# *Supporting Information*

## Ammonolytic transfer dehydrogenation of amines and amides: a versatile method to valorize nitrogen compounds to nitriles

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# 1. Experimental details

## 1.1. Materials

With the exception of the long-chain polyamide samples, all materials were used as obtained commercially.

## 1.2. Reactions

Reactions were performed in a 25 mL pressure Parr batch reactor. In a typical transfer dehydrogenation reaction, the reactor is filled with an amine substrate (e.g. 1 mmol octylamine), Pt/C catalyst (2.5 mol% Pt), dodecane (internal standard, 20 µL) and cyclopentyl methyl ether (CPME, 10 mL). Next, the reactor is sealed, purged, pressurized with 3 bar $NH_3$ and 10 bar $H_2$, and kept at the desired temperature (160°C, stirred at 830 rpm) for 15 minutes. In this pre-activation step, a passive layer of platinum oxide is removed from the $Pt^0$ surface. After a cool-down period, the reactor is depressurized and subsequently repressurized with the desired amount of $NH_3$ and ethylene ($C_2H_4$) gas. After an appropriate reaction time at a temperature of typically 200°C, the reactor is cooled down in an ice bath and the pressure is released. If the substrate was a polyamide, 10 mL ethanol was added to the reaction mixture after which the reactor was resealed and stirred for 30 minutes to redissolve any monomer products. The reaction mixture is then transferred to one or more glass reaction vials (11 mL) which is/are then sealed and centrifuged. The mixture is analyzed via GC, GC-MS and/or NMR.

## 1.3. Product analysis and identification

The crude reaction mixtures (described in section 1.2) were quantitatively analysed by gas chromatography (GC). A few samples were additionally checked via nuclear magnetic resonance (NMR) spectroscopy. NMR samples were prepared by mixing 275 µL of the reaction mixture with 275 µL methanol-d4. $^1$H-NMR spectra were recorded on a Bruker Ascend 400 MHz spectrometer equipped with a Bruker Ascend$^{TM}$ 400 magnet, a 5 mm PABBO BB/19F-1H/D probe and a sample case. Aside from GC and NMR, the products were also identified by gas chromatography coupled to mass spectrometry (GC-MS) with an Agilent 6890 GC, equipped with a HP-5ms column, coupled to a 5973 MSD mass spectrometer. The gas phase was analyzed via IR spectroscopy using a Gasmet DX4000 FTIR gas analyzer. The IR data were processed with Calcmet Standard software version 12.161.

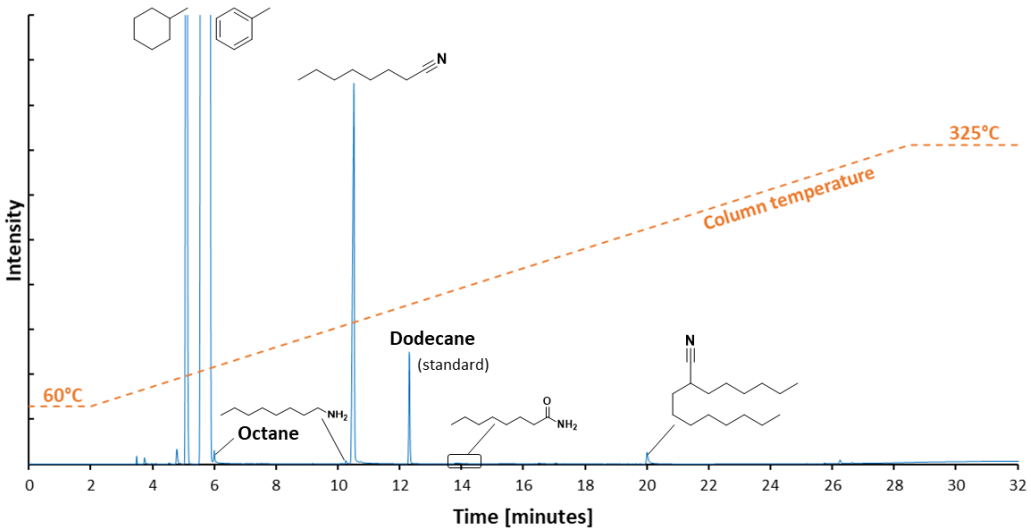



**Figure S 1** — GC chromatogram of a crude reaction mixture after a transfer-dehydrogenation reaction of n-octylamine reaching nearly complete conversion.

## 1.4. Catalyst synthesis

$Nb_2O_5$ was hydrothermally synthesized as described in a previous report by Coeck *et al.*[(1)] To a glass-lined Parr reactor (600 mL) 15 g ammonium niobium oxalate hydrate ($C_4H_4NNbO_9.xH_2O$) was added along with 300 mL deionized water. The reactor was sealed and stirred (500 rpm) for 3 days at 175°C. The resulting precipitate was isolated via filtration and excessively washed with deionized water. Instead of pure white, the precipitate had a very light pale yellow color due to some metal ions leaching from the stirrer and being incorporated into the $Nb_2O_5$ structure. This HT synthesis method was repeated 2 more times and the crude $Nb_2O_5$ from all three runs was combined. Any metal ions on the outer surface of the crude $Nb_2O_5$ were leached off by stirring the powder in a solution of 5 g citric acid in 250 mL deionized water at 80°C overnight. The wet powder was isolated via centrifugation, decanted and excessively washed with deionized water. After drying the powder overnight at 80°C, the material was calcined in air at 400°C for 4 h after which the $Nb_2O_5$ (HT bulk) was ready to use.

$Pt/Nb_2O_5$, $Pt/SiO_2$ and $Pd/Nb_2O_5$ were prepared via incipient wetness impregnation. In a typical synthesis, the appropriate amount of $[Pt(NH_3)_4](NO_3)_2$ or $[Pd(NH_3)_4]Cl_2{\cdot}H_2O$ was dissolved in water and mixed into the catalyst support (i.e. *ortho*-$Nb_2O_5$ or $SiO_2$). Next, the resulting pre-catalyst is dried overnight in an oven at 80°C, after which the material is granulated (250-500 µm). Finally, in a quartz U-tube, the material is calcined in oxygen at 400°C (2°C $min^{-1}$, 100 mL $min^{-1}$ $O_2$, for 1 h) followed by a reduction at the same temperature (400°C, 2°C $min^{-1}$, 100 mL $min^{-1}$ $H_2$, for 1 h).

### 1.5. Catalyst and polyamide characterization

*Ortho*-$Nb_2O_5$ was characterized with X-ray powder diffraction (XRD). Any XRD measurements were performed with the Malvern PANalytical Empyrean equipped with a Cu X-ray tube and a Pixcel3D detector. Additional characterization of $Nb_2O_5$ can be found in our previous report.(1) CO adsorption experiments were performed to determine the dispersion of the supported Pt nanoparticles. The experiments were performed with a ChemBet Pulsar TPR/TPD. Before every measurement, the catalyst was first pre-treated with $H_2$ at 200°C for approximately an hour. Next, the samples were cooled to room temperature and CO and He were then alternately pulsed over the sample. An adsorption stoichiometry of 0.5 molecules of CO per Pt atom is assumed.(2) Using a Bruker Alpha benchtop infrared spectrometer, with a resolution of 2 $cm^{-1}$ and spectral range of 4000-500 $cm^{-1}$, ATR-FTIR spectra of Pt/C samples were measured. The data were exported and processed in Excel. $N_2$ physisorption measurements were performed using a Micromeritics 3Flex surface analyzer at -196°C. Before the measurements, around 80 mg of each sample was degassed at 200°C for 3 h under vacuum. Polyamide samples were characterized via thermogravimetric analysis (TGA). A small amount of polymer (5 - 25 mg) was placed in a STA 449F3 Jupiter (Netzsch, 2017) TGA. Subsequently, the sample was degassed under a continuous flow of $N_2$, after which it was heated under air from 35°C to 800°C at a heating rate of 10°C/min.

### 1.6. Recycling test

After each reaction, the catalyst was separated from the reaction mixture and washed 4 times with ethanol. The catalyst was dried in an oven at 100°C for 4 hours and was reused afterwards. Small quantities of catalyst (< 5%) that were lost in the process, were replenished with fresh catalyst.

## 2. Thermodynamic calculations for the dehydrogenation of amines

Based on the thermodynamic values described by Stull *et al.*,(3) Ghahremanpour *et al.*(4) and the NIST webbook database(5), the temperature dependent equilibria were calculated, as expressed in the Gibbs free energy of the reaction and corresponding equilibrium constant. The values from the calculations are listed in Table S 1 . All calculations were performed with the assumption $\Delta_fG°_{gas} \approx \Delta_fG°_{liquid} \approx \Delta_fG°_{solid}$ and the formulas: $\Delta G° = \Delta H° - T\Delta S°$

$$\Delta G° = -RT.\ln(K_{298°C})$$

$$\ln\left(\frac{K_1}{K_2}\right) = -\frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

**Table S 1** — Thermodynamic values of organic model compounds for (ammonolytic) dehydrogenation reactions (values determined at 298K).

| | $\Delta_fH°$[a] | state[b] | S°[c] | State[d] | $\Delta_fG°$[e] | State[f] |
|---|---|---|---|---|---|---|
| $NH_3$ | -46.1 kJ.mol$^{-1}$ | g | 193 J.mol$^{-1}$K$^{-1}$ | n.d. | -16.5 kJ.mol$^{-1}$ | g |
| Ethylamine | -46 kJ.mol$^{-1}$ | g | 286.2 J.mol$^{-1}$K$^{-1}$ | g | 37.3 kJ.mol$^{-1}$ | g |
| Diethylamine | - 72.4 kJ.mol$^{-1}$ | g | 354.35 J.mol$^{-1}$K$^{-1}$ | g | 72.1 kJ.mol$^{-1}$ | g |
| Triethylamine | - 99.6 kJ.mol$^{-1}$ | g | 277.4 J.mol$^{-1}$K$^{-1}$ | g | 110.3 kJ.mol$^{-1}$ | g |
| Acetonitrile | 40.6 kJ.mol$^{-1}$ | L | 149.6 J.mol$^{-1}$K$^{-1}$ | L | 86.5 kJ.mol$^{-1}$ | L |
| Ethylene | 52,5 kJ.mol$^{-1}$ | g | 219,3 J.mol$^{-1}$K$^{-1}$ | g | n.d. | n.d. |
| Ethane | - 84.5 kJ.mol$^{-1}$ | g | 231,65 J.mol$^{-1}$K$^{-1}$ | g | - 33 kJ.mol$^{-1}$ | g |
| Benzene | 82.8 kJ.mol$^{-1}$ | L | 269,8 J.mol$^{-1}$K$^{-1}$ | L | 129,7 kJ.mol$^{-1}$ | L |
| Cyclohexane | -156,2 kJ.mol$^{-1}$ | L | 206,7 J.mol$^{-1}$K$^{-1}$ | L | 26,7 kJ.mol$^{-1}$ | L |
| C (grafite) | 0 kJ.mol$^{-1}$ | s | 5.7 J.mol$^{-1}$K$^{-1}$ | s | n.d. | n.d. |
| $N_2$ | 0 kJ.mol$^{-1}$ | g | 191.5 J.mol$^{-1}$K$^{-1}$ | g | n.d. | n.d. |
| $H_2$ | 0 kJ.mol$^{-1}$ | g | 131 J.mol$^{-1}$K$^{-1}$ | g | n.d. | n.d. |
| $O_2$ | 0 kJ.mol$^{-1}$ | g | 205 J.mol$^{-1}$K$^{-1}$ | g | n.d. | n.d. |

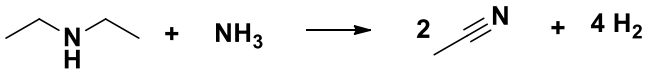
Values in **blue** are calculated values based on the other thermodynamic values. n.d. meaning not determined. [a]$\Delta_fH°$= Standard enthalpy of formation. [b]state for the $\Delta_fH°$ value with s=solid, L=liquid, g=gas. [c]S°= Standard molar entropy. [d]state for the S° value with L=liquid or g=gas. [e]$\Delta_fG°$= Standard Gibbs free energy of formation. [f]state for the ΔfG° value with L=liquid or g=gas.[g]

Ammonolysis of secondary amines

| $\Delta H°^{a}$ | $\Delta G°^{b}$ | $K^{c}$ | $\Delta G°_{200°C}{}^{d}$ | $K_{200°C}{}^{e}$ |
|---|---|---|---|---|
| 26.5 kJ.mol$^{-1}$ | 19 kJ.mol$^{-1}$ | 0.00047 | **14.6 kJ.mol$^{-1}$** | **0.024** |

[a]ΔH°= Standard (reaction) enthalpy of formation. [b]ΔG°= Standard (reaction) Gibbs free energy. [c]K=reaction equilibrium constant at 25°C. [d]ΔG°= (reaction) Gibbs free energy at 200°C. [e]K=reaction equilibrium constant at 200°C.

Acceptorless ammonolytic dehydrogenation

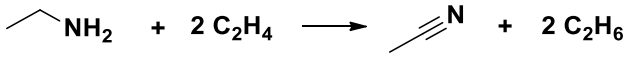


| $\Delta H°^{a}$ | $\Delta G°^{b}$ | $K^{c}$ | $\Delta G°_{200°C}{}^{d}$ | $K_{200°C}{}^{e}$ |
|---|---|---|---|---|
| 199.6 kJ.mol$^{-1}$ | 117.4 kJ.mol$^{-1}$ | 2.7*10$^{-21}$ | **69 kJ.mol$^{-1}$** | **2.4*10$^{-8}$** |

[a]ΔH°= Standard (reaction) enthalpy of formation. [b]ΔG°= Standard (reaction) Gibbs free energy. [c]K=reaction equilibrium constant at 25°C. [d]ΔG°= (reaction) Gibbs free energy at 200°C. [e]K=reaction equilibrium constant at 200°C.

Ammonolytic transfer dehydrogenation

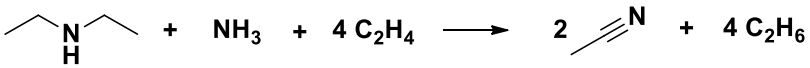
A) Ethylamine with ethylene



| $\Delta H°^{a}$ | $\Delta G°^{b}$ | $K^{c}$ | $\Delta G°_{200°C}{}^{d}$ | $K_{200°C}{}^{e}$ |
|---|---|---|---|---|
| - 187.4 kJ.mol$^{-1}$ | - 324.7 kJ.mol$^{-1}$ | 7.7*10$^{56}$ | - 405.3 kJ.mol$^{-1}$ | 5.5*10$^{44}$ |

[a]ΔH°= Standard (reaction) enthalpy of formation. [b]ΔG°= Standard (reaction) Gibbs free energy. [c]K=reaction equilibrium constant at 25°C. [d]ΔG°= (reaction) Gibbs free energy at 200°C. [e]K=reaction equilibrium constant at 200°C.

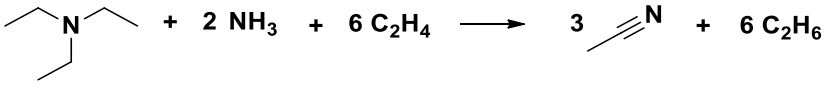
B) Diethylamine with ethylene



| $\Delta H°^{a}$ | $\Delta G°^{b}$ | $K^{c}$ | $\Delta G°_{200°C}{}^{d}$ | $K_{200°C}{}^{e}$ |
|---|---|---|---|---|
| - 348.3 kJ.mol$^{-1}$ | -289 kJ.mol$^{-1}$ | 4.3*10$^{50}$ | - 254.2 kJ.mol$^{-1}$ | 1.2*10$^{28}$ |

[a]ΔH°= Standard (reaction) enthalpy of formation. [b]ΔG°= Standard (reaction) Gibbs free energy. [c]K=reaction equilibrium constant at 25°C. [d]ΔG°= (reaction) Gibbs free energy at 200°C. [e]K=reaction equilibrium constant at 200°C.

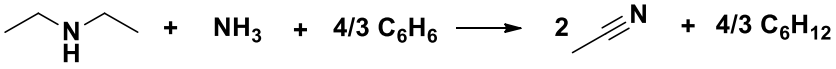
C) Triethylamine with ethylene



| $\Delta H°^{a}$ | $\Delta G°^{b}$ | $K^{c}$ | $\Delta G°_{200°C}{}^{d}$ | $K_{200°C}{}^{e}$ |
|---|---|---|---|---|
| - 508.3 kJ.mol$^{-1}$ | - 466.5 kJ.mol$^{-1}$ | 5.3*10$^{81}$ | - 441.9 kJ.mol$^{-1}$ | 6.1*10$^{48}$ |

[a]ΔH°= Standard (reaction) enthalpy of formation. [b]ΔG°= Standard (reaction) Gibbs free energy. [c]K=reaction equilibrium constant at 25°C. [d]ΔG°= (reaction) Gibbs free energy at 200°C. [e]K=reaction equilibrium constant at 200°C.

B) Diethylamine with benzene



| $\Delta H°^{a}$ | $\Delta G°^{b}$ | $K^{c}$ | $\Delta G°_{200°C}{}^{d}$ | $K_{200°C}{}^{e}$ |
|---|---|---|---|---|
| - 119 kJ.mol$^{-1}$ | - 20 kJ.mol$^{-1}$ | 3.1*10$^{3}$ | **38.2 kJ.mol$^{-1}$** | **6.1*10$^{-5}$** |

[a]ΔH°= Standard (reaction) enthalpy of formation. [b]ΔG°= Standard (reaction) Gibbs free energy. [c]K=reaction equilibrium constant at 25°C. [d]ΔG°= (reaction) Gibbs free energy at 200°C. [e]K=reaction equilibrium constant at 200°C.

## 3. Additional (ammonolytic) transfer dehydrogenation experiments

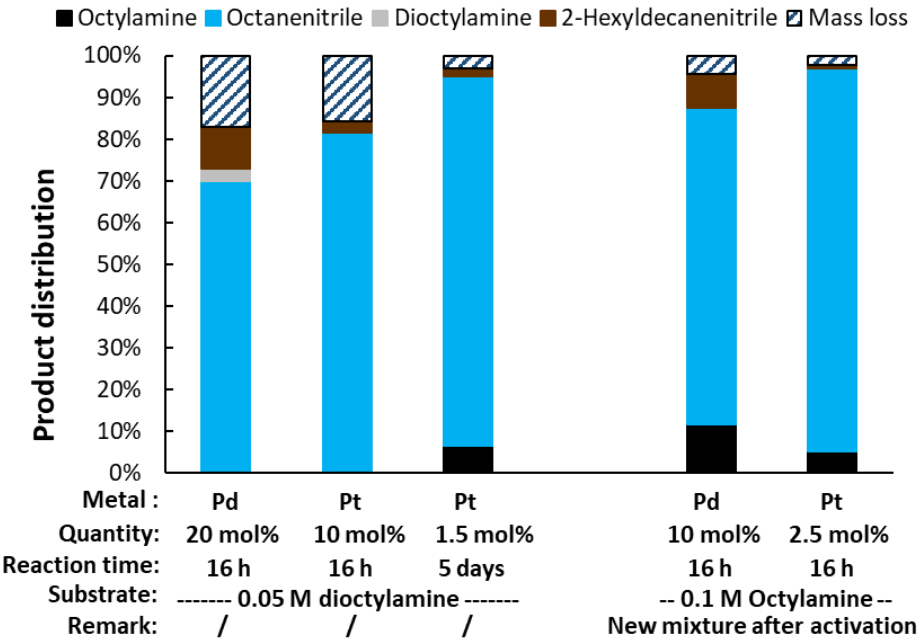
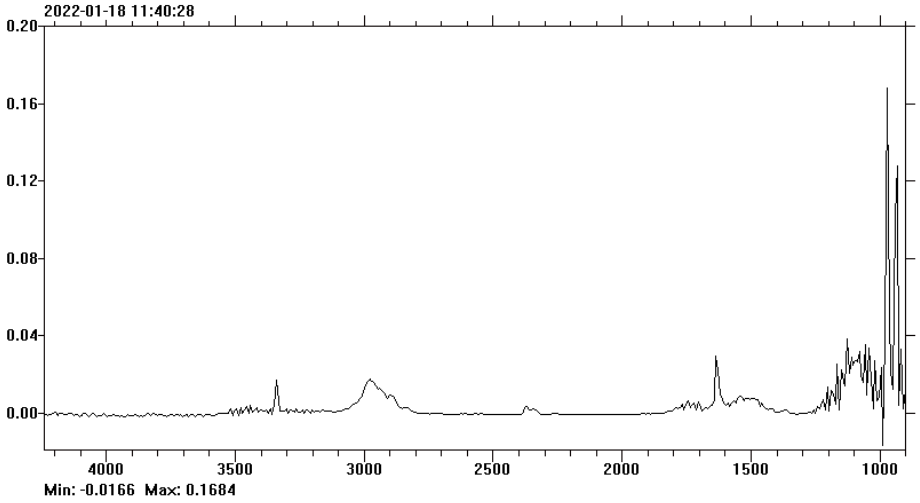



**Figure S 2** — The ammonolytic transfer dehydrogenation of amines to the corresponding nitriles. Reaction conditions: 200°C, 6 bar $NH_3$, 1 bar ethylene, noble metal catalyst, dodecane (20 µL), CPME (10 mL). Before the reaction, the catalysts were pre-activated under 10 bar $H_2$, at 160°C for 15 minutes.




Analysis Results - DEFAULT_V12.LIB: RC_test1_69071.SPE

| Ch | Component | Concentration | Unit | Ch(A) | Ch(M) | Compensation | Range | Residual |
|---|---|---|---|---|---|---|---|---|
| 4 | Methane CH4 | 0.00 | ppm | | | wet | 100 | 0.0047 |
| 8 | Ammonia NH3 | 140.56 | ppm | | | wet | 100 | 0.0082 |
| 9 | Ethane C2H6 | 9.21 | ppm | | | wet | 100 | 0.0022 |
| 10 | Ethylene C2H4 | 2.97 | ppm | | | wet | 100 | 0.0079 |
| 14 | Isobutene | 0.00 | ppm | | | wet | 100 | 0.0082 |
| 15 | cis-2-Butene | 0.11 | ppm | | | wet | 100 | 0.0082 |
| 16 | trans-2-Butene | 0.00 | ppm | | | wet | 100 | 0.0080 |
| 17 | 1-Butene | 0.00 | ppm | | | wet | 100 | 0.0081 |
| 19 | Butane C4H10 | 5.01 | ppm | | | wet | 100 | 0.0022 |

**Figure S 3** — FTIR analysis of gas phase after an (ammonolytic) transfer-hydrogenation reaction. Top: crude FTIR spectrum. Bottom: analysis of the FTIR spectrum.

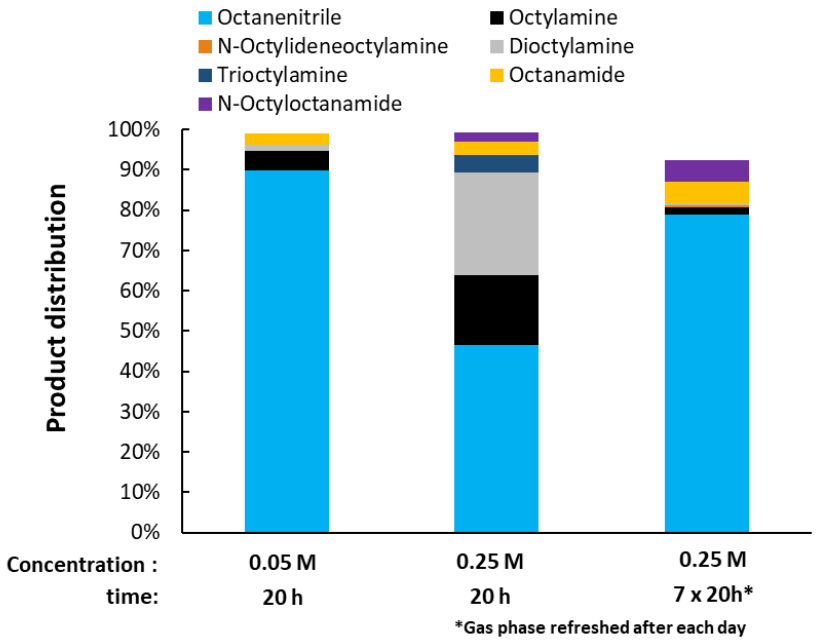



**Figure S 4** — The ammonolytic transfer dehydrogenation of dioctylamine with variable amine concentration. Reaction conditions: dioctylamine, 200°C, 6 bar $NH_3$, 2 bar ethylene, 2.5 mol% Pt (commercial Pt/C, 5 wt% Pt), dodecane (20 µL), CPME (10 mL). Before the reaction, the catalysts were pre-activated under 10 bar $H_2$, 1 bar $NH_3$, at 160°C for 15 minutes.

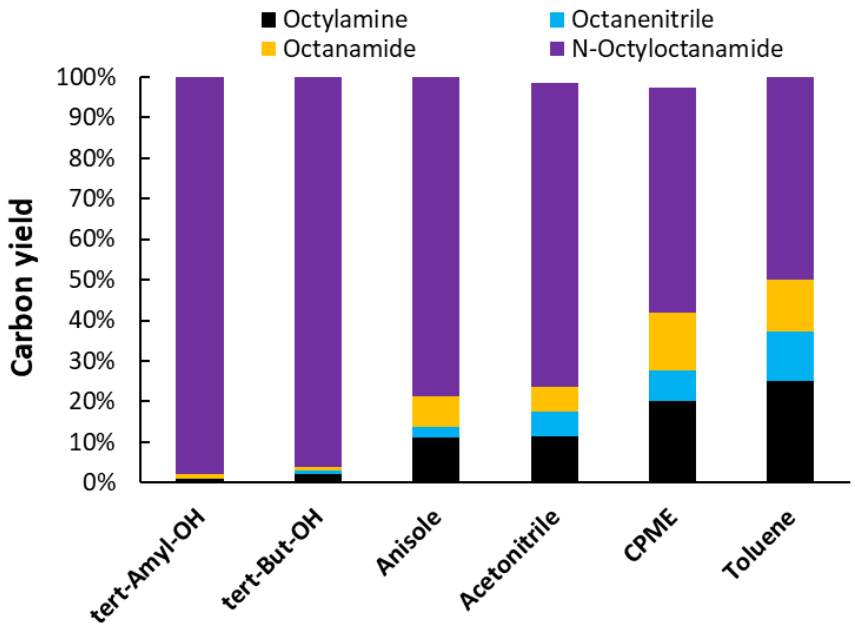



**Figure S 5** — Ammonolysis of *N*-octyloctanamide with *ortho*-$Nb_2O_5$ catalyst. Reaction conditions: *N*-octyloctanamide (0.5 mmol), 200°C, 6 bar $NH_3$, $Nb_2O_5$-catalyst, dodecane (20 µL), solvent (10 mL), 5 hours. tert-Amyl-OH: *tert*-amylalcohol. tert-But-OH: *tert*-butylalcohol.

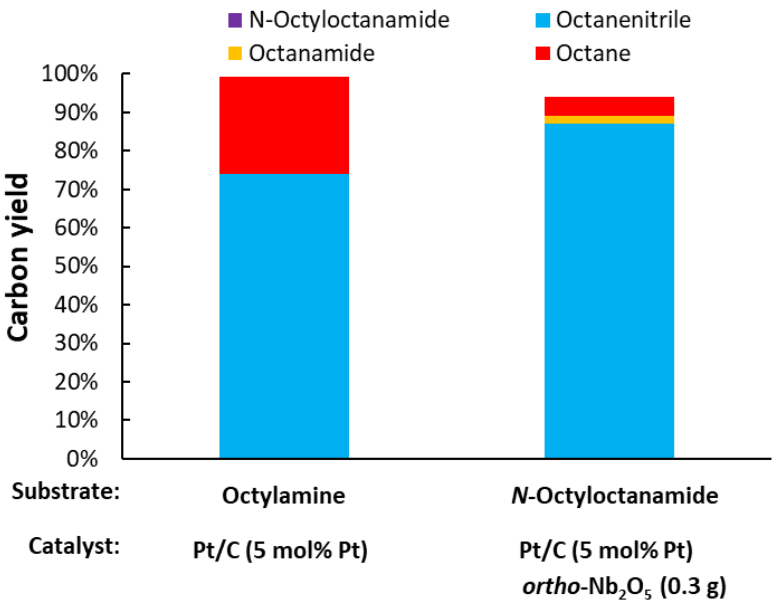



**Figure S 6** — (Ammonolytic) transfer dehydrogenation of different substrates at high temperature (i.e. 250°C) with pulsed additions of ethylene in $N_2$. Reaction conditions: *N*-octyloctanamide (0.5 mmol) or octylamine (1 mmol), 250°C, 6 bar $NH_3$, catalysts as specified in figure, dodecane (20 µL), toluene (10 mL), 7.5 hours. Over the course of the reactions, every half hour the pressure inside the reactor was increased with approximately 1.5 bar, by adding a pulse of 15% ethylene in $N_2$. Before the reaction, the catalysts were pre-activated under 10 bar $H_2$, 1 bar $NH_3$, at 160°C for 15 minutes.

## 4. Catalyst characterization

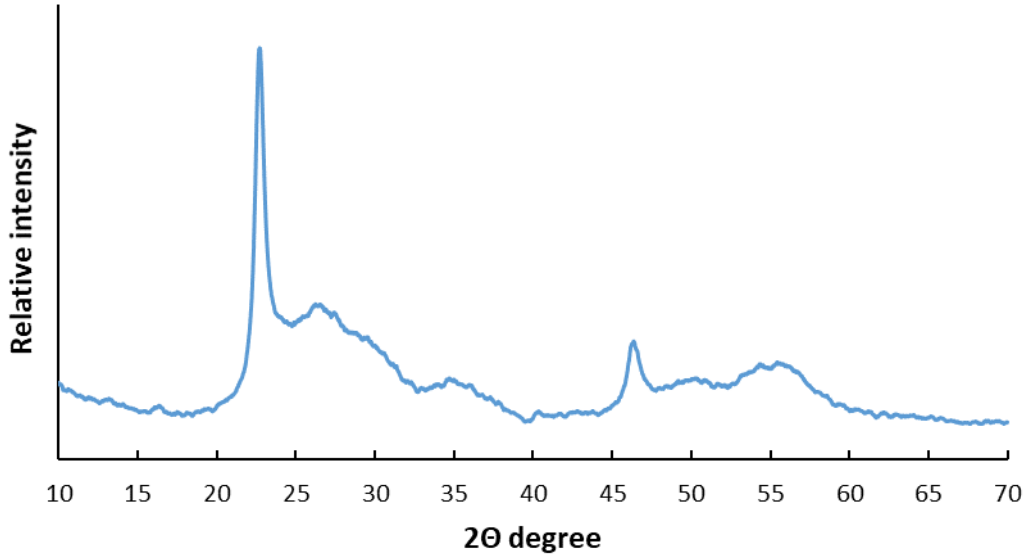



**Figure S 7** — XRD diffractogram of the synthesized $Nb_2O_5$. The diffractogram matches the pattern of a deformed orthorhombic structure for $Nb_2O_5$.

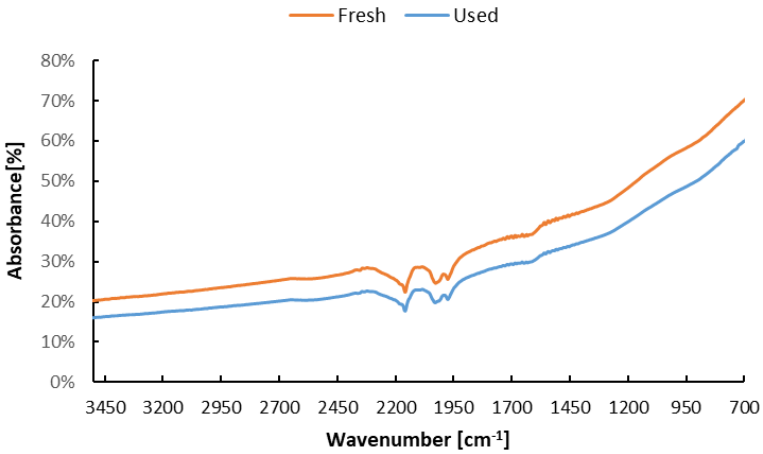



**Figure S 8** — ATR-FTIR spectrum of Pt/C before and after an ammonolytic transfer-hydrogenation reaction.

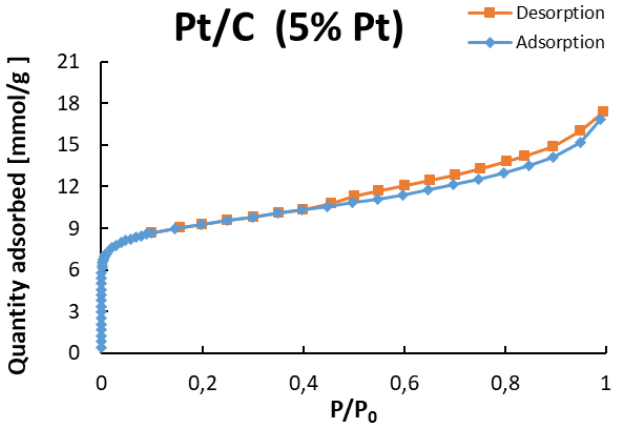



**Figure S 9** — $N_2$ adsorption and desorption isotherm of Pt/C (5wt% Pt). BET surface area of Pt/C (5wt% Pt) is 669 m²/g.

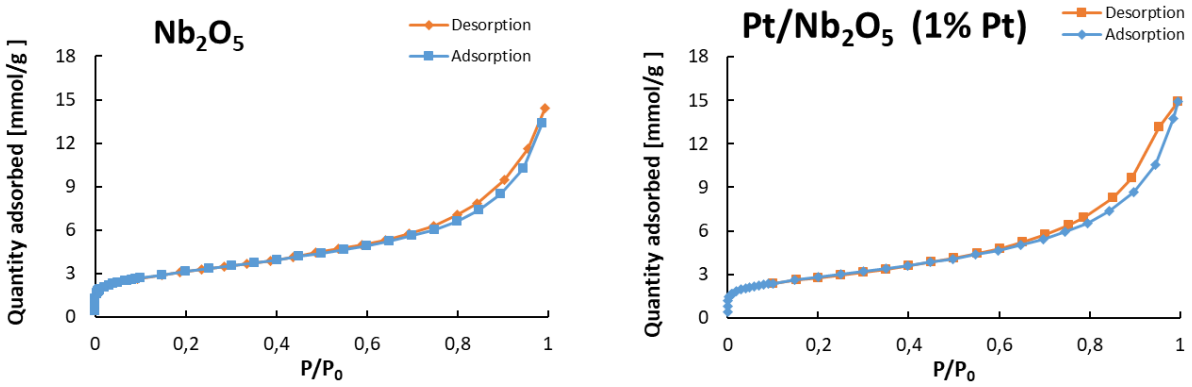



**Figure S 10** — $N_2$ adsorption and desorption isotherm of *ortho*-$Nb_2O_5$ (left) and Pt/$Nb_2O_5$ (1wt% Pt; right). BET surface area of *ortho*-$Nb_2O_5$ (left) and Pt/$Nb_2O_5$ (1wt% Pt) are respectively 245 m²/g and 223 m²/g.

## 5. Characterization of the polyamide samples

Samples of PA11 and PA12 were provided by Arkema and purified as we previously reported.[1]

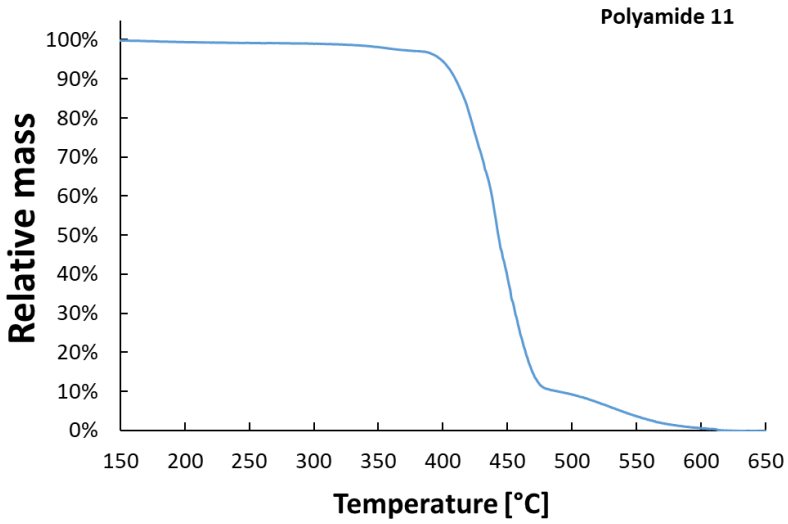



**Figure S 11** — TGA analysis of a purified industrial sample of polyamide 11.

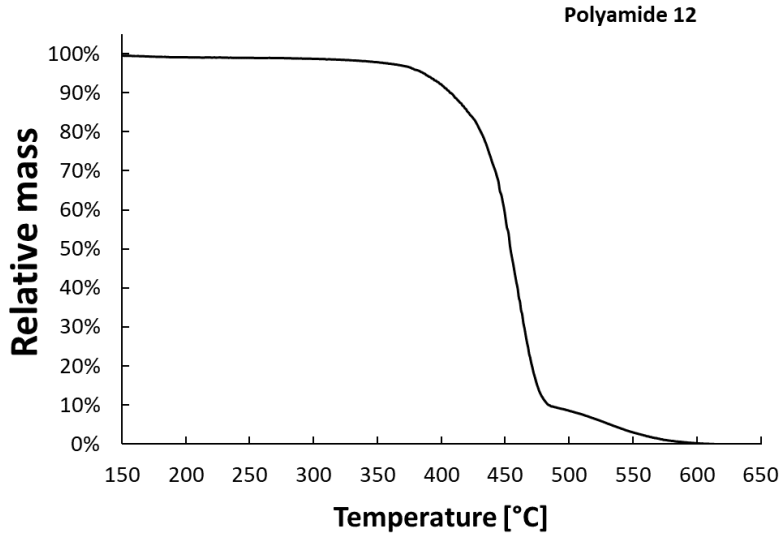



**Figure S 12** — TGA analysis of a purified industrial sample of polyamide 12.

## 6. Substrate scope investigation

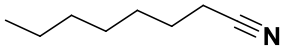
**Table S 2 –** Full list of substrate scope investigation. Exact reaction conditions are shown in the main text.

| | Substrate | Products distribution (yield)[a] |
|---|---|---|
| 1. | Hexylamine | Hexanenitrile (91%), Hexylamine (4%), Hexanamide (3%). |
| 2. | Octylamine | Octanenitrile (93%), Octylamine (4%), 2-Hexyldecanenitrile (1%). |
| 3. | Dodecylamine | Dodecanenitrile (88%), Dodecylamine (7%). |
| 4. | Hexahydrobenzylamine | Cyclohexanecarbonitrile (82%), Hexahydrobenzylamine (11%). |
| 5. | Dihexylamine | Hexanenitrile (81%), Hexylamine (8%), Dihexylamine (2%), Hexanamide (3%). |
| 6. | Dioctylamine | Octanenitrile (90%), Octylamine (5%), 2-Hexyldecanenitrile (1%). |
| 7. | Didodecylamine | Dodecanenitrile (94%), dodecanamide (1%). |
| 8. | Trihexylamine | Hexanenitrile (93%), Hexanamide (2%). |
| 9. | Trioctylamine | Octanenitrile (92%), Octylamine (1%), 2-Hexyldecanenitrile (2%). |
| 10. | *N,N*-Dimethylhexylamine | Hexanenitrile (6%), Hexylamine (5%), *N,N*-Dimethylhexylamine (67%), *N*-Methylhexylamine (11%). |
| 11. | Tris(2-ethylhexyl)amine | 2-Ethylhexylamine (4%), 2-Ethylhexanenitrile (18%), Bis(2-ethylhexyl)amine (10%), Tris(2-ethylhexyl)amine (69%). |
| 12. | Tris[2-(2-methoxyethoxy)-ethyl]amine | 2-(2-Methoxyethoxy)ethylamine (7%), Bis[2-(2-methoxyethoxy)ethyl]amine (19%), Tris[2-(2-methoxyethoxy)ethyl]amine (20%), 2-(2-Methoxyethoxy)acetonitrile (16%). |
| 13. | n-Decanol | n-Decanol (92%), Decanenitrile (5%). |
| 14. | Octanal | Octanenitrile (77%), Octylamine (10%), Octanamide (7%), 2-Hexyldecanenitrile (1%). |
| 15. | Benzylamine | Benzonitrile (89%), Benzamide (4%). |
| 16. | 1-Naphthylmethylamine | 1-Naphthonitrile (76%), 1-Naphthamide (3%), 1-Methylnaphthalene (13%). |
| 17. | 4-Fluorobenzylamine | 4-Fluorobenzonitrile (90%), 4-Fluorobenzamide (2%), benzonitrile (4%). |
| 18. | Dibenzylamine | Benzonitrile (91%), Benzamide (2%). |
| 19. | *N*-Benzylaniline | *N*-Benzylaniline (34%), Benzonitrile (63%); for every benzonitrile molecule, 1 eq. of aniline is generated; Aniline (64%). |
| 20. | Tribenzylamine | Benzonitrile (15%), Benzylamine (4%), Dibenzylamine (4%), Tribenzylamine (70%). |
| 21. | Benzaldehyde | Benzonitrile (71%), Benzamide (9%). |
| 22. | 1,10-diaminodecane | 1,10-Decanedinitrile (65%), 9-Cyanononanamide (5%), Decanenitrile (14%), Decanamide (2%), Nonanenitrile (4%). |
| 23. | Azonane | 1,8-Octanedinitrile (65%), Octanenitrile (15%), Cycloheptanecarbonitrile (6%), Azonane (2%). |
| 24. | Azacyclotridecane | Undecanenitrile (3%), Dodecanenitrile (3%),1,12-Dodecanedinitrile (88%), 11-Cyanoundecanamide (2%), |
| 25. | *N*-Octyloctanamide | Octanenitrile (74%), Octanamide (17%), *N*-Octyloctanamide (4%). |
| 26. | *N*-Octyloctanamide | Octanenitrile (75%), Octanamide (16%), *N*-Octyloctanamide (4%). |
| 27. | *N,N*-Dioctyloctanamide | *N,N*-Dioctyloctanamide (89%), Octanamide (3%), Octanenitrile (7%). |
| 28. | Nylon 11/Polyamide 11/PA11 | 1,11-Undecanedinitrile (39%), 10-Cyanodecanamide (54%), 1,11-Undecanediamide (4%). |
| 29. | Nylon 12/Polyamide 12/PA12 | 1,12-Dodecanedinitrile (30%), 11-Cyanoundecanamide (22%), 1,12-Dodecanediamide (5%). |
| 30. | Nylon 12/Polyamide 12/PA12 | 1,12-Dodecanedinitrile (43%), 11-Cyanoundecanamide (52%), 1,12-Dodecanediamide (3%). |
| 31. | Triethylamine | Mono-ethylamine (6%), Acetonitrile (20%).[b] |

[a]Carbon yield in case of an amide substrate. Due to traces of water in the solvent, substrate or on the catalyst, small quantities of primary amide are often found in samples were no water is generated. [b]A low mass balance was obtained due to the formation of very volatile compounds.

## 7. Product identification

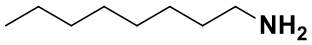
**Octanenitrile (1, MW = 125 g/mol)**



GC-MS (EI, 70eV): m/z (rel. int, %): 39 (19), 40 (5), 41 (54), 42 (9), 43 (22), 53 (5), 54 (33), 55 (31), 56 (7), 57 (8), 68 (7), 69 (33), 82 (100), 83 (39), 96 (53), 97 (23), 110 (13), 124 (3).

$^1$H-NMR (400 MHz, methanol-d4): δ (ppm) = 2.41 (t, 2H, NC-C**H$_2$**-), 1.89-1.78 (m, 2H, $NH_2$-$CH_2$-C**H$_2$**-), 1.39-1.25 (m, 8H, -(C**H$_2$**)$_5$-$CH_3$), 0.91 (t, 3H, -C**H$_3$**).

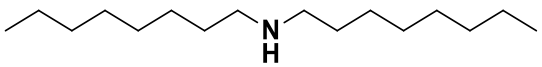
**Octylamine (2, MW = 129 g/mol)**



GC-MS (EI, 70eV): m/z (rel. int, %): 129 (13), 128 (8), 114 (5), 100 (26), 87 (5), 86 (52), 84 (8), 83 (12), 73 (6), 72 (17), 70 (16), 69 (33), 68 (5), 67 (6), 59 (15), 57 (9), 56 (40), 55 (48), 54 (7), 53 (10), 45 (62), 44 (75), 43 (47), 42 (39), 41 (100), 40 (8), 39 (42).

$^1$H-NMR (400 MHz, methanol-d4): δ (ppm) = 2.62 (t, 2H, $NH_2$-C**H$_2$**-), 1.46 (quint, 2H, $NH_2$-$CH_2$-C**H$_2$**-), 1.39-1.25 (m, 10H, -(C**H$_2$**)$_5$-$CH_3$), 0.91 (t, 3H, -C**H$_3$**).

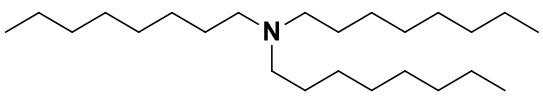
**Dioctylamine (3, MW = 241 g/mol)**



GC-MS (EI, 70eV): m/z (rel. int, %): 241 (5), 143 (11), 142 (100), 57 (6), 44 (32), 43 (10), 41 (8).

$^1$H-NMR (400 MHz, methanol-d4): δ (ppm) = 2.56 (t, 4H, -NH-C**H$_2$**-), 1.88-1.77 (quint, 4H, -NH-$CH_2$-C**H$_2$**-), 1.39-1.25 (m, 20H, -(C**H$_2$**)$_5$-$CH_3$), 0.91 (t, 6H, -C**H$_3$**).

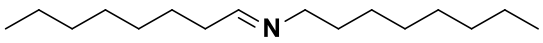
**Trioctylamine (4, MW = 354 g/mol)**



GC-MS (EI, 70eV): m/z (rel. int, %): 43 (4), 58 (3), 112 (3), 156 (7), 254 (100), 255 (19), 352 (2), 353 (1).

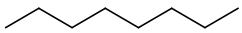
$^1$H-NMR (400 MHz, methanol-d4): δ (ppm) = 2.41 (t, 2H, NC-C**H$_2$**-), 1.89-1.78 (m, 2H, $NH_2$-$CH_2$-C**H$_2$**-), 1.39-1.25 (m, 10H, -(C**H$_2$**)$_5$-$CH_3$), 0.91 (t, 3H, -C**H$_3$**).

***N*-Octylideneoctylamine (5, MW = 239 g/mol)**



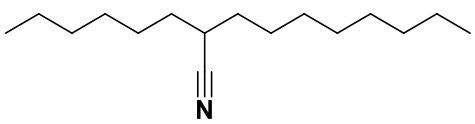
GC-MS (EI, 70eV): m/z (rel. int, %): 41 (20), 42 (8), 43 (15), 44 (5), 55 (11), 56 (13), 57 (12), 69 (6), 70 (11), 71 (5), 84 (12), 98 (13), 112 (9), 140 (100), 141 (10), 168 (17), 196 (5), 239 (1).

**Octane (6, MW = 114 g/mol)**



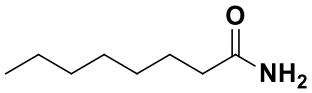
GC-MS (EI, 70eV): m/z (rel. int, %): 39 (19), 41 (57), 42 (17), 43 (100), 55 (17), 56 (26), 57 (46), 70 (21), 71 (35), 84 (17), 85 (73), 86 (5), 114 (12).

**2-Hexyldecanenitrile (7, MW = 237 g/mol)**



GC-MS (EI, 70eV): m/z (rel. int, %): 39 (10), 41 (57), 42 (9), 43 (44), 53 (5), 54 (13), 55 (34), 56 (10), 57 (17), 67 (9), 68 (8), 69 (19), 70 (9), 71 (7), 79 (5), 81 (8), 82 (28), 83 (74), 84 (7), 93 (5), 94 (6), 95 (7), 96 (68), 97 (100), 98 (14), 106 (6), 108 (5), 110 (53), 111 (32), 112 (5), 124 (29), 125 (14), 138 (37), 152 (12), 153 (11), 154 (5), 166 (52), 167 (9), 177 (15), 180 (24), 181 (5), 194 (24), 195 (6), 208 (18), 222 (4), 236 (4).

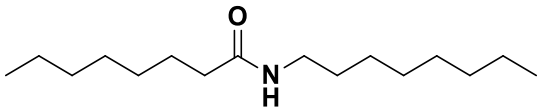
**Octanamide (8, MW = 143 g/mol)**



GC-MS (EI, 70eV): m/z (rel. int, %): 86 (9), 73 (5), 72 (29), 59 (100), 57 (8), 55 (9), 44 (20), 43 (14), 42 (5), 41 (14), 39 (5).

$^1$H-NMR (400 MHz, methanol-d4): δ (ppm) = 2.18 (t, 2H, -C(=O)-C**H$_2$**-), 1.78-1.47 (m, 4H, -C(=O)-CH$_2$-C**H$_2$**-C**H$_2$**-), 1.38-1.23 (m, 4H, -C**H$_2$**-C**H$_2$**-CH$_3$), 0.90 (t, 3H, -C**H$_3$**).

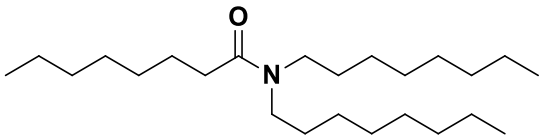
***N*-Octyloctanamide (9, MW = 255 g/mol)**



GC-MS (EI, 70eV): m/z (rel. int, %): 255 (16), 226 (20), 212 (20), 198 (25), 185 (13), 184 (100), 172 (7), 171 (55), 170 (6), 157 (16), 156 (49), 144 (13), 142 (17), 130 (7), 129 (8), 128 (29), 127 (39), 115 (10), 114 (44), 101 (19), 100 (38), 98 (5), 87 (30), 86 (47), 84 (8), 83 (5) 73 (63), 72 (21), 71 (17), 70 (5), 69 (12), 67 (5), 60 (9), 59 (5), 58 (15), 57 (87), 56 (11), 55 (37), 44 (41), 43 (60), 42 (12), 41 (51), 39 (8).

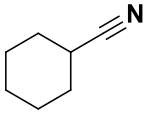
$^1$H-NMR (400 MHz, methanol-d4): δ (ppm) = 3.16 (t, 2H, -NH-C**H$_2$**-); 2.17 (t, 2H, -C(=O)-C**H$_2$**-); 1.60 (quint, 2H, -C(=O)-CH$_2$-C**H$_2$**-); 1.49 (quint, 2H, -NH-CH$_2$- C**H$_2$**-); 1.39-1.25 (m, 18H, CH$_3$-(C**H$_2$**)$_4$-R-C(=O)-NH-R'-(C**H$_2$**)$_5$-CH$_3$); 0.91 (t, 6H, -C**H$_3$**).

***N,N*-Dioctyloctanamide (10, MW = 368 g/mol)**



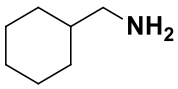
$^1$H-NMR (400 MHz, methanol-d4): δ (ppm) = 3.34-3.28 (m, 4H, -N[-C**H$_2$**-CH$_2$-]$_2$); 2.34 (t, 2H, -C(=O)-C**H$_2$**-); 1.65-1.55 (m, 4H, -N[-CH$_2$-C**H$_2$**-]$_2$); 1.53 (quint, 2H, -C(=O)-CH$_2$-C**H$_2$**-); 1.40-1.24 (m, 28H, CH$_3$-(C**H$_2$**)$_4$-R-C(=O)-N<[R'-(C**H$_2$**)$_5$-CH$_3$)]$_2$; 0.91 (t, 6H, -C**H$_3$**).

**Cyclohexanecarbonitrile (11, MW = 109 g/mol)**



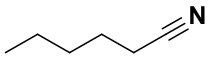
GC-MS (EI, 70eV): m/z (rel. int, %): 38 (8), 39 (63), 40 (15), 41 (100), 42 (16), 43 (21), 50 (9), 51 (16), 52 (16), 53 (26), 54 (85), 55 (24), 56 (96), 64 (5), 65 (6), 66 (10), 67 (47), 68 (24), 69 (25), 77 (6), 79 (8), 80 (31), 81 (42), 82 (33), 91 (18), 92 (35), 93 (5), 94 (57), 95 (5), 108 (41), 109 (17).

**Hexahydrobenzylamine (12, MW = 113 g/mol)**



GC-MS (EI, 70eV): m/z (rel. int, %): 38 (5), 39 (81), 40 (14), 41 (100), 42 (28), 43 (14), 44 (5), 50 (7), 51 (13), 52 (8), 53 (29), 54 (52), 55 (77), 56 (28), 65 (9), 66 (7), 67 (75), 68 (19), 70 (7), 77 (10), 79 (11), 80 (5), 81 (37), 82 (15), 83 (5), 95 (10), 96 (39), 113 (83), 114 (8).

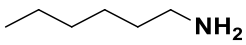
**Hexanenitrile (13, MW = 97 g/mol)**



GC-MS (EI, 70eV): m/z (rel. int, %): 97 (2), 96 (22), 82 (38), 78 (2), 70 (4), 69 (31), 68 (41), 57(30), 56 (5), 55 (48), 54 (90), 53 (6), 52(5), 51 (4), 50 (3), 44 (1), 43 (20), 42 (13), 41 (100), 40 (10), 39 (32), 38 (5).

$^1$H-NMR (400 MHz, $CD_3OD$): δ (ppm) = 2.43 (t, 2H, N≡C-C**H$_2$**-), 1.62 (quint, 2H, N≡C-$CH_2$-C**H$_2$**-), 1.41-1.26 (m, 4H, -C**H$_2$**-C**H$_2$**-$CH_3$), 0.91 (t, 3H, -C**H$_3$**).

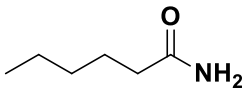
**Hexylamine (14, MW = 101 g/mol)**



GC-MS (EI, 70eV): m/z (rel. int, %): 101 (29), 100 (10), 86 (12), 72 (23), 69 (13), 59 (15), 56 (44), 55 (44), 54 (9), 53 (10), 51 (5), 45 (71), 44 (81), 43 (45), 42 (54), 41 (100), 40 (12), 39 (66), 38 (5).

$^1$H-NMR (400 MHz, $CD_3OD$): δ (ppm) = 2,63 (t, 2H, $NH_2$-C**H$_2$**-); 1,47 (quint, 2H, $NH_2$-$CH_2$C**H$_2$**-); 1,40-1,26 (m, 6H, -(C**H$_2$**)$_3$-$CH_3$); 0,92 (t, 3H, -C**H$_3$**).

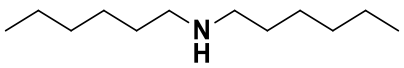
**Hexanamide (15, MW = 115 g/mol)**



GC-MS (EI, 70eV): m/z (rel. int, %): 39 (19), 41 (24), 42 (14), 43 (29), 44 (52), 55 (14), 59 (100), 72 (33), 73 (8), 86 (23).

$^1$H-NMR (400 MHz, $CD_3OD$): δ (ppm) = 2.19 (t, 2H, -C(=O)-C**H$_2$**-), 1.61 (quint, 2H, -C(=O)-$CH_2$-C**H$_2$**-), 1.41-1.26 (m, 4H, -C**H$_2$**-C**H$_2$**-$CH_3$), 0.91 (t, 3H, -C**H$_3$**).

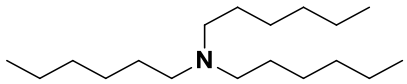
**Dihexylamine (16, MW = 185 g/mol)**



GC-MS (EI, 70eV): m/z (rel. int, %): 185 (6), 115 (9), 114 (100), 56 (5), 55 (6), 44 (53), 43 (21), 41 (11), 30 (9), 29 (6).

$^1$H-NMR (400 MHz, $CD_3OD$): δ (ppm) = 2.57 (t, 4H, -C**H$_2$**-NH-C**H$_2$**-), 1.47 (quint, 4H, -NH-$CH_2$-C**H$_2$**-), 1.40-1.26 (m, 12H, -(C**H$_2$**)$_3$-$CH_3$), 0.92 (t, 6H, -C**H$_3$**).

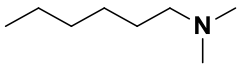
**Trihexylamine (17, MW = 269 g/mol)**



GC-MS (EI, 70eV): m/z (rel. int, %): 200 (15), 199 (100), 128 (13), 98 (5), 58 (5), 44 (5), 43 (12), 41 (5).

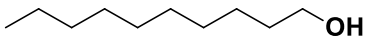
$^1$H-NMR (400 MHz, methanol-d4): δ (ppm) = 2.43 (t, 6H, -C**H$_2$**-NH-C**H$_2$**-), 1.47 (quint, 6H, -NH-$CH_2$-C**H$_2$**-), 1.40-1.26 (m, 18H, -(C**H$_2$**)$_3$-$CH_3$), 0.92 (t, 9H, -C**H$_3$**).

***N,N*-dimethylhexylamine (18, MW = 129 g/mol)**



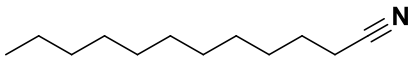
GC-MS (EI, 70eV): m/z (rel. int, %): 41 (4), 42 (9), 43 (3), 58 (100), 59 (4), 129 (7).

**n-Decanol (19, MW = 158 g/mol)**



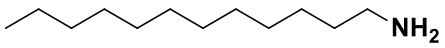
GC-MS (EI, 70eV): m/z (rel. int, %): 39 (28), 40 (6), 41 (100), 42 (31), 43 (70), 44 (5), 53 (9), 54 (9), 55 (98), 56 (72), 57 (39), 67 (14), 68 (26), 69 (73), 70 (81), 71 (14), 82 (24), 83 (64), 84 (41), 85 (7), 96 (5), 97 (36), 98 (14), 111 (19), 112 (22), 140 (2), 157 (0.1).

**Dodecanenitrile (20, MW = 181 g/mol)**



GC-MS (EI, 70eV): m/z (rel. int, %): 39 (27), 41 (100), 42 (21), 43 (58), 44 (6), 53 (9), 54 (32), 55 (60), 56 (23), 57 (42), 67 (11), 68 (10), 69 (46), 70 (28), 71 (11), 79 (9), 81 (7), 82 (71), 83 (56), 84 (11), 85 (6), 94 (5), 96 (89), 97 (95), 98 (10), 110 (79), 111 (33), 112 (5), 124 (57), 125 (8), 138 (43), 139 (5), 152 (22), 166 (5), 180 (3).

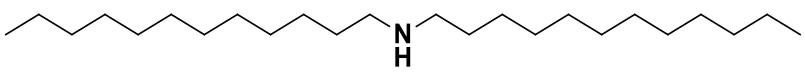
**Dodecylamine (21, MW = 185 g/mol)**



GC-MS (EI, 70eV): m/z (rel. int, %): 185 (12), 184 (9), 170 (5), 156 (14), 142 (15), 128 (12), 114 (15) 111 (6), 100 (34), 98 (6), 97 (13), 87 (7), 86 (59), 84 (10), 83 (18), 82 (6), 73 (9), 72 (21), 71 (5), 70 (16), 69 (36), 68 (6), 67 (8), 59 (20), 57 (23), 56 (41), 55 (67), 54 (7), 53 (8), 45 (59), 44 (78), 43 (71), 42 (27), 41 (100), 39 (21)

$^1$H-NMR (400 MHz, methanol-d4): δ (ppm) = 2.62 (t, 2H, $NH_2$-C**H$_2$**-), 1.47 (quint, 2H, $NH_2$-$CH_2$-C**H$_2$**-), 1.40-1.25 (m, 18H, -(C**H$_2$**)$_9$-$CH_3$), 0.92 (t, 3H, -C**H$_3$**).

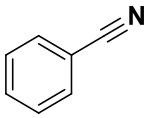
**Didodecylamine (22, MW = 354 g/mol)**



GC-MS (EI, 70eV): m/z (rel. int, %): 199 (15), 198 (100), 196 (5), 57 (8), 56 (5), 55 (7), 44 (19), 43 (9), 41 (7), 30 (5).

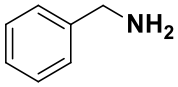
$^1$H-NMR (400 MHz, methanol-d4): δ (ppm) = 2.56 (t, 4H, -NH-C**H$_2$**-), 1.47 (quint, 4H, -NH-CH$_2$-C**H$_2$**-), 1.40-1.25 (m, 36H, -(C**H$_2$**)$_9$-CH$_3$), 0.92 (t, 6H, -C**H$_3$**).

**Benzonitrile (23, MW = 103 g/mol)**



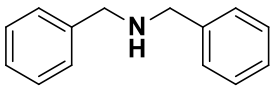
GC-MS (EI, 70eV): m/z (rel. int, %): 50 (14), 51 (8), 74 (5), 75 (10), 76 (35), 77 (6), 103 (100), 104 (8).

**Benzylamine (24, MW = 107 g/mol)**



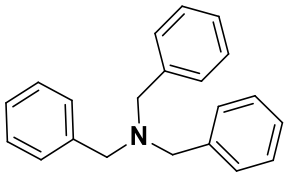
GC-MS (EI, 70eV): m/z (rel. int, %): 39 (6), 50 (9), 51 (16), 52 (5), 63 (5), 77 (24), 78 (14), 79 (39), 91 (12), 104 (5), 106 (100), 107 (52).

**Dibenzylamine (25, MW = 197 g/mol)**



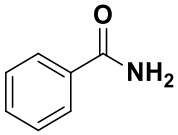
GC-MS (EI, 70eV): m/z (rel. int, %): 39 (8), 50 (6), 51 (13), 63 (8), 65 (20), 77 (13), 89 (15), 90 (10), 91 (100), 92 (28), 117 (12), 118 (5), 194 (35), 195 (32), 196 (5), 197 (1).

**Tribenzylamine (26, MW = 287 g/mol)**



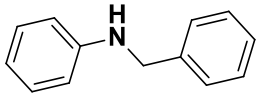
GC-MS (EI, 70eV): m/z (rel. int, %): 65 (14), 91 (100), 92 (13), 181 (5), 196 (25), 210 (33), 211 (5), 286 (6), 287 (26), 288 (6).

**Benzamide (27, MW = 121 g/mol)**



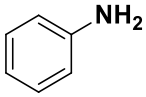
GC-MS (EI, 70eV): m/z (rel. int, %): 44 (10), 50 (22), 51 (37), 74 (10), 75 (6), 76 (8), 77 (91), 78 (12), 105 (100), 106 (8), 121 (76).

***N*-Benzylaniline (28, MW = 183 g/mol)**



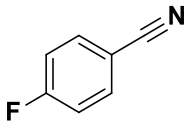
GC-MS (EI, 70eV): m/z (rel. int, %): 39 (7), 51 (11), 63 (5), 65 (23), 77 (22), 78 (5), 91 (93), 92 (10), 104 (10), 106 (19), 182 (38), 183 (100), 184 (14).

**Aniline (29, MW = 93 g/mol)**



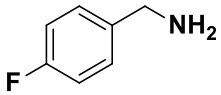
GC-MS (EI, 70eV): m/z (rel. int, %): 38 (6), 39 (13), 50 (6), 51 (5), 52 (6), 63 (7), 65 (18), 66 (38), 67 (5), 76 (5), 92 (11), 93 (100), 94 (8).

**4-Fluorobenzonitrile (30, MW = 121 g/mol)**



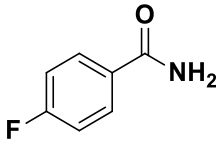
GC-MS (EI, 70eV): m/z (rel. int, %): 50 (8), 74 (5), 75 (8), 94 (33), 95 (5), 121 (100), 122 (8).

**4-Fluorobenzylamine (31, MW = 125 g/mol)**



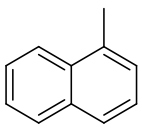
GC-MS (EI, 70eV): m/z (rel. int, %): 50 (11), 51 (9), 57 (7), 63 (5), 69 (5), 70 (5), 74 (8), 75 (19), 77 (13), 78 (5), 83 (10), 95 (14), 96 (13), 97 (37), 104 (8), 105 (46), 106 (6), 107 (8), 109 (25), 122 (7), 124 (100), 125 (31), 126 (2).

**4-Fluorobenzamide (32, MW = 139 g/mol)**



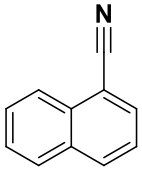
GC-MS (EI, 70eV): m/z (rel. int, %): 39 (5), 40 (19), 44 (28), 50 (14), 51 (7), 57 (5), 63 (5), 68 (7), 69 (10), 73 (6), 74 (13), 75 (39), 76 (5), 94 (10), 95 (83), 96 (11), 109 (9), 121 (5), 123 (100), 124 (13), 139 (67), 140 (5).

**1-Methylnaphthalene (33, MW = 142 g/mol)**



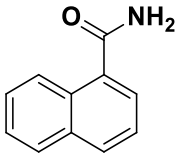
GC-MS (EI, 70eV): m/z (rel. int, %): 63 (8), 89 (6), 115 (44), 116 (5), 139 (11), 141 (88), 142 (100), 143 (11).

**1-Naphthonitrile (34, MW = 153 g/mol)**



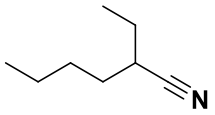
GC-MS (EI, 70eV): m/z (rel. int, %): 63 (5), 74 (5), 75 (5), 126 (18), 127 (6), 152 (6), 153 (100), 154 (12).

**1-Naphthamide (35, MW = 171 g/mol)**



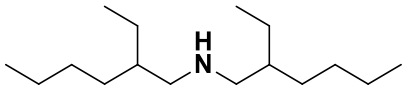
GC-MS (EI, 70eV): m/z (rel. int, %): 44 (7), 50 (6), 51 (7), 62 (5), 63 (11), 74 (12), 75 (12), 76 (7), 77 (13), 87 (6), 98 (5), 101 (10), 115 (10), 126 (33), 127 (100), 128 (15), 154 (7), 155 (77), 156 (10), 170 (34), 171 (87), 172 (12).

**2-Ethylhexanenitrile (36, MW = 125 g/mol)**



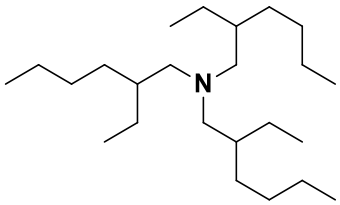
GC-MS (EI, 70eV): m/z (rel. int, %): 51 (5), 52 (6), 53 (9), 54 (100), 55 (24), 56 (8), 57 (36), 67 (6), 68 (15), 69 (88), 70 (6), 82 (56), 83 (6), 96 (93), 97 (87), 98 (6), 110 (8), 124 (2), 125 (0.3).

**Bis(2-ethylhexyl)amine (37, MW = 241 g/mol)**



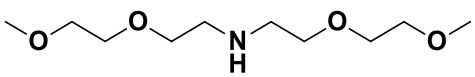
GC-MS (EI, 70eV): m/z (rel. int, %): 41 (16), 42 (6), 43 (9), 55 (9), 56 (5), 57 (9), 69 (8), 70 (6), 84 (28), 98 (5), 112 (11), 140 (100), 141 (11), 168 (15), 182 (6), 183 (10), 196 (6), 210 (7), 239 (0.4), 240 (0.1).

**Tris(2-ethylhexyl)amine (38, MW = 354 g/mol)**



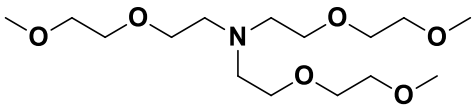
GC-MS (EI, 70eV): m/z (rel. int, %): 57 (5), 156 (11), 207 (10), 254 (100), 255 (19), 353 (1), 354 (0.1), 355 (0.2).

**Bis(2-(2-methoxyethoxy)ethyl)amine (39, MW = 221 g/mol)**



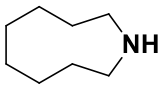
GC-MS (EI, 70eV): m/z (rel. int, %): 42 (7), 43 (10), 45 (17), 56 (24), 57 (8), 58 (24), 59 (26), 70 (8), 100 (33), 132 (100), 133 (6), 190 (4).

**Tris(2-(2-methoxyethoxy)ethyl)amine (40, MW = 323 g/mol)**



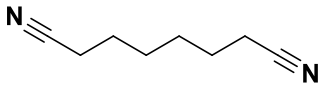
GC-MS (EI, 70eV): m/z (rel. int, %): 45 (6), 59 (18), 100 (7), 234 (100), 235 (13), 323 (0.1).

**Azonane (41, MW = 127 g/mol)**



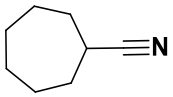
GC-MS (EI, 70eV): m/z (rel. int, %): 39 (27), 40 (6), 41 (41), 42 (31), 43 (100), 44 (58), 45 (5), 53 (7), 55 (20), 56 (100), 57 (34), 58 (6), 67 (9), 68 (10), 70 (98), 71 (13), 72 (15), 83 (17), 84 (44), 86 (28), 91 (5), 98 (29), 112 (16), 126 (10), 127 (50).

**1,8-Octanedinitrile (42, MW = 136 g/mol)**



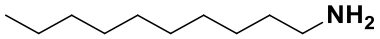
GC-MS (EI, 70eV): m/z (rel. int, %): 39 (31), 40 (13), 41 (73), 42 (18), 51 (5), 52 (9), 53 (10), 54 (38), 55 (60), 66 (5), 67 (8), 68 (14), 69 (42), 79 (10), 81 (5), 82 (27), 83 (20), 96 (100), 97 (7), 108 (6), 136 (0.1).

**Cycloheptanecarbonitrile (43, MW = 123 g/mol)**



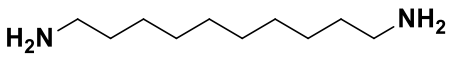
GC-MS (EI, 70eV): m/z (rel. int, %): 38 (6), 39 (64), 40 (17), 41 (81), 42 (44), 43 (12), 44 (5), 50 (5), 51 (11), 52 (12), 53 (28), 54 (64), 55 (100), 56 (53), 57 (5), 65 (9), 66 (12), 67 (45), 69 (17), 70 (15), 77 (6), 78 (5), 79 (7), 80 (48), 81 (54), 82 (38), 83 (14), 91 (14), 92 (5), 94 (93), 95 (71), 96 (26), 108 (34), 122 (36), 123 (3).

**Decylamine (44, MW = 157 g/mol)**



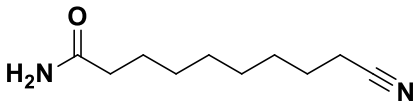
GC-MS (EI, 70eV): m/z (rel. int, %): 39 (36), 40 (8), 41 (100), 42 (20), 43 (42), 53 (11), 54 (44), 55 (52), 56 (18), 57 (31), 67 (10), 68 (12), 69 (55), 70 (15), 71 (9), 79 (9), 81 (7), 82 (94), 83 (64), 84 (9), 93 (5), 96 (97), 97 (70), 98 (7), 110 (74), 111 (18), 124 (35), 138 (6), 157 (0.02).

**1,10-Diaminodecane (45, MW = 172 g/mol)**



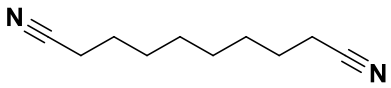
GC-MS (EI, 70eV): m/z (rel. int, %): 39 (12), 41 (40), 42 (17), 43 (23), 44 (75), 45 (38), 53 (5), 54 (6), 55 (44), 56 (60), 57 (8), 59 (27), 67 (10), 68 (6), 69 (32), 70 (20), 72 (26), 73 (11), 81 (7), 82 (6), 83 (12), 86 (45), 87 (11), 95 (5), 97 (9), 98 (6), 100 (45), 101 (5), 114 (31), 128 (36), 129 (5), 142 (21), 143 (72), 144 (8), 156 (100), 157 (12).

**9-Cyanononanamide (46, MW = 182 g/mol)**



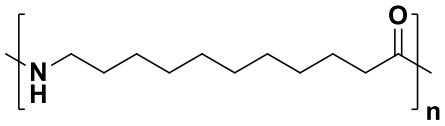
GC-MS (EI, 70eV): m/z (rel. int, %): 39 (10), 41 (27), 42 (9), 43 (14), 44 (31), 53 (5), 54 (8), 55 (22), 56 (4), 57 (6), 59 (100), 60 (7), 69 (7), 72 (19), 73 (5), 82 (9), 83 (12), 86 (11), 96 (7), 97 (9), 182 (0.2).

**1,10-Decanedinitrile (47, MW = 164 g/mol)**



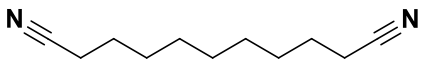
GC-MS (EI, 70eV): m/z (rel. int, %): 39 (23), 40 (7), 41 (58), 42 (10), 43 (6), 52 (5), 53 (9), 54 (25), 55 (41), 67 (8), 68 (7), 69 (21), 79 (10), 81 (8), 82 (100), 83 (88), 84 (5), 96 (30), 97 (8), 107 (5), 110 (5), 124 (20), 163 (1), 164 (0.1).

**Polyamide 11 (48, MW = 183 g/mol repeating unit)**



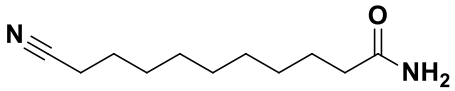
$^1$H-NMR (400 MHz, $CD_3OD$ and CHOOH/DCM): δ (ppm) = 2.84 (2H, -NH-C**H$_2$**-), 1.90 (2H, -C(=O)-C**H$_2$**-), 1.27-1.04 (4H, -NH-$CH_2$-C**H$_2$**-$(CH_2)_6$-C**H$_2$**-), 0.98-0.85 (12H, -NH-$CH_2$-$CH_2$-(C**H$_2$**)$_6$-).

**1,11-Undecanedinitrile (49, MW = 178 g/mol)**



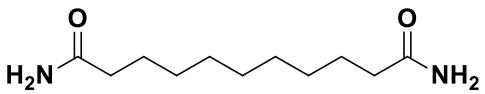
GC-MS (EI, 70eV): m/z (rel. int, %): 39 (26), 40 (7), 41 (70), 42 (12), 43 (8), 52 (5), 53 (10), 54 (30), 55 (49), 56 (6), 67 (10), 68 (8), 69 (36), 79 (7), 81 (6), 82 (100), 83 (97), 84 (6), 93 (7), 95 (5), 96 (65), 97 (37), 110 (17), 138 (17), 177 (1), 178 (0.2).

**10-Cyanodecanamide (50, MW = 196 g/mol)**



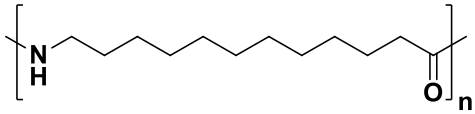
GC-MS (EI, 70eV): m/z (rel. int, %): 39 (9), 41 (27), 42 (7), 43 (13), 44 (28), 53 (4), 54 (7), 55 (22), 56 (4), 57 (5), 59 (100), 60 (8), 67 (4), 69 (8), 72 (23), 73 (6), 81 (3), 82 (6), 83 (10), 84 (3), 86 (11), 96 (7), 97 (8), 110 (3), 114 (3), 156 (7), 195 (0.1), 196 (0.02).

**1,11-Undecanediamide (51, MW = 214 g/mol)**



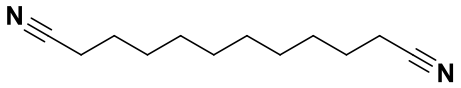
GC-MS (EI, 70eV): m/z (rel. int, %): 39 (10), 41 (34), 42 (12), 43 (28), 44 (69), 55 (37), 56 (6), 57 (15), 59 (79), 60 (6), 67 (8), 69 (24), 71 (6), 72 (59), 73 (10), 81 (7), 83 (10), 86 (19), 95 (7), 97 (21), 98 (7), 100 (20), 111 (7), 114 (16), 121 (7), 128 (7), 139 (19), 143 (11), 152 (6), 155 (16), 156 (100), 157 (10), 214 (1).

**Polyamide 12 (52, MW = 197 g/mol repeating unit)**



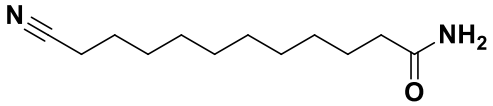
$^1$H-NMR (400 MHz, $CD_3OD$ and CHOOH/DCM): δ (ppm) = 2.84 (2H, -NH-C**H$_2$**-), 1.90 (2H, -C(=O)-C**H$_2$**-), 1.27-1.04 (4H, -NH-$CH_2$-C**H$_2$**-$(CH_2)_5$-C**H$_2$**-), 0.98-0.85 (14H, -NH-$CH_2$-$CH_2$-(C**H$_2$**)$_7$-).

**1,12-Dodecanedinitrile (53, MW = 192 g/mol)**



GC-MS (EI, 70eV): m/z (rel. int, %): 39 (28), 40 (8), 41 (88), 42 (14), 43 (13), 52 (5), 53 (11), 54 (36), 55 (63), 56 (9), 57 (6), 67 (12), 68 (10), 69 (53), 70 (5), 79 (8), 81 (6), 82 (100), 83 (100), 84 (7), 93 (5), 96 (82), 97 (86), 98 (6), 110 (42), 111 (5), 124 (9), 152 (16), 163 (5), 192 (0.4).

**11-Cyanoundecanamide (54, MW = 210 g/mol)**



GC-MS (EI, 70eV): m/z (rel. int, %): 39 (8), 41 (27), 42 (6), 43 (13), 44 (26), 54 (6), 55 (23), 56 (4), 57 (5), 59 (100), 60 (11), 67 (4), 69 (9), 72 (26), 73 (7), 82 (5), 83 (10), 86 (11), 96 (7), 97 (10), 98 (3), 100 (3), 110 (5), 114 (3), 170 (3), 209 (0.1), 210 (0.03).

**Ethylamine (55, MW = 45 g/mol)**

GC-MS (EI, 70eV): m/z (rel. int, %): 38 (8), 39 (11), 40 (27), 41 (29), 42 (53), 43 (16), 44 (100), 45 (88), 46 (3).

**Acetonitrile (56, MW = 41 g/mol)**

GC-MS (EI, 70eV): m/z (rel. int, %): 38 (17), 39 (23), 40 (56), 41 (100), 42 (6).

## 8. References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