

Supporting Information

Phytoextracted mining wastes for Ecocatalysis: Eco-Mn[®], an efficient and eco-friendly plant-based catalyst for reductive amination of ketones

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S1. General remarks

Reagents and methods

Reagents and solvents were purchased from Sigma-Aldrich, and were used without further purification. Flash column chromatography was performed using Chromagel Carlo Erba Reactifs SDS silica 60 A CC 35– 70 µm. Reactions were monitored using Merck Kieselgel 60 F254 aluminum. TLCs were visualized by UV fluorescence (254 nm) then by immersion in one of the following dyeing reagents: KMnO₄, vanillin, ninhydrin, phosphomolybdic acid solution, and phosphotungstic acid solution.

XRD analysis

X-ray diffraction (XRD) data measurements on the samples dried at 110 °C for 2 hours were performed by using a BRUKER diffractometer (D8 advance, with a Cu K α radiation $\lambda=1.54086$ Å) equipped with a Lynxeyes detector.

ICP-MS analysis

ICP-MS analyses were performed using the metal analysis of total dissolved solutes in water. The samples were acidified with nitric acid 2.5% and stirred for 30 min. The digestates were diluted to 0.005 g.L⁻¹ in nitric acid 2.5 %. Three blanks were recorded for each step of the digestion and dilution procedure on a HR-ICP-MS Thermo Scientific Element XR. Three analyses were performed for each sample in order to determine the standard deviation of the measurement.

GC-MS analysis

Gas chromatography and mass spectrometry analyses were performed using a Shimadzu QP2010SE apparatus, equipped with a 30 m x 0.25 mm x 0.25 μ m ZB-5MSi Guardian column (Phenomenex[®]) with hydrogen as carrier gas. Mass spectra were recorded in electron impact (EI) mode at 70 V and identified by comparison with data of the NIST 11 software library and by comparison of the retention time of the standard compounds.

NMR (Nuclear Magnetic Resonance) analysis

NMR spectra were recorded on a Brüker Avance 300 spectrometer at room temperature, ¹H frequency is at 300 MHz, ¹³C frequency is at 75 MHz.

IR (Infrared) analysis

IR spectra were recorded on a PerkinElmer Spectrum 100 FT-IR spectrometer, in ATR mode.

S2. Preparation of Eco-Mn[®]

Eco-Mn[®] was prepared from harvested leaves of *Grevillea exul rubiginosa*, a manganese hyperaccumulating plant present in New Caledonia. *Grevillea exul rubiginosa* was collected before flowering, at Col de Mouriange, near Le Mont-Dore, in the Southern province of the subtropical Pacific island of New Caledonia. The leaves were air-dried and ground. The obtained solid (50 g) was calcined to 400 °C for 5 h and the resulting ashes (1.5 g) were added to 20 mL of a diluted solution of HCl (1M). The solution was stirred for 2 h at 60 °C. During the heating, the color of the mixture changed from black to dark green. The reaction mixture was then filtered on a pad of celite. The resulting dark-green solution, composed of different metal chlorides, was concentrated under vacuum, yielding the ecocatalyst Eco-Mn[®] as a pale yellow powder (2.25 g). Eco-Mn[®] was stored in a desiccator under vacuum.

S3. Synthesis of inorganic salts present in Eco-Mn[®]: KMnCl_3 , $\text{CaMg}_2\text{Cl}_6(\text{H}_2\text{O})_{12}$, $\text{CaSO}_4(\text{H}_2\text{O})_{0.5}$

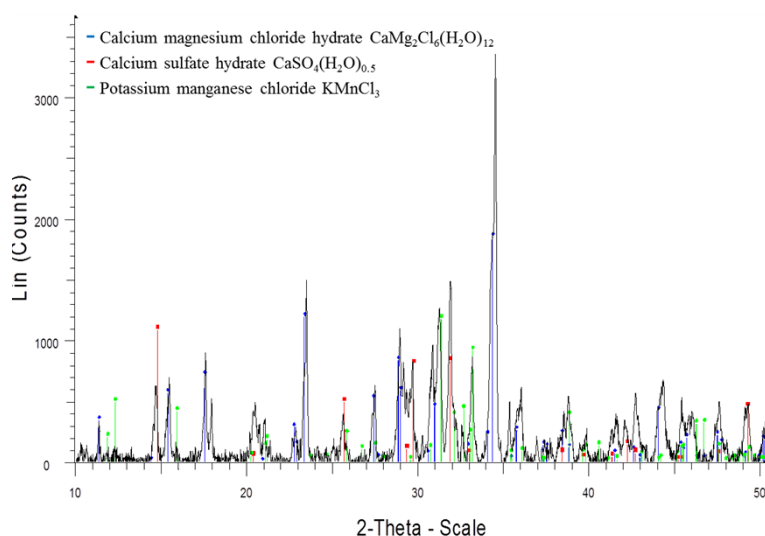
KMnCl_3 : the procedure followed is as described by Horowitz *et al.*¹ 1.86g of anhydrous KCl and 9.90g of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ were added in a round bottom flask, and dissolved in a minimum amount of a solution of HCl ($1\text{mol}\cdot\text{L}^{-1}$), at 100°C . Slow cooling of the mixture yielded $\text{KMnCl}_3 \cdot 2\text{H}_2\text{O}$ crystalline needles. Excess of solution was removed with a syringe, and the crystals were dried under vacuum at 90°C during 9 hours.

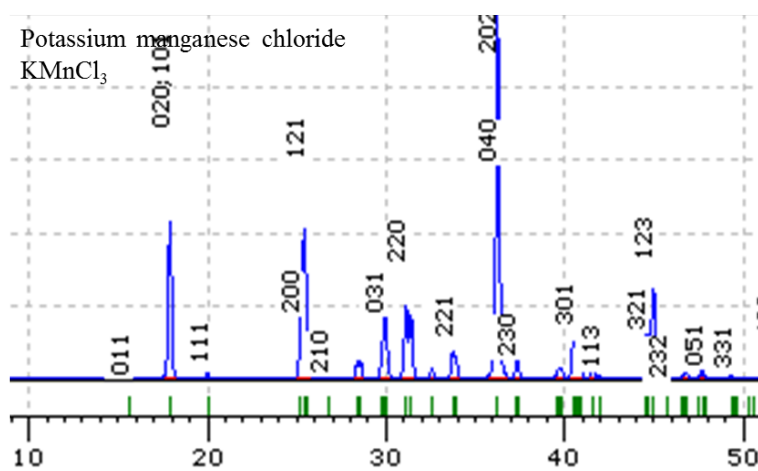
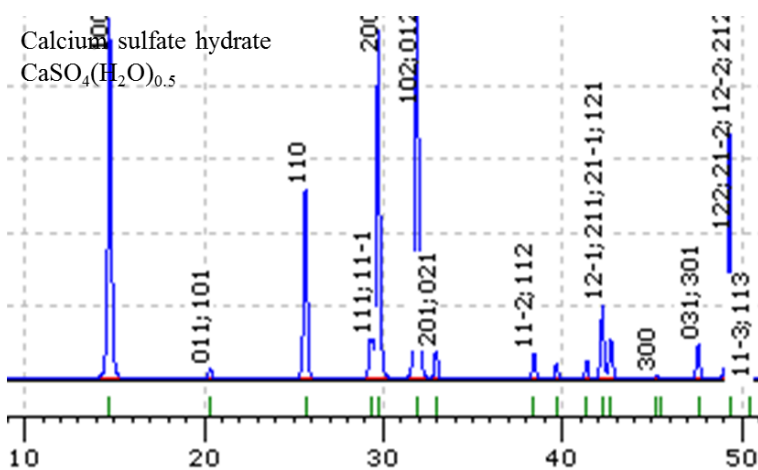
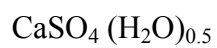
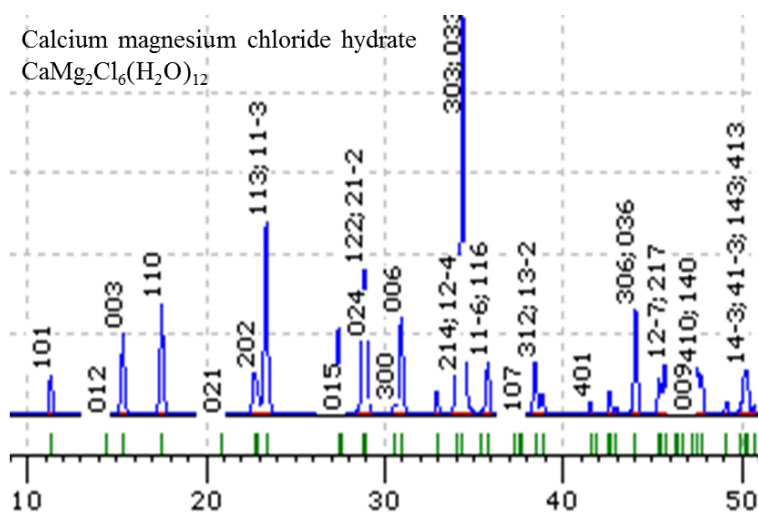
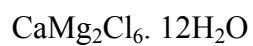
$\text{CaMg}_2\text{Cl}_6(\text{H}_2\text{O})_{12}$: the procedure is adapted from Erd *et al.*² 2g of anhydrous CaCl_2 were added in a round bottom flask with 2,4g of anhydrous MgCl_2 (these proportions of anhydrous salts are as cited by Erd *et al.*²). The salts were dissolved in a minimum amount of a solution of HCl ($1\text{mol}\cdot\text{L}^{-1}$) at 100°C . Slow cooling of the mixture yielded $\text{CaMg}_2\text{Cl}_6(\text{H}_2\text{O})_{12}$ crystals. Those very hygroscopic crystals were placed in a schlenk tube with P_2O_5 in order to dry them.

$\text{CaSO}_4(\text{H}_2\text{O})_{0.5}$: $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was dried under vacuum (50 mbars) at 175°C during three days. 0.5 equivalent of H_2O were then added to CaSO_4 .

S4. XRD patterns of Eco-Mn[®], KMnCl_3 , $\text{CaMg}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$ and $\text{CaSO}_4(\text{H}_2\text{O})_{0.5}$

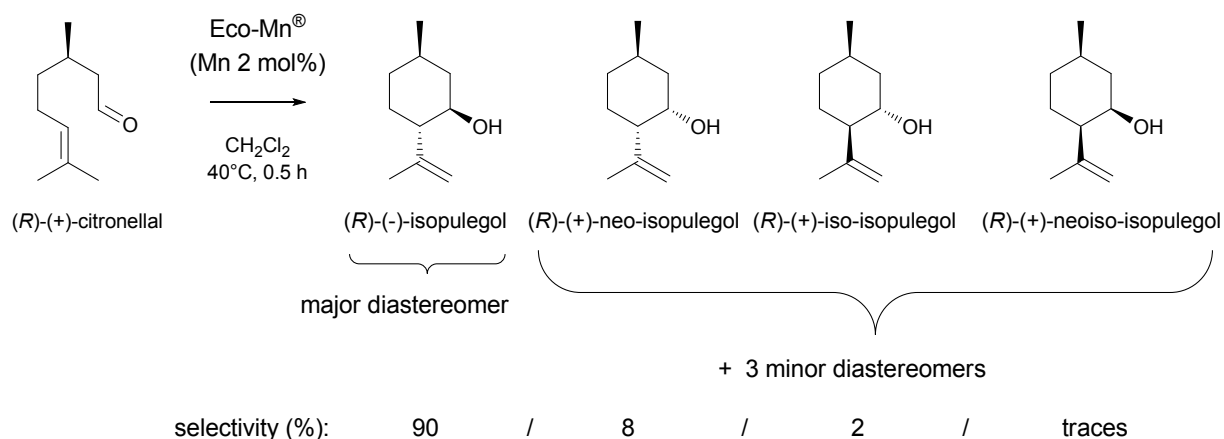
Eco-Mn[®]





S5. Cyclization of the monoterpene (+)-citronellal into isopulegol isomers

To a suspension of Mn catalyst (Table S4) (amount corresponding to 0.020 mmol of Mn, 2 mol%) in 5 mL of dichloromethane was added 180.4 μL of (+)-citronellal (1.0 mmol). After stirring for 0.5 h under reflux, the reaction mixture was filtered, washed with a saturated aqueous solution of NaHCO_3 . The organic layer was dried over Na_2SO_4 , filtered and concentrated under reduced pressure. 95% of yield and 90% of (-)-isopulegol stereoselectivity were estimated by GC-MS analysis. ^1H NMR and IR data were in accordance with those previously reported.³



Scheme S5. Carbonyl-ene cyclization of (+)-citronellal into isopulegol with Eco-Mn[®] as catalyst

Table S5. Carbonyl-ene cyclization of (+)-citronellal into isopulegol with a variety of Lewis acids.

Catalysts	Yield [%]	Ratio of (<i>R</i>)-(-)-isopulegol to other diastereomers [%]	References
Eco-Mn [®]	95 ^a	90	This work
MnCl ₂	-	-	This work
MnCl ₂ + 10 eq H ₂ O	-	-	This work
MnCl ₂ ·4H ₂ O	-	-	This work
ZnCl ₂	53 ^b	88	Nakatani <i>et al.</i> ⁴
Supported ZnCl ₂	94 ^c	86	Imachi <i>et al.</i> ³
ZnBr ₂	70 ^b	94	Nakatani <i>et al.</i> ⁴
ZnI ₂	50 ^b	95	Nakatani <i>et al.</i> ⁴
FeCl ₃	20 ^b	76	Nakatani <i>et al.</i> ⁴
AlCl ₃	30 ^b	71	Nakatani <i>et al.</i> ⁴
SbCl ₃	25 ^b	71	Nakatani <i>et al.</i> ⁴
SnCl ₄	81 ^b	69	Nakatani <i>et al.</i> ⁴
CuCl ₂	100 ^d	64	Alaerts <i>et al.</i> ⁵
TiCl ₄	60 ^b	50	Nakatani <i>et al.</i> ⁴

^a Reaction conditions: (+)-citronellal (1.0 mmol), Eco-Mn[®] (2 mol%, calculated in Mn mol%), dichloromethane (5 mL), 0.5 h under reflux. ^b Reaction conditions: (+)-citronellal (39.0 mmol), catalyst (39.0 mmol), benzene (20 mL), 0.3 h at 5-10 °C. ^c Reaction conditions: (+)-citronellal (1.0 mmol), ZnCl₂ (0.1 mmol) loading C16-HMS (Si/Zn = 16), dichloromethane (10 mL), 12 h at RT. ^d Reaction conditions: (+)-citronellal (3.2 mmol), catalyst (0.7 mmol), toluene (5 mL), 27 h at 100 °C

Almost no conversion of (+)-citronellal was observed with MnCl₂ with 10 eq of H₂O, as with dry MnCl₂ and MnCl₂·4H₂O.

S6. Fourier transform infrared spectroscopy of pyridine

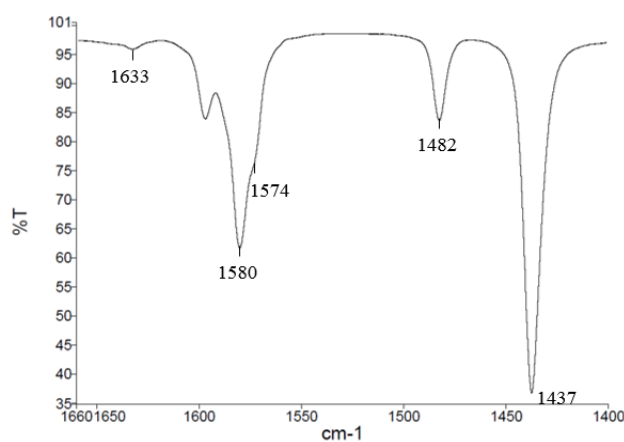
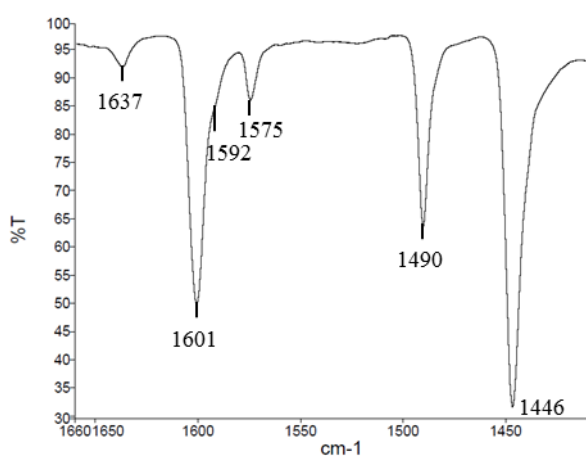


Fig. S6. Fourier transform infrared spectrum of pyridine

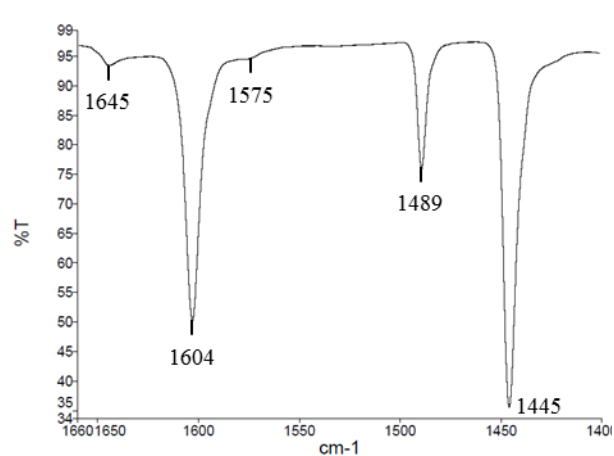
S7. Fourier transform infrared spectroscopy characterization of adsorbed pyridine on commercial manganese chlorides, Eco-Mn[®], and on salts present in Eco-Mn[®]

FTIR measurements were carried out using pyridine as a probe. A PerkinElmer Spectrum100 FT-IR spectrometer was used for recording the spectra. Excess pyridine was adsorbed, then the samples were degassed for 15 min at 25°C (4 mbar) and a first spectrum was recorded. The samples were then degassed for 30 min at 150°C (4 mbar) to eliminate the physisorbed pyridine and a second spectrum was recorded. Fig. S7 represents IR spectra of adsorbed pyridine on commercial manganese chlorides, on Eco-Mn[®], and on salts present in Eco-Mn[®], after outgassing at the indicated temperature.

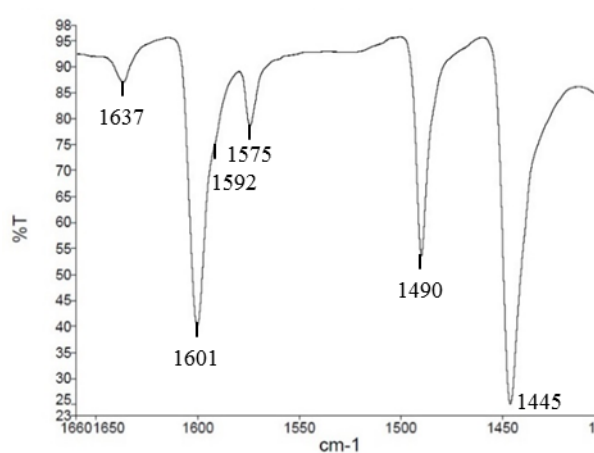
MnCl₂, 25°C



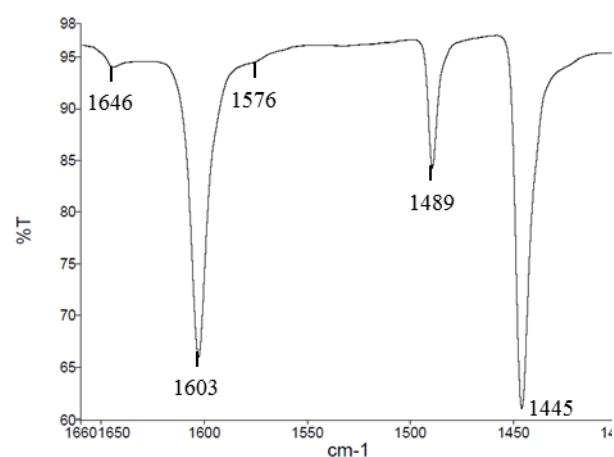
MnCl₂, 150°C



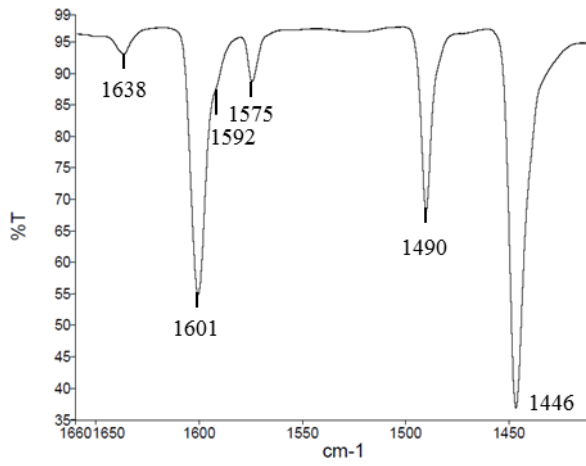
MnCl₂+10eq H₂O, 25°C



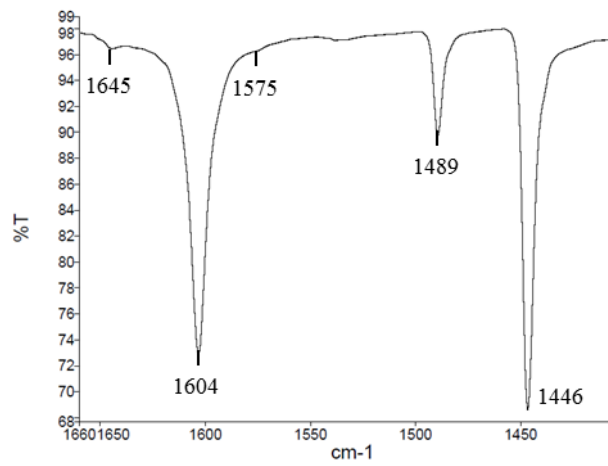
MnCl₂+10eq H₂O, 150°C



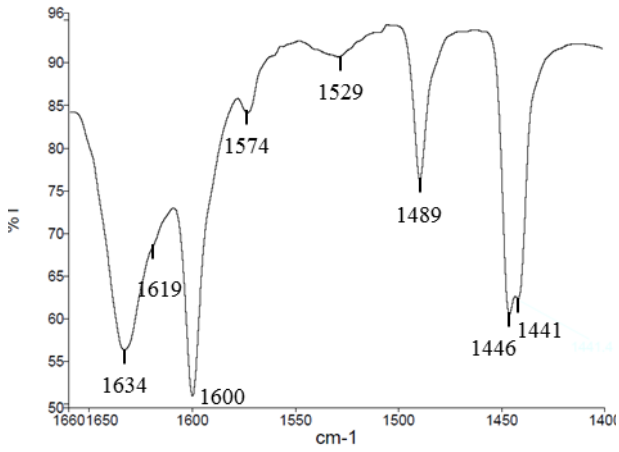
MnCl₂·4H₂O, 25°C



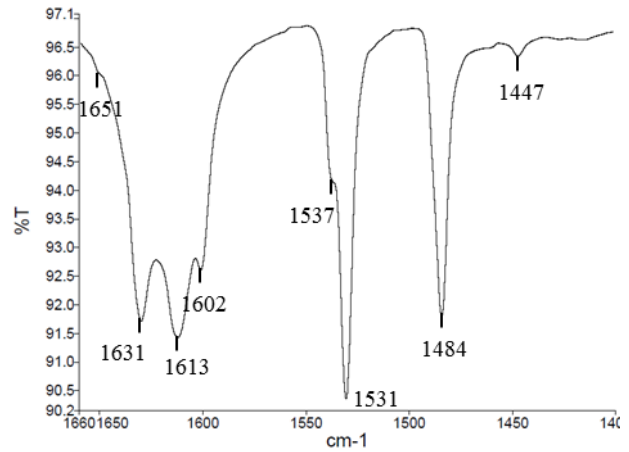
MnCl₂·4H₂O, 150°C



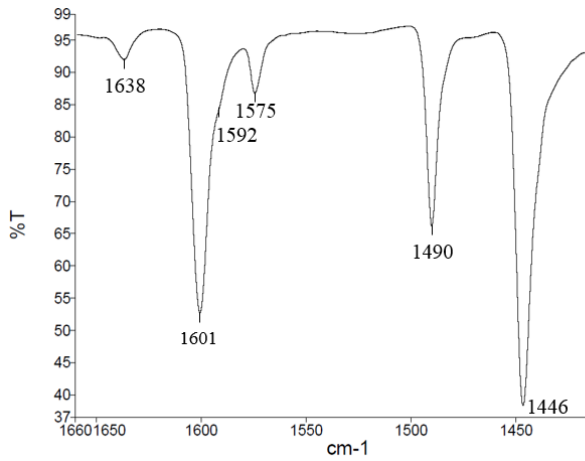
Eco-Mn[®], 25°C



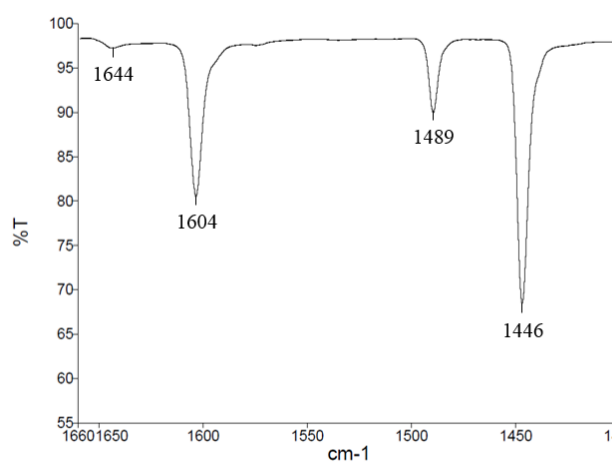
Eco-Mn[®], 150°C



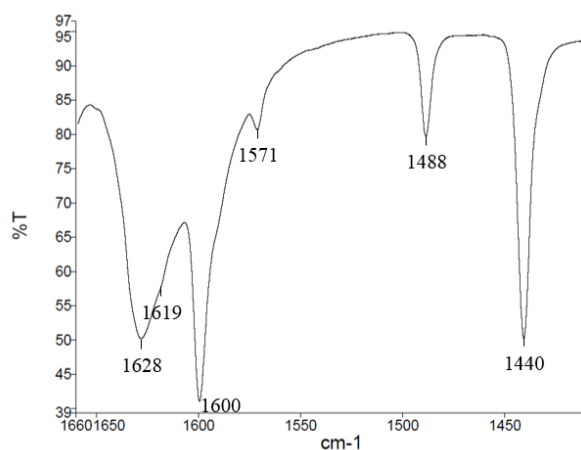
KMnCl₃, 25°C



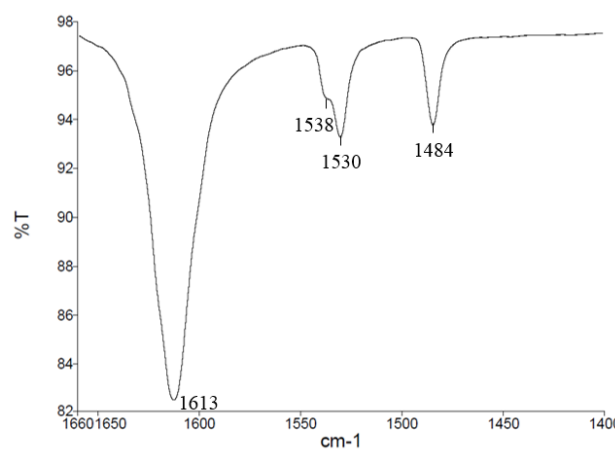
KMnCl₃, 150°C



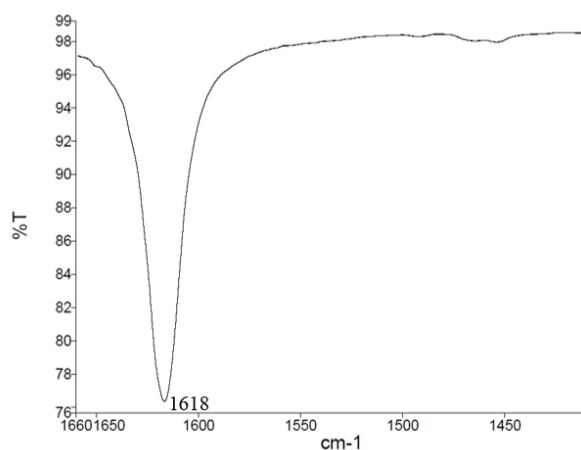
CaMg₂Cl₆(H₂O)₁₂, 25°C



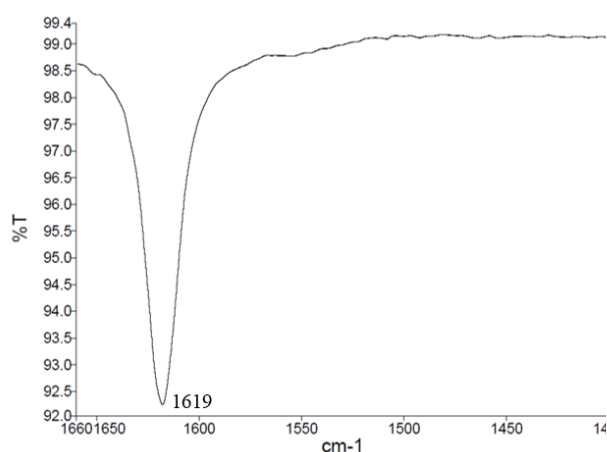
CaMg₂Cl₆(H₂O)₁₂, 150°C



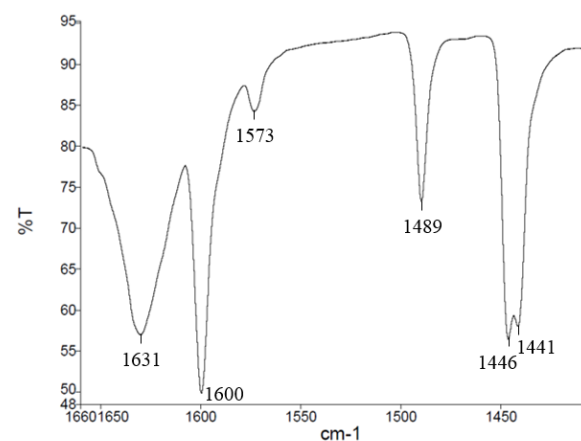
CaSO₄(H₂O)_{0.5}, 25°C



CaSO₄(H₂O)_{0.5}, 150°C



**Mixture of KMnCl₃, CaMg₂Cl₆(H₂O)₁₂,
CaSO₄(H₂O)_{0.5}, 25°C**



**Mixture of KMnCl₃, CaMg₂Cl₆(H₂O)₁₂,
CaSO₄(H₂O)_{0.5}, 150°C**

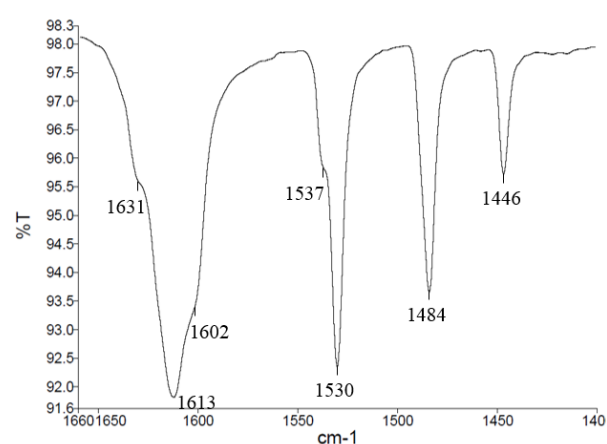
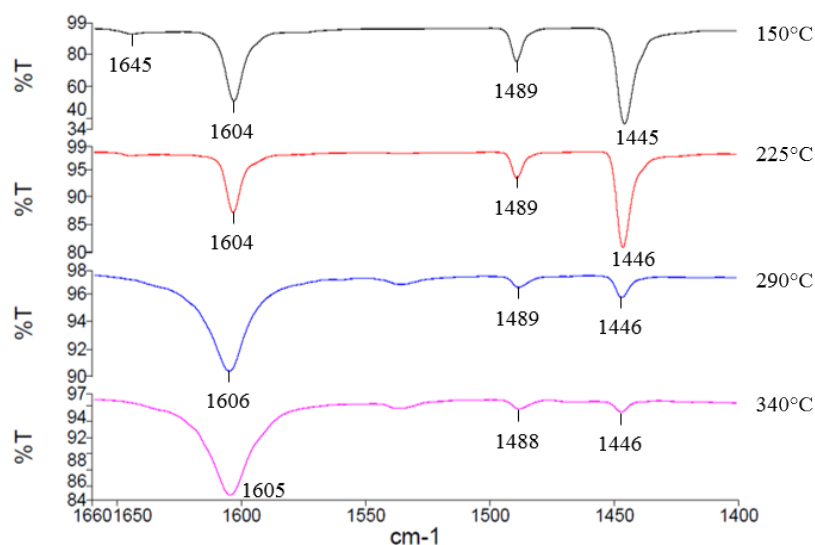


Fig. S7. IR spectra of adsorbed pyridine on commercial manganese chlorides, on Eco-Mn[®], and on salts present in Eco-Mn[®], registered following outgassing at the indicated temperatures.

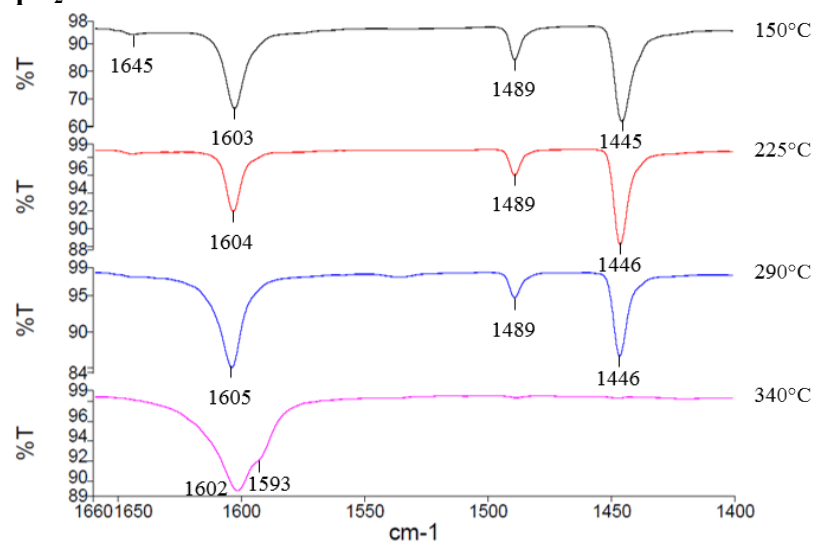
S8. Fourier transform infrared spectroscopy study of pyridine adsorbed on commercial manganese chlorides and Eco-Mn[®] after outgassing at different temperatures

FTIR measurements were carried out using pyridine as a probe. A PerkinElmer Spectrum100 FT-IR spectrometer was used for recording the spectra. Excess pyridine was adsorbed, then the samples were degassed for 15 min at 25°C (4 mbar) and a first spectrum was recorded. The samples were then degassed for 30 min at 150°C, or 225°C or 290°C or 340°C (4 mbar) to eliminate the physisorbed pyridine and a second spectrum was recorded. Fig. S8 represents IR spectra of adsorbed pyridine on manganese chlorides and on Eco-Mn[®] after outgassing at the indicated temperature.

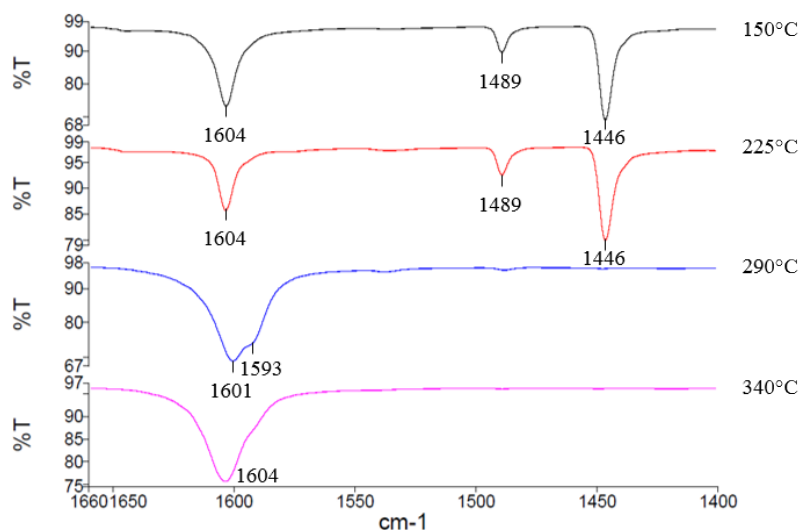
MnCl₂



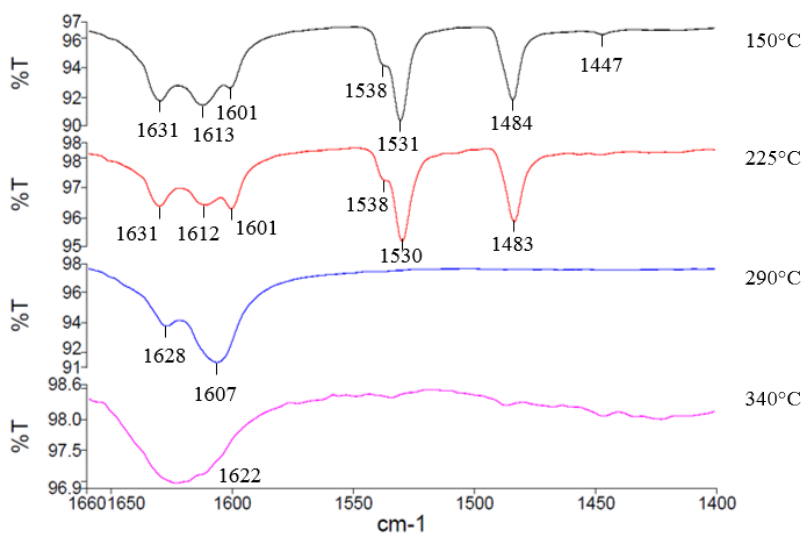
MnCl₂ + 10 eq H₂O



MnCl₂·4H₂O



Eco-Mn®

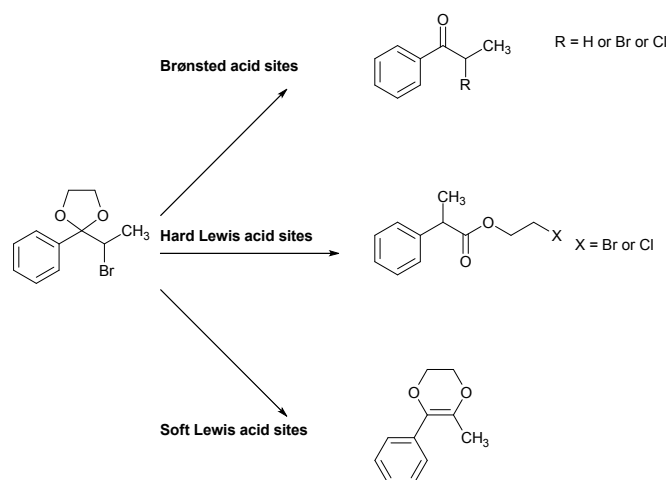


The infrared spectra registered after outgassing at 150°C and at 225°C are exactly the same; After outgassing at 290°C and 340°C, bands characteristic of pyridine were not present anymore on the spectra, pyridine was desorbed, except in the case of MnCl₂ with 10 eq H₂O. However, in this case, the spectrum is exactly the same as those recorded after outgassing at 150°C and 225°C. For these reasons, the temperatures of 25°C and 150°C have been selected to conduct IR/pyridine study of the different catalysts.

S9. Rearrangement of the ethylene acetal of 2-bromopropiophenone

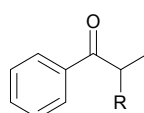
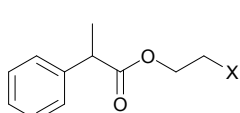
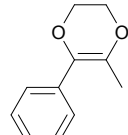
A solution of the ethylene acetal of 2-bromopropiophenone (75.8 mg, 0.29 mmol) in 1,2-dichlorobenzene (3.29 mL) was poured onto catalyst (mass corresponding to 0.012 mmol of Mn, 4 mol%), with water (5.31 μL, 0.29 mmol). The resulting suspension was magnetically stirred at 180 °C for 20 h. The mixture reaction was analyzed by GC-MS analysis, with the

following temperature program: 4 min isothermal at 80 °C, then increasing from 80 °C to 270 °C at 20 °C.min⁻¹.



Scheme S6. Rearrangement and hydrolysis of ethylene acetal of 2-bromopropiophenone depending on acid properties of the catalysts

Table S6. Conversion rates and selectivity of products coming from the rearrangement and hydrolysis of ethylene acetal of 2-bromopropiophenone with commercial manganese chlorides and with Eco-Mn[®].

Catalysts ^a	Conversion rate ^b [%]	Selectivity ^b [%]		
				
		Brønsted acidity products	Hard Lewis acidity products	Soft Lewis acidity products
MnCl ₂	20	14	72	14
MnCl ₂ + 10 eq H ₂ O	10	18	64	18
MnCl ₂ ·4H ₂ O	7	71	0	29
Eco-Mn [®]	62	29	69	2

^a Reaction conditions: 2-bromopropiophenone (0.29 mmol), catalyst (4 mol%), water (0.29 mmol), 1,2-dichlorobenzene (3.3 mL), 180°C, 20 h. ^b Determined by GC-MS analysis.

Results obtained with commercial MnCl_2 with 10 eq of H_2O are not so different from those obtained with dry MnCl_2 . Considering its reactivity toward the cyclic acetal, MnCl_2 with 10 eq of H_2O is in an intermediate position between commercial MnCl_2 and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$. Lewis acidity of MnCl_2 with 10 eq of H_2O is a bit softer than the one of MnCl_2 , and its Brønsted acid character is slightly higher than the one of dry MnCl_2 , which might be coherent with the presence of additional water.

S10. Synthesis of HEH

Paraformaldehyde (3.0 g, 100 mmol), ethyl acetoacetate (50.6 mL, 400 mmol) and ammonium acetate (15.4 g, 200 mmol) were added to 150 mL of degasified water. The mixture was vigorously stirred at reflux temperature, under argon atmosphere and away from light (flask protected with aluminum foil), for 2 h. A bright yellow solid precipitated and was collected by filtration after cooling to room temperature. The solid was washed with 20 mL of water twice and dried in a desiccator under vacuum, avoiding prolonged exposure to light. The obtained solid (22.1 g, 87% yield) was nearly pure and used in the next step without further purification.

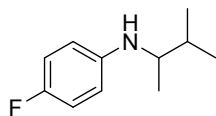
S11. Test reaction of HEH oxidation in presence of Mn(II) catalysts and water

HEH (253 mg, 1.0 mmol), Mn(II) catalyst (Mn 1 mol%) and water (1.8 μL , 10 mol%) were introduced into a 4 mL vial, open to air through a needle. After homogenization with a vortex mixer, the reaction mixture was heated to 110°C, 1 h, under stirring. An aliquot was taken and analyzed in GC-MS after dilution in DCM to determine the proportions of HEH and corresponding pyridine formed by oxidation.

S12. Reductive amination of ketones by Eco-Mn[®]/HEH

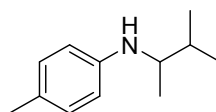
HEH (278 mg, 1.1 mmol), ketone (1.0 mmol), amine (1.0 mmol) and Eco-Mn[®] (8.3 mg, 1 mol% Mn) were introduced in a 4 mL vial. The solid mixture was homogenized with a vortex mixer, and then the reaction mixture was stirred at 110°C for 4 h (the solid melted quickly on heating). After cooling to room temperature, an aliquot was taken and analyzed in GC-MS after dilution in DCM. GC-MS calibration was performed by analysis of known quantities of pure products and biphenyl as internal standard. Products were isolated by flash column chromatography on silica gel (toluene/ethyl acetate, 9:1).

Products were identified by comparison of their spectroscopic data (¹H, ¹³C NMR, MS, IR) to those previously published. New spectroscopic data are given below:



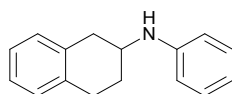
N-(1,2-dimethylpropyl)-4-fluorobenzeneamine (**3j**)

Orange oil; FT-IR (cm⁻¹): 3414, 2962, 1613, 1507; ¹H NMR (300 MHz, CDCl₃): δ_H = 6.90 (d, *J* = 8.9 Hz, 1H), 6.87 (d, *J* = 8.9 Hz, 1H), 6.53 (d, *J* = 8.9 Hz, 1H), 6.52 (d, *J* = 8.9 Hz, 1H), 3.28 (m, 1H), 1.85 (m, 1H), 1.11 (d, *J* = 6.4 Hz, 3H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.93 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ_C = 156.9, 153.8, 115.7, 115.5, 114.0, 113.9, 54.3, 32.1, 19.2, 17.4, 16.5; MS (EI): *m/z* 181, 166, 138, 122, 111, 95, 91, 83.



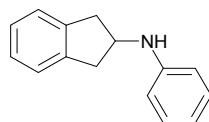
N-(1,2-dimethylpropyl)-4-methylbenzeneamine (**3n**)

Orange oil; FT-IR (cm⁻¹): 3404, 2960, 1618, 1517; ¹H NMR (300 MHz, CDCl₃): δ_H = 7.03 (d, *J* = 8.3 Hz, 2H), 6.57 (d, *J* = 8.3 Hz, 2H), 3.37 (m, 1H), 2.29 (s, 3H), 1.90 (m, 1H), 1.15 (d, *J* = 6.6 Hz, 3H), 1.03 (d, *J* = 6.8 Hz, 3H), 0.96 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ_C = 145.7, 129.8, 113.4, 53.8, 32.2, 20.4, 19.3, 17.5, 16.6; MS (EI): *m/z* 177, 162, 134, 119, 106, 91, 77.



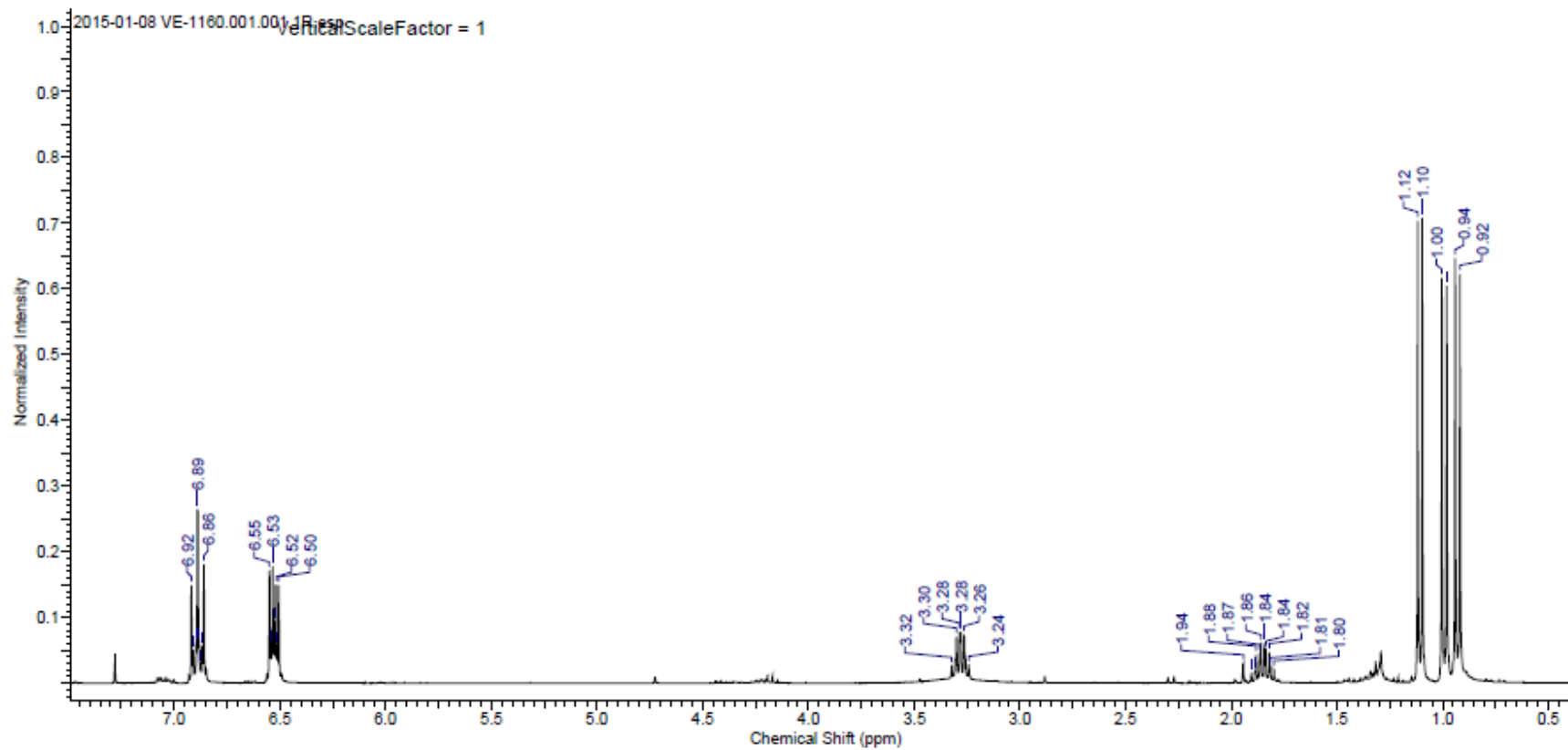
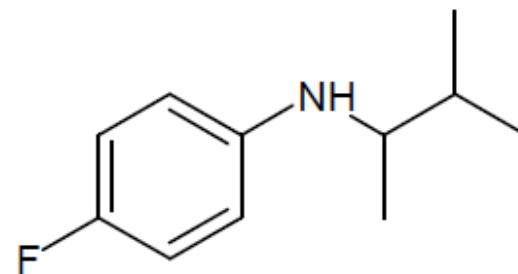
N-Phenyl-1,2,3,4-tetrahydro-2-naphthylamine (**3o**)

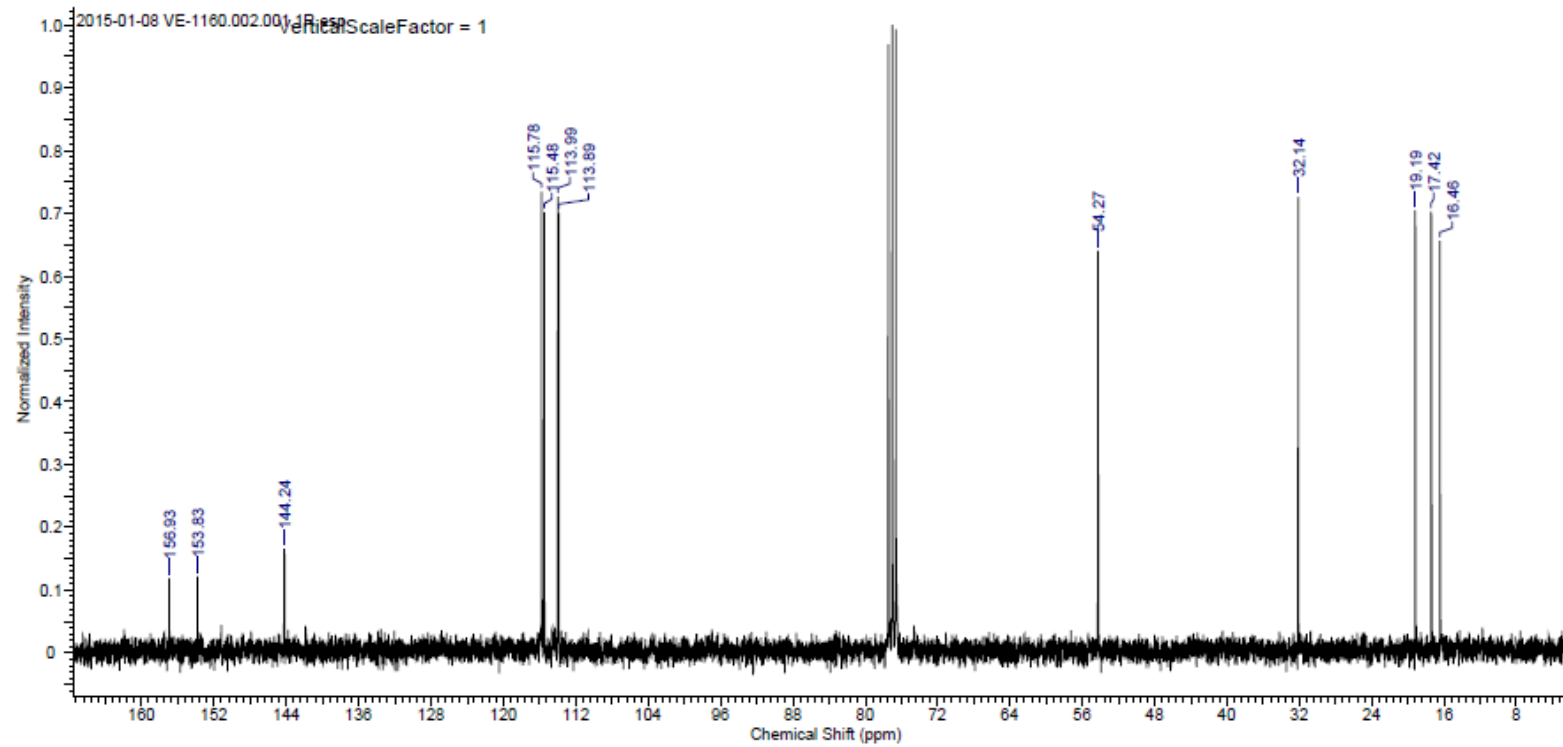
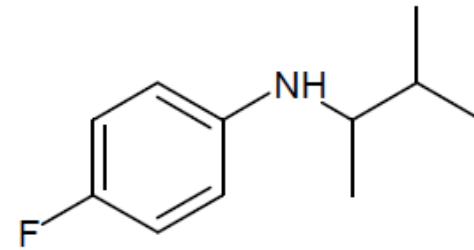
Red oil; FT-IR (cm⁻¹): 3390, 3053, 3019, 2923, 1599, 1494, 1265; ¹H NMR (300 MHz, CDCl₃): δ_H = 7.25-7.09 (m, 6H), 6.76-6.65 (m, 3H), 3.90-3.80 (m, 1H), 3.25 (ddd, *J* = 16.2, 4.9, 0.6 Hz, 1H), 2.95 (m, 2H), 2.72 (dd, *J* = 16.4, 8.3 Hz, 1H), 2.27-2.15 (m, 1H), 1.88-1.74 (m, 1H), 1.30 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ_C = 147.2, 135.9, 134.8, 129.6, 129.4, 128.9, 126.1, 125.9, 117.4, 113.4, 48.5, 36.5, 28.8, 27.5; MS (EI): *m/z* 223, 206, 130, 118, 104, 93, 77.

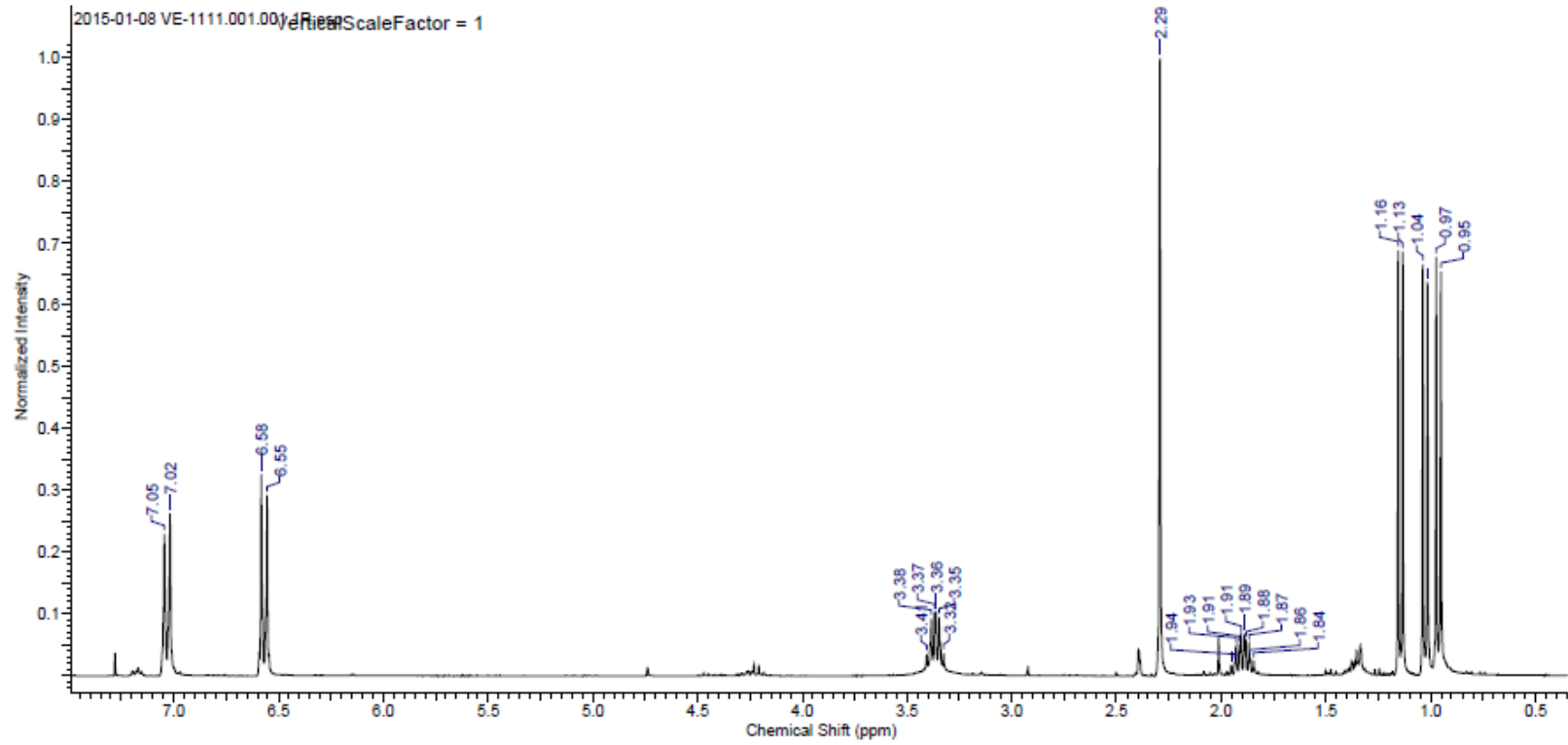
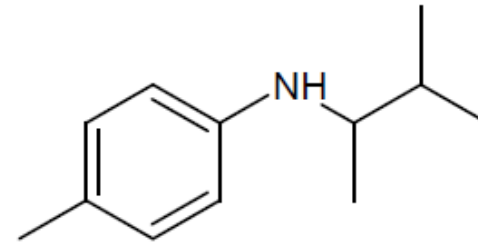


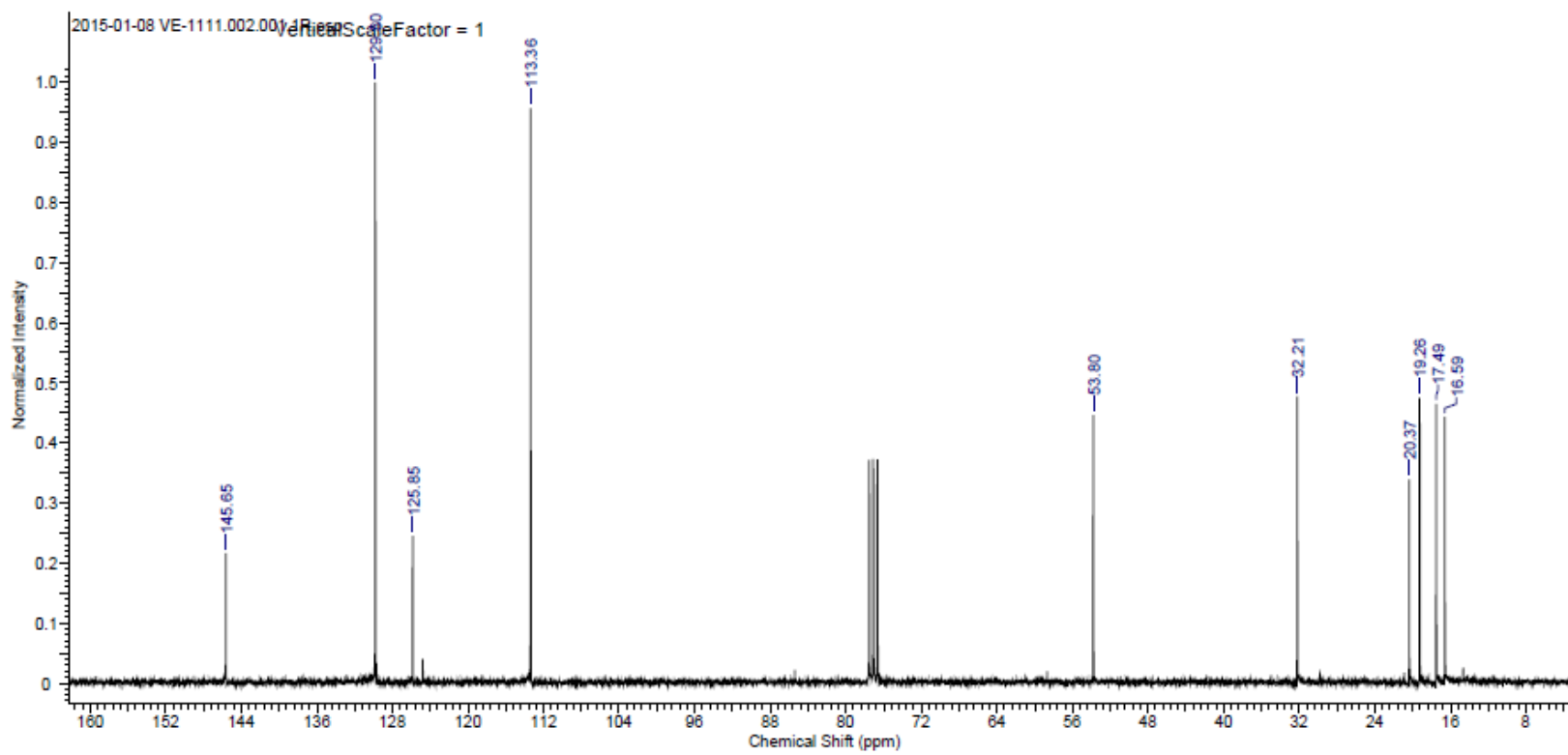
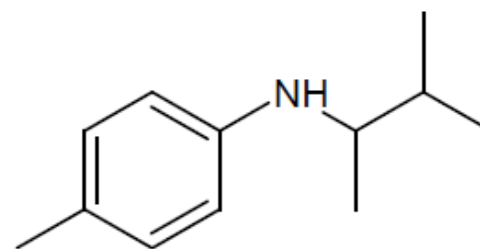
N-Phenyl-2-indanamine (**3p**)

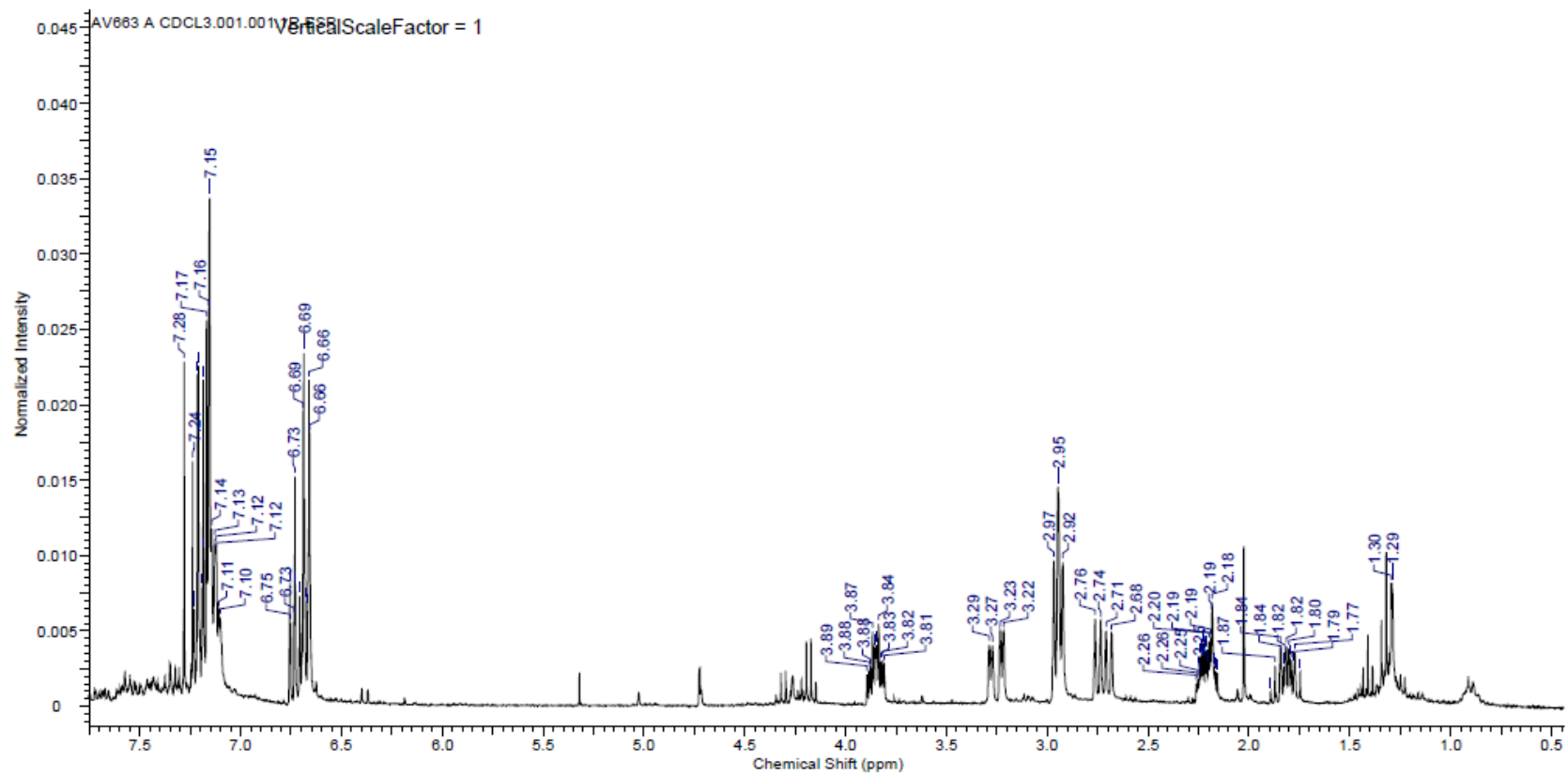
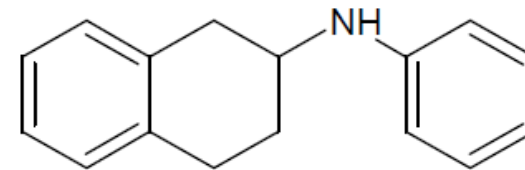
Red oil; FT-IR (cm⁻¹): 3396, 3048, 3021, 2935, 2902, 2838, 1600, 1502, 1311, 1257; ¹H NMR (300 MHz, CDCl₃): δ_H = 7.29-7.18 (m, 6H), 6.78-6.64 (m, 3H), 4.39 (m, 1H), 3.91 (brs, 1H), 3.40 (dd, *J* = 16.0, 6.8 Hz, 2H), 2.91 (dd, *J* = 16.0, 4.5 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ_C = 147.4, 141.5, 129.4, 129.7, 125.0, 117.5, 113.5, 54.1, 40.3; MS (EI): *m/z* 209, 116, 104, 77.

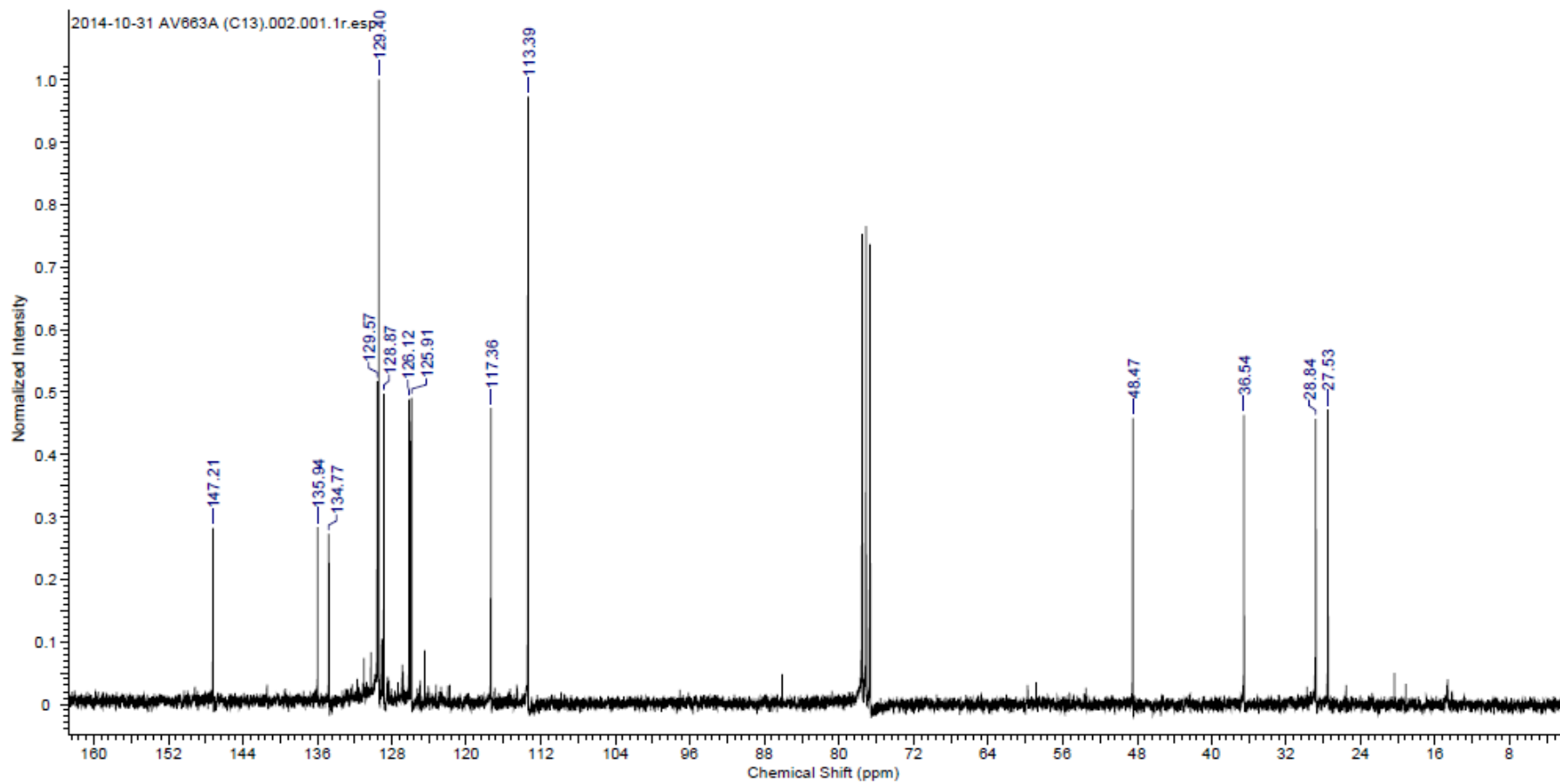
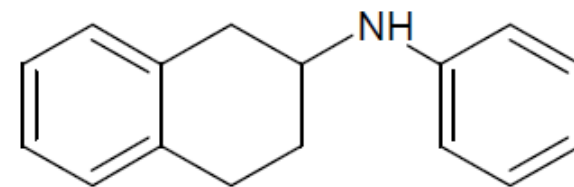


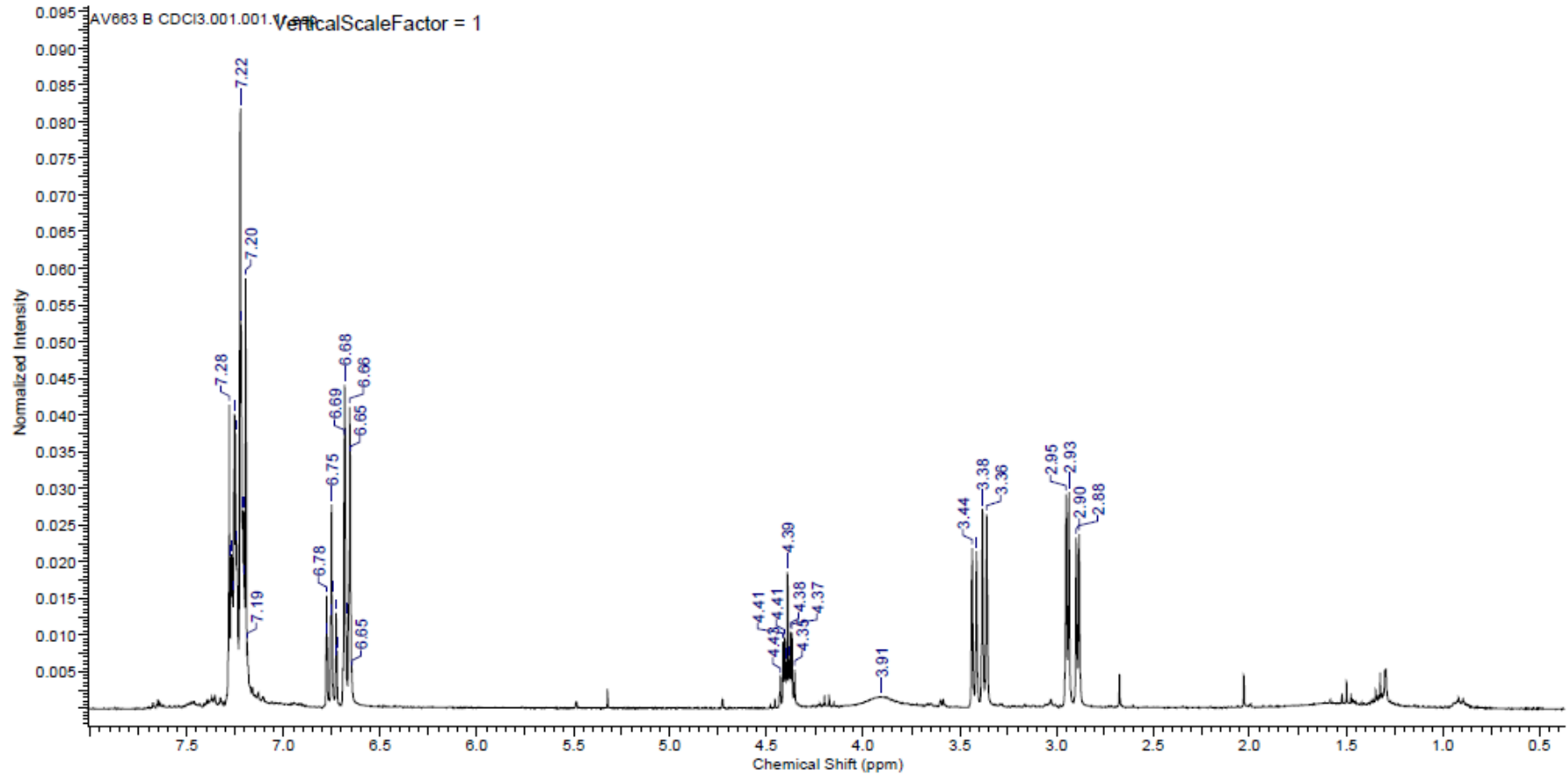
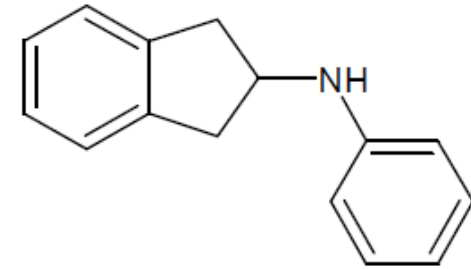


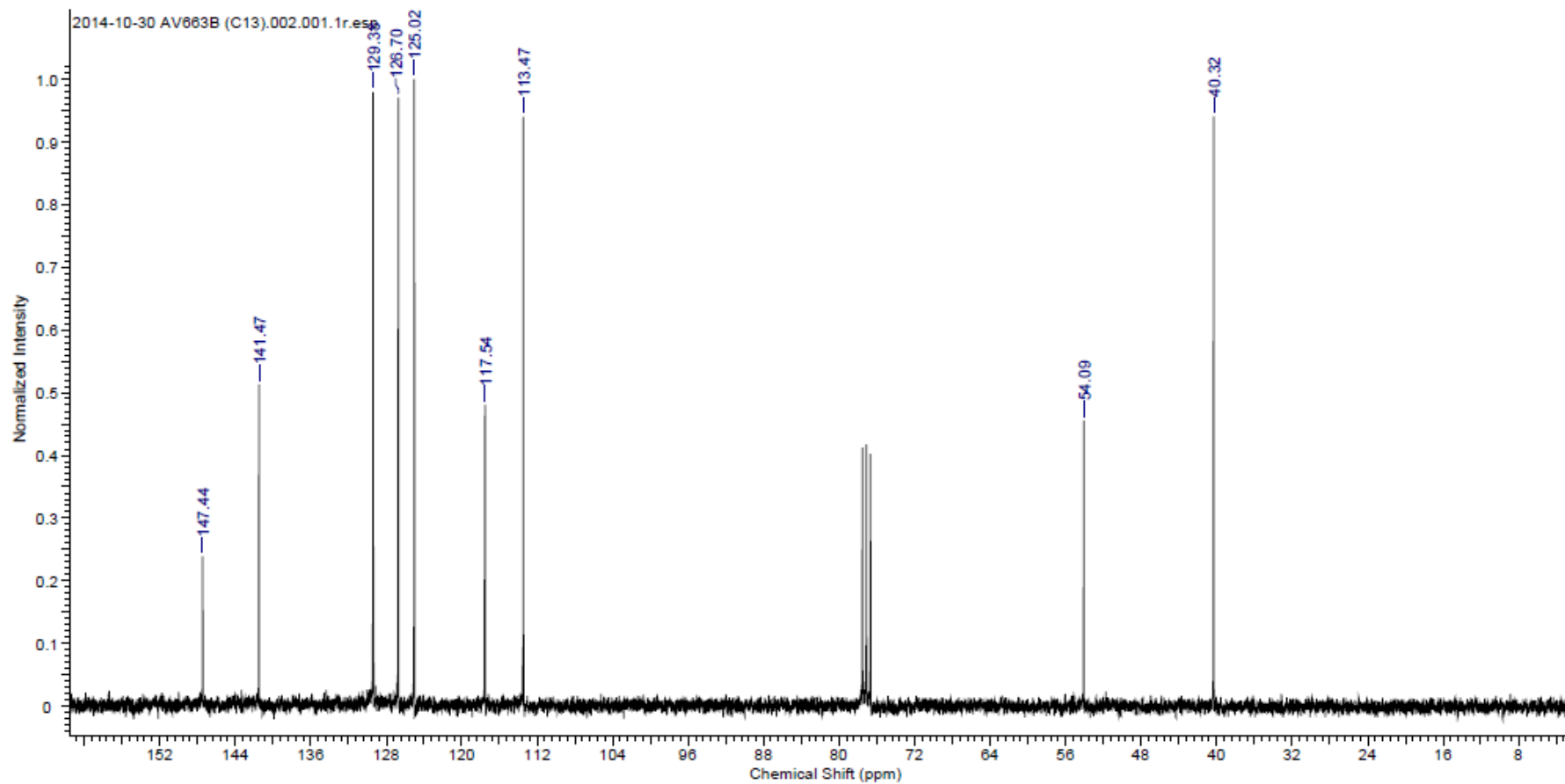
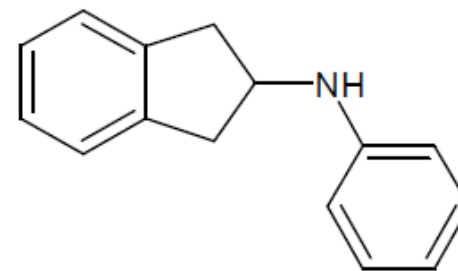












S13. ICP-MS analysis of residual metallic elements in purified products

After purification by flash chromatography, the presence of residual metallic elements in reaction products has been assessed by ICP-MS analysis. The following elements were detected on a representative sample (product **3i**, 10 mg).

Element	Content in analyzed sample (ppm)	Standard deviation (ppm)
K	40.81	0.38
Mg	122.45	6.82
Ca	510.20	7.49
Al	224.49	5.28
Mn	< 5	-
Fe	< 5	-
Ni	< 5	-

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