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Iridium-bipyridine periodic mesoporous organosilica catalyzed direct C-H borylation using a pinacolborane

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Heterogeneous catalysis for direct C-H borylation of arenes and heteroarenes in the combination of iridium (Ir) complex fixed on periodic mesoporous organosilica containing bipyridine ligands within the framework (Ir-BPy-PMO) and pinacolborane (HBpin) is reported. Ir-BPy-PMO showed higher catalytic activity toward the borylation of benzene with inexpensive HBpin compared to expensive bis(pinacolato)diboron (B_2pin_2). The precatalyst could be handled without use of a glove box. The catalyst was easily recovered from reaction mixtures by simple filtration under air. The recovered catalyst still had good catalytic activity for at least three more times for the borylation of benzene. A variety of arenes and heteroarenes were successfully borylated with high boron efficiency by Ir-BPy-PMO using HBpin, whereas almost no activity was observed for borylation of some heteroarenes with B_2pin_2. The system using Ir-BPy-PMO and HBpin was also utilized in syntheses of multi-boronated thiophene-based building blocks containing ladder-, acenefused-, and fused-thiophene skeletons. The combination of stable and reusable solid catalyst and inexpensive HBpin is expected to be superior to conventional approaches for the development of industrial applications.

Introduction

Transition-metal catalyzed direct C-H borylation has been developed as an efficient and straightforward synthetic strategies for aryl/heteroarylboronate esters,[1] which are valuable intermediates in organic synthesis.[2,3] In particular, the combination of an iridium(Ir)-bipyridine complex and bis(pinacolato)diboron (B_2pin_2, pin = $O_2C_2Me_4$) or pinacolborane (HBpin) has been established as one of the most reliable catalytic systems in terms of catalytic activity, boron efficiency, and functional group tolerance.[4,5] Unfortunately, this method still suffers from problems related to homogeneous systems such as fast deactivation of catalyst and difficult separation and recycling of residual catalyst from the reaction mixture. Thus, the development of synthetic approach of aryl/heteroarylboronate esters using a heterogeneous transition-metal catalyst is of paramount importance subject for sustainable organic synthesis.

Recently, we reported a unique solid chelating ligand, periodic mesoporous organosilica containing 2,2'-bipyridine groups within the framework (BPy-PMO). As the 2,2'-bipyridine ligands in BPy-PMO are regularly arranged and exposed on the pore surface, various metal complexes can be directly formed on the pore surface using the framework bipyridine as one of the ligands (Figure 1).[6] Iridium (Ir)-bipyridine complex formed on the pore surface of BPy-PMO showed high catalytic activity and durability for direct C-H borylation of arenes because of suppression of undesired interactions and aggregation of the metal centers due to the isolated binding of metals on the well-defined surface. The recovered Ir-BPy-PMO was available for recycle use. Independently, Copéret *et al*. reported a similar strategy to prepare a well-isolated catalytic active center on the pore surface of PMO where bipyridine groups were diluted with biphenylene units (Ir-bpy$^{1/10}$-PMO, Figure 1).[7] More recently, mesoporous silica and a metal-organic framework-supported Ir-bipyridine heterogeneous catalyst (bpy-SBA-15-Ir, bpy-UiO-Ir, Figure 1) have also been reported.[8,9] These findings indicate that ordered nanoporous materials containing bipyridine ligands in their frameworks have great potential for heterogenization of homogeneous Ir-bipyridine catalyst without loss of the activity.

In our preliminary results, we only showed the Ir-BPy-PMO catalyzed borylation of arenes in the combination with B_2pin_2 under neat conditions.[6] It should be required to evaluate the borylation reactions in the combination of Ir-BPy-PMO and HBpin, a cheaper boron source than B_2pin_2, as well as a wide

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† Electronic Supplementary Information (ESI) available: General procedure for C-H borylation of arenes and hetroarenes catalysed by Ir-BPy-PMO, NMR spectra of aryl and hetroarylboronate esters. See DOI: 10.1039/b000000x/

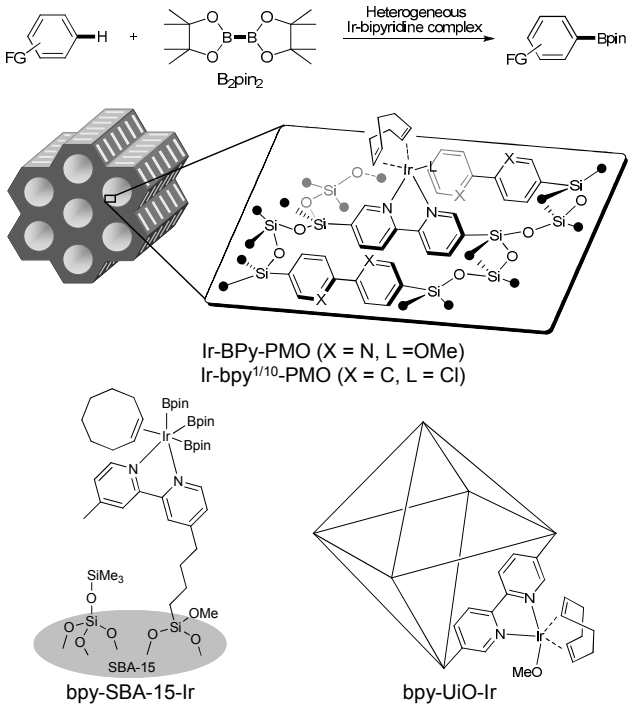


Fig 1. Representative heterogeneous Ir-bipyridine complex catalysts based on well-defined bipyridine solid chelating ligands for direct C-H borylation of arenes with bis(pinacolato)diboron.

range of substrate scope in order to develop the further potential of Ir-BPy-PMO for industrial applications.

Here, we report the Ir-BPy-PMO catalyzed borylation using an inexpensive HBpin for a wide range of arenes and heteroarenes. It was revealed that Ir-BPy-PMO showed higher catalytic activity for direct C-H borylation of a wide range of arenes and heteroarenes in the combination with HBpin rather than B_2pin_2. The combination with HBpin allowed multiple borylation of π-conjugated and/or fused-thiophene derivatives with high yields 95–99% while almost no reaction in the combination with B_2pin_2. The combination of Ir-BPy-PMO and HBpin has great potential for industrial applications affording useful molecular building blocks for the synthesis of functional π-conjugated materials using Suzuki-Miyaura coupling reaction.

Results and discussion

Direct C-H borylation of benzene

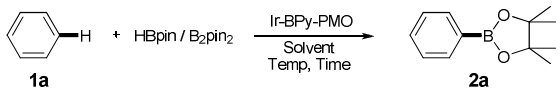
The heterogeneous Ir-BPy-PMO was prepared according to the literature with a slight modification. The Ir-bipyridine complex formed on the pore surface of BPy-PMO end-capped with trimethylsilyl group without loss of parent mesoporous structure. The density functional theory pore diameter (d_{DFT}), Brunauer-Emmett-Teller surface area (S_{BET}) and pore volume ware 3.5 nm, 519 m^2 g-1, and 0.23 cm^3 g^{-1}, respectively. The amount of Ir was 0.15-0.16 mmol g^{-1} which indicated that about 6 mol% of bipyridine groups in the BPy-PMO was coordinated with Ir.

The benchmark reactions between benzene and HBpin or B_2pin_2 (**1a**, 30 equiv relative to boron atom in boron reagent) were investigated using the heterogeneous Ir-BPy-PMO catalyst (0.75 mol % Ir relative to boron atom in boron reagent) under various conditions (Table 1). Unlike the homogeneous Ir-bipyridine system,[4b] the reaction with HBpin did not occur at room temperature even after a prolonged reaction time (Table 1, entry 1). However, increasing the reaction temperature gradually promoted the reaction with HBpin and produced the desired phenylboronate ester (**2a**) as the sole product (Table 1, entries 2-4). At 80 ºC, product **2a** was obtained in an excellent yield of 94% (Table 1, entry 4). These results suggest that heating is required for Ir-BPy-PMO, possibly due to the higher activation energy owing to lower flexible environment around the Ir catalysis centers and/or lower diffusion efficiency of the molecules around the catalyst compared to the homogeneous catalysis system. The loading amount of catalyst could be reduced to 0.125 mol % Ir without significant loss of product yield, which resulted in an increase in TON calculated as moles of product/moles of iridium in Ir-BPy-PMO to 728 (Table 1, entry 5). This value is higher than those for previously reported heterogeneous metal complex catalysts, such as BPDCA-cat (TON of 55)[10] and Silica-SMAP-Ir (TON of 204)[11] for the direct C-H borylation of benzene under almost the same reaction conditions. Although a high TON of 640 was reported for Ir-bpy$^{1/10}$-PMO[7], it was based on conversion of moles of diboron/moles of iridium in the catalyst. Furthermore, the amount of benzene relative to HBpin could be reduced to 2 equivalents with sufficient product yield (Table 1, entry 6).

The reaction efficiency of benzene with HBpin was higher than that with B_2pin_2. The maximum conversion of B_2pin_2 below 60 ºC was 28%, which is less than half the performance of the HBpin system under the same conditions (Table 1, entries 7-9 vs. entry 3). At temperatures higher than 80 ºC, the product yield increased up to 94% similar to the HBpin system (Table 1, entry 10). However, the reaction conducted in cyclohexane as the solvent at 80 ºC gave **2a** in only 26% yield (Table 1, entry 11).

The reaction kinetics were compared for HBpin and B_2pin_2 as the boron source for Ir-BPy-PMO catalyzed C-H borylation

Table 1. Catalytic activities of Ir-BPy-PMO catalyst in direct C-H borylation of benzene with HBpin and B_2pin_2.[a]



Entry	Boron reagent	Solvent	T (ºC)	Time [h]	Yield (%)[b]	TON[c]
1	HBpin	neat	25	24	0	0
2		neat	40	12	13	17
3		neat	60	12	66	88
4		neat	80	3	94	125
5		neat	80	24	91	728
6[d]		CyH	80	12	91	121
7	B_2pin_2	neat	25	24	0	0
8		neat	40	12	0	0
9		neat	60	12	28	38
10		neat	80	4	94	125
11[d]		CyH	80	12	26	34

[a] The reactions were conducted with benzene (**1a**, 30 equiv relative to boron atom in boron reagents) and HBpin (1 equiv) or B_2pin_2 (0.5 equiv) in the presence of Ir-BPy-PMO (0.125-0.75 mol % Ir). [b] Isolated yields based on boron atom in boron reagents. [c] TON was calculated as moles of product/moles of iridium in Ir-BPy-PMO. [d] The reaction was conducted with **1a** (2 equiv) in CyH (cyclohexane).

of benzene under neat conditions and diluted conditions with cyclohexane as shown in Figure 2. Under neat condition, both reactions proceeded efficiently without an induction period. The initial rate for the HBpin system was faster than that for the B_2pin_2 system. The TOF at initial 1 h for the HBpin system reached 113 h^{-1}, which is 1.7 times higher than that for the B_2pin_2 system (67 h^{-1}) (Figure 2). A similar trend was observed in the homogeneous catalysis system. This trend was also observed in the reaction conducted in cyclohexane as the solvent (Figure 2). The reaction with B_2pin_2 proceeded after an induction period of 1 h and the TOF was 8 h^{-1}. On the other hand, the reaction with HBpin proceeded without an induction period and the TOF for the HBpin system was 37 h^{-1}, which is 4.6 times higher than that for the B_2pin_2 system (Figure 2).

In the homogeneous system, the borylation was demonstrated to proceed through an Ir-boryl complex as an

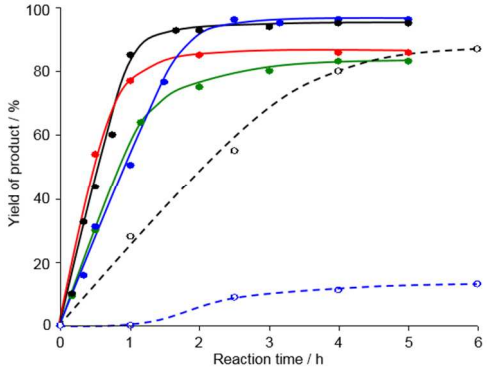


Fig 2. Reaction kinetic curves of C-H borylation of benzene catalyzed by Ir-BPy-PMO with HBpin (black line) or B_2pin_2 (blue line) and [Ir(bpy)(OMe)(cod)] with HBpin (red line) or B_2pin_2 (green line) under neat benzene condition and Ir-BPy-PMO with HBpin (black broken line) or B_2pin_2 (blue broken line). The reactions were conducted with benzene (**1a**, 30 equiv relative to boron atom in boron reagents) or benzene (**1a**, 2 equiv) in cyclohexane (2 mL) and HBpin (1 equiv) or B_2pin_2 (0.5 equiv) in the presence of Ir-BPy-PMO or [Ir(bpy)(OMe)(cod)] (0.75 mol % Ir).

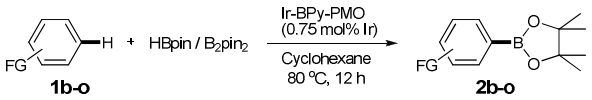
active intermediate. The Ir-boryl intermediate was generated by elimination of methoxy and cod ligands and formed more easily from HBpin than B_2pin_2.[12] We observed side products by GC/MS analysis, such as 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (MeOBpin) and cyclooctane from the eliminated methoxy and cod ligands in the filtrate after reaction (see Experimental section). The amount of side products was larger for the reaction system using HBpin than B_2pin_2 in cyclohexane, indicating higher reactivity of HBpin with Ir-BPy-PMO similar to the homogeneous system. These studies clearly indicate that the use of HBpin is effective for formation of an Ir-boryl complex on the pore surface of the Ir-BPy-PMO precatalyst.

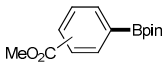
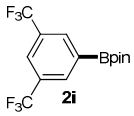
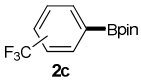
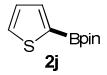
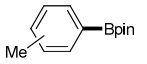
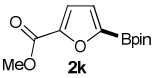
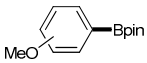
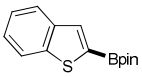
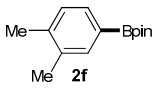
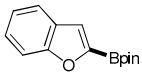
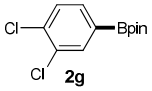
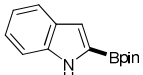
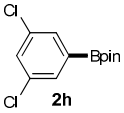
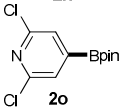
During the course of our studies, we found that the Ir-BPy-PMO precatalyst could be weighed under air. The recovery and reusability of Ir-BPy-PMO were also examined. After the reaction, the solid catalyst could be easily removed from the reaction mixture by simple filtration using a membrane filter (0.20 μm) without iridium contamination (<1.0 ppm) in the filtrate. We observed no elution of bipyridine ligand in the filtrate by GC-MS analyses. These results indicate the ratio of Ir/bipyridine was unchanged after the reaction. The X-ray diffraction patterns and the nitrogen adsorption/desorption isotherms showed that the mesoporous structure of Ir-BPy-PMO almost completely remained. We also found that the recovered Ir-BPy-PMO, which was quickly filtered under air, still showed high catalytic activity in the C-H borylation of benzene with HBpin. Successive recycle reactions could be performed under similar reaction conditions at least three times, although the reaction rate and product yield were gradually decreased (1st recycle: 88% after 5 h, 2nd recycle: 85% after 5 h, 3rd recycle: 69% after 8 h). The lowered catalytic performance might be due to partial deactivation of the active site during the recovery operation and/or recycle reaction.

Direct C-H borylation of substituted arenes and heteroarenes

The scope and limitations of Ir-BPy-PMO catalyzed direct C-H borylation were then examined with various types of arenes and heteroarenes with HBpin and B_2pin_2 under optimized conditions (Table 2). For electron-poor arenes such as methyl benzoate (**1b**) and benzotrifluoride (**1c**), the reactions proceeded effectively with HBpin even under dilute conditions in cyclohexane, providing the arylboronates **2b** and **2c** in 86% and 91% yields, respectively (Table 2, entries 1 and 2). In contrast, the reactions by B_2pin_2 provided the products in low yield, possibly due to the inefficient formation of active intermediates as observed for benzene. For electron-rich mono-substituted arenes such as toluene (**1d**) and anisole (**1e**), the reactions with HBpin and B_2pin_2 did not efficiently occur under dilution conditions, and resulted in formation of arylboronates **2d** and **2e** in low yield,

Table 2. Direct C-H borylation of arenes and heteroarenes with HBpin catalyzed by Ir-BPy-PMO.[a]



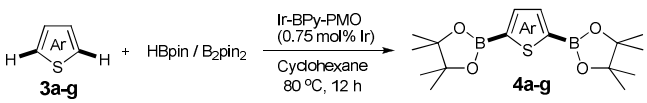
Entry	Arylboronate	Yield (%)[b]	Entry	Arylboronate	Yield (%)[b]
1	 **2b**	86[d] (7)	10	 **2i**	91 (47)
2	 **2c**	91[e] (52)	11	 **2j**	92 (0)
3 4[c]	 **2d**	23 (23) 92[f] (85)[g]	12	 **2k**	93[j] (0)
5 6[c]	 **2e**	17 (3) 86[h] (88)[i]	13	 **2l**	90 (0)
7[c]	 **2f**	68 (60)	14	 **2m**	92[k] (0)
8	 **2g**	95 (85)	15	 **2n**	93 (79)
9	 **2h**	94 (81)	16	 **2o**	92 (0)

[a] The reactions were conducted with arenes **1** (2 equiv), HBpin (1 equiv) or B_2pin_2 (0.5 equiv), and Ir-BPy-PMO (0.75 mol % Ir) in CyH. [b] Isolated yields based on HBpin. Isolated yields based on boron atom in B_2pin_2 are given in parentheses. [c] The reactions were carried out under neat conditions. [d] *m*:*p* = 53:47. [e] *m*:*p* = 69:31. [f] *m*:*p* = 60:40. [g] *m*:*p* = 63:37. [h] *m*:*p* = 51:49. [i] *m*:*p* = 63:37. [j] 2-isomer:3-isomer = 86:14. [k] 2-isomer:3-isomer = 80:20.

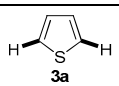
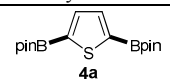
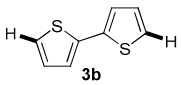
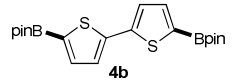
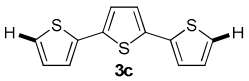
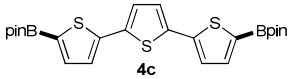
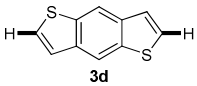
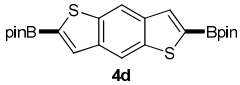
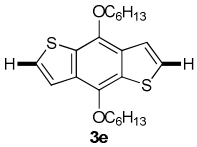
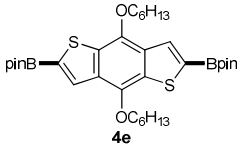
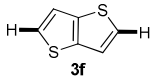
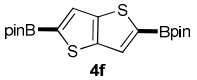
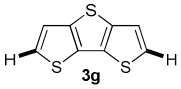
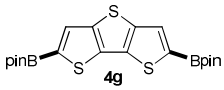
respectively (Table 2, entries 3 and 5). This result can be explained by the fact that reactivities of electron-rich arenes are usually lower than those of electron-poor arenes for direct C-H borylation (See Electronic Supplementary Information (ESI)). A similar trend has been observed for other homogeneous catalytic systems.[13] However, the neat reaction condition allowed for the borylations of **2d** and **2e** with HBpin or B_2pin_2 in high yields of 85-92% (Table 2, entries 4 and 6).

In the cases of mono-substituted arenes, the arylboronates were obtained as a mixture of regioisomers. Although the ratio of regioisomers was dependent on the substrates, the *m*-isomer was preferentially obtained, whereas the *o*-isomer did not form, possibly due to the steric hindrance of the substituents. This regioselectivity was commonly observed for the typical homogeneous catalysis system.[4] This suggests that the chemical environment of the active site is not strongly affected by the solid bipyridine ligand and the molecular nature of the active site is retained in the pore walls. For 1,2- and 1,3-disubstituted arenes, regioselective borylation occurred to afford a single regioisomer of the product in yields of 68-95% (Table 2, entries 7-10). The high regioselectivity can be explained by steric hindrance of the two substituents on the benzene ring.[4] Electron-poor arenes such

Table 3. Multiple borylation of heteroarenes with HBpin catalyzed by Ir-BPy-PMO.[a]



3a-g 4a-g

Entry	Heteroarene	Heteroarylboronate	Yield (%)[b]
1	 3a	 4a	99(0)
2	 3b	 4b	99(0)
3	 3c	 4c	99(0)
4	 3d	 4d	99(0)
5	 3e	 4e	95(0)
6	 3f	 4f	99(0)
7	 3g	 4g	89(0)

[a] All reactions were conducted with heteroarenes (**3**, 1 equiv) and HBpin (3.0 equiv) in the presence of Ir-BPy-PMO (1.1 mol % Ir per C-H bond in **3**). [b] Isolated yields. Isolated yields based on boron atom in B_2pin_2 are given in parentheses.

as **1g-1h** could be easily transformed into the corresponding arylboronates, whereas electron-rich arene **2f** showed sluggish reactivity even under neat conditions.

A variety of heteroarenes such as thiophene, furan, benzo[*b*]thiophene, benzofuran, indole, and pyridine were also transformed into the corresponding heteroarylboronates by combination of Ir-BPy-PMO and HBpin in cyclohexane (Table 2, entries 11-16). Thiophene, benzo[*b*]thiophene, and indole exclusively formed the corresponding α-substituted heteroarylboronate esters **2j**, **2l**, and **2n**, respectively, in yields of 90-93%. This is due to the high acidity of the α-positions from the electronegative heteroatom in the five-membered rings.[14] Furan derivatives **2k** and **2m** selectively gave the 2-isomer in

addition to a small amount of the 3-isomer. The reaction of 2,6-dichloropyridine occurred only at the 4-position, due to the substituents blocking the 2,6-positions to yield a pure regioisomer **2o**. It should be noted that the catalytic performance of Ir-BPy-PMO using HBpin is almost comparable with those of homogeneous Ir-bipyridine systems. However, almost no activity of Ir-BPy-PMO was observed for the reactions between B_2pin_2 and some kinds of heteroarenes containing thiophene, furan, and pyridine. The reason is not clear at this moment. A detailed investigation on these behaviors and the reaction mechanism are currently underway in our laboratory.

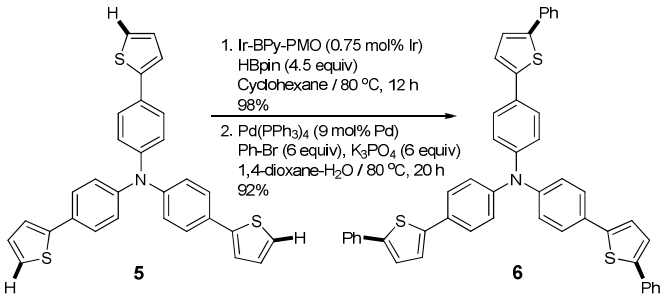
Multiple C-H borylation of thiophene derivatives

The development of an efficient synthetic method for arylene- and heteroarylene-bridged boronate esters has been of interest for fundamental organic chemistry. In particular, recent advances in polymer chemistry focused on thiophenes containing donor-acceptor molecular structures suitable for producing photoluminescence and energy-harvesting materials.[15] We utilized our Ir-BPy-PMO catalytic systems using HBpin and B_2pin_2 as a synthetic approach for multi-borated building blocks (Table 3).

For HBpin system, thiophene (**3a**) could be easily diborylated at the α-positions as well as the ladder-type derivatives such as 2,2'-bithiophene (**3b**) and 2,2':5',2''-terthiophene (**3c**) to afford the desired diboronates **3a**-**3c** (See ESI). The product yields were much higher than that of boronate syntheses via conventional magnesium or lithium intermediates.[16] Benzo[1,2-*b*:4,5-*b*']dithiophene (**3d**) could also be transformed into the diborated building block **4d**. The introduction of alkoxy groups on the benzo[1,2-*b*:4,5-*b*']dithiophene skeleton such as in **3e** did not significantly affect the product yield and regioselectivity. Moreover, diboronated fused-thiophene derivatives containing thieno[3,2-*b*]thiophene (**3f**) and dithieno[3,2-*b*:2',3'-*d*]thiophene (**3g**) were also borylated regioselectively. Notably, all reactions successfully occurred with complete conversion of substrates and excellent yields of 89-99%. The products could be easily isolated after evaporation of the reaction solvents and extraction with cold hexane to remove the excess HBpin. These diborylated products can be used as useful building blocks for

π-conjugated functional materials.[17] However, almost no activity was observed for borylation of all thiophene derivatives with B_2pin_2.

Starting from tris[4-(2-thienyl)phenyl]amine **5**,[18] high hole-transporting triarylamine derivative **6** could be readily obtained by direct C-H borylation followed by Suzuki-Miyaura coupling reaction to afford a 90% yield over two steps (Scheme 1). Unlike conventional approaches using the Grignard coupling reaction (9% yield), a remarkable improvement of product yield was achieved by adopting our approach.[19] This result demonstrated that thiophene-based boronated building blocks are effective and useful in the synthesis of functional organic materials.



Scheme 1. Synthesis of hole-transporting triarylamine derivative **6** by direct C-H borylation of **5** followed by Suzuki-Miyaura coupling reaction.

Conclusions

In conclusion, we developed efficient heterogeneous Ir-bipyridine-PMO catalysis using inexpensive pinacolborane as a boron source for direct C-H borylation. A wide range of arenes and heteroarenes were successfully borylated with high boron efficiency. The Ir-BPy-PMO catalyst could be weighed without inert atmosphere outside a glove box. The PMO catalyst after reaction could be easily recovered from the reaction mixture by filtration under air. The recovered PMO catalyst still showed good catalytic activity. The combination of Ir-BPy-PMO and pinacolborane could be applied to the synthesis of multi-boronated thiophene-based building blocks containing ladder-, acenefused-, and fused-thiophene skeletons. We demonstrated that one synthetic building block was readily utilized to give a functional hole-transporting organic material in high yield. The uses of solid catalyst and inexpensive pinacolborane are expected to be superior to conventional approaches in the development of industrial applications.

Acknowledgements

The authors thank Mr. Syuji Kajiya, Mr. Kenichi Yagi and Ms. Ayako Ohshima (Toyota Central R&D Laboratories, Inc.) for FI-HRMS and ESI-HRMS measurements and GC-MS analyses. This work was supported in part by a Grant-in-Aid for Scientific Research on Innovative Areas 'Artificial Photosynthesis' (No. 2406) from the Japan Society for the Promotion of Science (JSPS).

Experimental

Chemicals and characterization

Unless otherwise noted, all chemicals, including dry solvents, were purchased from commercial suppliers (Sigma-Aldrich, Tokyo Chemical Industry Co., Ltd., and Wako Pure Chemical Industries Ltd.) and used without further purification. BPy-PMO and end-capped BPy-PMO was prepared according to the literature.[6]

^{1}H, ^{13}C, and ^{19}F NMR spectra were obtained using a Jeol ECX-400 spectrometer operating at 400 MHz, 100 MHz, and 376 MHz, respectively. Chemical shifts are reported in δ parts per million referenced to tetramethylsilane (TMS) or residual protonated solvent as an internal standard.

Mass spectra were recorded on a Micromass GCT Premier mass spectrometer (FI: field ionization) and Micromass Q-TOF mass spectrometer (ESI: electrospray ionization).

GC mass analyses were performed on an Agilent 7890A GC instrument equipped with a capillary column (HP-5MS, 0.25 mm × 30 m) and a flame ionization detector.

IR spectra were collected on a Thermo Fisher Scientific Nicolet Avatar-360 FT-IR spectrometer using an attenuated total reflection (ATR) attachment.

XRD profiles were recorded on a Rigaku RINT-TTR diffractometer using Cu-Kα radiation (50 kV, 300 mV).

Nitrogen adsorption and desorption isotherms were measured using a Quantachrome Nova3000e sorptometer. BET surface areas were calculated from the linear sections of BET plots (P/P_0 = 0.1−0.2). Pore-size distributions were calculated using the DFT method (DFT kernel: N2 at 77 K on silica, cylindrical pores, nonlinear density functional theory (NLDFT) equilibrium model). Pore volumes were estimated by the *t*-plot method.

Synthetic procedure

All reactions were carried out under argon using standard high-vacuum and Schlenk-line techniques.

Preparation of Ir-BPy-PMO.

A 50 mL Schlenk tube was charged with a stir bar and end-capped BPy-PMO (77.5 mg, 0.226 mmol) and dry hexane (10 mL). A solution of $[Ir(OMe)(cod)]_2$ (5.0 mg, 0.015 mmol Ir) in dry hexane (20 mL) was added at room temperature. The reaction mixture was stirred at room temperature for 3-6 h. The resulting suspension was filtered and then washed with dry hexane. The material was dried over under reduced pressure to give Ir-BPy-PMO as a light grey powder (75 mg, Ir content: 0.15-0.16 mmol Ir/g).

General procedure for direct C-H borylation of arenes and heteroarenes.

A 20 mL Schlenk-tube assembled a stir bar and a septum inlet was charged with Ir-BPy-PMO (32.0 mg, 0.005 mmol Ir) and arenes or heteroarenes (1.33 mmol) then flushed with argon. Dry cyclohexane (2.0 mL) and pinacolborane (95 μL, 0.66 mmol) was added, and the mixture was stirred at 80 ºC for 12 h. The mixture was diluted with diethyl ether (5 mL) and filtered through a membrane filter (0.20 μm). Solvent was removed under reduced pressure. The crude product was purified by flash silica gel column chromatography (eluent: hexane/EtOAc = 100/0 to 70/30) provided analytically pure samples. The recovered catalyst was used for next reaction in the presence of pinacolborane and dry benzene under same reaction condition.

(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (2a): Yield: 94%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.35 (s, 12H), 7.37

(t, J = 7.4 Hz, 2H), 7.46 (t, J = 7.3 Hz, 1H), 7.81 (d, J = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.87, 83.75, 127.69, 131.23, 134.72.; IR (neat): υ_{max} 2983, 1604, 1437, 1350, 1137, 1092, 857, 705, 657 cm^{-1}; ESI-HRMS m/z calcd. for $C_{12}H_{21}BNO_2$ ($M+NH_4^+$): 222.1662; found: 222.1664.

Methyl (4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-benzoate (2b): Yield: 86% (p-isomer:m-isomer = 53:47). ^{1}H NMR (400 MHz, $CDCl_3$): δ (m-isomer) 1.36 (s, 12H), 3.91 (s, 3H), 7.44 (t, J = 8.0 Hz, 1H), 7.98 (d, J = 7.6 Hz, 1H), 8.12 (d, J = 8.0 Hz, 1H), 8.46 (s, 1H); (p-isomer) 1.36 (s, 12H), 3.92 (s, 3H), 7.86 (d, J = 8.4 Hz, 2H), 8.02 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (p-isomer) 24.83, 52.10, 84.15, 128.52, 132.23, 134.59, 167.10, (m-isomer) 24.83, 52.00, 84.06, 127.74, 129.47, 135.76, 139.09, 167.07.; IR (neat): υ_{max} 2952, 1726, 1461, 1362, 906 cm^{-1}; ESI-HRMS m/z calcd. for $C_{14}H_{23}BNO_4$ ($M+NH_4^+$): 280.1717; found: 280.1719.

(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)(trifluoromethyl)benzene (2c): Yield: 91% (p-isomer:m-isomer = 31:69). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (m-isomer) 1.36 (s, 12H), 7.48 (t, J = 7.6 Hz, 1H), 7.70 (d, J = 7.8 Hz, 1H), 7.97 (d, J = 7.6 Hz, 1H), 8.06 (s, 1H), (p-isomer) 1.36 (s, 12H), 7.61 (d, J =8.1 Hz, 2H), 7.91 (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (m-isomer) 24.85, 84.26, 124.29, 127.60, 127.99, 131.32, 137.96, (p-isomer) 24.53, 84.26, 124.15, 124. 29, 132.30, 134.96; ^{19}F NMR (376 MHz, $CDCl_3$): δ (m-isomer)-62.93, (p-isomer) -62.51.; IR (solution): υ_{max} 2976, 1584, 1552, 1334, 1144, 966 cm^{-1}; ESI-HRMS m/z calcd. for $C_{13}H_{20}BF_3NO_2$ ($M+NH_4^+$): 250.1539; found: 250.1539.

(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)toluene (2d): Yield: 92% (p-isomer:m-isomer = 40:60). ^{1}H NMR (400 MHz, $CDCl_3$): δ (m-isomer) 1.34 (s, 12H), 2.35 (s, 3H), 7.25-7.27 (m, 2H), 7.60 (t, J = 4.4 Hz, 1H), 7.63 (s, 1 H), (p-isomer) 1.34 (s, 12H), 2.36 (s, 3H), 7.18 (d, J = 7.6 Hz, 2H), 7.70 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (m-isomer) 21.27, 24.85, 83.71, 127.66, 131.73, 132.01, 135.29, 137.10, (p-isomer) 21.73, 24.85, 83.60, 128.49, 134.76, 141.37.; IR (solution): υ_{max} 2960, 1611, 1461, 1358, 1089 cm^{-1}; ESI-HRMS m/z calcd. for $C_{13}H_{23}BNO_2$ ($M+NH_4^+$): 236.1819; found: 236.1819.

(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)anisole (2e): Yield: 87% (p-isomer:m-isomer = 49:51). ^{1}H NMR (400 MHz, $CDCl_3$): δ (m-isomer) 1.34 (s, 12H), 3.83 (s, 3H), 7.00 (dd, J = 2.8, 8.4 Hz, 1H), 7.29 (t, J = 8.0 Hz, 1H), 7.32 (d, J = 2.8 Hz, 1H), 7.40 (d, J = 7.2 Hz, 1H), (p-isomer) 1.33 (s, 12H), 3.83 (s, 3H), 6.88 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (m-isomer) 24.85, 55.23, 83.80, 117.90, 118.61, 127.14, 128.91, 158.97, (p-isomer) 24.85, 55.08, 83.53, 113.27, 136.47, 162.08.; IR (solution): υ_{max} 2952, 1603, 1461, 1382, 1354, 1093 cm^{-1}; ESI-HRMS m/z calcd. for $C_{13}H_{23}BNO_3$ ($M+NH_4^+$): 252.1768; found: 252.1768.

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-*o*-xylene (2f): Yield: 60%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.34 (s, 12H), 2.27 (s, 3H), 2.28 (s, 3H), 7.14 (d, J = 7.6 Hz, 1H), 7.54 (d, J = 7.6 Hz, 1H), 7.58 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.47, 20.00, 24.83, 83.56, 129.13, 132.36, 135.88, 140.12.; IR (solution): υ_{max} 2952, 1611, 1465, 1374, 1350, 1093 cm^{-1}; ESI-HRMS m/z calcd. for $C_{14}H_{25}BNO_2$ ($M+NH_4^+$): 250.1975; found: 250.1975.

1,2-Dichloro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (2g): Yield: 95%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (s, 12H), 7.43 (d, J = 8.0 Hz, 1H), 7.59 (dd, J = 1.2 Hz, 8.0 Hz, 1H), 7.86 (d, J = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.15, 84.64, 130.29, 132.53, 134.04, 135.77, 136.83.; IR (solution): υ_{max} 2976, 1588, 1477, 1382, 1342, 1144, 1085, 1040, 960 cm^{-1}; ESI-HRMS m/z calcd. for $C_{12}H_{19}BNCl_2O_2$ ($M+NH_4^+$): 290.0883; found: 290.0882.

1,3-Dichloro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (2h): Yield: 94%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.34 (s, 12H), 7.42 (t, J = 2.0 Hz, 1H), 7.64 (d, J = 2.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.83, 84.48, 129.34, 131.04, 132.66, 134.68.; IR (solution): υ_{max} 2976, 1584, 1552, 1440, 1334, 144, 966 cm^{-1}; ESI-HRMS m/z calcd. for $C_{12}H_{19}BNCl_2O_2$ ($M+NH_4^+$): 290.0883; found: 290.0884.

1,3-Bis(trifluoromethyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (2i): Yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.37 (s, 12H), 7.94 (s, 1 H), 8.23 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.86, 84.83, 122.09, 124.66, 124.69, 130.68, 131.02, 134.61.; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.76.; IR (neat): υ_{max} 2983, 1618, 1279, 1123, 849, 677 cm^{-1}; ESI-HRMS m/z calcd. for $C_{14}H_{19}BNF_6O_2$ ($M+NH_4^+$): 358.1410; found: 358.1408.

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene (2j): Yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.35 (s, 12H), 7.19 (dd, J = 3.6 Hz, 4.4 Hz, 1H), 7.63 (d, J = 4.8 Hz, 1H), 7.64 (d, J = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 24.76, 84.07, 128.20, 132.34, 137.13.; IR (neat): υ_{max} 2966, 1519, 1423, 1358, 1132, 846 cm^{-1}; ESI-HRMS m/z calcd. for $C_{10}H_{19}BNO_2S$ ($M+NH_4^+$): 228.1224; found: 228.1224.

5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-furancarboxylic acid methyl ester (2k): Yield: 93%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (2-isomer) 1.35 (s, 12H), 3.89 (s, 3H), 7.07 (d, J = 3.6 Hz, 1H), 7.19 (d, J = 3.6 Hz, 1H), (3-isomer) 1.32 (s, 12H), 3.89 (s, 3H), 7.37 (s, 1H), 7.87 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$, TMS): δ (2-isomer) 24.70, 51.93, 84.70, 117.86, 124.00, 148.29, 159.03; (3-isomer) 24.75, 51,95, 83.91, 121.80, 123.9, 154.01, 159.07. 2:3 = 86/14.; IR (neat): υ_{max} 3112, 2977, 1714, 1575, 1527, 1437, 1358, 1324, 1284, 1103 , 780 cm^{-1}; ESI-HRMS m/z calcd. for $C_{12}H_{21}BNO_5$ ($M+NH_4^+$): 270.1507; found: 270.1508.

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[*b*]thiophene (2l): Yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.38 (s, 12H), 7.32-7.39 (m, 2H), 7.83-7.86 (m, 1H), 7.88 (s, 1H), 7.89-7.91 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 24.81, 84.42, 122.49, 124.07, 124.34, 125.27, 134.46, 140.39, 143.66.; IR (neat): υ_{max} 2977, 1595, 1553, 1522, 135, 1120, 849, 753, 662 cm^{-1}; ESI-HRMS m/z calcd. for $C_{14}H_{21}BNO_2S$ ($M+NH_4^+$): 278.1381; found: 278.1382.

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzofuran (2m): Yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (2-isomer) 1.39 (s, 12H), 7.22 (t, J = 7.2 Hz, 1H), 7.33 (dt, J = 1.2 Hz, 7.2 Hz, 1H), 7.40 (s, 1H), 7.56 (d, J = 8.4 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), (3-isomer) 1.37 (s, 12H), 7.26-7.29 (m, 2H), 7.91-7.93 (m, 2H), 7.95 (s, 1H) ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ (2-isomer) 24.77, 84.66, 111.93, 119.51, 121.85, 122.70, 125.90, 127.44, 157.46; (3-isomer) 24.87, 83.48, 111.0, 122,84, 122.92, 124.19, 153.5. 2:3 = 80:20.; IR (neat): υ_{max} 2971, 1612, 1561, 1471, 1321, 1132, 1069, 750 cm^{-1}; ESI-HRMS m/z calcd. for $C_{14}H_{21}BNO_3$ ($M+NH_4^+$): 262.1609; found: 272.1612.

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)indole (2n): Yield: 93%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.37 (s, 12H), 7.09 (t, J = 8.0 Hz, 1H), 7.11 (s, 1H), 7.22 (t, J = 8.0 Hz, 1H), 7.38 (d, J = 8.4 Hz, 1H), 7.66 (d, J = 8.4 Hz, 1H), 8.55 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 24.83, 84.13, 111.24, 113.82, 119.76, 121.58, 123.60, 128.24, 138.17.; IR (neat): υ_{max} 3333, 2977, 1615, 1581, 1539, 1372, 1313, 1137, 968, 852, 696 cm^{-1}; ESI-HRMS m/z calcd. for $C_{14}H_{19}BNO_2$ ($M+H^+$): 244.1503; found: 244.1507.

2,6-Dichloro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (2o): Yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.35 (s, 12H), 7.58 (s, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 24.82, 85.19, 127.75, 150.37.; IR (neat): υ_{max} 3007, 2983, 1516, 1369, 1341, 1163, 1137, 965, 807 cm^{-1}; ESI-HRMS *m/z* calcd. for $C_{11}H_{15}BCl_2NO_2$ (M+H$^+$): 274.0567; found: 274.0569.

General procedure for multiple-direct C-H borylation of thiophene derivatives

A 20 mL Schlenk-tube assembled a stir bar and a septum inlet was charged with Ir-BPy-PMO (32.0 mg, 0.005 mmol Ir) and thiophene derivatives **3** (0.22 mmol) and then flushed with argon. Dry cyclohexane (2.0 mL) and pinacolborane (95 μL, 0.66 mmol) was added, and the mixture was stirred at 80 ºC for 12 h. The mixture was diluted with chloroform (5 mL) and filtered through a membrane filter (0.20 μm). Solvent was removed under reduced pressure. The crude product was washed with cold hexane (1 mL) to afford analytically pure samples.

2,5-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene (4a): Yield: 99%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.34 (s, 24H), 7.66 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) : δ 24.76, 84.11, 137.64.; IR (neat): υ_{max} 2971, 1522, 1318, 1260, 1134, 1038, 855, 671 cm^{-1}; ESI-HRMS *m/z* calcd. for $C_{16}H_{27}B_2O_4S$ (M$^+$): 337.1811; found: 337.1718.

5,5'-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2'-bithiophene (4b): Yield: 99%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.35 (s, 24H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) : δ 24.76, 84.21, 125.60, 137.95, 143.83.; IR (neat): υ_{max} 2983, 1513, 1434, 1327, 1253, 1134, 1069, 852, 654 cm^{-1}; ESI-HRMS *m/z* calcd. for $C_{20}H_{29}B_2O_4S_2$ (M$^+$): 419.1688; found: 419.1698.

5,5''- Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2':5',2''-terthiophene (4c): Yield: 99%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.35 (s, 24H), 7.14 (s, 2H), 7.23 (d, *J* = 3.6 Hz, 2H), 7.52 (d, *J* = 3.6 Hz, 2H), ^{13}C NMR (100 MHz, $CDCl_3$, TMS) : δ 24.77, 84.22, 124.97, 125.11, 136.63, 137.95, 143.61.; IR (neat): υ_{max} 3056, 2977, 1510, 1448, 1349, 1321, 1137, 1067, 849, 660 cm^{-1}; FI-HRMS *m/z* calcd. for $C_{24}H_{31}B_2O_4S_3$ (M$^+$): 501.1565; found: 501.1577.

2,6-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[1,2-*b*:4,5-*b*']dithiophene (4d): Yield: 99%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.39 (s, 24H), 7.90 (s, 2H); 8.36 (s, 2H), ^{13}C NMR (100 MHz, $CDCl_3$, TMS) : δ 24.83, 84.54, 117.52, 133.59, 139.31, 140.56.; IR (neat): υ_{max}2983, 1539, 1443, 1395, 1298, 1137, 852, 660 cm^{-1}; ESI-HRMS *m/z* calcd. for $C_{22}H_{29}B_2O_4S_2$ (M$^+$): 443.1688; found: 443.1696.

2,6-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4,8-dihexyloxybenzo[1,2-*b*:4,5-*b*']dithiophene (4e): Yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.93 (t, *J* = 6.8 Hz, 6H), 1.36-1.38 (m, 12H), 1.38 (s, 24H), 1.50-1.55 (m, 4H), 1.84-1.91 (m, 4H), 4.30 (t, *J* = 6.8 Hz, 4H), 8.01 (s, 2H), ^{13}C NMR (100 MHz, $CDCl_3$, TMS) : δ 14.10, 22.65, 24.71, 24.81, 25.66, 30.53, 31.70, 73.94, 84.55, 130.82, 132.98, 133.77, 144.82.; IR (neat): υ_{max} 2981, 2926, 2853, 1553, 1448, 1348, 1307, 1129, 846, 665 cm^{-1}; ESI-HRMS *m/z* calcd. for $C_{34}H_{53}B_2O_6S_2$ (M$^+$): 643.3464; found: 643.3472.

2,5-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thieno[3,2-*b*]thiophene (4f): Yield: 99%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.36 (s, 24H), 7.75 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) : δ 24.79, 84.35, 128.87, 146.61.; IR (neat): υ_{max} 2983, 1485, 1338, 1259, 1134, 1030, 950, 849, 665 cm^{-1}; ESI-HRMS *m/z* calcd. for $C_{18}H_{27}B_2O_4S_2$ (M$^+$): 393.1531; found: 393.1539.

2,6- Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dithieno[3,2-*b*:2',3'-*d*]thiophene (4g): Yield: 89%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.36 (s, 24H), 7.76 (s, 2H), ^{13}C NMR (100 MHz, $CDCl_3$, TMS) : δ 24.78, 84.40, 130.27, 144.74.; IR (neat): υ_{max} 2977, 1499, 1383, 1250, 1132, 1020, 950, 849, 660 cm^{-1}; ESI-HRMS *m/z* calcd. for $C_{20}H_{27}B_2O_4S_3$ (M$^+$): 449.1252; found: 449.1259.

Synthesis of triarylamine derivative 6

A 20 mL Schlenk-tube assembled a stir bar and a septum inlet was charged with Ir-BPy-PMO (32.0 mg, 0.005 mmol Ir) and tris(4-(2-thienyl)phenyl)amine **5** (72 mg, 0.15 mmol) and then flushed with argon. Dry cyclohexane (2.0 mL) and pinacolborane (95 μL, 0.66 mmol) was added, and the mixture was stirred at 80 ºC for 12 h. The mixture was diluted with chloroform (5 mL) and filtered through a membrane filter (0.20 μm). Solvent was removed under reduced pressure. The crude product was washed with cold hexane (1 mL) to afford analytically pure tribolylated amine **5'**. Yield: 98%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.36 (s, 36H), 7.13 (d, *J* = 8.8 Hz, 6H), 7.32 (d, *J* = 3.6 Hz, 3H), 7.55 (d, *J* = 8.8 Hz, 6H), 7.58 (d, *J* = 3.6 Hz, 3H), ^{13}C NMR (100 MHz, $CDCl_3$, TMS) : δ 24.79, 84.11, 123.85, 124.42, 127.10, 129.13, 138.23, 146.73, 150.92.; IR (neat): υ_{max} 2977 1601, 1530, 1451, 1318, 1140, 1070, 950, 850, 804, 665 cm^{-1}; ESI-HRMS *m/z* calcd. for $C_{48}H_{55}B_3NO_6S_3$ (M$^+$): 870.3465; found: 870.3484.

A 50 mL two-neck flask connected to a condenser was charged with a stir bar, tribolylated amine **5'** (100 mg, 0.11 mmol), K_3PO_4 (146 mg, 0.69 mmol), and $Pd(PPh_3)_4$ (12 mg, 10.3 μmol). Dry 1,4-dioxane (7.5 mL), degassed distilled water (0.75 mL), and bromobenzene (108 mg, 0.69 mmol) were added. The reaction mixture was stirred at 80 °C for 20 h. After cooling to room temperature, the reaction mixture was diluted with water and extracted with dichloromethane. The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and then the solvent was completely evaporated. The residue was purified by silica gel column chromatography (eluent: hexane/CH_2Cl_2 = 10:1) to give **6** (77 mg, 92%) as a yellow powder. IR (neat): υ_{max} 3016, 2909, 1595, 1482, 1315, 1265, 798, 750, 690 cm^{-1}; ^{1}H NMR (400 MHz, THF-d_8) δ 7.15 (d, *J* = 8.8 Hz, 6H), 7.23 (t, *J* = 8.0 Hz, 3H), 7.32 (d, *J* = 3.6 Hz, 3H), 7.36 (d, *J* = 8.0 Hz, 6H), 7.37 (d, *J* = 3.6 Hz, 3H), 7.68 (d, *J* = 8.8 Hz, 6H), 7.64 (d, *J* = 8.4 Hz, 6H). ^{13}C NMR (100 MHz, THF-d_8) δ 124.44, 125.00, 125.31, 126.05, 127.22, 128.12, 129.67, 130.27, 135.28, 143.67, 143.96, 147.51.; ESI-HRMS *m/z* calcd. for $C_{48}H_{34}NS_3$ (M+H$^+$): 720.1848; found: 720.1842.

GC-MS analyses of side products after the reaction of Ir-BPy-PMO with boron reagent.

A 20 mL Schlenk-tube assembled a stir bar and a septum inlet was charged with Ir-BPy-PMO (173 mg, 27 μmol Ir) and then flushed with argon. Then, dry cyclohexane (3.0 mL) and HBpin (58 μL, 0.40 mmol) was added, and the mixture was stirred at 80 ºC for 3 h. In the case of B_2pin_2, B_2pin_2 (51 mg, 0.20 mmol) was directly charged with Ir-BPy-PMO in the Schlenk-tube. The mixture was filtered through a membrane filter (0.20 μm). The obtained reaction solution was analyzed by GC mass spectroscopy. The amount of side product was determined using the calibration curve obtained from known standard chemicals. In the case of HBpin system, cyclooctane (7.5 μmol), cyclooctene (0.03 μmol) and MeOBpin (1.8 μmol) were obtained. In the case of B_2pin_2 system, cyclooctane (0.94

μmol), cyclooctene (0.19 μmol), cyclooctadiene (0.008 μmol), and MeOBpin (1.35 μmol) were obtained.

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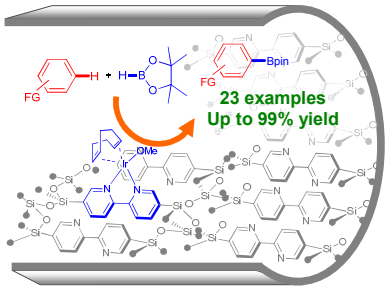
Graphical abstract



Iridium complex fixed on periodic mesoporous organosilica containing bipyridine ligands within the framework showed efficient heterogeneous catalysis for direct C-H borylation of arenes and heteroarenes in the combination with an inexpensive pinacolborane.