

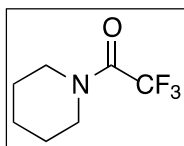
SUPPLEMENTARY MATERIAL

A Fortuitous, Mild Catalytic Carbon-Carbon Bond Hydrogenolysis by a Phosphine-Free Catalyst

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Synthesis of 2,2,2-trifluoro-1-(piperidin-1-yl)ethanone (2).^[1,2]

This is a modification of a literature procedure.^[1,2] 10.9 mL (7.9 g, 77.9 mmol) of triethylamine and 8.4 mL (7.3 g, 84.9 mmol) of piperidine were dissolved in 150 mL of stirred dichloromethane cooled in an ice/water bath. 10 mL (14.9 g, 70.8 mmol) of trifluoroacetic anhydride was then added dropwise. The mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was washed with 2x50 mL 1M HCl, with 2x50 mL distilled water, with 50 mL of brine, dried over sodium sulfate, and filtered. The organic solvent was removed under reduced pressure to yield the 2,2,2-trifluoro-1-(piperidin-1-yl)ethanone (65%, colourless oil). The product purified by vacuum distillation (water aspirator) at 90 °C (boiling point 53 °C at 2.6 torr).^[1] **¹H-NMR:** (CDCl₃, 400MHz, ppm): 3.54-3.64 (multiplet, 4H); 1.65-1.71 (multiplet, 6H). **¹³C {¹H} NMR:** (CDCl₃, 176MHz, ppm): 155.32, 116.65, 46.82, 44.56, 26.33, 25.36, 24.17. **HRMS (ESI)** m/z calculated for C₇H₁₀F₃ON: 181.0714. Found: 181.0716, 112.0762, and 69.0704. **EA:** Calculated for C₇H₁₀F₃ON: C 46.41, H 5.56, N 7.73. Found: 45.86, 5.56, and 7.62.

N, N-Diethyl-2,2,2-trifluoroacetamide.

Prepared as described above. 12.9 mL (9.3 g, 92.8 mmol) of triethylamine and 8 mL (5.6 g, 77.3 mmol) of diethylamine were dissolved in 150 mL of stirred dichloromethane cooled in an ice/water bath. 10.9 mL (16.2 g, 77.3 mmol) of trifluoroacetic anhydride was then added dropwise. The mixture was allowed to warm to room temperature and stirred overnight. The reaction

mixture was washed with 2x50 mL 1M HCl, 2x50 mL distilled water, 50 mL brine, dried over sodium sulfate, and filtered. The organic solvent was then removed under reduced pressure to yield the N, N-diethyl-2,2,2-trifluoroacetamide (60%, yellow oil). The product purified by passed through a neutral alumina plug. **¹H-NMR:** ^[3] (CDCl₃, 498.118MHz, ppm): 1.20-1.27 (multiplet, 6H); 3.45-3.47 (multiplet, 4H). The spectrum matches that reported for this compound.^[3]

Piperidine-1-carbaldehyde⁴: **¹H-NMR:** (CDCl₃, 400MHz, ppm): 8.01(singlet, 1H); 3.29-3.50 (multiplet, 4H); 1.52-1.78 (multiplet, 6H).

N,N-Diethylformamide⁵ : **¹H-NMR :** (CDCl₃, 400MHz, ppm): 8.05(singlet, 1H); 3.37 (q, *J*=7.2 Hz, 2H); 3.27 (q, *J*=7.2 Hz, 2H); 1.19 (t, *J*=7.2 Hz, 3H); 1.13 (t, *J*=7.2 Hz, 3H).

trans-RuCl₂((*S,S*)-skewphos)((*R,R*)-dpen) (**4**) was prepared as reported previously.^[6]

Figure S1. ¹H NMR spectrum (δ 6.5 to -2.0 ppm) of [Ru(H₂NCH(Ph)CH(Ph)NH)(η^{1,5}-C₈H₁₂)(η³-C₃H₅)]BF₄ (**6**) formed by the reaction of **1**, ((*R,R*)-dpen) and KO^tBu in ~1 atm H₂ in THF-*d*₈ at -80 °C.

Residual solvent, δ; coordinated (*R,R*)-dpen ligand, NH₂=●, NH=⊖ CH=○; Non coordinated (*R,R*)-dpen ligand =⊕, propylene, φ; Free hydrogen gas=H; (η³-C₃H₅)=α; (η^{1,5}-C₈H₁₂)=*

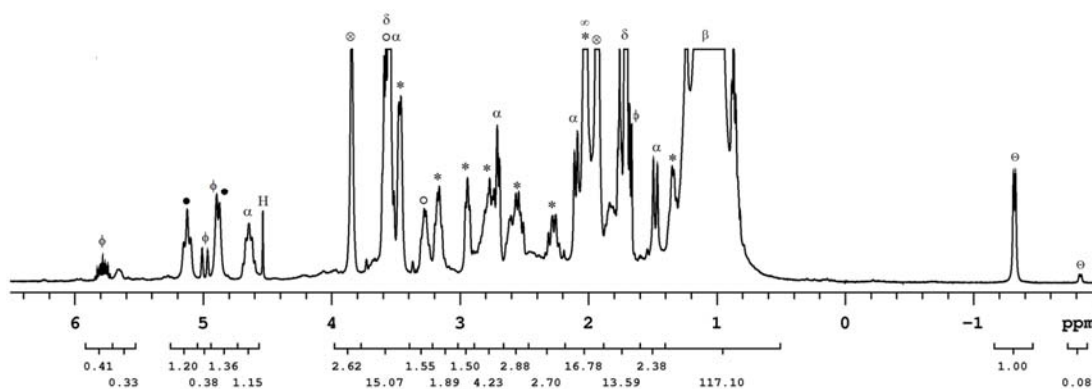


Figure S2. ¹H NMR and zTOCSYID spectrum (δ 6.5 to -2.0 ppm) of [Ru(H₂NCH(Ph)CH(Ph)NH)(η^{1,5}-C₈H₁₂)(η³-C₃H₅)]BF₄ (**6**) formed by the reaction of **1**, ((*R,R*)-dpen) and KO^tBu in ~1 atm H₂ in THF-*d*₈ at -80 °C.

Spectrum top to bottom

Spectrum 1: zTOCSY1D, sel.excite @ -1.34 ppm. (Coordinated (R,R)-dppe ligand)
 Spectrum 2: zTOCSY1D, sel.excite @ 2.94 ppm. ($\eta^{1,5}$ -C₈H₁₂)
 Spectrum 3: zTOCSY1D, sel.excite @ -1.34 ppm. (η^3 -C₃H₅)
 Spectrum 4: ¹H NMR of [Ru(H₂NCH(Ph)CH(Ph)NH)($\eta^{1,5}$ -C₈H₁₂)(η^3 -C₃H₅)]BF₄

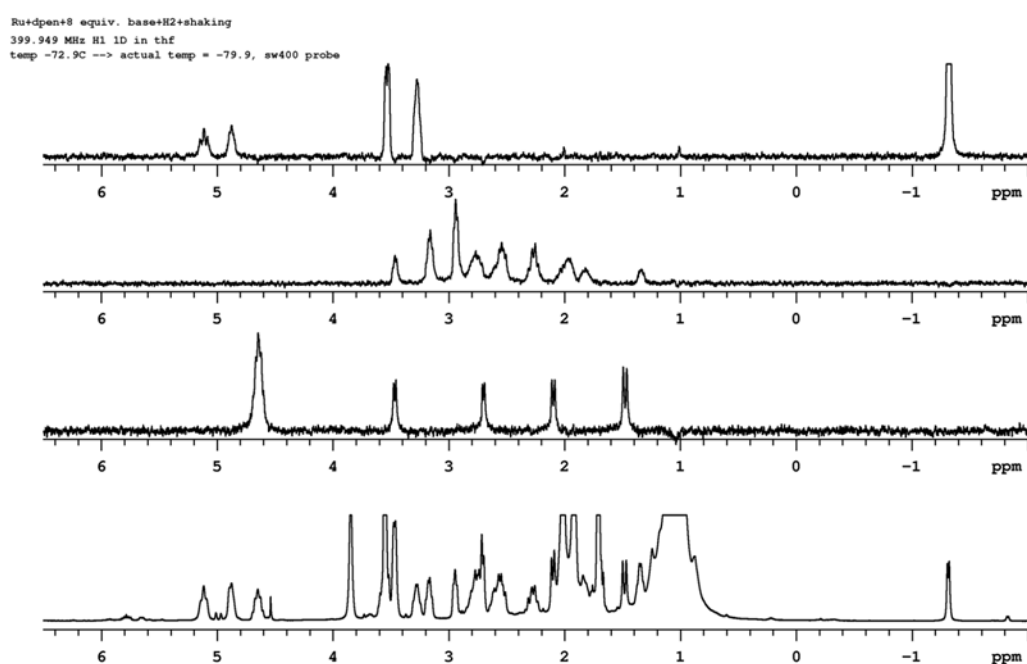


Figure S3. ¹H NMR spectrum (δ 6.5 to -2.0 ppm) of the product (**7**) formed by the reaction between **1**, ((R, R)-dppe) and KO^tBu in ~1 atm H₂ in THF-*d*₈ at -20 °C.

Top: @ -20 °C; middle: @ -20 °C (after an hour); bottom: @ -20 °C (after 4 hours)

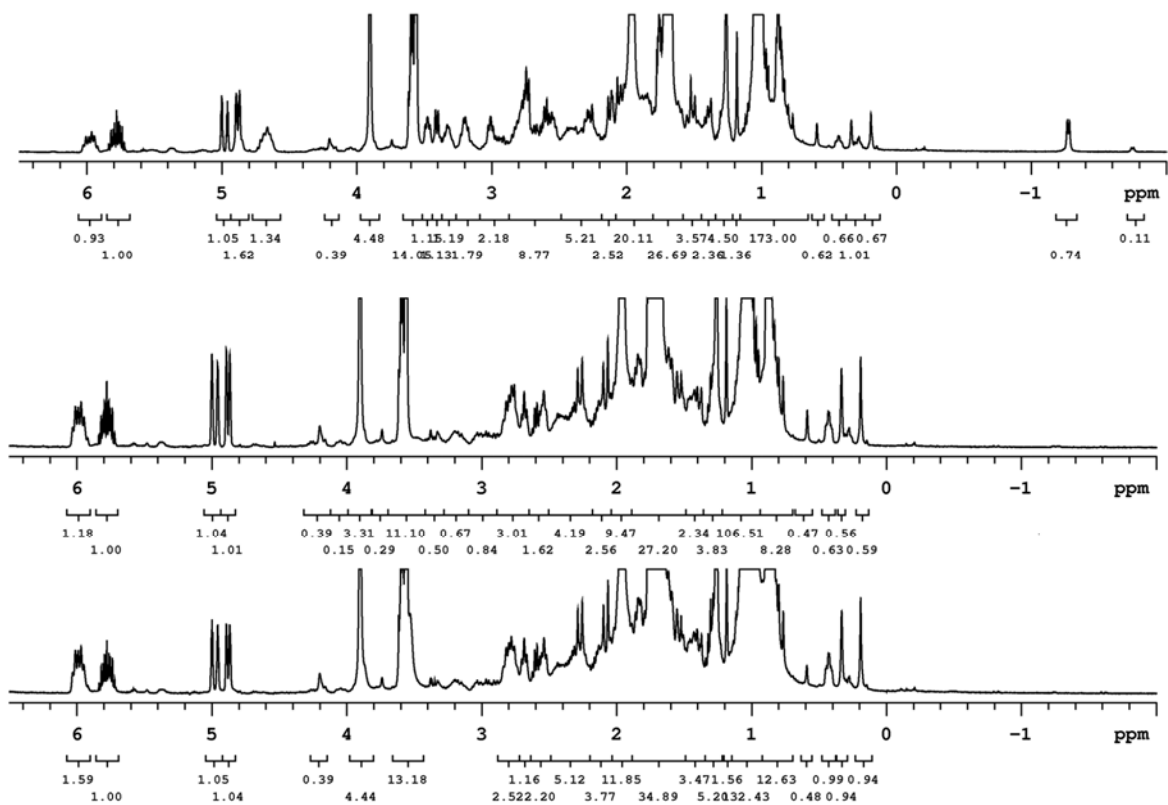


Figure S4. ^1H NMR spectrum (δ 9.0 to -12.0 ppm) of the product formed by the reaction between **1**, ((*R,R*)-*dpen*) and KO^tBu in ~ 1 atm H_2 in THF-d_8 at RT.

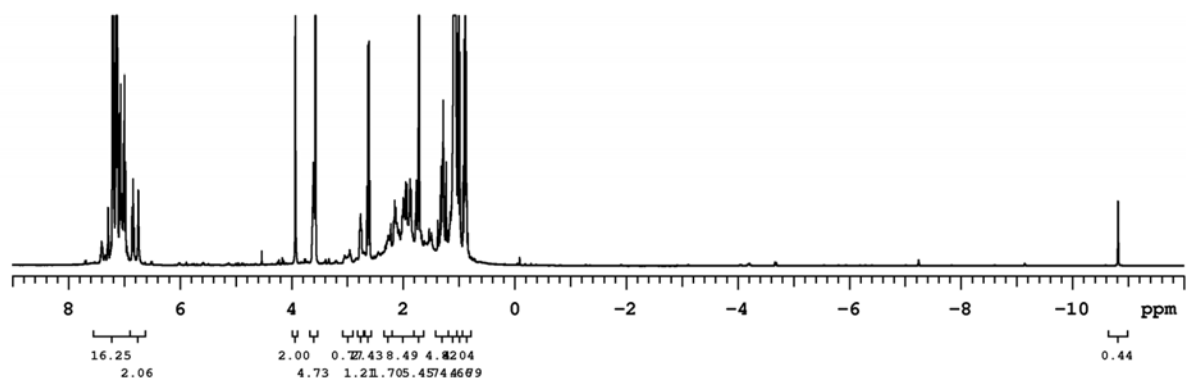


Figure S5. ^1H NMR spectrum (δ 5.0 to 0.0 ppm) of the product formed by the reaction between **1**, ((*R,R*)-*dpen*) and KO^tBu in ~ 1 atm H_2 in THF-d_8 at RT.

Residual solvent, δ ; Non-coordinated (R,R)-dpen ligand = \otimes , propane=P; Free hydrogen gas=H; Ethylamine=E

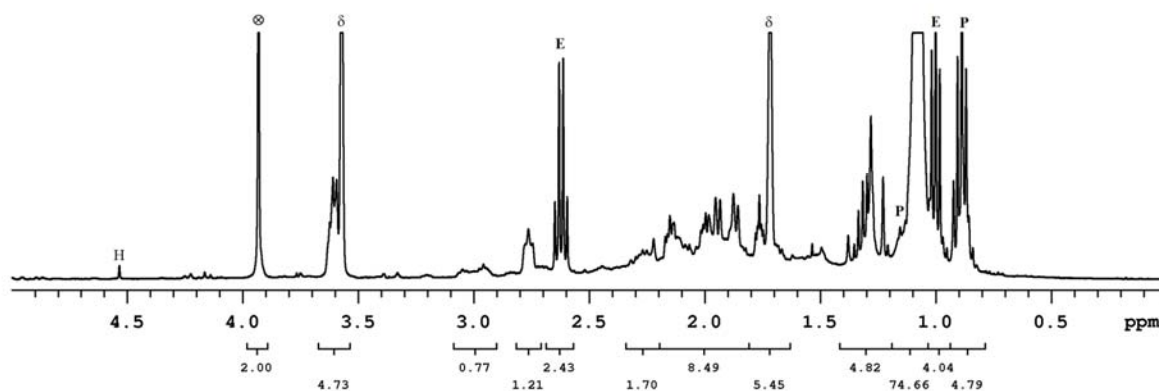


Figure S6. ^1H NMR and ^1H - ^{15}N NMR of a gHSQC spectrum (6 to -2 ppm) of $[\text{Ru}(\text{H}_2\text{NCH}(\text{Ph})\text{CH}(\text{Ph})\text{NH})(\eta^{1,5}\text{-C}_8\text{H}_{12})(\eta^3\text{-C}_3\text{H}_5)]\text{BF}_4$ (**6**) formed by the reaction of **1**, ((R, R)-dpen) and KO^tBu in ~ 1 atm H_2 in THF- d_8 at -80 °C. coordinated (R,R)-dpen ligand, $\text{NH}_2=\bullet$, $\text{NH}=\ominus$; Non coordinated (R, R)-dpen ligand = \otimes

Top: Only the first increment of ^1H - ^{15}N NMR of a gHSQC was recorded to show proton directly attached to nitrogen. The data were acquired at -80 °C using $^1J_{\text{H}-^{15}\text{N}}=90$ Hz with the ^{15}N decoupler set at 90 ppm.

Bottom: ^1H NMR of the mixture containing **6**.

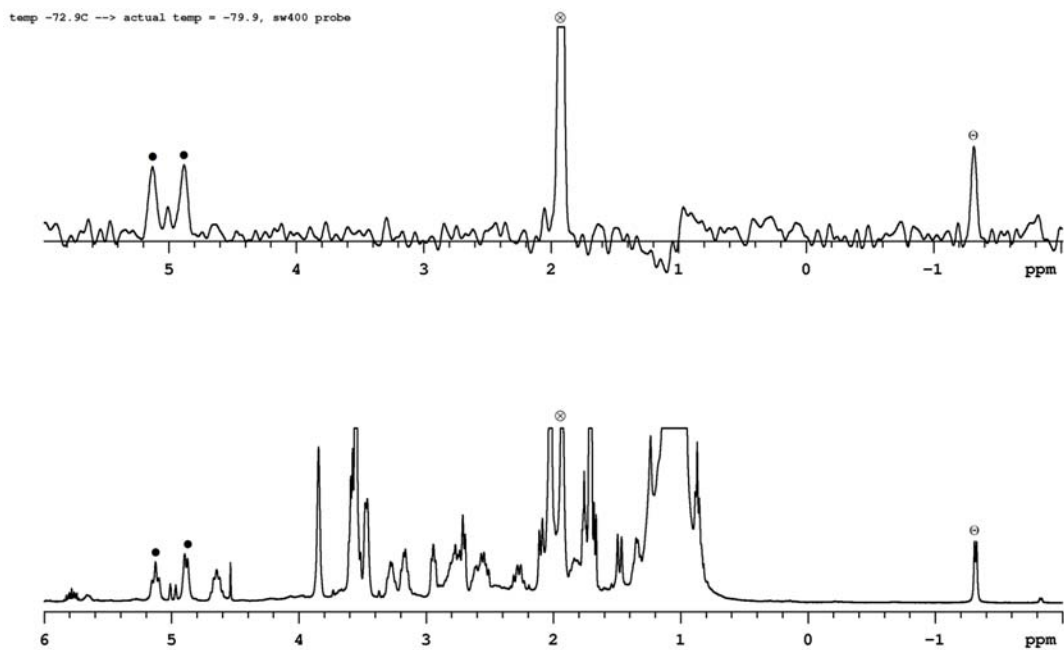


Figure S7. ^{19}F NMR spectrum (δ -65 to -85.0 ppm) of the product formed by the reaction between the catalyst and 10 equivalents of substrate in THF-d_8 at room temperature at different times. (Unidentified intermediate=U)

Top: After 15 min; middle: after 16 hours; bottom: after 20 hours

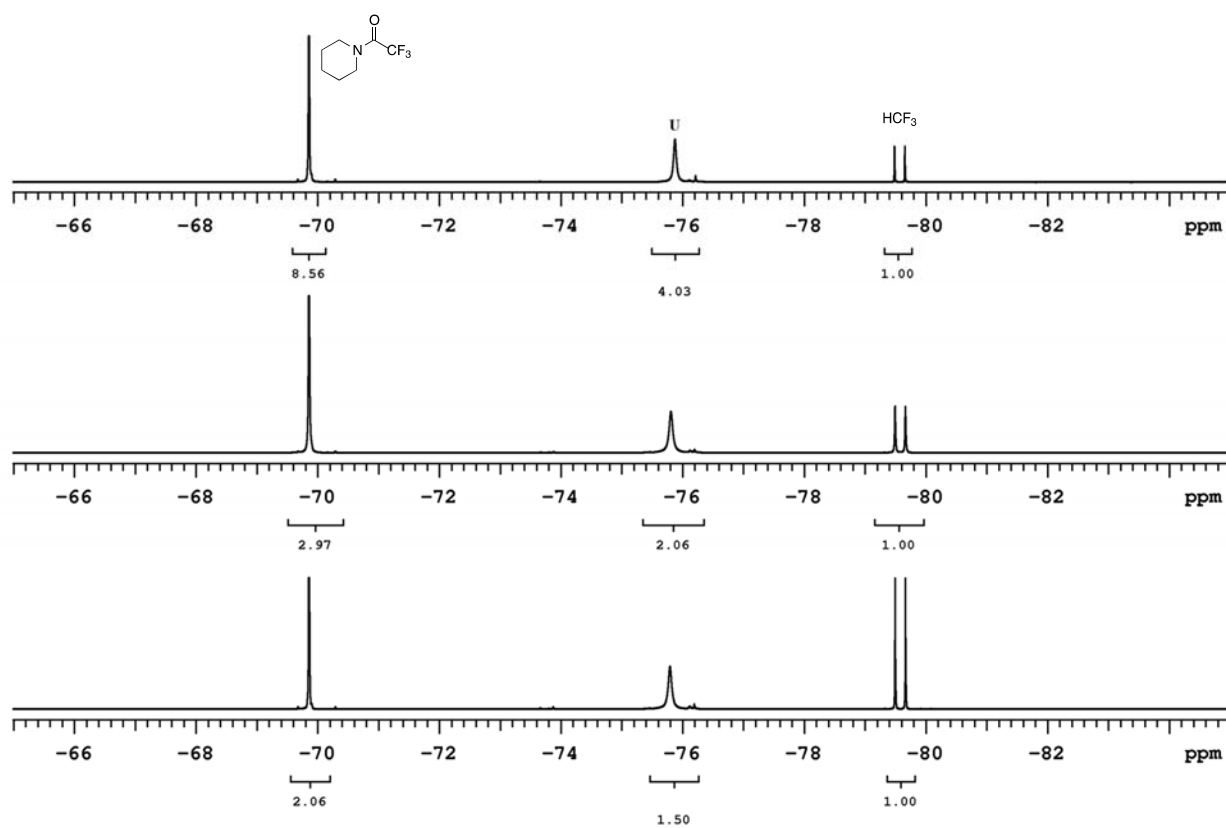


Figure S8. The δ 8.5 to 1 ppm ^1H NMR spectrum showing the formation of piperidine-1-carbaldehyde resulting from the hydrogenation of 2,2,2-trifluoro-(piperidin-1-yl)ethanone (**2**) using 4 atm H_2 pressure at RT.

Residual solvent = δ ; Starting material, **2** = Δ ; product = *

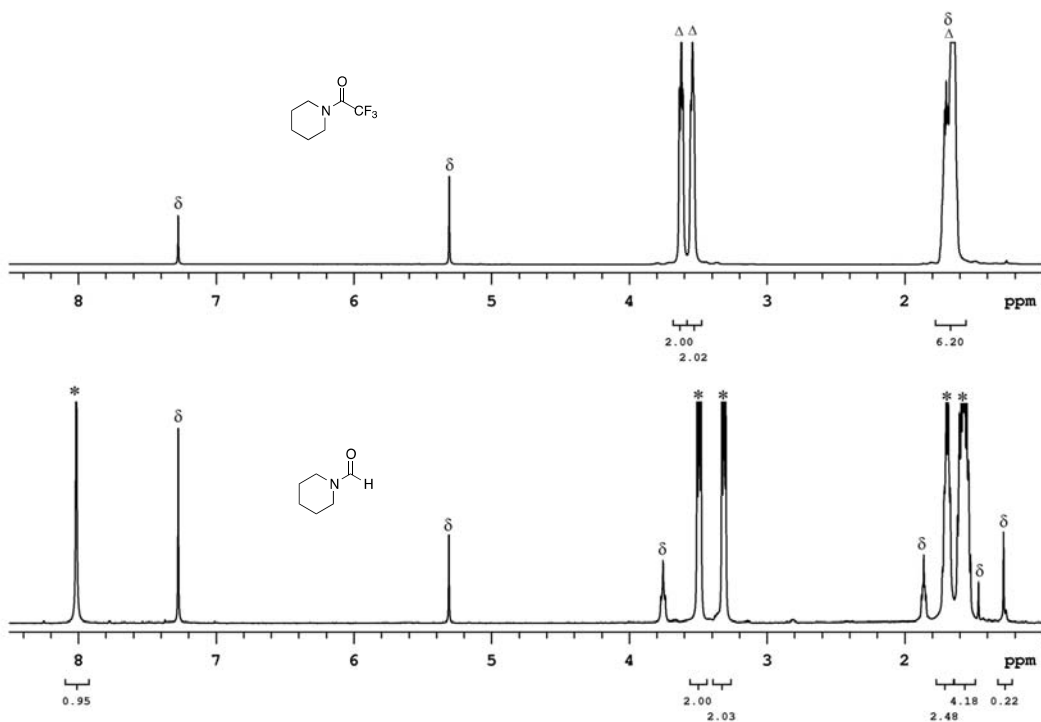
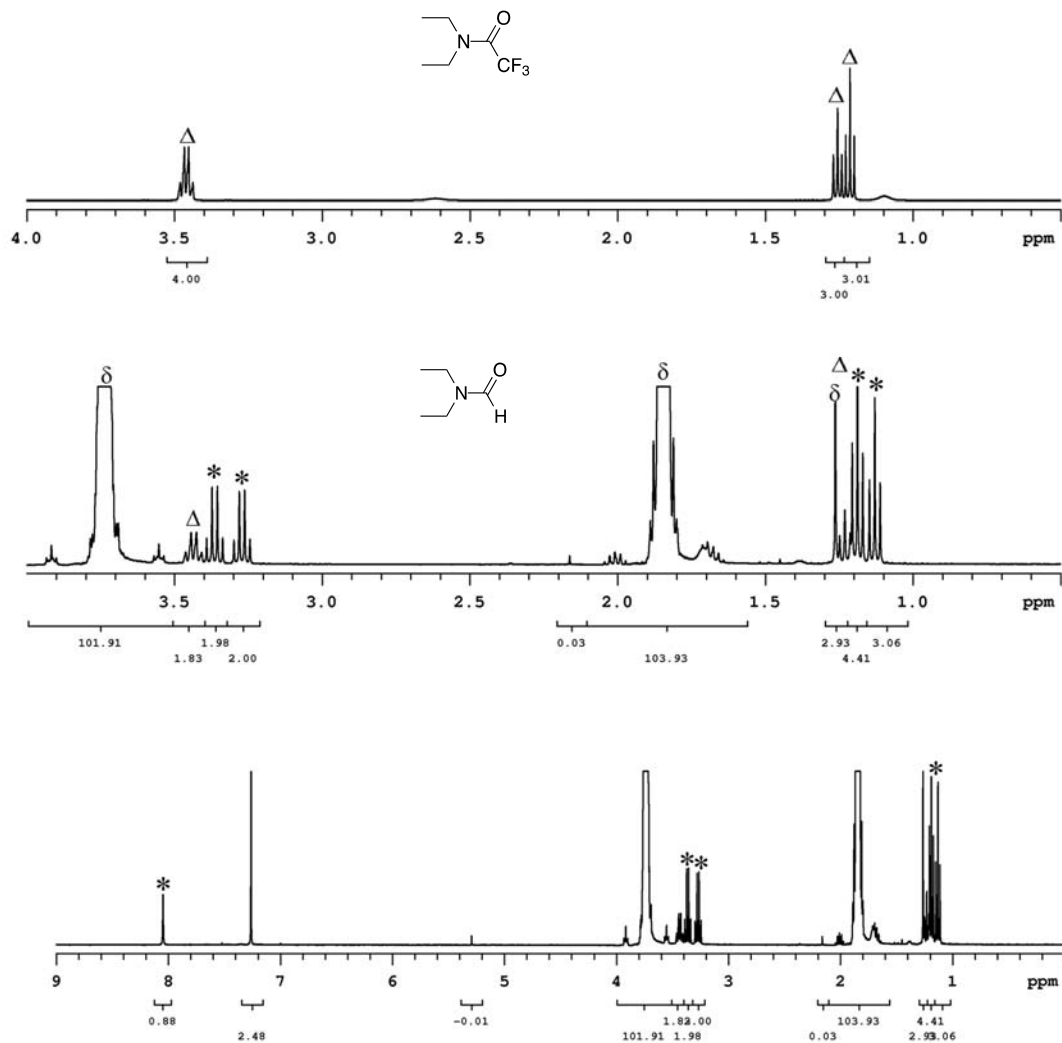


Figure S9. The ¹H NMR spectrum showing the formation of *N,N*-diethylformamide resulting from the hydrogenation of *N,N*-diethyl-2,2,2-trifluoroacetamide using 4 atm H₂ pressure at RT.

Residual solvent = δ; Starting material = Δ; product = *

Top: Starting material; middle: product (δ 4 to 0 ppm); bottom: product (δ 9 to 0 ppm)



Control Experiments.

Hydrogenation using ruthenium nanoparticles.

20.7 mg of Ruthenium black (0.014 mmol assuming 7% of Ru atoms are on the surface) were weighed into a test tube equipped with a magnetic stir bar and a rubber septum. After purging with hydrogen gas for 10 minutes the ruthenium black was reduced by heating at 60 °C for 30 minutes under hydrogen⁷. After 30 minutes the test tube placed inside the stainless steel autoclave equipped with the test tube holder and flushed with hydrogen using cannulas, needle lines, and bubblers. 2,2,2-trifluoro-1-(piperidin-1-yl)ethanone (**2**, 1.25 mmol, 90 equiv.) in THF (1.0 mL) and KO^tBu (0.1875 mmol, 14 equiv.) in THF (0.5 mL) were added using gas tight syringes under

1 atm hydrogen. Additional THF added to make the final volume to be 2.5 mL. Hydrogenated at 4 atm H₂ and stirred for 22 hours at room temperature.

Hydrogenations in the presence of Hg metal.

Cis-[Ru(η^3 -C₃H₅)(COD)(MeCN)₂]BF₄ (**1**, 0.007 mmol, 3mg), and 2 equiv. of (*R, R*)-dpen (0.014 mmol, 3.0 mg) were weighed out into a test tube equipped with stir bar and septum. Freshly distilled THF (0.5 mL) was then added by cannula under argon pressure into the test tube. It was then heated at 60 °C for 30 min while stirring (pale brown, clear liquid). After 30 minutes the resulting solution transferred to another test tube containing 200 equiv. of Hg (282.9 mg, 1.41 mmol) under 1 atm hydrogen atmosphere. 2,2,2-trifluoro-1-(piperidin-1-yl)ethanone (**2**, 129.6 mg, 0.715 mmol, 100 equiv.) in THF (1.0 mL) and KO^tBu (0.107 mmol, 15 equiv.) in THF (0.5 mL) were added using gas tight syringes under 1 atm hydrogen atmosphere. Additional THF added to make the final volume to be 2.5 mL. Hydrogenated at 4 atm H₂ and stirred for 22 hours at room temperature.

Crystallographic Experimental Details

Crystal Structure deposited on Crystallographic Data Centre (CCDC deposition number: 1442770)

Table 1. Crystallographic Experimental Details

A. Crystal Data

formula	C ₄₅ H ₅₀ Cl ₆ N ₂ P ₂ Ru
formula weight	994.58
crystal dimensions (mm)	0.19 × 0.08 × 0.03
crystal system	orthorhombic
space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (No. 19)
unit cell parameters ^a	
<i>a</i> (Å)	10.4622 (2)
<i>b</i> (Å)	17.2073 (3)
<i>c</i> (Å)	25.8113 (5)
<i>V</i> (Å ³)	4646.71 (15)
<i>Z</i>	4
ρ_{calcd} (g cm ⁻³)	1.422

μ (mm ⁻¹)	6.811
<i>B. Data Collection and Refinement Conditions</i>	
diffractometer	Bruker D8/APEX II CCD ^b
radiation (λ [Å])	Cu K α (1.54178) (microfocus source)
temperature (°C)	-100
scan type	ω and ϕ scans (1.0°) (5 s exposures)
data collection 2θ limit (deg)	140.48
total data collected	9431 (-12 $\leq h \leq$ 12, -20 $\leq k \leq$ 21, -31 $\leq l \leq$ 31)
independent reflections	9431 ($R_{\text{int}} = 0.1258$)
number of observed reflections (<i>NO</i>)	8751 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	intrinsic phasing (<i>SHELXT-2014</i> ^c)
refinement method	full-matrix least-squares on F^2 (<i>SHELXL-2013</i> ^c)
absorption correction method	multi-scan (<i>TWINABS</i>)
range of transmission factors	0.7533–0.5249
data/restraints/parameters	9431 / 0 / 522
Flack absolute structure parameter ^d	-0.010(7)
goodness-of-fit (<i>S</i>) ^e [all data]	1.051
final <i>R</i> indices ^f	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0415
wR_2 [all data]	0.1010
largest difference peak and hole	0.822 and -0.971 e Å ⁻³

^aObtained from least-squares refinement of 9510 reflections with $6.84^\circ < 2\theta < 139.46^\circ$.

^bPrograms for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker. The crystal used for data collection was found to display non-merohedral twinning. Both components of the twin were indexed with the program *CELL_NOW* (Bruker AXS Inc., Madison, WI, 2004). The second twin component can be related to the first component by 180° rotation about the [-0.03 1 0] axis in real space and about the [0 1 0] axis in reciprocal space. Integrated intensities for the reflections from the two components were written into a *SHELXL-2013* HKLF 5 reflection file with the data integration program *SAINTE* (version V8.34A), using all reflection data (exactly overlapped, partially overlapped and non-overlapped). The refined value of the twin fraction (*SHELXL-2014* BASF parameter) was 0.483(2).

^cSheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122.

^dFlack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876–881; Flack, H. D.; Bernardinelli, G. *Acta Crystallogr.* **1999**, *A55*, 908–915; Flack, H. D.; Bernardinelli, G. *J. Appl. Cryst.* **2000**, *33*, 1143–1148. The Flack parameter will refine to a value near zero if the structure is in the correct configuration and will refine to a value near one for the inverted configuration.

^e $S = [\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0653P)^2 + 0.5429P]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2] / 3$).

^f $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^4)]^{1/2}$.

Table 2. Selected Interatomic Distances (Å)*(a) within the [RuCl₂{2,4-(Ph₂P)₂-pentane}{1,2-diphenylethylenediamine}] molecule*

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Ru	Cl1	2.4163(13)	C21	C22	1.392(9)
Ru	Cl2	2.4148(14)	C21	C26	1.397(8)
Ru	P1	2.2638(13)	C22	C23	1.389(9)
Ru	P2	2.2816(12)	C23	C24	1.373(11)
Ru	N1	2.170(5)	C24	C25	1.398(12)
Ru	N2	2.185(4)	C25	C26	1.386(10)
P1	C1	1.851(6)	C31	C32	1.401(8)
P1	C11	1.834(6)	C31	C36	1.406(8)
P1	C21	1.832(6)	C32	C33	1.380(9)
P2	C3	1.868(6)	C33	C34	1.384(10)
P2	C31	1.835(6)	C34	C35	1.388(10)
P2	C41	1.852(6)	C35	C36	1.387(9)
N1	H1NA	0.92(9)	C41	C42	1.400(8)
N1	H1NB	0.88(10)	C41	C46	1.394(8)
N1	C6	1.492(6)	C42	C43	1.387(8)
N2	H2NA	0.94(8)	C43	C44	1.375(10)
N2	H2NB	0.85(9)	C44	C45	1.384(10)
N2	C7	1.491(7)	C45	C46	1.390(8)
C1	C2	1.535(8)	C51	C52	1.389(8)
C1	C4	1.529(8)	C51	C56	1.389(7)
C2	C3	1.537(8)	C52	C53	1.404(9)
C3	C5	1.535(9)	C53	C54	1.384(11)
C6	C7	1.540(7)	C54	C55	1.387(11)
C6	C51	1.514(7)	C55	C56	1.377(9)
C7	C61	1.520(6)	C61	C62	1.380(8)
C11	C12	1.398(8)	C61	C66	1.390(9)
C11	C16	1.386(8)	C62	C63	1.393(8)
C12	C13	1.388(9)	C63	C64	1.372(11)
C13	C14	1.389(12)	C64	C65	1.390(10)
C14	C15	1.380(12)	C65	C66	1.388(8)
C15	C16	1.393(9)			

Reference:

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