Supporting Information
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Supporting Information

Site-Selective and Stereoselective C(sp³)–H Borylation of Alkyl Side Chains on 1,3-Azoles with a Silica-Supported Monophosphine-Ir Catalyst

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1. Instrumentation and Chemicals

\(^1\)H (400 MHz), \(^{13}\)C (100 MHz) and \(^{11}\)B (128 MHz) NMR spectra were recorded on a JEOL JNM-ECX spectrometer. Chemical shift values for \(^1\)H, \(^{13}\)C and \(^{11}\)B NMR spectra are referenced to Me₄Si (0 ppm) and DMSO (2.50 ppm), the residual solvent resonances (77.0 ppm for CHCl₃, and 40.0 ppm for DMSO) and BF₃•OEt₂ (0 ppm), respectively. Chemical shifts are reported in δ ppm. High-resolution mass spectra were recorded on a Thermo Fisher Scientific Exactive, JEOL JMS-T100LP mass spectrometer or JEOL JMS-T100GCv mass spectrometer at the Instrumental Analysis Division, Equipment Management Center, Creative Research Institution, Hokkaido University. IR spectra were measured with a Perkin-Elmer Spectrum One. Melting points were determined on a micro melting point apparatus (Yanaco: MP-500D) using micro cover glass. GLC analyses were conducted on a Shimadzu GC-14B equipped with a flame ionization detector. Silica gel (Kanto Chemical Co., Silica gel 60 N, spherical, neutral) was used for column chromatography. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel 60F₂₅₄.

All reactions were carried out under a nitrogen atmosphere. Materials were obtained from commercial suppliers or prepared according to standard procedures unless otherwise noted. [Ir(OMe)(cod)]₂,¹ Ph-SMAP² and PS-TPP³ were prepared according to the literatures. Silica-SMAP,⁴ Silica-TRIP⁵ and Silica-TPP⁶ were prepared with CARiACT Q-10® according to the
reported procedures. CARiACT Q-10 (Catalyst grade, 75–150 µm) was purchased from Fuji Silysia Chemical Ltd. and dehydrated by heating at 150 °C for 10 h and stored in a glove box before use. All solvents for catalytic reactions were degassed via three freeze–pump–thaw cycles before use. Bis(pinacolato)diboron (2) was purchased from AllyChem Co., Ltd., and purified as follows: The diboron 2 was dissolved into hexane at room temperature, and traces of insoluble solids were removed by filtration. The filtrate was concentrated under vacuum, and the residue was recrystallized from pentane before use.

2. Experimental Procedures

Typical Procedure for the Borylation of 2-Ethylbenzo[d]thiazole (1a) with Immobilized Ligands (Table 1, Entry 1). In a glove box, Silica-SMAP (0.07 mmol/g, 57.1 mg, 0.0040 mmol, 2 mol%), bis(pinacolato)diboron (2) (50.8 mg, 0.20 mmol), and anhydrous, degassed THF (0.3 mL) were placed in a 10 mL glass tube containing a magnetic stirring bar. A solution of [Ir(OMe)(cod)]₂ (1.3 mg, 0.0020 mmol, 1 mol%) in THF (0.7 mL) and 2-ethylbenzo[d]thiazole (1a) (97.9 mg, 0.60 mmol) were added successively. The tube was sealed with a screw cap and removed from the glove box. The reaction mixture was stirred at 60 °C for 15 h, and filtered through a glass pipette equipped with a cotton filter. The solvent was removed under reduced pressure. An internal standard (1,1,2,2-tetrachloroethane) was added to the residue. The yields of the products 3a and 4a were determined by ¹H NMR spectroscopy (82% and 32% yields, respectively). The crude material was then purified by Kugelrohr distillation (1 mmHg, 145 °C), to give the corresponding product 3a (43.1 mg, 75% yield) contaminated with the diborylation product 4a (<1%) and traces of impurities, as estimated by ¹H NMR spectroscopy.

Procedure for the Borylation of 1a on a Gram Scale (Table 1, Entry 2). In a glove box, Silica-SMAP (0.07 mmol/g, 357 mg, 0.0250 mmol, 0.5 mol%), bis(pinacolato)diboron (2) (1.27 g, 5.0 mmol), and anhydrous, degassed THF (1 mL) were placed in a 50 mL glass tube containing a magnetic stirring bar. A solution of [Ir(OMe)(cod)]₂ (8.3 mg, 0.0125 mmol, 0.25 mol%) in THF (5 mL) and 2-ethylbenzo[d]thiazole (1a) (2.45 g, 15 mmol) were added successively. The tube was sealed with a screw cap and removed from the glove box. The reaction mixture was stirred at 90 °C for 24 h, and filtered through a glass pipette equipped with a cotton filter. Solvent was removed under reduced pressure. An internal standard (1,1,2,2-tetrachloroethane) was added to the residue. The yield of the product 3a was determined by ¹H NMR spectroscopy (71% yield). The crude material was then purified by Kugelrohr distillation (1 mmHg, 150 °C), to give the corresponding product 3a (780.8 mg, 2.7 mmol, 54% yield).
Procedure for the Geminal Borylation of 2-Ethylbenzo[d]thiazole (1a) (Table 1, Entry 3). In a glove box, Silica-SMAP (0.07 mmol/g, 57.1 mg, 0.0040 mmol, 2 mol%), bis(pinacolato)diboron (2) (101.6 mg, 0.40 mmol), and anhydrous, degassed THF (0.3 mL) were placed in a 10 mL glass tube containing a magnetic stirring bar. A solution of [Ir(OMe)(cod)]₂ (1.3 mg, 0.0020 mmol, 1 mol%) in THF (0.7 mL) and 2-ethylbenzo[d]thiazole (1a) (32.6 mg, 0.20 mmol) were added successively. The tube was sealed with a screw cap and removed from the glove box. The reaction mixture was stirred at 60 °C for 24 h, and filtered through a glass pipette equipped with a cotton filter. The solvent was removed under reduced pressure. An internal standard (1,1,2,2-tetrachloroethane) was added to the residue. The yields of the products 3a and 4a were determined by ¹H NMR spectroscopy (2% and 97% yields, respectively). The crude material was then purified by Kugelrohr distillation (1 mmHg, 180 °C), to give the corresponding product 4a [75.5 mg, 89% yield, contaminated with 3a (1.2 mg, 2% yield), as estimated by ¹H NMR spectroscopy.]

Typical Procedure for the Borylation of 2-Ethylbenzo[d]thiazole (1a) with Soluble Ligands (Table 1, Entry 7). In a glove box, bis(pinacolato)diboron (2) (50.8 mg, 0.20 mmol) was placed in a 10 mL glass tube containing a magnetic stirring bar. A solution of Ph-SMAP (0.9 mg, 0.0040 mmol, 2 mol%) in anhydrous, degassed THF (0.3 mL), a solution of [Ir(OMe)(cod)]₂ (1.3 mg, 0.0020 mmol, 1 mol%) in THF (0.7 mL) and 2-ethylbenzo[d]thiazole (1a) (97.9 mg, 0.60 mmol) were added successively. The tube was sealed with a screw cap and removed from the glove box. The reaction mixture was stirred at 60 °C for 15 h. Solvent was removed under reduced pressure. An internal standard (1,1,2,2-tetrachloroethane) was added to the residue. The yield of the product 3a was determined by ¹H NMR spectroscopy (0% yield).

Typical Procedure for the Borylation of 2-Alkyl-1,3-azole Derivatives (Table 2, Entry 1). In a glove box, Silica-SMAP (0.07 mmol/g, 57.1 mg, 0.0040 mmol, 2 mol%), bis(pinacolato)diboron (2) (50.8 mg, 0.20 mmol), and anhydrous, degassed THF (0.3 mL) were placed in a 10 mL glass tube containing a magnetic stirring bar. A solution of [Ir(OMe)(cod)]₂ (1.3 mg, 0.0020 mmol, 1 mol%) in THF (0.7 mL) and 2-ethylbenzo[d]oxazole (1b) (88.3 mg, 0.60 mmol) were added successively. The tube was sealed with a screw cap and removed from the glove box. The reaction mixture was stirred at 60 °C for 15 h, and filtered through a glass pipette equipped with a cotton filter. Solvent was removed under reduced pressure. An internal standard (1,1,2,2-tetrachloroethane) was added to the residue. The yield of the product 3b was determined by ¹H NMR spectroscopy (78% yield). The crude material was then purified by Kugelrohr distillation (1 mmHg, 130 °C), to give the corresponding product 3b (26.8 mg, 49% yield) contaminated with C(sp²)–H borylation products (4.6 mg, 9% yield) and a diborylation product (0.83 mg, 1% yield), as estimated by ¹H NMR spectroscopy.
Typical Procedure for the Borylation of 2-Alkyl-1,3-azole Derivatives Followed by Oxidation (Table 2, Entry 4). In a glove box, Silica-SMAP (0.07 mmol/g, 57.1 mg, 0.0040 mmol, 2 mol%), bis(pinacolato)diboron (2) (50.8 mg, 0.20 mmol), and anhydrous, degassed THF (0.3 mL) were placed in a 10 mL glass tube containing a magnetic stirring bar. A solution of [Ir(OMe)(cod)]2 (1.3 mg, 0.0020 mmol, 1 mol%) in THF (0.7 mL) and 2-isopropyl-1-methyl-1H-benzo[d]imidazole (1d) (88.3 mg, 0.60 mmol) were added successively. The tube was sealed with a screw cap and removed from the glove box. The reaction mixture was stirred at 80 °C for 15 h, and filtered through a glass pipette equipped with a cotton filter. Solvent was removed under reduced pressure. An internal standard (1,1,2,2-tetrachloroethane) was added to the residue. The yield of the product 3d was determined by ¹H NMR (83% yield). The resulting product was used to the next reaction without further purification. The crude boronate, THF (1.0 mL), water (1.0 mL) and NaBO₃•4H₂O (154 mg, 1.0 mmol) were placed in a round bottom flask containing a magnetic stirring bar, and the reaction mixture was stirred vigorously at room temperature for 5 h under air. The volatiles were evaporated under reduced pressure. The residue was suspended in CH₂Cl₂, filtered through a pipette equipped with a cotton plug. The filtrate was concentrated under reduced pressure, and the crude mixture was then purified by silica gel chromatography (CHCl₃/MeOH/Et₃N 97:2:1) to give the alcohol 5d (22.2 mg, 0.117 mmol, 59% yield in two steps).

Procedure for the Cu-Catalyzed Amination of 3a (Scheme 1). In a glove box, 3a (43.4 mg, 0.15 mmol), Cu(OAc)₂ (2.7 mg, 0.015 mmol, 10 mol%) and Ag₂CO₃ (82.7 mg, 0.3 mmol, 2 equiv) were placed in a 10 mL glass tube containing a magnetic stirring bar. N-Methylaniline (24.1 mg, 0.225 mmol, 1.5 equiv) and toluene (300 µL) were then added, and the tube was sealed with a screw cap and removed from the glove box. The reaction mixture was heated at 100 °C for 12 h. After cooling to room temperature, the solvents were removed under reduced pressure, and the resulting mixture was purified by silica gel chromatography (hexane/EtOAc 70:30) to give the desired product 6 as pale yellow oil (32.2 mg, 0.120 mmol, 80% yield).

Procedure for the Pd-Catalyzed Suzuki–Miyaura Coupling of 3a (Scheme 1). In a glove box, 3a (47.7 mg, 0.165 mmol, 1.1 equiv), 4-chloroanisole (21.4 mg, 0.15 mmol), a RuPhos-ligated palladacycle precatalyst (RuPhos-Pd-G3, 6.3 mg, 0.0075 mmol, 5 mol%) and K₂CO₃ (62.3 mg, 0.45 mmol, 3 equiv) were placed in a 10 mL glass tube containing a magnetic stirring bar. Toluene (150 µL) and H₂O (150 µL) were added, and the tube was sealed with a screw cap and removed from the glove box. The reaction mixture was heated at 90 °C for 24 h. After cooling to room temperature, water was added to the tube, and the mixture was extracted with Et₂O. The organic layer was washed with water, dried over MgSO₄, filtrate, and concentrated. The residue was purified by silica gel chromatography (hexane/EtOAc 80:20) to give the desired product 7 (25.4 mg,
63% yield) contaminated with 4,4'-dimethoxy-1,1'-biphenyl (<2%), as estimated by $^1$H NMR spectroscopy.

**Procedure for the One-Carbon Homologation Followed by Oxidation of 3a (Scheme 1).** Under Ar atmosphere, the boronate 3a (43.4 mg, 0.15 mmol), bromochloromethane (38.8 mg, 0.30 mmol, 2 equiv), and anhydrous THF (2 mL) were placed in a 10 mL glass tube containing a magnetic stirring bar. The tube was sealed with a screw cap with a Teflon-coated silicon rubber septum. After the mixture was cooled to –78 °C, nBuLi in hexane (1.6 M, 170 µL, 0.27 mmol, 1.8 equiv) was added. The mixture was stirred at –78 °C for 30 min, and stirred at room temperature for 3 h. The volatiles were evaporated under reduced pressure. An internal standard (1,1,2,2-tetrachloroethane) was added to the residue, and the yield of 1-methyl-2-(2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)cyclopropyl)-1H-benzo[d]imidazole was determined by $^1$H NMR (81% yield) in the crude mixture. The resulting product was used to the next reaction without further purification. The crude boronate, THF (0.5 mL), water (0.5 mL) and NaBO$_3$•4H$_2$O (55.8 mg, 0.36 mmol, 3 equiv) were placed in a round bottom flask containing a magnetic stirring bar, and the reaction mixture was stirred vigorously at room temperature for 3 h under air. The volatiles were evaporated under reduced pressure. The residue was suspended in CHCl$_3$, filtered through a pipette equipped with a cotton plug. The filtrate was concentrated under reduced pressure, and the crude mixture was then purified by silica gel chromatography (hexane/EtOAc 70:30) to give the alcohol 8 (19.1 mg, 0.099 mmol, 66% yield in two steps).

3. Preparation of Substrates
The starting material 1g is commercially available. The starting materials 1a, 7 1b, 8 1c, 9 1d, 10 1f, 11 1h, 12 1i, 13 1j, 14 1k, 15 and 1l 10 are reported in the literatures.

2-Cycloheptyl-1-methyl-1H-benzo[d]imidazole (1m)
The title compound (1m) was synthesized via the reaction of cycloheptylcarboxylic acid and o-phenylenediamine, followed by the methylation with MeI and NaH (92% yield).

![Structure](image)

Isolated by silica gel chromatography (CHCl$_3$/MeOH 98:2). White solids. **M.p.** 79.6–80.0 °C. $^1$H NMR (CDCl$_3$) $\delta$ 1.54–1.73 (m, 6H), 1.87–2.09 (m, 6H), 3.04 (sep, $J = 4.0$ Hz, 1H), 3.72 (s, 3H), 7.20–7.30 (m, 3H), 7.72–7.75 (m, 1H). $^{13}$C NMR (CDCl$_3$) $\delta$ 26.81 (2C), 27.96 (2C), 29.59, 33.20 (2C), 38.03, 108.77, 119.20, 121.58, 121.80, 135.60, 142.44, 160.12. **IR (ATR):** 2915, 2856, 1614,
4. Characterization of Products

2-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzo[d]thiazole (3a)

Isolated by Kugelrohr distillation [1 mmHg, 145 °C, 43.1 mg, 75% yield, contaminated with the diborylation product (<1%) and trace of impurities]. Colorless oil. $^1$H NMR (CDCl$_3$) δ 1.24 (s, 12H), 1.38 (t, $J = 7.6$ Hz, 2H), 3.24 (t, $J = 7.6$ Hz, 2H), 7.32 (td, $J = 8.4$, 1.2 Hz, 1H), 7.42 (td, $J = 7.6$, 0.8 Hz, 1H), 7.82 (d, $J = 8.0$ Hz, 1H), 7.94 (d, $J = 8.4$ Hz, 1H).

13C NMR (CDCl$_3$) δ 11.10 (br), 24.75 (4C), 28.85, 83.36 (2C), 121.42, 122.41, 124.42, 125.67, 135.19, 153.19, 173.81. $^{11}$B NMR (CDCl$_3$) δ 32.6. IR (ATR): 2976, 2931, 1519, 1436, 1370, 1313, 1142, 1082, 967, 845, 758 cm$^{-1}$. HRMS–ESI (m/z): [M+H]$^+$ Calcd for C$_{15}$H$_{21}$N$_2$, 229.1699; found, 229.1697.

2-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzo[d]oxazole (3b)

Isolated by Kugelrohr distillation [1 mmHg, 130 °C, 26.7 mg, 49% yield, contaminated with C(sp$^2$)–H borylation products (4.6 mg, 9% yield) and diborylation product (0.83 mg, 1% yield)]. Colorless oil. $^1$H NMR (CDCl$_3$) δ 1.24 (s, 12H), 1.36 (t, $J = 7.2$ Hz, 2H), 3.05 (t, $J = 7.2$ Hz, 2H), 7.26–7.28 (m, 2H), 7.44–7.47 (m, 1H), 7.64–7.66 (m, 1H). $^{13}$C NMR (CDCl$_3$) δ 23.24, 24.72 (4C), 83.40 (2C), 110.16, 119.46, 123.87, 124.20, 141.44, 150.86, 168.43. A signal for the carbon directly attached to the boron atom was not observed. $^{11}$B NMR (CDCl$_3$) δ 32.6. IR (ATR): 2977, 2932, 1615, 1571, 1456, 1358, 1316, 1241, 1141, 968, 849, 744 cm$^{-1}$. HRMS–EI (m/z): [M]$^+$ Calcd for C$_{15}$H$_{20}$O$_3$N$_{10}$B, 272.15725; found, 272.15662.

1-Methyl-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-1H-benzo[d]imidazole (3c)

Isolated by Kugelrohr distillation [1 mmHg, 160 °C, 30.8 mg, 54% yield, contaminated with the diborylation product (<1% yield)]. White solids. M.p. 111.3–112.2 °C. $^1$H NMR (CDCl$_3$) δ 1.23 (s, 12H), 1.38 (t, $J = 8.0$ Hz, 2H), 2.98 (t, $J = 8.0$ Hz, 2H), 3.72 (s, 3H), 7.19–7.24 (m, 2H), 7.25–7.29 (m, 1H), 7.67–7.71 (m, 1H). $^{13}$C NMR (CDCl$_3$) δ 8.97 (br), 21.87, 24.75 (4C), 29.59, 83.21 (2C), 108.68, 119.08, 121.45, 121.68, 135.93, 142.47, 156.62. $^{11}$B NMR (CDCl$_3$) δ 32.5. IR (ATR): 2976,
2902, 1615, 1512, 1406, 1379, 1142, 969, 749 cm$^{-1}$. **HRMS–EI** (m/z): [M]$^+$ Calcd for C$_{16}$H$_{24}$O$_2$N$_2^{10}$B, 286.19671; found, 286.19747.

**4,5-Dimethyl-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)thiazole (3g)**

Isolated by silica gel chromatography (hexane/EtOAc 80:20) (33.6 mg, 63% yield). Colorless oil.  
$^1$H NMR (CDCl$_3$) δ 1.21–1.26 (m, 14H), 2.26 (s, 3H), 2.29 (s, 3H), 3.00 (t, $J$ = 8.0 Hz, 2H).  
$^{13}$C NMR (CDCl$_3$) δ 11.21, 11.75 (br), 14.55, 24.75 (4C), 27.80, 83.22 (2C), 124.59, 147.01, 168.42.  
$^{11}$B NMR (CDCl$_3$) δ 32.7.  
IR (ATR): 2977, 2923, 1559, 1407, 1370, 1313, 1247, 1143, 967, 947, 672 cm$^{-1}$. **HRMS–EI** (m/z): [M]$^+$ Calcd for C$_{13}$H$_{22}$O$_2$N$_2^{10}$BS, 266.15006; found, 266.14926.

**2-(2,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzo[d]thiazole (4a)**

Isolated by Kugelrohr distillation [1 mmHg, 180 °C, 73.9 mg, 89% yield, contaminated with 3a (1.2 mg, 2% yield)]. Colorless oil.  
$^1$H NMR (CDCl$_3$) δ 1.21 (s, 12H), 1.24 (s, 12H), 1.44 (t, $J$ = 8.0 Hz, 1H), 3.37 (d, $J$ = 8.0 Hz, 2H), 7.30 (td, $J$ = 7.6, 1.2 Hz, 1H), 7.40 (td, $J$ = 7.6, 1.2 Hz, 1H), 7.80 (d, $J$ = 8.8 Hz, 1H), 7.91 (d, $J$ = 8.0 Hz, 1H).  
$^{13}$C NMR (CDCl$_3$) δ 10.48 (br), 24.48 (4C), 24.75 (4C), 30.36, 83.33 (4C), 121.33, 122.36, 124.22, 125.46, 135.36, 153.11, 173.89.  
IR (ATR): 2977, 2930, 1519, 1436, 1368, 1311, 1137, 968, 848, 758, 729 cm$^{-1}$. **HRMS–EI** (m/z): [M]$^+$ Calcd for C$_{21}$H$_{31}$O$_4$N$_2$$^{11}$B$_2$S, 415.21599; found, 415.21564.

**2-(1-Methyl-1H-benzo[d]imidazol-2-yl)propan-1-ol (5d)**

Isolated by silica gel chromatography (CHCl$_3$/MeOH/Et$_3$N 97:2:1) (22.2 mg, 0.117 mmol, 59% yield in two steps). Pale pink solids.  
**M.p.** 127.4–128.9 °C.  
$^1$H NMR (CDCl$_3$) δ 1.39 (d, $J$ = 7.2 Hz, 3H), 3.22–3.30 (m, 1H), 3.77 (s, 3H), 4.00–4.08 (m, 2H), 7.23–7.28 (m, 2H), 7.29–7.33 (m, 1H), 7.68–7.72 (m, 1H).  
$^{13}$C NMR (CDCl$_3$) δ 16.13, 29.68, 33.73, 65.56, 109.07, 119.14, 122.08, 122.31, 135.34, 141.99, 157.57.  
IR (ATR): 3129, 2972, 2832, 1615, 1507, 1472, 1315, 1239, 1075, 1047, 836, 741, 725 cm$^{-1}$. **HRMS–ESI** (m/z): [M+H]$^+$ Calcd for C$_{11}$H$_{15}$ON$_2$, 191.11789; found, 191.11802.
2-Methyl-2-(1-methyl-1\textit{H}-benzo[\textit{d}]imidazol-2-yl)propan-1-ol (5\text{e})

Isolated by silica gel chromatography (CHCl$_3$/MeOH/Et$_3$N 97:2:1) (27.6 mg, 0.135 mmol, 68% yield in two steps). White solids. \textbf{M.p.} 106.8–109.5 °C. $^1$\textit{H} NMR (CDCl$_3$) $\delta$ 1.47 (s, 6H), 3.85 (s, 2H), 3.90 (s, 3H), 5.18 (br, 1H), 7.24–7.33 (m, 3H), 7.67–7.69 (m, 1H). $^{13}$\textit{C} NMR (CDCl$_3$) $\delta$ 23.06 (2C), 31.75, 38.59, 72.61, 108.87, 119.19, 122.16, 122.46, 136.25, 141.02, 159.44. IR (ATR): 3142, 2921, 2823, 1724, 1612, 1452, 1325, 1289, 1070, 803, 744, 729 cm$^{-1}$. HRMS–ESI (m/z): [M+H]$^+$ Calcd for C$_{12}$H$_{17}$ON$_2$, 205.1335; found, 205.13358

Benzo[4,5]imidazo[1,2-\textit{a}]quinolin-6-ylmethanol (5\text{f})

Isolated by silica gel chromatography (CHCl$_3$/MeOH/Et$_3$N 97:2:1) (35.0 mg, 0.141 mmol, 71% yield in two steps). White solids. \textbf{M.p.} 206.7–207.3 °C. $^1$\textit{H} NMR (DMSO-\textit{d$_6$}) $\delta$ 4.97 (d, $J = 4.8$ Hz, 2H), 5.61 (dd, $J = 6.0$ Hz, 1H), 7.51–7.59 (m, 3H), 7.81 (t, $J = 7.6$ Hz, 1H), 7.94–7.96 (m, 2H), 8.09 (d, $J = 6.8$ Hz, 1H), 8.72 (d, $J = 7.6$ Hz, 1H), 8.80 (d, $J = 8.8$ Hz, 1H). $^{13}$\textit{C} NMR (DMSO-\textit{d$_6$}) $\delta$ 59.23, 115.11, 115.84, 120.36, 123.17, 123.45, 124.78, 124.96, 126.24, 129.40, 129.99, 131.00, 131.13, 134.37, 144.57, 146.71. IR (ATR): 3235, 2863, 1633, 1536, 1457, 1406, 1209, 1105, 1055, 759, 745 cm$^{-1}$. HRMS–ESI (m/z): [M+H]$^+$ Calcd for C$_{16}$H$_{12}$ON$_2$Na, 271.08418; found, 271.08402.

2-(1-Methyl-1\textit{H}-benzo[\textit{d}]imidazol-2-yl)-1-phenylethan-1-ol (5\text{h})

Isolated by silica gel chromatography (CHCl$_3$/MeOH/Et$_3$N 97:2:1) (34.8 mg, 0.138 mmol, 69% yield in two steps). White solids. $^1$\textit{H} NMR (CDCl$_3$) $\delta$ 3.12–3.21 (m, 2H), 3.59 (s, 3H), 5.38 (dd, $J = 8.0$, 4.4 Hz, 1H), 5.46 (br, 1H), 7.24–7.32 (m, 4H), 7.37 (t, $J = 7.2$ Hz, 2H), 7.45 (d, $J = 6.8$ Hz, 2H), 7.70–7.73 (m, 1H). $^{13}$\textit{C} NMR (CDCl$_3$) $\delta$ 29.53, 36.62, 71.46, 109.10, 119.09, 122.14, 122.38, 125.71 (2C), 127.66, 128.50 (2C), 135.20, 141.95, 143.24, 152.96.
1-(1-Methyl-1H-benzo[d]imidazol-2-yl)-3-phenylpropan-2-ol (5i)

Isolated by silica gel chromatography (CHCl₃/MeOH/Et₃N 97:2:1) (37.3 mg, 0.140 mmol, 70% yield in two steps). White solids. M.p. 128.3–131.9 °C. \(^1\)H NMR (CDCl₃) δ 2.87 (dd, \(J = 19.6, 13.6, 7.2\) Hz, 2H), 2.97 (dd, \(J = 16.0, 2.8\) Hz, 1H), 3.11 (dd, \(J = 14.0, 6.8\) Hz, 1H), 3.63 (s, 3H), 4.50–4.57 (m, 1H), 4.98 (br, 1H), 7.22–7.34 (m, 8H), 7.66–7.70 (m, 1H). \(^13\)C NMR (CDCl₃) δ 29.63, 32.84, 43.12, 70.34, 109.02, 119.04, 122.04, 122.26, 126.48, 128.52 (2C), 129.37 (2C), 135.20, 138.17, 141.98, 153.30. IR (ATR): 3575, 3140, 2988, 2901, 1614, 1475, 1447, 1395, 1243, 1078, 1049, 885, 699 cm\(^{-1}\). HRMS–ESI (m/z): [M+H]\(^+\) Calcd for C_{17}H_{19}ON₂, 267.14919; found, 267.14898.

1-(1-Methyl-1H-benzo[d]imidazol-2-yl)pentan-2-ol (5j)

Isolated by silica gel chromatography (CHCl₃/MeOH/Et₃N 97:2:1) (32.3 mg, 0.148 mmol, 74% yield in two steps). White solids. M.p. 125.1–126.8 °C. \(^1\)H NMR (CDCl₃) δ 0.98 (t, \(J = 6.8\) Hz, 3H), 1.43–1.62 (m, 3H), 1.63–1.76 (m, 1H), 2.83 (dd, \(J = 16.0, 9.6\) Hz, 1H), 2.96 (dd, \(J = 16.0, 2.8\) Hz, 1H), 3.70 (s, 3H), 4.26–4.32 (m, 1H), 4.88 (br, 1H), 7.22–7.31 (m, 3H), 7.67–7.70 (m, 1H). \(^13\)C NMR (CDCl₃) δ 14.05, 18.92, 29.61, 34.06, 38.97, 68.72, 108.98, 119.00, 121.98, 122.20, 135.22, 141.99, 153.62. IR (ATR): 3675, 3084, 2958, 2901, 1475, 1448, 1394, 1242, 1065, 1056, 741 cm\(^{-1}\). HRMS–ESI (m/z): [M+H]\(^+\) Calcd for C_{13}H_{19}ON₂, 219.14919; found, 219.14918.

cis-2-(1-Methyl-1H-benzo[d]imidazol-2-yl)cyclopentan-1-ol (5k)

Isolated by silica gel chromatography (CHCl₃/MeOH/Et₃N 97:2:1) (29.2 mg, 0.135 mmol, 67% yield in two steps). White solids. M.p. 114.0–116.9 °C. \(^1\)H NMR (CDCl₃) δ 1.79–1.91 (m, 2H), 1.98–2.08 (m, 2H), 2.10–2.21 (m, 2H), 3.10 (ddd, \(J = 11.2, 7.6, 3.6\) Hz, 1H), 3.76 (s, 3H), 4.65 (t, \(J = 4.0\) Hz, 1H), 6.21 (br, 1H), 7.24–7.30 (m, 2H), 7.31–7.34 (m, 1H), 7.68–7.71 (m, 1H). \(^13\)C NMR (CDCl₃) δ 22.62, 28.92, 29.70, 33.89, 41.98, 74.69, 108.97, 119.15, 122.18, 122.36, 134.97, 141.58, 156.35. IR (ATR): 3277, 2919, 2870, 1727, 1615, 1501, 1471, 1443, 1399, 1322, 1236, 1088, 1005, 734 cm\(^{-1}\). HRMS–ESI (m/z): [M+H]\(^+\) Calcd for C_{13}H_{17}ON₂, 217.13354; found, 217.13354. In the
NOESY NMR analysis, a strong correlation peak between the proton at the position $\alpha$ to the alcohol group (4.65 ppm) and the proton at the position $\alpha$ to theazole group (3.10 ppm) is assignable to cis configuration for 5k.

**trans-2-(1-Methyl-1H-benzo[d]imidazol-2-yl)cyclopentan-1-ol (5k')**

Isolated by silica gel chromatography (CHCl$_3$/MeOH/Et$_3$N 97:2:1) [6.9 mg, 0.032 mmol, 16% yield in two steps, contaminated with a phenol derivative derived from the corresponding arylboronate (0.53 mg, 1% yield)]. White solids. **M.p.** 166.2–168.9 °C. $^1$H NMR (CDCl$_3$) $\delta$ 1.69–1.97 (m, 4H), 2.17–2.29 (m, 2H), 3.19 (q, $J = 8.4$ Hz, 1H), 3.33 (br, 1H), 3.68 (s, 3H), 4.81 (q, $J = 7.2$ Hz, 1H), 7.19–7.23 (m, 3H), 7.67–7.72 (m, 1H). $^{13}$C NMR (CDCl$_3$) $\delta$ 21.71, 29.53, 29.73, 33.61, 45.73, 77.20, 108.92, 118.96, 121.80, 122.04, 135.80, 142.13, 156.79. IR (ATR): 3201, 2963, 1613, 1504, 1476, 1444, 1413, 1283, 1100, 768 cm$^{-1}$. HRMS–ESI ($m/z$): [M+H]$^+$ Calcd for C$_{13}$H$_{17}$O$_2$, 217.1335; found, 217.1339. In the NOESY NMR analysis, no correlation peak between the proton at the position $\alpha$ to the alcohol group (4.81 ppm) and the proton at the position $\alpha$ to the azole group (3.19 ppm) is assignable to trans configuration for 5k'.

**trans-2-(1-Methyl-1H-benzo[d]imidazol-2-yl)cyclohexan-1-ol (5l)**

Isolated by silica gel chromatography (CHCl$_3$/MeOH/Et$_3$N 98:1:1) [25.5 mg, 0.111 mmol, 55% yield in two steps, contaminated with a phenol derivative derived from the corresponding arylboronate (2.1 mg, 5% yield)]. White solids. **M.p.** 211.6–212.8 °C. $^1$H NMR (CDCl$_3$) $\delta$ 1.34–1.52 (m, 3H), 1.61 (qd, $J = 12.8$, 3.6 Hz 1H), 1.81–1.91 (m, 2H), 1.98–2.03 (m, 1H), 2.16–2.21 (m, 1H), 2.83 (ddd, $J = 12.0$, 9.2, 4.0 Hz, 1H), 3.15 (br, 1H), 3.76 (s, 3H), 4.28 (td, $J = 10.0$, 4.0 Hz, 1H), 7.22–7.33 (m, 3H), 7.69–7.73 (m, 1H). $^{13}$C NMR (CDCl$_3$) $\delta$ 24.70, 25.60, 29.78, 30.73, 33.74, 44.96, 72.08, 109.07, 119.13, 121.99, 122.19, 135.69, 142.24, 156.65. IR (ATR): 3197, 2924, 2852, 1598, 1471, 1447, 1275, 1071, 978, 785, 758, 736 cm$^{-1}$. HRMS–ESI ($m/z$): [M+H]$^+$ Calced for C$_{14}$H$_{19}$O$_2$, 231.14919; found, 231.14912. The $^1$H NMR resonance for the proton at the position $\alpha$ to the alcohol group (4.28 ppm) is a triplet of doublets ($J = 10.0$, 4.0 Hz), The coupling constant is assignable to trans configuration for 5l. In the NOESY NMR analysis, no correlation peak between the proton at the position $\alpha$ to the alcohol group (4.28 ppm) and the proton at the position $\alpha$ to the azole group (2.83 ppm) is also indicative of trans configuration for 5l.
trans-2-(1-Methyl-1H-benzo[d]imidazol-2-yl)cycloheptan-1-ol (5m)

Isolated by silica gel chromatography (CHCl₃/MeOH/Et₃N 98:1:1) [21.1 mg, 0.086 mmol, 43% yield in two steps, contaminated with a phenol derivative derived from the corresponding arylboronate (0.98 mg, 2% yield)]. Pale pink solids. M.p. 164.8–165.2 °C. ¹H NMR (CDCl₃) δ 1.62–1.90 (m, 9H), 2.15 (ddd, J = 12.8, 7.2, 4.0 Hz, 1H), 3.03 (td, J = 9.2, 2.8 Hz, 1H), 3.41 (br, 1H), 3.73 (s, 3H), 4.44 (td, J = 8.8, 3.6 Hz, 1H), 7.21–7.32 (m, 3H), 7.68–7.74 (m, 1H). ¹³C NMR (CDCl₃) δ 22.28, 26.41, 27.13, 29.69, 29.87, 35.88, 46.07, 74.39, 109.06, 119.08, 121.91, 122.13, 135.50, 142.15, 158.33. IR (ATR): 3300, 2922, 2856, 1612, 1496, 1467, 1436, 1317, 1052, 937, 769, 754 cm⁻¹. HRMS–ESI (m/z): [M+H]⁺ Calcd for C₁₅H₂₁ON₂, 245.16484; found, 245.16474.

N-(2-(Benzo[d]thiazol-2-yl)ethyl)-N-methylaniline (6)

Isolated by silica gel chromatography (EtOAc/hexane 70:30) (32.2 mg, 0.120 mmol, 80% yield). Pale yellow oil. ¹H NMR (CDCl₃) δ 2.97 (s, 3H), 3.36 (t, J = 8.0 Hz, 2H), 3.88 (t, J = 8.0 Hz, 2H), 6.75 (t, J = 7.2 Hz, 1H), 6.80 (d, J = 8.0 Hz, 2H), 7.24–7.28 (m, 2H), 7.36 (td, J = 8.4, 1.2 Hz, 1H), 7.47 (td, J = 8.4, 0.8 Hz, 1H), 7.84 (d, J = 7.6 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H). ¹³C NMR (CDCl₃) δ 31.34, 38.55, 52.44, 112.61 (2C), 116.92, 121.52, 122.60, 124.82, 126.01, 129.34 (2C), 135.27, 148.54, 153.32, 168.93. IR (ATR): 3059, 2902, 1912, 1597, 1503, 1434, 1353, 1193, 990, 745, 728 cm⁻¹. HRMS–ESI (m/z): [M+H]⁺ Calcd for C₁₆H₁₇N₂S, 269.11070; found, 269.11052.

2-(4-Methoxyphenethyl)benzo[d]thiazole (7)

Isolated by silica gel chromatography (EtOAc/hexane 70:30) [25.4 mg, 0.094 mmol, 63% yield, contaminated with 4,4'-dimethoxy-1,1'-biphenyl (<2%)]. White solids. M.p. 88.8–89.7 °C. ¹H
NMR (CDCl₃) δ 3.15 (t, J = 8.4 Hz, 2H), 3.40 (t, J = 8.0 Hz, 2H), 3.79 (s, 3H), 6.84 (d, J = 6.4 Hz, 2H), 7.17 (d, J = 6.4 Hz, 2H), 7.35 (td, J = 8.4, 0.8 Hz, 1H), 7.46 (td, J = 8.4, 1.6 Hz, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 7.6 Hz, 1H). ¹³C NMR (CDCl₃) δ 34.70, 36.28, 55.23, 113.95 (2C), 121.50, 122.55, 124.71, 125.90, 129.37 (2C), 132.22, 135.12, 153.18, 158.16, 171.04. IR (ATR): 3053, 2997, 2835, 1608, 1582, 1508, 1432, 1243, 1180, 1034, 822, 756 cm⁻¹. HRMS–ESI (m/z): [M+H]⁺ Calcd for C₁₆H₁₆ONS 270.09471; found, 270.09458.

3-(benzo[d]thiazol-2-yl)propan-1-ol (8)

![Chemical Structure](image)

Isolated by silica gel chromatography (EtOAc/hexane 70:30) (19.1 mg, 0.099 mmol, 66% yield in two steps). Pale yellow oil. ¹H NMR (CDCl₃) δ 2.15 (quin, J = 6.8 Hz, 2H), 2.76 (br, 1H), 3.27 (t, J = 7.6 Hz, 2H), 7.36 (td, J = 6.8, 1.2 Hz, 1H), 7.46 (td, J = 8.4, 1.2 Hz, 1H), 7.84 (d, J = 7.6 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H). ¹³C NMR (CDCl₃) δ 31.08, 31.61, 61.79, 121.50, 122.46, 124.84, 126.01, 135.06, 153.00, 171.66. IR (ATR): 3324, 2926, 1515, 1436, 1244, 1052, 756, 728 cm⁻¹. HRMS–ESI (m/z): [M+H]⁺ Calcd for C₁₀H₁₂ONS, 194.06341; found, 194.06369.

5. References


diborylation product
impurities

3a

S38
diborylation product

C(sp²)–H borylation products

3b

Bpin
diborylation product
monoborylation product
Me
 Me
 Me
 OH

S51
$\text{X: parts per Million: Carbon}^{13}$
phenol derivative