxidized into complex **B** by molecular oxygen.[60] Molecular oxygen that reacted with complex **D** would be reduced into hydroperoxy radical, followed by further redox reaction to give hydroperoxide. Hydroperoxide might have an ability to oxidize iron phthalocyanine into complex **B**. In addition, simple oxidation of triphenylphosphine by complex **B** would take place to give triphenylphosphine oxide as a competitive reaction.[27]

On the other hand, formation of the oxoiron(IV) complex from iron phthalocyanine by oxygen is not sure, unlike iron porphyrin complexes such as cytochrome P450.[15] As an alternative intermediate, iron(III) phthalocyanine cation radical **H**, which is probably the π-cation radical of the phthalocyanine ligand, might be formed from iron(III) phthalocyanine intermediate **G** by oxygen-mediated single electron oxidation. Highly reactive radical cation **H** would participate in the oxidation step of triphenylphosphine to give cation radical **E**.[61,62] In this case, superoxide or hydroperoxide anion generated by reduction of oxygen would deprive a proton from carboxylic acids **2**. In the esterification step, coupling of cation radical **E** and carboxylate **F** occurs with oxidation by molecular oxygen to give acyloxyphosphonium ion intermediate **I**. Intermediate **I** rapidly reacts with 4-methoxypyridine-*N*-oxide to generate activated ester intermediate **J** along with triphenylphosphine oxide.[34,35] Attack of alcohol **1** or carboxylic acid **2** to intermediate **J** affords ester product **3** or carboxylic anhydride **K**, which reacts with alcohol to give ester **3**.[63,64]

Scheme 4. A Modified Method of Esterification



The detection of anhydride **K** gave insight into improvement of the product yield.[63] We tested a catalytic generation of a reactive mixed anhydride in situ. Addition of a catalytic amount of 2-methyl-6-nitrobenzoic acid (**5**) (0.1 equiv) to the reaction system employing carboxylic acid **2s** improved the yield of ester **4s** (53% → 81%) (Scheme 4). Similarly, the yields of **4i** (35% → 51%), **4r** (47% → 75%), and **4t** (40% → 58%) were greatly improved (Scheme 4). Promotion of the reaction could be explained by the generation of mixed anhydride **L** developed by Shiina.[65]

CONCLUSION

We found a new method for esterification based on the concept of iron-catalyzed oxidative activation of triphenylphosphine by air. The use of an inexpensive and nontoxic iron catalyst and air is economical and environmentally beneficial. Although many examples of simple oxidation reactions with molecular oxygen have been reported, the application of molecular oxygen, especially

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air, to more complex reaction systems and the development of practical catalysts enabling it will be important subjects in the future. Our present work demonstrated a conceptually new approach to aerobic reactions and a large potential of an iron phthalocyanine as a catalyst. Further efforts will be continued to elucidate the whole aspect of the present catalytic system and extent of various reaction systems.

EXPERIMENTAL SECTION

General methods. All reagents were purchased commercially and used without further purification. Melting points are uncorrected. IR spectra were recorded on a commercial FT/IR spectrometer. ^{1}H NMR spectra were recorded on a 600 MHz spectrometer; chemical shifts (δ) are quoted relative to tetramethylsilane. ^{13}C NMR spectra were recorded on a 150 MHz spectrometer with complete proton decoupling; chemical shift (δ) are quoted relative to the residual signals of chloroform. Silica gel column chromatography was carried out on silica gel 60N. Mass spectra were recorded in electron ionization (EI), fast atom bombardment (FAB), or direct analysis in real time (DART).

Typical Procedure of Iron-Catalyzed Esterification. A mixture of 3-phenylpropanol (**1a**; 102 mg, 0.75 mmol), 4-nitrobenzoic acid (**2a**; 138 mg, 0.825 mmol), triphenylphosphine (394 mg, 1.50 mmol), iron(II) phthalocyanine (21.3 mg, 0.0375 mmol), and 4-methoxypyridine *N*-oxide (9.7 mg, 0.075 mmol) in MeCN (3 mL) was heated at reflux (bath temperature, 90 °C) under air (balloon) for 10 h. The mixture was filtered, and the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography (hexane−EtOAc, 15:1) to give ester 3-phenylpropyl 4-nitrobenzoate (**3a**; 199.9 mg, 94%) as a white solid. mp 44−45 °C (lit[66]. 44−45 °C). IR ($CHCl_3$) υ 1720, 1530, 1348, 1275 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.15 (2H, tt, J = 7.8, 6.6 Hz), 2.80 (2H, t, J = 7.8 Hz), 4.40 (2H, t, J = 6.6 Hz), 7.20−7.23 (3H, m), 7.29−7.31 (2H, m), 8.16 (2H, d-like, J = 8.4 Hz), 8.28 (2H, d-like, J = 8.4 Hz). ^{13}C NMR (150 MHz, $CDCl_3$) δ 30.0, 32.3, 65.3, 123.5, 126.1, 128.4, 128.5, 130.7, 135.6, 140.9, 150.5, 164.6. Anal. Calcd for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.91. Found: C, 67.50; H, 5.48; N, 4.91. Triphenylphosphine oxide was also isolated in reasonable yield, and spectral data accorded with the authentic sample.

Experiment with ^{18}O-Labeled 4-Nitrobenzoic Acid (2a′). ^{18}O-Labeled 4-nitrobenzoic acid (**2a′**) was used in a typical procedure. ^{18}O-Labeled 3-phenylpropyl 4-nitrobenzoate (**3a′**; 45% ^{18}O incorporation): IR ($CHCl_3$) υ 1720 (C=^{16}O), 1695 (C=^{18}O) cm^{-1}. MS (DART) ([M + H]$^+$, rel intensity, %) 286 (100), 288 (80). (Normal 3-phenylpropyl 4-nitrobenzoate (**3a**): MS (DART) ([M + H]$^+$, rel intensity, %) 286 (100), 288 (3.1)). ^{18}O-Labeled triphenylphosphine oxide (22% ^{18}O incorporation): MS (EI) (M$^+$, rel intensity, %) 278 (71), 280 (20). (Normal triphenylphosphine oxide: MS (EI) (M$^+$, rel intensity, %) 278 (68), 280 (1.6)).

Experiment with ^{18}O-Labeled 3-Phenylpropanol (1a′). ^{18}O-Labeled 3-phenylpropanol (**1a′**) was used in a typical procedure. ^{18}O-Labeled 3-phenylpropyl 4-nitrobenzoate (**3a″**) (91% ^{18}O incorporation): IR ($CHCl_3$) υ 1720 (C=^{16}O); MS (DART) ([M + H]$^+$, rel intensity, %) 286 (9.7), 288 (100). Triphenylphosphine oxide (<2% ^{18}O incorporation): MS (EI) (M$^+$, rel intensity, %) 278 (50), 280 (0.9).

ASSOCIATED CONTENT

Supporting Information. Expermental details and spectroscopic data for synthesized compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

(1) Valentine, D. H., Jr.; Hillhouse, J. H. *Synthesis* **2003**, 317–334.
(2) Appel, R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 801–811.
(3) Bergin, E.; O'Connor, C. T.; Robinson, S. B.; McGarrigle, E. M.; O'Mahony, C. P.; Gilheany, D. G. *J. Am. Chem. Soc.* **2007**, *129*, 9566–9567.
(4) Mukaiyama, T. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 94–103.
(5) Otera, J.; Nishikido, J. *Esterification: Methods, Reactions, and Applications: Completely Revised and Enlarged*, 2nd ed.; Wiley-VCH: Weinheim, Germany, 2010; Chapter 1, pp 3−157.
(6) Iranpoor, N.; Firouzabadi, H.; Khalili, D.; Motevalli, S. *J. Org. Chem.* **2008**, *73*, 4882–4887.
(7) Mukaiyama, T.; Kuroda, K.; Maruyama, Y. *Heterocycles* **2010**, *80*, 63–82.
(8) Morcillo, S. P.; Álvarez de Cienfuegos, L.; Mota, A. J.; Justicia, J.; Robles, R. *J. Org. Chem.* **2011**, *76*, 2277–2281.
(9) Mitsunobu, O. *Synthesis* **1981**, 1–28.
(10) Hughes, D. L. *Org. React.* **1992**, *42*, 335–656.
(11) Kumara Swamy, K. C.; Kumar Bhuvan, N. N.; Balaraman, E.; Pavan Kumar, K. V. P. *Chem. Rev.* **2009**, *109*, 2551–2651.
(12) But, T. Y. S.; Lu, J.; Toy, P. H. *Synlett* **2010**, 1115–1117.
(13) Stahl, S. S. *Angew. Chem., Int. Ed.* **2004**, *43*, 3400–3420.
(14) Punniyamurthy, T.; Velusamy, S.; Iqbal, J. *Chem. Rev.* **2005**, *105*, 2329–2364.
(15) Groves, J. T. In *Cytochrome P450: Structure, Mechanism, and Biochemistry*, 3rd ed.; Ortiz de Montellano, P. R., Ed.; Kluwer Academic/Plenum Publishers: New York, 2005; Chapter 1, pp 1−44.
(16) Costas, M.; Mehn, M. P.; Jensen, M. P.; Que, L., Jr. *Chem. Rev.* **2004**, *104*, 939–986.
(17) Chen, H.; Lai, W.; Shaik, S. *J. Phys. Chem. B* **2011**, *115*, 1727–1742.
(18) Krebs, C.; Fujimori, D. G.; Walsh, C. T.; Bollinger, J. M., Jr. *Acc. Chem. Res.* **2007**, *40*, 484–492.
(19) Gunay, A.; Theopold, K. H. *Chem. Rev.* **2010**, *110*, 1060–1081.
(20) Harischandra, D. N.; Lowery, G.; Newcomb, M. *Org. Lett.* **2009**, *11*, 2089–2092.
(21) Xue, G.; Hont, R. D.; Münck, E.; Que, L., Jr. *Nat. Chem.* **2010**, *2*, 400–405.
(22) Kotani, H.; Suenobu, T.; Lee, Y.-M.; Nam, W.; Fukuzumi, S. *J. Am. Chem. Soc.* **2011**, *133*, 3249–3251.
(23) Fürstner, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 1364–1367.
(24) Sarhan, A. A.; Bolm, C. *Chem. Soc. Rev.* **2009**, *38*, 2730–2744.
(25) Sun, C.-L.; Li, B.-J.; Shi, Z.-J. *Chem. Rev.* **2011**, *111*, 1293–1314.
(26) Kim, S. O.; Sastri, C. V.; Seo, M. S.; Kim., J.; Nam, W. *J. Am. Chem. Soc.* **2005**, *127*, 4178–4179.
(27) Ercolani, C.; Gardini, M.; Pennesi, G.; Rossi, G. *J. Mol. Catal.* **1985**, *30*, 135–144.

(28) Song, X.; She, Y.; Ji, H.; Zhang, Y. *Org. Process Res. Dev.* **2005**, *9*, 297–301.
(29) Wu, X.-F.; Darcel, C. *Eur. J. Org. Chem.* **2009**, 1144–1147.
(30) Rosa, J. N.; Reddy, R. S.; Candeias, N. R.; Cal, P. M. S. D.; Gois, P. M. *Org. Lett.* **2010**, *12*, 2686–2689.
(31) Petersen, T. B.; Khan, R.; Olofsson, B. *Org. Lett.* **2011**, *13*, 3462–3465.
(32) Berry, D. J.; DiGiovanna, C. V.; Metrick, S. S.; Murugan, R. *Arkivoc* **2001**, 201–226.
(33) Xu, S.; Held, I.; Kempf, B.; Mayr, H.; Steglich, W.; Zipse, H. *Chem.—Eur. J.* **2005**, *11*, 4751–4757.
(34) Efimov, V. A.; Chakhmakhcheva, O. G.; Ovchinnikov, Y. A. *Nucleic Acids Res.* **1985**, *13*, 3651–3666.
(35) Shiina, I.; Ushiyama, H.; Yamada, Y.-k.; Kawakita, Y.-j.; Nakata, K. *Chem.—Asian J.* **2008**, *3*, 454–461.
(36) Weng, S.-S.; Ke, C.-S.; Chen, F.-K.; Lyu, Y.-F.; Liu, G.-Y. *Tetrahedron* **2011**, *67*, 1640–1648.
(37) Chin, D.-H.; La Mar, G. N.; Balch, A. L. *J. Am. Chem. Soc.* **1980**, *102*, 5945–5947.
(38) Vasudevan, P.; Mann, S. N.; Tyagi, S. *Transition Met. Chem.* **1990**, *15*, 81–90.
(39) Liao, M.-S.; Watts, J. D.; Huang, M.-J. *J. Phys. Chem. A* **2005**, *109*, 7988–8000.
(40) In electrochemical reduction of oxygen, it is known that Fe(Pc) has the most highly catalytic activity in several metal phthalocyanines. See: Zagal, J.; Páez, M.; Tanaka, A. A.; dos Santos, J. R., Jr.; Linkous, C. A. *J. Electroanal. Chem.* **1992**, *339*, 13–30.
(41) Sharma, V. B.; Jain, S. L.; Sain, B. *Tetrahedron Lett.* **2003**, *44*, 383–386.
(42) Ebadi, A.; Safari, N.; Peyrovi, M. H. *Appl. Catal. Gen.* **2007**, *321*, 135–139.
(43) Ivšić, T.; Hameršak, Z. *Tetrahedron: Asymmetry* **2009**, *20*, 1095–1098.
(44) Calculated using Advanced Chemistry Development (ACD/Laboratories) Software, version 11.02 (1994−2011 ACD/Laboratories).
(45) De Silva, R. R.; Ramalho, T. C.; Santos, J. M.; Figueroa-Villar, J. D. *J. Phys. Chem. A* **2006**, *110*, 1031–1040.
(46) Torres-Lapasió, J. R.; García-Alvarez-Coque, M. C.; Bosch, E.; Rosés, M. *J. Chromatogr., A* **2005**, *1089*, 170–186.
(47) Xinglong, X.; Jinlong, W.; Jialu, L.; Wei-Min, D. *Synlett* **2006**, 2099–2103.
(48) Dodge, J. A.; Trujillo, J. I.; Presnell, M. *J. Org. Chem.* **1994**, *59*, 234–236.
(49) Hughes, D. L.; Reamer, R. A. *J. Org. Chem.* **1996**, *61*, 2967–2971.
(50) See the Supporting Information.
(51) Capretta, A.; Laritchv, V.; Dyck, J.; Robertson, A. J. *Angew. Chem., Int. Ed.* **2003**, *42*, 4051–4054. See also ref 11.
(52) Mekhryakova, N. G.; Gulina, T. Y.; Li, V. D.; Bundina, N. I.; Kaliya, O. L.; Luk'yanets, E. A. *Russ. J. Gen. Chem.* **2001**, *71*, 570–590.
(53) Martinsen, J.; Miller, M.; Trojan, D.; Sweigart, D. A. *Inorg. Chem.* **1980**, *19*, 2162–2165.
(54) It is known that a stable dimeric μ-oxo complex ($[Fe(Pc)]_2O$) is obtained as a main product in the reaction of iron (II) phthalocyanine with oxygen. However, this complex is presumed to be easily transformed into a monomeric complex, such as complex **A** or **D**, in the presence of PPh_3 and 4-methoxypyridine *N*-oxide (see refs 27 and 53). Perhaps $[Fe(Pc)]_2O$ itself might have the catalytic activity in the present reaction. See: Neu, H. M.; Zhadankin, V. V.; Nemykin, V. N. *Tetrahedron Lett.* **2010**, *51*, 6545–6548.
(55) Merzougui, B.; Berchadsky, Y.; Tordo, P.; Gronchi, G. *Electrochim. Acta* **1997**, *42*, 2445–2453.
(56) Alfassi, Z. B.; Neta, P. *J. Phys. Chem. A* **1997**, *101*, 2153–2158.
(57) Yasui, S.; Tojo, S.; Majima, T. *Org. Biomol. Chem.* **2006**, *4*, 2969–2973.
(58) Ohkubo, K.; Nanjo, T.; Fukuzumi, S. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1489–1500.
(59) Camp, D.; Hanson, G. R.; Jenkins, I. D. *J. Org. Chem.* **1995**, *60*, 2977–2980.
(60) Gupta, R.; Borovik, A. S. *J. Am. Chem. Soc.* **2003**, *125*, 13234–13242.
(61) Malek, A.; Latos-Grazynski, L.; Bartczak, T. J.; Zadlo, A. *Inorg. Chem.* **1991**, *30*, 3222–3230.
(62) Fedorova, T. M.; Topol', S. S.; Derkacheva, V. M.; Luk'yanets, E. A.; Kaliya, O. L. *Russ. Chem. Bull., Int. Ed.* **2004**, No. 53, 1655–1660.
(63) Acid anhydrides were detected by GC analysis in reactions of several carboxylic acids, such as benzoic acid (**2g**).
(64) Harvey, P. J.; von Itzstein, M.; Jenkins, I. D. *Tetrahedron* **1997**, *53*, 3933–3942.
(65) Shiina, I.; Miyao, R. *Heterocycles* **2008**, *76*, 1313–1328.
(66) Harned, A. M.; He, H. S.; Toy, P. H.; Flynn, D. L.; Hanson, P. R. *J. Am. Chem. Soc.* **2005**, *127*, 52–53.