Electronic Supplementary Information

Gold nanoparticle-catalysed functionalization of carbon-hydrogen bonds by carbene transfer reactions

Jonathan Martínez-Laguna,[a] Andrés Mollar-Cuni,[b] David Ventura-Espinosa,[b] Santiago Martín,[c,d] Ana Caballero,[*a] José A. Mata[*b] and Pedro J. Pérez[*a]

[a]Laboratorio de Catálisis Homogénea, Unidad Asociada al CSIC CIQSO-Centro de Investigación en Química Sostenible and Departamento de Química. Universidad de Huelva, Campus de El Carmen s/n, 21007-Huelva, Spain.

[b]Institute of Advanced Materials (INAM), Centro de Innovación en Química Avanzada (ORFEO-CINCA). Universitat Jaume I, Avda. Sos Baynat s/n, 12006-Castellón, Spain.

[c]Instituto de Nanociencia y Materiales de Aragón (INMA), CSIC-Universidad de Zaragoza, Zaragoza 50009, Spain

[d]Departamento de Química Física, Universidad de Zaragoza, 50009, Zaragoza (Spain) and Laboratorio de Microscopias Avanzadas (LMA). Universidad de Zaragoza, Edificio I+D+i. 50018, Zaragoza, Spain

Table of Contents

1.. Characterization of catalysts 1, 2 and 3

High-resolution images of transmission electron microscopy (**HRTEM**) and high-angle annular dark-field (**HAADF-STEM**) images of the samples were obtained using a Jem-2100 LaB6 (JEOL) transmission electron microscope coupled with an INCA Energy TEM 200 (Oxford) energy dispersive X-Ray spectrometer (EDX) operating at 200 kV. Samples were prepared by drying a droplet of a MeOH dispersion on a carbon-coated copper grid. X-ray photoelectron spectra (**XPS**) were acquired on a Kratos AXIS ultra DLD spectrometer with a monochromatic Al Kα X-ray source (1486.6 eV) using a pass energy of 20 eV. To provide a precise energy calibration, the XPS binding energies were referenced to the C1s peak at 284.6 eV.
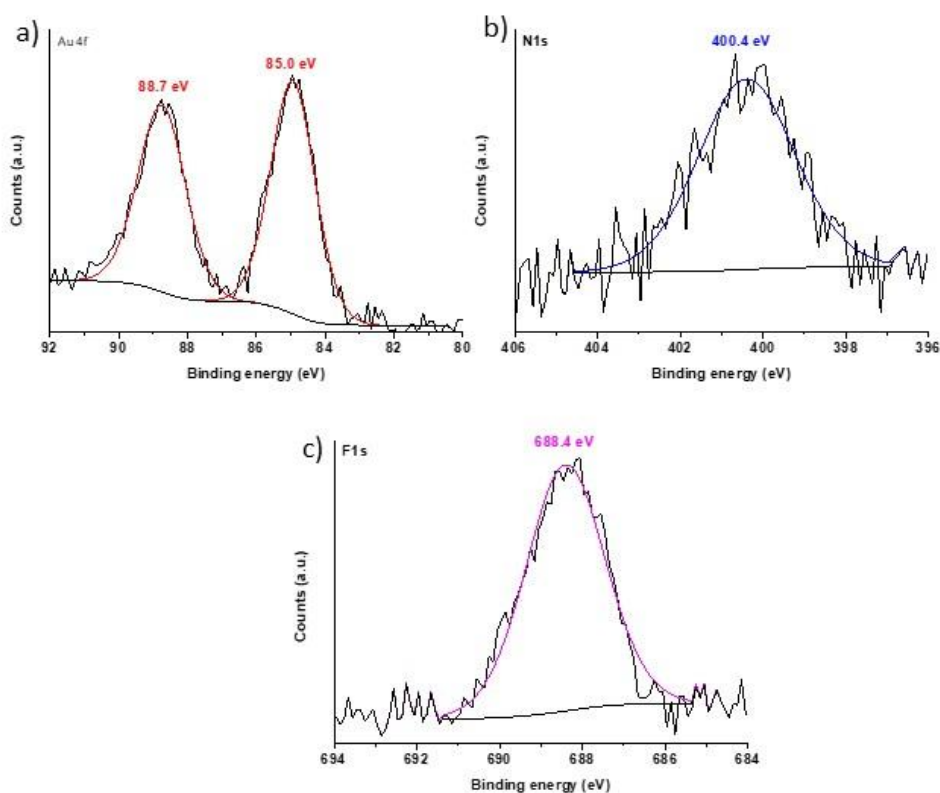

Figure S1. XPS spectra of catalyst **1** showing the high-resolution core-level peaks a) Au4f, b) N1s and c) F1s.[1]
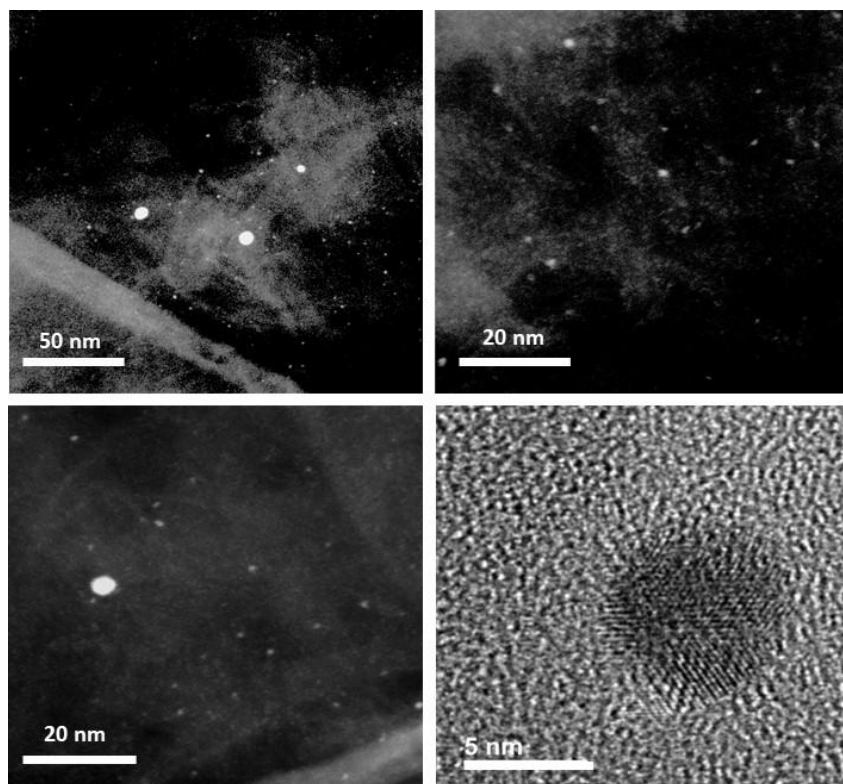
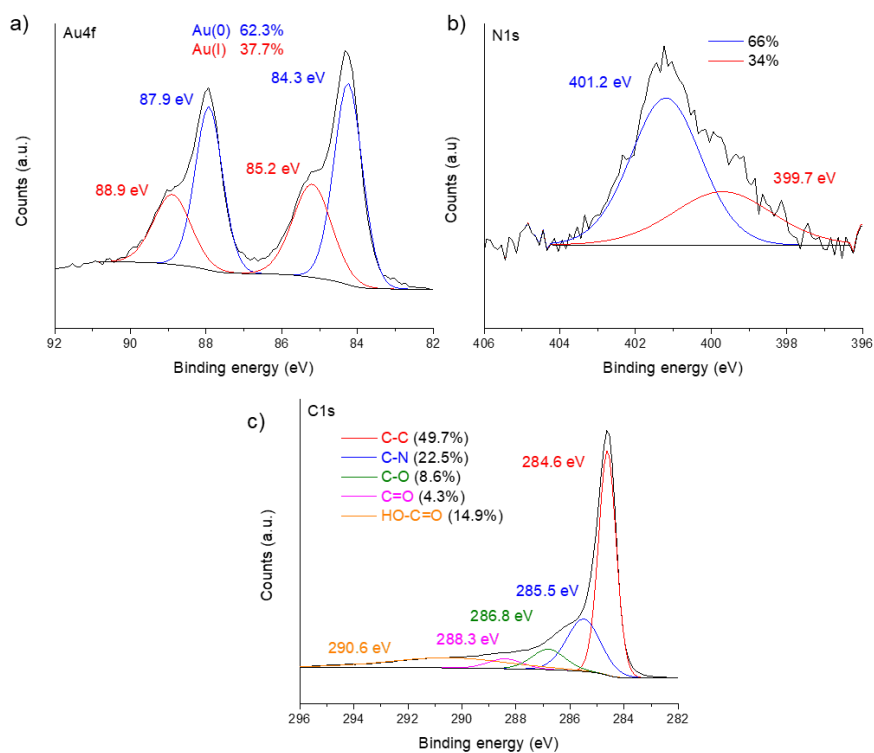Figure S2. Catalysts **1** STEM images at 50 and 20 nm and HRTEM at 5 nm

Figure S3. XPS spectra of catalyst **2** showing the high-resolution core-level peaks a) Au4f, b) N1s and c) C1s.
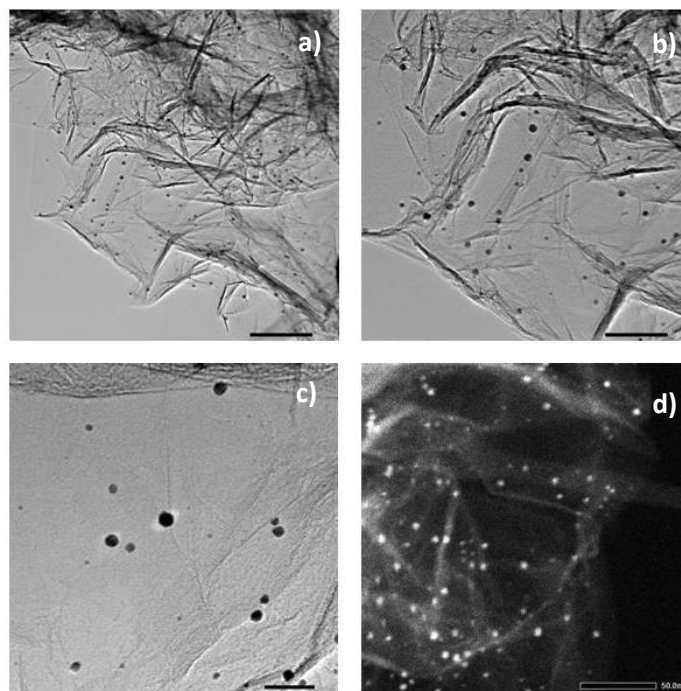
Figure S4. TEM images of **2** at different magnifications a) 100 nm, b) 50 nm, c) 20 nm and d) STEM image at 50 nm.
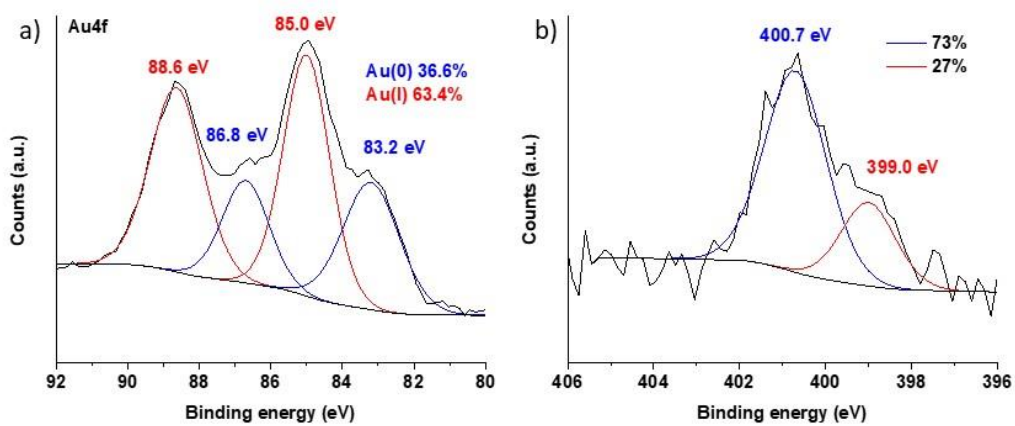

Figure S5. XPS spectra of catalyst **3** showing the high-resolution core-level peaks a) Au4f and b) N1s.
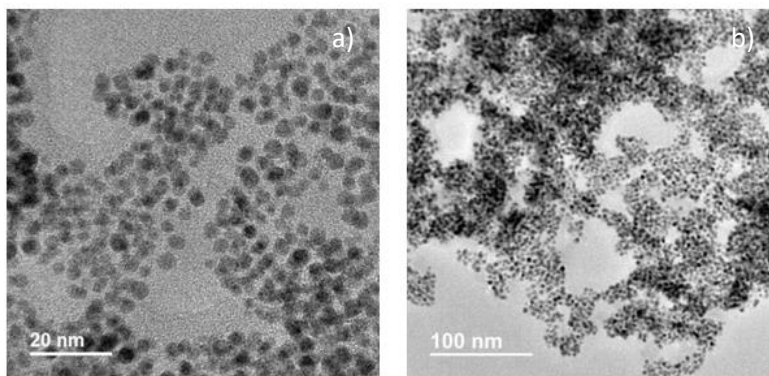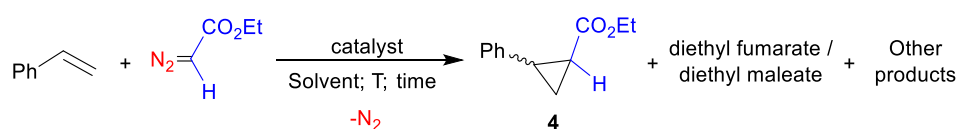
Figure S6. TEM images of **3** at different magnifications a) 20 nm and b) 100 nm.

2. Cyclopropanation of styrene with EDA

In a light-protected 50 mL J-Young ampoule charged with 10 mL of solvent, the corresponding amount of catalyst was added. For graphene-supported catalysts, the mixture was previously sonicated for 10 min. Then, 115 µL of styrene (1.0 mmol, 104 mg) were added and the mixture was stirred for 5 min. Afterwards, 12.5 µL of EDA (0.1 mmol) were added. The resulting mixture was stirred for the desired time and temperature. When the reaction was completed, the solid catalyst was filtered off and washed with 3x5 mL of DCM. The filtrates were collected, and volatiles were removed under vacuum resulting in a yellowish residue. Yields were determined by ^{1}H NMR analysis employing 1,2,3-trimetoxybenzene as internal standard and identified by its comparison with literature precedents.[2] The best results have been obtained employing DCM (10 mL) as solvent, 1.0 mmol of styrene and 0.1 mmol of EDA at 80 °C for 24 h.

Table S1. Results obtained for the cyclopropanation of styrene with EDA under different reaction conditions.

Entry	Catalyst	Solvent	Temperature	Time	EDA conv. (%)	4[g]	Diethyl fumarate / Diethyl maleate[h]	Other products
							Yields (%)[f]	
1[a]	**1**	DCM	RT	24	0	-	-	-
2[a]	**1**	DCM	80	5	70	46	10.5	10.5
3[a]	**1**	**DCM**	**80**	**24**	**100**	**70[i]**	**16[j]**	**14[k]**
4[a]	**1**	Styrene	RT	24	15	n.d.	n.d.	15
5[a,b]	**1**	Styrene	80	24	Undetermined		Undetermined	
6[c]	**2**	DCM	RT	24	0	-	-	-
7[c]	**2**	DCM	80	24	20	9	n.d.	11
8[d]	**3**	DCM	RT	24	0	-	-	-
9[d]	**3**	DCM	80	24	20	9	n.d.	11
10[e]	rGO	DCM	RT	24	0	-	-	-
11[e]	rGO	DCM	80	24	20	10	-	10
12	none	DCM	RT	24	0	-	-	-
13	none	DCM	80	24	16	9	-	7

[a]25 mg of the graphenic material **1**, corresponding to 4 x 10^{-5} mmol Au (0.04 mol% referred to EDA), were employed. [b]Polymers resulting from styrene polymerization were observed as major products. [c]75 mg of the graphenic material **2**, corresponding to 4 x 10^{-5} mmol Au (0.04 mol% referred to EDA), were employed. [d]0.5 mg of Au NPs **3**, corresponding to 4 x 10^{-5} mmol Au (0.04 mol% referred to EDA), were employed. [e]25 mg of pure rGO were employed. [f]Yields are referred to initial EDA and were determined by ^{1}H NMR employing 1,2,3-trimethoxybenzene as internal standard. [g]Given yields correspond to the sum of both isomers. [h]Given yields correspond to the sum of both isomers. [i]A 1.4:1 ratio was observed for trans/cis isomers. [j]A 1:1 ratio was observed for both isomers. [k]Other products include low-mass EDA oligomers (major) as well as decomposition species.

3. Reactions of cyclohexane and benzene with EDA catalysed by 1
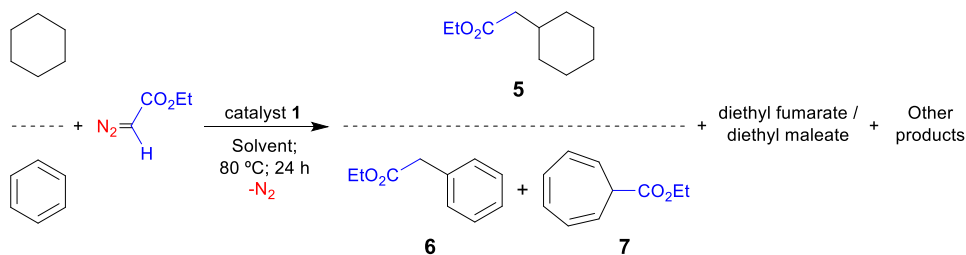
Following the previous procedure, 10 mL of cyclohexane or benzene and 50 mg of catalyst **1** (8x10^{-5} mmol Au; 0.08 mol% referred to EDA) were reacted with 12.5 µL of EDA (0.1 mmol). The

resulting mixture was heated for 24 hours at 80 °C. Yields were determined by GC (with an external standard for **5**) or NMR analysis (for **5**-**7**) employing 1,2,3-trimetoxybenzene as internal standard, and identified by comparison with literature data.[3]

Table S2. Results obtained for the reaction of cyclohexane or benzene with EDA catalysed by **1** under optimized reaction conditions.

Entry	Catalyst	Solvent	EDA conv. (%)	Yields (%)[a]				
				5	6	7	Ethyl fumarate / Ethyl maleate[b]	Other products[c]
1	**1**	Cyclohexane	100	20	-	-	27.2[d]	52.8
2	**1**	Benzene	100	-	6	17	18.7[e]	58.9

[a]Yields are referred to initial EDA and were determined by GC (external standard quantitation for **5**) and NMR analysis (for **5**-**7**) employing 1,2,3-trimetoxybenzene as internal standard. [b]Given yields correspond to the sum of both isomers. [c]Other products include low-mass EDA oligomers (major) as well as decomposition species. [d] A 1.3:1 ratio was observed for cis/trans isomers. [e]A 1.5:1 ratio was observed for cis/trans isomers.

4. Recycling studies with 1

Following the previous procedure for cyclohexane, when the reaction was finished, the mixture was allowed to decant, and an aliquot was taken for its analysis by GC. Then, the liquid fraction was filtered off and the resulting solid catalyst was washed with DCM (3x5 mL) and cyclohexane (3x5 mL). Fresh cyclohexane and EDA (10 mL and 12.5 µL, respectively) were added for the second run. The procedure was repeated up to six cycles.
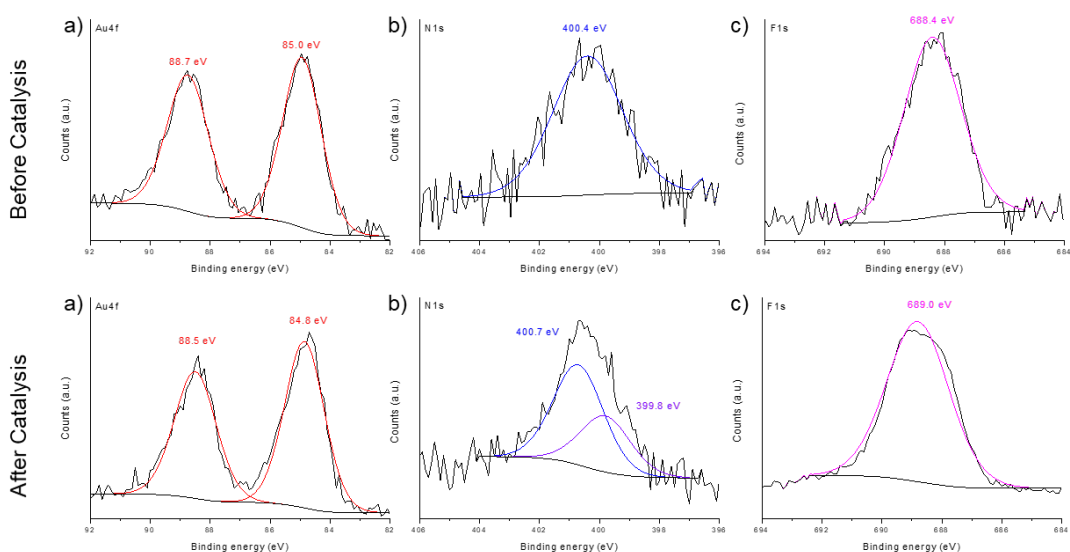

Figure S7. Comparative XPS spectra of catalyst **1** before and after 3 runs showing the high-resolution core-level peaks a) Au4f, b) N1s and c) F1s.
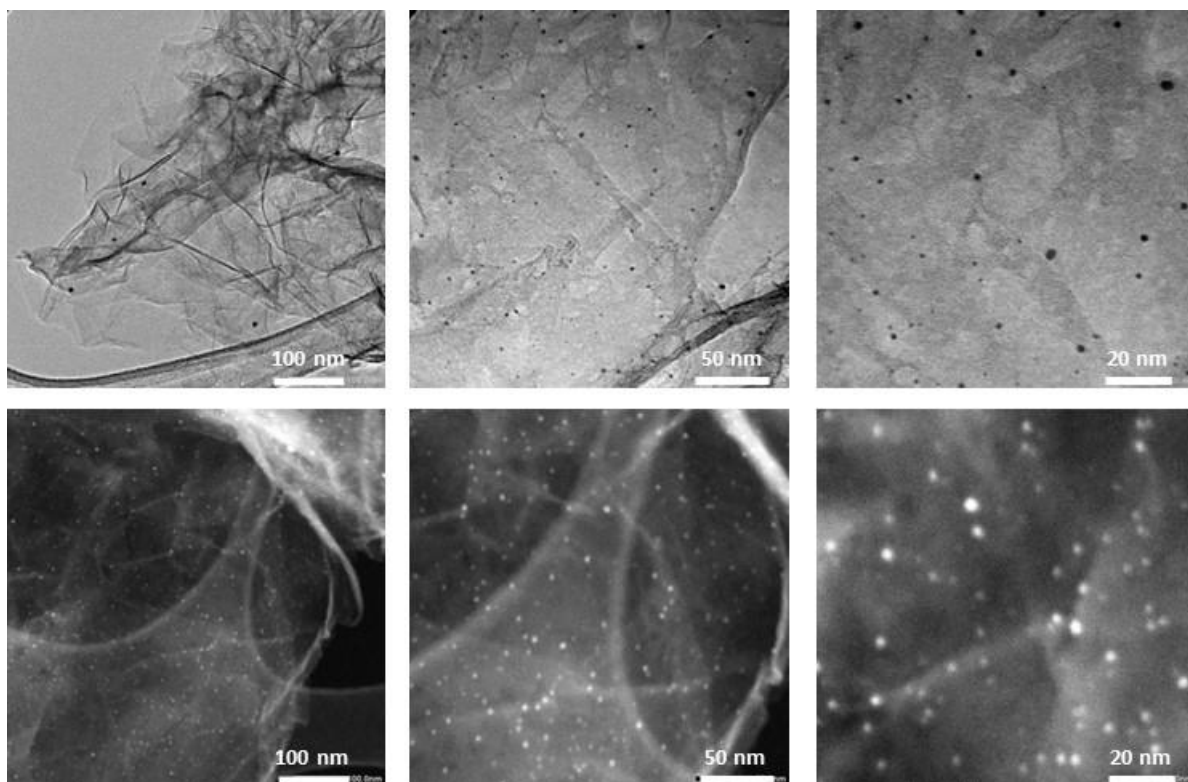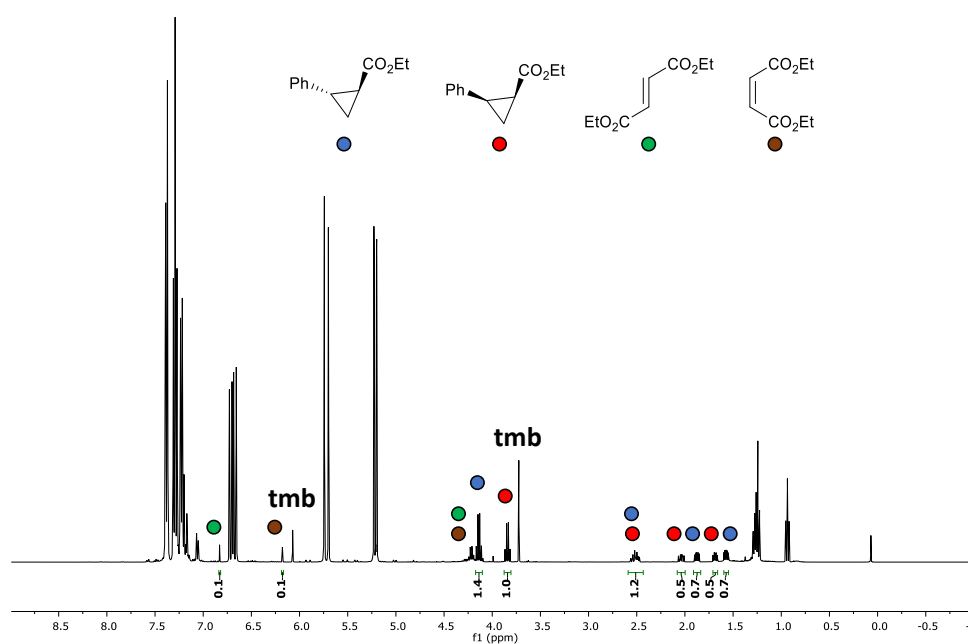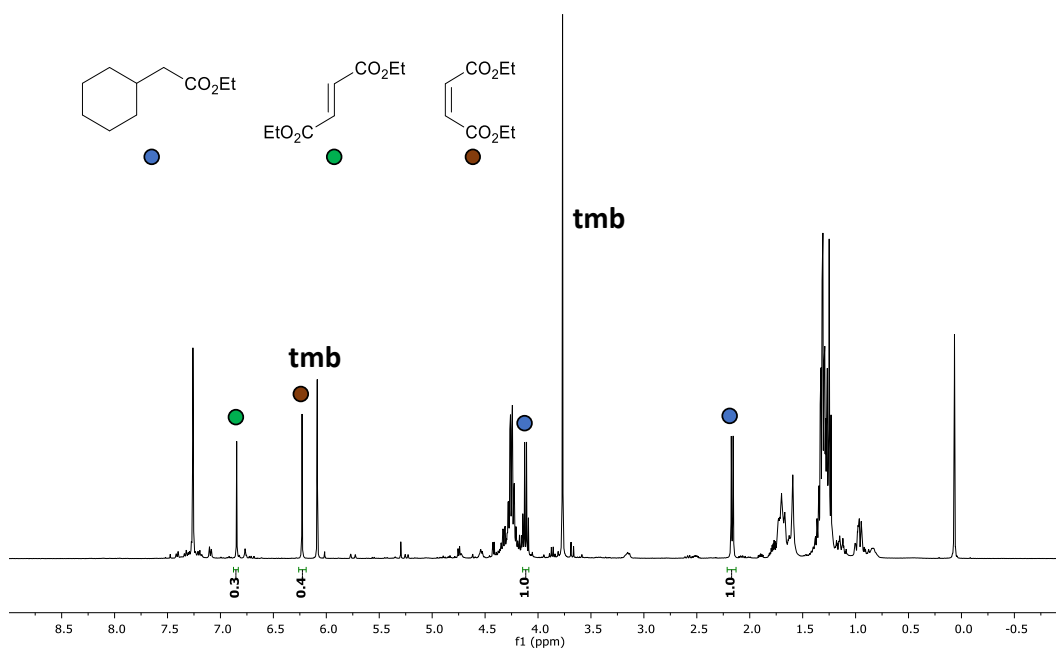
Figure S8. HRTEM (top) and STEM (down) images of catalyst **1** after 3 catalytic runs
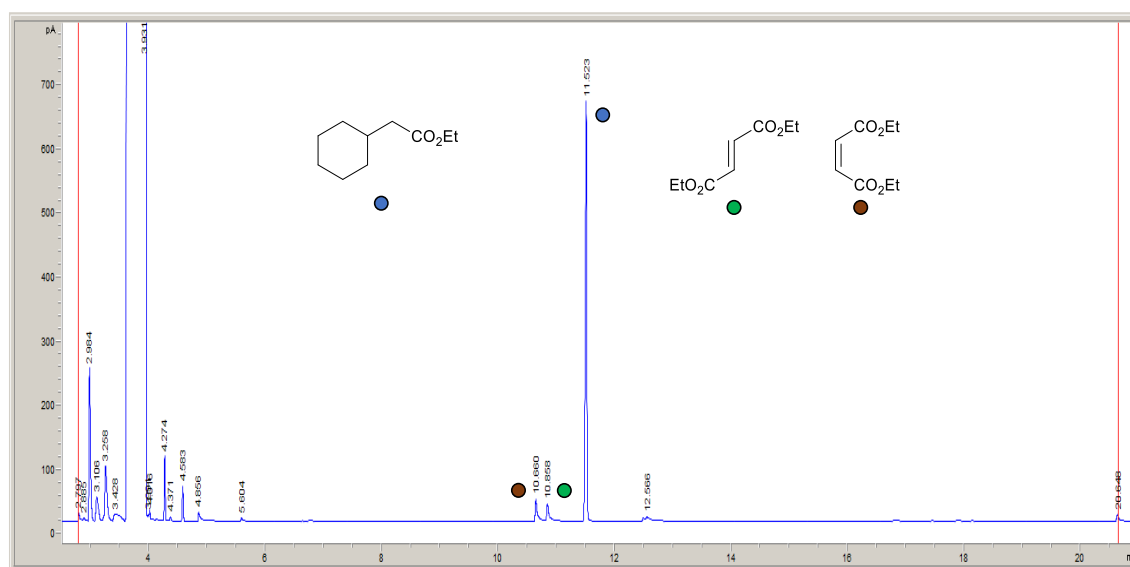
5. ¹H NMR spectra and GC traces of the reaction crudes

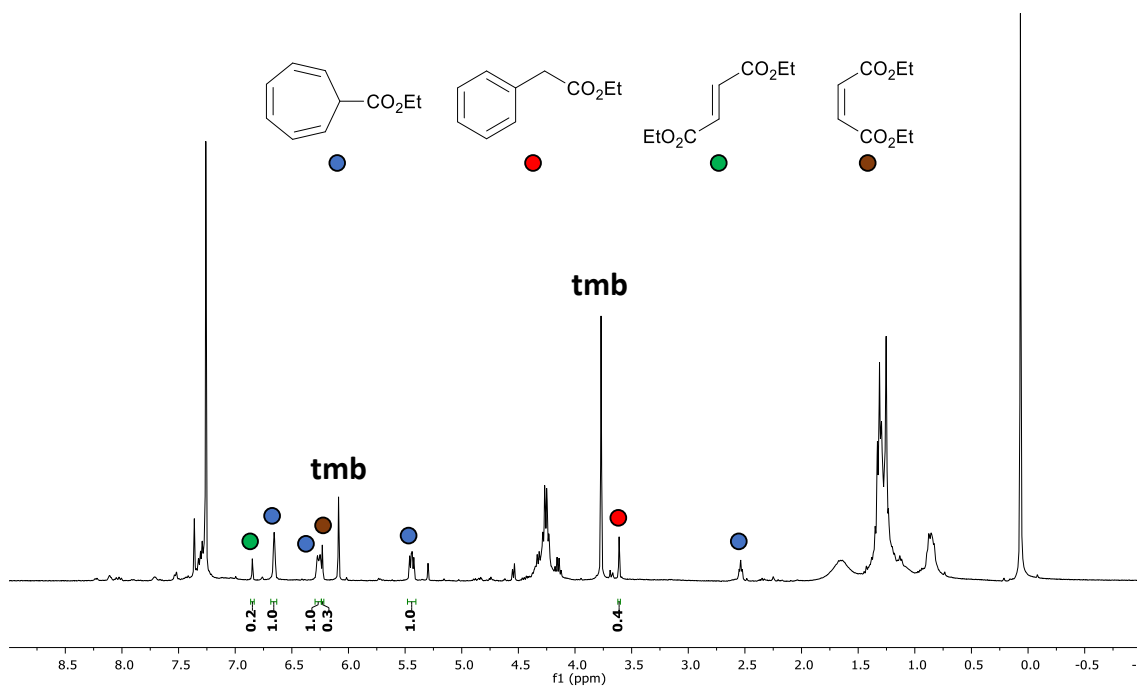¹H NMR spectrum of the cyclopropanation of styrene with EDA using catalyst **1**

^{1}H NMR spectrum of the reaction of cyclohexane with EDA using catalyst **1**.

GC trace of the reaction of cyclohexane with EDA using catalyst **1.**

^{1}H NMR spectrum of the reaction of benzene with EDA using catalyst **1**

6. References

[1]   D. Ventura-Espinosa, S. Martín and J. A. Mata, *J. Catal.*, 2019, **375**, 419.

[2]   P. J. Pérez, M. Brookhart and J. L. Templeton, *Organometallics*, 1993, **12**, 261 and references cited therein.

[3]   (a) M. M. Díaz-Requejo, T. R. Belderrain, M. C. Nicasio, S. Trofimenko and P. J. Pérez, *J. Am. Chem. Soc.*, 2002, **124**, 896 and references cited therein; (b) M. E. Morilla, M. M. Díaz-Requejo, T. R. Belderrain, M. C. Nicasio, S. Trofimenko and P. J. Pérez, *Organometallics*, 2004, **23**, 293 and references cited therein; (c) M. R. Fructos, T. R. Belderrain, P. de Fremont, N. M. Scott, S. P. Nolan, M. M. Díaz-Requejo and P. J. Pérez, *Angew. Chem. Int. Ed.*, 2005, **44**, 5284 and references cited therein.