

ELECTRONIC SUPPLEMENTARY INFORMATION

Enantioselective Hydrogenation of Ketones by Iridium Nanoparticles Ligated with Chiral Secondary Phosphine Oxides

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Contents

1. General procedures.....	S3
2. Synthetic procedures.....	S5
3. Catalytic hydrogenation.....	S7
4. Mercury poisoning test and molecular catalysis experiment.....	S8
5. Asymmetric hydrogenation of ethyl pyruvate using various Ir systems.	S9
6. Solid state NMR experiments.....	S9
7. Quantification of hydrides at the surface of IrNPs.....	S9
8. High resolution XPS spectrum of Ir signals for IrNPs.....	S11
9. EDX spectrum of IrNPs.....	S12
10. ECD spectra.....	S13
11. UV-Vis spectra.....	S15
12. ATR FT-IR spectra.....	S16
13. TEM images.....	S20
14. NMR spectra.....	S23
15. GC chromatograms of catalytic experiments.....	S30
16. References.....	S37

1. General procedures

All oxygen and moisture sensitive operations were carried out under an argon atmosphere using standard argon-vacuum-line and Schlenk techniques. Solvents were purchased from Sigma-Aldrich as HPLC grade and dried by means of an MBraun MB SPS800 purification system. Bis(1,5-cyclooctadiene)di- μ -methoxydiiridium(I) was purchased from Sigma-Aldrich. (*R*)-binol and (*S*)-binol were purchased from Impex Química. THF- d_8 was dried by distillation over Na/benzophenone under Ar and degassed by three freeze, pump, and thaw cycles. Chemical shifts of ^1H , ^{13}C and ^{31}P -NMR are reported in ppm, the solvent residual signal was used as internal standard. Signals are quoted as s (singlet), d (doublet), q (quartet), m (multiplet), dd (double doublet). Reaction conversion and enantiomeric excess were determined by NMR and GC analysis. Additional analyses of some catalytic reactions were performed on a GC-MS Agilent 6890N equipped with a 5973 MSD and a HP-5 MS column (30 m x 0.25 mm x 0.25 μm). Elemental analyses were performed by Kolbe (Mülheim, Germany).

Gas Chromatography (GC)

Analyses (determination of the reaction conversion and enantiomeric excess) of the reaction mixtures were performed on an Agilent Technologies 6890N/G1530N GC-FID equipped with a β -DEX 120 (20% permethylated β -cyclodextrin in SPB-35 poly(35% phenyl/65% dimethylsiloxane)).

X-ray Photoelectron Spectroscopy (XPS)

These experiments were carried out on our behalf by Dr. L. Calvo Barrio at the Centres Científics i Tecnològics, Universitat de Barcelona, using a PHI 5500 Multitechnique System (from Physical Electronics) with a monochromatic X-ray source (Aluminium Kalfa line of 1486.6 eV energy and 350 W), placed perpendicular to the analyzer axis and calibrated using the 3d $_{5/2}$ line of Ag with a full width at half maximum (FWHM) of 0.8 eV.

The analyzed area was a circle of 0.8 mm diameter, and the selected resolution for the spectra was 187.5 eV of Pass Energy and 0.8 eV/step for the general spectra and 23.5 eV of Pass Energy and 0.1 eV/step for the spectra of the different elements in the depth profile spectra. A low energy electron gun (less than 10 eV) was used in order to discharge the surface when necessary. All Measurements were made in an ultra-high vacuum (UHV) chamber pressure between 5×10^{-9} and 2×10^{-8} torr.

Energy Dispersive X-ray Spectroscopy (EDX)

EDX analyses were performed at the Universitat Rovira i Virgili on a FEI Quanta 600 ESEM equipped with an Oxford Instrument EDS Detector (20 kV accelerating voltage, 10 mm working distance) employing cobalt as internal standard. Samples were prepared by drop casting (from various THF solutions) onto an aluminum holder.

Electronic Circular Dichroism (ECD)

Circular Dichroism spectra measurements were carried out at the ICIQ on an Applied Photophysics Chirascan Circular Dichroism spectrometer equipped with a photomultiplier detector, dual polarizing prism design monochromator, photo-elastic modulator (PEM) and 150 W Xenon light source.

Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR measurements were carried out in a glove box at the LCC-Toulouse on a Bruker Optics FT-IR Alpha spectrometer equipped with a DTGS detector, KBr beamsplitter at 4 cm^{-1} resolution in the range 4000–400 cm^{-1} .

Transmission Electron Microscopy (TEM)

TEM analyses were performed at the Universitat Rovira i Virgili on a Zeiss 10 CA electron microscope at 100 kV with a resolution of 3 Å. Samples were prepared drop casting (from various THF) onto a holey Formvar/carbon-coated copper grid.

High Resolution Transmission Electron Microscopy (HRTEM)

HRTEM observations were performed at the “Toulouse characterization platform UMS-Castaing” on a JEOL JEM 2010 electron microscope working at 200 kV with a resolution point of 2.35 Å. FFT treatments have been carried out with Digital Micrograph Version 3.7.4. TEM grids were prepared by drop-casting of the crude colloidal solution in THF on a holey carbon-coated copper grid.

Magic Angle Spinning Solid State NMR (MAS-NMR)

MAS-NMR analyses with and without ^1H - ^{13}C cross-polarization (CP) were performed at the LCC-Toulouse on a Bruker Avance 400WB instrument equipped with a 2.5 mm probe with the sample rotation frequency of 12 kHz. Measurements were carried out in a 2.5 mm ZrO_2 rotor.

2. Synthetic procedures

Synthesis of *R*-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*] phosphepine-4-oxide (L_R)

2,2'-Di(lithiomethyl)-1,1'-binaphthyl-2-*N,N,N',N'*-tetramethylethylenediamine (10.48 g, 19.9 mmol), prepared from optically pure (*R*)-binol according to the literature procedures,¹ was treated with hexane (70 mL). Diethylphosphoramidous dichloride (3.3 mL, 22.5 mmol), in a small amount of hexane (~3 mL), was slowly added to the suspension with a Hamilton syringe at 0 °C external temperature (ice bath). The residual reagent from the Hamilton syringe was rinsed into the reaction mixture with hexane (5 mL + 3 mL). The reaction mixture was refluxed for 4 h. The hexane was removed in vacuum. The obtained yellow solid was extracted with toluene (3 x 50 mL). The toluene was removed from the combined extracts in vacuum, and the crude 4-diethylamino-4,5-dihydro-3*H*-dinaphtho(2,1-*c*; 1',2'-*e*)phosphepine was dissolved in THF (50 mL). Aqueous HCl solution (50 mL, 6 N, 300

mmol) was added at 0 °C external temperature. The ice bath was removed, and the reaction mixture was stirred at room temperature overnight. All the volatiles were removed in vacuum. The obtained yellow solid was extracted with a mixture of toluene (50 mL) and THF (60 mL). The insoluble residue, a yellowish waxy material, was washed again with toluene (50 mL). The extracts were combined, and solvents were removed in vacuum. The crude product was purified by column chromatography ((1) silica, CH₂Cl₂, CH₂Cl₂ : EtOH (v/v 9/1); (2) silica, CH₂Cl₂ : EtOH (v/v 9/1)). White solid. Yield: 2.82 g, 8.6 mmol, 43 %.

¹H NMR (400 MHz, CDCl₃): δ 8.03–7.92 (m, 4H, binaphthyl), 7.66 (d, *J*_{HH} = 8.2 Hz, 1H, binaphthyl), 7.56–7.45 (pseudo q, 3H, binaphthyl), 7.33– 7.19 (m, 4H, binaphthyl), 7.26 (dd, *J*_{PH} = 461 Hz, *J*_{HH} = 7.9 Hz, P(O)H), 3.47–3.26 (m, 2H, CHH, C'HH), 3.14–2.94 (m, 2H, CHH, C'HH).

³¹P{¹H} NMR (162 MHz, CDCl₃): δ 45.8 (s).

¹H and ³¹P{¹H} NMR data were consistent with those previously reported.²

Synthesis of *S*-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*] phosphepine-4-oxide (L_S)

This compound was prepared in an identical manner to above except optically pure (*S*)-binol was used in place of (*R*)-binol. White solid. Yield: 2.27 g, 6.9 mmol, 35 %.

¹H, ³¹P{¹H} NMR data were consistent with those previously reported for the (*R*) enantiomer.²

Synthesis of stabilized Ir nanoparticles, IrNPs

Bis(1,5-cyclooctadiene)di-μ-methoxydiiridium(I) (33.1 mg, 0.05 mmol) and **L** (*R* or *S* enantiomer, 16.4 mg, 0.05 mmol) were dissolved in THF (40 mL) and the solution was transferred *via* cannula to a Fischer–Porter reactor. The reactor was pressurized with 3 bar

of H₂ and vented twice. The reactor was then pressurized with 5 bar of H₂ and the reaction mixture was vigorously stirred overnight at room temperature. The colour of the solution turned from yellow to black. The hydrogen pressure was eliminated and the solvent was removed under vacuum. The **IrNPs** were precipitated and washed with methanol (2 x 30 mL) and dried under vacuum.

³¹P CP MAS NMR: δ 94 ppm.

Elemental analysis (%): C, 38.76; H, 3.76; Ir, 49.12; P, 4.42.

EDX (% , average of 3 measurements): C, 31.43; O, 9.00; Ir, 47.34; P, 4.94.

3. Catalytic hydrogenation experiments

Catalytic experiments were performed in a HEL 24–multireactor (volume of the tubes 1.5 mL). In a typical experiment, 1 mg of **IrNPs** (0.0025 mmol of Ir assuming % of Ir from elemental analysis) in 0.75 mL of THF (as a standard solution, freshly prepared prior to use) was mixed with 0.25 mmol of substrate in 1.5 mL vials and the reactor was sealed under nitrogen atmosphere in a glove box. The reactor was then pressurized with 20 bar of hydrogen and depressurized three times to purge and finally pressurized to 40 bar. The reactor was stirred overnight at room temperature. After 18 h, the reactor was slowly depressurized and samples from each reaction were filtered through a silica plug and analyzed by GC.

4. Mercury poisoning test and molecular catalysis experiments

Mercury poisoning test

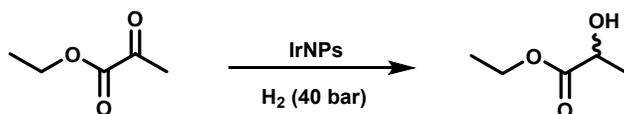
The experiment was performed in a Berghof Hastelloy autoclave. 7 mg of **IrNPs** (0.0175 mmol of Ir assuming % of Ir from elemental analysis), 1.75 mmol of acetophenone and 400 eq of Hg were mixed in 5 mL of THF and the reactor was sealed under nitrogen in a glove box. The reactor was then pressurized with 20 bar of hydrogen and depressurized three times to purge and finally pressurized to 40 bar. The reactor was stirred overnight at room temperature. After 18 h, the reactor was slowly depressurized and the reaction mixture was filtered through a silica plug and analyzed by GC.

Molecular catalysis experiments

The experiments were performed in a Berghof Hastelloy autoclave. Bis(1,5-cyclooctadiene)di- μ -methoxydiiridium(I) (3.3 mg, 0.005 mmol) and **L** (6.6 mg, 0.02 mmol) were dissolved in 3 mL of THF under nitrogen. After the required incubation time (0, 24 or 48 h), the solution was mixed with the required quantity of acetophenone and the reactor was sealed under nitrogen in a glove box. The reactor was then pressurized with 20 bar of hydrogen and depressurized three times to purge and finally pressurized to 40 bar. The reactor was stirred overnight at room temperature. After 18 h, the reactor was slowly depressurized and the reaction mixture was filtered through a silica plug and analyzed by GC.

5. Asymmetric hydrogenation of ethyl pyruvate using various Ir systems

Table S1 Summary of the attempted enantioselective hydrogenation of ethyl pyruvate using various iridium catalytic systems.^a



Entry	Catalyst	Conversion (%) ^b	ee (%) ^b	Configuration
1 ^c	IrNPs	100	26	S
2 ^c	IrNPs (unwashed)	100	19	S
3 ^d	[(COD)Ir(MeO)] ₂ + L	97	16	S

^a Conditions: 18 h, R. T. ^b Conversions and ee were determined by GC (average of two runs). ^c IrNPs (0.0025 mmol of Ir assuming % of Ir from elemental analysis), substrate (0.25 mmol), THF (0.75 mL). ^d [(COD)Ir(MeO)]₂ (0.005 mmol), **L** (0.02 mmol), substrate (1 mmol), THF (3 mL), 24 h incubation.

6. Solid state NMR experiments

30 mg of IrNPs were introduced in a Fisher-Porter bottle which was pressurized with 1 bar of ¹³CO. The nanoparticles were left under atmosphere of ¹³CO at room temperature during 20 h. The gas was then removed using a vacuum pump for 5 min and magic angle spinning solid-state NMR (MAS-NMR) with and without ¹H-¹³C cross-polarization (CP) were recorded.

7. Quantification of hydrides at the surface of IrNPs

The general procedure for the preparation of reaction mixtures for the quantification of hydrogen atoms adsorbed onto the surface of **IrNPs** by GC analyses was carried out

following a previously described methodology.³ On each fresh colloidal solution of **IrNPs** in THF, five cycles of 1 min vacuum/1 min bubbling of argon were performed in order to eliminate the H₂ dissolved into the solvent. Then, 1 or 5 equivalents of 2-norbornene, previously filtered through alumina, were added. Aliquots were regularly taken from the reacting solutions (after 2, 24, 48, 72 h and 1 week) for GC analysis and estimation of the olefin conversion into alkane (Table 2).

Table S2 Conversion (%) of 2-norbornene in relation to initial Ir.

Time	2h	24 h	48 h	72 h	1 week
1 eq. norbornene	24.2	33.2	40.1	40.7	42.5
5 eq. norbornene	4.9	7.0	7.1	7.4	8.6

We considered nanoparticles mean sizes and surface iridium atom contents as following:

Mean size: 1.45 nm / 66% surface atoms → 1.3 H / surface Ir atom

8. High resolution XPS spectrum of Ir signals for IrNPs

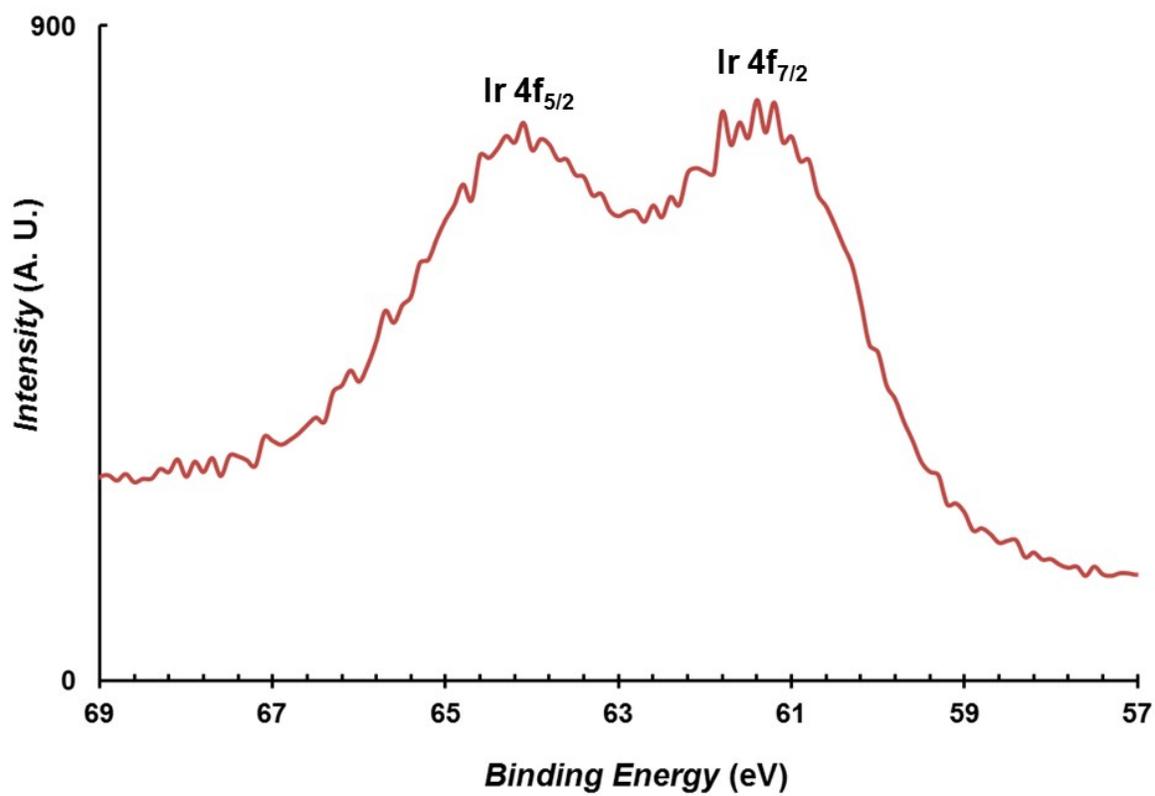


Figure S1. XPS spectrum of Ir 4f signals for IrNPs.

9. EDX spectrum of IrNPs

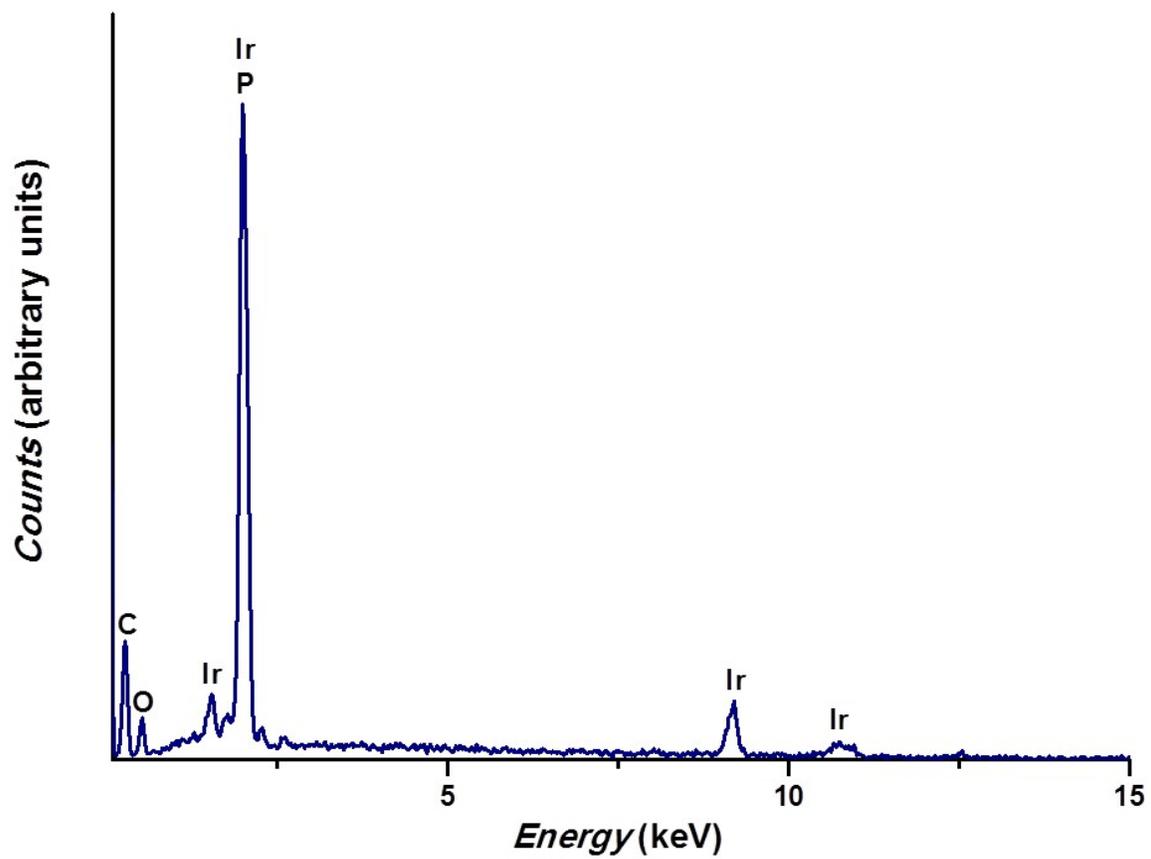


Figure S2. EDX spectrum of IrNPs.

10. CD spectra

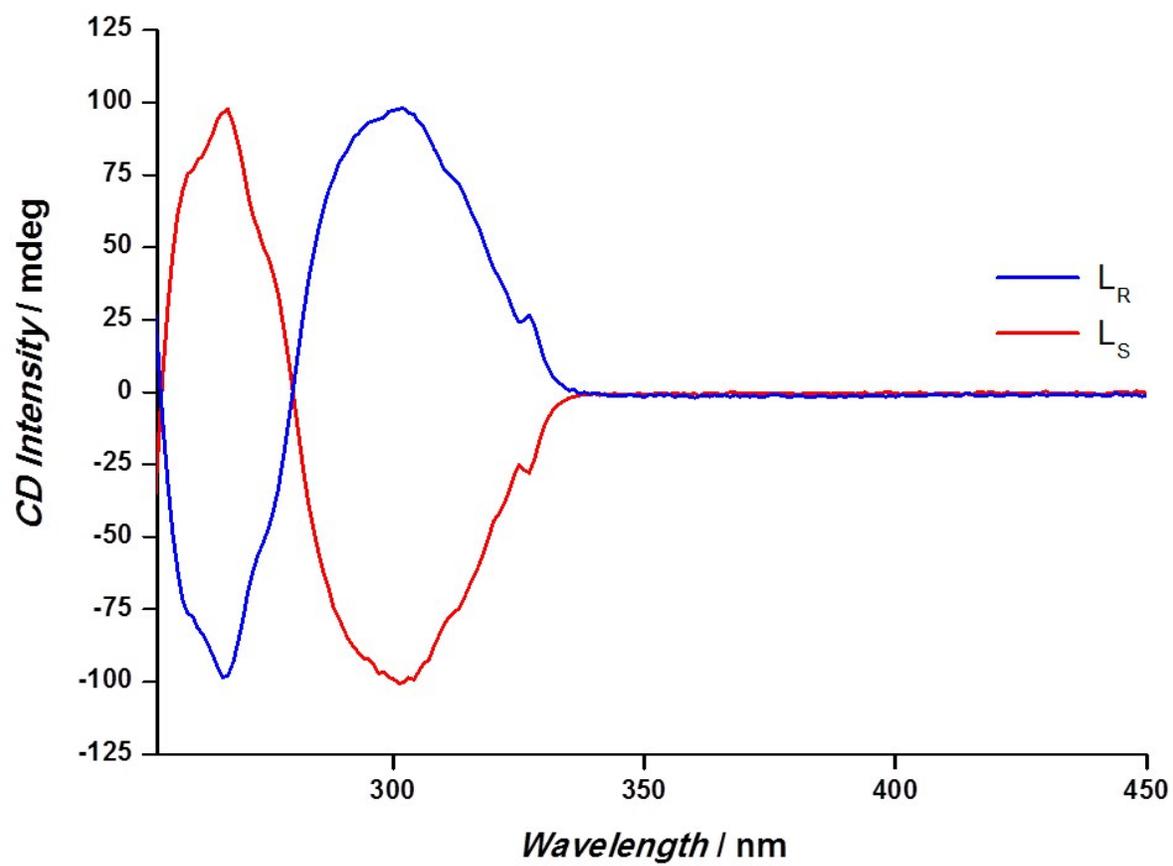


Figure S3. CD spectra of enantiomers L_R and L_S recorded in THF, $[L]$ ca. 2.5×10^{-4} M.

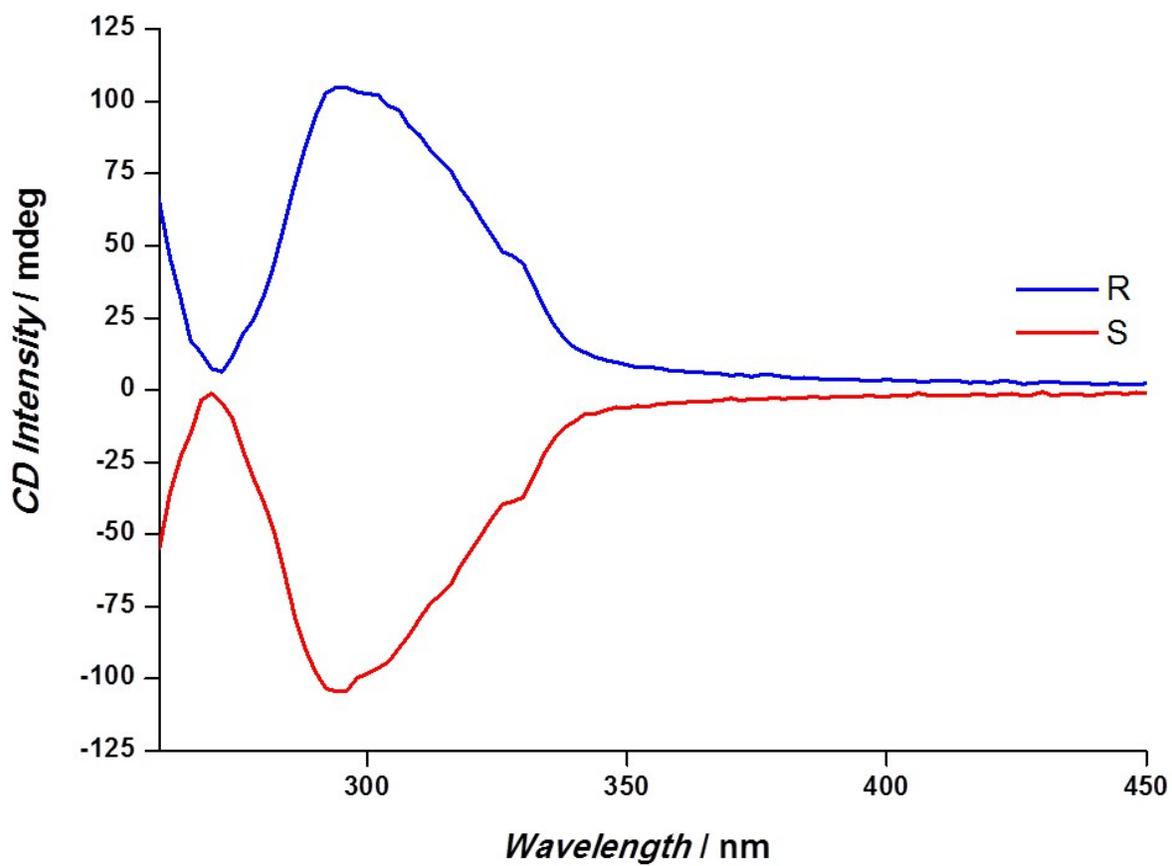


Figure S4. CD spectra of IrNPs (enantiomers **R** and **S**) recorded in THF, [IrNPs] ca. 2.5×10^{-4} M.

11. UV-Vis spectra

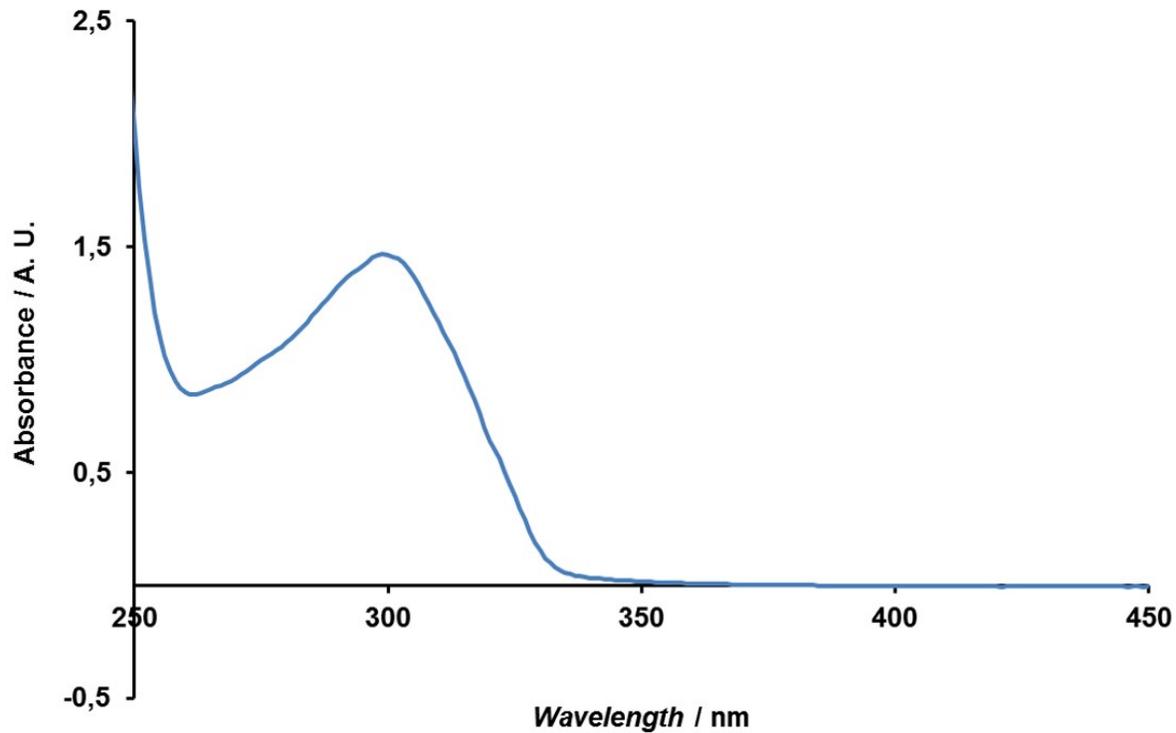


Figure S5. UV-Vis spectrum of L recorded in THF, [L] ca. 2×10^{-4} M.

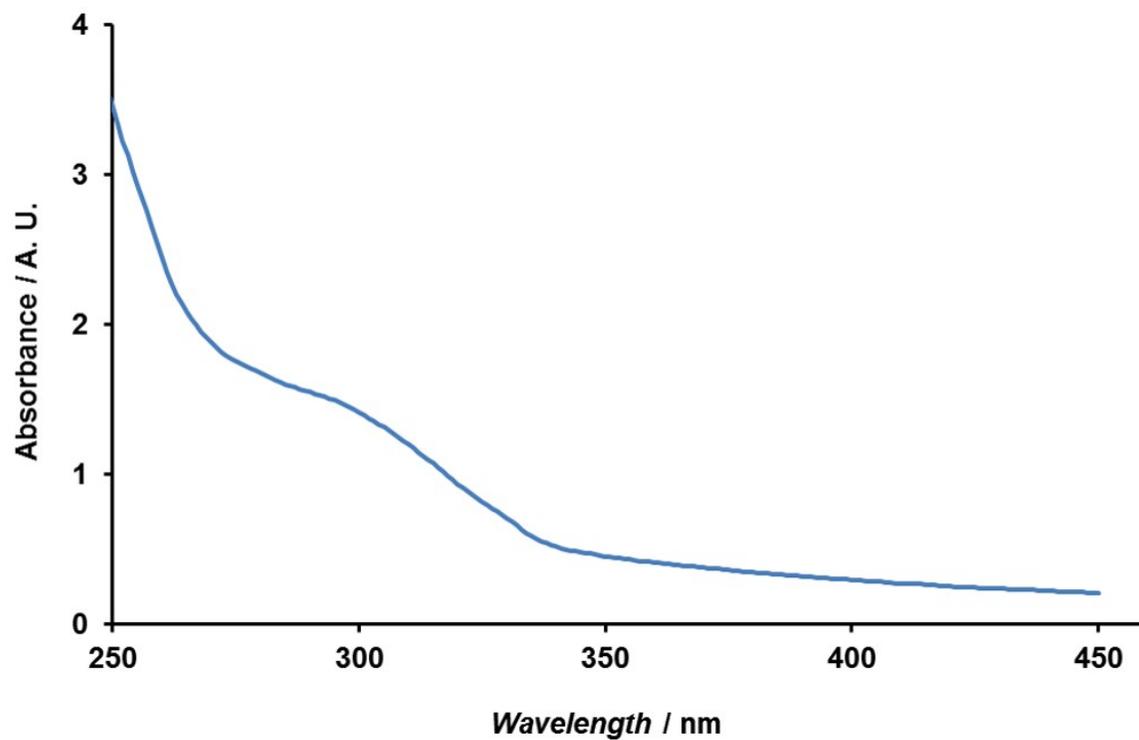


Figure S6. UV-Vis spectrum of IrNPs recorded in THF, [IrNPs] ca. 2×10^{-4} M.

12. ATR FT-IR spectra

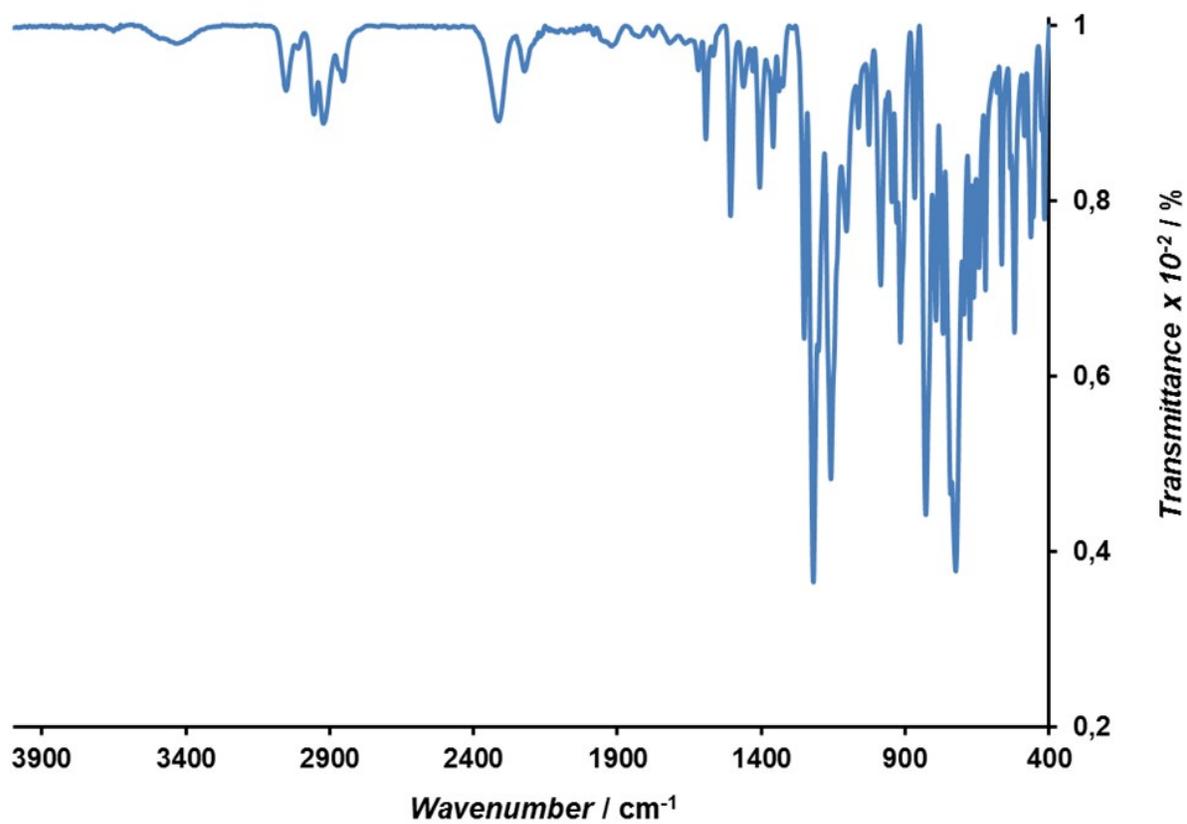


Figure S7. ATR FT-IR spectrum of **L**.

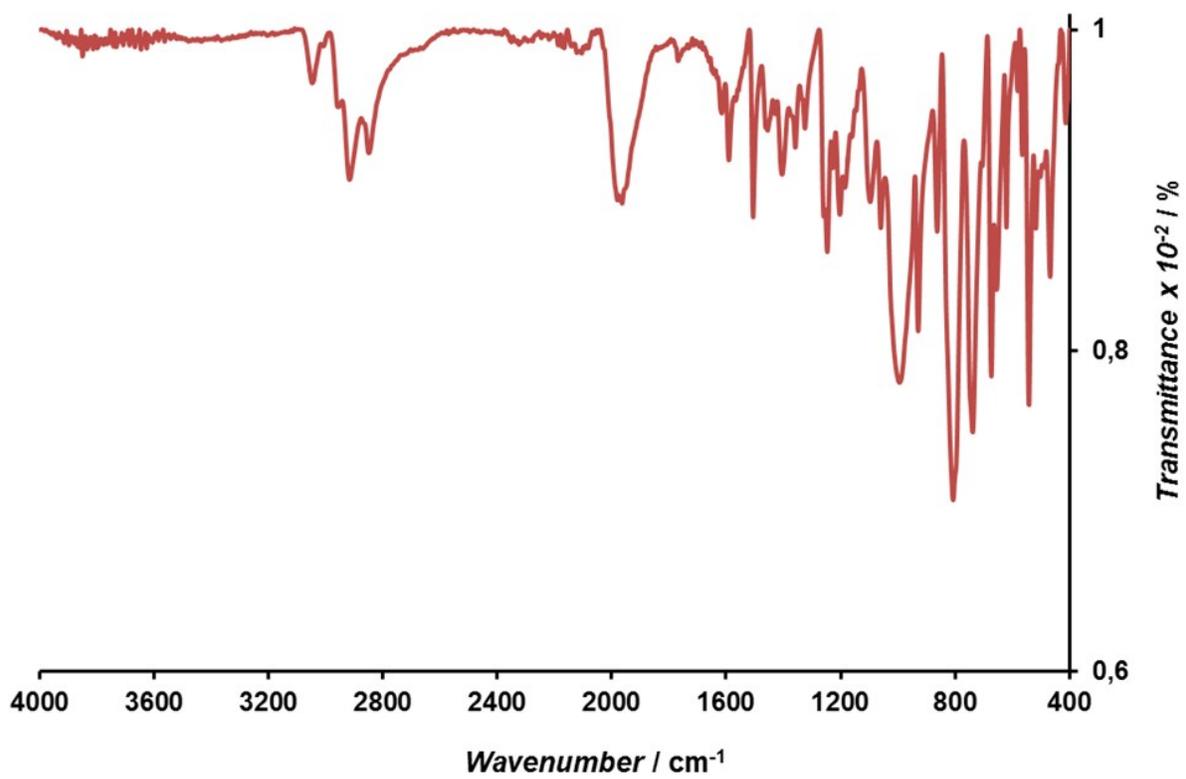


Figure S8. ATR FT-IR spectrum of IrNPs.

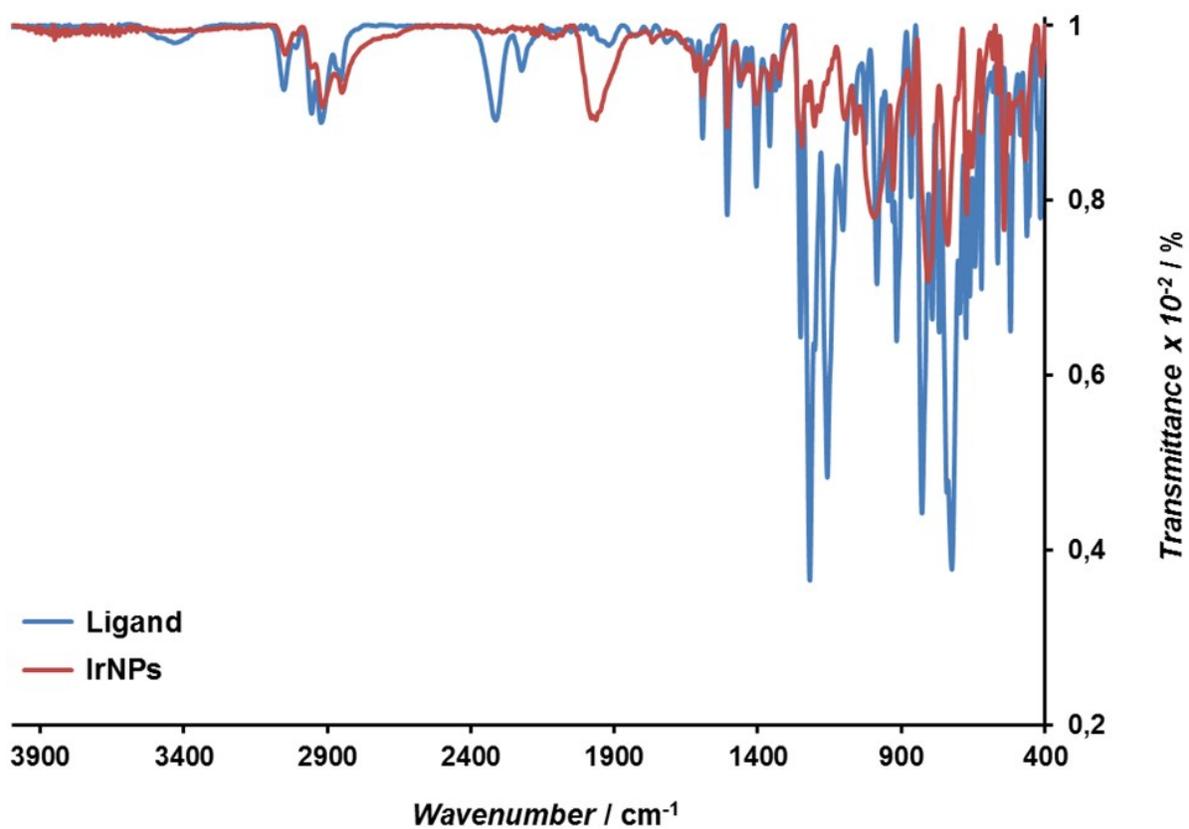


Figure S9. Overlay of ATR FT-IR spectra of L and IrNPs.

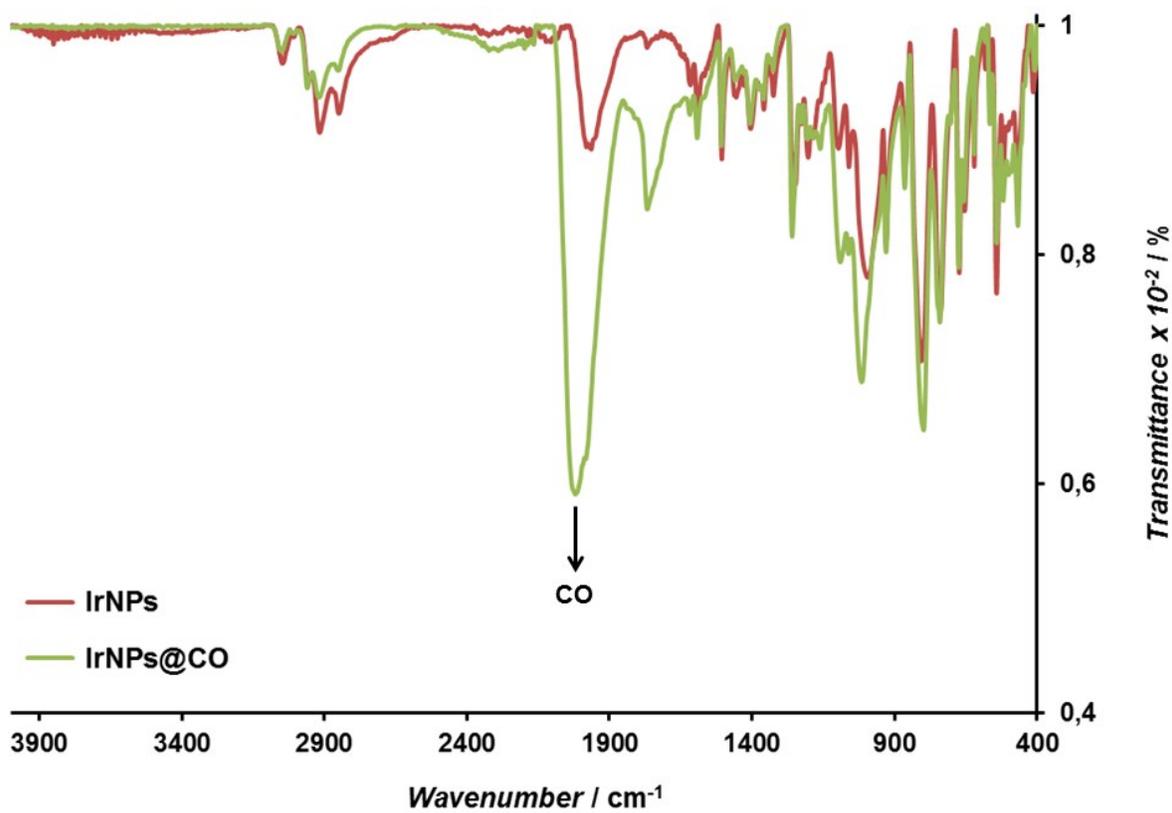
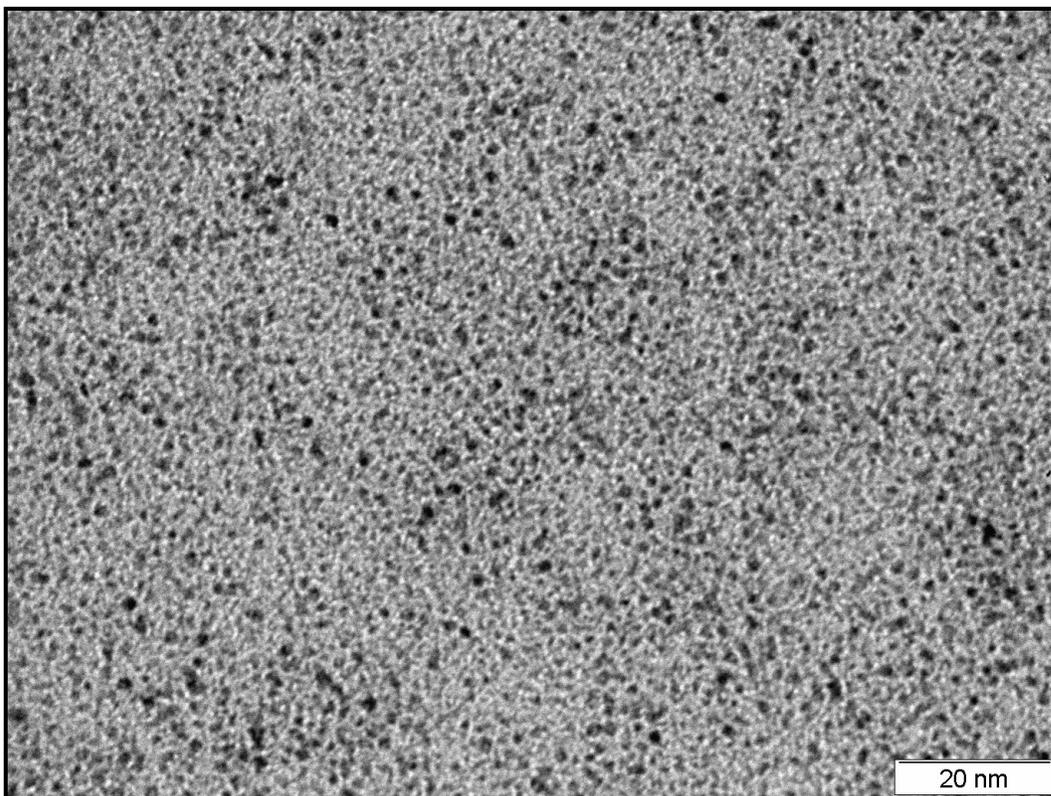
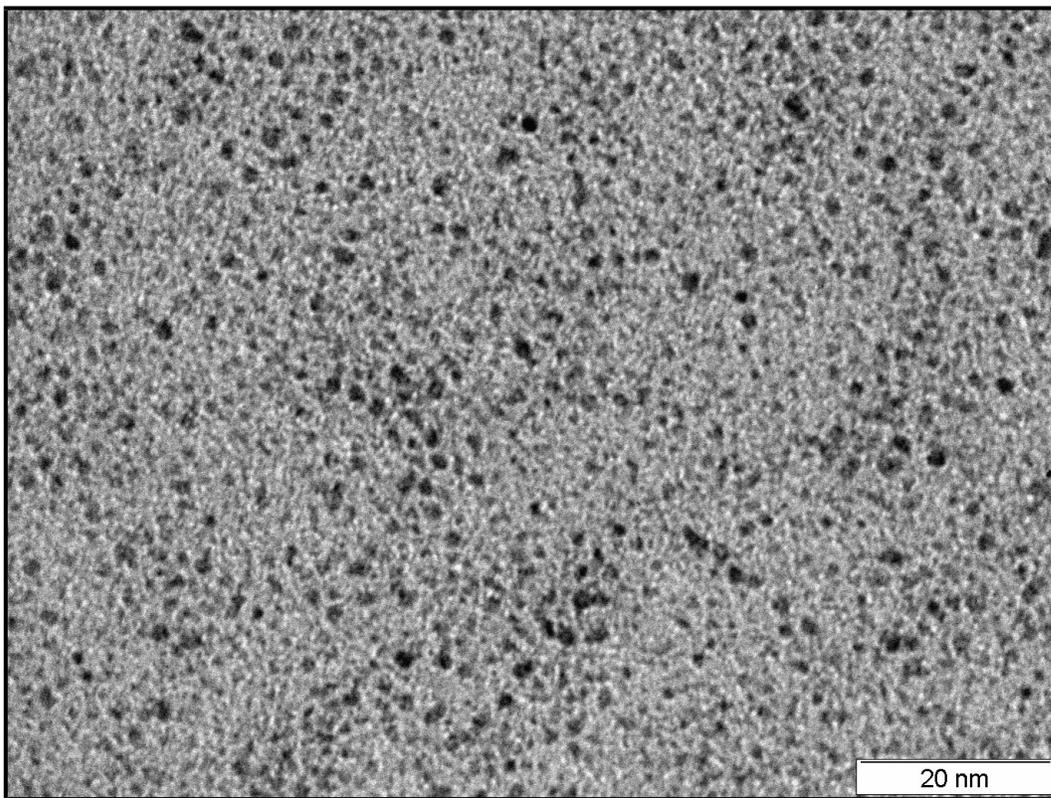
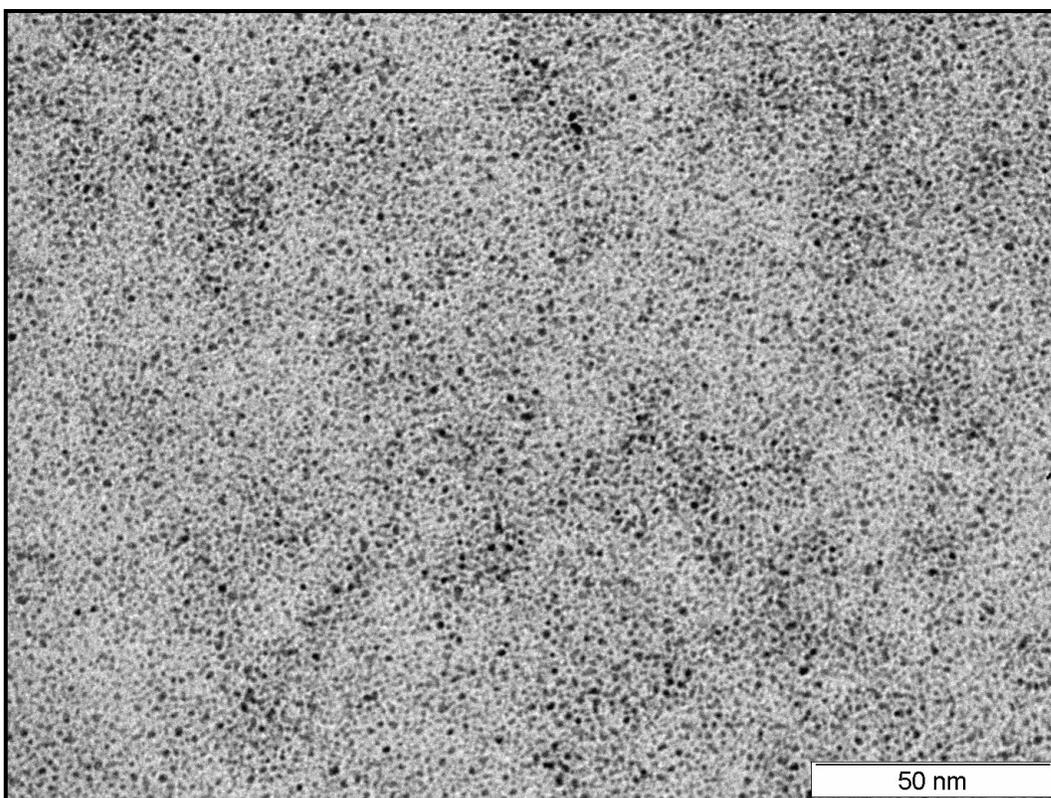
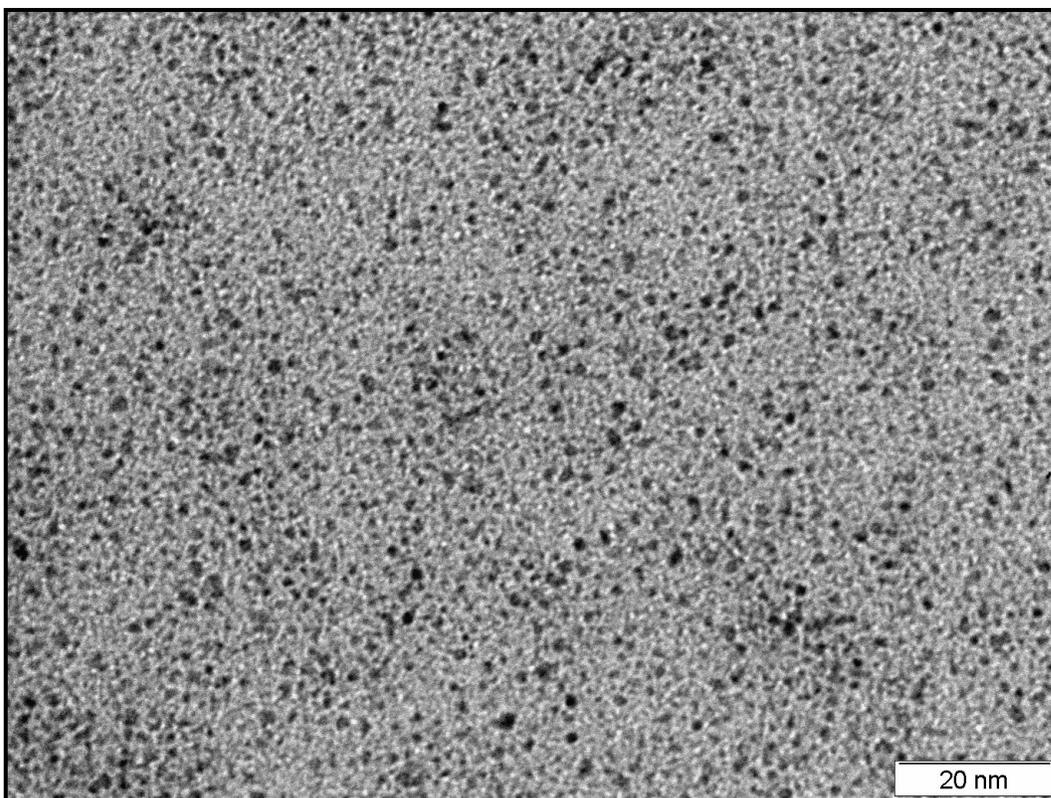


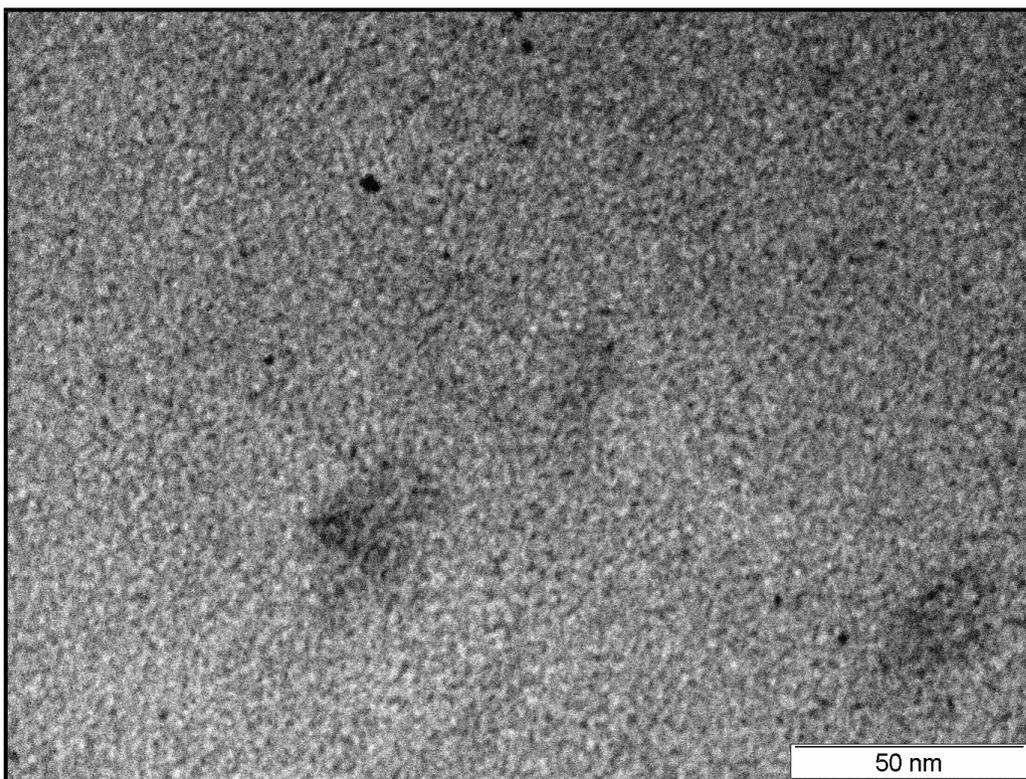
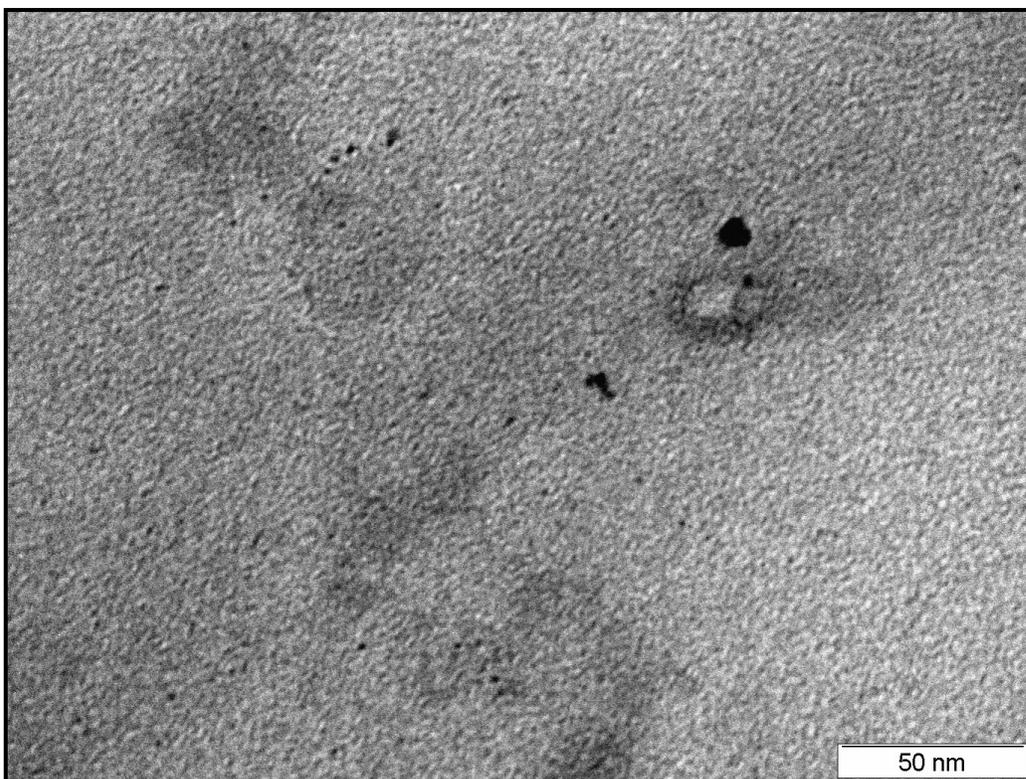
Figure S10. Overlay of ATR FT-IR spectra of **IrNPs** and **IrNPs** poisoned with CO.

13. TEM images





Figures S11-S14. Selected TEM images for IrNPs.



Figures S15-S16. Selected TEM images of a crude solution during a control catalytic reaction; hydrogenation of acetophenone catalyzed by a mixture of $[\text{Ir}(\text{OMe})(\text{COD})]_2 + \text{L}$.

14. NMR spectra

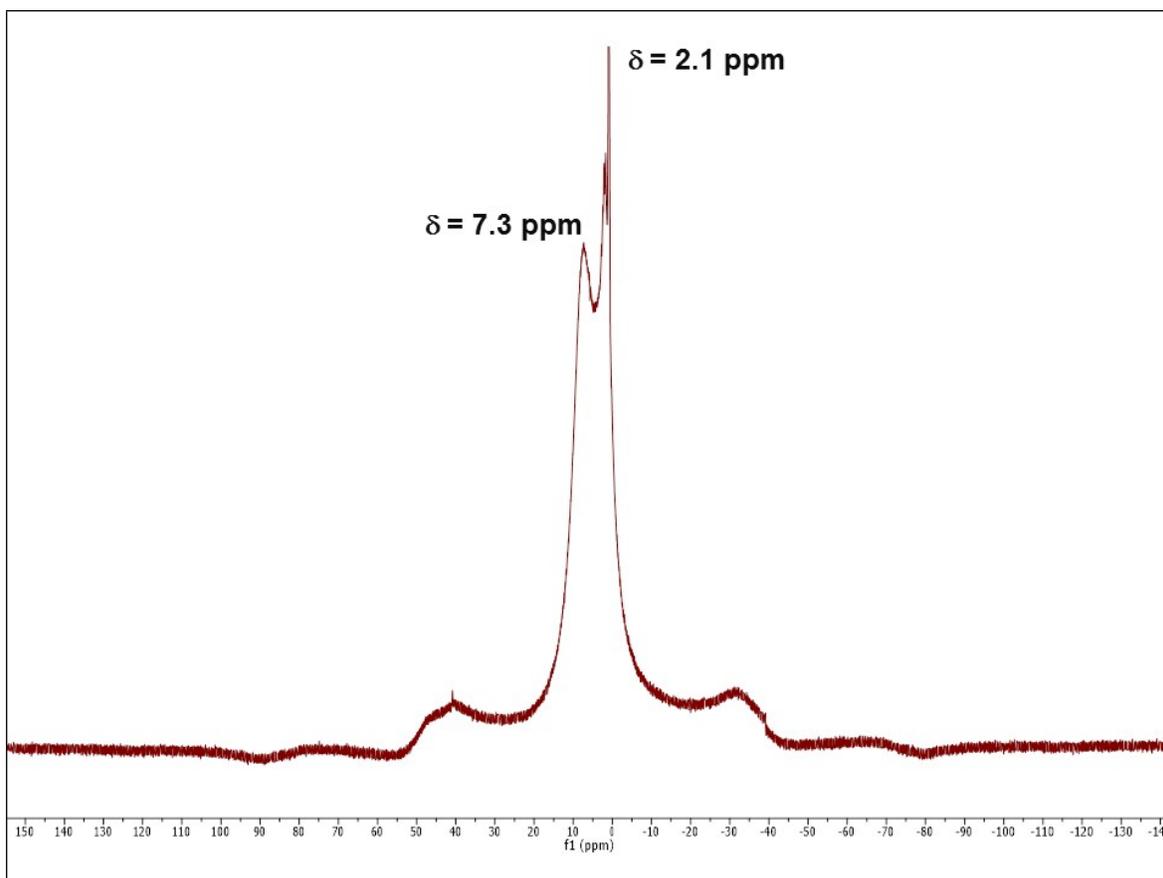


Figure S17. ^1H MAS NMR spectrum of IrNPs.

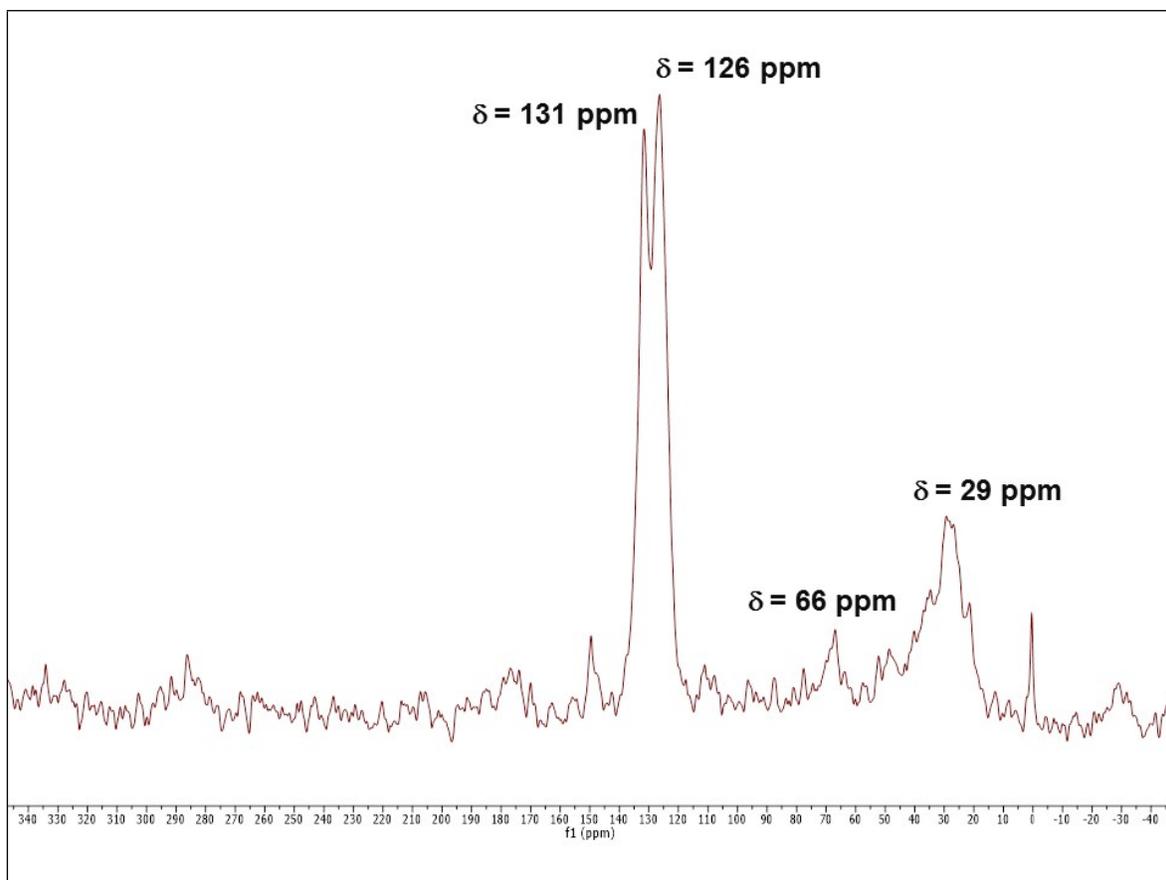


Figure S18. $^{13}\text{C}\{^1\text{H}\}$ MAS NMR spectrum of IrNPs.

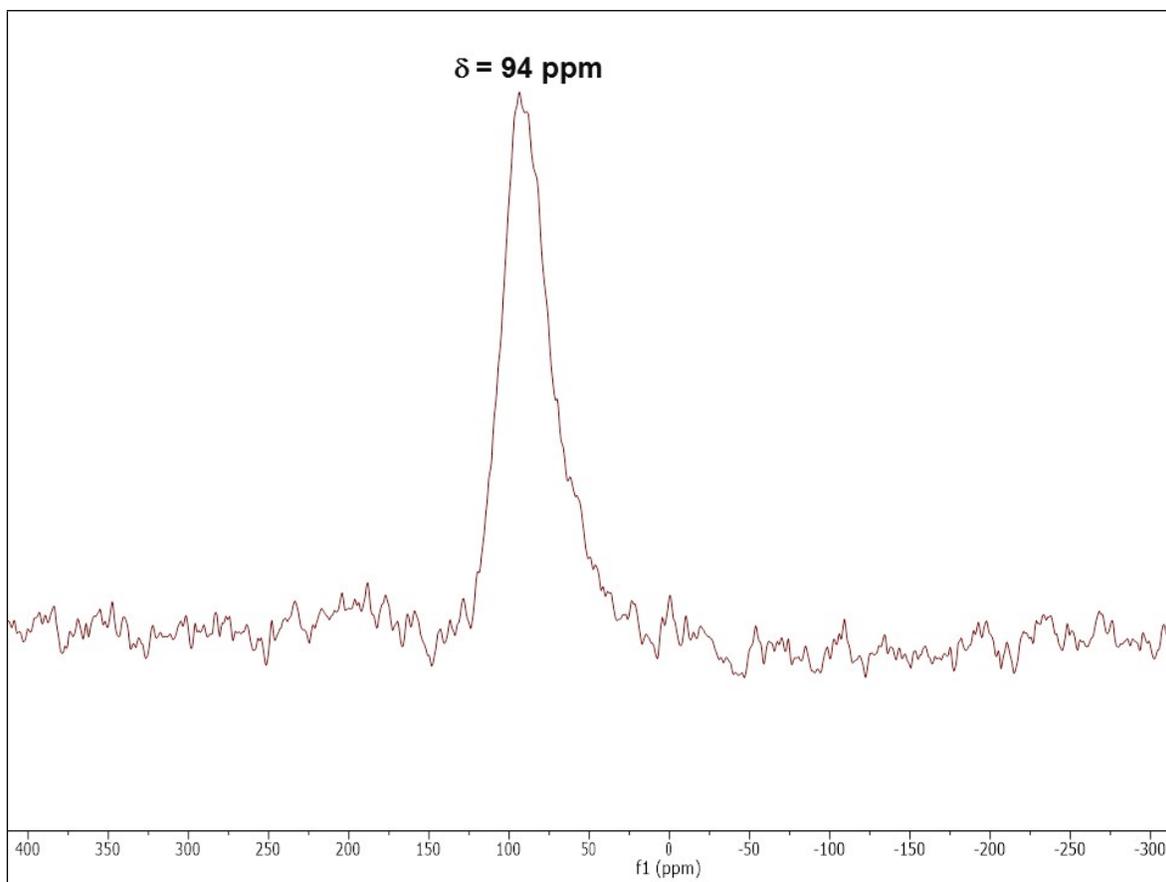


Figure S19. $^{31}\text{P}\{^1\text{H}\}$ MAS NMR spectrum of IrNPs.

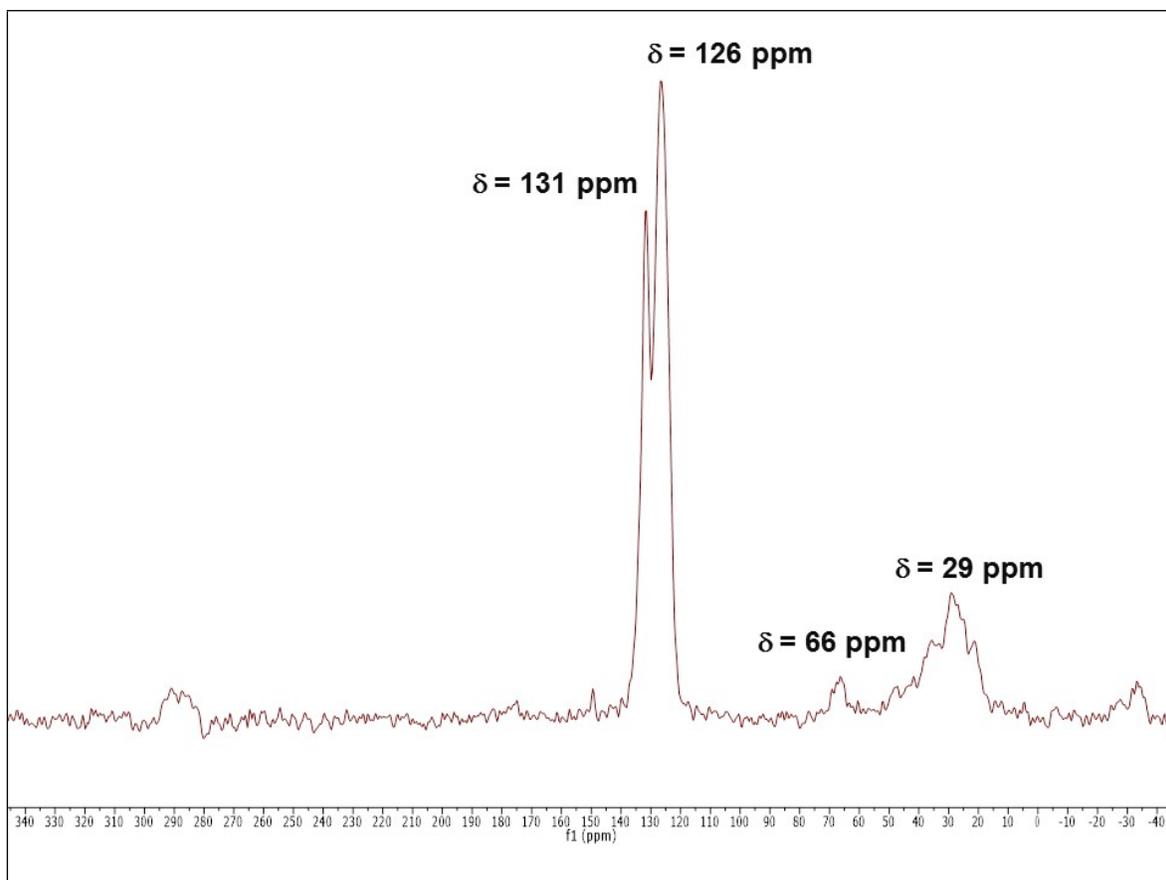


Figure S20. $^{13}\text{C}\{^1\text{H}\}$ CP-MAS NMR spectrum of IrNPs.

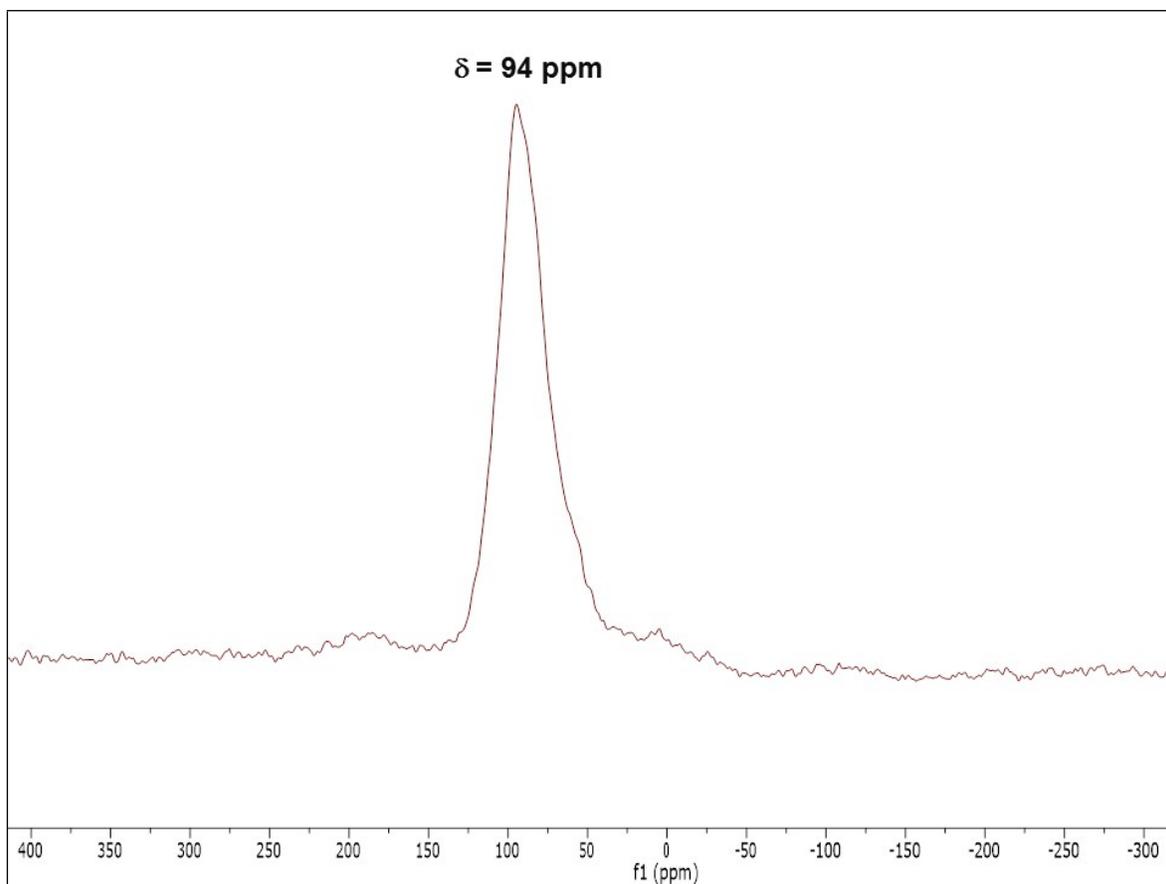


Figure S21. $^{31}\text{P}\{^1\text{H}\}$ CP-MAS NMR spectrum of IrNPs

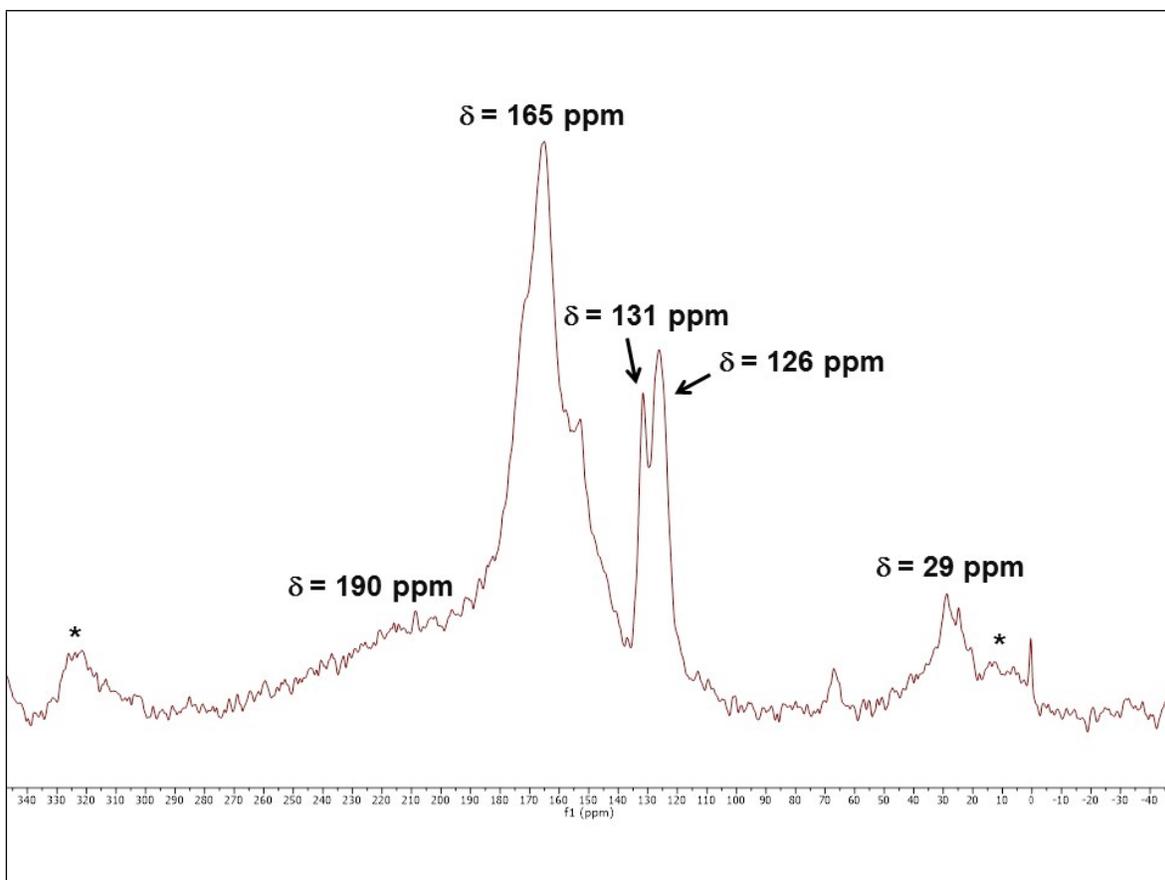


Figure S22. $^{13}\text{C}\{^1\text{H}\}$ MAS NMR spectrum of IrNPs + ^{13}CO . Asteriks denote spinning side bands.

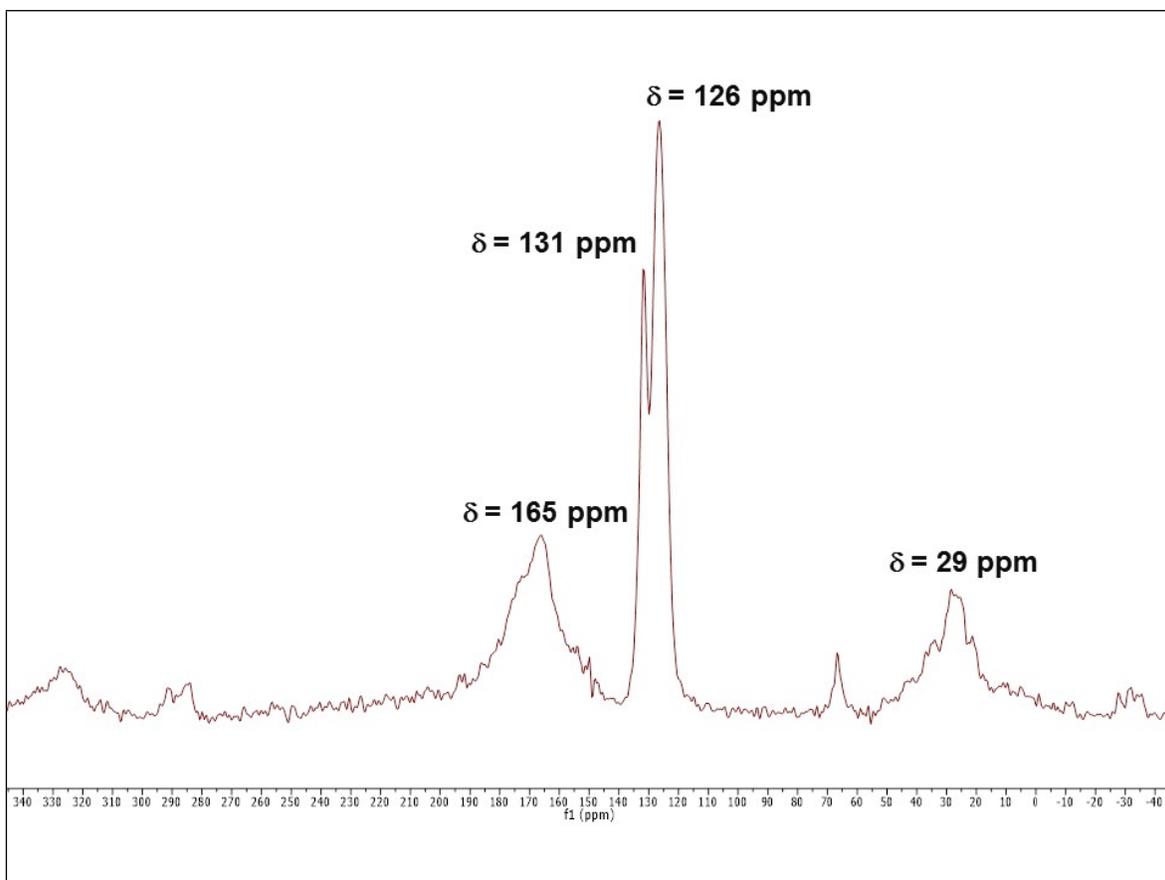
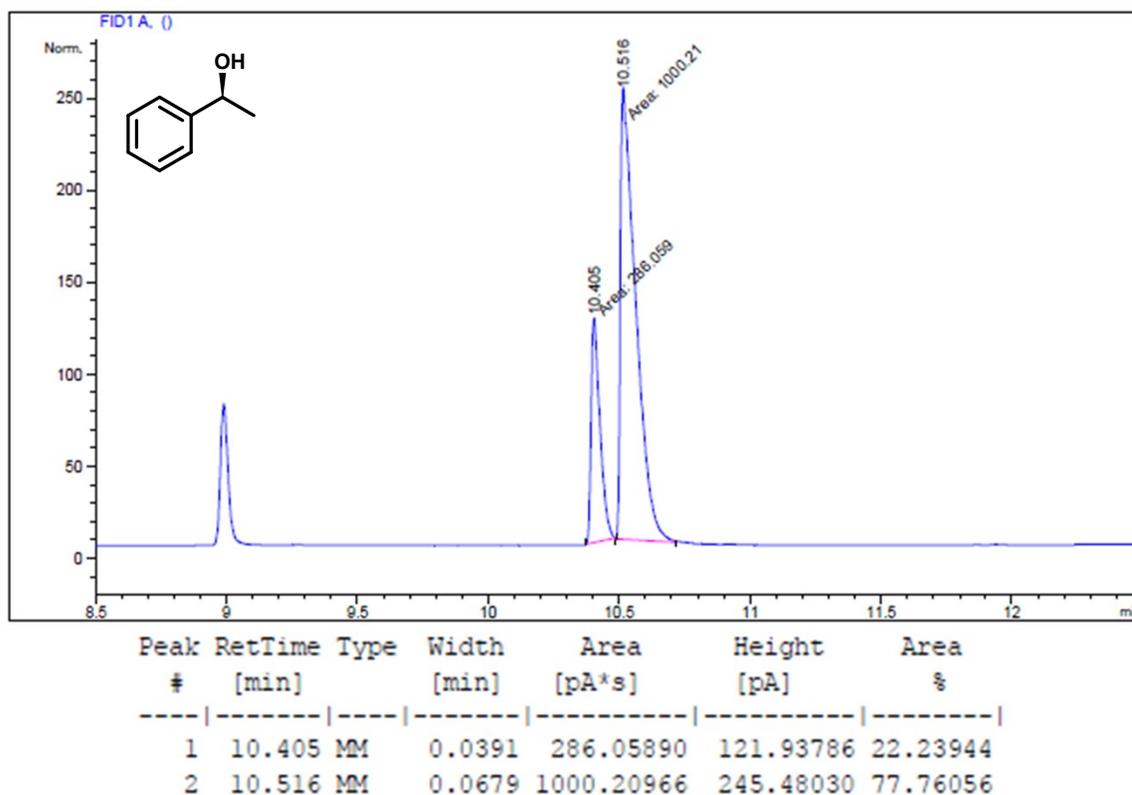


Figure S23. $^{13}\text{C}\{^1\text{H}\}$ CP-MAS NMR spectrum of IrNPs + ^{13}CO .

15. GC chromatograms of catalytic experiments

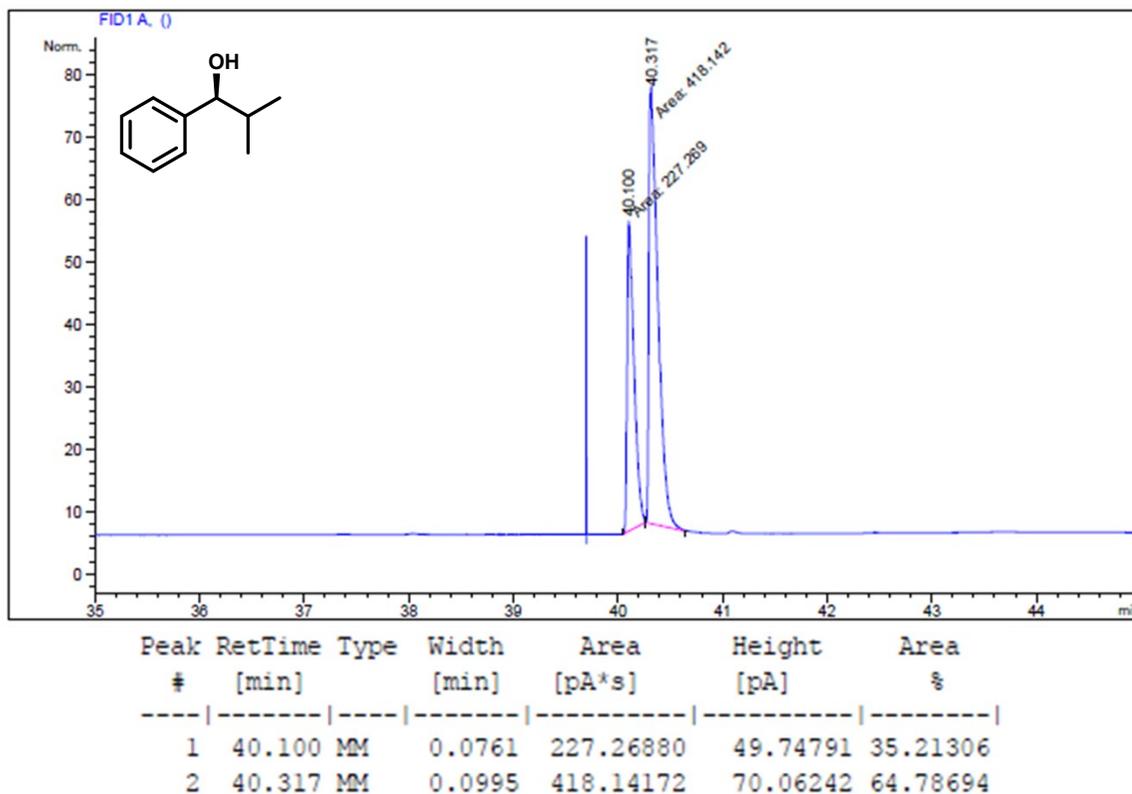
(S)-1-Phenylethanol (Table 2, entry 1)

Gas chromatography analyses were carried out on a GC-FID equipped with a β -DEX 120 (20% permethylated β -cyclodextrin in SPB-35 poly(35% phenyl/65% dimethylsiloxane); 30 m x 0.25 mm x 0.25 μ m). Gas flow, 1.0 mL/min; injection temperature, 280 °C; column temperature, 110 °C; t_R (R) = 10.40 min; t_R (S) = 10.52 min.



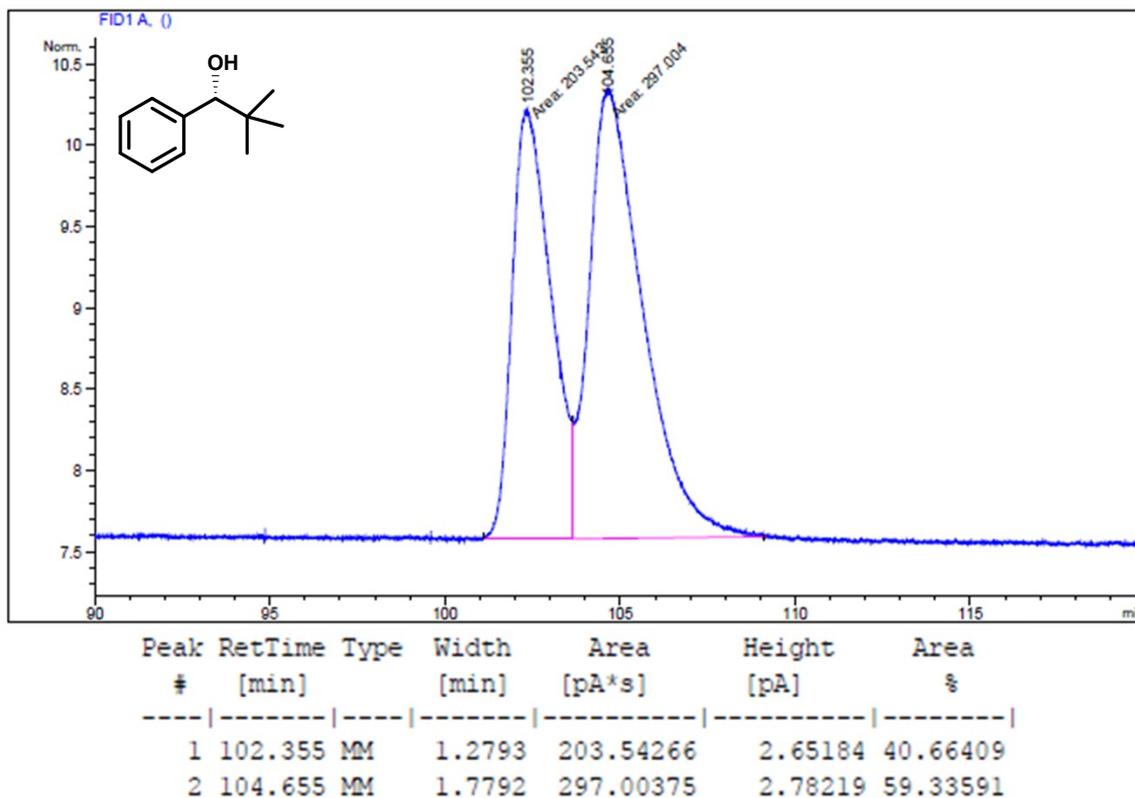
(S)-2-Methyl-1-phenyl-1-propanol (Table 2, entry 3)

The type of GC column and conditions (column temperature, 70 °C (30 min); 10 °C/min to 180 °C) were identical to those of (S)-1-phenylethanol; t_R (R) = 40.10 min; t_R (S) = 40.38 min.



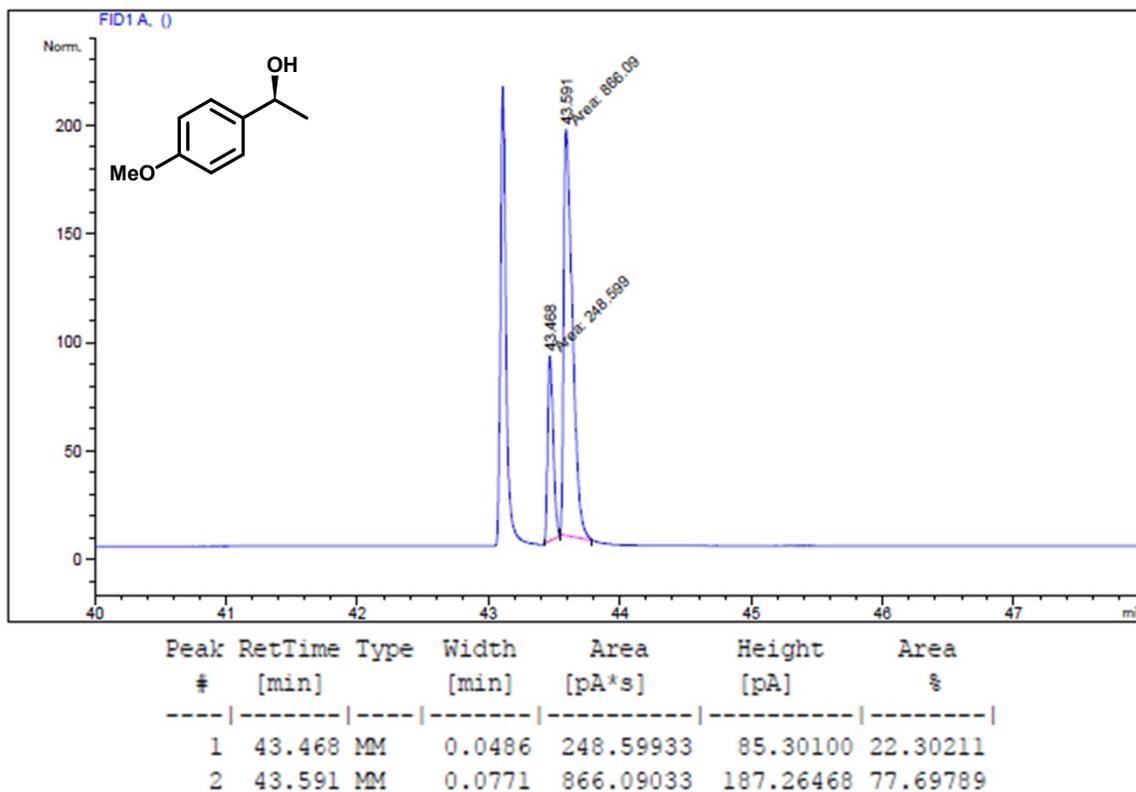
(R)-2,2-Dimethyl-1-phenyl-1-propanol (Table 2, entry 6)

The type of GC column and conditions (column temperature, 50 °C (80 min); 10 °C/min to 180 °C) were identical to those of (S)-1-phenylethanol; t_R (S) = 102.36 min; t_R (R) = 104.66 min.



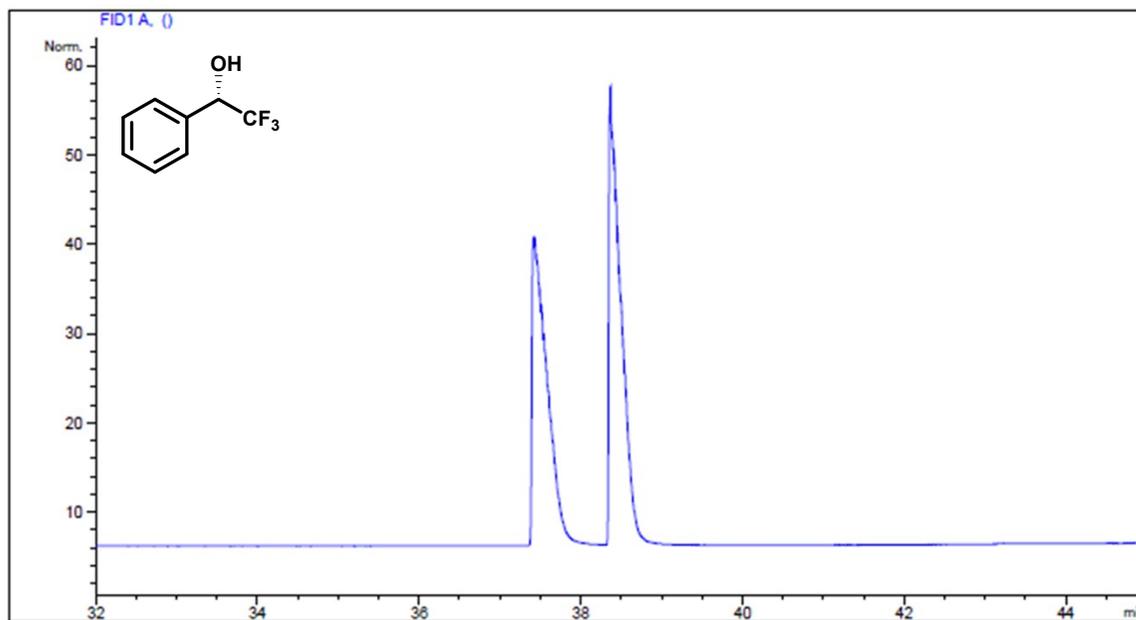
(S)-1-(4-Methoxyphenyl)ethanol (Table 2, entry 7)

The type of GC column and conditions (column temperature, 70 °C (30 min); 10 °C/min to 180 °C) were identical to those of (S)-1-phenylethanol; t_R (R) = 43.47 min; t_R (S) = 43.59 min.



(S)-1-phenyl-2,2,2-trifluoroethanol (Table 2, entry 9)

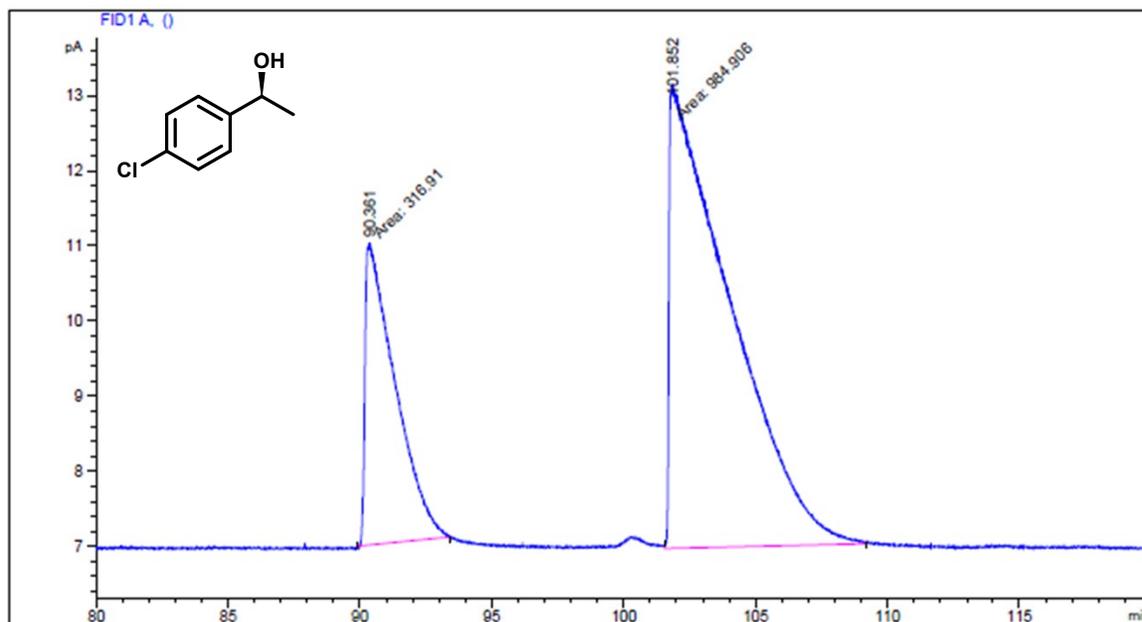
The type of GC column and conditions (column temperature, 70 °C (30 min); 10 °C/min to 180 °C) were identical to those of (S)-1-phenylethanol; t_R (R) = 37.44 min; t_R (S) = 38.37 min.



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	37.435	MM	0.2083	430.41510	34.43116	45.25996
2	38.373	MM	0.1688	520.56921	51.39795	54.74004

(S)-1-(3-Chlorophenyl)ethanol (Table 2, entry 11)

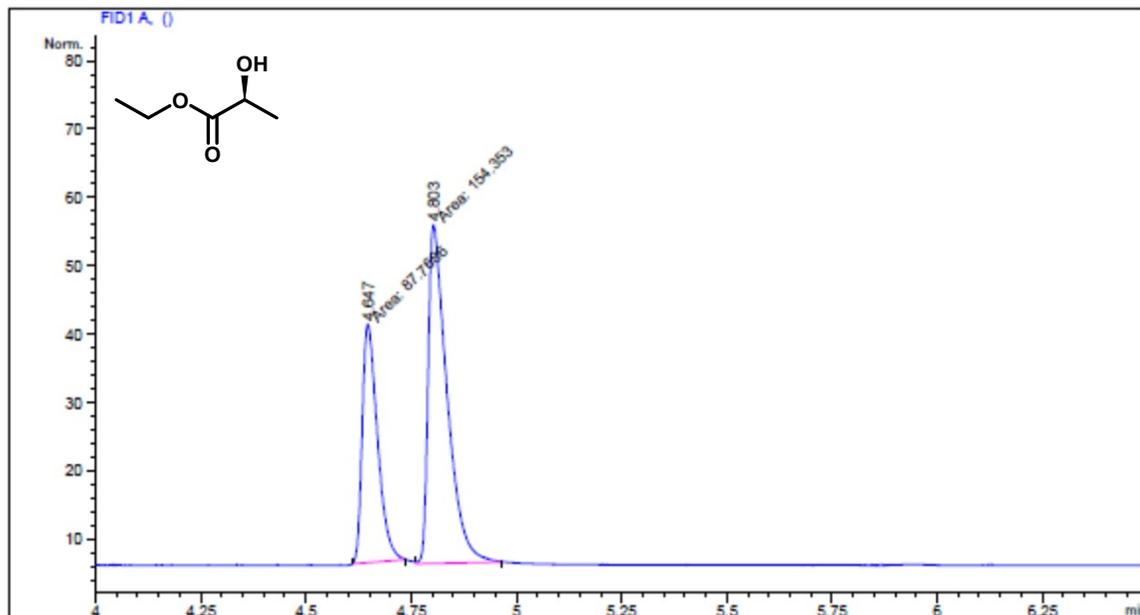
The type of GC column and conditions (column temperature, 50 °C (80 min); 10 °C/min to 180 °C) were identical to those of (S)-1-phenylethanol; t_R (R) = 90.36 min; t_R (S) = 101.85 min.



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	90.361	MM	1.3111	316.91013	4.02862	24.34369
2	101.852	MM	2.6526	984.90637	6.18821	75.65631

(S)-Ethyl 2-hydroxypropanoate (Table 2, entry 13)

The type of GC column and conditions (column temperature, 60 °C) were identical to those of (S)-1-phenylethanol; t_R (R) = 4.65 min; t_R (S) = 4.80 min.



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	4.647	MM	0.0419	87.76861	34.87364	36.24975
2	4.803	MM	0.0519	154.35333	49.57890	63.75025

16. References

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