Electronic Supplementary Material (ESI) for Dalton Transactions.

Mechanistic diversity in acetophenone transfer hydrogenation catalyzed by ruthenium iminophosphonamide complexes.

Alexander M. Kalsin,*[a] Tatyana A. Peganova,[a] Iana S. Sinopalnikova,[a,b] Ivan V. Fedyanin,[a] Natalia V. Belkova,[a] Eric Deydier,[b] Rinaldo Poli[b,c]*

[a] *A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov str., 119991 Moscow, Russia.*

[b] *CNRS, Laboratoire de Chimie de Coordination, Université de Toulouse, UPS, INPT, 205 Route de Narbonne, 31077 Toulouse Cedex 4, France. Email:* rinaldo.poli@lcc-toulouse.fr.

[c] *Institut Universitaire de France, 1, rue Descartes, 75231 Paris Cedex 05, France.*

SUPPORTING INFORMATION

Table S1. Selected geometrical parameters of complexes **1d** and **1e**: the distances (Å), angles and dihedrals (°).

	1d	**1e**
Ru…Arene(centroid)	1.673	1.647, 1.673
Ru...C (Arene)	2.167 – 2.242(2)	2.17 – 2.25(2)
Ru-N1	2.1373(14)	2.147(8)
Ru-N2	2.1736(14)	2.145(5)
P-N1	1.5887(15)	1.625(6)
P-N2	1.6173(15)	1.591(8)
Ru-Cl	2.4276(5)	2.411(2)
N1-Ru-N2	68.26(5)	67.9(2)
N1-P-N2	97.96(8)	96.3(4)
Ru-N1-P	98.04(7)	97.0(3)
Ru-N2-P	95.73(7)	98.2(3)
Ru-N1-N2-P	179.48(9)	171.8(5)
Arene(centroid)–Ru–P	145.7	140.2, 140.8
Σ(N1)	359.0	357.7
Σ(N2)	358.9	359.5

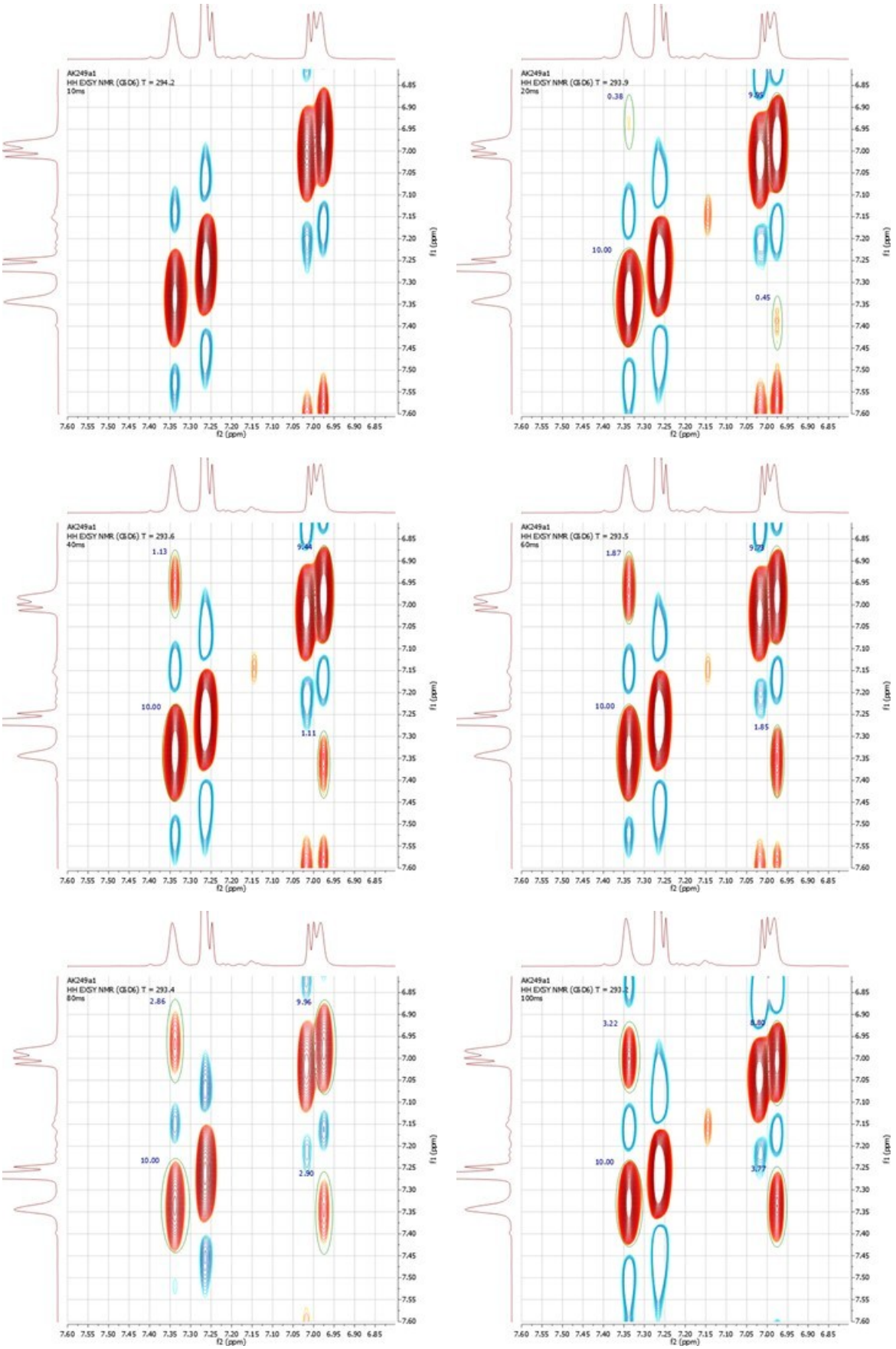
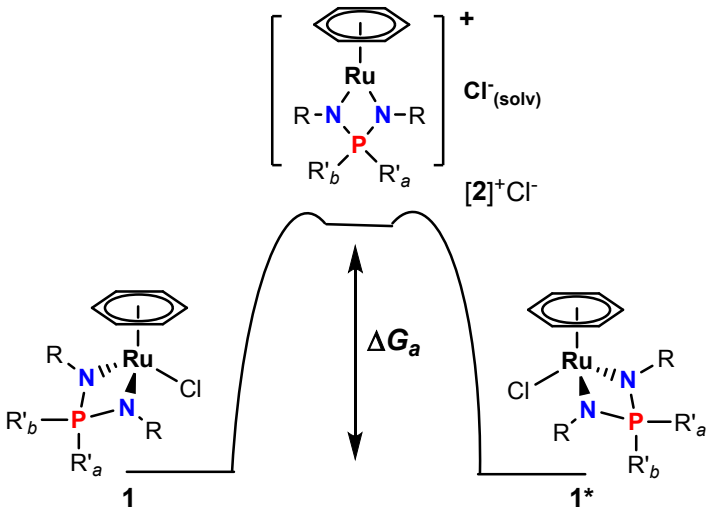


Figure S1. 2D EXSY ^{1}H NMR of **1d** in C_6D_6 at fixed concentration of the complex (10 mM), temperature (294K) and mixing times (10-100 ms).

Table S2. Experimentally measured peaks integral intensities and k_{ex} for **1d** (10 mM) in absolute C_6D_6 at 294 K.

entry	t_m, s	$I_{11}+I_{22}$	$I_{12}+I_{21}$	r(I)	k_{ex}, s^{-1}
1	0.01	10	0		
2	0.02	10	0.45	22.2	2.25
3	0.04	10	1.12	8.93	2.81
4	0.06	10	1.88	5.32	**3.17**
5	0.08	10	2.84	3.52	**3.65**
6	0.10	10	3.25	3.08	**3.37**
				k_{ex}(av)	**3.40 s^{-1}**
				$\Delta G_{ex}^{\neq}$	**16.5 kcal/mol**

The 2D ^{1}H-^{1}H EXSY spectra were collected on a Bruker Avance 600 spectrometer using the standard Bruker library *noesygpph* pulse program. Six experiments with different values of the mixing time t_m were performed to find an optimum mixing time, resulting in sufficiently large exchange cross-peaks without significant relaxation contribution (60-100 ms). The rate constants $k = k_{AB} + k_{BA}$ for the A ↔ B exchange reactions were calculated using simple two-site model [A.D. Bain, *Prog. Nucl. Magn. Reson. Spectrosc.* **2003**, *43*, 63-103] using Equations (1), (2), where k_{AB} and k_{BA} are the rate constants of the direct and inverse reactions, I_{AB}, I_{BA} and I_{AA}, I_{BB} are the cross-peak and the diagonal peak integral intensities, respectively. In case of exchange between equally populated states ($k_{AB} = k_{BA}$), the exchange rate constant is $k_{ex} = k/2$.



$$k = \frac{1}{t_m} ln(\frac{r+1}{r-1}) \qquad (1)$$

$$r = \frac{I_{AA} + I_{BB}}{I_{AB} + I_{BA}} \qquad (2)$$

The activation free energy $\Delta G^{\neq}$ was calculated from the Eyring equation (3) and the activation enthalpy $\Delta H^{\neq}$ and entropy $\Delta S^{\neq}$ were derived by linear fitting of $R\ln(k_{ex}/T)$ plotted *vs*. $1/T$ according to the equation (4).

$$\Delta G^{\neq} = -RT ln \frac{k_{ex} h}{k_b T} \quad (3)$$

$$R ln \frac{k_{ex}}{T} = -\frac{\Delta H^{\neq}}{T} + \Delta S^{\neq} + R ln \frac{k_b}{h} \quad (4)$$

As we noted before [I. S. Sinopalnikova, T. y. A. Peganova, V. V. Novikov, I. V. Fedyanin, O. A. Filippov, N. V. Belkova, E. S. Shubina, R. Poli, A. M. Kalsin, *Chem. Eur. J.* **2017**, 15424], the activation enthalpy $\Delta H_{ex}^{\neq}$ for the dissociative exchange mechanism should be close to the Ru–Cl bond dissociation enthalpy, ΔH_d. The latter depends predominantly on the Ru–Cl bond strength and on the solvent polarity. Hence, the ΔH_d value for complex **1d** in C_6D_6 may be estimated from its $\Delta G^{\neq}$ at 294 K as $\Delta H_d \sim \Delta H_{ex}^{\neq} = \Delta G_{ex}^{\neq} + T\Delta S_{ex}^{\neq}$, where $\Delta S_{ex}^{\neq}$ can be assumed the same as for **1b** (-29.2 cal/(mol·K)). This gives an estimate for the ΔH_d of **1d** as ca. 7.9 kcal/mol. The ΔH_d for **1a-f** expectedly lowers with an increase of the ligand donating ability: over 10 kcal/mol (**1a**, **1e, 1f**) > 8.4 kcal/mol (**1b**) > 7.9 kcal/mol (**1d**) > 5.7 kcal/mol (**1c**).

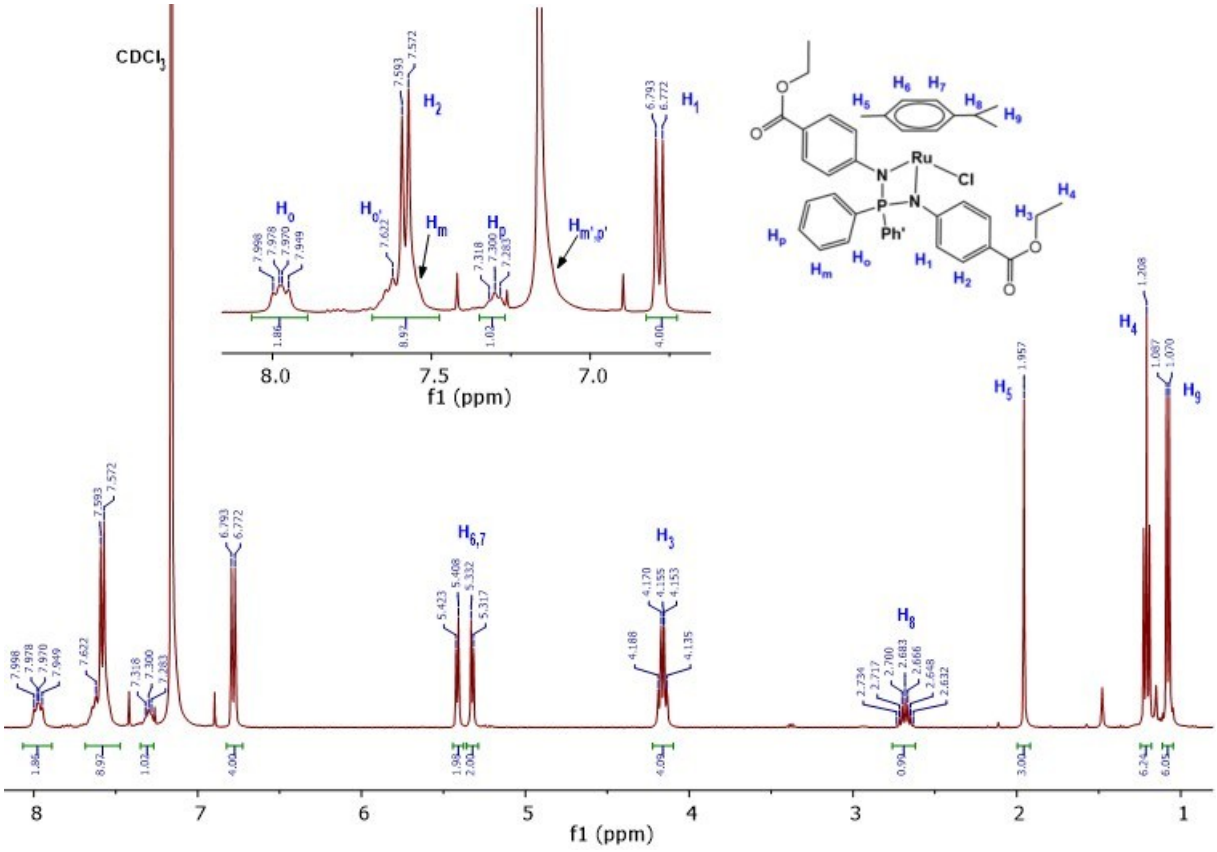


Figure S2. ^{1}H NMR spectrum of **1e** recorded in $CDCl_3$

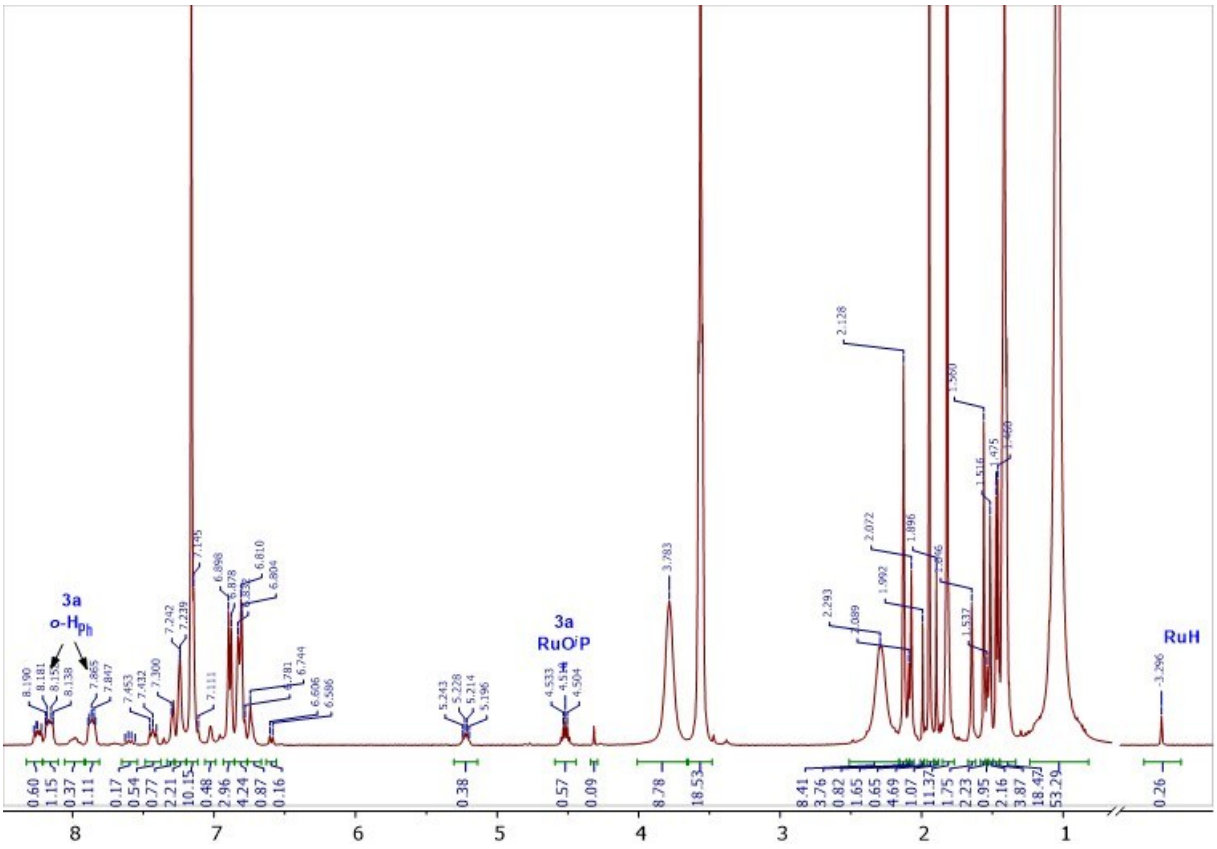


Figure S3. ^{1}H NMR spectrum of **3a**, generated *in situ* from **1a** in C_6D_6 recorded 10 min after the addition of base. Conditions: 0.5 mL of C_6D_6, 14 mg of **1a** (0.02 mmol), 10 µL of *i*PrOH (*i*PrOH/**1a** = 8), 15 µL of NaHDMS (2 M in THF; HMDS/**1a** = 1.5).

Figures S4a-c. NMR spectra of **2a** prepared from **1a** and NaHMDS (1.5 equiv.) in C_6D_6/^{i}PrOH (500/40 µL), followed by evaporation, extraction with Et_2O, filtration, evaporation and analysis in C_6D_6. About 5% of iminophosphonamine **A** is present as an impurity.

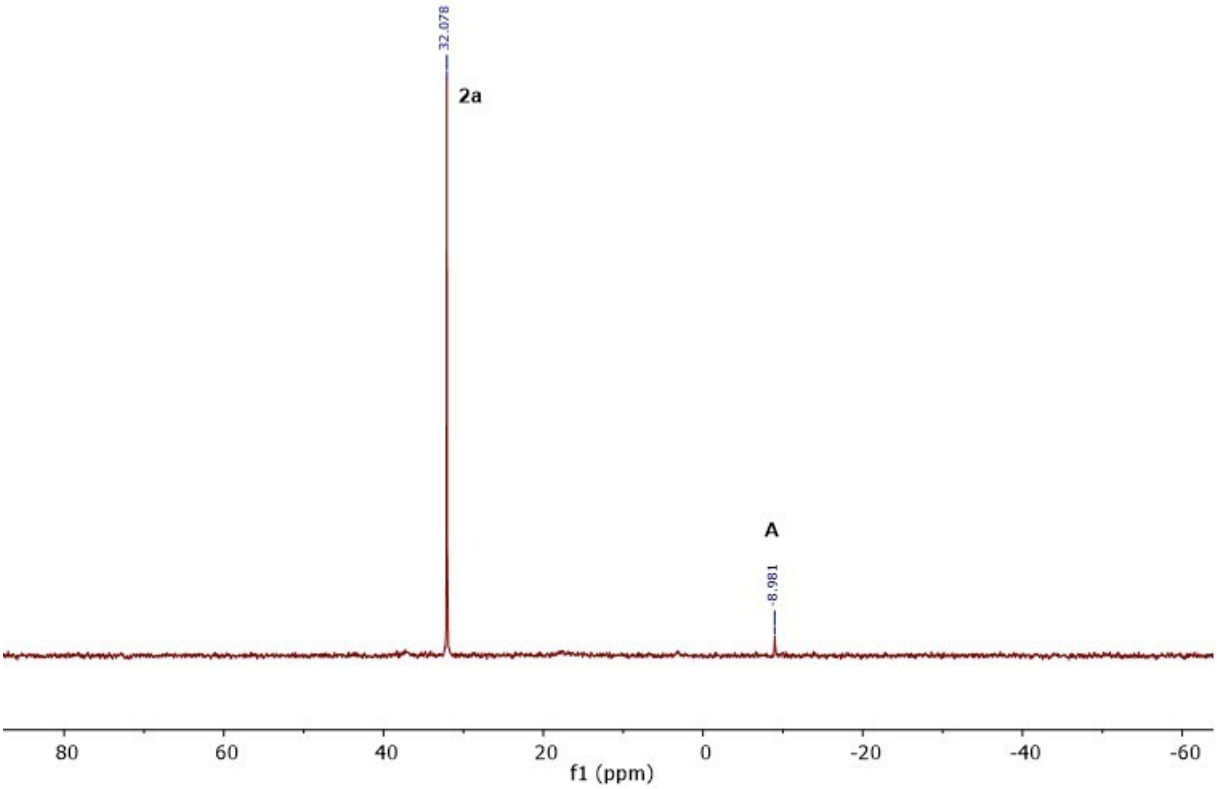


Figure S4a. $^{31}P\{^1H\}$ NMR spectrum of **2a**

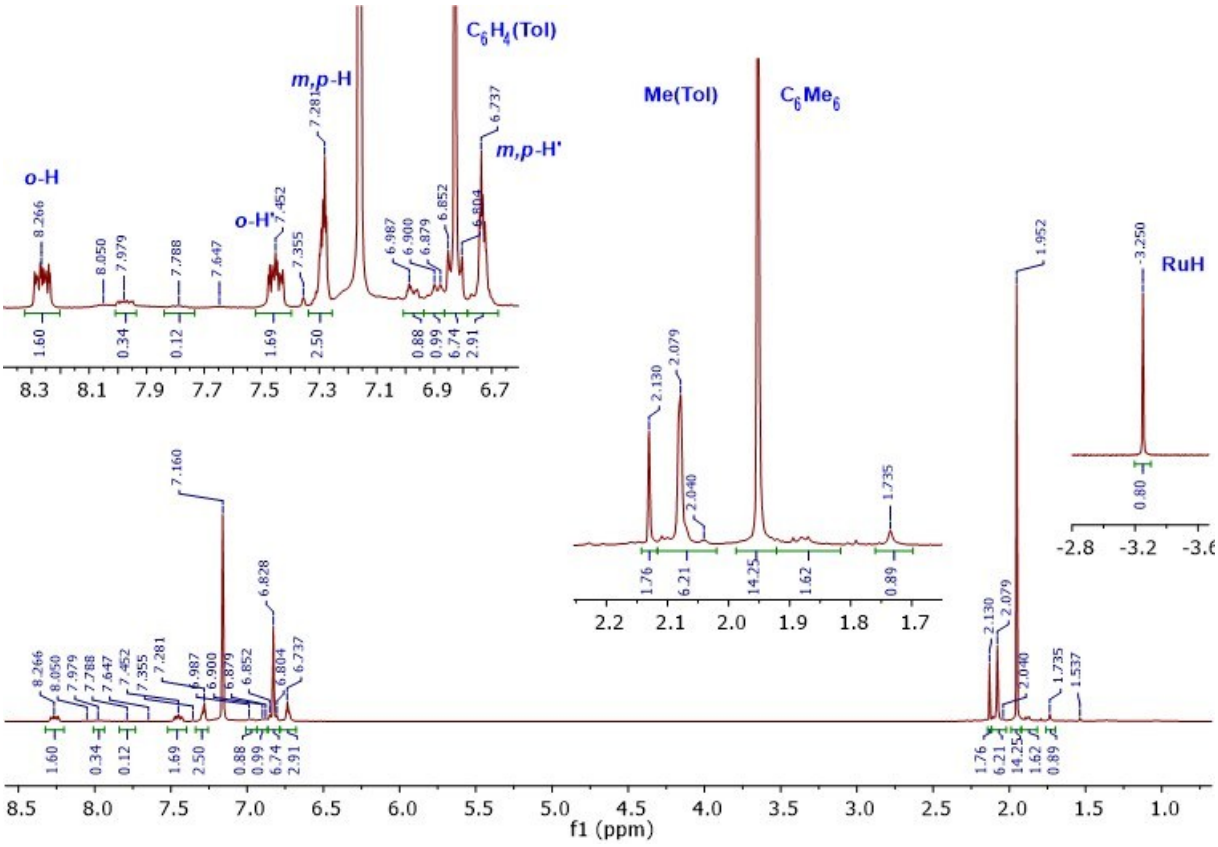


Figure S4b. ^{1}H NMR spectrum of **2a**.

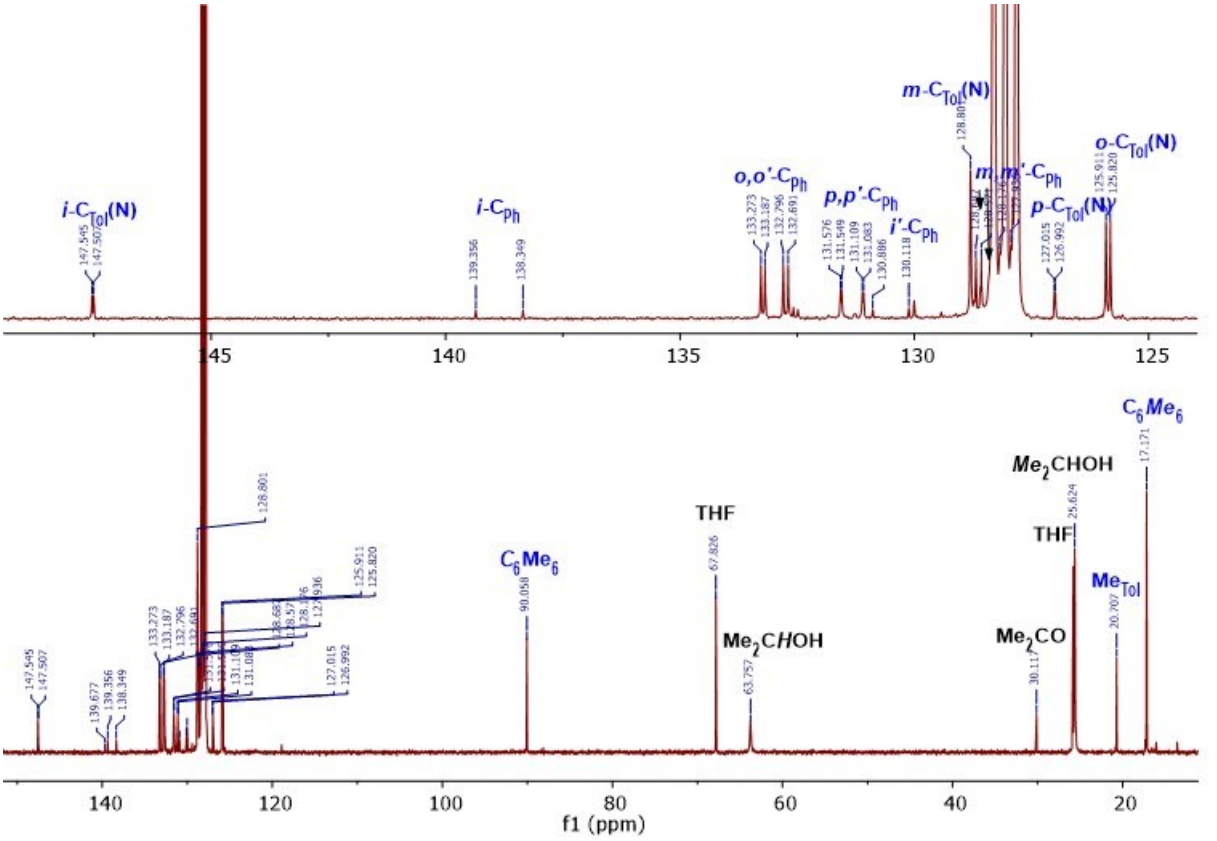


Figure S4c. $^{13}C\{^{1}H\}$ NMR spectrum of **2a** prepared from **1a** and NaHMDS (1.5 equiv.) in C_6D_6/^{i}PrOH (500/10 μL) without isolation.

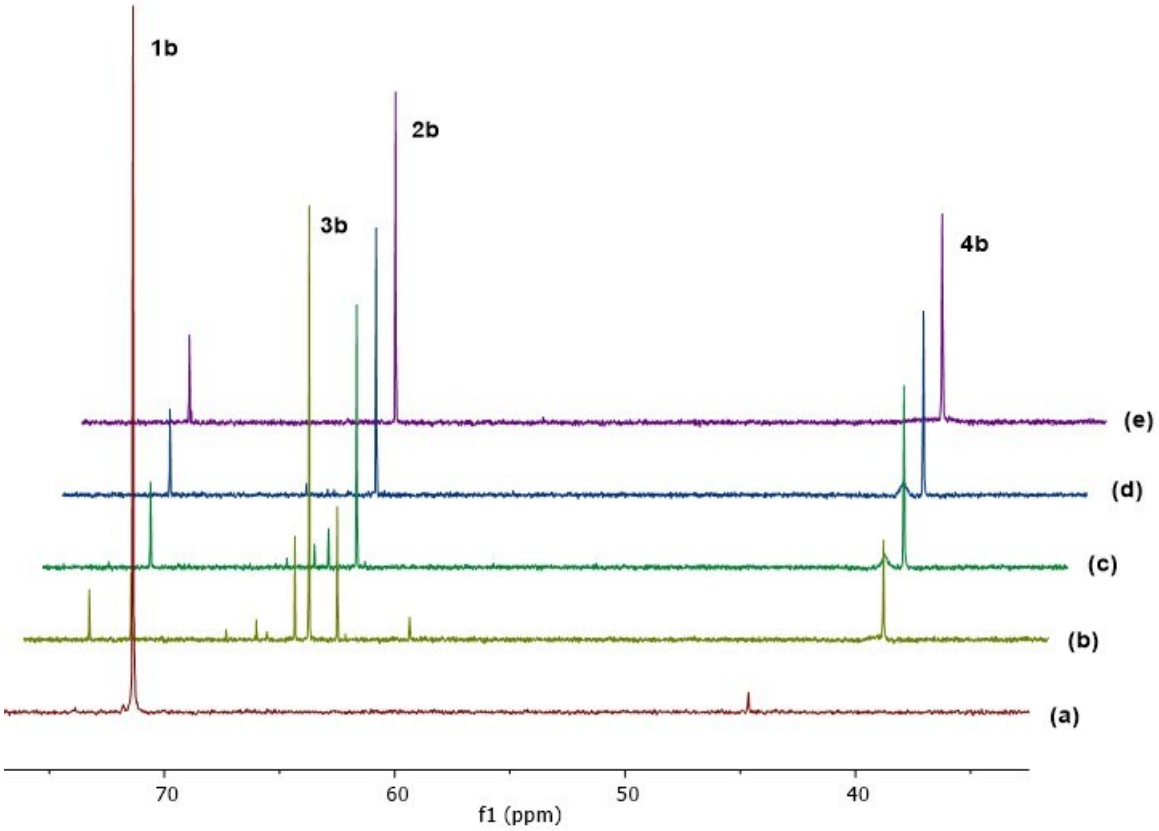


Figure S5. $^{31}P\{^{1}H\}$ NMR monitoring of the reaction of **1b** with NaHMDS/^{i}PrOH in C_6D_6. Conditions: 0.5 mL of C_6D_6, 14 mg of **1b** (0.02 mmol), 10 µL of *i*PrOH (*i*PrOH/**1b** = 8), 15 µL of NaHDMS (2 M in THF; HMDS/**1b** = 1.5). (a) 0 min, (b) 10 min, (c) 1 h, (d) 2 h, (e) 70 h.

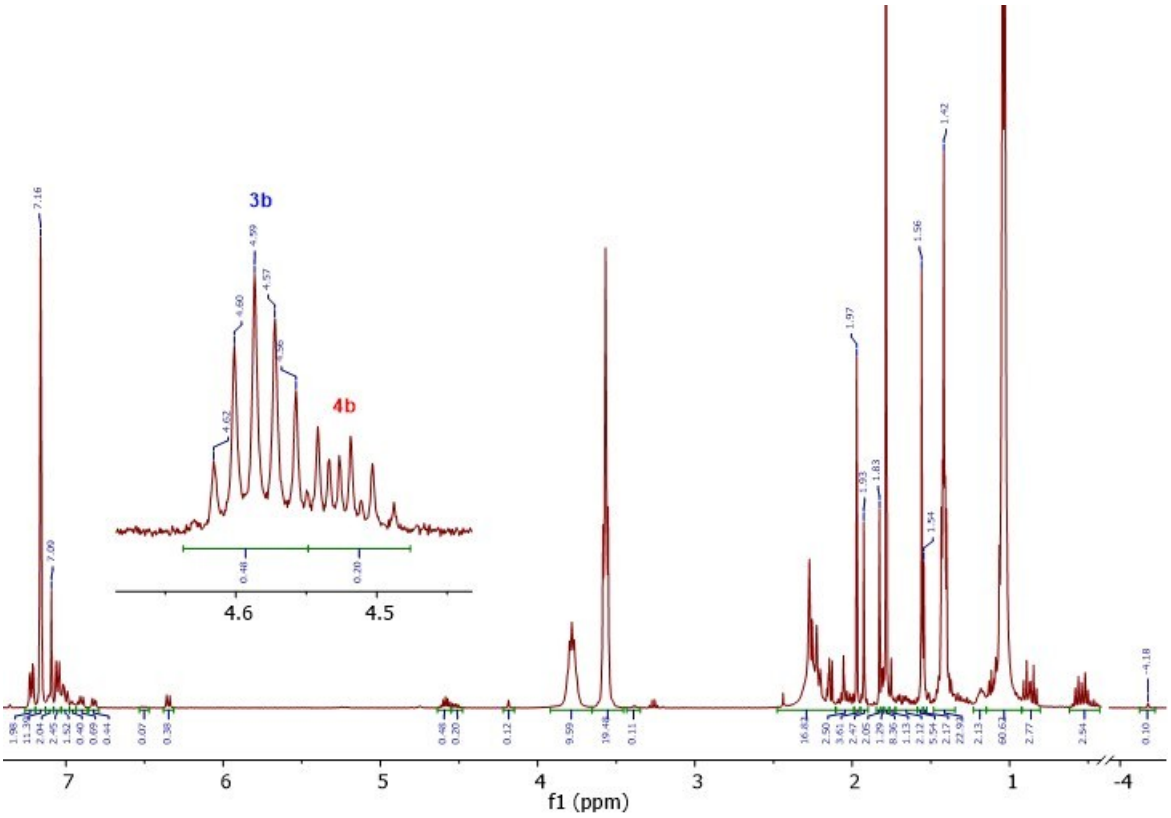


Figure S6. ^{1}H NMR spectrum of the reaction mixture of **1b** with NaHMDS (1.5 equiv.) in C_6D_6/^{i}PrOH (500/10 μL) recorded 5 minutes after mixing. The characteristic signals for **3b** and **4** are indicated.

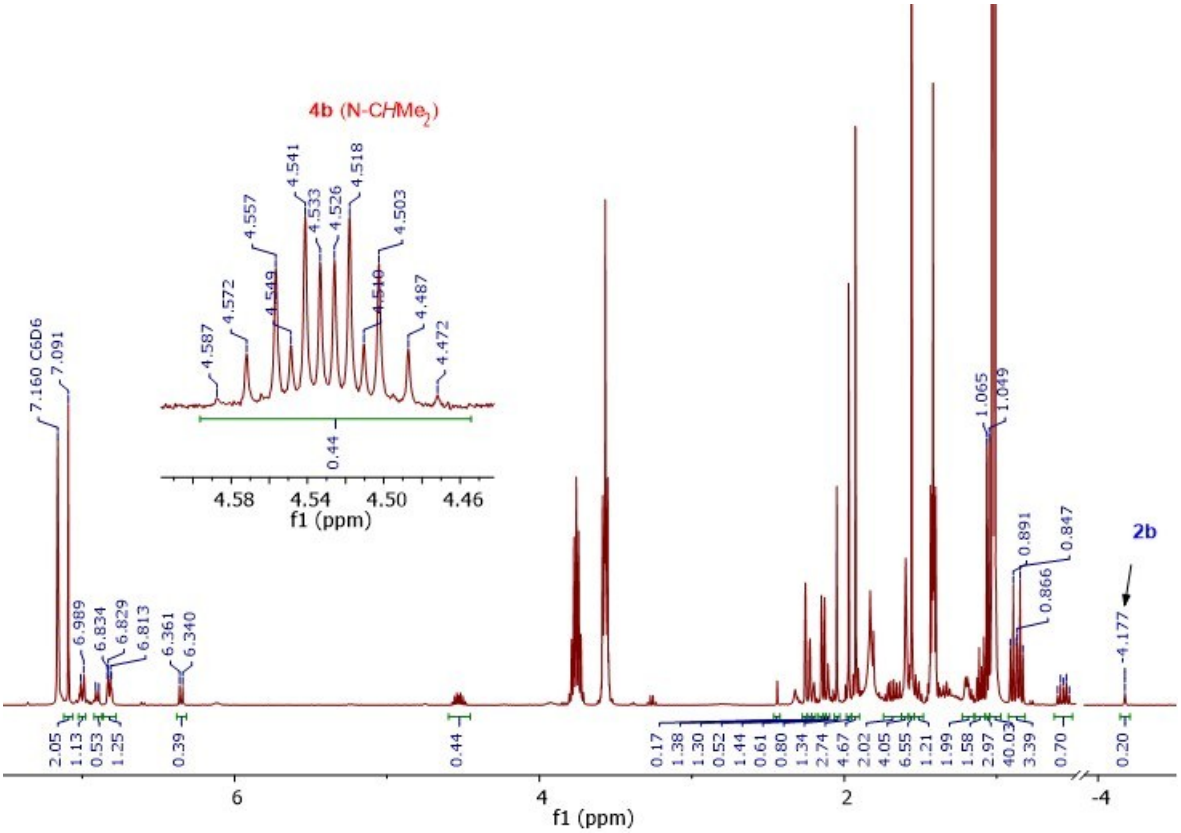


Figure S7. The ^{1}H NMR spectrum of the reaction mixture that corresponds to the ^{31}P NMR spectrum on the Figure S3d. The characteristic signals for **2b** and **4** are indicated.

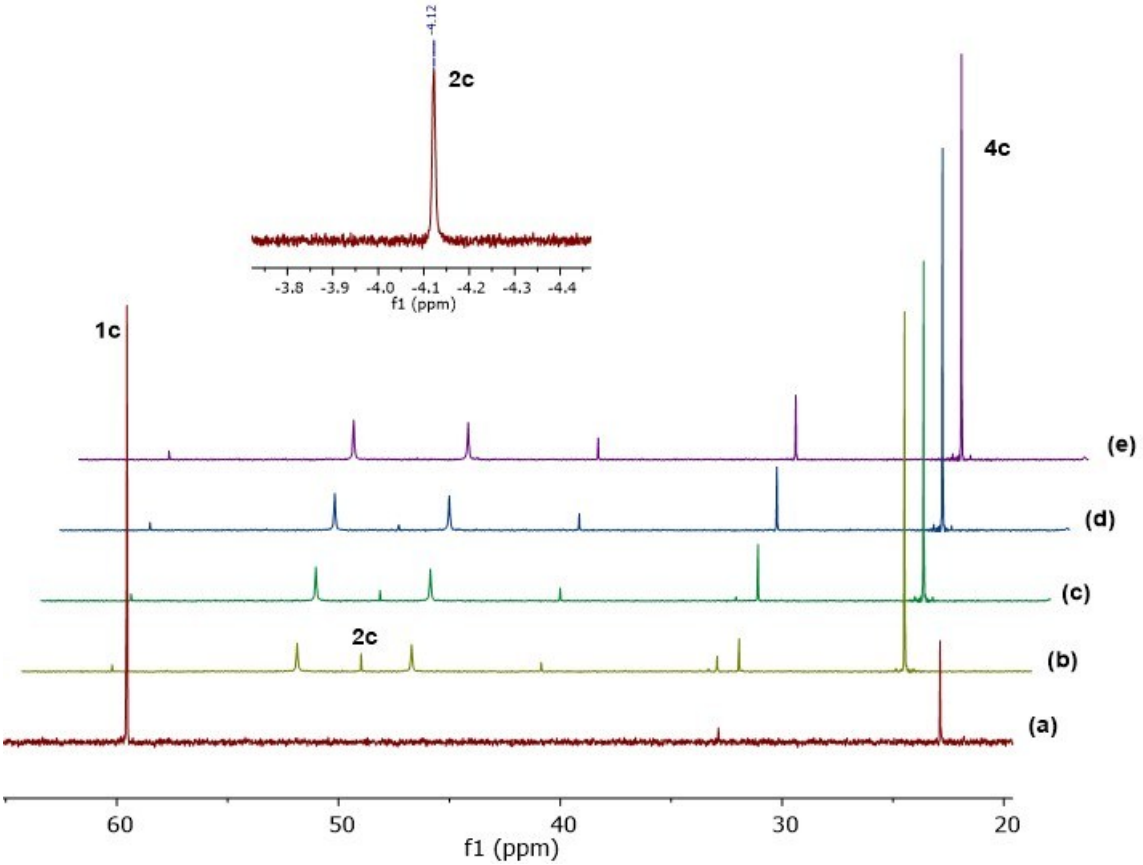


Figure S8. $^{31}P\{^{1}H\}$ NMR monitoring of the reaction of **1c** with NaHMDS/^{i}PrOH in C_6D_6. Conditions: 0.5 mL of C_6D_6, 14 mg of **1c** (0.02 mmol), 10 µL of *i*PrOH (*i*PrOH/**1c** = 8), 10 µL of NaHDMS (2 M in THF; HMDS/**1c** = 1.0). (a) 0 min, (b) 5 min, (c) 10 min, (d) 20 min, (e) 30 min. The insert shows the Ru-H resonance observed in ^{1}H NMR for spectrum (b).

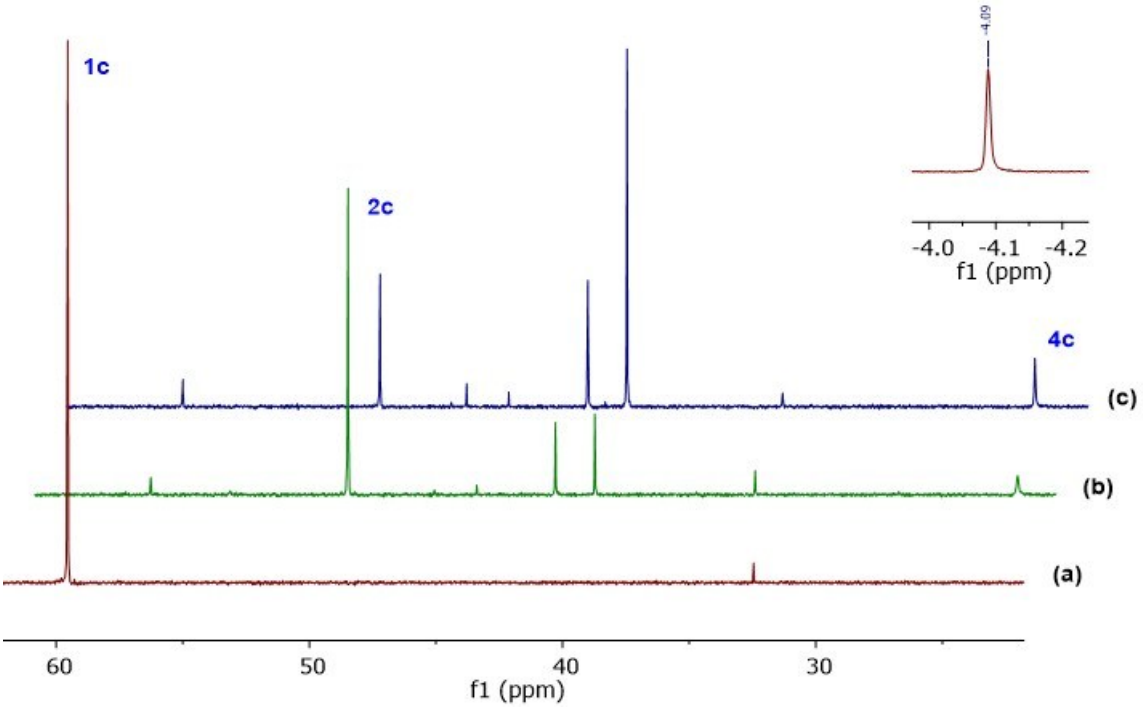


Figure S9a. $^{31}P\{^{1}H\}$ NMR monitoring of the reaction of **1c** with $NaHBEt_3$ (1 equiv.) in C_6D_6. (a) 0 min, (b) 20 min, (c) 2 h. The insert shows the Ru-H resonance observed in ^{1}H NMR for spectrum (b).

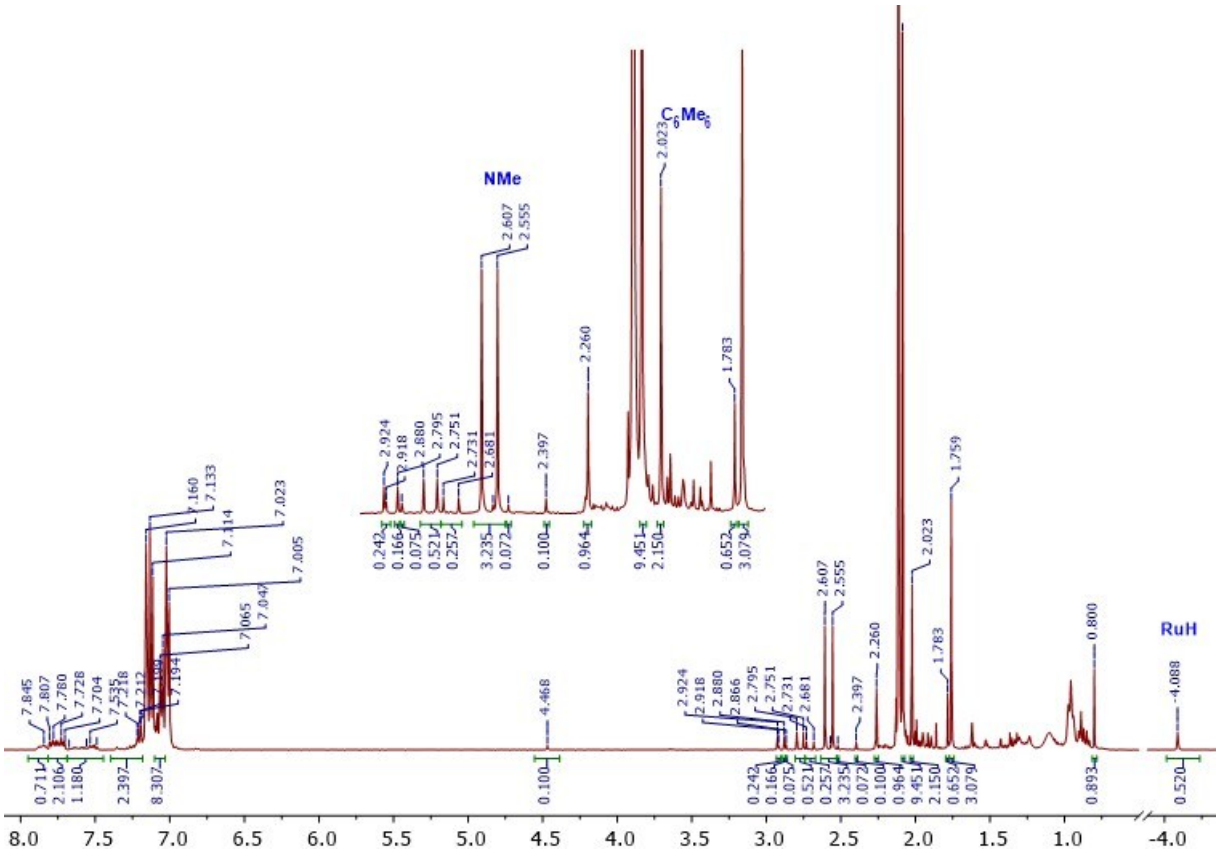


Figure S9b. ^{1}H NMR spectrum of the sample containing about 50% of **2c** that corresponds to the ^{31}P NMR spectrum on Figure S7a(b). Partial assignment for **2c** is given.

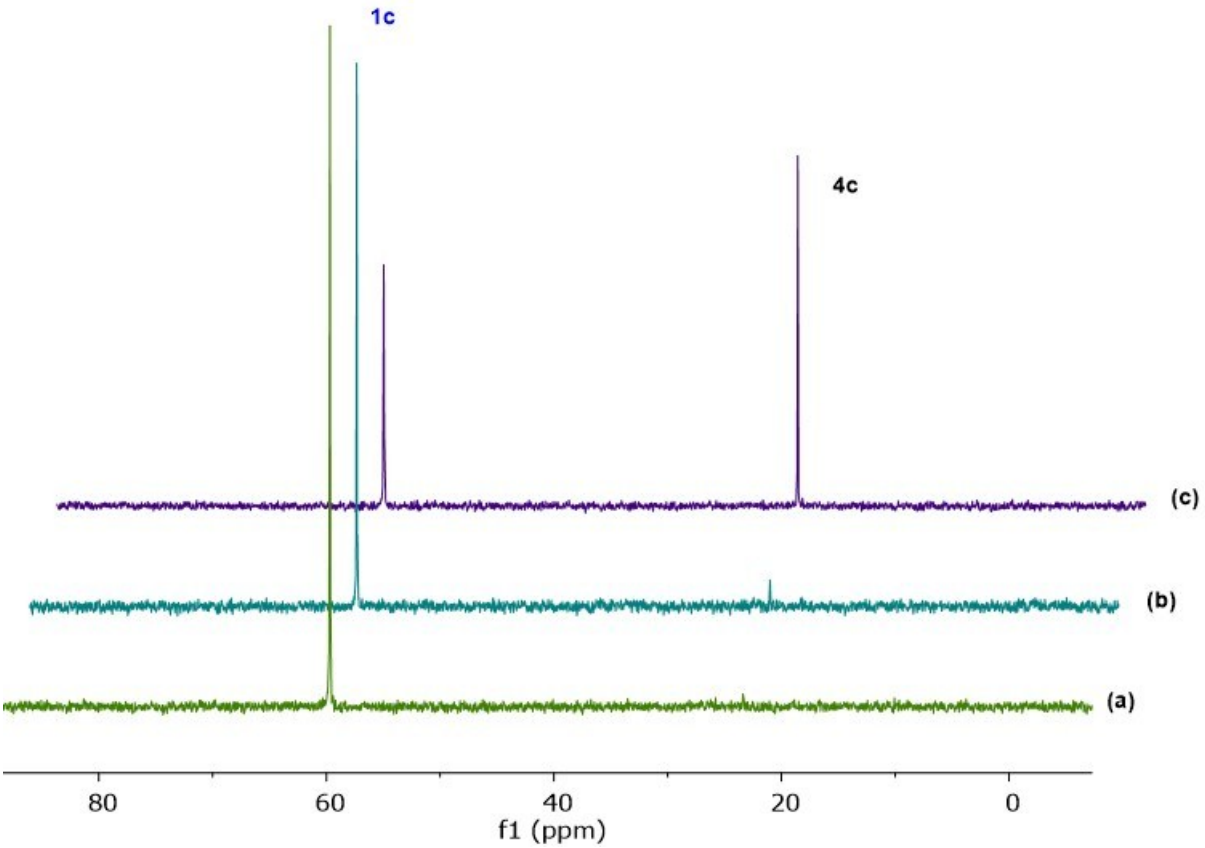


Figure S10. Stability of **1c** in C_6D_6 (0.50 ml) in the presence of isopropanol (6 equiv., 10 µl). (a) 0.5 h, (b) 2 h, (c) 96 h.

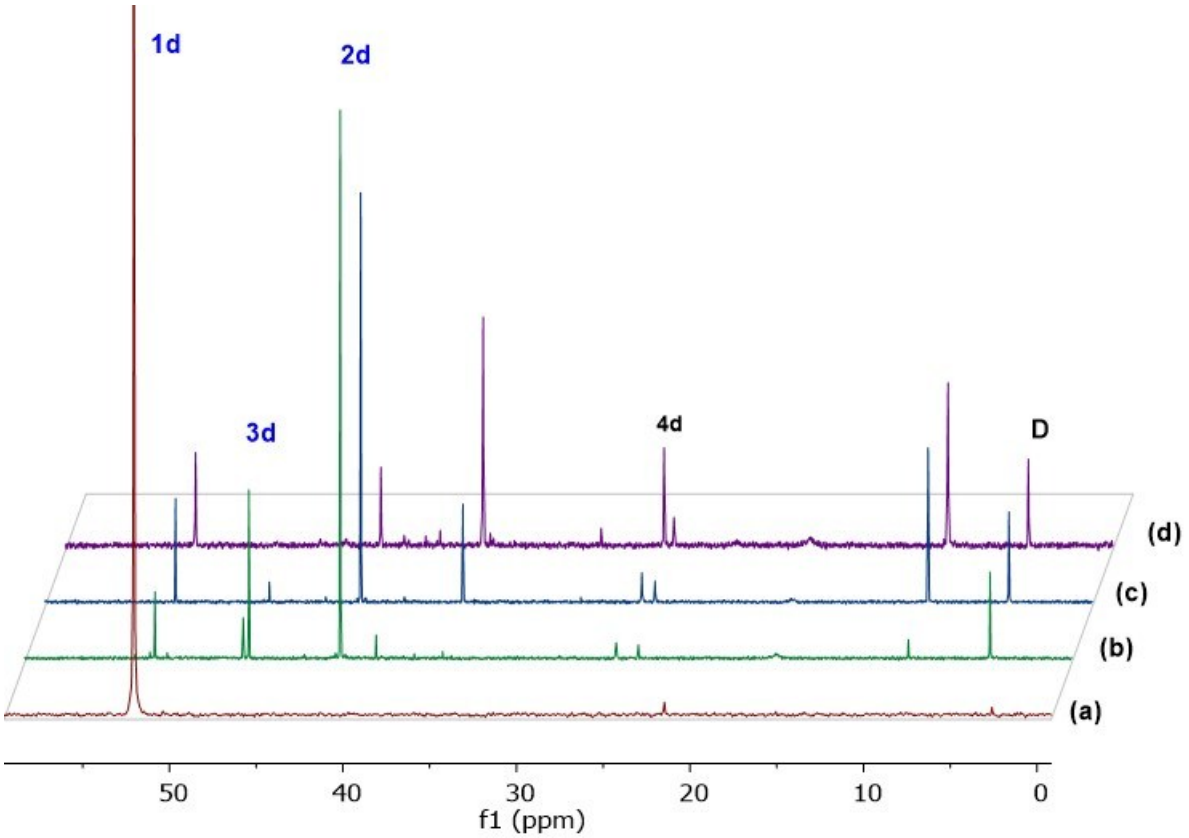


Figure S11. ^{31}P NMR monitoring of the reaction of **1d** with NaHMDS/^{i}PrOH in C_6D_6. Conditions: 0.5 mL of C_6D_6, 12 mg of **1d** (0.02 mmol), 10 μL of *i*PrOH (*i*PrOH/**1d** = 8), 10 μL of NaHDMS (2 M in THF; HMDS/**1d** = 1.0). (a) 0 min, (b) 5 min, (c) 1 h, (d) 72 h.

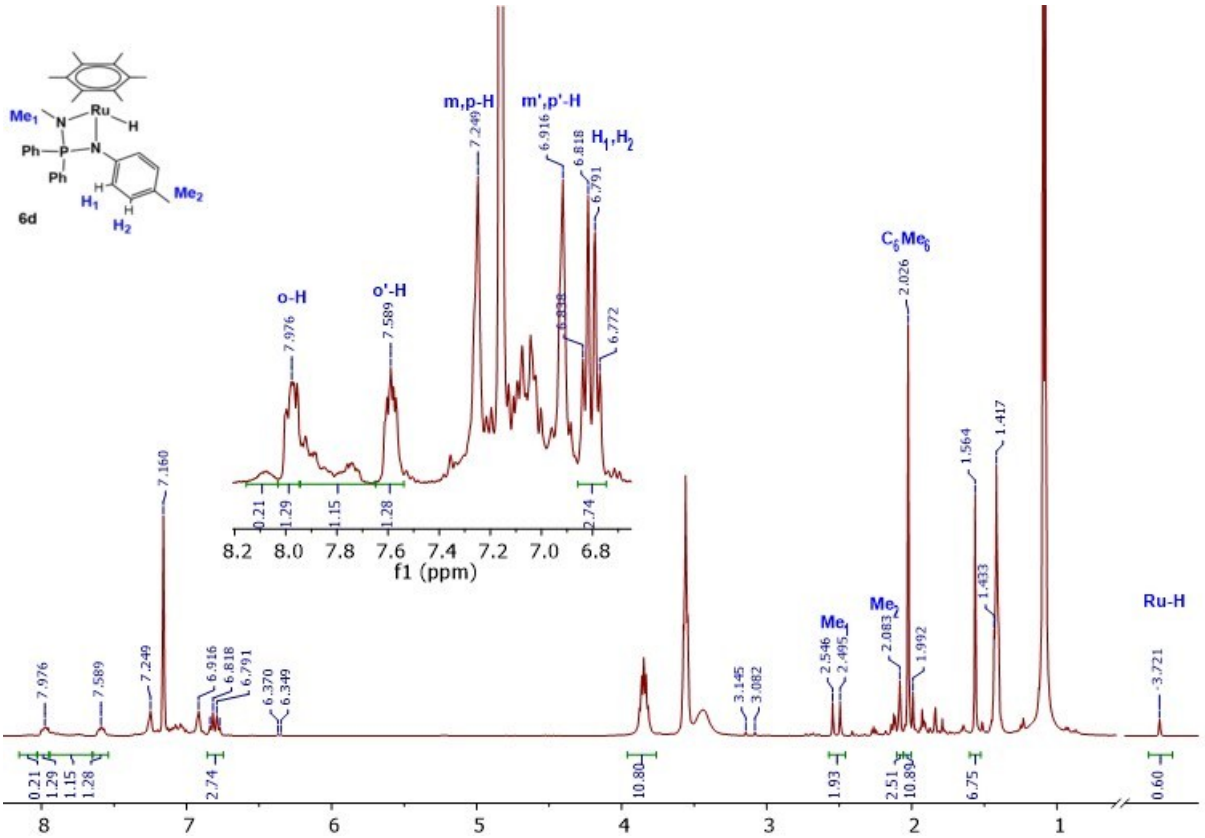


Figure S12. The ^{1}H NMR spectrum of **1d** in C_6D_6/^{i}PrOH (500/20 µL) recorded 1 hour after adding NaHMDS (1.5 equiv.) leading to **2d**. Assignment of resonances is given in blue.

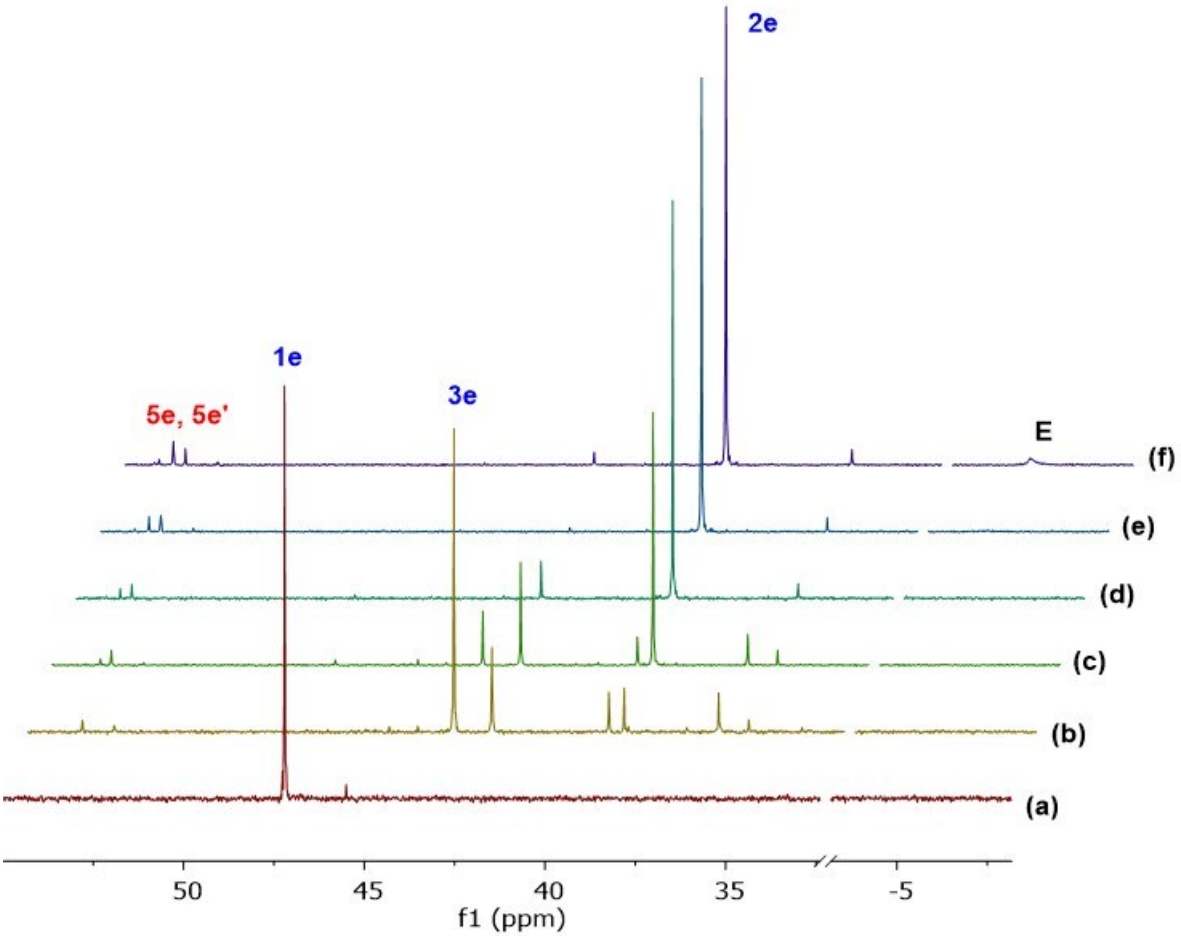


Figure S13. ^{31}P NMR monitoring of the reaction of **1e** with NaHMDS/^{i}PrOH in C_6D_6. Conditions: 0.5 mL of C_6D_6, 16 mg of **1e** (0.02 mmol), 10 µL of *i*PrOH (*i*PrOH/**1e** = 8), 10 µL of NaHDMS (2 M in THF; HMDS/**1e** = 1.0). (a) 0 min, (b) 15 min, (c) 1 h, (d) 2 h, (e) 4 h, (f) 24 h.

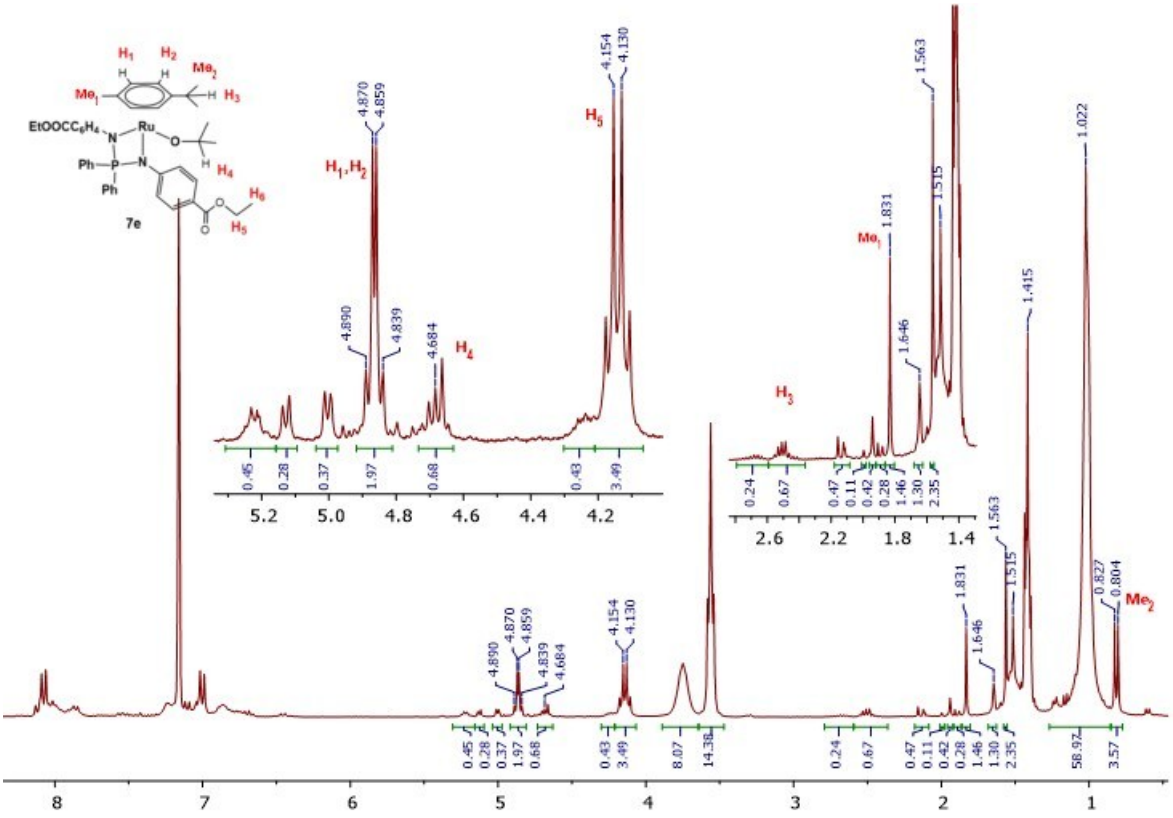


Figure S14. ^{1}H NMR spectrum of **3e** recorded 15 minutes after adding NaHMDS (1.0 equiv.) to **1e** in C_6D_6/^{i}PrOH (500/10 µL). The characteristic signals for compound **3e** are marked.

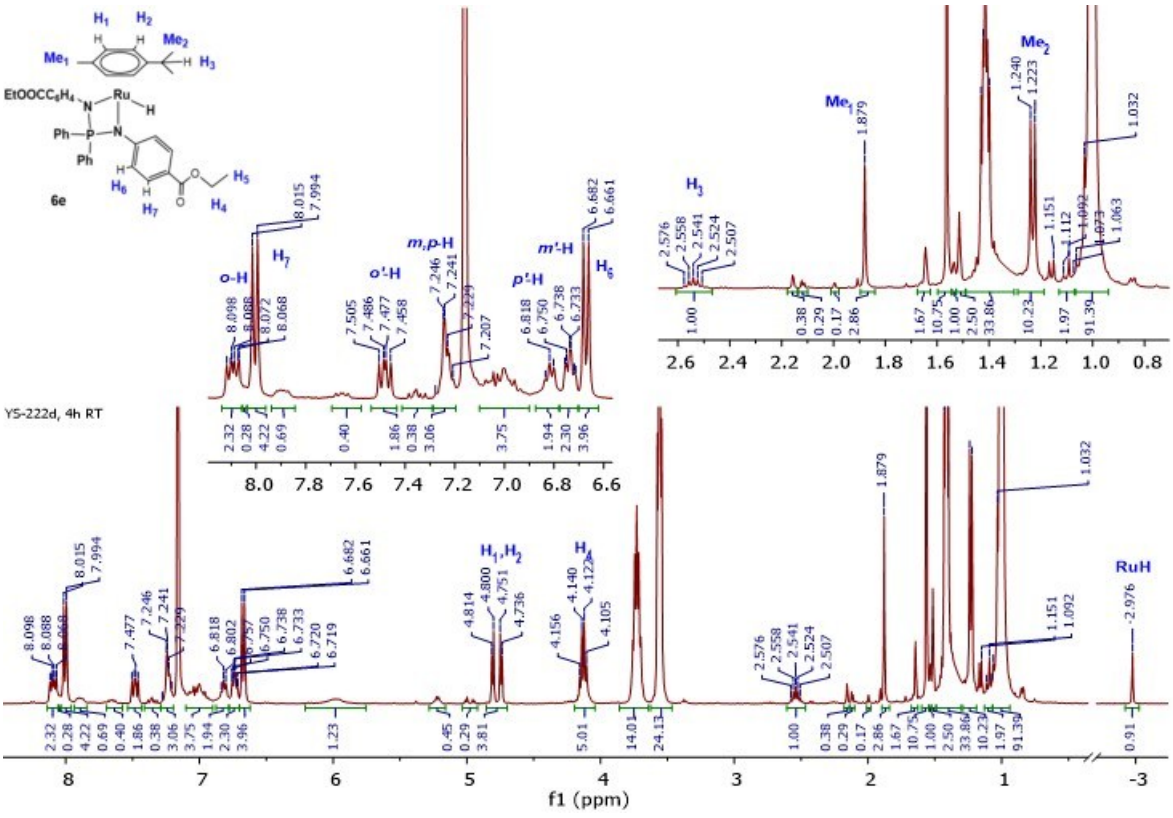


Figure S15. ^{1}H NMR spectrum of **2e** recorded 4 hours after adding NaHMDS (1.0 equiv.) to **1e** in C_6D_6/^{i}PrOH (500/10 µL). The characteristic signals for compound **2e** are marked.

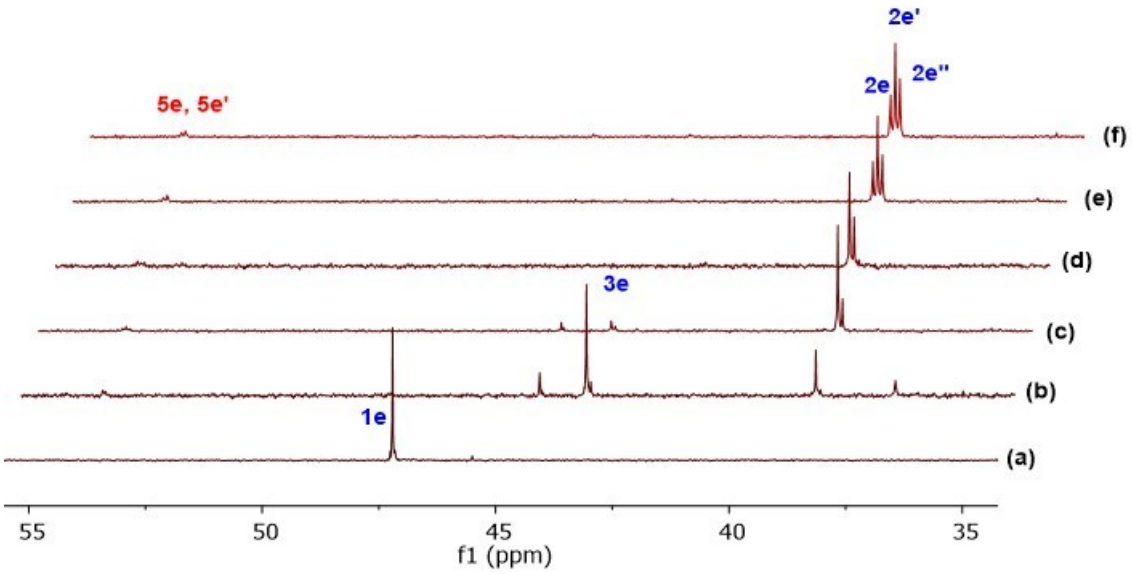
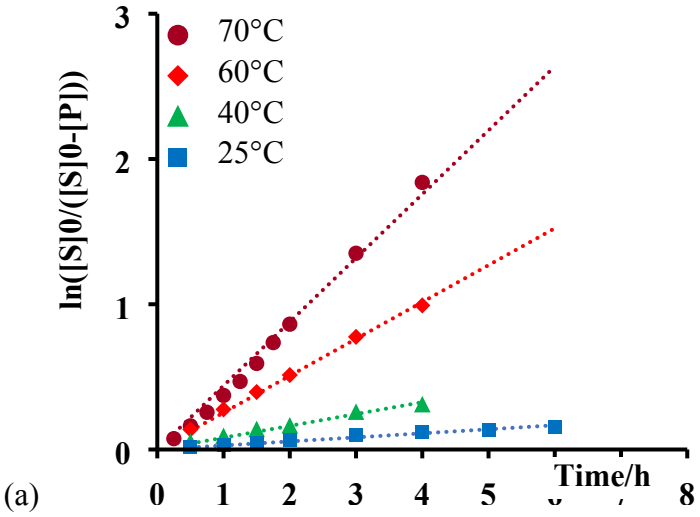
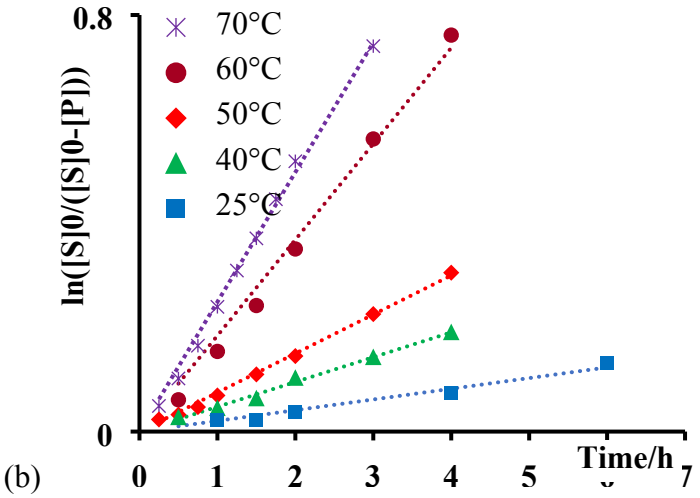


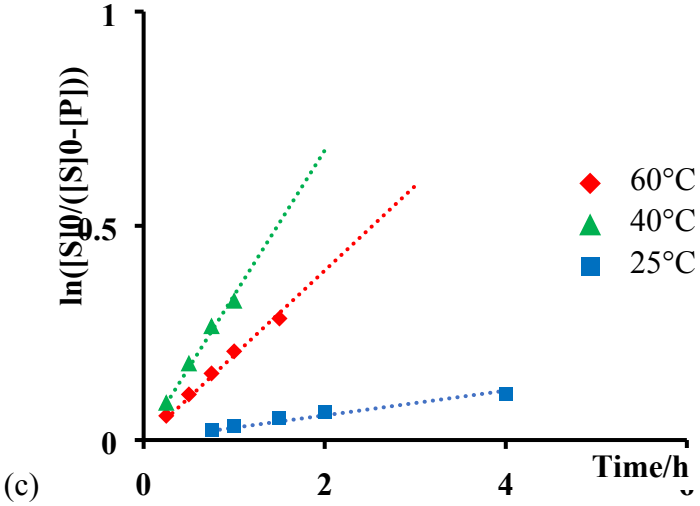
Figure S16. ^{31}P NMR monitoring of the reaction of **1e** with NaHMDS/^{i}PrOH in C_6D_6. Conditions: 0.5 mL of C_6D_6, 16 mg of **1e** (0.02 mmol), 40 µL of *i*PrOH (*i*PrOH/**1e** = 30), 15 µL of NaHDMS (2 M in THF; HMDS/**1e** = 1.5). (a) 0 min, (b) 20 min, (c) 1 h, (d) 2 h, (e) 24 h, (f) 48 h.


70°C
60°C
40°C
25°C
ln([S]0/([S]0-[P]))
Time/h
0
1
2
3
4
5
8

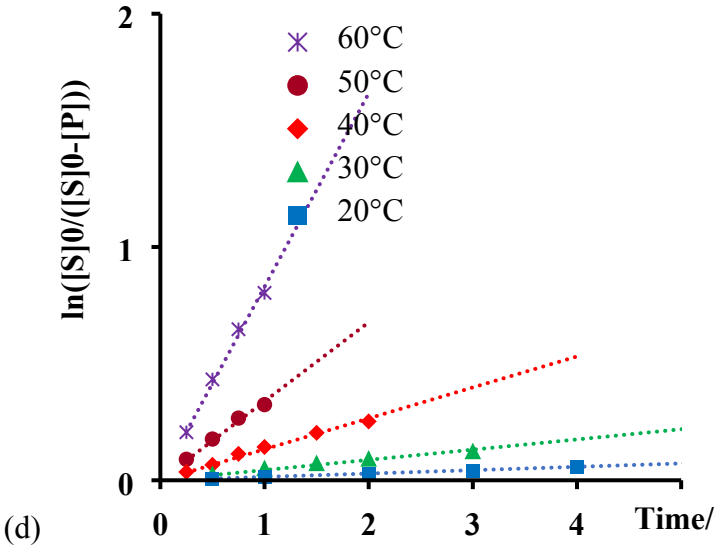
(a)


70°C
60°C
50°C
40°C
25°C
ln([S]0/([S]0-[P]))
Time/h
0.8
0
1
2
3
4
5
7

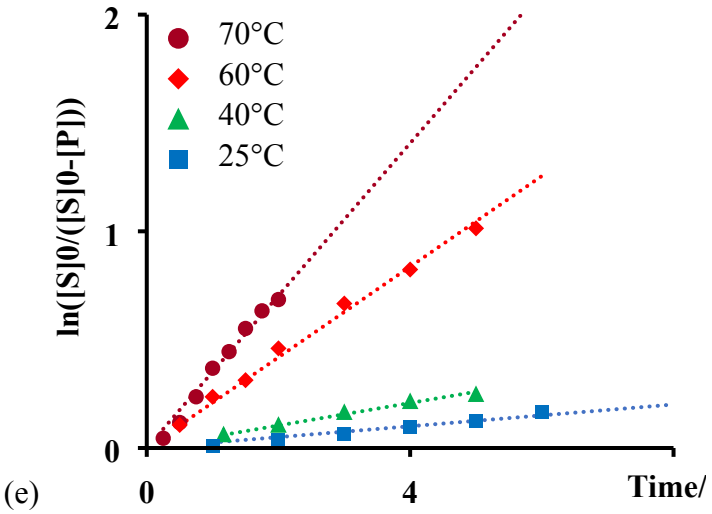
(b)


60°C
40°C
25°C
ln([S]0/([S]0-[P]))
Time/h
1
0.5
0
2
4

(c)



(d)



(e)

Figure S17. First order kinetics analyses of the acetophenone transfer hydrogenation in isopropanol catalyzed by **1a** (a), **1b** (b), **1c** (c), **1d** (d), **1e** (e) in the presence of base at different temperatures.

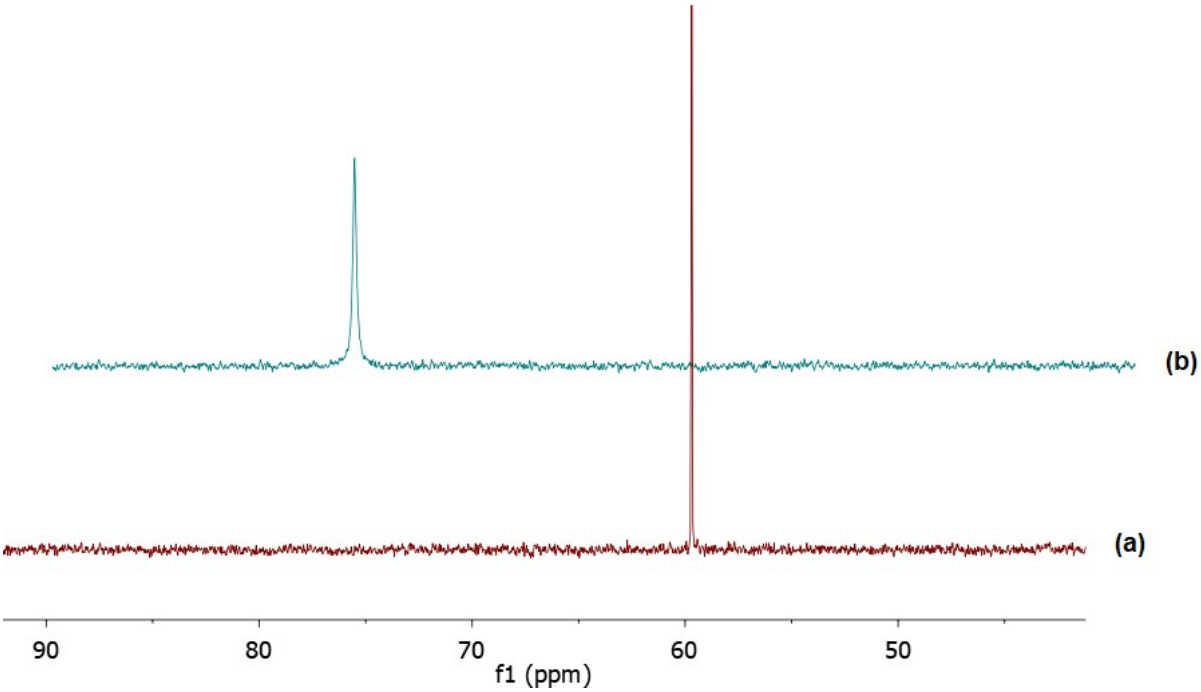


Figure S18. ^{31}P NMR spectra of **1d** recorded in C_6D_6 (**a**) and iPrOH (**b**).

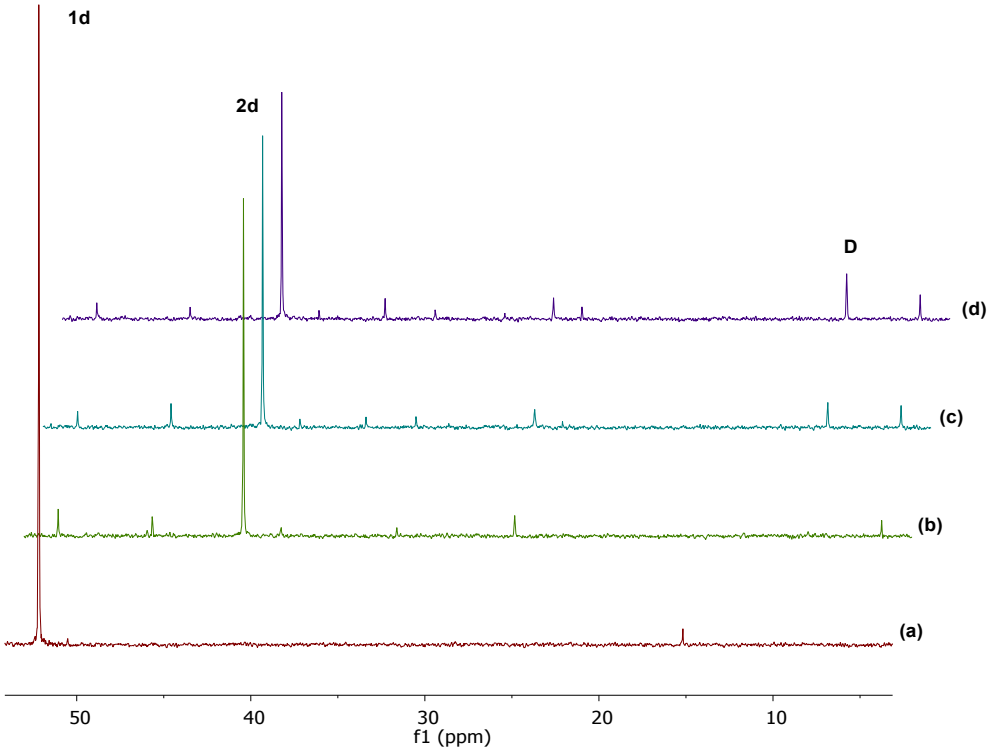


Fig. S19. ^{31}P NMR monitoring of **2d** generation followed by the addition of acetophenone. (a) **1d** in C_6D_6 (36 mM), (b) 10 min after addition of 10 equiv. of ^{i}PrOH (15 µL) and 1 equiv. of NaHMDS (0.5M in C_6D_6), (c) 10 min after addition of acetophenone (3 equiv.), (d) 50 min after the addition of acetophenone.

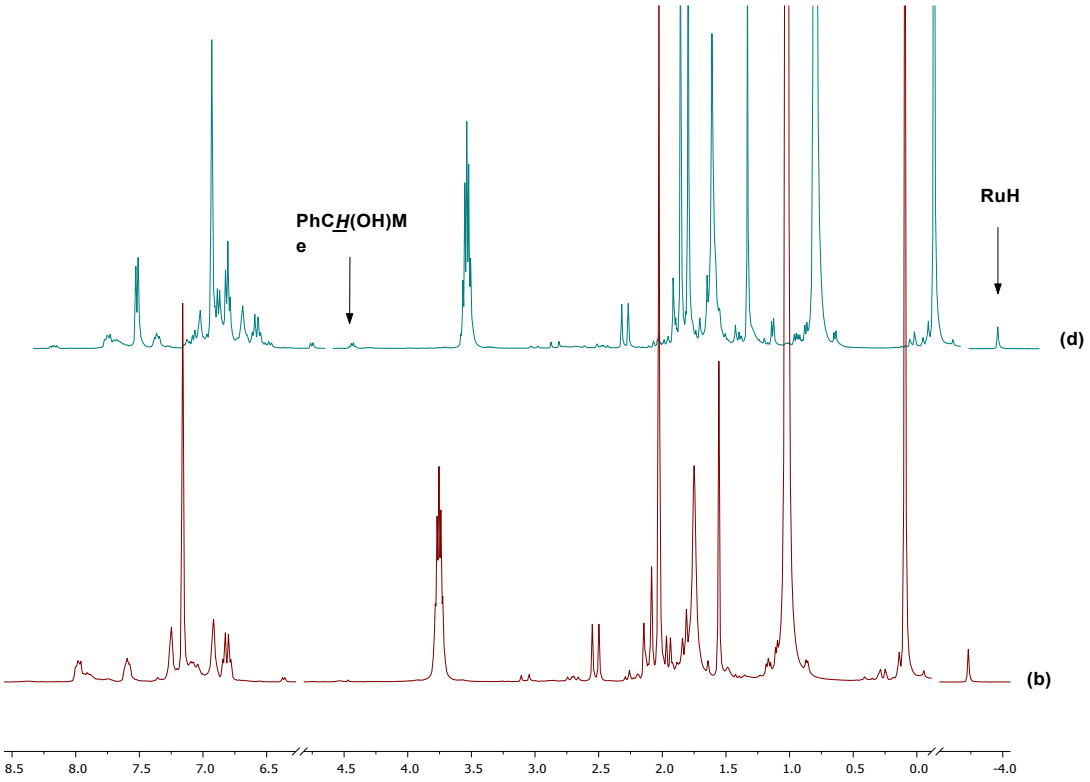


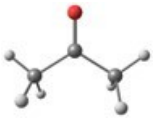
Fig. S20. ^{1}H NMR spectra for reaction of **2d** with acetophenone: the lower and the upper spectra correspond to (b) and (d) given on the Fig. S19.

Table S3. Crystal data and structure refinement parameters for **1d**, **1e**.

	1d	**1e**
Formula	$C_{32}H_{38}ClN_2PRu$	$C_{40}H_{42}ClN_2O_4PRu$
Formula weight	618.13	782.24
T, K	120	120
Crystal system	triclinic	triclinic
Space group	P-1	P-1
Z / Z'	2 / 1	2 / 1
a, Å	8.5677(4)	8.3234(4)
b, Å	10.2597(5)	9.3567(5)
c, Å	16.9517(8)	24.2732(13)
α, °	98.3850(10)	86.402(4)
β, °	98.0930(10)	84.285(3)
γ, °	104.7520(10)	74.464(3)
V, Å^3	1400.70(12)	1810.98(16)
d_{calc}, g cm^{-3}	1.466	1.435
Radiation type	MoKα	CuKα
μ, cm^{-1}	7.37	49.48
$2\theta_{max}$, °	60	135.4
Reflns. collected / independent	18805 / 8156	25523
Observed reflections [I>2σ(I)]	7131	23093
R_1	0.0283	0.0626
wR_2	0.0672	0.1534
GOF	1.027	1.029
Residual density, e Å^{-3} (d_{max}/d_{min})	0.537/-0.359	1.522/-1.072

Table S4. Cartesian coordinates, energies (gas-phase electronic energy and solvation-dispersion-corrected Gibbs energy in 1M isopropanol solution, in hartree) and views of all geometry-optimized molecules.

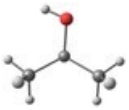
Acetone



E = -193.0912669
G = -193.0348469

8	0.000005000	1.411746000	0.000114000
6	0.000001000	0.185871000	-0.000402000
6	-1.286037000	-0.617998000	-0.003009000
1	-1.251523000	-1.392383000	-0.783589000
1	-1.380399000	-1.142451000	0.961131000
1	-2.151429000	0.038260000	-0.151154000
6	1.286031000	-0.618004000	0.003107000
1	1.251082000	-1.392291000	0.783771000
1	1.380911000	-1.142580000	-0.960911000
1	2.151347000	0.038263000	0.151656000

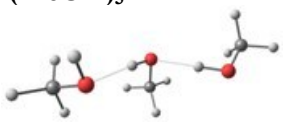
***i*PrOH**



E = -194.29732006
G = -194.2171981

6	-0.002807000	0.039775000	0.368185000
1	0.011239000	0.088046000	1.472138000
6	1.170050000	-0.825603000	-0.104790000
1	1.173794000	-0.889736000	-1.203364000
1	2.125815000	-0.389725000	0.224330000
1	1.094838000	-1.841938000	0.310080000
6	-1.350330000	-0.512646000	-0.090079000
1	-1.507425000	-1.520139000	0.319300000
1	-2.169996000	0.136315000	0.250202000
1	-1.380345000	-0.570405000	-1.188702000
8	0.098895000	1.381609000	-0.166944000
1	0.959440000	1.725555000	0.111671000

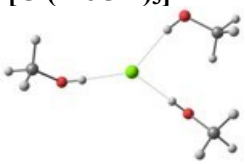
$(MeOH)_3$



E = -347.101986747
G = -346.982664

1	-0.040814000	1.314010000	-1.362833000
6	-0.019031000	1.587229000	-0.294974000
1	-0.914598000	2.185250000	-0.059510000
1	0.871625000	2.200063000	-0.105986000
8	0.065509000	0.424631000	0.550569000
1	-0.710639000	-0.140006000	0.321160000
1	-2.247427000	-1.724705000	0.446153000
8	-2.174969000	-0.995584000	-0.186579000
1	-4.235883000	-0.612178000	-0.002582000
6	-3.270798000	-0.089938000	0.083055000
1	-3.183983000	0.358789000	1.085286000
1	-3.222998000	0.700231000	-0.675186000
8	2.289512000	-0.765998000	-0.576672000
6	3.297838000	-0.277164000	0.313246000
1	3.324568000	0.827842000	0.348514000
1	3.160112000	-0.650219000	1.345169000
1	4.273017000	-0.630633000	-0.052033000
1	1.438550000	-0.453595000	-0.194656000

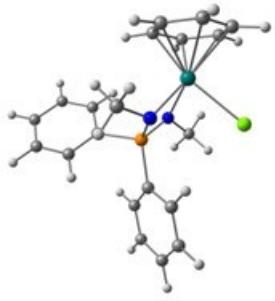
$[Cl(MeOH)_3]^-$



E = -807.513565383
G = -807.402813

1	1.164027000	-1.100124000	-0.504476000
8	1.928682000	-1.638801000	-0.795441000
1	3.348510000	-2.814838000	0.107745000
6	2.510457000	-2.167431000	0.402443000
1	2.899812000	-1.371412000	1.062099000
1	1.788204000	-2.773165000	0.978315000
8	1.596872000	2.372543000	-0.272486000
6	2.790115000	1.640602000	0.040549000
1	2.870047000	1.425329000	1.122453000
1	2.841271000	0.687072000	-0.509990000
1	3.647651000	2.265271000	-0.248840000
1	0.858840000	1.761735000	-0.076490000
17	-0.547684000	0.049244000	0.409221000
1	-2.578896000	-0.257157000	-0.483316000
6	-4.307926000	0.119487000	0.313689000
1	-4.093606000	1.175827000	0.560720000
1	-5.362286000	0.043935000	0.011110000
1	-4.165786000	-0.483618000	1.229651000
8	-3.508433000	-0.352735000	-0.775300000

$[(C_6H_6)RuCl(NPN)]$

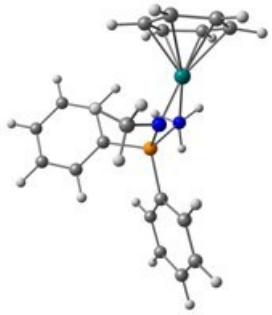


E = -1780.20870915
G = -1779.899948

17	-1.618874000	-2.725963000	-0.112978000
7	-0.122761000	-0.132204000	1.257776000
7	-0.096393000	-0.104438000	-1.242816000
15	0.949579000	0.015777000	0.023770000
6	1.795865000	1.638032000	0.086517000

6	1.241071000	2.661344000	0.876784000
6	2.903791000	1.911797000	-0.738377000
6	1.797781000	3.946456000	0.850204000
1	0.384280000	2.437692000	1.509826000
6	3.454915000	3.198850000	-0.763891000
1	3.336668000	1.123394000	-1.352339000
6	2.903413000	4.215852000	0.030236000
1	1.371763000	4.734947000	1.469699000
1	4.314984000	3.407702000	-1.399006000
1	3.335926000	5.215553000	0.010652000
6	2.279224000	-1.230269000	-0.029809000
6	3.446459000	-1.073274000	0.743143000
6	2.090883000	-2.397580000	-0.792831000
6	4.420251000	-2.079359000	0.746971000
1	3.596351000	-0.168890000	1.331057000
6	3.072056000	-3.396513000	-0.789778000
1	1.177599000	-2.510806000	-1.373436000
6	4.235222000	-3.238749000	-0.021273000
1	5.323756000	-1.956192000	1.342905000
1	2.928843000	-4.297304000	-1.385501000
1	4.997282000	-4.017454000	-0.021288000
6	-3.721912000	-0.000525000	1.211050000
6	-4.057999000	-0.472429000	-0.090826000
6	-3.686819000	0.248315000	-1.264912000
6	-2.865162000	1.406312000	-1.123328000
6	-2.485116000	1.891385000	0.167384000
6	-2.892827000	1.154319000	1.327000000
1	-3.972051000	-0.587492000	2.089542000
1	-4.564510000	-1.427997000	-0.194396000
1	-3.914513000	-0.148558000	-2.249429000
1	-2.464136000	1.889253000	-2.010067000
1	-1.819098000	2.743696000	0.261925000
1	-2.511626000	1.445184000	2.302868000
44	-1.847219000	-0.181624000	-0.027355000
6	0.067334000	-1.024910000	2.399853000
1	0.977625000	-0.752082000	2.961435000
1	-0.788816000	-0.905617000	3.079328000
1	0.132453000	-2.089656000	2.121065000
6	0.019537000	0.756722000	-2.420602000
1	-0.769979000	0.483581000	-3.134134000
1	-0.081575000	1.834323000	-2.196149000
1	0.989849000	0.604761000	-2.922653000

$[(C_6H_6)Ru(NPN)]^+$



E = -1319.79729392
G = -1319.484114

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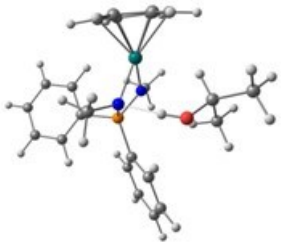
7	-0.116202000	-0.626969000	-1.226344000
15	0.910146000	-0.163830000	-0.004572000
6	1.184554000	1.629378000	-0.013728000
6	0.139483000	2.455056000	0.445599000
6	2.348678000	2.200682000	-0.561194000
6	0.265840000	3.845432000	0.366706000
1	-0.762700000	2.004080000	0.852355000
6	2.464634000	3.594445000	-0.640037000
1	3.154699000	1.567274000	-0.925016000
6	1.427872000	4.415717000	-0.175465000
1	-0.539996000	4.482733000	0.728060000
1	3.364039000	4.036731000	-1.065673000
1	1.523523000	5.498878000	-0.237152000
6	2.519850000	-0.988545000	0.010714000
6	3.536364000	-0.544726000	0.880419000
6	2.713328000	-2.130481000	-0.789555000
6	4.744748000	-1.246922000	0.944340000
1	3.386691000	0.340429000	1.495432000
6	3.930738000	-2.818652000	-0.726260000
1	1.919660000	-2.470822000	-1.452533000
6	4.942709000	-2.379154000	0.139784000
1	5.531738000	-0.908171000	1.616306000
1	4.088955000	-3.697027000	-1.349970000
1	5.887322000	-2.919132000	0.188395000
6	-3.667419000	-1.636881000	0.569090000
6	-3.672597000	-1.456562000	-0.858336000
6	-3.448437000	-0.176526000	-1.413717000
6	-3.149733000	0.920259000	-0.547211000
6	-3.187350000	0.744234000	0.880064000
6	-3.497924000	-0.530087000	1.438422000
1	-3.753297000	-2.639135000	0.979946000
1	-3.755916000	-2.323573000	-1.507399000
1	-3.352653000	-0.057553000	-2.488844000
1	-2.852671000	1.878850000	-0.963540000
1	-2.918238000	1.572240000	1.530066000
1	-3.439953000	-0.683493000	2.511648000
44	-1.764751000	-0.628016000	0.006741000
6	0.042551000	-0.235994000	2.607618000
1	1.034535000	-0.540721000	2.978282000
1	-0.062841000	0.852147000	2.757749000
1	-0.722657000	-0.744451000	3.207565000
6	0.006559000	-0.083586000	-2.581136000
1	-0.203286000	0.998893000	-2.618689000
1	1.017658000	-0.253417000	-2.984695000
1	-0.713957000	-0.598335000	-3.229193000

$[(C_6H_6)Ru(NPN)]^+\cdots HO\textit{i}Pr$



E = -1514.11658481
G = -1513.704813

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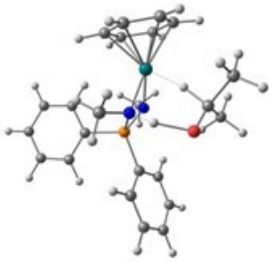
7	0.084278000	0.115783000	-1.154577000
15	-1.072597000	-0.038119000	0.035372000
6	-1.942897000	-1.623194000	-0.095550000
6	-1.269125000	-2.785738000	0.326320000
6	-3.208738000	-1.718662000	-0.704154000
6	-1.867059000	-4.037538000	0.149438000
1	-0.285909000	-2.700726000	0.782762000
6	-3.797522000	-2.976856000	-0.881404000
1	-3.727646000	-0.822790000	-1.038195000
6	-3.130487000	-4.133579000	-0.453891000
1	-1.349266000	-4.935734000	0.482602000

1	-4.775513000	-3.052246000	-1.354123000
1	-3.594236000	-5.109444000	-0.591416000
6	-2.312783000	1.278137000	0.094248000
6	-3.431789000	1.153375000	0.943370000
6	-2.115776000	2.452238000	-0.656776000
6	-4.349430000	2.205298000	1.035000000
1	-3.587166000	0.244008000	1.521321000
6	-3.047441000	3.492795000	-0.566815000
1	-1.236726000	2.559693000	-1.287147000
6	-4.160575000	3.370807000	0.276997000
1	-5.212755000	2.112942000	1.691995000
1	-2.899668000	4.399654000	-1.151085000
1	-4.881493000	4.184417000	0.345699000
6	3.729885000	-0.304936000	0.737155000
6	3.709633000	-0.403085000	-0.697094000
6	3.052652000	-1.487442000	-1.320006000
6	2.361790000	-2.447066000	-0.517390000
6	2.416640000	-2.364358000	0.917437000
6	3.147249000	-1.313815000	1.546569000
1	4.155866000	0.578862000	1.203466000
1	4.112042000	0.407678000	-1.296857000
1	2.941744000	-1.509168000	-2.400015000
1	1.752732000	-3.213691000	-0.988422000
1	1.851959000	-3.071952000	1.518279000
1	3.121087000	-1.200448000	2.625988000
44	1.606349000	-0.533094000	0.117870000
6	-0.166786000	-0.347783000	-2.525564000
1	-1.023505000	0.183563000	-2.969351000
1	0.724478000	-0.130909000	-3.127244000
1	-0.365605000	-1.430860000	-2.570337000
6	-0.297941000	-0.340649000	2.662954000
1	0.581424000	-0.136413000	3.286683000
1	-1.128444000	0.294097000	3.011521000
1	-0.588148000	-1.396255000	2.799781000
1	0.814407000	1.813956000	-1.312007000
6	1.910485000	2.964726000	-0.161858000
8	1.269978000	2.682058000	-1.424855000
6	3.010235000	3.993155000	-0.418998000
6	0.899916000	3.444972000	0.884129000
1	3.738737000	3.608688000	-1.147252000
1	0.146513000	2.670455000	1.076045000
1	3.539582000	4.229427000	0.515056000
1	2.575342000	4.923019000	-0.816734000
1	0.393181000	4.357706000	0.536625000
1	1.413087000	3.667785000	1.832391000

TS from $[(C_6H_6)Ru(NPN)]^+\cdots HO\textit{i}Pr$ to $[(C_6H_6)RuH(NPNH)]^+\cdots$acetone



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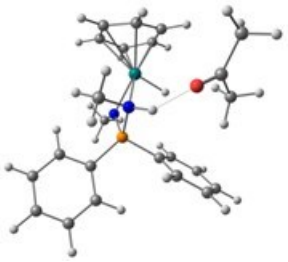
7	0.004082000	-0.158698000	-1.208903000
15	1.075004000	0.130376000	0.131082000
6	1.756242000	1.800903000	-0.011269000
6	0.877137000	2.879430000	0.215480000
6	3.115641000	2.040811000	-0.287863000
6	1.352591000	4.191253000	0.138674000
1	-0.163918000	2.680819000	0.447235000
6	3.581817000	3.358689000	-0.364071000
1	3.803680000	1.212823000	-0.439960000
6	2.703467000	4.431354000	-0.155668000
1	0.672182000	5.023508000	0.311722000
1	4.631685000	3.546183000	-0.582872000
1	3.072457000	5.454241000	-0.215253000
6	2.431340000	-1.062557000	0.135281000
6	2.698370000	-1.779576000	1.314785000
6	3.187759000	-1.287707000	-1.030894000
6	3.737332000	-2.717489000	1.328061000
1	2.096946000	-1.613540000	2.205810000
6	4.217457000	-2.234425000	-1.008075000
1	2.966004000	-0.740964000	-1.946166000
6	4.494110000	-2.944736000	0.169903000
1	3.949104000	-3.275123000	2.238959000
1	4.799887000	-2.420304000	-1.908975000
1	5.296282000	-3.681352000	0.182414000
6	-3.868277000	-0.211123000	0.556409000
6	-3.783417000	0.019087000	-0.857238000
6	-3.115005000	1.174452000	-1.333269000
6	-2.587620000	2.144280000	-0.414787000
6	-2.679083000	1.908650000	0.980051000
6	-3.333918000	0.729543000	1.475067000
1	-4.279224000	-1.147035000	0.923737000
1	-4.125184000	-0.739996000	-1.552878000
1	-2.948367000	1.299712000	-2.399623000
1	-2.039596000	3.004179000	-0.788505000
1	-2.194724000	2.587059000	1.676508000
1	-3.337660000	0.513558000	2.538941000
44	-1.744572000	0.115239000	0.052063000
6	0.184683000	0.597108000	-2.472805000
1	1.154129000	0.359406000	-2.931894000
1	-0.623814000	0.295663000	-3.147282000
1	0.119440000	1.673048000	-2.283259000
6	0.080477000	0.509017000	2.635762000
1	1.058569000	0.277871000	3.085337000
1	-0.045552000	1.604820000	2.628135000
1	-0.700071000	0.076004000	3.274987000
1	-0.007017000	-1.234945000	-1.393926000
6	-1.225915000	-2.818890000	-0.375023000
8	-0.231374000	-2.734474000	-1.229974000
6	-2.574828000	-3.295470000	-0.938556000
6	-0.881439000	-3.388120000	1.009300000
1	-2.807329000	-2.755895000	-1.865350000
1	-0.040982000	-2.829039000	1.438176000
1	-3.388444000	-3.145683000	-0.216572000
1	-2.496571000	-4.371097000	-1.165550000
1	-0.586872000	-4.442936000	0.890857000
1	-1.740659000	-3.331626000	1.692166000

$[(C_6H_6)RuH(NPNH)]^+\cdots$acetone



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G = -1513.698455

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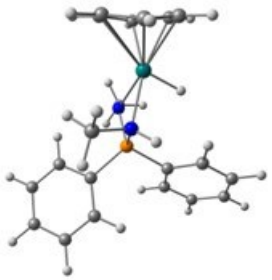
7	-0.073670000	-0.146030000	-1.085528000
15	-1.272399000	-0.141553000	0.187844000
6	-2.908262000	-0.726594000	-0.321633000
6	-3.056430000	-2.113943000	-0.534016000
6	-4.010240000	0.135735000	-0.485901000
6	-4.298229000	-2.628428000	-0.918533000
1	-2.206627000	-2.778997000	-0.393116000
6	-5.248082000	-0.389644000	-0.873465000
1	-3.908015000	1.202683000	-0.303257000
6	-5.392226000	-1.767319000	-1.091548000
1	-4.412443000	-3.698805000	-1.081935000
1	-6.100197000	0.276345000	-0.998582000
1	-6.358398000	-2.170807000	-1.391302000
6	-1.382605000	1.612879000	0.654261000
6	-1.157001000	1.958070000	1.997561000
6	-1.678885000	2.604795000	-0.299366000
6	-1.231409000	3.300801000	2.386822000
1	-0.914437000	1.185314000	2.724955000
6	-1.756496000	3.943917000	0.099851000
1	-1.835488000	2.336753000	-1.342844000
6	-1.532869000	4.290940000	1.440507000
1	-1.050981000	3.573430000	3.425461000
1	-1.980683000	4.714927000	-0.635503000
1	-1.588409000	5.334732000	1.746325000
6	3.342085000	-1.084574000	1.432097000
6	3.621376000	-0.618894000	0.103344000
6	3.128356000	-1.375934000	-0.996595000
6	2.584732000	-2.705226000	-0.810288000
6	2.319387000	-3.158066000	0.479837000
6	2.598778000	-2.288021000	1.604091000
1	3.619469000	-0.487537000	2.296301000
1	4.120009000	0.330914000	-0.059540000
1	3.238139000	-0.980284000	-2.002902000
1	2.293083000	-3.294482000	-1.676273000
1	1.819896000	-4.109977000	0.643460000
1	2.306136000	-2.592124000	2.605734000
44	1.455518000	-0.886265000	0.364760000
6	-0.298191000	-1.018678000	-2.270656000
1	-1.159726000	-0.669338000	-2.856545000
1	0.607213000	-0.977826000	-2.883859000
1	-0.463600000	-2.047272000	-1.937648000
6	-0.967519000	-1.828826000	2.353435000
1	-2.067980000	-1.848456000	2.401471000
1	-0.607172000	-2.868219000	2.373623000
1	-0.592394000	-1.319619000	3.256288000
1	0.174646000	0.805187000	-1.393533000
6	2.332285000	2.516637000	-1.544953000
8	1.471554000	1.971125000	-2.236380000
6	3.777214000	2.560591000	-1.985064000
6	2.009782000	3.177880000	-0.226923000
1	3.957472000	1.870724000	-2.817141000
1	0.940460000	3.396681000	-0.145293000
1	4.443969000	2.337989000	-1.140555000
1	4.007662000	3.589152000	-2.307241000
1	2.607471000	4.090252000	-0.093112000
1	2.291562000	2.477966000	0.575537000

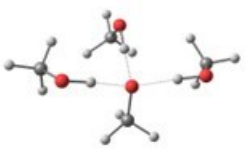
$[(C_6H_6)RuH(NPNH)]^+$



E = -1320.99517135
G = -1320.661195

1	-1.373144000	-1.581030000	0.003281000
7	-0.189313000	0.398235000	1.126982000
7	-0.142430000	0.256084000	-1.360881000
15	0.930519000	0.050951000	0.006137000
6	2.312259000	1.215427000	-0.012991000
6	2.186964000	2.409719000	0.722201000
6	3.462793000	0.970346000	-0.788966000
6	3.223504000	3.349287000	0.694141000
1	1.287922000	2.592997000	1.307414000
6	4.486988000	1.922252000	-0.820175000
1	3.556445000	0.046998000	-1.357748000
6	4.369584000	3.106957000	-0.076845000
1	3.134773000	4.269622000	1.269040000
1	5.377550000	1.738085000	-1.418785000
1	5.172541000	3.842533000	-0.099909000
6	1.626461000	-1.625865000	-0.090583000
6	2.746955000	-1.905753000	0.719180000
6	1.010507000	-2.663517000	-0.818362000
6	3.251109000	-3.209449000	0.786273000
1	3.226757000	-1.113723000	1.291226000
6	1.528769000	-3.961498000	-0.752926000
1	0.127688000	-2.472062000	-1.423346000
6	2.646036000	-4.236437000	0.048705000
1	4.117031000	-3.419887000	1.411813000
1	1.055365000	-4.757841000	-1.324869000
1	3.042109000	-5.249584000	0.099920000
6	-3.794343000	-0.856561000	0.740235000
6	-3.888408000	-0.817183000	-0.691659000
6	-3.637653000	0.417900000	-1.350372000
6	-3.541439000	1.658799000	-0.612506000
6	-3.459759000	1.620872000	0.776954000
6	-3.469661000	0.338068000	1.446980000
1	-3.893023000	-1.796808000	1.275120000
1	-4.065313000	-1.723396000	-1.263112000
1	-3.601744000	0.439930000	-2.436866000
1	-3.435200000	2.598274000	-1.149422000
1	-3.291951000	2.529828000	1.349734000
1	-3.310898000	0.291528000	2.521030000
44	-1.911832000	-0.095632000	-0.031110000
6	-0.132040000	1.591346000	-2.032350000
1	0.831186000	1.772832000	-2.528497000
1	-0.939206000	1.590149000	-2.771492000
1	-0.323392000	2.367541000	-1.285886000
6	0.009686000	0.173962000	2.559468000
1	0.981753000	0.569524000	2.896345000
1	-0.781392000	0.701881000	3.107690000
1	-0.040889000	-0.895762000	2.826048000
1	0.000153000	-0.470385000	-2.063073000

$[MeO(MeOH)_3]^-$



E = -462.316580067
G = -462.1669891

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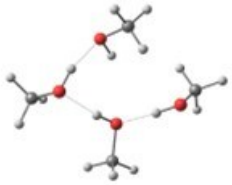
1	0.001387000	-0.318131000	1.956902000
6	-0.000162000	-1.224525000	1.313408000
1	-0.892865000	-1.818806000	1.604428000
1	-2.883617000	0.141995000	1.004595000
1	-4.127356000	0.127314000	-0.273906000
6	-3.041672000	0.084431000	-0.090586000
1	-2.576994000	0.977800000	-0.545522000
8	-2.536758000	-1.125762000	-0.650088000
1	-1.537221000	-1.087553000	-0.501241000
8	-0.000004000	-0.923532000	-0.064220000
1	0.000119000	0.627276000	-0.430329000
8	0.000263000	1.607311000	-0.697541000
1	0.894347000	2.157168000	1.132466000
6	-0.000208000	2.357295000	0.512081000
1	-0.000402000	3.430172000	0.260413000
1	-0.894951000	2.156762000	1.132047000
1	1.537340000	-1.087557000	-0.501163000
8	2.536851000	-1.125690000	-0.650122000
1	2.884051000	0.141639000	1.004861000
6	3.041772000	0.084405000	-0.090391000
1	2.576813000	0.977837000	-0.544909000
1	4.127396000	0.127487000	-0.274015000

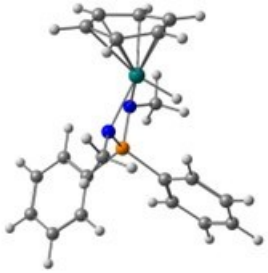
$(MeOH)_4$



E = -462.81100247
G = -462.6475785

1	0.221232000	2.988396000	0.915572000
6	0.218664000	2.689526000	-0.145967000
1	1.170774000	2.999351000	-0.607223000
1	-0.605948000	3.203836000	-0.656334000
8	0.007821000	1.275245000	-0.296419000
1	0.735860000	0.815140000	0.186176000
1	1.601796000	-0.994054000	0.320102000
8	2.061906000	-0.227726000	0.739914000
1	3.896657000	-0.698796000	-0.176259000
6	3.155423000	0.115761000	-0.134146000
1	2.803946000	0.334781000	-1.155842000
1	3.637305000	1.013078000	0.275055000
8	-2.352765000	0.440951000	0.827223000
6	-3.052695000	0.110607000	-0.377168000
1	-3.173200000	0.988433000	-1.037607000
1	-2.543239000	-0.685196000	-0.950144000
1	-4.052765000	-0.251636000	-0.099267000
1	-1.471359000	0.765498000	0.528517000
6	-0.557061000	-2.485779000	0.221492000
1	-1.312078000	-3.046144000	-0.351787000
1	-1.045735000	-1.672411000	0.775909000
1	-0.064349000	-3.168979000	0.924057000
8	0.475739000	-1.976398000	-0.657513000
1	0.073513000	-1.268563000	-1.181835000

$[(C_6H_6)Ru(NPNH)]$

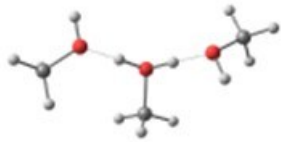


E = -1320.50913774
G = -1320.193867

1	-1.400963000	1.533553000	-0.050783000
7	-0.186674000	-0.387779000	-1.229175000
7	-0.212444000	-0.375354000	1.228576000
15	0.863668000	-0.134655000	0.019926000
6	2.258942000	-1.319354000	0.033415000
6	2.153652000	-2.490396000	-0.739775000
6	3.380889000	-1.125182000	0.863229000
6	3.168812000	-3.454277000	-0.693130000
1	1.279460000	-2.633991000	-1.374002000
6	4.386534000	-2.098551000	0.916728000
1	3.471850000	-0.216084000	1.455876000
6	4.283009000	-3.260493000	0.136865000
1	3.090080000	-4.354917000	-1.301064000
1	5.252357000	-1.948123000	1.560571000
1	5.070103000	-4.012913000	0.175164000
6	1.666072000	1.515558000	-0.011050000
6	2.849294000	1.732294000	-0.745416000
6	1.046287000	2.601886000	0.637631000
6	3.403231000	3.016114000	-0.827628000
1	3.338052000	0.900658000	-1.250449000
6	1.607952000	3.882521000	0.559976000
1	0.124845000	2.441613000	1.191280000
6	2.785449000	4.091815000	-0.172931000
1	4.316335000	3.175830000	-1.400120000
1	1.126099000	4.715715000	1.070442000
1	3.219632000	5.089157000	-0.234429000
6	-3.851945000	0.738630000	-0.767872000
6	-3.878095000	0.775073000	0.669628000
6	-3.600019000	-0.422535000	1.387942000
6	-3.539253000	-1.703535000	0.716675000
6	-3.519302000	-1.740637000	-0.675271000
6	-3.552131000	-0.496724000	-1.413693000
1	-3.997581000	1.644823000	-1.349691000
1	-4.039595000	1.710308000	1.199027000
1	-3.526592000	-0.383990000	2.472349000
1	-3.418667000	-2.614403000	1.299395000
1	-3.384620000	-2.681331000	-1.205355000
1	-3.444937000	-0.515445000	-2.495940000
44	-1.926602000	0.046353000	-0.005293000
6	0.039664000	-0.072420000	2.629979000
1	0.996232000	-0.510362000	2.967795000
1	0.071335000	1.010137000	2.855451000
1	-0.758958000	-0.516216000	3.242275000
6	0.058106000	0.223281000	-2.536079000
1	0.994222000	-0.149714000	-2.989648000
1	-0.766608000	-0.048488000	-3.210028000

1	0.114333000	1.328007000	-2.505253000

$[MeOH_2(MeOH)_2]^+$



E = -347.553337939
G = -347.4225579

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6	0.155057000	1.762204000	0.114173000
1	0.997490000	2.210243000	-0.419024000
1	-0.765377000	2.318910000	-0.082111000
8	-0.037841000	0.413320000	-0.440102000
1	0.802034000	-0.186050000	-0.239470000
1	2.057596000	-1.722955000	-0.570234000
8	1.986883000	-1.002077000	0.075115000
1	4.072599000	-0.901588000	0.248926000
6	3.227637000	-0.238561000	0.022943000
1	3.360919000	0.221733000	-0.966204000
1	3.151466000	0.537419000	0.791599000
8	-2.109111000	-0.570557000	0.577617000
6	-3.224877000	-0.442442000	-0.351978000
1	-3.435201000	0.614647000	-0.565614000
1	-2.922050000	-0.956274000	-1.270149000
1	-4.112099000	-0.929316000	0.072385000
1	-0.887172000	-0.022404000	0.008069000
1	-2.340141000	-0.093657000	1.390147000