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Palladium-Catalyzed Annulation Reaction of *o*-Bromobenzaldehydes with Carbonyl Compounds to Produce Naphthol and/or Naphthalene Derivatives

Yoshito Terao, Tetsuya Satoh, Masahiro Miura* and Masakatsu Nomura

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

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Abstract—*o*-Bromobenzaldehydes undergo annulation with 1,3-diaryl-2-propanones in the presence of a palladium catalyst to give the corresponding 1,3-diaryl-2-naphthols in fair to good yields. From the reaction of the aldehydes with 2-substituted 2-alkenals are formed 2,4-disubstituted 1-naphthols and/or 1,3-disubstituted naphthalenes accompanied by decarbonylation.

Introduction

Palladium-catalyzed arylation reactions using aryl halides and their synthetic equivalents such as aryl triflates are now recognized to be of genuine synthetic utility for preparing substituted aromatic compounds.[1–3] In particular, the reaction with alkenes (the Mizoroki–Heck reaction) and that with organometallic compounds, especially with organoboronates (the Suzuki–Miyaura coupling), are often employed. Meanwhile, the reaction of *ortho*-functionalized halobenzenes with unsaturated compounds, including alkenes, alkynes and dienes, i.e. palladium-catalyzed annulation, has also proven to be a powerful tool to construct various heterocyclic and carbocyclic compounds.[1–4]

Recently, several groups including ours have independently reported that aryl halides can efficiently react with ketones on their α-position without stoichiometric metalation under the conditions similar to those for the Mizoroki–Heck reaction.[5–8] We also demonstrated that the arylation of α,β-unsaturated carbonyl compounds regioselectively occurs on their γ-position.[9] It may be reasonable to consider that the arylation reaction of the carbonyl compounds can be extended to the annulation forming certain ring systems. Indeed we observed that when benzyl ketones and α,β-unsaturated carbonyl compounds are treated with *o*-dibromobenzenes, benzofuran derivatives and benzocyclobutane or indene derivatives, respectively, are formed.[10] In a further study of the annulation of carbonyl compounds, we have found that the reaction of *o*-bromobenzaldehydes with 1,3-diaryl-2-propanones affords the corresponding 1,3-diaryl-2-naphthols which are of interest as bulky oxygen ligands.[11–13] Furthermore, the bromoaldehydes have been observed to couple with 2-substituted 2-alkenals, interestingly accompanied by decarbonylation, to give 2,4-disubstituted 1-naphthols and/or 1,3-disubstituted naphthalenes. These new findings are described herein. While palladium-catalyzed reactions of *o*-halobenzaldehydes with alkynes,[14,15] allyl or homoallyl alcohols,[16] arylboronic acids[17] and active methylene compounds under carbon monoxide[18] to give indenones or indenols, indenes or dihydronaphthalenes, polycondensed aromatic compounds and benzofuranones, respectively, have been reported, the present method employing arylation of carbonyl compounds appears to be useful as a new, convenient route leading to naphthol and/or naphthalene derivatives.

Results and Discussion

When *o*-bromobenzaldehyde (**1a**) (1 mmol) was treated with 1,3-diphenyl-2-propanone (**2a**) (1 mmol) in the presence of $Pd(OAc)_2$ (0.05 mmol) and PPh_3 (0.2 mmol) together with K_2CO_3 (2 mmol) as base in refluxing *o*-xylene at a bath temperature of 160°C for 5 h, 1,3-diphenyl-2-naphthol (**3**) was produced in a yield of 54% (Scheme 1 and entry 1 in Table 1). The yield of product **3** was increased up to 72% by using 2 mmol of **2a** (Entry 2). Use of a relatively more effective base, Cs_2CO_3, in place of K_2CO_3 did not improve the reaction efficiency (Entry 3). The reaction in toluene at 120°C was very sluggish (Entry 4).

The treatment of 2-bromo-5-methoxy-, 2-bromo-4,5-dimethoxy-, 2-bromo-5,6-dimethoxybenzaldehydes, (**1b**),

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* Corresponding author. Tel.: +81-6-8797361; fax: +81-6-8797362; e-mail: miura@ap.chem.eng.osaka-u.ac.jp

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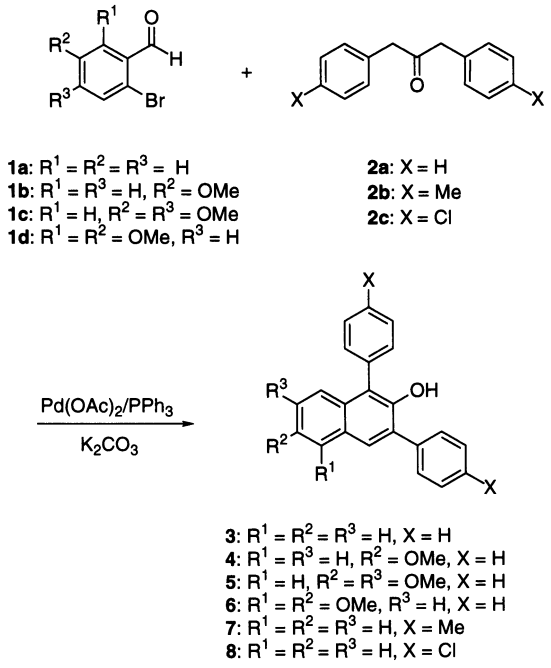


Scheme 1.

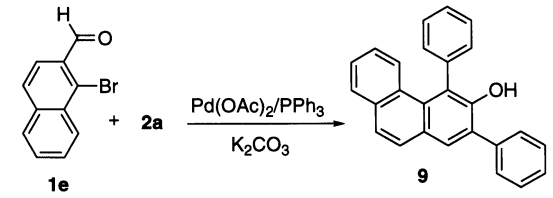
Table 1. Reaction of *o*-bromobenzaldehydes **1** with 1,3-diaryl-2-propanones **2** (reaction conditions: **1** (1 mmol), **2** (2 mmol), $Pd(OAc)_2$ (0.05 mmol), PPh_3 (0.2 mmol), K_2CO_3 (2 mmol) in *o*-xylene (5 cm^3) at 160°C (bath temperature))

Entry	1	2	Time/h	Product, % yield[a]
1[b]	**1a**	**2a**	5	**3**, 54[c]
2	**1a**	**2a**	5	**3**, 72 (59)[c]
3[d]	**1a**	**2a**	4	**3**, 64
4[d,e]	**1a**	**2a**	5	**3**, 18
5	**1b**	**2a**	7	**4**, 57 (45)[f]
6	**1c**	**2a**	4	**5**, 51 (43)
7	**1d**	**2a**	3	**6**, 90 (75)
8	**1a**	**2b**	3	**7**, 60 (44)
9	**1a**	**2c**	8	**8**, 48 (45)
10	**1e**	**2a**	2.5	**9**, 52 (44)

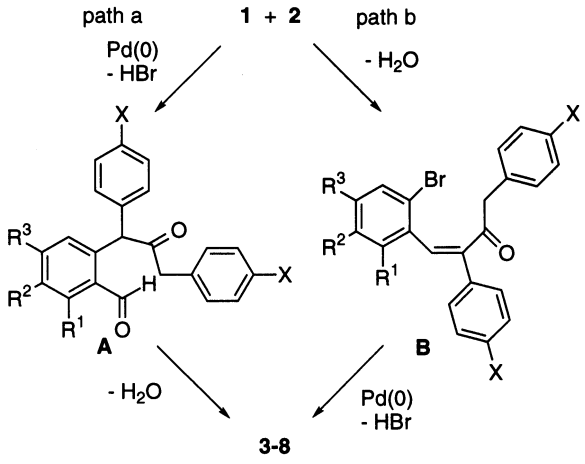
[a] GLC yield based on amount of **1** used. Value in parentheses indicates isolated yield.
[b] **2a** (1 mmol) was used.
[c] In entries 1 and 2, 0.32 and 1.23 mmol of **2a** were recovered, respectively. Recoveries of **2** in other entries were not determined.
[d] Cs_2CO_3 was used in place of K_2CO_3. Molecular sieves 4A (300 mg) was also added.
[e] Reaction in toluene at 120°C.
[f] Product **4** was isolated after acetylation.

(**1c**) and (**1d**) in place of **1a** with **2a** using K_2CO_3 in *o*-xylene gave the expected 1,3-diaryl-2-naphthols **4**–**6** (Entries 5–7). From the reactions of **1a** with 1,3-(4-methylphenyl)- and 1,3-(4-chlorophenyl)-2-propanones, **2b** and **2c**, in place of **2a** were also obtained naphthols **7** and **8** (Entries 8 and 9). The reaction of 1-bromo-2-naphthaldehyde (**1e**) with **2a** afforded 2,4-diphenyl-3-phenanthrol (**9**) (Scheme 2, Entry 10). These results may demonstrate generality of the present method as a route to 1,3-diaryl-2-naphthols.

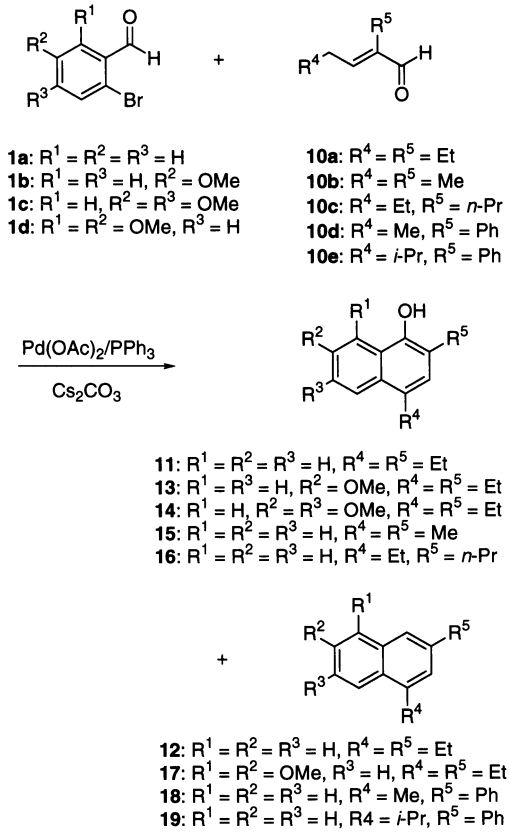
It seems reasonable to consider that the reaction of **1** with **2** proceeds via palladium-catalyzed arylation to give intermediate **A** followed by base-catalyzed condensation (path



Scheme 2.



Scheme 3.



Scheme 4.

Table 2. Reaction of *o*-bromobenzaldehyde (**1a**) with 2-ethyl-2-hexenal (**10a**) (reaction conditions: **1a** (2 mmol), **10a** (1 mmol), $Pd(OAc)_2$ (0.05 mmol), PPh_3 (0.1 mmol), Cs_2CO_3 (2 mmol), in Toluene-DMF (5 cm^3) at 120°C)

Entry	Toluene:DMF (cm^3)	Time/h	Yield (%)[a]	
			11	**12**
1	5:0	10	51	10
2	3:2	1	67 (57)[b]	10
3[c]	3:2	1	30	19
4	4:1	1	64	7
5	0:5	1	49	15
6[d]	0:5	6	5	50 (50)

[a] GLC yield based on amount of **10a** used. Value in parentheses indicates isolated yield.
[b] Product **11** was isolated after acetylation.
[c] **1a** (1 mmol) was used.
[d] $Pd(OAc)_2$ (0.01 mmol) and PPh_3 (0.04 mmol) were used.

a in Scheme 3).[5–8] Alternatively, dehydrative condensation to give intermediate **B** may occur before the arylation (path b). In order to determine which path is favorable, the reaction mixture of **1a** and **2a** at a reaction time of 2 h was analyzed by GC-MS. Neither **A** nor **B** could be detected, only **3** together with the starting materials being observed. This may be due to the fact that the intramolecular cyclization from **A** and/or **B** is relatively fast. Thus, the precedence of paths a and b is not definitive.

When **1a** (2 mmol) was treated with (*E*)-2-ethyl-2-hexenal (**10a**) (1 mmol) in the presence of $Pd(OAc)_2$ (0.05 mmol), PPh_3 (0.1 mmol) and Cs_2CO_3 (2 mmol) in toluene at 120°C for 10 h, 2,4-diethyl-1-naphthol (**11**) (51%) was produced as the major product together with 1,3-diethylnaphthalene (**12**) (10%) (Scheme 4 and entry 1 in Table 2). Analysis of the reaction mixture by GC also confirmed that **1a** completely disappeared and ca. 0.3 mmol of benzaldehyde was formed as a sole detectable by-product. Note that both **11** and **12** lack a carbonyl group in either **1a** or **10a**. The reaction in DMF was considerably faster than in toluene, while the relative product yields were comparable (Entry 5). It was observed that the yield of **11** was increased when the reaction was carried out in a mixed solvent of toluene–DMF (Entries 2 and 4). Decrease in the amount of **1a** to 1 mmol reduced the yield of **11** (Entry 3). Interestingly, with a reduced amount of $Pd(OAc)_2$ (0.01 mmol), **12** was selectively produced (Entry 6). On the other hand, use of K_2CO_3 in place of Cs_2CO_3 resulted in the formation of a significant amount of 2,2′-diformylbiphenyl, neither **11** nor **12** being detected by GC-MS. This may be due to the fact that the allylic hydrogen in **10a** is less acidic than the benzylic hydrogen in **2**.

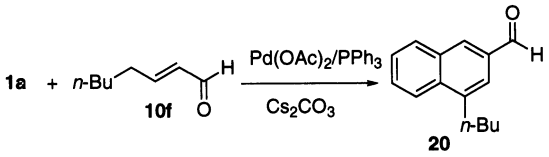
Table 3. Reaction of *o*-bromobenzaldehydes **1a**–**d** with 2-alkenals **10a**–**f** or isophorone (**10g**) (reaction conditions: **1** (2 mmol), **10** (1 mmol), $Pd(OAc)_2$ (0.05 mmol), PPh_3 (0.1 mmol), Cs_2CO_3 (2 mmol) in Toluene (3 cm^3)-DMF (2 cm^3) at 120°C)

Entry	**1**	**10**	Time/h	Product, % yield[a]
1	**1b**	**10a**	1	**13**, 60 (55)[b]
2	**1c**	**10a**	4	**14**, 65 (60)[b]
3	**1a**	**10b**	2	**15**, 52 (49)
4[c]	**1a**	**10c**	1	**16**, 43 (43)[b]
5	**1d**	**10a**	3	**17**, 76 (67)
6	**1a**	**10d**	2	**18**, 66 (62)
7	**1a**	**10e**	2	**19**, 77 (57)
8[d]	**1a**	**10f**	2	**20**, 46 (38)
9[d,e]	**1a**	**10g**	2	**21**, 78 (66)

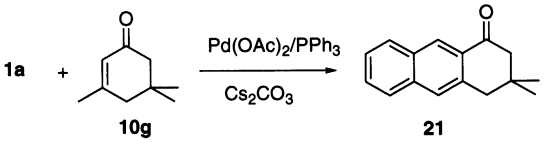
[a] GLC yield based on amount of **10** used. Value in parentheses indicates isolated yield.
[b] Isolated after acetylation.
[c] Reaction using **1a** (0.6 mmol), **10c** (0.3 mmol), $Pd(OAc)_2$ (0.015 mmol), PPh_3 (0.03 mmol), Cs_2CO_3 (0.6 mmol).
[d] Reaction in refluxing *o*-xylene.
[e] PPh_3 (0.2 mmol) was used.

Table 3 summarizes results for reactions using *o*-bromobenzaldehydes **1a**–**d** and 2-substituted (*E*)-2-alkenals **10a**–**e**, (*E*)-2-octenal (**10f**) or isophorone (**10g**). The reactions of **1b** and **1c** with **10a** and of **1a** with (*E*)-2-methyl-2-pentenal (**10b**) and (*E*)-2-propyl-2-hexenal (**10c**) using 0.05 mmol of $Pd(OAc)_2$ in 3:2 toluene–DMF mixture gave the expected 1-naphthols **13**–**16** as the predominant products (Entries 1–4). In each case a minor amount of the corresponding naphthalene derivative was detected by GC-MS. In contrast to these reactions, treatment of **1d** with **10a** gave 1,3-diethyl-5,6-dimethoxynaphthalene (**17**) in a yield of 76%, no 1-naphthol derivative being detected (Entry 5). The reactions of **1a** with 2-phenyl-2-pentenal (**10d**) and 5-methyl-2-phenyl-2-hexenal (**10e**) also produced naphthalenes **18** and **19** as the sole detectable coupling products (Entries 6 and 7). From the reactions of **1a** with **10f** and **10g** in refluxing *o*-xylene were obtained 4-butyl-2-naphthaldehyde (**20**) and 1,2,3,4-tetrahydro-3,3-dimethylanthracen-1-one (**21**) (Schemes 5 and 6).

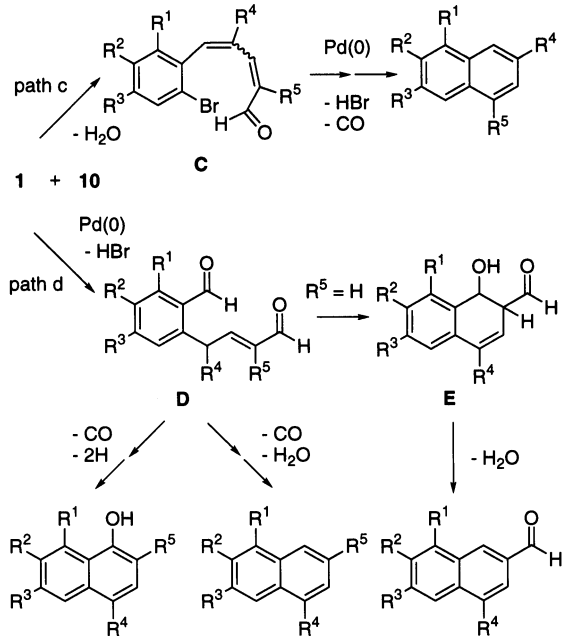
Possible reaction sequences from **1** and **10** to naphthols and naphthalenes are illustrated in Scheme 7. Base-catalyzed dehydrative condensation of **1** and **10** to give intermediate **C** followed by palladium-catalyzed decarbonylative cyclization involving cleavage of the aldehyde C–H bond[15,19–21] could produce naphthalenes (path c). However, this route may be excluded, since it is not consistent with the structures of products **18** and **19**. On the other hand, the structures of **16** and **20** as well as **18** and **19** may imply that the initial reaction in each coupling of **1** and **10** is palladium-catalyzed γ-arylation to give intermediate **D** (path d).[9] To form 1-naphthols and naphthalenes from **D**, decarbonylation from one of the formyl moieties should occur followed by dehydrogenative oxidation or dehydration. Palladium(0) and/or (II) species in the reaction



Scheme 5.



Scheme 6.



Scheme 7.

medium could participate in the decarbonylation[15,19–21] and oxidation,[22] while the detailed mechanisms as well as the reason why only naphthalenes are produced in the cases using **1d**, **10d** and **10e** are not clear at the present stage. Naphthaldehyde **20** may be formed by nucleophilic cyclization in intermediate **D** to give **E** followed by dehydration. The reaction using **1a** and **10g** may similarly take place.

Experimental

^{1}H and ^{13}C NMR spectra were recorded at 400 or 600 MHz and 100 MHz or 150 MHz, respectively, for $CDCl_3$ solutions. MS analysis was made by EI. GLC analysis was carried out using a Silicone OV-17 glass column (ϕ 2.6 mm×1.5 m). 1,3-Diaryl-2-propanones **2b**[23] and **2c**[23] and 2-propyl-2-hexenal (**10c**)[24] were prepared by the methods reported previously. Other starting materials were commercially available. The solvents employed were purified by standard methods before use. The structures of all new products were unambiguously determined by ^{1}H and ^{13}C NMR with the aid of NOESY, COSY and COLOC experiments.

General procedure for the reaction of *o*-bromobenzaldehydes 1 with carbonyl compounds 2 or 10

In a 100 cm^3 two-necked flask was placed K_2CO_3 or Cs_2CO_3 (2 mmol) which was then dried at 150°C in vacuo for 2 h. Then, $Pd(OAc)_2$ (0.01–0.05 mmol), PPh_3 (0.04–0.2 mmol), **1** (1–2 mmol), **2** or **10** (1–2 mmol), 1-methylnaphthalene (ca. 100 mg) as internal standard and a solvent (5 cm^3) were added. The resulting mixture was stirred under N_2 at 120–160°C (bath temperature) for 1–21 h. After cooling, the reaction mixture was extracted with diethyl ether and dried over sodium sulfate. Products were isolated by column chromatography on silica gel using hexane or hexane–diethyl ether as eluent. In some cases, naphthols were acetylated by treatment with acetic anhydride (2 mmol) in pyridine (5 cm^3) at room temperature for 2 h before the chromatographic purification.

Product data

1,3-Diphenyl-2-naphthol (3).[25] mp 69–71°C; ^{1}H NMR δ 5.32 (s, 1H), 7.35–7.44 (m, 4H), 7.48–7.55 (m, 5H), 7.59–7.63 (m, 2H), 7.69–7.71 (m, 2H), 7.84–7.87 (m, 2H); ^{13}C NMR δ 121.80, 123.66, 124.62, 126.41, 127.61, 128.04, 128.37, 128.44, 128.82, 129.46, 129.57, 129.63, 130.34, 131.20, 132.88, 134.61, 137.85, 147.65; MS *m*/*z* 296 (M^+). Anal. Calcd for $C_{22}H_{16}O$: C, 89.16; H, 5.44. Found: C, 89.06; H, 5.46.

1,3-Diphenyl-6-methoxy-2-naphthyl acetate (acetate of 4). mp 116–116.5°C; ^{1}H NMR δ 1.68 (s, 3H), 3.92 (s, 3H), 7.05 (dd, 1H, *J*=2.4, 9.2 Hz), 7.20 (d, 1H, *J*=2.4 Hz), 7.36–7.88 (m, 3H), 7.41–7.47 (m, 6H), 7.54–7.56 (m, 2H), 7.79 (s, 1H); ^{13}C NMR δ 20.23, 55.37, 106.00, 119.14, 127.46, 127.57, 127.66, 128.00, 128.14, 128.21, 128.27, 129.17, 130.24, 131.92, 133.17, 134.88, 135.59, 138.09, 141.79, 157.68, 169.44; MS *m*/*z* 368 (M^+). Anal. Calcd for $C_{25}H_{20}O_3$: C, 81.50; H, 5.47. Found: C, 81.37; H, 5.54.

1,3-Diphenyl-6,7-dimethoxy-2-naphthol (5). mp 164–165°C; ^{1}H NMR δ 3.74 (s, 3H), 3.99 (s, 3H), 5.15 (s, 1H), 6.70 (s, 1H), 7.14 (s, 1H), 7.38 (t, 1H, *J*=7.3, 7.8 Hz), 7.45–7.52 (m, 5H), 7.59 (t, 2H, *J*=7.3, 7.8 Hz), 7.65–7.68 (m, 3H); ^{13}C NMR δ 55.60, 55.86, 103.78, 106.70, 121.25, 124.18, 127.36, 127.93, 128.12, 128.31, 128.43, 128.58, 129.49, 129.52, 131.04, 135.07, 138.12, 146.54, 147.85, 150.00; MS *m*/*z* 356 (M^+). Anal. Calcd for $C_{24}H_{20}O_3$: C, 80.88; H, 5.66. Found: C, 80.79; H, 5.68.

1,3-Diphenyl-5,6-dimethoxy-2-naphthol (6). mp 149–150°C; ^{1}H NMR δ 3.95 (s, 3H), 4.02 (s, 3H), 5.19 (s, 1H), 7.14 (d, 2H, *J*=3.4 Hz), 7.38–7.52 (m, 6H), 7.56–7.60 (m, 2H), 7.68–7.71 (m, 2H), 8.13 (s, 1H); ^{13}C NMR δ 57.09, 61.23, 116.13, 120.88, 121.69, 123.04, 124.38, 127.60, 128.31, 128.42, 129.28, 129.38, 129.64, 130.80, 131.14, 134.77, 138.14, 143.42, 146.48, 146.73; MS *m*/*z* 356 (M^+). Anal. Calcd for $C_{24}H_{20}O_3$: C, 80.88; H, 5.66. Found: C, 80.69; H, 5.62.

1,3-Di(4-methylphenyl)-2-naphthol (7). Oil; ^{1}H NMR δ 2.42 (s, 3H), 2.47 (s, 3H), 5.33 (s, 1H), 7.28–7.42 (m, 9H), 7.56 (d, 2H, *J*=8.3 Hz), 7.79–7.82 (m, 2H); ^{13}C NMR δ 21.23, 21.34, 121.67, 123.51, 124.67, 126.18, 127.96, 128.82, 129.17, 129.26, 129.40, 130.15, 130.25, 131.03, 131.46, 132.91, 134.94, 137.35, 138.08, 147.84; HRMS *m*/*z* (M^+) calcd for $C_{24}H_{20}O$ 324.1514, found 324.1505.

1,3-Di(4-chlorophenyl)-2-naphthol (8). mp 159.5–160.5°C; ^{1}H NMR δ 5.16 (s, 1H), 7.34–7.46 (m, 7H), 7.56–7.61 (m, 4H), 7.80–7.84 (m, 2H); ^{13}C NMR δ 120.71, 123.99, 124.35, 126.83, 128.15, 128.64, 128.79, 129.15, 129.81, 129.91, 130.82, 130.88, 132.62, 132.83, 133.77, 134.64, 136.09, 147.47; MS *m*/*z* 364, 366, 368 (M^+). Anal. Calcd for $C_{22}H_{14}OCl_2$: C, 72.34; H, 3.86; Cl, 19.41, Found: C, 72.22; H, 4.01; Cl, 19.37.

2,4-Diphenyl-3-phenanthrol (9). mp 126–127°C; ^{1}H NMR δ 5.37 (s, 1H), 7.03–7.07 (m, 1H), 7.37–7.42 (m, 3H), 7.46–7.50 (m, 4H), 7.55–7.66 (m, 4H) 7.70–7.73 (m, 3H), 7.79 (dd, 1H, *J*=1.0, 7.8 Hz), 7.89 (s, 1H); ^{13}C NMR δ 123.83, 124.93, 125.51, 125.92, 127.32, 127.39, 127.55, 127.76, 128.38, 128.58, 128.73, 128.98, 129.00, 129.53, 129.94, 130.60, 130.67, 130.67, 133.87, 137.69, 138.13, 149.37; MS *m*/*z* 346 (M^+). Anal. Calcd for $C_{26}H_{18}O$: C, 90.14; H, 5.24. Found: C, 89.88; H, 5.08.

2,4-Diethyl-1-naphthyl acetate (acetate of 11). Oil; ^{1}H NMR δ 1.28 (t, 3H, *J*=7.3, 7.8 Hz), 1.39 (t, 3H, *J*=7.3, 7.8 Hz), 2.49 (s, 3H), 2.67 (q, 2H, *J*=7.3, 7.8 Hz), 3.09 (q, 2H, *J*=7.3, 7.8 Hz), 7.25 (s, 1H), 7.47–7.50 (m, 2H), 7.74–7.76 (m, 1H), 8.01–8.03 (m, 1H); ^{13}C NMR δ 14.32, 14.98, 20.66, 23.49, 25.68, 121.50, 124.00, 125.33, 126.03, 126.06, 127.23, 131.30, 131.58, 138.44, 142.10, 169.60; MS *m*/*z* 242 (M^+). Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.19; H, 7.44.

2,4-Diethylnaphthalene (12).[26] Oil; ^{1}H NMR δ 1.32 (t, 3H, *J*=7.3 Hz), 1.38 (t, 3H, *J*=7.3 Hz), 3.07 (q, 2H, *J*=7.3 Hz), 3.09 (q, 2H, *J*=7.3 Hz), 7.21 (s, 1H), 7.41–7.44 (m, 2H), 7.48 (s, 1H), 7.77–7.79 (m, 1H), 7.98–8.01 (m, 1H); ^{13}C NMR δ 15.10, 15.42, 25.90, 29.01, 123.55, 123.94, 124.82, 125.40, 126.20, 128.24, 130.25, 134.17, 140.15, 141.44.

2,4-Diethyl-7-methoxy-1-naphthyl acetate (acetate of 13). mp 79–80°C; ^{1}H NMR δ 1.26 (t, 3H, *J*=7.8 Hz), 1.36 (t, 3H, *J*=7.8 Hz), 2.47 (s, 3H), 2.64 (q, 2H, *J*=7.8 Hz), 3.01 (q, 2H, *J*=7.8 Hz), 3.90 (s, 3H), 7.00 (d, 1H, *J*=2.4 Hz), 7.09 (s, 1H), 7.13 (dd, 1H, *J*=2.4, 9.3 Hz) 7.91 (d, 1H, *J*=9.3 Hz); ^{13}C NMR δ 14.29, 15.07, 20.67, 23.58, 25.75, 55.16, 100.28, 117.42, 123.79, 125.78, 126.76, 128.44, 132.31, 138.42, 141.36, 157.84, 169.51; MS *m*/*z* 272 (M^+). Anal. Calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40. Found: C, 74.94; H, 7.34.

2,4-Diethyl-6,7-dimethoxy-1-naphthyl acetate (acetate of 14). mp 107–108°C; ^{1}H NMR δ 1.25 (t, 3H, *J*=7.3, 7.8 Hz), 1.38 (t, 3H, *J*=7.3, 7.8 Hz), 2.47 (s, 3H), 2.62 (q, 2H, *J*=7.3, 7.8 Hz), 3.01 (q, 2H, *J*=7.3, 7.8 Hz), 3.98 (s, 3H), 4.00 (s, 3H), 6.98 (s, 1H), 7.11 (s, 1H), 7.24 (s, 1H); ^{13}C NMR δ 14.42, 14.55, 20.71, 23.46, 25.90, 55.67, 55.83, 100.37, 103.20, 122.83, 124.45, 126.94, 130.04, 136.73, 141.36, 149.04, 149.63, 169.52; MS *m*/*z* 302 (M^+). Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.42; H, 7.26.

2,4-Dimethyl-1-naphthol (15).[27] mp 77–78°C; ^{1}H NMR δ 2.37 (s, 3H), 2.59 (s, 3H), 4.92 (s, 1H), 7.08 (s, 1H), 7.45–7.50 (m, 2H) 7.89–7.91 (m, 1H), 8.14–8.16 (m, 1H); ^{13}C NMR δ 15.52, 18.64, 115.70, 121.38, 124.15, 124.52, 124.98, 125.16, 126.12, 129.49, 132.11, 146.93; HRMS *m*/*z* (M^+) calcd for $C_{12}H_{12}O$ 172.0888, found 172.0883.

4-Ethyl-2-propyl-1-naphthyl acetate (acetate of 16). Oil; ^{1}H NMR δ 0.98 (t, 3H, *J*=7.3 Hz), 1.38 (t, 3H, *J*=7.3 Hz), 1.66–1.71 (m, 2H), 2.48 (s, 3H), 2.61 (t, 2H, *J*=7.8 Hz), 3.07 (q, 2H, *J*=7.3 Hz), 7.21 (s, 1H), 7.46–7.50 (m, 2H), 7.72–7.74 (m, 1H), 8.00–8.02 (m, 1H); ^{13}C NMR δ 14.17, 14.99, 20.69, 23.20, 25.66, 32.53, 121.56, 124.02, 125.33, 126.01, 126.69, 127.24, 130.21, 131.34, 138.23, 142.44, 169.61; HRMS *m*/*z* (M^+) calcd for $C_{17}H_{20}O_2$ 256.1463, found 256.1459.

1,3-Diethyl-5,6-dimethoxynaphthalene (17): Oil; ^{1}H NMR δ 1.33 (t, 3H, *J*=7.6 Hz), 1.37 (t, 3H, *J*=7.6 Hz), 2.79 (q, 2H, *J*=7.6 Hz), 3.04 (q, 2H, *J*=7.6 Hz), 3.98 (s, 3H), 3.99 (s, 3H), 7.09 (s, 1H), 7.23 (d, 1H, *J*=9.2 Hz), 7.65 (d, 1H, *J*=9.2 Hz), 7.79 (s, 1H); ^{13}C NMR δ 15.10, 15.54, 26.06, 29.39, 56.80, 61.03, 113.70, 117.09, 120.05, 124.51, 126.62, 129.80, 140.18, 142.04, 143.04, 148.11; MS *m*/*z* 244 (M^+). Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.52; H, 8.24.

1-Methyl-3-phenylnaphthalene (18). mp 68–69°C; ^{1}H NMR δ 2.76 (s, 3H), 7.37 (t, 1H, *J*=7.3, 7.8 Hz), 7.46–7,53 (m, 4H), 7.60 (s, 1H), 7.72 (d, 2H, *J*=8.3 Hz), 7.89–7.91 (m, 2H), 8.00–8.02 (m, 1H); ^{13}C NMR δ 19.53, 123.99, 124.24, 125.79, 125.99, 126.35, 127.25, 127.38, 128.79, 128.83, 131.83, 133.86, 134.83, 138.18, 141.22; MS *m*/*z* 218 (M^+). Anal. Calcd for $C_{17}H_{14}$: C, 93.54; H, 6.46. Found: C, 93.42; H, 6.51.

1-Isopropyl-3-phenylnaphthalene (19). Oil; ^{1}H NMR δ 1.46 (d, 6H, *J*=6.6 Hz), 3.78–3.84 (m, 1H), 7.36–7.40 (m, 1H), 7.47–7.54 (m, 4H), 7.68 (d, 1H, *J*=1.8 Hz), 7.72 (dd, 2H, *J*=1.1, 7.3 Hz), 7.89–7.93 (m, 2H), 8.14 (d, 1H, *J*=1.8 Hz); ^{13}C NMR δ 23.60, 28.68, 121.64, 123.21, 124.22, 125.70, 125.73, 127.24, 127.47, 128.79, 129.21, 130.58, 134.22, 138.22, 141.63, 145.22; MS *m*/*z* 246 (M^+). Anal. Calcd for $C_{19}H_{18}$: C, 92.64; H, 7.36. Found: C, 92.56; H, 7.53.

4-Butyl-2-naphthaldehyde (20). Oil; ^{1}H NMR δ 0.98 (t, 3H, *J*=7.3 Hz), 1.44–1.50 (m, 2H), 1.72–1.80 (m, 2H), 3.11 (t, 3H, *J*=7.8 Hz), 7.58 (t, 1H, *J*=8.3 Hz), 7.67 (t, 1H, *J*=8.3 Hz), 7.80 (s, 1H), 8.01 (t, 1H, *J*=8.3 Hz), 8.09 (d, 1H, *J*=8.3 Hz), 8.19 (s, 1H); ^{13}C NMR δ 13.95, 22.82, 32.62, 32.70, 122.08, 124.24, 126.54, 128.91, 130.41, 133.13, 133.35, 133.68, 135.23, 140.55, 192.55; HRMS *m*/*z*(M^+) calcd for $C_{15}H_{16}O$ 212.1201, found 212.1206.

1,2,3,4-Tetrahydro-3,3-dimethylanthracen-1-one (21). mp 105–105.5°C; ^{1}H NMR δ 1.10 (s, 6H), 2.59 (s, 2H), 3.00 (s, 2H), 7.46 (t, 1H, *J*=8.3 Hz), 7.55 (t, 1H, *J*=8.3 Hz), 7.66 (s, 1H), 7.79 (d, 1H, *J*=8.3 Hz), 7.95 (d, 1H, *J*=8.3 Hz), 8.60 (s, 1H); ^{13}C NMR δ 28.25, 33.52, 43.78, 52.92, 125.95, 127.02, 127.44, 128.35, 128.51, 129.82, 129.97, 131.68, 136.13, 137.66, 198.86; MS *m*/*z* 224 (M^+). Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.64; H, 7.21.

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