

Palladium-catalyzed cross-coupling reactions of arylboronic acids and 2-I-*p*-carborane

Ludvig Eriksson^{a,b}, Irina P. Beletskaya^{b,*}, Vladimir I. Bregadze^{c,*}, Igor B. Sivaev^{a,c},
Stefan Sjöberg^{a,*}

^a Department of Organic Chemistry, Institute of Chemistry, Uppsala University, P.O. Box 531, S-751 21 Uppsala, Sweden

^b Department of Chemistry, M.V. Lomonosov Moscow State University, Leninskie Gory, GSP-3, 119899 Moscow, Russia

^c A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov Str. 28, 119991 Moscow, Russia

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Abstract

p-Carborane has been arylated on the 2-*B*-atom in high yields, using the Suzuki–Miyaura reaction. Thus the reaction between 2-*I-p*-carborane and various arylboronic acids [1-naphthyl-, phenyl-, 4-MeO–C₆H₄–, 3-CH₃CONH–C₆H₄–, 4-NC–C₆H₄–, 3-NO₂–C₆H₄–], gave the corresponding 2-aryl-*p*-carboranes in DME solution when reacted in the presence of cesium fluoride and the catalytic Pd₂(dba)₃–dppb system. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: *p*-Carborane; Arylboronic acids; Suzuki–Miyaura reactions; Cross-coupling; Palladium

1. Introduction

The carboranes C₂B₁₀H₁₂ exhibit remarkable chemical stability and are generally biologically inactive [1]. The use of carboranes in boron neutron capture therapy (BNCT) for cancer has attracted much interest in recent years. For this purpose, numerous carborane-containing derivatives of biomolecules have been synthesized [2–5]. Besides for BNCT application, until recently, only a few cases have been described where use has been made of the carborane cages as hydrophobic pharmacophores in biologically active molecules. One of the most explored compounds in this respect is *o*-carboranylalanine, the *o*-carboranyl analogue of phenylalanine, which has been used to replace phenylalanine and tyrosine in biological active peptides, such as [4-carboranyl-alanine, 5-leucine]-enkephalin, angiotensins, bradykinins and substance-*P* octapeptides. This work has recently been reviewed [6]. Research on the use of carboranes as

hydrophobic pharmacophores has recently been intensified [7–9], in particular by Endo [10–13].

Another field of potential application of carborane derivatives is material science. High chemical and thermal stability in combination with the rigid structure of the carborane cage and the possibility of attachment of different types of substituents make them good candidates for synthesis of new interesting materials [14–18].

We are working on the synthesis of aryl- and heteroaryl derivatives of carboranes containing different functional groups, which we link directly to a boron atom.

The *C*-arylation of *p*-carborane via its *C*-copper derivatives has been widely studied during the last decade [11–13,16,19–21] and was there achieved, under the action of aryl- and pyridyl-halides on Li(Mg)-derivatives of carboranes under the catalysis of copper salts.

The *B*-arylation of *p*-carborane is much less studied. Synthesis of phenyl- and *p*-fluorophenyl-derivatives of *p*-carborane by the palladium-catalyzed cross-coupling reaction of 2-iodo-*p*-carborane with Grignard reagents were reported [22,23]. However, the application of Grignard reagents limits the introduction of substituents

* Corresponding authors. Tel.: +46-18-513563; fax: +46-18-512524.

E-mail addresses: beletska@org.chem.msu.ru (I.P. Beletskaya), bre@ineos.ac.ru (V.I. Bregadze), ssj@kemi.uu (S. Sjöberg).

containing functional groups. Besides, it is known, that using less active arylhalides in the reaction with organomagnesium compounds often yields a larger amount of homocoupling products. To overcome this problem, we have developed a mild method of the *B*-arylation using the Suzuki–Miyaura cross-coupling reaction with arylboronic acids and 2-*I-p*-carborane.

An attempt to use the Suzuki–Miyaura cross-coupling reaction for *B*-phenylation of *o*- and *m*-carborane was undertaken by Zakharkin et al. [24], but the yield of phenylcarborane derivatives in the case of 9-*I-m*-carborane was very low and 9-*I-o*-carborane did not produce any expected cross-coupling product. In both cases, biphenyl and the unsubstituted carboranes were formed.

2. Results and discussion

In the palladium catalyzed cross-coupling reactions of 2-*I-p*-carborane (**1**) with arylboronic acids, we have used CsF in DME, utilizing the facts that the fluoride ion is a good activating nucleophile and a mild base. The use of the fluoride ions in these reactions was supported by our preliminary exploratory coupling experiments of *B-I*-carboranes and phenylboronic acid with a variety of bases. Indeed, using K_2CO_3 in DMF as the base with $PdCl_2(PPh_3)_2$ as catalyst in the coupling of phenylboronic acid (**2**) and 2-*I-p*-carborane (**1**) was ineffective (the reaction stopped after 4 h), although the desired product was obtained in a yield of 30%.

Phenylboronic acid was used as a model boronic acid in the search for a good catalytic system for the cross-coupling reactions between arylboronic acids and 2-*I-p*-carborane. The results of these experiments are summarized in Table 1. Among boron containing side products, *p*-carborane could be detected by GC–MS analysis and ^{11}B -NMR.

Using the conventional $PdCl_2(PPh_3)_2$ catalyst, a rather good yield of 2-phenyl-*p*-carborane (**3**) (73%, 2 h) was obtained in the presence of a sufficiently large amount of the catalyst (Table 1, entry 2). Using the same amount of the catalyst (as in entry 2) but adding extra ligand (PPh_3) resulted in a sharp decrease of the reaction rate, a lower yield of the desired coupling product, and an increased yield of by-products (entry 3).

A change from $PdCl_2(PPh_3)_2$ to $Pd(PPh_3)_4$ as the catalyst did not significantly increase the desired product yield (entry 4). Changing CsF to Bu_4NF resulted in a fast and complete consumption of 2-iodo-*p*-carborane, but sharply increased the yield of by-products (entry 5).

To achieve an increase in the rate of the oxidative addition step and an increase of the stability of the palladium intermediate formed in this step, the monodentate ligand (PPh_3) was then changed to bidentate ligands. Using CsF as the base and $Pd_2(dba)_3$ as the catalyst precursor, the three bidentate ligands (BINAP,

entry 6; dppe, entry 7; and dppp, entry 9) resulted in lower reaction rates and lower yield of 2-phenyl-*p*-carborane (**3**), together with the formation of by-products. It should be noted that changing the base to K_2CO_3 gave no reaction with dppe as the ligand (entry 8).

However, when we used dppb as the ligand (entry 10), the reaction gave the desired product (**3**) in nearly quantitative yield without any detectable (^{11}B -NMR) boronated side products, when the reaction was run in the presence of only 2 mol% of the catalyst precursor (corresponding to 4 mol% of active catalyst).

These favorable reaction conditions were then applied to the reactions with various commercial arylboronic acids, containing both electron-donating and electron-withdrawing substituents. The reaction conditions and the isolated yields of the 2-aryl-*p*-carboranes are given in Table 2. The reaction with 1-naphthylboronic acid (entry 2) proceeds in the same smooth way as the reaction with phenylboronic acid (entry 1). A similar yield was obtained for *p*-methoxyphenyl boronic acid (entry 3). The introduction of the electron-withdrawing nitro group in the *meta* position (entry 6) did not decrease the yield of the desired product. In the case of *o*-nitrophenyl boronic acid (entry 7), however, we found no reaction.

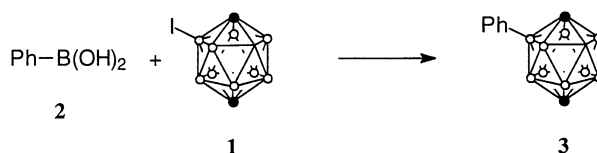
As expected, the introduction of an electron-withdrawing group in the *para* position sharply decreases the reaction rate. Indeed, in the case of *p*-cyano-phenylboronic acid (entry 5) a yield of 76% was obtained after 48 h only, whereas for other arylboronic acids besides *p*-acetamido-phenylboronic acid (entry 4), the reactions were completed over 10–12 h.

It is difficult to explain the decrease of the reaction rate in the case of *p*-acetamido-phenylboronic acid. The reaction proceeds selectively and gives the desired product in 28% yield after 24 h.

The large effect of the nature of the arylboronic acid on the reaction rate indicates that *trans*-metallation is the rate-determining step of the reaction. Concerning the first step, oxidative addition, it should be noted that no formation of a palladium(II) intermediate (corresponding to **A** in the Scheme 1) was observed in the ^{11}B -NMR spectrum of a mixture of one equivalent of $Pd(0)$, two equivalent of Ph_3P , and one equivalent of 2-iodo-*p*-carborane (**1**) in $CDCl_3$. This spectrum contains only signals from **1**. This observation is in accordance with observations reported by Marshall et al. [25], at the time when our study was in a final stage. These authors studied the reactivity of 9-*I-m*-carborane towards $Pd(0)$ complexes and were unable to observe the presence of a L_2I Pd -*B-m*-carboranyl Pd -complex as judged from the ^{31}P -NMR spectrum of a mixture of $(Ph_3P)_4Pd$ and 9-*I-m*-carborane in toluene- d_8 .

Our data regarding the oxidative addition step could be explained in a similar way as Marshall et al. [25]

Table 1

Reaction of 2-*I-p*-carborane with phenonylboronic acid in the presence of CsF

Entry ^a	Catalyst (mol%)	Time (h)	Ratio of boronated products ^b (3/1/side products)
1	PdCl ₂ (PPh ₃) ₂ (5)	4	48/41/11
2	PdCl ₂ (PPh ₃) ₂ (10)	2	73/23/4
3	PdCl ₂ (PPh ₃) ₂ /PPh ₃ (10/20)	10	51/13/36
4	Pd(PPh ₃) ₄ (10)	4	78/12/10
5 ^c	PdCl ₂ (PPh ₃) ₂ (10)	4	45/0/55
6	Pd ₂ (dba) ₃ /BINAP (2/5)	16	28/0/72
7	Pd ₂ (dba) ₃ /dppp (2/5)	18	33/52/15
8 ^d	Pd ₂ (dba) ₃ /dppp (2/5)	8	0/100/0
9	Pd ₂ (dba) ₃ /dppp (2/5)	10	26/72/2
10	Pd ₂ (dba) ₃ /dppb (2/4)	10	93/7/0

^a General conditions: 1 equivalent of 2-iodo-*p*-carborane (**1**), 1.5 equivalents of phenylboronic acid (**2**) and 3 equivalents of CsF in DME (2 ml/mmol **1**).

^b The ratios was determined by ¹¹B-NMR.

^c Bu₄NF.

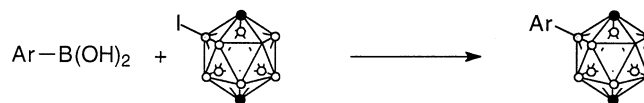
^d K₂CO₃.

explained their results, namely, that this step is reversible and that the complex (in our case **A**) is thermodynamically disfavored. Marshall et al. used this conclusion together with the known low nucleophilicity of arylboronic acids to explain the low yield of coupling product between 9-*I-m*-carborane and phenylboronic acid. The formation of unsubstituted carboranes (*meta*- as reported by Zakharkin et al. [24] and *para*- in our case) according to Marshall et al. [25] 'may involve *o*-palladation of coordinated PPh₃ to give a carboranyl

Pd-hydride which produces carborane upon B–H reductive elimination'.

The success of our reaction using cesium fluoride could be explained by assuming that a borate, formed via coordination of ArB(OH)₂ with F[−], moves the equilibrium in the initial oxidative addition step. It is not known which borate is the reactive species but in the Scheme we have indicated that it might be Ar–B(OH)₂F[−], although Wright et al. [26], in a paper introducing the use of fluoride ions in Suzuki–Miyaura

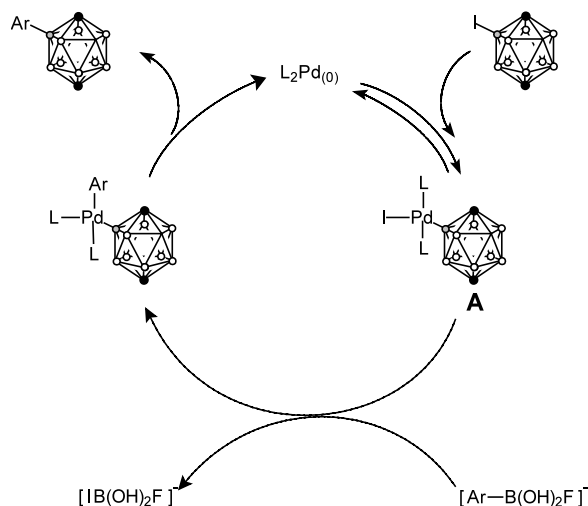
Table 2

Reaction of 2-*I-p*-carborane with various arylboronic acids

Entry ^a	Substrate Ar-B(OH) ₂	Reaction time (h)	Product (2-aryl- <i>p</i> -carborane)	Isolated yields (%)
1	Phenyl	12	3	90
2	1-Naphthyl	12	4	93
3	4-MeO-C ₆ H ₄	12	5	90
4	3-CH ₃ CONH-C ₆ H ₄	24	6	28/84 ^b
5	4-NC-C ₆ H ₄	48	7	76
6	3-NO ₂ -C ₆ H ₄	12	8	94
7	2-NO ₂ -C ₆ H ₄	24		No reaction

^a General conditions: 1 equivalent of 2-*I-p*-carborane (**2**), 1.5 equivalents of arylboronic acid, 3 equivalents of CsF, 2 mol% Pd₂(dba)₃, 4 mol % dppb, DME (2 ml/mmol **1**), reflux under argon.

^b Yield based on recovered **1**.



Scheme 1.

coupling reactions, suggest that Ar-BF_3^- is the species that undergoes the *trans*-metallation step. This has recently been questioned by Littke et al. [27], who showed that 4-bromo-*N,N*-dimethylaniline did not form any coupling product with $\text{K}[o\text{-tolyl-BF}_3]$ in the presence of $\text{Pd}_2(\text{dba})_3\text{-P}(t\text{-Bu})_3$ under conditions where the coupling reaction between 4-bromo-*N,N*-dimethylaniline and *o*-tolylboronic acid proceeds to completion in the presence of 3.3 equivalent of KF .

3. Conclusions

In this paper, we have shown that by a proper choice of the reaction conditions it is possible to use the Suzuki–Miyaura method for preparation of a number of functionalized 2-*B*-aryl-*p*-carboranes. Work on the corresponding cross-coupling reaction using other iodo-carboranes including 9-iodo-*m*-carborane, is in progress.

4. Experimental

All experiments were performed under argon atmosphere. DME was freshly distilled from sodium benzophenone. The arylboronic acids, ligands and palladium sources were purchased from Lancaster Synthesis Ltd.

Merck Silica Gel 60 (230–400 mesh) and Merck Silica 60 F₂₅₄ were used for flash chromatography and TLC, respectively. TLC-plates were developed with palladium chloride in acidified (hydrochloric acid) methanol solution.

Unless otherwise stated ^1H , ^{13}C and ^{11}B -NMR spectra were recorded in CDCl_3 with a Varian XL-400 spectrometer at 400, 100.6 and 128.3 MHz, respectively. ^{11}B -NMR spectra were acquired with $\text{BF}_3\cdot\text{Et}_2\text{O}$ as

external standard at 0 ppm. In the ^{13}C -NMR spectra of the compounds 5–7, the signals for the $\text{C}_{\text{ar-B}}$ atoms could not be detected. GC–MS analyses were performed with a non-polar column and a Thermquest GCQ mass spectrometer. Melting points were measured in sealed tubes using a Büchi capillary melting point apparatus. MIKRO KEMI AB, Uppsala, Sweden, performed the elemental analyses.

4.1. 2-Iodo-*p*-carborane (3)

2-Iodo-*p*-carborane was prepared in analogy with the procedure described by Jones et al. [28] for 9-iodo-*o*-carborane and adapted to *p*-carborane by Hawthorne et al. [23].

^1H -NMR (ppm) δ 3.21 (s, 1H, CH), 2.90 (s, 1H, CH), 1.50–3.00 (broad m, 9H, BH). ^{13}C -NMR (ppm) δ 67.9, 65.4. ^{11}B -NMR (ppm) δ –11.8 (2B, d, $J = 195$ Hz), –13.5 (4B, d, $J = 190$ Hz), –14.1 (2B, d, $J = 156$ Hz), –16.3 (1B, d, $J = 168$ Hz), –28.3 (1B, s).

5. General procedure for the cross-coupling reactions

5.1. Experiments in Table 1

2-*I-p*-Carborane (ca. 100 mg, one equivalent), arylboronic acid (1.5 equivalent), base (three equivalent) and catalyst were all weighted into a 10 ml reaction vial containing a magnetic stirring bar and connected to a reflux condenser. The equipment was evacuated and back-filled with argon, solvent (2 ml) was added and the mixture was heated to reflux. In each case, the progress of the reaction was monitored by TLC using pentane as the eluent. The reaction was stopped either after precipitation of palladium-black and decolorization of the supernatant or when all 2-*I-p*-carborane was consumed. The resulting mixture was diluted with diethyl ether, filtered through a pad of Celite and concentrated under reduced pressure. The reaction mixtures were analyzed by ^{11}B -NMR.

5.2. Syntheses of the aryl-*p*-carboranes 3–8 (Table 2)

The general procedure described above was followed, but in these experiments 300 mg (1.11 mmol) of 2-iodo-*p*-carborane, arylboronic acid (ca. 1.5 mmol), cesium fluoride 506 mg (3.33 mmol), $\text{Pd}_2(\text{dba})_3$ 20.3 mg (0.022 mmol, corresponding to 4 mol% Pd), dppb 18.9 mg (0.044 mmol), and 6 ml DME were used. The crude products were purified by flash chromatography.

5.3. 2-Phenyl-*p*-carborane (3)

2-Phenyl-*p*-carborane (1) was prepared according to the general procedure for syntheses of the aryl-*p*-

carboranes employing 203 mg (1.66 mmol) of phenylboronic acid. The reaction mixture was heated under reflux for 12 h. Purification of the residue by flash chromatography with pentane as the eluent gave 221 mg (90%) of **1** as a clear oil, which slowly crystallized when left unattended. The NMR data were in accordance with those reported in the literature [23].

5.4. 2-(1-Naphtyl)-*p*-carborane (**4**)

The naphtylcarborane (**4**) was prepared according to the general procedure for syntheses of the aryl-*p*-carboranes employing 287 mg (1.65 mmol) of 1-naphtylboronic acid. The reaction mixture was heated under reflux for 12 h. Purification of the residue by flash chromatography with 2% diethyl ether in pentane as the eluent gave 281 mg (93%) of **4** as a white solid. The sample for elemental analysis was obtained by recrystallization from hexane.

M.p. 109 °C. ¹H-NMR (ppm) δ 1.6–3.2 (broad m, BH, 9H), 2.99 (broad s, 1H), 3.39 (broad s, 1H), 7.41 (dd, *J* = 7.1, 8.1 Hz, 1H), 7.50 (ddd, *J* = 1.2, 6.8, 8.1 Hz, 1H), 7.56 (ddd, *J* = 1.2, 6.8, 8.4 Hz, 1H), 7.68 (d m, *J* = 7.1 Hz, 1H), 7.84 (d m, *J* = 8.1 Hz, 1H), 7.88 (dd, *J* = 8.1, 1.2 Hz, 1H). ¹³C-NMR (ppm) δ 63.3, 66.0, 125.0, 125.3, 126.0, 127.3, 129.1, 129.5, 133.6, 133.8, 136.2. ¹¹B-NMR (ppm) δ –5.4 (Ar–B, 1B), –13.1 (2B), –15.0 (6B), –16.7 (1B). Anal. Calc. for C₁₂H₁₈B₁₀ (272.23); C, 53.31; H, 6.71. Found: C, 53.6; H, 6.6%.

5.5. 2-(4-Methoxyphenyl)-*p*-carborane (**5**)

2-(4-Methoxyphenyl)-*p*-carborane (**5**) was prepared according to the general procedure for syntheses of the aryl-*p*-carboranes employing 253 mg (1.66 mmol) of 4-methoxyphenylboronic acid. The reaction mixture was heated under reflux for 12 h. Purification of the residue by flash chromatography with 5% EtOAc in pentane as the eluent gave 251 mg (90%) of **5** as a white solid. The sample for elemental analysis was obtained by recrystallization from hexane.

M.p. 99–100 °C. ¹H-NMR (ppm) δ 1.6–3.2 (broad multiple, BH, 9H), 2.90 (broad s, 1H), 3.03 (broad s, 1H), 3.82 (s, 3H), 6.87 (XX' part of AA'XX' system, 4-methoxyphenyl, 2H), 7.48 (AA' part of AA'XX' system, 4-methoxyphenyl, 2H). ¹³C-NMR (ppm) δ 55.1, 63.7, 65.8, 113.6, 134.7, 160.2. ¹¹B-NMR (ppm) δ –4.7 (Ar–B, 1B), –13.8 (2B), –14.8 (4B), –15.5 (2B), –18.0 (1B). Anal. Calc. for C₉H₁₈B₁₀O (250.34); C, 43.18; H, 7.25. Found: C, 43.2; H, 7.2%.

5.6. 2-(3-Acetamidophenyl)-*p*-carborane (**6**)

2-(3-Acetamidophenyl)-*p*-carborane (**6**) was prepared according to the general procedure for syntheses of the aryl-*p*-carboranes employing 298 mg (1.66 mmol) of 3-

acetamidophenylboronic acid. The reaction mixture was heated under reflux for 24 h. Purification of the residue by flash chromatography using first pentane as the eluent to give 201 mg of unreacted 2-*I-p*-carborane. Subsequent elution with diethyl ether gave 85 mg (28 or 84% based on recovered 2-*I-p*-carborane) of **6** as a white solid. The sample for elemental analysis was obtained by recrystallization from chloroform.

M.p. 193 °C. ¹H-NMR, CD₃OD, (ppm) δ 1.6–3.2 (broad m, BH, 9H), 2.15 (s, 3H), 3.40 (broad s, 1H), 3.61 (broad s, 1H), 7.24–7.31 (m, 2H), 7.58 (ddd, *J* = 2.2, 2.8, 7.2 Hz, 1H), 7.62 (m, 1H). ¹³C-NMR, CD₃OD, (ppm) δ 23.8, 65.1, 66.9, 121.2, 125.8, 129.3, 129.9, 139.4, 168.3. ¹¹B-NMR, CD₃OD, (ppm) δ –4.6 (Ar–B, 1B), –13.3 (2B), –14.5 (6B), –17.5 (1B). Anal. Calc. for C₁₀H₁₉B₁₀NO (277.37); C, 43.30; H, 6.90; N, 5.05. Found: C, 43.1; H, 6.7; N, 5.1%.

5.7. 2-(4-Cyanophenyl)-*p*-carborane (**7**)

2-(4-Cyanophenyl)-*p*-carborane (**7**) was prepared according to the general procedure for syntheses of the aryl-*p*-carboranes employing 245 mg (1.67 mmol) of 4-cyanophenylboronic acid. The reaction mixture was heated under reflux for 48 h. Purification of the residue by flash chromatography with 10% EtOAc in pentane as the eluent gave 208 mg (76%) of **7** as a white solid. The sample for elemental analysis was obtained by recrystallization from hexane.

M.p. 110 °C. ¹H-NMR (ppm) δ 1.6–3.2 (broad m, BH, 9H), 2.95 (broad s, 1H), 3.08 (broad s, 1H), 7.58 (XX' part of AA'XX' system, 4-cyanophenyl, 2H), 7.63 (AA' part of AA'XX' system, 4-cyanophenyl, 2H). ¹³C-NMR (ppm) δ 63.9, 65.2, 112.1, 118.9, 131.2, 133.7. ¹¹B-NMR (ppm) δ –6.0 (Ar–B, 1B), –13.8 (2B), –14.8 (6B), –17.0 (1B). Anal. Calc. for C₉H₁₅B₁₀N (245.32); C, 44.06; H, 6.16; N, 5.71. Found: C, 44.1; H, 6.1; N, 5.7%.

6. 2-(3-Nitrophenyl)-*p*-carborane (**8**)

2-(3-Nitrophenyl)-*p*-carborane (**8**) was prepared according to the general procedure for syntheses of the aryl-*p*-carboranes employing 279 mg (1.67 mmol) of 3-nitrophenylboronic acid. The reaction mixture was heated under reflux for 48 h. Purification of the residue by flash chromatography with 10% EtOAc acid in pentane as the eluent gave 276 mg (94%) of **8** as a slightly yellow solid. The sample for elementary analysis was obtained by recrystallization from hexane.

M.p. 105 °C. ¹H-NMR (ppm) δ 1.6–3.2 (broad m, BH, 9H), 2.99 (broad s, 1H), 3.15 (broad s, 1H), 7.51 (dd, *J* = 7.5, 8.2 Hz, 1H), 7.88 (d, m, *J* = 7.5 Hz, 1H), 8.20 (ddd, *J* = 8.2, 2.4, 1.2 Hz, 1H), 8.36 (m, 1H). ¹³C-NMR (ppm) δ 64.0, 65.4, 123.3, 127.6, 128.8, 139.3,

147.7. ^{11}B -NMR (ppm) δ –6.11 (Ar–B, 1B), –13.8 (2B), –14.7 (6B), –17.1 (1B). Anal. Calc. for $\text{C}_8\text{H}_{15}\text{B}_{10}\text{NO}_2$ (265.31); C, 36.22; H, 5.70; N, 5.28. Found: C, 36.1; H, 5.6; N, 5.3%.

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