

Supporting Information

An Asymmetric Dinuclear Bis(*ansa*-Zirconocene) Complex: Synthesis and Performance in Olefin (co-)Polymerization

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Figure S1: ¹ H NMR spectrum (CDCl ₃ , 400 MHz, 25 °C) of 1	3
Figure S2: ¹³ C{ ¹ H} NMR spectrum (CDCl ₃ , 100 MHz, 25 °C) of 1	3
Figure S3: ¹ H NMR spectrum (CDCl ₃ , 400 MHz, 25 °C) of 2	4
Figure S4: ¹ H NMR spectrum (CDCl ₃ , 400 MHz, 25 °C) of 4	5
Figure S5: ¹³ C{ ¹ H} NMR spectrum (CDCl ₃ , 100 MHz, 25 °C) of 4	5
Figure S6: ¹ H- ¹³ C HSQC NMR spectrum (CDCl ₃ , 400 MHz, 25 °C) of 4	5
Figure S7: ¹ H NMR spectrum (C ₆ D ₆ , 400 MHz, 25 °C) of 5	6
Figure S8: ¹³ C{ ¹ H} NMR spectrum (C ₆ D ₆ , 100 MHz, 25 °C) of 5	6
Figure S9: ¹ H- ¹³ C HSQC NMR spectrum (C ₆ D ₆ , 400 MHz, 25 °C) of 5	6
Figure S10: ¹ H NMR spectrum (CDCl ₃ , 400 MHz, 25 °C) of 6	7
Figure S11: ¹³ C{ ¹ H} NMR spectrum (CDCl ₃ , 100 MHz, 25 °C) of 6	7
Figure S12: Selected regions of the ¹³ C{ ¹ H} NMR spectrum (CD ₂ Cl ₂ , 100 MHz, 25 °C) of 6	
Figure S13: ¹ H- ¹³ C HSQC spectrum (CD ₂ Cl ₂ , 400 MHz, 25 °C) of 6	9
Figure S14: ¹ H- ¹³ C HMBC NMR spectrum (CD ₂ Cl ₂ , 400 MHz, 25 °C) of 6	9
Figure S15: ¹ H NMR spectrum (CDCl ₃ , 400 MHz, 25 °C) of 7	10
Figure S16: ¹³ C{ ¹ H} NMR spectrum (CDCl ₃ , 100 MHz, 25 °C) of 7	10
Figure S17: ¹ H- ¹³ C HSQC NMR spectrum (CDCl ₃ , 400 MHz, 25 °C) of 7	10
Figure S18: ¹ H NMR spectrum (CD ₂ Cl ₂ , 400 MHz, 25 °C) of 8	11
Figure S19: ¹³ C{ ¹ H} NMR spectrum (CD ₂ Cl ₂ , 100 MHz, 25 °C) of 8	11
Figure S20: ¹ H- ¹³ C HSQC NMR (CD ₂ Cl ₂ , 400 MHz, 25 °C) of 8	11
Figure S21: ¹ H- ¹³ C HMBC NMR spectrum (CD ₂ Cl ₂ , 400 MHz, 25 °C) of 8	12
Figure S22: ¹ H NMR spectrum (CD ₂ Cl ₂ , 400 MHz, 25 °C) of 9	13
Figure S23: ¹³ C{ ¹ H} NMR spectrum (CD ₂ Cl ₂ , 100 MHz, 25 °C) of 9	13
Figure S24: ¹ H- ¹³ C HSQC NMR spectrum (CD ₂ Cl ₂ , 400 MHz, 25 °C) of 9	14
Figure S25: ¹ H- ¹³ C HBC NMR spectrum (CD ₂ Cl ₂ , 400 MHz, 25 °C) of 9	14

Figure S26: Detail of the ^1H - ^1H COSY NMR spectrum (CD_2Cl_2 , 400 MHz, 25 °C) of 9	15
Figure S27: Detail of the ^1H - ^1H COSY NMR spectrum (CD_2Cl_2 , 400 MHz, 25 °C) of 9	15
Figure S28: ASAP mass spectrum (300 °C) of 9	16
Figure S29: MALDI-TOF mass spectrum (DCTB-Matrix) of 9	16
Table S1: Crystallographic Data for Compounds 5 , 6 , and 7	16
Figure S30: $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (1,2,5-trichlorobenzene/ C_6D_6 , 125 MHz, 135 °C) of ethylene/1-hexene copolymers prepared with complex 9 and corresponding composition determined thereof (Table 3, entries 11 and 12).	
Figure S31: $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (1,2,5-trichlorobenzene/ C_6D_6 , 125 MHz, 135 °C) of ethylene/1-hexene copolymers prepared with complexes 9 and M , and corresponding composition determined thereof (Table 3, entries 13–15).	
Figure S32: SEC trace of a PP prepared with complex 9 (Table 2, entry 6).	
Figure S33: SEC trace of a poly(ethylene- <i>co</i> -1-hexene) prepared with complex 9 (Table 3, entry 11).	
Figure S34: SEC trace of a poly(ethylene- <i>co</i> -1-hexene) prepared with complex 9 (Table 3, entry 12).	
Figure S35: SEC trace of a poly(ethylene- <i>co</i> -1-hexene) prepared with complex 9 (Table 3, entry 13).	
Figure S36: SEC trace of a poly(ethylene- <i>co</i> -1-hexene) prepared with complex M (Table 3, entry 14).	
Figure S37: SEC trace of a poly(ethylene- <i>co</i> -1-hexene) prepared with complex M (Table 3, entry 15).	
Figure S38: DSC trace of a polypropylene prepared with complex 9 (Table 2, entry 6).	
Figure S39: DSC trace of a polypropylene prepared with complex 9 (Table 2, entry 7).	
Figure S40: DSC trace of a polypropylene prepared with complex 9 (Table 2, entry 8).	
Figure S41: DSC trace of a polypropylene prepared with complex M (Table 2, entry 9).	
Figure S42: DSC trace of a polypropylene prepared with complex M (Table 2, entry 10).	
Figure S43: DSC trace of a poly(ethylene- <i>co</i> -1-hexene) prepared with complex 9 (Table 3, entry 11).	
Figure S44: DSC trace of a poly(ethylene- <i>co</i> -1-hexene) prepared with complex 9 (Table 3, entry 12).	
Figure S45: DSC trace of a poly(ethylene- <i>co</i> -1-hexene) prepared with complex 9 (Table 3, entry 13).	
Figure S46: DSC trace of a poly(ethylene- <i>co</i> -1-hexene) prepared with complex M (Table 3, entry 14).	
Figure S47: DSC trace of a poly(ethylene- <i>co</i> -1-hexene) prepared with complex M (Table 3, entry 15).	

1:

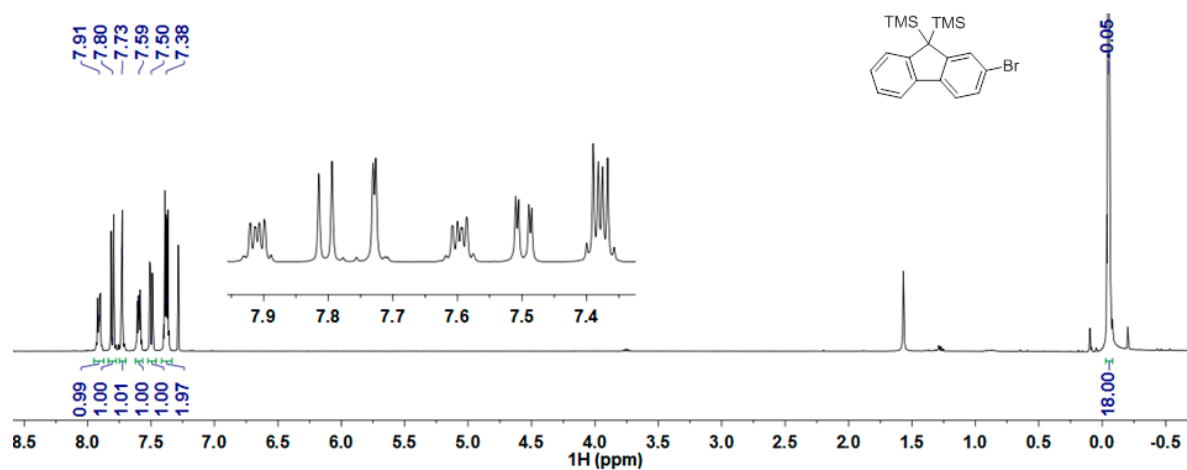


Figure S1: ¹H NMR spectrum (CDCl₃, 400 MHz, 25 °C) of **1**

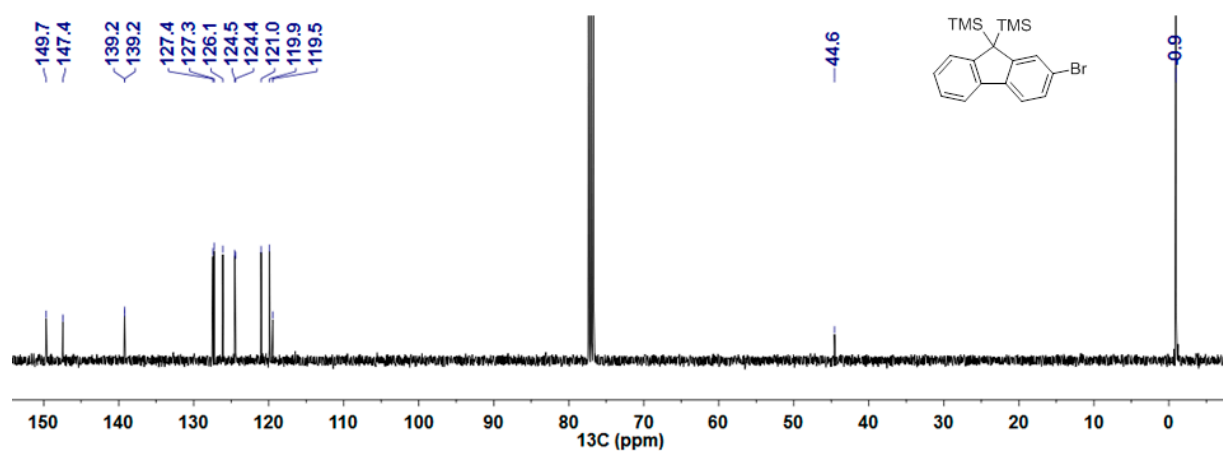


Figure S2: ¹³C{¹H} NMR spectrum (CDCl₃, 100 MHz, 25 °C) of **1**

2:

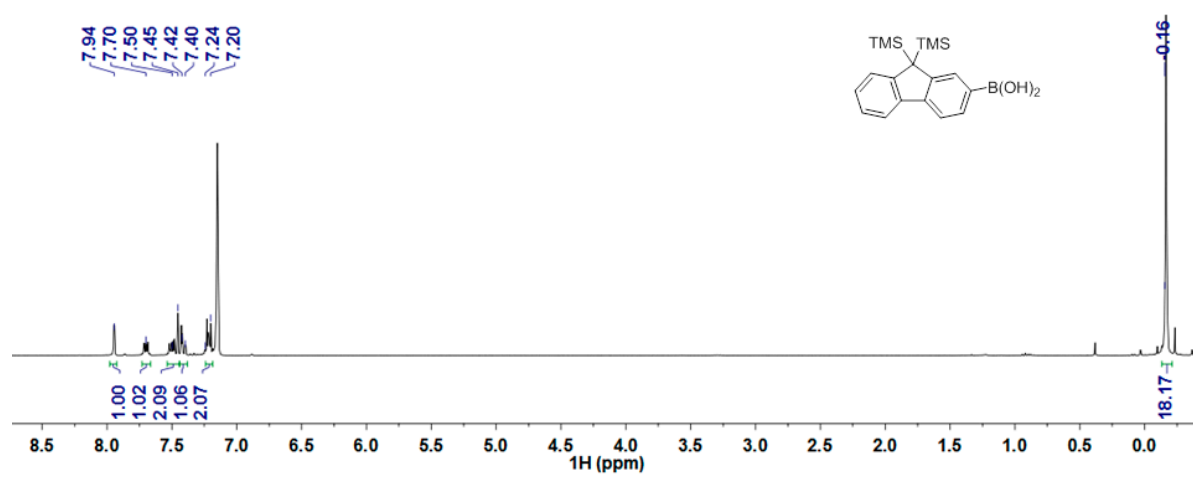


Figure S3: ^1H NMR spectrum (CDCl_3 , 400 MHz, 25 °C) of **2**

4:

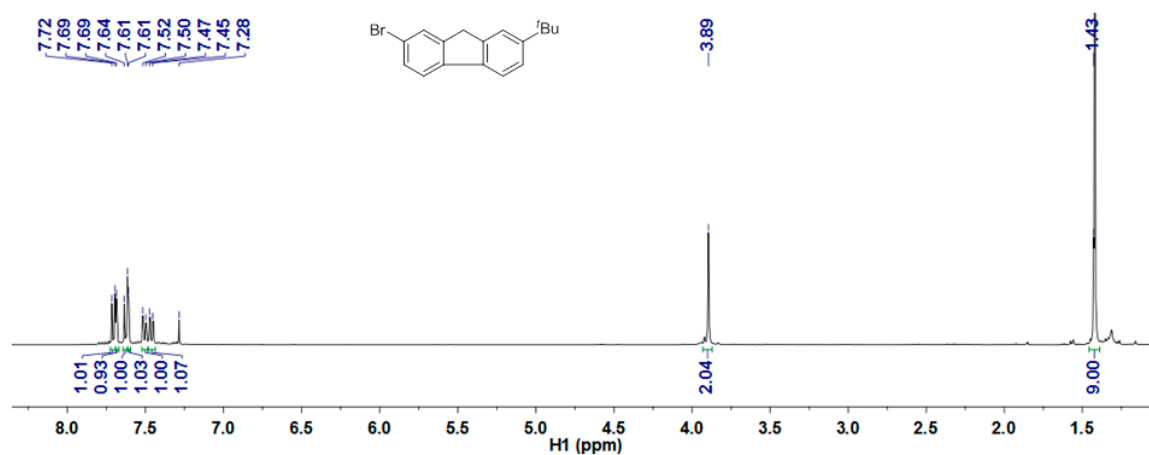


Figure S4: ¹H NMR spectrum (CDCl₃, 400 MHz, 25 °C) of 4

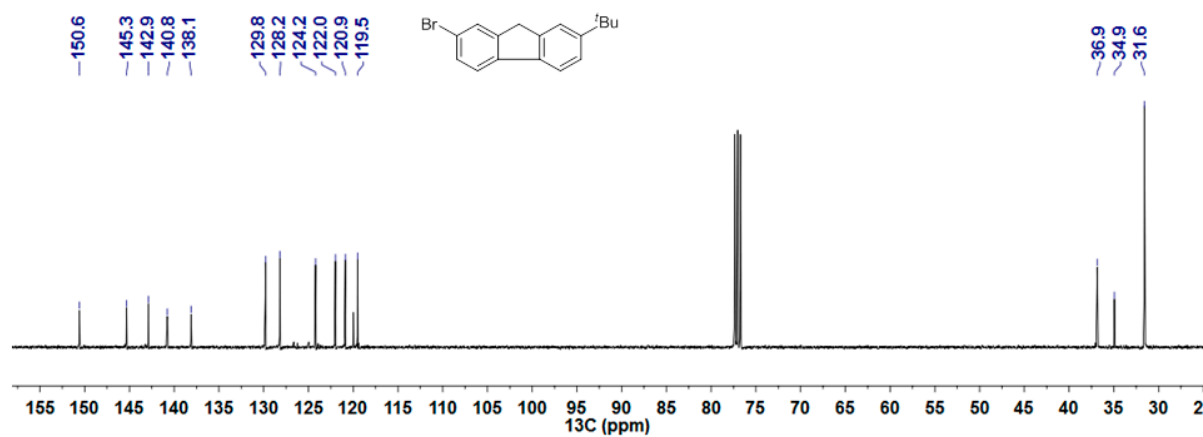


Figure S5: ¹³C{¹H} NMR spectrum (CDCl₃, 100 MHz, 25 °C) of 4

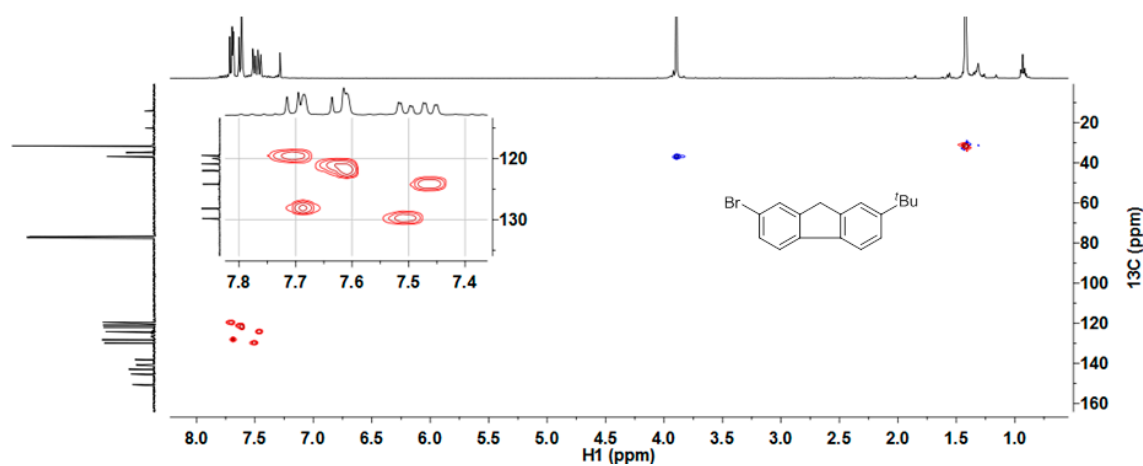


Figure S6: ¹H-¹³C HSQC NMR spectrum (CDCl₃, 400 MHz, 25 °C) of 4

5:

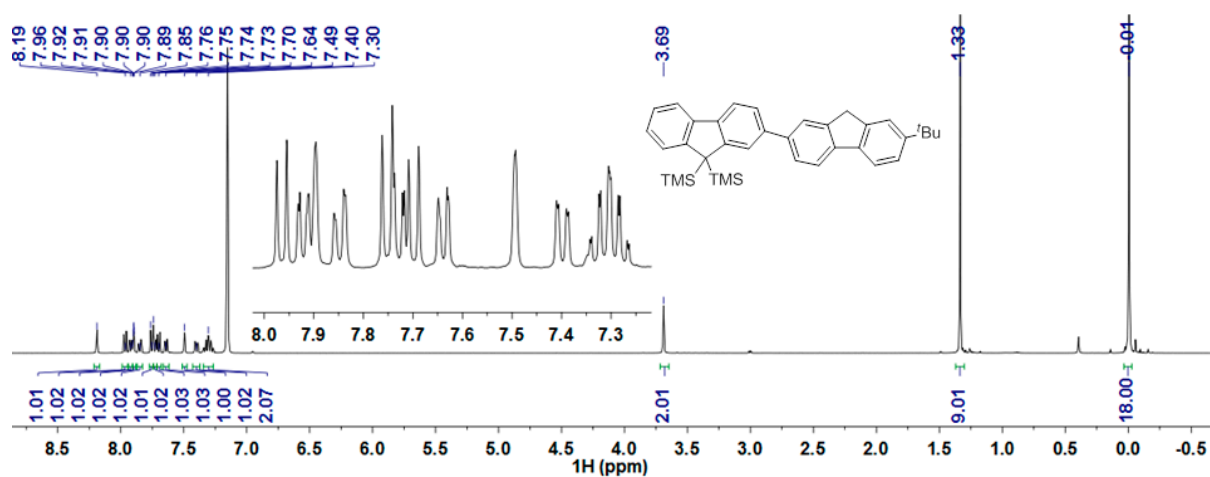


Figure S7: ¹H NMR spectrum (C₆D₆, 400 MHz, 25 °C) of **5**

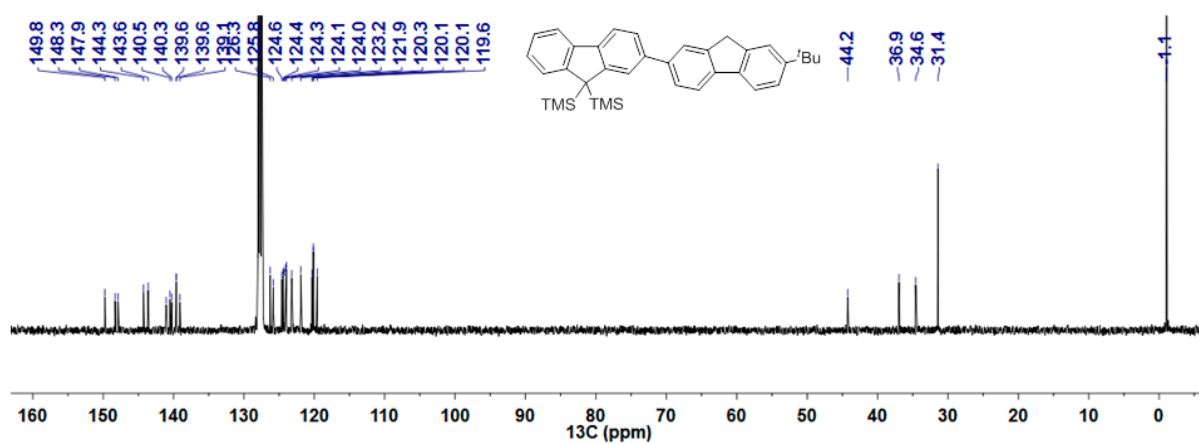


Figure S8: ¹³C{¹H} NMR spectrum (C₆D₆, 100 MHz, 25 °C) of **5**

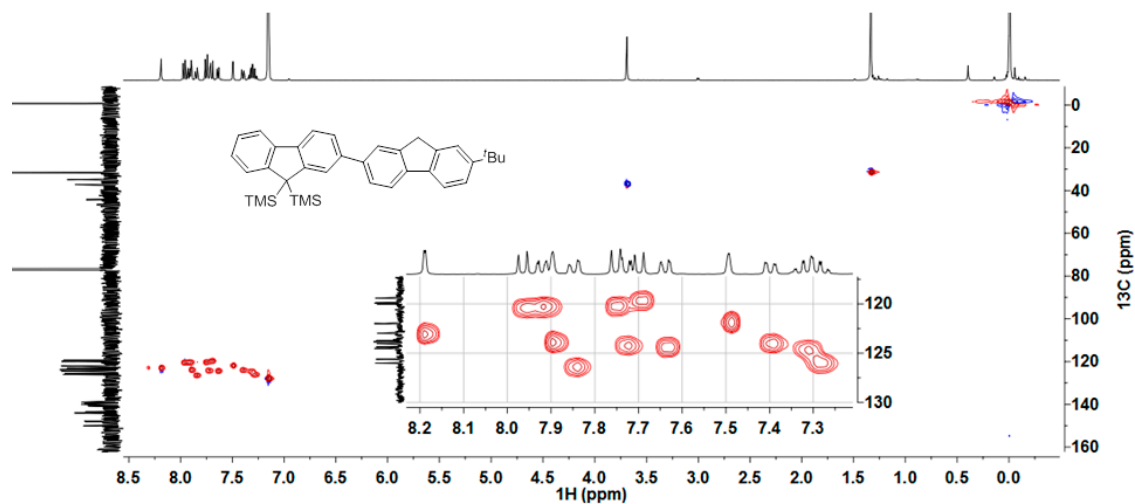


Figure S9: ¹H-¹³C HSQC NMR spectrum (C₆D₆, 400 MHz, 25 °C) of **5**

Chemical structure of compound 10 is shown above the spectrum. The structure is a fluorene derivative with two TMS groups at positions 9 and 10, and a tert-butyl group at position 1.

¹H NMR spectrum (CDCl₃) of compound 10. The x-axis represents the chemical shift in ppm, ranging from -0.5 to 8.5. The spectrum shows several peaks, with integrations provided below the baseline.

Peak list (ppm): 8.05, 8.02, 7.92, 7.83, 7.74, 7.72, 7.70, 7.68, 7.66, 7.45, 7.23, 7.09, 6.93, 6.61, 6.53, 6.23, 6.02, 4.32, 4.28, 3.30, 3.15, 1.37, 1.35, 1.34, 0.99, 0.03, 0.01.

Integration values (from left to right): 1.04, 1.03, 1.04, 1.07, 0.95, 1.13, 0.94, 1.05, 0.93, 3.12, 0.51, 0.99, 0.48, 0.50, 0.51, 0.49, 0.50, 0.51, 0.49, 0.50, 0.51, 1.04, 1.01, 3.05, 9.27, 3.00, 18.43.

Chemical structure of compound 10 is shown above the spectrum. The structure is a dimer of two fluorene units linked by a biphenyl group. One fluorene unit is substituted with a TMS group at the 9-position, and the other is substituted with a t-butyl group at the 9-position.

¹³C NMR spectrum (ppm): 157.9, 155.6, 149.3, 149.2, 148.2, 148.2, 147.9, 146.3, 146.2, 145.5, 145.5, 140.0, 139.3, 139.3, 139.3, 139.2, 139.1, 138.9, 134.3, 133.2, 133.2, 131.1, 126.6, 126.1, 126.1, 125.7, 125.2, 125.0, 124.8, 124.6, 124.4, 124.0, 123.7, 123.6, 123.5, 123.3, 123.0, 119.9, 119.8, 119.8, 119.4, 118.6, 58.0, 55.7, 44.3, 41.1, 40.8, 39.5, 34.7, 34.6, 31.3, 1.1, -1.1.

Figure S5: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 100 MHz, 25 °C) of **6**

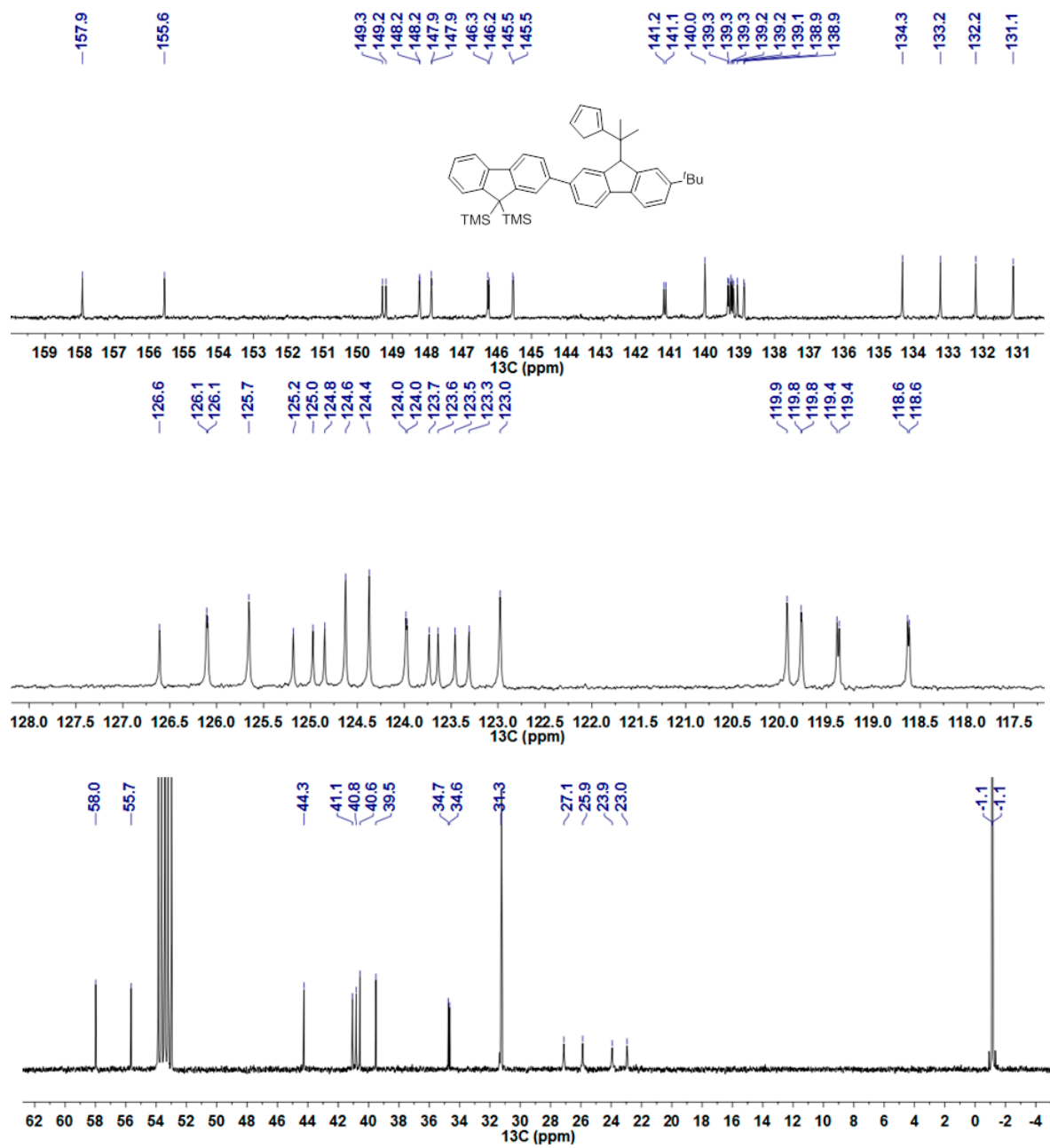


Figure S6: Selected regions of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CD_2Cl_2 , 100 MHz, 25 °C) of **6**

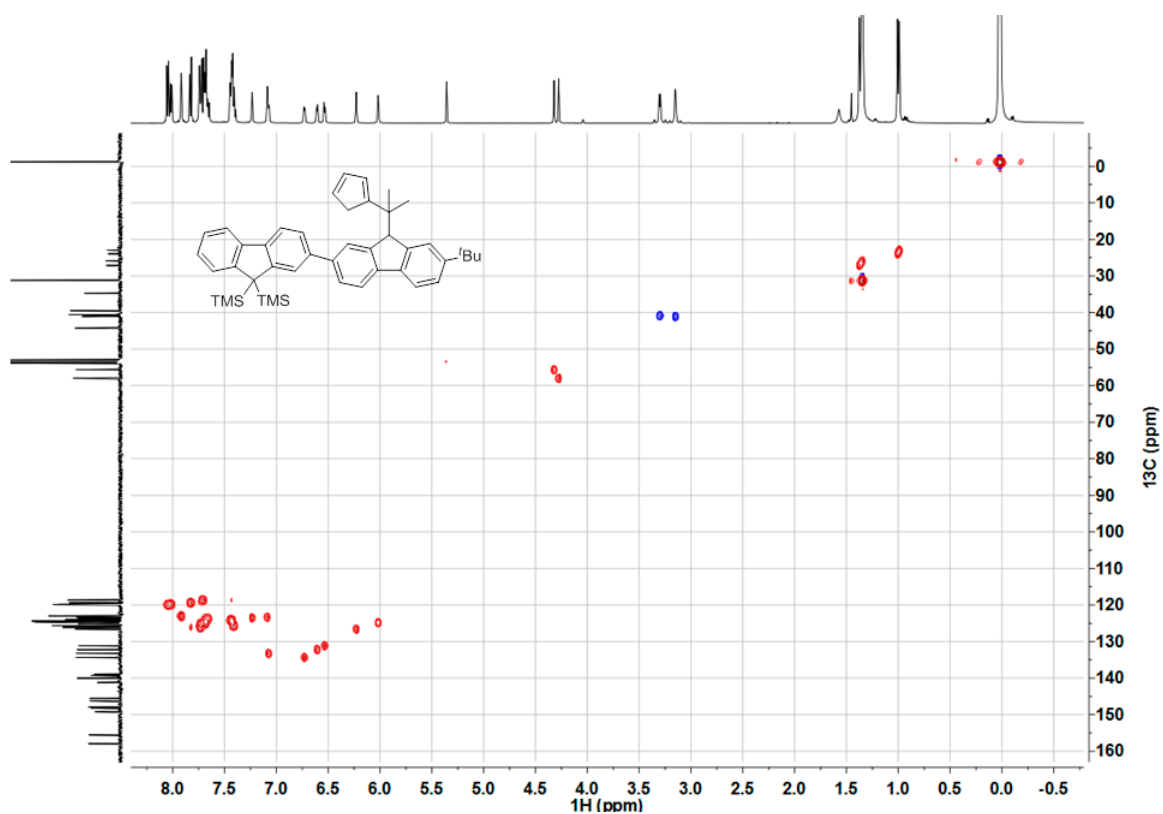


Figure S7: ^1H - ^{13}C HSQC spectrum (CD_2Cl_2 , 400 MHz, 25 $^\circ\text{C}$) of **6**

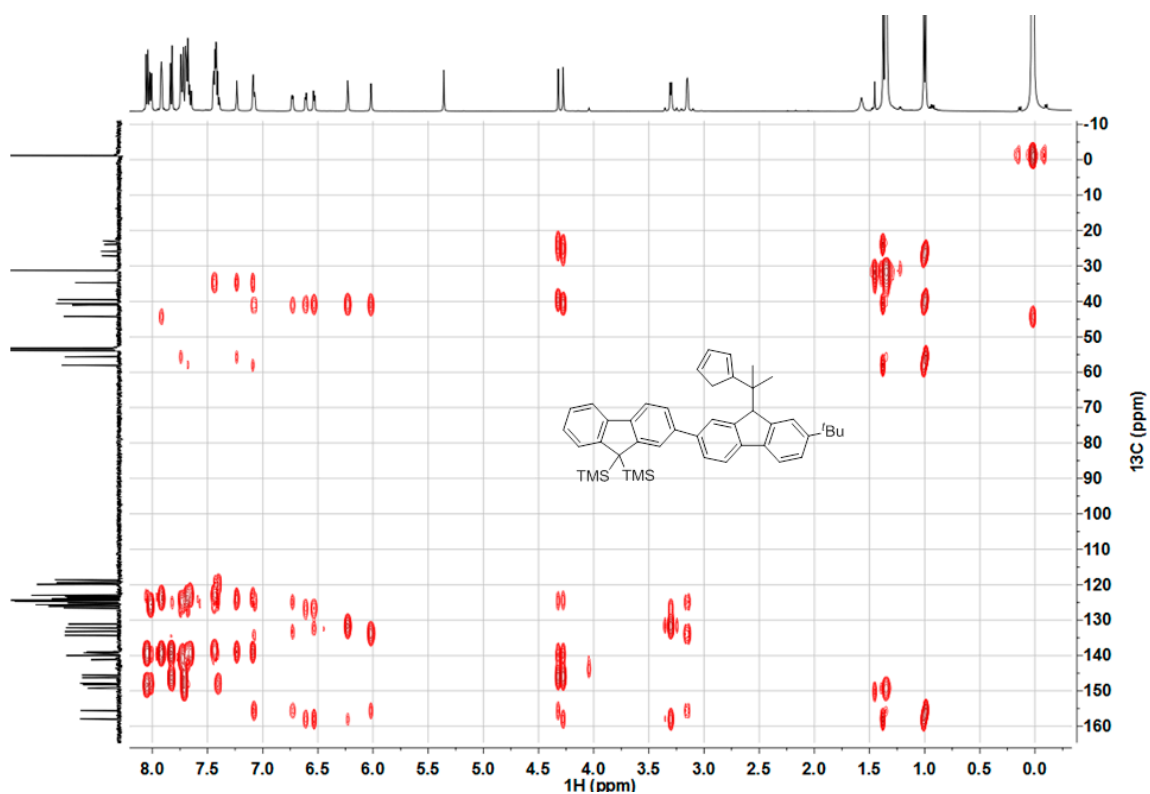


Figure S8: ^1H - ^{13}C HMBC NMR spectrum (CD_2Cl_2 , 400 MHz, 25 $^\circ\text{C}$) of **6**

7:

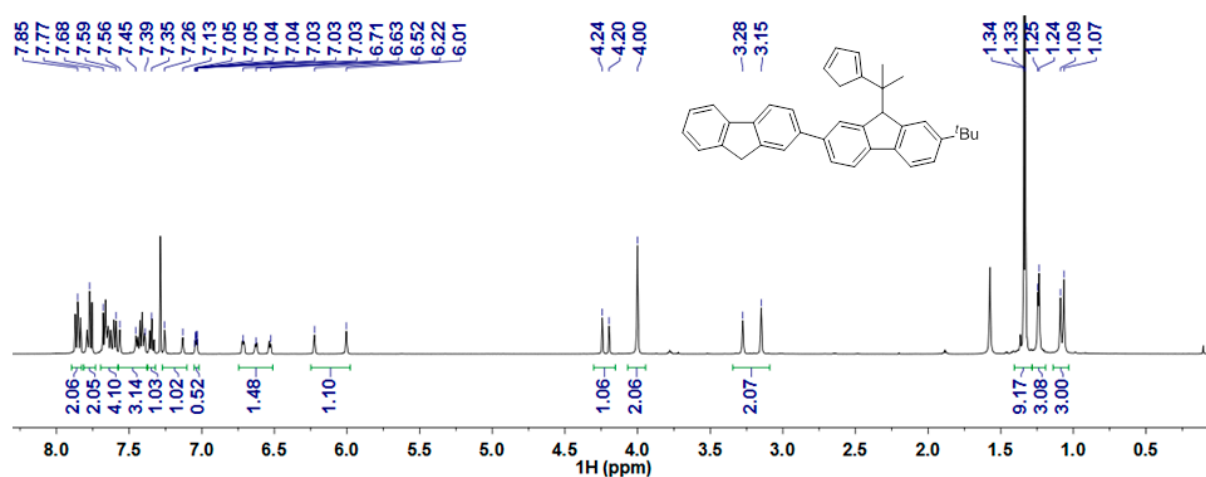


Figure S9: ¹H NMR spectrum (CDCl₃, 400 MHz, 25 °C) of 7

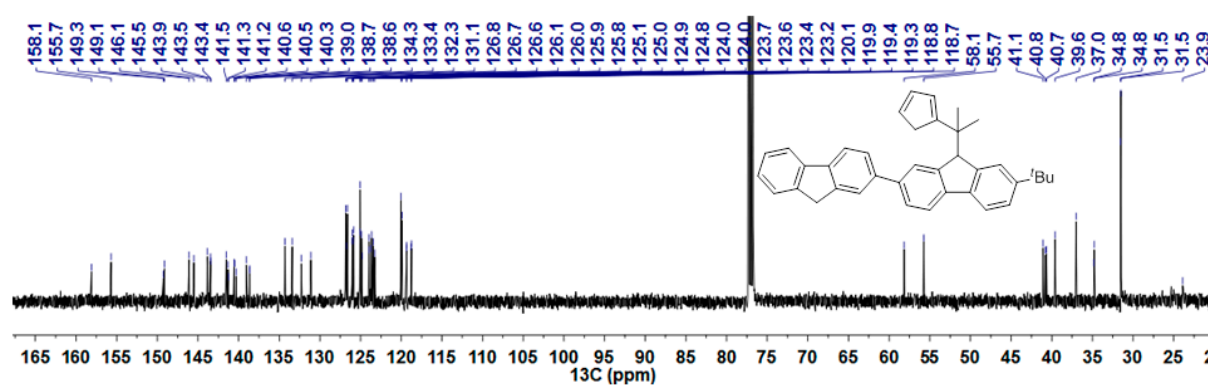


Figure S10: ¹³C{¹H} NMR spectrum (CDCl₃, 100 MHz, 25 °C) of 7

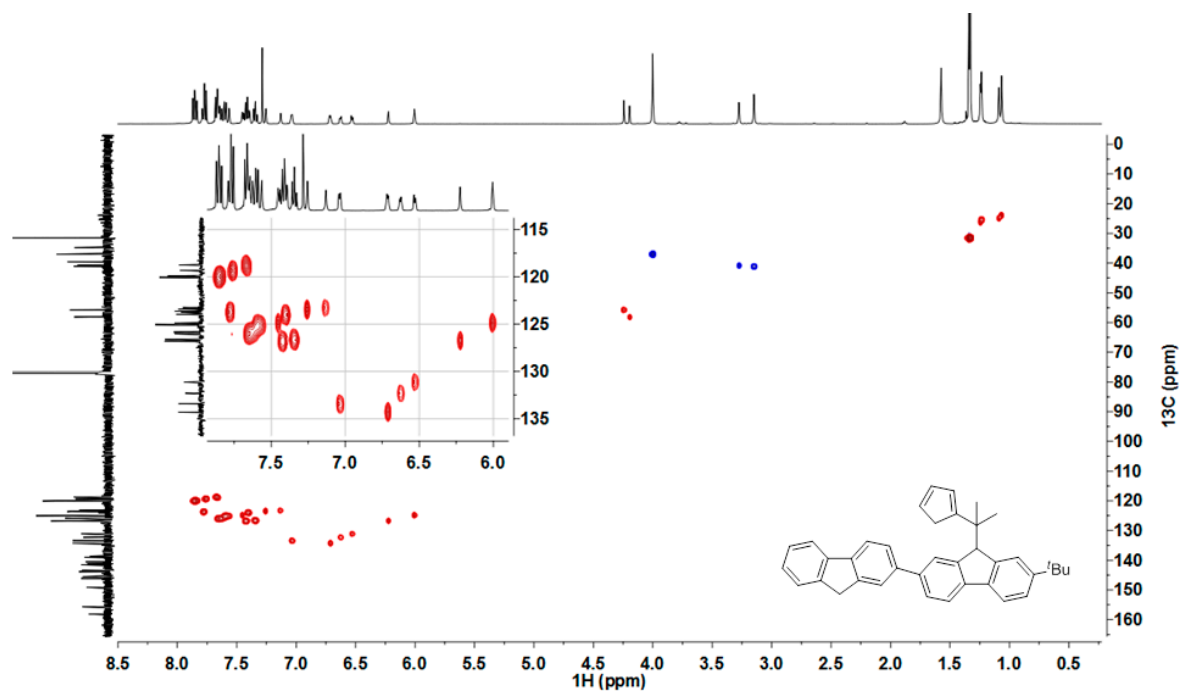


Figure S11: ¹H-¹³C HSQC NMR spectrum (CDCl₃, 400 MHz, 25 °C) of 7

8:

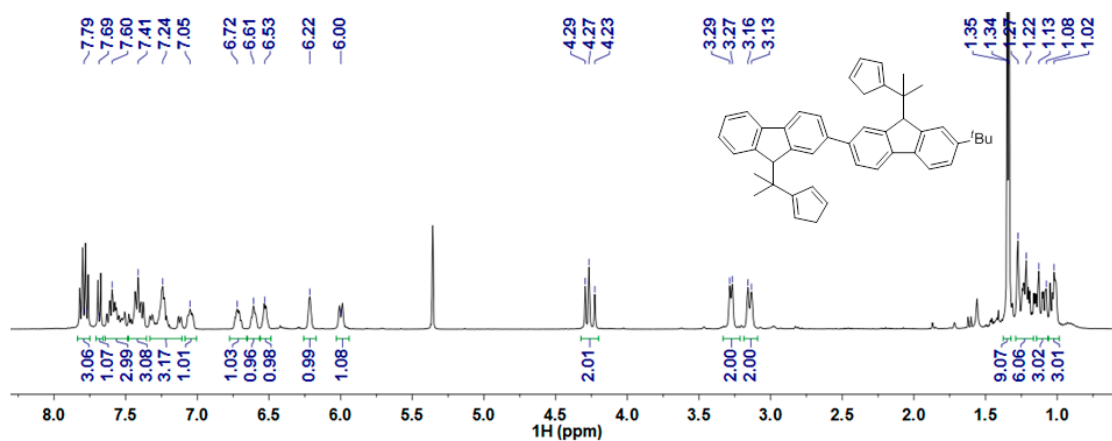


Figure S12: ¹H NMR spectrum (CD₂Cl₂, 400 MHz, 25 °C) of **8**

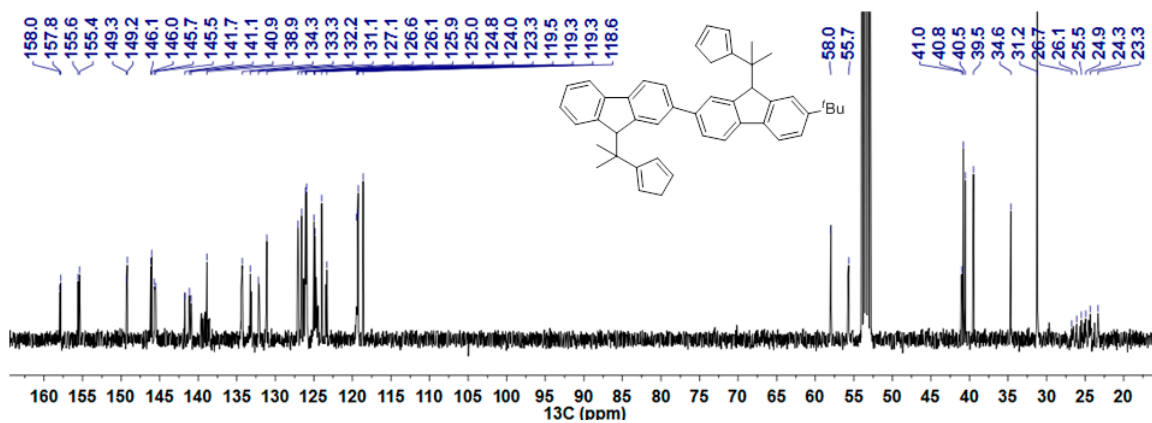


Figure S19: ¹³C{¹H} NMR spectrum (CD₂Cl₂, 100 MHz, 25 °C) of **8**

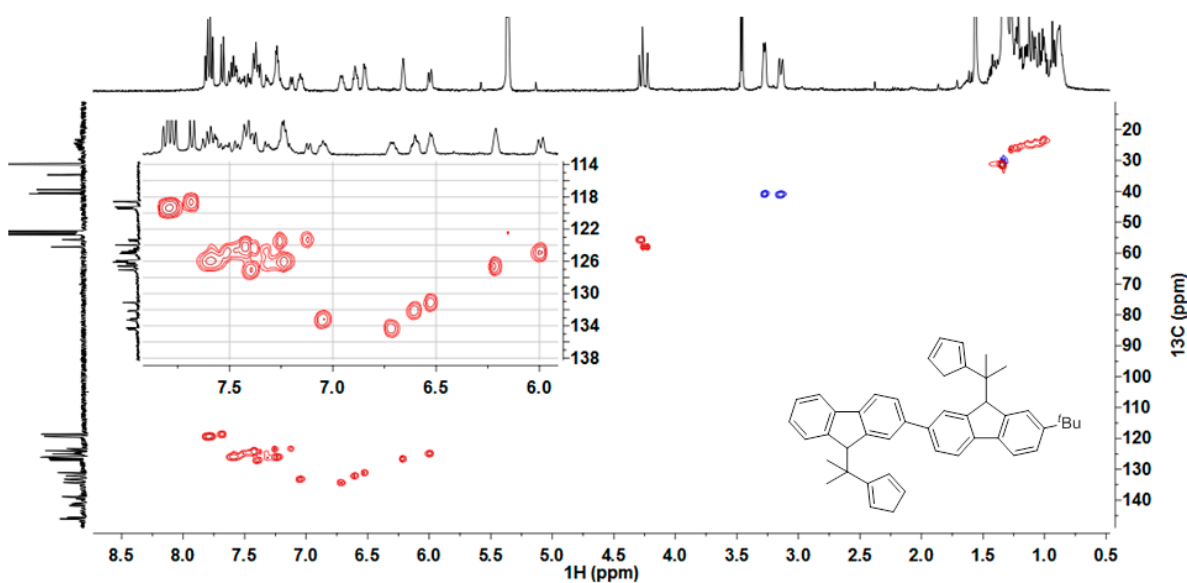


Figure S13: ¹H–¹³C HSQC NMR (CD₂Cl₂, 400 MHz, 25 °C) of **8**

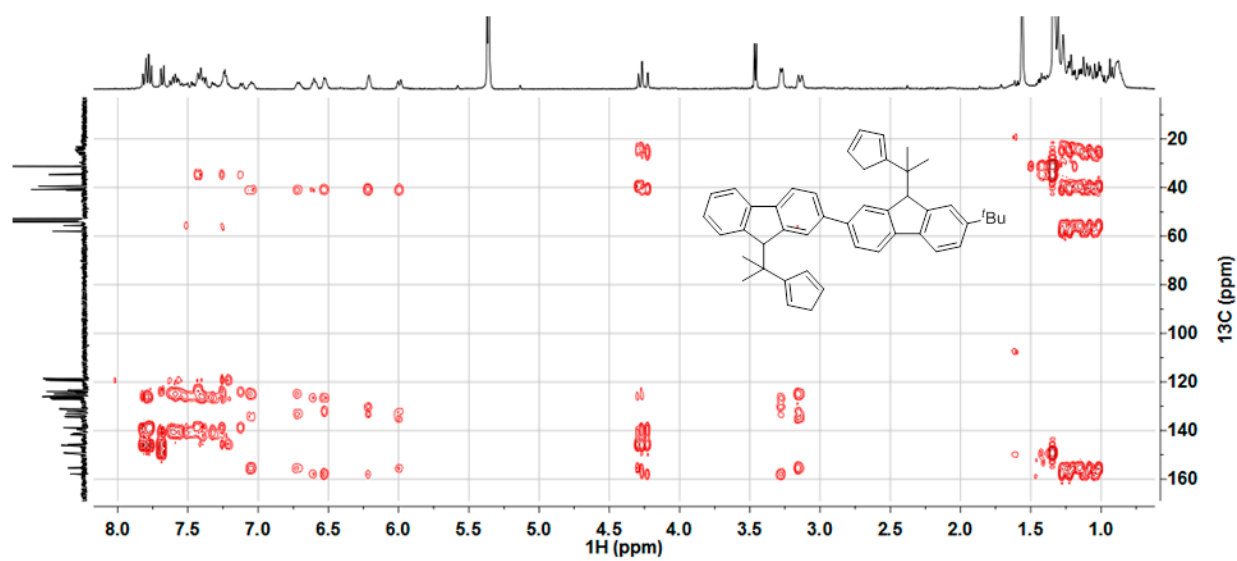


Figure S14: ^1H - ^{13}C HMBC NMR spectrum (CD_2Cl_2 , 400 MHz, 25 °C) of **8**

9:

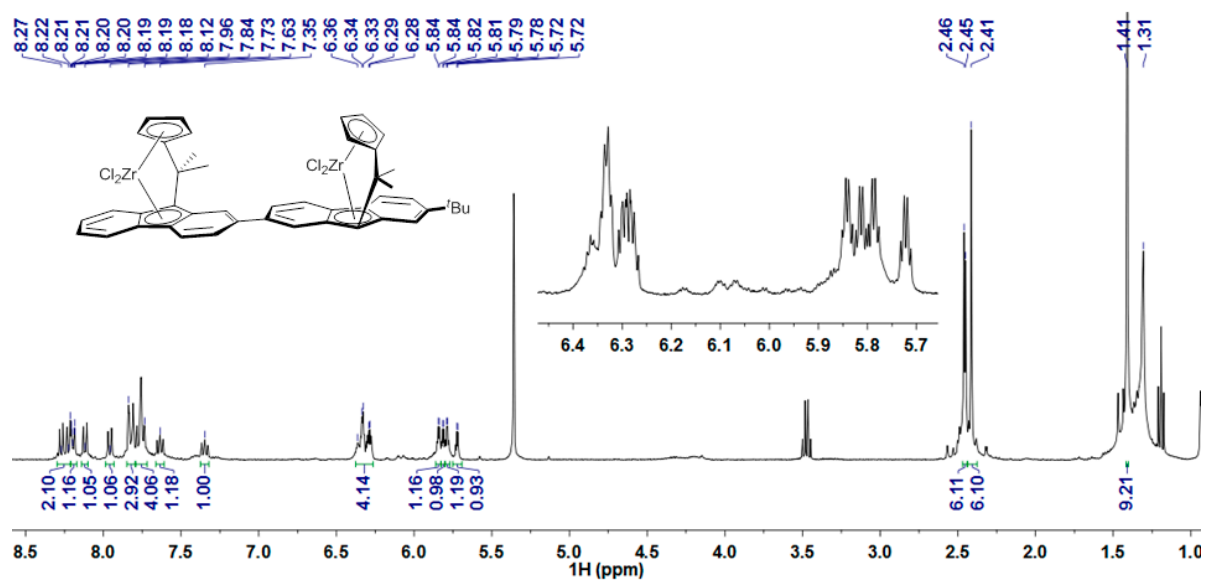


Figure S15: ¹H NMR spectrum (CD₂Cl₂, 400 MHz, 25 °C) of 9

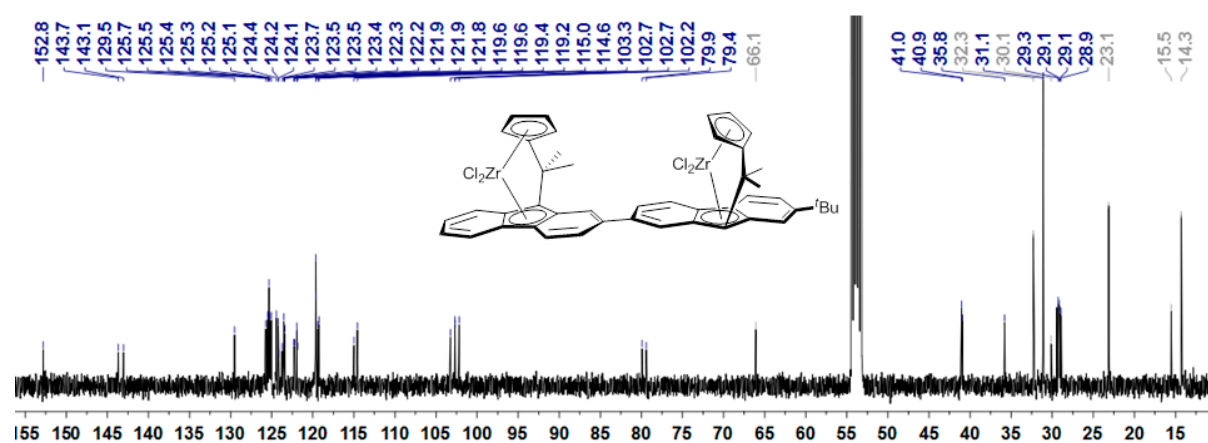


Figure S16: ¹³C{¹H} NMR spectrum (CD₂Cl₂, 100 MHz, 25 °C) of 9 (labels in light grey stand for signals of residual diethyl ether and *n*-hexane)

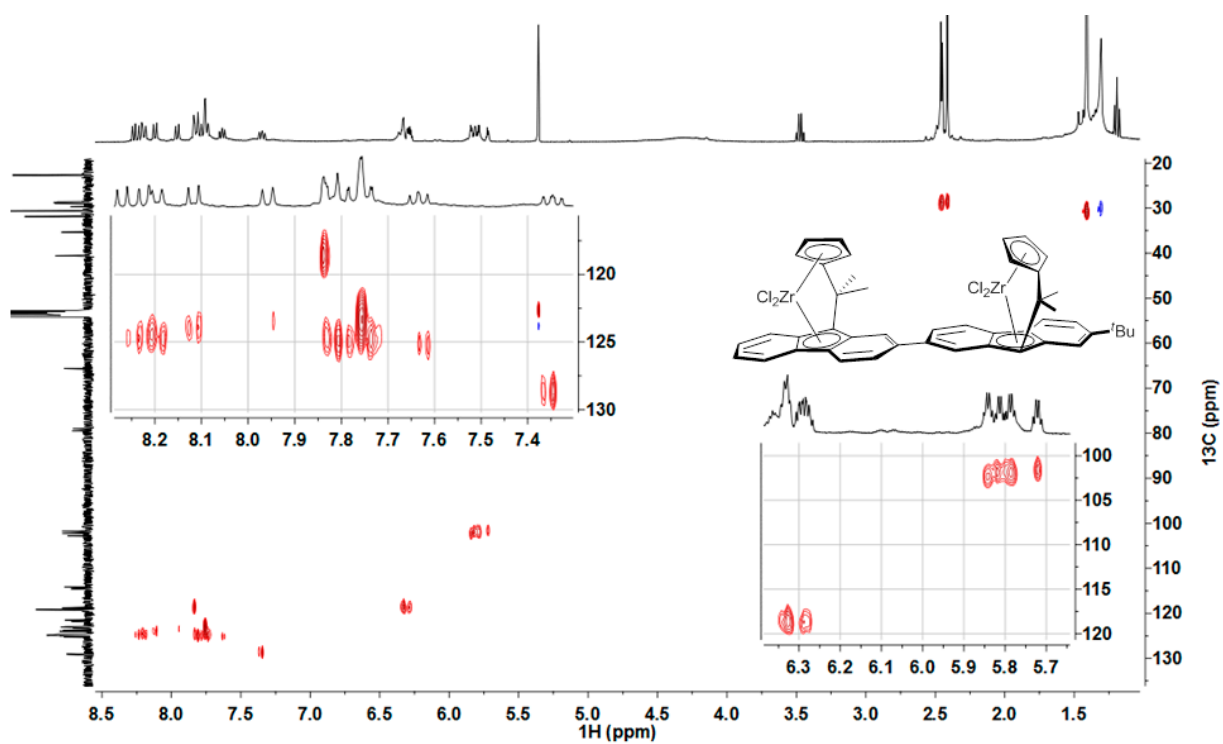


Figure S17: ^1H - ^{13}C HSQC NMR spectrum (CD_2Cl_2 , 400 MHz, 25 °C) of **9**

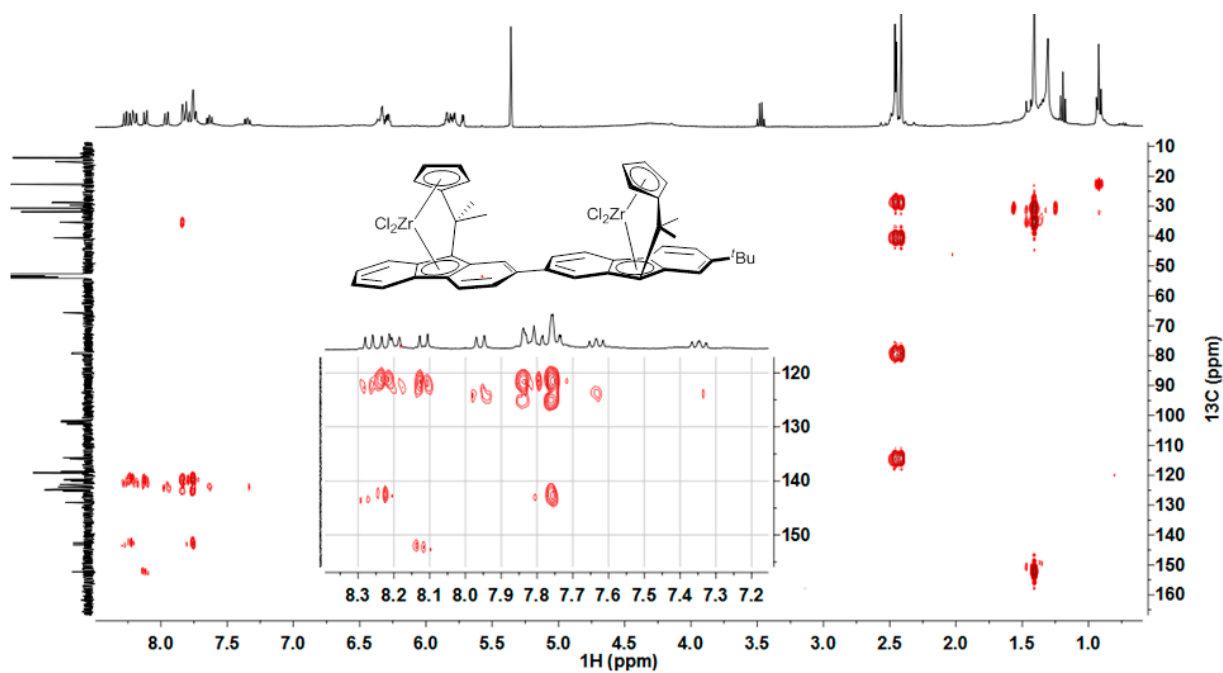


Figure S18: ^1H - ^{13}C HMBC NMR spectrum (CD_2Cl_2 , 400 MHz, 25 °C) of **9**

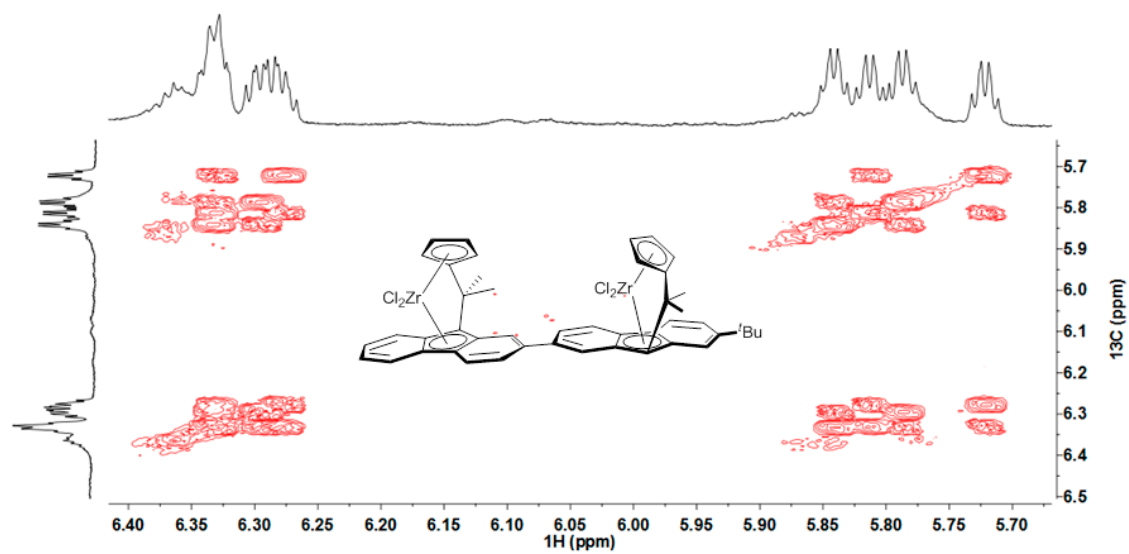


Figure S19: Detail (5.65–6.45 ppm) of the ^1H - ^1H COSY NMR spectrum (CD_2Cl_2 , 400 MHz, 25 °C) of **9**

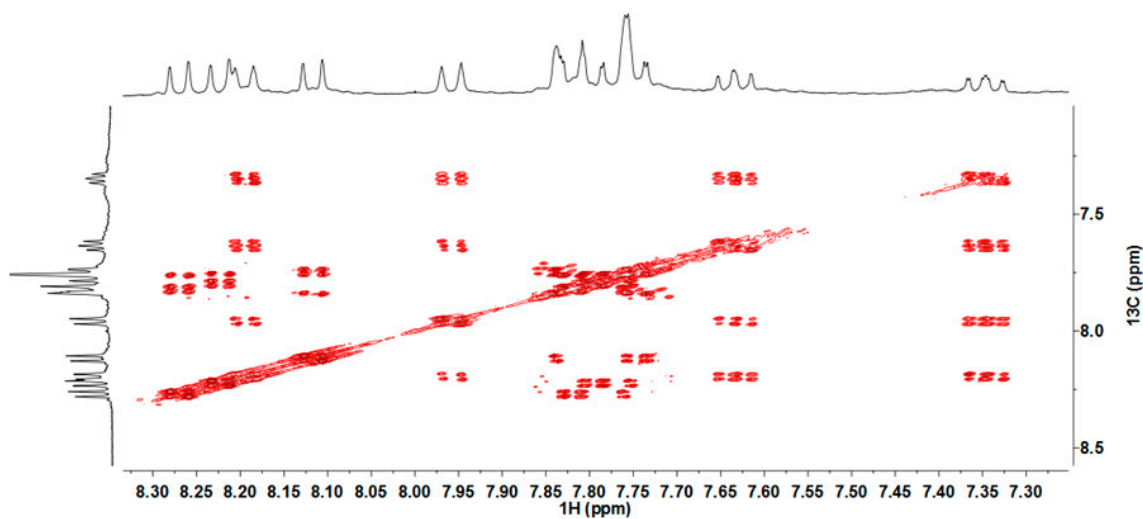


Figure S20: Detail (7.25–8.35 ppm) of the ^1H - ^1H COSY NMR spectrum (CD_2Cl_2 , 400 MHz, 25 °C) of **9**

Centre régional de mesures physiques de l'Ouest (CRMPO) - RAPPORT D'ANALYSE

Analysis Info

Analysis Name D:\Data\CRMPO\ASAP_7816_MS_02.d
Method ASAP_CRMPO_tune_mid.m
Sample Name LJ 294
Comment L. JENDE LJ 294 Température : 300°C

Acquisition Date 02/02/2018 8:14:41 PM

Operator Philippe JÉHAN
Instrument maXis

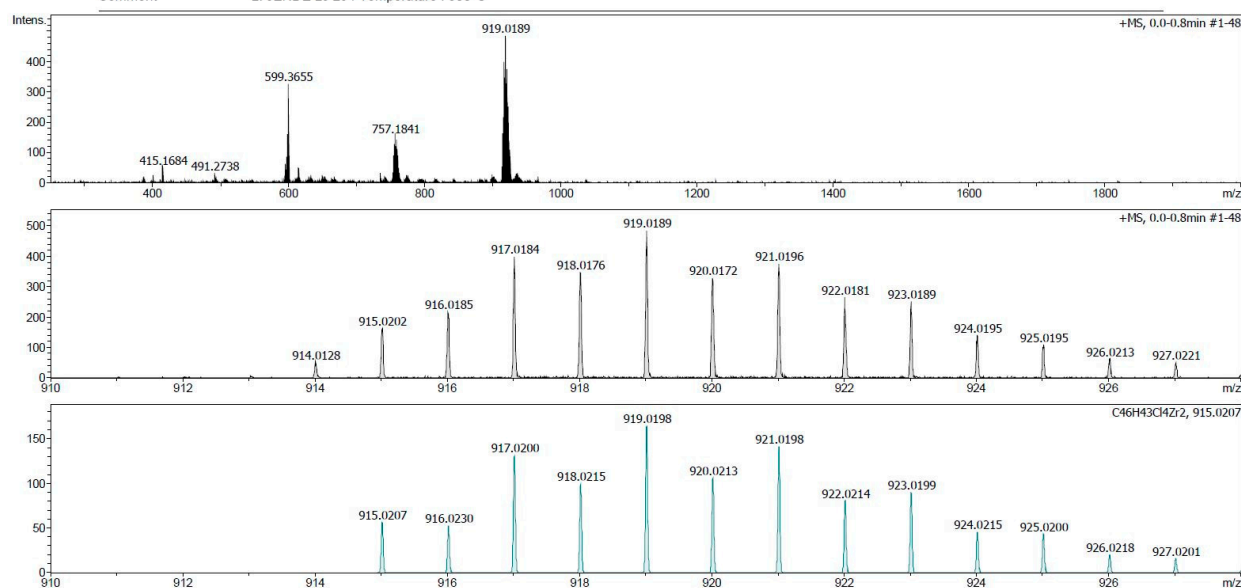
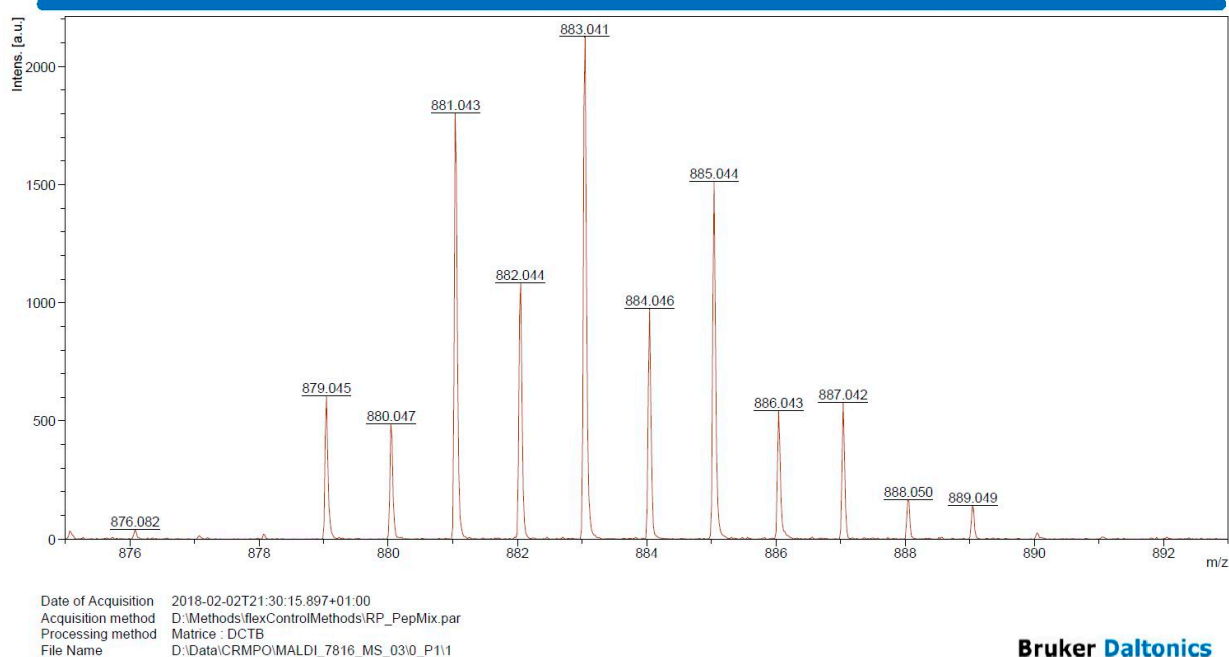


Figure S21: ASAP mass spectrum (300 °C) of 9

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L. JENDE LJ 294



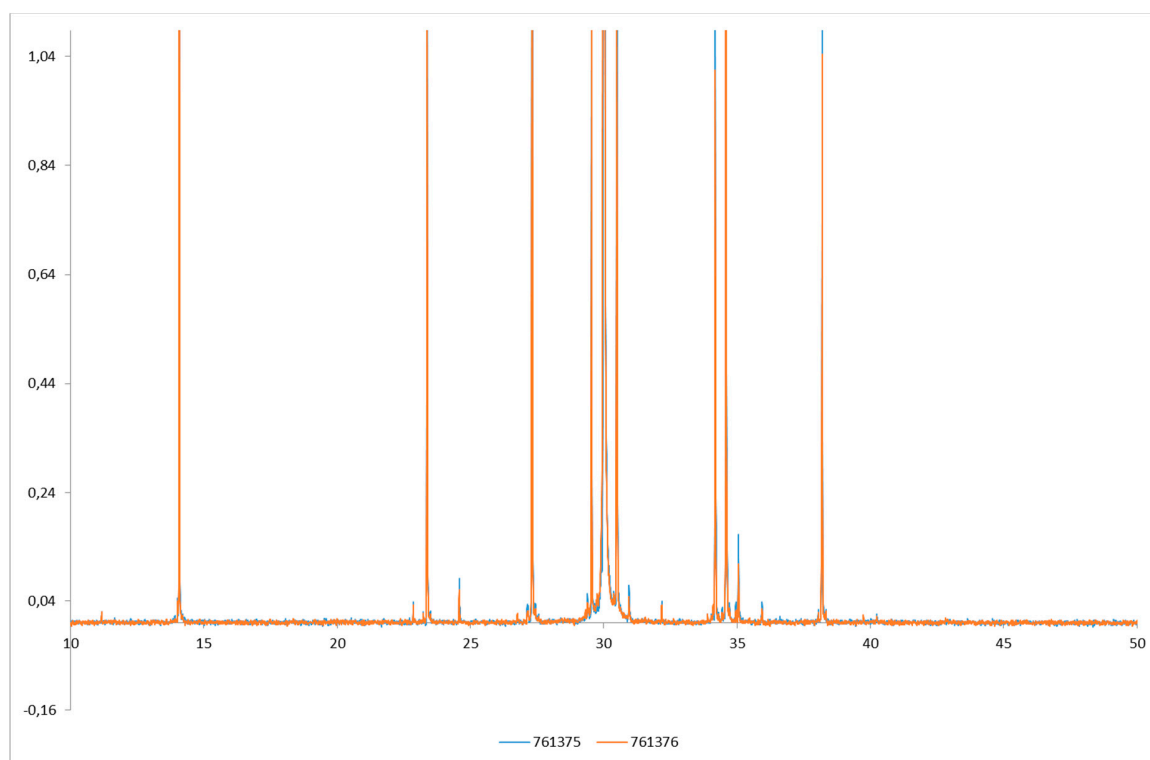
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Bruker Daltonics

Figure S29: MALDI-TOF mass spectrum (DCTB-Matrix) of 9

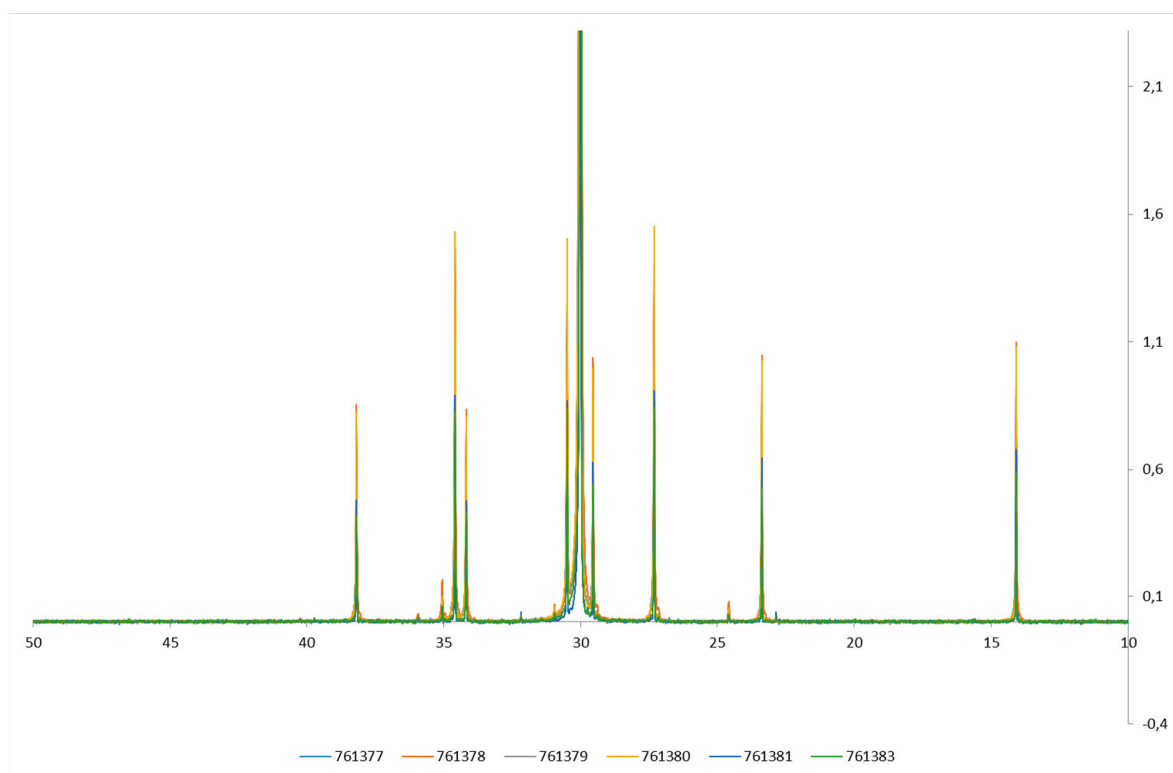
Table S1: Crystallographic Data for Compounds **5**, **6**, and **7**

	5	6	7
Empirical formula	C ₃₆ H ₄₂ Si ₂	C ₄₄ H ₅₂ Si ₂	C ₃₈ H ₃₆
CCDC	2268879	2268880	2268881
M _w [g mol ⁻¹]	530.87	637.03	492.67
T [K]	150	150	150
Crystal system	triclinic	triclinic	monoclinic
Space group	<i>P</i> -1	<i>P</i> 2 ₋₁	<i>P</i> 2 ₁ /c
a [Å]	10.7951(11)	9.7922(10)	18.2840(13)
b [Å]	12.1001(12)	13.3896(11)	6.5769(4)
c [Å]	13.5758(12)	15.6000(15)	22.8564(16)
α [°]	68.871(3)	70.243(3)	90.00
β [°]	82.082(3)	86.464(4)	97.671(3)
γ [°]	68.240(3)	79.205(3)	90.00
Volume [Å ³]	1536.2(3)	1890.9(3)	4878.7(12)
Z	2	2	4
density (calculated) ρ [mg mm ⁻³]	1.148	1.119	1.249
Absorption coefficient μ [mm ⁻¹]	0.138	0.123	0.067
R1 (obs) ^[a]	0.0406	0.0443	0.0661
wR2 (all) ^[b]	0.1124	0.1228	0.1622



	CPO-CPR-18-0045	CPO-CPR-18-0045
	761375	761376
	PE : Experimental Product	PE : Experimental Product
	CP1	CP2
C3 (m%)	0,0	0,0
C4 (m%)	0,1	0,1
C6 (m%)	4,7	3,9
C3 (w%)	0,0	0,0
C4 (w%)	0,1	0,1
C6 (w%)	12,8	10,8
Methyl br./1000C	0,0	0,0
Ethyl br. /1000C	0,4	0,3
Butyl br./1000C	21,7	18,3
Vinylidene /1000C	0	0
Vin ends/10000C	2	2
Sat ends/10000C	5	6

Figure S30: $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (1,2,5-trichlorobenzene/ C_6D_6 , 125 MHz, 135 °C) of ethylene/1-hexene copolymers prepared with complex **9** and corresponding composition determined thereof (Table 3, entries **13** and **14**).



			CPO-CPR-18-0045 761377	CPO-CPR-18-0045 761378	CPO-CPR-18-0045 761379
			PE : Experimental Product CP3	PE : Experimental Product CP4	PE : Experimental Product CP5
Hexene (mole%)			4,3	6,8	4,7
Ethylene (mole%)			95,7	93,2	95,3
Hexene (wt%)			11,9	17,9	12,9
Ethylene (wt%)			88,1	82,1	87,1
Butyl/1000C			19,8	29,6	21,4
Sat. Ends /10000C			5,2	9,0	4,3
Vin. Ends/10000C			0,0	0,0	0,0

Figure S31: $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (1,2,5-trichlorobenzene/ C_6D_6 , 125 MHz, 135 °C) of ethylene/1-hexene copolymers prepared with complexes **9** and **M**, and corresponding composition determined thereof (Table 3, entries 15–17).

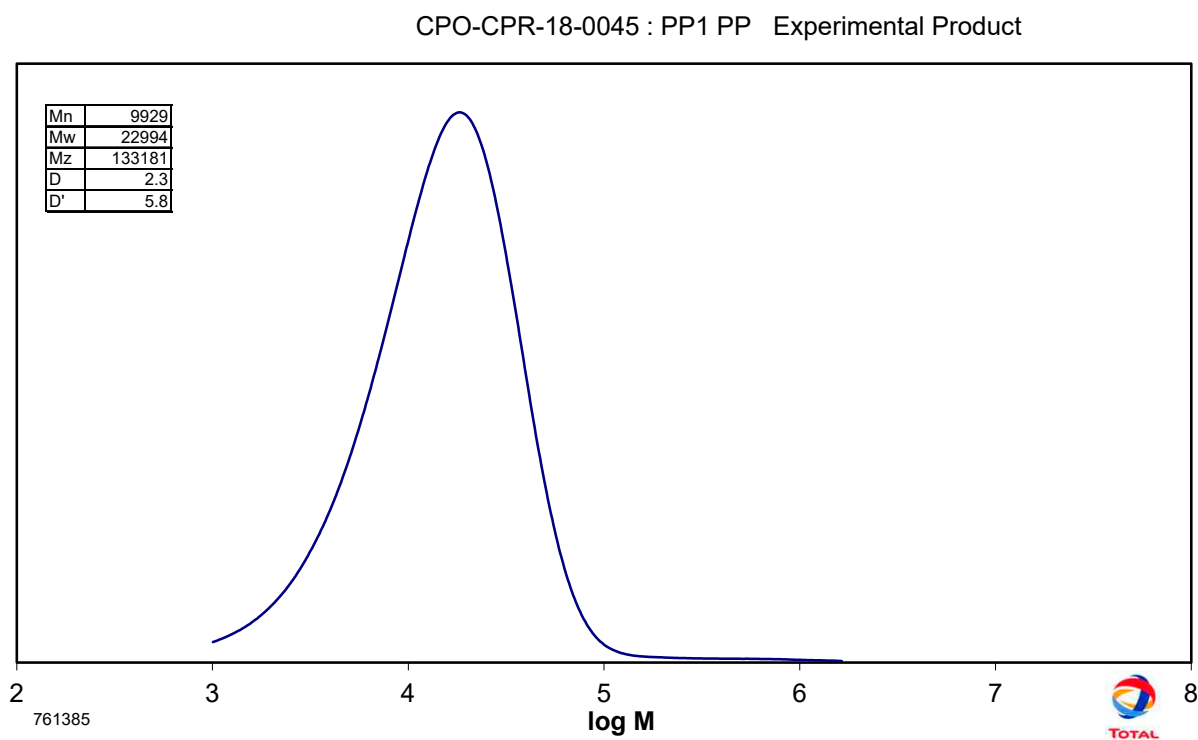


Figure S32: SEC trace of a PP prepared with complex **9** (Table 2, entry **7**).

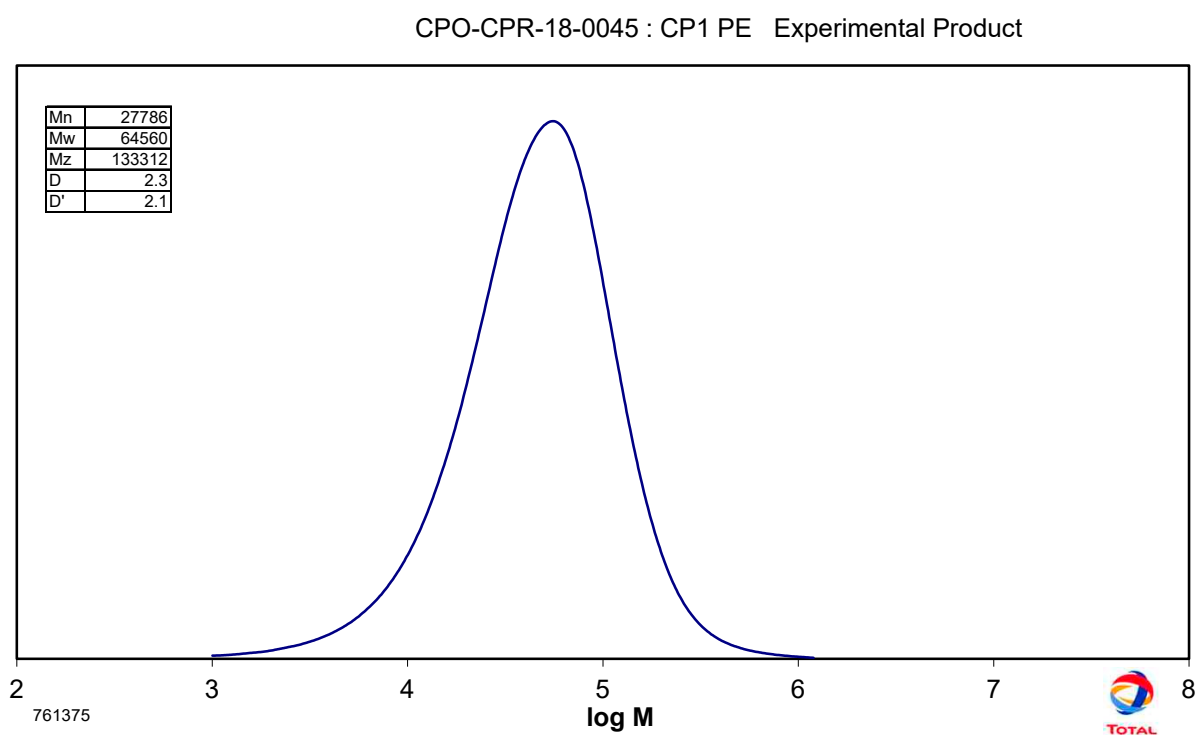


Figure S33: SEC trace of a poly(ethylene-*co*-1-hexene) prepared with complex **9** (Table 3, entry **13**).

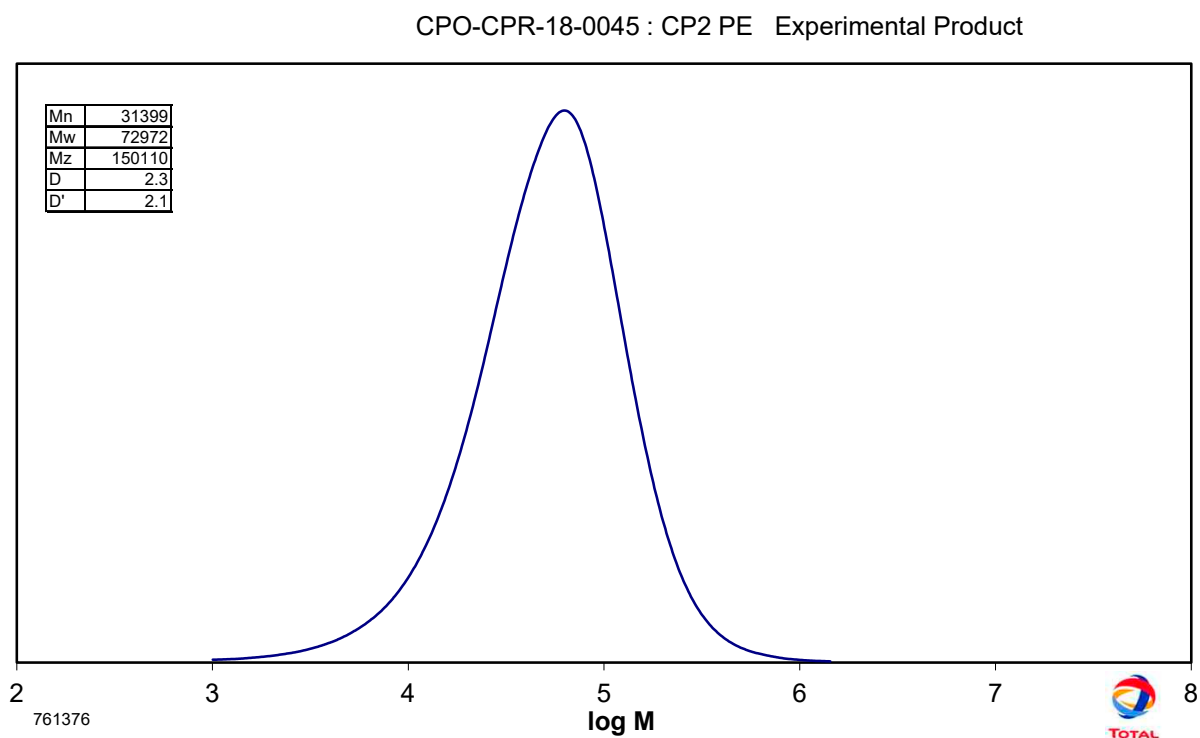


Figure S34: SEC trace of a poly(ethylene-*co*-1-hexene) prepared with complex **9** (Table 3, entry **14**).

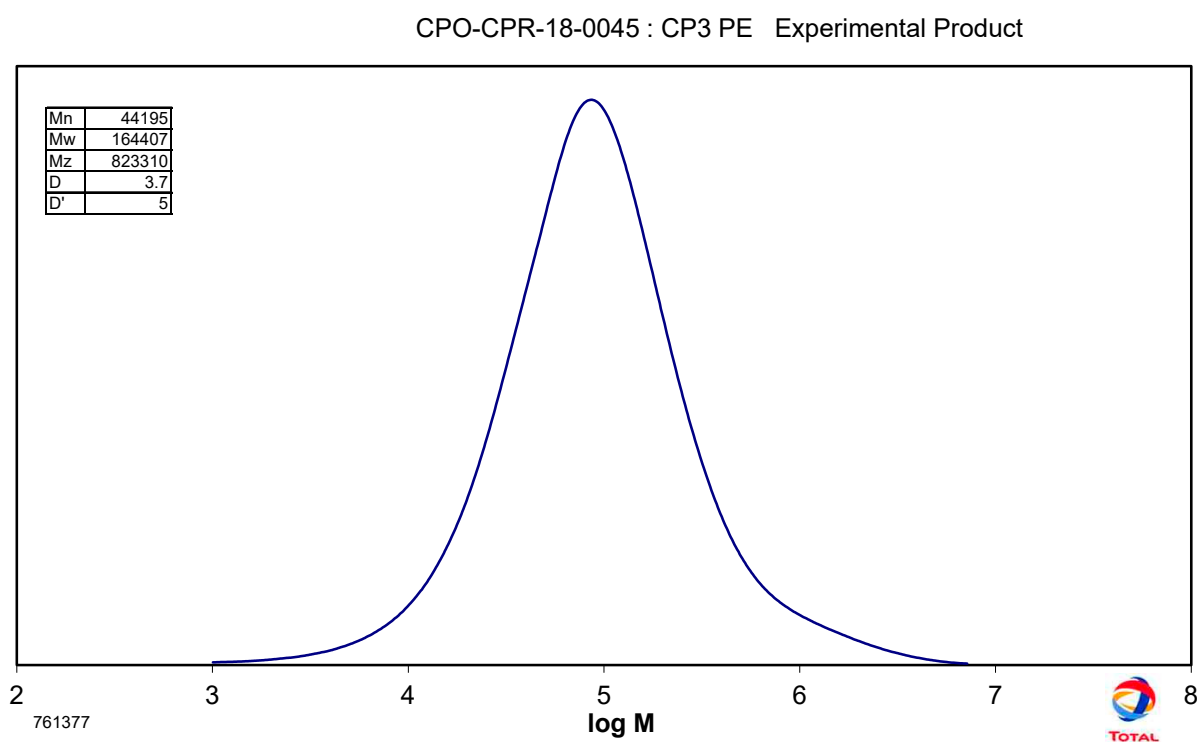


Figure S35: SEC trace of a poly(ethylene-*co*-1-hexene) prepared with complex **9** (Table 3, entry **15**).

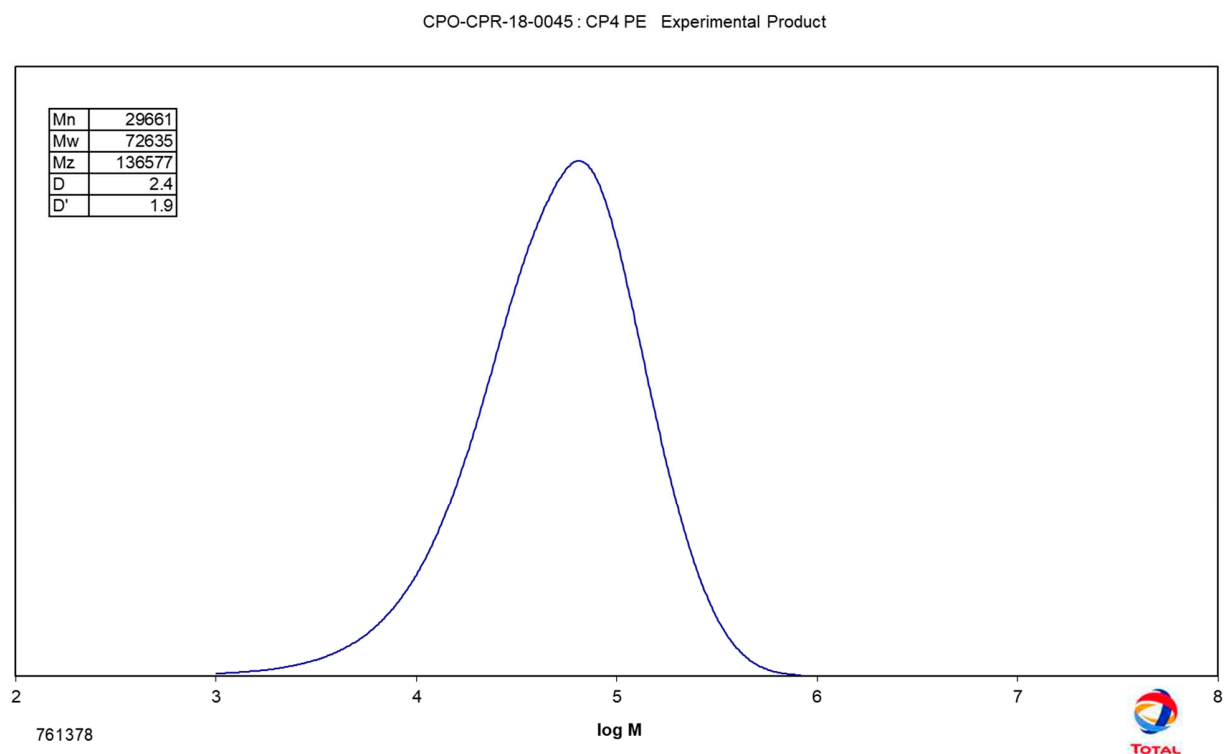


Figure S36: SEC trace of a poly(ethylene-*co*-1-hexene) prepared with complex **M** (Table 3, entry **16**).

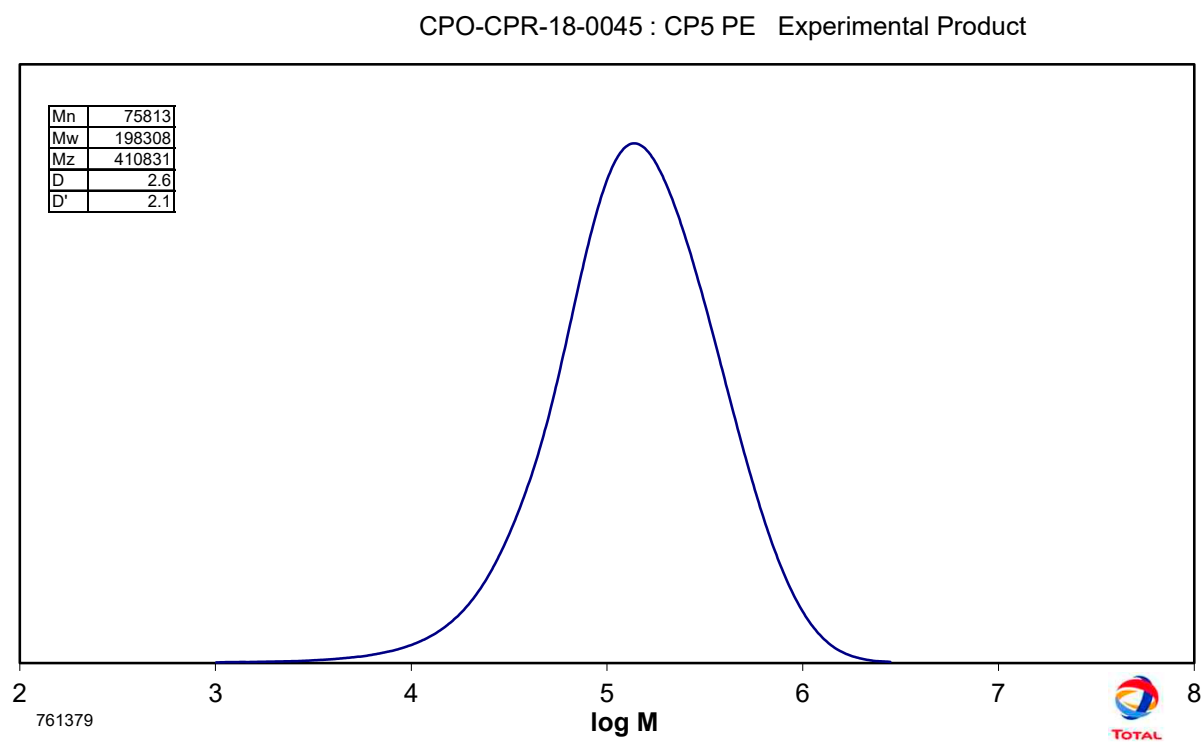


Figure S37: SEC trace of a poly(ethylene-*co*-1-hexene) prepared with complex **M** (Table 3, entry 17).

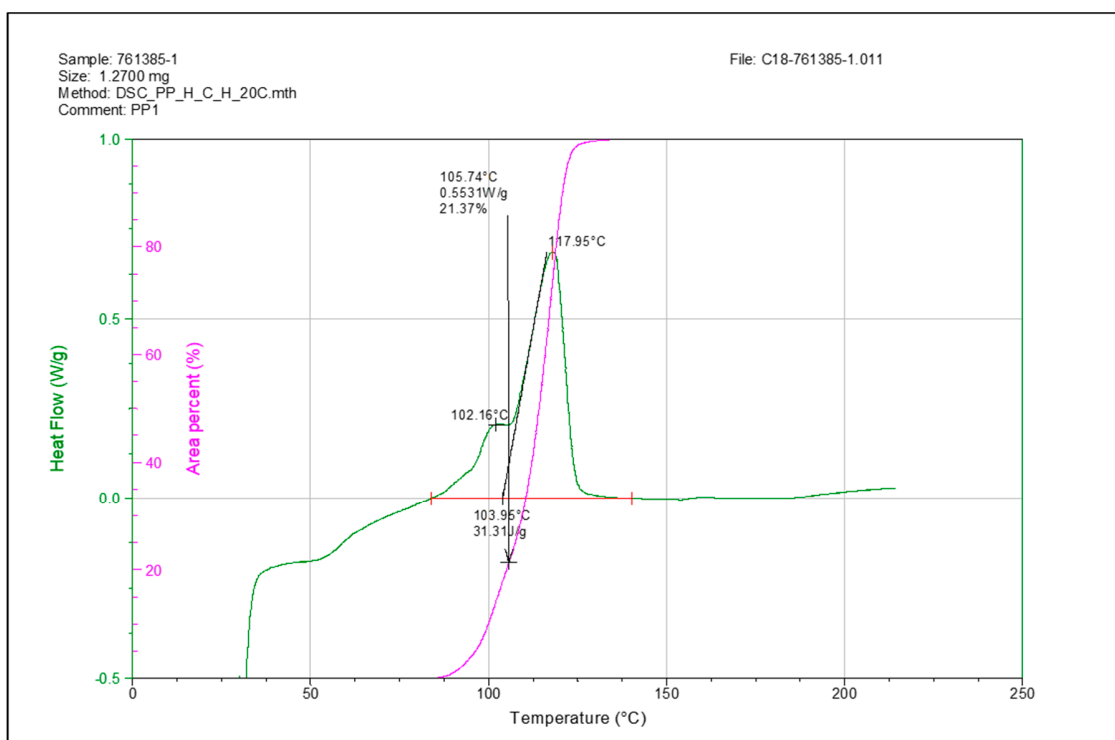


Figure S38: DSC trace of a polypropylene prepared with complex **9** (Table 2, entry **7**).

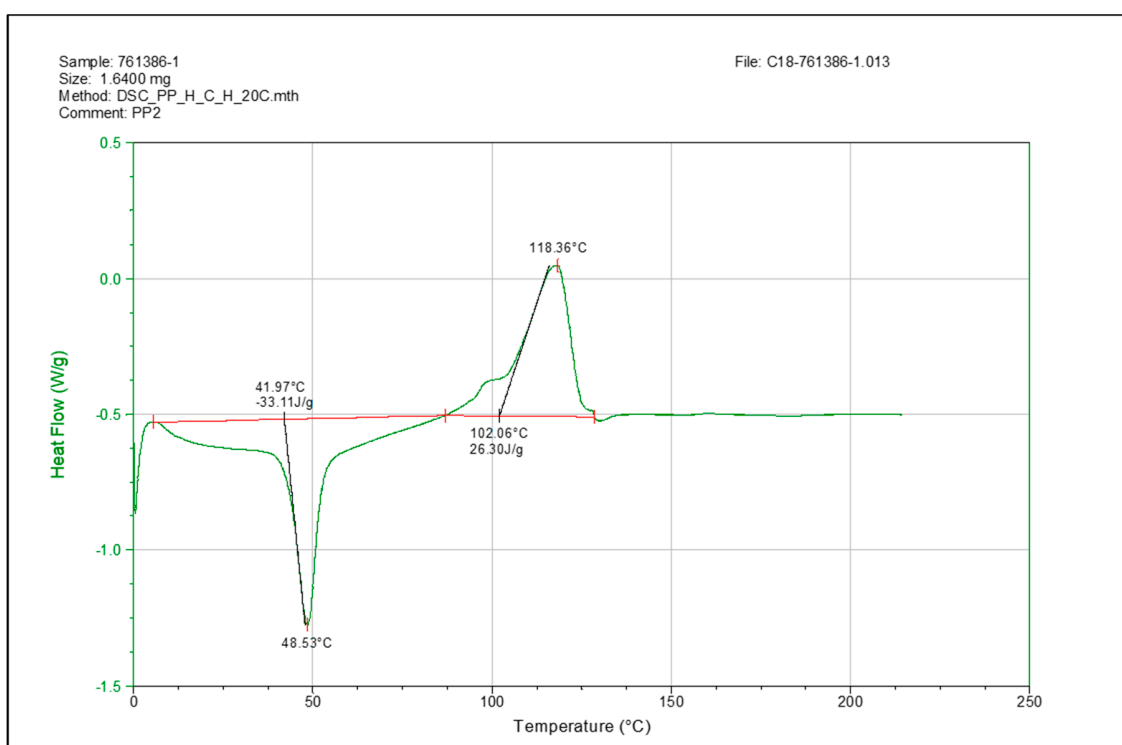


Figure S39: DSC trace of a polypropylene prepared with complex **9** (Table 2, entry **8**).

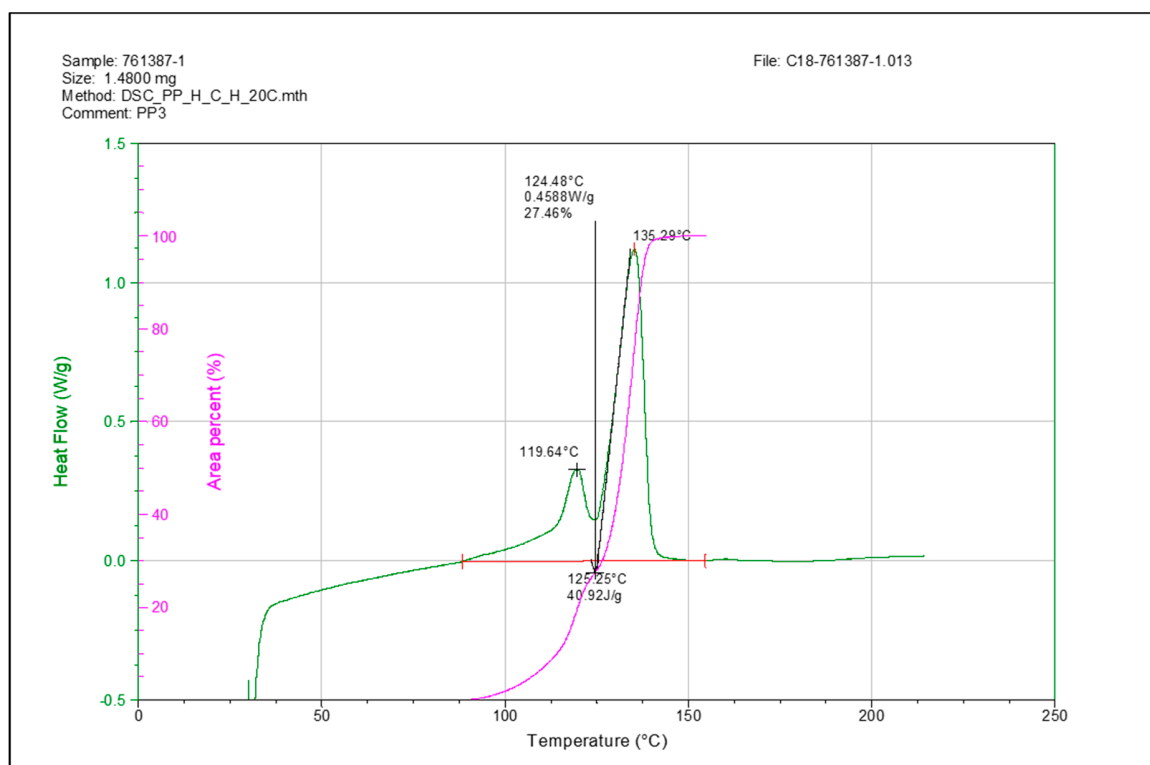


Figure S40: DSC trace of a polypropylene prepared with complex **9** (Table 2, entry **9**).

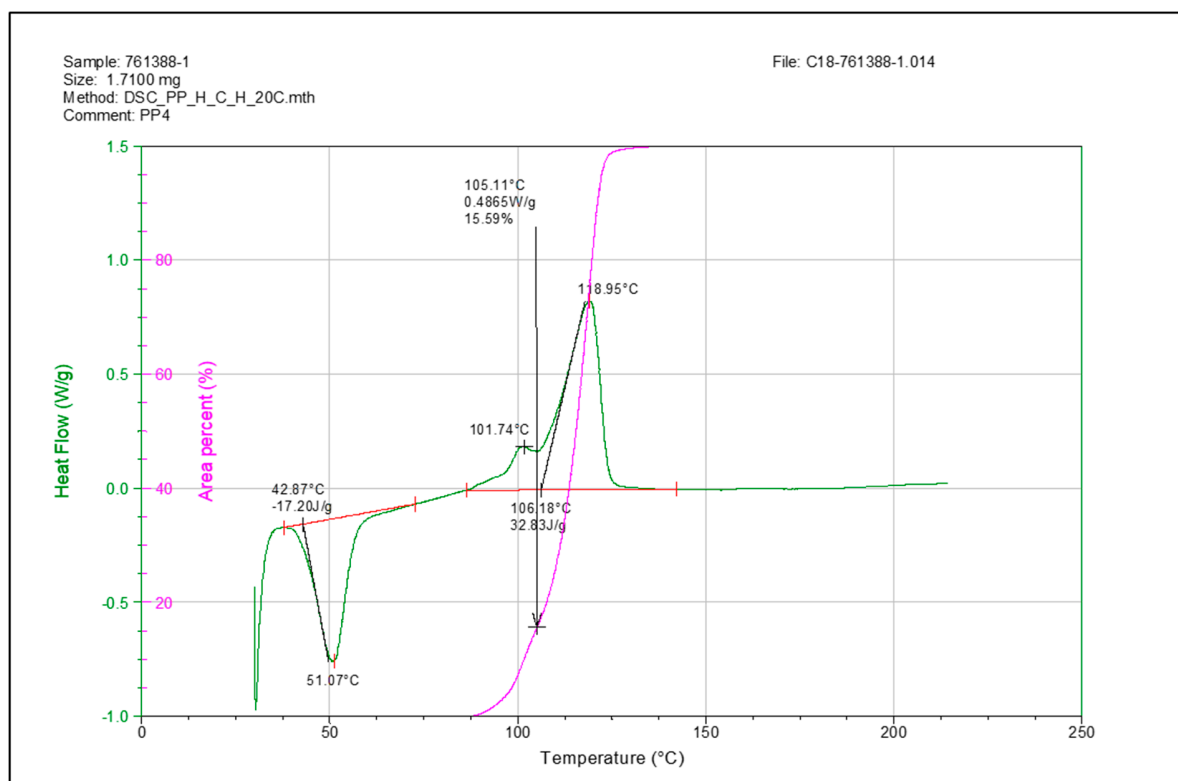


Figure S41: DSC trace of a polypropylene prepared with complex **M** (Table 2, entry **10**).

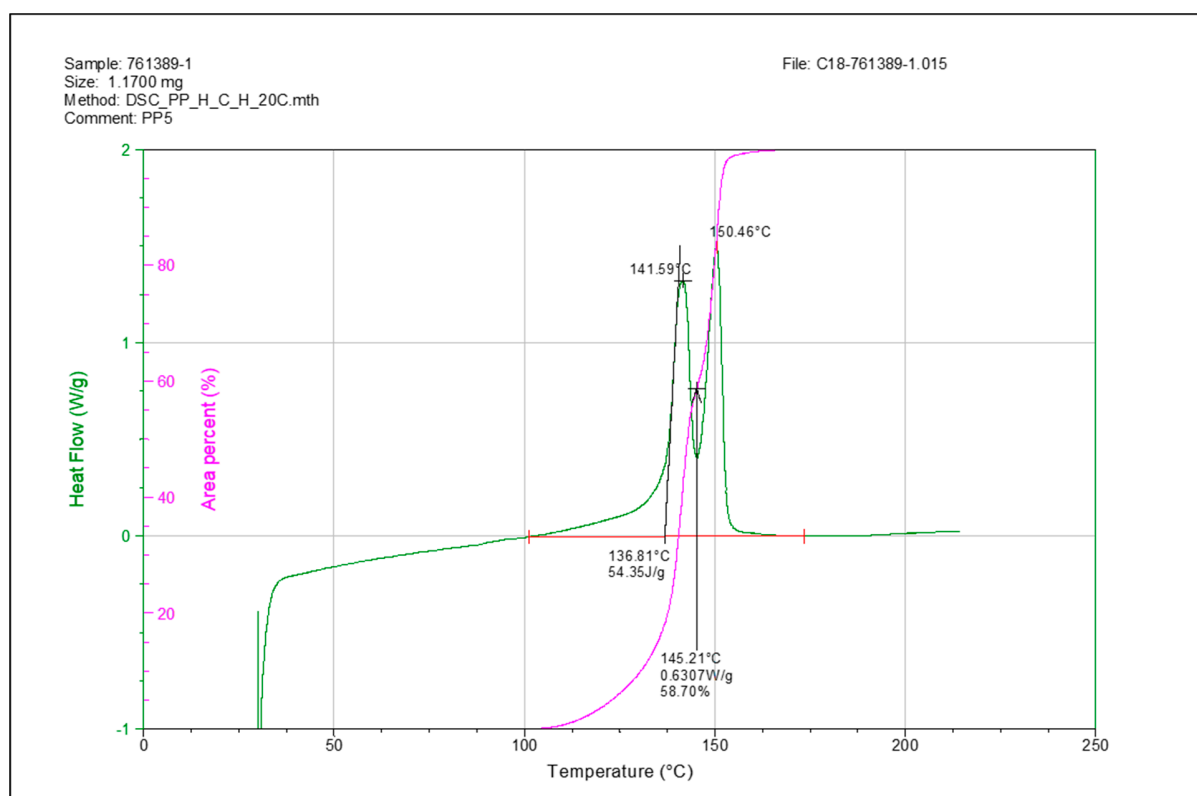


Figure S42: DSC trace of a polypropylene prepared with complex **M** (Table 2, entry 11).

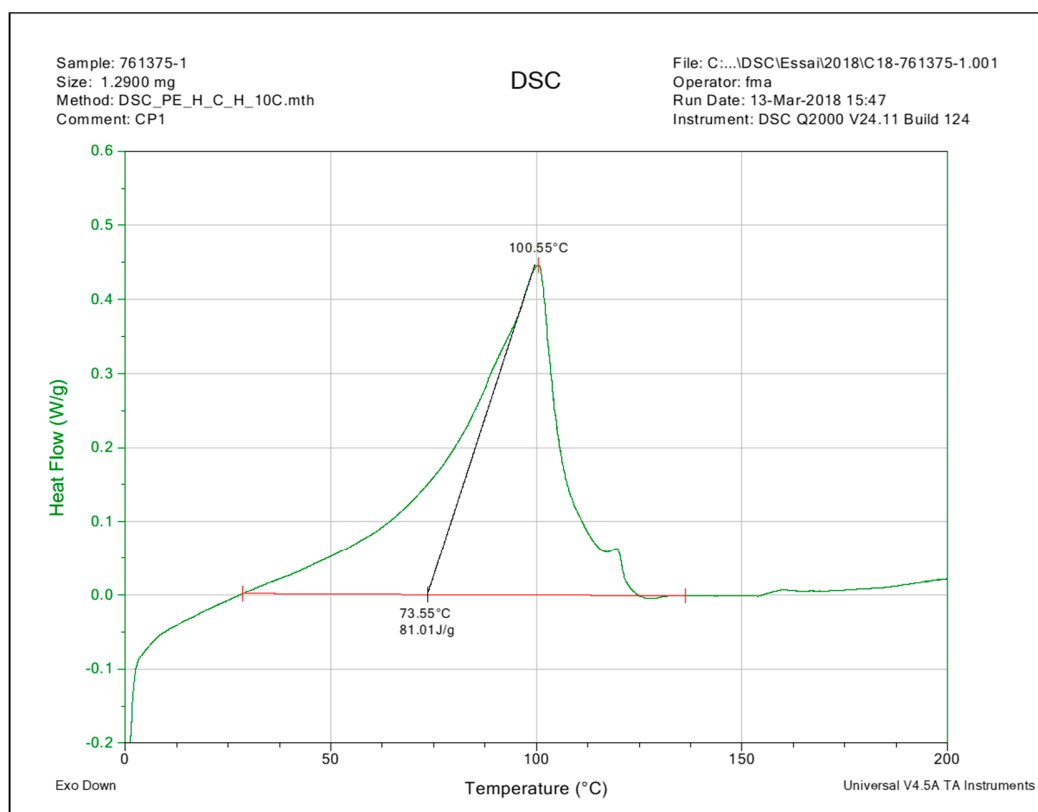


Figure S43: DSC trace of a poly(ethylene-*co*-1-hexene) prepared with complex **9** (Table 3, entry **13**).

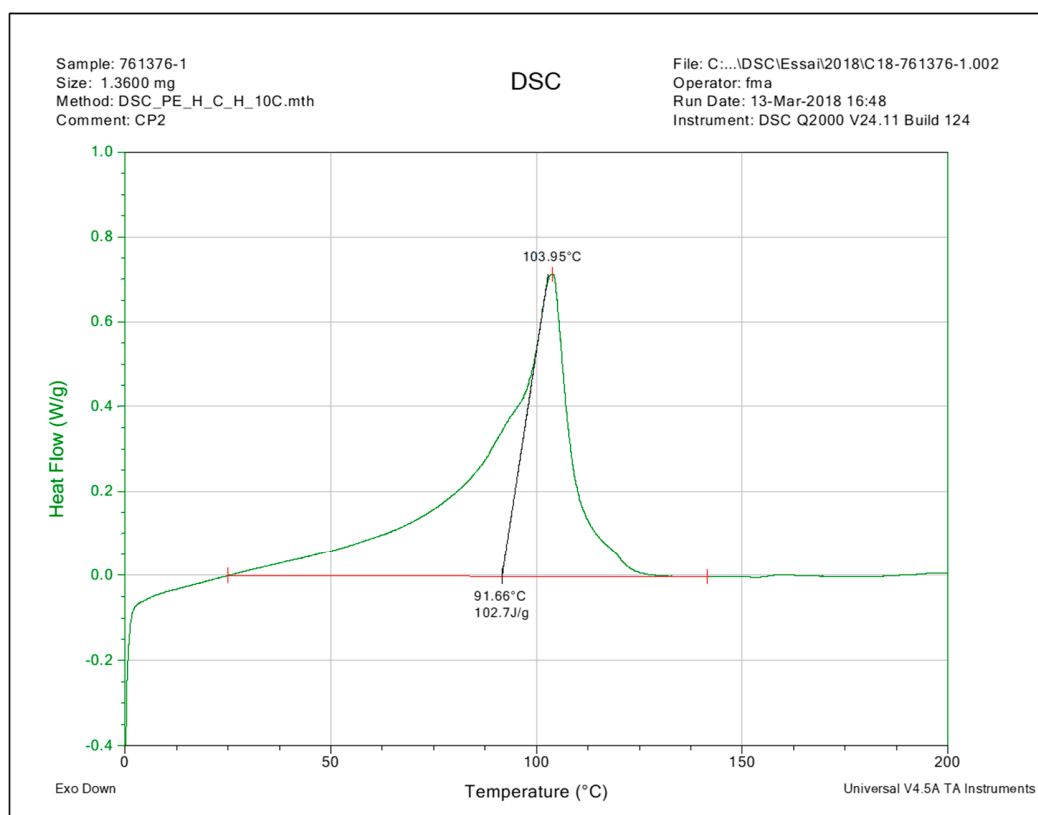


Figure S44: DSC trace of a poly(ethylene-*co*-1-hexene) prepared with complex **9** (Table 3, entry **14**).

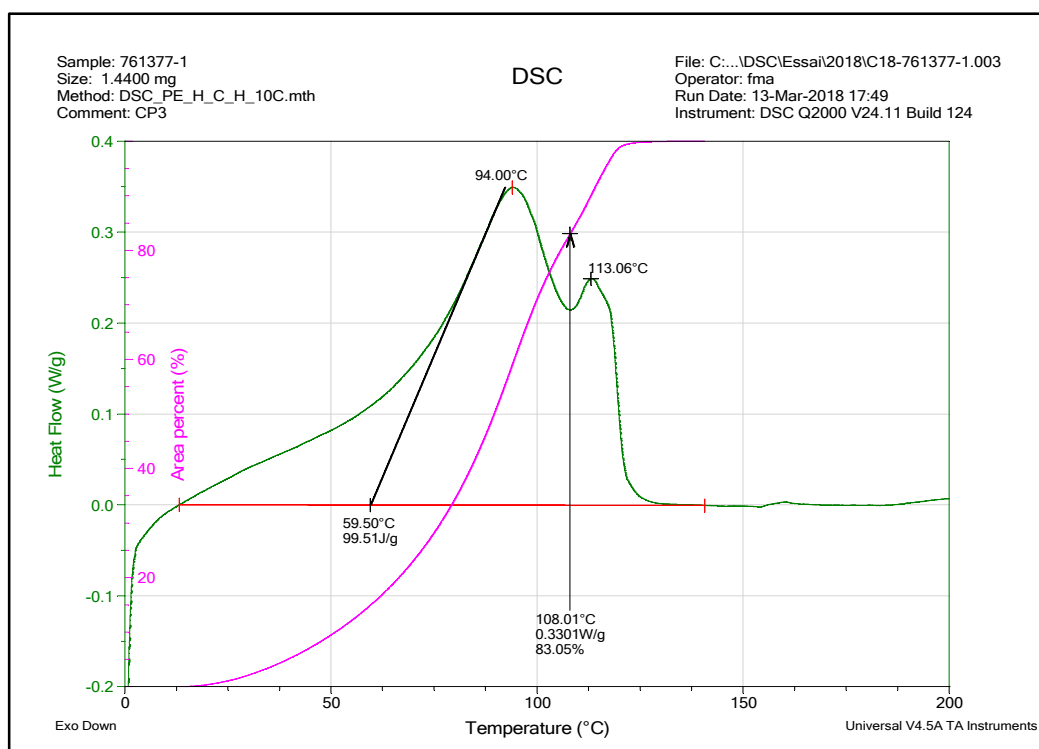


Figure S45: DSC trace of a poly(ethylene-*co*-1-hexene) prepared with complex **9** (Table 3, entry **15**).

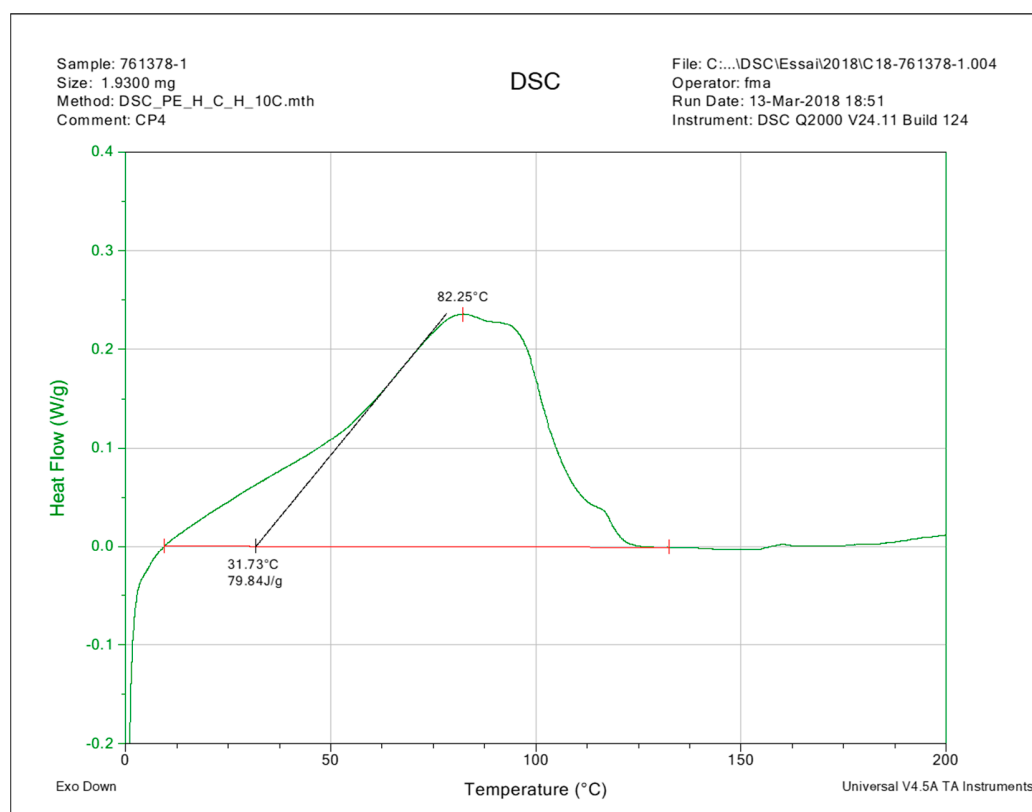


Figure S46: DSC trace of a poly(ethylene-*co*-1-hexene) prepared with complex **M** (Table 3, entry **16**).

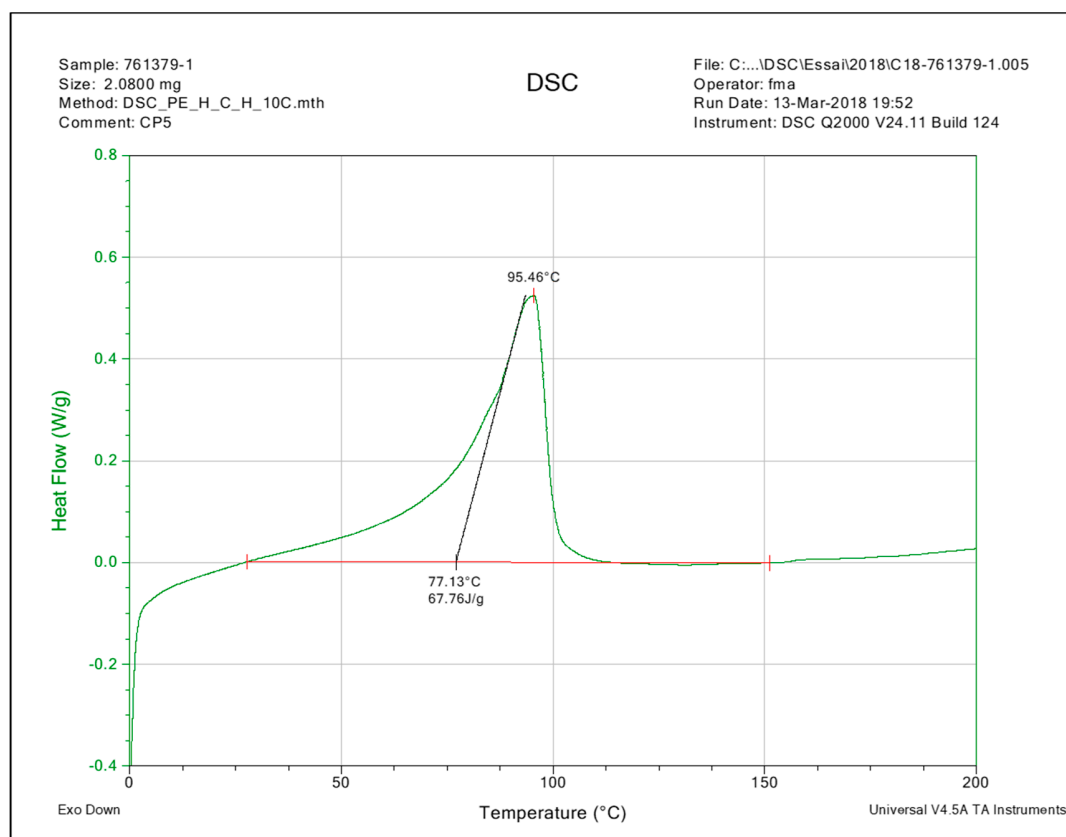


Figure S47: DSC trace of a poly(ethylene-*co*-1-hexene) prepared with complex **M** (Table 3, entry 17).