General Information

Chemicals were either purchased or purified by standard techniques without special instructions. All solvents were distilled prior to use. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. $^1$H NMR (300 MHz) and $^{13}$C NMR (75 MHz) were registered on Varian 300 M spectrometers; $^1$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) were registered on Bruker ARX 400 M spectrometer, all with CDCl$_3$ as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the $^1$H spectrum as 0.00 ppm and CDCl$_3$ resonance in the $^{13}$C spectrum as 77.0 ppm. All coupling constants ($J$ values) were reported in Hertz (Hz). HRMS were performed by Analytical Center of Peking University. IR spectra were recorded with a Nicolet 5MX-S infrared spectrometer. Fe$_2$O$_3$ magnetic nanoparticles (NanoArc®) was purchased from Alfa Aesar®.
Experimental Section

(1) Procedure for nano-Fe$_2$O$_3$-catalyzed ortho-borylation arene with B$_2$pin$_2$

A reflux tube equipped with a magnetic stir bar was charged with B$_2$pin$_2$ (254 mg, 1 mmol), K$_2$CO$_3$ (276 mg, 2 mmol), tBuOOtBu (292 mg, 2 mmol), Fe$_2$O$_3$ magnetic nanoparticles (NanoArc®, Alfa Aesar®) (32 mg, 0.2 mmol) and aryl substrate (5 mL). The reaction vessel was placed in an oil bath (80 °C) under open air. The reaction progress was monitored by GC-MS. The mixture was cooled to room temperature when B$_2$pin$_2$ disappeared completely, Yield and ratio was determined by GC using mesitylene or dodecane as the internal standard. After completion of borylation reaction, the mixture was first purified by a short silica gel column chromatography to removed iron catalyst and inorganic base. The solvent was evaporated in vacuo, and the residue was purified by flash column chromatography on silica gel (eluting with ethyl acetate/petroleum ether) to give pure product.

A large scale experiment: Benzene (20 mL) and B$_2$pin$_2$ (1 g, 4 mmol) were subjected to the above reaction conditions. PhBpin was isolated in 52% yield after column chromatography

(2) Procedure for Sequential Reactions

A reflux tube equipped with a magnetic stir bar was charged with B$_2$pin$_2$ (254 mg, 1 mmol), K$_2$CO$_3$ (276 mg, 2 mmol), tBuOOtBu (292 mg, 2 mmol), Fe$_2$O$_3$ magnetic nanoparticles (32 mg, 0.2 mmol) and benzene (5 mL). The reaction vessel was placed in oil bath (80 °C) under air. The solution was cooled to room temperature until B$_2$pin$_2$ was disappeared. The reaction progress was monitored and analyzed by GC-MS. After the completion of the borylation reaction, benzene was evaporated under reduced pressure. To this mixture were added aryl iodide(1 mmol), PdCl$_2$(dppf) (0.030 mmol), K$_3$PO$_4$(3 mmol), and DMF (5 mL), and the mixture was stirred at 60 °C under N$_2$. After the completion of the cross-coupling reaction, the mixture was extracted with EtOAc, washed with brine, and dried over MgSO$_4$. The residue was purified by flash column chromatography on a silica gel (eluting with ethyl acetate/petroleum ether) to give the product.

(3) Procedure for Nano Fe$_2$O$_3$ Catalyst preparation

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γ-Fe₂O₃ (20 nm) catalyst was prepared by co-precipitation of aqueous solutions of FeSO₄·7H₂O and FeCl₃·6H₂O by urea hydrolysis (All from Beijing Chemicals, AR grade). The cation (Fe²⁺ + Fe³⁺) concentration was kept at 0.60 M with [Fe²⁺]/[Fe³⁺] ratio of 1/2 and the urea concentration was kept at 6.0 M. The mixed solution was heated to 100 °C under N₂ atmosphere and maintained at 100 °C for 3 h to form precipitates. After filtration and thoroughly washing with deionized water until the filtrate was neutral, the precipitates were treated in ambient air at 110 °C overnight, and then at 300 °C for 3 h. A mixed crystal Fe₂O₃ (9 nm) with α and γ phases was obtained when the concentrations of the cation (Fe²⁺ + Fe³⁺) and urea improved to 1.20 M and 12.0 M respectively.

α-Fe₂O₃ catalysts were prepared in a similar way, in which Fe(NO₃)₃·9H₂O was used as the Fe³⁺ precursor salt instead of FeCl₃·6H₂O. The average crystallite size of α-Fe₂O₃ decreased from 18 nm to 14 nm by doubling the solution concentration as described above.

The crystalline phase of the catalysts was identified by X-ray diffraction (Rigaku D/MAX-2400 diffractometer) and the crystallite size of Fe₂O₃ was calculated by Scherrer equation, \( d = \frac{0.90 \lambda}{\beta \cos \theta} \), where \( \theta \) is the diffraction angle and \( \beta \) is the full width at half-maximum.

The X-ray diffraction patterns of Fe₂O₃ catalysts (the crystallite size of the commercial γ-Fe₂O₃ was 58 nm)

References

X-Ray Diffraction of Fe$_2$O$_3$ Catalysts
Spectral data for the products

4,4,5,5-Tetramethyl-2-phenyl-1,3,2-dioxaborolane
Colorless liquid
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.81 (d, $J$ = 6.7 Hz, 2H), 7.47–7.43 (m, 1H), 7.38–7.35 (m, 2H), 1.34 (s, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 131.7, 131.2, 127.7, 83.7, 24.8.

4,4,5,5-Tetramethyl-2-o-tolyl-1,3,2-dioxaborolane
Colorless liquid
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.77 (d, $J$ = 1.4 Hz, 1H), 7.33–7.29 (m, 1H), 7.16–7.14 (m, 2H), 2.54 (s, 3H), 1.34 (s, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 144.8, 135.8, 130.8, 129.7, 124.7, 83.4, 24.9, 22.2.

4,4,5,5-Tetramethyl-2-m-tolyl-1,3,2-dioxaborolane
White solid
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.64–7.60 (m, 2H), 7.28–7.26 (m, 2H), 2.35 (s, 3H), 1.34 (s, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 137.1, 135.3, 132.0, 131.8, 127.7, 83.7, 24.8, 21.2.

4,4,5,5-Tetramethyl-2-p-tolyl-1,3,2-dioxaborolane
White solid
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.70 (d, $J$ = 7.5 Hz, 2H), 7.18 (d, $J$ = 7.5 Hz, 2H), 2.36 (s, 3H), 1.33 (s, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 141.4, 134.8, 128.5, 83.6, 24.8, 21.7.

2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
Colorless liquid
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.76 (d, $J$ = 1.8 Hz, 2H), 6.89 (q, $J$ = 1.8 Hz, 2H), 3.82 (s, 3H), 1.33 (s, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.1, 136.5, 113.3, 83.5, 55.0, 24.8.

2-(3-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
Colorless liquid
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40 (d, $J$ = 11.2 Hz, 1H), 7.33–7.28 (m, 2H), 7.02–6.99 (m, 1H), 3.83 (s, 3H), 1.34 (s, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.0, 128.9, 127.1, 118.6, 117.9, 83.8, 55.2, 24.8.
2-(2-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
White solid
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.69–7.66 (m, 1H), 7.41–7.37 (m, 1H), 6.94 (t, $J$ = 7.4 Hz, 1H), 6.85 (d, $J$ = 8.3 Hz, 1H), 3.83 (s, 3H), 1.35 (s, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.1, 136.7, 132.4, 120.2, 110.4, 83.4, 55.8, 24.8.

4,4,5,5-Tetramethyl-2-(2,5-dimethylphenyl)-1,3,2-dioxaborolane
White solid
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.57 (s, 1H), 7.13–7.11 (m, 1H), 7.05 (d, $J$ = 7.7 Hz, 1H), 2.49 (s, 3H), 2.30 (s, 3H), 1.33 (s, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 141.7, 136.3, 133.9, 131.5, 129.8, 83.3, 24.9, 21.7, 20.8.

4,4,5,5-Tetramethyl-2-(2,3-dimethylphenyl)-1,3,2-dioxaborolane
White solid
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.60 (d, $J$ = 7.4 Hz, 1H), 7.20 (d, $J$ = 7.4 Hz, 1H), 7.08 (t, $J$ = 7.4 Hz, 1H), 2.47 (s, 3H), 2.26 (s, 3H), 1.34 (s, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 143.0, 136.4, 133.5, 132.3, 124.8, 83.4, 24.8, 20.4, 18.4; IR (film): 2978, 1429, 1379, 1346, 1304, 1138, 1034, 827, 785, 728, 669 cm$^{-1}$; EI-MS ($m/z$, relative intensity): 232 (M$^+$, 38), 217 (20), 175 (100), 159 (5), 146 (16), 132 (98), 117 (27), 105 (27), 91 (28), 77 (14), 41(44); HRMS calcd for C$_{14}$H$_{22}$BO$_2$ [M+H]$^+$ 233.1707, found 233.1706.

4,4,5,5-Tetramethyl-2-(3,4-dimethylphenyl)-1,3,2-dioxaborolane
White solid
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.58 (s, 1H), 7.5 (d, $J$ = 7.4 Hz, 1H), 7.14 (d, $J$ = 7.4 Hz, 1H), 2.27 (s, 3H), 2.26 (s, 3H), 1.33 (s, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 140.1, 135.9, 135.8, 132.4, 129.1, 83.5, 24.8, 20.0, 19.4.

4,4,5,5-Tetramethyl-2-(2,4-dimethylphenyl)-1,3,2-dioxaborolane
Colorless liquid
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.66 (d, $J$ = 8.1 Hz, 1H), 6.98 (d, $J$ = 7.0 Hz, 1H), 2.50 (s, 3H), 2.30 (s, 3H), 1.34 (s, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 144.9, 140.8, 136.1, 130.7, 125.5, 83.2, 24.9, 22.1, 21.5; IR (film): 2978, 1612, 1371, 1346, 1311, 1146, 1063, 963, 860, 659 cm$^{-1}$; EI-MS ($m/z$, relative intensity): 232 (M$^+$, 29), 217 (26), 175 (73), 159 (6), 146 (18), 132 (100), 117 (21), 105 (25), 91 (28), 77 (14), 41 (40); HRMS calcd for C$_{14}$H$_{22}$BO$_2$ [M+H]$^+$ 233.1707, found 233.1705.
4,4,5,5-Tetramethyl-2-(2,6-dimethylphenyl)-1,3,2-dioxaborolane
White solid
{\( ^1 \text{H} \text{ NMR} (400 \text{ MHz, CDCl}_3) \ \delta: 7.12 (t, J = 7.6 \text{ Hz, 1H}), 6.94 (d, J = 7.6 \text{ Hz, 2H}), 2.39 (s, 6H), 1.34 (s, 12H); ^{13} \text{C} \text{ NMR} (100 \text{ MHz, CDCl}_3) \ \delta: 141.7, 129.1, 126.4, 83.6, 24.9, 22.2.}\)

4,4,5,5-Tetramethyl-2-(3,5-dimethylphenyl)-1,3,2-dioxaborolane
White solid
{\( ^1 \text{H} \text{ NMR} (400 \text{ MHz, CDCl}_3) \ \delta: 7.44 (s, 2H), 7.10 (s, 1H), 2.32 (s, 6H), 1.34 (s, 12H); ^{13} \text{C} \text{ NMR} (100 \text{ MHz, CDCl}_3) \ \delta: 137.1, 133.0, 132.4, 83.7, 24.8, 21.1.\)

2-(2,5-Dimethoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
White solid, mp 58-60 °C.
{\( ^1 \text{H} \text{ NMR} (400 \text{ MHz, CDCl}_3) \ \delta: 7.21 (d, J = 3.3 \text{ Hz, 1H}), 6.93 (q, J = 3.3 \text{ Hz, 2H}), 2.78 (s, 6H), 1.35 (s, 12H); ^{13} \text{C} \text{ NMR} (100 \text{ MHz, CDCl}_3) \ \delta: 158.6, 153.3, 121.0, 118.0, 112.3, 83.5, 56.8, 55.8, 24.8; \text{IR (film): 2978, 1585, 1494, 1408, 1344, 1220,1139, 1066, 1048, 965, 90, 855, 812,727,672 cm}^{-1}; \text{EI-MS (m/z, relative intensity): 264 (M^+, 100), 249 (18), 191 (24), 164 (56), 149 (32), 135 (18), 121 (46), 105 (4), 91 (6), 77 (14), 41 (29); HRMS calcd for C_{14}H_{22}BO_4 [M+H]^+ 265.1606, found 265.1605.\)

2-Mesityl-4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane
White solid
{\( ^1 \text{H} \text{ NMR} (400 \text{ MHz, CDCl}_3) \ \delta: 6.76 (s, 2H), 2.36 (s, 6H), 2.23 (s, 3H), 1.36 (s, 12H); ^{13} \text{C} \text{ NMR} (100 \text{ MHz, CDCl}_3) \ \delta: 142.1, 138.9, 127.4, 83.4, 24.9, 22.1, 21.2.\)

2-(2,4,6-Trimethoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
White solid, mp 114-116 °C.
{\( ^1 \text{H} \text{ NMR} (400 \text{ MHz, CDCl}_3) \ \delta: 6.04 (s, 2H), 3.79 (s, 3H), 3.74 (s, 6H), 1.36 (s, 12H); ^{13} \text{C} \text{ NMR} (100 \text{ MHz, CDCl}_3) \ \delta: 164.5, 163.1, 90.2, 83.4, 55.6, 55.2, 24.6; \text{IR (film): 2996, 1607, 1581, 1457, 1356, 1327, 1295, 1221, 1204, 1124, 1037, 864, 804, 733; EI-MS (m/z, relative intensity): 294 (M^+, 100), 279 (16), 236 (42), 221 (52), 194 (69), 151 (40), 135 (56), 121 (59), 105 (10), 91 (20), 77 (24), 41 (44); HRMS calcd for C_{15}H_{24}BO_5 [M+H]^+ 295.1711, found 295.1708.\)
4-Nitro-biphenyl
\[ ^1\text{H NMR (300 MHz, CDCl}_3 \] \( \delta \) 8.31 (d, \( J = 9.0 \text{ Hz, 2H} \)), 7.76–7.65 (m, 2H), 7.24–7.20 (m, 2H), 7.45–7.53 (m, 3H); \( ^{13}\text{C NMR (75 MHz, CDCl}_3 \] \( \delta \) 147.6, 147.1, 138.8, 129.1, 128.9, 127.8, 127.4, 124.1.

4-Methoxy-biphenyl
\[ ^1\text{H NMR (300 MHz, CDCl}_3 \] \( \delta \) 7.57–7.52 (m, 4H), 7.44–7.39 (m, 2H), 7.33–7.28 (m, 1H), 6.98 (d, \( J = 8.7 \text{ Hz, 2H} \)), 3.85 (s, 3H); \( ^{13}\text{C NMR (75 MHz, CDCl}_3 \] \( \delta \) 159.2, 140.8, 133.8, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3.

4-Chloro-biphenyl
\[ ^1\text{H NMR (300 MHz, CDCl}_3 \] \( \delta \) 7.56–7.50 (m, 3H), 7.48–7.36 (m, 6H); \( ^{13}\text{C NMR (75 MHz, CDCl}_3 \] \( \delta \) 140.0, 139.7, 133.4, 129.0, 128.9, 128.4, 128.2, 127.0.

4-Acetyl-biphenyl
\[ ^1\text{H NMR (300 MHz, CDCl}_3 \] \( \delta \) 8.04 (q, \( J = 1.5 \text{ Hz, 2H} \)), 7.70–7.62 (m, 4H), 7.50–7.40 (m, 3H), 2.64 (s, 3H); \( ^{13}\text{C NMR (75 MHz, CDCl}_3 \] \( \delta \) 197.7, 145.7, 139.8, 135.8, 128.9, 128.8, 128.2, 127.2, 127.1, 26.6.

Biphenyl
\[ ^1\text{H NMR (300 MHz, CDCl}_3 \] \( \delta \) 7.60 (d, \( J = 7.5 \text{ Hz, 4H} \)), 7.47–7.37 (m, 4H), 7.35–7.32 (m, 2H); \( ^{13}\text{C NMR (75 MHz, CDCl}_3 \] \( \delta \) 141.2, 128.7, 127.2, 127.1.
$^1$H and $^{13}$C NMR spectra
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