Supplementary Information for:

Synthesis of Non-Symmetrically Sulphonated Phosphine Sulphonate Based Pd(II) Catalyst Salts for Olefin Polymerisation Reactions

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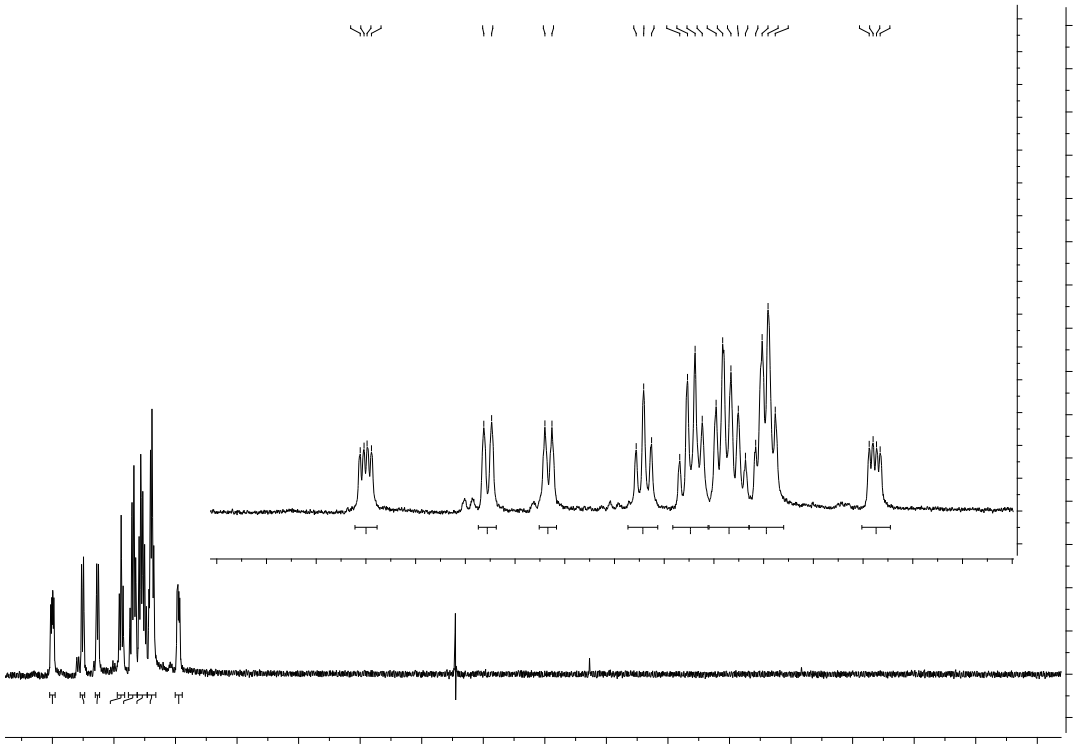
1. NMR spectra for newly synthesised compounds

1.1 $[K]_2$[*rac-o,m*-Triphenylphosphine disulphonate] (rac-*o,m*-TPPDS) 2b

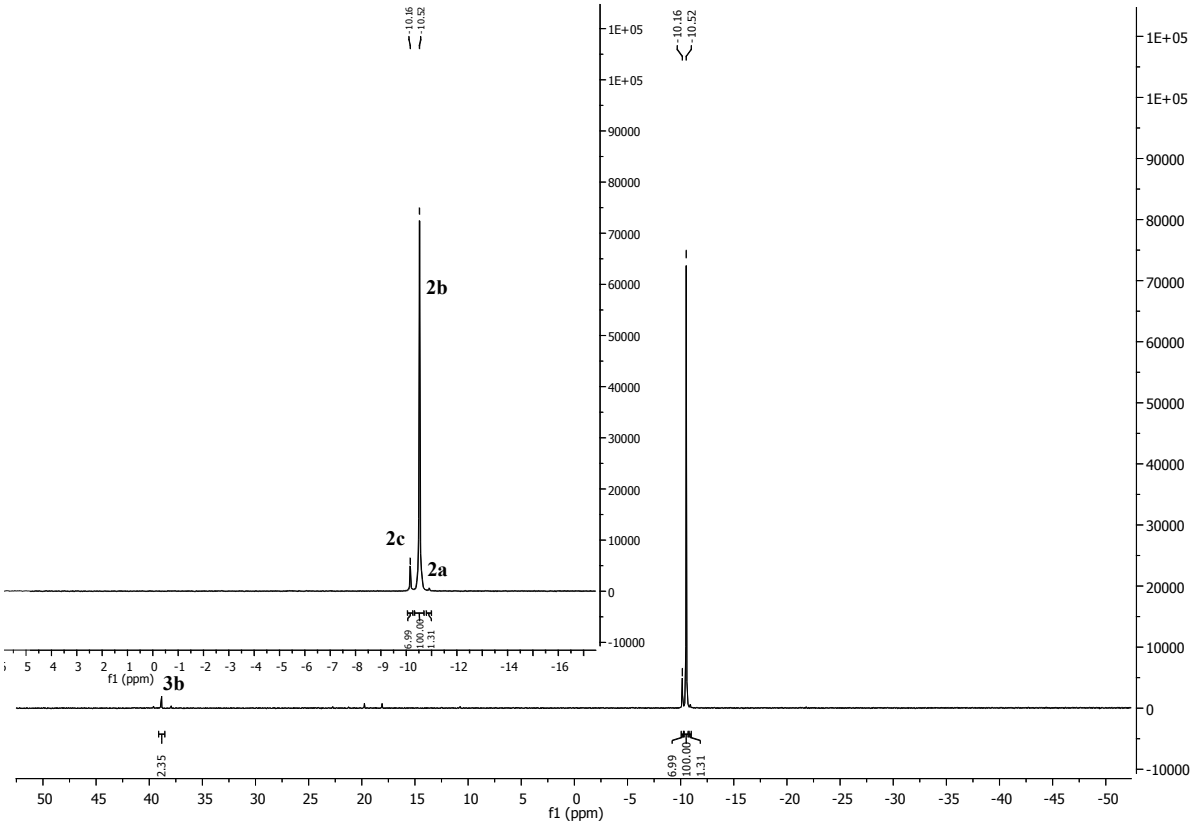
^{1}H NMR (500 MHz, D_2O) δ 8.06 (m, 1H), 7.82 (m, 1H), 7.70 (m, 1H), 7.51 (m, 1H), 7.41 (m, 2H), 7.37 – 7.29 (m, 3H), 7.26 (m, 3H), 7.04 (m, 1H).

^{31}P NMR (121 MHz, D_2O) δ -10.5

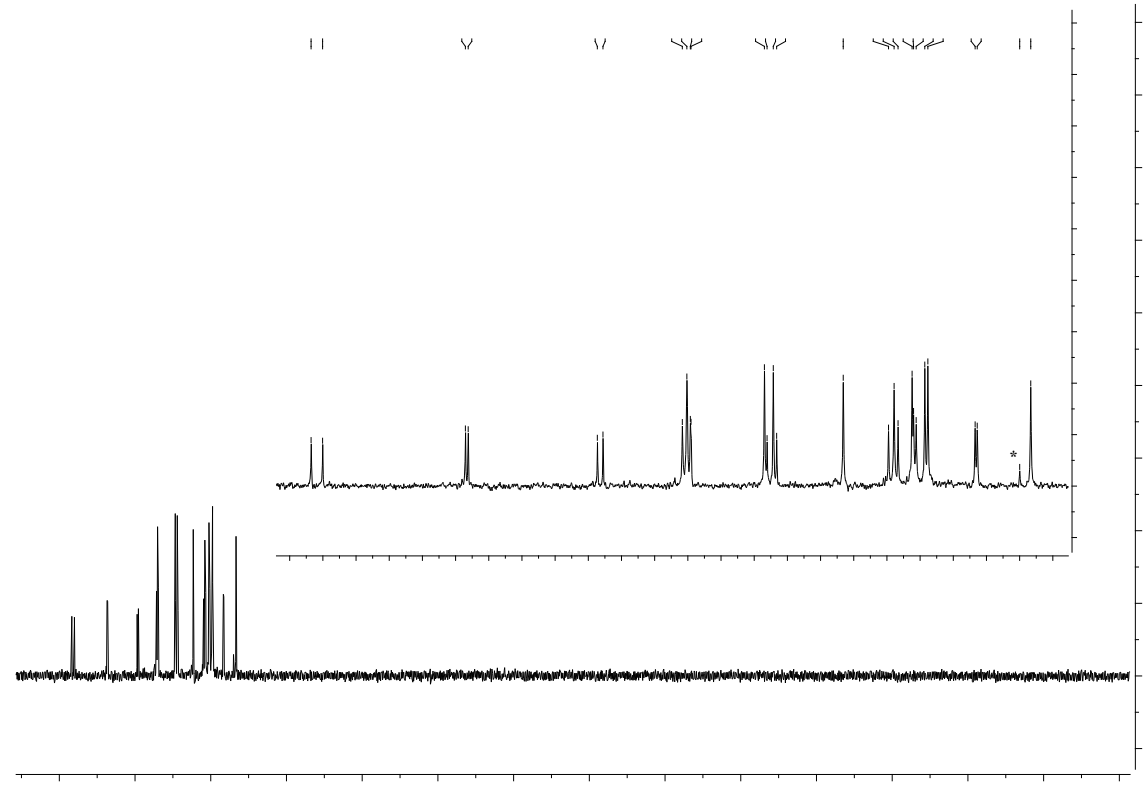
^{13}C{^{1}H} NMR (75 MHz, D_2O) δ 148.2 (d, *J(C-P)* = 26.2 Hz), 143.7 (d, *J(C-P)* = 6.4 Hz), 139.6 (d, *J(C-P)* = 12.8 Hz), 137.1 (d, *J(C-P)* = 10.3 Hz), 137.0 (d, *J(C-P)* = 7.9 Hz), 136.9 (s), 134.7 (s), 134.5 (d, *J (C-P)*= 21.8 Hz), 134.4 (s), 132.3 (s), 131. (s), 130.8 (s), 130.7 (s), 130.2 (s), 130.2 (d, *J(C-P)* = 5.9 Hz), 129.8 (d, *J(C-P)* = 7.0 Hz), 128.3 (d, *J(C-P)* = 4.7 Hz), 126.7 (s).



^{1} H NMR (500 MHz, D_2O, water suppression)



^{31}P {^{1}H} NMR (121 MHz, D_2O)



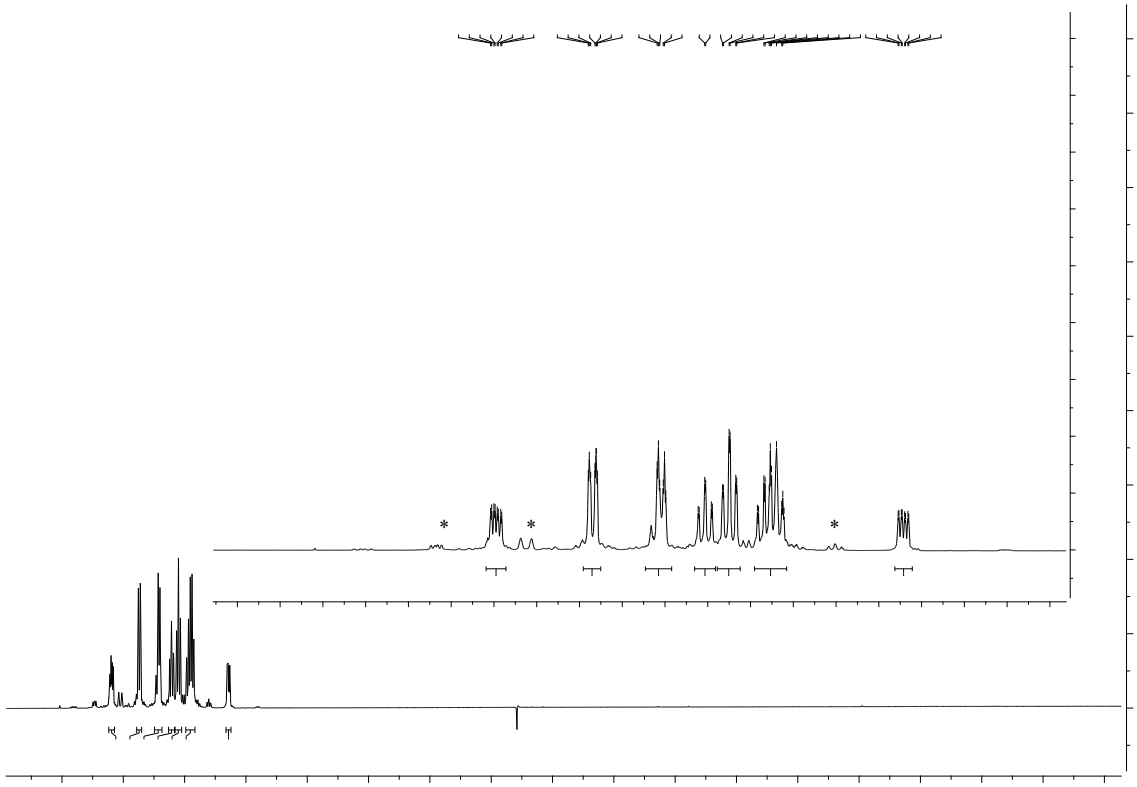
^{13}C{^{1}H} NMR (75 MHz, D_2O)

1.2 $[Na]_3$[*o,m,m*-Triphenylphosphine trisulphonate] (o,m,m-TPPTS) 2c

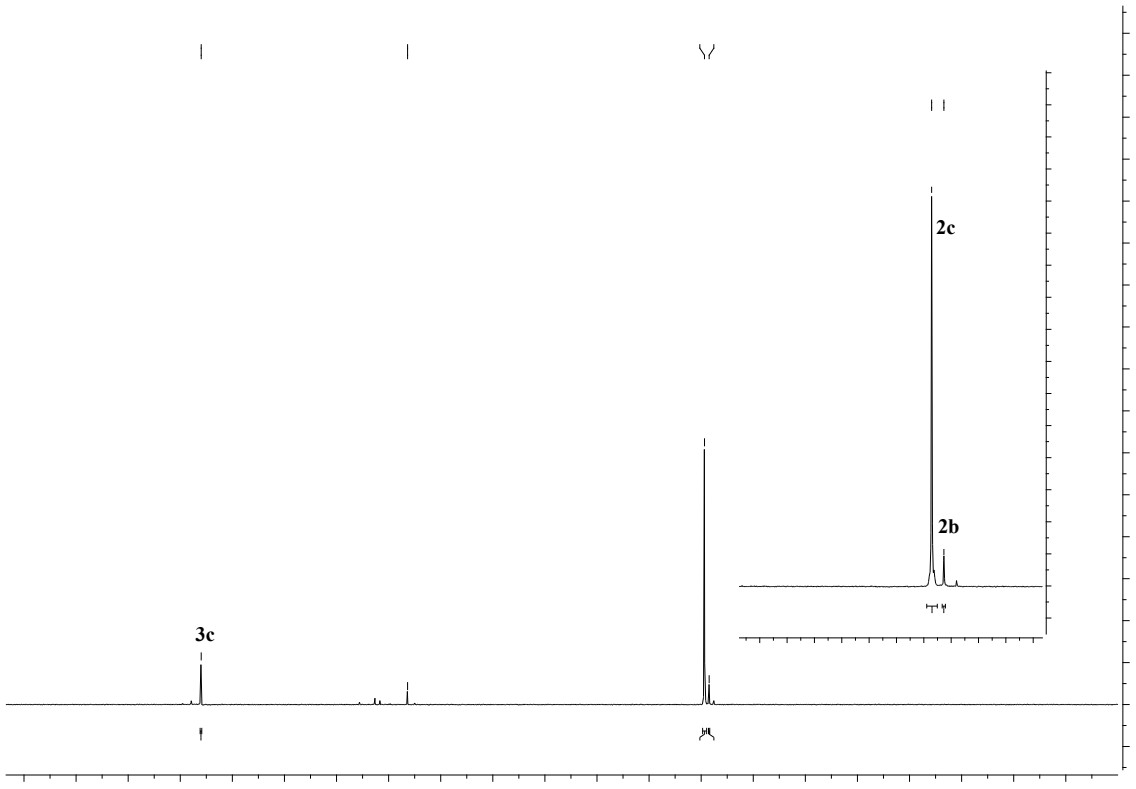
^{1}H NMR (500 MHz, D_2O) δ 8.09 (m, 1H), 7.89 – 7.85 (m, 2H), 7.73 – 7.69 (m, 2H), 7.61 (m, 1H), 7.55 (m, 2H), 7.49 – 7.42 (m, 3H), 7.14 (m, 1H).

^{31}P NMR (121 MHz, D_2O) δ -10.3

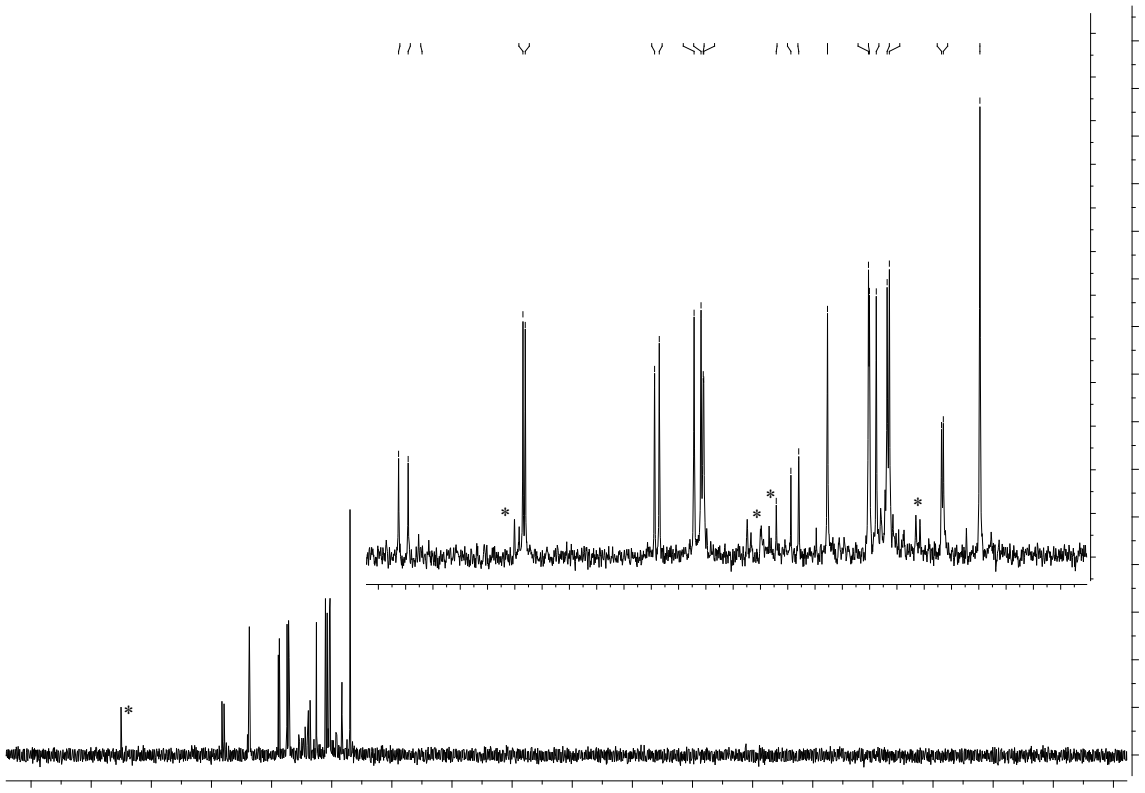
^{13}C{^{1}H} NMR (75 MHz, D_2O) δ 148.1 (d, *J (C-P)* = 26.5 Hz), 143.7 (d, *J (C-P)* = 6.4 Hz), 138.8 (d, *J (C-P)* = 13.0 Hz), 137.3 (d, *J (C-P)* = 19.2 Hz), 137.1 (d, *J (C-P)* = 1.3 Hz), 133.7 (d, *J (C-P)* = 21.7 Hz), 132.5 (s), 131.0 (d, *J (C-P)* = 2.6 Hz), 130.8 (s), 130.3 (d, *J (C-P)* = 6.2 Hz), 128.3 (d, *J (C-P)* = 4.9 Hz), 127.0 (s).



^{1} H NMR (500 MHz, D_2O, water suppression)



^{31}P {^{1}H} NMR (121 MHz, D_2O)



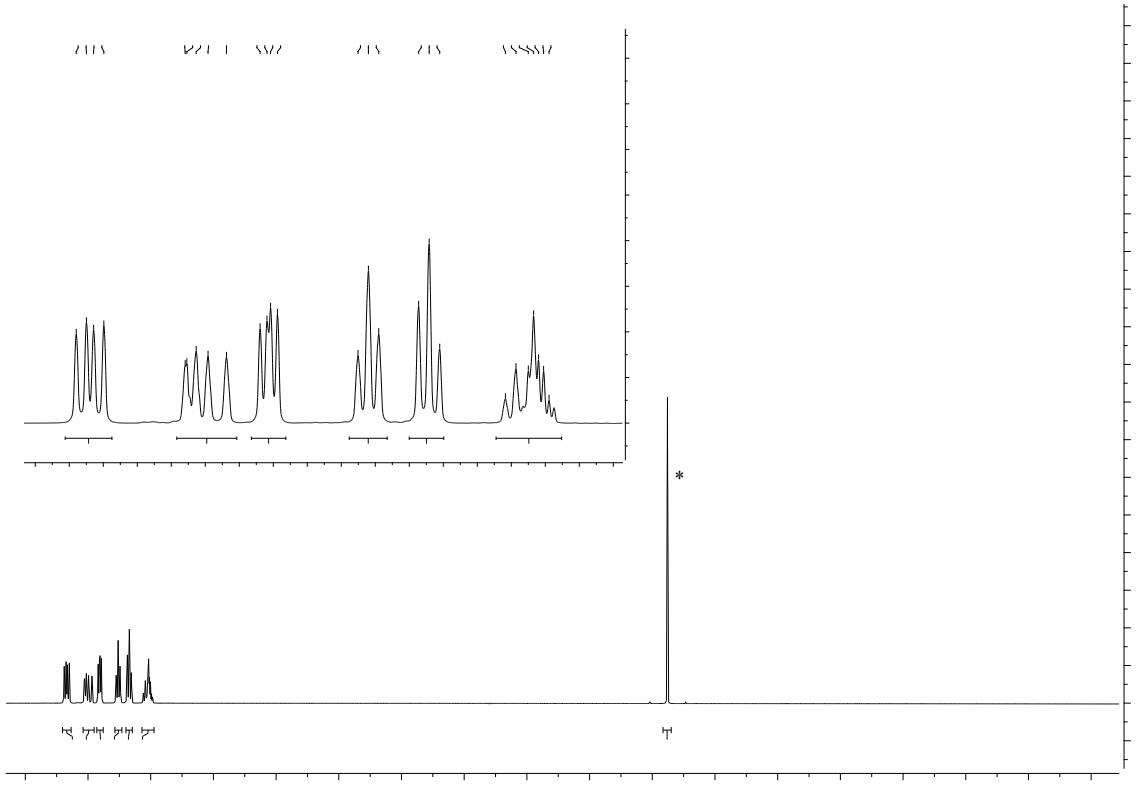
^{13}C {^{1}H} NMR (75 MHz, D_2O)

1.3 10-(3-Sulphonatophenyl)-10*H*-9-thia-10-phosphaanthracene-9.9.10-trioxide 4, sodium salt

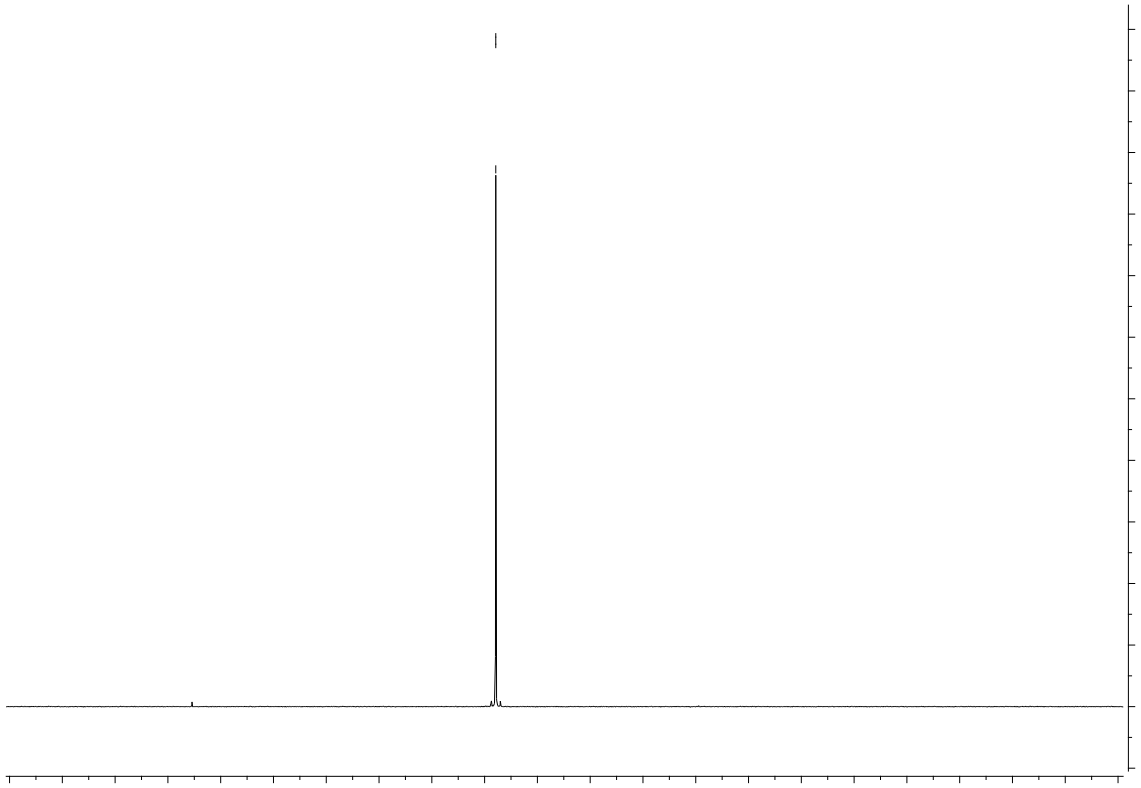
^{1}H NMR (500 MHz, D_2O) δ 8.17 (m, 2H), 8.05 – 8.01 (m, 2H), 7.98 (m, 2H), 7.91 (m, 2H), 7.76 (m, 2H), 7.67 (m, 2H), 7.57 – 7.48 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, D_2O) δ 144.7 (d, *J(C-P)* = 13.6 Hz), 141.3 (d, *J(C-P)* = 7.6 Hz), 135.3 (s), 135.2 (d, *J(C-P)* = 11.5 Hz), 134.8 (d, *J(C-P)* = 11.9 Hz), 134.0 (d, *J(C-P)* = 4.9 Hz), 132.2 (d, *J(C-P)* = 113.7 Hz), 131.5 (s), 130.9 (d, *J(C-P)* = 13.5 Hz), 129.1 (d, *J(C-P)* = 12.8 Hz), 128.9 (d, *J(C-P)* = 102.0 Hz), 126.3 (d, *J(C-P)* = 7.5 Hz).

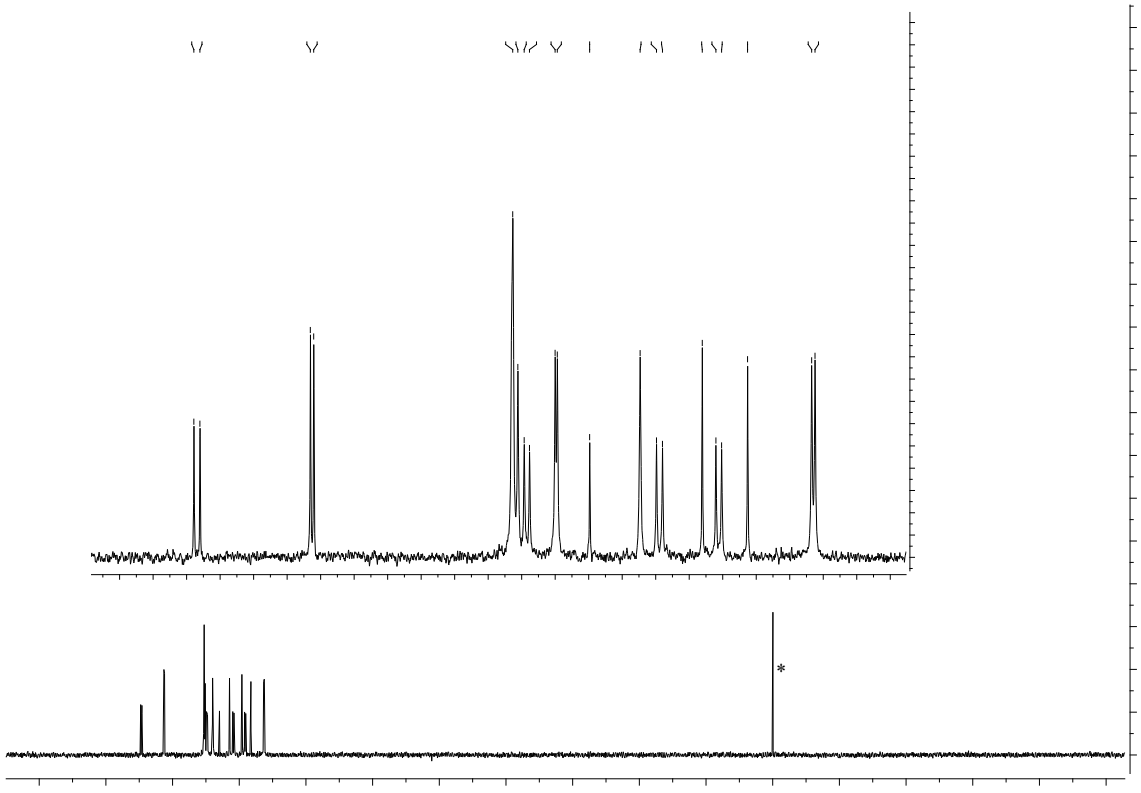
^{31}P{^{1}H} NMR (121 MHz, D_2O) δ 8.9 (s).



^{1}H NMR (500 MHz, D_2O, water suppression)



^{31}P $\{^{1}H\}$ NMR (121 MHz, D_2O)



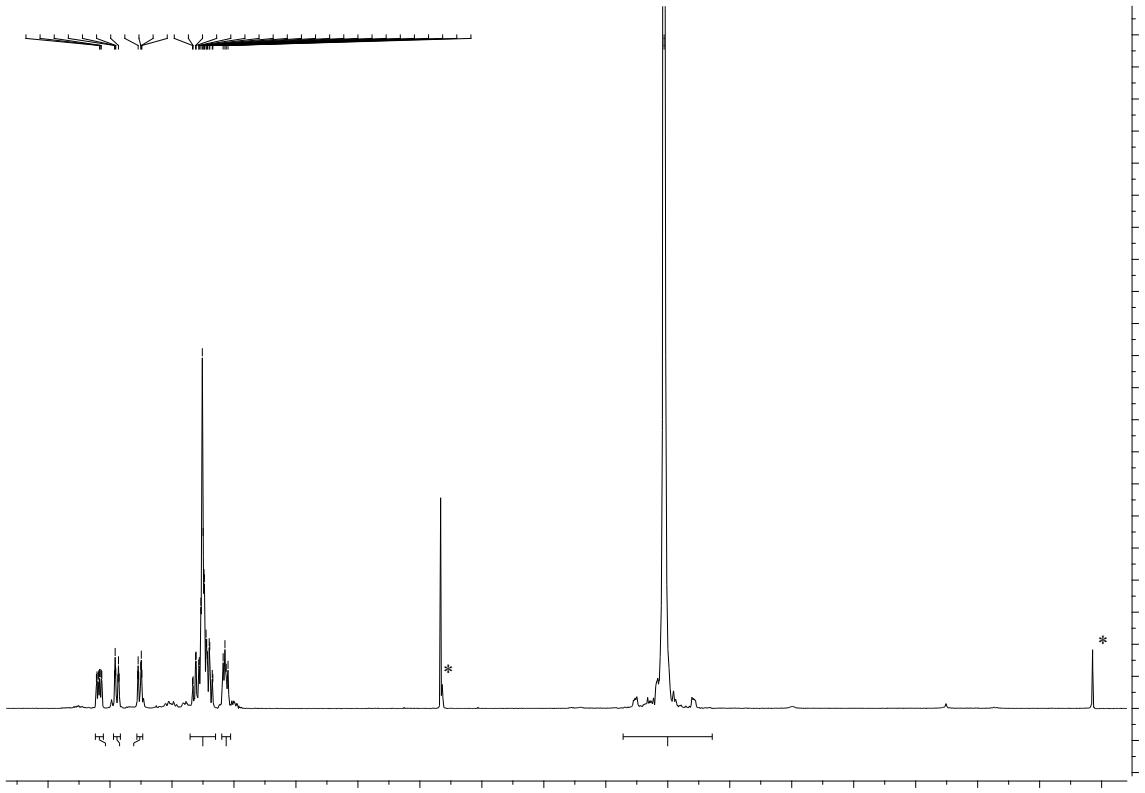
$^{13}C\{^{1}H\}$ NMR (75 MHz, D_2O)

1.4 [K(18-crown-6)]$_2$[*rac-o,m*-TPPDS] 5b

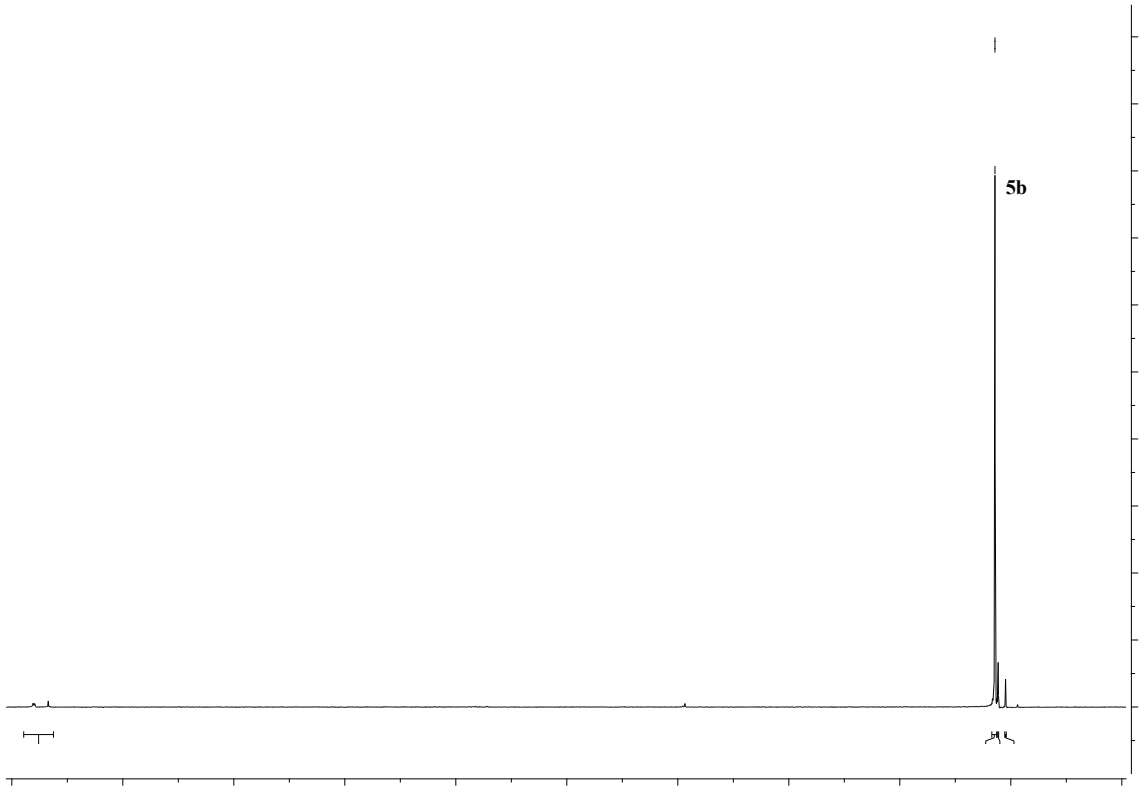
^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.09 (m, 1H), 7.95 (m, 1H), 7.76 (m, 1H), 7.35 – 7.15 (m, 8H), 7.10 – 7.03 (m, 2H), 3.53 (s, 57H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 152.8 (d, *J(C-P)* = 27.3 Hz), 147.7 (d, *J(C-P)* = 7.9 Hz), 139.9 (d, *J(C-P)* = 14.2 Hz), 139.5 (d, *J(C-P)* = 16.7 Hz), 136.1 (d, *J(C-P)* = 2.5 Hz), 135.0 (d, *J(C-P)* = 23.5 Hz), 134.6 (d, *J(C-P)* = 11.7 Hz), 134.0 (d, *J(C-P)* = 19.4 Hz), 131.7 (d, *J(C-P)* = 29.2 Hz), 129.4 (s), 128.8 (s), 128.4 (d, *J(C-P)* = 6.1 Hz), 128.2 (s), 128.1 (d, *J(C-P)* = 3.6 Hz), 128.0 (d, *J(C-P)* = 6.1 Hz), 126.4 (s), 70.4 (s).

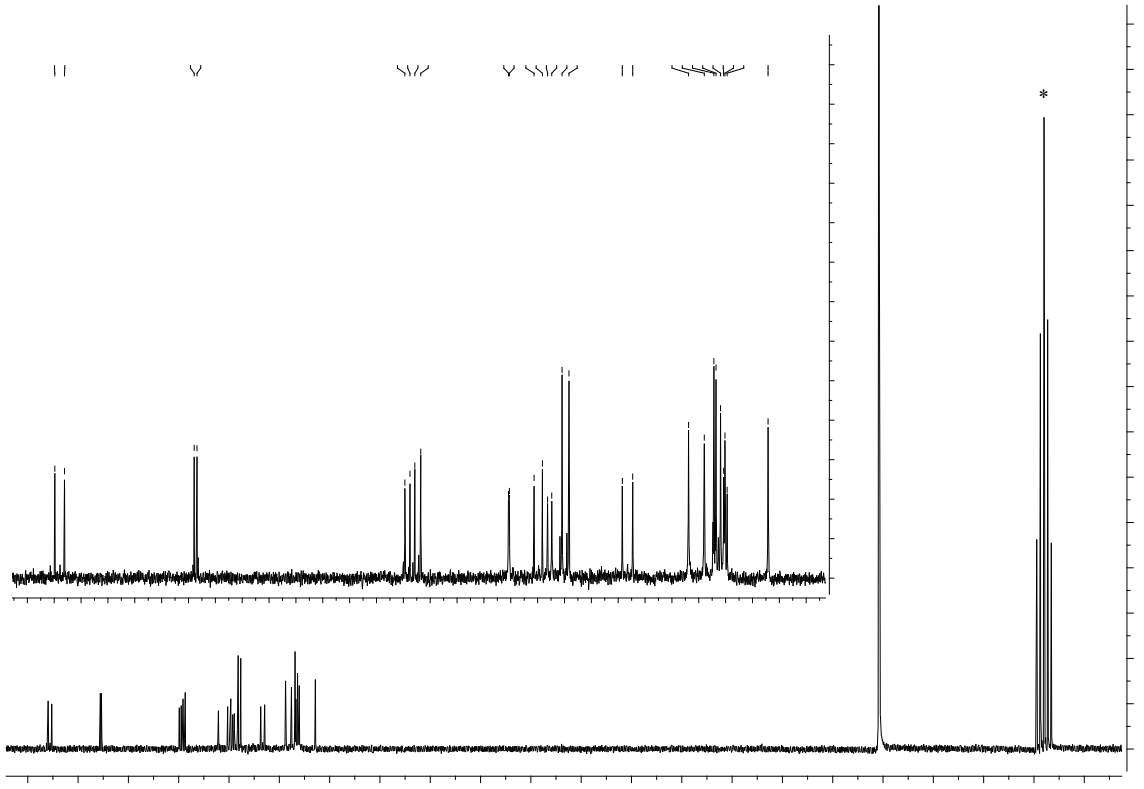
^{31}P NMR (121 MHz, CD_2Cl_2) δ -9.3 (s).



^{1}H NMR (300 MHz, CD_2Cl_2)



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



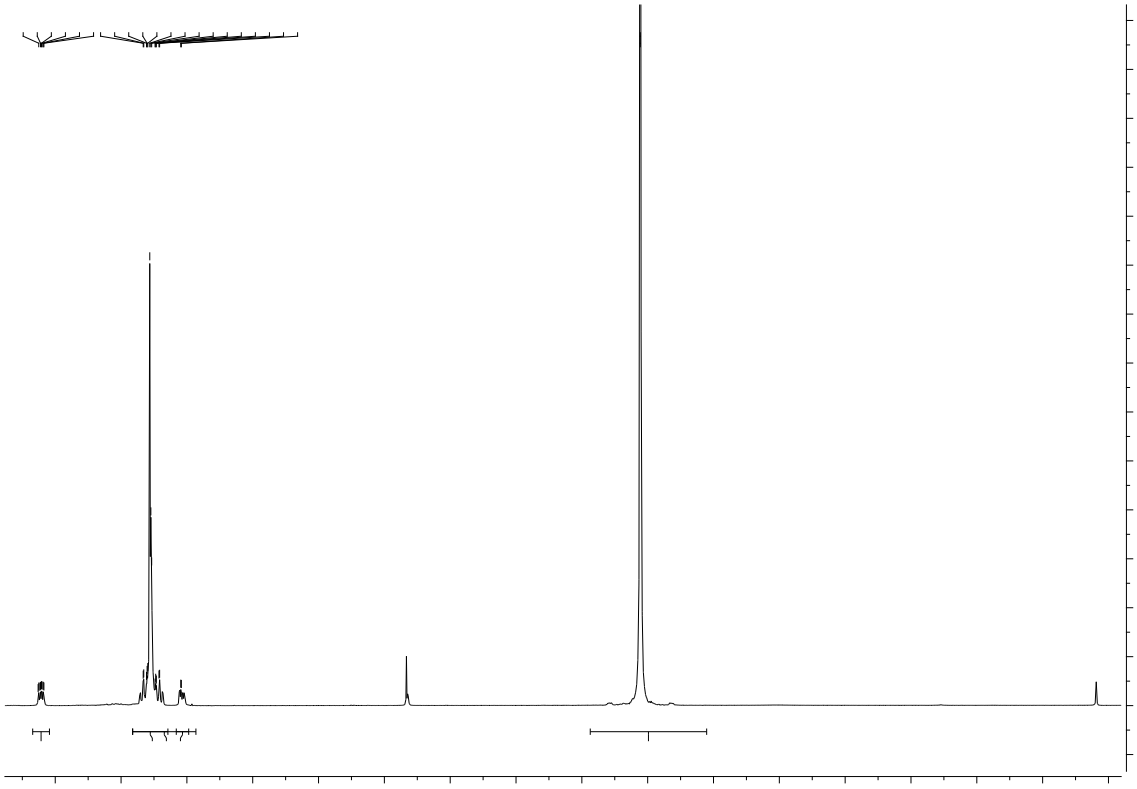
$^{13}C\{^{1}H\}$ NMR (75 MHz, CD_2Cl_2)

1.5 [K(18-crown-6)][*o*-TPPMS] 5a

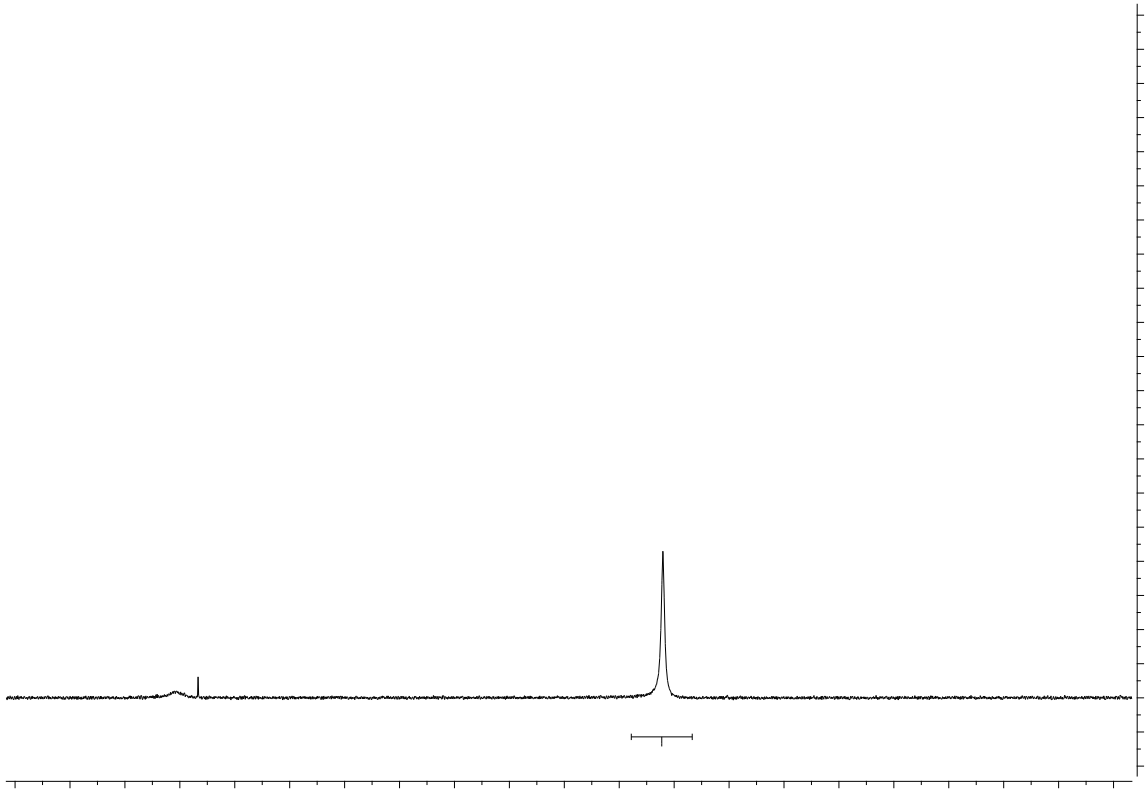
^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.11 (m, 1H), 7.42 – 7.15 (m, 12H), 7.04 (m, 1H), 3.56 (s, 27H).

^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2) δ 152.7 (d, *J(C-P)* = 27.1 Hz), 139.9 (d, *J(C-P)* = 14.5 Hz), 135.9 (d, *J(C-P)* = 2.4 Hz), 135.0 (d, *J(C-P)* = 23.2 Hz), 134.2 (s), 133.9 (s), 129.4 (s), 128.9 (s), 128.5 (d, *J(C-P)* = 6.1 Hz), 128.3 (s), 128.0 (d, *J(C-P)* = 5.1 Hz), 70.5 (s).

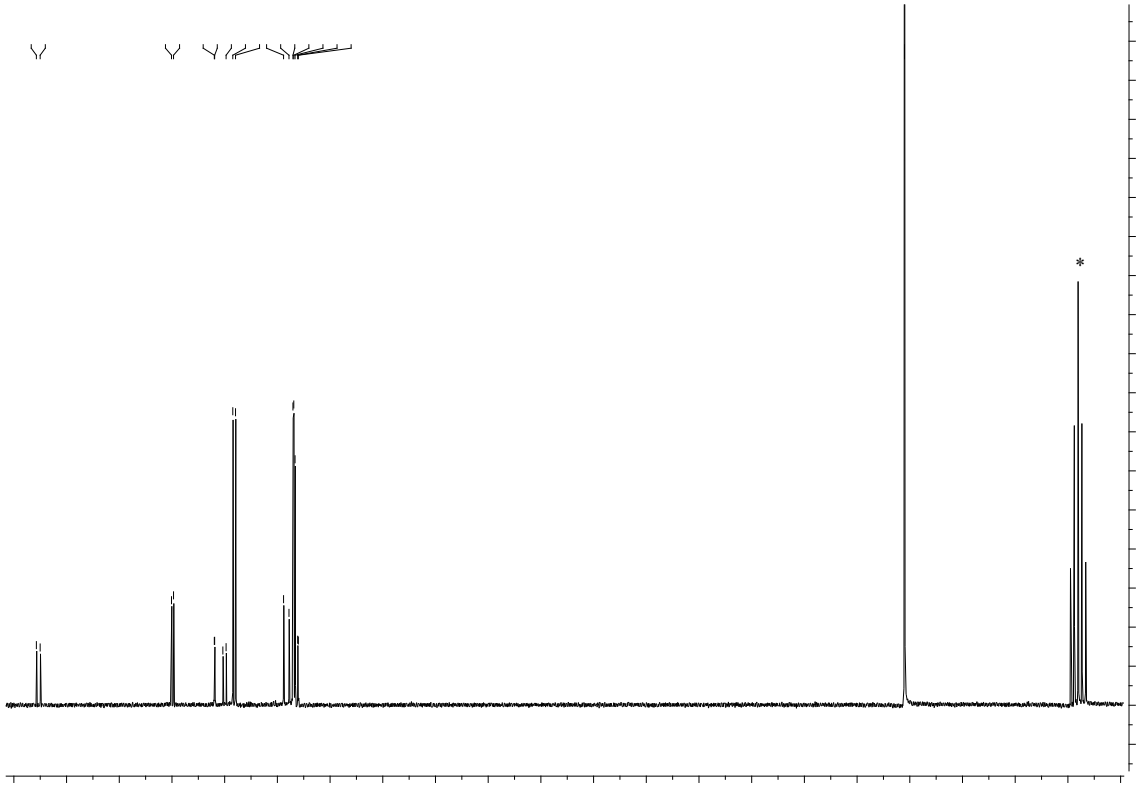
^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2) δ -9.0 (s).



^{1}H NMR (300 MHz, CD_2Cl_2)



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



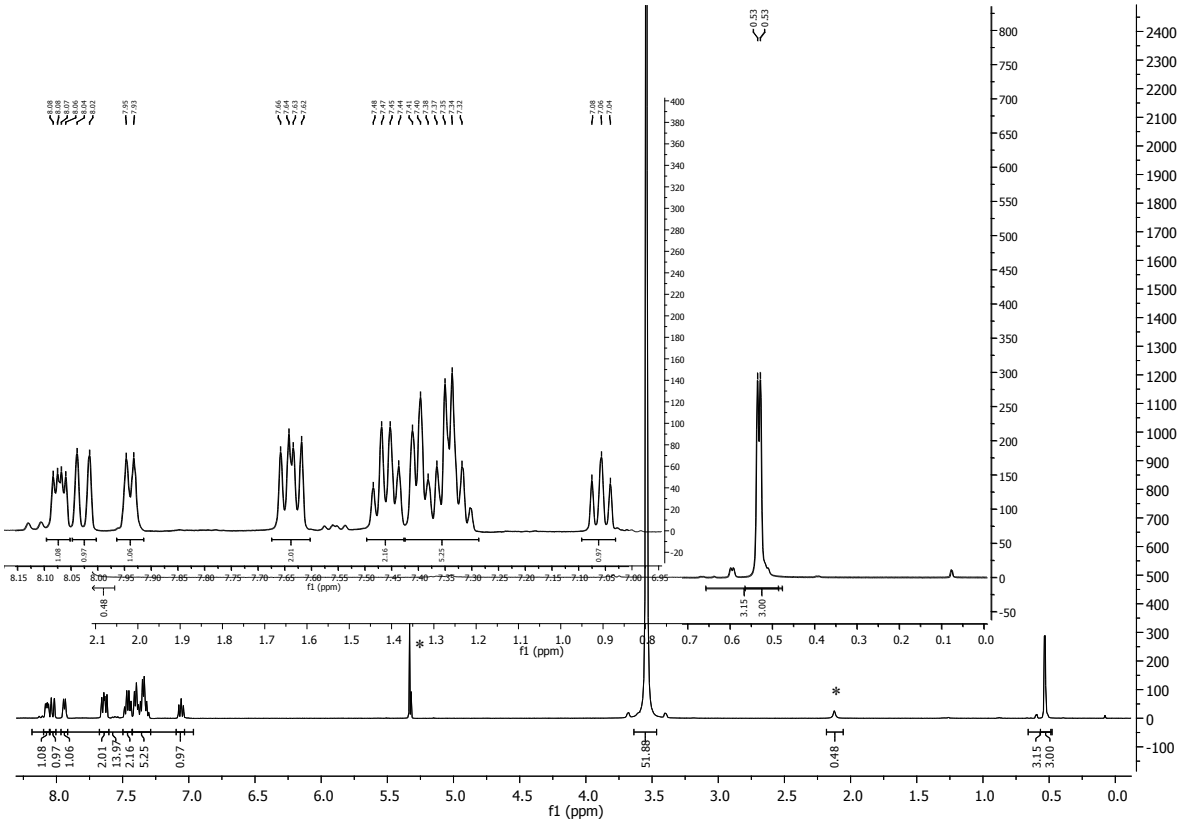
$^{13}C\{^{1}H\}$ NMR (75 MHz, CD_2Cl_2)

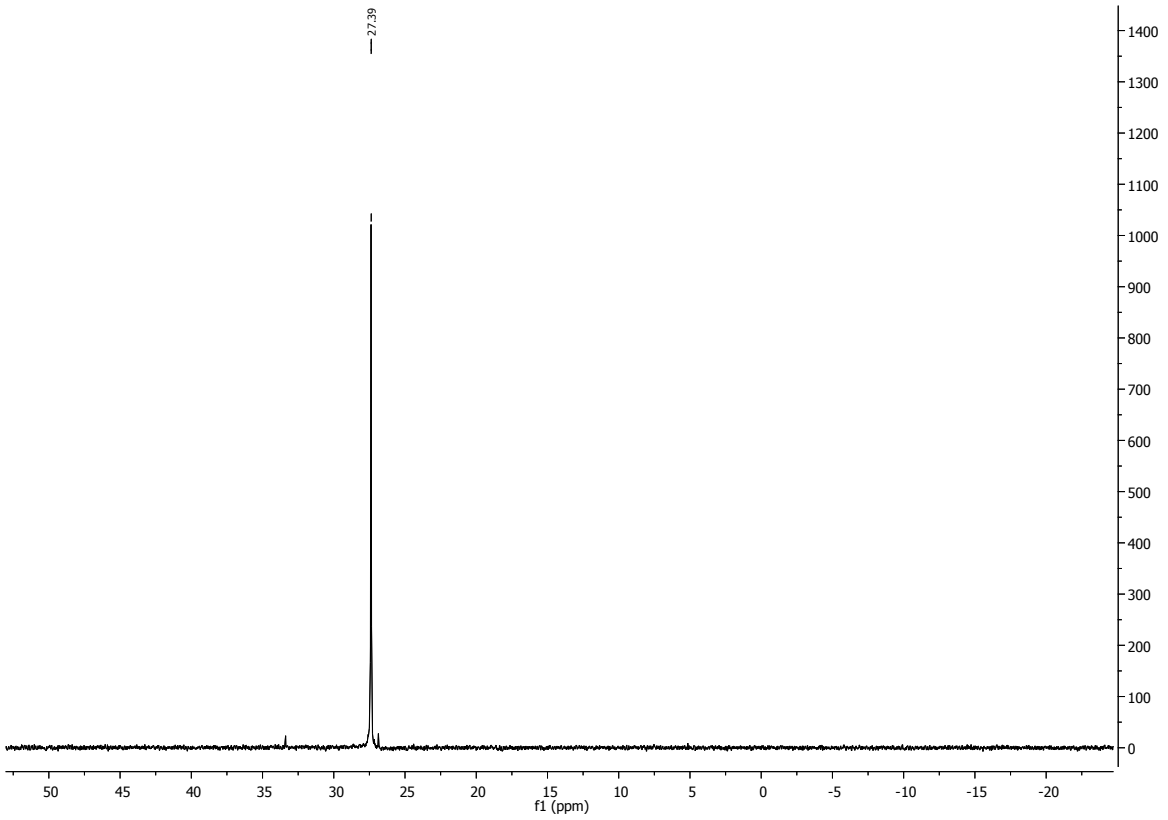
1.6 [K(18-crown-6)]$_2$[κ^2(P,O){*rac-o,m*-TPPDS}] 6

^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.07 (m, 1H), 8.03 (m, 1H), 7.94 (m, 1H), 7.64 (m, 2H), 7.46 (m, 2H), 7.36 (m, 5H), 7.06 (m, 1H), 3.54 (s, 48H), 0.53 (d, ^3J *(H-P)* = 3.2 Hz, 3H).

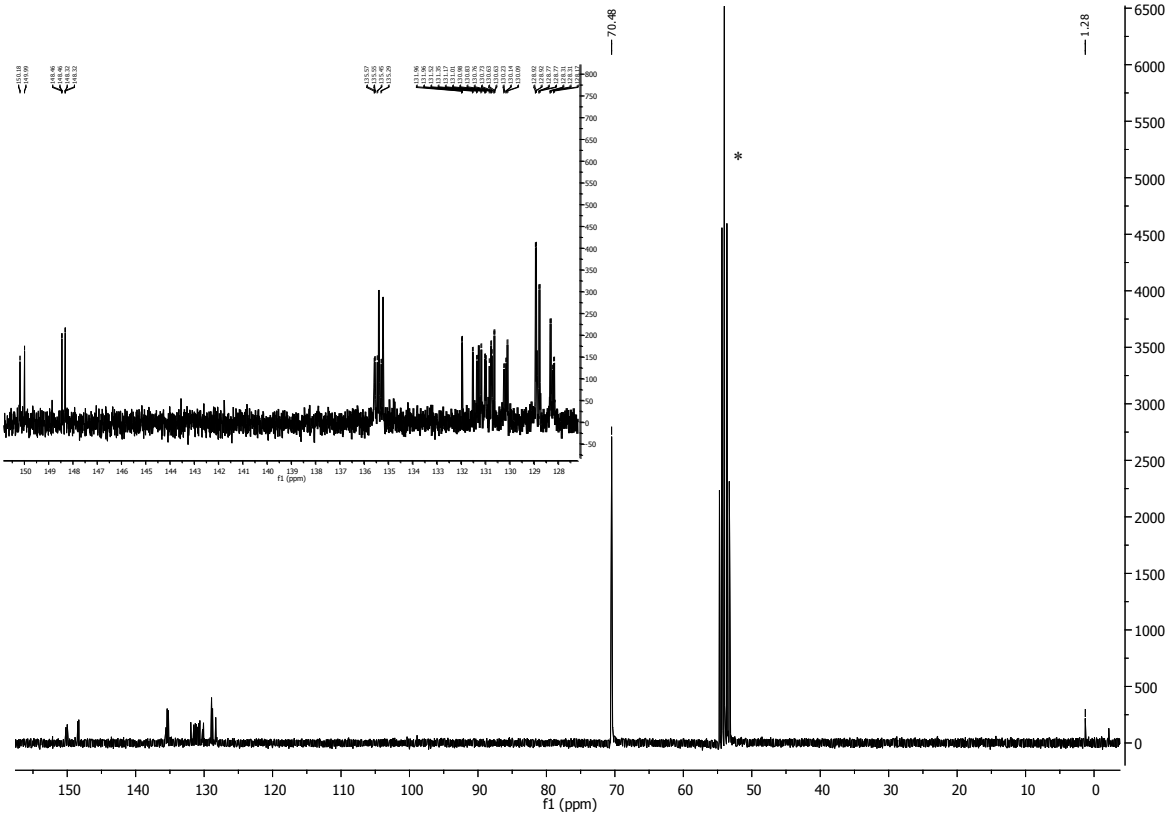
^{13}C NMR (75 MHz, CD_2Cl_2) δ 150.1 (d, *J(C-P)* = 14.0 Hz), 148.4 (d, *J(C-P)* = 10.5 Hz), 135.6 (d, *J(C-P)* = 1.5 Hz), 135.5 (s), 135.4 (d, *J(C-P)* = 11.9 Hz), 135.4 – 135.2 (m), 132.0 – 131.5 (m), 131.3 (d, *J(C-P)* = 13.4 Hz), 131.3 – 130.8 (m), 131.0 (d, *J(C-P)* = 2.6 Hz), 130.8 (d, *J(C-P)* = 2.1 Hz), 130.7 – 129.8 (m), 130.2 (d, *J(C-P)* = 6.4 Hz), 129.0 – 128.9 (m), 128.9 – 128.8 (m), 128.4 – 128.3 (m), 128.2 (d, *J(C-P)* = 3.6 Hz).

^{31}P NMR (121 MHz, CD_2Cl_2) δ +27.4.





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



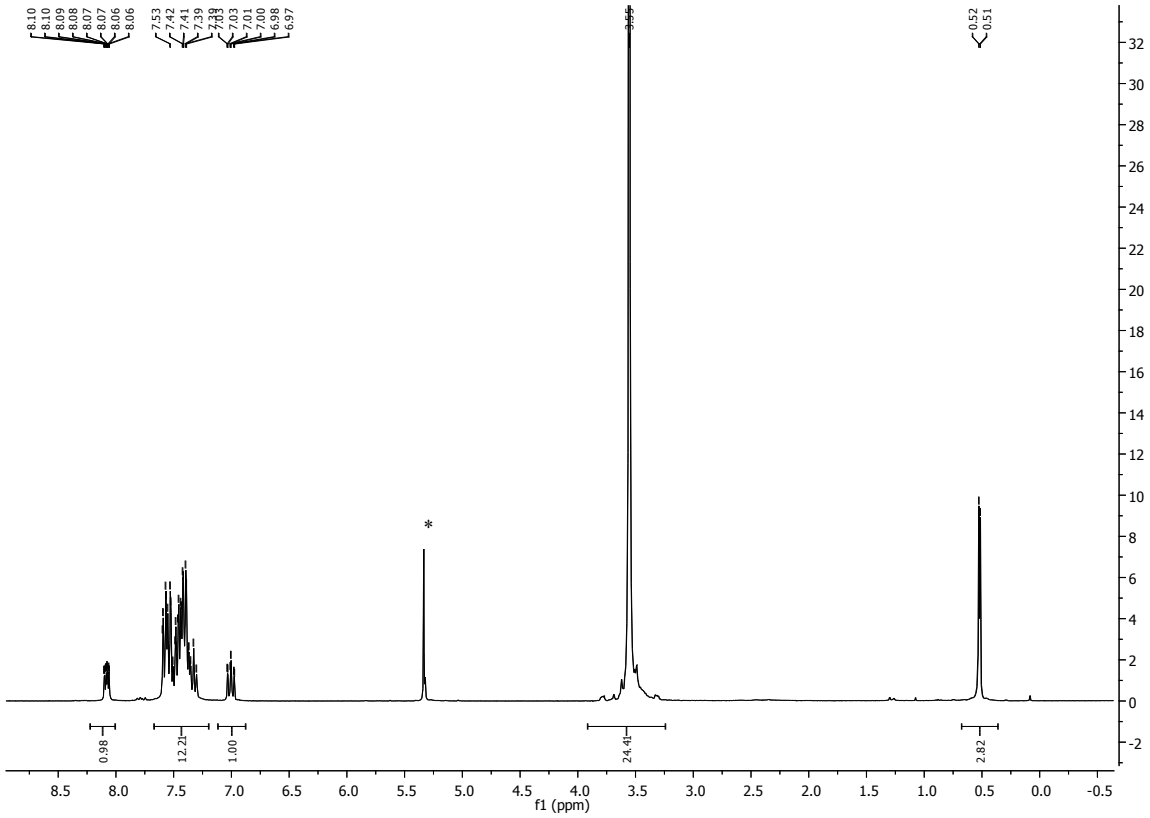
$^{13}C\{^{1}H\}$ NMR (75 MHz, CD_2Cl_2)

1.7 [K(18-crown-6)][κ^2(P,O){*o*-TPPMS}] 7

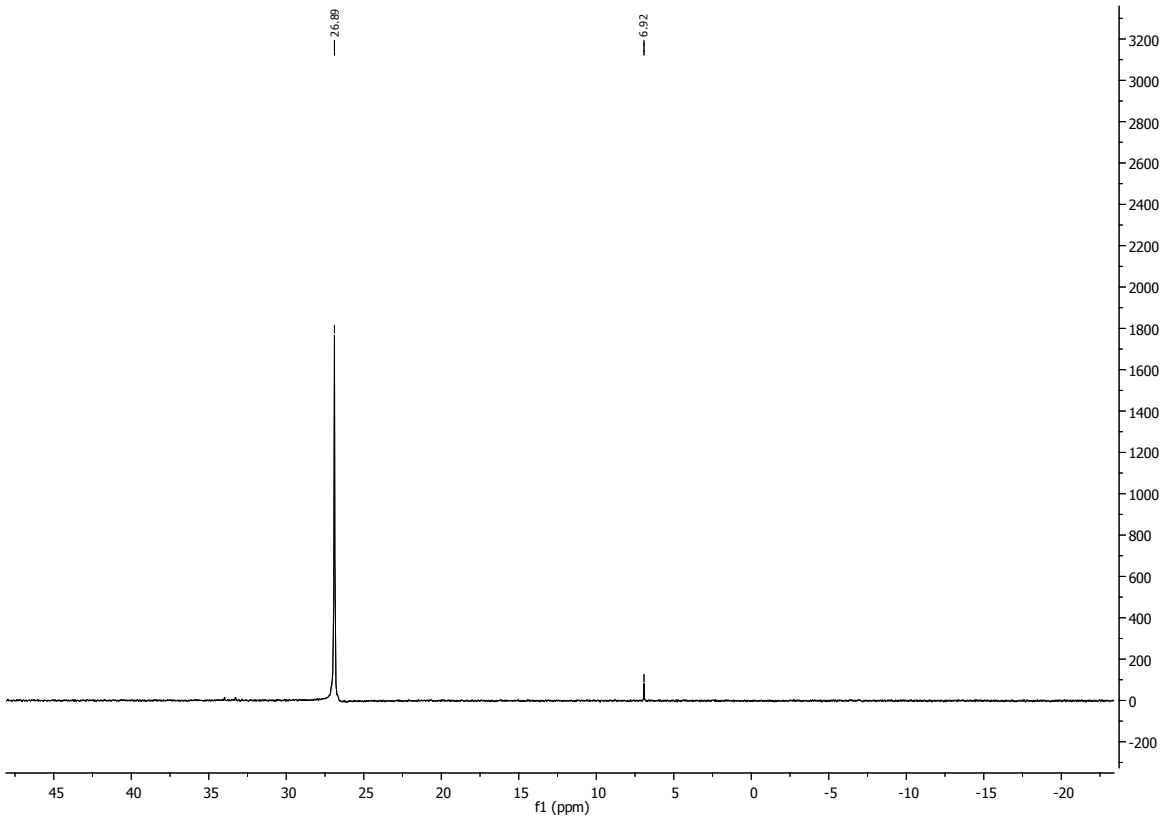
^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.00 (m, 1H), 7.55 – 7.18 (m, 12H), 6.91 (m, 1H), 3.47 (s, 24H), 0.44 (d, ^3J *(H-P)* = 3.4 Hz, 3H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 150.1 (d, *J (C-P)* = 14.0 Hz), 135.3 (d, *J (C-P)* = 1.4 Hz), 134.9 (d, *J (C-P)* = 12.5 Hz), 131.6 (d, *J (C-P)* = 52.5 Hz), 130.9 (d, *J (C-P)* = 2.4 Hz), 130.8 (d, *J (C-P)* = 2.1 Hz), 130.4 (d, *J (C-P)* = 41.0 Hz), 130.0 (d, *J (C-P)* = 6.3 Hz), 128.8 (d, *J (C-P)* = 11.0 Hz), 128.3 (d, *J (C-P)* = 7.5 Hz), 70.5 (s), -2.5 (s).

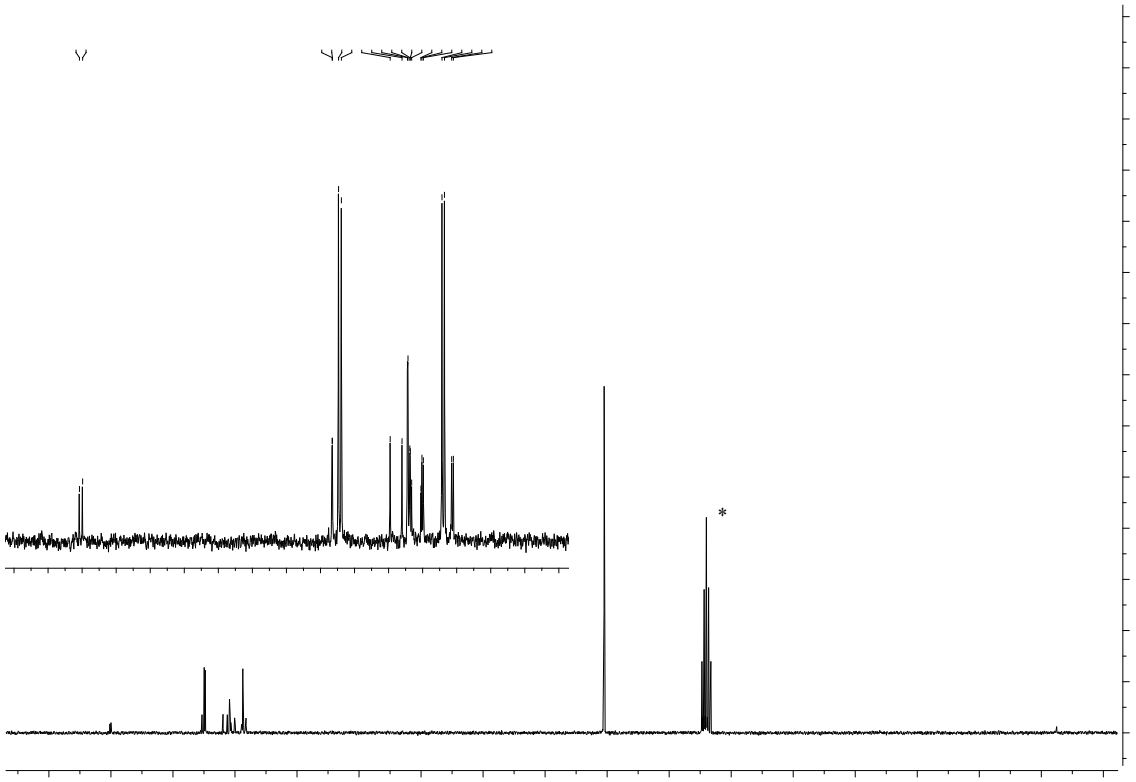
^{31}P NMR (121 MHz, CD_2Cl_2) δ +26.6.



^{1}H NMR (300 MHz, CD_2Cl_2)



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



$^{13}C\{^{1}H\}$ NMR (75 MHz, CD_2Cl_2)

2. Polymer analysis

2.1 Selected GPC data

2.1.1 Polyethylene

The depicted GPC plots show a representative behaviour of the synthesised polyethylene with observed bimodal distribution of molecular weights. Multi detection was employed to facilitate separate processing of the high and low molecular weight traces.

PE of Entry 9 in Table 3:

GPC Report

Freitag, 19. November 2010 14:14

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

Sample Details

Sample Name: AST 272 | Batch Name: 2010-11-18

Filename: C:\Cirrus Workbooks\Olexis_2010-07-26_658nm\2010-11-18-0005.cgrm

Acquired: 18.11.2010 21:20:20 | Eluent: TCB stabilised with 0.0125% BHT

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

Temperature: 160 ℃

Column Set: Olexis | Column Set Length: 60600 mm

Calculated concentration: 2.573987 mg/ml | Concentration used: 2.57 mg/ml

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

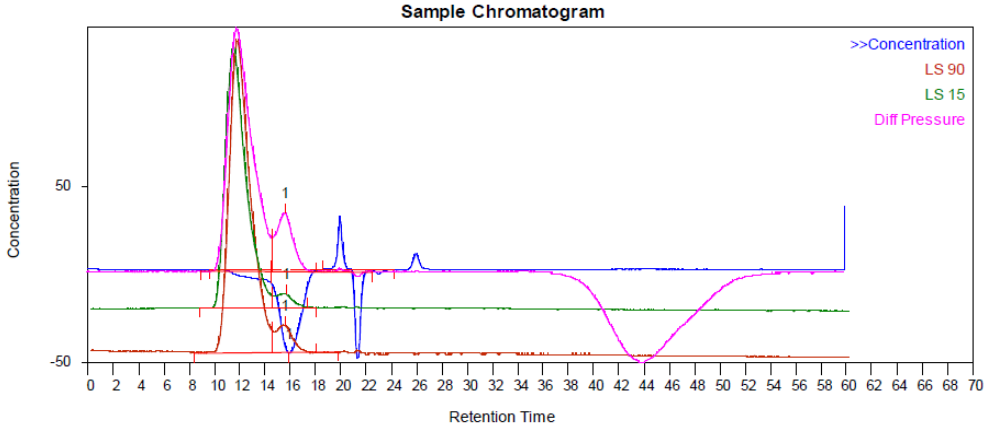
Analysis Using Method: Triple

Results File: C:\Cirrus Workbooks\Olexis_2010-07-26_658nm\2010-11-18-0005-Repeat (03).rst

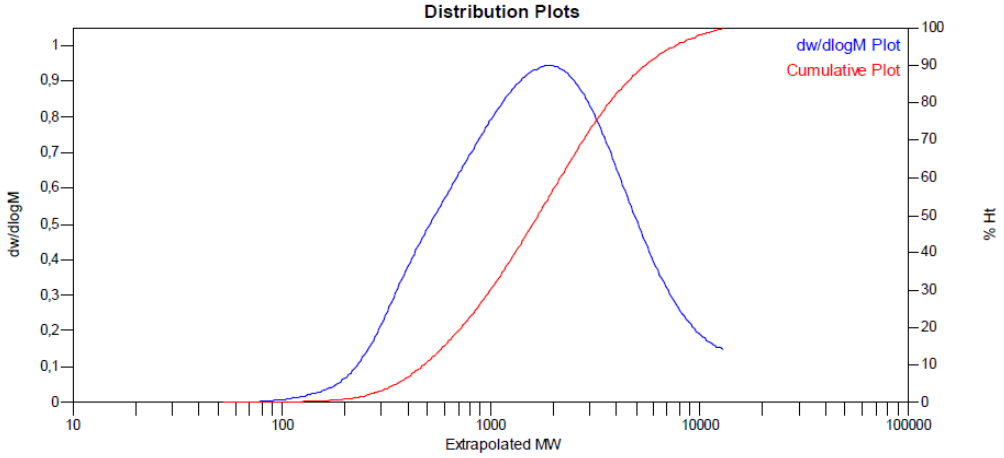
Ligt Scattering and IV Results: | Bulk IV: 0.113623

LS 15°Mw: 2314 | LS 90°Mw: 2417

Sample Chromatogram

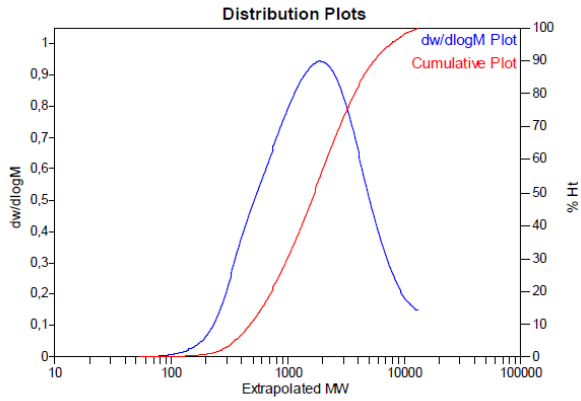


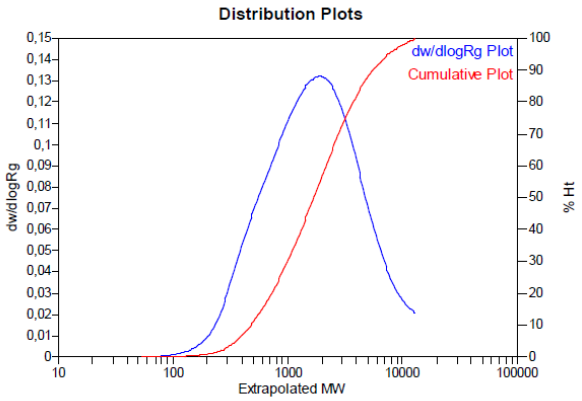
Distribution Plots

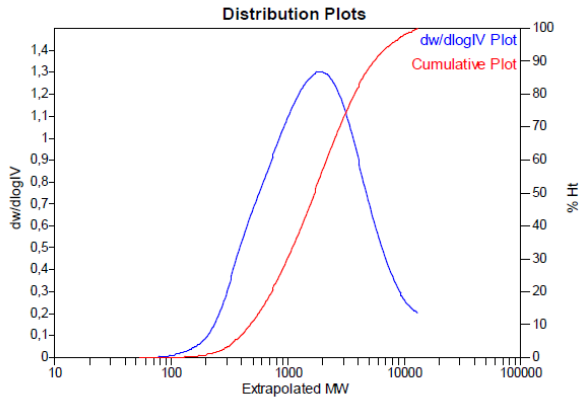


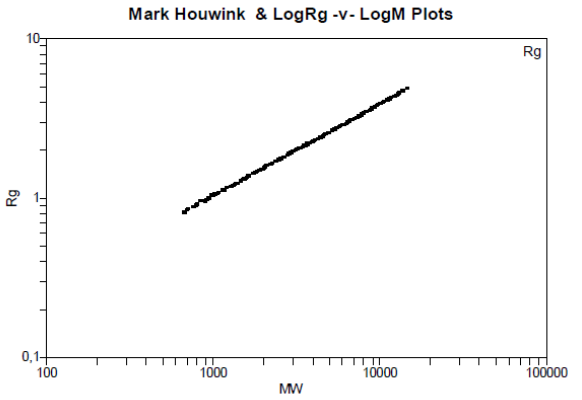
MW Averages

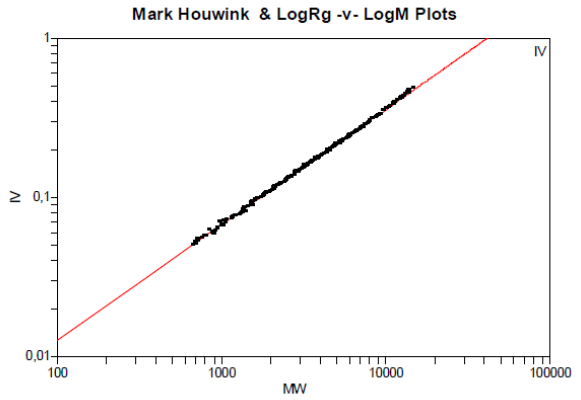
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1909	1066	2435	4640	6881	2194	2.28255

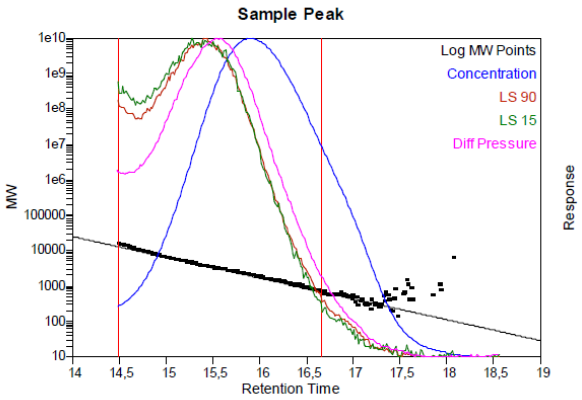

Distribution Plots
dw/dlogM Plot
Cumulative Plot
dw/dlogM
% Ht
Extrapolated MW


Distribution Plots
dw/dlogRg Plot
Cumulative Plot
dw/dlogRg
% Ht
Extrapolated MW


Distribution Plots
dw/dlogIV Plot
Cumulative Plot
dw/dlogIV
% Ht
Extrapolated MW


Mark Houwink & LogRg -v- LogM Plots
Rg
Rg
MW


Mark Houwink & LogRg -v- LogM Plots
IV
IV
MW


Sample Peak
Log MW Points
Concentration
LS 90
LS 15
Diff Pressure
MW
Response
Retention Time

Sample: AST 272 Batch: 2010-11-18

Workbook: Olexis 2010-07-26_658nm.mplw

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1909	1066	2435	4640	6881	2194	2.28255

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	14.48	15.90	18.55	-47.5241	0	5128.1	100
2	LS 90	14.57	15.55	18.08	0.861477	0	82.0527	100
3	LS 15	14.55	15.63	17.35	0.237069	0	23.1206	100
4	Diff Pressure	14.57	15.60	18.08	13.6299	0	1298.01	100

No	Start RT (mins)	End RT (mins)	Start Height	End Height	Is St Mod	Is End Mod
1	9.68	24.20	2.55	2.31	No	No
2	8.47	19.77	3.79	3.80	No	No
3	8.85	18.08	-1.03	-1.02	No	No
4	8.93	22.53	-2.77	-2.79	No	No

Peak No	IVp	IVn	IVw	IVz	IVz+1	IVv	Disp
1	0.107466	0.0766284	0.118855	0.173088	0.228141	0.0647774	1.55106

Peak No	Rgp	Rgn	Rgw	Rgz	Rgz+1	Rgv	Disp
1	1.48507	1.18857	1.55919	1.99589	2.438	0.977809	1.31182

GPC Report

Freitag, 19. November 2010 13:51

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

Sample Details

Sample Name: AST 272
Batch Name: 2010-11-18
Filename: C:\Cirrus Workbooks\Olexis_2010-07-26_658nm\2010-11-18-0005.cgrm
Acquired: 18.11.2010 21:20:20
Eluent: TCB stabilised with 0.0125% BHT
Injection Volume: 200.0 ul
Flow Rate: 1.0 ml/min
Temperature: 160 ℃
Column Set: Olexis
Column Set Length: 60600 mm

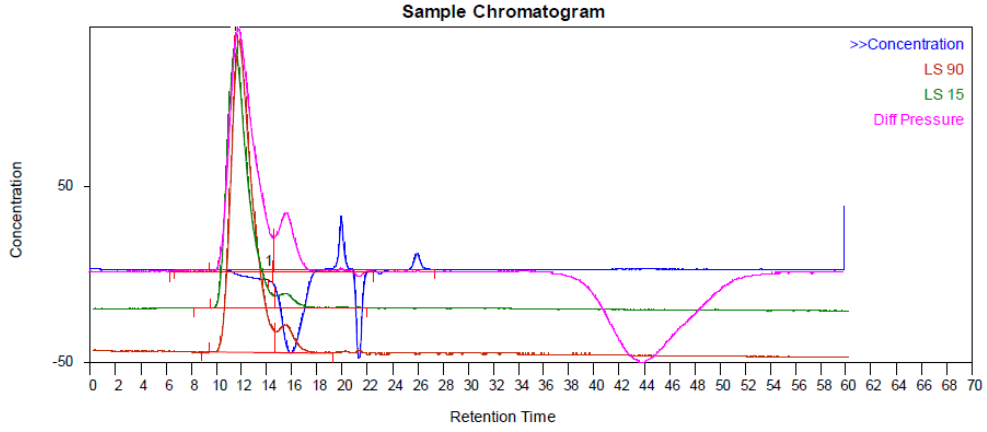
Calculated concentration: 0.472764 mg/ml
Concentration used: 0.47 mg/ml
Calculated dn/dc: 0.10000
dn/dc Used: 0.10000

Analysis Using Method: Triple

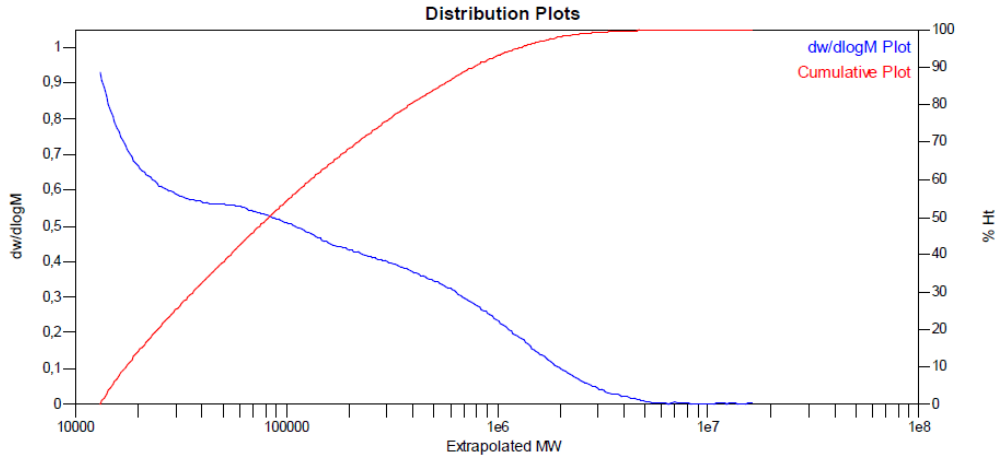
Results File: C:\Cirrus Workbooks\Olexis_2010-07-26_658nm\2010-11-18-0005-Repeat (01).rst

Ligt Scattering and IV Results:
Bulk IV: 3.694729
LS 15°Mw: 301471
LS 90°Mw: 190010

Sample Chromatogram

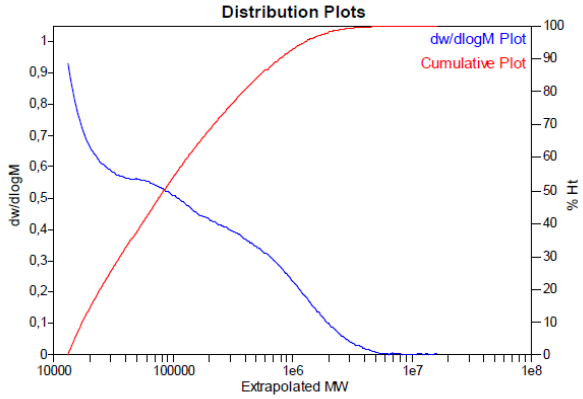


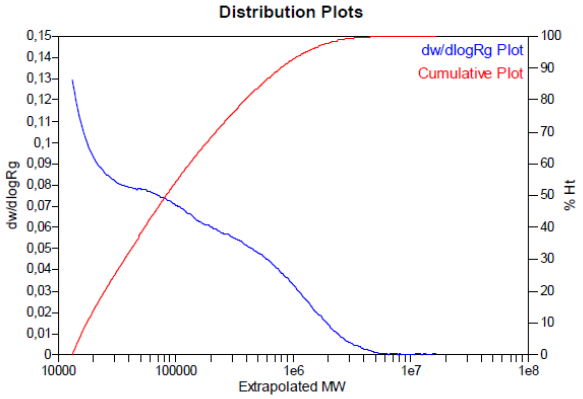
Distribution Plots

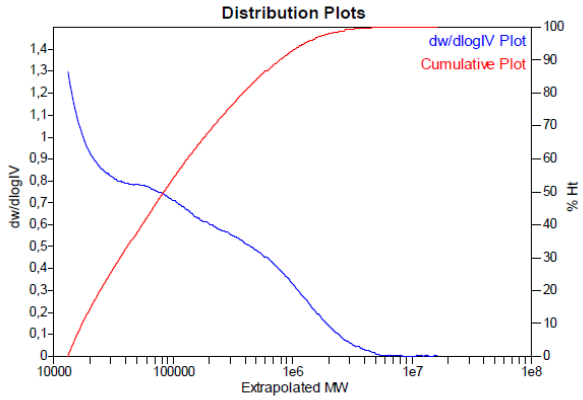


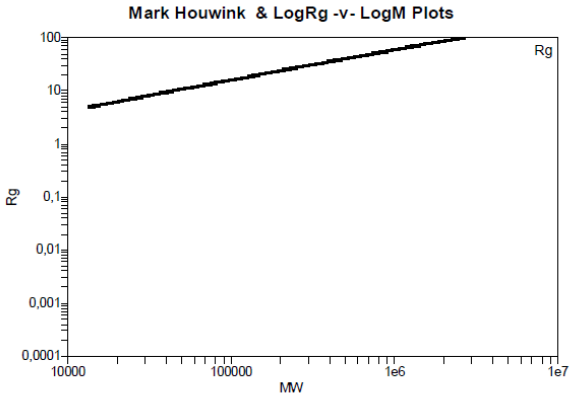
MW Averages

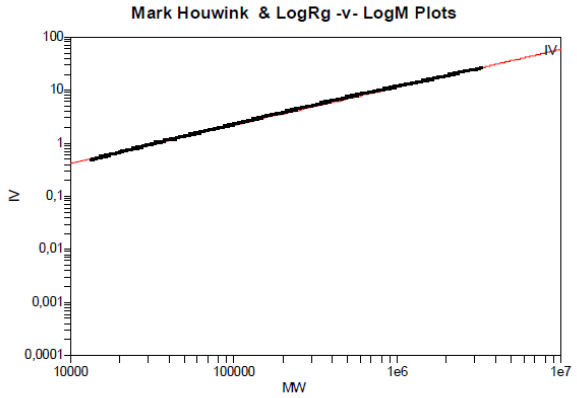
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	13138	47331	285009	1483057	4399009	213622	6.0216

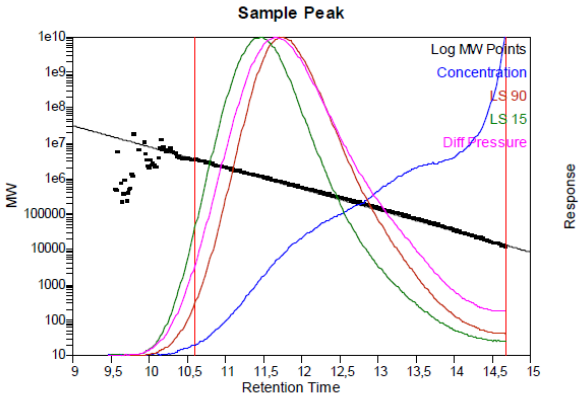

Distribution Plots
dw/dlogM Plot
Cumulative Plot
dw/dlogM
% Ht
Extrapolated MW


Distribution Plots
dw/dlogRg Plot
Cumulative Plot
dw/dlogRg
% Ht
Extrapolated MW


Distribution Plots
dw/dlogIV Plot
Cumulative Plot
dw/dlogIV
% Ht
Extrapolated MW


Mark Houwink & LogRg -v- LogM Plots
Rg
Rg
MW


Mark Houwink & LogRg -v- LogM Plots
IV
IV
MW


Sample Peak
Log MW Points
Concentration
LS 90
LS 15
Diff Pressure
MW
Response
Retention Time

Sample: AST 272 Batch: 2010-11-18

Workbook: Olexis 2010-07-26_658nm.mplw

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	13138	47331	285009	1483057	4399009	213622	6.0216

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	10.17	14.17	14.48	-6.26866	0	941.878	100
2	LS 90	9.48	11.75	14.67	9.85164	0	1184.4	100
3	LS 15	9.55	11.47	14.65	4.70726	0	553.054	100
4	Diff Pressure	9.48	11.67	14.57	56.5379	0	7733.95	100

No	Start RT (mins)	End RT (mins)	Start Height	End Height	Is St Mod	Is End Mod
1	6.65	27.37	2.55	2.63	No	No
2	8.88	19.30	3.81	3.79	No	No
3	8.20	21.98	-1.03	-1.03	No	No
4	6.32	22.53	-2.79	-2.79	No	No

Peak No	IVp	IVn	IVw	IVz	IVz+1	IVv	Disp
1	0.504535	1.4171	3.72438	9.86635	19.285	1.10422	2.62817

Peak No	Rgp	Rgn	Rgw	Rgz	Rgz+1	Rgv	Disp
1	5.13827	12.348	22.3274	41.8411	66.577	9.25121	1.80819

RI only detection:

GPC Report

Freitag, 19. November 2010 13:26

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

Sample Details

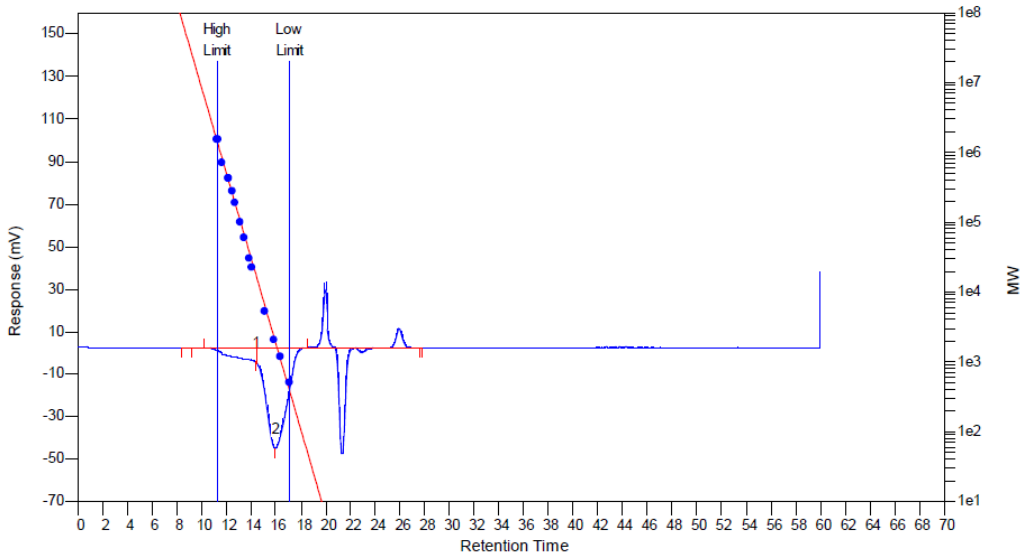
Sample Name: AST 272 — Batch Name: 2010-11-18
Filename: C:\Cirrus Workbooks\Olexis_2010-07-26_RI\2010-11-18-0005.cgrm
Acquired: 19.11.2010 08:41:50 — Eluent: TCB stabilised with 0.0125% BHT
Injection Volume: 200.0 ul — Flow Rate: 1.0 ml/min
Concentration: mg/ml — Temperature: 160 ℃
Column Set: Olexis — Column Set Length: 60600 mm

Analysis Using Method: RI-Auswert_PE_K_a

Results File: C:\Cirrus Workbooks\Olexis_2010-07-26_RI\2010-11-18-0005-Repeat (01).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	15350	58967	299909	1234234	2332861	232062	5.08605
2	2092	1101	2696	5305	7903	2413	2.44868

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.17	14.40	14.48	-7.03677	12.8653	0	0
2		14.48	15.90	18.55	-47.6589	87.1347	5162.77	100

2.1.2 GPC plot of an AN/ethene copolymerisation (Entry 16)

GPC Report

Donnerstag, 2. September 2010 09:31

Workbook: X:\GPC220\Olexis_2010-07-26_RI\Olexis_2010-07-26_RI.plw

Sample Details

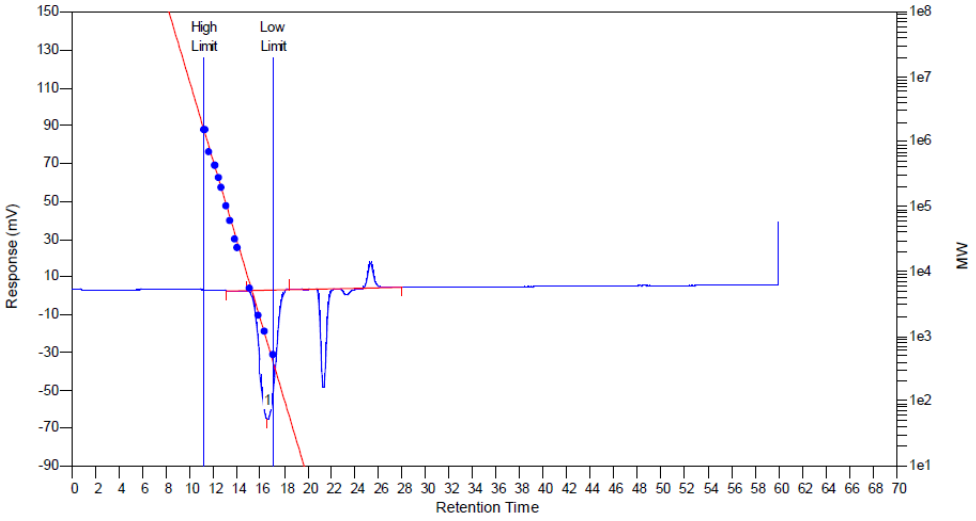
Sample Name: AST 250-filtriert
Batch Name: 2010-09-01
Filename: X:\GPC220\Olexis_2010-07-26_RI\2010-09-01-0003.cgrm
Acquired: 02.09.2010 09:23:12
Eluent: TCB stabilised with 0.0125% BHT
Injection Volume: 200.0 ul
Flow Rate: 1.0 ml/min
Concentration: mg/ml
Temperature: 160 °C
Column Set: Olexis
Column Set Length: 60600 mm

Analysis Using Method: RI-Auswert_PE_K_a

Results File: X:\GPC220\Olexis_2010-07-26_RI\2010-09-01-0003.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 calibration = 40.600000
Alpha calibration = 0.725000
High limit Mw = 1449749
Low limit Mw = 360



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	800	646	1100	1832	2793	1021	1.70279

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		14.83	16.58	18.45	-68.3459	0	5783.18	100

2.2 High temperature ^{1}H-NMR spectroscopic assignment for the AN/ethene copolymerisation (Entry 16)