

Synthetic Methods

Catalytic Borylation of SCF₃-Functionalized Arenes by Rhodium(I) Boryl Complexes: Regioselective C–H Activation at the *ortho*-Position**

Sabrina I. Kalläne and Thomas Braun*

Dedicated to Professor Helmut Werner on the occasion of his 80th birthday

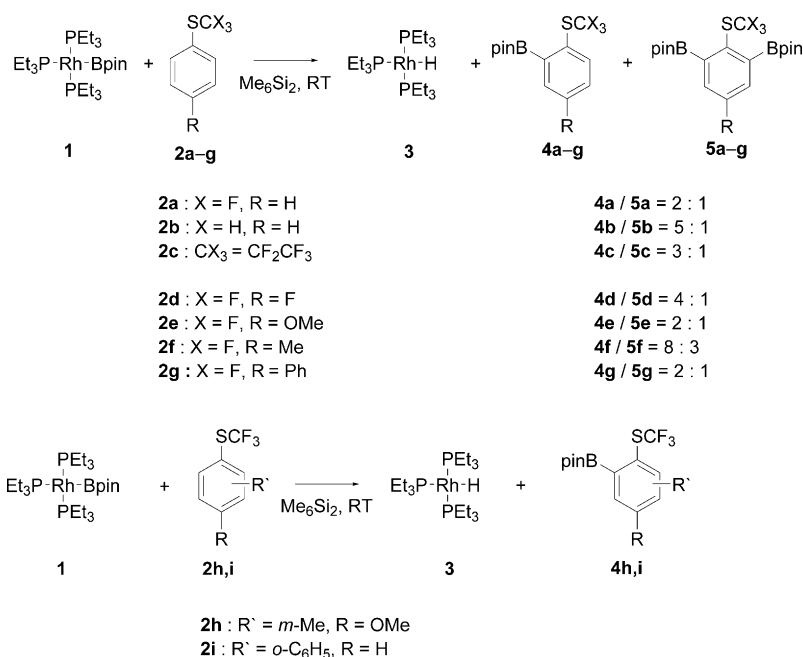
Abstract: An unprecedented reaction pathway for the borylation of SCF₃-containing arenes using [Rh(Bpin)(PEt₃)₃] (pin = pinacolato) is reported. Catalytic processes were developed and the functionalizations proceed under mild reaction conditions. The C–H activations occur with a unique regioselectivity for the position *ortho* to the SCF₃ group, which apparently serves as directing group. Borylated SCF₃ compounds can serve as versatile building blocks.

The trifluoromethylthio group is of considerable interest, because to some extent SCF₃ compounds are often characterized by a high lipophilicity, which can in turn enhance the ability of SCF₃ derivatives to cross lipid membranes and thus their biodisponibility.^[1] Moreover, the high electronegativity of a SCF₃ group ensures their stability in acidic environments.^[2] Thus, the use of the SCF₃-containing compounds as building blocks can lead to unique molecular properties and creates opportunities for the design of new bioactive substrates.^[3,4] SCF₃-functionalized compounds are, for instance, of interest in isostere-based drug design.^[5]

Numerous methods to construct the SCF₃ moiety are reported. Typical procedures involve halogen–fluorine exchange reactions at the sulfur atom or the trifluoromethylation of sulfur-containing compounds.^[6] In addition, in recent years several routes to introduce a SCF₃ building block by formation of a C–S bond were developed.^[1,4,7] However, an alternative route to access unique SCF₃ compounds consists of a functionalization of derivatives which already contain a SCF₃ group. Such an

approach can also involve the introduction of highly valuable entities, such as boryl groups, which might be beneficial for further derivatization reactions.

Herein, we report on the catalytic borylation of SCF₃-containing arenes by C–H activation on using the highly reactive rhodium(I) boryl complex [Rh(Bpin)(PEt₃)₃] (**1**) (pin = pinacolato) as the catalyst.^[8,9] The reactions proceed under mild reaction conditions and are distinguished by their



Scheme 1. Selective C–H borylation of phenyl sulfides at the position *ortho* to the thioether group.

selectivity for functionalization at the position *ortho* to the SCF₃ moiety,^[7e] which presumably serves as a directing group.

Treatment of [Rh(Bpin)(PEt₃)₃] (**1**) with an equimolar amount of phenyltrifluoromethyl sulfide (**2a**) at room temperature resulted in the formation of [Rh(H)(PEt₃)₃] (**3**)^[8–10] as well as the borylated aromatics **4a** and **5a**, which are functionalized at the *ortho* position to the SCF₃ group (Scheme 1). The latter were formed in a ratio of 2:1 and were identified by ¹H, ¹¹B, ¹³C and ¹⁹F NMR spectroscopy. The

[*] Dipl.-Chem. S. I. Kalläne, Prof. Dr. T. Braun
 Department of Chemistry, Humboldt-Universität zu Berlin
 Brook-Taylor-Strasse 2, 12489 Berlin (Germany)
 E-mail: thomas.braun@chemie.hu-berlin.de

[**] We thank the Cluster of Excellence “Unifying Concepts in Catalysis” funded by the DFG for financial support. The DFG research training group “Fluorine as a Key Element” is gratefully acknowledged. We thank Dr. Beatrice Braun for the X-ray crystal structure analysis.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201406424>.

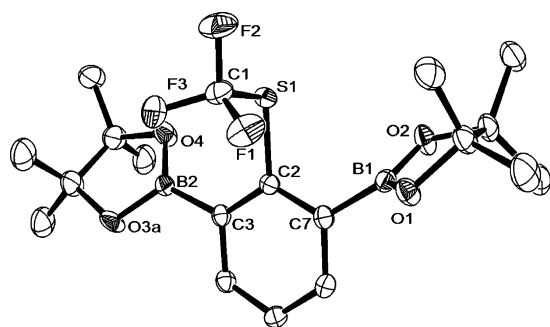


Figure 1. Molecular structure of **5a** (ORTEP, ellipsoids are set at a 50% probability).^[34] All hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: S1–C1 1.790(2), S1–C2 1.7932(19), B1–C7 1.571(3), B2–C3 1.576(3).

molecular structure of **5a** was determined by X-ray diffraction analysis (Figure 1).

To investigate the scope of the reaction, **1** was treated with the phenyl sulfides **2b** and **2c**, which contain a SCH₃ and a SCF₂CF₃ moiety, respectively. An excellent selectivity for a functionalization at the *ortho* positions was observed to give the mono- and bisborylated products **4b** and **5b** as well as **4c** and **5c**, along with **3** (Scheme 1). The conversion of **2c** is lower than that of either **2a** or **2b**. The *para*-substituted SCF₃ arenes **2d–f** can also be borylated with an analogous regioselectivity and the corresponding products **4d–f** and **5d–f** were obtained. The reaction of **1** with **2d**, which exhibits the electron-withdrawing fluorine atom at the *para* position, is faster than that with **2f** bearing an electron-donating group. No benzylic borylation was observed in the reaction of **2f**. Note that Marder et al. reported a rhodium-catalyzed borylation of toluene to primarily give benzyl boronate esters.^[11] Although **1** was used in C–F bond-activation reactions, no C–F bond-cleavage reaction was observed, neither at the SCF₃ group nor at the aromatic C–F bond of **2d**.^[8,12] The *ortho* borylation was also successful for the compounds **2h** and **2i**, bearing a methyl group at the *meta* position and a phenyl group at one *ortho* position, respectively, to the corresponding products **4h** and **4i**. Note that **2i** has no functional group at the *para* position and the selective *ortho* borylation is consistent with the results which were found for **2a–g**. For **2h** no double borylation was observed, and might be explained by the steric hindrance caused by the *meta* substituent. With the exception of **4b**^[13] all the borylated compounds **4** and **5** have not been synthesized previously.^[14] 4-Bpin-C₆H₄SCF₃, which is an isomer to **4a**, can be synthesized by Suzuki–Miyaura borylation of the aryl bromide with diboranes.^[15]

A variation of the boryl group is possible, too. Comparable regioselectivities were found upon treatment of [Rh{BO₂C₃H₄(CH₃)₂}(PET₃)₃] (**1'**)^[9a] with either **2a** or **2b** which led to the formation of the corresponding boronate esters **4a'** and **5a'**, and **4b'** and **5b'** (see the Supporting Information).

The stoichiometric C–H activation of benzene at **1** to yield PhBpin and **3** was reported before.^[8] In contrast, a reaction of **1** with 2,3,5,6-tetrafluoropyridine gave [Rh(4-C₅NF₄)(PET₃)₃] and HBpin. However, on treatment of **1** with

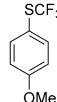
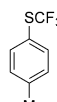
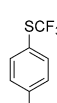
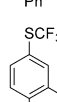
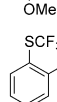
phenyl sulfides we did not observe any generation of an aryl complex.

According to the literature, the regioselectivity for C–H borylation reactions is predominantly determined by steric factors.^[16] Thus, the activation of monosubstituted arenes with transition-metal catalysts in the presence of B₂pin₂ or HBpin often leads to a mixture of functionalized arylboronate esters, in which *meta*-substituted aromatics are usually the main products.^[16,17] However, directing groups were used to achieve a catalytic borylation at the *ortho* position.^[18] These reactions involve, for instance silyl groups,^[19] carbonyl moieties,^[20] phosphines,^[21] or nitrogen-containing directing groups.^[22] The employment of the Bpin group as a traceless directing group for the borylation of nitrogen heterocycles and anilines was also demonstrated.^[23] We presume that the SCX₃ moieties also serve as directing groups.^[24,25] Although an initial coordination between rhodium and the SCX₃ moiety, which precedes the borylation at the *ortho* position, might be important, an interaction between the metal-bound Bpin entity and the sulfur atom of the SCX₃ group is also conceivable. Note that for the C–F activation of pentafluoropyridine a four-membered transition state, which involves an interaction of a fluorine atom with the boryl ligand, was suggested on the basis of DFT calculations.^[8,26] However, we did not observe any reactivity of **1** towards anisole or trifluoromethoxy benzene at room temperature, despite the assumption that the oxygen–boron interaction might be stronger than a sulfur–boron affinity. In addition, no reaction of **1** with **2a** takes place in the presence of free phosphine, thus indicating the dissociation of phosphine from **1**, presumably after precoordination of the substrate.

Based on the stoichiometric conversions, catalytic borylation reactions were developed. Treatment of **2a** with B₂pin₂ in cyclohexane at 40 °C^[27] in the presence of 12.5 mol % **1** (based on the amount of B₂pin₂) led to a mixture of **4a** and **5a**.^[28] An increase in the reaction time or the amount of B₂pin₂ yielded larger amounts of **5a** (Table 1, entries 1–5). Monitoring the reaction by NMR spectroscopy revealed that the C–H borylation of **4a** starts when the concentration of **4a** is high compared to that of **2a**. A ten-times excess of **2a** over B₂pin₂ gave only **4a**.^[18,20b,22d,e] The thioethers **2b** and **2c** are also viable substrates for producing *ortho*-borylated products under mild reaction conditions with excellent regioselectivities (entries 6–9). Moreover, the protocol is applicable to derivatives with functional groups at positions *ortho*, *meta*, or *para* to the SCF₃ group (entries 10–16). Competition experiments indicate that **2d** converts faster than **2a**, **2e**, **2f**, and **2g**, but no other relationship regarding the electronic influence of any substituent at the substrate is apparent (see the Supporting Information).

Upon using 2.5 mol % of **1** (based on the amount of B₂pin₂) as the catalyst, a three-times excess of **2a**, and cyclohexane as the solvent, the TON (based on the C–H activation steps) for the formation of **4a** and **5a** improved from 9 to 39 after 20 hours at 40 °C^[29] (Scheme 2). Comparable improvements were achieved for the thioethers **2d–f** as substrates. Kinetic traces show that the conversion of **2a** is complete after 18 hours when using a 2.5 mol % catalyst

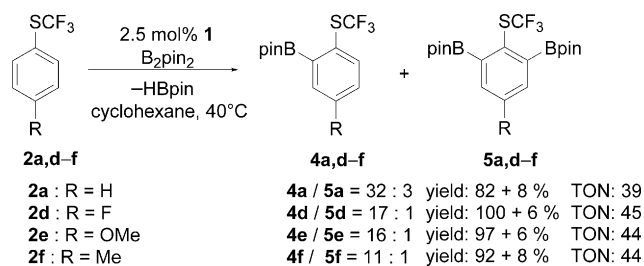
Table 1: Catalytic *ortho* borylation of **2a–i** using 12.5 mol% of the catalyst **1**.^[a,b]

$2 + B_2pin_2 \xrightarrow[\text{cyclohexane, 40}^\circ\text{C}]{12.5 \text{ mol\% } 1} 4 + 5$						
Entry	Substrate	B ₂ pin ₂ /2	t	Yield [%] ^[28,c] (4 + 5)	4/5	TON ^[d]
1		1:1	20 h	57 + 21	11:4	6
2		1:1	2 d	56 + 25	9:4	8
3		1:10	20 h	94	4a only	8
4		1:3	20 h	94 + 9	31:3	9
5		3:1	20 h	14 + 71	1:5	12
6		1:3	20 h	94 + 9	10:1	9
7		1:1	20 h	56 + 25	9:4	7
8		1:3	20 h	30 ^[e]	4c only	2
9		1:2	16 h ^[f]	76 + 5 ^[e]	14:1	7
10		1:8	14 h	94	4d only	8
11		1:3	11 h	91 + 5	18:1	8
12		1:3	20 h	99 + 5	20:1	9
13		1:3	20 h	99 + 13	15:2	10
14		1:1	20 h	60 + 14	17:4	7
15		1:1	20 h	86	4h only	7
16		1:1	20 h	87	4i only	7

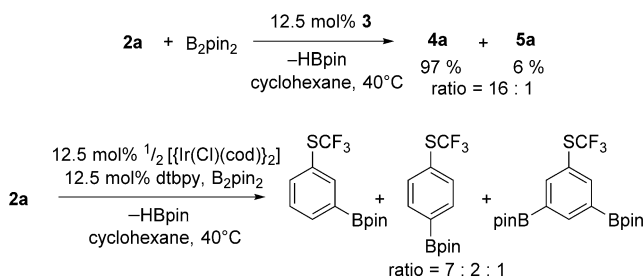
[a] Reactions were performed in a NMR tube which was equipped with a PFA inliner. [b] Yields and ratios were determined by ¹⁹F NMR spectroscopy; except for entries 6 and 7 for which by ¹H NMR spectroscopy was used. [c] Yields are based on the amount of B₂pin₂, except that for entry 5.^[28] [d] Turnover number = number of borylation steps per mole of **1**.^[28] [e] Reaction mixture also contains traces of PhBpin. [f] Reaction was performed at 50°C.

loading, whereas a higher loading led to completion after 8 hours.

Because [Rh(H)(PEt₃)₃] (**3**) was formed in the stoichiometric C–H activation reactions (Scheme 1), its capability for C–H activation at room temperature was also tested, but treatment of **3** with **2a** did not lead to any C–H bond cleavage. However, **3** is presumably an intermediate in a putative catalytic cycle and might, therefore, serve as a catalytic precursor. Indeed, **3** catalyzed the borylation of **2a** with *ortho*



Scheme 2. Catalytic borylation of phenyltrifluoromethyl sulfides.

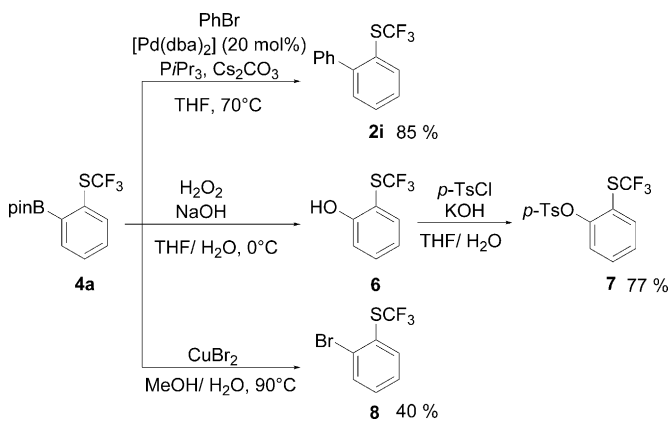


Scheme 3. Catalytic borylation of **2a** using **3** or [Ir(μ-Cl)(cod)]₂ as the catalyst.

selectivity (Scheme 3). Possibly, **1** as an active species can be generated from *fac*-[Rh(H)(Bpin)₂(PEt₃)₃], which can be furnished from **3** and B₂pin₂.^[8,9a]

The applicability of the catalytic system [Ir(μ-Cl)(cod)]₂/dtbpy (dtbpy = 4,4-di-*tert*-butylbipyridine, cod = 1,5-cyclooctadiene) in C–H borylation reactions is well known.^[16] Therefore, for comparison, its catalytic activity towards the borylation of **2a** with B₂pin₂ under the same reaction conditions was investigated. A mixture of three borylated products in a ratio of 7:2:1 was generated, and contained the *meta*-borylated arene as the major compound (Scheme 3). Interestingly, with **2b** no reaction was observed under these reaction conditions. These results with iridium are in sharp contrast to those of the borylation reactions with **1** as the catalyst, and indicate an influence of the CF₃ group. There is also no *ortho*-directed reaction step operating.

Further transformations of **4a** demonstrate its potential to serve as a building block (Scheme 4). Thus, a Suzuki–Miyaura



Scheme 4. Transformations of **4a**.

cross-coupling^[30] of **4a** with PhBr in the presence of [Pd(dba)₂] (dba = dibenzylideneacetone), P*i*Pr₃, and Cs₂CO₃ to give 2-Ph-C₆H₄SCF₃ (**2i**) was achieved. Moreover, the boronate ester **4a** was converted into the alcohol **6** by oxidation with H₂O₂. The compound **6** was treated in situ with *para*-toluenesulfonyl chloride under basic conditions to afford the tosylate **7**. The latter is presumably also a useful substrate for further reactions. In addition, it was shown that the Bpin moiety of **4a** can be replaced by a bromine atom on using CuBr₂.

In conclusion, a remarkable reaction route to access a range of SCF₃ aromatics which are borylated at the *ortho* position was developed. Doubly borylated compounds are also accessible, and are versatile building blocks.^[22g,31] The conversions impart catalytic borylation reactions of aromatic thioethers by C–H activation under mild reaction conditions. The boryl complex [Rh(Bpin)(PEt₃)₃] (**1**) serves as a catalyst and the SCX₃ groups presumably function as directing groups. Although rhodium-catalyzed arene borylation reactions are known,^[11a,32] they usually require fairly harsh reaction conditions, in contrast to iridium-catalyzed conversions.^[17,33] Moreover, the regioselectivities which were observed with **1** as catalyst are in sharp contrast to those which are typically found for iridium- or rhodium-catalyzed borylation reactions. In general, the conversions enable access to rare SCF₃ aromatics which were demonstrated to be useful starting compounds for further transformations.

Received: June 20, 2014

Published online: August 3, 2014

Keywords: boron · C–H activation · rhodium · sulfur · synthetic methods

- [1] a) A. Tlili, T. Billard, *Angew. Chem. Int. Ed.* **2013**, *52*, 6818–6819; *Angew. Chem.* **2013**, *125*, 6952–6954; b) X. Shao, X. Wang, T. Yang, L. Lu, Q. Shen, *Angew. Chem. Int. Ed.* **2013**, *52*, 3457–3460; *Angew. Chem.* **2013**, *125*, 3541–3544; c) E. V. V. Vinogradova, P. Müller, S. L. Buchwald, *Angew. Chem. Int. Ed.* **2014**, *53*, 3125–3128; *Angew. Chem.* **2014**, *126*, 3179–3192.
- [2] a) L. M. Yagupolskii, A. Y. Ilchenko, N. V. Kondratenko, *Russ. Chem. Rev.* **1974**, *32*, 32–34; b) C. Hansch, A. Leo, S. H. Unger, K. H. Kim, D. Nikaitani, E. J. Lien, *J. Med. Chem.* **1973**, *16*, 1207–1216.
- [3] a) F. Leroux, P. Jeschke, M. Schlosser, *Chem. Rev.* **2005**, *105*, 827–856; b) P. Jeschke, *Pest Manage. Sci.* **2010**, *66*, 10–27.
- [4] M. Rueping, N. Tolstoluzhsky, P. Nikolaienko, *Chem. Eur. J.* **2013**, *19*, 14043–14046.
- [5] V. N. Boiko, *Beilstein J. Org. Chem.* **2010**, *6*, 880–921.
- [6] a) E. A. Nodiff, S. Lipschutz, P. N. Craig, M. Gordon, *J. Org. Chem.* **1960**, *25*, 60–65; b) V. I. Popov, V. N. Boiko, L. M. Yagupolskii, *J. Fluorine Chem.* **1982**, *21*, 365–369; c) C. Wakselman, M. Tordeux, *J. Chem. Soc. Chem. Commun.* **1984**, 793; d) C. Wakselman, M. Tordeux, *J. Org. Chem.* **1985**, *50*, 4047–4051; e) M. Tordeux, B. Langlois, C. Wakselman, *J. Org. Chem.* **1989**, *54*, 2452–2453; f) T. Umamoto, S. Ishihara, *Tetrahedron Lett.* **1990**, *31*, 3579–3582; g) T. Umamoto, S. Ishihara, *J. Am. Chem. Soc.* **1993**, *115*, 2156–2164; h) T. Billard, B. R. Langlois, *Tetrahedron Lett.* **1996**, *37*, 6865–6868; i) S. Large, N. Roques, B. R. Langlois, *J. Org. Chem.* **2000**, *65*, 8848–8856; j) C. Pooput, M. Medebielle, W. R. Dolbier, *Org. Lett.* **2004**, *6*, 301–303; k) I. Kieltisch, P. Eisenberger, A. Togni, *Angew. Chem. Int. Ed.* **2007**, *46*, 754–757; *Angew. Chem.* **2007**, *119*, 768–771.
- [7] a) G. Teverovskiy, D. S. Surry, S. L. Buchwald, *Angew. Chem. Int. Ed.* **2011**, *50*, 7312–7314; *Angew. Chem.* **2011**, *123*, 7450–7452; b) C.-P. Zhang, D. A. Vicic, *J. Am. Chem. Soc.* **2012**, *134*, 183–185; c) F. Baert, J. Colomb, T. Billard, *Angew. Chem. Int. Ed.* **2012**, *51*, 10382–10385; *Angew. Chem.* **2012**, *124*, 10528–10531; d) C. Chen, Y. Xie, L. Chu, R.-W. Wang, X. Zhang, F.-L. Qing, *Angew. Chem. Int. Ed.* **2012**, *51*, 2492–2495; *Angew. Chem.* **2012**, *124*, 2542–2545; e) L. D. Tran, I. Popov, O. Daugulis, *J. Am. Chem. Soc.* **2012**, *134*, 18237–18240; f) Z. Weng, W. He, C. Chen, R. Lee, D. Tan, Z. Lai, D. Kong, Y. Yuan, K.-W. Huang, *Angew. Chem. Int. Ed.* **2013**, *52*, 1548–1552; *Angew. Chem.* **2013**, *125*, 1588–1592; g) S. Alazet, L. Zimmer, T. Billard, *Angew. Chem. Int. Ed.* **2013**, *52*, 10814–10817; *Angew. Chem.* **2013**, *125*, 11014–11017; h) T. Bootwicha, X. Liu, R. Pluta, I. Atodiresei, M. Rueping, *Angew. Chem. Int. Ed.* **2013**, *52*, 12856–12859; *Angew. Chem.* **2013**, *125*, 13093–13097; i) R. Pluta, P. Nikolaienko, M. Rueping, *Angew. Chem. Int. Ed.* **2014**, *53*, 1650–1653; *Angew. Chem.* **2014**, *126*, 1676–1679; j) G. Danoun, B. Bayarmagnai, M. F. Gruenberg, L. J. Goosen, *Chem. Sci.* **2014**, *5*, 1312–1316.
- [8] M. Teltewskoi, A. J. Panetier, S. A. Macgregor, T. Braun, *Angew. Chem. Int. Ed.* **2010**, *49*, 3947–3951; *Angew. Chem.* **2010**, *122*, 4039–4043.
- [9] a) M. Teltewskoi, S. I. Källäne, T. Braun, *Eur. J. Inorg. Chem.* **2013**, 5762–5768; b) S. I. Källäne, T. Braun, B. Braun, S. Mebs, *Dalton Trans.* **2014**, *43*, 6786–6801.
- [10] a) T. Braun, D. Noveski, M. Ahijado Salomon, F. Wehmeier, *Dalton Trans.* **2007**, 3820–3825; b) T. Yoshida, D. L. Thorn, T. Okano, S. Otsuka, J. A. Ibers, *J. Am. Chem. Soc.* **1980**, *102*, 6451–6457.
- [11] a) S. Shimada, A. S. Batsanov, J. A. K. Howard, T. B. Marder, *Angew. Chem. Int. Ed.* **2001**, *40*, 2168–2171; *Angew. Chem.* **2001**, *113*, 2226–2229; b) W. H. Lam, K. C. Lam, Z. Lin, S. Shimada, R. N. Perutz, T. B. Marder, *Dalton Trans.* **2004**, 1556–1562.
- [12] a) T. Braun, M. Ahijado Salomon, K. Altenhöner, M. Teltewskoi, S. Hinze, *Angew. Chem. Int. Ed.* **2009**, *48*, 1818–1822; *Angew. Chem.* **2009**, *121*, 1850–1854; b) T. Braun, F. Wehmeier, *Eur. J. Inorg. Chem.* **2011**, 613–625; c) M. F. Kuehnle, D. Lentz, T. Braun, *Angew. Chem. Int. Ed.* **2013**, *52*, 3328–3348; *Angew. Chem.* **2013**, *125*, 3412–3433; d) D. Noveski, T. Braun, B. Neumann, A. Stammeler, H. G. Stammeler, *Dalton Trans.* **2004**, 4106–4119; e) L. Zámotná, M. Ahrens, T. Braun, *J. Fluorine Chem.* **2013**, *155*, 132–142; f) L. Zámotná, T. Braun, B. Braun, *Angew. Chem.* **2014**, *126*, 2783–2787; *Angew. Chem. Int. Ed.* **2014**, *53*, 2745–2749.
- [13] H. Marom, S. Antonov, Y. Popowski, M. Gozin, *J. Org. Chem.* **2011**, *76*, 5240–5246.
- [14] Whereas it is possible to synthesize **4b** from thioanisole by an initial lithiation step at the *ortho* position, this strategy might not work for the preparation of **4d** and **4e** starting from **2d** or **2e** because of an *ortho*-directing effect of the fluorine atom and the methoxy group.^[24]
- [15] J. Takagi, T. Yamakawa, *Tetrahedron Lett.* **2013**, *54*, 166–169.
- [16] a) P. R. Rablen, J. F. Hartwig, S. P. Nolan, *J. Am. Chem. Soc.* **1994**, *116*, 4121–4122; b) I. A. I. Mkhali, J. H. Barnard, T. B. Marder, J. M. Murphy, J. F. Hartwig, *Chem. Rev.* **2010**, *110*, 890–931; c) J. F. Hartwig, *Chem. Soc. Rev.* **2011**, *40*, 1992–2002; d) M. A. Larsen, J. F. Hartwig, *J. Am. Chem. Soc.* **2014**, *136*, 4287–4299.
- [17] J.-Y. Cho, M. K. Tse, D. Holmes, R. E. Maleczka, M. R. Smith III, *Science* **2002**, *295*, 305–308.
- [18] a) P. C. Roosen, V. A. Kallepalli, B. Chattopadhyay, D. A. Singleton, R. E. Maleczka, M. R. Smith III, *J. Am. Chem. Soc.* **2012**, *134*, 11350–11353; b) A. Ros, R. Fernández, J. M. Lassale, *Chem. Soc. Rev.* **2014**, *43*, 3229–3243.

- [19] a) T. A. Boebel, J. F. Hartwig, *J. Am. Chem. Soc.* **2008**, *130*, 7534–7535; b) D. W. Robbins, T. A. Boebel, J. F. Hartwig, *J. Am. Chem. Soc.* **2010**, *132*, 4068–4069.
- [20] a) N. Miyaoura, *Bull. Chem. Soc. Jpn.* **2008**, *81*, 1535–1553; b) T. Ishiyama, H. Isou, T. Kikuchi, N. Miyaoura, *Chem. Commun.* **2010**, *46*, 159–161; c) H.-X. Dai, J.-Q. Yu, *J. Am. Chem. Soc.* **2012**, *134*, 134–137.
- [21] K. M. Crawford, T. R. Ramseyer, C. J. A. Daley, T. B. Clark, *Angew. Chem. Int. Ed.* **2014**, *53*, 7589–7593; *Angew. Chem.* **2014**, *126*, 7719–7723.
- [22] a) S. Paul, G. A. Chotana, D. Holmes, R. C. Reichle, R. E. Maleczka, M. R. Smith III, *J. Am. Chem. Soc.* **2006**, *128*, 15552–15553; b) S. Kawamorita, H. Ohmiya, K. Hara, A. Fukuoka, M. Sawamura, *J. Am. Chem. Soc.* **2009**, *131*, 5058–5059; c) S. Kawamorita, H. Ohmiya, M. Sawamura, *J. Org. Chem.* **2010**, *75*, 3855–3858; d) K. Yamazaki, S. Kawamorita, H. Ohmiya, M. Sawamura, *Org. Lett.* **2010**, *12*, 3978–3981; e) S. Kawamorita, T. Miyazaki, H. Ohmiya, T. Iwai, M. Sawamura, *J. Am. Chem. Soc.* **2011**, *133*, 19310–19313; f) A. Ros, B. Estepa, R. López-Rodríguez, E. Álvarez, R. Fernández, J. M. Lassaletta, *Angew. Chem. Int. Ed.* **2011**, *50*, 11724–11728; *Angew. Chem.* **2011**, *123*, 11928–11932; g) A. Ros, R. López-Rodríguez, B. Estepa, E. Álvarez, R. Fernández, J. M. Lassaletta, *J. Am. Chem. Soc.* **2012**, *134*, 4573–4576; h) Q. Jiang, D. Duan-Mu, W. Zhong, H. Chen, H. Yan, *Chem. Eur. J.* **2013**, *19*, 1903–1907.
- [23] S. M. Preshlock, D. L. Plattner, P. E. Maligres, S. W. Krska, R. E. Maleczka, M. R. Smith III, *Angew. Chem. Int. Ed.* **2013**, *52*, 12915–12919; *Angew. Chem.* **2013**, *125*, 13153–13157.
- [24] SCH₃ aromatics which bear an additional functional group show no selectivity for a metalation at the position *ortho* to SCH₃. See: a) S. Cabiddu, C. Fattuoni, C. Floris, G. Gelli, S. Melis, *J. Organomet. Chem.* **1991**, *419*, 1–8; b) S. Cabiddu, C. Fattuoni, C. Floris, G. Gelli, S. Melis, *Tetrahedron* **1993**, *49*, 4965–4974; c) M. G. Cabiddu, S. Cabiddu, E. Cadoni, R. Corrias, C. Fattuoni, C. Floris, S. Melis, *J. Organomet. Chem.* **1997**, *531*, 125–140.
- [25] Note that a predominant C–H borylation at the position *ortho* to a CN moiety on 4-CH₃S-C₆H₄CN is observed, despite the presence of the thioether group, when using an iridium catalyst. See: G. A. Chotana, M. A. Rak, M. R. Smith III, *J. Am. Chem. Soc.* **2005**, *127*, 10539–10544.
- [26] a) S. Erhardt, S. A. Macgregor, *J. Am. Chem. Soc.* **2008**, *130*, 15490–15498; b) A. Nova, S. Erhardt, N. A. Jasim, R. N. Perutz, S. A. Macgregor, J. E. McGrady, A. C. Whitwood, *J. Am. Chem. Soc.* **2008**, *130*, 15499–15511; c) A. Nova, M. Reinhold, R. N. Perutz, S. A. Macgregor, J. E. McGrady, *Organometallics* **2010**, *29*, 1824–1831; d) A. L. Raza, J. A. Panetier, M. Teltewskoi, S. A. Macgregor, T. Braun, *Organometallics* **2013**, *32*, 3795–3807.
- [27] An increase of the temperature to 60 °C led to marginal higher yields, whereas a temperature of 21 °C gave lower yields, but the ratio of **4a** to **5a** is slightly better (see the Supporting Information).
- [28] Note that the rhodium complex **1** is also a Bpin source which leads to higher yields. In addition HBpin might in principle act as a borylation agent, although the conversion is very low. Treatment of **3** with one equivalent **2a** and HBpin revealed the formation of **4a** in yield of 5% after 20 h at 40 °C.
- [29] The reactions can be run at considerably lower temperatures in comparison to most other *ortho* C–H borylation protocols which are described in the literature (typically 70–100 °C).^[19b,20b,22c,d,g,23]
- [30] N. Miyaoura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457–2483.
- [31] a) J. Hellberg, T. Remonen, F. Allared, J. Slätt, M. Svensson, *Synthesis* **2003**, 2199–2205; b) A. Åslund, A. Herland, P. Hammarström, K. P. R. Nilsson, B.-H. Jonsson, O. Inganäs, P. Konradsson, *Bioconjugate Chem.* **2007**, *18*, 1860–1868; c) T. Ohmura, A. Kijima, M. Sugimoto, *J. Am. Chem. Soc.* **2009**, *131*, 6070–6071; d) B. Avitia, E. MacIntosh, S. Muhia, E. Kelson, *Tetrahedron Lett.* **2011**, *52*, 1631–1634; e) L. Arnold, M. Baumgarten, K. Müllen, *Chem. Commun.* **2012**, *48*, 9640–9642; f) A. Osichow, I. Göttker-Schnetmann, S. Mecking, *Organometallics* **2013**, *32*, 5239–5242.
- [32] a) H. Chen, S. Schlecht, T. C. Semple, J. F. Hartwig, *Science* **2000**, *287*, 1995–1997; b) M. K. Tse, J.-Y. Cho, M. R. Smith III, *Org. Lett.* **2001**, *3*, 2831–2833; c) K. Mertins, A. Zapf, M. Beller, *J. Mol. Catal. A* **2004**, *207*, 21–25.
- [33] a) C. N. Iverson, M. R. Smith III, *J. Am. Chem. Soc.* **1999**, *121*, 7696–7697; b) J.-Y. Cho, C. N. Iverson, M. R. Smith III, *J. Am. Chem. Soc.* **2000**, *122*, 12868–12869; c) T. Ishiyama, J. Takagi, J. F. Hartwig, N. Miyaoura, *Angew. Chem. Int. Ed.* **2002**, *41*, 3056–3058; *Angew. Chem.* **2002**, *114*, 3182–3184; d) T. M. Boller, J. M. Murphy, M. Hapke, T. Ishiyama, N. Miyaoura, J. F. Hartwig, *J. Am. Chem. Soc.* **2005**, *127*, 14263–14278.
- [34] CCDC 990620 (**5a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.