# Reduction of hydrazines to amines with aqueous solution of titanium(III) trichloride

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## **General information**

<sup>1</sup>H NMR spectra were recorded on Bruker instruments (600 MHz, or 400 MHz). Chemical shifts are reported in ppm with tetramethylsilane as internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration. <sup>13</sup>C NMR data were collected on Bruker instruments (150, or 100 MHz) with complete proton decoupling. Chemical shifts are reported in ppm with tetramethylsilane as internal standard. IR spectra were recorded on a Perkin-Elmer FT-IR spectrometer. Elemental analyses were performed on a CARLO ERBA–1106 apparatus. High-resolution mass spectra were obtained on a Bruker Daltoics Bio TOF–Q mass spectrometer (ESI, MALDI-TOF). GC–MS were measured on Agilent Technologies 6890-5973N. Flash column chromatography was performed with silica gel (300–400 mesh). All reactions were carried out under an argon atmosphere. Commercially available materials were used without further purification unless otherwise noted.

## **Preparation of hydrazines**

Monosubstituted arylhydrazines were prepared from corresponding amines.<sup>1</sup> *N*-Alkyl-*N*-arylhydrazines were prepared from corresponding monosubstituted arylhydrazines.<sup>2</sup> *N*,*N*-Diarylhydrazines<sup>3</sup> and *N*,*N*-dialkylhydrazines<sup>4</sup> were prepared from corresponding secondary amines. *N*-Acyl-*N*-arylhydrazines were prepared from corresponding *N*-arylamines.<sup>5</sup>

## General procedure for the preparation of monosubstituted arylhydrazines.<sup>1</sup>

To the mixture of amine (20 mmol) and conc. HCl (15 mL) cooled in an ice-bath was added an aqueous solution of NaNO<sub>2</sub> (25%, 5.6 g) slowly. After cooling to -20 °C, a mixture of SnCl<sub>2</sub> (40 mmol) and conc. HCl (10 mL) was added dropwise. After 4 h, the reaction mixture was filtered. The residues were dissolved in aqueous KOH (25%), exacted with ether ( $3 \times 20$  mL). The extracts were combined and dried. The volatiles were removed to give corresponding hydrazines.

## 2-Methoxyphenylhydrazine (3)

White solid. Mp: 101–102 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 7.33 (t, J = 7.2 Hz, 1H), 7.21 (dd, J = 7.2 Hz, 12 Hz, 1H), 6.97 (t, J = 7.2 Hz, 1H), 6.92 (d, J = 7.2 Hz, 1H), 3.83 (s, 3H), 3.78 (s, 1H), 3.18 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 144.0, 129.2, 122.8, 120.0, 114.8, 110.0, 55.4; MS (ESI, m/z): 138 [M<sup>+</sup>].

## 4-Chlorophenylhydrazine (4)

White solid. Mp: 116–118 °C . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 7.03 (d, *J* = 8.0 Hz, 2H), 6.73 (d, *J* = 8.4 Hz, 2H), 3.66 (s, 1H), 2.27 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 143.0, 128.0, 124.2, 116.9; MS (ESI, *m/z*): 142 [M<sup>+</sup>].

## Cyclohexylhydrazine (6)

Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS) δ (ppm): 5.01 (s, 2H), 3.92 (s, 1H), 2.55–2.60 (m, 2H), 1.58–1.76 (m, 3H), 0.98–1.29 (m, 5H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS) δ (ppm): 61.1, 32.2, 25.0, 24.5; MS (ESI, *m/z*): 114 [M<sup>+</sup>].

## General procedure for the preparation of *N*-alkyl-*N*-arylhydrazines.<sup>2</sup>

An oven-dried flask was charged with sodium amide (0.43 g, 11 mmol), evacuated, backfilled with argon and then THF (50 mL) was added. The reaction mixture was cooled to 0  $^{\circ}$ C, then arylhydrazines (10 mmol) in THF (50 mL) was added dropwise and the resulting mixture was allowed to warm up to room temperature. The reaction mixture was stirred for 6 h at room temperature and turned brown. Methyl iodide (10 mmol) was added at 0  $^{\circ}$ C and the reaction mixture was stirred for additional 2 h. Then H<sub>2</sub>O (20 mL) was added to remove superfluous sodium amide. To the resulting mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> three times. The extracts were dried over MgSO<sub>4</sub>. After removal of the solvent, the residue was purified by column chromatography on silica.

#### N-Methyl-N-(2-naphthyl)hydrazine (11)

White solid. Mp:  $50-52 \,^{\circ}$ C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 7.68–7.73 (m, 3H), 7.44 (dd,  $J = 9.2 \,\text{Hz}$ , 2.4 Hz, 1H), 7.39 (t,  $J = 7.2 \,\text{Hz}$ , 1H), 7.26 (t,  $J = 8.0 \,\text{Hz}$ , 1H), 7.18 (d,  $J = 1.6 \,\text{Hz}$ , 1H), 3.89 (brs, 2H), 3.22 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 150.6, 134.7, 128.7, 128.0, 127.6, 126.7, 126.4, 123.2, 117.4, 107.3, 44.8; IR (KBr, v, cm<sup>-1</sup>): 3333.8, 3052.6, 2862.5, 1629.1, 1506.3, 1102.6, 834.4, 746.4; MS (ESI, *m/z*): 172 [M<sup>+</sup>].

#### N-Heptyl-N-(2-naphthyl)hydrazine (12)

Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 7.66–7.71 (m, 3H), 7.38 (t, J = 7.2 Hz, 1H), 7.33 (dd, J = 9.2 Hz, 2.4 Hz, 1H), 7.24 (t, J = 7.6 Hz, 1H), 7.19 (d, J = 2.4 Hz, 1H), 3.72 (brs, 2H), 3.48 (t, J = 7.2 Hz, 2H), 1.66–1.70 (m, 2H), 1.28–1.38 (m, 8H), 0.89 (t, J = 6.8 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 149.8, 135.0, 128.8, 127.8, 127.7, 126.7, 126.4, 122.7, 117.1, 106.9, 56.0, 32.1, 29.5, 27.3, 26.1, 22.9, 14.4; IR (film, v, cm<sup>-1</sup>): 3337.6, 3054.9, 2925.9, 2854.7, 1628.9, 1467.4, 830.7, 744.2; MS (ESI, *m/z*): 256 [M<sup>+</sup>].

#### General procedure for the preparation of N,N-diarylhydrazines.<sup>3</sup>

To a mixture of  $CH_2Cl_2$  and  $Et_2O$  (250 mL, 4:1 v/v), was added TiCl<sub>4</sub> (6.6 mL, 0.06 mol) slowly with stirring to give a yellow complex. Mg powder (1.5 g, 0.06 mol) was added under argon. The mixture was stirred for 2.5 h at room temperature to give a black solution. Then an ethereal solution of *N*-nitrosodiarylamine (0.015 mol) was added to the solution at room temperature with stirring. After 30 min, the reaction was quenched with dil. HCl and the mixture was stirred for 1 h. The resulting solution was made alkaline by addition of NaOH and extracted with Et<sub>2</sub>O to give *N*,*N*-diarylhydrazine.

#### General procedure for the preparation of N,N-dialkylhydrazines.<sup>4</sup>

*N*-Nitrosodialkylamine (10 mmol) were dissolved in EtOH (10 mL) under argon. Then aqueous solution of titanium trichloride (40 mmol) was added and the mixture was stirred for 1 h at room temperature. The mixture was basified to pH > 10 by adding aqueous NaOH (20%) dropwise under ice-bath extracted with CH<sub>2</sub>Cl<sub>2</sub> repeatedly. The extracts were combined and dried, and the volatiles were removed. The residue was purified by column chromatography on silica to obtain *N*,*N*-dialkylhydrazines.

## *N*-Acetyl-*N*-phenylhydrazine (14)<sup>5,6</sup>

A mixture of acetaldehyde phenylhydrazone (4.0 g), pyridine (2.4 g), and ether (30 mL) was

stirred and maintained at -88 °C and acetyl chloride (2.4 g) was added dropwise over 25 min. After stirring for an additional 4 h at room temperature, a white needle of acetaldehyde *N'*-acetylphenylhydrazone were obtained. A mixture of acetaldehyde *N'*-acetylphenylhydrazone (3.58 g), ethanol (5 mL) and ether (5 mL) were cooled under ice-bath and nearly saturated with gaseous hydrogen chloride. The addition of ether (15 ml) caused the precipitation of crystalline solids which were filtered, washed with ether, and dried under reduced pressure to give *N*-acetyl-*N*-phenylhydrazine hydrochloride (**17**). Mp: 186–189 °C dec..

## *N*,*N*-Dicyclohexylhydrazine (15)<sup>3</sup>

White solid. Mp: 163–165 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS) δ (ppm): 4.86–4.91 (m, 1H), 3.69–3.74 (m, 1H), 1.58–1.93 (m, 13H), 1.10–1.47 (m, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS) δ (ppm): 58.4, 52.1, 34.3, 29.3, 26.0, 25.4, 25.3, 25.2; MS (ESI, *m/z*): 196 [M]<sup>+</sup>.

## **Piperidin-1-amine** (17)<sup>4</sup>

Colorless liquid. Bp: 145–147 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 3.42 (s, 2H), 2.35 (s, 4H), 1.54–1.59 (m, 4H), 1.43–1.45 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm):62.5, 26.2, 24.8; MS (ESI, *m/z*): 196 [M]<sup>+</sup>.

## Procedure for the preparation of other types of substituted hydrazines.

## N,N'-Diphenylhydrazine (18)<sup>7</sup>

Hydrazine hydrate (100 mL) was added to a solution of azobenzene (3.64 g, 0.02 mol) in ethanol (500 mL). The reaction mixture was heated at 60 °C. After being stirred for 30 min, the solution was poured into ice. Then the crystals were collected and dried. The crude product was recrystallized from 95% ethanol to give a white solid (3.36 g, 92%). Mp: 124–125 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 7.19–7.25 (m, 4H), 6.82–6.86 (m, 6H), 5.61 (s, 2H).

#### *N*-Benzyl-*N'*-phenyllhydrazine (19)<sup>8</sup>

A solution of n-BuLi (10 mmol) in THF (10 mL) was added to a stirred solution of (2-phenylhydazino)triphenylphosphonium bromide (10 mmol) in THF (40 mL) under argon. Then a solution of benzyl bromide (10 mmol) in THF (10 mL) was added and stirring was continued for 8 h. An aqueous solution of NaOH (40 mL, 2 mol/L) was added and the mixture was heated at 60 °C for 2 h. The organic phase was dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated to afford the crude product. The hydrazine was isolated by distillation under reduce pressure (86% yield). Bp: 108–110 °C /0.2 mmHg; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 7.65–7.70 (m, 3H), 7.28–7.52 (m, 4H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.88 (t, *J* = 7.2 Hz, 1H), 4.52 (s, 2H), 1.65 (brs, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 150.8, 144.4, 129.6, 128.1, 126.7, 126.2, 119.2, 114.7, 52.3; MS (ESI, *m/z*): 199 [M + H]<sup>+</sup>.

#### N-Allyl-N'-phenylhydrazine (20)<sup>8</sup>

A solution of n-BuLi (10 mmol) in THF (10 mL) was added to a stirred solution of (2-phenylhydazino)triphenylphosphonium bromide (10 mmol) in THF (40 mL) under argon. Then a solution of allyl bromide (10 mmol) in THF (10 mL) was added and stirring was continued for 8 h. An aqueous solution of NaOH (40 mL, 2 mol/L) was added and the mixture was heated at  $60 \,^{\circ}$ C for 2 h. The organic phase was dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated to afford the crude product. The

hydrazine was isolated by distillation under reduce pressure (86% yield). Bp: 70–72 °C /0.2 mmHg; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 7.26–7.30 (m, 2H), 6.85 (d, *J* = 7.6 Hz, 1H), 6.72 (t, *J* = 7.6 Hz, 1H), 6.34 (brs, 2H), 5.92–6.01 (m, 1H), 5.30 (dd, *J* = 17.2 Hz, 1.6 Hz, 1H), 5.18 (dd, *J* = 10.4 Hz, 1.2 Hz, 1H), 3.31 (d, *J* = 5.2 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 148.7, 134.0, 128.8, 118.9, 118.0, 113.0, 53.3; MS (ESI, *m/z*): 149 [M + H]<sup>+</sup>.

#### *N*-Acetyl-*N'*-phenylhydrazine (21)<sup>9</sup>

Phenylhydrazine (5.0 g, 46.25 mmol) was added at room temperature to acetic acid (66 mL, 1.15 mol). The resulting mixture was heated at 80 °C for 1.5 h. Most of the acetic acid was then distilled. The residue was cooled to room temperature. A solid precipitated after addition of diethyl

ether (25 mL). The solid was then filtered and washed with diethyl ether (3×25 mL).

Recrystallization from ethanol afforded *N*-acetyl-*N'*-phenylhydrazine (**16**) (3.183 g, 47%) as a white solid. Mp: 128.5–129.5 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 7.35 (brs, 1H),

7.22–7.30 (m, 2H, major), 6.88–6.97 (m, 1H, minor), 6.79 & 6.86 (2×d, J = 8.0 Hz & 8.0 Hz, 3H,

major and minor), 3.20 (brs, 1H), 2.07 & 2.12 (2×s, 3H, major and minor); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 177.0, 170.3, 148.0, 147.2, 129.8, 129.4, 121.6, 113.8, 112.6, 21.2, 19.3; IR (KBr, v, cm<sup>-1</sup>): 3287, 3231, 3031, 2940, 1663, 1643, 1597; MS (ESI, *m/z*): 151 [M + H]<sup>+</sup>.

#### *N*-Phenyl-*N'*-benzyloxycarbonylhydrazine (22)<sup>10</sup>

To a solution of phenylhydrazine (5.1 g, 47 mmol) and triethylamine (5.0 g, 49 mmol) in THF (100 mL) cooled to -5 °C with an ice-bath was adde a solution of benzyl chlorofomate (8.2 g, 48 mmol) in THF (50 mL) with stirring at a rate that maintained the temperature below 0 °C. When the addition was complete, the reaction mixture was allowed to warm to room temperature. After filtration, the filtrate was concentrated in vacuo to afford a brown solid. Recrystallization from EtOH provided a white solid (60% yield). Mp: 94–96 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 7.39 (s, 4H), 7.25 (t, *J* = 7.6 Hz, 3H), 6.92 (t, *J* = 7.2 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 2H), 6.64 (s, 1H), 5.18 (s, 2H), 4.30 (brs, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 157.0, 147.8, 135.8, 129.4, 129.2, 128.9, 128.6, 128.3, 120.9, 113.0, 67.5; MS (ESI, *m/z*): 243 [M + H]<sup>+</sup>.

#### *N,N'*-Dibenzoylhydrazine (23)<sup>11</sup>

A solution of benzoyl chloride (11.0 mmol) in THF (30 mL) was added to the mixture of benzoyl hydrazide (10.0 mmol) and anhydrous sodium carbonate (1.02 g, 10.0 mmol) in THF (60 mL) and water (60 mL) at 0 °C. The resulting mixture was stirred at 0 °C for 1 h, and at room temperature for 4 h. A massive precipitation was observed. The product was harvested by filtration and washed three times with THF and ethyl ether, and dried in vacuo to give the product **18** as a white solid (1.45 g, 61%). Mp: 236–238 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 7.96–8.02 (m, 4H), 7.46–7.51 (m, 6H), 7.01 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm):166.3, 133.3, 132.4, 129.1, 128.0; IR (KBr, v ,cm<sup>-1</sup>): 3201, 3001, 1670, 1633, 1579, 1537, 1487, 1287, 687; MS (ESI, *m/z*): 241 [M + H]<sup>+</sup>.

## *N,N,N'*-Triphenylhydrazine (24)<sup>12</sup>

*N,N*-Diphenylhydrazine hydrochloride (1.35 g, 6 mmol), bromobenzene (0.5 mL, 5 mmol), Pd(OAc)<sub>2</sub> (20 mg, 0.05 mmol), BINAP (30 mg, 0.05 mmol) and NaO<sup>t</sup>Bu (1.34 g, 14 mmol) and toluene (30 mL) were added to an oven-dried flask with argon and then heated to 80 °C for 4 h. The reaction mixture was then cooled to room temperature, diluted with Et<sub>2</sub>O (20 mL), filtered through Celite and concentrated under vacuum. The crude product was purified by flash column chromatography on silica (EtOAc/hexane 1:19) to give the title product as a white solid (1.23 g, 95% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 7.27 (t, *J* = 8.0 Hz, 8H), 7.08 (d, *J* = 8.0 Hz, 5H), 6.94 (t, *J* = 7.2 Hz, 2H), 5.94 (brs, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 152.9, 146.9, 130.0, 129.6, 122.0, 121.1, 120.9, 113.3; MS (ESI, *m/z*): 261 [M + H]<sup>+</sup>.

#### *N*-Methyl-*N*,*N*'-diphenylhydrazine (25)<sup>13</sup>

An oven-dried flask was charged with *N*,*N'*-diphenylhydrazine (1.84 g, 10 mmol), evacuated, backfilled with argon, and then THF (50 mL) was added. The reaction mixture was cooled down to -78 °C, then 1.6 mol/L n-BuLi (12.5 mL, 20 mmol) solution in hexane was added dropwise and the resulting mixture was allowed to warm up to -60 °C for 15 min. Then MeI (0.63 mL, 10 mmol) was added and the reaction mixture was allowed to warm up to room temperature. The reaction was complete in 1 h. Then H<sub>2</sub>O (1 mL) was added and volatiles were evaporated. To the resulting mixture CHCl<sub>3</sub> (100 mL) and MgSO<sub>4</sub> were added. The mixture was filtered and volatiles were removed. The residue was purified by column chromatography on silica (EtOAc/hexane 1:8). The title compound **20** (1.68 g, 85%) was obtained as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 7.21–7.27 (q, *J* = 8.0 Hz, 4H), 6.96 (d, *J* = 8.4 Hz, 2H), 6.81–6.86 (m, 4H), 5.47 (s, 1H), 3.16 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 152.6, 152.5, 130.0, 122.9, 113.0, 39.5; MS (ESI, *m/z*): 199 [M + H]<sup>+</sup>.

#### *N*-Phenyl-*N*,*N'*-dibenzylhydrazine (26)<sup>14</sup>

*N*-Benzyl-*N*-phenylhydrazine (5 mmol) and benzyl chloride (5 mmol) were heated at 110 °C for 4 h. The mixture was cooled and ether (30 mL) was added. The solid hydrochloride of the starting hydrazine was removed by filtration. The filtrate was treated with diluted HCl and the precipitate was filtrate off, dissolved in 65% ethanol (10 mL), and treated with benzaldehyde (0.5 mL) on a steam bath for 5 min to remove unreacted *N*-benzyl-*N*-phenylhydrazine as hydrazone. The filtrate was concentrated on a rotary evaporator. The residue was treated with aqueous NaOH and extracted with ether. The extract was dried and volatiles were removed to give *N*-phenyl-*N*,*N*'-dibenzylhydrazine (**26**) as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 7.39–7.42 (m, 3H), 7.30–7.36 (m, 7H), 7.24–7.28 (m, 4H), 6.96 (t, *J* = 7.2 Hz, 1H), 5.19 (s, 2H), 3.83 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 152.0, 141.8, 134.8, 129.5, 128.8, 126.4, 126.1, 121.0, 114.9, 67.9, 53.0; MS (ESI, *m/z*): 289 [M + H]<sup>+</sup>.

## *N*-Benzyl-*N*,*N'*-diphenylhydrazine (27)<sup>13,15</sup>

An oven-dried flask was charged with *N*,*N'*-diphenylhydrazine (1.84 g, 10 mmol), evacuated, backfilled with argon and then THF (50 mL) was added. The reaction mixture was cooled down to -78 °C, then 1.6 mol/L n-BuLi (12.5 mL, 20 mmol) solution in hexane was added dropwise and the resulting mixture was allowed to warm up to -60 °C for 15 min. Then BnBr (1.2 mL, 10 mmol) was added and the reaction mixture was allowed to warm up to room temperature. The reaction was complete in 1 h. Then H<sub>2</sub>O (1 mL) was added and volatiles were evaporated. To the resulting

mixture CHCl<sub>3</sub> (100 mL) and MgSO<sub>4</sub> were added. The mixture was filtered and volatiles were removed. The residue was purified by column chromatography on silica (EtOAc/hexane 1:8). The title compound **27** (2.46 g, 90%) was obtained as a yellowish crystal. Mp: 68–70 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 7.20–7.34 (m, 9H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.77–6.87 (m, 4H), 5.67 (s, 1H), 4.76 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 151.6, 151.2, 140.4, 129.6, 128.9, 126.4, 126.0, 123.2, 113.2, 65.4; MS (ESI, *m/z*): 275 [M + H]<sup>+</sup>.

## *N*-Allyl-*N*,*N*'-diphenylhydrazine (28)<sup>13</sup>

An oven-dried flask was charged with *N,N'*-diphenylhydrazine (1.84 g, 10 mmol), evacuated, backfilled with argon and then THF (50 mL) was added. The reaction mixture was cooled down to -78 °C, then 1.6 mol/L n-BuLi (12.5 mL, 20 mmol) solution in hexane was added dropwise and the resulting mixture was allowed to warm up to -60 °C for 15 min. Then allyl bromide (0.9 mL, 10 mmol) was added and the reaction mixture was allowed to warm up to room temperature. The reaction was complete in 1 h. Then H<sub>2</sub>O (1 mL) was added and volatiles were evaporated. To the resulting mixture CHCl<sub>3</sub> (100 mL) and MgSO<sub>4</sub> were added. The mixture was filtered and volatiles were removed. The residue was purified by column chromatography on silica (EtOAc/hexane 1:8) to give the title compound **28** (2.14 g, 96%) as yellowish oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 7.20–7.25 (m, 4H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.79–6.86 (m, 4H), 5.85–5.95 (m, 1H), 5.69 (s, 1H), 5.20–5.27 (m, 2H), 4.13 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 150.0, 147.6, 132.4, 129.4, 129.2, 120.0, 119.1, 118.6, 113.4, 113.0, 54.0; IR (KBr, v, cm<sup>-1</sup>): 3326, 3054, 3018, 2977, 2905, 2859, 1595, 1492, 1302, 1256, 1225, 989, 922, 748, 686; MS (ESI, *m/z*): 225 [M + H]<sup>+</sup>.

#### *N,N'*-Dimethyl-*N,N'*-diphenylhydrazine (29)<sup>13</sup>

An oven-dried flask was charged with *N*,*N*'-diphenylhydrazine (1.84 g, 10 mmol), evacuated, backfilled with argon and then THF (50 mL) was added. The reaction mixture was cooled down to -78 °C, then 1.6 mol/L n-BuLi (12.5 mL, 20 mmol) solution in hexane was added dropwise and the resulting mixture was allowed to warm up to -60 °C for 15 min. Then MeI (0.63 mL, 10 mmol) was added and the reaction mixture was allowed to warm up to room temperature and stirred for another 1 h at room temperature. MeI (0.63 mL, 10 mmol) was added and the reaction was stirred for additional 3 h. Then H<sub>2</sub>O (1 mL) was added and volatiles were evaporated. To the resulting mixture CHCl<sub>3</sub> (100 mL) and MgSO<sub>4</sub> were added. Then mixture was filtered and volatiles were removed. The residue was purified by column chromatography on silica (EtOAc/hexane 1:8) to afford the title compound **29** (2.06 g 97%) as colorless crystals. Mp: 32–33 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 7.19–7.25 (m, 4H), 6.88 (d, *J* = 4.8 Hz, 2H), 6.74–6.79 (m, 4H), 2.92 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 149.1, 129.3, 118.6, 112.6, 33.7; IR (KBr, v, cm<sup>-1</sup>): 3095, 3064, 3023, 2982, 2951, 2869, 2802, 1600, 1492, 1318, 1102, 753, 686, 501; MS (ESI, *m*/z): 213 [M + H]<sup>+</sup>.

## *N*,*N*'-Dibenzyl-*N*,*N*'-diphenylhydrazine (30)<sup>13</sup>

An oven-dried flask was charged with N,N'-diphenylhydrazine (1.84 g, 10 mmol), evacuated, backfilled with argon and then THF (50 mL) was added. The reaction mixture was cooled down to -78 °C, then 1.6 mol/L n-BuLi (12.5 mL, 20 mmol) solution in hexane was added dropwise and the resulting mixture was allowed to warm up to -60 °C for 15 min. Then BnBr (1.25 mL, 10

mmol) was added and the reaction mixture was allowed to warm up to room temperature and stirred for another 1 h at room temperature. BnBr (1.25 mL, 10 mmol) was added and the reaction mixture was stirred for additional 3 h. Then H<sub>2</sub>O (1 mL) was added and volatiles were evaporated. To the resulting mixture CHCl<sub>3</sub> (100 mL) and MgSO<sub>4</sub> were added. Then mixture was filtered and volatiles were removed. The residue was purified by column chromatography on silica (EtOAc/hexane 1:8) to afford the title compound **30** (2.84 g, 78%) as colorless crystals. Mp: 126.5–127.0 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz, TMS)  $\delta$  (ppm): 7.18–7.25 (m, 14H), 6.80 (t, *J* = 8.4 Hz, 6H), 4.78 (s, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 151.0, 138.9, 131.5, 130.8, 128.3, 128.0, 125.1, 113.9, 62.0; MS (ESI, *m/z*): 365 [M + H]<sup>+</sup>.

#### *N,N,N',N'*-Tetraphenylhydrazine (31)<sup>16</sup>

CuCl (1.98 g, 0.02 mol) and pyridine (50 mL) were added in a glass flask immersed in a water bath under argon atmosphere with vigorous stirring, and then the atmosphere was replaced with oxygen. After the oxygen ceased, diphenylamine (1.69 g, 0.01 mol) in pyridine (10 mL) was added slowly with further absorption of oxygen. Pyridine was distilled off under reduce pressure after the reaction, and the residue was extracted with ether to give the crude product. The crude product was choromatographed on a silicon gel column with CH<sub>2</sub>Cl<sub>2</sub>-petroleum ether (1:3) to give N,N,N',N'-tetraphenylhydrazine (**31**) (1.4 g, 83%). Mp: 145–146 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz,

TMS)  $\delta$  (ppm): 7.31 (d, J = 8.0 Hz, 8H), 7.20 (t, J = 8.0 Hz, 8H), 6.90 (t, J = 8.0 Hz, 4H); MS

 $(ESI, m/z): 337 [M + H]^+.$ 

## *N*-Allyl-*N'*-methyl-*N*,*N'*-diphenylhydrazine (32)<sup>13</sup>

An oven-dried flask was charged with N,N'-diphenylhydrazine (1.84 g, 10 mmol), evacuated, backfilled with argon and then THF (50 mL) was added. The reaction mixture was cooled down to -78 °C, then 1.6 mol/L n-BuLi (12.5 mL, 20 mmol) solution in hexane was added dropwise and the resulting mixture was allowed to warm up to -60 °C for 15 min. Then allyl bromide (0.9 mL, 10 mmol) was added and the reaction mixture was allowed to warm up to room temperature. Then reaction mixture was stirred for another 1 h at room temperature. After this MeI (0.63 mL, 10 mmol) was added and the reaction was stirred for additional 3 h. Then H<sub>2</sub>O (1 mL) was added and volatiles were evaporated. To the resulting mixture CHCl<sub>3</sub> (100 mL) and MgSO<sub>4</sub> were added. Then mixture was filtered and volatiles were removed. The residue was purified by column chromatography on silica (EtOAc/hexane 1:8) to afford the title compound 27 (1.70 g, 71%) as yellowish oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS) δ (ppm): 7.20–7.25 (m, 4H), 6.76–6.80 (m, 6H), 5.93–6.03 (m, 1H), 5.28 (d, J = 7.2 Hz, 3H), 5.15 (d, J = 10.4 Hz, 1H), 4.05 (d, J = 5.6 Hz, 2H), 3.07 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS) δ (ppm): 149.2, 148.1, 134.8, 129.3, 122.9, 118.8, 118.3, 117.2, 113.1, 112.2, 52.7, 35.7; IR (KBr, v, cm<sup>-1</sup>): 3059, 3028, 2977, 2930, 2890, 2807, 1595, 1498, 1333, 1241, 994, 917, 743, 691, 501; HRMS (ESI<sup>+</sup>, *m/z*): calcd. for: C<sub>16</sub>H<sub>19</sub>N<sub>2</sub> [MH]<sup>+</sup> 239.1543, found: 239.1541.

#### The reduction of hydrazines

The reduction of 2-naphthylhydrazine (1)<sup>17</sup>

2-Naphthylhydrazine was dissolved in EtOH. 2-Naphthylamine (**1a**) was obtained as a white solid. Mp: 113–114 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 7.71 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.25 (t, *J* = 6.8 Hz, 1H), 7.01 (s, 1H), 6.97 (dd, *J* = 8.8 Hz, 2.0 Hz, 1H), 3.86 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 144.2, 135.0, 129.2, 128.0, 127.8, 126.4, 125.8, 122.5, 118.3, 108.6; GC–MS (EI, *m/z*): 143 [M<sup>+</sup>].

#### The reduction of phenylhydrazine (2)

Phenylhydrazine was dissolved in THF. Aniline (**2a**) was obtained as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 7.12–7.16 (m, 2H), 6.75 (t, *J* = 7.2 Hz, 1H), 6.66 (d, *J* = 7.2 Hz, 2H), 3.51 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 149.2, 129.7, 117.6, 115.2; GC–MS (EI, *m/z*): 93 [M<sup>+</sup>].

## The reduction of 2-methoxyphenylhydrazine (3)<sup>18</sup>

(2-Methoxyphenyl)hydrazine was dissolved in EtOH. 2-Methoxyanline (**3a**) was obtained as yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 6.81 (d, *J* = 6.8 Hz, 2H), 6.75 (t, *J* = 7.2 Hz, 2H), 3.87 (s, 3H), 3.75 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 147.3, 136.2, 121.1, 118.4, 115.0, 110.4, 55.4; GC–MS (EI, *m/z*): 123 [M<sup>+</sup>].

## The reduction of 4-chlorophenylhydrazine (4)<sup>19</sup>

(4-Chlorophenyl)hydrazine was dissolved in EtOH. 4-Choloroanline (**4a**) was obtained as a white solid. Mp: 68–71 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 7.10 (d, *J* = 8.4 Hz, 2H), 6.61 (d, *J* = 8.4 Hz, 2H), 3.64 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 145.0, 129.1, 122.9, 116.3; GC–MS (EI, *m/z*): 127 [M<sup>+</sup>].

#### The reduction of 6-bromo-2-naphthylhydrazine (5)

6-Bromo-2-naphthylhydrazine was dissolved in DMF. 6-Bromo-2-naphthylamine (**6a**) was obtained as a white solid. Mp: 127–128 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, TMS) δ (ppm): 7.83 (d, J = 1.2 Hz, 1H), 7.56 (d, J = 8.4 Hz, 1H), 7.46 (d, J = 9.0 Hz, 1H), 7.41 (dd, J = 8.4 Hz, 1.8 Hz, 1H), 6.94–6.97 (m, 2H), 3.89 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS) δ (ppm): 144.6, 133.4, 129.7, 129.6, 129.0, 128.4, 127.5, 119.1, 115.7, 108.4; GC–MS (EI, *m/z*): 221 [M<sup>+</sup>].

#### The reduction of cyclohexylhydrazine (6)<sup>20</sup>

Cyclohexylhydrazine was dissolved in EtOH. Cyclohexanamine (**5a**) was obtained as colorless oli. Bp: 132–134 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 2.61–2.68 (m, 1H), 1.83 (d, *J* = 12.4 Hz, 2H), 1.58–1.73 (m, 5H), 1.21–1.32 (m, 2H), 1.13–1.17 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 50.2, 36.6, 25.4, 24.9; GC–MS (EI, *m/z*): 99 [M<sup>+</sup>].

#### The reduction of *N*-methyl-*N*-phenylhydrazine (7)<sup>21</sup>

*N*-Methyl-*N*-phenylhydrazine was dissolved in THF. *N*-Methylaniline (**7a**) was obtained as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 7.18 (t, *J* = 7.2 Hz, 2H), 6.70 (t, *J* = 7.2 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 2H), 3.58 (brs, 1H), 2.81 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 149.4, 129.3, 117.3, 112.5, 30.8; GC–MS (EI, *m/z*): 107 [M<sup>+</sup>].

#### The reduction of *N*-heptyl-*N*-phenylhydrazine (8)<sup>22</sup>

*N*-Heptyl-*N*-phenylhydrazine was dissolved in THF. *N*-Heptylaniline (**8a**) was obtained as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 7.17 (t, *J* = 8.0 Hz, 2H), 6.68 (t, *J* = 7.2 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 2H), 3.61 (brs, 1H), 3.10 (t, *J* = 7.2 Hz, 2H), 1.57–1.65 (m, 2H), 1.25–1.43 (m, 8H), 0.89 (t, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 148.7, 129.3, 117.2, 112.8, 44.1, 32.0, 29.8, 29.3, 27.3, 22.8, 14.3; GC–MS (EI, *m/z*): 191 [M<sup>+</sup>].

## The reduction of *N*-cyclohexyl-*N*-phenylhydrazine (9)<sup>23</sup>

*N*-Cyclohexyl-*N*-phenylhydrazine was dissolved in THF. *N*-Cyclohexylaniline (**9a**) was obtained as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 7.12–7.17 (m, 2H), 6.65–6.67 (m, 1H), 6.57–6.60 (m, 2H), 3.54 (brs, 1H), 3.21–3.28 (m, 1H), 2.04–2.08 (m, 2H), 1.73–1.78 (m, 2H), 1.62–1.67 (m, 1H), 1.35–1.42 (m, 2H), 1.27–1.35 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 147.5, 129.3, 116.9, 113.2, 51.7, 33.6, 26.0, 25.1; GC–MS (EI, *m/z*): 175 [M<sup>+</sup>].

#### The reduction of *N*-benzyl-*N*-phenylhydrazine (10)<sup>24</sup>

*N*-Benzyl-*N*-phenylhydrazine was dissolved in THF. *N*-Benzylaniline (**10a**) was obtained as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 7.32–7.39 (m, 4H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 2H), 6.73 (t, *J* = 7.2 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 2H), 4.45 (brs, 1H), 4.33 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 148.1, 139.4, 129.3, 128.7, 127.6, 127.3, 117.6, 112.9, 48.4; GC–MS (EI, *m/z*): 183 [M<sup>+</sup>].

## The reduction of *N*-methyl-*N*-(2-naphthyl)hydrazine (11)<sup>25</sup>

*N*-Methyl-*N*-(2-naphthyl)hydrazine was dissolved in THF. *N*-Methyl-*N*-(2-naphthyl)amine (**11a**) was obtained as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 7.70–7.80 (m, 3H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 1H), 6.88 (s, 1H), 3.81 (brs, 1H), 2.96 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 147.1, 135.4, 128.9, 127.8, 127.6, 126.5, 126.1, 122.0, 118.1, 103.8, 30.8; GC–MS (EI, *m/z*): 157 [M<sup>+</sup>].

#### The reduction of *N*-heptyl-*N*-(2-naphthyl)hydrazine (12)

*N*-Heptyl-*N*-(2-naphthyl)hydrazine was dissolved in THF. *N*-Heptyl-*N*-(2-naphthyl)amine (**12a**) was obtained as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 7.65 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 8.4 Hz, 2H), 7.34 (t, J = 7.2 Hz, 1H), 7.17 (t, J = 7.2 Hz, 1H), 6.85 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 6.78 (d, J = 2.0 Hz, 1H), 3.76 (brs, 1H), 3.19 (t, J = 7.2 Hz, 2H), 1.63–1.69 (m, 2H), 1.25–1.48 (m, 8H), 0.90 (t, J = 6.8 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 146.4, 135.6, 129.0, 127.9, 127.6, 126.5, 126.1, 122.0, 118.3, 104.3, 44.2, 32.1, 29.7, 29.5, 27.5, 23.0, 14.4; IR (Film) v (cm<sup>-1</sup>): 3412.5, 3050.5, 2926.5, 2855.0, 1630.1, 1522.2, 1475.1, 1399.8, 1225.3, 827.4, 743.5; HRMS (MALDI-TOF): calcd. for: C<sub>17</sub>H<sub>23</sub>N [M<sup>+</sup>] 241.1830, found: 241.1825.

#### The reduction of *N*,*N*-diphenylhydrazine (13)<sup>26</sup>

*N,N*-Diphenylhydrazine was dissolved in THF. Diphenylamine (**13a**) was obtained as a white solid. Mp: 52–54 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 7.24–7.28 (m, 4H), 7.07 (d, *J* = 7.6 Hz, 4H), 6.92 (t, *J* = 7.2 Hz, 2H), 5.71 (brs, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 143.3, 129.5, 121.2, 118.0; GC–MS (EI, *m/z*): 169 [M<sup>+</sup>].

## The reduction of *N*-acetyl-*N*-phenylhydrazine (14)<sup>27</sup>

*N*-Acetyl-*N*-phenylhydrazine was dissolved in DMF. *N*-Phenylacetamide (**17a**) was obtained as a white solid. Mp: 115–116 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 7.49 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 8.0 Hz, 2H), 7.17 (brs, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 2.18 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 168.2, 137.9, 129.0, 124.3, 119.9, 24.6; GC–MS (EI, *m/z*): 135 [M<sup>+</sup>].

## The reduction of *N*,*N*-dicyclohexylhydrazine (15)<sup>28</sup>

*N,N*-Dicyclohexylhydrazine was dissolved in EtOH. *N,N*-Dicyclohexylamine (**14a**) was obtained as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 2.53 (t, *J* = 10.8 Hz, 2H), 1.58–1.86 (m, 11H), 0.96–1.28 (m, 11H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 52.8, 34.1, 26.0, 25.1;

GC–MS (EI, *m/z*): 181 [M<sup>+</sup>].

## The reduction of *N*,*N*-diisobutylhydrazine (16)<sup>29</sup>

*N,N*-Diisobutylhydrazine was dissolved in THF. *N,N*-Diisobutylamine (**15a**) was obtained as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 2.39 (d, *J* = 6.8 Hz, 4H), 1.72–1.79 (m, 2H), 1.33 (brs, 1H), 0.98 (d, *J* = 6.8 Hz, 12H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 58.0, 28.1, 20.5. GC–MS (EI, *m/z*): 129 [M<sup>+</sup>].

## The reduction of piperidin-1-amine (17)<sup>30</sup>

Piperidin-1-amine was dissolved in THF. Piperidine (**16a**) was obtained as colorless liquid. Bp: 104–106 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 2.77 (s, 4H), 2.19 (s, 2H), 1.51 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 47.1, 26.8, 24.8; GC–MS (EI, *m/z*): 85 [M<sup>+</sup>].

## The reduction of *N*,*N*'-diphenylhydrazine(18)

N,N'-Diphenylhydrazine was dissolved in DMF. Aniline (2a) was obtained as colorless oil.

## The reduction of *N*-benzyl-*N'*-phenyllhydrazine (19)<sup>31</sup>

*N*-Benzyl-*N*'-phenyllhydrazine was dissolved in THF. Aniline (**2a**) and benzylamine (**19b**) were obtained as colorless oils. Benzylamine: Bp: 184–185 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 7.24–7.30 (m, 3H), 7.16–7.20 (m, 2H), 3.73 (s, 2H), 1.72 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 143.2, 128.3, 127.0, 126.6, 46.4; GC–MS (EI, *m/z*): 107 [M<sup>+</sup>].

## The reduction of N-allyl-N'-phenylhydrazine (20)

*N*-Allyl-*N*'-phenylhydrazine was dissolved in THF. Aniline (**2a**) and allylamine (**20b**) were obtained as colorless oils. Allylamine: Bp: 56 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 5.73–6.21 (m, 1H), 5.19–5.28 (m, 1H), 4.92–5.12 (m, 1H), 3.22–3.39 (m, 2H), 1.26 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 136.1, 115.8, 18.7; GC–MS (EI, *m/z*): 57 [M<sup>+</sup>].

#### The reduction of N-acetyl-N'-phenylhydrazine (21)

*N*-Acetyl-*N'*-phenylhydrazine was dissolved in THF. Aniline (**2a**) was obtained as colorless oil, and acetamide (**21b**) was obtained as a white solid. Mp: 78–80 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 5.78–6.00 (br, 2H), 2.01 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 171.4, 15.6; GC–MS (EI, *m/z*): 59 [M<sup>+</sup>].

#### The reduction of N-phenyl-N'-benzyloxycarbonylhydrazine (22)

*N*-Phenyl-*N'*-benzyloxycarbonylhydrazine was dissolved in EtOH. Aniline (**2a**) and benzyl carbamate (**22b**) were obtained as a white solid. Benzyl carbamate: Mp: 86–89 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 7.32–7.37 (m, 5H), 5.11 (s, 2H), 4.78 (brs, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 157.2, 136.2, 128.5, 128.2, 128.1, 67.1; GC–MS (EI, *m/z*): 151 [M<sup>+</sup>].

## The reduction of N, N'-dibenzoylhydrazine (23)<sup>32</sup>

*N,N'*-Dibenzoylhydrazine was dissolved in DMF. Benzamide (**23a**) was obtained as a white solid. Mp: 125–128 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 7.82 (d, *J* = 7.6 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 6.13 (brs, 1H), 5.93 (brs, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 169.4, 135.1, 132.0, 128.9, 128.3; IR (KBr) v (cm<sup>-1</sup>): 3368, 3172, 2779, 1659, 1623, 1577, 1449, 1402, 1297, 1180, 1143, 1122, 1025, 918; GC-MS (EI, *m/z*): 121 [M<sup>+</sup>].

## The reduction of *N*,*N*,*N'*-triphenylhydrazine (24)

N,N,N'-Triphenylhydrazine was dissolved in THF. Aniline (2a) was obtained as colorless oil, and

diphenylamine (13a) was obtained as a white solid.

#### The reduction of *N*-methyl-*N*,*N'*-diphenylhydrazine (25)

*N*-Methyl-N,N'-diphenylhydrazine was dissolved in THF. Aniline (**2a**) was obtained as colorless oil, and *N*-methylaniline (**7a**) was obtained as colorless oil.

#### The reduction of *N*-phenyl-*N*,*N'*-dibenzylhydrazine (26)

*N*-Phenyl-*N*,*N*'-dibenzylhydrazine was dissolved in THF. *N*-benzylaniline (**10a**) was obtained as colorless oil, and benzylamine (**19b**) was obtained as colorless oil.

#### The reduction of *N*-benzyl-*N*,*N'*-diphenylhydrazine (27)

*N*-Benzyl-*N*,*N*'-diphenylhydrazine was dissolved in THF. Aniline (**2a**) was obtained as colorless oil, and *N*-benzylaniline (**10a**) was obtained as colorless oil.

## The reduction of *N*-allyl-*N*,*N'*-diphenylhydrazine (28)<sup>33</sup>

*N*-Allyl-*N*,*N*'-diphenylhydrazine was dissolved in THF. Aniline (**2a**) was obtained as colorless oil, and *N*-allylaniline (**28b**) was obtained as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 7.18 (t, *J* = 7.6 Hz, 2H), 6.72 (t, *J* = 7.6 Hz, 1H), 6.64 (d, *J* = 7.6 Hz, 2H), 5.92–6.01 (m, 1H), 5.29 (dd, *J* = 17.2 Hz, 1.6 Hz, 1H), 5.17 (dd, *J* = 10.4 Hz, 1.2 Hz, 1H), 4.03 (brs, 1H), 3.78 (d, *J* = 5.2 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 147.7, 135.2, 128.7, 117.0, 115.5, 112.6, 46.2; IR (KBr) v (cm<sup>-1</sup>): 3431, 3082, 3052, 3020, 2980, 2914, 2841, 1603, 1506, 1316, 1262, 1180, 994, 919, 749, 692; GC–MS (EI, *m/z*): 133 [M<sup>+</sup>]. HRMS (EI): calcd. for: C<sub>9</sub>H<sub>11</sub>N [M+1] 133.0891, found: 133.0891.

#### The reduction of *N*,*N*'-dimethyl-*N*,*N*'-diphenylhydrazine (29)

*N,N'*-Dimethyl-*N,N'*-diphenylhydrazine was dissolved in THF. *N*-methylaniline (**7a**) was obtained as colorless oil.

#### The reduction of *N*,*N*'-dibenzyl-*N*,*N*'-diphenylhydrazine (30)

*N,N'*-Dibenzyl-*N,N'*-diphenylhydrazine was dissolved in THF. *N*-benzylaniline (**10a**) was obtained as colorless oil.

#### The reduction of *N*,*N*,*N'*,*N'*-tetraphenylhydrazine (31)

N,N,N',N'-Tetraphenylhydrazine was dissolved in THF. Diphenylamine (13a) was obtained as a white solid.

#### The reduction of *N*-allyl-*N'*-methyl-*N*,*N'*-diphenylhydrazine (32)

N-Allyl-N'-methyl-N,N'-diphenylhydrazine was dissolved in THF. N-Methylaniline (7a) and N-allylaniline (28b) were obtained as colorless oils.

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## NMR spectra of hydrazines









































































NMR spectra of amine products



















































