Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for

An air and moisture tolerant iminotrihydroquinoline-ruthenium(II) catalyst for the transfer hydrogenation of ketones

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Contents

1. General Considerations

All manipulations involving ruthenium complexes, unless stated otherwise, were carried out under a nitrogen atmosphere using standard Schlenk techniques. 2-Propanol (analytical reagent) was either used directly from the bottle or was dried over sodium wire, distilled and stored under nitrogen before being degassed prior to use. ^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz) and ^{31}P (202 MHz) spectra were recorded on a Bruker AVШ–500 NMR spectrometer. GC measurements, with dodecane as an internal standard with respect to the ketone.[1-3] GC analysis was carried out on an Agilent 6820 instrument using a polar capillary column (part number 19091N-113 HP-INNOWAX): injector temp. 300 °C; detector temp. 300 °C; column temp. 40 ºC; withdraw time 2 min, then 20 ºC/min to 270 ºC over 20 min.

2. NMR spectra

2.1 NMR spectra of 5,6,7,8-tetrahydroquinolin-8-amine

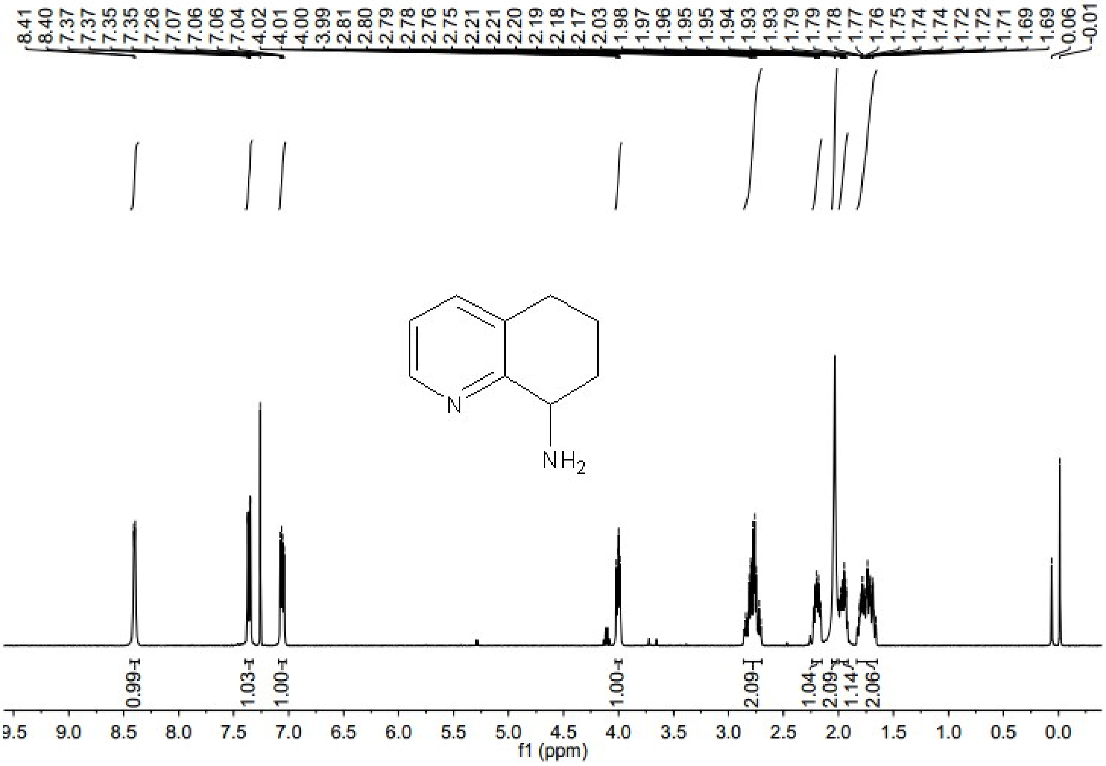

Figure S1 ^{1}H NMR spectrum of 5,6,7,8-tetrahydroquinolin-8-amine[4] in $CDCl_3$

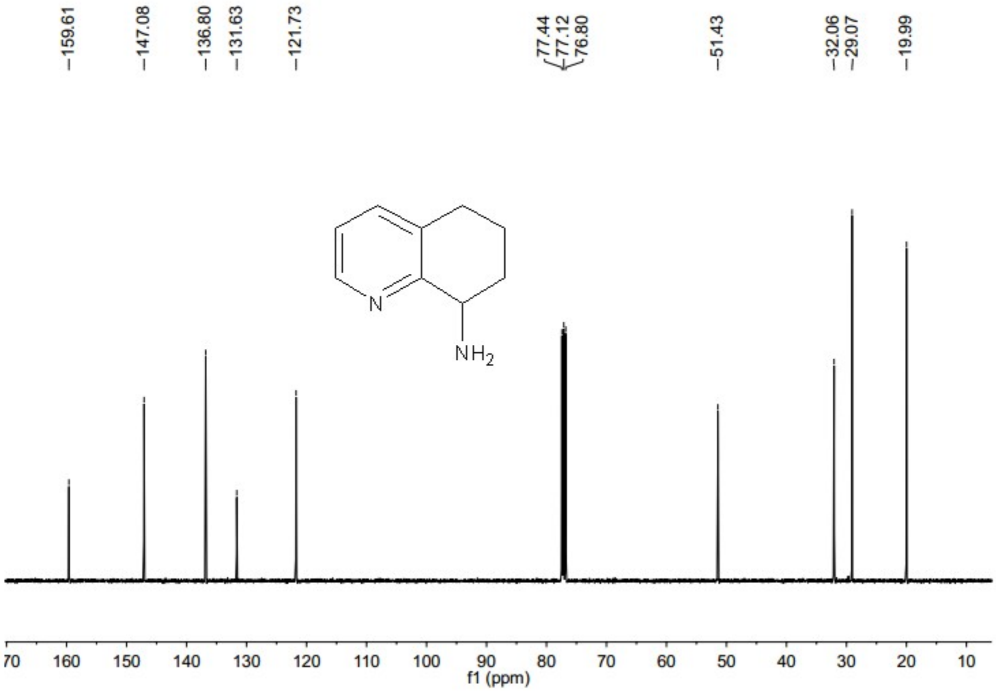

Figure S2 $^{13}C\{^{1}H\}$ NMR spectrum of 5,6,7,8-tetrahydroquinolin-8-amine in $CDCl_3$

2.2 NMR spectra for E and F

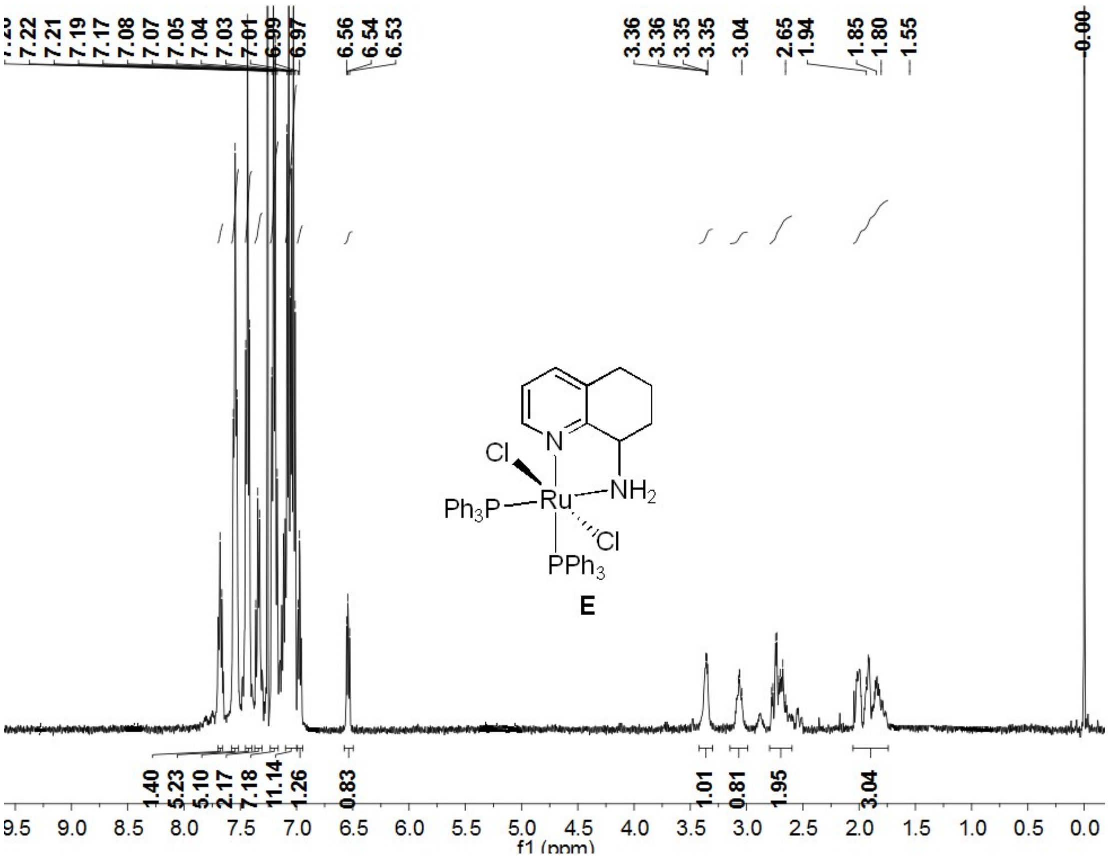

Figure S3 ^{1}H NMR spectrum of **E** in $CDCl_3$

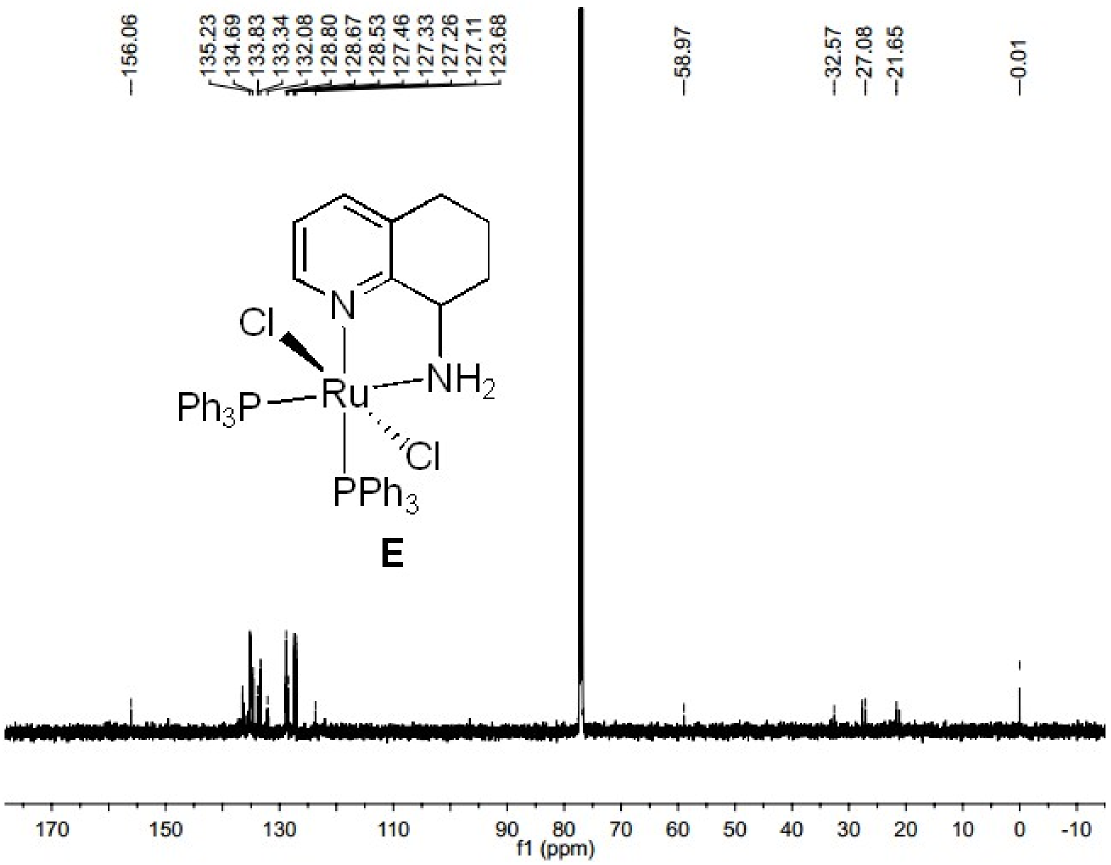

Figure S4 $^{13}C\{^{1}H\}$ NMR spectrum of **E** in $CDCl_3$

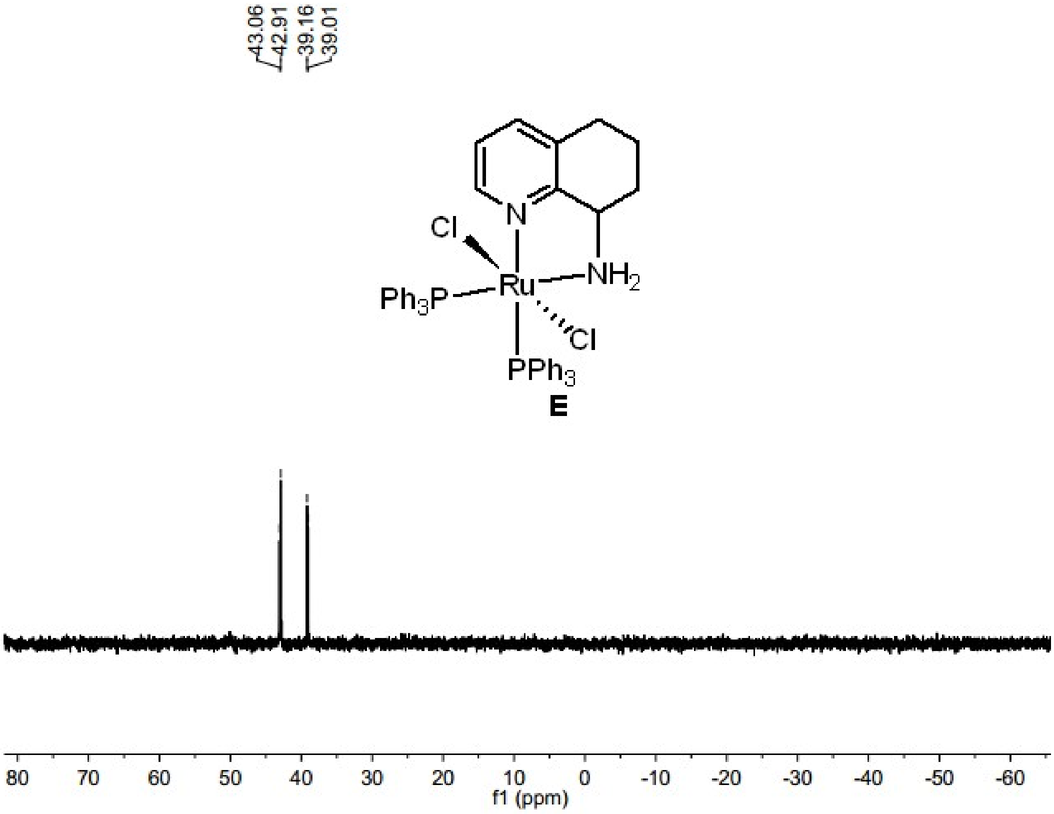

Figure S5 $^{31}P\{^{1}H\}$ NMR spectrum of **E** in $CDCl_3$

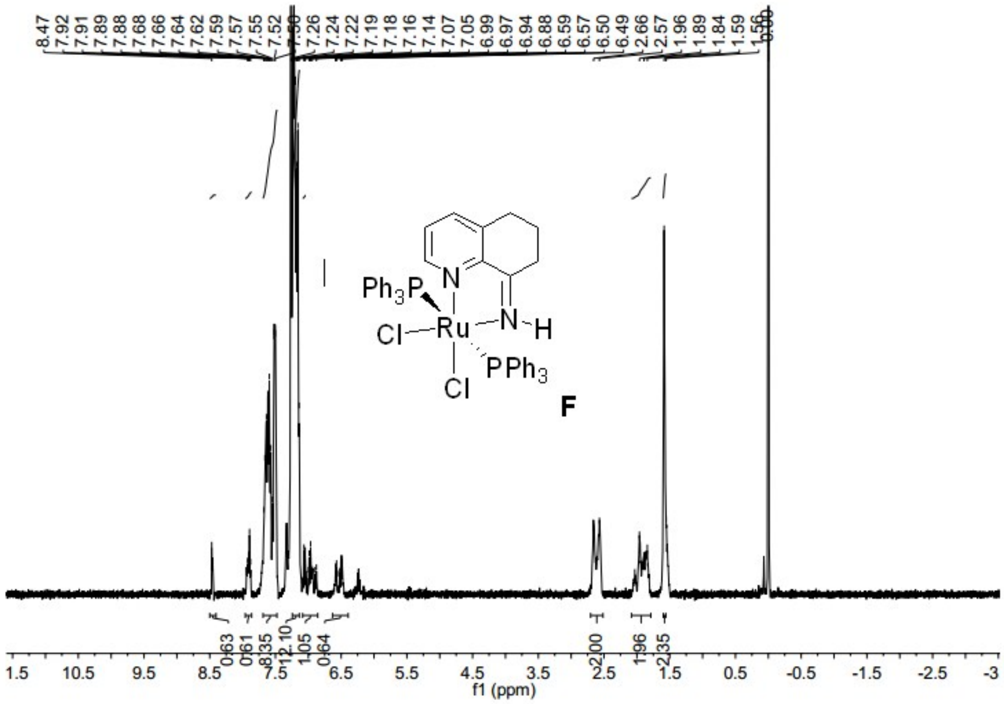

Figure S6 ^{1}H NMR spectrum of **F** in $CDCl_3$

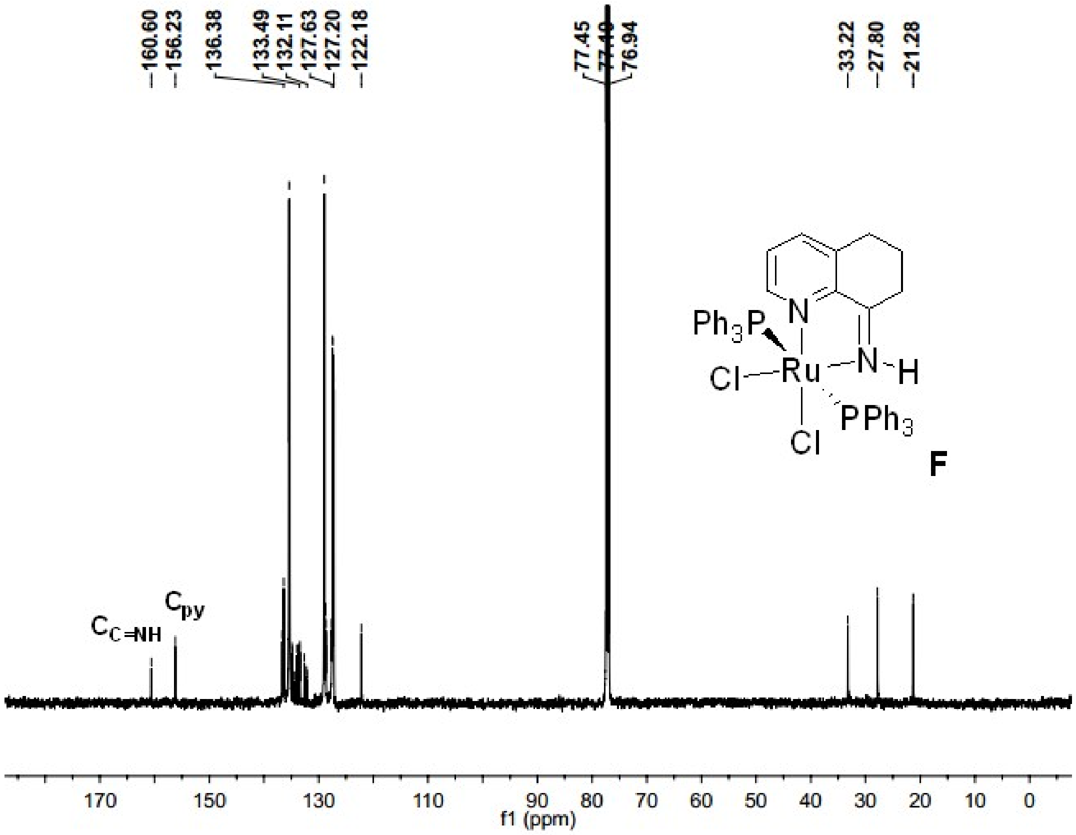

Figure S7 $^{13}C\{^{1}H\}$ NMR spectrum of **F** in $CDCl_3$

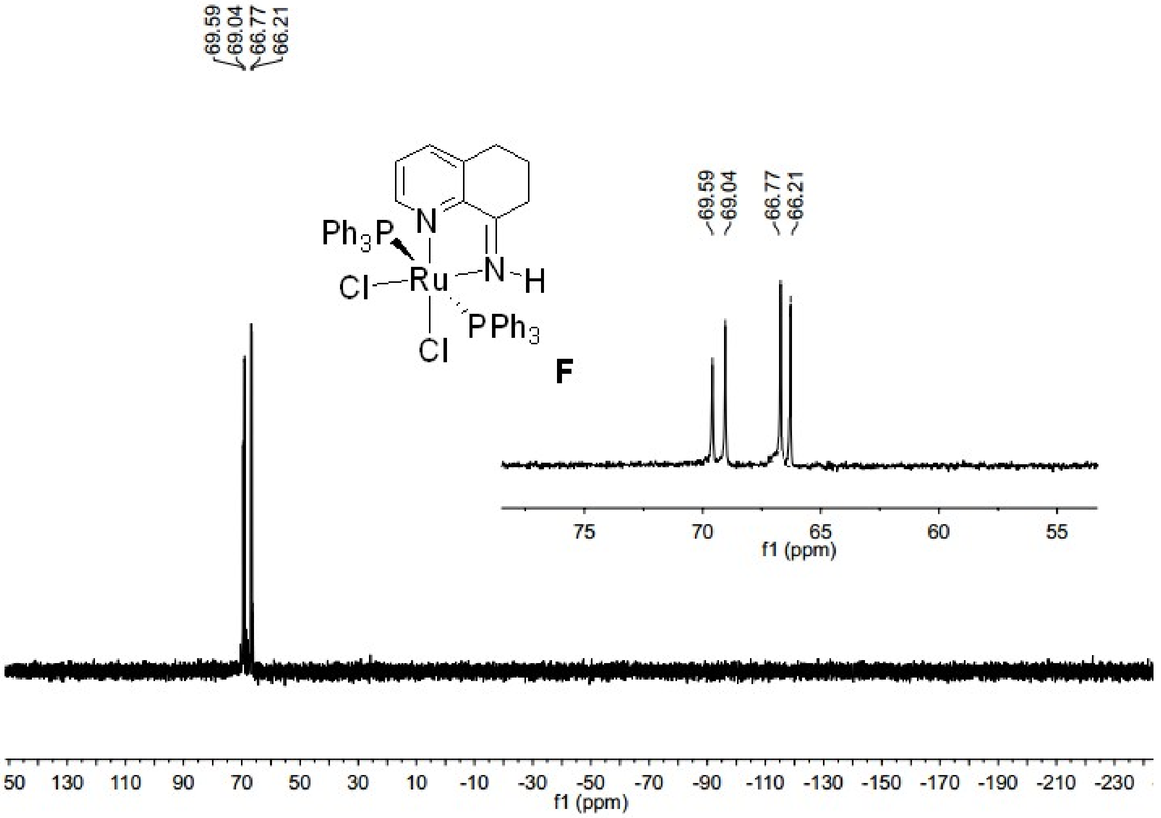

Figure S8 $^{31}P\{^1H\}$ NMR spectrum of **F** in $CDCl_3$

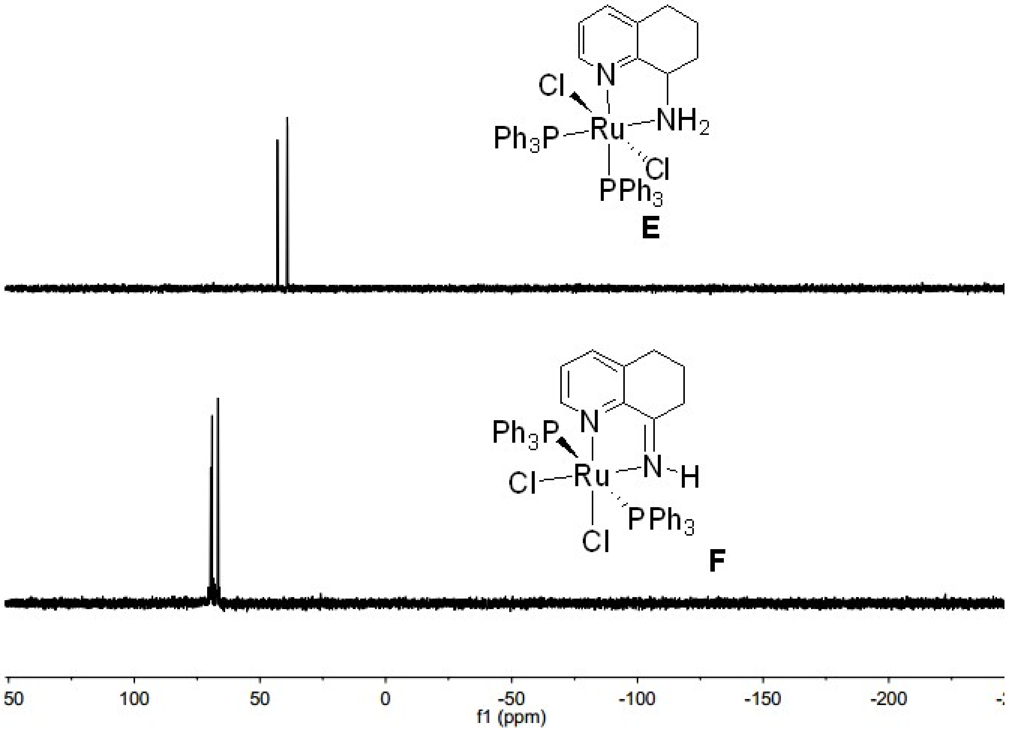

Figure S9 $^{31}P\{^1H\}$ NMR spectrum of **E** in $CDCl_3$ (top) and after heating this solution to 100 °C for 1 hour to give **F** (bottom)

2.3 NMR spectra showing deactivation of catalyst E over time

Method: Under an oxygen atmosphere, a mixture of **E** (40 mg), *t*-BuOK (8 mg) and 2-propanol (5 mL) were stirred at 82 ^{o}C. Aliquots of the reaction mixture were taken at 1 min, 5 min, 15 min, and 30 min and their ^{31}P NMR spectra immediately recorded.

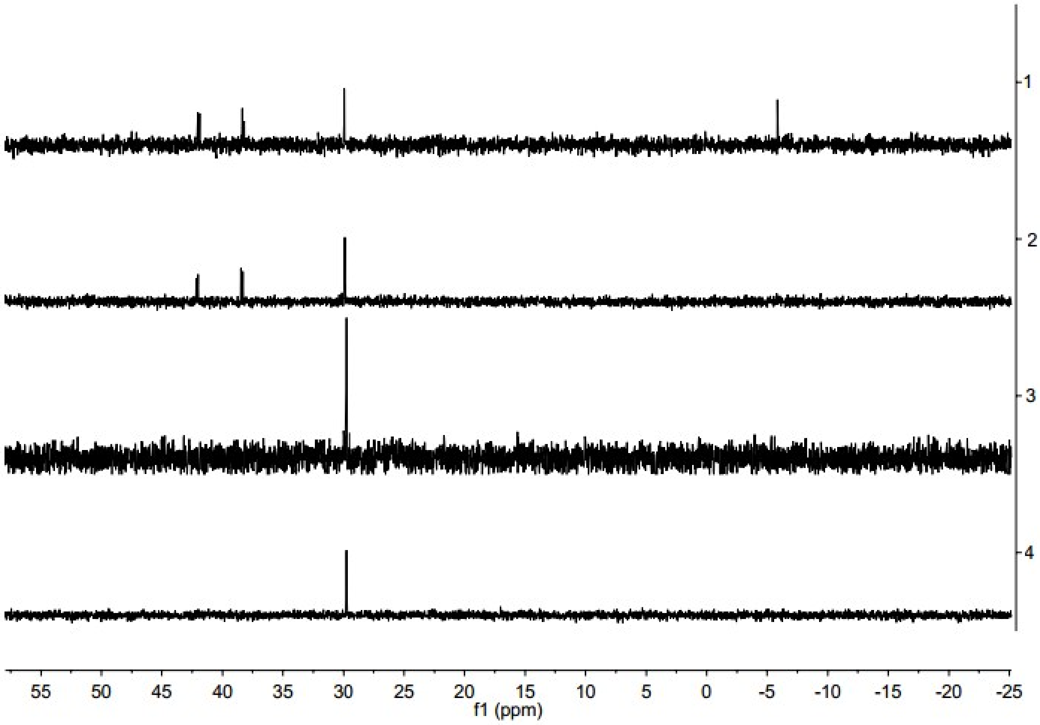

Figure S10 Stacked ^{31}P{^{1}H} NMR spectra of a sample of **E** that had been heated to 82 ^{o}C under an O_2 atmosphere. Spectra recorded after 1 min (1), 5 min (2), 10 min (3) and 30 min (4)) showing catalyst deactivation of **E** and formation of Ph_3PO.

2.4 NMR spectra of triphenylphosphine oxide isolated during catalyst deactivation

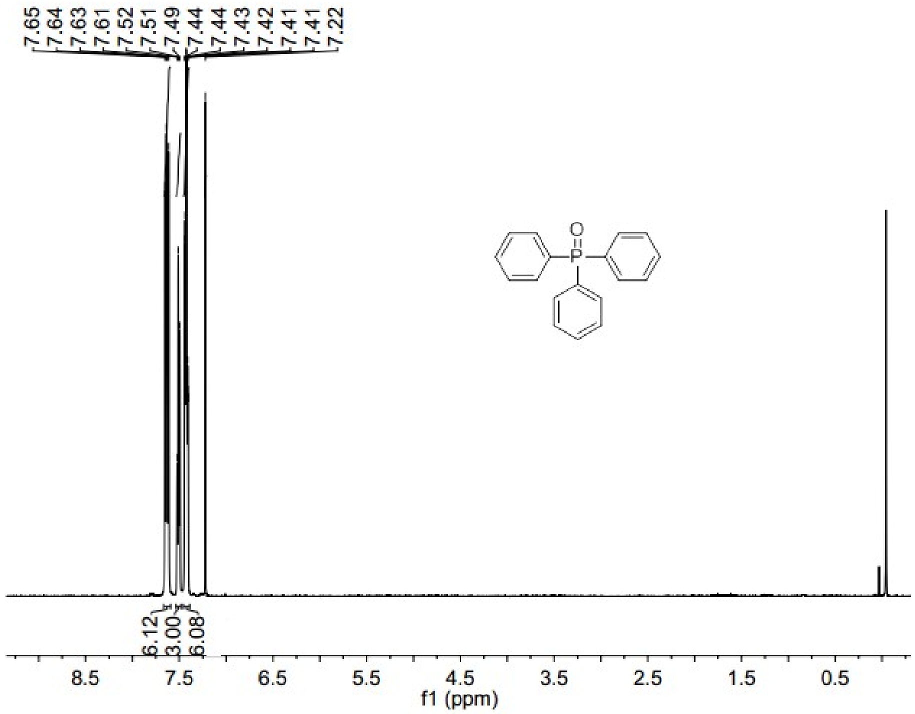

Figure S11 ^{1}H NMR spectrum of triphenylphosphine oxide[4] isolated during catalyst deactivation

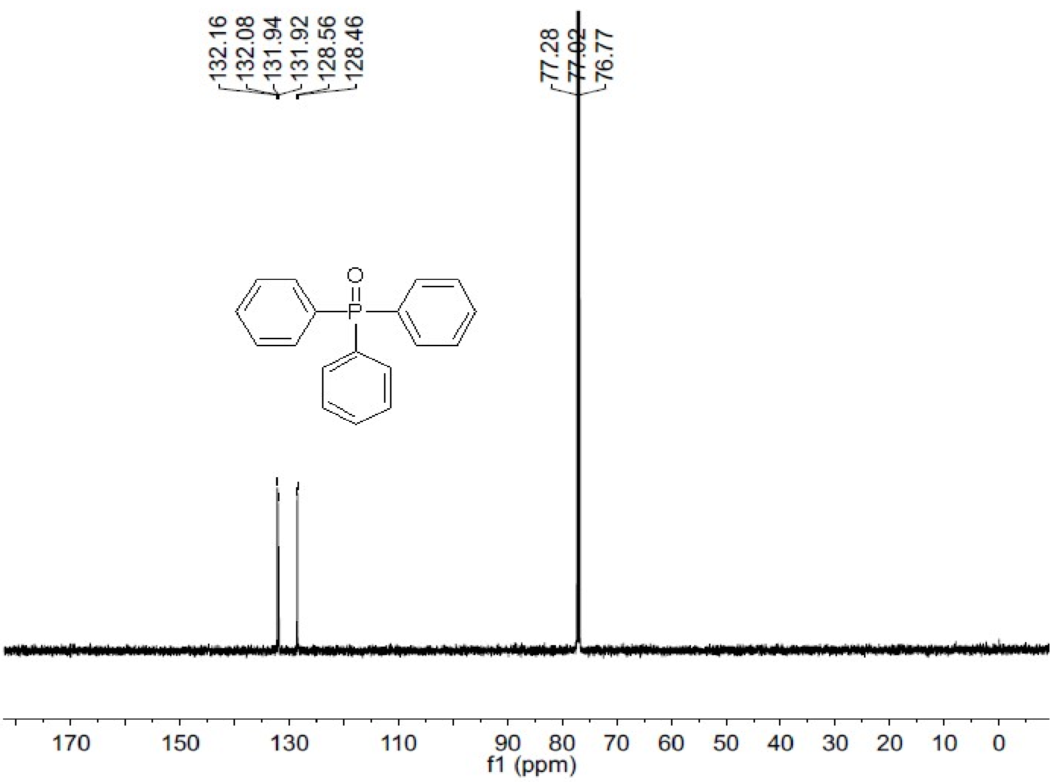

Figure S12 $^{13}C\{^1H\}$ NMR spectrum of triphenylphosphine oxide[4] isolated during catalyst deactivation

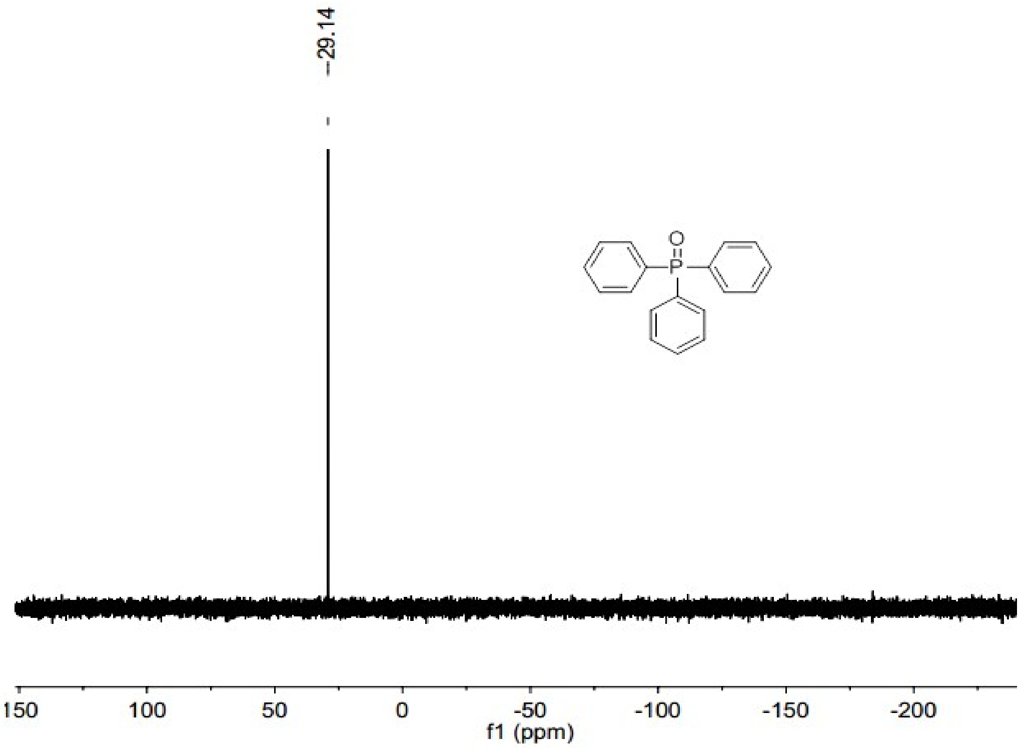

Figure S13 $^{31}P\{^{1}H\}$ NMR spectrum of triphenylphosphine oxide[4] isolated during catalyst deactivation

2.4 NMR spectra of *tert*-butyl-4-hydroxypiperidine-1-carboxylate[5]

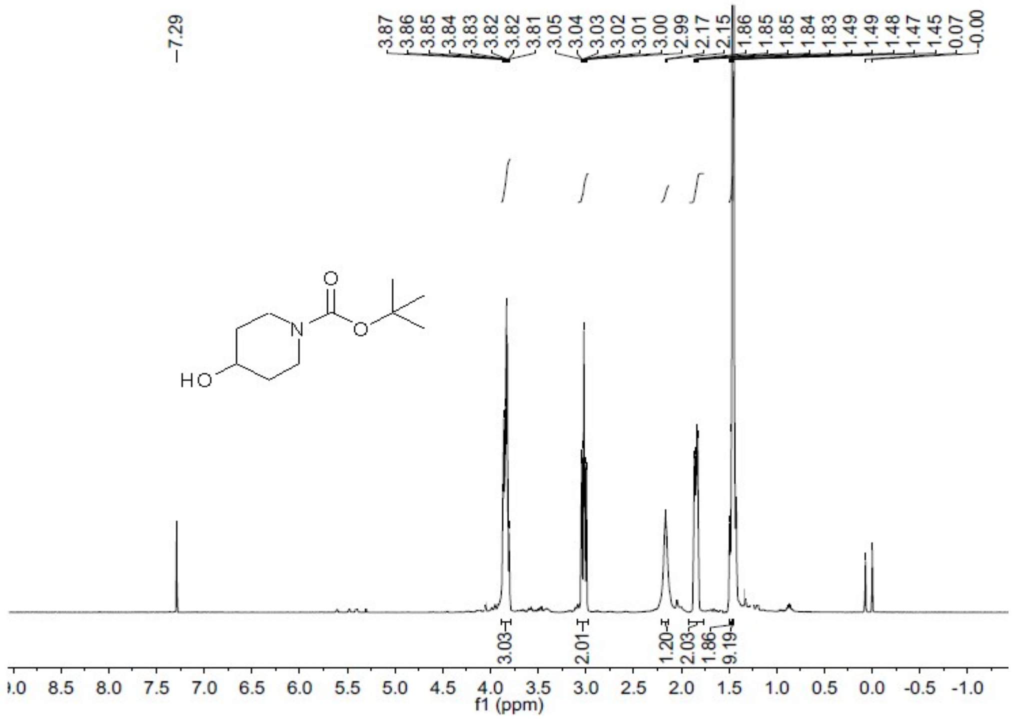

Figure S14 ^{1}H NMR spectrum of *tert*-butyl-4-hydroxypiperidine-1-carboxylate[5] in $CDCl_3$ (entry 17, Table 5)

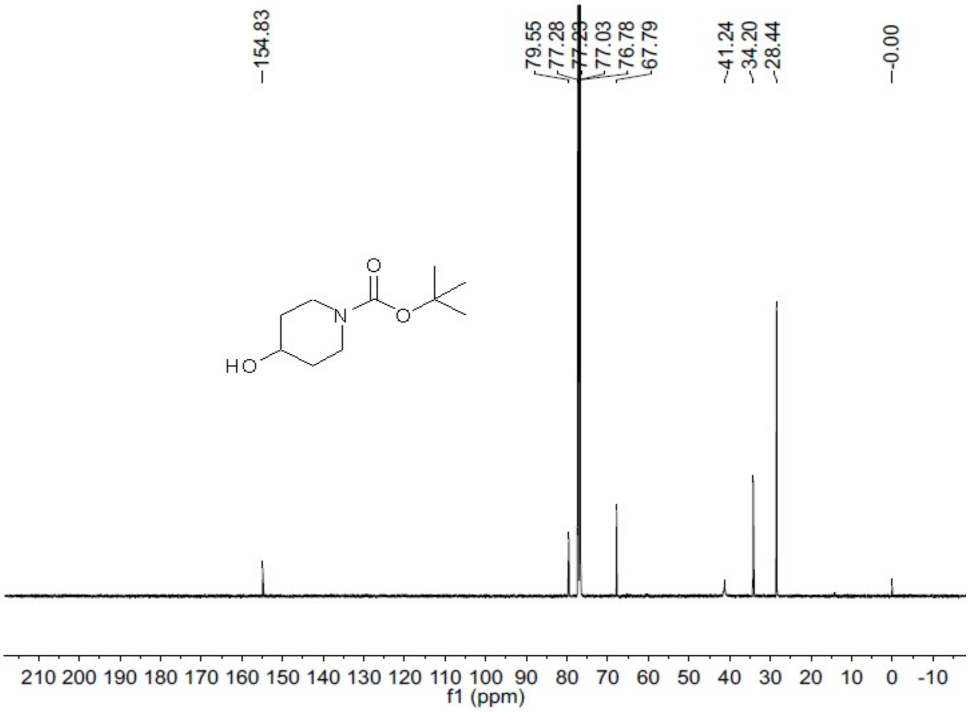

Figure S15 ^{13}C NMR spectrum of *tert*-butyl-4-hydroxypiperidine-1-carboxylate[5] in $CDCl_3$ (entry 17, Table 5)

3. X-Ray crystallographic studies

Table S1. Crystal data and structure refinement for **E** and **F**

Complex	**E**	**F**
Empirical formula	$C_{45}H_{42}Cl_2N_2P_2Ru$	$C_{45}H_{40}Cl_2N_2P_2Ru$
Formula weight	844.72	842.75
Temperature/K	173.1500	173.1500
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	$Pna2_1$
a/Å	12.296(3)	25.282(5)
b/Å	10.957(2)	9.6695(19)
c/Å	33.036(7)	15.833(3)
α/°	90.00	90.00
β/°	97.24(3)	90.00
γ/°	90.00	90.00
Volume/Å^3	4415.4(15)	3870.9(13)
Z	4	4
ρcalcg/cm^3	1.271	1.444
μ/mm^{-1}	0.580	0.661
F(000)	1736.0	1724.0
Crystal size/mm^3	0.303 × 0.159 × 0.082	0.327 × 0.276 × 0.081
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.48 to 54.98	4.5 to 54.98
Index ranges	$-15 \leq h \leq 15$, $-14 \leq k \leq 14$, $-42 \leq l \leq 42$	$-32 \leq h \leq 32$, $-12 \leq k \leq 12$, $-20 \leq l \leq 20$
Reflections collected	46059	43776
Independent reflections	10099 [R_{int} = 0.1138, R_{sigma} = 0.0840]	8873 [R_{int} = 0.0522, R_{sigma}= 0.0309]
Data/restraints/parameters	10099/0/469	8873/1/470
Goodness-of-fit on F2	1.125	1.054
Final R indexes [I>=2σ (I)]	R_1 = 0.0962, wR_2 = 0.2214	R_1 = 0.0352, wR_2= 0.0859
Final R indexes [all data]	R_1 = 0.1128, wR_2 = 0.2319	R_1 = 0.0368, wR_2= 0.0867
Largest diff. peak/hole / e Å^{-3}	2.20/-1.13	0.93/-0.68

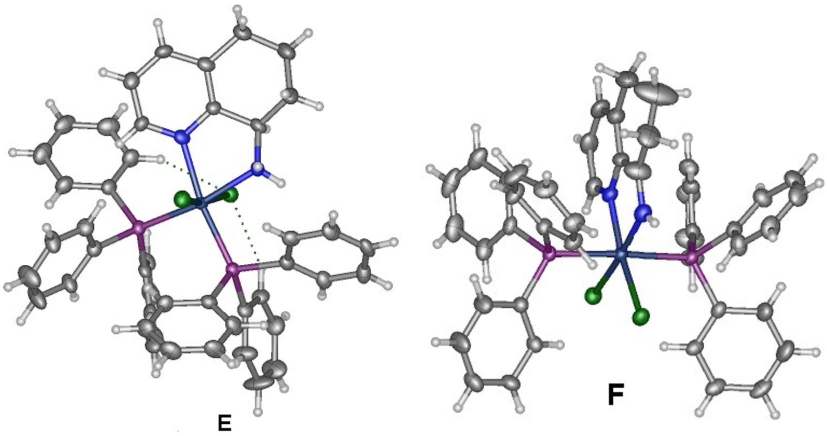

Figure S16 Olex2 representations of **E** and **F**. Thermal ellipsoids are shown at 30% probability.

4. References

(1) (a) Wang, Z.; Pan, B.; Liu, Q.; Yue, E.; Solan, G. A.; Ma, Y.; Sun, W.-H. *Catal. Sci. Technol.* **2017**, 7, 1654-1661; (b) S. Muthaiahb, S. H. Honga, *Adv. Synth. Catal*. **2012,** 354, 3045; (c) S. Shahane, C. Fischmeister, C. Bruneau, *Catal. Sci. Technol*. **2012**, 2, 1425.

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(3) (a) Baratta, W.; Ballico, M.; Del Zotto, A.; Herdtweck, E.; Rigo, P. *Organometallics* 2007, 26, 5636-5642; (b) Baratta, W.; Herdtweck, E.; Siega, K.; Toniutti, M.; Rigo, P. *Organometallics* **2005**, 24, 1660-1669.

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