Supporting Information

Direct Transformation from Arylamines to Aryl Naphthalene-1,8-diamino Boronamides: A Metal-Free Sandmeyer-type Process

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1.1 Proposed mechanism for this process

A radical mechanism has been proposed to account for this borylation reaction [47-61] as shown in the following Scheme. Firstly, the amino group is transformed to generate the diazonium salt A in the presence of t-BuONO through the Sandmeyer reaction, which was well documented as a radical mechanism [29-32]. On the other hand, the acetate anion reacts with Bpin-Bdan to form the tetra-coordinated boron complex C. Then a single-electron transformation (SET) process occurred between aryl diazonium ion B and complex C to generate aryl radical F through N₂ extrusion from radical D together with the formation of complex E. Finally, the reaction between aryl radical F with complex E gave the borylated product aryl-Bdan.

1.2 General Procedure for the synthesis of nonsymmetrical diboron reagent Bpin-Bdan

In air, B₂pin₂ (254.2 mg, 1.0 mmol, 1.0 eq.), 1,8-diaminonaphthalene (158.1 mg, 1.0 mmol, 1.0 eq.), and CH₃ONa (54.0 mg, 1.0 mmol, 1.0 eq.) were sequentially weighed and...
added to a screw-capped Schenk tube containing a magnetic stir bar. The vessel was evacuated and refilled with nitrogen for three times. MeOH (10.0 mL) were added in turn under N2 atmosphere using syringes through a septum which was temporarily used to replace the screw cap. The reaction mixture was then vigorously stirred at 70 °C for 4 hours. The resulting mixture was evaporated under vacuum to dryness and the residue was purified by column chromatography to yield the desired product Bpin-Bdan 235.4 mg, 80 %.

Melting point: 186.7–187.4 °C;
IR (cm⁻¹) 3382, 3053, 2975, 1627, 1603, 1372, 1316, 1291, 1267, 1250, 1212, 1165, 1144, 1106, 962, 849, 821, 765, 635;
¹H NMR (400 MHz, CDCl₃) δ 1.29 (s, 12H), 6.19 (br s, 2H), 6.26 (dd, J = 7.2, 0.8 Hz, 2H), 6.97 (dd, J = 8.4, 0.8 Hz, 2H), 7.07 (dd, J = 8.4, 7.2, 2H);
¹³C NMR (100 MHz, CDCl₃) δ 25.6, 83.8, 105.9, 118.1, 121.6, 128.0, 136.9, 141.0;
¹¹B NMR (128 MHz, CDCl₃) δ 32.7;

1.3 General Procedure for the application of 3-bromophenyl B(dan) 1j in the selective Suzuki-Miyaura cross-coupling reaction

2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (2)³

An oven dried test tube was charged with 2j (151 mg, 0.47 mmol), B₂pin₂ (130 mg, 0.51 mmol), Pd₂(dba)₃ (8.0 mg, 0.014 mmol), PCy₃ (9.4 mg, 0.033 mmol) and K₂CO₃ (68.3 mg, 0.7 mmol). The reaction tube was evacuated and backfilled with argon, and 1,4-dioxane (1.3 mL) was added via a syringe. The reaction mixture was stirred for 5h at 80 °C. The reaction mixture was diluted with EtOAc, and filtered through a pad of celite, and the filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography by PE/EA (10:1) to get the product as light grey solid (128.3 mg, 88 %).

Melting point: 106.1~107.2 °C;
IR (cm⁻¹): 3420.2, 3402.4, 1594.6, 1508.8, 1489.6, 1315.5, 1167.3;
¹H NMR (400 MHz, CDCl₃) δ 7.76 (s, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 7.4 Hz, 1H), 7.31 (t, J = 7.7 Hz, 1H), 7.14 (t, J = 7.8 Hz, 2H), 7.07 (d, J = 8.2 Hz, 2H), 6.42 (d, J = 7.2 Hz, 2H), 5.98 (s, 2H), 1.26 (s, 12H);
¹³C NMR (100 MHz, CDCl₃) δ 140.7, 136.3, 134.4, 133.2, 131.4, 130.0, 129.9, 127.6, 123.1, 119.9, 118.2, 106.2, 83.5, 25.0;
HRMS (APCI) m/z calcd for C₂₂H₂₄B₂N₂O₂ (M⁺): 370.2029, found: 370.2026.
2-(4'-methoxy-[1,1'-biphenyl]-3-yl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (3)

An oven dried test tube was charged with 2j (80.5 mg, 0.25 mmol), p-methoxylphenylboronic acid (77 mg, 0.50 mmol), PdCl₂ (dppf)CH₂Cl₂ (21 mg, 0.025 mmol) and K₃PO₄ (160 mg, 0.76 mmol). The reaction tube was evacuated and backfilled with argon, and 1,4-dioxane (1.3 mL) was added via a syringe. The reaction mixture was stirred for 5h at 80 °C. The reaction mixture was diluted with EtOAc, and filtered through a pad of celite, and the filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography by PE/EA (10:1) to get the product (78.8 mg, 90 %).

Melting point: 163.2~165.6 °C;
IR (cm⁻¹): 3407.2, 1594.4, 1495.9, 1407.7, 1224.1, 1181.2, 1029.0;
¹H NMR (400 MHz, CDCl₃) δ 7.80 (s, 1H), 7.65 (d, J = 7.1 Hz, 1H), 7.57 (m, 3H), 7.50 (t, J = 7.4 Hz, 1H), 7.15 (t, J = 7.7 Hz, 2H), 7.07 (d, J = 8.2 Hz, 2H), 7.02 (d, J = 8.4 Hz, 2H), 6.44 (d, J = 7.2 Hz, 2H), 6.08 (s, 2H), 3.88 (s, 3H);
¹³C NMR (100 MHz, CDCl₃) δ 159.3, 141.1, 140.8, 136.4, 133.7, 129.9, 129.8, 128.8, 128.7, 128.3, 127.6, 119.9, 117.9, 114.3, 106.1, 55.4;
HRMS (APCI) m/z calcd for C₂₃H₁₉BN₂O (M⁻): 350.1596, found: 350.1599.

4-methoxy-4''-(trifluoromethyl)-1,1'3',1''-terphenyl (4)

A round-bottomed flask was charged with 2-(4'-methoxy-[1,1'-biphenyl]-3-yl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (140.0 mg, 0.4 mmol) and THF (4 mL), and the reaction mixture was stirred for 5 min at room temperature. Then 1N HCl (4.0 mL, 0.4 mmol) was added. The mixture was stirred for another 12 h at room temperature and washed with Et₂O. The aqueous layer was washed twice with Et₂O. The aqueous layer was adjusted to pH 12 by aqueous NaOH and washed by Et₂O to remove 1,8-diaminonaphthalene. The aqueous layer was neutralized with HCl and extracted with EtOAc three times. The combined EtOAc layers were dried over anhydrous Na₂SO₄, and
the solvent was removed under reduced pressure to give the corresponding boronic acid, which was used for the next reaction without further purification.

An oven dried test tube was charged with the corresponding boronic acid (57.0 mg, 0.25 mmol), 3-bromothiophene (81.0 mg, 0.50 mmol), PdCl2 (dppe)CH2Cl2 (21 mg, 0.025 mmol) and K3PO4 (160 mg, 0.76 mmol). The reaction tube was evacuated and backfilled with argon, and 1,4-dioxane (1.3 mL) was added via a syringe. The reaction mixture was stirred for 5h at 80 °C. The reaction mixture was diluted with EtOAc, and filtered through a pad of celite, and the filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography by PE/EA (10:1) to get the target product (54.5 mg, 82%).

Melting point: 126.4~127.8 °C;
IR (cm⁻¹): 3096.2, 3004.0, 2954.8, 2837.2, 1603.2, 1513.4, 1441.4;
¹H NMR (400 MHz, CDCl₃) δ 7.78 (s, 1H), 7.47 (m, 8H), 7.01 (d, J = 8.6 Hz, 2H), 3.87 (s, 3H);
¹³C NMR (100 MHz, CDCl₃) δ 159.3, 142.4, 141.5, 136.4, 133.7, 129.2, 128.3, 126.5, 126.2, 125.7, 125.0, 124.9, 120.5, 114.3, 55.4;
HRMS (APCI) m/z calcd for C₁₇H₁₅OS [(M+H)⁺]: 267.0838, found: 267.0841.

References:
2. Copy of NMR spectra

Bpin-Bdan
HNMR CDCl₃
$\text{F}_3\text{C}-\text{B}-\text{NH}\text{N}$

$1c \text{ CNMR}$

$\text{CDCl}_3$
1e CNMR
CDCl$_3$
1f HNMR
CDCl₃
1f CNMR
CDCl₃
1h CNMR
CDCl₃
$^{1}$H NMR
CDCl$_3$
1H CNMR
CDCl₃
1H NMR
CDCl₃
1H NMR
CDCl₃
1n HNMR
CDCl₃
2 CNMR
CDCl₃