EurJOC European Journal of Organic Chemistry

FULL PAPER

DOI: 10.1002/ejoc.201201276

Palladium-Catalyzed Allylic Arylation of Allylic Ethers with Arylboronic Acids Using Hydrazone Ligands

Takashi Mino,*[a] Taketo Kogure,[a] Taichi Abe,[a] Tomoko Koizumi,[a] Tsutomu Fujita,[a] and Masami Sakamoto[a]

Keywords: Palladium / Hydrazones / Cross-coupling / N ligands / Homogeneous catalysis / Arylation

Unsymmetrical 1,3-diarylpropenes were synthesized in good to high yields by the palladium-catalyzed allylic arylation of allylic ethers, such as a cinnamyl phenyl ether, with a variety of arylboronic acids using a hydrazone **1a**–$Pd(OAc)_2$ system in $DMAc/H_2O$. Using this catalyst, eugenol was also synthesized from allyl phenyl ether with (4-hydroxy-3-methoxyphenyl)boronic acid pinacol ester.

Introduction

The 1,3-diarylpropenes, which are known as intermediates in the synthesis of natural products and biologically active compounds, have attracted considerable attention from medicinal chemists.[1] Recently, 1,3-diarylpropenes were synthesized by Tsukamoto et al.[2] by a palladium-catalyzed allylic arylation of cinnamyl phenyl ether derivatives using $Pd(PPh_3)_4$ in THF, and by Lipshutz et al.[3] using $PdCl_2$(DPEphos) in water with polyoxyethanyl-α-tocopheryl sebacate (MW > 1200) as an amphiphilic additive. However, the phosphanes in palladium complexes are often air-sensitive, toxic, or quite expensive. To the best of our knowledge, examples of the palladium-catalyzed allylic arylation of cinnamyl phenyl ether derivatives under phosphane-ligand-free conditions have not been explored. We previously demonstrated that easily prepared and air-stable hydrazones are effective ligands for palladium-catalyzed C–C bond formation reactions[4] including the allylic arylation of allylic esters with arylboronic acids.[5] The palladium-catalyzed allylic arylation of allylic acetates or carbonates with arylboronic acids or sodium tetraphenylborate have also been reported by the Uozumi group,[6] the Zhang group,[7] and the Sawamura group.[8] We now report the synthesis of 1,3-diarylpropenes by a palladium-catalyzed allylic arylation of cinnamyl phenyl ether derivatives with a variety of arylboronic acids using air-stable phosphane-free hydrazones **1** and **2** as ligands (Figure 1).

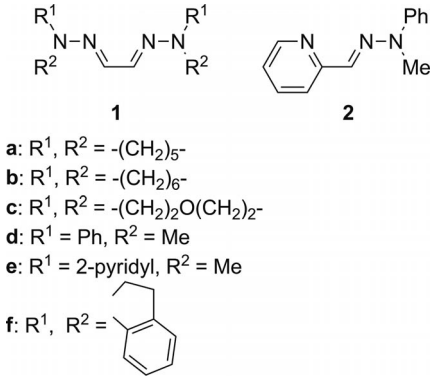


Figure 1. Hydrazones **1** and **2**.

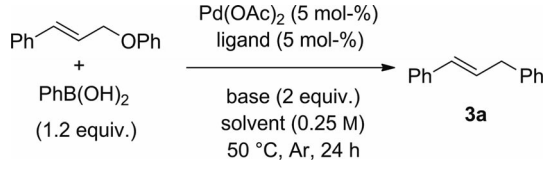
Results and Discussion

Initially, we sought the optimal reaction conditions for a palladium-catalyzed allylic arylation using hydrazone–$Pd(OAc)_2$ systems. Cinnamyl phenyl ether and phenylboronic acid were chosen as model substrates with 5 mol-% Pd catalyst and a reaction time of 24 h under an argon atmosphere at 50 °C (Table 1). Using 5 mol-% hydrazone **1a** as a ligand, we observed that the allylic arylation in the presence of K_2CO_3 as a base in DMF/H_2O as a solvent proceeded to give the corresponding product (i.e., **3a**) in 76% yield (Table 1, entry 1). We also tested other hydrazones **1b**–**f** and **2** (Table 1, entries 2–7), and found that hydrazone **1a** was a more effective ligand for this reaction (Table 1, entry 1). Without any ligand, the reaction gave a low yield of the desired product (Table 1, entry 8). Several bases were tested (Table 1, entries 1 and 9–14). $Ca(OH)_2$ was the most effective base in this reaction (Table 1, entry 12). Next, the effect of various solvents was investigated (Table 1, entries 12 and 15–17). When we used $DMAc/H_2O$ (DMAc = *N,N*-dimethylacetamide) instead of DMF/H_2O,

[a] Department of Applied Chemistry and Biotechnology, Graduate School of Engineering, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan
Fax: +81-43-290-3401
E-mail: tmino@faculty.chiba-u.jp
Homepage: http://chem.tf.chiba-u.jp/gacb06/index.html
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201201276.

the yield increased to 94% (Table 1, entry 17). The effect of the ratio of DMAc and H_2O was also investigated (Table 1, entries 17–19). When the ratio of DMAc/H_2O was 4:1 or 1:1 in the reaction, the yields decreased to 91 and 64%, respectively. When the ratio of $Pd(OAc)_2$/ligand **1a** was 1:2 or 2:1 in the reaction, the yields also decreased to 90 and 61%, respectively (Table 1, entries 20 and 21). Without any base in DMAc/H_2O, the reaction gave a low yield of the desired product (Table 1, entry 22). When we used $Pd_2(dba)_3$ (dba = dibenzylideneacetone) instead of $Pd(OAc)_2$, the yield slightly decreased to 87% (Table 1, entry 23). When the reaction was carried out under an air atmosphere, the yield also decreased to 79% (Table 1, entry 24). Finally, when the reaction was carried out using 3 mol-% palladium catalyst, the yield decreased to 68% (Table 1, entry 25).

Table 1. Optimization of the palladium-catalyzed allylic arylation of cinnamyl phenyl ether with phenylboronic acid.[a]

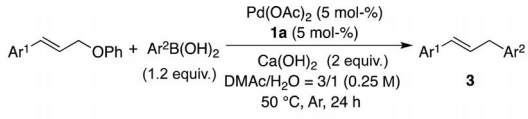


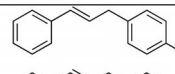
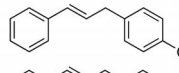
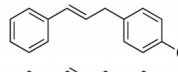
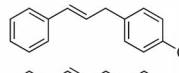
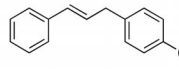
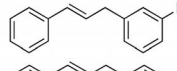
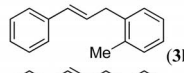
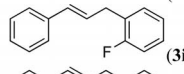
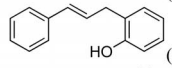
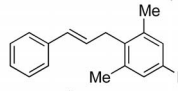
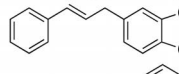
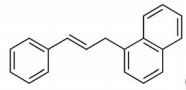
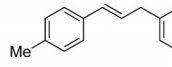
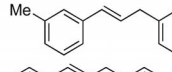
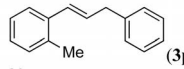
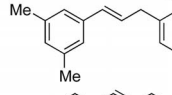
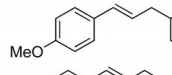
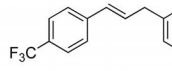
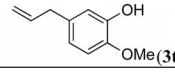
Entry	Ligand	Base	Solvent (v/v)	Yield of **3a** [%][b]
1	**1a**	K_2CO_3	DMF/H_2O (3:1)	76
2	**1b**	K_2CO_3	DMF/H_2O (3:1)	44
3	**1c**	K_2CO_3	DMF/H_2O (3:1)	69
4	**1d**	K_2CO_3	DMF/H_2O (3:1)	9
5	**1e**	K_2CO_3	DMF/H_2O (3:1)	75
6	**1f**	K_2CO_3	DMF/H_2O (3:1)	10
7	**2**	K_2CO_3	DMF/H_2O (3:1)	70
8	–	K_2CO_3	DMF/H_2O (3:1)	7
9	**1a**	Cs_2CO_3	DMF/H_2O (3:1)	56
10	**1a**	Na_2CO_3	DMF/H_2O (3:1)	73
11	**1a**	K_3PO_4	DMF/H_2O (3:1)	85
12	**1a**	$Ca(OH)_2$	DMF/H_2O (3:1)	86
13	**1a**	$CaCO_3$	DMF/H_2O (3:1)	42
14	**1a**	KOH	DMF/H_2O (3:1)	52
15	**1a**	$Ca(OH)_2$	DMSO:H_2O (3:1)	39
16	**1a**	$Ca(OH)_2$	MeCN:H_2O (3:1)	70
17	**1a**	***$Ca(OH)_2$***	***DMAc/H_2O (3:1)***	***94***
18	**1a**	$Ca(OH)_2$	DMAc/H_2O (4:1)	91
19	**1a**	$Ca(OH)_2$	DMAc/H_2O (1:1)	64
20	**1a**[c]	$Ca(OH)_2$	DMAc/H_2O (3:1)	90
21	**1a**[d]	$Ca(OH)_2$	DMAc/H_2O (3:1)	61
22	**1a**	–	DMAc/H_2O (3:1)	36
23[e]	**1a**	$Ca(OH)_2$	DMAc/H_2O (3:1)	87
24[f]	**1a**	$Ca(OH)_2$	DMAc/H_2O (3:1)	79
25[g]	**1a**	$Ca(OH)_2$	DMAc/H_2O (3:1)	68

[a] Reaction conditions: cinnamyl phenyl ether (0.25 mmol), phenylboronic acid (0.30 mmol), $Pd(OAc)_2$ (5 mol-%), ligand (5 mol-%), base (0.5 mmol), solvent (1.0 mL) at 50 °C for 24 h under Ar. [b] Isolated yields. [c] 10 mol-% **1a** was used. [d] 2.5 mol-% **1a** was used. [e] 2.5 mol-% $Pd_2(dba)_3$ (i.e., 5 mol-% Pd) was used. [f] Reaction temperature was 60 °C. [g] Arylboronic acid (0.35 mmol) was used. [i] The reaction was carried out under air. [j] 3 mol-% $Pd(OAc)_2$ and 3 mol-% **1a** were used.

Under the optimized reaction conditions (Table 1, entry 17), the scope and limitations of the reaction with respect to both the cinnamyl phenyl ether derived and the arylboronic acid components were explored (Table 2).

Table 2. Palladium-catalyzed allylic arylation of allylic ethers with arylboronic acids.[a]



Entry	Ar^1	Ar^2	Product	Yield (%)[b]
1	Ph	4-MeC_6H_4	 (**3b**)	86
2	Ph	4-$MeOC_6H_4$	 (**3c**)	92
3	Ph	4-ClC_6H_4	 (**3d**)	83
4	Ph	4-HOC_6H_4	 (**3e**)	69
5	Ph	4-$CF_3C_6H_4$	 (**3f**)	80 (**3f**+**3s**)[c]
6	Ph	3-MeC_6H_4	 (**3g**)	89
7	Ph	2-MeC_6H_4	 (**3h**)	84
8	Ph	2-FC_6H_4	 (**3i**)	85
9	Ph	2-HOC_6H_4	 (**3j**)	60[d]
10	Ph	2,4,6-$Me_3C_6H_2$	 (**3k**)	83
11	Ph	3,4-(methylene-dioxy)phenyl	 (**3l**)	73[e]
12	Ph	1-naphthyl	 (**3m**)	92
13	Ph	3-thiophenyl	–	n.r.
14	4-MeC_6H_4	Ph	 (**3n**)	94[f,g]
15	3-MeC_6H_4	Ph	 (**3o**)	94
16	2-MeC_6H_4	Ph	 (**3p**)	93
17	3,5-$Me_2C_6H_2$	Ph	 (**3q**)	94
18	4-$MeOC_6H_4$	Ph	 (**3r**)	60[g,h]
19	4-$CF_3C_6H_4$	Ph	 (**3s**)	63 (**3s**+**3f**)[i]
20	H	3-hydroxy-4-methoxyphenyl[j]	 (**3t**)	40

[a] Reaction conditions: allyl ether (0.25 mmol), arylboronic acid (0.30 mmol), $Pd(OAc)_2$ (5 mol-%), ligand **1a** (5 mol-%), $Ca(OH)_2$ (0.5 mmol), DMAc (0.75 mL), and H_2O (0.25 mL) at 50 °C for 24 h under Ar. [b] Isolated yields. [c] Reaction time was 6 h; Ratio of **3f**/**3s** was 92:8 by ^1H NMR spectroscopy. [d] Reaction temperature was 80 °C. [e] 10 mol-% $Pd(OAc)_2$ and ligand **1a** were used. [f] Reaction temperature was 60 °C. [g] Arylboronic acid (0.35 mmol) was used. [h] Reaction time was 48 h at 60 °C. [i] Reaction time was 6 h; ratio of **3s**/**3f** was 94:6 by ^1H NMR spectroscopy. [j] Pinacol ester was used.

Using cinnamyl phenyl ether with 4-substituted arylboronic acids such as 4-tolyl-, (4-methoxyphenyl)-, (4-chlorophenyl)-, and (4-hydroxyphenyl)boronic acid led to moderate to good yields of the corresponding products (Table 2, entries 1–4). When the reaction of (4-trifluoromethylphenyl)boronic acid was carried out for 24 h, **3f** (Ar^1 = Ph, Ar^2 = 4-$CF_3C_6H_4$) and **3s** (Ar^1 = 4-$CF_3C_6H_4$, Ar^2 = Ph) were obtained in 80% yield (ratio of **3f**/**3s** = 73:27). On the other hand, the reaction for 6 h gave **3f** with only a small amount of **3s** in 80% yield (Table 2, entry 5). The reaction of 3- and 2-substituted arylboronic acids such as 3-tolyl-, 2-tolyl-, (2-fluorophenyl)-, and (2-hydroxyphenyl)boronic acid also gave the corresponding products in moderate to good yields (Table 2, entries 6–9). Moreover, (2,4,6-trimethylphenyl)-, [3,4-(methylenedioxy)phenyl]-, and 1-naphthylboronic acid gave good yields (Table 2, entries 10–12). On the other hand, the reaction of a heteroarylboronic acid, 3-thiopheneboronic acid, did not gave the desired product, unfortunately (Table 2, entry 13). We also tested the reaction of various cinnamyl phenyl ether derivatives, which were easily prepared by the hydrazone–palladium-catalyzed Mizoroki–Heck reaction[4e] of allyl phenyl ether with the corresponding aryl iodides, with phenylboronic acid (Table 2, entries 14–19). The reaction of methyl-substituted cinnamyl phenyl ethers and 4-methoxycinnamyl phenyl ether gave the corresponding unsymmetrical 1,3-diphenylpropene derivatives in moderate to good yields (Table 2, entries 14–18). When phenyl 4-(trifluoromethyl)-cinnamyl ether was used, the reaction gave the corresponding product (i.e., **3s**) with small amount of **3f** as a by-product (Table 2, entry 19). We also tested the synthesis of eugenol using allyl phenyl ether with (4-hydroxy-3-methoxyphenyl)boronic acid pinacol ester (Table 2, entry 20). The reaction gave the corresponding product in moderate yield.

Conclusions

In conclusion, we succeeded with the synthesis of unsymmetrical 1,3-diarylpropenes in good to high yields by a palladium-catalyzed allylic arylation of cinnamyl phenyl ether derivatives with a variety of arylboronic acids using 5 mol-% of a hydrazone **1a**–$Pd(OAc)_2$ system in DMAc/H_2O at 50 °C. We also obtained eugenol by the allylic arylation of allyl phenyl ether with (4-hydroxy-3-methoxyphenyl)boronic acid pinacol ester using a hydrazone **1a**–$Pd(OAc)_2$ system.

Experimental Section

General Procedure for the Palladium-Catalyzed Allylic Arylation of Allylic Ethers with Arylboronic Acids: Arylboronic acid (0.30 mmol) was added to a mixture of allylic ether (0.25 mmol), $Ca(OH)_2$ (0.5 mmol), $Pd(OAc)_2$ (12.5 μmol), and ligand **1a** (12.5 μmol) in DMAc (0.75 mL) and H_2O (0.25 mL) at room temperature under an argon atmosphere. The mixture was stirred at 50 °C. After 24 h, the mixture was diluted with ethyl acetate and water. The organic phase was washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography [hexane, hexane/ethyl acetate (40–5:1), or hexane/diethyl ether (100:1)].

(3-Phenyl-1-propen-1-yl)benzene (3a):[5a] 94% as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.17–7.37 (m, 10 H), 6.46 (d, J = 15.9 Hz, 1 H), 6.35 (dt, J = 15.9 and 6.3 Hz, 1 H), 3.55 (d, J = 6.3 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.1, 137.4, 131.0, 129.2, 128.6, 128.5 ×2, 127.1, 126.2, 126.1, 39.3 ppm. MS (EI): m/z (%) = 194 (100) $[M]^+$.

1-Methyl-4-(3-phenyl-2-propen-1-yl)benzene (3b):[5a] 86% as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.10–7.37 (m, 9 H), 6.45 (d, J = 15.9 Hz, 1 H), 6.34 (dt, J = 15.9 and 6.3 Hz, 1 H), 3.51 (d, J = 6.3 Hz, 2 H), 2.32 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.5, 137.0, 135.7, 130.8, 129.5, 129.2, 128.53, 128.46, 127.0, 126.1, 38.9, 21.0 ppm. MS (EI): m/z (%) = 208 (100) $[M]^+$.

1-Methoxy-4-(3-phenyl-2-propen-1-yl)benzene (3c):[5a] 92% as a white solid; m.p. 25–27 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.14–7.37 (m, 7 H), 6.86 (dt, J = 8.7 and 2.8 Hz, 2 H), 6.43 (d, J = 15.9 Hz, 1 H), 6.33 (dt, J = 15.9 and 6.3 Hz, 1 H), 3.79 (s, 3 H), 3.49 (d, J = 6.2 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.0, 137.5, 132.2, 130.7, 129.7, 129.6, 128.5, 127.0, 126.1, 113.9, 55.3, 38.4 ppm. MS (EI): m/z (%) = 224 (100) $[M]^+$.

1-Chloro-4-(3-phenyl-2-propen-1-yl)benzene (3d):[5b] 83% as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.15–7.37 (m, 9 H), 6.44 (d, J = 15.6 Hz, 1 H), 6.30 (dt, J = 15.6 and 6.6 Hz, 1 H), 3.51 (d, J = 6.6 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.6, 137.2, 131.9, 131.5, 130.0, 128.55, 128.52, 127.2, 126.1, 38.6 ppm. MS (EI): m/z (%) = 228 (63) $[M]^+$.

4-(3-Phenyl-2-propen-1-yl)phenol (3e):[9] 69% as a yellow solid; m.p. 60–62 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.12–7.40 (m, 5 H), 7.08 (d, J = 2.9 Hz, 2 H), 6.78 (dt, J = 8.5 and 2.9 Hz, 2 H), 6.43 (d, J = 15.8 Hz, 1 H), 6.32 (dt, J = 15.8 and 6.2 Hz, 1 H), 4.88 (s, 1 H), 3.47 (d, J = 6.2 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.9, 137.5, 132.3, 130.7, 129.8, 129.6, 128.5, 127.0, 126.1, 115.3, 38.4 ppm. MS (EI): m/z (%) = 210 (100) $[M]^+$.

4-(3-Phenyl-2-propen-1-yl)-1-(trifluoromethyl)benzene (3f):[5a] 80% as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56 (d, J = 8.0 Hz, 2 H), 7.20–7.37 (m, 7 H), 6.48 (d, J = 15.7 Hz, 1 H), 6.32 (dt, J = 15.7 and 6.7 Hz, 1 H), 3.60 (d, J = 6.7 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.3, 137.1, 131.9, 129.0, 128.58 (q, J = 32.3 Hz), 128.56, 127.9, 127.4, 126.2, 125.4 (q, J = 3.7 Hz), 124.3 (q, J = 271.9 Hz), 39.1 ppm. MS (EI): m/z (%) = 262 (100) $[M]^+$.

1-Methyl-3-(3-phenyl-2-propen-1-yl)benzene (3g):[2] 89% as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.03–7.37 (m, 9 H), 6.46 (d, J = 15.8 Hz, 1 H), 6.34 (dt, J = 15.8 and 6.6 Hz, 1 H), 3.51 (d, J = 6.6 Hz, 2 H), 2.33 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.1, 138.1, 137.5, 130.9, 129.4, 129.3, 128.5, 128.4, 127.1, 126.9, 126.1, 125.7, 39.3, 21.4 ppm. MS (EI): m/z (%) = 208 (100) $[M]^+$.

1-Methyl-2-(3-phenyl-2-propen-1-yl)benzene (3h):[5a] 84% as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.13–7.35 (m, 9 H), 6.28–6.40 (m, 2 H), 3.53 (d, J = 4.9 Hz, 2 H), 2.33 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.2, 137.5, 136.4, 130.9, 130.2, 129.2, 128.51, 128.46, 127.0, 126.4, 126.1, 126.0, 36.8, 19.4 ppm. MS (EI): m/z (%) = 208 (100) $[M]^+$.

1-Fluoro-2-(3-phenyl-2-propen-1-yl)benzene (3i): 85% as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.17–7.37 (m, 7 H), 7.01–7.11 (m, 2 H), 6.46 (d, J = 15.8 Hz, 1 H), 6.33 (dt, J = 15.8 and 6.6 Hz, 1 H), 3.57 (d, J = 6.6 Hz, 2 H) ppm. ^{13}C NMR (75 MHz,

$CDCl_3$): δ = 161.0 (d, J = 244.2 Hz), 137.3, 131.4, 130.6 (d, J = 4.8 Hz), 128.5, 127.9 (d, J = 8.4 Hz), 127.6, 127.2, 127.1 (d, J = 16.7 Hz), 126.1, 32.2 (d, J = 3.3 Hz), 124.1 (d, J = 3.6 Hz), 115.3 (d, J = 21.5 Hz) ppm. MS (EI): *m/z* (%) = 212 (100) $[M]^+$. HRMS (APCI): calcd. for $C_{15}H_{14}F$ $[M + H]^+$ 213.1074; found 213.1084.

2-(3-Phenyl-2-propen-1-yl)phenol (3j):[9] 60% as a yellow solid; m.p. 47–49 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.12–7.37 (m, 7 H), 6.91 (td, J = 7.4 and 1.1 Hz, 1 H), 6.82 (d, J = 8.0 Hz, 1 H), 6.51 (d, J = 15.9 Hz, 1 H), 6.39 (dt, J = 15.9 and 6.2 Hz, 1 H), 4.93 (s, 1 H), 3.57 (d, J = 6.2 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.0, 137.0, 128.5, 131.5, 130.4, 127.9, 127.3, 126.2, 125.6, 125.3, 121.0, 115.7, 34.1 ppm. MS (EI): *m/z* (%) = 210 (100) $[M]^+$.

2,4,6-Trimethyl-1-(3-phenyl-2-propen-1-yl)benzene (3k): 83% as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.14–7.30 (m, 5 H), 6.87 (s, 2 H), 6.19–6.32 (m, 2 H), 3.51 (d, J = 4.0 Hz, 2 H), 2.30 (s, 6 H), 2.27 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.6, 136.6, 135.5, 133.1, 129.8, 128.9, 128.4, 127.7, 126.9, 126.0, 32.6, 20.9, 19.9 ppm. MS (EI): *m/z* (%) = 236 (100) $[M]^+$. HRMS (APCI): calcd. for $C_{18}H_{20}$ $[M]^+$ 236.1560; found 236.1556.

3,4-Methylenedioxy-1-(3-phenyl-2-propen-1-yl)benzene (3l):[9] 73% as a white solid; m.p. 38–40 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.17–7.36 (m, 5 H), 6.68–6.77 (m, 3 H), 6.43 (d, J = 15.8 Hz, 1 H), 6.31 (dt, J = 15.8 and 6.5 Hz, 1 H), 5.92 (s, 2 H), 3.46 (d, J = 6.5 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.7, 145.9, 137.4, 133.9, 130.9, 129.3, 128.5, 127.1, 126.1, 121.4, 109.2, 108.2, 100.8, 39.0 ppm. MS (EI): *m/z* (%) = 238 (100) $[M]^+$.

1-(3-Phenyl-2-propen-1-yl)naphthalene (3m):[5a] 92% as a white solid; m.p. 73–74 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.07–8.11 (m, 1 H), 7.84–7.88 (m, 1 H), 7.74–7.77 (m, 1 H), 7.15–7.54 (m, 9 H), 6.43–6.56 (m, 2 H), 4.00 (d, J = 4.8 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.4, 136.2, 133.8, 132.0, 131.3, 128.9, 128.7, 128.5, 127.1, 126.4, 126.1, 125.9, 125.63, 125.56, 124.0, 36.4 ppm. MS (EI): *m/z* (%) = 244 (73) $[M]^+$.

1-Methyl-4-(3-phenyl-1-propen-1-yl)benzene (3n):[5a] 94% as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.19–7.33 (m, 7 H), 7.10 (d, J = 8.0 Hz, 2 H), 6.43 (d, J = 15.8 Hz, 1 H), 6.30 (dt, J = 15.8 and 6.6 Hz, 1 H), 3.54 (d, J = 6.6 Hz, 2 H), 2.32 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.3, 136.8, 134.7, 130.9, 21.1, 129.2, 128.6, 128.4, 128.1, 126.1, 126.0, 39.3 ppm. MS (EI): *m/z* (%) = 208 (100) $[M]^+$.

1-Methyl-3-(3-phenyl-1-propen-1-yl)benzene (3o):[5b] 94% as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.15–7.33 (m, 8 H), 7.02 (d, J = 6.4 Hz, 1 H), 6.29–6.46 (m, 2 H), 3.54 (d, J = 6.1 Hz, 2 H), 2.32 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.2, 138.0, 137.4, 131.1, 129.0, 128.6, 128.5, 128.4, 127.9, 126.8, 126.1, 123.3, 39.3, 21.4 ppm. MS (EI): *m/z* (%) = 208 (100) $[M]^+$.

1-Methyl-2-(3-phenyl-1-propen-1-yl)benzene (3p):[10] 93% as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.44 (m, 1 H), 7.12–7.34 (m, 8 H), 6.66 (d, J = 15.6 Hz, 1 H), 6.23 (dt, J = 15.6 and 6.9 Hz, 1 H), 3.57 (d, J = 6.9 Hz, 2 H), 2.34 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.3, 136.6, 135.1, 130.5, 130.2, 129.0, 128.6, 128.5, 127.0, 126.1, 126.0, 125.6, 39.6, 19.8 ppm. MS (EI): *m/z* (%) = 208 (100) $[M]^+$.

1,3-Dimethyl-5-(3-phenyl-1-propen-1-yl)benzene (3q): 94% as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.18–7.33 (m, 5 H), 6.98 (s, 2 H), 6.85 (s, 1 H), 6.27–6.43 (m, 2 H), 3.53 (d, J = 5.8 Hz, 2 H), 2.28 (s, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.3, 137.9, 137.4, 131.1, 128.8 ×2, 128.7, 128.4, 126.1, 124.0, 39.4, 21.2 ppm. MS (EI): *m/z* (%) = 222 (100) $[M]^+$. HRMS (ESI): calcd. for $C_{17}H_{19}$ $[M + H]^+$ 223.1481; found 223.1484.

1-Methoxy-4-(3-phenyl-1-propen-1-yl)benzene (3r):[5a] 60% as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.19–7.33 (m, 7 H), 6.81–6.86 (m, 2 H), 6.40 (d, J = 15.8 Hz, 1 H), 6.21 (dt, J = 15.8 and 6.8 Hz, 1 H), 3.79 (s, 3 H), 3.53 (d, J = 6.8 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.8, 140.4, 130.4, 130.3, 128.6, 128.4, 127.2, 127.0, 126.1, 113.9, 55.3, 39.3 ppm. MS (EI): *m/z* (%) = 224 (100) $[M]^+$.

4-(3-Phenyl-1-propen-1-yl)-1-(trifluoromethyl)benzene (3s): 63% as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.53 (d, J = 8.3 Hz, 2 H), 7.43 (d, J = 8.2 Hz, 2 H), 7.23–7.32 (m, 5 H), 6.45–6.48 (m, 2 H), 3.57 (d, J = 3.9 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.9, 139.5, 132.1, 129.8, 128.7, 128.6, 129.0 (q, J = 32.3 Hz), 126.4, 126.2, 125.4 (q, J = 3.8 Hz), 124.2 (q, J = 271.6 Hz), 39.3 ppm. MS (EI): *m/z* (%) = 262 (100) $[M]^+$. HRMS (ESI): calcd. for $C_{16}H_{12}F_3$ $[M + H]^+$ 261.0897; found 261.0896.

Eugenol (3t):[11] 40% as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 6.83–6.86 (m, 1 H), 6.67–6.70 (m, 2 H), 5.95 (ddt, J = 6.6, 10.1, and 16.9 Hz, 1 H), 5.50 (s, 1 H), 5.04–5.11 (m, 2 H), 3.87 (s, 3 H), 3.32 (d, J = 6.6 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.4, 143.9, 137.8, 131.9, 121.1, 115.5, 114.2, 111.1, 55.8, 39.9 ppm. MS (EI): *m/z* (%) = 164 (100) $[M]^+$.

Supporting Information (see footnote on the first page of this article): Copies of ^1H and ^{13}C NMR spectra of the products.

Acknowledgments

The Authors gratefully acknowledge the financial support by Chiba University (Iodine Research Project and COE Start-up Program).

[1] a) B. Kramer, S. R. Waldvogel, *Angew. Chem.* **2004**, *116*, 2501–2503; *Angew. Chem. Int. Ed.* **2004**, *43*, 2446–2449; b) J. C. Anderson, C. Headly, P. D. Stapleton, P. W. Taylor, *Tetrahedron* **2005**, *61*, 7703–7711; c) M. Belley, C. C. Chan, Y. Gareau, M. Gallant, H. Juteau, K. Houde, N. Lachance, M. Labelle, N. Sawyer, N. Tremblay, S. Limontage, M.-C. Carrière, D. Denis, G. M. Greig, D. Slipez, R. Gordon, N. Chauret, C. Lo, R. J. Zamboni, K. M. Metters, *Bioorg. Med. Chem. Lett.* **2006**, *16*, 5639–5642; d) C.-R. Su, Y.-C. Shen, P.-C. Kuo, Y.-L. Leu, A. G. Damu, Y.-H. Wang, T.-S. Wu, *Bioorg. Med. Chem. Lett.* **2006**, *16*, 6155–6160; e) C. Ito, M. Itoigawa, T. Kanematsu, Y. Imamura, H. Tokuda, H. Nishino, H. Furukawa, *Eur. J. Med. Chem.* **2007**, *42*, 902–909; f) S. Cheenpracha, C. Karalai, C. Ponglimanont, A. Kanjana-Opas, *J. Nat. Prod.* **2009**, *72*, 1395–1398; g) K. N. Mewett, S. P. Fernandez, A. K. Pasricha, A. Pong, S. O. Devenish, D. E. Hibbs, M. Chebib, G. A. R. Johnston, J. R. Hanrahan, *Bioorg. Med. Chem.* **2009**, *17*, 7156–7173; h) K. Umehara, K. Nemoto, A. Matsushita, E. Terada, O. Monthakantirat, W. De-Eknamkul, T. Miyase, T. Warashina, M. Degawa, H. Noguchi, *J. Nat. Prod.* **2009**, *72*, 2163–2168; i) F. M. Abdel Bar, M. A. Khanfar, A. Y. Elnagar, F. A. Badria, A. M. Zaghloul, K. F. Ahmad, P. W. Sylvester, K. A. El Sayed, *Bioorg. Med. Chem.* **2010**, *18*, 496–507; j) M. Moriyasu, N. Nakatani, M. Ichimaru, Y. Nishiyama, A. Kato, S. G. Mathenge, F. D. Juma, P. B. C. Mutiso, *J. Nat. Med.* **2011**, *65*, 313–321; k) J. C. Anderson, R. McCarthy, S. Paulin, P. W. Taylor, *Bioorg. Med. Chem. Lett.* **2011**, *21*, 6996–7000.

[2] H. Tsukamoto, T. Uchiyama, T. Suzuki, Y. Kondo, *Org. Biomol. Chem.* **2008**, *6*, 3005–3013.

[3] a) T. Nishikata, B. H. Lipshutz, *J. Am. Chem. Soc.* **2009**, *131*, 12103–12105; b) B. H. Lipshutz, S. Ghorai, A. R. Abela, R. Moser, T. Nishikata, C. Duplais, A. Krasovskiy, R. D. G. Gaston, R. C. Gadwood, *J. Org. Chem.* **2011**, *76*, 4379–4391.

[4] a) T. Mino, Y. Shirae, M. Sakamoto, T. Fujita, *Synlett* **2003**, 882–884; b) T. Mino, Y. Shirae, M. Sakamoto, T. Fujita, *J. Org. Chem.* **2005**, *70*, 2191–2194; c) T. Mino, Y. Shirae, Y. Sasai, M.

Sakamoto, T. Fujita, *J. Org. Chem.* **2006**, *71*, 6834–6839; d) T. Mino, Y. Shirae, T. Saito, M. Sakamoto, T. Fujita, *J. Org. Chem.* **2006**, *71*, 9499–9502; e) T. Mino, H. Shindo, T. Kaneda, T. Koizumi, Y. Kasashima, M. Sakamoto, T. Fujita, *Tetrahedron Lett.* **2009**, *50*, 5358–5360; f) T. Mino, S. Suzuki, K. Hirai, M. Sakamoto, T. Fujita, *Synlett* **2011**, 1277–1280; g) T. Mino, M. Shibuya, S. Suzuki, K. Hirai, M. Sakamoto, T. Fujita, *Tetrahedron* **2012**, *68*, 429–432.

[5] a) T. Mino, K. Kajiwara, Y. Shirae, M. Sakamoto, T. Fujita, *Synlett* **2008**, 2711–2715; b) T. Mino, T. Koizumi, S. Suzuki, K. Hirai, K. Kajiwara, M. Sakamoto, T. Fujita, *Eur. J. Org. Chem.* **2012**, 678–680.

[6] a) Y. Uozumi, H. Danjo, T. Hayashi, *J. Org. Chem.* **1999**, *64*, 3384–3388; b) Y. M. A. Yamada, T. Watanabe, K. Torii, Y. Uozumi, *Chem. Commun.* **2009**, 5594–5596; c) Y. M. A. Yamada, T. Watanabe, T. Beppu, N. Fukuyama, K. Torii, Y. Uozumi, *Chem. Eur. J.* **2010**, *16*, 11311–11319; d) Y. M. A. Yamada, S. M. Sarkar, Y. Uozumi, *J. Am. Chem. Soc.* **2012**, *134*, 3190–3198.

[7] The Zhang group reported palladium-catalyzed α-selective and stereospecific allylic arylation: C. Li, J. Xing, J. Zhao, P. Huynh, W. Zhang, P. Jiang, Y. J. Zhang, *Org. Lett.* **2012**, *14*, 390–393.

[8] The Sawamura group reported palladium-catalyzed γ-selective and stereospecific allylic arylation: a) H. Ohmiya, Y. Makida, T. Tanaka, M. Sawamura, *J. Am. Chem. Soc.* **2008**, *130*, 17276–17277; b) H. Ohmiya, Y. Makida, D. Li, T. Tanaka, M. Sawamura, *J. Am. Chem. Soc.* **2010**, *132*, 879–889; c) Y. Makida, H. Ohmiya, M. Sawamura, *Chem. Asian J.* **2011**, *6*, 410–414.

[9] A. V. Malkov, S. L. Davis, I. R. Baxendale, W. L. Mitchell, P. Kocovsky, *J. Org. Chem.* **1999**, *64*, 2751–2764.

[10] J. Barluenga, L. Florentino, F. Aznar, C. Valdés, *Org. Lett.* **2011**, *13*, 510–513.

[11] C. R. Larsen, D. B. Grotjahn, *J. Am. Chem. Soc.* **2012**, *134*, 10357–10360.

Received: September 25, 2012
Published Online: January 29, 2013

