



Synthesis of 6-hydroxy-2-naphthoic acid from 2,6-diisopropynaphthalene 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-diisopropynaphthalene and *p*-cymene, respectively, was developed using the NHPI-catalyzed aerobic oxidation as a principal reaction. 2,6-Diisopropynaphthalene was oxidized by the oxidation with O₂ (1 atm) by NHPI (10 mol %) combined with Co(OAc)₂ (0.5 mol %) to give 6-acetyl-2-isopropynaphthalene, which then was converted to 6-isopropyl-2-naphthoic acid under O₂ (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-isopropynaphthalene 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.

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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 CO₂.² 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-diisopropynaphthalene (**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.

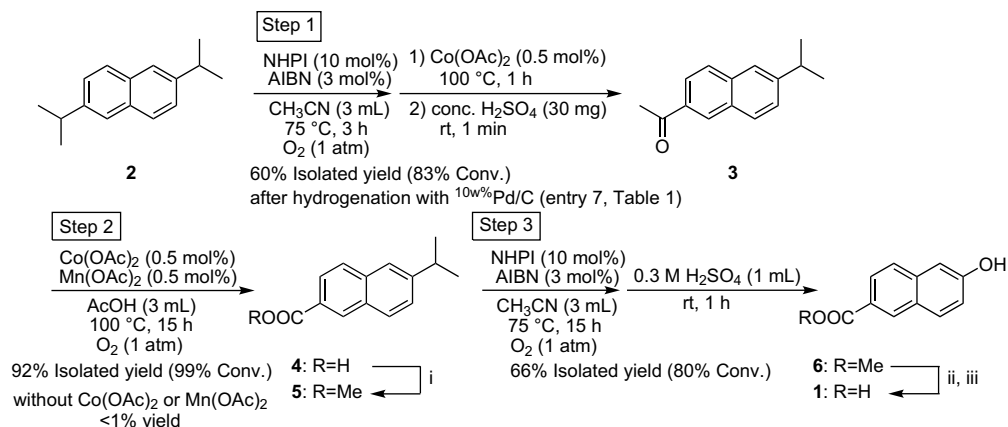
2. Results and discussion

The first synthetic approach to HNPA (**1**) from **2** is outlined in Scheme 1. The oxidation of **2** with O₂ 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-isopropynaphthalene (**3**). The oxidation of the **3** with O₂ by Co(OAc)₂ and Mn(OAc)₂ afforded 6-isopropyl-2-naphthoic acid (**4**). Esterification of **4** to methyl 6-isopropyl-2-naphthoate (**5**) followed by the oxidation with O₂ 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-isopropynaphthalene (**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-diisopropynaphthalene (**2**) (first approach). Reagents and conditions: (i) H₂SO₄ (50 mg), MeOH (20 mL), at 100 °C for 24 h, quant.; (ii) NaOH (120 mg), H₂O (30 mL), at 90 °C for 15 h; (iii) HCl (1 mL), quant.

Table 1
Oxidation of **2** to **3** with O₂ by NHPI under various conditions^a

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

^a Compound **2** (3 mmol) was reacted under O₂ (1 atm) in the presence of NHPI (10 mol %) and Co(OAc)₂ (0.5 mol %) in CH₃CN (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.

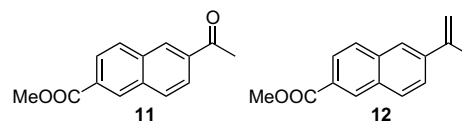
^e NHPI (10 mol %) and AIBN (3 mol %) were used as catalysts, and the reaction mixture was treated with Co(OAc)₂ (0.5 mol %) at 100 °C for 1 h before the treatment with sulfuric acid.

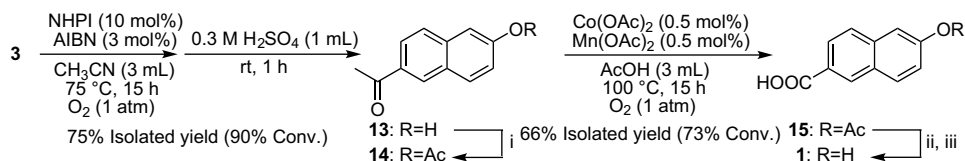
^f After the reaction, the reaction mixture was reacted under H₂ (1 atm) in the presence of 10 wt % Pd/C (100 mg) in EtOAc (20 mL) at room temperature for 6 h. Approximately 10% of **2** was increased after hydrogenation.

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-isopropynaphthalene (**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-diisopropynaphthalene (**8**) were converted into the starting **2**, which can be recycled as the starting material. We next tried the aerobic oxidation of **3** under O₂ (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 O₂ (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.

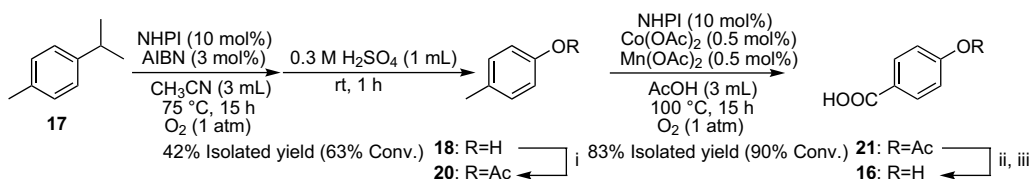




Scheme 2. Synthesis of 6-hydroxy-2-naphthoic acid (HNPA) (**1**) from 2,6-diisopropynaphthalene (**2**) via 6-acetyl-2-naphthol (**13**) (second approach). Reagents and conditions: (i) Ac_2O (10 mL), Pyridine (10 mL), at 100°C for 15 h, quant.; (ii) NaOH (120 mg), H_2O (30 mL), at 90°C for 15 h; (iii)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

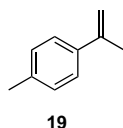
Scheme 2 shows another synthetic approach of **1** from **3**. The oxidation of **3** with O_2 under the influence of catalytic amounts of AIBN and NHPI in acetonitrile at 75°C for 15 h followed by treatment with dilute sulfuric acid produced 6-acetyl-2-naphthol (**13**) in 85% yield (75% isolated yield) at 90% conversion. Acetylation of **13** with acetic anhydride and then the aerobic oxidation by $\text{Co}(\text{OAc})_2$ and $\text{Mn}(\text{OAc})_2$ 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-acetoxyp-cymene (**20**) followed by the oxidation in the presence of NHPI, $\text{Co}(\text{OAc})_2$, and $\text{Mn}(\text{OAc})_2$ and then the treatment with 0.3 M sulfuric acid afforded **16** in 83% isolated yield at 90% conversion.



In conclusion, a new approach to 6-hydroxy-2-naphthoic acid and 4-hydroxybenzoic 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 $0.22\text{ mm} \times 25\text{ m}$ 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 $\text{DMSO}-d_6$ with Me_4Si as the internal standard. TLC was performed on TLC plastic sheets F₂₅₄ 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 $\text{C}_{15}\text{H}_{14}\text{O}$ [M^+] 210.1045, found 210.1049.

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

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

A mixture of 2,6-diisopropynaphthalene (**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 $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (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-isopropynaphthalene (**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-isopropynaphthalene (**3**) (637 mg, 3 mmol), $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (3.7 mg, 0.015 mmol, 0.5 mol%), and $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (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 NaHCO₃ 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 O₂. 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 H₂O (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-diisopropyl-naphthalene (**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-isopropyl-naphthalene (**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 O₂. 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 NaHCO₃ 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)₂·4H₂O (1.2 mg, 0.005 mmol, 0.5 mol %), and Mn(OAc)₂·4H₂O (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 O₂. 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 NaHCO₃ 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 H₂O (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 O₂. 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 NaHCO₃ 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)₂·4H₂O (1.2 mg, 0.005 mmol, 0.5 mol %), and Mn(OAc)₂·4H₂O (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 O₂. 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 NaHCO₃ 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 H₂O (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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