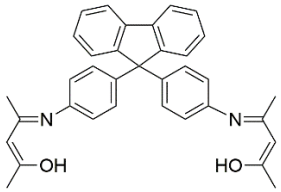
Instrumentation and materials

All manipulations were carried out using Schlenk techniques under an atmosphere of argon.
2,4-pentandione (99%), 4,4-diaminodiphenylmethane (97%), acetophenone, 4,4′-(9-Fluorenylidene)dianiline, ethanol (90%) was obtained from ABCR. Hydrogen chloride 1.25 M in ethanol was purchased by Acros. Cyclohexene oxide was obtained from ABCR 98% and was distilled over CaH_2 prior to use. Toluene was obtained from the solvent purification system MBraun (typ: MB SPS).
NMR-spectra were recorded on a Bruker ARX-300 spectrometer. All spectra were referenced to TMS or deuterated solvent as an internal standard.
GPC was performed with a PolymerLaboratoriesGPC-50 Plus chromatograph running with HPLC-grade in THF at a flow rate of 1 mL/min and PLgel-Mixed-C as the Column Set (by Varian, Inc. Company). Polystyrene standards were used for calibration.
In-situ IR-measurements were carried out on Mettler-Toledo system under argon atmosphere.
$Zn(N(SiMe_3)_2)_2$ and complex **1** and **3** were prepared according to the literature procedure.[5d]

Ligand and complex synthesis

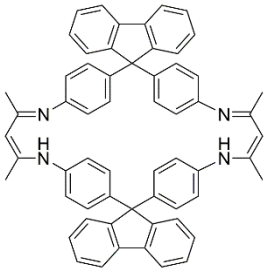
(2Z,2'Z,4E,4'E)-4,4'-(((9H-Fluorene-9,9-diyl)bis(4,1-phenylene))bis(azanylylidene))bis(pent-2-en-2-ol)



4,4′-(9-Fluorenylidene)dianiline (2.50 g, 7.17 mmol, 1. 0 eq.) and acetylacetone (1.47 ml, 14.35 mmol, 2.0 eq.) were dissolved in toluene (30 mL). p-Toluenesulfonic acid was added and the resulting reaction mixture was heated to 115 °C with a DeanStark trap for three hours. The reaction mixture was washed with saturated $NaHCO_3$-solution and the solvent was removed under reduced pressure. The product was obtained as a yellow solid and used without further purification (3.52 g, 96%).

^{1}H NMR (300 MHz, $CDCl_3$, 292 K): δ [ppm] = 12.37 (s, 2H), 7.00 (m, 8H), 5.13 (s, 2H), 2.04 (s, 3H), 1.91 (s, 3H).
^{13}C NMR (75.5 MHz, $CDCl_3$, 292 K): δ [ppm] = 196.2, 160.1, 150.7, 142.8, 140.1, 137.4, 128.8, 127.9, 127.7, 126.0, 124.2, 120.4, 97.8, 64.6, 29.2, 20.0.

$Bd(fluorenyl)_2H_2$



$Bd(fluorenyl)_2H2$/2 (1.00 g, 1.71 mmol, 1.0 eq.) and 4,4'-(9H-fluoren-9,9-diyl)dibenzenammonium chloride (0.72 g, 1.71 mmol, 1.0 eq.) were dissolved in hexafluoro-2-propanol$_{abs}$ (8.0 ml). Subsequent the reaction mixture was heated to 60 °C over night. The solvent is removed under reduced pressure. The residual solid was dissolved in methylene chloride and washed with saturated $NaHCO_3$-solution. The solvent is removed under reduced pressure to yield a yellow solid. After adding a small amount of methylene chloride (5 ml) the product precipitated and was finally recrystallized from toluene (0.30 g, 17%).

^{1}H NMR (300 MHz, THF 292 K): δ [ppm] = 12.37 (s, 2H), 7.00 (m, 8H), 5.13 (s, 2H), 2.04 (s, 3H), 1.91 (s, 3H).
^{13}C NMR (75.5 MHz, THF, 292 K): δ [ppm] = solubility not sufficient enough
EA (für $C_{60}H_{48}N_4$ + 2 toluene): calculated [%]: C 87.74, H 6.15, N 6.11
found [%]: C 87.35 , H 5.86 , N 6.79

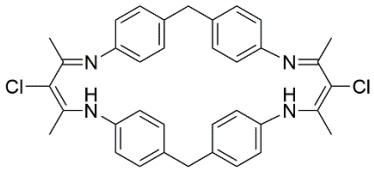
Bdm(Fluorenyl)$_2$H$_2$ (**2**)

Bd(fluorenyl)$_2$H$_2$ (0.23 g, 0.23 mmol, 1.0 eq.) was dissolved in toluene (20 ml) and bis[bis(trimethyl-silyl)amido]zinc (0.18 ml, 0.46 mmol, 2.0 eq.) was added at RT. The yellow suspension was heated to 90 °C for 24 hours. The solvent was removed in vacuo. The residue was washed with diethylether (20 ml) and the product is obtained as a yellow powder. (0.11 g, 35%)

^{1}H NMR (300 MHz, CDCl$_3$, 292 K): δ [ppm] = 7.80 (m, 8H), 7.42 (m, 8H), 7.14 (m, 8H), 6.62 (m, 8H), 4.93 (s, 2H), 1.88 (s, 12H), -0.17 (s, 36H).

EA (für C$_{48}$H$_{36}$F$_6$N$_4$): calculated [%]: C 67.85, H 6.48, N 6.59
found [%]: C 66,27 H 6.53, N 5.98

Bdm(Cl)$_2$H$_2$



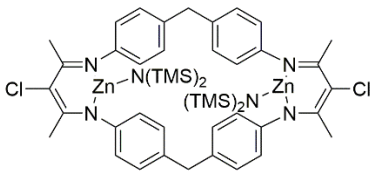
Diisopropylamine (0.06 ml, 0.41 mmol, 2.5 eq.) was dissolved in THF at 0°C. *n*-BuLi (0.25 mL, 0.41 mmol, 2.5 eq.) was dropwise added and the reaction mixture was stirred for two hours at ambient temperature. Subsequently, the addition of BdmH$_2$ (0.10 g, 0.16 mmol, 1.0 eq.) took place. After two more hours p-toluenesulfonyl chloride (0.08 g, 0.41 mmol, 2.5 eq.) was added and stirred for 24 hours at room temperature. The reaction mixture was dissolved in methylene chloride. After washing with saturated NaCl-solution, the solid was recrystallized from toluene (0.06 g, 61%).

^{1}H-NMR (300 MHz, CDCl$_3$, 295 K): δ [ppm] = 13.20 (s, 2H, NH), 7.02 (d, ^{3}J = 8.1 Hz, 8H, C$_{ar}$H), 6.67 (d, ^{3}J = 8.1 Hz, 8H, C$_{ar}$H), 3.77 (s, 4H, CH$_2$), 2.24 (s, 12H, CH$_3$).

^{13}C-NMR (75.5 MHz, CDCl$_3$, 294 K): δ [ppm] = 158.2, 142.2, 138.1, 128.4, 123.6, 103.9, 41.6, 18.9.

EA (für C$_{45}$H$_{42}$N$_6$ mit Toluol): calculated [%]: C 72.84, H 5.77, N 9.44
found [%]: C 72.76, H 5.86, N 9.38

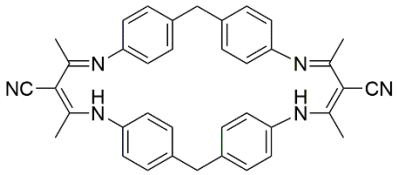
$Bdm(Cl)_2(Zn(N(TMS)_2)_2$ (**4**)



$Bdm(Cl)_2H_2$ (0.10 g 0.15 mmol, 1.0 eq.) was suspended in toluene (20 ml) and bis[bis(trimethylsilyl)amido]zinc (0.12 ml, 0.30 mmol, 2.0 eq.) was added at RT. The yellow suspension was heated to 90 °C for 24 hours. The solvent was removed in vacuo. The residue was washed with diethylether (20 ml) and the product is obtained as yellow powder. (0.08 g, 0.08 mmol, 51%)

^{1}H-NMR (300 MHz, $CDCl_3$, 295 K): δ [ppm] = 7.01 (s br, 16, $C_{ar}H$), 3.76 (s, 4H, CH_2), 2.32 (s, 12H, CH_3), -0.31 (s br, 36H)
EA (für $C_{45}H_{42}N_6$ mit Toluol): calculated [%]: C 55.27, H 6.57, N 8.06
found [%]: C 54.30, H 6.66, N 7.87

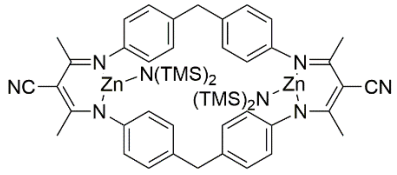
$Bdm(CN)_2H_2$



Diisopropylamine (0.28 ml, 2.03 mmol, 2.5 eq.) was dissolved in THF (20 ml) at room temperature. n-BuLi (0.81 mL, 2.03 mmol, 2.5 eq.) was dropwise added and the reaction mixture was stirred for two hours. Subsequently, the addition of $BdmH_2$ (0.50 g, 0.81 mmol, 1.0 eq.) took place. After two more hours p-toluenesulfonyl chloride (0.37 g, 2.03 mmol, 2.5 eq.) was added and stirred for 24 hours at room temperature. The orange solid was filtered and dissolved in methylene chloride. After washing with saturated $NaHCO_3$-solution, the solid was recrystallized from toluene (0.76 g, 65%).

^{1}H-NMR (300 MHz, $CDCl_3$, 297 K): δ [ppm] = 14.94 (s, 2H, N-H), 7.13 – 7.08 (d, ^{3}J = 8.35 Hz, 8H, C-H), 6.76 – 6.81 (d, ^{3}J = 8.35 Hz, 8H, C-H), 3.85 (s, 4H, CH_2), 2.33 (s, 12H, CH_3).
^{13}C-NMR (75.5 MHz, $CDCl_3$, 294 K): δ [ppm] = 164.6, 140.6, 140.0, 129.2, 128.4, 123.9, 122.0, 81.0, 41.7, 19.0.
EA (für $C_{45}H_{42}N_6$ mit Toluol): calculated [%]: C 82.29, H 6.64, N 11.07
found [%]: C 81.36, H 6.71, N 10.94

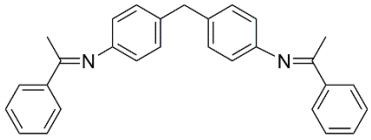
$Bdm(Cl)_2(Zn(N(TMS)_2)_2$ (**5**)



$Bdm(CN)_2H_2$ (0.09 g, 0.15 mmol, 1.0 eq.) was suspended in toluene (20.0 mL) and bis[bis(trimethyl-silyl)amido]zinc (0.12 ml, 0.30 mmol, 2.0 eq.) was added. The yellow suspension was heated to 90 °C for 24 hours. The suspension was separated into a solid and a solution which is dried under reduced pressure. Both fractions were washed with diethylether and dried. Both samples were analytically identical. Due to low solubility NMR spectroscopy was not possible.

EA (für $C_{58}H_{68}F_6N_6Si_4Zn_2$): calculated [%]: C 58.63, H 6.69, N 10.94
found [%]: C 59.58, H 6.72, N 10.58

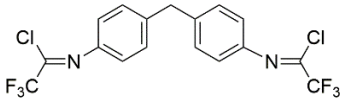
(N,N‘)-4,4'-Methylene-bis(N-(1-phenylethyliden)anilin) (**6**)



4,4-Diaminodiphenylmethane (5.00 g, 25.22 mmol, 1.0 eq.) was dissolved in methylene chloride (100 mL) and molecular sieve (3 Å) is added, following the addition of acetophenone (5.91 mL, 50.44 mmol, 2.0 eq.). The reaction was stored at room temperature for two days. After filtration and removal of the solvents under reduced pressure, recrystallization in ethanol led to the final product (5.94 g, 58%).

^{1}H-NMR (300 MHz, $CDCl_3$, 297 K): δ [ppm] = 7.93-8.01 (m, 4H), 7.48-7.38 (m, 6H), 7.18 (d, ^{3}J=8.4 Hz, 4H), 6.74 (d, ^{3}J=8.4 Hz, 4H), 3.97 (s, 2H), 2.25 (s, 6H).
^{13}C-NMR (75.5 MHz, $CDCl_3$, 294 K): δ [ppm] = 165.9, 149.6, 139.62 (s), 136.5, 133.3, 130.7, 129.7, 128.6, 127.4, 119.8, 115.6, 41.0, 17.7.
EA (für $C_{36}H_{34}Cl_2N_4$): calculated [%]: C 86.53, H 6.51, N 6.96
found [%]: C 86.14, H 6.61, N 7.04

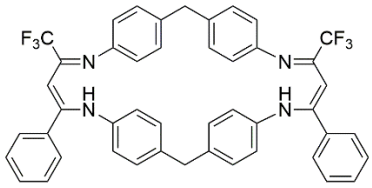
N',N''-(4,4'-Methylene-bis(4,1-phenylene))bis(2,2,2-trifluoroacetimidoyl chloride) (**7**)



Triphenylphosphine (34.60 g, 131.92 mmol, 4.8 eq), triethylamine (7.40 mL, 54.97 mmol, 2.0 eq) were dissolved in tetrachloromethane (150 mL). Trifluoroacetic acid (3.27 mL, 43.97 mmol, 1.6 eq.) is dropwise added at 0 °C and stirred for 20 min. Afterwards, 4-4-diaminophenylmethane (5.45 g, 37.48 mmol, 1.0 eq.) was added and the reaction mixture was stirred overnight at 85 °C. After removing the solvents under reduced pressure, the reaction mixture was filtrated and washed several times with hexane. The solvent were removed and the raw product was distilled ($1\cdot10^{-1}$ mmbar, 190 °C) to receive a clear solution (3.12 g, 29%).

^{1}H-NMR (300 MHz, $CDCl_3$, 297 K): δ [ppm] = 7.33-7.24 (m, 2H), 7.16-7.08 (m, 2H), 4.06 (s, 1H).
^{13}C-NMR (75.5 MHz, $CDCl_3$, 294 K): δ [ppm] = 141.7, 140.4, 131.4 (q, ^{2}J = 43.0 Hz), 129.8, 121.6, 117.1 (q, ^{1}J = 277.0 Hz), 41.2.
EA (für $C_{36}H_{34}Cl_2N_4$): calculated [%]: C 47.80, H 2.36, N 6.56
found [%]: C 47.71, H 2.28, N 6.41

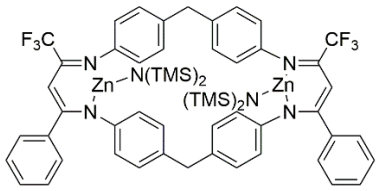
Bdm$(CF_3)_2(Ph)_2H_2$ (**8**)



n-BuLi (11.9 mL, 29.8 mmol, 4.0 eq.) was mixed with diisopropylamine (4.20 mL, 29.8 mmol, 4.0 eq.) in THF (100 mL) at -78 °C. After two hours 4,4'-methylen-bis-(N-(phenyl-2-yliden)aniline) (3.02 g, 7.45 mmol, 1.0 eq.) was added and the reaction mixture is stirred for 16 hours at room temperature before the addition N',N''-(4,4'-methylene-bis-(4,1-phenylene))bis(2,2,2-trifluoroacetimidoylchlorid) (3.00 g, 7.45 mmol, 1 eq.) was conducted. After two more hours the reaction was stopped via addition of saturated NH_4Cl-solution. The organic phase was separated, dried over magnesium sulfate and filtered. The organic solvent was removed under reduced pressure, following a recrystallization in acetone and finally in acetonitrile (0.18 g, 3%).

^{1}H-NMR (300 MHz, $CDCl_3$, 297 K): δ [ppm] = 12.76 (s, 2H), 7.44-7.50 (m, 4H), 7.30-7.40 (m, 6H), 7.15 (d, ^{3}J = 8.3 Hz, 4H), 6.84-6..78 (m, 8H), 6.52 (d, ^{3}J = 8.3 Hz, 4H), 5.58 (s, 2H), 3.83 (s, 2H), 3.62 (s, 2H).
^{13}C-NMR (75.5 MHz, $CDCl_3$, 294 K): δ [ppm] = 158.7, 149.9, 149.5, 144.4, 139.4, 138.8, 138.4, 135.8, 129.9, 129.3, 128.8, 128.8, 128.5, 123.5, 122.0, 94.2, 41.9, 41.0.
EA (für $C_{46}H_{34}F_6N_4$): calculated [%]: C 73.01, H 4.53, N 7.40
found [%]: C 72.60, H 4.46, N 7.63

$Bdm(CF_3)_2(Ph)_2(Zn(N(TMS)_2)_2$ (**9**)



$Bdm(CF_3)_2(Ph)_2H_2$ (0.25 g, 0.33 mmol, 1.0 eq.) was dissolved in toluene (50.0 ml) and bis[bis(trimethylsilyl)amido]zinc (0.26 mL, 0.67 mmol, 2.0 eq.) was added at RT. The yellow solution was heated to 90 °C for 24 hours. The solvent was removed in vacuo. The residue was washed with pentane (10 ml) and the product is obtained as a orange powder (0.30 g, 31%).

^{1}H-NMR (300 MHz, $CDCl_3$, 295 K): δ [ppm] = 7.43-7.46 (m, 4H), 7.38 – 7.21 (m, 6H), 7.03 (s, 4H), 6.81 (m, 8H), 6.57 (m, 4H), 5.70 (s, 2H), 3.80 (s, 2H), 3.54 (s, 2H). -0.27 (s br., 36H)
^{13}C-NMR (75.5 MHz, $CDCl_3$, 294 K): δ [ppm] = 169.7, 145.7, 144.6, 139.5, 138.7, 138.3, 130.5, 130.0, 129.2, 128.9, 128.4, 124.9, 123.6, 41.8, 4.86

EA (für $C_{58}H_{68}F_6N_6Si_4Zn_2$):	calculated [%]:	C 57.75, H 5.68, N 6.97
	found [%]:	C 56.81, H 6.09, N 6.89

Copolymerization with in situ IR

Catalyst was dissolved in cyclohexene oxide (5.0 mL, 49.4 mmol, 1.0 eq.) and toluene (5 – 7.5 mL). The reaction mixture was put in the preheated autoclave and pressurized with carbon dioxide (1, 10, 30, 40 bar). The reaction was terminated after the appropriate reaction time by releasing the gaseous CO_2 and addition of methanol (1.0 mL) and methylene chloride (10 mL). The organic phase was washed with HCl (1 M) and dried with Na_2SO_4. After evaporation of the solvent the poly(carbonate) is dissolved in a small amount of methylene chloride and precipitated via addition of methanol. Finally, the poly(carbonate) is dried in an oven to constant weight.

Poly(cyclohexene carbonate)

^{1}H-NMR (300 MHz, CDCl3, 292K): δ [ppm] = 4.58 (s, 2 H), 1.30-2.04 (m, 8 H).

Poly(cyclohexene oxide)

^{1}H-NMR (300 MHz, CDCl3, 292 K): δ [ppm]c = 3.50 (s, br., 2 H);

Copolymerization at one atmosphere CO_2

Catalyst was dissolved in cyclohexene oxide (2.5 mL, 24.7 mmol, 1.0 eq.) and put into a pressure flask. Afterwards, CO_2 is bubbled through the reaction mixture for 4 min, before the pressure of 1 bar CO_2 is adjusted. After a reaction time of 1 h at 100 °C, the reaction was terminated by adding methanol (1.0 mL) and methylene chloride (10 mL). The organic phase was washed with HCl (1 M) and dried with Na_2SO_4. After evaporation of the solvent the poly(carbonate) is dissolved in a small amount of methylene chloride and precipitated via addition of methanol. Finally, the poly(carbonate) is dried in an oven to constant weight.

Table S 1: Copolymerization of cyclohexene oxide and CO_2 with catalyst 1 and 9 at one atmosphere CO_2 pressure[a]

entry	Cat.	TON[b]	TOF[c] [h^{-1}]	%PCHC	%conversion
1	1	409	409	85	10
2	9	939	939	47	23

[a] Copolymerizations were conducted in a preheated schlenk flask for 60 minutes at a catalyst loading of catalyst/epoxide of 1/4000 in neat cyclohexene oxide at one atmosphere CO_2 pressure and 100 °C (1 bar CO_2) [b] The turnover number (TON) is calculated by the number of moles of consumed epoxide divided by the moles of catalyst. [c] TOF = TON/time

Homopolymerization of cyclohexene oxide

Catalyst was dissolved in cyclohexene oxide (2.5 mL, 24.7 mmol, 1.0 eq.) and put into a pressure flask. After a reaction time of 1 h at 100 °C, the reaction was terminated by adding methanol (1.0 mL) and methylene chloride (10 mL). The organic phase was washed with HCl (1 M) and dried with Na_2SO_4. After evaporation of the solvent the poly(carbonate) is dissolved in a small amount of methylene chloride and precipitated via addition of methanol. Finally, the poly(carbonate) is dried in an oven to constant weight.

Table S 2: Homopolymerization of cyclohexene oxide with catalyst 1 and 9[a]

entry	Cat.	TON[b]	TOF[c] [h^{-1}]	%conversion
1	1	44	44	1
2	9	211	211	5

[a] Copolymerizations were conducted in a preheated schlenk flask for 60 minutes at a catalyst loading of catalyst/epoxide of 1/4000 in neat cyclohexene oxide at 100 °C [b] The turnover number (TON) is calculated by the number of moles of consumed epoxide divided by the moles of catalyst. [c] TOF = TON/time

GPC-Reports (of table 1)

Entry 1:

Sample Details

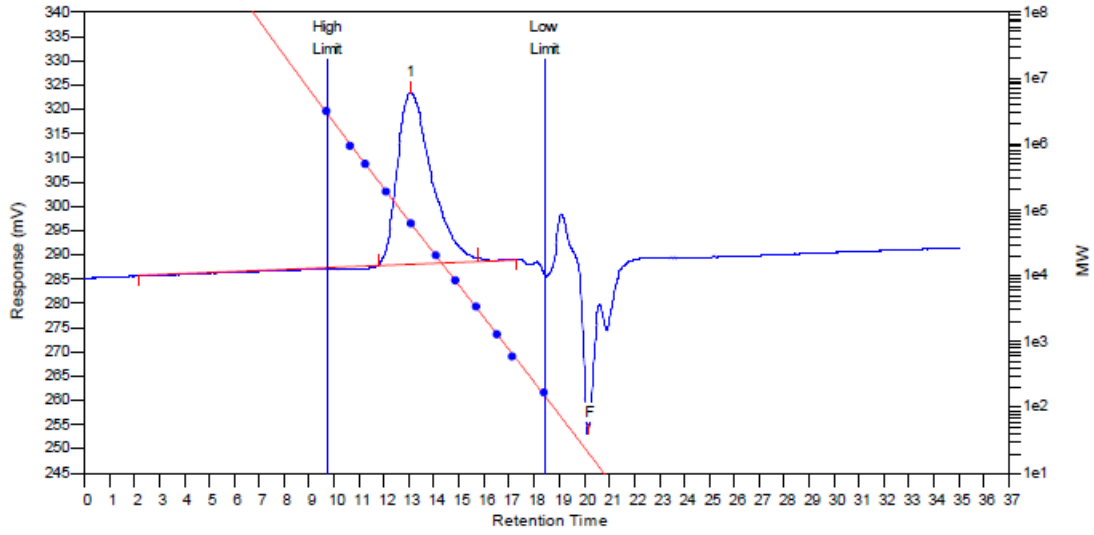
Sample Name: KSS-516thf
Batch Name: 2014-7-24
Filename: C:\Cirrus Workbooks\RI-THF-2013-03-22\2014-7-24-0001.cgrm
Acquired: 29.07.2014 09:42:43
Eluent: THF stablised with 250 ppm BHT
Injection Volume: 100.0 ul
Flow Rate: 1.000000 ml/min
Concentration: mg/ml
Temperature: 35
Column Set: PLgel-Mixed-C
Column Set Length: 600.000000 mm

Analysis Using Method: RI-Auswertung

Results File: C:\Cirrus Workbooks\RI-THF-2013-03-22\2014-7-24-0001-Repeat (01).rst

Calibration Used: 22.03.2013 13:51:19

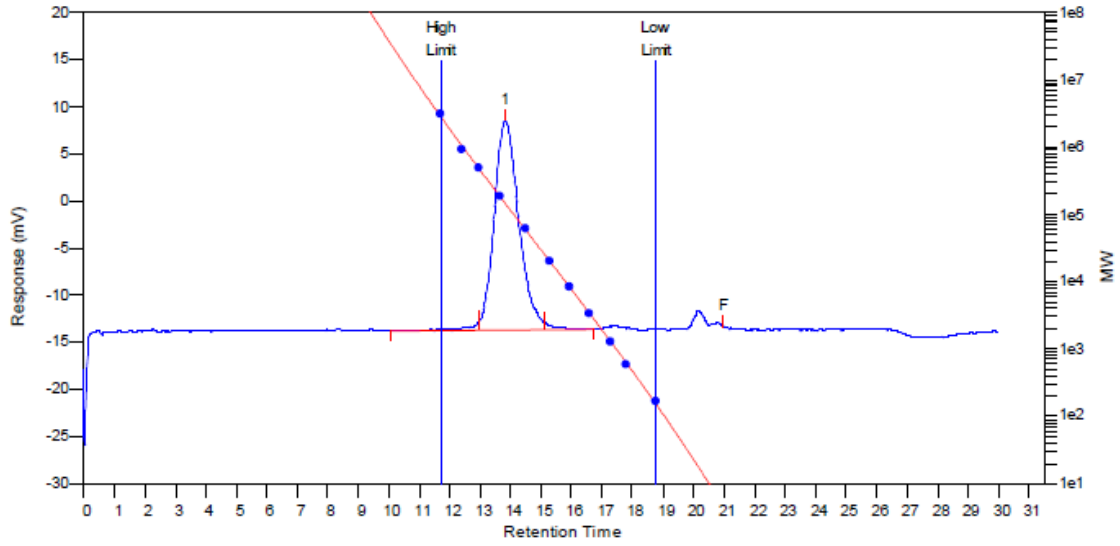
Calibration Type: Narrow Standard
Curve Fit Used: 3
Calibration Curve: y = 11.880254 - 0.627940x^1 + 0.009128x^2 - 0.000197x^3



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	63568	32042	58540	85062	109039	54701	1.82698

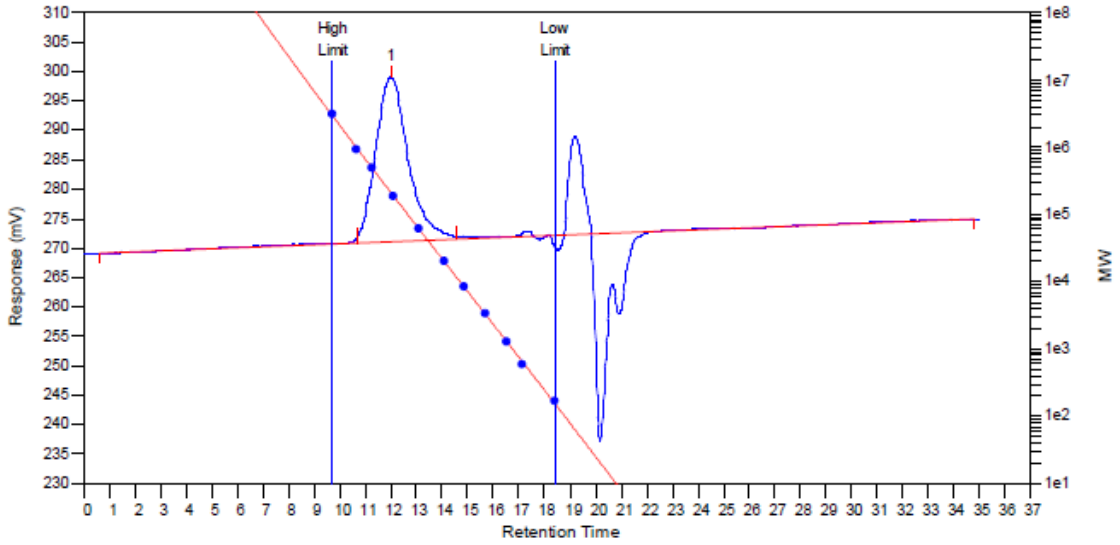
Entry 2:



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	146517	113667	147864	185218	222637	142470	1.30085

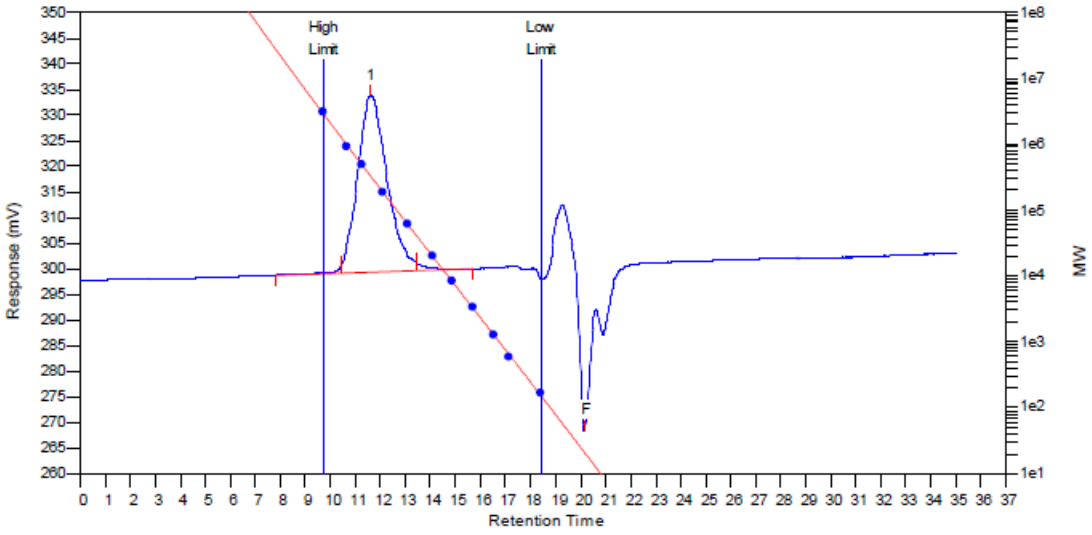
Entry 3:



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	208784	132266	230232	332454	432198	215909	1.74067

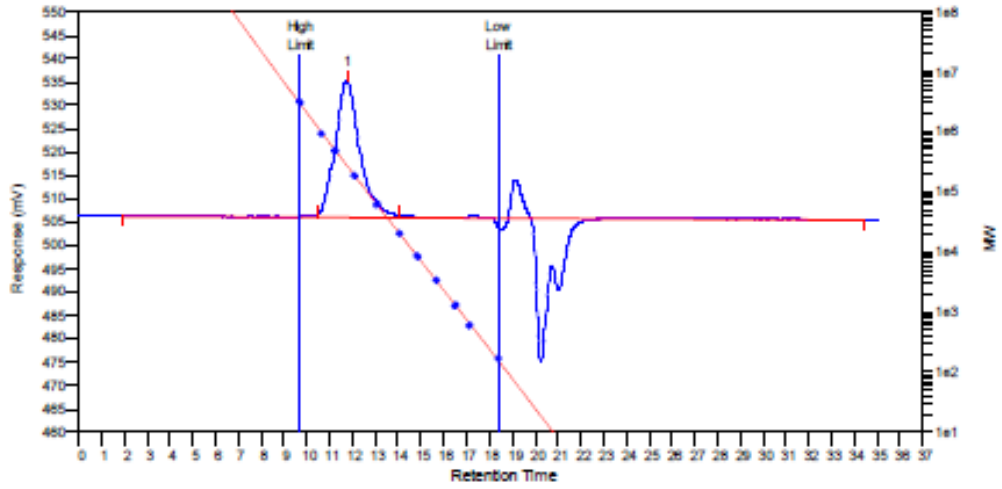
Entry 4:



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	323072	227981	340007	467499	594166	322222	1.49138
2	0	0	0	0	0	0	0

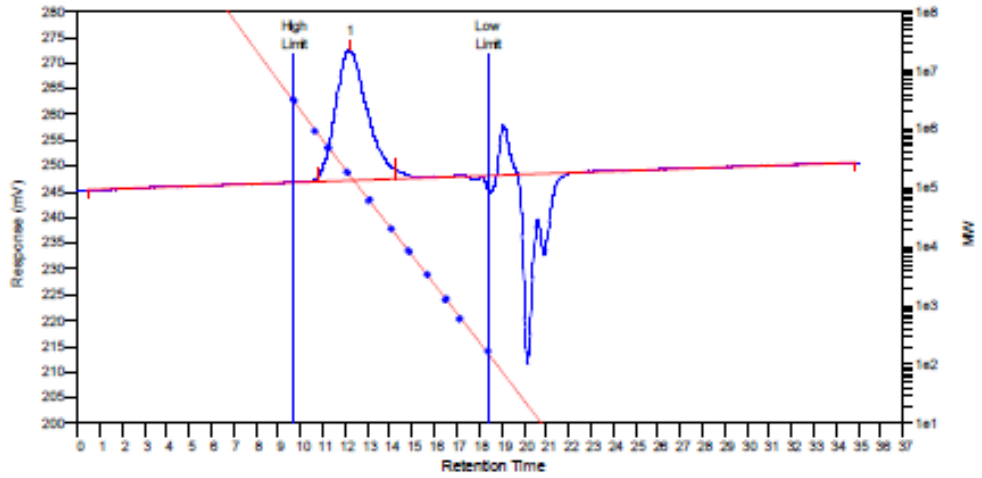
Entry 5:



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	277510	193359	296907	404144	513164	281827	1.53552

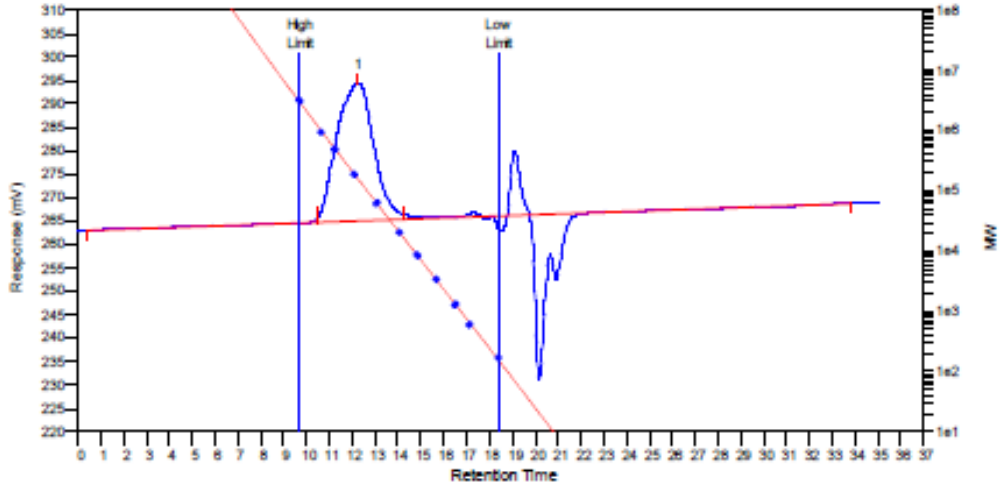
Entry 6:



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	169526	103487	179577	271314	361470	167109	1.73526

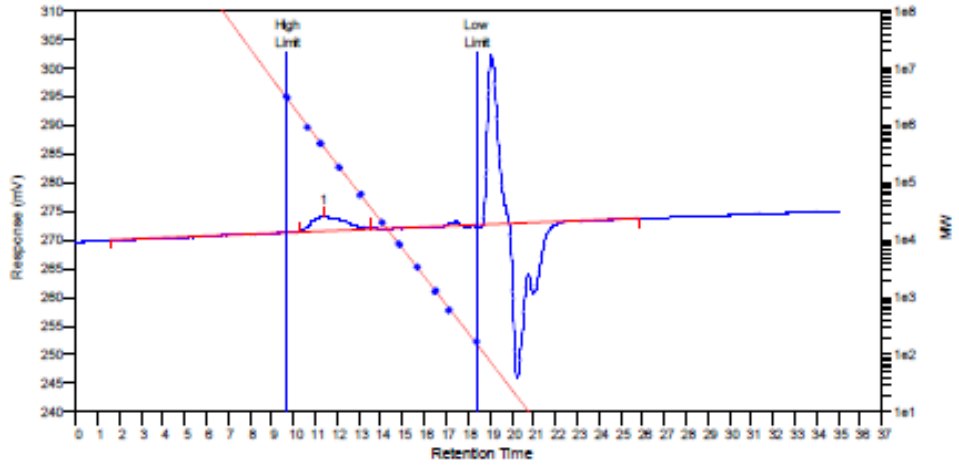
Entry 7:



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	157171	127823	235657	381350	526163	216849	1.84362

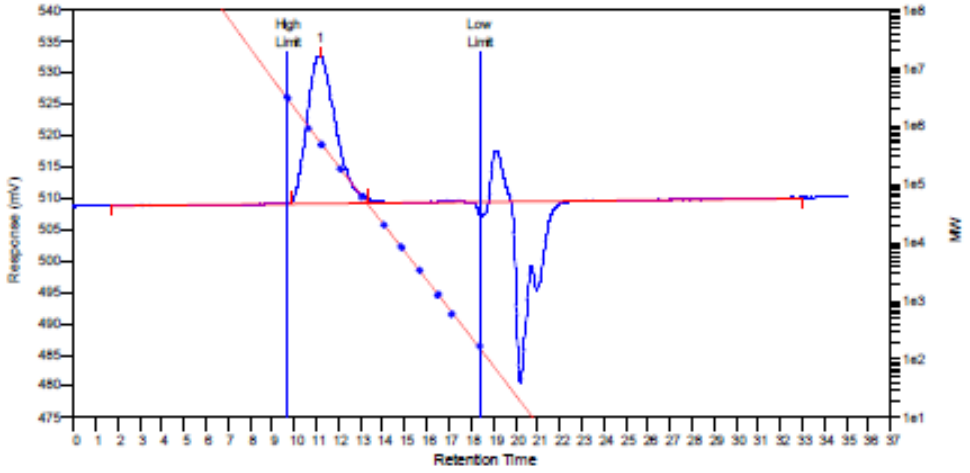
Entry 8:



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	429842	206858	381461	581903	746867	352735	1.84407

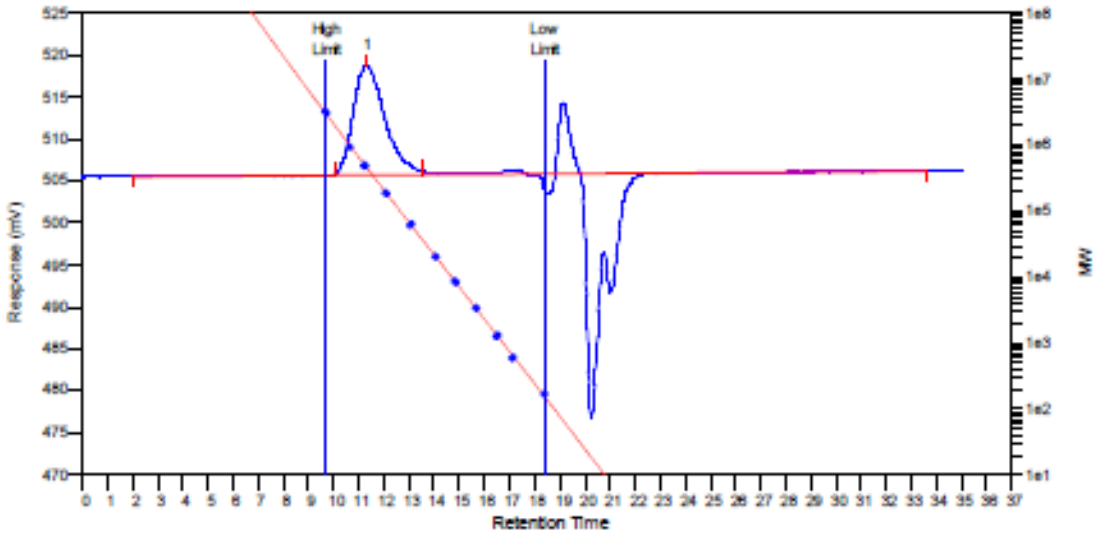
Entry 9:



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	561466	349850	574202	816958	1047078	539947	1.64128

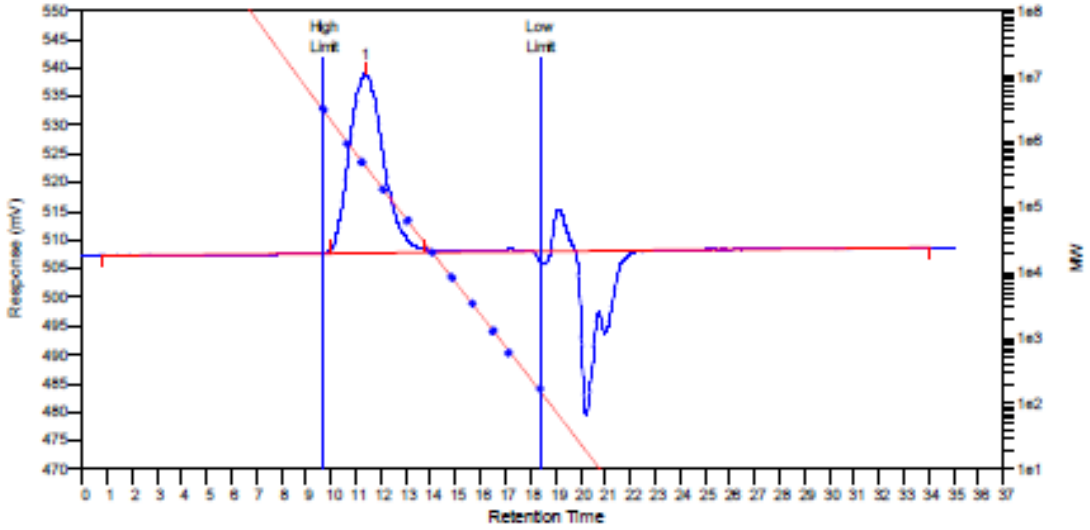
Entry 10:



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	446545	278093	454121	636623	807702	427955	1.63298

Entry 11:



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	421728	278906	474867	694643	908764	444600	1.70261