B(C₆F₅)₃-catalyzed methylation of amines using CO₂ as a C₁ building block

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1. General experimental methods

Materials
All reagents and solvents were purchased from commercial sources (J&K®, Beijing InnoChem Science & Technology Co., Sigma-Aldrich®) and were used without further purification, unless indicated otherwise.

Instrumentation
Liquid NMR spectra was recorded on Bruck 400 spectrometer using CDCl₃ as solvent. The composition of the reaction mixture was analyzed by means of GC (Agilent 4890D) with a FID detector and a nonpolar capillary column (DB-5) (30 m × 0.25 mm × 0.25 μm). The column oven was temperature-programmed with a 2 min initial hold at 323 K, followed by the temperature increase to 538 K at a rate of 20 K/min and kept at 538 K for 10 min. High purity nitrogen was used as a carrier gas.

2. Typical procedures for the methylation reaction of N-methylaniline catalyzed by B(C₆F₅)₃ in the presence of CO₂ and PhSi₃H

To a stainless steel autoclave (25 mL inner volume), B(C₆F₅)₃ (5 mol%), CH₃CN 2 mL, PhSiH₃ (1 mmol) and N-methylaniline (0.5 mmol) were added successively. CO₂ was then charged into the reactor up to a desired pressure (e.g., 0.5 MPa) at room temperature. The autoclave was heated at 140 °C for 24 h. After reaction, the autoclave was cooled to room temperature, and then CO₂ was vented. The product yields were determined by GC with a flame ionization detector and were further identified using GC-MS by comparing retention times and fragmentation patterns with authentic samples. The products were also isolated by column chromatography on silica gel (eluent: petroleum ether and dichloromethane) and identified by NMR spectra for substrate scope screening.
3. Characterization (NMR) of the methylamine products and byproducts

\[
\begin{align*}
\text{H NMR (CDCl}_3, 400 \text{ MHz) } & \delta \ 3.19 \text{ (s, 6H), 6.80 (d, } J = 7.6 \text{ Hz, 4H), 6.93 (t, } J = 7.2 \text{ Hz, 2H),} \\
& \ 7.04 \text{ (t, } J = 7.6 \text{ Hz, 4H); } \text{C NMR (CDCl}_3, 100.6 \text{ MHz) } \delta \ 39.29, 124.76, 125.67, 128.58, 145.63, 161.26.
\end{align*}
\]
$^{13}$C NMR (CDCl$_3$, 100.6 MHz) δ 32.02, 122.36, 126.37, 129.59, 142.19, 162.30.

$^1$H NMR (CDCl$_3$, 400 MHz) δ 3.32 (s, 3H), 7.16-7.18 (m, 2H), 7.26-7.29 (m, 1H), 7.39-7.43 (m, 2H), 8.48 (s, 1H); $^{13}$C NMR (CDCl$_3$, 100.6 MHz) δ 32.02, 122.36, 126.37, 129.59, 142.19, 162.30.
^1^H NMR (CDCl$_3$, 400 MHz) $\delta$ 2.93 (s, 6H), 6.70-6.75 (m, 3H), 7.24 (t, $^2J = 8.4$ Hz, 2H); $^{13}$C NMR (CDCl$_3$, 100.6 MHz) $\delta$ 40.59, 112.66, 116.63, 129.04, 150.65.
\(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 2.36 (s, 3H), 2.73 (s, 6H), 6.97 (t, \(J = 7.2\) Hz, 1H), 7.06 (t, \(J = 8\) Hz, 1H), 7.18 (t, \(J = 7.2\) Hz, 2H); \(^{13}\)C NMR (CDCl\(_3\), 100.6 MHz) \(\delta\) 18.33, 44.21, 118.34, 122.52, 126.40, 131.12, 132.10, 152.75.
$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 2.36 (s, 3H), 2.97 (s, 6H), 6.59-6.61 (m, 3H), 7.17 (t, $^3J =$ 7.6 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100.6 MHz) $\delta$ 21.85, 40.65, 109.93, 113.47, 117.63, 128.89, 138.66, 150.77.
$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 2.28 (s, 3H), 2.92 (s, 6H), 6.72 (d, $^3J = 8.8$ Hz, 2H), 7.08 (d, $^3J = 8.4$ Hz, 2H); $^{13}$C NMR (CDCl$_3$, 100.6 MHz) $\delta$ 20.21, 41.05, 113.21, 126.11, 129.56, 148.82.
\[^1\text{H NMR (CDCl}_3, 400 \text{ MHz)} \delta 2.88 (s, 6H), 3.78 (s, 3H), 6.76-6.79 (m, 2H), 6.85-6.87 (m, 2H);\]

\[^1\text{C NMR (CDCl}_3, 100.6 \text{ MHz)}\]

\[^1\text{H NMR (CDCl}_3, 400 \text{ MHz)} \delta 2.88 (s, 6H), 3.78 (s, 3H), 6.76-6.79 (m, 2H), 6.85-6.87 (m, 2H);\]
\[ ^{13}C \text{NMR (CDCl}_3, 100.6 \text{ MHz)} \delta 41.81, 55.71, 114.58, 114.90, 145.69, 151.98. \]

\[ ^{1}H \text{NMR (CDCl}_3, 400 \text{ MHz)} \delta 2.90 \text{ (s, 6H), 6.67-6.70 (m, 2H), 6.93-6.97 (m, 2H); } ^{13}C \text{NMR} \]
(CDCl₃, 100.6 MHz) δ 41.37, 113.8 (d, ³J = 7.3 Hz), 115.36 (d, ³J = 22.0 Hz), 147.52, 154.47, 156.81.
\[^1\text{H NMR (CDCl}_3, 400 \text{ MHz)} \delta 2.92 (s, 3H), 6.59 (d, ^3\text{J} = 8.8 \text{ Hz, 2H}), 7.28 (d, ^3\text{J} = 9.2 \text{ Hz, 2H}); \]

\[^{13}\text{C NMR (CDCl}_3, 100.6 \text{ MHz)} \delta 40.55, 108.53, 114.11, 131.67, 149.53.\]
$^1$H NMR (CDCl$_3$, 400 MHz) δ 2.93 (s, 6H), 6.64 (d, 3J = 8.8 Hz, 2H), 7.17 (d, 3J = 9.2 Hz, 2H);

$^{13}$C NMR (CDCl$_3$, 100.6 MHz) δ 40.64, 113.64, 121.44, 128.78, 149.19.

$^1$H NMR (CDCl$_3$, 400 MHz) δ 2.81 (s, 1H), 6.91-6.95 (m, 1H), 7.05-7.07 (m, 1H), 7.13-7.24 (m,
1H), 7.33-7.35 (m, 1H); $^{13}$C NMR (CDCl$_3$, 100.6 MHz) δ 43.72, 119.96, 123.15, 127.36, 130.62, 144.94, 150.36.
$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 2.95 (s, 1H), 6.58-6.60 (m, 1H), 6.67-6.69 (m, 2H), 7.14 (t, $^3J = 8.4$ Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100.6 MHz) $\delta$ 40.34, 110.44, 112.17, 116.14, 129.91, 134.94, 151.47.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 1.14 (t, $^3J = 7.2$ Hz, 3H), 2.92 (s, 3H), 3.39-3.44 (m, 2H), 6.69-6.76
(m, 3H), 7.25 (t, $^3J = 7.2$ Hz, 2H); $^{13}$C NMR (CDCl$_3$, 100.6 MHz) δ 14.09, 37.45, 46.85, 112.48, 116.11, 129.14, 149.11.
$^1$H NMR (CDCl$_3$, 400 MHz) δ 2.27 (s, 6H), 3.45 (s, 2H), 7.29-7.35 (m, 5H); $^{13}$C NMR (CDCl$_3$, 100.6 MHz) δ 45.31, 64.36, 126.98, 128.17, 129.05, 138.80.

$^1$H NMR (CDCl$_3$, 400 MHz) δ 3.33 (s, 3H), 6.97 (t, $^3J = 7.6$ Hz, 2H), 7.04 (d, $^3J = 8$ Hz, 4H), 7.29
(t, 3J = 8 Hz, 4H); $^1$H NMR (CDCl$_3$, 400 MHz) δ 4.02, 4.06, 4.09, 4.11.

$^{13}$C NMR (CDCl$_3$, 100.6 MHz) δ 40.22, 120.45, 121.26, 129.17, 149.04.