CHEMISTRY
AN ASIAN JOURNAL

DOI: 10.1002/asia.200900639

Synthesis of Naphtho[1,8-*bc*]pyran Derivatives and Related Compounds through Hydroxy Group Directed C–H Bond Cleavage under Rhodium Catalysis

Satoshi Mochida, Masaki Shimizu, Koji Hirano, Tetsuya Satoh,* and Masahiro Miura*[a]

Abstract: The straightforward and efficient synthesis of naphtho[1,8-*bc*]pyran derivatives and related polycyclic compounds is achieved by the rhodium-catalyzed oxidative coupling of 1-naphthols or other phenolic and alcoholic substrates with alkynes. In these annulation reactions, the hydroxy groups effectively act as the key function for the regioselective C–H bond cleavage.

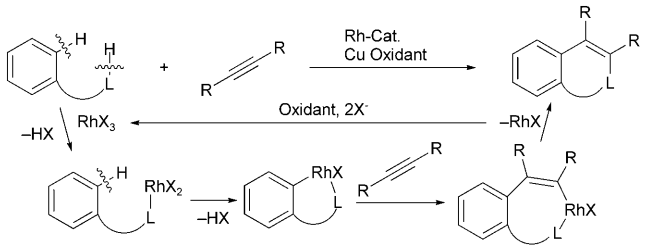
Keywords: annulation · C–H activation · fused-ring systems · homogeneous catalysis · rhodium

Introduction

A naphtho[1,8-*bc*]pyran skeleton can be seen in various naturally occurring and synthetic compounds that exhibit a broad range of interesting biological[1] and optoelectronic properties.[2] The skeleton has been constructed through a complicated multistep process. Thus, easier, more general approaches towards the skeleton are strongly desired.

Transition-metal-catalyzed direct C–H functionalization reactions have been significantly developed in recent years and have enabled various synthetic routes to be shortened for a range of complex molecules.[3] As an example, we recently disclosed the one-step synthesis of isocoumarin[4] and isoquinoline derivatives[5] from readily available substrates, such as benzoic acids and aromatic imines, respectively. As shown in Scheme 1, these frameworks can be constructed by the rhodium-catalyzed oxidative coupling with alkynes, involving regioselective C–H bond cleavage directed by carboxyl and imino groups (LH = CO_2H, C=NH).

During our further study of rhodium-catalyzed oxidative coupling,[6] it has been revealed that our catalyst system is applicable to the one-step construction of the naphtho[1,8-*bc*]pyran skeleton by using 1-naphthols and alkynes as the substrates. The hydroxy group also acts as the directing group for the aromatic C–H bond cleavage at the *peri*-position.[7] Expectedly, some naphtho[1,8-*bc*]pyran derivatives obtained have been found to show solid-state fluorescence. Furthermore, the couplings of 2-phenylphenol and 9-phenylxanthen-9-ol with alkynes also proceed smoothly by means of C–H cleavage around the hydroxy functions. These new findings are described herein.



Scheme 1. The rhodium-catalyzed oxidative coupling of aromatic substrates with internal alkynes.

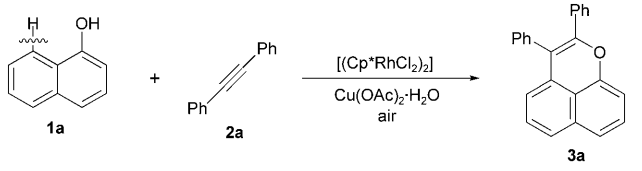
Results and Discussion

In an initial attempt, 1-naphthol (**1a**) (1 mmol) was treated with diphenylacetylene (**2a**) (0.5 mmol) in the presence of $[Cp^*RhCl_2]_2$ (0.005 mmol) and $Cu(OAc)_2 \cdot H_2O$ (0.025 mmol) (OAc = acetate) in *o*-xylene at 140 °C (bath temperature) for 6 h under air ($Cp^* = \eta^5$-pentamethylcyclopentadienyl). As a result, an oxidative coupling product, 2,3-diphenylnaphtho-[1,8-*bc*]pyran (**3a**), was formed in 64% yield (Table 1, entry 1). Decreasing the reaction temperature to 120 and

[a] S. Mochida, M. Shimizu, Dr. K. Hirano, Prof. Dr. T. Satoh, Prof. Dr. M. Miura
Department of Applied Chemistry
Faculty of Engineering, Osaka University
Suita, Osaka 565-0871 (Japan)
Fax: (+81) 6-6879-7362
E-mail: satoh@chem.eng.osaka-u.ac.jp
miura@chem.eng.osaka-u.ac.jp

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/asia.200900639.

Table 1. Reaction of 1-naphthol (**1a**) with diphenylacetylene (**2a**).[a]



Entry	*T* [°C]	Yield [%][b]
1	140	64
2	120	73
3	100	73(70)
4	80	57
5[c]	100	50

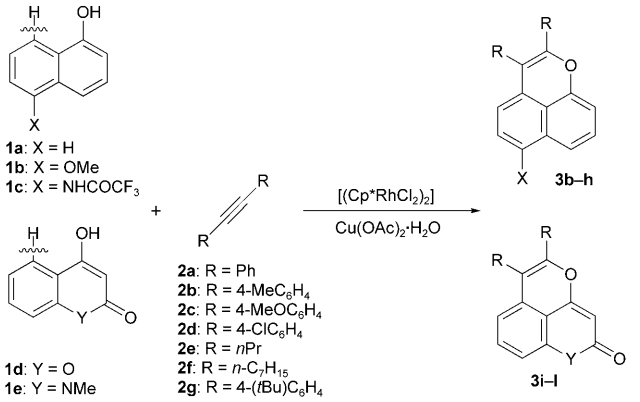
[a] The reaction of **1a** (1 mmol) with **2a** (0.5 mmol) was conducted with $[\{Cp^*RhCl_2\}_2]$ (0.005 mmol) and $Cu(OAc)_2{\cdot}H_2O$ (0.025 mmol) in *o*-xylene (2.5 mL) under air for 6 h. [b] Yield determined by GC. The value in parentheses indicates the yield after purification. [c] **1a** (0.5 mmol) and **2a** (1 mmol) were used.

100 °C somewhat improved the product yield (Table 1, entries 2 and 3). At 80 °C, however, the yield was reduced (Table 1, entry 4). Under the conditions using an excess amount of **2a** ([**1a**] = 0.5 mmol, [**2a**] = 1 mmol), the yield of **3a** was significantly lower (Table 1, entry 5).

Under the conditions for entry 3 of Table 1 (conditions A: $Cu(OAc)_2{\cdot}H_2O$ (0.025 mmol) in *o*-xylene (2.5 mL) under air), the couplings of various 1-naphthols and related hydroxy compounds **1a–e** with alkynes **2a–g** were examined (Scheme 2 and Table 2). Methyl, methoxy, and chloro-substituted diphenylacetylenes **2b–d** reacted with **1a** to form the corresponding 2,3-diarylnaphtho[1,8-*bc*]pyrans **3b–d** in 65–74% yield (Table 2, entries 1–3). Similarly, 2,3-dialkylnaphthopyrans **3e** and **3f** were also obtained from the reactions of **1a** with 4-octyne (**2e**) and 8-hexadecyne (**2f**), respectively (Table 2, entries 4 and 5). 5-Methoxy- (**1b**) and 5-trifluoroacetylamino- (**1c**) 1-naphthols underwent the coupling with **2a** to form 6-substituted 2,3-diphenylnaphthopyrans **3g** and **3h** (Table 2, entries 6 and 7).

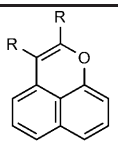
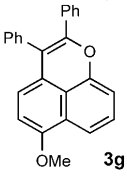
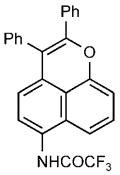
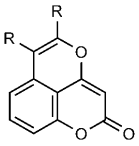
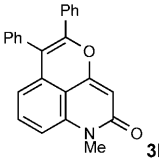
Treatment of 4-hydroxycoumarin (**1d**), which possesses a similar *peri* C–H bond to those of 1-naphthols, with **2a** under conditions A did not give any coupling product (Table 2, entry 8).[8] When using conditions B (conditions B: with a stoichiometric amount of $Cu(OAc)_2{\cdot}H_2O$ (1 mmol) in DMF (2.5 mL) under N_2), the desired coupling product **3i** was obtained in 74% yield (Table 2, entry 9). The reactions of **1d** with **2c** and bis(4-*tert*-butylphenyl)acetylene (**2g**) pro-

Abstract in Japanese:
ロジウム触媒を用いる1-ナフトールあるいは他のフェノールおよびアルコール類とアルキンとの酸化的カップリングにより、ナフト[1,8-*bc*]ピラン誘導体および関連する多環化合物を、直接的に効率よく合成することに成功した。これらの環化反応における位置選択的炭素–水素結合切断に対し、水酸基が鍵官能基として有効に機能する。



Scheme 2. The reaction of 1-naphthols and analogues **1a–e** with alkynes **2a–g**.

Table 2. Reaction of 1-naphthols and analogues **1** with alkynes **2**.[a]

Entry	**1**	**2**	Conditions	Product	Yield [%][b]
					
1	**1a**	**2b**	A	**3b**: R = 4-MeC_6H_4	(68)
2	**1a**	**2c**	A	**3c**: R = 4-$MeOC_6H_4$	(74)
3	**1a**	**2d**	A	**3d**: R = 4-ClC_6H_4	(65)
4	**1a**	**2e**	A	**3e**: R = *n*Pr	61 (54)
5	**1a**	**2f**	A	**3f**: R = *n*-C_7H_{15}	58 (49)
6	**1b**	**2a**	A	 **3g**	60 (52)
7	**1c**	**2a**	A	 **3h**	42 (41)
					
8	**1d**	**2a**	A	**3i**: R = Ph	0
9	**1d**	**2a**	B		74 (70)
10	**1d**	**2c**	B	**3j**: R = 4-$MeOC_6H_4$	77 (73)
11	**1d**	**2g**	B	**3k**: R = 4-(*t*Bu)C_6H_4	48 (46)
12	**1e**	**2a**	B	 **3l**	96 (92)

[a] The reaction of **1** (1 mmol) with **2** (0.5 mmol) was conducted with $[\{Cp^*RhCl_2\}_2]$ (0.005 mmol) at 100 °C for 6-8 h. Conditions A: with $Cu(OAc)_2{\cdot}H_2O$ (0.025 mmol) in *o*-xylene (2.5 mL) under air. Conditions B: with $Cu(OAc)_2{\cdot}H_2O$ (1 mmol) in DMF (2.5 mL) under N_2. [b] Yield determined by GC. The value in parentheses indicates the yield after purification.

ceeded similarly to give **3j** and **3k**, respectively (Table 2, entries 10 and 11). 4-Hydroxy-1-methylquinolin-2-one (**1e**) also underwent the coupling with **2a** under conditions B to produce 1-methyl-5,6-diphenylpyrano[2,3,4-*de*]quinolin-2-one (**3l**) in 96% yield (Table 2, entry 12).

Some tricyclic products **3** obtained above showed solid-state fluorescence in a range of 410–560 nm (see the Supporting Information). Notably, **3c** exhibited a relatively strong emission compared to a typical emitter, Coumarin 153, by a factor of 2.1 ($\lambda_{emis}=484$ nm, A versus B in Figure 1).

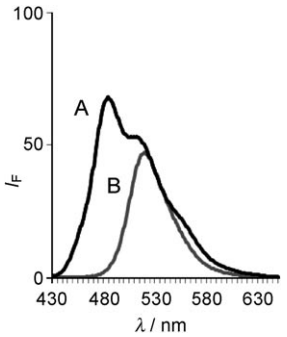
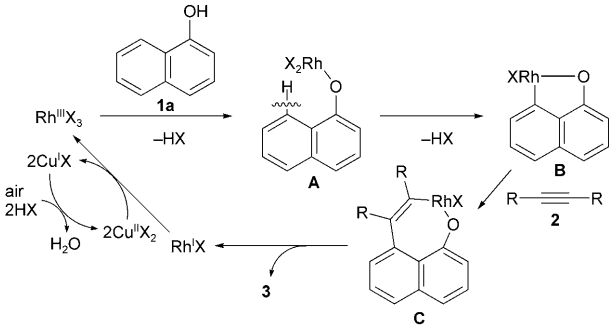


Figure 1. The fluorescence spectra of **3c** (A) and Coumarin 153 (B) in the solid-state upon excitation at 421 nm.

A plausible mechanism for the reaction of 1-naphthol (**1a**) with alkynes **2** is illustrated in Scheme 3, in which neutral ligands are omitted for clarity. Coordination of the phenolic oxygen to an $Rh^{III}X_3$ species gives a rhodium(III) naphtholate **A**. Directed C–H rhodation to form a rhodacycle intermediate **B** is then followed by alkyne insertion and reductive elimination to form a naphthopyran **3**. The resulting $Rh^{I}X$ species is oxidized by the copper(II) salt to regenerate $Rh^{III}X_3$. Under air, Cu^{I} species may also be reoxidized to Cu^{II}.

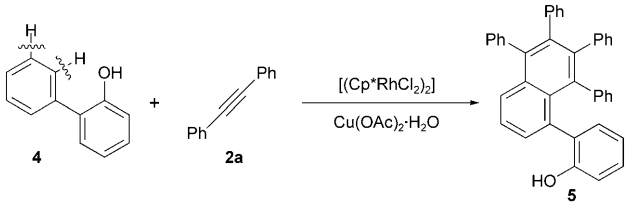
As described above, the hydroxy group can act as a good anchor for directed C–H bond cleavage by Rh^{III} species, such as **A** to **B** in Scheme 3. Therefore, we next examined the reactions of other phenolic and alcoholic substrates with



Scheme 3. A plausible mechanism for the reaction of **1a** with alkyne **2**.

our catalyst system. Among several substrates employed, 2-phenylphenol (**4**) was found to undergo the oxidative coupling with **2a**. In this case, these substrates were coupled in the ratio of 1:2, in contrast to the 1:1 coupling of **1** with **2**. Thus, treatment of **4** (0.5 mmol) with **2a** (0.5 mmol) in the presence of $[Cp^*RhCl_2]_2$ (0.005 mmol) and $Cu(OAc)_2{\cdot}H_2O$ (0.025 mmol) in *o*-xylene at 120°C (bath temperature) for 8 h under air gave product **5** in 9% yield (Table 3, entry 1). Similar 1:2 oxidative coupling, accompanied by double C–H bond cleavages, was also observed in our previous work on the reaction of phenylazoles, such as 1-phenylpyrazole with

Table 3. Reaction of 2-phenylphenol (**4**) with diphenylacetylene (**2a**).[a]



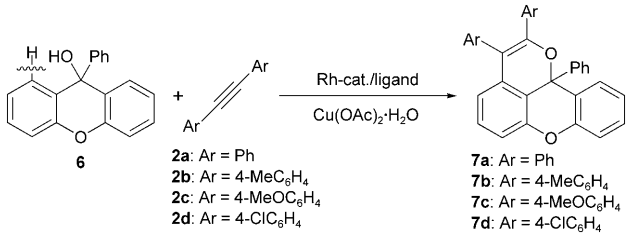
Entry	$Cu(OAc)_2{\cdot}H_2O$ [mmol]	*T* [°C]	Yield [%][b]
1[c]	0.025	120	9
2	0.5	120	68
3	0.5	100	33
4	0.5	150	54
5	1	150	57
6[d]	0.5	120	81 (72)

[a] The reaction of **4** (0.5 mmol) with **2a** (0.5 mmol) was conducted with $[\{Cp^*RhCl_2\}_2]$ (0.005 mmol) in *o*-xylene (2.5 mL) under N_2 for 6–8 h. [b] GC yield based on the amount of **2a** used. The value in parentheses indicates the yield after purification. [c] Under air. [d] KI (0.5 mmol) was added.

alkynes.[6c] The yield of **5** was improved to 68% by using a stoichimetric amount of $Cu(OAc)_2{\cdot}H_2O$ (0.5 mmol) under N_2 (Table 3, entry 2). Both decrease and increase of the reaction temperature reduced the yield of **5** (Table 3, entries 3 and 4). Further increase of the amount of $Cu(OAc)_2{\cdot}H_2O$ to 1 mmol at 150°C did not improved the product yield (Table 3, entry 5). Finally, addition of KI (0.5 mmol) was found to increase the yield up to 81% (Table 3, entry 6).[9]

Not only such phenolic substrates **1** and **4** but also a tertiary alcohol, 9-phenylxanthen-9-ol (**6**), underwent the oxidative coupling with diarylacetylenes **2a–d** involving regioselective C–H bond cleavage at its 1-position to form the corresponding annulated products. First, **6** (0.5 mmol) was treated with **2a** (0.5 mmol) in the presence of $[Cp^*RhCl_2]_2$ (0.005 mmol), 1,2,3,4-tetraphenyl-1,3-cyclopentadiene ($C_5H_2Ph_4$: 0.02 mmol), and $Cu(OAc)_2{\cdot}H_2O$ (1 mmol) in *o*-xylene at 160°C (bath temperature) for 8 h under N_2. As a result, pyranoxanthene **7a** was produced in 18% yield (Table 4, entry 1). Without $C_5H_2Ph_4$, the reaction did not take place at all (Table 4, entry 2). The catalyst system, $[RhCl(cod)]_2/C_5H_2Ph_4$ (cod = 1,5-cyclooctadiene), gave the significantly better yield of **7a** (72%) than $[Cp^*RhCl_2]_2/C_5H_2Ph_4$ (Table 4, entry 3 versus entry 1). As a ligand, $C_5H_2Ph_4$ was found to be more effective than 1,2,3,4,5-pentaphenyl-1,3-cyclopentadiene (C_5HPh_5) and 1,2,4-triphenyl-

Table 4. Reaction of 9-phenylxanthen-9-ol (**6**) with diarylacetylene **2a**–**d**.[a]

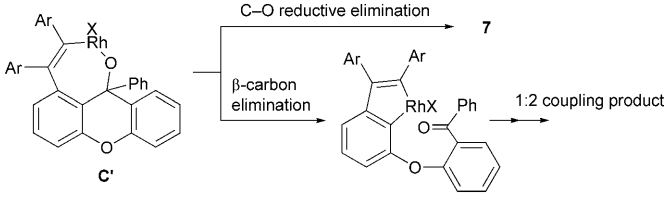


Entry	2	Rh catalyst	Ligand	Product, Yield [%][b]
1	**2a**	$[\{Cp^*RhCl_2\}_2]$	$C_5H_2Ph_4$	**7a**, 18
2	**2a**	$[\{Cp^*RhCl_2\}_2]$	–	–, 0
3	**2a**	$[RhCl(cod)]_2$	$C_5H_2Ph_4$	**7a**, 72
4	**2a**	$[RhCl(cod)]_2$	C_5HPh_5	**7a**, 21
5	**2a**	$[RhCl(cod)]_2$	$C_5H_3Ph_3$	**7a**, 61
6[c]	**2a**	$[RhCl(cod)]_2$	$C_5H_2Ph_4$	**7a**, 20
7[d]	**2a**	$[RhCl(cod)]_2$	$C_5H_2Ph_4$	**7a**, 83 (77)
8[d]	**2b**	$[RhCl(cod)]_2$	$C_5H_2Ph_4$	**7b**, 82 (72)
9[d]	**2c**	$[RhCl(cod)]_2$	$C_5H_2Ph_4$	**7c**, (76)
10[d]	**2d**	$[RhCl(cod)]_2$	$C_5H_2Ph_4$	**7d**, (46)

[a] The reaction of **6** (0.5 mmol) with **2** (0.5 mmol) was conducted with Rh catalyst (0.005 mmol), ligand (0.02 mmol), and $Cu(OAc)_2{\cdot}H_2O$ (1 mmol) in *o*-xylene (2.5 mL) under N_2 at 160 °C for 6–8 h. [b] Yield determined by GC. The value in parentheses indicates the yield after purification. [c] At 140 °C. [d] **6** (1 mmol) was used.

1,3-cyclopentadiene ($C_5H_3Ph_3$) (Table 4, entries 3–5) for which steric factors may be important. At 140 °C, the yield decreased (Table 4, entry 6). The best result was obtained if an excess amount of **6** was used, the yield being enhanced to 83 % (Table 4, entry 7). Under similar conditions, **6** reacted with substituted diphenylacetylenes **2b–d** to afford the corresponding pyranoxanthenes **7b–d** (Table 4, entries 8–10).

Previously, we reported that related acyclic tertiary alcohols, triarylmethanols, underwent the oxidative coupling with alkynes in the presence of a similar Rh/Cu catalyst system via successive C–H and C–C bond cleavages to afford 1,2,3,4-tetrasubstituted naphthalenes as 1:2 coupling products.[6d] In the reactions of **6**, however, only trace amounts of the 1:2 coupling products were detected by GCMS. The present reaction appears to proceed via a seven-membered rhodacycle intermediate **C′**, generated in a manner similar to that in the reaction of **1a** (**C** in Scheme 3). Then, C–O reductive elimination seems to occur in preference to β-carbon elimination to selectively form **7** (Scheme 4). The latter may be suppressed, owing to the rigidity of tetracyclic **C′**, in which the interaction between the Rh center and *ipso*-aromatic carbon seems to be difficult.[10]



Scheme 4. A plausible mechanism for the formation of **7**.

Conclusions

In summary, we have demonstrated that the oxidative coupling of 1-naphthols with internal alkynes can be performed in the presence of a rhodium/copper catalyst system under air to selectively give the corresponding naphtho[1,8-*bc*]pyran derivatives accompanied by C–H bond cleavage at the *peri* position. Using similar catalyst systems, 2-phenylphenol and 9-phenylxanthen-9-ol can also be coupled with alkynes in 1:2 and 1:1 ratios, respectively. Some of the fused polycyclic products exhibit intense fluorescence in the solid state.

Experimental Section

General

^1H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, for $CDCl_3$ solutions, respectively. MS data were obtained by using electron ionization (EI). GC analysis was carried out by using a silicon OV-17 column (i.d. 2.6 mm × 1.5 m) or a CBP-1 capillary column (i.d. 0.5 mm × 25 m). GC-MS analysis was carried out using a CBP-1 capillary column (i.d. 0.25 mm × 25 m). The structures of all products were unambiguously determined by using ^1H and ^{13}C NMR spectroscopy with the aid of NOE, COSY, HMQC, and HMBC experiments.

Diarylacetylenes **2b–d**,**g**,[11] naphthols **1b**,**c**,[7e] and $C_5H_3Ph_3$ (1,2,4-triphenyl-1,3-cyclopentadiene)[12] were prepared according to published procedures. Other starting materials and reagents were commercially available. Copies of the ^1H- and ^{13}C NMR spectra of **3a–l**, **5**, and **7a–d** are given in the Supporting Information.

Synthesis

General Procedure for Oxidative Coupling of 1-Naphthols and Analogues with Internal Alkynes

Under Conditions A: To a 20 mL two-necked flask were added ArOH **1** (1 mmol), alkyne **2** (0.5 mmol), $[\{Cp^*RhCl_2\}_2]$ (0.005 mmol, 3 mg), $Cu(OAc)_2{\cdot}H_2O$ (0.025 mmol, 5 mg), 1-methylnaphthalene (≈50 mg) as internal standard, and *o*-xylene (2.5 mL). The resulting mixture was stirred under air at 100 °C (bath temperature) for 6–8 h.

Under conditions B: To a 20 mL two-necked flask were added ArOH **1** (1 mmol), alkyne **2** (0.5 mmol), $[\{Cp^*RhCl_2\}_2]$ (0.005 mmol, 2.5 mg), $Cu(OAc)_2{\cdot}H_2O$ (1 mmol, 199 mg), 1-methylnaphthalene (≈50 mg) as internal standard, and DMF (2.5 mL). The resulting mixture was stirred under N_2 at 100 °C (bath temperature) for 6 h. GC and GCMS analyses of the mixture confirmed formation of **3**. The product was also isolated by chromatography on silica gel using hexane-ethyl acetate. The solid obtained was recrystallized from hexane/ethyl acetate. Characterization data of products are summarized in the Supporting Information.

Acknowledgements

This work was partly supported by Grants-in-Aid from the Ministry of Education, Culture, Sports, Science and Technology, Japan and the Kurata Memorial Hitachi Science and Technology Foundation.

[1] For selected papers, see: a) D.-Y. Shin, S. N. Kim, J.-H. Chae, S.-S. Hyun, S.-Y. Seo, Y.-S. Lee, K.-O. Lee, S.-H. Kim, Y.-S. Lee, J. M. Jeong, N.-S. Choi, Y.-G. Suh, *Bioorg. Med. Chem. Lett.* **2004**, *14*, 4519; b) Y.-G. Suh, D.-Y. Shin, K.-H. Min, S.-S. Hyun, J.-K. Jung, S.-Y. Seo, *Chem. Commun.* **2000**, 1203; c) Y. Miki, H. Hachiken, K. Noguchi, M. Ohta, A. Nakano, K. Takahashi, S. Takemura, *Chem.*

Pharm. Bull. **1990**, *38*, 3257; d) W. M. Best, D. Wege, *Aust. J. Chem.* **1986**, *39*, 647; e) S. O′Brien, D. C. C. Smith, *J. Chem. Soc.* **1963**, 2907.

[2] For selected papers, see: a) D. S. Tyson, E. F. Fabrizio, M. J. Panzner, J. D. Kinder, J.-P. Buisson, J. B. Christensen, M. A. Meador, *J. Photochem. Photobiol. A* **2005**, 172, 97; b) J. B. Christensen, I. Johannsen, K. Bechgaard, *J. Org. Chem.* **1991**, *56*, 7055.

[3] For selected reviews concerning C–H bond functionalization, see: a) D. A. Colby, R. G. Bergman, J. A. Ellman, *Chem. Rev.* **2010**, *110*, 624; b) F. Kakiuchi, T. Kochi, *Synthesis* **2008**, 3013; c) J. C. Lewis, R. G. Bergman, J. A. Ellman, *Acc. Chem. Res.* **2008**, *41*, 1013; d) E. M. Ferreira, H. Zhang, B. M. Stoltz, *Tetrahedron* **2008**, *64*, 5987; e) Y. J. Park, J.-W. Park, C.-H. Jun, *Acc. Chem. Res.* **2008**, *41*, 222; f) C. I. Herrerias, X. Yao, Z. Li, C.-J. Li, *Chem. Rev.* **2007**, *107*, 2546; g) F. Kakiuchi, *Top. Organomet. Chem.* **2007**, *24*, 1; h) L. Ackermann, *Top. Organomet. Chem.* **2007**, *24*, 35; i) T. Satoh, M. Miura, *Top. Organomet. Chem.* **2007**, *24*, 61; j) D. Kalyani, M. S. Sanford, *Top. Organomet. Chem.* **2007**, *24*, 85; k) D. Alberico, M. E. Scott, M. Lautens, *Chem. Rev.* **2007**, *107*, 174; l) C.-H. Jun, E.-A. Jo, J.-W. Park, *Eur. J. Org. Chem.* **2007**, 1869; m) T. Satoh, M. Miura, *Chem. Lett.* **2007**, *36*, 200; n) T. Satoh, M. Miura, *J. Synth. Org. Chem.* **2006**, *64*, 1199; o) B. L. Conley, W. J. Tenn III, K. J. H. Young, S. K. Ganesh, S. K. Meier, V. R. Ziatdinov, O. Mironov, J. Oxgaard, J. Gonzales, W. A. Goddard, III, R. A. Periana, *J. Mol. Catal. A* **2006**, *251*, 8; p) F. Kakiuchi, N. Chatani, *Adv. Synth. Catal.* **2003**, *345*, 1077; q) V. Ritleng, C. Sirlin, M. Pfeffer, *Chem. Rev.* **2002**, *102*, 1731; r) F. Kakiuchi, S. Murai, *Acc. Chem. Res.* **2002**, *35*, 826; s) C. Jia, T. Kitamura, Y. Fujiwara, *Acc. Chem. Res.* **2001**, *34*, 633; t) G. Dyker, *Angew. Chem.* **1999**, *111*, 1808; *Angew. Chem. Int. Ed.* **1999**, *38*, 1698; u) A. E. Shilov, G. B. Shul′pin, *Chem. Rev.* **1997**, *97*, 2879.

[4] a) M. Shimizu, K. Hirano, T. Satoh, M. Miura, *J. Org. Chem.* **2009**, *74*, 3478; b) T. Satoh, K. Ueura, M. Miura, *Pure Appl. Chem.* **2008**, *80*, 1127; c) K. Ueura, T. Satoh, M. Miura, *J. Org. Chem.* **2007**, *72*, 5362; d) K. Ueura, T. Satoh, M. Miura, *Org. Lett.* **2007**, *9*, 1407.

[5] T. Fukutani, N. Umeda, K. Hirano, T. Satoh, M. Miura, *Chem. Commun.* **2009**, 5141.

[6] a) S. Mochida, K. Hirano, T. Satoh, M. Miura, *J. Org. Chem.* **2009**, *74*, 6295; b) M. Shimizu, H. Tsurugi, T. Satoh, M. Miura, *Chem. Asian J.* **2008**, *3*, 881; c) N. Umeda, H. Tsurugi, T. Satoh, M. Miura, *Angew. Chem.* **2008**, *120*, 4083; *Angew. Chem. Int. Ed.* **2008**, *47*, 4019; d) T. Uto, M. Shimizu, K. Ueura, H. Tsurugi, T. Satoh, M. Miura, *J. Org. Chem.* **2008**, *73*, 298.

[7] Rh-Catalyzed arylation of phenols: a) R. B. Bedford, M. E. Limmert, *J. Org. Chem.* **2003**, *68*, 8669; b) R. B. Bedford, S. J. Coles, M. B. Hursthouse, M. E. Limmert, *Angew. Chem.* **2003**, *115*, 116; *Angew. Chem. Int. Ed.* **2003**, *42*, 112; c) S. Oi, S.-I. Watanabe, S. Fukita, Y. Inoue, *Tetrahedron Lett.* **2003**, *44*, 8665. Rh-Catalyzed alkylation of phenols: d) J. C. Lewis, J. Wu, R. G. Bergman, J. A. Ellman, *Organometallics* **2005**, *24*, 5737. Ir-Catalyzed vinylation of naphthols: e) Y. Nishinaka, T. Satoh, M. Miura, H. Morisaka, M. Nomura, H. Matsui, C. Yamaguchi, *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1727. Pd-Catalyzed arylation of phenols and naphthols: f) Y. Kawamura, T. Satoh, M. Miura, M. Nomura, *Chem. Lett.* **1999**, 961; g) T. Satoh, J.-I. Inoh, Y. Kawamura, Y. Kawamura, M. Miura, M. Nomura, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2239; h) T. Satoh, Y. Kawamura, M. Miura, M. Nomura, *Angew. Chem.* **1997**, *109*, 1820; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1740.

[8] Even in DMF, the reaction of **1d** did not proceed at all under the aerobic conditions. Thus, the use of a stoichiometric amount of the copper salt was essential for the efficient production of **3i**.

[9] It has been reported that the addition of KI can enhance the efficiency of Pd-catalyzed oxidative coupling and cyclization: a) C. Martínez, R. Álvarez, J. M. Aurrecoechea, *Org. Lett.* **2009**, *11*, 1083; b) S. Ma, Z. Yu, Z. Gu, *Chem. Eur. J.* **2005**, *11*, 2351; c) B. Gabríele, G. Salerno, A. Fazio, *Org. Lett.* **2000**, *2*, 351. As in the Pd systems, it would be possible that I_2, formed in-situ by the oxidation of I^-, acts as a re-oxidant in our system. See also: d) N. G. Connelly, S. J. Raven, *J. Chem. Soc. Dalton Trans.* **1986**, 1613.

[10] The C–H bond cleavage at the first step seems to be directed not on the phenyl group but on the xanthene ring exclusively, owing to the rigidity of the alcohol **6**, although the details are not clear at the present stage.

[11] Z. Novák, P. Nemes, A. Kotschy, *Org. Lett.* **2004**, *6*, 4917.

[12] S. S. Hirsch, W. J. Bailey, *J. Org. Chem.* **1978**, *43*, 4090.

Received: November 13, 2009
Published online: February 23, 2010

