

**Supporting Information**  
**For**  
**Kinetic and Microstructural Studies of Cp<sub>2</sub>ZrCl<sub>2</sub> and Cp<sub>2</sub>HfCl<sub>2</sub>-**  
**Catalyzed Oligomerization of Higher  $\alpha$ -Olefins in mPAO Oil Base**  
**Stocks Production**

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982144787021.

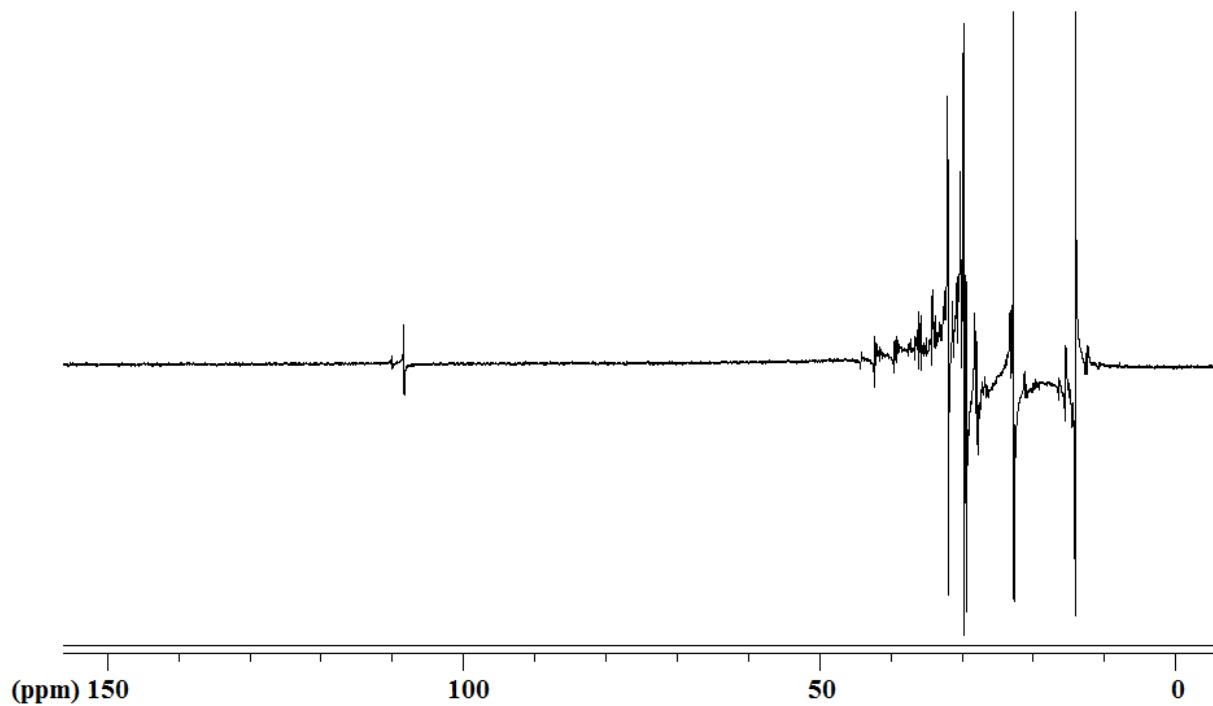


Fig S1. DEPT-135 spectrum of Zr-H sample

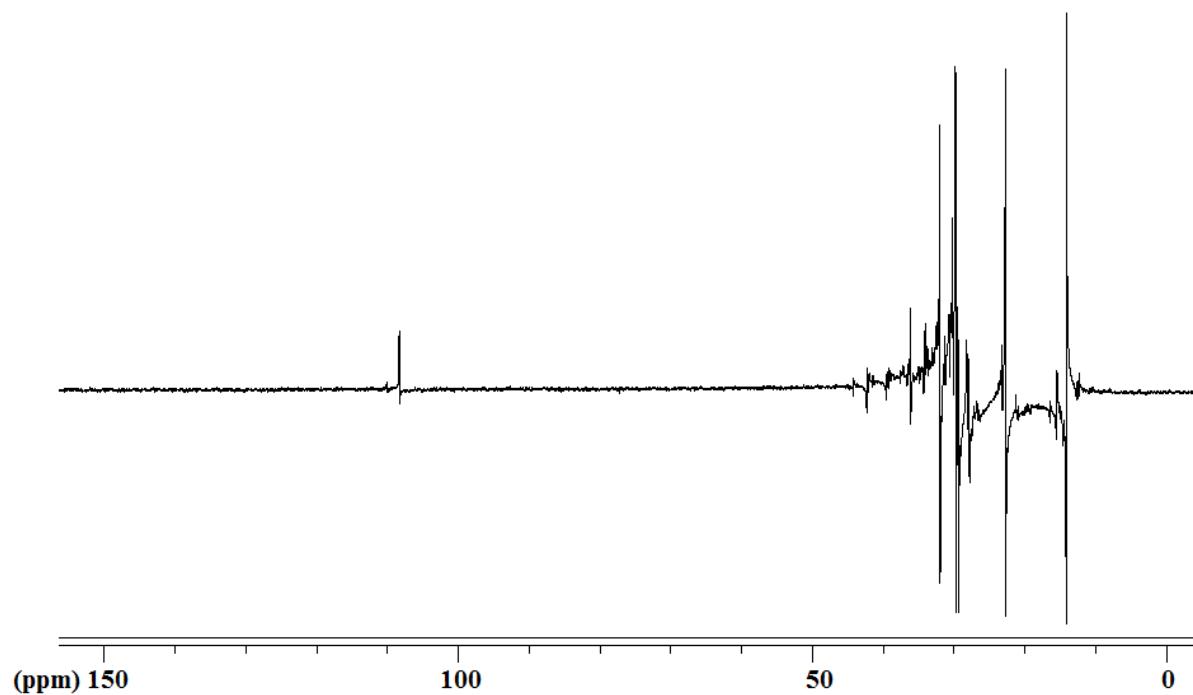


Fig S2. DEPT-135 spectrum of Zr-O sample

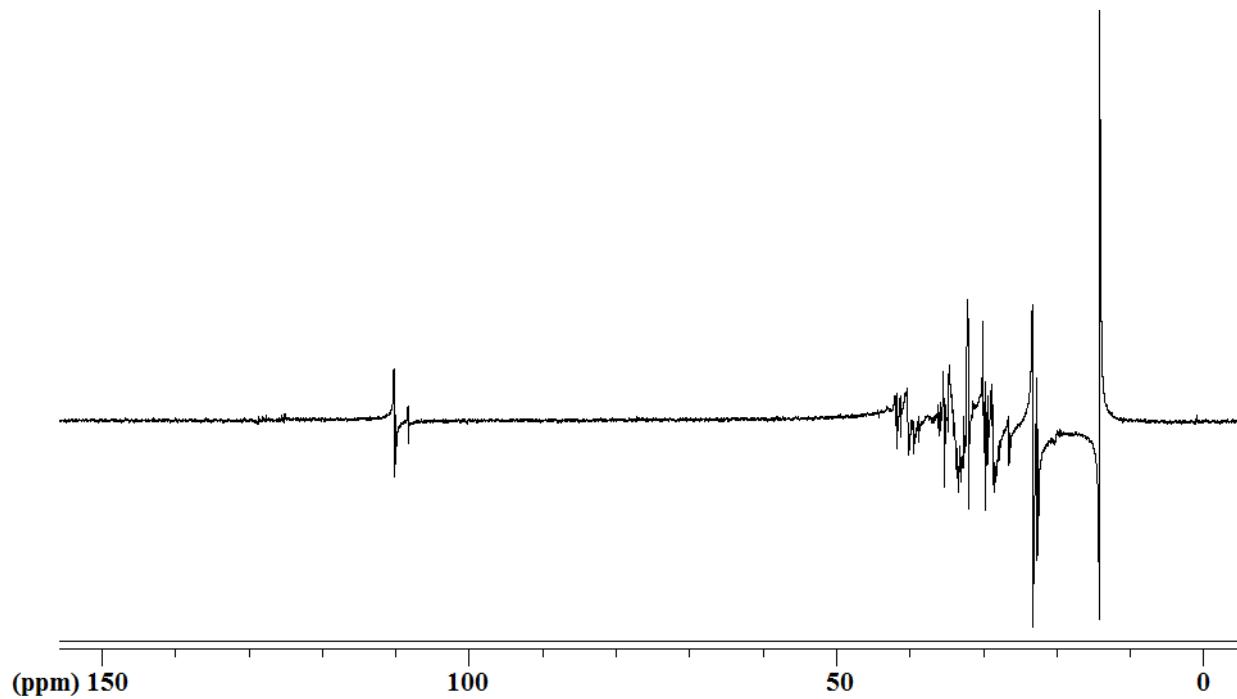


Fig S3. DEPT-135 spectrum of Hf-H sample

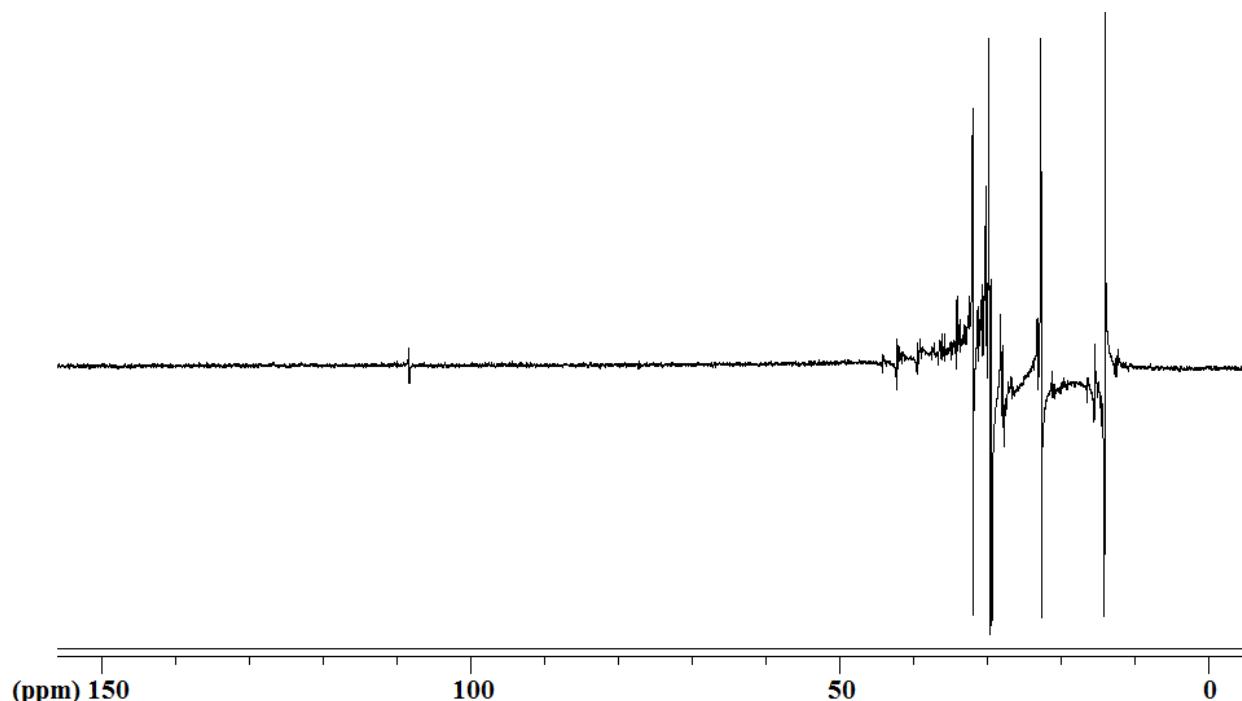


Fig S4. DEPT-135 spectrum of Hf-O sample

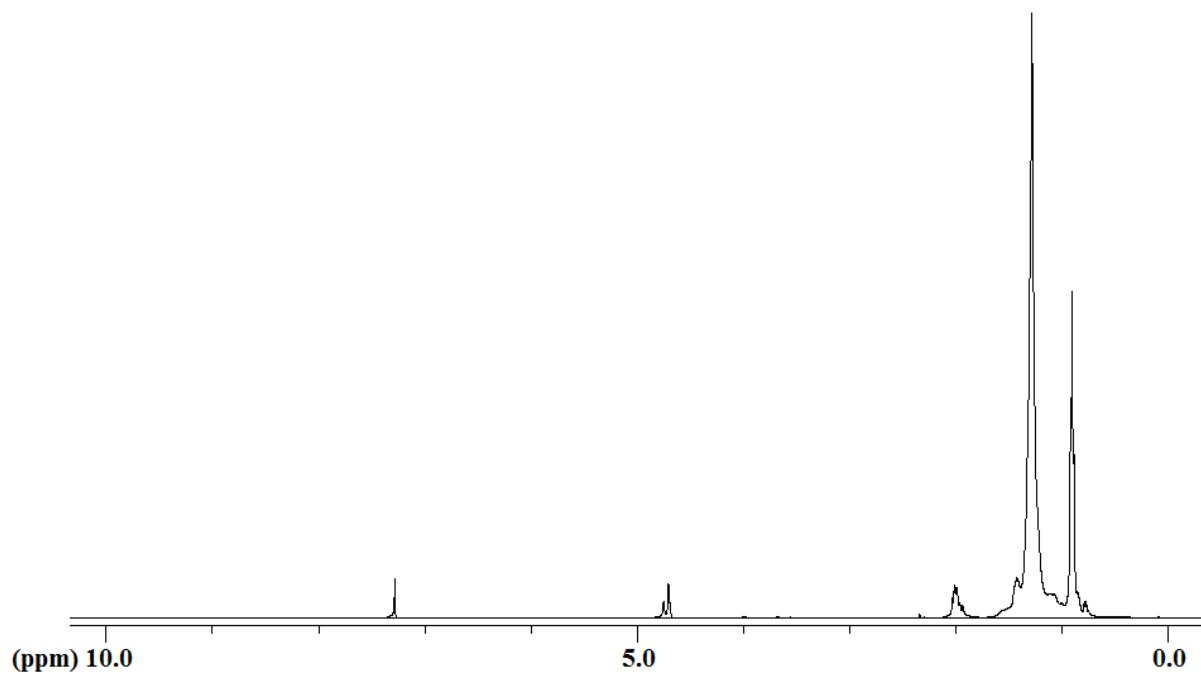


Fig S5. <sup>1</sup>H-NMR spectrum of Zr-H sample

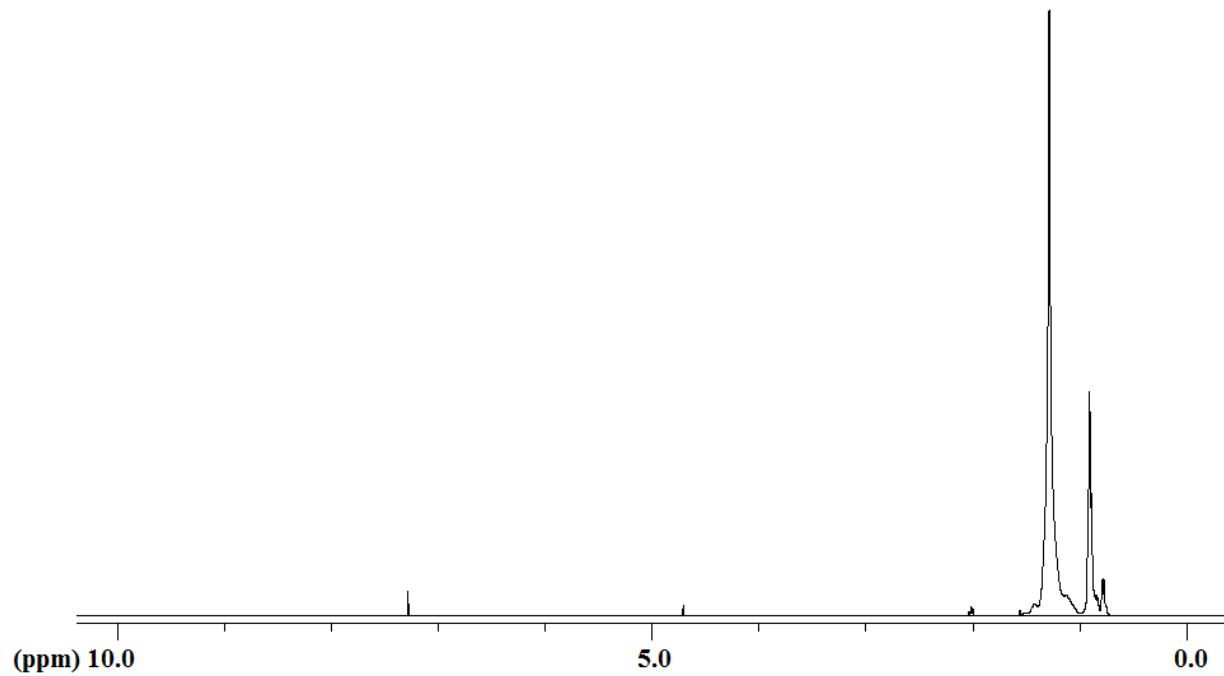


Fig S6. <sup>1</sup>H-NMR spectrum of Zr-O sample

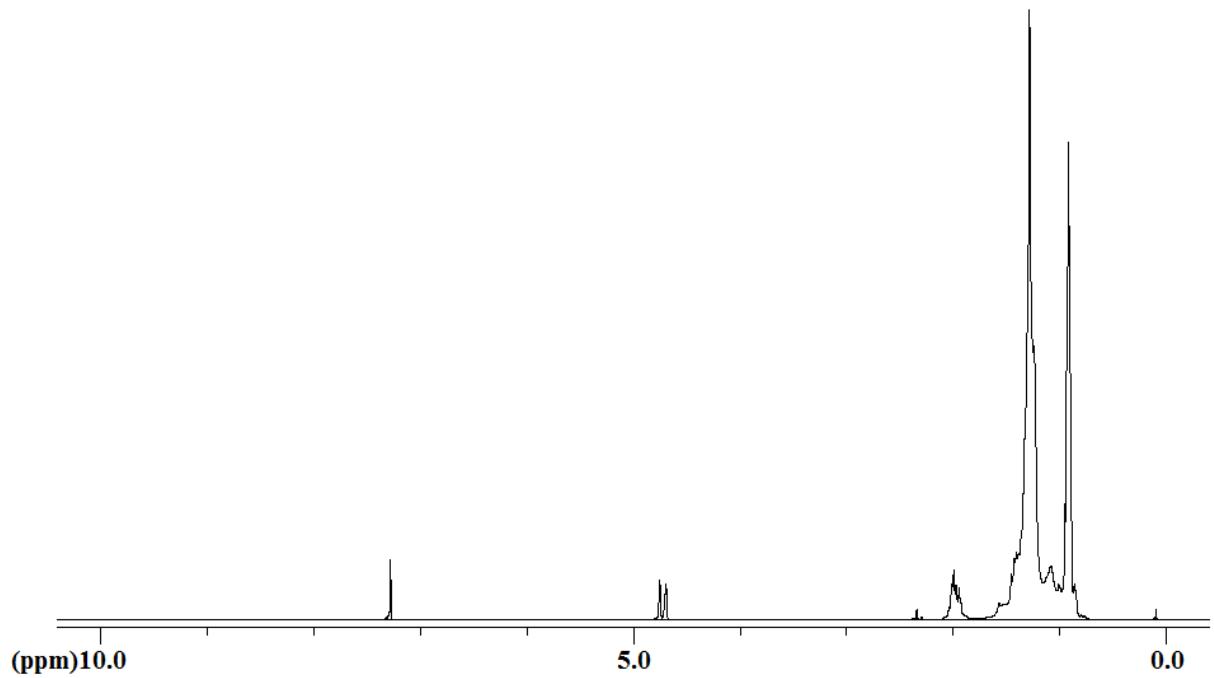


Fig S7. <sup>1</sup>H-NMR spectrum of Hf-H sample

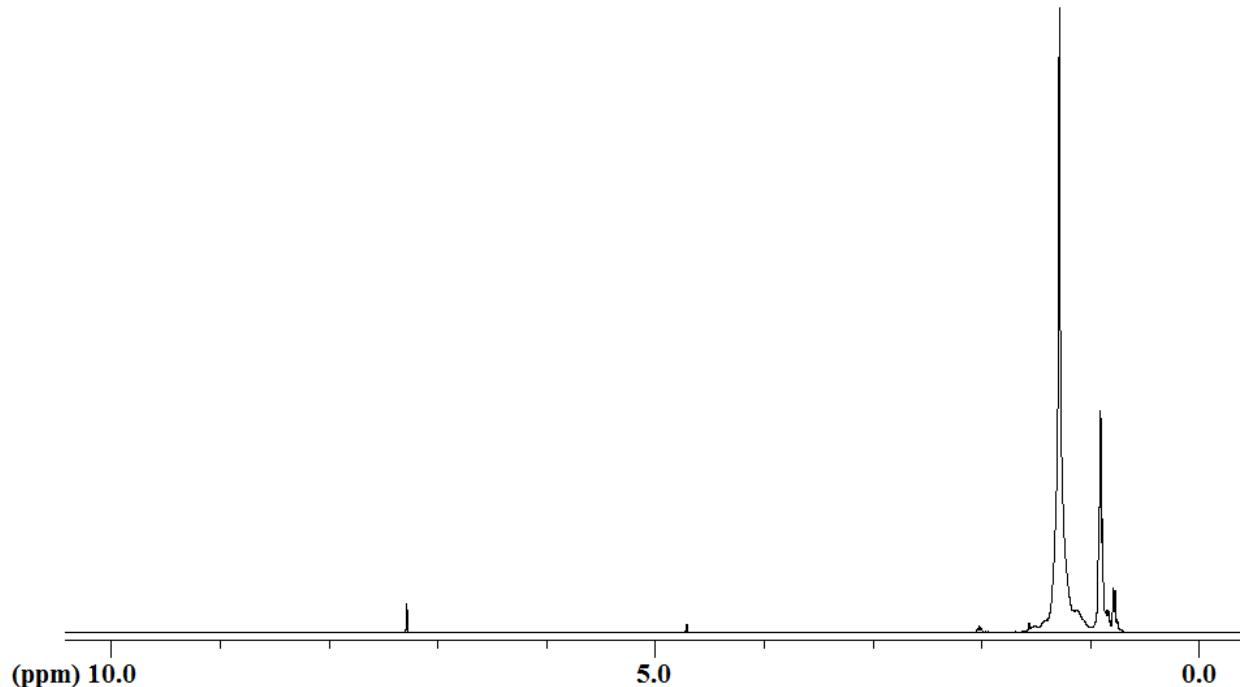
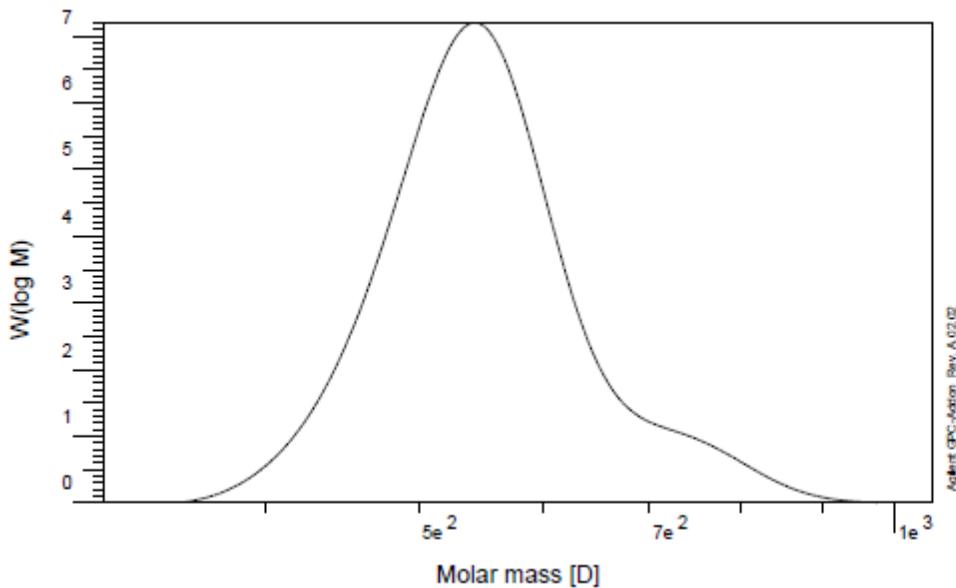


Fig S8. <sup>1</sup>H-NMR spectrum of Hf-O sample



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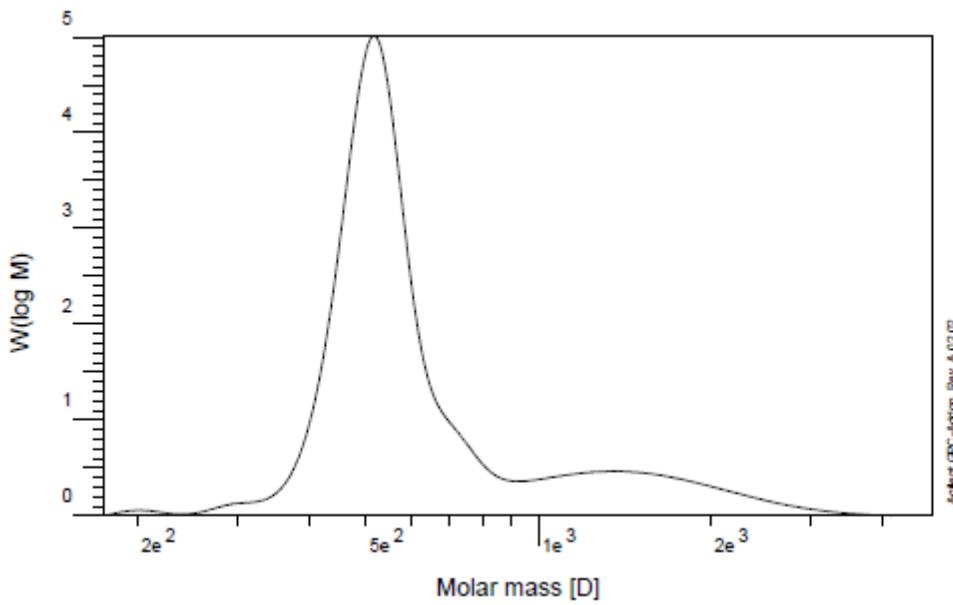
Sample : 6
Injection Date : 18-Jun-20, 08:50:56
Calibration File : C:\HPCHEM\1\DATA\KAZEMICAL990312.CAL
Calibration Date : Tuesday 20/06/09 13:51:38
Baseline from : 17.950 min
Integration from : 17.950 min
MHK - A (Cal.): 0.000000E+0
Eluent : THF
Concentration : 1.000 g/l
Column 1 : PLgel OH-MIXED C
Detector 1 : RID A, Refractive Index Signal
Operator : IPPI
rid1A

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Mn :	5.4328e2	g/mol
Mw :	5.5555e2	g/mol
Mz :	5.6900e2	g/mol
Mv :	0.000000	g/mol
D :	1.0226e0	
In:	0.000000	ml/g
Vp :	1.8612e1	ml
Mp :	5.4254e2	g/mol
A :	5.1335e3	ml <sup>3</sup> /V
< 316	0.00	
w% :	100.00	
> 1058	0.00	

Fig S9. GPC curve of prepared oligomer with  $\text{Cp}_2\text{ZrCl}_2$ , [cat]= 10  $\mu\text{mol}$ , [1-hexene]= 0.08 mol,

$t=3$  h,  $\text{Al}/\text{M}= 500$ ,  $T=80$   $^{\circ}\text{C}$



Agilent GPC-Action Rev A.02.02

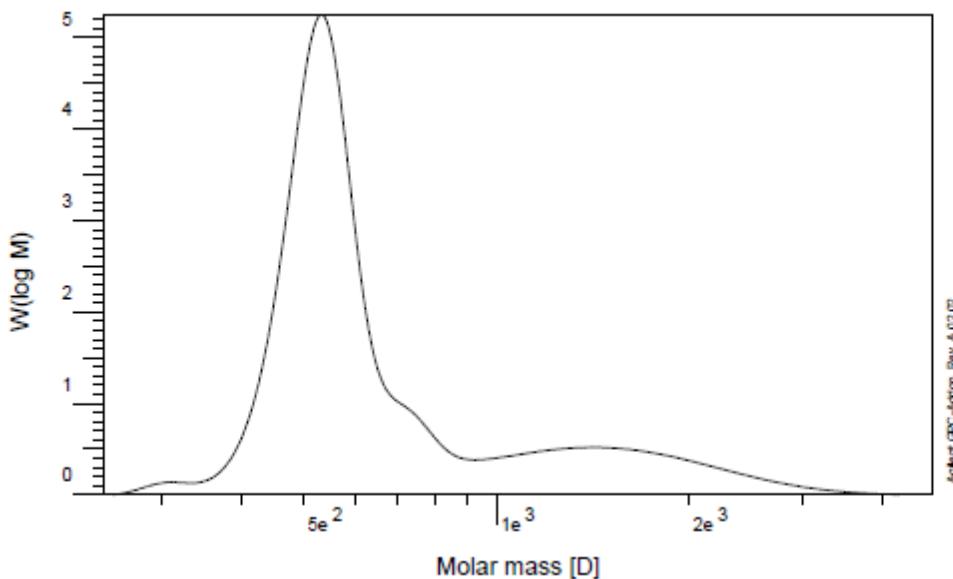
```

Sample : /
Injection Date :
Calibration File : CAL990312.CAL
Calibration Date :
Baseline from : 16.447 min
Integration from: 16.447 min
MHK - A (Cal.): 0.000000E+0
Eluent : THF
Concentration : 1.000 g/l
Column 1 : ....?
Detector 1 : RID A, Refractive Index Signal
Operator : IPPI
rid1A
Mn : 5.7779e2 g/mol
Mw : 7.2206e2 g/mol
Mz : 1.0356e3 g/mol
Mv : 0.000000 g/mol
D : 1.2497e0
[n]: 0.000000 ml/g
Vp : 1.8662e1 ml
Mp : 5.1572e2 g/mol
A : 4.2152e3 ml^V
< 174 0.00
w% : 100.00
> 4893 0.00

```

Fig S10. GPC curve of prepared oligomer with  $\text{Cp}_2\text{ZrCl}_2$ , [cat]= 10  $\mu\text{mol}$ , [1-hexene]= 0.08 mol,

$t=9$  h,  $\text{Al}/\text{M}= 500$ ,  $T=80$  °C



Sample : 8-SECOND  
 Injection Date : 18-Jun-20, 11:17:22  
 Calibration File : C:\HPCHEM\1\DATA\KAZEMI\CAL990312.CAL  
 Calibration Date : Tuesday 20/06/09 13:51:38  
 Baseline from : 16.465 min  
 Integration from: 16.465 min  
 MHK - A (Cal.): 0.00000E+0  
 Eluent : THF  
 Concentration : 1.000 g/l  
 Column 1 : PLgel OH-MIXED C  
 Detector 1 : RID A, Refractive Index Signal  
 Operator : IPPI

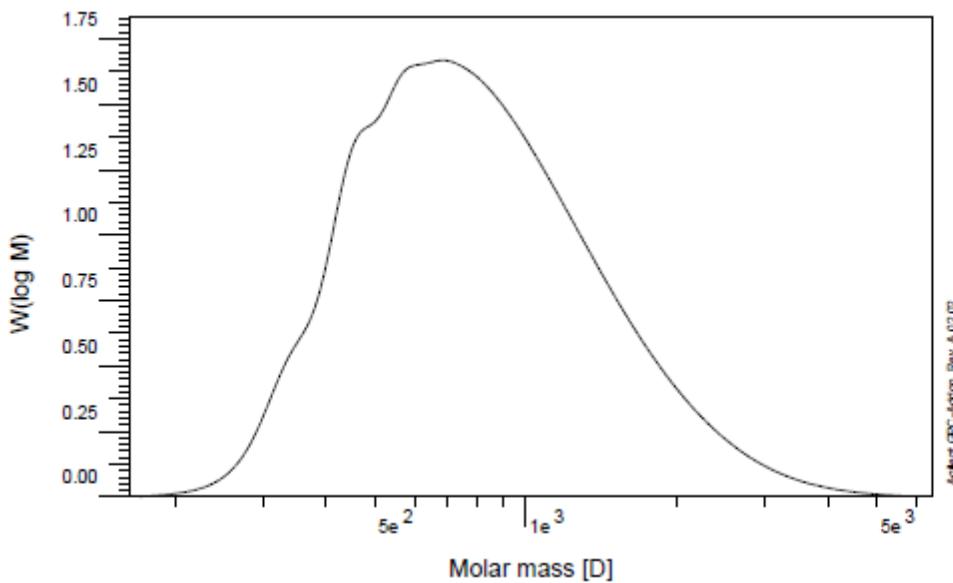
rid1A

Baseline to :	19.409 min
Integration to :	19.409 min
MHK - K (Cal.):	1.00000E+0 ml/g
Flowrate :	1.000 ml/min
Inject volume :	20.000 ul
Temperature :	29.980 C
Delay volume :	0.000 ml
Acquisition interval :	0.430 sec

<u>Mn</u> :	6.1039e2	g/mol
<u>Mw</u> :	7.8793e2	g/mol
<u>Mz</u> :	1.1045e3	g/mol
<u>Mv</u> :	0.000000	g/mol
D :	1.2581e0	
[n]:	0.000000	ml/g
Vp :	1.8833e1	ml
Mp :	5.3092e2	g/mol
A :	4.9604e3	ml <sup>2</sup> /V
< 243	0.00	
w% :	100.00	
> 4807	0.00	

Fig S11. GPC curve of prepared oligomer with Cp<sub>2</sub>ZrCl<sub>2</sub>, [cat]= 10 μmol, [1-hexene]= 0.08 mol,

t=18 h, Al/M= 500, T=80 °C



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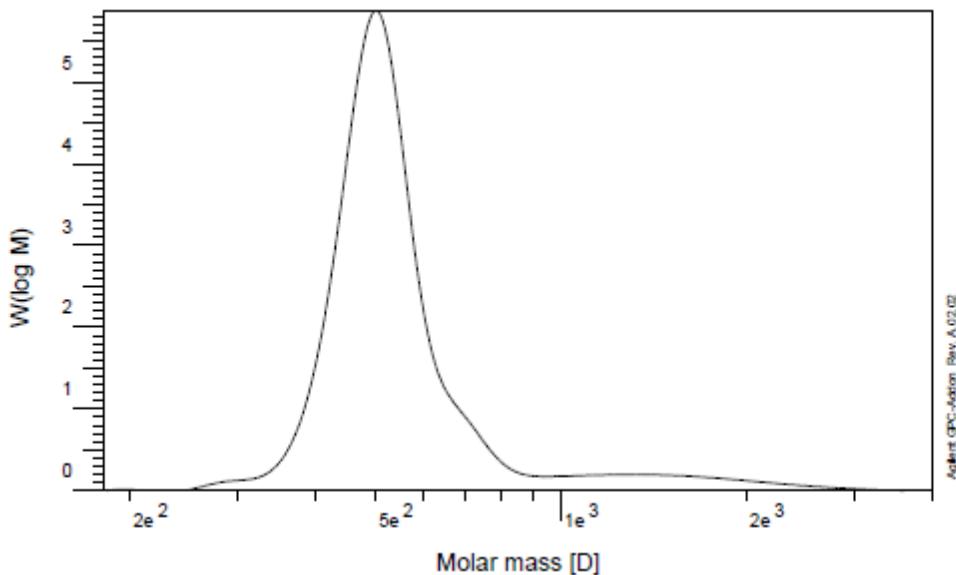
Sample : ZR-HEX-80  
 Injection Date : 12-Dec-17, 12:58:56  
 Calibration File : C:\HPCHEM\11\DATA\13960802\96-09-01-cal-01.CAL  
 Calibration Date : Thursday 17/11/30 09:46:40  
 Baseline from : 16.080 min Baseline to : 19.654 min  
 Integration from: 16.080 min Integration to : 19.654 min  
 MHK - A (Cal.): 0.000000E+0 MHK - K (Cal.): 1.000000E+0 ml/g  
 Eluent : THF Flowrate : 1.000 ml/min  
 Concentration : 1.000 g/l Inject volume : 20.000  $\mu$ l  
 Column 1 : PLgel OH-MIXED C Temperature : 29.970 °C  
 Detector 1 : RID A, Refractive Index Signal Delay volume : 0.000 ml  
 Operator : IPPI Acquisition interval : 0.430 sec

#### rid1A

<u>Mn</u> :	6.9167e2	g/mol
<u>Mw</u> :	9.2053e2	g/mol
<u>Mz</u> :	1.2805e3	g/mol
<u>Mv</u> :	0.000000	g/mol
D :	1.3309e0	
[n]:	0.000000	ml/g
Vp :	1.8259e1	ml
Mp :	6.8406e2	g/mol
A :	1.7531e4	ml <sup>2</sup> /V
< 162	0.00	
w% :	100.00	
> 6475	0.00	

Fig S12. GPC curve of prepared oligomer with  $Cp_2ZrCl_2$ , [cat]= 10  $\mu$ mol, [1-hexene]= 0.08 mol,

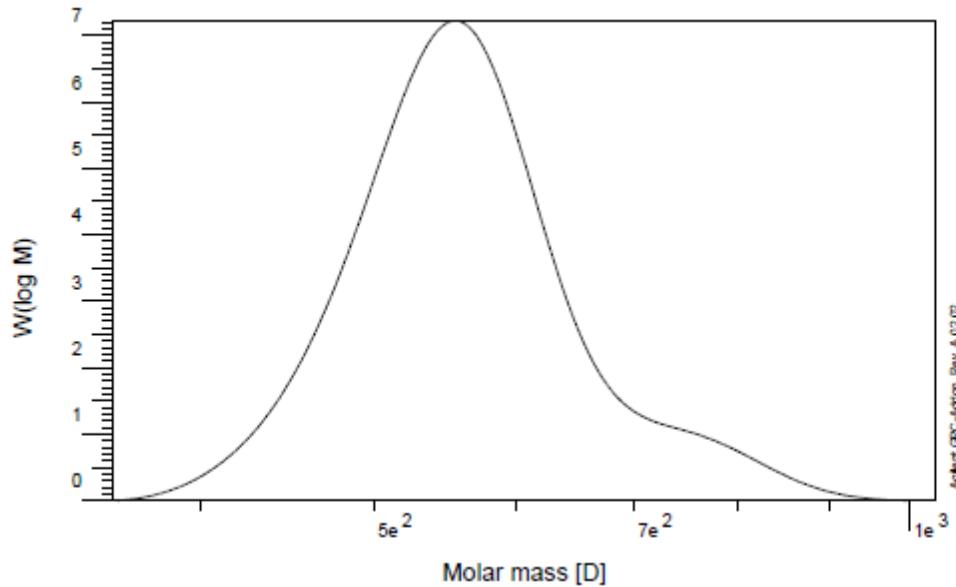
t=24 h, Al/M= 500, T=80 °C



Sample : 7  
 Injection Date : 09-Jun-20, 08:59:01  
 Calibration File : C:\HPCHEM\11\DATA\KAZEM\CAL990312.CAL  
 Calibration Date : Tuesday 20/06/09 13:51:38  
 Baseline from : 16.638 min Baseline to : 19.699 min  
 Integration from : 16.638 min Integration to : 19.699 min  
 MHK - A (Cal.): 0.000000E+0 MHK - K (Cal.): 1.000000E+0 ml/g  
 Eluent : THF Flowrate : 1.000 ml/min  
 Concentration : 1.000 g/l Inject volume : 20.000  $\mu$ l  
 Column 1 : PLgel OH-MIXED C Temperature : 29.930 C  
 Detector 1 : RID A, Refractive Index Signal Delay volume : 0.000 ml  
 Operator : IPPI Acquisition interval : 0.430 sec  
**rid1A**  
Mn : 5.2525e2 g/mol  
Mw : 5.9471e2 g/mol  
Mz : 7.6838e2 g/mol  
Mv : 0.000000 g/mol  
D : 1.1322e0  
[n] : 0.000000 ml/g  
Vp : 1.8691e1 ml  
Mp : 5.0096e2 g/mol  
A : 4.1071e3 ml/V  
< 180 0.00  
w% : 100.00  
> 4024 0.00

Fig S13. GPC curve of prepared oligomer with  $Cp_2ZrCl_2$ , [cat]= 10  $\mu$ mol, [1-octene]= 0.08 mol,

t=3 h, Al/M= 500, T=80 °C



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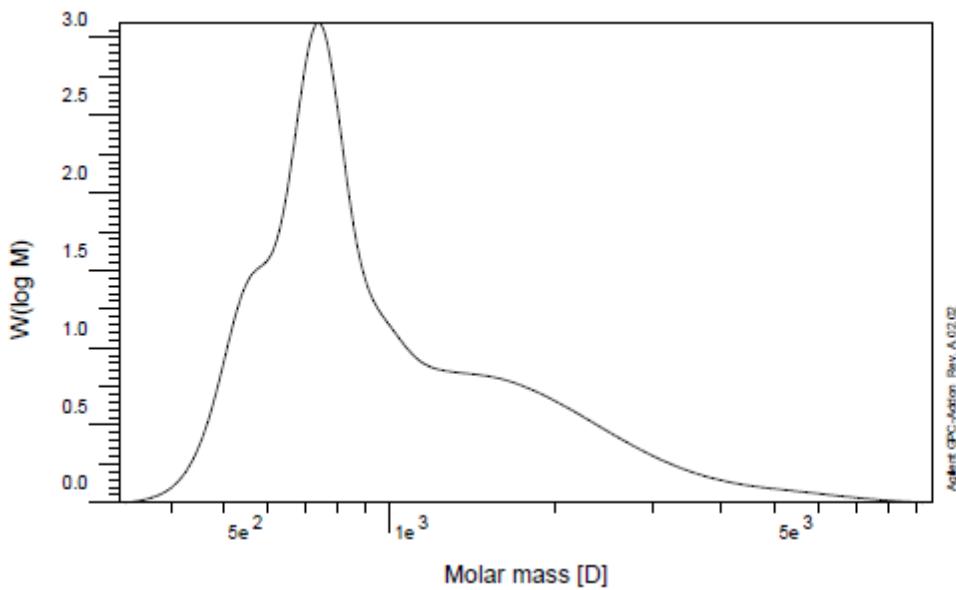
Sample : 4
Injection Date : 18-Jun-20, 07:56:51
Calibration File : C:\HPCHEM\11\DATA\KAZEMI\CAL990312.CAL
Calibration Date : Tuesday 20/06/09 13:51:38
Baseline from : 17.973 min
Integration from: 17.973 min
MHK - A (Cal.): 0.000000E+0
Eluent : THF
Concentration : 1.000 g/l
Column 1 : PLgel OH-MIXED C
Detector 1 : RID A, Refractive Index Signal
Operator : IPPI
rid1A

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<u>Mn</u> :	5.5501e2	g/mol
<u>Mw</u> :	5.6812e2	g/mol
<u>Mz</u> :	5.8183e2	g/mol
<u>Mv</u> :	0.000000	g/mol
D :	1.0225e0	
[n]:	0.000000	ml/g
Vp :	1.8590e1	ml
Mp :	5.5451e2	g/mol
A :	3.7559e3	ml <sup>2</sup> /V
< 356	0.00	
w% :	100.00	
> 1034	0.00	

Fig S14. GPC curve of prepared oligomer with  $\text{Cp}_2\text{ZrCl}_2$ , [cat]= 10  $\mu\text{mol}$ , [1-octene]= 0.08 mol,

t=9 h, Al/M= 500, T=80 °C

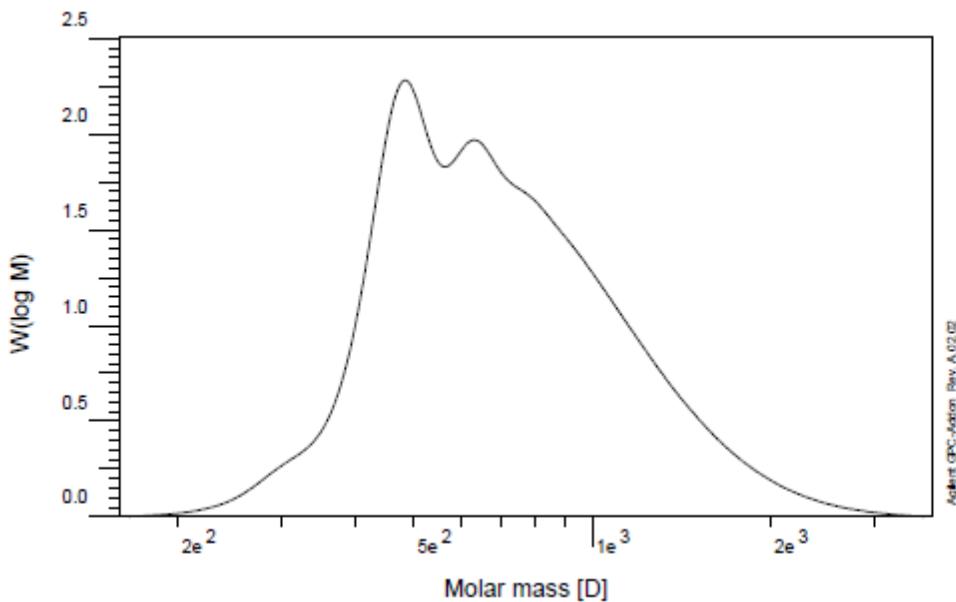


Sample : 2  
 Injection Date : 18-Jun-20, 10:15:41  
 Calibration File : C:\HPCHEM\1\DATA\KAZEMICAL990312.CAL  
 Calibration Date : Tuesday 20/06/09 13:51:38  
 Baseline from : 15.784 min Baseline to : 19.130 min  
 Integration from : 15.784 min Integration to : 19.130 min  
 MHK - A (Cal.): 0.000000E+0 MHK - K (Cal.): 1.000000E+0 ml/g  
 Eluent : THF Flowrate : 1.000 ml/min  
 Concentration : 1.000 g/l Inject volume : 20.000 ul  
 Column 1 : PLgel OH-MIXED C Temperature : 29.990 C  
 Detector 1 : RID A, Refractive Index Signal Delay volume : 0.000 ml  
 Operator : IPPI Acquisition interval : 0.430 sec  
rid1A

<b>Mn :</b>	8.7898e2	g/mol
<b>Mw :</b>	1.2015e3	g/mol
<b>Mz :</b>	1.9092e3	g/mol
<b>Mv :</b>	0.000000	g/mol
<b>D :</b>	1.3670e0	
<b>In:</b>	0.000000	ml/g
<b>Vp :</b>	1.8302e1	ml
<b>Mp :</b>	7.4127e2	g/mol
<b>A :</b>	5.4024e3	ml <sup>3</sup> /V
< 322	0.00	
w% :	100.00	
> 9680	0.00	

Fig S15. GPC curve of prepared oligomer with Cp<sub>2</sub>ZrCl<sub>2</sub>, [cat]= 10 μmol, [1-octene]= 0.08 mol,

t=18 h, Al/M= 500, T=80 °C



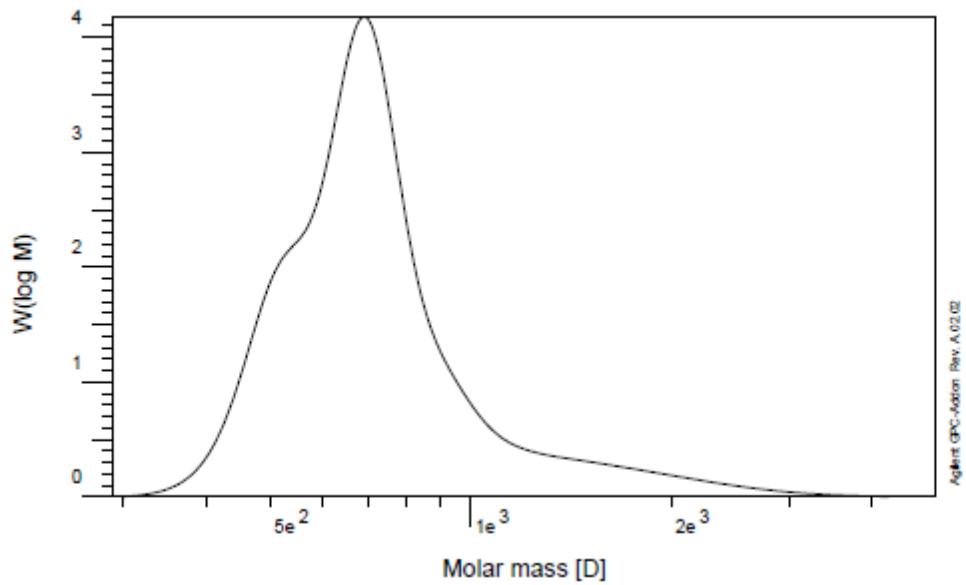
Sample : r-zr-oct-80  
 Injection Date : 22-Jan-18, 12:57:18  
 Calibration File : C:\HPCHEM\1\DATA\13960802\96-10-01-cal-01.CAL  
 Calibration Date : Thursday 18/01/18 08:55:00  
 Baseline from : 16.619 min Baseline to : 19.693 min  
 Integration from: 16.619 min Integration to : 19.693 min  
 MHK - A (Cal.): 0.00000E+0 MHK - K (Cal.): 1.00000E+0 ml/g  
 Eluent : THF Flowrate : 1.000 ml/min  
 Concentration : 1.000 g/l Inject volume : 20.000 ul  
 Column 1 : PLgel OH-MIXED C Temperature : 30.000 C  
 Detector 1 : RID A, Refractive Index Signal Delay volume : 0.000 ml  
 Operator : IPPI Acquisition interval : 0.430 sec

rid1A

Mn :	6.3162e2	g/mol
Mw :	7.7529e2	g/mol
Mz :	9.7806e2	g/mol
Mv :	0.000000	g/mol
D :	1.2275e0	
[n]:	0.000000	ml/g
Vp :	1.8612e1	ml
Mp :	4.8413e2	g/mol
A :	4.5502e3	ml <sup>2</sup> /V
< 160	0.00	
w% :	100.00	
> 3760	0.00	

Fig S16. GPC curve of prepared oligomer with Cp<sub>2</sub>ZrCl<sub>2</sub>, [cat]= 10 μmol, [1-octene]= 0.08 mol,

t=24 h, Al/M= 500, T=80 °C



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Sample : 8
Injection Date :
Calibration File : CAL990312.CAL
Calibration Date :
Baseline from : 16.428 min
Integration from: 16.428 min
MHK - A (Cal.): 0.000000E+0
Eluent : ....?
Concentration : 1.000 g/l
Column 1 : ....?
Detector 1 : RID A, Refractive Index Signal
Operator : IPPI

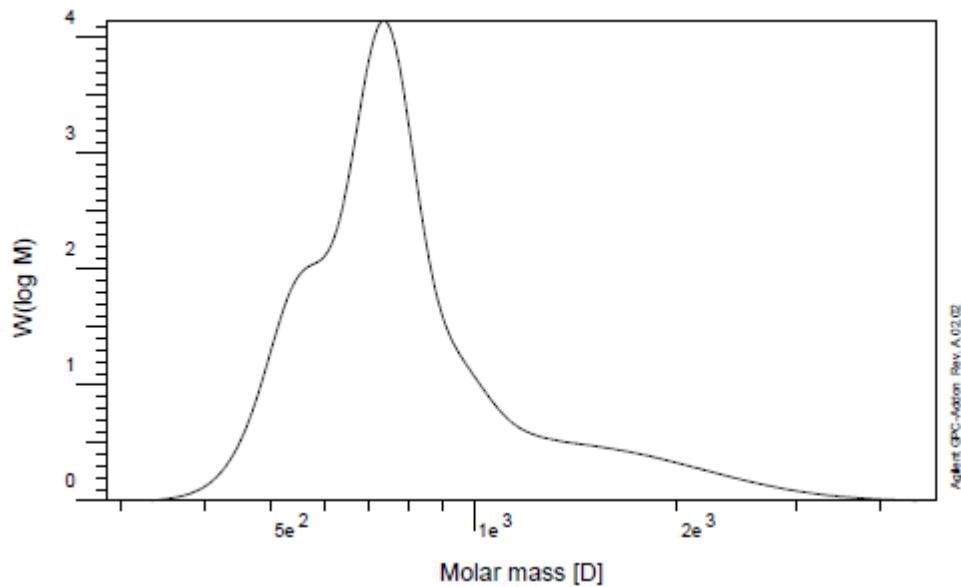
rid1A

Mn : 6.8284e2      g/mol
Mw : 7.7689e2      g/mol
Mz : 9.5505e2      g/mol
Mv : 0.000000      g/mol
D : 1.1377e0
[η]: 0.000000      ml/g
Vp : 1.8374e1      ml
Mp : 6.8934e2      g/mol
A : 4.8463e3      ml/V
10% 4.9251e2      g/mol
30% 6.0480e2      g/mol
60% 7.2664e2      g/mol
85% 9.5542e2      g/mol
90% 1.1248e3      g/mol

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Fig S17. GPC curve of prepared oligomer with Cp<sub>2</sub>HfCl<sub>2</sub>, [cat]= 10 μmol, [1-hexene]= 0.08 mol,

t=3 h, Al/M= 500, T=80 °C



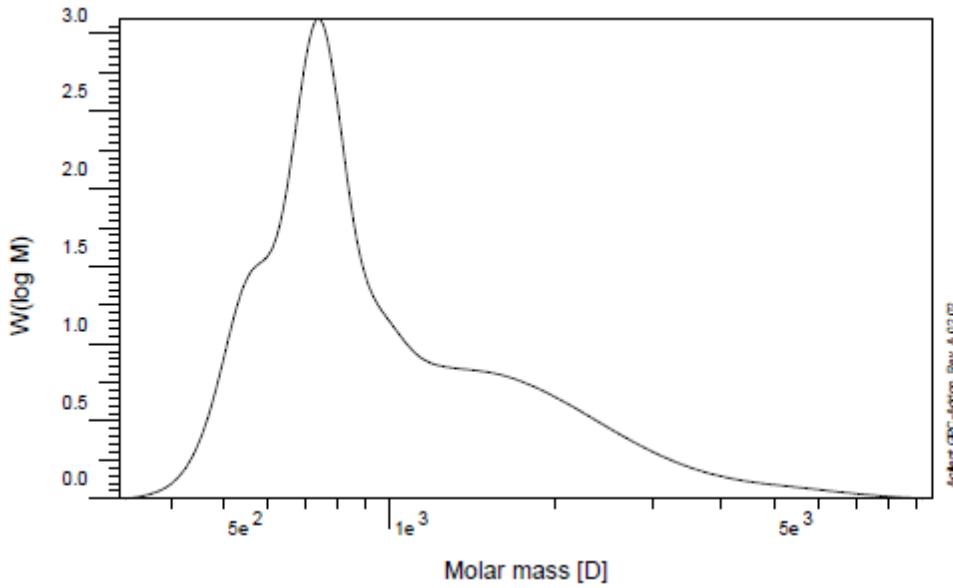
Sample : 7-SECOND  
 Injection Date : 18-Jun-20, 10:44:35  
 Calibration File : C:\HPCHEM\11\DATA\KAZEMI\CAL990312.CAL  
 Calibration Date : Tuesday 20/06/09 13:51:38  
 Baseline from : 16.457 min      Baseline to : 19.247 min  
 Integration from: 16.457 min      Integration to : 19.247 min  
 MHK - A (Cal.): 0.000000E+0      MHK - K (Cal.): 1.000000E+0 ml/g  
 Eluent : THF      Flowrate : 1.000 ml/min  
 Concentration : 1.000 g/l      Inject volume : 20.000  $\mu$ l  
 Column 1 : PLgel OH-MIXED C      Temperature : 30.010 C  
 Detector 1 : RID A, Refractive Index Signal      Delay volume : 0.000 ml  
 Operator : IPPI      Acquisition interval : 0.430 sec

#### rid1A

<b>Mn</b> :	7.5435e2	g/mol
<b>Mw</b> :	8.8157e2	g/mol
<b>Mz</b> :	1.1188e3	g/mol
<b>Mv</b> :	0.000000	g/mol
D :	1.1688e0	
[n]:	0.000000	ml/g
V <sub>p</sub> :	1.8310e1	ml
M <sub>p</sub> :	7.3592e2	g/mol
A :	5.8023e3	ml <sup>2</sup> /V
< 286	0.00	
w% :	100.00	
> 4845	0.00	

Fig S18. GPC curve of prepared oligomer with  $\text{Cp}_2\text{HfCl}_2$ , [cat]= 10  $\mu\text{mol}$ , [1-hexene]= 0.08 mol,

t=9 h, Al/M= 500, T=80 °C



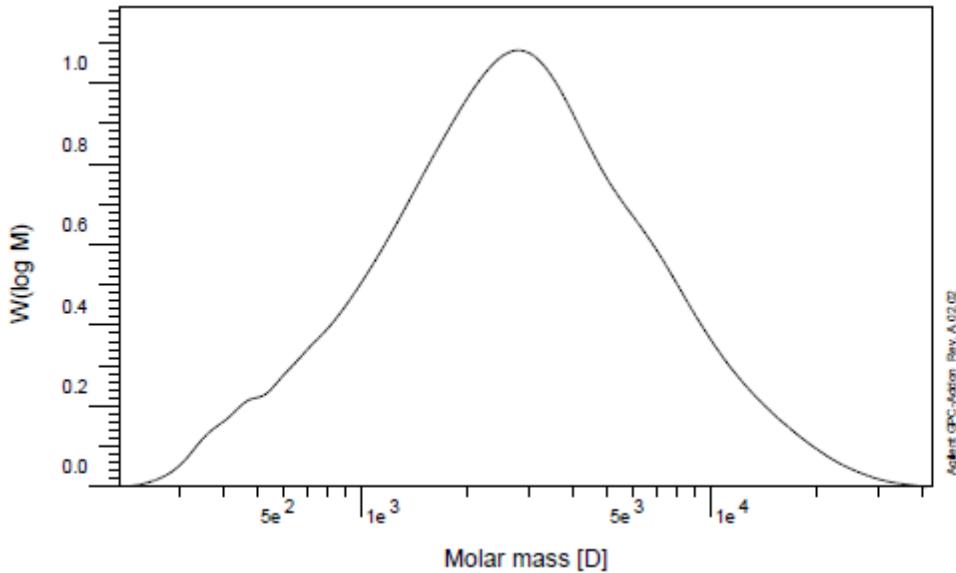
Sample : 2  
 Injection Date : 18-Jun-20, 10:15:41  
 Calibration File : C:\HPCHEM\11\DATA\KAZEMI\CAL990312.CAL  
 Calibration Date : Tuesday 20/06/09 13:51:38  
 Baseline from : 15.784 min Baseline to : 19.130 min  
 Integration from: 15.784 min Integration to : 19.130 min  
 MHK - A (Cal.): 0.000000E+0 MHK - K (Cal.): 1.000000E+0 ml/g  
 Eluent : THF Flowrate : 1.000 ml/min  
 Concentration : 1.000 g/l Inject volume : 20.000  $\mu$ l  
 Column 1 : PLgel OH-MIXED C Temperature : 29.990 °C  
 Detector 1 : RID A, Refractive Index Signal Delay volume : 0.000 ml  
 Operator : IPPI Acquisition interval : 0.430 sec

#### rid1A

M <sub>n</sub> :	8.7898e2	g/mol
M <sub>w</sub> :	1.2015e3	g/mol
M <sub>z</sub> :	1.9092e3	g/mol
M <sub>v</sub> :	0.000000	g/mol
D :	1.3670e0	
[n]:	0.000000	ml/g
V <sub>p</sub> :	1.8302e1	ml
M <sub>p</sub> :	7.4127e2	g/mol
A :	5.4024e3	ml <sup>2</sup> /V
< 322	0.00	
w% :	100.00	
> 9680	0.00	

Fig S19. GPC curve of prepared oligomer with Cp<sub>2</sub>HfCl<sub>2</sub>, [cat]= 10  $\mu$ mol, [1-hexene]= 0.08 mol,

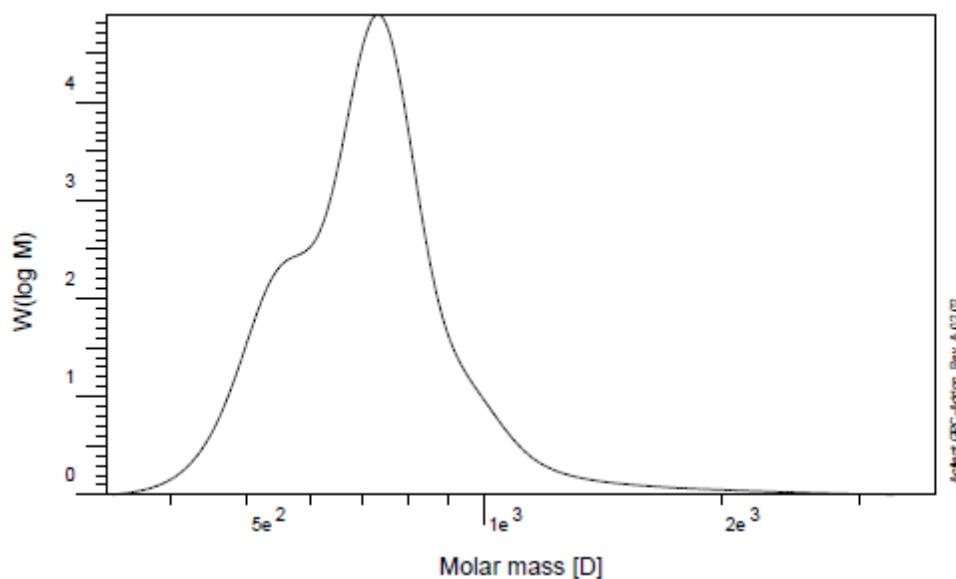
t=18 h, Al/M= 500, T=80 °C



Sample : HF-HEX-RT  
 Injection Date : 19-Dec-17, 09:25:29  
 Calibration File : C:\HPCHEM\1\DATA\13960802\96-09-01-cal-01.CAL  
 Calibration Date : Thursday 17/11/30 08:46:40  
 Baseline from : 14.241 min Baseline to : 19.443 min  
 Integration from: 14.241 min Integration to : 19.443 min  
 MHK - A (Cal.): 0.000000E+0 MHK - K (Cal.): 1.000000E+0 ml/g  
 Eluent : THF Flowrate : 1.000 ml/min  
 Concentration : 1.000 g/l Inject volume : 20.000 ul  
 Column 1 : PLgel OH-MIXED C Temperature : 29.980 C  
 Detector 1 : RID A, Refractive Index Signal Delay volume : 0.000 ml  
 Operator : IPPI Acquisition interval : 0.430 sec  
rid1A  
Mn : 1.8180e3 g/mol  
Mw : 3.9828e3 g/mol  
Mz : 7.9717e3 g/mol  
Mv : 0.000000 g/mol  
D : 2.1932e0  
Inl: 0.000000 ml/g  
Vp : 1.6891e1 ml  
Mp : 2.8052e3 g/mol  
A : 6.0696e3 ml/V  
< 200 0.00  
w%: 100.00  
> 43180 0.00

Fig S20. GPC curve of prepared oligomer with  $\text{Cp}_2\text{HfCl}_2$ , [cat]= 10  $\mu\text{mol}$ , [1-hexene]= 0.08 mol,

t=24 h, Al/M= 500, T=80 °C



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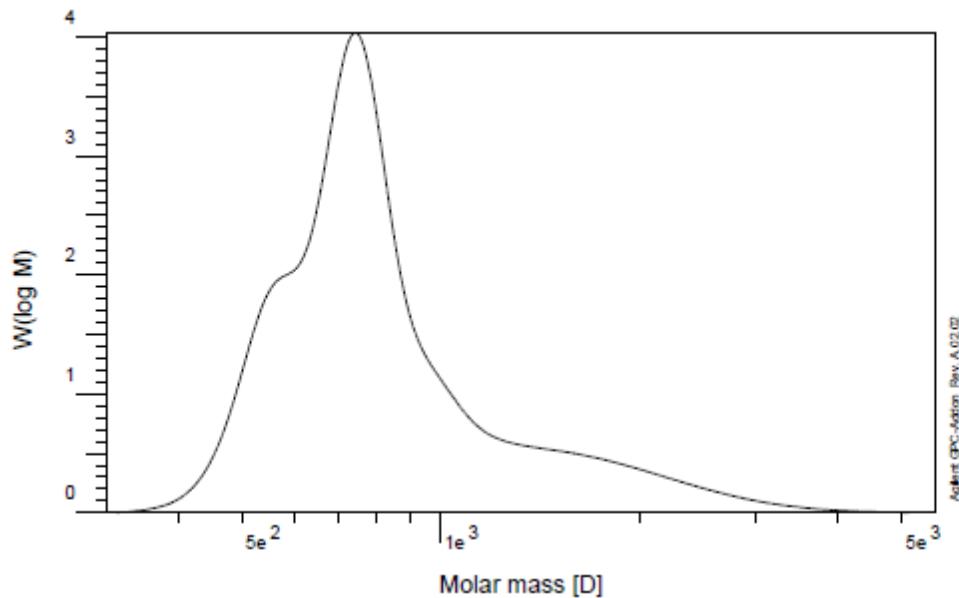
Sample : 1
Injection Date : 18-Jun-20, 09:18:44
Calibration File : C:\HPCHEM\11\DATA\KAZEMI\CAL990312.CAL
Calibration Date : Tuesday 20/06/09 13:51:38
Baseline from : 16.709 min
Integration from: 16.709 min
MHK - A (Cal.): 0.000000E+0
Eluent : THF
Concentration : 1.000 g/l
Column 1 : PLgel OH-MIXED C
Detector 1 : RID A, Refractive Index Signal
Operator : IPPI
rid1A

Mn : 6.8952e2 g/mol
Mw : 7.3789e2 g/mol
Mz : 8.0995e2 g/mol
Mv : 0.000000 g/mol
D : 1.0701e0
[n]: 0.000000 ml/g
Vp : 1.8317e1 ml
Mp : 7.3082e2 g/mol
A : 5.6647e3 ml^V
< 330 0.00
w% : 100.00
> 3744 0.00

```

Fig S21. GPC curve of prepared oligomer with  $\text{Cp}_2\text{HfCl}_2$ , [cat]= 10  $\mu\text{mol}$ , [1-octene]= 0.08 mol,

$t=3$  h,  $\text{Al}/\text{M}= 500$ ,  $T=80$  °C



```

Sample : 3
Injection Date : 18-Jun-20, 09:47:49
Calibration File : C:\HPCHEM\1\DATA\KAZEMICAL990312.CAL
Calibration Date : Tuesday 20/06/09 13:51:38
Baseline from : 16.311 min
Integration from: 16.311 min
MHK - A (Cal.): 0.000000E+0
Eluent : THF
Concentration : 1.000 g/l
Column 1 : PLgel OH-MIXED C
Detector 1 : RID A, Refractive Index Signal
Operator : IPPI
rid1A

```

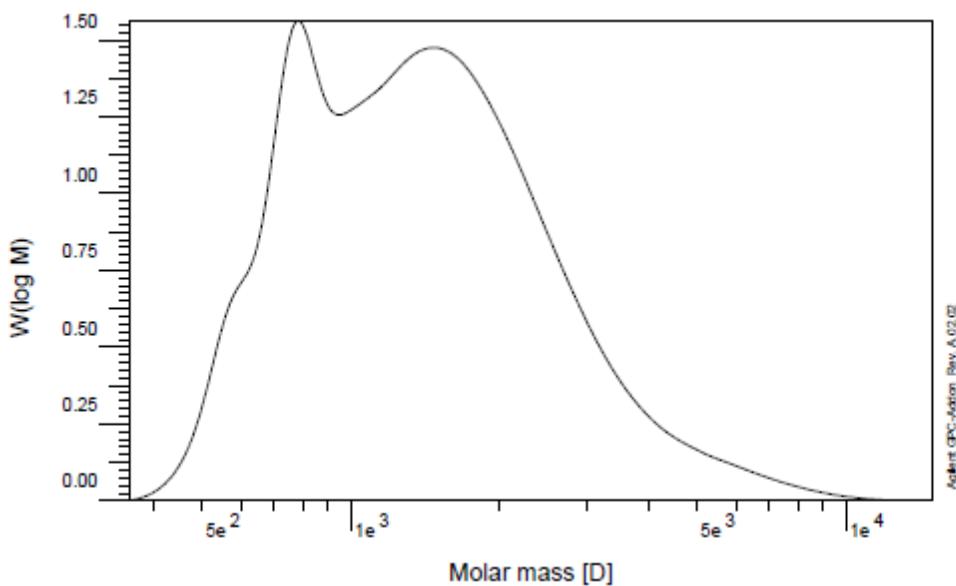
```

Mn : 7.6988e2 g/mol
Mw : 9.1024e2 g/mol
Mz : 1.1746e3 g/mol
Mv : 0.000000 g/mol
D : 1.1823e0
In: 0.000000 ml/g
Vp : 1.8302e1 ml
Mp : 7.4127e2 g/mol
A : 4.9706e3 ml^V
< 312 0.00
w% : 100.00
> 5630 0.00

```

Fig S22. GPC curve of prepared oligomer with  $\text{Cp}_2\text{HfCl}_2$ , [cat]= 10  $\mu\text{mol}$ , [1-octene]= 0.08 mol,

$t=9$  h,  $\text{Al}/\text{M}= 500$ ,  $T=80$  °C



```

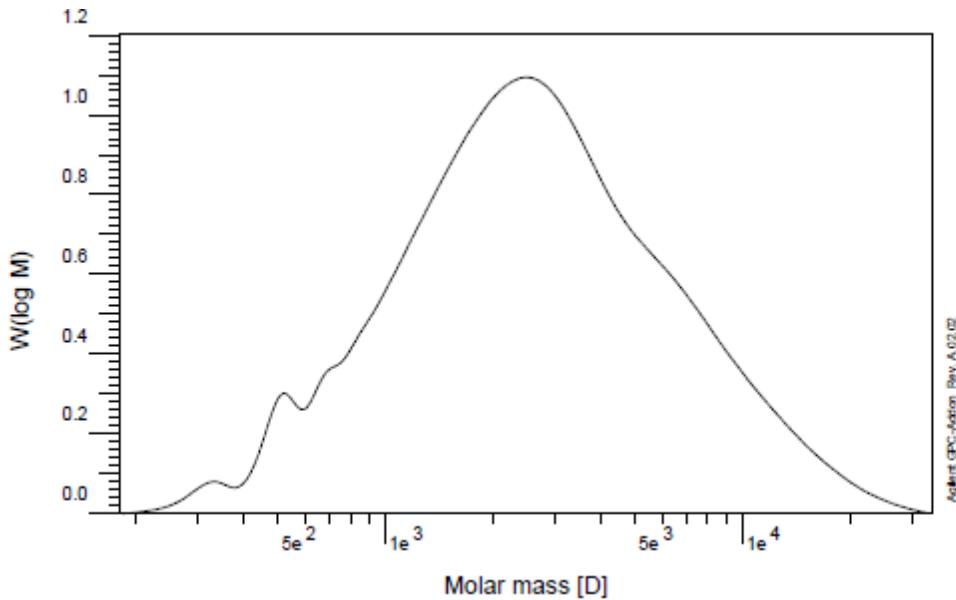
Sample :      5
Injection Date : 18-Jun-20, 07:28:56
Calibration File : C:\HPCHEM\1\DATA\KAZEMI\CAL990312.CAL
Calibration Date : Tuesday 20/06/09 13:51:38
Baseline from : 15.360 min
Integration from: 15.360 min
MHK - A (Cal.): 0.000000E+0
Eluent : THF
Concentration : 1.000 g/l
Column 1 : PLgel OH-MIXED C
Detector 1 : RID A, Refractive Index Signal
Operator : IPPI
rid1A

Mn : 1.1865e3 g/mol
Mw : 1.6566e3 g/mol
Mz : 2.4828e3 g/mol
Mv : 0.000000 g/mol
D : 1.3963e0
In: 0.000000 ml/g
Vp : 1.8245e1 ml
Mp : 7.8569e2 g/mol
A : 4.0481e3 ml^V
< 356 0.00
w% : 100.00
> 15012 0.00

```

Fig S23. GPC curve of prepared oligomer with Cp<sub>2</sub>HfCl<sub>2</sub>, [cat]= 10 μmol, [1-octene]= 0.08 mol,

t=18 h, Al/M= 500, T=80 °C



Sample : R-hf-OCT-80  
 Injection Date : 22-Jan-18, 09:15:45  
 Calibration File : C:\HPCHEM\1\DATA\13960802\96-10-01-cal-01.CAL  
 Calibration Date : Thursday 18/01/18 08:55:00  
 Baseline from : 14.473 min Baseline to : 19.575 min  
 Integration from : 14.473 min Integration to : 19.575 min  
 MHK - A (Cal.): 0.00000E+0 MHK - K (Cal.): 1.00000E+0 ml/g  
 Eluent : THF Flowrate : 1.000 ml/min  
 Concentration : 1.000 g/l Inject volume : 20.000  $\mu$ l  
 Column 1 : PLgel OH-MIXED C Temperature : 29.990 C  
 Detector 1 : RID A, Refractive Index Signal Delay volume : 0.000 ml  
 Operator : IPPI Acquisition interval : 0.430 sec  
**rid1A**  
Mn : 1.7754e3 g/mol  
Mw : 3.7812e3 g/mol  
Mz : 7.4847e3 g/mol  
Mv : 0.000000 g/mol  
D : 2.1288e0  
[n] : 0.000000 ml/g  
Vp : 1.7021e1 ml  
Mp : 2.4882e3 g/mol  
A : 3.3221e3 ml/V  
< 180 0.00  
w% : 100.00  
> 34213 0.00

Fig S24. GPC curve of prepared oligomer with  $Cp_2HfCl_2$ , [cat]= 10  $\mu$ mol, [1-octene]= 0.08 mol,

t=24 h, Al/M= 500, T=80 °C