Electronic Supporting Information for

Synthesis and Characterization of Rhenium(III) Complexes with $(Ph_2PCH_2CH_2)_2NR$ Diphosphinoamine Ligands

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CONTENTS

SYNTHESIS OF $(PH_2PCH_2CH_2)_2NR$ DIPHOSPHINOAMINE LIGANDS (PNPme, PNPet, PNPpr, PNPbu)

The diphosphinoamine ligands were prepared, in high yield, according to the literature (see main article, ref. 6) by alkylation of the diphenylphosphine lithium salt with the appropriate dichloride amine. The reaction were performed in anhydrous oxolane at −78 °C. The ligands were characterized by elemental analyses and ^{1}H, ^{13}C, ^{31}P NMR (see main article, Physical Measurements). ^{1}H, ^{13}C and ^{31}P NMR spectra of the complexes were acquired at 298 K in $CDCl_3$ on a Bruker AMX 300 instrument, using $SiMe_4$ as internal reference (^{1}H, ^{13}C) and 85% aqueous H_3PO_4 as external reference (^{31}P). Thin-layer chromatography (TLC) analyses were carried out on SiO_2 F254S plates (Merck). Column chromatography purifications were accomplished on a SiO_2 column (5 x 2.5 cm; SiO_2 grade 9385, pore size 60 Å; 230 – 400 mesh particles).

All the operations were carried out under a dinitrogen atmosphere.

Bis[(2-diphenylphosphino)ethyl]methylamine (PNPme).

PNPme was synthetized following the previously reported procedure.[6] Briefly, to a three-neck flask containing diphenylphosphine (3 g, 16.11 mmol) dissolved in anhydrous oxolane (50 mL), n-butyllithium 2.5 M in hexane (6.5 mL, 16.11 mmol) was slowly added by a syringe through a rubber septum. The red solution was cooled at −78 °C. After that, in a dropping funnel containing bis(2-chloroethyl)methylamine hydrochloride (1.55 g, 8.055 mmol) dissolved in anhydrous oxolane (30 mL) was added, drop-by-drop by a syringe, and under shaking, n-butyllithium 2.5 M in hexane (3.75 mL, 8.055 mmol), to neutralize the chloridric acid. The obtained pale-yellow solution was quickly poured into the flask. The gold-yellow mixture was then allowed to reach room temperature overnight. The resulting pale-yellow solution was cooled in an ice bath and quenched by slowly adding water (50 mL). The mixture was transferred in a separating funnel and further water (40 mL) was added. After separation, the upper organic layer was collected and the aqueous layer was extracted again with diethyl ether (3 x 40 mL). The organic phases were gathered and dried with anhydrous magnesium sulfate and, after filtration, the solvent was removed by rotary evaporator giving an oil. Other solvent traces were removed under vacuum, and then the residue was treated with methanol (5 mL) and vigorously stirred until a white solid formed. The crude product was dissolved in chloroform, charged onto a silica column preconditioned with chloroform and eluted with a mixture of chloroform and diethyl ether (1:1). The pure product was collected in the first fraction, which after concentration and treatment with methanol, gave a white solid. Yield 68%. Elem. Anal. Found: C, 76.4%; H, 6.6%; N, 3.4%. Calc. for $C_{29}H_{31}NP_2$: C, 76.5%; H, 6.9%; N, 3.1%. ^{31}P NMR (121.44 MHz, $CDCl_3$): δ −19.1 (s). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.2 – 7.4 (20H, H aromatic), 2.93 (m, 4H $NCH_2CH_2PPh_2$), 2.42 (m, 4H $NCH_2CH_2PPh_2$), 2.68

(s, 3H NC*H*$_3$). ^{13}C NMR (75.43 MHz, $CDCl_3$): δ 132.7 (d, *C* aromatic, $^1J_{CP}$ = 13 Hz), 130.5 (d, *o*-*C*H aromatic, $^2J_{CP}$ = 19 Hz), 129.5 (s, *p*-*C*H aromatic), 128.9 (d, *m*-*C*H aromatic, $^3J_{CP}$ = 7 Hz), 52.4 (d, N*C*H$_2$CH$_2$PPh$_2$, $^2J_{CP}$ = 23 Hz), 39.6 (s, N*C*H$_3$), 22.1 (d, NCH$_2$*C*H$_2$PPh$_2$, $^1J_{CP}$ = 12 Hz).

Bis[(2-diphenylphosphino)ethyl]ethylamine (PNPet).

Bis(2-hydroxyethyl)ethylamine (HOCH$_2$CH$_2$)$_2$NCH$_2$CH$_3$. To a solution of bis(2-hydroxyethyl)amine (28.27 g, 269 mmol) in ethanol (60 mL) were added potassium carbonate (37.2 g, 269 mmol) and ethylbromide (30.1 mL, 269 mmol). The mixture was refluxed under stirring for 3 days. The solid was filtered off and the filtrate reduced to half the volume using a rotary evaporator and stored overnight at 4 °C. The further white solid precipitate was filtered off quickly and the ethanol was eliminated by rotary evaporator. The obtained residue was distilled under vacuum. A first fraction containing unreacted reagents was collected in the range 60 – 65 °C (0.1 mmHg), while the expected product was collected at 80 – 85 °C (0.1 mmHg). Yield 79.4%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.57 (t, 4H, NCH$_2$C*H*$_2$OH), 2.57 (t, 4H, NC*H*$_2$CH$_2$OH), 2.50 (q, 2H, NC*H*$_2$CH$_3$), 0.91 (t, 3H, NCH$_2$C*H*$_3$).

Bis(2-chloroethyl)ethylamine (ClCH$_2$CH$_2$)$_2$NCH$_2$CH$_3$. (HOCH$_2$CH$_2$)$_2$NCH$_2$CH$_3$ (14.2 g, 107 mmol) was placed in a two-neck flask and cooled in an ice bath. Then, thionyl chloride (31 mL, 428 mmol) was added drop-by-drop within 20 minutes. The mixture was refluxed for 2 hours, then cooled again in an ice bath. Methanol (65 mL) was added to favor the precipitation of the white chlorohydrate salt of (ClCH$_2$CH$_2$)$_2$NCH$_2$CH$_3$. The filtrate, after further concentration by rotary evaporator, eventually gave another amount of chlorohydrate salt. Finally, this solid was dissolved in water (100 mL) and the pH was adjusted to 9 with aqueous sodium hydroxide (2 M). The alkaline solution was transferred in a separating funnel and the desired product was extracted with diethyl ether (3x100 mL). The organic phases were collected and dried with anhydrous magnesium sulfate, then the diethyl ether was removed by rotary evaporator. The crude compound was distilled under vacuum (64 – 67 °C, 4 mmHg). Yield 52%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.50 (t, 4H NCH$_2$C*H*$_2$Cl), 2.86 (t, 4H, NC*H*$_2$CH$_2$Cl), 2.65 (q, 2H, NC*H*$_2$CH$_3$), 1.05 (t, 3H, NCH$_2$C*H*$_3$).

(Ph$_2$PCH$_2$CH$_2$)$_2$NCH$_2$CH$_3$ (PNPet). The preparation procedure was almost identical to that reported for the preparation of PNPme, however in this case it was unnecessary to neutralize the dichloroamine since it was available in the neutral form. Yield 85%. Elem. Anal. Found: C, 76.6%; H, 7.0%; N, 3.1%. Calc. for $C_{30}H_{33}NP_2$: C, 76.7%; H, 7.1%; N, 3.0%. ^{31}P NMR (121.44 MHz, $CDCl_3$): δ −18.9 (s). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40 – 7.30 (m, 20H, H aromatic), 2.53 (m, 6H, NC*H*$_2$CH$_3$ and NC*H*$_2$CH$_2$PPh$_2$), 2.10 (m, 4H, NCH$_2$C*H*$_2$PPh$_2$), 0.89 (t, 3H, NCH$_2$C*H*$_3$). ^{13}C NMR (75.43 MHz, $CDCl_3$): δ 138.5 (d, *C* aromatic, $^1J_{CP}$ = 13 Hz), 132.7 (d, *o*-*C*H aromatic, $^2J_{CP}$ = 19 Hz), 128.6 (s, *p*-*C*H aromatic), 128.4 (d, *m*-*C*H aromatic, $^3J_{CP}$ = 7

Hz), 49.1 (d, N*C*$H_2CH_2PPh_2$, $^2J_{CP}$ = 23 Hz), 47.0 (s, N*C*H_2CH_3), 25.2 (d, NCH_2*C*H_2PPh_2, $^1J_{CP}$ = 12 Hz), 11.9 (s, NCH_2*C*H_3).

Bis[(2-diphenylphosphino)ethyl]propylamine (PNPpr).

The compound was prepared by a procedure identical to that reported for PNPet.

Bis(2-hydroxypropeyl)ethylamine $(HOCH_2CH_2)_2NCH_2CH_2CH_3$. To maximize the yield, a 20% excess of propyl bromide was used. Boiling point: 105 – 107 °C, $5x10^{-2}$ mmHg. Yield 88%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.61 (t, 4H, NCH_2CH_2OH), 2.65 (t, 4H, NCH_2CH_2OH), 2.49 (t, 2H, $NCH_2CH_2CH_3$), 1.47 (m, 2H, $NCH_2CH_2CH_3$), 0.89 (t, 3H, $NCH_2CH_2CH_3$).

Bis(2-chloropropyl)ethylamine $(ClCH_2CH_2)_2NCH_2CH_2CH_3$. The pure final product was recovered directly after diethyl ether removal, and no further purification was required. Yield 49%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.50 (t, 4H, NCH_2CH_2Cl), 2.86 (t, 4H, NCH_2CH_2Cl), 2.52 (t, 2H, $NCH_2CH_2CH_3$), 1.47 (m, 2H, $NCH_2CH_2CH_3$), 0.89 (t, 3H, $NCH_2CH_2CH_3$).

$(Ph_2PCH_2CH_2)_2NCH_2CH_2CH_3$ (PNPpr). Yield 82%. Elem. Anal. Found: C, 77.1%; H, 7.4%; N, 3.0%. Calc. for $C_{31}H_{35}NP_2$: C, 77.0%; H, 7.3%; N, 2.9%. ^{31}P NMR (121.44 MHz, $CDCl_3$): δ −18.9 (s). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42 – 7.30 (m, 20H, H aromatic), 2.55 (m, 4H, $NCH_2CH_2PPh_2$), 2.38 (t, 2H, $NCH_2CH_2CH_3$), 2.11 (m, 4H, $NCH_2CH_2PPh_2$), 1.28 (m, 2H, $NCH_2CH_2CH_3$), 0.82 (t, 3H, $NCH_2CH_2CH_3$). ^{13}C NMR (75.43 MHz, $CDCl_3$): δ 138 .5 (d, *C* aromatic, $^1J_{CP}$ = 13 Hz), 132.7 (d, *o-C*H aromatic, $^2J_{CP}$ = 18 Hz), 128.5 (s, *p-C*H aromatic), 128.4 (d, *m-C*H aromatic, $^3J_{CP}$ = 7 Hz); 55.5 (s, $NCH_2CH_2CH_3$); 49.6 (d, $NCH_2CH_2PPh_2$, $^2J_{CP}$ = 23 Hz), 25.18 (d, $NCH_2CH_2PPh_2$, $^1J_{CP}$ = 12 Hz), 20.18 (s, $NCH_2CH_2CH_3$), 11.9 (s, $NCH_2CH_2CH_3$).

Bis[(2-diphenylphosphino)ethyl]n-butylamine (PNPbu).

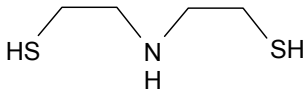
The compound was prepared by a procedure identical to that reported for PNPet.

Bis(2-hydroxybuthyl)ethylamine $(HOCH_2CH_2)_2NCH_2CH_2CH_2CH_3$. No purification was required. Yield 91%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.61 (t, 4H, NCH_2CH_2OH), 2.65 (t, 4H, NCH_2CH_2OH), 2.53 (t, 2H, $NCH_2CH_2CH_2CH_3$), 1.45 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.32 (m, 2H, $NCH_2CH_2CH_2CH_3$), 0.92 (t, 3H, $NCH_2CH_2CH_2CH_3$).

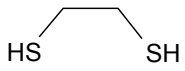
Bis(2-chlorobuthyl)ethylamine $(ClCH_2CH_2)_2NCH_2CH_2CH_2CH_3$. The pure crude compound was purified by distillation under vacuum (78 – 80 °C, 3 mmHg). Yield 54%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.50 (t, 4H, NCH_2CH_2Cl), 2.86 (t, 4H, NCH_2CH_2Cl), 2.55 (t, 2H, $NCH_2CH_2CH_2CH_3$), 1.42 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.33 (m, 2H, $NCH_2CH_2CH_2CH_3$); 0.91 (t, 3H, $NCH_2CH_2CH_2CH_3$).

$(Ph_2PCH_2CH_2)_2NCH_2CH_2CH_2CH_3$ (PNPbu). Yield 80%. Elem. Anal. Found: C, 77.1%; H, 7.35%; N, 2.75%. Calc. for $C_{32}H_{37}NP_2$: C, 77.2%; H, 7.5%; N, 2.8%. ^{31}P NMR (121.44 MHz, $CDCl_3$): δ −18.9 (s). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43 – 7.04 (m, 20H, H aromatic), 2.61 – 2.54 (4H, m, NCH_2CH_2P), 2.39 (t, 2H,

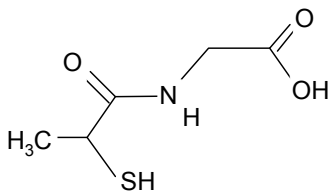
NC*H*$_2$CH$_2$CH$_2$CH$_3$), 2.13 – 2.08 (m, 4H, NCH$_2$C*H*$_2$PPh$_2$), 1.25 – 1.19 (m, 4H, NCH$_2$C*H*$_2$C*H*$_2$CH$_3$), 0.85 (t, 3H, NCH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C NMR (75.43 MHz, CDCl$_3$): δ 138.6 (d, *C* aromatic, $^1J_{CP}$ = 13 Hz), 132.7 (d, *o*-*C*H aromatic, $^2J_{CP}$ = 19 Hz), 128.5 (s, *p*-*C*H aromatic), 128.37 (d, *o*-*C*H aromatic, $^3J_{CP}$ = 8 Hz), 52.25 (s, N*C*H$_2$CH$_2$CH$_2$CH$_3$), 49.5 (d, N*C*H$_2$CH$_2$P, $^2J_{CP}$ = 23 Hz), 29.2 (s, NCH$_2$*C*H$_2$CH$_2$CH$_3$), 25.3 (d, NCH$_2$*C*H$_2$P, $^1J_{CP}$ = 15 Hz), 20.6 (s, NCH$_2$CH$_2$*C*H$_2$CH$_3$), 14.0 (s, NCH$_2$CH$_2$CH$_2$*C*H$_3$).



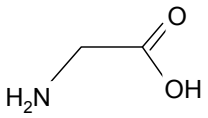
SNS-dimercaptoethanolamine



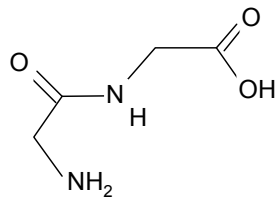
SS-1,2-ethanedithiol



SNO-tiopronin



NO-gly



NNO-gly-gly

Figure S1. Polydentate ligands used in substitution reactions with *fac*-[$ReCl_3$(PNPet)] (**2**) and *mer*-[$ReCl_3$(PNPH)] (**10**).

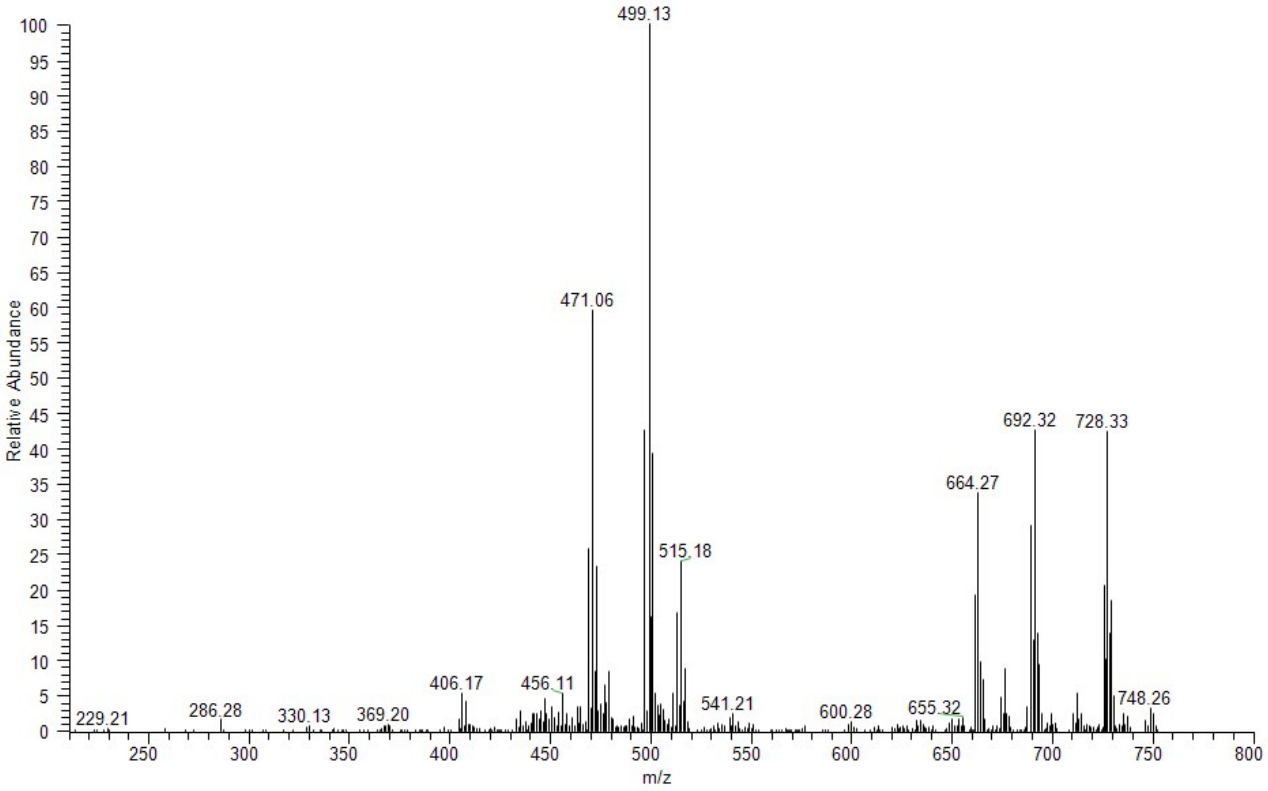


Figure S2. MS/MS spectrum of the ion $[Re^{V}(O)Cl_3(PNPme)+H]^+$ at m/z 764.

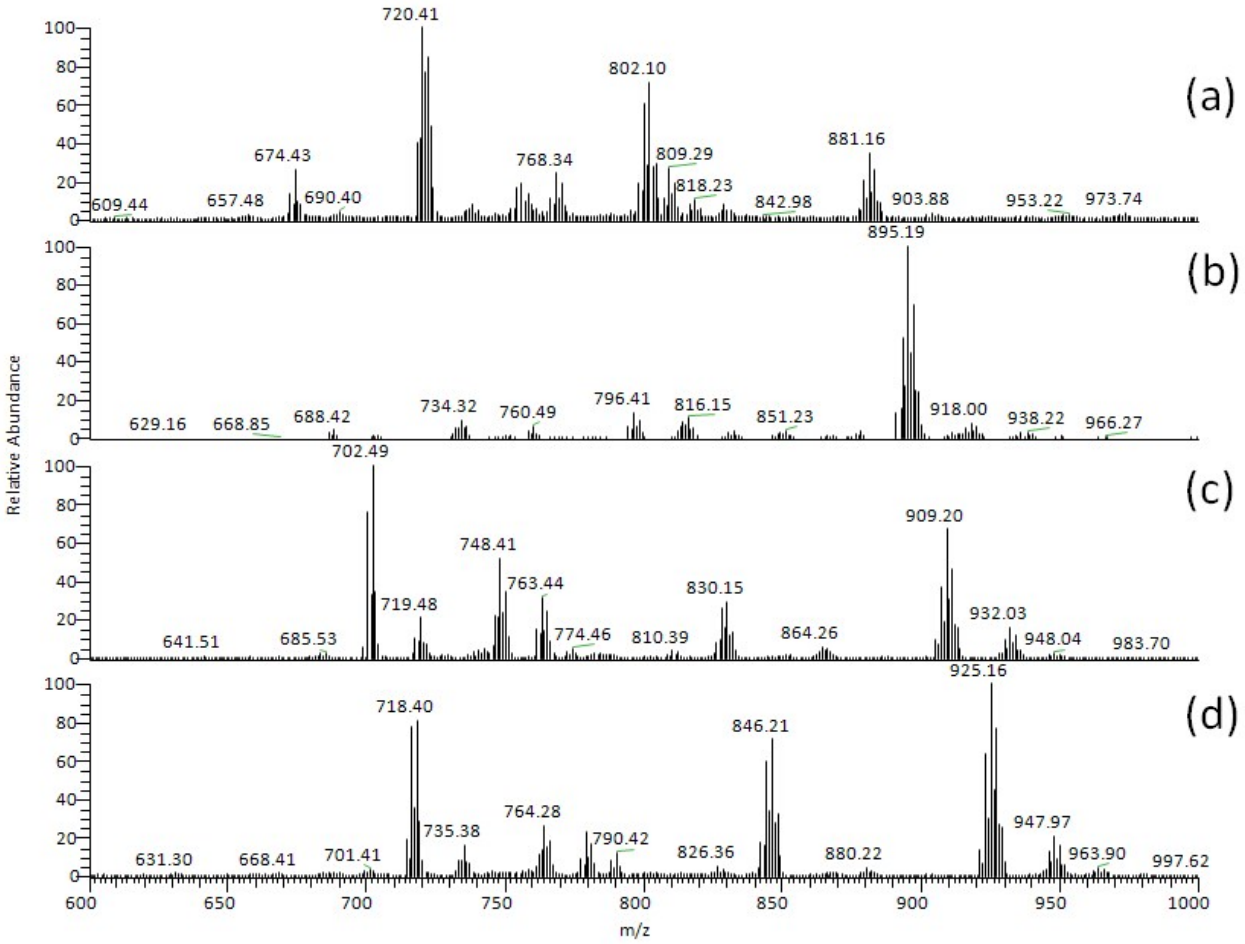


Figure S3. Partial full scan Full ESI(+)-MS spectra (range: 600-1000 m/z) of: (a) [$ReBr_3$(PNPme)] (**11**); (b) [$ReBr_3$(PNPet)] (**3**); (c) [$ReBr_3$(PNPpr)] (**5**) and (d) [$ReBr_3$(PNP2)] (**9**).

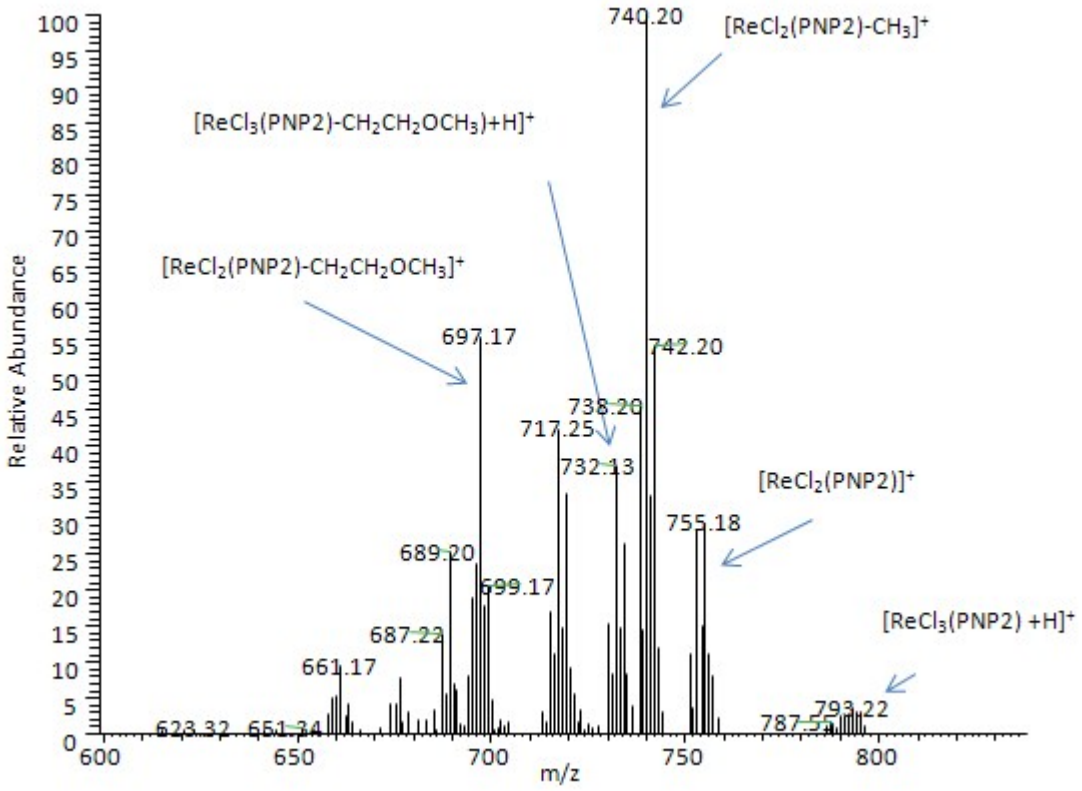


Figure S4. MS/MS spectrum of the $[ReCl_3(PNP2)+H]^+$ ion at m/z 791.

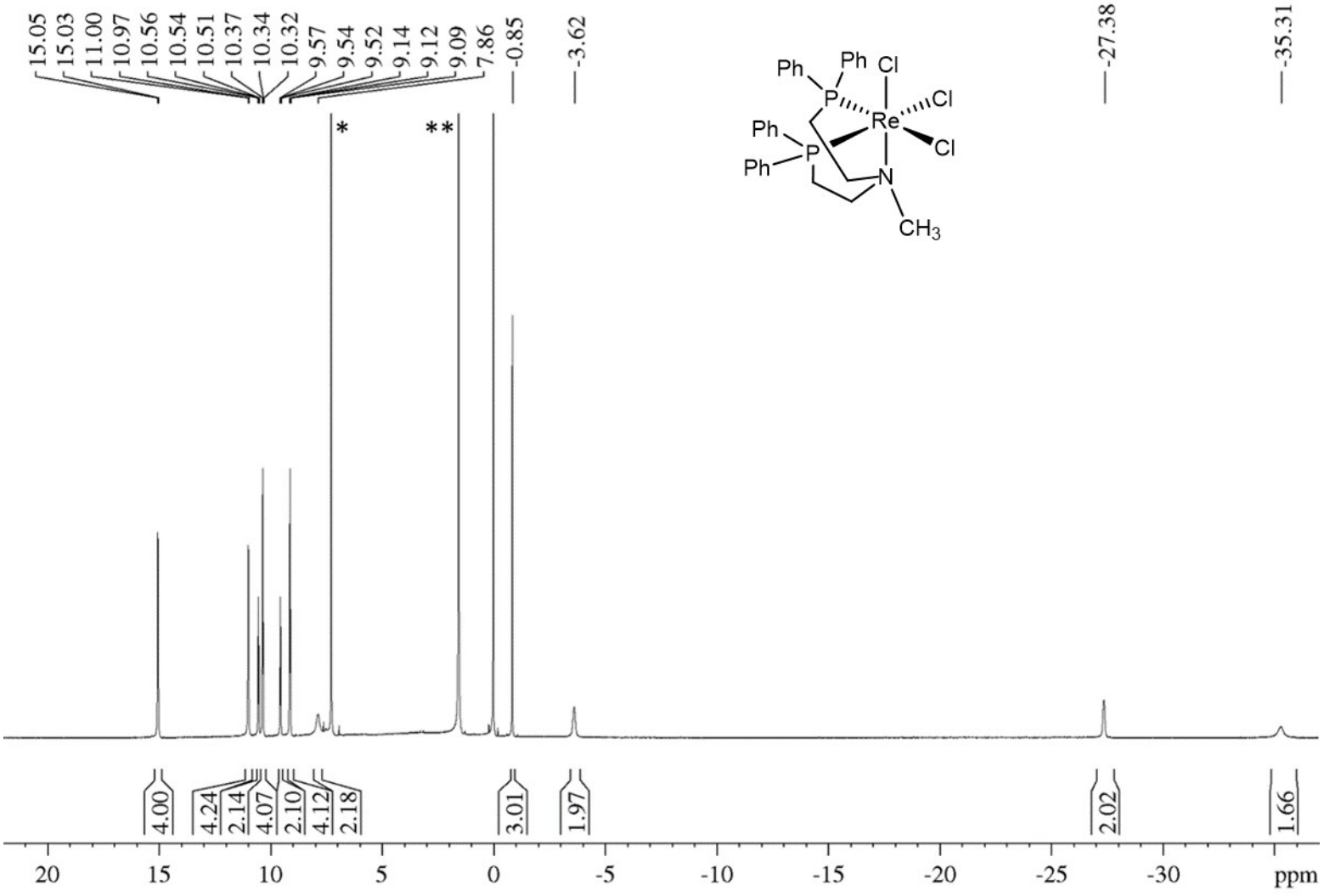


Figure S5. ^{1}H NMR spectrum (300 Mhz, $CDCl_3$, 298 K) of **1**. *$CHCl_3$. **Water.

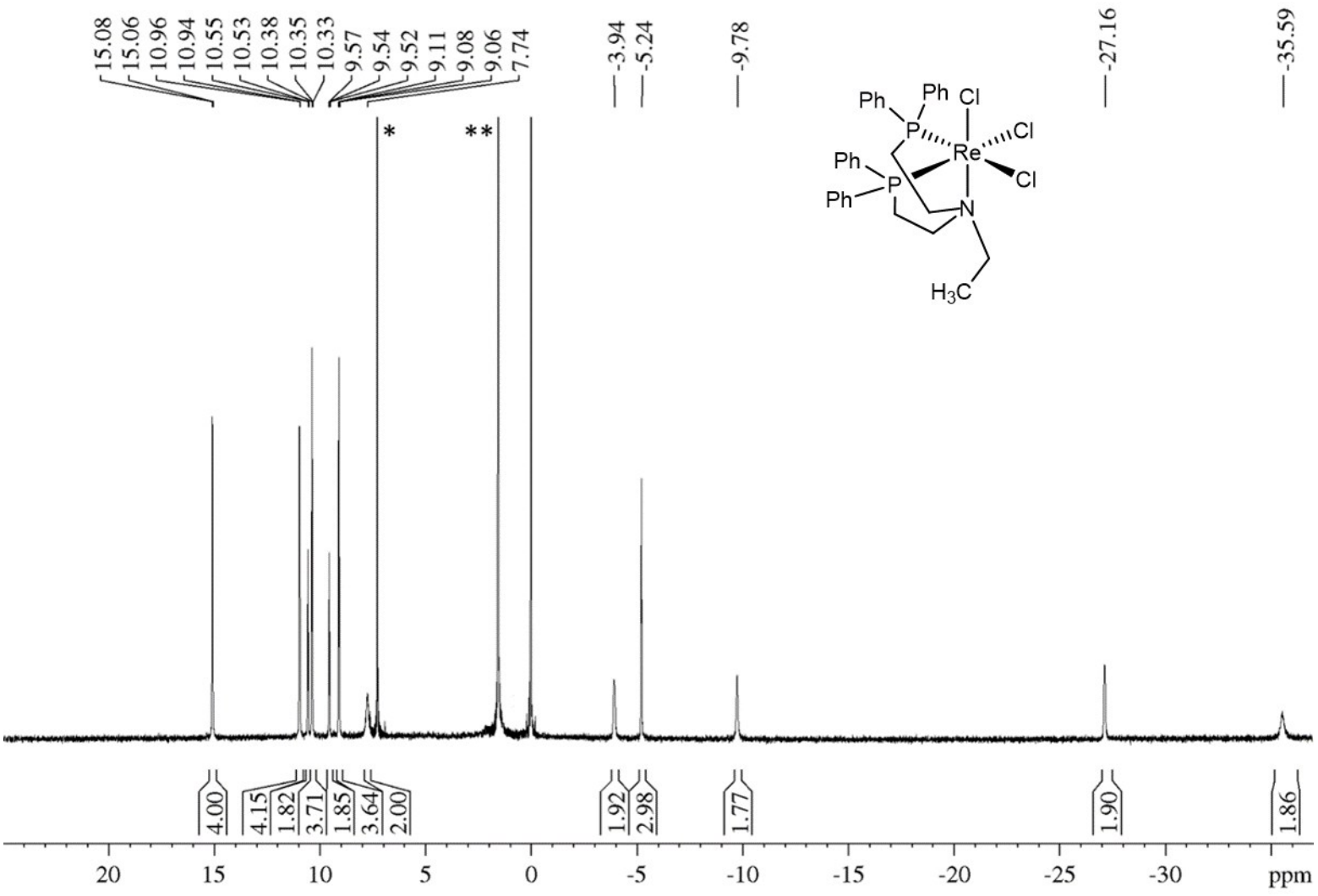


Figure S6. ^{1}H NMR spectrum (300 Mhz, $CDCl_3$, 298 K) of **2**. *$CHCl_3$. **Water.

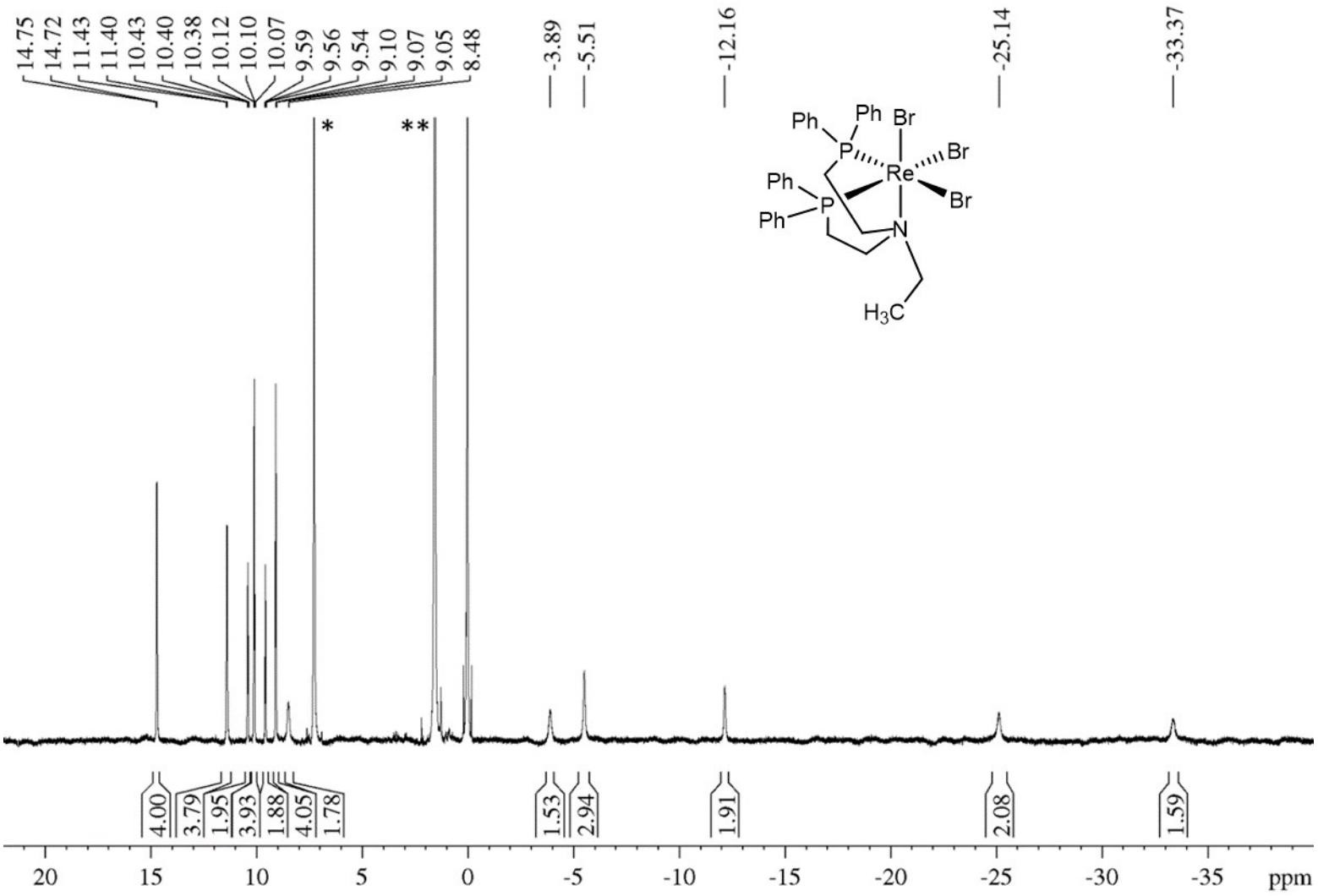


Figure S7. ^{1}H NMR spectrum (300 Mhz, $CDCl_3$, 298 K) of **3**. *$CHCl_3$. **Water.

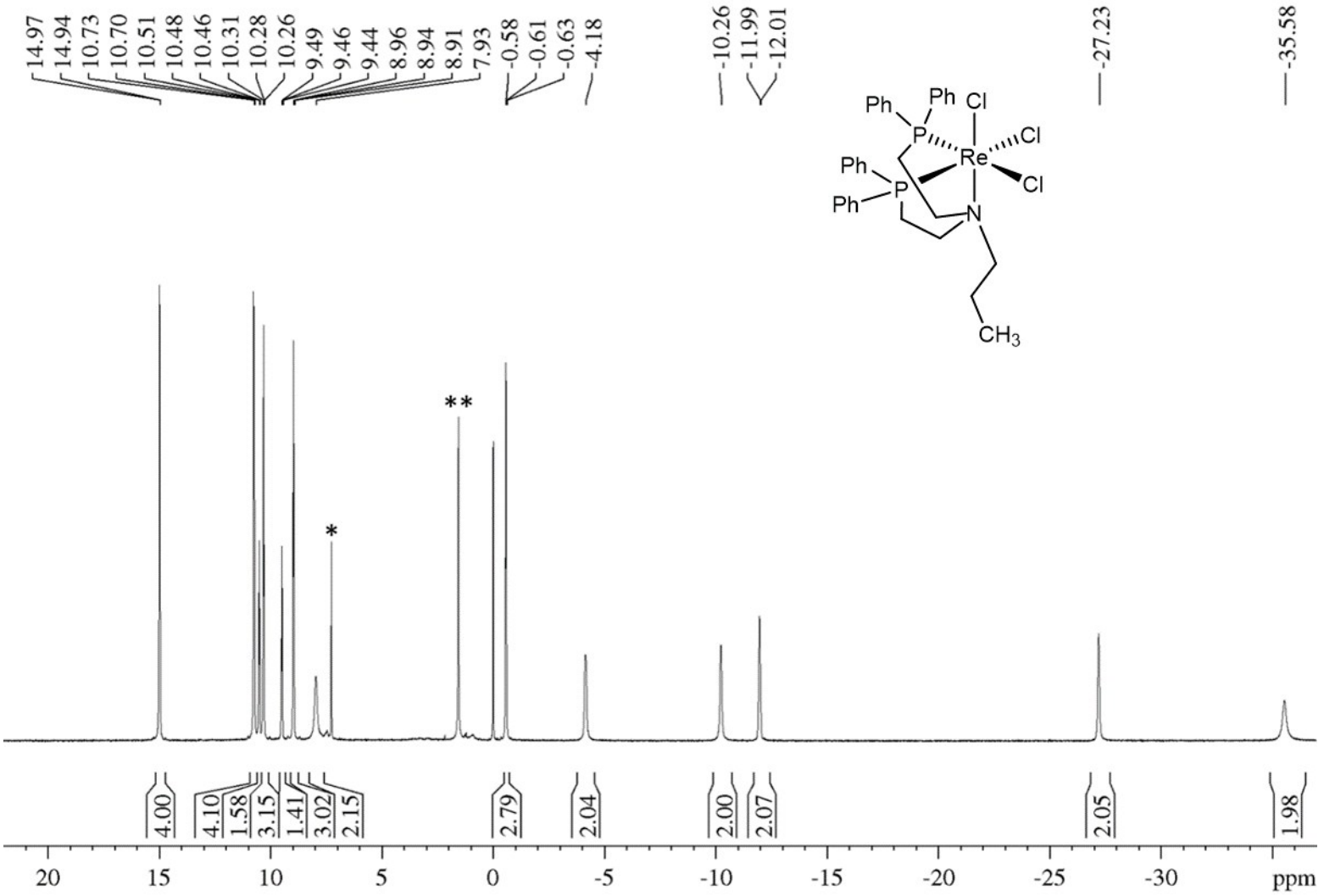


Figure S8. ^{1}H NMR spectrum (300 Mhz, $CDCl_3$, 298 K) of **4**. *$CHCl_3$. **Water.

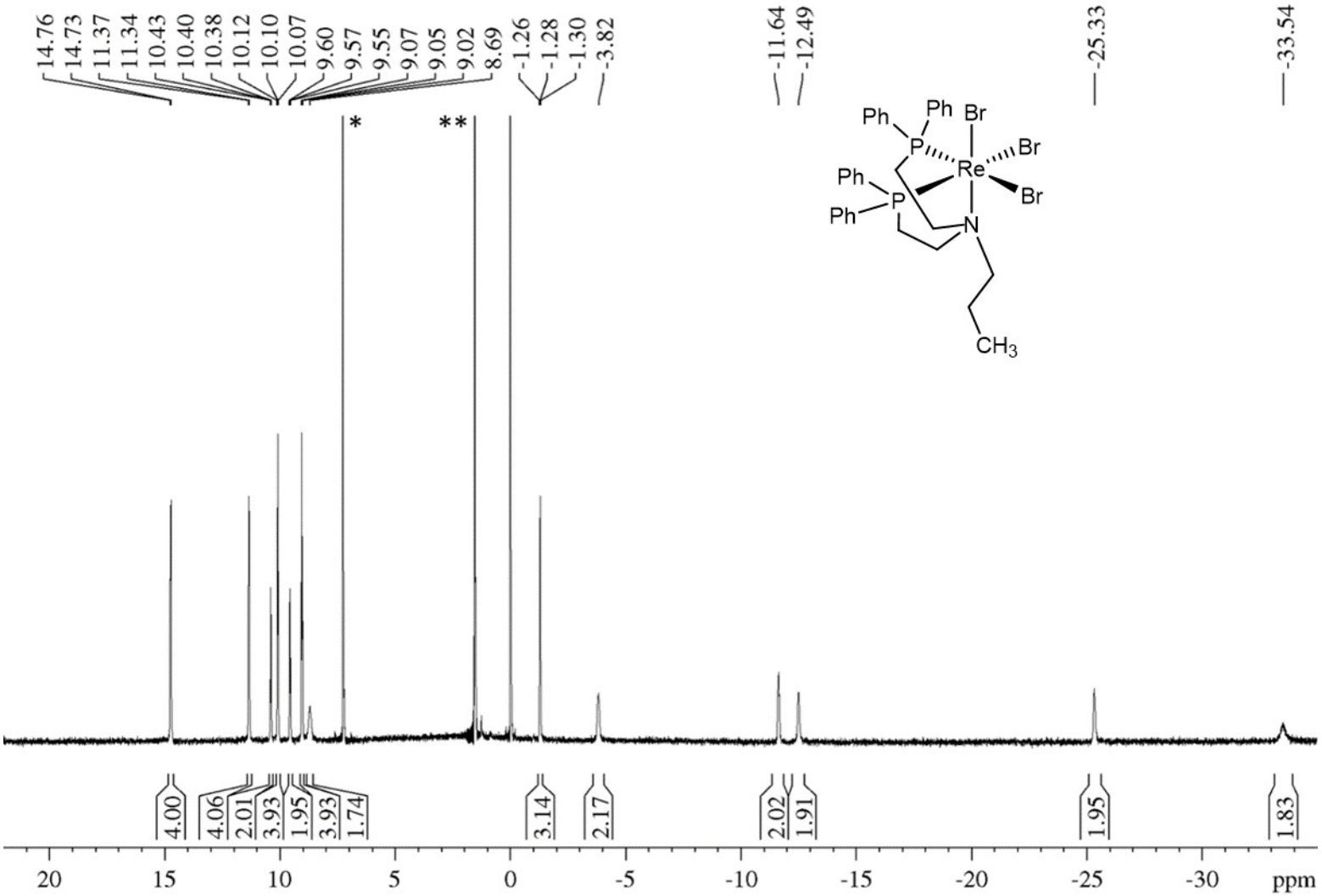


Figure S9. ^{1}H NMR spectrum (300 Mhz, $CDCl_3$, 298 K) of **5**. *$CHCl_3$. **Water.

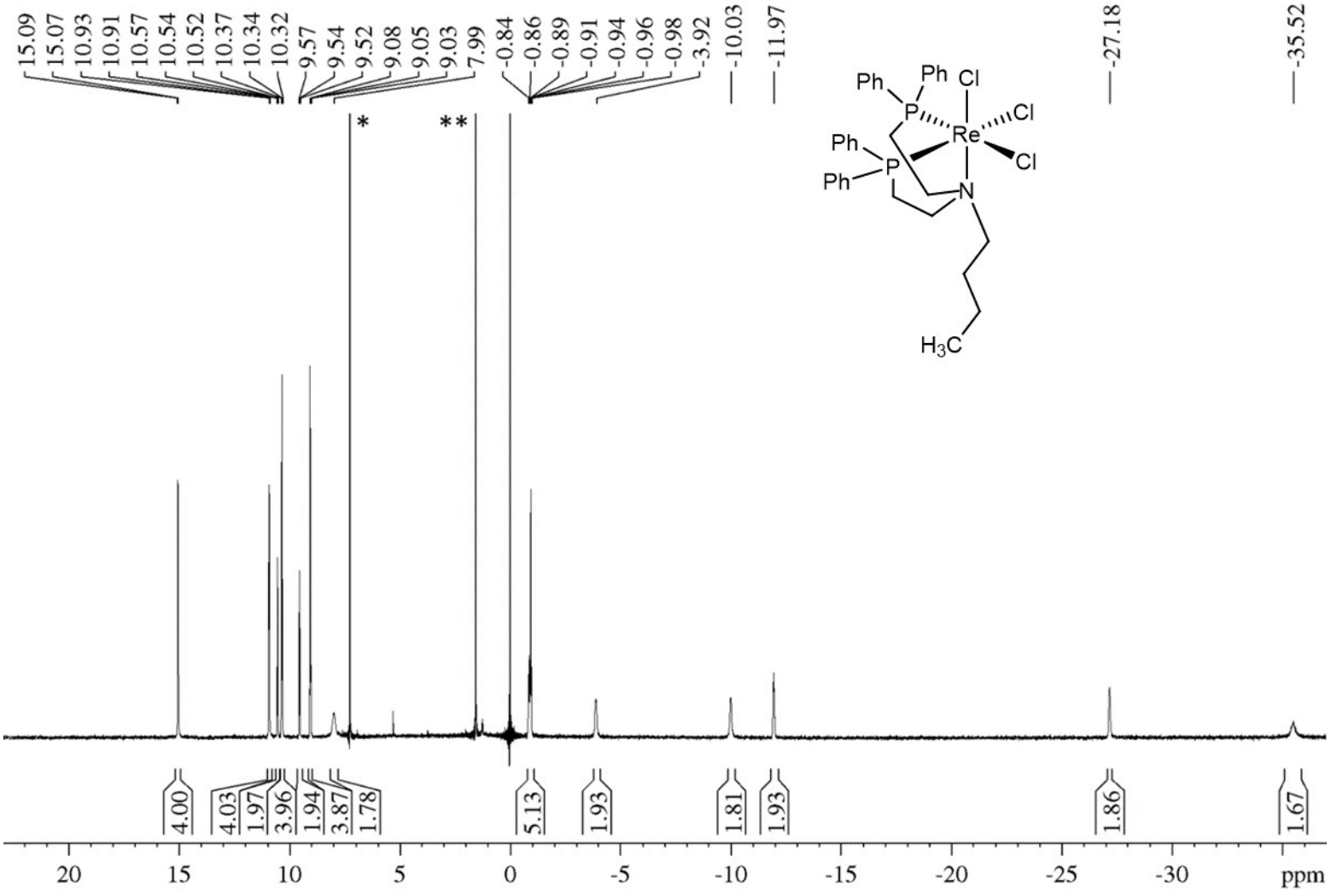


Figure S10. ^{1}H NMR spectrum (300 Mhz, $CDCl_3$, 298 K) of **6**. *$CHCl_3$. **Water.

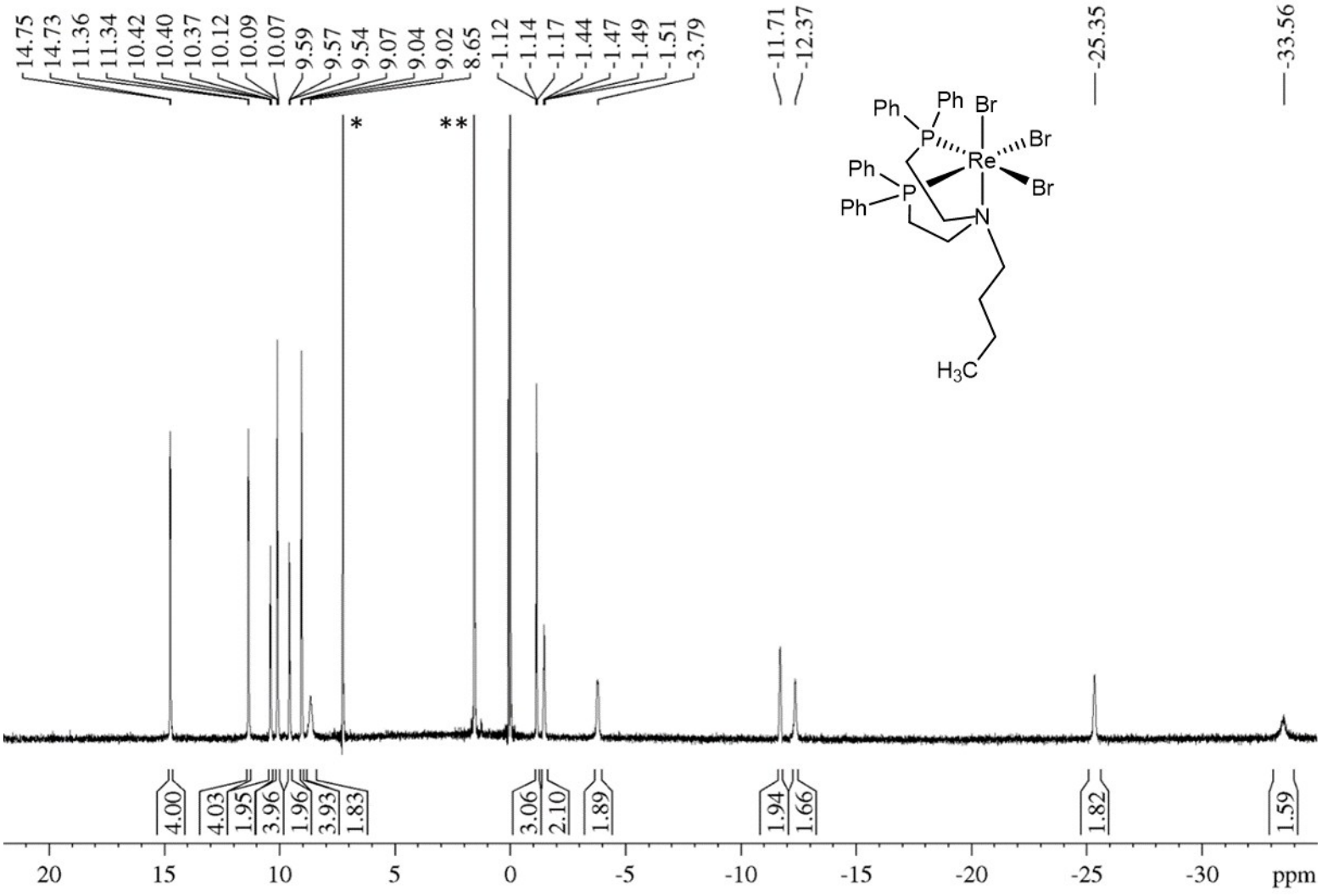


Figure S11. ^{1}H NMR spectrum (300 Mhz, $CDCl_3$, 298 K) of **7**. *$CHCl_3$. **Water.

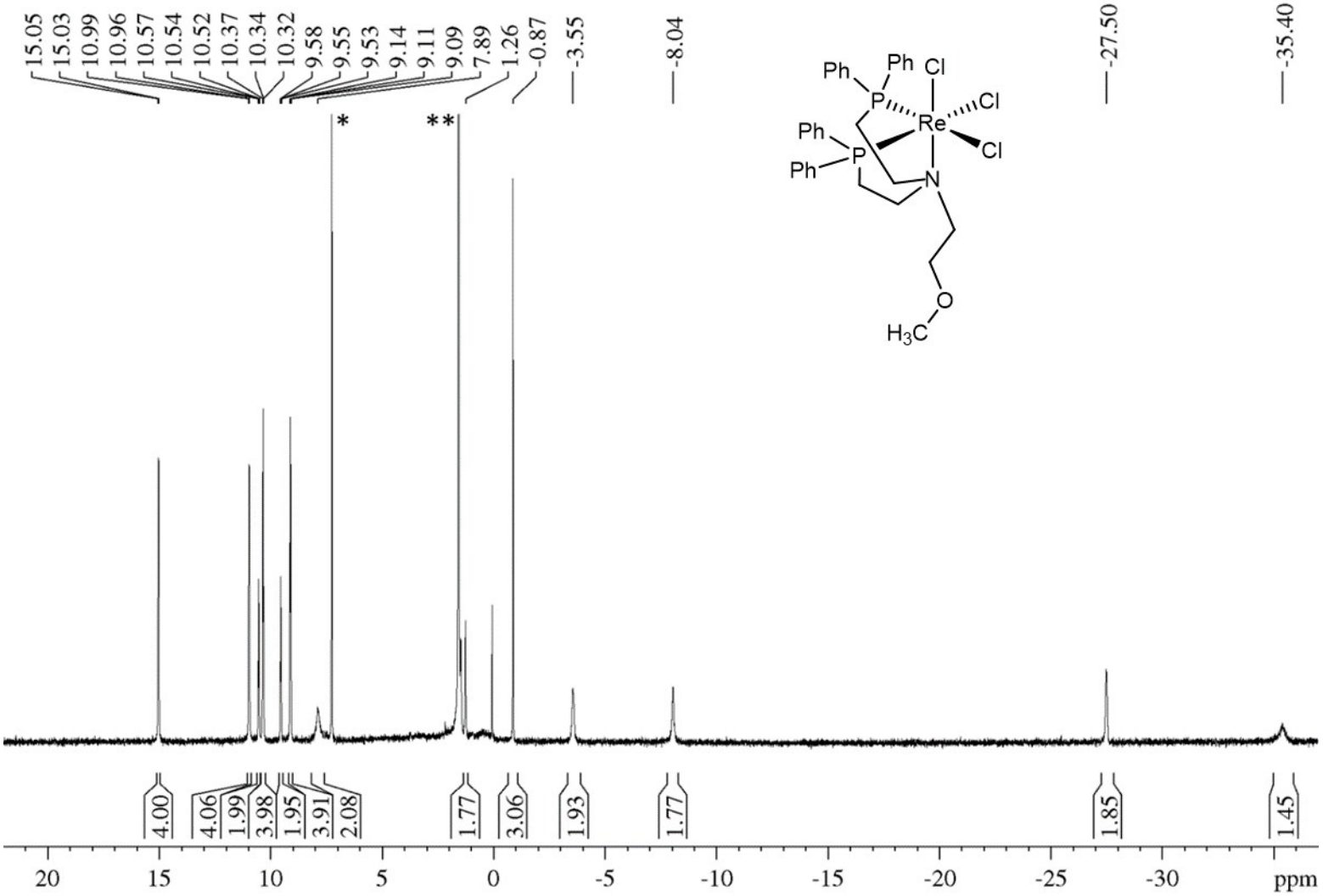


Figure S12. ^{1}H NMR spectrum (300 Mhz, $CDCl_3$, 298 K) of **8**. *$CHCl_3$. **Water.

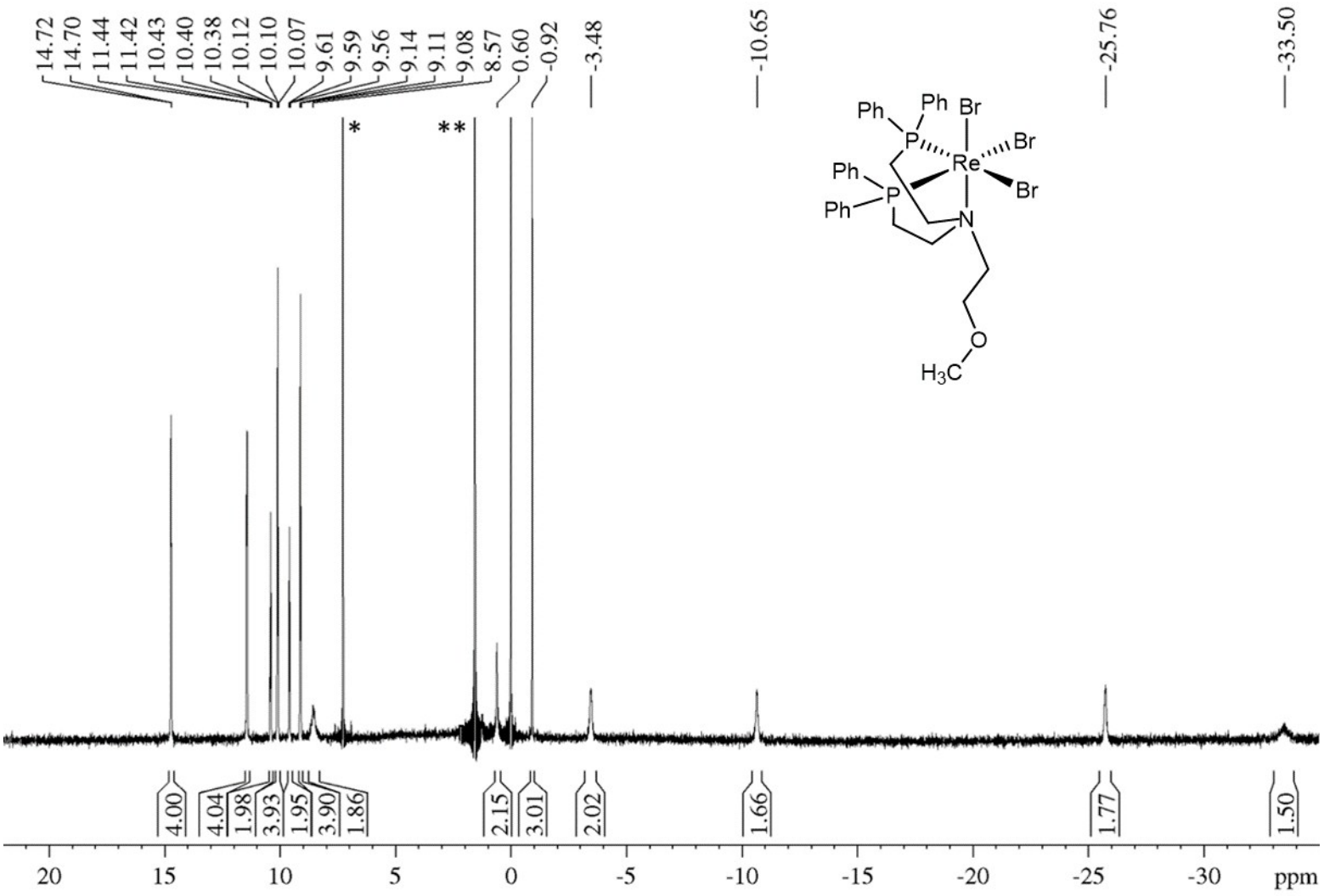


Figure S13. ^{1}H NMR spectrum (300 Mhz, $CDCl_3$, 298 K) of **9**. *$CHCl_3$. **Water.

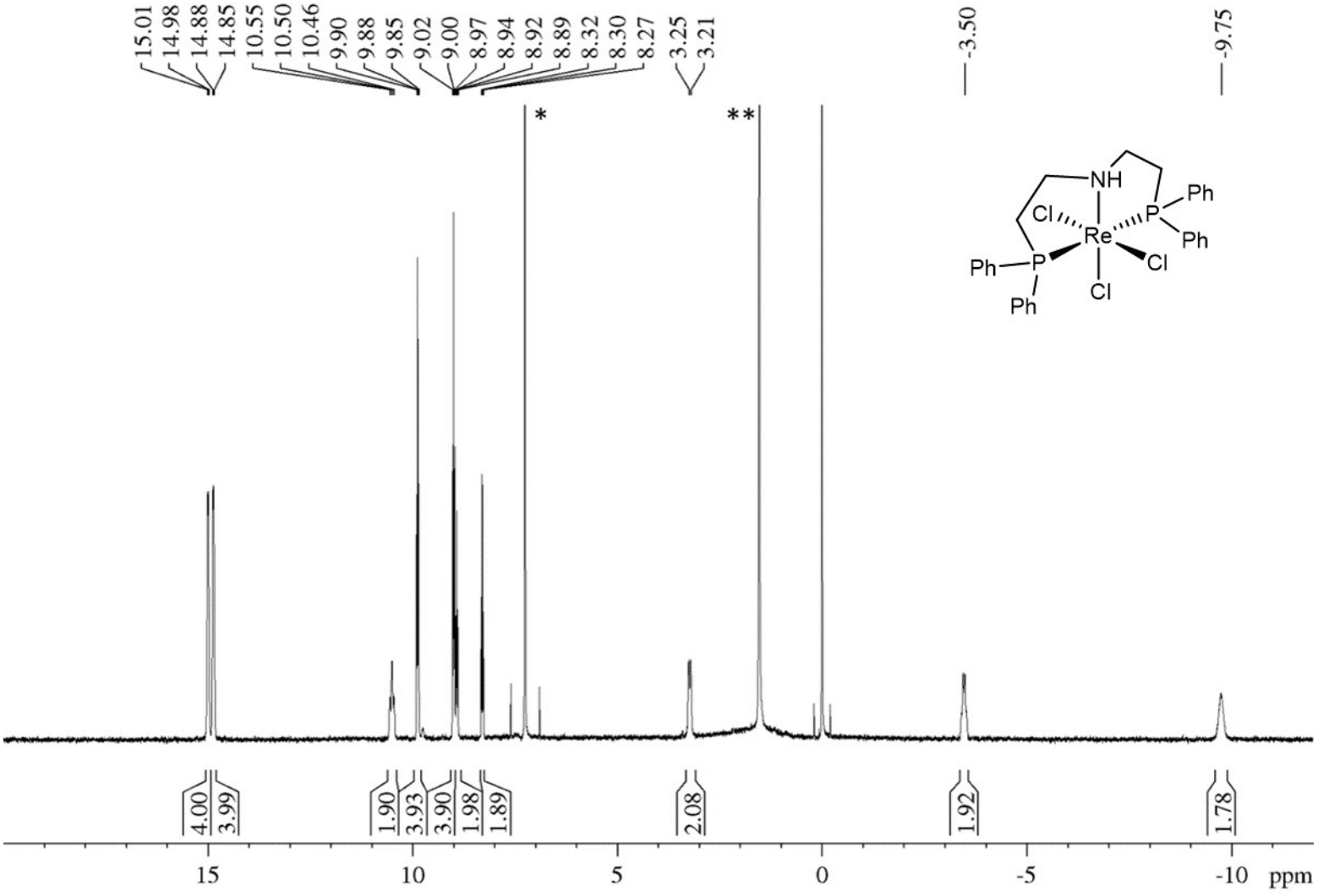


Figure S14. ^{1}H NMR spectrum (300 Mhz, $CDCl_3$, 298 K) of **10**. *$CHCl_3$. **Water.

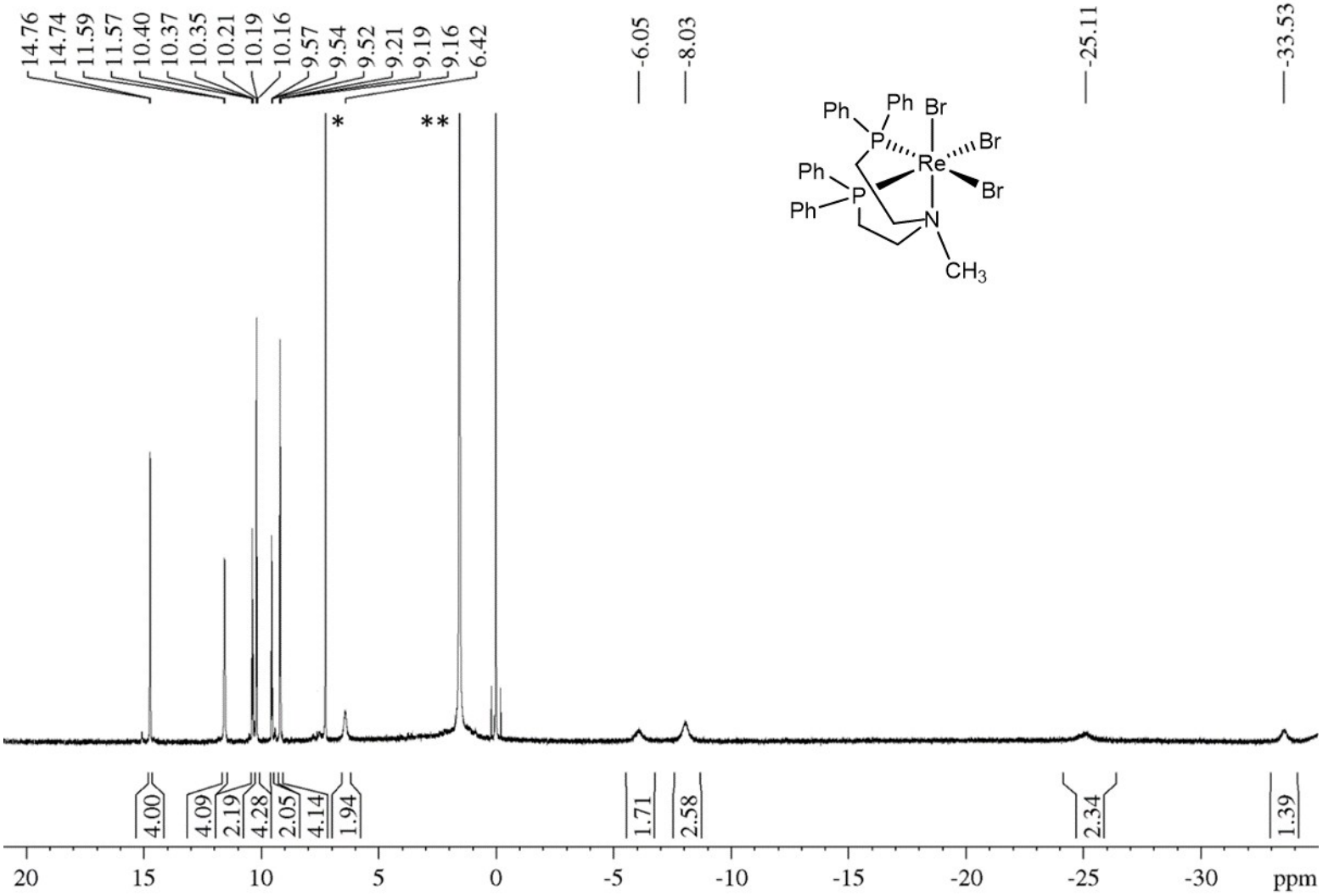


Figure S15. ^{1}H NMR spectrum (300 Mhz, $CDCl_3$, 298 K) of **11**. *$CHCl_3$. **Water.

Table S1. Summary of ^{1}H NMR data for the alkyl chains of complexes **1 – 11**. Spectra collected at 298 K in $CDCl_3$.

Compound		**Bridge PCH_2CH_2P (each signal integrates for 2H)**				**R-chain N- - -CH_3**	**R-chain -N-CH_2-**	**R-chain -$NCH_2C\underline{H}_2$-**	**R-chain -$NCH_2CH_2C\underline{H}_2$-**	**R-chain -$NCH_2C\underline{H}_2OCH_3$**
***mer*-[$ReCl_3PNPH$]**	**10**	−9.75 (bs)	−3.50 (bs);	3.23 (m)	10.50 (m)					
***fac*-[$ReCl_3PNPme$]**	**1**	−35.31 (bs)	−27.38 (bs)	−3.62 (bs)	7.86 (bs)	−0.85 (s)				
***fac*-[$ReBr_3PNPme$]**	**11**	−33.52 (bs)	−25.10 (bs)	−6.05 (bs)	6.42 (bs)	−8.03 (bs)				
***fac*-[$ReCl_3PNPet$]**	**2**	−35.59 (bs)	−27.16 (bs)	−3.94 (bs)	7.74 (bs)	−5.24 (t)	−9.78 (bs)			
***fac*-[$ReBr_3PNPet$]**	**3**	−33.37 (bs)	−25.14 (bs)	−3.89 (bs)	8.48 (bs)	−5.51 (bs)	−12.16 (bs)			
***fac*-[$ReCl_3PNPpr$]**	**4**	−35.58 (bs)	−27.23 (bs)	−4.18 (bs)	7,93 (bs)	−0.61 (t)	−10.26 (bs)	−12.00 (m)		
***fac*-[$ReBr_3PNPpr$]**	**5**	−33.54 (bs)	−25.33 (bs)	−3.82 (bs)	8.69 (bs)	−1.28 (t)	−12.49 (m)	−11.64 (m)		
***fac*-[$ReCl_3PNPbu$]**	**6**	−35.52 (bs)	−27.18 (bs)	−3.92 (m)	7.99 (s)	−0.96 (t)	−10.03 (bs)	−11.97 (m)	−0.87 (m)	
***fac*-[$ReBr_3PNPbu$]**	**7**	−33.56 (bs)	−25.35 (bs)	−3.79 (bs)	8.65 (bs)	−1.14 (t)	−12.36 (bs)	−11.71 (s)	−1.48 (m)	
***fac*-[$ReCl_3PNP2$]**	**8**	−35.40 (bs)	−27.50 (bs)	−3.55 (bs)	7.89 (m)	−0.87 (s)	−8.04 (bs)			1.26 (m)
***fac*-[$ReBr_3PNP2$]**	**9**	−33.50 (bs)	−25.76 (bs)	−3.48 (bs)	8.57 (bs)	−0.93 (s)	−10.65 (bs)			−0.60 (bs)

Table S2. Summary of ^{1}H NMR data for phenyl rings of complexes **1 – 11**. Spectra collected at 298 K in $CDCl_3$.

Compound		***o*-H**	***m*-H**	***p*-H**
***mer*-[$ReCl_3$PNPH]**	**10**	14.99 (d, 4H); 14.86 (d, 4H)	9.88 (t, 4H); 9.00 (t, 4H)	8.92 (t, 2H); 8.30 (t, 2H)
***fac*-[$ReCl_3$PNPme]**	**1**	15.04 (d, 4H); 10.98 (d, 4H)	10.34 (t, 4H); 9.11 (t, 4H)	10.54 (t, 2H); 9.54 (t, 2H)
***fac*-[$ReBr_3$PNPme]**	**11**	14.75 (d, 4H); 11.58 (d, 4H)	10.19 (t, 4H); 9.19 (t, 4H)	10.37 (t, 2H); 9.54 (t, 2H)
***fac*-[$ReCl_3$PNPet]**	**2**	15.07 (d, 4H); 10.95 (d, 4H)	10.35 (t, 4H); 9.08 (t, 4H)	10.55 (t, 2H); 9.54 (t, 2H)
***fac*-[$ReBr_3$PNPet]**	**3**	14.73 (d, 4H); 11.41 (d, 4H)	10.10 (t, 4H); 9.07 (t, 4H)	10.40 (t, 2H); 9.56 (t, 2H)
***fac*-[$ReCl_3$PNPpr]**	**4**	14.95 (d, 4H); 10.71 (d, 4H)	10.28 (t, 4H); 8.94 (t, 4H)	10.48 (t, 2H); 9.46 (t, 2H)
***fac*-[$ReBr_3$PNPpr]**	**5**	14.74 (d, 4H); 11.35 (d, 4H)	10.10 (t, 4H); 9.05 (t, 4H)	10.40 (t, 2H); 9.57 (t, 2H)
***fac*-[$ReCl_3$PNPbu]**	**6**	15.08 (d, 4H); 10.92 (d, 4H)	10.34 (t, 4H); 9.05 (t, 4H)	10.54 (t, 2H); 9.54 (t, 2H)
***fac*-[$ReBr_3$PNPbu]**	**7**	14.74 (d, 4H); 11.35 (d, 4H)	10.09 (t, 4H); 9.04 (t, 4H)	10.40 (t, 2H); 9.57 (t, 2H)
***fac*-[$ReCl_3$PNP2]**	**8**	15.04 (d, 4H); 10.97 (d, 4H)	10.34 (t, 4H); 9.11 (t, 4H)	10.54 (t, 2H); 9.55 (t, 2H)
***fac*-[$ReBr_3$PNP2]**	**9**	14.71 (d, 4H); 11.43 (d, 4H)	10.10 (t, 4H); 9.11 (t, 4H)	10.40 (t, 2H); 9.59 (t, 2H)

Table S3. Selected Bond Lengths (Å) and angles (deg) for the complexes **1** – **4**, **10** and **11**.

	***fac*-complexes**				***mer*-complexes**	
	[$ReCl_3$(PNPme)] 1	**[$ReCl_3$(PNPet)] 2**	**[$ReBr_3$(PNPet)] 3**	**[$ReCl_3$(PNPpr)] 4**	**[$ReCl_3$(PNPH)] 10**	**[$ReBr_3$(PNPme)] 11**
Re–N(1)[a, b]	2.2301(17)	2.274(3)	2.277(2)	2.2803(17)	2.156(2)	2.252(4)
Re–P(1)	2.3869(5)	2.3997(9)	2.4035(8)	2.3847(6)	2.4073(7)	2.4186(15)
Re–P(2)	2.3920(5)	2.4073(10)	2.4148(8)	2.3808(6)	2.4249(7)	2.4118(15)
Re–X(1)	2.4358(5)	2.4218(9)	2.5625(3)	2.4248(6)	2.3791(7)	2.5146(7)
Re–X(2)	2.4309(5)	2.4201(9)	2.5690(3)	2.4184(6)	2.3552(7)	2.5038(6)
Re–X(3)	2.3433(5)	2.3412(9)	2.4814(3)	2.3375(6)	2.3843(7)	2.5302(6)
P(1)–C(1)	1.838(2)	1.829(4)	1.827(3)	1.813(2)	1.835(3)	1.847(6)
P(2)–C(3)	1.840(2)	1.827(4)	1.823(3)	1.824(2)	1.830(3)	1.845(6)
P(1)–Re–N(1)	82.55(5)	82.59(8)	82.47(7)	82.85(5)	81.39(6)	81.42(13)
P(2)–Re–N(1)	81.59(5)	82.45(8)	82.56(6)	82.24(5)	81.45(6)	82.45(13)
P(1)–Re–P(2)	102.40(2)	105.48(3)	105.28(3)	100.42(2)	162.84(3)	163.78(5)
X(1)–Re–P(1)	166.66(2)	169.43(3)	170.00(2)	171.43(2)	90.04(3)	91.23(4)
X(2)–Re–P(2)	168.96(2)	165.11(3)	165.46(2)	166.99(2)	90.20(3)	89.82(4)
X(3)–Re–P(1)	92.20(2)	90.90(3)	90.07(2)	92.92(2)	97.99(3)	97.80(4)
X(3)–Re–P(2)	92.11(2)	94.69(3)	94.64(2)	96.01(2)	99.15(3)	98.37(4)
X(3)–Re–N(1)	170.69(5)	171.88(8)	170.99(6)	175.02(5)	177.44(6)	178.15(12)
X(1)–Re–X(2)	84.58(2)	85.04(3)	85.10(1)	86.37(2)	173.27(2)	177.02(2)
X(1)–Re–X(3)	98.01(2)	94.57(3)	94.84(1)	93.54(2)	91.65(3)	91.18(2)

[a]The precision of the data listed in the above table was, whenever possible, as following: four decimal digits for distances involving Re; three decimal digits for other distances; two decimal digit for bond angles of the type A–Re–B; one decimal digit for other angles. [b]Starred figures refer to angles of the disordered part of the molecule with C(2A), C(4A), C(5A) in place of C(2), C(4), C(5), hence to Re–N(1)–C(4A), Re–N(1)–C(5A), C(2A)–N(1)–C(5A), C(4A)–N(1)–C(5A).

CRYSTALLOGRAPHIC REFINEMENT DETAILS FOR COMPLEXES 1, 4, 10 AND 11.

Complex 1. The structure has been solved in the noncentrosymmetric and also enantiomorphic *P* $2_12_12_1$ space group; refinement performed alternatively with the MERG2 and MERG3 instructions of SHELXL allowed the calculation of the correct number of Friedel pairs to be 4986. The final value of the Flack parameter was -0.018(3). At the end of refinement, some peaks compatible with alternate arrangements of the C(2), C(4) and C(5) atoms appeared close to N(1). These carbon atoms were refined as disordered over two sites, with occupancies constrained to sum to 1.0. The presence of the alternate C(2A) and C(4A) atoms made necessary to consider also disordered over two sites (with identical occupancy restraints) the hydrogen atoms bound to C(1) and C(3). The final site occupation factors of the alternate arrangements were 0.824 and 0.176, respectively. No additional restraints were imposed on disordered atoms. A molecule of the crystallization solvent (dimethylformamide) is present in the unit cell. The C(31) and C(32) carbon atoms bound to N(2) in this anisotropically refined molecule show rather high final U_{eq} values (0.110, 0.125). The involved atoms were left unsplit because attempts to split them did not gave any better model.

Complex 4. The structure has been solved in the *P* $2_1/n$ space group. During the refinement, we found that one of the phenyl rings was disordered; the involved atoms were C(14) to C(19). We managed to resolve the disorder by modelling two alternate arrangements of the ring, with site occupation factors constrained to sum to unity. Final partial occupancies turned out to be 0.505 and 0.495; additional SHELX restraints (DELU, SIMU, SADI and FLAT) were also imposed on disordered atoms to improve the final model. In this case, disordered atoms were refined only isotropically because anisotropic refinement yielded a somewhat less satisfactory model. At this point, some residual peaks, likely due to a crystallization solvent molecule, were still present. This highly disordered methanol molecule could not be modelled efficiently. Accordingly, its contribution to the overall scattering was removed by means of the MASKS facility of OLEX. The routine showed the presence of two voids, each one with a void volume of 135 cubic Angstroms, large enough to fit 0.75 methanol molecules, as estimated from the electron count (nearly 26 electrons per void).

Complex 10. The structure has been solved in the *I* 2/*a* space group. At the end of the refinement, we found that three of the four phenyl rings in the complex were disordered. We split nearly all atoms of the rings in two arrangements, with site occupation factors constrained to sum to 1.0. The involved atoms were C(5) to C(10); C(11) to C(16); C(18) to C(22). For the above three sets the refined sofs were, respectively, 0.477/0.523; 0.399/0.601; 0.599/0.401. Additional SHELX restraints (RIGU, SIMU, SADI and FLAT) were also imposed on disordered atoms. The proposed solution, in which all disordered atoms have been refined anisotropically, has been selected after comparing the results of several

attempts as a reasonable compromise, however, the C(13), C(13A), C(14) and C(15) atoms remain affected by rather high thermal motions, with Ueq values of 0.137, 0.136, 0.140 and 0.135, respectively. At this point, some small solvent accessible voids, barely compatible with a crystallization water molecule, are still recognizable in the unit cell. However, the recrystallization solvent is CH_2Cl_2 and the positions of the very low residual density peaks do not collimate with such voids. We hence considered the refinement terminated at this stage.

Complex 11. The structure has been solved in the *Pbca* space group. In the final stages of refinement, some peaks appeared in positions compatible with alternate arrangements of C(2), C(4) and C(5) atoms, that were modelled as disordered over two sites with occupancies constrained to sum to unity. Final partial occupancies turned out to be 0.570 and 0.430. Further SHELX restraints (DELU, SIMU and SADI) were also imposed on the involved atoms, which have then been refined anisotropically. The phenyl rings were affected by some degree of thermal motion. The motion was more appreciable for atoms C(24)-C(29), in particular, for C(27)-C(28). We did not try to split these atoms and we refined them anisotropically (U_{eq} 0.102 and 0.104 for C(27) and C(28), respectively).

X–RAY STRUCTURE CHARACTERIZATION OF THE COMPLEXES 1 – 4, 10 AND 11: NONBONDING INTERACTIONS.

The packing diagrams of complexes **1** – **6** shows that intermolecular contacts are nor very much represented, possibly because of the neutral nature of the compounds, nor, in most cases, very efficient. In most cases, the distance between contacting atoms is above 2.6 Å and the contacts appear rather loose. Besides, some contacts involve H and C atoms of the disordered part of the molecules; these contacts will not be commented (except for **1**, see below).

Complex **1** is exceptional because it is the only one for which a dimethylformamide (DMF) crystallization molecule is present in the unit cell. The latter is the main responsible for the nonbonding interaction network in this complex. Several nonbonding contacts involve the O(1) atom of DMF and the H atoms of the disordered alkyl linkers of the PNPR ligand. The tightest contact is between the DMF O(1) atom and the H(9) atom of a nearby molecule (1/2–x, 1–y, 1/2+z) at 2.431 Å, backed by the contacts established with the H(4AA), H(5AA), H(4B), H(5B) (1–x, –1/2+y, 3/2–z) at ca. 2.50 – 2.60 Å; a softer interaction exists between the H(30) of DMF with the Cl(3) atom of the same unit at 2.890 Å. As a result, a DMF molecule bridges adjacent complexes molecules along all crystallographic axes and substantiate a rather efficient 3D network. The packing is also influenced by the presence of a well defined intramolecular π–π interaction between the C(12)/C(17) and C(24)/C(29) phenyl rings. By investigating the pertinent parameters within OLEX, we found that the centroids of the rings lie at a distance of 3.83 Å and are shifted by 1.21 Å; their mean planes make a dihedral angle of 12.5°.

The situation found in complexes **2** and **3** is alike as expected, given that the two compounds are isostructural and isomorphous. In both cases there are two rather loose halogen bonds, in which Cl(2) (in **2**) or Br(2) (in **3**) engage the H(4A) atom of the PNPR ligand of a nearby molecule (1/2+x, 3/2–y, 1/2+z in **2**, 1/2+x, 1/2–y, 1/2+z in **3**) at 2.885 and 2.976 Å, respectively. These two interactions propagate along a direction approximately coincident with the bisector of the β angle. In both cases, the 'tightest' contacts, at ca. 2.7 – 2.8 Å, involve the C(10) and the H(3B) atoms, propagating along the crystallographic b axis, and the C(15) atoms and H(2B) atoms, coupling adjacent units linked by the inversion operator. In these complexes the overall crystal packing looks less efficient than in **1**.

Complex **4** shows only two halogen bonds, involving the Cl(1) and Cl(2) atoms. The first one is rather tight; it develops along the crystallographic b axis and engages the H(1B) atom of the PNPR ligand at 2.582 Å (1/2–x, 1/2+y, 1/2–z). The second one approaches the H(11) atom of a phenyl ring at 2.808 Å (1–x, 1–y, –z); it links by the inversion operator two adjacent units and together with the previous one creates a zigzag motif growing along a direction approximately parallel to the diagonal of the ac face of the cell. Like in **1** above, also in **4** the disordered C(14)/C(19) (alternate positions: C(14A)/C(19A)) and the C(26)/C(31) phenyl rings

establish an intramolecular π–π interaction. In this case, the centroids of the rings lie at a distance of 3.95 (3.80) Å and are shifted by 0.96 (1.16) Å; their mean planes make a dihedral angle of 22.0 (7.2)°.

In the *mer* complex **10**, not considering the contacts involving the disordered phenyl rings, we found two interactions concerning Cl(1) and a further one involving the phenyl C(16) atom. Cl(1) makes a proper H–bond with the H(1) bound to N(1) (3/2–x, 3/2–y, 1/2–z) at 2.391 Å and has a softer contact with the H(25) atom (–1/2+x, 1–y, z) at 2.826 Å; another soft contact is given by C(16) and H(8). The first two interactions cooperate in giving a 2D motif that propagates along a direction that parallel the diagonal of the ab face of the cell; the last one propagates instead a zigzag motif along the crystallographic a axis. In this complex, the OLEX investigation revealed an intermolecular π–π interaction between the C(23)/C(28) ring of a molecule with the same residue of an adjacent unit at 5/2–x, 3/2–y, 1/2–z. Notably, this is the only phenyl ring not showing disorder. The centroids of the rings lie at a distance of 3.80 Å and are shifted by 1.88 Å; their mean planes make a crystallographically imposed dihedral angle of 0.0°.

The most relevant interactions in the other *mer* complex **11** are longer and softer compared with those in **10**; half of them are made by the disordered PNPR ligand, including the closest contact found between C(5) and H(5) at 2.669 Å. The bromide anions Br(3) and Br(2) make two not very tight halogen bonds with H(29) (1/2–x, 1/2+y, z) at 2.892 Å and with H(9) (–1/2+x, 1/2–y, 2–z) at 2.931 Å, respectively. The Br(3) interaction grows along the crystallographic b axis; the Br(2) contact creates a zigzag motif propagating along the crystallographic a axis. The two interactions together define a bidimensional network along the ab plane.

Table S4. Tightest intermolecular interactions for the complexes **1 – 4**, **10** and **11.**

Complex	acceptor (A)	donor (D)	donor parent (DP)	distance A–D, Å	angle A–D–DP, °	distance – sum of vdW radia, Å	disorder involved	symmetry
$[ReCl_3(PNPme)]$	O(1)	H(9)	C(9)	2.431	152.0	-0.289		1/2-x, 1-y, 1/2+z
1	O(1)	H(5AA)	C(5A)	2.457	159.7	-0.263	yes	1-x, -1/2+y, 3/2-z
	O(1)	H(4B)	C(4)	2.501	155.1	-0.219	yes	1-x, -1/2+y, 3/2-z
	C(5A)	H(14)	C(14)	2.601	139.4	-0.299	yes	1-x, -1/2+y, 3/2-z
	O(1)	H(4AA)	C(4A)	2.602	153.0	-0.118	yes	1-x, -1/2+y, 3/2-z
	O(1)	H(5B)	C(5)	2.627	153.2	-0.093	yes	1-x, -1/2+y, 3/2-z
	C(10)	H(2AA)	C(2A)	2.772	125.3	-0.128	yes	-1/2+x, 3/2-y, 1-z
	C(9)	H(2AA)	C(2A)	2.777	140.4	-0.123	yes	-1/2+x, 3/2-y, 1-z
	Cl(3)	H(30)	C(30)	2.890	133.4	-0.060		x, y, z
$[ReCl_3(PNPet)]$	C(10)	H(3B)	C(3)	2.668	157.9	-0.232		1/2-x, 1/2+y, 1/2-z
2	C(15)	H(2B)	C(2)	2.740	154.8	-0.160		-x, 2-y, -z
	Cl(2)	H(4A)	C(4)	2.885	151.5	-0.065		1/2+x, 3/2-y, 1/2+z
$[ReBr_3(PNPet)]$	C(15)	H(2B)	C(2)	2.773	155.5	-0.127		1-x, 1-y, -z
3	C(10)	H(3B)	C(3)	2.790	158.8	-0.110		3/2-x, 1/2+y, 1/2-z
	Br(2)	H(4A)	C(4)	2.976	153.4	-0.074		1/2+x, 1/2-y, 1/2+z
$[ReCl_3(PNPpr)]$	Cl(1)	H(1B)	C(1)	2.582	139.4	-0.368		1/2-x, 1/2+y, 1/2-z
4	Cl(2)	H(11)	C(11)	2.808	141.5	-0.142		1-x, 1-y, -z
$[ReCl_3(PNPH)]$	Cl(1)	H(1)	N(1)	2.391	153.8	-0.559		3/2-x, 3/2-y, 1/2-z
10	Cl(1)	H(25)	C(25)	2.826	143.7	-0.124		-1/2+x, 1-y, z
	C(7A)	H(22A)	C(22)	2.556	153.4	-0.074	yes	3/2-x, 3/2-y, 1/2-z
	C(15A)	H(16A)	C(16A)	2.603	153.3	-0.297	yes	2-x, 1-y, 1-z
	C(16A)	H(15A)	C(15A)	2.655	137.0	-0.245	yes	2-x, 1-y, 1-z
	C(16)	H(8)	C(8)	2.723	168.5	-0.177		-1/2+x, 1-y, z
$[ReBr_3(PNPme)]$	C(5)	H(5C)	C(5)	2.669	105.0	-0.231	yes	1-x, -y,2- z
11	Br(3)	H(29)	C(29)	2.892	161.5	-0.158		1/2-x, 1/2+y, z
	Br(2)	H(9)	C(9)	2.931	156.0	-0.119		-1/2+x, 1/2-y, 2-z
	Br(3)	H(3AA)	C(3)	2.987	143.7	-0.063	yes	1/2-x, 1/2+y, z
	Br(3)	H(3BC)	C(3)	2.991	143.2	-0.059	yes	1/2-x, 1/2+y, z