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Iron-Catalyzed Regioselective Direct Oxidative Aryl−Aryl Cross-Coupling

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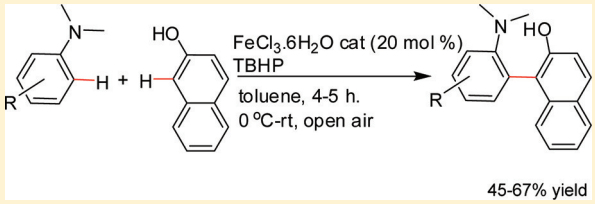
Supporting Information

ABSTRACT: Regioselective iron-catalyzed cross-dehydrogenative coupling (CDC) of two aromatic compounds using *tert*-BuOOH as oxidant under mild conditions has been reported. The direct oxidative coupling reaction is selective toward creation of a carbon−carbon bond at the position *ortho* to the functional groups of the substrates, completely preventing the homocoupled products. The C−C bond-forming reaction makes the method versatile, leading to functionalized 2,2′ -disubstituted biaryls.



INTRODUCTION

Development of novel methods toward the formation of C−C bonds is an important issue in the area of organic chemistry research, and C−C bond-formation reactions leading to dimerizations by self-coupling or cross-dehydrogenative couplings have been thoroughly investigated. Several stoichiometric as well as catalytic versions of transition-metal-mediated conversions are known to effect this fundamental reaction. Among various types of C−C bond-formation reactions, aryl−aryl bond formation is one of the most important tools in organic synthesis owing to the occurrence of biaryl building blocks in several biologically active molecules and functional materials such as light-emitting diodes, electron transport devices, liquid crystals, etc.[1] Despite the availability of several literature methods, selective cross-dehydrogenative coupling (CDC) is still a challenge in organic chemistry for the construction of a C−C bond without using prefunctionalized substrates.[2] Although transition-metal-catalyzed aryl−aryl cross-coupling reactions have been known over the past few decades, the mild and selective Suzuki coupling involving preactivation of both coupling partners has almost completely replaced classical methods of biaryl synthesis.[3] Such a preactivation needs inclusion of few more steps and hence serious efforts have been made in the past decade, wherein one of two coupling partners is preactivated while the second one is subjected to direct coupling.[4] In search of better alternatives, increased attention is being further focused on direct arylation processes that replace both of the preactivated substrates of the cross-coupling partners with the simple arene itself.[5] Although several reports have been published on homocoupling of either phenols/naphthols[6] or aniline[7] derivatives, to the best of our knowledge generalized methods for the regioselective cross-coupling of their unactivated analogues leading to functionalized biaryls under practical catalytic conditions are very rare. In this regard, a copper-catalyzed selective cross-coupling of various substituted 2-naphthols and 2-naphthylamines for the synthesis of tetrasubstituted 1,1′-binaphthyls has been reported without preactivation of either of the coupling partners.[8] Subsequently the reaction has been further explored using iron-catalyzed cross-coupling as well.[9]

In recent years iron, known to be a "cheap metal for noble task", has been extensively exploited in organic transformations because of its inexpensive, nontoxic, and environmentally benign characters.[10,11] Sarhan and Bolm, in their excellent recent article critically reviewed the use of iron(III) chloride in oxidative C−C coupling of arenes and related unsaturated compounds leading to highly selective dimerizations of phenol derivatives, naphthols, and heterocyclic compounds.[12] Although the iron-catalyzed formation of C−C[13] and C−heteroatom bonds[14] has been developed recently, the direct formation of C−C bonds without preactivation of the substrates especially with control over chemo-, regio-, and stereoselectivity appears to be a challenge.

In continuation of our program on various C−C and C−N bond-forming reactions,[15] we found that the regioselective formation of biaryls by iron-catalyzed direct oxidative cross-coupling is very interesting to explore, and in this article we present a CDC reaction of various substituted *N*,*N*-dialkylanilines with 2-naphthol/1-naphthol under different catalytic and solvent conditions.

RESULTS AND DISCUSSION

We discovered that stirring a toluene solution of equimolar quantities of the *N*,*N*-dimethylaniline and 2-naphthol in $FeCl_3 \cdot 6H_2O$ (20 mol %) and TBHP (2.0 equiv) for 4−5 h at 0 °C to room temperature under aerial conditions resulted in the formation of cross-coupling product (Scheme 1). The reaction proceeded with high regioselectivity under mild conditions. Our Initial studies using variety of Lewis acid

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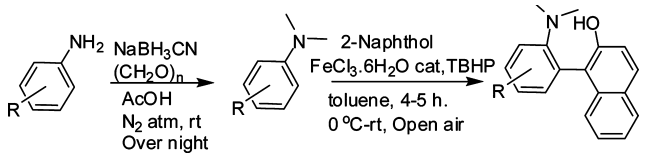
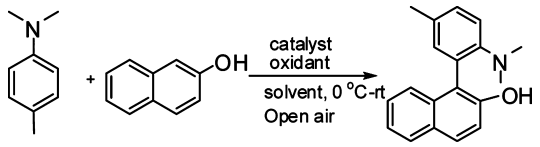
Scheme 1



catalysts for the coupling reaction of *N*,*N*-dimethyl *p*-toluidine (DMT) and 2-naphthol in the presence of TBHP revealed that copper, nickel, and other iron salts (Table 1, entries 2−8) were ineffective in giving desired product, whereas $Pd(OAc)_2$ afforded the product albeit in low yields (Table 1, entry 1). The cross-coupling reaction with $AlCl_3$ as catalyst also worked and gave good yields of the product next to $FeCl_3$ (Table 1, entry 9). TBHP was identified as the best-suited oxidant, while other oxidants turned out to be unreactive or failed to produce the desired outcome (Table 1, entries 11−15), except for $K_2S_2O_8$, which produced moderate yields of the coupling product (Table 1, entry 18). Oxidants such as H_2O_2 and DTBP found to be unreactive even after prolonged reaction times (Table 1, entries 16 and 17). The stoichiometric oxidant benzoyl peroxide proved to be the second best in terms of yield (Table 1, entry 19). Influence of solvents was also tested by screening the reaction with several nonpolar (hydrocarbon) and polar solvents (Table 1, entries 20−27), the latter suppressed the yields drastically and led to the formation of trace amounts of self-coupled products as well. Temperature also played a crucial role in the formation of desired products. When the reaction was performed at room temperature, few unseparable complex mixtures of products were produced, thereby diminishing the product yield. This problem was circumvented by initially carrying out the reaction at 0 °C and gradually allowing it to come to room temperature, thereby reducing the formation of undesirable byproducts to a considerable extent. In the course of the above reaction, absence of either Fe(III) catalyst or TBHP rendered the transformation unsuccessful, indicating that both catalyst and oxidant were essential for the reaction to proceed. Loading 20% of the catalyst proved to be optimal for the reaction and brought about the best outcome.

Further, oxygen did not play any significant role in the reaction course, as not much difference was observed in yields when operated under the absence of oxygen. With these

Table 1. Optimization of Reaction Conditions[a]



1a 2-Naphthol **1b**

entry	catalyst (20 mol %)	oxidant (2 equiv)	solvent	time	yield[b] (%)
1[c]	$Pd(OAc)_2$	TBHP	toluene	24 h	<10
2	CuCl	TBHP	toluene	30 min	0
3	CuBr	TBHP	toluene	30 min	0
4	CuI	TBHP	toluene	30 min	0
5	$NiCl_2$	TBHP	toluene	90 min	traces
6	$Fe_2(SO_4)_3{\cdot}9H_2O$	TBHP	toluene	5 h	traces
7	$NH_4Fe(SO_4)_2{\cdot}12H_2O$	TBHP	toluene	5 h	traces
8	$NH_4FeCl_4{\cdot}6H_2O$	TBHP	toluene	5 h	traces
9	$AlCl_3$	TBHP	toluene	5 h	60
10	$FeCl_3{\cdot}6H_2O$	TBHP	toluene	5 h	67
11	$FeCl_3{\cdot}6H_2O$	$PhI(OAc)_2$	toluene	45 min	0
12	$FeCl_3{\cdot}6H_2O$	*m*-CPBA	toluene	30 min	0
13	$FeCl_3{\cdot}6H_2O$	O_2	toluene	12 h	0
14	$FeCl_3{\cdot}6H_2O$	NBS	toluene	5 h	NR
15	$FeCl_3{\cdot}6H_2O$	DDQ	toluene	24 h	NR
16	$FeCl_3{\cdot}6H_2O$	H_2O_2 (30% aq)	toluene	24 h	NR
17	$FeCl_3{\cdot}6H_2O$	DTBP	toluene	overnight	NR
18	$FeCl_3{\cdot}6H_2O$	$K_2S_2O_8$	toluene	60 min	20
19	$FeCl_3{\cdot}6H_2O$	$(C_6H_5CO)_2O$	toluene	2 h	40
20	$FeCl_3{\cdot}6H_2O$	TBHP	DMSO	60 min	0
21	$FeCl_3{\cdot}6H_2O$	TBHP	AcOH	30 min	0
22	$FeCl_3{\cdot}6H_2O$	TBHP	CH_2Cl_2	2 h	30
23	$FeCl_3{\cdot}6H_2O$	TBHP	THF	2 h	29
24	$FeCl_3{\cdot}6H_2O$	TBHP	DME	2 h	22
25	$FeCl_3{\cdot}6H_2O$	TBHP	Et_2O	2 h	46
26	$FeCl_3{\cdot}6H_2O$	TBHP	CH_3CN	30 min	59
27	$FeCl_3{\cdot}6H_2O$	TBHP	benzene	90 min	60

[a]All reactions were carried out with 0.4 mmol of **1a** and 0.4 mmol of 2-naphthol. NR = no reaction. DTBP = di-*tert*-butyl peroxide, NBS = *N*-bromo succinimide. DME = 1,2-dimethoxyethane, DDQ= 2,3-dichloro-5,6-dicyano-*p*-benzoquinone. TBHP used in all cases is 70% aq solution. [b]Isolated yields. [c]Only 50% of the starting materials were consumed.

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Table 2. Substrate Scope[a]

Entry	Substrate	Product	Yield (%)
1	R=H, 2a	(2b)	62
2	R=4-Me, 1a	(1b)	67
3	R=3,4-diMe, 3a	(3b)	60
4	R=4-Et, 4a	(4b)	59
5	R=4-*i*-Pr, 5a	(5b)	56
6	R=4-*t*-Bu, 6a	(6b)	56
7	R=4-F, 7a	(7b)	49
8	R=4-Cl, 8a	(8b)	59
9*	R=4-Br, 9a	(9b)	57
10	R=4-I, 10a	(10b)	47
11	R=4-OMe, 11a	(11b)	60
12	R=2-OMe, 12a	–	NR
13	R=3.4,5-triOMe, 13a	–	NR
14	R=4-CN, 14a	(14b)	45
15	R=4-NO_2, 15a	–	NR
16	R=4-CF_3, 16a	–	NR
17	17a	(17b)	55
18	18a	(18b)	59
19	19a	(19b)	55

[a]Substituted *N*-alkyl aniline (1 equiv), 2-naphthol (1 equiv), TBHP (2 equiv), and [Fe] (20 mol %); otherwise are mentioned. Reported yields are based on *N*-alkyl aniline. NR = no reaction. (*) 12 h reaction.

optimal conditions in hand, reactions of various substituted *N*,*N*-dialkylaniline derivatives with 2-naphthol were examined for the generation of biaryls, and the results obtained are listed in Table 2. Alkyl-substituted anilines **1a**−**6a** afforded good yields (Table 2, entries 1−6). Interestingly, in contrary to our expectations, electron-donating alkoxy-substituted anilines show a reduction in yield, which can be attributed to the interference of oxygen that might have dampened their reactivity (Table 2, entries 11, 19). 2-Substituted aniline **12a** failed to produce the biaryl product, indicating that the presence of the *ortho* C−H is vital for the coupling reaction to proceed. The steric factors also played a role in the reaction course as 3,4-dimethylaniline derivative **3a** participated in CDC reaction at the less crowded 6-position (Table 2, entry-3), as opposed to the 2-position, and 3,4,5-trimethoxyaniline **13a** derivative failed to react presumably due to steric hindrance. Fluoro-, chloro-, bromo-, and iodo-substituted anilines were tolerated in the reaction course (Table 2, entries 7−10), thereby allowing room for further modifications at these halogenated positions. The electron-withdrawing fluoro- and bulky iodo-substituted aniline derivatives **7a** and **10a** delivered lower yields of the coupling products **7b** and **10b**, respectively. In the case of 4-cyano *N*,*N*-dimethylaniline **14a**, drastically reduced yield of the product (Table 2, entry 14) was observed, while other electron-withdrawing moieties at the 4-position of the *N*,*N*-dialkyl-substituted aniline such as *p*-nitro- and *p*-trifluoromethyl *N*,*N*-dimethylanilines **15a** and **16a** completely prevented the reaction from proceeding (Table 2, entries 15 and 16) due to decreased electron density of the phenyl ring. In general it is noticed that electron-donating alkyl groups on the aniline ring lower the E_{ox} value and allow easy oxidation of the substrate, giving higher yields compared to the substrates with electron-withdrawing groups. 3-Substituted aniline derivatives such as *m*-methoxy- and *m*-chloroanilines failed to produce the cross-coupling product (not shown). The overall yields of the reactions are in the range of 45−67%, and in most of the reactions, the starting aniline is completely consumed and part of the aniline is converted into unidentifiable complex mixture, whereas the unreacted 2-naphthol is recovered in all the cases. In order to gain insights into the effect of different *N*-substitutions such as *N*-allyl and *N*-benzyl groups on the reaction course, substrates **17a** and **18a** (Table 2, entries 17, 18) were also examined for the desired transformation under similar conditions and produced **17b** and **18b**, respectively. However, an attempt to extend the scope of the reaction to hetero aromatic compound, *N*,*N*-dimethylamino pyridine met with a failure (not shown). *N*-Methyl aniline and aniline also failed to give the cross-coupling product with 2-naphthol under these reaction conditions presumably because of their higher E_{ox} values of 1053 and 1135 mV, respectively,[16] thus making it

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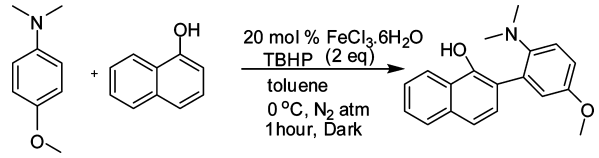
difficult for the substrate to generate easily the radical cation by oxidation. The structures of all the new compounds were confirmed by IR, ^{1}H NMR, ^{13}C NMR, and HRMS. The regioselectivity of the coupling presumably arising from hydrogen bonding between amino and hydroxyl groups was unambiguously established from the single crystal X-ray studies carried out on the cross-coupled product **1b**.

To broaden the scope of the oxidative direct cross coupling reaction, 1-naphthol was used in place of 2-naphthol, and it was found that the desired product **20b** was formed in good yield (Scheme 2).

Scheme 2



(20b)

In our hands simple phenols were found to be inert under the reaction conditions. Oxidation at sp^3 carbon on the nitrogen of the substituted aniline was also envisioned; however, no product resulting from such reaction was observed in this case, proving this reaction to be chemoselective.[17]

To establish the mechanistic evidence for the $FeCl_3 \cdot 6H_2O$-catalyzed direct oxidative cross-coupling reaction, the ESR spectrum of the reaction mixture was measured while the reaction was under progress (Figure 1). Initially no radical was

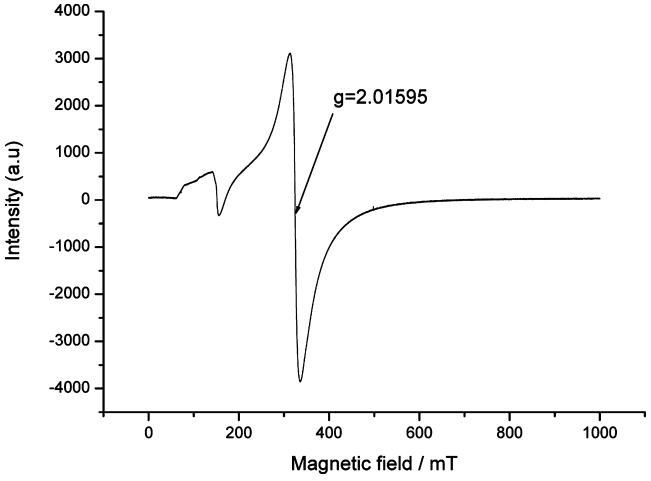
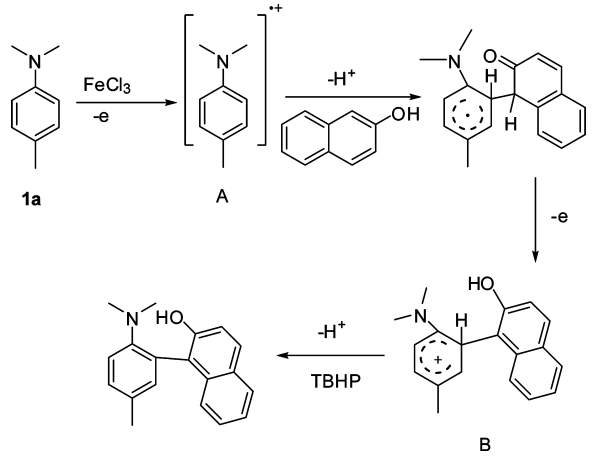


Figure 1. ESR spectrum of $FeCl_3 \cdot 6H_2O$-catalyzed oxidative coupling of *N*,*N*-dimethyl toluidine and 2-naphthol.

detected when measured at room temperature, and hence the reaction mixture was then cooled to −146 °C. The above figure shows the sharp signal observed at g = 2.01595, which is assigned to the radical species generated from **1a**.[18]

We propose the following tentative radical mechanism for the iron-catalyzed formation of cross-coupled products (Scheme 3).[19] Initial one electron transfer from *N*,*N*-dialkyl aniline to $FeCl_3$ gives rise to reduced form (Fe^{2+}) and a radical cationic species **A**. Subsequently the C−C bond is created by electrophilic attack of 2-naphthol on the radical cationic species at the *ortho* position. Finally dehydroaromatization of **B** takes place by losing one electron to form the cross-coupled product.

Scheme 3. Proposed Reaction Pathway for the Oxidative Coupling Reaction



$FeCl_3$ is regenerated by the reaction of the reduced catalyst with the oxidant TBHP. Finally we conclude that sufficiently different oxidation potentials (difference 440 mV) of the two coupling partners favors the cross-coupled product and that the lower oxidation potential (E_{ox}) of DMT (500 mV) compared to that of 2-naphthol (940 mV) supports initial ready oxidation of DMT to form the corresponding radical cation.[20]

CONCLUSION

In summary a promising protocol for a CDC coupling of *N*,*N*-dimethylanilines with 2-naphthol/1- naphthol has been established using an inexpensive catalyst oxidant Fe(III)/*tert*-BuOOH system under mild conditions. The coupling reactions are not sensitive to moisture or air and produced a variety of dialkyl amino- and hydroxy-substituted biaryls. The reaction was observed to be chemo- and regioselective, preventing the formation of any of the homocoupled biaryls. This is a C−C bond-forming reaction that is synthetically important for the generation of functionalized biaryls, and further the aryl substrates are not subjected to prefunctionalization and defunctionalization or use of organometallic reagents. Interestingly $AlCl_3$ also promoted the cross-coupling reaction with good catalytic activity, and detailed studies on the mechanism and substrate scope of the $AlCl_3$-catalyzed cross-coupling reaction of aryl amines with naphthols need further investigation.

EXPERIMENTAL SECTION

General Considerations. All commercially available chemicals were used as received, and $FeCl_3 \cdot 6H_2O$ (Purity 97%) was purchased from Sigma Aldrich. Thin-layer chromatography plates were visualized by exposure to UV light/iodine and/or by immersion in an acidic staining solution of phosphomolybdic acid followed by heating on a hot plate. ^{1}H and ^{13}C NMR spectra were obtained on 300 and 500 MHz spectrometers with tetramethylsilane and chloroform-d_1, respectively, as the internal standard. Chemical shifts (δ) are reported in ppm relative to the residual solvent signal (δ = 7.26 for ^{1}H NMR and δ = 77.0 for ^{13}C NMR). Data for ^{1}H NMR are reported as follows: chemical shift (multiplicity, coupling constant, number of hydrogens). Multiplicity is abbreviated as follows: s (singlet), d (doublet), dd (double doublet), t (triplet), q (quartet), m (multiplet). IR samples were analyzed as thin films on KBr plates. **CAUTION:** Mixing a metal salt and peroxide can cause explosion.[21] However in our experiments, we did not encounter this problem.

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General Procedure for CDC Reaction of *N,N*-Dialkylaniline Derivatives with 2-Naphthol. A 10-mL round bottomed flask was charged with *N,N*-dialkylaniline (1.0 mmol), 2-naphthol (1.0 mmol), and toluene (2 mL). The resulting mixture was kept at 0 °C, and $FeCl_3·6H_2O$ (20 mol %) and TBHP were added via syringe dropwise under atmospheric air. Then the resulting solution was allowed to stir at room temperature for 4−5 h. The reaction mixture obtained was then Celite filtered and washed with ethyl acetate and water. The combined organic layers were dried over Na_2SO_4, and solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (100−200 mesh/60−120 mesh) using hexane−ethyl acetate as eluent to give the product.

General Procedure for the Formation of *N,N*-Dimethylaniline Derivatives from Various Substituted Anilines. *Formation of (4-Methoxy-phenyl)-dimethylamine (**11a**).* To a purple solution of 4-methoxyaniline (1.02 g, 8.28 mmol) in glacial acetic acid (50 mL) under Ar(g) were added paraformaldehyde (2.44 g, 81.3 mmol) and sodium cyanoborohydride (2.46 g, 39.1 mmol). The addition of sodium cyanoborohydride caused vigorous bubbling. After stirring overnight, the reaction mixture was poured into a water−ice mixture (∼100 mL) containing NaOH (40 g). The addition was exothermic, and more ice was added to bring the total volume of the quench mixture to ∼300 mL. This mixture (pH = 14) was extracted with CH_2Cl_2 (350 mL). The combined organic layers were dried over $MgSO_4$(s), filtered, and concentrated under reduced pressure to obtain a purple solid. Flash chromatographic purification of the crude product provided a colorless solid (1.06 g, 7.01 mmol, 85%).

General Procedure for CDC Reaction of (4-Methoxy-phenyl)-dimethylamine with 1-Naphthol. To an oven-dried 10-mL two neck round bottomed flask equipped with a magnetic stir bar were added 0.151 g (1.0 mmol, 1 equiv) of (4-methoxy-phenyl)-dimethylamine and toluene (1.5 mL). The solution was kept in a dark place, and 0.144 g (1.0 mmol, 1equiv) of 1-naphthol was added under nitrogen atmosphere. The resulting solution was then kept at 0 °C, and 0.030 g (20 mol %) of $FeCl_3·6H_2O$ and 0.085 mL (2.0 mmol, 2equiv) of TBHP were added via syringe dropwise under nitrogen atmosphere. The resulting solution was allowed to stir at 0 °C for 1 h. The reaction mixture was then Celite filtered and washed with ethyl acetate and water. The combined organic layers were dried over Na_2SO_4, and solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (100−200 mesh/60−120 mesh) using hexane−ethyl acetate as eluent to give the product **20b**.

*1-(2-(Dimethylamino)-5-methylphenyl)naphthalen-2-ol (**1b**).* Isolated by column chromatography (ethyl acetate−hexane = 1:9, R_f = 0.7). The title compound was obtained as colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.83−7.75 (m, 3H), 7.39−7.14 (m, 6H), 2.65 (s, 6H), 2.31 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$, ppm): δ 152.1, 147.5, 135.7, 133.3, 132.4, 130.4, 129.9, 129.2, 128.9, 128.1, 125.9, 125.3, 123, 121.1, 120.7, 117.9, 43.7, 20.6; FTIR (cm^{-1}): 3034, 2922, 2743, 1727, 1658, 1620, 1587, 1501, 1460, 1430, 1403, 1341, 1273, 1233, 1179, 1151, 1113, 1036, 986, 956, 925, 892, 819, 747, 633, 585, 544, 472; MS (ESI) *m/z*: 278(M + H)$^+$; HRMS (ESI) calcd for $C_{19}H_{19}NO$ (M + H)$^+$: 278.1544; found: 278.1548.

*1-(2-(Dimethylamino)phenyl)naphthalen-2-ol (**2b**).* Isolated by column chromatography (ethyl acetate−hexane = 1:9, R_f = 0.6). The title compound was obtained as yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.77−7.71 (m, 3H), 7.39−7.26 (m, 4H), 7.22−7.19 (m, 2H), 7.14−7.09 (m, 1H), 2.69 (s, 6H); ^{13}C NMR (300 MHz, $CDCl_3$, ppm): δ 152, 149.9, 135.3, 133.3, 130.6, 129.9, 129.3, 128.4, 128.1, 126, 125.3, 123, 122.9, 120.9, 120.6, 118, 43.5; FTIR (cm^{-1}): 3418, 3016, 2920, 2865, 2792, 1927, 1736, 1589, 1459, 1401, 1365, 1330, 1298, 1234, 1202, 1149, 1117, 1091, 1038, 981, 922, 819, 752, 669, 621, 554; MS (ESI) *m/z*: 264(M + H)$^+$; HRMS (ESI) calcd for $C_{18}H_{17}NO$ (M + H)$^+$: 264.1388; found: 264.1376.

*1-(2-(Dimethylamino)-4,5-dimethylphenyl)naphthalen-2-ol (**3b**).* Isolated by column chromatography (ethyl acetate−hexane = 1:9, R_f = 0.6). The title compound was obtained as brownish viscous liquid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.76−7.68 (m, 3H), 7.33−7.13 (m, 4H), 6.97 (s, 1H), 2.66 (s, 6H), 2.34 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$, ppm): δ 153.8, 148.9, 137, 134.5, 130.1, 129.5, 128.5, 127.6, 126.7, 126.2, 123.2, 117.9, 116.1, 112, 109.4, 41.7, 20.1, 18.6; FTIR (cm^{-1}): 2923, 2852, 1611, 1507, 1459, 1369, 1231, 815, 751, 408; MS (ESI) *m/z*: 292(M + H)$^+$; HRMS (ESI) calcd for $C_{20}H_{21}NO$ (M + H)$^+$: 292.1701; found: 292.1706.

*1-(2-(Dimethylamino)-5-ethylphenyl)naphthalen-2-ol (**4b**).* Isolated by column chromatography (ethyl acetate−hexane = 1:9, R_f = 0.6). The title compound was obtained as brownish solid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.78−7.72 (m, 3H), 7.33−7.28 (m, 2H), 7.23−7.18(m, 3H), 7.15−7.14(m, 1H), 2.69(s, 6H), 2.66−2.61 (m, 2H), 1.24−1.18 (m, 3H); ^{13}C NMR (300 MHz, $CDCl_3$, ppm): δ 152.2, 141.3, 137.8, 133.4, 132.3, 130.8, 129, 128.4, 127.8, 126.8, 122.9, 122.4, 119.3, 117.3, 41, 28.9, 14.2; FTIR (cm^{-1}): 3435, 2959, 2926, 2855, 1737, 1625, 1503, 1459, 1346, 1272, 1120, 1082, 965, 893, 821, 750, 699, 551; MS (ESI) *m/z*: 292(M + H)$^+$; HRMS (ESI) calcd for $C_{20}H_{21}NO$ (M + H)$^+$: 292.1701; found: 292.1706.

*1-(2-(Dimethylamino)-5-isopropylphenyl)naphthalen-2-ol (**5b**).* Isolated by column chromatography (ethyl acetate−hexane = 1:9, R_f = 0.5). The title compound was obtained as reddish brown solid. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.82−7.77 (m, 3H), 7.37−7.31 (m, 2H), 7.28−7.25 (m, 3H), 7.20−7.19 (m, 1H), 2.91−2.86(m, 1H), 2.67 (s, 6H), 1.24−1.22 (m, 6H); ^{13}C NMR (300 MHz, $CDCl_3$, ppm): δ 152.1, 147.7, 143.3, 133.5, 130.5, 129.9, 129.2, 128.1, 126.2, 125.9, 125.3, 122.9, 121.3, 120.7, 117.9, 43.6, 33.4, 23.9; FTIR (cm^{-1}): 3418, 3051, 2959, 2925, 2870, 2797, 1666, 1613, 1588, 1496, 1461, 1390, 1361, 1332, 1302, 1268, 1228, 1182, 1137, 1093, 1042, 954, 926, 899, 819, 753, 683, 615, 570, 506, 474, 431; MS (ESI) *m/z*: 306(M + H)$^+$; HRMS (ESI) calcd for $C_{21}H_{23}NO$ (M + H)$^+$: 306.1857; found: 306.1850.

*1-(5-tert-Butyl-2-(dimethylamino)phenyl)naphthalen-2-ol (**6b**).* Isolated by column chromatography (ethyl acetate−hexane = 1:9, R_f = 0.6). The title compound was obtained as pale yellowish solid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.84−7.77 (m, 3H), 7.44−7.25 (m, 5H), 7.21−7.18 (m, 1H), 2.67 (s, 6H), 1.29 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$, ppm): δ 152.2, 147.4, 145.5, 133.5, 132.8, 130, 129.9, 129.2, 128.1, 125.9, 125.3, 125, 123, 121.4, 120.6, 117.6, 43.6, 34.3, 31.3; FTIR (cm^{-1}): 3421, 3054, 2954, 2866, 1903, 1732, 1588, 1501, 1463, 1400, 1355, 1263, 1229, 1193, 1147, 1088, 1037, 925, 864, 819, 748, 680, 622, 566; MS (ESI) *m/z*: 320(M + H)$^+$; HRMS (ESI) calcd for $C_{22}H_{25}NO$ (M + H)$^+$: 320.2014; found: 320.2010.

*1-(2-(Dimethylamino)-5-fluorophenyl)naphthalen-2-ol (**7b**).* Isolated by column chromatography (ethyl acetate−hexane = 1:9, R*f* = 0.3). The title compound was obtained as brownish viscous liquid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.84−7.77 (m, 3H), 7.43−7.28 (m, 3H), 7.23−7.07 (m, 3H), 2.67 (s, 6H); ^{13}C NMR (300 MHz, $CDCl_3$, ppm): δ 152.3, 146.3, 146.24, 146.20, 133.2, 130, 128.4, 126.6, 124.9, 123.5, 121.9, 120.9, 119.7, 119.4, 115.2, 114.8, 44; FTIR (cm^{-1}): 3431, 3060, 2923, 2851, 2796, 1735, 1616, 1595, 1493, 1461, 1410, 1360, 1337, 1273, 1231, 1171, 1148, 1089, 1042, 1009, 959, 929, 889, 817, 751, 676, 637, 601, 568, 541, 478, 432; MS (ESI) *m/z*: 282(M + H)$^+$; HRMS (ESI) calcd for $C_{18}H_{16}NOF$ (M + H)$^+$: 282.1294; found: 282.1284.

*1-(5-Chloro-2-(dimethylamino)phenyl)naphthalen-2-ol (**8b**).* Isolated by column chromatography (ethyl acetate−hexane = 1:9, R*f* = 0.4). The title compound was obtained as brownish yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.78−7.69 (m, 3H), 7.40−7.28 (m, 4H), 7.21−7.13 (dd, *J* = 16.1 Hz, 2H), 2.68 (s, 6H); ^{13}C NMR (300 MHz, $CDCl_3$, ppm): δ 152, 148.6, 134.6, 132.9, 132.3, 129.8, 128.2, 128, 126.5, 124.8, 123.3, 120.5, 119.7, 119.4, 43.5; FTIR (cm^{-1}): 3048, 2925, 2740, 1730, 1663, 1622, 1591, 1482, 1400, 1339, 1270, 1234, 1149, 1114, 1038, 991, 952, 924, 888, 853, 817, 746, 718, 633, 586, 540, 513; MS (ESI) *m/z*: 298(M + H)$^+$; HRMS (ESI) calcd for $C_{18}H_{16}NOCl$ (M + H)$^+$: 298.0998; found: 298.0994.

*1-(5-Bromo-2-(dimethylamino)phenyl)naphthalen-2-ol (**9b**).* Isolated by column chromatography (ethyl acetate−hexane = 1:9, R_f = 0.5). The title compound was obtained as reddish sticky solid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.77−7.69 (m, 4H), 7.42−7.18 (m, 4H), 7.08−7.06 (m, 1H), 2.65 (s, 6H); ^{13}C NMR (300 MHz, $CDCl_3$, ppm): δ 152.1, 149.2, 137.6, 133, 132.7, 131.2, 129.97, 129.93, 129.3, 128.3, 126.7, 124.7, 123.4, 120.5, 119.7, 96.2, 43.5; FTIR (cm^{-1}):

3422, 3062, 2924, 2853, 1663, 1620, 1594, 1506, 1463, 1399, 1343, 1310, 1271, 1215, 1167, 1030, 949, 815, 751, 515; MS (ESI) *m/z*: 342(M + H)$^+$, 344(M + 2 + H)$^+$; HRMS (ESI) calcd for $C_{18}H_{16}NOBr$ (M + H)$^+$: 342.0493; found: 342.0501.

1-(2-(Dimethylamino)-5-iodophenyl)naphthalen-2-ol (**10b**). Isolated by column chromatography (ethyl acetate−hexane = 1:9, R_f = 0.6). The title compound was obtained as brownish solid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.77−7.65 (m, 4H), 7.41−7.17 (m, 4H), 6.97−6.93 (m, 1H), 2.66 (s, 6H); ^{13}C NMR (300 MHz, $CDCl_3$, ppm): δ 152.1, 150, 143.5, 137.2, 133.1, 132.9, 129.9, 128.3, 126.7, 124.8, 123.4, 120.5, 120, 119.5, 96.3, 86.4, 43.4; FTIR (cm^{-1}): 3422, 2924, 2853, 1741, 1593, 1461, 1356, 1230, 1156, 1099, 930, 816, 750, 557; MS (ESI) *m/z*: 390(M + H)$^+$; HRMS (ESI) calcd for $C_{18}H_{16}NOI$ (M + H)$^+$: 390.0354; found: 390.0339.

1-(2-(Dimethylamino)-5-methoxyphenyl)naphthalen-2-ol (**11b**). Isolated by column chromatography (ethyl acetate−hexane = 1:9, R_f = 0.4). The title compound was obtained as brownish solid. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.79−7.71 (m, 3H), 7.33−7.24 (m, 2H), 7.21−7.19 (d, *J* = 8.76 Hz, 1H), 7.14−7.13 (d, *J* = 8.76 Hz, 1H), 6.92−6.89 (m, 2H), 3.73 (s, 3H), 2.65 (s, 6H); ^{13}C NMR (300 MHz, $CDCl_3$, ppm): δ 155, 152.2, 143.4, 133.3, 132.1, 129.8, 129.4, 128.1, 126, 125.2, 123, 120.8, 120.7, 119.9, 119, 114, 55.6, 43.9; FTIR (cm^{-1}): 3418, 2924, 2855, 1744, 1596, 1500, 1459, 1335, 1237, 1164, 1035, 920, 869, 815, 748, 606, 541; MS (ESI) *m/z*: 294(M + H)$^+$; HRMS (ESI) calcd for $C_{19}H_{19}NO_2$(M + H)$^+$: 294.1494; found: 294.1504.

4-(Dimethylamino)-3-(2-hydroxynaphthalen-1-yl)benzonitrile (**14b**). Isolated by column chromatography (ethyl acetate−hexane = 3:7, R_f = 0.4). The title compound was obtained as brownish solid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 8.11−8.08 (m, 1H), 7.79−7.76 (m, 2H), 7.56−7.53 (m, 1H), 7.45−7.31 (m, 3H), 7.21 (s, 1H), 7.18 (s, 1H), 2.71 (s, 6H); ^{13}C NMR (300 MHz, $CDCl_3$, ppm): δ 153.8, 151.5, 138.9, 133.7, 132.4, 130.4, 130.1, 129.8, 129.4, 128.4, 127, 124.4, 123.7, 119.8, 118.5, 43; FTIR (cm^{-1}): 3418, 3062, 2924, 2855, 2219, 1696, 1597, 1507, 1457, 1344, 1275, 1224, 1135, 953, 817, 749, 715, 606, 606, 548; MS (ESI) *m/z*: 289(M + H)$^+$; HRMS (ESI) calcd for $C_{19}H_{16}N_2O$ (M + H)$^+$: 289.1340; found: 289.1353.

1-(2-(Benzyl(methyl)amino)phenyl)naphthalen-2-ol (**17b**). Isolated by column chromatography (ethyl acetate−hexane =1:9, R_f = 0.7). The title compound was obtained as brownish solid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.78−7.74 (m, 3H), 7.43−7.33 (m, 4H), 7.28−7.27 (m, 1H), 7.19−7.18 (m, 5H), 6.94−6.93 (m, 2H), 3.92−3.85 (m, 2H), 2.64 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$, ppm): δ 153.3, 134.5, 130.9, 129.7, 129.2, 129, 128.8, 128.7, 128.6, 127.7, 127.2, 126.7, 126.4, 126.2, 123.5, 123.1, 123, 119.6, 117.9, 117.7, 112.9, 109.4, 59.5, 39.9; FTIR (cm^{-1}): 3420, 3059, 2923, 2853, 1735, 1595, 1494, 1455, 1366, 1223, 1166, 1079, 816, 752, 698, 555, 469; MS (ESI) *m/z*: 340(M + H)$^+$; HRMS (ESI) calcd for $C_{24}H_{21}NO$ (M + H)$^+$: 340.1701; found: 340.1699.

1-(2-(Allyl(methyl)amino)-5-methoxyphenyl)naphthalen-2-ol (**18b**). Isolated by column chromatography (ethyl acetate−hexane = 1:9, R_f = 0.3). The title compound was obtained as red viscous liquid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.84−7.78 (m, 3H), 7.40−7.30 (m, 3H), 7.23−7.20 (m, 1H), 6.99−6.94 (m, 2H), 5.63−5.52 (m, 1H), 5.08−4.98 (m, 2H), 3.76 (s, 3H), 3.42−3.32 (m, 2H), 2.76 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$, ppm): δ 158.4, 151.8, 140.2, 133.7, 132.8, 129.6, 128.2, 126.1, 125, 123, 120.7, 120.2, 119.8, 119.5, 119.9, 115.3, 114, 60.4, 55.6, 39.5, 29.7; FTIR (cm^{-1}): 3377, 2924, 2854, 1726, 1619, 1509, 1461, 1246, 1031, 821, 749; MS (ESI) *m/z*: 320(M + H)$^+$; HRMS (ESI) calcd for $C_{21}H_{21}NO_2$ (M + H)$^+$: 320.1650; found: 320.1665.

1-(5-Methoxy-2-(pyrrolidin-1-yl)phenyl)naphthalen-2-ol (**19b**). Isolated by column chromatography (ethyl acetate−hexane = 1:9, R_f = 0.3). The title compound was obtained as colorless crystalline solid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.83−7.77 (m, 3H), 7.40−7.28 (m, 3H), 7.22−7.19 (m, 1H), 6.95−6.92 (m, 2H), 3.749 (s, 3H), 3.12−2.89 (m, 4H), 1.80 (s, 4H); ^{13}C NMR (300 MHz, $CDCl_3$, ppm): δ 153.5, 134.6, 129.7, 128.1, 127.7, 126.4, 126.3, 125.2, 123.4, 123.2, 119.9, 119.5, 118.4, 117.8, 114.4, 109.4, 55.7, 52.3, 24.2; FTIR (cm^{-1}): 3428, 2927, 2853, 1617, 1502, 1463, 1341, 1278, 1233, 1170, 1039, 958, 870, 817, 752, 611; MS (ESI) *m/z*: 320(M + H)$^+$; HRMS (ESI) calcd for $C_{21}H_{21}NO_2$ (M + H)$^+$: 320.1650; found: 320.1645.

2-(2-(Dimethylamino)-5-methoxyphenyl)naphthalen-1-ol (**20b**). Isolated by column chromatography (ethyl acetate−hexane = 1:9, R_f = 0.8). The title compound was obtained as red suspension. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 8.40−8.38 (m, 1H), 7.73−7.72 (m, 1H), 7.45−7.37 (m, 4H), 7.13−7.11 (m, 1H), 6.98−6.97 (m, 1H), 6.86−6.84 (m, 1H), 3.76 (s, 3H), 2.62 (s, 6H); ^{13}C NMR (300 MHz, $CDCl_3$, ppm): δ 156.4, 151.7, 141.6, 136.5, 134.3, 128.5, 127, 126.9, 126.4, 125, 123.7, 120.4, 119.6, 119.2, 118.7, 113.2, 55.6, 43.9; FTIR (cm^{-1}): 3449, 3054, 2924, 2853, 1736, 1660, 1603, 1576, 1509, 1460, 1378, 1333, 1289, 1247, 1177, 1091, 1040, 935, 870, 810, 755, 720, 676, 581, 533, 477, 430; MS (ESI) *m/z*: 294(M + H)$^+$.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

IR, ^{1}H and ^{13}CNMR, HRMS data for all new compounds and CIF file of **1b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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