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Synthesis of masked haloareneboronic acids via iridium-catalyzed aromatic C–H borylation with 1,8-naphthalenediaminatoborane (danBH)

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ABSTRACT

"Masked" areneboronic acids have been prepared by Ir-catalyzed C–H borylation of arenes. A [Ir(OMe)(cod)]$_2$ complex with a DPPE ligand showed the highest catalytic activity in the C–H borylation of benzene at 80 °C. The reaction system can be applied to substituted arenes, including halogen-substituted arenes. 1,3-Dihalobenzenes undergo the C–H borylation at their 5-positions in a regioselective fashion, affording 3,5-dihaloareneboronic acid derivatives, which serve as useful coupling modules for the convergent dendrimer synthesis.

1. Introduction

Organoboronic acids play indispensable roles in the synthesis of conjugated organic molecules including oligoarenes and oligo(phenylene–vinylene)s through Suzuki–Miyaura coupling [1]. Particular attention has been focused on the synthesis and utilization of functionalized organoboronic acid derivatives, because they serve not only as good starting materials for highly functionalized products [2], but also as "coupling modules" which enables repetitive or iterative cross-coupling processes [3–5]. We [4] and others [5] have recently reported the iterative Suzuki–Miyaura coupling systems on the basis of the new protective groups for the boronyl group (B(OH)$_2$) in the Suzuki–Miyaura coupling. To make this iterative cross-coupling system really practical, it seems important to find convenient synthetic routes to the coupling modules, i.e., masked haloareneboronic acids.

In our iterative cross-coupling system, 1,8-diaminonaphthalene serves as a highly efficient masking group, which is robust but quantitatively removable by treatment with aqueous acids [4]. The masked coupling modules are typically synthesized from the corresponding haloareneboronic acids by condensation with 1,8-diaminonaphthalene [4,6]. The synthesis seems convenient because it is easy, high yielding, and highly applicable. However, in case no starting organoboronic acids are easily available, the coupling modules have to be synthesized. Although the synthesis of the coupling modules can be made through preparation of the corresponding organoboronic acids, it seems more desirable to introduce the masked boronyl group directly into simple starting organic molecules. With this idea, our recent interest has been focused on the use of 1,8-naphthalenediaminatoborane ((dan)BH), whose reactivity is not fully explored. In this paper, we disclose the synthesis of masked haloareneboronic acids via iridium-catalyzed C–H borylation, which allowed us to synthesize coupling modules for convergent dendrimer synthesis.

2. Results and discussion

Transition-metal catalyzed C–H borylations of arenes have been developed rapidly [7], because they are highly efficient for the synthesis of areneboronic acid derivatives in comparison with reactions of organometallic reagents with boron nucleophiles and catalytic borylations in which haloarenes are used as starting materials [8]. We examined iridium-catalyzed C–H borylation of aromatic compounds [9], utilizing 1,8-naphthalenediaminatoborane (dan)BH (**1**) as a hydroborane [10,11]. To optimize the reaction condition, benzene (60 equiv.) was reacted with **1** in the presence of Ir complexes at 80 °C. The combination of [Ir(OMe)(cod)]$_2$ with a bipyridine-based ligand, DTBPY, which was utilized as the best catalyst in the original C–H borylation with pinacolborane, gave the corresponding C–H borylation product only in low yield (Table 1, entry 1) [12]. When no ligand or triphenylphosphine was used, only a trace amount of borylation product was detected by GC analysis (entries 2 and 3). Among the bidentate phosphine ligand examined (entries 4–10), DPPE showed the highest catalytic activity to afford the borylation product in moderate yield with use of

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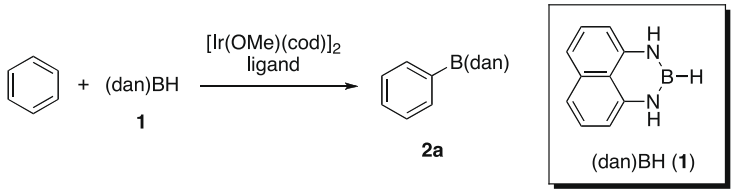
Table 1
Optimization of Ir-catalyzed C–H borylation of benzene with (dan)BH.[a]



Entry	Ligand[b]	Ir complex	Benzene (equiv.)	Temperature (°C)	% Yield[c]
1	DTBPY	$[Ir(OMe)(cod)]_2$	60	80	12
2	None	$[Ir(OMe)(cod)]_2$	60	80	4
3	PPh_3	$[Ir(OMe)(cod)]_2$	60	80	2
4	BINAP	$[Ir(OMe)(cod)]_2$	60	80	3
5	DPPF	$[Ir(OMe)(cod)]_2$	60	80	3
6	DPPM	$[Ir(OMe)(cod)]_2$	60	80	3
7	DPPE	$[Ir(OMe)(cod)]_2$	60	80	62
8	DMPE	$[Ir(OMe)(cod)]_2$	60	80	2
9	DPPP	$[Ir(OMe)(cod)]_2$	60	80	10
10	DPPB	$[Ir(OMe)(cod)]_2$	60	80	4
11	DPPE	$[Ir(OMe)(cod)]_2$	60	60	14
12	DPPE	$[Ir(OMe)(cod)]_2$	30	80	32
13	DPPE	$[Ir(OMe)(cod)]_2$	90	80	83
14	DPPE	$[Ir(OMe)(cod)]_2$	120	80	93 (87)
15	DPPE	$[IrCl(cod)]_2$	120	80	30
16	DPPE	$[Ir(cod)_2]BF_4$	120	80	5

[a] A mixture of (dan)BH, benzene, an iridium complex (5 mol% Ir), and ligand (5 mol% for the bidentate ligands and 10 mol% for PPh_3) was stirred.
[b] DTBPY: 4,4′-di-*t*-butyl-2,2′-bipyridyl; BINAP: 2,2′-bis(diphenylphosphino)-1-1′-binaphthyl; DPPF: 1,1′-bis(diphenylphosphino)ferrocene; DPPM: bis(diphenylphosphino)methane; DPPE: 1,2-bis(diphenylphosphino)ethane; DMPE: 1,2-bis(dimethylphosphino)ethane; DPPP: 1,3-bis(diphenylphosphino)propane; DPPB: 1,4-bis(diphenylphosphino)butane.
[c] GC yield. Isolated yield in the parenthesis.

60 equiv. of benzene (entry 7). Lowering the reaction temperature to 60 °C decreased the reaction yield significantly (entry 11). The amount of benzene used in the reaction also affected the yield (entries 12–14). Use of a smaller amount of benzene (30 equiv.) resulted in the formation of insoluble white precipitates, which were hardly identifiable (entry 12). Use of 120 equiv. benzene at 80 °C finally afforded the borylation product in 93% yield (entry 14). The product could be isolated by column chromatography on silica gel in 87% yield. Other iridium(I) complexes were also examined as catalysts for the C–H borylation of benzene with **1**. Neither the neutral chloroiridium complex nor the cationic complex showed remarkable catalytic activities (entries 15 and 16) [7c,9c,13].

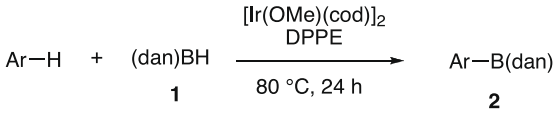
In the presence of $[Ir(OMe)(cod)]_2$ with DPPE as the optimized catalyst, C–H borylation of substituted arenes was carried out (Table 2). Monosubstituted arenes such as toluene, anisole, and trifluoromethylbenzene afforded the corresponding borylation products (entries 1–3). Note that C–H borylation took place at the *p*- and *m*-positions with the latter forming predominantly. *Meta*-dihalobenzenes underwent the C–H borylation in high yields at the most sterically favorable positions selectively (entries 4 and 5). *Ortho*-dibromobenzene afforded product **2g**, in which the boryl group was introduced to the 4-position regioselectively. With the 3-functionalized bromobenzenes, selective borylation at their 5-positions was observed, giving 1,3,5-trisubstituted arenes selectively (entries 7 and 8). Thiophene also underwent the C–H borylation selectively at the 2-position, giving the 2-borylated thiophene in good yield (entry 9).

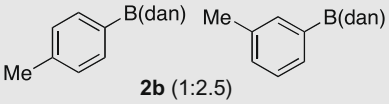
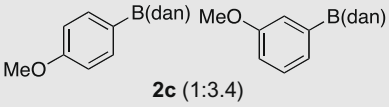
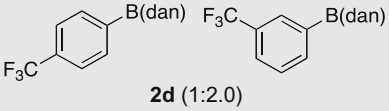
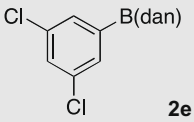
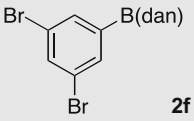
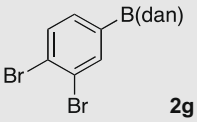
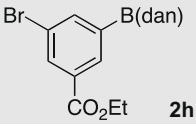
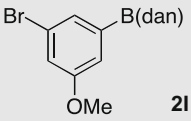
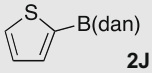
The dan-protected haloareneboronic acids are expected to serve as the coupling modules for the synthesis of oligoarene derivatives through iterative Suzuki–Miyaura coupling. We demonstrated the synthesis of new building blocks for the convergent dendrimer synthesis [14], taking **2f** as a dan-protected coupling module (Scheme 1). Initially, **2f** was coupled with *m*-hexyloxybenzeneboronic acid to obtain terphenyl derivative **4** bearing a protected boronyl group at the central benzene ring. As reported previously [4], Suzuki–Miyaura coupling at the unprotected boronyl group took place with high selectivity, leaving the masked boronyl group untouched. Prior to the synthesis of the second generation, **4** was treated with aqueous acid for unmasking. The resultant organoboronic acid was coupled with **2f** to afford the second generation **5** in good yield. The unmasking and coupling procedures were repeated once again, leading to the isolation of the third generation building block **6** in good yield. The module **6** can be used to finalize the dendrimer synthesis by the coupling with the core block or even to extend the generation to the higher dendrimers. It should be remarked that, in each step, no formation of undesirable side products was appreciable, when the unmasked organoboronic acids are used in excess. The coupling modules are easy to purify by recrystallization or silica gel chromatography, being expected to make the dendrimer synthesis more efficient and easier. A similar convergent synthesis of 1,3,5-phenylene-based dendrimers through Suzuki–Miyaura coupling was reported by using (3,5-dibromophenyl)trimethylsilane as a building block [15]. In their dendrimer synthesis, the silyl groups in the building blocks were converted into the boronyl group by treatment with BBr_3 followed by hydrolysis, before every Suzuki–Miyaura coupling processes. Our new method has obvious advantage over the previous method in that the use of the strong Lewis acid is avoidable, which may cleave the alkoxy side chains in our building blocks.

3. Conclusions

We have disclosed iridium-catalyzed C–H borylation of arenes with 1,8-naphthalenediaminatoborane ((dan)BH, **1**), which showed

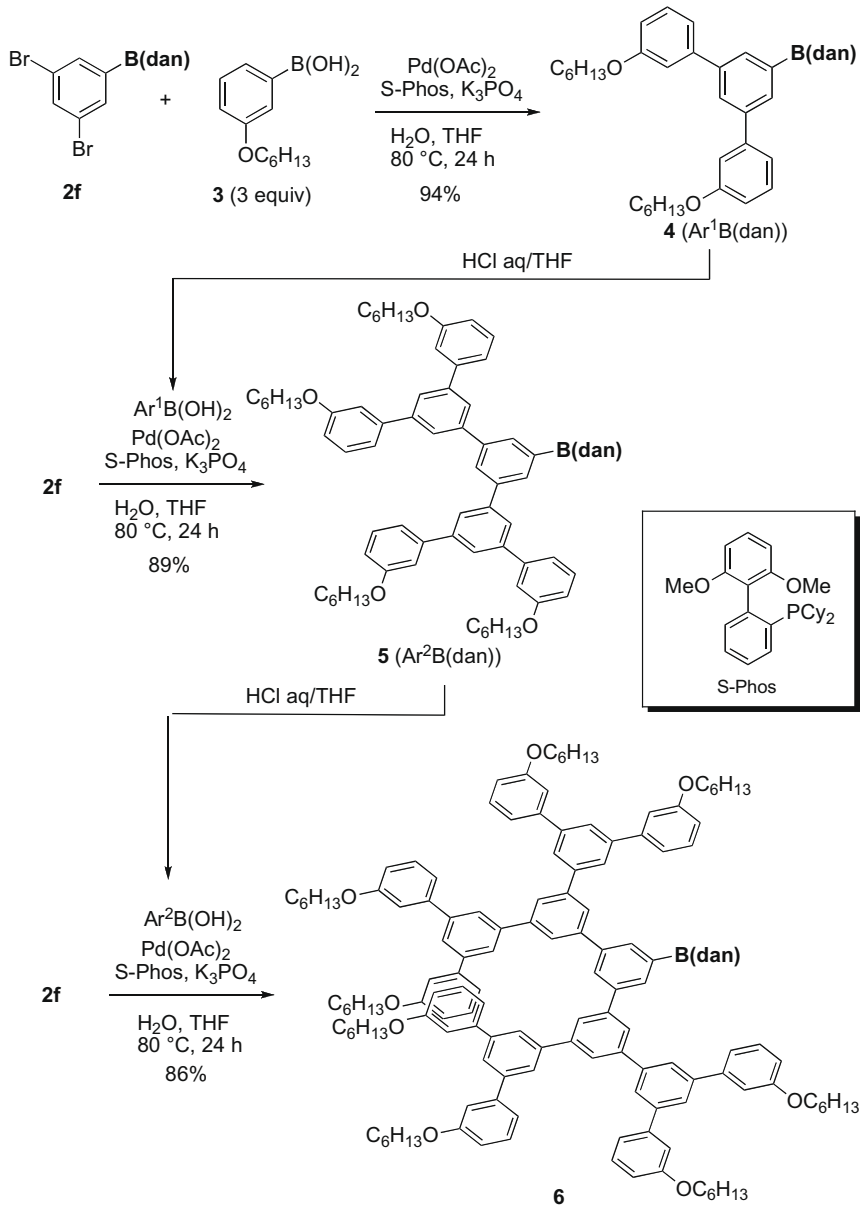
Table 2
Optimization of Ir-catalyzed C–H borylation of benzene with (dan)BH.[a]



Entry	Ar–H (equiv.)	Product(s)	%Yield[b]
1	Toluene (120)	 **2b** (1:2.5)	81
2	Anisol (120)	 **2c** (1:3.4)	61
3	Trifluoromethylbenzene (120)	 **2d** (1:2.0)	50
4	*m*-Dichlorobenzene (30)	 **2e**	80
5	*m*-Dibromobenzene (30)	 **2f**	83
6	*o*-Dibromobenzene (30)	 **2g**	73
7	Ethyl m-bromobenzoic acid (30)	 **2h**	58
8	*m*-Bromoanisol (30)	 **2l**	71
9	Thiophene (30)	 **2J**	77

[a] A mixture of (dan)BH, aromatic compound, an iridium complex (5 mol% Ir), and DPPE (5 mol%) was stirred at 80 °C for 24 h.
[b] Isolated yields.

lower reactivity than pinacolborane. The C–H borylation was significantly affected by the phosphine ligands used with the $[Ir(OMe)(cod)]_2$ catalyst: DPPE showed remarkable catalytic activity in comparison with other ligands such as DTBPY, DPPF, DPPM, DPPP, DMPE, and PPh_3. The C–H borylation of halobenzene derivatives afforded "masked" haloareneboronic acids, which may serve as coupling modules for the iterative cross-coupling. Taking the masked 1,3-dibromobenzeneboronic acid as a coupling module, iterative synthesis of new building blocks for the convergent dendrimer synthesis has been demonstrated. Synthesis of new coupling modules and their application to the synthesis of functionalized dendrimers is now being undertaken in this laboratory.



Scheme 1. Iterative synthesis of building blocks for the convergent dendrimer synthesis using **2f** as the cross-coupling module.

4. Experimental

4.1. Synthesis of (dan)BH (*1*)

To a solution of 1,8-diaminonaphthalene (20.0 mmol, 31.6 g) in dry CH_2Cl_2 (60 mL) at 0 °C was added a solution of $BH_3 \cdot SMe_2$ (20.0 mmol, 10.0 M) dropwise over 30 min. The reaction mixture was stirred for 30 min at 0 °C and for 24 h at room temperature. After evaporation of volatile materials, the title compound (28.4 g, 84%) was isolated by distillation (110 °C/0.3 mmHg) as spectroscopically pure material. Although **1** is the known compound, its spectral data is shown below. **1**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85 (br s, 2H), 6.32 (d, J = 6.8 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 7.16 (t, J = 7.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 106.2, 118.3, 120.9, 128.0, 136.8, 141.0; ^{11}B NMR (128 MHz, non-decoupled, $CDCl_3$) δ 26.7 (d, J = 109 Hz); IR (KBr) 3398, 2544 cm^{-1}; HRMS (EI) *m/z* Calc. for $C_{10}H_9BN_2$ (M+): 168.0859, found: 168.0861.

4.2. Typical procedure for the C–H borylation with *1*. Synthesis of *2f*

A mixture of **1** (50 mg, 0.30 mmol), $[Ir(OMe)(cod)]_2$ (3.3 mg, 5.0 mmol), DPPE (4.0 mg, 10 mmol), and 1,3-dibromobenzene (2.1 g, 9.0 mmol) was stirred at 80 °C for 24 h and cooled to room temperature. The solution was directly subjected to column chromatography on silica gel (hexane/CH_2Cl_2 = 2/1) to give **2f** (101 mg, 83%). Compound **2f**: ^{1}H NMR ($CDCl_3$) δ 5.93 (br s, 2H), 6.42 (dd, J = 7.2 Hz, 0.8 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 7.15 (dd, J = 8.0, 7.2 Hz, 2H), 7.67 (d, J = 1.6 Hz, 2H), 7.76 (t, J = 1.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 106.9, 118.9, 120.4, 124.0, 128.1, 133.4, 136.0, 136.8, 140.9; ^{11}B NMR (128 MHz, $CDCl_3$) δ 28.7; IR (KBr) 3436, 1600, 1402, 1235, 1095 cm^{-1}; HRMS (EI) *m/z* Calc. for $C_{16}H_{11}BBr_2N_2$ (M+): 399.9382, found: 399.9384. Following is the selected spectral and analytical data for compounds **2**. Compound **2g**: ^{1}H NMR ($CDCl_3$) δ 5.93 (br s, 2H), 6.41 (dd, J = 7.2 Hz, 0.8 Hz, 2H), 7.07 (dd, J = 8.4, 0.8 Hz, 2H), 7.15 (dd, J = 7.2, 8.4 Hz, 2H), 7.38 (dd, J = 8.0, 1.6 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.85 (d,

J = 1.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 106.8, 118.8, 120.4, 125.8, 127.3, 128.1, 131.8, 134.2, 136.8, 137.0, 141.0; ^{11}B NMR (128 MHz, $CDCl_3$) δ 28.9; IR (KBr) 3421, 1599, 1409, 1237, 1087 cm^{-1}; HRMS (EI) *m/z* Calc. for $C_{16}H_{11}BBr_2N_2$ (M+): 399.9382, found: 399.9391. Compound **2h**: ^{1}H NMR ($CDCl_3$) δ 1.43 (t, J = 7.2 Hz, 3H), 4.43 (q, J = 7.2 Hz, 2H), 6.04 (br s, 2H), 6.42 (d, J = 6.8 Hz, 2H), 7.07 (d, J = 8.4 Hz, 2H), 7.14 (dd, J = 6.8, 8.4 Hz, 2H), 7.91 (s, 1H), 8.21 (s, 1H), 8.24 (d, J = 1.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.8, 62.1, 106.8, 118.8, 120.4, 123.4, 128.1, 131.5, 132.6, 134.4, 136.7, 138.9, 140.9, 165.8; ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.0; IR (KBr) 3378, 1708, 1605, 1405, 1222, 1034 cm^{-1}; HRMS (EI) *m/z* Calc. for $C_{19}H_{16}BBrN_2O_2$ (M+): 394.0488, found: 394.0488. Compound **2i**: ^{1}H NMR (400.0 Hz, $CDCl_3$) δ 3.84 (s, 3H), 5.94 (br s, 2H), 6.40 (d, J = 7.2 Hz, 2H), 7.06–7.08 (m, 3H), 7.13–7.16 (m, 3H), 7.32 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 56.01, 106.7, 116.6, 118.6, 118.8, 120.4, 123.8, 126.7, 128.1, 136.8, 141.1, 160.7; ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.1; IR (KBr) 3412, 1602, 1406, 1049 cm^{-1}; HRMS (EI) *m/z* Calc. for $C_{17}H_{14}BBrN_2O$ (M+): 352.0383, found: 352.0382. Compound **2j**: ^{1}H NMR ($CDCl_3$) δ 5.98 (br s, 2H), 6.42 (dd, J = 7.2, 1.0 Hz, 2H), 7.09 (dd, J = 7.8, 1.0 Hz, 3H), 7.17 (dd, J = 7.8, 7.2 Hz, 2H), 7.25–7.27 (m, 1H), 7.51 (dd, J = 3.2, 0.8 Hz, 1H), 7.63 (dd, 4.4, 0.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 106.6, 118.4, 120.2, 128.0, 129.0, 130.5, 133.3, 136.8, 141.2; ^{11}B NMR (128 MHz, $CDCl_3$) δ 27.2; IR (KBr) 3402, 1598, 1415, 1233, 1067 cm^{-1}; HRMS (EI) *m/z* Calc. for $C_{14}H_{11}BN_2S$ (M+): 250.0736, found: 250.0744.

4.3. Typical procedure for the cross-coupling. Synthesis of *4*

To a solution of $Pd(OAc)_2$ (34 mg, 0.15 mmol), S-Phos (2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl, 123 mg, 0.300 mmol), and K_3PO_4 (0.96 g, 4.5 mmol) in THF (13 mL) were added **2f** (603 mg, 1.50 mmol), arylboronic acid **3** (1.0 g, 4.50 mmol), and then water (0.27 mL, 15 mmol), and the mixture was stirred at 80 °C for 24 h. To the cooled mixture was added water, and the organic material was extracted with CH_2Cl_2. The organic layer was dried over sodium sulfate and the solvent was evaporated under vacuum. The crude product was purified by silica gel column chromatography (hexane/CH_2Cl_2 = 2:1), affording coupling product **4** (842 mg, 94%). Compound **4**: ^{1}H NMR ($CDCl_3$) δ 0.911–0.95 (m, 6H), 1.35–1.40 (m, 8H), 1.50–1.53 (m, 4H), 1.84 (quint, J = 7.2 Hz, 4H), 4.06 (t, J = 6.4 Hz, 4H), 6.13 (br s, 2 H), 6.46 (dd, J = 7.6, 0.8 Hz, 2H), 6.95 (ddd, J = 8.0, 2.4, 0.8 Hz, 2H), 7.08 (dd, J = 8.4, 0.8 Hz, 2H), 7.17 (dd, J = 7.6, 8.4 Hz, 2H), 7.22–7.27 (m, 4H), 7.41 (t, J = 8.0 Hz, 2H), 7.81 (t, J = 0.8 Hz, 2H), 7.88 (t, J = 1.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.5, 23.1, 26.3, 29.8, 32.1, 68.7, 106.6, 113.8, 114.4, 118.4, 120.1, 120.4, 128.1, 128.6, 129.9, 130.3, 136.8, 141.5, 142.1, 143.0, 160.1; ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.8; IR (KBr) 3402, 2929, 1602, 1415, 1203 cm^{-1}; HRMS (EI) *m/z* Calc. for $C_{40}H_{45}BN_2O_2$ (M+): 596.3574, found: 596.3574. Compound **5**: ^{1}H NMR ($CDCl_3$) δ *0.88–0.91* (m, 12H), 1.33–1.36 (m, 16H), 1.46–1.48 (m, 8H), 1.81 (quint, J = 7.4 Hz, 8H), 4.03 (t, J = 6.4 Hz, 8H), 6.18 (br s, 2H), 6.49 (d, J = 7.2 Hz, 2H), 6.94 (m, 4H), 7.08 (d, J = 7.6 Hz, 2H), 7.16 (dd, J = 7.2, 7.6 Hz, 2H), 7.24–7.26 (m, 4H), 7.30 (d, J = 8.0 Hz, 4H), 7.40 (t, J = 8.0 Hz, 4H), 7.83 (t, J = 1.6 Hz, 2H), 7.86 (d, J = 2.0 Hz, 4H), 7.94 (d, J = 2.0 Hz, 2H), 8.05 (t, J = 1.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.5, 23.1, 26.2, 29.8, 32.1, 68.6, 106.7, 114.0, 114.3, 118.5, 120.2, 120.5, 126.0, 126.1, 128.1, 129.0, 130.3, 130.4, 136.8, 141.4, 142.4, 142.7, 142.9, 143.0, 160.1; HRMS (FAB) *m/z* Calc. for $C_{76}H_{85}BN_2O_4$ (M+): 1100.6602, found: 1100.6597. Compound **6**: ^{1}H NMR (500.0 MHz, C_6D_6) δ 0.85 (t, J = 7.0 Hz, 24H), 1.17–1.25 (m, 32H), 1.28–1.34 (m, 16H), 1.62 (quint, J = 6.5 Hz, 16H), 3.67 (t, J = 6.3 Hz, 16H), 5.66 (br s, 2H), 6.02 (d, 5.5 Hz, 2H), 6.91 (dd, J = 8.5, 1.5 Hz, 8H), 7.05–7.10 (m, 4H), 7.20 (t, J = 8.0 Hz, 8H), 7.26 (d, J = 8.0 Hz, 8H), 7.41 (s, 8H), 7.90 (s, 2H), 8.03 (s, 4H), 8.10 (d, J = 1.5 Hz, 8H), 8.15 (s, 2H), 8.19 (d, J = 1.5 Hz, 4H), 8.30 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.5, 23.1, 26.2, 29.8, 32.1, 68.6, 106.7, 114.0, 114.2, 118.4, 120.2, 120.5, 126.0, 126.1, 126.5, 128.1, 129.2, 130.3, 130.5, 136.8, 141.4, 142.4, 142.6, 142.9, 143.0, 143.1, 143.2, 160.1; HRMS (FAB) *m/z* Calc. for $C_{76}H_{85}BN_2O_4$ (M+): 2109.2659, found: 2110.2773.

4.4. Typical procedure for the unmasking

To a solution of **4** (1.02 g, 1.7 mmol) in THF (41 mL) was added HCl aq (5 N, 4.1 mL, 21 mmol) at room temperature. The homogeneous mixture was stirred at room temperature for 8 h, leading to the formation of precipitation in the solution. To the mixture was added HCl aq (3 N, 30 mL), and the suspension was filtered through a pad of Celite. The filtrate was extracted with Et_2O twice. The organic layer was dried over magnesium sulfate and evaporated under vacuum. The material (843 mg, 95% yield) was essentially pure by ^{1}H NMR determination and used for the cross-coupling reaction without further purification.

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