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Short Synthesis of Sulfur Analogues of Polyaromatic Hydrocarbons through Three Palladium-Catalyzed C−H Bond Arylations

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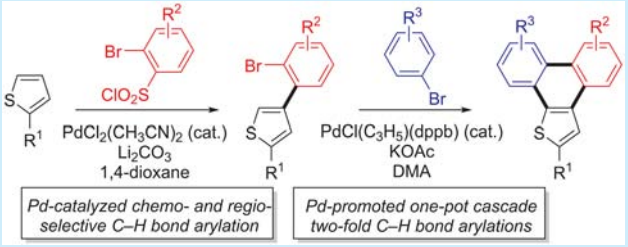
Supporting Information

ABSTRACT: An expeditious synthesis of a wide range of phenanthro[9,10-*b*]thiophene derivatives, which are a class of polyaromatic hydrocarbon (PAH) containing a sulfur atom, is reported. The synthetic scheme involves only two operations from commercially available thiophenes, 2-bromobenzenesulfonyl chlorides and aryl bromides. In the first step, palladium-catalyzed desulfitative arylation using 2-bromobenzenesulfonyl chlorides allows the synthesis of thiophene derivatives, which are substituted at the C4 position by an aryl group containing an *ortho*-bromo substituent. Then, a palladium-catalyzed one-pot cascade intermolecular C5-arylation of thiophene using aryl bromides followed by intramolecular arylation led to the corresponding phenanthro[9,10-*b*]thiophenes in a single operation. In addition, PAHs containing two or three sulfur atoms, as well as both sulfur and nitrogen atoms, were also designed by this strategy.



Sulfur analogues of polyaromatic hydrocarbones (thio-PAHs) represent an important class of molecules (Figure 1a). Especially phenanthro[9,10-*b*]thiophenes, which are subunits embedded in many important chemicals, have found numerous applications, for example, in solar cells,[1] as motifs in helicenes,[2] and in nanographenes.[3] Some of these phenanthro[9,10-*b*]thiophenes displayed unusual optical and electronic properties;[4] therefore, the discovery of a general, simple, and straightforward synthetic route of decorated thio-PAHs remains an important challenge. One of the most common routes to thio-PAHs involves a photochemical cyclization promoted by iodine, or by light (Figure 1b).[5] However, its scope is very limited due to both challenging access to starting materials and poor functional group tolerance. Photocyclodehydrofluorination has also been reported for the synthesis of 4,5,6,7-tetrafluorophenanthro[9,10-*b*]thiophene, but only one example of synthesis of thio-PAH has been described.[5f] Annulation reactions were also described for the synthesis of such thio-PAHs.[6]

During the last decades, transition-metal catalyzed direct C−H bond functionalization has emerged as a powerful methodology for the straightforward synthesis and the easy modifications of organic molecules, especially for those containing an heterocyclic motif.[7] In 2015, Kanai, Kuninobu and co-workers reported the synthesis of a phenanthro[9,10-*b*]thiophene, in which pd-catalyzed oxidative intramolecular C−H bond arylation was used as the key step (Figure 1c).[8] However, the synthesis of the precursor remains difficult and involves the pd-catalyzed cross-coupling reaction of an organometallic reagent (e.g., Grignard or boronic acid reagents). A similar strategy involving double C−H coupling for ring closing promoted by a stoichiometric amount of molybdenum(V) chloride for the synthesis of thio-PAH has been reported.[9] The starting material was also prepared via a Suzuki reaction from 3-bromobenzothiophene. These synthetic schemes, in which direct C−H bond arylation was used as the key step, provide a very powerful access to novel phenanthro-[9,10-*b*]thiophene.[8−10] In 2014, Bach and co-workers reported a novel synthetic route for the preparation of phenanthro[9,10-*c*]thiophenes involving C−H bond activation, Suzuki cross-coupling, and photocyclization.[11] However, to the best of our knowledge, there is no example of a general route involving only successive C−H bond arylation reactions from commercially available starting materials.

Originally reported by Dong and co-workers,[12] our group and others have exploited the reactivity of benzenesulfonyl chlorides for Pd-catalyzed direct regioselective arylation of several heteroarenes.[13] One of the major advantages of this methodology is that it tolerates C−X bonds (X = F, Cl, Br, I) allowing orthogonal functionalizations,[14] especially programmed synthesis by successive C−H bond functionalizations.[15] In addition, desulfitative couplings allowed the regioselective arylation of

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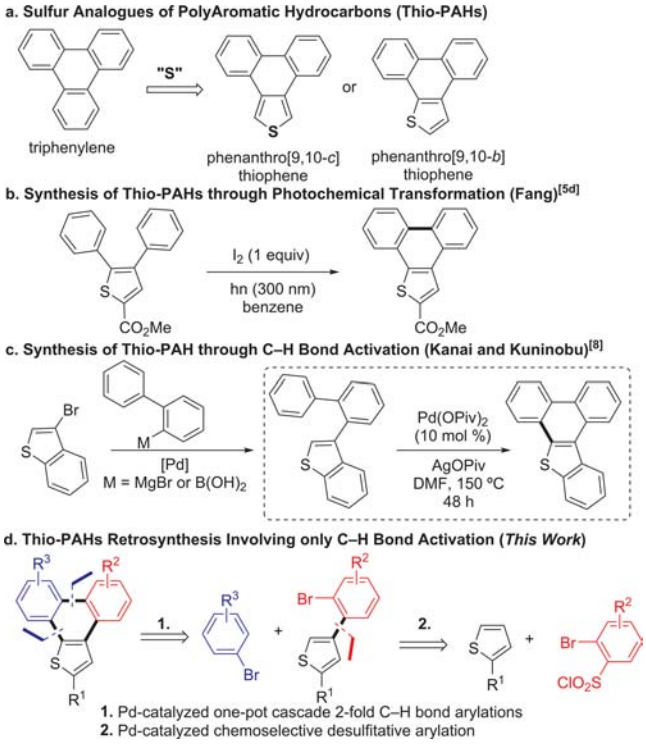
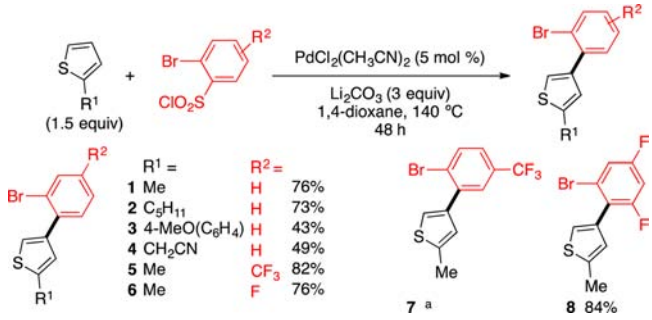


Figure 1. Thio-PAHs and their Synthesis Strategies.

electronically rich thiophenes at β-position. Recently, we succeeded in applying this orthogonal approach to the elaboration of medium-size heterocycles with a bridgehead nitrogen atom.[16] This strategy consisted in the first step to perform a direct arylation using 2-bromobenzenesulfonyl chlorides via a Pd-catalyzed desulfitative arylation followed by a Pd-catalyzed cyclization. Here, our retro-synthesis analysis to thio-PAHs first involves the preparation of 4-(2-bromophenyl)-thiophene derivatives as key intermediates. It is important to note that the access to such molecules is very challenging, owing to both the presence of the aryl C−Br bond and the unusual arylation at the C4 position of thiophenes. Then, from these derivatives and in the presence of aryl bromides, a Pd-promoted 2-fold C−H bond arylation (intermolecular at C5 position of the thiophene ring followed by an intramolecular reaction) gives a direct access to the desired thio-PAH (Figure 1d).[17]

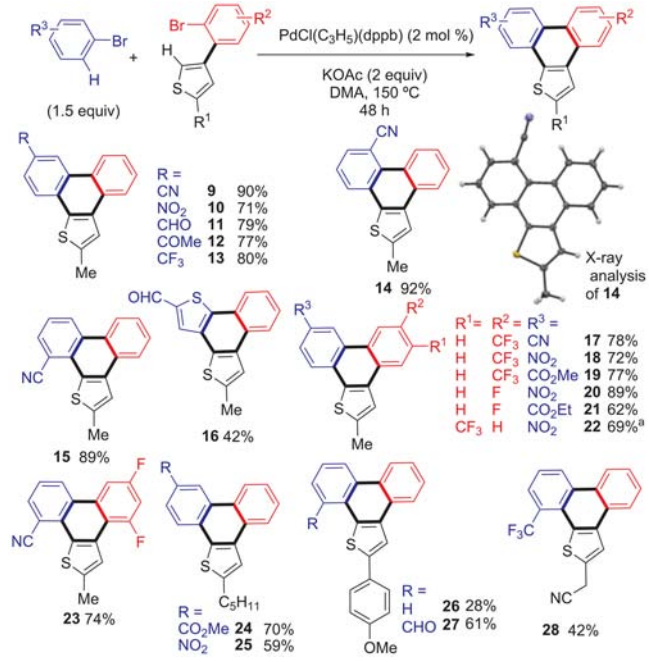
We started our study with the preparation of 4-(2-bromophenyl)thiophene derivatives, using Pd-catalyzed desulfitative direct arylation, from 2-substituted thiophenes with diversely substituted 2-bromobenzenesulfonyl chlorides (Scheme 1). In the presence of 5 mol % $PdCl_2(CH_3CN)_2$ and 3 equiv of inexpensive and safe base (Li_2CO_3), 2-methylthiophene was nicely coupled with 2-bromobenzenesulfonyl chloride to afford the C4-arylated thiophene **1** in 76% yield, without C−Br bond cleavage. Using the same reaction conditions, thiophenes substituted at C2 position by pentyl, 4-methoxyphenyl, or 2-cyanomethyl groups gave the desired product **2**-**4** in 73−43% yields. 4-Trifluoromethyl- or 4-fluoro-substituted 2-bromobenzenesulfonyl chlorides underwent desulfitative coupling with 2-methythiophene to deliver the 4-arylthiophenes **5** and **6** in 82% and 75% yields, respectively. 2-Bromo-5-trifluoromethylbenzenesulfonyl chloride also reacted nicely. However, the desired product **7** could not be isolated in a pure form and was directly used in the second step (see Scheme 2). 3-Bromo-2,4-difluorobenzenesulfonyl chloride afforded the 4-arylthiophene **8** in 84% yield.

Scheme 1. Pd-Catalyzed Direct C4 Arylation of Thiophenes Using 2-Bromobenzenesulfonyl Chlorides



[a]The product has not been isolated as pure form and it was directly used in the next step without further purification.

Scheme 2. Pd-Catalyzed One-Pot Two-Fold Direct Arylations of 4-(2-Bromophenyl)thiophene Derivatives 1−8



[a]Overall yield over two steps.

With the 4-(2-bromophenyl)thiophene derivatives **1**−**8** in hand, we next moved on to the second reaction, namely Pd-catalyzed one-pot cascade inter- and intramolecular direct arylations to allow the formation of the sulfur analogues PAHs in a single operation (Scheme 2). Notably, electron-deficient aryl bromides (i.e., more reactive than **1**−**8** regarding the oxidative addition to palladium) should be selected to favor the intermolecular C5-direct arylation and avoid the dimerization of thiophenes **1**−**8**. Initially, we selected our previous optimized reaction conditions for the direct arylation of thiophenes, namely, 2 mol % of $Pd(OAc)_2$ in the presence of KOAc in DMA.[18] However, using these conditions, the reaction between the thiophene **1** and 4-bromobenzonitrile gave a complex mixture, which included, among others, the targeted thio-PAH **9** and also the intermediate before cyclization. Using a diphosphine-

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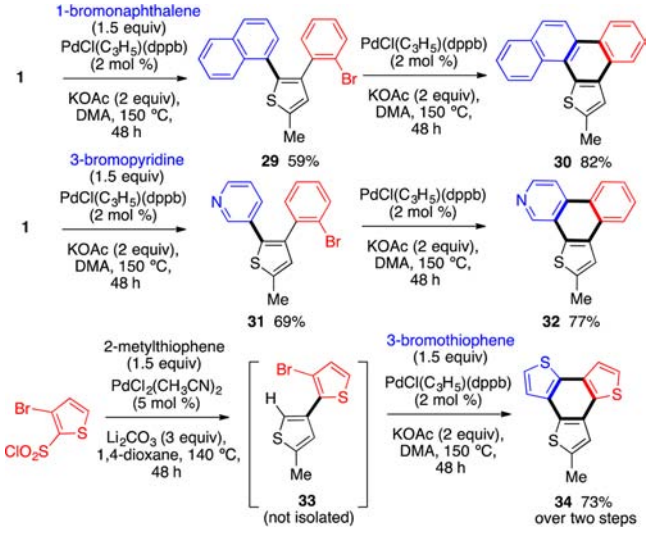
palladium catalyst [$PdCl(C_3H_5)$ (dppb)], we were pleased to find that only the desired product **9** was obtained in 90% yield. We then evaluated other *para*-substituted aryl bromides in this reaction. Functional groups such as nitro, formyl, acetyl, and trifluoromethyl were tolerated and allowed the synthesis of thio-PAHs **10**−**13** in a range of yields between 71% and 80%. Interestingly, when 3-bromobenzonitrile was used, the 2-fold C−H bond arylation afforded the single regioisomer **14** in 92% yield. Unexpectedly, the cyclization occurred at the *ortho*-position of the cyano group and not at the less sterically hindered position. The structure of **14** was secured by X-ray analysis.[19] This regioselectivity might be explained by electronic factors, such as the repulsing effect between sulfur atom and CN group,[20] or a directing group effect of the CN group. However, other *meta*-substituted aryl bromides (e.g., 3-bromobenzaldehyde, 1-bromo-3-nitrobenzene) gave complex mixtures that contained the two regioisomers in poor yields with other unidentified side-products. 2-Bromobenzonitrile allowed the synthesis of the thio-PAH **15**, again in a single operation, in 89% yield. This novel synthetic route also allowed the use of a heteroaryl bromide such as 4-bromothiophene-2-carbaldehyde for the one pot synthesis of naphtho[1,2-*b*:3,4-*b*′]dithiophene **16** in a moderate yield. Generally, such derivatives, which exhibit important applications in electronic devices, were obtained via multistep syntheses.[21] Then, we investigated the reactivity of other 4-(2-bromophenyl)-thiophene derivatives, bearing various substituents on the aryl group. The thiophene derivative **5**, which bears a trifluoromethyl substituent at the C4 position of the 4-aryl group, nicely underwent the Pd-catalyzed 2-fold C−H arylation with different aryl bromides to deliver the corresponding thio-PAHs **17**−**19** in excellent yields. A fluoro substituent was also tolerated, as the desired products **20** and **21** resulting from the coupling of the thiophene derivative **6** with 1-bromo-4-nitrobenzene or ethyl 4-bromobenzoate were obtained in 89% and 62% yields, respectively. From starting material **7**, which had not been isolated in the previous step, optimized conditions provided the thio-PAH **22** in 69% yield over the two steps. Under these reaction conditions, the thiophene derivative **8**, containing both *ortho*- and *para*-fluoro substituents on the C4-aryl ring, could also be transformed into the desired phenanthro[9,10-*b*]thiophene **23** in high yield, using 2-bromobenzonitrile as coupling partner. Then we investigated the effect of the C2 thienyl substituent. The 4-arylthiophene derivative **2**, which contains a *n*-pentyl substituent at the C2 position instead of a methyl, displayed a similar reactivity, as its reaction with methyl 4-bromobenzoate or 1-bromo-4-nitrobenzene afforded, through the 2-fold C−H bond arylations, the corresponding thio-PAH **24** and **25** in 70% and 59% yields, respectively. From thiophene **3** and bromobenzene the corresponding thio-PAH **26** was isolated in only 28% yield due to the oligomerization of **3**. Thio-PAH **27** resulting from the coupling of **3** with sterically demanding 2-bromobenzaldehyde was isolated in 61% yield. A similar reactivity trend in the coupling of 1-bromo-2-(trifluoromethyl)benzene with **4** allowed the formation of **28** in 42% overall yield.

We also investigated the reactivity of **1** for coupling with 1-bromonaphthalene in order to obtain π-extend aromatic thiaarenes such as chryseno[5,6-*b*]thiophene (Scheme 3a). Unfortunately, under the previous reaction conditions, namely 2 mol % $PdCl(C_3H_5)$(dppb) as catalyst in the presence of KOAc as base in DMA, the reaction stopped after the first step leading to compound **29** in 59% yield. Hence, we decided to perform the cyclization reaction under the same reaction conditions but from **29** (i.e., a two operation synthesis). We were pleased to find that

Scheme 3. Synthesis of thio-PAHs through Pd-Catalyzed Successive C−H Bond Arylations



cyclization reaction regioselectively occurred to afford the desired six-membererd ring cyclized product **30** in 82% yield. We next evaluated the reactivity of 3-bromopyridine under similar conditions (Scheme 3b). In the same way as that of the previous example, a two-pots procedure should be employed. Pd-catalyzed intermolecular C5 arylation of thiophene **1** with 3-bromopyridine afforded the intermediate product **31** in 69% yield. Pd-catalyzed direct arylation via C−H bond activation on a pyridine unit seems to be more challenging as only very few examples are reported in both intermolecular[22] or intramolecular versions.[23] Using the standard reaction conditions, the intermediate **31** was cyclized into **32** as a single regioisomer, resulting from the activation of the C4−H bond of the pyridine unit. Such benzo[*f*]thieno[3,2-*h*]isoquinoline units were found to have applications in electronic devices.[24] Finally, we applied this two operation synthesis to the preparation of a benzo[1,2-*b*:3,4-*b*′:5,6-*b*″]trithiophene derivative, which also finds many applications as a core unit in electronic devices, especially in solar cells (Scheme 3c).[25] 2-Methylthiophene was arylated at the C4 position using our Pd-catalyzed desulfitative arylation conditions with 3-bromothiophene-2-sulfonyl chloride to afford the bis-thiophene intermediate **33** which was found to be quite unstable.[26] To overcome its rapid decomposition, we decided to directly use it in the next step without purification. In the presence of 2 mol % $PdCl(C_3H_5)$(dppb) as catalyst associated with KOAc as base in DMA, the intermediate **33** was arylated using 3-bromothiophene as coupling partner followed by a one-pot cyclization affording the benzo[1,2-*b*:3,4-*b*′:5,6-*b*″]-trithiophene **34** in 73% yield.

In summary, we have developed a short synthetic route to the highly valuable thiophene-containing PAH frameworks involving Pd-catalyzed desulfitative regioselective C4 arylation of thiophenes with 2-bromobenzenesulfonyl chlorides followed by a Pd-promoted one-pot cascade C−H direct arylation of thiophene ring−cyclization reaction. A wide range of diversely substituted thio-PAHs have been synthesized in high yields. Additional flexibility of this synthetic approach has been demonstrated in the synthesis of PAHs containing more than one heteroatom and could be further applied in the development of novel preparations of structurally diverse PAHs. This is currently being developed in our laboratory.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b01735.

X-ray crystallographic data for **14** (CIF)

Experimental procedures, characterization data, ^{1}H and ^{13}C NMR spectra for all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Davy, N. C.; Man, G.; Kerner, R. A.; Fusella, M. A.; Purdum, G. E.; Sezen, M.; Rand, B. P.; Kahn, A.; Loo, Y.-L. *Chem. Mater.* **2016**, *28*, 673−681. (b) Zhou, W.; Zhang, Z.-G.; Ma, L.; Li, Y.; Zhan, X. *Sol. Energy Mater. Sol. Cells* **2013**, *112*, 13−19.

(2) Fujikawa, T.; Segawa, Y.; Itami, K. *J. Am. Chem. Soc.* **2016**, *138*, 3587−3595.

(3) (a) Daigle, M.; Picard-Lafond, A.; Soligo, E.; Morin, J.-F. *Angew. Chem., Int. Ed.* **2016**, *55*, 2042−2047. (b) Zhang, Q.; Peng, H.; Zhang, G.; Lu, Q.; Chang, J.; Dong, Y.; Shi, X.; Wei, J. *J. Am. Chem. Soc.* **2014**, *136*, 5057−5064.

(4) (a) Fang, K.; Huang, Y.; Chang, G.; Yang, J.; Shen, Y.; Ye, X. *Macromol. Res.* **2015**, *23*, 545−551. (b) Chen, L.; Mali, K. S.; Puniredd, S. R.; Baumgarten, M.; Parvez, K.; Pisula, W.; De Feyter, S.; Müllen, K. *J. Am. Chem. Soc.* **2013**, *135*, 13531−13537.

(5) (a) Buquet, A.; Couture, A.; Lablache-Combier, A.; Pollet, A. *Tetrahedron* **1981**, *37*, 75−81. (b) Del Mazza, D.; Reinecke, M. G. *J. Org. Chem.* **1988**, *53*, 5799−806. (c) Fischer, E.; Larsen, J.; Christensen, J. B.; Fourmigue, M.; Madsen, H. G.; Harrit, N. *J. Org. Chem.* **1996**, *61*, 6997−7005. (d) Yang, S.-M.; Shie, J.-J.; Fang, J.-M.; Nandy, S. K.; Chang, H.-Y.; Lu, S.-H.; Wang, G. *J. Org. Chem.* **2002**, *67*, 5208−5215. (e) Chiu, C.-Y.; Kim, B.; Gorodetsky, A. A.; Sattler, W.; Wei, S.; Sattler, A.; Steigerwald, M.; Nuckolls, C. *Chem. Sci.* **2011**, *2*, 1480−1486. (f) Li, Z.; Twieg, R. J. *Chem. - Eur. J.* **2015**, *21*, 15534−15539.

(6) Nagao, I.; Shimizu, M.; Hiyama, T. *Angew. Chem., Int. Ed.* **2009**, *48*, 7573−7576.

(7) (a) Kakiuchi, F.; Kochi, T. *Synthesis* **2008**, *2008*, 3013−3039. (b) Ackermann, L.; Vicente, R.; Kapdi, A. R. *Angew. Chem., Int. Ed.* **2009**, *48*, 9792−9826. (c) Bellina, F.; Rossi, R. *Tetrahedron* **2009**, *65*, 10269−10310. (d) Chen, X.; Engle, K. M.; Wang, D.-H.; Yu, J.-Q. *Angew. Chem., Int. Ed.* **2009**, *48*, 5094−5115. (e) Lyons, T. W.; Sanford, M. S. *Chem. Rev.* **2010**, *110*, 1147−1169. (f) Beck, E. M.; Gaunt, M. J. *Top. Curr. Chem.* **2009**, *292*, 85−121. (g) Satoh, T.; Miura, M. *Synthesis* **2010**, *2010*, 3395−3409. (h) Sun, C.-L.; Li, B.-J.; Shi, Z.-J. *Chem. Commun.* **2010**, *46*, 677−685. (i) Cho, S. H.; Kim, J. Y.; Kwak, J.; Chang, S. *Chem. Soc. Rev.* **2011**, *40*, 5068−5083. (j) Kuhl, N.; Hopkinson, M. N.; Wencel-Delord, J.; Glorius, F. *Angew. Chem., Int. Ed.* **2012**, *51*, 10236−10254. (k) Li, B.-J.; Shi, Z.-J. *Chem. Soc. Rev.* **2012**, *41*, 5588−5598. (l) White, M. C. *Synlett* **2012**, *23*, 2746−2748. (m) Yamaguchi, J.; Yamaguchi, A. D.; Itami, K. *Angew. Chem., Int. Ed.* **2012**, *51*, 8960−9009. (n) Kozhushkov, S. I.; Ackermann, L. *Chem. Sci.* **2013**, *4*, 886−896. (o) Rossi, R.; Bellina, F.; Lessi, M.; Manzini, C. *Adv. Synth. Catal.* **2014**, *356*, 17−117. (p) Zhang, M.; Zhang, Y.; Jie, X.; Zhao, H.; Li, G.; Su, W. *Org. Chem. Front.* **2014**, *1*, 843−895. (q) Yadav, M. R.; Rit, R. K.; Shankar, M.; Sahoo, A. K. *Asian J. Org. Chem.* **2015**, *4*, 846−864. (r) Hirano, K.; Miura, M. *Chem. Lett.* **2015**, *44*, 868−873. (s) Yuan, K.; Soulé, J.-F.; Doucet, H. *ACS Catal.* **2015**, *5*, 978−991. (t) Bheeter, C. B.; Chen, L.; Soulé, J.-F.; Doucet, H. *Catal. Sci. Technol.* **2016**, *6*, 2005−2049.

(8) Saito, K.; Chikkade, P. K.; Kanai, M.; Kuninobu, Y. *Chem. - Eur. J.* **2015**, *21*, 8365−8368.

(9) Schubert, M.; Trosien, S.; Schulz, L.; Brandscheid, C.; Schollmeyer, D.; Waldvogel, S. R. *Eur. J. Org. Chem.* **2014**, *2014*, 7091−7094.

(10) Iitsuka, T.; Hirano, K.; Satoh, T.; Miura, M. *J. Org. Chem.* **2015**, *80*, 2804−2814.

(11) Schnapperelle, I.; Bach, T. *Chem. - Eur. J.* **2014**, *20*, 9725−9732.

(12) Zhao, X.; Dimitrijević, E.; Dong, V. M. *J. Am. Chem. Soc.* **2009**, *131*, 3466−3467.

(13) (a) Zhang, M.; Zhang, S.; Liu, M.; Cheng, J. *Chem. Commun.* **2011**, *47*, 11522−11524. (b) Yu, X.; Li, X.; Wan, B. *Org. Biomol. Chem.* **2012**, *10*, 7479−7482. (c) Jafarpour, F.; Olia, M. B. A.; Hazrati, H. *Adv. Synth. Catal.* **2013**, *355*, 3407−3412. (d) Miao, T.; Li, P.; Wang, G.-W.; Wang, L. *Chem. - Asian J.* **2013**, *8*, 3185−3190. (e) Yuan, K.; Doucet, H. *Chem. Sci.* **2014**, *5*, 392−396. (f) Jin, R.; Yuan, K.; Chatelain, E.; Soulé, J.-F.; Doucet, H. *Adv. Synth. Catal.* **2014**, *356*, 3831−3841. (g) Hfaiedh, A.; Yuan, K.; Ben Ammar, H.; Ben Hassine, B.; Soulé, J.-F.; Doucet, H. *ChemSusChem* **2015**, *8*, 1794−1804.

(14) Skhiri, A.; Beladhria, A.; Yuan, K.; Soulé, J.-F.; Ben Salem, R.; Doucet, H. *Eur. J. Org. Chem.* **2015**, *2015*, 4428−4436.

(15) (a) Shibahara, F.; Yamauchi, T.; Yamaguchi, E.; Murai, T. *J. Org. Chem.* **2012**, *77*, 8815−8820. (b) Abdelmalek, F.; Derridj, F.; Djebbar, S.; Soulé, J.-F.; Doucet, H. *Beilstein J. Org. Chem.* **2015**, *11*, 2012−2020. (c) Suzuki, S.; Segawa, Y.; Itami, K.; Yamaguchi, J. *Nat. Chem.* **2015**, *7*, 227−233.

(16) Hagui, W.; Yuan, K.; Besbes, N.; Srasra, E.; Soulé, J.-F.; Doucet, H. *ChemCatChem* **2015**, *7*, 3544−3554.

(17) Iwasaki, M.; Iino, S.; Nishihara, Y. *Org. Lett.* **2013**, *15*, 5326−5329.

(18) Abdellaoui, F.; Youssef, C.; Ben Ammar, H.; Soulé, J.-F.; Doucet, H. *Synthesis* **2014**, *46*, 3341−3350.

(19) *CCDC 1485385*; Cambridge Crystallographic Data Centre.

(20) Distefano, G.; Granozzi, G.; Olivato, P. R. *J. Chem. Soc., Perkin Trans. 2* **1985**, 2037−2040.

(21) (a) Kashiki, T.; Kohara, M.; Osaka, I.; Miyazaki, E.; Takimiya, K. *J. Org. Chem.* **2011**, *76*, 4061−4070. (b) Yang, C.; Li, H.; Tong, J.; Li, J.; Zhang, P.; Xia, Y. *J. Appl. Polym. Sci.* **2016**, *133*, 43288−43296.

(22) Wasa, M.; Worrell, B. T.; Yu, J.-Q. *Angew. Chem., Int. Ed.* **2010**, *49*, 1275−1277.

(23) (a) Garcia-Cuadrado, D.; Braga, A. A. C.; Maseras, F.; Echavarren, A. M. *J. Am. Chem. Soc.* **2006**, *128*, 1066−1067. (b) Hostyn, S.; Maes, B. U. W.; Van Baelen, G.; Gulevskaya, A.; Meyers, C.; Smits, K. *Tetrahedron* **2006**, *62*, 4676−4684. (c) Garcia-Cuadrado, D.; de Mendoza, P.; Braga, A. A. C.; Maseras, F.; Echavarren, A. M. *J. Am. Chem. Soc.* **2007**, *129*, 6880−6886. (d) Marquise, N.; Harford, P. J.; Chevallier, F.; Roisnel, T.; Dorcet, V.; Gagez, A.-L.; Sable, S.; Picot, L.; Thiery, V.; Wheatley, A. E. H.; Gros, P. C.; Mongin, F. *Tetrahedron* **2013**, *69*, 10123−10133.

(24) (a) He, B.; Pun, A. B.; Klivansky, L. M.; McGough, A. M.; Ye, Y.; Zhu, J.; Guo, J.; Teat, S. J.; Liu, Y. *Chem. Mater.* **2014**, *26*, 3920−3927. (b) He, B.; Dai, J.; Zherebetskyy, D.; Chen, T. L.; Zhang, B. A.; Teat, S. J.; Zhang, Q.; Wang, L.; Liu, Y. *Chem. Sci.* **2015**, *6*, 3180−3186.

(25) (a) Meng, L.; Wu, F.; Liu, H.; Zhao, B.; Zhang, J.; Zhong, J.; Pei, Y.; Chen, H.; Tan, S. *RSC Adv.* **2015**, *5*, 14540−14546. (b) Gu, C.; Huang, N.; Chen, Y.; Qin, L.; Xu, H.; Zhang, S.; Li, F.; Ma, Y.; Jiang, D. *Angew. Chem., Int. Ed.* **2015**, *54*, 13594−13598. (c) Yin, J.; Chaitanya, K.; Ju, X.-H. *J. Theor. Comput. Chem.* **2015**, *14*, 1550058. (d) Molina-Ontoria, A.; Zimmermann, I.; Garcia-Benito, I.; Gratia, P.; Roldan-Carmona, C.; Aghazada, S.; Graetzel, M.; Nazeeruddin, M. K.; Martin, N. *Angew. Chem., Int. Ed.* **2016**, *55*, 6270−6274. (e) Riano, A.; Arrechea-Marcos, I.; Mancheno, M. J.; Mayorga Burrezo, P.; de la Pena, A.; Loser, S.; Timalsina, A.; Facchetti, A.; Marks, T. J.; Casado, J.; Lopez Navarrete, J. T.; Ponce Ortiz, R.; Segura, J. L. *Chem. - Eur. J.* **2016**, *22*, 6374−6381. (f) Ringk, A.; Lignie, A.; Hou, Y.; Alshareef, H. N.; Beaujuge, P. M. *ACS Appl. Mater. Interfaces* **2016**, *8*, 12091−12100.

(26) For Pd-catalyzed desulfitative heteroarylation see: Saoudi, B.; Debache, A.; Soulé, J.-F.; Doucet, H. *RSC Adv.* **2015**, *5*, 65175−65183.

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