Structural Modification of Functionalized Phosphine Sulfonate-Based Pd(II) Olefin Polymerization Catalysts

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1. Compound characterization by NMR spectroscopy

1.1. Synthesis of 2-(bis-2-thiomethoxyphenylphosphine)benzenesulfonic acid 5.

^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.34 – 8.17 (m, 1H), 7.85 – 7.59 (m, 4H), 7.46 (t, *J* = 7.1 Hz, 1H), 7.42 – 7.22 (m, 3H), 7.18 – 6.86 (m, 3H), 2.48 (s, 6H).

^{31}P NMR (121 MHz, CD_2Cl_2) δ -8.4 (s, br).

The compound was used as received for complexation reactions without further purification and due to a dynamic process on the NMR timescale the ^{13}C NMR spectra could not be unambiguously assigned.

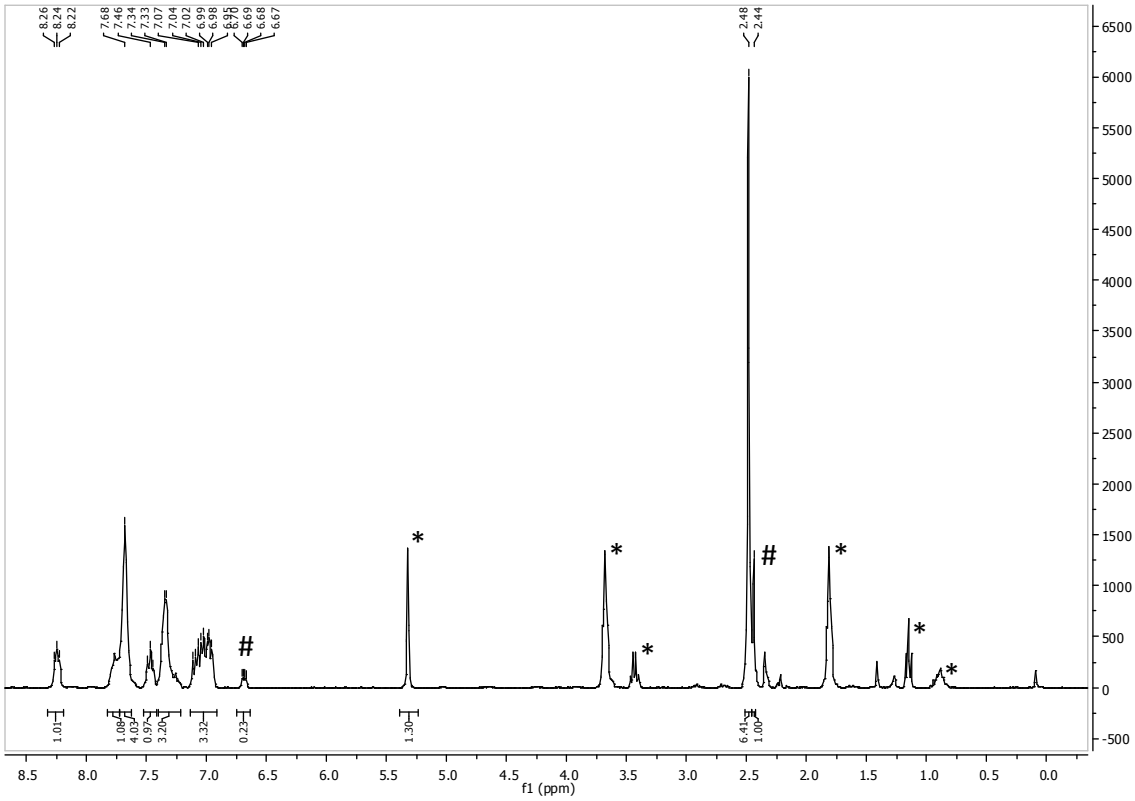


Figure 1: ^{1}H NMR (300 MHz, CD_2Cl_2), #, * impurities and residual solvent.

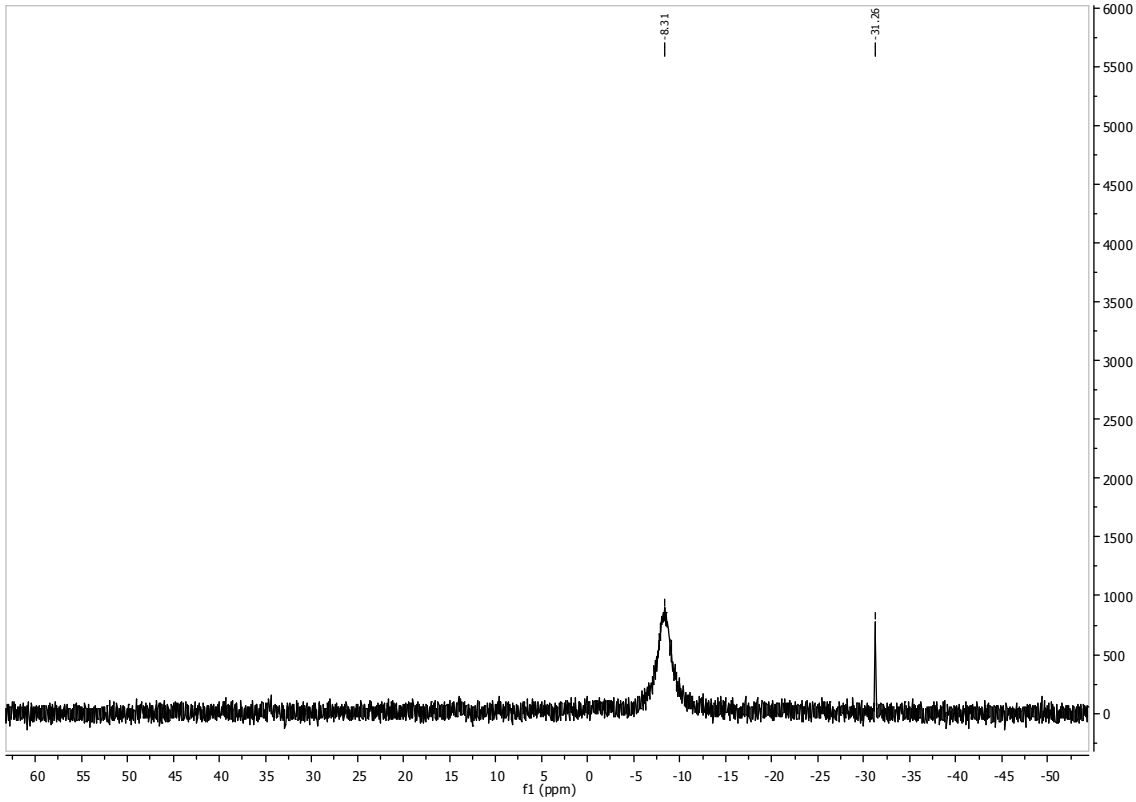


Figure 2: ^{31}P NMR (CD_2Cl_2)

1.2. Synthesis of 2-(bis-8-methoxynaphthalene-1-phosphine)benzenesulfonic acid 7.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.62 (d, ^{1}J (H-P) = 674.3 Hz, 1H, *H*-P), 8.50 (dd, ^{3}J (H-H) = 7.7 Hz, ^{4}J (H-P) = 4.8 Hz, 1H, *H3*), 8.12 – 8.05 (m, 2H, *H14, 24*), 7.73 (m, 1H, *H4*), 7.60 – 7.56 (m, 3H. *H11, 12, 22*), 7.47 (m, 2H, *H21, 25*), 7.36 – 7.28 (m, 2H, *H5, 15*), 7.26 (d, ^{3}J (H-H) = 7.3 Hz, 1H, *H26*), 7.12 (dd, ^{3}J (H-P) = 18.0 Hz, ^{3}J (H-H) = 7.3 Hz, 1H, *H16*), 7.00 (dd, *J* (H-H) = 6.7, 2.0 Hz, 1H, *H10*), 6.93 (dd, ^{3}J (H-P) = 14.4Hz, ^{3}J (H-H) = 7.7 Hz, 1H, *H6*), 6.80 (d, ^{3}J (H-H) = 7.7 Hz, 1H, *H20*), 3.89 (s, 3H, *OMe1*), 3.22 (s, 3H, *OMe2*).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 154.9 (s, *C9*), 154.2 (s, *C19*), 151.3 (d, ^{2}J (C-P) = 8.2 Hz, *C2*), 136.8 (d, ^{2}J (C-P) = 9.2 Hz, *C26*), 135.9 (d, ^{2}J (C-P) = 9.1 Hz, *C16*), 135.5 (s, *C23*), 135.4 (s, *C13*), 134.5 (d, ^{4}J (C-P) = 3.2 Hz, *C24*), 134.3 (s, *C14*), 133.9 (d, ^{4}J (C-P) = 3.3 Hz, *C4*), 133.9 (d, ^{2}J (C-P) = 4.1 Hz, *C6*), 130.4 (d, ^{3}J (C-P) = 8.7 Hz, *C3*), 129.8 (d, ^{3}J (C-P) = 12.2 Hz, *C5*), 128.3 (s, *C11*), 127.7 (s, *C21*), 126.3 (d, ^{3}J (C-P) = 15.0 Hz, *C25*), 125.8 (d, ^{3}J (C-P) = 14.7 Hz, *C15*), 125.4 (d, ^{2}J (C-P) = 5.1 Hz, *C8*), 124.6 (d, ^{2}J (C-P) = 5.3 Hz, *C18*), 122.5 (s, *C12*), 121.8 (s, *C22*), 118.1 (d, ^{1}J (C-P) = 94.7 Hz, *C17*), 117.0 (d, ^{1}J (C-P) = 89.7 Hz, *C7*), 115.9 (d, ^{1}J (C-P) = 92.8 Hz, *C1*), 107.9 (s, *C10*), 107.8 (s, *C20*), 56.3 (s, *OMe1*), 55.08 (s, *OMe2*).

^{31}P NMR (121 MHz, $CDCl_3$) δ +16.5 (ddd, ^{1}J (H-P) = 674.3, *J* (H-P) 32.2, 15.5 Hz).

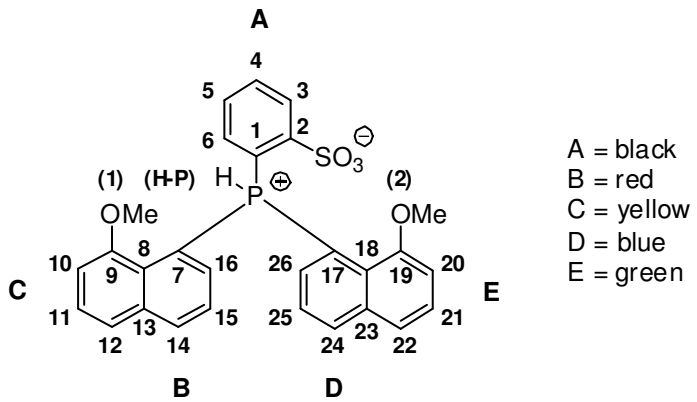


Figure 3: Labeling system employed for assignment of NMR signals and observed spin systems (color code).

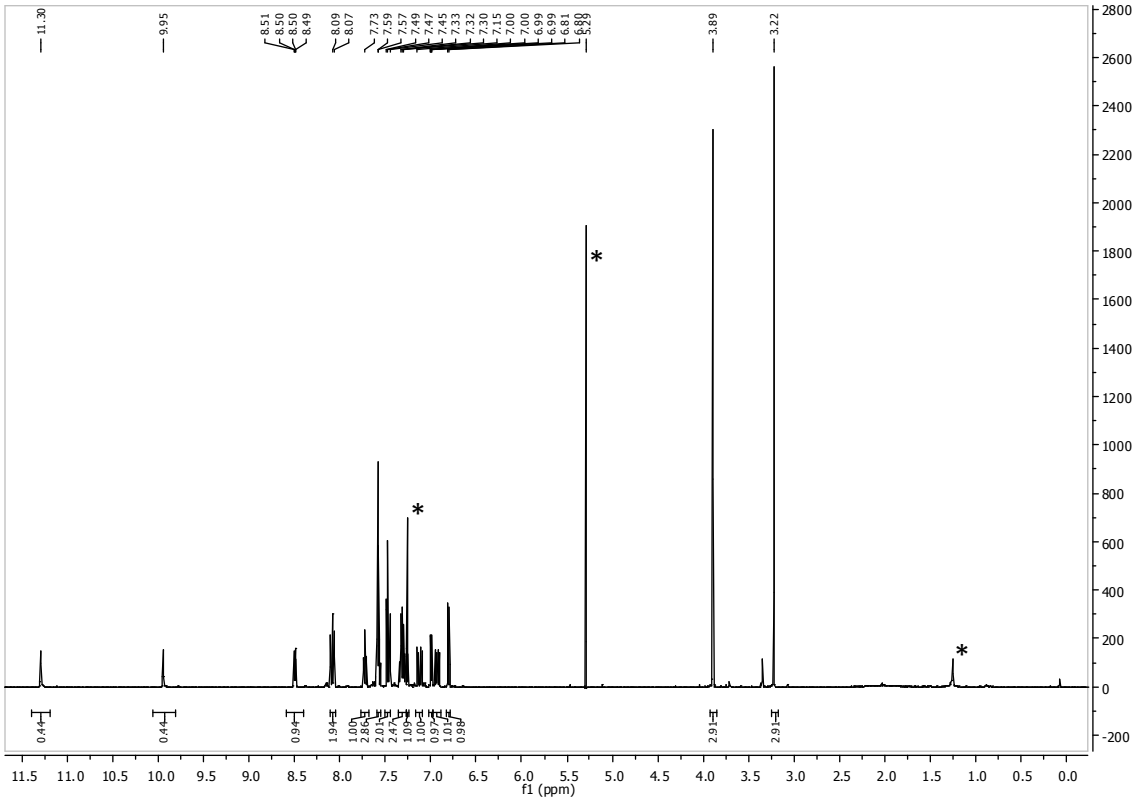


Figure 4: ^{1}H NMR (500 MHz, $CDCl_3$).

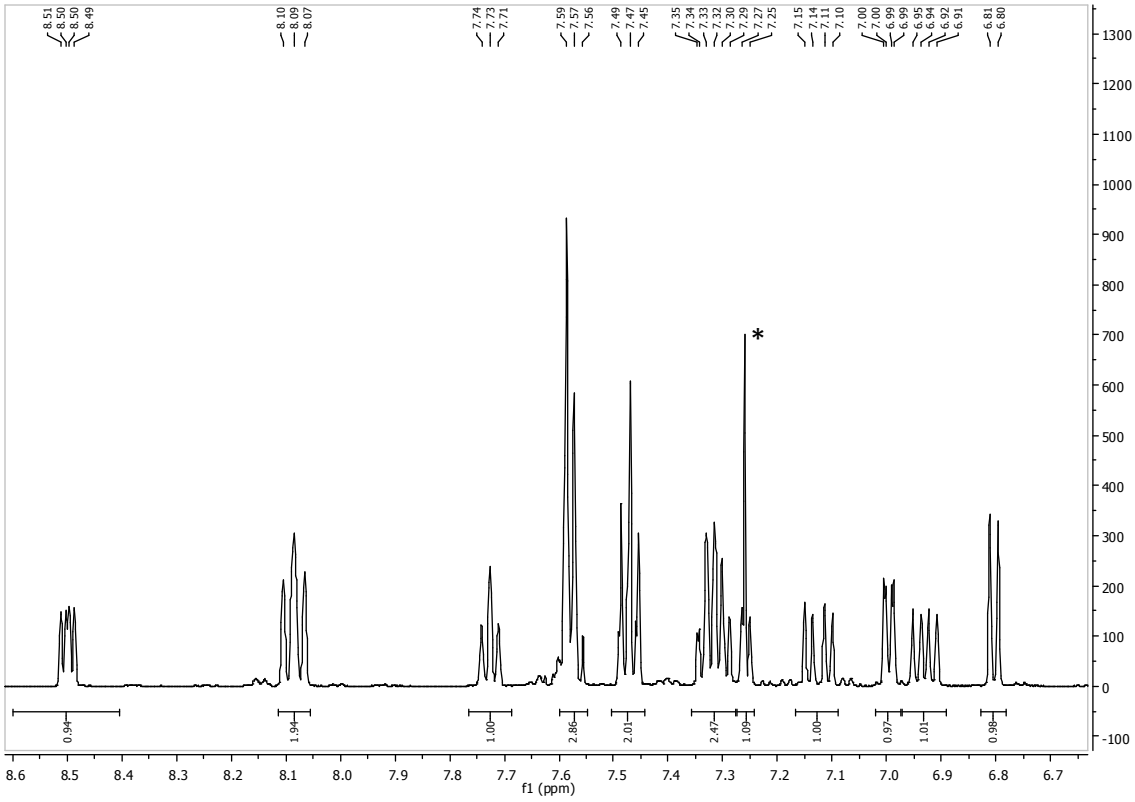


Figure 5: ^{1}H NMR aromatic region (500 MHz, $CDCl_3$).

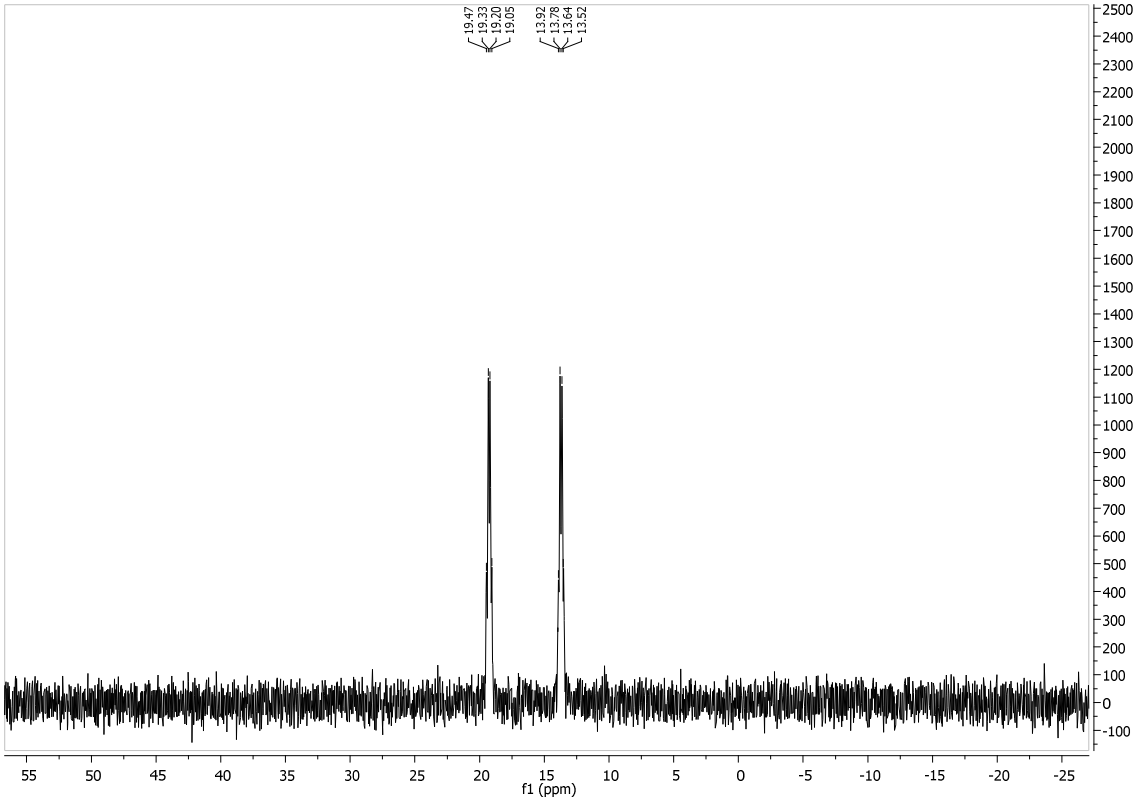


Figure 6: ^{31}P NMR (121 MHz, $CDCl_3$).

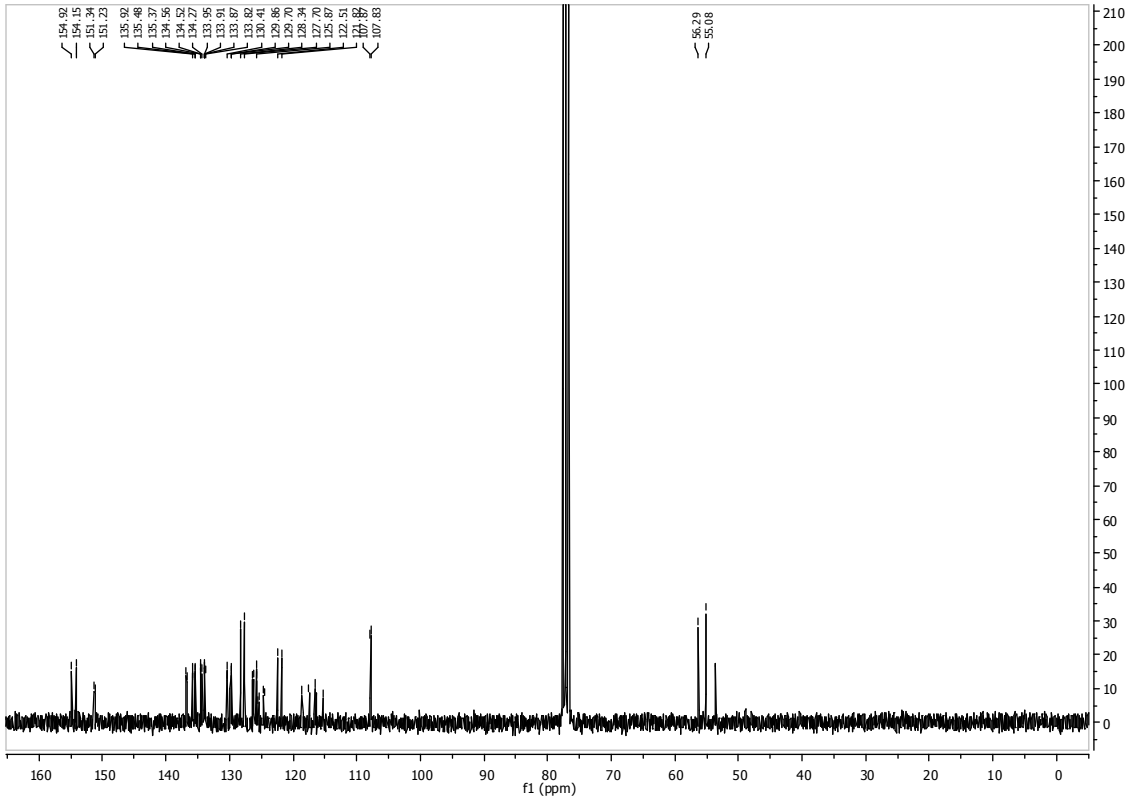


Figure 7: $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$).

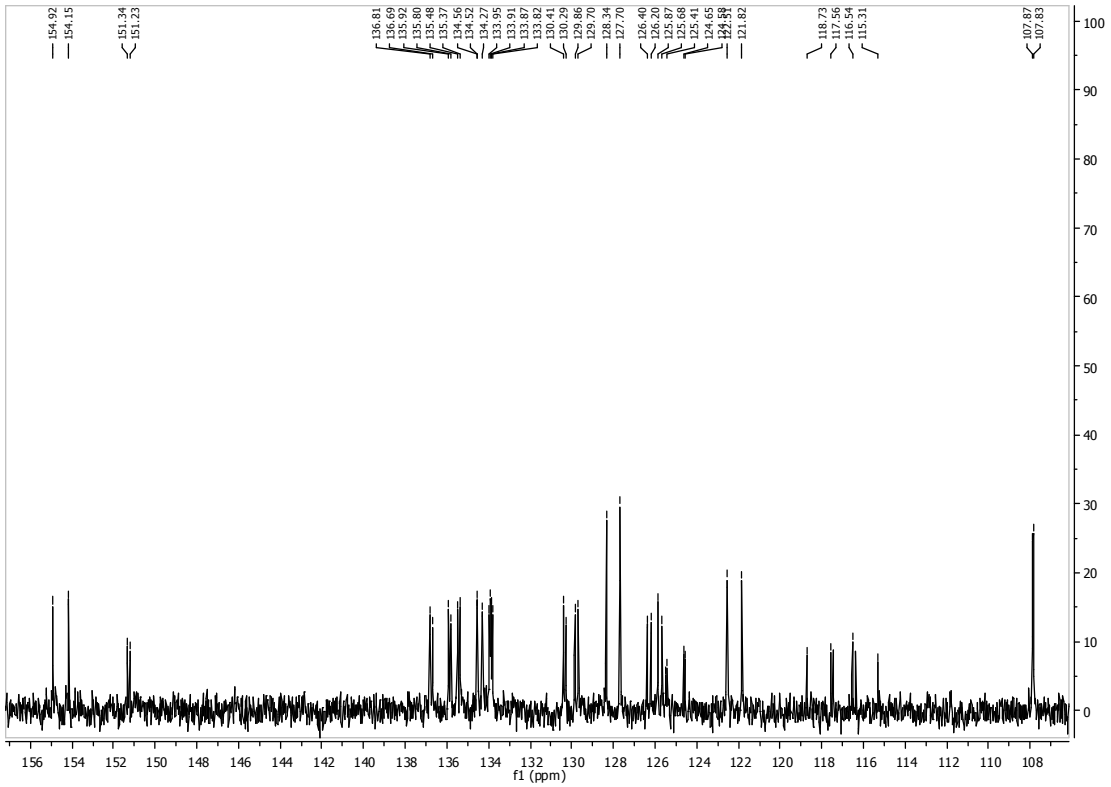


Figure 8: $^{13}C\{^{1}H\}$ NMR aromatic region (75 MHz, $CDCl_3$).

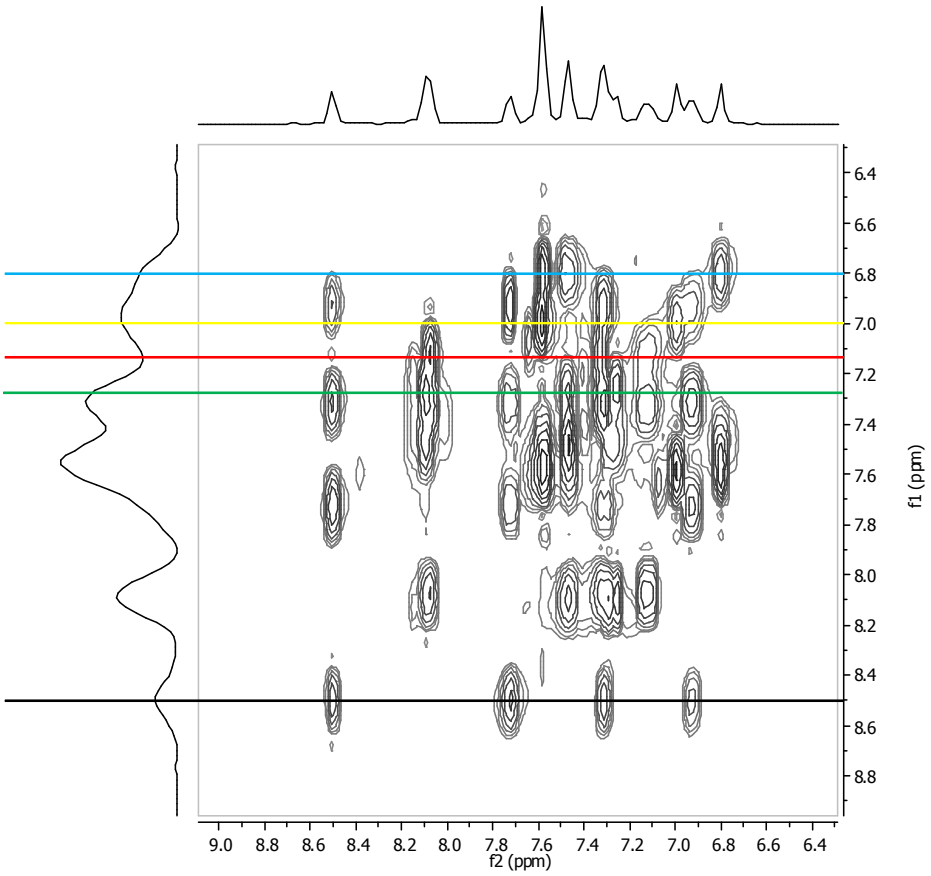


Figure 9: TOCSY NMR (500 MHz, $CDCl_3$).

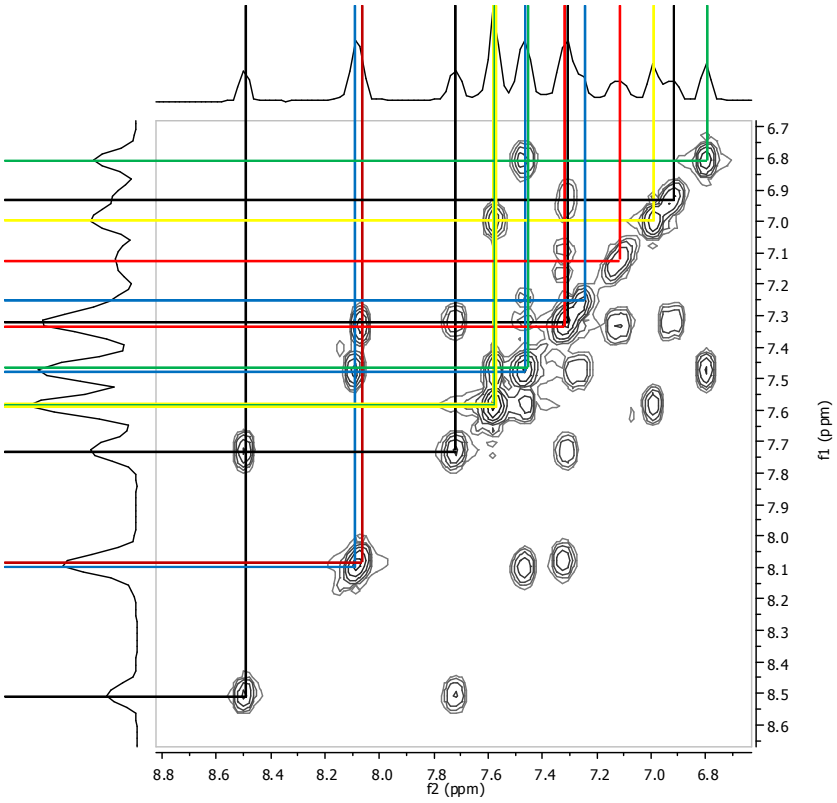


Figure 10: COSY NMR (500 MHz, $CDCl_3$).

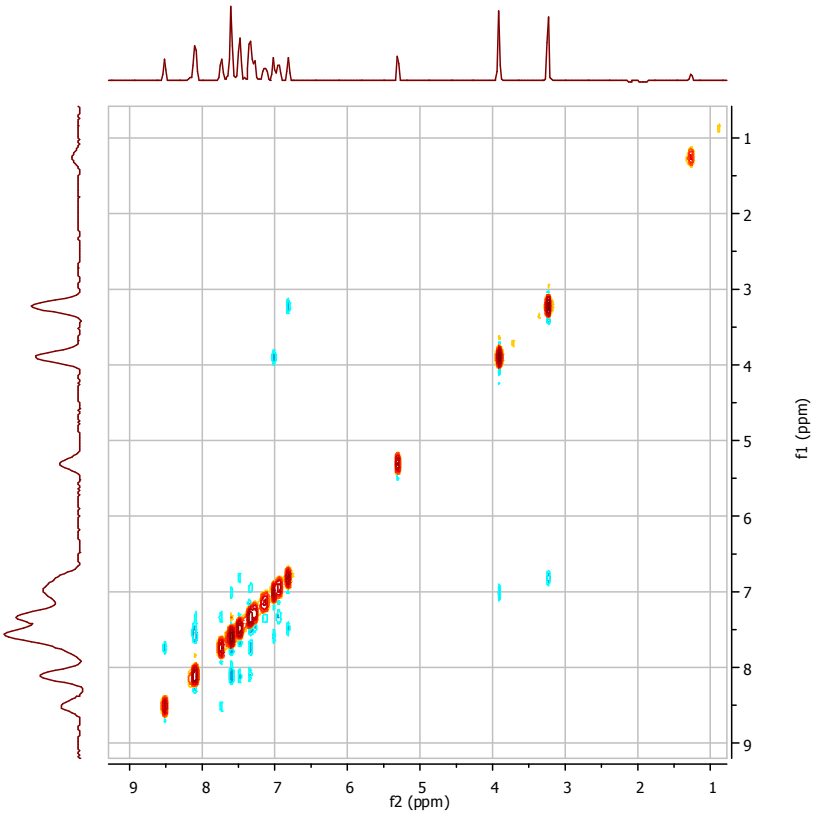


Figure 11: NOESY NMR (500 MHz, $CDCl_3$).

1.3. Synthesis of [{κ^2-(P,O)-2-(bis-2-thiomethoxyphenylphosphine)benzene-sulfonate}PdMe(pyridine)] 7.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.40 (s, 1H), 7.85 (s, 1H), 7.67 – 7.08 (m, 10H), 2.42 (s, 4H), 0.69 (s, 2H).

^{31}P NMR (121 MHz, CD_2Cl_2) δ 34.5.

Due to a dynamic process on the NMR timescale the observed peaks are broadened and the ^{13}C NMR spectra could not be unambiguously assigned.

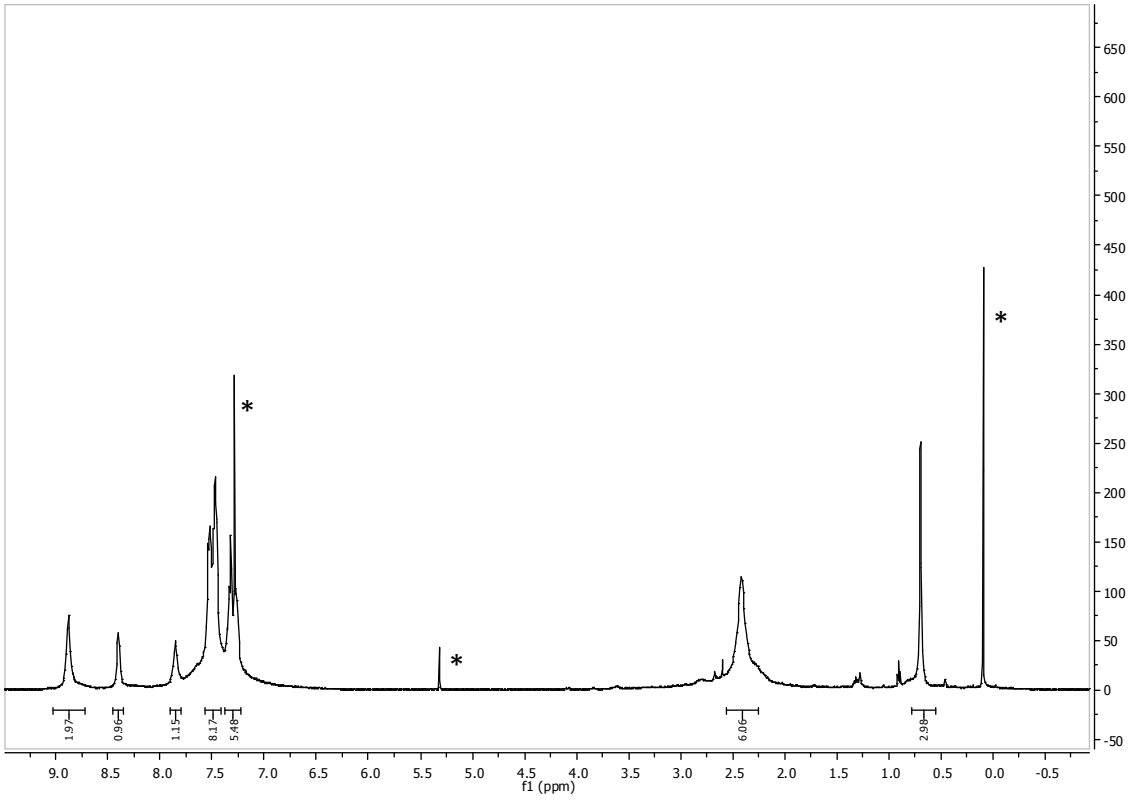


Figure 12: ^{1}H NMR (500 MHz, $CDCl_3$).

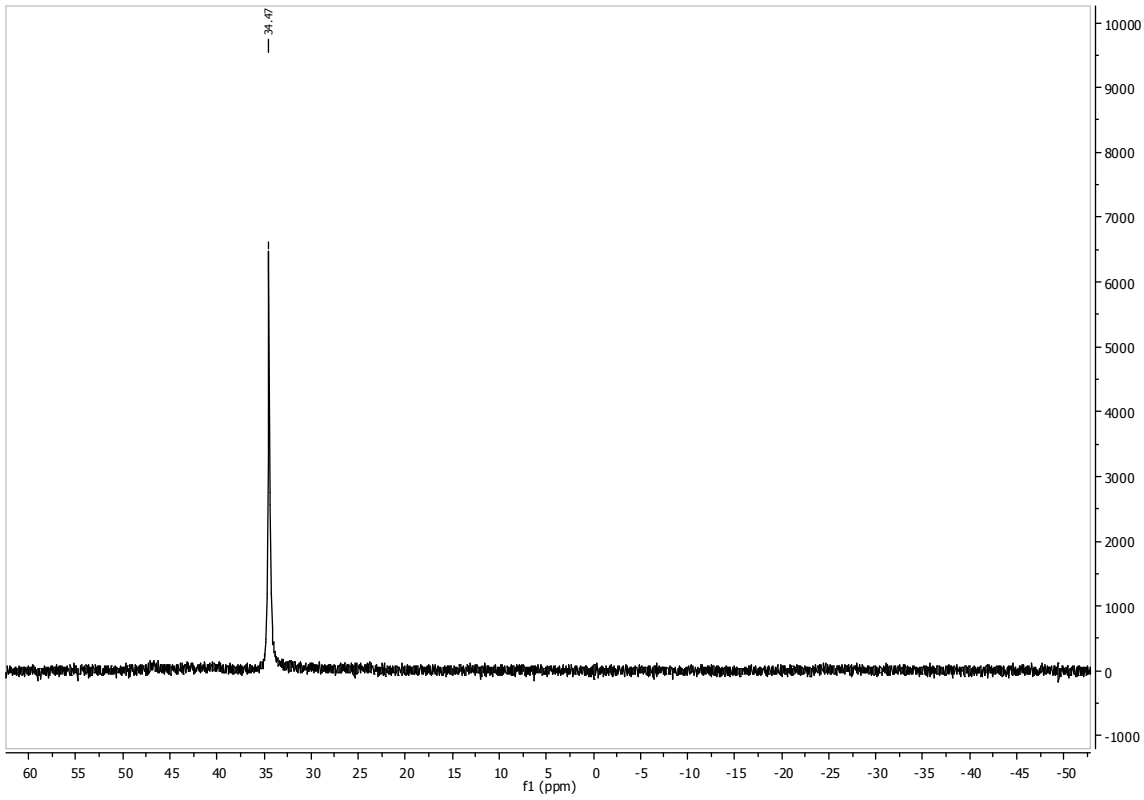


Figure 13: $^{31}P\{^{1}H\}$ NMR (121 MHz, CD_2Cl_2)

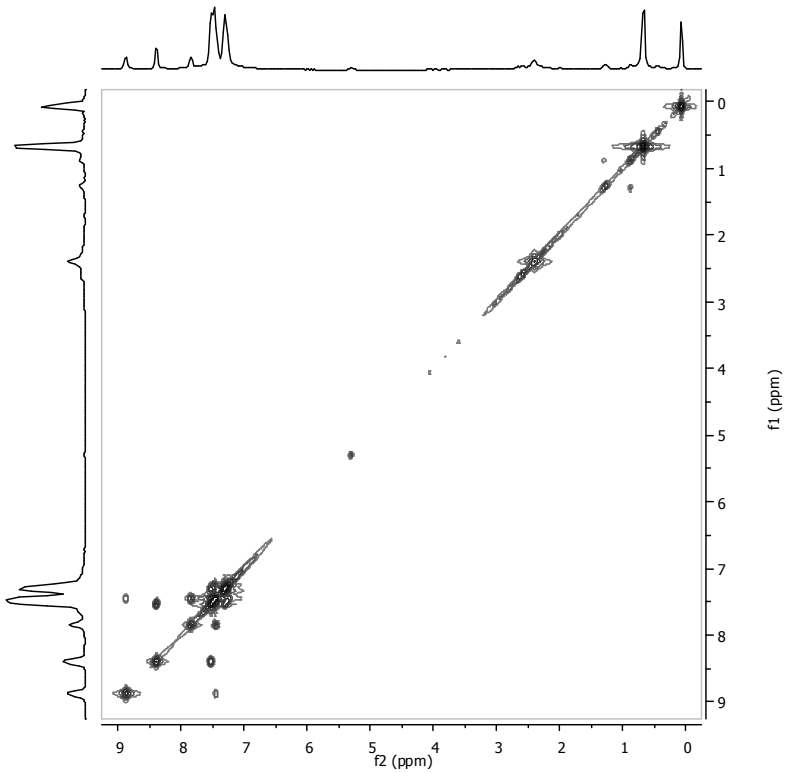


Figure 14: COSY NMR (500 MHz, $CDCl_3$)

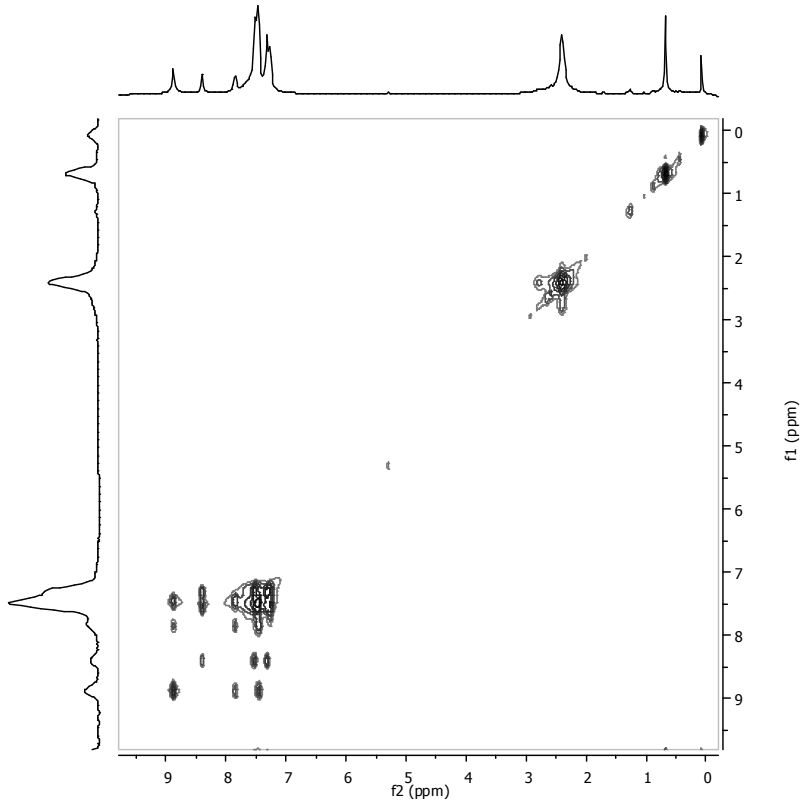


Figure 15: TOCSY NMR (500 MHz, $CDCl_3$)

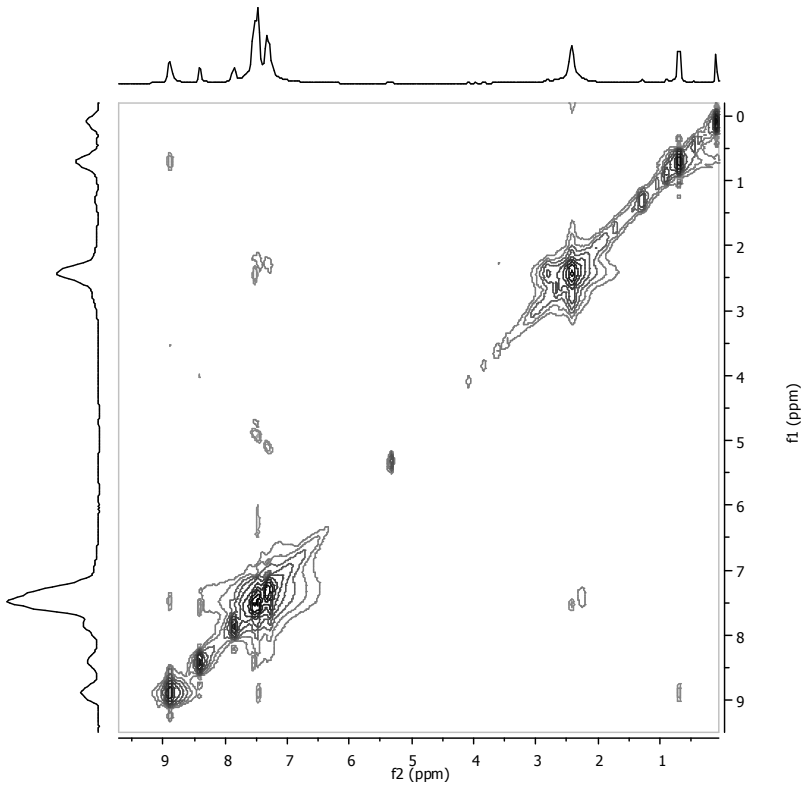


Figure 16: NOESY NMR (500 MHz, $CDCl_3$)

1.4. Synthesis of [{κ²-(P,O)-2-(bis-8-methoxynaphthalene-1-phosphine)benzene sulfonate}PdMe(pyridine)] 9.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.75 (d, ^{3}J (H-H) = 5.3 Hz, 2H, *Hpy1*), 8.39 – 8.28 (m, 1H, *H3*), 7.94 (d, ^{3}J (H-H) = 8.1 Hz, 1H, *H14*), 7.86 (d, ^{3}J (H-H) = 8.1 Hz, 1H, *H24*), 7.67 (t, ^{3}J (H-H) = 7.6 Hz, 1H, *Hpy3*), 7.55 – 7.39 (m, 5H, *H4, 11, 12, 21, 22*), 7.39 – 7.32 (m, 1H, *H15*), 7.32 – 7.23 (m, 4H, *Hpy2, 16, 25*), 7.16 (t, ^{3}J (H-H) = 7.6 Hz, 1H, *H5*), 7.13 – 7.07 (s, 1H, *H26*), 7.07 – 7.01 (m, 1H, *H6*), 6.85 (d, ^{3}J (H-H) = 7.6 Hz, 1H, *H20*), 6.70 (d, ^{3}J (H-H) = 7.6 Hz, 1H. *H10*), 3.71 (s, br, 3H,), 3.05 (s, 3H, *OMe2*), 0.49 (s, 3H, *PdMe*).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 156.1 (s, *C19*), 155.8 (s, *C9*), 150.9 (s, *py1*), 137.7 (s, *py3, C16*), 136.2 (d, *J* = 7.5 Hz), 135.5 (d, *J* = 5.2 Hz, *C26*), 135.4 (d, *J* = 7.6 Hz), 133.4 (d, ^{2}J (C-P) = 1.6 Hz. *C6*), 132.0 (s), 131.8 (s, *C24*), 131.3 (s, *C14*), 130.3 (s, *C4*), 129.9 (s, br, *C3, 5*), 127.1 (s), 126.9 (s, *C11*), 126.4 (s, *C21*), 126.0 (d, ^{3}J (C-P) = 8.5 Hz, *C25*), 125.5 (d, ^{3}J (C-P) = 10.5 Hz, *C15*), 125.1 – 124.7 (m, *py2, C16*), 122.0 (s, *C22*), 120.9 (s, *C12*), 107.1 (s, *C20*), 105.3 (s, *C10*), 56.5 (s, br, *OMe2*), 53.7 (s, *OMe1*), -0.17 (s, *Pd-Me*).

^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) δ +47.0.

Due to overlapping peaks most quaternary carbon atoms could not be assigned and detected.

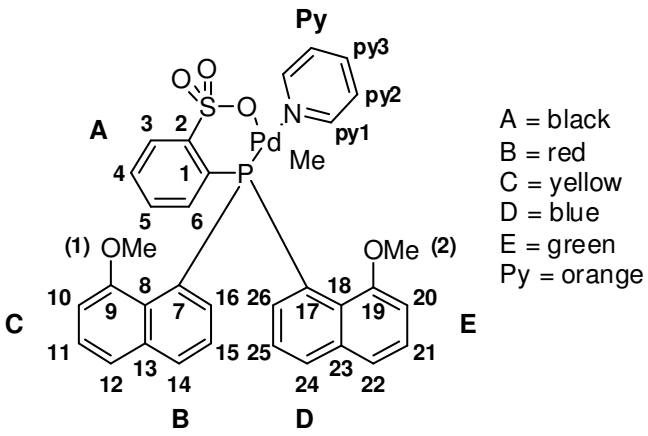


Figure 17: Labeling system employed for assignment of NMR signals and observed spin systems (color code).

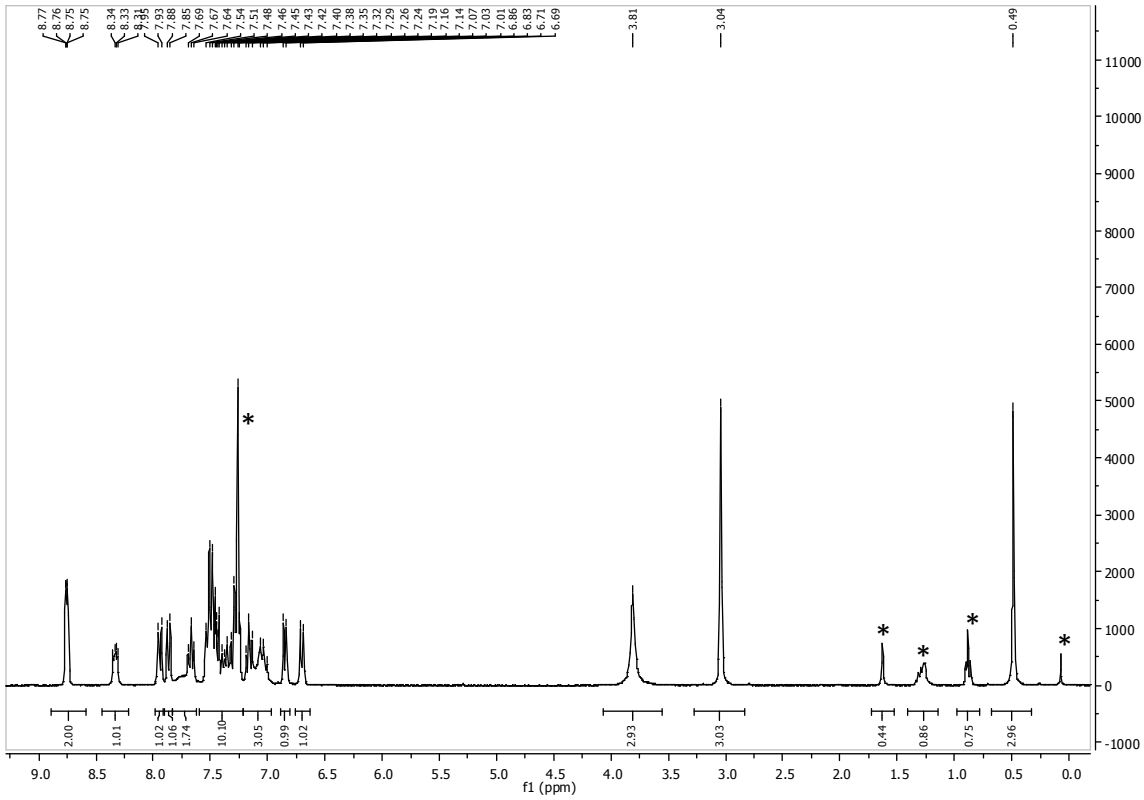


Figure 18: ^{1}H NMR (500 MHz, $CDCl_3$)

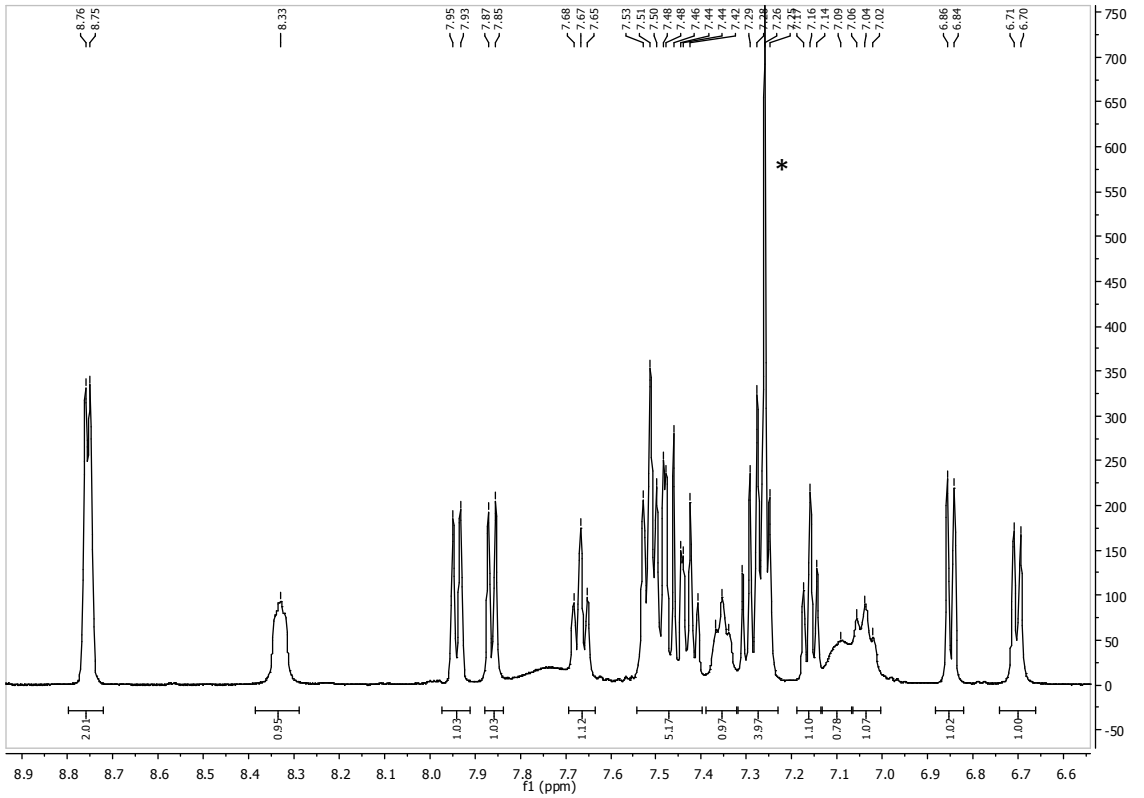


Figure 19: ^{1}H NMR aromatic region (500 MHz, $CDCl_3$)

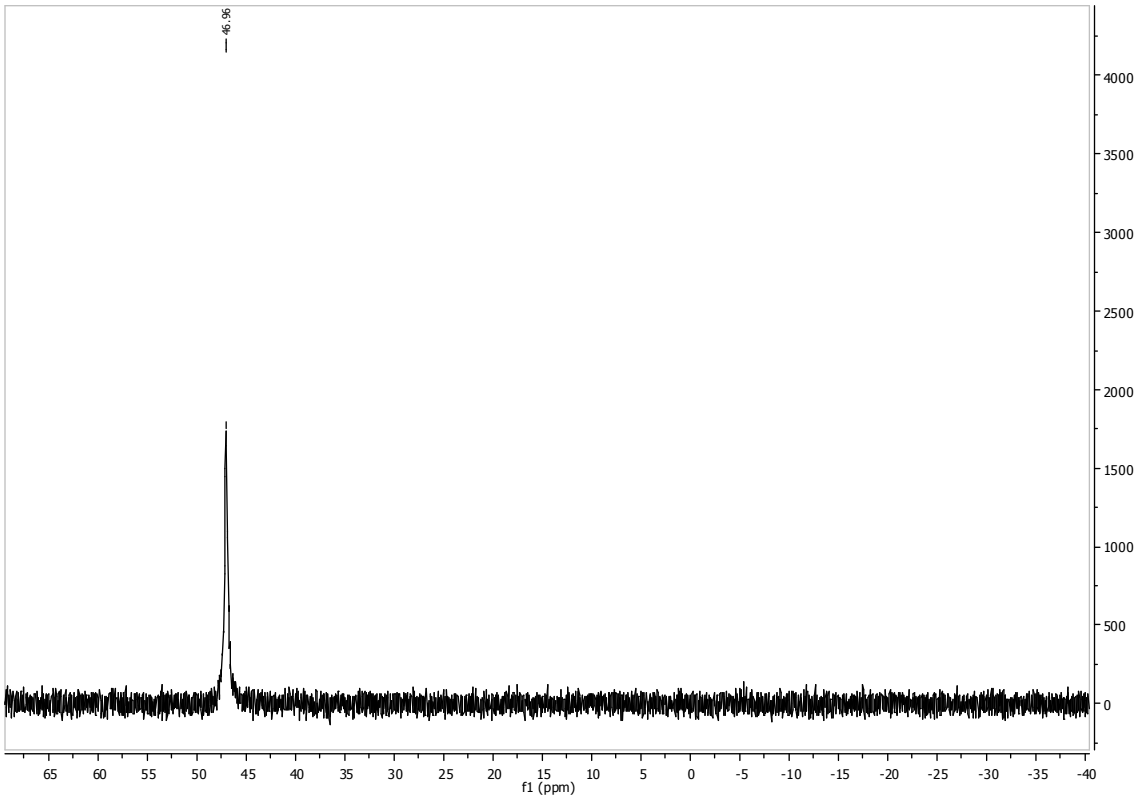


Figure 20: $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$)

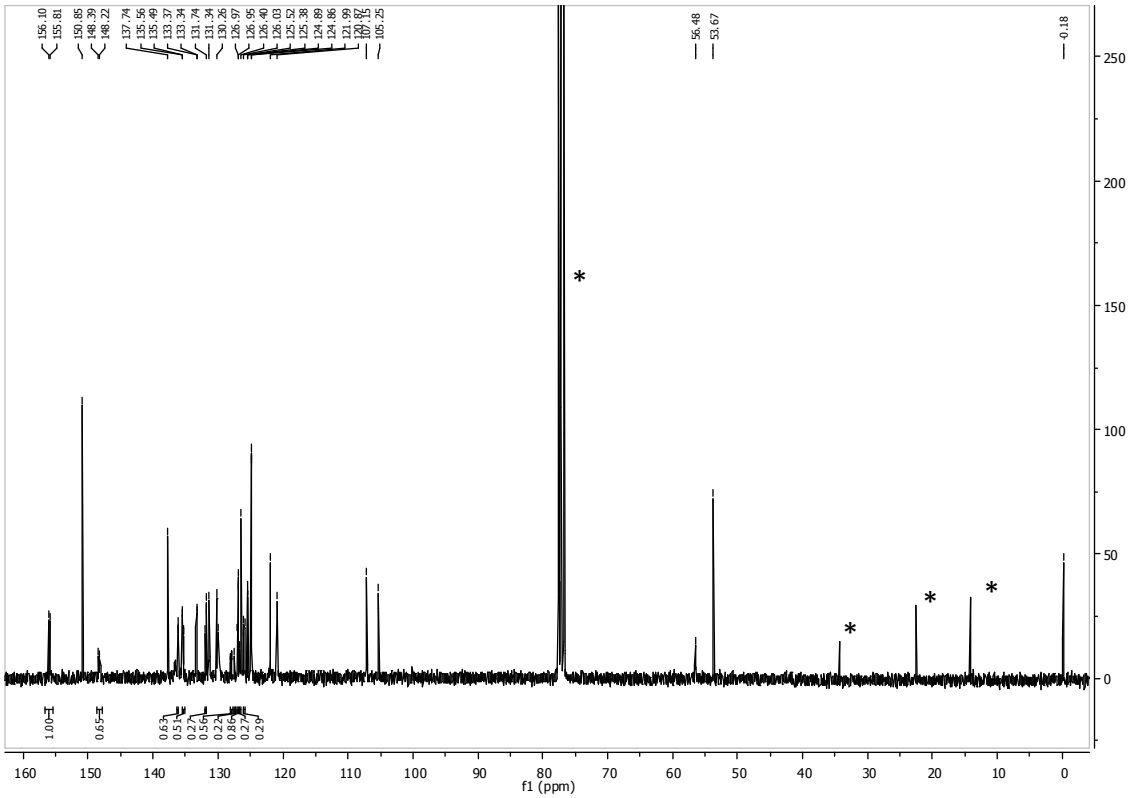


Figure 21: $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

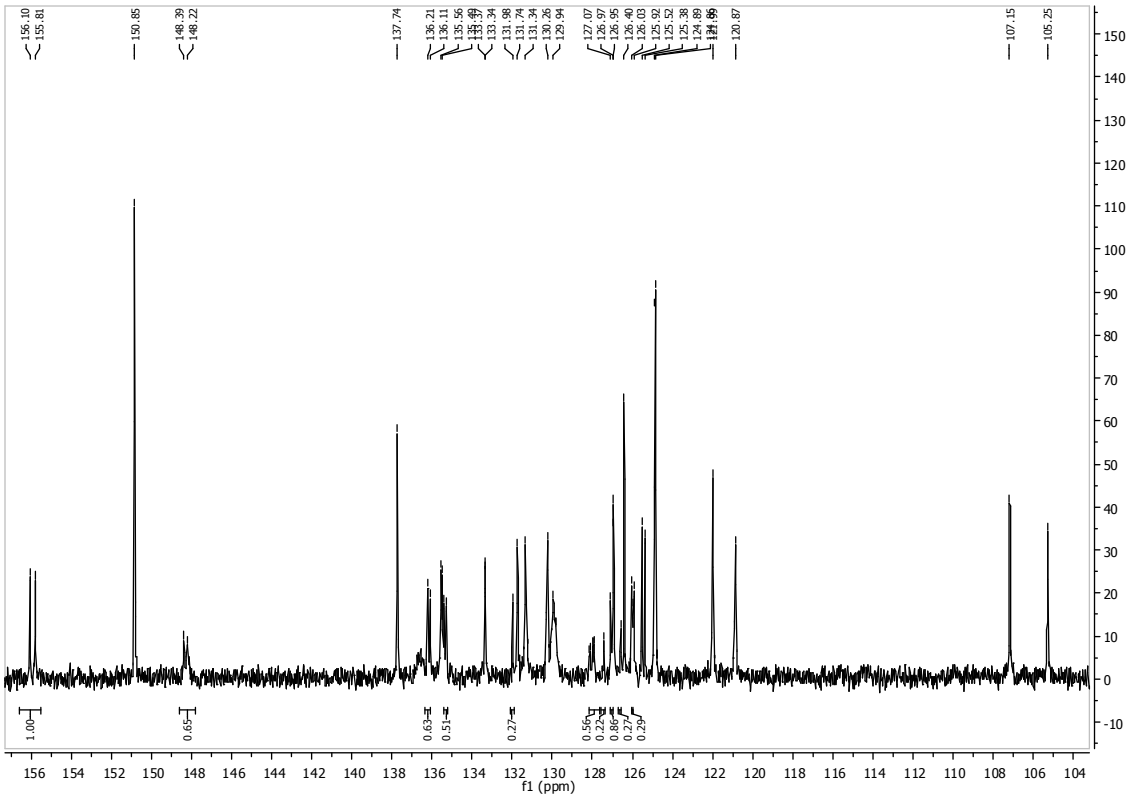


Figure 22: $^{13}C\{^{1}H\}$ NMR aromatic region (75 MHz, $CDCl_3$)

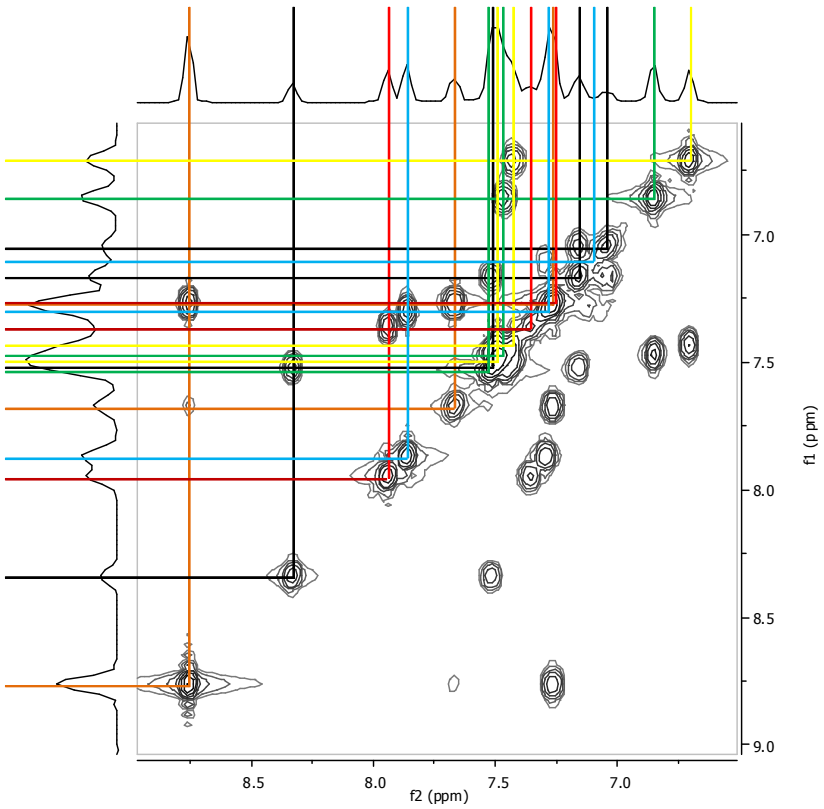


Figure 23: COSY NMR (500 MHz, $CDCl_3$)

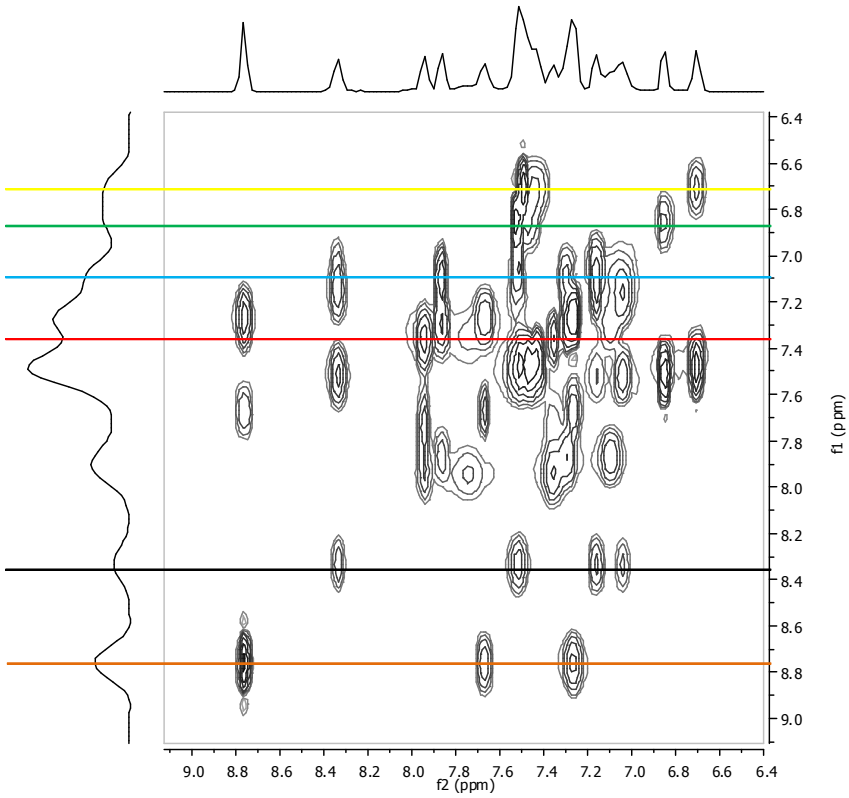


Figure 24: TOCSY NMR (500 MHz, $CDCl_3$

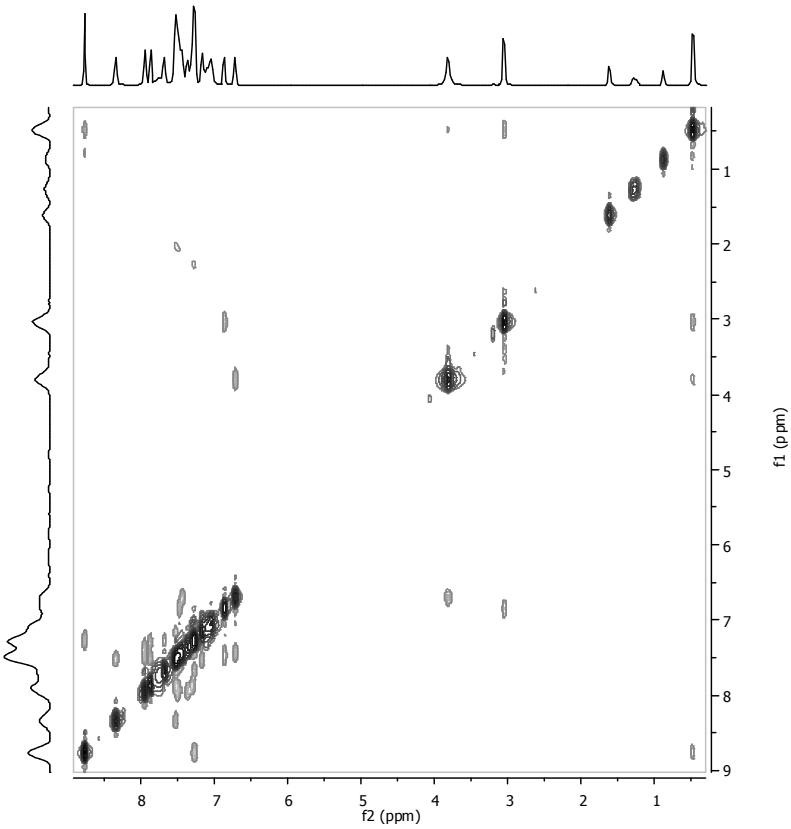


Figure 25: NOESY NMR (500 MHz, $CDCl_3$).

1.5. Synthesis of [κ-(N, N')-tmeda][{ κ^2-(P,O)-2-(bis-8-methoxynaphthalene-1-phosphine)benzene sulfonate} $PdMe]_2$ 10.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 7.4, 3.7 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.65 (dd, *J* = 14.0, 7.3 Hz, 1H), 7.53 – 7.36 (m, 5H), 7.34 – 7.19 (m, 4H), 7.09 (t, *J* = 7.5 Hz, 1H), 7.03 – 6.86 (m, 3H), 6.66 (d, *J* = 6.6 Hz, 1H), 3.68 (s, 3H), 2.98 (s, 3H), 2.17 (s, 3H), 1.55 (s, 3H), 0.16 (s, 3H).

^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) δ +47.6.

The low solubility of **10** in $CDCl_3$ prevented measurement of ^{13}C NMR spectra.

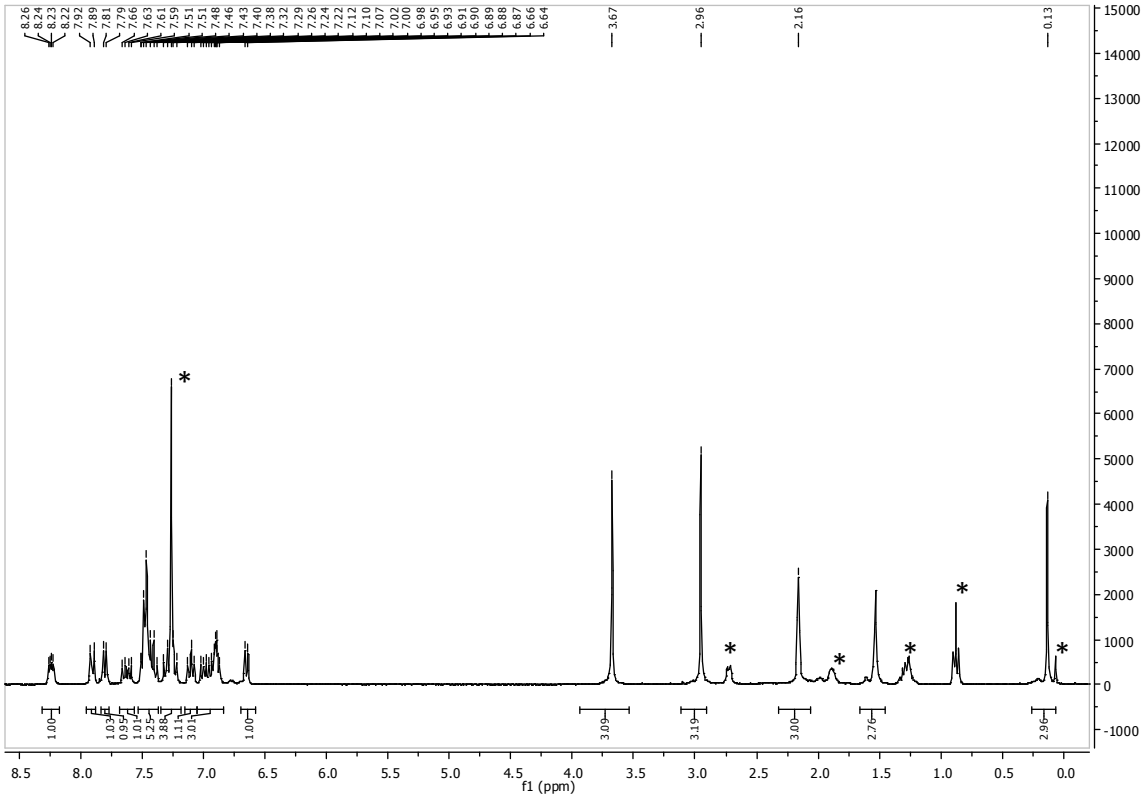


Figure 26: ^{1}H NMR (300 MHz, $CDCl_3$)

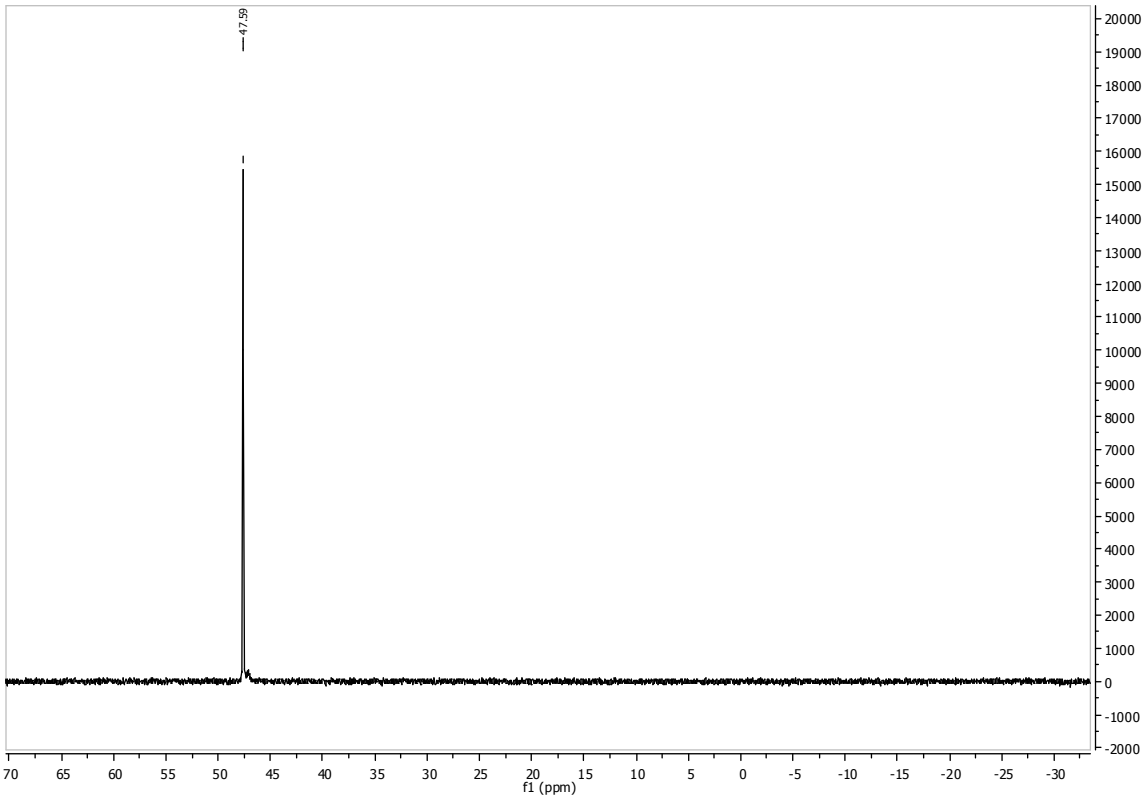


Figure 27: $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$)

2. H-H Distance determination by NOESY NMR spectroscopy and comparison to the molecular structure of phosphine sulfonate-based Pd(II) complexes

3.1. General Considerations

NOESY NMR spectra were employed to determine the solution distances of protons with close spatial contact. Due to the dependency of the nOe intensity on the proximity of protons (~ $1/d^6$) crosspeaks for signals between 2 and 4 Å are observed. In relation to a reference signal with known H-H distance the comparison of NOESY NMR crosspeaks gives an approximation for the distance between corresponding protons in solution. As the dependency of the distance d to the crosspeak integral I is not linear the observed average values for dynamic processes is weighted towards shorter H-H distances. Equation 1 shows the general formula for the intensity of a NOESY signal and its dependence on the corresponding proton distance. The calibration constant C can be determined by a reference relation giving Equation 2.[1]

In the present case the H-H distance of the *ortho* and *meta* pyridine H-atoms is an ideally suitable reference signal for distance approximation in phosphine sulfonate-based palladium catalysts with coordinated pyridine. Comparison of different reported molecular structures shows only minor variation, as expected.[2] Due to minor errors in phase- and baseline-correction the integrals of observed NOESY NMR crosspeaks differ slightly in f1 and f2 direction. Therefore only average values from f1 and f2 are compared to H-H distances determined from the molecular structure.

Equation 1:

$$I_{ij} = \frac{C}{d_{ij}^6}$$

with: C = calibration constant

I_{ij} = integral value of nOe signal *ij*

Equation 2:

$$d_{ij} = \sqrt[6]{\frac{I_{no}}{I_{ij}}} \cdot d_{no}$$

with: I_{no} = integral value of nOe signal *no* (reference signal)

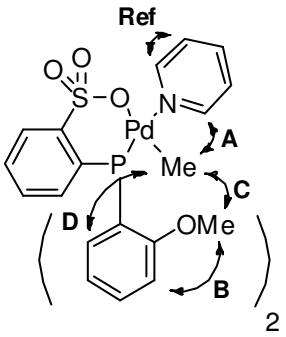
I_{ij} = integral value of nOe signal *ij* (x)

d_{no} = reference distance *no* (r)

d_{ij} = determined distance *ij* (x)

2.1. NOESY NMR spectra interpretation and correlation to solid state structures

Evaluation of [{κ²-(P,O)-2-(bis-2-methoxyphenylphosphine)benzene-sulfonate}PdMe (pyridine)] 1a



1a

Figure 28: Labeling of observed proton relations and correlation to the NOESY NMR crosspeaks for **1a**.

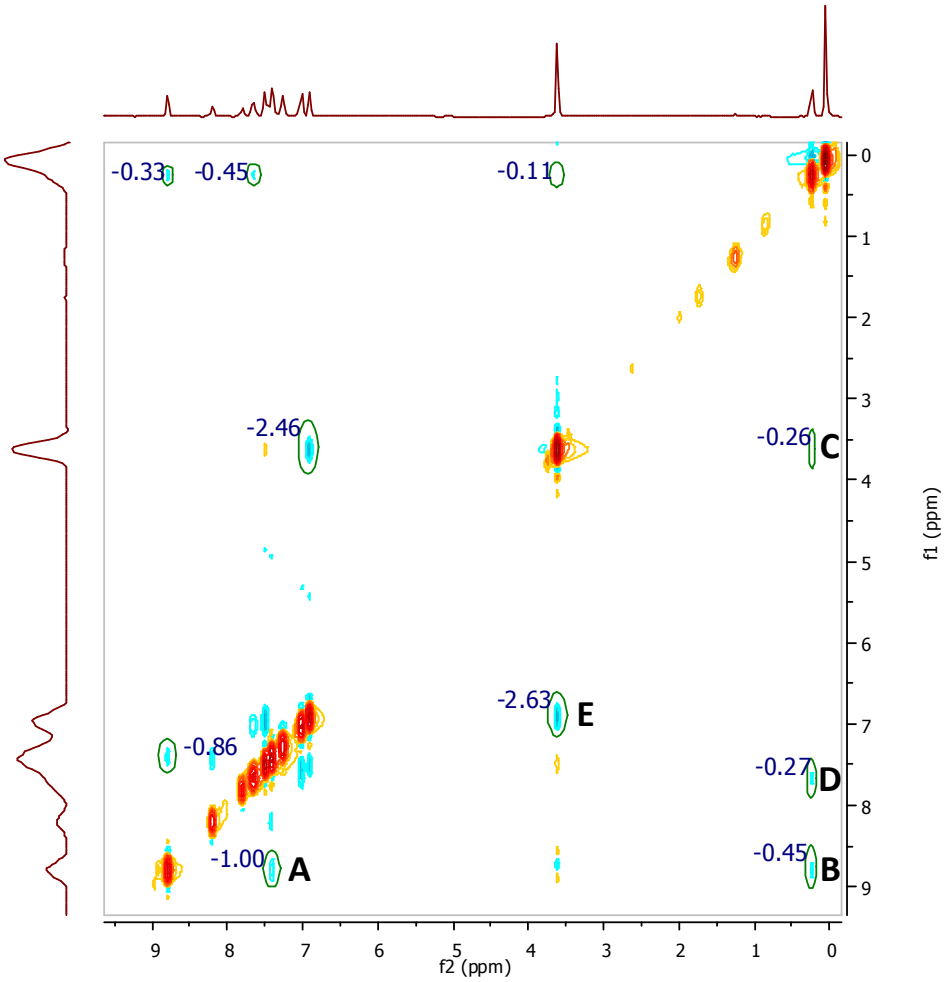


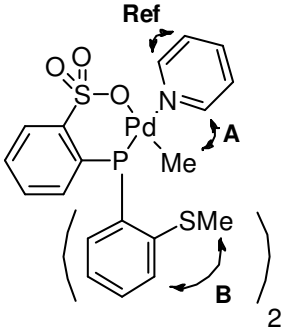
Figure 29: NOESY NMR spectrum of **1a** with labeled crosspeaks for correlation to H-H relations.

Table 1: Determination of solution H-H relation distances and comparison to values from the molecular structure[2a] of **1a**.

Relation[1]	I_x (f1)[2]	I_x (f2)[2]	d_x (nOe, f1) / Å[3]	d_x (nOe, f2) / Å[3]	**d_x (average) / Å**[4]	**d_x (mol. struc.) / Å**[5]
A	0.86	1.00	2.3[6]	2.3[6]	**2.3**[6]	**2.3**[6]
B	0.33	0.45	2.7	2.6	**2.7**	**2.6**
C	0.11	0.26	3.3	2.9	**3.1**	**3.7**
D	0.45	0.27	2.6	2.9	**2.7**	**2.8**
E	2.46	2.63	1.9	2.0	**2.0**	**2.2**

[1]nOe relation as defined in Figure 28, [2]nOe integral in f1 and f2 direction, [3]distance d_x for f1 and f2, [4]average distance d_x from f1 and f2, [5]determined from the molecular structure, [6]reference from the molecular structure.

Evaluation of [{κ^2-(P,O)-2-(bis-2-thiomethoxyphenylphosphine)benzene-sulfonate} PdMe(pyridine)] 8



7

Figure 30: Labeling of observed proton relations and correlation to the NOESY NMR crosspeaks for **8**.

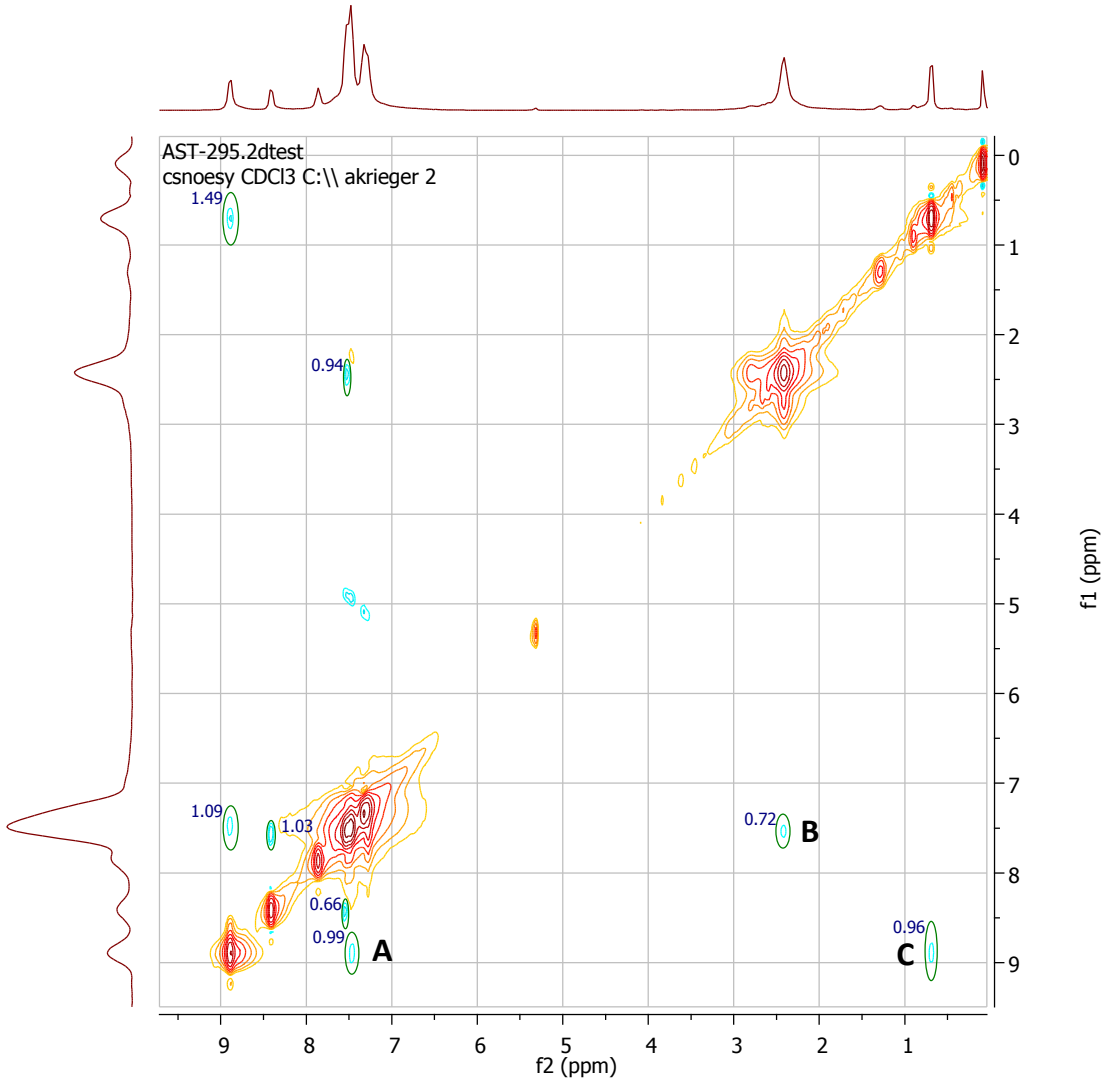


Figure 31: NOESY NMR spectrum of **8** with labeled crosspeaks for correlation to H-H relations.

relation[1]	I_x (f1)[2]	I_x (f2)[2]	d_x (nOe, f1) / Å[3]	d_x (nOe, f2) / Å[3]	**d_x (average) / Å**[4]	**d_x (mol. struc.) / Å**
A	0,99	1,09	2.3[5]	2.3[5]	**2.3**[5]	**2,3**[5]
B	0,96	1,09	2,3	2,3	**2,3**	**n.d.**
C	0,72	0,94	2,4	2,4	**2,4**	**n.d.**

[1]nOe relation as defined in Figure 30, [2]nOe integral in f1 and f2 direction, [3]distance d_x for f1 and f2 direction, [4]average distance d_x, [5]reference value for related compounds, n.d. = not determined.

[{κ²-(P,O)-2-(bis-8-methoxynaphthalene-1-phosphine)benzene sulfonate}PdMe (pyridine)] 9

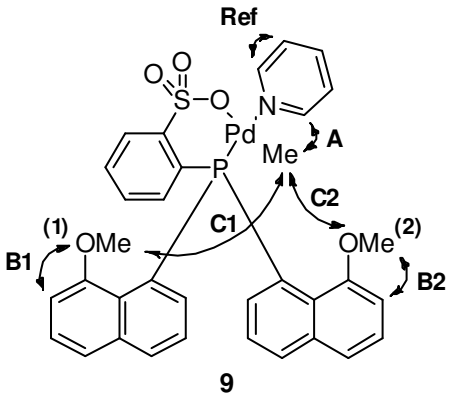


Figure 32: Labelling of observed proton relations and correlation to the NOESY NMR crosspeaks for **9**

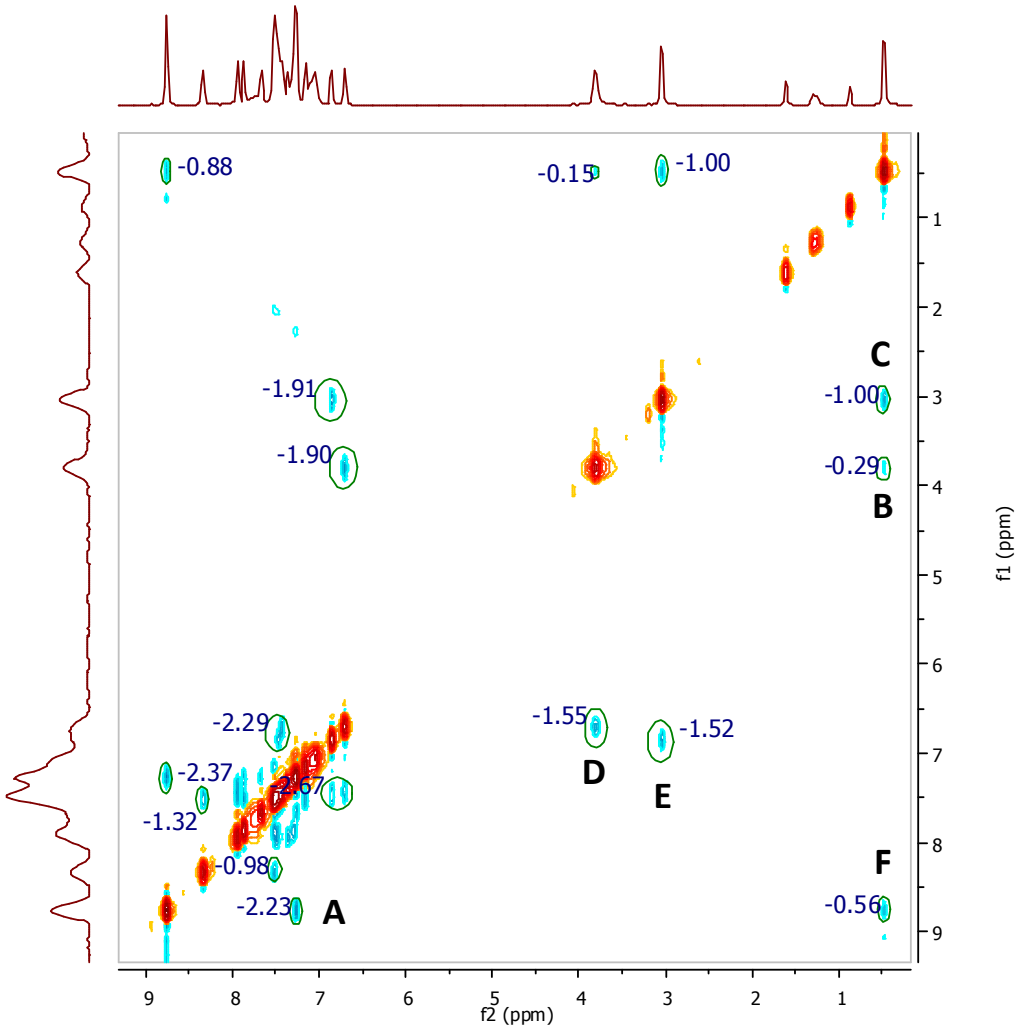


Figure 33: NOESY NMR spectrum of **9** with labeled crosspeaks for correlation to H-H relations.

relation x[1]	V_x (f1)[2]	V_x (f2)[2]	d_x (nOe, f1) / Å[3]	d_x (nOe, f2) / Å[3]	d_x (average) / Å[4]	d_x (mol. struc.) / Å[5]
A	2.37	2.23	2.3[6]	2.3[6]	2.3[6]	2.3
B	0.15	0.29	3.7	3.2	3.4	2.4
C	1.00	1.00	2.7	2.6	2.7	2.3
D	1.90	1.55	2.4	2.5	2.4	2.3
E	1.91	1.52	2.4	2.5	2.4	3.0
F	0.88	0.56	2.7	2.9	2.8	2.5

[1]nOe relation as defined in Figure 32, [2]nOe integral in f1 and f2 direction, [3]distance d_x for f1 and f2 direction, [4]average distance d_x, [5]determined from the molecular structure, [6]reference value from the molecular structure.

3. Analytical Data for selected polymer samples

3.1. NMR spectra

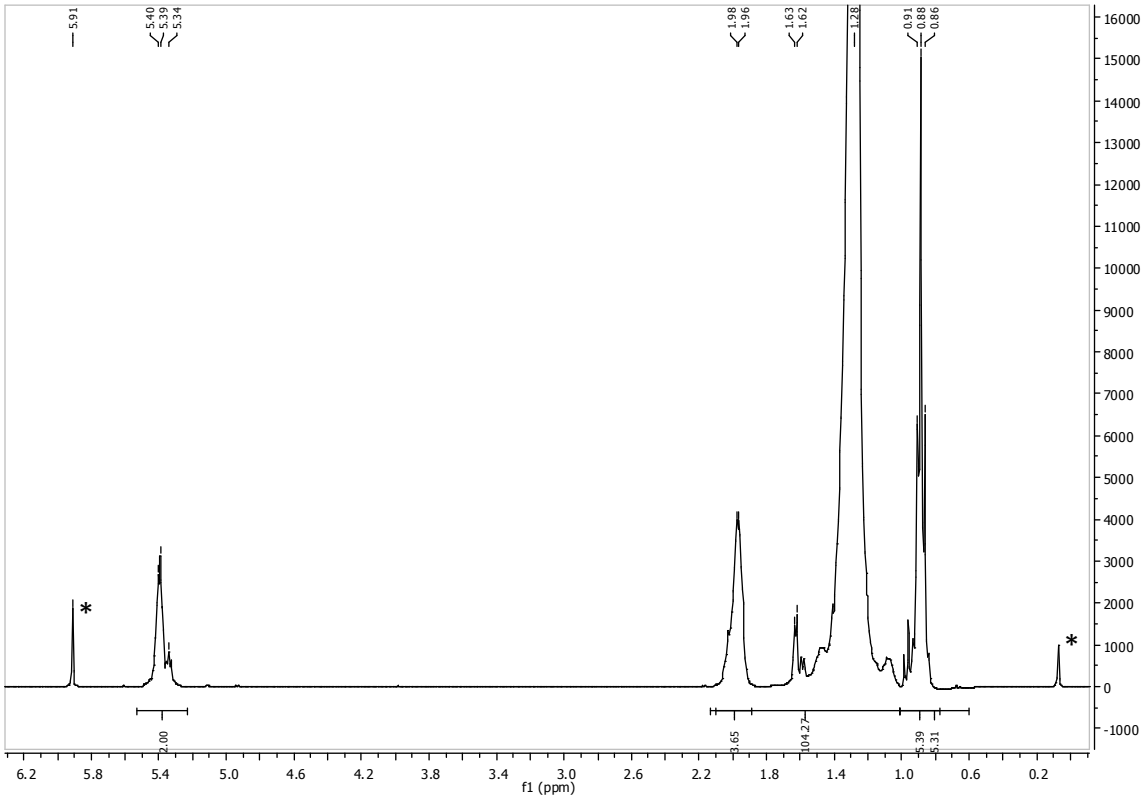


Figure 34: ^{1}H NMR (300 MHz, 120 °C, $C_2D_2Cl_4$) Sample Table 2, Entry 2.

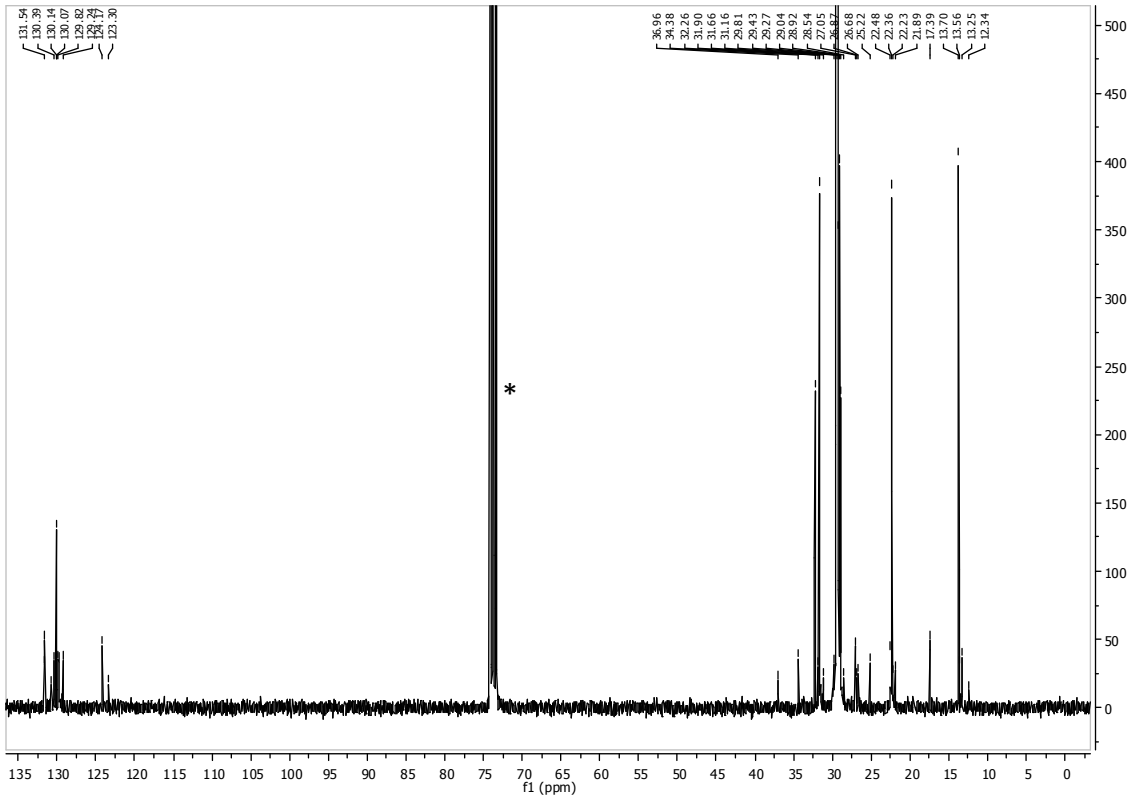


Figure 35: ^{13}C NMR (75 MHz, 120 °C, $C_2D_2Cl_4$) Sample Table 2, Entry 2.

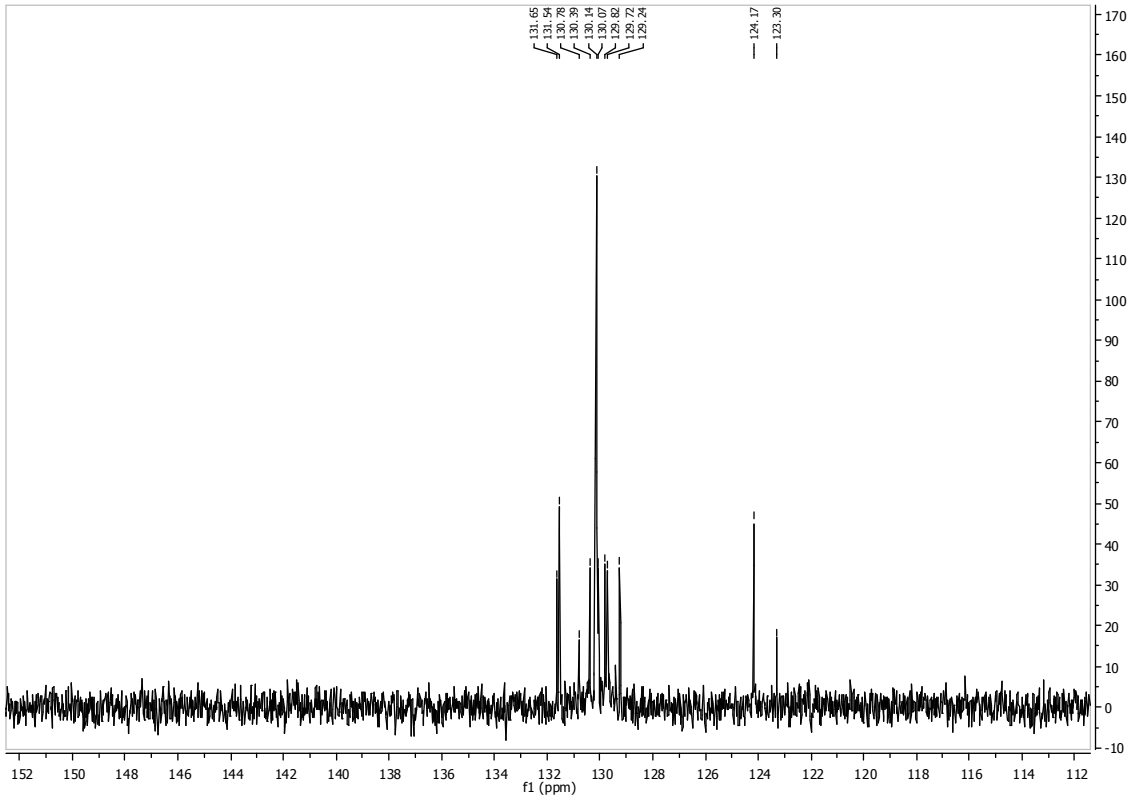


Figure 36: ^{13}C NMR olefinic region (75 MHz, 120 °C, $C_2D_2Cl_4$) Sample Table 2, Entry 2.

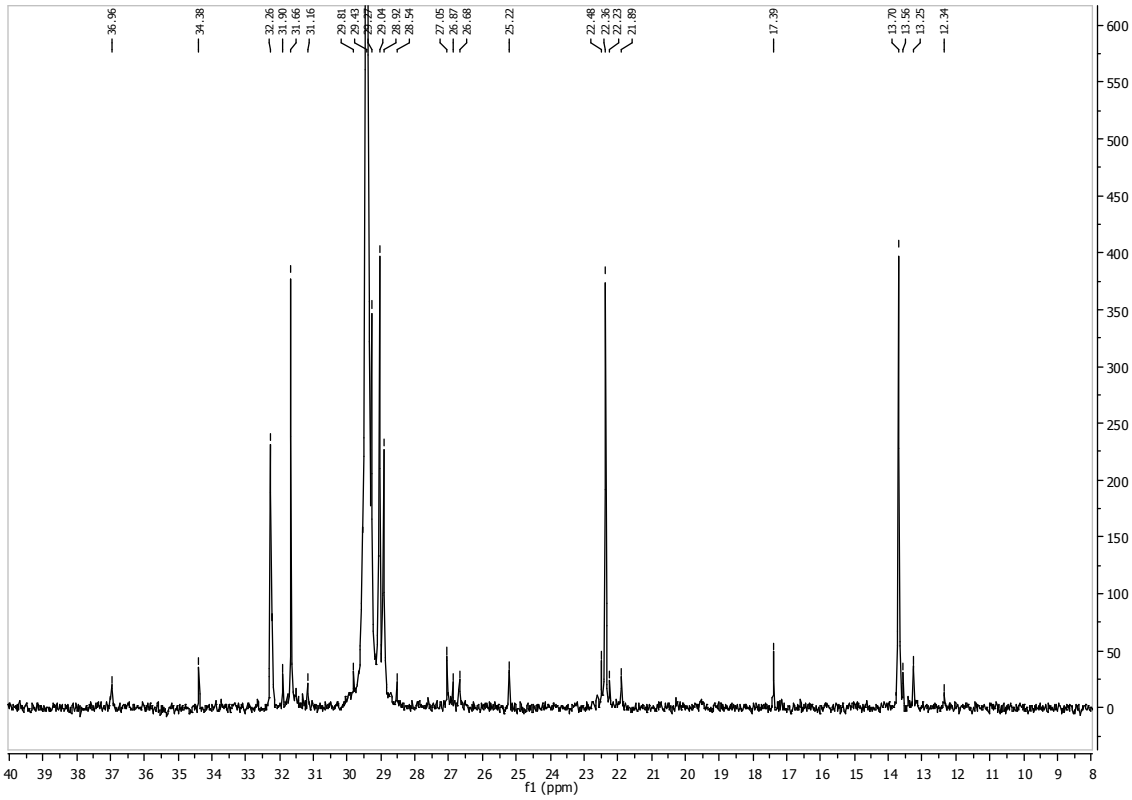


Figure 37: ^{13}C NMR aliphatic region (75 MHz, 120 °C, $C_2D_2Cl_4$) Sample Table 2, Entry 2.

3.2. GPC plots

- **Low molecular weight PE (Table 2, Entry 2).**

GPC Report **Freitag, 26. November 2010 13:08**

Workbook: C:\Cirrus Workbooks\Olexis_2010-07-26_RI\Olexis_2010-07-26_RI.plw

Sample Details

Sample Name: AST-342 Batch Name: 2010-11-25

Filename: C:\Cirrus Workbooks\Olexis_2010-07-26_RI\2010-11-25-0003.cgrm

Acquired: 26.11.2010 13:04:52 Eluent: TCB stabilised with 0.0125% BHT

Injection Volume: 200.0 ul Flow Rate: 1.0 ml/min

Concentration: mg/ml Temperature: 160 °C

Column Set: Olexis Column Set Length: 60600 mm

Analysis Using Method: RI-Auswert_PE_K_a

Results File: C:\Cirrus Workbooks\Olexis_2010-07-26_RI\2010-11-25-0003.rst

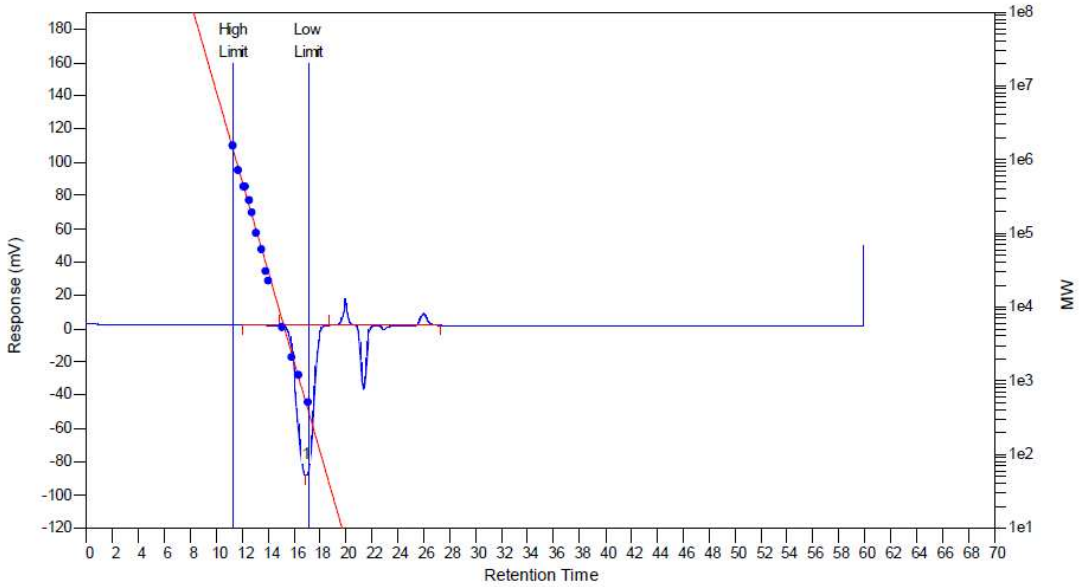
Calibration Used: 10.08.2010 14:34:17

Calibration Type: Narrow Standard Curve Fit Used: 1

Calibration Curve: y = 13.033703 - 0.610881x^1

K (user predefined) = 40.600000 alpha (user predifined) = 0.725000

High limit Mw = 1449749 Low limit Mw = 360



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	524	474	776	1296	2094	723	1.63713

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		14.90	16.88	18.67	-90.4028	0	7170.23	100

Figure 38: GPC plot of polymer sample from Table 2, Entry10; RI detection

- **High molecular weight PE (Table 2, Entry 10).**

GPC Report **Freitag, 26. November 2010 13:34**

Workbook: C:\Cirrus Workbooks\Olexis_2010-07-26_658nm\Olexis 2010-07-26_658nm.mplw

Sample Details

Sample Name: AST-313 Batch Name: 2010-11-24

Filename: C:\Cirrus Workbooks\Olexis_2010-07-26_658nm\2010-11-24-0006.cgrm

Acquired: 25.11.2010 21:45:40 Eluent: TCB stabilised with 0.0125% BHT

Injection Volume: 200.0 ul Flow Rate: 1.0 ml/min

Temperature: 160 °C

Column Set: Olexis Column Set Length: 60600 mm

Calculated concentration: 2.188513 mg/ml Concentration used: 2.19 mg/ml

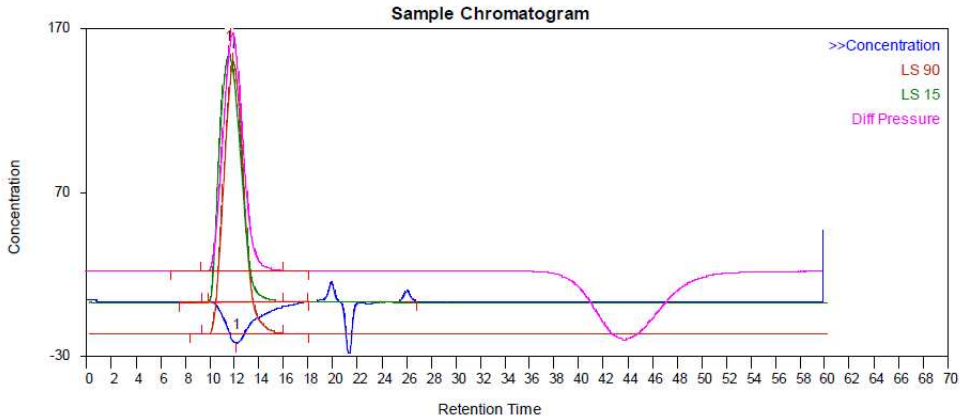
Calculated dn/dc: 0.10000 dn/dc Used: 0.10000

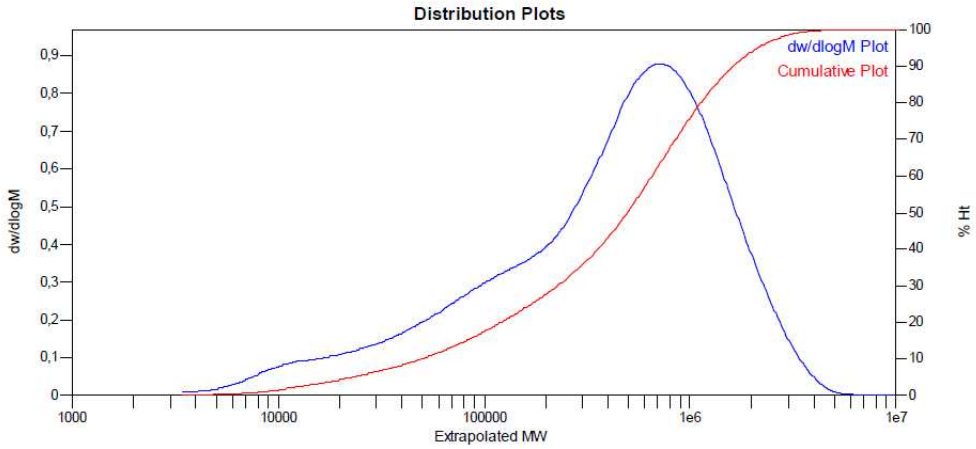
Analysis Using Method: Triple

Results File: C:\Cirrus Workbooks\Olexis_2010-07-26_658nm\2010-11-24-0006-Repeat (01).rst

Ligt Scattering and IV Results: Bulk IV: 8.364496

LS 15°Mw: 660289 LS 90°Mw: 332415





MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	718355	111026	695015	1421125	2111561	564160	6.25989

Cirrus GPC Version 3.1 Page 1 26.11.2010 13:34

Figure 39: GPC plot of polymer sample from Table 2, Entry10; multi detection.

4. Single Crystal X-Ray Structure Determinations of Compound 9, and 10

General:

Data were collected on an X-ray single crystal diffractometer equipped with a CCD detector (APEX II, κ–CCD), a rotating anode (Bruker AXS, FR591) with MoK_{α} radiation (λ = 0.71073 Å), and a graphite monochromator by using the SMART software package.[3] The measurements were performed on single crystals coated with perfluorinated ether. The crystals were fixed on the top of a glass fiber and transferred to the diffractometer. Crystals were frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorenz and polarization effects, scan speed, and background using SAINT 4.15.[4] Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS.[4] Space group assignments were based upon systematic absences, *E* statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps, and were refined against all data using WinGX[9] based on SIR-92.[5] Hydrogen atoms were assigned to ideal positions and refined using a riding model with an isotropic thermal parameter 1.2 times that of the attached carbon atom (1.5 times for methyl hydrogen atoms). If not mentioned otherwise, non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2-F_c^2)^2$ with SHELXL-97[7] weighting scheme. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*.[6] Images of the crystal structures were generated by PLATON[8].

4.1 Single Crystal X-Ray Structure Determination of Compound 9

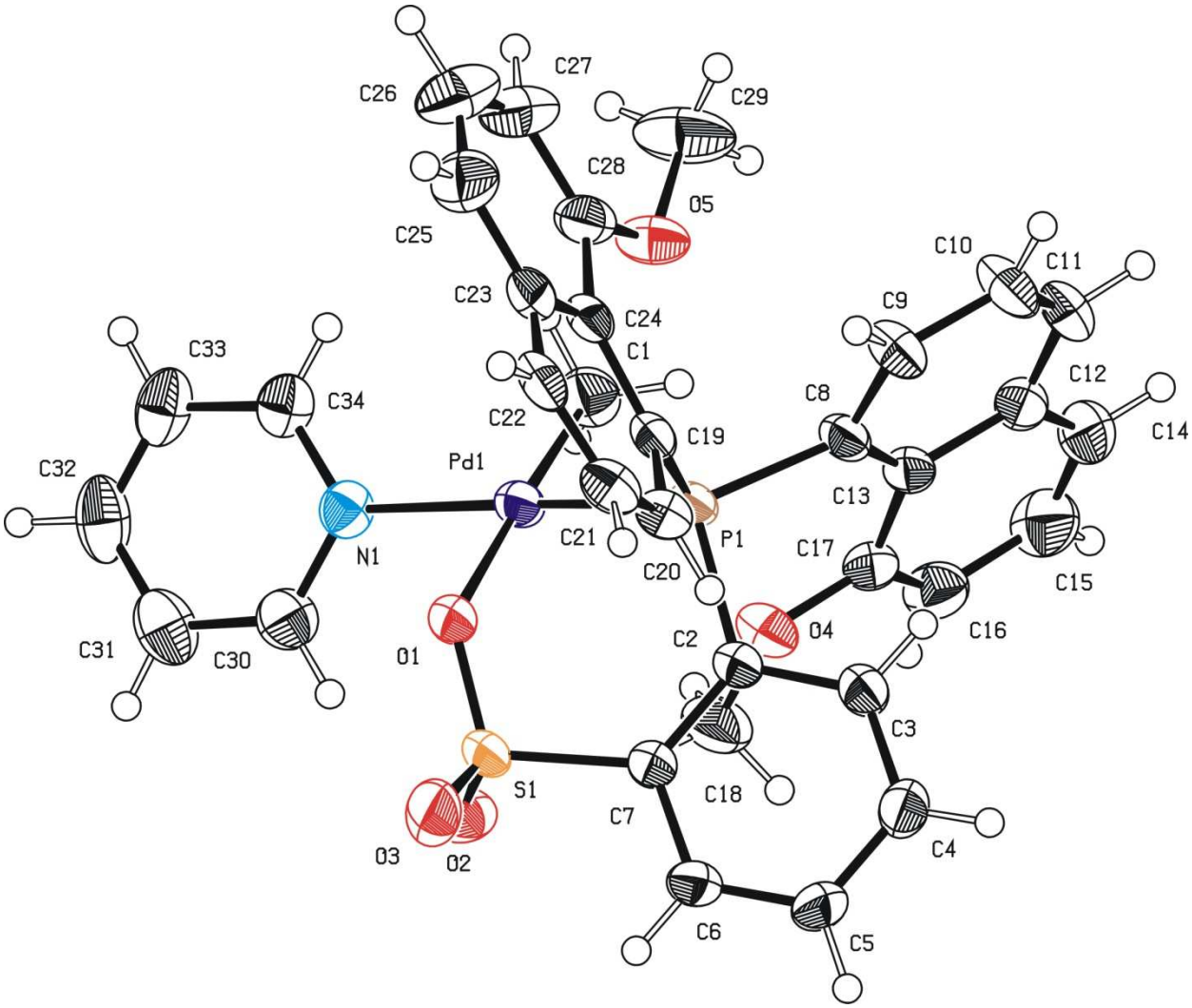


Figure F1 – Ortep drawing drawing of compound **9** with 50% ellipsoids.[8]

Operator:	*** Herdtweck ***
Molecular Formula:	C_{34} H_{30} N O_5 P Pd S
Crystal Color / Shape	Yellow prism
Crystal Size	Approximate size of crystal fragment used for data collection: 0.23 × 0.30 × 0.36 mm
Molecular Weight:	702.03 a.m.u.
F_{000}:	2864
Systematic Absences:	hkl: h+k≠2n; h0l: l≠2n
Space Group:	Monoclinic *C* 2/*c* (I.T.-No.: 15)

Cell Constants:	Least-squares refinement of 9868 reflections with the programs "APEX suite" and "SAINT"[3,4]; theta range 1.65° < θ < 25.47°; Mo(K$\overline{\alpha}$); λ = 71.073 pm
	a = 1830.19(3) pm
	b = 1552.60(3) pm β = 93.5722(9)°
	c = 2466.90(5) pm
	V = 6996.2(2)· 10^6 pm^3; Z = 8; D_{calc} = 1.333 g cm^{-3}; Mos. = 0.67
Diffractometer:	Kappa APEX II (Area Diffraction System; BRUKER AXS); sealed tube; graphite monochromator; 50 kV; 30 mA; λ = 71.073 pm; Mo(K$\overline{\alpha}$)
Temperature:	(-100±1) °C; (173±1) K
Measurement Range:	1.65° < θ < 25.47°; h: -22/22, k: -18/18, l: -29/29
Measurement Time:	2 × 10 s per film
Measurement Mode:	measured: 9 runs; 3070 films / scaled: 9 runs; 3070 films
	φ– and ω–movement; Increment: $\Delta\varphi/\Delta\omega$ = 0.50°; dx = 60.0 mm
LP - Correction:	Yes [4]
Intensity Correction	No/Yes; during scaling [4]
Absorption Correction:	Multi-scan; during scaling; μ = 0.674 mm^{-1} [4]
	Correction Factors: T_{min} = 0.6922 T_{max} = 0.7452
Removing solvent molecules	Unresolved solvent molecules had to be removed with the SQUEEZE procedure. [8]
Reflection Data:	58095 reflections were integrated and scaled
	1133 reflections systematic absent and rejected
	56962 reflections to be merged
	6482 independent reflections
	0.019 R_{int}: (basis F_o^2)
	6482 independent reflections (all) were used in refinements
	5970 independent reflections with $I_o > 2\sigma(I_o)$
	99.7 % completeness of the data set
	391 parameter full-matrix refinement
	16.6 reflections per parameter
Solution:	Direct Methods[5, 9]; Difference Fourier syntheses

Refinement Parameters:	In the asymmetric unit:
	43 Non-hydrogen atoms with anisotropic displacement parameters
Hydrogen Atoms:	In the difference map(s) calculated from the model containing all non-hydrogen atoms, not all of the hydrogen positions could be determined from the highest peaks. For this reason, the hydrogen atoms were placed in calculated positions (d_{C-H} = 95, 98 pm). Isotropic displacement parameters were calculated from the parent carbon atom ($U_H = 1.2/1.5\ U_C$). The hydrogen atoms were included in the structure factor calculations but not refined.
Atomic Form Factors:	For neutral atoms and anomalous dispersion [6, 7, 9]
Extinction Correction:	no
Weighting Scheme:	$w^{-1} = \sigma^2(F_o^2)+(a*P)^2+b*P$
	with a: 0.0274; b: 7.7977; P: [Maximum(0 or F_o^2)+2$*F_c^2$]/3
Shift/Err:	Less than 0.003 in the last cycle of refinement:
Resid. Electron Density:	+0.32 $e_{0;}^{-}$ /Å^3; -0.34 $e_{0;}^{-}$ /Å^3
R1:	$\Sigma(\lvert\lvert F_o\rvert-\lvert F_c\rvert\rvert)/\Sigma\lvert F_o\rvert$
[$F_o > 4\sigma(F_o)$; N=5970]:	= 0.0225
[all reflctns; N=6482]:	= 0.0244
wR2:	$[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$
[$F_o > 4\sigma(F_o)$; N=5970]:	= 0.0579
[all reflctns; N=6482]:	= 0.0589
Goodness of fit:	$[\Sigma w(F_o^2-F_c^2)^2/(NO-NV)]^{1/2}$ = 1.060
Remarks:	Refinement expression $\Sigma w(F_o^2-F_c^2)^2$

4.2 Fold angle determination for the naphthalene substituents in compound 9

```
+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
 +  SHELXL-97 - CRYSTAL STRUCTURE REFINEMENT - WINDOWS VERSION  +
 +  Copyright(C) George M. Sheldrick 1993-7       Release 97-2  +
 +  shelxl                  started at 10:32:46 on 05-Aug-2011  +
 +++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++

 TITL ANSE 7038-173 31. Januar 2011 sealed tube APEX II 50/30/0.50-Kollimator
 CELL 0.71073 18.3019 15.5260 24.6690 90 93.5722 90
 ZERR 8        0.0003  0.0003  0.0005  0  0.0009  0
 LATT 7
 SYMM -X, Y, 0.50000-Z
 SFAC C   H   N O  P Pd S
 UNIT 272 240 8 40 8 8  8

 MPLA 6  c8  c9  c10 c11 c12 c13 c14 c15 c16 c17
```

```
MPLA 6  c12 c13 c14 c15 c16 c17 c8  c9  c10 c11
MPLA 6  c19 c20 c21 c22 c23 c24 c25 c26 c27 c28
MPLA 6  c23 c24 c25 c26 c27 c28 c19 c20 c21 c22
MPLA 10 c8  c9  c10 c11 c12 c13 c14 c15 c16 c17
MPLA 10 c19 c20 c21 c22 c23 c24 c25 c26 c27 c28

L.S. 2
WGHT      0.0274      7.7977
FVAR       0.44016
PD1   6    0.245085    0.094988    0.385201    11.00000    0.03647    0.02677 =
         0.03049    0.00291    0.00879    0.00103
etc...
```

Least-squares planes (x,y,z in crystal coordinates) and deviations from them
(* indicates atom used to define plane)

1.6349 (0.0156) x - 15.4614 (0.0012) y + 0.3049 (0.0203) z = 0.7750 (0.0063)

```
*   -0.0208 (0.0013)  C8
*    0.0076 (0.0015)  C9
*    0.0127 (0.0017)  C10
*   -0.0185 (0.0016)  C11
*    0.0043 (0.0014)  C12
*    0.0147 (0.0013)  C13
     0.0249 (0.0033)  C14
     0.0709 (0.0039)  C15
     0.0977 (0.0037)  C16
     0.0851 (0.0029)  C17
```

Rms deviation of fitted atoms = 0.0143

2.2556 (0.0152) x - 15.4074 (0.0016) y - 0.0560 (0.0207) z = 0.8693 (0.0051)

Angle to previous plane (with approximate esd) = 2.08(0.03)

```
*    0.0056 (0.0014)  C12
*   -0.0100 (0.0012)  C13
*    0.0006 (0.0016)  C14
*   -0.0025 (0.0017)  C15
*   -0.0023 (0.0015)  C16
*    0.0085 (0.0013)  C17
    -0.0181 (0.0029)  C8
     0.0601 (0.0037)  C9
     0.0901 (0.0039)  C10
     0.0339 (0.0033)  C11
```

Rms deviation of fitted atoms = 0.0060

- 10.8178 (0.0099) x + 3.5706 (0.0109) y + 19.9439 (0.0098) z = 2.9553 (0.0083)

Angle to previous plane (with approximate esd) = 72.73 (0.06)

```
*    0.0311 (0.0012)  C19
*   -0.0035 (0.0013)  C20
*   -0.0253 (0.0013)  C21
*    0.0244 (0.0012)  C22
*    0.0047 (0.0012)  C23
*   -0.0314 (0.0011)  C24
    -0.0119 (0.0031)  C25
```

```
    -0.0831 (0.0039)  C26
    -0.1902 (0.0036)  C27
    -0.1879 (0.0028)  C28

Rms deviation of fitted atoms =   0.0232


- 11.5094 (0.0127) x + 4.3402 (0.0134) y + 18.8298 (0.0139) z = 2.2311 (0.0112)
```

Angle to previous plane (with approximate esd) = 4.50(0.11)

```
*   -0.0161 (0.0013)  C23
*    0.0308 (0.0012)  C24
*   -0.0094 (0.0017)  C25
*    0.0201 (0.0019)  C26
*   -0.0038 (0.0018)  C27
*   -0.0215 (0.0014)  C28
     0.0666 (0.0029)  C19
    -0.0725 (0.0036)  C20
    -0.1748 (0.0036)  C21
    -0.1018 (0.0029)  C22

Rms deviation of fitted atoms =   0.0190


 1.9961 (0.0077) x - 15.4322 (0.0008) y + 0.1310 (0.0153) z = 0.8585 (0.0035)

Angle to previous plane (with approximate esd) = 70.27 ( 0.06 )

*   -0.0382 (0.0015)  C8
*    0.0184 (0.0017)  C9
*    0.0360 (0.0019)  C10
*   -0.0110 (0.0018)  C11
*   -0.0172 (0.0018)  C12
*   -0.0199 (0.0016)  C13
*   -0.0128 (0.0018)  C14
*    0.0052 (0.0019)  C15
*    0.0186 (0.0017)  C16
*    0.0209 (0.0015)  C17

Rms deviation of fitted atoms =   0.0221


- 11.1577 (0.0086) x + 4.0300 (0.0061) y + 19.3776 (0.0086) z = 2.5611 (0.0074)

Angle to previous plane (with approximate esd) = 71.61 ( 0.04 )

*    0.0804 (0.0014)  C19
*   -0.0119 (0.0015)  C20
*   -0.0736 (0.0015)  C21
*   -0.0066 (0.0015)  C22
*    0.0322 (0.0016)  C23
*    0.0373 (0.0015)  C24
*    0.0332 (0.0019)  C25
*    0.0178 (0.0022)  C26
*   -0.0478 (0.0020)  C27
*   -0.0612 (0.0016)  C28

Rms deviation of fitted atoms =   0.0468



etc...
```

```
+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
+  shelxl            finished at 10:32:48   Total CPU time:       1.4 secs  +
+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
```

4.3 Single Crystal X-Ray Structure Determination of Compound 10

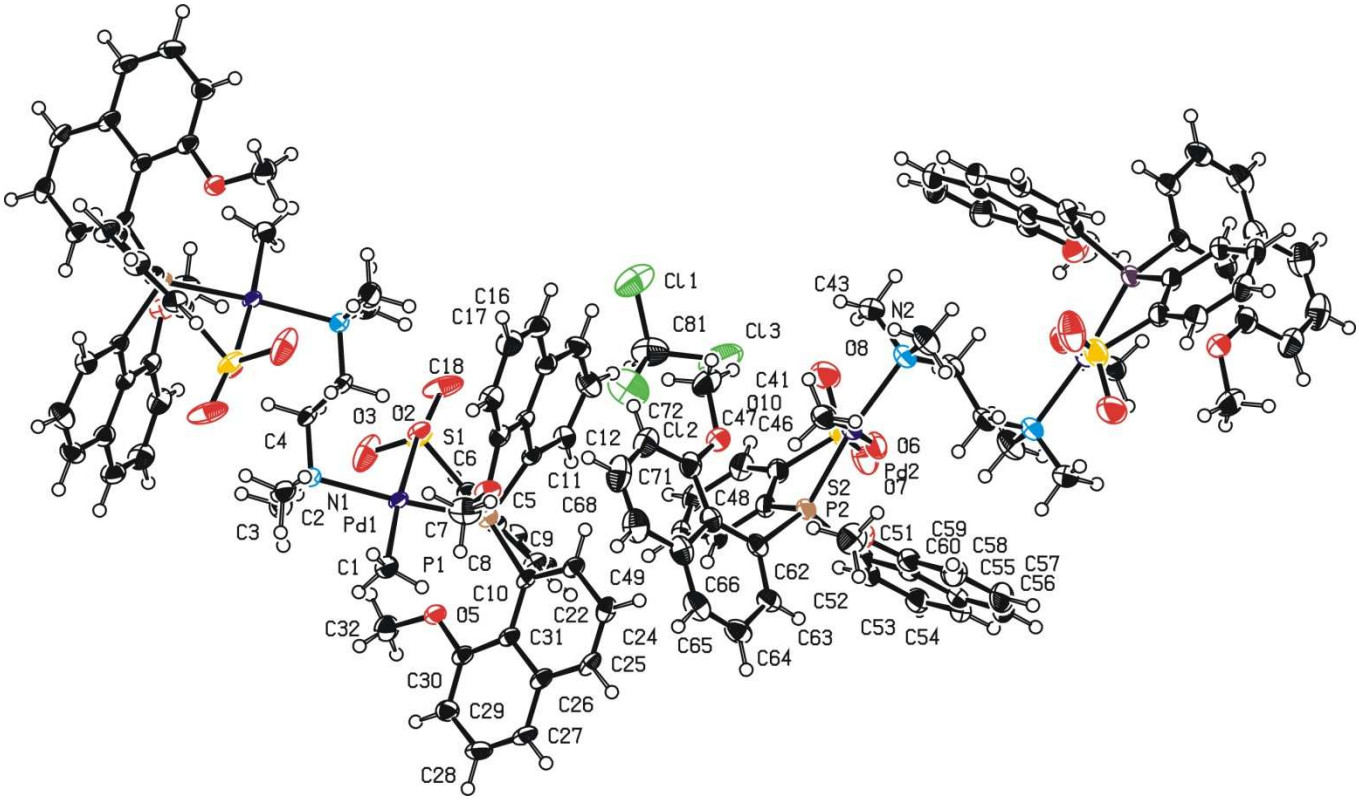


Figure F2 – Ortep drawing of compound **10** with 50% ellipsoids. [8]

Operator:	*** Herdtweck ***
Molecular Formula:	$C_{65}\ H_{67}\ Cl_3\ N_2\ O_{10}\ P_2\ Pd_2\ S_2$
	$(C_{64}\ H_{66}\ N_2\ O_{10}\ P_2\ Pd_2\ S_2)$, $(C\ H\ Cl_3)$
Crystal Color / Shape	Yellow fragment
Crystal Size	Approximate size of crystal fragment used for data collection: 0.30 × 0.36 × 0.46 mm
Molecular Weight:	1481.44 a.m.u.
F_{000}:	3024
Systematic Absences:	h0l: l≠2n; 0k0: k≠2n
Space Group:	Monoclinic *P* $2_1/c$ (I.T.-No.: 14)

Cell Constants:	Least-squares refinement of 9272 reflections with the programs "APEX suite" and "SAINT" [3,4]; theta range 1.64° < θ < 25.46°; Mo(K$\overline{\alpha}$); λ = 71.073 pm
	a = 2315.06(9) pm
	b = 1473.12(6) pm β = 110.6878(17)°
	c = 2453.48(9) pm
	V = 7827.7(5)· 10^6 pm^3; Z = 4; D_{calc} = 1.257 g cm^{-3}; Mos. = 0.66
Diffractometer:	Kappa APEX II (Area Diffraction System; BRUKER AXS); sealed tube; graphite monochromator; 50 kV; 30 mA; λ = 71.073 pm; Mo(K$\overline{\alpha}$)
Temperature:	(-150±1) °C; (123±1) K
Measurement Range:	1.64° < θ < 25.46°; h: -27/26, k: -17/17, l: -29/29
Measurement Time:	2 × 5 s per film
Measurement Mode:	measured: 11 runs; 5777 films / scaled: 11 runs; 5777 films
	φ– and ω–movement; Increment: $\Delta\varphi/\Delta\omega$ = 0.50°; dx = 65.0 mm
LP - Correction:	Yes [4]
Intensity Correction	No/Yes; during scaling [4]
Absorption Correction:	Multi-scan; during scaling; μ = 0.705 mm^{-1} [4]
	Correction Factors: T_{min} = 0.6507 T_{max} = 0.7452
Removing solvent molecules	Besides the solvent molecule, well located in the difference Fourier maps, unresolved solvent molecules remained and had to be removed with the SQUEEZE procedure. [8]
Reflection Data:	212318 reflections were integrated and scaled
	5706 reflections systematic absent and rejected
	1 ?
	206611 reflections to be merged
	14451 independent reflections
	0.027 R_{int}: (basis F_o^2)
	14451 independent reflections (all) were used in refinements
	13066 independent reflections with $I_o > 2\sigma(I_o)$
	99.6 % completeness of the data set
	785 parameter full-matrix refinement
	18.4 reflections per parameter

Solution:	Direct Methods [5]; Difference Fourier syntheses	
Refinement Parameters:	In the asymmetric unit:	
	86	Non-hydrogen atoms with anisotropic displacement parameters
Hydrogen Atoms:	In the difference map(s) calculated from the model containing all non-hydrogen atoms, not all of the hydrogen positions could be determined from the highest peaks. For this reason, the hydrogen atoms were placed in calculated positions (d_{C-H} = 95, 98, 99, 100 pm). Isotropic displacement parameters were calculated from the parent carbon atom (U_H = 1.2/1.5 U_C). The hydrogen atoms were included in the structure factor calculations but not refined.	
Atomic Form Factors:	For neutral atoms and anomalous dispersion [6]	
Extinction Correction:	no	
Weighting Scheme:	$w^{-1} = \sigma^2(F_o^2)+(a*P)^2+b*P$	
	with a: 0.0465; b: 10.7405; P: [Maximum(0 or F_o^2)+2$*F_c^2$]/3	
Shift/Err:	Less than 0.001 in the last cycle of refinement:	
Resid. Electron Density:	+1.65 $e_{0;}^{-}$ /Å^3; -1.01 $e_{0;}^{-}$ /Å^3	
R1:	$\Sigma(\|\|F_o\|-\|F_c\|\|)/\Sigma\|F_o\|$	
[$F_o > 4\sigma(F_o)$; N=13066]:		= 0.0344
[all reflctns; N=14451]:		= 0.0382
wR2:	$[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$	
[$F_o > 4\sigma(F_o)$; N=13066]:		= 0.0913
[all reflctns; N=14451]:		= 0.0935
Goodness of fit:	$[\Sigma w(F_o^2-F_c^2)^2/(NO-NV)]^{1/2}$	= 1.056
Remarks:	Refinement expression $\Sigma w(F_o^2-F_c^2)^2$	

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