Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary information

Influence of Copper Precursor on the Catalytic Transformation of Oleylamine during Cu Nanoparticles Synthesis

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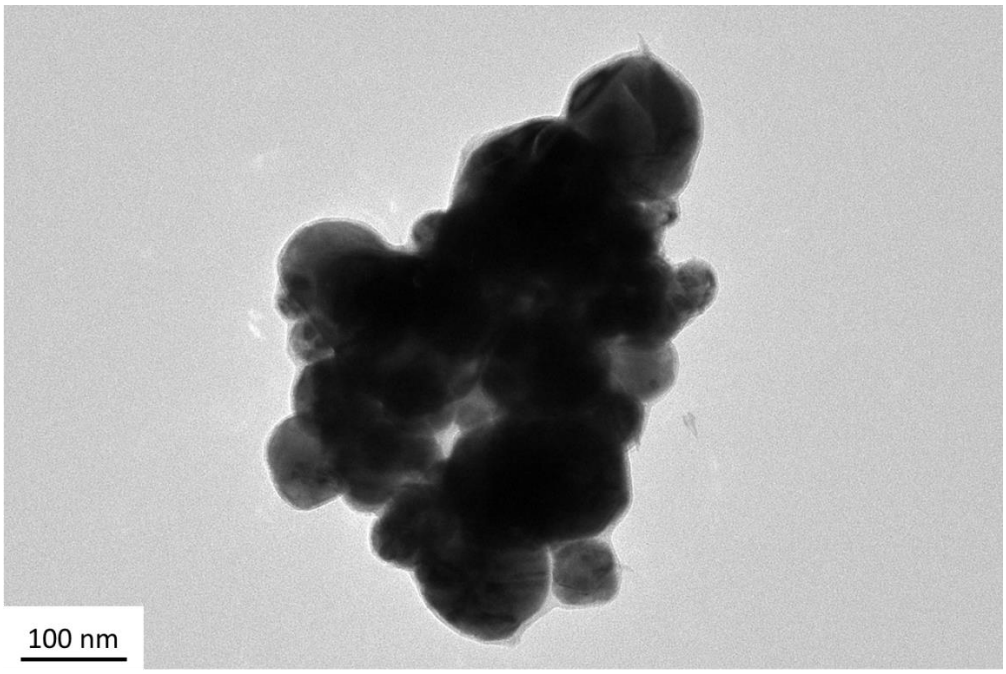


Figure S1: TEM micrograph of ***Cu_A*** nanoparticles before washing steps.

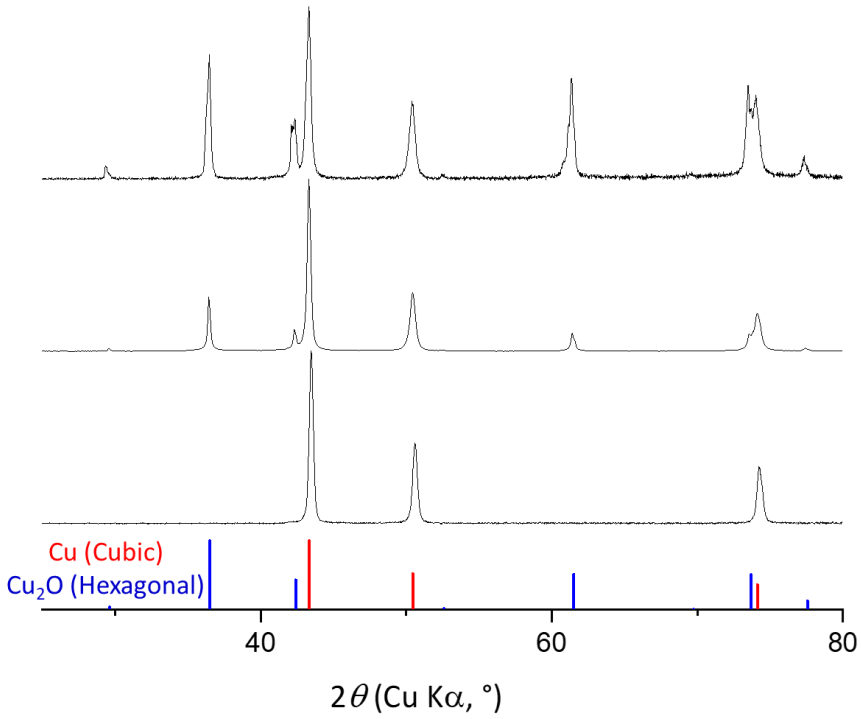


Figure S2: XRD patterns of several samples of copper nanoparticles ***Cu_A*** synthesized with $Cu(OAc)_2$ as precursor. XRD reference pattern for cubic Cu in red (COD number: 9008468) and for cubic Cu_2O in blue (COD number: 1010941) (bottom).

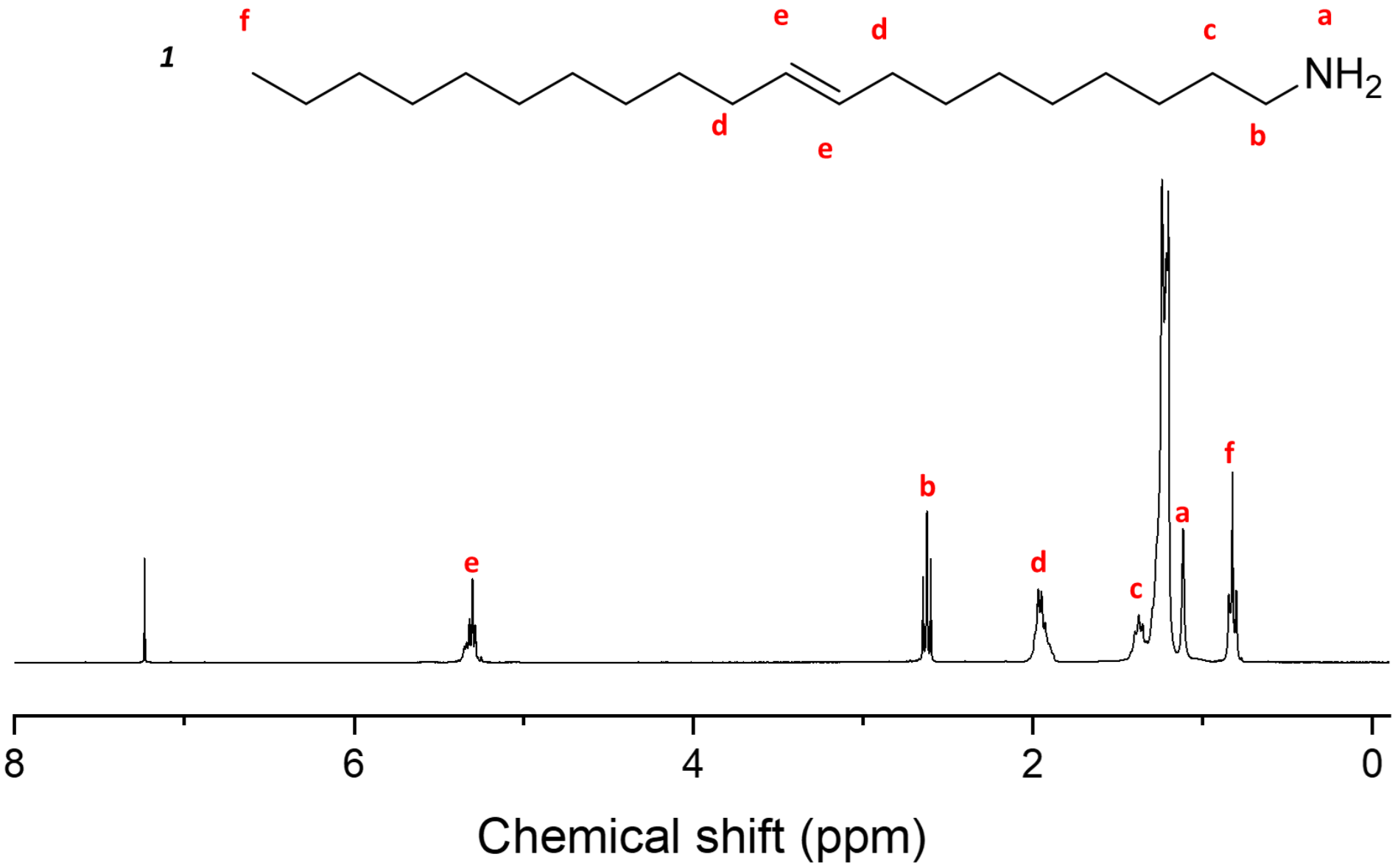


Figure S3: (Top) Molecular structure of oleylamine, (bottom) ^{1}H NMR spectrum of commercial oleylamine.

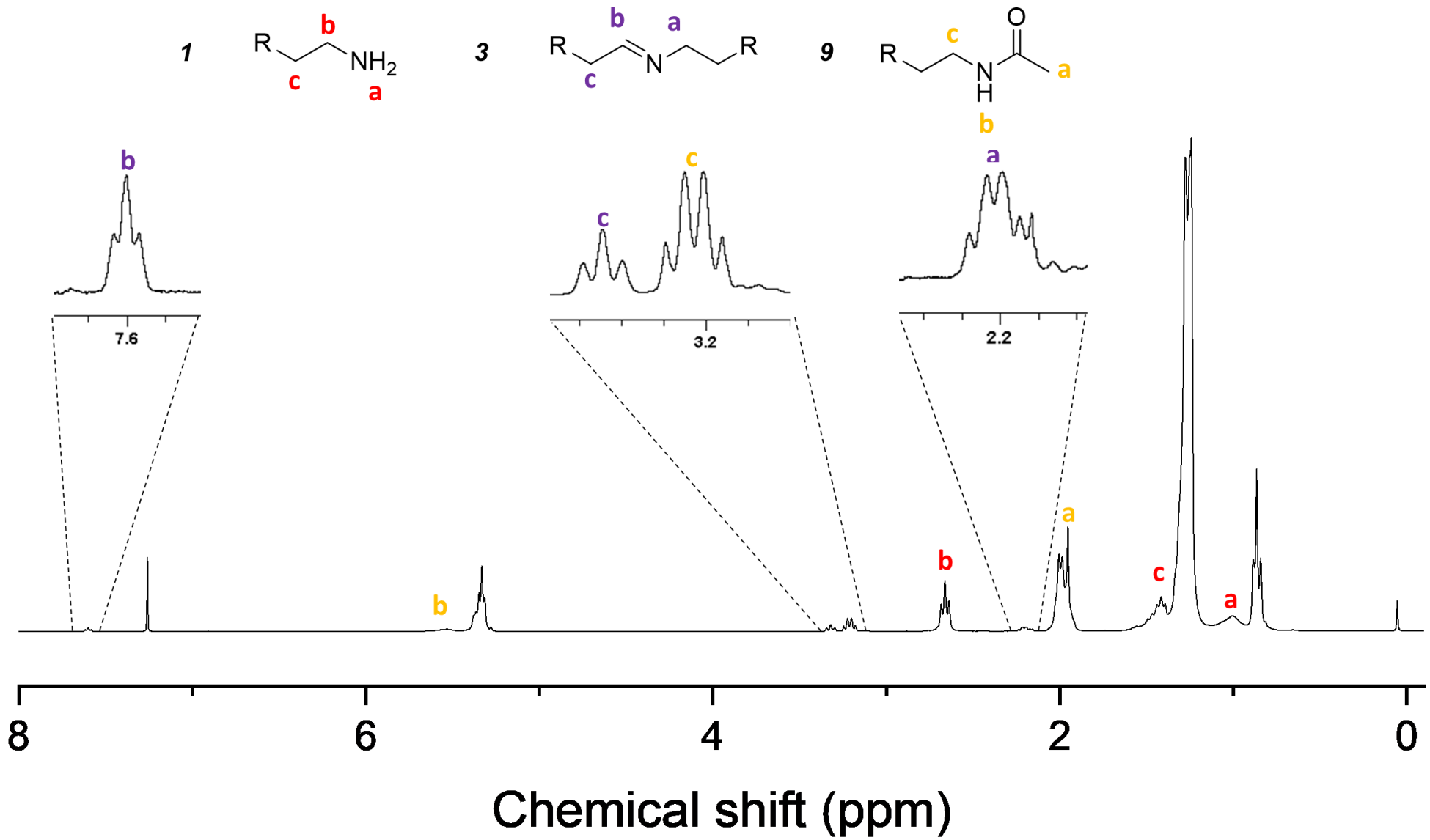


Figure S4: (Top) Molecular structure of species detected in the ^{1}H NMR spectrum. (Bottom) ^{1}H NMR spectrum of the supernatant of synthesis ***A*** centrifugated at 9000 RPM during 15 min.

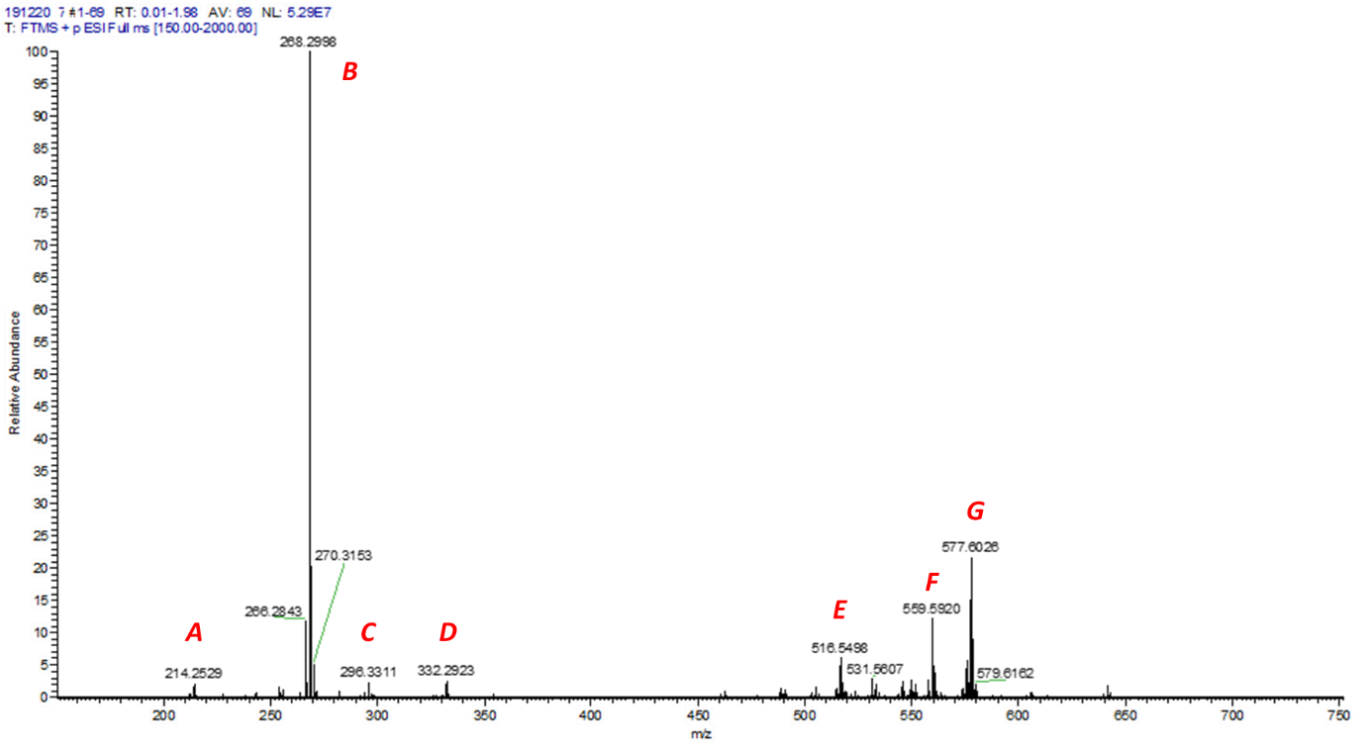


Figure S5: ESI-MS of the supernatant of synthesis ***A*** centrifuged at 9000 RPM during 15 min. Peaks interpreted are marked with a red letter and their interpretation are given in Table S1.

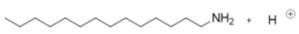
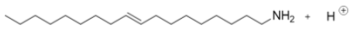
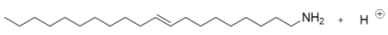
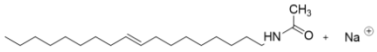
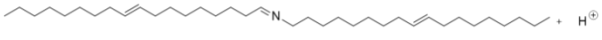
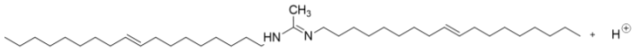
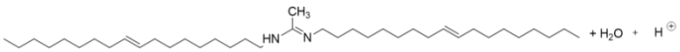
Entry	Measured Mass	Proposed chemical formula	Corresponding theoritical mass	Proposed ionized structure
A	214.2529	$C_{14}H_{32}N + H^+$	214.2534	
B	268.2998	$C_{18}H_{38}N + H^+$	268.3004	
C	296.3311	$C_{20}H_{42}N + H^+$	296.3317	
D	332.2923	$C_{20}H_{39}NO + Na^+$	332.2929	
E	516.5498	$C_{36}H_{70}N + H^+$	516.5508	
F	559.5920	$C_{38}H_{75}N_2 + H^+$	559.5930	
G	577.6026	$C_{38}H_{75}N_2^+ + H_2O$	577.6035	

Table S1: Ionized structure interpreted from mass spectrogram S6.

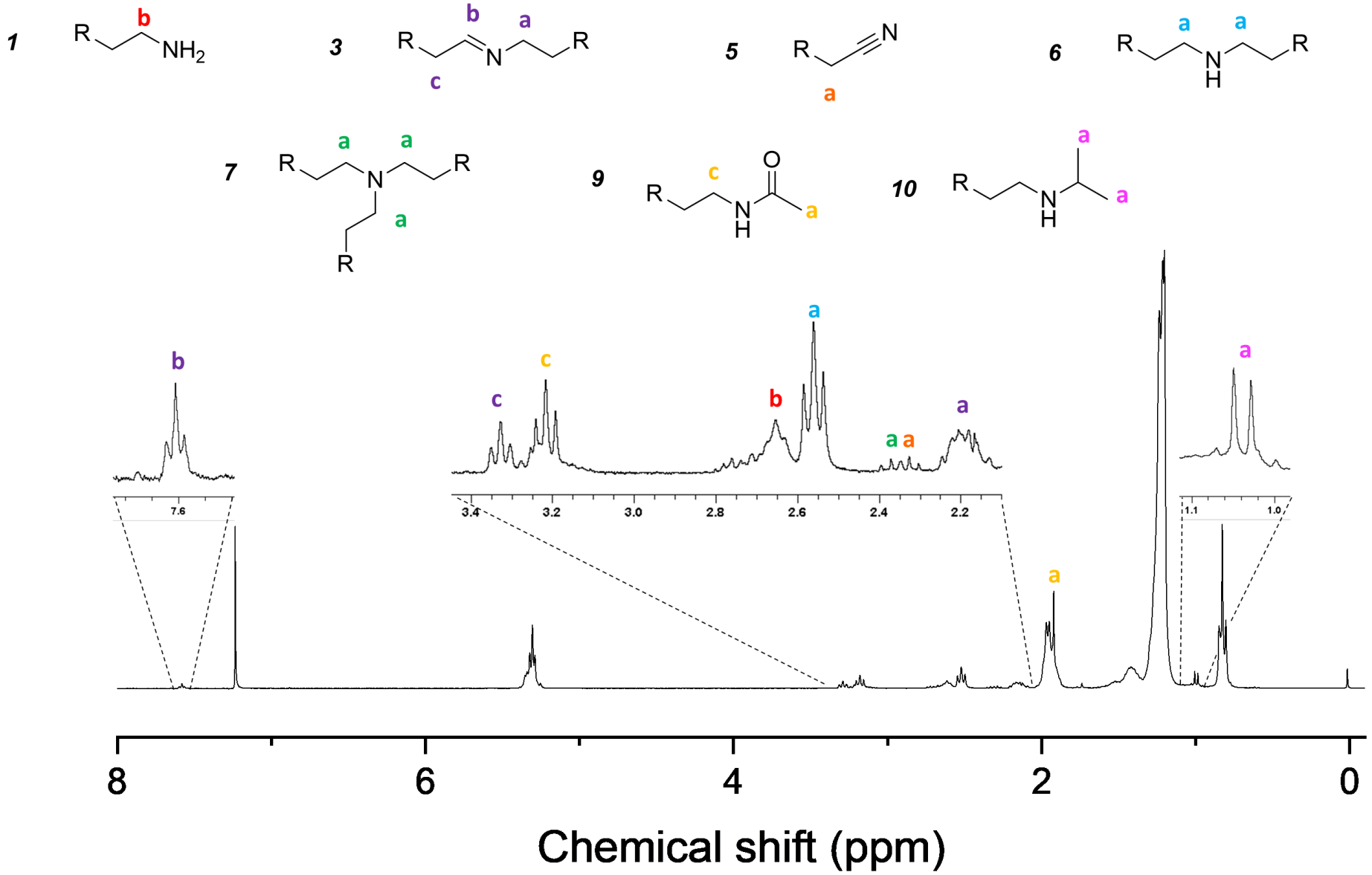


Figure S6: (Top) Molecular structure of species detected in the ^{1}H NMR spectrum. (Bottom) ^{1}H NMR spectrum of the supernatant of synthesis ***B*** centrifuged at 9000 RPM during 15 min.

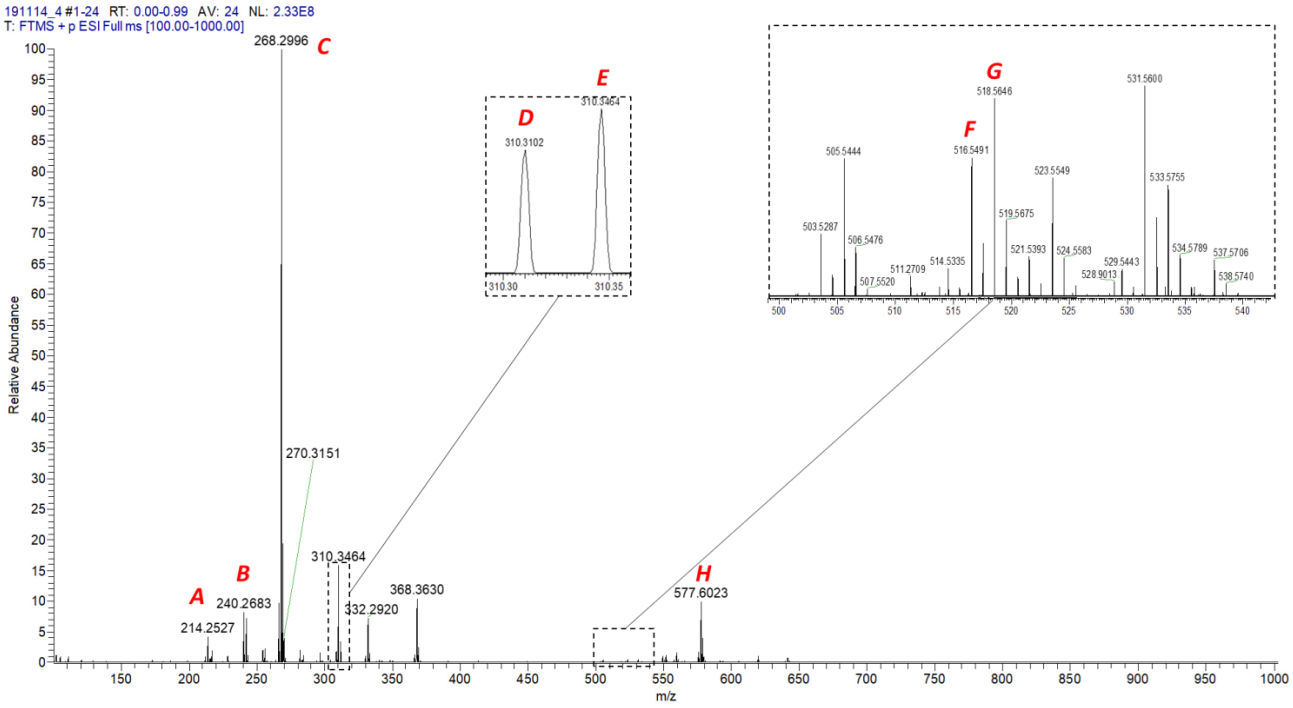


Figure S7: ESI-MS of the supernatant of synthesis ***B*** centrifuged at 9000 RPM during 15 min. Peaks interpreted are marked with a red letter and their interpretation are given in Table S2.

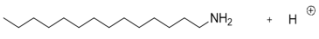
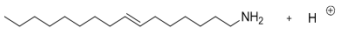
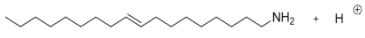
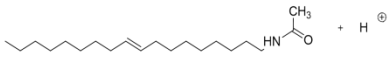
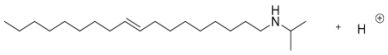
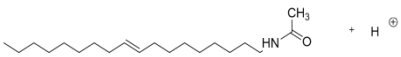
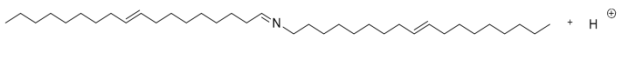
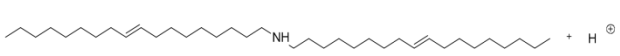
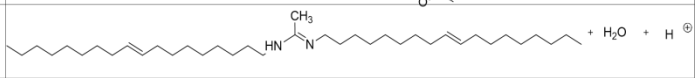
Entry	Measured Mass	Proposed chemical formula	Corresponding theoritical mass	Proposed ionized structure
A	214.2529	$C_{14}H_{31}N + H^+$	214.2534	
B	240.2683	$C_{16}H_{33}N + H^+$	240,2691	
C	268.2998	$C_{18}H_{37}N + H^+$	268.3004	
D	310.3102	$C_{20}H_{39}ON + H^+$	310,3104	
E	310,3464	$C_{21}H_{43}N + H+$	310,3468	
F	332.2923	$C_{20}H_{39}NO + Na^+$	332.2929	
G	368,363	$C_{23}H_{43}ON + H_2O + H^+$	368,3529	
H	516,5491	$C_{36}H_{69}N + H^+$	516,5508	
I	518,5646	$C_{36}H_{71}N + H^+$	518,5659	
J	577.6023	$C_{38}H_{75}N + H_2O + H^+$	577.6035	

Table S2: Ionized structure interpreted from mass spectrogram S6.

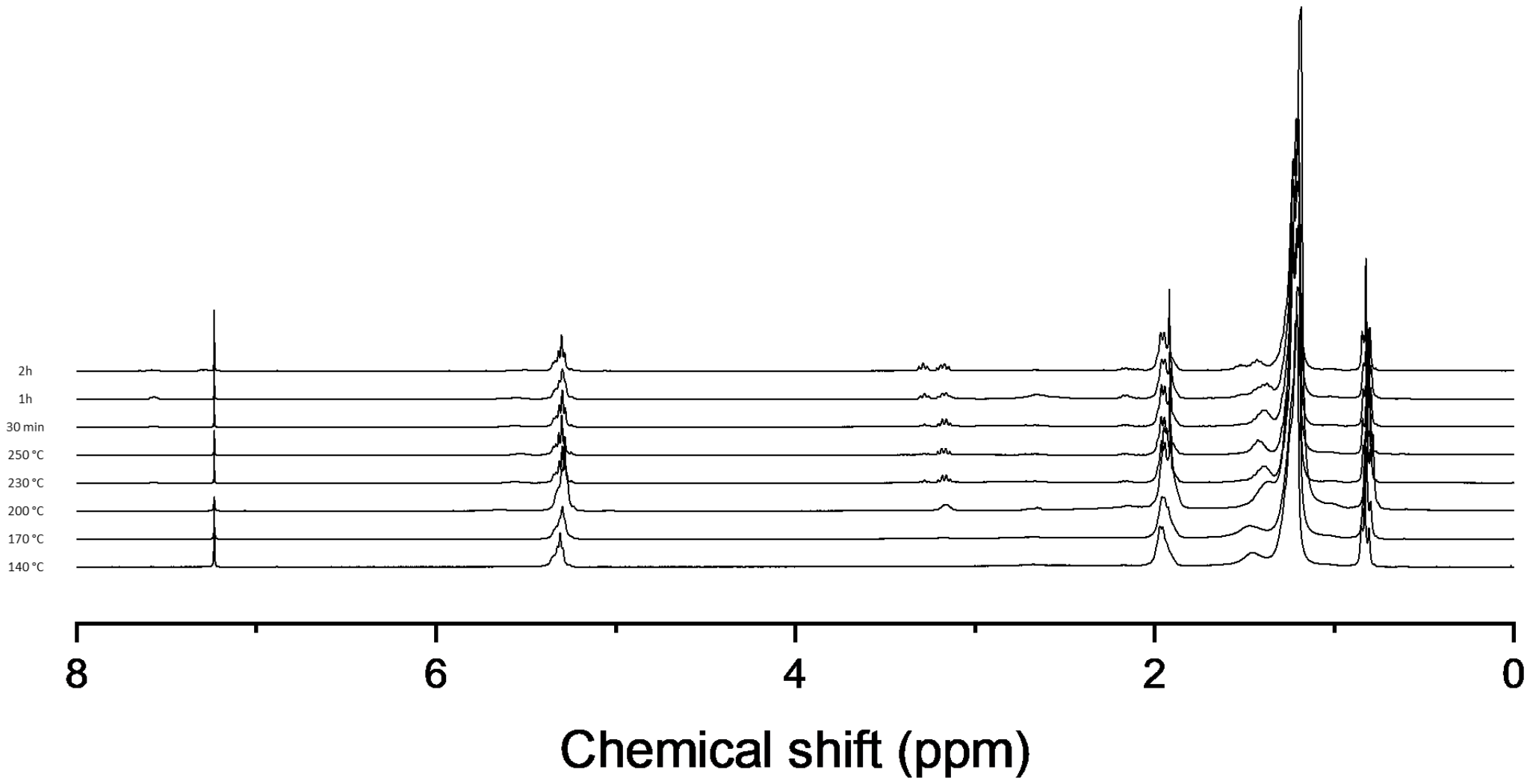


Figure S8a : ^{1}H NMR spectra from synthesis ***A*** *in situ* study. From bottom to top are displayed spectrum made from samples taken at 140 °C, 170 °C, 200 °C, 230 °C, 250 °C and after 30 min, 1h and 2h of plateau.

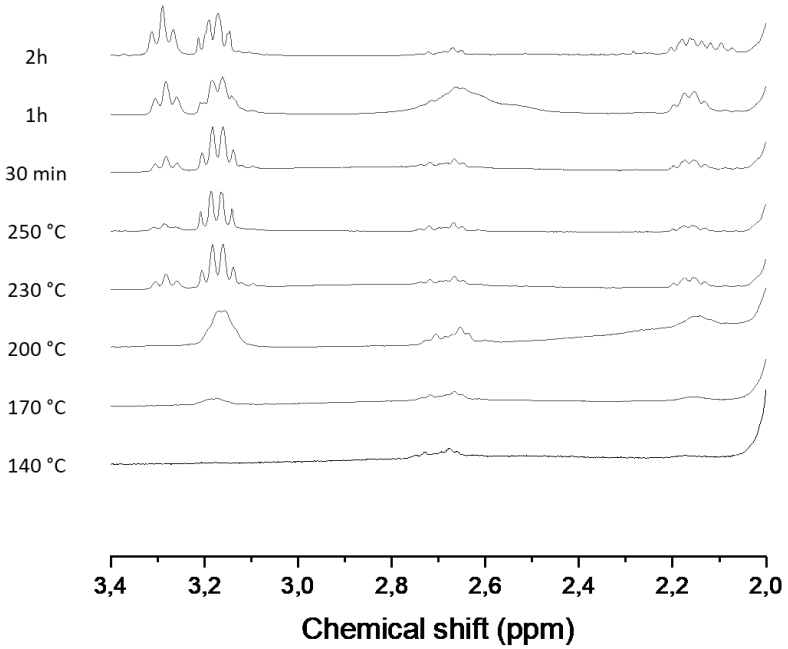


Figure S8b: Zoom in of ^{1}H NMR spectra in the CH_2 region from synthesis ***A*** *in situ* study. From bottom to top are displayed spectrum made from samples taken at 140 °C, 170 °C, 200 °C, 230 °C, 250 °C and after 30 min, 1h and 2h of plateau.

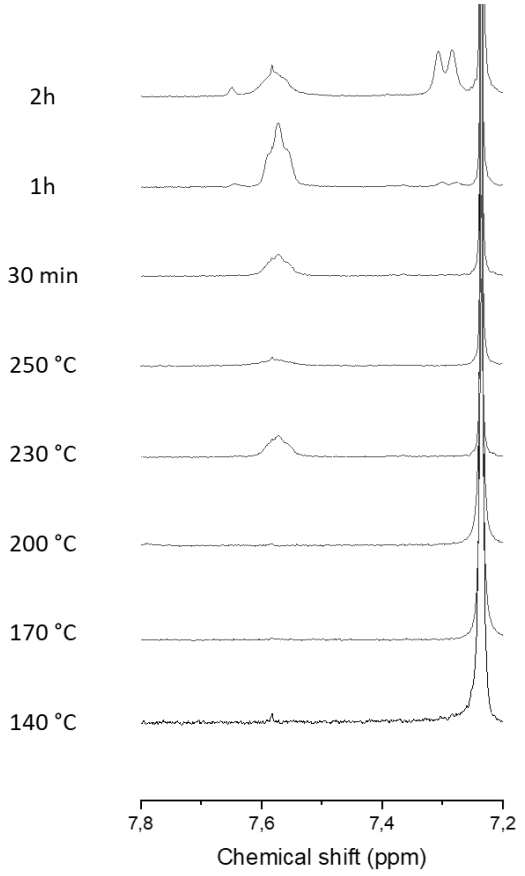


Figure S8c: Zoom in of ^{1}H NMR spectra in the H of secondary aldimine region from synthesis ***A*** *in situ* study. From bottom to top are displayed spectrum made from samples taken at 140 °C, 170 °C, 200 °C, 230 °C, 250 °C and after 30 min, 1h and 2h of plateau.

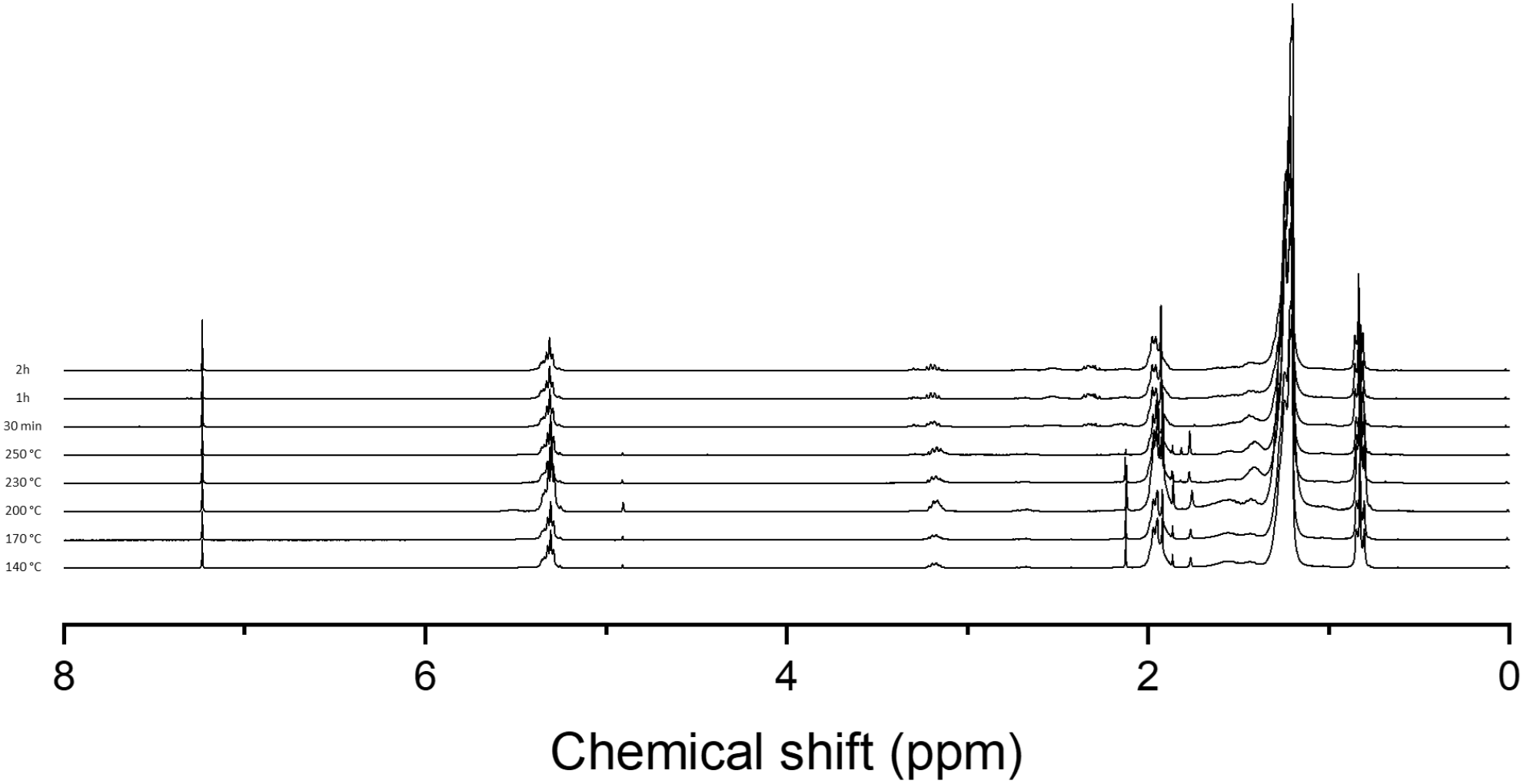


Figure S9a: ^{1}H NMR spectra from synthesis ***B*** *in situ* study. From bottom to top are displayed spectrum made from samples taken at 140 °C, 170 °C, 200 °C, 230 °C, 250 °C and after 30 min, 1 h and 2 h of plateau.

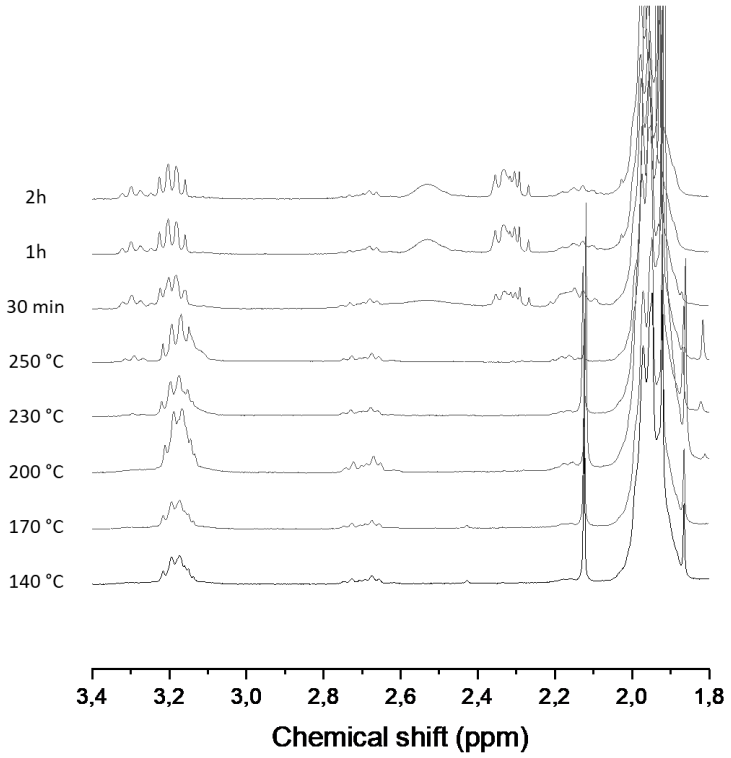


Figure S9b: Zoom of ^{1}H NMR spectra in the CH_2 region from synthesis ***B*** *in situ* study. From bottom to top are displayed spectrum made from samples taken at 140 °C, 170 °C, 200 °C, 230 °C, 250 °C and after 30 min, 1 h and 2 h of plateau.

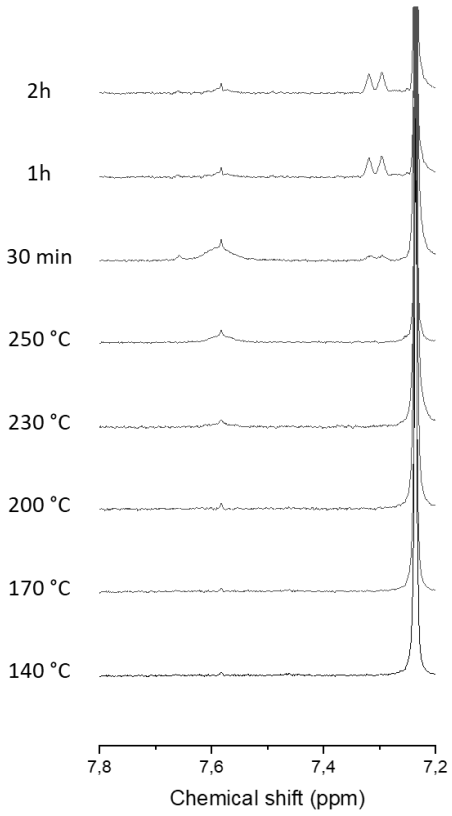


Figure S9c: Zoom of ^{1}H NMR spectra in the H of secondary aldimine from synthesis ***B*** *in situ* study. From bottom to top are displayed spectrum made from samples taken at 140 °C, 170 °C, 200 °C, 230 °C, 250 °C and after 30 min, 1 h and 2 h of plateau.

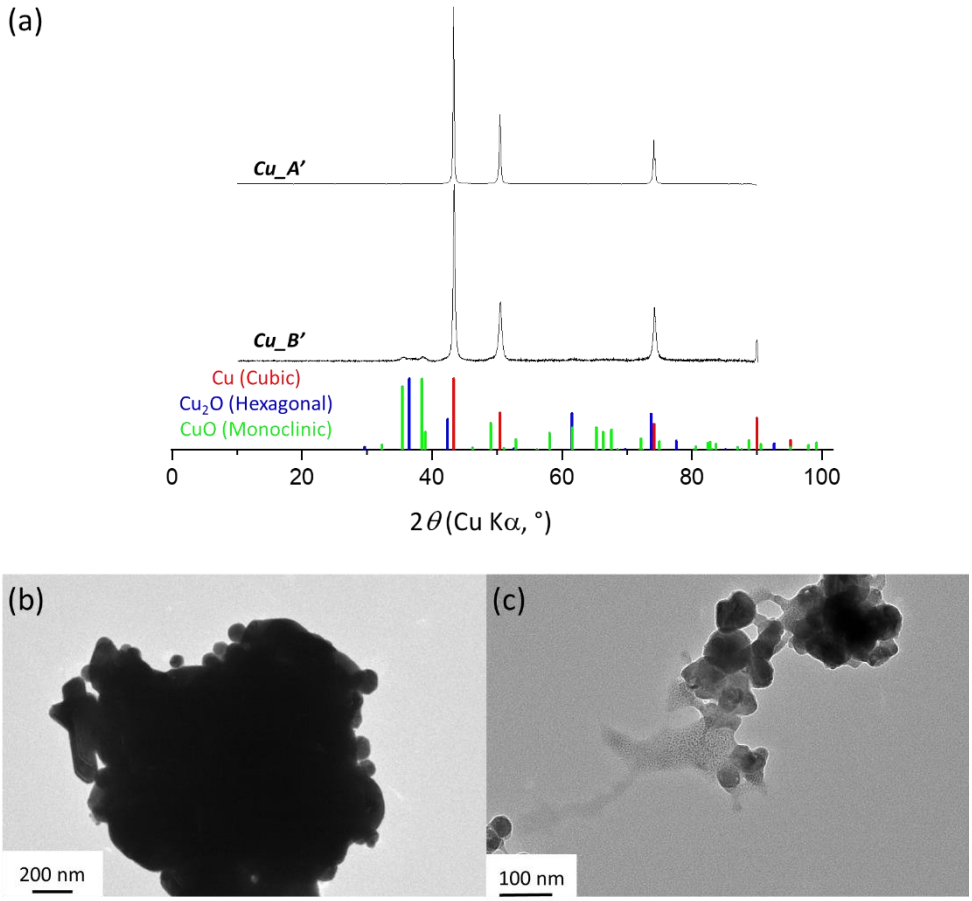


Figure S10 : (a) XRD pattern of ***Cu_A'*** and ***Cu_B'.*** XRD reference pattern for cubic Cu in red (COD number: 9008468) for cubic Cu_2O in blue (COD number: 1010941) and for monoclinic CuO in green (COD number : 9015822).TEM micrograph of nanoparticules obtained from (b) synthesis ***A'*** and (c) synthesis ***B'***.

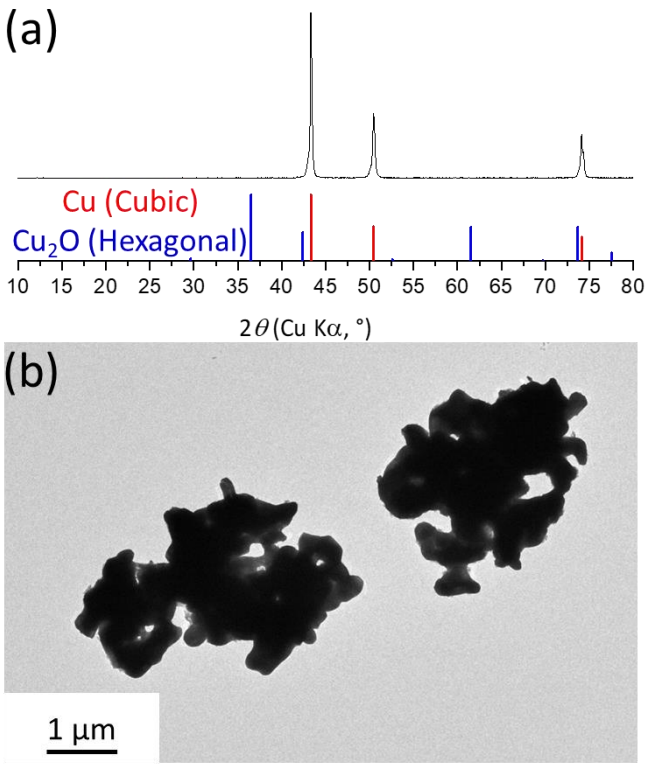


Figure S11: XRD pattern of copper nanoparticles ***Cu_A*** synthesized with the modified synthesis ***A*** to remove water from the reaction medium. XRD reference pattern for cubic Cu in red (COD number: 9008468) and for cubic Cu_2O in blue (COD number: 1010941), (b) TEM micrograph of the nanoparticles.

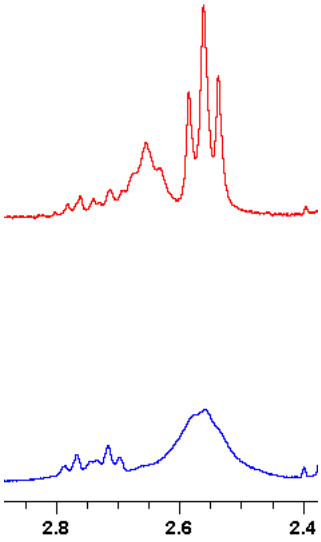


Figure S12: NMR ^{1}H spectra of the supernatant of synthesis ***B***: (a) before centrifugation, (b) after centrifugation at 9000 RPM for 15 minutes.

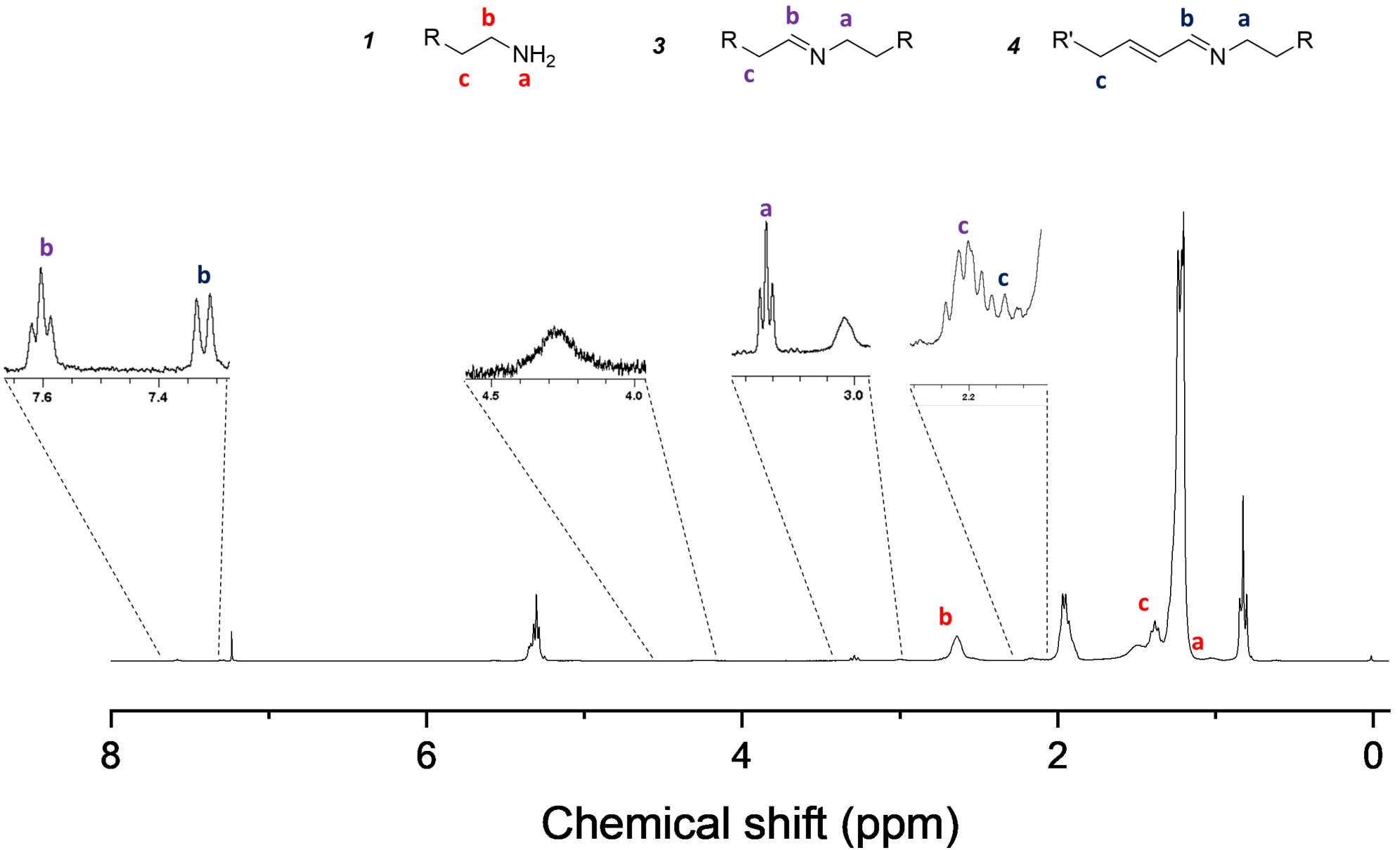


Figure S13: (Top) Molecular structure of species detected in the ^{1}H NMR spectrum. (Bottom) ^{1}H NMR of ***Cu_A*** catalysed transformation of oleylamine reaction crude centifuged at 9000 RPM during 15 min.

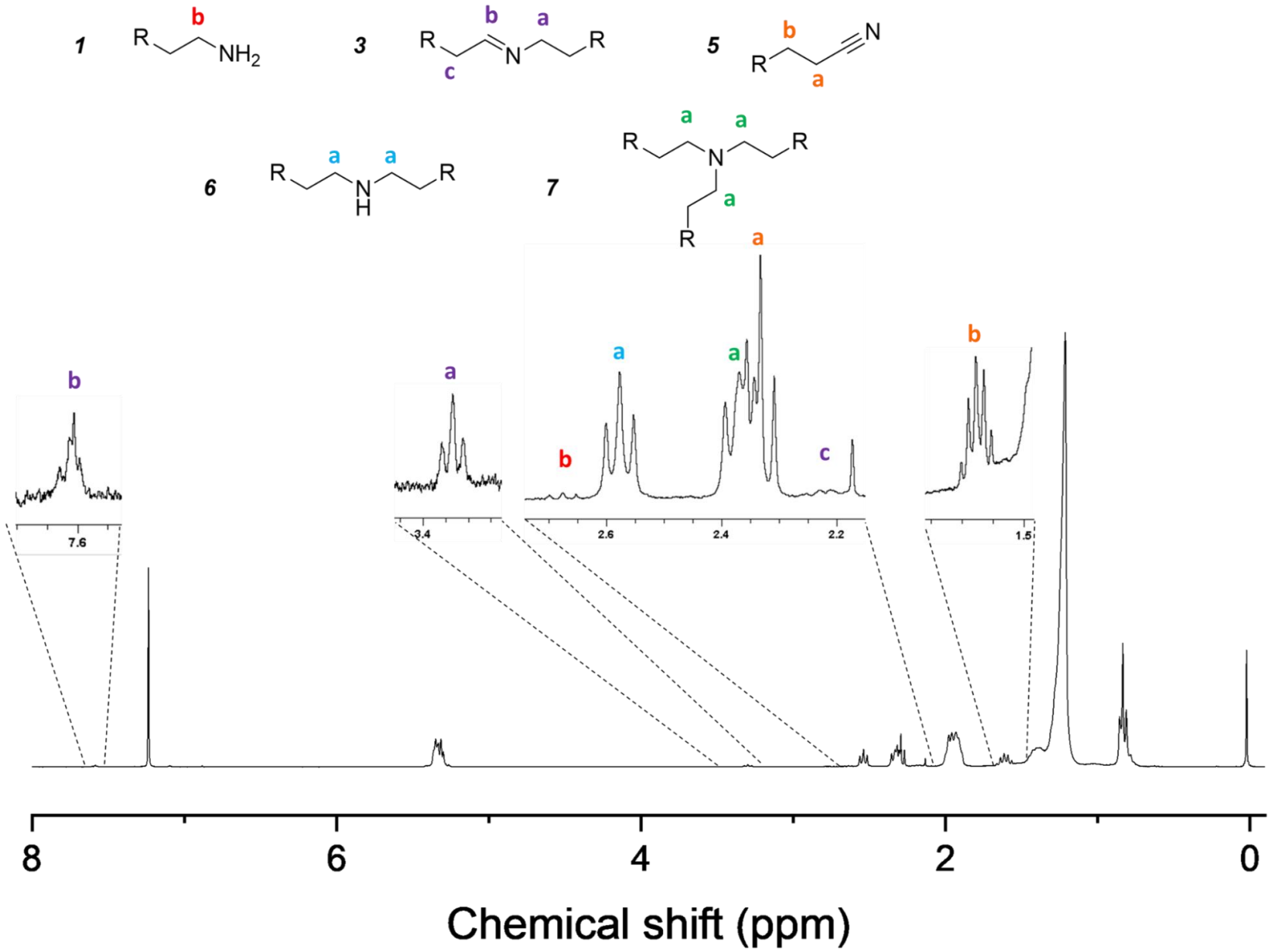


Figure S14: (Top) Molecular structure of species detected in the ^{1}H NMR spectrum. (Bottom) ^{1}H NMR of ***Cu_B*** catalysed transformation of oleylamine reaction crude centifuged at 9000 RPM during 15 min.

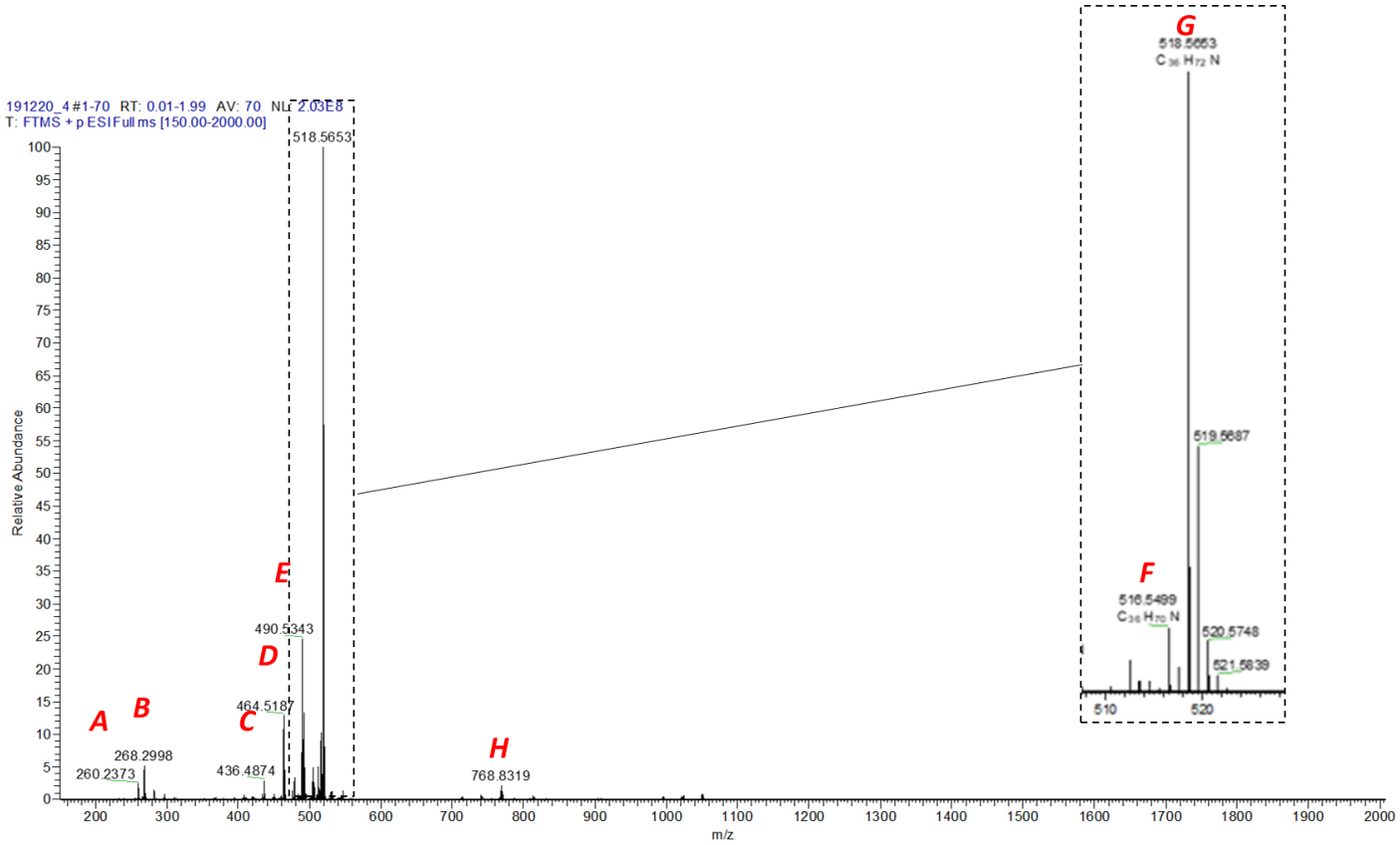


Figure S15: ESI-MS of ***Cu_B*** catalysed transformation of oleylamine reaction crude centifuged at 9000 RPM during 15 min. Peaks interpreted are marked with a red letter and their interpretation are given in Table S3.

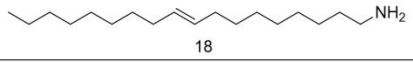
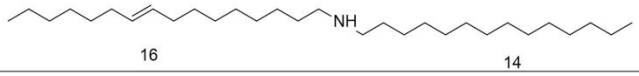
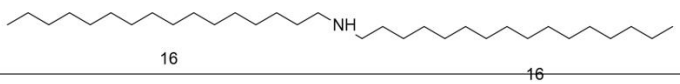
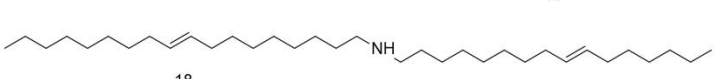
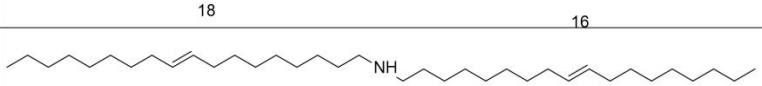
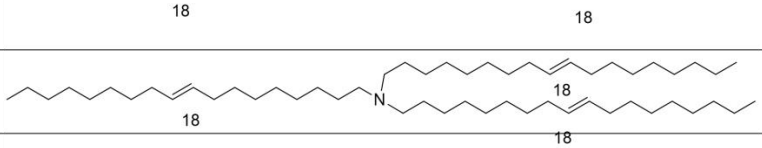
Entry	Measured Mass	Proposed chemical formula	Corresponding theoritical mass	Proposed ionized structure
A	260,2373	$C_{18}H_{29}N + H^+$	260,2378	Dehydrogenated derivative of oleylamine
B	268.2998	$C_{18}H_{37}N + H^+$	268.3004	
C	436.4874	$C_{30}H_{61}N + H^+$	436,4882	
D	464.5187	$C_{32}H_{65}N + H^+$	463,5117	
E	490.5343	$C_{34}H_{67}N + H^+$	490,5351	
F	518.5653	$C_{36}H_{71}N + H^+$	518,5659	
G	768.8319	$C_{54}H_{105}N + H^+$	768,8325	

Table S3 : Ionized structure interpreted from mass spectrogram S16.

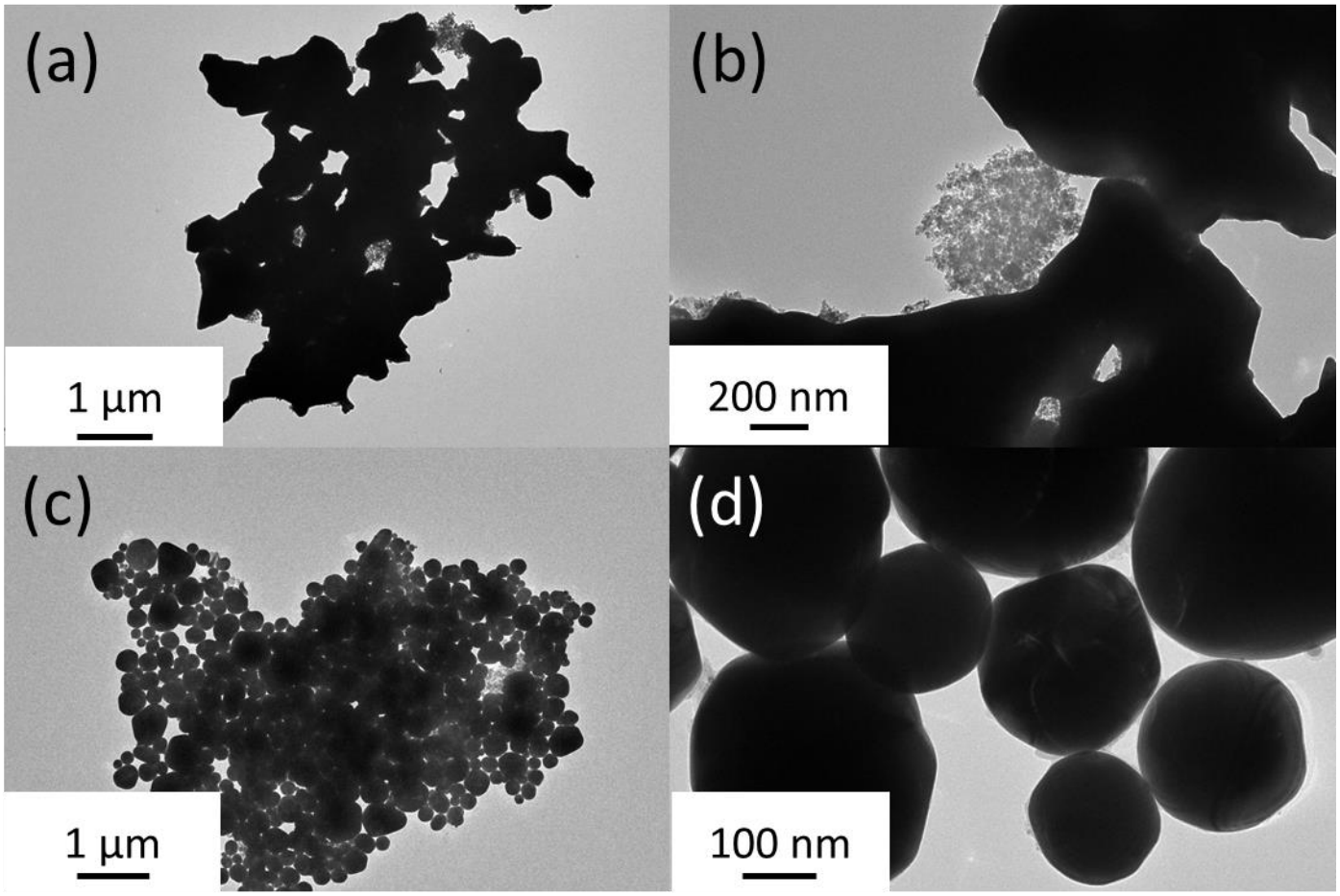


Figure S16 : TEM micrograph of (a),(b) ***Cu_A*** and (c),(d) ***Cu_B*** after catalytic transformation of oleylamine.

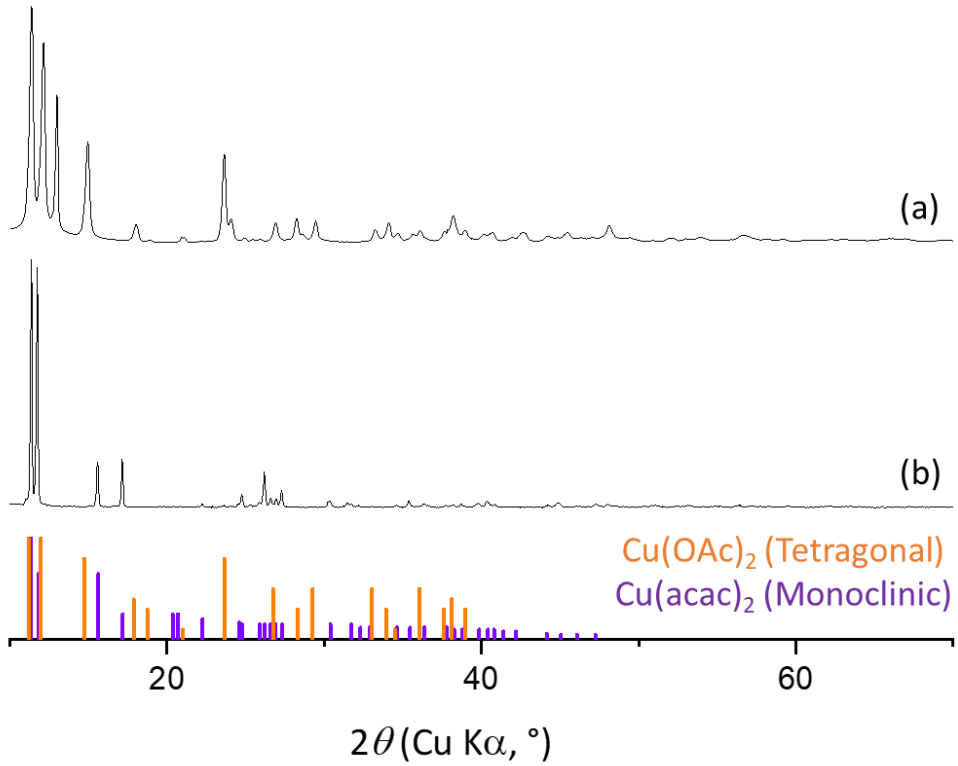


Figure S17: XRD patterns of commercial (a) $Cu(OAc)_2$ and (b) $Cu(acac)_2$ as precursor. XRD reference pattern for $Cu(OAc)_2$ in orange (PDF 00-011-0800) and for $Cu(acac)_2$ in purple (PDF 00-011-0800) (bottom).

Element	$Cu(OAc)_2$	$Cu(acac)_2$
Cu	98	96.5
Ni	0	2
Al	1.5	1
Si	0.5	0

Table S4: Elemental analysis of commercial $Cu(OAc)_2$ and $Cu(acac)_2$ performed by energy dispersive X-ray spectroscopy. Carbon and oxygen were not quantified. The data correspond to molar ratio of Cu, Ni, Al and Si in each compound.