Supporting Information

3*H*-1,3-Azaphospholo[4,5-*b*]pyridines - Novel Heterocyclic P,N-Bridging or Hybrid Ligands: Synthesis and First d^8-Transition Metal Complexes

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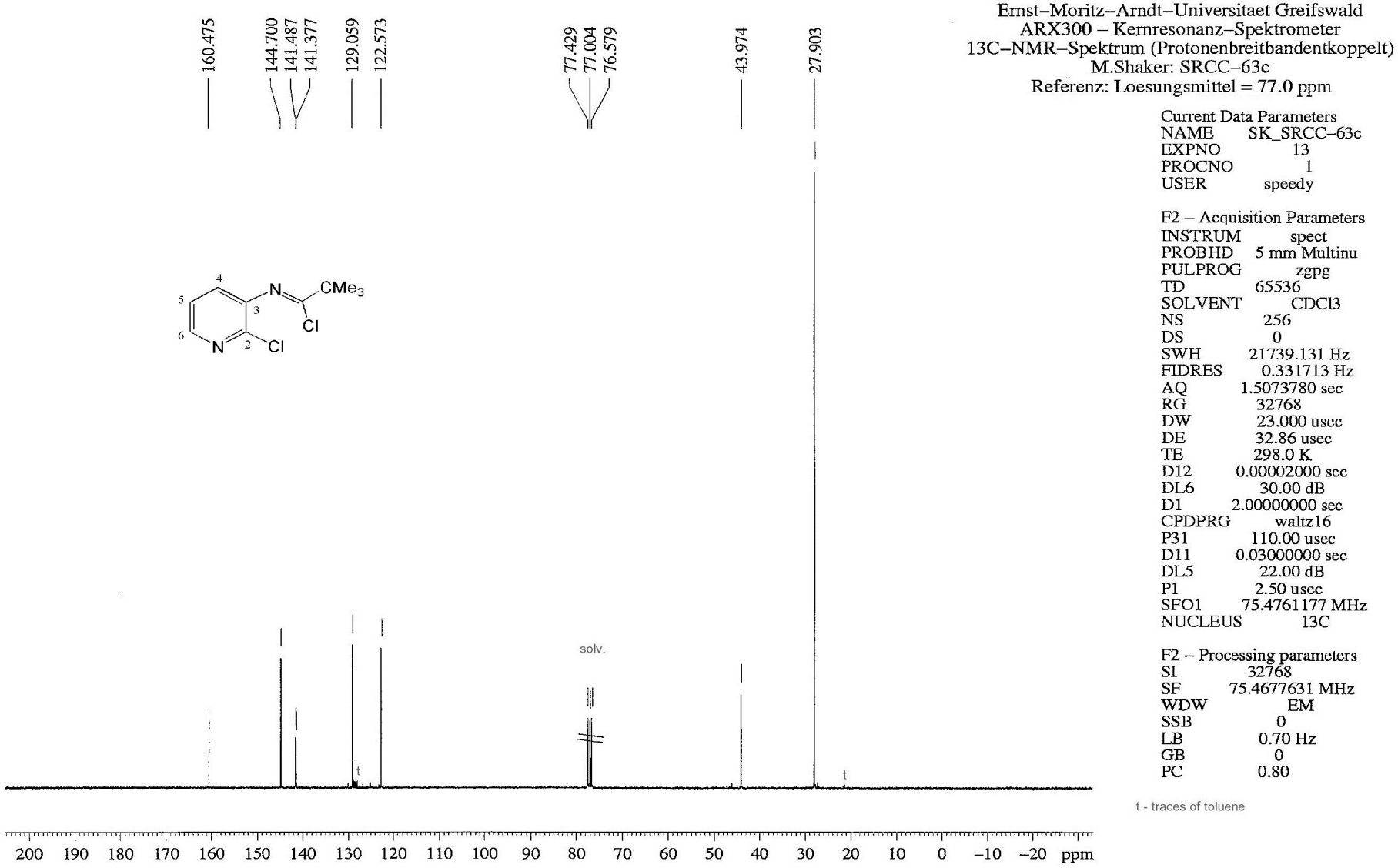
1. Selected NMR spectra of compounds **1-11** (Fig. S1-S25)
2. Crystal structures - Tables with positional parameters, bond lengths and angles of **6a**, **9b**·2$CDCl_3$, **10b**·2(D_6-acetone) and **10b**·4.5THF and figures of the packing of **6a** and the crude structure of **9a** (Fig.S26, S27).

1. Selected NMR spectra:

Fig. S1. ^{13}C NMR Spectrum of compound **1**.



Ernst–Moritz–Arndt–Universitaet Greifswald
ARX300 – Kernresonanz–Spektrometer
13C–NMR–Spektrum (Protonenbreitbandentkoppelt)
M.Shaker: SRCC–63c
Referenz: Loesungsmittel = 77.0 ppm

Current Data Parameters

NAME	SK_SRCC–63c
EXPNO	13
PROCNO	1
USER	speedy

F2 – Acquisition Parameters

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PROBHD	5 mm Multinu
PULPROG	zgpg
TD	65536
SOLVENT	CDCl3
NS	256
DS	0
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FIDRES	0.331713 Hz
AQ	1.5073780 sec
RG	32768
DW	23.000 usec
DE	32.86 usec
TE	298.0 K
D12	0.00002000 sec
DL6	30.00 dB
D1	2.00000000 sec
CPDPRG	waltz16
P31	110.00 usec
D11	0.03000000 sec
DL5	22.00 dB
P1	2.50 usec
SFO1	75.4761177 MHz
NUCLEUS	13C

F2 – Processing parameters

SI	32768
SF	75.4677631 MHz
WDW	EM
SSB	0
LB	0.70 Hz
GB	0
PC	0.80

t - traces of toluene

Fig. S2. ^{1}H NMR Spectrum of compound **2a**.

Acquisition Time (sec)	5.2953	***Comment***	M. Shaker: SRRY-2 1H-Spektrum Loesungsmittel: DMSO-d6 Referenz: LM = 2.5 ppm Messzeit: 4 min. EMAU, Avance II - 300		
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File Name	C:\Users\JoHei\				
Frequency (MHz)	300.13	***Nucleus***	1H	***Number of Transients***	32
Origin	spect	***Original Points Count***	32768	***Owner***	nmr
Points Count	16384	***Pulse Sequence***	zg30	***Receiver Gain***	203.00
SW(cyclical) (Hz)	6188.12	***Solvent***	DMSO-d6	***Spectrum Offset (Hz)***	1858.7338
Spectrum Type	STANDARD	***Sweep Width (Hz)***	6187.74	***Temperature (degree C)***	25.000

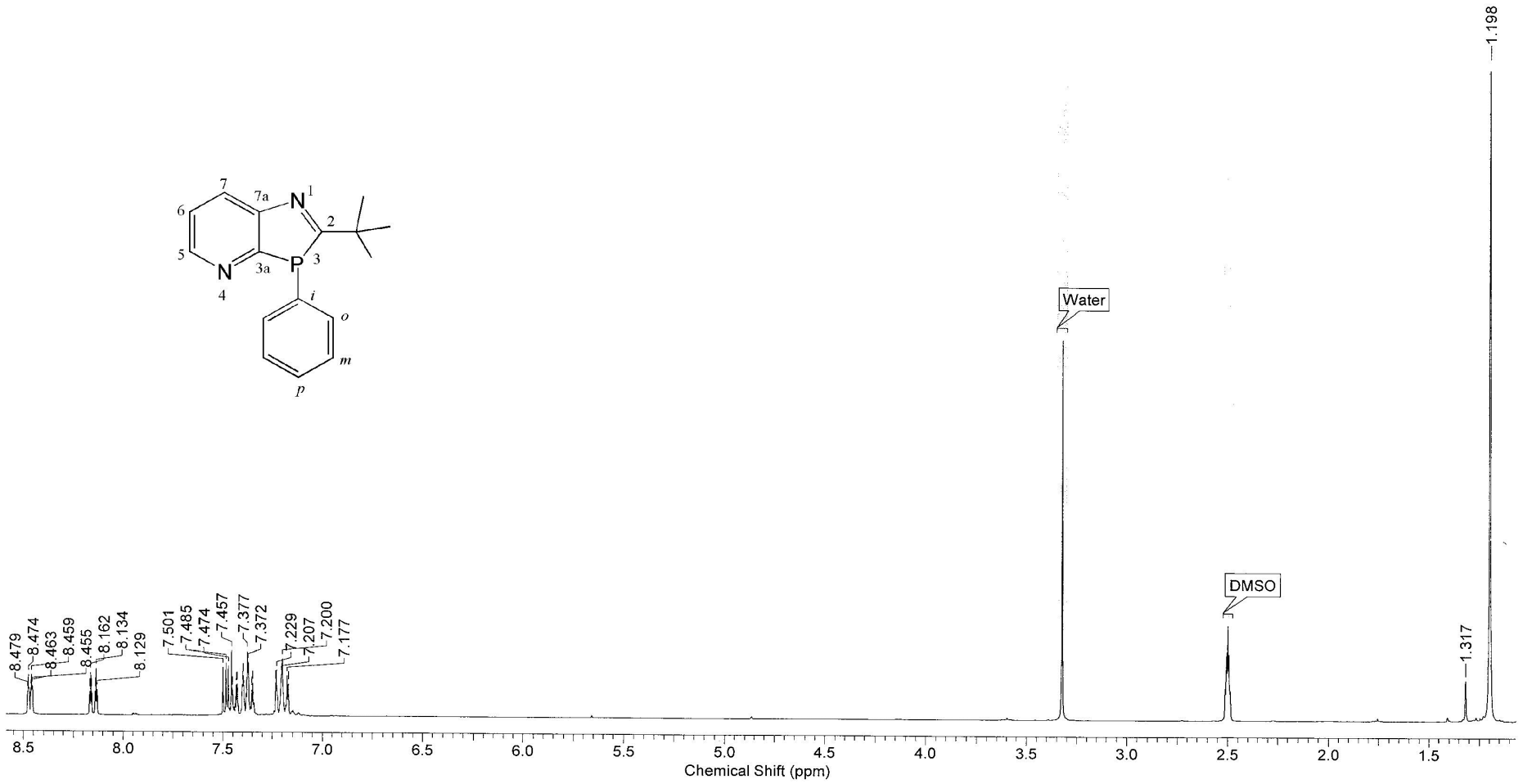
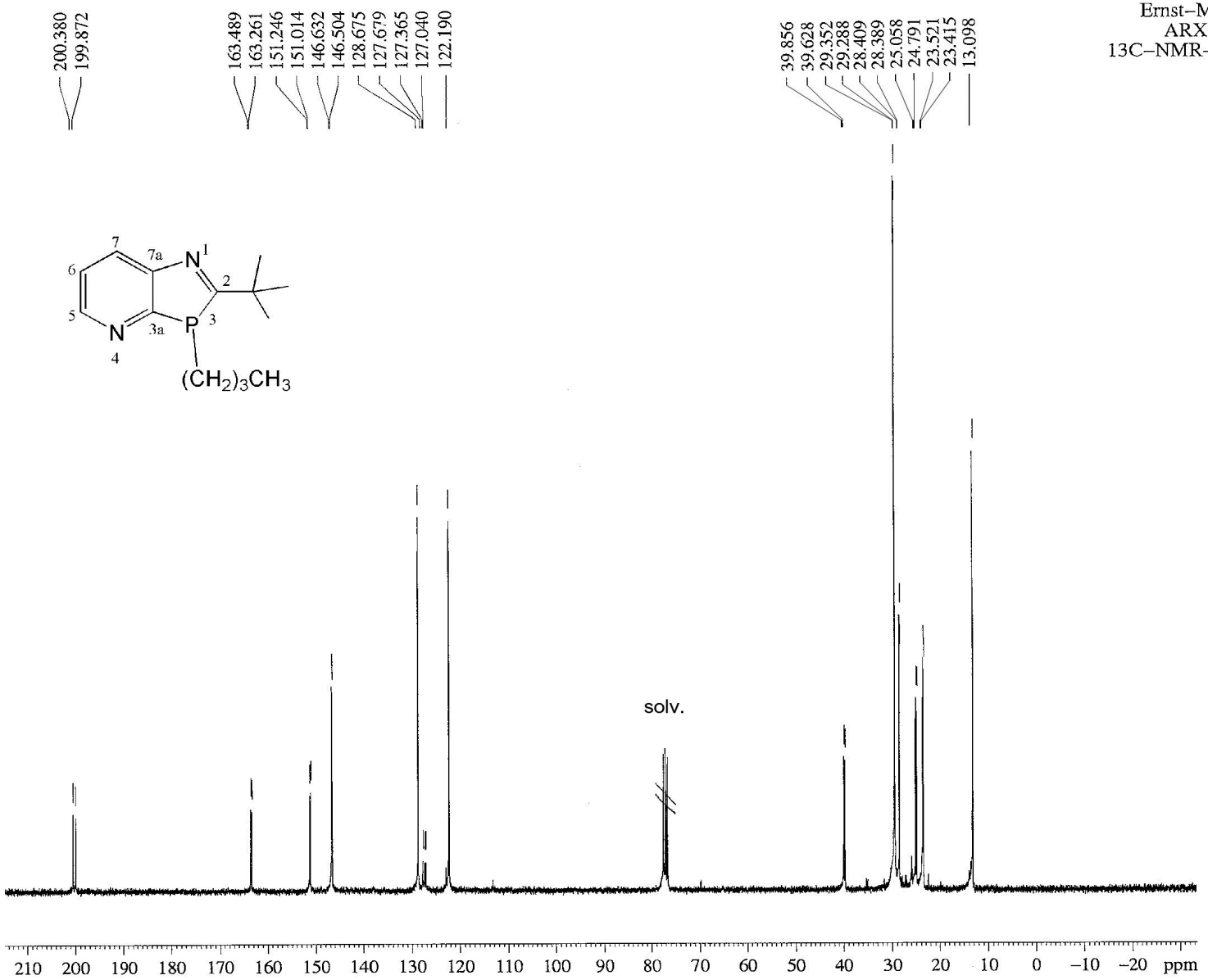


Fig. S3. ^{13}C NMR Spectrum of compound **2b** (in $CDCl_3$, C_6H_6).



Ernst–Moritz–Arndt–Universitaet Greifswald
ARX300 – Kernresonanz–Spektrometer
13C–NMR–Spektrum (Protonenbreitbandentkoppelt)
Shaker:SRPC–70d
Referenz: LM

Current Data Parameters	
NAME	SK_SRPC–70d
EXPNO	13
PROCNO	1
USER	speedy

F2 – Acquisition Parameters	
INSTRUM	spect
PROBHD	5 mm Multinu
PULPROG	zgpg
TD	65536
SOLVENT	CDCl3
NS	1024
DS	0
SWH	21739.131 Hz
FIDRES	0.331713 Hz
AQ	1.5073780 sec
RG	32768
DW	23.000 usec
DE	32.86 usec
TE	298.0 K
D12	0.00002000 sec
DL6	30.00 dB
D1	2.00000000 sec
CPDPRG	waltz16
P31	110.00 usec
D11	0.03000000 sec
DL5	22.00 dB
P1	2.50 usec
SFO1	75.4761177 MHz
NUCLEUS	13C

F2 – Processing parameters	
SI	65536
SF	75.4677698 MHz
WDW	EM
SSB	0
LB	0.70 Hz
GB	0
PC	1.00

Fig. S4. ^{13}C NMR Spectrum of compound **2c**.

Acquisition Time (sec)	1.5073				
Comment	Ernst-Moritz-Arndt-Universitaet Greifswald ARX300 - Kernresonanz-Spektrometer 13C-NMR-Spektrum (Protonenbreitbandentkoppelt) M.Shaker: SRCP-66c Loesungsmittel: Deuterobenzol, C6D6 Referenz: Loesungsmittel = 128.7 Messtemperatur: 298K (25 oC) Messzeit: 1				
Date		***Date Stamp***			
File Name	C:\Users\JoHei\Documents\150626 Arbeitsdokus\Arbeitsdateien\Fo-G15 P\Mitarbeiter& Koop\Adam M. Shaker\Pub5 3Npy 4N-3R-PAP +complex\NMR-Spektren zu ShakerPub5\SK_SRCP-66c\13\pdata\1\1r				
Frequency (MHz)	75.47	***Nucleus***	13C	***Number of Transients***	16384
Origin	spect	***Original Points Count***	32768	***Owner***	root
Points Count	32768	***Pulse Sequence***	zgpg	***Receiver Gain***	16384.00
SW(cyclical) (Hz)	21739.13	***Solvent***	CHLOROFORM-d	***Spectrum Offset (Hz)***	8440.8994
Spectrum Type	STANDARD	***Sweep Width (Hz)***	21738.47	***Temperature (degree C)***	25.000

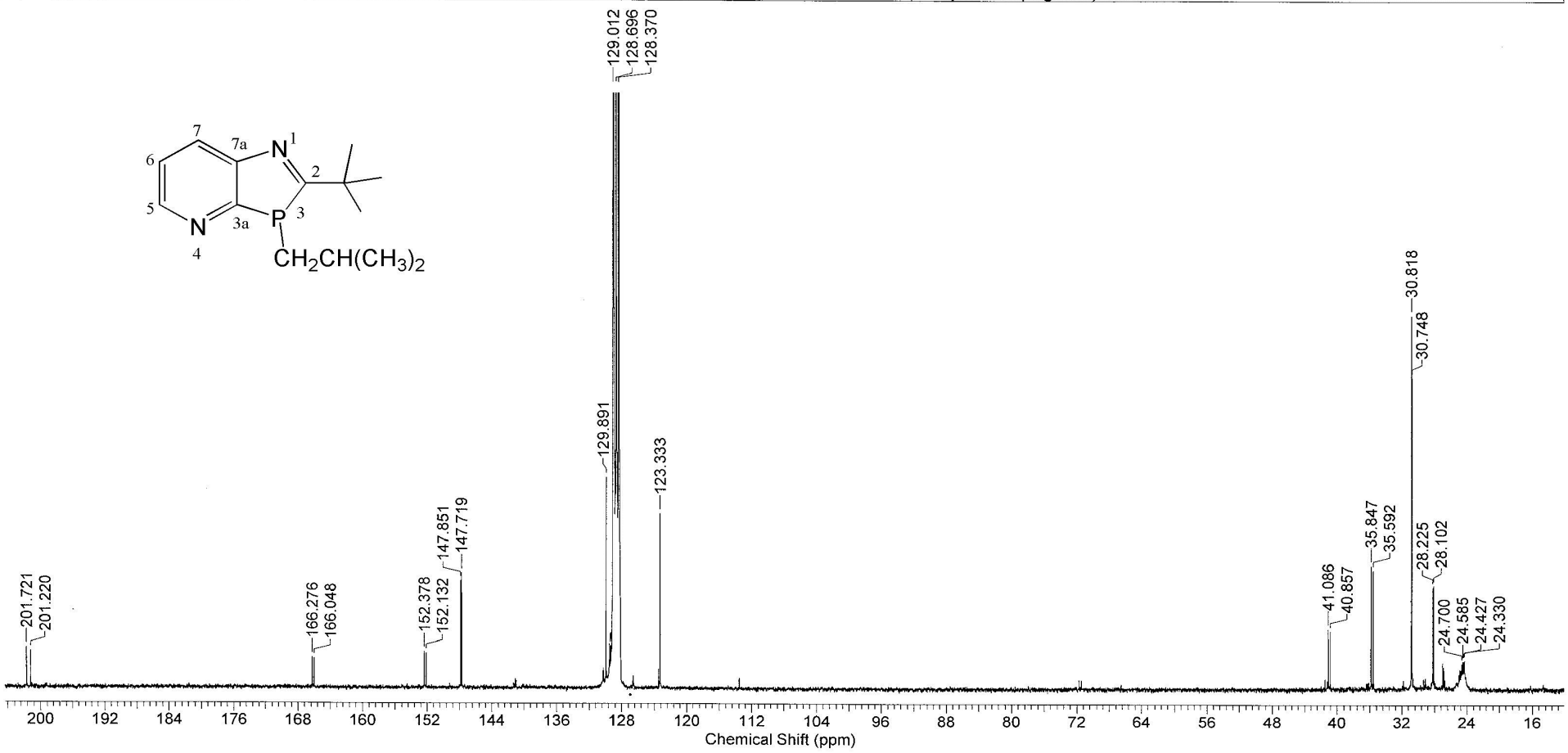


Fig. S5. ^{1}H NMR Spectrum of complex **3a**.

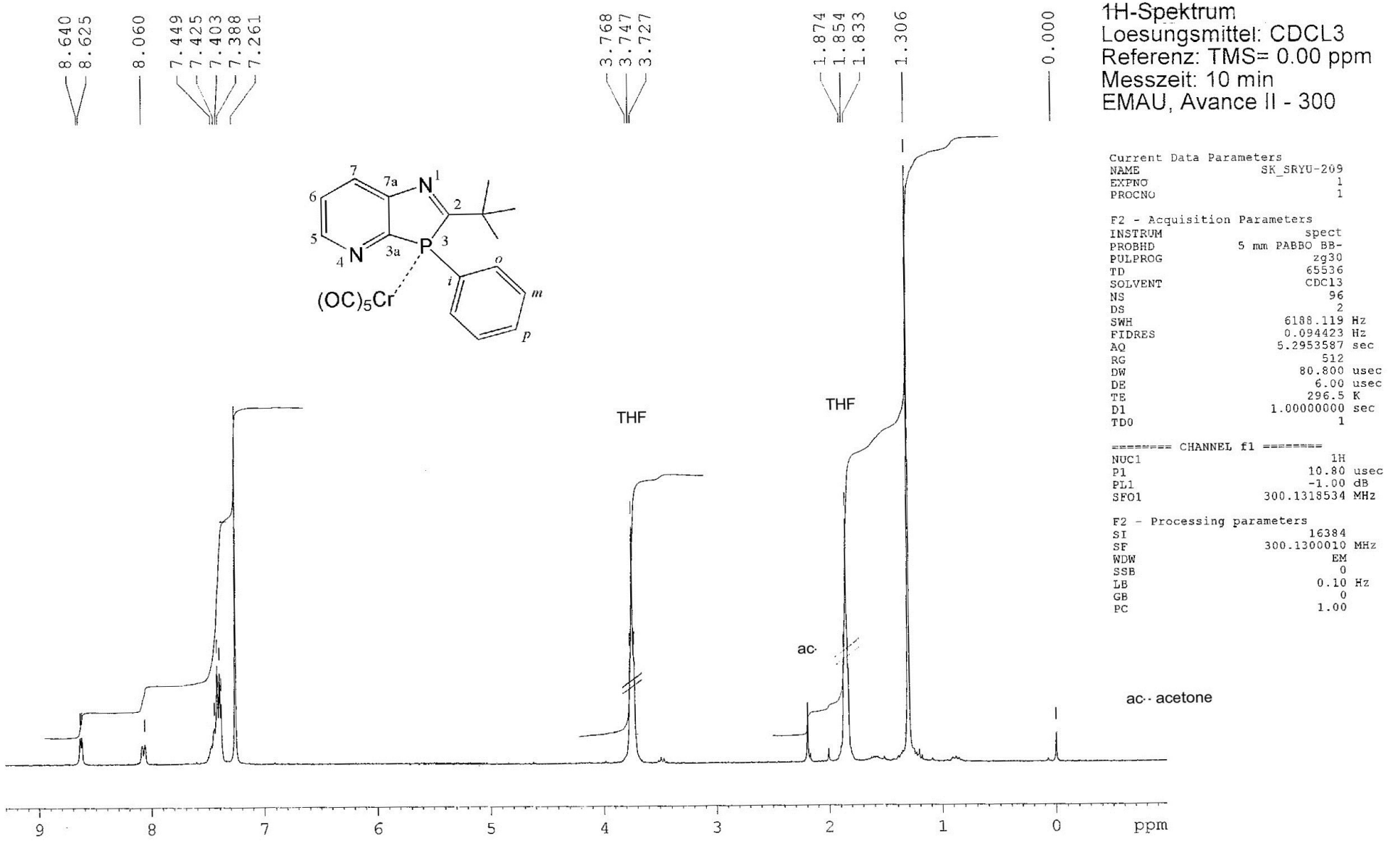
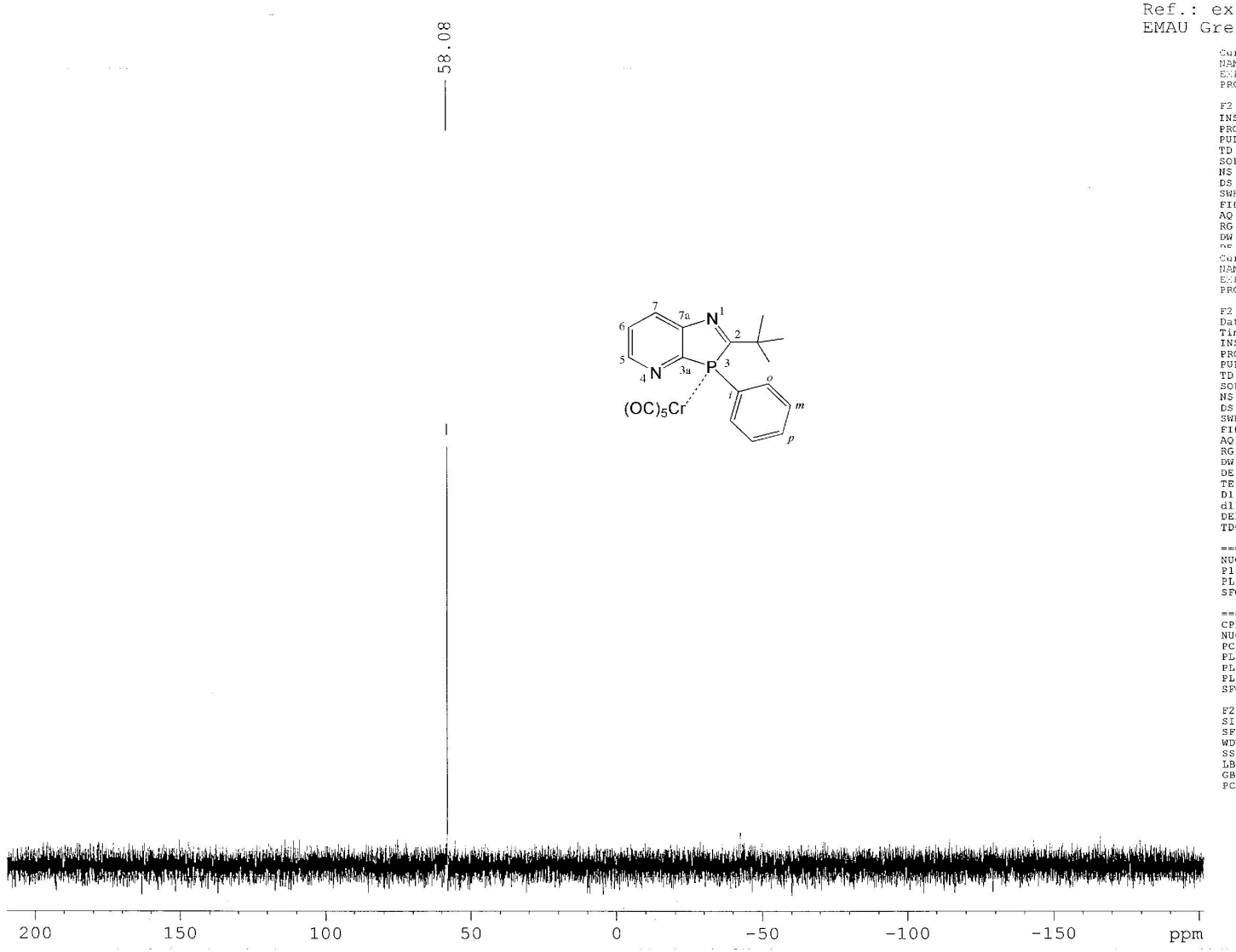


Fig. S6. ^{31}P NMR Spectrum of complex **3a**.

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M. Shaker: SRYU-209
31P{1H}-Spektrum
Loesungsmittel: CDCl3
Ref.: extern, H3PO4 = 0.0 ppm
EMAU Greifswald - Avance 300

Current Data Parameters
NAME                  SK_SRYU-209
EXPNO                          31
PROCNO                          1

F2 - Acquisition Parameters
INSTRUM                      spect
PROBHD          5 mm PABBO BB-
PULPROG                    zgpg30
TD                          32768
SOLVENT                     CDCl3
NS                            128
DS                              4
SWH                   50000.000 Hz
FIDRES                 1.525879 Hz
AQ                    0.3277300 sec
RG                        23100
DW                       10.000 usec
DE                        6.00 usec
Current Data Parameters       K
NAME                  SK_SRYU-209 sec
EXPNO                          31 sec
PROCNO                          1 sec

F2 - Acquisition Parameters
Date_                    20070806
Time                         9.46
INSTRUM                      spect usec
PROBHD          5 mm PABBO BB- dB
PULPROG                    zgpg30 MHz
TD                          32768
SOLVENT                     CDCl3
NS                            128
DS                              4
SWH                   50000.000 Hz
FIDRES                 1.525879 Hz
AQ                    0.3277300 sec
RG                        23100
DW                       10.000 usec
DE                        6.00 usec
TE                       296.8 K
D1                    2.00000000 sec
d11                   0.03000000 sec
DELTA                 1.89999998 sec
TD0                             1

======== CHANNEL f1 ========
NUC1                          31P
P1                          10.25 usec
PL1                          2.00 dB
SFO1                121.4953510 MHz

======== CHANNEL f2 ========
CPDPRG2                   waltz16
NUC2                          1H
PCPD2                       80.00 usec
PL12                        19.00 dB
PL13                        22.00 dB
PL2                         -1.00 dB
SFO2                300.1312005 MHz

F2 - Processing parameters
SI                           32768
SF                  121.4948510 MHz
WDW                             EM
SSB                              0
LB                           1.00 Hz
GB                               0
PC                            1.40
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Fig. S7. ^{1}H NMR Spectrum of complex **4a**.

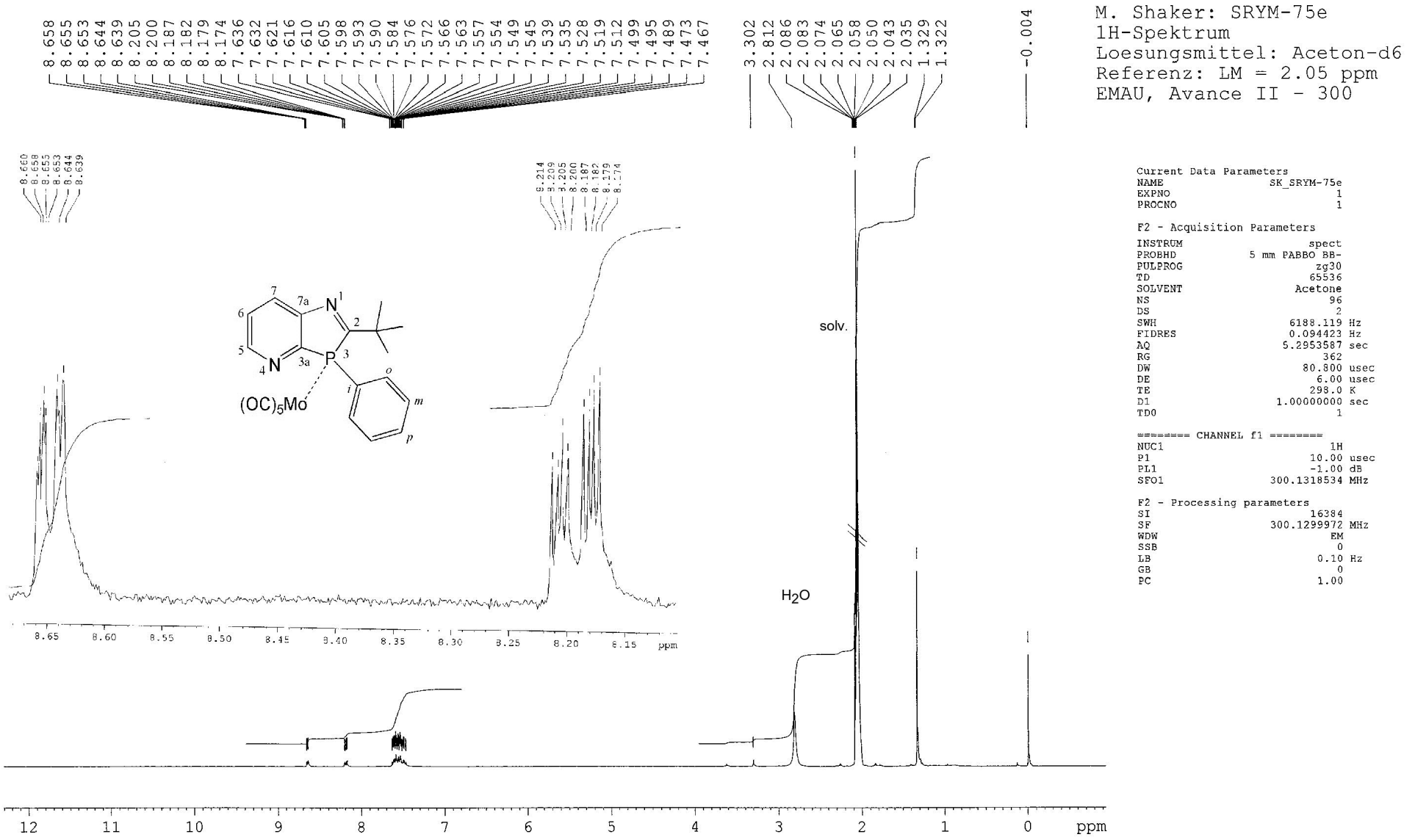


Fig. S8. ^{13}C NMR Spectrum of complex **4c**.

Acquisition Time (sec)	0.7537	*Comment*	M.Ghalib: MSRISOPMob 13C{1H}-NMR-Spektrum LM: CDCl3 Referenz: LM=77,0 ppm Messzeit: 15 Stunden EMAU, AVANCE II - 300		
Date	29 Nov 2012 08:23:44	*Date Stamp*	29 Nov 2012 08:23:44		
File Name	C:\Users\JoHei\Documents\141201 Arbeitsdokus\				
Frequency (MHz)	75.47	*Nucleus*	13C	*Number of Transients*	18944
Origin	spect	*Original Points Count*	16384	*Owner*	nmr
Points Count	16384	*Pulse Sequence*	zgpg30	*Receiver Gain*	32800.00
SW(cyclical) (Hz)	21739.13	*Solvent*	CHLOROFORM-d	*Spectrum Offset (Hz)*	8369.8350
Spectrum Type	STANDARD	*Sweep Width (Hz)*	21737.80		

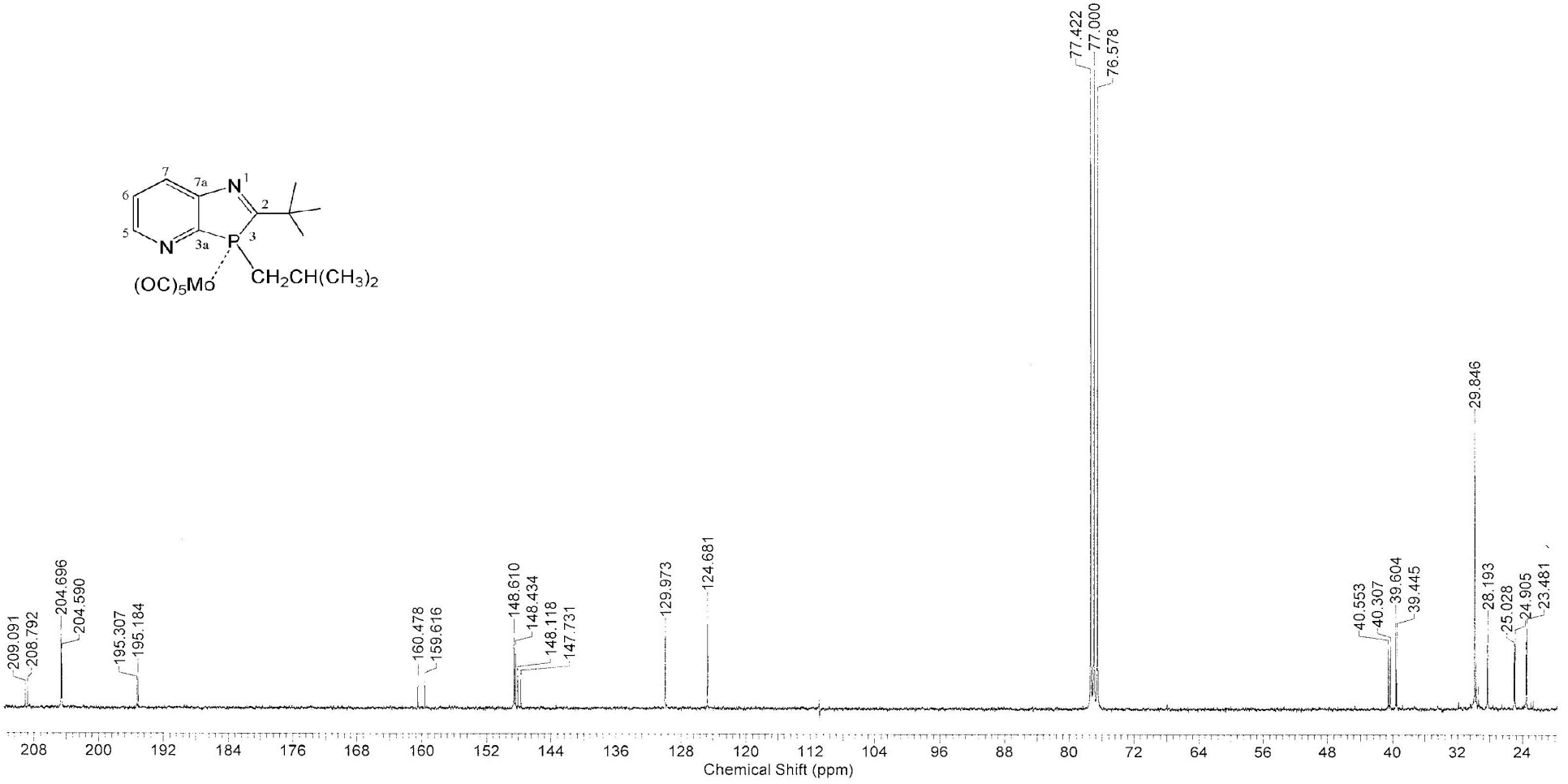


Fig. S9. ^{31}P NMR Spectrum of complex **4c**.

Acquisition Time (sec)	0.3277				
Comment	M. Ghalib:MSRISOPMob 31P{1H}-Spektrum Loesungsmittel: CDCl3 Ref.: extern, H3PO4 = 0.0 ppm (+/- 0.3) Messzeit: 10 min. EMAU Greifswald - Avance II - 300				
Date	28 Nov 2012 10:48:48	*Date Stamp*	28 Nov 2012 10:48:48		
File Name	C:\Users\JoHei\Documents\141201 Arbeitsdokus				
Frequency (MHz)	121.49	*Nucleus*	31P	*Number of Transients*	128
Origin	spect	*Original Points Count*	16384	*Owner*	nmr
Points Count	32768	*Pulse Sequence*	zgpg30	*Receiver Gain*	23100.00
SW(cyclical) (Hz)	50000.00	*Solvent*	CHLOROFORM-d	*Spectrum Offset (Hz)*	499.9960
Spectrum Type	STANDARD	*Sweep Width (Hz)*	49998.47	*Temperature (degree C)*	24.600

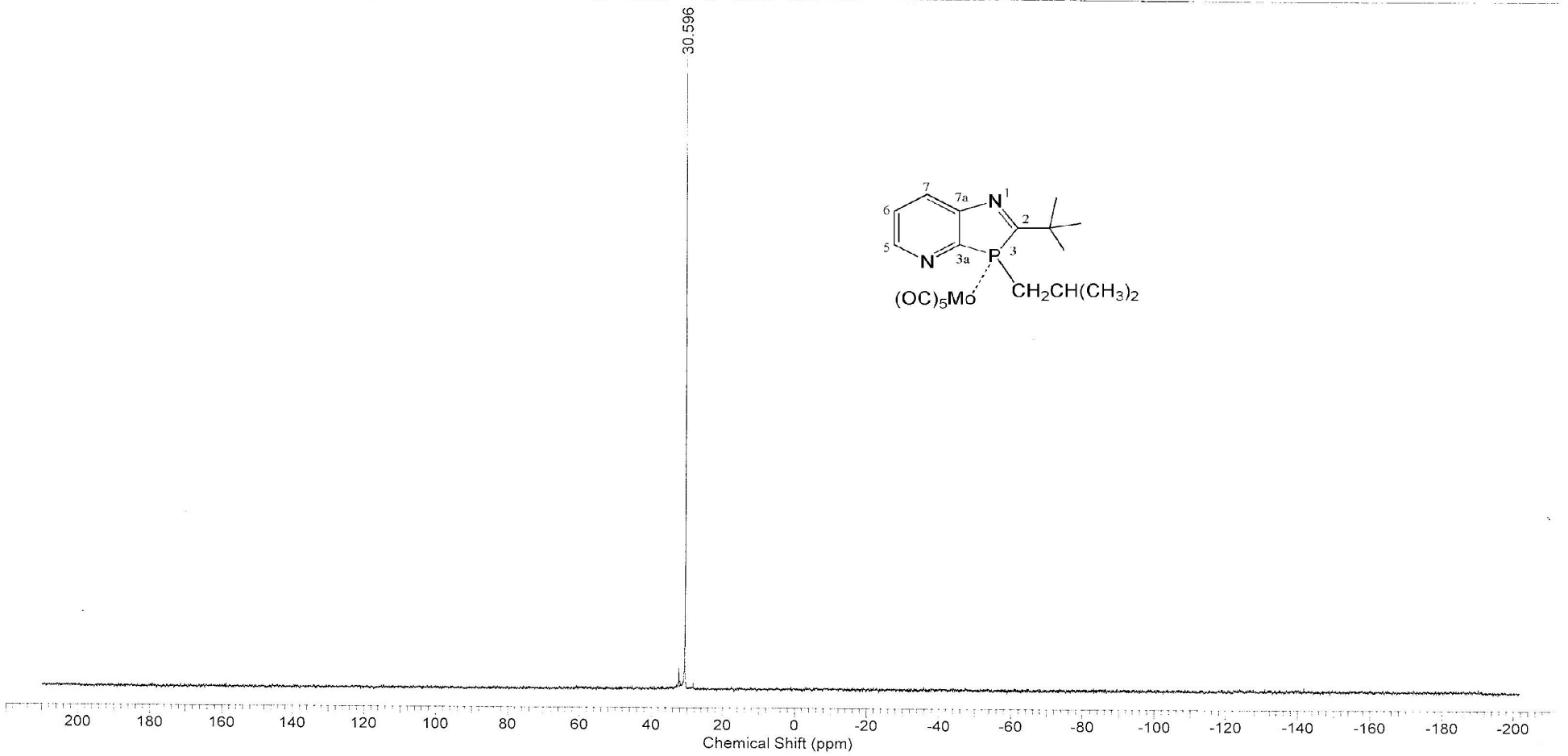
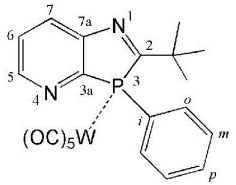


Fig. S10. ^{13}C NMR Spectrum of complex **5a**.

Acquisition Time (sec)	0.7537				
Comment	M.Shaker: SRYW-172 13C{1H}-NMR-Spektrum LM: CDCl3 Ref.: LM = 77.0 ppm (kein TMS) EMAU, AVANCE II - 300 Messzeit: 14 h				
Date		***Date Stamp***			
File Name	C:\Users\JoHei\				
Frequency (MHz)	75.47	***Nucleus***	13C	***Number of Transients***	16384
Origin	spect	***Original Points Count***	16384	***Owner***	nmr
Points Count	16384	***Pulse Sequence***	zgpg30	***Receiver Gain***	32800.00
SW(cyclical) (Hz)	21739.13	***Solvent***	CHLOROFORM-d	***Spectrum Offset (Hz)***	8369.9414
Spectrum Type	STANDARD	***Sweep Width (Hz)***	21737.80	***Temperature (degree C)***	23.700



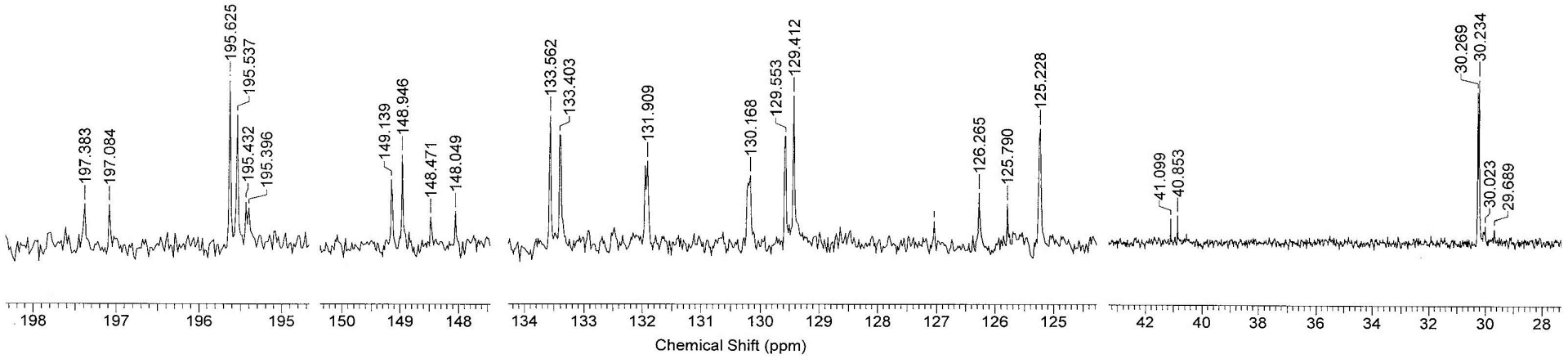
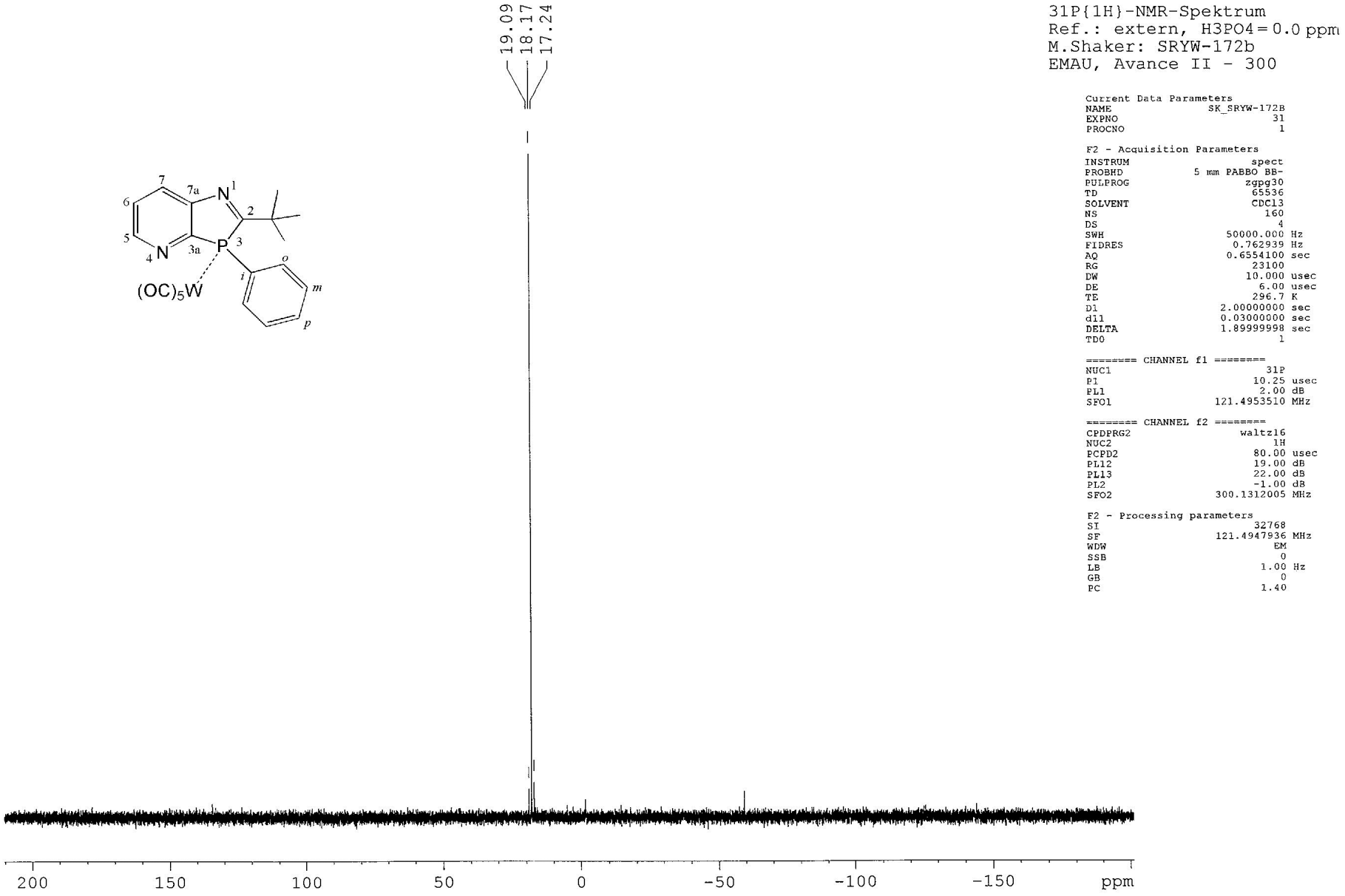


Fig. S11. ^{31}P NMR Spectrum of complex **5a** (with ^{31}P-^{183}W satellites).




```
31P{1H}-NMR-Spektrum
Ref.: extern, H3PO4 = 0.0 ppm
M.Shaker: SRYW-172b
EMAU, Avance II - 300

Current Data Parameters
NAME                  SK_SRYW-172B
EXPNO                           31
PROCNO                           1

F2 - Acquisition Parameters
INSTRUM                       spect
PROBHD          5 mm PABBO BB-
PULPROG                     zgpg30
TD                           65536
SOLVENT                      CDCl3
NS                             160
DS                               4
SWH                    50000.000 Hz
FIDRES                     0.762939 Hz
AQ                       0.6554100 sec
RG                           23100
DW                          10.000 usec
DE                           6.00 usec
TE                          296.7 K
D1                       2.00000000 sec
d11                      0.03000000 sec
DELTA                    1.89999998 sec
TD0                              1

======== CHANNEL f1 ========
NUC1                           31P
P1                          10.25 usec
PL1                          2.00 dB
SFO1                 121.4953510 MHz

======== CHANNEL f2 ========
CPDPRG2                    waltz16
NUC2                           1H
PCPD2                       80.00 usec
PL12                        19.00 dB
PL13                        22.00 dB
PL2                         -1.00 dB
SFO2                 300.1312005 MHz

F2 - Processing parameters
SI                            32768
SF                   121.4947936 MHz
WDW                              EM
SSB                               0
LB                           1.00 Hz
GB                                0
PC                            1.40
```

Fig. S12. ^{1}H NMR Spectrum of complex **6a** (and equilibrium amount of exchange product).

Acquisition Time (sec)	5.2953	***Comment***	M.Shaker: SRYR-168 1H-Spektrum Ernst-Moritz-Arndt-Universitaet Avance II - 300		
Date		***Date Stamp***			
File Name	C:\Users\JoHei\				
Frequency (MHz)	300.13	***Nucleus***	1H	***Number of Transients***	32
Origin	spect	***Original Points Count***	32768	***Owner***	nmr
Points Count	65536	***Pulse Sequence***	zg30	***Receiver Gain***	90.50
SW(cyclical) (Hz)	6188.12	***Solvent***	CHLOROFORM-d	***Spectrum Offset (Hz)***	1856.2401
Spectrum Type	STANDARD	***Sweep Width (Hz)***	6188.02	***Temperature (degree C)***	23.100

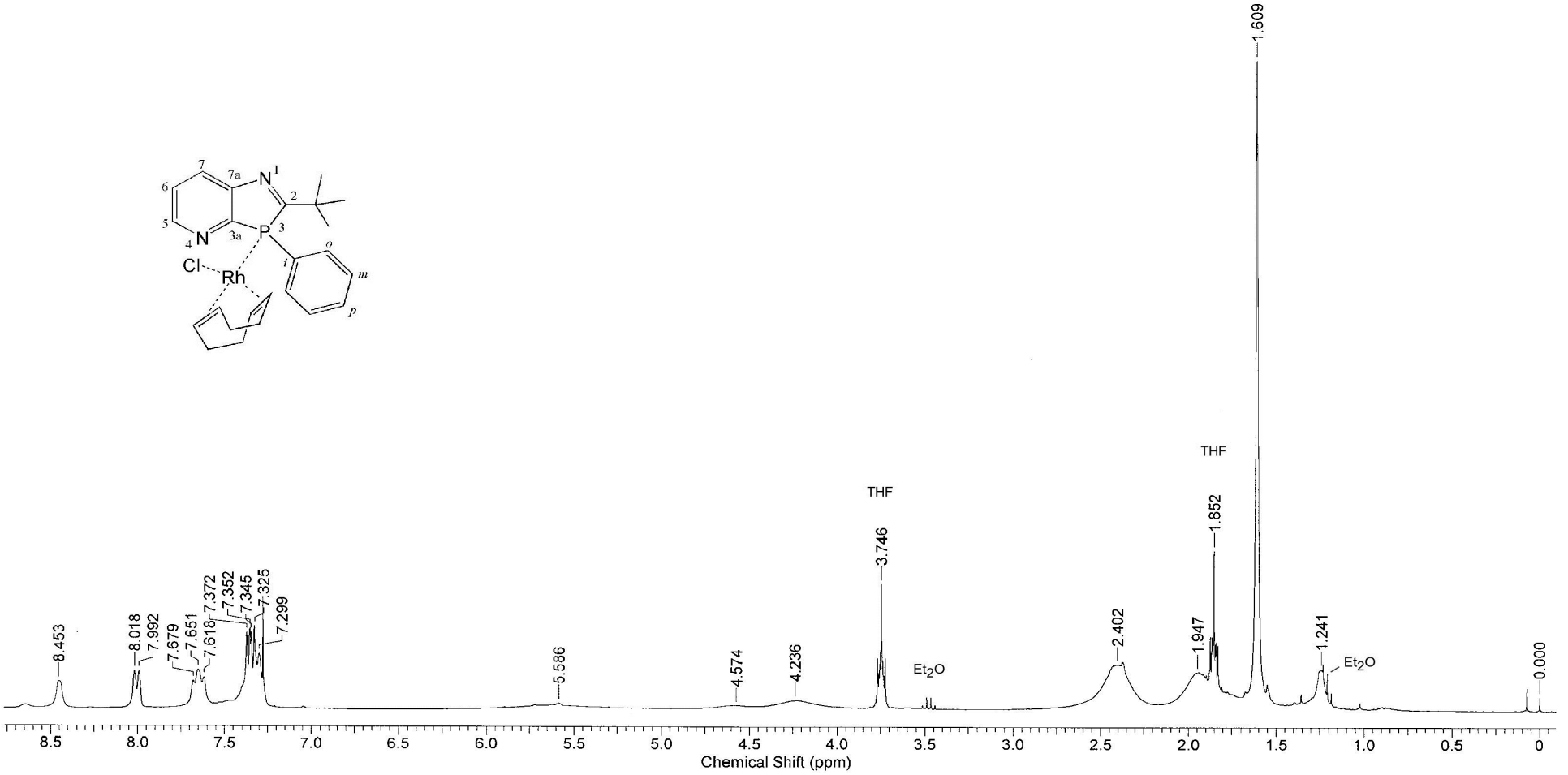


Fig. S13. ^{13}C NMR Spectrum of complex **6a** (and equilibrium amount of exchange product).

Acquisition Time (sec)	1.4156	***Comment***	M.Shaker: SRYR-168 13C{1H}-NMR-Spektrum LM: CDCl3 Ref.: EMAU, AVANCE II - 300		
Date		***Date Stamp***			
File Name	C:\Users\JoHei\				
Frequency (MHz)	75.47	***Nucleus***	13C	***Number of Transients***	17408
Origin	spect	***Original Points Count***	32768	***Owner***	nmr
Points Count	32768	***Pulse Sequence***	zgpg30	***Receiver Gain***	32800.00
SW(cyclical) (Hz)	23148.15	***Solvent***	CHLOROFORM-d	***Spectrum Offset (Hz)***	10451.9219
Spectrum Type	STANDARD	***Sweep Width (Hz)***	23147.44	***Temperature (degree C)***	23.800

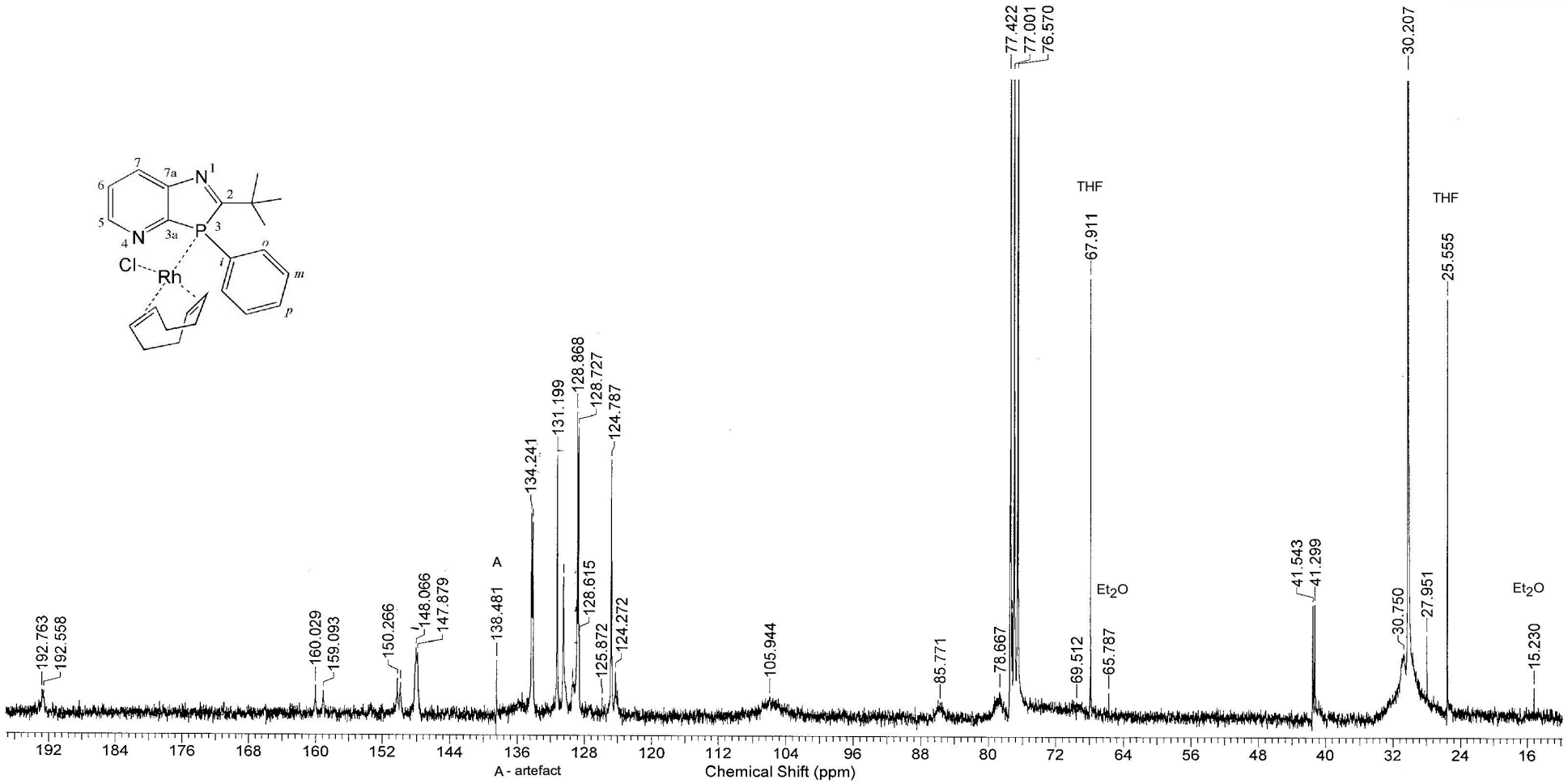


Fig. S14. ^{31}P NMR Spectrum of complex **6a**, showing exchange processes with *N*-Rh(COD)Cl-coordinated **2b** and possibly *P*,*N*-bis[Rh(COD)Cl]L complex **7a** .

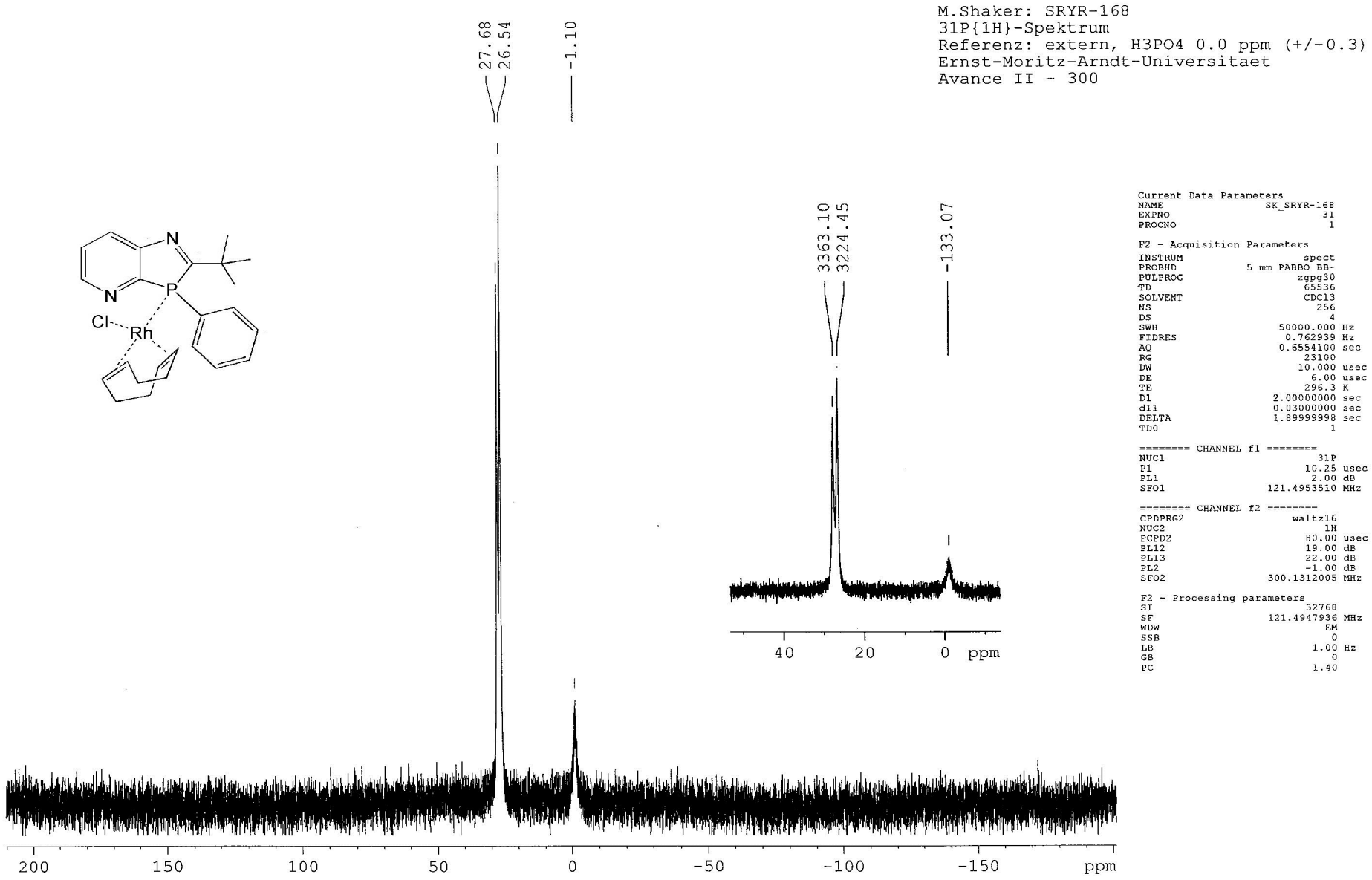


Fig. S15. ^{1}H NMR Spectrum of Rh(COD)Cl complex **6b** (95 mol%).

Acquisition Time (sec)	5.2953	***Comment***	M. Shaker: SRYO-184 1H-Spektrum Loesungsmittel:CDCL3 Referenz:TMS EMAU, Avance II - 300		
Date		***Date Stamp***			
File Name	C:\Users\JoHei\				
Frequency (MHz)	300.13	***Nucleus***	1H	***Number of Transients***	16
Origin	spect	***Original Points Count***	32768	***Owner***	nmr
Points Count	16384	***Pulse Sequence***	zg30	***Receiver Gain***	181.00
SW(cyclical) (Hz)	6188.12	***Solvent***	CHLOROFORM-d	***Spectrum Offset (Hz)***	1854.2772
Spectrum Type	STANDARD	***Sweep Width (Hz)***	6187.74	***Temperature (degree C)***	23.900

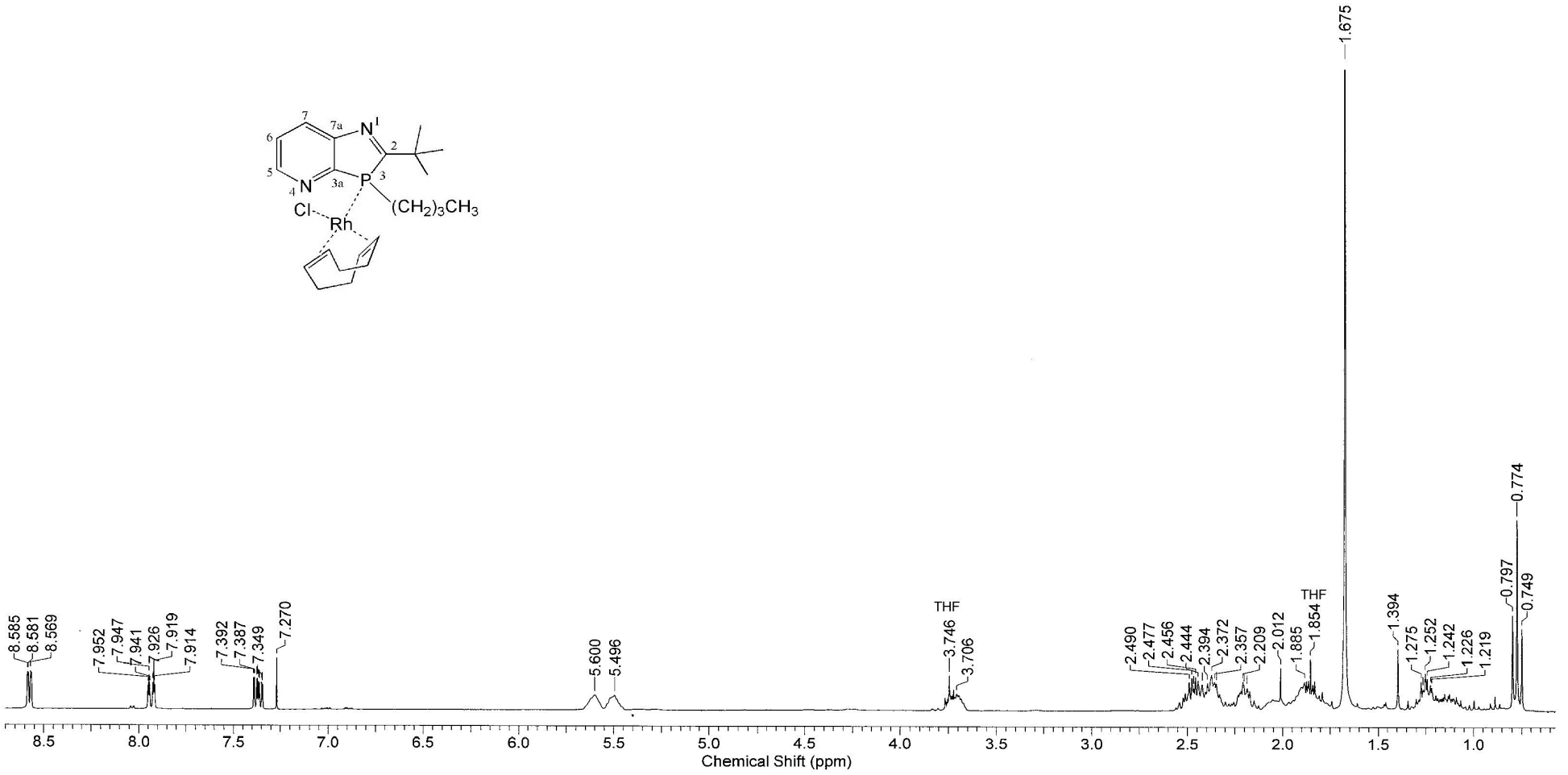


Fig. S16. ^{13}C NMR Spectrum of Rh(COD)Cl complex **6b** (95 mol%).

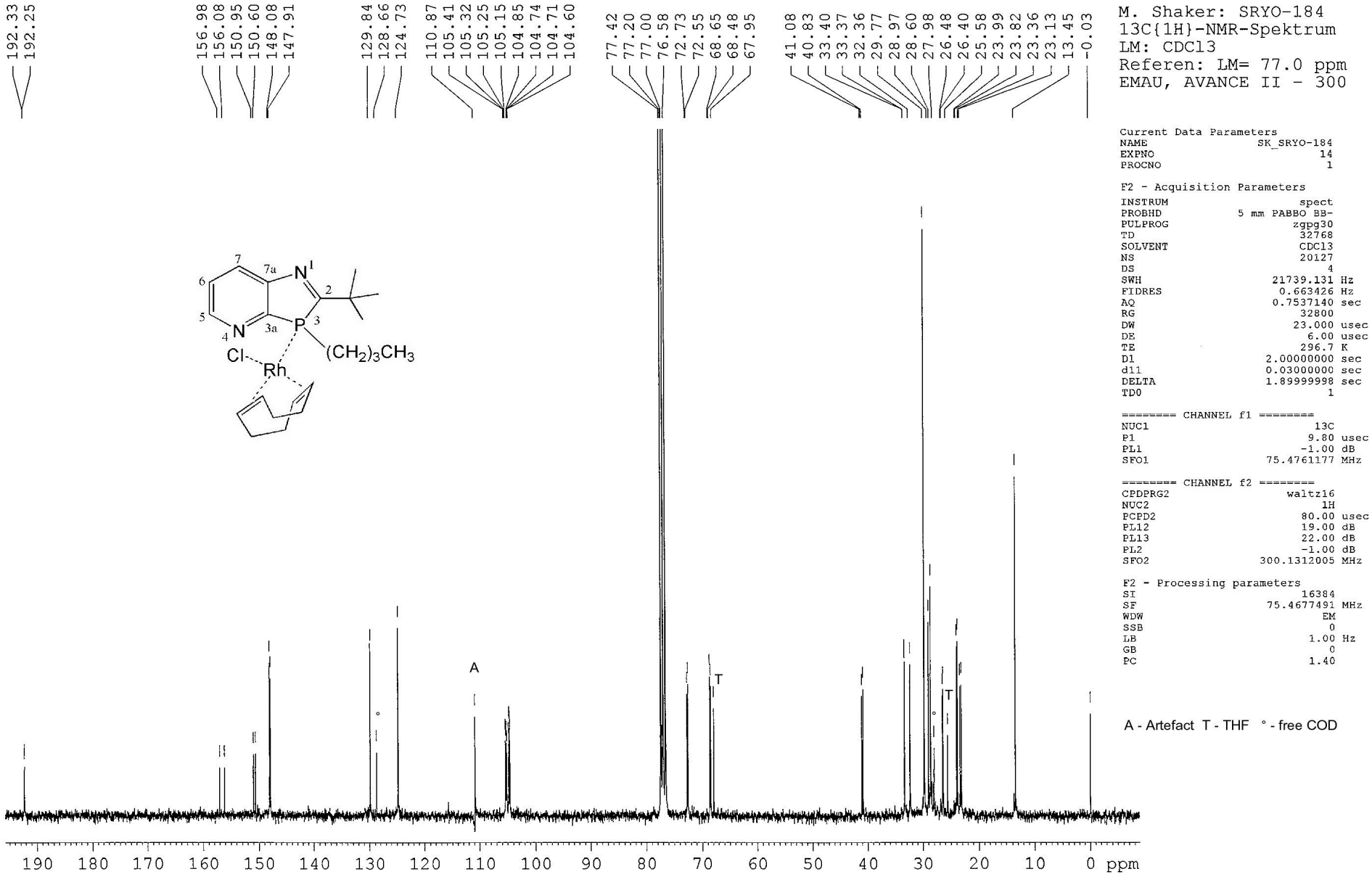


Fig. S17. ^{31}P NMR Spectrum of Rh(COD)Cl complex **6b** (95 mol%) containing 5 mol% *P,N*-bis[Rh(COD)Cl]L complex **7b**.

Acquisition Time (sec)	0.3277				
Comment	M. Shaker: SRYO-184 31P{1H}-Spektrum - Loesungsmittel:CDCL3 Ref.: extern, H3PO4 = 0.0 ppm (+/- 0.3) EMAU, Avance II - 300 Messzeit: 10 min.				
Date		***Date Stamp***			
File Name	C:\Users\JoHei\				
Frequency (MHz)	121.49	***Nucleus***	31P	***Number of Transients***	256
Origin	spect	***Original Points Count***	16384	***Owner***	nmr
Points Count	32768	***Pulse Sequence***	zgpg30	***Receiver Gain***	456.00
SW(cyclical) (Hz)	50000.00	***Solvent***	CHLOROFORM-d	***Spectrum Offset (Hz)***	499.9960
Spectrum Type	STANDARD	***Sweep Width (Hz)***	49998.47	***Temperature (degree C)***	24.000

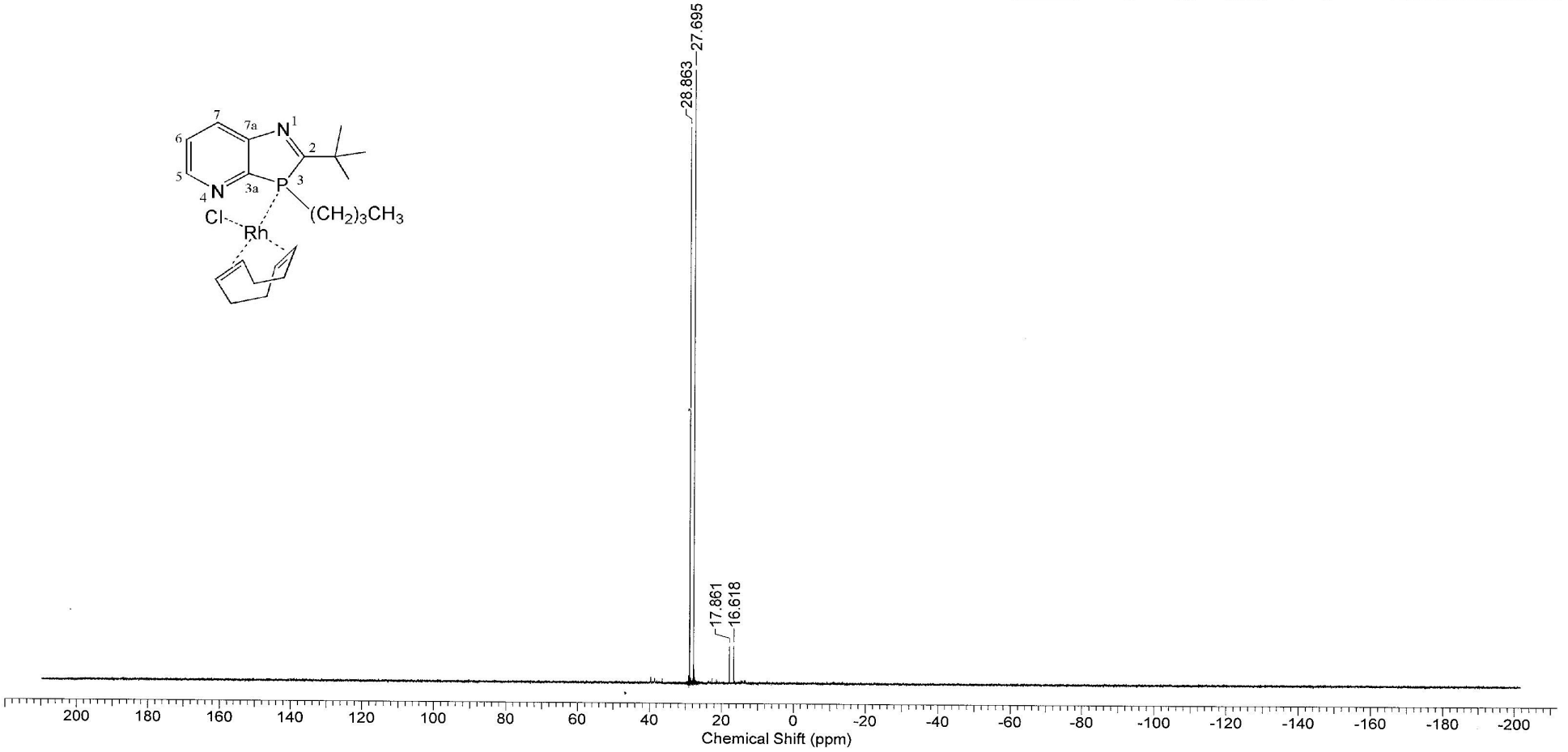


Fig. S18. ^{1}H NMR Spectrum of **8a** and/or **9a**.

Acquisition Time (sec)	5.2953	***Comment***	M.Shaker: SRYN-164 1H-Spektrum Ernst-Moritz-Arndt-Universitaet Avance II - 300		
Date		***Date Stamp***			
File Name	C:\Users\JoHei\				
Frequency (MHz)	300.13	***Nucleus***	1H	***Number of Transients***	16
Origin	spect	***Original Points Count***	32768	***Owner***	nmr
Points Count	32768	***Pulse Sequence***	zg30	***Receiver Gain***	90.50
SW(cyclical) (Hz)	6188.12	***Solvent***	CHLOROFORM-d	***Spectrum Offset (Hz)***	1860.8622
Spectrum Type	STANDARD	***Sweep Width (Hz)***	6187.93	***Temperature (degree C)***	23.600

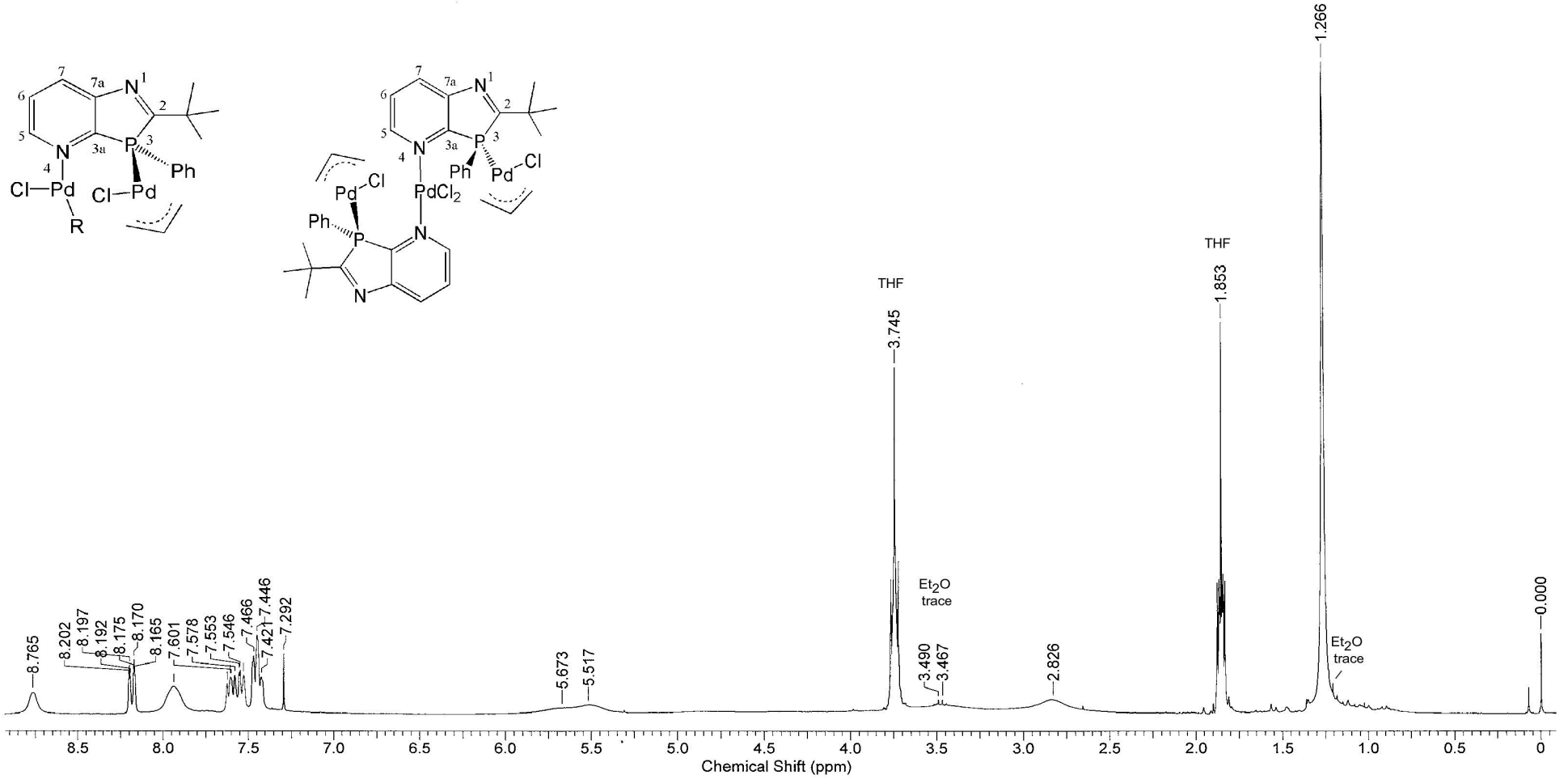


Fig. S19. ^{13}C NMR Spectrum of **8a** and/or **9a**.

Acquisition Time (sec)	1.1010				
Comment	Ernst-Moritz-Arndt-Universitaet, Avance II - 300 13C{1H}-NMR-Spektrum Referenz: TMS = 0.0ppm M.Shaker: SRYN-164 Messzeit: 68 Stunden				
Date		***Date Stamp***			
File Name	C:\Users\JoHei\				
Frequency (MHz)	75.47	***Nucleus***	13C	***Number of Transients***	70656
Origin	spect	***Original Points Count***	32768	***Owner***	nmr
Points Count	32768	***Pulse Sequence***	zgpg30	***Receiver Gain***	32800.00
SW(cyclical) (Hz)	29761.90	***Solvent***	CHLOROFORM-d	***Spectrum Offset (Hz)***	7548.2139
Spectrum Type	STANDARD	***Sweep Width (Hz)***	29761.00	***Temperature (degree C)***	23.500

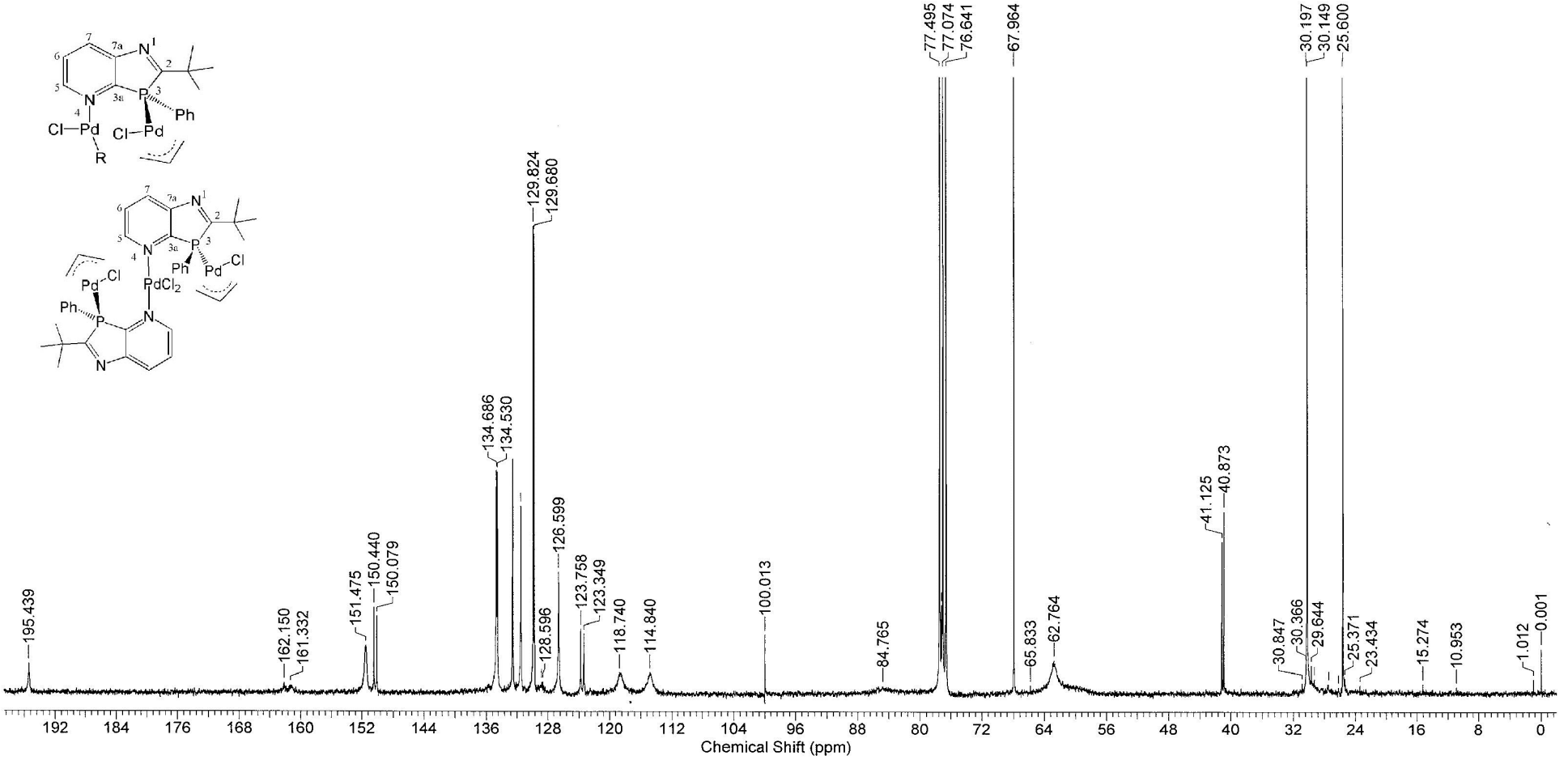


Fig. S20. ^{31}P NMR Spectrum of **8a**/**9a**.

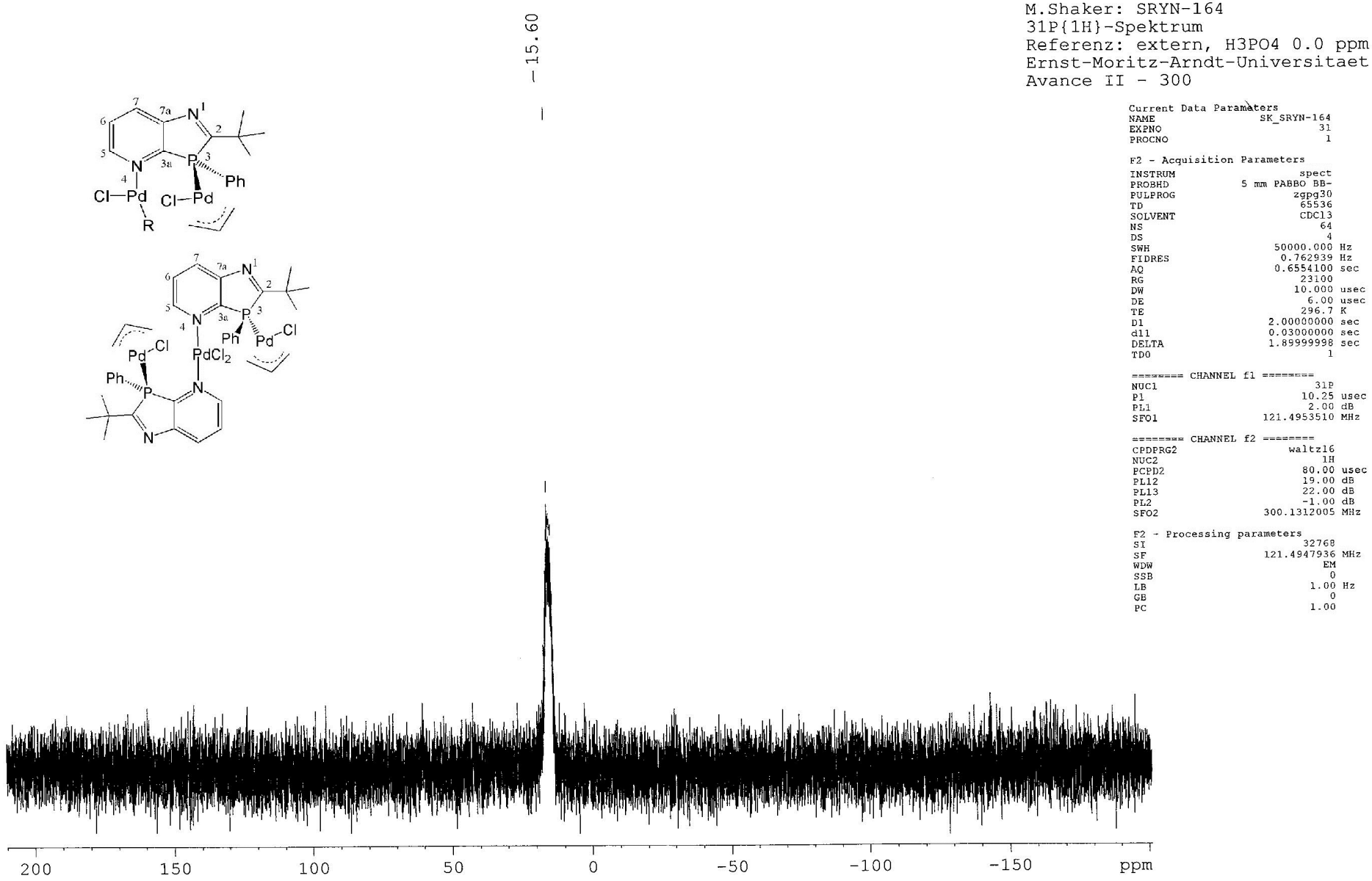


Fig. S21. ^{1}H NMR Spectrum of compound **9b**.

Acquisition Time (sec)	5.2953	***Comment***	M. Shaker: SRYI-188 1H-Spektrum Loesungsmittel: CDCl3 Referenz: TMS = 0.0 ppm EMAU, Avance II - 300		
Date		***Date Stamp***			
File Name	C:\Users\JoHei\				
Frequency (MHz)	300.13	***Nucleus***	1H	***Number of Transients***	80
Origin	spect	***Original Points Count***	32768	***Owner***	nmr
Points Count	16384	***Pulse Sequence***	zg30	***Receiver Gain***	203.00
SW(cyclical) (Hz)	6188.12	***Solvent***	CHLOROFORM-d	***Spectrum Offset (Hz)***	1856.5551
Spectrum Type	STANDARD	***Sweep Width (Hz)***	6187.74	***Temperature (degree C)***	23.600

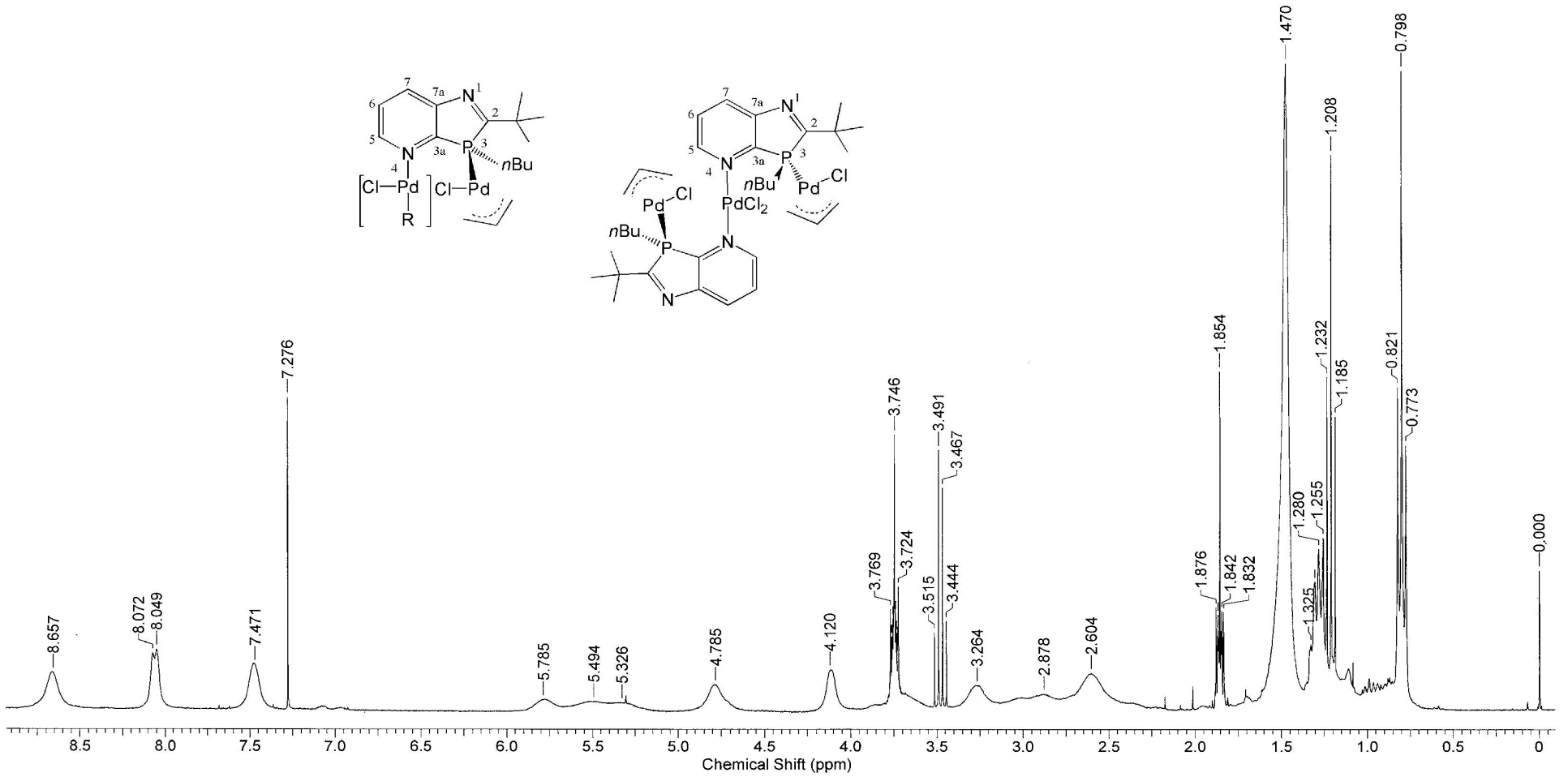


Fig. S22. ^{13}C NMR Spectrum of compound **9b**.

Acquisition Time (sec)	1.4156	***Comment***	M.Shaker: SRYI-188 13C{1H}-NMR-Spektrum LM: CDCl3 Ref.: LM = 77.0 ppm Messzeit: 14 Stunden EMAU, AVANCE II - 300		
Date		***Date Stamp***			
File Name	C:\Users\JoHei\				
Frequency (MHz)	75.47	***Nucleus***	13C	***Number of Transients***	14336
Origin	spect	***Original Points Count***	32768	***Owner***	nmr
Points Count	65536	***Pulse Sequence***	zgpg30	***Receiver Gain***	32800.00
SW(cyclical) (Hz)	23148.15	***Solvent***	CHLOROFORM-d	***Spectrum Offset (Hz)***	10454.1855
Spectrum Type	STANDARD	***Sweep Width (Hz)***	23147.79	***Temperature (degree C)***	25.400

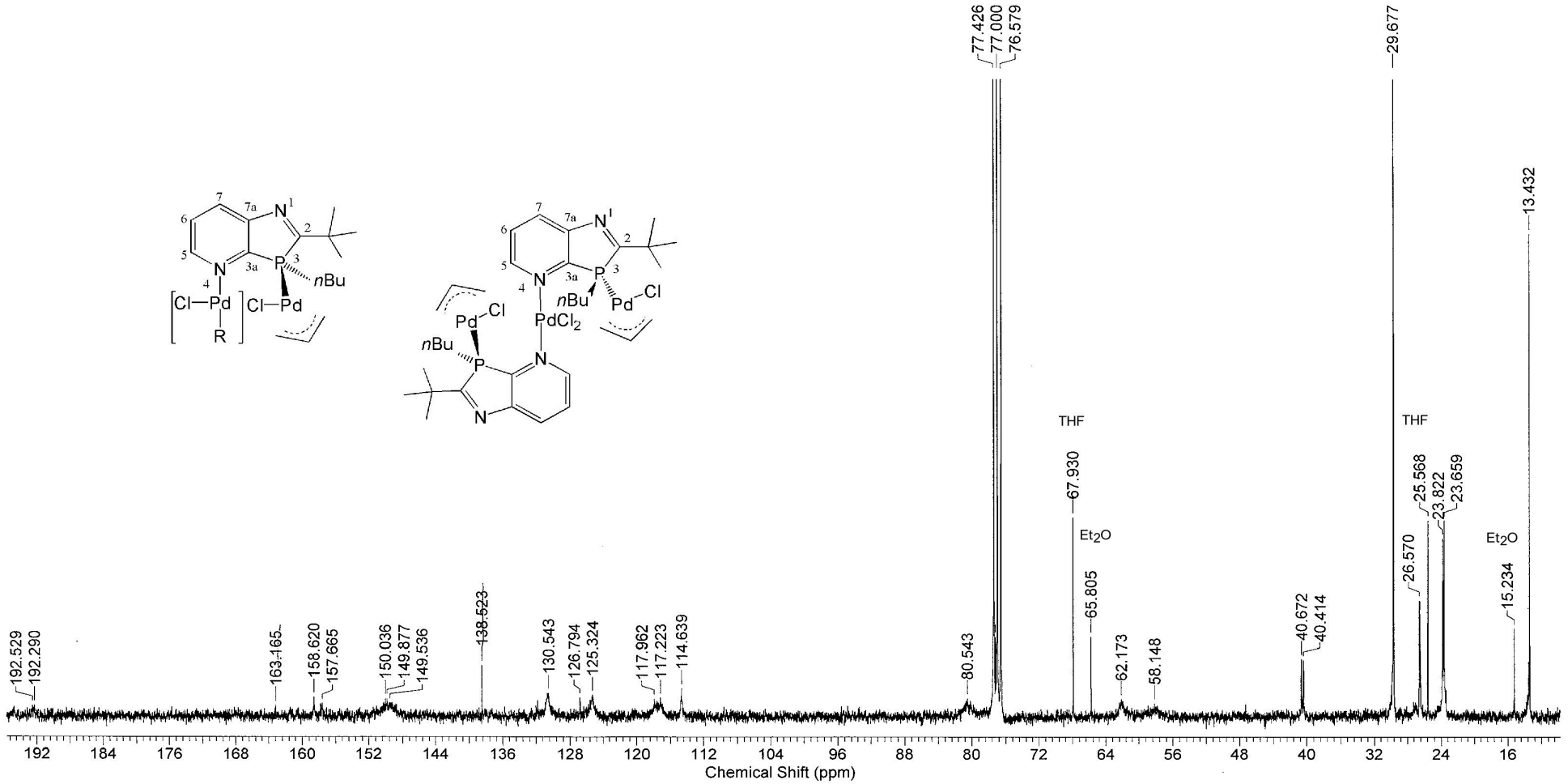


Fig. S23. ^{31}P NMR Spectrum of compound **9b**.

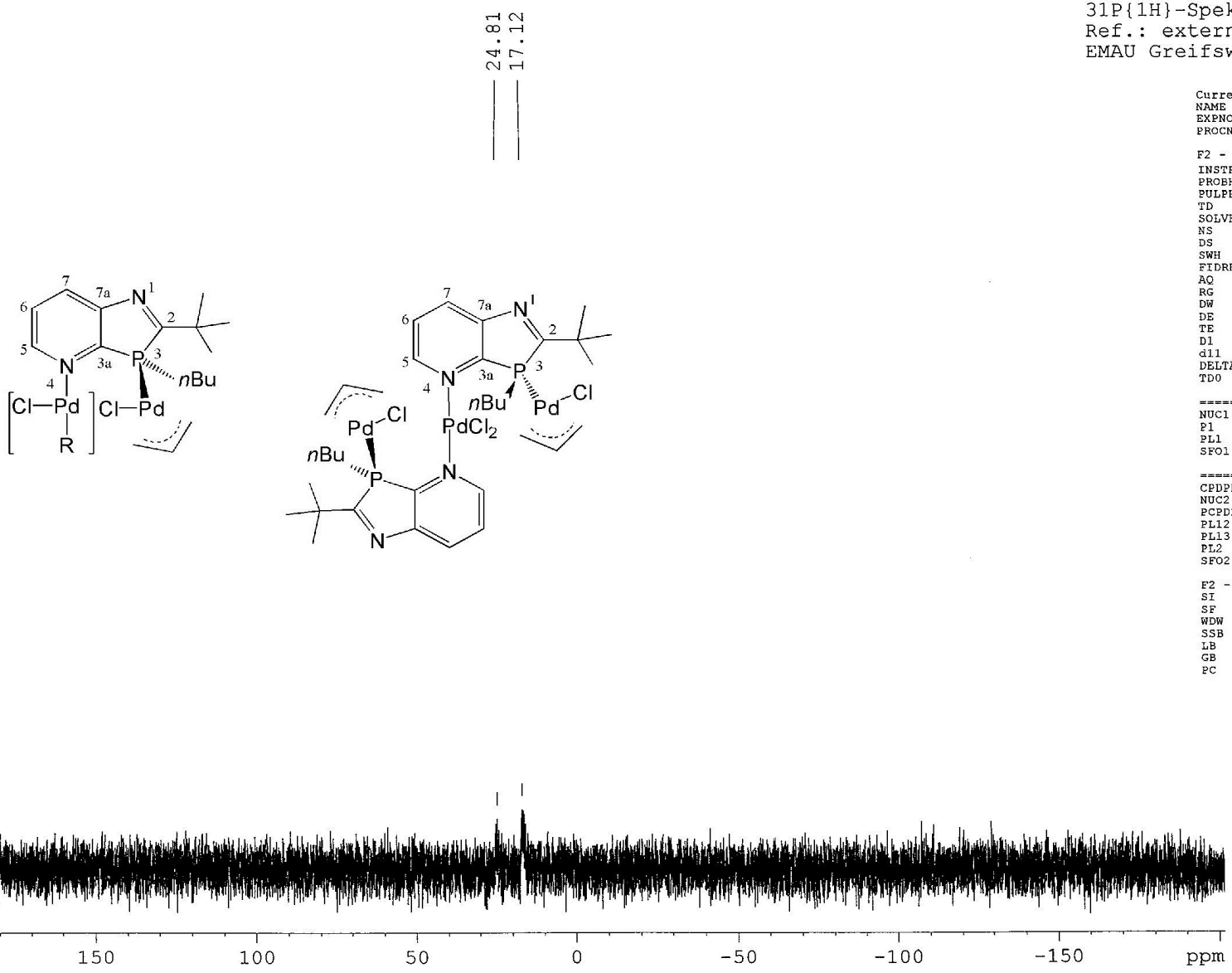


Fig. S24. ^{13}C NMR Spectrum of compound **10b**.

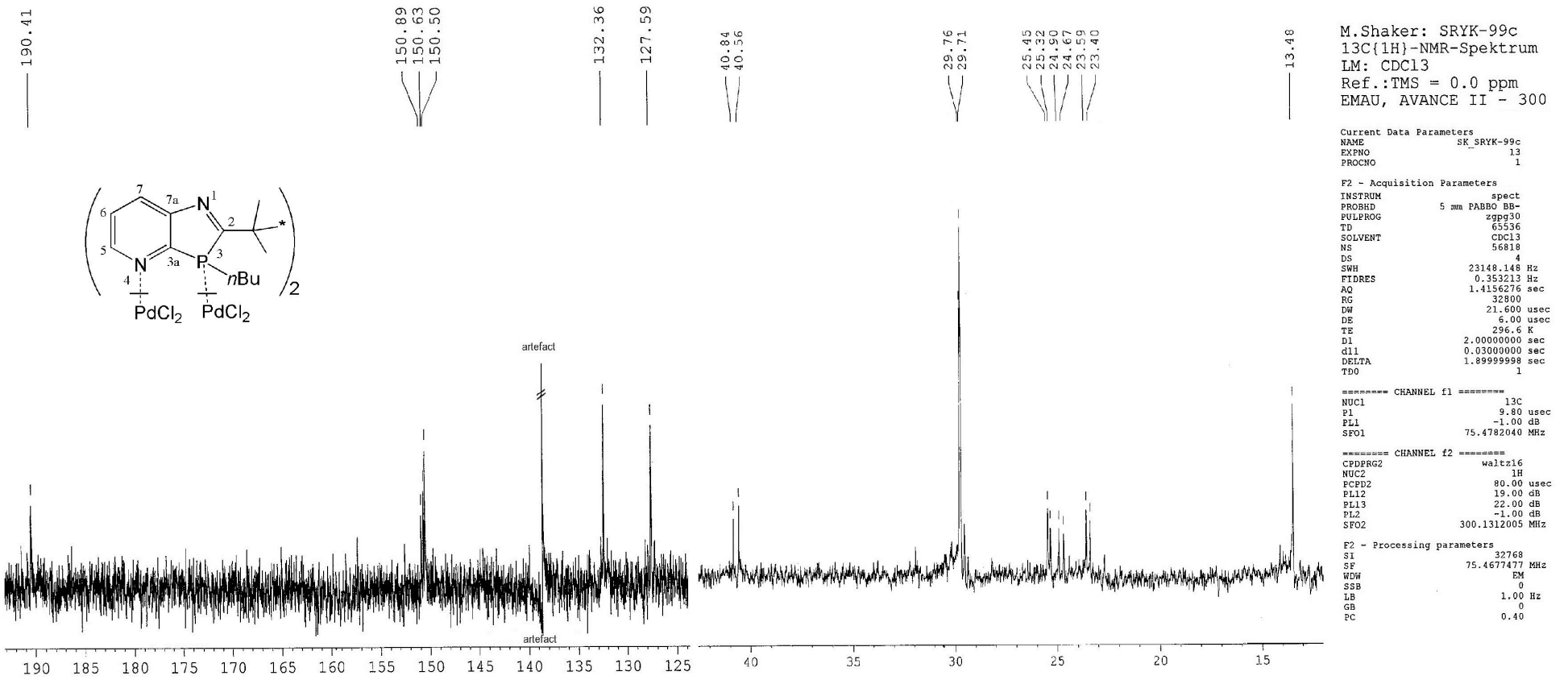
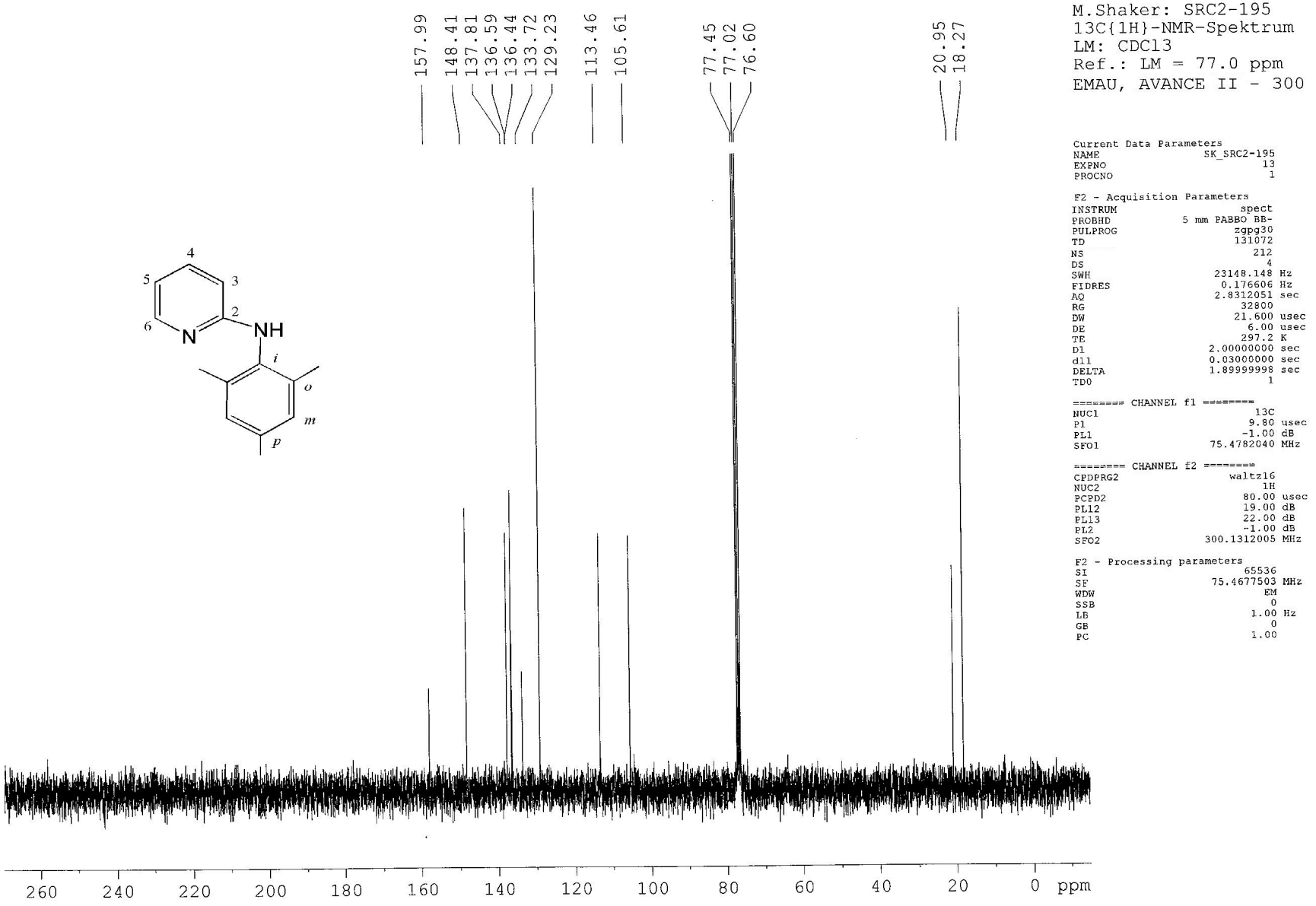


Fig. S25. ^{13}C NMR Spectrum of compound **11**.

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M.Shaker: SRC2-195
13C{1H}-NMR-Spektrum
LM: CDCl3
Ref.: LM = 77.0 ppm
EMAU, AVANCE II - 300

Current Data Parameters
NAME                  SK_SRC2-195
EXPNO                          13
PROCNO                          1

F2 - Acquisition Parameters
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PROBHD          5 mm PABBO BB-
PULPROG                    zgpg30
TD                         131072
NS                            212
DS                              4
SWH                     23148.148 Hz
FIDRES                  0.176606 Hz
AQ                      2.8312051 sec
RG                          32800
DW                         21.600 usec
DE                          6.00 usec
TE                          297.2 K
D1                     2.00000000 sec
d11                    0.03000000 sec
DELTA                  1.89999998 sec
TD0                             1

======== CHANNEL f1 ========
NUC1                          13C
P1                           9.80 usec
PL1                         -1.00 dB
SFO1                  75.4782040 MHz

======== CHANNEL f2 ========
CPDPRG2                   waltz16
NUC2                          1H
PCPD2                       80.00 usec
PL12                        19.00 dB
PL13                        22.00 dB
PL2                         -1.00 dB
SFO2                 300.1312005 MHz

F2 - Processing parameters
SI                            65536
SF                    75.4677503 MHz
WDW                              EM
SSB                              0
LB                            1.00 Hz
GB                               0
PC                            1.00
```

2. Crystal structures - Tables with positional parameters, bond lengths and angles of **6a**, **9b**·2$CDCl_3$, **10b**·2(D_6-acetone) and **10b**·4.5THF and figures of the packing of **6a** and the crude structure of **9a** (S26, S27).

Table S1. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor of **6a**.

	x	y	z	U(eq)
Rh	2875.1(1)	4769.2(1)	2382.9(1)	13.5(1)
Cl	78.4(3)	5818.0(3)	2563.2(2)	24.4(1)
N(1)	4209.8(10)	225.7(9)	3557.5(6)	14.8(2)
C(2)	2956.1(11)	1404.8(10)	3559.4(7)	13.8(2)
P(3)	2792.5(3)	2496.0(3)	2335.4(2)	11.6(1)
C(3A)	4573.1(11)	1038.5(10)	1841.8(7)	11.9(2)
N(4)	5252.9(10)	971.4(9)	900.2(6)	13.8(1)
C(5)	6565.9(11)	-226.0(11)	704.1(7)	15.0(2)
C(6)	7235.3(12)	-1313.1(11)	1425.8(8)	16.0(2)
C(7)	6522.4(12)	-1209.6(11)	2406.3(8)	15.2(2)
C(7A)	5131.2(11)	-14.1(10)	2612.8(7)	12.8(2)
C(11)	1271.9(11)	2200.3(10)	1758.0(7)	14.1(2)
C(12)	870.8(13)	969.4(11)	2029.4(8)	19.1(2)
C(13)	-208.2(14)	713.8(13)	1523.7(10)	23.4(2)
C(14)	-862.7(13)	1664.5(13)	734.2(9)	22.3(2)
C(15)	-451.7(13)	2875.4(12)	453.6(8)	20.4(2)
C(16)	604.8(12)	3155.5(11)	970.5(8)	17.3(2)
C(17)	1860.1(12)	1912.9(11)	4508.0(8)	17.6(2)
C(18)	2045.1(14)	614.1(13)	5272.3(8)	23.8(2)
C(19)	2370.1(16)	3038.0(13)	4922.0(9)	25.7(2)
C(20)	120.5(13)	2639.3(14)	4295.9(9)	26.0(2)
C(21)	2886.8(15)	6991.2(11)	1990.5(9)	22.6(2)
C(22)	3062.0(19)	6684.3(13)	2992.4(9)	29.2(3)
C(23)	4623(2)	6274.5(17)	3409.5(11)	40.6(4)
C(24)	5511(2)	4616.5(17)	3531.4(11)	37.8(3)
C(25)	5256.2(14)	3788.6(13)	2737.6(10)	23.9(2)
C(26)	5280.0(13)	4188.2(12)	1713.2(9)	20.7(2)
C(27)	5678.1(15)	5492.3(13)	1231.9(10)	26.3(2)
C(28)	4202.8(15)	6896.5(13)	1162.2(9)	24.4(2)

Table S2. Bond lengths [Å] and angles [°] of **6a**.

Rh-C(25)	2.1274(11)	C(11)-C(16)	1.3945(14)
Rh-C(26)	2.1364(11)	C(11)-C(12)	1.3976(14)
Rh-C(21)	2.2085(11)	C(12)-C(13)	1.3895(15)
Rh-C(22)	2.2176(11)	C(13)-C(14)	1.3913(17)
Rh-P(3)	2.2855(3)	C(14)-C(15)	1.3858(16)
Rh-Cl	2.3547(3)	C(15)-C(16)	1.3937(14)
N(1)-C(2)	1.2902(13)	C(17)-C(18)	1.5346(15)
N(1)-C(7A)	1.4159(12)	C(17)-C(20)	1.5351(16)
C(2)-C(17)	1.5137(14)	C(17)-C(19)	1.5400(16)
C(2)-P(3)	1.8733(10)	C(21)-C(22)	1.3791(17)
P(3)-C(3A)	1.8144(10)	C(21)-C(28)	1.5033(17)
P(3)-C(11)	1.8181(10)	C(22)-C(23)	1.507(2)
C(3A)-N(4)	1.3323(12)	C(23)-C(24)	1.533(2)
C(3A)-C(7A)	1.3998(13)	C(24)-C(25)	1.5128(18)
N(4)-C(5)	1.3473(13)	C(25)-C(26)	1.4022(17)
C(5)-C(6)	1.3934(14)	C(26)-C(27)	1.5253(16)
C(6)-C(7)	1.3884(14)	C(27)-C(28)	1.5338(17)
C(7)-C(7A)	1.3877(13)		

C(25)-Rh-C(26)	38.40(5)	C(17)-C(2)-P(3)	124.45(7)
C(25)-Rh-C(21)	96.88(5)	C(3A)-P(3)-C(11)	101.39(4)
C(26)-Rh-C(21)	81.32(4)	C(3A)-P(3)-C(2)	87.53(4)
C(25)-Rh-C(22)	81.30(5)	C(11)-P(3)-C(2)	106.34(4)
C(26)-Rh-C(22)	89.02(5)	C(3A)-P(3)-Rh	118.56(3)
C(21)-Rh-C(22)	36.31(4)	C(11)-P(3)-Rh	122.16(3)
C(25)-Rh-P(3)	89.64(3)	C(2)-P(3)-Rh	114.88(3)
C(26)-Rh-P(3)	95.34(3)	N(4)-C(3A)-C(7A)	125.04(9)
C(21)-Rh-P(3)	164.30(3)	N(4)-C(3A)-P(3)	125.95(7)
C(22)-Rh-P(3)	159.39(3)	C(7A)-C(3A)-P(3)	109.00(7)
C(25)-Rh-Cl	161.21(4)	C(3A)-N(4)-C(5)	115.44(8)
C(26)-Rh-Cl	159.88(3)	N(4)-C(5)-C(6)	123.72(9)
C(21)-Rh-Cl	87.76(3)	C(7)-C(6)-C(5)	119.87(9)
C(22)-Rh-Cl	92.13(4)	C(7A)-C(7)-C(6)	117.15(9)
P(3)-Rh-Cl	90.624(10)	C(7)-C(7A)-C(3A)	118.69(9)
C(2)-N(1)-C(7A)	113.10(8)	C(7)-C(7A)-N(1)	124.64(9)
N(1)-C(2)-C(17)	121.62(9)	C(3A)-C(7A)-N(1)	116.67(8)
N(1)-C(2)-P(3)	113.53(7)	C(16)-C(11)-C(12)	119.81(9)

C(16)-C(11)-P(3)	118.79(7)	C(28)-C(21)-Rh	108.41(7)
C(12)-C(11)-P(3)	121.15(8)	C(21)-C(22)-C(23)	123.64(13)
C(13)-C(12)-C(11)	119.91(10)	C(21)-C(22)-Rh	71.49(7)
C(12)-C(13)-C(14)	120.06(10)	C(23)-C(22)-Rh	111.09(9)
C(15)-C(14)-C(13)	120.22(10)	C(22)-C(23)-C(24)	113.06(10)
C(14)-C(15)-C(16)	120.04(10)	C(25)-C(24)-C(23)	113.06(10)
C(15)-C(16)-C(11)	119.93(10)	C(26)-C(25)-C(24)	125.92(10)
C(2)-C(17)-C(18)	110.00(9)	C(26)-C(25)-Rh	71.15(6)
C(2)-C(17)-C(20)	111.14(9)	C(24)-C(25)-Rh	110.15(10)
C(18)-C(17)-C(20)	109.91(9)	C(25)-C(26)-C(27)	123.93(10)
C(2)-C(17)-C(19)	106.68(9)	C(25)-C(26)-Rh	70.45(7)
C(18)-C(17)-C(19)	109.60(9)	C(27)-C(26)-Rh	113.51(8)
C(20)-C(17)-C(19)	109.44(10)	C(26)-C(27)-C(28)	112.88(10)
C(22)-C(21)-C(28)	125.78(12)	C(21)-C(28)-C(27)	113.77(9)
C(22)-C(21)-Rh	72.21(6)		

Table S3. Hydrogen bonds [Å and °] of **6a**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(20)-H(20A)...Cl	0.98	2.74	3.7094(13)	169.1
C(6)-H(6)...Cl#1	0.95	2.79	3.4435(10)	126.3
C(7)-H(7)...Cl#1	0.95	2.89	3.4805(10)	121.6
C(19)-H(19B)...Cl#2	0.98	2.85	3.8204(12)	173.1

Symmetry transformations used to generate equivalent atoms: #1 x+1,y-1,z; #2 -x,-y+1,-z+1

Table S4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor of **9b**·2$CDCl_3$.

	x	y	z	U(eq)
Pd(1)	5665.7(2)	1405.3(2)	8565.3(1)	13.7(1)
Cl(1)	2752.4(6)	349.5(6)	8548.1(3)	21.9(1)
Pd(2)	5000	5000	10000	11.2(1)
Cl(2)	6567.9(6)	3776.0(6)	10505.7(3)	19.4(1)
N(1)	8024.7(19)	4864.8(18)	7246.7(10)	13.1(3)
C(2)	6767(2)	3622(2)	7092.5(11)	12.4(3)
P(3)	5550.8(6)	3309.8(5)	7987.4(3)	10.9(1)
C(3A)	6906(2)	5157.1(19)	8554.6(11)	11.0(3)
N(4)	6853.4(19)	5880.1(17)	9335.3(10)	12.1(3)
C(5)	8066(2)	7217(2)	9666.8(12)	15.6(3)
C(6)	9369(2)	7835(2)	9222.6(12)	17.3(4)
C(7)	9437(2)	7101(2)	8410.7(12)	15.8(4)
C(7A)	8162(2)	5745(2)	8069.4(11)	12.4(3)
C(8)	6447(2)	2448(2)	6272.7(12)	15.2(3)
C(9)	7509(3)	1476(2)	6367.7(13)	21.3(4)
C(10)	6977(3)	3231(3)	5557.1(13)	24.5(4)
C(11)	4607(3)	1433(3)	6087.5(14)	25.2(5)
C(12)	3559(2)	3521(2)	7721.4(12)	14.7(3)
C(13)	3726(2)	4822(2)	7303.3(13)	17.2(4)
C(14)	2074(3)	5044(3)	7151.7(14)	22.8(4)
C(15)	2256(3)	6353(3)	6742.4(17)	33.0(6)
C(16)	6470(3)	-72(3)	9200.1(18)	31.7(5)
C(17)	7616(3)	482(3)	8669.9(17)	30.4(5)
C(18)	8304(3)	2037(3)	8747.6(15)	23.7(4)
C(99)	8527(3)	7495(3)	6077.2(15)	25.5(4)
Cl(3)	6474.9(7)	7411.0(7)	6195.1(5)	35.2(1)
Cl(4)	9962.6(8)	9134.4(7)	6727.2(5)	36.0(1)
Cl(5)	8865.3(13)	7319.8(14)	5030.5(5)	67.9(3)

Table S5. Bond lengths [Å] and angles [°] of **9b**·2$CDCl_3$.

Pd(1)-C(18)	2.125(2)	N(4)-C(5)	1.347(2)
Pd(1)-C(17)	2.157(2)	C(5)-C(6)	1.390(3)
Pd(1)-C(16)	2.197(2)	C(6)-C(7)	1.388(3)
Pd(1)-P(3)	2.2685(5)	C(7)-C(7A)	1.385(3)
Pd(1)-Cl(1)	2.3542(5)	C(8)-C(10)	1.530(3)
Pd(2)-N(4)	2.0121(15)	C(8)-C(11)	1.531(3)
Pd(2)-Cl(2)	2.2976(5)	C(8)-C(9)	1.536(3)
N(1)-C(2)	1.288(2)	C(12)-C(13)	1.524(3)
N(1)-C(7A)	1.417(2)	C(13)-C(14)	1.519(3)
C(2)-C(8)	1.519(3)	C(14)-C(15)	1.520(3)
C(2)-P(3)	1.8506(19)	C(16)-C(17)	1.384(4)
P(3)-C(3A)	1.8027(18)	C(17)-C(18)	1.396(4)
P(3)-C(12)	1.8305(19)	C(99)-Cl(5)	1.737(3)
C(3A)-N(4)	1.337(2)	C(99)-Cl(4)	1.750(2)
C(3A)-C(7A)	1.400(2)	C(99)-Cl(3)	1.751(2)
C(18)-Pd(1)-C(17)	38.05(10)	C(3A)-P(3)-Pd(1)	114.31(6)
C(18)-Pd(1)-C(16)	67.44(10)	C(12)-P(3)-Pd(1)	121.33(6)
C(17)-Pd(1)-C(16)	37.05(10)	C(2)-P(3)-Pd(1)	116.46(6)
C(18)-Pd(1)-P(3)	97.89(7)	N(4)-C(3A)-C(7A)	122.45(16)
C(17)-Pd(1)-P(3)	131.02(7)	N(4)-C(3A)-P(3)	127.97(14)
C(16)-Pd(1)-P(3)	165.00(8)	C(7A)-C(3A)-P(3)	109.47(13)
C(18)-Pd(1)-Cl(1)	167.66(7)	C(3A)-N(4)-C(5)	118.54(16)
C(17)-Pd(1)-Cl(1)	131.73(8)	C(3A)-N(4)-Pd(2)	120.86(12)
C(16)-Pd(1)-Cl(1)	100.35(7)	C(5)-N(4)-Pd(2)	120.59(13)
P(3)-Pd(1)-Cl(1)	94.182(19)	N(4)-C(5)-C(6)	121.50(17)
N(4)#1-Pd(2)-N(4)	180.0	C(7)-C(6)-C(5)	120.60(18)
N(4)#1-Pd(2)-Cl(2)#1	89.37(5)	C(7A)-C(7)-C(6)	117.37(17)
N(4)-Pd(2)-Cl(2)#1	90.63(5)	C(7)-C(7A)-C(3A)	119.50(17)
Cl(2)#1-Pd(2)-Cl(2)	180.0	C(7)-C(7A)-N(1)	124.65(17)
C(2)-N(1)-C(7A)	112.59(16)	C(3A)-C(7A)-N(1)	115.85(16)
N(1)-C(2)-C(8)	121.76(17)	C(2)-C(8)-C(10)	109.74(16)
N(1)-C(2)-P(3)	114.44(14)	C(2)-C(8)-C(11)	111.13(16)
C(8)-C(2)-P(3)	123.46(14)	C(10)-C(8)-C(11)	110.25(18)
C(3A)-P(3)-C(12)	105.39(9)	C(2)-C(8)-C(9)	107.25(16)
C(3A)-P(3)-C(2)	87.36(8)	C(10)-C(8)-C(9)	109.57(17)
C(12)-P(3)-C(2)	106.44(9)	C(11)-C(8)-C(9)	108.84(17)

C(13)-C(12)-P(3)	113.70(13)	C(18)-C(17)-Pd(1)	69.71(13)
C(14)-C(13)-C(12)	112.44(16)	C(17)-C(18)-Pd(1)	72.25(14)
C(13)-C(14)-C(15)	112.05(18)	Cl(5)-C(99)-Cl(4)	112.42(14)
C(17)-C(16)-Pd(1)	69.92(14)	Cl(5)-C(99)-Cl(3)	110.38(13)
C(16)-C(17)-C(18)	119.4(2)	Cl(4)-C(99)-Cl(3)	111.01(13)
C(16)-C(17)-Pd(1)	73.03(14)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+2

Table S6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor of **10b**·2(D_6-acetone).

	x	y	z	U(eq)
Pd(1)	5347.4(1)	6341.6(2)	4184.6(1)	15.4(1)
Pd(2)	5561.0(1)	8702.7(2)	4391.3(1)	15.9(1)
Cl(1)	5459.1(3)	6134.8(6)	3231.8(3)	28.2(2)
Cl(2)	5945.4(3)	5402.8(5)	4426.3(3)	21.2(2)
Cl(3)	6303.0(3)	8984.7(6)	4045.3(4)	28.6(2)
Cl(4)	5199.0(3)	9617.6(5)	3758.2(3)	21.3(2)
N(1)	3903.2(10)	7072.6(17)	4482.0(12)	20.3(6)
C(2)	4134.5(12)	6736.1(19)	4073.8(14)	18.3(6)
P(3)	4742.5(3)	7179.7(5)	3953.2(3)	15.3(2)
C(3A)	4612.4(11)	7891.3(18)	4516.6(13)	15.9(6)
N(4)	4901.9(10)	8471.9(15)	4729.5(11)	15.4(5)
C(5)	4739.2(12)	8907.1(19)	5178.0(13)	19.0(6)
C(6)	4287.8(12)	8772(2)	5417.7(14)	19.6(6)
C(7)	3998.2(13)	8159(2)	5208.1(14)	22.1(7)
C(7A)	4163.6(12)	7715.1(19)	4746.0(13)	18.0(6)
C(8)	3935.8(12)	6016(2)	3751.5(14)	21.2(7)
C(9)	4070.6(15)	6047(2)	3116.9(14)	28.6(8)
C(10)	4161.8(16)	5260(2)	4021.0(17)	32.9(9)
C(11)	3388.5(14)	5990(3)	3804.9(18)	37.6(10)
C(12)	4718.1(12)	7734(2)	3279.5(13)	18.9(6)
C(13)	4267.1(12)	8248(2)	3207.3(14)	20.5(7)
C(14)	4232.2(14)	8617(2)	2607.9(14)	25.9(7)
C(15)	3793.7(15)	9153(2)	2535.3(16)	31.8(9)
N(1')	5727.1(10)	7940.0(17)	6123.9(11)	19.3(6)
C(2')	5996.7(12)	8275.7(19)	5748.2(14)	18.3(6)
P(3')	5911.8(3)	7848.6(5)	5012.8(3)	15.2(2)
C(3A')	5494.2(11)	7134.6(18)	5316.1(13)	14.9(6)
N(4')	5244.1(9)	6555.1(15)	5039.4(11)	14.9(5)
C(5')	4937.2(12)	6111.6(19)	5348.7(14)	18.7(6)
C(6')	4866.3(12)	6238(2)	5936.1(13)	19.4(6)
C(7')	5120.2(12)	6849(2)	6217.0(14)	20.0(7)
C(7A')	5439.7(11)	7301.0(19)	5895.9(13)	16.7(6)
C(8')	6318.0(12)	8987(2)	5893.0(14)	20.3(6)

C(9')	6785.9(13)	8963(2)	5549.6(16)	28.7(8)
C(10')	6037.9(15)	9754(2)	5739.8(18)	32.1(9)
C(11')	6446.5(14)	8973(2)	6530.6(15)	28.0(8)
C(12')	6450.5(12)	7286(2)	4835.8(14)	20.2(6)
C(13')	6648.3(12)	6783(2)	5336.1(15)	22.9(7)
C(14')	7122.9(14)	6391(2)	5190.7(17)	32.1(8)
C(15')	7342.0(15)	5934(3)	5688(2)	41.5(11)
O(111)	5000	7711(2)	7500	25.1(7)
C(112)	5413.1(13)	8213(2)	7604.8(16)	27.2(8)
C(113)	5265.8(13)	9056(2)	7432.1(17)	29.6(8)
O(121)	6888.3(12)	11734(2)	3969.0(14)	47.1(8)
C(122)	7050.0(15)	10918(3)	4006.3(17)	35.7(9)
C(123)	7049.2(14)	10580(3)	3409.4(17)	36.3(9)
C(124)	6624.4(19)	11059(3)	3145(2)	51.7(12)
C(125)	6695(2)	11868(3)	3416(2)	53.1(13)
O(131)	5978.5(13)	6287(2)	7021.8(16)	61.0(10)
C(132)	6458.9(17)	6539(3)	7130(2)	47.9(12)
C(133)	6643.4(18)	5997(3)	7598(2)	53.3(13)
C(134)	6196.7(19)	5889(3)	7962(2)	60.1(14)
C(135)	5781.0(19)	6027(3)	7553(2)	54.8(13)
O(141)	7399.3(16)	10706(2)	6213(2)	78.0(13)
C(142)	7155.9(19)	11447(3)	6127(2)	54.0(13)
C(143)	7317(2)	11761(5)	5572(3)	85(2)
C(144)	7817(3)	11397(5)	5521(3)	98(2)
C(145)	7791(2)	10677(4)	5829(3)	88(2)
O(151)	7489(2)	6769(3)	2729(3)	66.8(19)
C(152)	7222(3)	6108(4)	2934(3)	43.5(17)
C(153)	6916(3)	6425(4)	3404(4)	50(2)
C(154)	6794(3)	7262(5)	3187(4)	60(2)
C(155)	7201(4)	7449(5)	2787(5)	68(3)
O(161)	7404(5)	7117(9)	3523(6)	103(5)
C(162)	7183(6)	6360(9)	3501(7)	59(4)
C(163)	6860(6)	6340(9)	3000(8)	68(5)
C(164)	6792(7)	7224(10)	2840(9)	79(5)
C(165)	7214(7)	7621(10)	3110(9)	79(5)

Table S7. Bond lengths [Å] and angles [°] (excluding solvent) of **10b**·2(D_6-acetone).

Pd(1)-N(4')	2.048(3)	C(8)-C(10)	1.535(5)
Pd(1)-P(3)	2.2397(9)	C(12)-C(13)	1.522(5)
Pd(1)-Cl(1)	2.2725(9)	C(13)-C(14)	1.527(4)
Pd(1)-Cl(2)	2.3396(8)	C(14)-C(15)	1.515(5)
Pd(2)-N(4)	2.038(3)	N(1')-C(2')	1.287(4)
Pd(2)-P(3')	2.2396(9)	N(1')-C(7A')	1.426(4)
Pd(2)-Cl(3)	2.2704(9)	C(2')-C(8')	1.515(5)
Pd(2)-Cl(4)	2.3346(8)	C(2')-P(3')	1.866(3)
N(1)-C(2)	1.284(4)	P(3')-C(3A')	1.810(3)
N(1)-C(7A)	1.424(4)	P(3')-C(12')	1.816(3)
C(2)-C(8)	1.513(5)	C(3A')-N(4')	1.346(4)
C(2)-P(3)	1.865(3)	C(3A')-C(7A')	1.390(4)
P(3)-C(3A)	1.808(3)	N(4')-C(5')	1.344(4)
P(3)-C(12)	1.821(3)	C(5')-C(6')	1.402(4)
C(3A)-N(4)	1.345(4)	C(6')-C(7')	1.393(5)
C(3A)-C(7A)	1.393(4)	C(7')-C(7A')	1.389(4)
N(4)-C(5)	1.354(4)	C(8')-C(11')	1.523(5)
C(5)-C(6)	1.397(4)	C(8')-C(10')	1.533(5)
C(6)-C(7)	1.381(5)	C(8')-C(9')	1.535(5)
C(7)-C(7A)	1.389(4)	C(12')-C(13')	1.529(5)
C(8)-C(11)	1.525(5)	C(13')-C(14')	1.512(5)
C(8)-C(9)	1.532(5)	C(14')-C(15')	1.506(5)

N(4')-Pd(1)-P(3)	90.62(8)	N(1)-C(2)-P(3)	113.7(2)
N(4')-Pd(1)-Cl(1)	178.70(8)	C(8)-C(2)-P(3)	124.1(2)
P(3)-Pd(1)-Cl(1)	88.39(3)	C(3A)-P(3)-C(12)	106.86(15)
N(4')-Pd(1)-Cl(2)	89.47(8)	C(3A)-P(3)-C(2)	87.61(15)
P(3)-Pd(1)-Cl(2)	176.55(3)	C(12)-P(3)-C(2)	107.96(15)
Cl(1)-Pd(1)-Cl(2)	91.57(3)	C(3A)-P(3)-Pd(1)	112.92(10)
N(4)-Pd(2)-P(3')	90.78(7)	C(12)-P(3)-Pd(1)	122.68(11)
N(4)-Pd(2)-Cl(3)	177.85(8)	C(2)-P(3)-Pd(1)	113.13(11)
P(3')-Pd(2)-Cl(3)	88.49(3)	N(4)-C(3A)-C(7A)	122.7(3)
N(4)-Pd(2)-Cl(4)	89.30(7)	N(4)-C(3A)-P(3)	127.8(2)
P(3')-Pd(2)-Cl(4)	178.67(3)	C(7A)-C(3A)-P(3)	109.3(2)
Cl(3)-Pd(2)-Cl(4)	91.38(3)	C(3A)-N(4)-C(5)	117.6(3)
C(2)-N(1)-C(7A)	113.0(3)	C(3A)-N(4)-Pd(2)	121.7(2)
N(1)-C(2)-C(8)	122.0(3)	C(5)-N(4)-Pd(2)	120.6(2)

N(4)-C(5)-C(6)	122.3(3)	C(12')-P(3')-Pd(2)	122.04(11)
C(7)-C(6)-C(5)	119.8(3)	C(2')-P(3')-Pd(2)	113.56(11)
C(6)-C(7)-C(7A)	117.9(3)	N(4')-C(3A')-C(7A')	123.0(3)
C(7)-C(7A)-C(3A)	119.6(3)	N(4')-C(3A')-P(3')	127.6(2)
C(7)-C(7A)-N(1)	124.2(3)	C(7A')-C(3A')-P(3')	109.2(2)
C(3A)-C(7A)-N(1)	116.2(3)	C(5')-N(4')-C(3A')	117.5(3)
C(2)-C(8)-C(11)	109.7(3)	C(5')-N(4')-Pd(1)	121.7(2)
C(2)-C(8)-C(9)	111.1(3)	C(3A')-N(4')-Pd(1)	120.8(2)
C(11)-C(8)-C(9)	109.7(3)	N(4')-C(5')-C(6')	122.7(3)
C(2)-C(8)-C(10)	107.6(3)	C(7')-C(6')-C(5')	119.4(3)
C(11)-C(8)-C(10)	110.2(3)	C(7A')-C(7')-C(6')	117.6(3)
C(9)-C(8)-C(10)	108.6(3)	C(7')-C(7A')-C(3A')	119.7(3)
C(13)-C(12)-P(3)	113.5(2)	C(7')-C(7A')-N(1')	124.0(3)
C(12)-C(13)-C(14)	111.5(3)	C(3A')-C(7A')-N(1')	116.2(3)
C(15)-C(14)-C(13)	112.2(3)	C(2')-C(8')-C(11')	109.5(3)
C(2')-N(1')-C(7A')	113.4(3)	C(2')-C(8')-C(10')	107.7(3)
N(1')-C(2')-C(8')	122.2(3)	C(11')-C(8')-C(10')	110.5(3)
N(1')-C(2')-P(3')	113.2(2)	C(2')-C(8')-C(9')	111.2(3)
C(8')-C(2')-P(3')	124.5(2)	C(11')-C(8')-C(9')	108.8(3)
C(3A')-P(3')-C(12')	106.51(15)	C(10')-C(8')-C(9')	109.2(3)
C(3A')-P(3')-C(2')	87.90(14)	C(13')-C(12')-P(3')	113.3(2)
C(12')-P(3')-C(2')	108.20(15)	C(14')-C(13')-C(12')	111.6(3)
C(3A')-P(3')-Pd(2)	113.22(10)	C(15')-C(14')-C(13')	112.8(3)

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor of **10b**·4.5THF.

	x	y	z	U(eq)
Pd(1)	6298.9(2)	5534.3(1)	7229.8(2)	13.1(1)
Pd(2)	7213.2(2)	6845.4(1)	7836.5(2)	14.2(1)
Cl(1)	7174.7(7)	5200.5(2)	8975.7(6)	22.3(2)
Cl(2)	4324.5(6)	5273.5(2)	6891.0(6)	18.7(2)
Cl(3)	6500.7(7)	7040.2(2)	9132.9(6)	24.5(2)
Cl(4)	9192.4(7)	7128.1(2)	8972.8(6)	24.6(2)
N(1)	8879(2)	5614.6(7)	5851.6(18)	15.4(5)
C(2)	8820(2)	5400.7(8)	6686(2)	15.2(6)
P(3)	8203.4(7)	5755.1(2)	7503.6(6)	13.9(2)
C(3A)	8172(2)	6227.2(8)	6607(2)	11.9(6)
N(4)	7796.1(19)	6655.7(7)	6645.3(17)	13.0(5)
C(5)	7800(2)	6946.3(8)	5851(2)	16.1(6)
C(6)	8136(2)	6818.2(9)	5010(2)	17.4(6)
C(7)	8497(2)	6376.5(8)	4954(2)	17.5(6)
C(7A)	8521(2)	6078.5(8)	5782(2)	14.1(6)
C(8)	9126(3)	4899.0(8)	6882(2)	16.7(6)
C(9)	9858(3)	4804.3(9)	8152(2)	26.3(7)
C(10)	7895(3)	4637.5(9)	6432(2)	25.9(7)
C(11)	9868(3)	4747.3(9)	6252(3)	32.9(8)
C(12)	9398(2)	5871.0(8)	8924(2)	16.2(6)
C(13)	10644(3)	6016.6(10)	8998(2)	25.4(7)
C(14)	11673(3)	6000.8(10)	10209(3)	32.1(8)
C(15)	11408(3)	6313.9(11)	11027(3)	40.5(9)
N(1')	4368(2)	6964.4(6)	4557.7(17)	15.2(5)
C(2')	4548(2)	7098.6(8)	5548(2)	14.6(6)
P(3')	5258.4(7)	6654.5(2)	6668.3(6)	13.7(2)
C(3A')	5161(2)	6273.2(8)	5558(2)	12.4(6)
N(4')	5547.0(19)	5837.0(6)	5676.2(17)	12.3(5)
C(5')	5446(2)	5619.5(8)	4730(2)	15.2(6)
C(6')	4987(2)	5827.4(8)	3681(2)	17.8(6)
C(7')	4622(3)	6280.0(9)	3567(2)	18.9(6)
C(7A')	4702(2)	6501.4(8)	4529(2)	14.4(6)
C(8')	4311(3)	7582.7(8)	5798(2)	17.4(6)

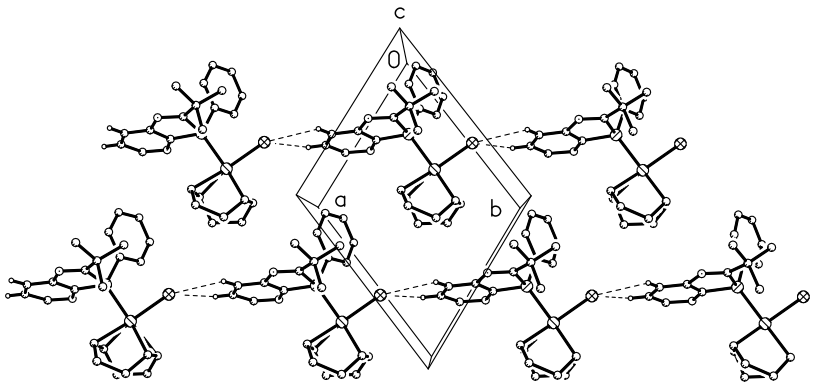
C(9')	3606(3)	7593.2(9)	6529(2)	25.4(7)
C(10')	5574(3)	7820.9(8)	6444(2)	23.0(7)
C(11')	3573(3)	7834.9(9)	4685(2)	25.2(7)
C(12')	4108(2)	6462.9(8)	7131(2)	16.1(6)
C(13')	2855(2)	6343.7(9)	6139(2)	18.3(6)
C(14')	1844(3)	6268.0(9)	6525(2)	25.8(7)
C(15')	1403(3)	6704.6(9)	6843(2)	27.2(7)
O(1)	5013(3)	8912.4(8)	6371(2)	56.5(8)
C(94)	4556(4)	9387.5(13)	4790(3)	63.4(12)
C(95)	5393(4)	9205.7(11)	5944(3)	42.7(9)
C(96)	6654(3)	9413.4(11)	6568(3)	51.1(10)
O(2)	9513(3)	3550.8(8)	6500(2)	63.2(8)
C(97)	9251(3)	2883.8(11)	7391(3)	57.3(11)
C(98)	9964(3)	3253.5(11)	7194(3)	38.8(9)
C(99)	11324(3)	3229.4(12)	7878(3)	50.7(10)

Table S9. Bond lengths [Å] and angles [°] of **10b**·4.5THF.

Pd(1)-N(4')	2.035(2)	C(14)-C(15)	1.546(4)
Pd(1)-P(3)	2.2427(8)	N(1')-C(2')	1.279(3)
Pd(1)-Cl(1)	2.2789(7)	N(1')-C(7A')	1.428(3)
Pd(1)-Cl(2)	2.3347(7)	C(2')-C(8')	1.518(3)
Pd(2)-N(4)	2.042(2)	C(2')-P(3')	1.871(3)
Pd(2)-P(3')	2.2370(8)	P(3')-C(3A')	1.799(3)
Pd(2)-Cl(3)	2.2774(7)	P(3')-C(12')	1.817(3)
Pd(2)-Cl(4)	2.3327(7)	C(3A')-N(4')	1.353(3)
N(1)-C(2)	1.288(3)	C(3A')-C(7A')	1.386(3)
N(1)-C(7A)	1.424(3)	N(4')-C(5')	1.351(3)
C(2)-C(8)	1.519(3)	C(5')-C(6')	1.379(3)
C(2)-P(3)	1.862(3)	C(6')-C(7')	1.392(3)
P(3)-C(3A)	1.809(2)	C(7')-C(7A')	1.383(3)
P(3)-C(12)	1.816(3)	C(8')-C(9')	1.525(4)
C(3A)-N(4)	1.349(3)	C(8')-C(11')	1.527(3)
C(3A)-C(7A)	1.387(3)	C(8')-C(10')	1.541(4)
N(4)-C(5)	1.348(3)	C(12')-C(13')	1.536(3)
C(5)-C(6)	1.378(3)	C(13')-C(14')	1.516(4)
C(6)-C(7)	1.384(3)	C(14')-C(15')	1.517(4)
C(7)-C(7A)	1.384(3)	O(1)-C(95)	1.220(4)
C(8)-C(11)	1.518(4)	C(94)-C(95)	1.500(5)
C(8)-C(9)	1.528(3)	C(95)-C(96)	1.498(5)
C(8)-C(10)	1.534(4)	O(2)-C(98)	1.207(3)
C(12)-C(13)	1.513(4)	C(97)-C(98)	1.474(5)
C(13)-C(14)	1.525(4)	C(98)-C(99)	1.477(5)
N(4')-Pd(1)-P(3)	90.48(6)	Cl(3)-Pd(2)-Cl(4)	92.32(3)
N(4')-Pd(1)-Cl(1)	178.97(7)	C(2)-N(1)-C(7A)	113.5(2)
P(3)-Pd(1)-Cl(1)	88.50(3)	N(1)-C(2)-C(8)	121.5(2)
N(4')-Pd(1)-Cl(2)	89.11(6)	N(1)-C(2)-P(3)	113.12(19)
P(3)-Pd(1)-Cl(2)	177.11(3)	C(8)-C(2)-P(3)	125.21(19)
Cl(1)-Pd(1)-Cl(2)	91.92(3)	C(3A)-P(3)-C(12)	107.63(11)
N(4)-Pd(2)-P(3')	90.73(6)	C(3A)-P(3)-C(2)	87.82(12)
N(4)-Pd(2)-Cl(3)	177.89(6)	C(12)-P(3)-C(2)	111.18(12)
P(3')-Pd(2)-Cl(3)	87.32(3)	C(3A)-P(3)-Pd(1)	112.75(9)
N(4)-Pd(2)-Cl(4)	89.71(6)	C(12)-P(3)-Pd(1)	120.66(9)
P(3')-Pd(2)-Cl(4)	173.46(3)	C(2)-P(3)-Pd(1)	111.95(9)

N(4)-C(3A)-C(7A)	122.8(2)	C(12')-P(3')-Pd(2)	124.62(9)
N(4)-C(3A)-P(3)	127.6(2)	C(2')-P(3')-Pd(2)	109.99(9)
C(7A)-C(3A)-P(3)	109.41(18)	N(4')-C(3A')-C(7A')	122.9(2)
C(5)-N(4)-C(3A)	117.0(2)	N(4')-C(3A')-P(3')	127.12(19)
C(5)-N(4)-Pd(2)	122.02(17)	C(7A')-C(3A')-P(3')	109.81(18)
C(3A)-N(4)-Pd(2)	120.94(17)	C(5')-N(4')-C(3A')	117.2(2)
N(4)-C(5)-C(6)	122.7(2)	C(5')-N(4')-Pd(1)	122.00(17)
C(5)-C(6)-C(7)	120.4(2)	C(3A')-N(4')-Pd(1)	120.76(16)
C(6)-C(7)-C(7A)	117.2(2)	N(4')-C(5')-C(6')	122.5(2)
C(7)-C(7A)-C(3A)	119.8(2)	C(5')-C(6')-C(7')	120.2(2)
C(7)-C(7A)-N(1)	124.3(2)	C(7A')-C(7')-C(6')	117.4(2)
C(3A)-C(7A)-N(1)	115.9(2)	C(7')-C(7A')-C(3A')	119.7(2)
C(11)-C(8)-C(2)	110.5(2)	C(7')-C(7A')-N(1')	124.5(2)
C(11)-C(8)-C(9)	110.0(2)	C(3A')-C(7A')-N(1')	115.8(2)
C(2)-C(8)-C(9)	110.1(2)	C(2')-C(8')-C(9')	111.1(2)
C(11)-C(8)-C(10)	109.5(2)	C(2')-C(8')-C(11')	109.7(2)
C(2)-C(8)-C(10)	107.7(2)	C(9')-C(8')-C(11')	109.8(2)
C(9)-C(8)-C(10)	109.0(2)	C(2')-C(8')-C(10')	108.4(2)
C(13)-C(12)-P(3)	115.66(19)	C(9')-C(8')-C(10')	108.9(2)
C(12)-C(13)-C(14)	112.6(2)	C(11')-C(8')-C(10')	108.8(2)
C(13)-C(14)-C(15)	112.6(2)	C(13')-C(12')-P(3')	113.02(18)
C(2')-N(1')-C(7A')	113.4(2)	C(14')-C(13')-C(12')	112.2(2)
N(1')-C(2')-C(8')	123.0(2)	C(13')-C(14')-C(15')	112.9(2)
N(1')-C(2')-P(3')	113.26(18)	O(1)-C(95)-C(96)	121.9(3)
C(8')-C(2')-P(3')	123.57(18)	O(1)-C(95)-C(94)	119.7(4)
C(3A')-P(3')-C(12')	106.36(12)	C(96)-C(95)-C(94)	118.3(3)
C(3A')-P(3')-C(2')	87.59(11)	O(2)-C(98)-C(97)	124.5(4)
C(12')-P(3')-C(2')	109.09(12)	O(2)-C(98)-C(99)	120.2(3)
C(3A')-P(3')-Pd(2)	112.93(9)	C(97)-C(98)-C(99)	115.3(3)

Fig. S26. Homochiral chains of 3*S*-enantiomers of **6a**; chains of 3*R*-enantiomers occupy the other half of the unit cell.



XRD studies of a crystal of the analogous complex **9a**, crystallised with THF, confirmed the crude structure of **9a**, but severe disorder of the allyl group and unexpected peaks, possibly caused by twinning, prevented satisfactory refinement.

Figure S27. Crude structural information on the unrefinable structure **9a**.