Supporting Information for

Stereospecific Ring-Opening Metathesis Polymerization (ROMP) of *Endo*-Dicyclopentadiene by Molybdenum and Tungsten Catalysts

by

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Figure S36. WAXRD measurement profile for *syndiotactic* H-poly(DCPD) made from **2** and 200 equiv. of DCPD.

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Figure S40. ROMP of 8 equivalents DCPD by **13** at 20 °C in CD_2Cl_2 to give atactic poly(DCPD); $k_p/k_i \sim 14$.

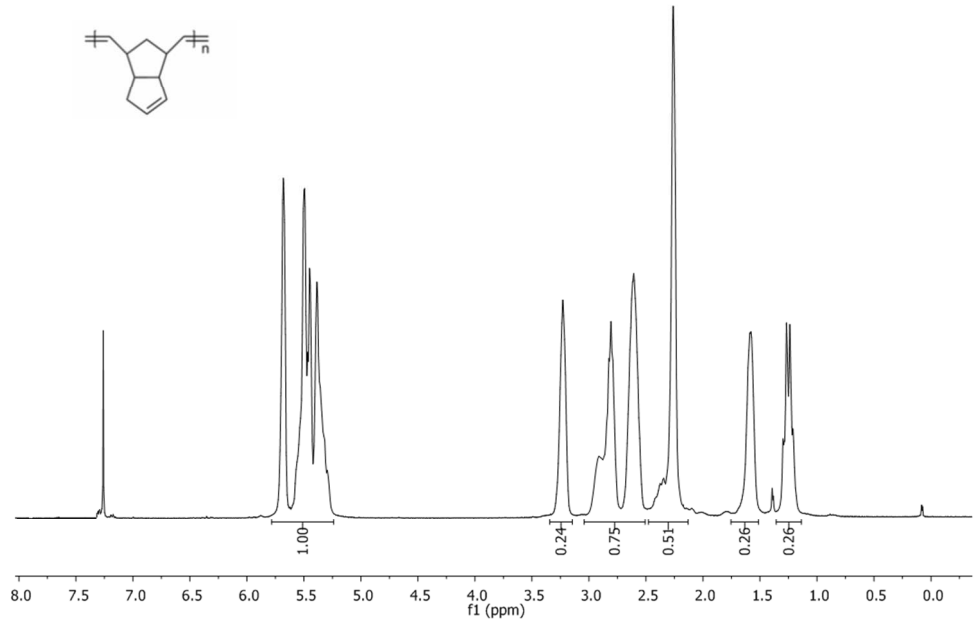

Figure S1. ^{1}H NMR spectrum ($CDCl_3$) of linear, atactic poly(DCPD) made from **1**. The ratio of the olefinic to the aliphatic region is 1:2.

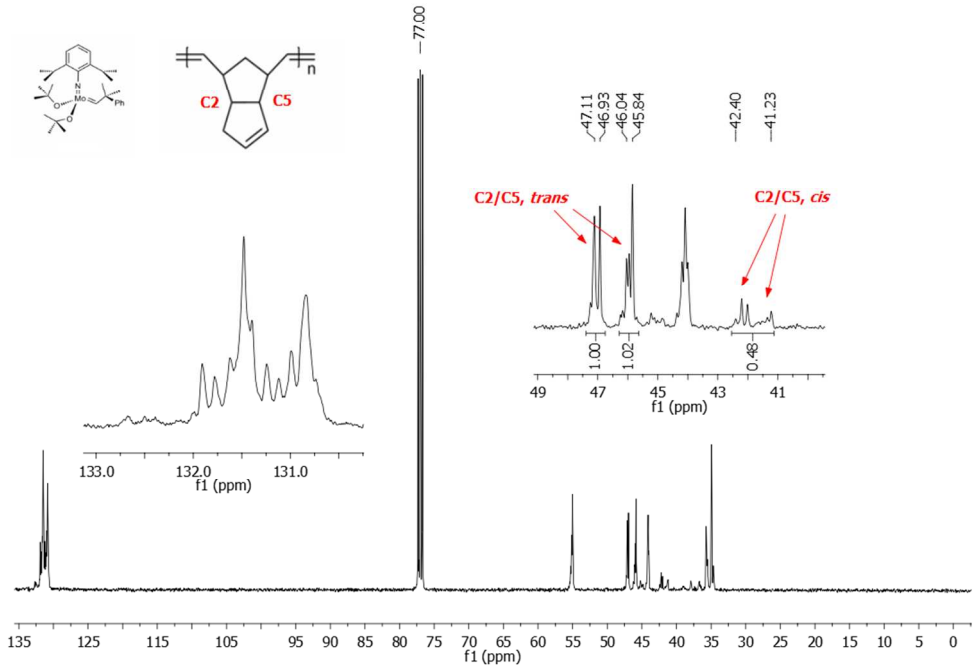

Figure S2. ^{13}C NMR spectrum ($CDCl_3$) of atactic poly(DCPD) made from **1**.

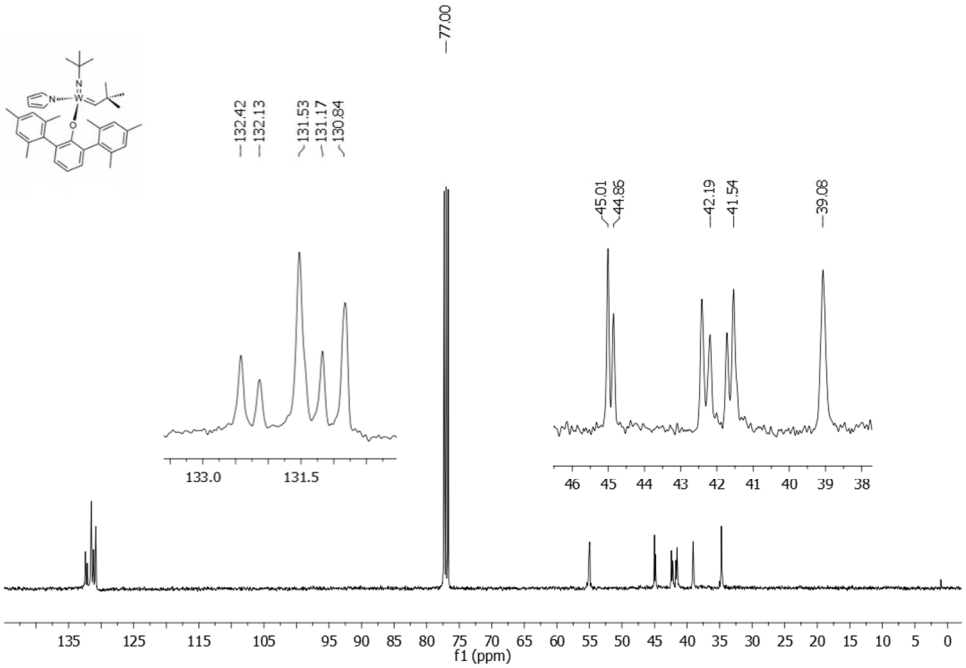

Figure S3. ^{13}C NMR spectrum ($CDCl_3$) of *cis, syndio*tactic poly(DCPD) made from **2**. The signals for C3/C4 at 45.0/44.9 ppm are indicative for a *cis, syndiotactic* structure.

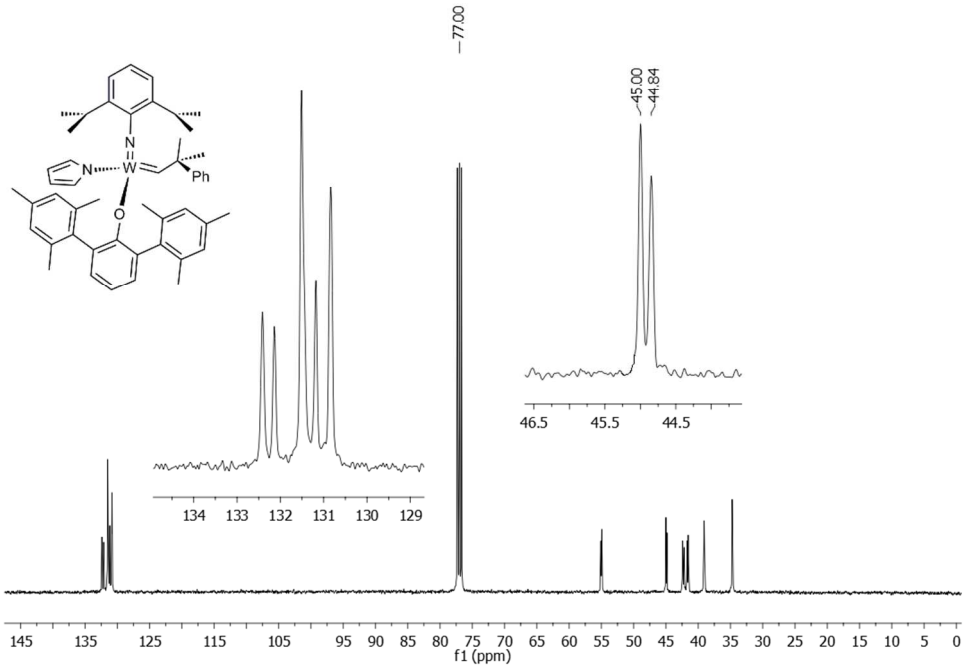

Figure S4. ^{13}C NMR spectrum ($CDCl_3$) of *cis, syndiotactic* poly(DCPD) made from **3**. The signals for C3/C4 at 45.0/44.9 ppm are indicative for a *cis, syndiotactic* structure.

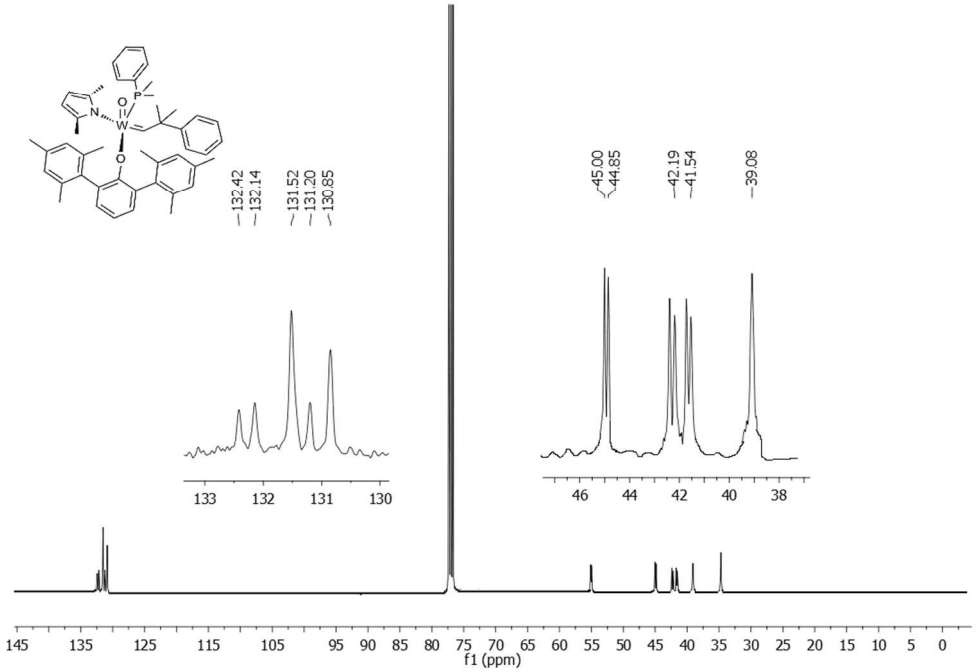

Figure S5. ^{13}C NMR spectrum ($CDCl_3$) of *cis, syndiotactic* poly(DCPD) made from **7**. The signals for C3/C4 at 45.0/44.9 ppm are indicative for a *cis, syndiotactic* structure.

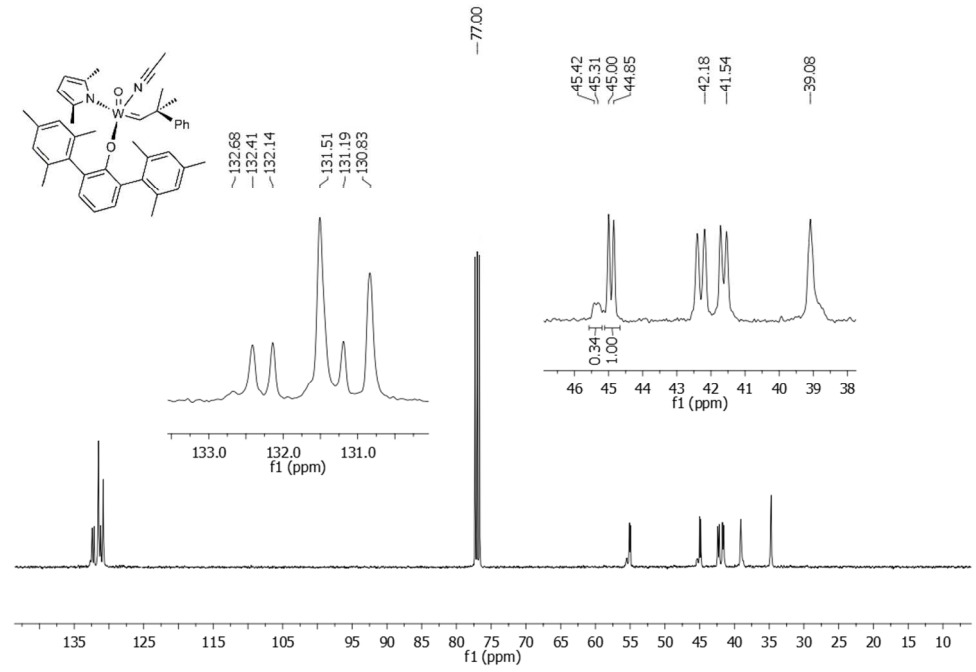

Figure S6. ^{13}C NMR spectrum ($CDCl_3$) of >98% *cis,* 75% *syndiotactic* poly(DCPD) made from **8**. The signals for C3/C4 at 45.0/44.9 ppm are indicative for a *cis, syndiotactic* structure, the signals for C3/C4 at 45.4/45.3 ppm are indicative for a *cis, isotactic* structure.

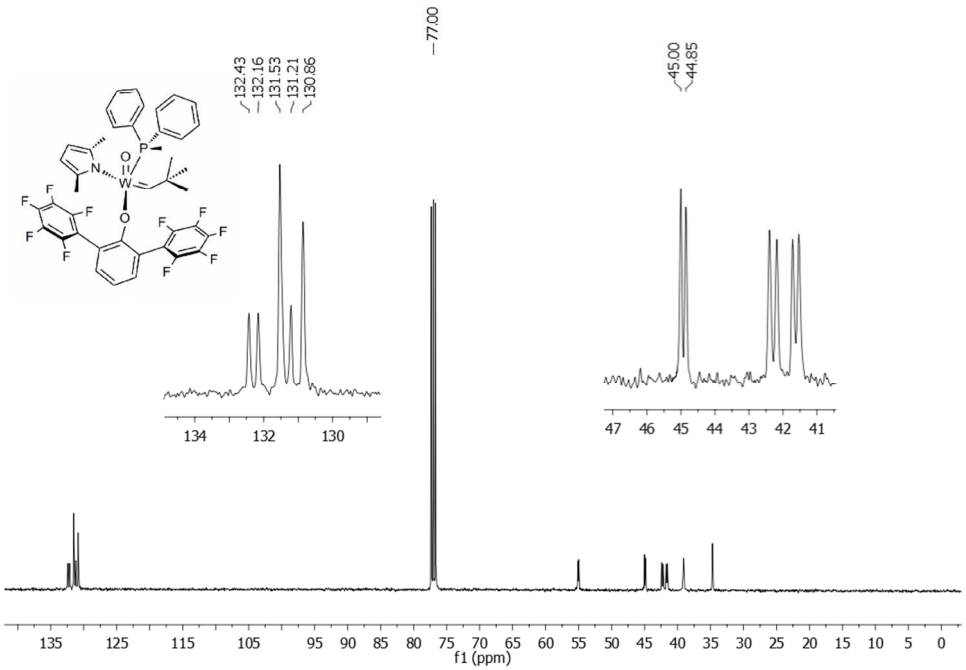

Figure S7. ^{13}C NMR spectrum ($CDCl_3$) of *cis, syndiotactic* poly(DCPD) made from **9**. The signals for C3/C4 at 45.0/44.9 ppm are indicative for a *cis, syndiotactic* structure.

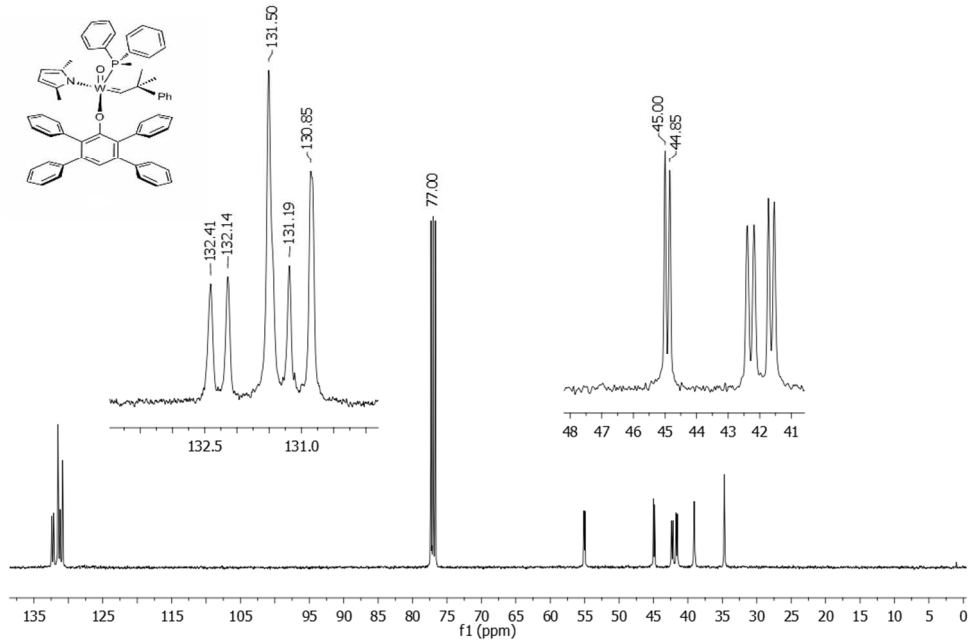

Figure S8. ^{13}C NMR spectrum ($CDCl_3$) of *cis, syndiotactic* poly(DCPD) made from **10**. The signals for C3/C4 at 45.0/44.9 ppm are indicative for a *cis, syndiotactic* structure.

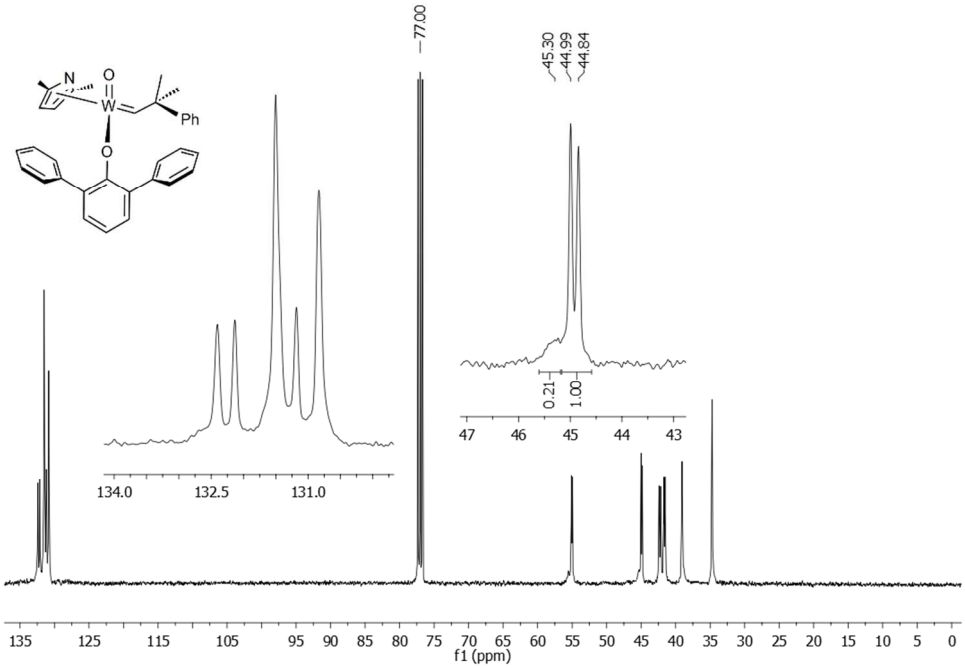

Figure S9. ^{13}C NMR spectrum ($CDCl_3$) of >98% *cis,* 90% *syndiotactic* poly(DCPD) made from **11**.

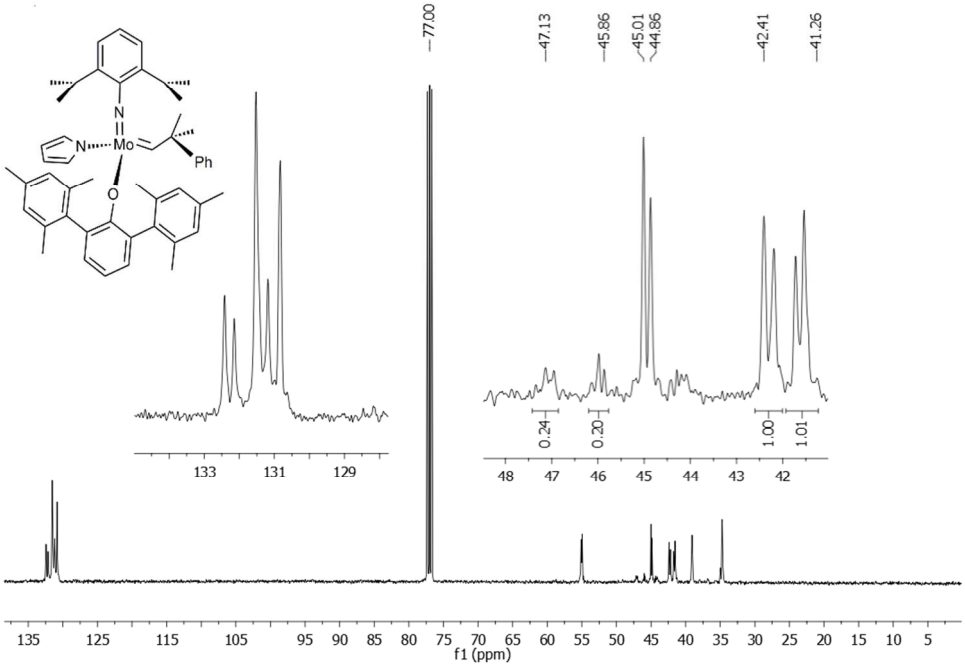

Figure S10. ^{13}C NMR spectrum ($CDCl_3$) of 80% *cis,* 90% *syndio*tactic poly(DCPD) made from **15**.

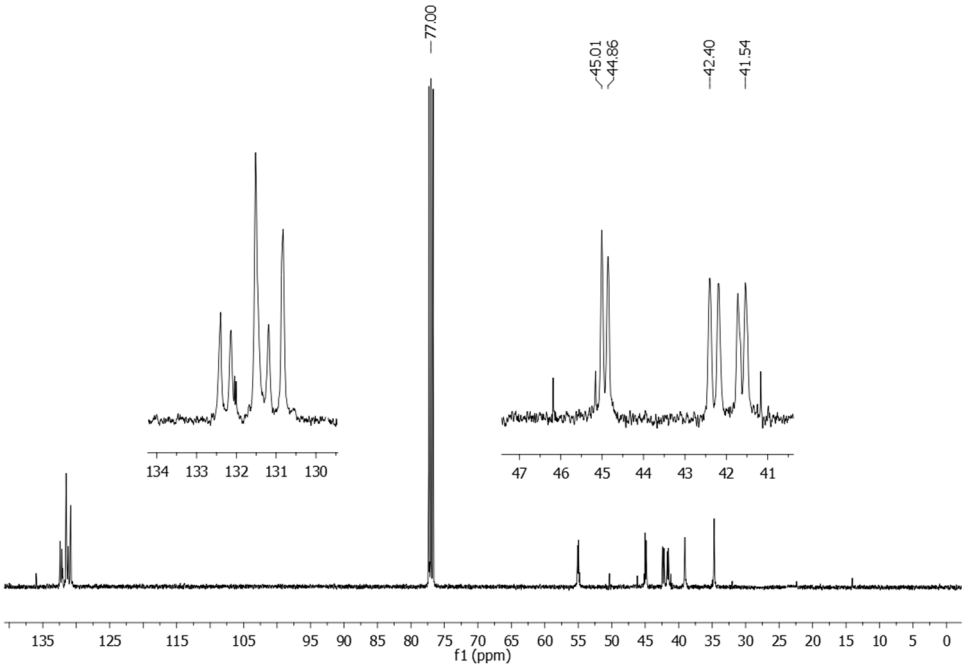

Figure S11. ^{13}C NMR spectrum ($CDCl_3$) of *cis, syndiotactic* poly(DCPD) made using **9** in the presence of 5 mol-% 1-hexene (**9hex**). The signals for C3/C4 at 45.0/44.9 ppm are indicative for a *cis,syndiotactic* structure.

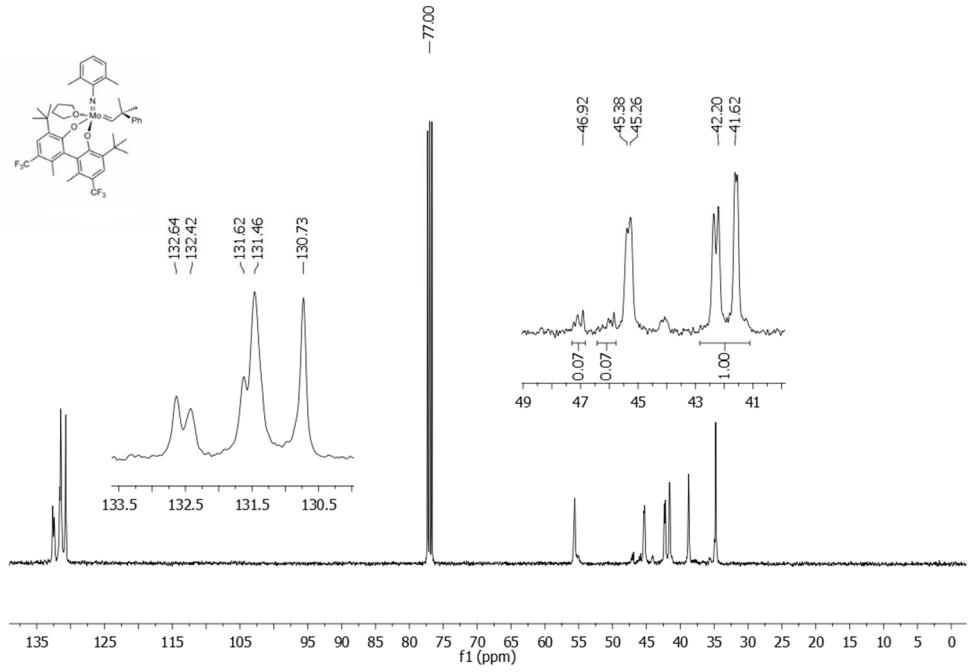

Figure S12. ^{13}C NMR spectrum ($CDCl_3$) of 90% *cis,* 95% *isotactic* poly(DCPD) made using **20**. The signals for C3/C4 at 45.4/45.3 ppm are indicative for a *cis, isotactic* structure.

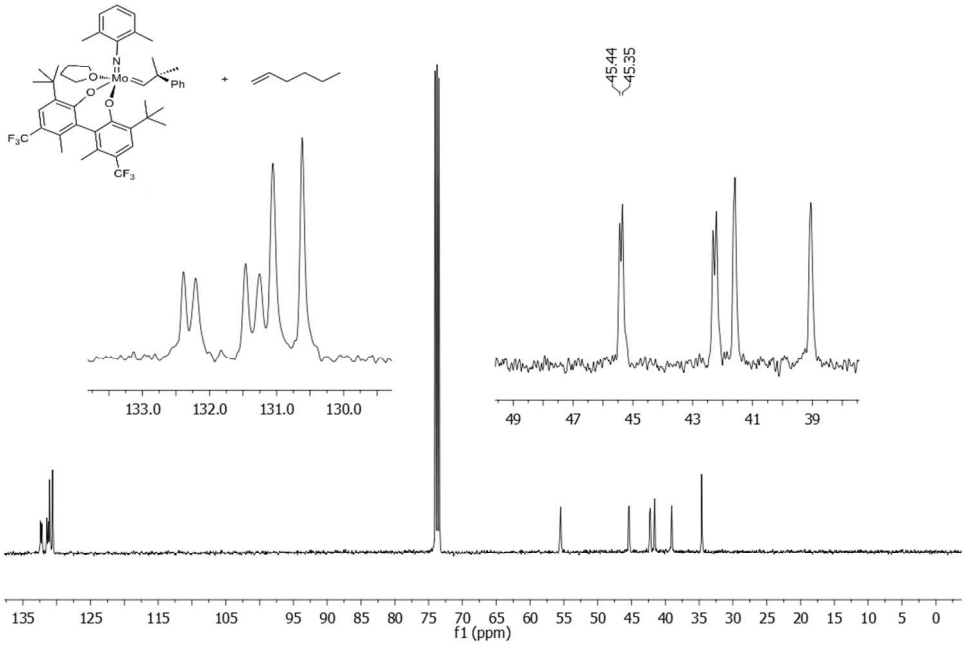

Figure S13. ^{13}C NMR spectrum ($C_2D_2Cl_4$, 140 °C) of *cis, isotactic* poly(DCPD) derived by the action of **20** in the presence of 5 mol-% 1-hexene (**20hex**). The signals for C3/C4 at 45.4/45.3 ppm are indicative for a *cis, isotactic* structure; no *trans* olefin carbon resonances are visible.

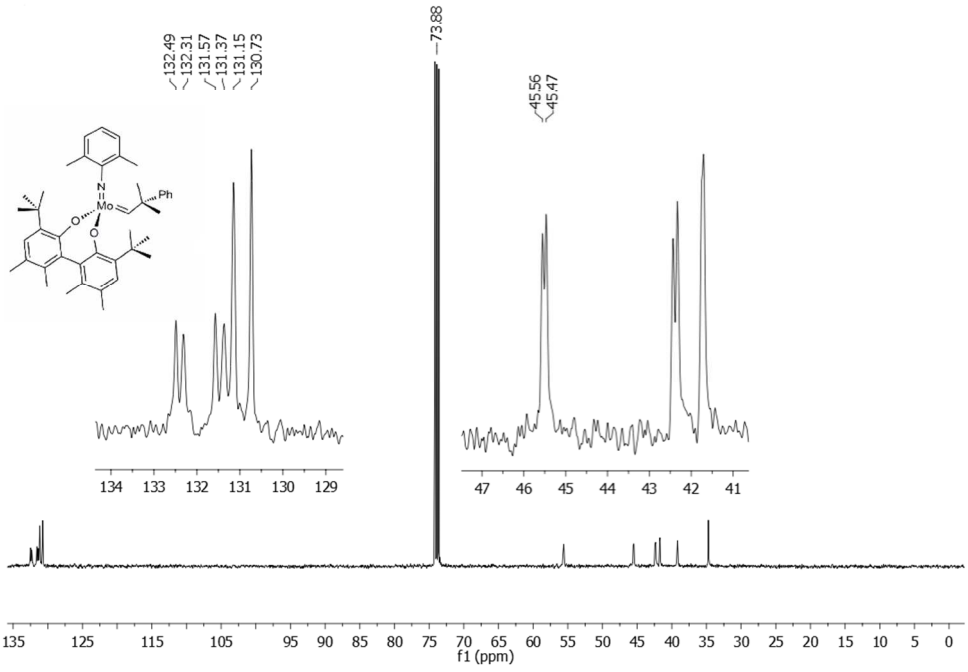

Figure S14. ^{13}C NMR ($C_2D_2Cl_4$, 140 °C) of *cis, isotactic* poly(DCPD) derived by the action of **17**. The signals for C3/C4 at 45.6/45.5 ppm are indicative for a *cis, isotactic* structure; no *trans* olefin carbon resonances are visible.

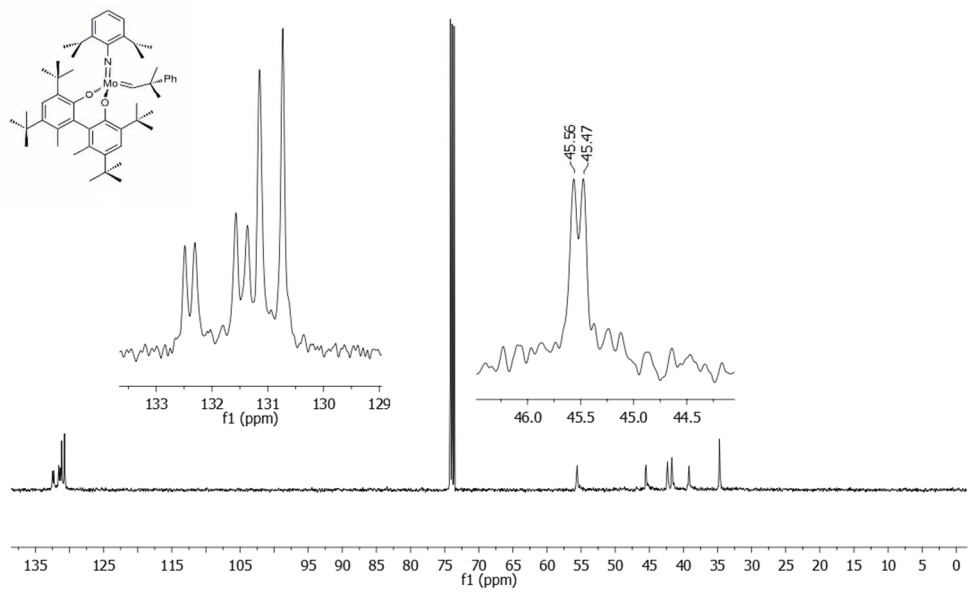

Figure S15. ^{13}C NMR spectrum ($C_2D_2Cl_4$, 140 °C) of *cis,* 90% *isotactic* poly(DCPD) made using **18**.

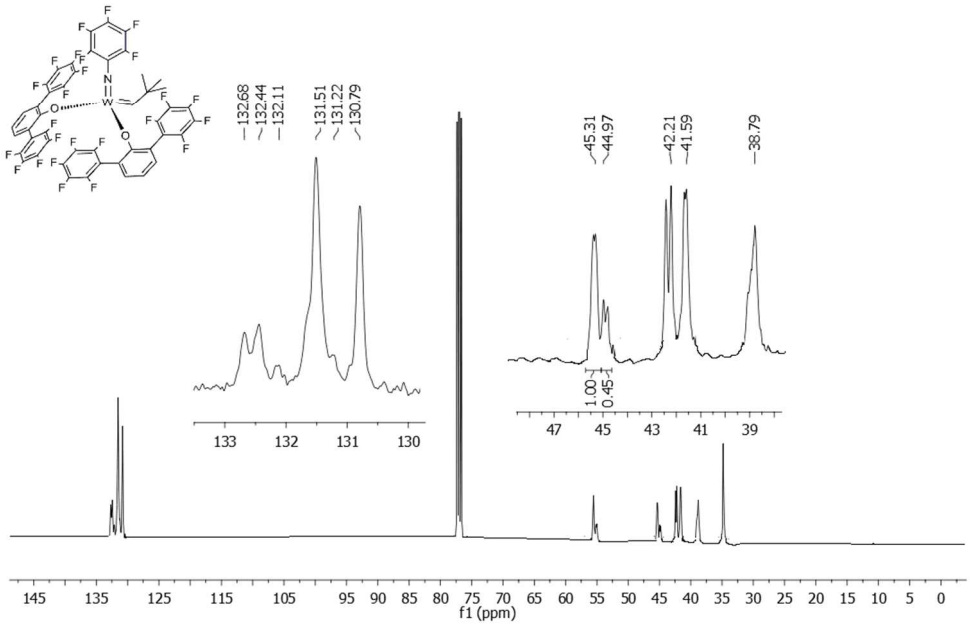

Figure S16. ^{13}C NMR spectrum ($CDCl_3$) of >98% *cis,* 70% *iso*tactic poly(DCPD) made using **25**. The signals for C3/C4 at 45.4/45.3 ppm are indicative for a *cis, isotactic* structure, the signals for C3/C4 at 45.0/44.9 ppm are indicative for a *cis, syndiotactic* structure.

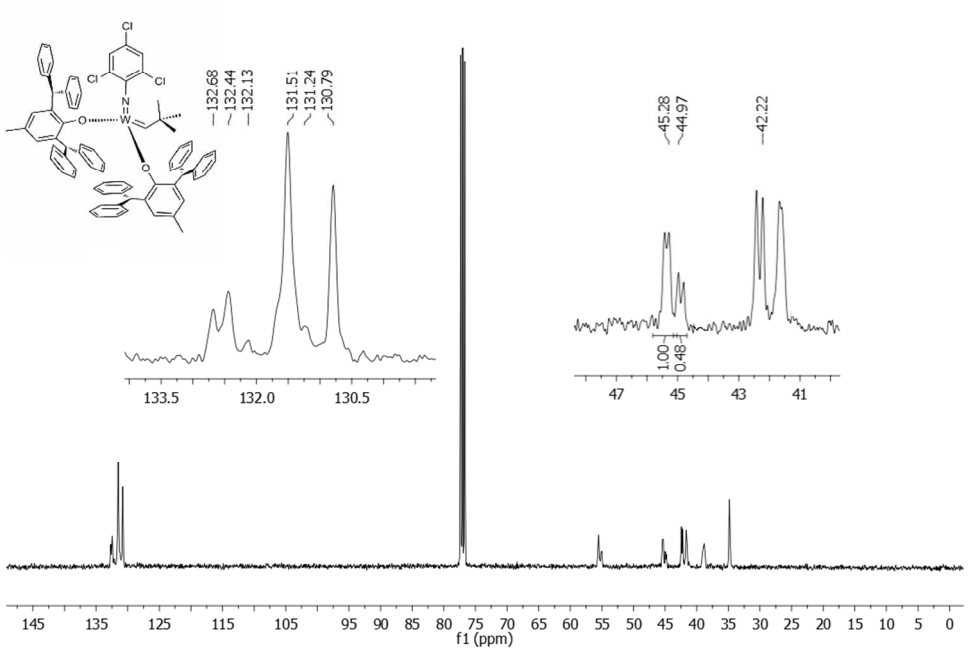

Figure S17. ^{13}C NMR spectrum ($CDCl_3$) of 100% *cis,* 70% *isotactic* poly(DCPD) derived by the action of **26a**. The signals for C3/C4 at 45.4/45.3 ppm are indicative for a *cis, isotactic* structure, the signals for C3/C4 at 45.0/44.9 are indicative for a *cis, syndiotactic* structure.

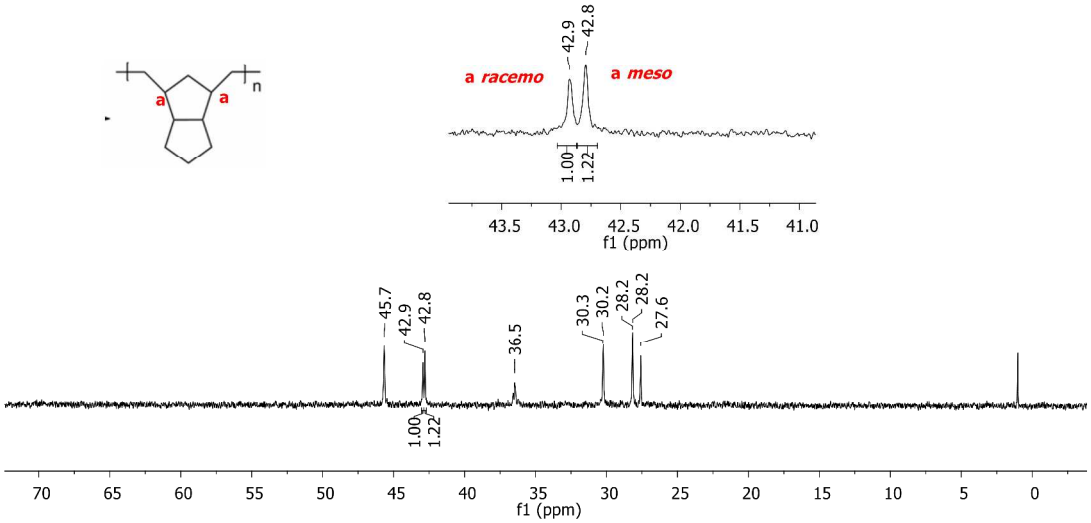

Figure S18. ^{13}C NMR **spectrum** ($CDCl_3$, r.t.) of atactic H-poly(DCPD) made using **1** (Table 1, entry 2). The signal for C(a) at 42.9 ppm is indicative for a *syndiotactic* structure, the signal at 42.8 ppm is indicative for an *isotactic* structure [8,10,28].

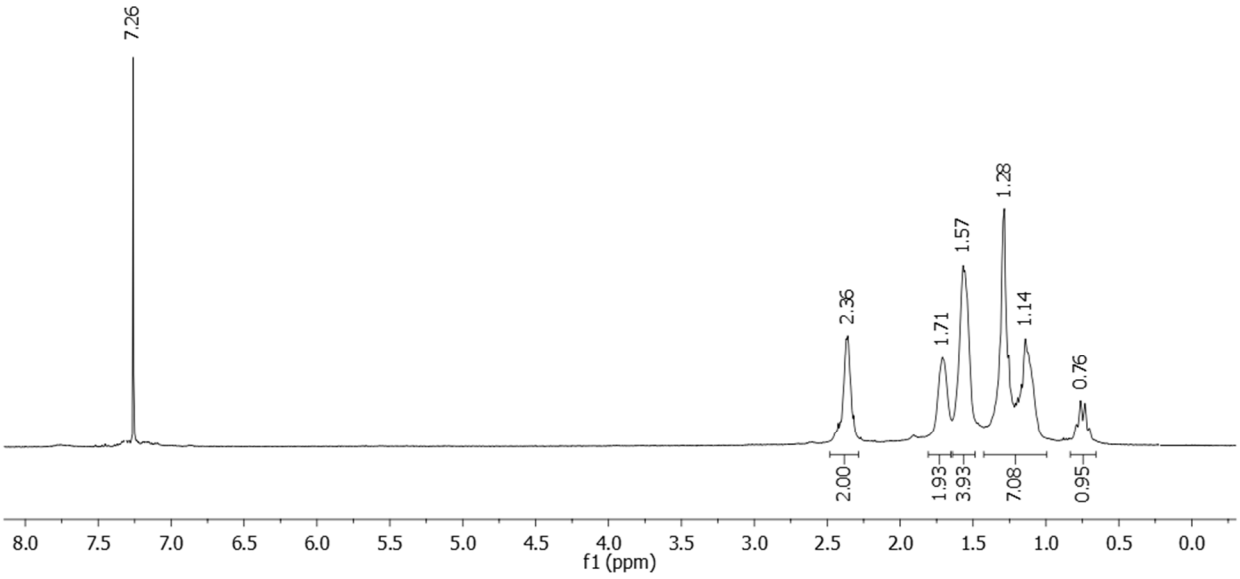

Figure S19. ^{1}H NMR spectrum ($CDCl_3$, 22 °C) of atactic H-poly(DCPD) made from **1**.

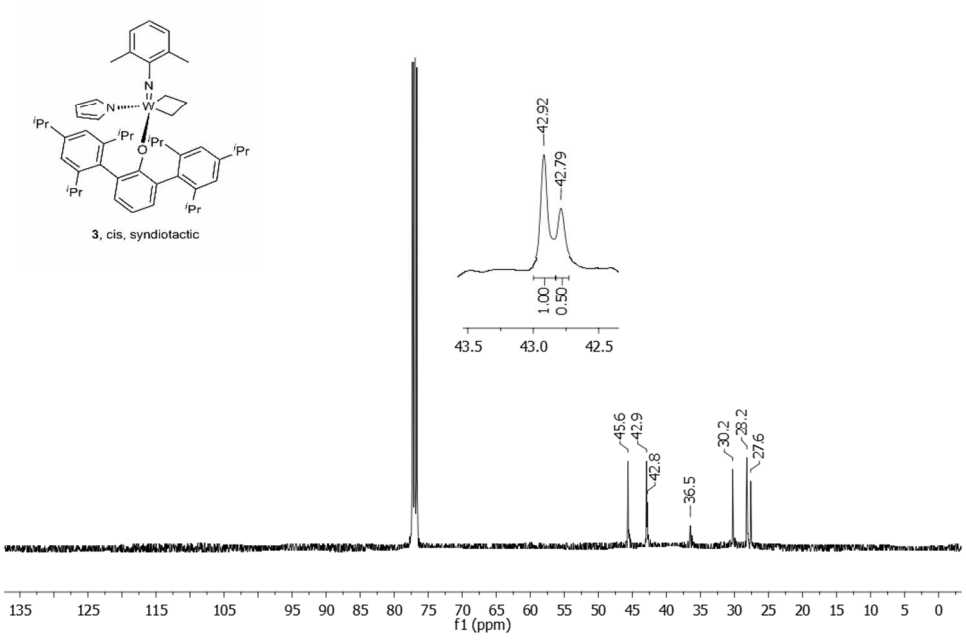

Figure S20. ^{13}C NMR spectrum ($CDCl_3$, r.t.) of 70% *syndiotactic* H-poly(DCPD) made from **4**.

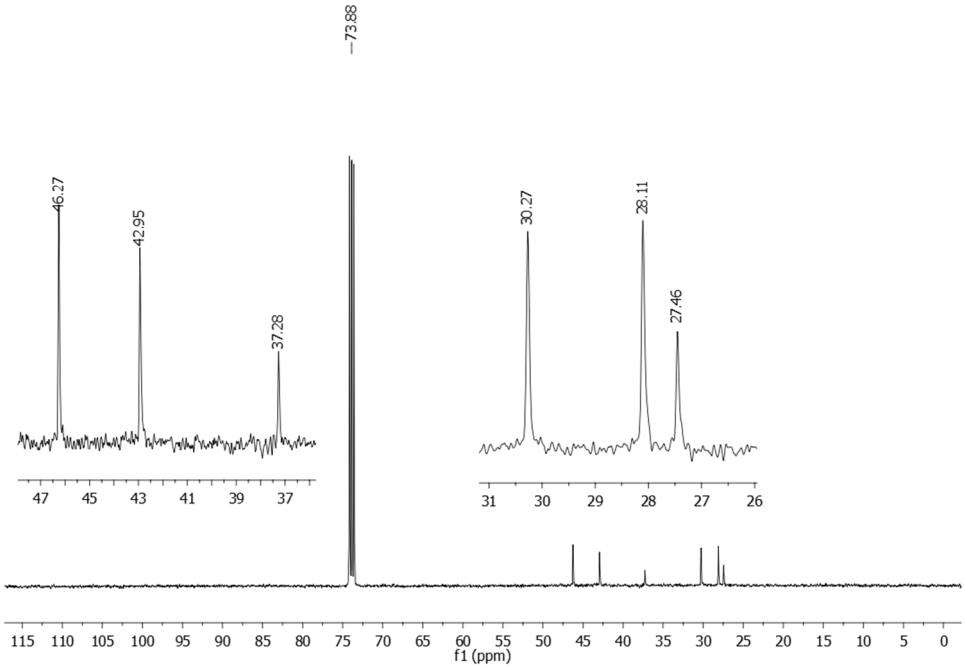

Figure S21. ^{13}C NMR spectrum ($C_2D_2Cl_4$, 140 °C) of *syndiotactic* H-poly(DCPD) made from **2**.

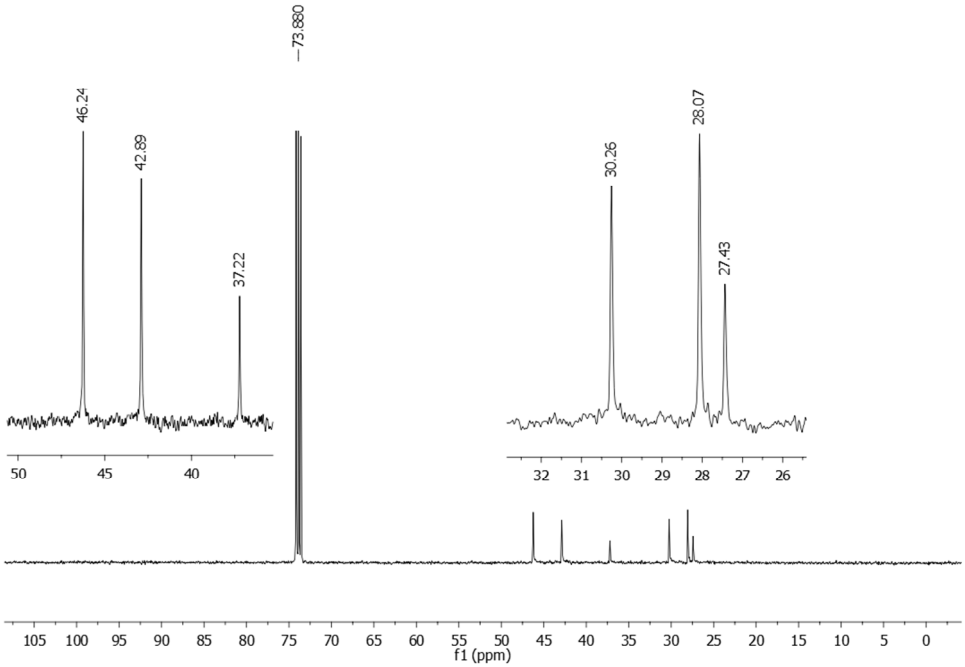

Figure S22. ^{13}C NMR spectrum ($C_2D_2Cl_4$, 140 °C) of *isotactic* H-poly(DCPD) made with **20(hex)**.

DSC Thermograms

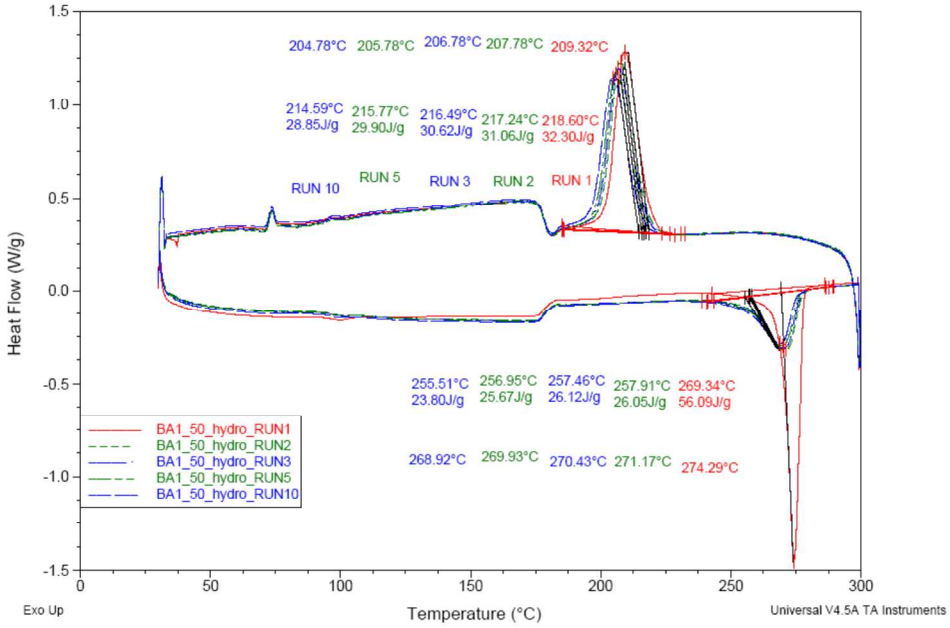

Figure S23. DSC thermogram of *syndiotactic* H-poly(DCPD) (50 equiv. DCPD) derived by the action of **2**. 10 heating/cooling cycles. Heating: 10 K/min. Cooling: 20 K/min.

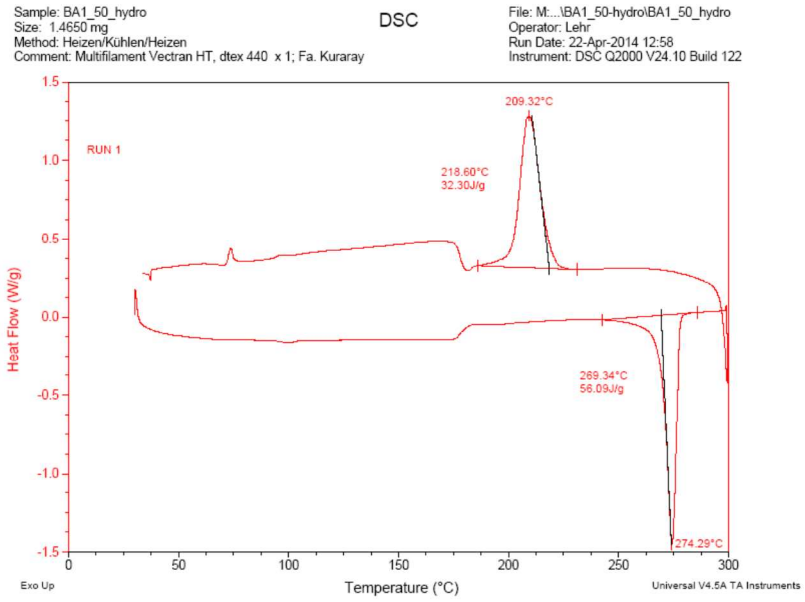

Figure S24. First heating/cooling cycle for *syndiotactic* H-poly(DCPD) (50 equiv. DCPD) derived by the action of **2**. Heating: 10 K/min. Cooling: 20 K/min.

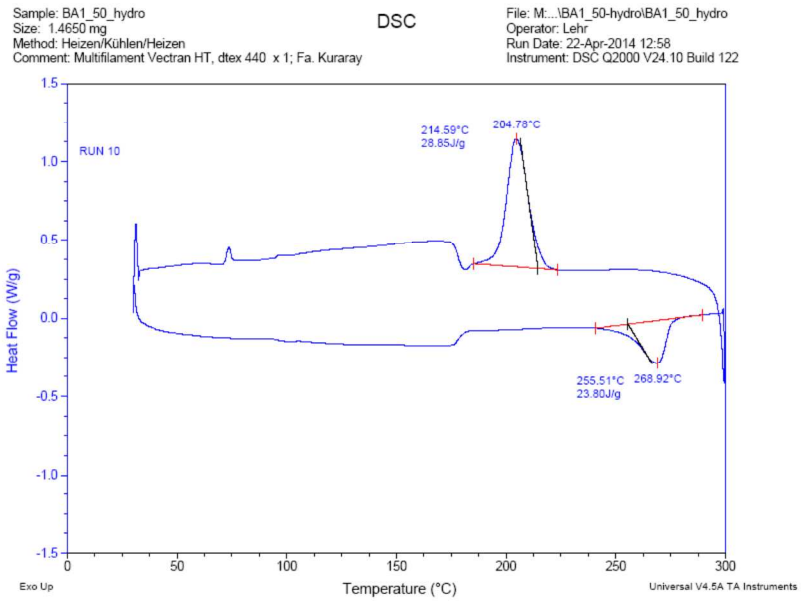

Figure S25. Tenth heating/cooling cycle for *syndiotactic* H-poly(DCPD) (50 equiv. DCPD) made from **2**. Heating: 10 K/min. Cooling: 20 K/min.

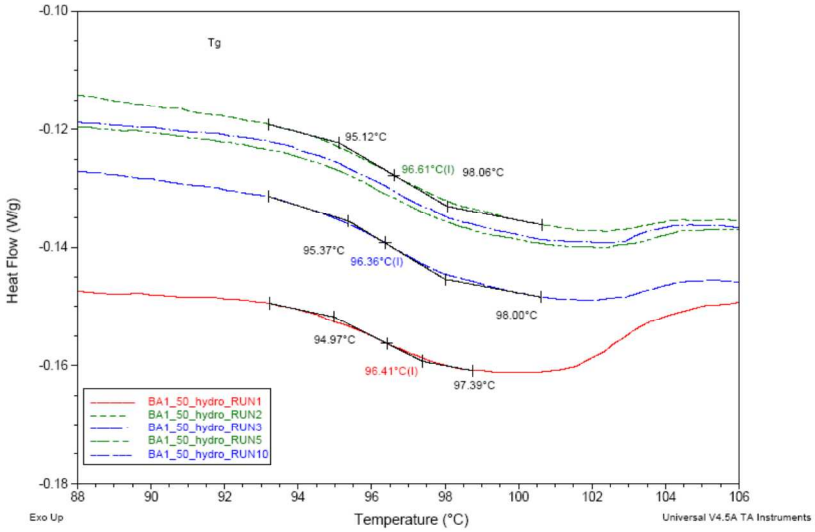

Figure S26. Determination of T_g for *syndiotactic* H-poly(DCPD) (50 equiv. DCPD) made from **2**.

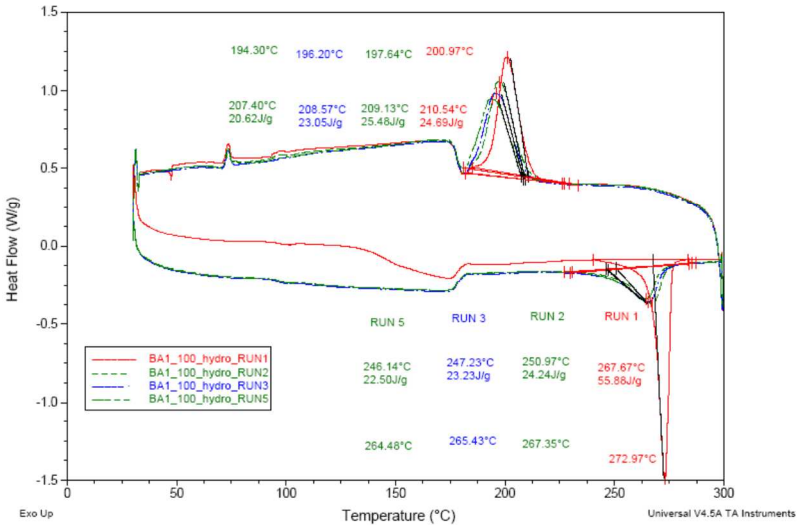

Figure S27. DSC thermogram of *syndiotactic* H-poly(DCPD) (100 equiv. DCPD) made from **2**. Heating: 10 K/min. Cooling: 20 K/min.

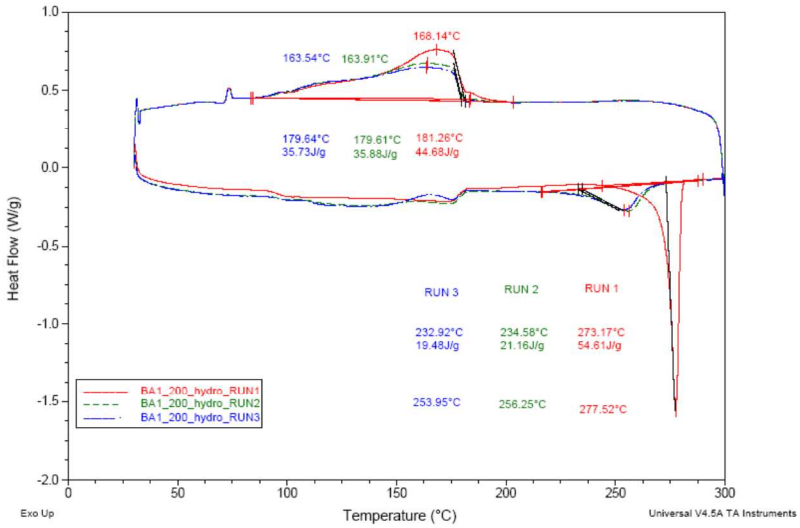

Figure S28. DSC thermogram of *syndiotactic* H-poly(DCPD) (200 equiv. DCPD) made with **2**. Heating: 10 K/min. Cooling: 20 K/min.

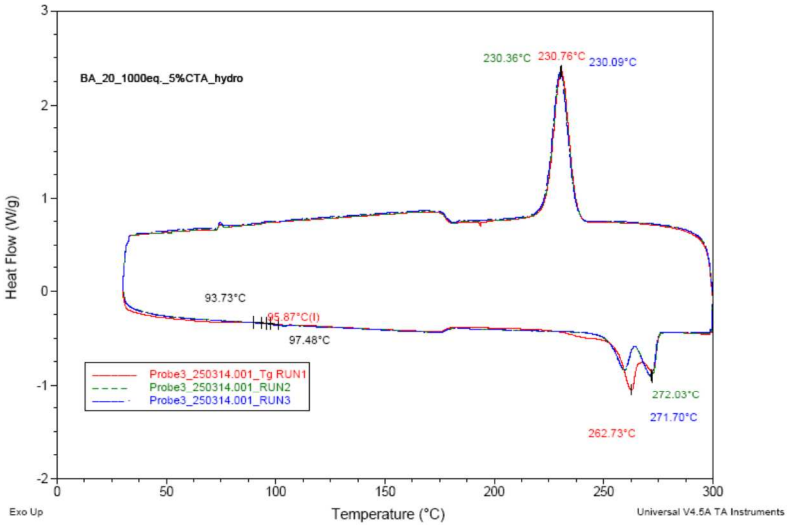

Figure S29. DSC thermogram of *syndiotactic* H-poly(DCPD) (1000 equiv. DCPD + 5 mol-% 1-hexene) made employing **9(hex)**. Heating: 10 K/min. Cooling: 20 K/min.

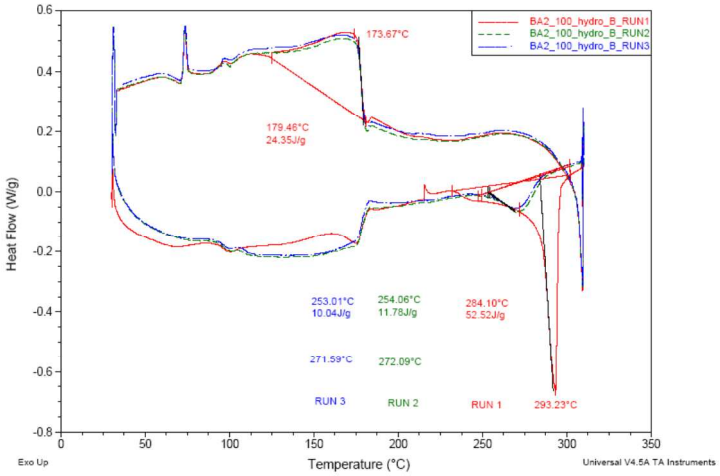

Figure S30. DSC thermogram of *isotactic* H-poly(DCPD) (100 equiv. DCPD) made from **17**. Heating: 10 K/min. Cooling: 20 K/min.

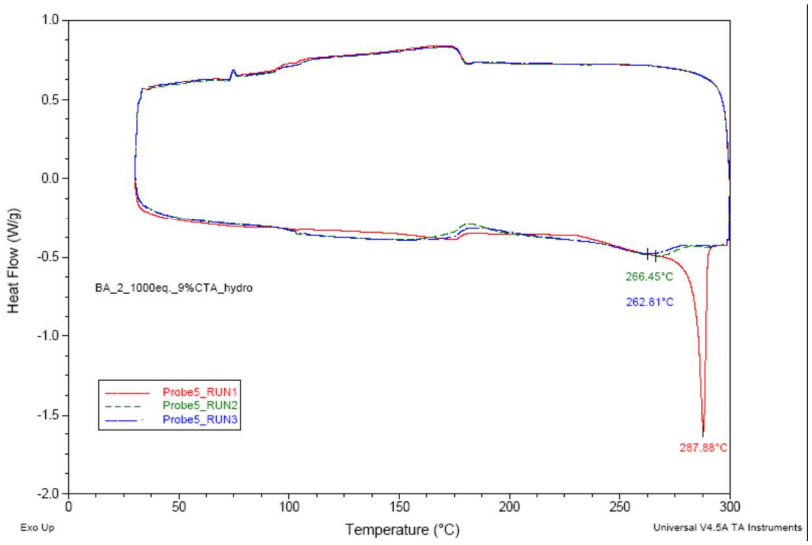

Figure S31. DSC thermogram of *isotactic* H-poly(DCPD) (1000 equiv. DCPD + 5 mol-% 1-hexene) made employing **20(hex)**. Heating: 10 K/min. Cooling: 20 K/min.

Crystallinity of H-poly(DCPD)s

Table S1. Peak list for *syndiotactic* H-poly(DCPD) made with **2** and 50 equiv. of monomer.

No.	2-theta(deg)	d(ang.)	Height(cps)	FWHM(deg)	Int. I(cps deg)	Int. W(deg)	Asym. factor
1	6.446(19)	13.70(4)	108.3(7)	0.520(16)	60(3)	0.55(3)	0.86(12)
2	11.54(6)	7.66(4)	61.7(6)	2.23(15)	160(13)	2.6(2)	1(2)
3	13.27(5)	6.66(3)	84.6(6)	3(7)	276(20)	3.3(3)	0.30(7)
4	15.882(9)	5.576(3)	610.7(17)	0.718(19)	573(28)	0.94(5)	1.20(8)
5	16.05(5)	5.517(18)	403.4(14)	2.42(12)	1039(58)	2.58(15)	1.20(13)
6	18.475(5)	4.7986(14)	1452(3)	0.864(16)	2067(84)	1.42(6)	1.43(8)
7	19.46(5)	4.559(11)	368.3(13)	2.17(9)	849(43)	2.31(12)	0.5(2)
8	21.62(3)	4.108(6)	133.6(8)	2.31(6)	366(11)	2.74(10)	0.23(3)
9	26.02(3)	3.421(4)	121.1(8)	0.88(5)	200(7)	1.65(7)	1.2(2)
10	32.18(5)	2.779(4)	54.9(5)	0.97(5)	65(3)	1.19(7)	1.3(3)
11	37.9(3)	2.37(2)	7.00(19)	1.3(3)	10(34)	1(5)	2(2)
12	38.7(3)	2.324(16)	20.0(3)	8.0(12)	171(50)	9(3)	0.2(4)
13	40.57(11)	2.222(6)	36.8(4)	2.0(3)	141(49)	3.8(14)	0.37(14)
14	46.6(3)	1.949(10)	15.0(3)	3.2(6)	67(24)	4.5(17)	0.5(4)

Crystallinity

Data set name	Crystallinity(%)
Aut004_BG	83(12)

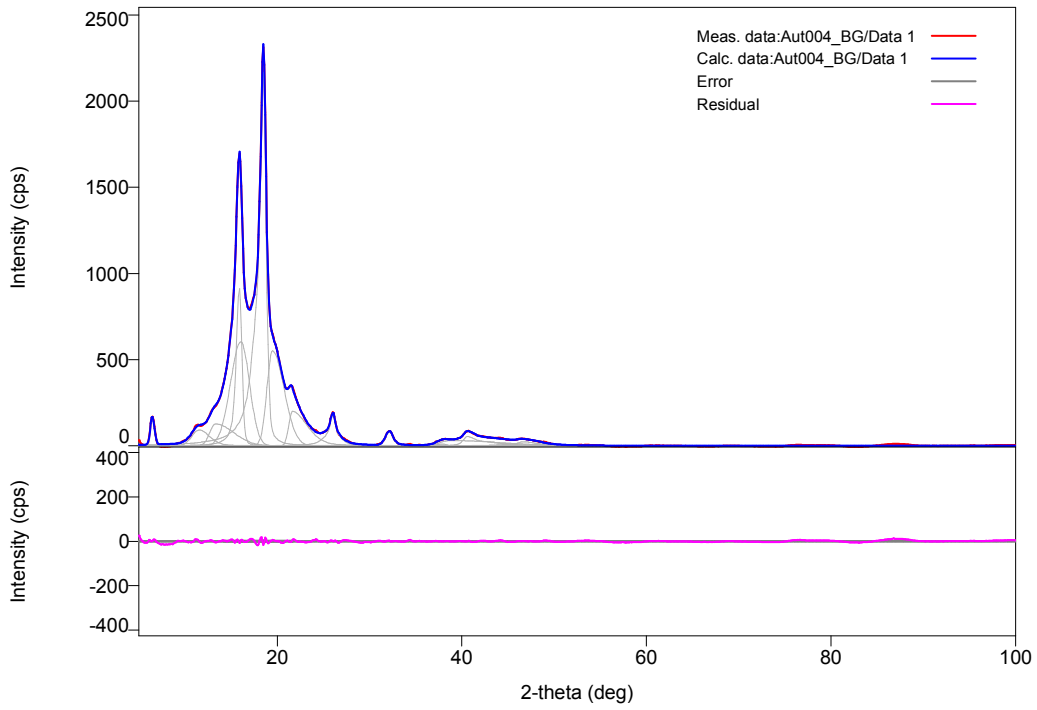

Figure S32. WAXRD measurement profile for *syndiotactic* H-poly(DCPD) made from **2** and 50 equiv. of DCPD.

Table S2. Peak list for *isotactic* H-poly(DCPD) made from **17** and 50 equivalents of DCPD.

No.	2-theta(deg)	d(ang.)	Height(counts)	FWHM(deg)	Int. I(counts deg)	Int. W(deg)	Asym. factor
1	12.26(6)	7.21(4)	41.9(15)	2.06(18)	184(29)	4.4(8)	1.8(5)
2	14.551(14)	6.082(6)	332(4)	0.710(10)	268(23)	0.81(8)	1.10(8)
3	15.82(5)	5.596(18)	236(4)	2.87(18)	1087(118)	4.6(6)	1.46(18)
4	18.447(12)	4.806(3)	331(4)	0.82(4)	492(58)	1.5(2)	2.0(2)
5	19.08(3)	4.648(8)	317(4)	1.18(5)	495(20)	1.56(8)	1(3)
6	20.068(14)	4.421(3)	223(3)	0.81(5)	269(19)	1.21(10)	1.23(19)
7	21.314(17)	4.165(3)	91(2)	0.79(5)	128(9)	1.41(13)	1.8(2)
8	24.52(3)	3.628(4)	19.2(10)	0.51(5)	11.1(13)	0.58(10)	1.4(4)
9	25.34(3)	3.513(3)	47.6(16)	0.82(5)	64(3)	1.35(10)	0.74(13)
10	36.43(8)	2.465(5)	23.8(11)	1.32(12)	55(11)	2.3(6)	1.8(5)
11	38.63(14)	2.329(8)	27.4(12)	3.7(2)	137(187)	5(7)	1.5(3)
12	40.81(5)	2.209(3)	19.2(10)	2(3)	70(6)	3.6(5)	0.29(8)
13	44.42(12)	2.038(5)	18.8(10)	2.5(3)	61(10)	3.2(7)	2.8(10)
14	47.94(8)	1.896(3)	13.3(8)	4.7(4)	115(15)	8.7(17)	0.32(9)

Crystallinity

Data set name	Crystallinity(%)
Aut008_BG	68(21)

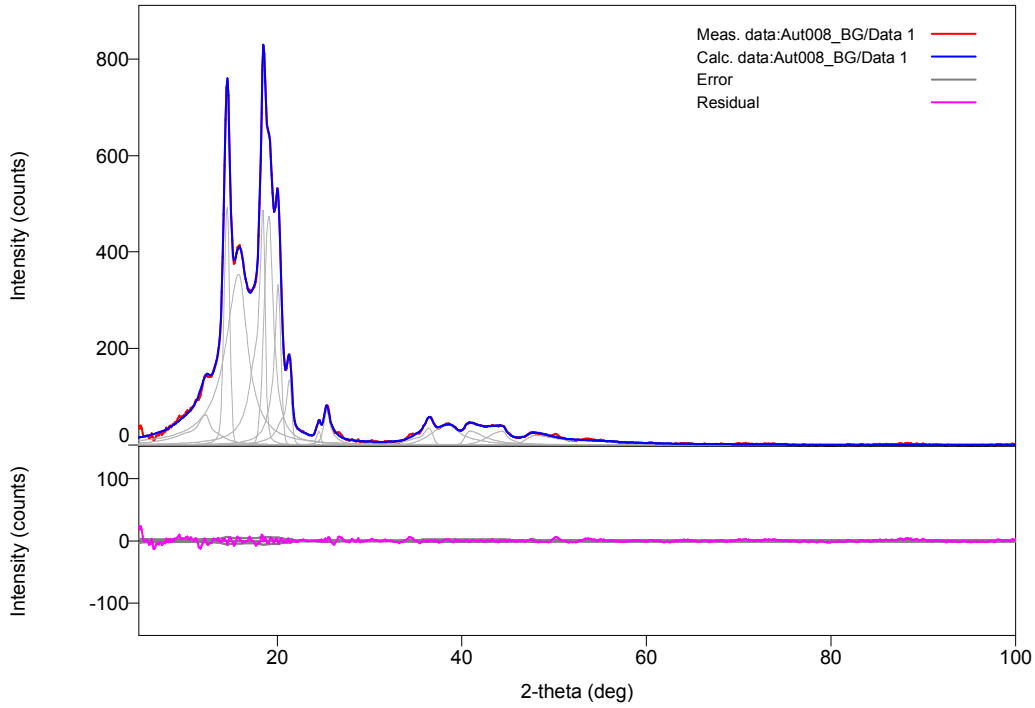

Figure S33. WAXRD measurement profile for *isotactic* H-poly(DCPD) made from **17** and 50 equivalents of DCPD.

Table S3. Peak list for *syndiotactic* H-poly(DCPD) derived by **9(hex)**, 1000 equiv. DCPD + 5 mol% 1-hexene.

No.	2-theta(deg)	d(ang.)	Height(counts)	FWHM(deg)	Int. I(counts deg)	Int. W(deg)	Asym. factor
1	6.50(2)	13.59(5)	80(2)	0.47(2)	48(3)	0.60(6)	0.9(2)
2	11.27(4)	7.85(3)	23.7(12)	0.80(12)	29(6)	1.2(3)	0.56(15)
3	12.97(5)	6.82(3)	13.4(9)	0.8(2)	15(7)	1.1(6)	2(6)
4	16(2)	5.6(7)	100(2)	4.2(6)	451(68)	4.5(8)	1.4(4)
5	15.934(8)	5.557(3)	478(5)	0.611(12)	431(11)	0.90(3)	1.10(7)
6	17.61(5)	5.031(15)	66(2)	1.8(3)	126(30)	1.9(5)	5(6)
7	18.541(6)	4.7815(14)	596(6)	0.588(16)	472(22)	0.79(4)	1.11(7)
8	19.44(5)	4.562(11)	123(3)	1.88(7)	363(44)	3.0(4)	1(4)
9	21.660(9)	4.0997(18)	30.3(13)	0.57(3)	24.0(8)	0.79(6)	1.4(5)
10	26.06(2)	3.416(3)	43.5(16)	0.42(2)	26.1(7)	0.60(4)	0.86(18)
11	32.20(3)	2.778(3)	39.6(15)	0.63(3)	35.2(14)	0.89(7)	1.1(2)
12	38.69(17)	2.326(10)	10.6(8)	5.1(6)	114(16)	11(2)	5(5)
13	40.63(3)	2.2185(18)	18.6(10)	1.06(11)	31(15)	1.7(9)	0.9(6)
14	42.9(2)	2.106(11)	16.2(10)	4.7(3)	120(12)	7.4(12)	1.0(2)

Crystallinity

Data set name	Crystallinity(%)
Aut005_BG	81(18)

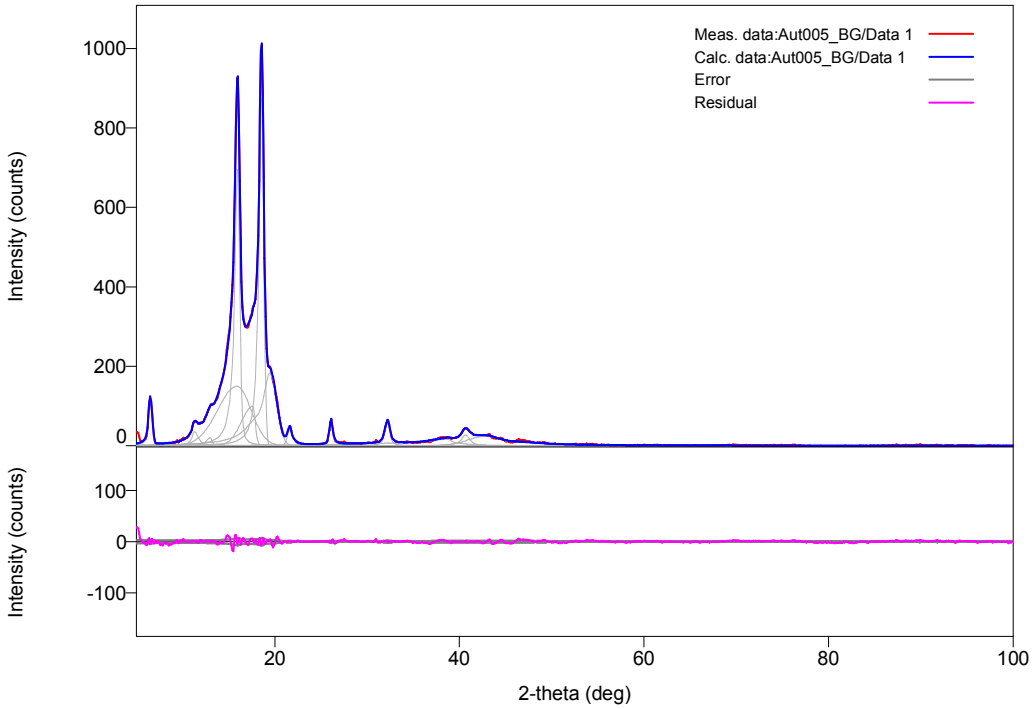

Figure S34. WAXRD measurement profile for *syndiotactic* H-poly(DCPD) derived by **9(hex)**, 1000 equivalents DCPD + 5 mol% 1-hexene.

Table S4. Peak list for *syndiotactic* H-poly(DCPD) made from **2** and 100 equiv. of DCPD.

No.	2-theta(deg)	d(ang.)	Height(cps)	FWHM(deg)	Int. I(cps deg)	Int. W(deg)	Asym. factor
1	6.45(2)	13.69(5)	154.6(7)	0.64(2)	116(4)	0.75(3)	0.83(13)
2	11.5(2)	7.66(14)	64.8(5)	4.0(6)	277(76)	4.3(12)	0.4(11)
3	15.850(16)	5.587(6)	1033.3(18)	1.48(5)	2684(219)	2.6(2)	0.90(7)
4	15.99(8)	5.54(3)	383.1(11)	3.5(2)	1708(143)	4.5(4)	1(6)
5	18.466(9)	4.801(2)	1483(2)	0.973(19)	2273(76)	1.53(5)	1.13(6)
6	20.45(8)	4.340(17)	232.3(9)	5(11)	1217(404)	5.2(18)	1.28(8)
7	25.97(4)	3.428(6)	153.3(7)	0.96(6)	248(10)	1.62(8)	1.0(2)
8	32.13(11)	2.784(9)	53.4(4)	1.74(13)	123(8)	2.30(17)	1.3(4)
9	38.25(19)	2.351(11)	24.5(3)	2.5(6)	78(20)	3.2(9)	0.7(16)
10	40.57(10)	2.222(5)	39.9(4)	2.8(3)	131(26)	3.3(7)	0.4(5)
11	44.8(7)	2.02(3)	29.1(3)	9(3)	298(70)	10(3)	1.4(8)
12	47.6(6)	1.91(2)	10.88(19)	10(11)	119(77)	11(7)	4(207)
13	52(4)	1.75(12)	15.9(2)	9.8(7)	241(17)	15.1(13)	1(19)
14	77.7(2)	1.227(3)	11.08(19)	8.6(6)	103(6)	9.3(7)	1.4(5)

Crystallinity

Data set name	Crystallinity(%)
Aut009_BG	80(15)

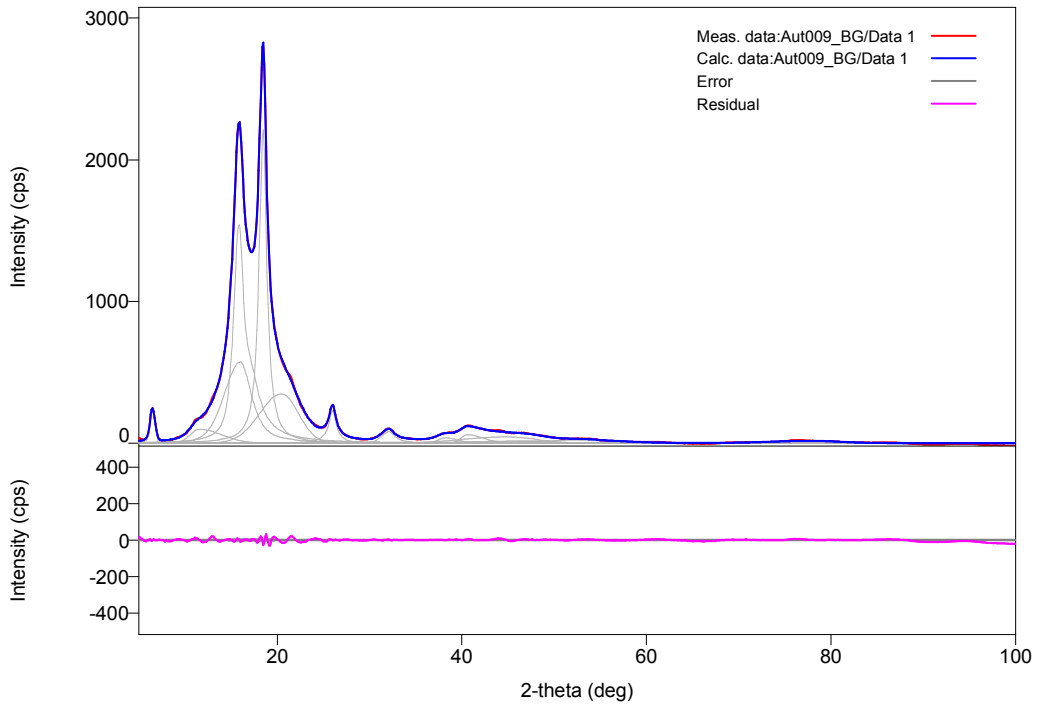

Figure S35. WAXRD measurement profile for *syndiotactic* H-poly(DCPD) made from **2** and 100 equiv. of DCPD.

Table S5. Peak list for *syndiotactic* H-poly(DCPD) made from **2** and 200 equiv. of DCPD.

No.	2-theta(deg)	d(ang.)	Height(cps)	FWHM(deg)	Int. I(cps deg)	Int. W(deg)	Asym. factor
1	6.55(2)	13.49(5)	40.7(4)	0.72(2)	31(2)	0.76(6)	1.22(16)
2	15.6(4)	5.66(15)	130.1(6)	4.9(7)	685(112)	5.3(9)	1.2(5)
3	15.815(17)	5.599(6)	478.7(12)	1.94(7)	1328(141)	2.8(3)	0.70(3)
4	18.531(8)	4.784(2)	499.2(12)	1.50(7)	1237(127)	2.5(3)	1.4(4)
5	20.8(5)	4.26(10)	87.2(5)	3.63(16)	337(22)	3.9(3)	0.80(11)
6	25.95(3)	3.430(4)	54.7(4)	1.25(5)	108(4)	1.98(10)	1.01(13)
7	32.03(11)	2.792(9)	14.2(2)	1.75(10)	27(2)	1.9(2)	1.1(3)
8	40.52(13)	2.225(7)	21.0(3)	8.32(17)	186(4)	8.9(3)	0.34(3)
9	69.7(8)	1.348(13)	1.95(8)	20(3)	41(5)	21(3)	3(3)

Crystallinity

Data set name	Crystallinity(%)
Aut011_BG	83(16)

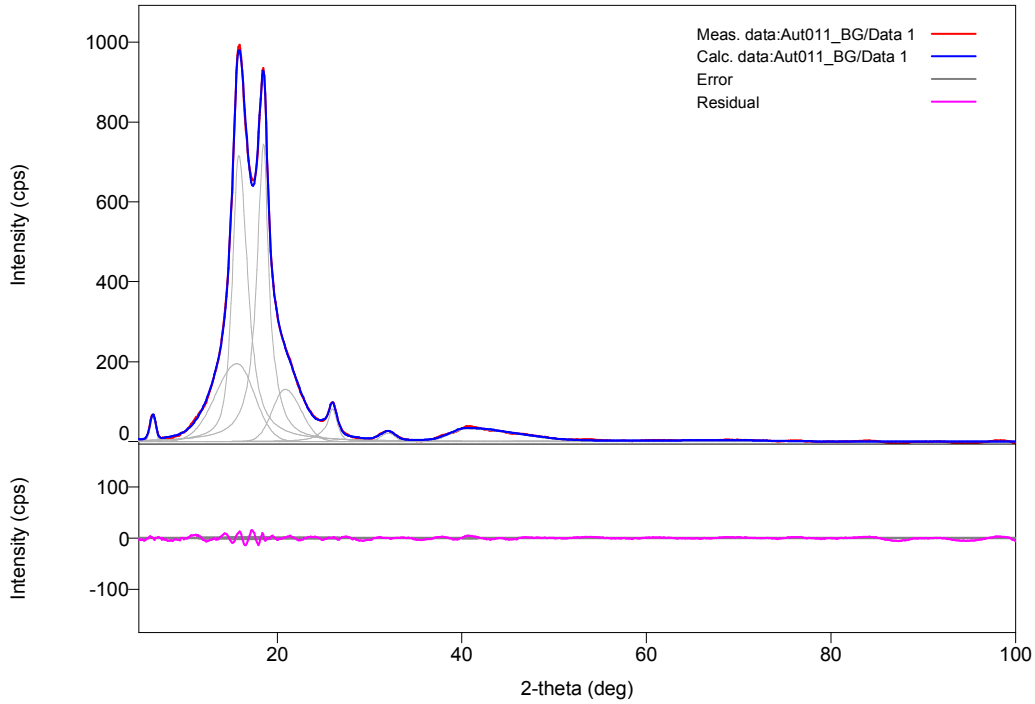

Figure S36. WAXRD measurement profile for *syndiotactic* H-poly(DCPD) made from **2** and 200 equiv. of DCPD.

Table S6. Peak list for *isotactic* H-poly(DCPD) made from **17** and 100 equiv. of DCPD.

No.	2-theta(deg)	d(ang.)	Height(cps)	FWHM(deg)	Int. I(cps deg)	Int. W(deg)	Asym. factor
1	10.78(19)	8.20(14)	10.4(2)	2.9(7)	32(8)	3.1(9)	1.5(10)
2	12.27(7)	7.21(4)	41.5(4)	2.05(16)	109(142)	3(3)	0.5(6)
3	14.61(2)	6.058(8)	125.9(8)	0.85(2)	125(14)	1.00(12)	0.98(9)
4	16.09(5)	5.504(16)	266.9(11)	4.3(17)	1223(15)	4.58(7)	0.69(4)
5	18.51(5)	4.789(12)	199.9(10)	1.39(17)	395(122)	2.0(6)	0.67(9)
6	20.00(8)	4.435(17)	99.6(7)	1.5(5)	159(99)	1.6(10)	2.1(8)
7	21.04(11)	4.22(2)	75.7(6)	1.54(19)	127(24)	1.7(3)	2(5)
8	21.63(11)	4.10(2)	46.8(5)	2.2(3)	111(20)	2.4(4)	0.26(10)
9	24.68(7)	3.605(11)	36.0(4)	2.09(15)	110(23)	3.1(7)	0.4(4)
10	25.49(6)	3.491(8)	25.4(4)	1.21(18)	61(14)	2.4(6)	0.7(3)
11	36.59(5)	2.454(3)	6.97(18)	0.91(18)	7(2)	1.0(4)	1.7(15)
12	37.3(4)	2.41(2)	10.2(2)	3.8(2)	41(4)	4.0(5)	1.1(3)
13	40.95(10)	2.202(5)	3.44(13)	0.9(3)	3.5(11)	1.0(4)	0.8(13)
14	43.32(12)	2.087(5)	17.2(3)	7.4(2)	193(6)	11.2(5)	1(4)

Crystallinity

Data set name	Crystallinity(%)
Aut013_BG	55(28)

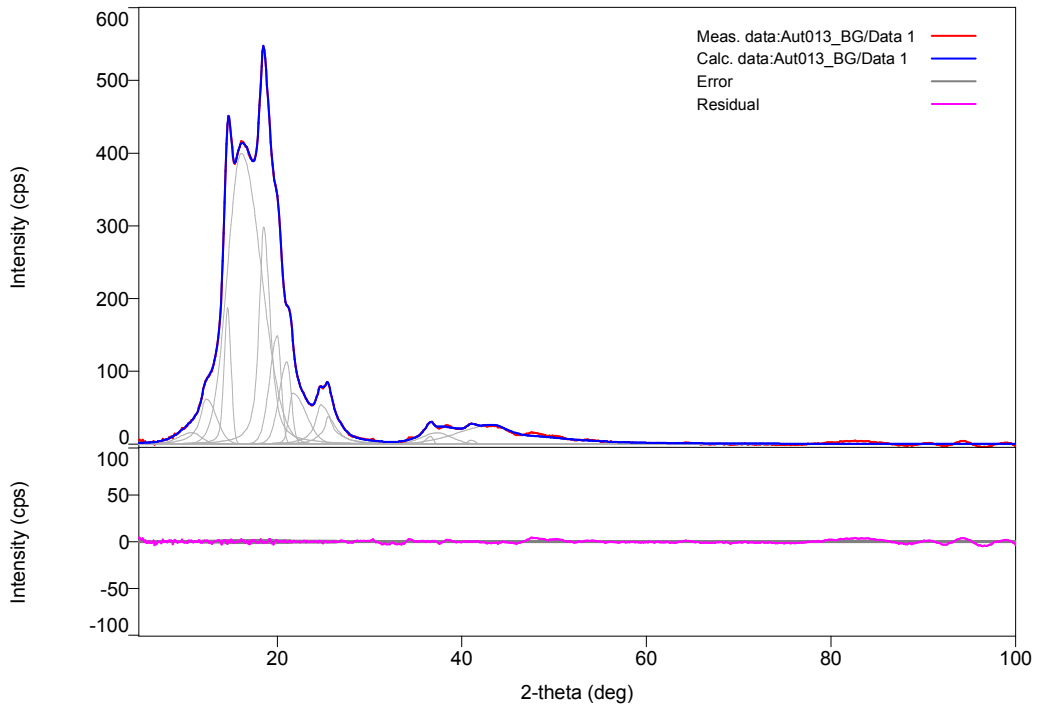

Figure S37. WAXRD measurement profile for *isotactic* H-poly(DCPD) made from **17** and 100 equiv. of DCPDs.

Table S7. Peak list for *iso*tactic H-poly(DCPD) derived by **20(hex)**, 1000 equiv. DCPD + 5 mol% 1-hexene.

No.	2-theta(deg)	d(ang.)	Height(cps)	FWHM(deg)	Int. I(cps deg)	Int. W(deg)	Asym. factor
1	12.06(6)	7.33(4)	31.9(5)	1.4(4)	67(23)	2.1(8)	0.6(3)
2	14.54(2)	6.085(8)	224.4(13)	0.75(3)	194(32)	0.86(15)	1.08(9)
3	15.75(8)	5.62(3)	169.8(11)	3.4(4)	645(101)	3.8(6)	1.0(3)
4	18.42(2)	4.812(6)	274.2(14)	1.04(6)	387(74)	1.4(3)	0.55(7)
5	20.07(4)	4.420(9)	265.5(14)	2.3(4)	674(127)	2.5(5)	3.1(7)
6	21.33(3)	4.163(6)	93.9(8)	0.90(6)	122(12)	1.29(13)	0.79(19)
7	24.39(7)	3.646(10)	22.5(4)	0.74(13)	19(4)	0.84(18)	0.7(3)
8	25.39(5)	3.505(7)	49.0(6)	1.12(8)	89(8)	1.81(18)	1.6(3)
9	26.3(7)	3.38(8)	17.6(4)	1.65(13)	33(3)	1.9(2)	1(19)
10	35.1(3)	2.557(19)	8.8(3)	1.8(5)	17(5)	1.9(6)	1(13)
11	36.53(9)	2.458(6)	26.2(4)	1.5(12)	58(14)	2.2(6)	1(2)
12	38.50(12)	2.337(7)	13.1(3)	2.1(4)	29(9)	2.2(7)	0.7(6)
13	41.02(15)	2.199(8)	15.6(3)	4.2(7)	70(17)	4.5(12)	0.23(7)
14	45(9)	2.0(3)	6.2(2)	11.6(17)	77(24)	12(4)	0.5(12)
15	48.02(16)	1.893(6)	6.3(2)	3.2(8)	24(10)	3.8(17)	0.4(2)

Crystallinity

Data set name	Crystallinity(%)
Aut006_BG	74(28)

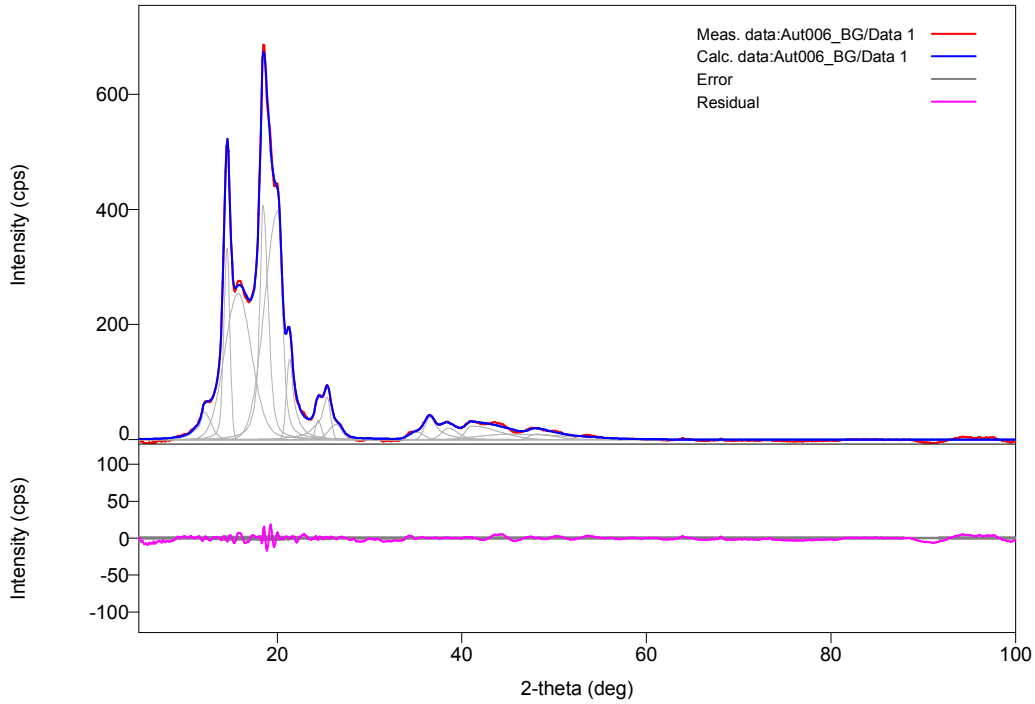

Figure S38. WAXRD measurement profile for *isotactic* H-poly(DCPD) derived by **20(hex)**, 1000 equiv. DCPD + 5 mol% 1-hexene.

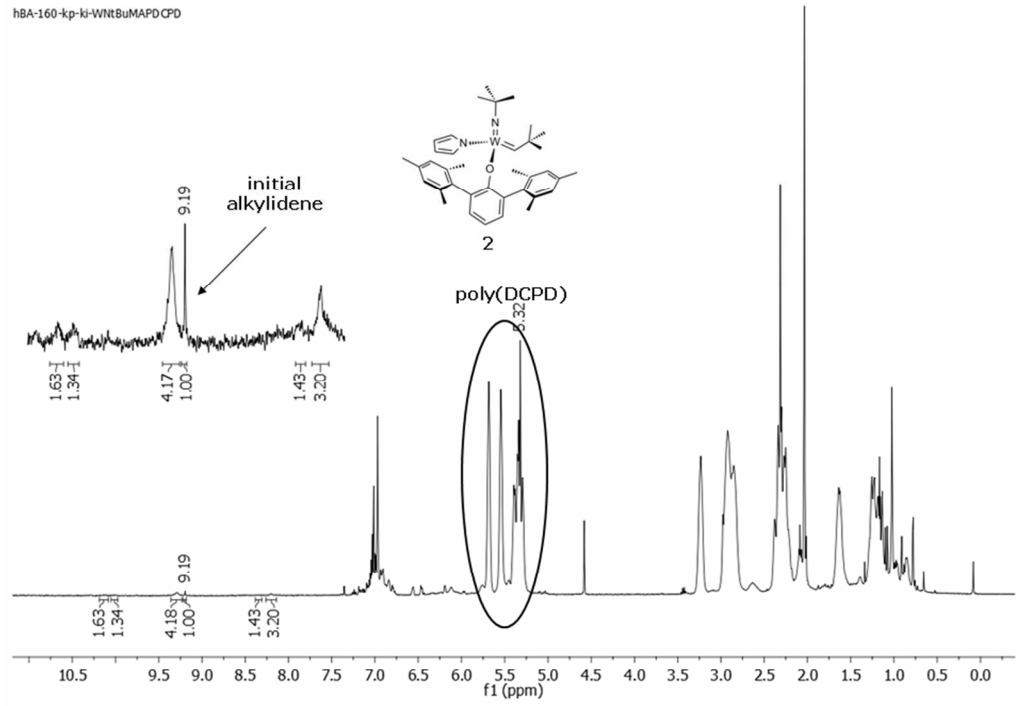

Figure S39. ROMP of 8 equivalents DCPD by **2** at 20 °C in CD_2Cl_2 to give *cis, syndiotactic* poly(DCPD); $k_p/k_i \sim 1$.

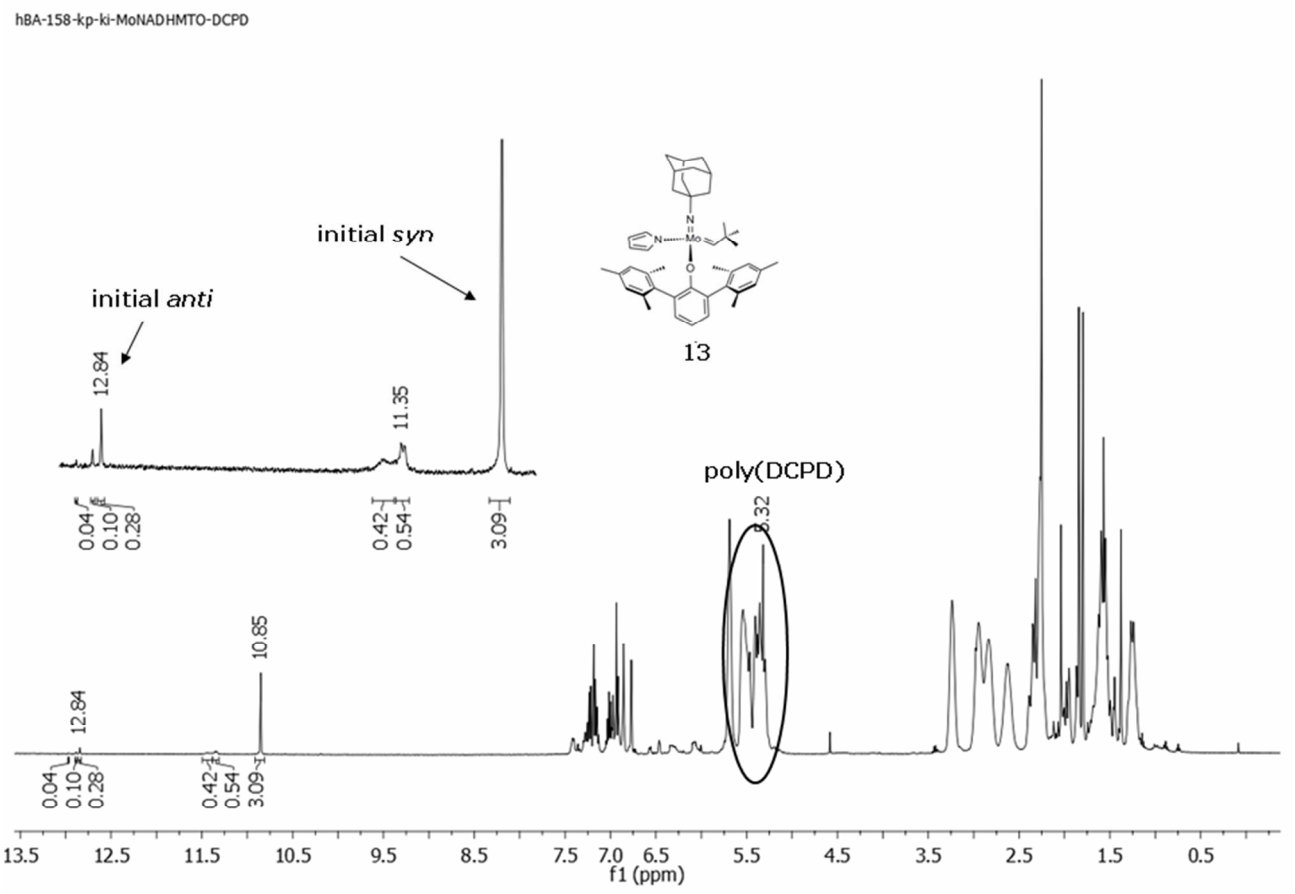

Figure S40. ROMP of 8 equivalents DCPD by **13** at 20 °C in CD_2Cl_2 to give atactic poly(DCPD); $k_p/k_i \sim 14$.