Angewandte Chemie
International Edition

Aromatic Compounds

International Edition: DOI: 10.1002/anie.201501992
German Edition: DOI: 10.1002/ange.201501992

Palladium-Assisted “Aromatic Metamorphosis” of Dibenzothiophenes into Triphenylenes**

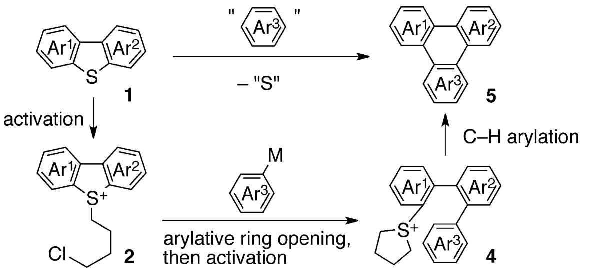
Dhananjayan Vasu, Hideki Yorimitsu, and Atsuhiro Osuka*

Abstract: *Two new palladium-catalyzed reactions of aromatic sulfur compounds enabled the conversion of dibenzothiophenes into triphenylenes in four steps. This transformation of one aromatic framework into another consists of 1) 4-chlorobutylation of the dibenzothiophene to form the corresponding sulfonium salt, 2) palladium-catalyzed arylative ring opening of the sulfonium salt with a sodium tetraarylborate, 3) an intramolecular S_N2 reaction to form a teraryl sulfonium salt, and 4) palladium-catalyzed intramolecular C−S/C−H coupling through electrophilic palladation. Symmetrical as well as unsymmetrical triphenylenes of interest were synthesized in a tailor-made fashion in satisfactory overall yields.*

The fundamental nature of aromatic compounds is governed by the specific characteristics of the aromatic rings they contain. Aromatic rings are generally stable and thus unbreakable except under harsh or special conditions. The conversion of an aromatic system into a different aromatic system is challenging.[1] Developments in transition-metal catalysis in the last decade now enable some transformations of this type. Specifically, triazoles and related high-energy triazaarenes undergo catalytic denitrogenative transannulation with unsaturated compounds, such as alkynes and nitriles, to afford other aromatic systems.[2] There still remains ample room to develop novel strategies for the conversion of aromatic systems into other aromatic systems with the aid of catalysts.

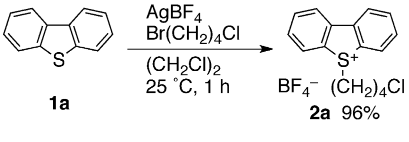
Sulfur-containing heteroaromatic skeletons, such as thiophene, are found widely in bioactive compounds and organic electronics as well as abundantly in unrefined oils.[3] The catalytic cleavage of thiophenes is usually difficult because sulfur species strongly poison transition-metal catalysts. Although desulfurization–hydrogenation is an important heterogeneous catalytic process in oil refining,[4] there are no reports on the catalytic conversion of thiophene units into other aromatic molecules.[5,6] Herein we report a strategy for the transformation of dibenzothiophenes into triphenylenes with the aid of palladium catalysis. Triphenylenes have been attracting increasing attention owing to their broad application in liquid crystals, OLEDs, and photoconductive and optical data-storage devices.[7] However, the tailor-made synthesis of multisubstituted triphenylenes remains a challenge because of their symmetrical and planar structures.[8,9]

Our strategy began with the activation of dibenzothiophenes **1** as sulfonium salts **2** with diminishment of the Lewis basicity of the sulfur atom (Scheme 1). The activated sulfonium salt **2** had been expected to undergo smooth cross-coupling with an aryl nucleophile.[10–12] The product of ring opening, a 4-chlorobutyl teraryl sulfide **3**, would be activated again through the formation of the corresponding cyclic sulfonium salt **4**. Intramolecular C−H arylation of **4** should finalize our aromatic metamorphosis, although there have been no reports of catalytic C−H arylation[13] with an aromatic sulfur compound as an electrophilic partner.



Scheme 1. Strategy for the aromatic metamorphosis of dibenzothiophenes into triphenylenes (M = metal).

The first step occurred readily through a $AgBF_4$-mediated S_N2 reaction[14] of dibenzothiophenes with a 1-halo-4-chlorobutane [Eq. (1); see also the Supporting Information].



(1)

We next examined the arylative ring opening of **2**. However, **2** suffered from rapid dealkylative decomposition owing to the high leaving-group ability of the dibenzothiophene unit. Typical Suzuki–Miyaura or Migita–Kosugi–Stille conditions were ineffective and provided **1a** as the unwanted main product (see the Supporting Information for details). The former reaction requires basic conditions that are not

---

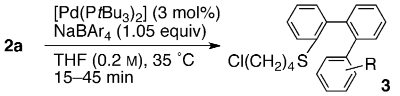
[*] Dr. D. Vasu, Prof. Dr. H. Yorimitsu, Prof. Dr. A. Osuka
Department of Chemistry, Graduate School of Science
Kyoto University
Sakyo-ku, Kyoto 606-8502 (Japan)
E-mail: yori@kuchem.kyoto-u.ac.jp
Prof. Dr. H. Yorimitsu
ACT-C, JST
Sakyo-ku, Kyoto 606-8502 (Japan)

[**] This research was supported by Grants-in-Aid from MEXT (No. 25107002 “Science of Atomic Layers”) and from the JSPS (Nos. 24685007 (Young Scientists (A)) and 26620081 (Exploratory Research)). D.V. acknowledges a JSPS Postdoctoral Fellowship.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201501992.

compatible with **2**, and the latter led to the direct dealkylation of **2** with a phenyltin reagent. These unsuccessful results suggested that desired aryl metal species should show exquisite reactivity in the smooth transfer of their aryl group to palladium without the aid of an additional base and should remain unreactive toward the sulfonium salt **2**. With these guidelines in mind, we eventually devised a combination of a sodium tetraarylborate[15] and a $[\mathrm{Pd}(\mathrm{P}t\mathrm{Bu}_3)_2]$ catalyst[16] for the desired transformation under mild additive-free conditions (Table 1). A variety of tetraarylborates participated in the arylative ring-opening reaction. All reactions proceeded to completion within 45 min at 35 °C, which highlights the high efficiency of the ring opening.

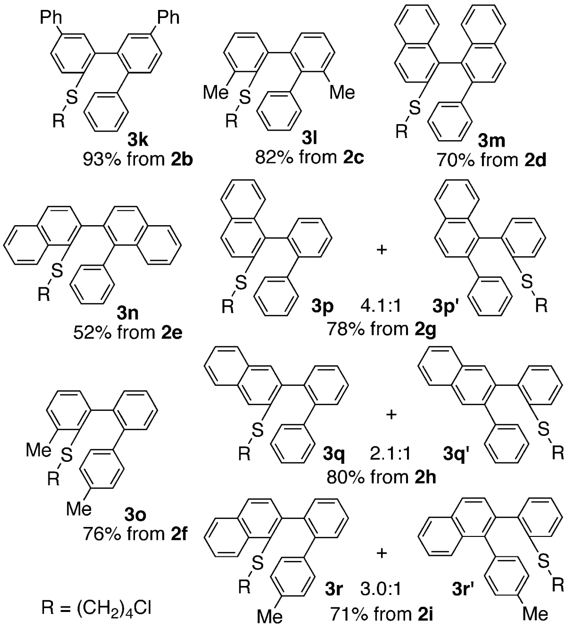
Table 1: Arylative ring opening of **2a** with NaBAr_4.



R	3	Yield [%]	R	3	Yield [%]
H	**3a**	81	4-F	**3f**	88
3-Me	**3b**	79	4-Cl	**3g**	77
4-Me	**3c**	80	3,4-$\mathrm{OCH_2O}$	**3h**	84
3-MeO	**3d**	89	(2-naphthyl)[a]	**3i**	73
4-MeO	**3e**	83	4-CHO[b]	**3j**	88

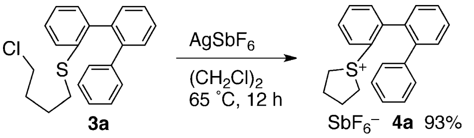
[a] $\mathrm{NaB(2\text{-}C_{10}H_7)_4}$ was used. [b] $\mathrm{NaB[C_6H_4\text{-}4\text{-}CH(OMe)_2]_4}$ was used. Compound **3j** was obtained after hydrolysis with $\mathrm{I_2}$ in aqueous acetone.

The results of the arylative ring opening of substituted dibenzothiophene sulfonium salts are shown in Scheme 2. The ring-opening reaction was powerful enough to yield the highly crowded products **3l** and **3n** as well as the quinquephenyl derivative **3k**. Unsymmetrical **2f** underwent regioselective ring opening at the less hindered C–S bond to form **3o** exclusively. This kinetic control also operated in the reactions of benzonaphthothiophenes **2g–i**, albeit with modest regioselectivity.[17]



Scheme 2. Products of the arylative ring opening of **2b–i** (the structures of which are shown in the Supporting Information).

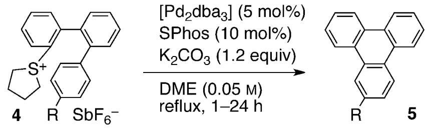
The treatment of **3** with $\mathrm{AgSbF_6}$ led to highly efficient $\mathrm{S_N2}$ cyclization to give the corresponding teraryl sulfonium salts **4** [Eq. (2); see also the Supporting Information].



(2)

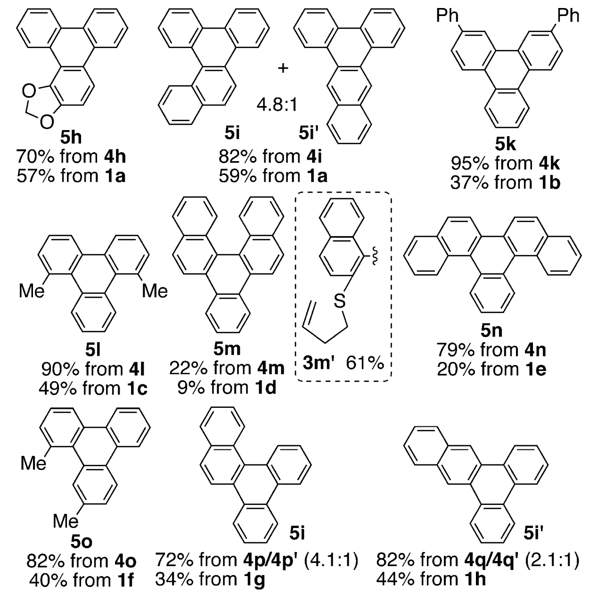
With compounds **4** in hand, we screened reaction conditions extensively for the final intramolecular C–H arylation (see the Supporting Information for details). Fortunately, a Pd/SPhos catalyst[18] proved to be uniquely effective for the generation of triphenylenes **5** (Table 2, Scheme 3; see also the Supporting Information). This transformation is a rare example of C–H arylation involving organosulfur compounds as electrophilic arylating agents.[19] The reactions generally furnished the desired triphenylenes **5** in high to excellent yields. The four-step overall yields are satisfactory in most cases. The electronic nature of a substituent at the 4-position had little effect on the reaction efficiency (Table 2). The compatibility of a formyl group with the reaction conditions enabled the formation of **5j**. The cyclization reactions of 3-substituted substrates **4b**, **4d**, **4h**, and **4i** posed a regioselectivity issue (Scheme 3; see also the Supporting Information). The regioselectivity was broadly in favor of the formation of the more congested triphenylenes. Notably, the cyclization of 3,4-methylenedioxy-substituted **4h** yielded **5h** with exclusive regioselectivity. The regioselectivity of the formation of naphthyl-derived **5i**/**5i′** was as high as 4.8:1, whereas that observed for the reactions of **4b** and **4d** (R = 3-Me and 3-OMe, respectively, in the precursor structure **3** in Table 1) was almost negligible. Steric repulsion around the sulfur atom in **4l**, **4n**, and **4o** had no influence on the efficiency of the cyclization. In contrast, **5m** was obtained in only 22 % yield along with the elimination product **3m′**, probably because of the outer-sphere steric repulsion in the binaphthyl backbone. The reaction of an isomeric mixture of **4p** and **4p′** led to the convergent formation of **5i**. Similarly, a mixture of **4q** and **4q′**

Table 2: Palladium-catalyzed cyclization of **4**.



R	5	Yield from **4** [%] (yield from **1** [%])	R	5	Yield from **4** [%] (yield from **1** [%])
H	**5a**	92 (70)	F	**5f**	98 (70)
Me	**5c**	89 (66)	Cl	**5g**	84 (54)
MeO[a]	**5e**	98 (73)	CHO	**5j**	86 (52)

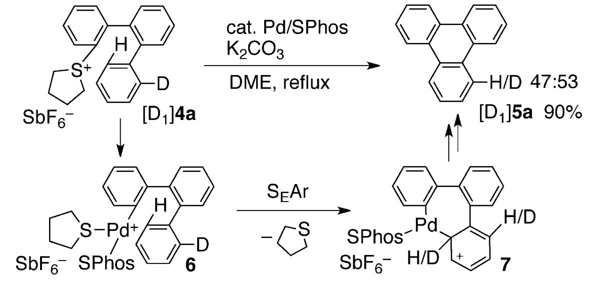
[a] The reaction was carried out with 6 mol % of $[\mathrm{Pd_2dba_3}]$ and 12 mol % of SPhos. dba = dibenzylideneacetone, DME = dimethoxyethane, SPhos = 2-dicyclohexylphosphanyl-2′,6′-dimethoxybiphenyl.



Scheme 3. Triphenylene products **5h**, **5i**, and **5k–o**. Reaction conditions are described in Table 2. For the reaction of **4h**, 10 mol% of $[Pd_2dba_3]$ and 20 mol% of SPhos were used.

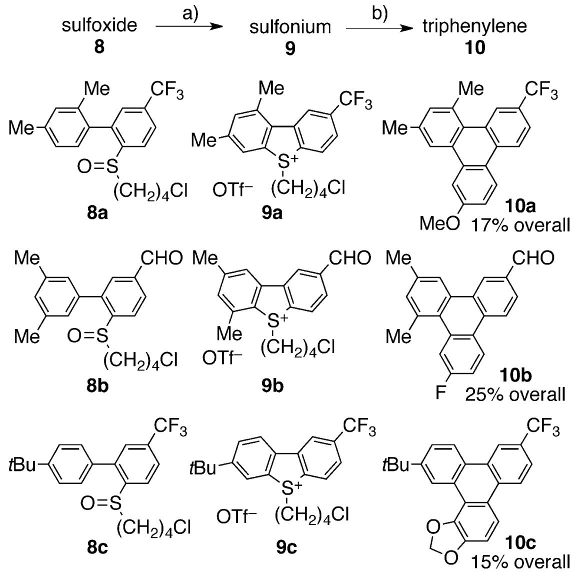
converged into the sole product **5i′**. Given that a mixture of **5i**/**5i′** was obtained from **4i**, well-designed synthetic pathways would offer tailor-made syntheses of appropriately substituted triphenylenes.

To clarify the reaction mechanism for the C–H arylation process, *ortho*-monodeuterated $[D_1]$**4a** was prepared and subjected to the cyclization conditions (Scheme 4). We found that half of the deuterium remained in the product and observed only a small kinetic isotope effect. This result indicates that the reaction mechanism includes oxidative addition of the $C(sp^2)$–S bond to form the corresponding cationic aryl palladium intermediate **6**, which would then undergo electrophilic aromatic substitution via **7** as the C–H palladation step.[13,20,21]



Scheme 4. Deuterium-labeling experiment.

Dibenzothiophene sulfonium salts were alternatively accessible by the cyclization of 2-arylphenyl sulfoxides under Pummerer-like conditions.[22,23] Sulfoxides **8**, readily prepared by cross-coupling biaryl synthesis, underwent Tf_2O-mediated electrophilic cyclization to provide sulfonium triflates **9** efficiently (Scheme 5; see Schemes S4–S6 in the Supporting Information for details). Sulfonium triflates **9** were converted into triphenylenes **10** in good overall yields in five steps from **8**. This strategy will be useful for synthesizing multisubstituted triphenylenes in a precisely controlled manner.



Scheme 5. Synthesis of multisubstituted triphenylenes through Tf_2O-mediated sulfonium formation: a) Tf_2O (2 equiv), $(CH_2Cl)_2$, 25 °C, 15–30 min; b) see reaction conditions in Table 1, Equation (2), and Table 2. Tf = trifluoromethanesulfonyl.

In conclusion, we have developed an "aromatic metamorphosis" of dibenzothiophenes into triphenylenes by inventing two new palladium-catalyzed arylation reactions. Owing to the invaluable roles played by aromatic core structures, aromatic metamorphosis could be a game-changing strategy in organic chemistry. Investigations to develop new forms of aromatic metamorphosis are under way in our laboratory.

Keywords: C–H arylation · C–S cleavage · cross-coupling · palladium · sulfur

---

[1] For Diels–Alder reactions of five-membered heteroaromatic rings and azines with alkenes or alkynes to provide the corresponding aromatic rings with extrusion of their heteroatomic units, see: a) A. Criado, M. Vilas-Varela, A. Cobas, D. Pérez, D. Peña, E. Guitián, *J. Org. Chem.* **2013**, *78*, 12637; b) X. Ding, S. T. Nguyen, J. D. Williams, N. P. Peet, *Tetrahedron Lett.* **2014**, *55*, 7002; c) S. P. J. T. Bachollet, J. F. Vivat, D. C. Cocker, H. Adams, J. P. A. Harrity, *Chem. Eur. J.* **2014**, *20*, 12889; d) S. Suzuki, Y. Segawa, K. Itami, J. Yamaguchi, *Nat. Chem.* **2015**, *7*, 227.

[2] a) S. Chuprakov, F. W. Hwang, V. Gevorgyan, *Angew. Chem. Int. Ed.* **2007**, *46*, 4757; *Angew. Chem.* **2007**, *119*, 4841; b) T. Horneff, S. Chuprakov, N. Chernyak, V. Gevorgyan, V. V. Fokin, *J. Am. Chem. Soc.* **2008**, *130*, 14972; c) M. Miura, M. Yamauchi, M. Murakami, *Chem. Commun.* **2009**, 1470; d) M. Miura, M. Yamauchi, M. Murakami, *Org. Lett.* **2008**, *10*, 3085; e) S. Chuprakov, S. W. Kwok, V. V. Fokin, *J. Am. Chem. Soc.* **2013**,

135, 4652; for reviews, see: f) B. Chattopadhyay, V. Gevorgyan, *Angew. Chem. Int. Ed.* **2012**, *51*, 862; *Angew. Chem.* **2012**, *124*, 886; g) P. Anbarasan, D. Yadagiri, S. Rajasekar, *Synthesis* **2014**, *46*, 3004.

[3] a) S. Gronowitz, A.-B. Hörnfeldt, *Thiophenes*, Elsevier, Oxford, **2004**; b) E. Block, *Advances in Sulfur Chemistry*, JAI Press, Greenwich, **1994**; c) R. J. Cremlyn, *An Introduction of Organosulfur Chemistry*, Wiley, Chichester, **1996**; d) *Organic Sulfur Chemistry: Biochemical Aspects* (Eds.: S. Oae, T. Okuyama), CRC Press, Boca Raton, FL, **1992**.

[4] a) C. Song, *Catal. Today* **2003**, *86*, 211; b) I. V. Babich, J. A. Moulijn, *Fuel* **2003**, *82*, 607; c) R. T. Yang, A. Hernández-Maldonado, F. H. Yang, *Science* **2003**, *301*, 79.

[5] For the cross-coupling of thiophenes as 1,4-butadienyl dication equivalents, see: a) E. Wenkert, T. W. Ferreira, E. L. Michelotti, *J. Chem. Soc. Chem. Commun.* **1979**, 637; b) E. Wenkert, M. H. Leftin, E. L. Michelotti, *J. Chem. Soc. Chem. Commun.* **1984**, 617; c) M. Tiecco, M. Tingoli, E. Wenkert, *J. Org. Chem.* **1985**, *50*, 3828; d) L. Hintermann, M. Schmitz, Y. Chen, *Adv. Synth. Catal.* **2010**, *352*, 2411.

[6] For uncatalyzed transformations, see: a) Y. Li, T. Thiemann, T. Sawada, S. Mataka, M. Tashiro, *J. Org. Chem.* **1997**, *62*, 7926; b) T. Thiemann, H. Fujii, D. Ohira, K. Arima, Y. Li, S. Mataka, *New J. Chem.* **2003**, *27*, 1377; see also Ref. [1c] and [1d].

[7] a) S. Laschat, A. Baro, N. Steinke, F. Giesselmann, C. Hägele, G. Scalia, R. Judele, E. Kapatsina, S. Sauer, A. Schreivogel, M. Tosoni, *Angew. Chem. Int. Ed.* **2007**, *46*, 4832; *Angew. Chem.* **2007**, *119*, 4916; b) S. Sergeyev, W. Pisula, Y. H. Geerts, *Chem. Soc. Rev.* **2007**, *36*, 1902; c) K. Togashi, S. Nomura, N. Yokoyama, T. Yasuda, C. Adachi, *J. Mater. Chem.* **2012**, *22*, 20689; d) H. Wettach, S. S. Jester, A. Colsmann, U. Lemmer, N. Rehmann, K. Meerholz, S. Höger, *Synth. Met.* **2010**, *160*, 691; e) R. Freudenmann, B. Behnisch, M. Hanack, *J. Mater. Chem.* **2001**, *11*, 1618; f) S. Tanaka, C. Adachi, T. Koyama, Y. Taniguchi, *Chem. Lett.* **1998**, 975.

[8] For review on the synthesis of triphenylenes, see: a) D. Pérez, E. Guitián, *Chem. Soc. Rev.* **2004**, *33*, 274; b) D. Pérez, D. Peña, E. Guitián, *Eur. J. Org. Chem.* **2013**, 5981.

[9] For palladium-catalyzed annulation reactions to give triphenylenes, see: a) Y. Terao, H. Wakui, M. Nomoto, T. Satoh, M. Miura, M. Nomura, *J. Org. Chem.* **2003**, *68*, 5236; b) Z. Liu, X. Zhang, R. C. Larock, *J. Am. Chem. Soc.* **2005**, *127*, 15716; c) T. T. Jayanth, C.-H. Cheng, *Chem. Commun.* **2006**, 894; d) Z. Liu, R. C. Larock, *J. Org. Chem.* **2007**, *72*, 223; e) I. Nagao, M. Shimizu, T. Hiyama, *Angew. Chem. Int. Ed.* **2009**, *48*, 7573; *Angew. Chem.* **2009**, *121*, 7709; f) A. A. Cant, L. Roberts, M. F. Greaney, *Chem. Commun.* **2010**, *46*, 8671; g) M. Shimizu, I. Nagao, Y. Tomioka, T. Kadowaki, T. Hiyama, *Tetrahedron* **2011**, *67*, 8014; h) M. Iwasaki, S. Iino, Y. Nishihara, *Org. Lett.* **2013**, *15*, 5326; i) K. Ozaki, K. Kawasumi, M. Shibata, H. Ito, K. Itami, *Nat. Commun.* **2015**, *6*, 6251.

[10] For the activation of compounds as sulfonium salts, see: a) J. Srogl, G. D. Allred, L. S. Liebeskind, *J. Am. Chem. Soc.* **1997**, *119*, 12376; b) S. Zhang, D. Marshall, L. S. Liebeskind, *J. Org. Chem.* **1999**, *64*, 2796; c) A. Zapf, *Angew. Chem. Int. Ed.* **2003**, *42*, 5394; *Angew. Chem.* **2003**, *115*, 5552; d) H. Lin, X. Dong, Y. Li, Q. Shen, L. Lu, *Eur. J. Org. Chem.* **2012**, 4675.

[11] For reviews on the cross-coupling of organosulfur compounds, see: a) S. R. Dubbaka, P. Vogel, *Angew. Chem. Int. Ed.* **2005**, *44*, 7674; *Angew. Chem.* **2005**, *117*, 7848; b) L. Wang, W. He, Z. Yu, *Chem. Soc. Rev.* **2013**, *42*, 599; c) S. G. Modha, V. P. Mehta, E. V. Van der Eycken, *Chem. Soc. Rev.* **2013**, *42*, 5042; d) F. Pan, Z.-J. Shi, *ACS Catal.* **2014**, *4*, 280; e) H. Prokopcová, C. O. Kappe, *Angew. Chem. Int. Ed.* **2008**, *47*, 3674; *Angew. Chem.* **2008**, *120*, 3732; f) E. C. Garnier-Amblard, L. S. Liebeskind, *Boronic Acids*, 2nd ed. (Ed.: D. G. Hall), Wiley-VCH, Weinheim, **2011**, chap. 7.

[12] For our cross-coupling reactions of aryl sulfides, see: a) Y. Ookubo, A. Wakamiya, H. Yorimitsu, A. Osuka, *Chem. Eur. J.* **2012**, *18*, 12690; b) K. Murakami, H. Yorimitsu, A. Osuka, *Angew. Chem. Int. Ed.* **2014**, *53*, 7510; *Angew. Chem.* **2014**, *126*, 7640; c) T. Sugahara, K. Murakami, H. Yorimitsu, A. Osuka, *Angew. Chem. Int. Ed.* **2014**, *53*, 9329; *Angew. Chem.* **2014**, *126*, 9483; d) S. Otsuka, D. Fujino, K. Murakami, H. Yorimitsu, A. Osuka, *Chem. Eur. J.* **2014**, *20*, 13146; e) A. Baralle, S. Otsuka, V. Guérin, K. Murakami, H. Yorimitsu, A. Osuka, *Synlett* **2015**, *26*, 327.

[13] a) D. Alberico, M. E. Scott, M. Lautens, *Chem. Rev.* **2007**, *107*, 174; b) T. Satoh, M. Miura, *Chem. Lett.* **2007**, *36*, 200; c) L. C. Campeau, D. R. Stuart, K. Fagnou, *Aldrichimica Acta* **2007**, *40*, 35; d) I. V. Seregin, V. Gevorgyan, *Chem. Soc. Rev.* **2007**, *36*, 1173; e) L. C. Lewis, R. G. Bergman, J. A. Ellman, *Acc. Chem. Res.* **2008**, *41*, 1013; f) F. Kakiuchi, T. Kochi, *Synthesis* **2008**, 3013; g) O. Daugulis, H.-Q. Do, D. Shabashov, *Acc. Chem. Res.* **2009**, *42*, 1074; h) A. A. Kulkarni, O. Daugulis, *Synthesis* **2009**, 4087; i) X. Chen, K. M. Engle, D.-H. Wang, J.-Q. Yu, *Angew. Chem. Int. Ed.* **2009**, *48*, 5094; *Angew. Chem.* **2009**, *121*, 5196; j) L. Ackermann, R. Vicente, A. R. Kapdi, *Angew. Chem. Int. Ed.* **2009**, *48*, 9792; *Angew. Chem.* **2009**, *121*, 9976; k) F. Bellina, R. Rossi, *Tetrahedron* **2009**, *65*, 10269; l) C.-L. Sun, B.-J. Li, Z.-J. Shi, *Chem. Commun.* **2010**, *46*, 677; m) T. W. Lyons, M. S. Sanford, *Chem. Rev.* **2010**, *110*, 1147; n) A. Lei, W. Liu, C. Liu, M. Chen, *Dalton Trans.* **2010**, *39*, 10352; o) K. Hirano, M. Miura, *Synlett* **2011**, 294; p) C. Liu, H. Zhang, W. Sui, A. Lei, *Chem. Rev.* **2011**, *111*, 1780; q) J. Wencel-Delord, T. Dröge, F. Liu, F. Glorius, *Chem. Soc. Rev.* **2011**, *40*, 4740; r) L. Ackermann, *Chem. Rev.* **2011**, *111*, 1315; s) J. Yamaguchi, A. D. Yamaguchi, K. Itami, *Angew. Chem. Int. Ed.* **2012**, *51*, 8960; *Angew. Chem.* **2012**, *124*, 9092; t) H. Yorimitsu, A. Osuka, *Asian J. Org. Chem.* **2013**, *2*, 356; u) F. Shibahara, T. Murai, *Asian J. Org. Chem.* **2013**, *2*, 624; v) G. Rouquet, N. Chatani, *Angew. Chem. Int. Ed.* **2013**, *52*, 11726; *Angew. Chem.* **2013**, *125*, 11942; w) R. Rossi, F. Bellina, M. Lessi, C. Manzini, *Adv. Synth. Catal.* **2014**, *356*, 17; x) M. He, J.-F. Soulé, H. Doucet, *ChemCatChem* **2014**, *6*, 1824; y) R. Rossi, F. Bellina, M. Lessi, C. Manzini, L. A. Perego, *Synthesis* **2014**, *46*, 2833; z) M. Miura, T. Satoh, K. Hirano, *Bull. Chem. Soc. Jpn.* **2014**, *87*, 751; aa) Y. Segawa, T. Maekawa, K. Itami, *Angew. Chem. Int. Ed.* **2015**, *54*, 66; *Angew. Chem.* **2015**, *127*, 68.

[14] K. K. Laali, J.-H. Chun, T. Okazaki, S. Kumar, G. L. Borosky, C. Swartz, *J. Org. Chem.* **2007**, *72*, 8383.

[15] For pioneering work on NaBAr$_4$ in palladium-catalyzed coupling, see: a) H. Kurosawa, S. Ogoshi, Y. Kawasaki, S. Murai, M. Miyoshi, I. Ikeda, *J. Am. Chem. Soc.* **1990**, *112*, 2813; b) J.-Y. Legros, J.-C. Fiaud, *Tetrahedron Lett.* **1990**, *31*, 7453; c) M. Catellani, G. P. Chiusoli, F. Vilma, *Gazz. Chim. Ital.* **1990**, *120*, 779; for base-free coupling with NaBAr$_4$, see: d) Y. M. A. Yamada, T. Watanabe, T. Beppu, N. Fukuyama, K. Torii, Y. Uozumi, *Chem. Eur. J.* **2010**, *16*, 11311; e) J. Yan, Z. Zhou, M. Zhu, *Synth. Commun.* **2006**, *36*, 1495.

[16] a) M. Matsumoto, H. Yoshioka, K. Nakatsu, T. Yoshida, S. Otsuka, *J. Am. Chem. Soc.* **1974**, *96*, 3322; b) A. F. Littke, C. Dai, G. C. Fu, *J. Am. Chem. Soc.* **2000**, *122*, 4020; c) C. Dai, G. C. Fu, *J. Am. Chem. Soc.* **2001**, *123*, 2719.

[17] The structures were determined by X-ray crystallographic analysis of the corresponding sulfonium salts **3** (see the Supporting Information for details).

[18] T. E. Barder, S. L. Buchwald, *Org. Lett.* **2004**, *6*, 2649.

[19] Just before the submission of this manuscript, the palladium-catalyzed arylation of azoles or thiazoles with aryl sulfides was reported: F. Zhu, Z.-X. Wang, *Org. Lett.* **2015**, *17*, 1601.

[20] a) M. Catellani, G. P. Chiusoli, *J. Organomet. Chem.* **1992**, *425*, 151; b) S. Pivsa-Art, T. Satoh, Y. Kawamura, M. Miura, M. Nomura, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 467; c) G. Dyker, *Angew. Chem. Int. Ed.* **1999**, *38*, 1698; *Angew. Chem.* **1999**, *111*,

1808; d) B. Martín-Matute, C. Mateo, D. J. Cárdenas, A. M. Echavarren, *Chem. Eur. J.* **2001**, *7*, 2341; e) B. S. Lane, M. A. Brown, D. Sames, *J. Am. Chem. Soc.* **2005**, *127*, 8050; f) V. Farina, in *Comprehensive Organometallic Chemistry II, Vol. 12* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, Oxford, **1995**, chap. 3.4.

[21] M. Gómez-Gallego, M. A. Sierra, *Chem. Rev.* **2011**, *111*, 4857.

[22] For reviews on extended Pummerer reactions, see: a) L. H. S. Smith, S. C. Coote, H. F. Sneddon, D. J. Procter, *Angew. Chem. Int. Ed.* **2010**, *49*, 5832; *Angew. Chem.* **2010**, *122*, 5968; 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.

[23] For the TfOH-mediated cyclization of 2-arylphenyl sulfoxides, which was not successful with our substrates, see: a) A. Haryono, K. Miyatake, J. Natori, E. Tsuchida, *Macromolecules* **1999**, *32*, 3146; b) H. Sirringhaus, R. H. Friend, C. Wang, J. Leuninger, K. Müllen, *J. Mater. Chem.* **1999**, *9*, 2095; c) T. Iwasaki, Y. Kohinata, H. Nishide, *Org. Lett.* **2005**, *7*, 755; d) S. Zhang, X. Qiao, Y. Chen, Y. Wang, R. M. Edkins, Z. Liu, H. Li, Q. Fang, *Org. Lett.* **2014**, *16*, 342.

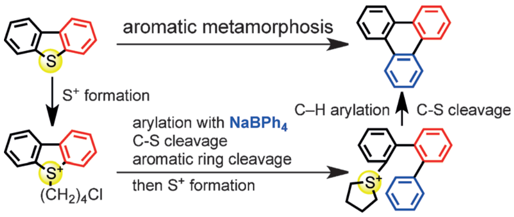
Received: March 3, 2015

Communications

Aromatic Compounds

D. Vasu, H. Yorimitsu,*
A. Osuka ________________ ▮▮▮▮–▮▮▮▮

Palladium-Assisted “Aromatic Metamorphosis” of Dibenzothiophenes into Triphenylenes



A change of heart: The invention of two palladium-catalyzed arylation reactions of organosulfur compounds enabled the transformation of dibenzothiophenes into triphenylenes and thus a fundamental change in the core aromatic structure (see scheme). Both symmetrical and unsymmetrical triphenylenes were synthesized in a tailor-made fashion in satisfactory overall yield.