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Electronic Supporting Information

Phosphine-functionalised Tris(pyrazolyl)methane Ligands and their Mono- and Heterobimetallic complexes

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S1. X-Ray crystallography

Crystal data collection and processing parameters are given below. In order to avoid degradation, single crystals were mounted in perfluoropolyalkyletheroil on top of the edge of an open Mark tube and then brought into the cold nitrogen stream of a low- temperature device (Oxford Cryosystems Cryostream unit) so that the oil solidified. Diffraction data were measured using a Stoe IPDS II diffractometer and graphite-monochromated MoK_α (0.71073 Å) radiation. The structures were solved by dual-space direct methods with SHELXT,[S5] followed by full-matrix least-squares refinement using SHELXL-2014/7.[S6] All non-hydrogen atoms were refined anisotropically, with organic hydrogen atoms placed in calculated positions using a riding model. Absorption corrections were applied for compounds **3**-**6** (multi-scan). Crystallographic data, data collection, and refinement details are summarized in Table S2-1. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1898143-1898147. Copies of the data can be obtained from https://summary.ccdc.cam.ac.uk/structure-summary-form.

[S1] G. M. Sheldrick, *Acta Cryst. Sect. A*, 2015, **71**, 3–8.

[S2] G. M. Sheldrick, *Acta Cryst. Sect. C*, 2015, **71**, 3–8.

Table S1-1 Crystallographic data, data collection and refinement details for **2a**-**2c**.

Compound	**2a**	**2b**	**2c**
Empirical formula	$C_{22}H_{19}N_6P$	$C_{18}H_{27}N_6P$	$C_{16}H_{23}N_6P$
M	398.40	358.42	330.37
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	*Pna*2$_1$	*P*-1	*P*2$_1$/*c*
a /pm	1741.6(4)	812.93(16)	898.30(18)
b /pm	843.90(17)	863.11(17)	1143.8(2)
c /pm	4080.6(8)	1558.2(3)	1681.2(3)
α /°	90	77.76(3)	90
β /°	90	86.99(3)	97.07(3)
γ /°	90	66.40(3)	90
V /·10^6 pm^3	5997(2)	978.5(4)	1714.3(6)
μ /mm^{-1}	0.159	0.154	0.169
D_{calcd} /g cm^{-3}	1.324	1.217	1.280
Crystal dim. /mm^3	0.4 × 0.3 × 0.3	0.6 × 0.3 × 0.3	0.3 × 0.3 × 0.3
Z	12	2	4
T /K	200	200	200
$2\theta_{max}$ /°	51.998	58.532	58.65
Refls. measured	80621	18987	32515
Refls. unique	11783 (R_{int} = 0.0935)	5275 (R_{int} = 0.0458)	4632 (R_{int} = 0.0911)
Param./restraints	786 / 1	228 / 0	212 / 0
*R*1 [$I \geq 2\sigma(I)$]	0.0580	0.0408	0.0393
*wR*2 (all data)	0.1613	0.1196	0.1014
max./min. res. elec. dens. /e ·10^{-6} pm^{-3}	1.38 / –0.28	0.32 / –0.32	0.26 / –0.37
CCDC	1916045	1916046	1916047

Table S1-2 Crystallographic data, data collection and refinement details for **3a-3c**.

Compound	**3a**	**3b**	**3c**
Empirical formula	$C_{23}H_{20}ClN_6OPRh$	$C_{19}H_{27}ClN_6OPRh$	$C_{17}H_{23}ClN_6OPRh$
M	565.78	524.79	496.74
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1$
a /pm	1043.0(2)	1796.9(4)	863.20(17)
b /pm	1544.2(3)	893.00(18)	1292.7(3)
c /pm	1438.2(3)	1540.8(3)	1000.3(2)
α /°	90	90	90
β /°	104.0(3)	110.01(3)	114.42(3)
γ /°	90	90	90
V /$\cdot 10^6$ pm^3	2247.2(8)	2323.1(9)	1016.3(4)
μ /mm^{-1}	0.980	0.941	1.070
D_{calcd} /g cm^{-3}	1.672	1.500	1.623
Crystal dim. /mm^3	$0.3 \times 0.2 \times 0.2$	$0.5 \times 0.5 \times 0.4$	$0.6 \times 0.6 \times 0.5$
Z	4	4	2
T /K	200	200	200
$2\theta_{max}$ /°	51.996	51.998	58.444
Refls. measured	15146	14865	19391
Refls. unique	4393 (R_{int} = 0.0375)	4548 (R_{int} = 0.1361)	5438 (R_{int} = 0.0528)
Param./restraints	298 / 0	265 / 0	249 / 1
$R1$ [$I \geq 2\sigma(I)$]	0.0240	0.0565	0.0290
*wR*2 (all data)	0.0648	0.1632	0.0687
max./min. res. elec. dens. /e $\cdot 10^{-6}$ pm^{-3}	0.35 / −0.66	0.93 / −1.17	0.54 / −0.67
CCDC	1916048	1916049	1916050

Table S1-3 Crystallographic data, data collection and refinement details for **4-6**.

Compound	**4**	**5**	**6**
Empirical formula	$C_{21}H_{28}F_6N_6P_2Ru$	$C_{22}H_{19}AuClN_6P$	$C_{25}H_{24}ClN_6PPd$
M	641.50	630.82	581.32
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	*Pbcn*	$P2_1/n$	$P2_12_12_1$
a /pm	1762.9(4)	876.40(18)	902.70(18)
b /pm	1842.8(4)	1560.4(3)	1594.2(3)
c /pm	1530.9(3)	1609.1(3)	1722.5(3)
α /°	90	90	90
β /°	90	90.76(3)	90
γ /°	90	90	90
V /·10^6 pm^3	4976.1(17)	2200.3(8)	2478.8(9)
μ /mm^{-1}	0.827	6.903	0.947
D_{calcd} /g cm^{-3}	1.713	1.904	1.558
Crystal dim. /mm^3	0.4 × 0.4 × 0.4	0.5 × 0.3 × 0.2	0.25 × 0.2 × 0.1
Z	8	4	4
T /K	200	200	200
$2\theta_{max}$ /°	58.53	54	53.994
Refls. measured	91924	12511	9518
Refls. unique	6718 (R_{int} = 0.0415)	4760 (R_{int} = 0.0548)	5395 (R_{int} = 0.0552)
Param./restraints	332 / 70	281 / 0	317 / 36
$R1$ [$I \geq 2\sigma(I)$]	0.0302	0.0327	0.0503
$wR2$ (all data)	0.0821	0.1086	0.1489
max./min. res. elec. dens. /e ·10^{-6} pm^{-3}	0.95 / −0.48	1.02 / −1.34	0.80 / −1.48
CCDC	1916051	1916052	1916053

Table S1-4 Crystallographic data, data collection and refinement details for **7**-**8**.

Compound	**7**	**8**
Empirical formula	$C_{22}H_{19}Cl_2N_6PPd$	$C_{22}H_{19}Cl_4CuN_6PPd \cdot 2\ C_2H_3N$
M	575.70	792.25
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a /pm	1481.8(3)	1126.8(2)
b /pm	927.10(19)	1481.9(3)
c /pm	1699.8(3)	1865.9(4)
α /°	90	90
β /°	100.998(3)	98.36(3)
γ /°	90	90
V /·10^6 pm^3	2292.7(8)	3082.6(11)
μ /mm^{-1}	1.136	1.704
D_{calcd} /g cm^{-3}	1.668	1.707
Crystal dim. /mm^3	0.4 × 0.3 × 0.25	0.15 × 0.1 × 0.05
Z	4	4
T /K	200	200
$2\theta_{max}$ /°	58.348	51.996
Refls. measured	15955	18940
Refls. unique	6154 (R_{int} = 0.0289)	6055 (R_{int} = 0.0960)
Param./restraints	290 / 0	373 / 0
$R1$ [$I \geq 2\sigma(I)$]	0.0296	0.0626
$wR2$ (all data)	0.0817	0.01639
max./min. res. elec. dens. /e ·10^{-6} pm^{-3}	0.72 / −0.76	1.97 / −1.58
CCDC	1916054	1916055

S2. NMR-spectra

Compound **2a**

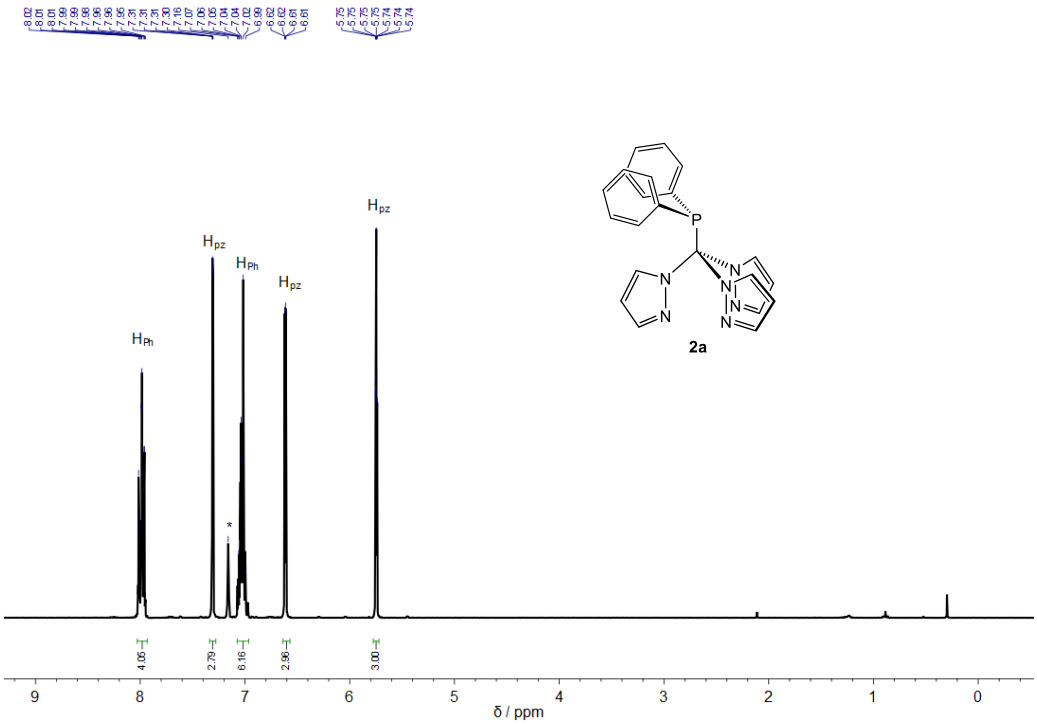


Figure 1 ^{1}H NMR spectrum of **2a** in C_6D_6 (*).

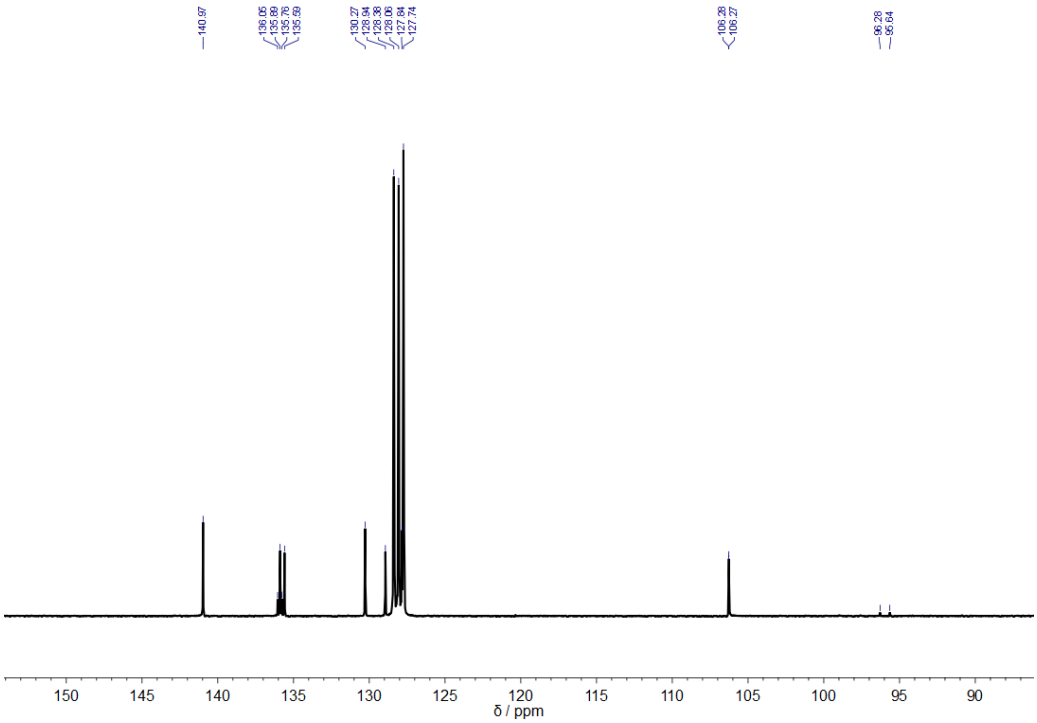


Figure 2 $^{13}C\{^{1}H\}$ NMR spectrum of **2a** in C_6D_6.

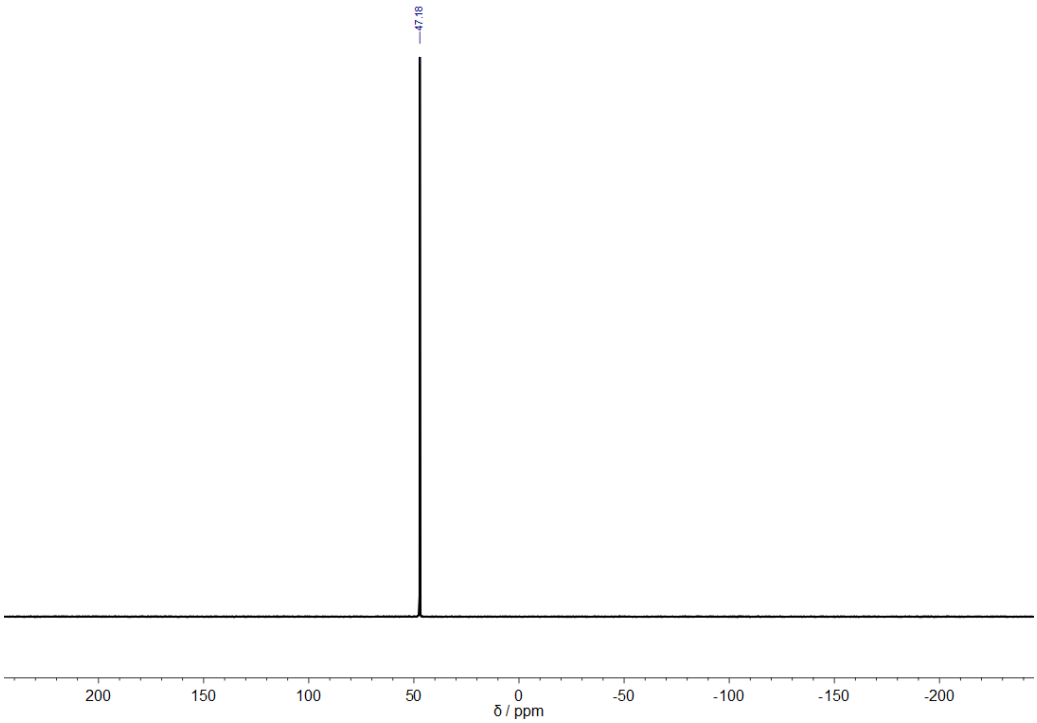


Figure 3 $^{31}P\{^{1}H\}$ NMR spectrum of **2a** in C_6D_6.

Compound **2b**

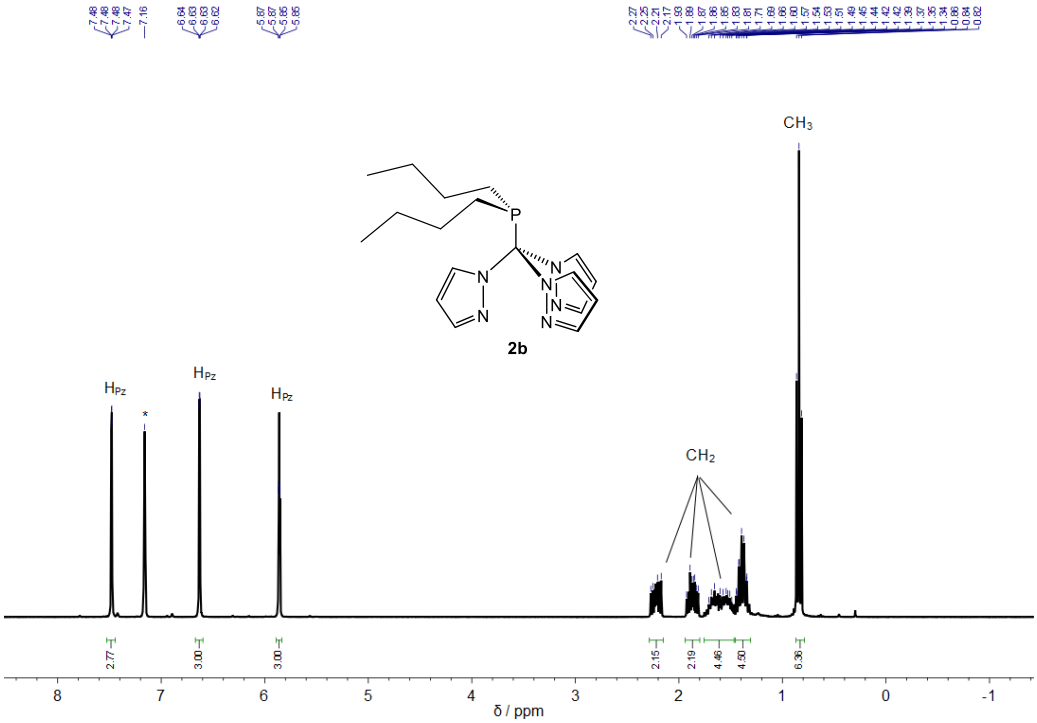


Figure 4 ^{1}H NMR spectrum of **2b** in C_6D_6 (*).

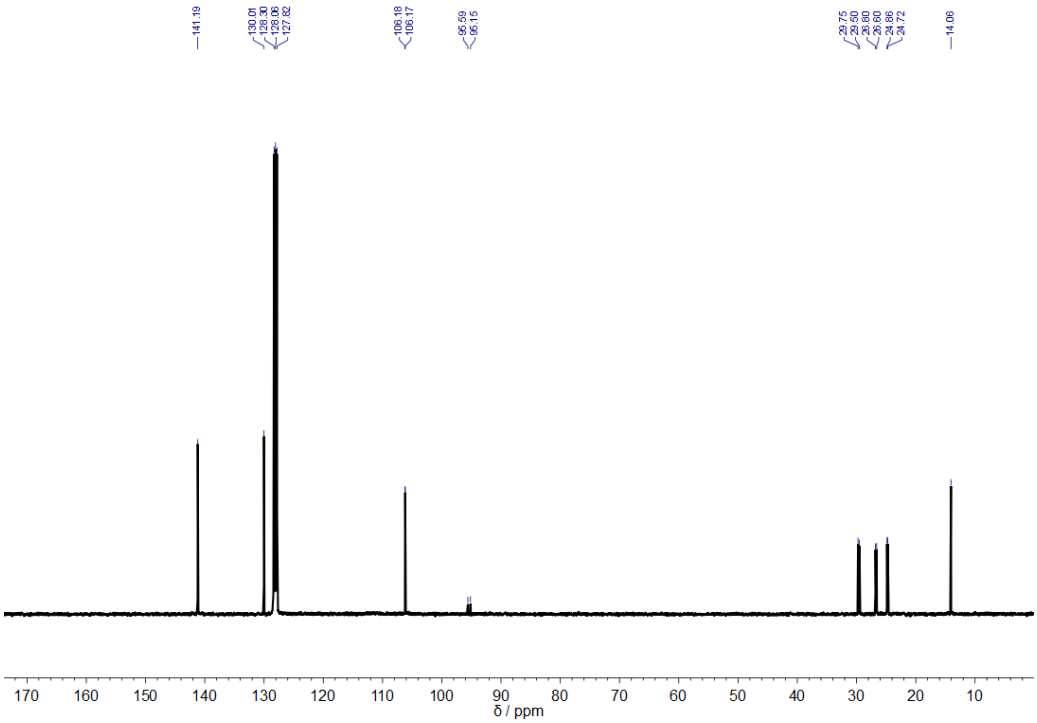


Figure 5 $^{13}C\{^{1}H\}$ NMR spectrum of **2b** in C_6D_6.

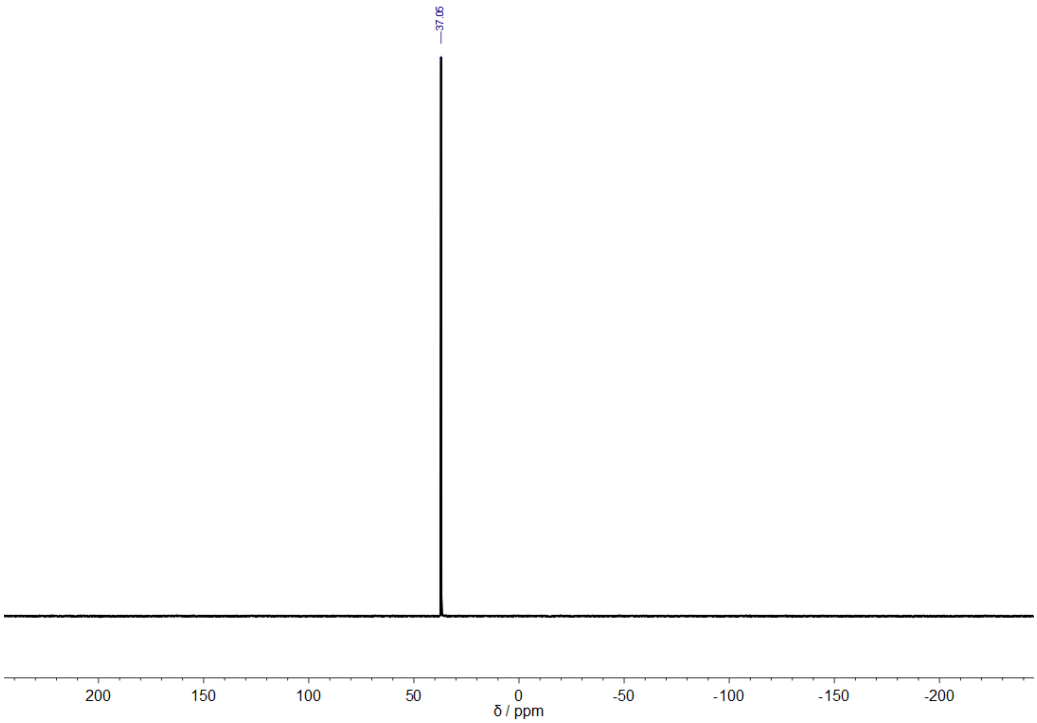


Figure 6 $^{31}P\{^{1}H\}$ NMR spectrum of **2b** in C_6D_6.

Compound **2c**

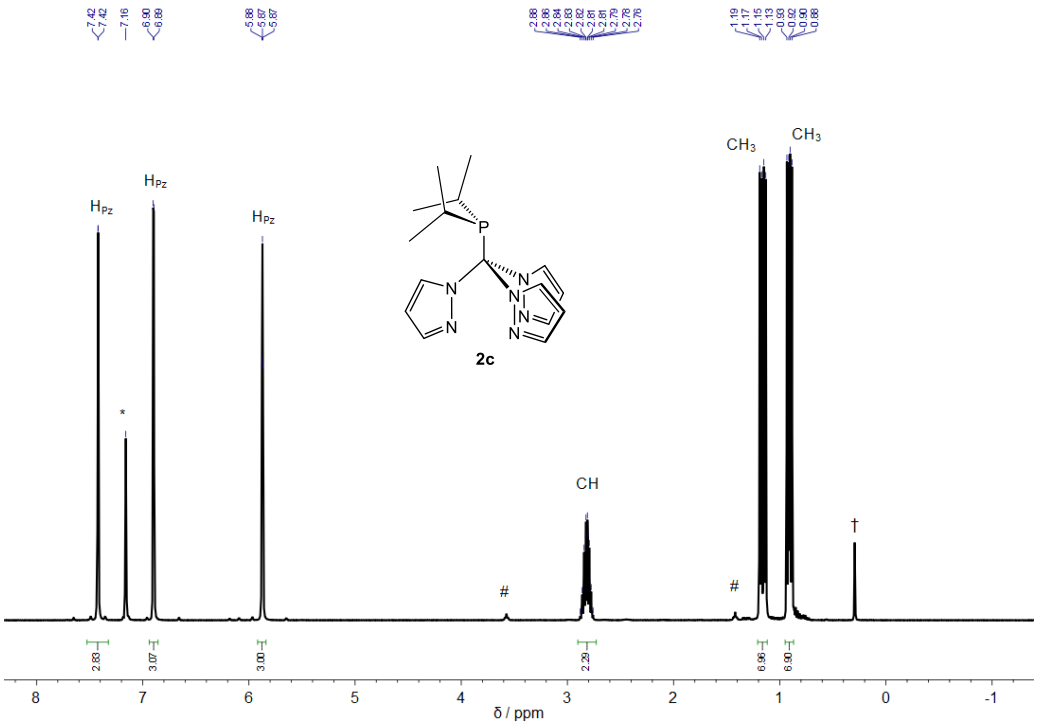


Figure 7 ^{1}H NMR spectrum of **2c** in C_6D_6 (*). Signals marked with # correspond to THF and † to silicon grease.

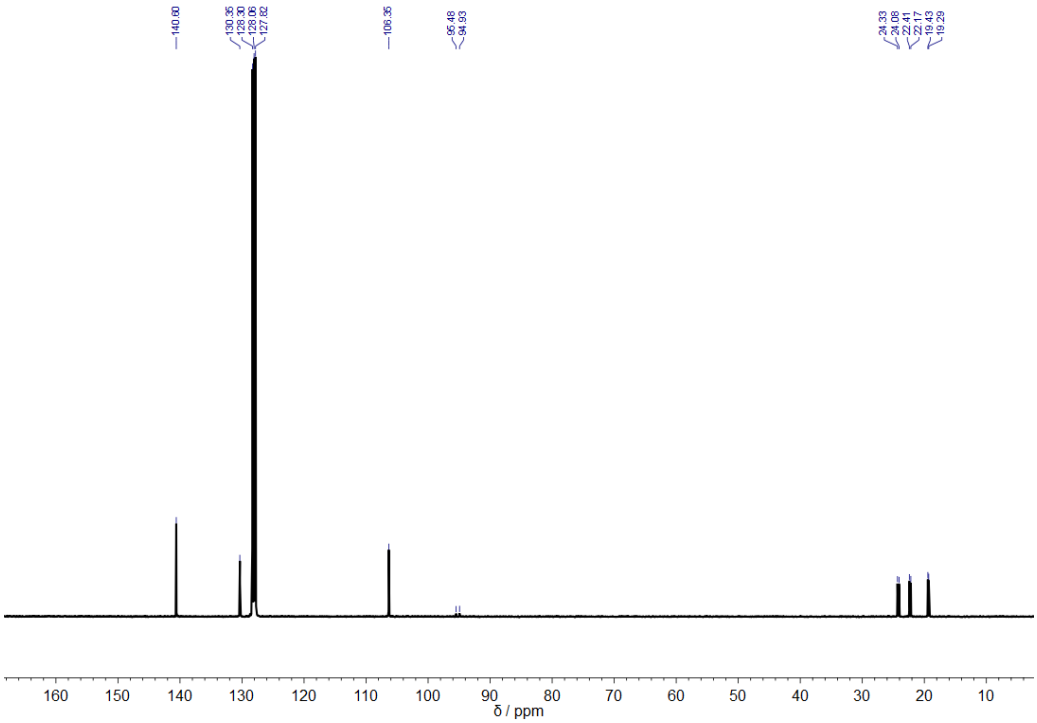


Figure 8 ^{13}C{^{1}H} NMR spectrum of **2c** in C_6D_6.

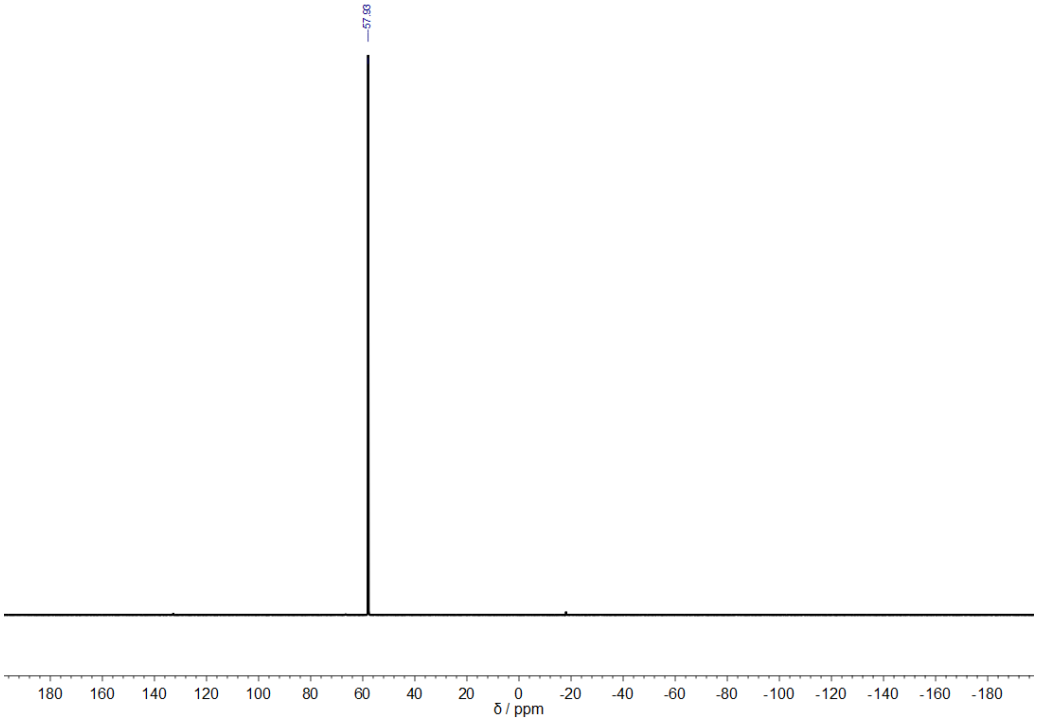
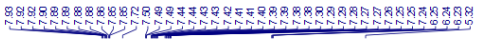
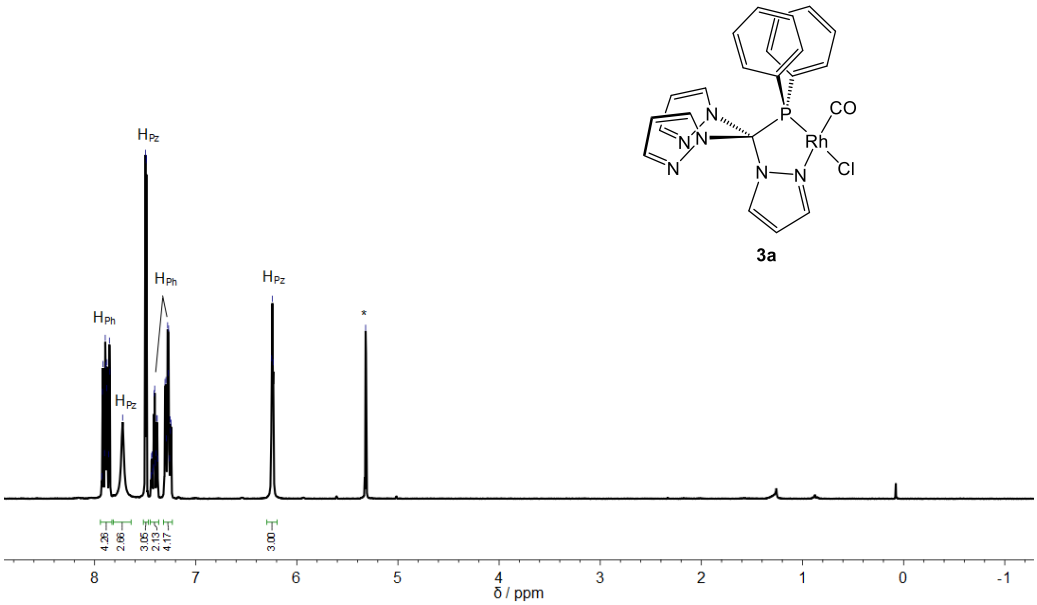


Figure 9 $^{31}P\{^{1}H\}$ NMR spectrum of **2c** in C_6D_6.

Compound **3a**





3a

Figure 10 ^{1}H NMR spectrum of **3a** in CD_2Cl_2 (*).

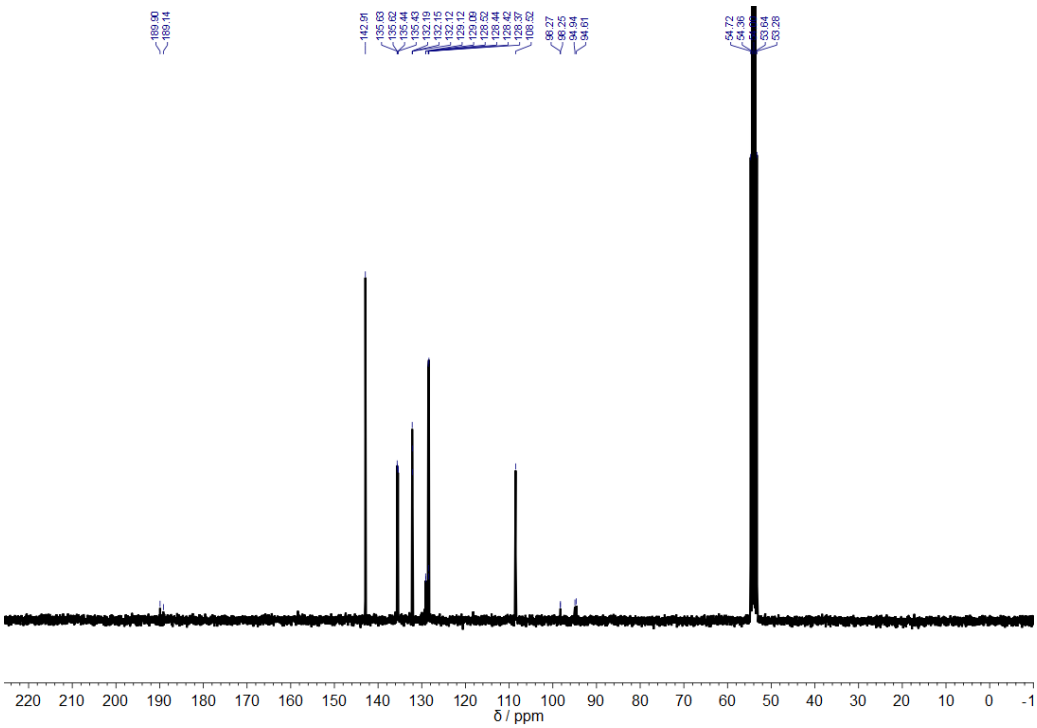


Figure 11 $^{13}C\{^{1}H\}$ NMR spectrum of **3a** in CD_2Cl_2.

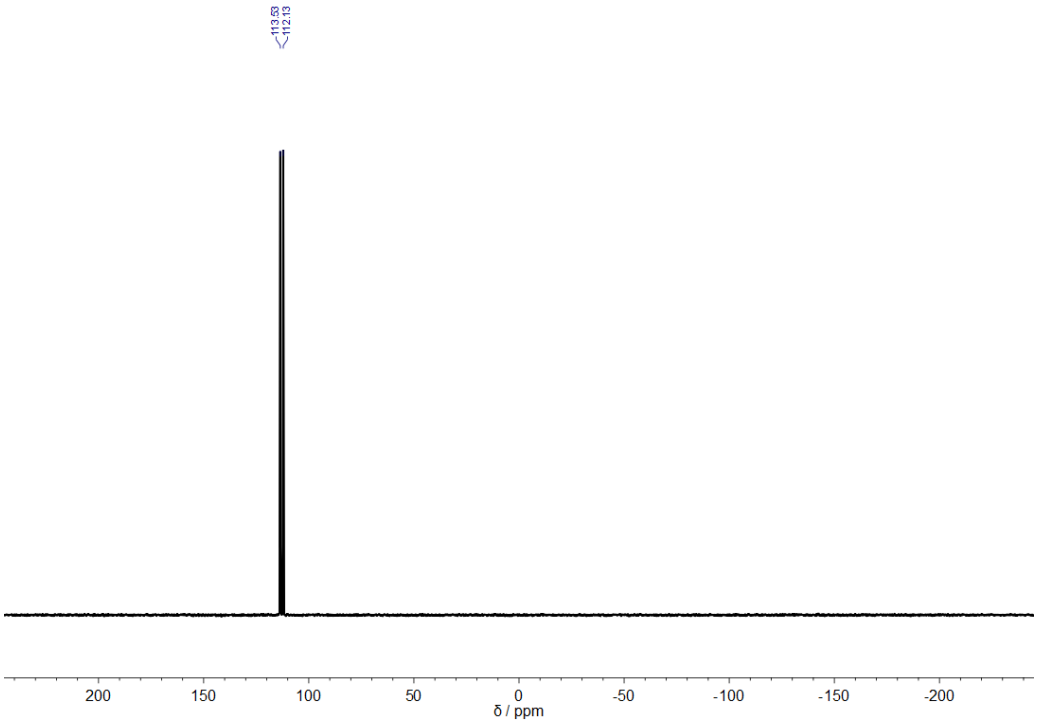


Figure 12 $^{31}P\{^{1}H\}$ NMR spectrum of **3a** in CD_2Cl_2.

Compound **3b**

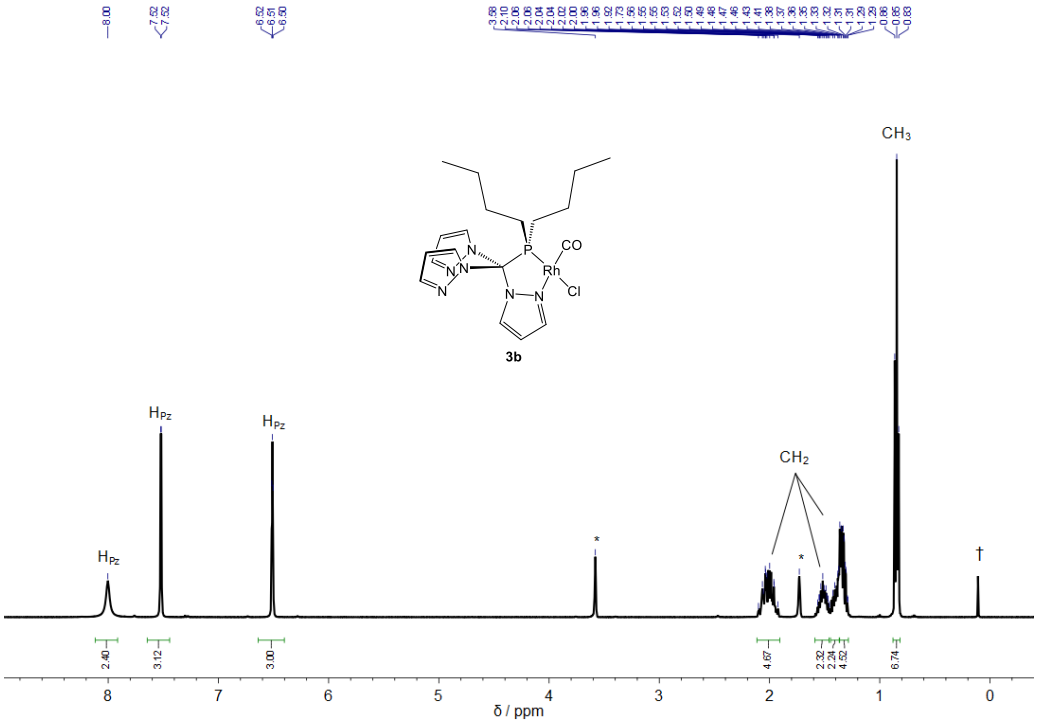


Figure 13 ^{1}H NMR spectrum of **3b** in THF-*d*8 (*). Signals marked with † correspond to silicon grease.

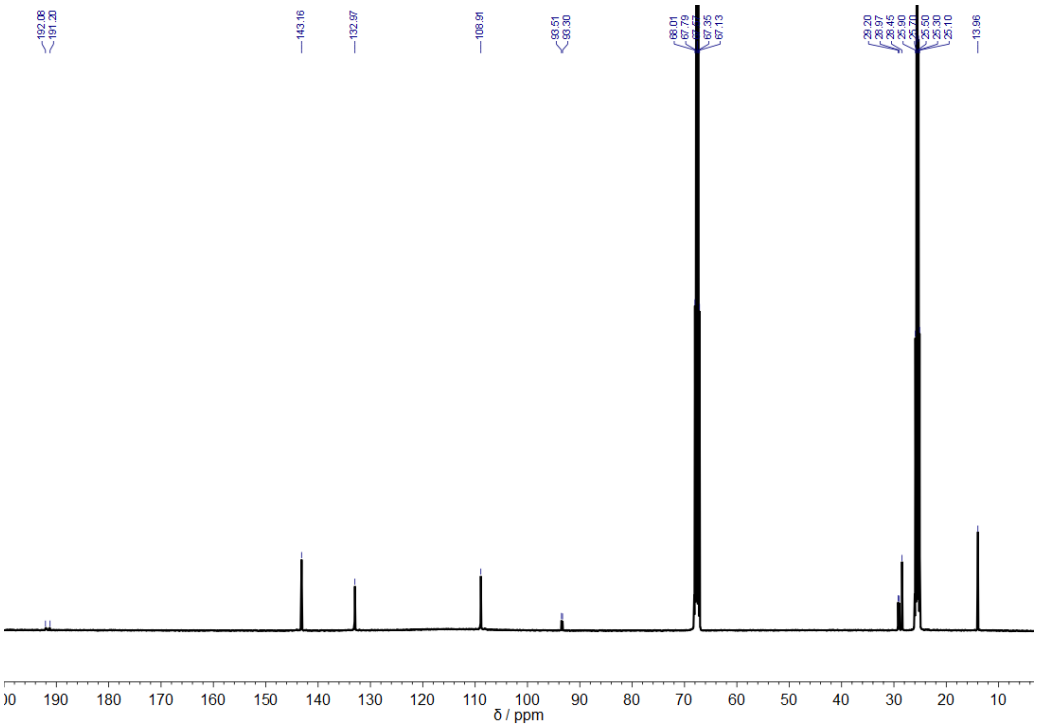


Figure 14 ^{13}C{^{1}H} NMR spectrum of **3b** in THF-*d*8.

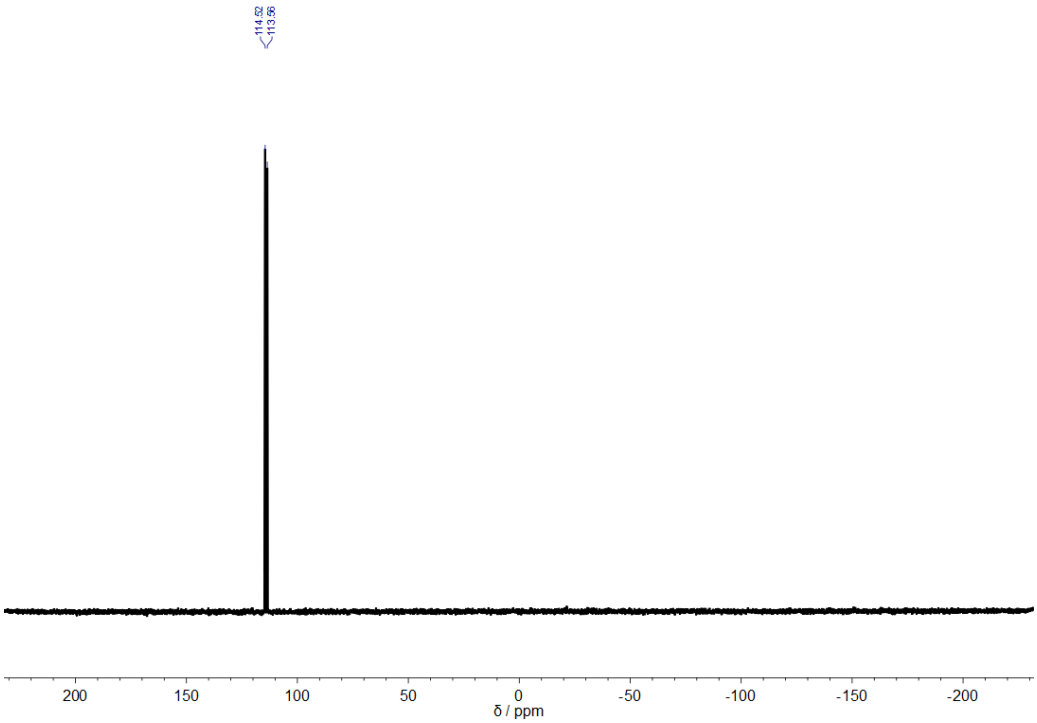


Figure 15 $^{31}P\{^{1}H\}$ NMR spectrum of **3b** in thf-*d*8.

Compound **3c**

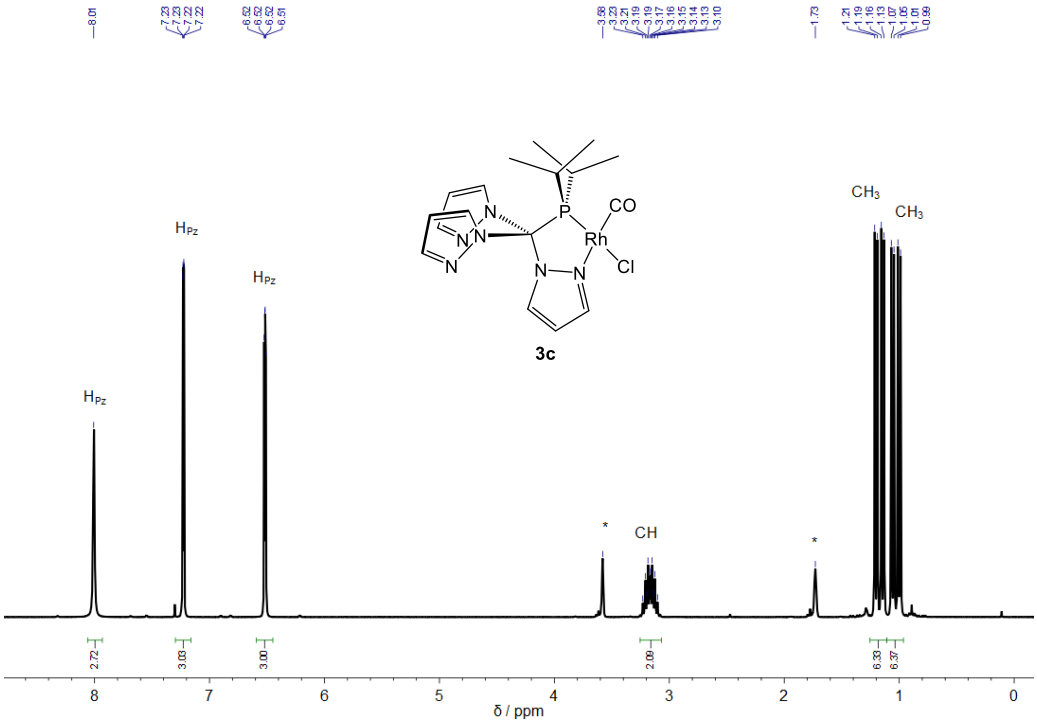


Figure 16 ^{1}H NMR spectrum of **3c** in THF-*d*8 (*).

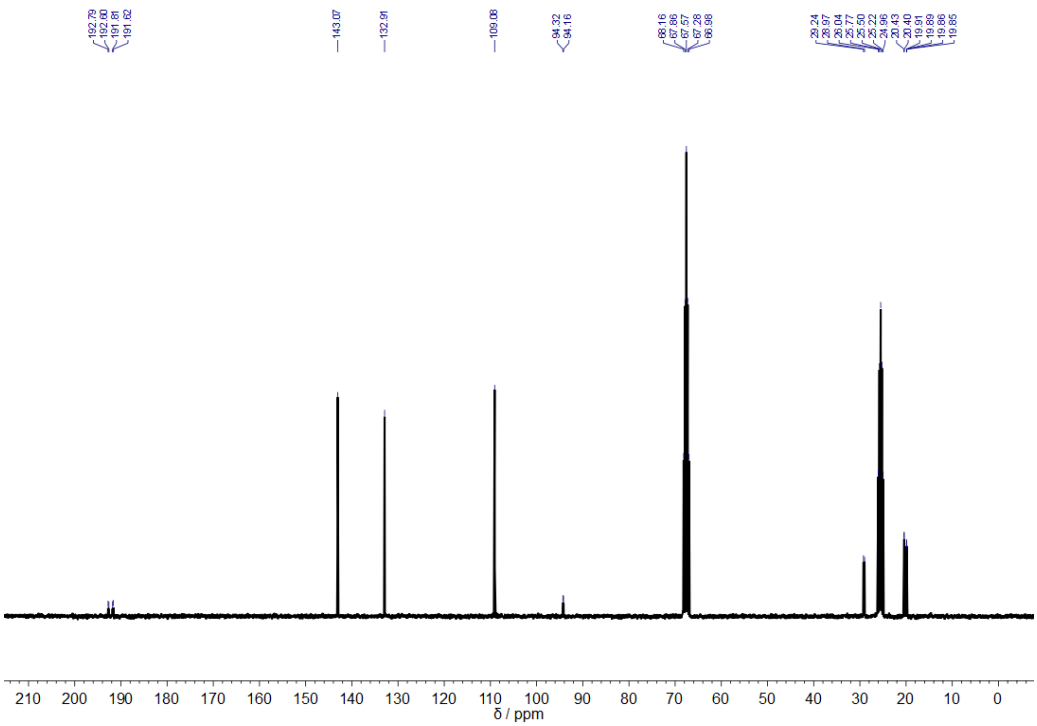


Figure 17 $^{13}C\{^{1}H\}$ NMR spectrum of **3c** in THF-*d*8.

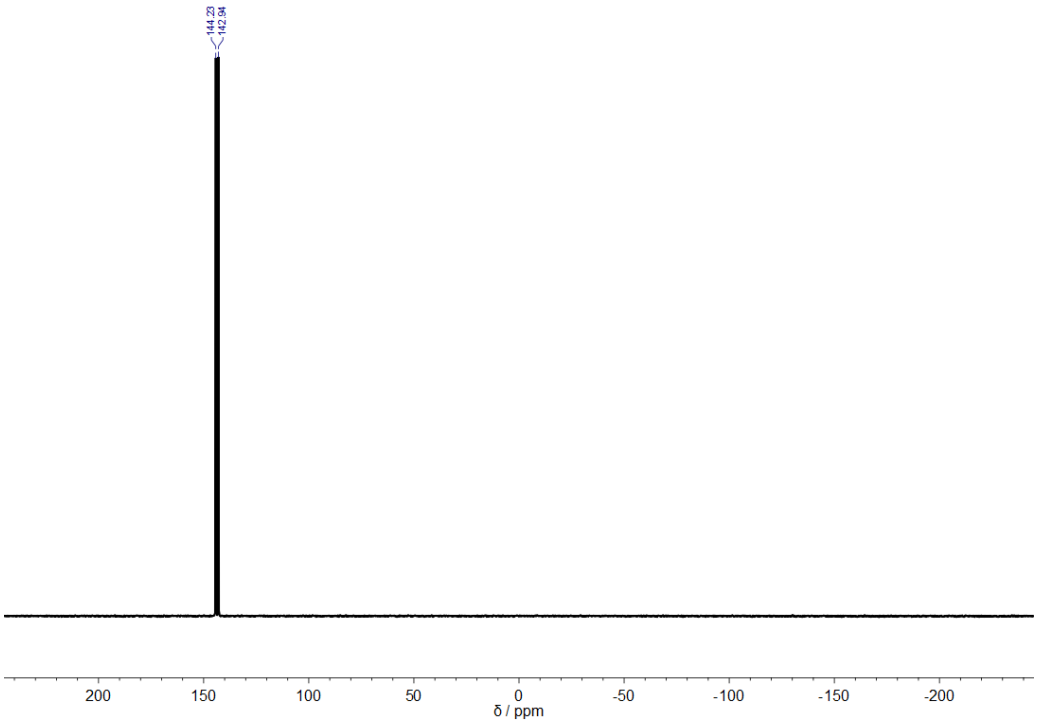


Figure 18 $^{31}P\{^{1}H\}$ NMR spectrum of **3c** in thf-*d*8.

Compound **4**

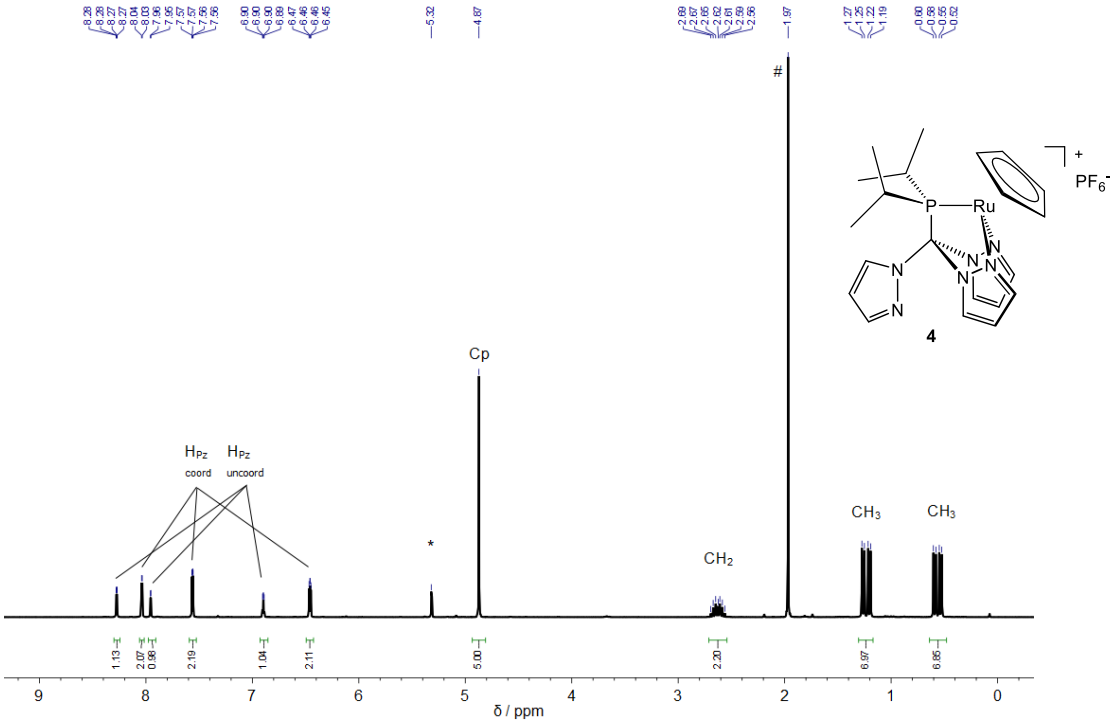


Figure 19 ^{1}H NMR spectrum of **4** in CD_2Cl_2 (*). Signals marked with # correspond to MeCN.

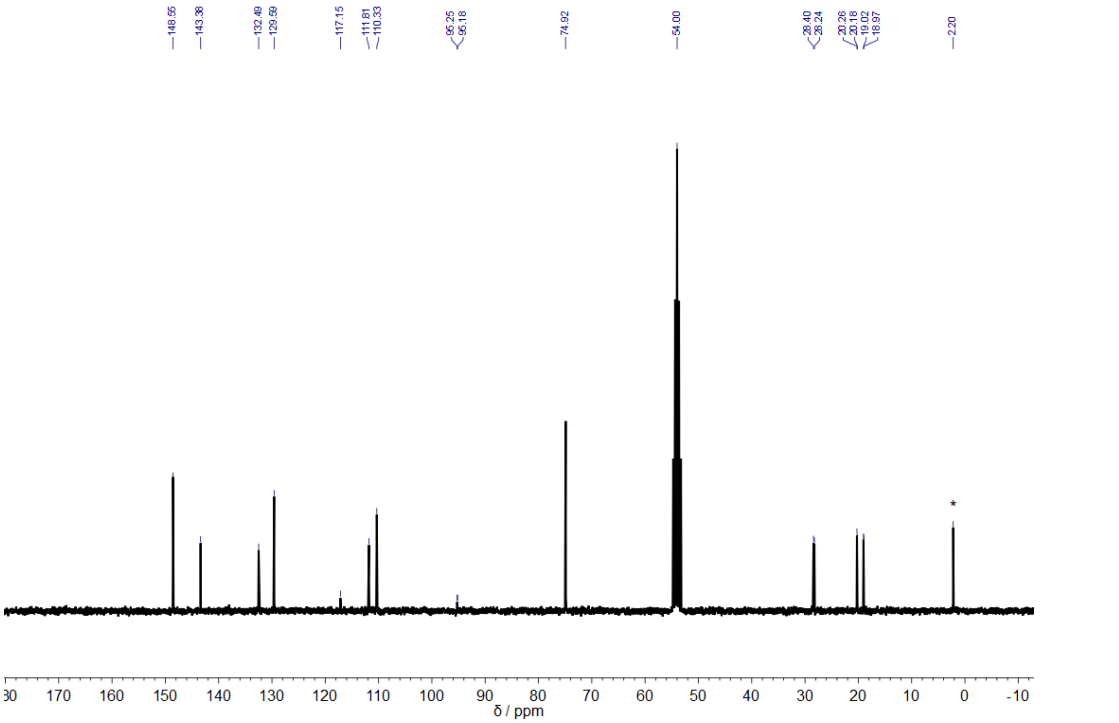


Figure 20 $^{13}C\{^{1}H\}$ NMR spectrum of **4** in CD_2Cl_2. Signals marked with * correspond to MeCN.

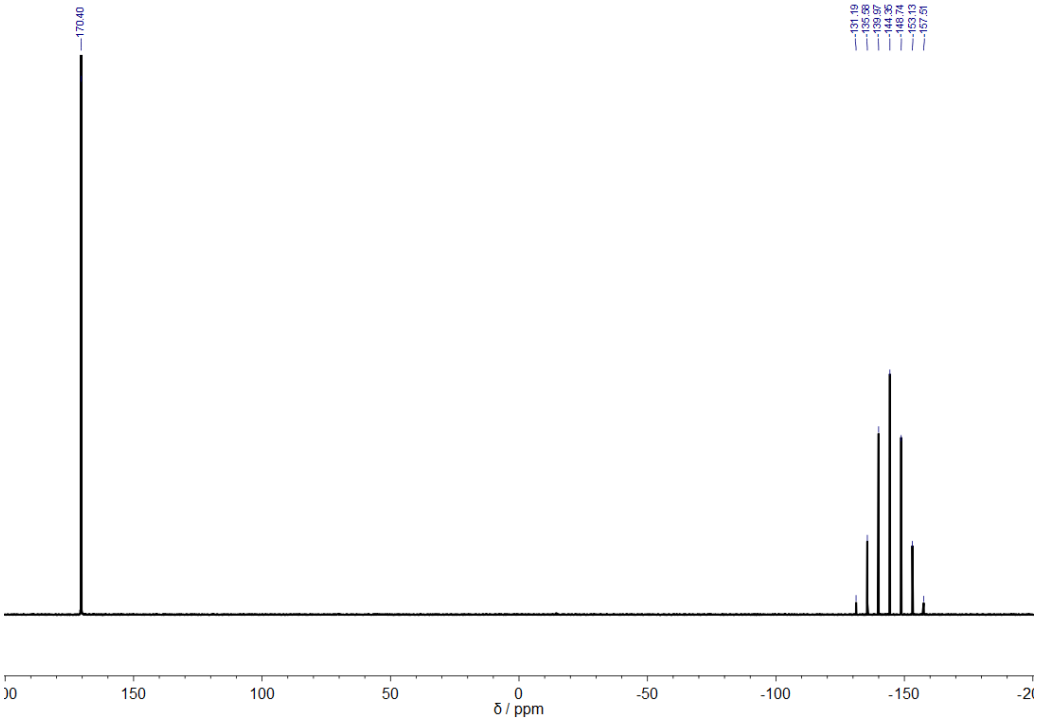


Figure 21 $^{31}P\{^{1}H\}$ NMR spectrum of **4** in CD_2Cl_2.

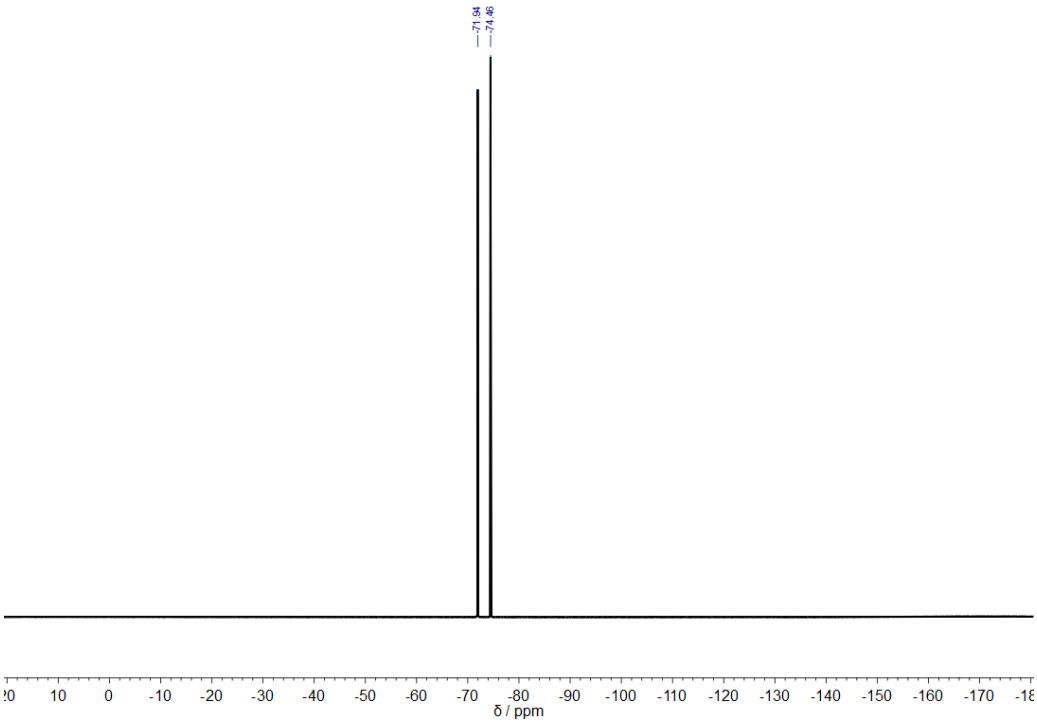


Figure 22 ^{19}F NMR spectrum of **4** in CD_2Cl_2.

Compound **5**

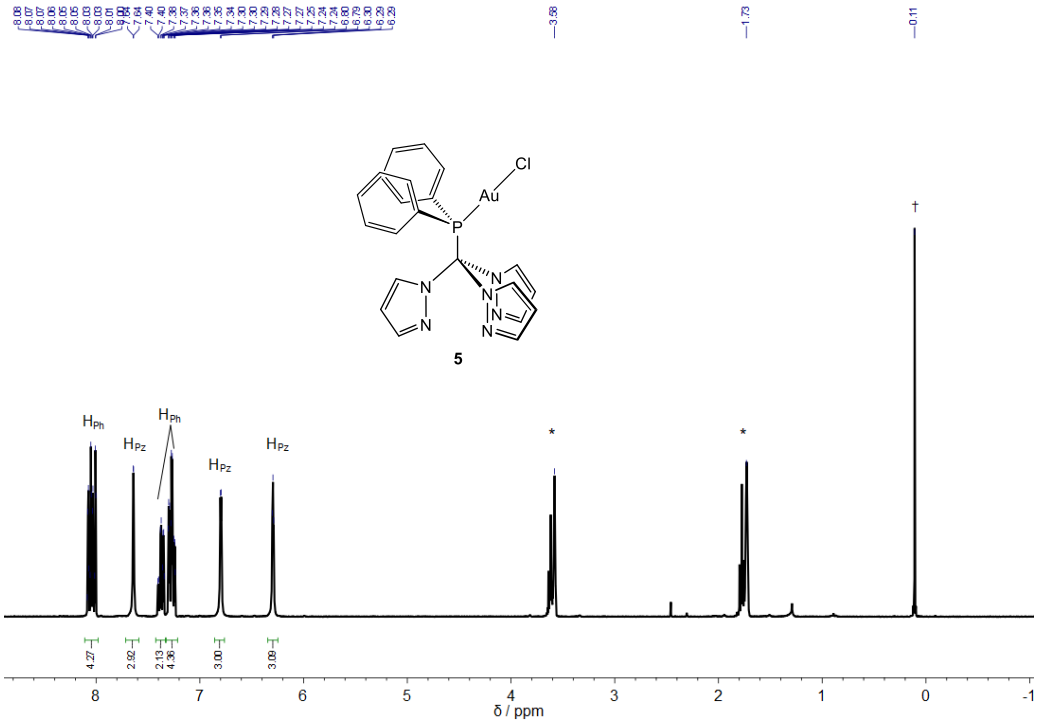


Figure 23 ^{1}H NMR spectrum of **5** in THF-*d*8 (*). Signals marked with † correspond to silicon grease.

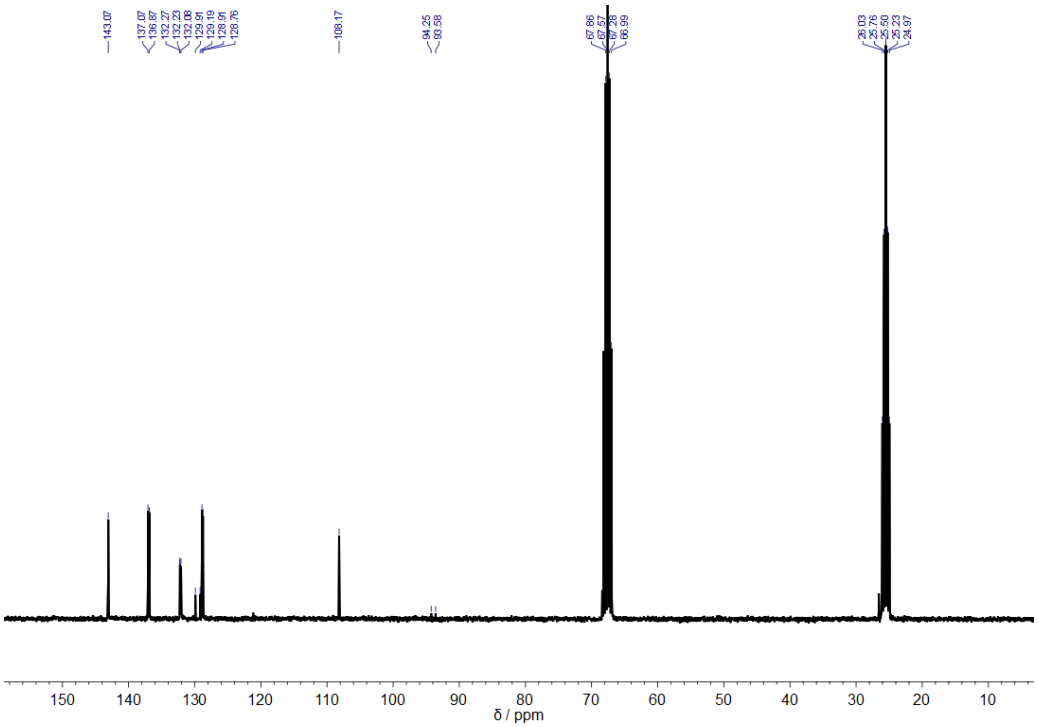


Figure 24 ^{13}C NMR spectrum of **5** in THF-*d*8.

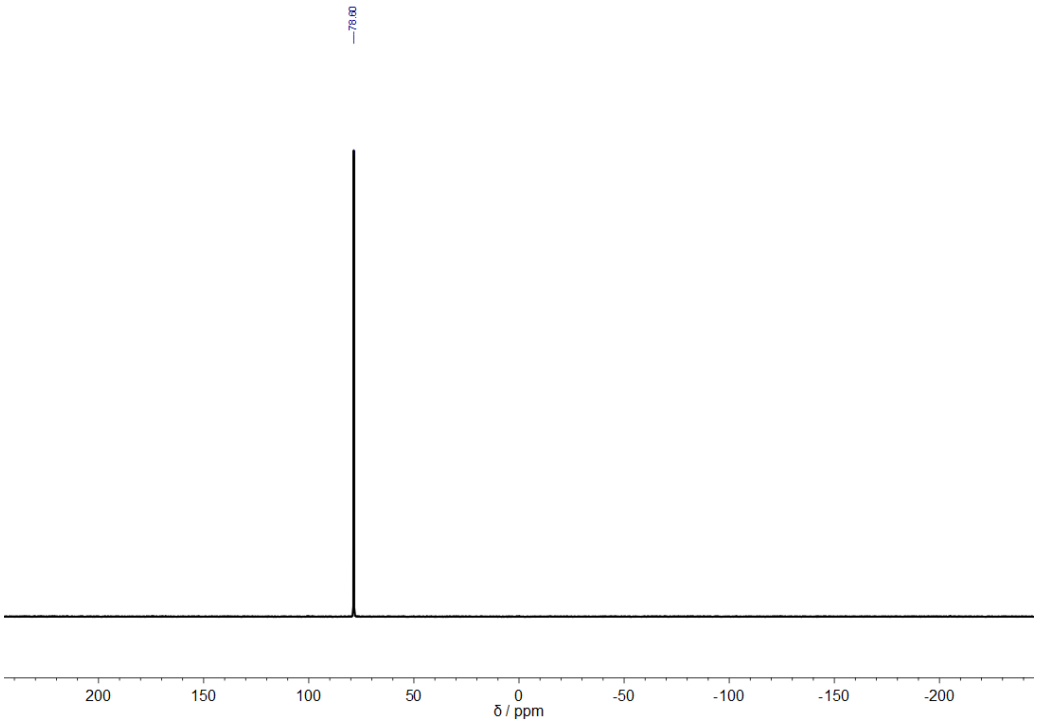


Figure 25 $^{31}P\{^{1}H\}$ NMR spectrum of **5** in thf-*d*8.

Compound **6**

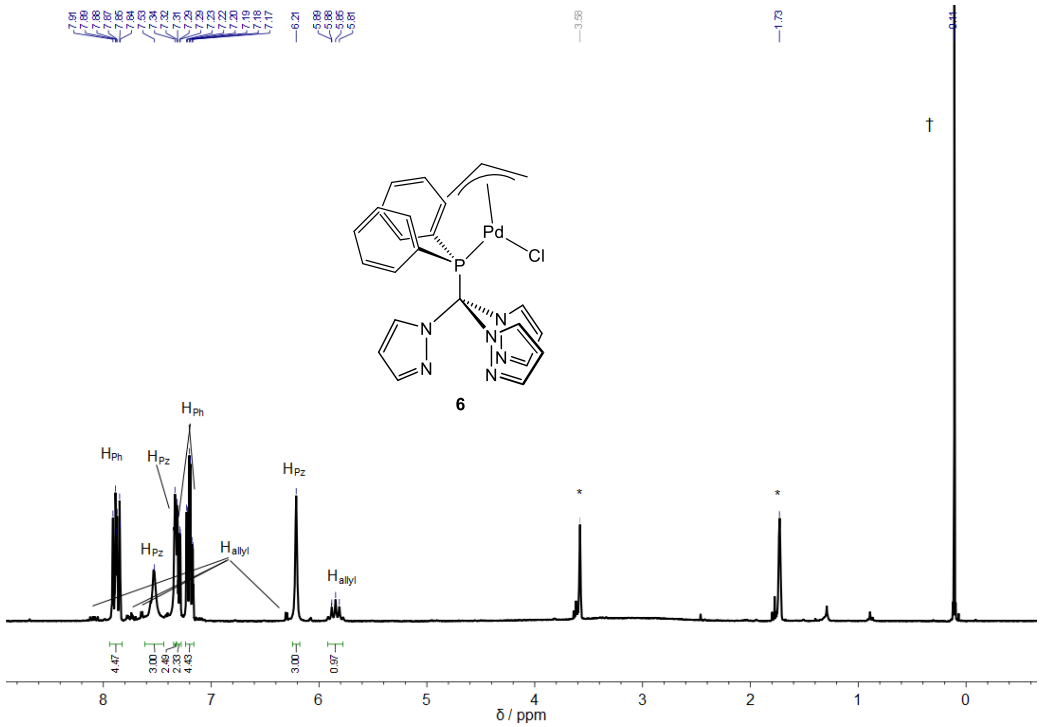


Figure 26 ^{1}H NMR spectrum of **6** in THF-*d*8 (*). Signals marked with † correspond to silicon grease.

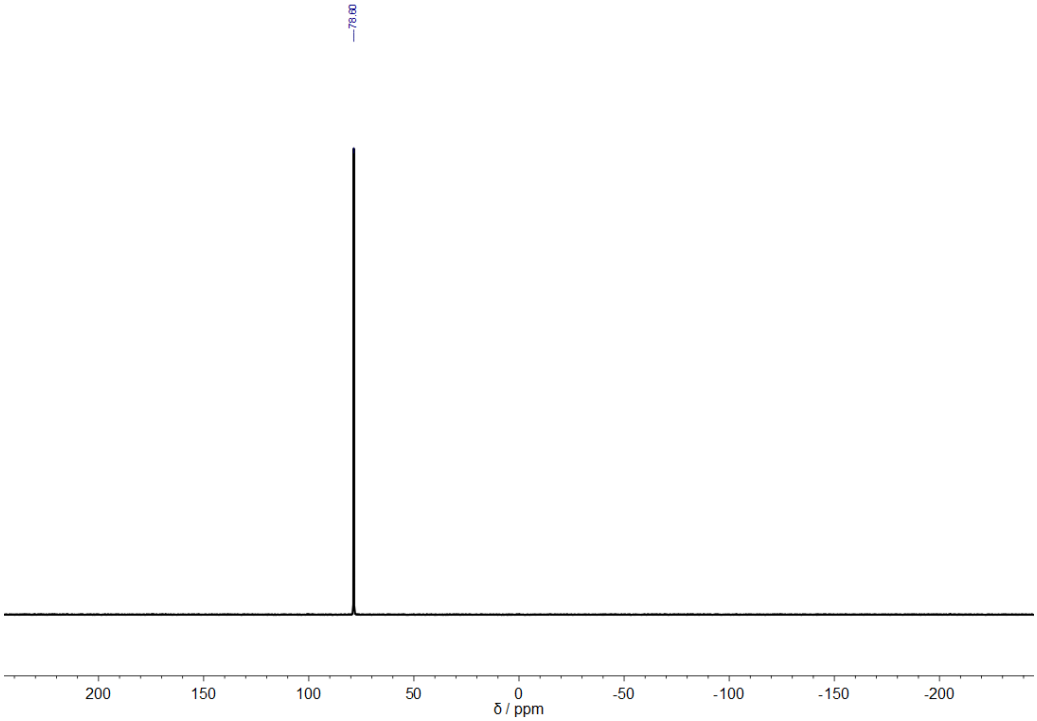


Figure 27 $^{31}P\{^{1}H\}$ NMR spectrum of **6** in thf-*d*8.

Compound **7**

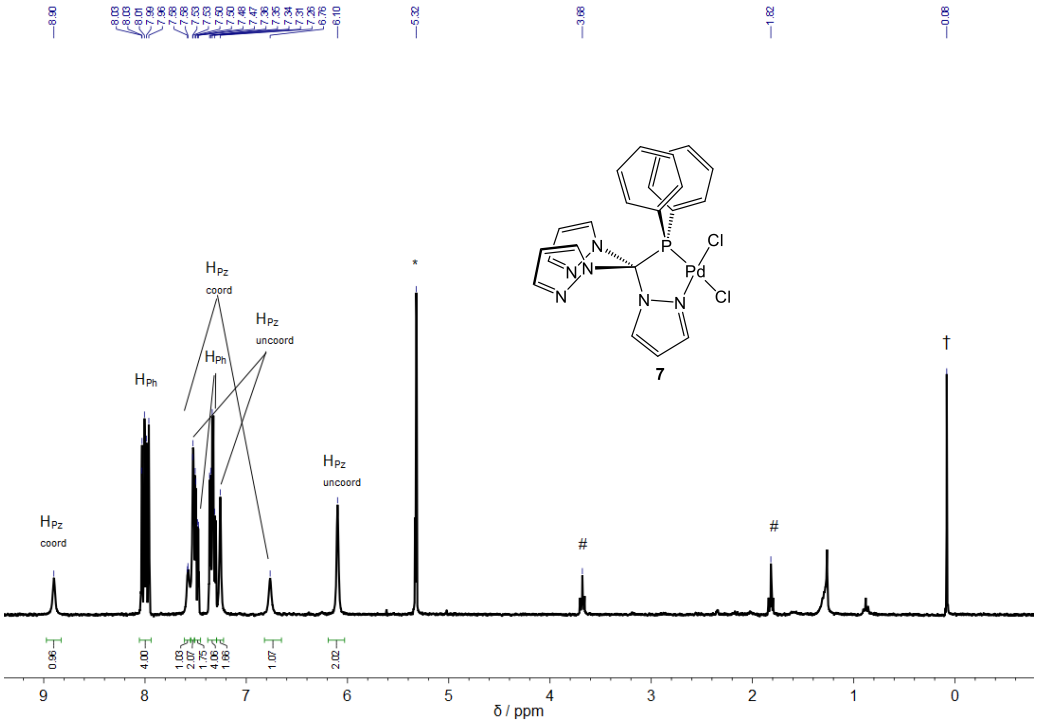


Figure 28 ^{1}H NMR spectrum of **7** in CD_2Cl_2 (*). Signals marked with # correspond to THF and † to silicon grease.

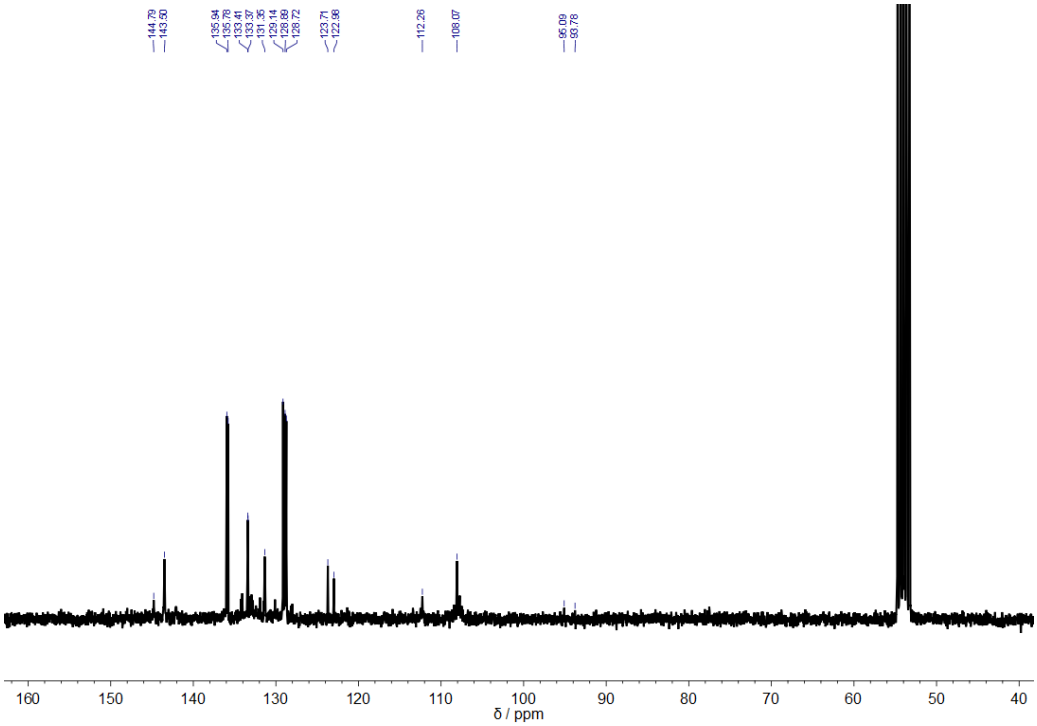


Figure 29 $^{13}C\{^{1}H\}$ NMR spectrum of **7** in CD_2Cl_2.

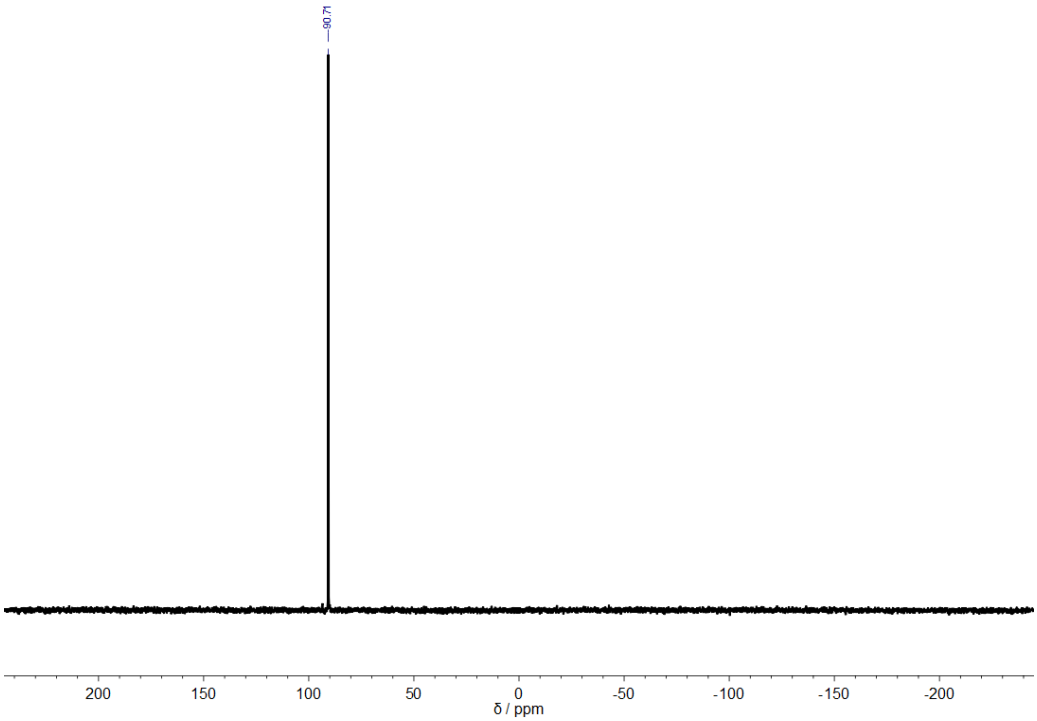


Figure 30 $^{31}P\{^{1}H\}$ NMR spectrum of **7** in CD_2Cl_2.