Electronic Supplementary Material (ESI) for Green Chemistry.

Ni-catalyzed reductive amination of phenols with ammonia or amines into cyclohexylamines

Supporting information

1. General information

All chemicals were obtained from commercial sources and were used without further purification: toluene (≥99.8%, Acros Organics), methanol (>99.8%, VWR), 2-propanol (≥99.8%, Sigma Aldrich), *tert*-amyl alcohol (>98%, TCI Europe), *tert*-amyl methyl ether (>99%, Sigma Aldrich), cyclopentyl methyl ether (>99%, VWR), 2-methyltetrahydrofuran (≥99%, Sigma Aldrich), methylcyclohexane (>98%, Sigma Aldrich), phenol (>99%, Sigma Aldrich), *o*-cresol (≥99%, Sigma Aldrich), *m*-cresol (99%, Sigma Aldrich), *p*-cresol (99%, Alfa Aesar), 2-methoxyphenol (≥98%, Sigma Aldrich), 3-methoxyphenol (97%, Fisher Scientific), 4-methoxyphenol (>99%, TCI Europe), 4-*n*-propylphenol (98%, J&K Scientific), 4-*tert*-butylphenol (99%, Sigma Aldrich), diphenyl ether (99%, Acros Organics), benzyl phenyl ether (>98%, TCI Europe), bisfenol F (>99%, TCI Europe), NH_3 (gas, 99.98%, Air Liquide), 2-ethyl-1-hexylamine (98%, Sigma Aldrich), *n*-octylamine (99%, Sigma Aldrich), piperidine (99%, Acros Organics), pyrrolidine (99%, Sigma Aldrich), n-nonane (99%, Acros Organics), cyclohexanol (99%, Sigma Aldrich), cyclohexylamine (>99%, TCI Europe), Aniline (>98%, TCI Europe), $Ni(NO_3)_2.6H_2O$ (99%, Acros Organics), $Pd(NH_3)_4Cl_2.H_2O$ (≥99.99%, Sigma Aldrich), $RhCl_3.H_2O$ (38.5-45.5% Rh, Alfa Aesar), SiO_2 (Evonik, Aerosil 380), γ-Al_2O_3 (Alfa Aesar), Al_2O_3 (CONDEA Chemie, Puralox NGa-150), TiO_2 (rutile, Sigma Aldrich), ZrO_2 (Alfa Aesar, 1/8" pellets), SiO_2-Al_2O_3 (Grace Silica GmbH, 13% Al_2O_3), Nb_2O_5 (99.9%, Alfa Aesar), $Ba(NO_3)_2$ (>99%, Acros Organics), $Mg(NO_3)_2.6H_2O$ (99%, Acros Organics), $Ca(NO_3)_2.4H_2O$ (99%, Sigma Aldrich), polyvinyl alcohol (98-99% hydrolyzed, MW of 13.000 g/mol, Alfa Aesar), aqueous ammonia (28-30 wt% in H_2O, Chem-lab Analytical).

2. General procedures

2.1. Catalyst preparation

Self-prepared supported palladium and rhodium catalysts (5 wt% metal on support) were prepared by incipient wetness impregnation, in the same way as the supported Ni catalysts in this manuscript. In a typical procedure, the supporting material was impregnated with an aqueous solution of $Pd(NH_3)_4Cl_2.H_2O$ or $RhCl_3.H_2O$ in deionized water. The impregnated supports were then dried overnight at 60 °C, granulated to particles (250-500 μm), calcined at 400 °C (30 min, 2 °C/min, 100 mL/min O_2) and reduced at 400 °C (1 h, 2 °C/min, 100 mL/min H_2) in a quartz U-tube. All catalysts were stored under an Ar atmosphere.

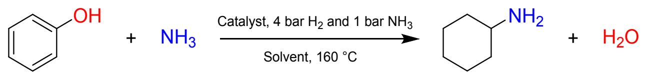
2.2. Catalyst characterization

Powder X-Ray diffraction (XRD) patterns were recorded on a Malvern PANalytical Empyrean diffractometer in reflection mode over a 5–45° 2θ range, using a PIXcel3D solid state detector and Cu anode (Cu Kα1: 1.5406 Å; Cu Kα2: 1.5444 Å). Scanning electron microscopy (SEM) was carried out on a Philips XL 30 FEG microscope equipped with a EDAX EDX system after coating the samples with Au. N_2 adsorption/desorption isotherms were measured with a Micromeritics 3Flex Surface Characterization Analyzer at -196 °C. Before the measurements, around 100 mg of sample was degassed under vacuum at 150 °C for 6 h. CO pulse titration experiments were performed using a Quantachrome ChemBET pulsar equipped with a TCD. Prior to each measurement, the catalyst (200 mg) was reduced in 5% H_2/Ar (20 mL/min) at 450 °C for 1 h. After purging with He (20 mL/min) at 450 °C for 30 min, the catalyst was exposed to pulses of CO (75 μL) in He (20 mL/min) at 40 °C.

3. Expanded catalyst screening

Like in the catalyst screening experiments with Ni, the activities of Pd and Rh were affected by the acidity of the supporting material. In order of increasing acidity (Al_2O_3 < ZrO_2 < SiO_2-Al_2O_3), phenol conversion dropped noticeably. While Rh displayed a comparable selectivity as Ni, non-negligible amounts of the secondary amines (selectivity of ≥ 20%) were observed for Pd, as described in prior research by Murahashi and co-workers.[1] Ru and Pt are expected to display similar trends as Rh and Pd, respectively, as studied in our previous work,[2] albeit at a lower phenol conversion.

Table S1. Expanded table for screening of supported catalysts for the direct amination of phenol with ammonia to cyclohexylamine.[a]



1a **2a** **3a**

Entry	Catalyst	Substrate	X[b] [%]	Y_{CHA} (S_{CHA})[b] [%]	Y_{CHOL} (S_{CHOL})[b] [%]	Y_{Sec} (S_{Sec})[b] [%]	Y_{An} (S_{An})[b] [%]	Y_{CHO} (S_{CHO})[b] [%]
1	Ni/$MgAl_2O_4$-800 °C	Phenol	57	51 (89)	6 (11)	-	-	-
2	Ni/Al_2O_3-600 °C	Phenol	27	26 (95)	1 (5)	-	-	-
3	Ni/Al_2O_3-1000 °C	Phenol	31	30 (97)	1 (3)	-	-	-
4[b]	Pd/SiO_2-Al_2O_3	Phenol	71	51 (71)	-	20 (28)	< 1 (1)	-
5[b]	Pd/Al_2O_3	Phenol	>99	74 (74)	-	19 (19)	7 (7)	-
6[b]	Pd/ZrO_2	Phenol	81	58 (72)	-	22 (27)	1 (1)	-
7[b]	Rh/SiO_2-Al_2O_3	Phenol	45	45 (99)	-	< 1 (1)	-	-
8[b]	Rh/Al_2O_3	Phenol	86	84 (98)	-	1 (2)	-	-
9[b]	Rh/ZrO_2	Phenol	66	65 (99)	1 (1)	-	-	-
10	Ni/Al_2O_3-800 °C	Cyclohexanone	>99	>99 (>99)	-	-	-	*substrate*
11[c]			92	81 (88)	11 (12)	-	-	*substrate*
12		2-Cyclohexen-1-one	>99	>99 (>99)	-	-	-	-
13[d]	Ni/Al_2O_3-800 °C	Phenol	81	-	62 (76)	-	-	19 (24)
14[d]		Cyclohexanol	17	-	*substrate*	-	-	17 (>99)
15		Cyclohexanol	97	97 (>99)	*substrate*	-	-	-

[a] Reaction conditions: phenol (**1a**, 2 mmol) in toluene (20 mL), 10 mol% Ni (5 wt% Ni on support), 4 bar H_2 and 1 bar NH_3 (**2a**) for 3 h at 160 °C. CHA: cyclohexylamine (**3a**), CHOL: cyclohexanol, Sec: secondary amines (dicyclohexylamine and *N*-cyclohexylaniline). Conversions (X), yields (Y) and selectivities (S) were determined by GC-FID analysis with n-nonane as the external standard. [b] 5 mol% metal (5 wt% metal on support) for 1 h. [c] 1 h. [d] 0 bar NH_3 for 3 h.

4. Solubility of NH_3

In order to determine the ammonia concentration in the liquid phase at a certain NH_3 partial pressure, a calibration curve was made. For this, the reactor was loaded with 10 mol% catalyst, phenol (2 mmol) in 20 mL of the solvent and a magnetic stirring rod, analogous to the procedure for the amination reactions. After purging three times with N_2 and NH_3, the reactor was pressurized with 1 bar of N_2 and weighed, m(N_2). Next, the reactor was loaded with different NH_3 partial pressures and weighed again, m(N_2 + xNH_3). Finally, the ammonia concentration can be obtained by subtracting the weight of NH_3 in the gas phase (approximated by the ideal gas law) from the total NH_3 weight, m(N_2 + xNH_3).

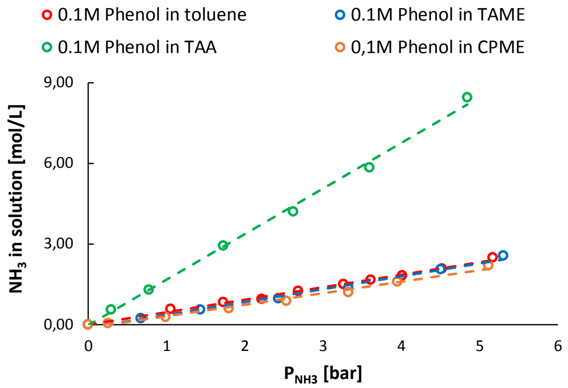


Figure S1. Solubility of NH_3 in different solvents (○ toluene, ○ TAA, ○ TAME, ○ CPME)

5. FTIR of aniline-saturated ZrO_2

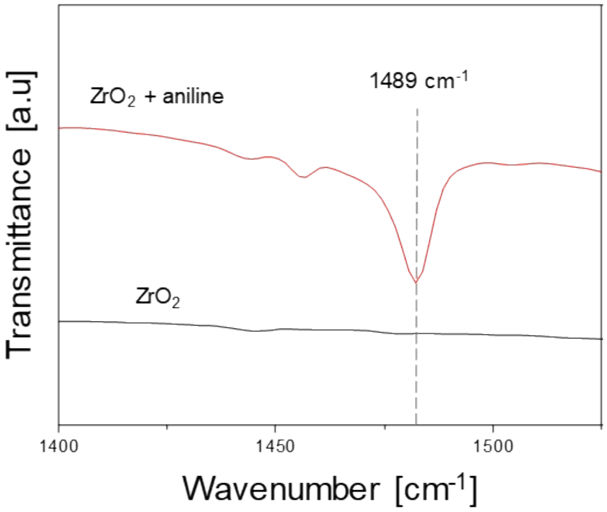


Figure S2. FTIR spectra of a ZrO_2 (black) and an aniline-saturated ZrO_2 sample (red) collected on a Bruker IFS 66 v/S Vacuum FTIR spectrometer.

6. ICP-OES analyses

Table S2. Ni-content of the reaction solution after recycling by ICP-OES analysis.

Reaction	Ni [ppm] [a] / Leaching [wt%] [b]
Fresh catalyst	0 / < 0.05
1st recycle	0 / < 0.05
2nd recycle	0 / < 0.05
3rd recycle	0 / < 0.05

[a] Ni content in the reaction solution determined by ICP-OES (detection limit for Ni of 5 ppb). [b] wt% Ni leaching with respect to the Ni content of the fresh catalyst.

7. CO pulse titration

Table S3. Metal dispersion (D) and average Ni particle size (d_{av}) determined by CO pulse titration.[a]

Reaction	D [%]	d_{av} [nm]
Fresh catalyst	12.9	6.5
1st recycle	12.1	6.9
2nd recycle	11.9	7.1
3rd recycle	11.3	7.4

[a] Assuming CO:Ni ratio of 1 and cubic Ni particles.

8. Catalyst characterization

8.1. Powder X-Ray diffraction (XRD)

For Ni/$MgAl_2O_4$, the characteristic peaks are present, as reported by Guo *et al*. (2004).[3] In the case of Ni/γ-Al_2O_3 and Ni/$MgAl_2O_4$, small NiO peaks are present.

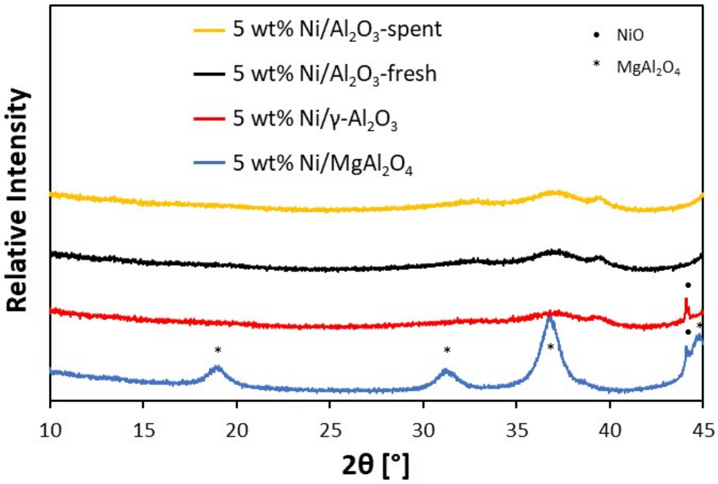


Figure S3. Powder X-Ray diffraction (XRD) patterns of Ni/Al_2O_3-fresh (black), Ni/Al_2O_3-spent (yellow), Ni/γ-Al_2O_3 (red) and Ni/$MgAl_2O_4$ (blue).

8.2. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX)

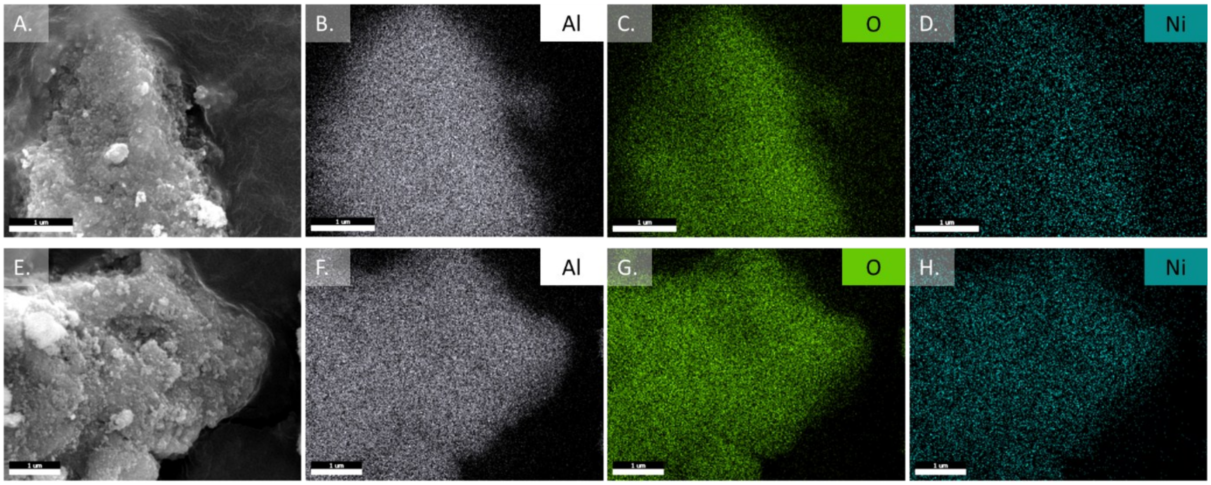


Figure S4. SEM images (A and E) and EDX elemental mapping (B-D and F-H) of 5 wt% Ni/Al_2O_3-fresh (A-D) and 5 wt% Ni/Al_2O_3-spent (E-H).

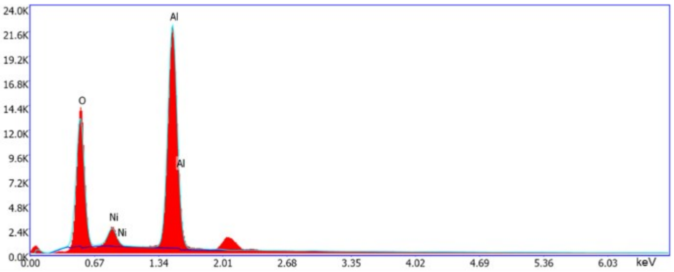


Figure S5. EDX spectrum of 5 wt% Ni/Al_2O_3-spent.

8.3. Scanning Transmission Electron Microscopy (STEM)

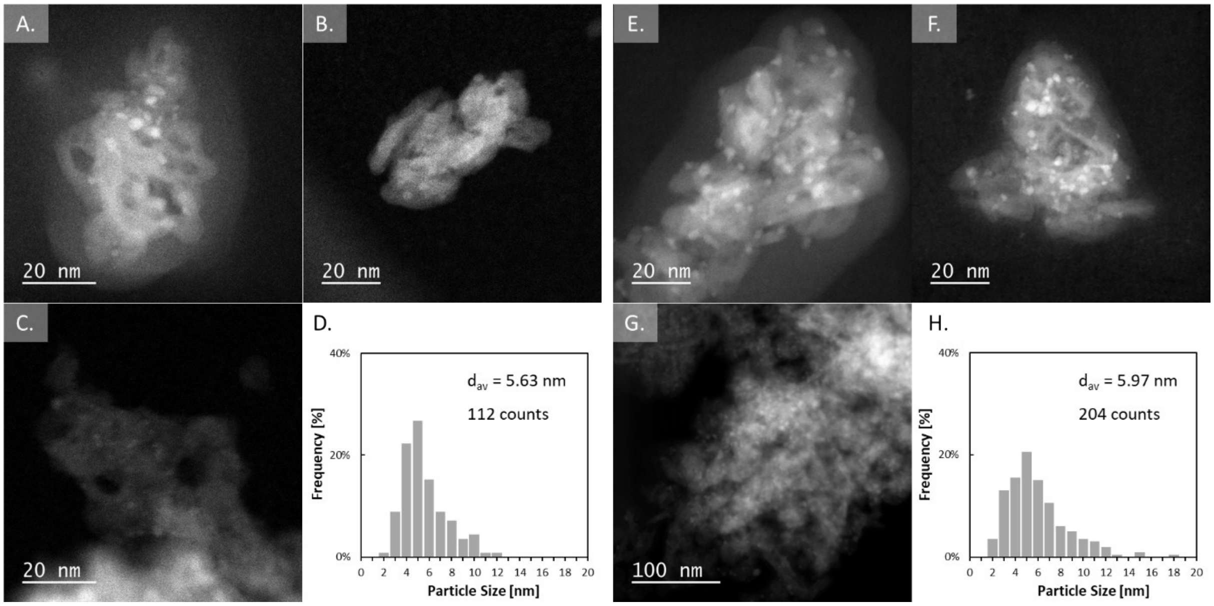


Figure S6. STEM images (A-C and E-H) and Ni particle distribution (D and H) of 5 wt% Ni/Al_2O_3-fresh (A-D) and 5 wt% Ni/Al_2O_3-spent (E-H).

8.4. N_2 physisorption

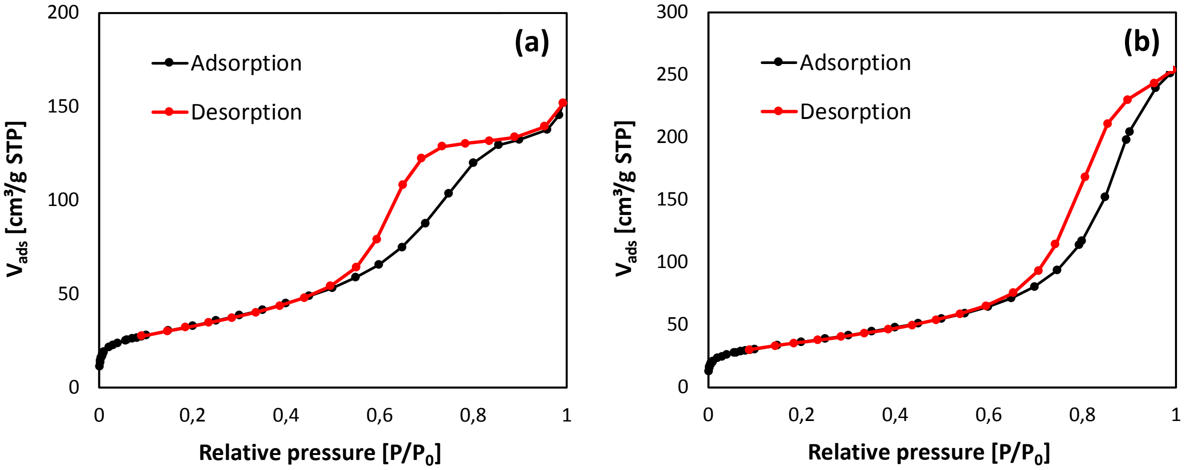


Figure S7. N_2 adsorption/desorption isotherms of (a) 5 wt% Ni/$MgAl_2O_4$ reduced at 600 °C (BET surface area = 120 m^2/g) and (b) 5 wt% Ni/Al_2O_3 reduced at 800 °C (BET surface area = 130 m^2/g).

9. Product analysis & identification

9.1. GC-FID

The reaction products were analyzed using a Shimadzu GC-2010 gas chromatograph instrument equipped with a AOC-20s Autosampler and AOC-20i Auto-injector. For every analysis, 1 mL of the reaction mixture was transferred together with *n*-nonane as external standard into a GC-vial (1.8 mL). The various reaction products were separated after 1 µL of the sample was injected via split-injection (30:1) at 315 °C on an Agilent CP-Sil 5 CB capillary column (length: 60 m; internal diameter: 0.32 mm and film thickness: 0.25 µm). The volatile components were carried through the column by a constant N_2 flow of 2.39 mL/min, before it reached a FID detector (Flame Ionisation Detector) at 325 °C. The temperature profile of the column is shown in the table below:

Step	Rate [°C/min]	Temperature [°C]	Hold-time [min]
1	-	70	7
2	1.5	100	-
3	20	320	5
Total time = 43 min			

The concentrations of different reaction products were obtained by the effective carbon number (ECN) concept, as described in a prior report,[4] with n-nonane as external standard. Conversion (X), yield (Y) and selectivity (S) of the products in all the reaction mixtures were calculated by normalizing the concentration of each product to the initial phenol concentration.

$$X\,(\%) = 100\,x\left(1 - \frac{[Phenol]}{[Phenol]_{t\,=\,0}}\right)$$

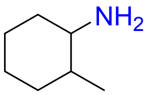
$$Y_{CHA}\,(\%) = \;100\,x\,\frac{[CHA]}{[Phenol]_{t\,=\,0}}$$

$$S_{CHA}\,(\%) = \;100\,x\,\frac{Y_{CHA}\,(\%)}{X\,(\%)}$$

9.2. GC-MS

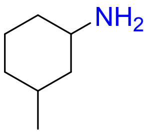
The different reaction products were identified using a Agilent 6890 gas chromatograph equipped with a HP-1 MS column (length: 30 m; internal diameter: 0.25 mm and film thickness: 0.25 µm) connected to a 5973 MSD mass spectrometer. The used instrumental parameters were identical to those for GC-FID analysis. The resulting fragmentation spectra were matched to those in databases, such as the database of the National Institute of Standards and Technology (NIST), resulting in the identification of all desired products in the reaction mixtures.

2-Methylcyclohexylamine (MW = 113.20 g/mol)



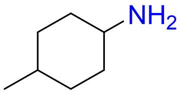
GC/MS (EI, 70 eV): m/z (rel. int., %): 54 (5), 56 (100), 57 (15), 67 (6), 70 (60), 84 (8), 113 (36).

3-Methylcyclohexylamine (MW = 113.20 g/mol)



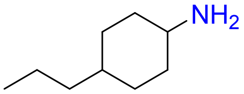
GC/MS (EI, 70 eV): m/z (rel. int., %): 53 (5), 56 (65), 57 (6), 70 (100), 71 (5), 81 (12), 96 (22), 98 (9), 113 (12).

4-Methylcyclohexylamine (MW = 113.20 g/mol)



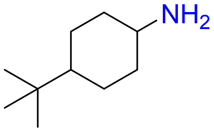
GC/MS (EI, 70 eV): m/z (rel. int., %): 56 (100), 57 (6), 67 (5), 81 (5), 84 (5), 113 (19).

4-*n*-Propylcyclohexylamine (MW = 141.25 g/mol)



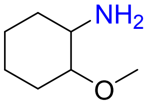
GC/MS (EI, 70 eV): m/z (rel. int., %): 55 (8), 56 (100), 57 (6), 67 (5), 70 (10), 81 (7), 82(7), 141 (13).

4-*tert*-Butylcyclohexylamine (MW = 155.28 g/mol)



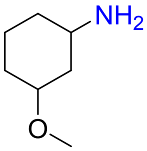
GC/MS (EI, 70 eV): m/z (rel. int., %): 55 (9), 56 (100), 57 (11), 67 (7), 69 (10), 81 (15), 84 (9), 98 (13), 123 (15), 140 (4), 155 (11).

2-Methoxycyclohexylamine (MW = 129.20 g/mol)



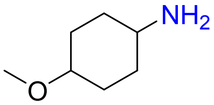
GC/MS (EI, 70 eV): m/z (rel. int., %): 55 (9), 56 (100), 57 (8), 58 (11), 67 (12), 69 (32), 70 (20), 71 (11), 79 (21), 82 (13), 86 (19), 96 (9), 98 (12), 99 (24)114 (49), 129 (13).

3-Methoxycyclohexylamine (MW = 129.20 g/mol)



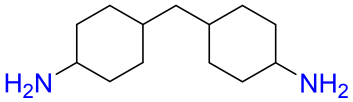
GC/MS (EI, 70 eV): m/z (rel. int., %): 56 (45), 58 (35), 69 (21), 82 (27), 86 (100), 96 (20), 97 (33), 98 (12), 112 (34), 114 (10), 129 (6).

4-Methoxycyclohexylamine (MW = 129.20 g/mol)



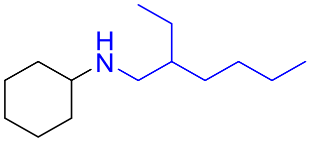
GC/MS (EI, 70 eV): m/z (rel. int., %): 56 (100), 57 (19), 59 (5), 68 (7), 69 (7), 73 (64), 79 (5), 82 (5), 97 (6), 112 (14), 129 (5).

4,4’-Diaminodicyclohexyl methane (H_{12}MDA) (MW = 210.36 g/mol)



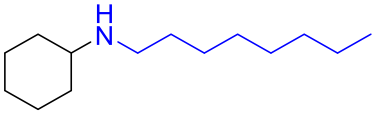
GC/MS (EI, 70 eV): m/z (rel. int., %): 55 (12), 56 (100), 57 (7), 67 (14), 69 (8), 79 (12), 81 (18), 82 (17), 95 (13), 96 (20), 97 (8), 99 (14), 110 (13), 112 (7) 138 (11), 147 (9), 152 (7), 164 (29), 176 (28), 192 (35), 193 (65), 194 (12), 210 (8).

***N*-(2-Ethyl-1-hexyl)-cyclohexylamine** (MW = 211.39 g/mol)



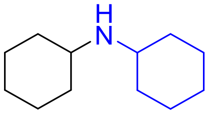
GC/MS (EI, 70 eV): m/z (rel. int., %): 55 (7), 56 (6), 57 (2), 70 (3), 82 (2), 83 (5), 112 (100), 113 (10), 168 (12), 211 (4).

***N*-Octyl-cyclohexylamine** (MW = 211.39 g/mol)



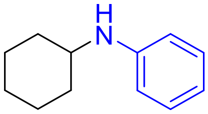
GC/MS (EI, 70 eV): m/z (rel. int., %): 55 (11), 56 (11), 70 (6), 83 (5), 112 (83), 113 (7), 140 (11), 168 (100), 169 (14), 211 (11).

Dicyclohexylamine (MW = 181.32 g/mol)



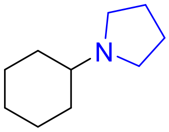
GC/MS (EI, 70 eV): m/z (rel. int., %): 55 (7), 56 (12), 138 (100), 139 (11), 152 (5), 181 (16).

***N*-Cyclohexylaniline** (MW = 175.27 g/mol)



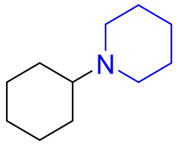
GC/MS (EI, 70 eV): m/z (rel. int., %): 51 (5), 55 (5), 65 (8), 66 (5), 77 (12), 79 (7), 91 (17), 92 (14), 93 (16), 104 (9), 106 (9), 118 (18), 119 (18), 132 (100), 133 (11), 152 (6), 153 (5), 174 (7), 175 (33), 176 (5).

***N*-Pyrrolidine-cyclohexylamine** (MW = 153.26 g/mol)



GC/MS (EI, 70 eV): m/z (rel. int., %): 69 (5), 96 (10), 97 (11), 110 (100), 111 (9), 153 (18).

***N*-Piperidine-cyclohexylamine** (MW = 167.29 g/mol)



GC/MS (EI, 70 eV): m/z (rel. int., %): 55 (5), 96 (8), 110 (7), 124 (100), 125 (11), 167 (16).

References

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