Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting information

1. Experimental details

1.1. Materials

All chemicals were used as received: hexanamide (Tokyo Chemical Industries, >98%), hexylamine (Sigma-Aldrich, 99%), hexylamine (Tokyo Chemical Industries, >98%), 1-hexanol (Sigma-Aldrich, >99%), trihexylamine (Alfa Aesar, 97%), benzyl alcohol (Alfa Aesar, 99.9%), cyclopentyl methyl ether (VWR Chemicals, 99.9%), 1,2-dimethoxyethane (J&K Scientific, 99.5%), 2-methyltetrahydrofuran (Sigma-Aldrich, 99%), tert-amyl alcohol (TCI, >98%), tert-amyl methyl ether (Sigma-Aldrich, 97%), undecane (Acros, 99%), methanol-d4 (Sigma-Aldrich, 99.8% D), N_2 (Air Liquide, α1), H_2 (Air liquide, N40), ammonia (Air Liquide, N38), Ru/C (5 wt%, Alfa Aesar), Pd/C (5 wt%, Alfa Aesar), Rh/C (5 wt%, Alfa Aesar), Pt/C (5 wt%, Alfa Aesar), SiO_2 – Aerosil 380 (Evonik, >99.8%), rutile (TiO_2, nanopowder, <100 nm particle size) (Sigma-Aldrich, 99.5%), hydroxyapatite (nanopowder, <200 nm particle size) (Sigma-Aldrich, >97%), ruthenium(III) chloride hydrate (Alfa Aesar, min 38% Ru, 99.9% PGM basis), ammonium tungsten oxide (Alfa Aesar, 99.99+%), platinum(II) acetylacetonate (Acros, 98%), vanadyl(IV) acetylacetonate (Acros, 99%), ammonium molybdate tetrahydrate (Sigma-Aldrich, 81-83% MoO_3 basis), tetraammineplatinum(II) chloride hydrate (Sigma-Aldrich, ≥ 99.99%), rhodium chloride trihydrate (Alfa Aesar, 38.5-45.5% Rh), ammonium metavanadate (Sigma Aldrich, 99%), sodium hydroxide (Acros, micropearls), calcium hydroxide (Acros, 98%), potassium hydroxide (Acros, pellets, 85%), cesium hydroxide hydrate (Sigma-Aldrich, >90%, >99.5% metal basis), adipamide (Tokyo Chemical Industries, >98%), propionamide (J&K Scientific, 99%), *N*-methylpropionamide (Tokyo Chemical Industries, >99%), *N,N*-dimethylpropionamide (Acros, >99%), octanamide (Tokyo Chemical Industries, >98%), lauramide (Tokyo Chemical Industries, >96%), cyclohexanecarboxamide (J&K Scientific, >97%), malonamide (Sigma-Aldrich, 97%), ε-caprolactam (Sigma-Aldrich, >99%), *N*-acetylmorpholine (J&K Scientific, 98%), hexanoyl chloride (Fisher, 97%), azepane (Alfa Aesar, >98%), polyvinyl alcohol (PVA, Acros, M.W. ~ 13,000 >98%, hydrolysed), $Al(NO_3)_3.9H_2O$ (Carl Roth, >98%), NH_4OH (Sigma-Aldrich, aqueous solution, 25% NH_3) and $Mg(NO_3)_2.6H_2O$ (Sigma-Aldrich, 99%).

1.2. Product analysis and identification

Crude reaction mixtures were analyzed by gas chromatography (GC) and nuclear magnetic resonance (NMR) spectroscopy. NMR samples were prepared by mixing 300 µL of the reaction mixture with 300 µL methanol-d4. ^{1}H-NMR spectra, as well as ^{1}H,^{1}H-COSY and ^{1}H,^{13}C-HSQC spectra, were recorded on a Bruker Ascend 400 MHz spectrometer equipped with a BBO 5 mm atma probe and a sample case. One of the signals of CPME was suppressed by applying an adapted zgpr pulse program: p1 9.75 µs; plw1 15W; plw9 5.7-05W; o1P on the resonance signal of CPME (around 3.27 ppm). Besides 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. For a reaction with octanamide, we illustrated that the amine product can easily be isolated by destilation; after a hydrogenation reaction, an isolated yield of 0.116 g amines was obtained (91% yield, with a molar primary - secondary amine ratio of 4.1 – 1; determined via NMR).

1.3. Catalyst characterization

Characterized was performed by N_2 physisorption, Ammonia temperature-programmed desorption (NH_3-TPD), X-ray powder diffraction (XRD), inductively coupled plasma optical emission spectrometry (ICP-OES), transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDX). N_2 physisorption measurements were performed using a Micromeritics 3Flex surface analyzer at -196°C. Before the measurements, the ~ 100 mg samples were degassed at 140°C for 3 h under vacuum. NH_3-TPD was conducted in a tubular gas phase reactor (with ~ 200 mg sample) connected to a Gasmet DX4000 FTIR gas analyzer. The IR data were processed with Calcmet Standard software version 12.161. XRD measurements were performed with the Malvern PANalytical Empyrean equipped with a Cu X-ray tube and a Pixcel3D detector. Possible Ru and W leaching was measured by ICP using a Varian 720-ES with the Varian SPS3 sample preparation system and applying the calibration curve method. For 1 mL of the supernatant of the reaction mixture, the solvent was evaporated and leftover ions were redissolved in 20 mL aqua regia. For TEM-EDX experiments, measurements were recorded with a probe aberration corrected JEOL ARM-200F microscope equipped with a cold-FEG and operated at 200 kV. Particles were deposited on a holey carbon-coated Cu-grid. These TEM experiments also confirmed the elemental composition of the catalyst.

1.4. Spinel synthesis and characterization

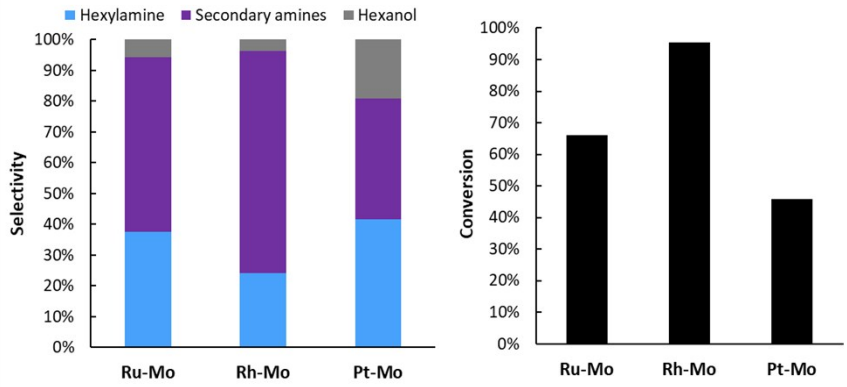
$MgAl_2O_4$ (spinel) was synthesized via the procedure described by Guo et al. (2003).[1] First, an aqueous solution of 2 wt% polyinylalcohol was prepared (9.3 g PVA, 465 mL water). To increase the dissolution rate of PVA, the dispersion was heated to 75°C and cooled when fully clear. Next, $Mg(NO_3)_2.6H_2O$ (18.0 g) and $Al(NO_3)_3.9H_2O$ (52.7 g) were added and dissolved, resulting in a mixture with a molar ratio Mg-Al-PVA (repeating unit) of 1-2-3. Then, ammonia solution was added under vigorous stirring until a pH value of 10 was reached. The resulting gel was stirred for 3 h at room temperature and aged afterwards overnight. The solid spinel was isolated by filtration and washed with water. Finally, the wet $MgAl_2O_4$ was lyophilized until a dry (non-sticky) white powder was obtained and then calcined in air at 800°C for 8h (5°C min^{-1}). The synthesized spinel was characterized by N_2 physisorption and X-ray powder diffraction (XRD).

1.5. Most significant metal catalysts

Table S 1 – Composition and source of most significant metal catalysts

Catalyst	wt% M	Ratio M/M'O	Source
Pt/C – Pd/C – Rh/C – Ru/C	5	/	Commercial catalysts
Ru-MnO_x/C	5	10	Edited commercial catalyst
Ru-WO_x/C	5	10	Edited commercial catalyst
Pt-VO_x/HAP	7	1	Homemade
Ru/SiO_2	4	/	Homemade
Ru-WO_x/SiO_2	4	8	Homemade
Ru-WO_x/SiO_2-Ca^{2+}(or other ions)	4	8	Homemade
Ru-WO_x/$MgAl_2O_4$	4	8	Homemade
Ru/rutile	4	/	Homemade
Ru-WO_x/rutile	4	8	Homemade

2. Preliminary hydrogenation experiments with different noble metals



Metal prices (5 April 2019)	
Ru	~ 7,000 EUR/kg
Pt	~ 23,000 EUR/kg
Rh	~ 65,000 EUR/kg

Figure S 1 – Preliminary hydrogenation experiments with PGM-Mo catalysts on SiO_2-aerosil-380 support (4 wt% PGM, molar PGM-Mo ratio of 1). Reaction conditions: hexanamide (1 mmol), 180°C, 40 bar H_2, 3 mol% PGM, undecane (20 µL), DME (10 mL), 16 h.

3. Kinetic experiments in DME and CPME

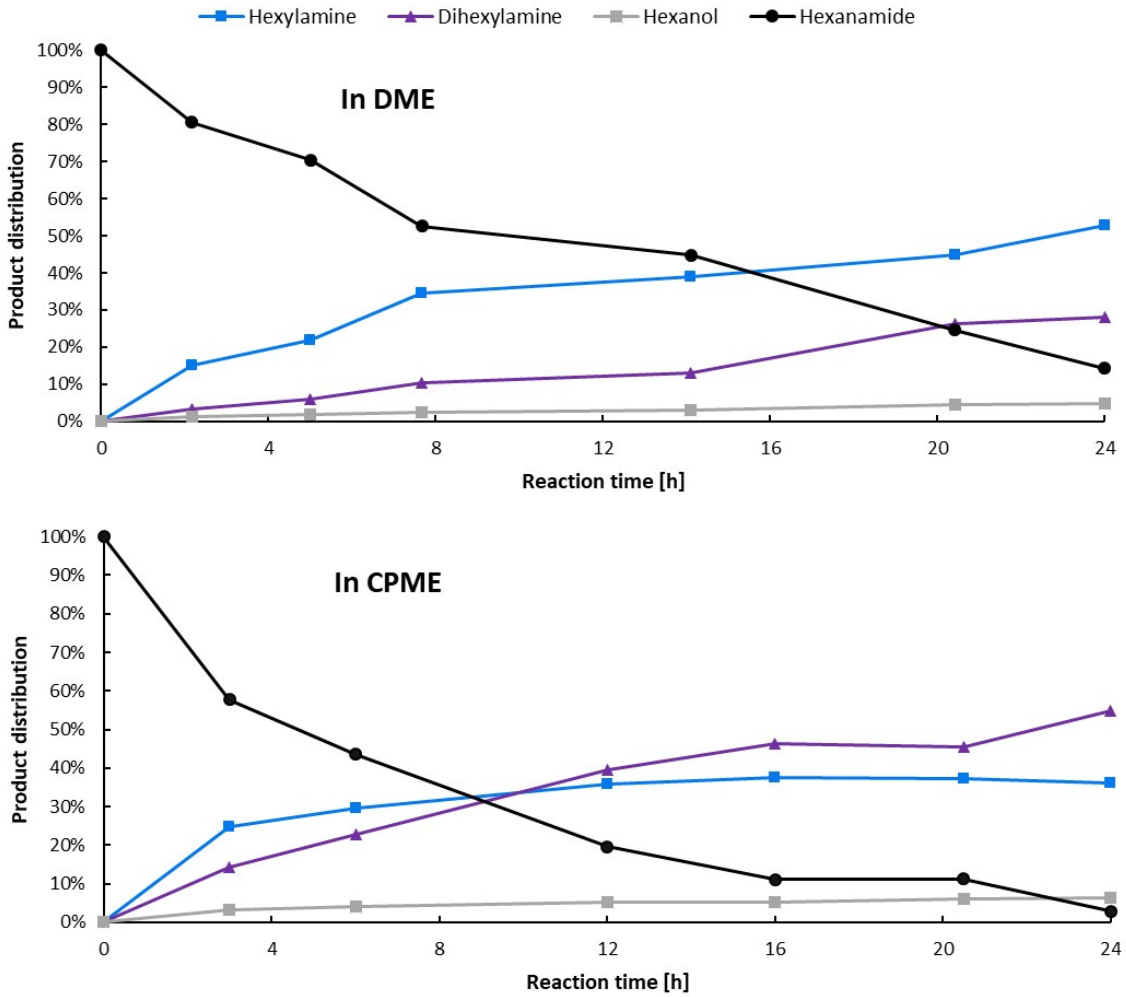


Figure S 2 – Time profile of hydrogenation experiments in dimethoxyethane (DME, top) and cyclopentyl methyl ether (CPME, botom). Reaction conditions: hexanamide (1 mmol), 160°C, 60 bar H_2, 1 mol% Ru ($RuWO_x/SiO_2$), undecane (20 µL), solvent (10 mL).

4. Search for suitable amide hydrogenation catalyst and determining the product stability

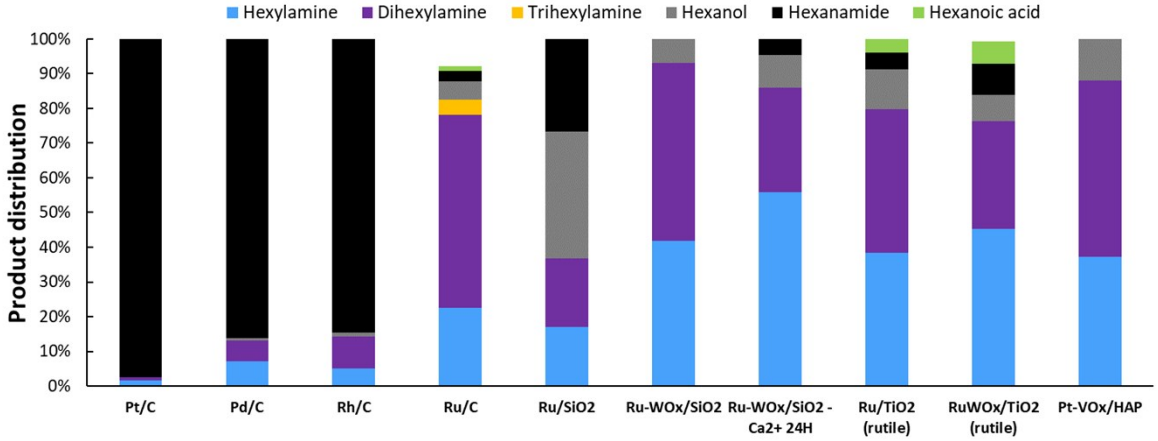


Figure S 3 – Variation of the amide hydrogenation catalyst. Reaction conditions: hexanamide (1 mmol), 180°C, 50 bar H_2; 0.5 bar NH_3; 1 mol% Ru (or same weight other PGM), undecane (20 µL), CPME (10 mL), 16 h.

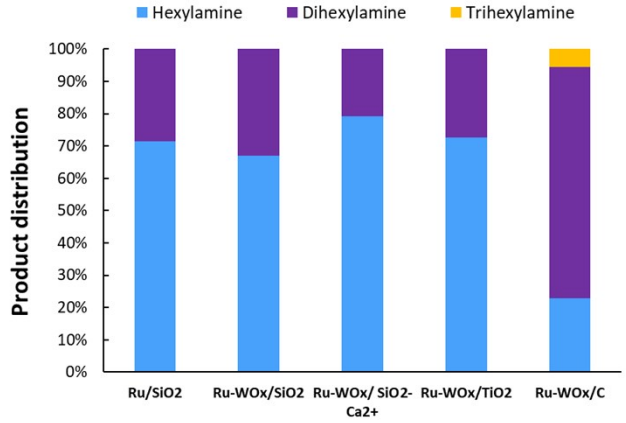


Figure S 4 – Screening of the product stability (hexylamine) in the presence of different hydrogenation catalysts. Reaction conditions: hexylamine (1 mmol), 180°C, 50 bar H_2; 0.5 bar NH_3, 0.5 mol% Ru, undecane (20 µL), CPME (10 mL), 16 h.

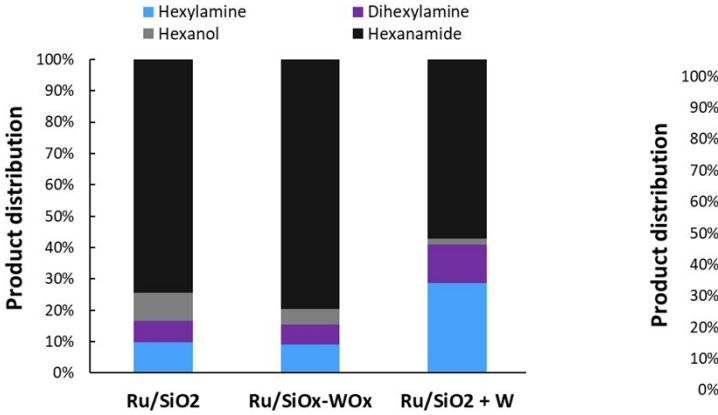


Figure S 5 – Hydrogenation experiments with Ru catalyst: (left) Ru/SiO_2, (middle) Ru deposited on W-modified SiO_2 support and (right) Ru/SiO_2 with post W-deposition. Reaction conditions: hexanamide (1 mmol), 180°C, 40 bar H_2, 0.5 mol% Ru, undecane (20 µL), DME (10 mL), 16 h.

5. Variation of the reaction conditions (temperature and hydrogen pressure)

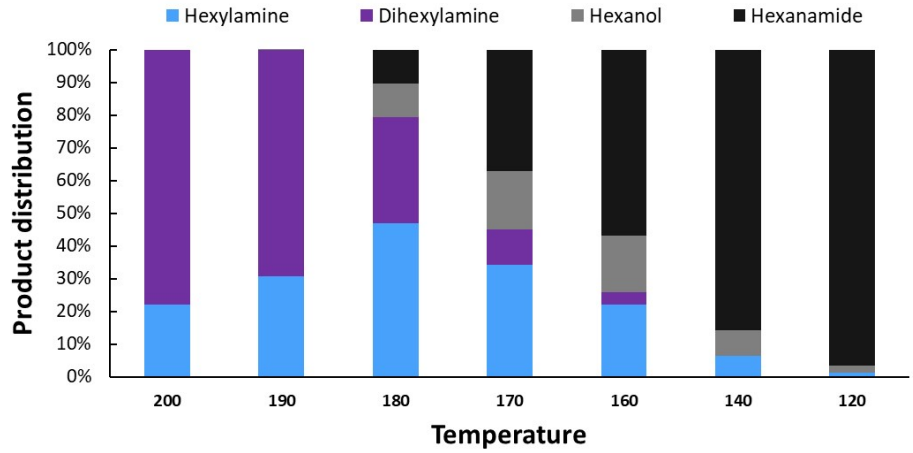


Figure S 6 – Variation of the reaction temperature. Reaction conditions: hexanamide (1 mmol), 50 bar H_2; 0.5 bar NH_3, 5 mol% Ru ($RuWO_x/SiO_2$-Ca^{2+}), undecane (20 µL), CPME (10 mL), 5 h.

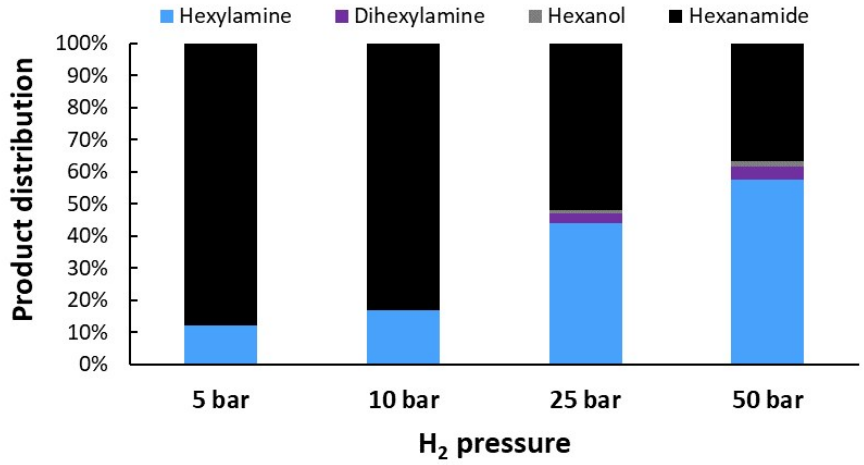


Figure S 7 – Variation of the hydrogen pressure. Reaction conditions: hexanamide (1 mmol), 200°C, 6 bar NH_3, 5 mol% Ru ($RuWO_x/SiO_2$-Ca^{2+}), undecane (20 µL), CPME (10 mL), 8 h.

6. Kinetics – first order hydrogenation

Under the assumption that the hydrogenation proceeds according to a first order reaction (with P_{H2} = constant);

$$\frac{d[\text{amide}]}{dt} = -k[\text{amide}] \leftrightarrow \ln(\text{amide}_{t=0}) - \ln(amide_{t=t}) = k.t \quad (1)$$

and the Arrhenius equation;

$$k = k_0.e^{\frac{-Ea}{R.T}} \leftrightarrow \ln(k) = \ln(k_0) - \frac{E_a}{R.T} \quad (2)$$

Plotting ln(k) derived from function (1) in function of T^{-1}, should give a straight curve (2) if the assumption of a first order reaction is correct. This indeed appeared to be the case.

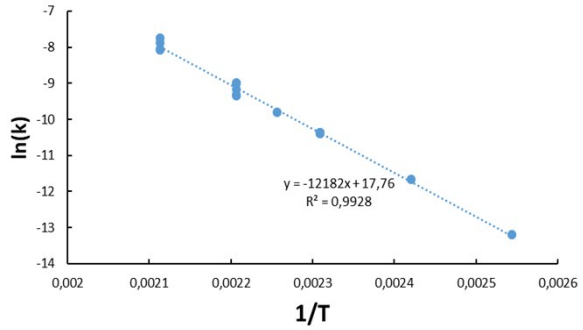


Figure S 8 – ln(k) in function of 1/T. For the determination of k, all experiments were performed with: hexanamide (1 mmol), 50 bar H_2; 0.5 bar NH_3, 5 mol% Ru ($RuWO_x/SiO_2$-Ca^{2+}), undecane (20 µL), CPME (10 mL).

7. Kinetics – influence of ammonia

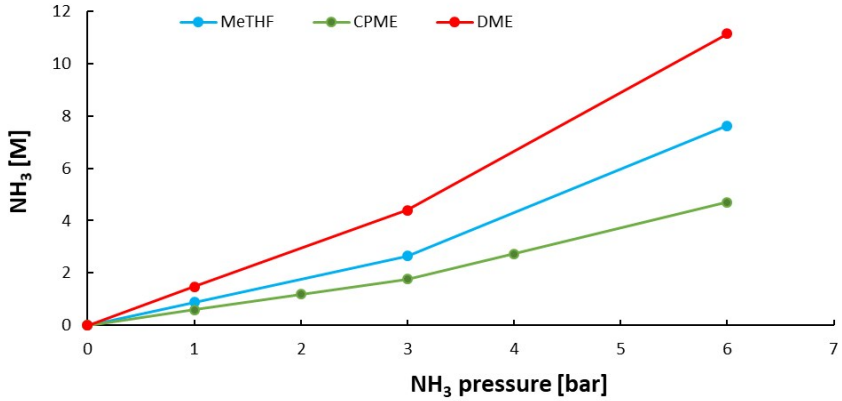


Figure S 9 – Ammonia concentration in different solvents (DME, MeTHF and CPME) as a function of the ammonia pressure.

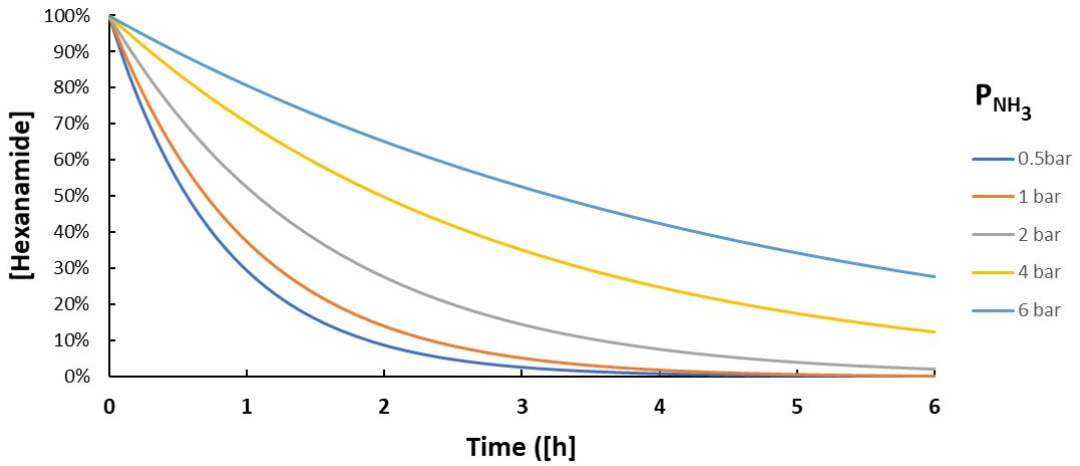


Figure S 10 – Hexanamide concentration in function of time for different ammonia pressures. Reaction conditions: hexanamide (1 mmol), 200°C, 50 bar H_2, 5 mol% Ru ($RuWO_x/SiO_2$-Ca^{2+}), undecane (20 µL), CPME (10 mL).

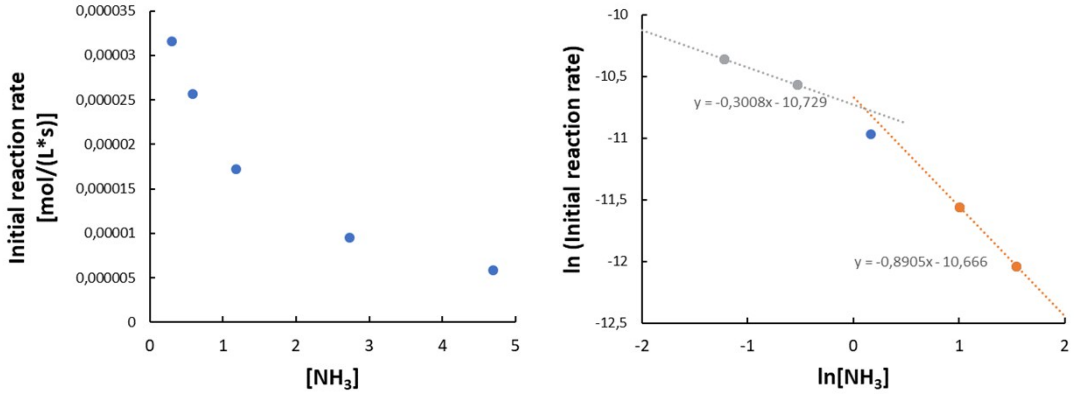


Figure S 11 – The initial reaction rate (see Figure S 10) in function of [NH3] (left) and ln(initial reaction rate) i.f.o. ln[-NH3] (right).

8. Characterization of the $RuWO_x$-catalysts

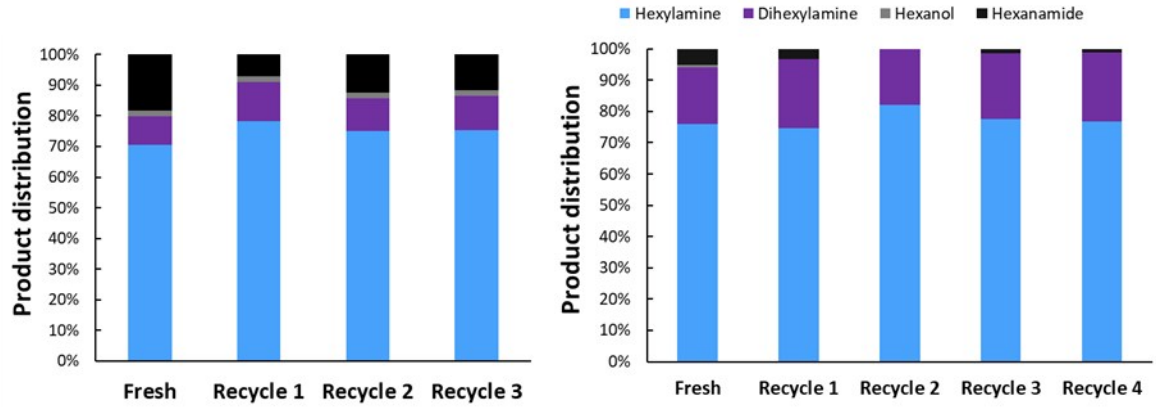


Figure S 12 – Recycling test of $RuWO_x$-catalysts: (left) $RuWO_x/SiO_2$ (7 mol% Ru per run, 7 h) and (right) $RuWO_x/MgAl_2O_4$ (5 mol% Ru per run, 6 h). Reaction conditions: hexanamide (1 mmol), 200°C, 50 bar H_2, 6 bar NH_3, undecane (20 µL), CPME (10 mL).

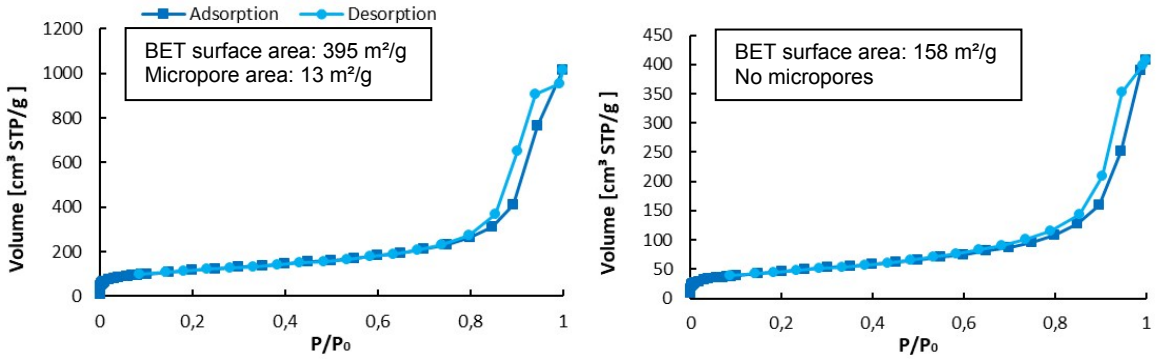


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Figure S 13 – BET surface area determination from N_2-physisorption isotherm for $RuWO_x/SiO_2$ (left) and $RuWO_x/MgAl_2O_4$ (right).

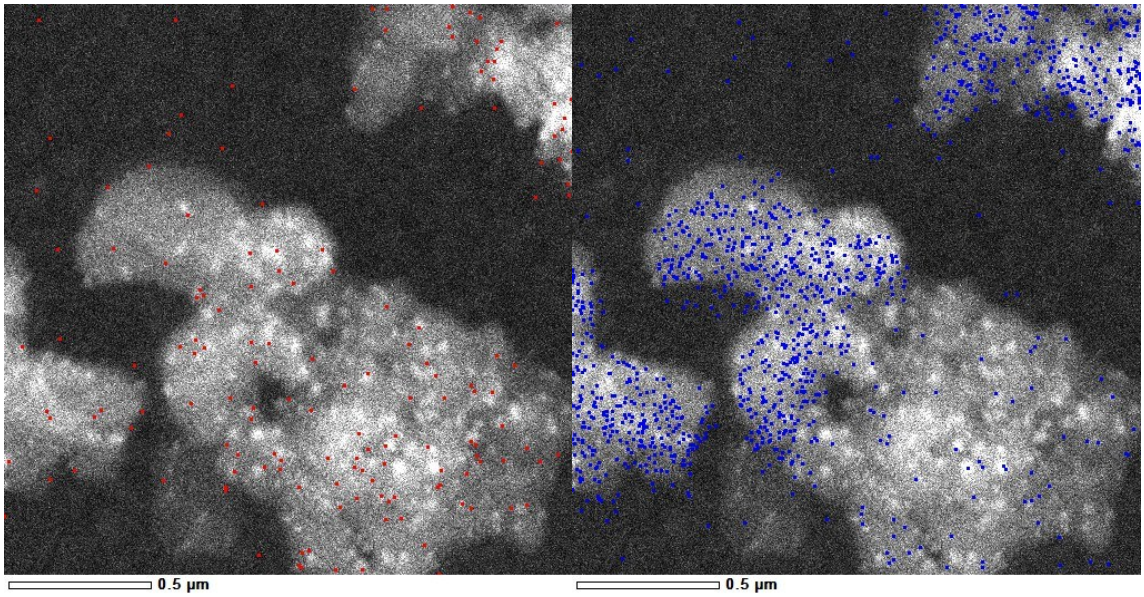


Figure S 14 – TEM-EDX image of $RuWO_x/MgAl_2O_4$: (left) overlap with the detected ruthenium (white spots = ruthenium particles); (right) overlap with the detected tungsten (homogeneously distributed).

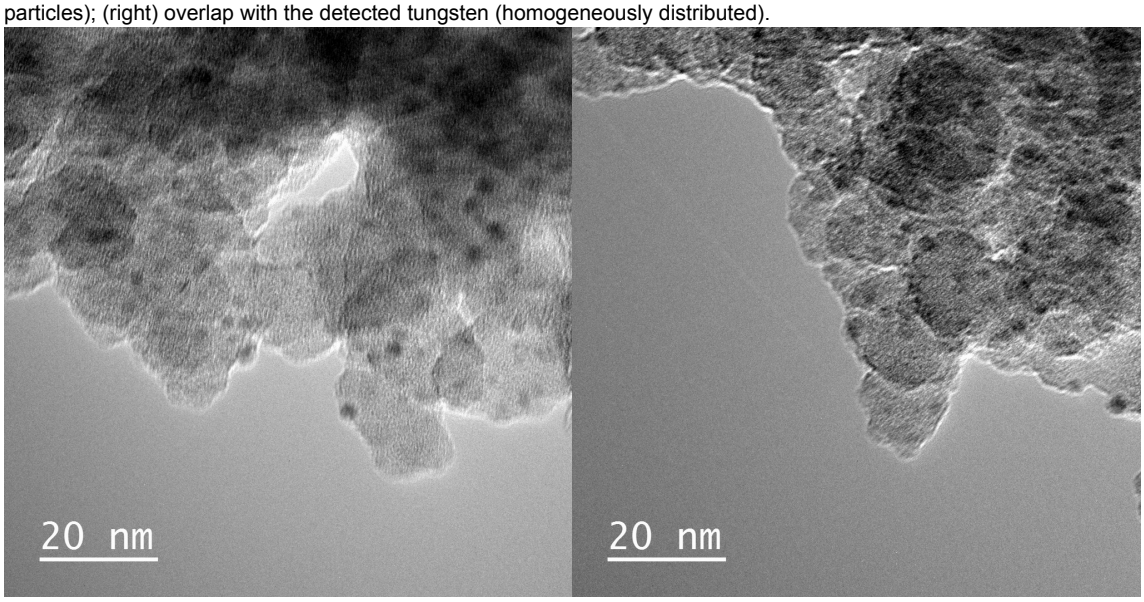


Figure S 15 – TEM images of $RuWO_x/SiO_2$ (black dots are Ru particles).

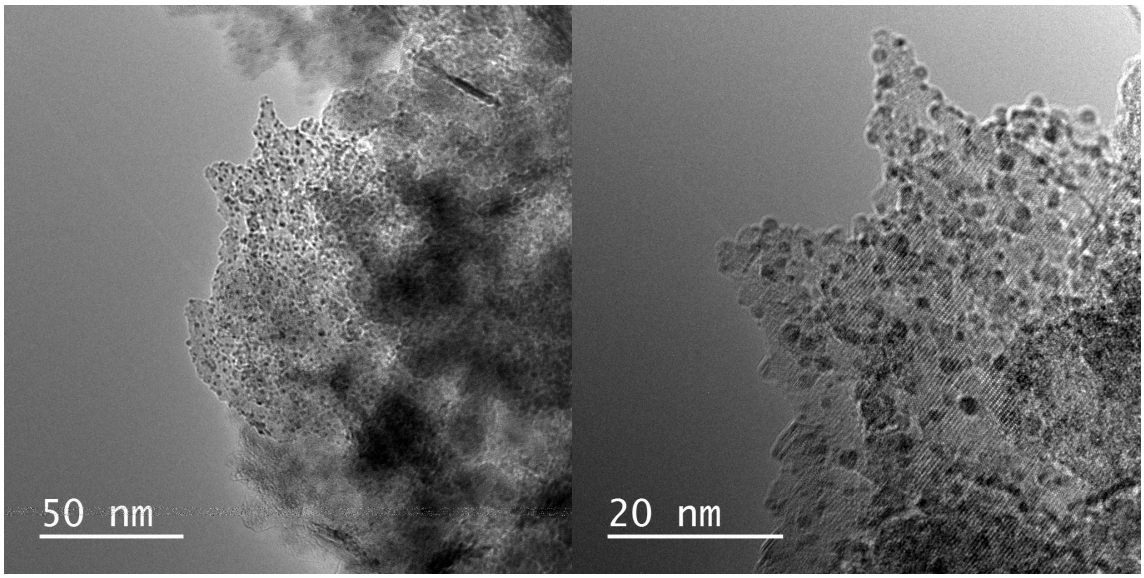


Figure S 16 – TEM images of $RuWO_x/MgAl_2O_4$ catalyst (black dots are Ru particles).

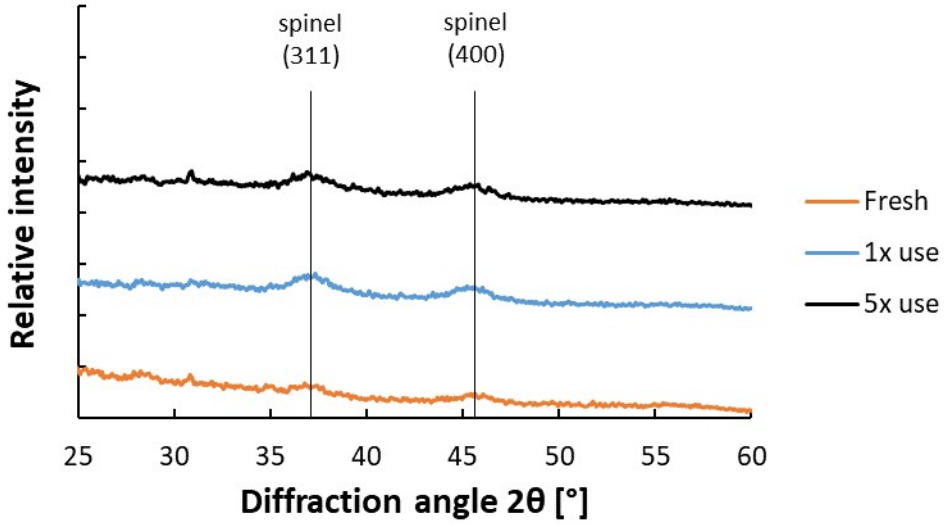


Figure S 17 – XRD pattern of $RuWO_x/MgAl_2O_4$ catalyst after 0, 1 and 5 times used. The catalyst remains essentially the same. No peak for Ru detected since the Ru nanoparticles are too small.

9. Characterization of the $MgAl_2O_4$ spinel

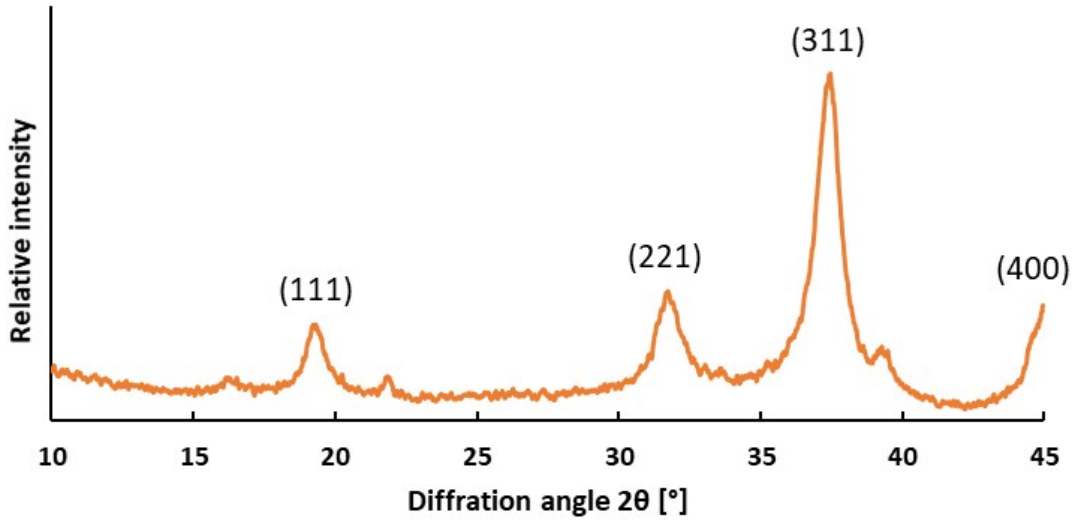


Figure S 18 – XRD pattern of synthesized $MgAl_2O_4$ spinel. Diffraction planes are marked on figure.

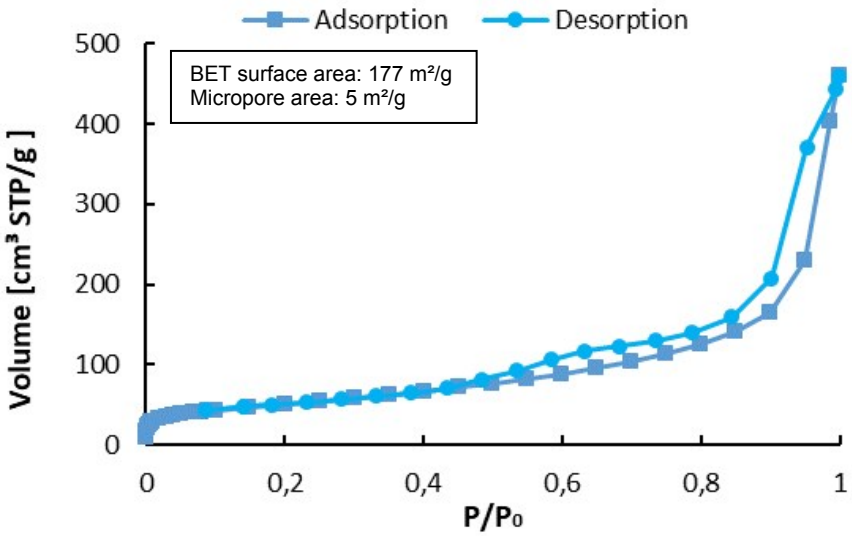


Figure S 19 – BET surface area determination from N_2-physisorption isotherm for $MgAl_2O_4$.

10. Substrate scope investigation

Substrate	Products distribution (yield)
Hexanamide	Hexylamine (83%), dihexylamine (17%)
Malonamide	Ethylamine (23%)[a], propylamine (30%)
ε-Caprolactam	Hexamethylenediamine (4%), azepane (85%), hexylamine (6%), 6-(azepan-1-yl)hexan-1-amine (5%)
Cyclohexanecarboxamide	Cyclohexylmethanamine (80%), bis(cyclohexylmethyl)amine (18%), 1-cyclohexyl-N-(cyclohexylmethyl)-N-methylmethanamine (1%), N-(cyclohexylmethyl)cyclopentanamine (1%)
Propionamide	Propylamine (81%), dipropylamine (15%), propionamide (4%), tripropylamine (1%)
Octanamide	Octylamine (80%), dioctylamine (17%), *N*-octyloctanamide (3%)
Adipamide	Hexamethylenediamine (4%), azepane (85%), hexylamine (8%), 6-(azepan-1-yl)hexan-1-amine (3%)
Lauramide	Laurylamine (80%), dilaurylamine (14%), *N*-dodecyldodecaneamide (3%) , dodecane (1%)
N-methylpropionamide [b]	Propylamine (80%), dipropylamine (12%), propionamide (4%)
N,N-dimethylpropionamide[b]	Propylamine (50%), dipropylamine (5%), 37%), propionamide (6%), *N,N*-dimethylpropylamine (2%)
N-acetylmorpholine [c]	Morpholine (45%), diethylamine (17%), *N*-ethylacetamide (7%), *N*-ethylmorpholine (4%), *N*-methylethanamine (2%)
N-Hexylhexanamide	Hexylamine (6%)

[a]Compound is very volatile: therefore, yields are underestimated by analyzing the liquid phase.
[b]Methylamine, dimethylamine and trimethylamine are extremely volatile and weren't observed.
[c]High concentration of ethanol and ethylamine (0.04 M and 0.085 M respectively).

11. Ammonolysis of secondary amines

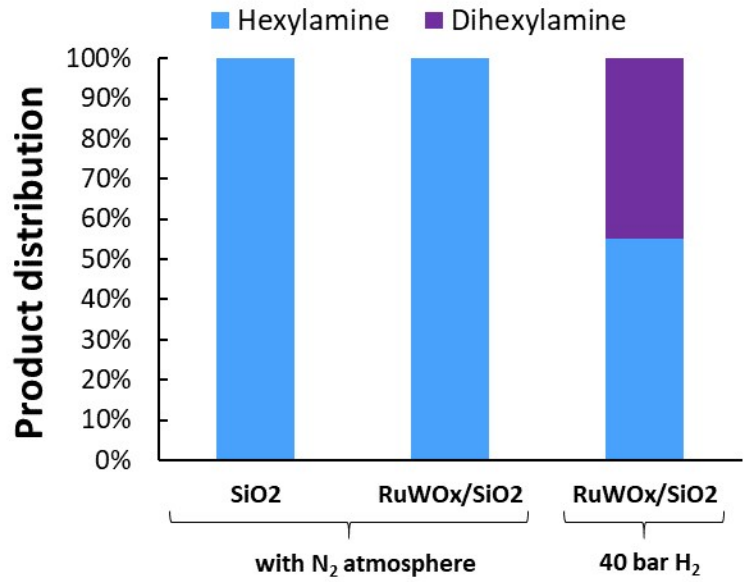
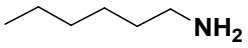


Figure S 20 – Ammonolysis of dihexylamine. Reaction conditions: hexylamine (1 mmol), 180°C, 1 mol% Ru ($RuWO_x/SiO_2$ or equal weight of SiO_2 support), undecane (20 µL), DME (10 mL), 16 h.

12. Product identification

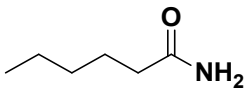
General information: ^{1}H-NMR spectra were calibrated by setting the singlet signal of the external standard (benzyl alcohol) to 4.59 ppm.[2]

Hexylamine (1, MW = 101 g/mol)



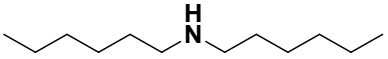
^{1}H-NMR (400 MHz, methanol-d4): δ (ppm) = 2.63 (t, 2H, NH_2-C**H$_2$**-), 1.47 (quint, 2H, NH_2-CH_2-C**H$_2$**-), 1.40-1.26 (m, 6H, -(C**H$_2$**)$_3$-CH_3), 0.92 (t, 3H, -C**H$_3$**).
^{13}C-NMR (400 MHz, H2O/D2O): δ (ppm) = 41.3 (NH_2-**C**H_2-), 32.5 (NH_2-CH_2-**C**H_2-), 31.5 (-$(CH_2)_2$-**C**H_2-), 26.3 (-**C**H_2-CH_2-CH_3), 22.4 (-**C**H_2-CH_3), 13.6 (-**C**H_3).
GC-MS (EI, 70eV): m/z (rel. int, %): 55 (3), 45 (5), 44 (9), 43 (4), 42 (5), 41 (8), 39 (6), 30 (100), 28 (8), 27 (7).

Hexanamide (2, MW = 115 g/mol)



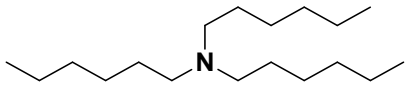
^{1}H-NMR (400 MHz, methanol-d4): δ (ppm) = 2.19 (t, 2H, -C(=O)-C**H$_2$**-), 1.61 (quint, 2H, -C(=O)-CH_2-C**H$_2$**-), 1.41-1.26 (m, 4H, -C**H$_2$**-C**H$_2$**-CH_3), 0.91 (t, 3H, -C**H$_3$**).
^{13}C-NMR (400 MHz, H2O/D2O): δ (ppm) = 178.0 (-**C**(=O)-), 35.3 (-C(=O)-**C**H_2-), 31.2 (-**C**H_2-CH_3), 25.3 (-C(=O)-CH_2-**C**H_2-), 22.2 (-**C**H_2-CH_2-CH_3), 13.4 (-**C**H_3).
GC-MS (EI, 70 eV): m/z (rel. int., %): 39 (19), 41 (24), 42 (14), 43 (29), 44 (52), 55 (14), 59 (100), 72 (33), 73 (8), 86 (23).

Dihexylamine (3, MW = 185 g/mol)



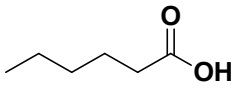
^{1}H-NMR (400 MHz, methanol-d4): δ (ppm) = 2.57 (t, 4H, -C**H$_2$**-NH-C**H$_2$**-), 1.47 (quint, 4H, -NH-CH_2-C**H$_2$**-), 1.40-1.26 (m, 12H, -(C**H$_2$**)$_3$-CH_3), 0.92 (t, 6H, -C**H$_3$**).
GC-MS (EI, 70eV): m/z (rel. int, %): 185 (6), 115 (9), 114 (100), 56 (5), 55 (6), 44 (53), 43 (21), 41 (11), 30 (9), 29 (6).

Trihexylamine (4, MW = 269 g/mol)



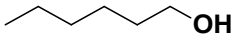
^{1}H-NMR (400 MHz, methanol-d4): δ (ppm) = 2.43 (t, 6H, -C**H$_2$**-NH-C**H$_2$**-), 1.47 (quint, 6H, -NH-CH_2-C**H$_2$**-), 1.40-1.26 (m, 18H, -(C**H$_2$**)$_3$-CH_3), 0.92 (t, 9H, -C**H$_3$**).
GC-MS (EI, 70eV): m/z (rel. int, %): 200 (15), 199 (100), 128 (13), 98 (5), 58 (5), 44 (5), 43 (12), 41 (5).

Hexanoic acid (5, MW = 116 g/mol)



^{1}H-NMR (400 MHz, methanol-d4): δ (ppm) = 2.16 (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$_3$**).
GC-MS (EI, 70eV): m/z (rel. int, %): 87 (16), 74 (8), 73 (53), 70 (6), 61 (10), 60 (100), 57 (11), 56 (10), 55 (15), 45 (16), 43 (20), 42 (14), 41 (29), 39 (14).

Hexanol (6, MW = 102 g/mol)

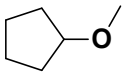


GC-MS (EI, 70eV): m/z (rel. int, %): 84 (5), 69 (31), 57 (9), 56 (100), 55 (52), 44 (5), 43 (54), 42 (39), 41 (42), 39 (13).

Hexane (7, MW = 72 g/mol)

GC-MS (EI, 70eV): m/z (rel. int, %): 39 (26), 41 (77), 42 (27), 43 (51), 55 (8), 56 (52), 57 (100).

Cyclopentyl methyl ether (8, MW = 100 g/mol)

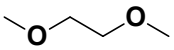


^{1}H-NMR (400 MHz, methanol-d4): δ (ppm) = 3.81 (m, 1H, -O-C**H**<), 3.26 (s, 3H, -C**H$_3$**), 1.79-1.48 (m, 8H, -C**H$_2$**-).
GC-MS (EI, 70eV): m/z (rel. int, %): 100 (17), 72 (11), 71 (100), 69 (8), 68 (5), 67 (9), 58 (12), 57 (11), 43 (11), 42 (7), 41 (36), 39 (20).

Cyclopentane (9, MW = 70 g/mol)

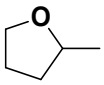
GC-MS (EI, 70eV): m/z (rel. int, %): 39 (21), 41 (31), 40 (7), 42 (100), 43 (6), 55 (43), 70 (33).

1,2-Dimethoxyethane (10, MW = 90 g/mol)



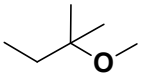
^{1}H-NMR (400 MHz, methanol-d4): δ (ppm) = 3.49 (s, 4H, -O-C**H$_2$**-), 3.30 (s, 6H, -O-C**H$_3$**).
GC-MS (EI, 70eV): m/z (rel. int, %): 45 (100), 58 (10), 60 (16), 90 (10).

2-Methyltetrahydrofuran (11, MW = 86 g/mol)



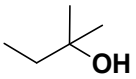
^{1}H-NMR (400 MHz, methanol-d4): δ (ppm) = 3.98-3.82; 3.72-3.64 (m, 3H, -C**H$_2$**-O-C**H**-), 2.07-1.82; 1.47-1.35 (m, 4H, -CH-C**H$_2$**-C**H$_2$**-), 1.21 (d, 3H, -C**H$_3$**).

tert-Amyl methyl ether (12, MW = 102 g/mol)



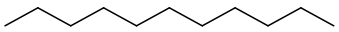
^{1}H-NMR (400 MHz, methanol-d4): δ (ppm) =3.17 (s, 3H, -O-C**H**$_3$), 1.52 (quart, 2H, -C**H**$_2$-CH$_3$), 1.13 (s, 6H, >C<(C**H**$_3$)$_2$), 0.88 (t, 3H, -CH$_2$-C**H**$_3$).

tert-Amyl alcohol (13, MW = 88 g/mol)



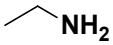
^{1}H-NMR (400 MHz, methanol-d4): δ (ppm) =1.46 (quart, 2H, -C**H**$_2$-CH$_3$), 1.13 (s, 6H, >C<(C**H**$_3$)$_2$), 0.88 (t, 3H, -CH$_2$-C**H**$_3$).

Undecane (14, MW = 156 g/mol)



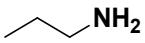
GC-MS (EI, 70eV): m/z (rel. int, %): 156 (6), 99 (5), 98 (7), 85 (32), 84 (9), 71 (51), 70 (14), 69 (6), 58 (5), 57 (100), 56 (18), 55 (16), 43 (81), 42 (12), 41 (40), 39 (9).

Ethylamine (15, MW = 45 g/mol)



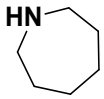
GC-MS (EI, 70eV): m/z (rel. int, %): 45 (100), 44 (100), 43 (14), 42 (47), 41 (22), 40 (21), 39 (8), 38 (6).

Propylamine (16, MW = 59 g/mol)



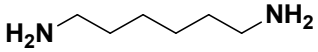
GC-MS (EI, 70eV): m/z (rel. int, %): 59 (100), 58 (21), 56 (11), 54 (5), 52 (6), 44 (9), 43 (19), 42 (33), 41 (51), 40 (8), 39 (24), 38 (6).

Azepane (17, MW = 99 g/mol)



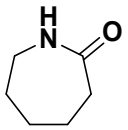
^{1}H-NMR (400 MHz, methanol-d4): δ (ppm) = 2.87-2.71 (m, 4H, -C**H**$_2$-NH-C**H**$_2$-), 1.74-1.49 (m, 8H, -NH-CH$_2$-C**H**$_2$-C**H**$_2$-).
GC-MS (EI, 70eV): m/z (rel. int, %): 99 (64), 98 (28), 84 (15), 71 (9), 70 (100), 68 (6), 57 (39), 56 (51), 55 (8), 44 (25), 43 (66), 42 (24), 41 (25), 39 (17).

Hexamethylenediamine (18, MW = 116 g/mol)



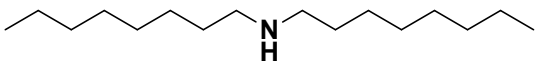
GC-MS (EI, 70eV): m/z (rel. int, %): 108 (5), 100 (20), 99 (14), 98 (8), 87 (58), 86 (27), 82 (6), 79 (9), 77 (5), 73 (10), 72 (14), 70 (30), 69 (13), 67 (7), 59 (17), 57 (10) 56 (100), 55 (19), 54 (5), 53 (5), 45 (29), 44 (31), 43 (23), 42 (32), 41 (30), 39 (13).

Caprolactam (19, MW = 113 g/mol)



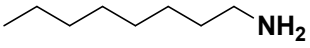
^{1}H-NMR (400 MHz, methanol-d4): δ (ppm) = 3.22-3.15 (m, 2H, -NH-C**H$_2$**-), 2.48-2.39 (m, 2H, -C(=O)-C**H$_2$**-), 1.82-1.48 (m, 6H, -NH-CH$_2$-(C**H$_2$**)$_3$-CH$_2$-C(=O)-).
GC-MS (EI, 70eV): m/z (rel. int, %): 114 (7), 113 (100), 86 (5), 85 (60), 84 (54), 83 (10), 69 (5), 68 (8), 67 (13), 59 (13), 57 (11), 56 (84), 55 (84), 55 (25), 54 (6), 53 (5), 44 (17), 43 (21), 42 (56), 41 (54), 40 (11), 39 (31).

Dioctylamine (20, MW = 241 g/mol)



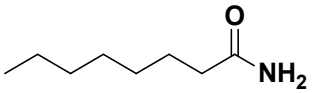
GC-MS (EI, 70eV): m/z (rel. int, %): 241 (5), 143 (11), 142 (100), 57 (6), 44 (32), 43 (10), 41 (8).

Octylamine (21, MW = 129 g/mol)



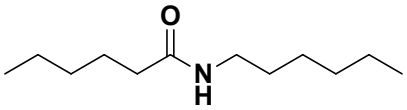
GC-MS (EI, 70eV): m/z (rel. int, %): 129 (13), 128 (8), 114 (5), 100 (26), 87 (5), 86 (52), 84 (8), 83 (12), 73 (6), 72 (17), 70 (16), 69 (33), 68 (5), 67 (6), 59 (15), 57 (9), 56 (40), 55 (48), 54 (7), 53 (10), 45 (62), 44 (75), 43 (47), 42 (39), 41 (100), 40 (8), 39 (42).

Octanamide (22, MW = 143 g/mol)



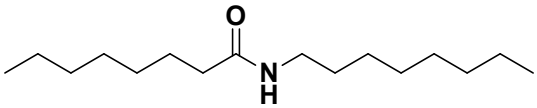
^{1}H-NMR (400 MHz, methanol-d4): δ (ppm) = 2.18 (t, 2H, -C(=O)-C**H$_2$**-), 1.78-1.47 (m, 4H, -C(=O)-CH$_2$-C**H$_2$**-C**H$_2$**-), 1.38-1.23 (m, 4H, -C**H$_2$**-C**H$_2$**-CH$_3$), 0.90 (t, 3H, -C**H$_3$**).
GC-MS (EI, 70eV): m/z (rel. int, %): 86 (9), 73 (5), 72 (29), 59 (100), 57 (8), 55 (9), 44 (20), 43 (14), 42 (5), 41 (14), 39 (5).

***N*-Hexylhexanamide (23, MW = 199 g/mol)**



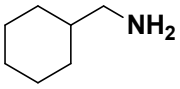
^{1}H-NMR (400 MHz, methanol-d4): δ (ppm) = 7.29 (s, 1H, -N**H**-), 3.15 (t, 2H, -NH-C**H$_2$**-), 2.16 (t, 2H, -C(=O)-C**H$_2$**-), 1.60 (quint, 2H, -C(=O)-CH$_2$-C**H$_2$**-), 1.49 (quint, 2H, -NH-CH$_2$-C**H$_2$**-), 1.38-1.25 (m, 10H, -CH$_3$-(C**H$_2$**)$_2$-R-C(=O)-NH-R'-(C**H$_2$**)$_3$-CH$_3$), 0.91 (t, 6H, -C**H$_3$**).
GC-MS (EI, 70eV): m/z (rel. int, %): 199 (8), 170 (31), 157 (10), 156 (86), 144 (7), 143 (71), 142 (6), 129 (18), 128 (52), 116 (16), 115 (5), 114 (35), 101 (29), 100 (43), 99 (62), 87 (37), 86 (54), 85 (12), 73 (53), 72 (24), 71 (35), 69 (5), 60 (9), 59 (5), 58 (15), 57 (10), 56 (10), 55 (27), 44 (40), 43 (100), 42 (13), 41 (42), 39 (11).

***N*-Octyloctanamide (24, MW = 255 g/mol)**



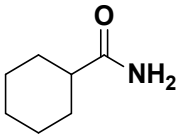
GC-MS (EI, 70eV): m/z (rel. int, %): 255 (16), 226 (20), 212 (20), 198 (25), 185 (13), 184 (100), 172 (7), 171 (55), 170 (6), 157 (16), 156 (49), 144 (13), 142 (17), 130 (7), 129 (8), 128 (29), 127 (39), 115 (10), 114 (44), 101 (19), 100 (38), 98 (5), 87 (30), 86 (47), 84 (8), 83 (5) 73 (63), 72 (21), 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).

Cyclohexylmethanamine (25, MW = 113 g/mol)



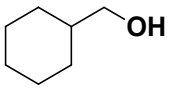
GC-MS (EI, 70eV): m/z (rel. int, %): 114 (12), 113 (100), 96 (43), 95 (11), 83 (5), 82 (16), 81 (38), 79 (9), 77 (8), 70 (6), 68 (18), 67 (73), 66 (5), 65 (7), 56 (23), 55 (70), 54 (43), 53 (21), 52 (5), 51 (8), 43 (10), 42 (19), 41 (77), 39 (53).

Cyclohexanecarboxamide (26, MW = 127 g/mol)



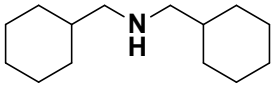
GC-MS (EI, 70eV): m/z (rel. int, %): 127 (39), 126 (13), 112 (15), 99 (9), 98 (40), 86 (18), 85 (10), 84 (5), 83 (38), 82 (6), 81 (7), 79 (5), 73 (10), 72 (96), 69 (5), 67 (14), 59 (64), 56 (16), 55 (100), 54 (11), 53 (11), 44 (31), 43 (7), 42 (7), 41 (50), 39 (25).

Cyclohexylmethanol (27, MW = 114 g/mol)



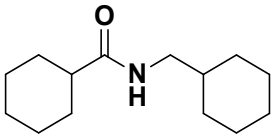
GC-MS (EI, 70eV): m/z (rel. int, %): 96 (22), 84 (5), 83 (68), 82 (28), 81 (57), 68 (15), 67 (45), 66 (5), 56 (6), 55 (100), 54 (13), 53 (9), 43 (7), 42 (7), 41 (45), 39 (21).

Bis(cyclohexylmethyl)amine (28, MW = 209 g/mol)



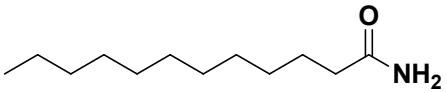
GC-MS (EI, 70eV): m/z (rel. int, %): 209 (5), 127 (9), 126 (100), 97 (6), 55 (23), 44 (33), 43 (7), 41 (11).

***N*-(cyclohexylmethyl)cyclohexanecarboxamide (29, MW = 223 g/mol)**



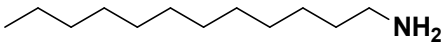
GC-MS (EI, 70eV): m/z (rel. int, %): 223 (10), 168 (17), 141 (20), 140 (8), 129 (8), 128 (100), 112 (10), 111 (17), 97 (6), 86 (9), 83 (43), 81 (7) 73 (8), 67 (9), 55 (42), 44 (11), 41 (19), 39 (5).

Dodecanamide (30, MW = 199 g/mol)



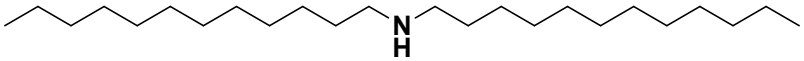
GC-MS (EI, 70eV): m/z (rel. int, %): 128 (5), 114 (5), 86 (8), 73 (6), 72 (40), 60 (6), 59 (100), 57 (7), 55 (11), 44 (15), 43 (17), 41 (15).

Dodecylamine (31, MW = 185 g/mol)



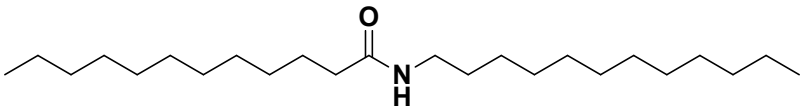
GC-MS (EI, 70eV): m/z (rel. int, %): 185 (12), 184 (9), 170 (5), 156 (14), 142 (15), 128 (12), 114 (15) 111 (6), 100 (34), 98 (6), 97 (13), 87 (7), 86 (59), 84 (10), 83 (18), 82 (6), 73 (9), 72 (21), 71 (5), 70 (16), 69 (36), 68 (6), 67 (8), 59 (20), 57 (23), 56 (41), 55 (67), 54 (7), 53 (8), 45 (59),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

Didodecylamine(32, MW = 354 g/mol)



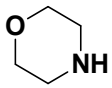
GC-MS (EI, 70eV): m/z (rel. int, %): 199 (15), 198 (100), 196 (5), 57 (8), 56 (5), 55 (7), 44 (19), 43 (9), 41 (7), 30 (5).

***N*-Dodecyldodecanamide (33, MW = 368 g/mol)**



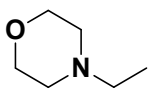
GC-MS (EI, 70eV): m/z (rel. int, %): 368 (5), 367 (18), 338 (10), 324 (15), 310 (9), 296 (20), 282 (19), 268 (12), 254 (22), 241 (17), 240 (100), 228 (12), 227 (61), 213 (14), 212 (55), 207 (5), 200 (9), 198 (11), 186 (14), 184 (20), 183 (15), 170 (13), 156 (12), 142 (16), 129 (5), 128 (18), 115 (9), 114 (36), 101 (16), 100 (27), 98 (8), 97 (7), 87 (23), 86 (34), 85 (13), 84 (8), 83 (11), 81 (5), 73 (47), 72 (16), 71 (21), 70 (6), 69 (19), 60 (8), 58 (9), 57 (55), 55 (39), 44 (27), 43 (71), 42 (8), 41 (37).

Morpholine (34, MW = 87 g/mol)



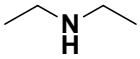
GC-MS (EI, 70eV): m/z (rel. int, %): %): 87 (77), 86 (37), 58 (7), 57 (100), 56 (49), 43 (6), 42 (17), 41 (6).

***N*-Ethylmorpholine (35, MW = 115 g/mol)**



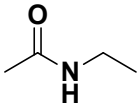
GC-MS (EI, 70eV): m/z (rel. int, %): 115 (37), 101 (6), 100 (100), 84 (5), 70 (12), 58 (7), 57 (85), 56 (25), 54 (6), 43 (6), 42 (88), 41 (8).

Diethylamine (36, MW = 73 g/mol)



GC-MS (EI, 70eV): m/z (rel. int, %): 39 (8), 41 (14), 42 (43), 44 (24), 55 (14), 56 (5), 58 (100), 70 (12), 72 (14), 73 (25).

***N*-Ethylacetamide (37, MW = 87 g/mol)**

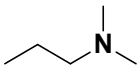


GC-MS (EI, 70eV): m/z (rel. int, %): 87 (100), 72 (21), 44 (65), 43 (85), 42 (20), 41 (6).

***N*-Methylethanamide (38, MW = 59 g/mol)**

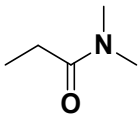
GC-MS (EI, 70eV): m/z (rel. int, %): 59 (42), 58 (27), 56 (7), 44 (100), 43 (8), 42 (14), 41 (4), 30 (23), 29 (8), 27 (9).

***N,N*-Dimethylpropanamine (39, MW = 87 g/mol)**



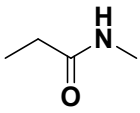
GC-MS (EI, 70eV): m/z (rel. int, %): 87 (13), 58 (100), 44 (9), 42 (12).

***N,N*-Dimethylpropanamide (40, MW = 101 g/mol)**



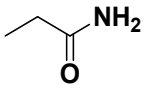
^{1}H-NMR (400 MHz, methanol-d4): δ (ppm) = 3.07 (s, 3H, -N-C**H**$_3$), 2.94 (s, 3H, -N-C**H**$_3$), 2.40 (quart, 2H, -C(=O)-C**H**$_2$-), 1.11 (t, 3H, -CH$_2$-C**H**$_3$).
GC-MS (EI, 70eV): m/z (rel. int, %): 101 (100), 73 (5), 72 (79), 58 (11), 57 (36), 56 (6), 55 (5), 46 (7), 45 (44), 44 (78), 43 (6), 42 (23).

***N*-Methylpropanamide (41, MW = 87 g/mol)**



^{1}H-NMR (400 MHz, methanol-d4): δ (ppm) = 2.68 (s, 3H, -NH-C**H**$_3$), 2.17 (quart, 2H, -C(=O)-C**H**$_2$-), 1.07 (t, 3H, -CH$_2$-C**H**$_3$).
GC-MS (EI, 70eV): m/z (rel. int, %): 87 (75), 86 (6), 59 (5), 58 (100), 57 (33), 56 (33), 55 (6), 44 (15).

Propionamide (42, MW = 73 g/mol)

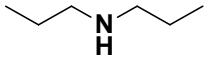


^{1}H-NMR (400 MHz, methanol-d4): δ (ppm) =2.21 (quart, 2H, -C(=O)-C**H$_2$**-), 1.12 (t, 3H, -C**H$_3$**).
GC-MS (EI, 70eV): m/z (rel. int, %): 99 (7), 73 (60), 72 (14), 70 (34), 57 (21), 56 (5), 55 (7), 44 (100), 42 (6).

Ethanol (43, MW = 46 g/mol)

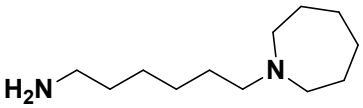
GC-MS (EI, 70eV): m/z (rel. int, %): 42 (11), 43 (20), 44 (10), 45 (100), 46 (35).

Dipropylamine (44, MW = 101 g/mol)



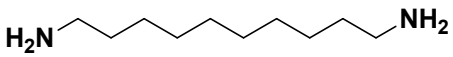
GC-MS (EI, 70eV): m/z (rel. int, %): 39 (5), 41 (15), 42 (5), 43 (20), 44 (11), 58 (6), 72 (100), 73 (5), 101 (15).

6-(azepan-1-yl)hexan-1-amine (45, MW = 198 g/mol)



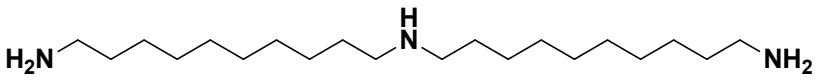
GC-MS (EI, 70eV): m/z (rel. int, %): 41 (6), 42 (5), 55 (6), 58 (8), 112 (100), 113 (8).

1,10-Diaminodecane (46, MW = 172 g/mol)



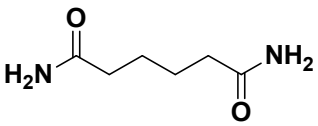
GC-MS (EI, 70eV): m/z (rel. int, %): 39 (12), 41 (40), 42 (17), 43 (23), 44 (75), 45 (38), 53 (5), 54 (6), 55 (44), 56 (60), 57 (8), 59 (27), 67 (10), 68 (6), 69 (32), 70 (20), 72 (26), 73 (11), 81 (7), 82 (6), 83 (12), 86 (45), 87 (11), 95 (5), 97 (9), 98 (6), 100 (45), 101 (5), 114 (31), 128 (36),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

***N*^{1}-(10-aminodecyl)decane-1,10-diamine (47, MW = 327 g/mol)**



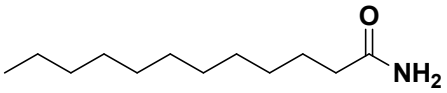
GC-MS (EI, 70eV): m/z (rel. int, %): 44 (11), 55 (7), 56 (6), 156 (6), 171 (6), 185 (100), 186 (13).

Adipamide (48, MW = 144 g/mol)



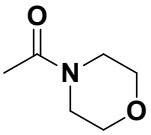
^{1}H-NMR (400 MHz, methanol-d4): δ (ppm) = 2.32 (t, 2H, -C(=O)-C**H$_2$**-), 1.76-1.70 (m, 4H, -C(=O)-CH$_2$-C**H$_2$**-).

Lauramide (49, MW = 144 g/mol)



^{1}H-NMR (400 MHz, methanol-d4): δ (ppm) = 2.19 (t, 2H, -C(=O)-C**H$_2$**-), 1.60 (quint, 2H, -C(=O)-CH$_2$-C**H$_2$**-), 1.38-1.22 (m, 8H, -(C**H$_2$**)$_8$-CH$_3$), 0.90 (t, 3H, -C**H$_3$**).

***N*-Acetylmorpholine (50, MW = 129 g/mol)**



GC-MS (EI, 70eV): m/z (rel. int, %): 41 (6), 42 (22), 43 (75), 44 (6), 54 (5), 55 (6), 56 (63), 57 (100), 58 (9), 70 (5), 71 (5), 72 (10), 86 (59), 87 (16), 99 (5), 114 (36), 129 (53).

13. References supporting information

(1) Guo, J., Lou, H., Zhao, H., Wang, X., & Zheng, X. *Materials Letters*, **2004**, *58*, 1920–1923.
(2) Babij, N. R., et al. *Organic Process Research and Development*, **2016**, *20*, 661–667.