Supplementary Material

Selective hydration of nitriles to amides in air with Rh(I)-*N*-heterocyclic catalysts

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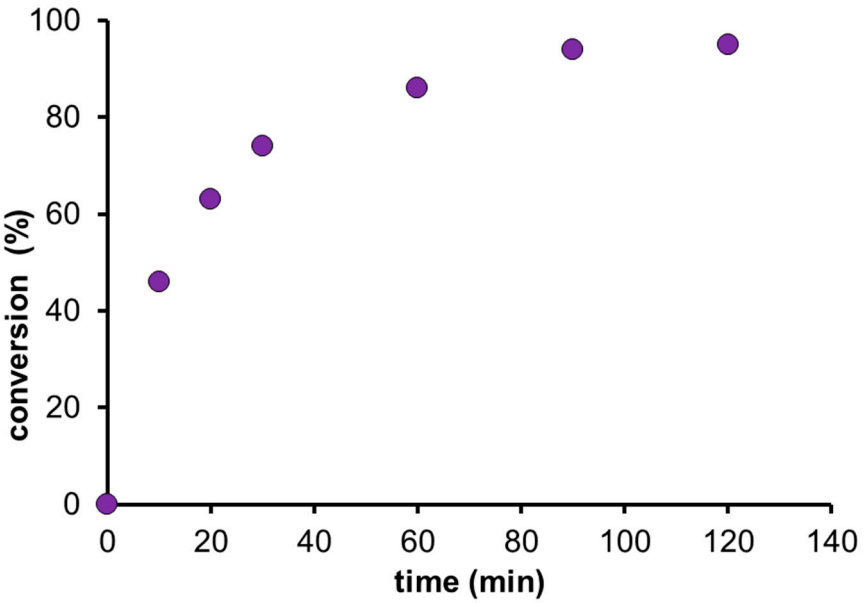

Figure S1. The time course of benzonitrile hydration with 1 mol % of [RhCl(cod)(IMes)] (**1**) *Conditions:* 1 mmol benzonitrile, 1 mol % **1**, 0.01 mmol NaOH, 1 mL *2*-PrOH, 1 mL H_2O, 80 °C.

Gas chromatographic determination of the compounds

The gas chromatographic measurements were done on an Agilent Technologies 7890 A instrument HP-5, 0.25µm x 30 m x 0.32 mm, FID 300 °C (Agilent Technologies, Santa Clara, California, USA); carrier gas: nitrogen (1.9 mL/min). T_{inj}= 250 °C, T_{det}= 300 °C, V_{inj}= 1 µL, split ratio = 350:1. Initial column temperature: 130 °C, held for 4 minutes, ramp to 250 °C (60 °C /min), then held at this temperature for 1 minute.

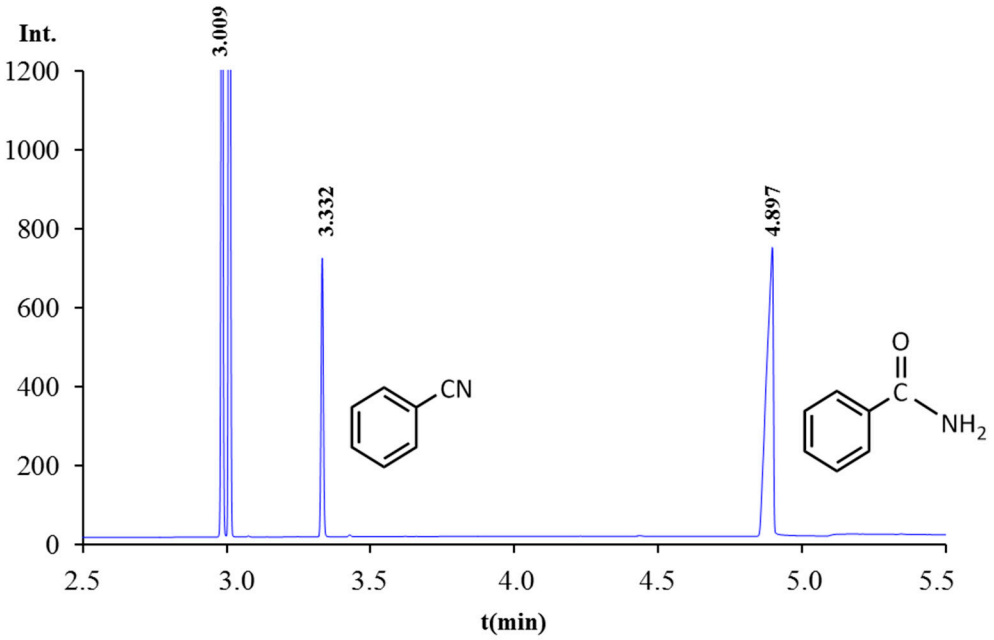

Figure S2. Gas chromatographic separation of benzonitrile and benzamide

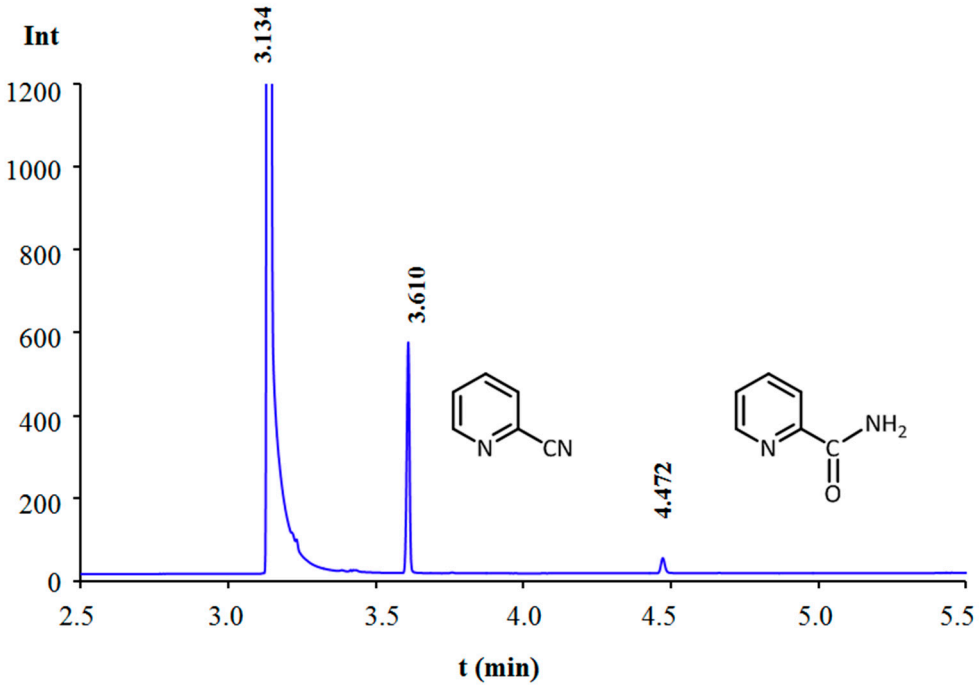

Figure S3. Gas chromatographic separation of 2-pyridinecarbonitrile and 2-pyridine-carboxamide

Table S1. Retention times of the nitriles and amides used in this study

Retention time (min)			
Starting material		***Product***	
benzonitrile	3.3	benzamide	4.9
4-chlorobenzonitrile	3.8	4-chlorobenzamide	5.6
4-chloropheny-acetonitrile	4.8	4-chlorophenyl-acetamide	5.9
4-methylbenzotrile	3.7	4-methylbezamide	5.3
2-pyridinecarbonitrile	3.6	picolinamide	4.5
3-pyridinecarbonitrile	3.5	nicotinamide	5.1
4-pyridinecarbonitrile	3.4	isonicotinamide	5.1

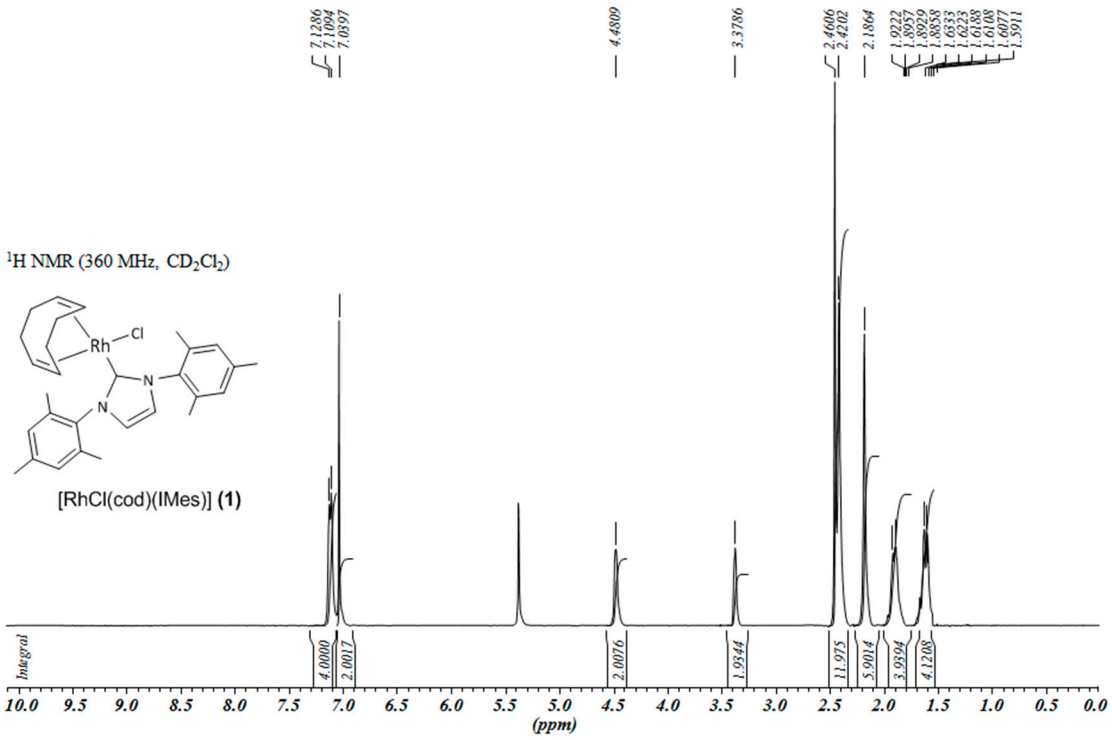

Figure S4. ^{1}H NMR spectrum of [RhCl(cod)(IMes)] (**1**)

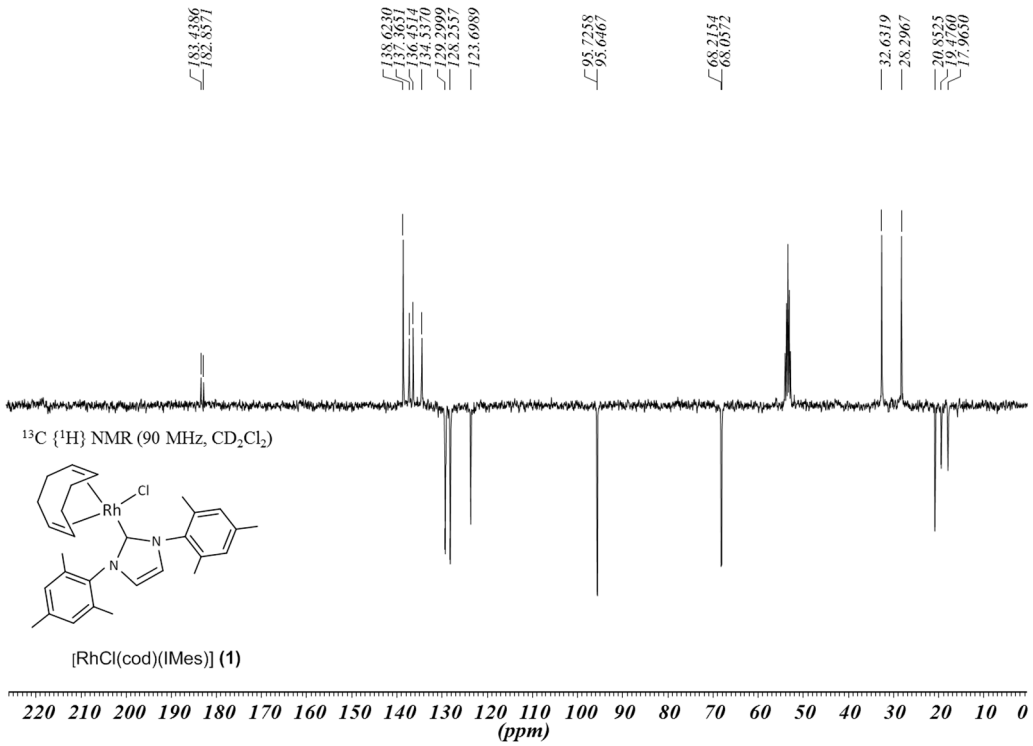

Figure S5. ^{13}C{^{1}H} NMR spectrum of [RhCl(cod)(IMes)] (**1**)

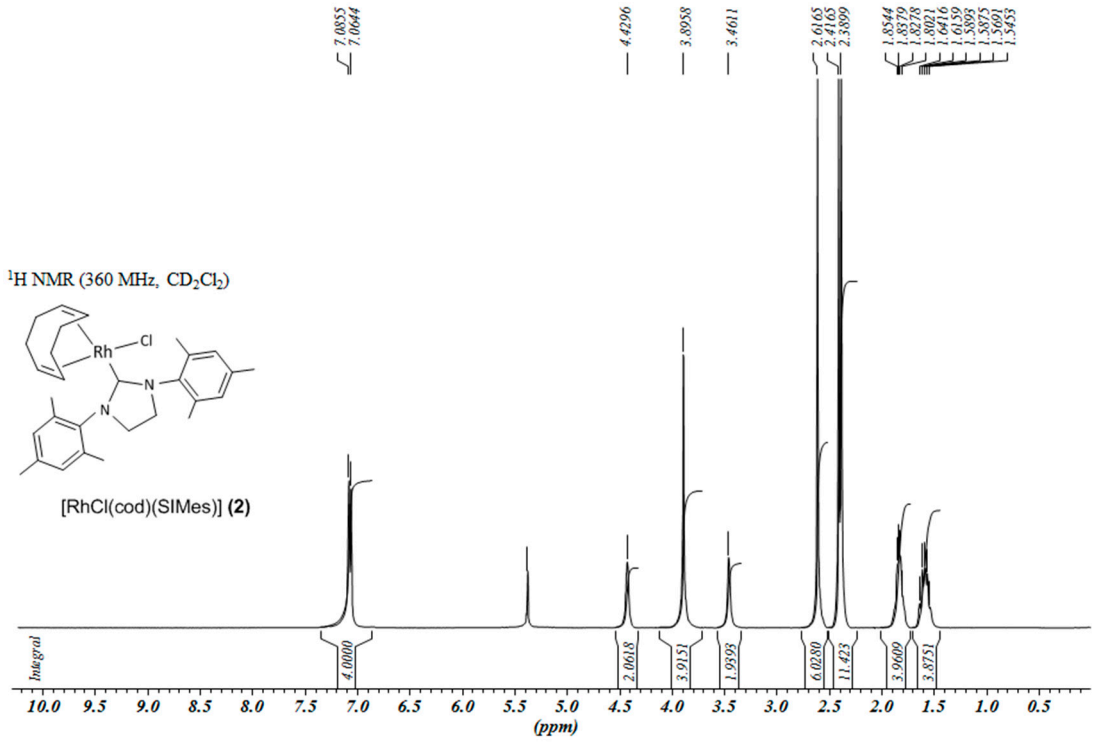

Figure S6. ^{1}H-NMR spectrum of [RhCl(cod)(SIMes)] (**2**)

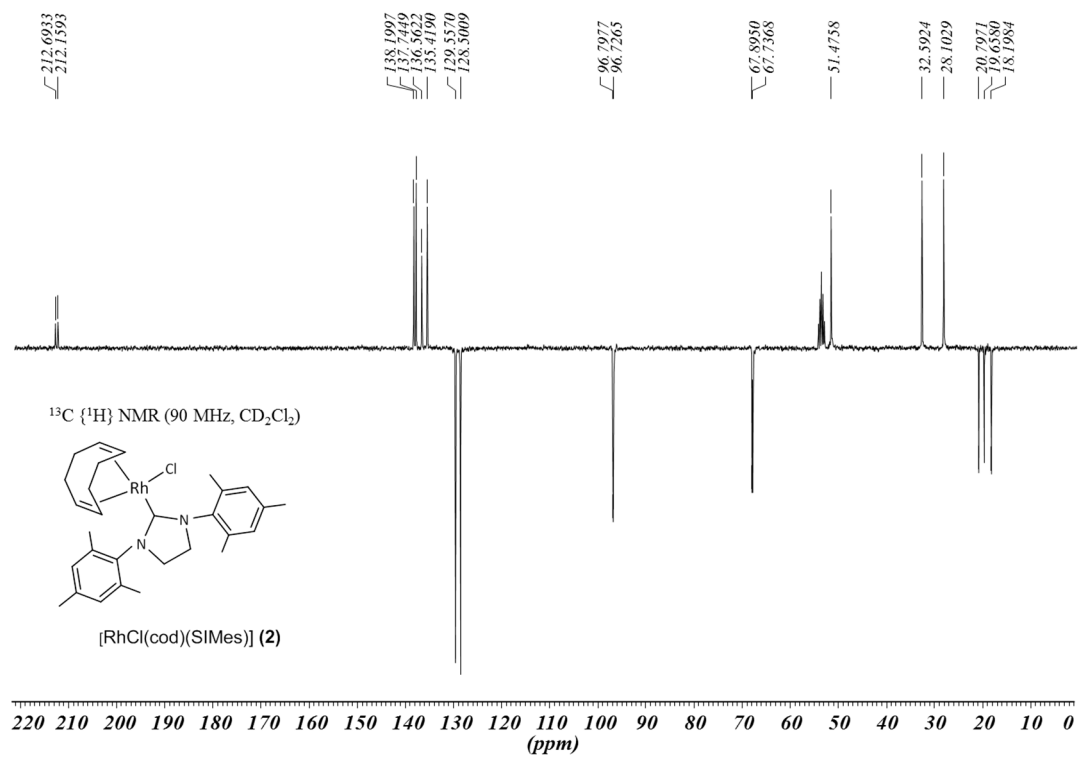

Figure S7. ^{13}C{^{1}H} NMR spectrum of [RhCl(cod)(SIMes)] (**2**)

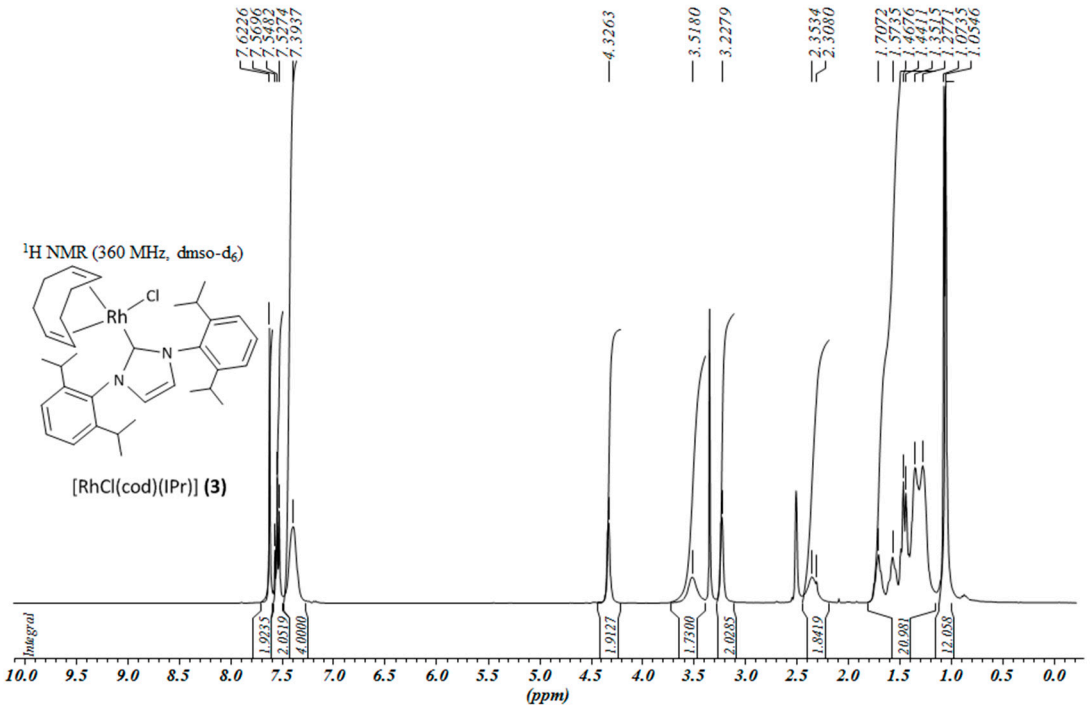

Figure S8. ^{1}H-NMR spectrum of [RhCl(cod)(IPr)] (**3**)

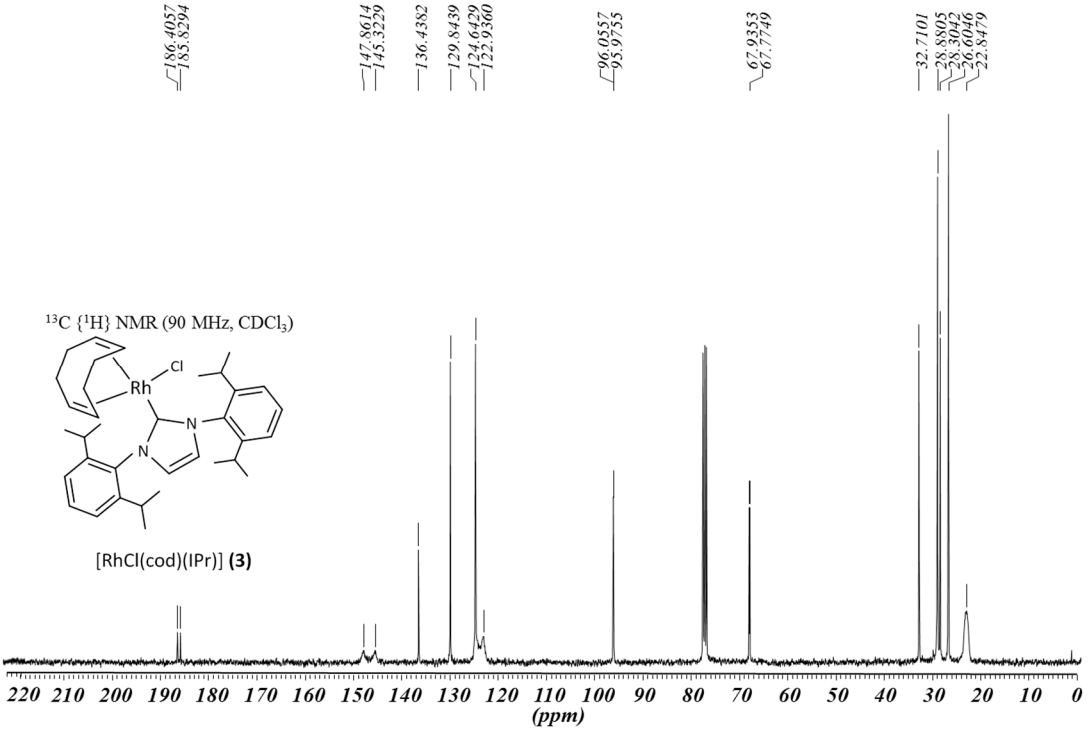

Figure S9. ^{13}C{^{1}H} NMR spectrum of [RhCl(cod)(IPr)] (**3**)

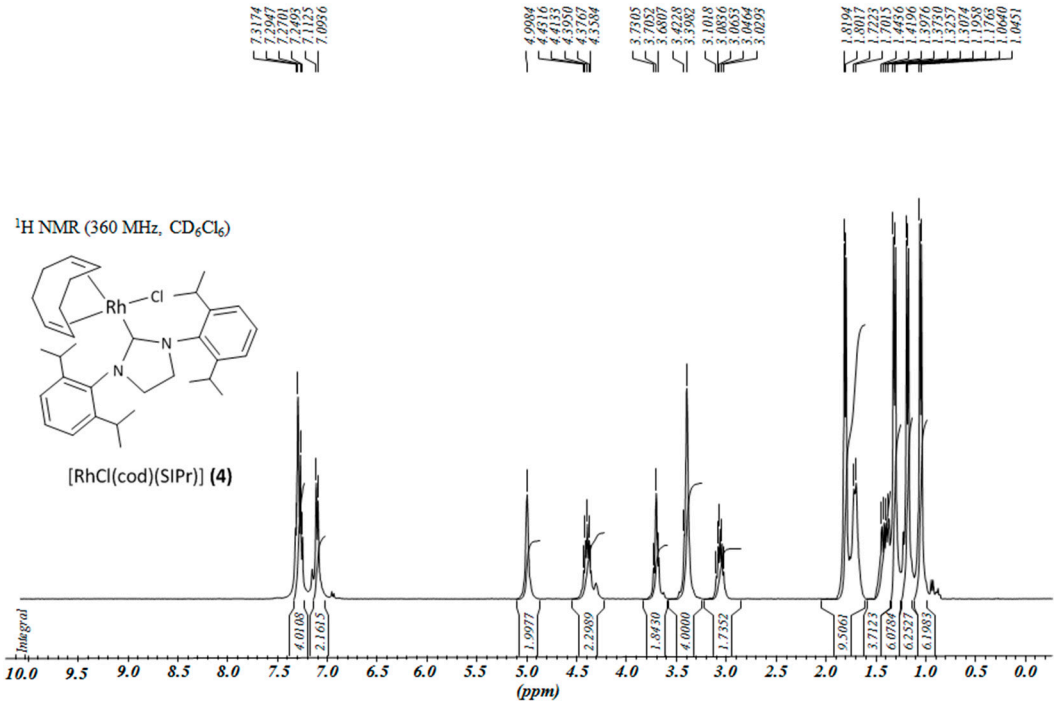

Figure S10. ^{1}H-NMR spectrum of [RhCl(cod)(SIPr)] (**4**)

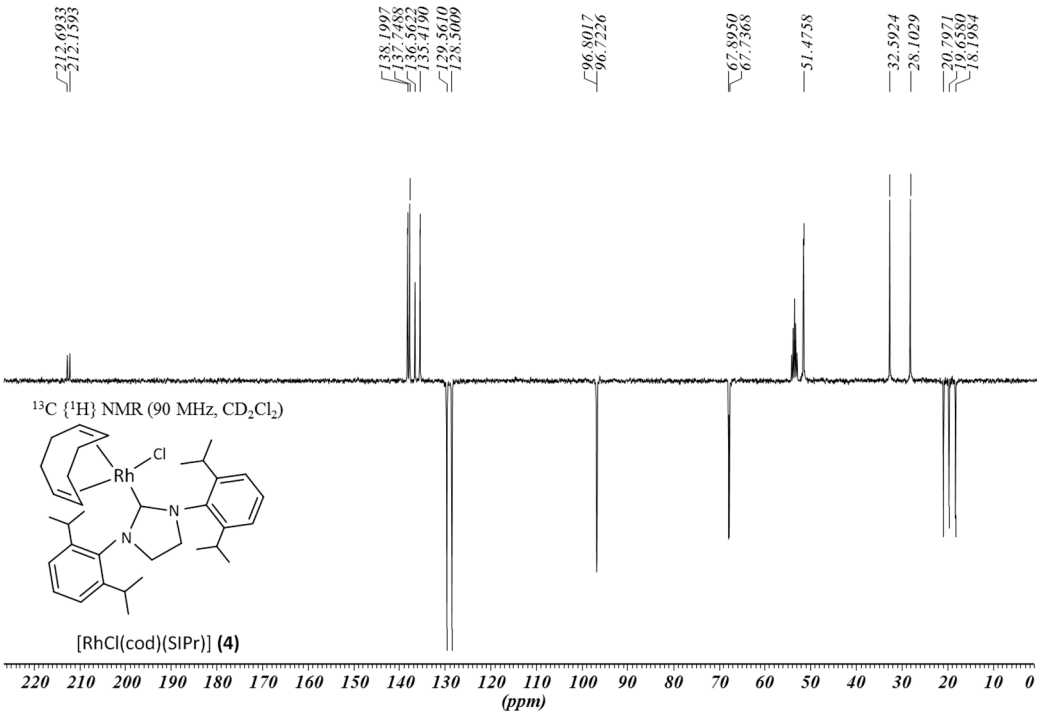

Figure S11. ^{13}C{^{1}H} NMR spectrum of [RhCl(cod)(SIPr)] (**4**)

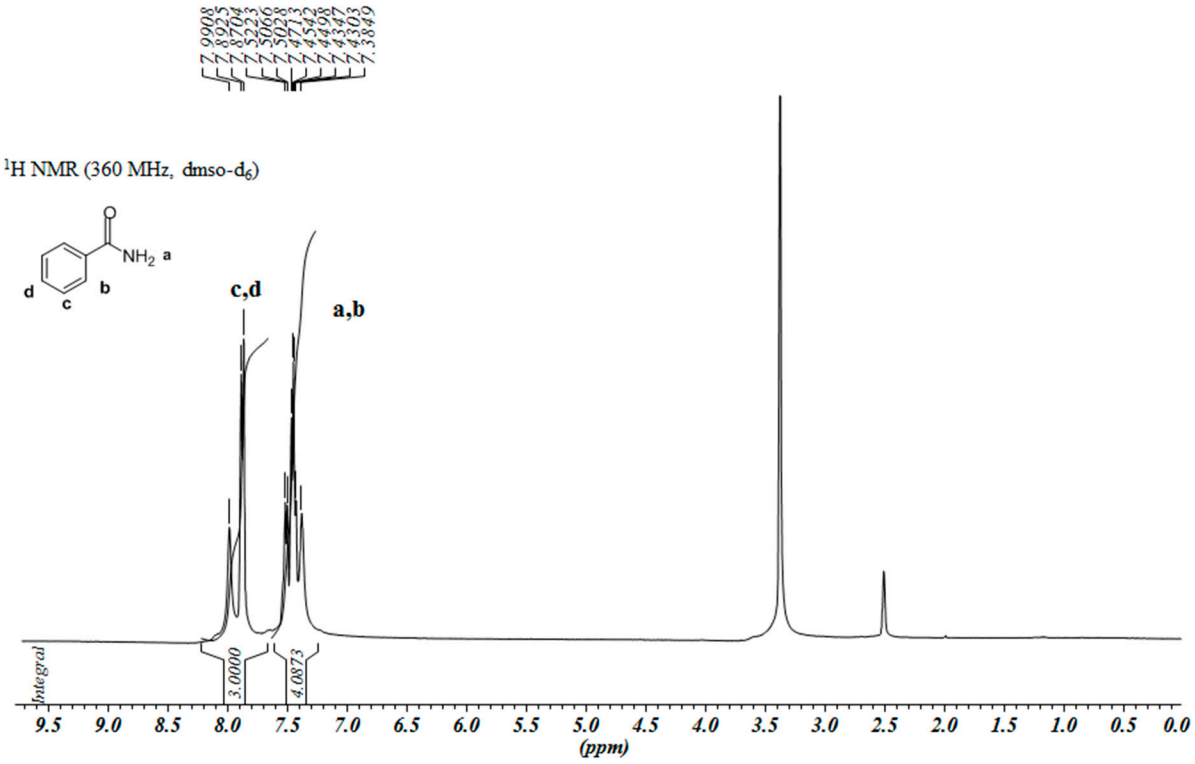

Figure S12. ^{1}H NMR spectrum of benzamide in dmso-d6 obtained by hydration of benzonitrile with catalyst **1**.
Conditions: 200 µL (2 mmol) benzonitrile, 11 mg (0.02 mmol) [RhCl(cod)(IMes)] (**1**), 0.8 mg (0.02 mmol) NaOH, 1.5 mL *2*-PrOH, 1.5 mL deionized water, 80 °C, 3 h.

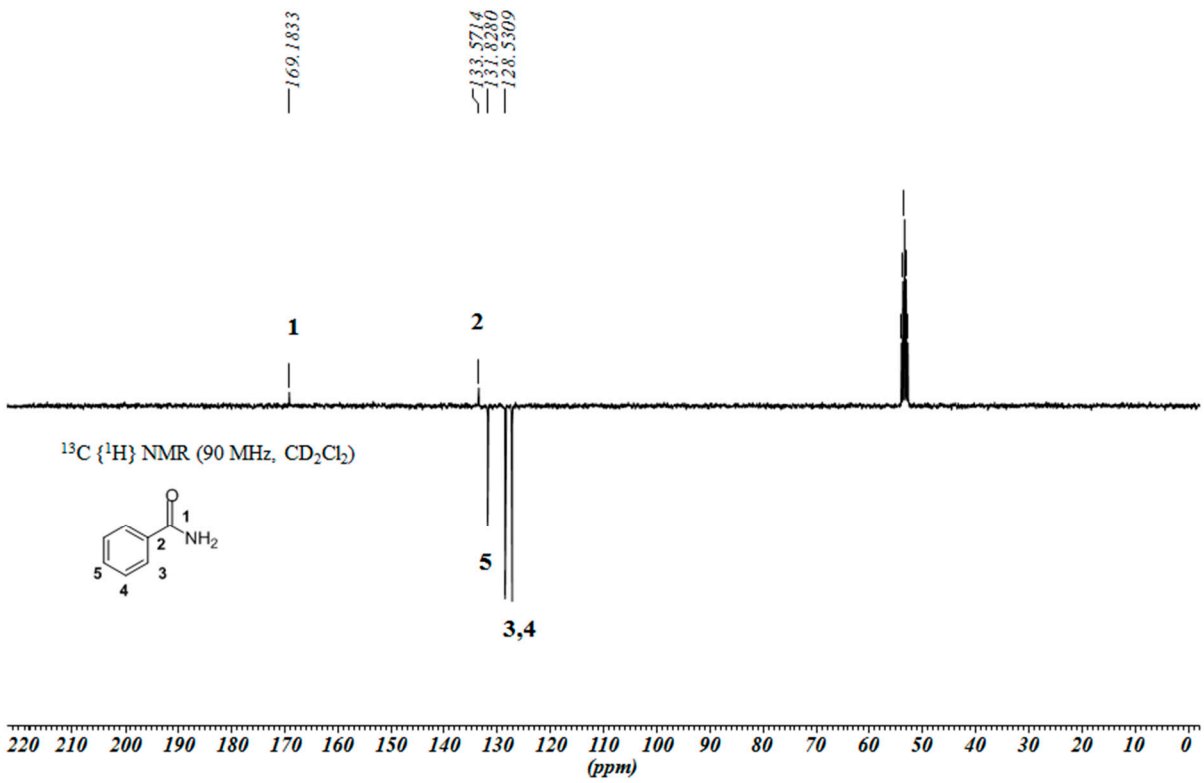

Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum of benzamide obtained by hydration of benzonitrile with catalyst **1**. For the conditions. see Figure S12.

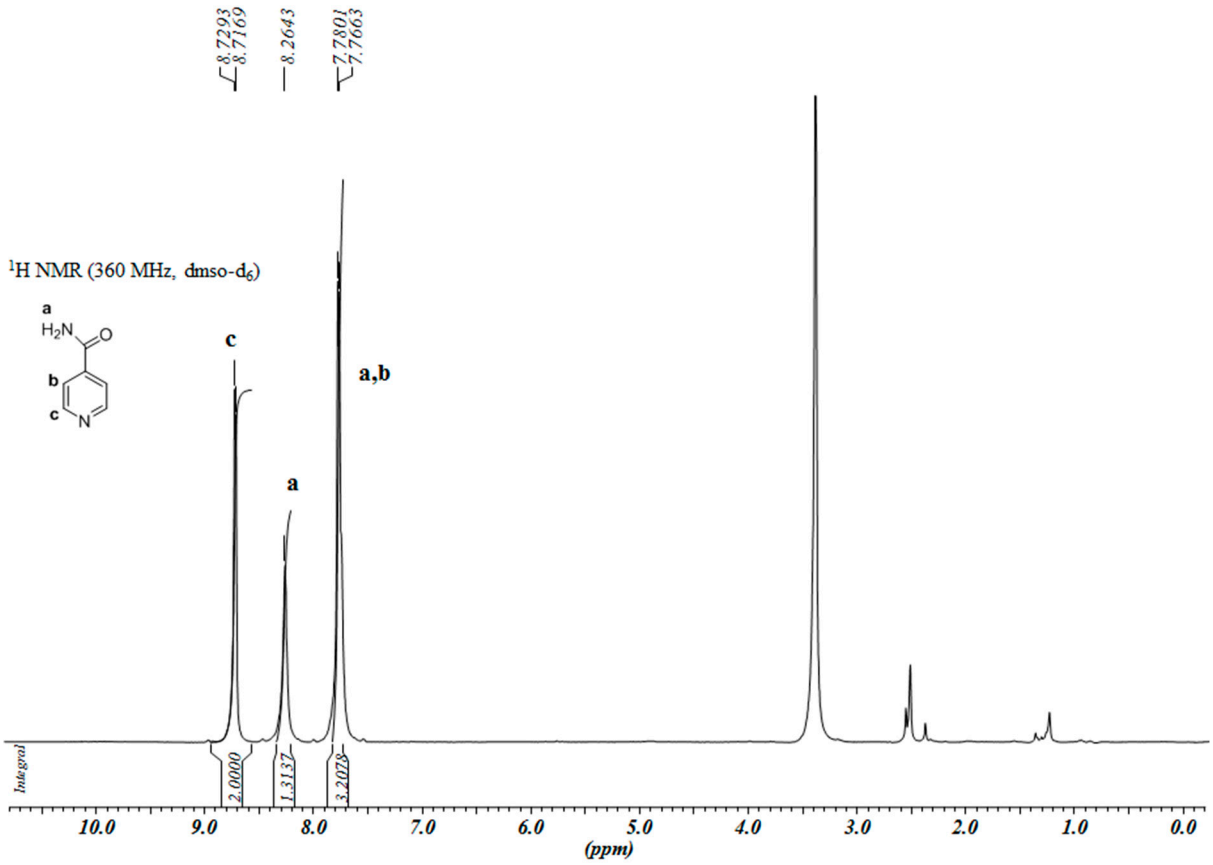

Figure S14. [1]H NMR spectrum of isonicotinamide in dmso-d6 obtained by hydration of 4-pyridinecarbonitrile with catalyst **1**.

Conditions:
104 mg (1 mmol) of 4-pyridinecarbonitrile, 5.5 mg (0.01 mmol) [RhCl(cod)(IMes)] (**1**), 1.5 mL *2*-PrOH, 1.5 mL deionized water, reflux, 2 h.

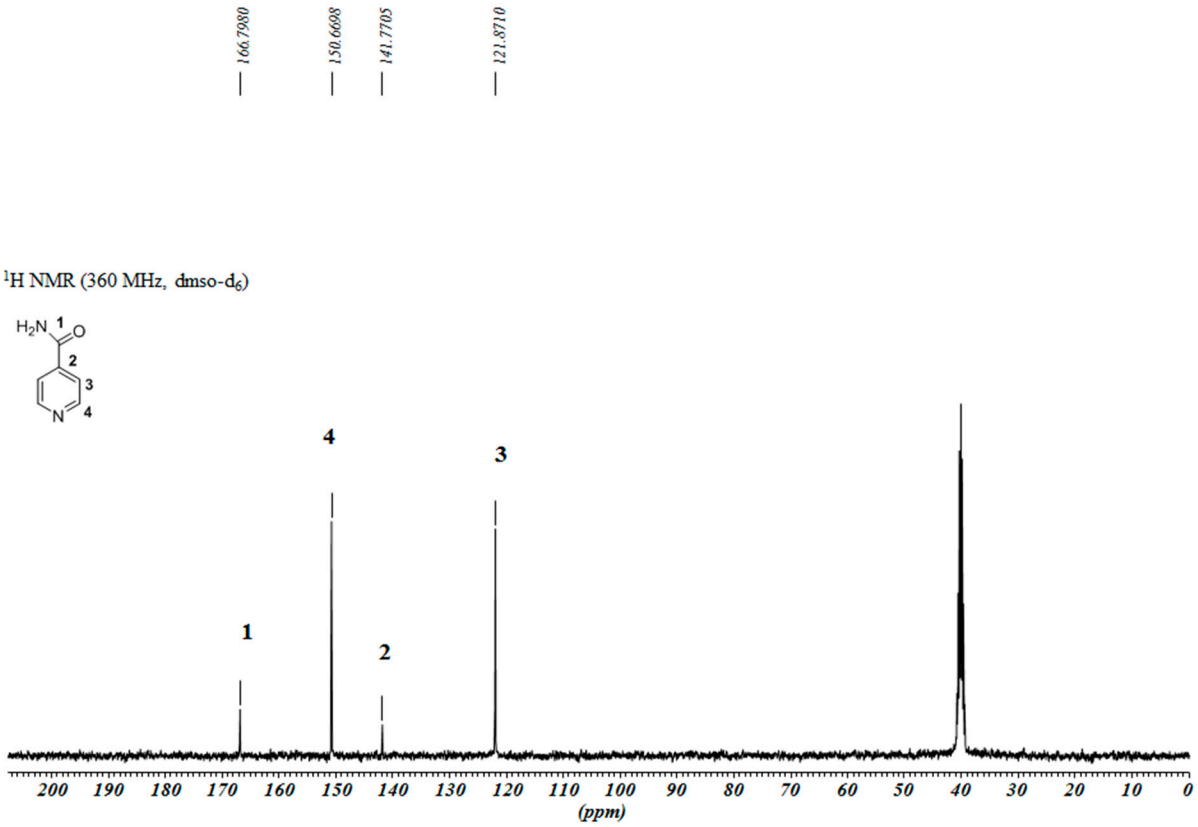

Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of isonicotinamide in dmso-d6 obtained by hydration of 4-pyridinecarbonitrile with catalyst **1**. For the conditions, see Figure S14.

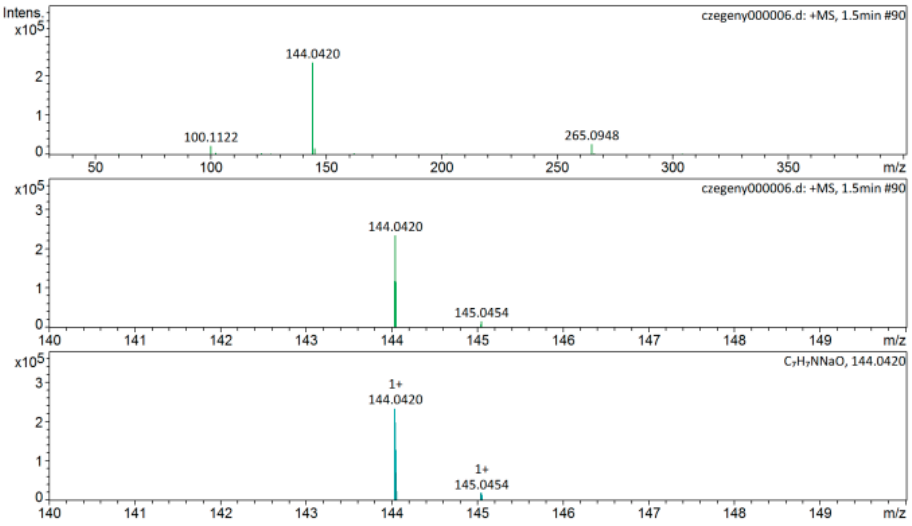

Figure S16. MS(ESI), positive mode, in MeOH, *m/z* for benzamide, $[M\text{-}Na]^+$ (C_7H_7NNaO), Calculated: 144.0420, Found: 144.0420.

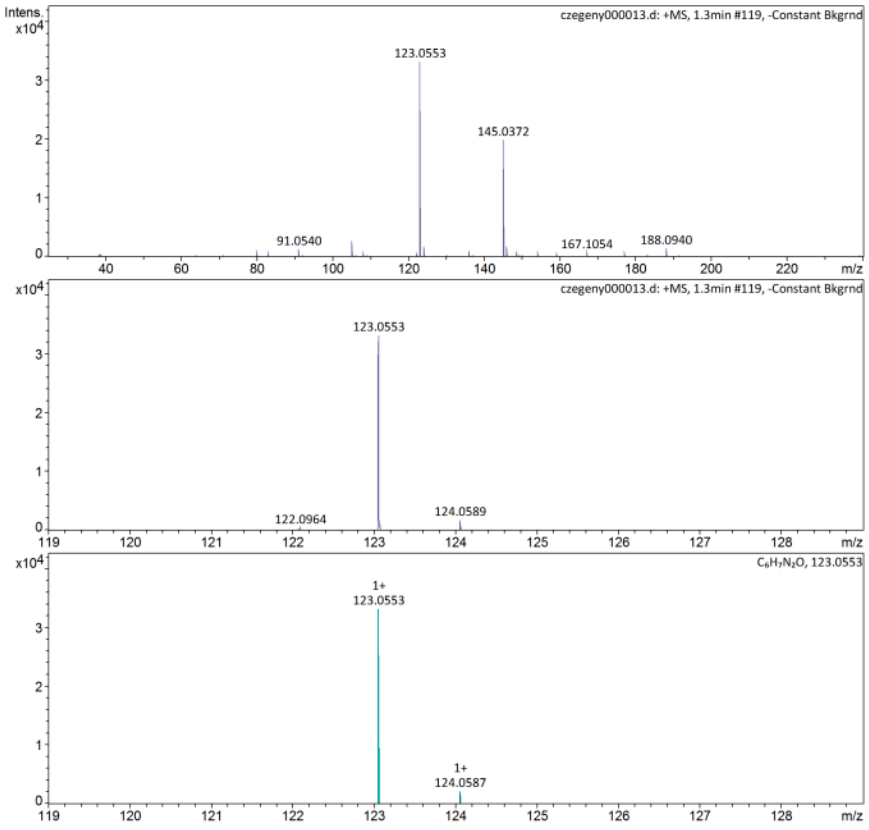

Figure S17. MS(ESI), positive mode, in MeOH, *m/z* for isonicotinamide, $[M\text{-}H]^+$ (C_6H_7NO), Calculated: 123.0553, Found: 123.0553 and $[M\text{-}Na]^+$ (C_6H_6NNaO), Calculated: 145.0378, Found: 145.0372.

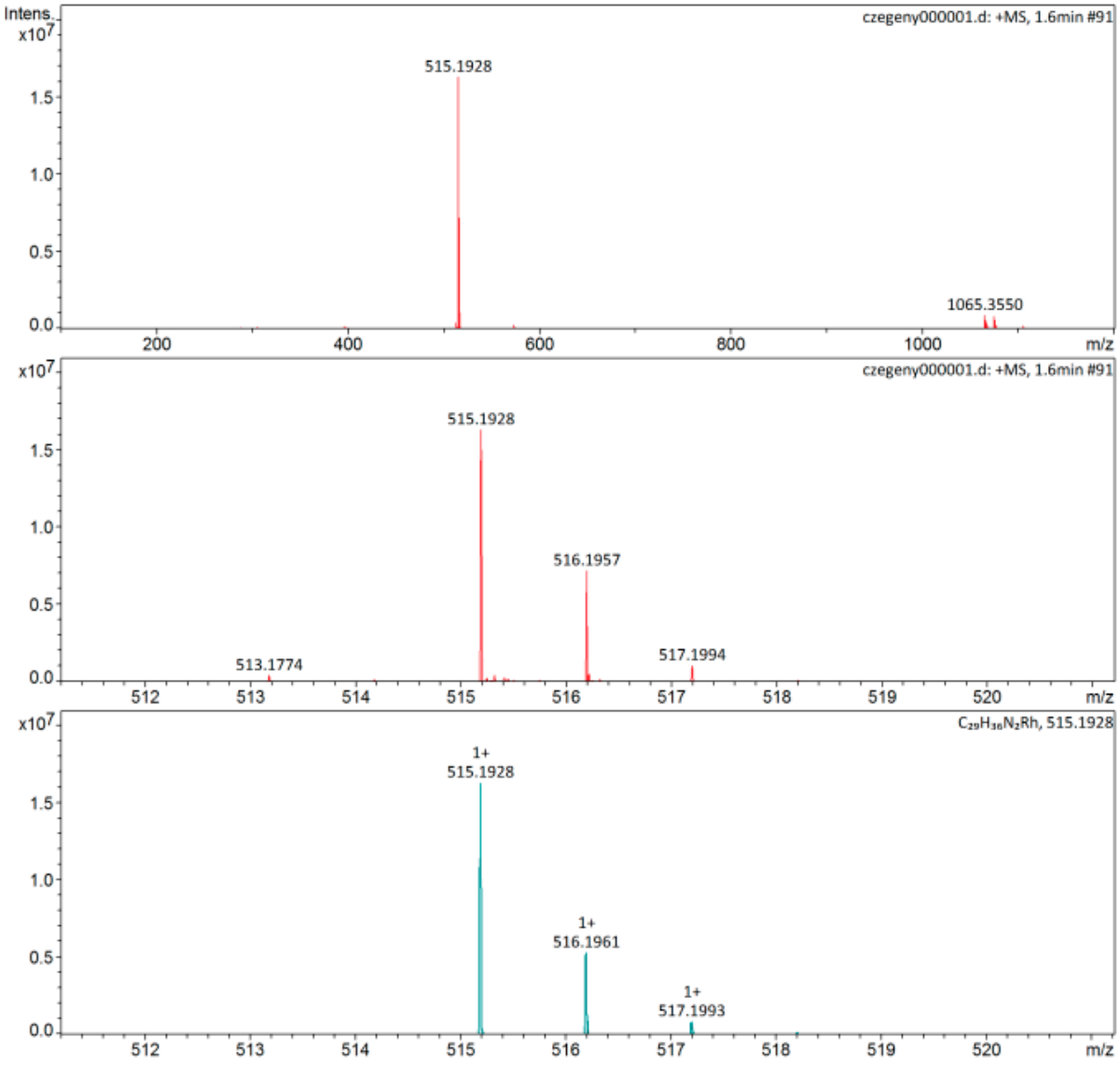

Figure S18. MS(ESI), positive mode, in MeOH, *m/z* for **1**, $[M]^+$ ($C_{29}H_{36}N_2Rh$), Calculated: 515.1928, Found: 515.1928.

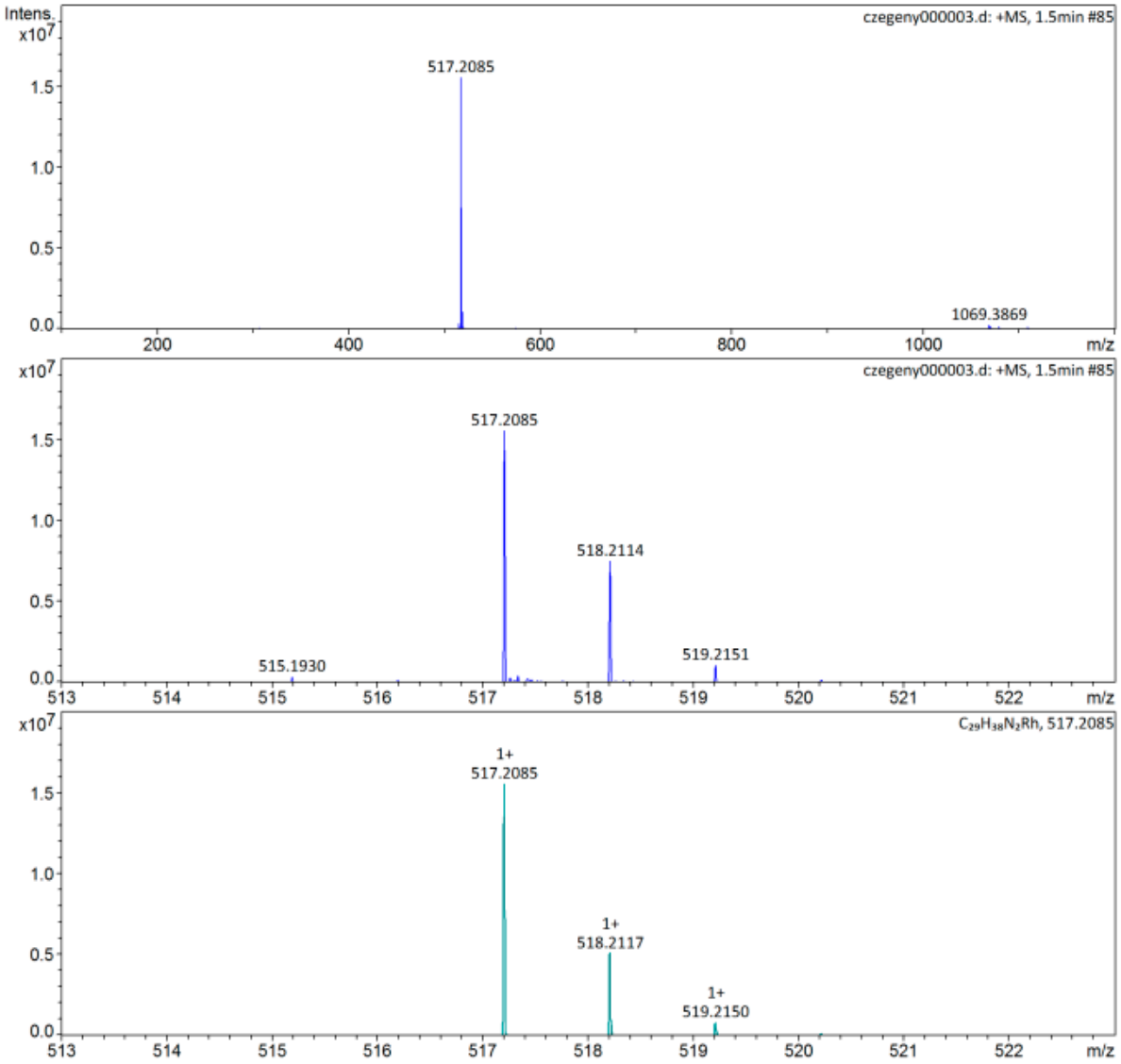

Figure S19. MS(ESI), positive mode, in MeOH, *m/z* for **2**, $[M]^+$ ($C_{29}H_{38}N_2Rh$), Calculated: 517.2085, Found: 517.2085.

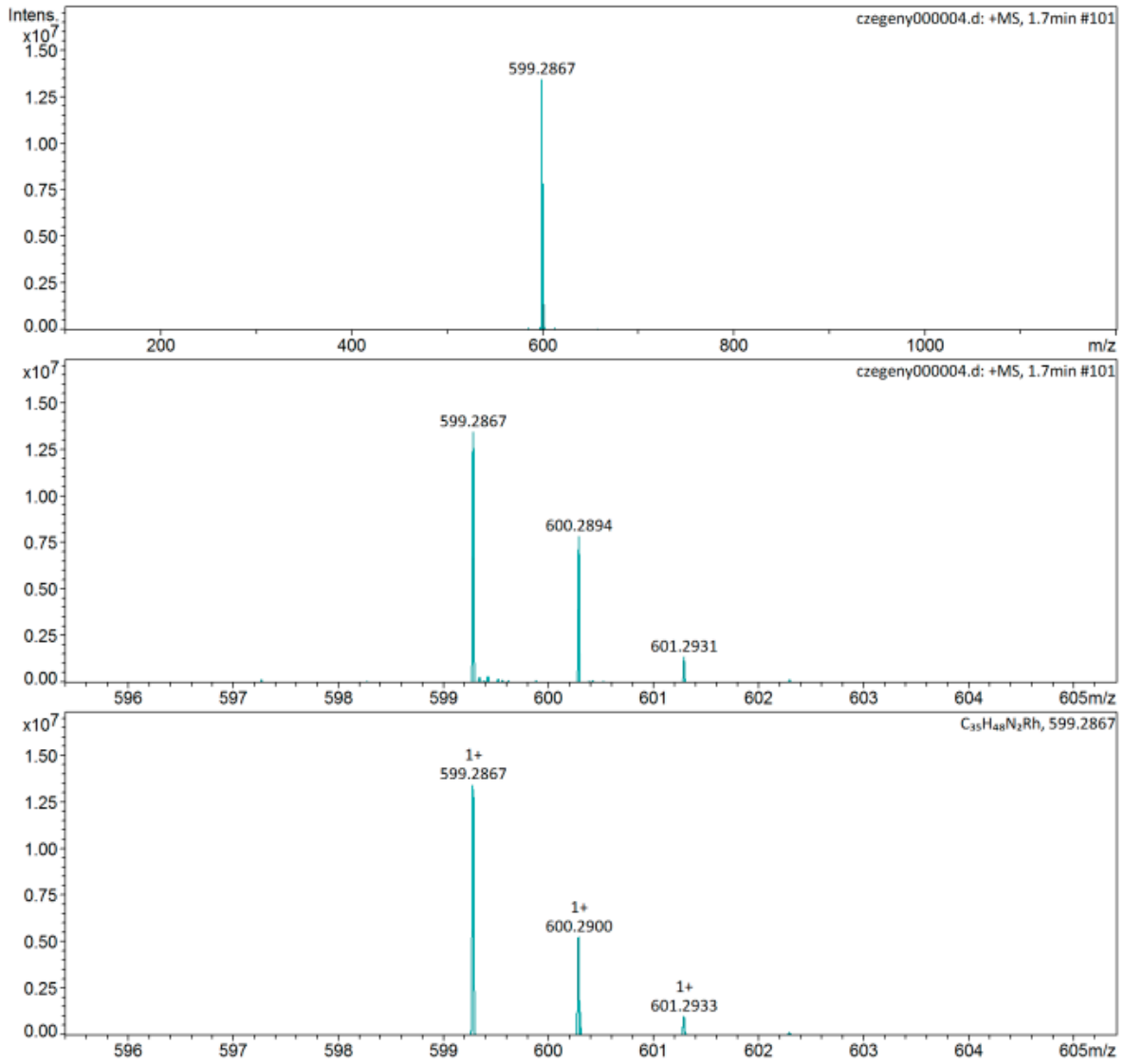

Figure S20. MS(ESI), positive mode, in MeOH, *m/z* for **3**, $[M]^+$ ($C_{35}H_{48}N_2Rh$), Calculated: 599.2867, Found: 599.2867.

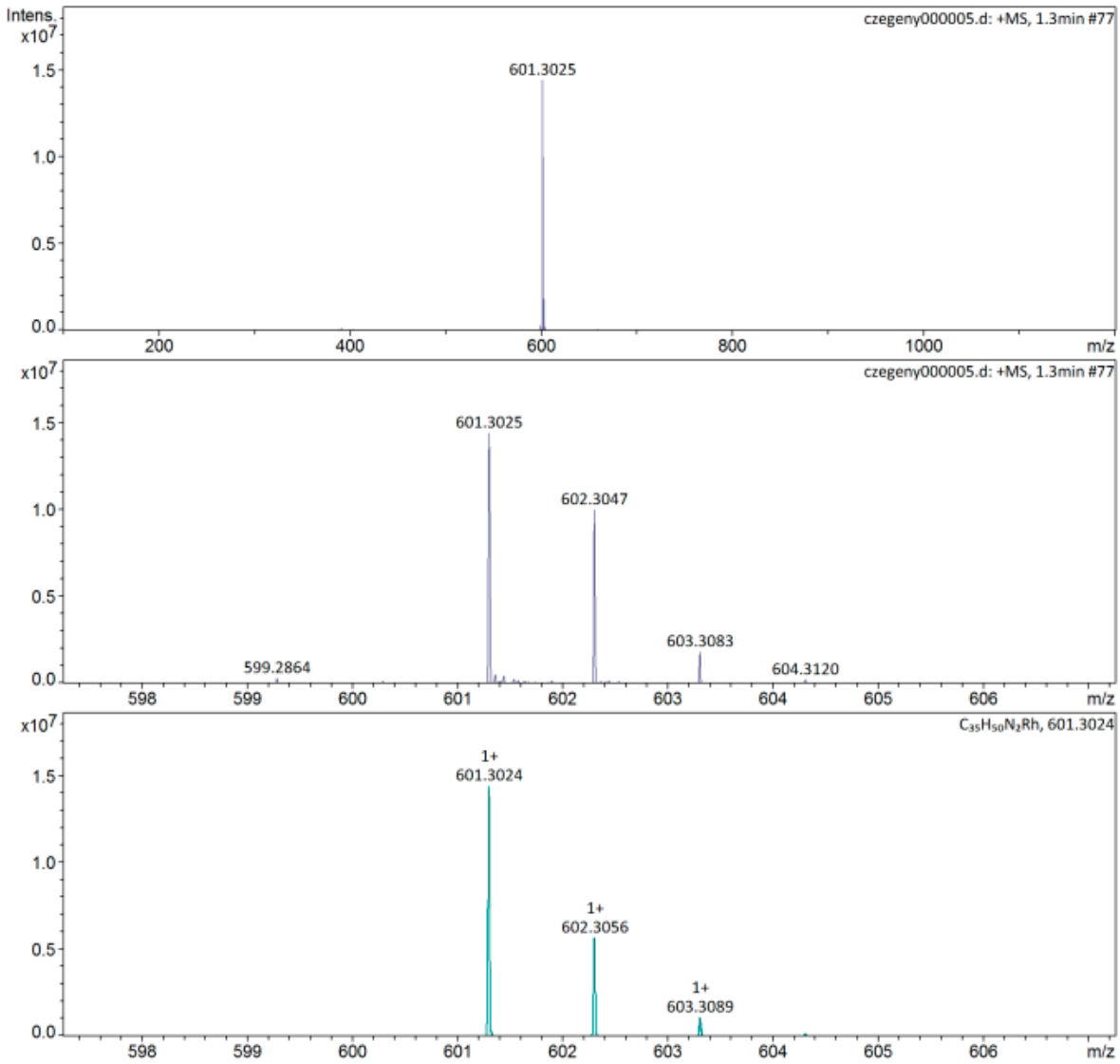

Figure S21. MS(ESI), positive mode, in MeOH, *m/z* for **4**, $[M]^+$ ($C_{35}H_{50}N_2Rh$), Calculated: 601.3024, Found: 601.3025.

Experimental details for molecular structure determinations of Rh(I)-complexes by SCXRD

X-ray diffraction data were collected by a Bruker-D8 Venture diffractometer equipped with a Photon II Charge-integrating Pixel Array detector and INCOATEC IμS 3.0 dual (Cu or Mo) sealed tube microsources. Mo Kα (λ = 0.7107 Å) radiation was used for [RhCl(cod)(IPr)]_benzene_**3**; Complexes of [RhCl(cod)(SIPr)]_**4** and [RhCl(cod)(SIPr)]_benzene_**4** were radiated with Cu Kα (λ = 1.54178Å) Diffraction data collection and integration of the frames were performed by APEX3 packages [1]. Using the Olex^2 [2]. the structures were solved with the SIR-97 and SIR-2014 [3] and the SHELXT [4] structure solution programs and refined by full-matrix least-squares method of F^2. Non-hydrogen atoms were refined with anisotropic thermal parameters using the SHELXL package [5] and hydrogen atoms were placed into their geometric positions. The solid state structure of [RhCl(cod)(IPr)]_benzene_**3** and [RhCl(cod)(SIPr)]_benzene_**4** have several unsolved disorder parts; lattice benzene as solvent molecules and very dynamic side-chains (i-propyl groups) and the coordinated 1.5-cyclooctadiene rings. RIGU restraints were not used. We tried to get some new better quality crystals; but collected data were the same. The publication materials (figures) were prepared by the PublCIF4 [6] and the Mercury [7] programs.

Table S2. Experimental conditions of X-ray diffraction measurements of Rh(I)-complexes

	[RhCl(cod)(SIPr)] **4**	[RhCl(cod)(IPr)] benzene **3**	[RhCl(cod)(SIPr)] benzene **4**
Chemical formula	$C_{70}H_{100}Cl_2N_4Rh_2$	$C_{188}H_{240}Cl_4N_8Rh_4$	$C_{188}H_{248}Cl_4N_8Rh_4$
FW (g mol^{-1})	1274.25	3165.31	3173.37
T (K)	295(2)	150(2)	150(2)
λ (Å)	1.54178	0.71073	1.54178
Crystalsize (mm)	0.24×0.15×0.11	0.210×0.054×0.024	0.360×0.190×0.007
Crystal habit. colour	block. yellow	block. yellow	block. yellow
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/_n$ (no.14)	*CC* (no. 9)	*CC* (no. 9)
a (Å)	16.7559(3)	73.009(3)	72.862(3)
b (Å)	10.5333(2)	11.6924(4)	11.6662(4)
c (Å)	38.6218(7)	19.8553(7)	19.8192(7)
α (°)	90	90	90
β (°)	102.53	96.876(2)	96.4800(10)
γ (°)	90	90	90
V (Å^3)	6654.2(2)	16827.5(10)	16739.2(10)
Z	4	4	4
ρ_{calc} (g/cm^3)	1.272	1.249	1.259
μ (mm^{-1})	5.057	0.53	4.125
Θ range	2.70-74.32	2.70-26.49	2.44-70.17
Index range	-20 ≤ h ≤ 20 -12 ≤ k ≤ 12 -47 ≤ l ≤ 47	-91 ≤ h ≤ 91 -14 ≤ k ≤ 14 -24 ≤ l ≤ 24	-88 ≤ h ≤ 80 -13 ≤ k ≤ 14 -24 ≤ l ≤ 24
Reflns collected	50613	126215	105384
Independent reflns	7941 [R_{int}=0.086]	33965 [R_{int}=0.0371]	29836 [R_{int}=0.0371]
Data / restraints / parameters	7971/0/719	33965/2/1870	29193/2/1860
Goodness-offiton**F**^{2}	1.024	1.041	1.070
R_1 [I>2σ(I)]	0.0419	0.036	0.0510
wR_2 [all data]	0.1016	0.064	0.1314
CCDC	1972109	1972110	1972111

Table S3. Unit cell data of [RhCl(cod)(IPr)] [8] and [IrCl(cod)(IPr)] [9]

	[RhCl(cod)(IPr)] [8]	[IrCl(cod)(IPr)] [9]
Chemical formula	$C_{70}H_{96}Cl_2N_4Rh_2$	$C_{70}H_{96}Cl_2N_4Ir_2$
Crystal system	monoclinic	monoclinic
Space group	$P2_1/_c$	$P2_1/_n$
a (Å)	16.8738(3)	16.7211(8)
b (Å)	10.5374(3)	10.5462(5)
c (Å)	38.3162(9)	38.526(2)
α (°)	90	90
β (°)	102.1240	102.4810(10)
γ (°)	90	90
V (Å^3)	6660.9(3)	6487.56

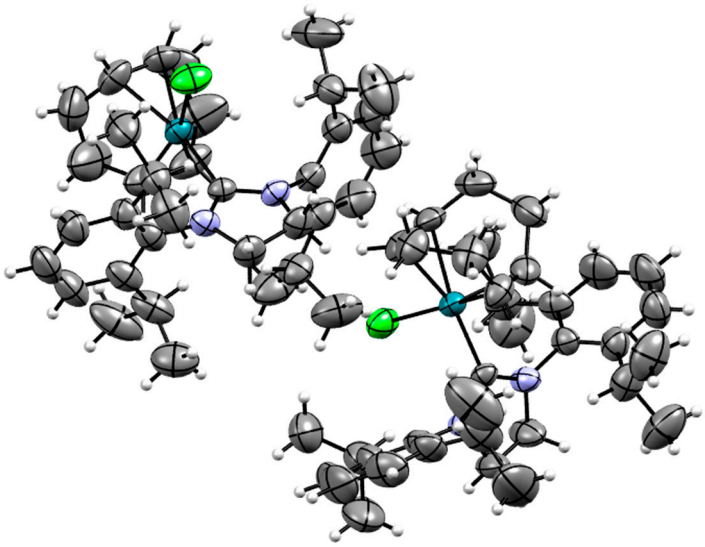

Figure S22. ORTEP view of [RhCl(cod)(SIPr)]_**4** (50% ellipsoid level)

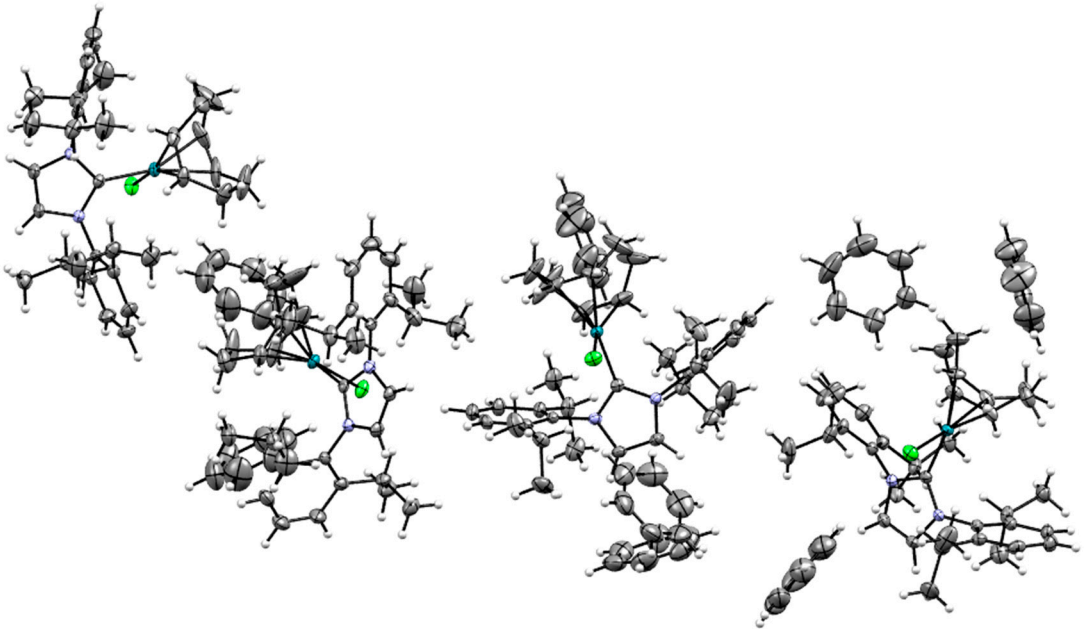

Figure S23. ORTEP view of [RhCl(cod)(IPr)]_benzene_**3** (50% ellipsoid level**)**

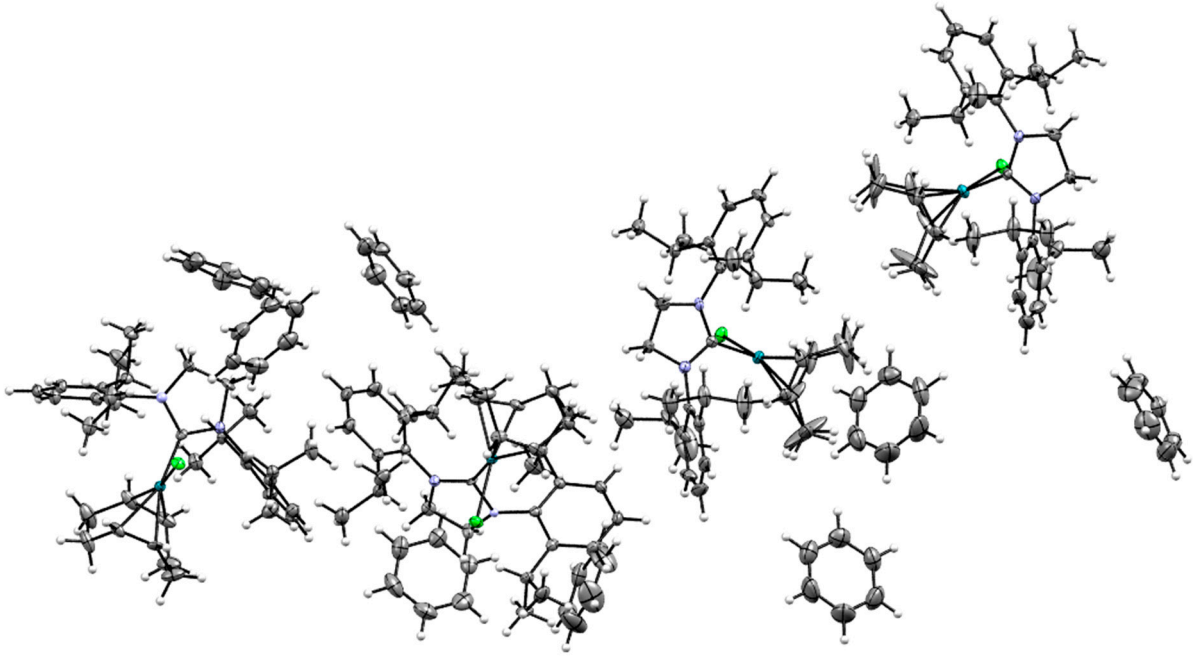

Figure S24. ORTEP view of [RhCl(cod)(SIPr)]_benzene_**4** (50% ellipsoid level)

References

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