

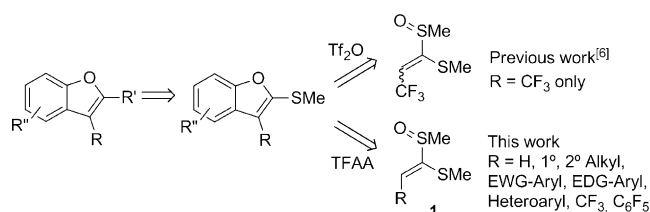
Practical, Modular, and General Synthesis of Benzofurans through Extended Pummerer Annulation/Cross-Coupling Strategy**

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Abstract: Operationally simple, efficient, and widely applicable Pummerer annulations of simple phenols with ketene dithioacetal monoxides, with the aid of trifluoroacetic anhydride, have been shown to provide a variety of benzofurans having a methylthio group at the 2-position. Subsequent and newly developed nickel-catalyzed arylation at the methylthio group culminates in diversity-oriented synthesis of multisubstituted benzofurans. Our extended Pummerer annulation/cross-coupling sequence is powerful enough to synthesize biologically active natural products as well as highly fluorescent benzofuran derivatives.

Benzofuran is an ubiquitous core found in various natural products,^[1] biologically active molecules,^[2] and organic functional molecules.^[3] Development of straightforward and diversity-oriented reactions to construct benzofurans^[4] would therefore have a big impact for pharmaceutical chemists as well as materials chemists who need libraries for novel molecules. While recent active investigations on direct two-component annulations of simple phenols describe an ideal route,^[5] it has still been difficult to achieve modular and precise syntheses of substituted benzofurans.

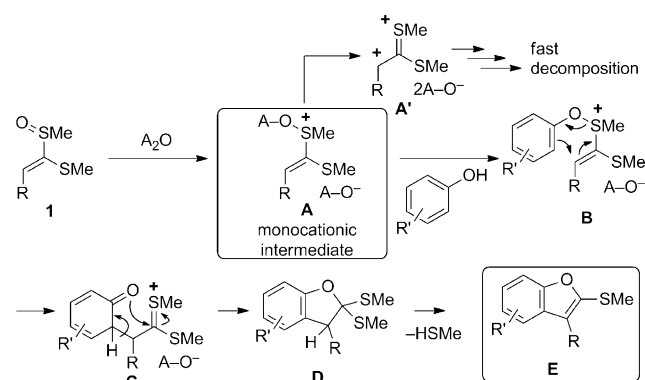
We recently reported the synthesis of 3-trifluoromethylbenzofurans,^[6] which have a convertible alkylthio group^[7] at the 2-position, from simple phenols and perfluoroalkyl-substituted ketene dithioacetal monoxide (KDM) through an extended Pummerer annulation (Scheme 1).^[8–10] Our diversity-oriented synthesis of substituted benzofurans was accomplished through an extended Pummerer annulation/cross-coupling^[11] sequence. Although the annulation is metal-free, rapid, efficient, and regioselective, only perfluoroalkyl-substituted KDM is applicable and the scope is thus very limited. Naturally, we envisioned that the development of new extended Pummerer annulations, which proceed with



Scheme 1. Modular synthesis of substituted benzofurans. EDG = electron-donating group, EWG = electron-withdrawing group, Tf = trifluoromethanesulfonyl, TFAA = trifluoroacetic anhydride.

a wide range of KDMs,^[12] would provide a tailor-made^[13] multisubstituted benzofurans.

A proposed mechanism of the extended Pummerer annulation with the acid anhydride A_2O is shown in Scheme 2. First, the KDM **1** is activated with A_2O to give the monocationic intermediate **A**. Unless an appropriate combination of A_2O and the R group is employed, **A** readily



Scheme 2. Proposed mechanism.

decomposes through the dicationic intermediate **A'**.^[9d] The intermediate **A** reacts with a phenol to provide **B**. Charge-accelerated [3,3]-sigmatropic rearrangement of **B**^[14] gives **C**, which smoothly cyclizes into **D**. Methanethiol is eliminated from **D** to afford the corresponding benzofuran **E**. Since the choice of acid anhydride directly affects the stability and reactivity of **A**, we first screened acid anhydrides. After the screening, we found trifluoroacetic anhydride (TFAA) to be the best activator (see the Supporting Information).

In contrast to the previous report^[6,9a–d] where only CF_3 -substituted KDM could be applied, a wide variety of KDMs have become applicable with the aid of TFAA (Table 1). Treatment of 4-*tert*-butylphenol with **1a** in the presence of TFAA afforded the corresponding benzofuran **2a** in 87%

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Table 1: Scope with regard to KDM and substituted phenol.

Entry	R	1: R'	2 or 3	Yield [%]
1	4- <i>t</i> Bu	1a : Ph	2a	87
2 ^[a]	4- <i>t</i> Bu	1b : H	2b	67
3	4- <i>t</i> Bu	1c : Me	2c	78
4	4- <i>t</i> Bu	1d : Cyclohexyl	2d	63
5	4- <i>t</i> Bu	1e : 4-CF ₃ C ₆ H ₄	2e	95
6	4- <i>t</i> Bu	1f : 4-MeOC ₆ H ₄	2f	51
7	4- <i>t</i> Bu	1g : 4-ClC ₆ H ₄	2g	96
8	4- <i>t</i> Bu	1h : 1-naphthyl	2h	78
9	4- <i>t</i> Bu	1i : 3-thienyl	2i	85
10 ^[a,b]	4- <i>t</i> Bu	1j : C ₆ F ₅	2j	54
11 ^[a,b]	4- <i>t</i> Bu	1k : CF ₃ ^[c]	2k	61
12	4-Br	1a : Ph	3a	87
13	4-Bpin	1a : Ph	3b	76
14	4-CF ₃	1a : Ph	3c	60
15 ^[d]	4-MeO	1a : Ph	3d	72
16	4-EtO ₂ C	1a : Ph	3e	77
17 ^[e]	4-CHO	1a : Ph	3f	60
18 ^[a]	4-TIPSO	1a : Ph	3g	65
19	3-MeO	1a : Ph	3h ^[f]	63
20	2-Ph	1a : Ph	3i ^[g]	70

[a] **1** (1 equiv), TFAA (2 equiv), phenol (2 equiv). [b] 40 °C, 1.5 h. [c] The *E/Z* ratio of **1k** was 4:1. [d] **1a** (1 equiv), TFAA (1.2 equiv), phenol (1.2 equiv). [e] **1a** (1 equiv), TFAA (2 equiv), phenol (2 equiv), K₂CO₃ (2 equiv), 1 h. [f] 6-Methoxy-2-methylthio-3-phenylbenzo[*b*]furan. [g] 2-Methylthio-3,7-diphenylbenzo[*b*]furan. TIPSO = triisopropylsilyl.

yield. The unsubstituted KDM **1b** or KDM having other alkyl groups such as methyl and bulky cyclohexyl groups participated to give **2b–d** in good yields (entries 2–4). The reactions with various substituents on the aryl groups of the KDMs, groups such as electron-withdrawing and electron-donating moieties and halogens, were successful (entries 5–7). Bulky 1-naphthyl- and heteroaryl-substituted **1h** and **1i** reacted to provide **2h** and **2i**, respectively, in high yields (entries 8 and 9). KDMs having perfluorinated substituents also reacted similarly (entries 10 and 11). The scope of substituted phenols was also studied and showed high functional-group compatibility (entries 12–20). Phenols having halogen, boron, electron-withdrawing, or electron-donating groups smoothly reacted (entries 12–15). While the reaction of 4-ethoxycarbonylphenol provided **3e** with the ester group intact (entry 16), a formyl group did not tolerate the original reaction conditions because the resulting trifluoroacetic acid catalyzed dithioacetalization of the carbonyl moiety with methanethiol. An addition of K₂CO₃ suppressed this side reaction to afford **3f** (entry 17). A bulky triisopropylsiloxy group remained untouched (entry 18). To our delight, the reaction of 3-methoxyphenol proceeded at the 6-position, the less crowded *ortho* position, regioselectively to yield 6-methoxy-2-methylthio-3-phenylbenzo[*b*]furan (**3h**) (entry 19). Bulky *ortho*-substituted 2-phenylphenol reacted smoothly (entry 20).

The reactions were applied to various hydroxy-substituted aromatics (Table 2). The reactions of 2-naphthols regioselectively proceeded to give **4a–c** in high yield.^[15] In the presence

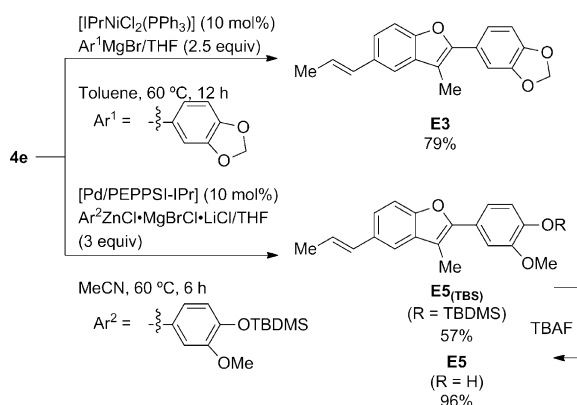
Table 2: Reaction of various hydroxyaromatics.

	R	1: R'	4	Yield (Starting Material)
	2-naphthol	1a : Ph	4a	92%
	2-naphthol	1a : Ph	4b	62% ^[a]
	2-naphthol	1a : Ph	4c	83% ^[b]
	Vanillin	1a : Ph	4d	45%
	Vanillin	1a : Ph	4d'	22%
	Vanillin	1a : Ph	4e	79%
	Resolcinol	1a : Ph	4f	49% ^[d]
	2,7-naphthalenediol	1a : Ph	4g	60% ^[d]
	2,6-naphthalenediol	1a : Ph	4h	40% ^[e]

[a] Alcohol (2 equiv), **1** (1 equiv) TFAA (2 equiv). [b] Alcohol (1 equiv), **1** (2 equiv), TFAA (2 equiv). [c] Vanillin (2 equiv), **1a** (1 equiv), TFAA (2 equiv), K₂CO₃ (2 equiv). [d] Diol (1 equiv), **1** (3 equiv), TFAA (3 equiv). [e] Diol (2 equiv), **1a** (1 equiv), TFAA (1.5 equiv).

of K₂CO₃, vanillin participated to furnish the corresponding benzofuran **4d** in 45% yield with concomitant formation of **4d'** in 22% yield. The reaction of 4-[(*E*)-1-propenyl]phenol with **1c** smoothly proceeded in the presence of TFAA to give **4e** in 79% yield. Gratifyingly, the reactions of dihydroxylated arenes such as resolcinol and naphthalenediols afforded the corresponding difurans **4f–h** directly in one pot. Since the solubility of 2,6-naphthodiol in dichloromethane is poor, employment of an excess amount of 2,6-naphthodiol provided the corresponding difuran **4h** in moderate yield. To demonstrate the robustness of the extended Pummerer annulation, the reaction of 2,6-naphthalenediol was performed on a 5 mmol scale, thus affording 1.4 grams of **4g** after simple filtration through a pad of silica gel and recrystallization from CH₂Cl₂/MeOH (1:2).

We applied the Pummerer annulation/coupling strategy toward the diversity-oriented syntheses of Eupomatenoids (Scheme 3),^[16] which were first isolated from *Eupomatia laurina* and have interesting biological activities such as anticancer^[17a] or anti-*Trypanosoma cruzi* activity.^[17b] In the recent report by Bach and Bartels,^[18] the linear syntheses of eupomatenoids started from the arylation of the bromo group at the 2-position of 2,3,5-tribromobenzo[*b*]furan. Since the eupomatenoid family has variety of aryl groups, installation of an aryl group at the 2-position should be ideally done at the late stage of a synthesis. In contrast, our convergent strategy centers on the synthesis of the core benzofuran (i.e., **4e**), which is then transformed into eupomatenoids. To realize the



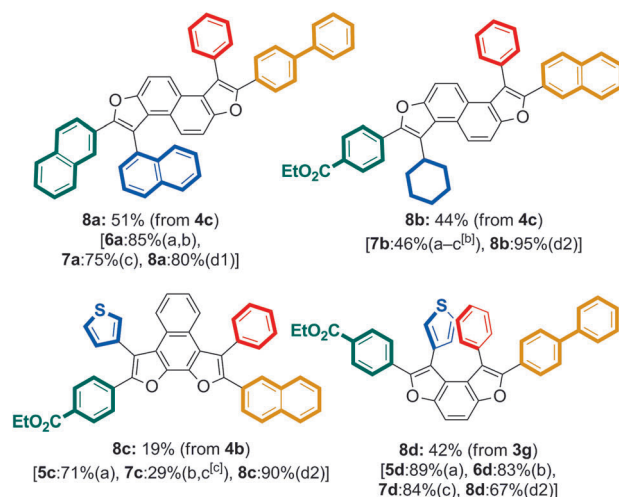
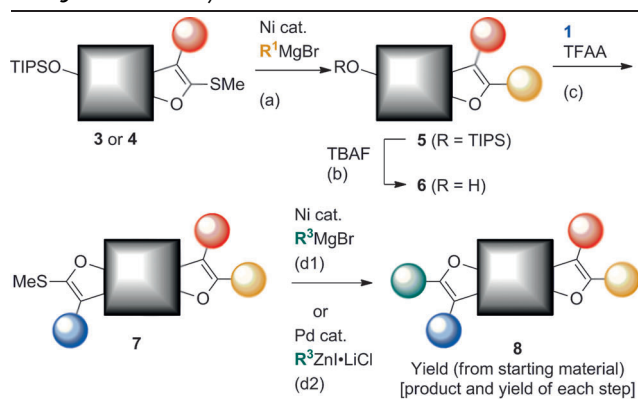
Scheme 3. Syntheses of Eupomatenoids. IPr = 1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2 H-imidazol-2-ylidene, PEPPSI = pyridine-enhanced precatalyst preparation stabilization and initiation, TBDMS = *tert*-butyldimethylsilyl.

strategy, we developed new Kumada–Tamao–Corriu conditions for bulky thioethers^[7,8,19] catalyzed by [IPrNiCl₂(PPh₃)].^[20] Treatment of **4e** with a Grignard reagent in toluene at 60 °C for 12 h in the presence of the [IPrNiCl₂(PPh₃)] catalyst furnished Eupomatenoid-3 (**E3**) in 79% yield. Since methoxy moieties are not tolerated by the highly active Ni/IPr catalyst,^[20c] the synthesis of Eupomatenoid-5 (**E5**) was accomplished under our Negishi conditions.^[6] The reaction of **4e** with the 3-methoxy-4-siloxyphenylzinc reagent^[21] provided TBS-protected **E5**_(TBS) in 57% yield, and was smoothly deprotected with TBAF to give **E5** in 96% yield.

Finally, we performed modular and tailor-made syntheses of multisubstituted difurans because substituents on the furan cores significantly alter their photophysical properties.^[3,6] Our iterative Pummerer annulation/cross-coupling strategy leads to the construction multisubstituted difurans at will (Table 3). The details of the strategy are as follows. The siloxy-substituted 2-methylthiofuran **3** or **4** is subjected to our [IPrNiCl₂(PPh₃)]-catalyzed Kumada–Tamao–Corriu coupling with an organomagnesium reagent. The siloxy group on furan **5** is then removed with TBAF to yield **6**. The second furan structure is constructed under the extended Pummerer annulation conditions with the KDM **1**. The resulting difuran **7** is then converted, by the Kumada–Tamao–Corriu or Negishi reaction, to afford the tetrasubstituted difuran **8**. By using this strategy, we synthesized various multisubstituted difurans which have four different substituents at the designated positions. The structure of **8a** was confirmed by X-ray crystallographic analysis (Figure S7 in the Supporting Information). Gratifyingly, the resulting multisubstituted furans **8** showed a bright blue fluorescence with high quantum yields [quantum yield Φ_F = 0.71 (**8a**), 0.81 (**8b**), 0.71 (**8c**), 0.62 (**8d**); see the Supporting Information]. Overall, the results clearly demonstrate the iterative annulation/coupling strategy is promising for accessing a library of multisubstituted difurans for materials science.

In summary, we invented the extended Pummerer annulation/coupling strategy toward diversity-oriented syntheses of multisubstituted benzofurans. Our improved nickel-cata-

Table 3: Tailor-made synthesis of difurans.^[a]



[a] Reaction conditions: a) [IPrNiCl₂(PPh₃)] (10 mol %), R¹ MgBr/THF (1 M, 2.5 equiv), toluene (0.1 M), 100 °C, 12 h; b) TBAF/THF (1 M, 3 equiv), THF (0.1 M), 25 °C, 3 h; c) **1** (2 equiv), TFAA (2 equiv), CH₂Cl₂, 25 °C, 1 h; d1) [IPrNiCl₂(PPh₃)] (10 mol %), R³ MgBr/THF (1 M, 2.5 equiv), toluene (0.1 M), 100 °C, 12 h; d2) [Pd/PEPPSI-IPr] (10 mol %), R³ Zn·LiCl/THF^[21] (1 M, 2.5 equiv), toluene/MeCN (1:1, 0.05 M), 60 °C, 12 h. [b] E/Z ratio of **1d** used in this reaction was 3:2. [c] CH₂Cl₂/MeCN (5:1, 0.08 M) was used as a solvent. TBAF = *tert*-*n*-butylammonium fluoride.

lyzed Kumada–Tamao–Corriu and palladium-catalyzed Negishi conditions were broadly applicable to the bulky thioethers. The newly developed strategy was powerful enough to synthesize highly fluorescent benzofuran molecules and Eupomatenoid natural products.

Experimental Section

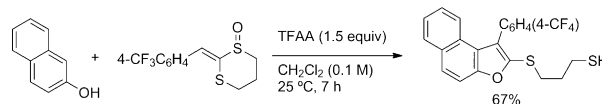
Preparation of **2a** is representative (Table 1). A dichloromethane (2 mL) solution of 4-*tert*-butylphenol (30 mg, 0.20 mmol) and **1a** (51 mg, 0.24 mmol) was placed in a flask. Trifluoroacetic anhydride (33 μ L, 0.24 mmol) was added at 25 °C, and the resulting mixture was stirred for 30 min. The mixture was filtered through a pad of alumina and concentrated in vacuo. Purification by chromatography on silica gel (*n*-hexane/CH₂Cl₂ = 5:1) provided 5-*tert*-butyl-2-methylthio-3-phenylbenzo[*b*]furan (**2a**, 51 mg, 0.17 mmol, 87 %).

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- [1] a) A. L. Ososki, E. J. Knelly, *Phytother. Res.* **2003**, *17*, 845; b) K. Baba, K. Takeuchi, F. Hamasaki, M. Kozawa, *Chem. Pharm. Bull.* **1985**, *33*, 416.
- [2] a) D. A. Horton, G. T. Bourne, M. L. Smythe, *Chem. Rev.* **2003**, *103*, 893; b) B. L. Flynn, G. S. Gill, D. W. Grobely, J. H. Chaplin, D. Paul, A. F. Leske, T. C. Lavranos, D. K. Chalmers, S. A. Charman, E. Kostewicz, D. M. Shackelford, J. Morizzi, E. Hamel, M. K. Jung, G. Kremmidiotis, *J. Med. Chem.* **2011**, *54*, 6014.
- [3] a) H. Tsuji, C. Mitsui, L. Ilies, Y. Sato, E. Nakamura, *J. Am. Chem. Soc.* **2007**, *129*, 11902; b) H. Tsuji, C. Mitsui, Y. Sato, E. Nakamura, *Adv. Mater.* **2009**, *21*, 3776; c) S. Shinamura, I. Osaka, E. Miyazaki, A. Nakao, M. Yamagishi, J. Takeya, K. Takimiya, *J. Am. Chem. Soc.* **2011**, *133*, 5024; d) C. Mitsui, J. Soeda, K. Miwa, H. Tsuji, J. Takeya, E. Nakamura, *J. Am. Chem. Soc.* **2012**, *134*, 5448.
- [4] Reviews: a) G. Zeni, R. C. Larock, *Chem. Rev.* **2006**, *106*, 4644; b) O. Miyata, N. Takeda, T. Naito, *Heterocycles* **2009**, *78*, 843; c) S. Cacchi, G. Fabrizi, A. Goggiani, *Org. Biomol. Chem.* **2011**, *9*, 641; Recent examples: d) M. Furusawa, T. Imahori, K. Igawa, K. Tomooka, R. Irie, *Chem. Lett.* **2013**, *42*, 1134; e) H. Tsuji, K. Shoyama, E. Nakamura, *Chem. Lett.* **2012**, *41*, 957; f) W. Yuan, S. Ma, *Org. Lett.* **2014**, *16*, 193; g) L. Meng, G. Zhang, C. Liu, K. Wu, A. Lei, *Angew. Chem.* **2013**, *125*, 10385; *Angew. Chem. Int. Ed.* **2013**, *52*, 10195.
- [5] Reaction with ketoesters: a) X. Guo, R. Yu, H. Li, Z. Li, *J. Am. Chem. Soc.* **2009**, *131*, 17387; b) U. A. Kshirsagar, R. Parnes, H. Goldshtein, R. Ofir, R. Zarivach, D. Pappo, *Chem. Eur. J.* **2013**, *19*, 13575; Reaction with 1,2-diol: c) D.-H. Lee, K.-H. Kwon, C. S. Yi, *J. Am. Chem. Soc.* **2012**, *134*, 7325; Reaction with alkene: d) U. Sharma, T. Naveen, A. Maji, S. Manna, D. Maiti, *Angew. Chem.* **2013**, *125*, 12901; *Angew. Chem. Int. Ed.* **2013**, *52*, 12669; Reaction with alkyne: e) M. R. Kuram, M. Bhanuchandra, A. K. Sahoo, *Angew. Chem.* **2013**, *125*, 4705; *Angew. Chem. Int. Ed.* **2013**, *52*, 4607; f) W. Zeng, W. Wu, H. Jiang, L. Huang, Y. Sun, Z. Chen, X. Li, *Chem. Commun.* **2013**, *49*, 6611; g) R. Zhu, J. Wei, Z. Shi, *Chem. Sci.* **2013**, *4*, 3706.
- [6] a) T. Kobatake, D. Fujino, S. Yoshida, H. Yorimitsu, K. Oshima, *J. Am. Chem. Soc.* **2010**, *132*, 11838; b) Y. Ookubo, A. Wakamiya, H. Yorimitsu, A. Osuka, *Chem. Eur. J.* **2012**, *18*, 12690.
- [7] Reviews on transformations of alkylthio groups: a) S. R. Dubbaka, P. Vogel, *Angew. Chem.* **2005**, *117*, 7848; *Angew. Chem. Int. Ed.* **2005**, *44*, 7674; b) T.-Y. Luh, Z.-J. Ni, *Synthesis* **1990**, 89; c) T.-Y. Luh, *Acc. Chem. Res.* **1991**, *24*, 257; d) F. Pan, Z.-J. Shi, *ACS Catal.* **2014**, *4*, 280.
- [8] Reviews: a) L. H. S. Smith, S. C. Coote, H. F. Sneddon, D. J. Procter, *Angew. Chem.* **2010**, *122*, 5968; *Angew. Chem. Int. Ed.* **2010**, *49*, 5832; b) S. Akai, Y. Kita, *Top. Curr. Chem.* **2007**, *274*, 35; c) K. S. Feldman, *Tetrahedron* **2006**, *62*, 5003; d) S. K. Bur, A. Padwa, *Chem. Rev.* **2004**, *104*, 2401; e) *Sulfur-Mediated Rearrangements I* (Ed.: E. Schaumann), Springer, Heidelberg, **2007**; f) H. Yorimitsu, *J. Synth. Org. Chem. Jpn.* **2013**, *71*, 341.
- [9] Recent examples from our group: a) S. Yoshida, H. Yorimitsu, K. Oshima, *Chem. Lett.* **2008**, *37*, 786; b) S. Yoshida, H. Yorimitsu, K. Oshima, *Org. Lett.* **2007**, *9*, 5573; c) S. Yoshida, H. Yorimitsu, K. Oshima, *Org. Lett.* **2009**, *11*, 2185; d) T. Kobatake, S. Yoshida, H. Yorimitsu, K. Oshima, *Angew. Chem.* **2010**, *122*, 2390; *Angew. Chem. Int. Ed.* **2010**, *49*, 2340; e) K. Murakami, J. Imoto, H. Matsubara, S. Yoshida, H. Yorimitsu, K. Oshima, *Chem. Eur. J.* **2013**, *19*, 5625.
- [10] From other groups: a) A. J. Eberhart, C. Cicoira, D. J. Procter, *Org. Lett.* **2013**, *15*, 3994; b) X. Huang, N. Maulide, *J. Am. Chem. Soc.* **2011**, *133*, 8510; c) X. Huang, M. Patil, C. Fares, W. Thiel, N. Maulide, *J. Am. Chem. Soc.* **2013**, *135*, 7312; d) A. J. Eberhart, J. E. Imbriglio, D. J. Procter, *Org. Lett.* **2011**, *13*, 5882; e) A. J. Eberhart, D. J. Procter, *Angew. Chem.* **2013**, *125*, 4100; *Angew. Chem. Int. Ed.* **2013**, *52*, 4008; f) K. S. Feldman, M. D. Fodor, *J. Org. Chem.* **2009**, *74*, 3449; g) S. Akai, N. Kawashita, Y. Wada, H. Satoh, A. H. Alinejad, K. Kakiguchi, I. Kuriwaki, Y. Kita, *Tetrahedron Lett.* **2006**, *47*, 1881.
- [11] *Applied Cross-Coupling Reactions* (Ed.: Y. Nishihara), Springer, Heidelberg, **2013**.
- [12] a) K. Murakami, H. Yorimitsu, A. Osuka, *Bull. Chem. Soc. Jpn.* **2013**, *86*, 1193; b) K. Murakami, H. Yorimitsu, A. Osuka, *Bull. Chem. Soc. Jpn.* **2014**, *87*, 441; c) K. Ogura, Y. Ito, G. Tsuchihashi, *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2013.
- [13] a) K. Itami, J. Yoshida, *Bull. Chem. Soc. Jpn.* **2006**, *79*, 811; b) S. Tani, T. N. Uehara, J. Yamaguchi, K. Itami, *Chem. Sci.* **2014**, *5*, 123.
- [14] a) R. F. de La Pradilla, M. Tortosa, A. Viso, *Top. Curr. Chem.* **2007**, *275*, 103; b) X. Huang, S. Klimczyk, N. Maulide, *Synthesis* **2012**, 175.
- [15] The reaction of KDMs which have cyclic structure also proceeded smoothly to provide the corresponding benzofuran.



- [16] B. F. Bowden, E. Ritchie, W. C. Taylor, *Aust. J. Chem.* **1972**, *25*, 2659.
- [17] a) G. B. Longato, L. Y. Rizzo, I. M. de Oliveira Sousa, S. V. Tinti, A. Possenti, G. M. Figueira, A. L. T. G. Ruiz, M. A. Foglio, J. E. de Carvalho, *Planta Med.* **2011**, *77*, 1482; b) P. S. Luize, T. Ueda-Nakamura, B. P. Filho, G. D. Cortéz, C. V. Nakamura, *Biol. Pharm. Bull.* **2006**, *29*, 2126.
- [18] T. Bach, M. Bartels, *Synthesis* **2003**, 925.
- [19] Recent examples: a) S. Kanemura, A. Kondoh, H. Yorimitsu, K. Oshima, *Synthesis* **2008**, 2659; b) K. Itami, D. Yamazaki, J. Yoshida, *J. Am. Chem. Soc.* **2004**, *126*, 15396; c) A. Ghaderi, T. Iwasaki, A. Fukuoka, J. Terao, N. Kambe, *Chem. Eur. J.* **2013**, *19*, 2951.
- [20] a) K. Matsubara, K. Ueno, Y. Shibata, *Organometallics* **2006**, *25*, 3422; b) S. Tanaka, D. Tanaka, G. Tatsuta, K. Murakami, S. Tamba, A. Sugie, A. Mori, *Chem. Eur. J.* **2013**, *19*, 1658; c) M. J. Iglesias, A. Prieto, M. C. Nicasio, *Org. Lett.* **2012**, *14*, 4318.
- [21] a) A. Krasovskiy, V. Malakhov, A. Gavryushin, P. Knochel, *Angew. Chem.* **2006**, *118*, 6186; *Angew. Chem. Int. Ed.* **2006**, *45*, 6040; b) F. M. Piller, A. Metzger, M. A. Schade, B. A. Haag, A. Gavryushin, P. Knochel, *Chem. Eur. J.* **2009**, *15*, 7192.