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Electronic Supplementary Information (ESI)

Intimate ruthenium–platinum nanoalloys supported on carbon catalyze the hydrogenation and one–pot hydrogenation–coupling reaction of oxidized amino derivatives

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Experimental Procedures

General

Reinforced glass reactors were dried in an oven at 175 ^{0}C before use and the ducts of the microrreactor were cleaned with hexane. Reagents and solvents were obtained from commercial sources and were used without further purification otherwise indicated. All the products obtained were characterized by gas chromatography/mass spectrometry (GC–MS) and compared with authentic samples. Gas chromatography (GC) analyses were performed in an instrument equipped with a 25 m capillary column of 5% phenylmethylsilicone, and *n*-dodecane was used as an external standard. GC–MS analyses were performed on a spectrometer equipped with the same column as the GC and operated under the same conditions.

The metal content of the solids was determined by the inductively coupled plasma-atomic emission spectroscopy (ICP–AES) by disaggregation of the solid in aqueous acid mixture and filtration, or after extraction of the filtrates in 5 ml of freshly prepared aqua regia. X–Ray photoelectron spectra (XPS) of the solids were recorded with a SPECS spectrometer equipped with a Phoibos 150MCD multichannel analyzer using MgKα (1253.6 eV) irradiation. The spectra were recorded at -175 ºC and with an X–ray power of 50 mW in order to avoid photoreduction of the Ru and Pt species. The residual pressure in the analytical chamber was maintained below 10^{-9} mbar during data acquisition. The binding energies were corrected for surface charging by referencing them to the energy of C1s peak of adventitious carbon set at 284.5 eV. The samples were prepared by dropping a solid water suspension onto a molybdenum plate followed by air drying. The field–emission scanning electron microscopy (FESEM) images of the RuPt-C catalysts were obtained in a ZEISS Ultra 55 SEM. High resolution transmission electron microscopy (HR–TEM) measurements were performed in a 200 KeV Jeol JEM–2100 microscope by impregnating a copper–carbon filmed grid with a drop of the corresponding solid after dispersing in dichloromethane and leaving evaporation for at least 5 hours. HR HAADF-STEM imaging was performed on a double-aberration-corrected, monochromated, FEI Titan3 Themis 60–300 microscope working at 300 kV. To limit the damage by the electron beam, a fast image-recording protocol was used with a beam current of 100 pA. The microscope was also used to perform chemical mapping using the high-efficiency SuperX G2 detection system equipped in the microscope, which integrates four windowless detectors surrounding the sample and high-performance signal-processing hardware. Temperature–programmed reduction (TPR) experiments were performed between -100 and 600 ºC under a 10% H_2/Ar stream at 50 ml·min^{-1}, after previous oxidation of the sample under air. X–Ray diffraction spectra of the different catalysts were recorded in a CubiX PRO (PAN Analytical) spectrometer, with a Cu K(α) radiation source, 1.5406 Å wavelength.

Synthesis of the catalysts.

The corresponding amounts of H_2PtCl_4 and $RuCl_3$ were dissolved in water and activated charcoal was impregnated with this solution. The order of addition is catalytically irrelevant, since characterization and catalytic activity remain consistently similar. The wet solid was dried in a muffle at 100 °C for 18 h, and then hydrogenated with an atmosphere of 10% H_2 in N_2 at 360 °C (10 °C/min slope) for 1 h.

Reaction procedures.

*Typical reaction procedure: hydrogenation reaction of nitrobenzene **21**.* The corresponding amount of solid catalyst and hexane (0.5 mL) were placed into the reactor (2 mL capacity) equipped with a magnetic stirrer. **21** (11 µL, 0.1 mmol) was added, and after the micro–reactor was sealed, air was purged by flushing out 4 times with hydrogen and then pressurized with ~8–10 bar of H_2 (~10 eq.). The resulting mixture was magnetically stirred overnight in static pressure at 60 ºC. During the experiment, H_2 pressure decreases as reaction evolves. The mixture composition was determined by means of GC and GC–MS, once the catalyst particles were removed from the solution by filtration and *n*–dodecane (11 µl, 0.05 mmol) was added.

Reusability of the solid catalyst and hot filtration. RuPt–C (5 mol%), diethyl ether and oxime **25** (0.2 M solution) were placed into the reactor (2 mL capacity) equipped with a magnetic stirrer. The micro–reactor was sealed, air was purged by flushing out 4 times with hydrogen and then pressurized with ~8-10 bar of H_2. The resulting mixture was magnetically stirred overnight in static pressure at 60 ºC. After 18 h, the mixture composition was determined by means of GC and GC–MS, once the catalyst particles were removed from the solution by filtration and *n*–dodecane (11 µl, 0.05 mmol) was added. For the hot filtration test, two reactions were run in parallel and, at 30 min reaction time (18% yield), one of the reaction mixtures was taken out with a syringe and added to a new micro–reactor at the same temperature (60 ºC) and under H_2 atmosphere, after passing through a PTFE filter. Both reactions were followed by GC and GC–MS.

Kinetic experiments for hydrogenation reactions. Solid catalyst, reagent (0.24 mmol) and solvent (1.2 ml) were introduced into a 4 ml glass vial. The vial was coupled to a pressure gauge and loaded with hydrogen by means of a capillary, at a total pressure of 10 bars, keeping the reaction in constant magnetic agitation for 24 h at room temperature. To start the kinetic study, the reaction was considered initiated at the time of adding the hydrogen gas, taking this moment as a zero point. Once the reaction began, samples were taken at approximately 10, 30 and 60 minutes and several points at longer times. The total volume extracted at the end of the kinetics should not exceed 20% of the initial volume. Each aliquot was diluted in dichloromethane (DCM) to be analyzed by gas chromatography after addition of *n*–dodecane (11 µl, 0.05 mmol) as an external standard.

Figures.

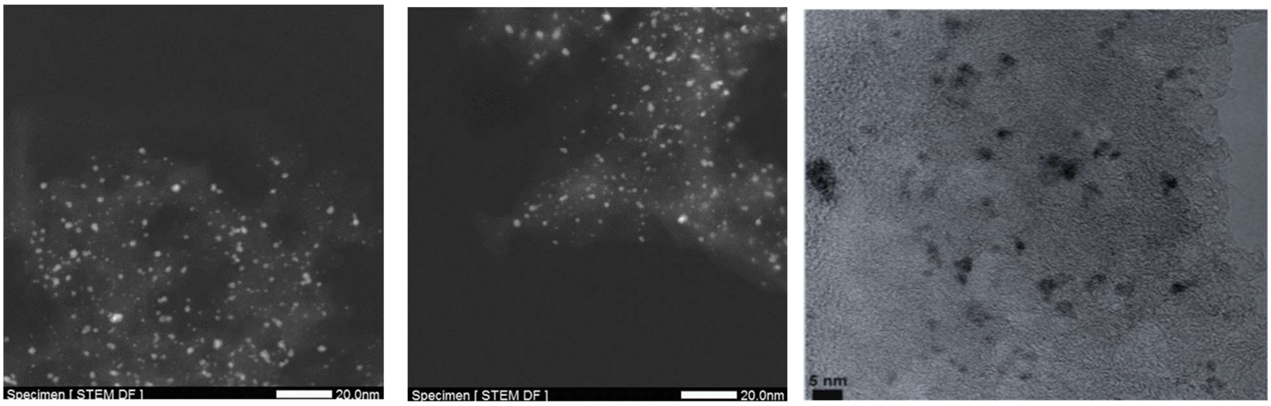


Figure S1 Representative STEM DF images of Pt–C (left and middle) and HR–TEM image of Ru–C (right).

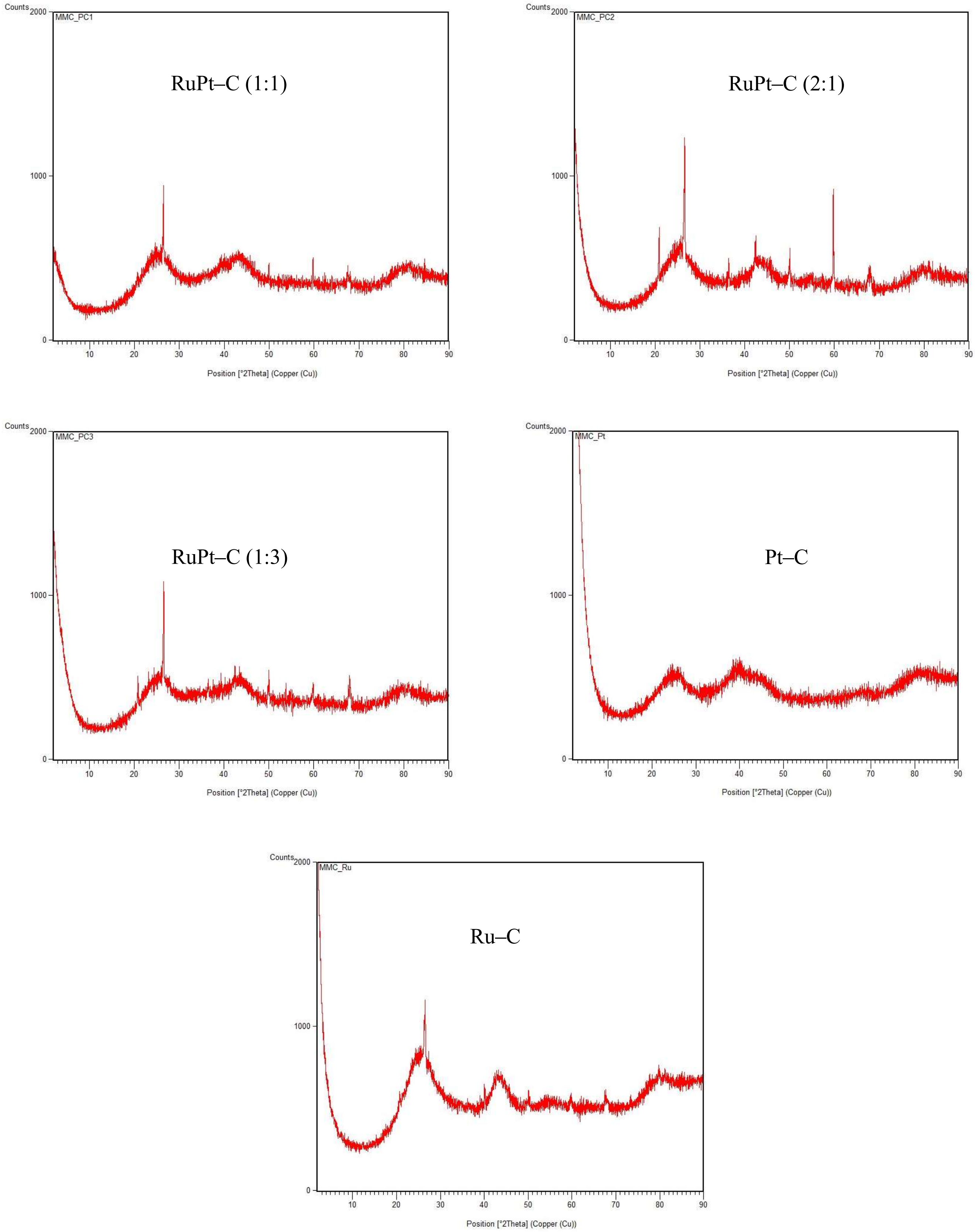


Figure S2 Powder XRD patterns of the RuPt–C, Ru–C and Pt–C catalysts. The Scherrer equation was applied on the peaks featuring around 2θ= 43 degrees (i.e. crystallographic plane [111] for Pt).

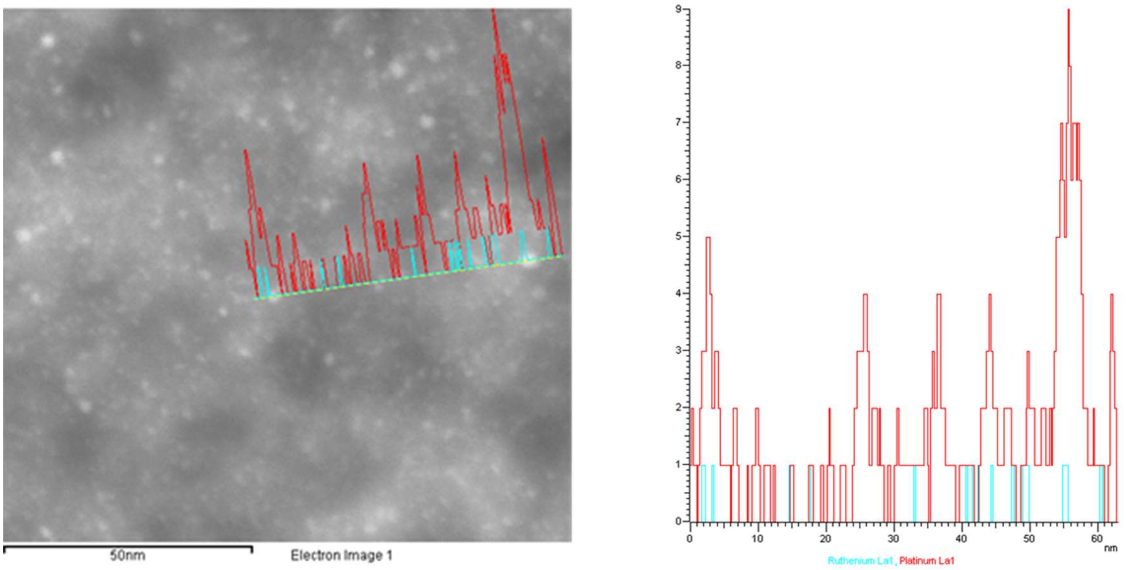


Figure S3 Linear (50 nm) EDX sweeping of the RuPt–C (1:3) sample in a representative FESEM image.

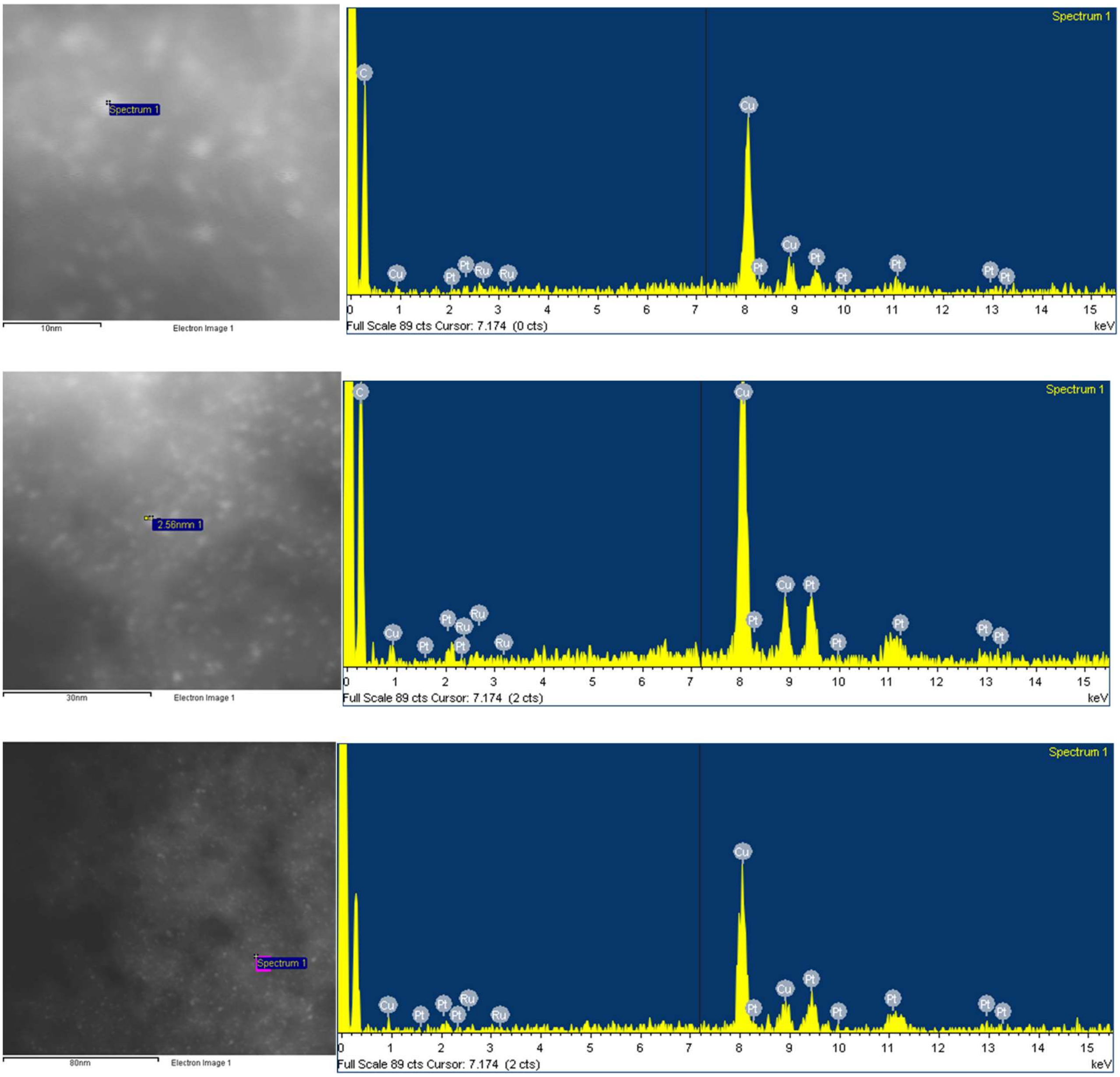
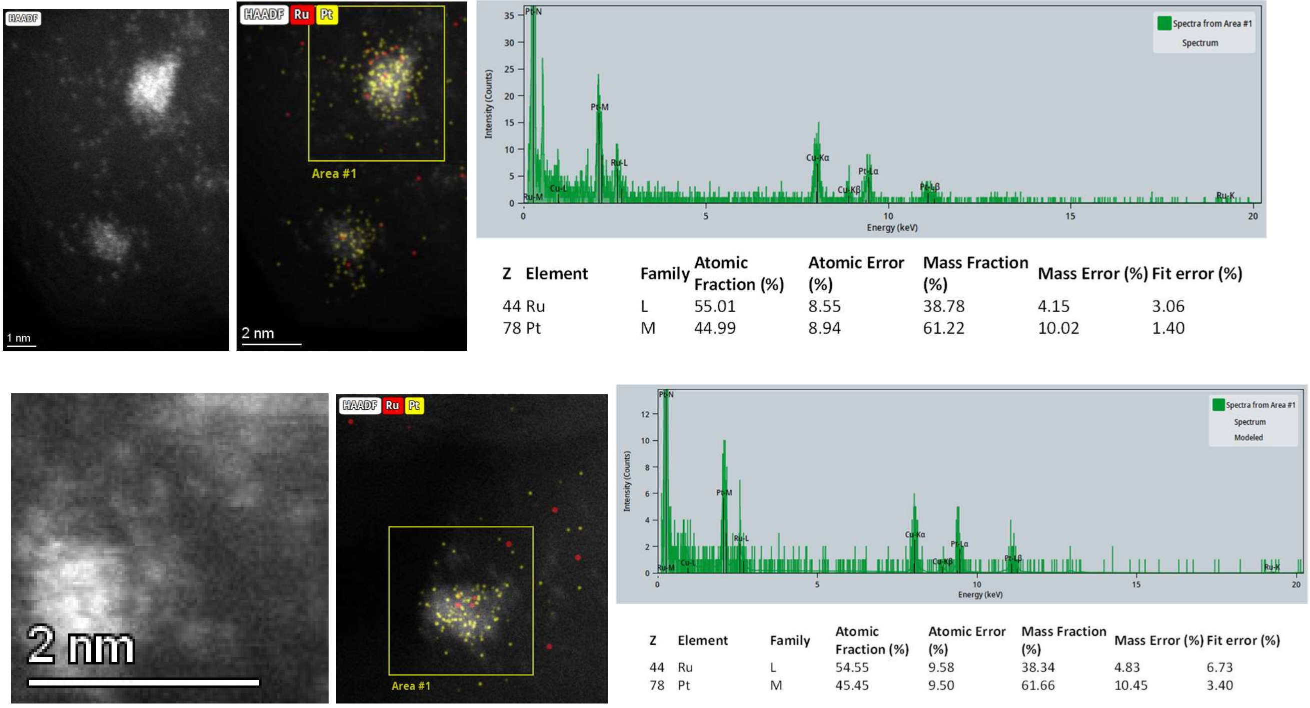


Figure S4 EDX spectra for three different discrete nanoparticles of RuPt–C (1:1) in FESEM, at decreasing magnifications (from top to bottom, 10 to 80 nm bars). Quantification is ~1:1 Ru:Pt in the three cases.



Z	Element	Family	Atomic Fraction (%)	Atomic Error (%)	Mass Fraction (%)	Mass Error (%)	Fit error (%)
44	Ru	L	55.01	8.55	38.78	4.15	3.06
78	Pt	M	44.99	8.94	61.22	10.02	1.40

Z	Element	Family	Atomic Fraction (%)	Atomic Error (%)	Mass Fraction (%)	Mass Error (%)	Fit error (%)
44	Ru	L	54.55	9.58	38.34	4.83	6.73
78	Pt	M	45.45	9.50	61.66	10.45	3.40

Figure S5 High-angle annular dark field scanning transmission electron microscopy (HAADF–STEM) with EDX spectra of the squared areas for two different individual nanoparticles of RuPt–C (1:1). Quantification is ~1:1 Ru:Pt in both cases.

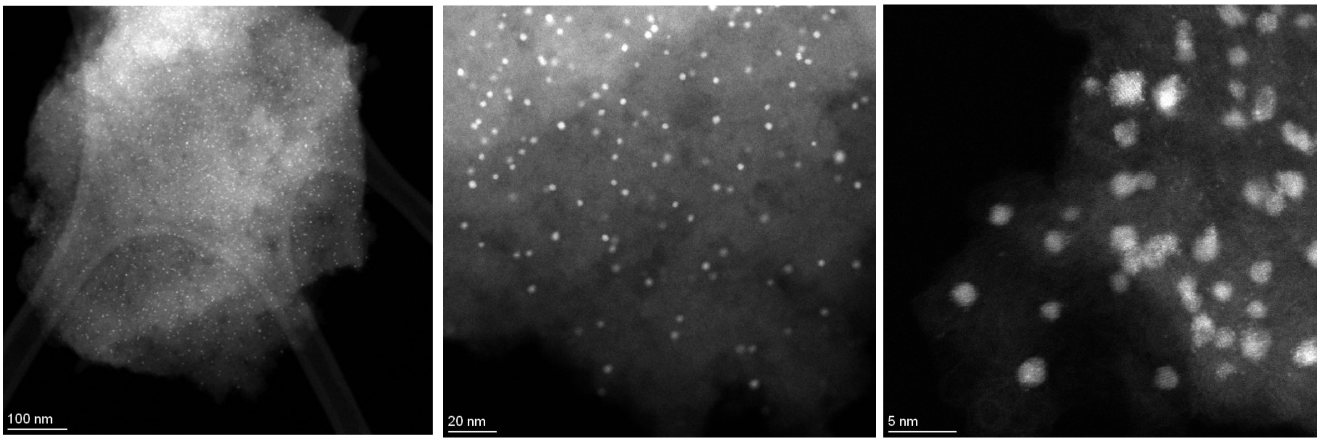


Figure S6 HAADF–STEM images at increasing magnifications (from left to right) of the RuPt–C (1:1) material.

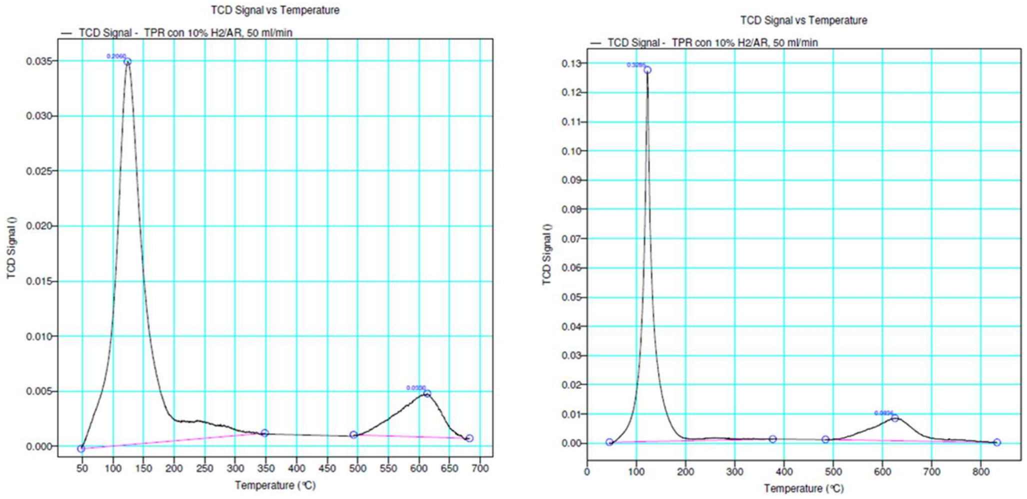


Figure S7 TPR spectra of 2:1 (left) and 1:3 (right) RuPt–C, after previous oxidation of the samples.

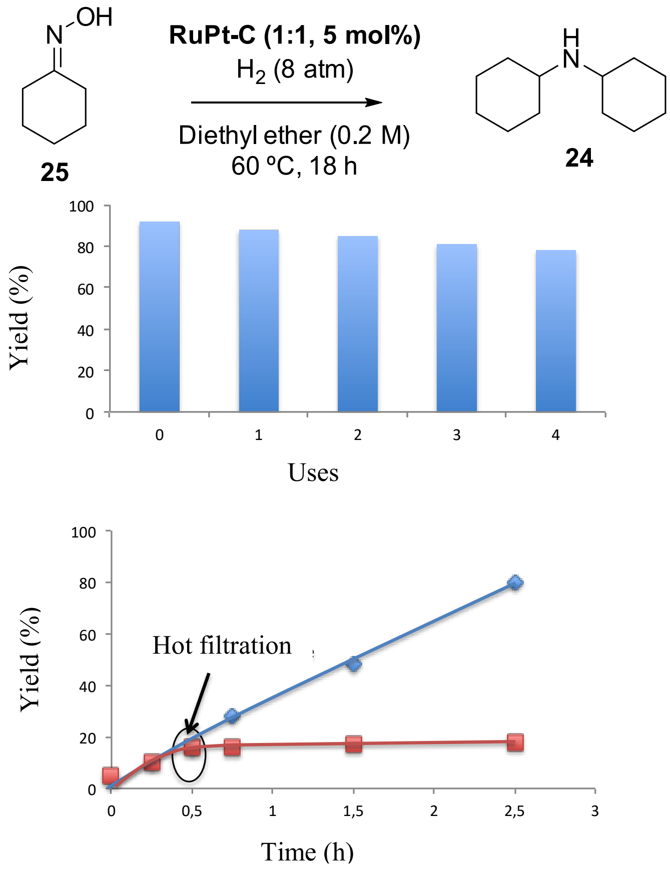


Figure S8 Reuse (top) and hot filtration test (bottom) of RuPt–C (1:1) during the hydrogenation and coupling of oxime **25**.

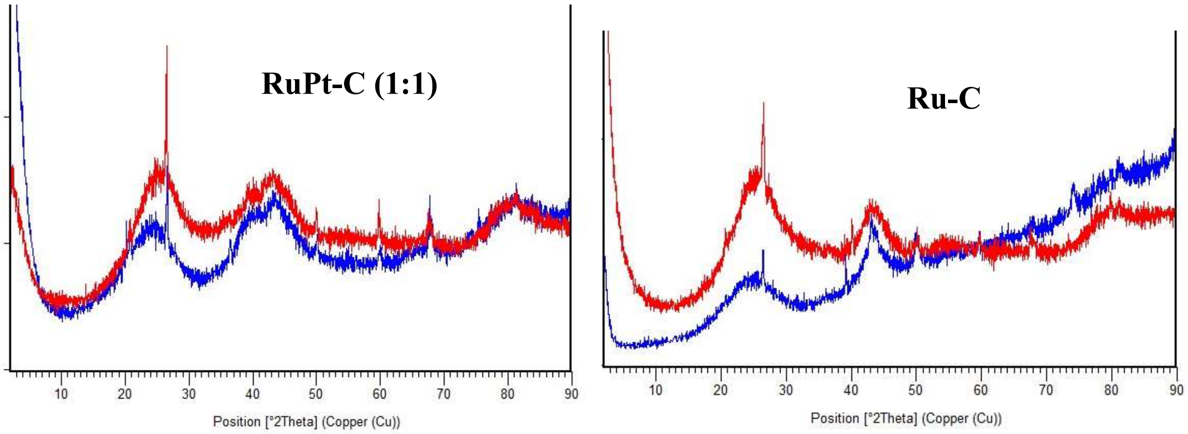


Figure S9 Powder XRD patterns of RuPt-C (1:1, left) and Ru-C (right) catalysts before (red) and after (blue) hydrogenation and coupling reaction of oxime **25**.

Taken the diameter of the nanoparticle (d) from HR–TEM experiments, we can calculate the number of total atoms (N_{total}) in the (Ru)Pt nanoparticle with the following equation (where the rest of values are taken from the typical crystallographic distances for Ru and Pt):

$d = 1.105 \text{ x } 0.29 \text{ x } N_{total}^{1/3}$.

Example: Pt/C (d=2.3 nm), $N_{total} = \left(\frac{3 \text{ x } 2.3167}{1.105 \text{ x } 0.29}\right)^3 = 10203$

Once N_{total} is obtanied, we can calculate the number of surface atoms ($N_{surface}$) in the (Ru)Pt nanoparticle by solving the following equations through the parameter “m“:

$N_{total} = (10\,m^3 - 15m^2 + 11m - 3) / 3$.

$N_{surface} = 10\,m^2 - 20\,m + 12$.

Example: Pt/C, $10202 = (10\,m^3 - 15m^2 + 11m - 3) / 3, \; m = 14.77$

$N_{surface} = 10(14.77)^2 - 20(14.77) + 12 = 1900$

Finally, we calculate the percentage of atoms in surface with the simple formula:

% atoms in surface = $(N_{surface} / N_{total})\cdot 100$.

Example: Pt/C, $\frac{\text{Nsurface}}{\text{Ntotal}} x\ 100 = \frac{1900}{10203}\ x\ 100 = 18.6$

Figure S10 Calculations for the % of atoms in surface for a given nanoparticle size and supposing perfect nanocubes, using as an example the Pt/C material.

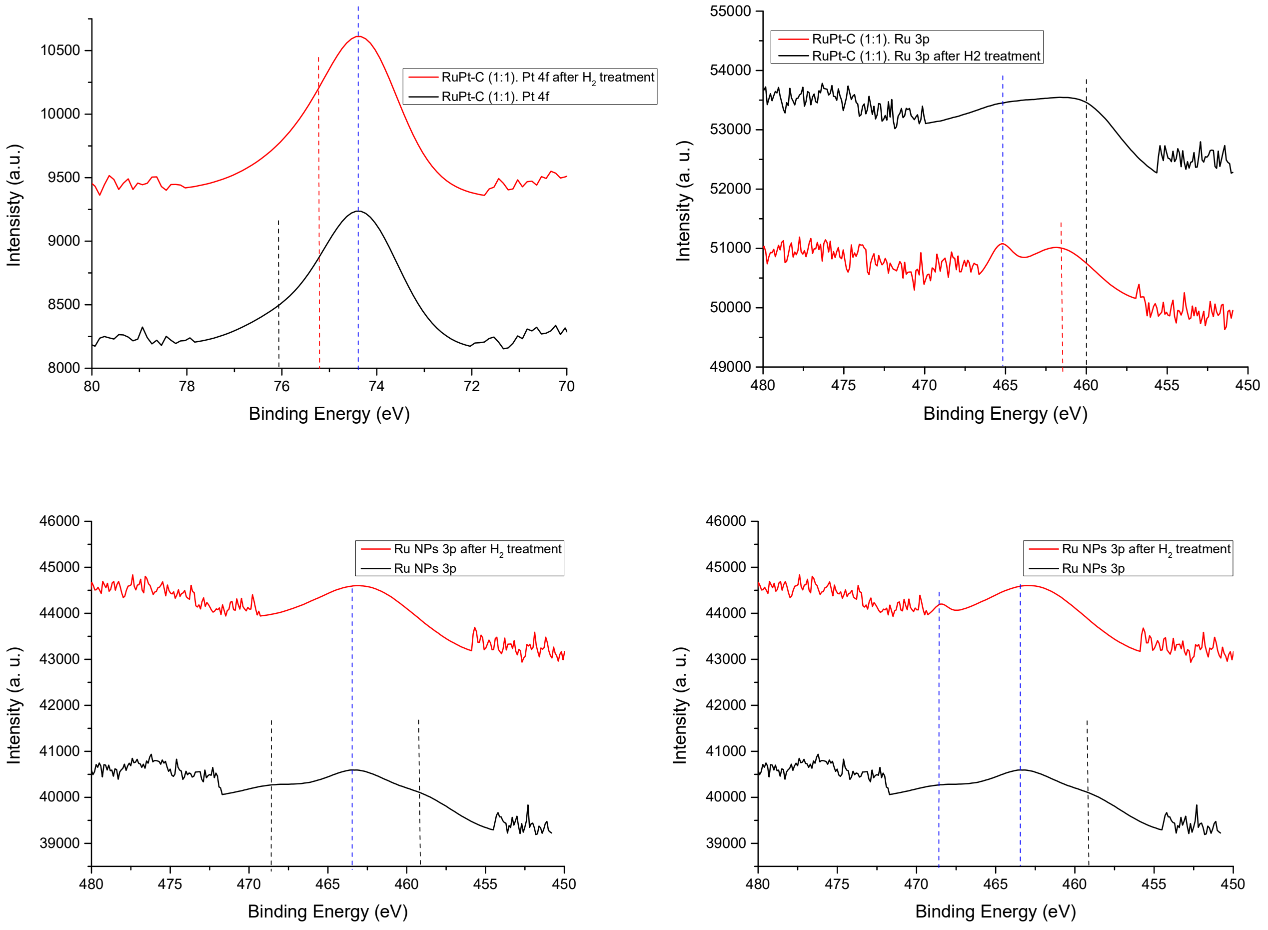


Figure S11 Pt$_{4f}$ and Ru$_{3p}$ XPS of RuPt–C (1:1, top) and two reproductions of a Ru–C sample (bottom) after in-situ treatment with an atmosphere of H$_2$ in the pre-chamber of the XPS instrument. Lines are a guide to the eye. Blue dashed line means that the peak is common for both spectra, black and red lines show slight variations.

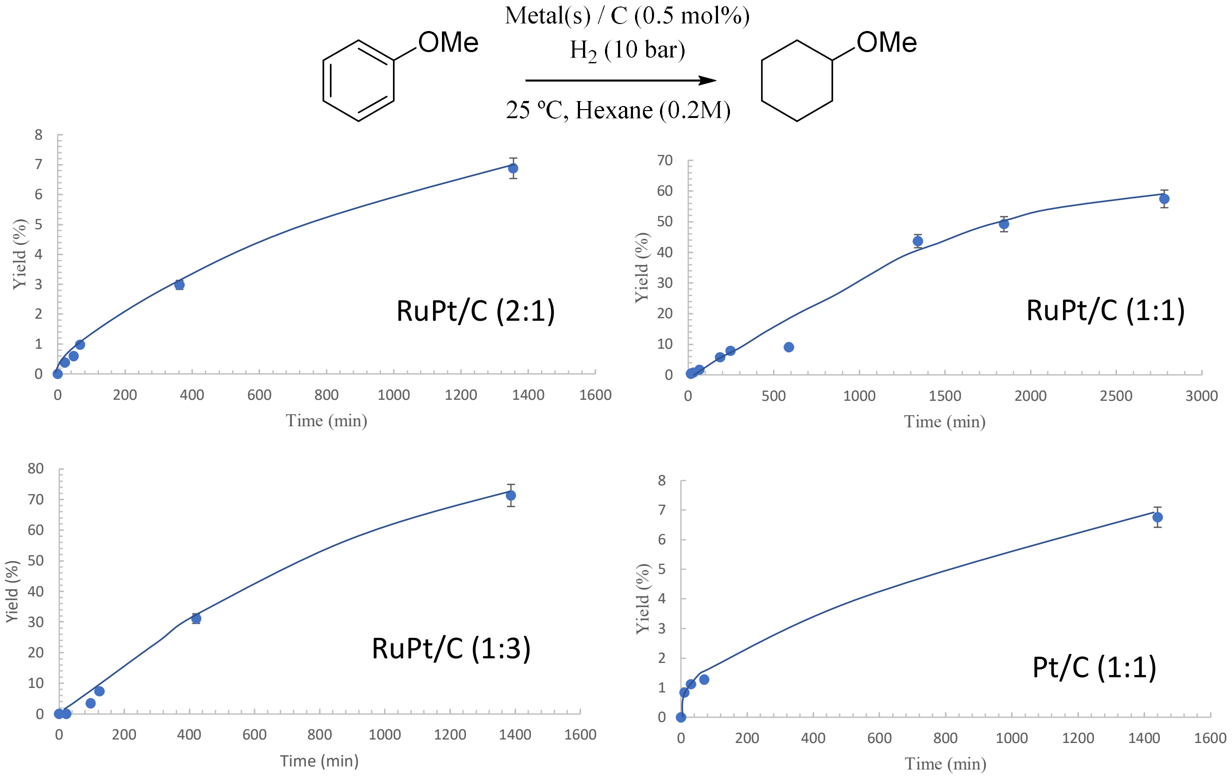
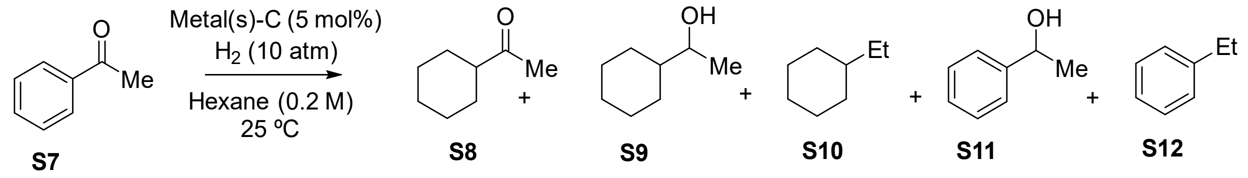


Figure S12 Kinetic curves for the hydrogenation reaction of anisole catalysed by different (Ru)Pt–C nanoalloy catalysts, in increasing order of Pt content (from top left to bottom right). Notice the different scale in yield axis for RuPt–C (2:1) and Pt–C. The kinetic curves for Ru–C and the physical mixture of Ru–C + Pt–C gave final yields below 5% (not shown).



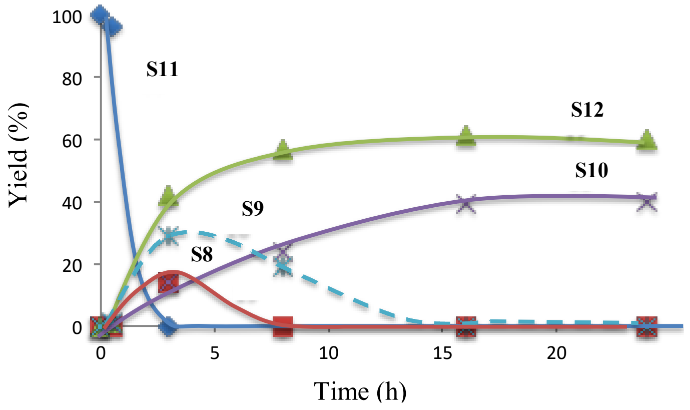


Figure S13 Kinetic curves for the acetophenone reduction reaction catalysed by the RuPt–C (1:1) nanoalloy material.

Tables.

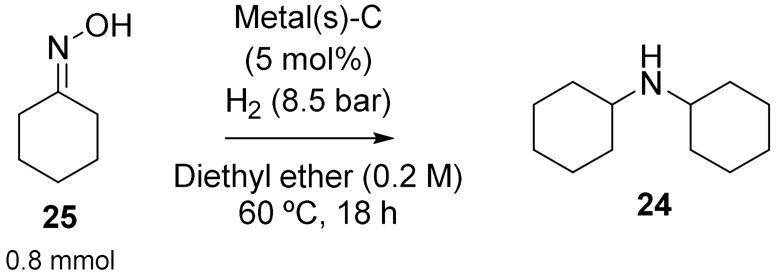


Table S1 Elemental analysis of the RuPt-C (1:1) and Ru-C catalysts after reaction.

Entry	Catalyst	Conversion (%)	24 (%)	Amine (%)	Alcohol (%)	Carbon (%)	Hydrogen (%)	Nitrogen (%)
1	RuPt–C (1:1)	100.0	88.1	5.3	6.6	72.8	2.04	1.71
2	Ru–C	100.0	10.4	40.3	49.3	73.2	2.24	2.22

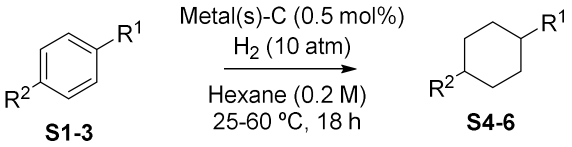


Table S2 Hydrogenation of aromatics with Ru, Pt or RuPt–C catalysts. GC measurements using *n*–dodecane as an external standard. Initial turnover frequency (TOF_0) calculated respect to superficial atoms, with access to reagents. Anisole **S1** was reacted at 25 ºC, and the other two substrates **S2–S3** were reacted at 60 ºC. ^{t}Bu–benzene **S2** reacts sluggishly due to the Taft rule (see main text), and **S3** reacted sluggishly due to strong electron withdrawing effect of the CF_3 group.

Entry	R^1 / R^2	Substrate / product	Metal(s)	TOF_0 (h^{-1})	Final yield (%)
1	OMe / H	**S1 / S4**	Ru	<5	<5
2			Pt	52	7
3			Ru + Pt (1:1)	86	5
4			RuPt (2:1)	243	12
5			RuPt (1:1)	4375	72
6			RuPt (1:3)	7500	57
7	^{t}Bu / H	**S2 / S5**	Ru	<10	<5
8			Pt	105	3
9			Ru + Pt (1:1)	32	3
10			RuPt (2:1)	49	13
11			RuPt (1:1)	500	9
12			RuPt (1:3)	875	25
13	CF_3 / Et		Ru	<5	<5
14			Pt	7	21

Entry	R^1 / R^2	Substrate / product	Metal(s)	TOF_0 (h^{-1})	Final yield (%)
15		**S3 / S6**	Ru + Pt (1:1)	7	27
16			RuPt (2:1)	5	100
17			RuPt (1:1)	5	100
18			RuPt (1:3)	52	100

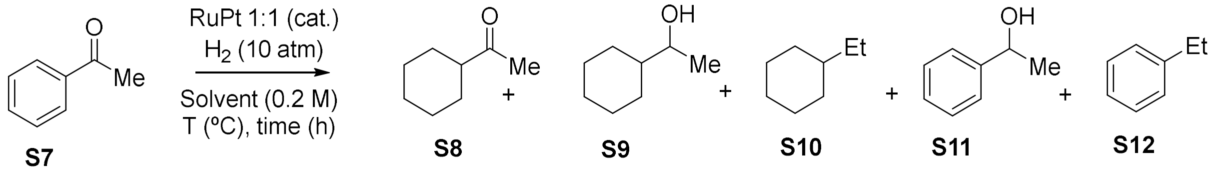


Table S3 Distribution of products in the hydrogenation of acetophenone **S7** with RuPt–C (1:1) catalyst under different reaction conditions. GC measurements using *n*–dodecane as an external standard.

Entry	Mol %	Solvent	T (°C)	t (h)	S8	S9	S10	S11	S12	Conversion (%)
1	15	Mesytilene	145	2	18	6	63	-	13	100
2	20	EtOH	45	24	-	28	71	-	-	99
3	1	Hexane	25	0.5	2	3	1	51	2	41
4	10	Hexane	25	3	4	14	5	48	26	97
5	10	Hexane	25	24	1	50	48	-	-	100
6	10	DMSO	100	24	39	1	8	44	8	100
7	10	Water	100	24	-	-	-	50	50	100

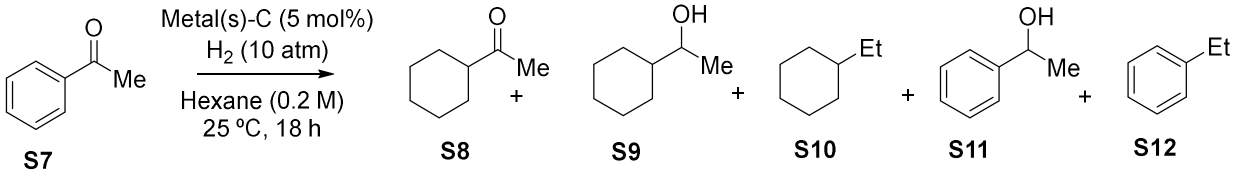


Table S4 Distribution of products in the hydrogenation of acetophenone **S7** with Ru, Pt or RuPt–C catalysts. GC measurements using *n*–dodecane as an external standard.

Entry	Metal(s)	Mol (%)	S8	S9	S10	S11	S12	Conversion (%)
1	RuPt (1:1)	1	0.5	70	30	-	-	100
2		0.25	6	38	5	45	6	100
3		0.1	2	3	-	17	-	22
4	Ru	1	6	94	-	-	-	100
5	Pt	1	15	33	5	39	8	100

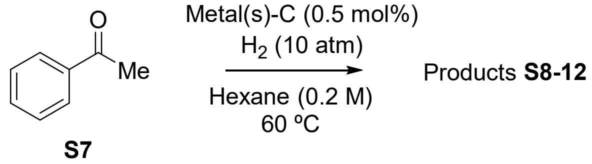


Table S5 Initial rate for the hydrogenation of acetophenone **S7** with Ru, Pt or RuPt–C catalysts.

Entry	Metal	TOF_0 (h^{-1})[a]
1	Ru	25
2	Pt	980
3	RuPt (2:1)	2600
4	RuPt (1:1)	2367
5	RuPt (1:3)	3333

[a] Initial turnover frequency (TOF_0) calculated respect to the superficial atoms. GC measurements using *n*–dodecane as an external standard.

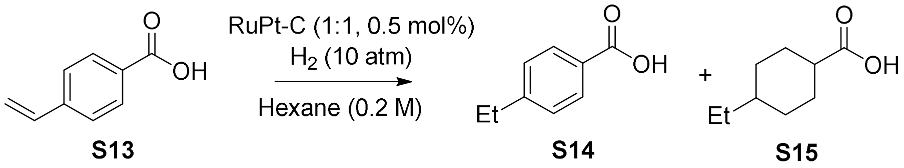


Table S6 Results for the hydrogenation of *para*–vinyl benzoic acid **S13** with Ru, Pt or RuPt–C catalysts.

Entry	T (ºC)	Time (h)	S14 (%)	S15 (%)
1	25	0.5	82	-
2		2	99	-
3		24	91	9
4	60	0.5	93	7
5		2	24	76
6		24	-	100

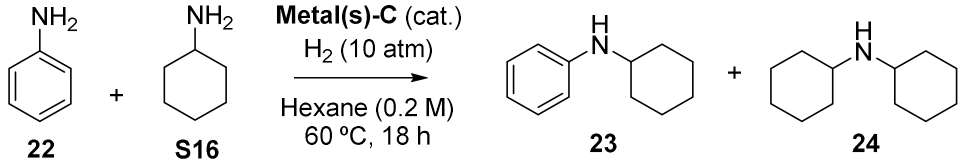


Table S7 Results for the hydrogen–borrowing coupling reaction of **22** and **S16** (equimolar) with Ru, Pt or RuPt–C catalysts.

Entry	Metal	23 (%)	24 (%)	Conversion of 22 (%)
1[a]	Ru	-	-	-
2		60	-	80
3	Pt	-	-	-
3	RuPt (1:1)	-	36	36

[a] Cyclohexylamine **S16** was not added to the reaction.