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Microwave-assisted Suzuki–Miyaura cross-coupling of 2-alkyl and 2-alkenyl-benzo-1,3,2-diazaborolanes

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ABSTRACT

Nitrogen-based boronate esters, such as 2-octyl-benzo-1,3,2-diazaborolane, 2-phenethyl-benzo-1,3,2-diazaborolane, and 2-{(1*E*)-hexenyl}-benzo-1,3,2-diazaborolane have been shown to be suitable coupling partners with arylhalides in microwave accelerated Suzuki cross-coupling reactions. Reaction yields of up to 89% were achieved. The use of a silicon group attached to the nitrogen atom, proved to enhance the reactivity of 2-octyl-benzo-1,3,2-diazaborolane.

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1. Introduction

For two decades there has been intense research into the palladium-catalyzed cross-coupling reaction also known as the Suzuki–Miyaura cross-coupling reaction since its discovery by Miyaura, Yanagi, and Suzuki.[1] The Suzuki-coupling methodology has proven to be extremely powerful and versatile in the formation of carbon–carbon bonds,[2a–d] and for the production of building blocks of pharmaceutical importance.[2e–h]

Recently, a number of research groups have focused on the development of new palladium catalyst systems,[3–5] more effective ligands[6] and bases[7] with the aim of enhancing the applicability of the Suzuki type chemistry. Much emphasis has been on investigating the effects of different solvents, additives, ligand[8,9,10a,b] and more recently the use of microwave irradiation.[10c] However, literature precedent accumulated in this area has been based almost exclusively on the utility of boronic acids and boronate esters.[1,2] To date, only a few research groups have directed their attention toward expanding the scope of other potential Suzuki-coupling type organoboranes.[8,11,12] Specifically, nitrogen-based organoboranes have not been investigated in Suzuki–Miyaura chemistry. To the best of our knowledge, only a few publications have been reported on the synthesis of nitrogen-based organoboranes.[13]

We have recently published a new route to the synthesis of nitrogen-based organoboranes via rhodium-catalyzed hydroboration to afford organoboranes in high yields.[14]

The success of our new approach prompted our research into the synthesis of a range of nitrogen-based organoboranes (Table 1) and to explore their respective Pd-mediated coupling reactions with a range of arylhalides as shown in Scheme 1.

2. Results and discussion

Nitrogen-based organoboranes, namely 2-octyl-benzo-1,3,2-diazaborolane **2**, 2-phenethyl-benzo-1,3,2-diazaborolane **3**, and 2-[2-(4-methoxyphenyl)-ethyl]benzo-1,3,2-diazaborolane **4** were synthesized from benzo-1,3,2-diazaborolane **1**, which is readily prepared from commercially available borane–methyl sulfide complex and inexpensive *o*-phenylenediamine, as shown in Table 1. It was interesting to note that **1** was very robust to air and moisture when compared to the widely utilized oxygen analogues benzo-1,3,2-dioxaborolane (catecholborane) and 4,4,6,6-tretramethyl-1,3,2-dioxaborolane (pinacolborane). Benzo-1,3,2-diazaborlane **1** could be handled in an open vessel for several hours without notable oxidation to boric acid.[14]

We were delighted at the ease with which we were able to prepare the novel organoboranes **2**, **3**, and **4** in excellent yields, via Rh(I) catalyzed hydroboration of the corresponding alkenes. Rh(I) catalyzed reactions of similar alkenes with catecholborane have previously been intensively investigated and have been found to lead to a mixture of both internal and terminal products, which is

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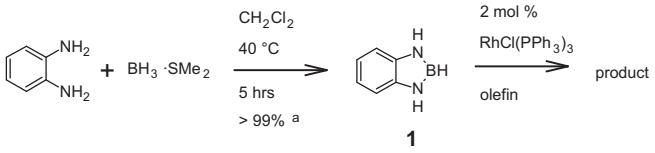
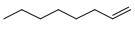
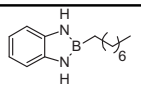
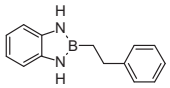
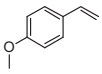
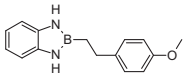
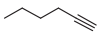
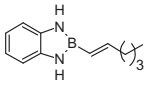
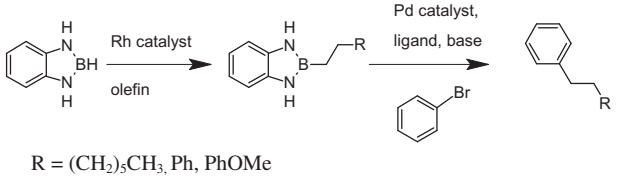
Table 1
$RhCl(PPh_3)_3$-catalyzed synthesis of nitrogen-based organoboranes



1

Entry	Olefin	Conditions	Product	Yield (%)
1		25 °C, 24 h	 **2**	92[b]
2		40–65 °C, 48 h	 **3**	81[b]
3		40–65 °C, 60 h	 **4**	79[b]
4		10–15 °C $HBBr_2$, 3 h	 **5**	78[b]

[a] ^{11}B NMR spectroscopy was used to monitor the formation of benzo-1,3,2-diazaborolane **1**, the yields are based on ^{11}B NMR spectroscopy.
[b] Isolated yields after flash column chromatography on silica gel. All reactions were conducted under a dry nitrogen atmosphere.



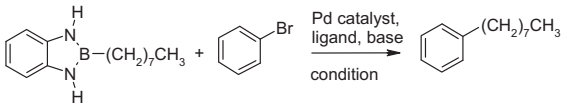
Scheme 1. Rhodium-catalyzed hydroboration and Pd-mediated coupling reactions.

not the case in our study.[15] In addition, our research group has also successfully developed a convenient procedure for the synthesis of 2-alkenyl-benzo-1,3,2-diazaboranes from terminal alkynes without the use of Rh(I) catalyst (Table 1, entry 4).

A model study was conducted in order to optimize the conditions for Suzuki–Miyaura coupling reactions. In this study 2-octyl-benzo-1,3,2-diazaborolane **2** was reacted with bromobenzene as a substrate (Table 2). This reaction was repeated several times varying commonly used Suzuki-coupling reagents (Table 2, entries 1–7), however, all attempts failed to improve the coupling reaction in yields greater than ca. 5%. Changing the solvent to THF and allowing the reaction to reflux for 48 h gave a moderately improved yield of 30% (Table 2, entry 8).

The low reactivity of **2** was attributed to the reduced Lewis acidity of the boron atom, due to pronounced overlap of the nitrogen lone pair of electrons into the vacant p_z-boron orbital. In order to enhance the reactivity of this species, it was envisaged that the introduction of a silicon hetero-atom α to the nitrogen would diminish this orbital overlap. Consequently, 2-octyl-1,3-bis-trimethylsilanyl-benzo-1,3,2-diazaborole **7** (Scheme 2) was synthesized. As anticipated, **7** was more reactive than **2** giving ca. 50% of **6a** when treated similarly to entry 8 of Table 2. Despite the increased reactivity, **7** was also more susceptible to oxidation during purification which made it difficult to work with.

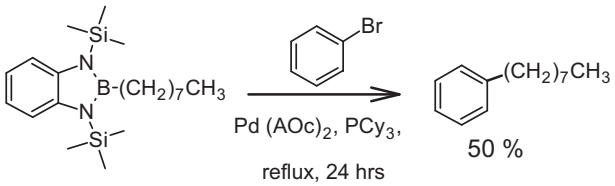
Table 2
Pd-catalyzed coupling reaction of bromobenzene with 2-octyl-benzo-1,3,2-diazaborolane, optimum condition survey



2 **5a** **6a**

Entry	Catalyst	Base	Ligand	Condition	Yield[a] (%)
1	$Pd(PPh_3)_4$	Aq Na_2CO_3	None	A	0
2	$Pd(PPh_3)_4$	Aq K_2CO_3	None	A	0
3	$Pd(PPh_3)_4$	K_2CO_3	None	A[b]	2
4	$Pd(PPh_3)_4$	K_2CO_3	None	B	2
5	$Pd(OAc)_2$	K_2CO_3	PPh_3	A[b]	5
6	$Pd(OAc)_2$	K_2CO_3	PPh_3	B	2
7	$Pd(OAc)_2$	$K_3PO_4·H_2O$	PCy_3	A[b]	0
8	$Pd(OAc)_2$	$K_3PO_4·H_2O$	PCy_3	A[c]	30
9	$Pd(OAc)_2$	$K_3PO_4·H_2O$	PCy_3	B[d]	50
10	$Pd(OAc)_2$	$K_3PO_4·H_2O$	PCy_3	C	88

Reaction conditions: (A) 1.0 equiv of **2**, 1.0 equiv of bromobenzene, 3.0 equiv of base, benzene, 4 mol % $Pd(PPh_3)_4$ or $Pd(OAc)_2$, reflux for 24 h. (B) Same as (A) but DMF was used and the mixture was capped in a closed vessel and irradiated with 100 W of microwave energy for 1 h. (C) Solvent free, 4 mol % $Pd(OAc)_2$, and 8 mol % PCy_3 was used, closed vessel 50 W microwave irradiation, 5 min.
[a] Isolated yields after flash column chromatography on silica gel.
[b] DMF used instead.
[c] 48 h reflux in THF.
[d] 2 h reflux in THF.



7 **6a**

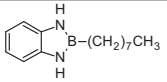
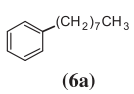
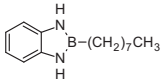
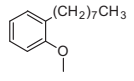
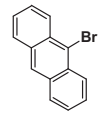
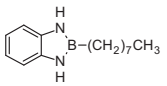
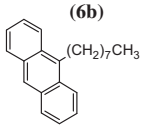
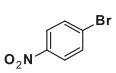
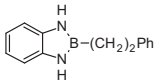
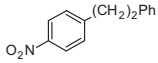
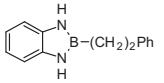
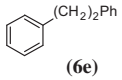
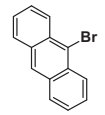
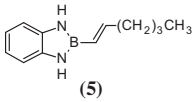
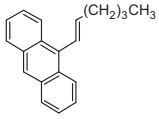
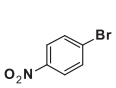
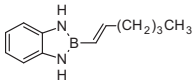
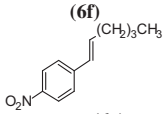
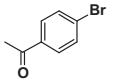
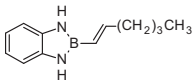
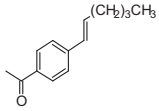
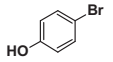
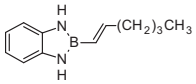
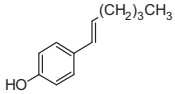
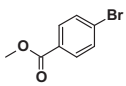
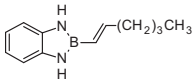
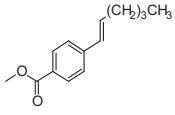
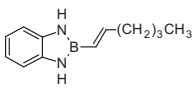
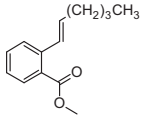
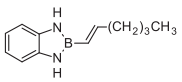
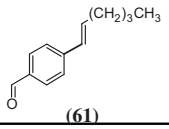
Scheme 2. Coupling reaction of silylated diazaborolane **7**.

Further investigations with 2-octyl-benzo-1,3,2-diazaborolane **2** incorporating the use of $K_3PO_4·H_2O$, PCy_3, $Pd(OAc)_2$ in conjunction with microwave irradiation afforded a slightly higher yield of 50% in 2 h (Table 2, entry 9) compared to conventional heating (ca. 30% in 48 h; Table 2, entry 8). The reaction yields were improved significantly to 88% when solvent free conditions were employed, furthermore, reaction completion was reached in only 5 min with microwave irradiation (Table 2, entry 10).

Having achieved optimal reaction conditions (Table 2, entry 10), we investigated the utility of diazaborolane **2**, **3**, and **5** with different arylhalides (X=Cl, Br, and I) in order to assess the scope and the limitations of such unusual Suzuki-coupling partners. The results obtained are summarized in Table 3. Working with optimized reaction conditions, diazaborolane **2** afforded the coupled-product **6b** in low 35% yield with an electron donating substituted substrate (Table 3, entry 2), however, an appreciably high yield of 89% was achieved with a more conjugated substrate (Table 3, entry 3). An arylhalide bearing an electron-withdrawing substituent reacted moderately with diazaborolane **3** in toluene affording the cross-coupled product **6d** in 57% yield (Table 3, entry 4). A solvent free cross-coupling reaction of diazaborolane **3** with bromobenzene furnished **6e** in 79% (Table 3, entry 5).

Applying the same optimal reaction conditions to couple diazaborolane **5** to different arylhalides, however, failed to give the coupled-product in excellent yields. Under these conditions, the coupling reaction of diazaborolane **5** with 9-bromoanthracene and *p*-bromonitrobenzene afforded the desired product in 34% and 64%,

Table 3
Palladium-catalyzed cross-coupling reactions of **2** and **3** with arylhalides

Entry	Bromide	Diazaborolane	Product	Yield (%)
1		 **(2)**	 **(6a)**	88[a]
2		 **(2)**	 **(6b)**	35[a]
3		 **(2)**	 **(6c)**	89[a]
4		 **(3)**	 **(6d)**	57[b]
5		 **(3)**	 **(6e)**	79[c]
6		 **(5)**	 **(6f)**	(34) 84[d]
7		 **(5)**	 **(6g)**	(64) 81[d]
8		 **(5)**	 **(6h)**	67[d]
9		 **(5)**	 **(6i)**	62[d]
10		 **(5)**	 **(6j)**	67[d]
11		 **(5)**	 **(6k)**	74[d]
12		 **(5)**	 **(6l)**	NR[e]

[a] Reaction condition C: $Pd(OAc)_2$ (4 mol %), PCy_3 (8 mol %), $K_3PO_4 \cdot H_2O$ (3 equiv), solvent free, closed vessel, 100 °C, 50 W microwave irradiation, 5 min.

[b] Reaction condition D: $Pd(OAc)_2$ (4 mol %), PCy_3 (8 mol %), $K_3PO_4 \cdot H_2O$ (3 equiv), toluene, 100 °C, closed vessel, 200 W microwave irradiation, 15 min.

[c] Reaction ondition E: same as condition C, however, 200 W of microwave irradiation was used.

[d] Reaction condition F: Pd $(OAc)_2$ (4 mol %), PCy_3 (8 mol %), $K_3PO_4 \cdot H_2O$ (3 equiv), closed vessel, 50 W microwave irradiation, 1,4-dioxane, 100 °C, 20 min. All yields refer to isolated material. Yields in parenthesis were obtained under condition D.

[e] NR refers to no reaction.

respectively (Table 3, entries 6 and 7). As a result, this encouraged us to screen more well known Suzuki reagents. In summary, the combination of $Pd(OAc)_2$, PCy_3, $K_2PO_4 \cdot H_2O$, diazaborolane **5** (2 equiv), and arylhalide (1 equiv) in 1,4-dioxane proved to be suitable reaction conditions for the cross-coupling of diazaborolane **5** to arylhalides.

Under these new improved reaction conditions, diazaborolane **5** was smoothly coupled to 9-bromoanthracene to provide **6f** in 84% yield (Table 3, entry 6). The cross-coupling reaction of a strongly deactivated substrate (*p*-bromonitrobenzene) in the presence of diazaborolane **5** (2 equiv) in 1,4-dioxane afforded **6g** quantitatively (Table 3, entry 7).

As shown in Table 3 (entry 8), the coupling reaction between diazaborolane **5** and *p*-bromoacetophenone afforded the coupled-product in moderate 67% yield. This yield is lower than the 86% yield reported by Yamada et al.[16] however, it is worth noting that, our yield was achieved in 20 min compared to 9 h of reflux documented by Yamada et al.[16]

Under the developed optimal reaction conditions, *p*-bromophenol and *p*-bromoacetophenone reacted moderately affording the coupled-product **6i** and **6j** in 62% and 67% yields, respectively (Table 3, entries 9 and 10). However, the coupling reaction of *o*-iodomethylbenzoate furnished **6k** in 74% yield (Table 3, entry 11).

Lastly, we investigated the coupling reaction of *p*-chlorobenzaldehyde, however, attempts failed to give any desired product even after 40 min (Table 3, entry 12). It is not surprising though, as it is well documented in the literature that arylchlorides are significantly less reactive due to their slow oxidative addition to palladium (0) catalyst.[11,17]

3. Conclusions

In Summary, 2-alkenyl and 2-alkyl-benzo-1,3,2-diazaborolanes are noticeably uncommon coupling partners in the Suzuki–Miyaura cross-coupling reactions. We have successfully developed standard reaction conditions for the cross-coupling of such diazaborolane compounds with a wide range of arylhalides These reactions proceed smoothly in the presence of an inexpensive and widely used combination of $Pd(OAc)_2$ and PCy_3, affording the coupled-products in moderate to excellent yields in only 20 min. Our standard reaction conditions have proven to be versatile and general tolerating a variety of functional groups, such as OMe, NO_2, OH, COOMe, and COMe.

4. Experimental

4.1. General

All glassware was thoroughly dried in an oven at ca. 150 °C overnight. The glassware was further flame dried by heating with a hot air gun under reduced pressure and allowed to cool under a stream of dry nitrogen, which was passed through a mixture of silica gel and 0.4 nm molecular sieves prior to use. Glass syringes, cannulae, and needles were oven dried and stored in a desiccator (charged with a mixture of silica gel and 0.4 nm molecular sieves) prior to use. Disposable syringes and needles were stored in the desiccator before use, and they were discarded after single use. On assembling of the glassware, all joints were wrapped with Teflon® tape and were subsequently sealed. ^1H, ^{13}C, and ^{11}B NMR spectra were recorded on a Varian Unity-Inova 500 MHz and/or Bruker 400 MHz UltraShield spectrometers. ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ and were referenced using the residual chloroform signal at 7.25 ppm and 77.0 ppm, respectively. ^{29}Si NMR spectra were referenced to TMS as an external standard (0.0 ppm). All ^{11}B NMR spectra were referenced to $BF_3 \cdot OEt_2$ as an external standard (0.0 ppm) contained

within a sealed capillary insert. ^{11}B spectroscopy was utilized in order to identify the compounds as well as to monitor the progress of the reactions.

GC–MS analyses were performed on a Thermofinnigan® (GC) coupled with a PolarisQ® (MS) system. Thin layer chromatography was performed on silica gel (60 F_{254}) plates from Merck. Flash column chromatography was performed on SP Silica Gel 60 (230–400-mesh ASTM) from Merck. HRMS were conducted on a Perkin–Elmer® Spectrum 100 FT-IR spectrometer (with universal ATR sampling accessory). All solvents were purified by distillation and dried prior to use. CH_2Cl_2 was distilled over P_2O_5 under dry nitrogen, THF, DMF, and 1-octene were all distilled over sodium wire in the presence of an indicator benzophenone.

The solvents were distilled and transferred via cannula to a flame dried, nitrogen flushed flask containing 0.4 nm molecular sieves (activated in the furnace at 600 °C and cooled under dry nitrogen) prior to use. *o*-Phenylenediamine was obtained from Merck-Schuchardt. $BH_3\cdot SMe_2$ (1 M solution in CH_2Cl_2) and Tris–(triphenylphosphine)–rhodium(I)-chloride were obtained from Sigma–Aldrich Co. All these reagents were used without further purification.

4.2. Synthesis

4.2.1. Benzo-1,3,2-diazaborolane ***1***. *o*-Phenylenediamine (541 mg, 5.0 mmol) was dissolved in dichloromethane (5.0 ml) in a flame-dried round-bottom flask. After complete dissolution of the solid, borane–dimethyl sulfide complex (1 M solution in dichloromethane, 5.0 ml, 5.0 mmol) was introduced drop wise through the septum. The resulting mixture was stirred under reflux for 5 h under a dry atmosphere of nitrogen. Benzo-1,3,2-diazaborolane was obtained as a clear liquid (95%). ^{11}B NMR (160 MHz, $BF_3\cdot OEt_2$): δ ppm 23.9 (d, J=153.2 Hz, ^1H, BH).

4.2.2. 2-Octyl-benzo-1,3,2-diazaborolane ***2*** *(method A).* Freshly prepared benzo-1,3,2-diazaborolane (20.0 ml, 46.2 mmol) in dichloromethane was injected into an oven dried, nitrogen purged two necked round-bottom flask, followed by 1-octene (7.3 ml, 46.2 mmol), with continuous stirring. To this solution was added $RhCl(PPh_3)_3$ (2 mol %, 855 mg), which had been dissolved in dichloromethane (5.0 ml) in a separate flame dried, nitrogen flushed flask. The reaction mixture was allowed to stir at 25 °C for 24 h. The solvent was then removed in vacuo, and the remaining orange-yellow waxy material was purified through flash column chromatography on silica gel with hexane as an eluting solvent. Removal of solvent in vacuo afforded 2-octyl-benzo-1,3,2-diazaborolane **2**, as low melting orange-yellow wax (92%), mp 26.2–28.9 °C. ^{11}B NMR (160 MHz, $BF_3\cdot OEt_2$): δ ppm 31.6 (s). MS (EI): m/z (%) 231 [M^+] (18), 230 (100), 229 (15), 145 (15), 132 (16), 119 (17), 118 (31).

4.2.3. 2-Phenethyl-benzo-1,3,2-diazaborolane ***3***. Method A was followed, benzo-1,3,2-diazaborolane (20.0 ml, 46.2 mmol) in CH_2Cl_2, styrene (5.3 ml, 46.2 mmol), and $RhCl(PPh_3)_3$ (2 mol %, 855 mg). However, in this case the reaction mixture was heated to ca. 60 °C and kept at that temperature for 48 h. ^{11}B NMR analysis of the product mixture showed that the starting material had disappeared completely. The boronate emitted an intense blue color under UV light, consequently, migration of this boronate ester during radial chromatography was followed using a standard hand held UV lamp (350 nm). Compound **3** was obtained as a cream powder (81%), mp 53–54 °C. ^{11}B NMR (128 MHz, $BF_3\cdot OEt_2$): δ ppm 31.2 (s). ^1H NMR (400 MHz, $CDCl_3$): δ ppm 1.49 (t, J=7.9 Hz, 2H), 2.80 (t, J=8.1 Hz, 2H), 6.18 (s, 2H, 2× *NH*), 6.77–6.81 (m, 2H), 6.82–6.87 (m, 2H), 7.09–7.25 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 31.9, 110.6, 118.9, 125.7, 128.0, 128.4, 136.1, 144.3. MS (EI): m/z (%) 223 [M^+] (16), 222 (100), 221 (27), 132 (17), 131 (44), 118 (29). HRMS found: [M^+] 221.1247, calculated for $C_{14}H_{14}N_2B$ 221.1250. IR (ν_{max}) neat 3385, 3364, 3027, 1621 cm^{-1}.

4.2.4. 2-{2-(4-Methoxyphenyl)-ethyl}-benzo-1,3,2-diazaborolane ***4***. Method A was followed, benzo-1,3,2-diazaborolane (20.0 ml, 46.2 mmol) in CH_2Cl_2, 4-vinylanisole (5.61 ml, 46.2 mmol), and $RhCl(PPh_3)_3$ (2 mol %, 855 mg). However, in this case the reaction mixture was heated to ca. 60 °C, and kept at that temperature for 60 h. ^{11}B NMR analysis of the product mixture showed that the starting material had disappeared completely. The boronate emitted an intense blue color under UV light, consequently, migration of this boronate ester during radial chromatography was followed using a standard hand held UV lamp (350 nm). Compound **4** was obtained as a cream-white powder (79%), mp 128–130 °C. ^{11}B NMR (128 MHz, $BF_3\cdot OEt_2$): δ ppm 31.2 (s). ^1H NMR (400 MHz, $CDCl_3$): δ ppm 1.56 (t, J=8.1 Hz, 2H), 2.85 (t, J=8.0 Hz, 2H), 3.82 (s, 3H), 6.29 (s, 2H, 2× *NH*), 6.87 (d, J=8.5 Hz, 2H), 6.90–6.94 (m, 2H), 6.98–7.03 (m, 2H), 7.19 (d, J=8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 30.9, 55.2, 110.5, 113.5, 114.0, 118.8, 128.8, 136.0, 136.3, 157.7. HRMS found: [M^+] 251.1360, $C_{15}H_{17}BN_2O$ required 251.1356.

4.2.5. 2-(1E-1-Hexenyl)-benzo-1,3,2-diazaborolane ***5***. 1*E*-1-Hexenylboronic acid was prepared according to known procedures.[17] A round-bottom flask fitted with Dean and Stark apparatus, a magnetic stirrer bar and reflux condenser was charged with freshly prepared 1*E*-1-hexenylboronic acid (0.40 g, 0.313 mmol), *o*-phenylenediamine (0.30 g, 0.313 mmol), and toluene (20 ml). The reaction mixture was heated under reflux for 1 h followed by the removal of solvent in vacuo. The remaining light-brown solid was purified through a radial chromatography to afford the desired product as fluffy white plate-like crystals (78%), mp 45–47 °C. ^{11}B NMR (128 MHz, $BF_3\cdot OEt_2$): δ ppm 27.2 (s). ^1H NMR (400 MHz, $CDCl_3$): δ ppm 0.93 (t, J=7.3 Hz, 3H), 1.33–1.52 (m, 4H), 2.19–2.27 (m, 2H), 5.88 (dt, J=18.1 Hz, 1H), 6.51 (dt, J=18.3 Hz, 1H), 6.77–6.84 (m, 2H), 6.98–7.05 (m, 2H), 7.87 (s, 2H, 2× *NH*). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 13.3, 21.9, 30.9, 35.6, 110.5, 118.2, 137.1, 148.0. HRMS found: [M^+] 199.1404, $C_{12}H_{17}BN_2$ required 199.1407. IR (ν_{max}) neat 3381, 3360, 2961, 2928, 2874, 2856, 1634.

4.2.6. Octylbenzene ***6a***. *Representative procedure for solvent-free Suzuki cross-coupling reactions (method B).* To a flame dried, nitrogen purged microwave pressure tube (10 ml) equipped with a magnetic stirring bar, was placed bromobenzene (0.23 ml, 2.17 mmol), $K_3PO_4\cdot H_2O$ (1.0 g, 4.34 mmol), PCy_3 (48.7 mg, 0.173 mmol), and $Pd(OAc)_2$ (19.5 mg, 86.8 μmol), the vial was agitated in order to mix the reagents, then purged with nitrogen. To this heterogeneous mixture was added 2-octyl-benzo-1,3,2-diazaborolane (0.50 g, 2.17 mmol), and subsequent nitrogen purging for 5 min. The tube was sealed with a snap on cap and inserted into the CEM Discovery® synthetic microwave reactor cavity.[18] The microwave cavity was then close with an Intellivent pressure control system.[19] The sample was irradiated with microwave energy (50 W) for 5 min, and the sample temperature was monitored by a non-contact, infrared sensor. After 5 min, TLC analysis showed no evidence of unreacted boronate ester or arylbromide. The remaining material solidified at the bottom of the vial, and the target octylbenzene was decanted as clear oil. The remaining solid was washed with ethyl acetate (2.0 ml), which was eventually concentrated in vacuo, combined with the decanted oil, and purified on column chromatography using hexane as an eluting solvent to afford octylbenzene **6a** (88%). ^1H NMR, ^{13}C NMR spectroscopic analysis and GC–MS traces of this sample were identical to the commercial samples. ^1H NMR (400 MHz, $CDCl_3$): δ ppm 0.85 (t, J=6.7 Hz, 3H), 1.21–1.40 (m, 10H), 1.60–1.69 (m, 2H), 3.65 (t, J=7.8 Hz, 2H), 7.18–7.31 (m, 2H), 7.42–7.56 (m, 2H), 7.63–7.69 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 14.2, 22.7, 29.3, 29.5, 29.6, 29.7, 31.5, 31.9, 125.6, 128.3, 128.4, 143.0. MS (EI): m/z (%) 191

[M^+] (3), 190 (5), 133 (10), 92 (100), 91 (72), 65 (7), 41(12). All the characterizations of the titled compound are consistent with the reported data.[20,21]

4.2.6.1. 1-Methoxy-2-octyl-benzene ***6b***. Method B was employed, 1-bromo-2-methoxy-benzene (0.27 ml, 2.17 mmol), $K_3PO_4 \cdot H_2O$ (1.00 g, 4.34 mmol), PCy_3 (48.7 mg, 0.173 mmol), $Pd(OAc)_2$ (19.5 mg, 86.8 μmol), and 2-octyl-benzo-1,3,2-diazaborolane (0.50 g, 2.17 mmol). However, the reaction mixture was irradiated with microwave energy (50 W) for 40 min to afford 1-methoxy-2-octyl-benzene as a clear oil (35%). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.78 (t, J=7.0 Hz, 3H), 1.10–1.47 (m, 10H), 1.55–1.62 (m, 2H), 2.50 (t, J=7.6 Hz, 2H), 3.71 (s, 3H), 6.71–7.23 (m, 4H). The ^{1}H NMR of **6a** is consistent with the ^{1}H NMR data reported in literature.[6]

4.2.6.2. 9-Octyl-anthracene ***6c***. Method B was employed, 9-bromoanthracene (0.60 g, 2.17 mmol), $K_3PO_4 \cdot H_2O$ (1.00 g, 4.34 mmol), PCy_3 (48.7 mg, 0.17 mmol), $Pd(OAc)_2$ (19.50 mg, 86.8 μmol), and 2-octyl-benzo-1,3,2-diazaborolane (0.50 g, 2.17 mmol). The solid product obtained was dissolved in hexane, chromatographed, and afforded 9-octyl-anthracene as glassy crystals (89%), mp 60–63 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.79 (t, J=7.3 Hz, 3H), 1.11–1.34 (m, 8H), 1.40–1.47 (m, 2H), 1.63–1.73 (m, 2H), 3.46 (t, J=7.3 Hz, 2H), 7.28–7.40 (m, 4H), 7.82–7.89 (m, 2H), 8.12–8.20 (m, 2H), 8.27 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 14.2, 22.8, 28.2, 29.4, 29.7, 30.5, 31.5, 32.0, 124.6, 124.8, 125.4, 128.2, 129.3, 131.8, 135.5. All the characterizations of the titled compound are consistent with the reported data.[22,23]

4.2.6.3. 1-(4-Nitrophenyl)-2-phenylethane ***6d***. *Representative procedure for solvent-free Suzuki cross-coupling reactions (method C).* A microwave tube equipped with a magnetic stirrer bar was charged with 4-bromonitrobenzene (0.10 g, 0.49 mmol), $K_3PO_4 \cdot H_2O$ (0.34 g, 1.47 mmol), PCy_3 (11 mg, 0.039 mmol), $Pd(OAc)_2$ (4.40 mg, 0.020 mmol), 2-phenethyl-benzo-1,3,2-diazaborolane **3** (2 equiv), and toluene (0.1 ml). The reaction tube was fitted with a snap on cap and irradiated with microwave energy (200 W) for 15 min. After the completion of the reaction, acetone was added to the tube and the content of the tube was filtered into a round-bottom flask. The solvent was removed in vacuo and the remaining black residue was purified with a flash column using hexane/ethyl acetate (8:2) as an eluting solvent to afford the title compound **6d** as a colorless crystals (57%), mp 55–56 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 2.98 (t, J=7.7 Hz, 2H), 3.06 (t, J=7.7 Hz, 2H), 7.15 (d, J=7.6 Hz, 2H), 7.23 (t, J=6.9 Hz, 1H), 7.27–7.33 (m, 4H), 8.14 (d, J=8.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 37.2, 37.6, 123.6, 126.3, 128.5, 129.4, 140.5, 146.5, 149.4. HRMS found: [M^++Na] 250.0847, $C_{14}H_{13}NNaO_2$ required 250.0844.[24]

4.2.7. Dibenzyl ***6e***. *Representative procedure for solvent-free Suzuki cross-coupling reactions (method D).* A microwave tube equipped with a magnetic stirrer bar was charged with bromobenzene (0.1 ml), $K_3PO_4 \cdot H_2O$ (0.34 g, 1.47 mmol), PCy_3 (11 mg, 0.039 mmol), $Pd(OAc)_2$ (4.40 mg, 0.020 mmol), and 2-phenethyl-benzo-1,3,2-diazaborolane **3** (0.11 g, 0.49 mmol). The reaction tube was fitted with a snap on cap and irradiated with microwave energy (200 W) for 15 min. After the completion of the reaction, acetone was added to the tube and the content of the tube was filtered into a round-bottom flask. The solvent was removed in vacuo and the remaining black residue was purified with a flash column using hexane as an eluting solvent to afford the title compound as a colorless crystals (79%), mp 52 °C [lit.[24] 51 °C]. MS (EI): m/z (%) 65.04 (24), 91.07 (100), 92.06 (7), 104.07 (22), 182.04 [M^+] (32). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 2.95 (s, 4H), 7.18–7.25 (m, 5H), 7.26–7.34 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 37.9, 125.9, 138.2, 138.3, 141.8.The characterizations of the titled compound are consistent with the reported data.[25,26]

4.2.8. Representative procedure for Suzuki cross-coupling of diazaborolane ***5*** *(method E).* A microwave tube equipped with a magnetic stirring bar was charged with diazaborolane **5** (0.20 g, 0.10 mmol), $K_3PO_4 \cdot H_2O$ (0.35 g, 1.50 mmol), PCy_3 (11.2 mg, 0.040 mmol), $Pd(OAc)_2$ (4.40 mg, 0.020 mmol), 1,4-dioxane (0.2 ml), and the corresponding arylhalide (0.5 mmol). The reaction tube was fitted with a snap on cap and irradiated with microwave energy (15 W) for 20 min at 100 °C. After the completion of the reaction, acetone was added to the tube and the content of the tube was filtered into a round-bottom flask. The solvent was removed in vacuo and the remaining black residue was purified by silica gel column chromatography using hexane/ethyl acetate (9:1) mixture as an eluting solvent.

4.2.8.1. 9-{(1E)-Hexenyl}anthracene ***6f***. *Method E was followed using 9-bromoanthracene (0.13 g, 0.5 mmol).* Compound **6f** was obtained as a light yellow solid (84%), mp 53–54 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 1.06 (t, J=7.3 Hz, 3H), 1.52–1.62 (m, 2H), 1.64–1.75 (m, 2H), 2.50–2.58 (m, 2H), 6.08 (dt, J=16.1, 6.7 Hz, 1H), 7.14 (d, J=16.0 Hz, 1H), 7.46–7.51 (m, 4H), 7.99–8.05 (m, 2H), 8.32–8.39 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 14.12, 22.51, 31.67, 33.41, 125.02, 125.07, 125.31, 125.33, 125.76, 126.24, 128.17, 128.56, 129.65, 131.54, 133.73, 139.62. MS (EI): m/z (%) 189.17 (6), 201.21 (10), 202.20 (66), 217.18 (100), 218.16 (71), 231.16 (63), 260.08 [M^+] (79), 261.11 (20). HRMS: found [M^+] 260.1565, calculated for $C_{20}H_{20}$ 260.1570.

4.2.8.2. 4-{(1E)-Hexenyl}nitrobenzene ***6g***. *Method E was followed using 4-bromonitrobenzene (0.10 g, 0.5 mmol).* Compound **6g** was obtained as a clear-yellow oil (81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.95 (t, J=7.5 Hz, 3H), 1.34–1.56 (m, 4H), 2.25–2.31 (m, 2H), 6.44–6.47 (m, 2H), 7.46 (d, J=8.9 Hz, 2H), 8.16 (d, J=9.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 13.87, 22.26, 31.11, 32.86, 123.94, 126.30, 128.09, 136.64, 144.47, 146.44. MS (EI): m/z (%) 98.11 (6), 91.14 (18), 116.15 (33), 119.08 (42), 149.01 (100), 150.02 (15), 188.01 (6), 205.02 [M^+] (28). HRMS: found [M^++Na] 228.0999, calculated for $C_{12}H_{15}NO_2Na$ 228.1000. IR (ν_{max}) neat 2957, 2928, 1595, 1512, 1337, 1108 cm^{-1}.[27]

4.2.8.3. 4-{(1E)-Hexenyl}acetophenone ***6h***. *Method E was followed using 4-bromoacetophenone (0.10 g, 0.5 mmol).* Compound **6h** was obtained as a colorless oil (67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.95 (t, J=7.3 Hz, 3H), 1.33–1.43 (m, 2H), 1.43–1.56 (m, 2H), 2.21–2.29 (m, 2H), 2.58 (s, 3H), 6.42 (m, 2H), 7.41 (d, J=8.3 Hz, 2H), 7.89 (d, J=8.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 13.89, 22.26, 26.46, 31.27, 32.82, 125.89, 128.72, 134.49, 135.43, 142.69, 197.49. MS (EI): m/z (%) 103.16 (8), 115.15 (25), 131.10 (80), 146.02 (39), 159.11 (10), 187.14 (100), 202.03 [M^+] (60), 203.04 (10). HRMS: found [M^++Na] 225.1255, calculated for $C_{14}H_{18}ONa$ 225.1255. IR (ν_{max}) neat 2957, 2927, 1678, 1601, 1265 cm^{-1}.[28]

4.2.8.4. 4-{(1E)-Hexenyl}phenol ***6i***. *Method E was followed using 4-bromophenol (0.086 g, 0.5 mmol).* Compound **6i** was obtained as a colorless oil (62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.93 (t, J=7.0 Hz, 3H), 1.36–1.50 (m, 4H), 2.16–2.23 (m, 2H), 6.08 (dt, J=15.8, 6.9 Hz, 1H), 6.30 (d, J=15.8 Hz, 1H), 6.77 (d, J=8.6 Hz, 2H), 7.23 (d, J=8.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 13.95, 22.27, 31.27, 32.66, 67.03, 115.43, 127.19, 129.01, 129.07, 154.58. MS (EI): m/z (%) 79.16 (16), 103.10 (21), 105.11 (71), 133.09 (100), 134.11 (15), 147.09 (6), 176.04 [M^+] (57), 177.04 (9). HRMS: found [M^+] 175.1125, calculated for $C_{12}H_{15}O$ 175.1123. IR (ν_{max}) neat 3313, 2956, 2928, 1600, 1511, 1218 cm^{-1}.[29]

*4.2.8.5. 4-{(1E)-Hexenyl}methylbenzoate **6j**. Method E was followed using 4-bromomethylbenzoate (0.11 g, 0.5 mmol).* Compound **6j** was obtained as a colorless oil (67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.95 (t, J=7.2 Hz, 3H), 1.35–1.44 (m, 2H), 1.44–1.55 (m, 2H), 2.25 (q, J=6.6 Hz, 2H), 3.92 (s, 3H), 6.32–6.48 (m, 2H), 7.40 (d, J=8.1 Hz, 2H), 7.97 (d, J=8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 13.89, 22.26, 31.30, 32.80, 51.93, 125.73, 129.02, 129.87, 134.20, 142.50, 167.00. MS (EI): m/z (%) 91.17 (25), 115.19 (31), 131.14 (77), 162.03 (100), 187.11 (14), 218.07 [M^+] (58), 219.04 (11). HRMS: found [M^++Na] 241.1204, calculated for $C_{14}H_{18}O_2Na$ 241.1204. IR (ν_{max}) neat 2954, 2927, 1718, 1272, 1107 cm^{-1}.[30]

*4.2.8.6. 2-{(1E)-Hexenyl}methylbenzoate **6k**. Method E was followed using 2-iodomethylbenzoate (0.13 g, 0.5 mmol).* Compound **6k** was obtained as a colorless oil (74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.95 (t, J=7.2 Hz, 3H), 1.35–1.55 (m, 4H), 2.24–2.31 (m, 2H), 3.91 (s, 3H), 6.15 (dt, J=15.6, 6.8 Hz, 1H), 7.15 (d, J=15.9 Hz, 1H), 7.26 (dd, J=7.6, 1.5 Hz, 1H), 7.41–7.47 (m, 1H), 7.55 (dd, J=7.2, 0.84 Hz, 1H), 7.87 (dd, J=7.9, 1.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 13.92, 22.26, 31.41, 32.86, 51.91, 126.40, 127.16, 128.18, 128.40, 130.25, 131.85, 134.05, 139.71, 168.09. MS (EI): m/z (%) 91.19 (14), 115.21 (24), 144.15 (100), 161.11 (69), 162.08 (12), 186.08 (7), 218.00 [M^+] (36), 219.11 (22). HRMS: found [M^++Na] 241.1205, calculated for $C_{14}H_{18}O_2Na$ 241.1204. IR (ν_{max}) neat 2954, 2927, 1720, 1247, 1076 cm^{-1}.[31]

*4.2.8.7. 2-Octyl-1,3-bis-trimethylsilanyl-benzo-1,3,2-diazaborolane **7***. Freshly prepared 2-octyl-benzo-1,3,2-diazaborolane (3.00 g, 13.04 mmol) was placed in a flame dried, nitrogen purged two necked round-bottom flask and then dissolved in THF (15 ml). To this solution was injected gradually, tetramethyl ethylenediamine (TMEDA) (3.88 ml, 26.1 mmol) via a syringe. The mixture was stirred for 5 min and a slight excess of butyl lithium (17.4 ml, 1.6 M) was added drop wise for 30 min, followed by continuous stirring for 24 h at ambient temperature. ^{11}B NMR spectroscopic analysis of the reaction mixture showed complete conversion of the starting boronate. The solvent was removed in vacuo, and the light-brown solid was purified without quenching, using flash column chromatography on silica gel with hexane. Subsequent removal of hexane in vacuo afforded 2-octyl-1,3-bis-tetramethylsilanyl-benzo-1,3,2-diazaborolane (83%). ^{11}B NMR (160 MHz, $BF_3{\cdot}OEt_2$): δ ppm 37.6 (s). ^{29}Si NMR (99 MHz, TMS): δ ppm 6.31 (s). ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 0.74 (s, 18H), 1.13–1.20 (m, 13H), 1.57 (m, 4H), 7.18 (dd, 2H), 7.48 (dd, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ ppm 2.0, 14.2, 22.9, 29.3, 30.4, 32.2, 113.4, 118.4, 142.2. This compound was sensitive to air and moisture, thus decomposed gradually after flash column chromatography.

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