Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Fullerenes for Catalysis: Metallofullerenes in Hydrogen Transfer Reactions

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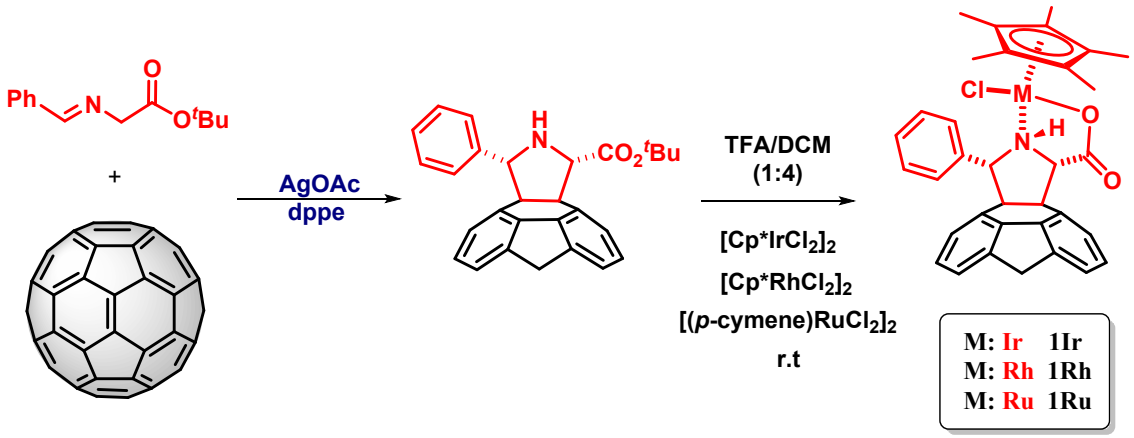
Contents

General Methods and Materials.

The commercially available reagents and solvents were used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a BRUKER AVANCE AMX-700 in $CDCl_3$ or CD_2Cl_2 at 25°C, and referenced to $CDCl_3$ or CD_2Cl_2; coupling constants (*J*) are reported in Hz and the chemical shifts (δ) in ppm. Mass spectra were reported on a HP1100EMD (ESI), and BRUKER-REFLEX (MALDI-TOF). Reactions were monitored by thin-layer chromatography carried out on 0.2 mm TLC-aluminium sheets of silica gel (Merck, TLC Silica gel 60 F_{254}). Flash column chromatographies were performed using silica gel (230-400 mesh). The relative yield of some products was carried out in HPLC, column: Buckyprep Waters (4.6 x 250 mm).

FTIR spectra were carried out using ATR of the solid compounds. The instrument used was a Bruker TENSOR FTIR. The spectral range was 4000-550 cm^{-1}.

Procedure for the synthesis of [(η^n-ring)M(Pyrrolidino[3,4:1,2][60]fullerene carboxylate)Cl].



Synthesis of *cis tert*-butyl 5-phenylpyrrolidine[3,4:1,2][60]fullerene-2-carboxylate.

Starting ^{t}Bu-pyrrolidino[3,4:1,2][60]fullerene esters were prepared following a similar procedure described previously by our research group:[1] A suspension of a mixture of silver acetate (0.023 mmol, 0.1 eq.) and dppe ligand (0.023 mmol, 0.1 eq.) in 50 mL of anhydrous toluene is prepared in a 100 ml one-neck round bottom flask. After 30 min of stirring at 25°C, α-iminoester (50 mg, 0.228 mmol, 1 eq.) is added to the solution. Later, [60]fullerene (160 mg, 0.228 mmol, 1 eq.) is added and the purple mixture stirred at 25°C for 2 h. Finally, the solvent is evaporated under vacuum and the dark residue is purified by silica-gel column chromatography using CS_2 as eluent (recovering unreacted [60]fullerene). Then, mixtures of hexane/DCM (2:1 to 1:1) and DCM were employed to obtain the desired products (20-25 % yield).

^{1}H NMR (700 MHz, $CDCl_3$): δ 7.77 (d, J = 7.5 Hz, 2H, Ph), 7.45 (t, J = 7.5 Hz, 2H, Ph), 7.37 (t, J = 7.5 Hz, 1H, Ph), 5.84 (br s, 1H, C_5H-pyrrolidine), 5.55 (br s, 1H, C_2H-pyrrolidine), 4.04 (br s, 1H, NH), 1.51 (s, 9H, ^{t}Bu) ppm.

^{13}C NMR (175MHz, $CDCl_3$): δ 168.51, 153.16, 153.05, 152.39, 150.93, 147.17, 147.06, 146.93, 146.43, 146.32, 146.29, 146.24, 146.22, 146.06, 146.03, 145.93, 145.76, 145.66, 145.60, 145.49, 145.44, 145.36, 145.33, 145.27, 145.24, 145.15, 144.48, 144.43, 144.34, 144.25, 143.16, 143.00, 142.71, 142.64, 142.38, 142.34, 142.22, 142.12, 142.08, 142.04, 141.99, 141.70, 141.59, 139.98, 139.68, 139.66, 138.91,

[1] Filippone, S.; Maroto, E.E.; Martín-Domenech, Á.; Suarez, M.; Martín, N. *Nat. Chem.* **2009,** *1*, 578.

137.13, 136.21, 136.16, 135.96, 135.41, 128.81, 128.72, 128.09, 83.77, 79.68, 76.01, 75.89, 73.61, 28.24 ppm.

HRMS (ESI+) $[M+H]^+$ Calc. for $C_{73}H_{18}NO_2$: 940.13321; found: 940.12899.

ATR-FTIR ν (C=O) = 1733 cm^{-1}.

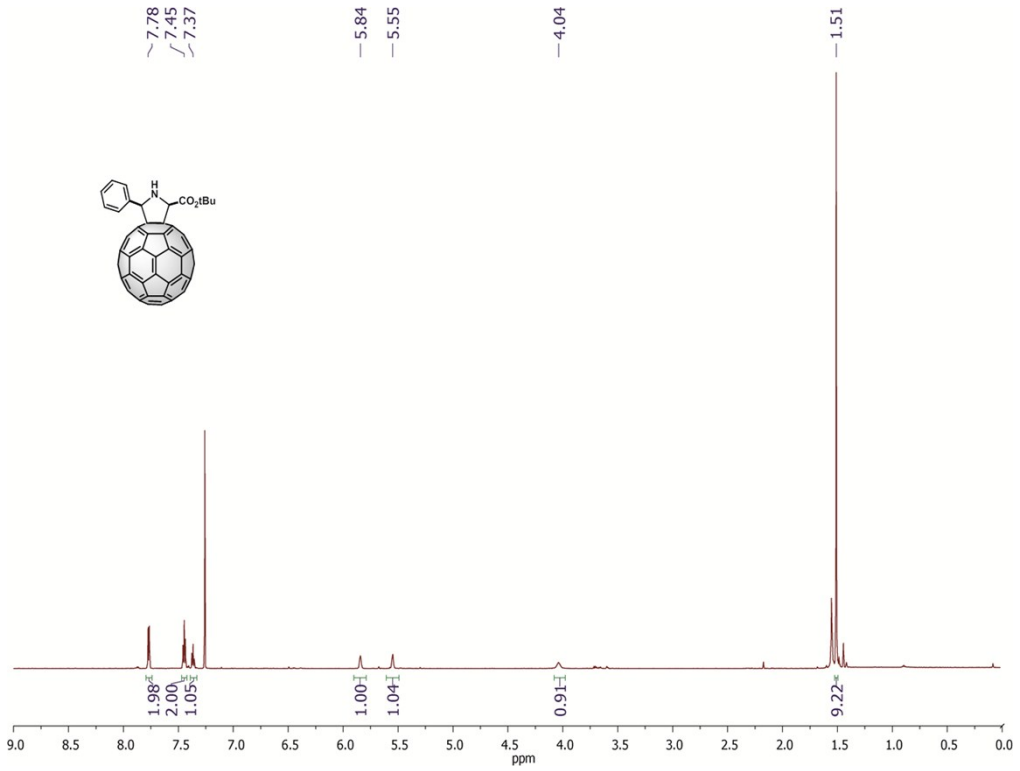


Figure S1. ^1H NMR (700 MHz, 298K, $CDCl_3$) of *cis tert*-butyl 5-phenylpyrrolidine[3,4:1,2][60]fullerene-2-carboxylate.

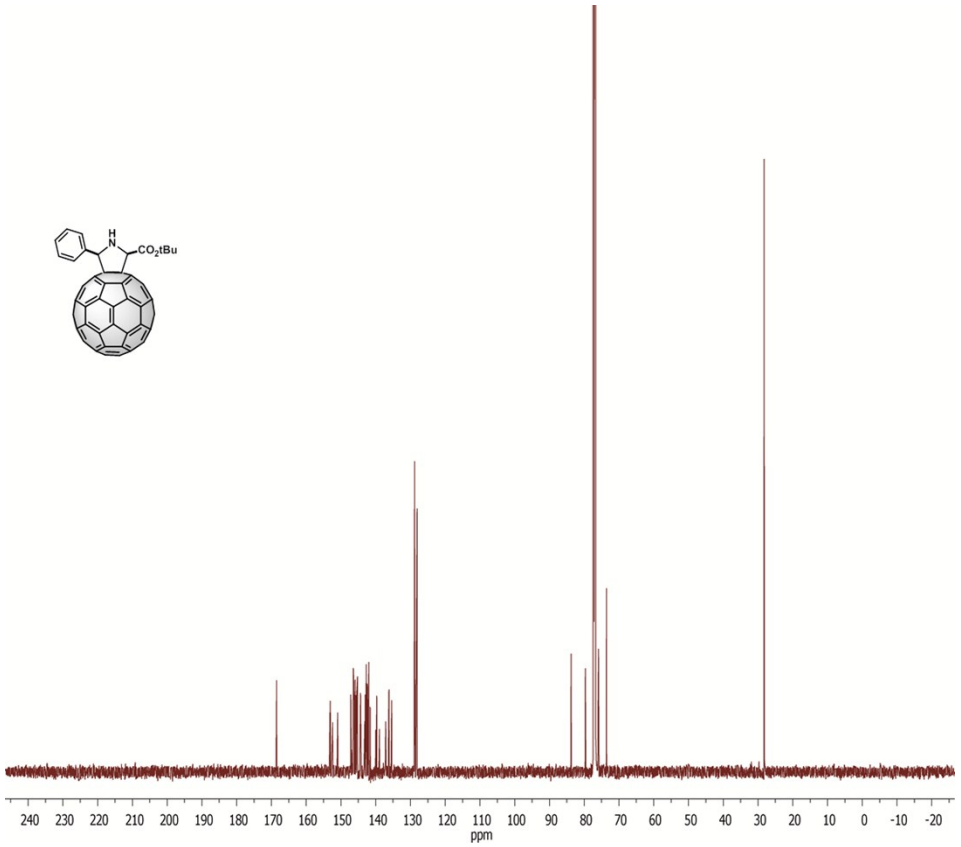
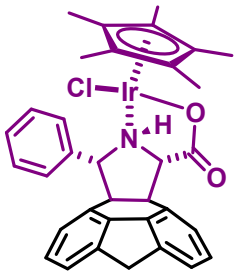


Figure S2. ^{13}C NMR (175 MHz, 298 K, $CDCl_3$) of *cis tert*-butyl 5-phenylpyrrolidine[3,4:1,2][60]fullerene-2-carboxylate.

Synthesis of [(η^n-ring)Ir(Pyrrolidino[3,4:1,2][60]fullerene carboxylate)Cl] 1.

Thereafter, a solution of the starting ^{t}Bu-pyrrolidino[3,4:1,2][60]fullerene ester (25 mg, 0.027 mmol, 1 eq.) and the corresponding metal dimer, (Ir, Rh or Ru, 0.5 eq.) in a mixture of DCM/TFA (2.5 mL, 4:1) is stirred for 2 h. Finally, the solvent is evaporated under vacuum and the dark residue is purified by silica-gel column chromatography in DCM and mixtures of DCM/MeOH (indicated in each case) to obtain the desired products. In all cases, dark brown solids were obtained and centrifuged in dry MeOH (2 x 2 mL, 15 min at 60 rpm) and dried under vacuum.



1Ir

^{1}H NMR (700 MHz, $CDCl_3$): δ 8.21 (d, *J* = 7.5 Hz, 1H, Ph), 7.55 (m, 2H, Ph), 7.38 (m, 2H, Ph), 6.88 (t, *J* = 13.1 Hz, 1H, NH), 6.12 (d, *J* = 13.1 Hz, 1H, C_5H-pyrrolidine), 5.69 (d, *J* = 13.1 Hz, 1H, C_2H-pyrrolidine), 1.64 (s, 15H, Me-Cp*) ppm.

^{13}C NMR (175MHz, $CDCl_3$): δ 171.01, 151.49, 150.17, 149.96, 149.71, 148.33, 147.89, 147.34, 147.17, 146.54, 146.39, 146.33, 146.27, 146.18, 146.09, 145.92, 145.84, 145.80, 145.72, 145.62, 145.38, 145.34, 144.96, 144.75, 144.51, 144.22, 144.04, 143.02, 142.86, 142.81, 142.77, 142.72, 142.62, 142.45, 142.02, 141.98, 141.78, 141.75, 141.67, 141.60, 141.56, 140.02, 139.83, 139.61, 139.00, 136.51, 136.20, 135.64, 132.69, 129.77, 129.31, 129.05, 128.75, 128.35, 85.35, 79.15, 77.61, 77.18, 72.28, 9.42 ppm.

MS (MALDI+) $[M\text{-}2H\text{-}Cl]^+$ Calc. for $C_{79}H_{21}NO_2Ir$: 1208.1; found: 1208.1. (MALDI-) $[M\text{-}2H]^+$ Calc. for $C_{79}H_{21}ClNO_2Ir$: 1243.1; found: 1243.1.

ATR-FTIR ν (C=O) = 1662 cm^{-1}.

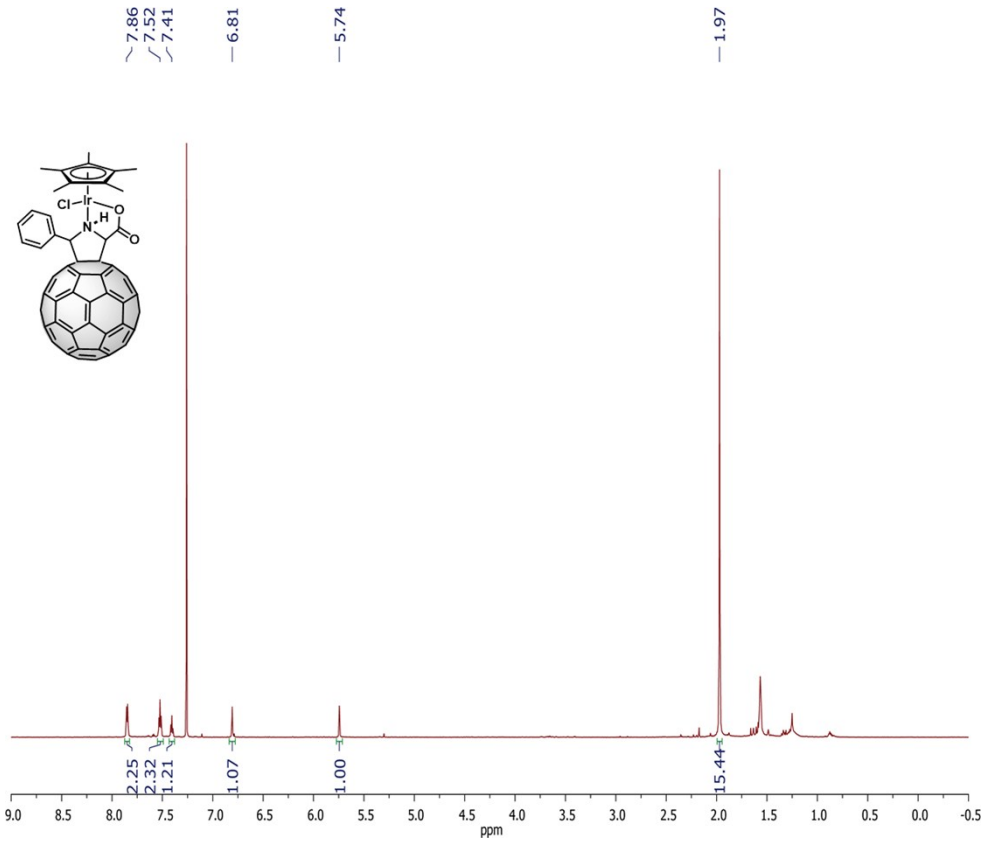


Figure S3. ^{1}H NMR (700 MHz, 298K, $CDCl_3$) of compound **1Ir**.

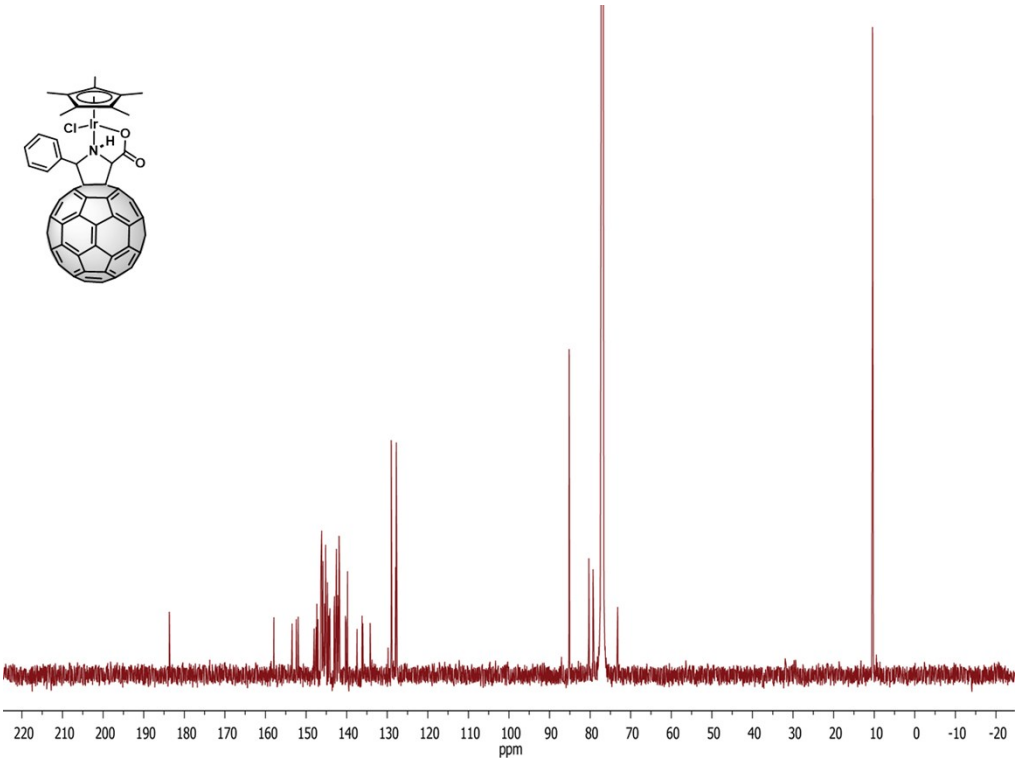
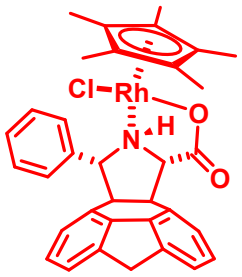


Figure S4. ^{13}C NMR (175 MHz, 298K, $CDCl_3$) of compound **1Ir**.



1Rh

^{1}H NMR (700 MHz, $CDCl_3$): δ 8.27 (s, 1H, Ph), 7.60-7.50 (m, 2H, Ph), 7.42-7.30 (m, 2H, Ph), 6.23 (d, J = 13.4 Hz, 1H, C_5H-pyrrolidine), 6.08 (t, J = 13.4 Hz, 1H, NH), 5.87 (d, J = 13.4 Hz, 1H, C_2H-pyrrolidine), 1.67 (s, 15H, Me-Cp*) ppm.

^{13}C NMR (175MHz, $CDCl_3$): δ 170.69 (C=O), 152.20, 150.63, 150.37, 150.11, 148.58, 148.23, 147.27, 147.15, 146.49, 146.41, 146.34, 146.29, 146.25, 146.14, 146.05, 145.88, 145.83, 145.59, 145.55, 145.34, 145.25, 145.10, 144.74, 144.47, 144.22, 144.06, 143.00, 142.84, 142.76, 142.69, 142.59, 142.37, 142.05, 142.01, 141.99, 141.85, 141.75, 141.60, 139.81, 139.60, 138.78, 136.62, 136.57, 136.12, 135.78, 133.14, 129.23, 94.13, 79.28, 77.23, 76.18, 72.58, 9.36 ppm.

MS (MALDI+) $[M+H_3O]^+$ Calc. for $C_{79}H_{23}ClNO_2Rh$: 1155.047; found: 1175.215.

ATR-FTIR ν (C=O) = 1647 cm^{-1}.

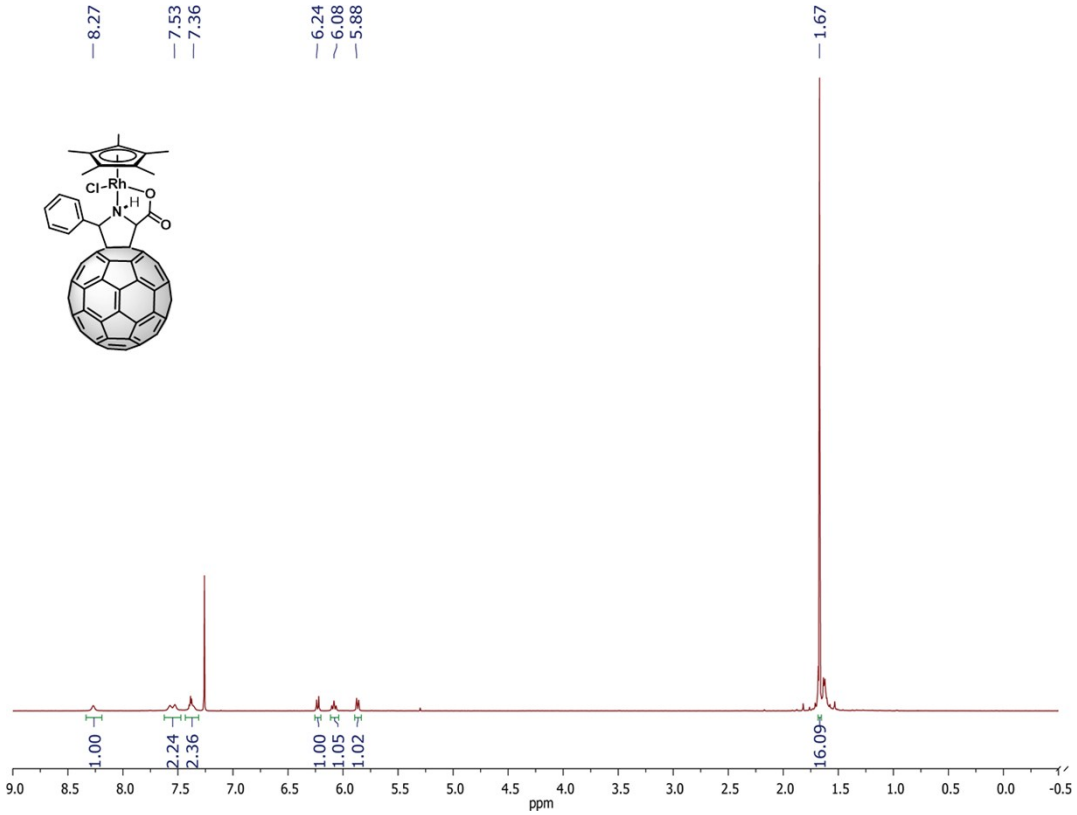


Figure S5. ^{1}H NMR (700 MHz, 298K, $CDCl_3$) of compound **2Rh**.

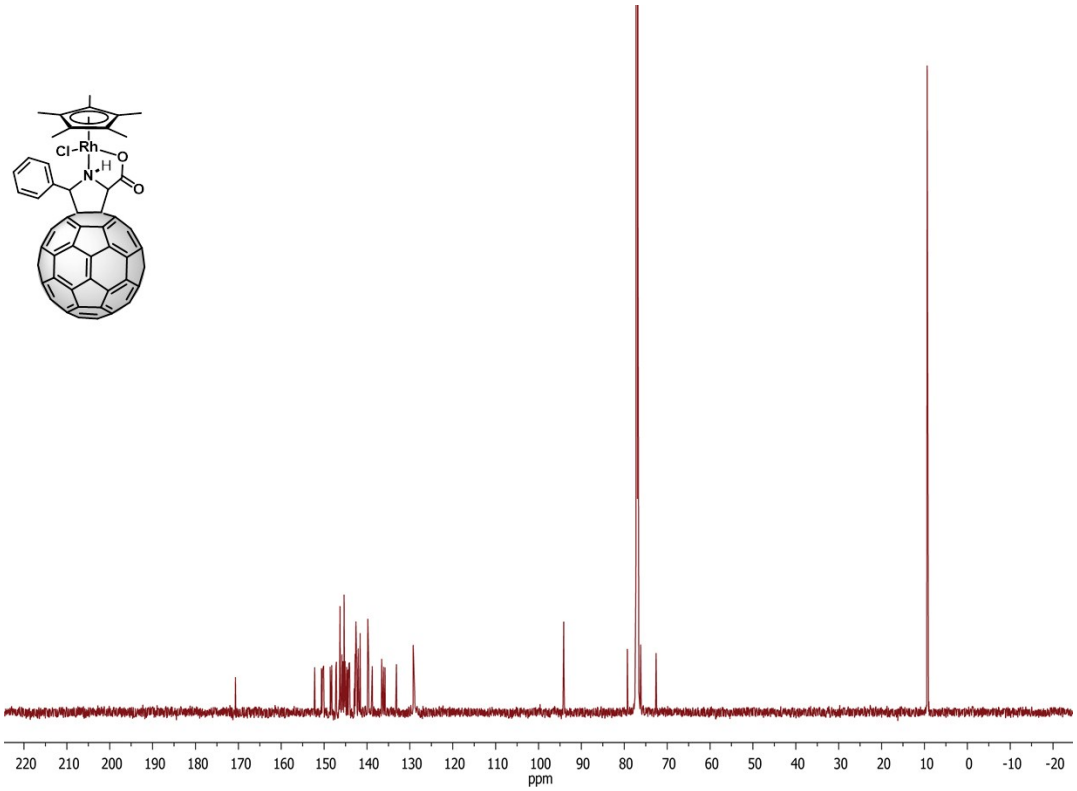
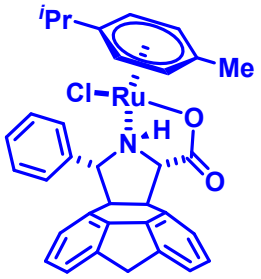


Figure S6. ^{13}C NMR (175 MHz, 298K, $CDCl_3$) of compound **2Rh**.



1Ru

^{1}H NMR (700 MHz, $CDCl_3$): δ 7.97 (d, *J* = 7.5 Hz, 1H, Ph), 7.76 (d, *J* = 7.3 Hz, 1H, Ph), 7.59 (t, *J* = 7.5 Hz, 1H, Ph), 7.50 (t, *J* = 7.5 Hz, 1H, Ph), 7.47 (t, *J* = 7.5 Hz, 1H, Ph), 6.26 (d, *J* = 13.1 Hz, 1H, C_5H-pyrrolidine), 5.77 (t, *J* = 13.1 Hz, 1H, NH), 5.74 (d, *J* = 5.8 Hz, 1H, $C_{3'\text{-}5'}$Hcym), 5.70 (d, *J* = 5.8 Hz, 1H, $C_{2'\text{-}6'}$Hcym), 5.65 (d, *J* = 13.1 Hz, 1H, C_2H-pyrrolidine), 5.34 (d, *J* = 6.0 Hz, 1H, $C_{3'\text{-}5'}$Hcym), 5.21 (d, *J* = 5.0 Hz, 1H, $C_{2'\text{-}6'}$Hcym), 2.71 (ht, *J* = 7.0 Hz, 1H, CH ^{i}Pr-cym), 2.11 (s, 3H, Me-cym), 1.38 (d, *J* = 6.8 Hz, 3H, Me-^{i}Pr), 1.23 (d, *J* = 6.9 Hz, 3H, Me-^{i}Pr) ppm.

^{13}C NMR (175MHz, $CDCl_3$): δ 170.22 (C=O), 151.43, 150.40, 149.75, 149.47, 148.22, 147.56, 147.37, 147.17, 146.55, 146.41, 146.26, 146.19, 146.10, 145.92, 145.78, 145.73, 145.65, 145.40, 145.36, 145.33, 145.29, 144.88, 144.74, 144.51, 144.21, 144.00, 143.03, 142.86, 142.81, 142.76, 142.72, 142.61, 142.53, 142.02, 141.95, 141.84, 141.73, 141.61, 141.48, 140.15, 139.96, 139.69, 139.14, 136.46, 136.22, 135.35, 132.97, 129.83, 129.71, 129.31, 129.12, 129.06, 128.89, 128.25, 104.60, 94.43, 82.84, 80.94, 80.31, 79.32, 78.37, 78.15, 77.34, 71.79, 31.24, 22.54, 22.38, 18.47 ppm.

HRMS (MALDI+) $[M+Na]^+$ Calc. for $C_{79}H_{22}ClNNaO_2Ru$: 1176.0293; found: 1176.0250.

ATR-FTIR ν (C=O) = 1657 cm^{-1}.

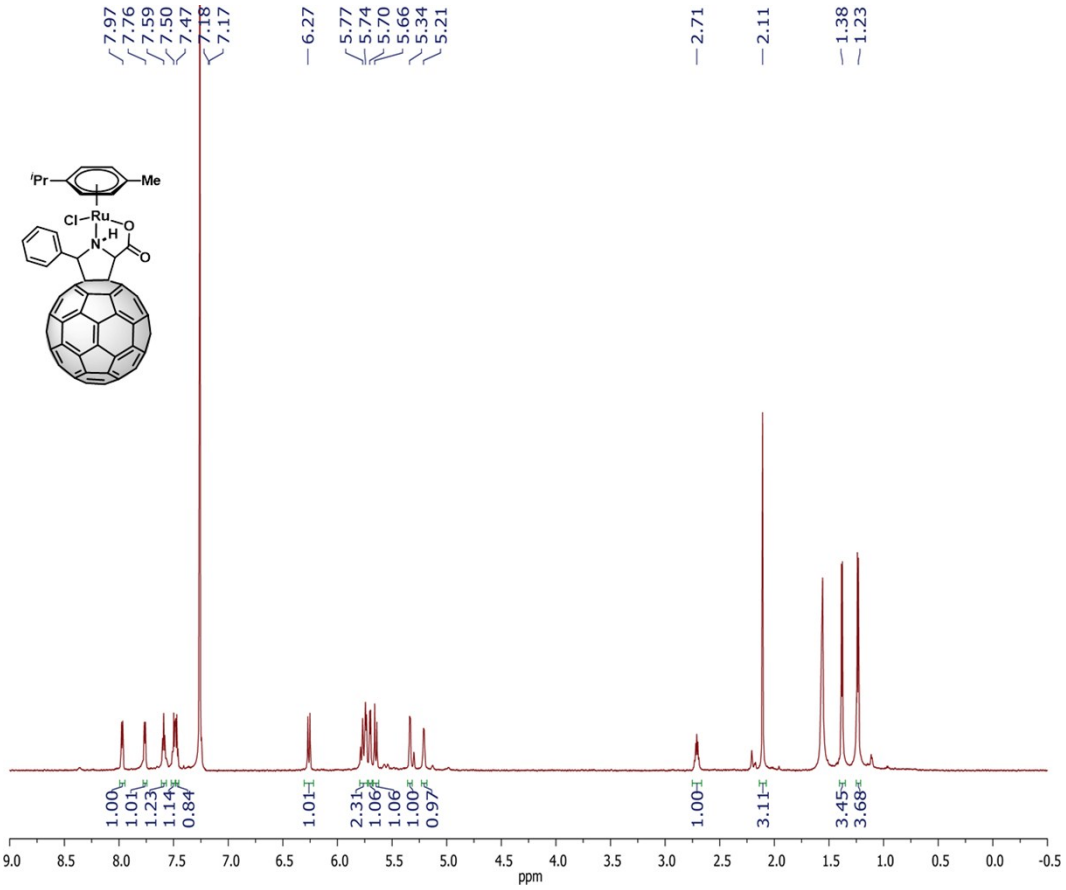


Figure S7. ^{1}H NMR (700 MHz, 298K, $CDCl_3$) of compound **3Ru**.

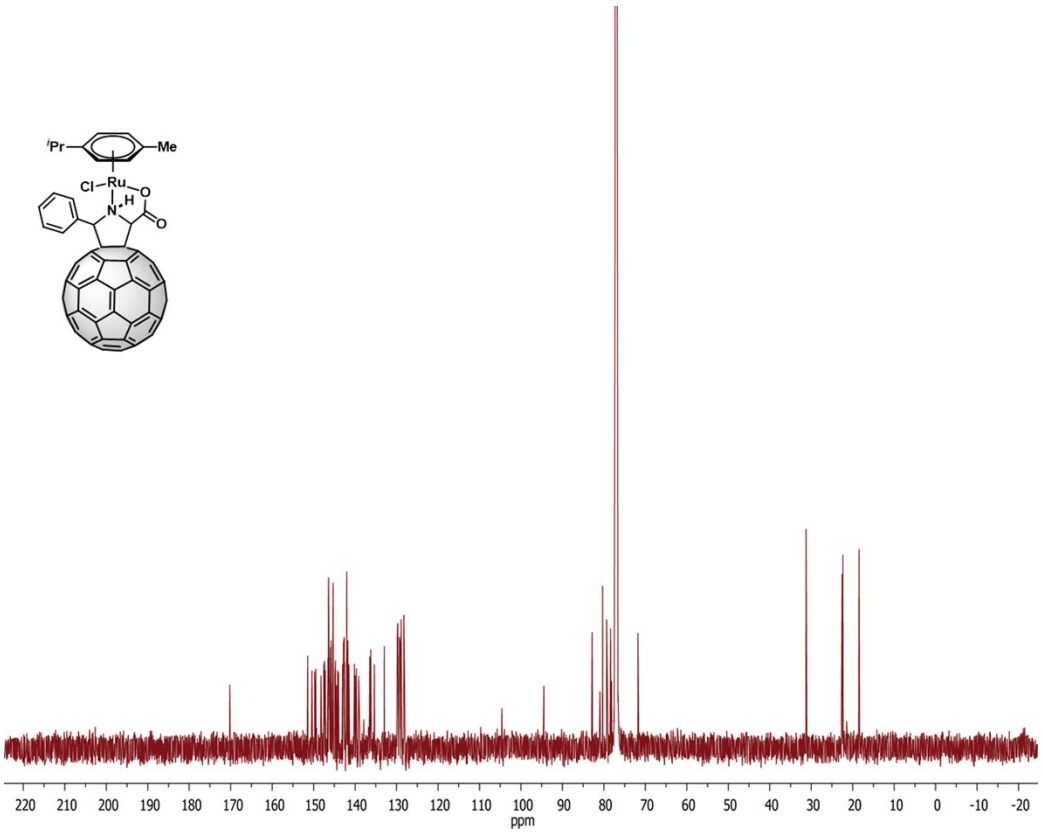


Figure S8. ^{13}C NMR (175 MHz, 298K, $CDCl_3$) of compound **3Ru**.

General procedure for Ketones Reduction with Isopropanol.

A suspension of prepared metallo-fulleropyrrolidines (**1Ir**, **1Rh**, **1Ru**) ($1.6 \cdot 10^{-3}$ mmol, 0.5%), or iridium dimer complex ($1.6 \cdot 10^{-3}$ mmol, 0.5%), K_2CO_3 ($1.6 \cdot 10^{-3}$ mmol, 0.5%) and acetophenone (0.32 mmol, 1 eq.) in 2 mL of isopropanol is bubbled with argon for 15 min and then, refluxed for 18 h. Once separated from the catalyst by mechanical means (filtration or centrifugation, see below), the product is isolated by solvent removal and analyzed without any further purification.

General procedure to recover the catalyst

Once carried out the reaction, the catalyst is precipitated at room temperature by adding methanol to the crude of reaction. The solution is centrifuged at 6000 rpm during 20 minutes and this procedure is repeated for three times. Finally, after solvent evaporation, the product formed is fully characterized by spectroscopic techniques and the yield determined by ^{1}H-NMR. The isolated solid catalyst is employed (recycled) in a new reaction without any further purification. **It is important to note that the recovered catalyst should be used immediately (or stored under argon atmosphere) to prevent catalyst oxidation!**

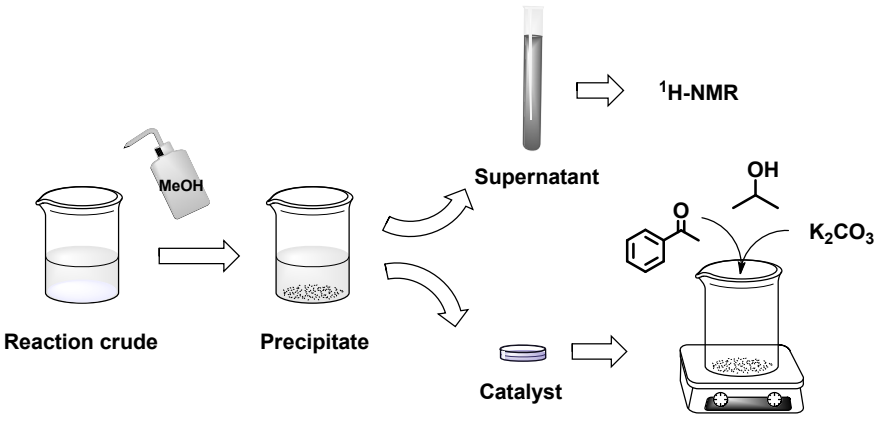


Figure S9. Procedure to recycle the catalyst from the reaction medium.

Representative ^{1}H-NMR spectra.

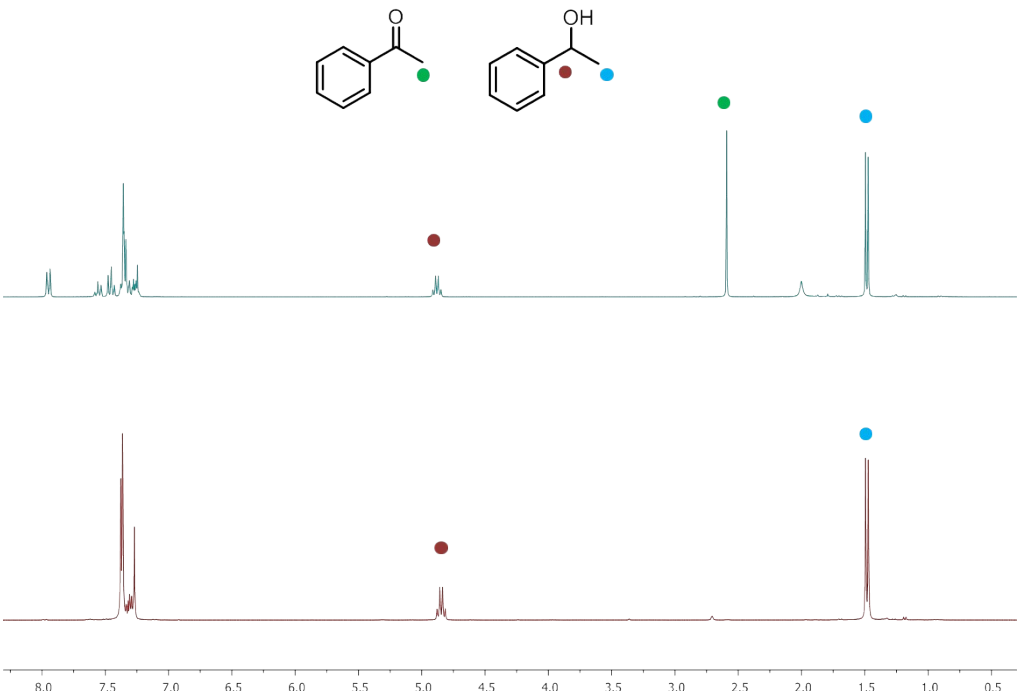


Figure S10. ^{1}H NMR (300 MHz, 298K, $CDCl_3$) spectra from the reaction crude (without any purification) of acetophenone catalyzed by iridium dimer complex (top) and **1Ir** (bottom) (table 1, entries 1 and 2). Please, note than in the second case (bottom), the reagent (acetophenone) has been totally consumed (> 99%).

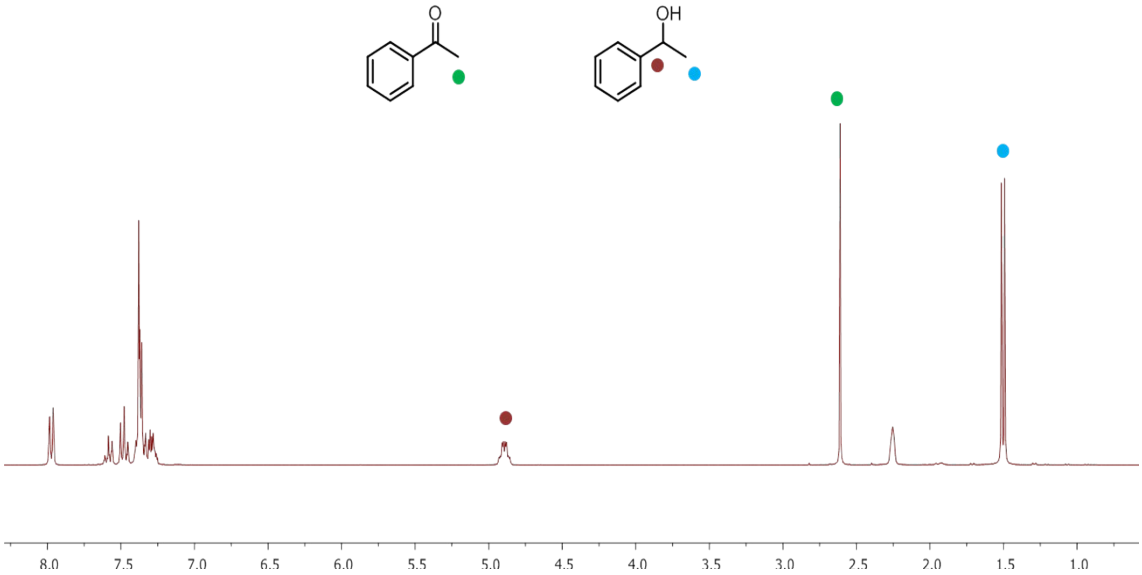


Figure S11. ^{1}H NMR (300 MHz, 298K, $CDCl_3$) spectrum of the reaction crude catalyzed by 0.1% of **1Ir** (table 1, entry 3).

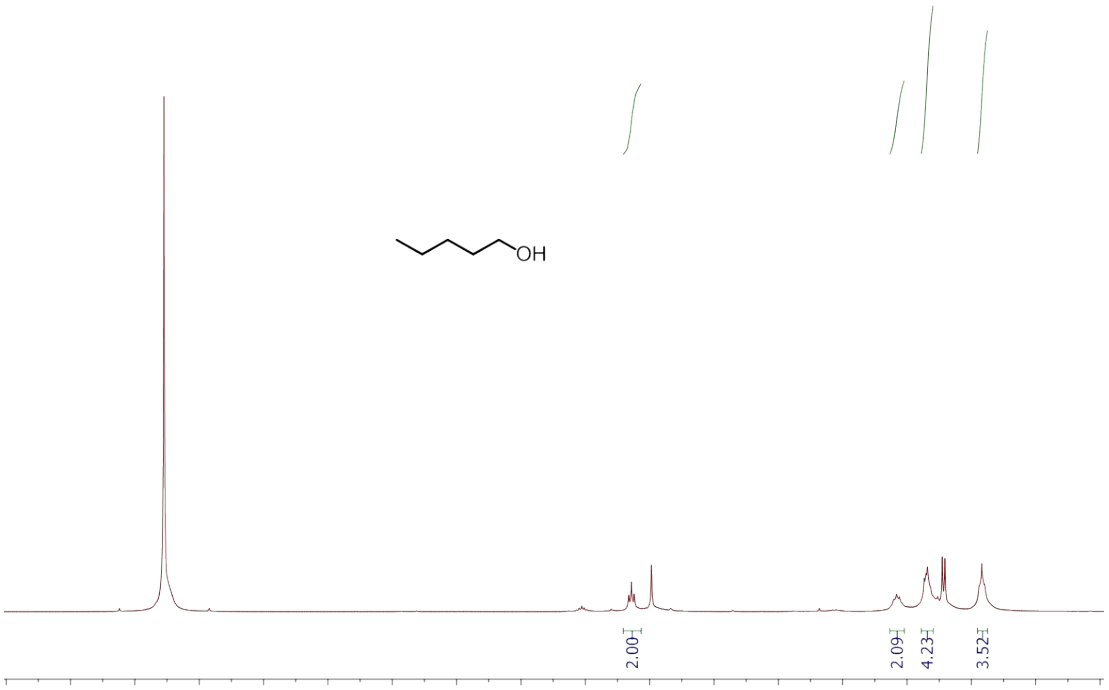


Figure S12. ^{1}H NMR (300 MHz, 298K, $CDCl_3$) spectrum of the reaction crude catalyzed by 0.5% of **1Ir** (table 1, entry 10).

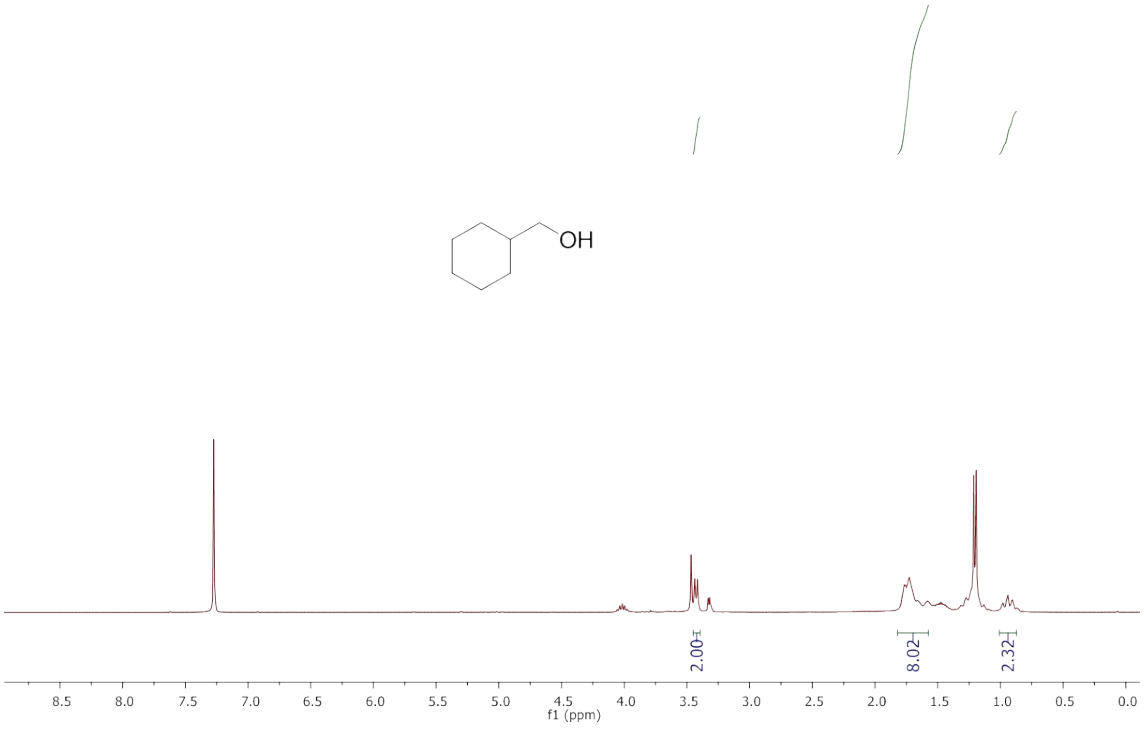


Figure S13. ^{1}H NMR (300 MHz, 298K, $CDCl_3$) spectrum of the reaction crude catalyzed by 0.5% of **1Ir** (table 1, entry 11).

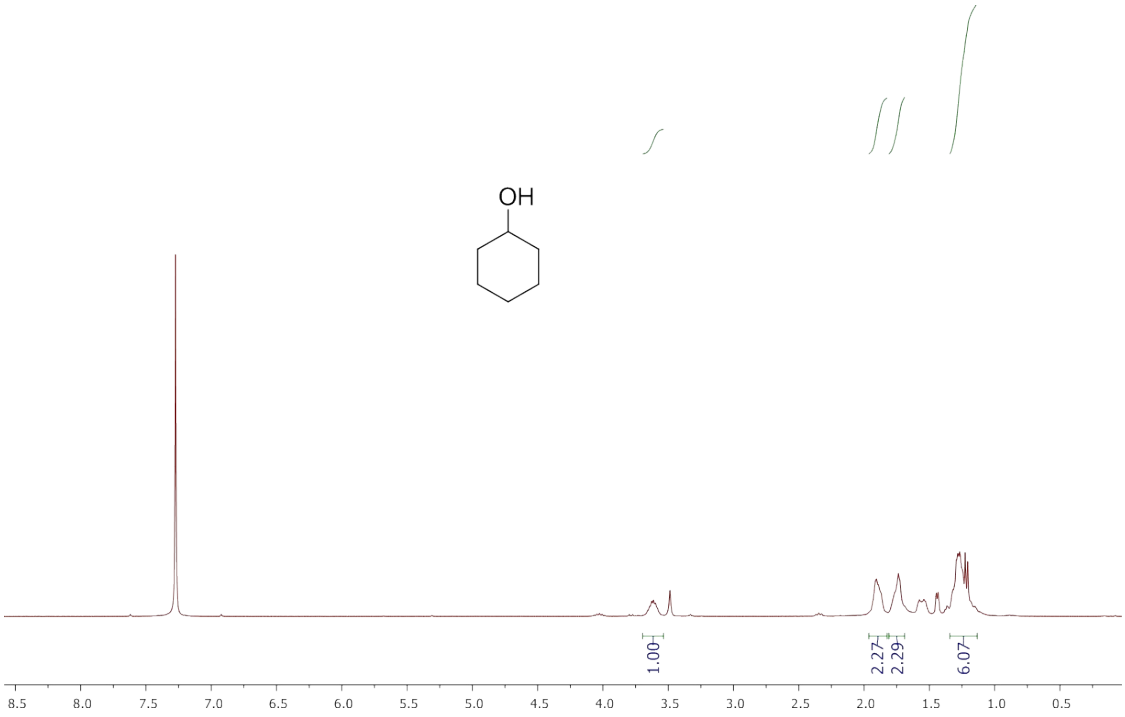


Figure S14. ^{1}H NMR (300 MHz, 298K, $CDCl_3$) spectrum of the reaction crude catalyzed by 0.5% of **1Ir** (table 1, entry 12).

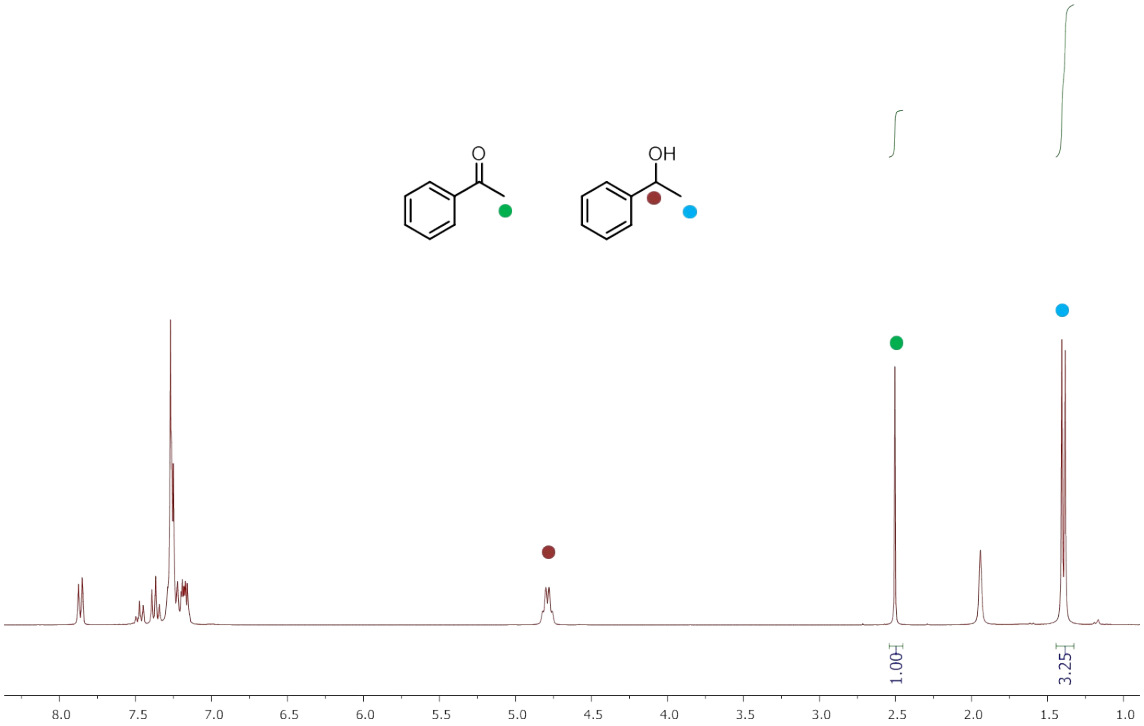


Figure S15. ^{1}H NMR (300 MHz, 298K, $CDCl_3$) spectrum of the reaction crude catalyzed by 0.5% of **1Rh** (table 1, entry 13).

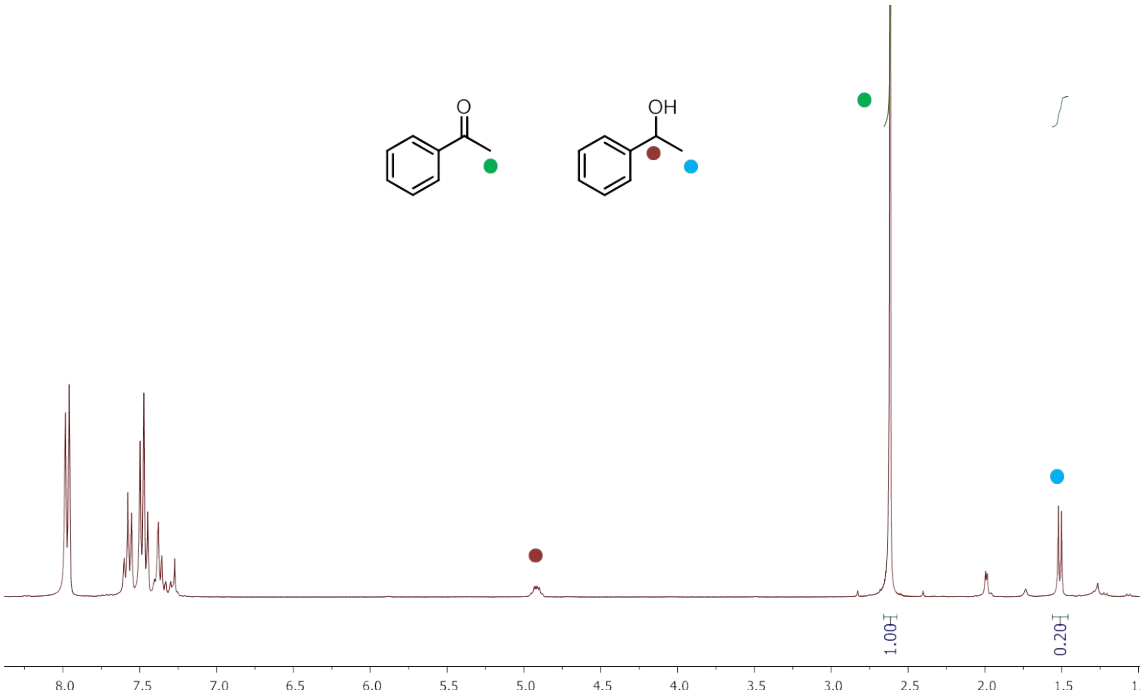


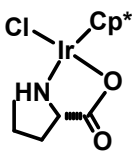
Figure S16. ^{1}H NMR (300 MHz, 298K, $CDCl_3$) spectrum of the reaction crude catalyzed by 0.5% of **1Ru** (table 1, entry 14).

General Procedure for the *N*-alkylation of Amines with Alcohols by Hydrogen Borrowing Mechanism.

A mixture of amine (1eq.), alcohol (1.2 eq.), base (same equivalent as that of the catalyst) and catalyst, in 0.5 mL of dry toluene, was refluxed into a 1 mL sealed vial for 17 h. In the case of secondary alcohols, the reaction was carried out in a ratio 1:1 amine:alcohol in 0.1 mL of dry toluene.

Procedure for the synthesis of Cp*-Iridium prolinate 2.

The iridium complex **2** was prepared following the methodology described in the literature.[2]



2

[2] (a) Wetzel, A.; Wöckel, S.; Schelwies, M.; Brinks, M. K.; Rominger, F.; Hofmann, P.; Limbach, M. *Org. Lett.* **2013**, *15*, 266. (b) Carmona, D.; Pilar Lamata, M.; Viguri, F.; San José, E.; Mendoza, A.; Lahoz, F. J.; García-Orduña, P.; Atencio, R.; Oro, L. A. *J. Organomet. Chem.* **2012**, *717*, 152.

Representative ^{1}H NMR spectra.

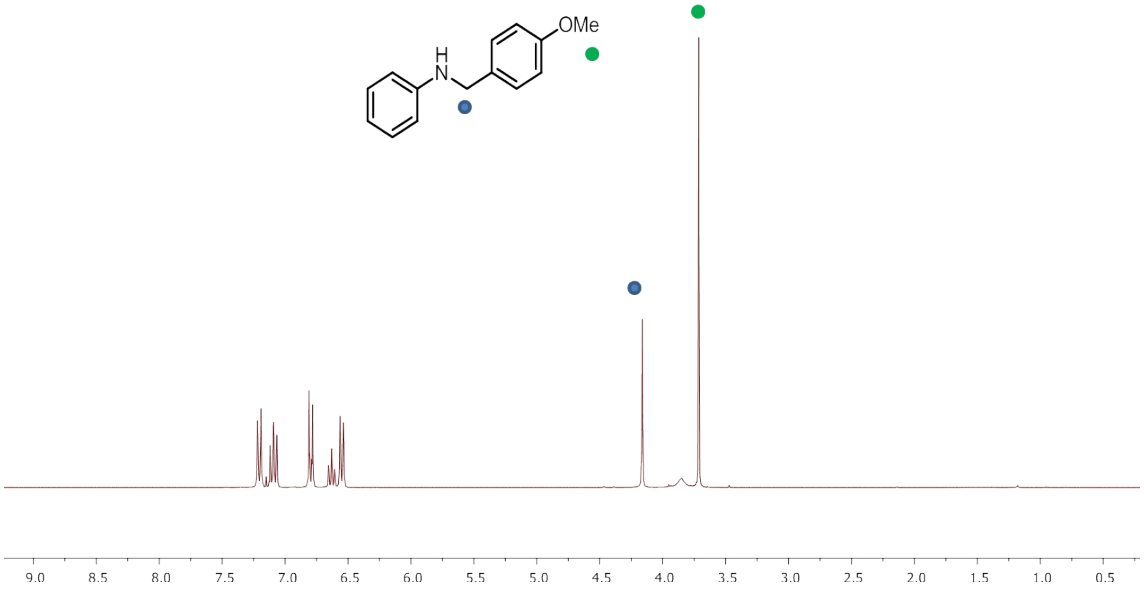


Figure S17. ^{1}H NMR (300 MHz, 298K, $CDCl_3$) spectrum of the reaction crude catalyzed by 1.25% of **1Ir** (table 2, entry 3).

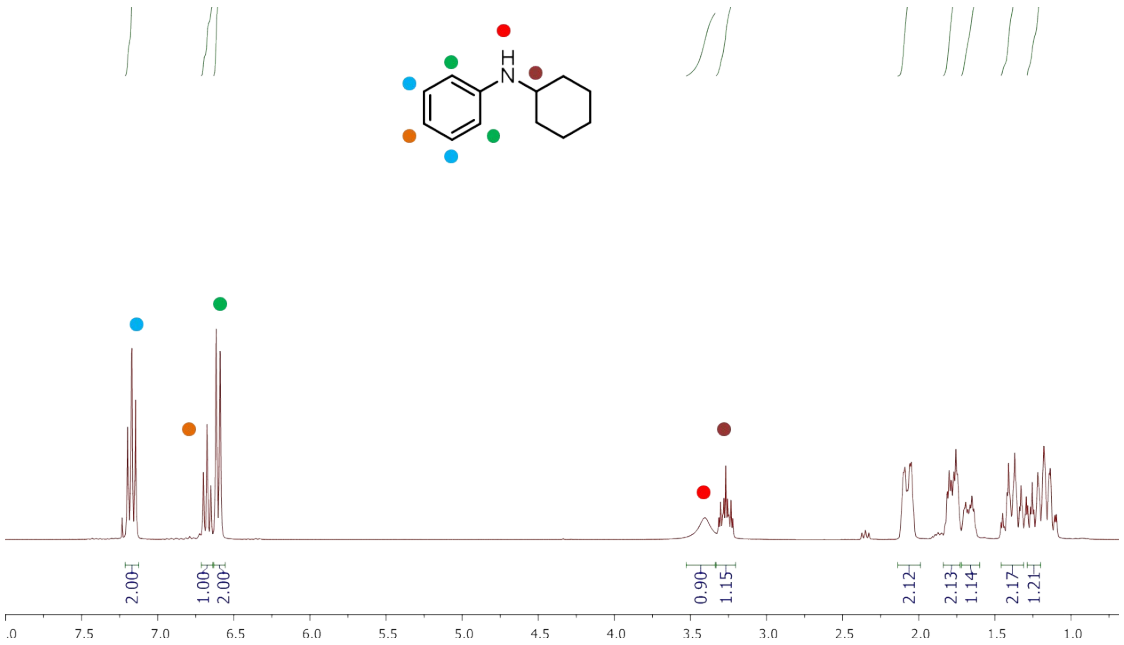


Figure S18. ^{1}H NMR (300 MHz, 298K, $CDCl_3$) spectrum of the reaction crude catalyzed by 1.25% of **1Ir** (table 2, entry 4).

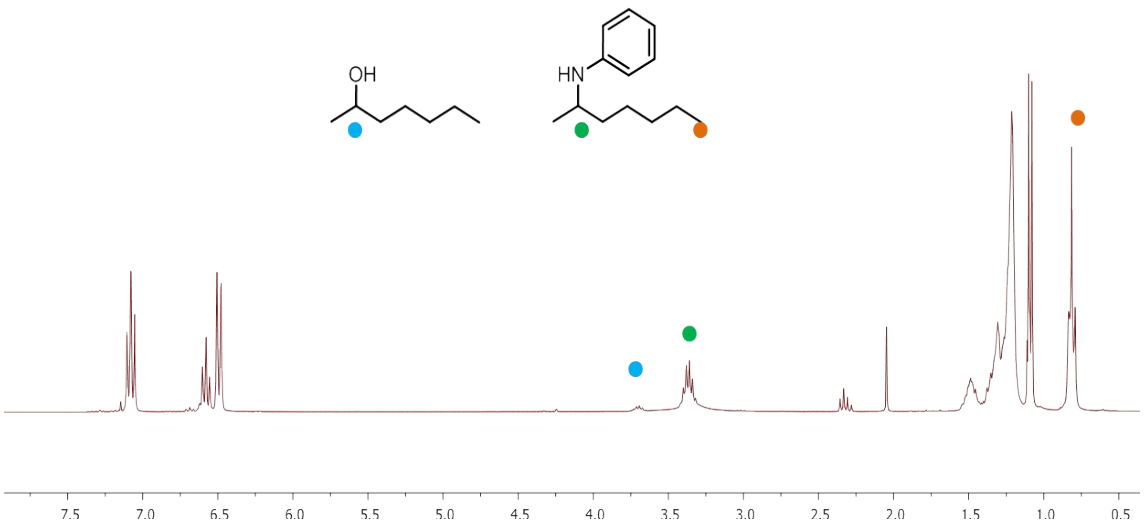


Figure S19. ^{1}H NMR (300 MHz, 298K, $CDCl_3$) spectrum of the reaction crude catalyzed by 1.25% of **1Ir** (table 2, entry 5).

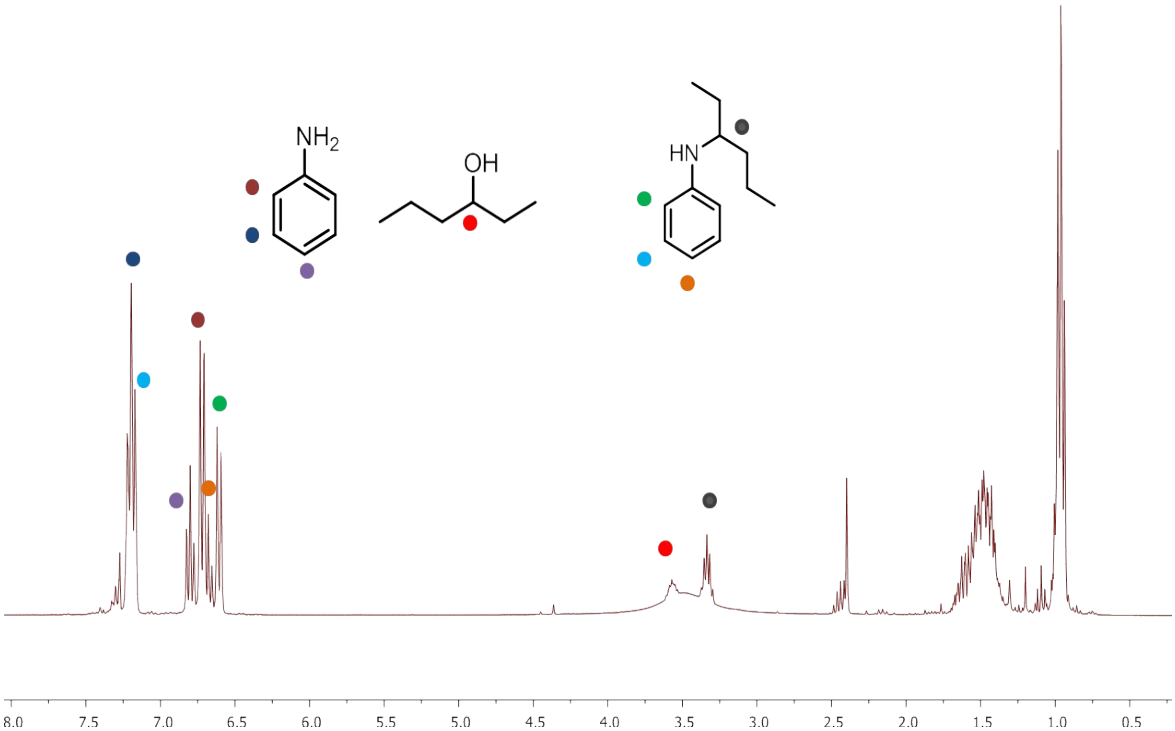


Figure S20. ^{1}H NMR (300 MHz, 298K, $CDCl_3$) spectrum of the reaction crude catalyzed by 1.25% of **1Ir** (table 2, entry 6).

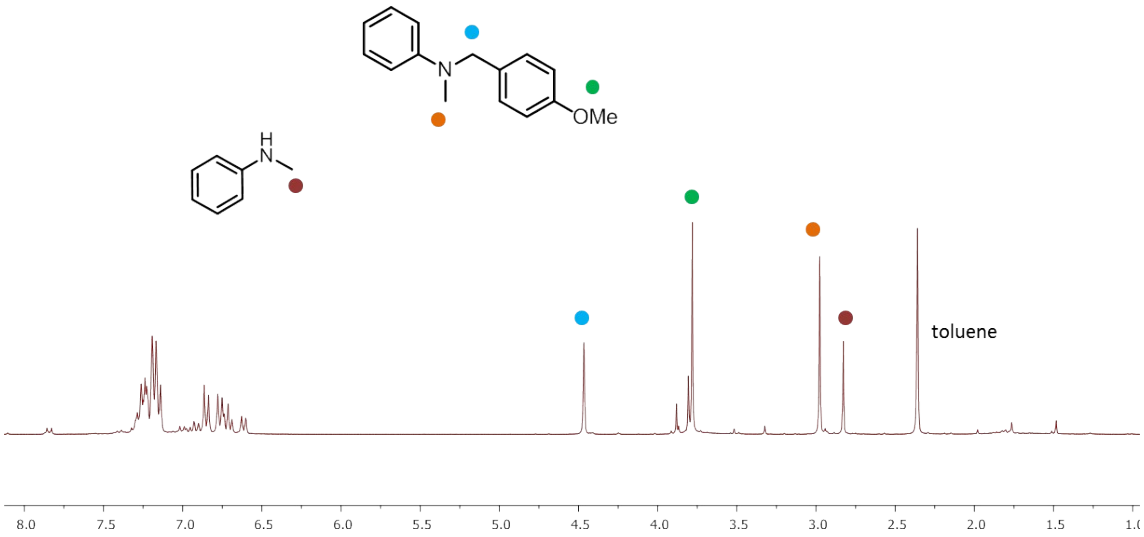


Figure S21. ^{1}H NMR (300 MHz, 298K, $CDCl_3$) spectrum of the reaction crude catalyzed by 4% of iridium dimer complex (table 2, entry 7).

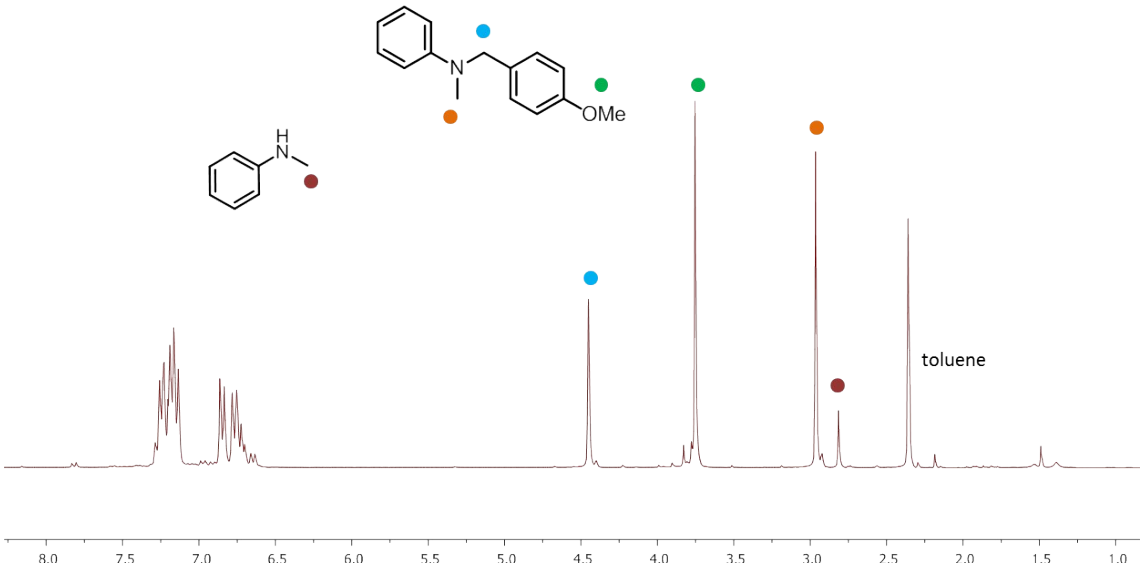


Figure S22. ^{1}H NMR (300 MHz, 298K, $CDCl_3$) spectrum of the reaction crude catalyzed by 4% of **1Ir** (table 2, entry 8).

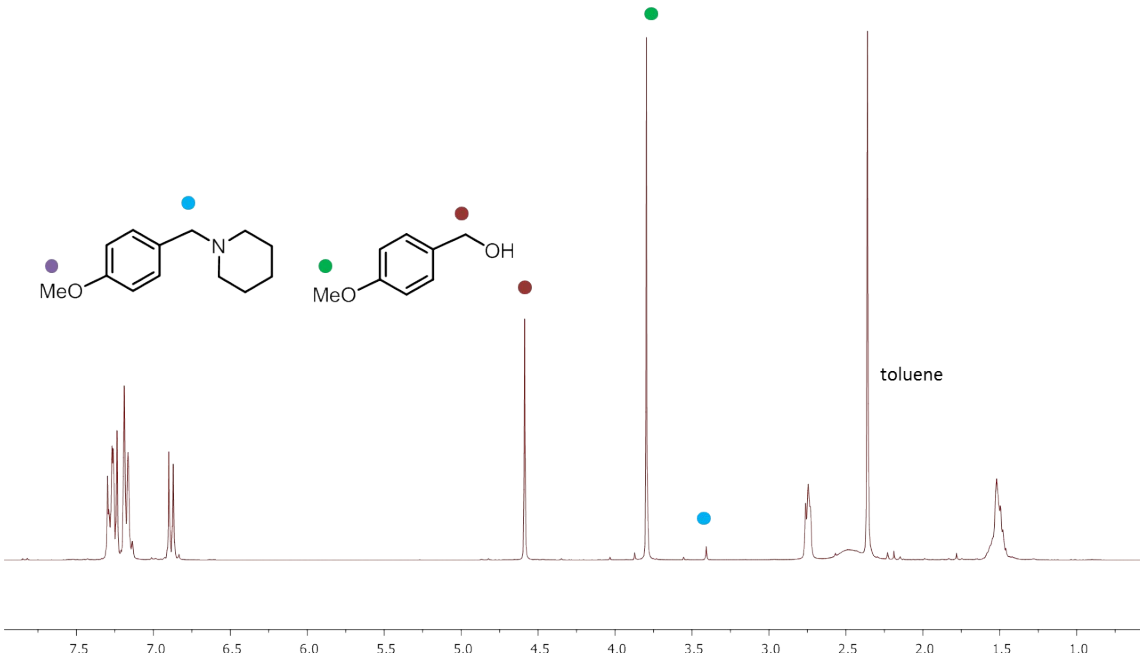


Figure S23. ^{1}H NMR (300 MHz, 298K, $CDCl_3$) spectrum of the reaction crude catalyzed by 2% of iridium dimer complex (table 2, entry 9).

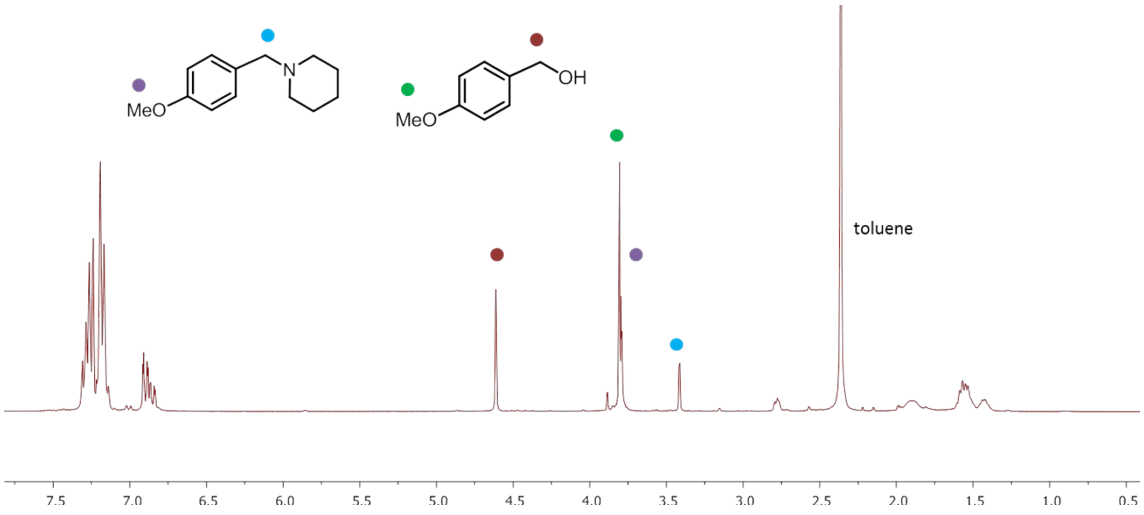


Figure S24. ^{1}H NMR (300 MHz, 298K, $CDCl_3$) spectrum of the reaction crude catalyzed by 2% of **1Ir** (table 2, entry 10).

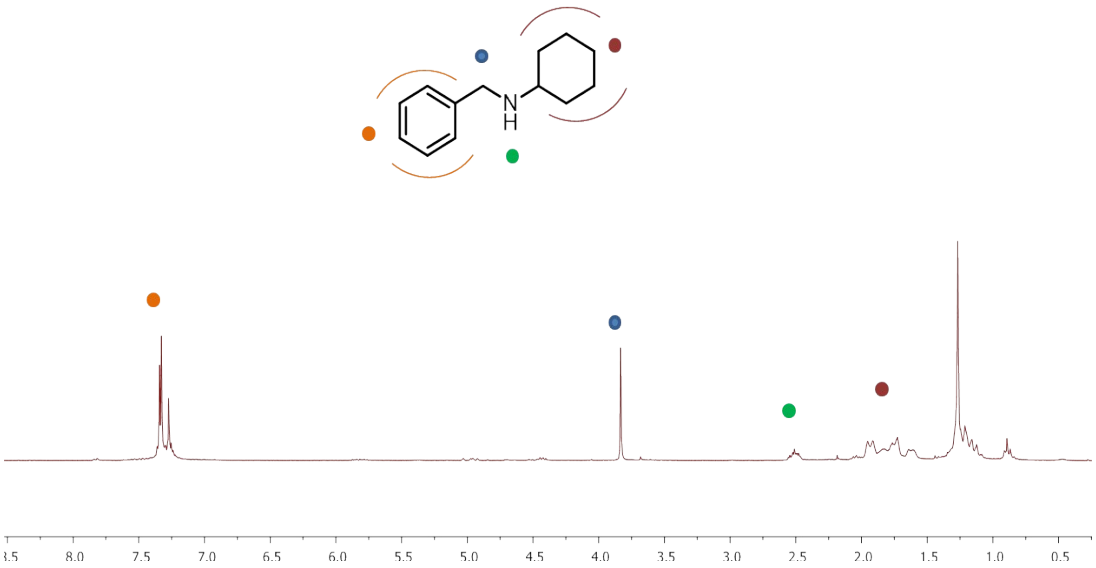


Figure S25. ^{1}H NMR (300 MHz, 298K, $CDCl_3$) spectrum of the reaction crude catalyzed by 1.25% of **1Ir** (table 2, entry 11).