The Direct Dimesitylborylation of Benzofuran Derivatives via an Iridium-Catalyzed C–H Activation with Silyldimesitylborane

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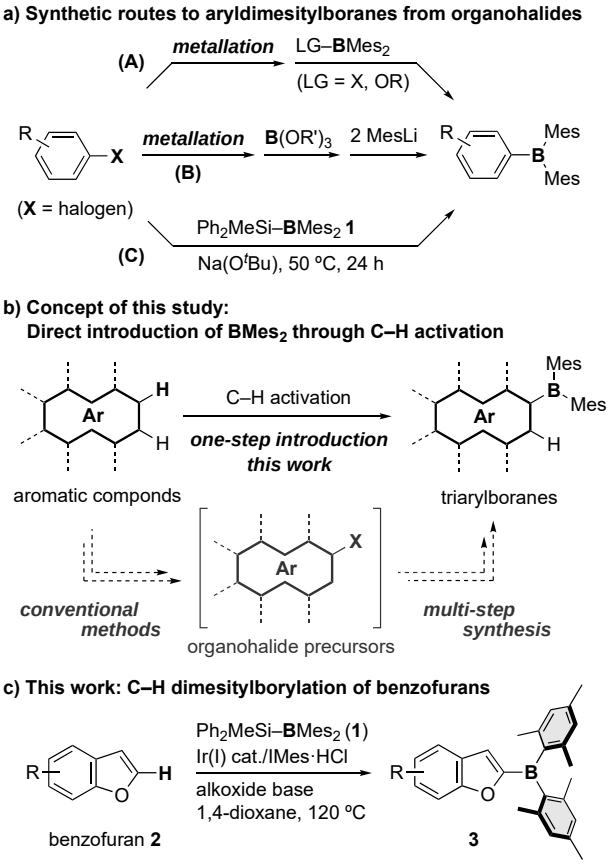
Abstract: The direct dimesitylborylation of benzofuran derivatives *via* a C–H activation catalyzed by an iridium(I)/*N*-heterocyclic carbene (NHC) complex in the presence of $Ph_2MeSi–BMes_2$ afforded the corresponding dimesitylborylation products in good to high yield with excellent regioselectivity. This method provides a straightforward route to donor-(π-spacer)-acceptor systems with intriguing solvatochromic luminescence properties.

Boron-containing π-conjugated compounds such as triarylboranes have attracted much attention due to their unique photophysical and electronic properties. These properties arise from the pπ-π* conjugation between the vacant p-orbital of the boron atom and the π*-orbital of the connected carbon-based π-conjugated moieties.[1] The dimesitylboryl ($BMes_2$) group is frequently used in this context due to its high π-electron-accepting abilities and its desirable stability in air. However, methods to introduce $BMes_2$ groups into aromatic compounds remain highly limited. A popular method for the transfer of $BMes_2$ groups is the nucleophilic substitution of $BMes_2$ electrophiles ($Mes_2B–X$; X = halogen or OR) with organometallic reagents (Ar–M; M = Li, Mg) generated from organic halides via halogen-metal exchange [Scheme 1a, (A)].[2,3] $BMes_2$ groups can also be introduced into aromatic compounds by the reaction of aryl boronic acid esters with MesLi [Scheme 1a, (B)].[2,4] Recently, our group has reported the direct dimesitylborylation of aryl halides with silyldimesitylborane $Ph_2MeSi–BMes_2$ and Na(O^{t}Bu), i.e., a base-mediated borylation with silylborane (BBS reaction) [Scheme 1a, (C)].[5,6] Although the corresponding dimesitylborylation products are obtained in good yield using both methods, a stoichiometric amount of base or organometallic reagent is needed. Furthermore, in both reactions, the availability of the $BMes_2$ compounds relies on the availability of the preceding organohalide precursors, which are often difficult to access, especially in case of highly functionalized organic halides. Hence, more efficient and direct methods are required to improve the availability of triarylboron compounds for the introduction into organic compounds.



Scheme 1. a) Synthetic routes to aryldimesitylboranes from organohalides. b) Schematic illustration of the concept of this study. c) This work: Direct dimesitylborylation of benzofurans via an iridium-catalyzed C–H activation.

Iridium-catalyzed aromatic C–H borylations[7,8] using diboron or silylborane compounds[9] represent a powerful method for the preparation of arylboron compounds, and have often been used for the synthesis of organic materials,[10] natural products,[11] and fine chemicals.[11] This method enables the direct borylation of C–H bonds in aromatic compounds without requiring any halogenated intermediates and providing the corresponding arylboronates in high yield with excellent regioselectivity. Therefore, the direct introduction of $BMes_2$ into aromatic compounds via iridium-catalyzed C–H borylations may potentially provide a new method for the synthesis of boron-containing organic compounds with a triarylboron structure [Scheme 1b]. This method thus allows a late-stage introduction of the $BMes_2$ group,[12] which would be advantageous especially for the compilation of compound libraries with complicated structures for screening purposes. However, previous examples of the synthesis of triarylboranes with this strategy have not yet been reported. Most examples of C–H borylations introduce boronate

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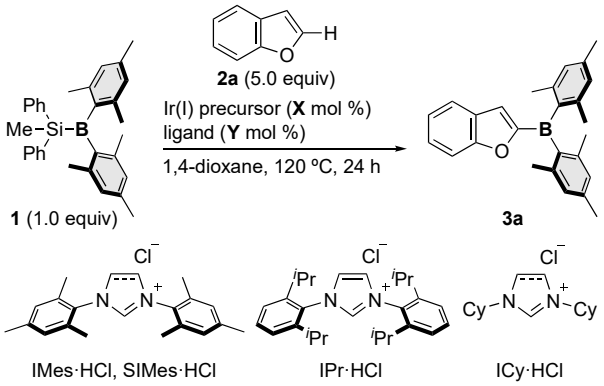
groups [B(OR)$_2$] such as B(pin), and only one example for the introduction of B(9-BBN)$_2$ (9-BBN: 9-borabicyclo[3.3.1]nonan) has been reported.[13] Herein, we report the first example of the direct introduction of BMes$_2$ into heteroaromatic benzofuran derivatives (**2**) via an iridium-catalyzed C–H activation using Ph$_2$MeSi–BMes$_2$ (**1**)[14] as the borylation reagent [Scheme 1c]. The C–H dimesitylborylation proceeds smoothly in the presence of [Ir(Cl)(coe)$_2$]$_2$/IMes (IMes: 1,3-dimesitylimidazol-2-ylidene; coe: cyclooctene) to afford the corresponding products in good to high yield with excellent regioselectivity. Some of the dimesitylborylation products obtained exhibit a pronounced solvatochromic luminescence properties due to their donor-(π-spacer)-acceptor (D-π-A) structure.

Table 1. Optimization of the reaction conditions for the iridium-catalyzed C–H borylation of benzofuran (**2a**) using **1**.[a]



Entry	Ir(I) precursor [**X** mol %]	ligand [**Y** mol %]	Yield[b]
1	[Ir(OMe)(cod)]$_2$ (2.5)	IMes·HCl (10)[c]	48
2	[Ir(OMe)(cod)]$_2$ (2.5)	dtbpy (5.0)	0
3	[Ir(OMe)(cod)]$_2$ (2.5)	Me$_4$phen (5.0)	0
4	[Ir(OMe)(cod)]$_2$ (2.5)	PPh$_3$ (10)	0
5	[Ir(OMe)(cod)]$_2$ (2.5)	P^{t}Bu$_3$ (10)	13
6	[Ir(OMe)(cod)]$_2$ (2.5)	dcpe (5.0)	0
7	[Ir(Cl)(coe)$_2$]$_2$ (2.5)	IMes·HCl (10)[c]	69
8	[Ir(Cl)(cod)]$_2$ (2.5)	IMes·HCl (10)[c]	58
9	[Ir(cod)(Py)(PCy$_3$)][PF$_6$] (5.0)	IMes·HCl (10)[c]	5
10	[Ir(cod)$_2$][BAr$^F_4$] (5.0)	IMes·HCl (10)[c]	65
11	[Ir(Cl)(coe)$_2$]$_2$ (2.5)	IMes·HCl (5.0)[c]	75 (59)
12	[Ir(Cl)(coe)$_2$]$_2$ (2.5)	SIMes·HCl (5.0)[c]	64
13	[Ir(Cl)(coe)$_2$]$_2$ (2.5)	IPr·HCl (5.0)[c]	10
14	[Ir(Cl)(coe)$_2$]$_2$ (2.5)	ICy·HCl (5.0)[c]	11
15	[Ir(Cl)(coe)$_2$]$_2$ (2.5)	-	0

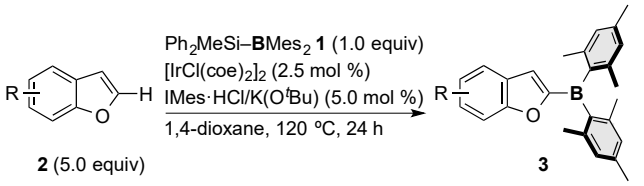
[a] Conditions: **1** (0.10 mmol), **2a** (0.50 mmol), [Ir(OMe)(cod)]$_2$ (0.0025 mmol), and ligand (0.005 or 0.01 mmol) in 1,4-dioxane (0.5 mL) at 120 ºC for 24 h. [b] ^{1}H NMR yield of **3a**. 1,1,2,2-Tetrachloroethane was used as an internal standard. The isolated yield of **3a** is shown in parentheses. [c] K(O^{t}Bu) (**Y** mol %) was added to the reaction mixture.

We initially investigated the optimization of the reaction conditions for the Ir-catalyzed C–H dimesitylborylation of benzofuran (**2a**) with **1** (Table 1),[15] starting by screening a series of different ligands (Table 1; entries 1–6). For that purpose, a 1,4-dioxane solution of **1** and **2a** was heated to 120 ºC in the presence of [Ir(OMe)(cod)]$_2$ (2.5 mol %; cod: 1,5-cyclooctadiene) and a variety of different ligands. The use of IMes·HCl/K(O^{t}Bu) (10 mol %) furnished **3a** in 48% yield (Table 1; entry 1). The silylated product was also detected as a side product. The presence of K(O^{t}Bu) was required to generate the Ir–NHC complex catalyst *in situ*. 4,4-Di-*tert*-butyl-2,2'-bipyridine (dtbpy; 5.0 mol %) and 3,4,7,8-tetramethyl-1,10-phenanthroline (Me$_4$phen; 5.0 mol %), which are effective ligands for typical Ir-catalyzed C–H borylation reactions, did not facilitate the dimesitylborylation of the C–H bonds of **2a** (entries 2 and 3). Using monodentate (10 mol %) or bidentate (5.0 mol %) phosphines such as triphenylphosphine (PPh$_3$), tri-*tert*-butylphosphine (P^{t}Bu$_3$) and 1,2-bis(dicyclohexylphosphino)ethane (dcpe) did not generate **3a** efficiently (entries 4–6; 0–13%). These results suggest that the presence of NHC ligands is crucial to promote the dimesitylborylation of **2a** efficiently. Therefore, we further examined various Ir(I) precursors and NHC ligands (Table 1; entries 7–15). In the presence of [Ir(Cl)(coe)$_2$]$_2$ (2.5 mol %) and IMes·HCl/K(O*t*Bu) (10 mol %), **3a** was obtained in 69% yield (entry 7). The use of [Ir(Cl)(cod)]$_2$ (2.5 mol %) resulted in a slightly lower yield of **3a** (58% yield; entry 8). Using Crabtree's catalyst [Ir(cod)(Py)(PCy$_3$)][PF$_6$] (5.0 mol %; Py: pyridine) furnished **3a** in merely 5% yield (entry 9). The cationic iridium catalyst [Ir(cod)$_2$][BAr$^F_4$] [5.0 mol %; Ar^F: 3,5-bis(trifluoromethyl)phenyl] showed good reactivity (65% yield; entry 10), similar to that of [Ir(Cl)(coe)$_2$]$_2$. Diminishing the catalyst loading {[Ir(Cl)(coe)$_2$]$_2$ (2.5 mol %) and IMes·HCl/K(O*t*Bu) (5.0 mol %)} also afforded **3a** in high yield (75% ^{1}H NMR yield; 59% isolated yield; entry 11). The use of other NHC ligands such as SIMes, IPr, or ICy decreased the yield of **3a** (SIMes: 64%; IPr: 10%; ICy: 11%; entries 12–14). **3a** was not obtained in the absence of IMes (entry 15). Moreover, using H–BMes$_2$ instead of Ph$_2$MeSi–BMes$_2$ did not furnish any **3a** (Table S5).[16] Therefore, the optimal conditions to obtain a maximum of **3a** involve [Ir(Cl)(coe)$_2$]$_2$ (2.5 mol %) and IMes (5.0 mol %).[17] Under these conditions, the silylation side product was formed in 29% yield.

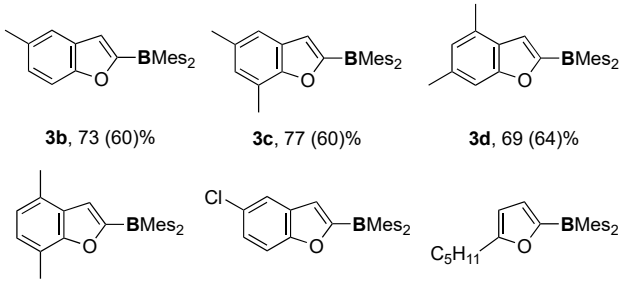
With the optimized conditions in hand, we proceeded to investigate the substrate scope for this C–H dimesitylborylation (Table 2).[18] 5-Methylbenzofuran (**2b**) reacted with **1** to give the corresponding borylation product (**3b**) in high yield (73%). Substrates bearing two methyl groups such as 5,7-dimethyl- (**2c**), 4,6-dimethyl- (**2d**), and 4,7-dimethylbenzofuran (**2e**) afforded **3c**, **3d**, and **3e**, respectively, in good yield (**3c**: 77%; **3d**: 69%; **3e**: 62%). The reaction of 5-chlorobenzofuran (**2f**) proceeded smoothly without any side reactions involving the C–Cl bond, even though some transition-metal catalysts show high reactivity for the cleavage of such C–Cl bonds. Unfortunately, furan substrate **2g** did not readily engage in the C–H dimesitylborylation.[19] The optimized catalyst system also worked well for benzofuran derivatives bearing aromatic rings at the 5-position (**2h**–**2k**) to furnish the corresponding products in good

yield (**3h**: 62%; **3i**: 68%; **3j**: 67%; **3k**: 58%). The reaction of 9-carbazolyl-substituted benzofuran **2l** afforded **3l** in good yield (66%). The molecular structure of **3l** was confirmed by a single-crystal x-ray diffraction analysis (Figure 1). This result indicates high reactivity of this C–H dimesitylborylation only toward benzofuran derivatives. This unique reactivity enabled the site-selective C–H dimesitylborylation of the benzofuran moiety in **2m**, which bears an additional furan substituent (Scheme 2).

Table 2. Substrate scope for the Ir-catalyzed C–H dimesitylborylation of substituted benzofuran derivatives.[a]



2 (5.0 equiv) **3**



3b, 73 (60)% **3c**, 77 (60)% **3d**, 69 (64)%

3e, 62 (52)% **3f**, 74 (42)% **3g**, 16%[b]

3h, 62 (40)% **3i**, 68 (60)%

3j, 67 (57)%

3k, 58 (53)% **3l**, 66 (59)%

[a] Conditions: **1** (0.10 mmol), **2** (0.50 mmol), $[Ir(Cl)(coe)_2]_2$ (0.0025 mmol), and IMes·HCl (0.01 mmol) in 1,4-dioxane (0.5 mL) at 120 ºC. The yield of the products was determined by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane as the internal standard. Isolated product yield values are shown in parentheses. [b] Identified based on ^{1}H NMR spectroscopy and GC-MS spectrometry.

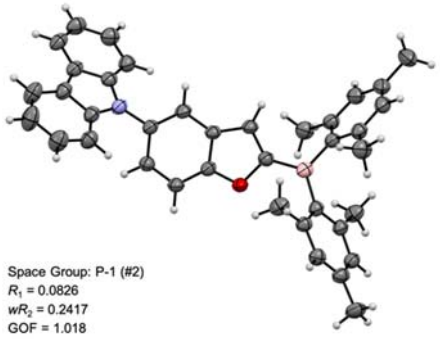
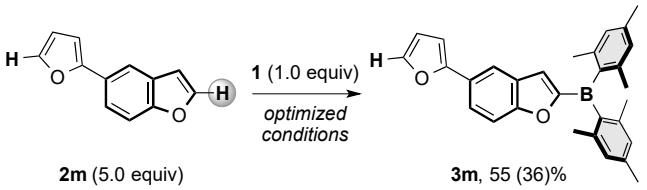


Figure 1. Crystal structure of **3l** with thermal ellipsoids at 50% probability. Color code: grey: carbon; white: hydrogen; pink: boron; red: oxygen; pale purple: nitrogen.



2m (5.0 equiv) **3m**, 55 (36)%

Scheme 2. Site-selective C–H dimesitylborylation of benzofuran **2m**, which bears an additional furan substituent.

Dimesitylborylation product **3i** exhibited pronounced solvatochromic luminescence properties due to the D-π-A structure, which includes the benzofuran moiety and the phenyl spacer (Figure 2). The absorption and emission spectra of **3i** were measured in various solvents. Two absorption maxima (λ_{abs} = 290 and 350 nm) were observed that were relatively unaffected by the solvent polarity (Figure S1). Yet, we obtained seven different emission spectra for **3i** (λ_{ex} = 365 nm) in seven different solvents (hexane, toluene, Et_2O, CH_2Cl_2, THF, acetone and CH_3CN) (Figure 2). All spectra of **3i** exhibited a broad band with a distinct emission maximum ($\lambda_{em,\ max}$) ranging from 455 nm to 722 nm (hexane: $\lambda_{em,\ max}$ = 455 nm, Φ_{em} = 29.4%; toluene: $\lambda_{em,\ max}$ = 504 nm, Φ_{em} = 43.5%; Et_2O: $\lambda_{em,\ max}$ = 536 nm, Φ_{em} = 43.5%; CH_2Cl_2: $\lambda_{em,\ max}$ = 587 nm, Φ_{em} = 59.4%; THF: $\lambda_{em,\ max}$ = 602 nm, Φ_{em} = 50.0%; acetone: $\lambda_{em,\ max}$ = 667 nm, Φ_{em} = 29.4%; CH_3CN: $\lambda_{em,\ max}$ = 722 nm, Φ_{em} = 43.5%), which demonstrates that $\lambda_{em,\ max}$ changes with the solvent polarity. These results indicate that **3i** shows properties that are characteristic for push-pull solvatoluminescent dyes. Therefore, the Ir-catalyzed C–H dimesitylborylation of substituted benzofuran derivatives described in this article permits the rapid construction of the D-π-A systems found in such dyes.

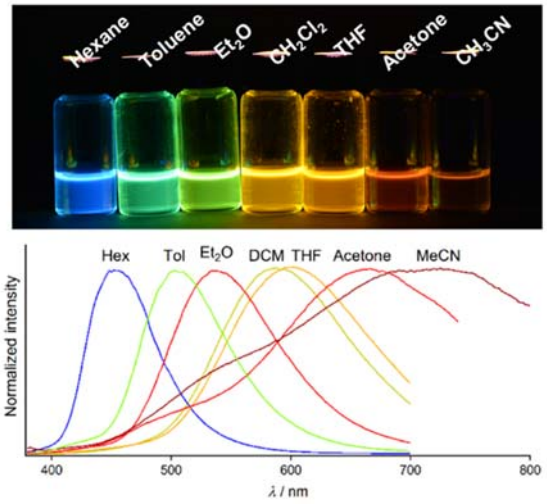
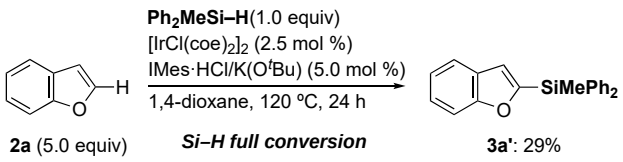


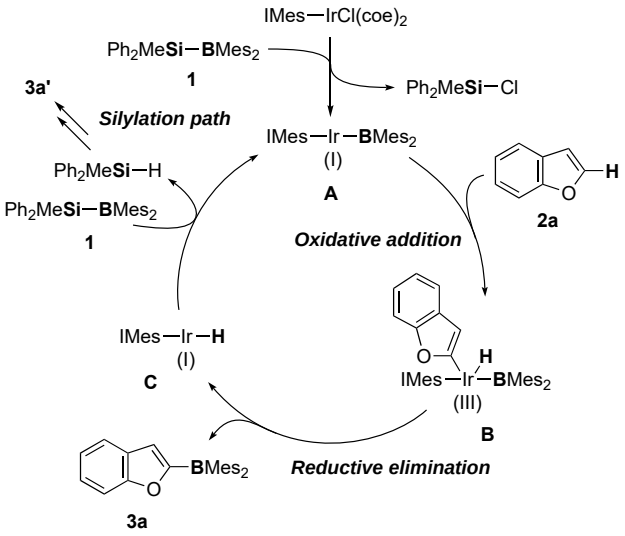
Figure 2. Photograph and emission spectra of **3i** in various solvents under irradiation from UV light (λ_{ex} = 365 nm; 2.5 mM).

Silylation products were detected as the main side products of the dimesitylborylation reactions. To gain insight into the mechanism of their generation, a control experiment was carried out (Scheme 3). The reaction between **2a** and Ph_2MeSi–H instead of Ph_2MeSi–$BMes_2$ led to the formation of the silylation product **3a'** in 29% yield.[20–22] This result suggests that Ph_2MeSi–H, which would be produced as a by-product in the borylation reaction, reacts with **2a** to give the silylation side product.



Scheme 3. Control experiment using $PhMe_2Si$–H instead of **1**.

Based on previous mechanistic studies[9, 23] for the Ir-catalyzed C–H borylation of aromatic compounds with bis(pinacolate)diboron and silylborane, and considering the results of our control experiments, we would like to propose a plausible reaction mechanism for this C–H dimesitylborylation (Scheme 4). The NHC-Ir(I) complex generated *in situ* could initially react with Ph_2MeSi–$BMes_2$ (**1**) to afford monoboryliridium(I) complex **A** as an active catalyst species. The subsequent oxidative addition of a C–H bond at the 2-position in **2a** to complex **A** would produce Ir(III) complex **B**. This regioselectivity could be assigned to the high acidity of the C–H bond in the benzofuran ring.[24] Reductive elimination of the desired dimesitylborylation product (**3a**) would lead to the formation of Ir(I)-hydride complex **C**. Finally, the oxidative addition of **1** to complex **C**, followed by a reductive elimination of Ph_2MeSi–H, would regenerate Ir(I) complex **A**. Additionally, Ph_2MeSi–H would rapidly engage in a side reaction of **2a** to provide the silylated benzofuran **3a'** via a C–H activation process. Moreover, it seems feasible to assume that the Ir(III) complexes $[Ir(B)_n(Si)_{3-n}]$ (n = 1 or 2) are generated *in situ* and act as actual active catalytic species.[9, 23] At present, we speculate that the generation of the monoboryliridium(I) complex **A** would be favored relative to that of $[Ir(B)_n(Si)_{3-n}]$ (n = 1 or 2) due to the presence of bulky boryl and silyl groups.[25]



Scheme 4. Possible reaction mechanism for the Ir(I)-catalyzed C–H dimesitylborylation of benzofuran derivatives.

In summary, we have developed a novel method for the C–H dimesitylborylation of benzofuran derivatives, which is the first example of a direct dimesitylborylation of aromatic compounds through C–H activation using a catalyst system based on an Iridium(I)/*N*-heterocyclic carbene complex. These reactions afford the corresponding dimesitylborylation products in good to high yield with excellent regioselectivity. This method thus enables the one-step introduction of luminescent functionality into non-luminescent heteroarenes at a late stage in their synthesis, which should significantly promote the synthesis of novel organic materials. Detailed mechanistic studies and efforts to expand the substrate scope are currently in progress in our laboratory.

Acknowledgements

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Keywords: C–H borylation • Iridium catalyst • Dimesitylboryl group • Silyldimesitylborane • Benzofuran

[1] For reviews on boron-containing π-conjugated compounds, see: a) A. Wakamiya, S. Yamaguchi, *Bull. Chem. Soc. Jpn.* **2015**, *88*, 1357; b) F.

Qiu, W. Zhao, S. Han, X. Zhuang, H. Lin, F. Zhang, *Polymers* **2016**, *8*, 191; c) G. Turkoglu, M. E. Cinar, T. Ozturk, *Molecules* **2017**, *22*, 1522; d) S.-Y. Li, Z.-B. Sun, C.-H. Zhao, *Inorg. Chem.* **2017**, *56*, 8705; d) Z. M. Hudson, S. Wang, *Acc. Chem. Res.* **2009**, *42*, 1584. For selected practical examples, see: e) S. Hashimoto, T. Ikuta, K. Shiren, S. Nakatsuka, J. Ni, M. Nakamura, T. Hatakeyama, *Chem. Mater.* **2014**, *26*, 6265; f) H. Hirai, K. Nakajima, S. Nakatsuka, K. Shiren, J. Ni, S. Nomura, T. Ikuta, T. Hatakeyama, *Angew. Chem., Int. Ed.* **2015**, *54*, 13581; g) T. Hatakeyama, K. Shiren, K. Nakajima, S. Nomura, S. Nakatsuka, K. Kinoshita, J. Ni, Y. Ono, T. Ikuta, *Adv. Mater.* **2016**, *28*, 2777. For selected reports for dimesitylboryl ($BMes_2$) compounds, see: h) Z.-Q. Liu, Q. Fang, D. Wang, G. Xue, W.-T. Yu, Z.-S. Shao, M.-H. Jiang, *Chem. Commun.* **2002**, 2900; i) Z.-Q. Liu, Q. Fang, D. Wang, D.-X. Cao, G. Xue, W.-T. Yu, H. Lei, *Chem. Eur. J.* **2003**, *9,* 5074.

[2] For selected reviews, see: D. G. Hall, Boronic Acids: *Preparation and Applications in Organic Synthesis Medicine and Materials,* 2nd ed., Wiley-VCH, Weinheim, **2011**.

[3] a) J. C. Doty, B. Babb, P. J. Grisdale, M. Glogowski, J. L. R. Williams, *J. Organomet. Chem.* **1972**, *38*, 229; b) Z. Yuan, C. D. Entwistle, J. C. Collings, D. Albedsa-Jové, A. S. Batsanov, J. A. K. Howard, N. J. Taylor, H. M. Kaiser, D. E. Kaufmann, S.-Y. Poon, W.-Y. Wong, J.-F. Halet, T. B. Marder, *Chem.-Eur. J.* **2006**, *12*, 2758; c) Z. Zhang, R. M. Edkins, J. Nitsch, K. Fucke, A. Eichhorn, A. Steffen, Y. Wang, T. B. Marder, *Chem.-Eur. J.* **2015**, *21*, 177.

[4] a) K. Albrecht, V. Kaiser, R. Boese, J. Adams, D. E. Kaufmann, *J. Chem. Soc. Perkin Trans. 2* **2000**, 2153; b) Y. Gu, H. Pritzkow, W. Siebert, *Eur. J. Inorg. Chem.* **2001**, 373; c) M. Ito, E. Ito, M. Hirai, S. Yamaguchi, *J. Org. Chem.* **2018**, *83*, 8449.

[5] E. Yamamoto, K. Izumi, R. Shishido, T. Seki, N. Tokodai, H. Ito, *Chem.-Eur. J.* **2016**, *22*, 17547.

[6] For reports on base-mediated borylations with silylborane (BBS reactions), see: a) E. Yamamoto, K. Izumi, Y. Horita, H. Ito, *J. Am. Chem. Soc.* **2012**, *134*, 19997; b) E. Yamamoto, S. Ukigai, H. Ito, *Chem. Sci.* **2015**, *6*, 2943; c) R. Uematsu, E. Yamamoto, S. Maeda, H. Ito, T. Taketsugu, *J. Am. Chem. Soc.* **2015**, *137*, 4090; d) E. Yamamoto, S. Maeda, T. Taketsugu, H. Ito, *Synlett* **2017**, *28*, 1258; e) E. Yamamoto, R. Shishido, T. Seki, H. Ito, *Organometallics* **2017**, *36*, 3019; f) A. B. Cuenca, R. Shishido, H. Ito, E. Fernández, *Chem. Soc. Rev.* **2017**, *46*, 415.

[7] For reviews on transition-metal-catalyzed C–H bond activation reactions, see: a) J. Wencel-Delord, F. Glorius, *Nat. Chem.* **2013**, *5*, 369; b) Y. Kuninobu, *J. Synth. Org. Chem., Jpn.* **2016**, *74*, 1058; c) J. F. Hartwig, *Acc. Chem. Res.* **2017**, *50*, 549; d) T. Gensch, M. J. James, T. Dalton, F. Glorius, *Angew. Chem., Int. Ed.* **2018**, *57*, 2269; *Angew. Chem.* **2018**, *130*, 2318; e) P. Wedi, M. V. Gemmeren, *Angew. Chem., Int. Ed.* **2018**, *57*, 13016; *Angew. Chem.* **2018**, *130*, 13198.

[8] For reviews on transition-metal-catalyzed C–H borylations, see: a) T. Ishiyama, N. Miyaura, *J. Organomet. Chem.* **2003**, *680*, 3; b) I. A. I. Mkhalid, J. H. Barnard, T. B. Marder, J. M. Murphy, J. F. Hartwig, *Chem. Rev.* **2010**, *110*, 890; c) J. F. Hartwig, *Chem. Soc. Rev.* **2011**, *40*, 1992; c) J. F. Hartwig, *Acc. Chem. Res.* **2012**, *45*, 864; d) L. Xu, G. Wang, S. Zhang, H. Wang, L. Wang, L. Liu, J. Jiao, P. Li, *Tetrahedron* **2017**, *73*, 7123.

[9] a) T. A. Boebel, J. F. Hartwig, *Organometallics* **2008**, *27*, 6013; b) M. A. Larsen, C. V. Wilson, J. F. Hartwig, *J. Am. Chem. Soc.* **2015**, *137*, 8633; c) M. A. Larsen, S. H. Cho, J. F. Hartwig, *J. Am. Chem. Soc.* **2016**, *138*, 762. For a review on transition-metal-catalyzed reactions with silylboranes, see: d) M. Oestreich, E. Hartmann, *Chem. Rev.* **2013**, *113*, 402.

[10] a) S. Shinamura, R. Sugimoto, N. Yanai, N. Takemura, T. Kashiki, I. Osaka, E. Miyazaki, K. Takimiya, *Org. Lett.* **2012**, *14*, 4718; b) Y. Segawa, T. Maekawa, K. Itami, *Angew. Chem., Int. Ed.* **2015**, *54*, 66; c) L. Ji, I. Krummenacher, A. Friedrich, A. Lorbach, M. Haehnel, K. Dekins, H. Braunschweig, T. B. Marder, *J. Org. Chem.* **2018**, *83*, 3599.

[11] C. Yuan, B. Liu, *Org. Chem. Front.* **2018**, *5*, 106.

[12] For selected examples of electrophilic aromatic C–H borylation reactions, see: a) A. C. Shaikh, D. S. Ranade, S. Thorat, A. Maity, P. P. Kulkarni, R. G. Gonnade, P. Munshi, N. T. Patil, *Chem. Commun.* **2015**, *51*, 16115; b) M. Yusuf, K. Liu, F. Guo, R. A. Lalancette, F. Jäkle, *Dalton Trans.* **2016**, *45*, 4580; c) K. Liu, R. A. Lalancette, F. Jäkle, *J. Am. Chem. Soc.* **2017**, *139*, 18170; d) K. Yang, G. Zhang, Q. Song, *Chem. Sci.* **2018**, *9*, 7666; e) B. P. Dash, I. Hamilton, D. J. Tate, D. L. Crossley, J.-S. Kim, M. J. Ingleson, M. L. Turner, *J. Mater. Chem. C,* **2019**, *7*, 718.

[13] a) Y. Kuninobu, T. Iwanaga, T. Omura, K. Takai, *Angew. Chem., Int. Ed.* **2013**, *52*, 4431; b) Y. Yoshigoe, Y. Kuninobu, *Org. Lett.* **2017**, *19*, 3450.

[14] a) E. Bonnefon, M. Birot, J. Dunogues, J.-P. Pillot, C. Courseille, F. Taulelle, *Main Group Met. Chem.* **1996**, *19,* 761; b) J. Carlos Araujo Da Silva, M. Birot, J.-P. Pillot, M. Pétraud, *J. Organomet. Chem.* **2002**, *646,* 179.

[15] For further optimizations of the reaction conditions, see the supporting information.

[16] Preliminary experiments for the reaction using H–$BMes_2$ instead of Ph_2MeSi–$BMes_2$ were also conducted. For details, see the supporting information (Table S5).

[17] For examples of aromatic C–H borylation reactions using Ir/NHC catalyst systems, see: a) G. D. Rey, C. F. Rentzsch, D. V. Preysing, T. Scherg, M. Mühlhofer, E. Herdtweck, W. A. Herrmann, *J. Organomet. Chem.* **2006**, *691*, 5725; b) C. F. Rentzsch, E. Tosh, W. A. Herrmann, F. E. Kühn, *Green Chem.* **2009**, *11*, 1610.

[18] Reactions of heteroaromatic substrates other than benzofuran and furan were also investigated. However, these compounds did not effectively engage in this reaction. For details, see the supporting information.

[19] The presence of the borylation product in the reaction mixture was ascertained based on a combined GC, GC-MS, and ^{1}H NMR analysis.

[20] Other silicon-derived by-products such as Ph_2MeSi–$SiMePh_2$, Ph_2MeSi–O–$SiMePh_2$, and Ph_2MeSi–OH were not observed by GC and GC-MS in the reaction mixture. For details, see the supporting information.

[21] For reviews on transition-metal-catalyzed C–H silylation reactions, see: a) C. Cheng, J. F. Hartwig, *Chem. Rev.* **2015**, *115*, 8946; b) R. Sharma, R. Kumar, I. Kumar, B. Singh, U. Sharma, *Synthesis* **2015**, *47*, 2347; c) Z. Xu, W.-S. Huang, J. Zhang, L.-W. Xu, *Synthesis* **2015**, *47*, 3645.

[22] a) B. Lu, J. R. Falck, *Angew. Chem., Int. Ed.* **2008**, *47*, 7508; *Angew. Chem.* **2008**, *120*, 7618; b) C. Cheng, J. F. Hartwig, *J. Am. Chem. Soc.* **2015**, *137*, 592; c) M. Murai, N. Nishinaka, K. Takai, *Angew. Chem., Int. Ed.* **2018**, *57*, 5843; *Angew. Chem.* **2018**, *130*, 5945.

[23] a) H. Tamura, H. Yamazaki, H. Sato, S. Sasaki, *J. Am. Chem. Soc.* **2003**, *125*, 16114; b) T. M. Boller, J. M. Murphy, M. Hapke, T. Ishiyama, N. Miyaura, J. F. Hartwig, *J. Am. Chem. Soc.* **2005**, *127*, 14263; c) A. G. Green, P. Liu, C. A. Merlic, K. N. Houk, *J. Am. Chem. Soc.* **2014**, *136*, 4575.

[24] a) T. Ishiyama, J. Takagi, J. F. Hartwig, N. Miyaura, *Angew. Chem., Int. Ed.* **2002**, *41*, 3056; b) J. Takagi, K. Sato, J. F. Hartwig, T. Ishiyama, N. Miyaura, *Tetrahedron Lett.* **2002**, *43*, 5649; c) T. Ishiyama, J. Takagi, Y. Yonekawa, J. F. Hartwig, N. Miyaura, *Adv. Synth. Catal.* **2003**, *345*, 1103; d) T. Ishiyama, Y. Nobuta, J. F. Hartwig, N. Miyaura, *Chem. Commun.* **2003**, 2924.

[25] a) Y. Saito, Y. Segawa, K. Itami, *J. Am. Chem. Soc.* **2015**, *137*, 5193; b) B. E. Haines, Y. Saito, Y. Segawa, K. Itami, D. G. Musaev, *ACS Catal.* **2016**, *6*, 7536; c) L. Zhu, X. Qi, Y. Li, M. Duan, L. Zou, R. Bai, Y. Lan, *Organometallics* **2017**, *36*, 2107.

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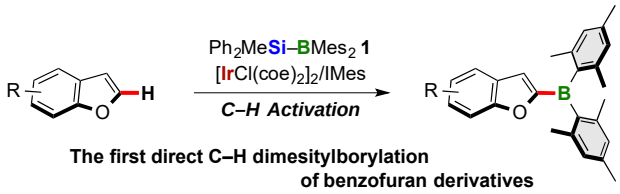

The first direct C–H dimesitylborylation of benzofuran derivatives

The first dimesitylborylation of benzofuran derivatives via an Ir-catalyzed C–H activation has been accomplished. This reaction provides direct access to donor-(π-spacer)-acceptor systems with intriguing luminescence properties.

*Ryosuke Shishido, Ikuo Sasaki, Tomohiro Seki, Tatsuo Ishiyama, Hajime Ito**

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The Direct Dimesitylborylation of Benzofuran Derivatives via an Iridium-Catalyzed C–H Activation with Silyldimesitylborane