DOI: 10.1002/adsc.201((will be filled in by the editorial staff))

Synthesis of Benzo[*b*]thiophenes through Rhodium-Catalyzed Three-Component Reaction using Elemental Sulfur

Sanghun Moon,[a] Moena Kato,[a] Yuji Nishii,[b]* and Masahiro Miura[a]*

[a] Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan
Phone: (+81)-6-6879-7360, FAX: (+81)-6-6879-7362, e-mail: miura@chem.eng.osaka-u.ac.jp
[b] Frontier Research Base for Global Young Researchers, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan
Phone: (+81)-6-6879-7361, FAX: (+81)-6-6879-7362, e-mail: y_nishii@chem.eng.osaka-u.ac.jp

Received: ((will be filled in by the editorial staff))

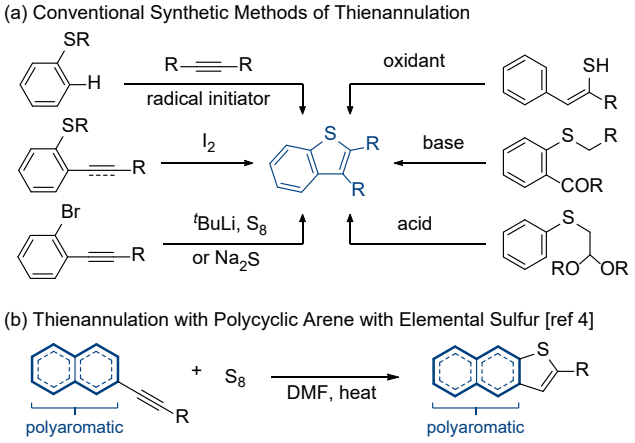
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201######.

Abstract. A benzo[*b*]thiophene synthesis by Rh-catalyzed three-component coupling reaction of arylboronic acids, alkynes, and elemental sulfur (S_8) is developed. A notable feature of this protocol is that the thienannulation (thiophene annulation) proceeds with high regioselectivity via the sequential alkyne insertion, C–H activation, and then sulfur atom transfer to the metallacycle intermediate. In a similar manner, dibenzothiophenes can be synthesized from the parent biarylboronic acids and S_8.

Keywords: Rhodium; C-H activation; Thiophene; Elemental sulfur; Multicomponent reactions

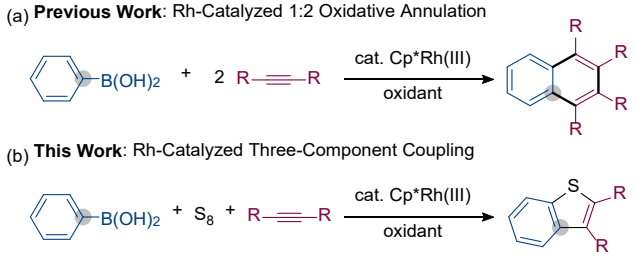
Benzo[*b*]thiophene skeleton is frequently found as a core component of many bioactive compounds and drug candidates.[1] Additionally, densely-fused benzo[*b*]thiophene derivatives have been of vital use in organic electronic devices such as field-effect transistors (OFETs), light-emitting diodes (OLEDs), and photovoltaics (OPVs).[2] To meet the increasing demand in these research fields, the development of efficient synthetic methods for benzo[*b*]thiophene and their analogues has been a substantial topic in recent years. Conventional approaches to the thiophene ring closure (thienannulation) require the appropriate pre-functionalized compounds bearing sulfur-containing substituents (thiol, thioether, disulfide, etc.) (Scheme 1a).[3] In some cases, the sulfur functionalities can be installed *in situ* from the parent haloarenes via halogen-lithium exchange reaction or substitution with Na_2S; however, cumbersome multi-step synthesis of ortho-disubstituted precursors is inevitable. Recently, Itami and coworkers developed an excellent method for the construction of thiophene-fused π-conjugated scaffolds using elemental sulfur (S_8) (Scheme 1b),[4] which is inexpensive, readily available, and highly user-friendly (stable, non-toxic, non-volatile, non-hygroscopic, and non-odorous) sulfur source.[5,6] This reaction calls for the presence of only one alkynyl substituent, whereas the polyaromatic scaffold is essential to trigger the thienannulation.

Meanwhile, transition-metal-catalyzed C–H activation[7] and the subsequent oxidative carbon-carbon as well as carbon-heteroatom bond forming reactions have been of versatile synthetic tool over the past decades.[8] A number of catalytic protocols for the C–S bond formation have been established mainly adopting disulfides as the sulfur source.[9] In contrast, the use of elemental sulfur in the direct C–H functionalization strategy have rarely been achieved despite the fact that sulfur atom transfer from S_8 into the metal-carbon linkage of a Ni(II) metallacycle species was realized by Hillhouse more than 20 years ago.[10] To the best of our knowledge, there have been only two reports for the thia-heterocycle construction through the transition-metal-mediated C–H activation. Shi achieved a Cu-mediated benzoisothiazolone synthesis using the (pyridin-2-yl)isopropylamine (PIP-amine) bidentate directing group.[11] Afterward, Gong and Song developed a catalytic variant adopting a Ni complex with the aid of 2-amino alkylbenzimidazole (MBIP-amine) directing group.[12,13]



Scheme 1. Representative Synthetic Methods for Benzo[*b*]thiophene Derivatives.

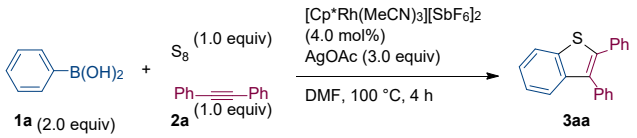
We previously reported a Rh-catalyzed oxidative coupling of arylboronic acids with two equivalents of alkynes, leading to the formation of 1,2,3,4-tetrasubstituted naphthalenes (Scheme 2a).[14,15] As a consequence of our research interest in this area, we assumed that the sulfur atom migration to the corresponding metallacycle intermediate would result in the assembly of benzo[*b*]thiophene skeletons (Scheme 2b). In this manuscript, a Rh-catalyzed three-component coupling reaction[16] of arylboronic acids, alkynes, and elemental sulfur is described. This reaction proceeds with high regio-selectivity since the sulfur atom migration takes place only after the insertion of alkynes, achieving the first successful use of elemental sulfur in thiophen ring formation via the C–H activation under transition-metal catalysis.



Scheme 2. Rh-Catalyzed Oxidative Annulation of Arylboronic Acids with Alkynes.

At the outset, we carried out an optimization study for the model reaction utilizing phenylboronic acid (**1a**), diphenylacetylene (**2a**), and elemental sulfur (Table 1). The desired product (2,3-diphenylbenzo[*b*]thiophene, **3aa**) was obtained in 54% yield in the presence of $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (4.0 mol %) catalyst and AgOAc (2.0 equiv) oxidant in DMF solvent (entry 1). Intriguingly, 1,2,3,4-tetraphenylnaphthalene, a 1:2 coupling product of **1a** with **2a**, was not detected during the course of the study. Boronic esters (entries 2 and 3) as well as a phenyl(trifluoro)borate salt (entry 4) failed to trigger the reaction. $AgOCOCF_3$ and Ag_2CO_3 were not suitable oxidants for the present transformation (entries 5 and 6). The productivity was slightly improved with a increased amount of AgOAc (entry 7). An analogous neutral Rh(III) catalyst was totally inactive (entry 8). Ethanol, 2-propanol, acetone, and DMPU (*N,N'*-dimethylpropyleneurea) were also suitable solvents, but the yields were lower than that in DMF (entries 9-12). The amount of S_8 could be decreased to 0.25 equiv (2.0 equiv as S) without significant drop of the reactivity (entries 13,14), but lower yield was given with 0.125 equiv of sulfur (1.0 equiv as S) (entry 15). Although non-polar solvents (toluene, $PhCF_3$, DCE) alone were not effective (not shown), a mixed solvent system of DMF and $PhCF_3$ gave a considerably high 81% yield of **3aa** (entry 16), probably due to the higher solubility of S_8 in $PhCF_3$. This reaction could be conducted in 1.0 mmol scale to give **3aa** in 66% isolated yield (entry 17).

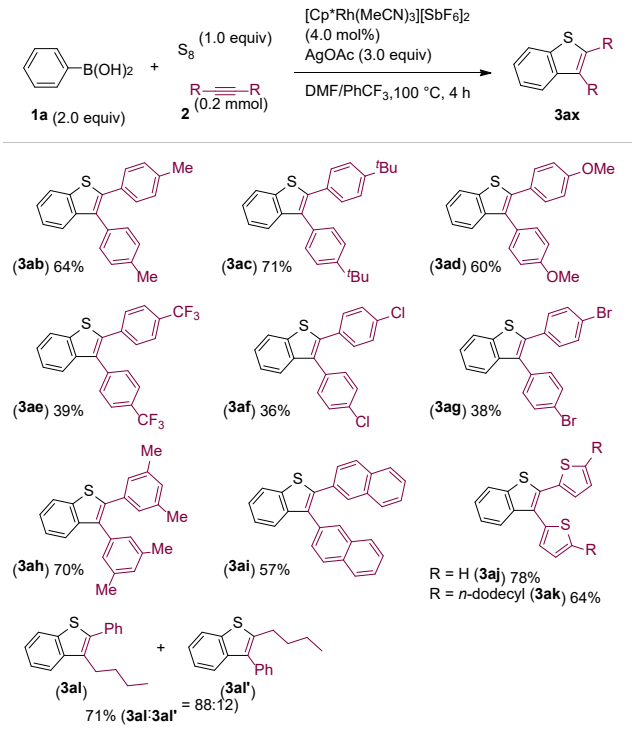
Table 1. Optimization Study [a]



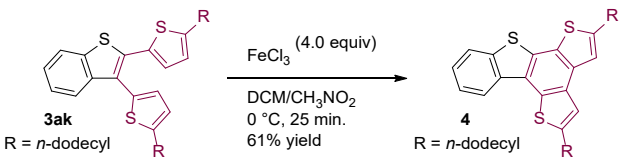
entry	deviation from the standard conditions	yield [b]
1	AgOAc (2.0 equiv)	54% [c]
2	AgOAc (2.0 equiv) PhBpin instead of **1a**	n.d.
3	AgOAc (2.0 equiv) PhBnep instead of **1a**	n.d.
4	AgOAc (2.0 equiv) $PhBF_3K$ instead of **1a**	trace
5	$AgOCOCF_3$ (2.0 equiv) instead of AgOAc	4%
6	Ag_2CO_3 (1.0 equiv) instead of AgOAc	7%
7	--	64%
8	$[Cp^*RhCl_2]$ (2.0 mol%) as catalyst	n.d.
9	ethanol solvent	38%
10	2-propanol solvent	41%
11	acetone solvent	36%
12	DMPU solvent	41%
13	S_8 (0.5 equiv)	66%
14	S_8 (0.25 equiv)	57%
15	S_8 (0.125 equiv)	28%
16	DMF (0.1 mL)/$PhCF_3$ (0.2 mL) solvent	81%[c] (75%)
17	DMF (0.1 mL)/$PhCF_3$ (0.2 mL) solvent	(66%)[d]

[a] Standard conditions: **1a** (0.4 mmol), S_8 (0.2 mmol), **2a** (0.2 mmol), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (4.0 mol%), AgOAc (0.4 mmol), DMF (0.5 mL). [b] Determined by GC analysis. Isolated yield in parentheses. [c] Average of two runs. [d] 1.0 mmol scale. n.d. = not detected, pin = pinacolato, nep = neopentyl glycolato.

With the optimized reaction conditions of entry 16 in Table 1, we then examined the applicability of a series of alkynes (Scheme 3). Para-substituted alkynes bearing electron donating groups gave the desired products (**3ab**–**3ad**) in high yields, whereas electron-withdrawing functionalities considerably retarded the reaction (**3ae**–**3ag**). A meta-substituted alkyne **2h** as well as a 2-naphthyl alkyne **2i** were successfully transformed. For alkynes with low product yield, the corresponding naphthalene derivatives were not detected, and the unreacted alkynes were recovered. It was notable that the catalytic protocol was applicable to the reaction of 2-thienyl alkynes **2j** and **2k** to afford **3aj** and **3ak**, respectively, of which terthiophene skeleton is of precursors for benzo[1,2-*b*:3,4-*b'*:6,5-*b''*]trithiophene derivatives.[17] Actually, **3ak** could be converted to the corresponding trithiophene **4** in 61% yield upon treatment with $FeCl_3$ (Scheme 4). The present method was not applicable to terminal alkynes and aliphatic alkynes (not shown). The reaction of 1-phenyl-1-hexyne (**2l**) produced the desired product **3al** in 72% yield with considerably high regioselectivity (**3al**:**3al'** = 88:12).



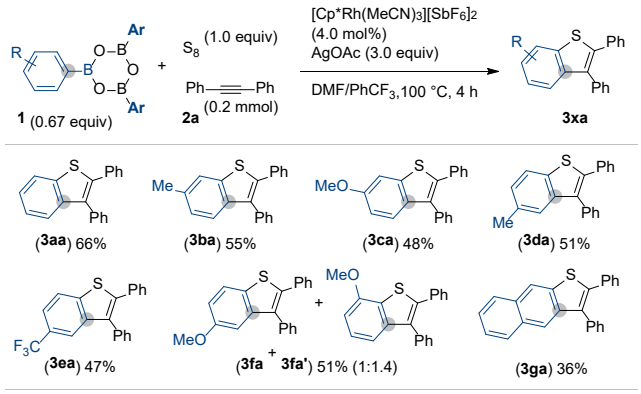
Scheme 3. Substrate Scope for Alkynes.



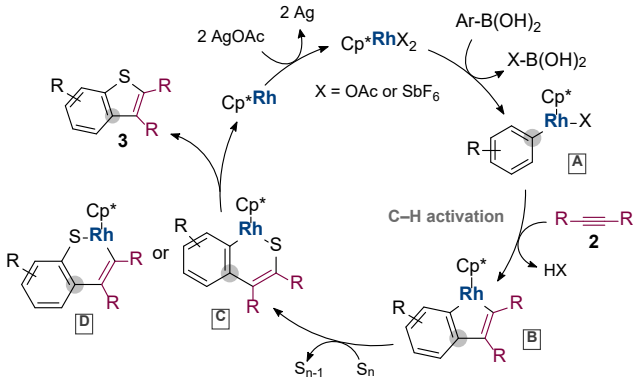
Scheme 4. Synthesis of a Benzotrithiophene through $FeCl_3$-Mediated Oxidative Cyclization.

Next, we evaluated the scope for arylboronic acids. Because of the better reproducibility, boroxines **1** were used (Scheme 5).[18] Phenylboroxine afforded a comparable 66% yield for the production of **3aa**. The para-substituted boroxines **1b** and **1c** were respectively converted to the C6-substituted benzo[*b*]thiophenes **3ba** and **3ca**, indicating that the alkyne firstly reacted with the aryl-rhodium species before the sulfur atom insertion (see below). In a similar manner, the substituents at the meta position (**1d**–**1f**) fell into the C5 position (**3da**–**3fa**) where the sterically more accessible C–H bond preferentially reacted, while **1f** gave a mixture of isomers. A naphtho[2,3-*b*]thiophene core could be constructed in the single step to give **3ga**.

A proposed reaction mechanism for the three-component coupling is illustrated in Scheme 6. A catalytically active Rh(III) species, probably [Cp*RhOAc][SbF_6], undergo transmetalation with the boronic acid to generate the corresponding aryl complex **A**. The following alkyne insertion and the proximal C–H activation give a five-membered rhodacycle **B**. This is consistent with the reaction outcome described in Scheme 5, where the substituents at the para-position placed at the C6 position of the benzo[*b*]thiophene ring. Sulfur atom migration into one of the Rh–C bonds leads to the formation of six-membered metallacycle complexes **C** or **D**.[19] Thereafter, C–S reductive elimination is affected to liberate the coupling product **3** along with the Rh(I) species, which is then oxidized by AgOAc to regenerate the reactive Rh(III) complex, closing the catalytic cycle.



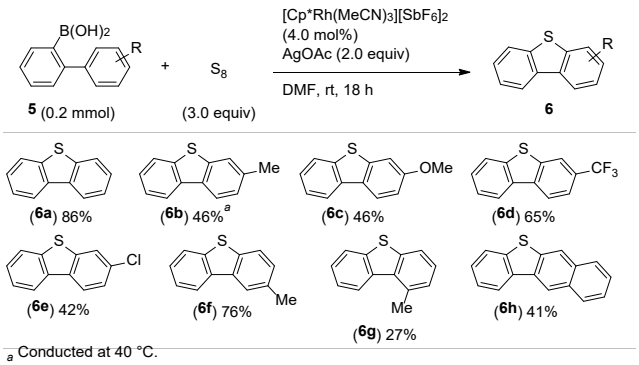
Scheme 5. Substrate Scope for Boroxines.



Scheme 6. Proposed Reaction Mechanism.

On the basis of the proposed reaction mechanism, we assumed that the reaction of 2-biphenylboronic acid (**5a**)[20] with elemental sulfur would produce dibenzothiophene (**6a**) through the formation of similar metallacycle intermediates.[21] As expected, **6a** was isolated in 86% yield under the slightly modified reaction conditions at ambient temperature (Scheme 7). Higher reaction temperature did not improve the yield due to the competing protodeboronation. Subsequently, we examined the reaction with various biarylboronic acids **5**. A series of functional groups such as alkyl (**5b**), alkoxy (**5c**), trifluoromethyl (**5d**), and chloro (**5e**) were compatible to the present method, giving the corresponding dibenzothiophenes in moderate to good yields. For a meta-substituted substrate, **6f** was obtained in 76% yield as a sole product. This reaction system was also applicable to the boronic acids with *ortho*-methyl (**5g**) and 2-naphthyl (**5h**) substituents.

In summary, we have introduced a benzo[*b*]thiophene synthesis by rhodium-catalyzed three-component coupling reaction of arylboronic acids, alkynes, and elemental sulfur. The reaction proceeds high regio-selectivity via the sequential alkyne insertion, C–H activation, and then sulfur atom transfer. Thus, this report represents the first successful use of elemental sulfur for the thienannulation relying on the transition-metal-catalyzed C–H activation technique.



Scheme 7. Dibenzothiophene Synthesis using Elemental Sulfur.

Experimental Section

Synthesis of **3aa** through the three-component coupling: To an oven-dried glass tube were added phenylboronic acid (**1a**, 0.4 mmol, 2.0 equiv), diphenylacetylene (**2a**, 0.2 mmol, 1.0 equiv), sulfur powder (51 mg, 0.2 mmol, 1.0 equiv as S_8), $[Cp^*Rh(MeCN_3)][SbF_6]_2$ (4.0 mol%), and AgOAc (0.6 mmol, 3.0 equiv). The tube was refilled with N_2 and sealed. DMF (0.1 mL) and $PhCF_3$ (0.2 mL) were added to the tube via a syringe, and the mixture was stirred for 4 h at 100 °C with an oil bath. After cooling to room temperature, the resulting mixture was diluted with ethyl acetate and filtered through a pad of Celite and activated alumina. The filtrate was concentrated in *vacuo*, and the residue was purified by column chromatography (eluent: hexane) and GPC ($CHCl_3$) to give the **3aa** as white solid (43.0 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.76 (m, 1H), 7.51-7.49 (m, 1H), 7.31-7.23 (m, 9H), 7.14-7.13 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 139.7, 139.0, 135.6, 134.4, 133.4, 130.6, 129.7, 128.8, 128.5, 127.8, 127.5, 124.7, 124.6, 123.5, 122.2. These values were identical to those reported in the literature.[22] For other compounds, see the Supporting Information.

Acknowledgements

This work was supported by JSPS KAKENHI Grant No. JP 19K15586 (Grant-in-Aid for Young Scientists) to Y.N. and JP 17H06092 (Grant-in-Aid for Specially Promoted Research) to M.M.

References

[1] For selected reviews, see: a) D. A. Horton, G. T. Bourne, M. L. Smythe, *Chem. Rev.* **2003**, *103*, 893-930; b) G. H. Veeneman, *Curr. Med. Chem.* **2005**, *12*, 1077-1136; c) H. Brown, P. Thomas, C. Lindsley, *Nat. Rev. Drug Discov.* **2017**, *16*, 351-367; d) R. S. Keri, K. Chand, S. Budagumpi, S. B. Somappa, S. A. Patil, B. N. Nagaraja, *Eur. J. Med. Chem.* **2017**, *138*, 1002-1033.

[2] For selected reviews, see: a) J. E. Anthony, *Chem. Rev.* **2006**, *106*, 5028-5048; b) S. Allard, M. Forster, B. Souharce, H. Thiem, U. Scherf, *Angew. Chem., Int. Ed.* **2008**, *47*, 4070-4098; *Angew. Chem.* **2008**, *120*, 4138-4167; c) K. Takimiya, S. Shinamura, I. Osaka, E. Miyazaki, *Adv. Mater.* **2011**, *23*, 4347-4370; d) J. Mei, Y. Diao, A. L. Appleton, L. Fang, Z. Bao, *J. Am. Chem. Soc.* **2013**, *135*, 6724-6746; f) W. Jiang, Y. Li, Z. Wang, *Chem. Soc. Rev.* **2013**, *42*, 6113-6127.

[3] See the reviews and the references therein: a) K. Takimiya, M. Nakano, M. J. Kang, E. Miyazaki, I. Osaka, *Eur. J. Org. Chem.* **2013**, 217-227; b) M. E. Cinar, T. Ozturk, *Chem. Rev.* **2015**, *115*, 3036-3140; c) B. Wu, N. Yoshikai, *Org. Biomol. Chem.* **2016**, *14*, 5402-5416.

[4] L. Meng, T. Fujikawa, M. Kuwayama, Y. Segawa, K. Itami, *J. Am. Chem. Soc.* **2016**, *138*, 10351-10355.

[5] For a comprehensive review, see: T. B. Nguyena, *Adv. Synth. Catal.* **2017**, *359*, 1066-1130.

[6] For recent examples of thienannulation using elemental sulfur, see: a) T. B. Nguyen, P. Retailleau, *Org. Lett.* **2017**, *19*, 4858-4860; b) T. B. Nguyen, P. Retailleau, *Org. Lett.* **2018**, *20*, 186-189; c) H. Huang, Z. Xu, X. Ji, B. Li, G.-J. Deng, *Org. Lett.* **2018**, *20*, 4917-4920; d) Z. Liu, R. Gao, J. Lou, Y. He, Z. Yua, *Adv. Synth. Catal.* **2018**, *360*, 3097-3108; e) J. R. Zhang, L. Z. Zhan, L. Wei, Y.-Y. Ning, X.-L. Zhong, J.-X. Lai, L. Xu, R.-Y. Tang, *Adv. Synth. Catal.* **2018**, *360*, 533-543; f) L. Chen, H. Min, W. Zeng, X. Zhu, Y. Liang, G. Deng, Y. Yang, *Org. Lett.* **2018**, *20*, 7392-7395; g) J. Liu, Y. Zhang, Y. Yue, Z. Wang, H. Shao, K. Zhuo, Q. Lv, Z. Zhang, *J. Org. Chem.* **2019**, *84*, 12946-12959; h) P. Zhou, Y. Huang, W. Wu, W. Yu, J. Li, Z. Zhu, H. Jiang, *Org. Biomol. Chem.* **2019**, *17*, 3424-3432; i) H. Huang, Q. Wang, Z. Xu, G. J. Deng, *Adv. Synth. Catal.* **2019**, *361*, 591-596; j) T. T. T. Nguyen, Z. A. Le, P. Retailleau, T. B. Nguyen, *Adv. Synth. Catal.* **2019**, *361*, 160-165.

[7] For a recent comprehensive review, see: C. Sambiagio, D. Schönbauer, R. Blieck, T. Dao-Huy, G. Pototschnig, P. Schaaf, T. Wiesinger, M. F. Zia, J. Wencel-Delord, T. Besset, B. U. W. Maes, M. Schnürch, *Chem. Soc. Rev.* **2018**, *47*, 6603-6743.

[8] For selected reviews, see: a) T. Satoh, M. Miura, *Chem. –Eur. J.* **2010**, *16*, 11212-11222; b) D. A. Colby, R. G. Bergman, J. A. Ellman, *Chem. Rev.* **2010**, *110*, 624-655; c) V. P. Boyarskiy, D. S. Ryabukhin, N. A. Bokach, A. V. Vasilyev, *Chem. Rev.* **2016**, *116*, 5894-5986; d) R. Santhoshkumar, C.-H. Cheng, *Chem. –Eur. J.* **2019**, *25*, 9366-9384.

[9] For selected examples, see: a) X. Chen, X.-S. Hao, C. E. Goodhue, J.-Q. Yu, *J. Am. Chem. Soc.* **2006**, *128*, 6790-6791; b) L. D. Tran, I. Popov, O. Daugulis, *J. Am. Chem. Soc.* **2012**, *134*, 18237-18240; c) Y. Yang, W. Hou, L. Qin, J. Du, H. Feng, B. Zhou, Y. Li, *Chem. Eur. J.* **2014**, *20*, 416-420; d) M. Iwasaki, M. Iyanaga, Y. Tsuchiya, Y.

Nishimura, W. Li, Z. Li, Y. Nishihara, *Chem. Eur. J.* **2014**, *20*, 2459-2462; e) V. P. Reddy, R. Qiu, T. Iwasaki, N. Kambe, *Org. Biomol. Chem.* **2015**, *13*, 6803-6813; f) S.-Y. Yan, Y.-J. Liu, B. Liu, Y. H. Liu, B.-F. Shi, *Chem. Commun.* **2015**, *51*, 4069-4072; g) K. Yang, Y. Wang, X. Chen, A. A. Kadi, H.-K. Fun, H. Sun, Y. Zhang, H. Lu, *Chem. Commun.* **2015**, *51*, 3582-3585; h) W. Xie, B. Li, B. Wang, *J. Org. Chem.* **2016**, *81*, 396-403; i) T. Müller, L. Ackermann, *Chem. –Eur. J.* **2016**, *22*, 14151-14154.

[10] R. Han, G. L. Hillhouse, *J. Am. Chem. Soc.* **1998**, *120*, 7657-7658.

[11] F.-G. Chen, G. Liao, X. Li, J. Wu, B.-F. Shi, *Org. Lett.* **2014**, *16*, 5644-5647.

[12] J.-R. Guo, J.-F. Gong, M.-P. Song, *Org. Biomol. Chem.* **2019**, *17*, 5029-5037.

[13] For a related example of the use of elemental selenium in C–H activation strategy, see: M. Iwasaki, N. Miki, Y. Tsuchiya, K. Nakajima, Y. Nishihara, *Org. Lett.* **2017**, *19*, 1092-1095.

[14] T. Fukutani, K. Hirano, T. Satoh, M. Miura, *J. Org. Chem.* **2011**, *76*, 2867-2874.

[15] A similar reaction was reported under electro-catalytic conditions: W.-J. Kong, L. H. Finger, J. C. A. Oliveira, L. Ackermann, *Angew. Chem. Int. Ed.* **2019**, 58, 6342-6346; *Angew. Chem.* **2019**, *131*, 6408-6412.

[16] For related benzo[*b*]thiophene synthesis via formal three-component reactions, see: a) S. L. Buchwald, Q. Fang, *J. Org. Chem.* **1989**, *54*, 2793-2797; b) B. Wu, N. Yoshikai, *Angew. Chem. Int. Ed.* **2013**, *52*, 10496-10499; *Angew. Chem.* **2013**, *125*, 10690-10693.

[17] For recent examples, see: a) Y. Wang, S. Zou, J. Gao, H. Zhang, G. Lai, C. Yang, H. Xie, R. Fang, H. Li, W. Hu, *Chem. Commun.* **2015**, *51*, 11961-11963; b) D. Dang, J. Fan, X. Wang, M. Xiao, J. Shi, P. Zhou, X. Duan, G. Lei, Y. Liu, W. Zhu, *New J. Chem.* **2015**, *39*, 2224-2232; c) D. Dang, M. Xiao, P. Zhou, J. Zhong, J. Fan, N. Su, W. Xiong, C. Yang, Q. Wang, Y. Wang, Y. Pei, R. Yang, W. Zhu, *Eur. J. Org. Chem.* **2015**, *2015*, 820-827; d) M. L. Keshtov, Y. Geng, S. A. Kuklin, A. R. Khokhlov, E. N. Koukaras, G. D. Sharma, *Org. Electron.* **2015**, *17*, 167-177; e) H. Y. Cho, L. T. Scott, *Tetrahedron Lett.* **2015**, *56*, 3458-3462; f) F. Magnan, B. Gabidullin, J. L. Brusso, *RSC Advances* **2016**, *6*, 97420-97429; g) I. García-Benito, I. Zimmermann, J. Urieta-Mora, J. Aragó, A. Molina-Ontoria, E. Ortí, N. Martín, M. K. Nazeeruddin, *J. Mater. Chem. A* **2017**, *5*, 8317-8324; h) S.-Y. Chen, Y.-C. Pao, S. K. Sahoo, W.-C. Huang, Y.-Y. Lai, Y.-J. Cheng, *Chem. Commun.* **2018**, *54*, 1517-1520; i) J. Urieta-Mora, I. Zimmermann, J. Aragó, A. Molina-Ontoria, E. Ortí, N. Martín, M. K. Nazeeruddin, *Chem. Mater.* **2019**, *31*, 6435-6442.

[18] One of the possible reasons for the reproducibility issue of the reaction with arylboronic acids is due to the inhibition by varying amount of water in the medium. Actually, addition of H_2O (1.0 equiv) to the reaction of **1a** with **2a** under the standard conditions significantly decreased the yield of **3aa** (<5% yield). However, addition of desiccants such as molecular sieves and calcium sulfate could not improve the product yield.

[19] Sulfur atom transfer from polysulfide to the Rh(III)-C bond was reported: a) M. Arisawa, M. Ashikawa, A. Suwa, M. Yamaguchi, *Tetrahedron Lett.* **2005**, *46*, 1727-1729; b) M. Arisawa, K. Tanaka, M. Yamaguchi, *Tetrahedron Lett.* **2005**, *46*, 4797-4800; c) M. Arisawa, T. Ichikawa, M. Yamaguchi, *Org. Lett.* **2012**, *14*, 5318-5321.

[20] a) T. Nagata, T. Satoh, Y. Nishii, M. Miura, *Synlett* **2016**, *27*, 1707-1710; b) S.; Xu, B. Huang, G. Qiao, Z. Huang, Z. Zhang, Z. Li, P. Wang, Z. Zhang, *Org. Lett.* **2018**, *20*, 5578-5582.

[21] Cyclic hypervalent iodonium reagents were reported to react with elemental sulfur to give dibenzothiophenes: a) M. Shimizu, M. Ogawa, T. Tamagawa, R. Shigitani, M. Nakatani, Nakano, Y. *Eur. J. Org. Chem.* **2016**, 2785-2788; b) M. Wang, Q. Fan, X. Jiang, *Org. Lett.* **2016**, *18*, 5756-5759.

[22] Y. Masuya, M. Tobisu, N. Chatani, *Org. Lett.* **2016**, *18*, 4312-4315.

Synthesis of Benzo[*b*]thiophenes through Rhodium-Catalyzed Three-Component Reaction using Elemental Sulfur

Adv. Synth. Catal. **Year**, *Volume*, Page – Page

Sanghun Moon, Moena Kato, Yuji Nishii,* Masahiro Miura*