原著論文　１４）

Synthesis of a Novel Potential Tridentate Anthracene Ligand, 1,8-Bis(dimethylamino)-9-bromoanthracene, and its Application as Chelete Ligand for Synthesis of the Corresponding Boron and Palladium Compounds**

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Abstract

A novel potential tridentate ligand, 1,8-bis(dimethylamino)-9-bromoanthracene, was synthesized. Key steps are the following; (i) dimethylamination of 1,8-dibromo-9-methoxyanthracene by a modified Buchwald's method to afford 1,8-bis(dimethylamino)-9-methoxyanthracene, (ii) reduction of the methoxy group by LDBB (lithium di-*tert*-butylbiphenylide) followed by treatment with $BrCF_2CF_2Br$. The corresponding 1,8-bis(dimethylamino)-9-lithioanthracene, which should be a useful versatile tridentate ligand, could be generated by treatment of the bromide with 1 equiv. of *n*BuLi. The lithioanthracene reacted with *B*-chloroborane derivatives to give three 9-boryl derivatives. Although we recently reported that the crystal structure of 1,8-dimethoxy-9-*B*-catecholateborylanthracene showed the symmetrical nature of the compound with the almost identical two O--B distances {2.379(2) and 2.441(2)Å}, the newly prepared 1,8-bis(dimethylamino)-9-borylanthracene derivatives clearly showed the unsymmetrical structures with coordination of only one NMe_2 group toward the central boron atom. But the energy difference between the unsymmetrical structure and the symmeterical one was found to be very small based on the ^1H NMR measurement, showing symmetrical anthracene patterns in the aromatic region (two kinds of doublets and a triplet) and a sharp singlet signal of the two NMe_2 groups even at -80 $^\circ$C. 1,8-Bis(dimethylamino)-

9-bromoanthracene itself can be a versatile ligand for transition metal compounds. In fact, direct palladation of the bromide took place by the reaction with $Pd_2dba_3 \cdot CHCl_3$ in THF to give the 9-palladated product. X-ray crystallographic analysis of the Pd compound showed symmetrical tetracoordinate planar palladium atom by coordination of the both NMe_2 groups {Pd-N bonds are 2.138(5) and 2.146(5) Å}.

Introduction

Recently, we reported synthesis of hypervalent pentacoordinate carbon compound bearing a rigid anthracene skeleton, which was prepared from 1,8-dimethoxy-9-trifluoromethanesulfonyloxyanthracene,[1a] and of hypervalent pentacoordinate boron compounds (2) from 1,8-dimethoxy-9-bromoanthracene (1).[1b] Although anthracene bearing only two dimethylamino groups at 1,8-positions (3) has been synthesized in trace amounts by Haenel et al,[2] 3 has not been used as a potential tridentate ligand probably because of the inefficient synthetic method and inertness toward introduction of transition metal compounds. However, such rigid potential tridentate anthracene ligand has eagerly been desired since several bi-[3] and tri-dentate ligands bearing dimethylamino groups, especially van Koten type tridentate ligand such as 2,6-bis(dimethylaminomethyl)phenyl ligand (4), have been effectively applied for stabilization of highly-coordinated main group element compounds,[4] and for transition

metal catalysts of various reactions[5] such as organoplatinum crystals for gas-triggered switches.[6]

Figure 1
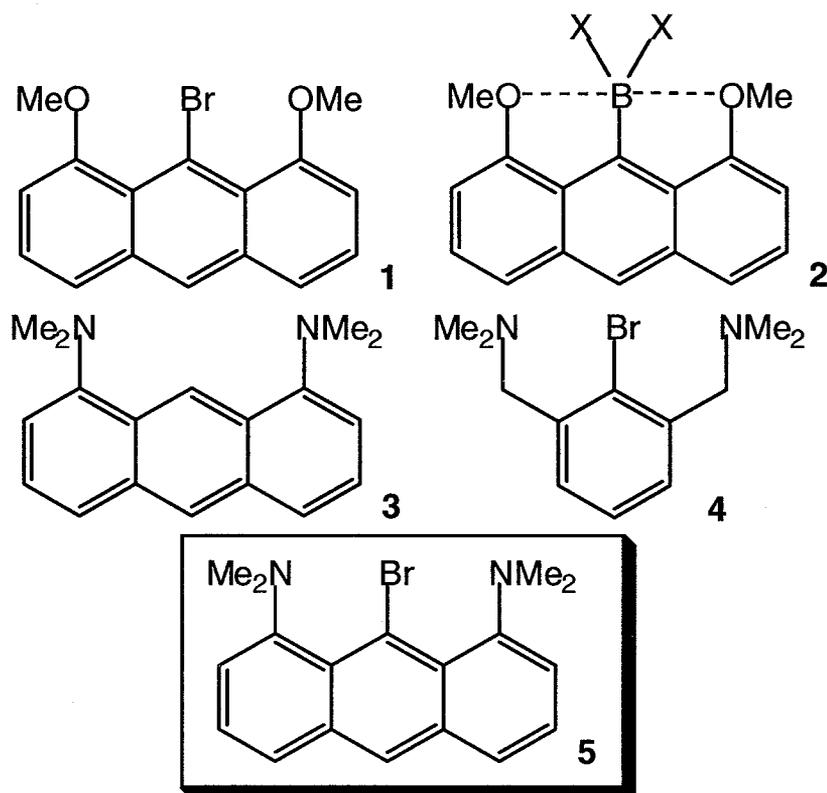
Here, we report first synthesis of the potential anthracene ligand bearing two dimethylamino groups at 1,8 positions with a Br atom at 9-position (**5**). The bromide should be a very useful versatile potential tridentate ligand, and in fact, **5** could be easily lithiated with nBuLi to introduce a boron atom to the 9-position and could be converted to the corresponding palladium compound.
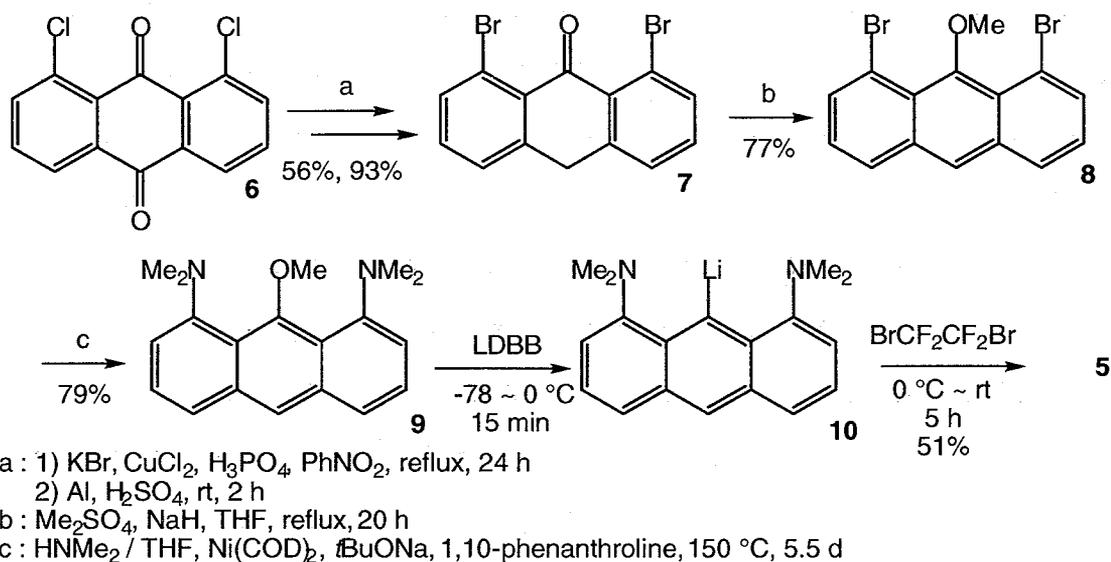
Results and Discussion

In order to prepare **5**, we examined the possibility for direct lithiation of 1,8-bis(dimethylamino)anthracene (**3**)[2] with various base (*n*BuLi, *s*BuLi and *t*BuLi) in various solvents (ether, THF and hexane) with or without addition of TMEDA, but the lithiation at the 9 position did not take place at all. In addition, a strategy to use 1,8-bis(dimethylamino)anthrone as a synthetic intermediate which is based on our previous synthesis of 1,8-dimethoxy-9-bromoanthracene,[1b] did not work because reduction of 1,8-bis(dimethylamino)anthraquinone to the corresponding anthrone was not successful.

Finally, **5** could be prepared by a completely new route as illustrated in Scheme 1. Bromine substitution[7] and reduction[8] of commercially available dichloroanthraquinone **6** afforded dibromoanthrone (**7**) in good yield. Deprotonation of **7** followed by methylation gave 1,8-dibromo-9-methoxyanthracene (**8**) in 77 % yield. Pd(0) mediated coupling reaction of **8** with various nucleophiles (Bu_3SnNMe_2, Me_3SnNMe_2, $LiNMe_2$ and $HNMe_2$) did not give an expected bis-dimethylaminated compound (**9**), instead only mono-dimethylaminated product was obtained in most cases and reduction of the C-Br bonds took place in some cases. However, dibromoanthracene **8** could be converted to desired 1,8-bis(dimethyamino)-9-methoxyanthracene **9** in 79 % yield by heating a $HNMe_2$-THF solution of **8** up to 150 °C in a pressure-resistant vessel with Ni(0)-catalyst, which is a modified Buchwald's method.[9] To our knowledge, this is the first example for direct dimethylamination of aryl bromides. LDBB (lithium di-*tert*-butylbiphenylide) reduction of the

methoxy group at the 9-position[1b,10] worked well for **9** to afford the novel anthracene ligand **5** in 51% yield after reaction with $BrCF_2CF_2Br$.

Scheme 1

a : 1) KBr, $CuCl_2$, H_3PO_4, $PhNO_2$, reflux, 24 h
    2) Al, H_2SO_4, rt, 2 h
b : Me_2SO_4, NaH, THF, reflux, 20 h
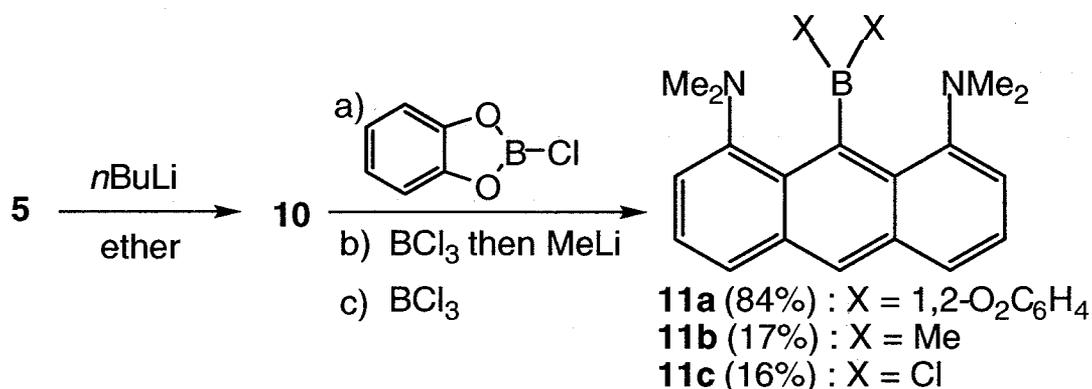c : $HNMe_2$ / THF, Ni(COD)$_2$, *t*BuONa, 1,10-phenanthroline, 150 °C, 5.5 d

LDBB = lithium di-*tert*-butylbiphenylide

After regeneration of the lithium derivative **10** by the reaction of **5** with *n*BuLi in ether, **10** was reacted with various boron reagents to give 9-boryl derivatives (**11a-c**) (Scheme 2). These boryl derivatives (**11a-c**) were air and moisture stable and the single crystals of **11a-c** suitable for X-ray analysis were obtained from CH_2Cl_2-hexane solution. X-ray crystallographic analysis of **11a-c** (Figure 2) showed the unsymmetrical structures with coordination of only one NMe_2 group toward the central boron atom. Shorter N–B bond lengths are 1.809(2) Å in **11a**, 1.739(2) Å in **11b**, and 1.664(3) Å in **11c**, and the longer N–B bonds are 2.941(2) Å in **11a**, 3.124(3) Å in

11b, and 3.129(3) Å in **11c,** respectively. The results are somewhat surprising because almost symmetrical structures were observed in the corresponding boron compounds (**2**) bearing the OMe group at 1,8-positions,[1b] although similar unsymmetrical structure was recently observed by us in the corresponding boron

Scheme 2

5 $\xrightarrow[\text{ether}]{n\text{BuLi}}$ 10 $\xrightarrow[\substack{\text{b) BCl}_3 \text{ then MeLi} \\ \text{c) BCl}_3}]{\text{a)}}$

11a (84%) : X = 1,2-O$_2$C$_6$H$_4$
**11b** (17%) : X = Me
11c (16%) : X = Cl

compound with phosphorus donors {P(*i*Pr)$_2$} at 1,8-position of the anthracene skeleton.[10] The reason why **11** showed unsymmetrical structures in contrast to **2** with oxygen donors is not clear yet, but the unsymmetrical structures observed in **11** may be related to the stronger N–B bonding energy in comparison with the corresponding O–B energy as was reported for F$_3$B-NMe$_3$ (26.6 kcalmol^{-1}) and F$_3$B-OEt$_2$ (13.9 kcalmol^{-1}).[11] But the energy difference between the unsymmetrical structure and the symmetrical one should be very small (vide infra).

In ^{1}H NMR (CDCl$_3$ or CD$_2$Cl$_2$), **11a-c** showed symmetrical anthracene patterns in the aromatic region (two kinds of doublets and a triplet) and a sharp singlet signal of the two NMe$_2$ groups at room temperature. The peaks kept its sharpness and symmetrical pattern even at -80 $^\circ$C even in the most unsymmetrical dichloro compound **11c** (CD$_2$Cl$_2$). Since the energy barrier of the N-B bond switching process in **11c** was too small to measure by coalescence method, the energy difference between the unsymmetrical tetracoordinate dichloroboron **11c** and the pentacoordinate one **11c**‡, which should be the transition state


11a   11b   11c
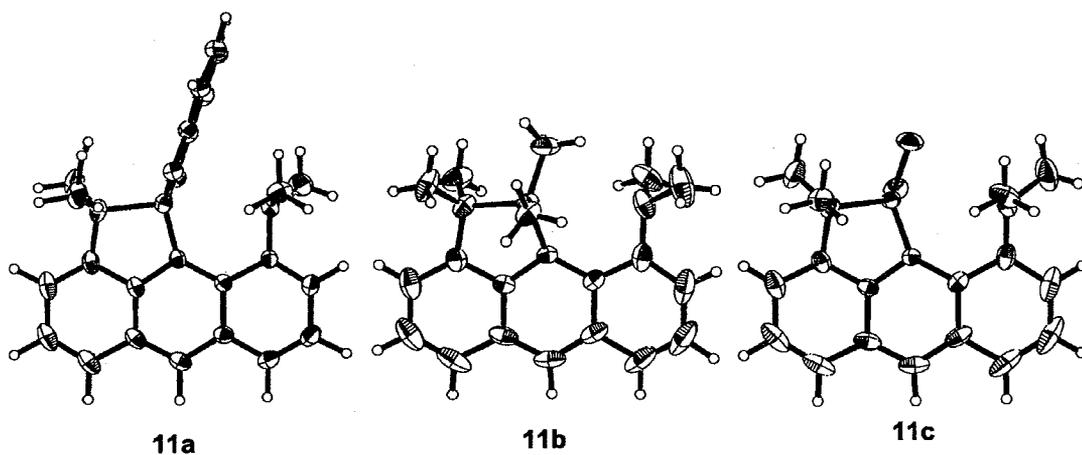
of the bond switching process named as _bell-clapper_ mechanism[12], must be very small (Scheme 3). The result is in contrast to the relatively high energy barrier of the similar S$_N$2 type reaction of BCl$_2$[2,6-(NEt$_2$CH$_2$)$_2$C$_6$H$_3$] (**12**)[13a], which showed two kinds of NEt$_2$ groups in C$_6$D$_6$ or THF-d$_8$ solvents at 25 $^\circ$C.

Scheme 3

11c   11c‡

hypervalent
5-coordinate boron

11c
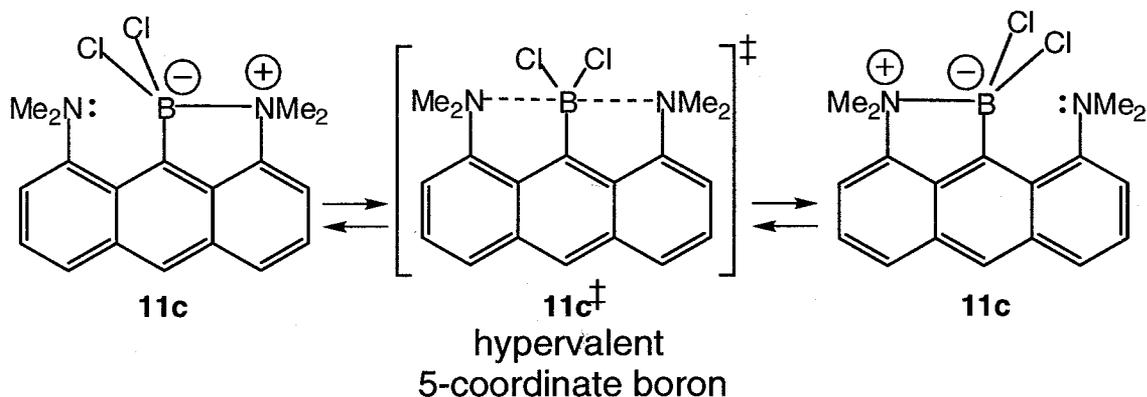
In order to show the versatility of the newly prepared potential ligand (5), direct palladation of 5 was examined. Although the reaction with Pd(PPh$_3$)$_4$ gave a complicated mixture, reaction of 5 with Pd$_2$dba$_3$·CHCl$_3$ in THF gave the expected 9-palladated product 13 in 33 % yield

12
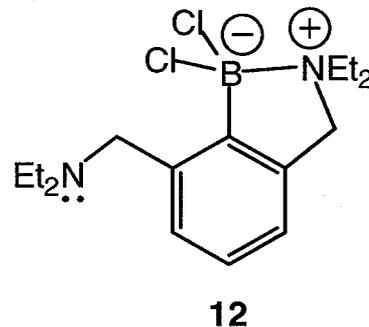
(Scheme 4). Although 13 was not stable under air in solution and decomposed during purification with silica gel, it could be purified by recycle HPLC (Japan Analytical Industry). The single crystals of 13 suitable for X-ray analysis were obtained from CH$_2$Cl$_2$-hexane. ORTEP drawing of 13 is illustrated in Figure 3, showing symmetrical tetracoordinate planar palladium atom by coordination of the both NMe$_2$ groups. The bond lengths of the two Pd-N bonds are 2.138(5) and 2.146(5) Å. These lengths are slightly longer than a sum of the covalent radii (1.98 Å),[14] and are also longer than the reported Pd-N (or Pt-N) bond lengths in NCN pincer type tridentate compounds, for

example, Pd-N(sp^2) (2.06 Å),[15] Pt-N(sp^3) (2.08-2.11 Å) [5a,6c,16] although we did not find examples for N(sp^3)-Pd-N(sp^3) type compounds. The longer Pd-N length may be due to the strain of the anthracene skeleton, and efficient reactivities of **13** as catalysts may be anticipated. The investigation toward the direction is under way.
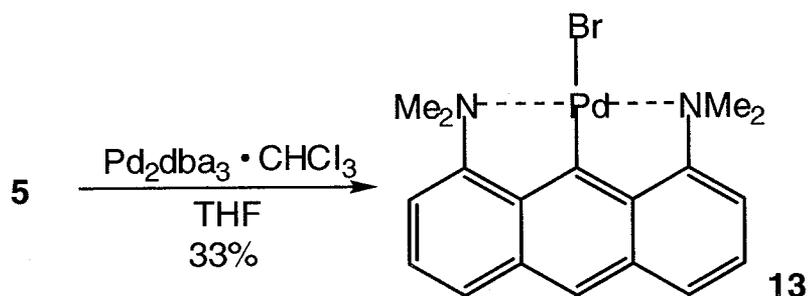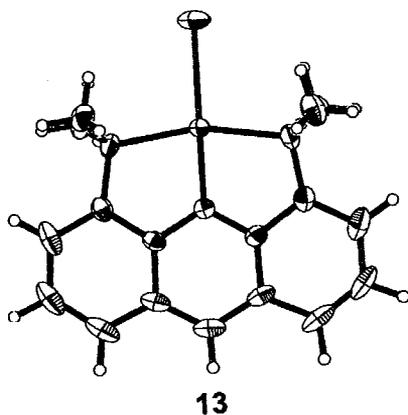

Figure 3

13

Experimental Section

General

Ether and tetrahydrofuran were freshly distilled from sodium-benzophenone and other solvents were distilled from calcium hydride under argon atmosphere. Merck silica gel 9385

and 7730 was used for column chromatography and preparative TLC. LC908-C60 and LC-918 (Japan Analytical Industry, JAIGEL-2H, $ClCH_2CH_2Cl$) and LC908 (Japan Analytical Industry, JAIGEL-ODS-AP, $CH_3CN/THF = 9/1$) were used for HPLC purification. Melting points were taken on a Yanagimoto micro melting point apparatus. ^{1}H NMR (400 MHz), ^{11}B NMR (127 MHz) and ^{13}C NMR (99 MHz) spectra were recorded on a JEOL EX-400 and AL-400 spectrometer. Chemical shifts (δ) are reported as parts per million from internal $CHCl_3$ for [1]H (δ 7.26) or from external $BF_3 \cdot OEt_2$ for [11]B (δ 0.0) or from internal $CDCl_3$ for [13]C (δ 77.0). Elemental analysis was performed on Perkin-Elmer 2400CHN elemental analyzer.

Synthesis of 9 : A mixture of **8**[10] (9.15 g, 25 mmol) and $Ni(COD)_2$ (687 mg, 2.5 mmol) and tBuONa (9.60 g, 100 mmol) and 1,10-phenanthroline (905 mg, 5.0 mmol) and THF solution of $HNMe_2$ (100 mL, 2.0 M, 200 mmol) was stirred for 5.5 d at 150 °C in a pressure-resistant vessel under Ar. The crude product was purified by column chromatography (CH_2Cl_2) to give yellow-orange powder of **9** (5.8 g, 79%); m.p. 98-100 °C (dec.); ^{1}H NMR (400MHz, $CDCl_3$, 25 °C, $CHCl_3$) δ 2.94 (s, 12H; NMe_2), 3.59 (s, 3H; OMe), 6.90 (d, [3]J (H, H) = 8 Hz, 2H; aromatic CH), 7.30 (t, [3]J (H, H) = 8 Hz, 2H; aromatic CH), 7.49 (d, [3]J (H, H) = 8 Hz, 2H; aromatic CH), 8.07 (s, 1H; aromatic CH); ^{13}C NMR (99 MHz, $CDCl_3$, 25 °C, $CDCl_3$) δ 45.4, 62.8, 111.0, 120.6, 121.5, 122.5, 125.2, 134.9, 150.2, 154.3; MS (FAB[+]): m/z : 294 [M+1[+]]; elemental analysis calcd for $C_{19}H_{22}N_2O$: C 77.52, H 7.53, N 9.52; found: C 77.82, H 7.61, N 9.44.

Synthesis of 5 : THF (100 mL) was added to a mixture of Li (278 mg, 40 mmol) and di-*tert*-butylbiphenyl (DTBB; 10.7 g, 40 mmol) at 0 °C under Ar. The mixture was stirred for 6 h at 0 °C to give lithium di-*tert*-butylbiphenylide (LDBB) solution. The LDBB solution was added to a solution of **9** (5.49 g, 19 mmol) in THF (100 mL) at −78 °C within 5 min. The reaction mixture was quickly allowed to warm to 0 °C and was stirred for 15 min at 0 °C. Then, $BrCF_2CF_2Br$ (3.6 mL, 30 mmol) was added dropwise to the reaction mixture at 0 °C. The reaction mixture was allowed to warm to rt and was stirred for 5 h at rt. The product was purified by column chromatography (CH_2Cl_2 : hexane = 1 : 5) to give red-orange powder of pure **5** (3.3 g, 51%); m.p. 142-144 °C (dec.); ^{1}H NMR (400MHz, $CDCl_3$, 25 °C, $CHCl_3$) δ 2.93 (s, 12H; NMe_2), 7.03 (d, ^3J (H, H) = 8 Hz, 2H; aromatic CH), 7.36 (t, ^3J (H, H) = 8 Hz, 2H; aromatic CH), 7.54 (d, ^3J (H, H) = 8 Hz, 2H; aromatic CH), 8.26 (s, 1H; aromatic CH); ^{13}C NMR (99 MHz, $CDCl_3$, 25 °C, $CDCl_3$) δ 43.8, 113.3, 115.8, 121.3, 125.3, 127.0, 127.2, 134.3, 150.3; MS (FAB$^+$): m/z : 342/344 [M$^+$]; elemental analysis calcd for $C_{18}H_{19}BrN_2$: C 62.98, H 5.58, N 8.16; found: C 62.95, H 5.31, N 8.03.

Synthesis of 11a-c : A solution of *n*BuLi in *n*hexane (0.35 mL, 0.55 mmol) was added dropwise to a solution of **5** (172 mg, 0.5 mmol) in THF (10 mL) at −78 °C under Ar. The reaction mixture was stirred for 1.5 h at −78 °C and **10** was generated in situ. Boron reagent [*B*-chlorocatecholborane (85.3 mg, 0.55 mmol) in THF (2 mL) for **11a**; a solution of BCl_3 in heptane (0.5 mL, 0.5 mmol) for **11b** and **11c**] was added dropwise to the solution of

10. The reaction mixture was stirred for 2 h at −78 °C [followed by an addition of a solution of MeLi in ether (1.3 mL, 1.5 mmol) for **11b**] and for 3 h at rt. Solvents were removed from the reaction mixture under reduced pressure. The crude products were purified [by HPLC (LC908-C60) for **11a** (RT = 64 min), by preparative TLC for **11b** (CH_2Cl_2 : hexane = 1 : 3 eluent), and by HPLC for **11c** (RT = 69 min)] to give **11a** (84 mg, 49%), **11b** (36 mg, 17%) and **11c** (28 mg, 16%). The single crystals of **11a-c** suitable for X-ray analysis were obtained from their CH_2Cl_2/hexane solution under Ar; **11a**; yellow-green solid, m.p. 194-196 °C (dec.); ^1H NMR (400MHz, $CDCl_3$, 25 °C, $CHCl_3$) δ 2.65 (s, 12H, NMe_2), 6.82 (dd, ^3J (H, H) = 6 Hz, ^4J (H, H) = 3 Hz, 2H; catechol CH), 6.92 (dd, ^3J (H, H) = 6 Hz, ^4J (H, H) = 3 Hz, 2H; catechol CH), 7.28 (d, ^3J (H, H) = 8 Hz, 2H; aromatic CH), 7.45 (t, ^3J (H, H) = 8 Hz, 2H; aromatic CH), 7.87 (d, ^3J (H, H) = 8 Hz, 2H; aromatic CH), 8.44 (s, 1H; aromatic CH); ^{11}B NMR (127 MHz, $CDCl_3$, 25 °C, $BF_3 \cdot Et_2O$) δ 17-20 (br); **11b**; yellow solid, m.p. 186-187 °C (dec.); ^1H NMR (400MHz, $CDCl_3$, 25 °C) δ 0.19 (s, 6H, BMe_2), 2.83 (s, 12H, NMe_2), 7.21 (d, ^3J (H, H) = 8 Hz, 2H; aromatic CH), 7.39 (t, ^3J (H, H) = 8 Hz, 2H; aromatic CH), 7.80 (d, ^3J (H, H) = 8 Hz, 2H; aromatic CH), 8.17 (s, 1H); ^{11}B NMR (127 MHz, $CDCl_3$, 25 °C, $BF_3 \cdot Et_2O$) δ 8-14 (br); **11c**; yellow solid, m.p. 132-134 °C (dec.); ^1H NMR (400MHz, $CDCl_3$, 25 °C, $CHCl_3$) δ 3.04 (s, 12H, NMe_2), 7.38 (d, ^3J (H, H) = 8 Hz, 2H; aromatic CH), 7.47 (t, ^3J (H, H) = 8 Hz, 2H; aromatic CH), 7.87 (d, ^3J (H, H) = 8 Hz, 2H; aromatic CH), 8.38 (s, 1H; aromatic CH); ^{11}B NMR (127 MHz, $CDCl_3$, 25 °C, $BF_3 \cdot Et_2O$) δ 12-15 (br).

Synthesis of 13 : THF (1 mL) was added to a mixture of **5** (34 mg, 0.1 mmol) and $Pd_2dba_3 \cdot CHCl_3$ (78 mg, 0.75 mmol) at rt under Ar. After the reaction mixture was stirred at 75 °C for 1 h, the mixture was filtered. The solid was purified by HPLC (LC908 and LC918) to afford yellow solids of **13** (14.4 mg, 33%). Single crystals suitable for X-ray analysis were obtained from CH_2Cl_2-hexane; m.p. 154–162 °C (dec.); ^1H NMR (400MHz, $CDCl_3$, 25 °C, $CHCl_3$) δ 3.55 (s, 12H; NMe_2), 7.26 (d, ^3J (H, H) = 8 Hz, 2H; aromatic CH), 7.45 (t, ^3J (H, H) = 8 Hz, 2H; aromatic CH), 7.77 (d, ^3J (H, H) = 8 Hz, 2H; aromatic CH), 8.03 (s, 1H; aromatic CH); ^{13}C NMR (99 MHz, $CDCl_3$, 25 °C, $CDCl_3$) δ 54.5, 114.6, 116.3, 126.7, 126.9, 132.7, 134.6, 156.8, 158.7.

X-ray structural analysis of 11a–c and 13. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallogrphic Data Centre as supplmentary publication nos. CCDC-176315, 176316, 176317, and 176318. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). Data were collected at 298K on a Mac Science DIP2030 imaging plate equipped with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Unit cell parameters were determined by autoindexing several images in each data set separately with program DENZO. For each data set, rotation images were collected in 3° increments with a total rotation of 180° about ϕ. Data were processed by using SCALEPACK. The structure was solved using the teXsan system and refined

by full-matrix least-squares. Crystal data for **11a**: monoclinic system, space group $P2_1/n$ (no. 14), a = 16.3780(6) Å, b = 7.4670(2) Å, c = 16.9660(6) Å, β = 105.007(2)°, V = 2004.1(1) Å^3, Z = 4, ρ_{calc} = 1.267 g cm^{-3}. R = 0.0661 (Rw = 0.1247) for 4022 observed reflections (262 parameters) with $I>2\sigma(I)$. Goodness of fit = 1.308; Crystal data for **11b**: monoclinic system, space group $P2_1/n$ (no. 14), a = 10.7260(4) Å, b = 12.5420(4) Å, c = 13.0800(4) Å, β = 91.437(2)°, V = 1759.04(9) Å^3, Z = 4, ρ_{calc} = 1.149 g cm^{-3}. R = 0.0699 (Rw = 0.1271) for 3321 observed reflections (208 parameters) with $I>2\sigma(I)$. Goodness of fit = 1.584; Crystal data for **11c**: monoclinic system, space group $P2_1/n$ (no. 14), a = 12.7770(4) Å, b = 12.5510(6) Å, c = 10.7200(4) Å, β = 90.546(3)°, V = 1719.0(1) Å^3, Z = 4, ρ_{calc} = 1.333 g cm^{-3}. R = 0.0667 (Rw = 0.1344) for 3323 observed reflections (208 parameters) with $I>2\sigma(I)$. Goodness of fit = 1.516; Crystal data for **13**: tetragonal system, space group $P4_1$ (no. 76), a = 10.3490(2) Å, c = 16.1520(4) Å, V = 1729.91(5) Å^3, Z = 4, ρ_{calc} = 1.726 g cm^{-3}. R = 0.0426 (Rw = 0.0668) for 2081 observed reflections (200 parameters) with $I>3\sigma(I)$. Goodness of fit = 1.054. The programs (DENZO and SCALEPACK) are available from Mac Science Co. Z. Otwinowski, University of Texas, Southwestern Medical Center. The program teXsan is available from Rigaku Co.

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