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Palladium-imidazolinium carbene-catalyzed arylation of aldehydes with arylboronic acids in water

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ABSTRACT

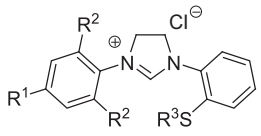
The catalytic arylation of aldehydes with arylboronic acids in only water was found to be achieved using the palladium/thioether-imidazolinium chloride system in good to excellent yields. This catalytic process showed high tolerance for a broad range of substrates, giving a variety of carbinol derivatives with 2.0–3.0 mol % of the catalyst.

1. Introduction

Powerful and environmentally benign synthetic methods are desirable from the viewpoint of green chemistry.[1] Organic chemical reactions in aqueous media have been focused due to various advantages of water as a solvent, such as its low cost, safety, and innocuousness in addition to unique reactivity observed in it.[2,3] Especially, the discovery and development of more efficient and sustainable transition-metal catalysts that are effective in only water has been still desired.[4] However, the achievement of high selectivity and yields with metal catalysts in water is not easy.[2b,4a] In order to overcome the poor solubility of compounds and deleterious effects for metal catalysts in pure water, the aids of ingenious methods such as sonication, microwave heating, organic co-solvents, surfactants, and ligands with hydrophilic auxiliaries are often necessary.[2,4]

Transition metal catalysts are one of the most important tools for C–C bond formation.[5] Since Miyaura and co-workers found the rhodium-catalyzed 1,2-addition to aldehydes in 1998,[6] transition metal-catalyzed arylation of aldehydes with organoboron reagents have attracted much attention.[7] Because of the advantages of organoboron reagents, such as low toxicity and easy manipulation,[8] several types of active catalysts have been developed for this kind of reaction.[9,10] In spite of these efforts, only two examples of transition metal-catalyzed arylation of aldehydes with organoboron reagents in only water have been reported.[11] Sweigart found the anionic rhodium quinonoid catalyst was effective,[11a] and Wu developed the cyclopalladated complex-catalyzed arylation of aldehydes with SDS.[11b] However, there is still room for improvement in reaction systems and substrate generality.

More recently, we have developed thioether-imidazolinium salts **1** as heterobidentate ligand precursors (Fig. 1).[12] In the course of our investigation on the palladium-catalyzed 1,2-addition of organoboron reagents with *N*-heterocyclic carbene precursors **1**,[13] we found the palladium/thioether-imidazolinium chloride system had the ability to tolerate water and achieved high catalyst performance even in the arylation of aldehydes using arylboronic acids in only water without further assistance such as co-solvents, surfactants, and hydrophilic auxiliaries. Herein, we would like to describe the full details on this investigation.



1a: R^1= Me, R^2= Me, R^3= Me
1b: R^1= Me, R^2= Me, R^3= Ph
1c: R^1= Me, R^2= Me, R^3= *i*-Pr
1d: R^1= H, R^2= *i*-Pr, R^3= Me
1e: R^1= H, R^2= *i*-Pr, R^3= Ph
1f: R^1= H, R^2= *i*-Pr, R^3= *i*-Pr

Figure 1. Precursors of *N*-heterocyclic carbene ligands.

2. Results and discussion

Our initial study was focused on optimization of reaction conditions using 2-naphthaldehyde **2a** and phenylboronic acid **3a** (Table 1). The 1,2-addition with 1.0 mol % of the catalysts generated in situ from thioether-imidazolinium chloride **1a**–**f** and allylpalladium(II) chloride dimer in the presence of cesium carbonate was examined in water at 100 °C for 2 h. Then, only thioether-imidazolinium chloride **1e** was proven to be an effective *N*-heterocyclic carbene ligand precursor (entries 1–6). The arylation reactions at 80 and 120 °C led to decrease in yields, affording the adduct **4aa** with 45% and 73% yields, respectively (entries 7 and 8). The screening of palladium sources was conducted, and allylpalladium(II) chloride dimer showed the highest catalytic activity (entries 5 and 9–12).

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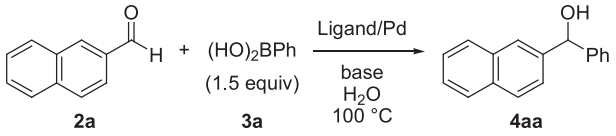
While the examination of bases revealed that cesium carbonate was the reagent of choice, cheaper potassium carbonate and sodium carbonate also provided good results (entries 5 and 13–18). Evaluation on the effect of organic solvents gave the information that the smooth reaction progress required the appropriate solvent polarity (entries 19–21). Interestingly, DMSO gave the quite poor result although the reaction in more highly polar water proceeded efficiently, which could be achieved by hydrophobic effects. As expected, the decrease of water had no influence on the reaction rate, which could make the large-scale synthesis easier to conduct (entry 22). The gram-scale reaction with 10 mmol of the aldehyde **2a** was achieved with excellent efficacy to afford the desired product **4aa** in 91% yield (entry 23). Thus, this catalytic system could be quite advantageous for the practical synthesis of carbinol derivatives.

Table 1
Optimization of Reaction Conditions[a]



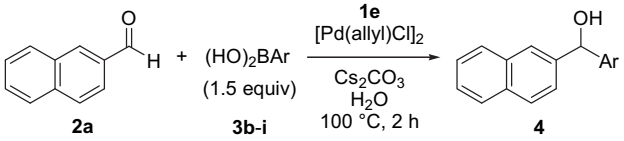
2a **3a** **4aa**

Entry	Ligand	Pd	Base	Yield[b] (%)
1	**1a**	$[Pd(allyl)Cl]_2$	Cs_2CO_3	0
2	**1b**	$[Pd(allyl)Cl]_2$	Cs_2CO_3	5
3	**1c**	$[Pd(allyl)Cl]_2$	Cs_2CO_3	20
4	**1d**	$[Pd(allyl)Cl]_2$	Cs_2CO_3	9
5	**1e**	$[Pd(allyl)Cl]_2$	Cs_2CO_3	90
6	**1f**	$[Pd(allyl)Cl]_2$	Cs_2CO_3	13
7[c]	**1e**	$[Pd(allyl)Cl]_2$	Cs_2CO_3	45
8[d]	**1e**	$[Pd(allyl)Cl]_2$	Cs_2CO_3	73
9	**1e**	$PdCl_2$	Cs_2CO_3	5
10	**1e**	$Pd(OAc)_2$	Cs_2CO_3	6
11	**1e**	$Pd(dba)_2$	Cs_2CO_3	33
12	**1e**	$Pd_2(dba)_3$	Cs_2CO_3	36
13	**1e**	$[Pd(allyl)Cl]_2$	K_2CO_3	78
14	**1e**	$[Pd(allyl)Cl]_2$	Na_2CO_3	80
15	**1e**	$[Pd(allyl)Cl]_2$	$BaCO_3$	33
16	**1e**	$[Pd(allyl)Cl]_2$	$CaCO_3$	43
17	**1e**	$[Pd(allyl)Cl]_2$	CsF	27
18	**1e**	$[Pd(allyl)Cl]_2$	K_3PO_4	60
19[e]	**1e**	$[Pd(allyl)Cl]_2$	Cs_2CO_3	90
20[f]	**1e**	$[Pd(allyl)Cl]_2$	Cs_2CO_3	95
21[g]	**1e**	$[Pd(allyl)Cl]_2$	Cs_2CO_3	25
22[h]	**1e**	$[Pd(allyl)Cl]_2$	Cs_2CO_3	90
23[i]	**1e**	$[Pd(allyl)Cl]_2$	Cs_2CO_3	91

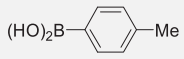
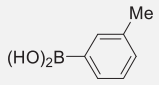
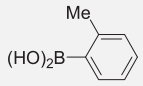
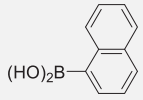
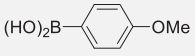
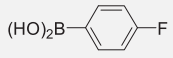
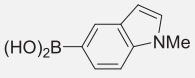
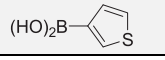
[a] Reaction conditions: 2-naphthaldehyde **2a** (1.0 mmol), phenylboronic acid **3a** (1.5 mmol), ligand (1.0 mol %), Pd (1.0 mol %), base (2.0 mmol), water (2 mL), 100 °C, 2 h.
[b] Isolated yield.
[c] The reaction was carried out at 80 °C.
[d] The reaction was carried out at 120 °C.
[e] Toluene was used as a solvent.
[f] Dioxane was used as a solvent.
[g] DMSO was used as a solvent.
[h] 1 mL of water was used as a solvent.
[i] Large-scale reaction conditions: 2-naphthaldehyde **2a** (10 mmol), phenylboronic acid **3a** (15 mmol), **1e** (1.0 mol %), Pd (1.0 mol %), Cs_2CO_3 (20 mmol), water (15 mL), 100 °C, 8 h.

Investigation of arylboronic acids in the arylation reactions of 2-naphthaldehyde **2a** with 2.0 mol % of the catalyst was examined (Table 2). The reactions using 4-methylphenylboronic acid **3b** or 3-methylphenylboronic acid **3c** took place smoothly to give the desired products in high yields (entries 1 and 2). On the other hand, sterically hindered 2-methylphenylboronic acid **3d** led to 35% yield (entry 3). The arylation with 1-naphthylboronic acid **3e** gave the adduct **4ae** in moderate yield (entry 4). While the electron-rich 4-methoxyphenylboronic acid **3f** was less reactive to afford 61% yield (entry 5), the 1,2-addition reaction of electron-poor arylboronic acid **3g** proceeded efficiently with 96% yield (entry 6). In addition, heteroarylboronic acids were examined. The arylation reactions using 1-methyl-5-indolylboronic acid **3h** and 3-thiopheneboronic acid **3i** gave the products **4ah** and **4ai** in 55% and 76% yields, respectively (entries 7 and 8).

Table 2
Palladium-imidazolinium carbene-catalyzed arylation of 2-naphthaldehyde in water[a]



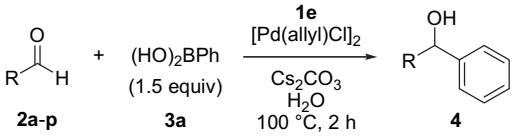
2a **3b-i** **4**

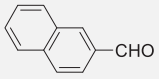
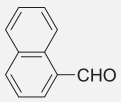
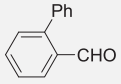
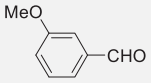
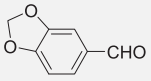
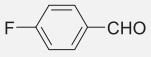
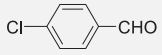
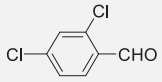
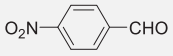
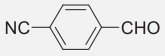
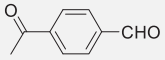
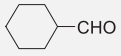
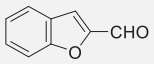
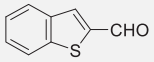
Entry	$(HO)_2BAr$	Product	Yield[b] (%)
1	**3b** 	**4ab**	81
2	**3c** 	**4ac**	85
3[c]	**3d** 	**4ad**	35
4	**3e** 	**4ae**	61
5	**3f** 	**4af**	61
6	**3g** 	**4ag**	96
7	**3h** 	**4ah**	55
8	**3i** 	**4ai**	76

[a] Reaction conditions: 2-naphthaldehyde **2a** (1.0 mmol), arylboronic acid **3** (1.5 mmol), **1e** (2.0 mol %), $[Pd(allyl)Cl]_2$ (1.0 mol %), Cs_2CO_3 (2.0 mmol), water (2 mL), 100 °C, 2 h.
[b] Isolated yield.
[c] The catalyst (3.0 mol %) was used.

The influence of varying aldehydes in the 1,2-addition reactions of phenylboronic acid **3a** with 2.0 mol % of the catalyst was also investigated (Table 3). In the case of the reaction using 2-naphthaldehyde **2a** with 2.0 mol % catalyst loading, the result was slightly improved to afford 93% yield (entry 1). The sterically hindered aromatic aldehydes **2b** and **2c** led to the excellent yields (entries 2 and 3). Then, no significant decrease in yields for the arylation of electron-rich aromatic aldehydes such as **2d**, **2e**, and **2f** was observed, giving the desired products **4da**–**fa** in high yields (entries 4–6). The 1,2-addition to the electron-poor aromatic aldehyde **2g** proceeded smoothly with 99% yield (entry 7). Both of 4-chlorobenzaldehyde **2h** and 2,4-dichlorobenzaldehyde **2i** were converted efficiently without the generation of Suzuki/Miyaura coupling or dehalogenation products (entries 8 and 9).[14] Other electron-withdrawing functionalities such as nitro, cyano, and acetyl groups were also tolerated under the reaction conditions (entries 10–12), though they have high reactivity toward Grignard or organolithium reagents. In the reaction using terephthalaldehyde **2m**, the monophenylated product **4ma** was formed with 80% yield, while the diphenylated compound **5ma**[15] was

Table 3
Palladium-imidazolinium carbene-catalyzed phenylation of aldehydes in water[a]



Entry	RCHO		Product	Yield[b] (%)
1	**2a**		**4aa**	93
2	**2b**		**4ba**	95
3	**2c**		**4ca**	92
4[c]	**2d**		**4da**	81
5	**2e**		**4ea**	99
6[c]	**2f**		**4fa**	78
7	**2g**		**4ga**	99
8	**2h**		**4ha**	92
9	**2i**		**4ia**	92
10	**2j**		**4ja**	93
11	**2k**		**4ka**	87
12	**2l**		**4la**	94
13[d]	**2m**		**4ma**	80
14[c]	**2n**		**4na**	96
15	**2o**		**4oa**	92
16[c]	**2p**		**4pa**	93

[a] Reaction conditions: aldehyde **2** (1.0 mmol), phenylboronic acid **3a** (1.5 mmol), ligand **1e** (2.0 mol %), $[Pd(allyl)Cl]_2$ (1.0 mol %), Cs_2CO_3 (2.0 mmol), water (2 mL), 100 °C, 2 h.
[b] Isolated yield.
[c] The catalyst (3.0 mol %) was used.
[d] 1,4-Bis(phenylhydroxylmethyl)benzene **5ma** was obtained in 17% yield as a side product.

observed in 17% yield (entry 13). The arylation of the aliphatic aldehyde **2n** took place without difficulty with excellent yield (entry 14). The heteroaromatic aldehydes **2o** and **2p** were also proved to be good acceptors, affording the addition products **4oa** and **4pa** in high yields (entries 15 and 16).

3. Conclusion

In summary, we found the thioether-imidazolinium chloride **1e** led to the high level of catalyst performance for the palladium-catalyzed 1,2-addition of arylboronic acids to aldehydes even in only water with no further aid. This process was carried out readily with 2.0–3.0 mol % of catalyst loading, giving various carbinol compounds bearing a diverse range of functionalities with good to excellent yields.

4. Experimental

4.1. General

All melting points are not corrected. ^1H NMR spectra were taken at 300 or 400 MHz. ^{13}C NMR spectra were taken at 75 or 100 MHz. Chemical shift values are expressed in parts per million relative to internal or external TMS. Abbreviations are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. Mass spectra (MS) and high-resolution mass spectra (HRMS) were recorded using electron ionization (EI) mass spectrometry. The products were isolated by silica gel column chromatography. Organoboronic acids and palladium sources were used as received. Degassed ultrapure water was used as a solvent. Cesium carbonate, potassium carbonate, sodium carbonate, calcium carbonate, barium carbonate, and cesium fluoride were used as received. Potassium phosphate tribasic was ground to a fine powder prior to use.

4.2. General procedure for the palladium-imidazolinium carbene-catalyzed arylation of aldehydes with arylboronic acids in water

Under an argon atmosphere, a reaction tube was charged with thioether-imidazolinium chloride **1e** (9.02 mg, 0.02 mmol), $[Pd(allyl)Cl]_2$ (3.66 mg, 0.01 mmol), and cesium carbonate (652 mg, 2.0 mmol). To this mixture was added water (2.0 mL). The mixture was stirred for 15 min at 80 °C and cooled to room temperature. Then, aldehyde (1.0 mmol) and arylboronic acid (1.5 mmol) were added, and the reaction mixture was stirred at 100 °C for 2 h. The mixture was cooled to room temperature. Water and saturated NH_4Cl were added and the resulting mixture was extracted with AcOEt. The combined organic layers were washed with brine, and then dried over $MgSO_4$. Concentration and purification through silica gel column chromatography gave the product.

4.2.1. 4-Methylphenyl(2-naphthyl)methanol[10a] (***4ab***) *(Table 2, entry 1).* Silica gel column chromatography (hexane/AcOEt=10/1) gave 200 mg (0.81 mmol, 81% yield) of the product as a colorless solid of mp 91–92 °C. IR (neat): 3300 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 2.32 (br s, 4H), 5.95 (s, 1H), 7.12–7.14 (m, 2H), 7.22–7.29 (m, 2H), 7.39–7.49 (m, 3H), 7.74–7.88 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): 21.1, 76.2, 124.8, 124.9, 125.9, 126.1, 127.0, 127.6, 128.1, 128.2, 129.2, 132.8, 133.3, 137.4, 140.8, 141.3. EIMS *m*/*z*: 248 (M^+).

4.2.2. 3-Methylphenyl(2-naphthyl)methanol (***4ac***) *(Table 2, entry 2).* Silica gel column chromatography (hexane/AcOEt=10/1) gave 211 mg (0.85 mmol, 85% yield) of the product as a colorless solid of mp 77–78 °C. IR (neat): 3330 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 2.28 (s, 1H), 2.33 (s, 3H), 5.97 (s, 1H), 7.09 (d, *J*=5.8 Hz, 1H), 7.23 (d, *J*=5.8 Hz, 3H), 7.41–7.50 (m, 3H), 7.78–7.85 (m, 3H), 7.91 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 21.4, 76.3, 123.8, 124.8, 124.9, 125.9, 126.1, 127.3, 127.6, 128.0, 128.2, 128.4, 132.8, 133.2, 138.2, 141.2, 143.6. HRMS (EI) *m*/*z*: calcd for $C_{18}H_{16}O$ (M^+): 248.1201. Found: 248.1189.

4.2.3. 2-Methylphenyl(2-naphthyl)methanol[13b] (***4ad***) *(Table 2, entry 3).* Silica gel column chromatography (hexane/AcOEt=10/1) gave

87 mg (0.35 mmol, 35% yield) of the product as a colorless solid of mp 77–78 °C. IR (neat): 3310 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 2.22 (s, 1H), 2.30 (s, 3H), 6.18 (s, 1H), 7.15–7.27 (m, 3H), 7.40–7.42 (m, 1H), 7.45–7.48 (m, 2H), 7.52–7.55 (m, 1H), 7.78–7.81 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): 19.4, 73.4, 125.2, 125.6, 125.9, 126.08, 126.12, 126.5, 127.6, 128.0, 128.2, 130.6, 132.8, 133.2, 135.5, 140.2, 141.2. EIMS *m*/*z*: 248 (M^+).

*4.2.4. 1-Naphthyl(2-naphthyl)methanol (**4ae**) (Table 2, entry 4).* Silica gel column chromatography (hexane/AcOEt=10/1) gave 172 mg (0.61 mmol, 61% yield) of the product as a colorless solid of mp 107–108 °C. IR (neat): 3480 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 2.43 (s, 1H), 6.70 (s, 1H), 7.42–7.51 (m, 6H), 7.65 (d, *J*=7.1 Hz, 1H), 7.77–7.88 (m, 5H), 7.93 (s, 1H), 8.11 (d, *J*=7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 73.6, 124.0, 124.9, 125.1, 125.3, 125.6, 125.6, 126.0, 126.1, 126.2, 127.6, 128.1, 128.2, 128.6, 128.7, 130.8, 132.9, 133.3, 134.0, 138.6, 140.5. HRMS (EI) *m*/*z*: calcd for $C_{21}H_{16}O$ (M^+): 284.1201. Found: 284.1183.

*4.2.5. 4-Methoxyphenyl(2-naphthyl)methanol[13b] (**4af**) (Table 2, entry 5).* Silica gel column chromatography (hexane/AcOEt=10/1) gave 161 mg (0.61 mmol, 61% yield) of the product as a colorless solid of mp 78–79 °C. IR (neat): 1250, 3390 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 2.27 (s, 1H), 3.79 (s, 3H), 5.97 (s, 1H), 6.87 (d, *J*=8.8 Hz, 2H), 7.32 (d, *J*=8.8 Hz, 2H), 7.41 (d, *J*=8.8 Hz, 1H), 7.46–7.47 (m, 2H), 7.78–7.85 (m, 3H), 7.90 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 55.3, 75.9, 113.9, 124.7, 125.9, 126.1, 127.6, 128.0, 128.1, 128.2, 132.8, 133.2, 136.0, 141.3, 159.1. EIMS *m*/*z*: 264 (M^+).

*4.2.6. 4-Fluorophenyl(2-naphthyl)methanol[13b] (**4ag**) (Table 2, entry 6).* Silica gel column chromatography (hexane/AcOEt=10/1) gave 243 mg (0.96 mmol, 96% yield) of the product as a colorless solid of mp 67–68 °C. IR (neat): 1220, 3300 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): 2.31 (br s, 1H), 6.00 (s, 1H), 6.99–7.05 (m, 2H), 7.36–7.40 (m, 3H), 7.44–7.51 (m, 2H), 7.79–7.85 (m, 3H), 7.87 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 75.6, 115.3 (d, *J*=22.2 Hz), 124.6, 125.0, 126.1, 126.3, 127.7, 128.0, 128.4 (d, *J*=8.2 Hz), 132.9, 133.2, 139.4, 141.0, 162.2 (d, *J*=244.5 Hz). EIMS *m*/*z*: 252 (M^+).

*4.2.7. (1-Methyl-5-indolyl)(2-naphthyl)methanol[13a] (**4ah**) (Table 2, entry 7).* Silica gel column chromatography (hexane/AcOEt=10/1) gave 157 mg (0.55 mmol, 55% yield) of the product as a colorless solid of mp 92–93 °C. IR (neat): 3450 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 2.29 (s, 1H), 3.77 (s, 3H), 6.13 (s, 1H), 6.46 (d, *J*=3.0 Hz, 1H), 7.05 (d, *J*=3.0 Hz, 1H), 7.23–7.30 (m, 2H), 7.42–7.49 (m, 3H), 7.67 (s, 1H), 7.76–7.85 (m, 3H), 7.97 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 32.7, 76.7, 101.1, 109.4, 119.3, 120.9, 124.6, 125.0, 125.7, 125.9, 127.7, 127.9, 128.0 128.3, 129.3, 132.7, 133.2, 135.0, 136.2, 141.9. EIMS *m*/*z*: 287 (M^+).

*4.2.8. 3-Thienyl(2-naphthyl)methanol[13a] (**4ai**) (Table 2, entry 8).* Silica gel column chromatography (hexane/AcOEt=10/1) gave 183 mg (0.76 mmol, 76% yield) of the product as colorless oil. IR (neat): 3300 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 2.38 (br s, 1H), 6.02 (s, 1H), 7.00 (d, *J*=4.9 Hz, 1H), 7.18–7.27 (m, 2H), 7.43–7.48 (m, 3H), 7.79–7.86 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): 72.7, 121.7, 124.6, 124.9, 125.9, 126.08, 126.13, 126.4, 127.6, 128.0, 128.2, 132.9, 133.1, 140.7, 145.1. EIMS *m*/*z*: 240 (M^+).

*4.2.9. 2-Naphthyl(phenyl)methanol[13b] (**4aa**) (Table 3, entry 1).* Silica gel column chromatography (hexane/AcOEt=10/1) gave 218 mg (0.93 mmol, 93% yield) of the product as a colorless solid of mp 87–88 °C. IR (neat): 3560 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 2.31 (br s, 1H), 6.02 (s, 1H), 7.28–7.29 (m, 1H), 7.35 (m, 2H), 7.42–7.44 (m, 3H), 7.46–7.49 (m, 2H), 7.78–7.85 (m, 3H), 7.90 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 76.2, 124.7, 125.0, 125.9, 126.1, 126.6, 127.5, 127.6, 128.0, 128.2, 128.4, 132.8, 133.2, 141.1, 143.6. EIMS *m*/*z*: 234 (M^+).

*4.2.10. 1-Naphthyl(phenyl)methanol[10q] (**4ba**) (Table 3, entry 2).* Silica gel column chromatography (hexane/AcOEt=10/1) gave 222 mg (0.95 mmol, 95% yield) of the product as yellow oil. IR (neat): 3700 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 2.60 (br s, 1H), 6.43 (s, 1H), 7.20–7.28 (m, 3H), 7.32–7.43 (m, 5H), 7.55 (d, *J*=7.0 Hz, 1H), 7.75 (d, *J*=8.0 Hz, 1H), 7.81 (d, *J*=7.0 Hz, 1H), 7.96 (d, *J*=8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 73.5, 124.0, 124.6, 125.3, 125.5, 126.0, 127.0, 127.5, 128.36, 128.41, 128.7, 130.7, 133.9, 138.8, 143.1. EIMS *m*/*z*: 234 (M^+).

*4.2.11. 2-Biphenyl(phenyl)methanol (**4ca**) (Table 3, entry 3).* Silica gel column chromatography (hexane/AcOEt=10/1) gave 239 mg (0.92 mmol, 92% yield) of the product as colorless oil. IR (neat): 3590 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 2.04 (br s, 1H), 5.94 (s, 1H), 7.17 (d, *J*=7.1 Hz, 2H), 7.21–7.27 (m, 6H), 7.31–7.41 (m, 5H), 7.56 (d, *J*=7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 72.1, 126.5, 126.9, 127.0, 127.1, 127.2, 127.7, 128.04, 128.09, 129.2, 129.8, 140.7, 140.9, 141.1, 143.8. HRMS (EI) *m*/*z*: calcd for $C_{19}H_{16}O$ (M^+): 260.1201. Found: 260.1192.

*4.2.12. 4-Methoxyphenyl(phenyl)methanol[10a] (**4da**) (Table 3, entry 4).* Silica gel column chromatography (hexane/AcOEt=20/1) gave 173 mg (0.81 mmol, 81% yield) of the product as colorless oil. IR (neat): 1170, 3570 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): 2.14 (d, *J*=3.3 Hz, 1H), 3.79 (s, 3H), 5.82 (d, *J*=3.3 Hz, 1H), 6.84–6.89 (m, 2H), 7.26–7.39 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$): 55.2, 75.8, 113.9, 126.4, 127.3, 127.9, 128.4, 136.2, 144.0, 159.0. EIMS *m*/*z*: 214 (M^+).

*4.2.13. 3-Methoxyphenyl(phenyl)methanol[10e] (**4ea**) (Table 3, entry 5).* Silica gel column chromatography (hexane/AcOEt=10/1) gave 212 mg (0.99 mmol, 99% yield) of the product as colorless oil. IR (neat): 1260, 3480 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): 2.21 (d, *J*=3.3 Hz, 1H), 3.79 (s, 3H), 5.82 (d, *J*=3.3 Hz, 1H), 6.79–6.82 (m, 1H), 6.94–6.97 (m, 2H), 7.22–7.40 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 55.0, 76.0, 111.9, 112.8, 118.7, 126.4, 127.4, 128.3, 129.3, 143.5, 145.3, 159.6. EIMS *m*/*z*: 214 (M^+).

*4.2.14. 3,4-Methylenedioxyphenyl(phenyl)methanol[13a] (**4fa**) (Table 3, entry 6).* Silica gel column chromatography (hexane/AcOEt=10/1) gave 178 mg (0.78 mmol, 78% yield) of the product as yellow oil. IR (neat): 3390 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 2.15 (s, 1H), 5.77 (s, 1H), 5.93 (s, 2H), 6.76 (d, *J*=8.3 Hz, 1H), 6.85–6.86 (m, 2H), 7.26–7.28 (m, 1H), 7.32–7.38 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): 75.8, 100.9, 107.1, 107.9, 119.9, 126.2, 127.4, 128.3, 138.0, 143.8, 146.8, 147.7. EIMS *m*/*z*: 228 (M^+).

*4.2.15. 4-Fluorophenyl(phenyl)methanol[10a] (**4ga**) (Table 3, entry 7).* Silica gel column chromatography (hexane/AcOEt=10/1) gave 200 mg (0.99 mmol, 99% yield) of the product as a colorless solid of mp 42–43 °C. IR (neat): 3310 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 2.71 (br s, 1H), 5.68 (s, 1H), 6.93–6.97 (m, 2H), 7.23–7.28 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$): 75.5, 115.2 (d, *J*=21.4 Hz), 126.4, 127.7, 128.2 (d, *J*=8.2 Hz), 128.5, 139.5 (d, *J*=2.5 Hz), 143.6, 162.1 (d, *J*=244.5 Hz). EIMS *m*/*z*: 202 (M^+).

*4.2.16. 4-Chlorophenyl(phenyl)methanol[10h] (**4ha**) (Table 3, entry 8).* Silica gel column chromatography (hexane/AcOEt=10/1) gave 200 mg (0.92 mmol, 92% yield) of the product as a colorless solid of mp 55–56 °C. IR (neat): 3310 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 2.24 (s, 1H), 5.81 (s, 1H), 7.27–7.35 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): 75.3, 126.4, 127.7, 127.8, 128.4, 128.5, 133.1, 142.1, 143.3. EIMS *m*/*z*: 218 (M^+, ^{35}Cl).

*4.2.17. 2,4-Dichlorophenyl(phenyl)methanol[10h] (**4ia**) (Table 3, entry 9).* Silica gel column chromatography (hexane/AcOEt=20/1) gave

232 mg (0.92 mmol, 92% yield) of the product as colorless oil. IR (neat): 3290 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): 2.30 (d, J=4.0 Hz, 1H), 6.17 (d, J=4.0 Hz, 1H), 7.26–7.38 (m, 7H), 7.59 (d, J=8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 72.1, 126.8, 127.3, 127.9, 128.5, 128.8, 129.1, 132.9, 133.7, 139.5, 141.7. EIMS m/z: 252 (M^+, $^{35}Cl\times2$).

4.2.18. 4-Nitrophenyl(phenyl)methanol[10e] (**4ja**) *(Table 3, entry 10).* Silica gel column chromatography (hexane/AcOEt=10/1) gave 212 mg (0.93 mmol, 93% yield) of the product as a colorless solid of mp 52–53 °C. IR (neat): 1350, 1540, 3340 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 2.39 (d, J=2.4 Hz, 1H), 5.92 (d, J=2.4 Hz, 1H), 7.31–7.39 (m, 5H), 7.58 (d, J=8.3 Hz, 2H), 8.19 (d, J=8.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 75.2, 123.4, 126.5, 126.9, 128.1, 128.7, 142.5, 146.8, 150.8. EIMS m/z: 229 (M^+).

4.2.19. 4-Cyanophenyl(phenyl)methanol[10e] (**4ka**) *(Table 3, entry 11).* Silica gel column chromatography (hexane/AcOEt=20/1) gave 181 mg (0.87 mmol, 87% yield) of the product as a colorless solid of mp 58–59 °C. IR (neat): 2240, 3660 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 3.05 (br s, 1H), 5.78 (s, 1H), 7.23–7.33 (m, 5H), 7.45 (d, J=8.3 Hz, 2H), 7.53 (d, J=8.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 75.3, 110.7, 118.7, 126.5, 126.9, 128.0, 128.7, 132.1, 142.7, 148.9. EIMS m/z: 209 (M^+).

4.2.20. 4-Acetylphenyl(phenyl)methanol[6b] (**4la**) *(Table 3, entry 12).* Silica gel column chromatography (hexane/AcOEt=10/1) gave 212 mg (0.94 mmol, 94% yield) of the product as colorless oil. IR (neat): 3330 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 2.40 (s, 1H), 2.57 (s, 3H), 5.89 (s, 1H), 7.26–7.37 (m, 5H), 7.49–7.51 (m, 2H), 7.91–7.93 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 26.4, 75.5, 126.4, 126.5, 127.6, 128.4, 128.5, 135.8, 143.2, 149.2, 198.2. EIMS m/z: 226 (M^+).

4.2.21. 4-Formylphenyl(phenyl)methanol[10s] (**4ma**) *(Table 3, entry 13).* Silica gel column chromatography (hexane/AcOEt=20/1) gave 170 mg (0.80 mmol, 80% yield) of the product as colorless oil. IR (neat): 1710, 3490 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 3.47 (br s, 1H), 5.83 (s, 1H), 7.23–7.32 (m, 5H), 7.52 (d, J=8.3 Hz, 2H), 7.78 (d, J=8.3 Hz, 2H), 9.89 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 75.7, 126.6, 126.8, 127.9, 128.6, 129.9, 135.4, 143.0, 150.5, 192.1. EIMS m/z: 212 (M^+).

4.2.22. Cyclohexyl(phenyl)methanol[13a] (**4na**) *(Table 3, entry 14).* Silica gel column chromatography (hexane/AcOEt=10/1) gave 182 mg (0.96 mmol, 96% yield) of the product as a colorless oil. IR (neat): 3340 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 0.85–1.26 (m, 5H), 1.33–1.37 (m, 1H), 1.53–1.65 (m, 3H), 1.72–1.76 (m, 1H), 1.94–1.97 (m, 1H), 2.14 (br s, 1H), 4.30 (d, J=7.0 Hz, 1H), 7.23–7.32 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): 25.9, 26.0, 26.4, 28.8, 29.2, 44.8, 79.2, 126.6, 127.2, 128.0, 143.6. EIMS m/z: 190 (M^+).

4.2.23. 2-Benzofuranyl(phenyl)methanol[13a] (**4oa**) *(Table 3, entry 15).* Silica gel column chromatography (hexane/AcOEt=10/1) gave 205 mg (0.92 mmol, 92% yield) of the product as a colorless solid of mp 67–68 °C. IR (neat): 1450, 1490, 1590, 3350 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 2.51 (s, 1H), 5.96 (s, 1H), 6.53 (s, 1H), 7.20–7.26 (m, 2H), 7.38–7.51 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$): 70.6, 104.0, 111.3, 121.1, 122.8, 124.3, 126.8, 128.0, 128.4, 128.6, 140.2, 155.1, 158.5. EIMS m/z: 224 (M^+).

4.2.24. 2-Benzothienyl(phenyl)methanol[13b] (**4pa**) *(Table 3, entry 16).* Silica gel column chromatography (hexane/AcOEt=20/1) gave 224 mg (0.93 mmol, 93% yield) of the product as a colorless solid of mp 74–75 °C. IR (neat): 3330 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 2.49 (d, J=3.9 Hz, 1H), 6.13 (d, J=3.9 Hz, 1H), 7.13 (s, 1H), 7.28–7.41 (m, 5H), 7.50 (d, J=7.3 Hz, 2H), 7.68 (d, J=7.3 Hz, 1H), 7.78 (d, J=7.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 72.9, 121.1, 122.3, 123.5, 124.1, 124.2, 126.4, 128.1, 128.5, 139.3, 139.8, 142.5, 148.6. EIMS m/z: 240 (M^+).

4.2.25. 1,4-Bis(phenylhydroxymethyl)benzene (**5ma**) *(Table 3, entry 13).* Silica gel column chromatography (hexane/AcOEt=20/1) gave 49 mg (0.17 mmol, 17% yield) of the product as a colorless solid of mp 134–135 °C. IR (neat): 3390 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 2.18 (d, J=3.4 Hz, 2H), 5.83 (d, J=3.4 Hz, 2H), 7.27–7.37 (m, 14H). ^{13}C NMR (100 MHz, $CDCl_3$): 76.1, 126.5, 126.7, 127.6, 128.5, 143.2, 143.7. HRMS (EI) m/z: calcd for $C_{20}H_{18}O_2$ (M^+): 290.1307. Found: 290.1316.

4.3. Procedure for the large-scale synthesis of 2-naphthyl (phenyl)methanol (Table 1, entry 23)

Under an argon atmosphere, a reaction tube was charged with thioether-imidazolinium chloride **1e** (45.1 mg, 0.1 mmol), $[Pd(allyl)Cl]_2$ (18.3 mg, 0.05 mmol), and cesium carbonate (6.52 g, 20 mmol). To this mixture was added water (15 mL). The mixture was stirred for 60 min at 80 °C and cooled to room temperature. Then, 2-naphthaldehyde (1.56 g, 10 mmol) and phenylboronic acid (1.83 g, 15 mmol) were added, and the reaction mixture was stirred at 100 °C for 8 h. The mixture was cooled to room temperature. Water and saturated NH_4Cl were added and the resulting mixture was extracted with AcOEt. The combined organic layers were washed with brine, and then dried over $MgSO_4$. Concentration and purification through silica gel column chromatography (hexane/AcOEt=10/1) gave 2.12 g of **4aa** (91% yield).

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Supplementary data

Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.06.049.

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