Supporting Information

Carboxylate-promoted reductive functionalization of CO₂ with amine and hydrosilane under mild conditions

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1. General Experimental Section

The starting materials were commercially available and were used without further purification except solvents. The products were isolated by column chromatography on silica gel (200-300 mesh) using petroleum ether (60-90 °C) and ethyl acetate. All compounds were characterized by $^1$H NMR, $^{13}$C NMR and mass spectroscopy, which are consistent with those reported in the literature. NMR spectra were determined on Bruker 400 in CDCl$_3$ or C$_6$D$_6$. $^1$H NMR spectra was recorded on 400 MHz spectrometers using CDCl$_3$ as solvent referenced to tetramethylsilane (TMS, 0 ppm). The $^{13}$C NMR chemical shifts were reported in ppm relative to the carbon resonance of CDCl$_3$ (central peak is 77.0 ppm). $^1$H NMR peaks are labeled as singlet (s), doublet (d), triplet (t), and multiplet (m). The coupling constants, $J$, are reported in Hertz (Hz). GC-MS data were performed on Finnigan HP G1800 A. GC analyses were performed on a Shimadzu GC-2014 equipped with a capillary column (RTX-17 30 m × 0.25 μm) using a flame ionization detector.
2. Cesium formate-catalyzed hydrosilation of CO$_2$ in the absence of amines

$$\text{CO}_2 + \text{Ph}_2\text{SiH}_2 \xrightarrow{\text{HCOOCs, CH}_3\text{CN, 50 °C}} \text{HCOO}[\text{Si}] + [\text{SiOCH}_2\text{O}[\text{Si}] + \text{CH}_3\text{O}[\text{Si}]]$$

Under inert atmosphere (Ar), a 10 mL Schlenk flask was charged with cesium formate (2.3 mg), diphenylsilane (186 μL, 1 mmol) and CH$_3$CN (2 mL) successfully. The reaction mixture was stirred at 50 °C under an atmosphere of CO$_2$ (99.999%, balloon). Samples were taken for the desired time (6 h) to be analyzed through $^1$H NMR. It was found that diphenylsilane (4.90 ppm) was consumed in 6 h, giving rise to peaks at ~8.1, ~5.5 and ~3.5 ppm, indicative of CO$_2$ reduction to silyl formates, silyl acetals and silyl methoxides.\(^1\)

3. Experimental procedure for reductive functionalization of CO\textsubscript{2} with aniline to \textit{N}-methylaniline and \textit{N},\textit{N}-methylaniline

Under inert atmosphere (Ar), a 50 mL Schlenk flask was charged successively with cesium formate (9.2 mg, 5 mol\% relative to amine), aniline (1 mmol), diphenylsilane (744 μL, 4 mmol) and CH\textsubscript{3}CN (8 mL). The reaction mixture was stirred at 50 °C for 6 h under an atmosphere of CO\textsubscript{2} (99.999%, balloon). After the reaction, the reaction mixture was concentrated and purified by silica gel column chromatography (petroleum ether-EtOAc). \textit{N}-methylaniline was obtained with 21\% isolated yield, and \textit{N},\textit{N}-methylaniline were with 28\% yield. The spectrum of \textit{N}-methylaniline are as below: \textit{\textsuperscript{1}H} NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.18 (t, \(J = 7.8\) Hz, 2H), 6.70 (t, \(J = 7.3\) Hz, 1H), 6.60 (d, \(J = 8.2\) Hz, 2H), 3.63 (s, 1H), 2.81 (s, 3H). \textit{\textsuperscript{13}C} NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 149.25, 129.14, 117.18, 112.36, 30.66.
4. Characterization Data for the Products

\[ \text{N,N-Dimethylaniline} \]

Yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\), 25°C, TMS) \(\delta\) 7.24 (dd, \(J = 8.8,\ 7.3\ \text{Hz},\ 2\text{H})\), 6.85 – 6.62 (m, 3H), 2.94 (s, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\), 25°C, TMS) \(\delta\) 150.58, 129.03, 116.60, 112.62, 40.61. GC-MS (EI, 70 eV) m/z (%) 121.15 (81.29), 120.15 (100.00), 77.05 (29.56).

\[ \text{4-Methoxy-N,N-dimethylaniline} \]

White solid. \(^1\)H NMR (400 MHz, CDCl\(_3\), 25°C, TMS) \(\delta\) 6.88 – 6.81 (m, 2H), 6.79 – 6.72 (m, 2H), 3.76 (s, 3H), 2.86 (s, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\), 25°C, TMS) \(\delta\) 152.12, 145.52, 115.04, 114.60, 55.72, 41.92. GC-MS (EI, 70 eV) m/z (%) 151.25 (59.49), 136.20 (100.00).

\[ \text{N,N-Dimethyl-p-toluidine} \]

Yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\), 25°C, TMS) \(\delta\) 7.05 (d, \(J = 8.1\ \text{Hz},\ 2\text{H})\), 6.69 (d, \(J = 8.2\ \text{Hz},\ 2\text{H})\), 2.89 (s, 6H), 2.25 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\), 25°C, 100.00).
4-Chloro-N,N-dimethylaniline

Yellow oil. $^1$H NMR (400 MHz, CDCl$_3$, 25°C, TMS) $\delta$ 7.17 (d, $J$ = 8.9 Hz, 2H), 6.64 (d, $J$ = 8.7 Hz, 2H), 2.92 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$, 25°C, TMS) $\delta$ 149.10, 128.75, 121.36, 113.59, 40.64. GC-MS (EI, 70 eV) m/z (%) 157.10 (25.27), 156.10 (39.00), 155.10 (82.99), 154.10 (100.00).

N-allyl-N-methylaniline

Yellow oil. $^1$H NMR (400 MHz, CDCl$_3$, 25°C, TMS) $\delta$ 7.25 – 7.20 (m, 2H), 6.74 – 6.68 (m, 3H), 5.89 – 5.80 (m, 1H), 5.18 – 5.13 (m, 2H), 3.92 (d, $J$ = 4.9 Hz, 2H), 2.93 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$, 25°C, TMS) $\delta$ 149.43, 133.75, 129.07, 116.36, 116.12, 112.40, 55.23, 37.97. HRMS (ESI, m/z) calcd. For C$_{10}$H$_{13}$N [M+H]$^+$: 148.1126, found: 148.1122.
**N-isopropyl-N-methylaniline**

Yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.22 (t, $J = 7.9$ Hz, 2H), 6.79 (d, $J = 8.2$ Hz, 2H), 6.69 (t, $J = 7.2$ Hz, 1H), 4.18 – 3.96 (m, 1H), 2.72 (s, 3H), 1.15 (d, $J = 6.6$ Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 150.10, 129.07, 116.38, 113.28, 48.87, 29.75, 19.26.

**1-Methylpiperidine**

Colourless oil. $^1$H NMR (400 MHz, CDCl$_3$, 25°C, TMS) $\delta$ 2.33 (s, 4H), 2.24 (s, 3H), 1.68 – 1.51 (m, 4H), 1.41 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$, 25°C, TMS) $\delta$ 56.46, 46.86, 25.95, 23.70. GC-MS (EI, 70 eV) m/z (%) 99.15 (42.36), 98.15 (100.00), 71.10 (22.54).

**4-methylmorpholine**

Colourless oil. $^1$H NMR (400 MHz, CDCl$_3$, 25°C, TMS) $\delta$ 3.80 – 3.61 (m, 4H), 2.41 (s, 4H), 2.29 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$, 25°C, TMS) $\delta$ 66.67, 55.20, 46.23. GC-MS (EI, 70 eV) m/z (%) 101.15 (100.00), 100.15 (36.36), 71.10 (60.10).

**4-Bromo-N,N-dimethylaniline**
White solid. $^1$H NMR (400 MHz, CDCl$_3$, 25°C, TMS) $\delta$ 7.30 (d, $J = 9.1$ Hz, 2H), 6.59 (d, $J = 8.8$ Hz, 2H), 2.92 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$, 25°C, TMS) $\delta$ 56.46, 46.86, 25.95, 23.70. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 149.46, 131.64, 114.06, 108.45, 40.53. GC-MS (EI, 70 eV) m/z (%) 201.00 (93.41), 200.00 (100.00), 199.00 (99.32), 198.00 (97.76), 118.15 (45.22), 77.10 (20.98).

![Structure of N,N-dimethylcyclohexanamine](image)

**N,N-dimethylcyclohexanamine**

Colourless oil. $^1$H NMR (400 MHz, CDCl$_3$, 25°C, TMS) $\delta$ 2.27 (s, 6H), 2.14 – 2.10 (m, 1H), 1.86 – 1.76 (m, 4H), 1.68 – 1.55 (m, 1H), 1.26 – 1.09 (m, 5H). $^{13}$C NMR (101 MHz, CDCl$_3$, 25°C, TMS) $\delta$ 63.60, 41.43, 28.82, 26.14, 25.60. GC-MS (EI, 70 eV) 127.20 (26.01), 84.15 (100.00), 71.10 (21.41).

![Structure of N,N'-dimethyl-N,N'-diphenylmethanedianine](image)

**N,N'-dimethyl-N,N'-diphenylmethanedianine**

Colourless liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.25 (dd, $J = 8.6, 7.4$ Hz, 4H), 6.84 (d, $J = 8.1$ Hz, 4H), 6.78 (t, $J = 7.3$ Hz, 2H), 4.76 (s, 2H), 2.87 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 149.31, 129.27, 117.86, 113.76, 70.44, 36.31. GC-MS (EI, 70 eV) m/z (%) 226.20 (2.83), 121.15 (16.02), 120.15 (100.00), 107.15 (61.88), 106.15 (71.81), 79.10 (21.17), 77.10 (39.67).
4. NMR Spectral Copies of the Products