Supporting Information for

Synthesis of *Cis,syndiotactic*-A-*alt*-B Copolymers from Two Enantiomerically Pure *trans*-2,3-Disubstituted-5,6-Norbornenes

Eun Sil Jang, Jeremy M. John and Richard R. Schrock*
Department of Chemistry 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Table of Contents

Experimental…….. S3–S5
General
Synthesis of $\mathbf{A_1}$, $\mathbf{A_2}$, $\mathbf{B_1}$, and $\mathbf{B_2}$
Representative ROMP Procedure

Relevant Spectra……. S6–S19
Figure S1. ^{1}H NMR of *cis,syndiotactic*-poly($\mathbf{A_1}$-*alt*-$\mathbf{B_1}$)
Figure S2. ^{13}C NMR of *cis,syndiotactic*-poly($\mathbf{A_1}$-*alt*-$\mathbf{B_1}$)
Figure S3. HSQC of *cis,syndiotactic*-poly($\mathbf{A_1}$-*alt*-$\mathbf{B_1}$)
Figure S4. gCOSY of *cis,syndiotactic*-poly($\mathbf{A_1}$-*alt*-$\mathbf{B_1}$)
Figure S5. ^{1}H HOMODEC of *cis,syndiotactic*-poly($\mathbf{A_1}$-*alt*-$\mathbf{B_1}$)
Figure S6. ^{19}F NMR of *cis,syndiotactic*-poly($\mathbf{A_1}$-*alt*-$\mathbf{B_1}$)
Figure S7. FTIR of *cis,syndiotactic*-poly($\mathbf{A_1}$-*alt*-$\mathbf{B_1}$)
Figure S8. ^{1}H NMR of *cis,syndiotactic*-poly($\mathbf{A_1}$-*alt*-$\mathbf{B_2}$)
Figure S9. ^{13}C NMR of *cis,syndiotactic*-poly($\mathbf{A_1}$-*alt*-$\mathbf{B_2}$)
Figure S10. HSQC of *cis,syndiotactic*-poly($\mathbf{A_1}$-*alt*-$\mathbf{B_2}$)
Figure S11. gCOSYof *cis,syndiotactic*-poly($\mathbf{A_1}$-*alt*-$\mathbf{B_2}$)
Figure S12. ^{1}H HOMODEC of *cis,syndiotactic*-poly($\mathbf{A_1}$-*alt*-$\mathbf{B_2}$)
Figure S13. FTIR of *cis,syndiotactic*-poly($\mathbf{A_1}$-*alt*-$\mathbf{B_2}$)
Figure S14. ^{1}H NMR of *cis,syndiotactic*-poly($\mathbf{A_2}$-*alt*-$\mathbf{B_2}$)
Figure S15. ^{13}C NMR of *cis,syndiotactic*-poly($\mathbf{A_2}$-*alt*-$\mathbf{B_2}$)
Figure S16. HSQC of *cis,syndiotactic*-poly($\mathbf{A_2}$-*alt*-$\mathbf{B_2}$)
Figure S17. gCOSY of *cis,syndiotactic*-poly($\mathbf{A_2}$-*alt*-$\mathbf{B_2}$)
Figure S18. ^{1}H HOMODEC of *cis,syndiotactic*-poly($\mathbf{A_2}$-*alt*-$\mathbf{B_2}$)
Figure S19. FTIR of *cis,syndiotactic*-poly($\mathbf{A_2}$-*alt*-$\mathbf{B_2}$)
Figure S20. ^{1}H NMR of *cis,syndiotactic*-poly($\mathbf{A_2}$-*alt*-$\mathbf{B_1}$)
Figure S21. ^{13}C NMR of *cis,syndiotactic*-poly($\mathbf{A_2}$-*alt*-$\mathbf{B_1}$)
Figure S22. ^{1}H NMR of *cis,syndiotactic*-poly($\mathbf{A_1}$-*alt*-$\mathbf{B_4}$)
Figure S23. ^{13}C NMR of *cis,syndiotactic*-poly($\mathbf{A_1}$-*alt*-$\mathbf{B_4}$)
Figure S24. ^{1}H NMR of *cis,syndiotactic*-poly($\mathbf{A_1}$-*alt*-$\mathbf{B_5}$)
Figure S25. ^{13}C NMR of *cis,syndiotactic*-poly($\mathbf{A_1}$-*alt*-$\mathbf{B_5}$)
Figure S26. ^{1}H NMR of *cis,syndiotactic*-poly($\mathbf{A_2}$-*alt*-$\mathbf{B_3}$)
Figure S27. ^{13}C NMR of *cis,syndiotactic*-poly($\mathbf{A_2}$-*alt*-$\mathbf{B_3}$)
Figure S28. ^{1}H NMR of *cis,syndiotactic*-poly($\mathbf{A_3}$-*alt*-$\mathbf{B_2}$)
Figure S29. ^{13}C NMR of *cis,syndiotactic*-poly($\mathbf{A_3}$-*alt*-$\mathbf{B_2}$)
Figure S30. ^{1}H NMR of *cis,syndiotactic*-poly($\mathbf{A_3}$-*alt*-$\mathbf{B_5}$)
Figure S31. ^{13}C NMR of *cis,syndiotactic*-poly($\mathbf{A_3}$-*alt*-$\mathbf{B_5}$)
Figure S32. ^{1}H NMR of *cis,syndiotactic*-poly($\mathbf{A_4}$-*alt*-$\mathbf{B_2}$)
Figure S33. ^{13}C NMR of *cis,syndiotactic*-poly($\mathbf{A_4}$-*alt*-$\mathbf{B_2}$)

Control Reactions…… S20
ROMP of $\mathbf{A_1}$
ROMP of $\mathbf{B_1}$
ROMP of *rac*-$\mathbf{A_1}$
ROMP of *rac*-$\mathbf{A_2}$
ROMP of *rac*-$\mathbf{B_1}$
ROMP of *rac*-$\mathbf{B_2}$

Catalyst Screen……. S21–S22
Table S1. Mo and W catalysts screened in this study

Monomer Screen…..…… S23–S30
Table S2. ROMP of enantiomerically pure monomers **A** and **B** catalyzed by **1a** or **1b**

ROMP using **1b**…..…….. S31–S37
Figure S34. ^{1}H NMR of *cis,syndiotactic,alt*-poly(*rac*-$\mathbf{A_1}$).
Figure S35. ^{13}C NMR of *cis,syndiotactic,alt*-poly(*rac*-$\mathbf{A_1}$).
Figure S36. ^{1}H NMR of *cis,syndiotactic*-poly($\mathbf{A_1}$).
Figure S37. ^{13}C NMR of *cis,syndiotactic*-poly($\mathbf{A_1}$).
Figure S38. ^{1}H NMR of *cis,syndiotactic,alt*-poly(*rac*-$\mathbf{A_2}$).
Figure S39. ^{1}H NMR of *cis,syndiotactic,alt*-poly(*rac*-$\mathbf{B_2}$).
Figure S40. ^{13}C NMR of *cis,syndiotactic,alt*-poly(*rac*-$\mathbf{B_2}$).
Figure S41. ^{1}H NMR of *cis,syndiotactic*-poly($\mathbf{B_2}$).
Figure S42. ^{1}H NMR of *cis,syndiotactic,alt*-poly(*rac*-$\mathbf{A_3}$).
Figure S43. ^{13}C NMR of *cis,syndiotactic,alt*-poly(*rac*-$\mathbf{A_3}$).
Figure S44. ^{1}H NMR of *cis,syndiotactic*-poly($\mathbf{B_3}$).
Figure S45. ^{13}C NMR of *cis,syndiotactic*-poly($\mathbf{B_3}$).

Comparison of **1a**, **1b** and $\mathbf{1b_w}$ initiators …… S38–S40
Figure S46. Comparison of *cis*,*syndiotactic*-poly($\mathbf{A_2}$-*alt*-$\mathbf{B_2}$) prepared from **1a**, **1b** and $\mathbf{1b_W}$.
Figure S47. Comparison of *cis*,*syndiotactic*-poly($\mathbf{A_1}$-*alt*-$\mathbf{B_2}$) prepared from **1b** and $\mathbf{1b_W}$.
Figure S48. Comparison of *cis*,*syndiotactic*-poly($\mathbf{A_3}$-*alt*-$\mathbf{B_2}$) prepared from **1a**, **1b** and $\mathbf{1b_W}$.
Figure S49. Comparison of *cis*,*syndiotactic*-poly($\mathbf{A_1}$-*alt*-$\mathbf{B_3}$) prepared from **1a** and $\mathbf{1b_W}$.
Figure S50. Comparison of *cis*,*syndiotactic*-poly($\mathbf{A_1}$-*alt*-$\mathbf{B_1}$) prepared from **1a**, **1b** and $\mathbf{1b_W}$.
Figure S51. Comparison of *cis*,*syndiotactic*-poly($\mathbf{A_2}$-*alt*-$\mathbf{B_3}$) prepared from **1a**, **1b** and $\mathbf{1b_W}$.

References…… S41

General

All procedures and manipulations were performed under a nitrogen atmosphere using standard Schlenk and glovebox techniques unless stated otherwise. All glassware was oven-dried or flame-dried prior to use unless stated otherwise. Ether, pentane, toluene, dichloromethane, toluene, and benzene were degassed with dinitrogen and passed through activated alumina columns under nitrogen unless stated otherwise. All dried and deoxygenated solvents were stored over molecular sieves in a nitrogen-filled glovebox. Deuterated solvents were purchased from Cambridge Isotope Laboratories, degassed, and dried over activated molecular sieves prior to use. NMR spectra were recorded on 500 or 400 MHz spectrometers at ambient temperature. The ^{1}H and ^{13}C NMR spectra were referenced relative to partially deuterated solvent peaks. All ^{19}F chemical shifts were measured relative to fluorobenzene (-113.15 ppm) as an external reference.

Mo(NAd)(CHCMe$_2$Ph)(pyr)(HMTO) **1a**[1], Mo(NAr')(CHCMe$_2$Ph)(pyr)(HMTO) **1b**[2],
Mo(NAd)(CHCMe$_2$Ph)(pyr)(HIPTO)[3], Mo(NAr')(CHCMe$_2$Ph)(Me$_2$pyr)(DFTO)[4],
Mo(NC$_6$F$_5$)(CHCMe$_2$Ph)(Me$_2$pyr)(HMTO)[4], Mo(NC$_6$F$_5$)(CHCMe$_3$)(Me$_2$pyr)(DFTO)[4],
Mo(NAr)(CHCMe$_2$Ph)(Me$_2$pyr)(OCCH$_3$(CF$_3$)$_2$)[5], Mo(NAr)(CHCMe$_2$Ph)(Me$_2$pyr)(TPPO)[6],
Mo(NAr')(CHCMe$_2$Ph)(OCCH$_3$(CF$_3$)$_2$)$_2$[7], Mo(NAr)(CHCMe$_2$Ph)(Me$_2$pyr)(HMTO)[8],
Mo(NAd)(CHCMe$_2$Ph)(Me$_2$pyr)(HIPTO)[3], W(O)(CHCMe$_2$Ph)(Me$_2$pyr)(HMTO)[9], W(N*t*Bu)(CHR)(pyr)(HMTO)[10],
W(NAr$^{2,6\text{-Cl2}}$)(CHCMe$_3$)(pyr)(HIPTO)[11], W(NAr')(CHCMe$_2$Ph)(pyr)(HMTO) **1b$_w$**[8] and (2*R*,3*R*) [2.2.1]bicyclohept-5-ene-2,3-dicarboxylic acid[12], and (2*S*,3*S*) [2.2.1]bicyclohept-5-ene-2,3-dicarboxylic acid[12] were synthesized according to literature procedures.

Ad – 1-adamantyl
Ar – 2,6-diisopropylphenyl
Ar' – 2,6-dimethylphenyl
C_6F_5 – 2,3,4,5,6-pentafluorophenyl
HIPT – 2,6-(2,4,6-triisopropylphenyl)C_6H_3
DFT – 2,6-(C_6F_5)$_2C_6H_3$
HMT – 2,6-(2,4,6-trimethylphenyl)C_6H_3
TPP – 2,3,5,6-tetraphenylC_6H
R – *o*-MeOC_6H_4
pyr – pyrrolide
Me$_2$pyr – 2,5-dimethylpyrrolide

Synthesis of Monomers A_x and B_y

All enantiomerically pure monomer **A** and **B** are synthesized from corresponding *endo*,*exo*- [2.2.1]bicyclohept-5-ene-2,3-dicarboxylic acid[12] or *endo*,*exo*-*di*-menthyl-[2.2.1]bicyclohept-5-ene-2,3-dicarboxylate[12]. Monomers **A$_1$**[13], **A$_2$/B$_4$**[13], **B$_1$**[14], and **B$_2$**[15] **A$_3$/B$_3$**[16], **A$_4$/A$_6$/A$_7$/B$_6$/B$_7$**[17], **A$_5$**[18], **B$_5$**[19] have been previously reported.

Representative Syntheses of Monomers **A$_x$** and **B$_y$**:

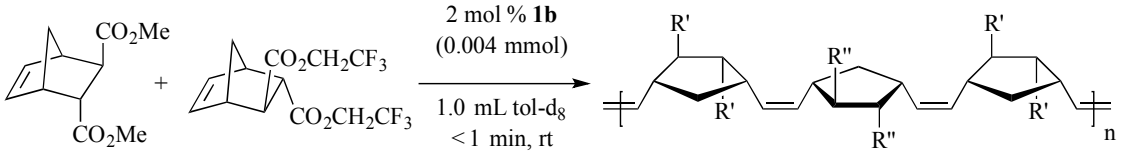
A$_1$ (dimethyl (1*R*,2*R*,3*R*,4*S*)-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate) was prepared by esterification of (2*R*,3*R*) [2.2.1]bicyclohept-5-ene-2,3-dicarboxylic acid adapted from a procedure reported in the literature.[20] To a stirring solution of 2.61 g (14.3 mmol) (2*R*,3*R*) [2.2.1]bicyclohept-5-ene-2,3-dicarboxylic acid in 50 mL CH_2Cl_2 was added 175.3 mg (1.4 mmol, 0.1 eq.) DMAP and 5.8 mL (143.5 mmol, 10 eq.) MeOH. The reaction was cooled to 0 ºC using an ice bath and 6.5 g (31.6 mmol, 2.2 eq.) DCC was added. After stirring for 5 min at 0 ºC then at room temperature for 3h, urea precipitates were filtered off and the solvent removed *in vacuo*. The resulting crude product was taken up in CH_2Cl_2, washed with 0.5N HCl followed by saturated Na_2CO_3 solution. The organic layer was dried over anhydrous $MgSO_4$, filtered and the solvent removed using a rotary evaporator. Flash chromatography on silica gel using CH_2Cl_2 as eluent gave the product as colorless oil (2.5 g, 83%, 11.9 mmol).

A_2 (((1*R*,2*R*,3*R*,4*S*)-bicyclo[2.2.1]hept-5-ene-2,3-diyl)bis(methylene) diacetate) was prepared according to a published procedure[21]. Flash chromatography on silica gel using 10% EtOAc:90% hexanes gave a colorless oil.

B_1 (bis(2,2,2-trifluoroethyl) (1*R*,2*S*,3*S*,4*S*)-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate) was prepared in an identical manner to **A_1**. 3.0 g (16.5 mmol) (2*S*,3*S*) [2.2.1]bicyclohept-5-ene-2,3-dicarboxylic acid, 201.2 mg (1.7 mmol) DMAP, 11.9 mL (164.7 mmol) 2,2,2-trifluoroethanol, and 7.5 g (36.2 mmol) DCC. Product was a colorless oil (5.0 g, 88%, 14.5 mmol).

B_2 (diethyl (1*R*,2*S*,3*S*,4*S*)-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate) was prepared in an identical manner to **A_1**. 1.5 g (8.2 mmol) (2*S*,3*S*) [2.2.1]bicyclohept-5-ene-2,3-dicarboxylic acid, 100.6 mg (0.8 mmol) DMAP, 4.8 mL (82 mmol) EtOH, and 3.7 g (18.1 mmol) DCC. Product was a colorless oil (1.6 g, 82%, 6.7 mmol).

Representative ROMP Procedure:



A_1 25 eq. **B_1** 25 eq.

cis,syndiotactic-poly(**A_1**-*alt*-**B_1**) R' =CO_2Me, R'' = $CO_2CH_2CF_3$

A mixture of 21.0 mg (0.1 mmol, 25 eq.) **A_1** and 34.6 mg (0.1 mmol, 25 eq.) **B_1** in 0.5 mL toluene-d_8 was prepared then added to a solution of 3.0 mg (0.004 mmol) **1b** in 0.5 mL toluene-d_8. The reaction mixture thickened within seconds of mixing. ^{1}H NMR spectroscopy was used to monitor the course of the reaction. Once complete, the reaction mixture was exposed to air and poured into 35 mL of MeOH. The precipitated polymer was allowed to settle, the solvent decanted, and dried under vacuum. The dried polymer was characterized in $CDCl_3$ at room temperature (20 °C) unless stated otherwise.

Cis,syndiotactic-poly(**A_1**-*alt*-**B_1**)
^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC): δ 5.35 (dt, *J* = 17.2, 9.8 Hz, 2H), 5.23 (dt, *J* = 14.4, 10.1 Hz, 2H), 4.42 (dq, *J* = 29.8, 8.4 Hz, 4H), 3.66 (s, 3H), 3.61 (s, 3H), 3.48 – 3.23 (m, 4H), 3.18 – 2.94 (m, 4H), 2.20 – 1.99 (m, 2H), 1.42 – 1.31 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$, 20 ºC): δ 174.11, 172.82, 171.72, 170.61, 133.71, 132.08, 131.30, 129.72, 126.17, 123.98, 121.77, 119.57, 61.04, 60.94, 60.75, 60.64, 60.45, 60.35, 60.16, 60.05, 52.69, 52.34, 52.05, 51.81, 42.04, 41.88, 40.73, 40.19, 39.08, 38.92, 29.85.

Cis,syndiotactic-poly(**A_1**-*alt*-**B_2**)
^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC): δ 5.32 (q, *J* = 9.6 Hz, 2H), 5.21 (dt, *J* = 16.4, 10.2 Hz, 2H), 4.17 – 3.99 (m, 4H), 3.65 (s, 3H), 3.59 (s, 3H), 3.40 – 3.25 (m, 3H), 3.22 (td, *J* = 9.5, 3.6 Hz, 1H), 3.06 (p, *J* = 9.6, 9.2 Hz, 2H), 2.95 (qd, *J* = 9.6, 4.6 Hz, 2H), 2.17 – 1.98 (m, 2H), 1.40 – 1.28 (m, 2H), 1.19 (dtd, *J* = 14.7, 7.3, 4.3 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$, 20 ºC) δ 174.15, 173.71, 172.93, 172.48, 133.23, 132.69, 130.87, 130.53, 60.78, 60.65, 52.80, 52.69, 52.33, 52.13, 52.01, 51.77, 42.03, 41.95, 40.77, 40.56, 39.01, 14.45, 14.41.

Cis,syndiotactic-poly(**A_2**-*alt*-**B_2**)
^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC): δ 5.37 (t, *J* = 9.9 Hz, 1H), 5.29 (t, *J* = 10.4 Hz, 1H), 5.26 – 5.19 (m, 2H), 4.16 – 4.01 (m, 6H), 3.96 (td, *J* = 11.1, 6.1 Hz, 2H), 3.24 (dt, *J* = 26.0, 7.5 Hz, 2H), 3.04 (p, *J* = 9.6 Hz, 2H), 2.95 (t, *J* = 9.3 Hz, 1H), 2.63 (p, *J* = 8.9 Hz, 1H), 2.19 (p, *J* = 7.0 Hz, 1H), 2.09 (dd, *J* = 15.0, 8.4 Hz, 1H), 2.04 (s, 3H), 2.01 (s, 3H), 1.93 (p, *J* = 5.7, 4.3 Hz, 1H), 1.82 – 1.71 (m, 1H), 1.41 (ddt, *J* = 18.3, 11.2, 5.7 Hz, 1H), 1.20 (dt, *J* = 17.3, 7.2 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$, 20 ºC): δ 174.00, 172.37, 171.01, 170.99, 134.35, 132.80, 131.16, 130.14, 65.51, 65.28, 60.79, 60.62, 52.84, 52.43, 48.18, 44.29, 42.12, 40.75, 40.70, 40.51, 39.09, 38.86, 21.13, 21.05, 14.44, 14.41.

cis,syndiotactic-poly(**A_2**-*alt*-**B_1**)
^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC) δ 5.47 – 5.14 (m, 4H), 4.63 – 4.28 (m, 4H), 4.20 – 3.85 (m, 4H), 3.48 – 3.25 (m, 2H), 3.21 – 2.95 (m, 3H), 2.61 (p, *J* = 9.7 Hz, 1H), 2.29 – 2.10 (m, 2H), 2.10 – 1.99 (m, 6H), 1.93 – 1.74 (m, 2H), 1.57 – 1.36 (m, 1H), 1.26 (d, *J* = 12.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$, 20 ºC) δ 171.95, 171.02, 171.00, 170.50, 135.44, 131.93, 131.66, 128.95, 126.19, 124.01, 123.99, 121.81, 121.78, 119.58, 65.41, 65.19, 61.01, 60.92, 60.72, 60.63, 60.43, 60.34, 60.14, 60.05, 52.43, 52.10, 48.17, 44.25, 42.00, 40.64, 40.44, 39.15, 38.90, 29.84, 21.10, 21.00.

cis,syndiotactic-poly(**A_1**-*alt*-**B_4**)
^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC) δ 5.32 (dt, *J* = 28.5, 10.4 Hz, 2H), 5.20 (dq, *J* = 19.4, 10.5 Hz, 2H), 4.13 – 3.99 (m, 2H), 3.99 – 3.88 (m, 2H), 3.61 (d, *J* = 31.3 Hz, 6H), 3.33 – 3.19 (m, 2H), 3.13 – 2.87 (m, 3H), 2.61 (p, *J* = 9.3 Hz, 1H), 2.24 – 2.05 (m, 2H), 2.01 (d, *J* = 13.7 Hz, 6H), 1.94 – 1.83 (m, 1H), 1.82 – 1.71 (m, 1H), 1.47 – 1.31 (m, 1H), 1.23 (q, *J* = 10.5 Hz, 1H).^{13}C NMR (126 MHz, $CDCl_3$, 20 ºC) δ 174.48, 172.79, 171.04, 134.51, 132.50, 131.37, 130.05, 65.52, 65.23, 52.54, 52.05, 51.78, 48.14, 44.27, 42.23, 40.60, 39.05, 38.87, 21.14, 21.08.

cis,syndiotactic-poly(**A_1**-*alt*-**B_5**)
^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC) δ 5.39 – 5.28 (m, 2H), 5.24 (t, *J* = 10.2 Hz, 1H), 5.15 (t, *J* = 10.2 Hz, 1H), 3.61 (d, *J* = 28.8 Hz, 6H), 3.40 – 3.17 (m, 12H), 3.07 (p, *J* = 9.5 Hz, 1H), 2.95 (q, *J* = 8.8, 7.9 Hz, 2H), 2.65 (p, *J* = 9.5 Hz, 1H), 2.17 – 2.00 (m, 2H), 1.90 – 1.75 (m, 1H), 1.75 – 1.63 (m, 1H), 1.48 – 1.31 (m, 1H), 1.27 – 1.14 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$, 20 ºC) δ 174.44, 173.17, 135.50, 132.44, 131.55, 129.47, 74.08, 73.69, 58.97, 58.78, 52.70, 52.32, 51.93, 51.68, 48.92, 45.51, 42.25, 40.83, 40.80, 40.17, 39.24, 38.84.

cis,syndiotactic-poly(**A_2**-*alt*-**B_3**)
^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.34 (t, *J* = 10.0 Hz, 1H), 5.30 – 5.16 (m, 3H), 4.13 – 3.86 (m, 4H), 3.18 (p, *J* = 8.7 Hz, 1H), 3.08 (p, *J* = 8.7 Hz, 1H), 2.98 (dt, *J* = 21.5, 9.3 Hz, 2H), 2.79 (t, *J* = 9.5 Hz, 1H), 2.63 (p, *J* = 8.8 Hz, 1H), 2.24 – 2.11 (m, 1H), 2.01 (d, *J* = 14.8 Hz, 8H), 1.76 (td, *J* = 9.0, 4.7 Hz, 1H), 1.38 (d, *J* = 15.5 Hz, 19H), 1.27 (dt, *J* = 14.5, 10.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$, 20 ºC) δ 173.23, 171.72, 171.03, 170.99, 133.98, 133.32, 130.79, 130.63, 80.64, 80.45, 65.44, 65.37, 53.93, 53.25, 48.20, 44.30, 41.83, 40.77, 40.68, 40.35, 39.08, 38.81, 28.28, 28.19, 21.13, 21.04.

cis,syndiotactic-poly(**A_3**-*alt*-**B_2**)
^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.35 – 5.23 (m, 3H), 5.19 (t, *J* = 10.4 Hz, 1H), 4.18 – 3.97 (m, 4H), 3.37 (p, *J* = 7.9 Hz, 1H), 3.29 – 3.17 (m, 2H), 3.12 – 2.88 (m, 4H), 2.79 (t, *J* = 9.7 Hz, 1H), 2.15 (h, *J* = 6.9 Hz, 1H), 2.04 (h, *J* = 7.3 Hz, 1H), 1.38 (d, *J* = 16.8 Hz, 20H), 1.20 (dt, *J* = 16.8, 7.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$, 20 ºC) δ 173.72, 172.92, 172.61, 171.90, 133.55, 132.66, 131.15, 130.28, 80.66, 80.48, 60.72, 60.59, 54.05, 53.04, 52.41, 41.92, 41.61, 40.79, 39.10, 28.31, 28.22, 14.47, 14.42.

cis,syndiotactic-poly(**A_3**-*alt*-**B_5**)
^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC) δ 5.39 – 5.16 (m, 4H), 3.39 – 3.15 (m, 12H), 3.07 – 2.94 (m, 2H), 2.79 (t, *J* = 9.8 Hz, 1H), 2.65 (p, *J* = 9.4 Hz, 1H), 2.13 – 2.00 (m, 2H), 1.93 (p, *J* = 7.4 Hz, 1H), 1.69 (td, *J* = 9.0, 4.6 Hz, 1H), 1.48 – 1.29 (m, 19H), 1.30 – 1.19 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$, 20 ºC) δ 173.17, 172.11, 134.93, 132.35, 131.82, 130.03, 80.43, 80.29, 74.15, 73.77, 58.93, 58.76, 54.02, 52.93, 48.98, 45.70, 41.87, 41.11, 40.78, 40.00, 39.21, 38.79, 28.29, 28.20.

cis,syndiotactic-poly(**A_4**-*alt*-**B_2**)
^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC) δ 5.53 – 5.08 (m, 4H), 4.22 – 3.96 (m, 4H), 3.68 – 3.39 (m, 4H), 3.29 (dt, *J* = 55.2, 9.3 Hz, 2H), 3.13 – 2.79 (m, 3H), 2.73 – 2.44 (m, 1H), 2.34 – 1.87 (m, 2H), 1.85 – 1.59 (m, 2H), 1.54 – 1.29 (m, 2H), 1.29 – 1.13 (m, 6H), 0.98 – 0.80 (m, 18H), 0.12 – -0.08 (m, 12H). ^{13}C NMR (126 MHz, $CDCl_3$, 20 ºC) δ 173.91, 172.49, 135.32, 132.92, 131.75, 129.61, 64.40, 63.63, 60.65, 60.55, 52.74, 52.48, 50.65, 47.39, 42.13, 41.75, 41.20, 40.20, 39.65, 38.53, 26.08, 18.38, 18.26, 14.43, -5.17, -5.23, -5.38.

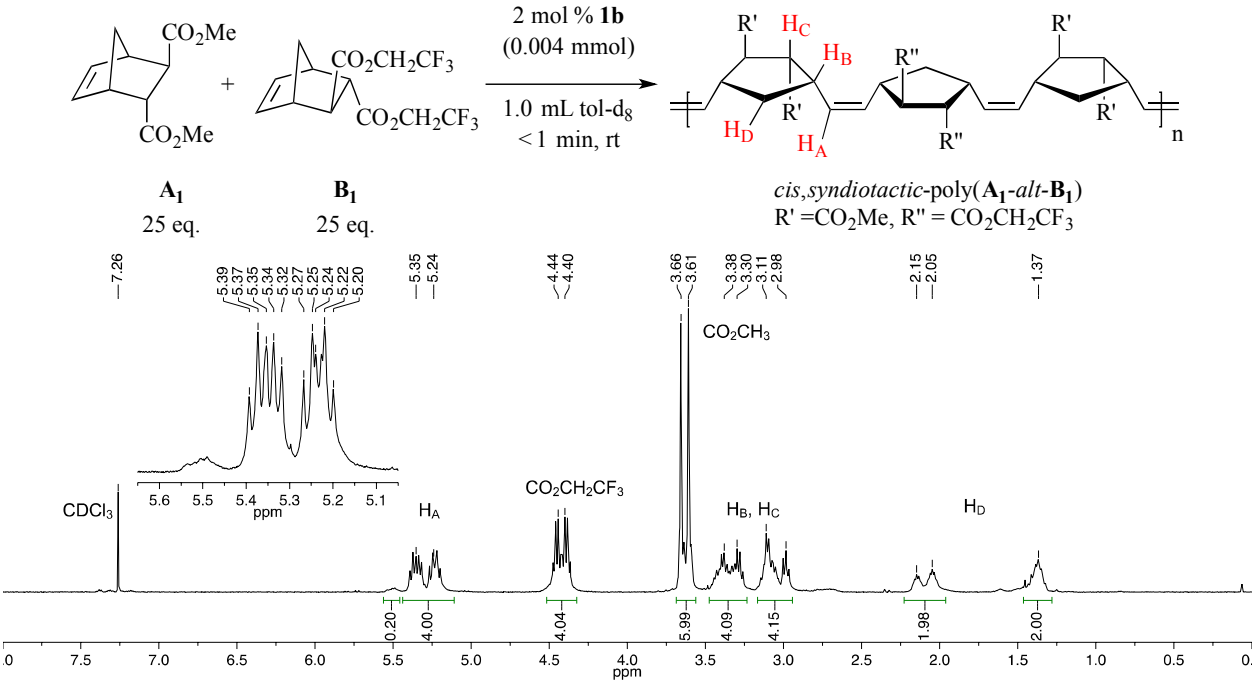


Figure S1. ^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC) of *cis,syndiotactic*-poly(**A$_1$**-*alt*-**B$_1$**).

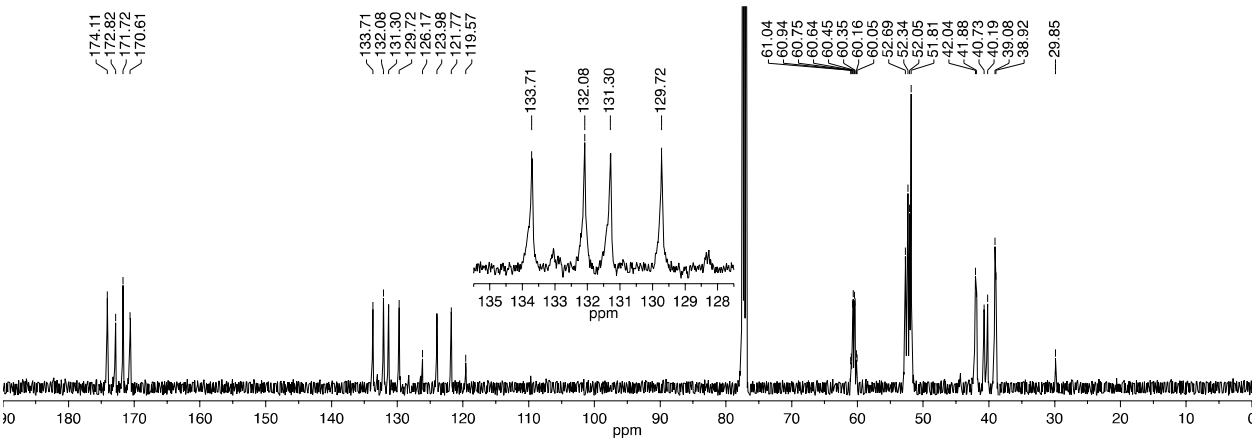


Figure S2. ^{13}C NMR (126 MHz, $CDCl_3$, 20 ºC) of *cis,syndiotactic*-poly(**A$_1$**-*alt*-**B$_1$**).

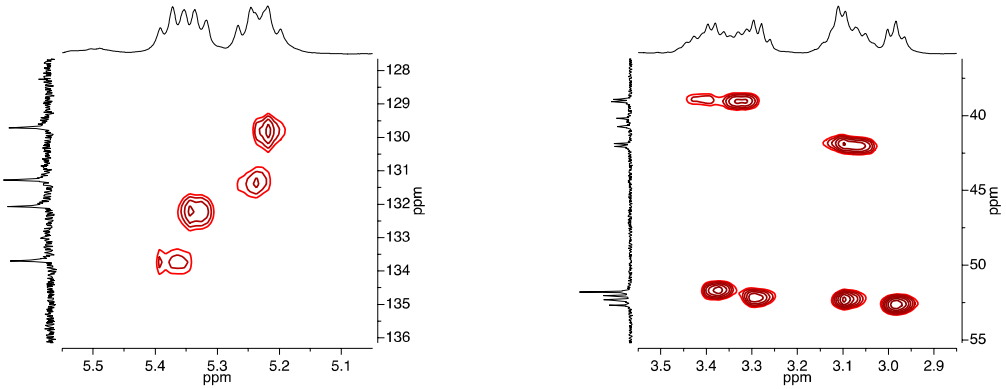


Figure S3. HSQC ($CDCl_3$, 20 ºC) of *cis,syndiotactic*-poly(**A$_1$**-*alt*-**B$_1$**). Olefinic (left) and methine (right) region.

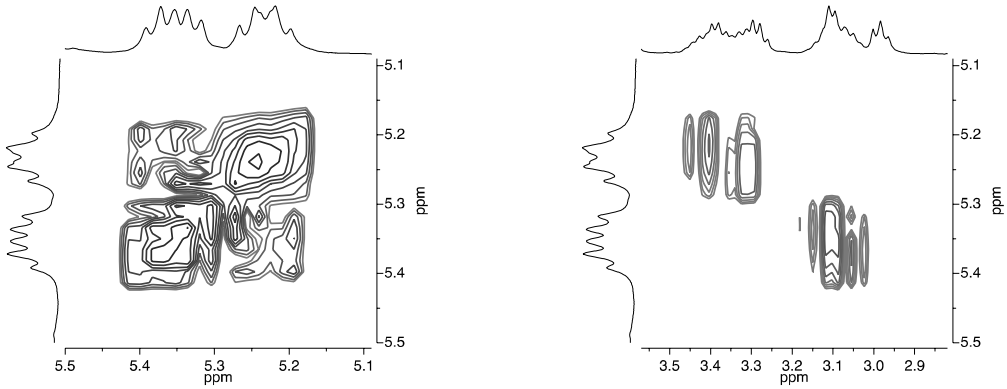


Figure S4. gCOSY (500 MHz, $CDCl_3$, 20 ºC) of *cis,syndiotactic*-poly(**A**$_1$-*alt*-**B**$_1$). Olefinic region (left) and olefinic/methine region (right).

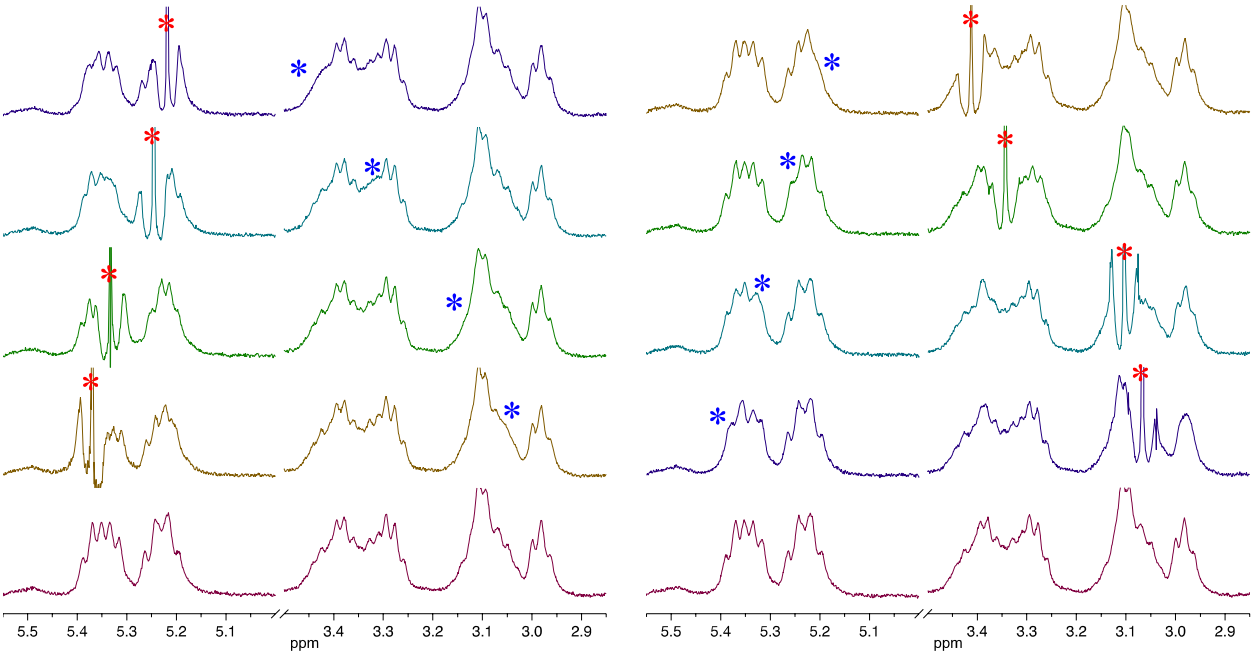


Figure S5. ^{1}H HOMODEC (500 MHz, $CDCl_3$, 20 ºC) of *cis,syndiotactic*-poly(**A**$_1$-*alt*-**B**$_1$). (*) irradiation, (*) decoupled resonance.

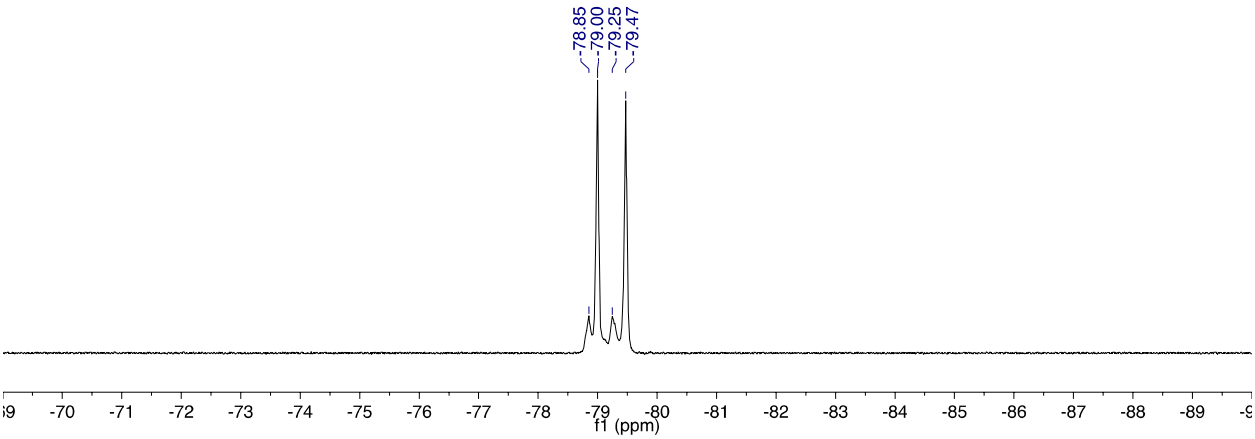


Figure S6. ^{19}F NMR (471 MHz, $CDCl_3$, 20 ºC) of *cis,syndiotactic*-poly(**A**$_1$-*alt*-**B**$_1$).

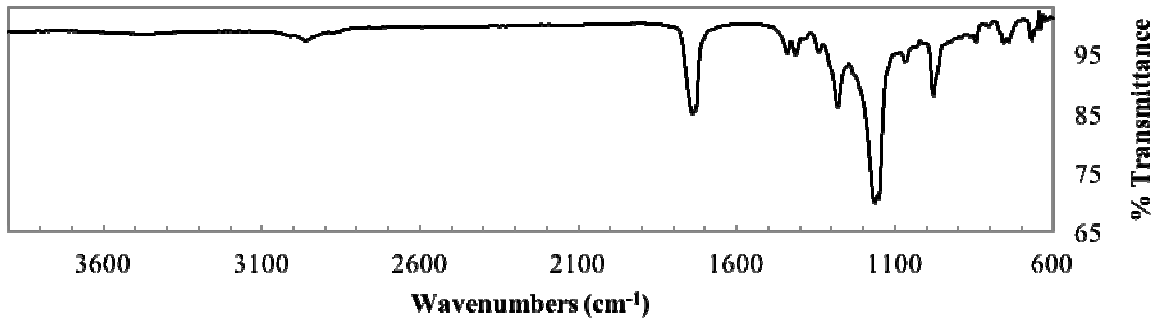


Figure S7. FTIR of *cis,syndiotactic*-poly(**A**$_1$-*alt*-**B**$_1$).

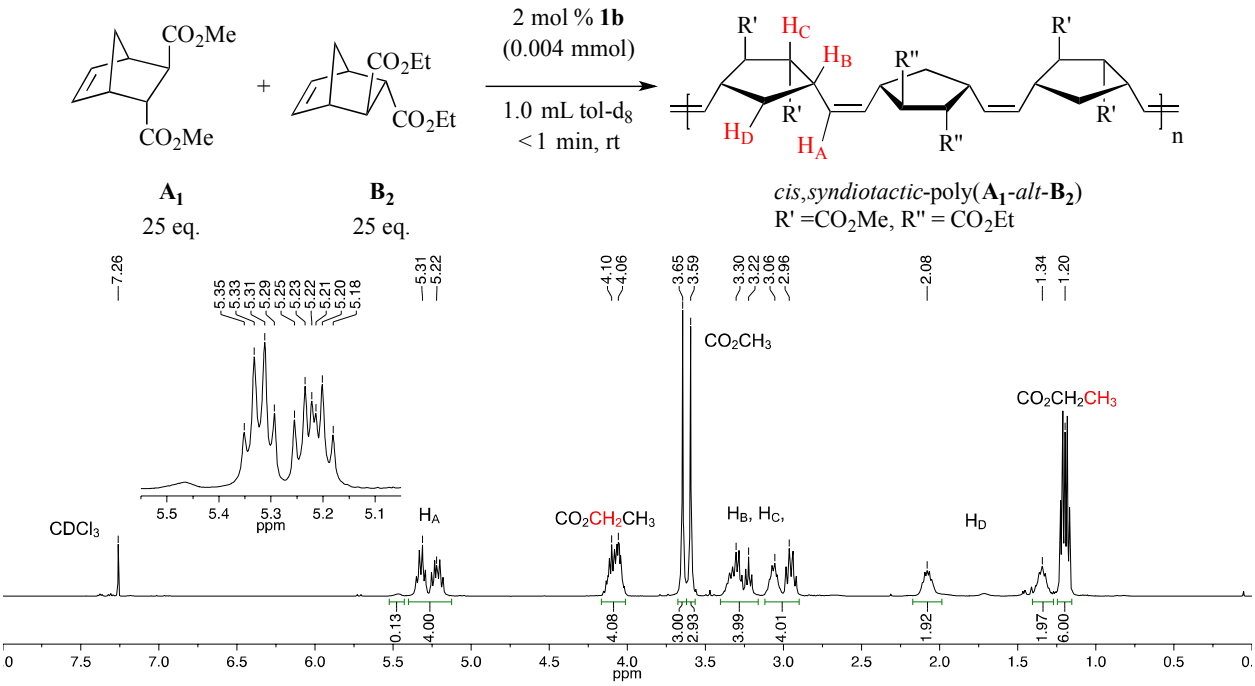


Figure S8. ^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC) of *cis,syndiotactic*-poly(**A$_1$**-*alt*-**B$_2$**).

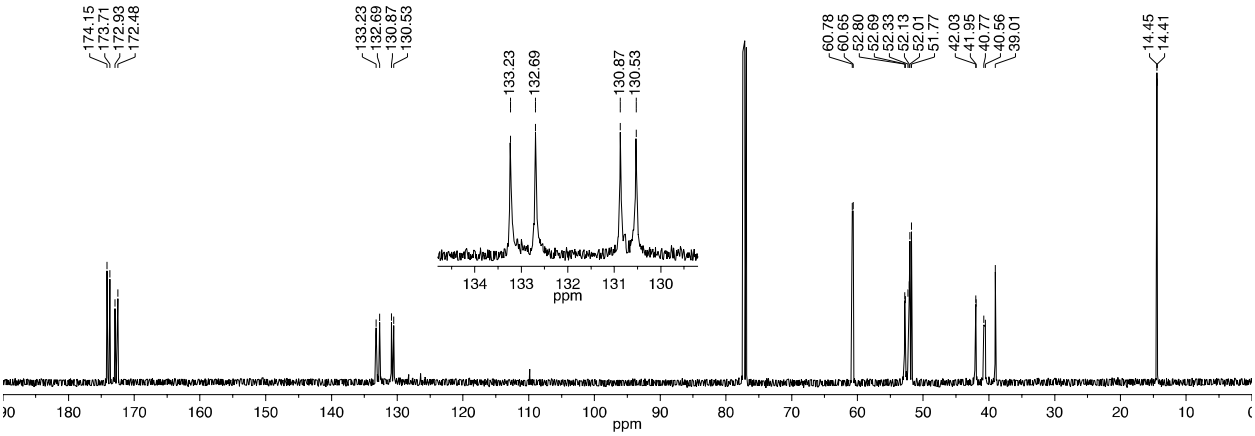


Figure S9. ^{13}C NMR (126 MHz, $CDCl_3$, 20 ºC) of *cis,syndiotactic*-poly(**A$_1$**-*alt*-**B$_2$**).

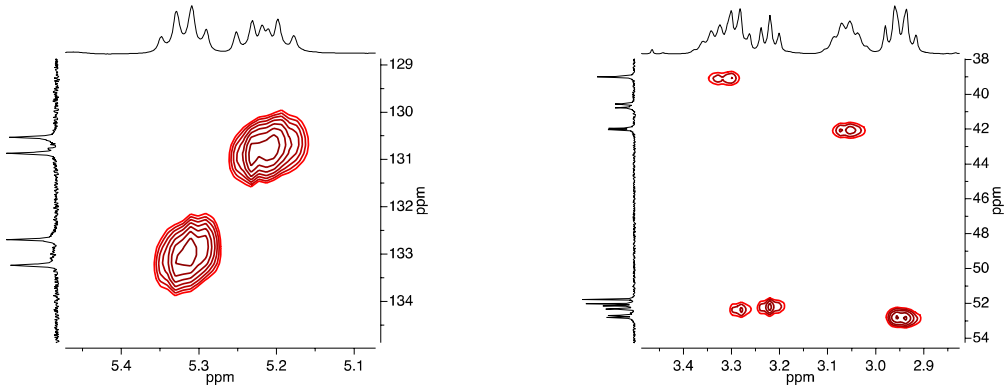


Figure S10. HSQC ($CDCl_3$, 20 ºC) of *cis,syndiotactic*-poly(**A$_1$**-*alt*-**B$_2$**). Olefinic (left) and methine (right) region.

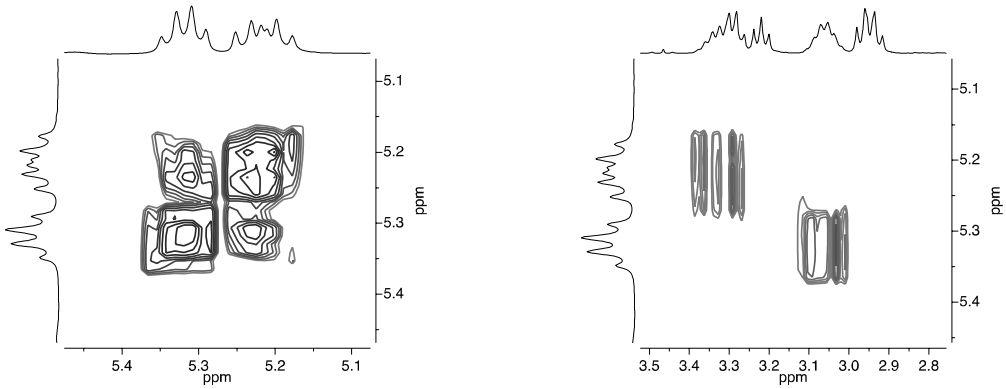


Figure S11. gCOSY (500 MHz, $CDCl_3$, 20 ºC) of *cis,syndiotactic*-poly(**A_1**-*alt*-**B_2**). Olefinic (left) and olefinic/methine (right).

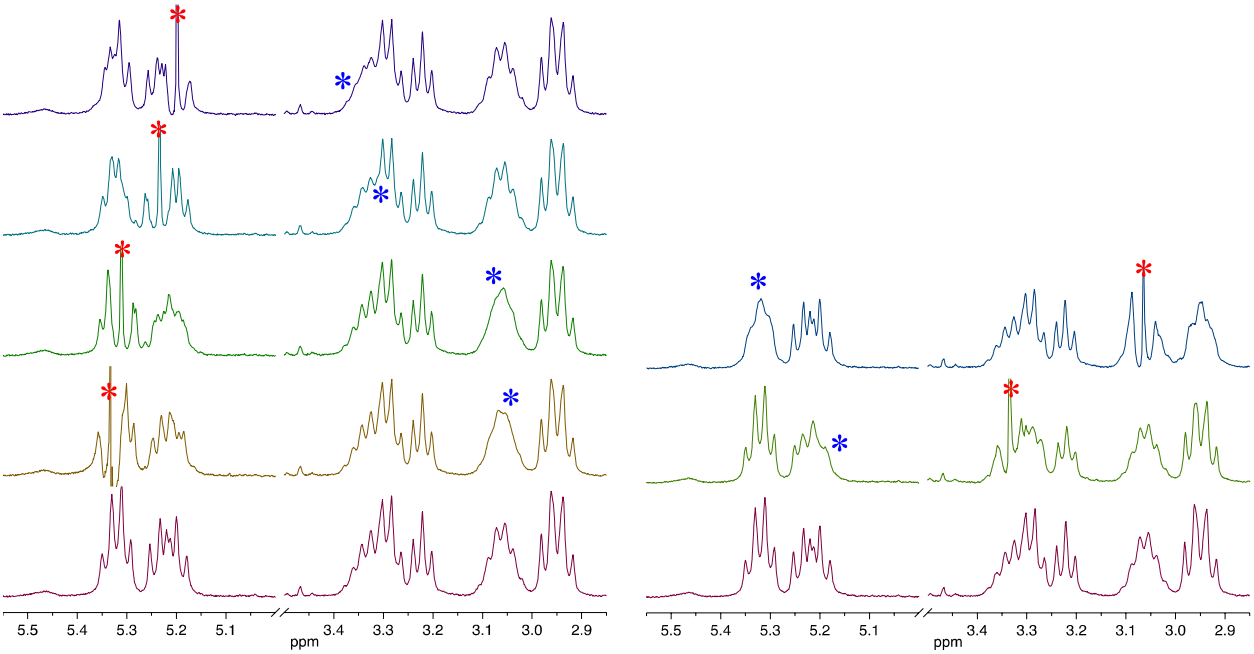


Figure S12. ^{1}H HOMODEC (500 MHz, $CDCl_3$, 20 ºC) of *cis,syndiotactic*-poly(**A_1**-*alt*-**B_2**). (*) irradiation, (*) decoupled resonance.

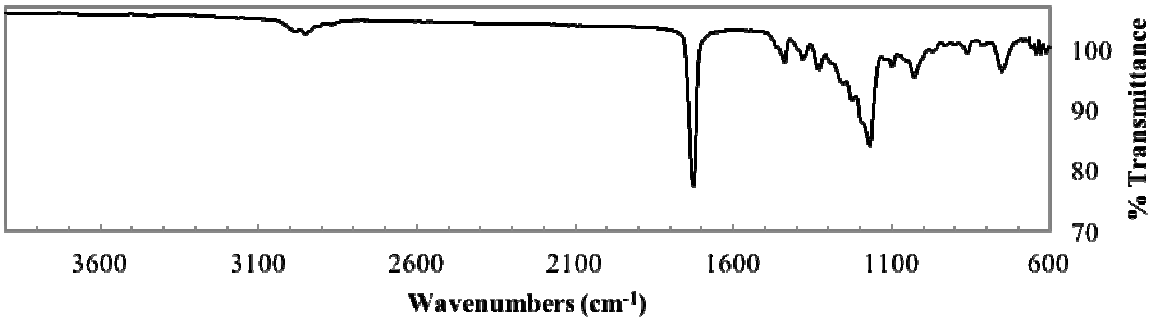


Figure S13. FTIR of *cis,syndiotactic*-poly(**A_1**-*alt*-**B_2**).

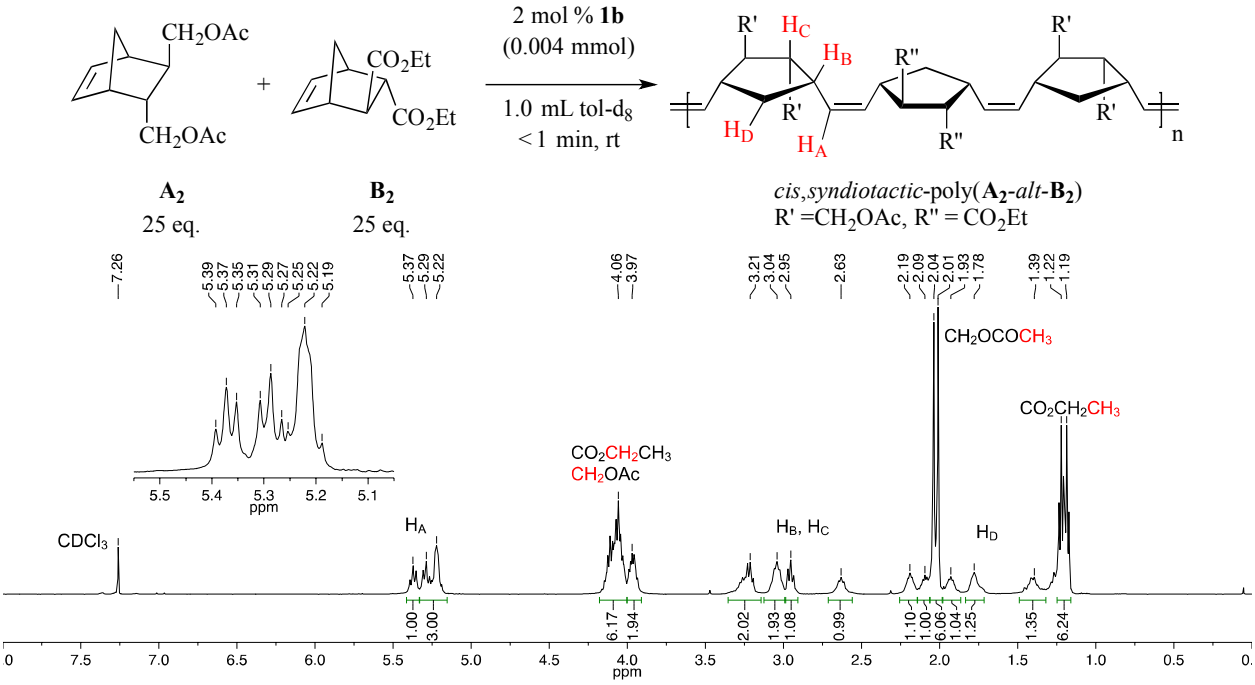


Figure S14. ^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC) of *cis,syndiotactic*-poly(**A$_2$**-*alt*-**B$_2$**).

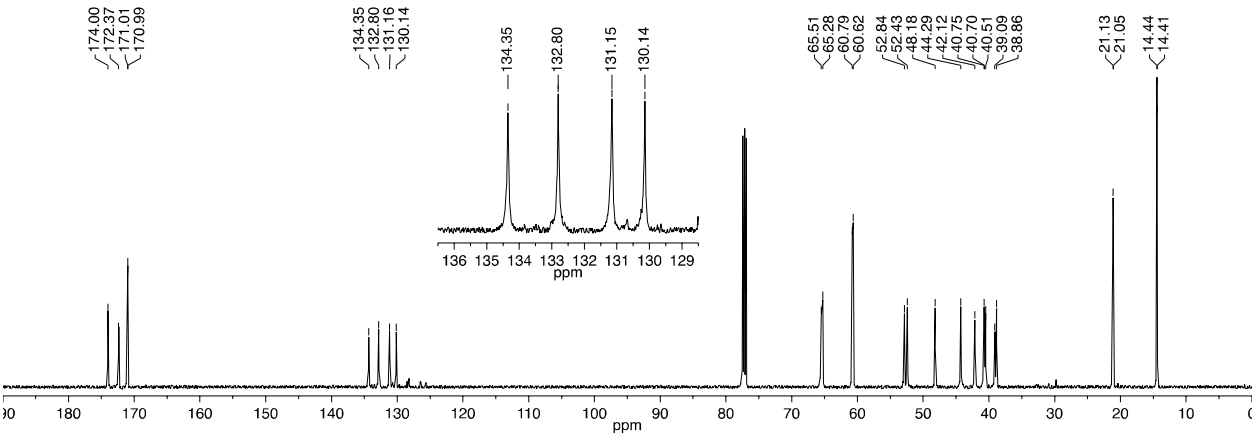


Figure S15. ^{13}C NMR (126 MHz, $CDCl_3$, 20 ºC) of *cis,syndiotactic*-poly(**A$_2$**-*alt*-**B$_2$**).

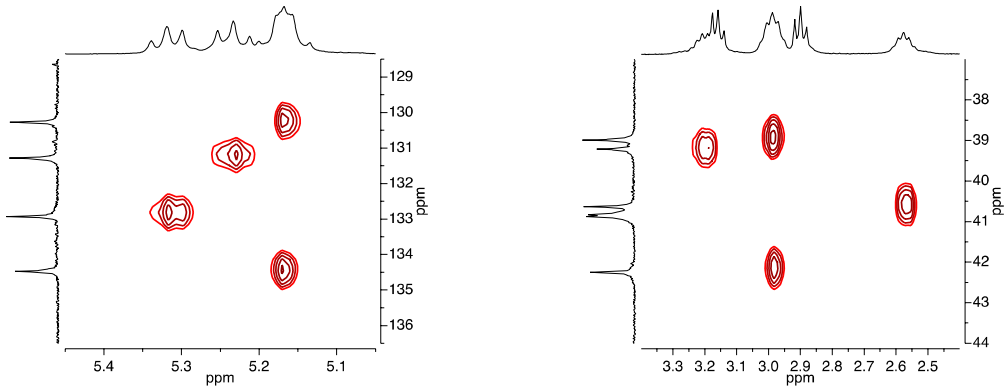


Figure S16. HSQC ($CDCl_3$, 20 ºC) of *cis,syndiotactic*-poly(**A$_2$**-*alt*-**B$_2$**). Olefinic (left) and methine region (right).

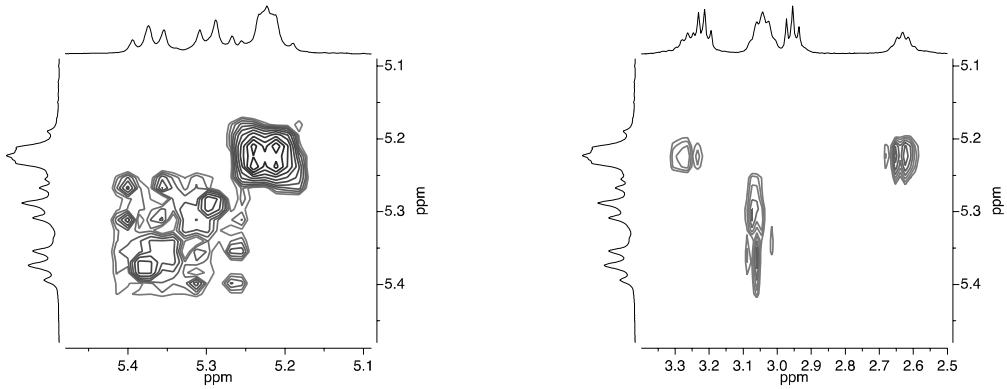


Figure S17. gCOSY ($CDCl_3$, 20 ºC) of *cis,syndiotactic*-poly(**A_2**-*alt*-**B_2**). Olefinic (left) and olefinic/methine region (right).

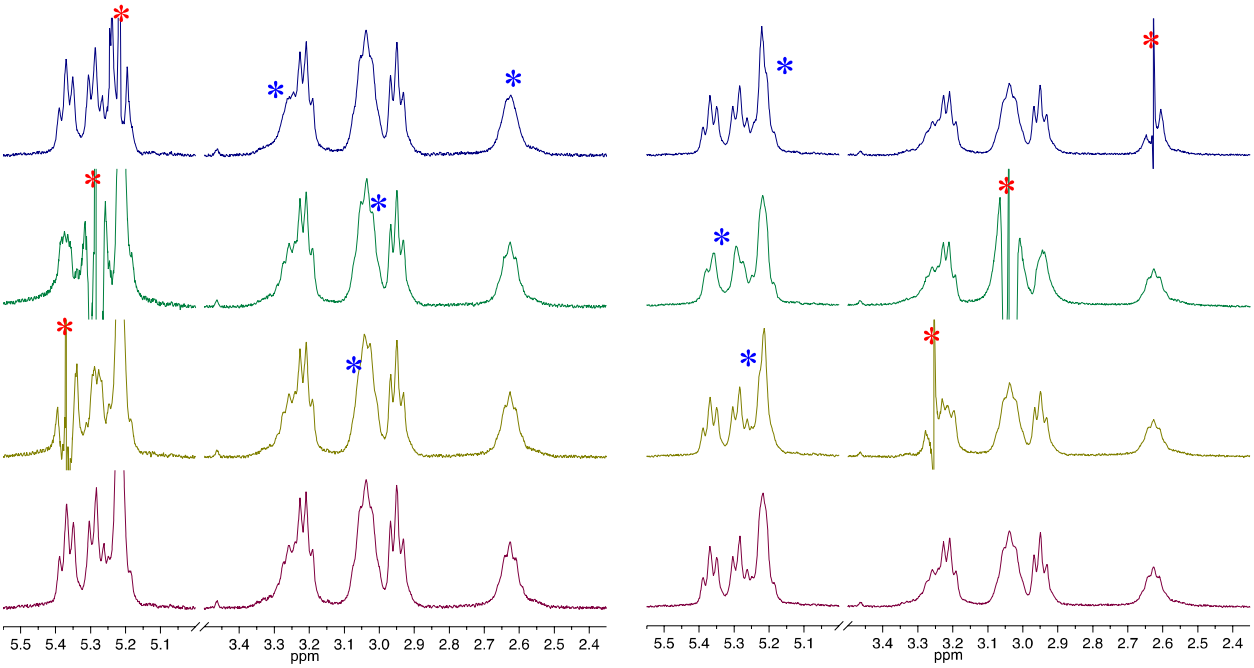


Figure S18. ^{1}H HOMODEC (500 MHz, $CDCl_3$, 20 ºC) of *cis,syndiotactic*-poly(**A_2**-*alt*-**B_2**). (*) irradiation, (*) decoupled resonance.

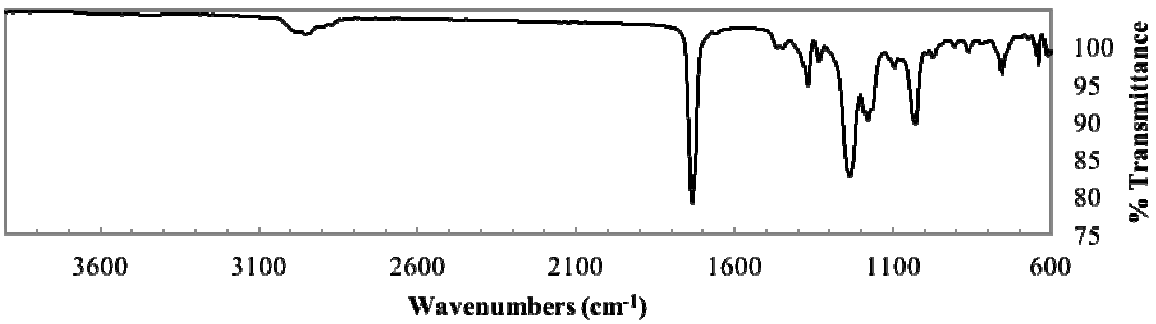


Figure S19. FTIR of *cis,syndiotactic*-poly(**A_2**-*alt*-**B_2**)

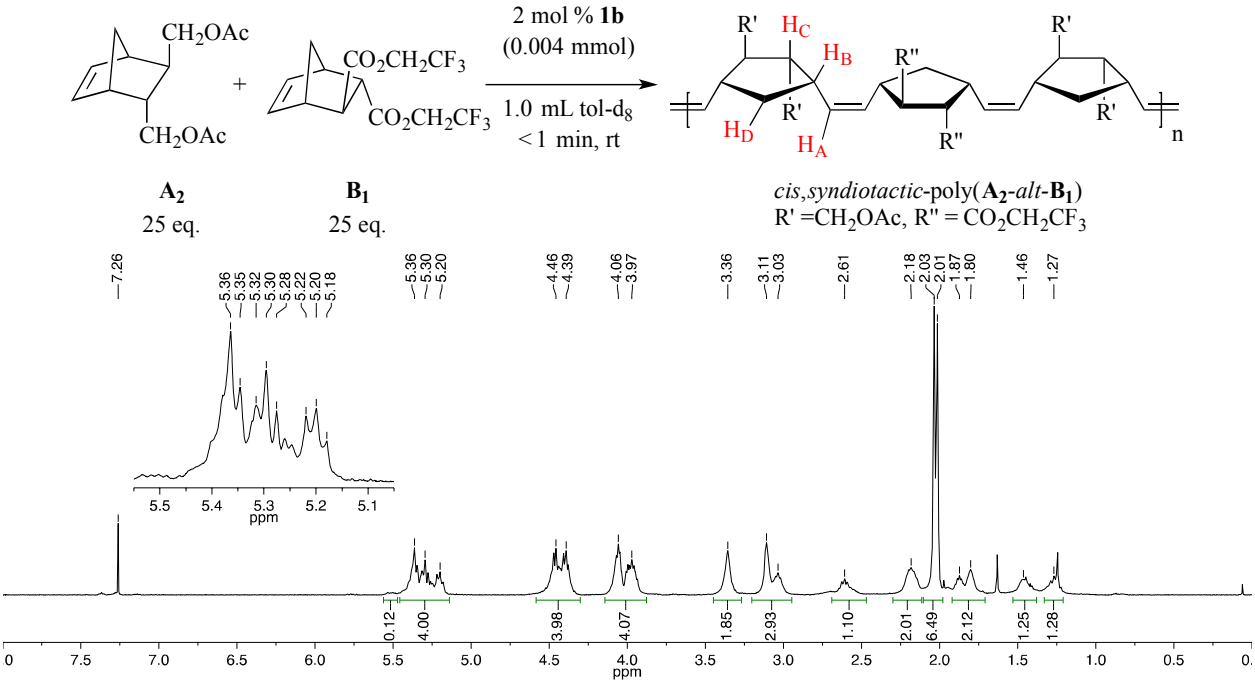


Figure S20. ^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC) of *cis,syndiotactic*-poly(**A**$_2$-*alt*-**B**$_1$).

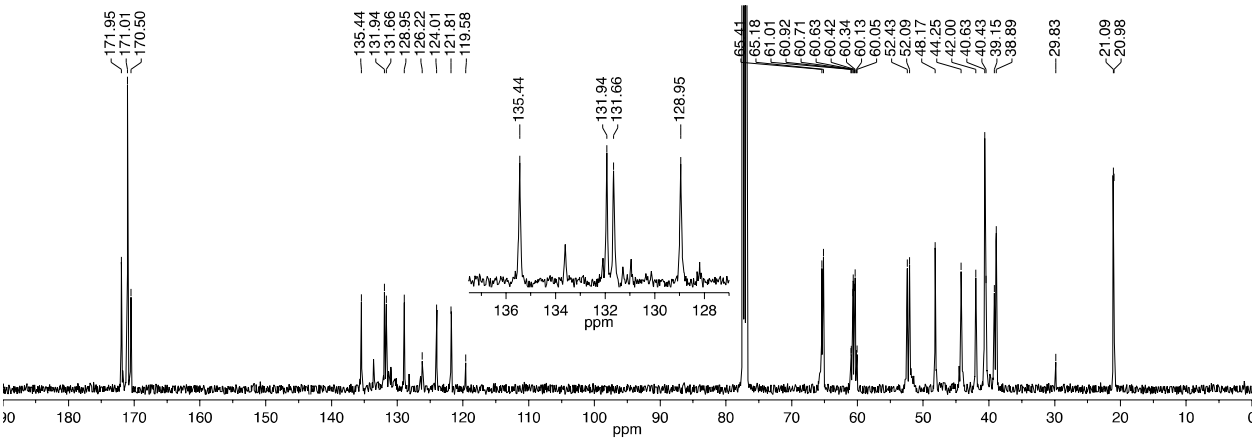


Figure S21. ^{13}C NMR (126 MHz, $CDCl_3$, 20 ºC) of *cis,syndiotactic*-poly(**A**$_2$-*alt*-**B**$_1$).

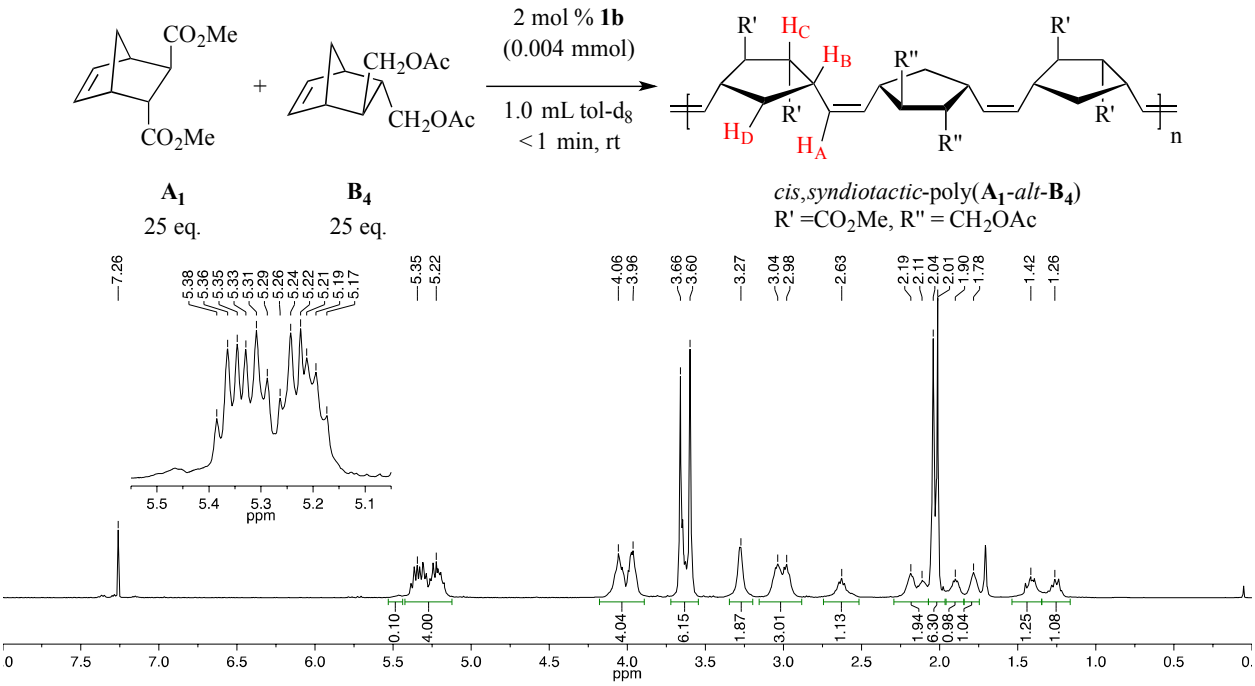


Figure S22. ^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC) of *cis,syndiotactic*-poly(**A**$_1$-*alt*-**B**$_4$).

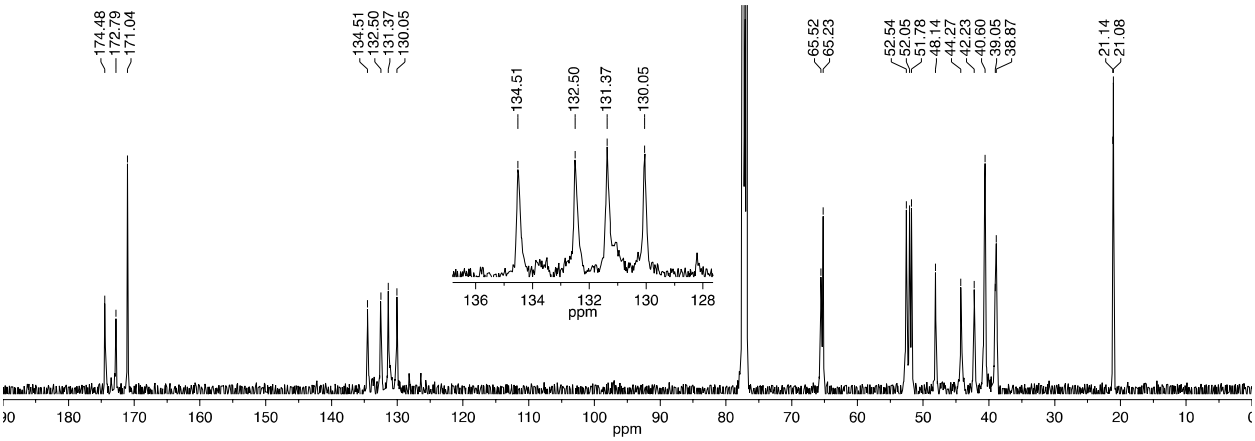


Figure S23. ^{13}C NMR (126 MHz, $CDCl_3$, 20 ºC) of *cis,syndiotactic*-poly(**A**$_1$-*alt*-**B**$_4$).

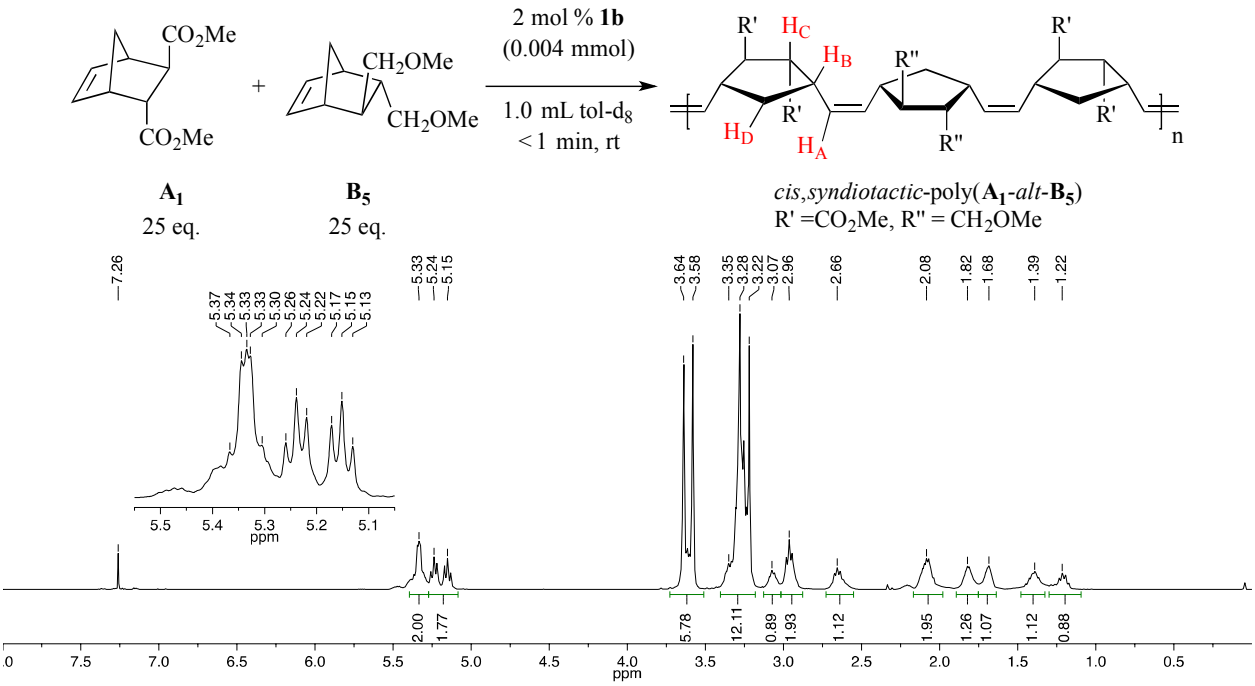


Figure S24. ^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC) of *cis,syndiotactic*-poly(**A**$_1$-*alt*-**B**$_5$).

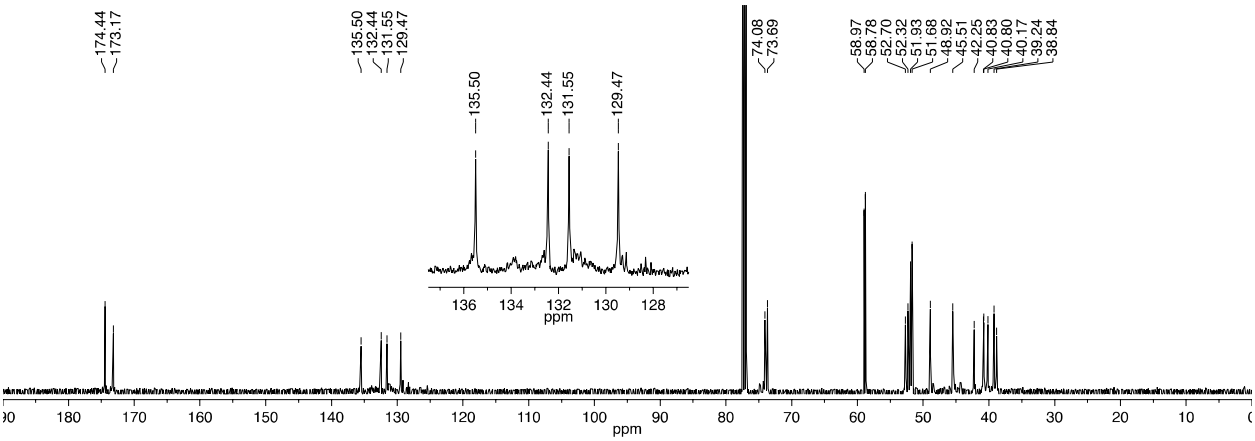


Figure S25. ^{13}C NMR (126 MHz, $CDCl_3$, 20 ºC) of *cis,syndiotactic*-poly(**A**$_1$-*alt*-**B**$_5$).

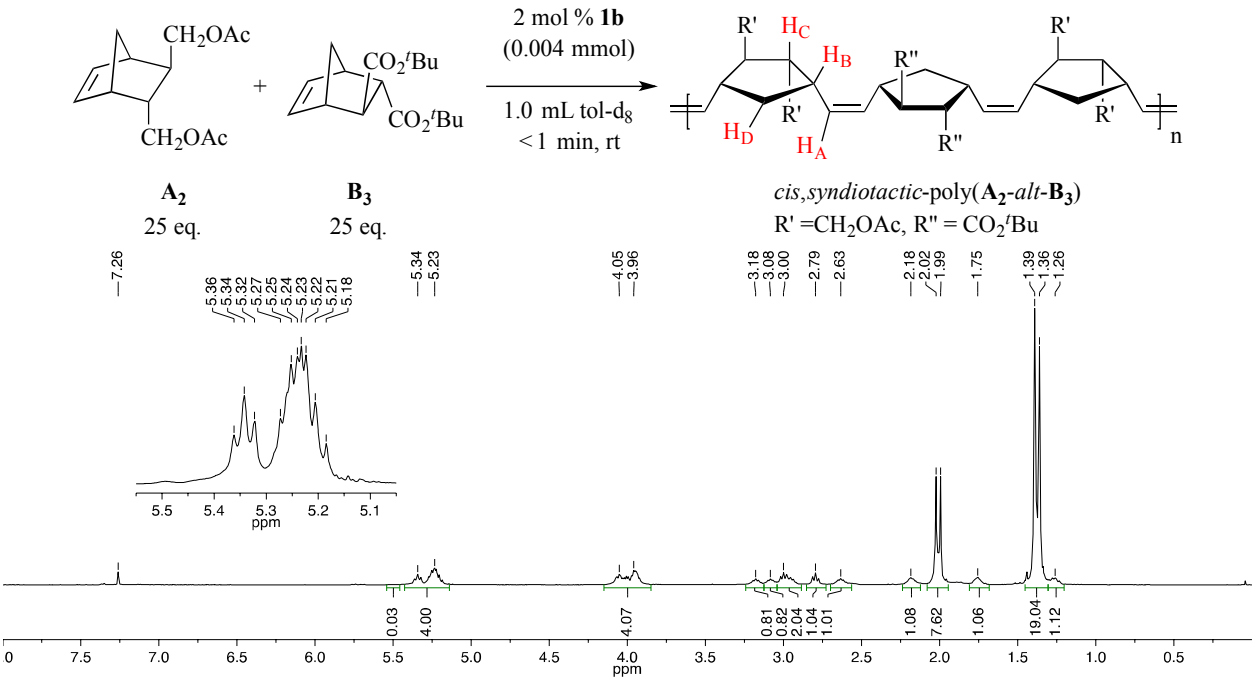


Figure S26. ^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC) of *cis,syndiotactic*-poly(**A_2**-*alt*-**B_3**).

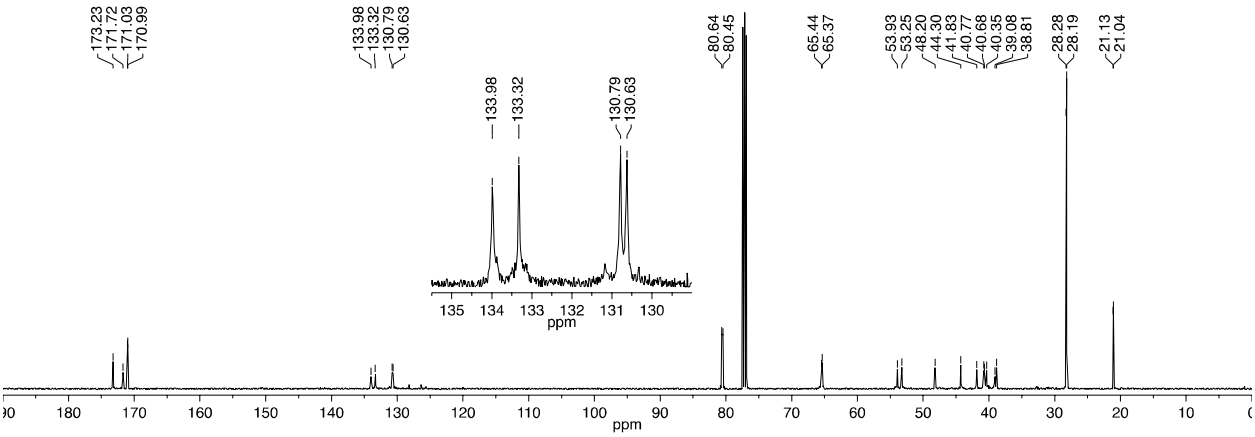


Figure S27. ^{13}C NMR (126 MHz, $CDCl_3$, 20 ºC) of *cis,syndiotactic*-poly(**A_2**-*alt*-**B_3**).

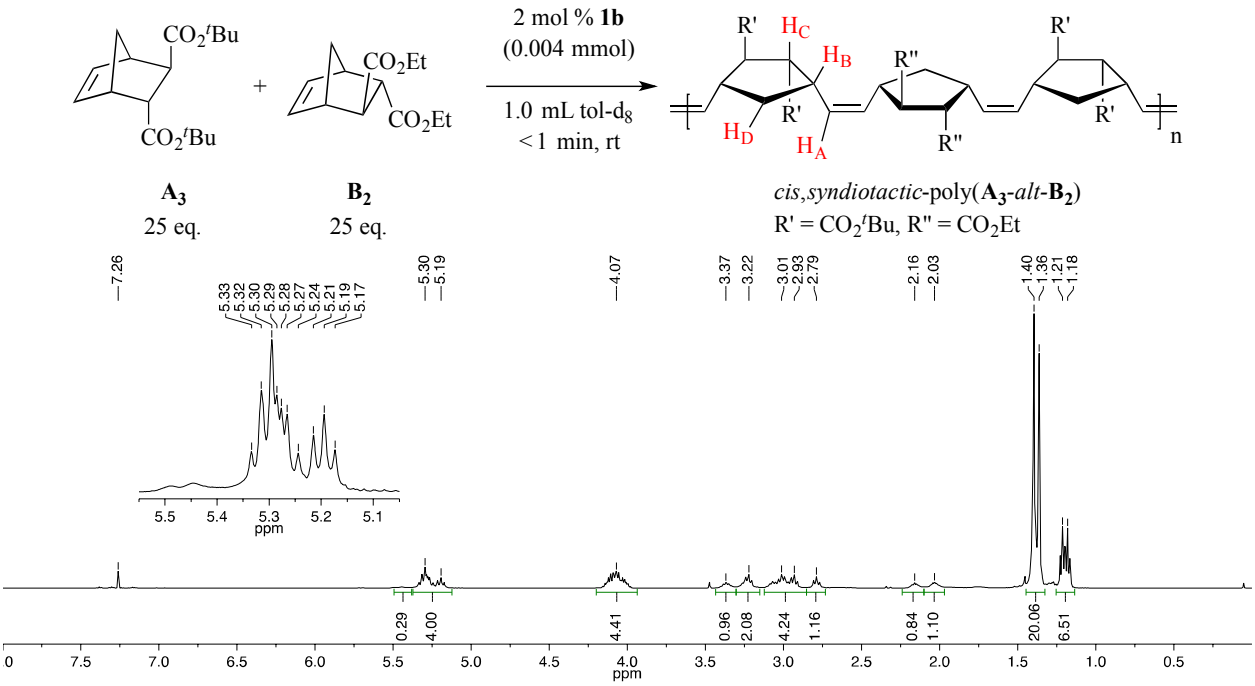


Figure S28. ^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC) of *cis,syndiotactic*-poly(**A$_3$**-*alt*-**B$_2$**).

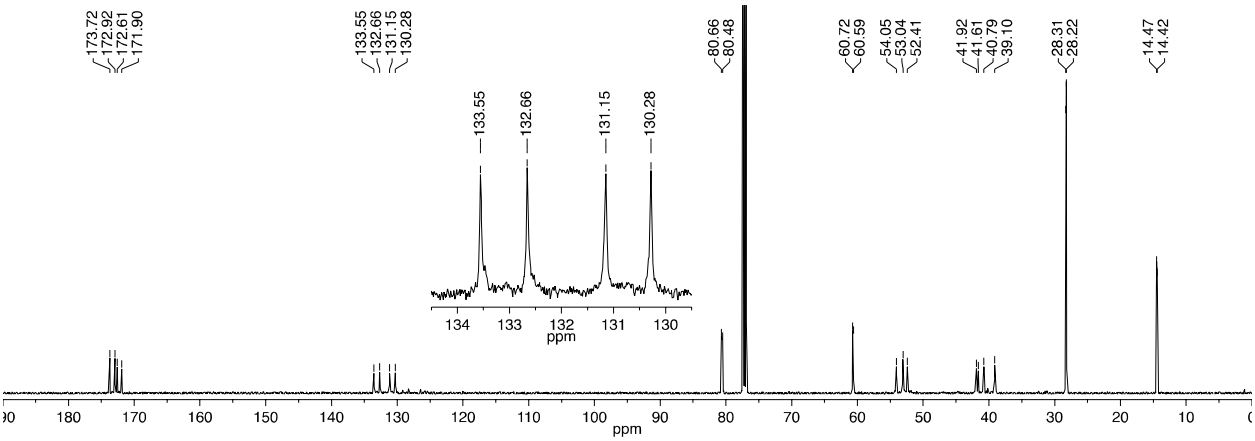


Figure S29. ^{13}C NMR (126 MHz, $CDCl_3$, 20 ºC) of *cis,syndiotactic*-poly(**A$_3$**-*alt*-**B$_2$**).

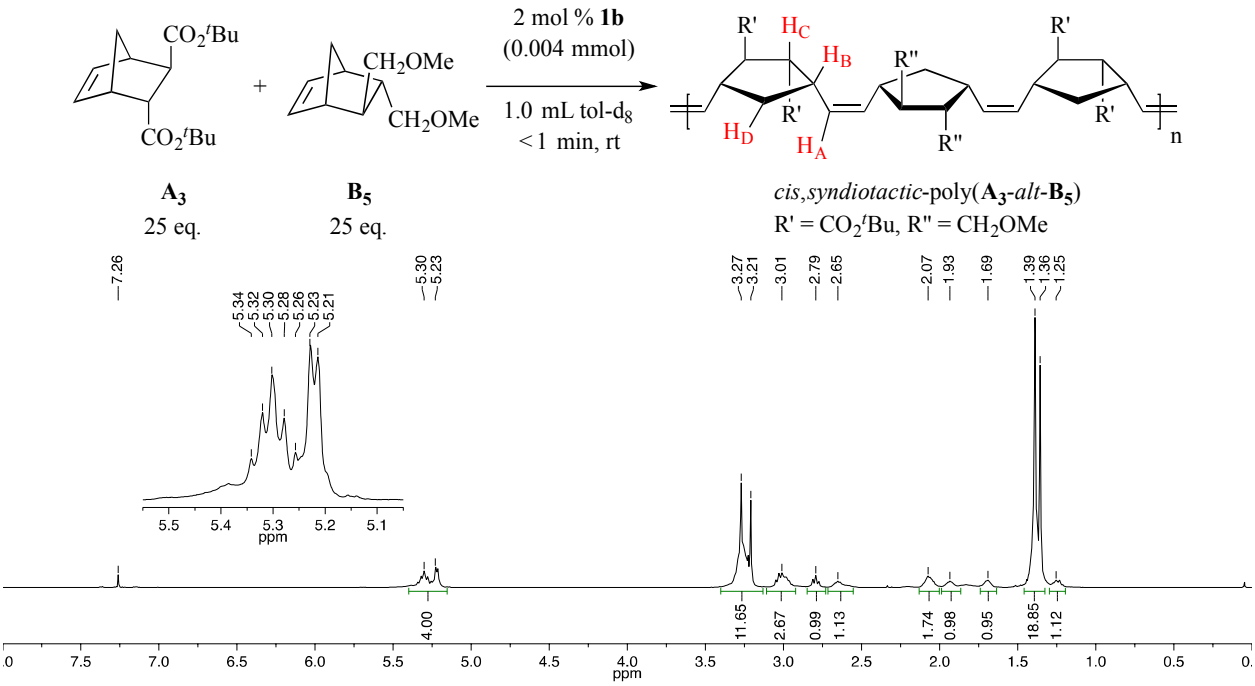


Figure S30. ^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC) of *cis,syndiotactic*-poly(**A$_3$**-*alt*-**B$_5$**).

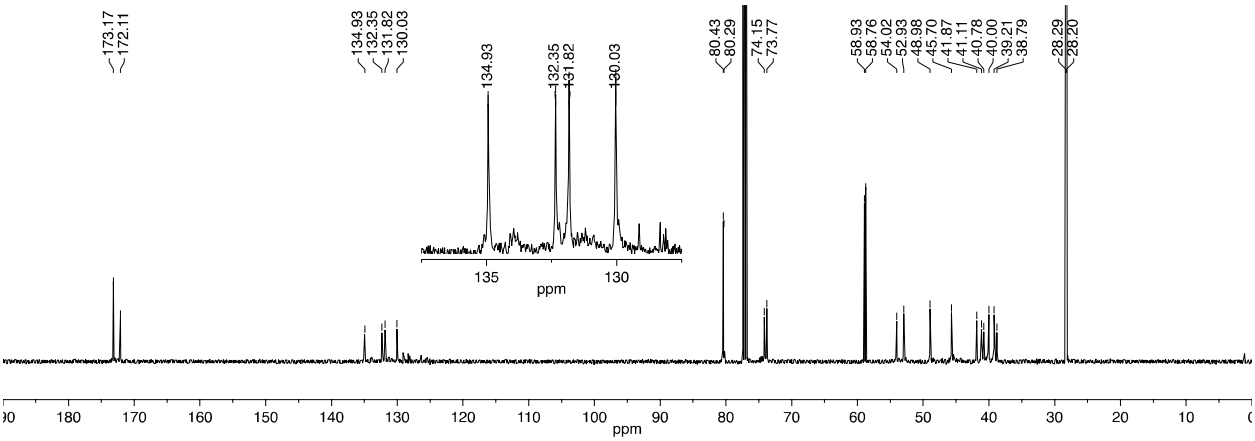


Figure S31. ^{13}C NMR (126 MHz, $CDCl_3$, 20 ºC) of *cis,syndiotactic*-poly(**A$_3$**-*alt*-**B$_5$**).

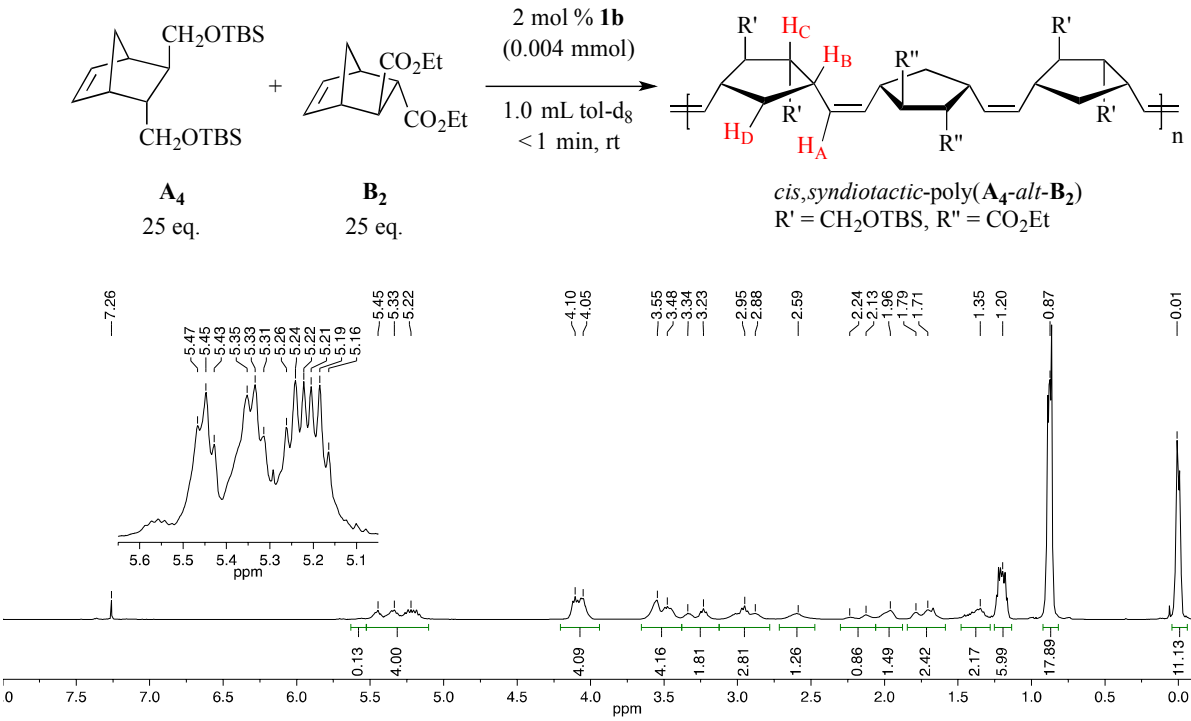


Figure S32. ^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC) of *cis,syndiotactic*-poly(**A$_4$**-*alt*-**B$_2$**).

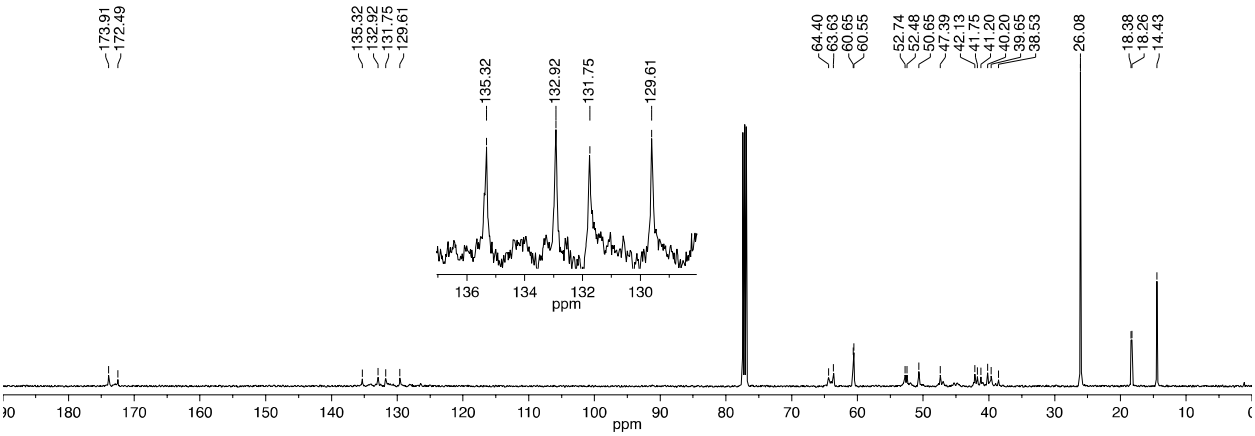
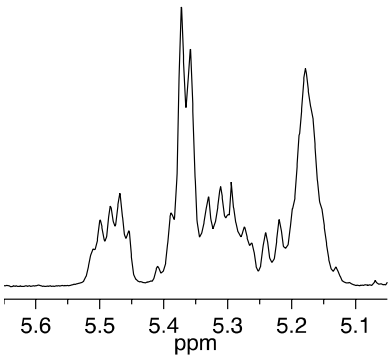


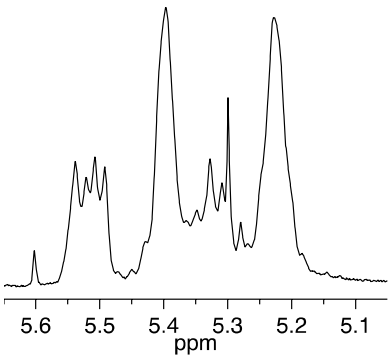
Figure S33. ^{13}C NMR (126 MHz, $CDCl_3$, 20 ºC) of *cis,syndiotactic*-poly(**A$_4$**-*alt*-**B$_2$**).

Control Reactions

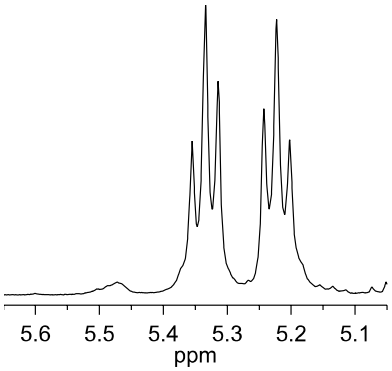
Standard Condition: 0.2 mol monomer, 2 mol % Mo initiator (0.004 mmol), rt, 1.0 mL toluene, overnight
^{1}H NMR spectra (500 MHz, $CDCl_3$, 20 ºC) – unless noted otherwise



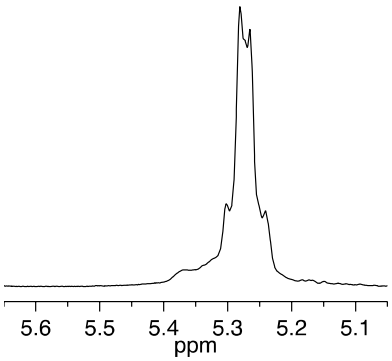
Mo(NAr')(CHCMe$_2$Ph)(pyr)(HMTO) **1b**
A$_1$



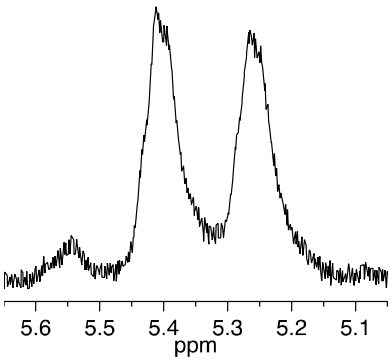
Mo(NAr')(CHCMe$_2$Ph)(pyr)(HMTO) **1b**
B$_1$



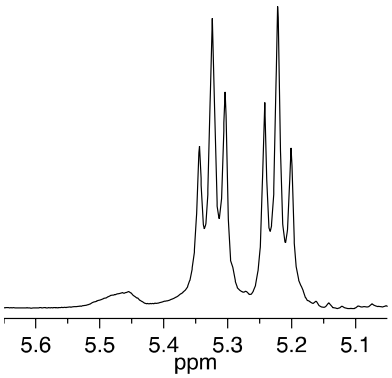
Mo(NAr')(CHCMe$_2$Ph)(pyr)(HMTO) **1b**
rac-**A$_1$**



Mo(NAd)(CHCMe$_2$Ph)(pyr)(HMTO) **1a**
rac-**A$_2$**



Mo(NAr')(CHCMe$_2$Ph)(pyr)(HMTO) **1b**
rac-**B$_1$**
(*limited solubility* in DMSO-d$_6$, 100 ºC)



Mo(NAd)(CHCMe$_2$Ph)(pyr)(HMTO) **1a**
rac-**B$_2$**

Catalyst Screen

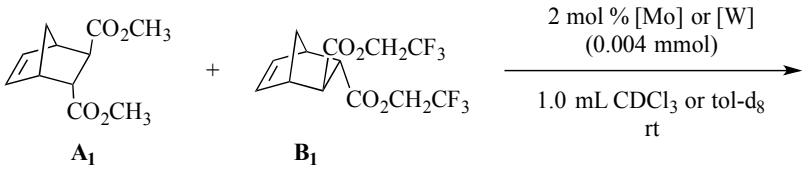
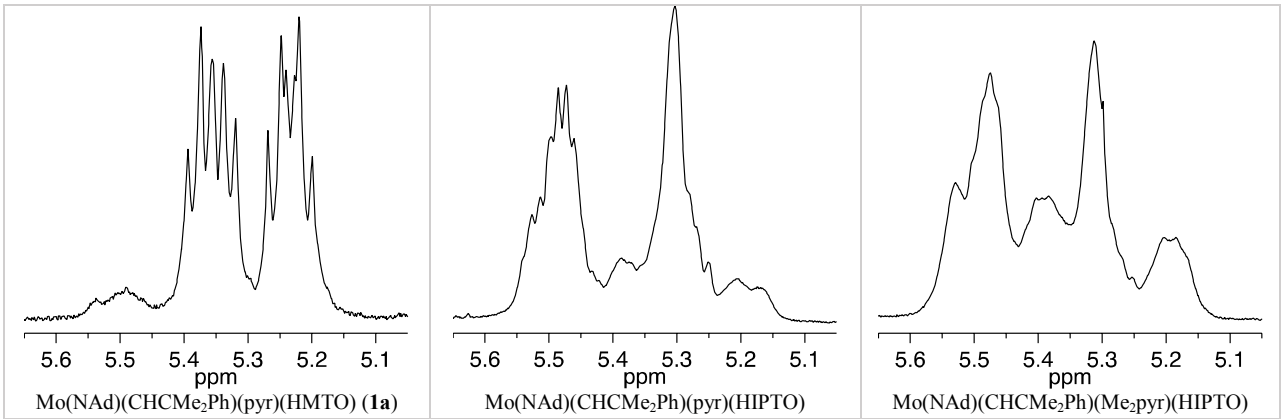
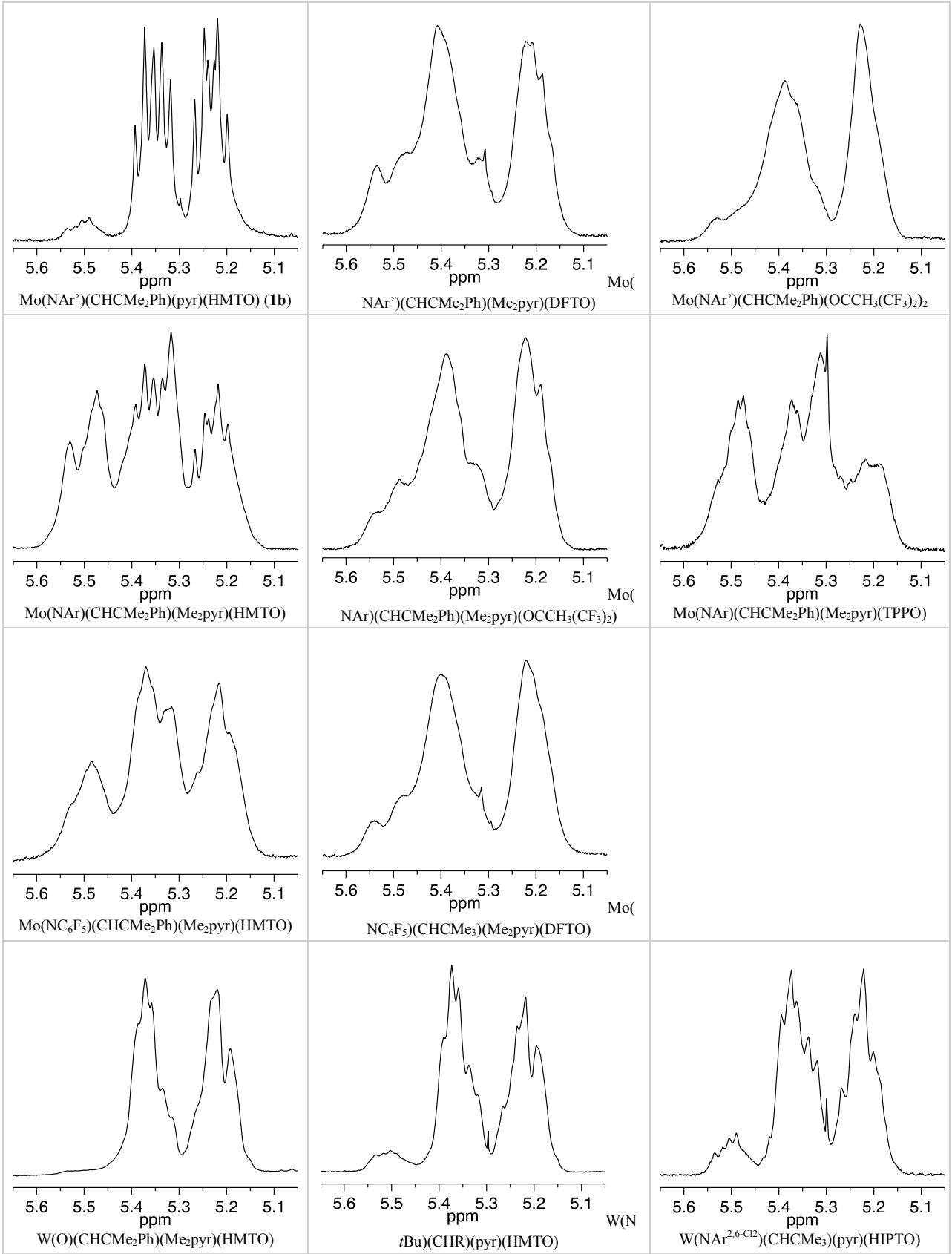


Table S1. Mo and W catalysts screened in this study.

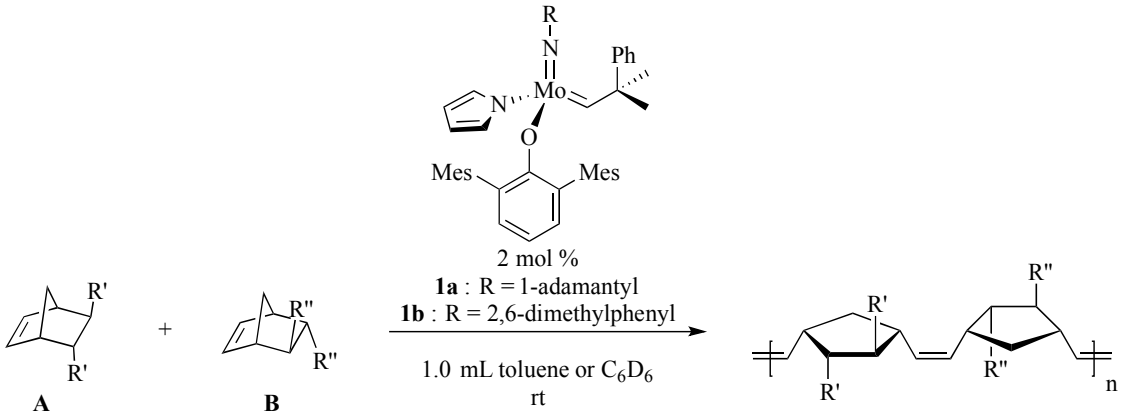
Catalyst	solvent	Polymer structure (as observed in ^{1}H NMR)
Mo(NAd)(CHCMe$_2$Ph)(pyr)(HMTO)	Tol-d$_8$	cis, tactic
Mo(NAd)(CHCMe$_2$Ph)(pyr)(HIPTO)	CDCl$_3$	atactic
Mo(NAd)(CHCMe$_2$Ph)(Me$_2$pyr)(HIPTO)	Tol-d$_8$	atactic
Mo(NAr')(CHCMe$_2$Ph)(pyr)(HMTO)	Tol-d$_8$	cis, tactic
Mo(NAr')(CHCMe$_2$Ph)(Me$_2$pyr)(DFTO)	CDCl$_3$	atactic
Mo(NAr')(CHCMe$_2$Ph)(OCCH$_3$(CF$_3$)$_2$)$_2$	Tol-d$_8$	atactic
Mo(NAr)(CHCMe$_2$Ph)(Me$_2$pyr)(HMTO)	Tol-d$_8$	atactic
Mo(NAr)(CHCMe$_2$Ph)(Me$_2$pyr)(OCCH$_3$(CF$_3$)$_2$)	CDCl$_3$	atactic
Mo(NAr)(CHCMe$_2$Ph)(Me$_2$pyr)(TPPO)	CDCl$_3$	atactic
Mo(NC$_6$F$_5$)(CHCMe$_2$Ph)(Me$_2$pyr)(HMTO)	CDCl$_3$	atactic
Mo(NC$_6$F$_5$)(CHCMe$_3$)(Me$_2$pyr)(DFTO)	CDCl$_3$	atactic
W(O)(CHCMe$_2$Ph)(Me$_2$pyr)(HMTO)	CDCl$_3$	atactic
W(N*t*Bu)(CHR)(pyr)(HMTO)	Tol-d$_8$	atactic
W(NAr$^{2,6\text{-Cl2}}$)(CHCMe$_3$)(pyr)(HIPTO)	Tol-d$_8$	atactic

^{1}H NMR spectra (500 MHz, CDCl$_3$, 20 ºC) – olefinic region

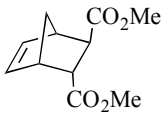



5.6 5.5 5.4 5.3 5.2 5.1
ppm
Mo(NAr')(CHCMe2Ph)(pyr)(HMTO) (1b)
NAr')(CHCMe2Ph)(Me2pyr)(DFTO)
Mo(
Mo(NAr')(CHCMe2Ph)(OCCH3(CF3)2)2
Mo(NAr)(CHCMe2Ph)(Me2pyr)(HMTO)
NAr)(CHCMe2Ph)(Me2pyr)(OCCH3(CF3)2)
Mo(
Mo(NAr)(CHCMe2Ph)(Me2pyr)(TPPO)
Mo(NC6F5)(CHCMe2Ph)(Me2pyr)(HMTO)
NC6F5)(CHCMe3)(Me2pyr)(DFTO)
Mo(
W(O)(CHCMe2Ph)(Me2pyr)(HMTO)
tBu)(CHR)(pyr)(HMTO)
W(N
W(NAr2,6-Cl2)(CHCMe3)(pyr)(HIPTO)

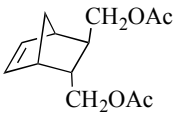
Monomer Screen



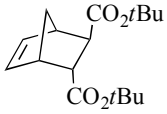
R,R



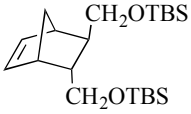
A$_1$



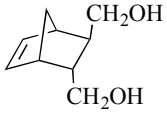
A$_2$



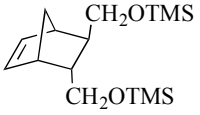
A$_3$



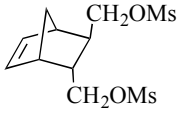
A$_4$



A$_5$

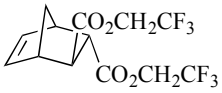


A$_6$

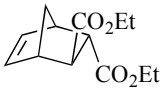


A$_7$

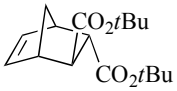
S,S



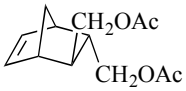
B$_1$



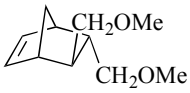
B$_2$



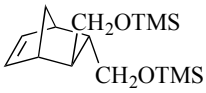
B$_3$



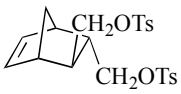
B$_4$



B$_5$



B$_6$

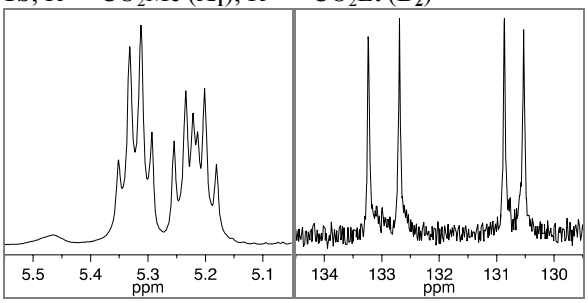


B$_7$

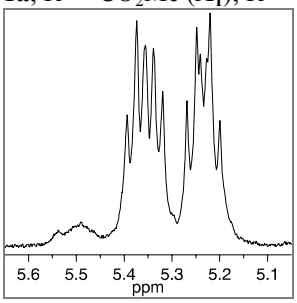
Table S2. ROMP of enantiomerically pure monomers **A** and **B** catalyzed by **1a** or **1b**.

SI Entry	Catalyst	R' (**A**)	R'' (**B**)	Polymer structure (^{1}H NMR)
1	**1b**	CO_2Me (**A_1**)	CO_2Et (**B_2**)	tactic
2	**1a**	CO_2Me (**A_1**)	$CO_2CH_2CF_3$ (**B_1**)	tactic
3	**1b**	CO_2Me (**A_1**)	$CO_2CH_2CF_3$ (**B_1**)	tactic
4	**1a**	CO_2Me (**A_1**)	CH_2OAc (**B_4**)	tactic
5	**1b**	CO_2Me (**A_1**)	CH_2OAc (**B_4**)	tactic
6	**1a**	CO_2Me (**A_1**)	CH_2OTMS (**B_6**)	atactic
7	**1b**	CO_2Me (**A_1**)	CH_2OTMS (**B_6**)	Insoluble in $CDCl_3$
8	**1b**	CO_2Me (**A_1**)	CH_2OMe (**B_7**)	tactic
9	**1b**	CO_2Me (**A_1**)	CH_2OTs (**B_7**)	atactic
10	**1a**	CH_2OAc (**A_2**)	CO_2Et (**B_2**)	tactic
11	**1b**	CH_2OAc (**A_2**)	CO_2Et (**B_2**)	tactic
12	**1b**	CH_2OAc (**A_2**)	$CO_2CH_2CF_3$ (**B_1**)	tactic
13	**1a**	CH_2OAc (**A_2**)	CO_2tBu (**B_3**)	atactic
14	**1b**	CH_2OAc (**A_2**)	CO_2tBu (**B_3**)	tactic
15	**1b**	CH_2OAc (**A_2**)	CH_2OMe (**B_5**)	tactic
16	**1b**	CH_2OAc (**A_2**)	CH_2OTs (**B_7**)	tactic
17	**1a**	CO_2tBu (**A_3**)	CO_2Et (**B_2**)	tactic
18	**1b**	CO_2tBu (**A_3**)	CO_2Et (**B_2**)	tactic
19	**1a**	CO_2tBu (**A_3**)	$CO_2CH_2CF_3$ (**B_1**)	atactic
20	**1b**	CO_2tBu (**A_3**)	CH_2OMe (**B_5**)	tactic
21	**1b**	CO_2tBu (**A_3**)	CH_2OTs (**B_7**)	atactic
22	**1a**	CH_2OTMS (**A_6**)	$CO_2CH_2CF_3$ (**B_1**)	atactic
23	**1b**	CH_2OTMS (**A_6**)	$CO_2CH_2CF_3$ (**B_1**)	atactic
24	**1a**	CH_2OTMS (**A_6**)	CO_2Et (**B_2**)	tactic
25	**1b**	CH_2OTMS (**A_6**)	CO_2Et (**B_2**)	atactic
26	**1a**	CH_2OTMS (**A_6**)	CO_2tBu (**B_3**)	atactic
27	**1b**	CH_2OTMS (**A_6**)	CO_2tBu (**B_3**)	atactic
28	**1a**	CH_2OTMS (**A_6**)	CH_2OAc (**B_4**)	atactic
29	**1b**	CH_2OTMS (**A_6**)	CH_2OAc (**B_4**)	atactic
30	**1b**	CH_2OTMS (**A_6**)	CH_2OMe (**B_5**)	atactic
31	**1b**	CH_2OTMS (**A_6**)	CH_2OTs (**B_7**)	No conversion
32	**1a**	CH_2OH (**A_5**)	$CO_2CH_2CF_3$ (**B_1**)	No conversion
33	**1a**	CH_2OH (**A_5**)	CO_2Et (**B_2**)	No conversion
34	**1a**	CH_2OH (**A_5**)	CO_2tBu (**B_3**)	No conversion
35	**1a**	CH_2OMs (**A_7**)	$CO_2CH_2CF_3$ (**B_1**)	atactic
36	**1a**	CH_2OMs (**A_7**)	CO_2Et (**B_2**)	tactic
37	**1a**	CH_2OMs (**A_7**)	CO_2tBu (**B_3**)	atactic
38	**1a**	CH_2OTBS (**A_4**)	$CO_2CH_2CF_3$ (**B_1**)	atactic
39	**1b**	CH_2OTBS (**A_4**)	$CO_2CH_2CF_3$ (**B_1**)	atactic
40	**1a**	CH_2OTBS (**A_4**)	CO_2Et (**B_2**)	tactic
41	**1b**	CH_2OTBS (**A_4**)	CO_2Et (**B_2**)	tactic
42	**1a**	CH_2OTBS (**A_4**)	CO_2tBu (**B_3**)	tactic
43	**1b**	CH_2OTBS (**A_4**)	CO_2tBu (**B_3**)	tactic
44	**1a**	CH_2OTBS (**A_4**)	CH_2OAc (**B_4**)	atactic
45	**1b**	CH_2OTBS (**A_4**)	CH_2OAc (**B_4**)	atactic
46	**1a**	CH_2OTBS (**A_4**)	CH_2OTMS (**B_6**)	atactic
47	**1b**	CH_2OTBS (**A_4**)	CH_2OTMS (**B_6**)	atacitc
48	**1b**	CH_2OTBS (**A_4**)	CH_2OMe (**B_5**)	tactic
49	**1b**	CH_2OTBS (**A_4**)	CH_2OTs (**B_7**)	atactic

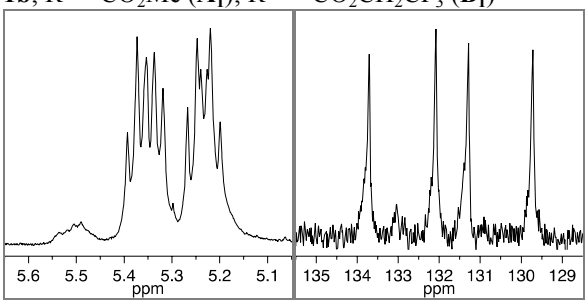
SI Entry 1:
1b; R' = CO_2Me (**A_1**); R'' = CO_2Et (**B_2**)



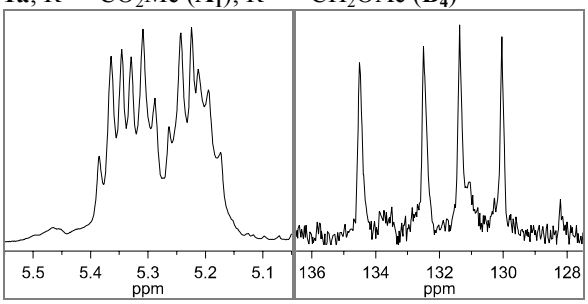
SI Entry 2:
1a; R' = CO_2Me (**A_1**); R'' = $CO_2CH_2CF_3$ (**B_1**)



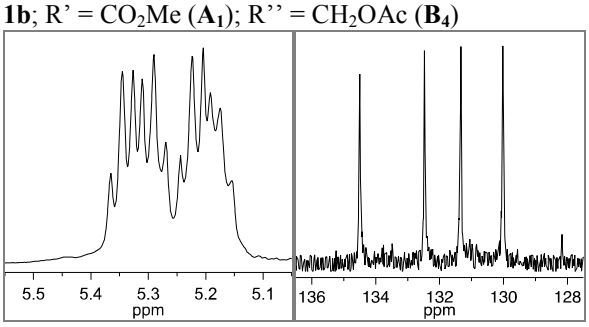
SI Entry 3:
1b; R' = CO_2Me (**A_1**); R'' = $CO_2CH_2CF_3$ (**B_1**)



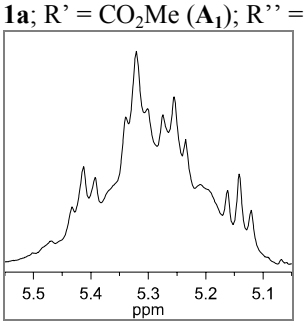
SI Entry 4:
1a; R' = CO_2Me (**A_1**); R'' = CH_2OAc (**B_4**)



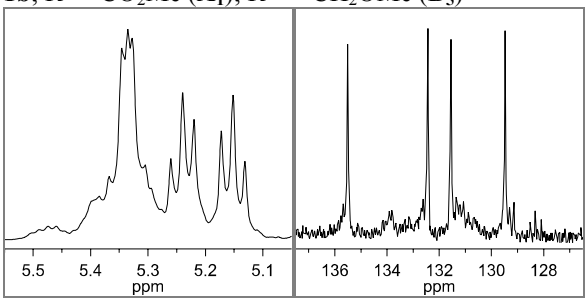
SI Entry 5:
1b; R' = CO_2Me (**A_1**); R'' = CH_2OAc (**B_4**)



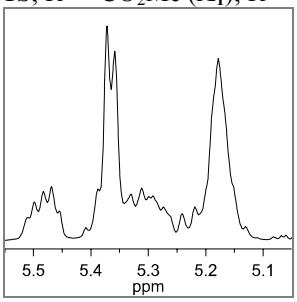
SI Entry 6:
1a; R' = CO_2Me (**A_1**); R'' = CH_2OTMS (**B_6**)



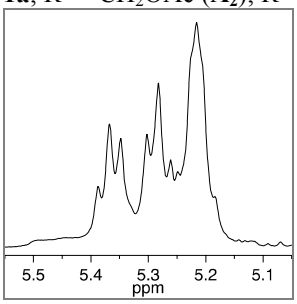
SI Entry 8:
1b; R' = CO_2Me (**A_1**); R'' = CH_2OMe (**B_5**)



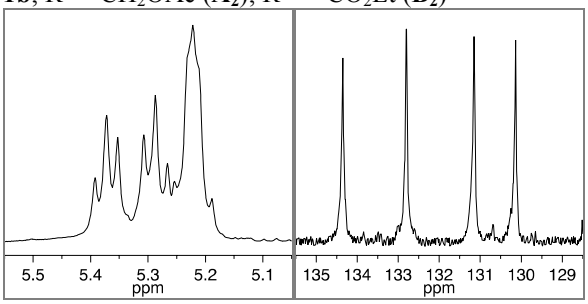
SI Entry 9:
1b; R' = CO_2Me (**A_1**); R'' = CH_2OTs (**B_7**)



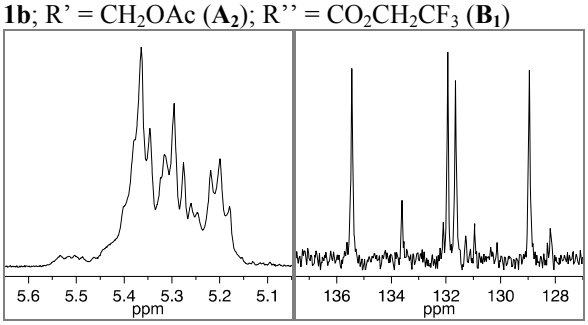
SI Entry 10:
1a; R' = CH_2OAc (**A_2**); R'' = CO_2Et (**B_2**)



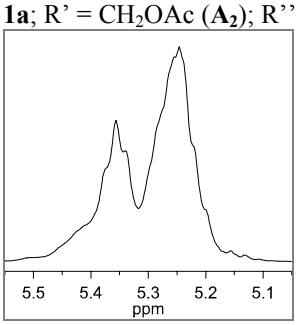
SI Entry 11:
1b; R' = CH_2OAc (**A_2**); R'' = CO_2Et (**B_2**)



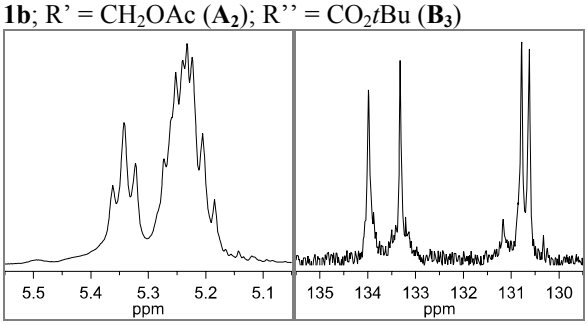
SI Entry 12:
1b; R' = CH_2OAc (**A_2**); R'' = $CO_2CH_2CF_3$ (**B_1**)



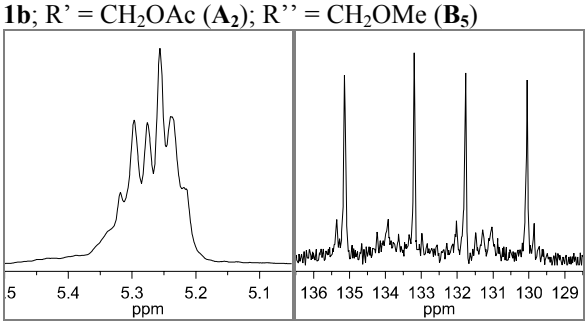
SI Entry 13:
1a; R' = CH_2OAc (**A_2**); R'' = CO_2tBu (**B_3**)



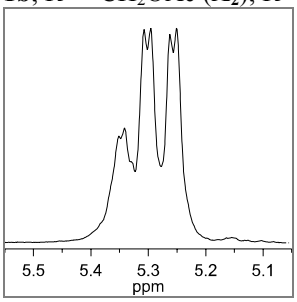
SI Entry 14:
1b; R' = CH_2OAc (**A_2**); R'' = CO_2tBu (**B_3**)



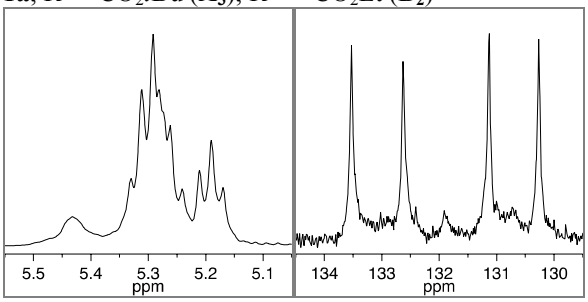
SI Entry 15:
1b; R' = CH_2OAc (**A_2**); R'' = CH_2OMe (**B_5**)



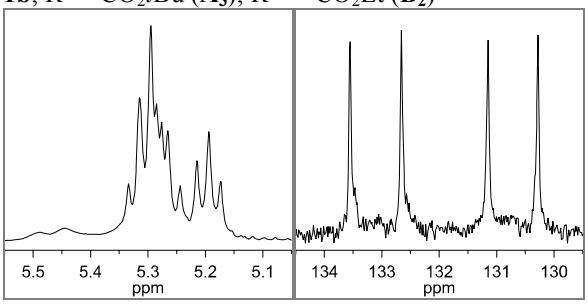
SI Entry 16:
1b; R' = CH_2OAc (**A_2**); R'' = CH_2OTs (**B_6**)



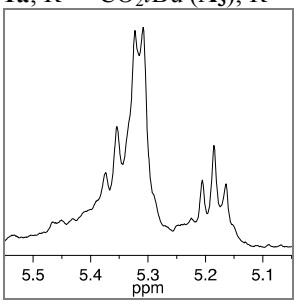
SI Entry 17:
1a; R' = CO_2tBu (**A_3**); R'' = CO_2Et (**B_2**)



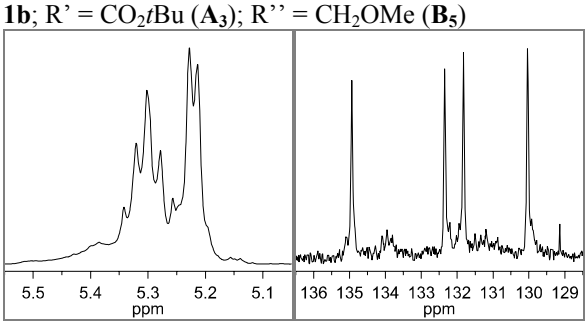
SI Entry 18:
1b; R' = CO_2tBu (**A_3**); R'' = CO_2Et (**B_2**)



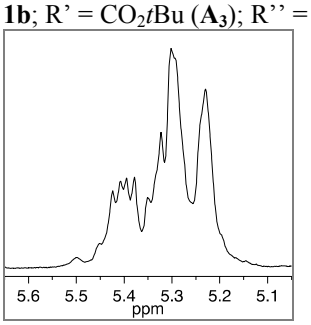
SI Entry 19:
1a; R' = CO_2tBu (**A_3**); R'' = $CO_2CH_2CF_3$ (**B_1**)



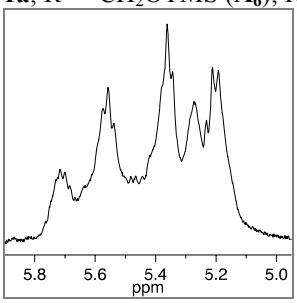
SI Entry 20:
1b; R' = CO_2tBu (**A_3**); R'' = CH_2OMe (**B_5**)



SI Entry 21:
1b; R' = CO_2tBu (**A_3**); R'' = CH_2OTs (**B_7**)

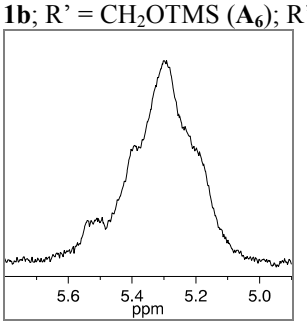


SI Entry 22:
1a; R' = CH_2OTMS (**A_6**); R'' = $CO_2CH_2CF_3$ (**B_1**)

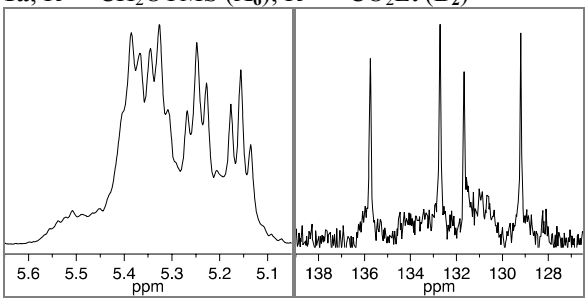


(Spectrum in tol-d_8)

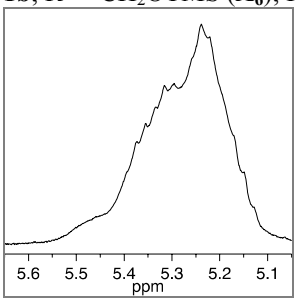
SI Entry 23:
1b; R' = CH_2OTMS (**A_6**); R'' = $CO_2CH_2CF_3$ (**B_1**)



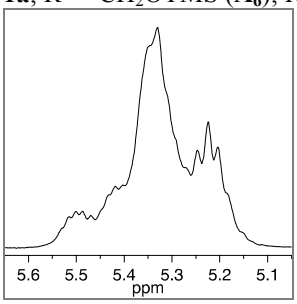
SI Entry 24:
1a; R' = CH_2OTMS (**A_6**); R'' = CO_2Et (**B_2**)



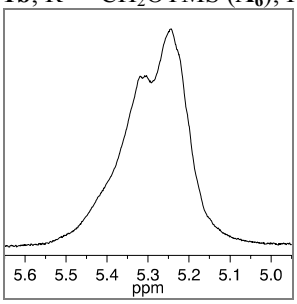
SI Entry 25:
1b; R' = CH_2OTMS (**A_6**); R'' = CO_2Et (**B_2**)



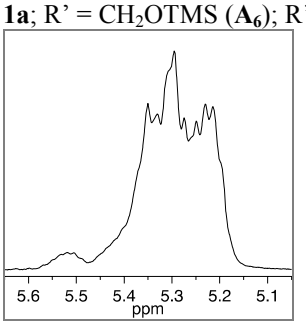
SI Entry 26:
1a; R' = CH_2OTMS (**A_6**); R'' = CO_2tBu (**B_3**)



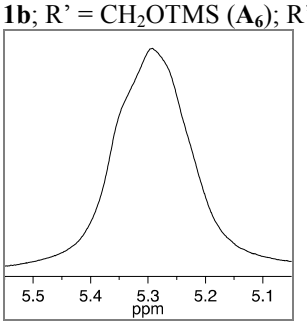
SI Entry 27:
1b; R' = CH_2OTMS (**A_6**); R'' = CO_2tBu (**B_3**)



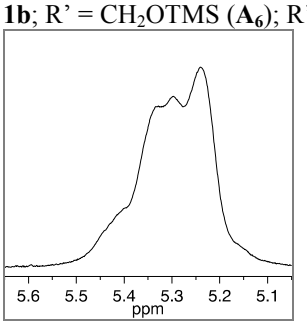
SI Entry 28:
1a; R' = CH_2OTMS (**A_6**); R'' = CH_2OAc (**B_5**)



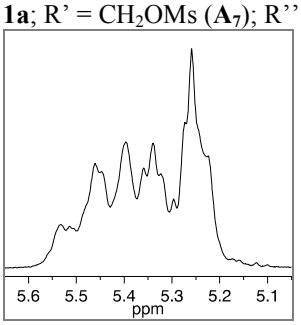
SI Entry 29:
1b; R' = CH_2OTMS (**A_6**); R'' = CH_2OAc (**B_5**)



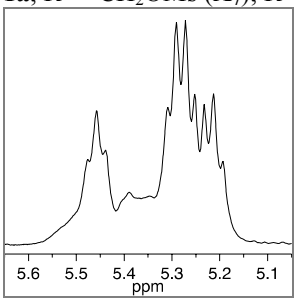
SI Entry 30:
1b; R' = CH_2OTMS (**A_6**); R'' = CH_2OMe (**B_7**)



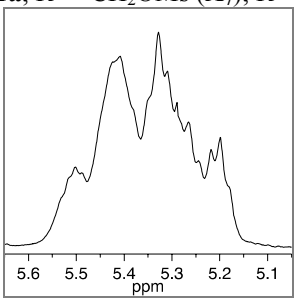
SI Entry 35:
1a; R' = CH_2OMs (**A_7**); R'' = $CO_2CH_2CF_3$ (**B_1**)



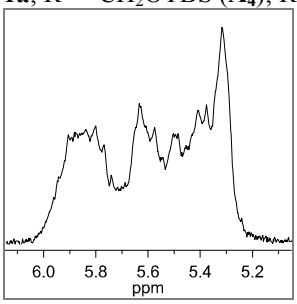
SI Entry 36:
1a; R' = CH_2OMs (**A_7**); R'' = CO_2Et (**B_2**)



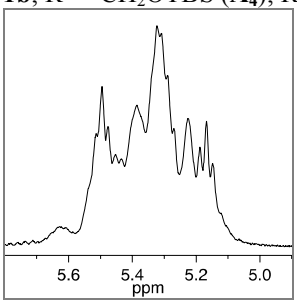
SI Entry 37:
1a; R' = CH_2OMs (**A_7**); R'' = CO_2tBu (**B_3**)



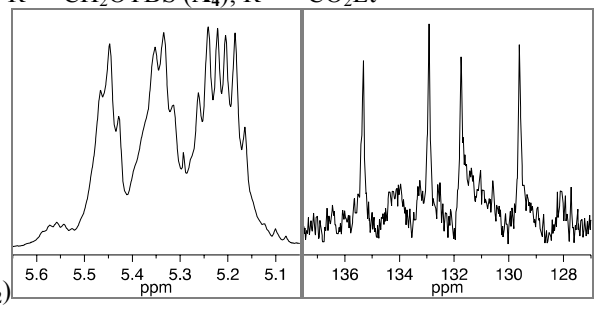
SI Entry 38:
1a; R' = CH_2OTBS (**A_4**); R'' = $CO_2CH_2CF_3$ (**B_1**)



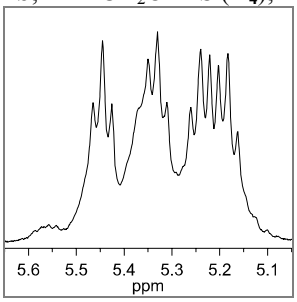
SI Entry 39:
1b; R' = CH_2OTBS (**A_4**); R'' = $CO_2CH_2CF_3$ (**B_1**)



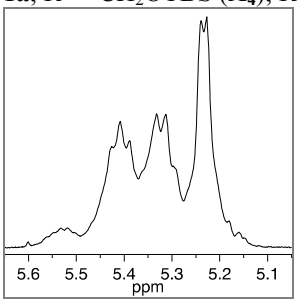
SI Entry 40:
1a; R' = CH_2OTBS (**A_4**); R'' = CO_2Et (**B_2**)



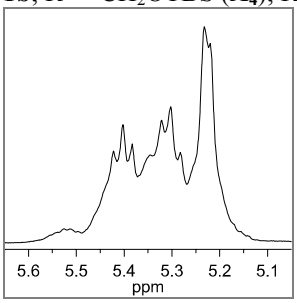
SI Entry 41:
1b; R' = CH_2OTBS (**A_4**); R'' = CO_2Et (**B_2**)



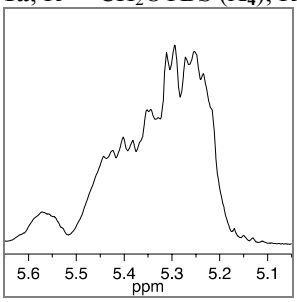
SI Entry 42:
1a; R' = CH_2OTBS (**A_4**); R'' = CO_2tBu (**B_3**)



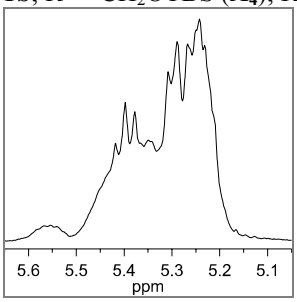
SI Entry 43:
1b; R' = CH_2OTBS (**A_4**); R'' = CO_2tBu (**B_3**)



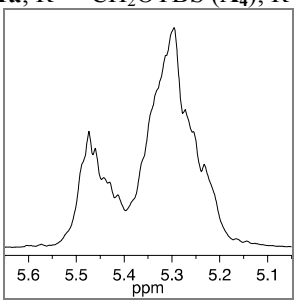
SI Entry 44:
1a; R' = CH_2OTBS (**A_4**); R'' = CH_2OAc(**B_5**)



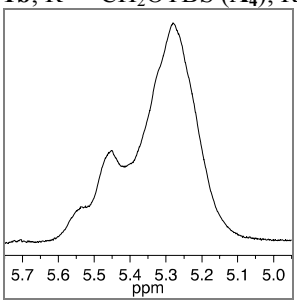
SI Entry 45:
1b; R' = CH_2OTBS (**A_4**); R'' = CH_2OAc (**B_5**)



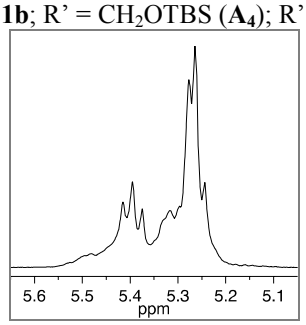
SI Entry 46:
1a; R' = CH_2OTBS (**A_4**); R'' = CH_2OTMS (**B_4**)



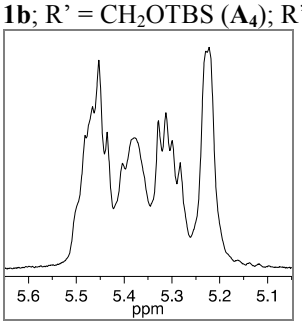
SI Entry 47:
1b; R' = CH_2OTBS (**A_4**); R'' = CH_2OTMS (**B_4**)



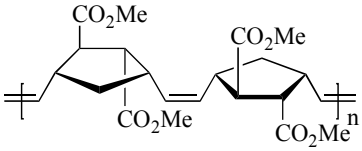
SI Entry 48:
1b; R' = CH_2OTBS (**A_4**); R'' = CH_2OMe (**B_7**)



SI Entry 49:
1b; R' = CH_2OTBS (**A_4**); R'' = CH_2OTs (**B_6**)



ROMP with $1b_w$



Cis,syndiotactic,alt-poly(*rac*-**A$_1$**)
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.33 (t, *J* = 10.2 Hz, 1H), 5.21 (t, *J* = 10.2 Hz, 1H), 3.65 (s, 3H), 3.60 (s, 3H), 3.31 (dq, *J* = 18.8, 9.5 Hz, 2H), 3.07 (p, *J* = 9.9 Hz, 1H), 2.97 (t, *J* = 9.5 Hz, 1H), 2.20 – 1.97 (m, 1H), 1.43 – 1.29 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.17, 172.91, 132.92, 130.75, 52.61, 52.22, 52.03, 51.78, 42.05, 40.59, 39.00.

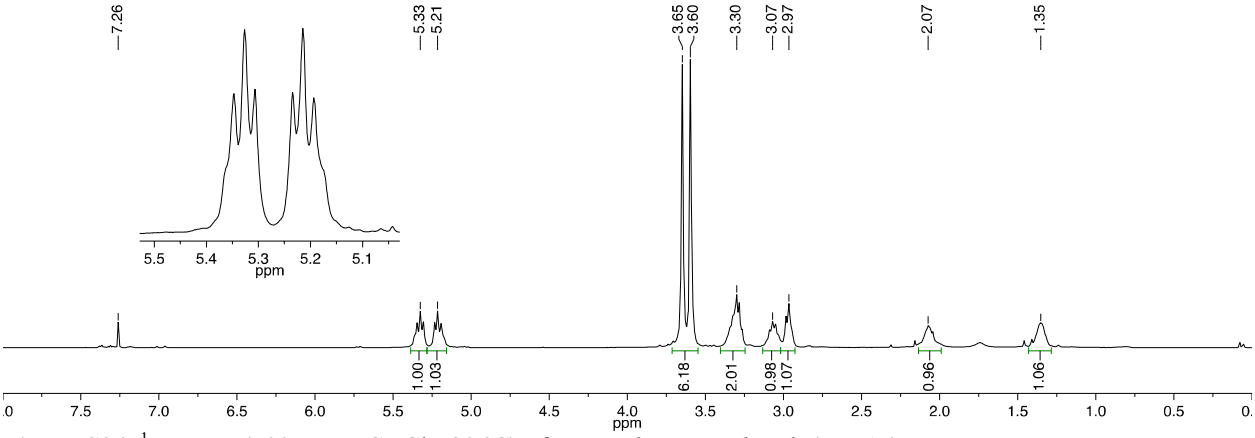


Figure S34. ^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC) of *cis,syndiotactic,alt*-poly(*rac*-**A$_1$**).

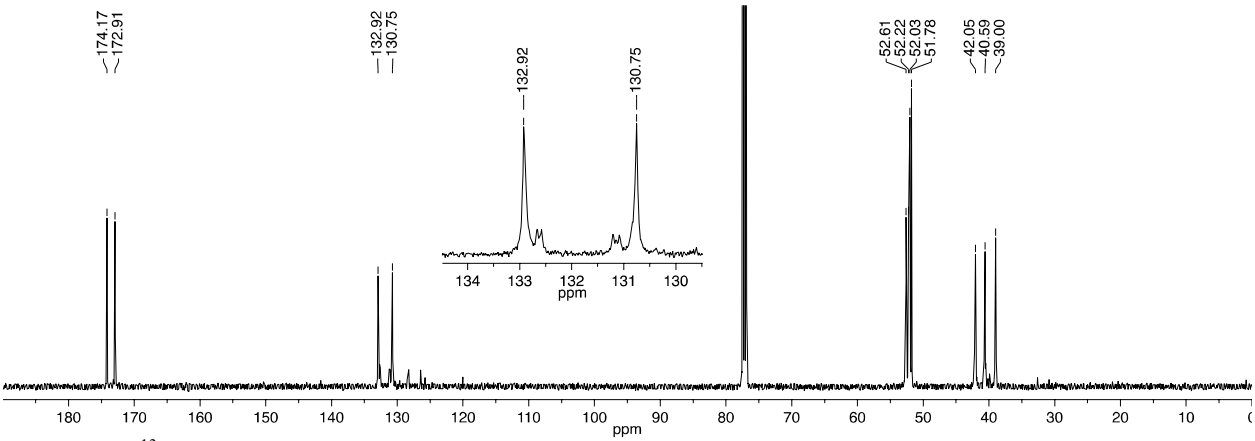
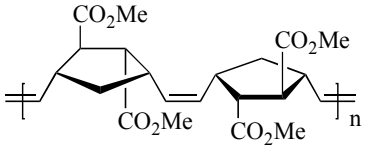


Figure S35. ^{13}C NMR (126 MHz, $CDCl_3$, 20 ºC) of *cis,syndiotactic,alt*-poly(*rac*-**A$_1$**).



Cis,syndiotactic-poly(**A_1**)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.34 (d, *J* = 7.0 Hz, 1H), 5.16 (d, *J* = 6.6 Hz, 1H), 3.63 (s, 3H), 3.58 (s, 3H), 3.37 – 3.23 (m, 2H), 3.05 (p, *J* = 8.9, 8.4 Hz, 1H), 2.95 (t, *J* = 9.5 Hz, 1H), 2.03 (p, *J* = 7.0 Hz, 1H), 1.45 – 1.24 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 174.10, 172.87, 132.58, 131.13, 52.61, 52.07, 51.97, 51.77, 42.20, 40.60, 38.90.

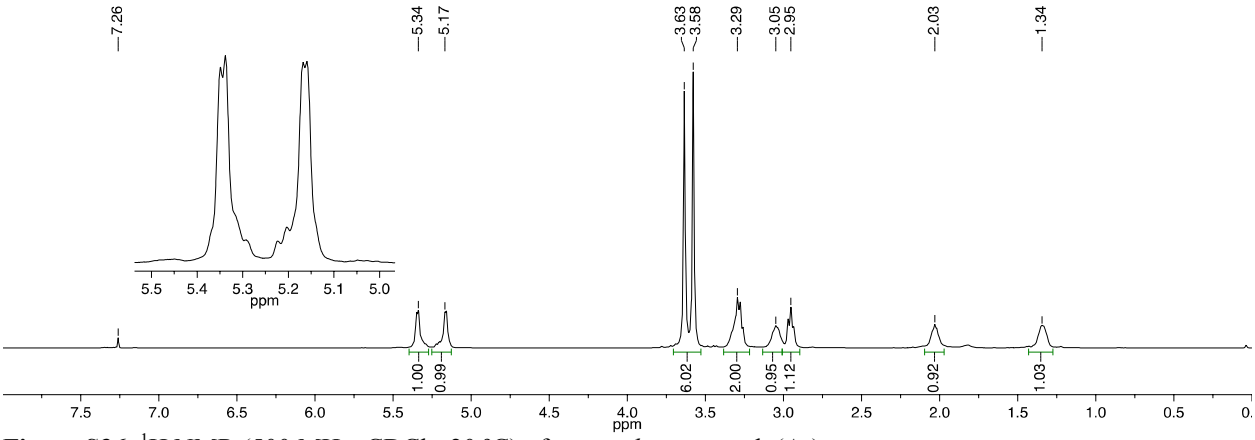


Figure S36. ^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC) of *cis,syndiotactic*-poly(**A_1**).

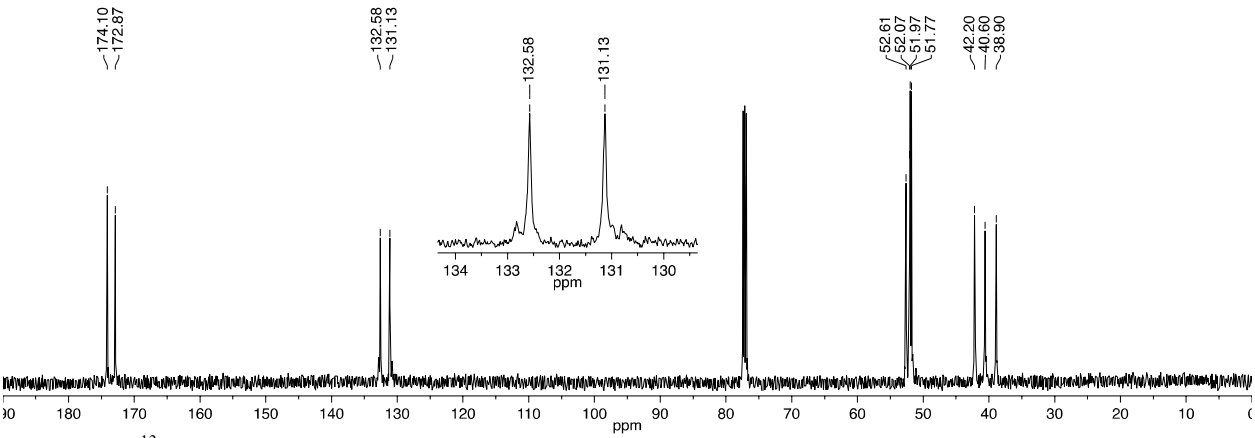
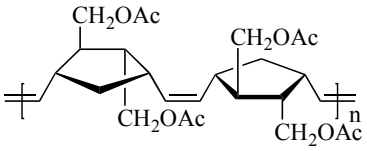


Figure S37. ^{13}C NMR (126 MHz, $CDCl_3$, 20 ºC) of *cis,syndiotactic*-poly(**A_1**).



Cis,syndiotactic,alt-poly(*rac*-**A$_2$**)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.27 (dt, *J* = 14.5, 7.6 Hz, 2H), 4.15 – 3.90 (m, 4H), 3.10 – 2.91 (m, 1H), 2.69 – 2.47 (m, 1H), 2.27 – 2.09 (m, 1H), 2.08 – 1.98 (m, 6H), 1.98 – 1.87 (m, 2H), 1.86 – 1.74 (m, 1H), 1.38 – 1.22 (m, 1H).

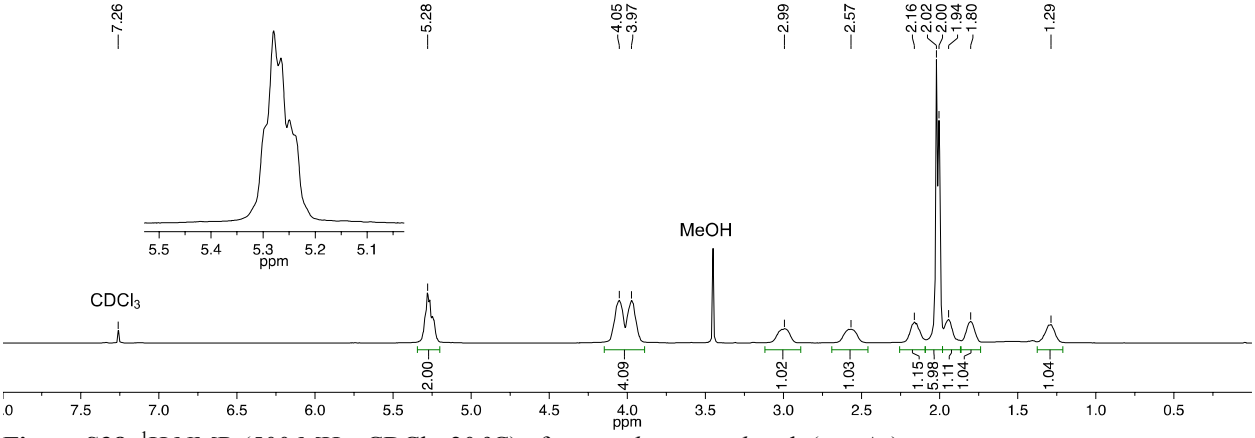
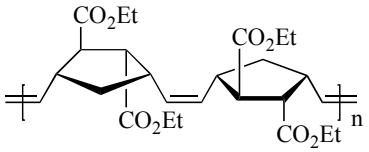


Figure S38. ^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC) of *cis,syndiotactic,alt*-poly(*rac*-**A$_2$**).



Cis,syndiotactic,alt-poly(*rac*-**B_2**)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.32 (t, *J* = 10.1 Hz, 1H), 5.21 (t, *J* = 10.4 Hz, 1H), 4.17 – 3.98 (m, 4H), 3.32 (p, *J* = 8.1 Hz, 1H), 3.22 (q, *J* = 9.5, 9.0 Hz, 1H), 3.06 (p, *J* = 9.7 Hz, 1H), 2.93 (t, *J* = 9.5 Hz, 1H), 2.16 – 1.98 (m, 1H), 1.40 – 1.28 (m, 1H), 1.19 (dt, *J* = 14.6, 7.2 Hz, 6H). ^{13}C NMR (126 MHz $CDCl_3$) δ 173.71, 172.54, 133.04, 130.63, 60.76, 60.63, 52.91, 52.24, 41.91, 40.72, 39.06, 14.45, 14.41.

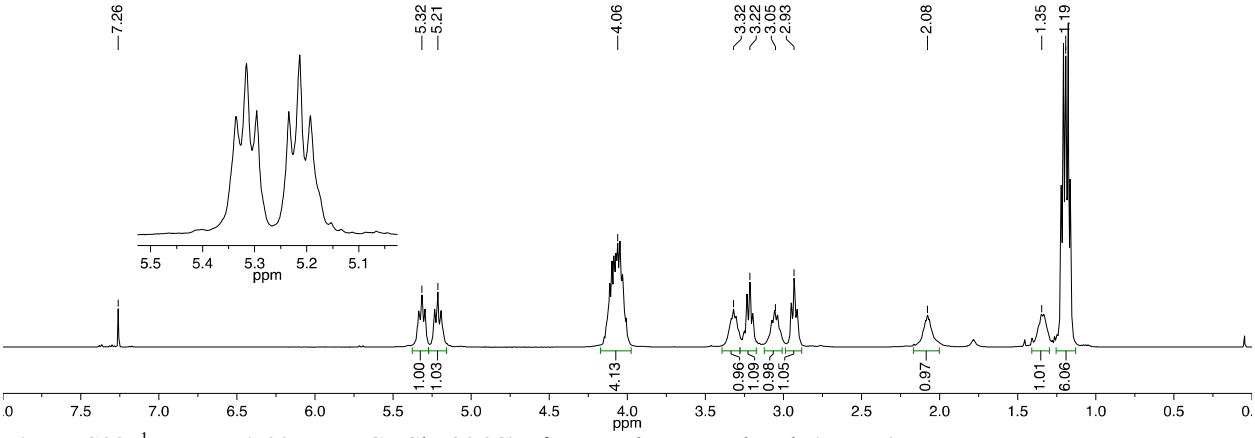


Figure S39. ^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC) of *cis,syndiotactic,alt*-poly(*rac*-**B_2**).

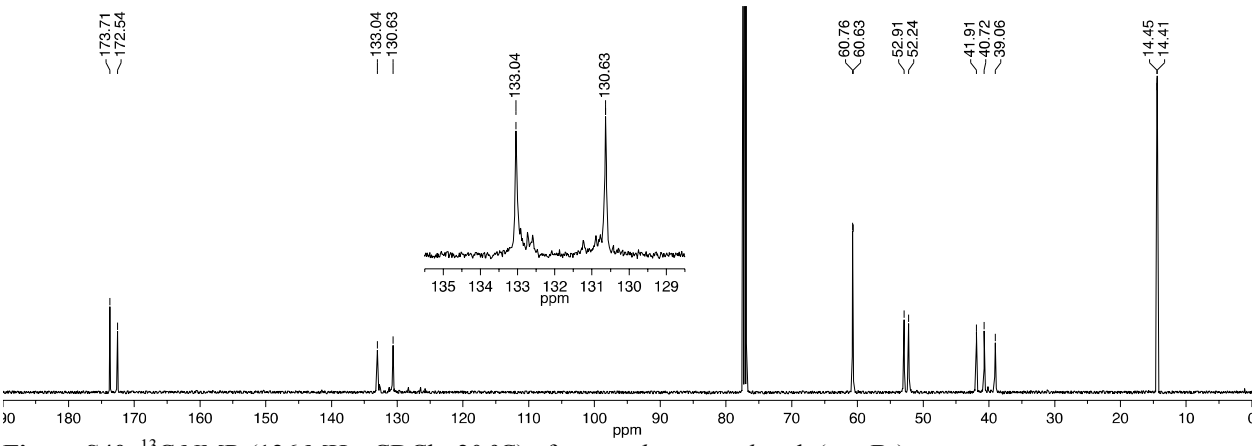
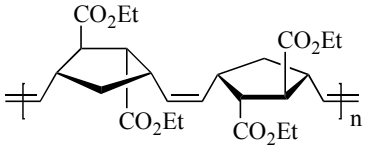


Figure S40. ^{13}C NMR (126 MHz, $CDCl_3$, 20 ºC) of *cis,syndiotactic,alt*-poly(*rac*-**B_2**).



Cis,syndiotactic-poly(**B_2**)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.33 (d, *J* = 7.6 Hz, 1H), 5.18 (d, *J* = 7.5 Hz, 1H), 4.18 – 3.95 (m, 4H), 3.30 (p, *J* = 8.3 Hz, 1H), 3.21 (t, *J* = 9.4 Hz, 1H), 3.06 (h, *J* = 9.1 Hz, 1H), 2.92 (t, *J* = 9.5 Hz, 1H), 2.05 (dt, *J* = 13.9, 7.3 Hz, 1H), 1.41 – 1.28 (m, 1H), 1.19 (dt, *J* = 18.5, 7.2 Hz, 6H).

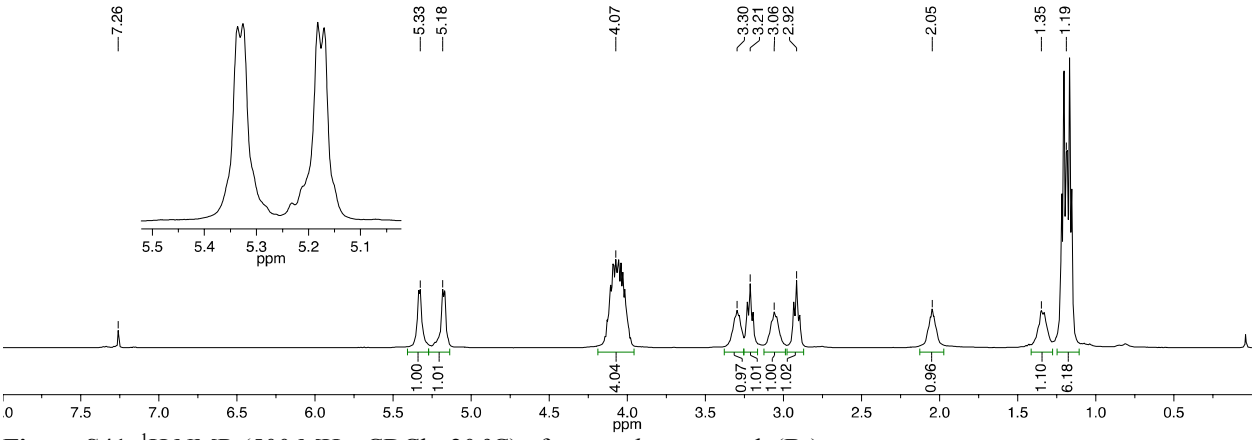
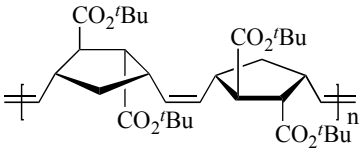


Figure S41. ^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC) of *cis,syndiotactic*-poly(**B_2**).



Cis,syndiotactic,alt-poly(*rac*-**A$_3$**)
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.26 (dt, *J* = 31.4, 10.4 Hz, 2H), 3.27 (p, *J* = 8.6 Hz, 1H), 2.99 (q, *J* = 7.7, 6.5 Hz, 2H), 2.78 (t, *J* = 9.5 Hz, 1H), 2.10 (p, *J* = 6.8 Hz, 1H), 1.37 (d, *J* = 19.9 Hz, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.88, 172.03, 133.24, 130.69, 80.58, 80.37, 54.26, 53.19, 41.63, 40.83, 39.18, 28.31, 28.22.

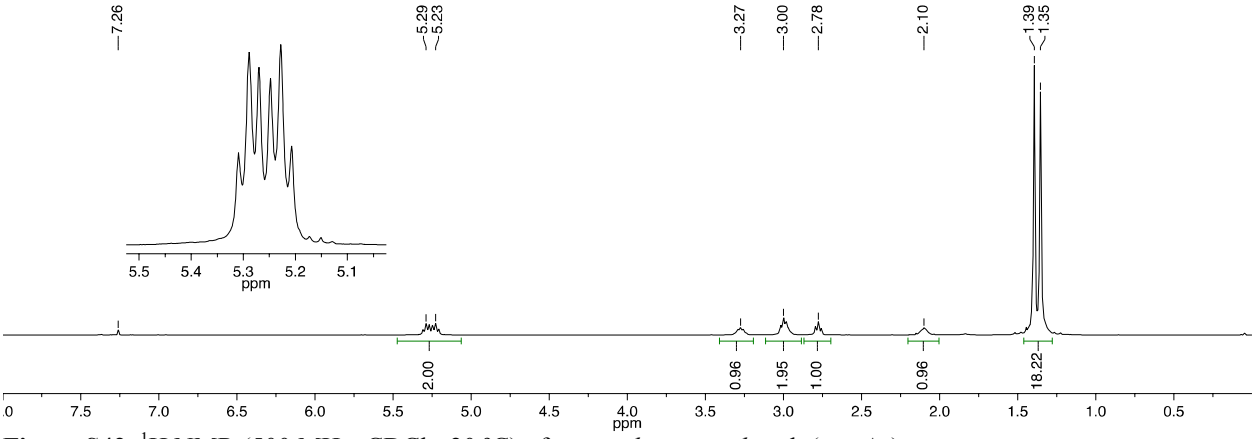


Figure S42. ^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC) of *cis,syndiotactic,alt*-poly(*rac*-**A$_3$**).

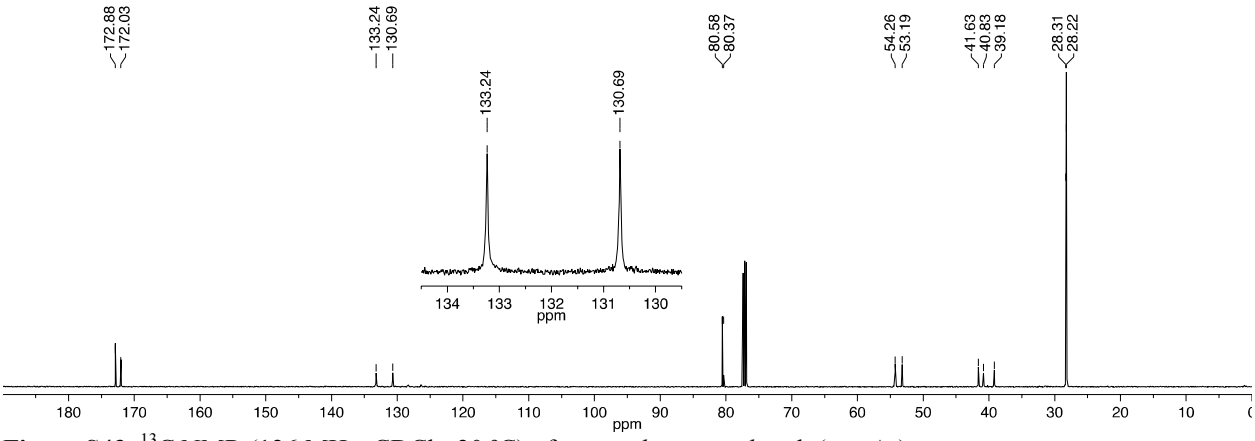
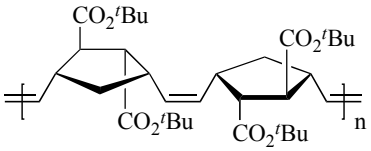


Figure S43. ^{13}C NMR (126 MHz, $CDCl_3$, 20 ºC) of *cis,syndiotactic,alt*-poly(*rac*-**A$_3$**).



Cis,syndiotactic-poly(**B_3**)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.26 (dd, *J* = 26.8, 7.4 Hz, 2H), 3.25 (p, *J* = 9.2, 8.2 Hz, 1H), 3.03 (dp, *J* = 26.9, 8.5 Hz, 2H), 2.76 (t, *J* = 9.5 Hz, 1H), 2.10 (dt, *J* = 14.3, 7.0 Hz, 1H), 1.39 (d, *J* = 21.7 Hz, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.97, 172.03, 132.77, 131.12, 80.61, 80.35, 54.19, 53.20, 41.69, 40.92, 39.00, 28.32, 28.26.

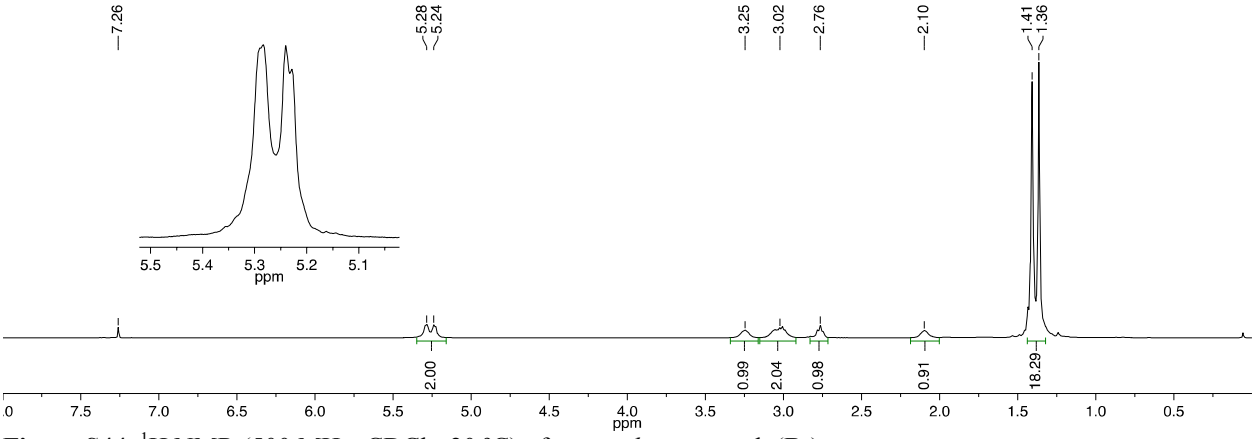


Figure S44. ^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC) of *cis,syndiotactic*-poly(**B_3**).

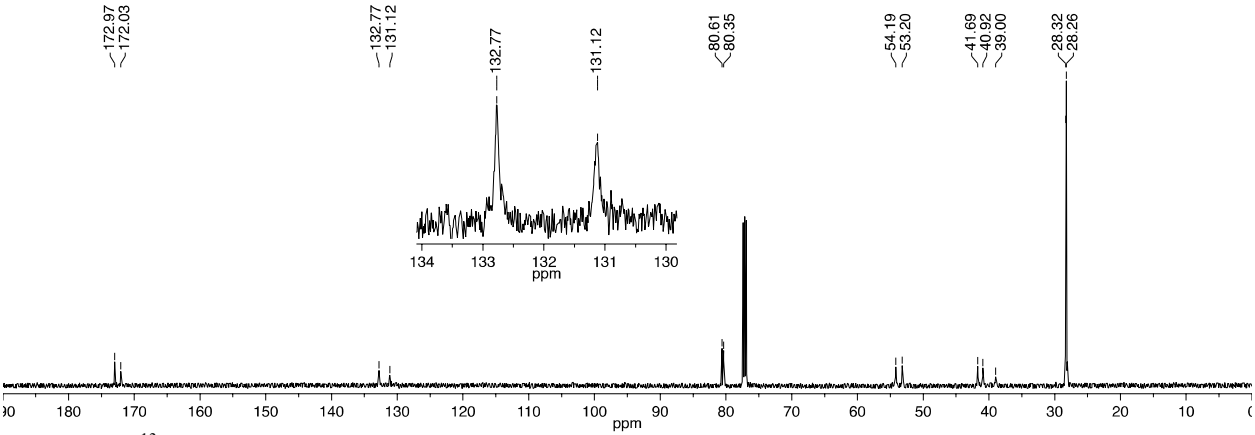
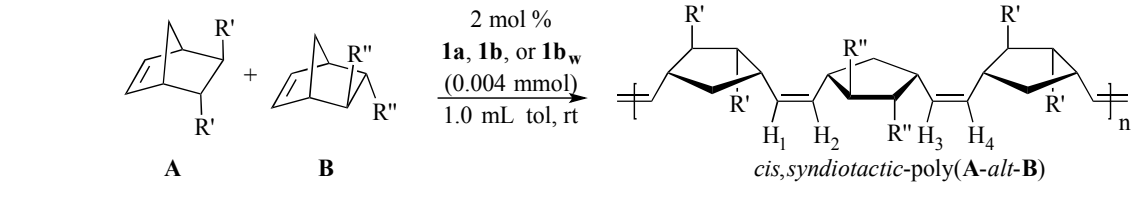
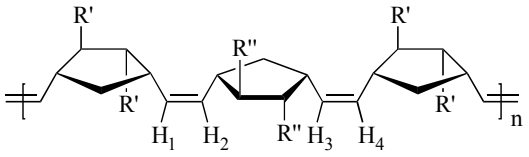


Figure S45. ^{13}C NMR (126 MHz, $CDCl_3$, 20 ºC) of *cis,syndiotactic*-poly(**B_3**).

Comparison of 1a, 1b and $1b_w$ initiators





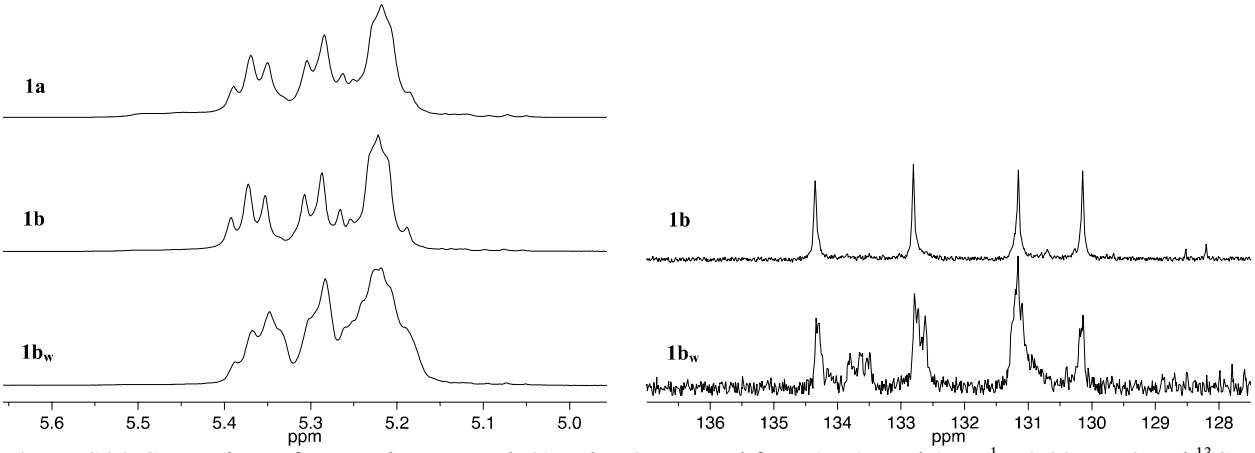
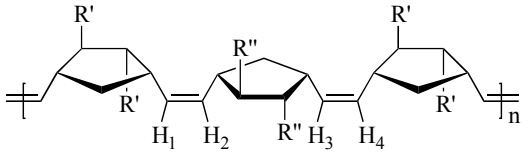


Figure S46. Comparison of *cis*,*syndiotactic*-poly($\mathbf{A_2}$-*alt*-$\mathbf{B_2}$) prepared from **1a**, **1b** and $\mathbf{1b_W}$. ^{1}H (500 MHz) and ^{13}C (126 MHz) NMR spectra ($CDCl_3$, 20 ºC) – olefinic region.



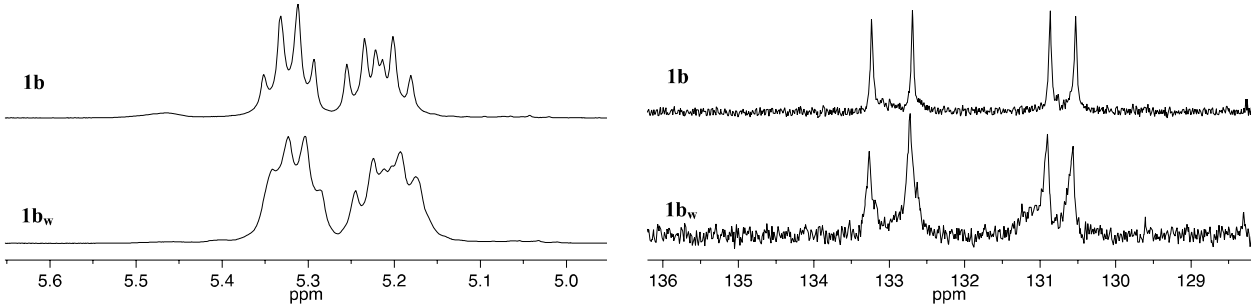


Figure S47. Comparison of *cis*,*syndiotactic*-poly($\mathbf{A_1}$-*alt*-$\mathbf{B_2}$) prepared from **1b** and $\mathbf{1b_W}$. ^{1}H (500 MHz) and ^{13}C (126 MHz) NMR spectra ($CDCl_3$, 20 ºC) – olefinic region

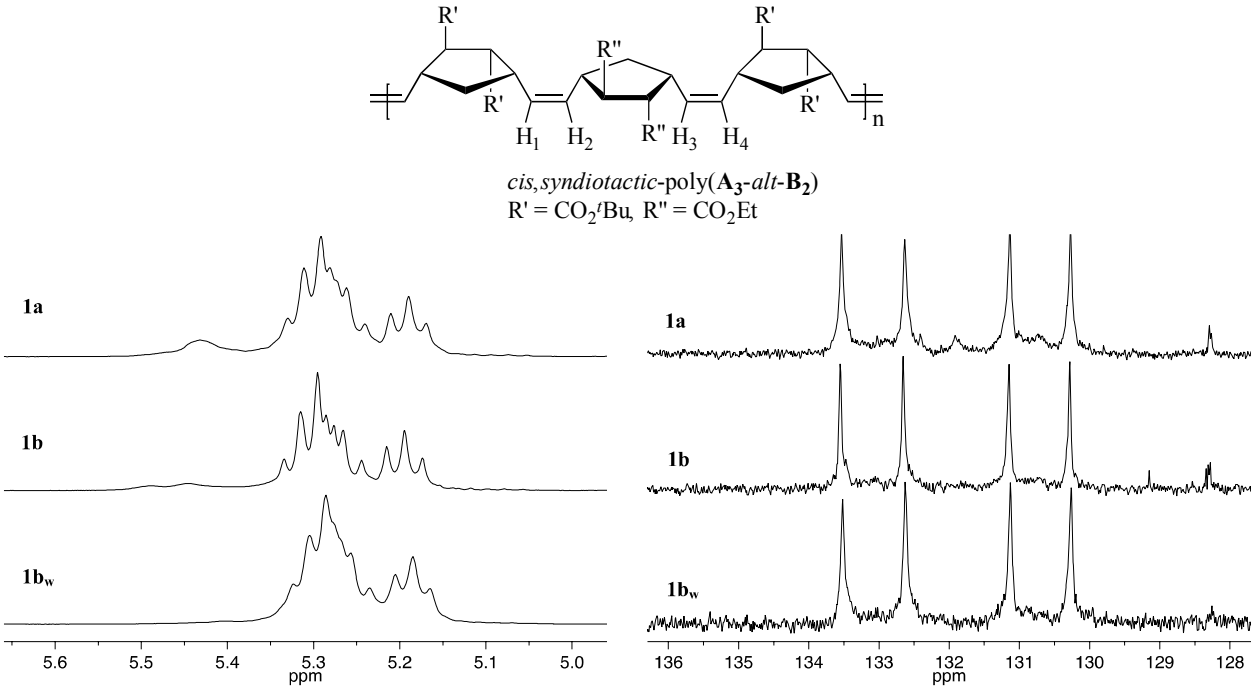


Figure S48. Comparison of *cis*,*syndiotactic*-poly(**A$_3$**-*alt*-**B$_2$**) prepared from **1a**, **1b** and **1b$_W$**. ^{1}H (500 MHz) and ^{13}C (126 MHz) NMR spectra ($CDCl_3$, 20 ºC) – olefinic region.

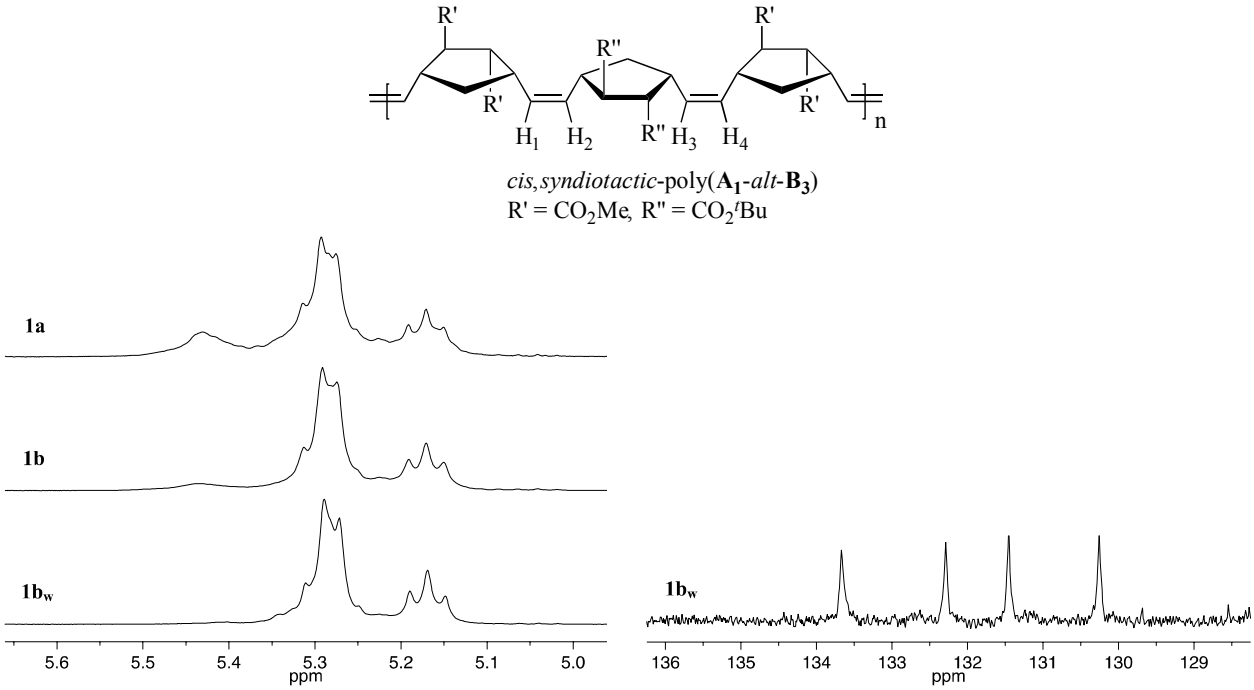


Figure S49. Comparison of *cis*,*syndiotactic*-poly(**A$_1$**-*alt*-**B$_3$**)prepared from **1a** and **1b$_W$**. ^{1}H (500 MHz) and ^{13}C (126 MHz) NMR spectra ($CDCl_3$, 20 ºC) – olefinic region

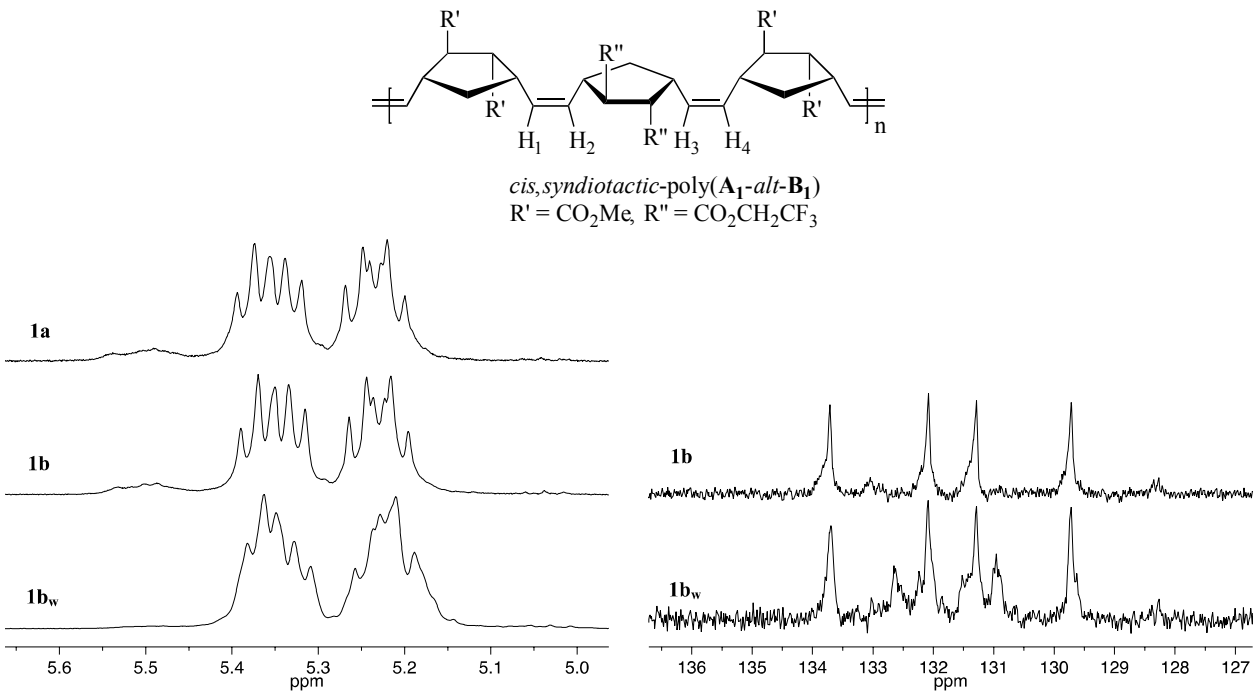


Figure S50. Comparison of *cis*,*syndiotactic*-poly(**A**$_1$-*alt*-**B**$_1$) prepared from **1a**, **1b** and **1b**$_W$. ^{1}H (500 MHz) and ^{13}C (126 MHz) NMR spectra ($CDCl_3$, 20 ºC) – olefinic region

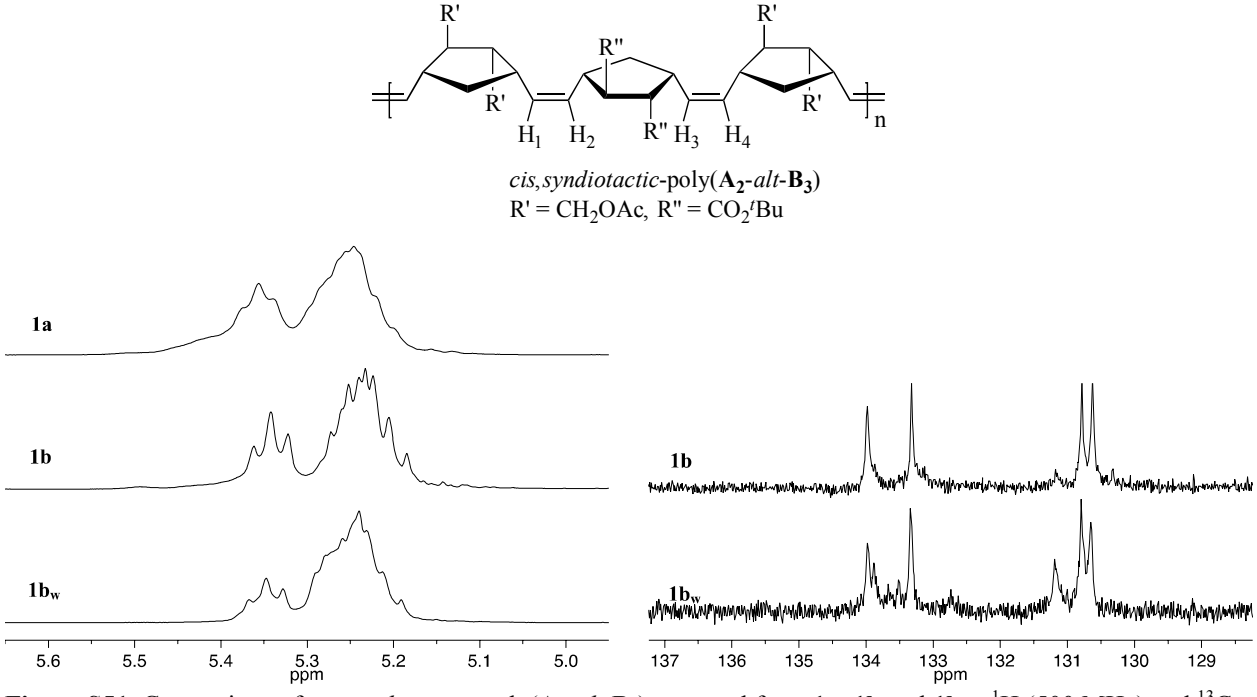


Figure S51. Comparison of *cis*,*syndiotactic*-poly(**A**$_2$-*alt*-**B**$_3$) prepared from **1a**, **1b** and **1b**$_W$. ^{1}H (500 MHz) and ^{13}C (126 MHz) NMR spectra ($CDCl_3$, 20 ºC) – olefinic region

References

(1) Flook, M. M.; Ng, V. W. L.; Schrock, R. R. Synthesis of *cis,syndiotactic* ROMP Polymers Containing Alternating Enantiomers *J. Am. Chem. Soc.* **2011**, *133*, 1784-1786.

(2) Lichtscheidl, A. G.; Ng, V. W. L.; Müller, P.; Takase, M. K.; Schrock, R. R.; Malcolmson, S. J.; Meek, S. J.; Li, B.; Kiesewetter, E. T.; Hoveyda, A. H. Bipyridine Adducts of Molybdenum Imido Alkylidene and Imido Alkylidyne Complexes" Lichtscheidl, A. G.; Ng, V. W. L.; Müller, P.; Takase, M. K.; Schrock, R. R.; Malcolmson, S. J.; Meek, S. J.; Li, B.; Kiesewetter, E. T.; Hoveyda, A. H. *Organometallics* **2012**, *31*, 4558–4564.

(3) Flook, M. M.; Jiang, A. J.; Schrock, R. R.; Hoveyda, A. H. *Z*-Selective Olefin Metathesis Processes Catalyzed by a Molybdenum Hexaisopropylterphenoxide Monopyrrolide Complex *J. Am. Chem. Soc.* **2009**, *131*, 7962–7963.

(4) Yuan, J.; Schrock, R. R.; Gerber, L. C. H.; Müller, P.; Smith, S. Synthesis and ROMP Chemistry of Decafluoroterphenoxide Molybdenum Imido Alkylidene and Ethylene Complexes *Organometallics* **2013**, *32*, 2983–2992.

(5) Singh, R.; Schrock, R. R.; Müller, P.; Hoveyda, A. H. Synthesis of Monoalkoxide Monopyrrolyl Complexes of the Type Mo(NR)(CHR')(OR")(pyrrolyl). Enyne Metathesis with High Oxidation State Catalysts *J. Am. Chem. Soc.* **2007**, *129*, 12654–12655.

(6) Lee, Y.-J.; Schrock, R. R.; Hoveyda, A. H. Efficient endo-Selective Enyne Ring-Closing Metathesis Reactions Promoted by Stereogenic-at-Mo Monoaryloxide Complexes. Synthesis of Cyclic Dienes Not Accessible through Reactions with Ru Carbenes *J. Am. Chem. Soc.* **2009**, *131*, 10652–10661.

(7) Oskam, J. H.; Fox, H. H.; Yap, K. B.; McConville, D. H.; O`Dell, R.; Lichtenstein, B. J.; Schrock, R. R. Ligand Variation in Alkylidene Complexes of the Type Mo(CHR)(NR')(OR")$_2$ *J. Organomet. Chem.* **1993**, *459*, 185–198.

(8) Townsend, E. M.; Schrock, R. R.; Hoveyda, A. H. *Z*-Selective Metathesis Homocoupling of 1,3-Dienes by Molybdenum and Tungsten Monoaryloxide Pyrrolide (MAP) Complexes *J. Am. Chem. Soc.* **2012**, *134*, 11334–11337.

(9) Forrest, W. P.; Axtell, J. C.; Schrock, R. R. Tungsten Oxo Alkylidene Complexes as Initiators for the Stereoregular Polymerization of 2,3-Dicarbomethoxynorbornadiene *Organometallics* **2014**, *33*, 2313–2325.

(10) Jeong, H.; Schrock, R. R.; Müller, P. Synthesis of Molybdenum and Tungsten Alkylidene Complexes that Contain a *tert*-Butylimido Ligand *Organometallics* **2015**, *34*, 4408–4418.

(11) Jiang, A. J.; Zhao, Y.; Schrock, R. R.; Hoveyda, A. H. Highly *Z*-Selective Metathesis Homocoupling of Terminal Olefins *J. Am. Chem. Soc.* **2009**, *131*, 16630–16631.

(12) Takacs, J. M.; Quincy, D. A.; Shay, W.; Jones, B. E.; Ross, C. R. Enantioselective Diels-Alder reactions: novel constrained bis(oxazoline) ligand-metal triflate catalysts *Tetrahedron Asymmetry* **1997**, *8*, 3079–3087.

(13) Van der Eycken, J.; Vandewalle, M.; Heinemann, G.; Laumen, K.; Schneider, M. P.; Kredel, J.; Sauer, J. Enzymatic preparation of optically active bicyclo[2.2.1]heptene derivatives, building blocks for terpenoid natural products. An attractive alternative to enantioselective Diels-Alder syntheses *J. Chem. Soc., Chem. Commun.* **1989**, 306–308.

(14) Mahender Reddy, K.; Bhimireddy, E.; Thirupathi, B.; Breitler, S.; Yu, S.; Corey, E. J. Cationic Chiral Fluorinated Oxazaborolidines. More Potent, Second-Generation Catalysts for Highly Enantioselective Cycloaddition Reactions *J. Am. Chem. Soc.* **2016**, *138*, 2443–2453.

(15) Ryu, D. H.; Lee, T. W.; Corey, E. J. Broad-Spectrum Enantioselective Diels−Alder Catalysis by Chiral, Cationic Oxazaborolidines *J. Am. Chem. Soc.* **2002**, *124*, 9992–9993.

(16) Flook, M. M.; Börner, J.; Kilyanek, S. M.; Gerber, L. C. H.; Schrock, R. R. Five-Coordinate Rearrangements of Metallacyclobutane Intermediates During Ring-Opening Metathesis Polymerization (ROMP) of 2,3-Dicarboalkoxynorbornenes by Molybdenum and Tungsten Monoalkoxide Pyrrolide (MAP) Initiators *Organometallics* **2012**, *31*, 6231–6243.

(17) Nomura, K.; Schrock, R. R. The Synthesis of ROMP Homopolymers and Multi-Block Copolymers Containing Sugars *Macromolecules* **1996**, *29*, 540–545.

(18) Xie, P.; Jiao, X.-Z.; Chen, S.-F.; Lian, X.-T. Study of Synthesis of Natural Product (-)-Patriscabrol and (+)-Isopatriscabrol *Chinese J. Org. Chem.* **2005**, *25*, 1094–1099.

(19) O'Dell, R.; McConville, D. H.; Hofmeister, G. E.; Schrock, R. R. Polymerization of Enantiomerically Pure 2,3-Dicarboalkoxy Norbornadienes and 5,6-Disubstituted Norbornenes by Well-Characterized Molybdenum ROMP Catalysts. Direct Determination of Tacticity in High Cis and High Trans, Highly Tactic Polymers *J. Am. Chem. Soc.* **1994**, *116*, 3414–3423.

(20) Neises, B.; Steglich, W. Simple Method for the Esterification of Carboxylic Acids *Angew. Chemie Int. Ed.* **1978**, *17*, 522–524.
(21) Kadam, S. T.; Lee, H.; Kim, S. S. TMEDA: Efficient and Mild Catalyst for the Acylation of Alcohols, Phenols and Thiols under Solvent-free Condition *Bull. Korean Chem. Soc.* **2009**, *30*, 1071–1076.