

Supporting Information

Immobilization of Rh(I)-N-Xantphos and Fe(II)-C-scorpionate onto magnetic nanoparticles: reusable catalytic system for sequential hydroformylation/acetalization

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Contents

1. General Information

2. Experimental data

2.1. Characterization of catalyst **CAT 1**

2.2. Magnetic nanoparticles TEM images and size distribution

2.3. Characterization of catalyst **CAT 6**

2.4. Catalysis products

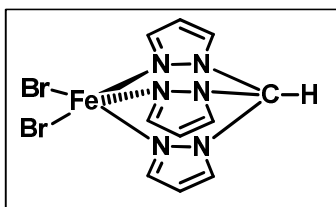
1. General Information

NMR spectra were recorded on Bruker Avance 400 spectrometer (Department of Chemistry, University of Coimbra), using CDCl_3 as deuterated solvent (unless otherwise stated). The ^1H and ^{13}C chemical shifts δ (ppm) are given relative to solvent residual peaks: references for CDCl_3 were 7.26 ppm (^1H -NMR) and 77.16 ppm (^{13}C -NMR) chemical shifts, expressed in ppm. Multiplets were assigned as *s* (singlet), *d* (doublet), *t* (triplet), *dd* (doublet of doublet), *m* (multiplet) and *br. s* (broad singlet), all measurements were carried out at room temperature. High-resolution mass spectrometry was carried out on a Bruker Microtof apparatus, equipped with selective ESI detector. Electron impact (EI) mass spectra were recorded on Agilent 5975 MSD mass spectrometer (70 eV). The data are given as mass units per charge (m/z). Transmission electron microscopy (TEM) analyses were performed on a JEOL JEM 2100 apparatus, at 200 kV, and size distributions of the materials were calculated by a statistical size distribution by manual analysis of enlarged images using the Imagetool sware (Version 3.0) program. Thermogravimetric analysis were made using a TG-DSC Perkin-Elmer STA6000 with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ to a maximum temperature of $900\text{ }^\circ\text{C}$ and 20 mL min^{-1} nitrogen flux. The infrared spectra were performed in a Pike Miracle spectrometer and each spectrum was obtained with a resolution of 4 cm^{-1} (64 scans). The inductively coupled plasma optical emission spectrometry (ICP-OES) analysis were conducted on an ICP-OES iCAP™ 7000 Series. The isolated reaction products were purified using a flash chromatography equipment PuriFlash XS 420® Interchim equipped with a UV diode array detector, a HP silica F0025 column ($0.15\text{ }\mu\text{m}$) was used as stationary phase and the appropriate eluent. Conversions and yields of hydroformylation/acetalization reactions were determined using Agilent 7820A chromatograph equipped with 30 m length and 0.32 mm inside diameter HP5 column and FID detector using nitrogen as carrier gas and isooctane as an external standard. Mass spectra were recorded on a GC-MS Agilent 7820A system equipped with a mass selective detector: an Agilent 7820 Gas Chromatograph system equipped with a HP5 MS column ($30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$) coupled to an Agilent 5975 MSD System Technologies (70 eV) using helium as carrier gas.

2. Experimental data

2.1. Characterization of catalyst CAT 1

FeBr₂{HC(pz)₃} (CAT1): FeBr₂{HC(pz)₃} was obtained from complexation of FeBr₂ and HC(pz)₃ (**2**) as purple powder (95%, 1.65 g).



¹H NMR (400 MHz, D₂O) δ(ppm): 9.22 (s, 1H), 8.56 (s, 3H), 7.83 (s, 3H), 7.09 (s 3H).

¹³C NMR (100 MHz, D₂O) δ(ppm): 159.8, 143.1, 114.6, 74.2.

HRMS (ESI): m/z = calcd for C₁₀H₁₀BrFeN₆⁺ [M-Br]⁺: 348.9494; found: 348.9489.

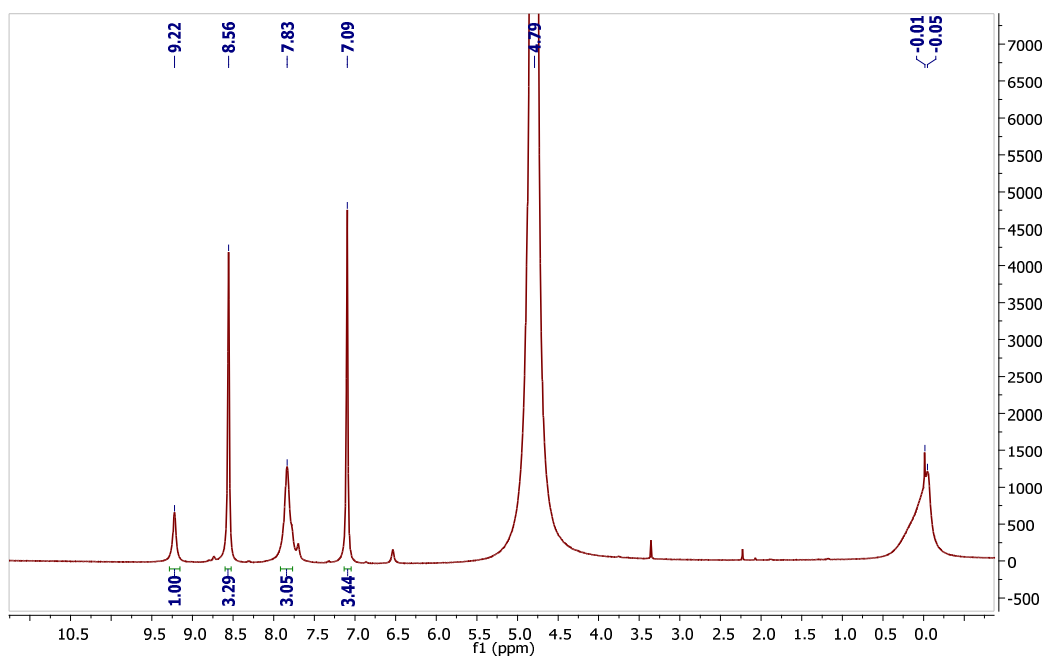


Figure S1. ¹H-NMR spectrum of **CAT1** in D₂O.

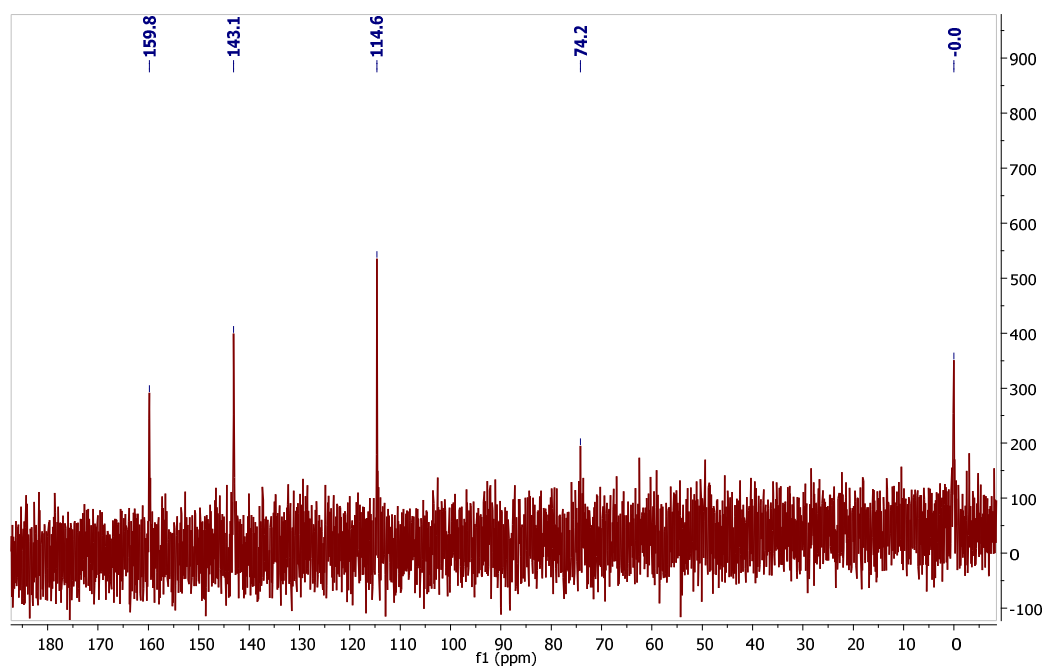


Figure S2. ¹³C-NMR spectrum of **CAT1** in D₂O.

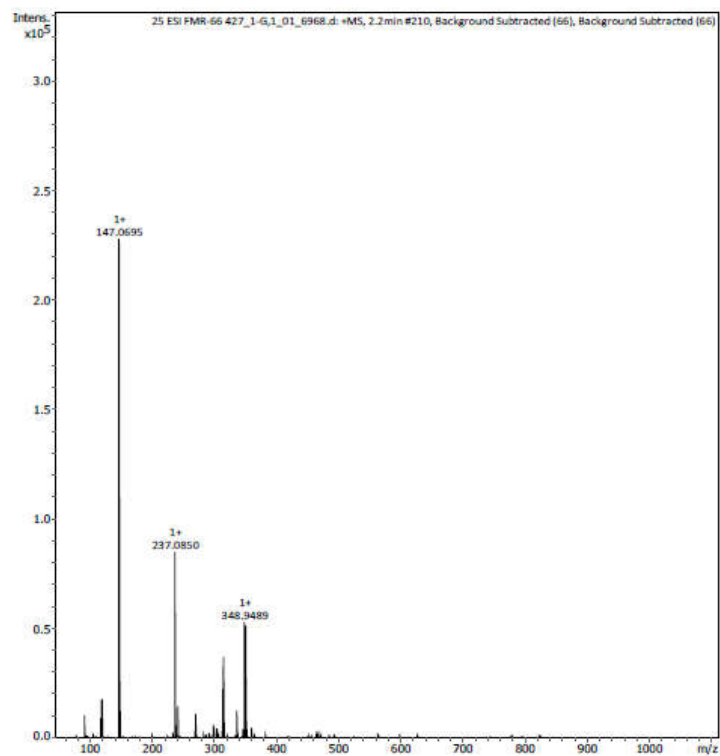


Figure S3. HRMS-ESI spectrum of **CAT1**.

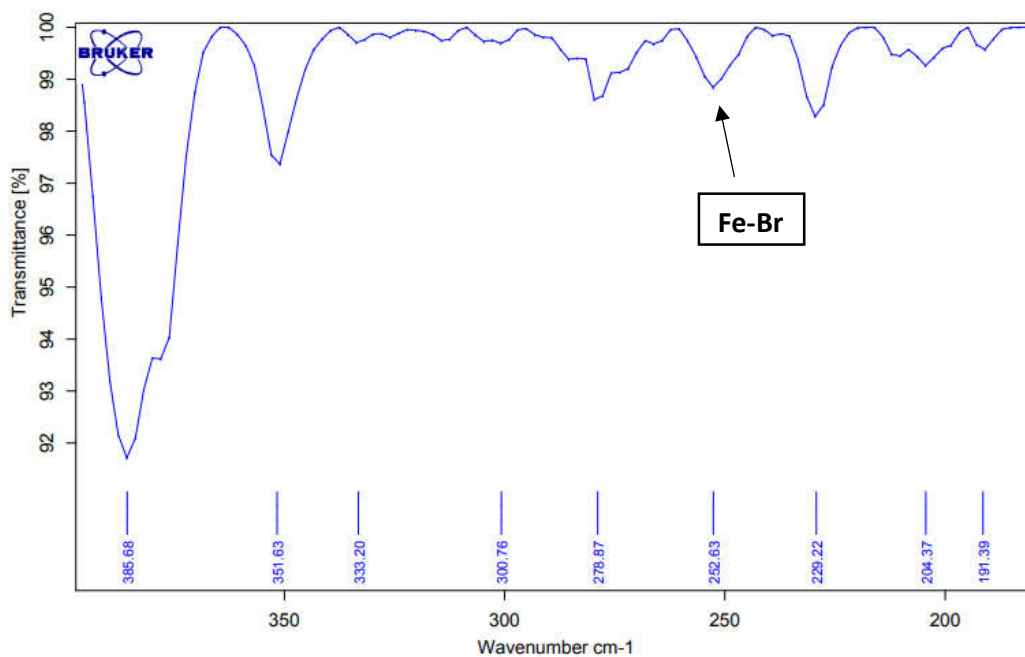


Figure S4. IR spectrum of **CAT1** (FAR region) were the 252.6 cm⁻¹ is attributed to Fe-Br.^[1]

2.2.Magnetic nanoparticles TEM images and size distribution

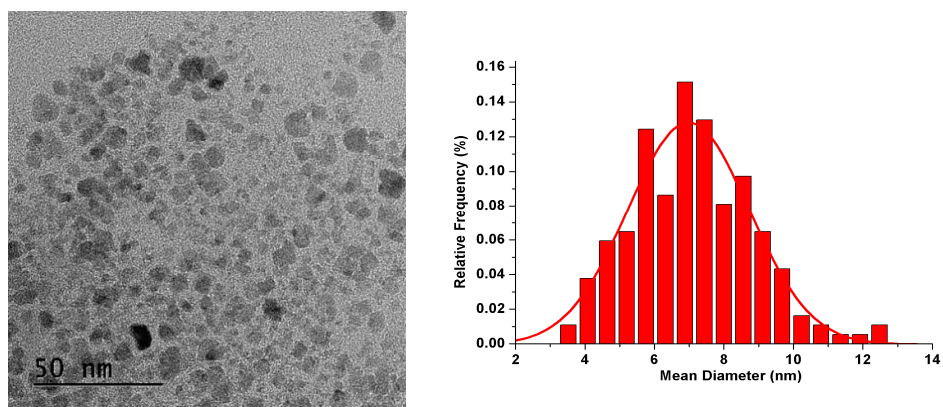


Figure S5. TEM image of MNP and their corresponding size distribution histogram (≈ 7 nm).

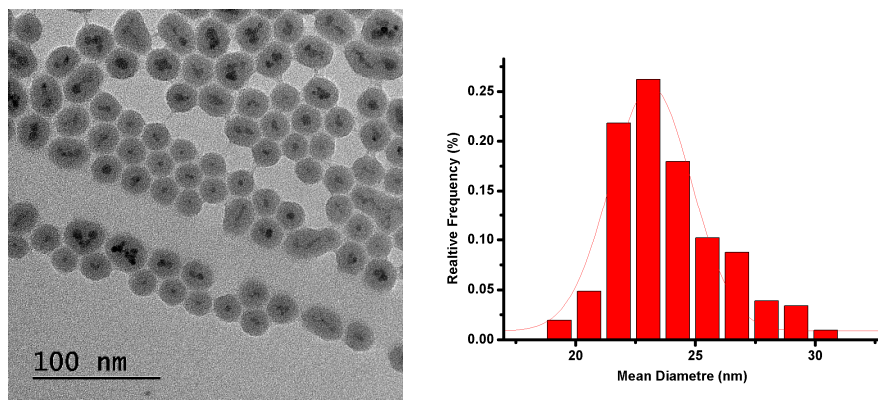


Figure S6. TEM image of MNP@SiO₂ and their corresponding size distribution histogram (≈ 23 nm).

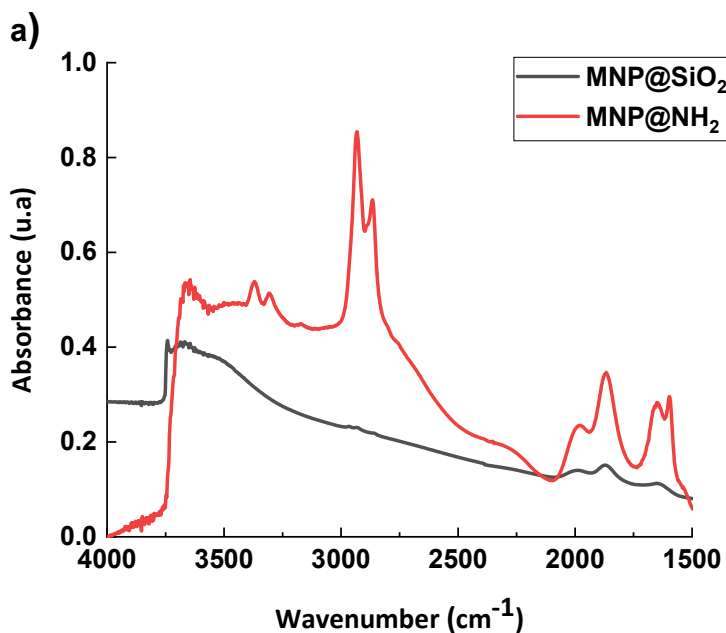


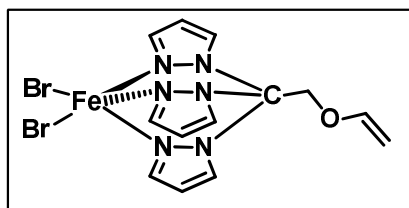
Figure S7. Comparative infrared spectra of MNP@SiO₂-NH₂ and MNP@SiO₂.

The FTIR spectra of MNP@SiO₂-NH₂ (red) and the MNP@SiO₂ (black) are presented in Figure S11. The FTIR spectra show the typical-OH silanol peak (3739 cm⁻¹), additional bands at 3369; 3309 and 1597 cm⁻¹ (attributed to antisymmetric, symmetric elongation, and deformation of the NH₂ group, respectively); 2935–2860 and 1450 cm⁻¹ (elongation and deformation of the CH₂ group, respectively) and 1410 cm⁻¹ (attributed to the deformation of the Si-CH₂ bond).

2.3. Characterization of catalyst CAT 6

[FeBr₂{allyl-HC(pz)₃}] (**4**)

Complex **3** was obtained from complexation of FeBr₂ with Tris-2,2,2-(1-pyrazoyl)ethoxyallyl (**3**) as orange powder (95%, 1.6 g).



HRMS (EI): m/z = calcd for C₁₄H₁₆BrFeN₆O⁺ [M-Br]⁺:
418,9918; found: 418,9911.

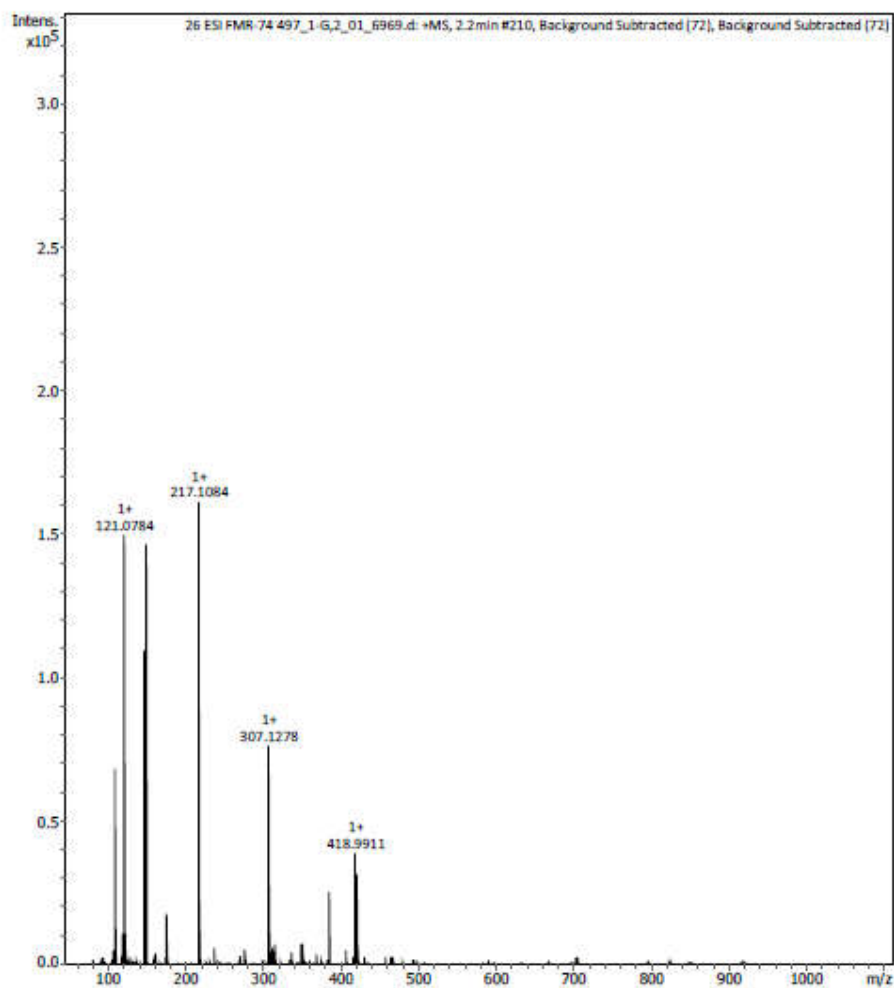


Figure S8. HRMS-ESI spectrum of compound **4**.

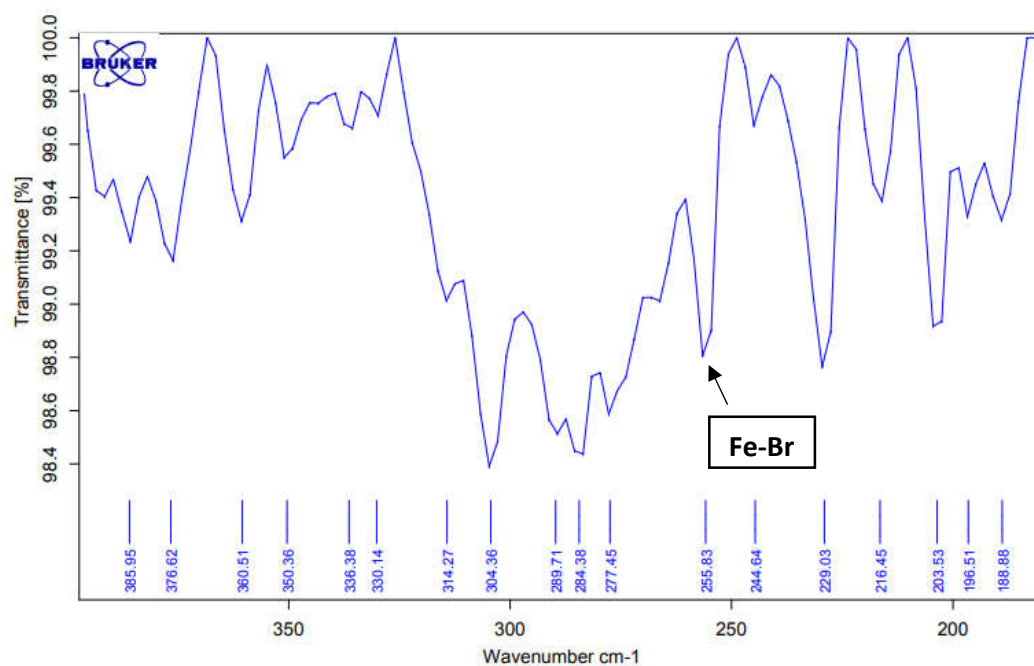
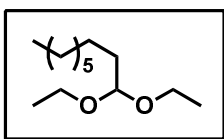


Figure S9. IR spectrum of complex **4** (FAR region).

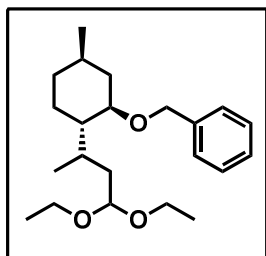
2.4. Catalysis products

1,1-Diethoxynonane (**7a**)



According to general procedure for the hydroformylation/acetalization of alkenes, (**7a**) was prepared from oct-1-ene and isolated as a colorless liquid in (70%, 360 mg) yield through normal phase silica flash chromatography using ethyl acetate/*n*-hexane as eluent. Data is in accordance with literature.^[2]

((1*R*,2*S*,5*R*)-2-(-4,4-diethoxybutan-2-yl)-5-methylcyclohexyl)oxy)methylbenzene (9a**)**



According to general procedure for the hydroformylation/acetalization of alkenes, (**9a**) was prepared from (-)-Isopulegol benzyl ether and isolated as a colorless liquid in (74%, 770 mg) yield through normal phase silica flash chromatography using ethyl acetate/*n*-hexane as eluent.

¹H NMR (400 MHz, CDCl₃) δ(ppm): 7.42-7.23 (*m*, 5H), 4.64 (*d*, *J* = 11.1 Hz, 1H), 4.56 (*dd*, *J* = 7.8, 3.9 Hz, 1H), 4.43 (*d*, *J* = 11.1 Hz, 1H), 3.63 (*dq*, *J* = 9.4, 7.1 Hz, 2H), 3.48 (*dq*, *J* = 9.3, 7.1 Hz, 2H), 3.25 (*dt*, *J* = 10.6, 4.1 Hz, 1H), 2.34-2.24 (*m*, 1H), 2.22-2.17 (*m*, 1H), 1.78-1.72 (*m*, 1H), 1.69-1.63 (*m*, 2H), 1.39-1.26 (*m*, 3H), 1.20 (*t*, *J* = 7.1 Hz, 3H), 1.12 (*t*, *J* = 7.1 Hz, 3H), 0.96 (*d*, *J* = 7.0 Hz 3H), 0.93 (*d*, *J* = 6.6 Hz 3H), overlap signals 1.06-0.81 (*m*, 3H)

¹³C NMR (100 MHz, (CD₃)₂CO) δ(ppm): 140.8, 129.0, 128.5, 128.0, 103.1, 79.2, 71.0, 61.6, 61.2, 50.0, 41.3, 36.7, 35.7, 32.3, 28.7, 25.9, 22.8, 18.6, 16.0, 15.9.

MS (EI): *m/z* = 347 [M]⁺, 319, 211, 194, 179, 165, 150, 103, 99, 91, 71, 55, 47, 28.

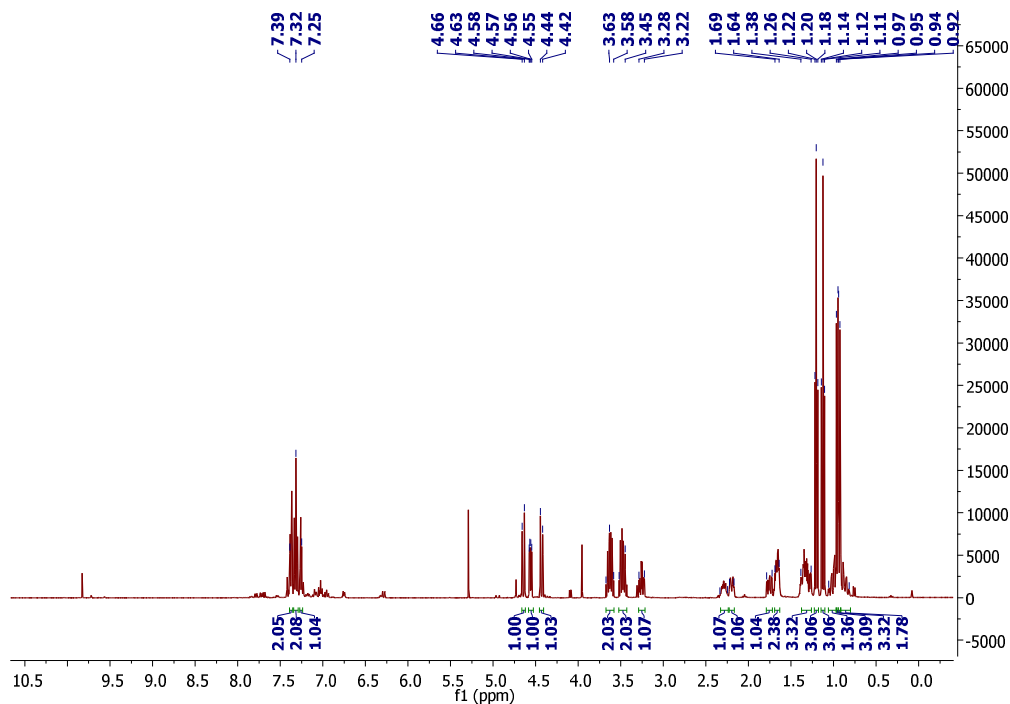


Figure S10. ¹H-NMR spectrum of compound **9a** in CDCl₃.

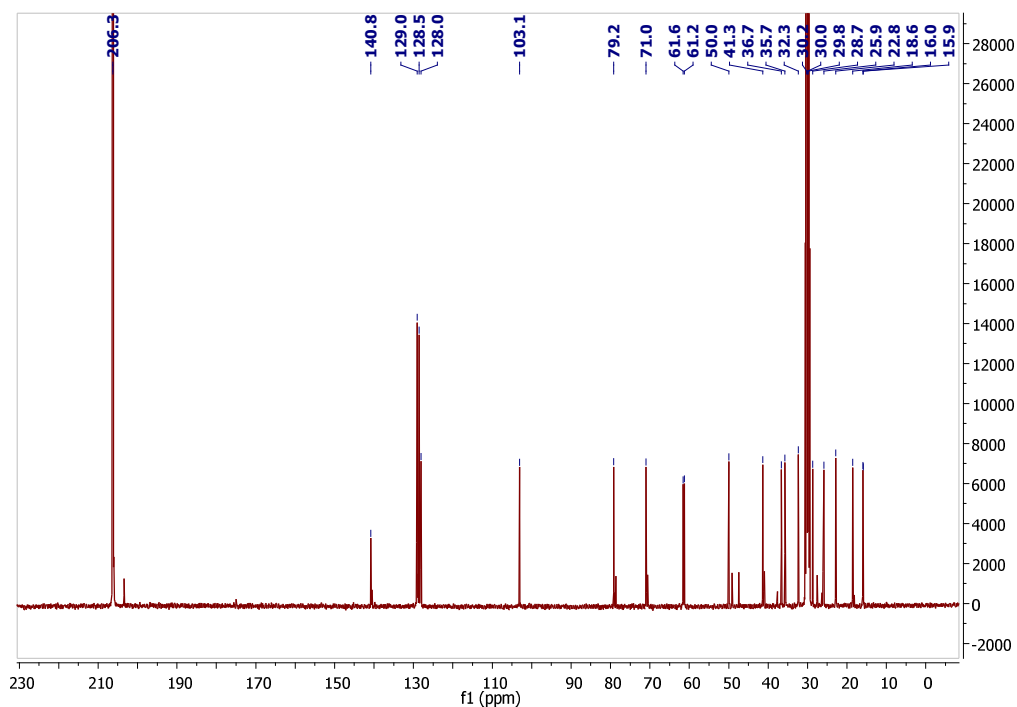
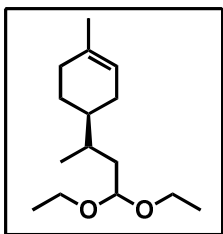


Figure S11. ^{13}C -NMR spectrum of compound **9a** in $(\text{CD}_3)_2\text{CO}$.

(S)-4-(4,4-diethoxybutan-2-yl)-1-methylcyclohex-1-ene (10a**)**



According to general procedure for the hydroformylation/acetalization of alkenes, (**10a**) was prepared from (+)-limonene and isolated as a colorless liquid in (40%, 230 mg) yield through normal phase silica flash chromatography using ethyl acetate/*n*-hexane as eluent. Data is in accordance with literature.^[3]

References

- [1] T. Birchall and M. F. Morris, *Can. J. Chem.* **1972**, *50*, 211-216.
- [2] O. Diebolt, C. Cruzeuil, C. Mueller, D. Vogt, *Adv. Synth. Catal.* **2012**, *354*, 670-677.
- [3] C. G. Vieira, J. G. da Silva, C. A. A. Penna, E. N. dos Santos, E. V. Gusevskaya, *Appl. Catal. A: Gen.* **2010**, *380*, 125-132