Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Rh(I) and Ru(II) phosphaamidine and phosphaguanidine (1,3-P,N) complexes and their activity for CO_2 hydrogenation

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Section S1: X-ray Crystallography

Table S1.1. Crystallographic Data and Structure Refinement for **1**, **2**, **3, 4**, and **6.**

	1	**2**	**3**	**4**	**6**
formula	$C_{51}H_{40}Cl_2N_2OP_2Rh_2$	$C_{50}H_{40}Cl_2N_2P_2Ru$	$C_{24}H_{38}BF_4NPRh$	$C_{20}H_{38}Cl_2NO_2PRuS_2$	$C_{22}H_{35}Cl_2N_2O_2PRuS_2$
formula weight	1035.51	902.75	561.24	591.57	626.58
crystal system	monoclinic	monoclinic	orthorhombic	monoclinic	orthorhombic
space group	*C*2/*n*	*P* 2_1/*c*	*Pbca*	*P* 2_1/*n*	*Pna*2_1
temperature (K)	180(2)	180(2)	180(2)	180(2)	180(2)
wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
a (Å)	19.2924(4)	13.9242(2)	15.4994(4)	9.6004(3)	20.9190(4)
b (Å)	18.3550(4)	19.2794(3)	17.8762(5)	20.3354(6)	8.78640(10)
c (Å)	16.0363(4)	15.9218(2)	18.5967(5)	14.1978(4)	15.0358(2)
α (°)	90	90	90	90	90
β (°)	102.5930(10)	96.5170(10)	90	107.5250(10)	90
γ (°)	90	90	90	90	90
V (Å^3)	5542.0(2)	4246.59(10)	5152.6(2)	2643.16(14)	2763.62(7)
Z	4	4	8	4	4
D_c (Mg m^{-3})	1.241	1.412	1.447	1.487	1.506
μ (Mo Kα), mm^{-1}	0.782	0.608	0.766	1.030	0.991
F(000)	2088	1848	2320	1224	1288
crystal size (mm^{-3})	0.250 × 0.060 × 0.040	0.280 × 0.119 × 0.061	0.178 × 0.143 × 0.121	0.256 × 0.227 × 0.108	0.176 × 0.107 × 0.092
θ range (°)	1.549 – 26.730	1.665 – 27.320	2.055 – 27.149	1.807 – 27.233	1.947 to 30.989
index ranges	–23 ≤ *h* ≤ 24 –23 ≤ *k* ≤ 233 –20 ≤ *l* ≤ 20	–17 ≤ *h* ≤ 17 –24 ≤ *k* ≤ 24 –20 ≤ *l* ≤ 20	–19 ≤ *h* ≤ 15 –22 ≤ *k* ≤ 22 –21 ≤ *l* ≤ 23	–11 ≤ *h* ≤ 12 –26 ≤ *k* ≤ 21 –17 ≤ *l* ≤ 18	–28 ≤ *h* ≤ 30 –12 ≤ *k* ≤ 11 –20 ≤ *l* ≤ 21
reflns collcd	35084	37468	42474	22480	21039
independent	5884	9506	5701	5871	7941
GooF on F^2	1.058	1.022	1.030	1.046	1.016
R_1 ($I > 2\sigma[I]$)[a]	0.0366	0.0286	0.0312	0.0261	0.0265
wR_2 (all data)[b]	0.0926	0.0724	0.0820	0.0675	0.0544
Largest diff. peak and hole (e$^-$/Å^3)	1.021 / –1.014	0.499 / -0.333	0.803 / –0.410	1.908 / –0.651	0.550 / –0.354

[a] $R_1 = [\Sigma||F_o|-|F_c||]/[\Sigma|F_o|]$ for $[F_o^2 > 2\sigma(F_o^2)]$. [b] $wR_2 = \{[\Sigma w(F_o^2-F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$ [all data].

Table S1.2. Interatomic Distances [Å] and Interatomic Angles [°] for Compound **1**

Rh(1)-C(26)	1.967(4)		
Rh(1)-N(1)	2.128(2)		
Rh(1)-P(1)	2.2147(8)		
Rh(1)-Cl(1)	2.3495(9)		
Rh(1)-Rh(1)*	2.6104(4)		
P(1)-C(20)	1.811(3)		
P(1)-C(14)	1.818(3)		
P(1)-C(7)	1.859(3)		
O(1)-C(26)	1.150(6)		
N(1)-C(7)*	1.283(4)		
N(1)-C(1)	1.41(2)	N(1)-C(1A)	1.49(3)
C(1)-C(2)	1.392(18)	C(1A)-C(2A)	1.37(2)
C(1)-C(6)	1.41(2)	C(1A)-C(6A)	1.36(3)
C(2)-C(3)	1.416(17)	C(2A)-C(3A)	1.36(2)
C(3)-C(4)	1.358(13)	C(3A)-C(4A)	1.442(17)
C(4)-C(5)	1.353(13)	C(4A)-C(5A)	1.380(17)
C(5)-C(6)	1.359(15)	C(5A)-C(6A)	1.41(2)
C(7)-N(1)*	1.283(4)		
C(7)-C(8)	1.490(4)		
C(8)-C(13)	1.390(4)		
C(8)-C(9)	1.397(4)		
C(9)-C(10)	1.381(4)		
C(10)-C(11)	1.381(5)		
C(11)-C(12)	1.359(5)		
C(12)-C(13)	1.385(4)		
C(14)-C(15)	1.386(5)		
C(14)-C(19)	1.401(4)		
C(15)-C(16)	1.390(4)		
C(16)-C(17)	1.378(5)		
C(17)-C(18)	1.360(6)		
C(18)-C(19)	1.386(5)		
C(20)-C(25)	1.389(4)		
C(20)-C(21)	1.402(4)		

C(21)-C(22)	1.378(5)
C(22)-C(23)	1.380(5)
C(23)-C(24)	1.369(5)
C(24)-C(25)	1.396(4)
C(26)-Rh(1)*	1.967(4)

C(26)-Rh(1)-N(1)	86.80(7)		
C(26)-Rh(1)-P(1)	96.22(3)		
N(1)-Rh(1)-P(1)	174.86(7)		
C(26)-Rh(1)-Cl(1)	152.72(11)		
N(1)-Rh(1)-Cl(1)	91.12(7)		
P(1)-Rh(1)-Cl(1)	88.09(3)		
C(26)-Rh(1)-Rh(1)*	48.44(11)		
N(1)-Rh(1)-Rh(1)*	94.23(6)		
P(1)-Rh(1)-Rh(1)*	84.75(2)		
Cl(1)-Rh(1)-Rh(1)*	158.66(3)		
C(20)-P(1)-C(14)	107.36(15)		
C(20)-P(1)-C(7)	100.87(13)		
C(14)-P(1)-C(7)	100.97(14)		
C(20)-P(1)-Rh(1)	114.72(10)		
C(14)-P(1)-Rh(1)	116.00(11)		
C(7)-P(1)-Rh(1)	115.02(10)		
C(7)*-N(1)-C(1)	118.9(12)	C(7)*-N(1)-C(1A)	119.9(15)
C(7)*-N(1)-Rh(1)	122.3(2)		
C(1)-N(1)-Rh(1)	118.0(12)	C(1A)-N(1)-Rh(1)	117.8(15)
C(2)-C(1)-N(1)	117.1(17)	C(6A)-C(1A)-N(1)	119.3(19)
C(2)-C(1)-C(6)	120.0(16)	C(6A)-C(1A)-C(2A)	124(2)
N(1)-C(1)-C(6)	122.8(14)	C(2A)-C(1A)-N(1)	117(2)
C(1)-C(2)-C(3)	120.3(12)	C(3A)-C(2A)-C(1A)	117.0(17)
C(4)-C(3)-C(2)	116.4(10)	C(2A)-C(3A)-C(4A)	120.7(13)
C(5)-C(4)-C(3)	124.2(11)	C(5A)-C(4A)-C(3A)	120.7(12)
C(4)-C(5)-C(6)	120.8(11)	C(4A)-C(5A)-C(6A)	117.2(13)
C(5)-C(6)-C(1)	118.3(12)	C(1A)-C(6A)-C(5A)	120.4(15)
N(1)*-C(7)-C(8)	123.9(3)		
N(1)*-C(7)-P(1)	116.3(2)		

C(8)-C(7)-P(1)	119.6(2)
C(13)-C(8)-C(9)	119.4(3)
C(13)-C(8)-C(7)	120.6(3)
C(9)-C(8)-C(7)	119.9(3)
C(10)-C(9)-C(8)	119.6(3)
C(9)-C(10)-C(11)	120.5(3)
C(12)-C(11)-C(10)	119.8(3)
C(11)-C(12)-C(13)	121.1(3)
C(12)-C(13)-C(8)	119.5(3)
C(15)-C(14)-C(19)	119.0(3)
C(15)-C(14)-P(1)	117.6(2)
C(19)-C(14)-P(1)	123.3(3)
C(14)-C(15)-C(16)	121.1(3)
C(17)-C(16)-C(15)	118.7(4)
C(18)-C(17)-C(16)	121.0(4)
C(17)-C(18)-C(19)	121.1(4)
C(18)-C(19)-C(14)	119.1(4)
C(25)-C(20)-C(21)	119.0(3)
C(25)-C(20)-P(1)	119.8(2)
C(21)-C(20)-P(1)	121.2(3)
C(22)-C(21)-C(20)	119.8(3)
C(21)-C(22)-C(23)	120.8(3)
C(24)-C(23)-C(22)	120.0(3)
C(23)-C(24)-C(25)	120.2(3)
C(20)-C(25)-C(24)	120.1(3)
O(1)-C(26)-Rh(1)	138.43(11)
O(1)-C(26)-Rh(1)*	138.44(11)
Rh(1)-C(26)-Rh(1)*	83.1(2)

Symmetry transformations used to generate equivalent atoms:

*: -x + 1, y, -z + ½

The carbon atoms (labelled as C1, C2, C3, C4, C5, C6, C1A, C2A, C3A, C4A, C5A, C6A) in one of the phenyl rings were disordered over two sites. The rigid body restraint RIGU was used in the refinement of these atoms. Their site occupancy factors were refined to 0.56(3) and 0.44(3), respectively.

Approximately 27% of the unit cell (1478 Å^3) comprises a region of disordered solvent molecules and their atoms could not be modeled as discrete atomic sites. Attempts to refine the peaks of the residual electron density as Et_2O solvent molecules were unsuccessful. The program PLATON/SQUEEZE was used to calculate the contribution from the solvent region to the diffraction. The data were corrected for the disordered electron density using the SQUEEZE [3] routine as implemented in PLATON [2] leading to set of solvent-free diffraction intensities. A total electron count of 98 electrons was found in the total solvent accessible void volume within the unit cell. The electron densities identified in the solvent accessible voids are as follows:

# of void	**Centre of Void**			**Volume [Å^3]**	**Volume [%] based on cell volume**	**Electron count/Void**
	x_{av}	y_{av}	z_{av}			
1	0.500	0.013	0.011	739	13.5	231
2	0.500	0.005	0.750	739	13.5	231

The expected molar volume for a diethyl ether molecule is 104.8 Å^3 [1] (electron count: 42 e$^-$). This means that there should be 5.5 molecules of Et_2O (total of 231 electrons) located in each of the voids of 739 Å^3. In total there should be 11 molecules of Et_2O within the unit cell.

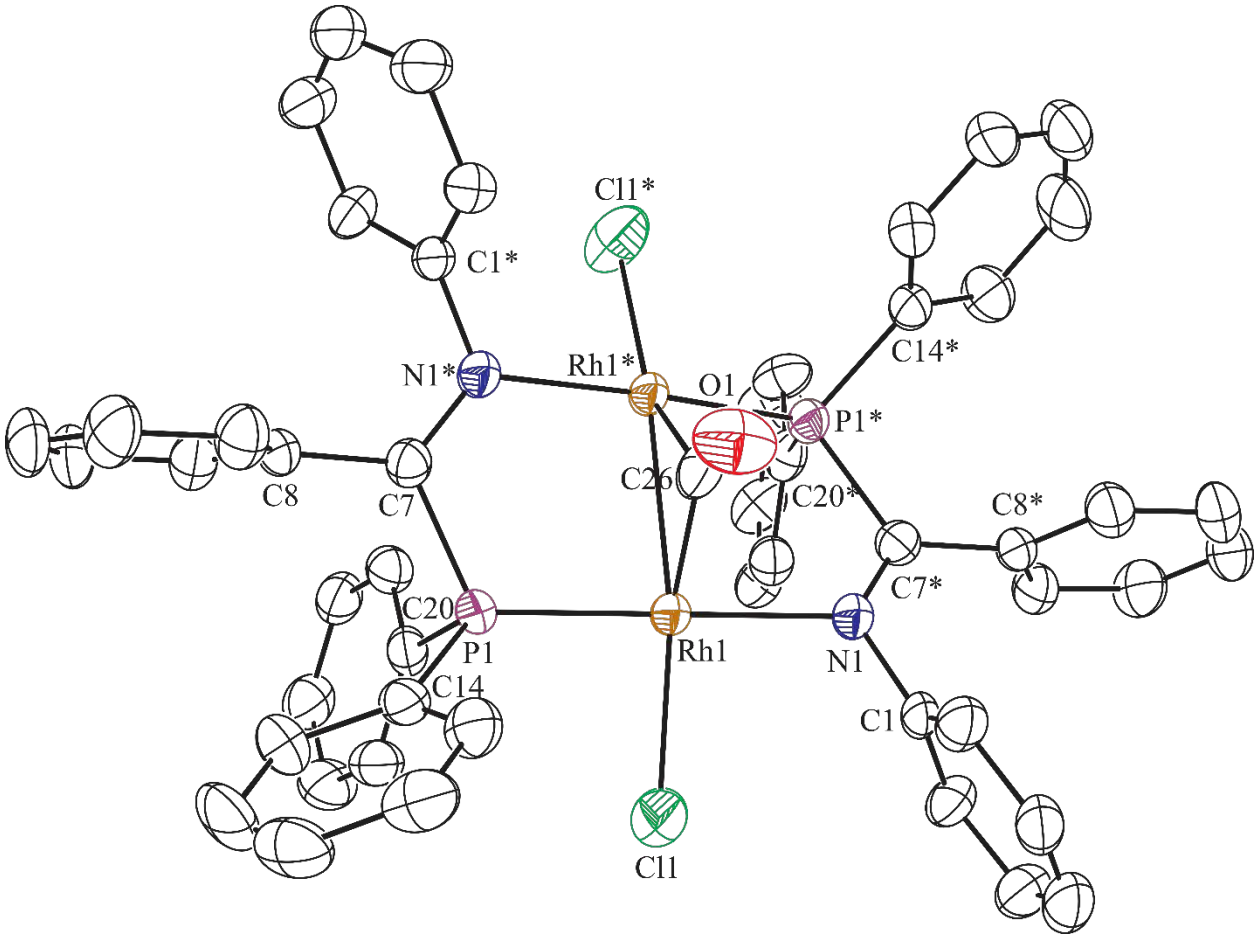
The modified data improved the *R*-factors (before SQUEEZE: R_1 = 0.0872, wR_2 = 0.2905; largest peak and hole, 4.801 and -1.104 e$^-$/Å^3; after SQUEEZE: R_1 = 0.0366, wR_2 = 0.0926; largest peak and hole, 1.021 and -1.014 e$^-$/Å^3). Derived values (formula weight, density, absorption coefficient) do not contain the contributions of the disordered solvent.

References:

[1] At 298.15 K (25 °C). *Hansen Solubility Parameters*: *A User's Handbook, 2nd Edition*, Charles M. Hansen, CRC Press, Boca Raton, FL, 2007.

[2] Spek, A. L., Single-crystal structure validation with the program *PLATON*. *J. Appl. Crystallogr*. 2003, *36*, 7-13.

[3] Spek, A. L., *PLATON SQUEEZE*: a tool for calculation of the disordered solvent contribution to the calculated structure factors. *Acta Cryst*. 2015, **C71**, 9-18.



Symmetry transformations used to generate equivalent atoms:

*: -x + 1, y, -z + ½

Figure S1.1. Molecular structure of **1.** Hydrogen atoms are omitted for clarity. The thermal ellipsoids are shown at the 50% probability level. Relevant bond distances and angles are given in Table S1.2.

Table S1.3. Interatomic Distances [Å] and Interatomic Angles [°] for Compound **2**

Ru(1)-N(2)	2.1378(15)	C(17)-C(18)	1.379(3)
Ru(1)-N(1)	2.1723(15)	C(18)-C(19)	1.388(3)
Ru(1)-P(2)	2.2514(5)	C(20)-C(21)	1.391(3)
Ru(1)-P(1)	2.2590(5)	C(20)-C(25)	1.396(3)
Ru(1)-Cl(1)	2.3944(5)	C(21)-C(22)	1.383(3)
Ru(1)-Cl(2)	2.4054(5)	C(22)-C(23)	1.377(3)
P(1)-C(20)	1.815(2)	C(23)-C(24)	1.381(3)
P(1)-C(14)	1.8151(19)	C(24)-C(25)	1.381(3)
P(1)-C(7)	1.8530(19)	C(26)-C(27)	1.384(3)
P(2)-C(45)	1.814(2)	C(26)-C(31)	1.388(3)
P(2)-C(39)	1.822(2)	C(27)-C(28)	1.388(3)
P(2)-C(32)	1.8703(19)	C(28)-C(29)	1.381(3)
N(1)-C(7)	1.293(2)	C(29)-C(30)	1.380(3)
N(1)-C(1)	1.430(2)	C(30)-C(31)	1.382(3)
N(2)-C(32)	1.289(2)	C(32)-C(33)	1.479(3)
N(2)-C(26)	1.430(2)	C(33)-C(38)	1.386(3)
C(1)-C(2)	1.381(3)	C(33)-C(34)	1.397(3)
C(1)-C(6)	1.384(3)	C(34)-C(35)	1.388(3)
C(2)-C(3)	1.392(3)	C(35)-C(36)	1.371(4)
C(3)-C(4)	1.363(4)	C(36)-C(37)	1.372(4)
C(4)-C(5)	1.376(4)	C(37)-C(38)	1.394(3)
C(5)-C(6)	1.387(3)	C(39)-C(50)	1.390(3)
C(7)-C(8)	1.481(3)	C(39)-C(46)	1.392(3)
C(8)-C(13)	1.378(3)	C(40)-C(41)	1.374(3)
C(8)-C(9)	1.392(3)	C(40)-C(45)	1.396(3)
C(9)-C(10)	1.391(3)	C(41)-C(42)	1.372(4)
C(10)-C(11)	1.371(3)	C(42)-C(43)	1.372(4)
C(11)-C(12)	1.373(3)	C(43)-C(44)	1.394(3)
C(12)-C(13)	1.390(3)	C(44)-C(45)	1.385(3)
C(14)-C(19)	1.387(3)	C(46)-C(47)	1.382(3)
C(14)-C(15)	1.397(3)	C(47)-C(48)	1.375(4)
C(15)-C(16)	1.385(3)	C(48)-C(49)	1.375(4)
C(16)-C(17)	1.375(3)	C(49)-C(50)	1.386(3)

N(2)-Ru(1)-N(1)	109.29(6)	C(2)-C(1)-N(1)	119.67(18)
N(2)-Ru(1)-P(2)	67.73(4)	C(6)-C(1)-N(1)	119.50(18)
N(1)-Ru(1)-P(2)	175.16(4)	C(1)-C(2)-C(3)	119.1(2)
N(2)-Ru(1)-P(1)	176.43(4)	C(4)-C(3)-C(2)	120.5(2)
N(1)-Ru(1)-P(1)	67.44(4)	C(3)-C(4)-C(5)	120.4(2)
P(2)-Ru(1)-P(1)	115.431(18)	C(4)-C(5)-C(6)	120.2(2)
N(2)-Ru(1)-Cl(1)	87.96(4)	C(1)-C(6)-C(5)	119.2(2)
N(1)-Ru(1)-Cl(1)	91.37(4)	N(1)-C(7)-C(8)	127.78(17)
P(2)-Ru(1)-Cl(1)	92.318(18)	N(1)-C(7)-P(1)	101.44(13)
P(1)-Ru(1)-Cl(1)	93.482(17)	C(8)-C(7)-P(1)	130.38(14)
N(2)-Ru(1)-Cl(2)	87.10(4)	C(13)-C(8)-C(9)	119.08(19)
N(1)-Ru(1)-Cl(2)	83.14(4)	C(13)-C(8)-C(7)	119.28(18)
P(2)-Ru(1)-Cl(2)	92.810(18)	C(9)-C(8)-C(7)	121.46(18)
P(1)-Ru(1)-Cl(2)	91.032(17)	C(10)-C(9)-C(8)	119.8(2)
Cl(1)-Ru(1)-Cl(2)	170.960(18)	C(11)-C(10)-C(9)	120.4(2)
C(20)-P(1)-C(14)	105.15(9)	C(10)-C(11)-C(12)	120.1(2)
C(20)-P(1)-C(7)	104.97(9)	C(11)-C(12)-C(13)	119.9(2)
C(14)-P(1)-C(7)	109.34(9)	C(8)-C(13)-C(12)	120.7(2)
C(20)-P(1)-Ru(1)	123.31(6)	C(19)-C(14)-C(15)	119.22(18)
C(14)-P(1)-Ru(1)	123.86(6)	C(19)-C(14)-P(1)	117.20(14)
C(7)-P(1)-Ru(1)	85.39(6)	C(15)-C(14)-P(1)	123.58(16)
C(45)-P(2)-C(39)	102.95(9)	C(16)-C(15)-C(14)	119.9(2)
C(45)-P(2)-C(32)	105.90(9)	C(17)-C(16)-C(15)	120.3(2)
C(39)-P(2)-C(32)	111.09(9)	C(16)-C(17)-C(18)	120.4(2)
C(45)-P(2)-Ru(1)	123.47(7)	C(17)-C(18)-C(19)	119.8(2)
C(39)-P(2)-Ru(1)	124.80(6)	C(14)-C(19)-C(18)	120.38(19)
C(32)-P(2)-Ru(1)	85.06(6)	C(21)-C(20)-C(25)	118.76(19)
C(7)-N(1)-C(1)	123.14(16)	C(21)-C(20)-P(1)	121.47(16)
C(7)-N(1)-Ru(1)	105.21(12)	C(25)-C(20)-P(1)	119.31(15)
C(1)-N(1)-Ru(1)	131.44(12)	C(22)-C(21)-C(20)	120.2(2)
C(32)-N(2)-C(26)	124.98(16)	C(23)-C(22)-C(21)	120.6(2)
C(32)-N(2)-Ru(1)	106.99(12)	C(22)-C(23)-C(24)	119.8(2)
C(26)-N(2)-Ru(1)	127.94(12)	C(23)-C(24)-C(25)	120.1(2)
C(2)-C(1)-C(6)	120.66(19)	C(24)-C(25)-C(20)	120.5(2)

C(27)-C(26)-C(31)	120.90(19)	C(33)-C(38)-C(37)	120.2(2)
C(27)-C(26)-N(2)	118.04(18)	C(50)-C(39)-C(46)	118.89(19)
C(31)-C(26)-N(2)	120.94(18)	C(50)-C(39)-P(2)	120.91(16)
C(26)-C(27)-C(28)	119.1(2)	C(46)-C(39)-P(2)	119.71(16)
C(29)-C(28)-C(27)	120.2(2)	C(41)-C(40)-C(45)	120.2(2)
C(30)-C(29)-C(28)	120.2(2)	C(42)-C(41)-C(40)	120.5(2)
C(29)-C(30)-C(31)	120.3(2)	C(41)-C(42)-C(43)	120.1(2)
C(30)-C(31)-C(26)	119.3(2)	C(42)-C(43)-C(44)	120.4(3)
N(2)-C(32)-C(33)	127.94(17)	C(45)-C(44)-C(43)	119.6(2)
N(2)-C(32)-P(2)	99.93(13)	C(44)-C(45)-C(40)	119.3(2)
C(33)-C(32)-P(2)	131.82(15)	C(44)-C(45)-P(2)	119.23(16)
C(38)-C(33)-C(34)	118.99(19)	C(40)-C(45)-P(2)	121.45(17)
C(38)-C(33)-C(32)	120.34(19)	C(47)-C(46)-C(39)	120.2(2)
C(34)-C(33)-C(32)	120.63(19)	C(48)-C(47)-C(46)	120.3(2)
C(35)-C(34)-C(33)	120.2(2)	C(47)-C(48)-C(49)	120.2(2)
C(36)-C(35)-C(34)	120.0(2)	C(48)-C(49)-C(50)	120.0(2)
C(35)-C(36)-C(37)	120.6(2)	C(49)-C(50)-C(39)	120.4(2)
C(36)-C(37)-C(38)	120.0(2)		

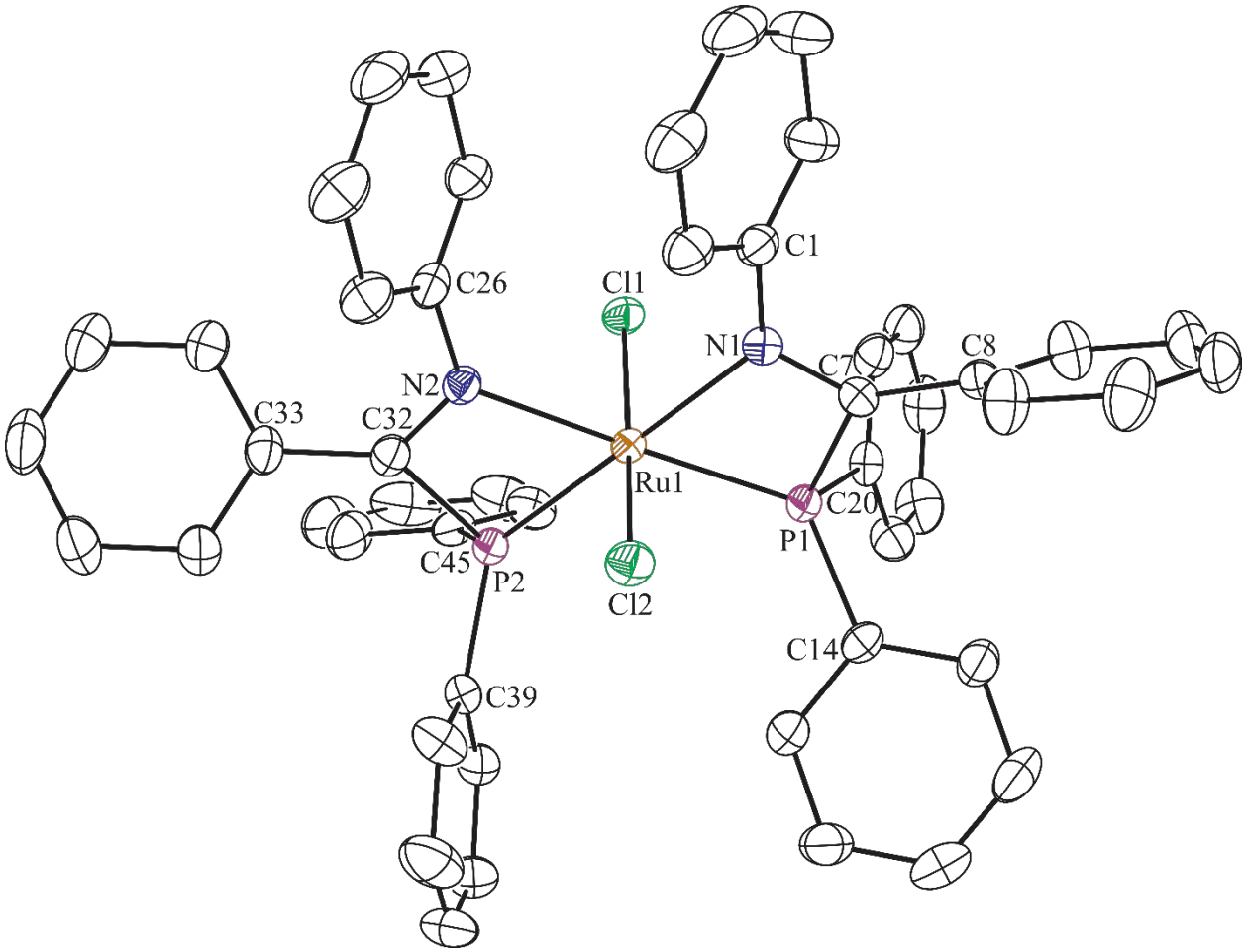


Figure S1.2. Molecular structure of **2.** Hydrogen atoms are omitted for clarity. The thermal ellipsoids are shown at the 30% probability level. Relevant bond distances and angles are given in Table S1.3.

Table S1.4. Interatomic Distances [Å] and Interatomic Angles [°] for Compound **3**

Rh(1)-C(18)	2.119(3)	C(6)-C(7)	1.389(4)
Rh(1)-C(17)	2.129(3)	C(7)-C(8)	1.375(5)
Rh(1)-N(1)	2.164(2)	C(8)-C(9)	1.379(4)
Rh(1)-C(22)	2.186(3)	C(9)-C(10)	1.386(4)
Rh(1)-C(21)	2.228(3)	C(11)-C(13)	1.528(4)
Rh(1)-P(1)	2.2738(6)	C(11)-C(12)	1.530(4)
P(1)-C(14)	1.833(3)	C(14)-C(16)	1.516(4)
P(1)-C(11)	1.833(3)	C(14)-C(15)	1.529(4)
P(1)-C(4)	1.840(2)	C(17)-C(18)	1.388(4)
N(1)-C(4)	1.289(3)	C(17)-C(24)	1.516(4)
N(1)-C(1)	1.488(3)	C(18)-C(19)	1.503(4)
C(1)-C(2)	1.508(4)	C(19)-C(20)	1.493(5)
C(1)-C(3)	1.512(4)	C(20)-C(21)	1.515(4)
C(4)-C(5)	1.481(3)	C(21)-C(22)	1.364(4)
C(5)-C(6)	1.389(4)	C(22)-C(23)	1.497(4)
C(5)-C(10)	1.395(3)	C(23)-C(24)	1.485(4)
F(1A)-B(1)	1.379(5)	F(1B)-B(1)	1.415(8)
F(2A)-B(1)	1.347(6)	F(2B)-B(1)	1.433(9)
F(3A)-B(1)	1.386(5)	F(3B)-B(1)	1.397(8)
F(4A)-B(1)	1.374(7)	F(4B)-B(1)	1.377(10)
C(18)-Rh(1)-C(17)	38.13(12)	C(17)-Rh(1)-P(1)	97.89(8)
C(18)-Rh(1)-N(1)	157.74(10)	N(1)-Rh(1)-P(1)	68.29(5)
C(17)-Rh(1)-N(1)	158.46(10)	C(22)-Rh(1)-P(1)	149.55(9)
C(18)-Rh(1)-C(22)	95.68(11)	C(21)-Rh(1)-P(1)	170.64(8)
C(17)-Rh(1)-C(22)	81.78(10)	C(14)-P(1)-C(11)	108.36(12)
N(1)-Rh(1)-C(22)	101.67(9)	C(14)-P(1)-C(4)	107.23(11)
C(18)-Rh(1)-C(21)	81.27(11)	C(11)-P(1)-C(4)	110.24(12)
C(17)-Rh(1)-C(21)	90.43(11)	C(14)-P(1)-Rh(1)	121.99(9)
N(1)-Rh(1)-C(21)	104.91(9)	C(11)-P(1)-Rh(1)	121.43(9)
C(22)-Rh(1)-C(21)	35.99(11)	C(4)-P(1)-Rh(1)	82.80(7)
C(18)-Rh(1)-P(1)	102.68(8)	C(4)-N(1)-C(1)	120.8(2)

C(4)-N(1)-Rh(1)	102.04(15)	C(16)-C(14)-C(15)	110.6(2)
C(1)-N(1)-Rh(1)	137.06(16)	C(16)-C(14)-P(1)	110.26(18)
N(1)-C(1)-C(2)	112.5(2)	C(15)-C(14)-P(1)	108.19(19)
N(1)-C(1)-C(3)	107.1(2)	C(18)-C(17)-C(24)	122.8(3)
C(2)-C(1)-C(3)	111.6(3)	C(18)-C(17)-Rh(1)	70.53(16)
N(1)-C(4)-C(5)	129.0(2)	C(24)-C(17)-Rh(1)	112.26(18)
N(1)-C(4)-P(1)	104.26(17)	C(17)-C(18)-C(19)	126.1(3)
C(5)-C(4)-P(1)	126.72(17)	C(17)-C(18)-Rh(1)	71.33(15)
C(6)-C(5)-C(10)	120.0(2)	C(19)-C(18)-Rh(1)	110.9(2)
C(6)-C(5)-C(4)	120.0(2)	C(20)-C(19)-C(18)	115.8(3)
C(10)-C(5)-C(4)	119.7(2)	C(19)-C(20)-C(21)	114.4(3)
C(7)-C(6)-C(5)	119.3(3)	C(22)-C(21)-C(20)	124.6(3)
C(8)-C(7)-C(6)	120.4(3)	C(22)-C(21)-Rh(1)	70.31(15)
C(7)-C(8)-C(9)	120.6(3)	C(20)-C(21)-Rh(1)	110.4(2)
C(8)-C(9)-C(10)	119.8(3)	C(21)-C(22)-C(23)	126.6(3)
C(9)-C(10)-C(5)	119.9(3)	C(21)-C(22)-Rh(1)	73.70(15)
C(13)-C(11)-C(12)	112.2(2)	C(23)-C(22)-Rh(1)	107.6(2)
C(13)-C(11)-P(1)	115.22(19)	C(24)-C(23)-C(22)	115.4(3)
C(12)-C(11)-P(1)	109.40(18)	C(23)-C(24)-C(17)	114.1(3)
F(2A)-B(1)-F(4A)	117.8(17)	F(4B)-B(1)-F(2B)	92(3)
F(2A)-B(1)-F(1A)	109.0(4)	F(1B)-B(1)-F(2B)	99.3(7)
F(4A)-B(1)-F(1A)	3.3(11)	F(4B)-B(1)-F(1B)	120(3)
F(2A)-B(1)-F(3A)	102.2(5)	F(3B)-B(1)-F(2B)	127.9(9)
F(4A)-B(1)-F(3A)	108.6(17)	F(4B)-B(1)-F(3B)	114(4)
F(1A)-B(1)-F(3A)	116.8(4)	F(3B)-B(1)-F(1B)	104.4(6)

The fluorine atoms [labelled as F(1A) to F(1A) and F(1B) to F(6B)] of one of the BF_4^- anions were disordered over two positions each. In order, to model the disorder satisfactory restraints on bond lengths and angles (DFIX) as well as on atomic displacement parameters (SIMU, DELU) were applied. The site occupancy factors were refined to 0.660(8) and 0.340(8), respectively.

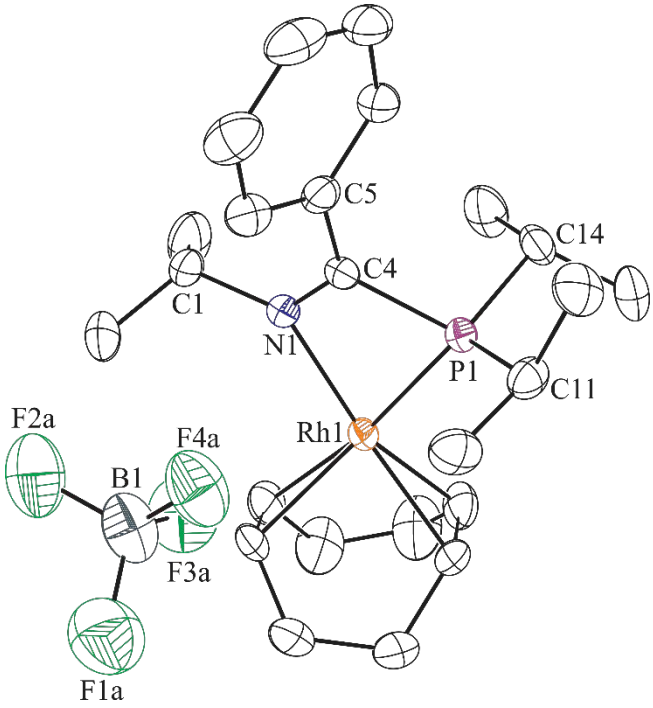


Figure S1.3. Molecular structure of **3.** Hydrogen atoms are omitted for clarity. The thermal ellipsoids are shown at the 50% probability level. Relevant bond distances and angles are given Table S1.4.

Table S1.5. Interatomic Distances [Å] and Interatomic Angles [°] for Compound **4**

Ru(1)-N(1)	2.1390(17)	N(1)-C(4)	1.302(3)
Ru(1)-S(1)	2.2542(5)	N(1)-C(1)	1.481(3)
Ru(1)-S(2)	2.2548(5)	C(1)-C(3)	1.510(3)
Ru(1)-P(1)	2.3207(5)	C(1)-C(2)	1.524(3)
Ru(1)-Cl(1)	2.4358(5)	C(4)-C(5)	1.491(3)
Ru(1)-Cl(2)	2.4568(5)	C(5)-C(10)	1.388(3)
S(1)-O(1)	1.4787(16)	C(5)-C(6)	1.391(3)
S(1)-C(19)	1.792(2)	C(6)-C(7)	1.392(4)
S(1)-C(20)	1.793(2)	C(7)-C(8)	1.375(5)
S(2)-O(2)	1.4740(17)	C(8)-C(9)	1.373(4)
S(2)-C(18)	1.787(3)	C(9)-C(10)	1.386(3)
S(2)-C(17)	1.790(3)	C(11)-C(12)	1.526(3)
P(1)-C(14)	1.851(2)	C(11)-C(13)	1.531(3)
P(1)-C(11)	1.857(2)	C(14)-C(15)	1.525(3)
P(1)-C(4)	1.860(2)	C(14)-C(16)	1.532(3)
N(1)-Ru(1)-S(1)	88.18(5)	C(19)-S(1)-C(20)	97.35(12)
N(1)-Ru(1)-S(2)	171.17(5)	O(1)-S(1)-Ru(1)	114.00(7)
S(1)-Ru(1)-S(2)	94.21(2)	C(19)-S(1)-Ru(1)	116.80(8)
N(1)-Ru(1)-P(1)	67.97(5)	C(20)-S(1)-Ru(1)	115.77(9)
S(1)-Ru(1)-P(1)	90.757(19)	O(2)-S(2)-C(18)	106.49(12)
S(2)-Ru(1)-P(1)	103.459(19)	O(2)-S(2)-C(17)	106.34(13)
N(1)-Ru(1)-Cl(1)	86.16(5)	C(18)-S(2)-C(17)	96.62(14)
S(1)-Ru(1)-Cl(1)	174.32(2)	O(2)-S(2)-Ru(1)	117.03(7)
S(2)-Ru(1)-Cl(1)	91.468(19)	C(18)-S(2)-Ru(1)	113.87(9)
P(1)-Ru(1)-Cl(1)	87.605(18)	C(17)-S(2)-Ru(1)	114.28(9)
N(1)-Ru(1)-Cl(2)	98.66(5)	C(14)-P(1)-C(11)	108.99(10)
S(1)-Ru(1)-Cl(2)	93.156(19)	C(14)-P(1)-C(4)	106.17(9)
S(2)-Ru(1)-Cl(2)	89.706(19)	C(11)-P(1)-C(4)	109.25(10)
P(1)-Ru(1)-Cl(2)	165.96(2)	C(14)-P(1)-Ru(1)	120.26(7)
Cl(1)-Ru(1)-Cl(2)	87.188(19)	C(11)-P(1)-Ru(1)	123.40(7)
O(1)-S(1)-C(19)	105.27(11)	C(4)-P(1)-Ru(1)	83.10(7)
O(1)-S(1)-C(20)	105.75(11)	C(4)-N(1)-C(1)	120.90(17)

C(4)-N(1)-Ru(1)	106.03(13)	C(5)-C(6)-C(7)	119.8(2)
C(1)-N(1)-Ru(1)	132.97(14)	C(8)-C(7)-C(6)	120.4(3)
N(1)-C(1)-C(3)	108.01(18)	C(9)-C(8)-C(7)	119.8(2)
N(1)-C(1)-C(2)	109.44(18)	C(8)-C(9)-C(10)	120.7(3)
C(3)-C(1)-C(2)	113.2(2)	C(9)-C(10)-C(5)	119.9(2)
N(1)-C(4)-C(5)	123.14(18)	C(12)-C(11)-C(13)	110.9(2)
N(1)-C(4)-P(1)	102.89(14)	C(12)-C(11)-P(1)	117.71(16)
C(5)-C(4)-P(1)	133.94(15)	C(13)-C(11)-P(1)	110.58(16)
C(10)-C(5)-C(6)	119.4(2)	C(15)-C(14)-C(16)	111.32(19)
C(10)-C(5)-C(4)	120.31(19)	C(15)-C(14)-P(1)	115.24(15)
C(6)-C(5)-C(4)	119.9(2)	C(16)-C(14)-P(1)	111.39(16)

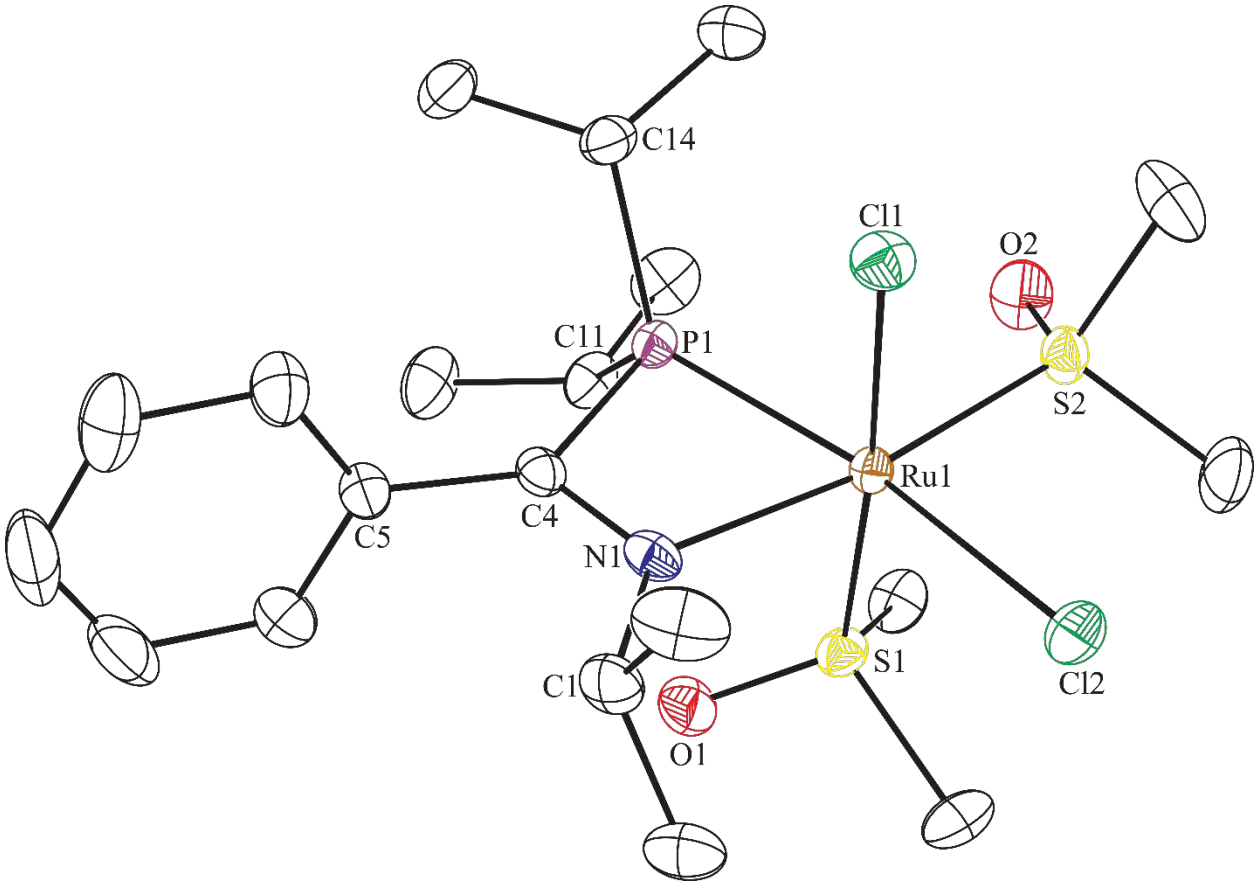


Figure S1.4. Molecular structure of **4**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are shown at the 30% probability level. Relevant bond distances and angles are given in Table S1.5.

Table S1.6. Interatomic Distances [Å] and Interatomic Angles [°] for Compound **6**

Ru(1)-N(2)	2.173(2)	N(1)-C(2)	1.457(4)
Ru(1)-S(1)	2.2556(7)	N(2)-C(3)	1.301(4)
Ru(1)-S(2)	2.2812(7)	N(2)-C(4)	1.479(4)
Ru(1)-P(1)	2.2874(8)	C(4)-C(6)	1.518(5)
Ru(1)-Cl(1)	2.4248(7)	C(4)-C(5)	1.527(5)
Ru(1)-Cl(2)	2.4331(7)	C(7)-C(8)	1.384(5)
S(1)-O(1)	1.482(2)	C(7)-C(12)	1.392(4)
S(1)-C(19)	1.784(3)	C(8)-C(9)	1.381(5)
S(1)-C(20)	1.787(3)	C(9)-C(10)	1.371(6)
S(2)-O(2)	1.476(2)	C(10)-C(11)	1.384(6)
S(2)-C(22)	1.786(4)	C(11)-C(12)	1.382(5)
S(2)-C(21)	1.790(3)	C(13)-C(18)	1.380(5)
P(1)-C(7)	1.818(3)	C(13)-C(14)	1.391(5)
P(1)-C(13)	1.834(3)	C(14)-C(15)	1.388(5)
P(1)-C(3)	1.854(3)	C(15)-C(16)	1.343(6)
N(1)-C(3)	1.348(4)	C(16)-C(17)	1.376(6)
N(1)-C(1)	1.457(4)	C(17)-C(18)	1.384(5)

N(2)-Ru(1)-S(1)	171.41(7)	O(1)-S(1)-C(19)	106.60(17)
N(2)-Ru(1)-S(2)	90.73(6)	O(1)-S(1)-C(20)	105.99(17)
S(1)-Ru(1)-S(2)	95.12(3)	C(19)-S(1)-C(20)	99.26(16)
N(2)-Ru(1)-P(1)	67.32(6)	O(1)-S(1)-Ru(1)	120.16(10)
S(1)-Ru(1)-P(1)	106.06(3)	C(19)-S(1)-Ru(1)	110.61(11)
S(2)-Ru(1)-P(1)	92.62(3)	C(20)-S(1)-Ru(1)	112.06(12)
N(2)-Ru(1)-Cl(1)	88.40(7)	O(2)-S(2)-C(22)	107.12(17)
S(1)-Ru(1)-Cl(1)	86.11(3)	O(2)-S(2)-C(21)	105.90(15)
S(2)-Ru(1)-Cl(1)	176.61(3)	C(22)-S(2)-C(21)	95.72(17)
P(1)-Ru(1)-Cl(1)	90.06(3)	O(2)-S(2)-Ru(1)	115.08(10)
N(2)-Ru(1)-Cl(2)	97.20(6)	C(22)-S(2)-Ru(1)	113.95(12)
S(1)-Ru(1)-Cl(2)	89.18(3)	C(21)-S(2)-Ru(1)	117.00(11)
S(2)-Ru(1)-Cl(2)	9.09(3)	C(7)-P(1)-C(13)	105.86(15)
P(1)-Ru(1)-Cl(2)	164.43(3)	C(7)-P(1)-C(3)	108.01(14)
Cl(1)-Ru(1)-Cl(2)	87.77(3)	C(13)-P(1)-C(3)	104.75(14)

C(7)-P(1)-Ru(1)	124.69(10)	C(8)-C(7)-P(1)	121.4(2)
C(13)-P(1)-Ru(1)	122.97(10)	C(12)-C(7)-P(1)	119.9(3)
C(3)-P(1)-Ru(1)	84.61(9)	C(9)-C(8)-C(7)	120.5(4)
C(3)-N(1)-C(1)	122.9(3)	C(10)-C(9)-C(8)	120.6(4)
C(3)-N(1)-C(2)	121.8(3)	C(9)-C(10)-C(11)	120.0(4)
C(1)-N(1)-C(2)	114.4(3)	C(12)-C(11)-C(10)	119.4(3)
C(3)-N(2)-C(4)	121.6(2)	C(11)-C(12)-C(7)	121.1(4)
C(3)-N(2)-Ru(1)	104.96(18)	C(18)-C(13)-C(14)	117.8(3)
C(4)-N(2)-Ru(1)	133.33(19)	C(18)-C(13)-P(1)	118.6(3)
N(2)-C(3)-N(1)	129.8(3)	C(14)-C(13)-P(1)	123.6(3)
N(2)-C(3)-P(1)	101.9(2)	C(15)-C(14)-C(13)	120.6(4)
N(1)-C(3)-P(1)	128.3(2)	C(16)-C(15)-C(14)	120.5(4)
N(2)-C(4)-C(6)	111.3(3)	C(15)-C(16)-C(17)	120.1(4)
N(2)-C(4)-C(5)	108.8(3)	C(16)-C(17)-C(18)	120.0(4)
C(6)-C(4)-C(5)	111.2(3)	C(13)-C(18)-C(17)	120.8(4)
C(8)-C(7)-C(12)	118.4(3)		

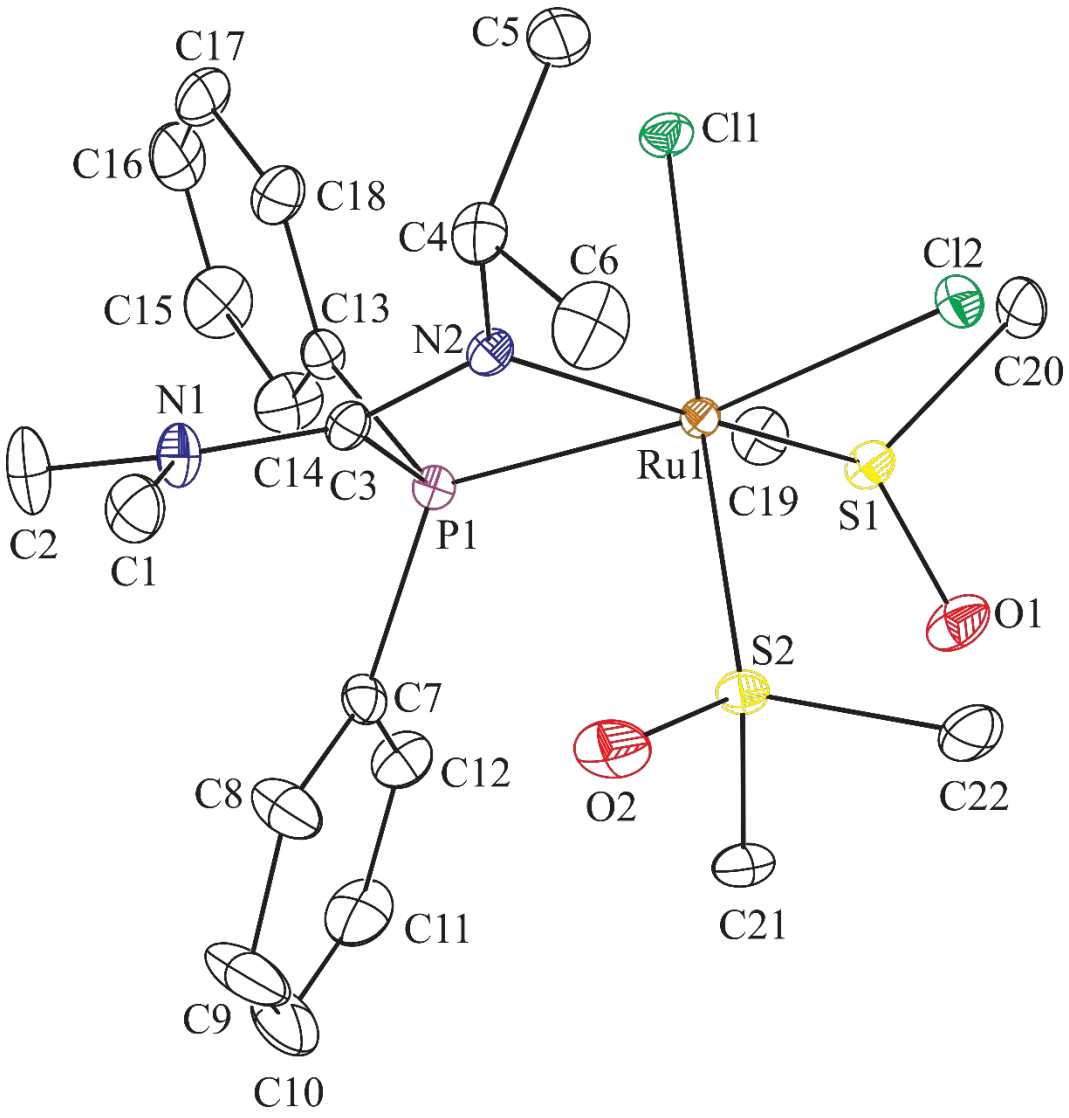
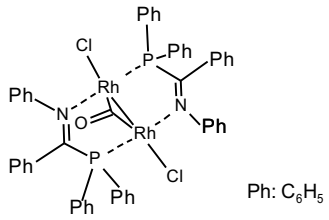


Figure S1.5. Molecular structure of **6.** Hydrogen atoms are omitted for clarity. The thermal ellipsoids are shown at the 30% probability level. Relevant bond distances and angles are given in the Supporting Information (Table S1.6).

Section S2: FT-IR and HRMS Spectra of 1.



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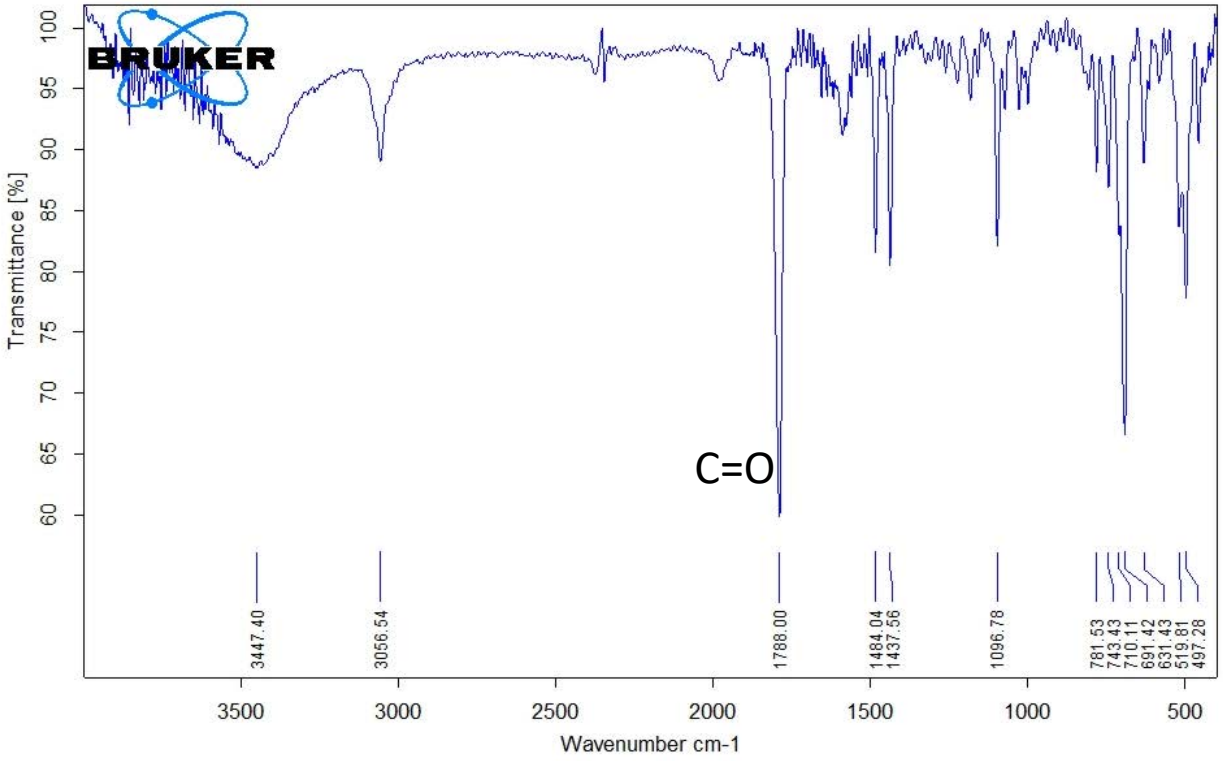


Figure S2.1. FT-IR spectrum of **1**.

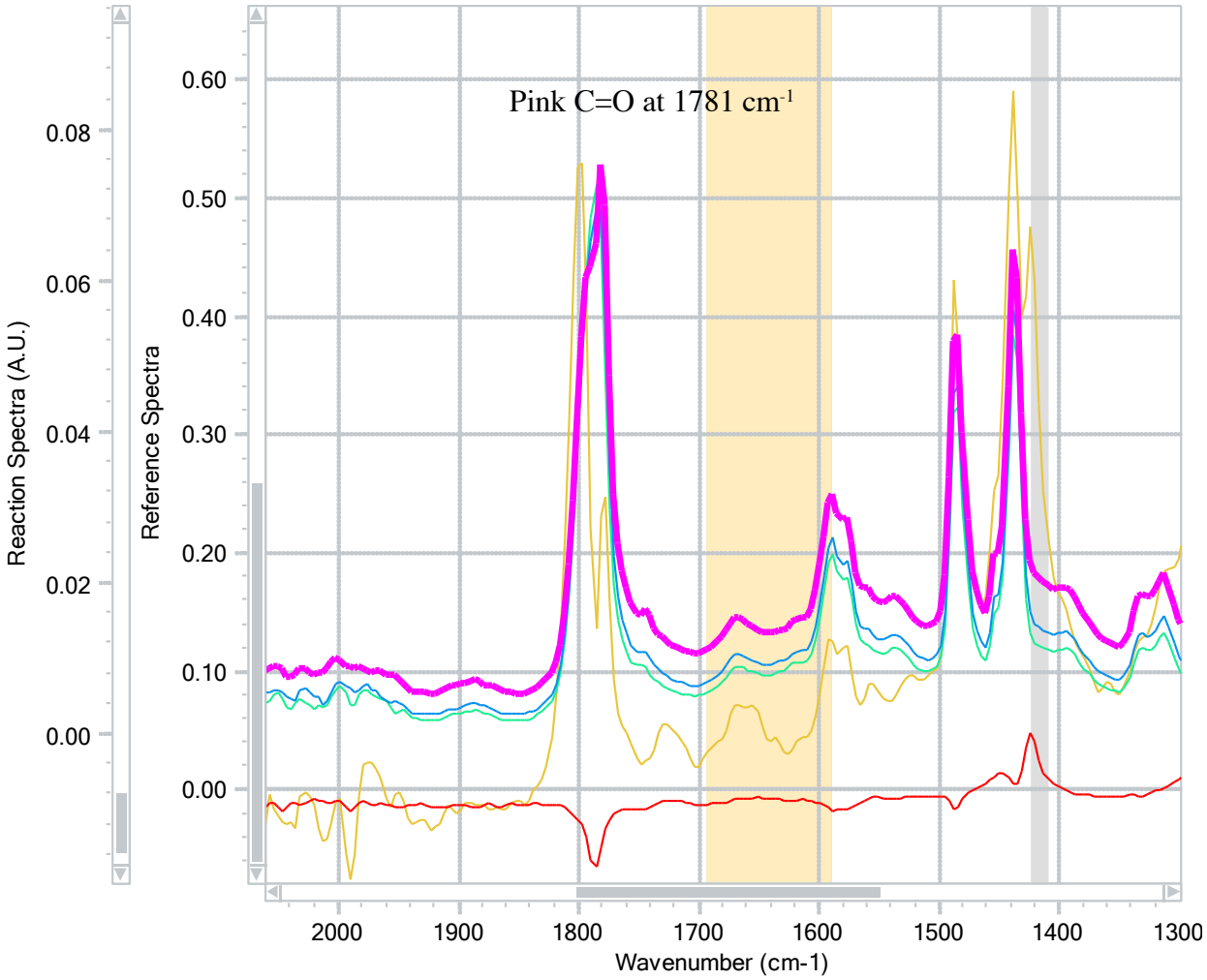


Figure S2.2. ReactIR spectrum of concentrated **1** in CH_2Cl_2.

Red spectrum for solvent (CH_2Cl_2). Pink, blue and green were collected as reference spectra in 1, 1.30 and 2 min to see whether the spectrum changes with solvent evaporation. Yellow in concentrated solution (reaction spectra) after 5 min.

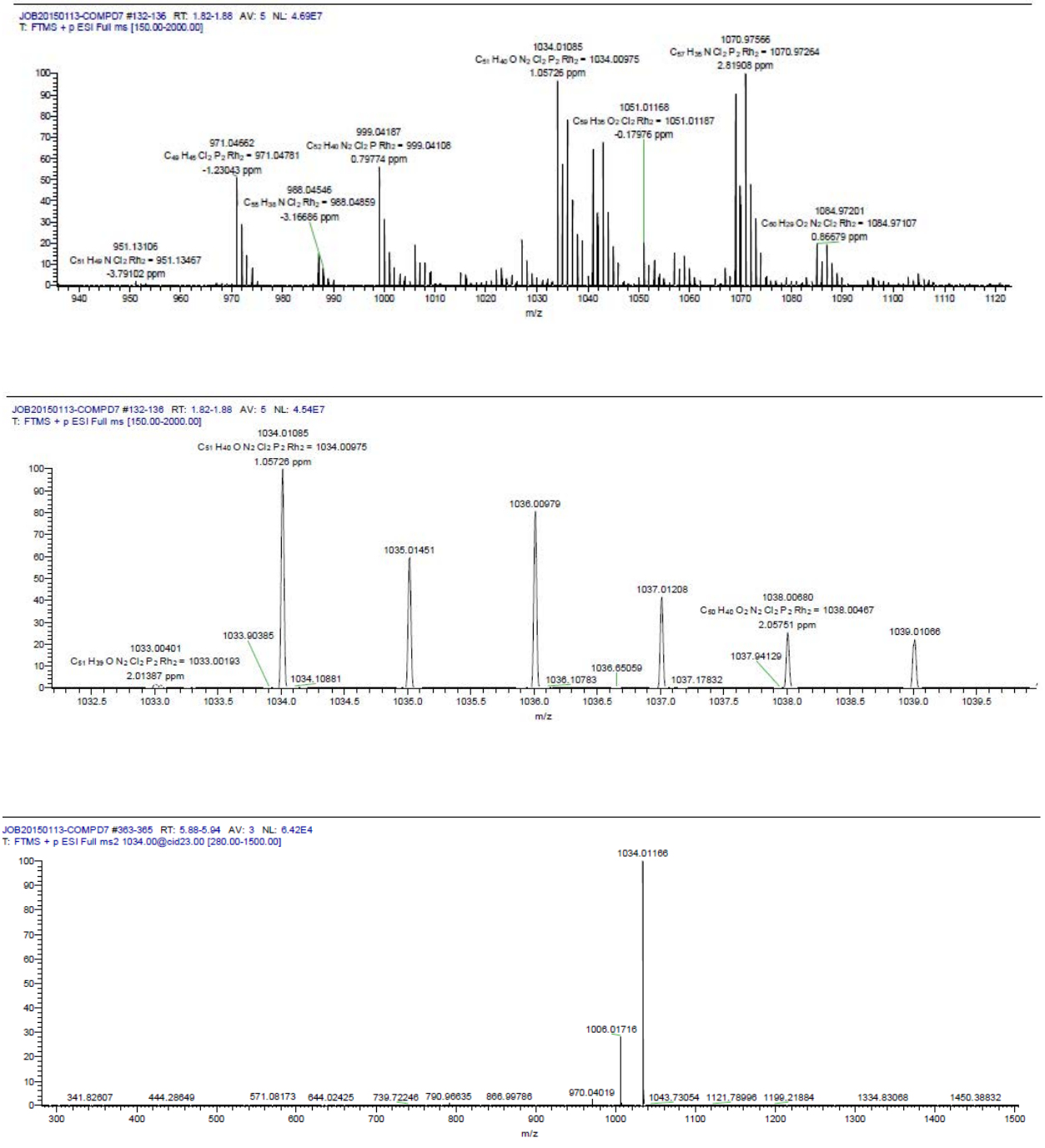
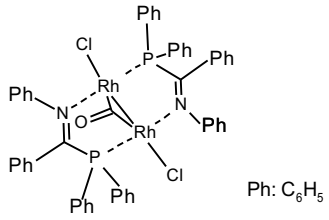


Figure S2.3. HRMS (top and middle) and MS/MS (bottom) spectra of **1**.

Section S3: NMR DATA.



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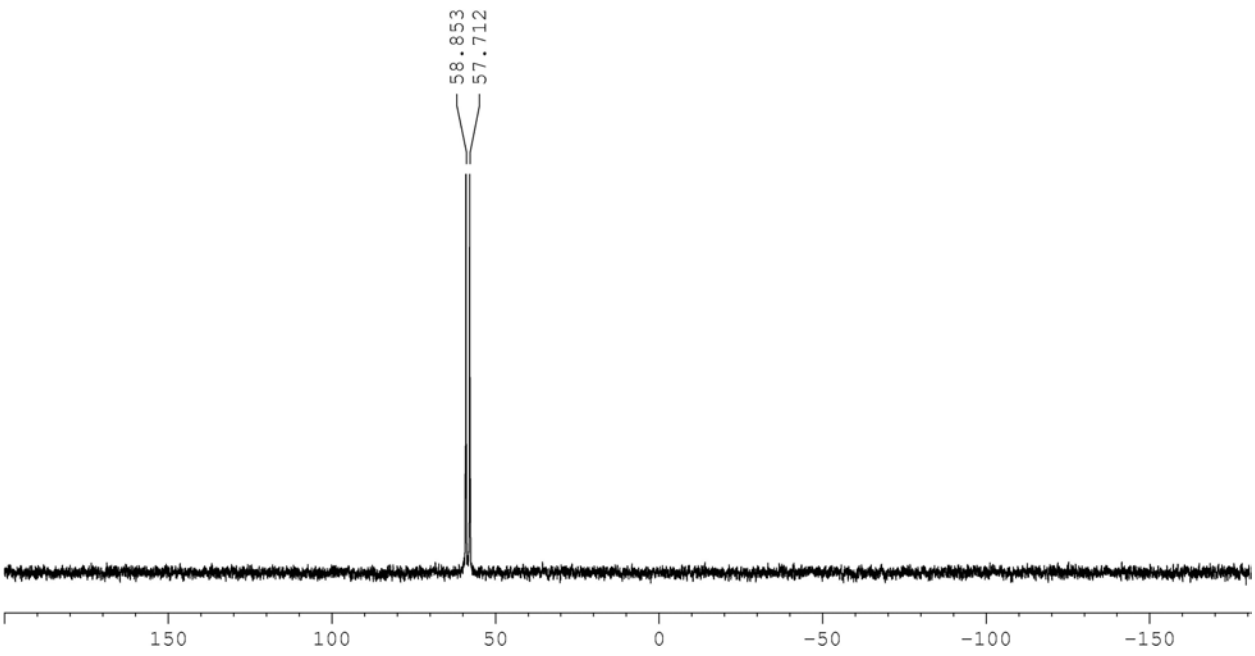
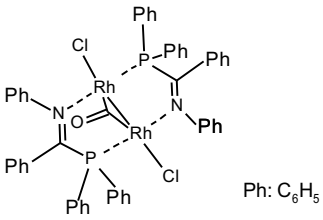


Figure S3.1. $^{31}P\{^{1}H\}$ NMR spectrum of **1**.



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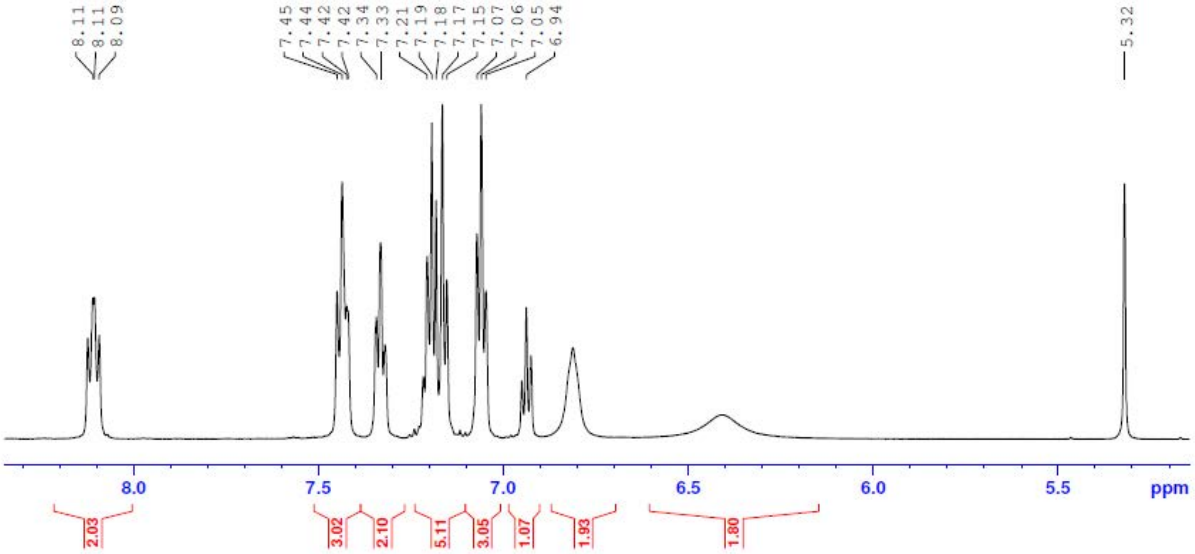
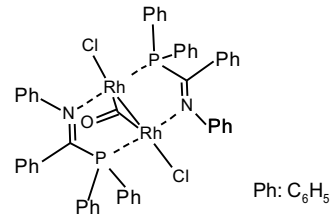


Figure S3.2. ^{1}H NMR spectrum of **1**.



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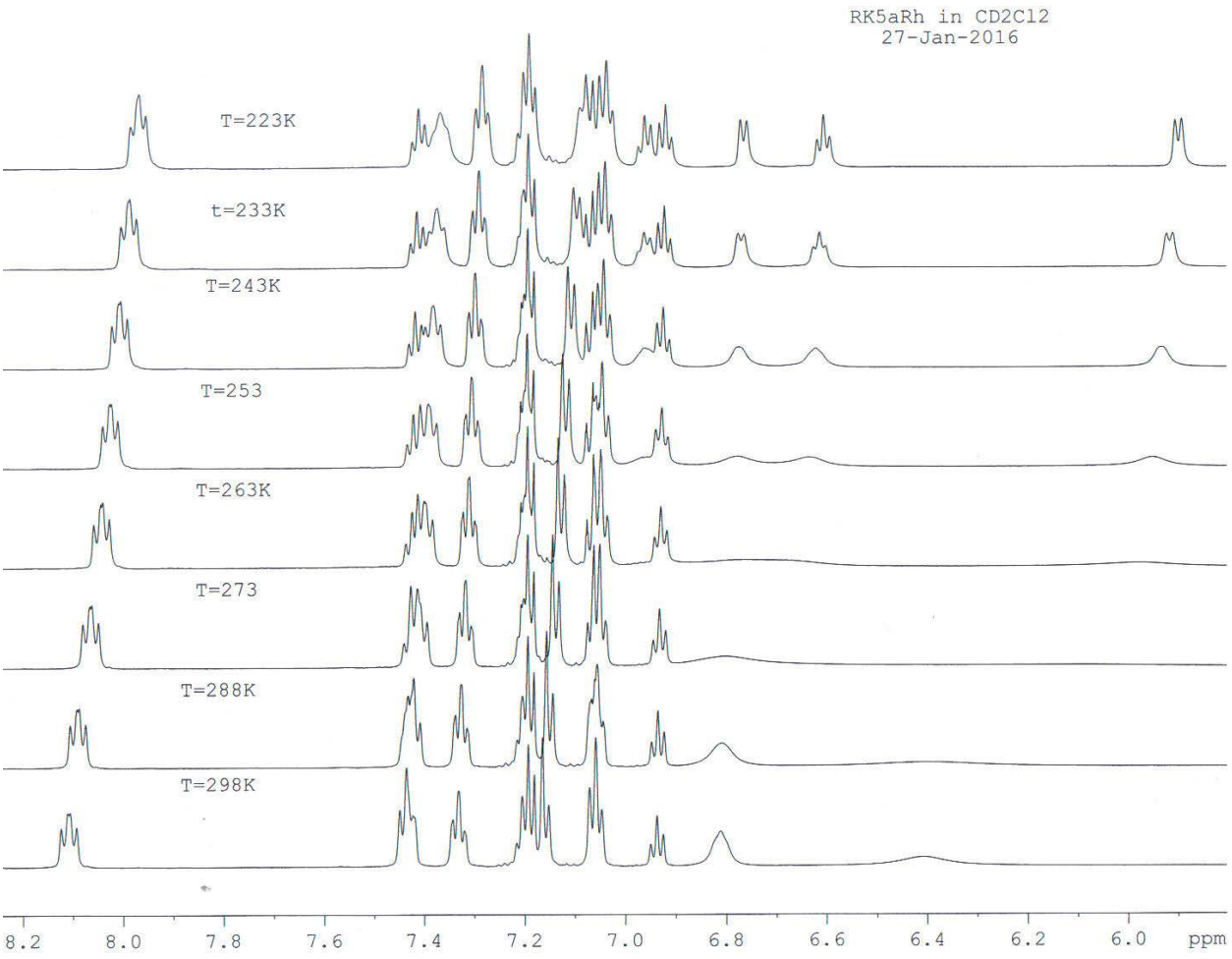
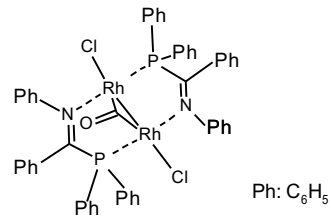


Figure S3.3. Variable temperature ^{1}H NMR spectra of **1**.



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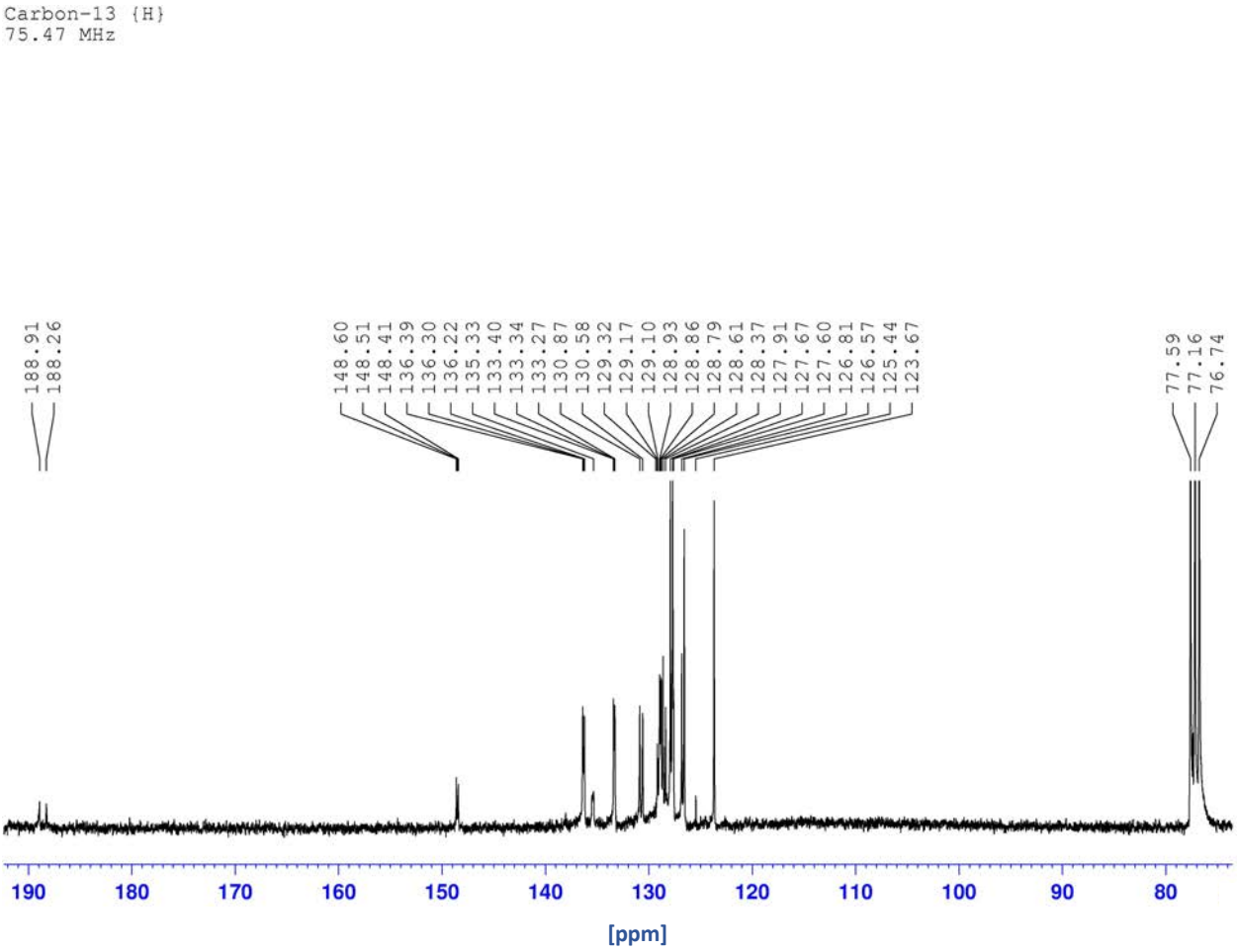
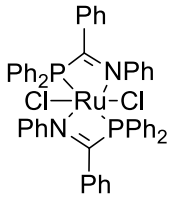


Figure S3.4. $^{13}C\{^{1}H\}$ NMR spectrum of **1**.



2

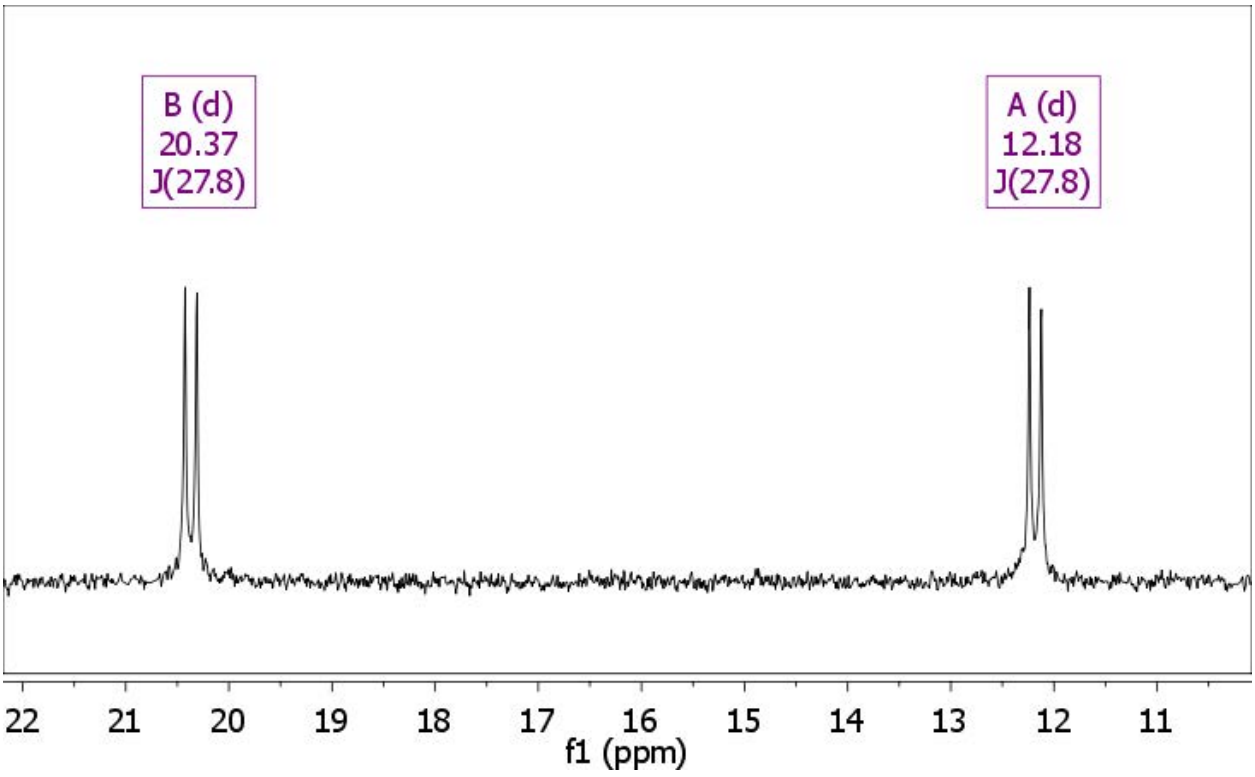
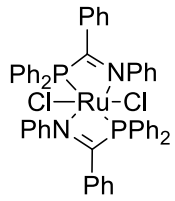
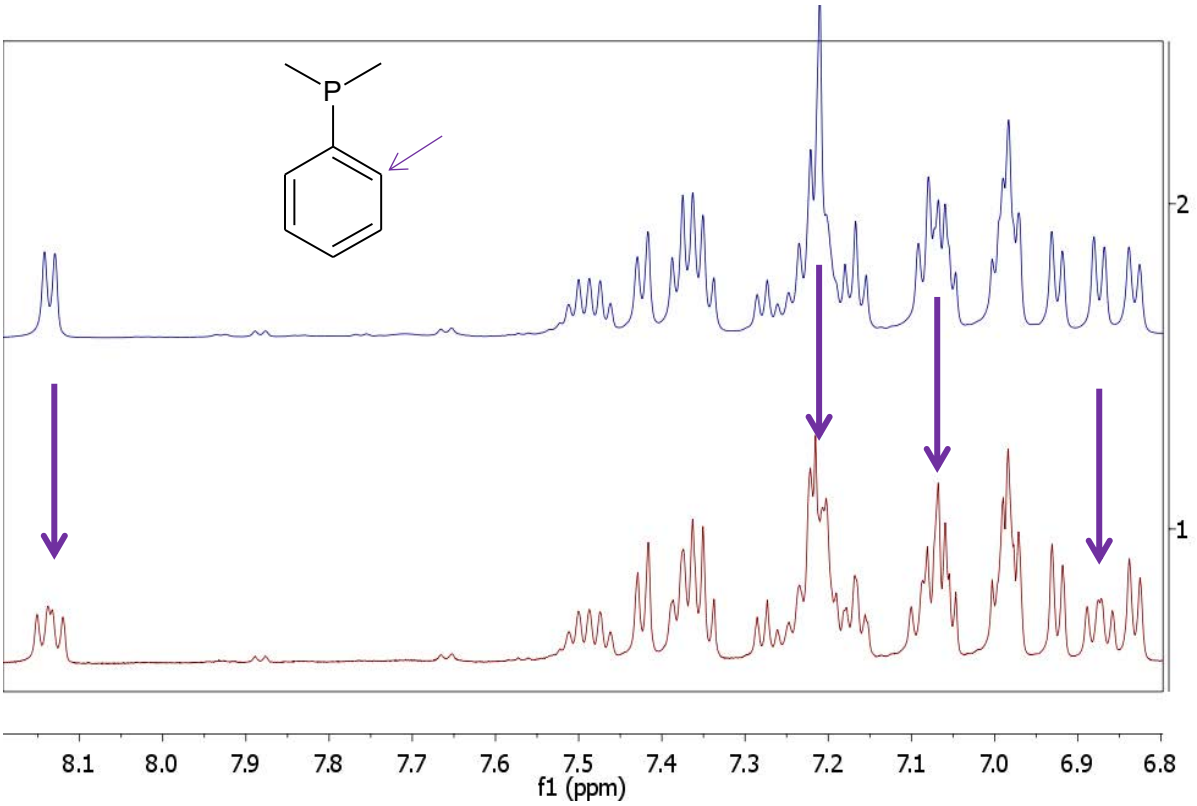


Figure S3.5. $^{31}P\{^{1}H\}$ NMR spectrum of **2**.



2



Ortho protons are coupled with large coupling to ^{31}P: 4 rings with 4 ortho protons.

Figure S3.6. $^{1}H\{^{31}P\}$ coupled (bottom) and $^{1}H\{^{31}P\}$ decoupled (top).

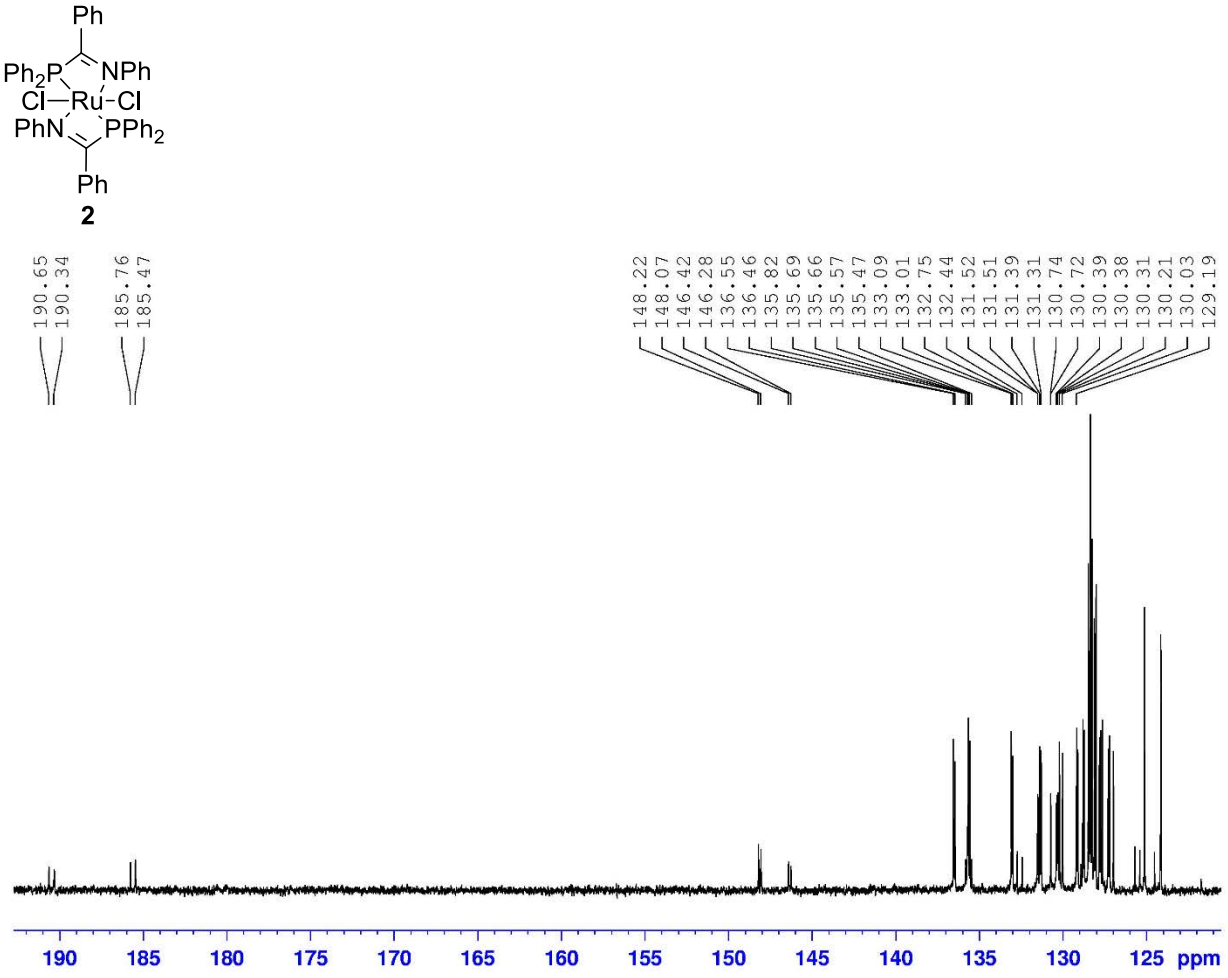


Figure S3.7. $^{13}C\{^{1}H\}$ NMR spectrum of **2**.

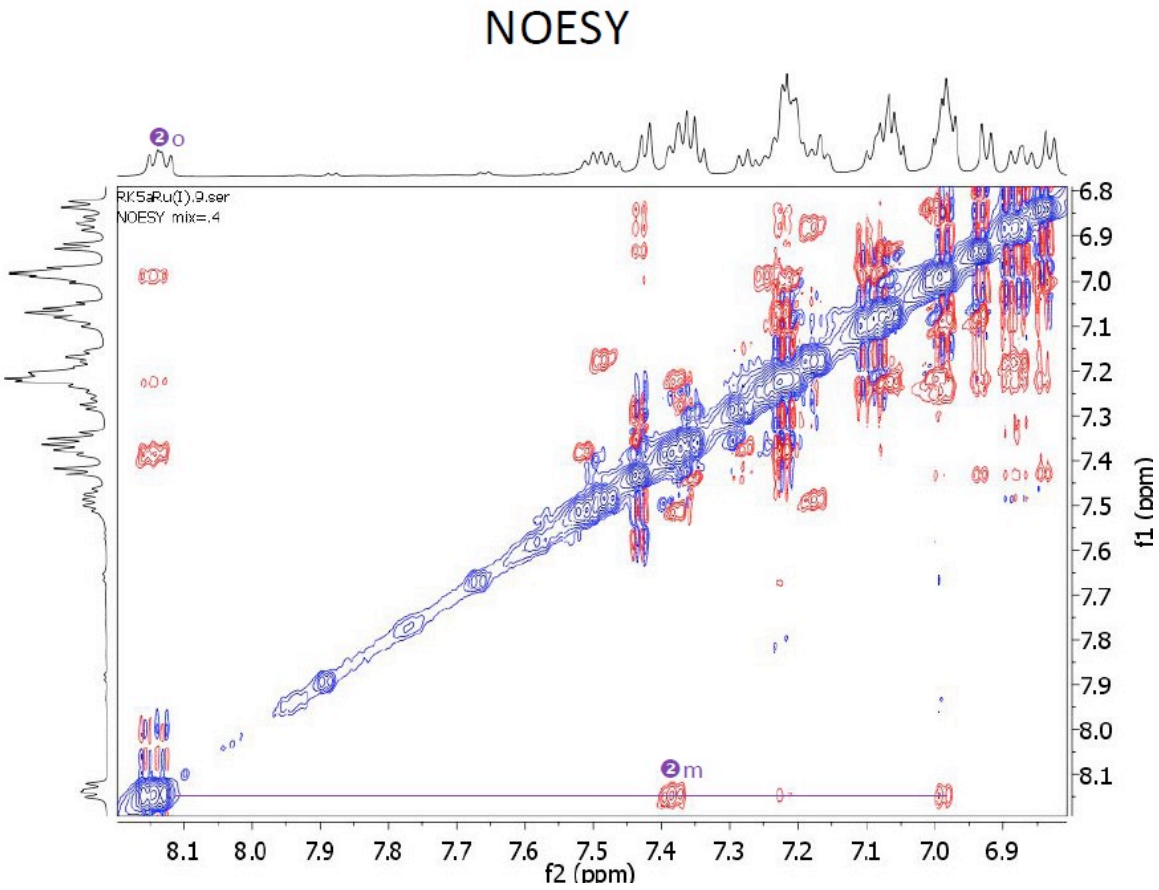
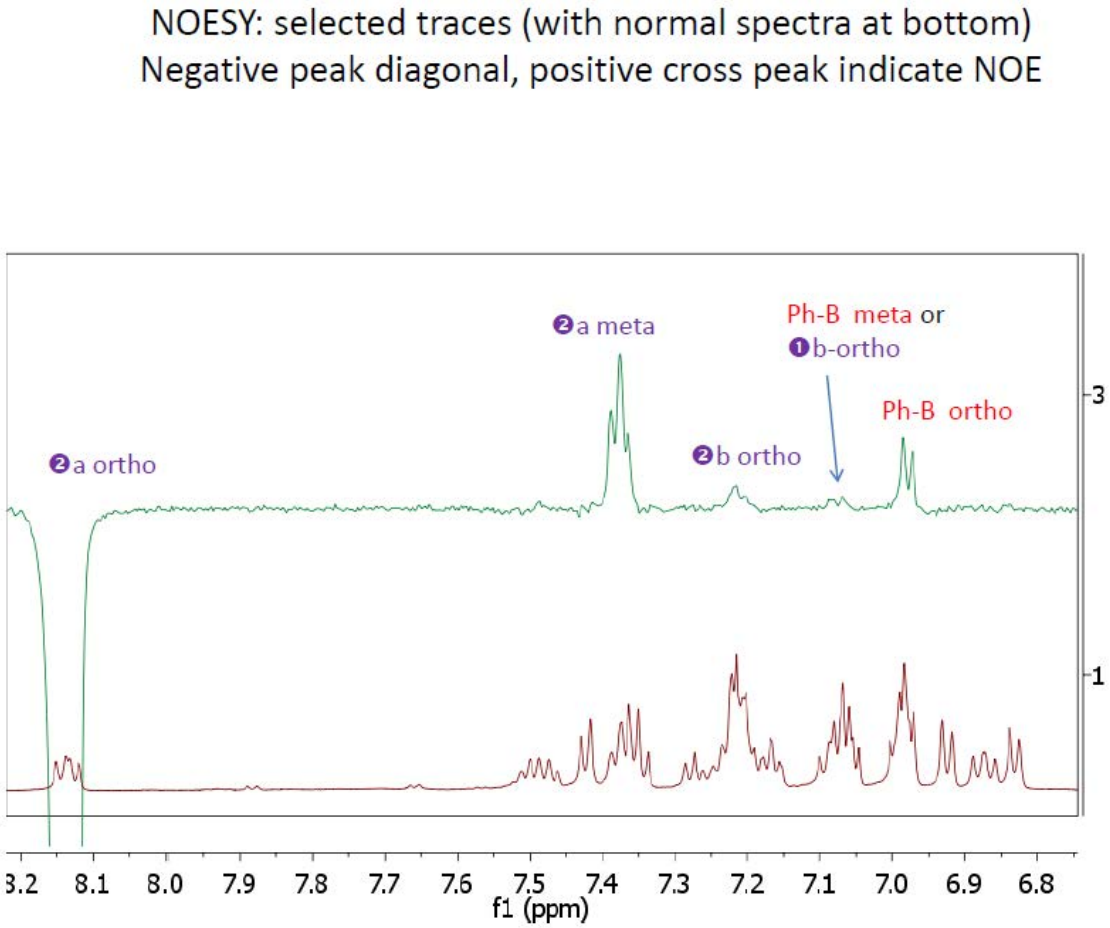
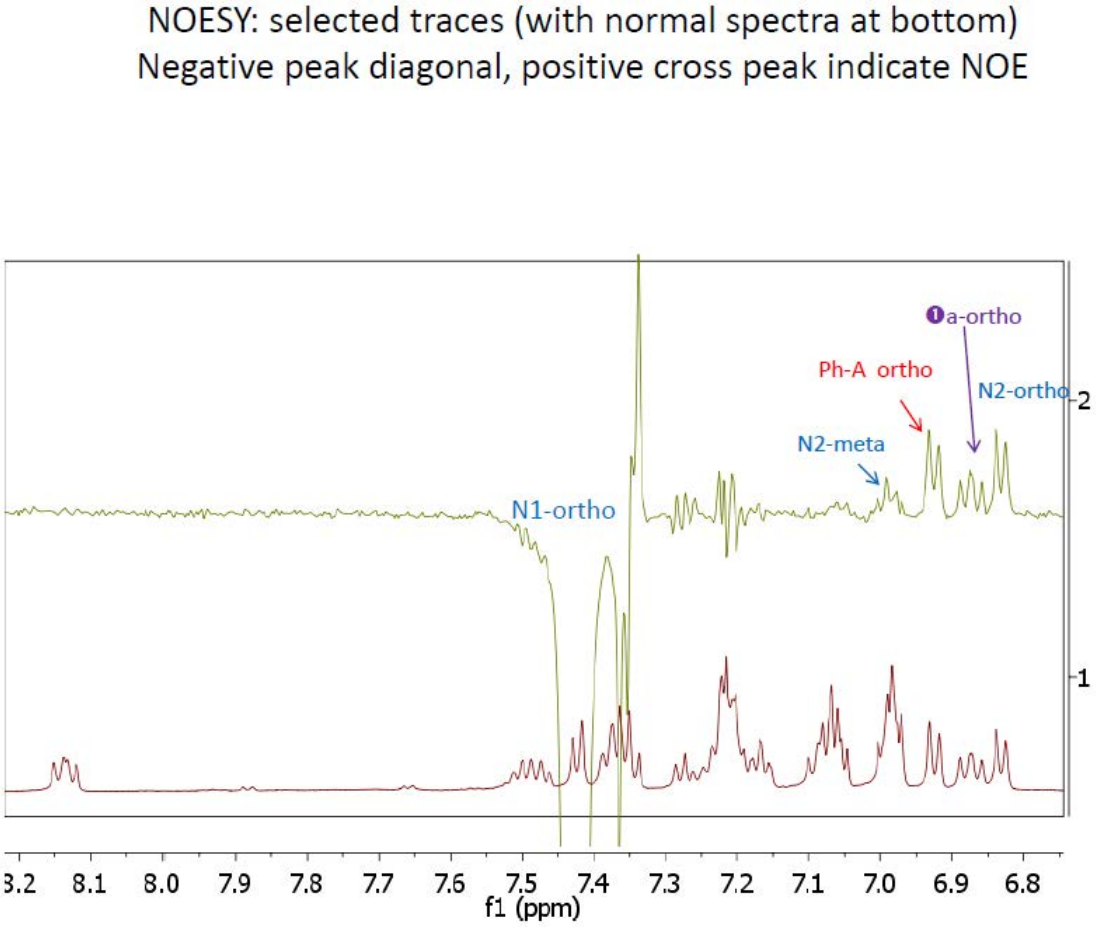


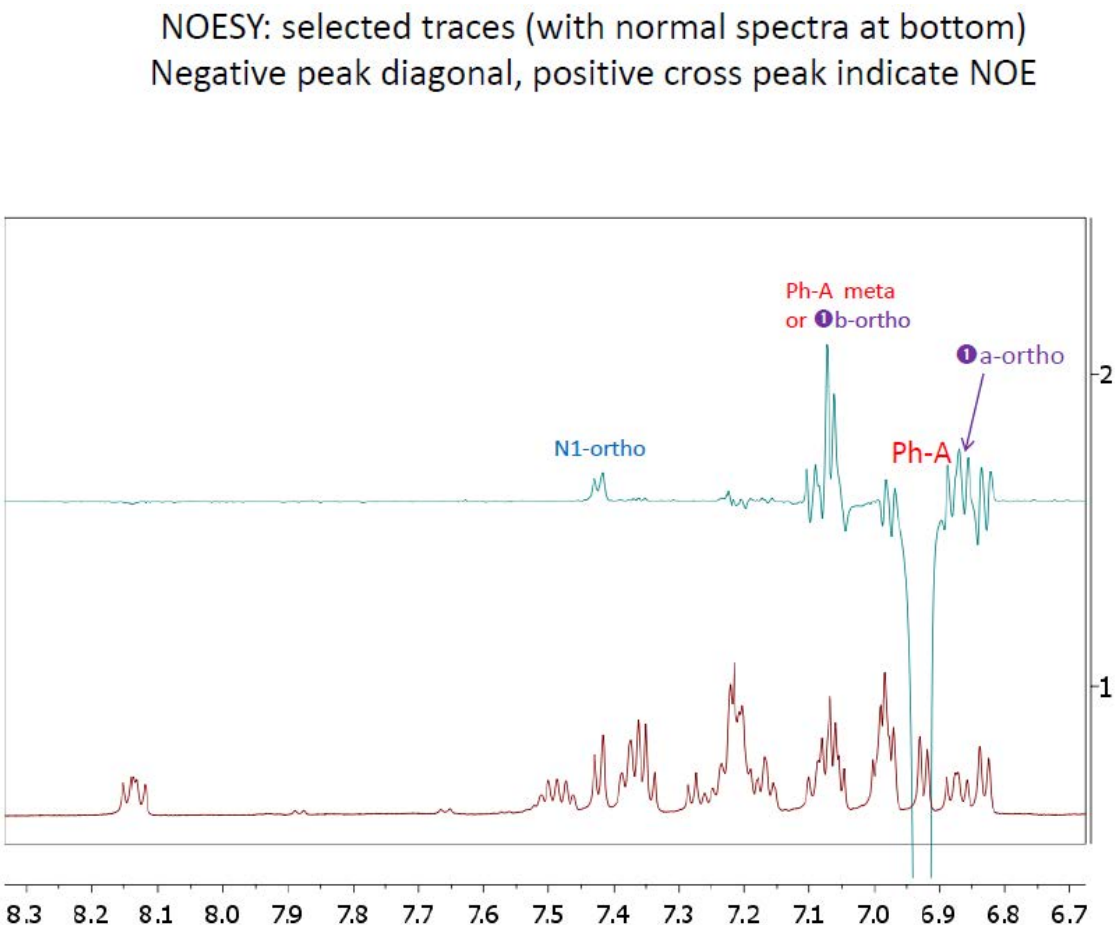
Figure S3.8. NOESY NMR spectrum of **2**.



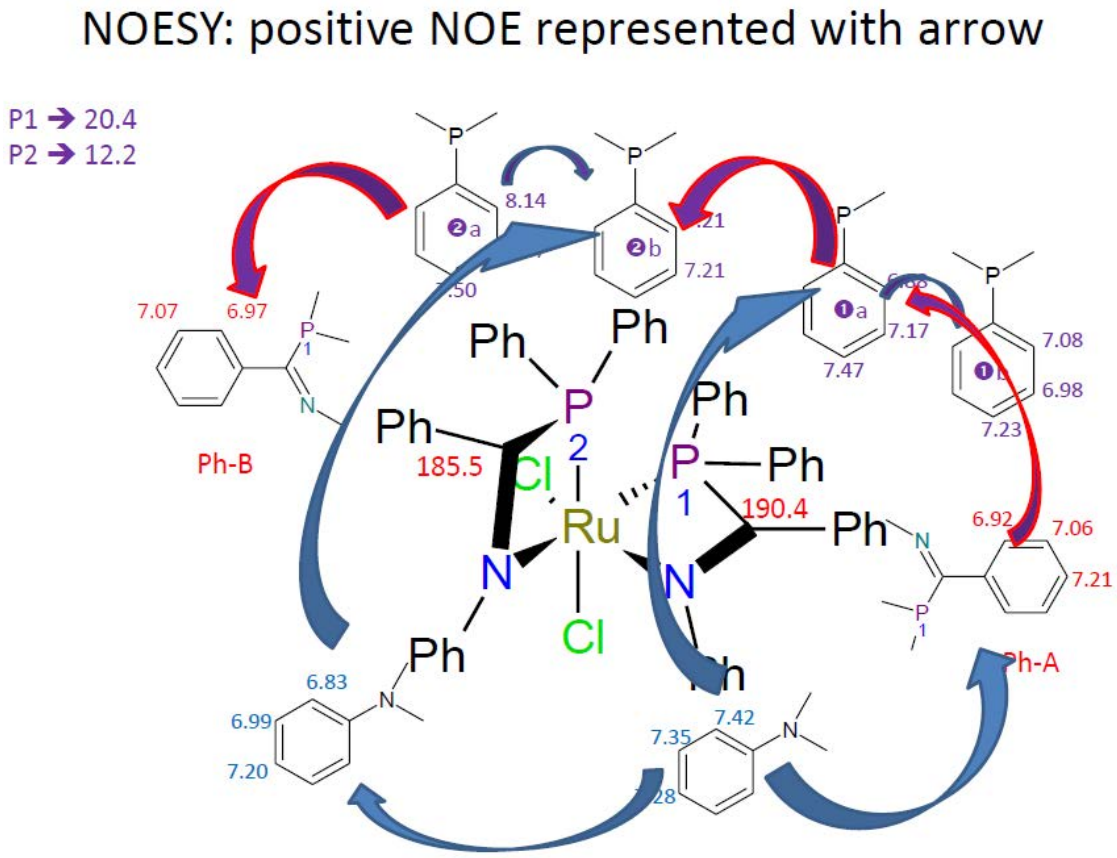
Selected NOESY NMR spectrum of **2**.



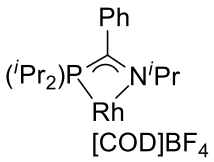
Selected NOESY NMR spectrum of **2**.



Selected NOESY NMR spectrum of **2**.



Arrow heads showing NOE contacts of **2**.



3

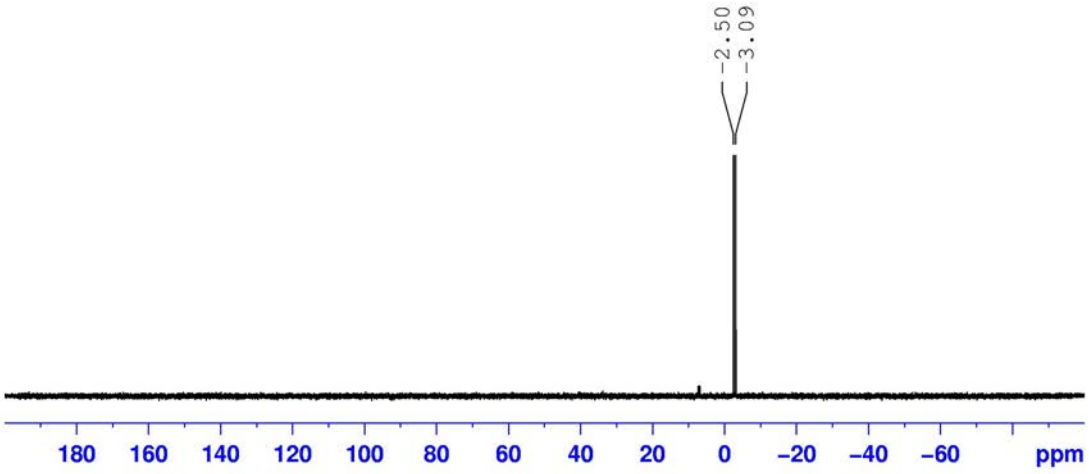


Figure S3.8. $^{31}P\{^{1}H\}$ NMR spectrum of **3**.

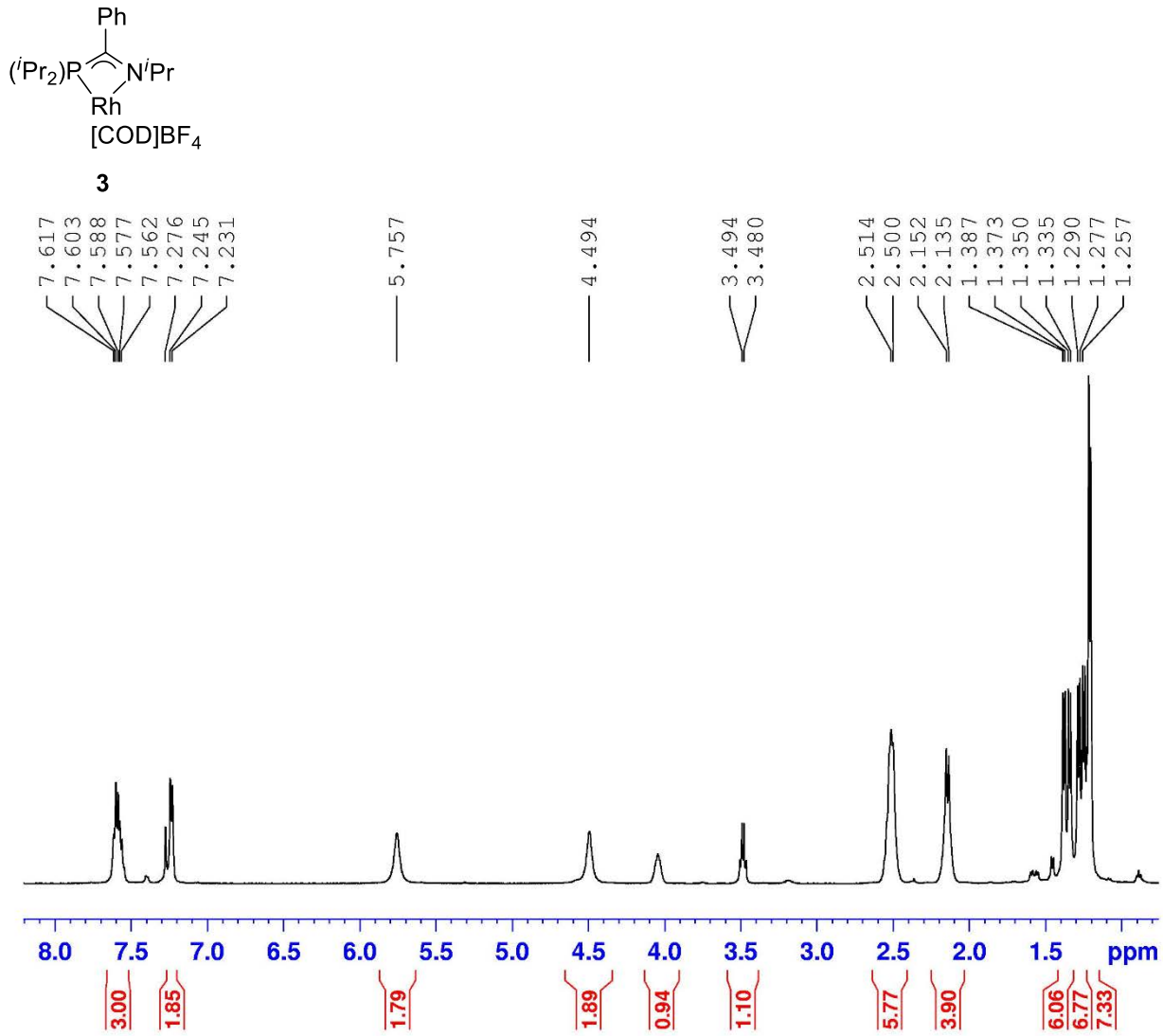


Figure S3.9. ^{1}H NMR spectrum of **3**.

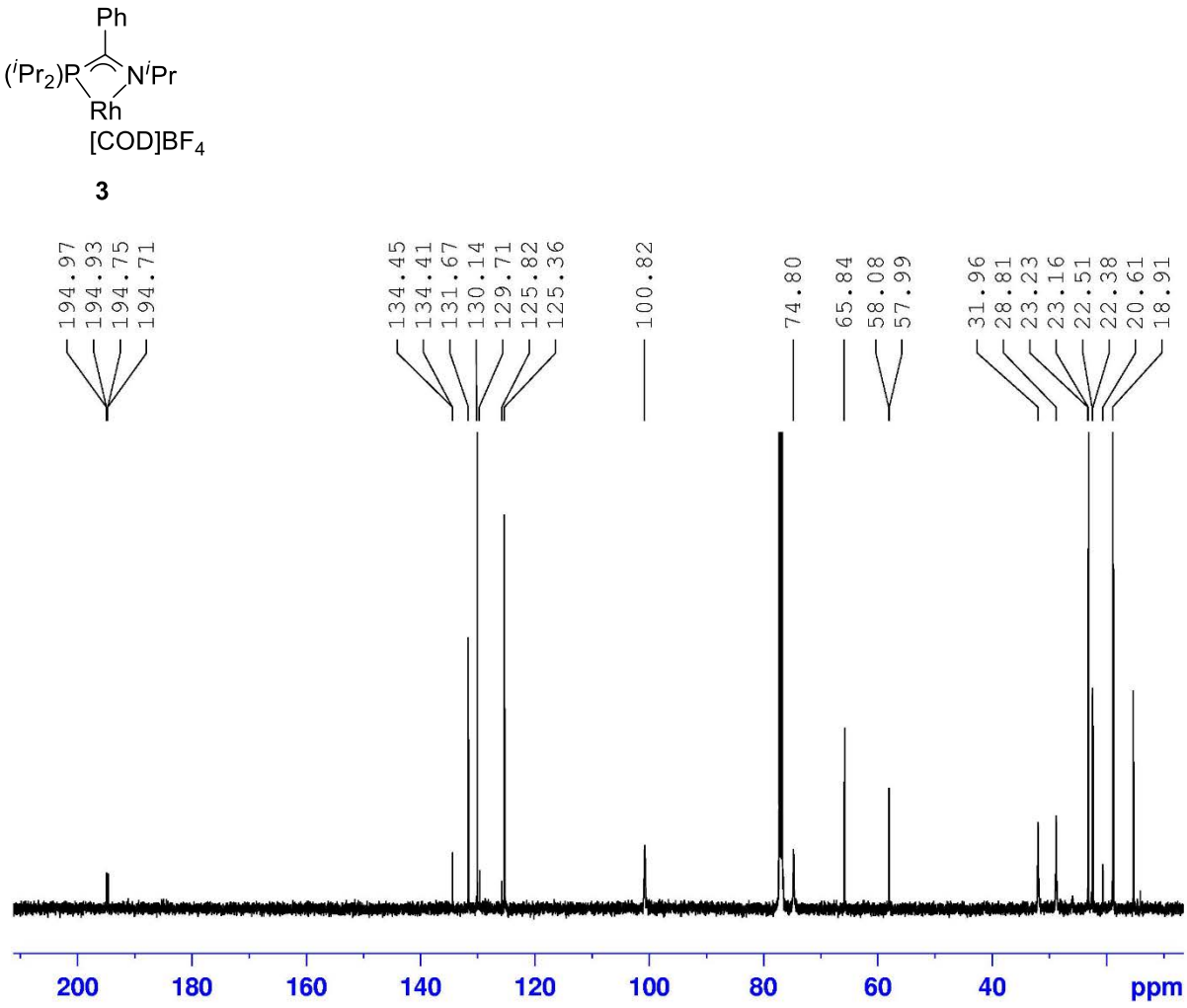
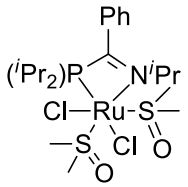


Figure S3.10. $^{13}C\{^{1}H\}$ NMR spectrum of **3**.



4

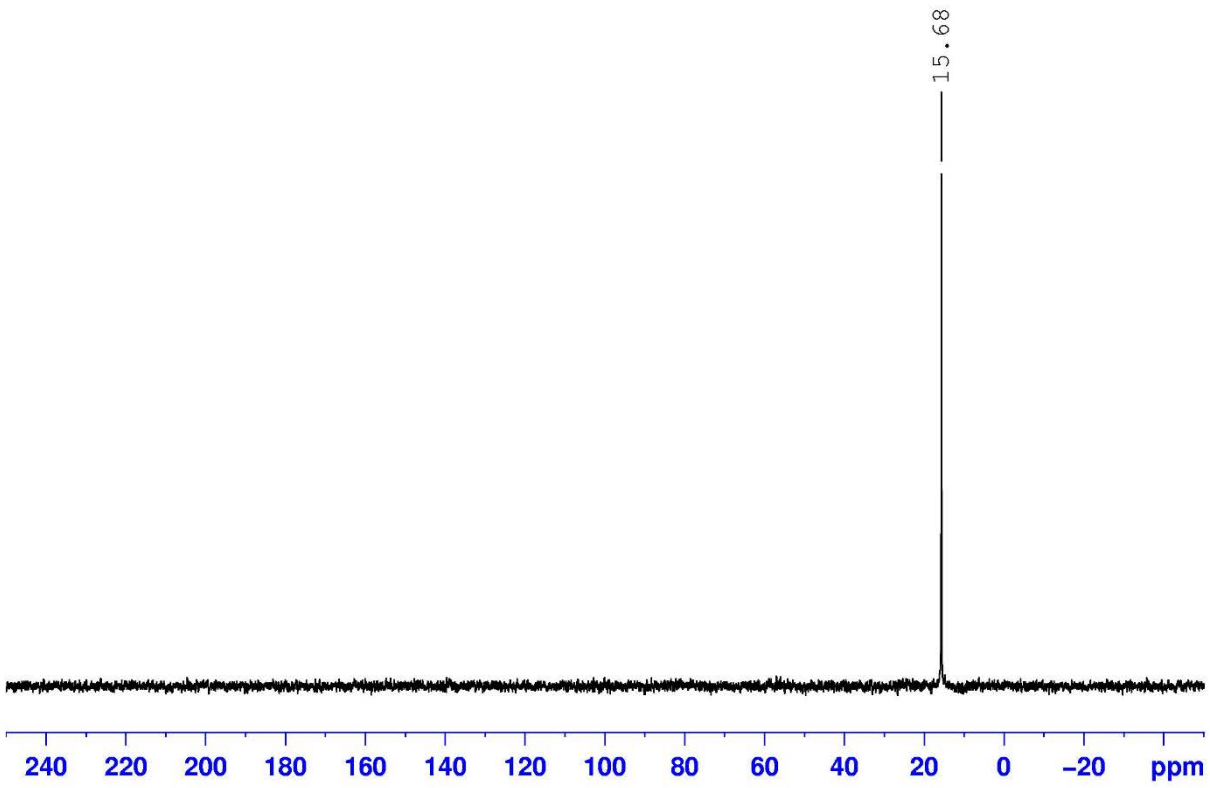


Figure S3.11. $^{31}P\{^{1}H\}$ NMR spectrum of **4**.

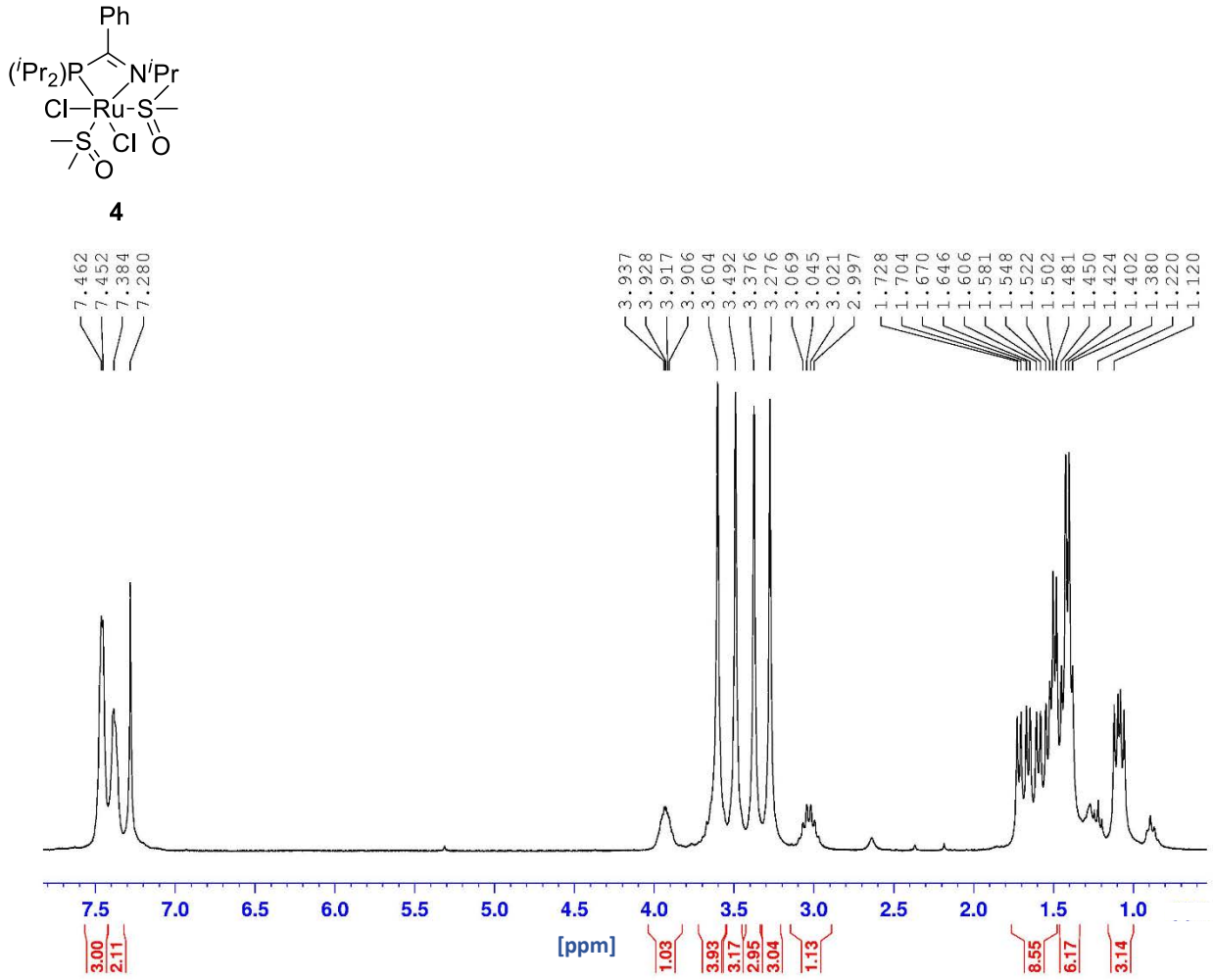


Figure S3.12. ^{1}H NMR spectrum of **4**.

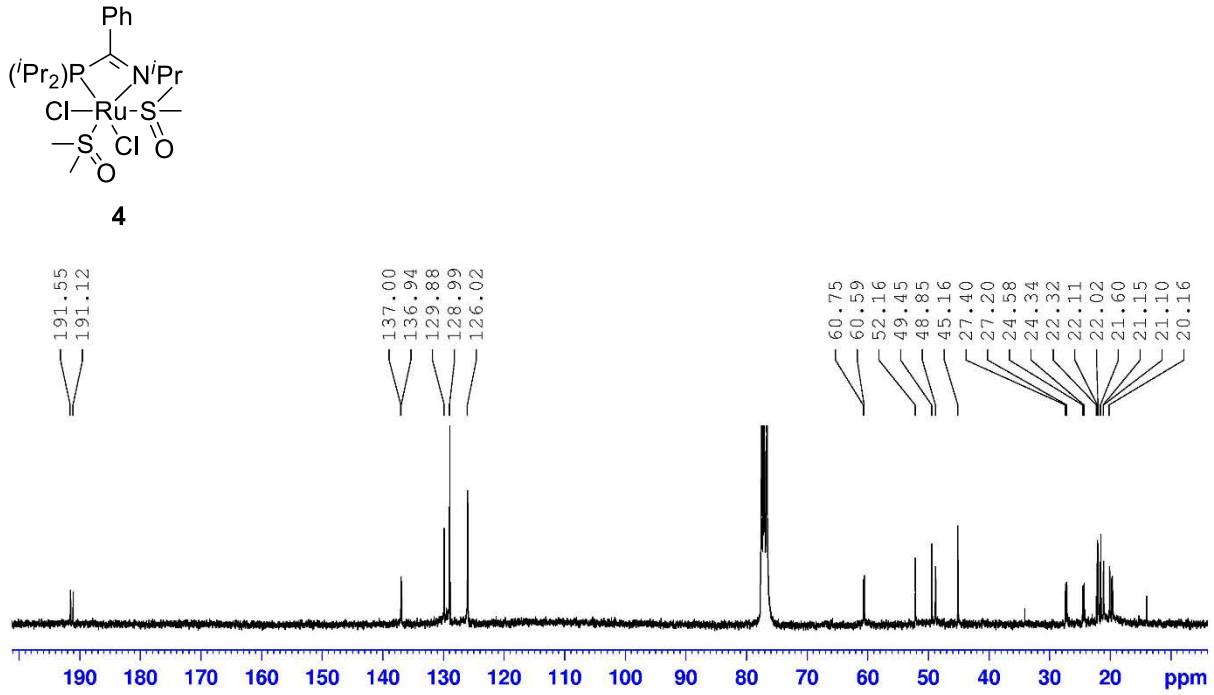


Figure S3.13. $^{13}C\{^{1}H\}$ NMR spectrum of **4**.

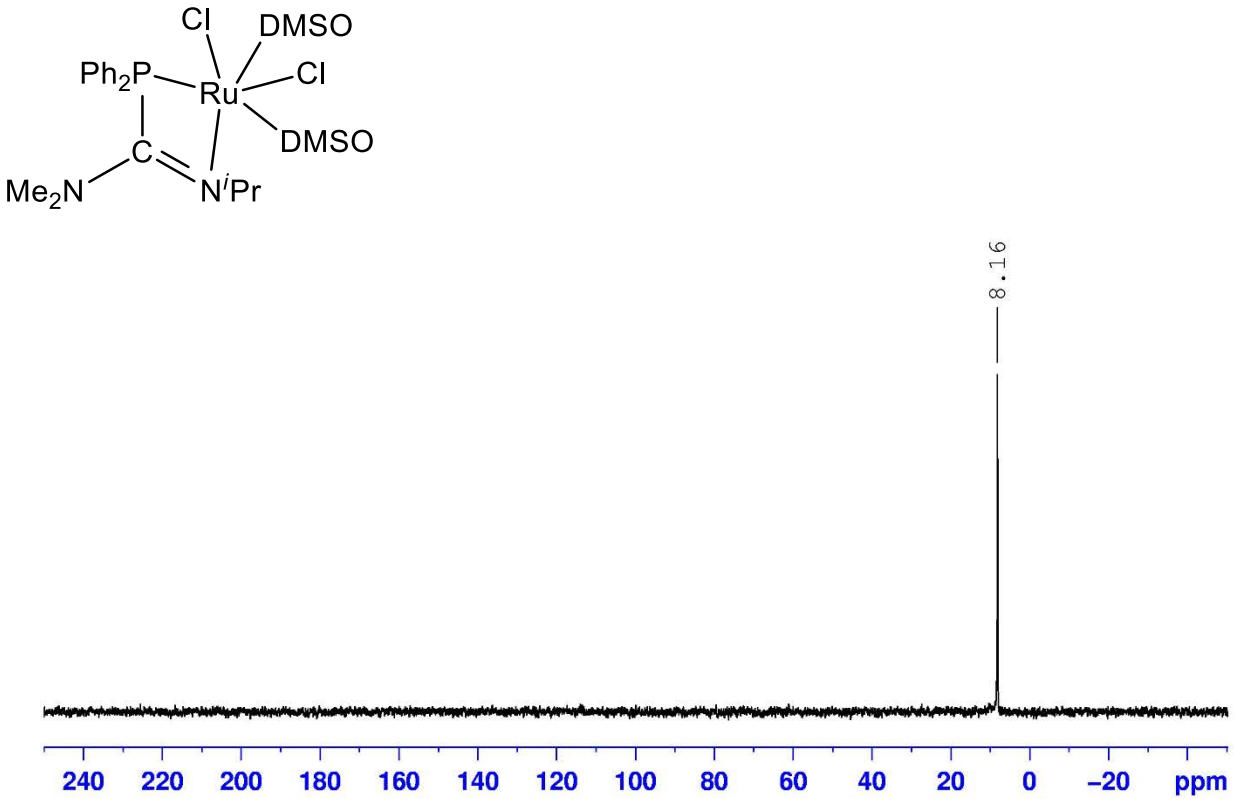


Figure S3.14. $^{31}P\{H\}$ NMR spectrum of complex **6**.

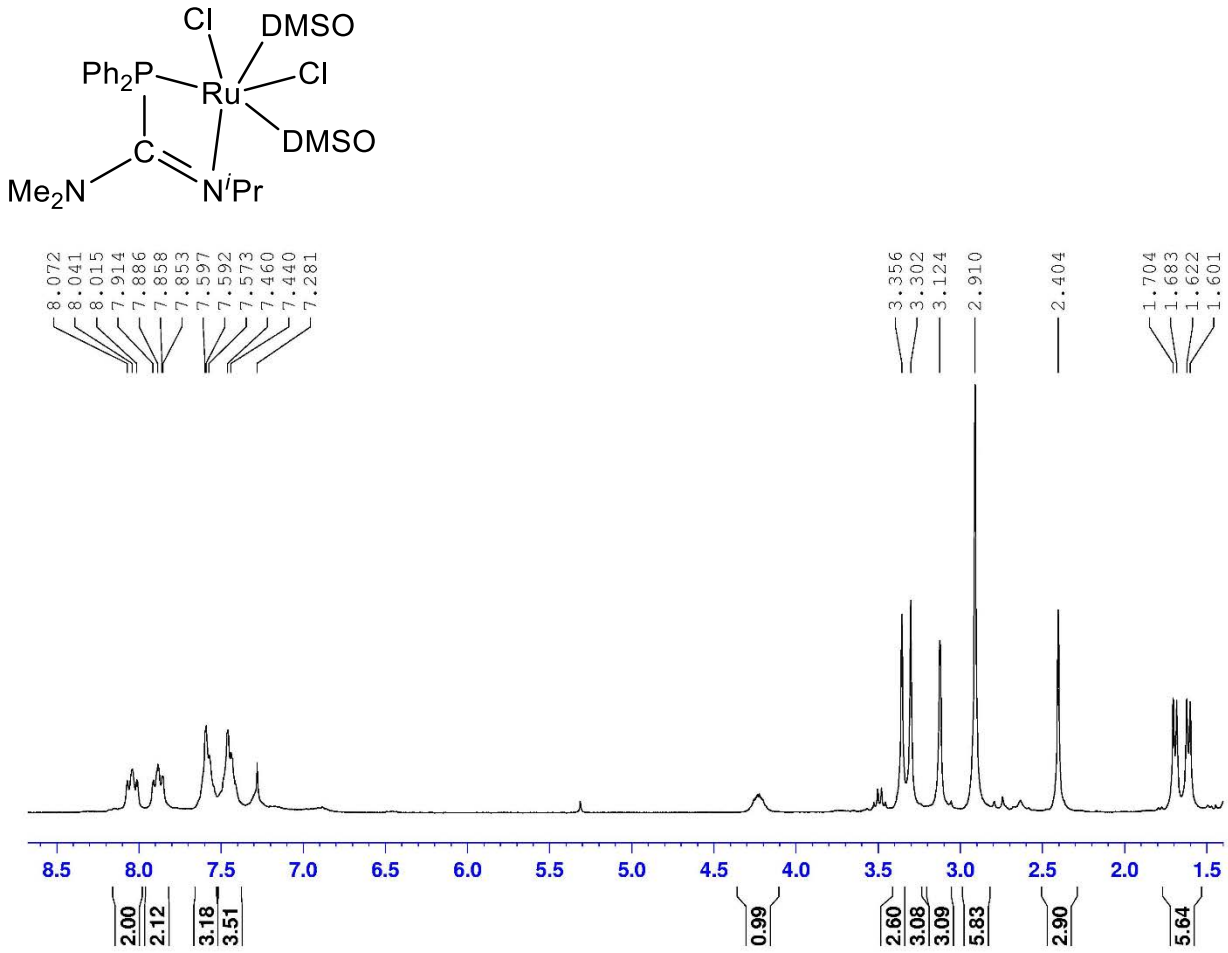


Figure S3.15. ^{1}H NMR spectrum of **6**.

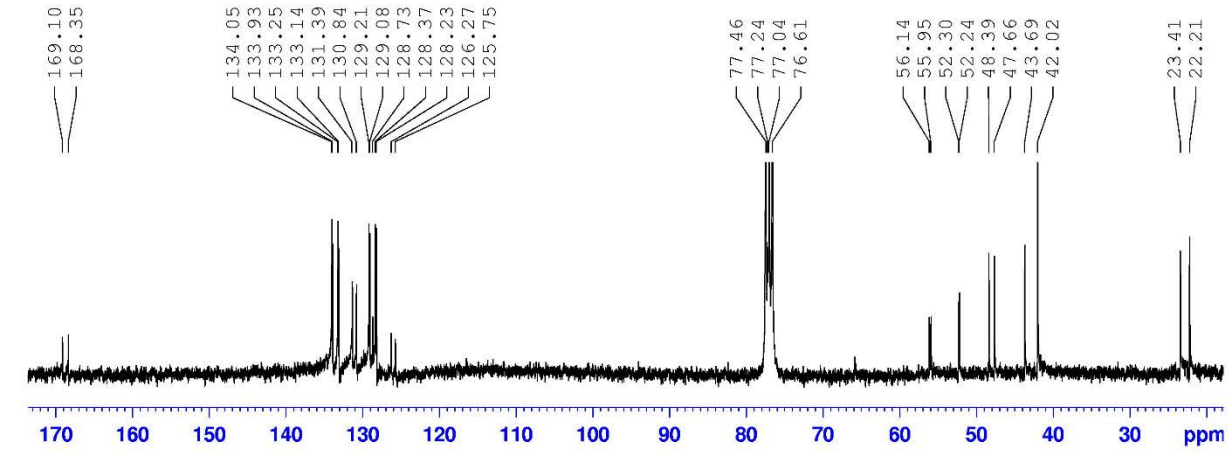


Figure S3.16. ^{13}C{^{1}H} NMR spectrum of **6**.

Air and water stability of **6**

Solid compound **6** is air stable for a month, while it is reasonably stable in the presence of water.

Compound **6** (6 mg) was dissolved in 0.5 mL of deuterated acetone in a NMR tube and 10 μL of degassed water was added under argon. No change in the $^{31}P\{^{1}H\}$ NMR spectrum was observed over 2 days. After two days a peak at 18.0 ppm appeared leaving 75% of unreacted **6** (8.2 ppm) as monitored by $^{31}P\{^{1}H\}$ NMR spectroscopy. This showed that **6** is slowly changing to an unidentified product.

Section S4: Turn over Number Calculation (TON)

Turn over Number Calculation (TON): An example

For complex **2**, where catalyst (**2**): DBU = 1: 20 molar ratio was used

Weight of **2** taken = 2.5 mg = 0.0025 g

Mol. Wt of **2** = 902.75 g/mole

Number of moles of **2** = $\frac{0.0025}{902.75}$ = 2.77×10^{-6} moles

Internal standard (**IS**) = 1,2,3-trimethoxybenzene

Weight of **IS** taken = 19.5 mg = 0.0195 g

Mol. Wt of **IS** = 168.19 g/mole

Number of moles of **IS** = $\frac{0.0195}{168.19}$ = 116×10^{-6} moles

The peaks from the ^{1}H NMR spectrum of the reaction mixture were integrated for the ratio of areas of peak of formate to the ratio of peak of **IS** as follows:

Ratio of area of peak of formate compared to **IS**

$$= \frac{\frac{\text{Integration}}{\text{Formate proton}}}{\frac{\text{Integration}}{\text{Protons of IS compared}}} = \frac{\frac{2.16}{1}}{\frac{2.06}{2}} = 2.09$$

So, moles of products = no of moles of **IS** × ratio of formate to **IS**

$$= 116 \times 10^{-6} \times 2.09 = 242.44 \times 10^{-6} \text{ g/mole}$$

$$\text{TON} = \frac{\text{moles of product}}{\text{moles of catalyst}} = \frac{2.42 \times 10^{-6}}{2.77 \times 10^{-6}} = 87.5$$

It was rounded to TON of 85 from two different experiments.