New ruthenium(II) coordination compounds possessing bidentate aminomethylphosphane ligands: synthesis, characterization and preliminary biological study *in vitro*

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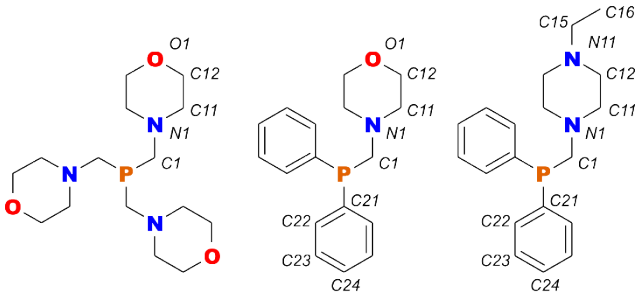
Addition of aminomethylphosphanes $P\{CH_2N(CH_2CH_2)_2O\}_3$ (**1**), $PPh_2\{CH_2N(CH_2CH_2)_2O\}$ (**2**) or $PPh_2\{CH_2N(CH_2CH_2)_2NCH_2CH_3\}$ (**3**) to methanolic solution of $RuCl_3$ results in reduction of ruthenium(III) ion giving finally *ttt*-$[RuCl_2(\mathbf{1})_2]$ (**1A**), *ttt*-$[RuCl_2(\mathbf{2})_2]$ (**2A**) and *ttt*-$[RuCl_2(\mathbf{3})_2]$ (**3A**). Synthesized complexes are the first examples of ruthenium(II) coordination compounds possessing aminomethylphosphanes chelating *via* phosphorus and nitrogen atoms. They were fully characterized (NMR, ESI-MS, IR, elemental analysis, X-ray crystallography). Preliminary studies of the *in vitro* cytotoxicity against A549 cell line (human lung adenocarcinoma) and interactions with human serum proteins (albumin and apotransferrin) showed the moderate activity of the complexes. Interestingly, the P,N-chelation leads to formation of strained 4-membered Ru-P-C-N-Ru rings, which in the case of **2A** and **3A** undergo opening in the presence of CH_3CN, which results in rearrangement to *ctc*-$[RuCl_2(\mathbf{2})_2(CH_3CN)_2]$ (**2B**) and *ctc*-$[RuCl_2(\mathbf{3})_2(CH_3CN)_2]$ (**3B**).



1 **2** **3**

Fig. S1 Structures of aminomethylphosphanes with atom numbering scheme (every hydrogen has the same number as directly bound carbon atom): $P\{CH_2N(CH_2CH_2)_2O\}_3$ (**1**), $PPh_2\{CH_2N(CH_2CH_2)_2O\}$ (**2**) and $PPh_2\{CH_2N(CH_2CH_2)_2NCH_2CH_3\}$ (**3**).

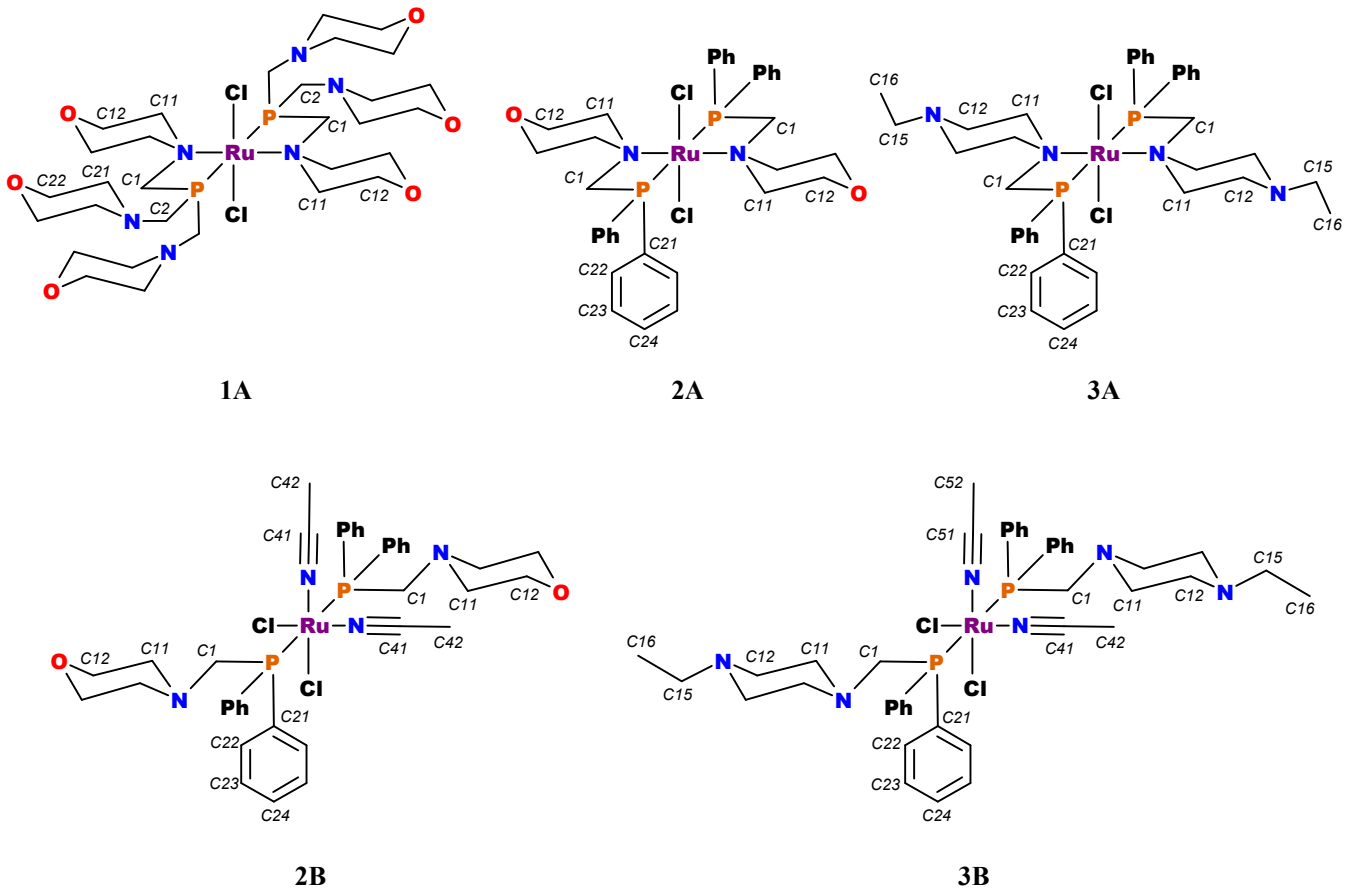


Fig. S2 Schematic structures of synthesized complexes (every hydrogen has the same number as directly bound carbon atom):
ttt-[$RuCl_2(P\{CH_2N(CH_2CH_2)_2O\}_3)_2$] (**1A**),
ttt-[$RuCl_2(PPh_2\{CH_2N(CH_2CH_2)_2O\})_2$] (**2A**),
ttt-[$RuCl_2(PPh_2\{CH_2N(CH_2CH_2)_2NCH_2CH_3\})_2$] (**3A**),
ctc-[$RuCl_2(PPh_2\{CH_2N(CH_2CH_2)_2O\})_2(CH_3CN)_2$] (**2B**) and
ctc-[$RuCl_2(PPh_2\{CH_2N(CH_2CH_2)_2NCH_2CH_3\})_2(CH_3CN)_2$] (**3B**)

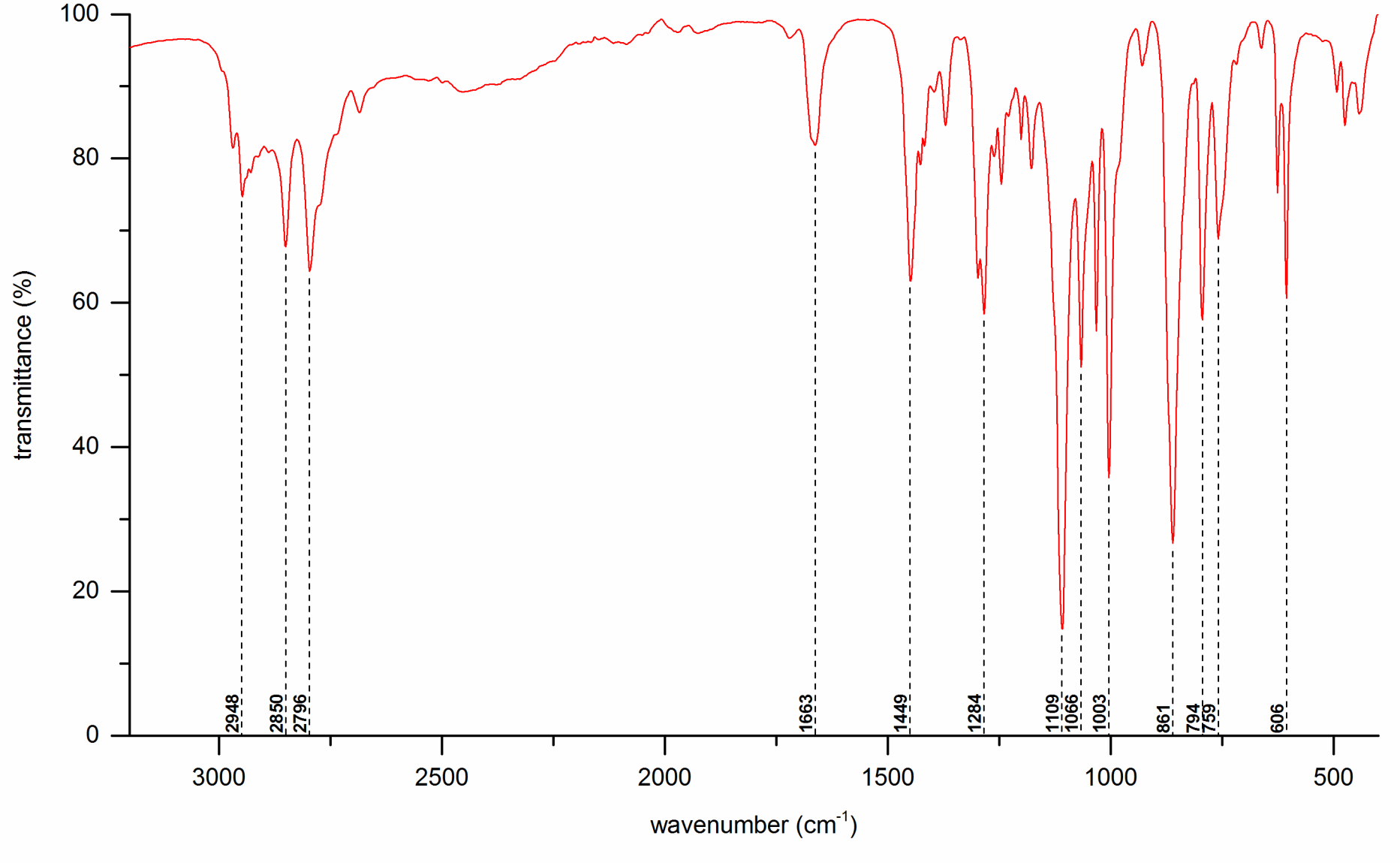


Fig. S3 Infrared spectrum of $P\{CH_2N(CH_2CH_2)_2O\}_3$ (**1**).

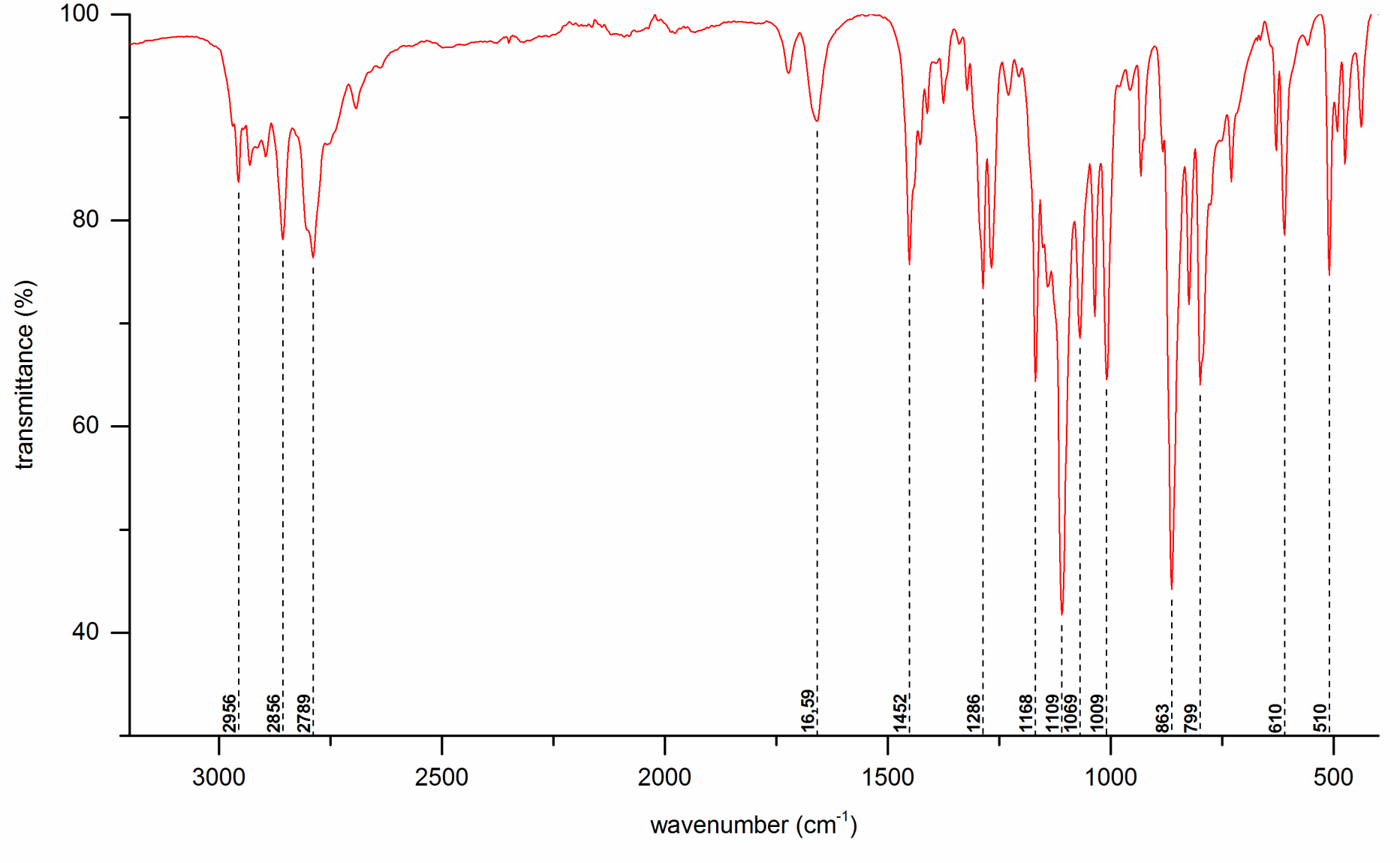


Fig. S4 Infrared spectrum of $OP\{CH_2N(CH_2CH_2)_2O\}_3$ (**1O**).

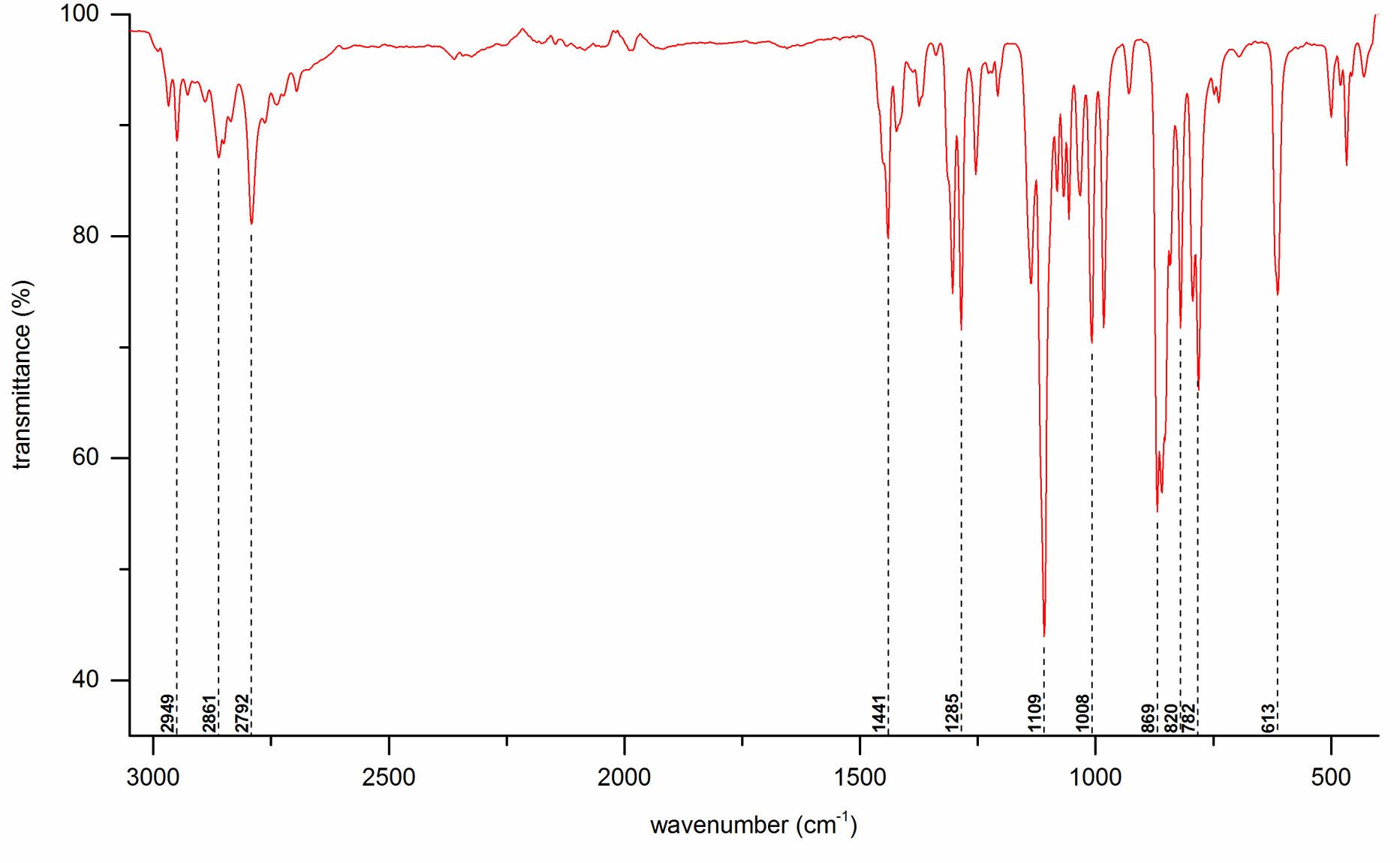


Fig. S5 Infrared spectrum of $[RuCl_2(P\{CH_2N(CH_2CH_2)_2O\}_3)_2]$ (**1A**).

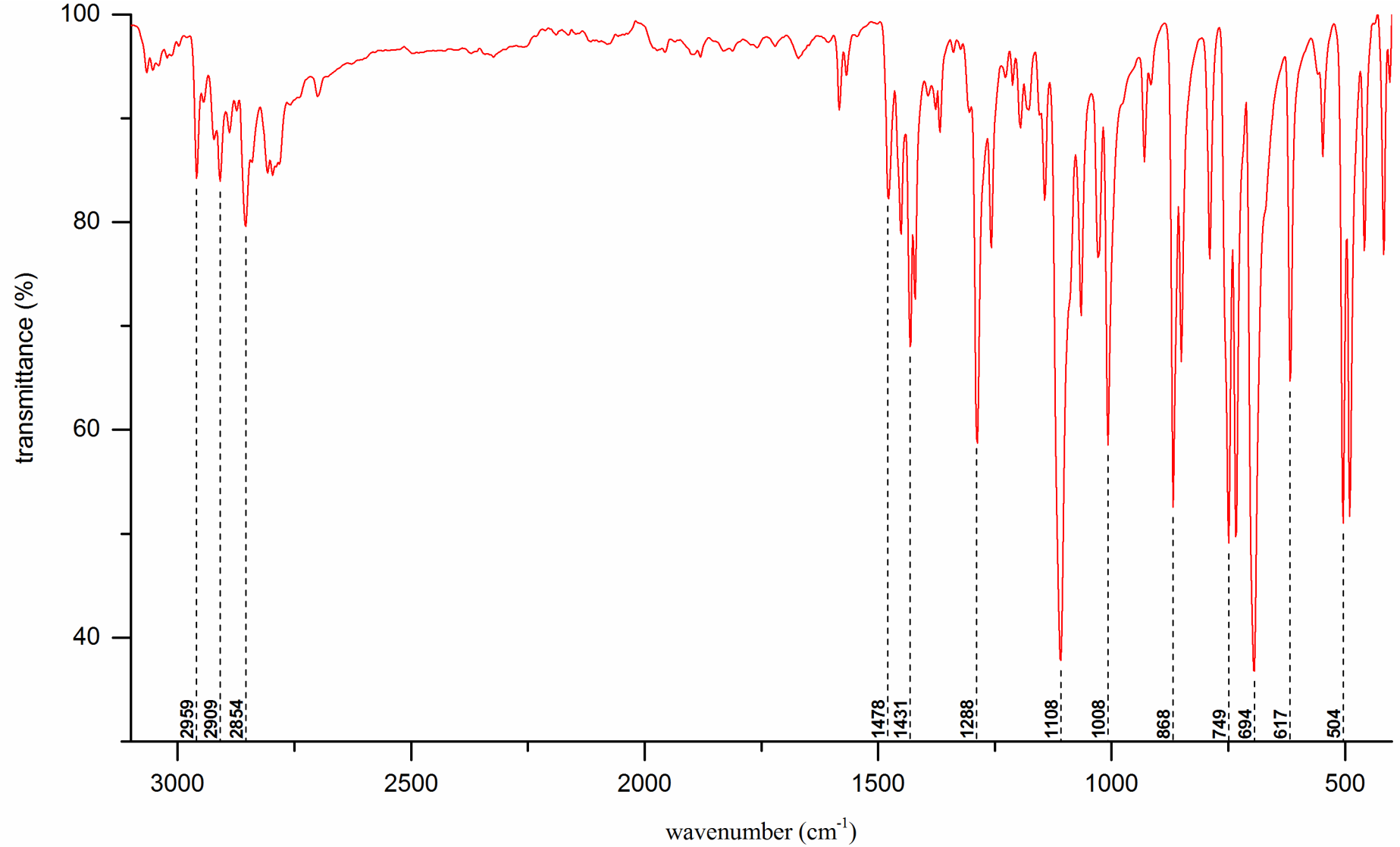


Fig. S6 Infrared spectrum of $PPh_2\{CH_2N(CH_2CH_2)_2O\}$ (**2**).

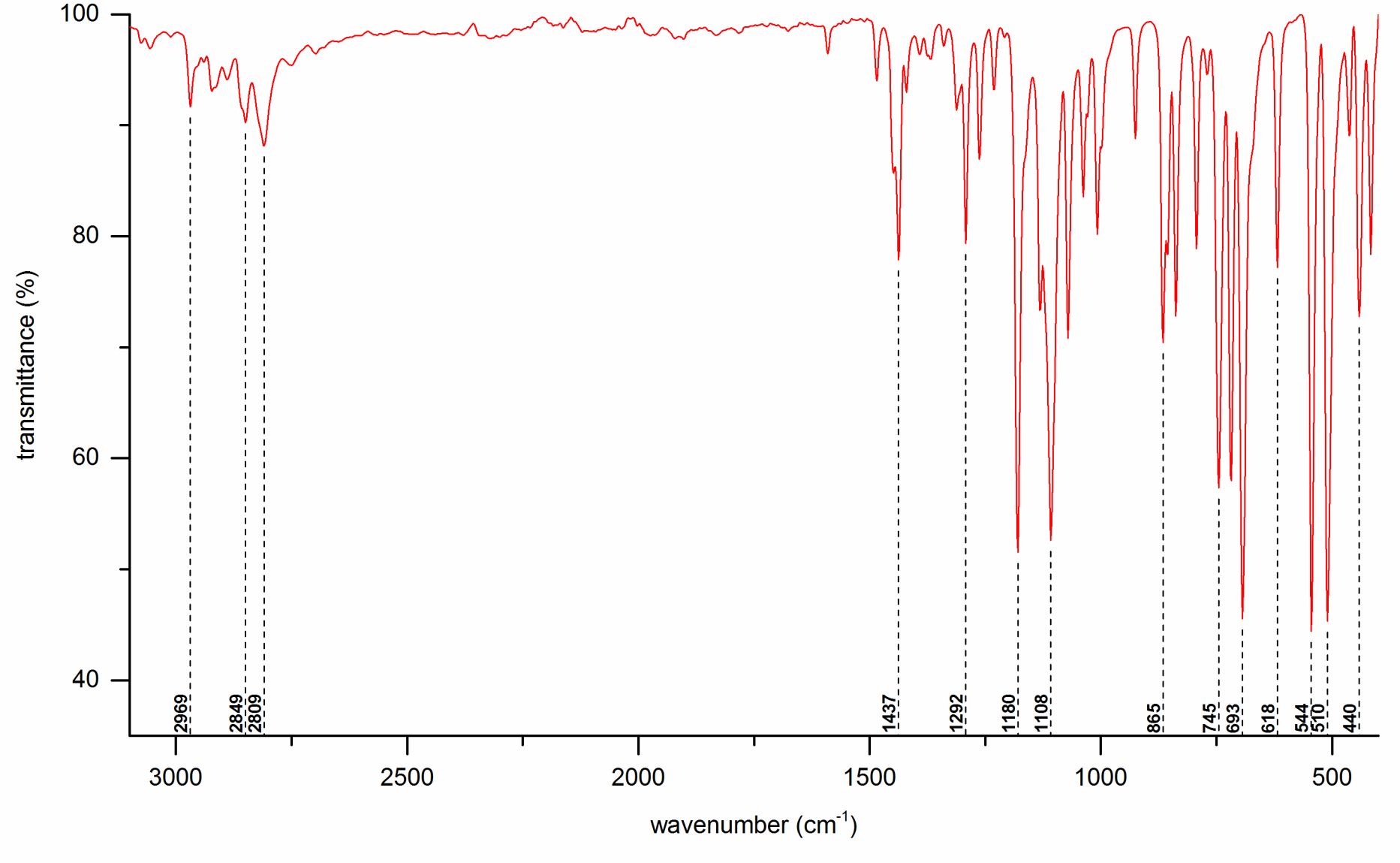


Fig. S7 Infrared spectrum of $OPPh_2\{CH_2N(CH_2CH_2)_2O\}$ (**2O**).

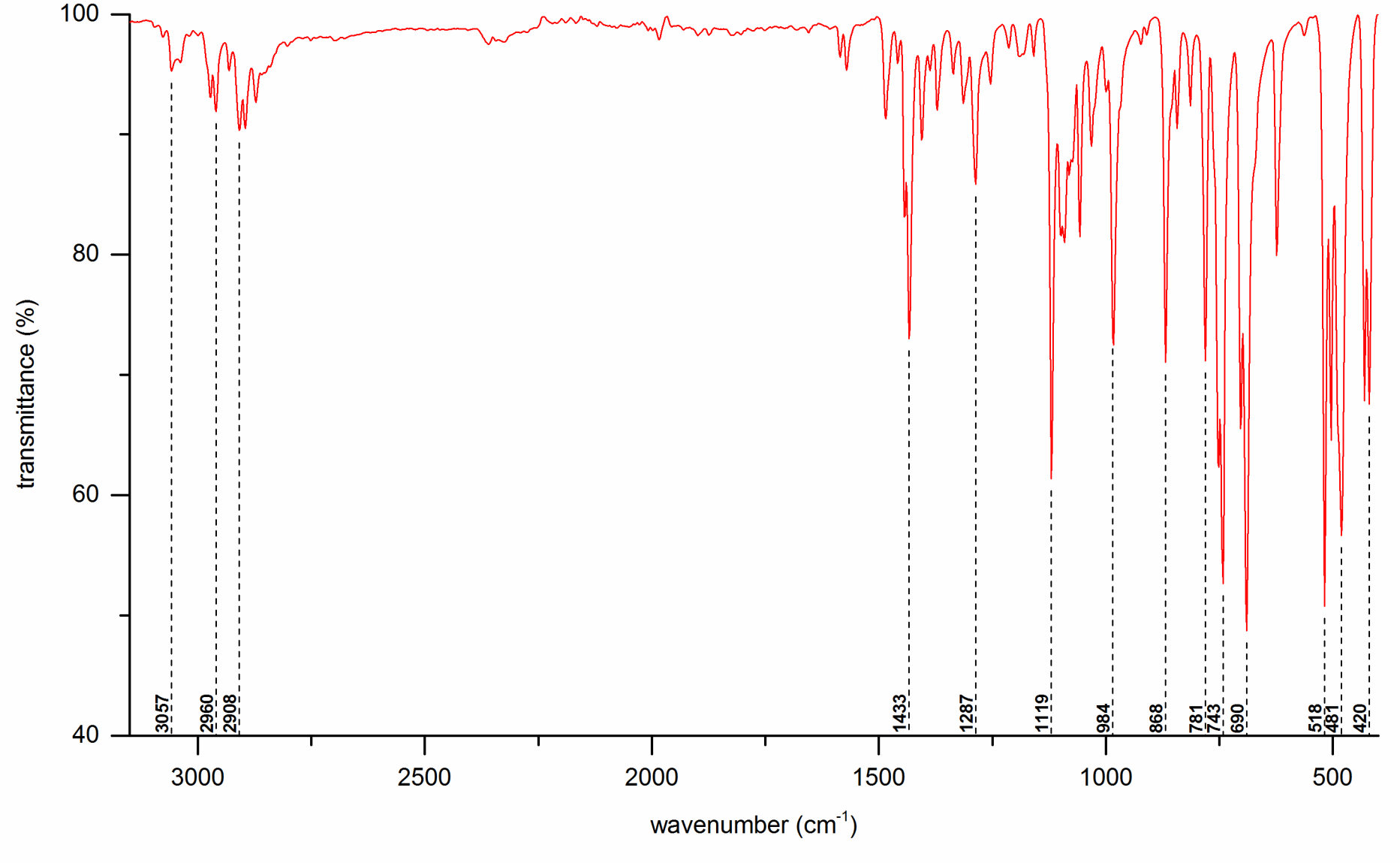


Fig. S8 Infrared spectrum of $[RuCl_2(PPh_2\{CH_2N(CH_2CH_2)_2O\})_2]$ (**2A**).

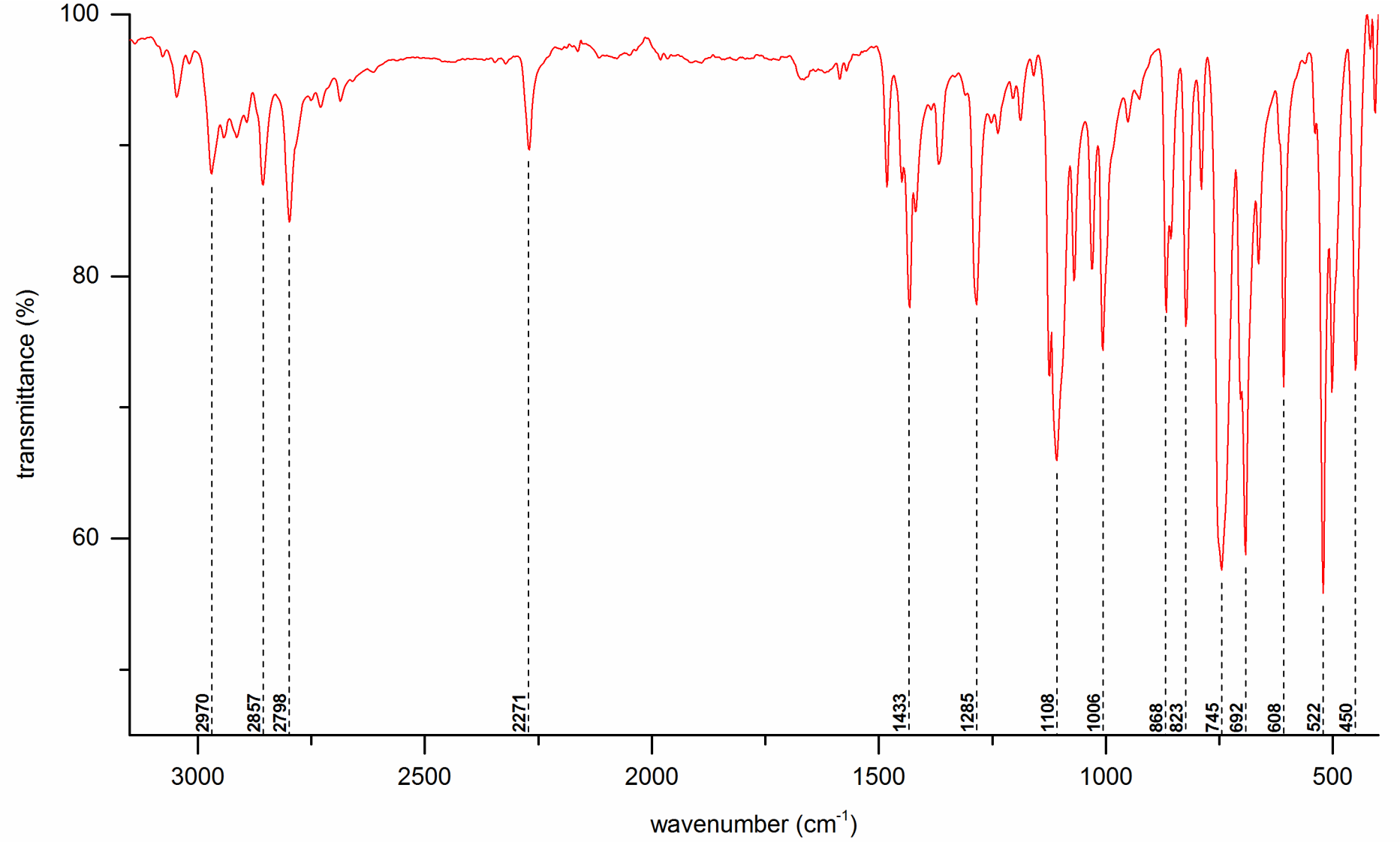


Fig. S9 Infrared spectrum of $[RuCl_2(PPh_2\{CH_2N(CH_2CH_2)_2O\})_2(CH_3CN)_2]$ (**2B**).

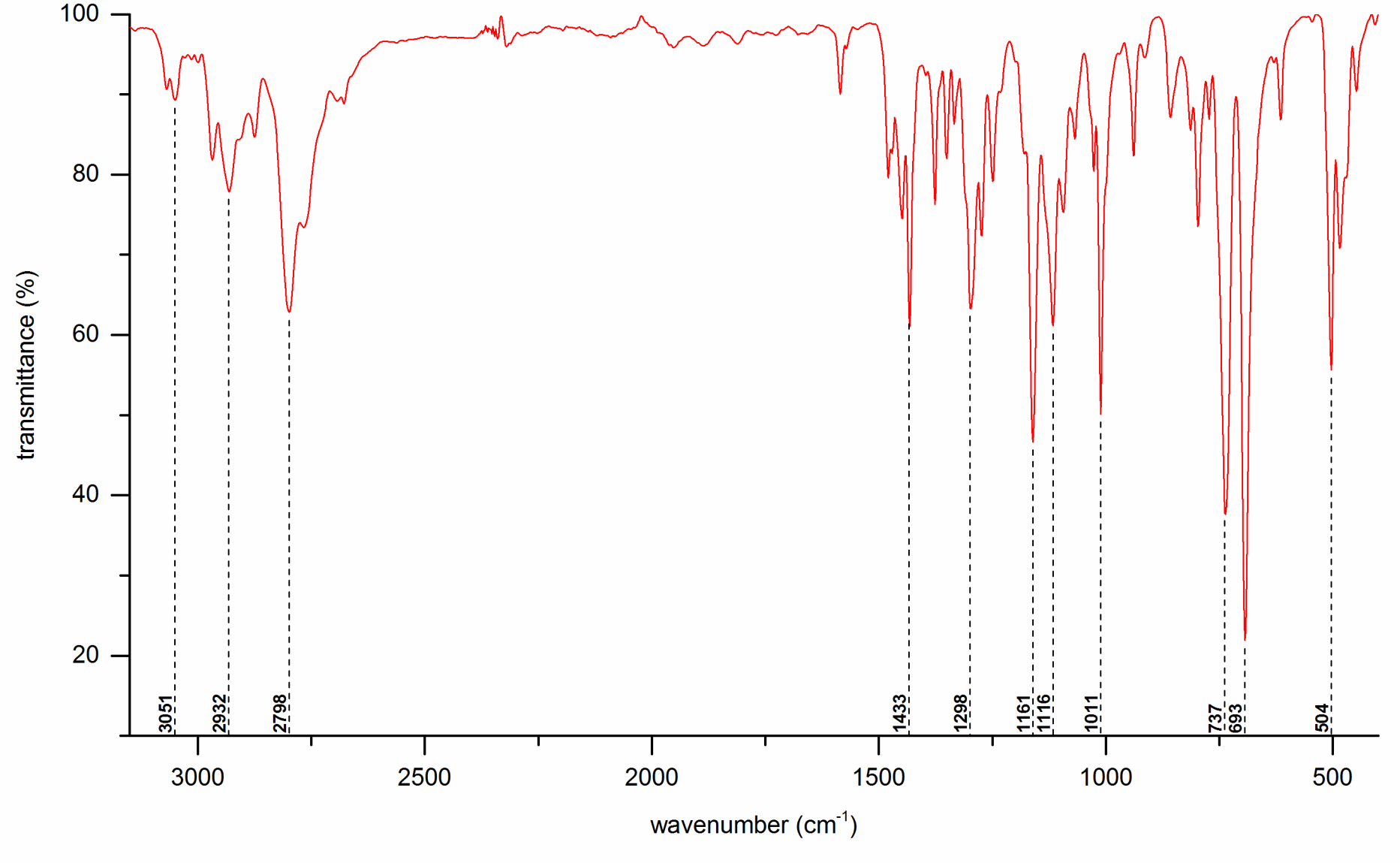


Fig. S10 Infrared spectrum of $PPh_2\{CH_2N(CH_2CH_2)_2NCH_2CH_3\}$ (**3**).

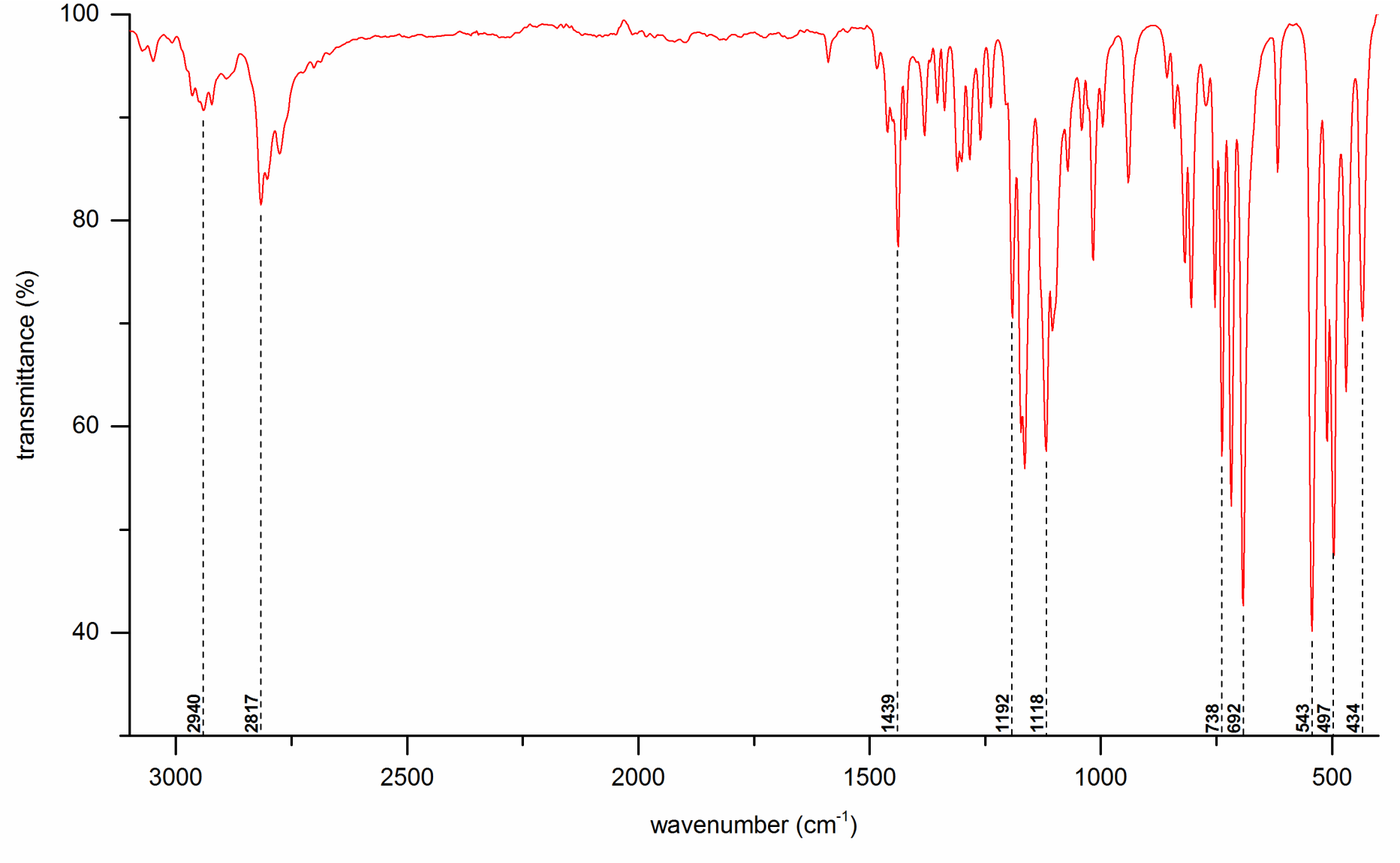


Fig. S11 Infrared spectrum of $OPPh_2\{CH_2N(CH_2CH_2)_2NCH_2CH_3\}$ (**3O**).

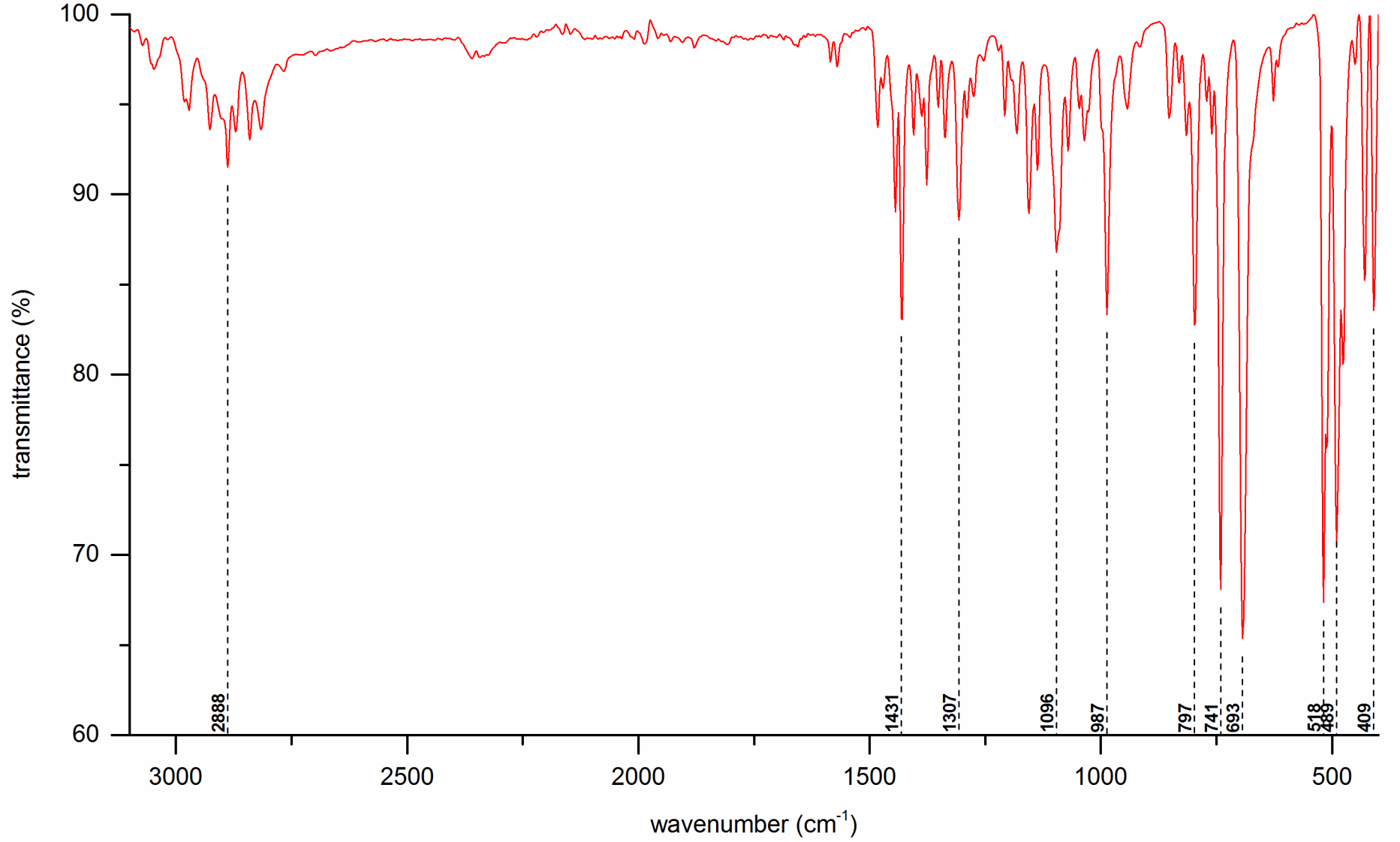


Fig. S12 Infrared spectrum of $[RuCl_2(PPh_2\{CH_2N(CH_2CH_2)_2NCH_2CH_3\})_2]$ (**3A**).

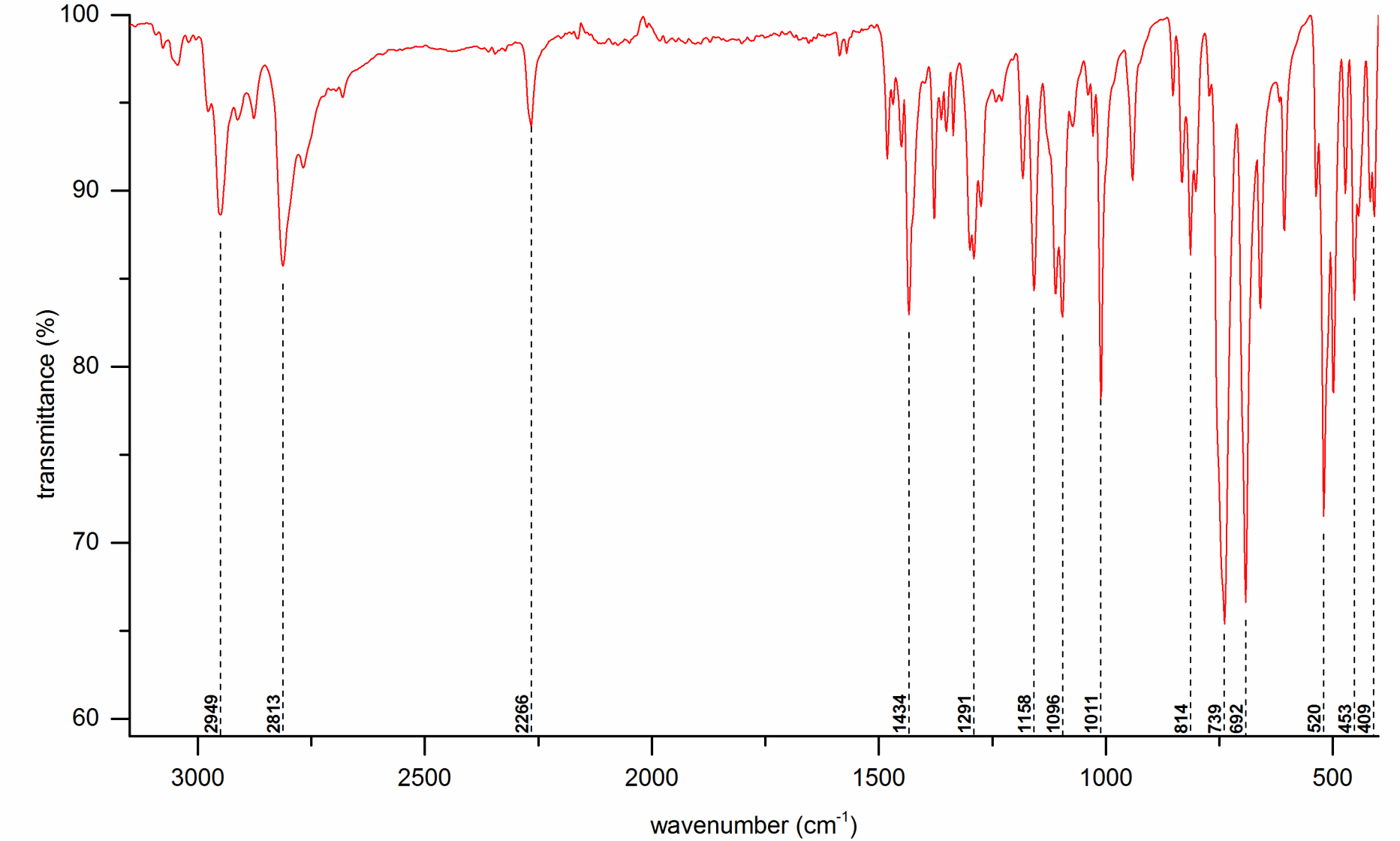


Fig. S13 Infrared spectrum of $[RuCl_2(PPh_2\{CH_2N(CH_2CH_2)_2NCH_2CH_3\})_2(CH_3CN)_2]$ (**3B**).

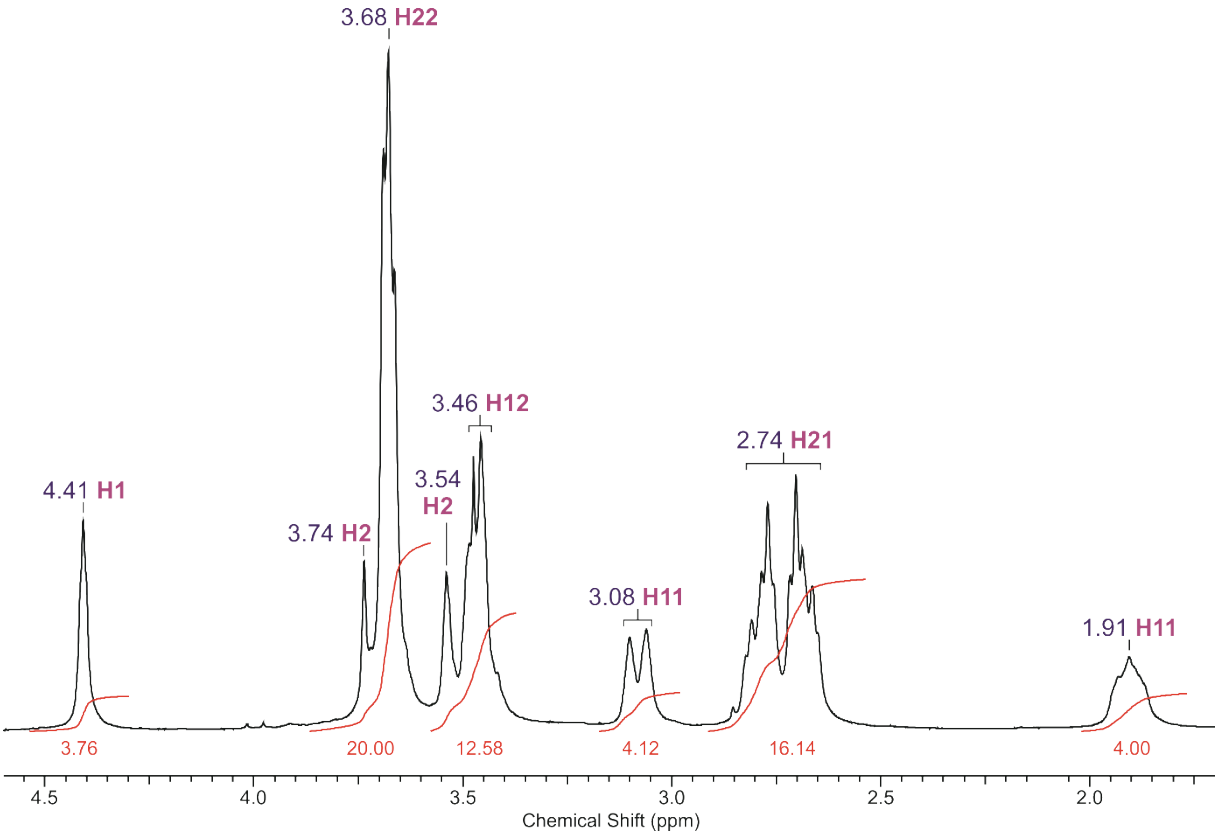


Fig. S14 ^{1}HNMR spectrum of $[RuCl_2(P\{CH_2N(CH_2CH_2)_2O\}_3)_2]$ (**1A**).

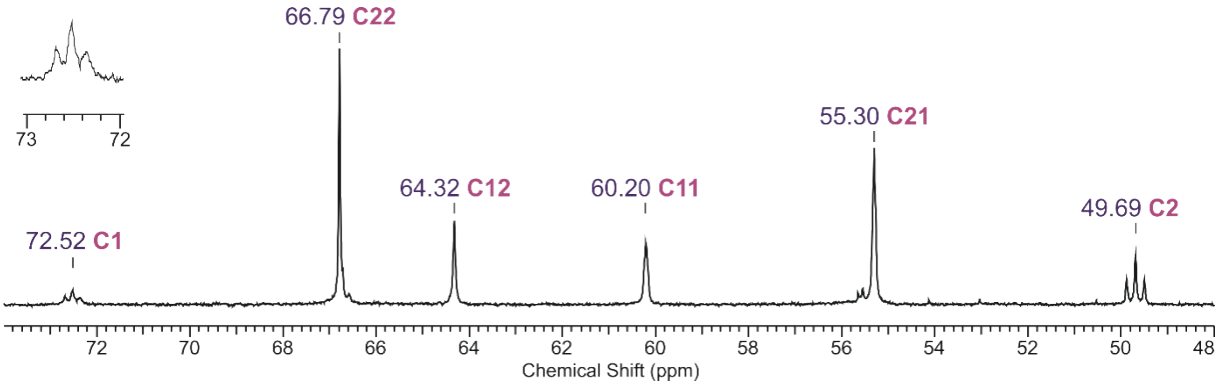


Fig. S15 ^{13}CNMR spectrum of $[RuCl_2(P\{CH_2N(CH_2CH_2)_2O\}_3)_2]$ (**1A**).

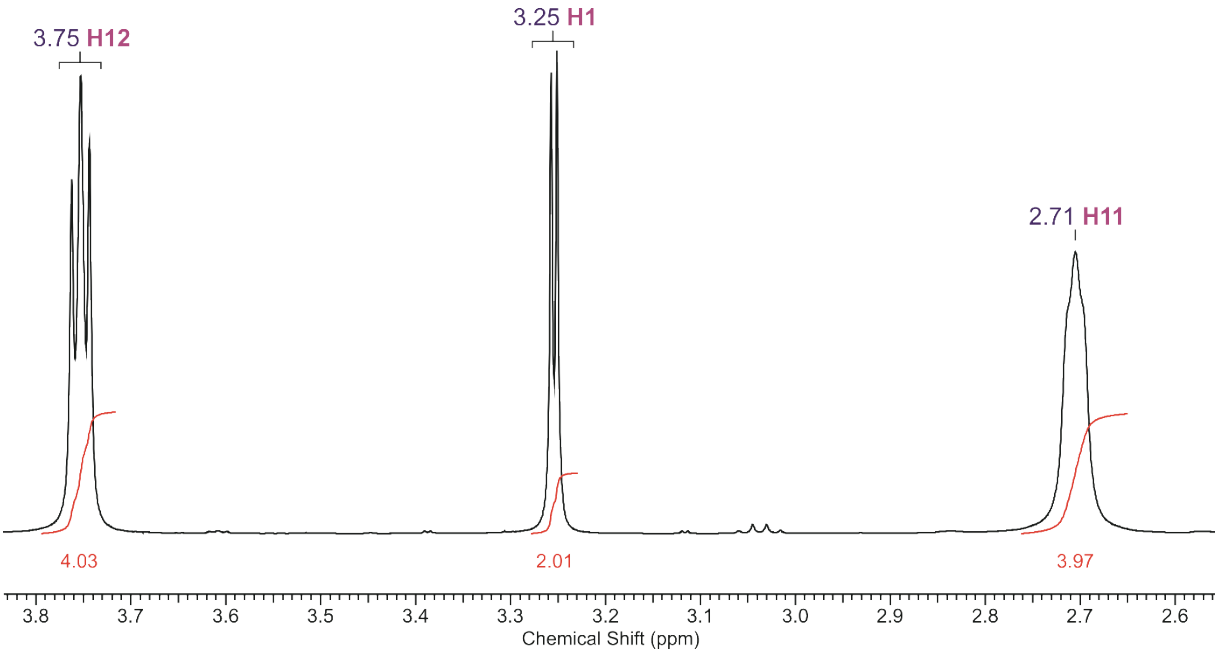


Fig. S16 ^{1}HNMR spectrum of $PPh_2\{CH_2N(CH_2CH_2)_2O\}$ (**2**) (aliphatic region).

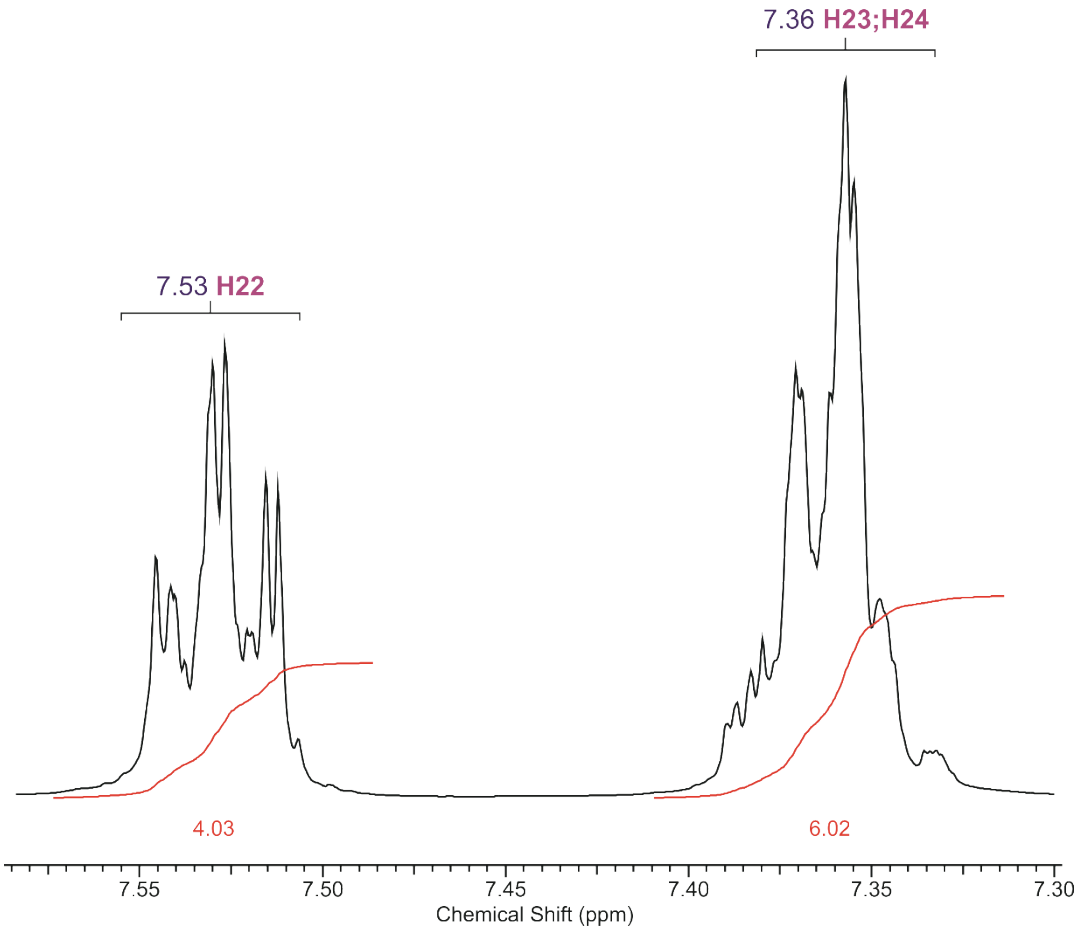


Fig. S17 ^{1}HNMR spectrum of $PPh_2\{CH_2N(CH_2CH_2)_2O\}$ (**2**) (aromatic region).

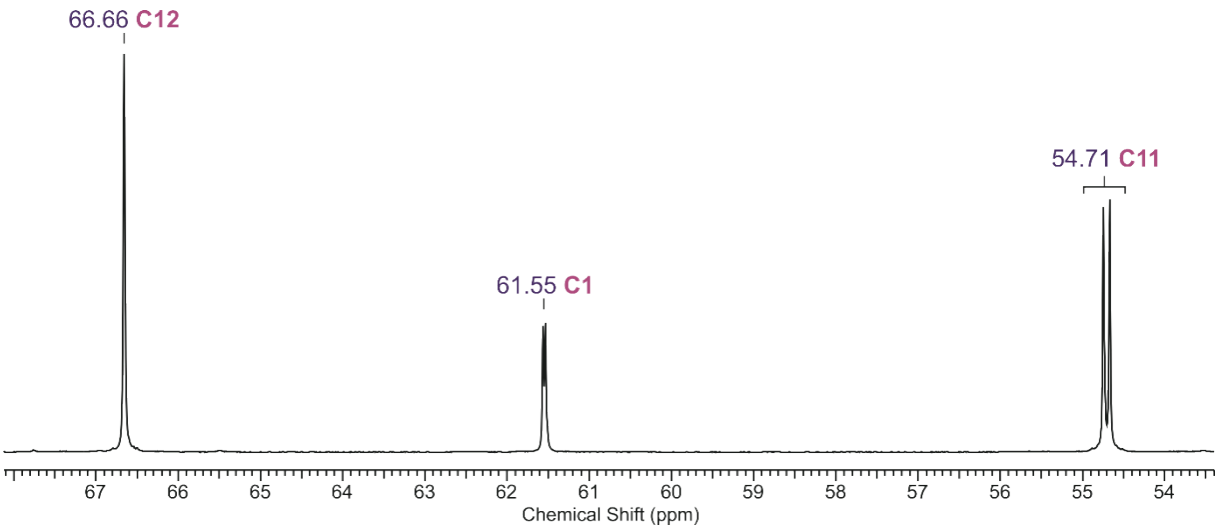


Fig. S18 ^{13}CNMR spectrum of $PPh_2\{CH_2N(CH_2CH_2)_2O\}$ (**2**) (aliphatic region).

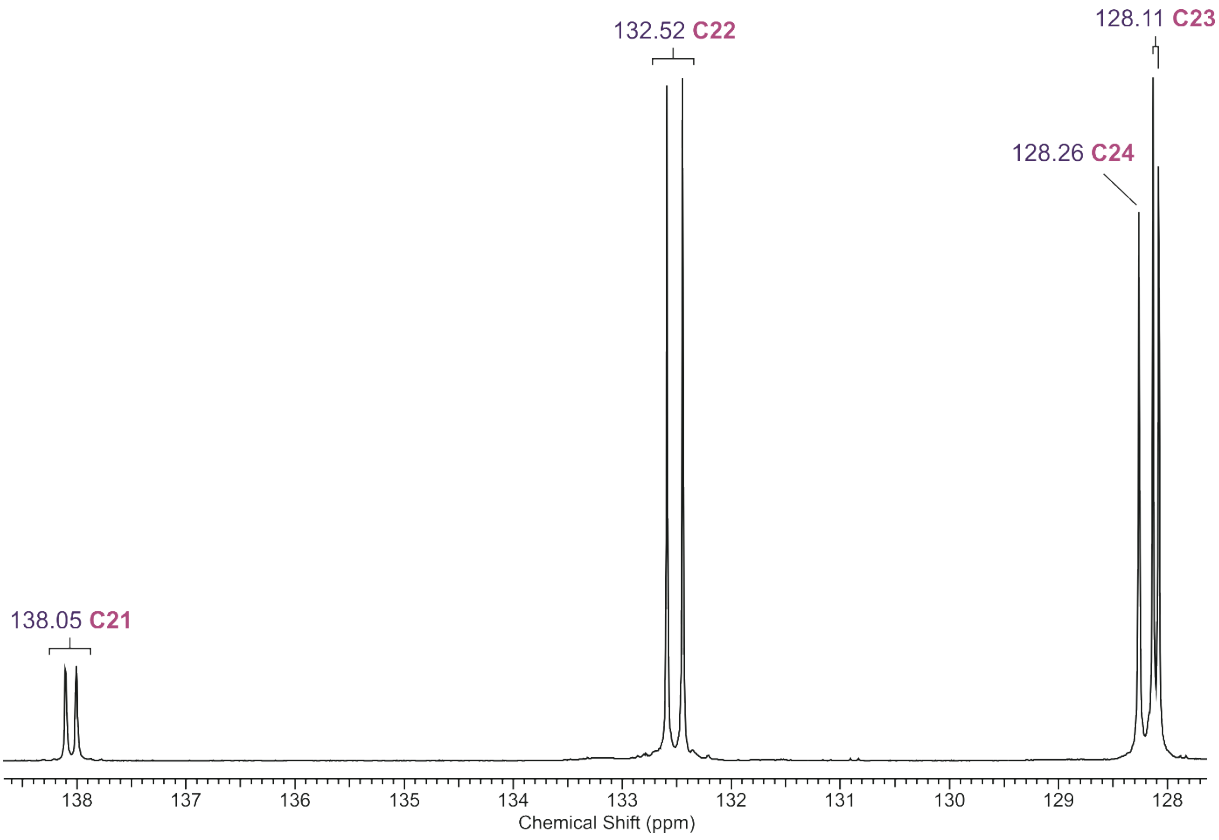


Fig. S19 ^{13}CNMR spectrum of $PPh_2\{CH_2N(CH_2CH_2)_2O\}$ (**2**) (aromatic region).

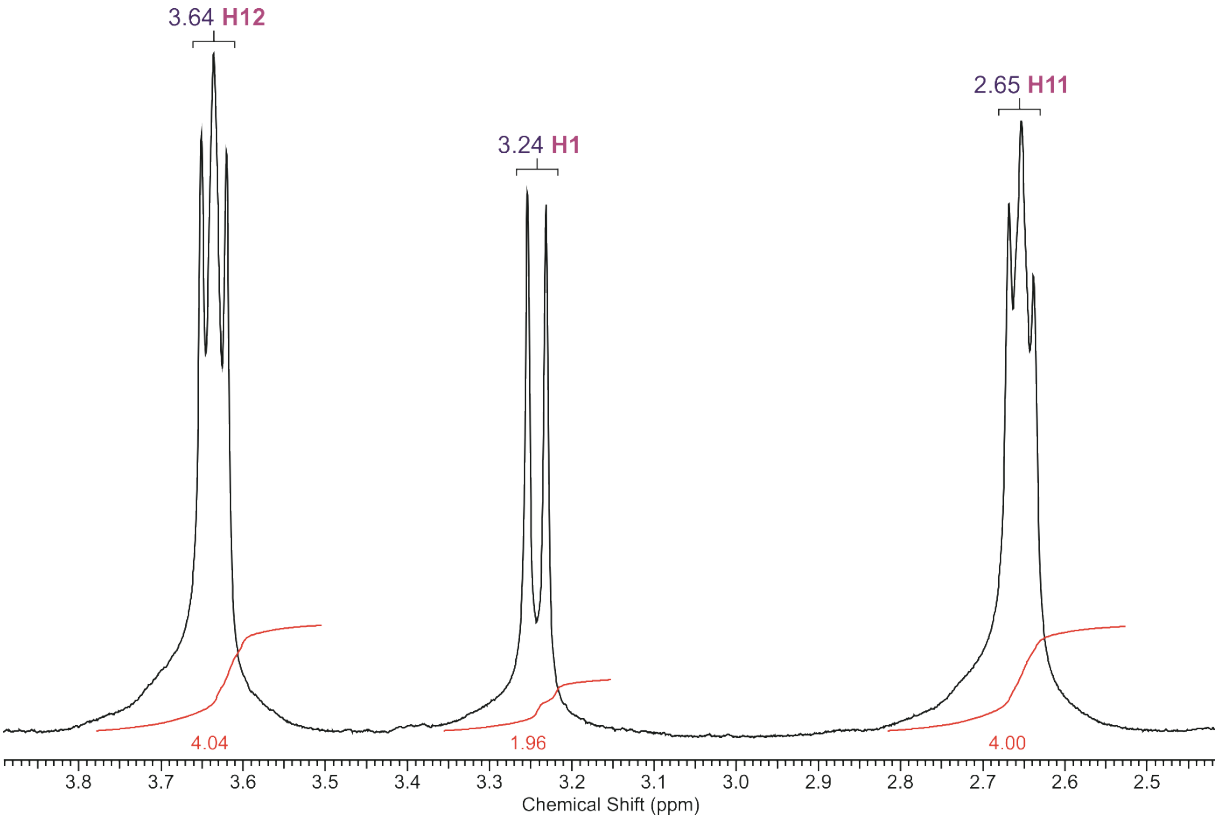


Fig. S20 ^{1}HNMR spectrum of $OPPh_2\{CH_2N(CH_2CH_2)_2O\}$ (**2O**) (aliphatic region).

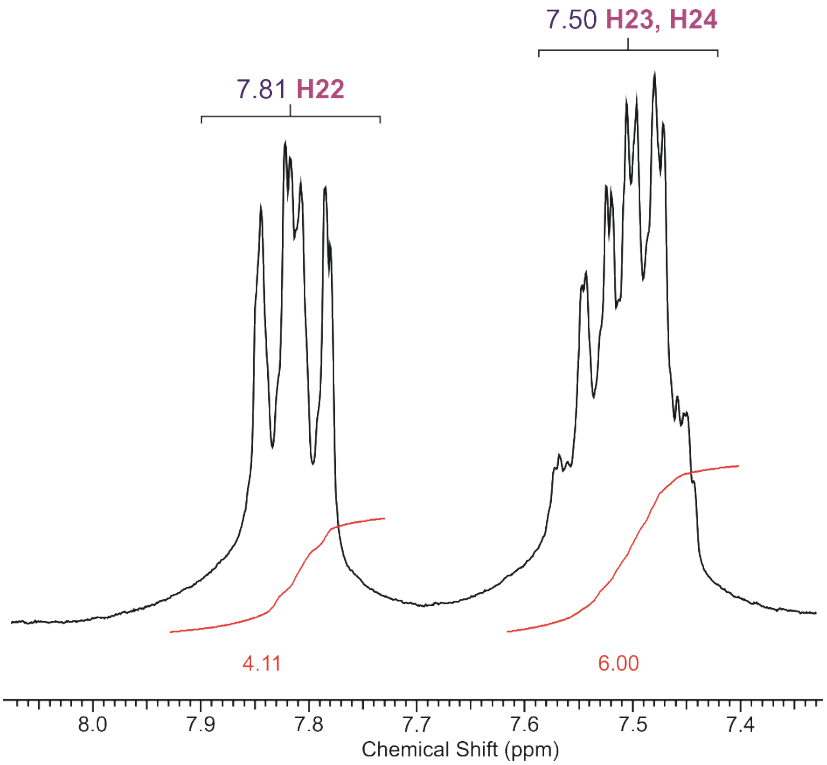


Fig. S21 ^{1}HNMR spectrum of $OPPh_2\{CH_2N(CH_2CH_2)_2O\}$ (**2O**) (aromatic region).

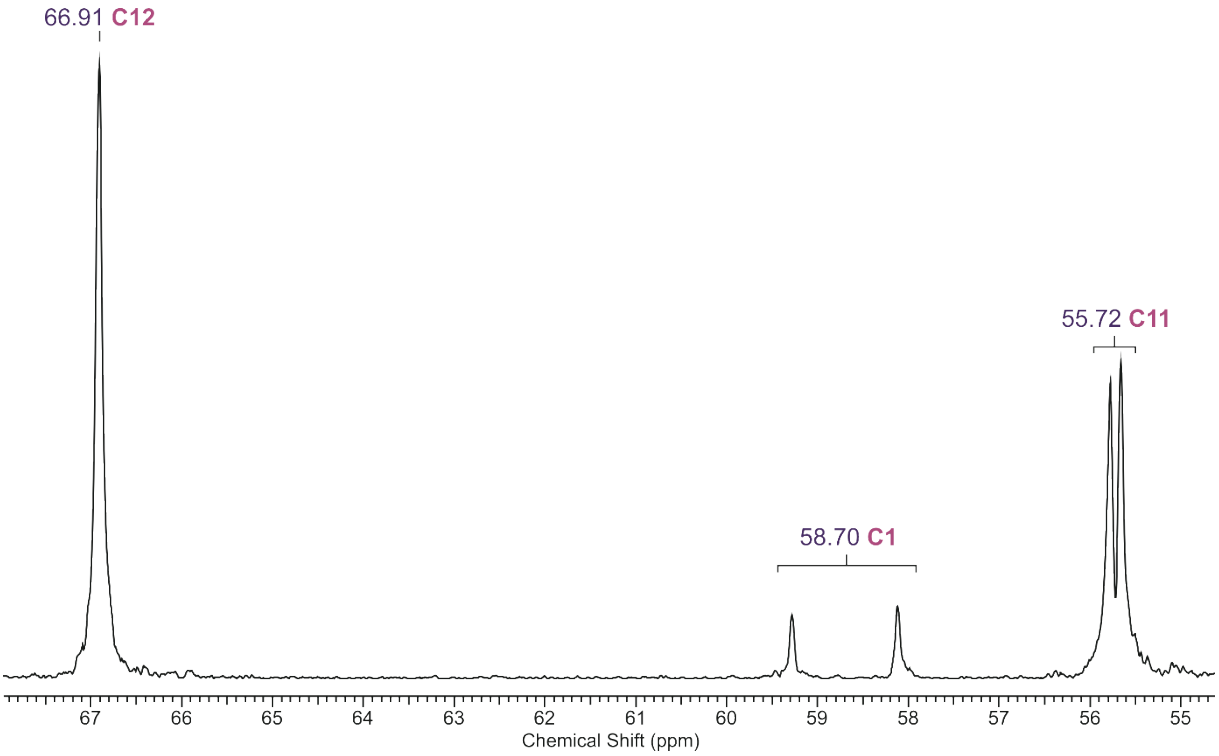


Fig. S22 ^{13}CNMR spectrum of $OPPh_2\{CH_2N(CH_2CH_2)_2O\}$ (**2O**) (aliphatic region).

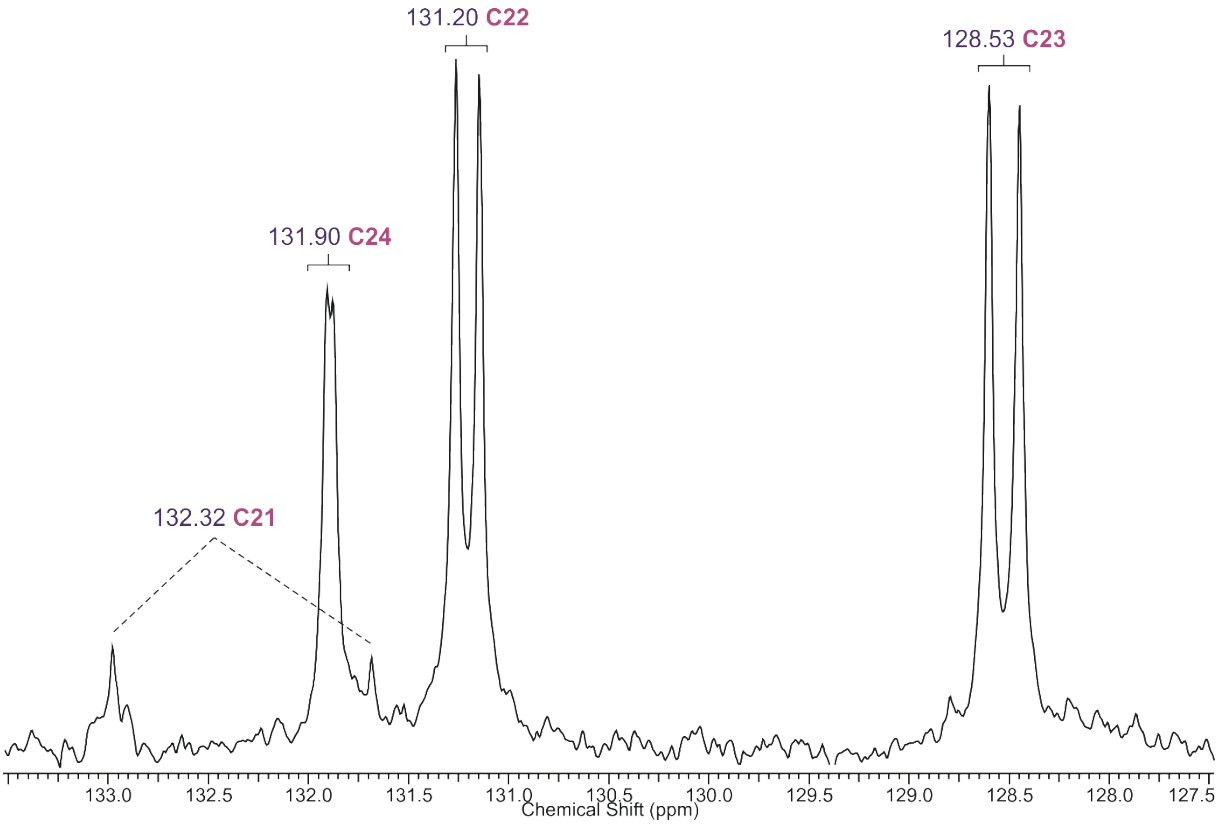


Fig. S23 ^{13}CNMR spectrum of $OPPh_2\{CH_2N(CH_2CH_2)_2O\}$ (**2O**) (aromatic region).

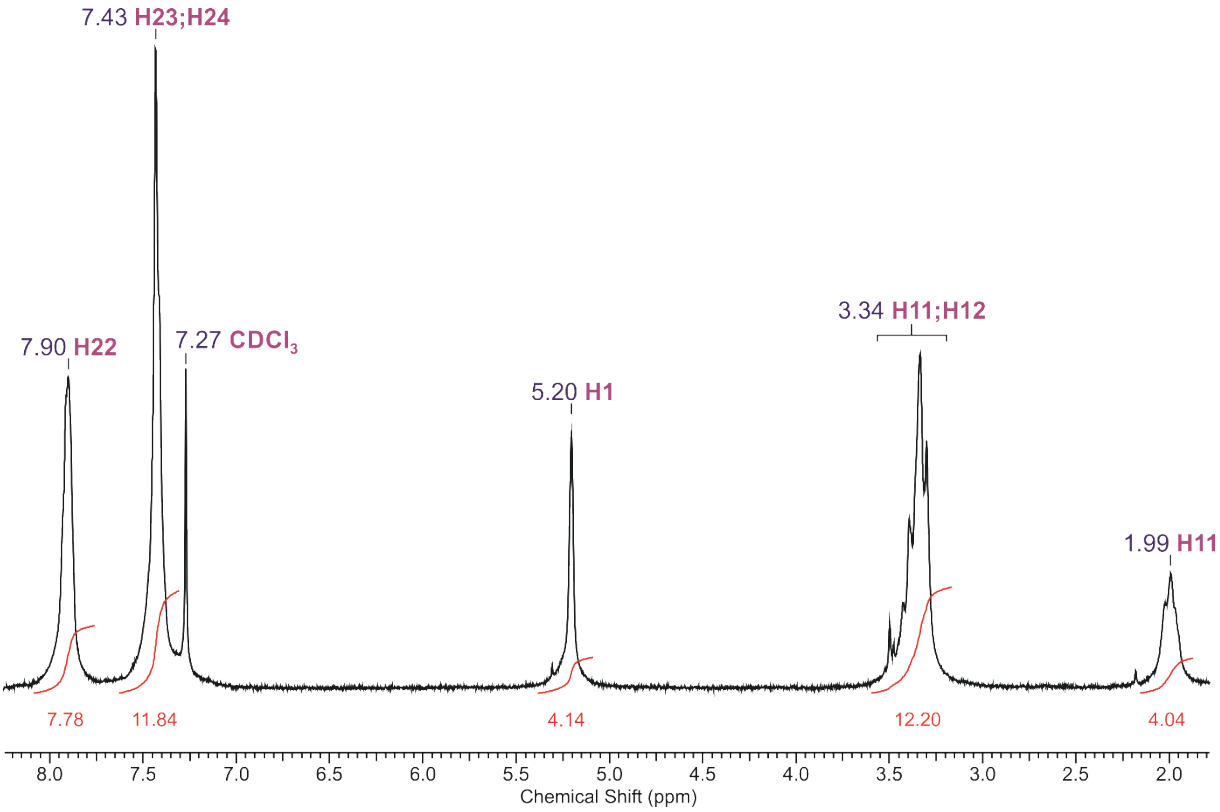


Fig. S24 ^{1}HNMR spectrum of $[RuCl_2(PPh_2\{CH_2N(CH_2CH_2)_2O\})_2]$ (**2A**).

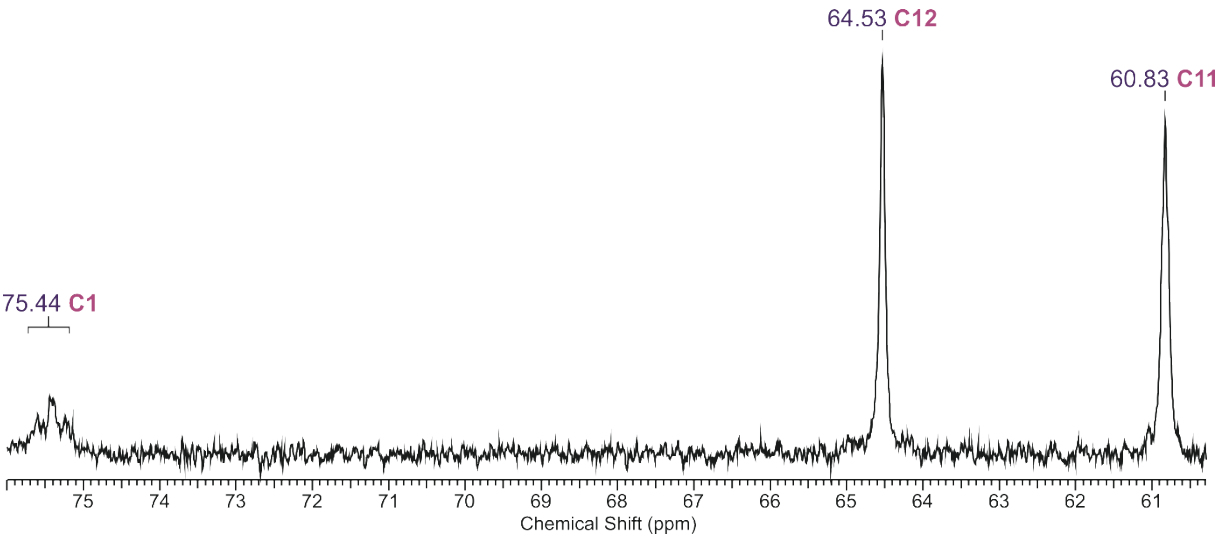


Fig. S25 ^{13}CNMR spectrum of $[RuCl_2(PPh_2\{CH_2N(CH_2CH_2)_2O\})_2]$ (**2A**) (aliphatic region).

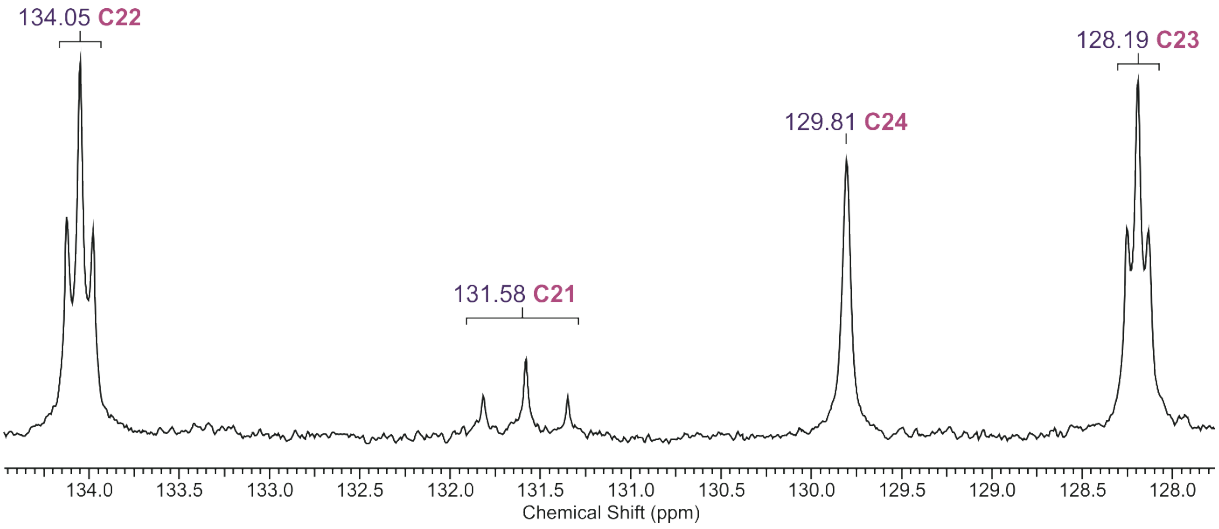


Fig. S26 ^{13}CNMR spectrum of $[RuCl_2(PPh_2\{CH_2N(CH_2CH_2)_2O\})_2]$ (**2A**) (aromatic region).

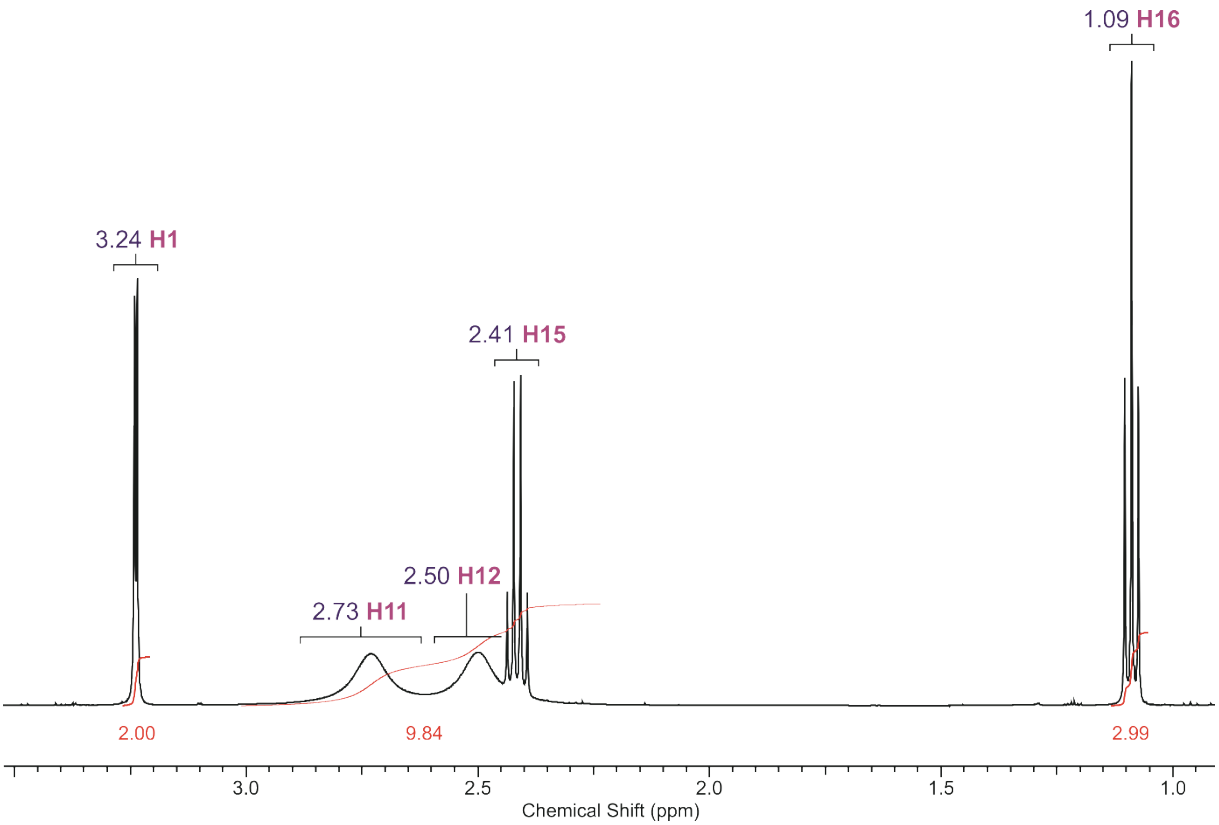


Fig. S27 ^{1}HNMR spectrum of $PPh_2\{CH_2N(CH_2CH_2)_2NCH_2CH_3\}$ (**3**) (aliphatic region).

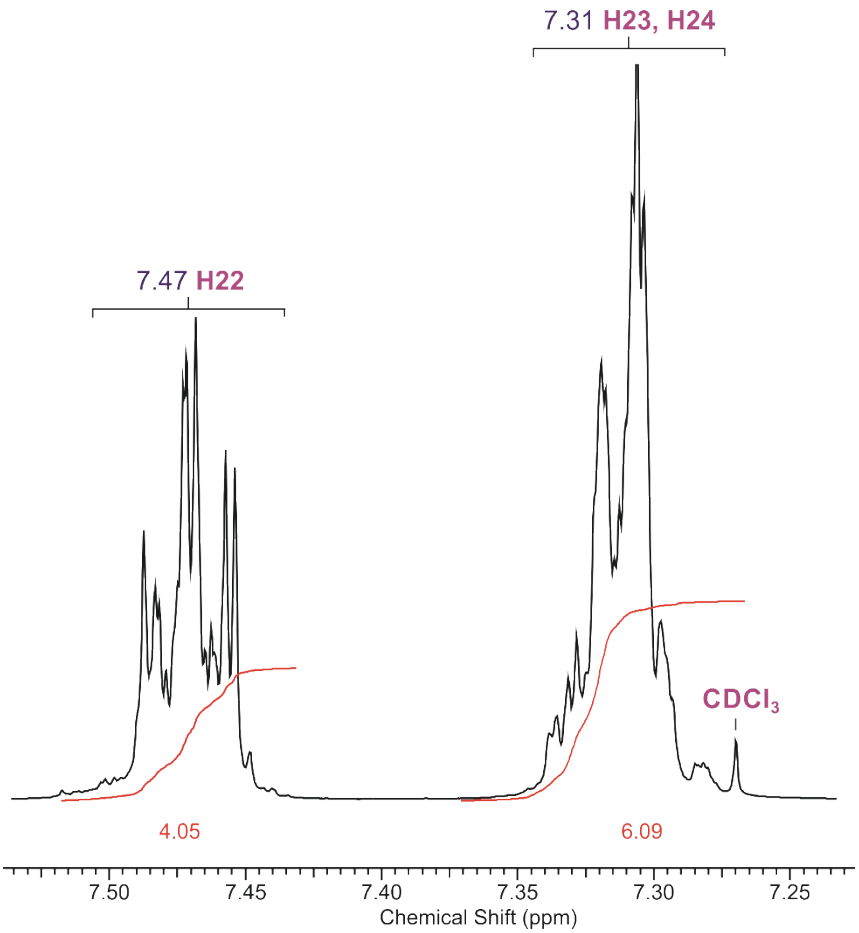


Fig. S28 ^{1}HNMR spectrum of $PPh_2\{CH_2N(CH_2CH_2)_2NCH_2CH_3\}$ (**3**) (aromatic region).

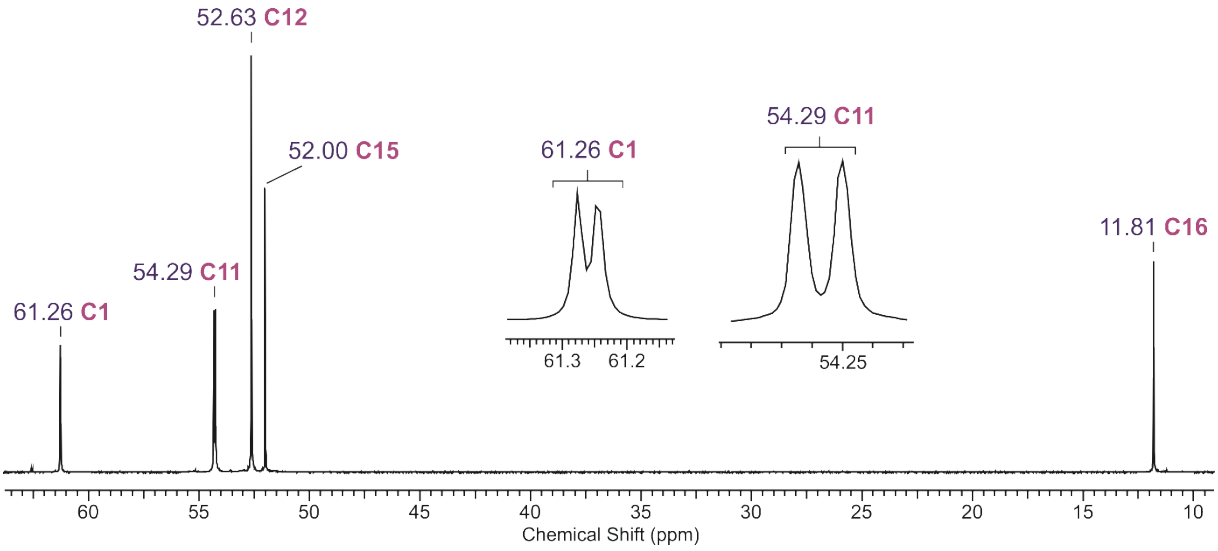


Fig. S29 ^{13}CNMR spectrum of $PPh_2\{CH_2N(CH_2CH_2)_2NCH_2CH_3\}$ (**3**) (aliphatic region).

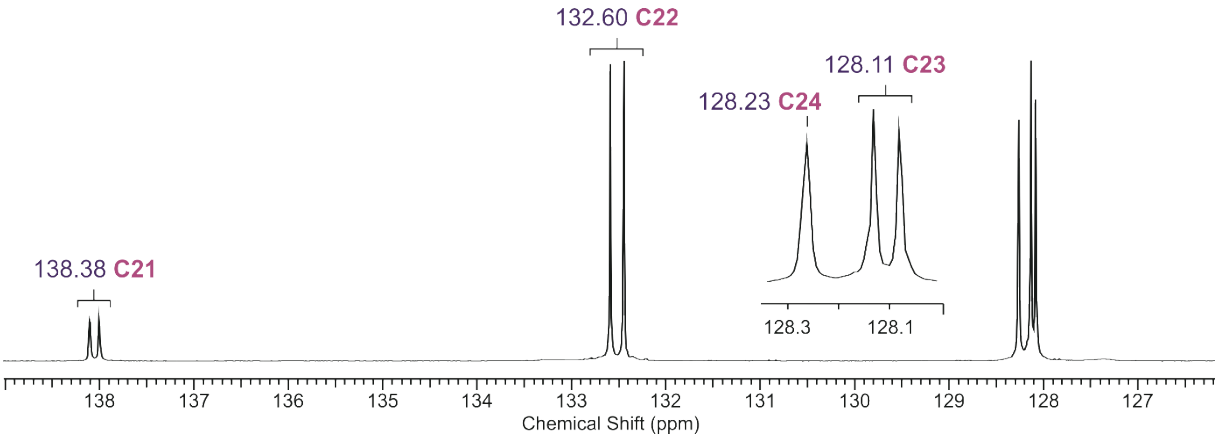


Fig. S30 ^{13}CNMR spectrum of $PPh_2\{CH_2N(CH_2CH_2)_2NCH_2CH_3\}$ (**3**) (aromatic region).

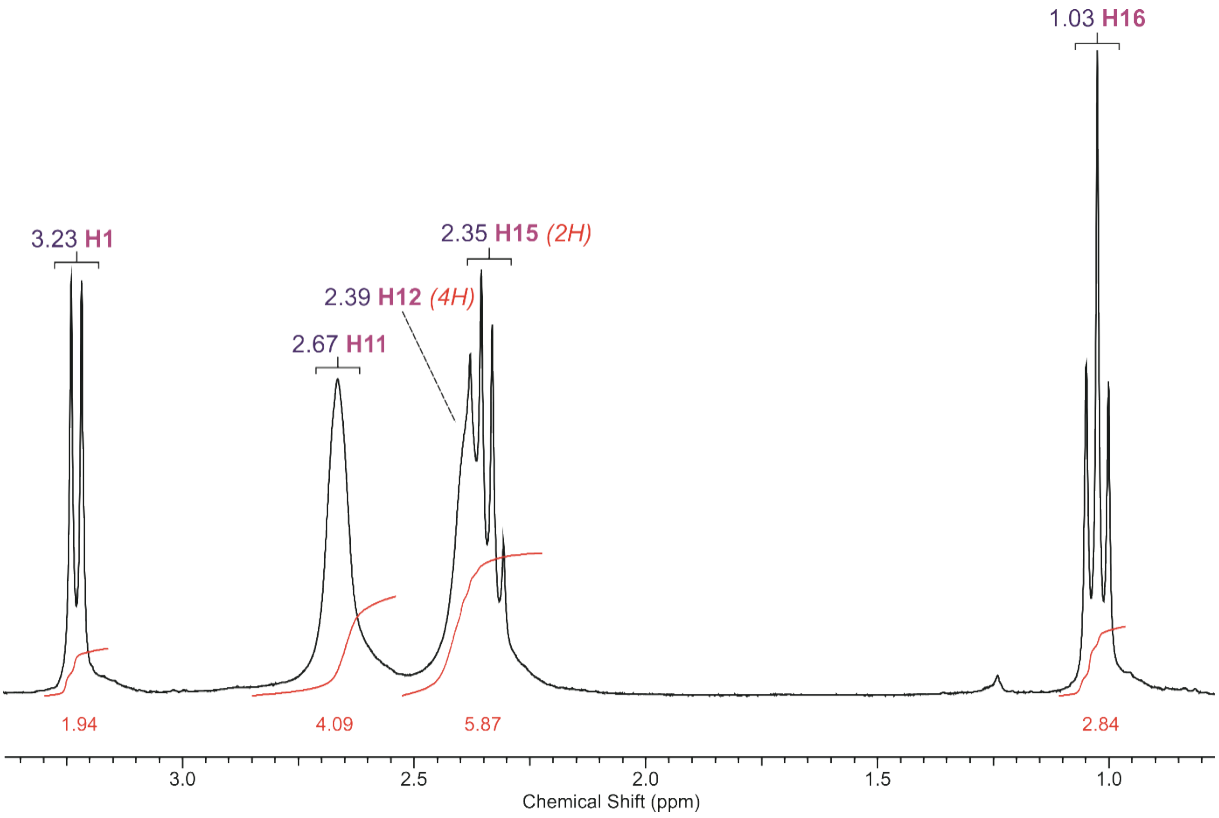


Fig. S31 ^{1}HNMR spectrum of $OPPh_2\{CH_2N(CH_2CH_2)_2NCH_2CH_3\}$ (**3O**) (aliphatic region).

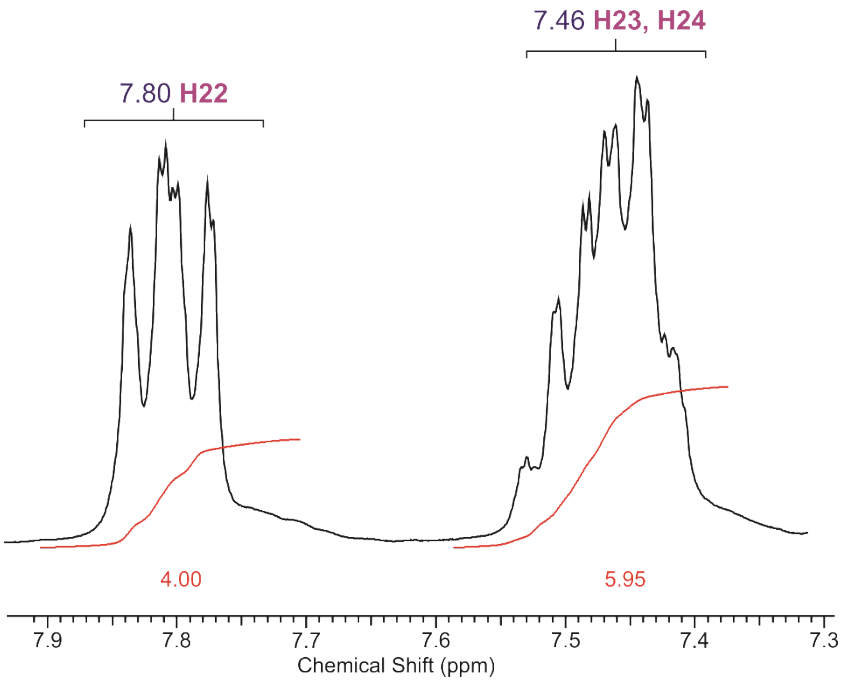


Fig. S32 ^{1}HNMR spectrum of $OPPh_2\{CH_2N(CH_2CH_2)_2NCH_2CH_3\}$ (**3O**) (aromatic region).

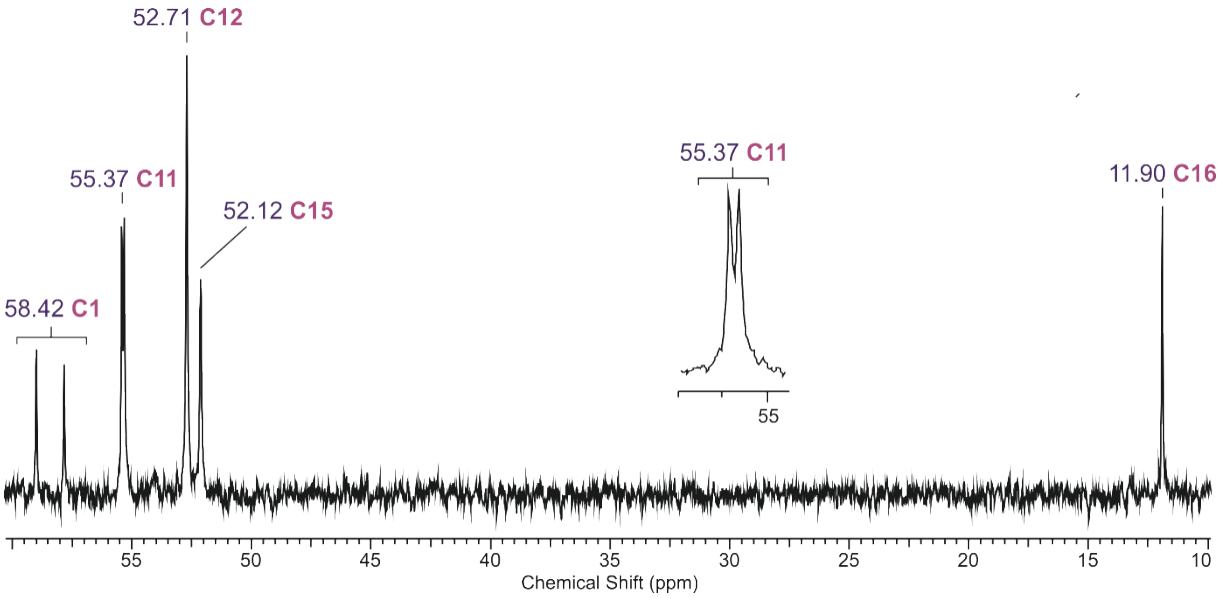


Fig. S33 ^{13}CNMR spectrum of $OPPh_2\{CH_2N(CH_2CH_2)_2NCH_2CH_3\}$ (**3O**) (aliphatic region).

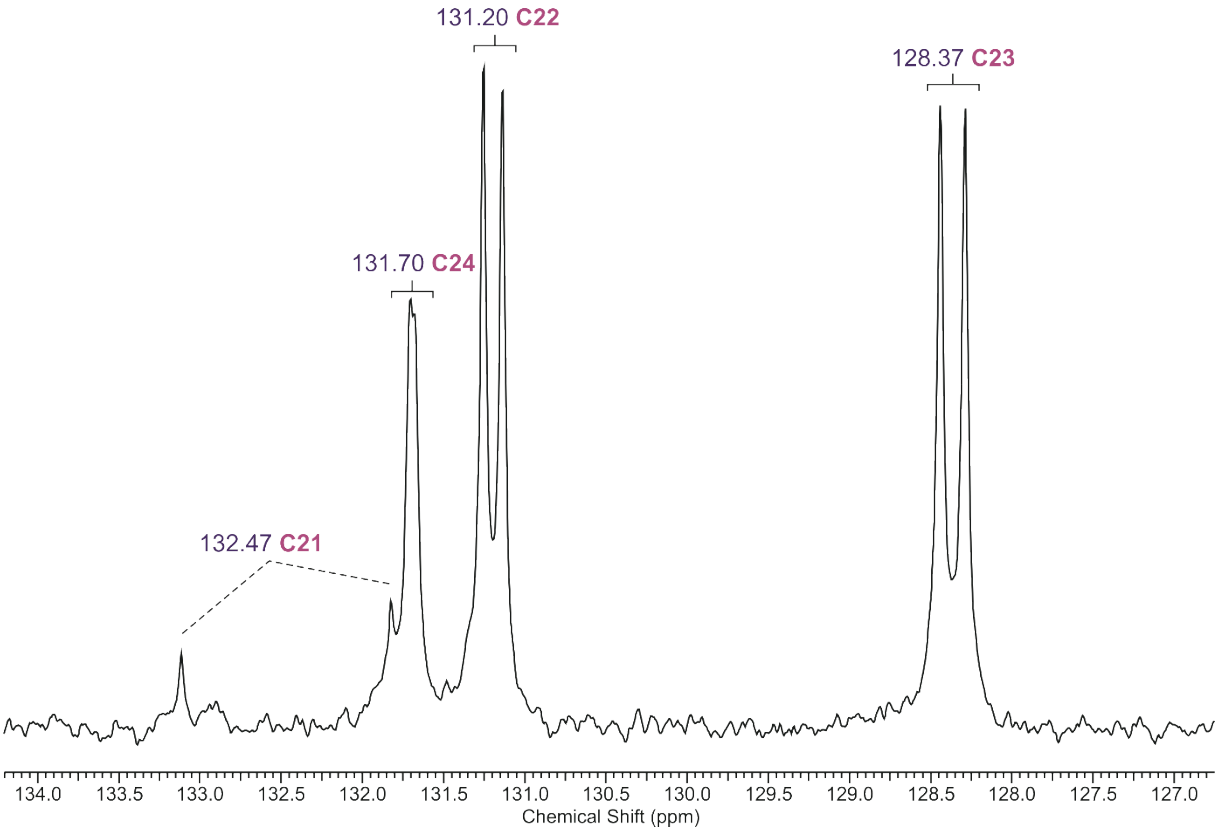


Fig. S34 ^{13}CNMR spectrum of $OPPh_2\{CH_2N(CH_2CH_2)_2NCH_2CH_3\}$ (**3O**) (aromatic region).

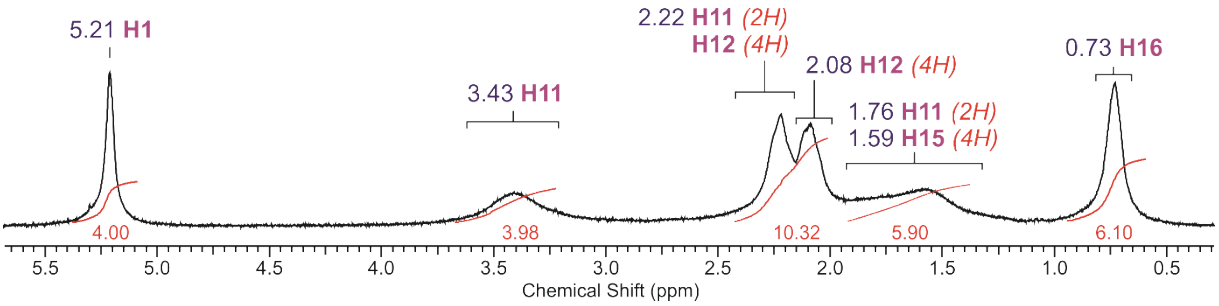


Fig. S35 ^{1}HNMR spectrum of $[RuCl_2(PPh_2\{CH_2N(CH_2CH_2)_2NCH_2CH_3\})_2]$ (**3A**) (aliphatic region).

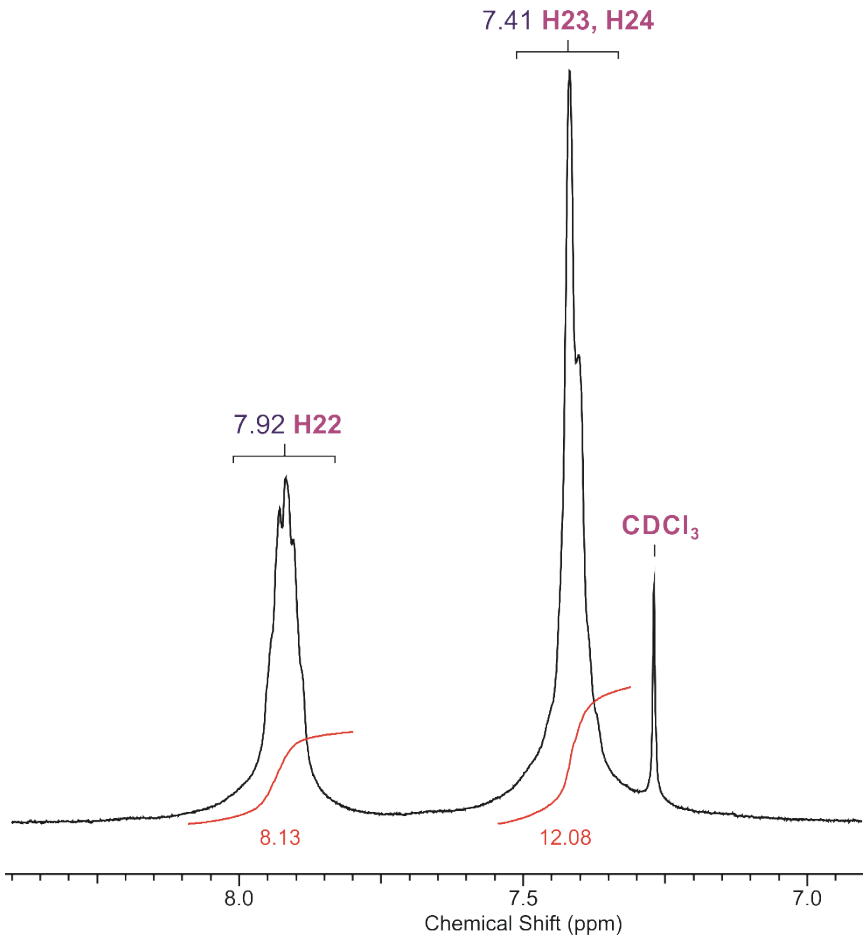


Fig. S36 ^{1}HNMR spectrum of [$RuCl_2(PPh_2\{CH_2N(CH_2CH_2)_2NCH_2CH_3\})_2$] (**3A**) (aromatic region).

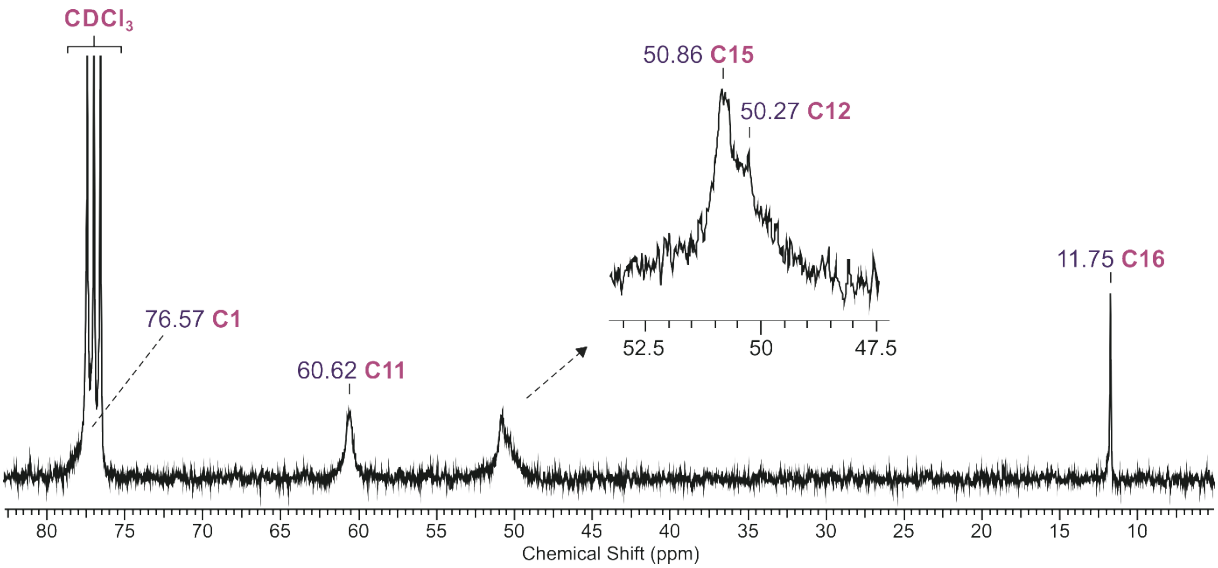


Fig. S37 ^{13}CNMR spectrum of [$RuCl_2(PPh_2\{CH_2N(CH_2CH_2)_2NCH_2CH_3\})_2$] (**3A**) (aliphatic region).

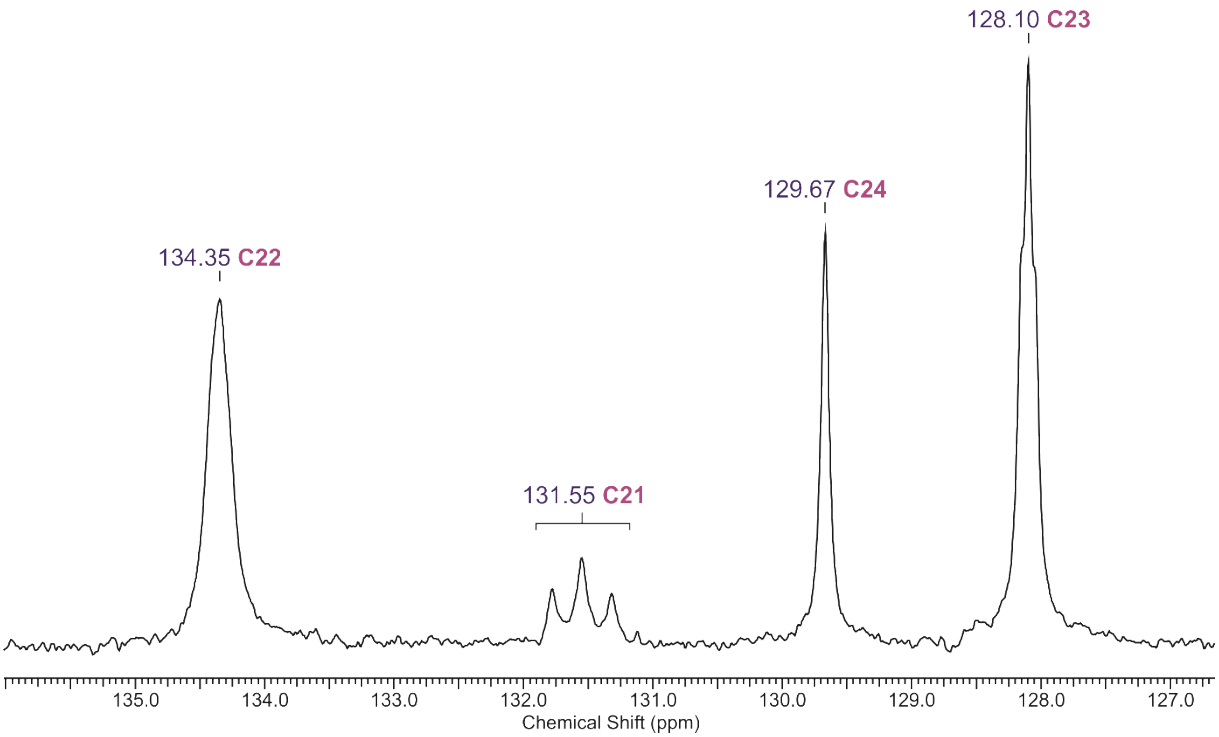


Fig. S38 ^{13}CNMR spectrum of $[RuCl_2(PPh_2\{CH_2N(CH_2CH_2)_2NCH_2CH_3\})_2]$ (**3A**) (aromatic region).

Table S1. Comparison of NMR data for $P\{CH_2N(CH_2CH_2)_2O\}_3$ (**1**), $OP\{CH_2N(CH_2CH_2)_2O\}_3$ (**1O**) and $[RuCl_2(P\{CH_2N(CH_2CH_2)_2O\}_3)_2]$ (**1A**).

	$P\{CH_2N(CH_2CH_2)_2O\}_3$ (1)		**$OP\{CH_2N(CH_2CH_2)_2O\}_3$ (1O)**		**$[RuCl_2(P\{CH_2N(CH_2CH_2)_2O\}_3)_2]$ (1A)**	
	σ [ppm]	**multiplicity J [Hz]**	**σ [ppm]**	**multiplicity J [Hz]**	**σ [ppm]**	**multiplicity J [Hz]**
			^{1}HNMR			
H^1	2.59 (6H)	d $^2J(H^1\text{-}P^1)$ = 2.1	2.83 (6H)	d $^2J(H^1\text{-}P^1)$ = 6.8	4.41 (2H*)	bm
H^{11}	2.50 (12H)	m	2.65 (12H)	bs	1.91 (2H) 3.08 (2H)	m d $^3J(H^{11}\text{-}H^{12})$ = 11.9
H^{12}	3.63 (12H)	m	3.67 (12H)	bt	3.46 (4H)	m
H^2	-	-	-	-	3.54 (2H) 3.74 (2H)	m s
H^{21}	-	-	-	-	2.74 (8H)	m
H^{22}	-	-	-	-	3.68 (8H)	m
			$^{13}C\{^1H\}$ NMR			
C^1	55.8	d $^1J(C^1\text{-}P^1)$ = 7.8	53.9	d $^1J(C^1\text{-}P^1)$ =82.3	72.5	T 12.7
C^{11}	54.6	d $^3J(C^{11}\text{-}P^1)$ = 8.3	55.9	d $^3J(C^{11}\text{-}P^1)$ = 7.2	60.2	T 2.8
C^{12}	66.5	s	67.0	s	64.3	s
C^2	-	-	-	-	49.7	T 14.3
C^{21}	-	-	-	-	55.3	T 2.2
C^{22}	-	-	-	-	66.8	s
			$^{31}P\{^1H\}$ NMR			
P^1	-61.47	s	47.11	s	-19.61	s

s – singlet, d – doublet, t – triplet, m – multiplet, b – broad, T – pseudo-triplets (virtual coupling)

* - due to equivalency of the coordinated phosphane molecules, the relative intensities are given per one molecule

Table S2. Comparison of NMR data for $PPh_2\{CH_2N(CH_2CH_2)_2O\}$ (**2**), $OPPh_2\{CH_2N(CH_2CH_2)_2O\}$ (**2O**) and $[RuCl_2(PPh_2\{CH_2N(CH_2CH_2)_2O\})_2]$ (**2A**).

	$PPh_2\{CH_2N(CH_2CH_2)_2O\}$ (2)		**$OPPh_2\{CH_2N(CH_2CH_2)_2O\}$ (2O)**		**$[RuCl_2(PPh_2\{CH_2N(CH_2CH_2)_2O\})_2]$ (2A)**	
	σ [ppm]	**multiplicity J [Hz]**	**σ [ppm]**	**multiplicity J [Hz]**	**σ [ppm]**	**multiplicity J [Hz]**
			$^{1}HNMR$			
H^{1}	3.25 (2H)	d $^{2}J(H^{1}\text{-}P^{1}) = 3.1$	3.24 (2H)	d $^{2}J(H^{1}\text{-}P^{1}) = 6.8$	5.20 (2H*)	s
H^{11}	2.71 (4H)	bt	2.65 (4H)	t $^{3}J(H^{11}\text{-}H^{12}) = 4.5$	1.99 (2H) 3.34 (2H)	m m
H^{12}	3.75 (4H)	t $^{3}J(H^{12}\text{-}H^{11}) = 4.7$	3.64 (4H)	t $^{3}J(H^{11}\text{-}H^{12}) = 4.5$	3.34 (4H)	m
H^{22}	7.53 (4H)	m	7.81 (4H)	m	7.90 (4H)	m
H^{23}, H^{24}	7.36 (6H)	m	7.50 (6H)	m	7.43 (6H)	m
			$^{13}C\{^{1}H\}$ NMR			
C^{1}	61.6	d $^{1}J(C^{1}\text{-}P^{1}) = 3.6$	58.7	d $^{1}J(C^{1}\text{-}P^{1}) = 87.9$	75.4	bT
C^{11}	54.7	d $^{3}J(C^{11}\text{-}P^{1}) = 9.1$	55.7	d $^{3}J(C^{11}\text{-}P^{1}) = 7.9$	60.8	s
C^{12}	66.7	s	66.9	s	64.5	s
C^{21}	138.1	d $^{1}J(C^{21}\text{-}P^{1}) = 12.7$	132.3	d $^{1}J(C^{21}\text{-}P^{1}) = 98.2$	131.6	T 17.7
C^{22}	132.5	d $^{2}J(C^{22}\text{-}P^{1}) = 18.2$	131.2	d $^{2}J(C^{22}\text{-}P^{1}) = 8.8$	134.1	T 5.0
C^{23}	128.1	d $^{3}J(C^{23}\text{-}P^{1}) = 6.4$	128.5	d $^{3}J(C^{23}\text{-}P^{1}) = 11.6$	128.2	T 3.9
C^{24}	128.3	s	131.9	d $^{4}J(C^{24}\text{-}P^{1}) = 1.9$	129.8	s
			$^{31}P\{^{1}H\}$ NMR			
P^{1}	-27.65	s	27.92	s	-23.68	s

s – singlet, d – doublet, t – triplet, m – multiplet, b - broad, T – pseudo-triplets (virtual coupling);

* - due to equivalency of the coordinated phosphane molecules, the relative intensities are given per one molecule.

Table S3. Comparison of NMR data for $PPh_2\{CH_2N(CH_2CH_2)_2NCH_2CH_3\}$ (**3**), $OPPh_2\{CH_2N(CH_2CH_2)_2NCH_2CH_3\}$ (**3O**) and $[RuCl_2(PPh_2\{CH_2N(CH_2CH_2)_2NCH_2CH_3\})_2]$ (**3A**).

	$PPh_2\{CH_2N(CH_2CH_2)_2NCH_2CH_3\}$ (3)		$OPPh_2\{CH_2N(CH_2CH_2)_2NCH_2CH_3\}$ (3O)		$[RuCl_2(PPh_2\{CH_2N(CH_2CH_2)_2NCH_2CH_3\})_2]$ (3A)	
	σ [ppm]	**multiplicity J [Hz]**	**σ [ppm]**	**multiplicity J [Hz]**	**σ [ppm]**	**multiplicity J [Hz]**
				^{1}HNMR		
H^1	3.24 (2H)	d $^2J(H^1\text{-}P^1)$ = 2.9	3.23 (2H)	d $^2J(H^1\text{-}P^1)$ = 6.8	5.21 (2H*)	s
H^{11}	2.73 (4H)	bm	2.67 (4H)	bm	1.76 (1H) 2.22 (1H) 3.43 (2H)	bm bm bm
H^{12}	2.50 (4H)	bm	2.39 (4H)	bm	2.08 (2H) 2.22 (2H)	bm bm
H^{15}	2.41 (2H)	q $^3J(H^{15}\text{-}H^{16})$ = 7.3	2.35 (2H)	q $^3J(H^{15}\text{-}H^{16})$ = 7.2	1.59 (2H)	bm
H^{16}	1.09 (3H)	t $^3J(H^{16}\text{-}H^{15})$ = 7.3	1.03 (3H)	t $^3J(H^{16}\text{-}H^{15})$ = 7.2	0.73 (3H)	bs
H^{22}	7.47 (4H)	m	7.80 (4H)	m	7.92 (4H)	m
H^{23}, H^{24}	7.31 (6H)	m	7.46 (6H)	m	7.41 (6H)	m
				$^{13}C\{^1H\}$ NMR		
C^1	61.3	d $^1J(C^1\text{-}P^1)$ = 3.6	58.4	d $^1J(C^1\text{-}P^1)$ = 88.4	76.6 under $CDCl_3$	-
C^{11}	54.3	d $^3J(C^{11}\text{-}P^1)$ = 9.1	55.4	d $^3J(C^{11}\text{-}P^1)$ = 7.9	60.6	bm
C^{12}	52.6	s	52.7	s	50.3	bm
C^{15}	52.0	s	52.1	s	50.9	bm
C^{16}	11.8	s	11.9	s	11.8	s
C^{21}	138.4	d $^1J(C^{21}\text{-}P^1)$ = 12.7	132.5	d $^1J(C^{21}\text{-}P^1)$ = 97.2	131.6	T 17.2
C^{22}	132.6	d $^2J(C^{22}\text{-}P^1)$ = 18.2	131.2	d $^2J(C^{22}\text{-}P^1)$ = 8.8	134.4	bm
C^{23}	128.1	d $^3J(C^{23}\text{-}P^1)$ = 6.4	128.4	d $^3J(C^{23}\text{-}P^1)$ = 11.6	128.1	bm
C^{24}	128.2	s	131.7	d $^4J(C^{24}\text{-}P^1)$ = 1.4	129.7	s
				$^{31}P\{^1H\}$ NMR		
P^1	-26.69	s	27.58	s	-25.28	s

s – singlet, d – doublet, t – triplet, m – multiplet, b – broad,T – pseudo-triplets (virtual coupling)

* - due to equivalency of the coordinated phosphane molecules, the relative intensities are given per one molecule

Table S4. Crystallographic experimental details.

Parameters	**1A**	**2A**	**2B**·2CH_3CN	**3A**·2CH_3OH·2H_2O	**3B**·$CHCl_3$
Moiety formula	$RuCl_2C_{30}H_{60}N_6O_6P_2$	$RuCl_2C_{34}H_{40}N_2O_2P_2$	$RuCl_2C_{42}H_{52}N_6O_2P_2$	$RuCl_2C_{40}H_{62}N_4O_4P_2$	$RuCl_5C_{43}H_{57}N_6P_2$
Formula weight ($g \cdot mol^{-1}$)	834.76	742.62	906.80	896.87	998.23
Crystal description	yellow-orange blocks	yellow-orange blocks	yellow needles	yellow-orange blocks	yellow needles
Temperature (K)	132	120	100	293	293
Type of radiation	Cu *Kα*	Mo *Kα*	Mo *Kα*	Mo *Kα*	Mo *Kα*
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	C2/c	C2/c	$P2_1/m$
Unit cell dimensions					
a (Å)	10.2331(1)	11.7180(3)	11.7701(3)	25.716(3)	9.2987(6)
b (Å)	17.3721(2)	10.6960(3)	15.4658(4)	10.5327(10)	25.2380(16)
c (Å)	10.6544(2)	13.4140(4)	23.8880(5)	15.7639(15)	10.4915(7)
β (°)	92.496(1)	104.386(2)	101.725(2)	91.084(9)	100.394(5)
Volume ($Å^3$)	1892.2(1)	1628.5(1)	4257.7(2)	4269.0(8)	2421.7(3)
Z	2	2	4	4	2
Density calc. (Mg/m^3)	1.465	1.514	1.415	1.395	1.396
Absorption coeff. (mm^{-1})	5.849	0.778	0.612	0.611	0.702
F(000)	876	764	1880	1880	1032
$\theta_{min} - \theta_{max}$ (°)	4.87 to 71.32	2.81 to 27.46	3.02 to 31.89	3.06 to 36.87	2.81 to 36.79
hkl range	-12 ← h ← 12 -21 ← k ← 21 -13 ← l ← 12	-15 ← h ← 15 -13 ← k ← 13 -17 ← l ← 17	-17 ← h ← 4 -11 ← k ← 19 -29 ← l ← 35	-34 ← h ← 43 -10 ← k ← 15 -24 ← l ← 21	-11 ← h ← 14 -34 ← k ← 33 -14 ← l ← 16
Reflections collected	27311	13237	9470	19269	26561
Independent reflections	3657	3718	6038	6956	7510
R_{int}	0.0493	0.0354	0.0202	0.0975	0.0454
Completeness to θ_{max} (%)	99.7	99.8	95.7	99.3	99.6
Absorption correction type	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
T_{max} and T_{min}	1.000 and 0.620	1.000 and 0.579	1.0000 and 0.9783	1.0000 and 0.8713	1.000 and 0.8855
Data/restraints/parameters	3657 / 0 / 214	3718 / 0 / 196	6038 / 0 / 252	6956 / 3 / 271	7510 / 0 / 276
Goodness of fit F^2	1.065	1.091	1.041	0.972	1.023
R_1, wR_2 [I>2σ(I)]	0.0257, 0.0625	0.0288, 0.0656	0.0402, 0.0978	0.0971, 0.2263	0.0465, 0.0989
R_1, wR_2 (all data)	0.0306, 0.0659	0.0392, 0.0703	0.0505, 0.1053	0.1713, 0.2634	0.0599, 0.1054
Largest diff. peak and hole ($e Å^{-3}$)	0.780, -0.524	0.824, -0.803	1.110, -0.641	6.759, -1.397	0.877, -0.862

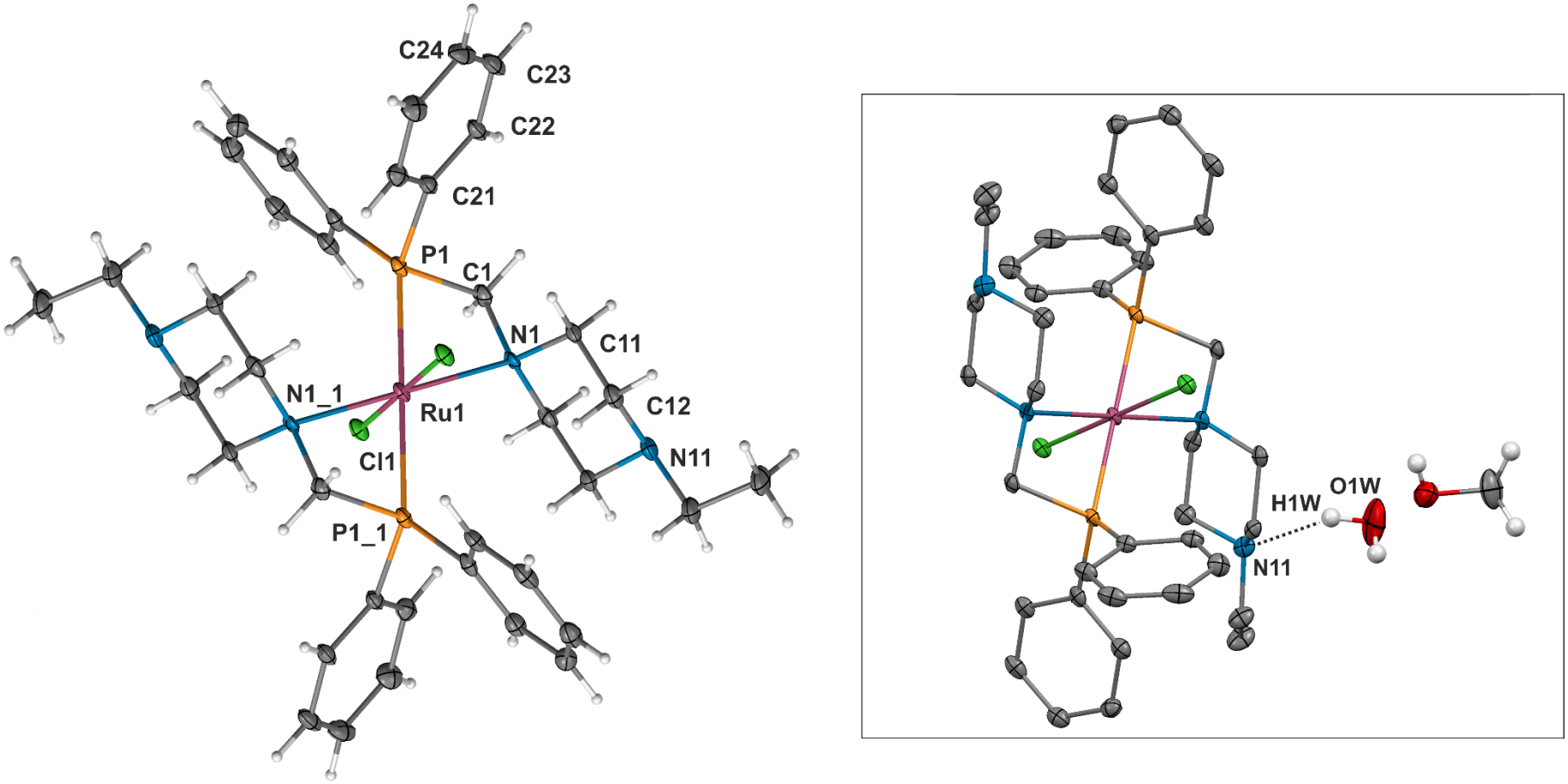


Fig. S39 Two views (30% probability ellipsoids) of the **3A** molecule in **3A**·2CH_3OH·2H_2O complex with the atoms numeration scheme. Hydrogen atoms for view in frame were omitted for clarity. The hydrogen bond parameters: O1W-H1W···N11 d(D-H)=0.89(2) Å, d(H···A)=1.91(5) Å, d(D···A)=2.78(1) Å, <(DHA)=162(13)º.

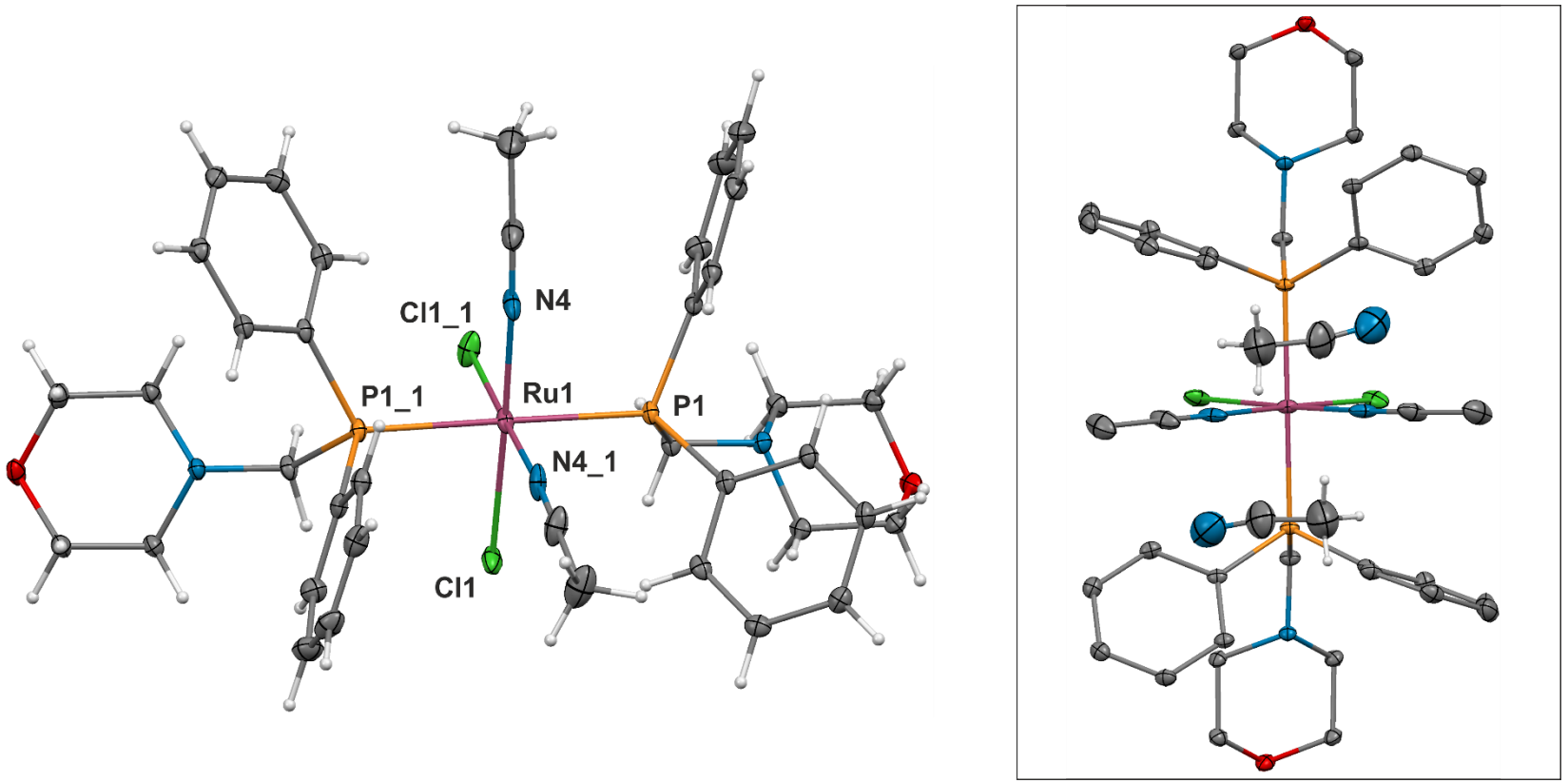


Fig. S40 Two views (30% probability ellipsoids) of the **2B** molecule in **2B**·2CH_3CN complex with the atoms numeration scheme. Hydrogen atoms for view in frame were omitted for clarity.

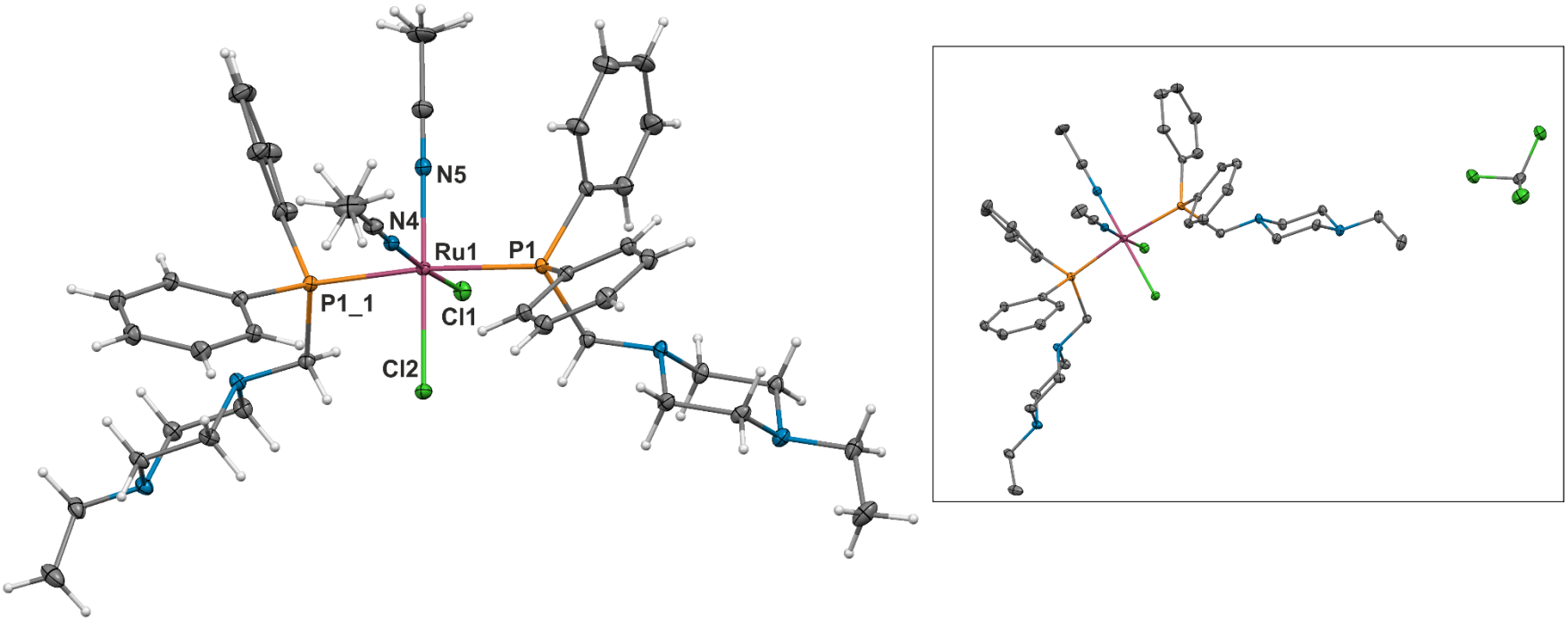


Fig. S41 Two views (30% probability ellipsoids) of molecule **3B** in **3B**·$CHCl_3$ complex with the atoms numeration scheme. Hydrogen atoms for view in frame were omitted for clarity.