Supporting Information

for

A versatile way for the synthesis of monomethylamines by reduction of \( N \)-substituted carbonylimidazoles with the \( \text{NaBH}_4/\text{I}_2 \) system

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Experimental part
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1. General information

All starting materials and solvents were obtained from commercial suppliers and were used without further purification unless otherwise stated. Reagents were used as purchased. NMR spectra were recorded on Bruker spectrometers operating at 400 MHz (1H resonance). Proton chemical shifts (δ) were given in parts per million (ppm) relative to tetramethylsilane (TMS) with the solvent resonance as internal standard: CDCl₃, δ = 7.26 ppm. Carbon chemical shifts were reported in ppm (δ) relative to TMS with the solvent resonance as internal standard: CDCl₃, δ = 77.16 ppm. Electron spray ionization mass spectra (ESI-MS) were recorded with a Shimadzu LC/MS–IT–TOF hybrid mass spectrometer (Kyoto, Japan) (1c–3c, 5c–7c, 10c, 14c, 18c–20c) and a Bruker MicroTOF-Q ESI time-of-flight system (4c, 8c, 9c 11c–13c, 15c–17c). Solutions were evaporated under reduced pressure with a rotary evaporator. Thin-layer chromatography (TLC) was performed on precoated plates silica gel GF 254; the spots were visualized under UV light (λ = 254 nm) and/or Ninhydrin (aq.) was used as revealing system.

2. Synthesis of N-substituted carbonylimidazoles

2.1 General procedure for the preparation of N-substituted carbonylimidazoles (1b–12b, 14b) starting from amines [1-4].

To a solution of amine (4.0 mmol) in THF (30 mL) was slowly added carbonyldiimidazole (CDI) (4.8 mmol) and the solution was heated to refluxed for 1–5 h. The reaction was monitored by TLC. After completion of the reaction, the mixture was concentrated under reduced pressure. The residue was extracted with CH₂Cl₂ (100 mL), washed with water and dried over anhydrous Na₂SO₄. The solvent
was evaporated under reduced pressure and the crude product was purified by column chromatography.

**Typical compound data are as follows:**

![Compound 1b](image)

**N-Phenethyl-1H-imidazole-1-carboxamide (1b)** Yield: 87% (748 mg); white solid; $R_f = 0.6$ (EtOAc/PE, 2.5/1, v/v). $^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta =$ 8.00 (s, 1H), 7.73 (t, $J =$ 5.6 Hz, 1H), 7.41-7.42 (m, 1H), 7.33 – 7.20 (m, 5H), 6.89 (s, 1H), 3.65 (dd, $J =$ 12.0 Hz, 8.0 Hz, 2H), 2.95 (t, $J =$ 8.0 Hz, 2H).

![Compound 5b](image)

**N-(Furan-2-ylmethyl)-1H-imidazole-1-carboxamide (5b)** Yield: 87% (666 mg); white solid; $R_f = 0.6$ (EtOAc/PE, 2.5/1, v/v). $^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta =$ 8.24 (s, 1H), 7.42 (s, 1H), 7.37 (d, $J =$ 0.8 Hz, 1H), 7.17 (br s, 1H), 7.03 (s, 1H), 6.35 – 6.32 (m, 2H), 4.59 (d, $J =$ 4.0 Hz, 2H).

![Compound 7b](image)

**N,N-Dibenzyl-1H-imidazole-1-carboxamide (7b)** Yield: 85% (990 mg); white solid; $R_f = 0.6$ (EtOAc/PE, 2.5/1, v/v). $^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta =$ 7.98 (s, 1H), 7.44 – 7.35 (m, 6H), 7.28 – 7.26 (m, 5H), 7.06 (s, 1H), 4.61 (s, 4H).
N-Methyl-N-phenyl-1H-imidazole-1-carboxamide (12b) [2] Yield: 89% (716 mg); white solid; \( R_f = 0.6 \) (EtOAc/PE, 2.5/1, v/v). \(^1\)H NMR (400 MHz, CDCl\(_3\), ppm): \( \delta = 7.55 \) (s, 1H), 7.35 (t, \( J = 7.2 \) Hz, 2H), 7.28 (t, \( J = 7.2 \) Hz, 1H), 7.09 (d, \( J = 7.2 \) Hz, 2H), 6.81 (s, 1H), 6.77 (s, 1H), 3.46 (s, 3H).

N, N-Diphenylimidazole-1-carboxamide (13b) [1].

To a solution of diphenylamine (1.69 g, 10.0 mmol), DBU (1.83 g, 12 mmol) in acetonitrile (60 mL) was added carbonyldiimidazole (CDI) (1.95 g, 12.0 mmol) and refluxed for 48 h. The reaction did not go to completion. Volatiles were distilled out under reduced pressure. The residue was extracted with CH\(_2\)Cl\(_2\) (200 mL), washed with water and dried over anhydrous Na\(_2\)SO\(_4\). The solvent was evaporated under reduced pressure and crude product was purified by column chromatography (\( R_f = 0.5 \), EtOAc/PE, 2/1, v/v) to get white solid; Yield: 57% (1.5 g). \(^1\)H NMR (400 MHz, CDCl\(_3\), ppm): \( \delta = 7.74 \) (s, 1H), 7.38 (t, \( J = 7.6 \) Hz, 4H), 7.29 (t, \( J = 7.6 \) Hz, 2H), 7.18 (d, \( J = 7.2 \) Hz, 4H), 7.00 (s, 1H), 6.88 (s, 1H).
2.2 General procedure for the preparation of N-substituted carbonylimidazoles (15b–20b) from isocyanates or carboxylic acids [7,8].

Carboxylic acid (10 mmol) was dissolved in dry THF (30 mL) and cooled to −10 °C to −15 °C. After addition of ethyl chloroformate (11 mmol) and Et₃N (12 mmol), the mixture was stirred for 20 min. A solution of NaN₃ (25 mmol) in H₂O (5 mL) was added and stirred for 1 h at −10 °C to −15 °C. The solution was then diluted with H₂O and extracted with EtOAc (150 mL). The organic layers were washed with brine (2 × 10 mL), dried over Na₂SO₄ and concentrated under reduced pressure to give crude acyl azide. The crude acyl azide was dissolved in toluene (35 mL) and heated to 80 °C under stirring for 2–3 h. The toluene was removed under reduced pressure to afford isocyanate.

Isocyanate (5 mmol) synthesized according to the above method or obtained from commercial suppliers was dissolved in CH₂Cl₂ (15 mL) at room temperature. The imidazole (5.5 mmol) dissolved in CH₂Cl₂ (5 mL) was added to this solution, which was stirred at room temperature for 1 h. The resulting mixture was concentrated in vacuo. The residue was purified by column chromatography.

Typical compound data are as follows:

\[ \text{N-Nonyl-1H-imidazole-1-carboxamide (18b)} \]

Yield: 72% (854 mg); white solid; \( R_f = 0.6 \) (EtOAc/PE, 2.5/1, v/v). \( ^1\)H NMR (400 MHz, CDCl₃, ppm): \( \delta = 8.22 \) (s, 1H), 7.83 (t, \( J = \) 0.6 (EtOAc/PE, 2.5/1, v/v). \( ^1\)H NMR (400 MHz, CDCl₃, ppm): \( \delta = 8.22 \) (s, 1H), 7.83 (t, \( J = \) 0.6 (EtOAc/PE, 2.5/1, v/v). \( ^1\)H NMR (400 MHz, CDCl₃, ppm): \( \delta = 8.22 \text{ (s, 1H), 7.83 (t, } J = 0.6 \text{ (EtOAc/PE, 2.5/1, v/v).} \)
4.0 Hz, 1H), 7.51 (s, 1H), 6.98 (s, 1H), 3.35 (dd, \( J = 12.0 \text{Hz}, 8.0 \text{Hz}, 2 \text{H} \)), 1.62 – 1.55 (m, 2H), 1.30 – 1.23 (m, 12H), 0.85 (t, \( J = 8.0 \text{ Hz}, 3 \text{H} \)).

![Chemical Structure](image)

**N-(5-Acetamidopentyl)-1H-imidazole-1-carboxamide (19b)** Yield: 91% (1.08 g), white solid; Rf = 0.6 (EtOAc/PE, 2.5/1, v/v); \(^1\text{H NMR (400 MHz, CDCl}_3, \text{ppm): } \delta = 8.33 (s, 1\text{H}), 8.00 (\text{br s}, 1\text{H}), 7.65 (s, 1\text{H}), 7.01 (s, 1\text{H}), 6.21 (\text{br s}, 1\text{H}), 3.38 (\text{dd}, \( J = 12.0 \text{ Hz}, 8.0 \text{ Hz}, 2 \text{H} \)), 3.24 (dd, \( J = 12.0 \text{ Hz}, 4.0 \text{ Hz}, 2 \text{H} \)), 1.96 (s, 3\text{H}), 1.69 – 1.62 (m, 2\text{H}), 1.55 – 1.48 (m, 2\text{H}), 1.41 – 1.33 (m, 2\text{H}).

### 3. General procedure for the preparation of N-methylamines

To a stirred solution of \( N \)-substituted carbonylimidazoles (b) (2 mmol) and THF (20 mL) cooled to 0 °C in an ice bath, NaBH₄ (378 mg, 10.0 mmol) was added in one portion. Then a solution of I₂ (508 mg, 2 mmol) in THF (5 mL) was added slowly and drop-wise over 5 min resulting in vigorous evolution of hydrogen. Once gas evolution had ceased, the flask was heated to reflux for 1–10 h. The reaction was monitored by TLC. After completion of the reaction, the mixture was cooled to 0 °C with ice water, 6 M HCl was added carefully till pH = 1–2. After stirring for 1 h, NaOH (10% aq.) was added till pH = 12–13. The resulting solution was extracted with CH₂Cl₂ (3 × 50 mL). The organic extract was washed with brine, dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography.
data of N-methylamines

\[ \text{N-Methyl-2-phenylethanamine (1c) [10]} \]

yellow liquid (200 mg, 74\%); Rf: 0.4 (MeOH/CH\(_2\)Cl\(_2\), 1/9, v/v). \(^1\)H NMR (400 MHz, CDCl\(_3\), ppm): \(\delta = 7.31 - 7.26\) (m, 2H), 7.21 – 7.20 (m, 3H), 2.86 – 2.78 (m, 4H), 2.42 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\), ppm): \(\delta = 139.94, 128.76, 128.51, 126.20, 53.07, 36.19, 36.03\).

ESI-MS: \(m/z\) calcd. for C\(_9\)H\(_{14}\)N [M+H]\(^+\) 136.1126; found 136.084.

\[ \text{N-Methylbenzylamine (2c) [11]} \]

yellow liquid (162 mg, 67\%); Rf: 0.4 (MeOH/CH\(_2\)Cl\(_2\), 1/9, v/v). \(^1\)H NMR (400 MHz, CDCl\(_3\), ppm): \(\delta = 7.37 - 7.26\) (m, 5H), 3.77 (s, 2H), 2.46 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\), ppm): \(\delta = 139.60, 128.45, 128.31, 127.12, 55.84, 35.74\). ESI-MS: \(m/z\) calcd. for C\(_8\)H\(_{12}\)N [M+H]\(^+\) 122.0970; found 122.067.

\[ \text{N-Methyl-4-chlorobenzylamine (3c) [12]} \]

yellow liquid (208 mg, 67\%); Rf: 0.4 (MeOH/CH\(_2\)Cl\(_2\), 1/9, v/v). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.27\) (d, \(J = 8.0\) Hz, 2H), 7.23 (d, \(J = 8.0\) Hz, 2H), 3.69 (s, 2H), 2.41 (s, 3H). \(^{13}\)C NMR
(100 MHz, CDCl$_3$, ppm): $\delta = 138.26$, 132.74, 129.59, 128.52, 55.16, 35.79. ESI-MS: $m/z$ calcd. for C$_8$H$_{11}$ClN [M+H]$^+$ 156.0580 (Cl 35); found 156.028.

$4c$

$N$-Methyl-$\alpha$-phenylethylamine (4c) [13,14]
yellow liquid (176 mg, 65%); R$_f$: 0.4 (MeOH/CH$_2$Cl$_2$, 1/9, v/v). $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.38 - 7.35$ (m, 4H), 7.32 - 7.27 (m, 1H), 3.99 (br s, 1H), 3.78 (q, $J = 6.7$ Hz, 1H), 2.35 (s, 3H), 1.49 (d, $J = 6.7$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) $\delta = 142.77$, 128.70, 127.59, 126.92, 60.08, 33.44, 22.83. ESI-MS: $m/z$ calcd. for C$_9$H$_{14}$N [M+H]$^+$ 136.1126; found 136.1091.

$5c$

$N$-Methylfurfurylamine (5c) [15]
yellow liquid (155 mg, 70%); R$_f$: 0.4 (MeOH/CH$_2$Cl$_2$, 1/9, v/v). $^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta = 7.34$ (d, $J = 1.2$ Hz, 1H), 6.29 (dd, $J = 2.8$ Hz, 2.0, 1H), 6.16 (d, $J = 2.8$ Hz, 1H), 3.71 (s, 2H), 2.39 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta = 153.50$, 141.86, 110.10, 107.12, 47.87, 35.51. ESI-MS: $m/z$ calcd. for C$_6$H$_{10}$NO [M+H]$^+$ 112.0757; found 112.052.
**N,N-Dimethyl-2-phenylethanamine (6c)** [16]

yellow liquid (247 mg, 83%); R$_f$: 0.4 (MeOH/CH$_2$Cl$_2$, 1/9, v/v). $^1$H NMR (400 MHz, CDCl$_3$, ppm): δ = 7.32 – 7.26 (m, 2H), 7.23 – 7.18 (m, 3H), 2.80 (t, J = 8.0 Hz, 2H), 2.54 (t, J = 8.0 Hz, 2H), 2.31 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ = 140.40, 128.68, 128.42, 126.04, 61.65, 45.52, 34.45. ESI-MS: m/z calcd. for C$_{10}$H$_{16}$N [M+H]$^+$ 150.1283; found 150.099.

**N-Methyldibenzylamine (7c)** [17]

yellow liquid (253 mg, 60%); R$_f$: 0.4 (MeOH/CH$_2$Cl$_2$, 1/9, v/v). $^1$H NMR (400 MHz, CDCl$_3$, ppm): δ = 7.44 – 7.36 (m, 8H), 7.33 – 7.29 (m, 2H), 3.59 (s, 4H), 2.25 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ = 132.90, 131.42, 128.99, 128.14, 66.41, 45.97. ESI-MS: m/z calcd. for C$_{15}$H$_{18}$N [M+H]$^+$ 212.1439; found 212.121.

**N-Methylaniline (8c)** [18]

yellow liquid (154 mg, 72%); R$_f$: 0.6 (EA/PE, 1/4, v/v). $^1$H NMR (400 MHz, CDCl$_3$) δ = 7.26 (dd, J = 8.0 Hz, 7.2 Hz, 2H), 6.78 (t, J = 7.2 Hz, 1H), 6.67 (d, J = 7.6 Hz, 2H), 3.56 (br s, 1H), 2.87 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ = 149.38, 129.29, 117.33, 112.52, 30.81. ESI-MS: m/z calcd. for C$_7$H$_{13}$N [M+H]$^+$ 108.0813; found 108.0789.
**N,3-Dimethylbenzenamine (9c) [18,19]**

Yellow liquid (206 mg, 85%); R_f: 0.6 (EA/PE, 1/4, v/v). 1H NMR (400 MHz, CDCl_3) δ = 7.18 (t, J = 8.0 Hz, 1H), 6.64 (d, J = 8.0 Hz, 1H), 6.52 – 6.51 (m, 2H), 3.56 (br s, 1H), 2.89 (s, 3H), 2.39 (s, 3H). 13C NMR (100 MHz, CDCl_3, ppm): δ = 149.51, 139.05, 129.18, 118.28, 113.28, 109.73, 30.86, 21.76. ESI-MS: m/z calcd. for C_8H_12N [M+H]^+ 122.0970; found 122.0951.

**N,4-Dimethylbenzenamine (10c) [18]**

Yellow liquid (194 mg, 80%); R_f: 0.6 (EA/PE, 1/4, v/v). 1H NMR (400 MHz, CDCl_3, ppm) δ = 7.04 (d, J = 8.0 Hz, 2H), 6.58 (d, J = 8.0 Hz, 2H), 3.23 (br s, 1H), 2.84 (s, 3H), 2.28 (s, 3H). 13C NMR (100 MHz, CDCl_3, ppm): δ = 147.25, 129.79, 126.51, 112.71, 31.17, 20.49. ESI-MS: m/z calcd. for C_8H_12N [M+H]^+ 122.0970; found 122.069.

**N-Methyl-4-nitrobenzenamine (11c) [18]**
yellow liquid (213 mg, 70%); Rf: 0.6 (EA/PE, 1/4, v/v). $^1$H NMR (400 MHz, CDCl$_3$, ppm): δ = 8.08 (d, $J = 8.0$ Hz, 2H), 6.52 (d, $J = 8.0$ Hz, 2H), 4.67 (br s, 1H), 2.93 (d, $J = 4.7$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ = 154.25, 137.90, 126.42, 110.71, 30.15. ESI-MS: m/z calcd. for C$_7$H$_9$N$_2$O$_2$ [M+H]$^+$ 153.0664; found 153.0631.

![12c](image)

$N,N$-Dimethylaniline (12c) [17]

yellow liquid (172 mg, 71%); Rf: 0.6 (EA/PE, 1/4, v/v). $^1$H NMR (400 MHz, CDCl$_3$, ppm): δ = 7.29 – 7.25 (m, 2H), 6.79-6.74 (m, 3H), 2.97 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ = 150.61, 129.11, 116.76, 112.75, 40.71. ESI-MS: m/z calcd. for C$_8$H$_{12}$N [M+H]$^+$ 122.0970; found 122.0961.

![13c](image)

$N$-Methyl diphenylamine (13c) [17]

yellow liquid (245 mg, 67%); Rf: 0.6 (EA/PE, 1/4, v/v). $^1$H NMR (400 MHz, CDCl$_3$) δ = 7.30 – 7.26 (m, 4H), 7.04 (d, $J = 8.0$ Hz, 4H), 6.97 (t, $J = 8.0$ Hz, 2H), 3.33 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ = 148.92, 129.23, 121.41, 120.48, 40.36. ESI-MS: m/z calcd. for C$_{13}$H$_{14}$N [M+H]$^+$ 184.1126; found 184.1098.

![14c](image)
**N,N'-Dimethyl-1,4-benzenediamine (14c) [20]**

green solid (191 mg, 70%); Rf: 0.6 (EA/PE, 2.5/1, v/v). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 6.60 (s, 4H), 3.36 (br s, 2H), 2.80 (s, 6H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 141.89, 114.31, 31.95. ESI-MS: m/z calcd. for C₈H₁₃N₂ [M+H]⁺ 137.1079; found 137.078.

**N-Methylcyclohexanamine (15c) [13,14,21-23]**
colorless liquid (167 mg, 74%); Rf: 0.4 (MeOH/CH₂Cl₂, 1/9, v/v). ¹H NMR (400 MHz, CDCl₃, ppm) δ = 3.68 (br s, 1H), 2.76 – 2.69 (m, 1H), 2.48 (d, J = 8.0 Hz, 3H), 2.06 (d, J = 12.0 Hz, 1H), 1.91 (d, J = 12.0 Hz, 1H), 1.81 (d, J = 12.9 Hz, 2H), 1.68 – 1.62 (m, 1H), 1.48 – 1.44 (m, 1H), 1.33 – 1.23 (m, 3H), 1.16 – 1.09 (m, 1H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 63.12, 38.05, 29.46, 27.90, 25.49, 25.19, 25.17. ESI-MS: m/z calcd. for C₇H₁₆N [M+H]⁺ 114.1283; found 114.1254.

**4-Chloro-N-methylbenzenamine (16c) [18,24]**
yellow liquid (209 mg, 74%); Rf: 0.6 (EA/PE, 1/4, v/v). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.14 (d, J = 8.0 Hz, 2H), 6.53 (d, J = 12.0 Hz, 2H), 3.68 (br s, 1H), 2.81 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 152.77, 129.02, 121.73, 113.45, 30.82. ESI-MS: m/z calcd. for C₇H₆ClN [M+H]⁺ 142.0424 (Cl 35); found 142.0410.
yellow liquid (275 mg, 72%); Rf 0.6 (EA/PE, 1/4, v/v). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.07 (d, J = 8.0 Hz, 2H), 6.56 (d, J = 12.0 Hz, 2H), 3.68 (br s, 1H), 2.83 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 148.11, 140.34, 122.40, 120.79 (q, J = 255.1 Hz, CF₃), 112.54, 30.79. ESI-MS: m/z calcd. for C₈H₉F₃NO [M+H]+ 192.0636; found 192.0613.

yellow liquid (242 mg, 77%); Rf 0.4 (MeOH/CH₂Cl₂, 1/9, v/v). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 2.58 – 2.54 (m, 3H), 2.42 (s, 3H), 1.50 – 1.47 (m, 2H), 1.26 – 1.24 (m, 12H), 0.86 (t, J = 6.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 51.91, 36.12, 31.88, 29.55, 29.52, 29.28, 27.30, 22.67, 14.11. ESI-MS: m/z calcd. for C₁₀H₂₄N [M+H]+ 158.1909; found 158.163.

yellow liquid (206 mg, 65%); Rf 0.4 (MeOH/CH₂Cl₂, 1/9, v/v). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 6.11 (br s, 1H), 3.18 (dd, J = 4.0, 12.0 Hz, 2H), 2.53 (t, J = 8.0 Hz, 2H), 2.38 (s, 3H), 2.31 (br s, 1H), 1.92 (s, 3H), 1.51 – 1.43 (m, 4H), 1.36 – 1.28 (m, 2H). ¹³C NMR (100
MHz, CDCl₃, ppm): δ = 170.25, 51.63, 39.47, 36.27, 29.31, 29.20, 24.50, 23.26. ESI-MS:

m/z calcd. for C₈H₁₉N₂O [M+H]+ 159.1497; found 159.1514.

\[\text{N-[4-(Methylamino)phenyl]acetamide (20c) [27]}\]

green solid (223 mg, 68%); Rf 0.4 (EA/PE, 2.5/1, v/v). \(^1\)H NMR (400 MHz, CDCl₃, ppm): δ = 7.80 (br s, 1H), 7.25 (d, J = 8.0 Hz, 2H), 6.52 (d, J = 8.0 Hz, 2H), 3.45 (br s, 1H), 2.77 (s, 3H), 2.07 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl₃, ppm): δ = 168.66, 146.50, 128.26, 122.49, 112.58, 31.04, 24.13. ESI-MS: m/z calcd. for C₉H₁₃N₂O [M+H]+ 165.1028; found 165.073.
4. Data of the two intermediates

\[
\begin{align*}
\text{N-(2-Phenylethyl)formamide} \\
\end{align*}
\]

\(^1\)H NMR (400 MHz, CDCl\(_3\), ppm): \(\delta = 8.10\) (s, 1H), 7.35 – 7.21 (m, 5H), 6.01 (br s, 1H), 3.57 (dd, \(J = 13.6\) Hz, 6.8 Hz, 2H), 2.85 (t, \(J = 6.8\) Hz, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\), ppm): \(\delta = 161.37, 138.54, 128.78, 128.71, 126.66, 39.24, 35.49\).
$^1$H NMR (400 MHz, CDCl$_3$, ppm) (trans/cis=54/46): $\delta = 8.87$ (br s, 1H, *trans*), 8.70 (d, $J = 11.4$ Hz, 1H, *trans*), 8.35 (d, $J = 1.8$ Hz, 1H, *cis*), 7.96 (br s, 1H, *cis*), 7.55 (d, $J = 7.7$ Hz, 1H), 7.37 – 7.30 (m, 4H), 7.20 – 7.10 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta = 163.04, 159.45, 136.98, 136.80, 129.77, 129.12, 125.31, 124.83, 120.09, 118.81$. 

*N-Phenylformamide* [6,28]
5. Scheme S1

For amines

\[
R^1R^2\text{NH} \xrightarrow{\text{Curtius rearrangement}} R^1\text{NCO} \xrightarrow{[H]} R^1\text{NCH}_3
\]

For carboxylic acids or isocyanates

\[
R^1\text{COOH} \xrightarrow{\text{Curtius rearrangement}} R^1\text{NCO} \xrightarrow{[H]} R^1\text{NCH}_3
\]

The carbon source was marked in red.

**Scheme S1**: Schematic of the conversion process for N-CH$_3$ carbon source.
6. References

7. $^1$H and $^{13}$C NMR spectra of b and c

*N-Phenethyl-1H-imidazole-1-carboxamide (1b)*

*N-(Furan-2-ylmethyl)-1H-imidazole-1-carboxamide (5b)*
$N,N$-Dibenzyl-1H-imidazole-1-carboxamide (7b)

$N$-Methyl-$N$-phenyl-1H-imidazole-1-carboxamide (12b)
$N,N$-Diphenyl-$1H$-imidazole-$1$-carboxamide (13b)

$N$-Nonyl-$1H$-imidazole-$1$-carboxamide (18b)
$N$-(5-Azetidopentyl)-1$H$-imidazole-1-carboxamide (19b)
N-Methyl-2-phenylethanamine (1c)
$N$-Methyl-1-phenylmethanamine (2c)
1-(4-Chlorophenyl)-N-methylmethanamine (3c)
$N$-Methyl-1-phenylethalamine (4c)
1-(Furan-2-yl)-N-methylmethanamine (5c)
N,N-Dimethyl-2-phenylethanamine (6c)
$N$-Benzyl-$N$-methyl-1-phenylmethanamine (7c)
N-Methylaniline (8c)
N,3-Dimethylaniline (9c)
$N,4$-Dimethylaniline (10c)
$N$-Methyl-4-nitroaniline (11c)
$N,N$-Dimethylaniline (12c)
N-Methyl-N-phenylaniline (13c)
$N^1,N^4$-Dimethylbenzene-1,4-diamine (14c)

\[ \text{Diagram of molecule} \]

\[ \text{NMR spectrum with peaks at 7.26, 6.60, 3.36, and 2.86 ppm} \]

\[ \text{NMR spectrum with peaks at 4.09, 2.08, and 6.04 ppm} \]

\[ \text{NMR spectrum with peaks at 14.43 and 31.95 ppm} \]
N-Methyl-cyclohexylamine (15c)
4-Chloro-N-methylaniline (16c)
$N$-Methyl-4-(trifluoromethoxy)aniline (17c)
$N$-Methylnonan-1-amine (18c)
$N$-(5-(Methylamino)pentyl)acetamide (19c)
$N$-(4-(Methylamino)phenyl)acetamide (20c)
8. ESI–MS

**N-Methyl-2-phenylethanamine (1c)**

![Graph of N-Methyl-2-phenylethanamine (1c)](image)

**N-Methylbenzylamine (2c)**

![Graph of N-Methylbenzylamine (2c)](image)

**N-Methyl-4-chlorobenzylamine (3c)**

![Graph of N-Methyl-4-chlorobenzylamine (3c)](image)
$N$-Methyl-$\alpha$-phenylethylamine (4c)

$N$-Methylfuranylamine (5c)

$N,N$-Dimethyl-2-phenylethanamine (6c)
$N$-Methyldibenzylamine (7c)

$N$-Methylaniline (8c)

$N,3$-Dimethylbenzenamine (9c)
$N,4$-Dimethylbenzenamine (10c)

$N$-Methyl-4-nitrobenzenamine (11c)

$N,N$-Dimethylaniline (12c)
N-Methyldiphenylamine (13c)

N',N'-Dimethyl-1,4-benzenediamine (14c)

N-Methylcyclohexylamine (15c)
$N$-Methyl-4-chlorobenzenamine (16c)

$N$-Methyl-4-(trifluoromethoxy)benzenamine (17c)

$N$-Methylnonylamine (18c)
$N$-[5-(Methylamino)pentyl]acetamide (19c)

$N$-[4-(Methylamino)phenyl]acetamide (20c)