Supporting Information

Catalyst-free N-methylation of amines using CO₂

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Table of Contents

| I . General InformationS2 |
|---|
| II . Experimental DetailsS3 |
| III. Control experiments ······S5 |
| IV. Labelling experiments·····S6 |
| V. Detailed descriptions for productsS7 |
| VI. Copies of Product ¹ H NMR and ¹³ C NMR······S15 |
| VII. ReferencesS35 |

I . General Information

All reactions were isolated from moisture and oxygen by a nitrogen atmosphere on a Schlenk tube. All glassware was oven dried at 110 °C for hours and cooled down under vacuum. All solvents were dried and distilled before use according to the standard methods. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. All reactions were carried out under a carbon dioxide atmosphere with a balloon fitted on a Schlenk tube unless otherwise noted. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 60-90 °C). Gas chromatographic analyses were performed on Varian GC 3900 gas chromatography instrument with a FID detector and biphenyl was added as internal standard. GC-MS spectra were recorded on a Varian GC-MS 3900-2100T. High Resolution MS data report were performed on Waters Micromass GCT Premier, ionization mode: EI⁺. ¹H and ¹³C NMR data were recorded with Bruker Advance 400 MHz spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. All chemical shifts are reported relative to tetramethylsilane and *d*-solvent peaks (77.00 ppm, chloroform), respectively.

II . Experimental Details

General procedure for the methylation of amines using carbon dioxide and phenylsilane

$$R^{1} N^{H} + CO_{2} \xrightarrow{\text{phenylsilane}} R^{1} N^{H} \text{ or } R^{1} N^{H}$$

An over-dried Schlenk tube was equipped with a stir-bar. A balloon filled with CO₂ was connected to the Schlenk tube via the side tube and purged 3 times. Then DMF (3.0 mL) was added into the tube via a syringe, subsequently amine (0.5 mmol) was combined. At last, phenylsilane (105 mg, 1.0 mmol) was added to the tube. The Schlenk tube was heated at 90 °C for 24 h (900 rpm) and then cooled to room temperature. After the balloon gas was released, the reaction mixture was quenched by water and extracted with CH₂Cl₂ three times. The combined organic layers were dried over anhydrous Na₂SO₄ and evaporated under vacuum. The desired products were obtained in the corresponding yields after purification by flash chromatography on silica gel with petroleumether/ethyl acetate.

Gram scale Reaction

An over-dried Schlenk tube was equipped with a stir-bar. A balloon filled with CO_2 was connected to the Schlenk tube via the side tube and purged 3 times. Then DMF (50 mL) was added into the tube via a syringe, subsequently *N*-methylaniline (1.07 g, 10.0 mmol) was combined. At last, phenylsilane (2.10 g, 20.0 mmol) was added to the tube. The Schlenk tube was heated at 90 °C for 24 h (900 rpm) and then cooled to room temperature. After the balloon gas was released, the reaction mixture was quenched by water and extracted with CH_2Cl_2 three times. The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under vacuum. The desired products were obtained in the corresponding yields after purification by flash chromatography on silica gel with petroleumether/ethyl acetate.

III. Control experiments

Reaction of CO₂ and phenylsilane in d⁶-DMSO

An over-dried Schlenk tube was equipped with a stir-bar. A balloon filled with CO_2 was connected to the Schlenk tube via the side tube and purged 3 times. Then d⁶-DMSO (1.0 mL) was added into the tube via a syringe, subsequently *N*-methylaniline (0.2 mmol, 21.4 mg) was combined. At last, phenylsilane (42 mg, 0.4 mmol) was added to the tube. The Schlenk tube was heated at 90 °C for 1 h (900 rpm) and then cooled to room temperature. And 0.5 mL reaction liquid was transferred into an NMR tube for ¹³C NMR analysis.



Fig. 1¹³C NMR spectra of the reaction of CO₂ and phenylsilane in d⁶-DMSO

IV. Labelling experiment



An over-dried Schlenk tube was equipped with a stir-bar. A balloon filled with ¹³CO₂ was connected to the Schlenk tube via the side tube and purged 1 time. Then DMF (3.0 mL) was added into the tube via a syringe, subsequently amine (0.5 mmol) was combined. At last, phenylsilane (105 mg, 1.0 mmol) was added to the tube. The Schlenk tube was heated at 90 °C for 24 h (900 rpm) and then cooled to room temperature. After the balloon gas was released, the reaction mixture was quenched by water

and extracted with CH_2Cl_2 three times. The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under vacuum. The desired products were obtained in the corresponding yields after purification by flash chromatography on silica gel with petroleumether/ethyl acetate.



The EI-MS spectra of ¹³C-labelled 2a:

V. Detailed descriptions for products



N, N-dimethylaniline

2a was obtained according to the general procedure in 80% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.68 – 7.45 (m, 2H), 7.15 – 6.90 (m, 3H), 3.27 – 3.11 (m, 6H) ppm.

 ^{13}C NMR (101 MHz, CDCl₃) δ 150.40, 128.86, 116.40, 112.41, 40.31 ppm. The NMR data agree with

those in a literature report.¹



N, N, 4-trimethylaniline

2b was obtained according to the general procedure in 70% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.05 (d, J = 8.4 Hz, 2H), 6.68 (d, J = 8.6 Hz, 2H), 2.89 (s, 6H), 2.25 (s, 6H

3H) ppm.

 13 C NMR (101 MHz, CDCl₃) δ 148.77, 129.53, 126.05, 113.17, 41.03, 20.21 ppm. The NMR data agree with those in a literature report.¹





N, N-dimethyl-4-nitroaniline²

2c was obtained according to the general procedure in 49% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, J = 9.4 Hz, 2H), 6.59 (d, J = 9.4 Hz, 2H), 3.11 (s, 6H) ppm.

 13 C NMR (101 MHz, CDCl₃) δ 151.14, 136.82, 126.08, 110.15, 40.25 ppm. The NMR data agree with those in a literature report.²



2d

4-methoxy-N, N-dimethylaniline

2d was obtained according to the general procedure in 45% yield.

¹H NMR (400 MHz, CDCl₃) δ 6.95 – 6.86 (m, 2H), 6.86 – 6.77 (m, 2H), 3.81 (s, 3H), 2.91 (s, 6H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 151.90, 145.66, 114.84, 114.52, 55.64, 41.76 ppm. The NMR data agree with those in a literature report.¹



N-ethyl-N-methylaniline

2e was obtained according to the general procedure in 80% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.22 (t, J = 7.9 Hz, 2H), 6.69 (dd, J = 17.7, 7.8 Hz, 3H), 3.41 – 3.36 (m,

2H), 2.89 (s, 3H), 1.11 (t, *J* = 7.1 Hz, 3H) ppm.

 13 C NMR (101 MHz, CDCl₃) δ 129.10, 115.96, 112.32, 46.74, 37.38, 11.13 ppm. The NMR data agree with those in a literature report.³



N-isopropyl-*N*-methylaniline

2f was obtained according to the general procedure in 95% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.22 (t, J = 8.0 Hz, 2H), 6.79 (d, J = 8.3 Hz, 2H), 6.69 (t, J = 7.2 Hz,

1H), 4.14 – 4.04 (m, 1H), 2.72 (s, 3H), 1.15 (d, *J* = 6.6 Hz, 6H) ppm.

¹³C NMR (101 MHz, CDCl₃) δ 150.11, 129.04, 116.32, 113.23, 48.82, 29.69, 19.25 ppm. The NMR data agree with those in a literature report.⁴



N-cyclohexyl-N-methylaniline

2g was obtained according to the general procedure in 88% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.21 (t, *J* = 7.9 Hz, 2H), 6.77 (d, *J* = 8.3 Hz, 2H), 6.67 (t, *J* = 7.2 Hz, 1H), 3.55 (t, *J* = 11.2 Hz, 1H), 2.75 (s, 3H), 1.80 (dd, *J* = 20.2, 14.3 Hz, 4H), 1.67 (d, *J* = 13.0 Hz, 1H),

1.48 - 1.32 (m, 4H), 1.16 - 1.07 (m, 1H) ppm.

¹³C NMR (101 MHz, CDCl₃) δ 150.06, 129.01, 116.14, 113.06, 58.03, 31.08, 29.97, 26.15, 25.88 ppm.

The NMR data agree with those in a literature report.5



N-allyl-N-methylaniline

2h was obtained according to the general procedure in 87% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.29 – 7.16 (m, 2H), 6.81 – 6.64 (m, 3H), 5.93 – 5.76 (m, 1H), 5.24 – 5.06 (m, 2H), 3.91 (d, *J* = 5.0 Hz, 2H), 2.93 (s, 3H) ppm.
¹³C NMR (101 MHz, CDCl₃) δ 149.41, 133.74, 129.06, 116.33, 116.10, 112.37, 55.21, 37.96 ppm. The NMR data agree with those in a literature report.⁶



1-methyl-1,2,3,4-tetrahydroquinoline

2i was obtained according to the general procedure in 77% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.06 (t, *J* = 7.7 Hz, 1H), 6.94 (d, *J* = 7.1 Hz, 1H), 6.60 (t, *J* = 7.9 Hz, 2H), 3.22 – 3.17 (m, 2H), 2.87 (s, 3H), 2.76 (t, *J* = 6.4 Hz, 2H), 1.97 (p, *J* = 6.2 Hz, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 146.68, 128.76, 126.98, 122.79, 116.14, 110.90, 51.22, 39.08, 27.74, 22.41 ppm. The NMR data agree with those in a literature report.⁷



1-methylindoline

2j was obtained according to the general procedure in 73% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.17 – 7.01 (m, 2H), 6.67 (t, *J* = 7.3 Hz, 1H), 6.50 (d, *J* = 8.0 Hz, 1H), 3.36 – 3.22 (m, 2H), 2.94 (t, *J* = 8.1 Hz, 2H), 2.76 (s, 3H) ppm.

¹³C NMR (101 MHz, CDCl₃) δ 153.41, 130.35, 127.32, 124.28, 117.80, 107.28, 56.20, 36.34, 28.76 ppm. The NMR data agree with those in a literature report.¹



N, N-dimethylnaphthalen-1-amine

2k was obtained according to the general procedure in 47% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.23 (d, J = 7.7 Hz, 1H), 7.81 (d, J = 7.7 Hz, 1H), 7.57 – 7.42 (m, 3H),

7.38 (t, J = 7.8 Hz, 1H), 7.06 (d, J = 7.4 Hz, 1H), 2.89 (d, J = 1.6 Hz, 6H) ppm.

¹³C NMR (101 MHz, CDCl₃) δ 150.75, 134.74, 128.72, 128.29, 125.71, 125.65, 125.09, 124.07, 122.84,

113.85, 45.18 ppm. The NMR data agree with those in a literature report.⁸



N-methyl-N-phenylaniline

21 was obtained according to the general procedure in 34% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.27 (t, *J* = 7.2 Hz, 4H), 7.02 (d, *J* = 8.2 Hz, 4H), 6.95 (t, *J* = 7.3 Hz, 2H), 3.30 (s, 3H) ppm.

 13 C NMR (101 MHz, CDCl₃) δ 148.96, 129.14, 121.20, 120.39, 40.21 ppm. The NMR data agree with those in a literature report.³



2m

N-benzyl-N-methyl-1-phenylmethanamine

2m was obtained according to the general procedure in 59% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.28 (m, 8H), 7.28 – 7.20 (m, 2H), 3.52 (s, 4H), 2.18 (d, *J* = 1.1 Hz, 3H). ppm.

 13 C NMR (101 MHz, CDCl₃) δ 139.24, 128.90, 128.18, 126.89, 61.82, 42.21 ppm. The NMR data agree with those in a literature report.⁶



N, N-dimethylpyridin-3-amine

2n was obtained according to the general procedure in 34% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.17 (d, J = 3.8 Hz, 1H), 7.45 (t, J = 8.7 Hz, 1H), 6.61 – 6.43 (m, 2H),

3.08 (s, 6H) ppm.

 13 C NMR (101 MHz, CDCl₃) δ 159.30, 147.81, 137.08, 111.38, 105.82, 38.11 ppm. The NMR data agree with those in a literature report.⁹



1,2,2,6,6-pentamethylpiperidine

20 was obtained according to the general procedure in 95% yield.

¹H NMR (400 MHz, CDCl₃) δ 2.76 (d, *J* = 4.8 Hz, 3H), 2.47 (t, *J* = 13.4 Hz, 2H), 2.00 – 1.65 (m, 10H),

1.37 (s, 6H) ppm.

 ^{13}C NMR (101 MHz, CDCl₃) δ 63.83, 36.77, 28.78, 20.87, 15.82 ppm. The NMR data agree with those in a literature report.⁴



(3s,5s,7s)-N, N-dimethyladamantan-1-amine

2p was obtained according to the general procedure in 70% yield.

¹H NMR (400 MHz, CDCl₃) δ 3.32 (s, 6H), 2.40 (s, 2H), 2.18 – 1.98 (m, 5H), 1.87 – 1.53 (m, 8H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 73.00, 48.47, 35.03, 34.92, 29.93 ppm. The NMR data agree with those in a literature report.¹⁰



1-(4-(dimethylamino)phenyl)ethan-1-one

2q was obtained according to the general procedure in 60% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, J = 9.1 Hz, 2H), 6.65 (d, J = 9.1 Hz, 2H), 3.06 (s, 6H), 2.51 (s,

3H). ppm.

 13 C NMR (101 MHz, CDCl₃) δ 196.38, 153.32, 130.47, 125.25, 110.52, 39.99, 25.96 ppm. The NMR data agree with those in a literature report.¹¹



2r

Ethyl 4-(dimethylamino)benzoate

2r was obtained according to the general procedure in 69% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, J = 9.0 Hz, 2H), 6.63 (d, J = 9.0 Hz, 2H), 4.31 (q, J = 7.1 Hz,

2H), 3.01 (s, 6H), 1.36 (t, *J* = 7.1 Hz, 3H) ppm.

 13 C NMR (101 MHz, CDCl₃) δ 166.92, 153.11, 131.07, 117.14, 110.53, 59.99, 39.92, 14.39 ppm. The NMR data agree with those in a literature report.¹¹



N, N-dimethyl-4-vinylaniline

2s was obtained according to the general procedure in 38% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.27 (d, J = 8.7 Hz, 2H), 6.63 (d, J = 9.0 Hz, 2H), 6.59 (d, J = 10.9 Hz,

1H), 5.52 (d, J = 17.6 Hz, 1H), 5.00 (d, J = 10.9 Hz, 1H), 2.89 (s, 6H) ppm.

¹³C NMR (101 MHz, CDCl₃) δ 150.09, 136.52, 127.03, 126.02, 112.17, 109.15, 40.33 ppm. The NMR

data agree with those in a literature report.¹²



4-ethynyl-N, N-dimethylaniline

2t was obtained according to the general procedure in 58% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.36 (d, J = 8.9 Hz, 2H), 6.61 (d, J = 8.9 Hz, 2H), 2.98 (s, 1H), 2.96 (s, 1H

6H). ppm.

 ^{13}C NMR (101 MHz, CDCl_3) δ 150.32, 133.15, 111.62, 108.65, 84.82, 74.75, 40.13 ppm. The NMR

data agree with those in a literature report.¹³



$\rm VI$. Copies of Product ^{1}H NMR and ^{13}C NMR





















































VI. References

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