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ORIGINAL PAPER

$KHSO_4$: a highly efficient and reusable heterogeneous catalyst for hydroarylation of styrenes

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Abstract Hydroarylation of styrenes with arenes/heteroarenes using $KHSO_4$ (10 mol%) as an efficient heterogeneous catalyst is described. High conversion and selectivity (>99%) were observed for hydroarylation of styrenes with 2-naphthol at reflux temperature of 1,2-dichloroethane. Yields were quantitative with all styrenes. Moderate to good conversions and selectivities were achieved with other aromatics and heteroaromatics under the same conditions. Regeneration and reusability of $KHSO_4$ were demonstrated. Addition of a trace amount of water could help to reactivate the $KHSO_4$ through dispersion and to facilitate the hydroarylation reaction.

Keywords $KHSO_4$ · Heterogeneous catalysis · Hydroarylation · Styrenes · Aromatics

Introduction

Functionalization of arenes and heteroarenes is of great importance in synthesis of pharmaceuticals, and agro- and fine chemicals; therefore, various procedures for their acylation and alkylation have been reported. Transition-metal-catalyzed hydroarylation of alkenes is of particular importance due to its high selectivity, synthetic efficiency, and environmental friendliness. Traditionally, these transformations are performed by Friedel–Crafts reactions with acyl or alkyl halides in combination with at least equimolar quantities of a Lewis acid. Recently, promising transition-metal- and acid-catalyzed C–H transformations of arenes and heteroarenes have been reported [1–6]. A number of catalytic systems, including ruthenium [7–10], palladium [11–17], platinum [18–20], nickel [21], and indium [22], have been employed for functionalization of heterocycles through carbon–carbon bond formation. Prominent systems, $Bi(OTf)_3$ [23], $BiCl_3$ [24], and $FeCl_3$ [25] catalyzed hydroarylation of styrenes were also reported for synthesis of a variety of 1,1-diarylalkanes in good yields. Boronic esters/acids with palladium complex [26], iodine [27], and an ion-exchange resin [28] are recent developments in the hydroarylation of alkenes. However, these methods require use of stoichiometric or excess amounts of strong acids/bases and air/moisture-sensitive organometallic reagents. In most studies, the halide salts obtained as byproducts are drawbacks of these reactions.

Results and discussion

In view of our ongoing quest for green and sustainable processes for functionalization of alkenes [29–33] and alkynes [34] for diverse applications, we envisioned a metal-free catalyst system for hydroarylation of styrenes with aromatic compounds in the presence of $KHSO_4$ (10 mol%) as an efficient catalyst under mild conditions (Scheme 1).

These reactions are particularly interesting from the viewpoint of green chemistry because hydroarylation exhibits perfect atom efficiency and relies on the use of simple arene reactants and safe catalysts, no production of toxic waste material, applicability of various substrates, and heterogeneous catalysis, allowing facile catalyst/product separation. Careful choice of inorganic acid, solvent, and reaction conditions enabled us to develop a

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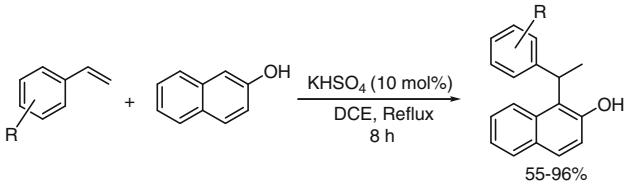


Scheme 1

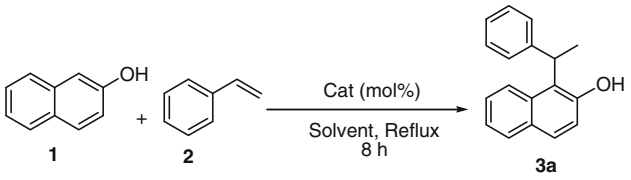
convenient protocol, which allows for efficient reaction of various alkenes with various arene functionalities to give the corresponding regioselectively alkylated product in a number of cases.

Initially, to determine the optimum reaction conditions, the reaction of β-naphthol (**1**) with styrene (**2**) using a catalytic amount of $KHSO_4$ and in different solvent media was investigated, and the reaction progress and yield were monitored by gas chromatography (GC) (Table 1). The reaction of equimolar amount of **1** with **2** in 5 cm^3 1,2-dichloroethane at reflux for 8 h in presence of 10 mol% $KHSO_4$ resulted in complete conversion to **3** (Table 1, entry 1). GC and GC-mass spectrometry (GC–MS) analyses of the reaction mixture revealed 98% conversion of **1** to yield the arylated product **3** with more than 99% selectivity. Use of excess amount of $KHSO_4$ under the same conditions resulted in less conversion and the formation of undesired products (Table 1, entries 2–4). When neat reaction was carried out, it indeed gave >99% selective product **3**, but led to less conversion (Table 1, entry 5). Use of 10 mol% $KHSO_4$ showed the highest catalytic activity and selectivity for hydroarylation of styrene with β-naphthol (Table 1, entry 1). Switching to other solvents led to lower conversion and yields under these conditions (Table 1, entries 6–10). Various other catalysts were also applied to the hydroarylation reaction, but showed lower catalytic activity and lower yield of the desired product (Table 1, entries 11–17) than that of $KHSO_4$.

The effect of temperature on the formation of **3** under the conditions of Table 1 was also studied. This study showed that, at room temperature and at 40 °C, there is no conversion by GC analysis even when the reaction continued up to 15 h (Table 2, entries 1 and 2). However, at 60 °C, 9% conversion and 100% selectivity of the desired product were observed (entry 3). At reflux temperature of 1,2-dichloroethane the best conversion and selectivity were observed (entry 4). Therefore the rest of the experiments were carried out under these optimized conditions.

The scope of the $KHSO_4$-catalyzed hydroarylation reactions of various styrenes with β-naphthol was examined under the optimized conditions, and results are indicated in Table 3. The hydroarylation reaction of various styrenes having electron-donating substituents with β-naphthol proceeded efficiently to give the corresponding

Table 1 Screening of various catalysts and solvents for hydroarylation of styrene with β-naphthol



Entry	Cat. (mol%)	Solvent	Conv. (%)[a]	Yield (%)[b]	Sel.[c]
1	$KHSO_4$ (10)	DCE	98	100	>99:1
2	$KHSO_4$ (12.5)	DCE	93	100	>99:1
3	$KHSO_4$ (50)	DCE	85	95	97:3
4	$KHSO_4$ (100)	DCE	84	100	93:7
5	$KHSO_4$ (10)	Neat	63	100	100
6	$KHSO_4$(10)	DCM	65	98	94:6
7	$KHSO_4$ (10)	Cyclohexane	91	100	99:1
8	$KHSO_4$ (10)	CH_3CN	–	–	–
9	$KHSO_4$ (10)	CH_3OH	61	81	62:38
10	$KHSO_4$ (10)	THF	–	–	–
11	$NaHSO_4$ (10)	DCE	88	99	98:2
12	HCl (10)	DCE	77	95	98:2
13	HCl (10)	Neat	91	100	89:11
14	H_2SO_4 (10)	DCE	56	97	11:89
15	HNO_3 (10)	DCE	30	78	–
16	PTS	DCE	68	99	1:99
17	PTS	Neat	28	84	31:69

Reaction conditions: 3.5 mmol of **1**, 3.5 mmol of **2,** cat, 5 cm^3 solvent/neat, reflux, 8 h

DCE 1,2-dichloroethane, *DCM* dichloromethane, *PTS* *p*-toluenesulfonic acid

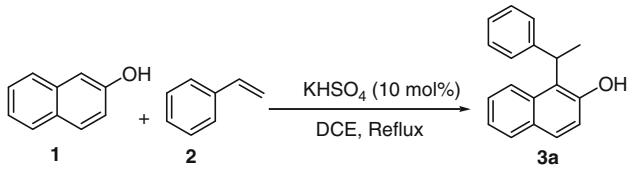
[a] GC conversions based on **1**

[b] GC yields of arylated products based on conversion

[c] Selectivity determined by GC of **3a** to others

arylated products in good to high yields with high selectivity (>99:1) (Table 3, entries 1–3). However, hydroarylation reaction of β-naphthol with styrenes having electron-withdrawing substituents also offered high yields and high selectivity (Table 3, entries 4 and 5), except with 4-acetoxystyrene (Table 3, entry 6) for which it gave product **3f** with 93% selectivity, which may be due to the strong electron-withdrawing property of the acetoxy group. All products of Table 3 were formed with high selectivity (except entry 6) of the desired product **3a**–**3f** as determined by ^{1}H nuclear magnetic resonance (NMR) of the purified products. Note that hydroarylation of various styrenes with β-naphthol provided the desired product as major isomer with all styrenes in excellent yields compared with the reported procedures [33–35]. These facts indicate the efficiency, selectivity, and catalytic activity of the present system.

Table 2 Effect of temperature on hydroarylation of styrene with β-naphthol



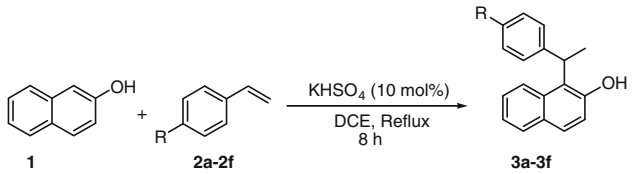
Entry	Temp. (°C)	Time (h)	Conv. (%)[a]	Yield (%)[b]	Sel.[c]
1	RT	15	0	–	–
2	40	15	0	–	–
3	60	15	9	9	100
4	Reflux	8	98	98	>99:1

[a] GC conversions based on **1**

[b] GC yields of arylated products

[c] Selectivity determined by GC of **3a** to others

Table 3 Hydroarylation of different styrenes with β-naphthol



Entry	R	Time (h)	Product	Yield (%)[a]	Selectivity[b]	Reference[c]
1	–H	8.0	**3a**	96	>99:1	
2	$-CH_3$	7.0	**3b**	93	99:1	[28]
3	–*t*-Bu	6.0	**3c**	88	99:1	
4	–Br	5.0	**3d**	93	98:2	
5	–Cl	8.0	**3e**	94	96:4	
6	$-OCOCH_3$	8.0	**3f**	73	93:7	

Reaction conditions: 3.5 mmol of **1**, 3.5 mmol of **2a**–**2f**, 5 cm^3 DCE

[a] Isolated yields

[b] Determined by ^1H NMR of desired product to other isomer

[c] Identity confirmed by comparison of spectroscopic data

To assess the reusability of $KHSO_4$, after completion of the reaction, the $KHSO_4$ was retrieved from the reaction mixture by simple filtration, dried, and recycled under the same experimental conditions, but GC analysis showed no formation of hydroarylated product. Furthermore, to corroborate the reusability of the catalyst, another reaction was carried out by the addition of a trace amount of water (through a syringe) to the recovered catalyst under the same conditions; GC analysis showed 85% conversion with 97% selectivity of the desired product (Fig. 1). This suggests that the hydrated form of the catalyst is active for this

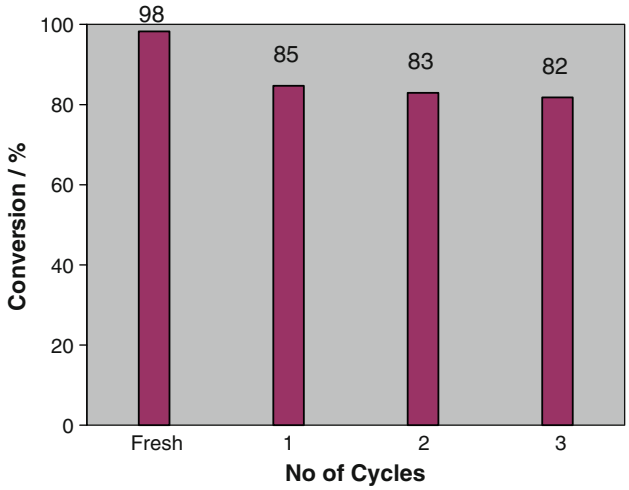


Fig. 1 $KHSO_4$ recyclability chart

transformation. Although a small amount of water was beneficial for recycling the catalyst ($KHSO_4$), when the reaction was tested without $KHSO_4$, on the addition of a drop of water no product was detected by GC–MS analysis.

This fact helps to rule out the contribution of H_2O alone to promote the hydroarylation reactions. In another set of recycling of $KHSO_4$, when D_2O was added instead of H_2O, no deuterated product was detected, however the desired hydroarylated product was obtained. We reasoned that a trace amount of water could help to disperse the $KHSO_4$ to facilitate the hydroarylation reaction [35].

As can be evidenced from the scanning electron microscope (SEM) images (Fig. 2) of fresh and recovered $KHSO_4$, the fresh $KHSO_4$ is surrounded by a number of H_2O molecules, which is not the case for the recovered $KHSO_4$. The surrounding water molecules help the dispersion of the catalyst, and thus activate the hydroarylation reaction.

As evident from the recyclability chart of $KHSO_4$ (Fig. 1), the catalyst could be easily recovered and reused for up to three consecutive cycles with good conversions. Therefore a reaction mechanism for electrophilic substitution of styrenes with 2-naphthol is proposed in Scheme 2.

To explore the scope and limitations of the present catalytic procedure, representative examples of functionalized aromatic and heteroaromatic compounds were treated with styrene and substituted styrenes, and the results are summarized in Table 4.

As shown in Table 4, various substituted styrenes reacted smoothly with α-naphthol to give corresponding hydroarylated products in 48–72% isolated yields with 90–98% selectivity (Table 4, entries 1–3). The reaction of phenol with *t*-butylstyrene (Table 4, entry 4) and styrene (Table 4, entry 5) gave moderate yields (43% and 42%) of

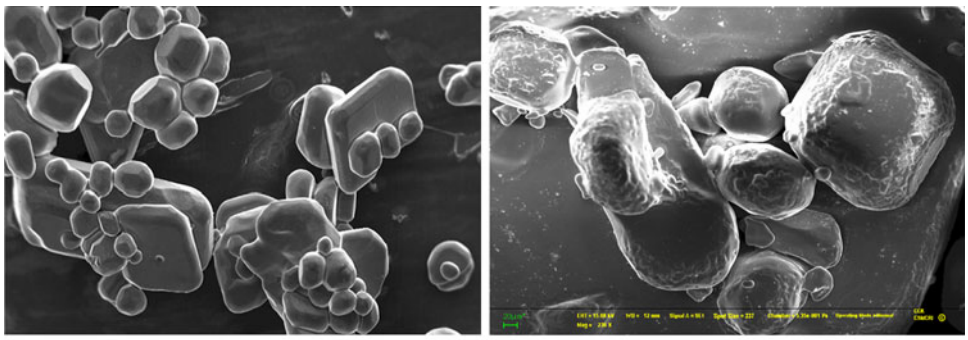
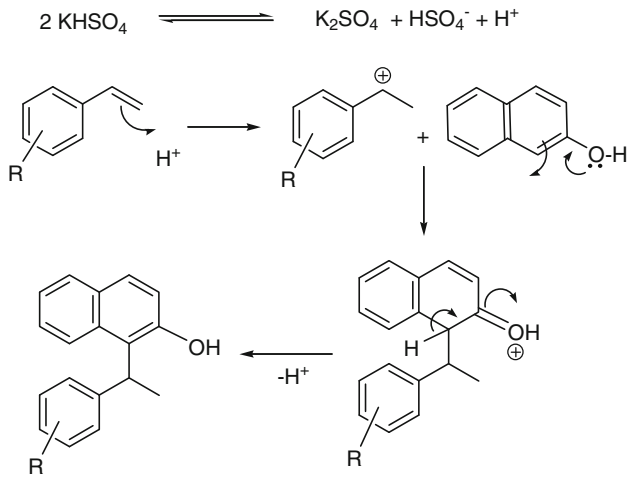


Fig. 2 Scanning electron microscope (SEM) images of $KHSO_4$ catalyst



Scheme 2

hydroarylated product with high selectivity (>99:1) in the former case. The same trend is observed in the reaction of *p*-cresol with methylstyrene and *t*-butylstyrene (Table 4, entries 6 and 7), but with good yields. The relatively low yield of thiophene with styrene is due its lower reactivity compared with naphthols and phenols under the present conditions (Table 4, entry 8). However, the reaction of 2-methythiophene with *t*-butylstyrene gave the corresponding hydroarylated product in good yield with high selectivity (Table 4, entry 9).

Conclusions

Herein we describe a general, mild, and efficient method for hydroarylation of styrenes with various aromatics and heteroaromatics using $KHSO_4$ (10 mol%) as a highly efficient and selective heterogeneous catalyst. Styrenes with electron-donating substituents showed higher selectivity for the hydroarylation reaction than those with electron-withdrawing substituents. $KHSO_4$ could be recovered and reused up to a minimum of three consecutive cycles with good conversion under the conditions studied. The present catalytic system has remarkable advantages such as: good activity and selectivity in a number of cases, no need to maintain dry or inert atmospheric conditions, ready availability, low cost, and recoverable and reusable catalyst, and importantly, it does not generate any toxic waste. This simple procedure offers a very attractive alternative for synthesis of motifs that are found in various bioactive molecules.

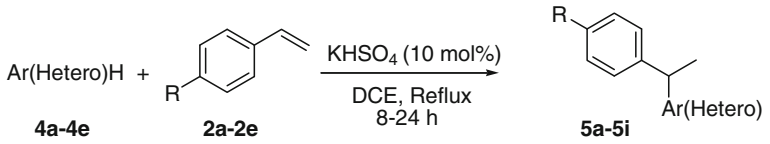
Experimental

All products from Table 1 were analyzed by GC–MS using a Shimadzu GCMS-QP2010. Gas chromatograms of compounds listed in Table 1 were recorded on a Thermo Trace GC Ultra using HP-5 column. ^1H and ^{13}C NMR spectra were recorded on a spectrometer operating at 500 and 125 MHz, respectively, in $CDCl_3$ unless otherwise stated. Chemical shifts are reported in ppm relative to the appropriate standard tetramethylsilane (TMS). Fourier-transform infrared (FT-IR) spectra were recorded on a Perkin Elmer GX-2000 spectrometer. Mass spectra were recorded on a micromass Q-Tof micro^{TM} in ES+ mode. Analytical thin-layer chromatography (TLC) was performed on Aluchrosep Silica Gel 60/UV_{254} plates. Purification of compounds (Tables 3, 4) was carried out by column chromatography using 100–200 mesh silica gel. All reactions were carried out in air without any special precautions. Unless otherwise stated, all reactions were carried out in an oil bath with magnetic stirring, and yield refers to isolated yields in Tables 3 and 4. Scanning electron microscope (SEM, LEO 1430 UP model) was used to observe the morphology of $KHSO_4$ before and after reaction.

General procedure for hydroarylation of styrenes

All reactions were carried out in air without any special precautions. To a stirred solution of **1** or **4** (3.5 mmol) and substituted styrene (3.5 mmol) in 5 cm^3 1,2-dichloroethane

Table 4 Hydroarylation of styrenes with arenes and heteroarenes



4a-4e **2a-2e** **5a-5i**

4a = 1-Naphthol, **4b** = Phenol, **4c** = 4-Me-phenol, **4d** = Thiophene, **4e** = 2-Me-thiophene

2a R = H, **2b** R = CH_3, **2c** R = *t*-Bu, **2d** R = Br, **2e** R = Cl

5a Ar = 1-HO-2-naphthyl, R = H; **5b** Ar = 1-HO-2-naphthyl, R = Cl; **5c** Ar = 1-HO-2-naphthyl, R = Br; **5d** Ar = 2-HO-phenyl, R = *t*-Bu; **5e** Ar = 2-HO-phenyl, R = H; **5f** Ar = 2-HO-5-Me-phenyl, R = CH_3; **5g** Ar = 2-HO-5-Me-phenyl, R = *t*-Bu; **5h** Ar = 2-Thienyl, R = CH_3; **5i** Ar = 5-Me-2-thienyl, R = *t*-Bu

Entry	4	2	Time (h)	5	Yield (%)[a]	Selectivity[b]	Reference[c]
1	**4a**	**2a**	8	**5a**	72	91:9	[28]
2	**4a**	**2e**	12	**5b**	67	90:10	
3	**4a**	**2d**	24	**5c**	48	98:2	
4	**4b**	**2c**	14	**5d**	43	>99:1	
5	**4b**	**2a**	15	**5e**	42	77:23	[27]
6	**4c**	**2b**	10	**5f**	72	68:32	
7	**4c**	**2c**	10	**5g**	73	70:30	
8	**4d**	**2b**	15	**5h**	33	73:27	[27]
9	**4e**	**2c**	14	**5i**	53	>99:1	

Reaction conditions: 3.5 mmol of **4a**–**4e**, 3.5 mmol of **2a**–**2e**, 10 mol% $KHSO_4$, 5 cm^3 DCE, 80 °C, 8 h

[a] Isolated yield

[b] Determined by ^1H NMR of purified main product to other isomer

[c] Identity confirmed by comparison of spectroscopic data

(DCE), 47.0 mg commercially available $KHSO_4$ (10 mol%) was added. The mixture was allowed to reflux at 80 °C for 8 h. The progress of the reaction was monitored by TLC. The reaction mixture was cooled to room temperature and filtered to remove $KHSO_4$. The $KHSO_4$ was washed with 5 cm^3 DCE, and the filtrate was concentrated in vacuo. The residue was subjected to column chromatography on silica gel (hexane–ethyl acetate) to obtain pure hydroarylated products.

1-(1-Phenylethyl)-2-naphthol (**3a**, $C_{18}H_{16}O$)
Brown viscous liquid. ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.91$ (s, 3H), 5.23 (s, 1H), 5.31 (q, $J = 7.0$ Hz, 1H), 7.1 (d, $J = 9.0$ Hz, 1H), 7.35 (t, $J = 7.5$ Hz, 1H), 7.44 (q, $J = 8.0$ Hz, 3H), 7.51 (d, $J = 7.51$ Hz, 2H), 7.56 (t, $J = 8.0$ Hz, 1H), 7.77 (d, $J = 8.5$ Hz, 1H), 7.91 (d, $J = 8.0$ Hz, 1H), 8.14 (d, $J = 9.0$ Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 18.9$, 36.5, 121.0, 124.6, 124.8, 125.6, 128.3, 128.4, 128.9, 130.4, 130.6, 130.7, 131.5, 134.6, 145.6, 153.2 ppm; IR (neat): $\bar{\nu} = 3{,}499$, 3,059, 3,026, 2,969, 2,934, 2,876, 1,661, 1,623, 1,601, 1,512, 1,448, 1,374, 1,260, 1,210, 1,147, 1,075, 1,025, 933, 855, 813, 751, 701, 587, 529, 504, 450 cm^{-1}; GC–MS: *m/z* (%) = 248 (100) [M^+], 233 (92), 215 (72), 203 (20), 189 (10), 115 (28), 77 (18), 63 (7); LRMS: calcd 248.12, found 248.15.

1-[1-(4-tert-Butylphenyl)ethyl]-2-naphthol (**3c**, $C_{22}H_{24}O$)
Reddish-brown viscous liquid. ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.21$ (s, 9H), 1.67 (d, $J = 7.0$ Hz, 3H), 4.88 (s, 1H), 5.03 (q, $J = 7.0$ Hz, 1H), 6.90 (d, $J = 8.5$ Hz, 1H), 7.25 (m, 5H), 7.38 (t, $J = 8.0$ Hz, 1H), 7.57 (d, $J = 8.5$ Hz, 1H), 7.70 (d, $J = 8.0$ Hz 1H), 7.98 (d, $J = 5.0$ Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 17.2$, 31.3, 34.5, 119.5, 122.5, 123.1, 123.8, 126.1, 126.6, 126.9, 128.7, 128.9, 129.7, 132.9, 140.1, 149.9, 151.7 ppm; IR (neat): $\bar{\nu} = 3{,}452$, 3,056, 2,959, 2,872, 1,664, 1,602, 1,511, 1,463, 1,393, 1,366, 1,261, 1,206, 1,148, 1,019, 932, 813, 749, 687, 559, 429 cm^{-1}; GC–MS: *m/z* (%) = 304 (100) [M^+], 289 (95), 247 (40), 233 (30), 215 (25), 170 (60), 161 (15), 144 (27), 130 (15), 123 (38), 103 (18), 91 (12), 77 (8), 65 (3); LRMS: calcd 304.18, found 304.28.

1-[1-(4-Bromophenyl)ethyl]-2-naphthol (**3d**, $C_{18}H_{15}BrO$)
Dark-brown viscous liquid. ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.68$ (d, $J = 7.0$ Hz, 3H), 4.85 (s, 1H), 5.07 (q, $J = 7.0$ Hz, 1H), 6.88 (d, $J = 8.5$ Hz, 1H), 7.13 (t, $J = 7.0$ Hz, 1H), 7.22 (q, $J = 7.5$ Hz, 3H), 7.27 (d, $J = 7.5$ Hz, 2H), 7.34 (t, $J = 8.0$ Hz, 1H), 7.55 (d, $J = 8.5$ Hz, 1H), 7.68 (d, $J = 8.0$ Hz 1H), 7.92 (d, $J = 8.5$ Hz, 1H) ppm; ^{13}C NMR

(125 MHz, $CDCl_3$): δ = 17.2, 34.9, 119.4, 122.7, 123.1, 123.9, 126.6, 126.8, 127.2, 128.7, 128.9, 129.1, 129.7, 132.9, 143.8, 151.5 ppm; IR (neat): $\bar{\nu}$ = 3,397, 3,028, 2,998, 2,922, 2,837, 1,610, 1,510, 1,457, 1,369, 1,298, 1,246, 1,176, 1,109, 1,034, 827, 742, 688, 547, 419 cm^{-1}; GC–MS: *m/z* (%) = 326 (56) [M^+], 311 (52), 293 (3), 231 (55), 215 (12.5), 202 (25), 170 (100), 141 (15), 128 (2.5), 116 (27), 101 (35), 89 (12.5), 77 (13); LRMS: calcd for $C_{18}H_{15}BrO$ [K^+] 364.99, found 364.33.

1-[1-(4-Chlorophenyl)ethyl]-2-naphthol
(**3e**, $C_{18}H_{15}ClO$)
Dark-brown viscous liquid. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.69 (d, *J* = 7.0 Hz, 3H), 4.86 (s, 1H), 5.03 (q, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 9.0 Hz, 1H), 7.17 (m, 4H), 7.23 (t, *J* = 7.5 Hz, 1H) 7.32 (t, *J* = 7.5 Hz, 1H), 7.57 (d, *J* = 8.5 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.4, 34.3, 119.0, 123.0, 123.2, 123.4, 126.6, 128.5, 128.82, 128.88, 128.9, 129.8, 132.1, 132.7, 142.8, 151.2 ppm; IR (neat): $\bar{\nu}$ = 3,487, 3,058, 2,962, 2,873, 1,622, 1,511, 1,462, 1,395, 1,365, 1,260, 1,205, 1,149, 1,018, 932, 812, 745, 689, 592, 468 cm^{-1}; GC–MS: *m/z* (%) = 282 (98) [M^+], 267 (100), 249 (18), 231 (47), 215 (15), 170 (19), 139 (20), 116 (27), 101 (35), 88 (12), 77 (13), 63 (7); LRMS: calcd for $C_{18}H_{15}ClO$ [Na^+] 305.07, found 305.20.

4-[1-(2-Hydroxy-1-naphthyl)ethyl]phenyl acetate
(**3f**, $C_{20}H_{18}O_3$)
Dark-brown viscous liquid. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.77 (d, *J* = 7.0 Hz, 3H), 2.25 (s, 3H), 5.12 (q, *J* = 7.5 Hz, 1H), 5.20 (s, 1H), 6.95 (d, *J* = 9.0 Hz, 1H), 7.0 (d, *J* = 8.5 Hz, 2H), 7.31 (m, 3H), 7.40 (t, *J* = 7.0 Hz, 1H), 7.62 (d, *J* = 8.5 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.5, 21.1, 34.3, 119.1, 121.7, 123.0, 123.6, 126.5, 128.2, 128.7, 128.8, 129.7, 132.8, 141.9, 149.0, 151.4, 169.9 ppm; IR (neat): $\bar{\nu}$ = 3,434, 3,057, 2,966, 2,930, 1,739, 1,666, 1,625, 1,506, 1,436, 1,369, 1,199, 1,167, 1,017, 913, 848, 814, 744, 522, 463, 422 cm^{-1}; GC–MS: *m/z* (%) = 306 (5) [M^+], 264 (100), 249 (89), 231 (52), 171 (85), 115 (48), 101 (29), 94 (13), 77 (18), 65 (12); LRMS: calcd for $C_{20}H_{18}O_3$ [Na^+] 329.12, found 329.13.

2-[1-(4-Chlorophenyl)ethyl]-1-naphthol
(**5b**, $C_{18}H_{15}ClO$)
Dark-brown viscous liquid. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.6 (d, *J* = 7.0 Hz, 3H), 4.0 (q, *J* = 7.0 Hz, 1H), 5.1 (s, 1H), 7.1 (d, *J* = 8.5 Hz, 2H), 7.2 (d, *J* = 8.0 Hz, 2H), 7.3 (d, *J* = 8.0 Hz, 2H), 7.4 (t, *J* = 4.5 Hz, 2H), 7.7 (t, *J* = 5.5 Hz, 2H), 8.0 (d, *J* = 8.5 Hz, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.0, 38.2, 120.8, 121.0, 124.9, 125.2, 125.6, 125.7, 125.9, 127.8, 128.9, 132.4, 133.5, 143.7, 148.1 ppm; IR (neat): $\bar{\nu}$ = 3,538, 3,059, 2,970, 2,932, 2,875, 1,659, 1,576, 1,490, 1,389, 1,262, 1,198, 1,090, 1,055, 1,016, 895, 820, 784, 749, 566, 542 cm^{-1}; GC–MS: *m/z* (%) = 282 (86) [M^+], 267 (90), 249 (10), 231 (32), 215 (8), 202 (28), 170 (100), 141 (23), 115 (25), 101 (33), 89 (10), 77 (15); LRMS: calcd 282.08, found 282.85.

2-[1-(4-Bromophenyl)ethyl]-1-naphthol
(**5c**, $C_{18}H_{15}BrO$)
Dark-brown viscous liquid. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.6 (d, *J* = 7.5 Hz, 1H), 4.4 (q, *J* = 7 Hz, 1H), 5.1 (s, 1H), 7.1 (d, *J* = 8.0 Hz, 2H), 7.3 (d, *J* = 8.5 Hz, 1H), 7.3 (d, *J* = 8.5 Hz, 2H), 7.4 (m, 2H), 7.7 (m, 1H), 8.0 (t, *J* = 9.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.0, 38.4, 120.6, 120.9, 121.0, 124.9, 125.1, 125.71, 125.75, 126.0, 127.9, 129.4, 132.0, 133.5, 144.2, 148.1 ppm; IR (neat): $\bar{\nu}$ = 3,504, 3,059, 2,969, 2,871, 1,657, 1,573, 1,491, 1,352, 1,150, 1,016, 811, 786, 618, 450, 422 cm^{-1}; GC–MS: *m/z* (%) = 326 (55) [M^+], 311 (53), 293 (3), 231 (55), 215 (13), 202 (25), 170 (100), 141 (15), 128 (3), 116 (28), 101 (35), 89 (13), 77 (13); LRMS: calcd 326.03, found 326.75.

2-[1-(4-tert-Butylphenyl)ethyl]phenol (**5d**, $C_{18}H_{22}O$)
Dark-brown viscous liquid. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.3 (s, 9H), 1.4 (d, *J* = 7 Hz, 2H), 3.6 (t, *J* = 6.5 Hz, 1H), 6.3 (m, 1H), 6.4 (d, *J* = 15.5 Hz, 2H), 7.2 (m, 2H), 7.3 (m, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 22.8, 32.9, 43.6, 126.9, 127.0, 127.4, 128.5, 129.6, 136.3, 136.5, 144.3, 151.6 ppm; IR (neat): $\bar{\nu}$ = 3,413, 3,059, 3,019, 2,958, 2,869, 1,583, 1,511, 1,474, 1,447, 1,364, 1,270, 1,201, 1,098, 1,022, 820, 739, 693, 563, 479 cm^{-1}; GC–MS: *m/z* (%) = 254 (38) [M^+], 239 (100), 223 (8), 197 (25), 181 (8), 165 (5), 121 (20), 98 (25), 91 (13), 77 (8); LRMS: calcd for $C_{18}H_{22}O$ [–1] 253.17, found 252.83.

4-Methyl-2-[1-(4-methylphenyl)ethyl]phenol
(**5f**, $C_{16}H_{18}O$)
Colorless viscous liquid. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.58 (d, *J* = 7.0 Hz, 3H), 2.27 (s, 3H), 2.29 (s, 3H), 4.27 (q, *J* = 7.0 Hz, 1H), 4.61 (s, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 7.02 (s, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.9, 21.1, 21.2, 38.5, 116.0, 127.5, 127.9, 128.6, 129.5, 130.0, 131.9, 136.1, 142.4, 151.2 ppm; IR (neat): $\bar{\nu}$ = 3,502, 3,433, 3,021, 2,968, 2,926, 2,870, 1,611, 1,503, 1,457, 1,372, 1,328, 1,257, 1,190, 1,117, 1,047, 815, 781, 730, 511, 469, 419 cm^{-1}; GC–MS: *m/z* (%) = 226 (65) [M^+], 211 (100), 196 (18), 134 (50), 105 (8), 91 (18), 77 (12), 65 (7); LRMS: calcd 226.14, found 226.24.

2-[1-(4-tert-Butylphenyl)ethyl]-4-methylphenol
(**5g**, $C_{19}H_{24}O$)
Colorless viscous liquid. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.28$ (s, 9H), 1.60 (d, $J = 7.0$ Hz, 3H), 2.28 (s, 3H), 4.28 (q, $J = 6.5$ Hz, 1H), 4.56 (s, 1H), 6.64 (d, $J = 7.5$ Hz, 1H), 6.90 (d, $J = 8.0$ Hz, 1H), 7.04 (s, 1H), 7.17 (d, $J = 8.0$ Hz, 2H), 7.30 (d, $J = 8.0$ Hz, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 22.4$, 22.6, 33.0, 36.0, 40.0, 127.2, 128.7, 129.4, 130.1, 131.5, 133.4, 143.6, 150.8, 152.7 ppm; IR (neat): $\overline{\nu} = 3{,}438$, 2,963, 2,927, 1,632, 1,507, 1,383, 1,264, 1,114, 1,020, 669, 620, 421 cm^{-1}; GC–MS: *m/z* (%) = 268 (42) [M^+], 253 (100), 211 (15), 197 (14), 134 (9), 105, 91 (15), 77 (11), 65 (8); LRMS: calcd 268.18, found 268.24.

2-[1-(4-tert-Butylphenyl)ethyl]-5-methylthiophene
(**5i**, $C_{17}H_{22}S$)
Colorless viscous liquid. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.2$ (s, 9H), 1.5 (d, $J = 7.0$ Hz, 3H), 2.3 (s, 3H), 4.1 (q, $J = 7$ Hz, 1H), 6.5 (d, $J = 3$ Hz, 1H), 7.1 (d, $J = 8$ Hz, 2H), 7.2 (d, $J = 8$ Hz, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 15.3$, 23.2, 31.3, 31.4, 40.4, 42.0, 123.1, 124.4, 125.3, 125.8, 126.8, 126.9, 128.0, 134.7, 137.8, 143.1 ppm; IR (neat): $\overline{\nu} = 3{,}055$, 3,024, 2,964, 2,870, 1,656, 1,511, 1,456, 1,405, 1,365, 1,266, 1,109, 1,018, 831, 800, 671, 572, 463, 419 cm^{-1}; GC–MS: *m/z* (%) = 258 (48) [M^+], 243 (100), 228 (18), 213 (13), 201 (8), 187 (3), 152 (3), 125 (8), 100 (25), 91 (5), 77 (3); LRMS: calcd for $C_{17}H_{22}S$ [−1] 257.14, found 256.91.

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