Advanced Synthesis & Catalysis

DOI: 10.1002/adsc.201400154

Palladium-Catalyzed Intermolecular Allylic Dearomatization Reaction of α-Substituted β-Naphthol Derivatives: Scope and Mechanistic Investigation

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Received: February 20, 2014; Revised: March 15, 2014; Published online: ■■ ■■, 0000

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201400154.

Abstract: A highly efficient dearomatization reaction of α-substituted β-naphthols with excellent chemoselectivity and regioselectivity has been developed. Mechanistic studies demonstrated that the dearomatized alkylation product is the thermodynamically more stable compound. The etherification product could be further transformed to the dearomatization product.

Keywords: allylic substitution; chemoselectivity; dearomatization; naphthalenones; naphthols; palladium

Introduction

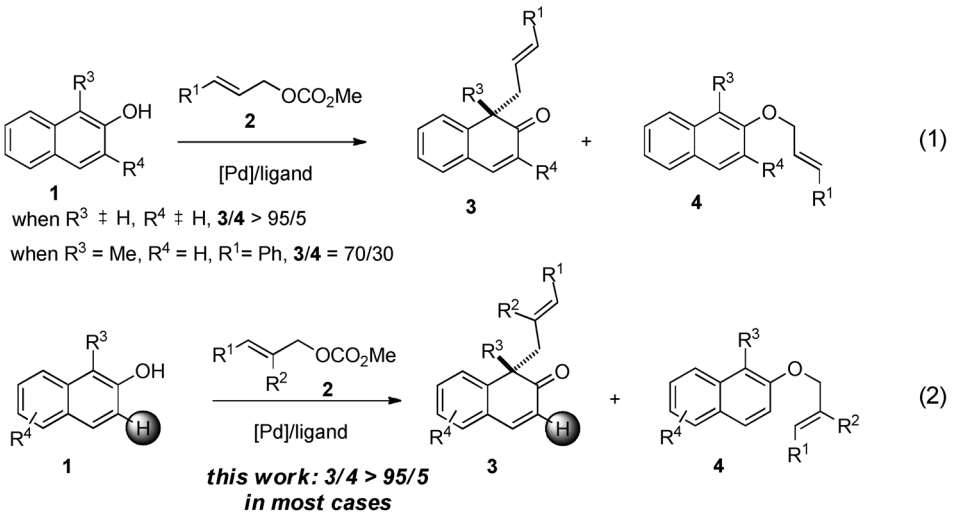
The dearomatization reaction of simple planar aromatic compounds is a powerful and straightforward strategy for the preparation of highly functionalized ring structures.[1] In this regard, the transition metal-catalyzed dearomatization reaction has received great attention and enormous efforts have been devoted to this area in recent years.[2]

Phenols are particular interesting in dearomatization reactions because of their abundance as starting materials and utility of the products.[3,4] However, due to the high energy barrier for breaking the aromaticity and the competitive *O*-alkylation or Friedel–Crafts alkylation reaction pathways, chemoselectivity and stereoselectivity remain challenging issues in the catalytic intermolecular dearomatization reaction. One solution to the problems mentioned above is to utilize the oxidative protocol to furnish the efficient dearomatization process of phenols.[5] The other is the intramolecular design that benefits the selectivities.[6] Despite the progress in the intramolecular dearomatization of phenols, catalytic intermolecular dearomatization reactions of phenol derivatives under the non-oxidative conditions have been rarely explored.[7]

The transition metal-catalyzed allylic substitution reaction is one of the most powerful methods for the construction of C–C and C–X bonds.[8] Recently, we reported a palladium-catalyzed intermolecular asymmetric allylic dearomatization of β-naphthols, affording highly enantioenriched β-naphthalenone derivatives.[9] Good chemoselectivities were obtained only with the 1,3-disubstituted 2-naphthols in which the steric hindrance of the disubstituted groups would prevent the competitive *O*-alkylation [Eq. (1), Scheme 1]. The chemoselectivity for substrates without substituent at the C-3 position suffered greatly. In addition, R^3 is limited with alkyl group, and electron-deficient substituents cannot be tolerated. In this paper, we present a highly efficient dearomatization reaction of simple 1-substituted 2-naphthol substrates with excellent chemoselectivity and regioselectivity and the related mechanistic study [Eq. (2), Scheme 1].

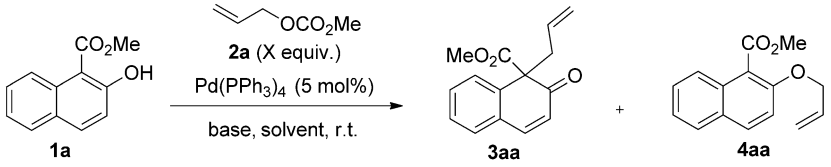
Results and Discussion

The initial exploration of the reaction conditions was performed using methyl 2-hydroxy-1-naphthoate (**1a**) and allylic carbonate (**2a**) as the model substrates. The results are summarized in Table 1. In the presence of 5 mol% of $Pd(PPh_3)_4$ and 2.0 equiv. of Li_2CO_3, the reaction proceeded smoothly in DCM for 21 h to provide **3aa** and **4aa** in a ratio of 88/12 with 72% conversion (entry 1, Table 1). To optimize the reaction conditions, various solvents such as CCl_4, benzene, toluene, THF and dioxane were screened (entries 2–6, Table 1). The results showed that chemoselectivity and conversion of this reaction varied re-



Scheme 1. Palladium-catalyzed intermolecular allylic dearomatization reaction of naphthols.

Table 1. Investigation of the reaction conditions.[a]

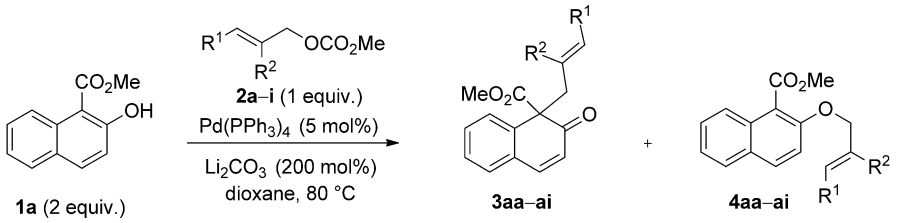


Entry	Solvent	Base	X	Time [h]	Conversion [%][b]	Ratio of **3aa**/**4aa**[b]
1	DCM	Li_2CO_3	1.2	21	72	88/12
2	CCl_4	Li_2CO_3	1.2	21	35	< 5/95
3	benzene	Li_2CO_3	1.2	21	71	> 95/5
4	toluene	Li_2CO_3	1.2	21	76	79/21
5	THF	Li_2CO_3	1.2	21	42	71/29
6	dioxane	Li_2CO_3	1.2	21	79	> 95/5
7	dioxane	Cs_2CO_3	1.2	41	68	> 95/5
8	dioxane	LiO-*t*-Bu	1.2	41	48	95/5
9	dioxane	DBU	1.2	41	> 95	17/83
10[c]	dioxane	LiHMDS	1.2	41	84	< 5/95
11	dioxane	Li_2CO_3	2.0	27	> 95	45/55
12	dioxane	Li_2CO_3	0.64	27	82	> 95/5
13[d]	dioxane	Li_2CO_3	0.5	27	89	> 95/5
14	dioxane	Li_2CO_3	0.33	27	91	> 95/5

[a] *Reaction conditions:* 5 mol% of $Pd(PPh_3)_4$, 0.2 mmol of **1a**, 0.24 mmol of **2a**, 0.4 mmol of base in solvent (2.0 mL) at room temperataure (for entries 1–10); 5 mol% of $Pd(PPh_3)_4$, 0.1 mmol of **1a**, 0.2 mmol of **2a**, 0.2 mmol of Li_2CO_3 in dioxane (2.0 mL) at room temperature (for entry 11); 5 mol% of $Pd(PPh_3)_4$, 0.2/X mmol of **1a**, 0.2 mmol of **2a**, 0.4 mmol of Li_2CO_3 in dioxane (2.0 mL) at room temperature (for entries 12–14).
[b] Determined by ^1H NMR of the crude reaction mixture.
[c] 1 equiv. of base was used.
[d] Isolated yield of **3aa** is 85%.

markably in different solvents. Dioxane was found to be the optimal solvent (79% conversion, **3aa**/**4aa**: > 95/5, entry 6, Table 1). The effect of base was examined next. Cs_2CO_3 and LiO-*t*-Bu could promote the reaction with good chemoselectivity, but in only moderate conversions (entries 7 and 8, Table 1). DBU and LiHMDS were effective in promoting the allylic substitution reaction but with low selectivity for **3aa** (entries 9 and 10, Table 1). Li_2CO_3 was found to be the optimal base (entry 6, Table 1). Investigation of the loading of **2a** demonstrated that an excess amount of **1a** gave satisfactory results in terms of yield and chemoselectivity (entries 11–14, Table 1). Overall, the optimized conditions for the reaction are the following:

Table 2. The substrate scope – allyl carbonates.[a]



Entry	**2**, R^1, R^2	Time [h]	Ratio of **3**/**4**[b]	**3**, Yield [%][c]
1[d]	**2a**, H, H	27	>95/5	**3aa**, 85
2[d]	**2b**, Ph, H	28	75/25	**3ab**, 72
3	**2b**, Ph, H	34	95/5	**3ab**, 94
4[e]	**2b**, Ph, H	24	>95/5	**3ab**, 84
5	**2c**, 4-$MeOC_6H_4$, H	11	>95/5	**3ac**, 98
6	**2d**, 3-$MeOC_6H_4$, H	7	>95/5	**3ad**, 87
7	**2e**, 2-ClC_6H_4, H	11	>95/5	**3ae**, 90
8	**2f**, 4-ClC_6H_4, H	18	>95/5	**3af**, 83
9	**2g**, 4-$CF_3C_6H_4$, H	7	>95/5	**3ag**, 69
10	**2h**, 2-thienyl, H	11	>95/5	**3ah**, 85
11	**2i**, H, Ph	18	78/22	**3ai**, 60

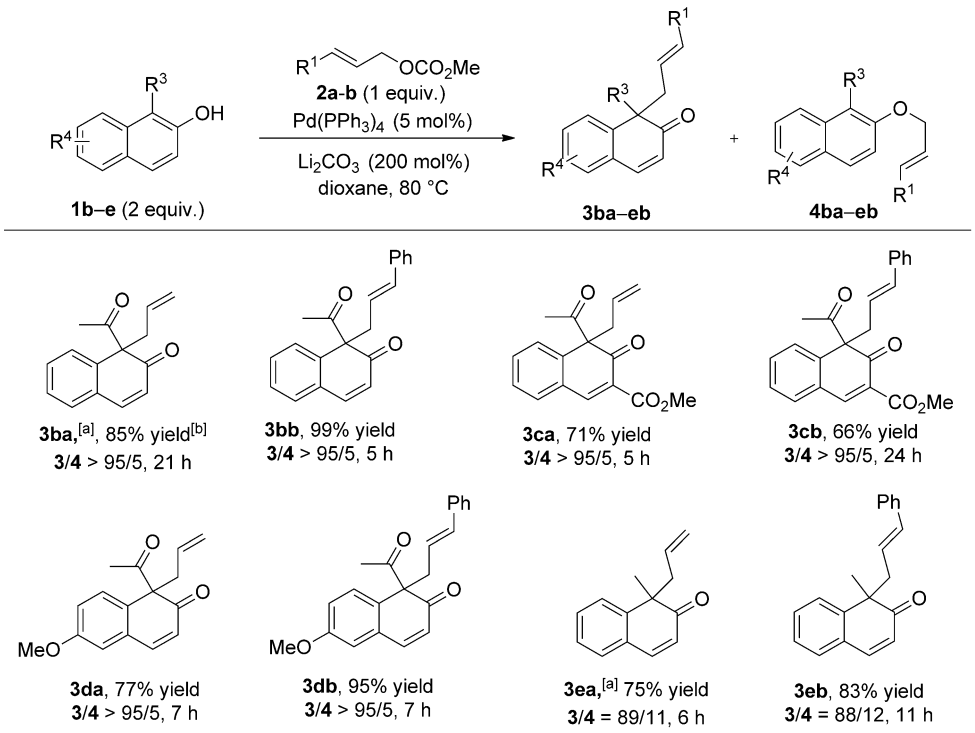
[a] *Reaction conditions:* 5 mol% of $Pd(PPh_3)_4$, 0.4 mmol of **1a**, 0.2 mmol of **2**, 0.4 mmol of Li_2CO_3 in dioxane (2.0 mL) at 80 °C.
[b] Determined by ^1H NMR of the crude reaction mixture.
[c] Isolated yield.
[d] Reaction was conducted at room temperature.
[e] *Reaction conditions:* 1 mol% of $Pd(PPh_3)_4$, 1.0 mmol of **1a**, 0.5 mmol of **2b**, 1.0 mmol of Li_2CO_3 in dioxane (5.0 mL) at 80 °C.

5 mol% of $Pd(PPh_3)_4$, 2 equiv. of Li_2CO_3, 2 equiv. of **1a** and 1 equiv. of **2a** at room temperature in dioxane (**3aa** was obtained in 85% yield with a ratio of **3aa**/**4aa** as >95/5, entry 13, Table 1).

Under the optimized reaction conditions, various substituted allylic carbonates **2** were reacted with methyl 2-hydroxy-1-naphthoate (**1a**) to examine the generality of the process (Table 2). When cinnamyl carbonate (**2b**) was utilized, the reaction occurred smoothly at room temperature in 72% yield with 3/1 chemoselectivity in favor of the dearomatized product (entry 2, Table 2). The yield and chemoselectivity could be improved to 94% and 95/5, respectively, when the reaction temperature was elevated to 80 °C (entry 3, Table 2). The reactions of allylic carbonates containing *para*-, *meta*-methoxyphenyl groups (**2c** and **2d**) occurred smoothly to give the desired products (**3ac** and **3ad**) in 98% and 87% yield with excellent chemoselectivity (entries 5 and 6, Table 2). Aryl allylic carbonates bearing an electron-withdrawing group on the aromatic ring (*o*-Cl, *p*-Cl, *p*-CF_3; **2e**–**g**) all gave their corresponding products (**3ae**–**ag**) in good to excellent yields with exclusive formation of the dearomatized product (entries 7–9, Table 2). The reaction of 2-thienyl allyl carbonate (**2h**) with **1a** afforded product **3ah** in 85% yield with excellent chemoselectivity (entry 10, Table 2). When methyl 2-(phenylallyl) carbonate (**2i**) was used, the reaction also went smoothly with moderate chemoselectivity (**3ai**/**4ai**: 78/22, 60% isolated yield of **3ai**, entry 11, Table 2). To be noted, when the reaction was performed with 1 mol% of $Pd(PPh_3)_4$ on a 0.5 mmol scale, the reaction proceeded with excellent chemoselectivity in favor of dearomatized product **3ab** (**3ab**/**4ab** >95/5, 84% yield, entry 4, Table 2).

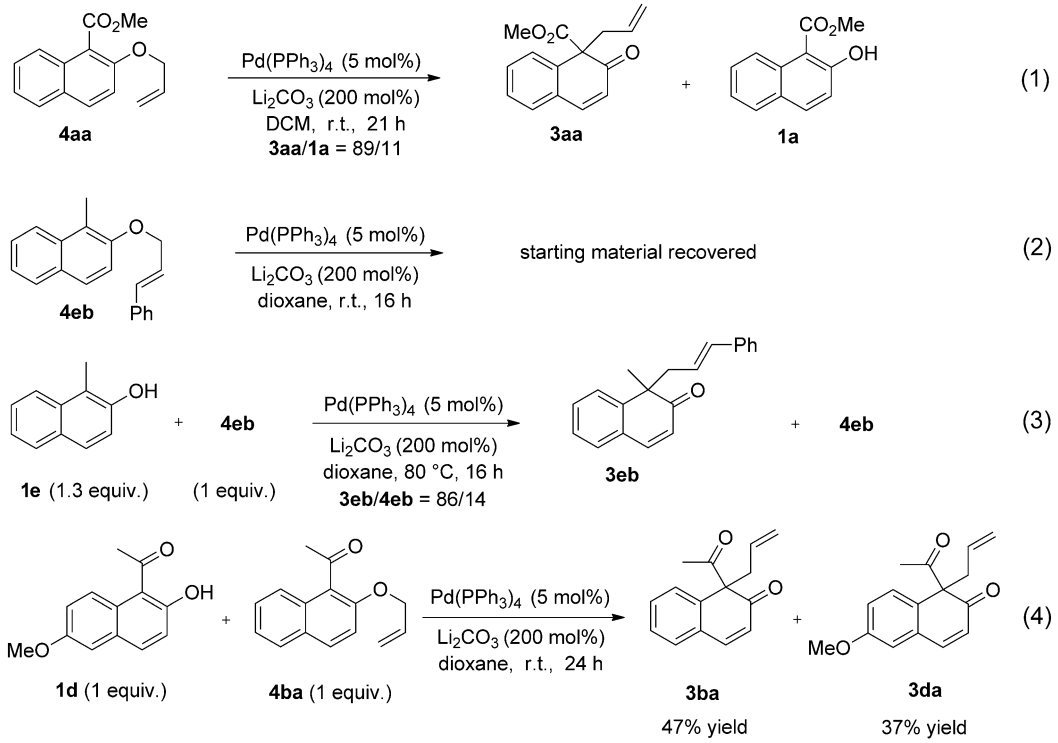
In addition, various β-naphthol derivatives **1b**–**e** were also tested in this reaction (Scheme 2). When the α-methyl ketone-bearing substrate (**1b**) was used, the reaction also occurred smoothly with either allyl carbonate (**2a**) or cinnamyl carbonate (**2b**) in excellent yields and chemoselectivity (85–99% yield, Scheme 2). β-Naphthol derivatives bearing either electron-withdrawing groups or electron-donating groups generally led to moderate to excellent yields (**3ca**–**3db**, 66–95% yield, Scheme 2) and excellent chemoselectivity (>95/5). Notably, the reaction could also occur smoothly when α-methyl-β-naphthol (**1e**) was utilized, affording the α-methyl-β-naphthalenone in good yields and chemoselectivity (**3ea** and **3eb**, 75–83% yield, Scheme 2).[10,11]

To gain insights into the reaction mechanism, we carried out the following experiments (Scheme 3). In the presence of the palladium catalyst and Li_2CO_3, product **4aa** could be converted to **3aa** and **1a** with a ratio of 89/11 [Eq. (1), Scheme 3]. Notably, no reaction occurred in the absence of the palladium catalyst.



[a] Reaction was conducted at room temperature.
[b] Isolated yield of **3**.

Scheme 2. The substrate scope – naphthols. *Reaction conditions:* 5 mol% of $Pd(PPh_3)_4$, 0.4 mmol of **1**, 0.2 mmol of **2**, 0.4 mmol of Li_2CO_3 in dioxane (2.0 mL) at 80 °C. Ratio of **3**/**4** was determined by ^1H NMR of the crude reaction mixture.



Scheme 3. Mechanistic study.

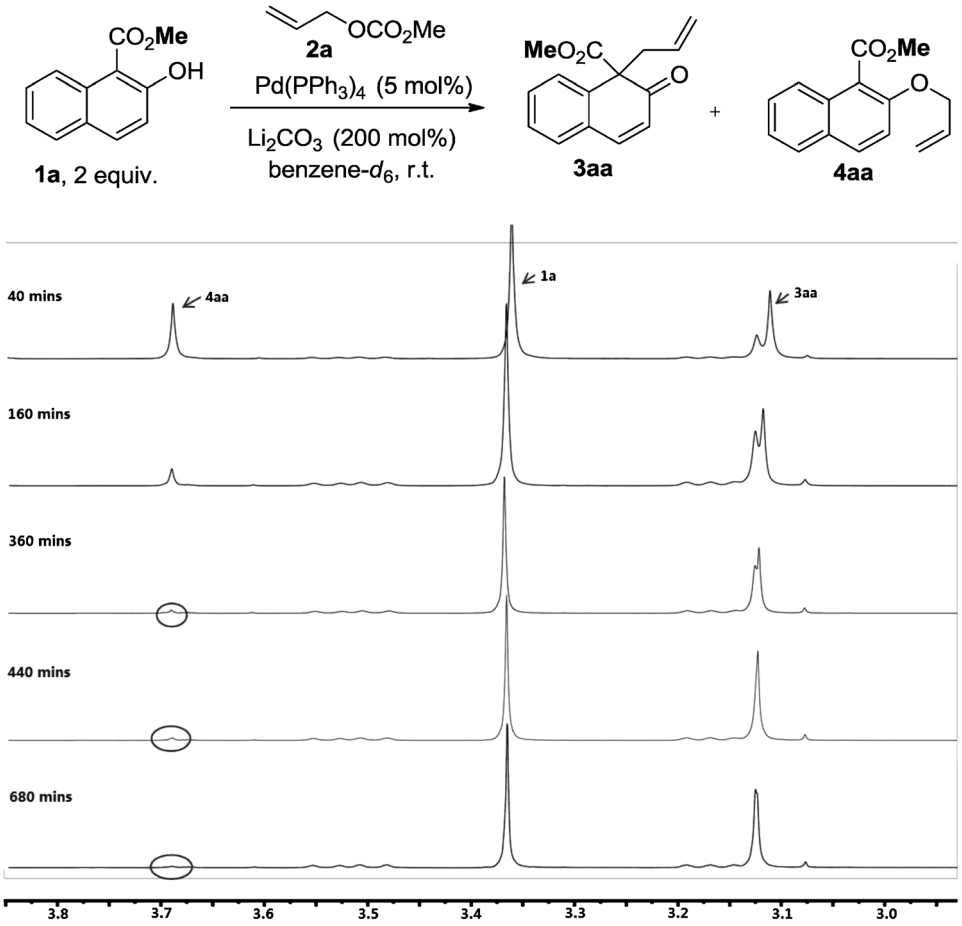
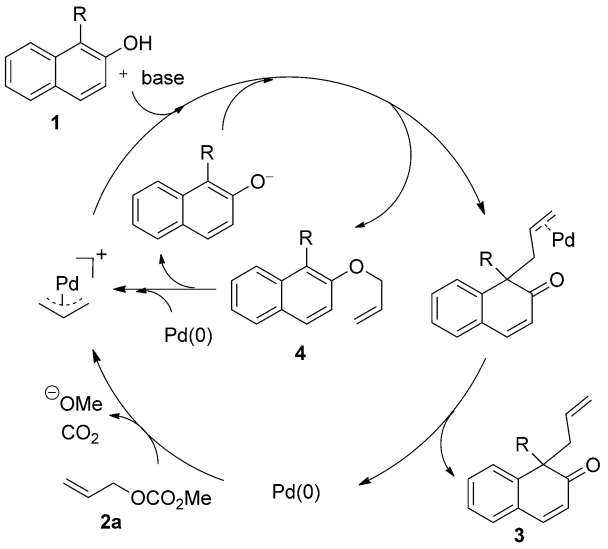


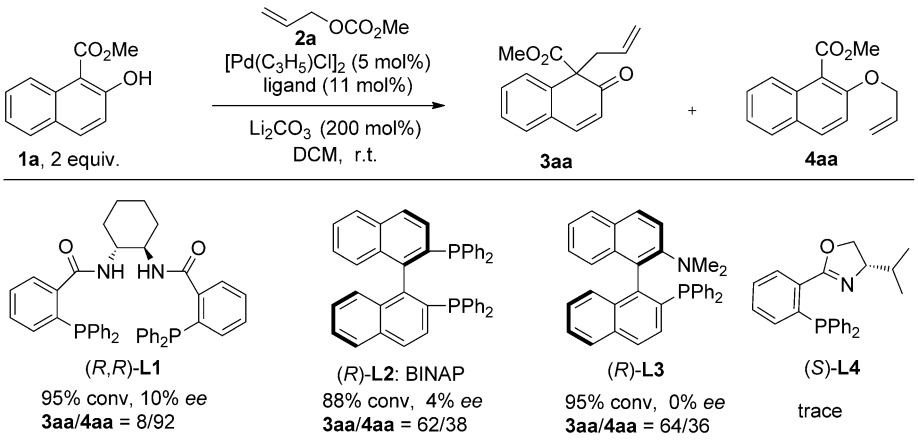
Figure 1. [1]H NMR monitoring of the reaction (*the peak at 3.69 ppm* refers to the chemical shift of the methyl group in **4aa**, *the peak at 3.37 ppm* refers to the chemical shift of the methyl group in **1a**, *the peak at 3.12 ppm* refers to the chemical shift of the methyl group in **3aa**).

In addition, product **3aa** could not be transformed to **4aa** under the same reaction conditions. Monitoring the reaction process in deuterated benzene by [1]H NMR was then carried out. The result also demonstrated that product **4aa** could be completely converted to **3aa** as the reaction proceeded (Figure 1). However, when product **4eb** was utilized in the presence of the palladium catalyst and Li_2CO_3, no reaction occurred [Eq. (2), Scheme 3]. Product **4eb** could be converted to **3eb** with only 6% conversion even when the temperature was elevated to 80 °C. This phenomenon indicated the reversible ionization of *O*-allylated product was greatly influenced by the induced effect of the α-substituted group of the β-naphthol. Interestingly, in the presence of an excess amount of α-methyl-β-naphthol, the *O*-allylated product **4eb** could be converted to the *C*-allylated product **3eb** with 86% conversion at 80 °C [Eq. (3), Scheme 3]. A cross-over experiment proved that the conversion from *O*-alkylated compounds to dearomatization products is not an intramolecular transformation or a contact ion pair process [Eq. (4), Scheme 3].

Based on the above experimental observations, a plausible reaction mechanism was proposed, as depicted in Scheme 4. Firstly, oxidative addition of allyl-



Scheme 4. A plausible reaction pathway.



Scheme 5. Attempt for the enantioselective reaction

ic carbonate **2a** to Pd(0) forms the π-allyl palladium species. Then nucleophilic attack by **1** gives products **3** and **4**, respectively. Product **4** can be further converted to π-allyl palladium species through oxidative addition to Pd(0).[12] The π-allyl palladium species leads to product **3** upon the nucleophilic attack by **1**.

Next, an initial attempt for the development of an asymmetric intermolecular allylic dearomatization reaction of **1a** was carried out. To our disappointment, low enantioselective control was observed when several readily available chiral ligands (**L1**–**L4**) were utilized in the reaction (Scheme 5).

Conclusions

In summary, we have developed an efficient palladium-catalyzed intermolecular allylic dearomatization reaction of β-naphthol derivatives to provide β-naphthalenones bearing an all-carbon quaternary center in good to excellent yields and chemoselectivity. Mechanistic studies demonstrated that the reaction for methyl 2-hydroxy-1-naphthoate went through both etherification and alkylation at first. Then the etherification product could be further transformed to the dearomatization product. For 1-alkylnaphthalen-2-ols, the transformation from their allylic etherification products to dearomatization products requires harsh reaction conditions.

Experimental Section

General Procedure for Palladium-Catalyzed Intermolecular Allylic Dearomatization Reaction of Naphthol Derivatives

A flame-dried Schlenk tube was cooled to room temperature and filled with argon. To this flask were added $Pd(PPh_3)_4$ (11.5 mg, 0.010 mmol, 5 mol%), lithium carbonate (29.6 mg, 0.40 mmol, 200 mol%), β-naphthol derivatives **1** (0.40 mmol, 200 mol%), allyl carbonate **2** (0.20 mmol, 100 mol%), dioxane (2 mL). The reaction mixture was stirred at 80 °C. After the reaction was complete (monitored by TLC), the crude reaction mixture was filtrated with celite and washed with DCM. The solvents were removed under reduced pressure. The ratio of **3**/**4** was determined by ^{1}H NMR of the crude reaction mixture. Then the residue was purified by silica gel column chromatography (PE/EtOAc = 23/1) to afford the desired product **3**. The characterization data of the products are summarized below.

3aa: Yield: 41.0 mg (85%); yellow solid; mp 95.1–97.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.48$ (d, $J = 10.2$ Hz, 1H), 7.42–7.27 (m, 4H), 6.21 (d, $J = 10.2$ Hz, 1H), 5.35–5.21 (m, 1H), 4.91–4.81 (m, 2H), 3.62 (s, 3H), 3.19–3.12 (m, 1H), 3.04–2.97 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 197.4$, 170.9, 146.1, 139.2, 130.7, 130.4, 129.7, 129.6, 128.0, 126.9, 125.4, 119.3, 62.3, 52.9, 44.6; IR (thin film): $\nu_{max} = 3075$, 2953, 2921, 1730, 1661, 1619, 1414, 1225, 934, 773, 693 cm^{-1}; MS (EI): $m/z =$ 242 $[M]^+$; HR-MS (EI): $m/z = 242.0945$, calcd. for $C_{15}H_{14}O_3$ $[M]^+$: 242.0943.

3ab: Yield: 63.0 mg (94%); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.49$–7.37 (m, 5H), 7.22–7.10 (m, 5H), 6.23–6.00 (m, 2H), 5.73–5.63 (m, 1H), 3.67 (s, 3H), 3.36–3.28 (m, 1H), 3.21–3.14 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 197.5$, 171.0, 146.1, 139.2, 137.0, 134.1, 130.5, 129.7, 129.6, 128.3, 128.1, 127.2, 126.9, 126.0, 125.3, 122.2, 62.7, 53.0, 44.0; IR (thin film): $\nu_{max} = 3026$, 2951, 2849, 1740, 1660, 1619, 1565, 1493, 1220, 1017, 742, 694 cm^{-1}; MS (EI): $m/z = 318$ $[M]^+$; HR-MS (EI): $m/z = 318.1260$, calcd. for $C_{21}H_{18}O_3$ $[M]^+$: 318.1256.

3ac: Yield: 62.5 mg (98%); yellow solid; mp 101.3–103.5; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.47$–7.34 (m, 5H), 7.02 (d, $J = 8.7$ Hz, 2H), 6.72 (d, $J = 8.7$ Hz, 2H), 6.18 (d, $J = 9.9$ Hz, 1H), 6.12 (d, $J = 15.6$ Hz, 1H), 5.56–5.45 (m, 1H), 3.73 (s, 3H), 3.63 (s, 3H), 3.30–3.23 (m, 1H), 3.15–3.08 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 197.5$, 171.0, 158.9, 146.0, 139.3, 133.4, 130.3, 129.8, 129.7, 129.6, 128.0, 127.2, 126.9, 125.3, 119.8, 113.7, 62.8, 55.1, 52.9, 44.0. IR (thin film): $\nu_{max} = 2966$, 2850, 1739, 1658, 1617, 1565, 1487, 1227, 1033, 762 645 cm^{-1}; MS (EI): $m/z = 348$ $[M]^+$; HR-MS (EI): $m/z =$ 348.1364, calcd. for $C_{22}H_{20}O_4$ $[M]^+$: 348.1362.

3ad: Yield: 61.1 mg (87%); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46–7.42 (m, 5H), 7.11 (t, J = 7.8 Hz, 1H), 6.71–6.62 (m, 3H), 6.20–6.13 (m, 2H), 5.70–5.59 (m, 1H), 3.73 (s, 3H), 3.64 (s, 3H), 3.32–3.24 (m, 1H), 3.17–3.10 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 197.5, 170.9, 159.5, 146.1, 139.1, 138.4, 133.9, 130.4, 129.7, 129.5, 129.2, 128.1, 126.9, 125.2, 122.5, 118.7, 112.6, 111.6, 62.6, 55.1, 52.9, 43.9; IR (thin film): ν_{max} = 2965, 1740, 1661, 1619, 1580, 1488, 1221, 1046, 765, 646 cm^{-1}; MS (EI): m/z = 348 [M]$^+$; HR-MS (EI): m/z = 348.1366, calcd. for $C_{22}H_{20}O_4$ [M]$^+$: 348.1362.

3ae: Yield: 63.8 mg (90%); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49–7.35 (m, 5H), 7.20–7.06 (m, 4H), 6.50 (d, J = 15.9 Hz, 1H), 6.21 (d, J = 10.2 Hz, 1H), 5.72–5.62 (m, 1H), 3.64 (s, 3H), 3.37–3.30 (m, 1H), 3.20–3.12 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.2, 170.8, 146.1, 139.1, 135.2, 132.6, 130.6, 130.5, 129.8, 129.5, 129.4, 128.2, 126.9, 126.8, 126.6, 125.4, 125.2, 62.7, 52.9, 43.8; IR (thin film): ν_{max} = 3064, 2960, 1741, 1661, 1620, 1565, 1489, 1221, 1050, 752, 644 cm^{-1}; MS (EI): m/z = 352 [M]$^+$; HR-MS (EI): m/z = 352.0867, calcd. for $C_{21}H_{17}O_3Cl$ [M]$^+$: 352.0866.

3af: Yield: 72.1 mg (83%); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47–7.34 (m, 5H), 7.15 (d, J = 8.7 Hz, 2H), 7.00 (d, J = 8.4 Hz, 2H), 6.20–6.11 (m, 2H), 5.69–5.59 (m, 1H), 3.64 (s, 3H), 3.31–3.24 (m, 1H), 3.15–3.08 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 197.3, 170.9, 146.1, 139.1, 135.3, 132.8, 130.5, 129.8, 129.5, 128.4, 128.2, 127.2, 126.9, 125.2, 123.0, 62.6, 53.0, 43.8; IR (thin film): ν_{max} = 3028, 2963, 1740, 1661, 1620, 1565, 1490, 1221, 1052, 761, 644 cm^{-1}; MS (EI): m/z = 352 [M]$^+$; HR-MS (EI): m/z = 352.0864, calcd. for $C_{21}H_{17}O_3Cl$ [M]$^+$: 352.0866.

3ag: Yield: 53.2 mg (69%); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50–7.36 (m, 7H), 7.17 (d, J = 8.1 Hz, 1H), 6.25–6.18 (m, 2H), 5.82–5.72 (m, 1H), 3.66 (s, 3H), 3.35–3.27 (m, 1H), 3.18–3.11 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 197.3, 170.8, 146.1, 140.3, 139.0, 132.8, 130.6, 129.8, 129.7, 129.5, 129.3, 128.8, 128.4, 128.3, 126.9, 126.2, 125.9, 125.6, 125.3, 125.2, 124.1 (q, J = 270.3 Hz), 62.6, 53.1, 43.8; ^{19}F NMR (282 MHz, $CDCl_3$): δ = −62.92 (3F); IR (thin film): ν_{max} = 2964, 1742, 1662, 1617, 1566, 1489, 1223, 1066, 762, 647 cm^{-1}; MS (EI): m/z = 386 [M]$^+$; HR-MS (EI): m/z = 386.1131, calcd. for $C_{22}H_{17}O_3F$ [M]$^+$: 386.1130.

3ah: Yield: 46.0 mg (85%); yellow solid; mp 86.3–88.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47–7.32 (m, 5H), 7.01 (d, J = 5.1 Hz, 1H), 6.85–6.82 (m, 1H), 6.71 (d, J = 3.6 Hz, 1H), 6.29 (d, J = 15.3 Hz, 1H), 6.19 (d, J = 9.6 Hz, 1H), 5.53–5.43 (m, 1H), 3.63 (s, 3H), 3.27–3.20 (m, 1H), 3.13–3.06 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 197.4, 170.9, 146.1, 141.9, 139.1, 130.4, 129.8, 129.6, 128.2, 127.2, 126.9, 125.2, 125.1, 123.7, 122.0, 62.6, 52.9, 43.8; IR (thin film): ν_{max} = 2964, 1730, 1656, 1619, 1564, 1488, 1220, 1044, 764, 647 cm^{-1}; MS (EI): m/z = 324 [M]$^+$; HR-MS (EI); m/z = 324.0818, calcd. for $C_{19}H_{16}O_3S$ [M]$^+$: 324.0820.

3ai: Yield: 38.3 mg (60%); white solid; mp 59.3–61.1 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.25–7.04 (m, 8H), 6.91–6.88 (m, 2H), 5.91 (d, J = 9.9 Hz, 1H), 4.92 (d, J = 1.5 Hz, 1H), 4.74 (s, 1H), 3.74 (d, J = 14.1 Hz, 1H), 3.62–3.57 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 197.4, 171.2, 145.5, 143.5, 140.9, 138.8, 129.9, 129.7, 129.4, 127.8, 127.5, 127.2, 127.0, 126.8, 125.4, 117.7, 62.2, 53.0, 45.0; IR (thin film): ν_{max} = 3024, 2964, 2851, 1734, 1651, 1624, 1566, 1491, 1240, 1055, 769, 700 cm^{-1}; MS (EI): m/z = 318 [M]$^+$; HR-MS (EI): m/z = 318.1260, calcd for $C_{21}H_{18}O_3$ [M]$^+$: 318.1256.

4ai: Yield: 12.4 mg (19%); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, J = 9.2 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.53–7.49 (m, 3H), 7.40–7.33 (m, 4H), 7.30 (d, J = 9.2 Hz, 1H), 5.61 (s, 1H), 5.50 (s, 1H), 5.08 (s, 2H), 3.89 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.3, 153.4, 142.7, 138.2, 131.6, 131.0, 128.7, 128.4, 128.0, 128.0, 127.6, 126.0, 124.3, 123.8, 118.2, 114.8, 114.4, 71.0, 52.2; IR (thin film): ν_{max} = 3081, 3030, 1723, 1626, 1511, 1437, 1282, 1229, 1136, 1062, 779, 704 cm^{-1}; HR-MS (ESI): m/z = 319.1330, calcd. for $C_{21}H_{19}O_3$ [M+H]$^+$: 319.1329.

3ba: Yield: 53.4 mg (85%); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59 (d, J = 9.9 Hz, 1H), 7.48–7.40 (m, 3H), 7.17 (d, J = 7.5 Hz, 1H), 6.29 (d, J = 9.9 Hz, 1H), 5.33–5.19 (m, 1H), 4.87–4.77 (m, 2H), 3.08–3.01 (m, 1H), 2.96–2.89 (m, 1H), 1.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.3, 198.6, 146.6, 138.3, 131.3, 130.7, 130.0, 129.9, 128.3, 127.2, 126.0, 118.7, 69.8, 44.1, 27.5; IR (thin film): ν_{max} = 3074, 2976, 2923, 1741, 1628, 1514, 1438, 1264, 986, 783, 669 cm^{-1}; MS (EI): m/z = 226 [M]$^+$; HR-MS (EI): m/z = 226.0998, calcd. for $C_{15}H_{14}O_2$ [M]$^+$: 226.0994.

3bb: Yield: 60.6 mg (99%); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54 (d, J = 9.6 Hz, 1H), 7.47–7.39 (m, 3H), 7.26–7.05 (m, 6H), 6.26 (d, J = 10.2 Hz, 1H), 6.16 (d, J = 15.3 Hz, 1H), 5.69–5.58 (m, 1H), 3.22–3.15 (m, 1H), 3.09–3.03 (m, 1H), 1.86 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.5, 198.7, 146.6, 138.4, 137.0, 133.6, 130.7, 130.1, 130.0, 128.3, 128.2, 127.2, 127.1, 126.0, 125.9, 122.9, 70.1, 43.4, 27.6; IR (thin film): ν_{max} = 3058, 3025, 2920, 1721, 1655, 1563, 1468, 1208, 965, 745, 694 cm^{-1}; MS (EI): m/z = 302 [M]$^+$; HR-MS (EI): m/z = 302.1302, calcd. for $C_{21}H_{18}O_2$ [M]$^+$: 302.1307.

3ca: Yield: 39.4 mg (71%); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.32 (s, 1H), 7.59–7.52 (m, 2H), 7.48–7.43 (m, 1H), 7.19 (d, J = 7.5 Hz, 1H), 5.37–5.23 (m, 1H), 4.87–4.79 (m, 2H), 3.90 (s, 3H), 3.10–3.03 (m, 1H), 2.94–2.87 (m, 1H), 1.87 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.3, 194.2, 164.6, 151.7, 140.0, 132.6, 131.9, 130.8, 128.7, 128.6, 127.2, 126.6, 119.2, 71.1, 52.5, 44.6, 27.9; IR (thin film): ν_{max} = 3077, 3004, 2953, 1722, 1678, 1616, 1438, 1220, 965, 761, 642 cm^{-1}; MS (EI): m/z = 284 [M]$^+$; HR-MS (EI): m/z = 284.1052, calcd. for $C_{17}H_{16}O_4$ [M]$^+$: 284.1049.

3cb: Yield: 22.4 mg (66%); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.27 (s, 1H), 7.59–7.56 (m, 2H), 7.48–7.43 (m, 1H), 7.27–7.16 (m, 4H), 7.08–7.06 (m, 2H), 6.18 (d, J = 15.6 Hz, 1H), 5.72–5.62 (m, 1H), 3.85 (s, 3H), 3.24–3.17 (m, 1H), 3.08–3.01 (m, 1H), 1.90 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.3, 194.5, 164.5, 151.6, 139.9, 136.8, 134.1, 132.6, 132.0, 128.7, 128.6, 128.3, 127.2, 126.6, 126.0, 122.3, 71.4, 52.5, 43.7, 28.0; IR (thin film): ν_{max} = 3058, 3026, 2952, 1721, 1667, 1615, 1495, 1217, 966, 746, 648 cm^{-1}; MS (EI): m/z = 360 [M]$^+$; HR-MS (EI): m/z = 360.1358, calcd. for $C_{23}H_{20}O_4$ [M]$^+$: 360.1362.

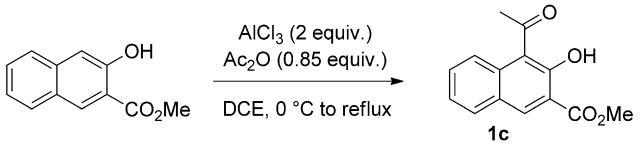
3da: Yield: 36.0 mg (77%); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53 (d, J = 9.6 Hz, 1H), 7.08 (d, J = 8.4 Hz, 1H), 7.07–6.94 (m, 2H), 6.28 (d, J = 10.2 Hz, 1H), 5.33–5.19 (m, 1H), 4.88–4.78 (m, 2H), 3.87 (s, 3H), 3.05–2.98 (m, 1H), 2.94–2.87 (m, 1H), 1.83 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.5, 198.8, 159.2, 146.4, 131.5, 131.0, 130.0, 128.3, 126.4, 118.6, 116.3, 114.8, 69.2, 55.4, 43.9, 27.3;

IR (thin film): ν_{max} = 3077, 3004, 2935, 1721, 1656, 1599, 1432, 1251, 997, 715, 668 cm^{-1}; MS (EI): *m/z* = 256 $[M]^+$; HR-MS (EI): *m/z* = 256.1104, calcd. for $C_{16}H_{16}O_3$ $[M]^+$: 256.1099.

3db: Yield: 65.4 mg (95%); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 9.9 Hz, 1H), 7.21–7.07 (m, 6H), 7.02–6.98 (m, 1H), 6.92–6.91 (m, 1H), 6.25 (d, *J* = 10.2 Hz, 1H), 6.18 (d, *J* = 15.9 Hz, 1H), 5.69–5.59 (m, 1H), 3.85 (s, 3H), 3.19–3.12 (m, 1H), 3.08–3.01 (m, 1H), 1.85 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.6, 198.9, 159.2, 146.5, 137.0, 133.3, 130.9, 129.9, 128.3, 128.2, 127.1, 126.3, 126.0, 123.1, 116.4, 114.9, 69.4, 55.4, 43.1, 27.3; IR (thin film): ν_{max} = 3057, 3026, 2919, 1720, 1652, 1599, 1448, 1246, 966, 743, 694 cm^{-1}; MS (EI): *m/z* = 332 $[M]^+$; HR-MS (EI): *m/z* = 332.1418, calcd. for $C_{22}H_{20}O_3$ $[M]^+$: 332.1412.

3ea:[10] Yield: 32.9 mg (75%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44–7.41 (m, 3H), 7.34–7.26 (m, 2H), 6.17 (d, *J* = 9.9 Hz, 1H), 5.37–5.23 (m, 1H), 4.87–4.79 (m, 2H), 2.89–2.82 (m, 1H), 2.60–2.53 (m, 1H), 1.47 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 203.8, 145.6, 145.1, 133.0, 129.9, 129.6, 129.4, 126.7, 125.2, 117.9, 51.5, 46.7, 26.8; IR (thin film): ν_{max} = 3058, 3026, 2971, 1720, 1656, 1620, 1448, 1240, 966, 745, 694 cm^{-1}; MS (EI): *m/z* = 198 $[M]^+$; HR-MS (EI): m/z = 198.1047, calcd. for $C_{14}H_{14}O$ $[M]^+$: 198.1045.

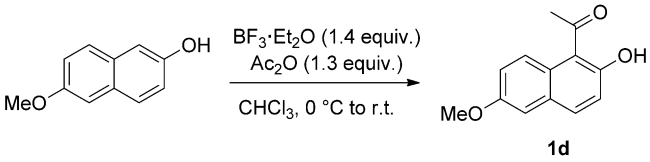
3eb:[9] Yield: 42.7 mg (83%); colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.52–7.45 (m, 2H), 7.42 (d, *J* = 10.2 Hz, 1H), 7.34–7.30 (m, 2H), 7.27–7.11 (m, 5H), 6.20 (d, *J* = 15.9 Hz, 1H), 6.17 (d, *J* = 9.6 Hz, 1H), 5.71 (d, *J* = 15.0, 7.2 Hz, 1H), 3.03–2.96 (m, 1H), 2.74–2.67 (m, 1H), 1.54 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.0, 145.6, 145.2, 137.2, 133.0, 130.0, 129.7, 129.6, 128.4, 127.1, 126.9, 126.8, 126.1, 125.2, 124.7, 52.0, 46.3, 26.5.



1c

Procedure for the Synthesis of Methyl 4-Acetyl-3-hydroxy-2-naphthoate (1c)

A flame-dried reaction flask was cooled to room temperature and filled with argon. To this flask were added methyl 3-hydroxy-2-naphthoate (2.02 g, 10.0 mmol), aluminum chloride (2.6 g, 19.5 mmol), 1,2-dichloroethane (DCE) (30 mL). The reaction mixture was cooled to 0 °C, and acetic anhydride (0.8 mL, 8.5 mmol) was added slowly. After that, the reaction mixture was stirred and heated to reflux for 46 h. After the reaction was complete (monitored by TLC), the reaction mixture was cooled to 0 °C and quenched with water. The product was partitioned between water and DCE. The layers were separated, and the aqueous layer was extracted with DCM. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under vacuum. The crude material was purified by column chromatography using PE/EtOAc (40:1) to give **1c** as a yellow solid; yield: 961 mg (40%); mp 136.0–138.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.00 (s, 1H), 8.52–8.51 (m, 1H), 7.84–7.78 (m, 2H), 7.55 (dt, *J* = 6.8, 1.2 Hz, 1H), 7.35 (t, *J* = 7.2 Hz, 1H), 4.02 (s, 3H), 2.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.0, 170.0, 154.0, 134.6, 133.8, 130.5, 129.8, 126.9, 124.4, 123.6, 123.3, 113.5, 52.8, 32.4; IR (thin film): ν_{max} = 3112, 3038, 2962, 2919, 1678, 1631, 1602, 1508, 1435, 1272, 1082, 791, 752 cm^{-1}; HR-MS (ESI): *m/z* = 245.0816, calcd. for $C_{14}H_{13}O_4$ $[M+H]^+$: 245.0808.



1d

Procedure for the Synthesis of 1-(2-Hydroxy-6-methoxynaphthalen-1-yl)ethanone (1d)

A flame-dried reaction flask was cooled to room temperature and filled with argon. To this flask were added 6-methoxynaphthalen-2-ol (700 mg, 4.0 mmol), chloroform (10 mL), boron trifluoride diethyl etherate (0.7 mL, 5.5 mmol). The reaction mixture was cooled to 0 °C, and acetic anhydride (0.5 mL, 5.3 mmol) was added slowly. After that, the reaction mixture was stirred at room temperature for 4 days. After the reaction was complete (monitored by TLC), the reaction mixture was cooled to 0 °C and quenched with water. The product was partitioned between water and $CHCl_3$. The layers were separated, and the aqueous layer was extracted with DCM. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under vacuum. The crude material was purified by column chromatography using PE/EtOAc (20:1) to give **1d** as a brown solid; yield: 589 mg (68%); mp 67.9–70.1 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 13.16 (s, 1H), 7.80 (d, *J* = 9.3 Hz, 1H), 7.59 (d, *J* = 9.3 Hz, 1H), 7.10–7.07 (m, 1H), 6.99–6.96 (m, 2H), 3.78 (s, 3H), 2.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.3, 162.2, 155.7, 136.3, 129.7, 126.5, 125.7, 120.2, 119.4, 115.1, 108.5, 55.3, 32.6; IR (thin film): ν_{max} = 3139, 3087, 2965, 2918, 1756, 1609, 1573, 1507, 1209, 1028, 809 cm^{-1}; HR-MS (ESI): *m/z* = 217.0863, calcd. for $C_{13}H_{13}O_3$ $[M+H]^+$: 217.0859.

Acknowledgements

We thank the National Basic Research Program of China (973 Program 2010CB833300), the National Natural Science Foundation of China (21025209, 21121062, 21332009), and the Science and Technology Commission of Shanghai Municipality (13JC1406900) for generous financial support.

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