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Advanced Synthesis & Catalysis

An Efficient Ni/Pd Catalyzed Chemoselective Synthesis of 1,3,2-Benzodiazaborininones from Boronic Acids and Anthranilamides

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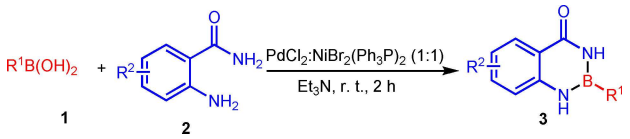
Abstract: An efficient Ni/Pd catalyzed chemoselective synthesis of 1,3,2-benzodiazaborininones from boronic acids and anthranilamide has been developed. This protocol allows for the rapid and straightforward access to a wide range of 1,3,2-benzodiazaborininones at roomtemperature with excellent functional group tolerance.

Keywords: 1,3,2-benzodiazaborininones; boronic acids; anthranilamide; Ni/Pd; green synthesis

Introduction

Organoboron compounds make up a group of the most versatile heteroatom-substituted organic molecules. They have received significant attention due to their unique structure, physical properties and diverse applications in medicinal chemistry[1] and materials science.[2] They also play an important role in organic synthesis, catalysis, and biochemistry.[3] Furthermore, boron-containing *N*-heterocyclic compounds with valuable B–N structural units exhibited useful behavior in materials and biomedical research as fluorescent dyes[4] and biological labeling.[5] In addition, since the B–N unit has a strong dipole moment, replacing the C=C with a B–N unit can reduce the HOMO-LUMO gap, which usually results in a chemiluminescent material.[6] As one of the major classes of valuable boron-containing heterocyclic compounds, 1,3,2-benzodiazaborininones have high stability toward moisture, oxygen, and even silica gel chromatography.[7] These compounds with an anthranilamide (aam) substituent on the boron center [Ar–B(aam)] are temporarily masked for their reactivity toward transmetalation, and have proven to be useful reagents in Suzuki-Miyaura cross-coupling reaction.[8] The B(aam) moieties also serve as directing groups for catalytic *ortho*-C(aryl)–H silylation.[9] They have been applied to iridium-catalyzed stereoselective hydroboration of alkynes.[10]

Conventional methods involve the construction of 1,3,2-benzodiazaborininones based on the condensation of boronic acid with commercially available anthranilamide in toluene under reflux.[11] This method requires high temperature and the yield is not ideal. Recently, Molander and co-workers reported the direct synthesis of these compounds by the defluorinative annulation of potassium organotrifluoroborates with anthranilamide in the presence of anhydrous $BF_3{\cdot}NH_2Et$ or SiO_2 in cyclopentyl methyl ether (CPME)/toluene.[12] Although this method represents important advances, the established protocol does not sufficiently meet the demands for green chemistry and still suffers from several limitations, such as: 1) high energy consumption under harsh reaction conditions; 2) the substrates are not commercially available and expensive; 3) the reaction time is too long. Therefore, in order to further improve the reaction efficiency, the search for a more mild and practical method with high generality for synthesis of 1,3,2-benzodiazaborininones under mild reaction conditions remains appealing and challenging. Based on our tremendous interest in developing of environmentally friendly approaches for various organic transformations,[13] herein, we report an efficient strategy for the synthesis of 1,3,2-benzodiazaborininones utilizing a Pd/Ni cocatalyst at room temperature (Scheme 1).



Scheme 1. Synthesis of 1,3,2-benzodiazaborininones.

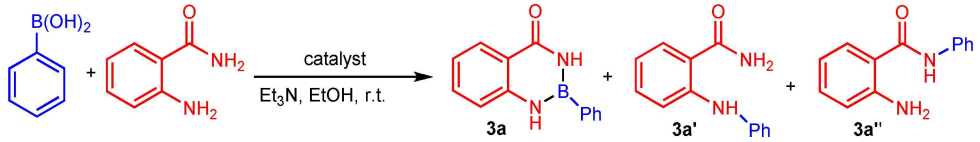
Results and Discussion

At the outset of this study, phenylboronic acid and 2-aminobenzamide were used as model substrates to optimize the reaction conditions. The results of screening different catalysts are summarized in Table 1. It is noteworthy that no product formation was observed, and the starting materials were completely recycled in the absence of a catalyst. Several Cu, Zn, Fe, Ni and Pd salts were screened in EtOH at room temperature in the present of 0.5 equiv. of Et_3N (Table 1, entries 2–7). When CuBr was as a catalyst, Chan-Evans-Lam reaction[14] occurred and *N*-arylation products **3 a′** and **3 a″** was obtained in 80% and 15% yield, respectively (Table 1, entry 2). After testing $ZnCl_2$, $FeCl_2$, $NiCl_2$, and $NiBr_2(PPh_3)_2$ as well as $PdCl_2$, to our surprise, only annulated product **3 a** was formed. Among them, $PdCl_2$ turned out to be the best catalyst with 90% isolated yield of **3 a** without the generation of **3 a′** and **3 a″** (entry 7). Encouraged by the above results, various catalytic systems combined with $PdCl_2$ were tested. After extensive screening, $NiBr_2(PPh_3)_2/PdCl_2$ (1:1, 5 mol%) was found to be optimal. When the amount of catalyst $NiBr_2(PPh_3)_2/PdCl_2$ was decreased to 2.5 mol%, the isolated yield was dropped to 83%.

Based on the results presented in entry 11 of Table 1, we subsequently tested the base, solvent and temperature effect on the reaction. When inorganic bases including NaOH, Na_2CO_3 and K_2CO_3 were selected, the reaction progressed with poor yields (Table 2, entries 2–4). Organic bases such as pyridine, 1,4-diazabicyclo[2.2.2]octane (DABCO) and a much-hindered organic base 1,8-diazabicyclo(5,4,0) undec-7-ene (DBU) also led to inferior results. Furthermore, the screening of different solvents such as methanol, tetrahydrofuran (THF) dimethylsulfoxide (DMSO), *N, N*-dimethylformamide (DMF), toluene (PhMe), PEG 400, choline chloride (ChCl)/urea did not help in improving the yield. Notably, increasing the reaction temperature has little effect on the reaction, only the reaction time is shortened. Thus, we chose 0.5 equivalent of triethylamine with 5 mol% each of $NiBr_2(PPh_3)_2$ and $PdCl_2$ in ethanol at room temperature as the standard conditions.

Having affirmed the optimized conditions, a series of boronic acids and 2-aminobenzamide were investigated to explore the universality and limitation of this method. The results are summarized in Tables 3 and 4.

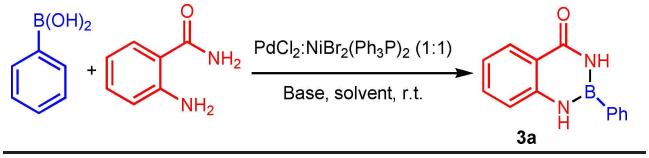
Table 1. Catalyst screening for the reaction of phenylboronic acid and 2-aminobenzamide.[a]



Entry	Catalyst	Time (h)	Yield of **3 a** (%)	Yield of **3 a'** (%)	Yield of **3 a''** (%)
1	no	12	0	0	0
2	CuBr	12	0	80	15
3	$ZnCl_2$	12	32	0	0
4	$FeCl_2$	12	41	0	0
5	$NiCl_2$	12	63	0	0
6	$NiBr_2(PPh_3)_2$	12	70	0	0
7	$PdCl_2$	12	90	0	0
8[b]	CuBr:$PdCl_2$ (1:1)	12	10	35	50
9[b]	$NiBr_2(PPh_3)_2$:CuBr (1:1)	12	10	35	45
10[b]	$NiCl_2$:$PdCl_2$ (1:1)	12	81	0	0
11[b]	$NiBr_2(PPh_3)_2$:$PdCl_2$ (1:1)	2	90	0	0
12[b]	$NiBr_2(PPh_3)_2$:$PdCl_2$ (2:1)	2	87	0	0
13[b]	$NiBr_2(PPh_3)_2$:$PdCl_2$ (3:1)	2	78	0	0
14[b]	$NiBr_2(PPh_3)_2$:$PdCl_2$ (4:1)	2	71	0	0
15[c]	$NiBr_2(PPh_3)_2$:$PdCl_2$ (1:1)	24	83	0	0

[a] Reaction conditions: phenylboronic acid (1.0 mmol), 2-aminobenzamide (1.0 mmol), Et_3N (0.5 mmol), catalyst (0.1 mmol) in EtOH (2 ml) at room temperature unless otherwise specified in the Table; isolated yields are given.
[b] Catalyst (0.05 mmol).
[c] Catalyst (0.025 mmol).

Table 2. Optimization of the reaction conditions for the synthesis of product **3a**.[a]

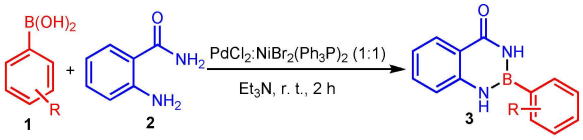


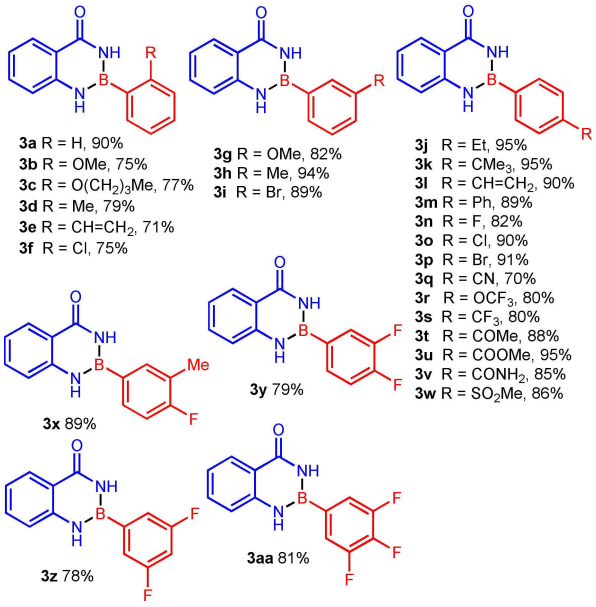
3a

Entry	Base	Solvent	Time (h)	Yield (%)[b]
1	no	EtOH	12	0
2	NaOH	EtOH	2	21
3	Na_2CO_3	EtOH	2	10
4	K_2CO_3	EtOH	2	12
5	EtONa	EtOH	2	39
6	DBU	EtOH	2	24
7	*t*-BuOK	EtOH	2	65
8	DABCO	EtOH	2	56
9	Pyridine	EtOH	2	50
10	Et_3N	EtOH	2	90
11	Et_3N	MeOH	2	87
12	Et_3N	THF	2	10
13	Et_3N	DMSO	2	21
14	Et_3N	DMF	2	30
15	Et_3N	PhMe	2	58
16	Et_3N	PEG 400	2	41
17	Et_3N	ChCl/urea	2	10
18[c]	Et_3N	EtOH	1.5	87
19[d]	Et_3N	EtOH	1	88

[a] Reaction conditions: phenylboronic acid (1.0 mmol), 2-aminobenzamide (1.0 mmol), base (0.5 mmol), $NiBr_2(PPh_3)_2$:$PdCl_2$ (1:1, 0.05 mmol) in solvent (2 ml) at room temperature unless otherwise specified in the Table.
[b] Isolated yields.
[c] The reaction was performed at 40 °C.
[d] The reaction was performed at 80 °C.

Table 3. Synthesis of 1,3,2-benzodiazaborininones from substituted phenylboronic acids.





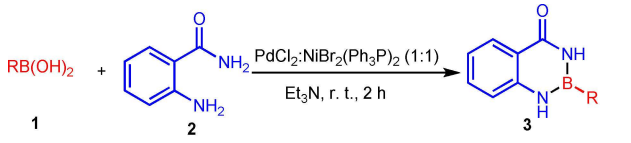
[a] Reaction conditions: substituted phenylboronic acid (1.0 mmol), 2-aminobenzamide (1.0 mmol), Et_3N (0.5 mmol), $NiBr_2(PPh_3)_2$:$PdCl_2$ (1:1, 0.05 mmol) in EtOH (2 ml) at room temperature for 2 h, and the yields were given in isolated yields.

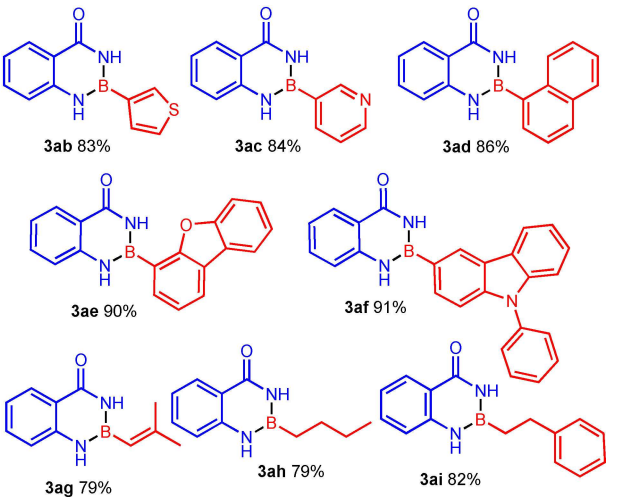
Generally, both electron-donating and electron-withdrawing (*ortho*-, *meta*- and *para*-) substituted phenylboronic acids performed well under the optimized reaction conditions and provided the desired products **3a**–**3w** in 70–95% yields. The vinyl group was tolerated, **3e** and **3l** was obtained in 90%. The use of (4-carbamoylphenyl)boronic acid, which has an amide group, was not a problem to give the desired product **3v** in 85% yield. Halogen-substituted phenylboronic acids, such as 4-fluoro, 4-chloro and 4-bromo-phenylboronic acids also participated in the reaction to provide the the anticipated products **3n**–**3p** with good to excellent yields. No coupling product was observed from the above reaction. The tolerance of halogen groups in this reaction provides an opportunity for further modifications toward the construction of structural diverse 1,3,2-benzodiazaborininones.

Furthermore, heterocyclic and fused-rings-substituted boronic acids such as thienyl-, pyridyl-, naphthyl-, dibenzo[*b*,*d*]furan-, and 9-phenyl-9*H*-carbazole-substituted boronic acids were amenable to the annulation process, giving the corresponding target products **3ab**–**3af** in 83–91% yield. This protocol is also applicable to alkenylboronic acids such as (2,2-dimethylethenyl)boronic acid, affording the desired product **3ag** in 79% yield. In addition, alkylboronic acids such as butylboronic acid, phenethylboronic acid were also examined, the corresponding product **3ah** and **3ai** were obtained in 79% and 82% yields, respectively.

Subsequently, the reactions of substituted anthranilamide were also further evaluated under the optimized reaction conditions. As shown in Table 5, a variety of anthranilamide with electron-donating and electron-withdrawing groups afford the corresponding products **3aj**–**3bn** in high yields. Even anthranilamide substituted at the *ortho* position of the amino group such as 2-amino-3-methylbenzamide also underwent the condensation reaction, forming the respective products **3bo**–**3bq** in moderate to high yields. However, anthranilamides bearing a substituent at the *ortho* position of the amide such as 2-amino-6-methylbenzamide and 2-amino-6-methoxybenzamide re-

Table 4. Synthesis of 1,3,2-benzodiazaborininones from various boronic acids.

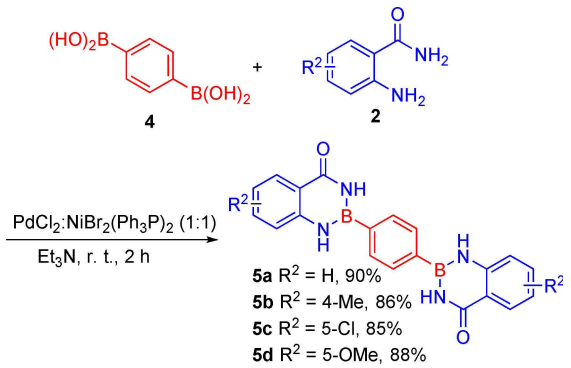




[a] Reaction conditions: boronic acid (1.0 mmol), 2-aminobenzamide (1.0 mmol), Et_3N (0.5 mmol), $NiBr_2(PPh_3)_2$:$PdCl_2$ (1:1, 0.05 mmol) in EtOH (2 ml) at room temperature for 2 h, and the yields were given in isolated yields.

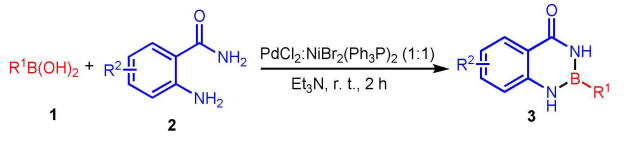
acted with phenylboronic acid, did not produce the desired products in synthetically useful yields (not shown in the Table).

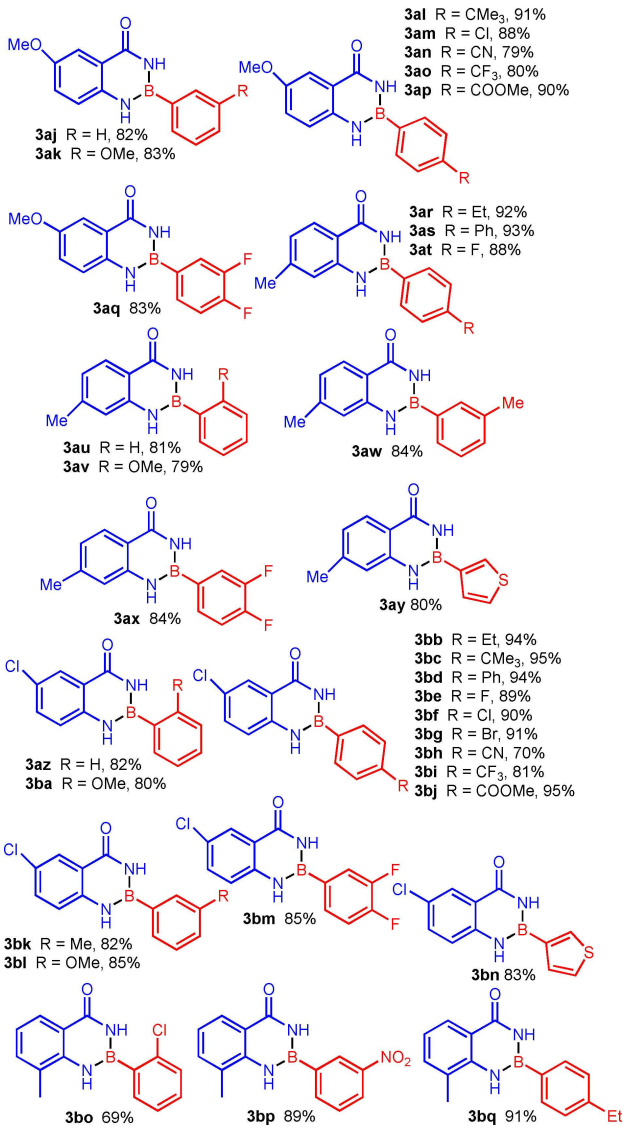
Stimulated by these results, we then extended the scope of this reaction to a substrate containing two boric acid groups, such as 1,4-phenylenediboronic acid. As shown in Scheme 2, treatment of 1,4-phenylenediboronic acid (1 mmol) with anthranilamide (2 mmol) under the above optimal conditions led to formation of the corresponding bis(1,3,2-benzodiazaborininones) **5a**–**5d** in 85%-90% yields.



Scheme 2. Synthesis of bis(1,3,2-benzodiazaborininones).

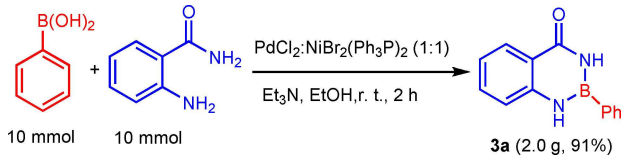
Table 5. Synthesis of 1,3,2-benzodiazaborininones from various anthranilamides and boronic acids.



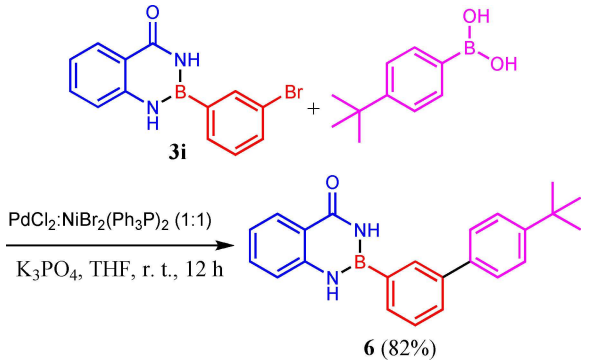


[a] Reaction conditions: boronic acid (1.0 mmol), 2-aminobenzamide (1.0 mmol), Et_3N (0.5 mmol), $NiBr_2(PPh_3)_2$:$PdCl_2$ (1:1, 0.05 mmol) in EtOH (2 ml) at room temperature for 2 h, and the yields were given in isolated yields.

To showcase the practical applications of this methodology, we carried out the model reaction on a 10 mmol scale under the corresponding optimized reaction conditions. We were pleased that 91% yield of the desired product **3a** (2.0 g) could be obtained, implying that this methodology is suitable for larger scale synthesis (Scheme 3).



Scheme 3. Gram-scale synthesis of **3 a.**



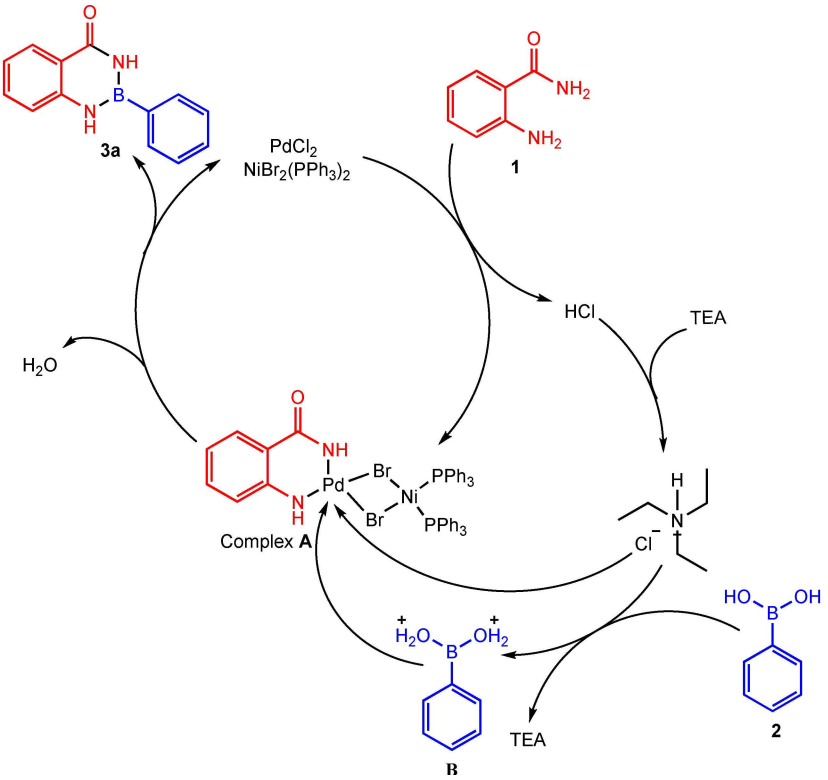
Scheme 4. Late-stage functionalization.

To further demonstrate the potential utility of this reaction, late-stage functionalization of product **3 i** was examined. Treatment of **3 i** with (4-(*tert*-butyl)phenyl) boronic acid in THF in the presence of $PdCl_2/NiBr_2(PPh_3)_2$ and K_3PO_4 at room temperature successfully afforded the cross-coupling product **6** in 82% yield (Scheme 5). The B(aam) group was completely retained in this process, and it may serve as directing group and protecting group for further C–H functionalization.[7]

On the basis of above results and previous reports,[15] a plausible mechanism is illustrated in Scheme 5. The initial step involves the formation of complex **A** generated from $PdCl_2/NiBr_2(PPh_3)_2$ and anthranilamide, in which Pd and Br are connected through coordinate bonds.[16] At the same time, the released hydrogen chloride reacts with triethylamine to form triethylamine hydrochloride. Subsequently, the interaction of triethylamine hydrochloride and phenylboronic acid transfers H^+ to -OH of phenylboronic acid to yield a protonated boric acid (**B**). Finally, protonated boric acid attacks complex **A** to produce target product **3 a** with elimination of 2 molecules of water and simultaneous regeneration of $PdCl_2/NiBr_2(PPh_3)_2$, thus completing the catalytic cycle.

Conclusion

In summary, we have disclosed a mild and efficient Ni/Pd catalyzed chemoselective synthesis of 1,3,2-benzodiazaborininones from boronic acids and anthranilamide. This catalytic system is applicable for various



Scheme 5. Proposed mechanism.

aromatic, heteroaromatic, alkenyl- and alkylboronic acids. This mild process has a high efficacy in large-scale reactions. Compared to previous methods, this protocol features wide range of substrates, largely reduced reaction time, and high yields. Further investigations on the synthetic applications of this methodology are ongoing in our laboratory.

Experimental Section

General

Unless otherwise stated, all reagents were purchased from commercial suppliers and used as received without further purification. Melting points were determined on an X-5 digital melting point apparatus and are not corrected. The FT-IR spectra were recorded on a Bruker Tensor 27 Fourier transform infrared spectroscope using a thin film supported on KBr pellets. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV III-500 or Zhongke Niujin AS 400 spectrometer using TMS as internal standard. The mass spectra were performed on a 3200 Qtrap instrument with an ESI source.

General Procedure for Synthesis of 1,3,2-Benzodiazaborininones

A mixture of boronic acid (1 mmol), anthranilamide (1 mmol), Et_3N (0.5 mmol) $NiBr_2(PPh_3)_2$ (0.05 mmol), $PdCl_2$ (0.05 mmol) in EtOH (2 ml) was stirred at room temperature. The reaction progress was monitored by thin-layer chromatography (TLC). Upon completion, water (10 ml) was added and the solid precipitate was filtered and purified by recrystallized from ethanol/water or by column chromatography (silica gel, 5:1 petroleum ether/ethyl acetate as an eluent) to give the desired pure products.

General Procedure for Synthesis of bis (1,3,2-Benzodiazaborininones)

A mixture of 1,4-phenylenediboronic acid (1 mmol), anthranilamide (2 mmol), Et_3N (1.0 mmol) $NiBr_2(PPh_3)_2$ (0.10 mmol), $PdCl_2$ (0.10 mmol) in EtOH (4 ml) was stirred at room temperature until the reaction was completed as monitored by TLC. Water was added and the solid precipitate was filtered and purified by recrystallized from ethanol/water to give the pure product **5**.

2,2′-(1,4-Phenylene)bis(2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one) (5a): White solid; 328 mg, 90% Yield; mp: >300 °C; IR (KBr): 3404, 3304, 1652, 1619, 1539, 1487, 1365, 1271, 826, 760 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.82 (s, 2H), 9.44 (s, 2H), 8.19 (s, 4H), 8.07 (d, J=6.8 Hz, 2H), 7.61 (t, J=7.2 Hz, 2H), 7.49 (d, J=8.0 Hz, 2H), 7.15 (t, J=7.6 Hz, 2H) ppm; ^{13}C NMR (DMSO-d_6, 100 MHz): δ 166.8, 145.9, 134.8, 133.9, 133.1, 128.4, 121.4, 119.3, 118.6 ppm; EI-MS: m/z=366 $(M+H)^+$.

2,2′-(1,4-Phenylene)bis(7-methyl-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1*H*)-one) (5b): Brown solid; 338 mg, 86% Yield; mp: >300 °C; IR (KBr): 3414, 3320, 1648, 1602, 1548, 1482, 1366, 1273, 870, 824, 743 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.68 (s, 2H), 9.30 (s, 2H), 8.13 (s, 4H), 7.92 (d, J=8.0 Hz, 2H), 7.25 (s, 2H), 6.95 (d, J=7.6 Hz, 2H), 2.39 (s, 6H) ppm; ^{13}C NMR (DMSO-d_6, 100 MHz): δ 166.7, 145.9, 144.0, 134.8, 133.0, 128.4, 122.7, 118.5, 117.1, 21.9 ppm; EI-MS: m/z=395 $(M+H)^+$.

2,2′-(1,4-Phenylene)bis(6-chloro-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1*H*)-one) (5c): White solid; 369 mg, 85% Yield; mp: >300 °C; IR (KBr): 3408, 3329, 1652, 1619, 1540, 1505, 1359, 1295, 848, 825, 717 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.87 (s, 2H), 9.48 (s, 2H), 8.14 (s, 4H), 7.99 (s, 2H), 7.85 (d, J=8.0 Hz, 2H), 7.48 (d, J=8.8 Hz, 2H) ppm; ^{13}C NMR (DMSO-d_6, 100 MHz): δ 170.5, 149.5, 138.6, 137.5, 132.0, 130.0, 125.6, 125.3 ppm; EI-MS: m/z=436 $(M+H)^+$.

2,2′-(1,4-Phenylene)bis(6-methoxy-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one) (5d): White solid; 374 mg, 88% Yield; mp: >300 °C; IR (KBr): 3404, 3301, 2839, 1645, 1609, 1542, 1506, 1351, 1255, 862, 824, 753 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.78 (s, 2H), 9.31 (s, 2H), 8.12 (s, 4H), 7.50 (s, 2H), 7.41 (d, J=8.8 Hz, 2H), 7.24 (d, J=8.8 Hz, 2H), 3.81 (s, 6H) ppm; ^{13}C NMR (DMSO-d_6, 100 MHz): δ 171.4, 158.8, 144.9, 137.7, 127.5, 124.8, 124.4, 114.1, 60.6 ppm; EI-MS: m/z=427 $(M+H)^+$.

Procedure for Synthesis of Product 6

A mixture of 2-(3-bromophenyl)-2,3-dihydrobenzo[*d*][1,3,2] diazaborinin-4(1*H*)-one (**3i**, 1 mmol), (4-(*tert*-butyl)phenyl)boronic acid (1 mmol), K_3PO_4 (1.0 mmol) $NiBr_2(PPh_3)_2$ (0.05 mmol), $PdCl_2$ (0.05 mmol) in THF (2 ml) was stirred at room temperature for 12 h. The reaction was quenched with water and extracted with ethyl acetate for three times. The combined organic layers were dried over anhydrous $MgSO_4$, concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc in petroleum ether) to afford the pure product **6**. White solid; 245 mg, 82% Yield; mp: 282–283 °C; IR (KBr): 3528, 1659, 1608, 1530, 1488, 1362, 1278, 825, 763 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.70 (s, 1H), 9.31 (s, 1H), 8.08–8.02 (m, 3H), 7.97 (s, 1H), 7.77 (d, J=8.8 Hz, 1H), 7.59 (t, J=8.0 Hz, 1H), 7.50–7.46 (m, 3H), 7.37 (d, J=8.0 Hz, 1H), 7.18-7.11 (m, 2H), 1.30 (s, 9H) ppm; ^{13}C NMR (DMSO-d_6, 100 MHz): δ 166.8, 153.6, 152.9, 146.0, 134.5, 133.7, 129.5, 128.4, 125.0, 124.6, 121.2, 119.2, 118.6, 35.0, 31.5 ppm; EI-MS: m/z=355 $(M+H)^+$.

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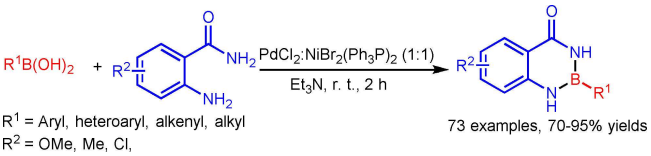
FULL PAPER

An Efficient Ni/Pd Catalyzed Chemoselective Synthesis of 1,3,2-Benzodiazaborininones from Boronic Acids and Anthranilamides



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H.-J. Wang, M. Zhang, W.-J. Li, Y. Ni, J. Lin*, Z.-H. Zhang*