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Synthesis of 6-hydroxy-2-naphthoic acid from 2,6-diisopropylnaphthalene using NHPI as a key catalyst

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ABSTRACT

A new strategy to 6-hydroxy-2-naphthoic acid (HNPA) and 4-hydroxybenzoic acid from 2,6-diisopropylnaphthalene and *p*-cymene, respectively, was developed using the NHPI-catalyzed aerobic oxidation as a principal reaction. 2,6-Diisopropylnaphthalene was oxidized by the oxidation with O_2 (1 atm) by NHPI (10 mol %) combined with $Co(OAc)_2$ (0.5 mol %) to give 6-acetyl-2-isopropylnaphthalene, which then was converted to 6-isopropyl-2-naphthoic acid under O_2 (1 atm) in the presence of $Co(OAc)_2$ (0.5 mol %) and $Mn(OAc)_2$ (0.5 mol %). Esterification of the resulting acid followed by the aerobic oxidation produced methyl 6-hydroxy-2-naphthoate whose hydrolysis led to the desired HNPA. An alternative route involves the oxidation of 6-acetyl-2-isopropylnaphthalene to 6-acetyl-2-naphthol on which subsequent oxidation and deacetylation gave HNPA. This method was successfully extended to the synthesis of 4-hydroxybenzoic acid from *p*-cymene.

1. Introduction

6-Hydroxy-2-naphthoic acid (HNPA) (**1**) is a very important class of compound as polymer materials for polyesters and polymeric liquid crystals having high performance properties like thermal stability.[1] HNPA (**1**) is merely prepared by the Kolbe–Schmitt reaction, which is a carboxylation of alkali and alkaline earth metal naphthoxides with CO_2.[2] The drawback of this method is the formation of a regioisomeric mixture of 2-hydroxy-1-naphthoic acid, 2-hydroxy-3-naphthoic acid, and HNPA (**1**). To our knowledge, however, there has been little study so far of HNPA (**1**) synthesis from readily available starting materials in spite of their synthetic importance.[3] Thus, our attention has been paid to the synthesis of HNPA (**1**) from 2,6-diisopropylnaphthalene (**2**), which is manufactured in large scale in industry.

In a previous paper, we reported that phenol can be prepared by the NHPI-catalyzed aerobic oxidation of isopropylbenzene (cumene) followed by treating with dilute sulfuric acid.[4] In this paper, this methodology has been applied to introducing a phenolic OH group to the naphthalene ring for the synthesis of HNPA (**1**). Here we wish to propose new routes to HNPA (**1**) from **2** using the NHPI-catalyzed aerobic oxidation as a key reaction.

2. Results and discussion

The first synthetic approach to HNPA (**1**) from **2** is outlined in Scheme 1. The oxidation of **2** with O_2 was examined by using NHPI/AIBN system, leading to isopropyl hydroperoxide on which subsequent decomposition with $Co(OAc)_2$ followed by the hydrogenation on Pd/C gave 6-acetyl-2-isopropylnaphthalene (**3**). The oxidation of the **3** with O_2 by $Co(OAc)_2$ and $Mn(OAc)_2$ afforded 6-isopropyl-2-naphthoic acid (**4**). Esterification of **4** to methyl 6-isopropyl-2-naphtoate (**5**) followed by the oxidation with O_2 under the influence of NHPI and AIBN produces methyl 6-hydroxy-2-naphthoate (**6**), which is easily hydrolyzed to **1**.

Table 1 shows the result for the oxidation of **2** by NHPI under various reaction conditions. The oxidation of **2** by NHPI combined with $Co(OAc)_2$ in acetonitrile at 75 °C for 6 h produced **3** in 31% yield (29% isolated yield) and 6-isopropenyl-2-isopropylnaphthalene (**7**) in 5% yield at 36% conversion (entry 1). When $Mn(OAc)_2$ in place of $Co(OAc)_2$ was added to the catalytic system, the conversion of **2** was increased to 51%. However, the reaction gave rise to **7**, but not **3**, as a major product (48% yield) (entry 3). This indicates that the catalytic potential of the Mn ion is very different from that of the Co ion. In order to improve the conversion and selectivity to **3**, the oxidation of **2** by NHPI in the presence of both $Mn(OAc)_2$ and $Co(OAc)_2$ was examined, but the selectivity of **3** did not increase (entry 4). The reaction in acetic acid resulted in low conversion of **2** (entry 5). Previously, we observed similar phenomena in the NHPI-catalyzed aerobic oxidation of *p*-cymene in acetic acid, because the acetic acid can induce the decomposition of the resulting isopropyl

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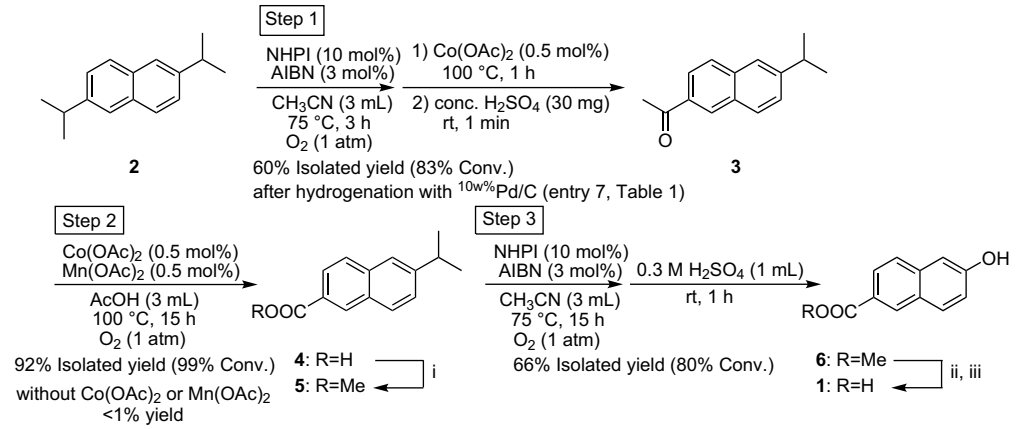
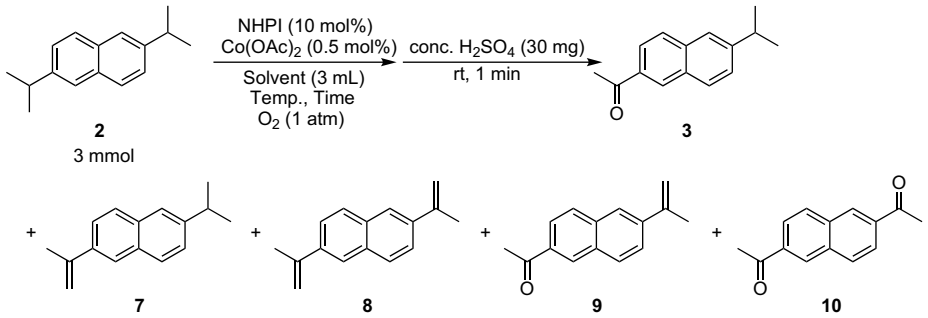


Scheme 1. Synthesis of 6-hydroxy-2-naphthoic acid (HNPA) (**1**) from 2,6-diisopropylnaphthalene (**2**) (first approach). Reagents and conditions: (i) H_2SO_4 (50 mg), MeOH (20 mL), at 100 °C for 24 h, quant.; (ii) NaOH (120 mg), H_2O (30 mL), at 90 °C for 15 h; (iii) HCl (1 mL), quant.

Table 1
Oxidation of **2** to **3** with O_2 by NHPI under various conditions[a]

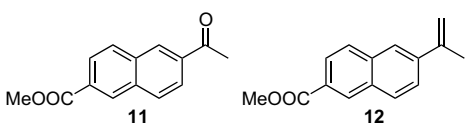


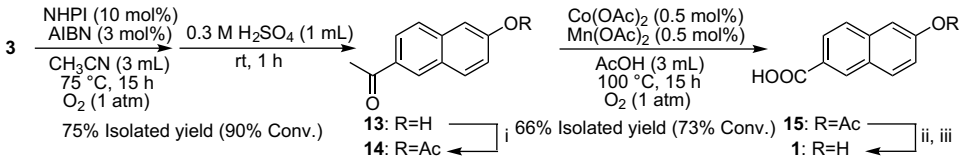
Entry	Solvent	Temp/°C	Time/h	Conv./%	Yield/%[b]				
					3	**7**	**8**	**9**	**10**
1	CH_3CN	75	6	36	31(29)	5	Trace	Trace	nd
2	CH_3CN	75	15	48	30	7	1	8	nd
3[c]	CH_3CN	75	6	51	Trace	48	nd	nd	nd
4[d]	CH_3CN	75	6	40	26	4	Trace	nd	nd
5	AcOH	100	6	8	6	1	Trace	Trace	nd
6[e]	CH_3CN	75	3	93	31	11	4	32	11
7[e,f]	CH_3CN	75	3	83	62(60)	3	1	1	10

[a] Compound **2** (3 mmol) was reacted under O_2 (1 atm) in the presence of NHPI (10 mol %) and $Co(OAc)_2$ (0.5 mol %) in CH_3CN (3 mL) at 75 °C for 3–15 h.
[b] Numbers in parentheses show isolated yields.
[c] $Mn(OAc)_2$ (0.5 mol %) was used in place of $Co(OAc)_2$.
[d] $Mn(OAc)_2$ (0.5 mol %) was added to the catalytic system.
[e] NHPI (10 mol %) and AIBN (3 mol %) were used as catalysts, and the reaction mixture was treated with $Co(OAc)_2$ (0.5 mol %) at 100 °C for 1 h before the treatment with sulfuric acid.
[f] After the reaction, the reaction mixture was reacted under H_2 (1 atm) in the presence of 10 wt % Pd/C (100 mg) in EtOAc (20 mL) at room temperature for 6 h. Approximately 10% of **2** was increased after hydrogenation.

hydroperoxide to phenol, which serves as a radical inhibitor.[4] The oxidation of **2** by NHPI combined with AIBN in acetonitrile at 75 °C for 3 h produced **3**, 2-acetyl-6-isopropenylnaphthalene (**9**), and 2,6-diacetylnaphthalene (**10**) in 31%, 32%, and 11% yields, respectively (entry 6). In this oxidation, **3** was found to be further oxidized to **9**. In order to improve the yield of **3**, the hydrogenation of the resulting reaction mixture was carried out. Thus, **3** was obtained as a major product in 60% isolated yield (entry 7). This is the first successful conversion of isopropyl group to acetyl group on the naphthalene ring. In this hydrogenation, **7** and 2,6-diisopropenylnaphthalene (**8**) were converted into the starting **2**, which can be recycled as the starting material. We next tried the aerobic oxidation of **3** under O_2 (1 atm) using $Co(OAc)_2$ (0.5 mol %) and $Mn(OAc)_2$ (0.5 mol %) in acetic acid at 100 °C for 15 h and gave 6-isopropyl-2-naphthoic acid (**4**) in 92% isolated yield. When either $Mn(OAc)_2$ or $Co(OAc)_2$ was removed from the catalytic system, **4** was formed in poor yield (<1%) (step 2). This indicates that remarkable synergy effect of Co and Mn ions appeared in this aerobic oxidation, although such a marked synergy effect of these metal ions was not observed in the oxidation of **2** by the NHPI as shown in entry 4 of Table 1.

The methyl ester (**5**) was allowed to react with O_2 (1 atm) under the influence of AIBN (3 mol %) and NHPI (10 mol %) in acetonitrile at 75 °C for 15 h followed by treatment with dilute sulfuric acid at room temperature for 1 h to lead to a mixture of **6** (66% isolated yield), methyl 6-acetyl-2-naphthoate (**11**) (4%), and methyl 6-isopropenyl-2-naphthoate (**12**) (4%) at 80% conversion (step 3). Treatment of **6** with a base gave rise to the desired **1** in quantitative yield.

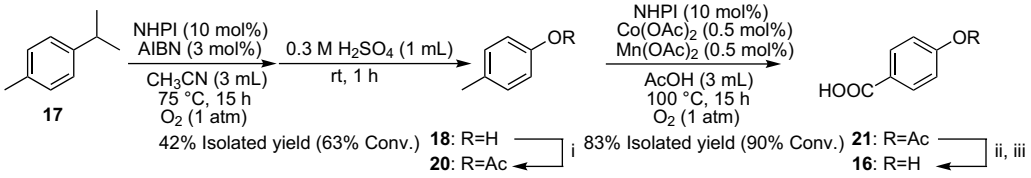




Scheme 2. Synthesis of 6-hydroxy-2-naphthoic acid (HNPA) (**1**) from 2,6-diisopropylnaphthalene (**2**) via 6-acetyl-2-naphthol (**13**) (second approach). Reagents and conditions: (i) Ac_2O (10 mL), Pyridine (10 mL), at 100 °C for 15 h, quant.; (ii) NaOH (120 mg), H_2O (30 mL), at 90 °C for 15 h; (iii) HCl (1 mL), quant.

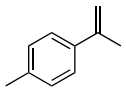
Scheme 2 shows another synthetic approach of **1** from **3**. The oxidation of **3** with O_2 under the influence of catalytic amounts of AIBN and NHPI in acetonitrile at 75 °C for 15 h followed by treatment with dilute sulfuric acid produced 6-acetyl-2-naphthol (**13**) in 85% yield (75% isolated yield) at 90% conversion. Acetylation of **13** with acetic anhydride and then the aerobic oxidation by $Co(OAc)_2$ and $Mn(OAc)_2$ gave **1** in 66% isolated yield at 73% conversion after hydrolysis.

This strategy can be extended to the synthesis of 4-hydroxybenzoic acid (**16**), which is an important compound for drugs, dyes, and polymer material, from *p*-cymene (**17**) (Scheme 3).



Scheme 3. Synthesis of 4-hydroxybenzoic acid (**16**) from *p*-cymene (**17**). Reagents and conditions: (i) Ac_2O (10 mL), Pyridine (10 mL), at 100 °C for 15 h, quant.; (ii) NaOH (120 mg), H_2O (30 mL), at 90 °C for 15 h; (iii) HCl (1 mL), quant.

The oxidation of **17** with O_2 in the presence of AIBN and NHPI in acetonitrile at 75 °C for 15 h followed by treatment with dilute sulfuric acid produced *p*-cresol (**18**) in 49% yield (42% isolated yield) along with 4-isopropenyltoluene (**19**) in 13% yield at 63% conversion. Acetylation of **18** to 4-acetoxytoluene (**20**) followed by the oxidation in the presence of NHPI, $Co(OAc)_2$, and $Mn(OAc)_2$ and then the treatment with 0.3 M sulfuric acid afforded **16** in 83% isolated yield at 90% conversion.



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In conclusion, a new approach to 6-hydroxy-2-naphthoic acid and 4-hydroxyl benzoic acid from easily available starting materials was achieved by using the NHPI-catalyzed aerobic oxidation as a key reaction and obtained desired products in fair yields.

3. Experimental

3.1. General procedure

All solvents, **2** and **17** were purchased from commercial sources. GC analysis was performed on GC equipped with a flame ionization detector using a 0.22 mm×25 m capillary column. Mass spectra were determined at ionization energy of 70 eV on GC–MS. ^1H and ^{13}C NMR were measured at 270/400 MHz and 67.5/100 MHz, respectively, in $CDCl_3$ or DMSO-d_6 with Me_4Si as the internal standard. TLC was performed on TLC plastic sheets F_{254} silica gel 60, using UV light and I_2. Infrared (IR) spectra were measured as thin films on NaCl plate. The product yields were estimated from the peak areas on the basis of the internal standard technique by using GC. All products except **9** were known compounds and reported previously.[5]

*3.1.1. 2-Acetyl-6-isopropenylnaphthalene (**9**)*

^1H NMR (270 MHz, $CDCl_3$, Me_4Si): 2.27 (s, 3H), 2.70 (s, 3H), 5.26 (s, 1H), 5.58 (s, 1H), and 8.41–7.66 (m, 6H); ^{13}C NMR (67.5 MHz, $CDCl_3$, Me_4Si): 21.8 (CH_3), 26.5 (CH_3), 114.4 (CH_2), 124.2 (CH), 124.5 (CH), 124.8 (CH), 129.2 (CH), 131.6 (CH), 135.6 (CH), 140.9 (C), 142.5 (C), 144.7 (C), 145.4 (C), 150.5 (C), and 198.2 (C); IR (neat, cm^{-1}) 3428, 2975, 1673, 1626, 1355, 1284, 1172, 1131, 889, 824, and 477; GC–MS (EI) *m*/*z* (relative intensity) 210 (M^+, 57), 195 (100%), 167 (40), 165 (22), 152 (24), 139 (5), 126 (5), and 115 (4); HRMS (EI) *m*/*z* calcd for $C_{15}H_{14}O$ [M^+] 210.1045, found 210.1049.

3.2. Synthesis of 6-hydroxy-2-naphthoic acid (HNPA) (1) from 2,6-diisopropylnaphthalene (2) (first approach, Scheme 1)

*3.2.1. Synthesis of 6-acetyl-2-isopropylnaphthalene (**3**)*

A mixture of 2,6-diisopropylnaphthalene (**2**) (637 mg, 3 mmol), NHPI (49 mg, 0.3 mmol, 10 mol %), and AIBN (14.7 mg, 0.09 mmol, 3 mol %) in acetonitrile (3.0 mL) was placed in a 30 mL pear-shaped flask equipped with a balloon filled with O_2. The mixture was stirred at 75 °C for 3 h. The reaction mixture was treated with $Co(OAc)_2{\cdot}4H_2O$ (3.7 mg, 0.015 mmol, 0.5 mol %) at 100 °C for 1 h under argon atmosphere. The reaction mixture was treated with a sulfuric acid (30 mg) at room temperature for 1 min. Removal of the solvent under reduced pressure afforded a crude mixture, and 10 wt % Pd/C (100 mg) in ethyl acetate (20 mL) was placed in a 50 mL pear-shaped flask equipped with a balloon filled with H_2. The mixture was stirred at the room temperature for 6 h. Removal of the solvent under reduced pressure afforded a crude mixture, which was purified by column chromatography on silica gel (*n*-hexane/AcOEt=15/1) to give 6-acetyl-2-isopropylnaphthalene (**3**) (382 mg, 1.8 mmol) in 60% isolated yield as a pure form.

*3.2.2. Synthesis of 6-isopropyl-2-naphthoic acid (**4**)*

A mixture of 6-acetyl-2-isopropylnaphthalene (**3**) (637 mg, 3 mmol), $Co(OAc)_2{\cdot}4H_2O$ (3.7 mg, 0.015 mmol, 0.5 mol %), and $Mn(OAc)_2{\cdot}4H_2O$ (3.6 mg, 0.015 mmol, 0.5 mol %) in acetic acid (3.0 mL) was placed in a 30 mL pear-shaped flask equipped with a balloon filled with O_2. The mixture was stirred at 100 °C for 15 h. Removal of the solvent under reduced pressure afforded a crude

mixture, which was extracted with $NaHCO_3$ solution followed by work up with hydrochloric acid (1 mL) to give 6-isopropyl-2-naphthoic acid (**4**) (591 mg, 2.76 mmol) in 92% isolated yield as a pure form.

*3.2.3. Synthesis of methyl 6-isopropyl-2-naphthoate (**5**)*

A mixture of 6-isopropyl-2-naphthoic acid (**4**) (214 mg, 1 mmol) and sulfuric acid (50 mg) in methanol (20 mL) was placed in a 50 mL pear-shaped flask. The mixture was stirred at 100 °C for 24 h. Removal of the solvent under reduced pressure afforded a crude mixture, which was purified by column chromatography on silica gel (*n*-hexane/AcOEt=15/1) to give methyl 6-isopropyl-2-naphthoate in quantitative yield.

*3.2.4. Synthesis of methyl 6-hydroxy-2-naphthoate (**6**)*

A mixture of methyl 6-isopropyl-2-naphthoate (**5**) (228 mg, 1 mmol), NHPI (16 mg, 0.1 mmol, 10 mol %), and AIBN (4.9 mg, 0.03 mmol, 3.0 mol %) in acetonitrile (3.0 mL) was placed in a 30 mL pear-shaped flask equipped with a balloon filled with O_2. The mixture was stirred at 75 °C for 15 h. The reaction mixture was treated with a solution of sulfuric acid (29 mg, 0.3 mmol) in acetonitrile (1 mL) at room temperature for 1 h. Removal of the solvent under reduced pressure afforded a crude mixture, which was purified by column chromatography on silica gel (*n*-hexane/AcOEt=15/1) to give the products, methyl 6-hydroxy-2-naphthoate (**6**) (133 mg, 0.66 mmol) in 66% isolated yield as a pure form.

*3.2.5. Synthesis of methyl 6-hydroxy-2-naphthoic acid (**1**)*

A mixture of 6-hydroxy-2-naphthoate (**6**) (202 mg, 1 mmol) and NaOH (120 mg, 3 mmol) in H_2O (30 mL) was placed in a 50 mL pear-shaped flask. The mixture was stirred at 90 °C for 15 h followed by work up with hydrochloric acid (1 mL) to give 6-hydroxy-2-naphthoic acid in quantitative yield.

3.3. Synthesis of 6-hydroxy-2-naphthoic acid (HNPA) (1) from 2,6-diisopropylnaphthalene (2) via 6-acetyl-2-naphthol (13) (second approach, Scheme 2)

*3.3.1. Synthesis of 6-acetyl-2-naphthol (**13**)*

A mixture of 6-acetyl-2-isopropylnaphthalene (**3**) (1061 mg, 5 mmol), NHPI (82 mg, 0.5 mmol, 10 mol %), and AIBN (25 mg, 0.15 mmol, 3.0 mol %) in acetonitrile (3.0 mL) was placed in a 30 mL pear-shaped flask equipped with a balloon filled with O_2. The mixture was stirred at 75 °C for 15 h. The reaction mixture was treated with a solution of sulfuric acid (29 mg, 0.3 mmol) in acetonitrile (1 mL) at room temperature for 1 h. Removal of the solvent under reduced pressure afforded a crude mixture, which was purified by column chromatography on silica gel (*n*-hexane/AcOEt=15/1) to give the products, 6-acetyl-2-naphthol (**13**) (698 mg, 3.75 mmol) in 75% isolated yield as a pure form.

*3.3.2. Synthesis of 2-acetoxy-6-acetylnaphthalene (**14**)*

6-Acetyl-2-naphthol (**13**) (559 mg, 3 mmol), in a mixture of acetic anhydride and pyridine (10 mL/10 mL) was placed in a 50 mL pear-shaped flask. The mixture was stirred at 100 °C for 15 h. Removal of the solvent under reduced pressure afforded a crude mixture, which was extracted with HCl solution followed by extracted with $NaHCO_3$ solution to give the products, which was purified by column chromatography on silica gel (*n*-hexane/AcOEt=15/1) to give 2-acetoxy-6-acetylnaphthalene (**14**) in quantitative yield.

*3.3.3. Synthesis of 6-acetoxy-2-naphthoic acid (**15**)*

A mixture of 2-acetoxy-6-acetylnaphthalene (**14**) (228 mg, 1 mmol), $Co(OAc)_2 \cdot 4H_2O$ (1.2 mg, 0.005 mmol, 0.5 mol %), and $Mn(OAc)_2 \cdot 4H_2O$ (1.2 mg, 0.005 mmol, 0.5 mol %) in acetic acid (3.0 mL) was placed in a 30 mL pear-shaped flask equipped with a balloon filled with O_2. The mixture was stirred at 100 °C for 15 h. Removal of the solvent under reduced pressure afforded a crude mixture, which was extracted with $NaHCO_3$ solution followed by extracted with HCl solution to give 6-acetoxy-2-naphthoic acid (**15**) (152 mg, 0.66 mmol) in 66% isolated yield as a pure form.

*3.3.4. Synthesis of 6-hydroxy-2-naphthoic acid (**1**)*

6-Acetoxy-2-naphthoic acid (**15**) (230 mg, 1 mmol) and NaOH (120 mg, 3 mmol) in H_2O (30 mL) were placed in a 50 mL pear-shaped flask. The mixture was reacted at 90 °C for 15 h followed by work up with hydrochloric acid (1 mL) to give 6-hydroxy-2-naphthoic acid (**1**) in quantitative yield.

3.4. Synthesis of 4-hydroxy-2-benzoic acid (16) from *p*-cymene (17) (Scheme 3)

*3.4.1. Synthesis of p-cresol (**18**)*

A mixture of *p*-cymene (**17**) (134 mg, 1 mmol), NHPI (16 mg, 0.1 mmol, 10 mol %), and AIBN (4.9 mg, 0.03 mmol, 3.0 mol %) in acetonitrile (3.0 mL) was placed in a 30 mL pear-shaped flask equipped with a balloon filled with O_2. The mixture was stirred at 75 °C for 15 h. The reaction mixture was treated with a solution of sulfuric acid (29 mg, 0.3 mmol) in acetonitrile (1 mL) at room temperature for 1 h. Removal of the solvent under reduced pressure afforded a crude mixture, which was purified by column chromatography on silica gel (*n*-hexane/AcOEt=15/1) to give the products, *p*-cresol (**18**) (45 mg, 0.42 mmol) in 42% isolated yield as a pure form.

*3.4.2. Synthesis of 4-acetoxytoluene (**20**)*

p-Cresol (**18**) (1081 mg, 10 mmol), in a mixture of acetic anhydride and pyridine (10 mL/10 mL) was placed in a 50 mL pear-shaped flask. The mixture was stirred at 100 °C for 15 h. Removal of the solvent under reduced pressure afforded a crude mixture, which was extracted with HCl solution followed by extracted with $NaHCO_3$ solution to give the products, which was purified by column chromatography on silica gel (*n*-hexane/AcOEt=15/1) to give 4-acetoxytoluene (**20**) in quantitative yield.

*3.4.3. Synthesis of 4-acetoxybenzoic acid (**21**)*

A mixture of 4-acetoxytoluene (**20**) (150 mg, 1 mmol), $Co(OAc)_2 \cdot 4H_2O$ (1.2 mg, 0.005 mmol, 0.5 mol %), and $Mn(OAc)_2 \cdot 4H_2O$ (1.2 mg, 0.005 mmol, 0.5 mol %) in acetic acid (3.0 mL) was placed in a 30 mL pear-shaped flask equipped with a balloon filled with O_2. The mixture was stirred at 100 °C for 15 h. Removal of the solvent under reduced pressure afforded a crude mixture, which was extracted with $NaHCO_3$ solution followed by work up with hydrochloric acid (1 mL) to give 4-acetoxybenzoic acid (**21**) (150 mg, 0.83 mmol) in 83% isolated yield as a pure form.

*3.4.4. Synthesis of 4-hydroxybenzoic acid (**16**)*

4-Acetoxybenzoic acid (**21**) (180 mg, 1 mmol) and NaOH (120 mg, 3 mmol) in H_2O (30 mL) were placed in a 50 mL pear-shaped flask. The mixture was stirred at 90 °C for 15 h followed by work up with hydrochloric acid (1 mL) to give 4-hydroxybenzoic acid (**16**) in quantitative yield.

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References and notes

1. (a) De Ruijter, C.; Bos, J.; Boerstoel, H.; Dingemans, T. J. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 6565; (b) Hsiue, L.-T.; Ma, C.-C. M.; Tsai, H.-B. *J. Appl. Polym. Sci.* **1995**, *56*, 471; (c) Nagata, M. *High Perform. Polym.* **2001**, *13*, S265; (d) Gao, P.; Lu, X. H.; Chai, C. K. *Polym. Eng. Sci.* **1996**, *36*, 2771.
2. (a) Lindsey, A. S.; Jeskey, H. *Chem. Rev.* **1957**, *57*, 583; (b) Rahim, M. A.; Matsui, Y.; Kosugi, Y. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 619; (c) Kumagai, H.; Ueda, S.; Hori, T. *Nippon Kagaku Kaishi* **1991**, 170; (d) Iijima, T.; Iwase, T.; Yamaguchi, T. *J. Jpn. Pet. Inst.* **2006**, *49*, 206; (e) Kolbe, H.; Lautemann, E. *Justus Liebigs Ann. Chem.* **1860**, *113*, 125; (f) Schmitt, R. *J. Prakt. Chem.* **1886**, *31*, 397.
3. (a) Minisci, F.; Recupero, F.; Fontana, F.; Bjørsvik, H.-R.; Liguori, L. *Synlett* **2002**, 610; (b) Kantam, M. L.; Ranganath, K. V. S.; Sateesh, M.; Kumar, K. B. S.; Choudary, B. M. *J. Mol. Catal. A: Chem.* **2005**, *225*, 15; (c) Melero, J. A.; van Grieken, R.; Morales, G.; Nuño, V. *Catal. Commun.* **2004**, *5*, 131; (d) Klein, C. D. P.; Tabeteh, G. F.; Laguna, A. V.; Holzgrabe, U.; Mohr, K. *Eur. J. Pharm. Sci.* **2001**, *14*, 167.
4. Fukuda, O.; Sakaguchi, S.; Ishii, Y. *Adv. Synth. Catal.* **2001**, *343*, 809.
5. (a) Compound **1**: Serrano-Wu, M. H.; Regueiro-Ren, A.; St. Laurent, D. R.; Carroll, T. M.; Balasubramanian, B. N. *Tetrahedron Lett.* **2001**, *42*, 8593; (b) Compound **3**: Zawadiak, J.; Orlinska, B.; Stec, Z. *Fresenius' J. Anal. Chem.* **2000**, *367*, 502; (c) Compound **4**: Huebner, C. F.; Jacobs, W. A. *J. Biol. Chem.* **1947**, *169*, 211; (d) Compound **5**: Zoeller, J. R.; Sumner, C. E. *J. Org. Chem.* **1990**, *55*, 319; (e) Compound **6**: Gao, Y.; Voigt, J.; Zhao, H.; Pais, G. C. G.; Zhang, X.; Wu, L.; Zhang, Z.-Y.; Burke, T. R., Jr. *J. Med. Chem.* **2001**, *44*, 2869; (f) Compound **7**: Aoki, Y.; Sakaguchi, S.; Ishii, Y. *Adv. Synth. Catal.* **2004**, *346*, 199; (g) Compound **8**: Minisci, F.; Recupero, F.; Cecchetto, A.; Gambarotti, C.; Punta, C.; Paganelli, R.; Pedulli, G. F.; Fontana, F. *Org. Process Res. Dev.* **2004**, *8*, 163; (h) Compound **10**: Zaccheria, F.; Ravasio, N.; Ercoli, M.; Allegrini, P. *Tetrahedron Lett.* **2005**, *46*, 7743; (i) Compound **11**: Ref. 5d; (j) Compound **12**: Shishido, Y.; Nakao, K.; Nagayama, S.; Tanaka, H.; Duncton, M. A. J.; Cox, M.; Kincaid, J.; Sahasrabudhe, K.; Estiarte-Martinez, M. PCT Int. Appl., 2007, WO 2007133637; (k) Compound **13**: Kim, H. M.; Jung, C.; Kim, B. R.; Jung, S.-Y.; Hong, J. H.; Ko, Y.-G.; Lee, K. J.; Cho, B. R. *Angew. Chem., Int. Ed.* **2007**, *46*, 3460; (l) Compound **14**: Rajarathnam, D.; Nadar, P. A. *Int. J. Chem. Kinet.* **2001**, *33*, 157; (m) Compound **15**: Teoh, M. M.; Chung, T.-S.; Pramoda, K. P. *Synth. Met.* **2004**, *147*, 191; (n) Compound **16**: Kshirsagar, V. S.; Vijayanand, S.; Potdar, H. S.; Joy, P. A.; Patil, K. R.; Rode, C. V. *Chem. Lett.* **2008**, *37*, 310; (o) Compound **18**: Kianmehr, E.; Yahyaee, M.; Tabatabai, K. *Tetrahedron Lett.* **2007**, *48*, 2713; (p) Compound **19**: Lebel, H.; Davi, M.; Díez-González, S.; Nolan, S. P. *J. Org. Chem.* **2007**, *72*, 144; (q) Compound **20**: Moghadam, M.; Tangestaninejad, S.; Mirkhani, V.; Mohammadpoor-Baltork, I.; Taghavi, S. A. *J. Mol. Catal. A: Chem.* **2007**, *274*, 217; (r) Compound **21**: Yeung, C. S.; Dong, V. M. *J. Am. Chem. Soc.* **2008**, *130*, 7826.