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Efficient 1,2-Addition of Aryl- and Alkenylboronic Acids to Aldehydes Catalyzed by the Palladium/Thioether−Imidazolinium Chloride System

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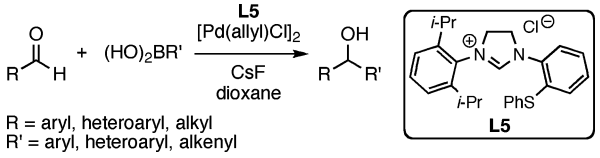
Received September 26, 2007



The high level of catalyst performance was attainable in the palladium-catalyzed 1,2-addition of aryl-, heteroaryl-, and alkenylboronic acids to aromatic, heteroaromatic, and aliphatic aldehydes using thioether−imidazolinium chloride **L5** as a heterobidentate carbene ligand precursor.

In metal-mediated organic synthesis, the transmetalation between organo-main group metal reagents and transition metal complexes is important for the generation of active organometallic species.[1] Particularly, organoboronic acids are known as useful reagents for carbon−carbon bond formations with various electrophiles in the presence of transition metal.[2] In 1998, Miyaura and co-workers reported that 1,2-addition of arylboronic acids to aldehydes was catalyzed by rhodium(I) complexes.[3] Because of the advantageous features of organoboronic acids such as low toxicity and easy manipulation[2] and the importance of the addition products as intermediates for the synthesis of biologically active compounds,[4] this type of reaction has been attracting much attention.[5] In terms of usefulness, more economically and practically advantageous processes are desirable.

Recently, Gibson and Cole-Hamilton found phosphapalladacyclic complex-catalyzed 1,2-addition of phenylboronic acid to 4-chlorobenzaldehyde as a side reaction.[6] On the basis of this finding, Ohta developed addition reactions of arylboronic acids to aromatic aldehydes catalyzed by palladium−triphenylphosphine complexes with chloroform.[7] Kondo and Aoyama reported (±)-tol-BINAP−palladium complex as a chloroform-free catalyst.[8] Hu found palladacycles containing phosphorus donors catalyzed addition reactions to aromatic and aliphatic aldehydes at room temperature.[9] Wu and Cheng found bulky tri(1-naphthyl)phosphine was effective, and achieved heteroarylation of aldehydes, in which only thienyl groups were examined.[10]

In spite of these efforts, examples of addition using heterocyclic and sterically hindered substrates are scarce and alkenylations have not been reported. Thus, it is still desirable to develop or find more active and efficient catalytic systems for 1,2-addition of organoboronic acids to aldehydes. Herein, we would like to describe efficient 1,2-addition reactions of aryl-, heteroaryl-, and alkenylboronic acids to aromatic, heteroaromatic, and aliphatic aldehydes catalyzed by 0.005−2.0 mol % of the palladium/thioether−imidazolinium chloride system.

First of all, the 1,2-addition of phenylboronic acid **2a** to benzaldehyde **1a** using 1.0 mol % of catalysts (Pd/L =1/1) generated in situ from thioether−imidazolinium chlorides[11] **L1**−**6** (Figure 1) and $[Pd(allyl)Cl]_2$ in the presence of cesium carbonate was examined in toluene at 80 °C for 20 min, and thioether−imidazolinium chloride **L5** was proven to be a superior heterobidentate[12] carbene ligand precursor (Table 1, entries 1−6). The reaction using SIPr·HCl (Figure 1), a simple monodentate carbene ligand precursor, gave the addition product **3aa** in only 8% yield (entry 7).

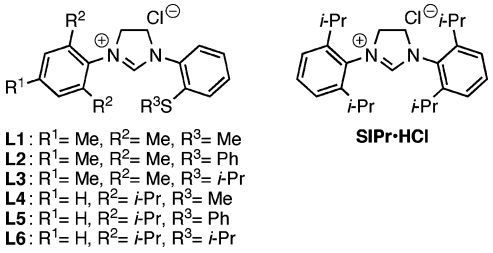


FIGURE 1. Precursors of *N*-heterocyclic carbene ligands.

A series of bases were examined, and we found cesium fluoride was the reagent of choice (Table 1, entries 5 and 8−11). Investigation into the influence of solvents proved that dioxane

(1) Beller, M.; Bolm, C. *Transition Metals for Organic Synthesis*: *Building Blocks and Fine Chemicals*; Wiley-VCH: New York, 1998.

(2) (a) Suzuki, A. *Acc. Chem. Res.* **1982**, *15*, 178−184. (b) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457−2483. (c) Suzuki, A. *J. Organomet. Chem*. **1998**, *576*, 147−168.

(3) (a) Sakai, M.; Ueda, M.; Miyaura, N. *Angew. Chem., Int. Ed*. **1998**, *37*, 3279−3281. (b) Ueda, M.; Miyaura, N. *J. Org. Chem*. **2000**, *65*, 4450−4452.

(4) (a) Casy, A. F.; Drake, A. F.; Ganellin, C. R.; Mercer, A. D.; Upton, C. *Chirality* **1992**, *4*, 356−366. (b) Spencer, C. M.; Foulds, D.; Peter, D. H. *Drugs* **1993**, *46*, 1055−1080. (c) Botta, M.; Summa, V.; Corelli, F.; Pietro, G. D.; Lombardi, P. *Tetrahedron*: *Asymmetry* **1996**, *7*, 1263−1266.

(5) Other examples: (a) Fürstner, A.; Krause, H. *Adv. Synth. Catal*. **2001**, *343*, 343−350. (b) Moreau, C.; Hague, C.; Weller, A. S.; Frost, C. G. *Tetrahedron Lett.* **2001**, *42*, 6957−6960. (c) Bolm, C.; Rudolph, J. *J. Am. Chem. Soc*. **2002**, *124*, 14850−14851. (d) Son, S. U.; Kim, S. B.; Reingold, J. A.; Carpenter, G. B.; Sweigart, D. A. *J. Am. Chem. Soc*. **2005**, *127*, 12238−12239. (e) Focken, T.; Rudolph, J.; Bolm, C. *Synthesis* **2005**, 429−436. (f) Duan, H.-F.; Xie, J.-H.; Shi, W.-J.; Zhang, Q.; Zhou, Q.-L. *Org. Lett*. **2006**, *8*, 1479−1481. (g) Suzuki, K.; Ishii, S.; Kondo, K.; Aoyama, T. *Synlett* **2006**, 648−650. (h) Suzuki, K.; Kondo, K.; Aoyama, T. *Synthesis* **2006**, 1360−1364. (i) Jagt, R. B. C.; Toullec, P. Y.; de Vries, J. G.; Feringa, B. L.; Minnaard, A. J. *Org. Biomol. Chem*. **2006**, *4*, 773−775. (j) Gois, P. M. P.; Trindade, A. F.; Veiros, L. F.; André, V.; Duarte, M. T.; Afonso, C. A. M.; Caddick, S.; Cloke, F. G. N. *Angew. Chem., Int. Ed*. **2007**, *46*, 5750−5753.

(6) Gibson, S.; Foster, D. F.; Eastham, G. R.; Tooze, R. P.; Cole-Hamilton, D. J. *Chem, Commun*. **2001**, 779−780.

(7) Yamamoto, T.; Ohta, T.; Ito, Y. *Org. Lett*. **2005**, *7*, 4153−4155.

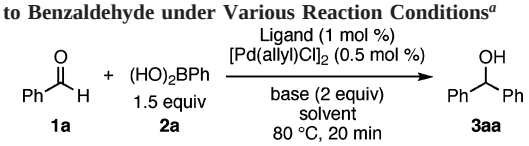
(8) Suzuki, K.; Arao, T.; Ishii, S.; Maeda, Y.; Kondo, K.; Aoyama, T. *Tetrahedron Lett.* **2006**, *47*, 5789−5792.

(9) (a) He, P.; Lu, Y.; Dong, C.-G.; Hu, Q.-S. *Org. Lett*. **2007**, *9*, 343−346. (b) He, P.; Lu, Y.; Hu, Q.-S. *Tetrahedron Lett.* **2007**, *48*, 5283−5288.

(10) Qin, C.; Wu, H.; Cheng, J.; Chen, X.; Liu, M.; Zhang, W.; Su, W.; Ding, J. *J. Org. Chem*. **2007**, *72*, 4102−4107.

10.1021/jo7020983 CCC: $40.75
Published on Web 01/11/2008

TABLE 1. Palladium-Catalyzed 1,2-Addition of Phenylboronic Acid to Benzaldehyde under Various Reaction Conditions[a]



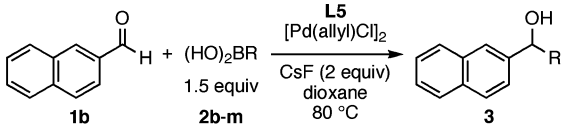
entry	ligand	base	solvent	yield (%)[b]
1	**L1**	Cs_2CO_3	toluene	12
2	**L2**	Cs_2CO_3	toluene	40
3	**L3**	Cs_2CO_3	toluene	20
4	**L4**	Cs_2CO_3	toluene	82
5	**L5**	Cs_2CO_3	toluene	95
6	**L6**	Cs_2CO_3	toluene	85
7	SIPr·HCl	Cs_2CO_3	toluene	8
8	**L5**	K_2CO_3	toluene	74
9	**L5**	Na_2CO_3	toluene	17
10	**L5**	K_3PO_4	toluene	71
11	**L5**	CsF	toluene	97
12	**L5**	CsF	dioxane	99
13	**L5**	CsF	DMA	39
14	**L5**	CsF	DMF	37
15	**L5**	CsF	DMSO	36
16	PhSMe	CsF	dioxane	0
17	none	CsF	dioxane	0
18[c]	**L5**	CsF	dioxane	99
19[d]	**L5**	CsF	dioxane	54

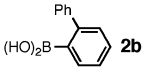
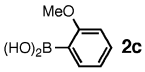
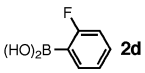
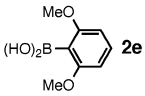
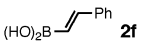
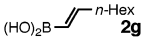
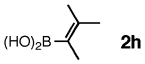
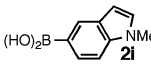
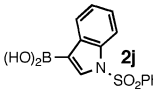
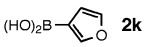
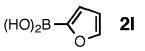
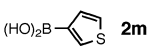
[a] Reaction conditions: benzaldehyde (1.0 mmol), phenylboronic acid (1.5 mmol), ligand (1 mol %), $[Pd(allyl)Cl]_2$ (0.5 mol %), base (2.0 mmol), solvent (2 mL), 80 °C, 20 min. [b] Isolated yield. [c] The reaction using 0.05 mol % of **L5** and 0.025 mol % of $[Pd(allyl)Cl]_2$ was carried out for 12 h. [d] The reaction using 0.005 mol % of **L5** and 0.0025 mol % of $[Pd(allyl)Cl]_2$ was carried out for 24 h.

was most suitable, affording the adduct **3aa** in 99% yield. Highly polar solvents such as DMA, DMF, and DMSO led to low yields (entries 11−15). It was suggested that active thioether−imidazolinium carbene−palladium species were formed in situ under basic conditions because the control experiment with thioanisole or no imidazolinium chloride gave no conversion (entries 16 and 17). The low catalyst loading conditions were conducted, and the addition reactions using 0.05 and 0.005 mol % of the catalyst under the optimized condition led to 99% and 54% yield, respectively (entries 18 and 19).

The influence of varying aryl- and alkenylboronic acids in the addition reactions with 0.5−2.0 mol % of the catalyst using 2-naphthaldehyde **1b** was investigated (Table 2). The reaction using sterically hindered 2-biphenylboronic acid **2b** gave the adduct **3bb** with 98% yield (entry 1). Both the electron-rich and -poor arylboronic acids substituted at the 2-position (**2c** and **2d**) were converted efficiently (entries 2 and 3). The sterically hindered 2,6-dimethoxyphenylboronic acid **2e** reacted to afford 95% yield (entry 4), although the palladium-catalyzed arylation with 2,6-disubstituted arylboronic acid was known as a difficult task.[10] The alkenylboronic acids **2f**−**h** also gave the adducts **3bf**−**3bh** with high yields (entries 5−7). Then, heteroaryl boronic acids containing nitrogen, oxygen, and sulfur atoms were examined. While the reaction with 1-methyl-5-indoleboronic acid **2i** proceeded smoothly, *N*-protected 3-indoleboronic acid **2j** was less reactive leading to 75% yield (entries 8 and 9). To obtain the adduct **3bk** with 82% yield, 2.5 equiv of

TABLE 2. Palladium-Catalyzed 1,2-Addition of Aryl-, Heteroaryl-, and Alkenylboronic Acids to 2-Naphthaldehyde Using Thioether−Imidazolinium Chloride[a]



entry	$(HO)_2BR$	product	cat. (mol %)	time (h)	yield (%)[b]
1	 **2b**	**3bb**	0.5	3	98
2	 **2c**	**3bc**	0.5	3	98
3	 **2d**	**3bd**	0.5	3	84
4[c]	 **2e**	**3be**	1.0	3.5	95
5	 **2f**	**3bf**	1.5	0.5	92
6	 **2g**	**3bg**	1.5	0.5	80
7	 **2h**	**3bh**	1.5	0.5	93
8	 **2i**	**3bi**	1.0	2	99
9	 **2j**	**3bj**	2.0	2	75
10[d]	 **2k**	**3bk**	1.0	2	82
11[e]	 **2l**	**3bl**	1.5	2	93
12	 **2m**	**3bm**	1.0	2	99

[a] Reaction conditions: 2-naphthaldehyde (1.0 mmol), boronic acid (1.5 mmol), **L5**/Pd = 1/1, CsF (2.0 mmol), dioxane (2 mL), 80 °C. [b] Isolated yield. [c] The reaction was carried out at 100 °C. [d] 2.5 equiv of boronic acid was used. [e] Water (0.2 mL) was added to dissolve precipitate.

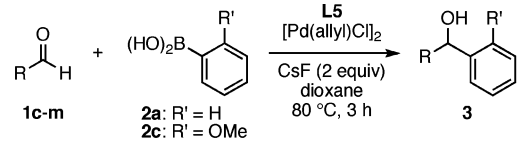
3-furanboronic acid **2k** was needed (entry 10). 2-Furanboronic acid **2*l*** and 3-thiophenboronic acid **2m** afforded excellent results (entries 11 and 12).

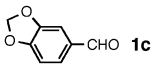
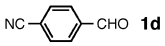
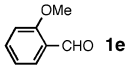
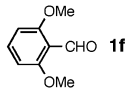
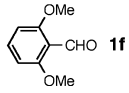
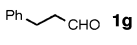
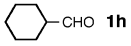
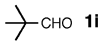
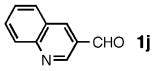
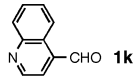
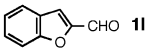
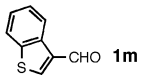
Investigation of aldehydes in the addition reactions of arylboronic acids using 0.5−1.5 mol % of the palladium/thioether−imidazolinium chloride system was also conducted (Table 3). Both the electron-rich and -poor aromatic aldehydes (**1c** and **1d**) were easily converted (entries 1 and 2). 2-Methoxybenzaldehyde **1e** reacted with the ortho-substituted phenylboronic acid **2c**, efficiently (entry 3). Moreover, the addition to electron-rich and sterically hindered 2,6-dimethoxybenzaldehyde **1f** with phenylboronic acid **2a** led to 98% yield (entry 4), although it was reported that the addition to this class of aromatic aldehyde was sluggish.[10] The addition reaction of **2c** to **1f** gave the product **3fc** with the acceptable yield (entry 5). Phenyl groups were introduced to the aliphatic aldehydes **1g**−**i**, affording the adducts **3ga**−**3ia** with good yields (entries 6−8). The heteroaromatic aldehydes **1j**−**m**, which have not been examined in previous reports,[6−10] were also good acceptors,

(11) Kuriyama, M.; Shimazawa, R.; Shirai, R. *Tetrahedron* **2007**, *63*, 9393−9400.

(12) Hemilabile behavior of thioether-functionalized NHC was investigated: Huynh, H. V.; Yeo, C. H.; Tan, G. K. *Chem. Commun.* **2006**, 3833−3835.

TABLE 3. Palladium-Catalyzed 1,2-Addition of Arylboronic Acids to Aromatic, Heteroaromatic, and Aliphatic Aldehydes Using Thioether−Imidazolinium Chloride[a]



entry	RCHO	boronic acid	product	cat. (mol %)	yield (%)[b]
1	 **1c**	**2a**	**3ca**	0.5	99
2	 **1d**	**2a**	**3da**	0.5	98
3	 **1e**	**2c**	**3ec**	1.0	99
4	 **1f**	**2a**	**3fa**	0.5	98
5[c]	 **1f**	**2c**	**3fc**	1.5	65
6	 **1g**	**2a**	**3ga**	0.5	82
7	 **1h**	**2a**	**3ha**	1.0	98
8	 **1i**	**2a**	**3ia**	1.0	85
9	 **1j**	**2a**	**3ja**	0.5	97
10	 **1k**	**2a**	**3ka**	0.5	98
11	 **1l**	**2a**	**3la**	0.5	99
12	 **1m**	**2a**	**3ma**	0.5	99

[a] Reaction conditions: aldehyde (1.0 mmol), boronic acid (1.5 mmol), **L5**/Pd = 1/1, CsF (2.0 mmol), dioxane (2 mL), 80 °C, 3 h. [b] Isolated yield. [c] The reaction was carried out at 100 °C.

being converted to the addition products **3ja**−**3ma** with excellent yields (entries 9−12).

In conclusion, we found that 1,2-addition of aryl-, heteroaryl-, and alkenylboronic acids to aromatic, heteroaromatic, and aliphatic aldehydes was catalyzed by 0.005−2.0 mol % of the palladium/thioether−imidazolinium chloride system quite efficiently. Further efforts are focused on mechanistic investigation and development of an asymmetric version in our laboratory.

Experimental Section

Typical Procedure of 1,2-Addition Reaction Catalyzed by the Palladium/Thioether−Imidazolinium Chloride System. Under argon atmosphere, a reaction tube was charged with $[Pd(allyl)Cl]_2$ (0.92 mg, 0.0025mmol), imidazolinium chloride **L5** (2.26 mg, 0.005 mmol), and cesium fluoride (304 mg, 2.0 mmol), and then dioxane (2.0 mL) was added. The mixture was stirred for 15 min at 80 °C and cooled to room temperature. Then, 2-naphthaldehyde **1b** (156 mg, 1.0 mmol) and 2-biphenylboronic acid **2b** (297 mg, 1.5 mmol) were added, and the reaction mixture was stirred at 80 °C for 3 h. The mixture was cooled to room temperature, and water and satd NH_4Cl were added, and then it was extracted with CH_2Cl_2. 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 **3bb**.

2-Biphenyl-2-naphthylmethanol (3bb). Silica gel column chromatography (hexane/AcOEt = 10/1) gave 305 mg (0.98 mmol, 98% yield) of the product as colorless viscous oil. ^{1}H NMR ($CDCl_3$) δ 2.20 (1H, d, J = 4.0 Hz), 6.10 (1H, d, J = 4.0 Hz), 7.24−7.40 (9H, m), 7.43−7.47 (2H, m), 7.58 (1H, dd, J = 1.0, 7.5 Hz), 7.64 (1H, s), 7.72 (1H, d, J = 8.5 Hz), 7.74−7.79 (2H, m). ^{13}C NMR ($CDCl_3$) δ 72.4, 124.9, 125.0, 125.8, 126.0, 127.2, 127.3, 127.5, 127.5, 127.9, 128.0, 128.1, 129.3, 130.0, 132.6, 133.1, 140.75, 140.81, 141.2, 141.4. IR (neat) 3370 cm^{-1}. HRMS (EI) calcd for $C_{23}H_{18}O$ (M^+) 310.1358, found 310.1362.

2,6-Dimethoxyphenyl-2-naphthylmethanol (3be). Silica gel column chromatography (hexane/AcOEt = 5/1) gave 279 mg (0.95 mmol, 95% yield) of the product as a pale yellow solid of mp 140−141 °C. ^{1}H NMR ($CDCl_3$) δ 3.79 (6H, s), 4.45 (1H, d, J = 12.0 Hz), 6.48 (1H, d, J = 12.0 Hz), 6.62 (2H, d, J = 8.5 Hz), 7.25 (1H, t, J = 8.5 Hz), 7.39−7.44 (2H, m), 7.49 (1H, dd, J = 1.5, 8.5 Hz), 7.74 (1H, d, J = 8.5 Hz), 7.77−7.79 (3H, m). ^{13}C NMR ($CDCl_3$) δ 55.8, 68.6, 104.6, 119.4, 123.6, 124.7, 125.3, 125.7, 127.5, 128.0, 129.0, 132.4, 133.2, 142.2, 157.8. IR (nujol) 1260, 3550 cm^{-1}. EIMS *m/z* 294 (M^+). Anal. Calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C, 77.30; H, 6.12.

(*E*)-1-Octenyl-2-naphthylmethanol (3bg). Silica gel column chromatography (hexane/AcOEt = 10/1) gave 215 mg (0.80 mmol, 80% yield) of the product as pale yellow oil. ^{1}H NMR ($CDCl_3$) δ 0.87 (3H, t, J = 7.0 Hz), 1.24−1.33 (6H, m), 1.37−1.42 (2H, m), 1.94 (1H, d, J = 3.5 Hz), 2.07 (2H, q, J = 7.0 Hz), 5.34 (1H, dd, J = 3.5, 6.5 Hz), 5.73 (1H, dd, J = 6.5, 15.0 Hz), 5.82 (1H, dt, J = 7.0, 15.0 Hz), 7.44−7.49 (3H, m), 7.82−7.84 (4H, m). ^{13}C NMR ($CDCl_3$) δ 14.1, 22.6, 28.9, 29.0, 31.7, 32.2, 75.3, 124.5, 125.8, 126.1, 127.6, 128.0, 128.2, 132.1, 132.9, 133.2, 133.3, 140.8. IR (neat) 3350 cm^{-1}. EIMS *m/z* 268 (M^+). Anal. Calcd for $C_{19}H_{24}O$: C, 85.03; H, 9.01. Found: C, 85.13; H, 9.26.

1-(1,2-Dimethyl)propenyl-2-naphthylmethanol (3bh). Silica gel column chromatography (hexane/AcOEt = 10/1) gave 210 mg (0.93 mmol, 93% yield) of the product (**3bh**) as a pale yellow solid of mp 87−88 °C. ^{1}H NMR ($CDCl_3$) δ 1.51 (3H, s), 1.77 (3H, s), 1.83 (1H, d, J = 3.5 Hz), 1.97 (3H, d, J = 1.5 Hz), 6.02 (1H, d, J = 3.5 Hz), 7.36 (1H, dd, J = 1.5, 8.5 Hz), 7.43−7.49 (2H, m), 7.78 (1H, d, J = 8.5 Hz), 7.82 (1H, d, J = 8.5 Hz), 7.84 (1H, d, J = 8.5 Hz), 7.88 (1H, s). ^{13}C NMR ($CDCl_3$) δ 12.3, 20.3, 21.2, 72.3, 123.7, 124.2, 125.5, 125.9, 127.6, 127.7, 128.0, 129.0, 129.3, 132.5, 133.3, 140.7. IR (nujol) 3320 cm^{-1}. EIMS *m/z* 226 (M^+). Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.72; H, 8.27.

(1-Methyl-5-indolyl)-2-naphthylmethanol (3bi). Silica gel column chromatography (hexane/AcOEt = 10/1) gave 283 mg (0.99 mmol, 99% yield) of the product as a pale yellow solid of mp 92−93 °C. ^{1}H NMR ($CDCl_3$) δ 2.29 (1H, d, J = 3.5 Hz), 3.77 (3H, s), 6.13 (1H, d, J = 1.5 Hz), 6.46 (1H, d, J= 3.5 Hz), 7.05 (1H, d, J = 3.5 Hz), 7.24 (1H, dd, J = 1.5, 8.5 Hz), 7.28 (1H, d, J = 8.5 Hz), 7.43−7.48 (3H, m), 7.67 (1H, s), 7.76 (1H, d, J = 8.5 Hz), 7.79−7.85 (2H, m), 7.97 (1H, s). ^{13}C NMR ($CDCl_3$) δ 32.8, 76.8, 101.2, 109.4, 119.4, 120.9, 124.6, 125.0, 125.7, 126.0, 127.6, 128.0, 128.1, 128.3, 129.4, 132.7, 133.3, 135.0, 136.3, 141.9. IR (nujol) 3440 cm^{-1}. EIMS *m/z* 287 (M^+). Anal. Calcd for $C_{20}H_{17}NO$: C, 83.59; H, 5.96; N, 4.87. Found: C, 83.30; H, 5.89; N, 4.78.

(1-Phenylsulfonyl-3-indolyl)-2-naphthylmethanol (3bj). Silica gel column chromatography (hexane/AcOEt = 3/1) gave 311 mg (0.75 mmol, 75% yield) of the product as a pale orange amorphous. ^{1}H NMR ($CDCl_3$) δ 2.30 (1H, d, J = 4.0 Hz), 6.19 (1H, d, J = 4.0 Hz), 7.11−7.14 (1H, m), 7.27−7.30 (1H, m), 7.41−7.47 (4H, m), 7.48−7.51 (3H, m), 7.55 (1H, t, J = 7.5 Hz), 7.81−7.84 (3H, m), 7.87−7.89 (2H, m), 7.91 (1H, s), 7.98 (1H, d, J = 8.5 Hz). ^{13}C NMR ($CDCl_3$) δ 70.4, 113.7, 120.6, 123.3, 123.9, 124.6, 124.9,

125.5, 125.6, 126.2, 126.3, 126.7, 127.7, 128.1, 128.5, 128.9, 129.2, 133.1, 133.2, 133.8, 135.6, 138.0, 139.3. IR (KBr) 1170, 3410 cm^{-1}. HRMS (EI) calcd for $C_{25}H_{19}NO_3S$ (M^+) 413.1086, found 413.1084.

3-Furanyl-2-naphthylmethanol (3bk). Silica gel column chromatography (hexane/AcOEt = 5/1) gave 184 mg (0.82 mmol, 82% yield) of the product as yellow oil. ^1H NMR ($CDCl_3$) δ 2.21 (1H, d, J = 4.0 H), 5.96 (1H, d, J = 4.0 Hz), 6.36 (1H, d, J = 1.0 Hz), 7.36 (1H, d, J = 1.0 Hz), 7.39 (1H, t, J = 1.5 Hz), 7.48−7.51 (3H, m), 7.83−7.85 (3H, m), 7.90 (1H, s). ^{13}C NMR ($CDCl_3$) δ 69.6, 109.2, 124.5, 124.9, 126.0, 126.2, 127.7, 128.0, 128.3, 128.8, 133.0, 133.2, 139.9, 140.3, 143.5. IR (neat): 1510, 1600, 3370 cm^{-1}. HRMS (EI) Calcd for $C_{15}H_{12}O_2$ (M^+) 224.0837, found 224.0838.

2-Furanyl-2-naphthylmethanol (3b*l*). Silica gel column chromatography (hexane/AcOEt = 10/1) gave 209 mg (0.93 mmol, 93% yield) of the product as pale yellow oil. ^1H NMR ($CDCl_3$) δ 2.47 (1H, d, J = 4.5 Hz), 6.01 (1H, d, J = 4.5 Hz), 6.15 (1H, d, J = 3.0 Hz), 6.33 (1H, dd, J = 2.0, 3.0 Hz), 7.41 (1H, d, J = 1.0 Hz), 7.47−7.51 (2H, m), 7.53 (1H, dd, J = 1.5, 8.5 Hz), 7.83−7.85 (3H, m), 7.93 (1H, s). ^{13}C NMR ($CDCl_3$) δ 70.2, 107.6, 110.3, 124.6, 125.3, 126.1, 126.2, 127.7, 128.1, 128.2, 133.1, 133.2, 138.1, 142.6, 155.8. IR (neat) 1500, 1600, 3370 cm^{-1}. HRMS (EI) calcd for $C_{15}H_{12}O_2$ (M^+) 224.0837, found 224.0841.

3-Thienyl-2-naphthylmethanol (3bm). Silica gel column chromatography (hexane/AcOEt = 5/1) gave 237 mg (0.99 mmol, 99% yield) of the product as yellow oil. ^1H NMR ($CDCl_3$) δ 2.32 (1H, d, J = 4.0 Hz), 6.07 (1H, d, J = 4.0 Hz), 7.03 (1H, dd, J = 1.0, 4.0 Hz), 7.23−7.24 (1H, m), 7.28 (1H, dd, J = 3.0, 5.0 Hz), 7.46−7.51 (3 H, m), 7.82−7.85 (3H, m), 7.89 (1H, s). ^{13}C NMR ($CDCl_3$) δ 72.9, 121.8, 124.6, 125.0, 126.0, 126.2, 126.3, 126.4, 127.7, 128.1, 128.3, 133.0, 133.2, 140.7, 145.2. IR (neat) 1420, 1510, 3360 cm^{-1}. HRMS (EI) calcd for $C_{15}H_{12}OS$ (M^+) 240.0609, found 240.0608.

2,6-Dimethoxyphenyl(2-methoxyphenyl)methanol (3fc). Silica gel column chromatography (benzene/AcOEt = 20/1) gave 177 mg (0.65 mmol, 65% yield) of the product as a colorless solid of mp 131−132 °C. ^1H NMR ($CDCl_3$) δ 3.80 (6H, s), 3.87 (3H, s), 4.33 (1H, d, J = 11.0 Hz), 6.60 (1H, d, J = 11.0 Hz), 6.61 (2H, d, J = 8.0 Hz), 6.83 (1H, dt, J = 1.0, 8.0 Hz), 6.89 (1H, d, J = 8.0 Hz), 7.10 (1H, dd, J = 1.5, 8.0 Hz), 7.20−7.25 (2H, m). ^{13}C NMR ($CDCl_3$) δ 55.67, 55.75, 64.8, 104.5, 110.8, 118.3, 119.8, 127.6, 128.3, 128.6, 131.5, 157.6, 158.1. IR (nujol) 3570 cm^{-1}. EIMS *m/z* 274 (M^+). Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.06; H, 6.61. Found: C, 70.18; H, 6.63.

Acknowledgment. This work was supported by Grant-in-Aid for Scientific Research (C) (No. 18590023) from the Japan Society for the Promotion of Science.

Supporting Information Available: General procedure of 1,2-addition catalyzed by the palladium/thioether−imidazolinium chloride system, spectral data of products, and copies of ^1H and ^{13}C NMR spectra of products. This material is available free of charge via the Internet at http://pubs.acs.org.

JO7020983