

Supporting Information  
©Wiley-VCH 2021  
69451 Weinheim, Germany

## Magnetically Induced Catalytic Amination of Aliphatic Alcohols with Cu-based Nanoparticles

Víctor Varela-Izquierdo,<sup>[a]</sup> Irene Mustieles-Marín,<sup>[a]</sup> Pier-Francesco Fazzini,<sup>[b]</sup> Gabriel Mencía,<sup>[a]</sup> Simon Guelen,<sup>[c]</sup> Rabih Ratchet,<sup>[c]</sup> and Bruno Chaudret<sup>\*,[a]</sup>

**Abstract:** Bimetallic nanoparticles (NPs) displaying a magnetic core (Co<sub>4</sub>Ni<sub>6</sub> and Fe<sub>3</sub>Ni<sub>7</sub>) and a Cu shell have been developed for the synthesis of tertiary amines in one-step from primary alcohols (i. e. heptanol, dodecanol) and secondary amines (Me<sub>2</sub>NH (DMA), <sup>n</sup>Pr<sub>2</sub>NH, <sup>t</sup>Bu<sub>2</sub>NH) using magnetically induced heating. This methodology strongly limits the redistribution reactions occurring on amines at high temperature as observed when using conventional heating therefore leading to high conversion and selectivity. Moreover, Co<sub>4</sub>Ni<sub>6</sub>@Cu NPs were found resistant to moisture, thereby allowing for performing the reaction with commercial DMA in water (40 % wt). As an additional advantage, the magnetic behavior of the NPs facilitates the separation of the catalyst by magnetic decantation.

DOI: 10.1002/anie.2021XXXXX

### Table of Contents

<b>1. Experimental Procedures</b> .....	<b>2</b>
1.1. Materials and Methods .....	2
1.2. Synthesis of the catalysts .....	2
1.3. Characterization of the catalysts:.....	3
<b>2. Catalytic experiments</b> .....	<b>8</b>
2.1. GC-MS Method .....	9
2.2. Selected Mass Spectrums .....	10
2.3. Selected Chromas for the reactions with dodecanol and dibutylamine .....	13
2.4. Selected Chromas for the reactions with dodecanol and dipropylamine.....	13
<b>2.5. Selected Chromatograms for the reaction with heptanol and dibutylamine</b> .....	<b>14</b>
<b>2.6. Selected Chromatogram for the reaction with benzylalcohol and dibutylamine</b> .....	<b>14</b>
<b>2.7. Selected Chromatogram for the reaction with cyclohexanone and dibutylamine</b> .....	<b>14</b>
<b>2.8. Chromatogram for the reactions with dodecanal and dibutylamine</b> .....	<b>14</b>
2.9. Recycling tests with dodecanol and dibutylamine. ....	15
2.10. <b>Selected Chromatograms for the reactions with dodecanol and DMA in water</b> .....	<b>15</b>
2.11. Selected Chromatograms for the reactions with dodecanol and DMA in THF .....	15
2.12. Scale-up reaction with DMA (40 wt% in water) .....	17
<b>3. Study of the catalyst after the catalysis by XRD and TEM</b> .....	<b>17</b>

4. Transalkylation reactions of secondary amines .....	19
5. References .....	20
6. Author Contributions .....	20

## 1. Experimental Procedures

### 1.1. Materials and Methods

**General methods.** All air-sensitive procedures were carried out either under an inert atmosphere of argon inside a glovebox or in a schlenck line. Mesitylene (99%) and toluene (99%) were purchased from VWR PROLABO. The solvents were purified on an alumina desiccant and degassed by bubbling Ar through the solution for ca. 40 minutes. Palmitic acid (PA, > 99 %) was purchased from Sigma Aldrich.  $\{\text{Co}[\text{N}(\text{SiMe}_3)_2]_2(\text{thf})\}$ ,  $\{\text{Fe}[\text{N}(\text{SiMe}_3)_2]_2\}$ ,  $\{\text{Ni}[\text{PrNC}(\text{CH}_3)\text{N}^i\text{Pr}]\}$  and  $\{\text{Cu}_2[\text{PrNC}(\text{CH}_3)\text{N}^i\text{Pr}]_4\}$  were obtained from Nanomeps. All these reactants were used without any additional purification and stored in a glove box under Ar atmosphere.

**Thermogravimetric analyses (TGA)** were performed in a TGA/DSC 1 STAR System equipped with an ultra-microbalance UMX5, a gas switch GC200 and DTA and DSC sensors. Chemical composition of the powder was determined by inductively coupled plasma mass spectrometry (ICP-MS, Pascher laboratory).

**Morphological and Chemical Characterization.** The size and the morphology of the NPs were studied by transmission electron microscopy (TEM), using a 120 kV JEOL microscope 1400, working at 120 kV. Scanning TEM (STEM) and energy X-ray dispersive analysis (STEM-EDX) were conducted on a Scanning Electron Microscopy JEOL 2100F equipped with an SSD Bruker detector to determine the relative metal content. Electron energy loss spectroscopy (EELS) measurements were performed on ARM-200F electron microscope equipped with a cold field emission gun (FEG) with a spatial resolution of  $\sim 0.8\text{\AA}$ . To prepare the TEM grids, 5 mg of the powder were dispersed in toluene and sonicated for 2 min. Then, few drops of the colloidal solution were deposited on a carbon-coated Cu grid or Au grid.

**X-ray diffraction (XRD)** measurements were performed on a PANalytical Empyrean diffractometer using Co-K $\alpha$  radiation ( $\lambda=0.1789$  nm) at 45 kV and 30 mA. In a glove box, few mg of the powder was placed between two Kapton sheets and sealed with grease to prevent air exposure.

**Vibrating Sample Magnetometer (VSM)** measurement Magnetic measurements were carried using a Vibrating Sample Magnetometer (VSM, Quantum Device PPMS Evercool II) by placing about 10 mg of dry powder sample in a sealed Teflon capsule inside the glovebox. The magnetization versus magnetic field measurements (hysteresis loop) were conducted at both 300 and 5 K, with an external field of up to  $\pm 3$  T

The catalytic mixtures were analyzed by **gas chromatography** (GC PerkinElmer 580) and a FID detector and using H<sub>2</sub> as carrier gas. The GC is coupled to a Clarus SQ8T mass spectrometer. Conversion and yields were obtained by comparison of the peak areas of reagent, products and internal standard. Specific absorption rate (SAR) of the NPs was measured by calorimetry using a coil with a fixed frequency of 93 kHz, following an already described procedure.[1]

**Specific absorption rate (SAR)** values were measured by calorimetry experiments following the protocol already described in our previous work[1] using a coil with a fixed frequency of 93 kHz. In a typical experiment under inert atmosphere, a sample tube was charged with the sample Mag-NPs (around 10 mg) and dry mesitylene (0.5 mL) was added. The tube was sealed with a Teflon lined screw cap and then the mixture was sonicated during a few seconds to disperse the Mag-NPs in the solvent. During the calorimetric experiments, the sample tube was placed inside a socket filled with 1.8 mL of deionized water, in the center of the magnetic coil. Two temperature probes are submerged in the water, one near the bottom of the socket and the other near the center. Then, the temperature increase after applying an AMF during 50 seconds is measured using different field amplitudes, which allows us to construct a curve of SAR ( $W \cdot g^{-1}$ ) against field amplitude (mT).

### 1.2. Synthesis of the catalysts

**Co<sub>3</sub>Ni<sub>6</sub> (1):** In a glovebox  $\{\text{Co}[\text{N}(\text{SiMe}_3)_2]_2(\text{thf})\}$  (418 mg, 0.96 mmol) and  $\{\text{Ni}[\text{PrNC}(\text{CH}_3)\text{N}^i\text{Pr}]\}$  (475 mg, 1.4 mmol) were dissolved separately in 4 and 6 mL of degassed mesitylene respectively. Both solutions were mixed in a 100 mL Fisher Porter (FP) bottle. Then, palmitic acid (593 mg, 2.3 mmol) was dissolved in 8 mL of mesitylene and was added to the mixture under vigorous magnetic stirring. The FP bottle was pressurized with 3 bar of H<sub>2</sub> and stirred at RT for 40 min. Then, the reaction mixture was heated at 120 °C for 24 hours under magnetic stirring. The NPs were recovered by magnetic decantation, washed with toluene (3 x 5 mL) and dried under vacuum. CoNi NPs were obtained as black powder (ca. 135 mg) The NPs were characterized by TEM, XRD and their SAR was determined by calorimetry. (78 % of metal content determined by TGA): Ni, 48 wt%;Co 32 %wt.

**Fe<sub>3</sub>Ni<sub>7</sub> (2):** In a glove box,  $\{\text{Ni}[\text{PrNC}(\text{CH}_3)\text{N}^i\text{Pr}]\}$  (692 mg, 2.00 mmol) and  $\{\text{Fe}[\text{N}(\text{SiMe}_3)_2]_2\}$  (301 mg, 0.40 mmol) were dissolved separately in 8 and 4 mL of degassed mesitylene respectively. Both solutions were mixed in a 100 mL FP bottle. Then, palmitic acid (185 mg, 0.72 mmol) dissolved in 8 mL of mesitylene was added to the mixture under vigorous magnetic stirring. The FP bottle was pressurized with 3 bar of H<sub>2</sub> and heated at 150 °C for 24 hours under magnetic stirring. The NPs were recovered by magnetic decantation, washed with toluene (3 x 5 mL) and dried under vacuum. Ni<sub>7</sub>Fe<sub>3</sub> NPs were obtained as a black powder (ca. 130 mg). (95 % of metal content determined by TGA): Ni, 67 wt%; Fe 28 %wt.

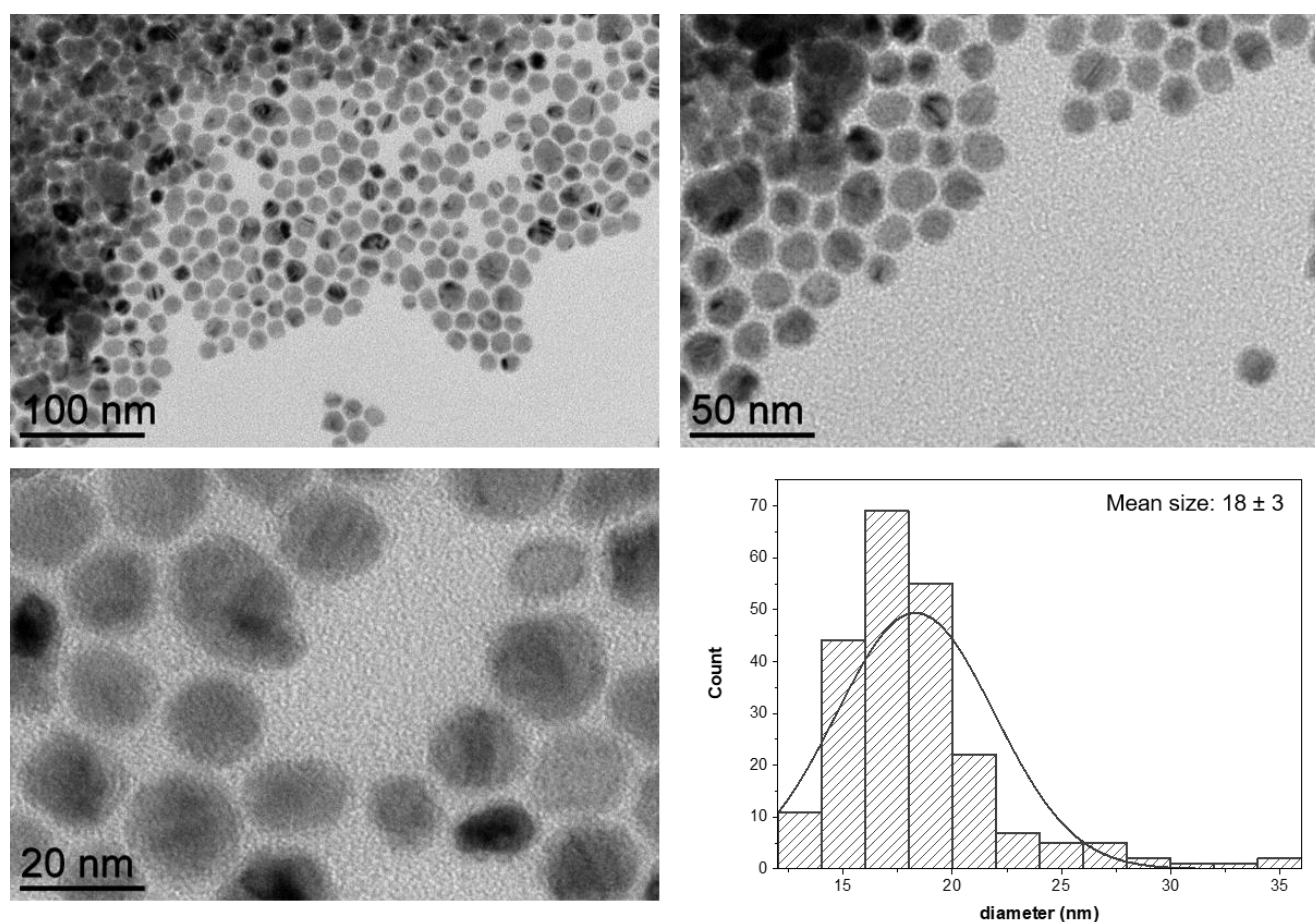
**Co<sub>4</sub>Ni<sub>6</sub>@Cu (3):** In a glovebox, 100 mg of NPs 1 (ca. 1.3 mmol of metal) were dispersed in 10 mL of mesitylene in a 180 mL FP bottle. Then, a solution of {Cu<sub>2</sub>[<sup>i</sup>PrNC(CH<sub>3</sub>)N<sup>i</sup>Pr]<sub>4</sub>} (327.6 mg, 0.80 mmol) in 8 mL of mesitylene was added. Afterwards, palmitic acid (410.2 mg, 1.6 mmol) was dissolved in 16 mL of mesitylene and was added to the mixture under vigorous magnetic stirring. The FP bottle was pressurized with 3 bar of H<sub>2</sub> and the reaction was heated at 80 °C for 3 hours and then, at 120 °C for 24 hours under magnetic stirring. The NPs were recovered by magnetic decantation, washed with toluene (4 x 5 mL) and dried under vacuum. NPs 3 were recovered as a reddish black powder (ca. 150 mg) and fully characterized. (90 % of metal content determined by TGA): Ni, 24 wt%; Co 16 %wt; Cu 49 %wt.

**Fe<sub>3</sub>Ni<sub>7</sub>@Cu (4):** In a glovebox, 50 mg of NPs 2 (ca. 0.86 mmol of metal) were dispersed in 5 mL of mesitylene in a 100 mL FP bottle. Then, a solution of {Cu<sub>2</sub>[<sup>i</sup>PrNC(CH<sub>3</sub>)N<sup>i</sup>Pr]<sub>4</sub>} (163.8mg, 0.40 mmol) in 5 mL of mesitylene was added. Afterwards, palmitic acid (205.1 mg, 0.8 mmol) was dissolved in 10 mL of mesitylene and was added to the mixture under vigorous magnetic stirring. The FP bottle was pressurized with 3 bar of H<sub>2</sub> and the reaction was heated at 120 °C for 24 hours under magnetic stirring. The NPs were recovered by magnetic decantation, washed with toluene (3 x 5 mL) and dried under vacuum. NPs 4 were recovered as a black powder (ca. 78 mg) and fully characterized. (96 % of metal content determined by TGA): Ni, 37 wt%; Fe 12 %wt; Cu 46 %wt.

**Supported catalyst general preparation:** In a glovebox, 117 mg of the support (Al<sub>2</sub>O<sub>3</sub> or C<sub>mes</sub>) and 15 mL of THF were added to a 180 mL FP bottle under magnetic stirring. After that, 50 mg of NPs 3 were added to the FP bottle. The mixture was stirred for 16 hours at room temperature, and 15 mL of pentane were added to aid the solid precipitation. The solid was recovered by magnetic decantation and the black powder obtained was washed twice with 10 mL of pentane. Finally, the remaining powder was further dried under vacuum and stored in a glovebox.

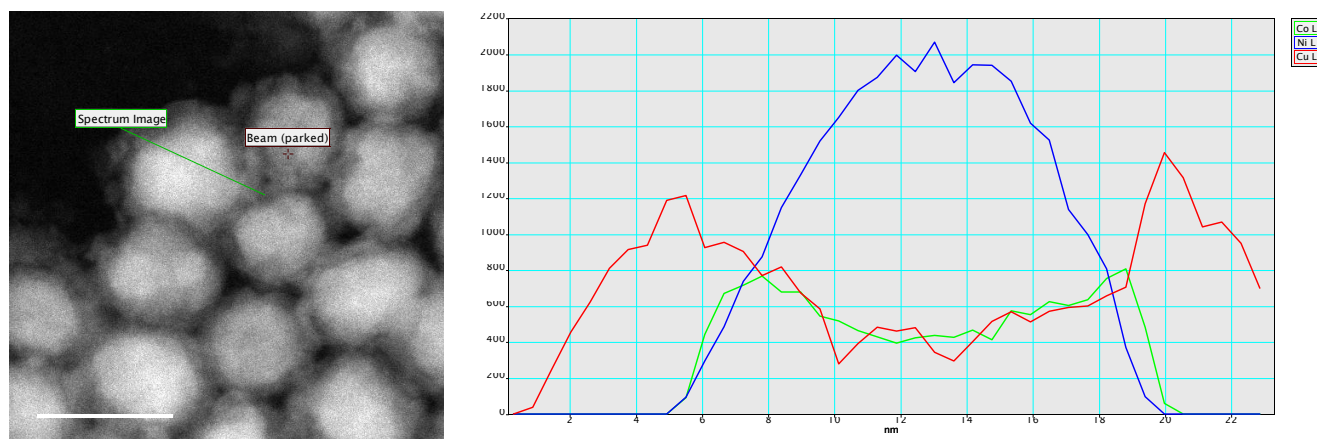
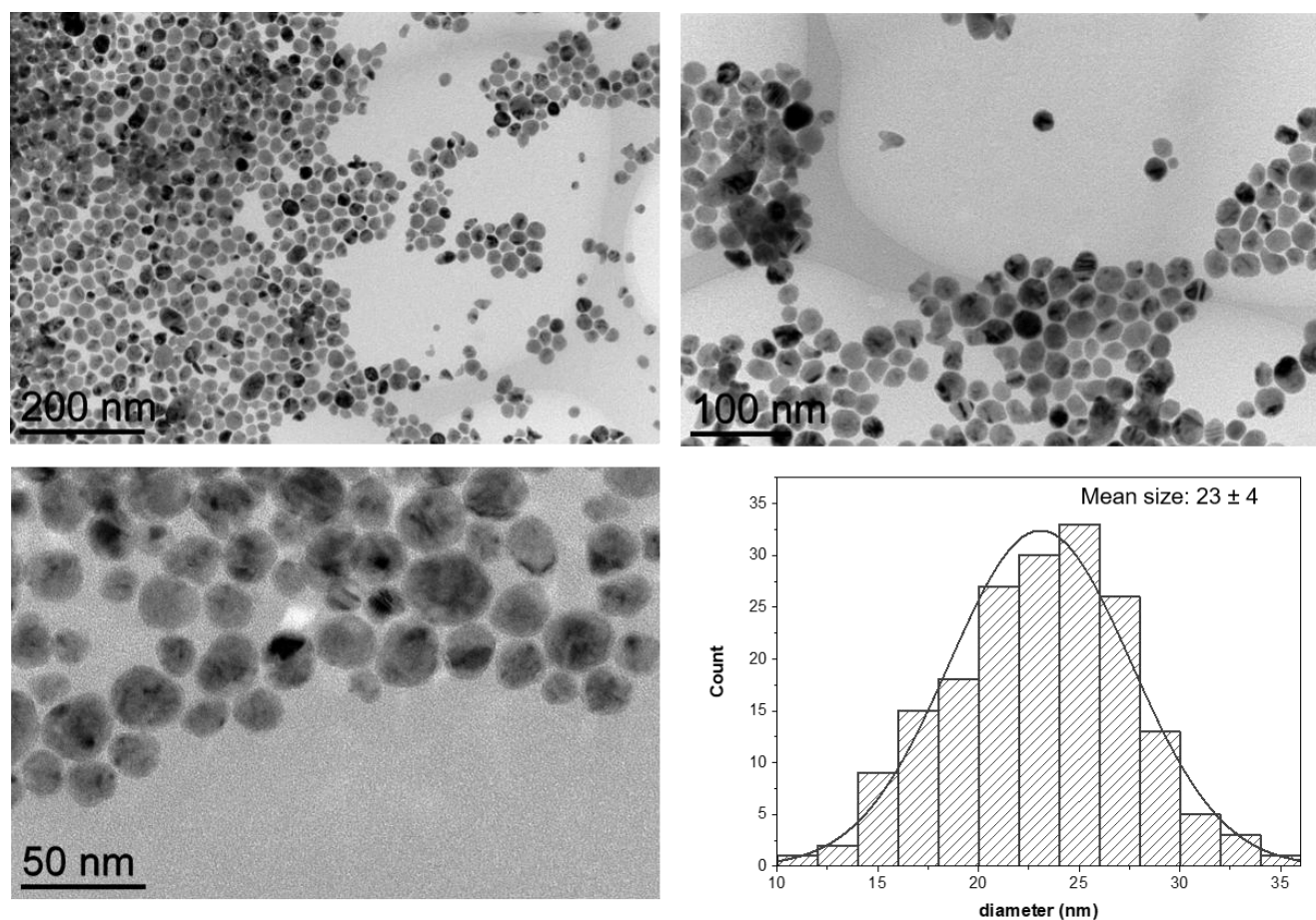
### 1.3. Characterization of the catalysts:

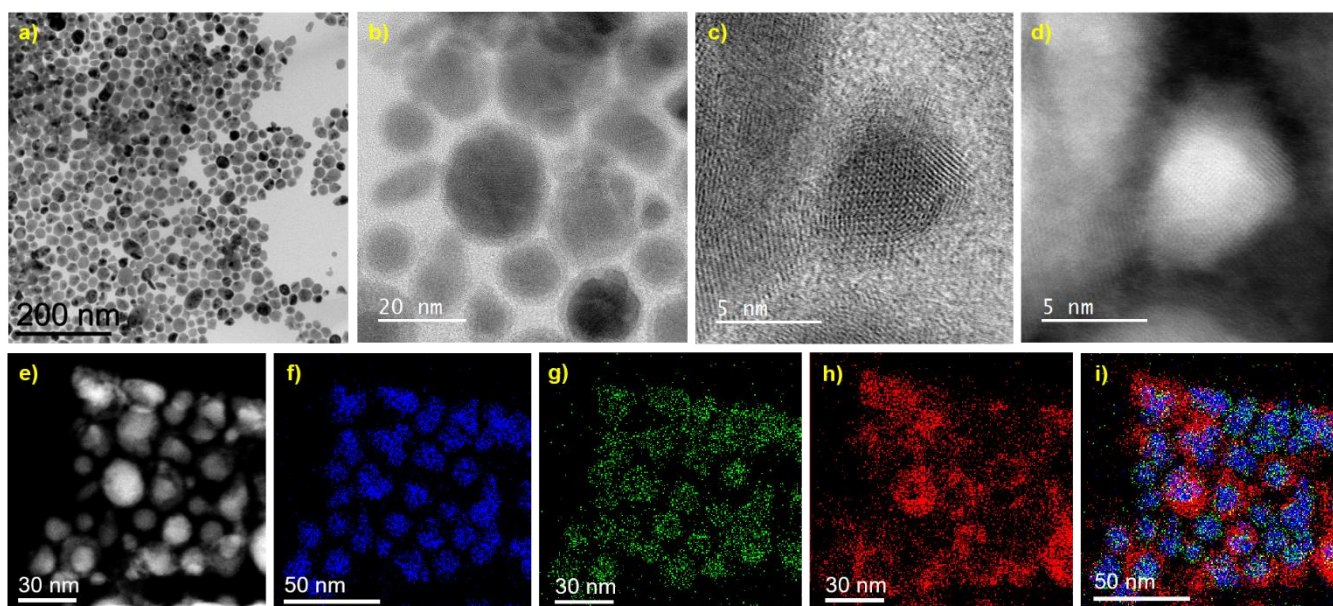
#### TEM pictures for Co<sub>4</sub>Ni<sub>6</sub>@Cu



**Figure S1.** TEM pictures for Co<sub>4</sub>Ni<sub>6</sub>@Cu

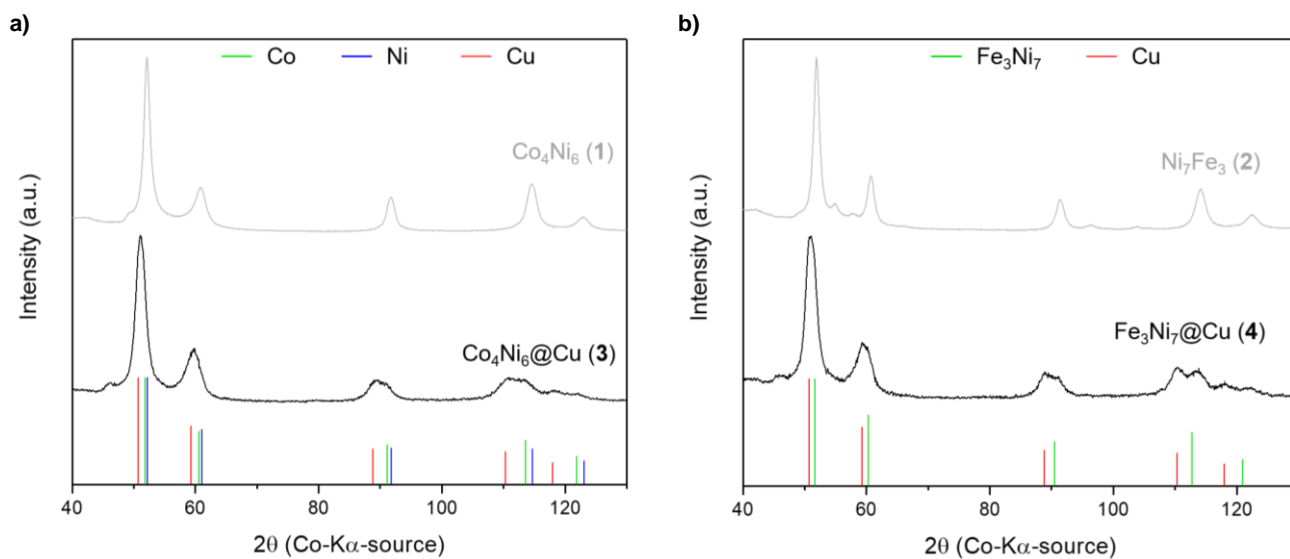


EELS experiment for  $\text{Co}_4\text{Ni}_6\text{@Cu}$ Figure S2. EELS experiment for  $\text{Co}_4\text{Ni}_6\text{@Cu}$ TEM pictures for  $\text{Fe}_3\text{Ni}_7\text{@Cu}$ Figure S3. TEM pictures for  $\text{Fe}_3\text{Ni}_7\text{@Cu}$



**Figure S4.** a) TEM image for  $\text{Fe}_3\text{Ni}_7@\text{Cu}$  NPs (Mean size =  $23 \pm 4$  nm). b-c) HR-STEM micrograph of isolated NPs. d-e) STEM-HAADF images for  $\text{Fe}_3\text{Ni}_7@\text{Cu}$ . f-i) Chemical mapping of  $\text{Fe}_3\text{Ni}_7@\text{Cu}$  showing f) Ni in blue, g) Fe in green, h) Cu in red, i) Overlapping Ni + Fe + Cu. The NPs exhibited a polycrystalline structure.

#### XRD measurements



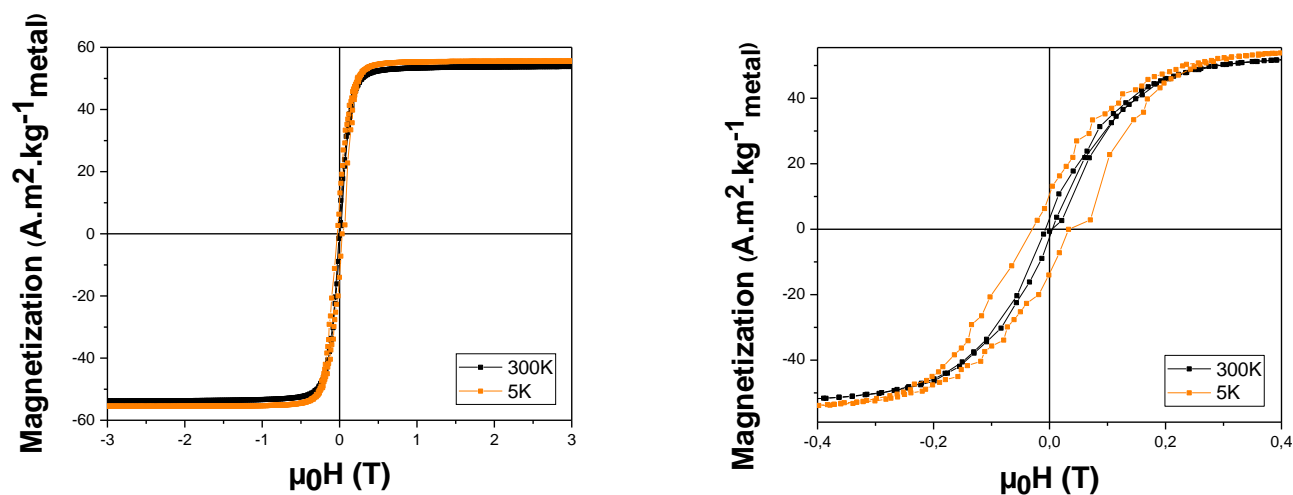
**Figure S5.** a) Powder XRD (X-Ray Diffraction) spectrum of  $\text{Co}_4\text{Ni}_6$  (1, top)  $\text{Co}_4\text{Ni}_6@\text{Cu}$  NPs (3, bottom). a) Powder XRD (X-Ray Diffraction) spectrum of  $\text{Fe}_3\text{Ni}_7$  (2, top)  $\text{Fe}_3\text{Ni}_7@\text{Cu}$  NPs (4, bottom).

## VSM measurements

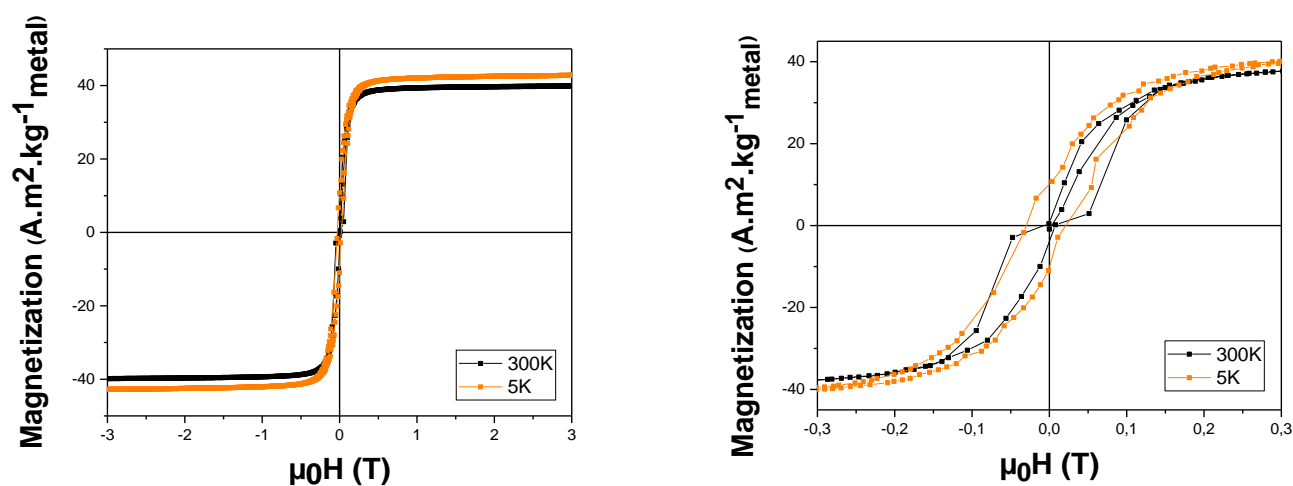
**Table S1.** Magnetic properties measurement for the Mag-NPs

Material	T (K)	$M_S$ ( $A \cdot m^2 \cdot kg^{-1}$ ) <sup>a</sup>	$M_R$ ( $A \cdot m^2 \cdot kg^{-1}$ ) <sup>b</sup>	$H_c$ (mT) <sup>c</sup>
Co <sub>4</sub> Ni <sub>6</sub> (1) <sup>2</sup>	5	98	31	69
	300	99	3	3
Fe <sub>3</sub> Ni <sub>7</sub> (2) <sup>3</sup>	5	98	16	41
	300	94	0.6	-
Co <sub>4</sub> Ni <sub>6</sub> @Cu (3)	5	56	10	33
	300	54	3	6
Fe <sub>3</sub> Ni <sub>7</sub> @Cu (4)	5	43	10	21
	300	40	1	7

<sup>a</sup>Saturation magnetization; <sup>b</sup> Remanence Magnetization. <sup>c</sup> coercive field.

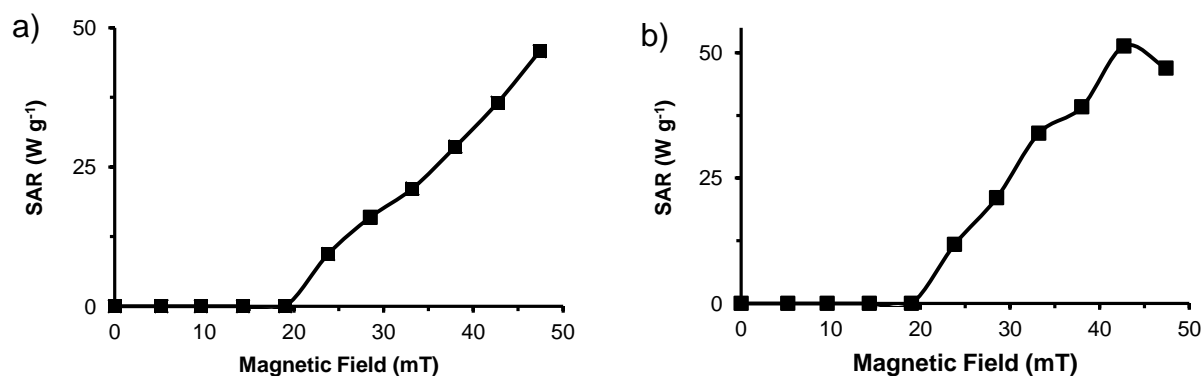


**Figure S6.** Hysteresis loop for Co<sub>4</sub>Ni<sub>6</sub>@Cu NPs determined by VSM and measured at 5 K (orange) and at 300 K (black).  $M_S$  (Magnetization at Saturation value) at 300 K = 54  $A \cdot m^2 \cdot kg^{-1}$ .  $M_S$  at 5 K = 56  $A \cdot m^2 \cdot kg^{-1}$ .



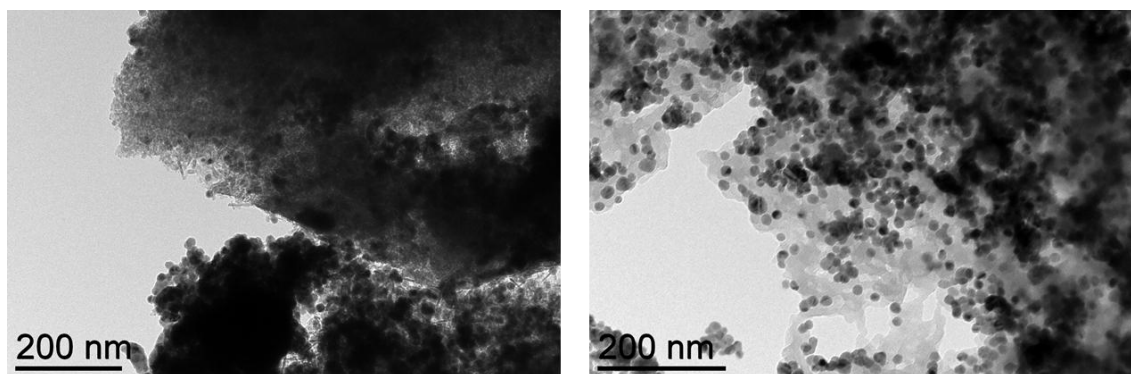
**Figure S7.** Hysteresis loop for  $\text{Fe}_3\text{Ni}_7@Cu$  NPs determined by VSM and measured at 5 K (orange) and at 300 K (black).  $M_s$  (Magnetization at Saturation value) at 300 K =  $43 \text{ A m}^2 \text{ kg}^{-1}$ .  $M_s$  at 5 K =  $40 \text{ A m}^2 \text{ kg}^{-1}$ .

#### SAR measurements



**Figure S8.** a) SAR of  $\text{Co}_4\text{Ni}_6@Cu$  NPs determined by calorimetry: 10 mg of NPs dispersed in 0.5 mL of mesitylene ( $C_p = 400 \text{ J.kg}^{-1}.\text{K}^{-1}$  for  $\text{Co}_4\text{Ni}_6@Cu$  alloy,  $C_p = 1750 \text{ J.kg}^{-1}.\text{K}^{-1}$  for mesitylene,  $C_p = 4186 \text{ J.kg}^{-1}.\text{K}^{-1}$  for water and  $C_p = 720 \text{ J.kg}^{-1}.\text{K}^{-1}$  for glass). b) SAR of  $\text{Fe}_3\text{Ni}_7@Cu$  NPs determined by calorimetry: 10 mg of NPs dispersed in 0.5 mL of mesitylene. ( $C_p = 418 \text{ J.kg}^{-1}.\text{K}^{-1}$  for  $\text{Fe}_3\text{Ni}_7@Cu$  alloy).

#### TEM pictures of the supported $\text{Co}_4\text{Ni}_6@Cu$ Mag-NPs



**Figure S9.** a) TEM image for  $\text{Co}_4\text{Ni}_6@Cu/\text{Al}_2\text{O}_3$  NPs, b) TEM image for  $\text{Co}_4\text{Ni}_6@Cu/C_{mes}$  NPs



## 2. Catalytic experiments

In a typical experiment, 5 mmol of substrate (alcohol/amine), 1 or 5 mmol of dodecane used as internal standard, and ca. 15, 30 or 45 mg of catalyst (2.3, 4.6 or 6.8 mol % respectively, based on Cu content) were mixed in a Fisher–Porter bottle in the glove box. The Fisher–Porter bottle was sealed and placed in the center of the magnetic coil and the amplitude settled to the desired value for the required time. At the end of the reaction, the FP was cool down and pressure was released (in some reactions with long chain amines, manometer pressure was > 1 bar). The gas was analyzed by GC-MS and identified as H<sub>2</sub> – due to oxidation of the alcohol to aldehyde). Temperature was recorded on the surface of the external glass of the FP with an IR camera after 1 h of reaction. The pressure was released and 8 mL of diethyl ether was added. The catalyst was separated by magnetic decantation and the reaction mixture was stirred for 20 minutes in the presence of MgSO<sub>4</sub> (to remove the water formed during the reaction) and filtered off through Celite®. After that, 20 µL were taken and diluted in 1.4 mL of diethyl ether for GC-MS analysis. The induction coil is equipped with a user interface, where the software permits continuous monitoring and adjust the percentage of magnetic field amplitude applied. The relation between the power in kW and the magnetic field amplitudes in % and mT is shown in the table below. In the blank reaction, the FP was placed in an oil bath at the indicated temperature

**Table S2.** Magnetic properties measurement for the Mag-NPs

Field (%)	Power (kW)	Field Amplitude (mT)
100	12.9	65
80	10.8	60
60	8.2	53
40	5.5	44
20	2.8	33
10	1.5	24
5	0.8	15

Conversion (%) was calculated with the remaining dibutylamine (C<sub>DBA</sub>) and alcohol (C<sub>dodecanol</sub>). Selectivity for DBDA (S<sub>DBDA</sub>) was calculated with the relative area by taking into account the different amines obtained due to inability of the compound. Selectivity for DMDA (S<sub>DMDA</sub>) was calculated with the number of moles at the end of the reaction.

$$C_{DBA} (\%) = \frac{n_{DBA,0} - n_{DBA}}{n_{DBA,0}} \times 100$$

$$C_{dodecanol} (\%) = \frac{n_{dodecanol,0} - n_{dodecanol}}{n_{dodecanol,0}} \times 100$$

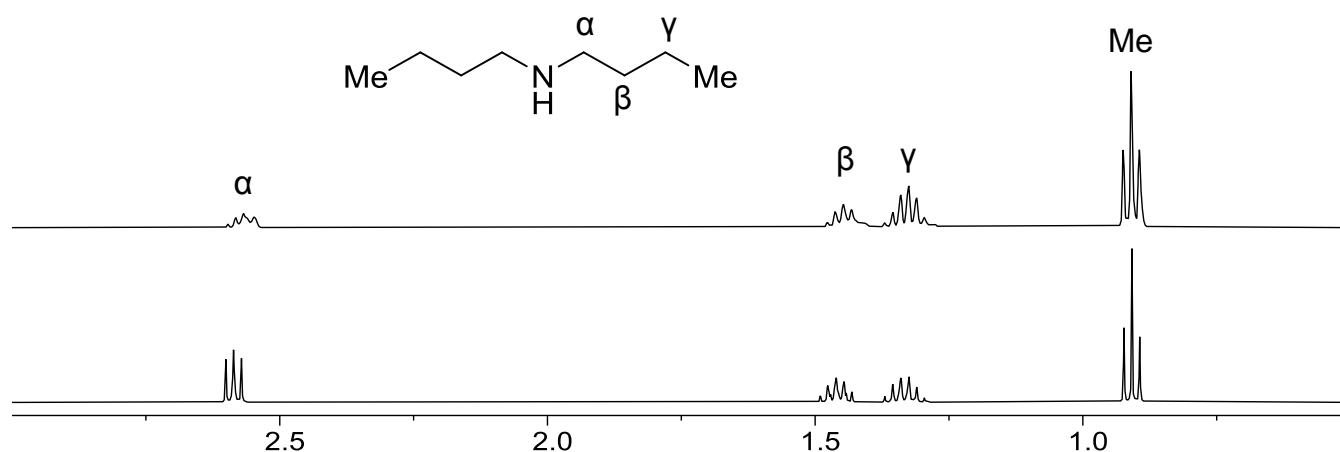
$$S_{DBDA} = \frac{A_{DBDA}}{A_{TBA} + A_{DBDA} + A_{BDA} + A_{BDDA}} \times 100$$

$$S_{DMDA} = \frac{n_{DMDA}}{n_{DMDA,T}} \times 100$$

n <sub>DBA,0</sub>	initial moles of dibutylamine
n <sub>DBA</sub>	moles of dibutylamine
n <sub>dodecanol,0</sub>	initial moles of dodecanol
n <sub>dodecanol</sub>	moles of dodecanol
A <sub>DBDA</sub>	area of dibutyldodecanamine
A <sub>TBA</sub>	area of tributylamine
A <sub>BDA</sub>	area of butyldodecanamine
A <sub>BDDA</sub>	area of butyldidodecanamine
n <sub>DMDA</sub>	moles of dimethyldodecanamine
n <sub>DMDA,T</sub>	theoretical moles of dimethyldodecanamine

The di(butyl-1,1-d<sup>2</sup>)amine was prepared as follows. In a Fisher Porter bottle a stirring bar, Ru/C<sub>mes</sub> (100 mg, 10 wt % Ru, C<sub>mes</sub> = mesoporous carbon) and dibutylamine were introduced (5 mL). Then, the F.P. bottle was charged with 4 bars of D<sub>2</sub> and stirred at 120 °C for 3 hours, the mixture was decanted and the colourless liquid was filtered off with a PTFE filter. The formation of di(butyl-1,1-d<sup>2</sup>)amine was analysed by GC-MS and <sup>1</sup>H-NMR. Dibutylamine was deuterated in the α-position in 67% yield. MS *m/z* calc. for C<sub>8</sub>H<sub>10</sub>D<sub>4</sub>N [M]<sup>+</sup>133.2681, found: 133.2927).





**Figure S10.** <sup>1</sup>H-NMR spectra of the dibutylamine (bottom) and the partial deuterated dibutylamine-*d*<sub>4</sub> (top). The product was deuterated in a 67% in  $\alpha$ -position and 41% in  $\beta$ -position.

### 2.1. GC-MS Method

The initial temperature, 50 °C, was increased to 100 °C at 10 °C min<sup>-1</sup>. Then, increased to 280 °C at 15 °C min<sup>-1</sup> and hold for 5 minutes. The injector temperature was settled at 250 °C and the carrier gas (hydrogen) flowed at 2 mL min<sup>-1</sup>. Retention time and isotopic mass founded of the chemical compounds are included in the following table:

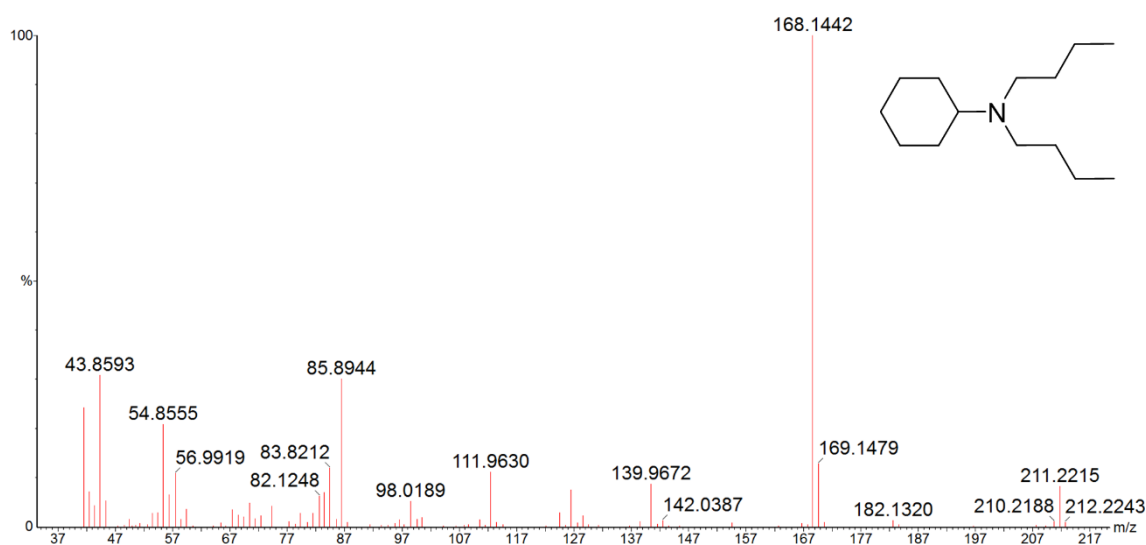
**Table S3.** Retention time, theoretical and founded isotopic mass for the catalytic products injected in the GC-MS.

Compound	Molecular formula	Retention Time (min)	Molecular Peak	Theoretical Isotopic Mass	Experimental Isotopic Mass
<sup>n</sup> Pr <sub>2</sub> NH	C <sub>6</sub> H <sub>15</sub> N	3.54	[M] <sup>+</sup>	101.1204	101.1911
Cyclohexanol	C <sub>6</sub> H <sub>12</sub> O	3.77	[M] <sup>+</sup>	100.0888	100.0290
Cyclohexanone	C <sub>6</sub> H <sub>10</sub> O	3.82	[M] <sup>+</sup>	98.0731	97.8933
Benzaldehyde	C <sub>7</sub> H <sub>12</sub> O	4.54	[M] <sup>+</sup>	106.0418	105.8706
Benzylalcohol	C <sub>7</sub> H <sub>14</sub> O	5.40	[M] <sup>+</sup>	108.0575	107.9433
<sup>n</sup> Bu <sub>2</sub> NH	C <sub>8</sub> H <sub>19</sub> N	5.49	[M] <sup>+</sup>	129.1571	129.1208
<sup>n</sup> Bu <sub>3</sub> NH	C <sub>12</sub> H <sub>27</sub> N	8.42	[M] <sup>+</sup>	185.2143	184.1582
Dodecane	C <sub>12</sub> H <sub>26</sub>	8.55	[M] <sup>+</sup>	170.2035	170.1711
N,N-dibutylcyclohexanamine	C <sub>12</sub> H <sub>29</sub> N	9.93	[M] <sup>+</sup>	211.2300	211.2215
Dodecanal	C <sub>12</sub> H <sub>24</sub> O	10.57	[M-CO] <sup>+</sup>	156.1878	156.1812
N,N-dibutylheptanamine	C <sub>15</sub> H <sub>33</sub> N	10.13	[M] <sup>+</sup>	227.2613	227.3164
N,N-dibutylbenzylamine	C <sub>15</sub> H <sub>25</sub> N	10.60	[M] <sup>+</sup>	219.1987	219.3053
N,N-dibutylhept-1-enamine	C <sub>15</sub> H <sub>31</sub> N	10.61	[M] <sup>+</sup>	225.2457	225.3201
Dodecanol	C <sub>12</sub> H <sub>26</sub> O	11.14	[M-H <sub>2</sub> O] <sup>+</sup>	168.1878	168.1014
N,N-dimethyldodecanamine	C <sub>14</sub> H <sub>31</sub> N	11.39	[M] <sup>+</sup>	213.2457	213.3192
N-butyl-diheptanamine	C <sub>18</sub> H <sub>39</sub> N	13.20	[M+H] <sup>+</sup>	270.3170	270.3111
N,N-dipropyldodecanamine	C <sub>18</sub> H <sub>39</sub> N	13.76	[M] <sup>+</sup>	269.3083	269.3844

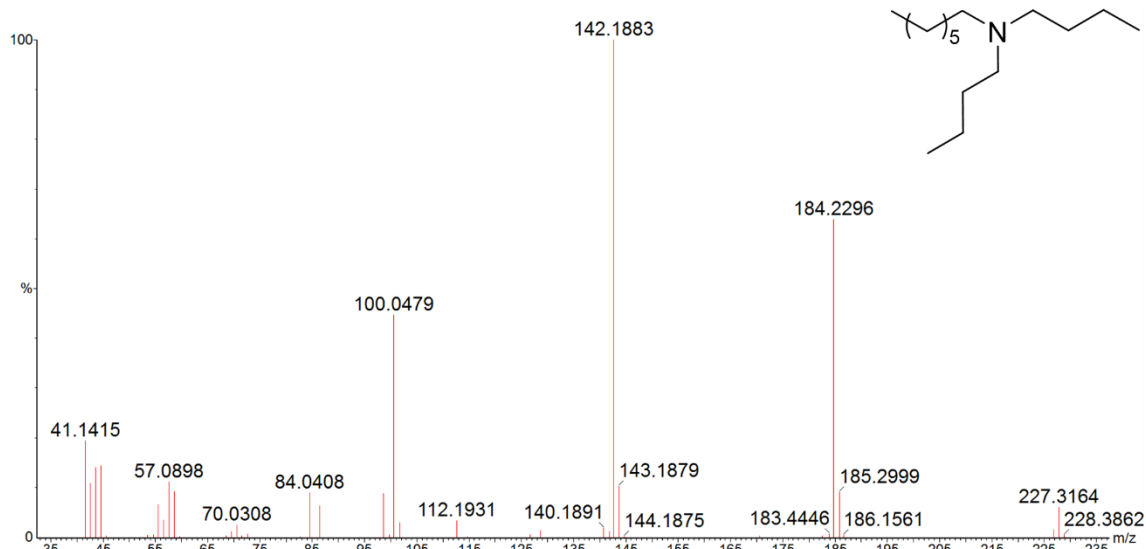
N,N-dibutyldodec-1-enamine	C <sub>20</sub> H <sub>41</sub> N	14.08	[M] <sup>+</sup>	295.3239	295.3085
N,N-dibutyldodecanamine	C <sub>20</sub> H <sub>43</sub> N	14.70	[M] <sup>+</sup>	297.3396	297.4411
<sup>a</sup> N,N-di(butyl-1,1-d <sup>2</sup> )dodecanamine	C <sub>20</sub> H <sub>39</sub> D <sub>4</sub> N	14.70	[M] <sup>D+</sup>	301.3395	301.3883
N-methyldidodecanamine	C <sub>25</sub> H <sub>53</sub> N	17.93	[M] <sup>+</sup>	367.4178	367.3762
N-butyldidodecanamine	C <sub>28</sub> H <sub>49</sub> N	18.90	[M] <sup>+</sup>	409.4648	408.4147

<sup>a</sup> Reaction with full deuterated <sup>n</sup>Bu<sub>2</sub>ND in α position.

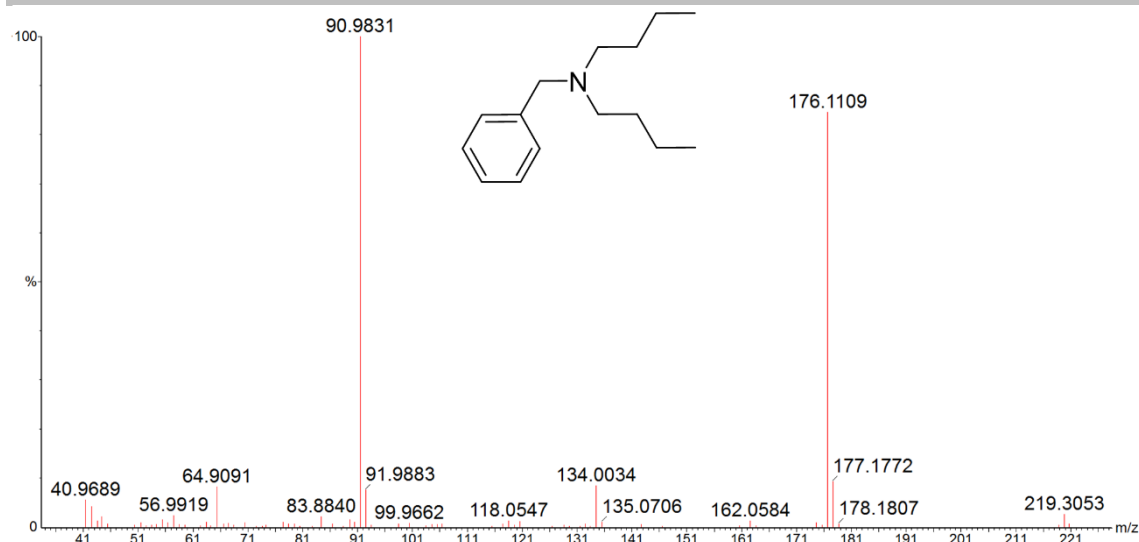
## 2.2. Selected Mass Spectrums



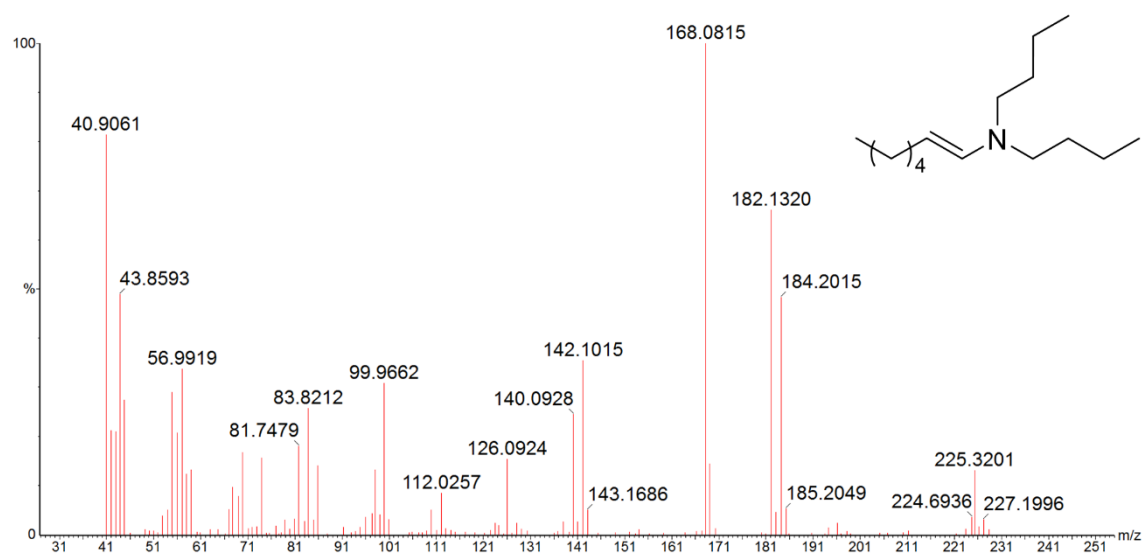
**Figure S11.** Registered MS spectrum of N,N-dibutylcyclohexanamine



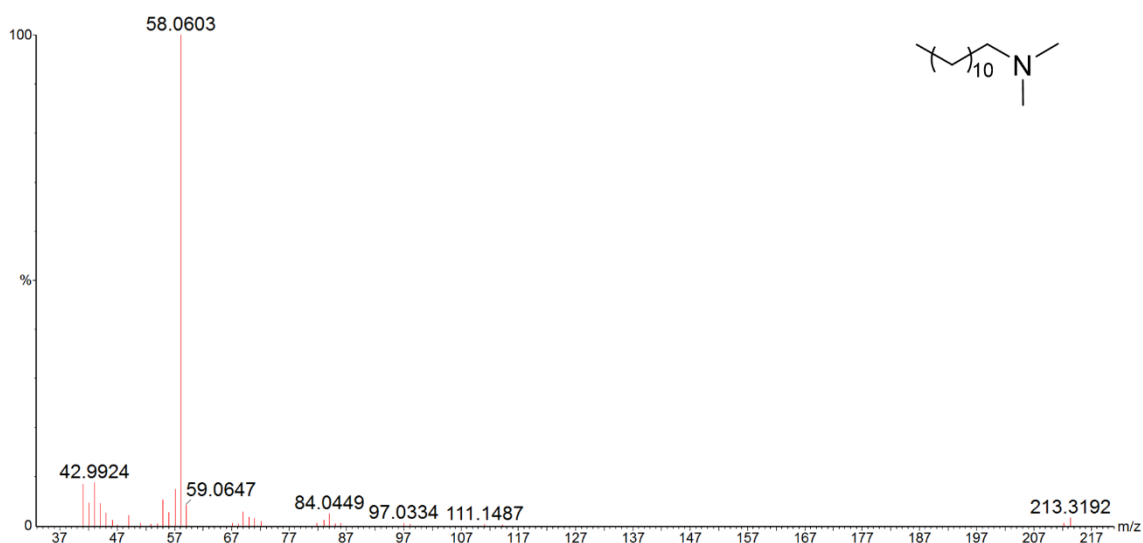
**Figure S12.** Registered MS spectrum of N,N-dibutylheptanamine



**Figure S13.** Registered MS spectrum of N,N-dibutylbenzylamine



**Figure S14.** Registered MS spectrum of N,N-dibutylhept-1-enamine



**Figure S15.** Registered MS spectrum of N,N-dimethyldodecanamine

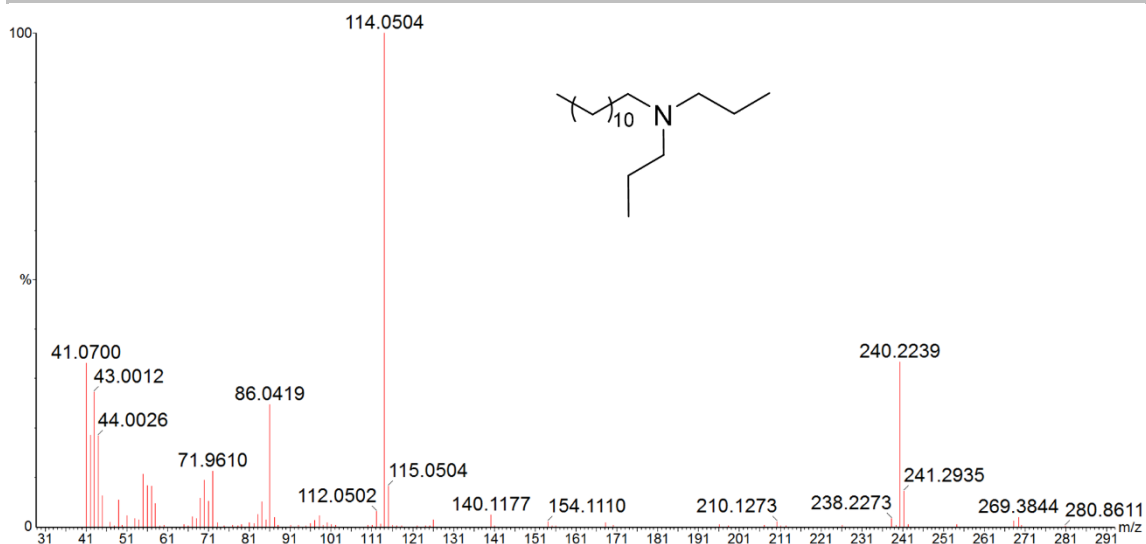


Figure S16. Registered MS spectrum of N,N-dipropyldodecanamine

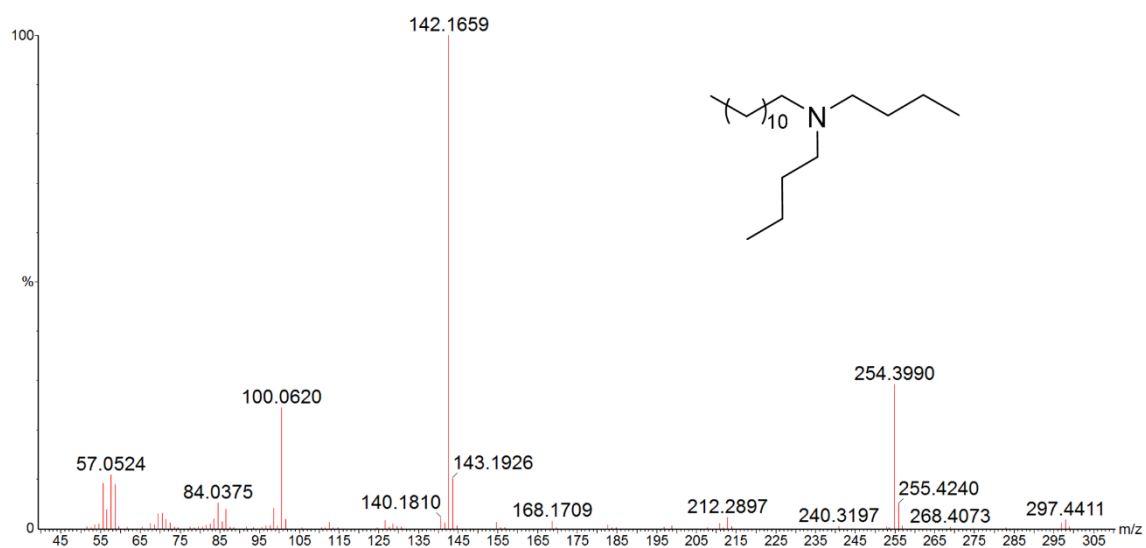
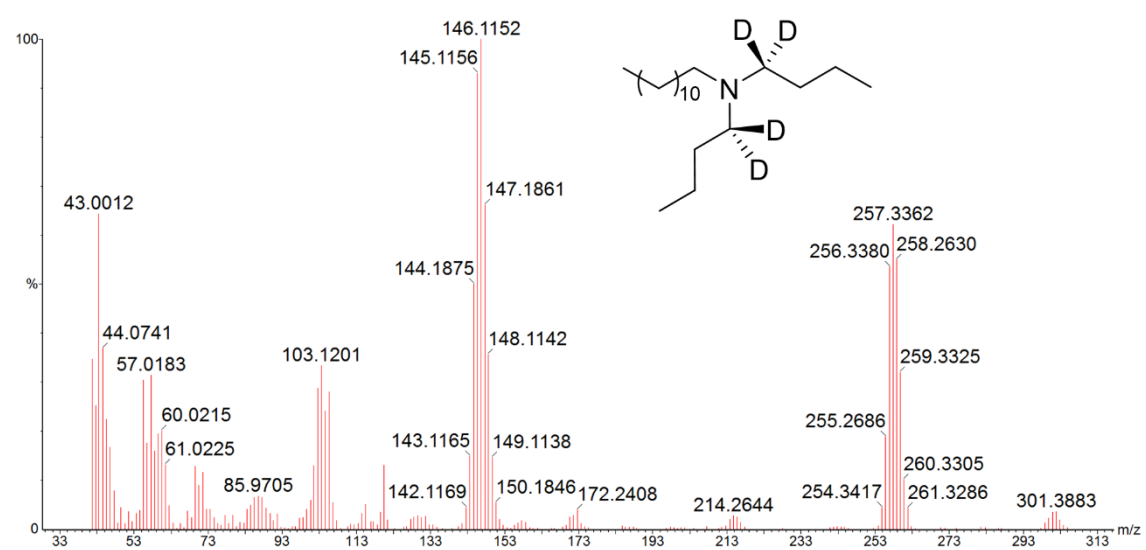


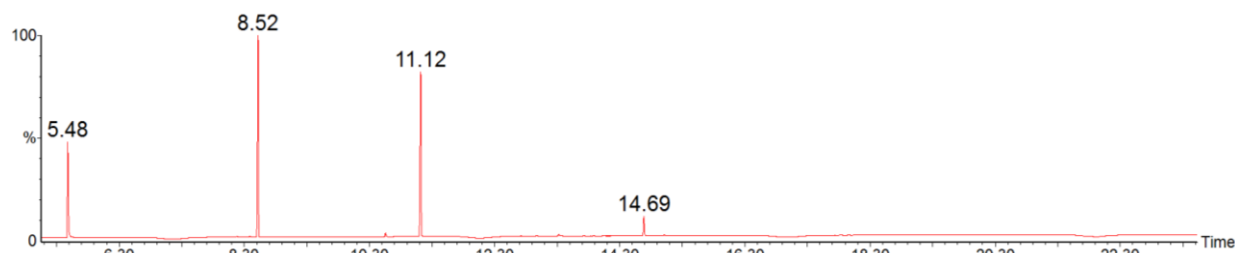
Figure S17. Registered MS spectrum of N,N-dibutyldodecanamine



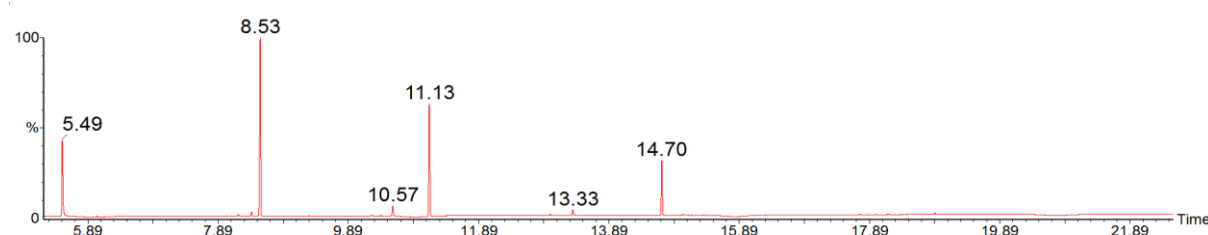


**Figure S18.** Registered MS spectrum of N,N-di(butyl-1,1-d<sup>2</sup>)dodecanamine. MS spectrum obtained from the reaction of dodecanol with di(butyl-1,1-d<sup>2</sup>)-amine

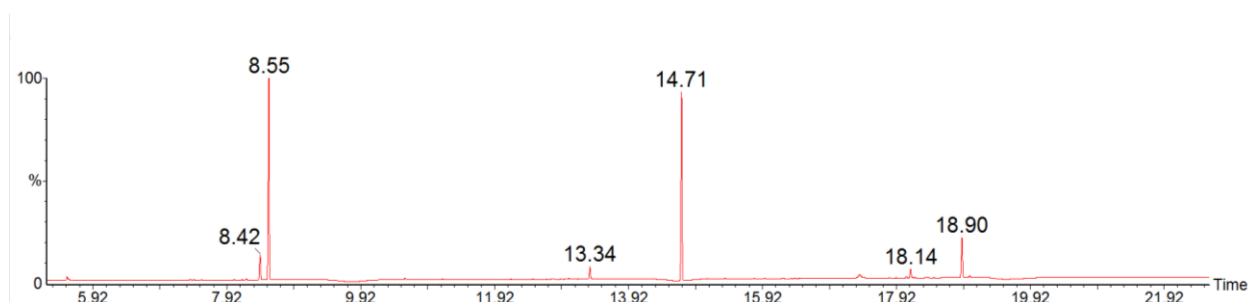
### 2.3. Selected Chromas for the reactions with dodecanol and dibutylamine



**Figure S19.** Registered chromatogram after 2 hours in the reaction of dodecanol with dibutylamine with 2.3 mol % of Cu (21% conversion). Reaction conditions: 5 mmol of dodecanol/ dibutylamineamine, 5 mmol of dodecane (227  $\mu$ L, internal standard), Co<sub>4</sub>Ni<sub>6</sub>@Cu (15 mg, 2.3 mol % Cu), neat, argon atmosphere, 39 mT (300 kHz coil), 2 h.

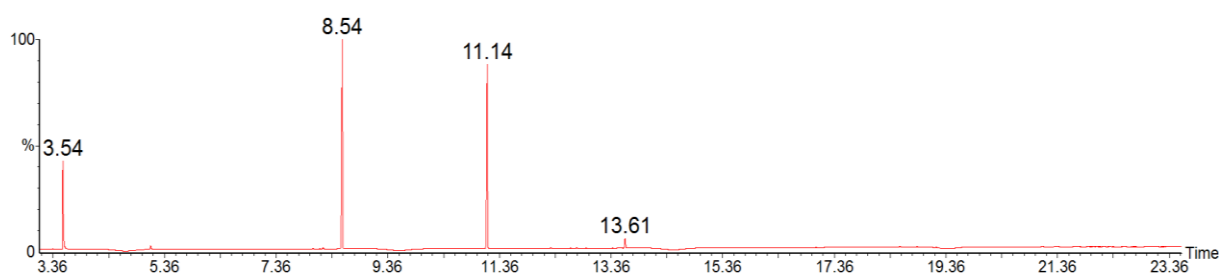


**Figure S20.** Registered chromatogram after 2 hours in the reaction of dodecanol with dibutylamine with 2.3 mol % of Cu (32% conversion). Reaction conditions: 5 mmol of dodecanol/ dibutylamineamine, 5 mmol of dodecane (227  $\mu$ L, internal standard), Co<sub>4</sub>Ni<sub>6</sub>@Cu (15 mg, 2.3 mol % Cu), neat, argon atmosphere, 49 mT (300 kHz coil), 2 h.

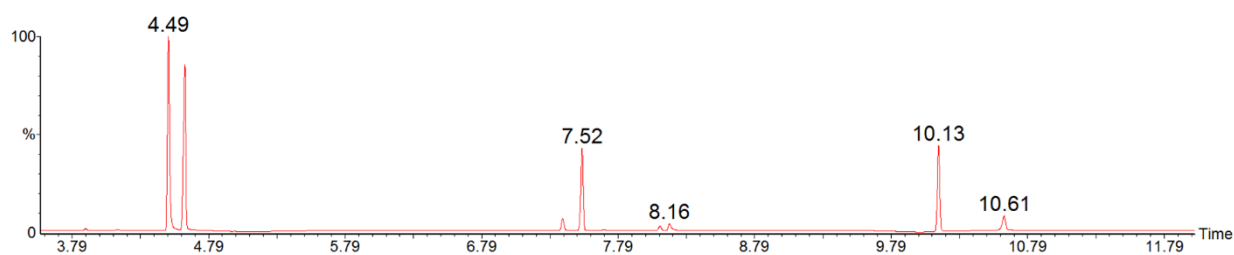


**Figure S21.** Registered chromatogram after 3 hours in the reaction of dodecanol with dibutylamine with 6.8 mol % of Cu (>99% conversion). Reaction conditions: 5 mmol of dodecanol/ dibutylamineamine, 5 mmol of dodecane (227  $\mu$ L, internal standard), Co<sub>4</sub>Ni<sub>6</sub>@Cu (45 mg, 6.8 mol % Cu), neat, argon atmosphere, 49 mT (300 kHz coil), 2 h.

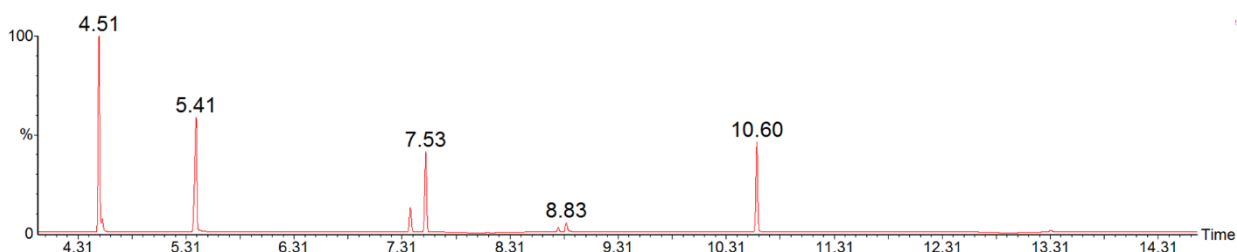
### 2.4. Selected Chromas for the reactions with dodecanol and dipropylamine



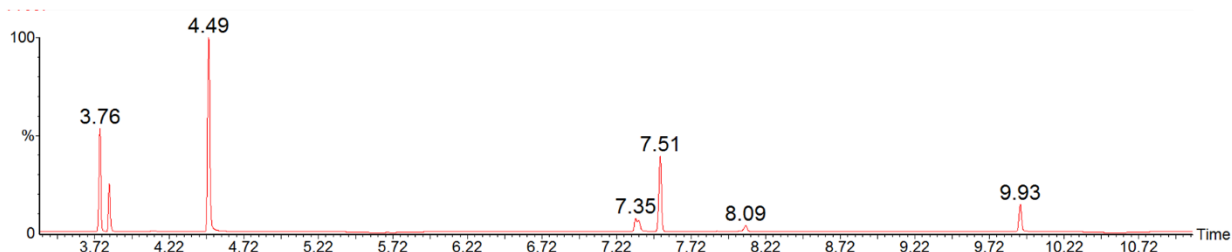
**Figure S22.** Registered chromatogram after 2 hours of reaction with 2.3 mol % of Cu (25% conversion). Reaction conditions: 5 mmol of dodecanol/ dipropylamineamine, 5 mmol of dodecane (227  $\mu$ L, internal standard), Co<sub>4</sub>Ni<sub>6</sub>@Cu (15 mg, 2.3 mol % Cu), neat, argon atmosphere, 39 mT (300 kHz coil), 2 h.

**2.5. Selected Chromatograms for the reaction with heptanol and dibutylamine**

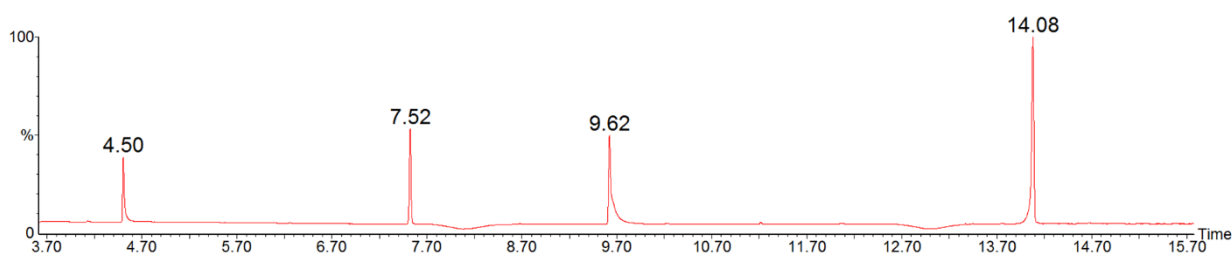
**Figure S23.** Registered chromatogram after 2 hours of reaction with 2.3 mol % of Cu (25 % of conversion). Registered chromatogram after 2 hours of reaction with 6.8 mol % of Cu (25% conversion). Reaction conditions: 5 mmol of heptanol/ dibutylamine, 1 mmol of dodecane (227  $\mu$ L, internal standard),  $\text{Co}_4\text{Ni}_6\text{@Cu}$  (15 mg, 2.3 mol % Cu), neat, argon atmosphere, 49 mT (300 kHz coil), 2 h.

**2.6. Selected Chromatogram for the reaction with benzylalcohol and dibutylamine**

**Figure S24.** Registered chromatogram after 2 hours of reaction with 6.8 mol % of Cu (30% conversion). Reaction conditions: 5 mmol of benzylalcohol/ dibutylamine, 1 mmol of dodecane (227  $\mu$ L, internal standard),  $\text{Co}_4\text{Ni}_6\text{@Cu}$  (15 mg, 2.3 mol % Cu), neat, argon atmosphere, 39 mT (300 kHz coil), 2 h.

**2.7. Selected Chromatogram for the reaction with cyclohexanone and dibutylamine**

**Figure S25.** Registered chromatogram after 2 hours of reaction with 6.8 mol % of Cu (56% conversion). Reaction conditions: 5 mmol of benzylalcohol/ dibutylamine, 1 mmol of dodecane (227  $\mu$ L, internal standard),  $\text{Co}_4\text{Ni}_6\text{@Cu}$  (15 mg, 2.3 mol % Cu), neat, argon atmosphere, 49 mT (300 kHz coil), 2 h.

**2.8. Chromatogram for the reactions with dodecanal and dibutylamine**

**Figure S26.** Registered chromatogram after 10 minutes of reaction. Reaction conditions: 5 mmol of dodecanal/ dibutylamine, 1 mmol of dodecane (227  $\mu$ L, internal standard), neat, argon atmosphere, 10 minutes.

## 2.9. Recycling tests with dodecanol and dibutylamine.

Table S4. Recycling tests with dodecanol and dibutylamine.

Cycle	Catalyst	Cu mol %	Mag. Field (mT)	Time (h)	Conv. (%)	Selec. (%)
1	3	2.3	49	2	35	98
2	3	2.3	49	2	21	>99
3	3	2.3	49	2	14	>99
4	3	2.3	49	2	9	>99

Reaction conditions: 5 mmol of dodecanol/ dibutylamine, 1 mmol of dodecane (227  $\mu$ L, internal standard),  $\text{Co}_4\text{Ni}_6\text{@Cu}$  (15 mg, 2.3 mol % Cu), neat, argon atmosphere, 49 mT (300 kHz coil), 2 h. After each run, 8 mL of  $\text{Et}_2\text{O}$  was added to the reaction mixture to extract the organic materials, and the Mag-NPs were separated from the solution by magnetic decanting. Afterwards, the NPs were washed with toluene (3 x 5 mL), dried under vacuum, and reused in the same reactor.

## 2.10. Selected Chromatograms for the reactions with dodecanol and DMA in water

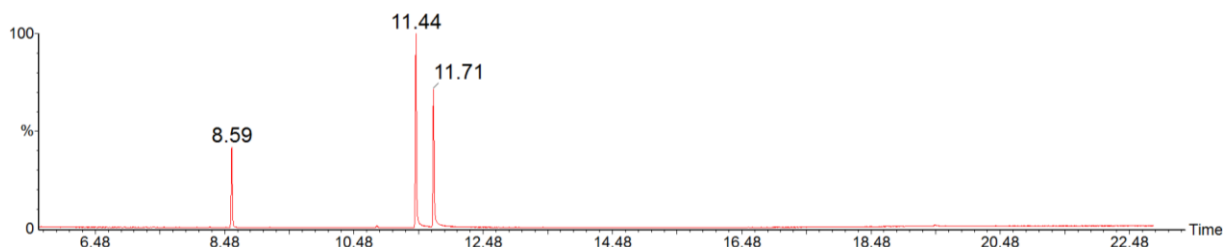


Figure S27. Registered chromatogram after 2 hours of reaction with 6.8 mol % of Cu (36% conversion). Reaction conditions: 5 mmol of dodecanol/ DMA, 1 mmol of dodecane (227  $\mu$ L, internal standard),  $\text{Co}_4\text{Ni}_6\text{@Cu}$  (45 mg, 6.8 mol % Cu), neat, argon atmosphere, 39 mT (300 kHz coil), 2 h.

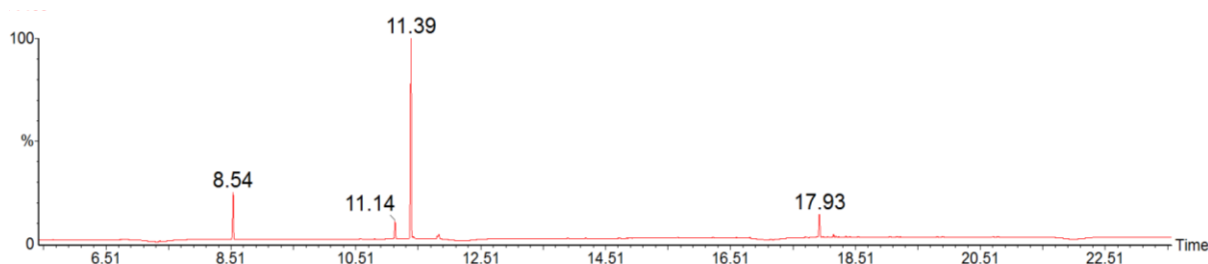


Figure S28. Registered chromatogram after 5 hours of reaction with 6.8 mol % of Cu (91% conversion). Reaction conditions: 5 mmol of dodecanol/ DMA, 1 mmol of dodecane (227  $\mu$ L, internal standard),  $\text{Co}_4\text{Ni}_6\text{@Cu}$  (45 mg, 6.8 mol % Cu), neat, argon atmosphere, 39 mT (300 kHz coil), 5 h.

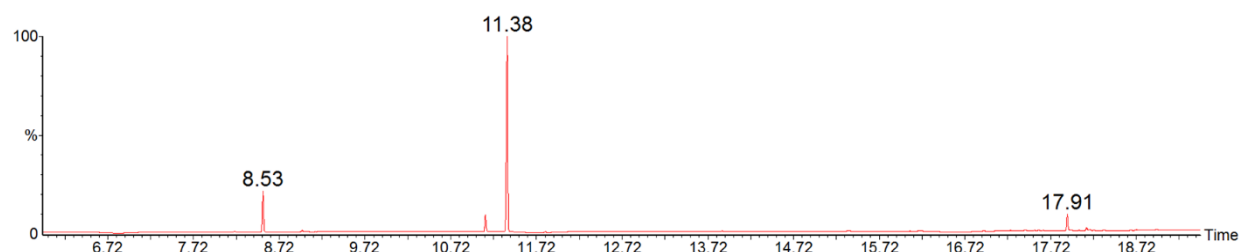
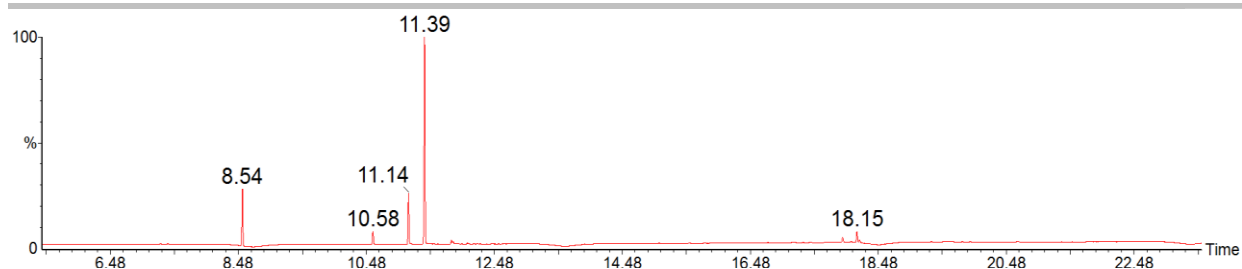
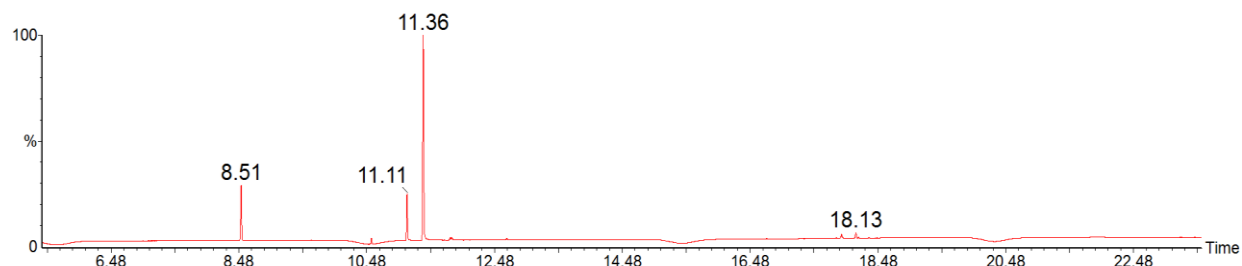


Figure S29. Registered chromatogram after 12 hours of reaction with 4.6 mol % of Cu (92% conversion). Reaction conditions: 5 mmol of dodecanol/ DMA, 1 mmol of dodecane (227  $\mu$ L, internal standard),  $\text{Co}_4\text{Ni}_6\text{@Cu}$  (30 mg, 6.8 mol % Cu), neat, argon atmosphere, 39 mT (300 kHz coil), 12 h.

## 2.11. Selected Chromatograms for the reactions with dodecanol and DMA in THF



**Figure S30.** Registered chromatogram after 8 hours of reaction with 6.8 mol % of Cu (82% conversion). Reaction conditions: 5 mmol of dodecanol/ DMA, 1 mmol of dodecane (227  $\mu$ L, internal standard),  $\text{Co}_4\text{Ni}_6@\text{Cu}$  (45 mg, 6.8 mol % Cu), THF, argon atmosphere, 49 mT (300 kHz coil), 8 h.



**Figure S31.** Registered chromatogram after 15 hours of reaction with 6.8 mol % of Cu (83% of conversion). Registered chromatogram after 15 hours of reaction with 6.8 mol % of Cu (83% conversion). Reaction conditions: 5 mmol of dodecanol/ DMA, 1 mmol of dodecane (227  $\mu$ L, internal standard),  $\text{Co}_4\text{Ni}_6@\text{Cu}$  (45 mg, 6.8 mol % Cu), THF, argon atmosphere, 49 mT (300 kHz coil), 15 h.

**Table S5.** Catalytic runs with DMA (40 wt% in  $\text{H}_2\text{O}$  or 2.5 M in THF).

Entry	Catalyst	Solvent	Cu mol %	Mag. Field (mT)	Time (h)	Temp. <sup>a</sup> (°C)	Conv. (%)	Selec. (%)
1	$\text{Co}_4\text{Ni}_6@\text{Cu}$	$\text{H}_2\text{O}$	2.3	39	2	89	19	>99
2	$\text{Co}_4\text{Ni}_6@\text{Cu}$	$\text{H}_2\text{O}$	6.8	49	5	118	91	88
3	$\text{Co}_4\text{Ni}_6@\text{Cu}$	$\text{H}_2\text{O}$	4.6	49	8	115	75	92
4	$\text{Co}_4\text{Ni}_6@\text{Cu}$	THF	2.3	49	2	93	11	>99
5	$\text{Co}_4\text{Ni}_6@\text{Cu}$	THF	6.8	49	15	121	83	97
6	$\text{Fe}_3\text{Ni}_7@\text{Cu}$	THF	6.8	65	8	117	42	94

Reaction conditions: 5 mmol of dodecanol/ DMA, 1 mmol of dodecane (227  $\mu$ L, internal standard),  $\text{Co}_4\text{Ni}_6@\text{Cu}$  (15 mg, 2.3 mol % Cu), argon atmosphere, 49 mT (300 kHz coil). [a] Temperature determined with IR camera on the Fisher-Porter external wall.



## 2.12. Scale-up reaction with DMA (40 wt% in water)

Table S6. Catalytic runs with DMA (40 wt% in H<sub>2</sub>O).

Entry	Solvent	Cu mol %	Mag. Field (mT)	Time (h)	Temp. <sup>a</sup> (°C)	Conv. (%)	Selec. (%)
1	H <sub>2</sub> O	6.8	49	8	131	86	82
2	H <sub>2</sub> O	6.8	49	8	134	89	76

Reaction conditions: 15 mmol of dodecanol/ DMA, 3 mmol of dodecane (681  $\mu$ L, internal standard), Co<sub>4</sub>Ni<sub>6</sub>@Cu (90 mg, 4.6 mol % Cu), argon atmosphere, 49 mT (300 kHz coil), 12 h. [a] Temperature determined with IR camera on the Fisher-Porter external wall.

The reaction was scaled up in the conditions previously described using 15 mmol of alcohol/amine with DMA in water, leading to 86 % conversion and lower selectivity to DMDA (82 %). This difference may be since the reactor is not prepared for large-scale reactions. In this example, the pressure increased up to 7 bar, and higher mean solution temperatures (131 °C) were recorded during the catalysis.

## 3. Study of the catalyst after the catalysis by XRD and TEM

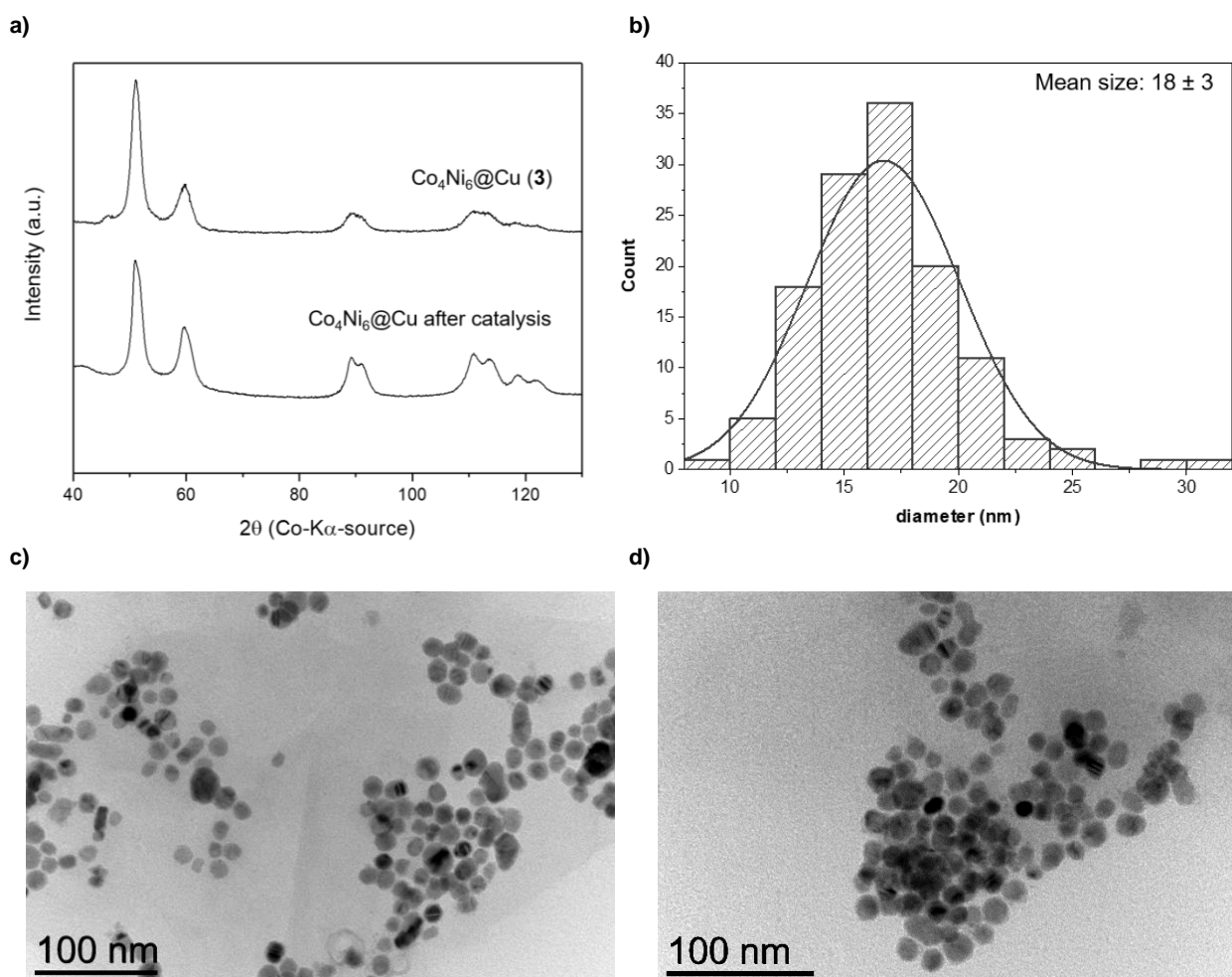


Figure S32. a) Powder XRD (X-Ray Diffraction) spectra of Co<sub>4</sub>Ni<sub>6</sub>@Cu NPs (3, top) and after catalysis (bottom) b-d) TEM images for Co<sub>4</sub>Ni<sub>6</sub>@Cu NPs after the fourth catalytic cycles. (Mean size = 17 ± 3 nm).

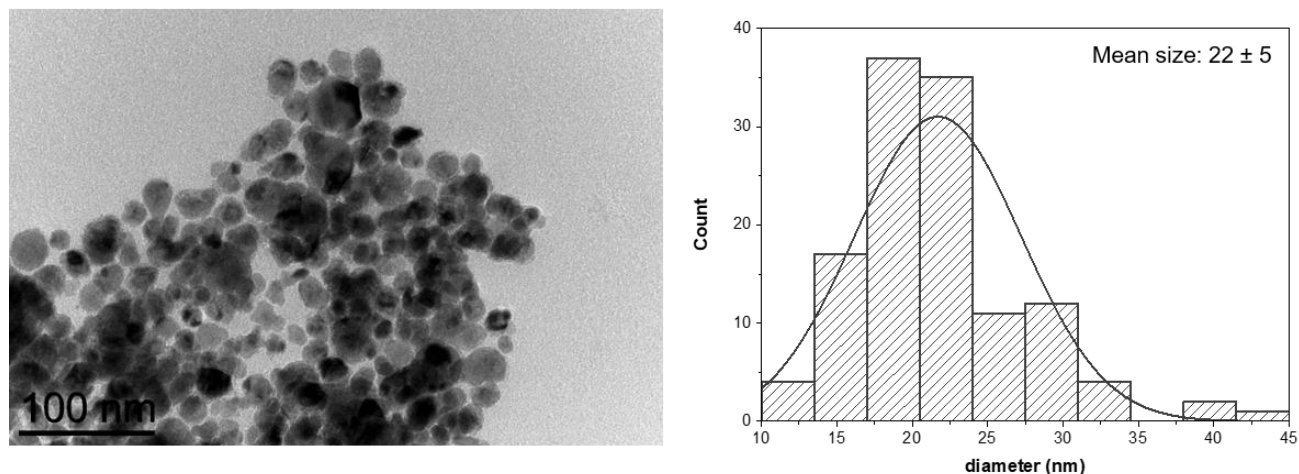
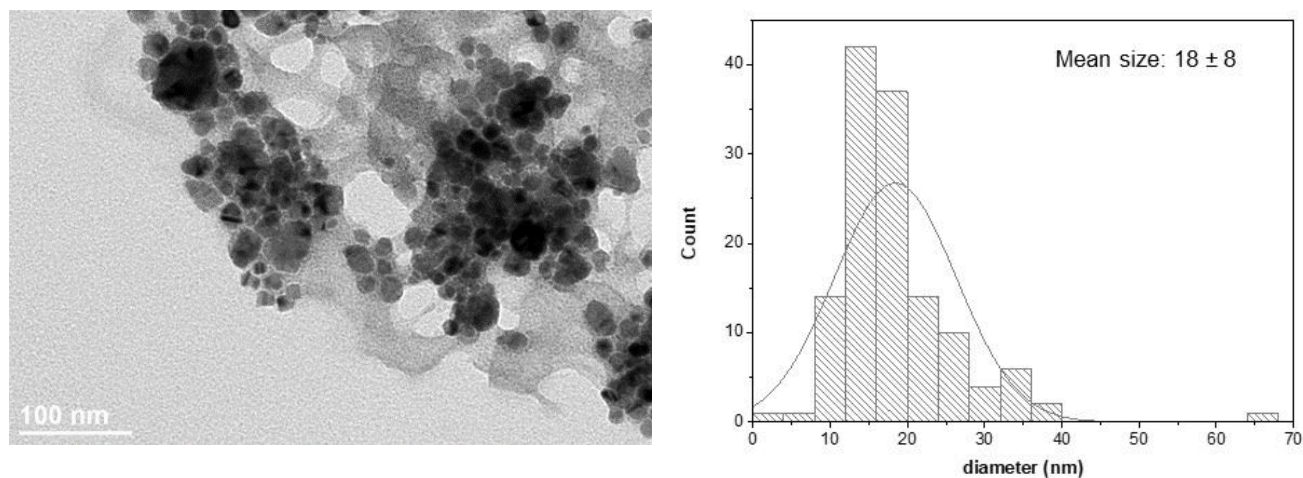
Table S7. ICP results before and after catalysis (metal-based)

Sample	% Ni	%Co	%Cu
Before Catalysis	27.9	17.80	54.26
After Catalysis	27.08	17.89	55.02

**Table S8.** ICP results for the reaction crude after extraction with acidic water

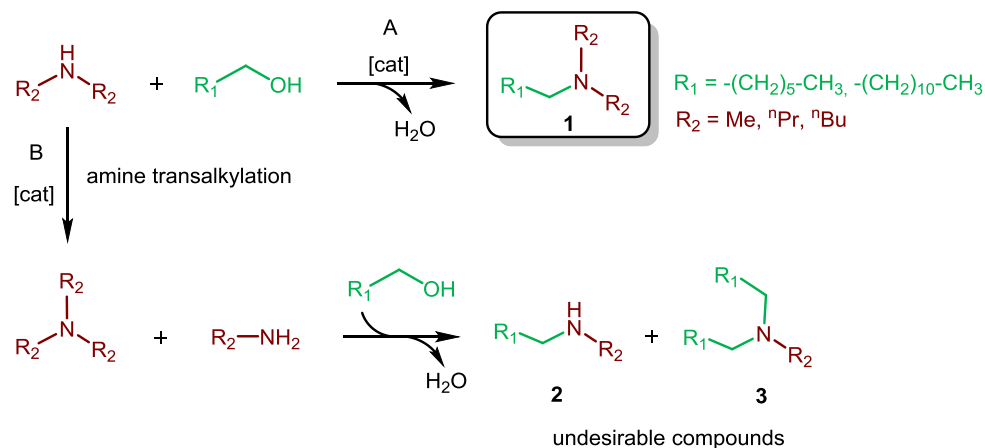
	Ni	Co	Cu
LOD (ppm)	0.0002	0.0001	0.0003
LOQ (ppm)	0.0006	0.0003	0.0009
Sample (ppm)	0.00635	0.0022	0
Sample (%)	0.009	0.004	0

After removing the NPs by magnetic decantation, 10 mL of acidic water ( $[H_2SO_4] = 0.04$  M) was added to the reaction crude. The mixture was stirred for 10 minutes and the metal content of the aqueous phase was analysed by ICP. LOD = limit of detection, LOQ = limit of quantification.

**Figure S33.** TEM images for  $Co_4Ni_6@Cu$  after the reaction with DMA in water (40 wt %). (Mean size =  $22 \pm 5$  nm).**Figure S34.** TEM images for  $Fe_3Ni_7@Cu$  after the fourth cycle of catalysis. (Mean size =  $18 \pm 8$  nm).

## 4. Transalkylation reactions of secondary amines

Regarding the main reaction with dodecanol and secondary amines  $R_2NH$  ( $R = \text{Me}, {}^n\text{Pr}, {}^n\text{Bu}$ ) as substrates (**Scheme S1**, via A), *N,N*-dialkyldodecylamines were obtained in excellent yield. Contrary, compounds **2** and **3** (**Scheme S1**, via B) were formed when two moles of  $R_2NH$  ( $R = \text{Me}, {}^n\text{Pr}, {}^n\text{Bu}$ ) were disproportionated to  $RNH_2$  and  $R_3N$  in the transalkylation reaction, followed by the reaction of fatty alcohol with one or two equivalents of  $RNH_2$  respectively. Selectivity of the catalysts mainly depended on their catalytic activity in the disproportionation reaction of the amine (**Scheme S1**, via B).<sup>[4]</sup>



**Scheme S1.** Formation of different products in alcohol amination reaction. The main by-product of this amination reaction was **3**, and in less grade compound **2**.

The stability of the the dibutylamine was studied under thermal conditions observing very low transalkylation reaction in the presence of  $\text{Co}_4\text{Ni}_6@\text{Cu}$  (**3**) catalyst after 2 and 24 h. (Table S9)

**Table S9.** Transalkylation reaction of the  ${}^n\text{Bu}_2\text{NH}$

Time	$\text{Bu}_2\text{NH}$ (%)	$\text{Bu}_3\text{N}$ (%)
2 h	99	1
24 h	94	6

*Reaction conditions:* 5 mmol dibutylamine, 1 mmol of dodecane (227  $\mu\text{L}$ , internal standard),  $\text{Co}_4\text{Ni}_6@\text{Cu}$  (**3**, 45 mg, 6.8 mol % Cu), neat, argon atmosphere, 160  $^\circ\text{C}$  (oil bath). Bu = butyl.

In addition, the transalkylation reaction under thermal conditions at 160  $^\circ\text{C}$  was studied in the presence of the same Cu catalyst observing that the tertiary amines seem quite stable under the studied reaction conditions (Table S10)

**Table S10.** Transalkylation reaction of the tertiary amines under thermal heating

Time	$\text{Bu}_3\text{N}$ (%)	$\text{Bu}_2\text{NDoc}$ (%)	$\text{BuNDoc}_2$ (%)
Starting point	7.5	75	17.5
2 h	7	77	16
24 h	5	78	17

*Reaction conditions:* Mixture of tertiary amines (5 mmol in total), 1 mmol of dodecane (227  $\mu\text{L}$ , internal standard),  $\text{Co}_4\text{Ni}_6@\text{Cu}$  (**3**, 45 mg, 6.8 mol % Cu), neat, argon atmosphere, 160  $^\circ\text{C}$  (oil bath). Bu = butyl, Doc = dodecyl. The mixture of the tertiary amines was obtained using the following reaction conditions: 5 mmol of dodecanol/ dibutylamine, 1 mmol of dodecane (227  $\mu\text{L}$ , internal standard),  $\text{Co}_4\text{Ni}_6@\text{Cu}$  (**3**, 45 mg, 6.8 mol % Cu), neat, argon atmosphere, 3 h, 49 mT (300 kHz coil)

**Table S11.** Transalkylation reaction of the tertiary amines under induction heating

Time	Bu <sub>3</sub> N (%)	Bu <sub>2</sub> NDoc (%)	BuNDoc <sub>2</sub> (%)	Doc <sub>3</sub> N (%)
Starting point	15.7	53.5	26.6	4.2
2 h	15.4	48.1	30.8	5.7

*Reaction Conditions:* 5 mmol of dodecanol/ dibutylamine, 1 mmol of dodecane (227  $\mu$ L, internal standard), Co<sub>4</sub>Ni<sub>6</sub>@Cu (**3**, 45 mg, 6.8 mol % Cu), neat, argon atmosphere, 2 h, 49 mT (300 kHz coil). Bu = butyl, Doc = dodecyl.

## 5. References

- [1] A. Bordet, L.-M. Lacroix, P.-F. Fazzini, J. Carrey, K. Soulantica, B. Chaudret, *Angew. Chem., Int. Ed.* **2016**, *55*, 15894-15898.
- [2] J. Mazarío, I. Mustieles Marin, G. Mencia, C.W. Lopes, V. Varela-Izquierdo, G. Agostini, P.F. Fazzini, N. Ratel-Ramond, B. Chaudret, *ACS Appl. Nano Mater.* **2024**, *7*, 8, 9412–9427.
- [3] D. De Masi, J. M. Asensio, P. -F. Fazzini, L. -M. Lacroix and B. Chaudret, *Angew. Chem. Int. Ed.*, **2020**, *59*, 6187–6191.
- [4] A. Baiker, A., W. Richarz, *Ind. Eng. Chem., Prod. Res. Dev.* **1977**, *16*, 261.

## 6. Author Contributions

Víctor Varela-Izquierdo synthesized the Co<sub>4</sub>Ni<sub>6</sub>@Cu and Fe<sub>3</sub>Ni<sub>7</sub>@Cu nanoparticles, carried out the catalytic experiments and did the initial writing of the work

Irene Mustieles-Marin synthesized the CoNi nanoparticles and participated to the initial synthesis of Co<sub>4</sub>Ni<sub>6</sub>@Cu and Fe<sub>3</sub>Ni<sub>7</sub>@Cu nanoparticles

Pier-Francesco Fazzini carried out all characterizations by HRTEM

Gabriel Mencia run the deuteration of dibutyl amine experiments

Simon Guelen and Rabih Rachet supervised the work from an industrial point-of-view

Bruno Chaudret supervised the research and wrote the article

((Please specify the contributions of each author including the type (e.g. data curation, funding acquisition, formal analysis, investigation, project administration, validation, writing of original draft) and the degree (e.g. lead, equal, supporting) of contribution.))