Supporting Information for

Syndioselective Ring-Opening Polymerization and Copolymerization of *trans*-1,4-Cyclohexadiene Carbonate Mediated by Achiral Metal- and Organo-Catalysts

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Figure S14. SEC trace ($CHCl_3$, 30 °C) of a PCHDC prepared by ROP of *rac*-CHDC with the [(NNO)ZnEt]/BnOH system (Table 1, entry 1).

Figure S15. SEC trace ($CHCl_3$, 30 °C) of a PCHDC prepared by ROP of *rac*-CHDC with the TBD/BnOH system (Table 1, entry 4).

Figure S16. SEC trace (THF, 30 °C) of a P(CHC-*co*-CHDC) prepared by ROP of *rac*-CHDC and *rac*-CHC with the [(NNO)ZnEt]/BnOH system (Table 2, entry 2).

Figure S17. DSC thermogram (second heating cycle; heating rate = 10 °C.min^{-1}; argon flow) of a P(CHC-*co*-CHDC) prepared by ROP of *rac*-CHDC and *rac*-CHC with the [(NNO)ZnEt]/BnOH system (Table 2, entry 2).

Figure S18. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 23 °C) of a P(CHC-*b*-CHDC) copolymer prepared by sequential copolymerization of *rac*-CHC followed by that of *rac*-CHDC (Table 3).

Figure S19. $^{13}C\{^1H\}$ NMR spectrum (100 MHz, CD_2Cl_2, 23 °C) of a P(CHC-*b*-CHDC) copolymer prepared by sequential copolymerization of *rac*-CHC followed by that of *rac*-CHDC (Table 3).

Figure S20. DSC thermogram (first heating cycle; heating rate = 10 °C.min^{-1}; argon flow) of a P(CHC-*b*-CHDC) prepared by sequential copolymerization of *rac*-CHC followed by that of *rac*-CHDC (Table 3).

Figure S21. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of a P(CHDC-*co*-LLA) copolymer prepared from *rac*-CHDC and L-LA (Table 4, entry 2).

Figure S22. $^{13}C\{^1H\}$ NMR spectrum (100 MHz, $CDCl_3$, 23 °C) of a P(CHDC-*co*-LLA) copolymer prepared from *rac*-CHDC and L-LA (Table 4, entry 2).

Figure S23. DSC thermogram (second heating cycle; heating rate = 10 °C.min^{-1}; argon flow) of a P(CHDC-*co*-LLA) copolymer prepared from *rac*-CHDC and L-LA (Table 4, entry 2).

Figure S24. DSC thermogram (second heating cycle; heating rate = 10 °C.min^{-1}; argon flow) of a P(CHDC-*co*-LLA) copolymer prepared from *rac*-CHDC and L-LA (Table 4, entry 3).

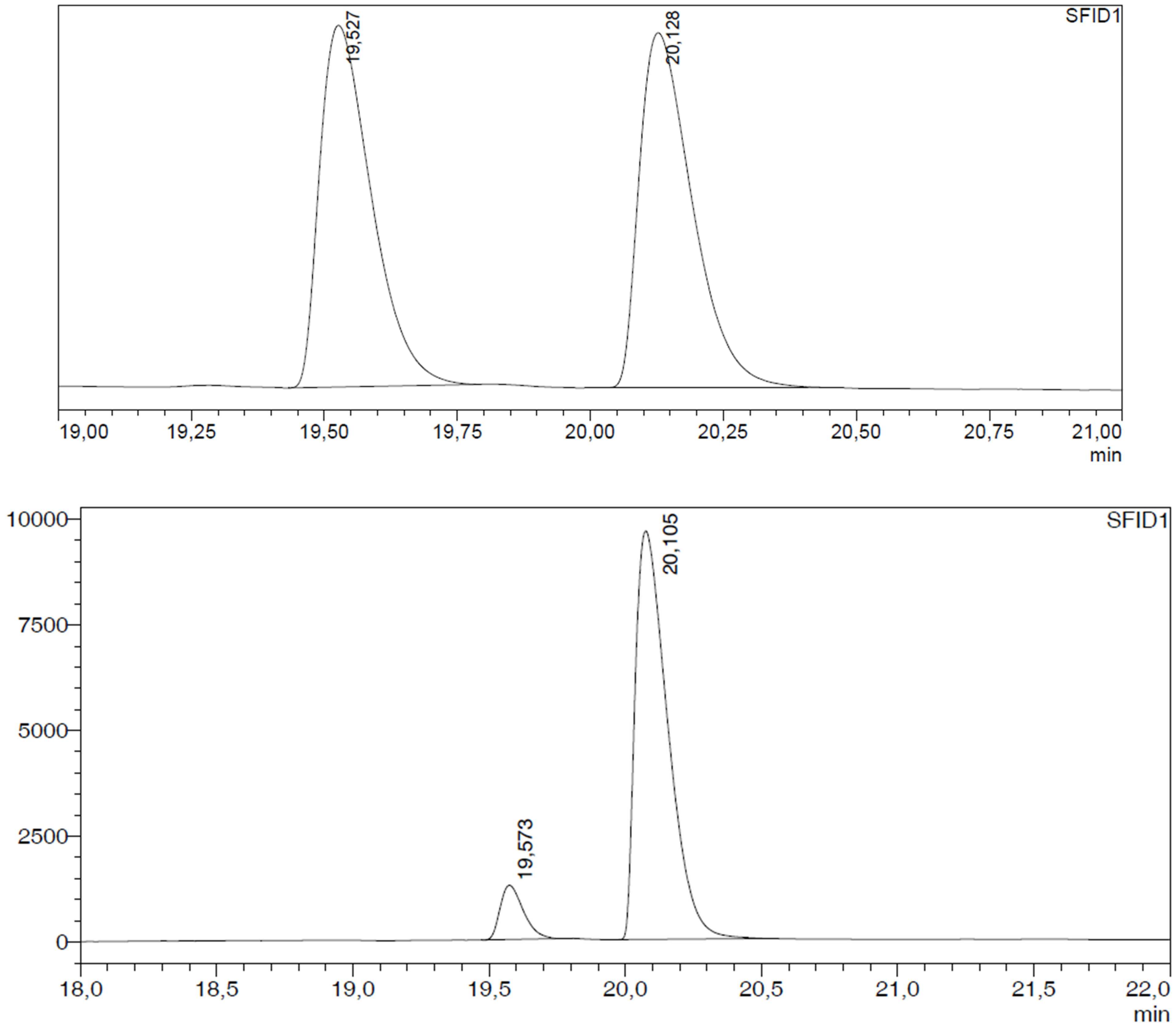

Figure S1. Chiral GC trace of racemic (top) and enantio-enriched (83% ee) (bottom) *trans*-(*R*,*R*)-1,2-cyclohex-4-ene-diol.

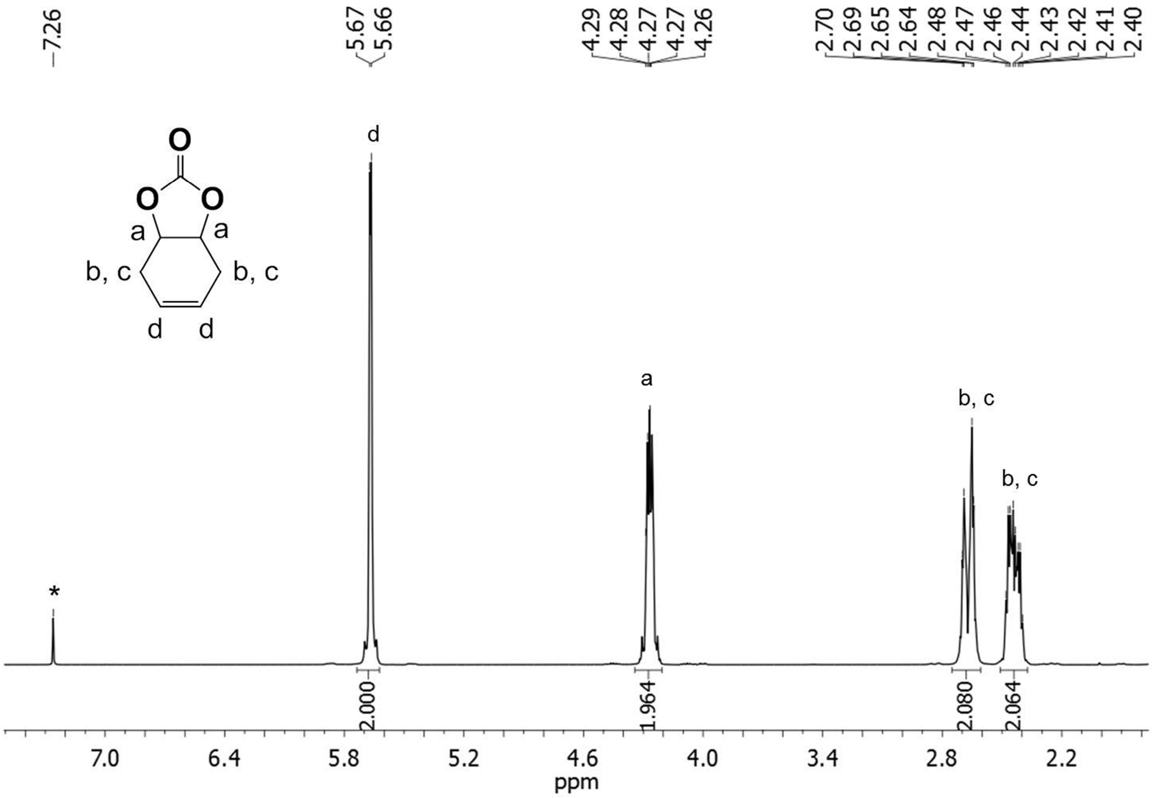

Figure S2. ^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 °C) of *trans*-*rac*-CHDC (* stands for residual CHCl$_3$).

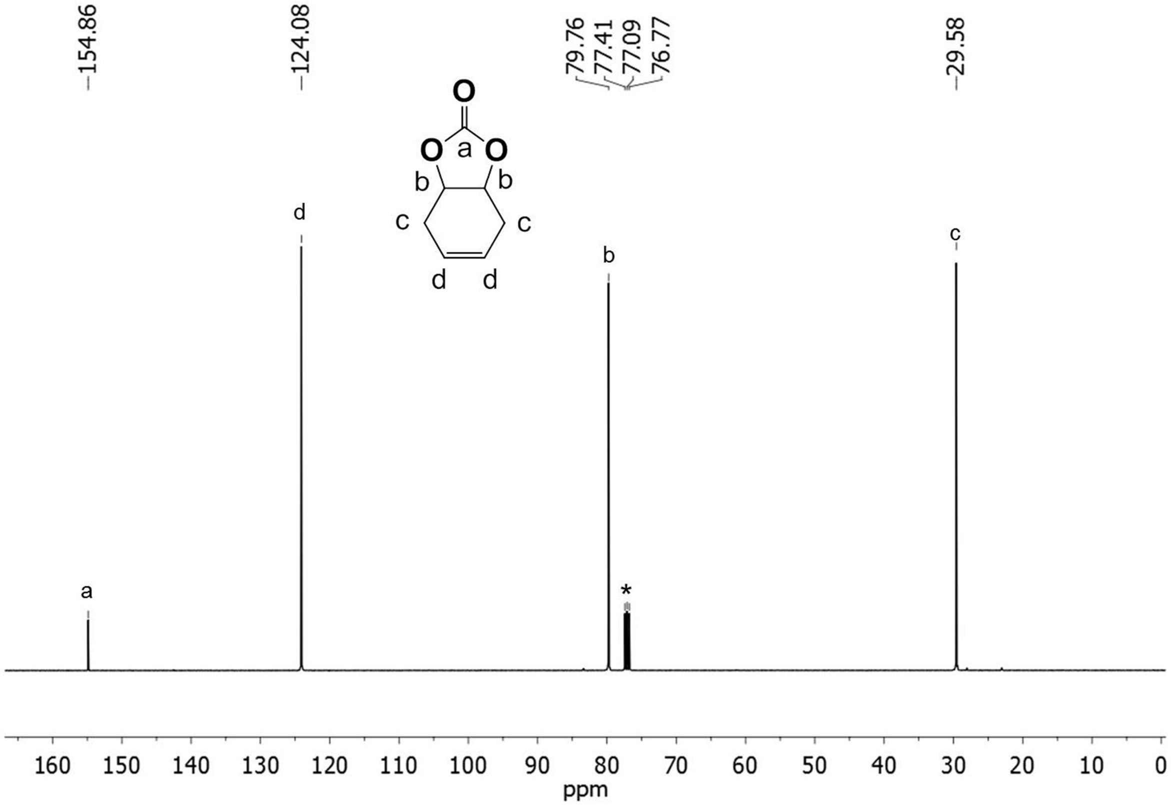

Figure S3. ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz, 23 °C) of *trans*-*rac*-CHDC (* stands for residual CHCl$_3$).

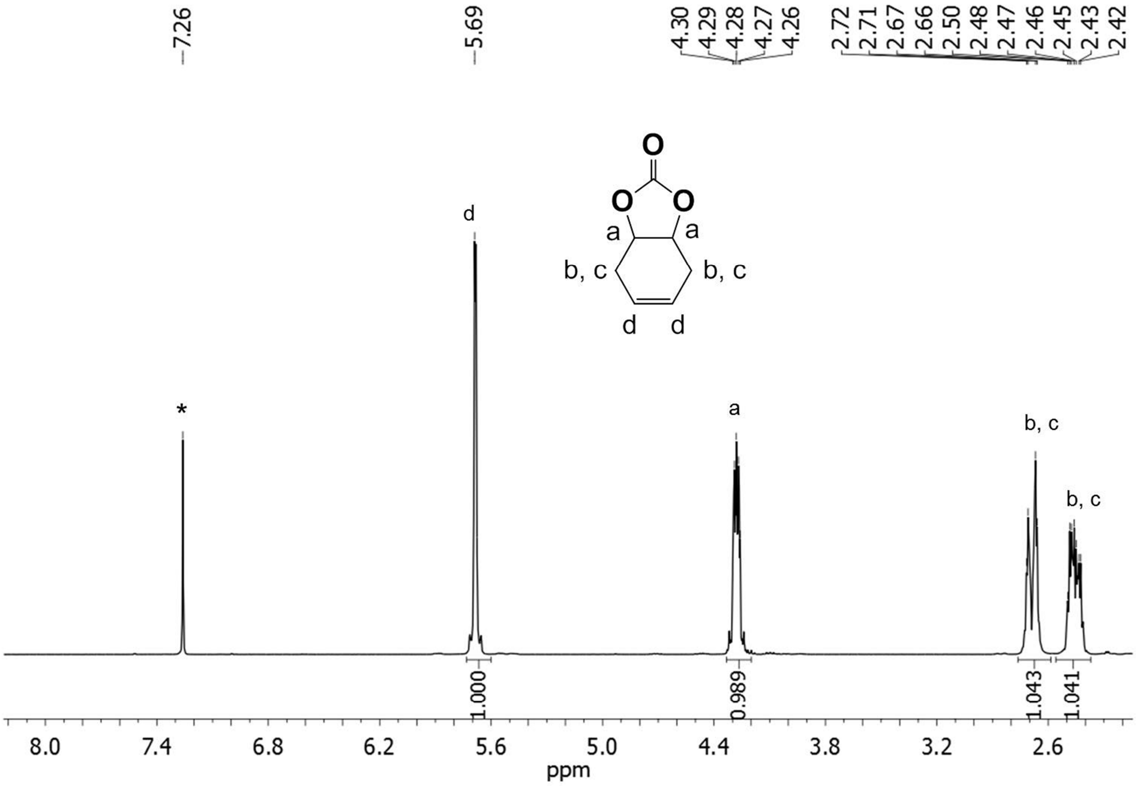

Figure S4. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of enantio-enriched (83% ee) *trans*-(*R,R*)-CHDC (* stands for residual $CHCl_3$).

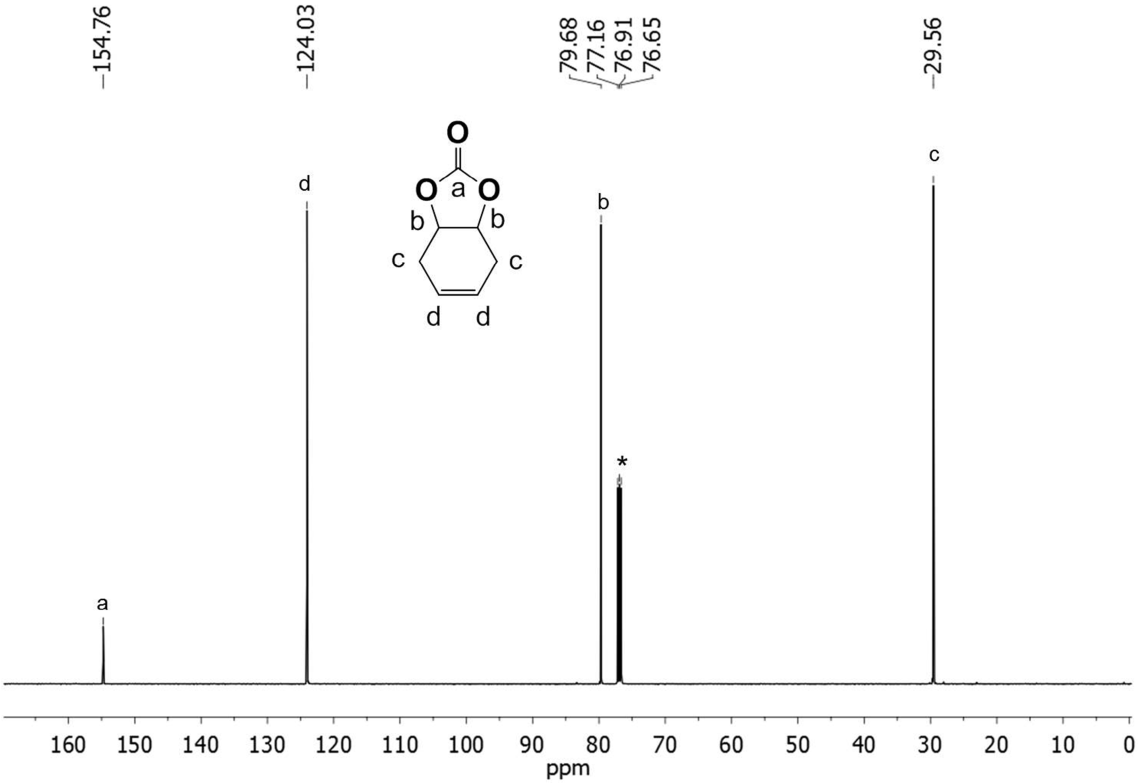

Figure S5. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 23 °C) of enantio-enriched (83% ee) *trans*-(*R*,*R*)-CHDC (* stands for residual $CHCl_3$).

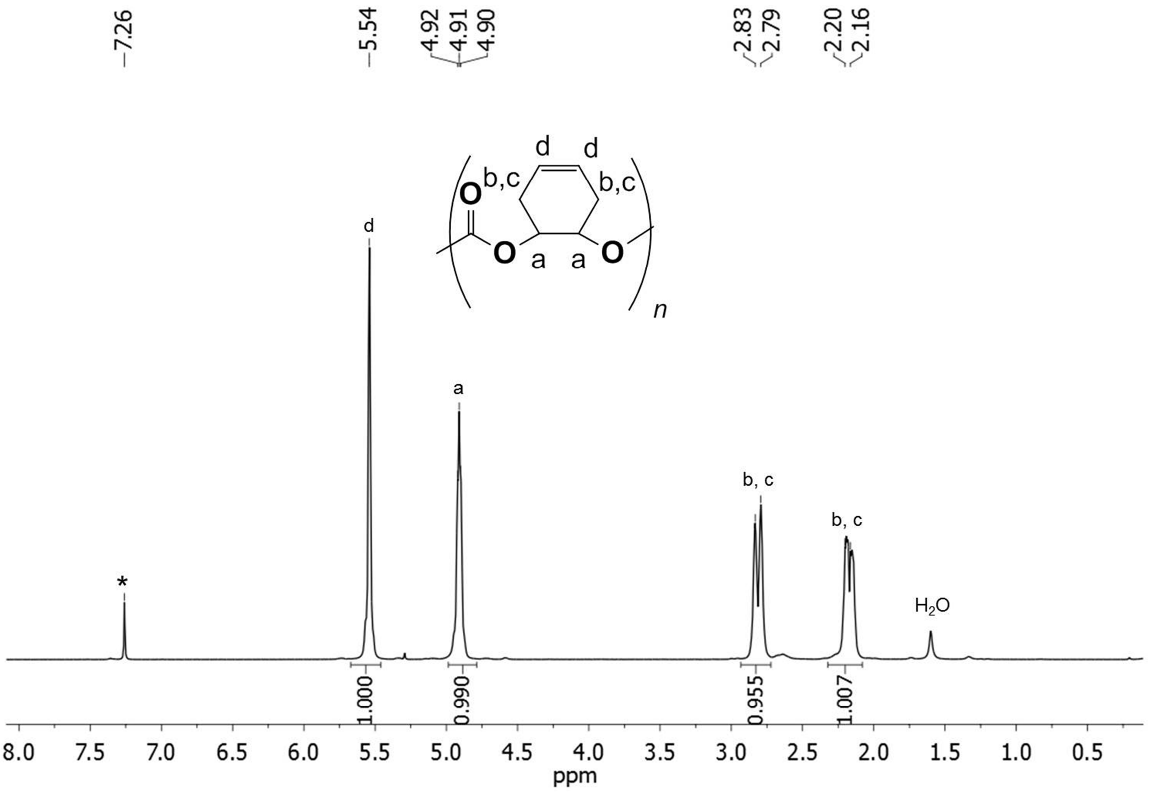

Figure S6. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of a PCHDC prepared by ROP of *rac*-CHDC with the [(NNO)ZnEt]/BnOH system (Table 1, entry 3) (* stands for residual $CHCl_3$).

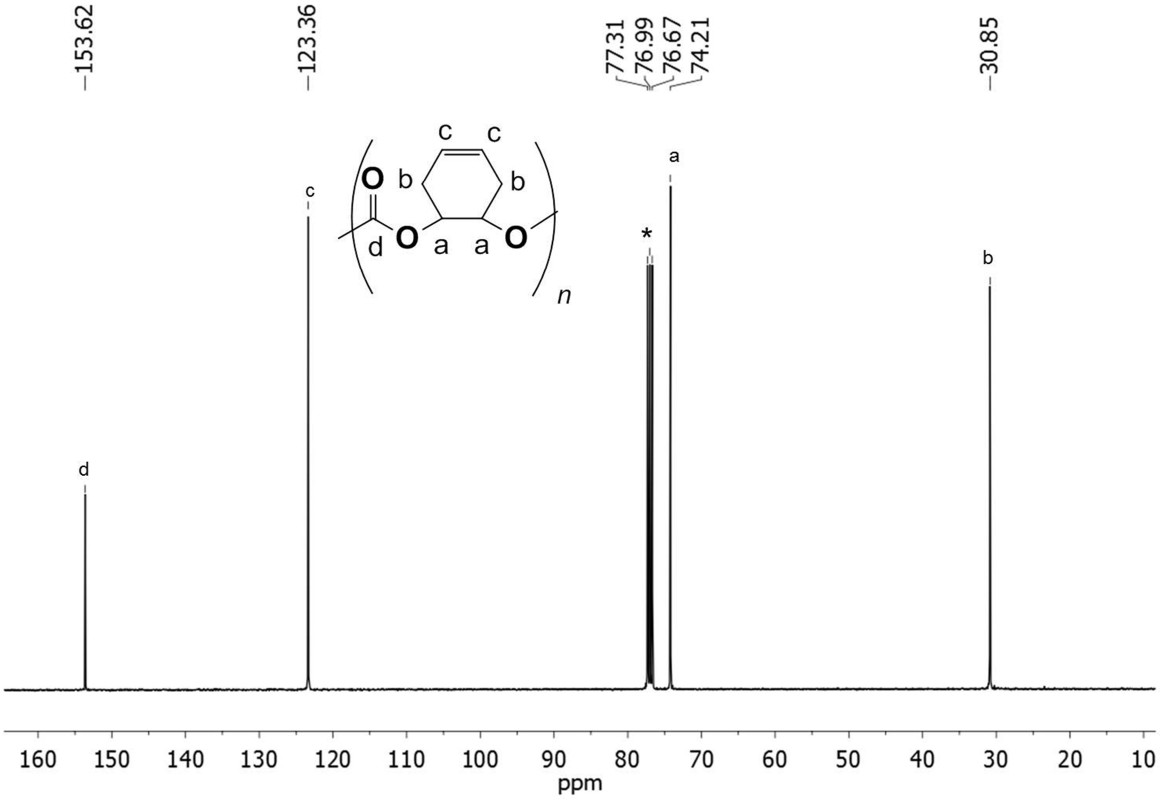

Figure S7. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 23 °C) of a PCHDC prepared by ROP of *rac*-CHDC with the [(NNO)ZnEt]/BnOH system (Table 1, entry 3) (* stands for residual $CHCl_3$).

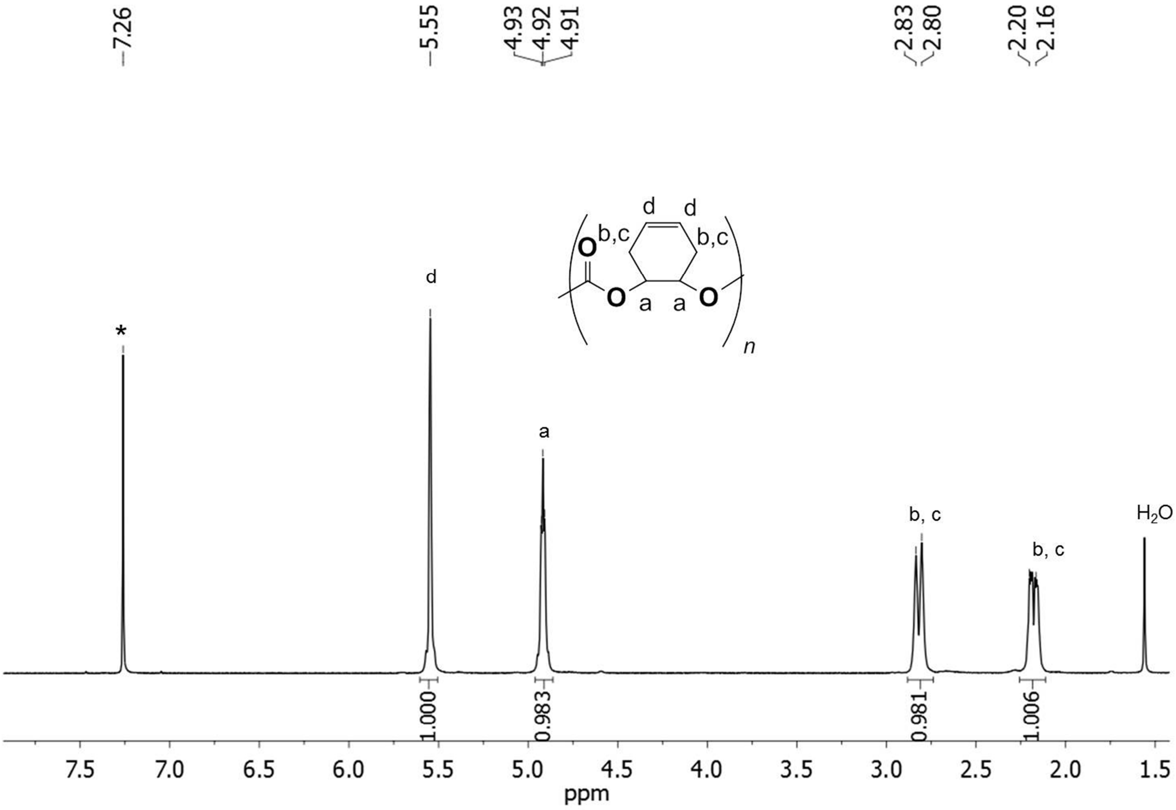

Figure S8. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of a PCHDC prepared by ROP of *rac*-CHDC with the TBD/BnOH system (Table 1, entry 4) (* stands for residual $CHCl_3$).

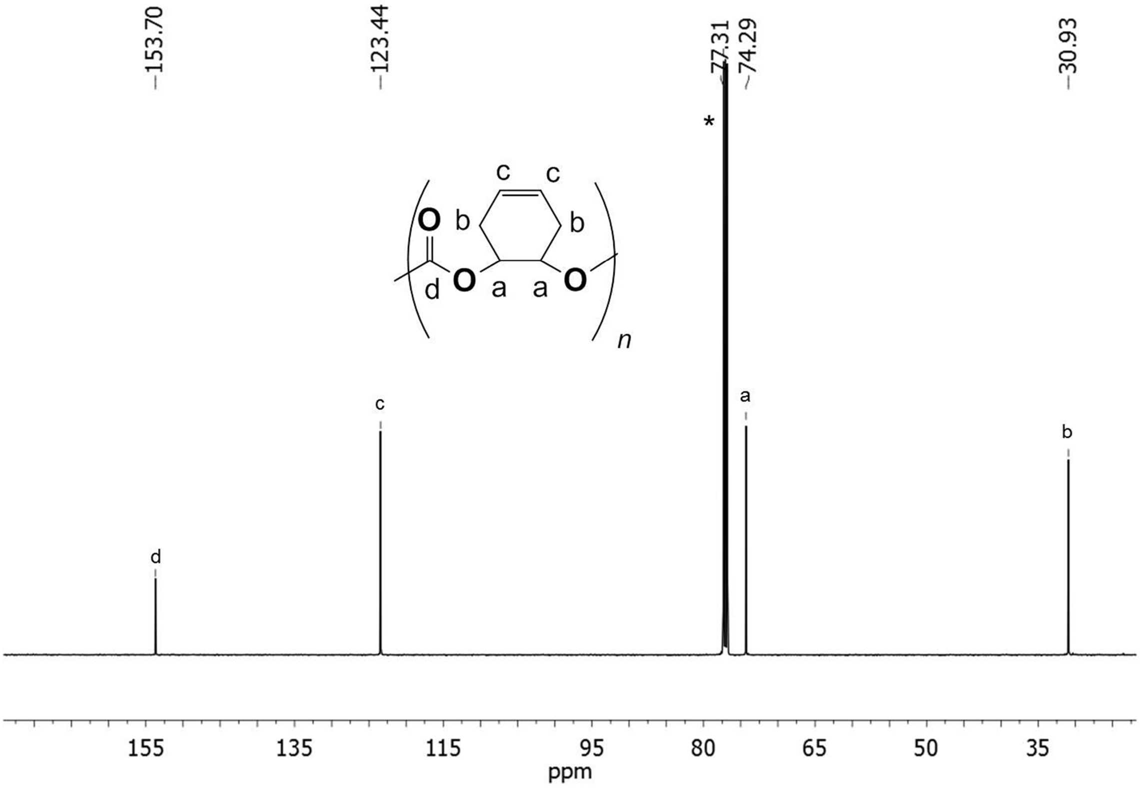

Figure S9. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 23 °C) of a PCHDC prepared by ROP of *rac*-CHDC with the TBD/BnOH system (Table 1, entry 4) (* stands for residual $CHCl_3$).

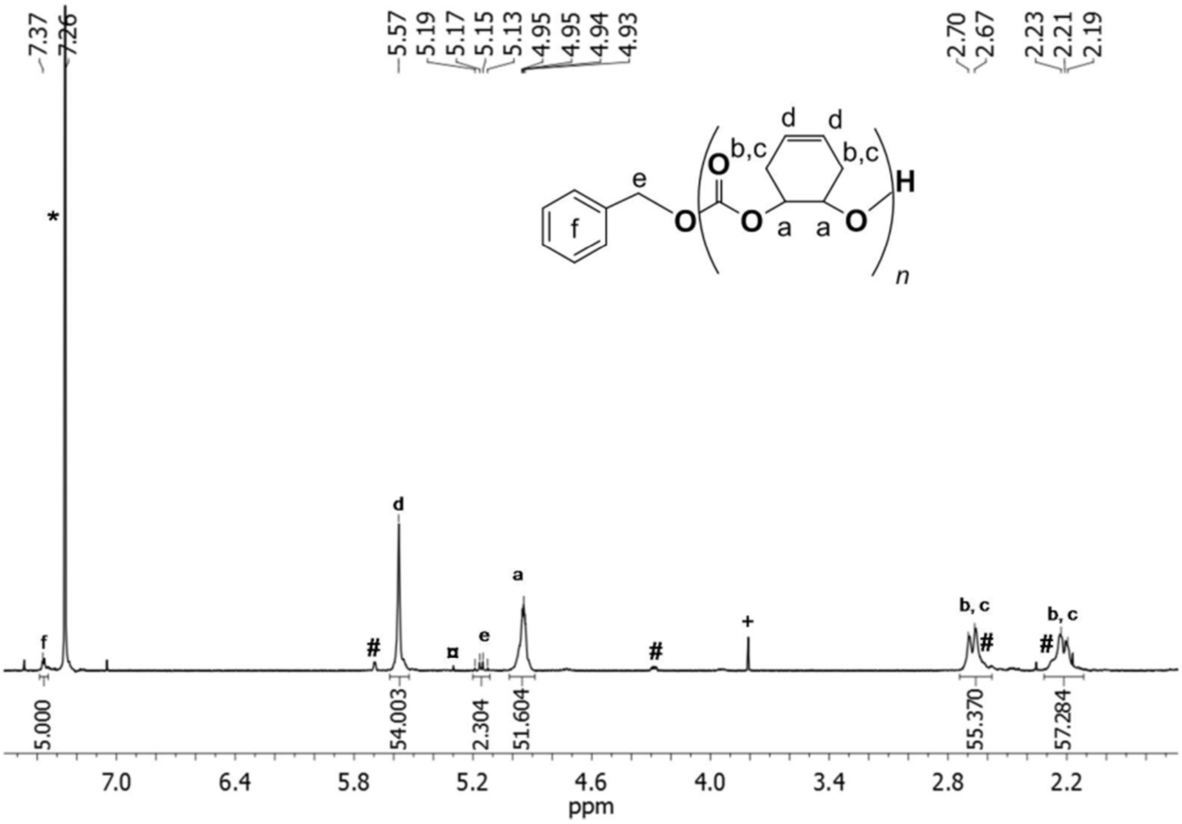

Figure S10. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of a PCHDC prepared by ROP of (*R*,*R*)-CHDC with the [(NNO)ZnEt]/BnOH system (Table 1, entry 7) (*, +, ¤ and # stand for residual $CHCl_3$, MeOH, CH_2Cl_2 and CHDC, respectively).

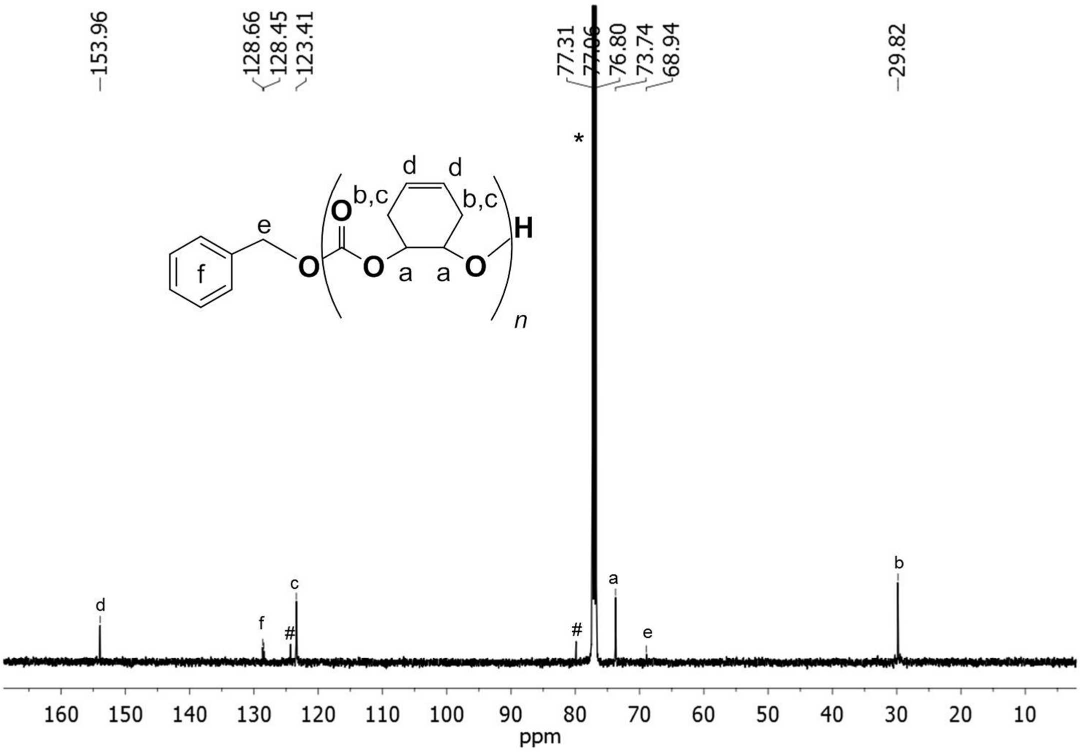

Figure S11. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 23 °C) of a PCHDC prepared by ROP of (*R*,*R*)-CHDC with the [(NNO)ZnEt]/BnOH system (Table 1, entry 7) (*and # stand for residual $CHCl_3$ and CHDC, respectively).

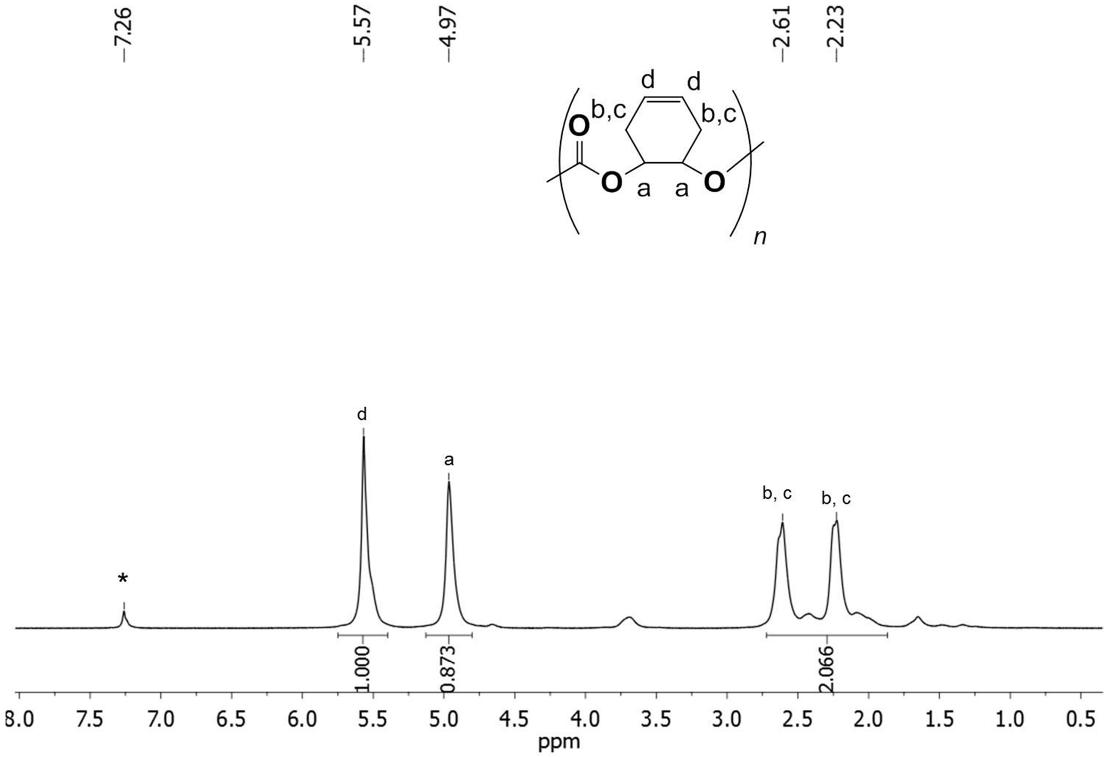

Figure S12. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of a PCHDC prepared from ROCOP of CHDO and CO_2 using a *rac*-(Salen)CoBr catalyst (* stands for residual $CHCl_3$).

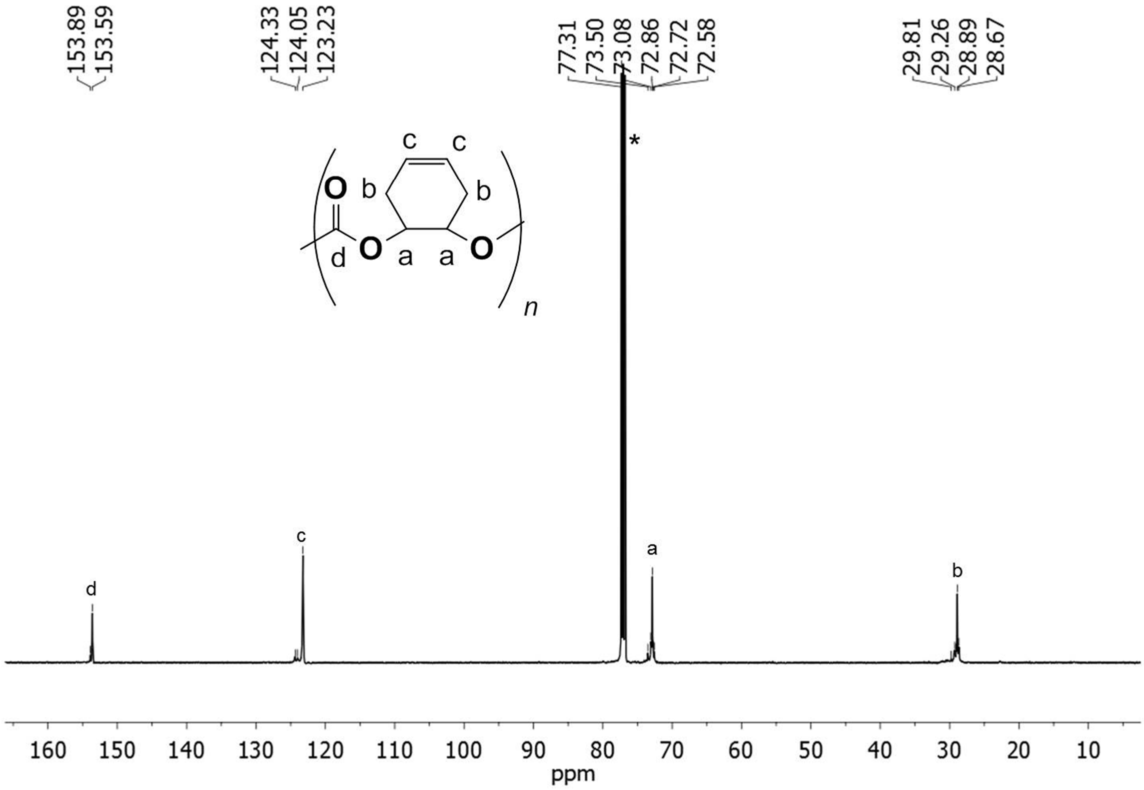

Figure S13. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 23 °C) of a PCHDC prepared from ROCOP of CHDO and CO_2 using a *rac*-(Salen)CoBr catalyst (* stands for residual $CHCl_3$).

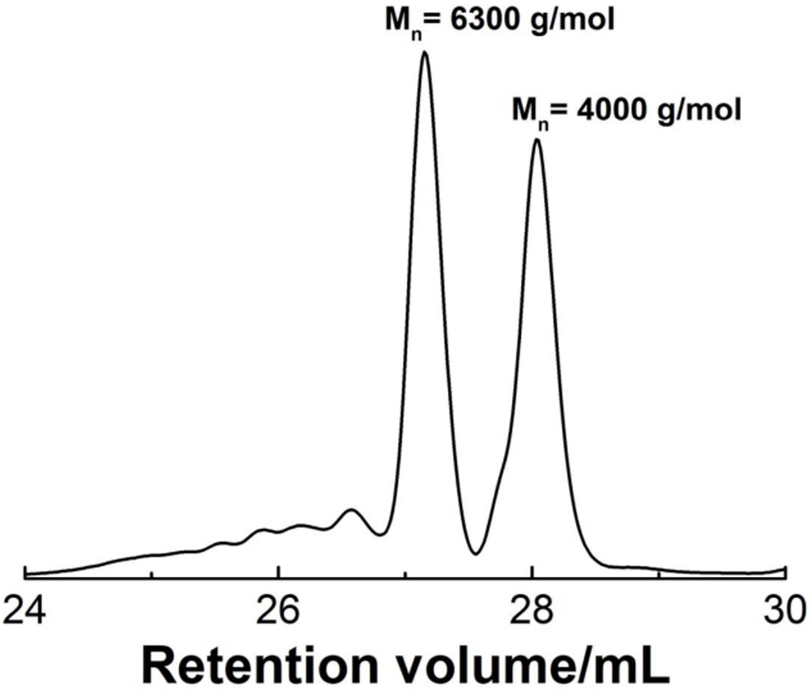

Figure S14. SEC trace ($CHCl_3$, 30 °C) of a PCHDC prepared by ROP of *rac*-CHDC with the [(NNO)ZnEt]/BnOH system (Table 1, entry 1).

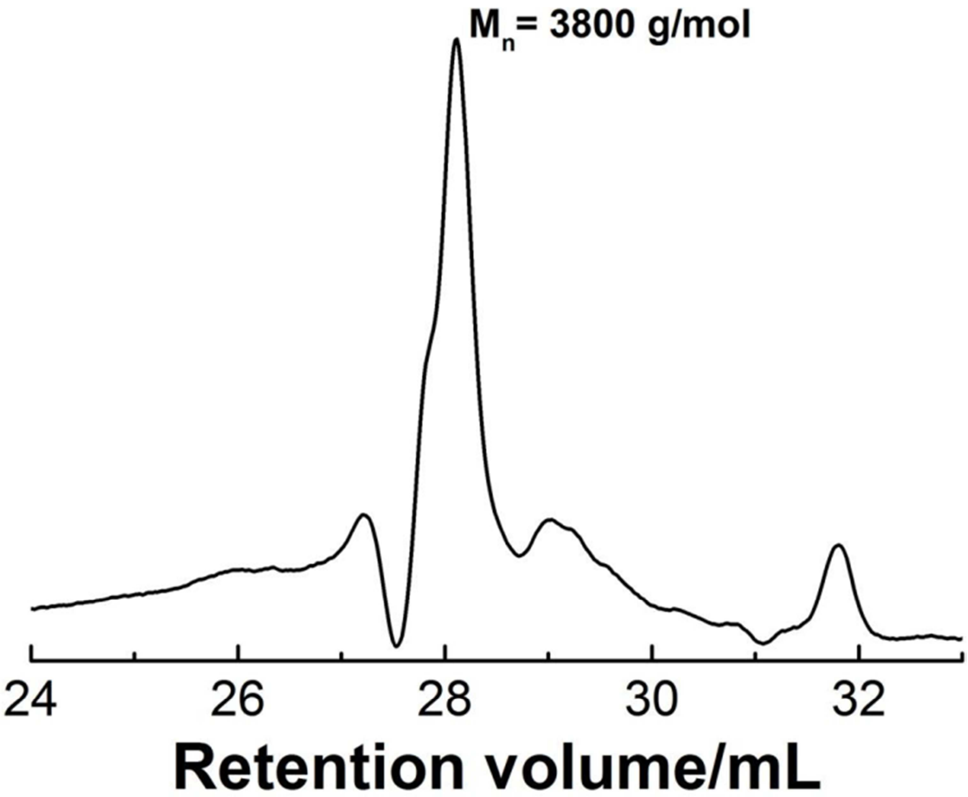

Figure S15. SEC trace ($CHCl_3$, 30 °C) of a PCHDC prepared by ROP of *rac*-CHDC with the TBD/BnOH system (Table 1, entry 4).

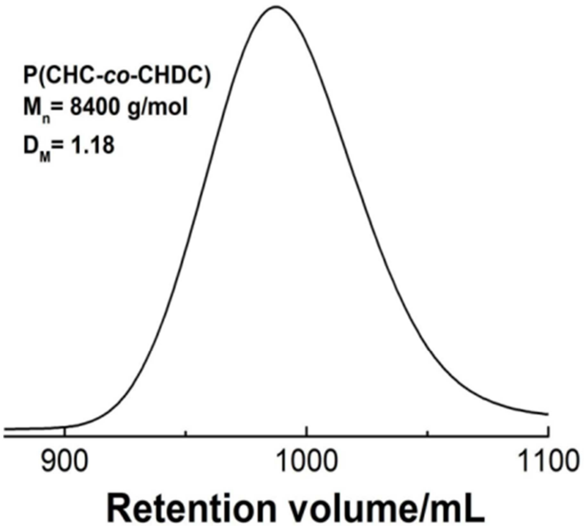

Figure S16. SEC trace (THF, 30 °C) of a P(CHC-*co*-CHDC) prepared by ROP of *rac*-CHDC and *rac*-CHC with the [(NNO)ZnEt]/BnOH system (Table 2, entry 2).

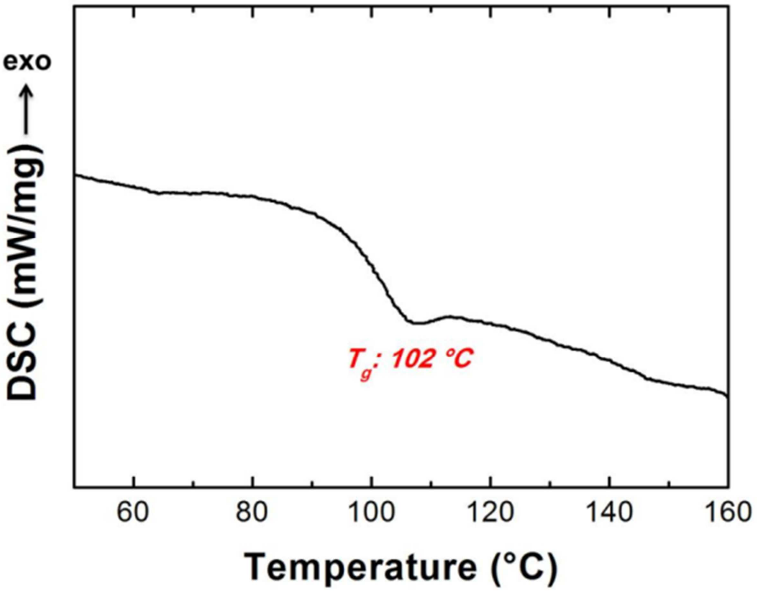

Figure S17. DSC thermogram (second heating cycle; heating rate = 10 °C.min^{-1}; argon flow) of a P(CHC-*co*-CHDC) prepared by ROP of *rac*-CHDC and *rac*-CHC with the [(NNO)ZnEt]/BnOH system (Table 2, entry 2).

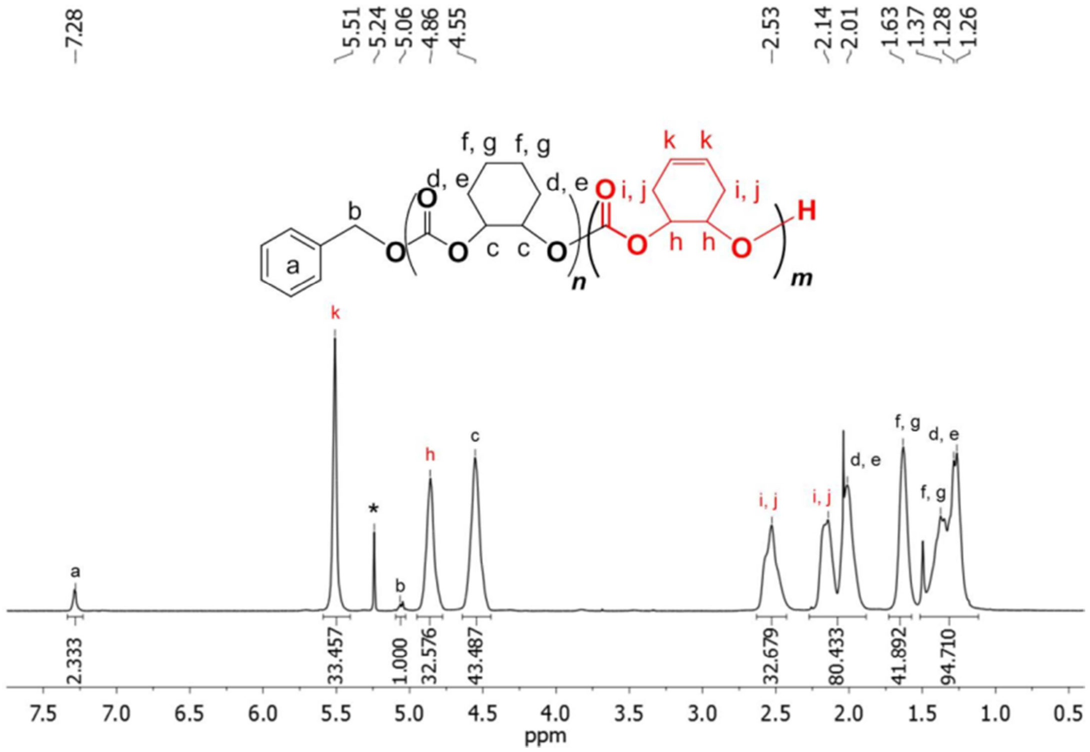

Figure S18. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 23 °C) of a P(CHC-*b*-CHDC) copolymer prepared by sequential copolymerization of *rac*-CHC followed by that of *rac*-CHDC (Table 3) (* stands for residual CH_2Cl_2 resonances).

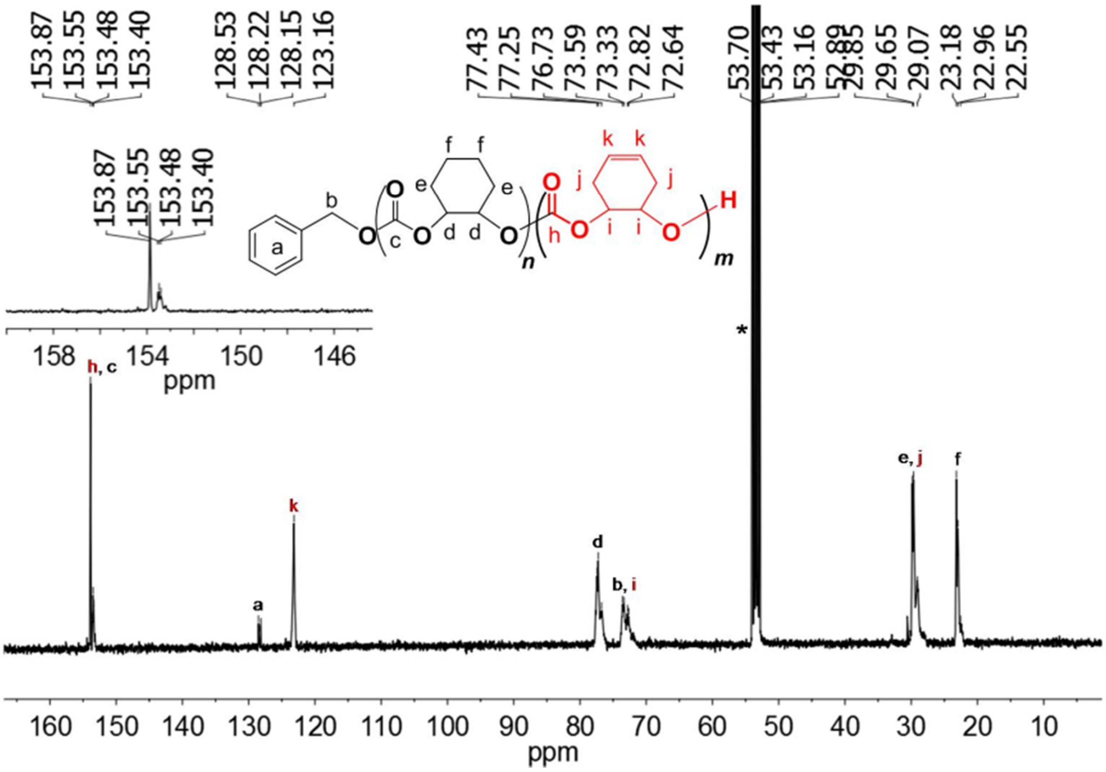

Figure S19. $^{13}C\{^1H\}$ NMR spectrum (100 MHz, CD_2Cl_2, 23 °C) of a P(CHC-*b*-CHDC) copolymer prepared by sequential copolymerization of *rac*-CHC followed by that of *rac*-CHDC (Table 3) (* stands for residual CD_2Cl_2 resonances).

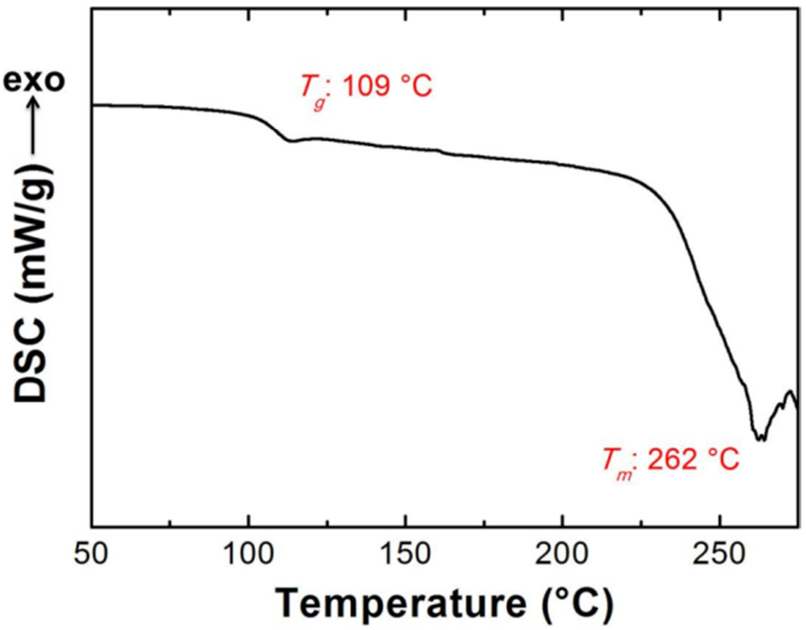

Figure S20. DSC thermogram (first heating cycle; heating rate = 10 °C.min^{-1}; argon flow) of a P(CHC-*b*-CHDC) prepared by sequential copolymerization of *rac*-CHC followed by that of *rac*-CHDC (Table 3).

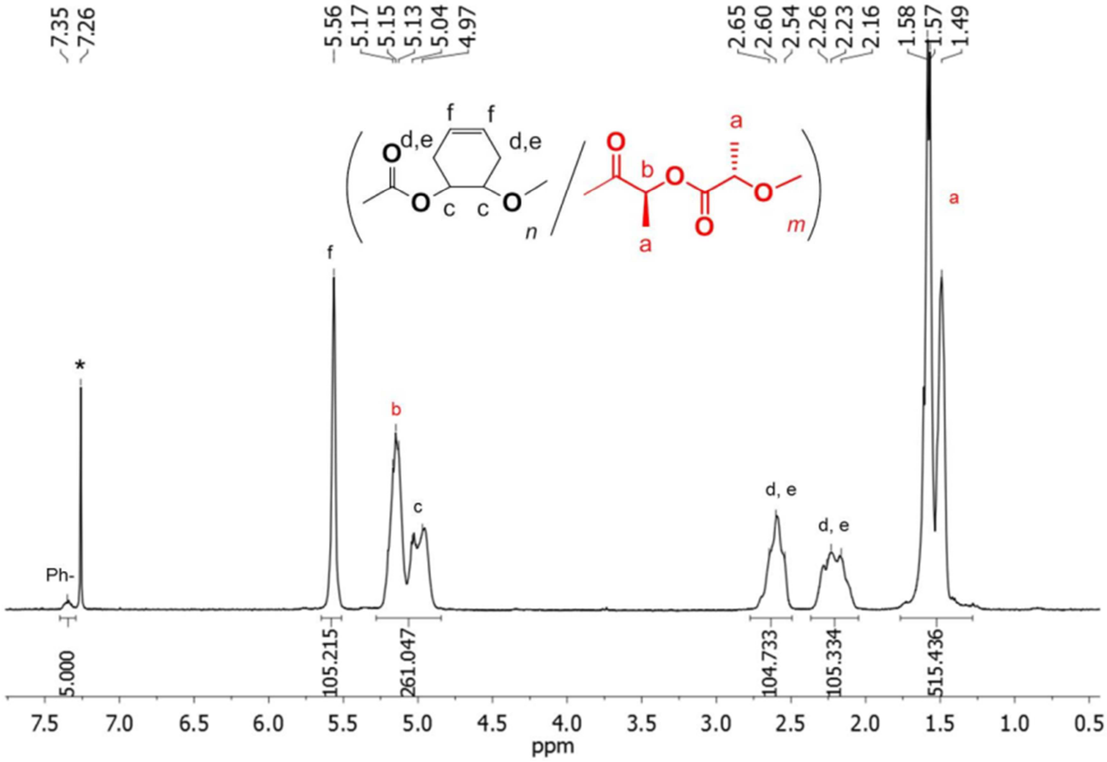

Figure S21. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of a P(CHDC-*co*-LLA) copolymer prepared from *rac*-CHDC and L-LA (Table 4, entry 2) (* stands for residual $CHCl_3$ resonances).

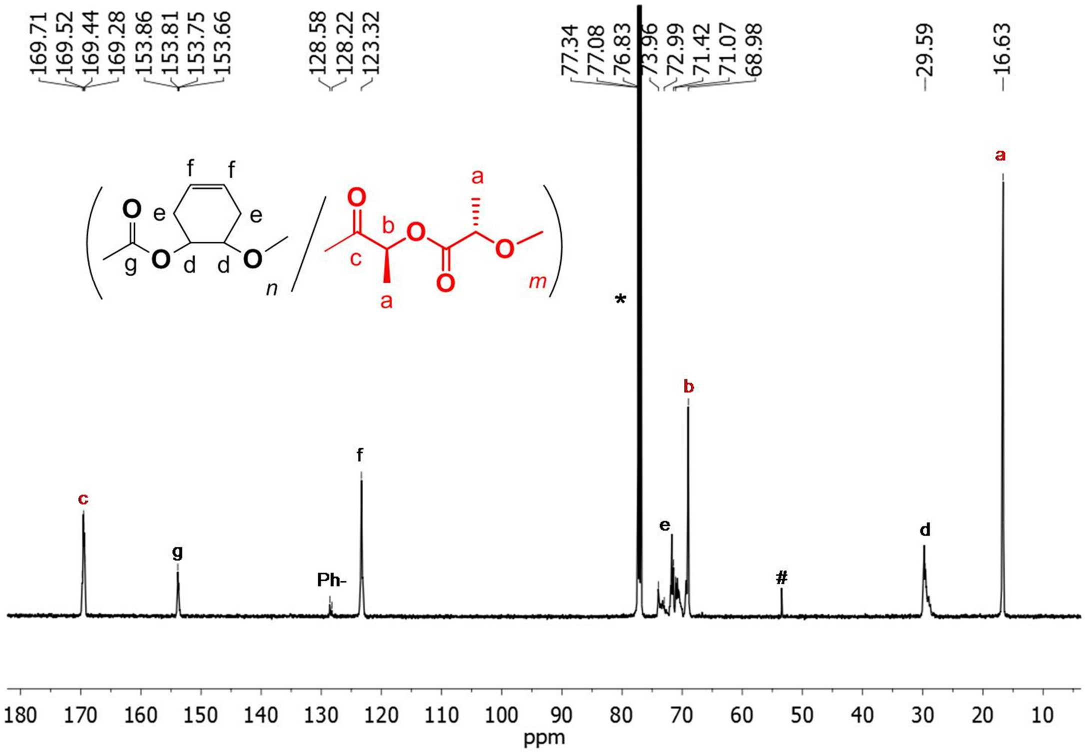

Figure S22. $^{13}C\{^1H\}$ NMR spectrum (100 MHz, $CDCl_3$, 23 °C) of a P(CHDC-*co*-LLA) copolymer prepared from *rac*-CHDC and L-LA (Table 4, entry 2) (# and * stand for residual CH_2Cl_2 and $CHCl_3$ resonances, respectively).

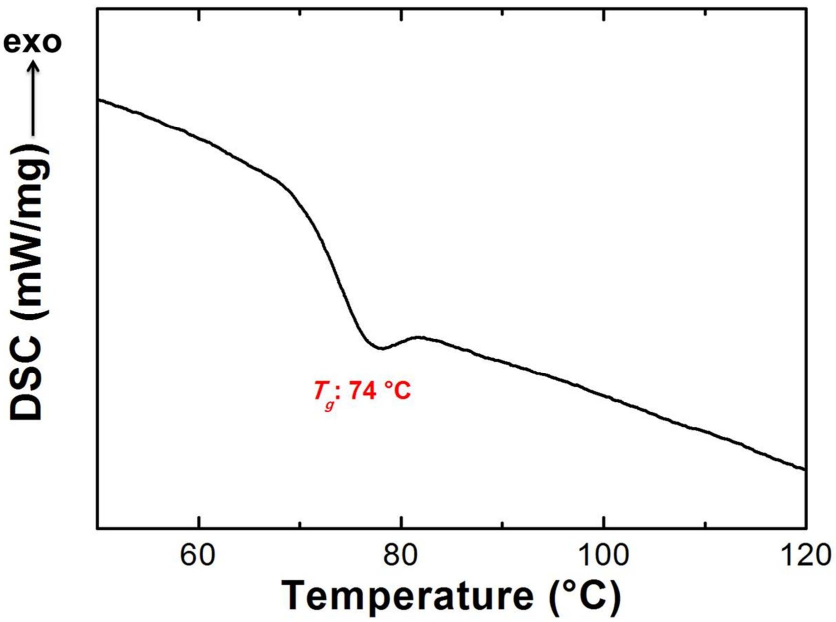

Figure S23. DSC thermogram (second heating cycle; heating rate = 10 °C.min^{-1}; argon flow) of a P(CHDC-*co*-LLA) copolymer prepared from *rac*-CHDC and L-LA (Table 4, entry 2).

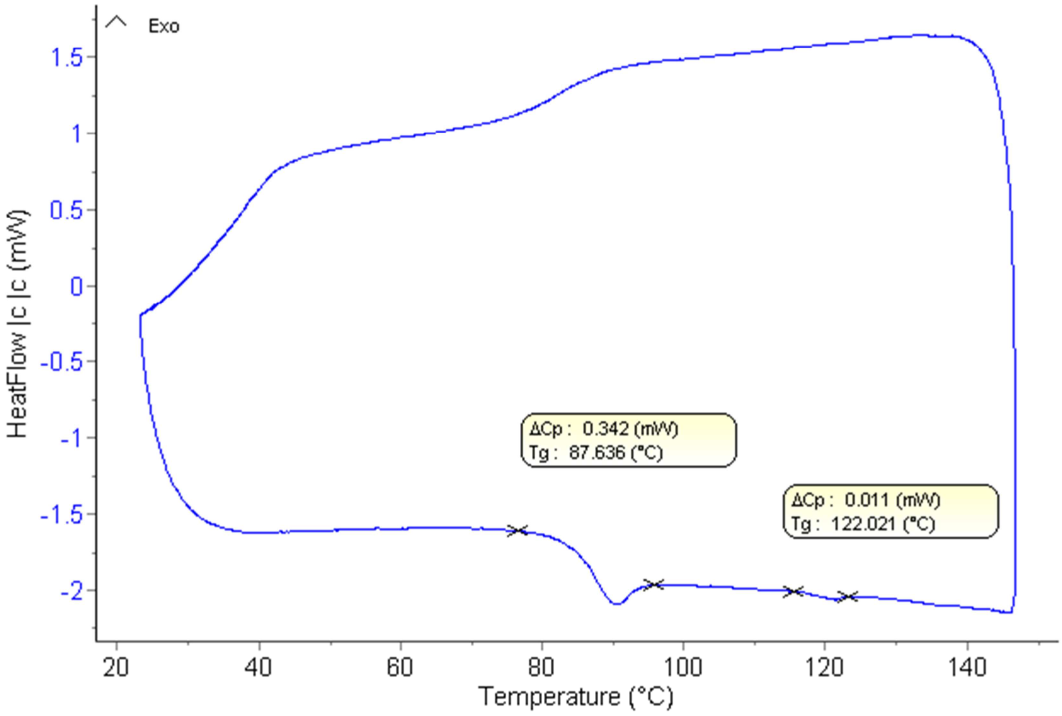

Figure S24. DSC thermogram (second heating cycle; heating rate = 10 °C.min^{-1}; argon flow) of a P(CHDC-*co*-LLA) copolymer prepared from *rac*-CHDC and L-LA (Table 4, entry 3).