Supporting Information - A Lewis acid ß-Diiminato-Zinc-Complex as All-Rounder for Co- and Terpolymerization of various Epoxides with Carbon Dioxide

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0. Experimental Section

General. All reactions containing air- and/or moisture sensitive compounds were performed under dry argon using standard Schlenk or glovebox techniques. All chemicals were purchased from Aldrich or ABCR. Solvents were obtained from an MBraun MB-SPS-800 solvent purification system. Monomers were dried over calcium hydride and distilled prior to polymerization. NMR spectra were recorded on a Bruker AVIII-300 and AVIII 500 Cryo spectrometer. ^{1}H NMR spectroscopic chemical shifts δ are reported in ppm relative to tetramethylsilane and calibrated to the residual proton signal of the deuterated solvent. Deuterated solvents were obtained from Sigma Aldrich and dried over 3 Å molecular sieves. ESI-MS analytical measurements were performed in acetonitrile solutions on a Varian 500 MS spectrometer. Gel permeation chromatography (GPC) analysis was performed on a Varian PL-GPC 50. As eluent, chloroform (HPLC grade) with 1.5 g L^{-1} tetrabutylammonium tetrafluoroborate was used. Polystyrene standards were used for calibration. Furthermore, gel permeation chromatography (GPC) analysis was performed on a Varian PL-GPC 50 Plus at 35 °C equipped with a PLgel-Mixed-C column set (600 mm). THF (HPLC grade) was used as solvent together with 2,6-di-tert-butyl-4-methylphenol at a flow rate of 1 mL/min and a polystryrene standard. DSC measurements were performed at a DSC Q2000 of TA Instruments with a heating rate of 5°C/min. UV-Vis spectra were recorded on a Varian Cary-50. *In situ* IR measurements were carried out under an argon atmosphere using an ATR IR MettlerToledo system. Elemental analysis was performed at the microanalytic laboratory of the Department of Inorganic Chemistry at the Technical University of Munich.

Monomer Synthesis. 84% *trans*-(+)-Limonene oxide was synthesized according to a literature procedure.[1] >99% *trans*-(+)-Limonene oxide was synthesized according to literature procedure, but purification was performed via silica gel chromatography (SiO_2, Hexane:EtOAc, 20:1; R_f=0.41).[2] Menthene oxide was prepared according to modified literature procedure (thf was used instead of MeOH).[3]

Ligand Synthesis. $CH(CCF_3NC_6H_4\text{-}2,6C_2H_5)_2$, ligand (**I**) was synthesized according to literature procedures.[4,5]

Complex Synthesis.

$[CH(CCF_3NC_6H_4\text{-}2,6C_2H_5)_2]ZnN(SiMe_3)_2$, Complex 1. 1.00 equiv of ligand **I** and 1.20 equiv of $Zn(NTMS_2)_2$ were dissolved in dry toluene and stirred at 110 °C under inert atmosphere for 3 days. After cooling to room temperature, the solvent was removed under vacuum and the yellow solid was twice recrystallized from toluene at -35 °C to yield yellow crystals (42%). Anal. Calcd for $C_{31}H_{45}F_6N_3Si_2Zn$: C, 53.55; H, 6.52; N, 6.04. Found: C, 53.22; H, 6.23; N, 5.86. ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ(ppm) = 7.12 – 7.02 (m, 6H, H_{Aromat}), 6.11 (s, 1H, C*H*), 2.73-2.58 (m, 8H, CH_2), 1.21 (t, J^3 = 7.5 Hz, 12*H*, CH_3), -0.13 (s, 18H, SiCH_3). ^{13}C NMR (126 MHz, C_6D_6, 298K): δ(ppm) = 157.88 (q, $^2J_{CF}$ = 27.3 Hz, N*C*(CF_3)CH*C*(CF_3)N)), 143.16 (s, C_{Ar}), 136.19 (s, C_{Ar}), 127.10 (s, C_{Ar}), 125.40 (s, C_{Ar}), 120.24 (q, $^1J_{CF}$ = 287 Hz, NC(*C*F_3)CHC(*C*F_3)N), 87.09 (m, NC(CF_3)*C*HC(CF_3)N), 24.63 (s, CH_2CH_3), 12.85 (s CH_2CH_3), 5.19 (s, Si(CH_3)$_3$). ^{29}Si NMR (99 MHz, C_6D_6, 298 K): δ(ppm) = -2.68.

$[[CH(CCF_3NC_6H_4\text{-}2,6C_2H_5)_2]ZnOSiMe_3]_2$, Complex 2. 300 mg of complex 1 were solved in 2.0 mL toluene-d_8 and pressurized with 40 bar CO_2 in an autoclave at 50 °C overnight. Carbon dioxide was released (0 °C) and the autoclave was opened in a glovebox. The slightly yellow precipitate (~100 mg) was recrystallized from 15 mL toluene. SC-XRD revealed that the complex is dimeric in the solid state (Figure 3). ^{1}H NMR (300 MHz, thf-d_8, 298 K): δ(ppm) = 7.16 (s, 12H, H_{Aromat}), 5.85 (s, 2H, C*H*), 2.79-2.50 (m, 16H, CH_2), 1.30 (t, J^3 = 7.6 Hz, 24H, CH_3), -0.51 (s, 18H, OSi(CH_3)$_3$). ^{13}C NMR (126 MHz, C_6D_6, 298K): δ(ppm) = 157.65 (q, $^2J_{CF}$ = 27.7 Hz, N*C*(CF_3)CH*C*(CF_3)N)), 143.87 (s, C_{Ar}), 137.58 (s, C_{Ar}), 127.33 (s, C_{Ar}), 126.17 (s, C_{Ar}), 120.80 (q, $^1J_{CF}$ = 291 Hz, NC(*C*F_3)CHC(*C*F_3)N), 85.70 (m, NC(CF_3)*C*HC(CF_3)N), 24.45 (s, CH_2CH_3), 13.84 (s, *C*H_2CH_3), 3.08 (s, OSi(CH_3)$_3$).

Polymerization procedure. Copolymerization experiments with *in situ* monitoring were performed using a React-IR/MultiMax four-autoclave system (Mettler-Toledo). 50 mL steel autoclaves equipped with a diamond window, a mechanic stirring and a heating device were heated under vacuum to 130 °C overnight prior to use. The required amount of catalyst was dissolved in 5.0 mL epoxide (+ toluene, if indicated in Table 1+3) in a vial equipped with an injection septum and afterwards rapidly transferred into the reactor using a syringe. The reactor was pressurized and the polymerization was finished by cooling the reactor to 20 °C and release of CO_2. The product was dissolved in methylene chloride and transferred to a flask. Afterwards methylene chloride was removed under vacuum and yield and selectivity were determined via NMR/weight of the polymer. The dissolved polymer (methylene chloride) was precipitated from methanol.

[1] O. Hauenstein, M. Reiter, S. Agarwal, B. Rieger and A. Greiner, *Green Chem.*, 2016, **18**, 760-770.
[2] D. Steiner, L. Ivison, C. T. Goralski, R. B. Appell, J. R. Gojkovic and B. Singaram, *Tetrahedron Asymmetry*, 2002, **13**, 2359-2363.

[3] K. Mori, *Tetrahedron Asymmetry*, 2006, **17**, 2133-2142.
[4] A. Kronast, M. Reiter, P. T. Altenbuchner, C. Jandl, A. Pöthig and B. Rieger, *Organometallics*, 2016, **35**, 681-685.
[5] D. T. Carey, E. K. Cope-Eatough, E. Vilaplana-Mafe, F. S. Mair, R. G. Pritchard, J. E. Warren and R. J. Woods, *Dalt. Trans.*, 2003, 1083-1093.

1. Pressurizing Catalyst (1) with CO_2.

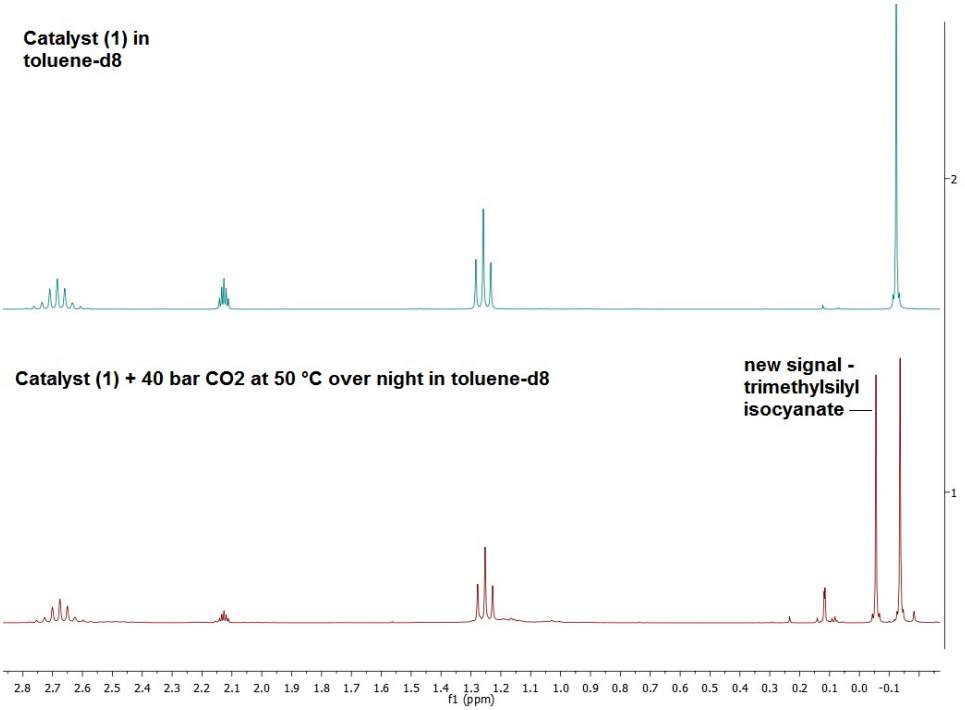
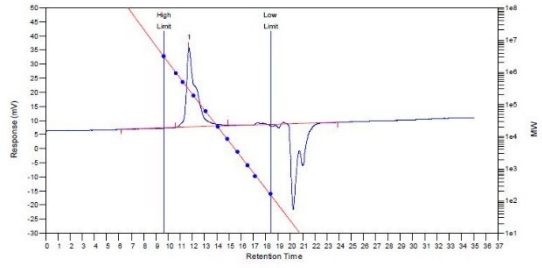


Figure S1. On the top: ^{1}H-NMR spectrum of catalyst (1) in toluene-d_8. On the bottom: ^{1}H-NMR spectrum of catalyst (1) + 40 bar CO_2 at 50 °C over night in toluene-d_8.

2. GPC results of Table 1 and Table 3.

Table 1

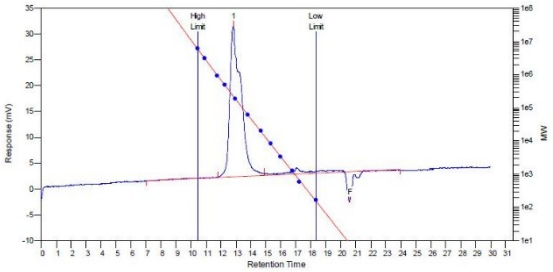
Entry 1



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	288254	134128	223217	283558	339300	213584	1.66421

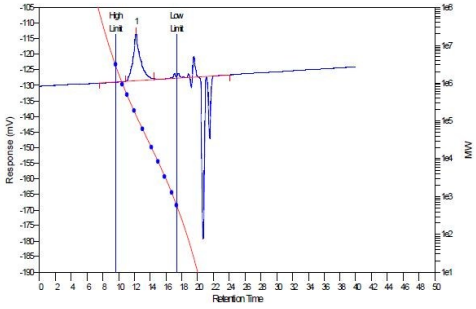
Entry 2



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	227930	134776	186847	234564	284109	179814	1.38635
2	0	0	0	0	0	0	0

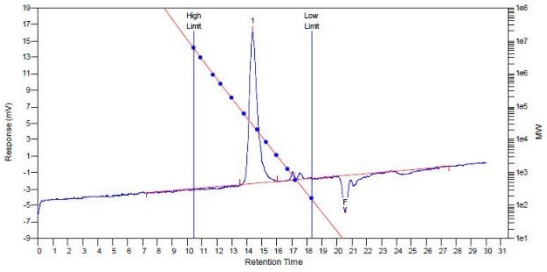
Entry 3



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	148007	97520	140558	185229	233077	134270	1.44132

Entry 5



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	27636	21444	25773	29187	32131	25227	1.20187
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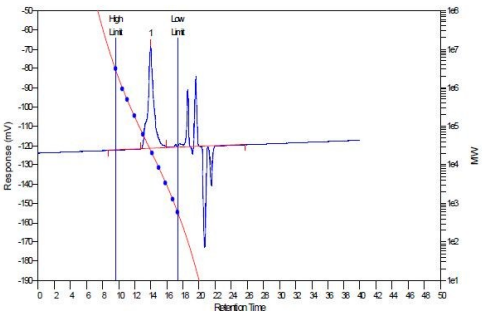
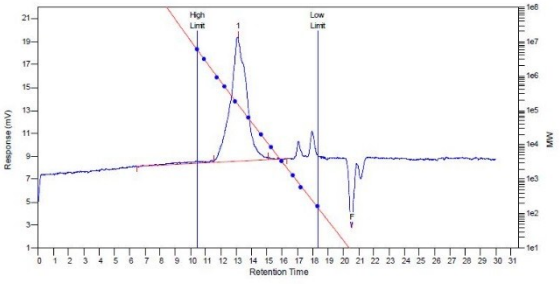
Entry 6



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	24494	19623	24762	29686	34717	24041	1.26189

Entry 7



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	151266	106526	186099	312723	476723	171604	1.74698
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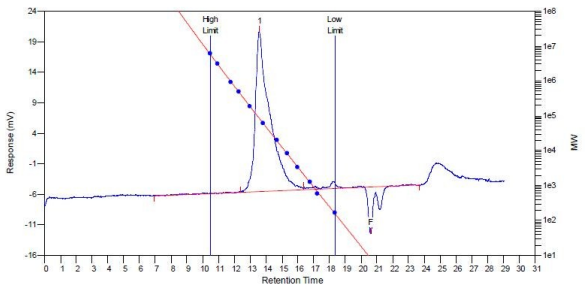
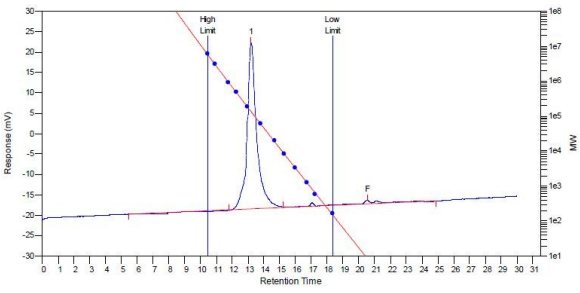
Entry 9



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	80821	32545	63213	90855	119531	59155	1.94233
2	0	0	0	0	0	0	0

Entry 10



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
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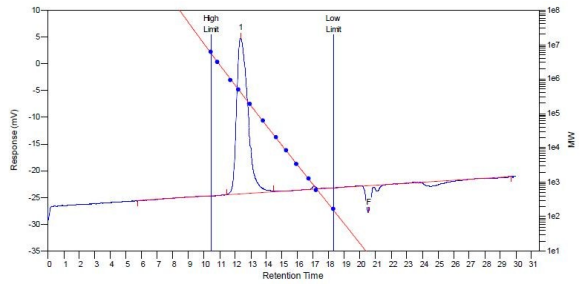
Entry 11

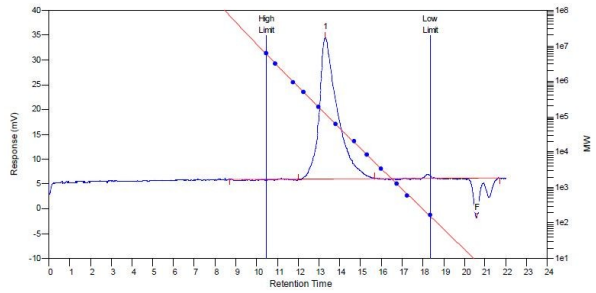


MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	411339	271984	360946	432723	497941	349791	1.32709
2	0	0	0	0	0	0	0

Table 3

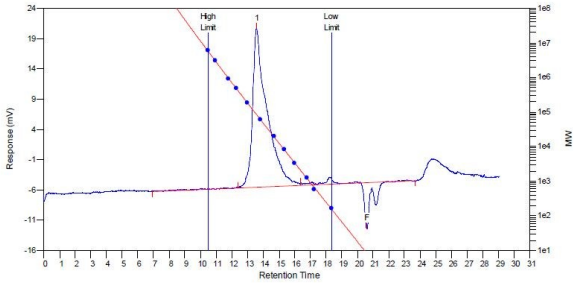
Entry 1



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	120730	61887	103822	146357	194488	97931	1.67761
2	0	0	0	0	0	0	0

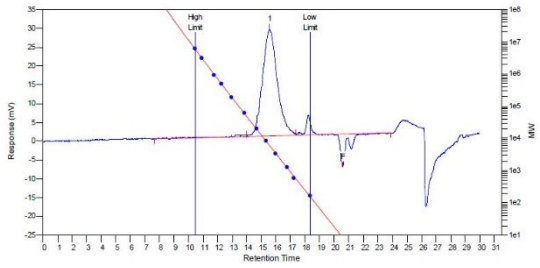
Entry 2



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	80821	32545	63213	90855	119531	59155	1.94233
2	0	0	0	0	0	0	0

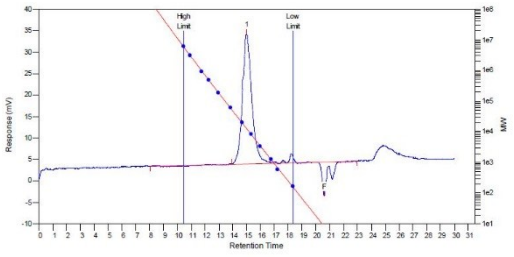
Entry 3



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	5980	4312	6812	10133	14715	6403	1.57978
2	0	0	0	0	0	0	0

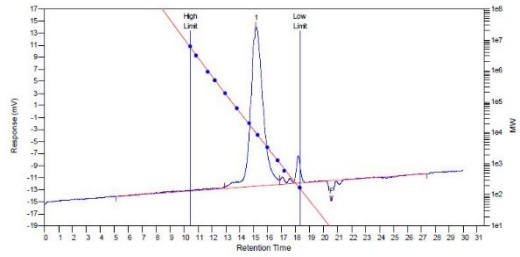
Entry 4



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	12611	9968	12708	15468	18491	12314	1.27488
2	0	0	0	0	0	0	0

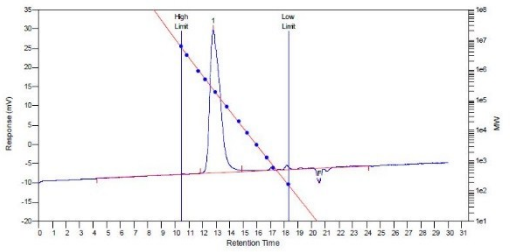
Entry 5



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	9643	7217	12319	32554	86356	11053	1.70694
2	0	0	0	0	0	0	0

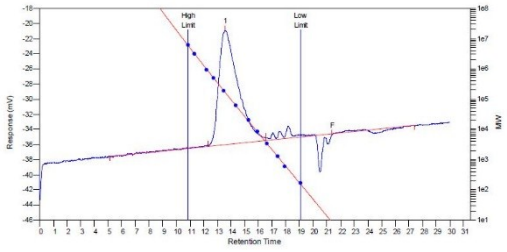
Entry 6



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	237109	145274	195978	238610	278149	189434	1.34902
2	0	0	0	0	0	0	0

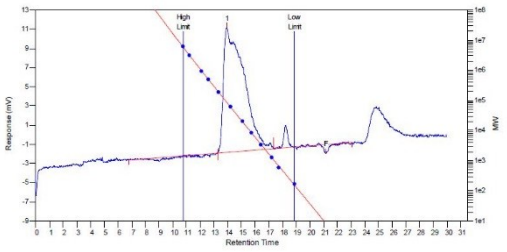
Entry 7



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	163243	56092	138489	223954	300881	126324	2.46896
2	0	0	0	0	0	0	0

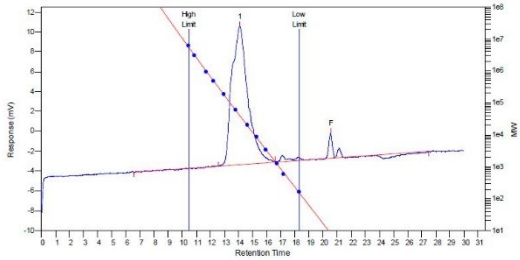
Entry 8



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	90308	18913	46651	73134	91357	42623	2.46661
2	0	0	0	0	0	0	0

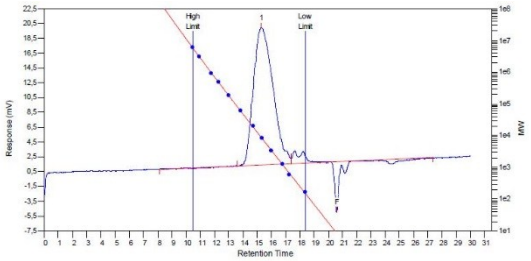
Entry 9



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	39942	24028	45232	66088	85701	42240	1.88247
2	0	0	0	0	0	0	0

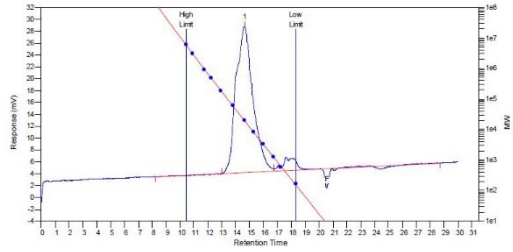
Entry 10



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	8493	4593	8949	14360	19826	8232	1.9484
2	0	0	0	0	0	0	0

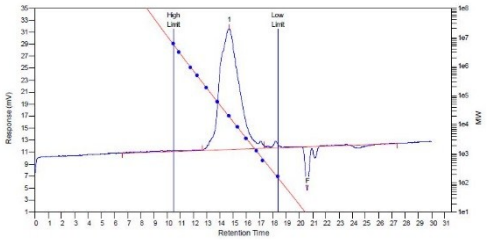
Entry 13



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	19528	12844	23614	36599	50315	21889	1.83852
2	0	0	0	0	0	0	0

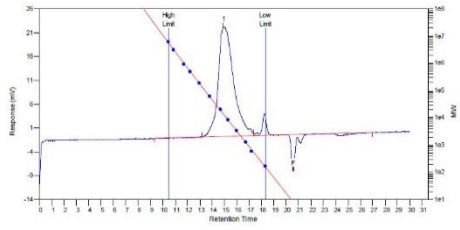
Entry 14



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	19587	9466	24633	48832	85455	22001	2.60226
2	0	0	0	0	0	0	0

Entry 15



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	13126	6014	12806	23068	39359	11665	2.12936
2	0	0	0	0	0	0	0

3. Ring Opening Polymerizations of CHO, PO, LO with catalyst 1-3 (Table 3).

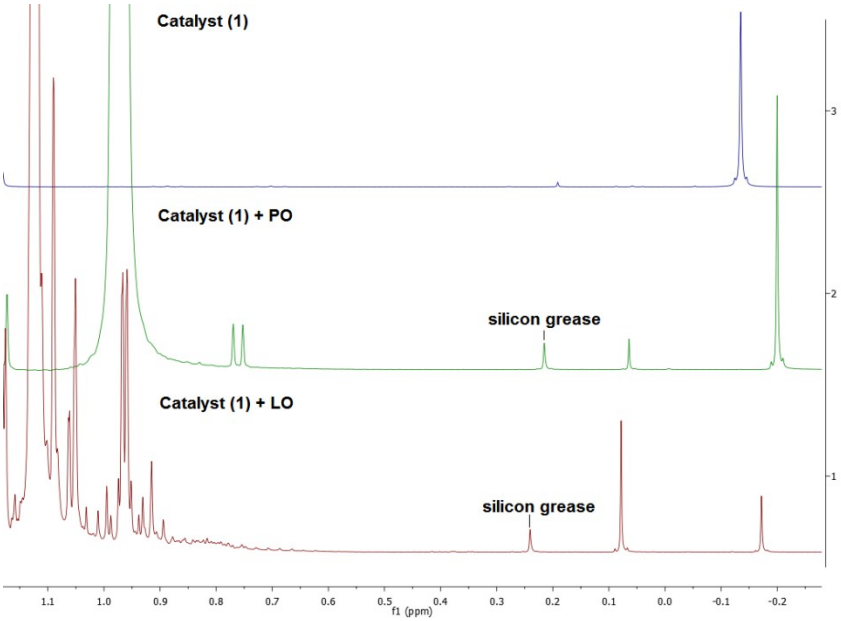


Figure S2. ^{1}H-NMR section (1.2ppm- (-0.2 ppm)) of Table 2, Entries 2+3. On top: ^{1}H NMR of Catalyst (1) in C_6D_6, -ZnNSi(CH_3)$_3$. In the middle: ^{1}H NMR of Catalyst (1) in C_6D_6 + 500 eq. propylene oxide. On the bottom: ^{1}H NMR of Catalyst (1) in C_6D_6 + 250 eq. limonene oxide.

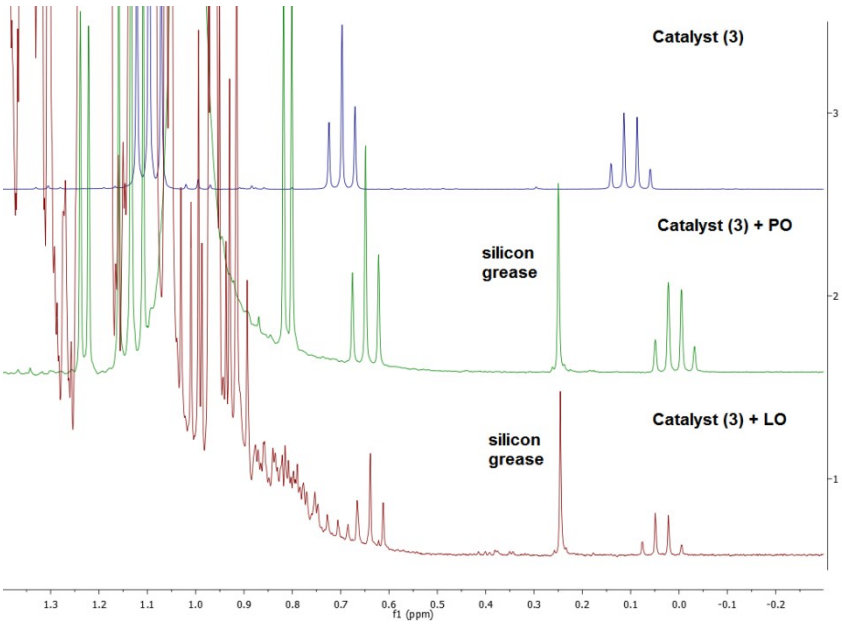


Figure S3. ^{1}H-NMR section (1.3ppm- (-0.3 ppm)) of Table 2, Entries 8+9. On top: ^{1}H NMR of Catalyst (3) in C_6D_6, -ZnNSi(CH_3)$_3$. In the middle: ^{1}H NMR of Catalyst (3) in C_6D_6 + 500 eq. propylene oxide. On the bottom: ^{1}H NMR of Catalyst (3) in C_6D_6 + 250 eq. limonene oxide.

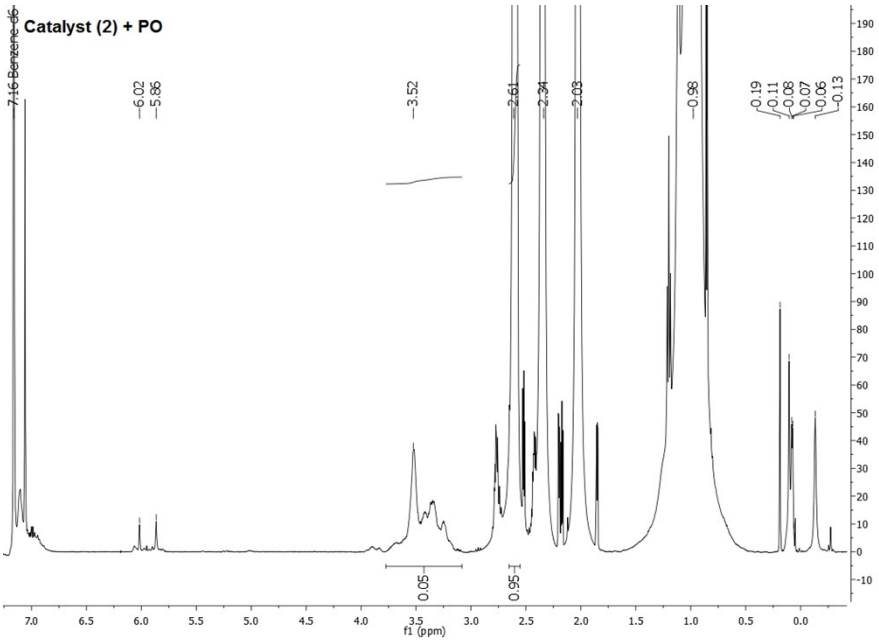
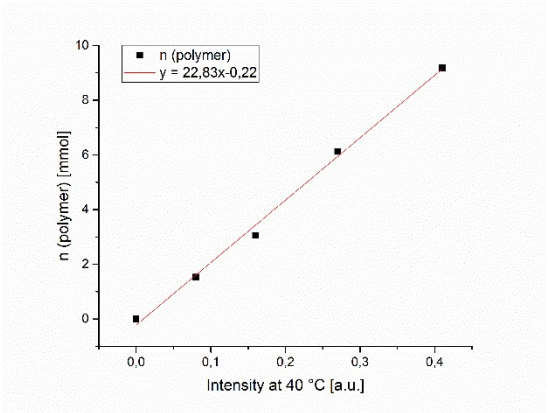


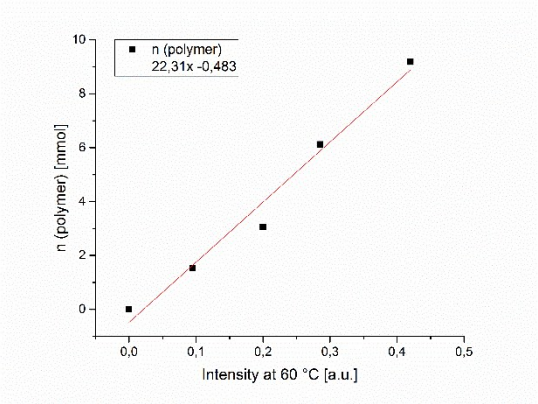
Figure S4. ^{1}H-NMR section of Table 2, Entry 5. Catalyst (2) + 500 eq. propylene oxide in C_6D_6. No NMR spectrum of the catalyst provided as it is insoluble in benzene.

4. Calibration curve for *in situ* determination of the TOF

a



b



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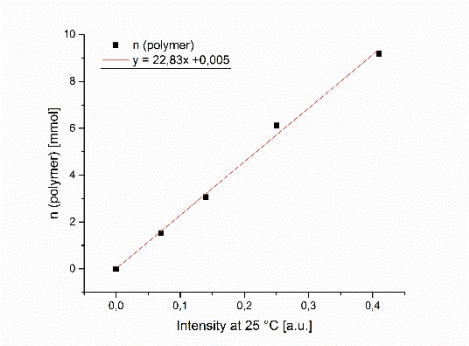


Figure S5. Calibration curve: Intensity of the carbonyl stretching bond v(C=O) of PLimC determined in the *in situ* IR autoclave reactor 1 against n(polymer) a) 40°C b) 60°C c) 25°C.

5. *In situ* IR spectra for Copolymerization results of CO_2 and Limonene oxide.

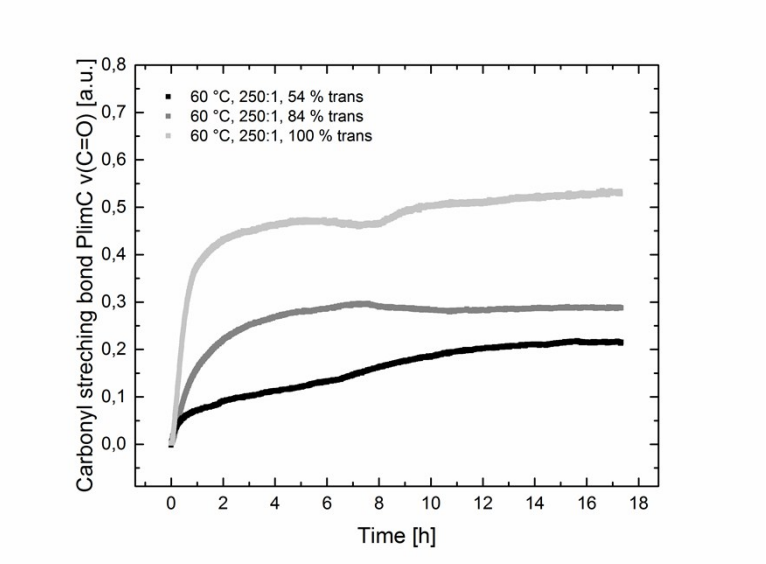


Figure S6. Intensity of the carbonyl stretching bond of PlimC in a.u. against time in hours. Data from Table 3, Entries 3+5+7 at 60 °C, 30 bar 250:1 (0.4 mol%).

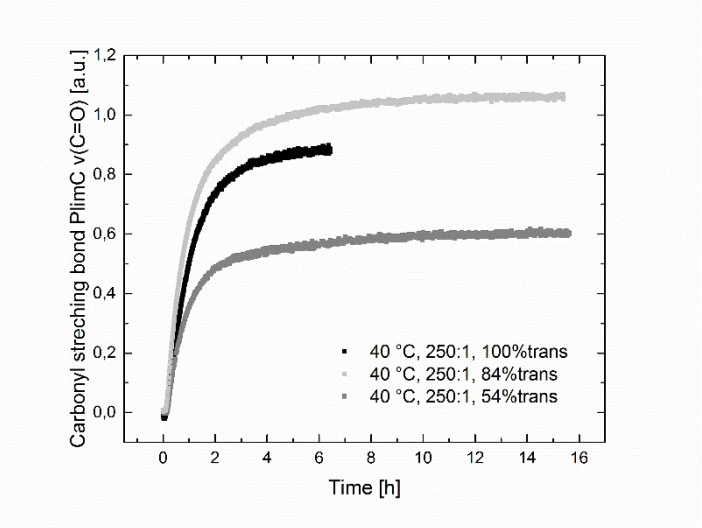
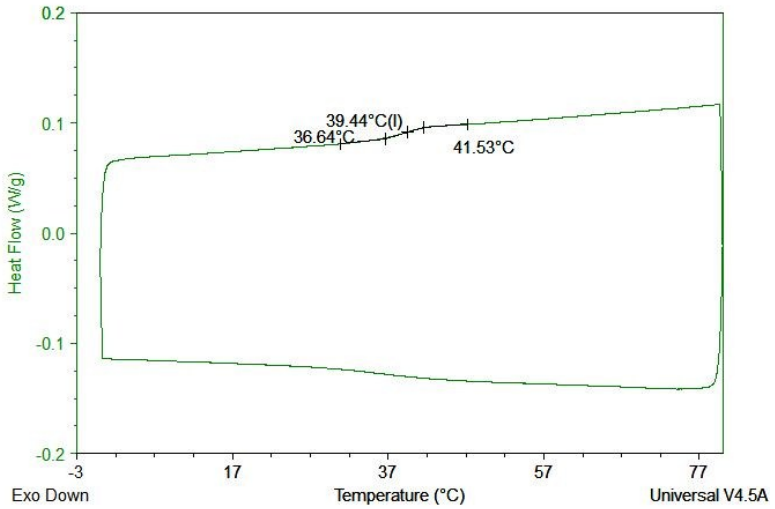


Figure S7. Intensity of the carbonyl stretching bond of PlimC in a.u. against time in hours. Data from Table 3, Entries 2+4+6 at 40 °C, 30 bar 250:1 (0.4 mol%).

6. DSC Analysis of the terpolymers



a)

b)

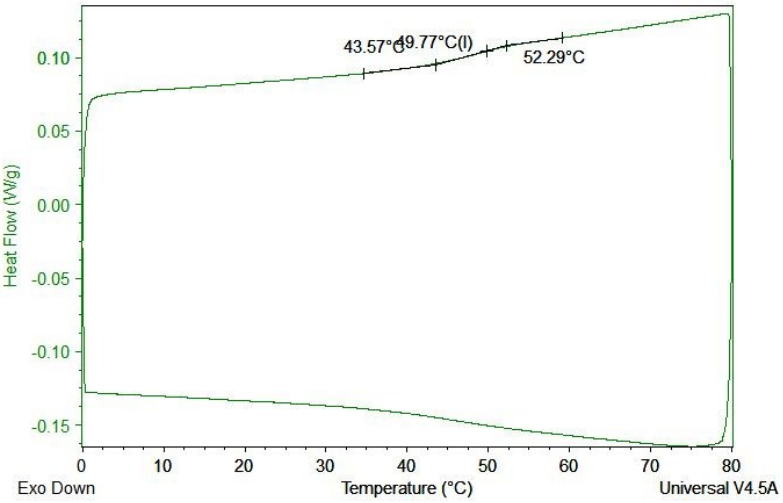


Figure S8. a) DSC curve (heating rate 5K/min) for terpolymer (PLimC-PPC), Table 1, Entry 10; b) DSC curve (heating rate 5K/min) for terpolymer (PCHC-PPC), Table 1, Entry 11.

7. UV-Vis Analysis of the terpolymers

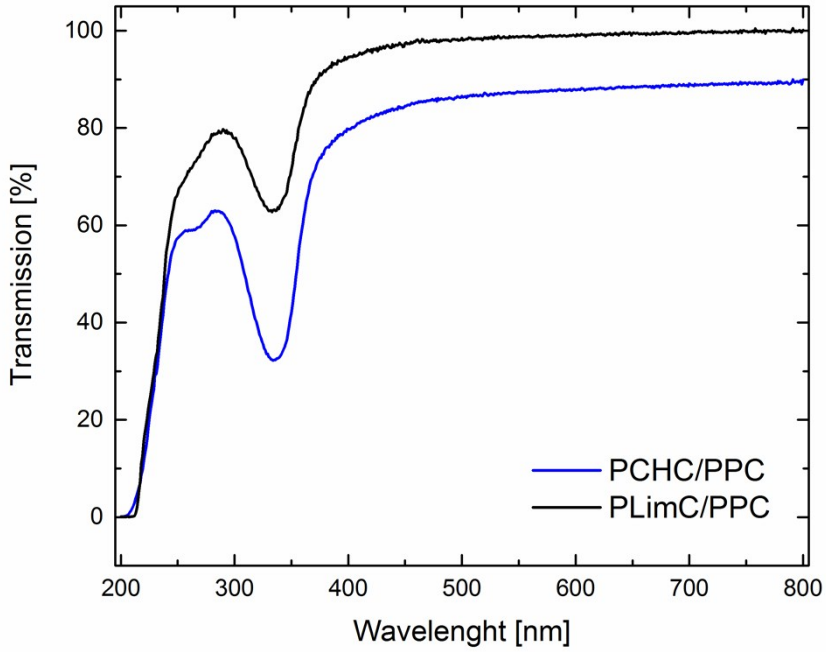
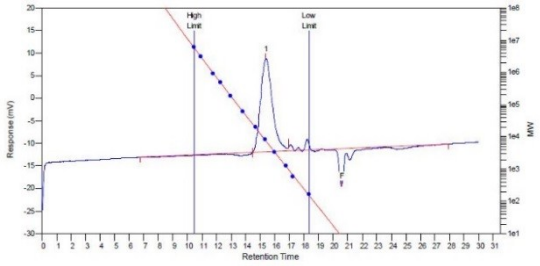


Figure S9. UV-Vis spectrum of two different terpolymers from 200-800 nm: blue line CHO/PO/CO_2. Black line LO/PO/CO_2.

8. Synthesis and analysis (GPC, NMR) of Poly(menthene carbonate)

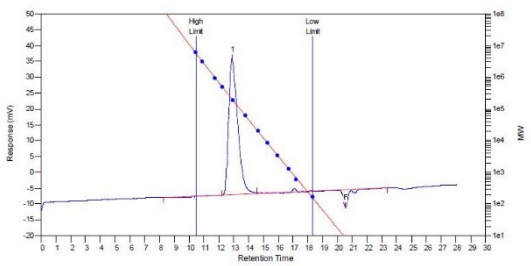
Table S1 Copolymerization of menthene oxide and carbon dioxide with catalyst (1).

Entry	[MenO]:[1]	%*trans* LO	V (tol) [mL]	Pressure [bar]	T[°C]	Time [h]	Yield [%]	Yield *trans*-LO [%]	Trans/Cis*/ Trans* [%]	M_n (PDI)[e] [g/mol]
1	250	54	2	30	25	16	43	80	100:0:0	149 000 (1.2)
2	250	54	2	30	60	16	4	8	-	5700 (1.3)



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	7324	5663	7512	9336	11093	7243	1.32651
2	0	0	0	0	0	0	0



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	200862	149126	180252	206178	228783	176165	1.20872
2	0	0	0	0	0	0	0

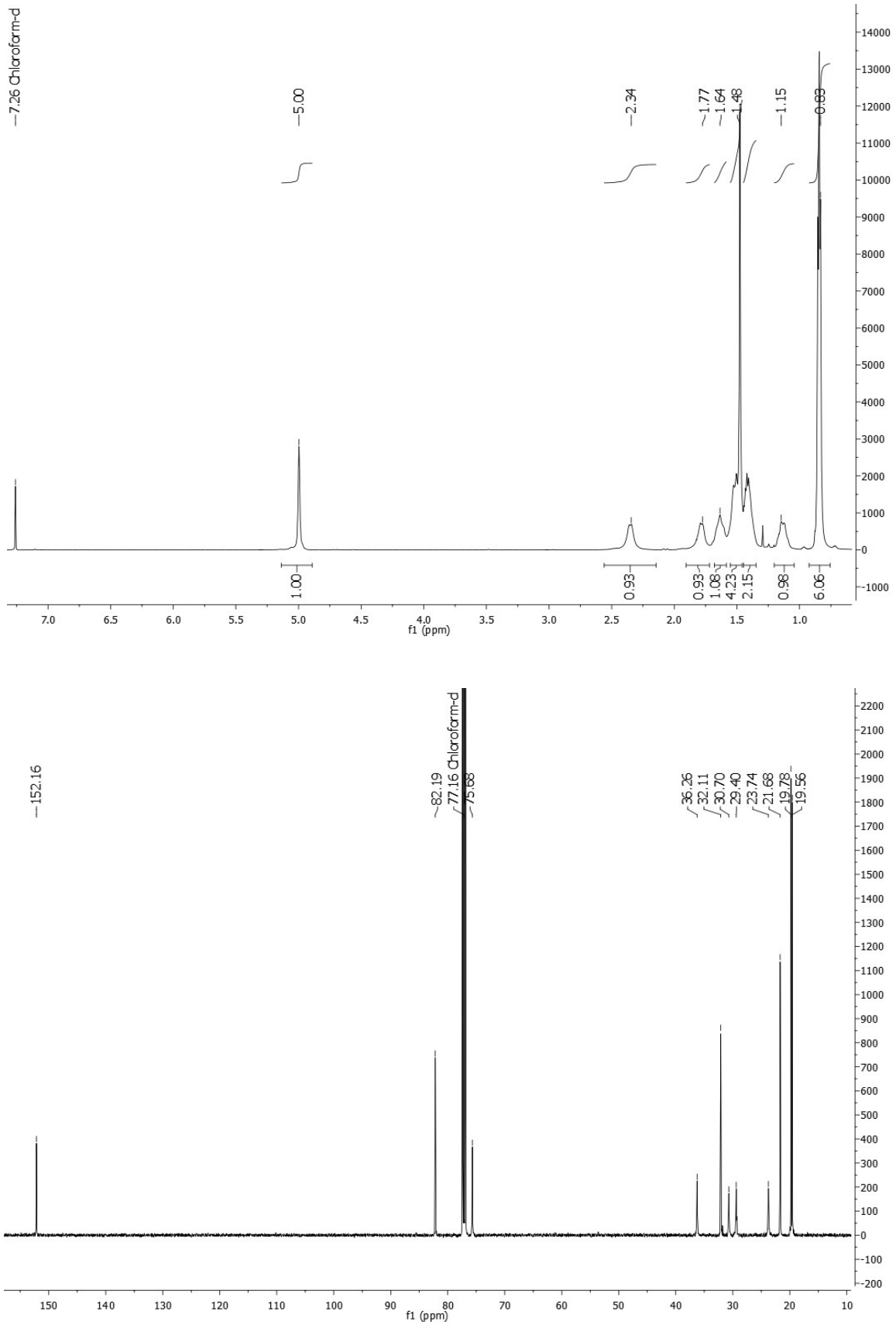


Figure S10. ^{1}H and ^{13}C NMR spectra of PMenC (Table S1, Entry 1).

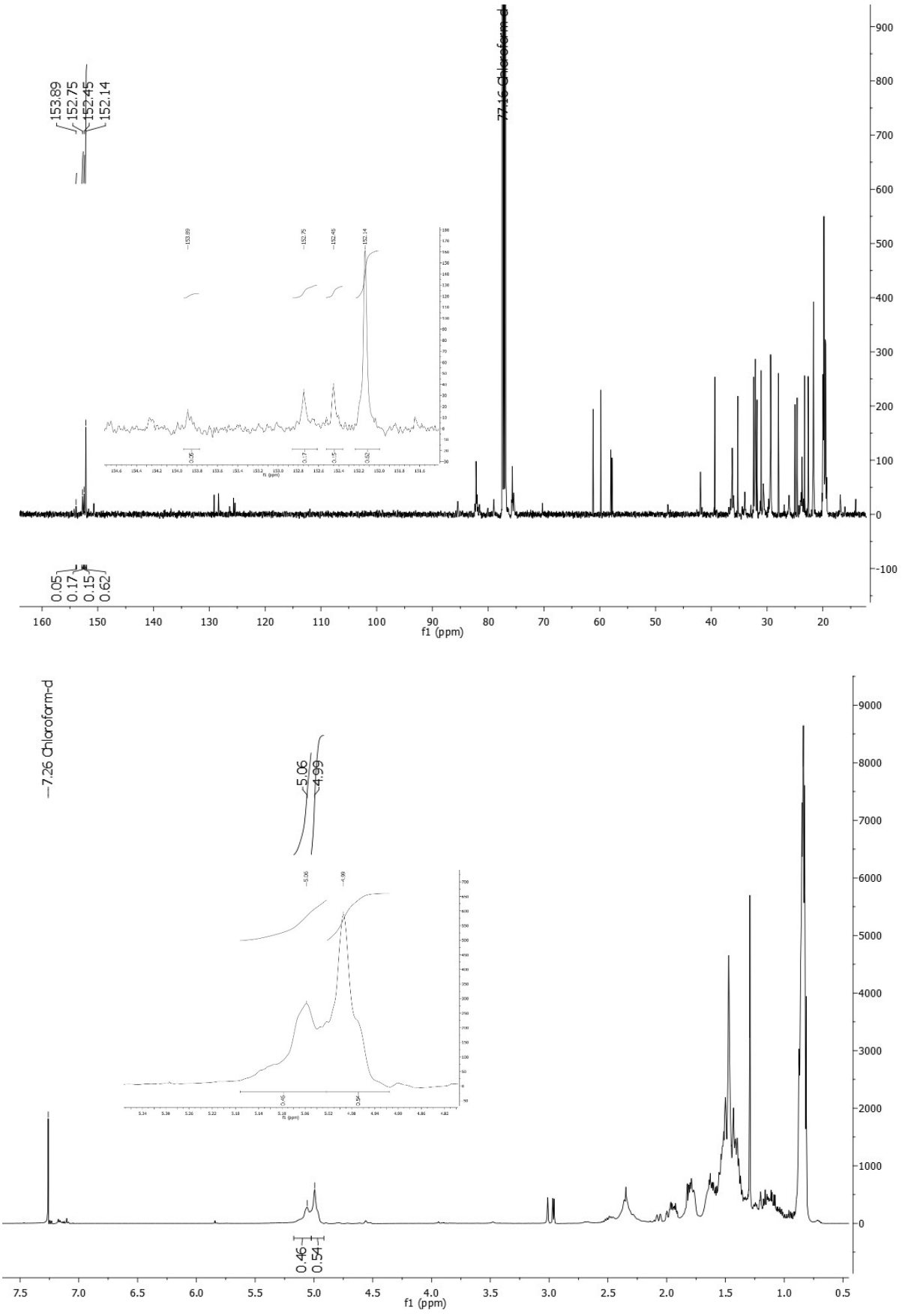


Figure S11. ^{1}H and ^{13}C NMR spectra of PMenC (Table S1, Entry 2).

9. ^{1}H and ^{13}C NMR spectra of selected precipitated polymer samples

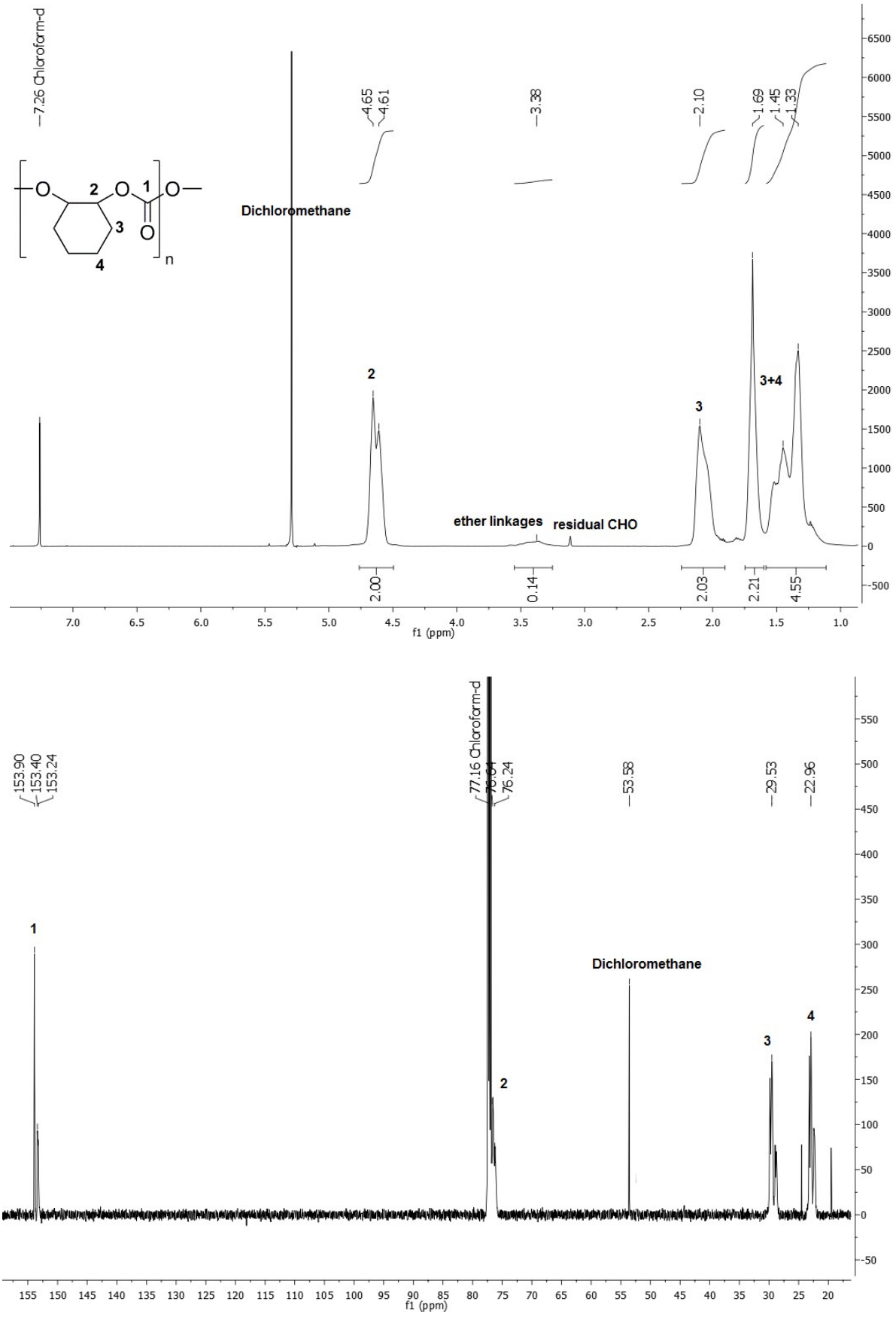


Figure S12. ^{1}H and ^{13}C NMR spectra of Poly(cyclohexene carbonate), Table 1, Entry 2.

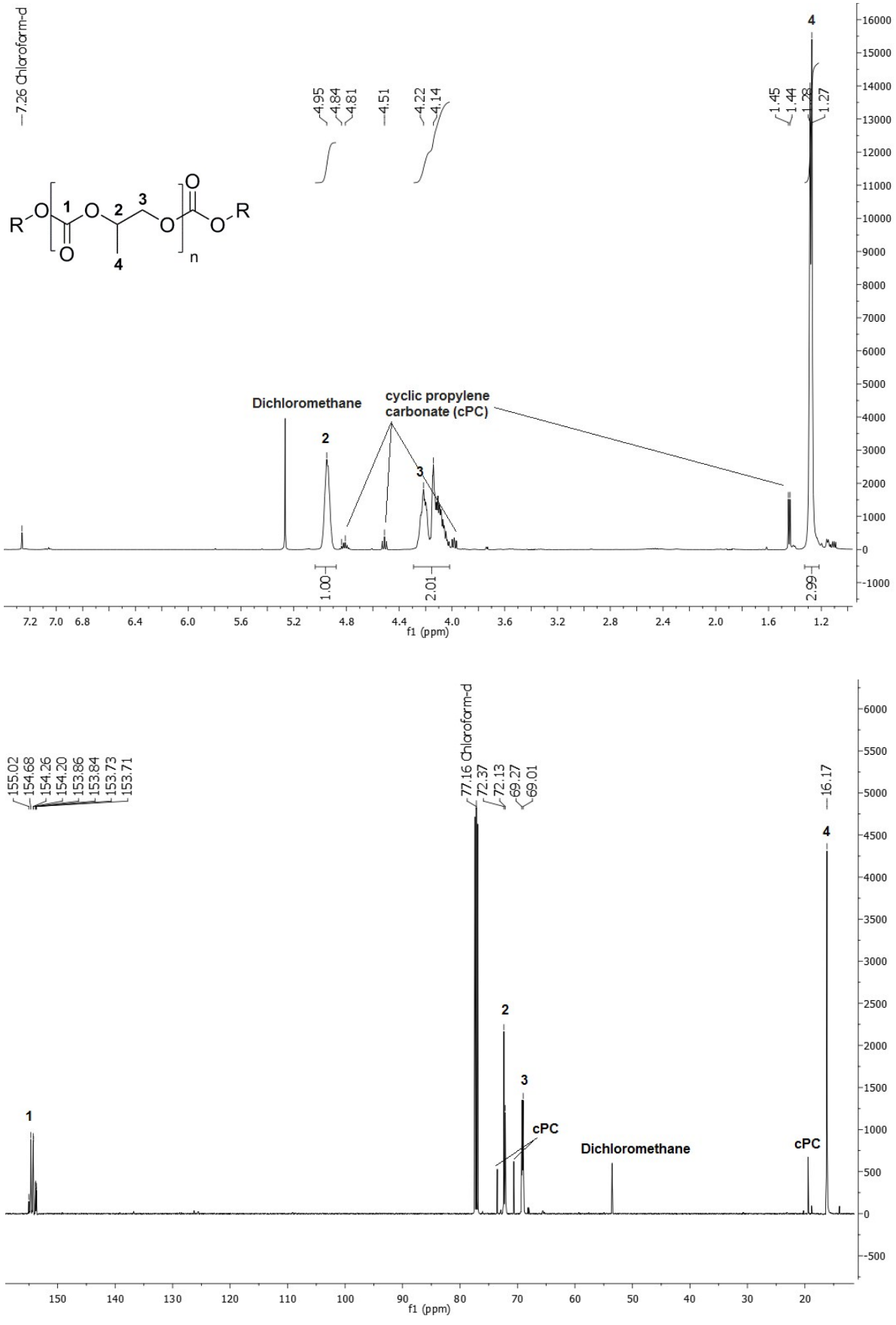


Figure S13. ^{1}H and ^{13}C NMR spectra of Poly(propylene carbonate), Table 1, Entry 5.

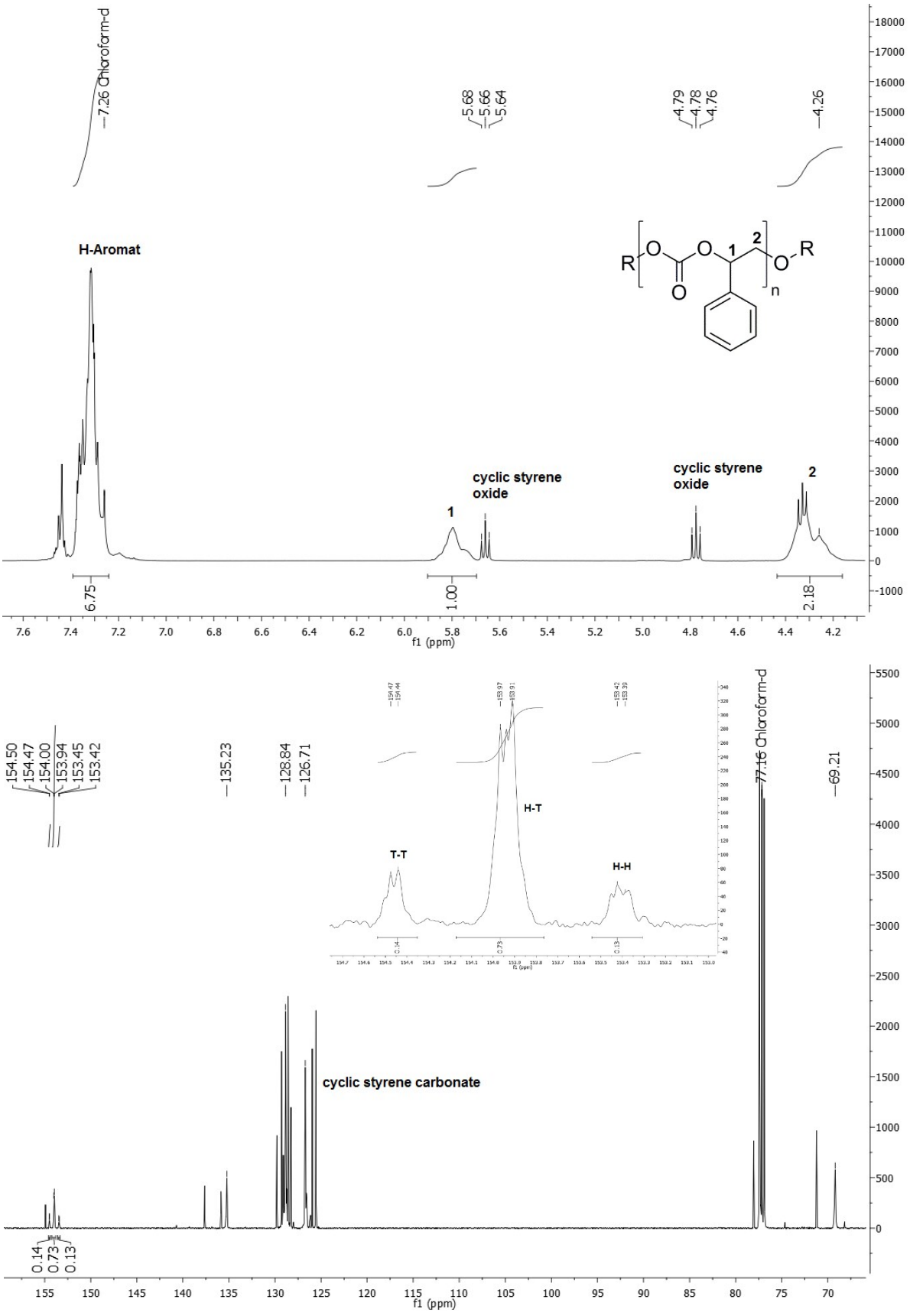


Figure S14. ^{1}H and ^{13}C NMR spectra of Poly(styrene carbonate), Table 1, Entry 6.

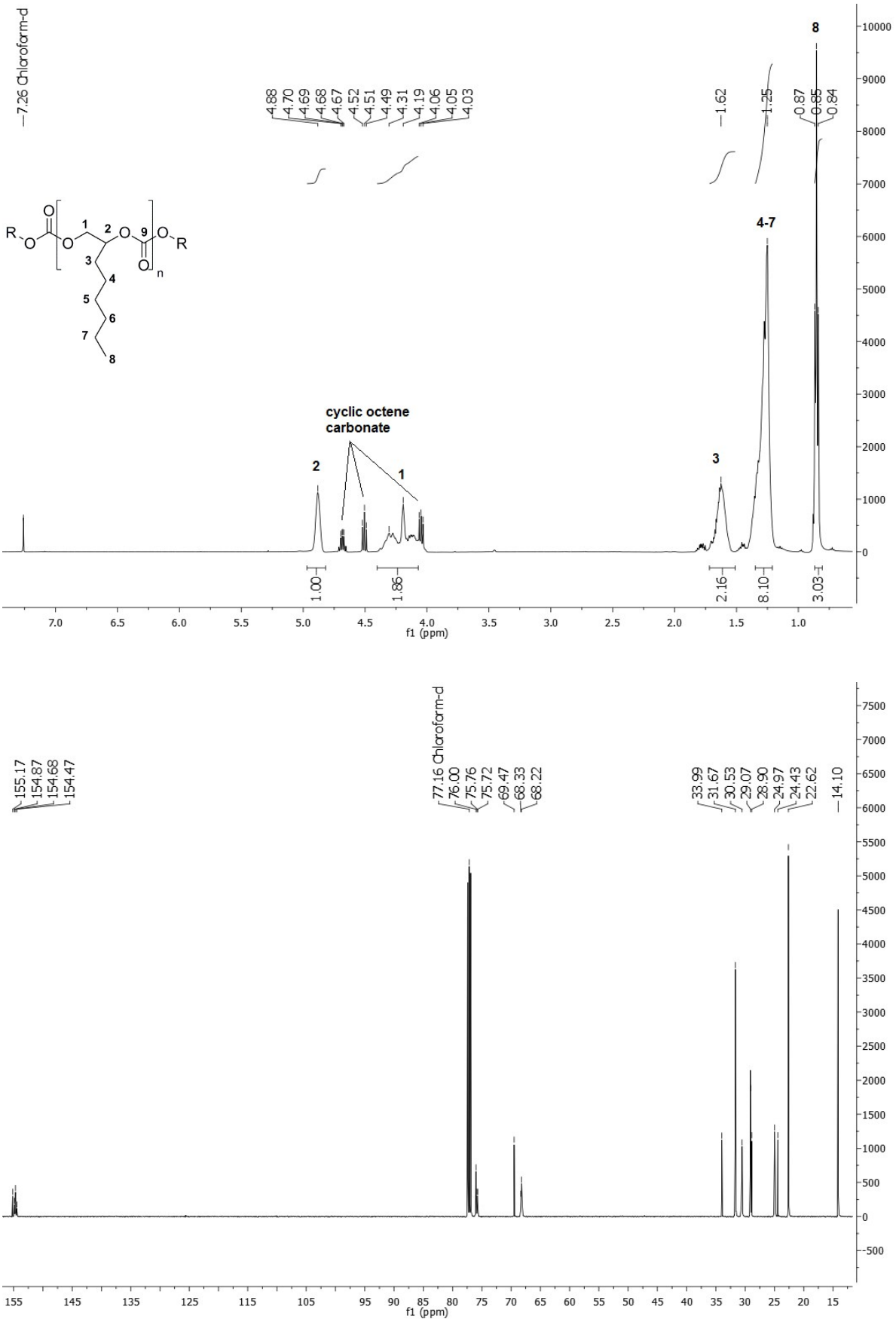


Figure S15. ^{1}H and ^{13}C NMR spectra of Poly(octene carbonate), Table 1, Entry 7.

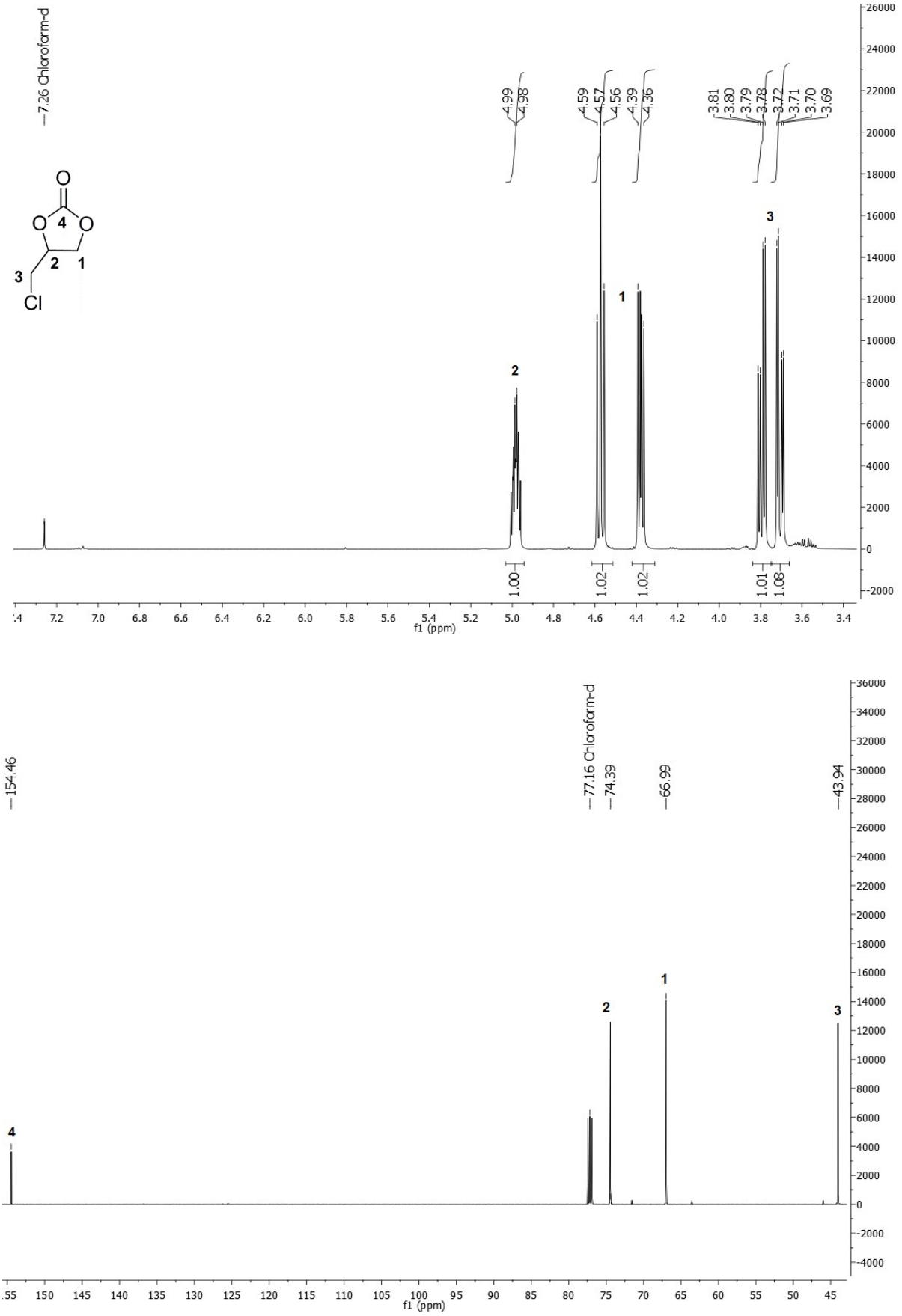


Figure S16. ^{1}H and ^{13}C NMR spectra of Cyclic epichlorohydrin carbonate, Table 1, Entry 8.

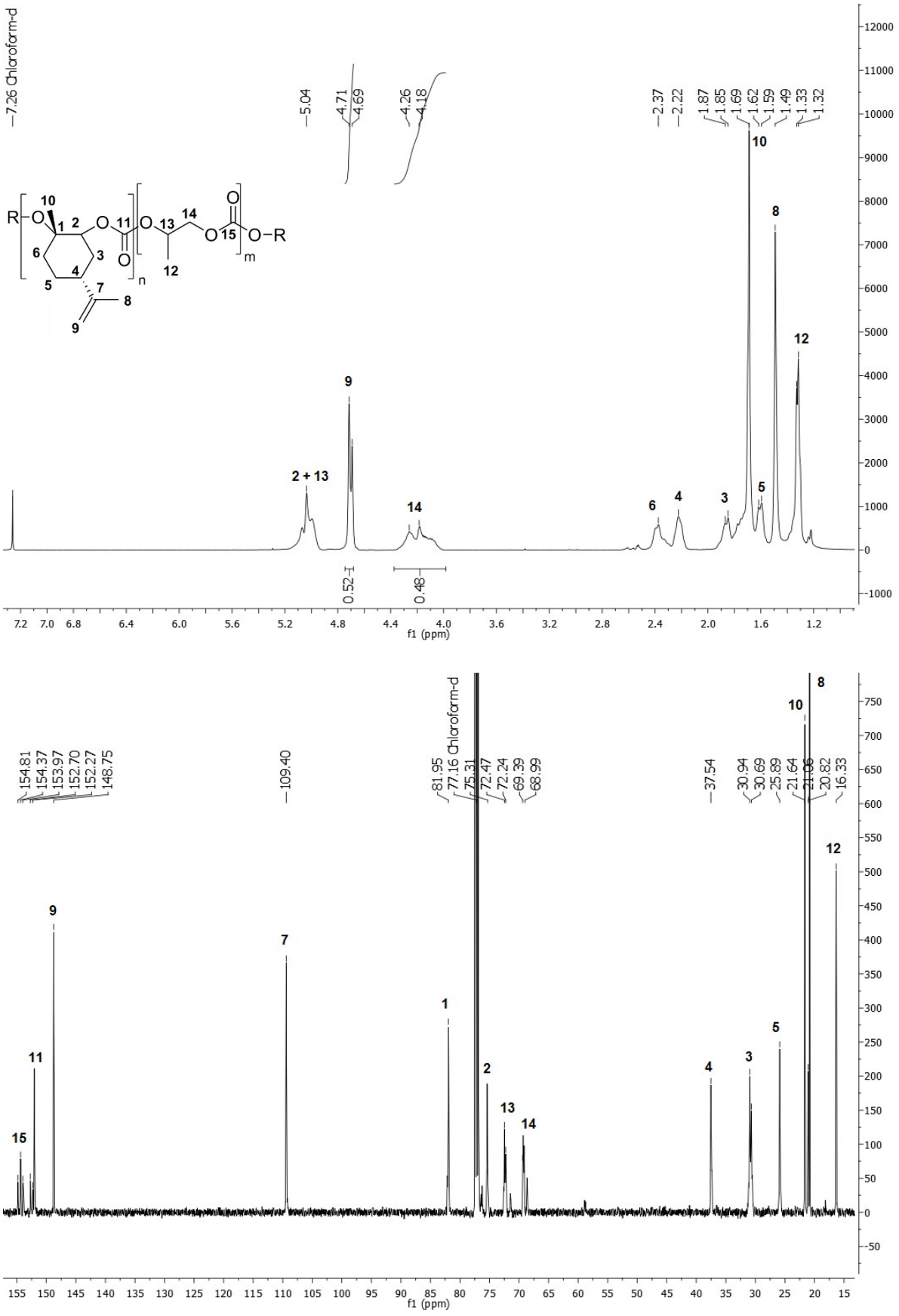


Figure S17. ^{1}H and ^{13}C NMR spectra of Terpolymer PLimC/PPC, Table 1, Entry 10.

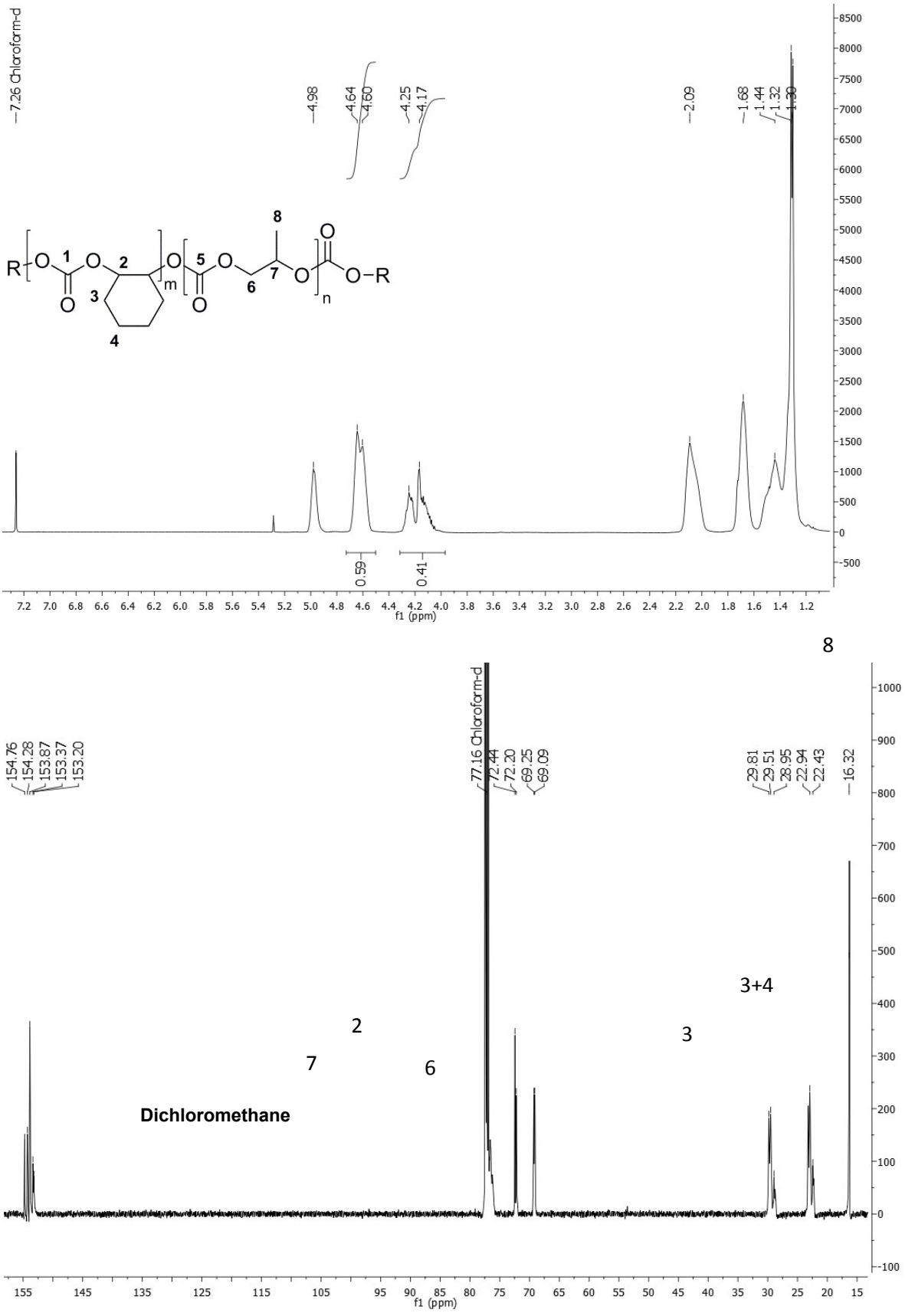
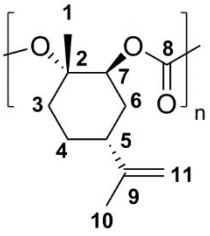


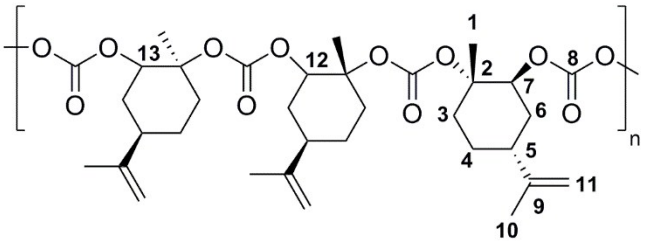
Figure S18. ^{1}H and ^{13}C NMR spectra of Terpolymer PCHC/PPC (precipitated), Table 1, Entry 11.

General ^{1}H and ^{13}C signal assignment for regioregular (*trans*-PLimC) and regioirregular (*trans*+*trans+*cis**-PLimC).[6],[7]**



Trans-PLimC

Group	^{1}H (δ, ppm)	^{13}C (δ, ppm)
1	1.69	21.65
2	-	81.97
3	2.38, 2.40	30.71
4	1.34, 1.60	25.90
5	2.23	37.55
6	1.62, 1.86	30.95
7	5.04	75.40
8	-	152.06
9	-	109.42
10	1.50	20.84
11	4.70, 4.72	148.76

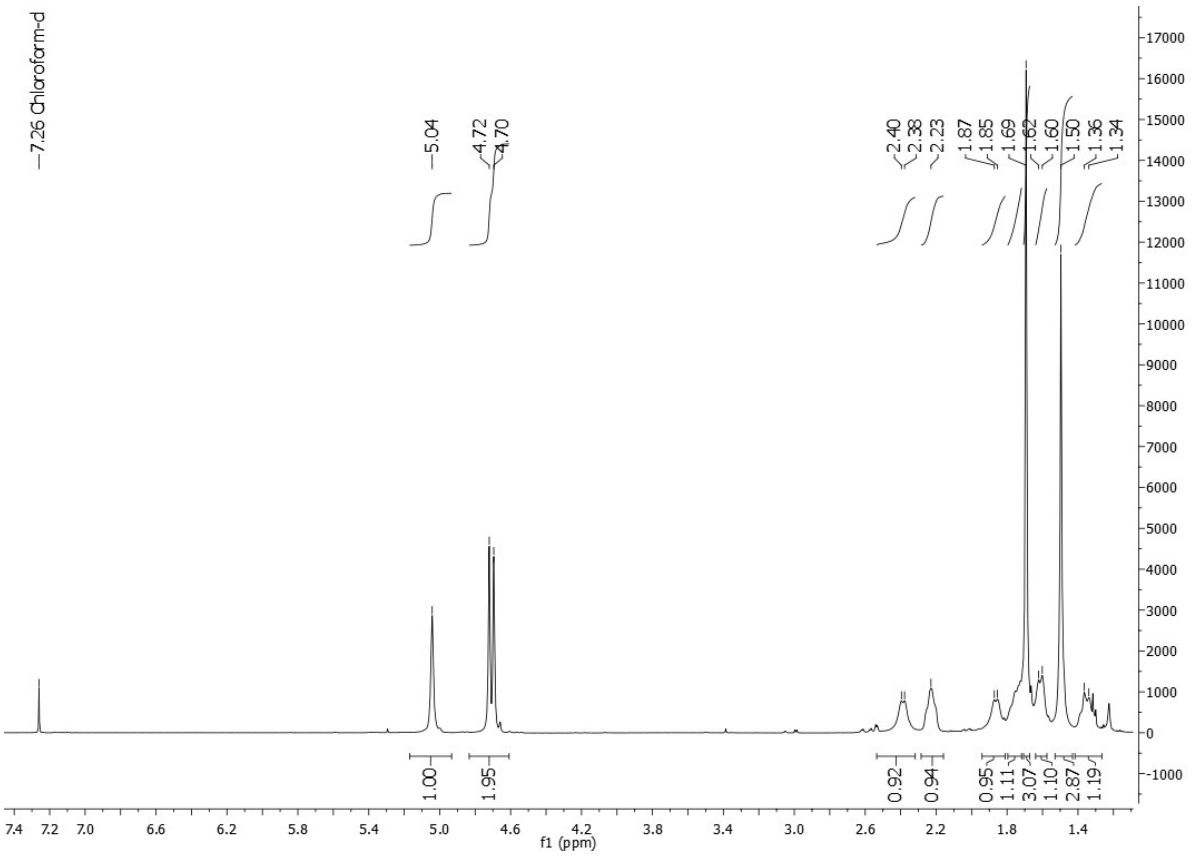


*trans**-PLimC *cis**-PLimC *trans*-PlimC

Group	^{1}H (δ, ppm)	^{13}C (δ, ppm)
1	1.69	21.65
2	-	81.97
3	2.38, 2.40	30.71
4	1.34, 1.60	25.90
5	2.23	37.55
6	1.62, 1.86	30.95
7	5.04	75.40
8	-	152.06
9	-	109.42
10	1.50	20.84
11	4.70, 4.72	148.76
12	5.08	152.43
13	5.12	153.77

[6] C. M. Byrne, S. D. Allen, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, **2004**, 126, 11404-11405.

[7] L. Peña Carrodeguas, J. González-Fabra, F. Castro-Gómez, C. Bo and A. W. Kleij, *Chem.-Eur. J.*, **2015**, 21, 6115-6122.



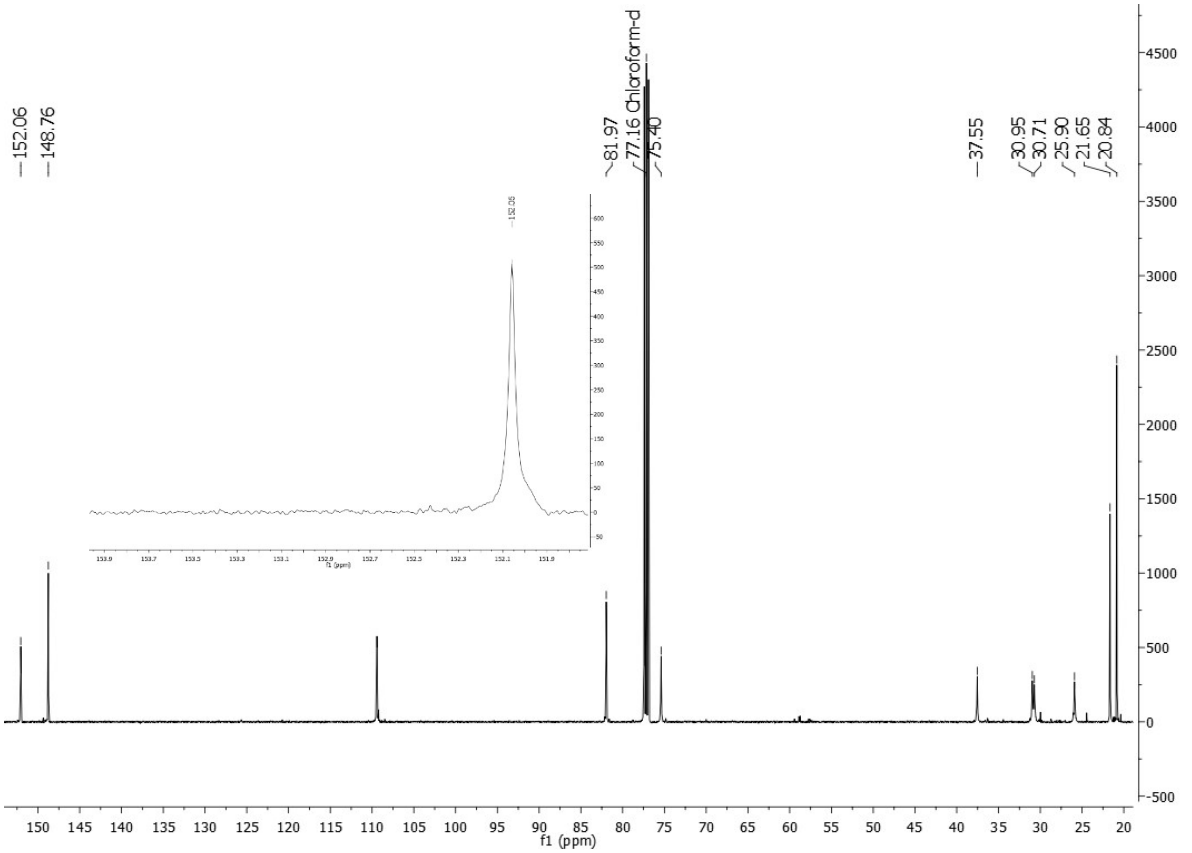
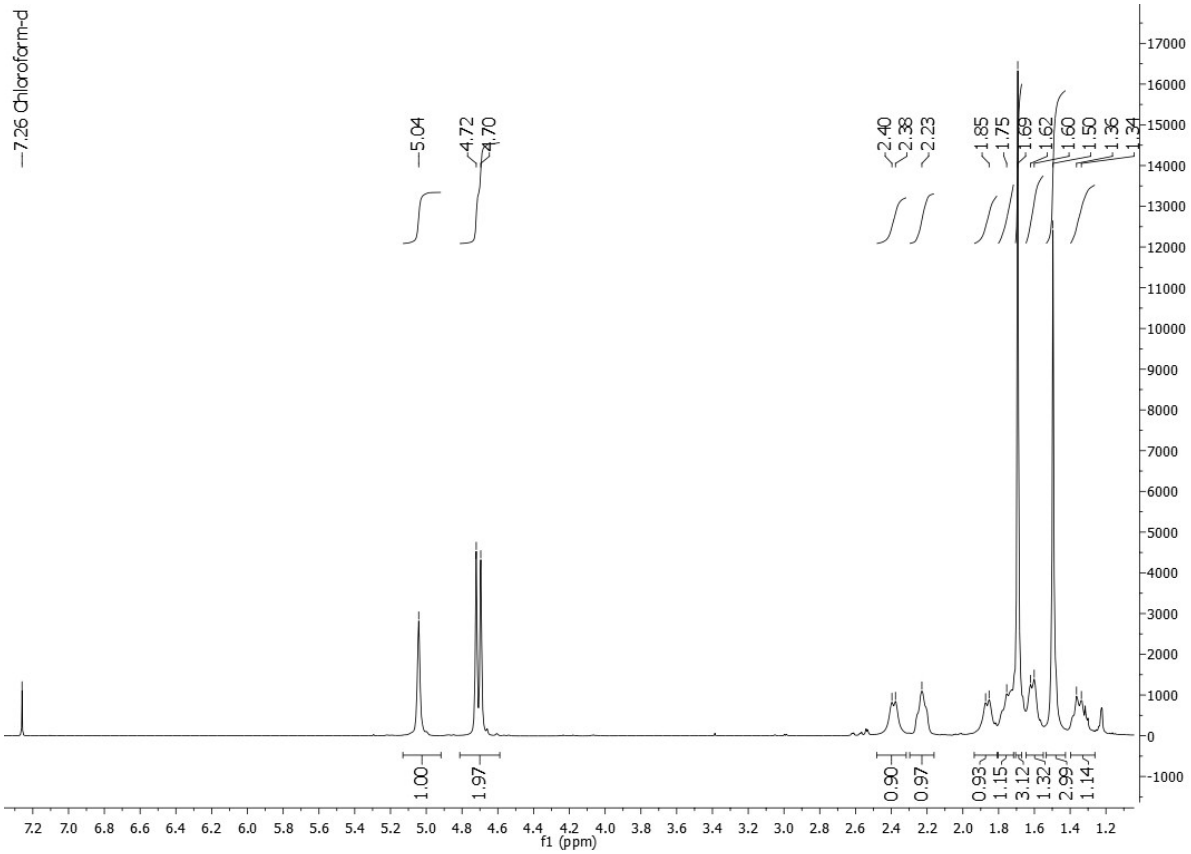


Figure S19. ^{1}H and ^{13}C NMR spectra of Poly(limonene carbonate), Table 3, Entry 1.



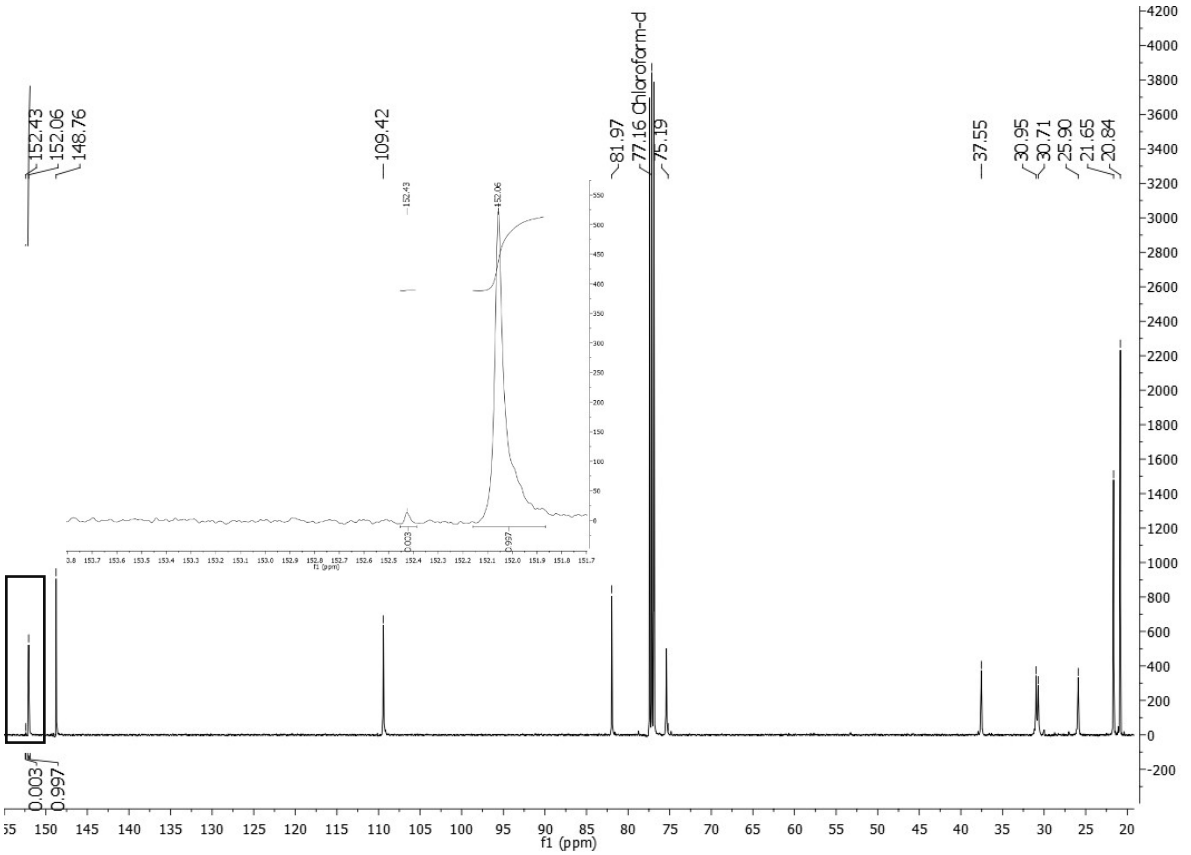
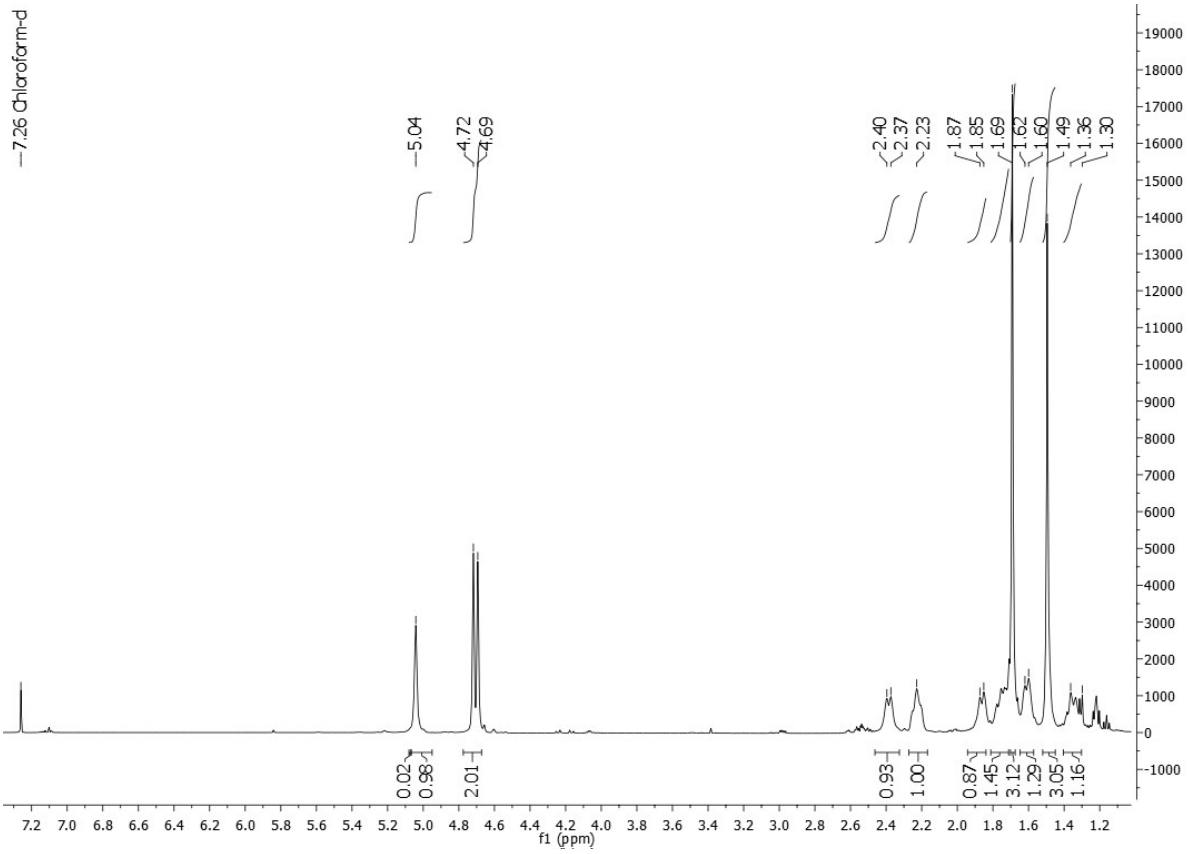
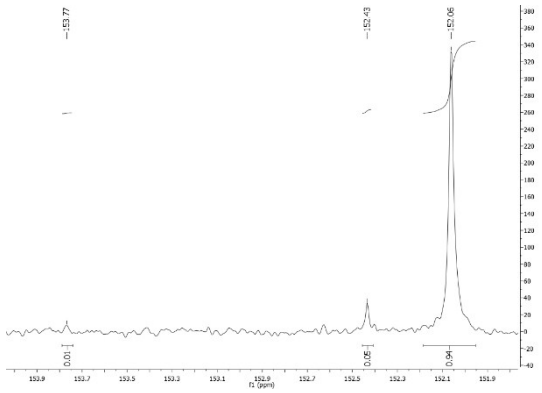


Figure S20. ^{1}H and ^{13}C NMR spectra of Poly(limonene carbonate), Table 3, Entry 2.





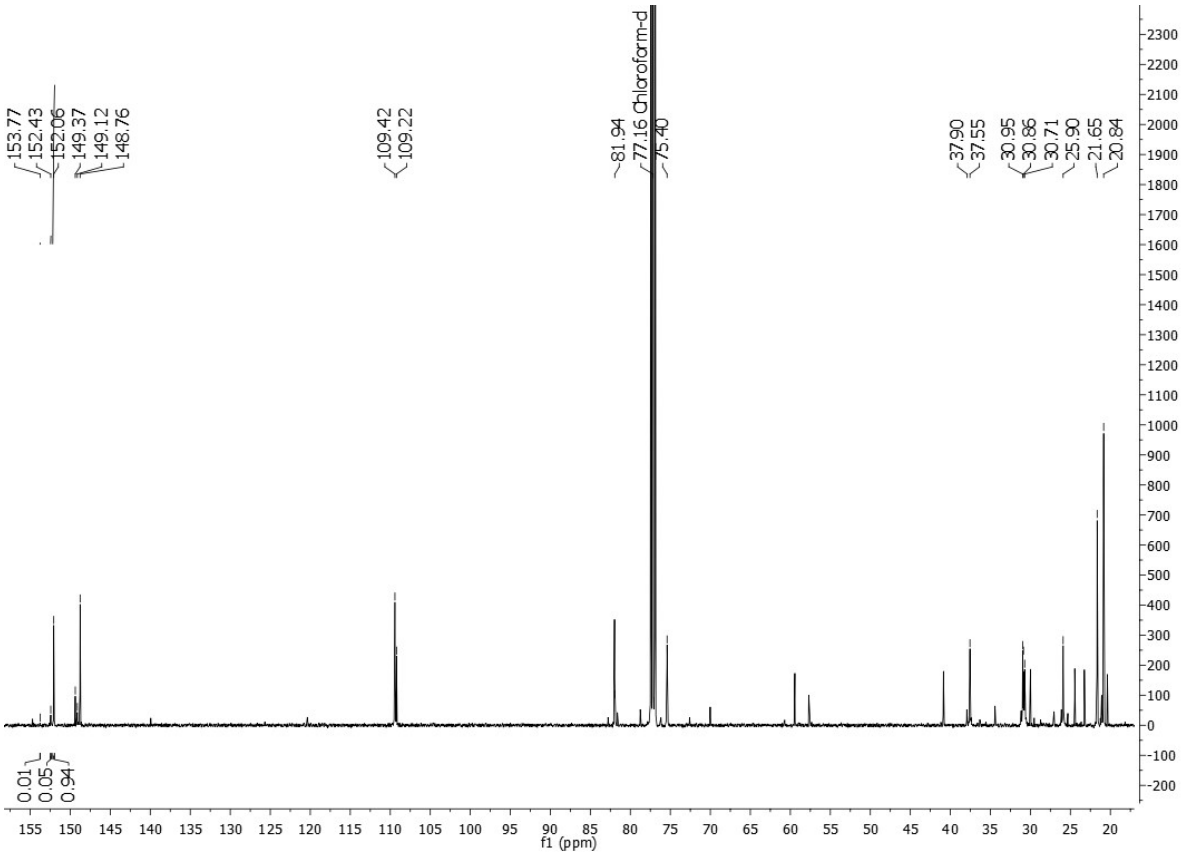


Figure S21. ^{1}H and ^{13}C NMR spectra of Poly(limonene carbonate), Table 3, Entry 3.

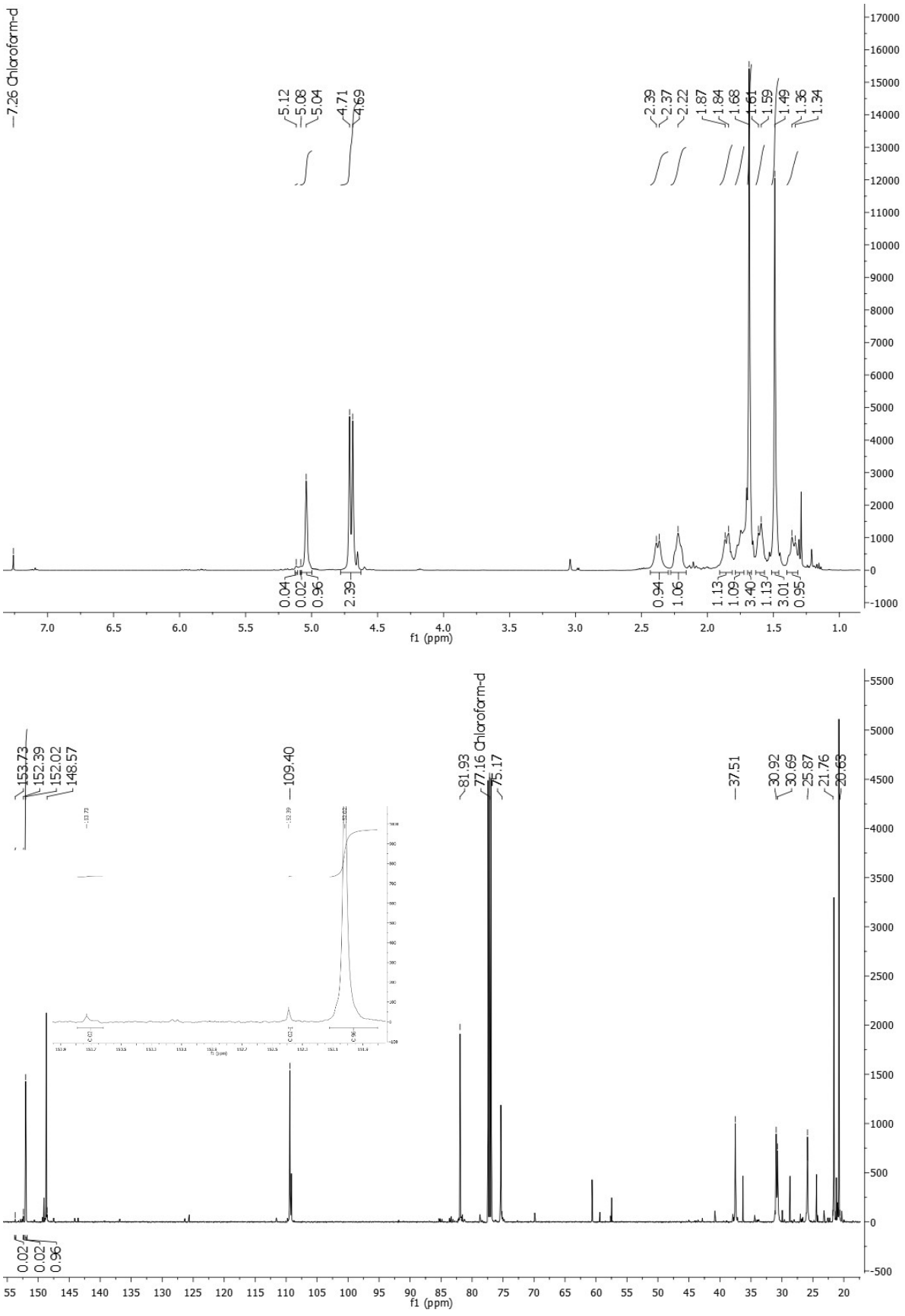


Figure S22. ^{1}H and ^{13}C NMR spectra of Poly(limonene carbonate), Table 3, Entry 4.

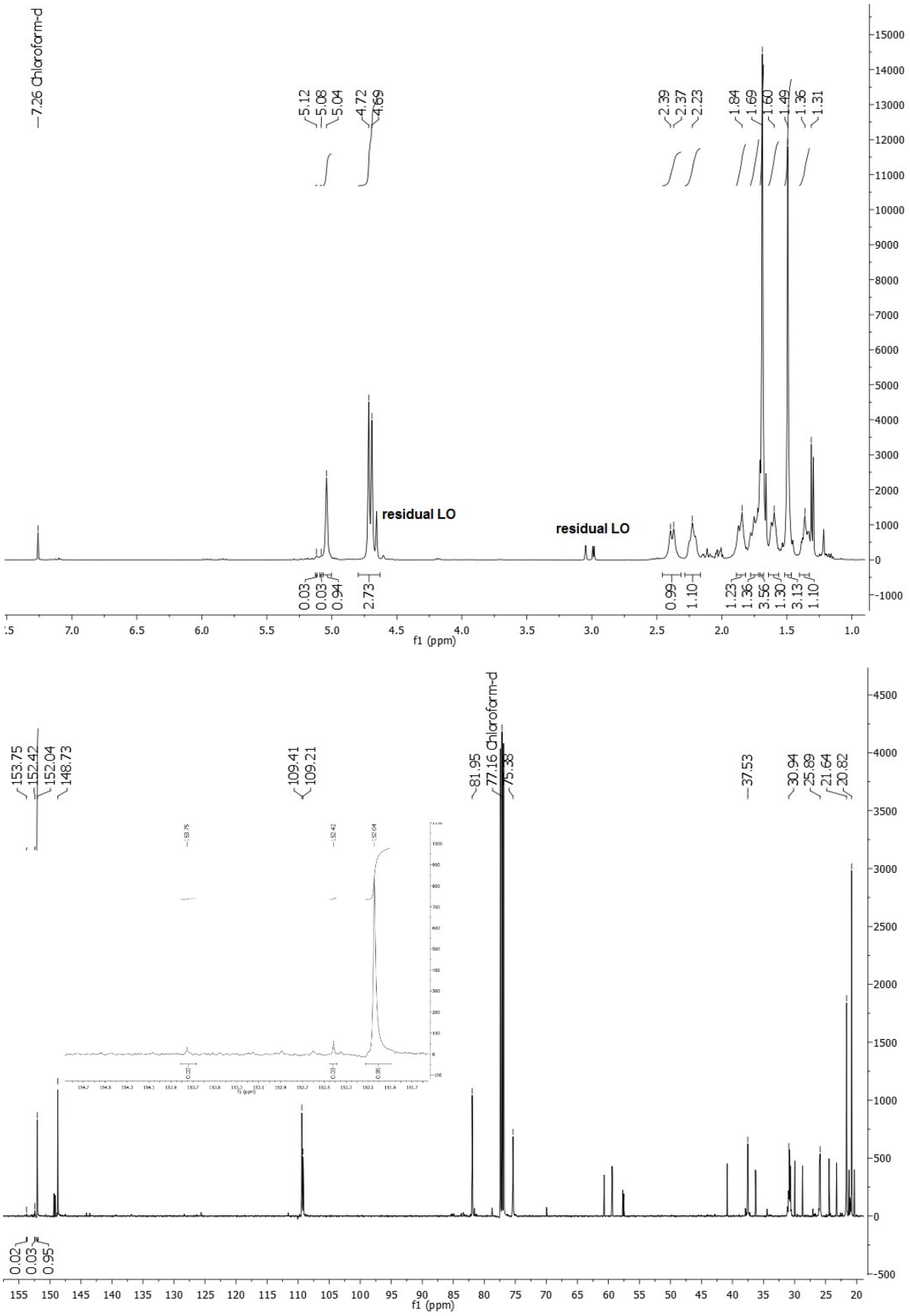


Figure S23. ^{1}H and ^{13}C NMR spectra of Poly(limonene carbonate), Table 3, Entry 5.

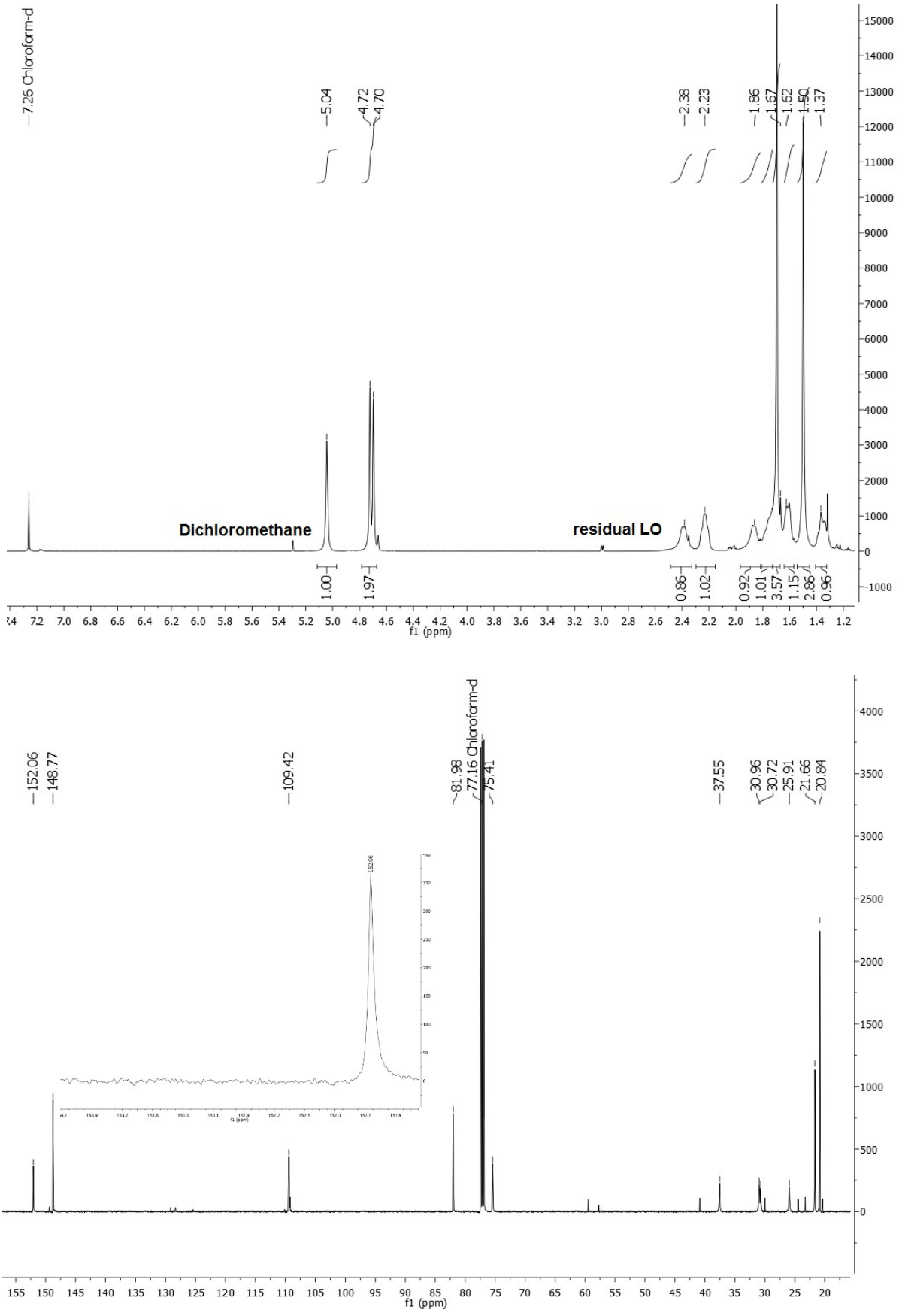


Figure S24. ^{1}H and ^{13}C NMR spectra of Poly(limonene carbonate), Table 3, Entry 6.

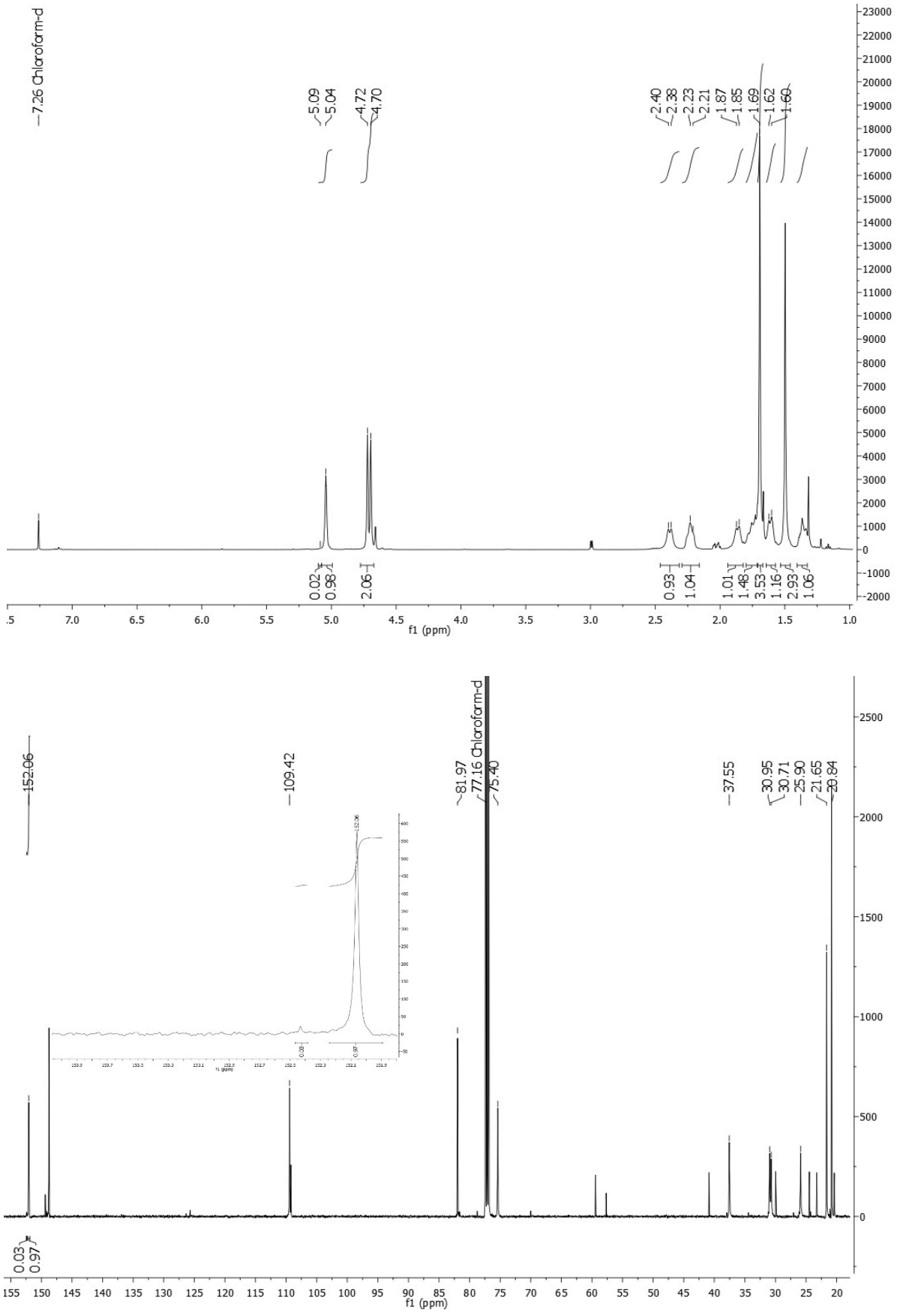


Figure S25. ^{1}H and ^{13}C NMR spectra of Poly(limonene carbonate), Table 3, Entry 7.

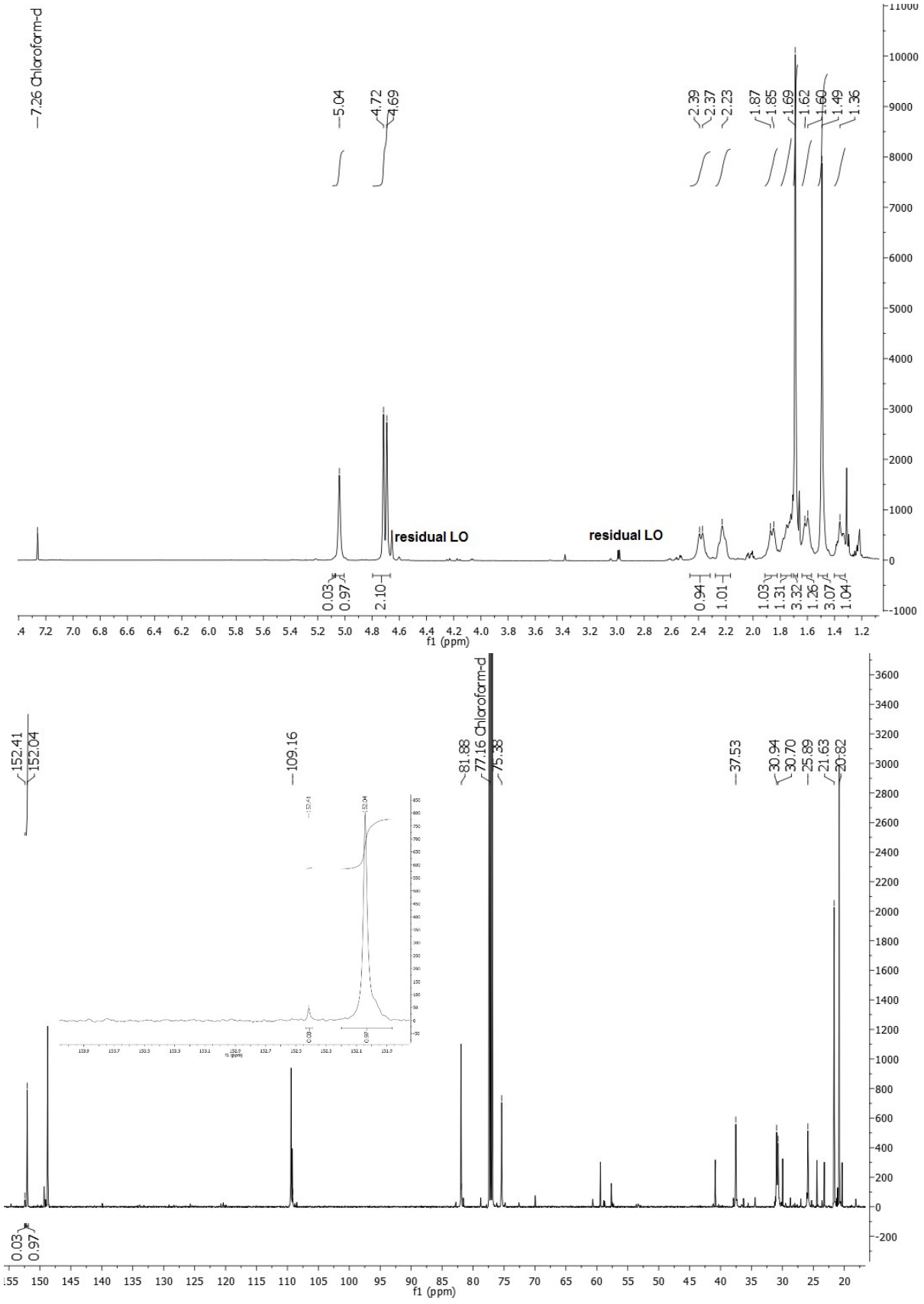


Figure S26. ^{1}H and ^{13}C NMR spectra of Poly(limonene carbonate), Table 3, Entry 8.

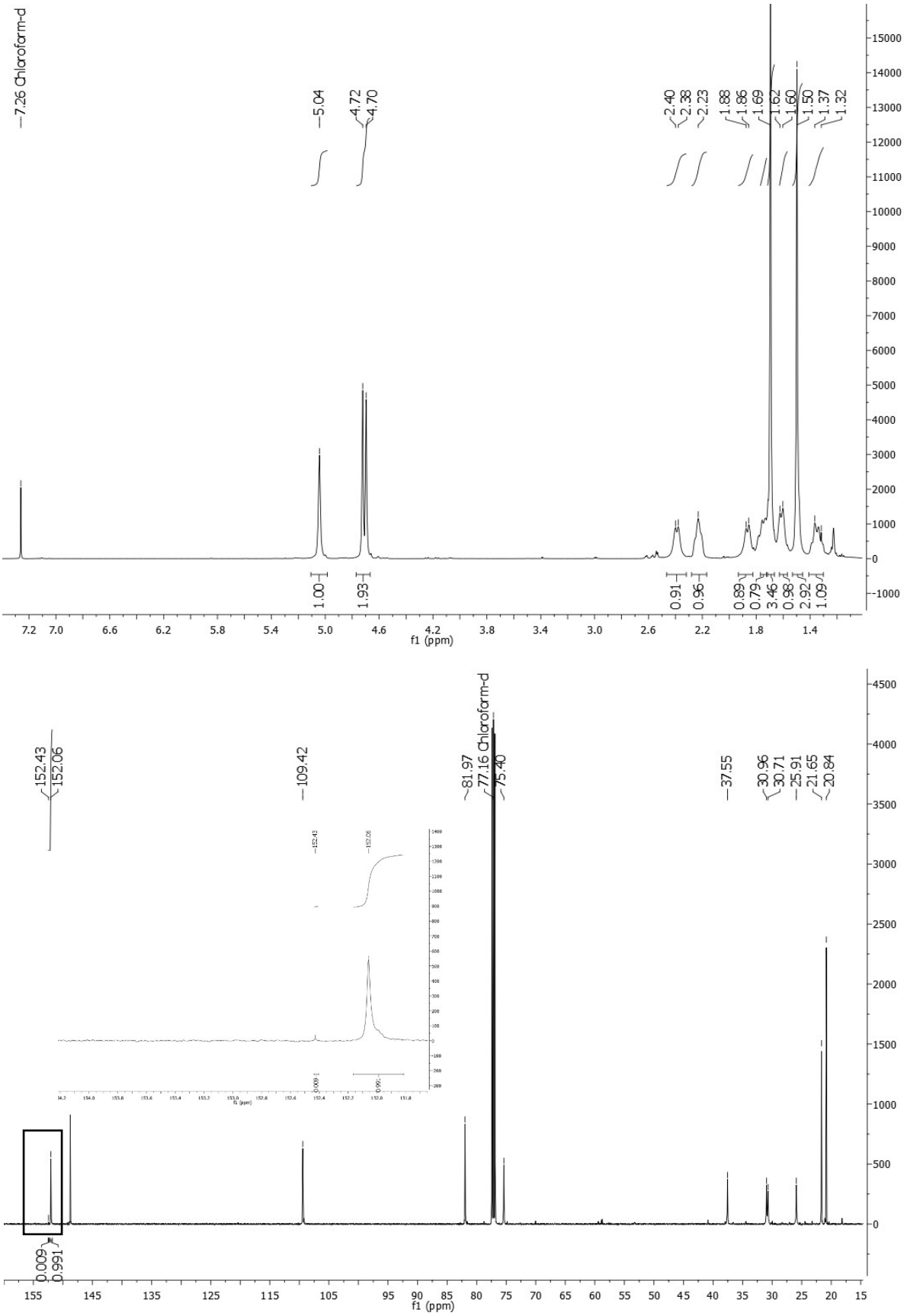


Figure S27. ^{1}H and ^{13}C NMR spectra of Poly(limonene carbonate), Table 3, Entry 9.

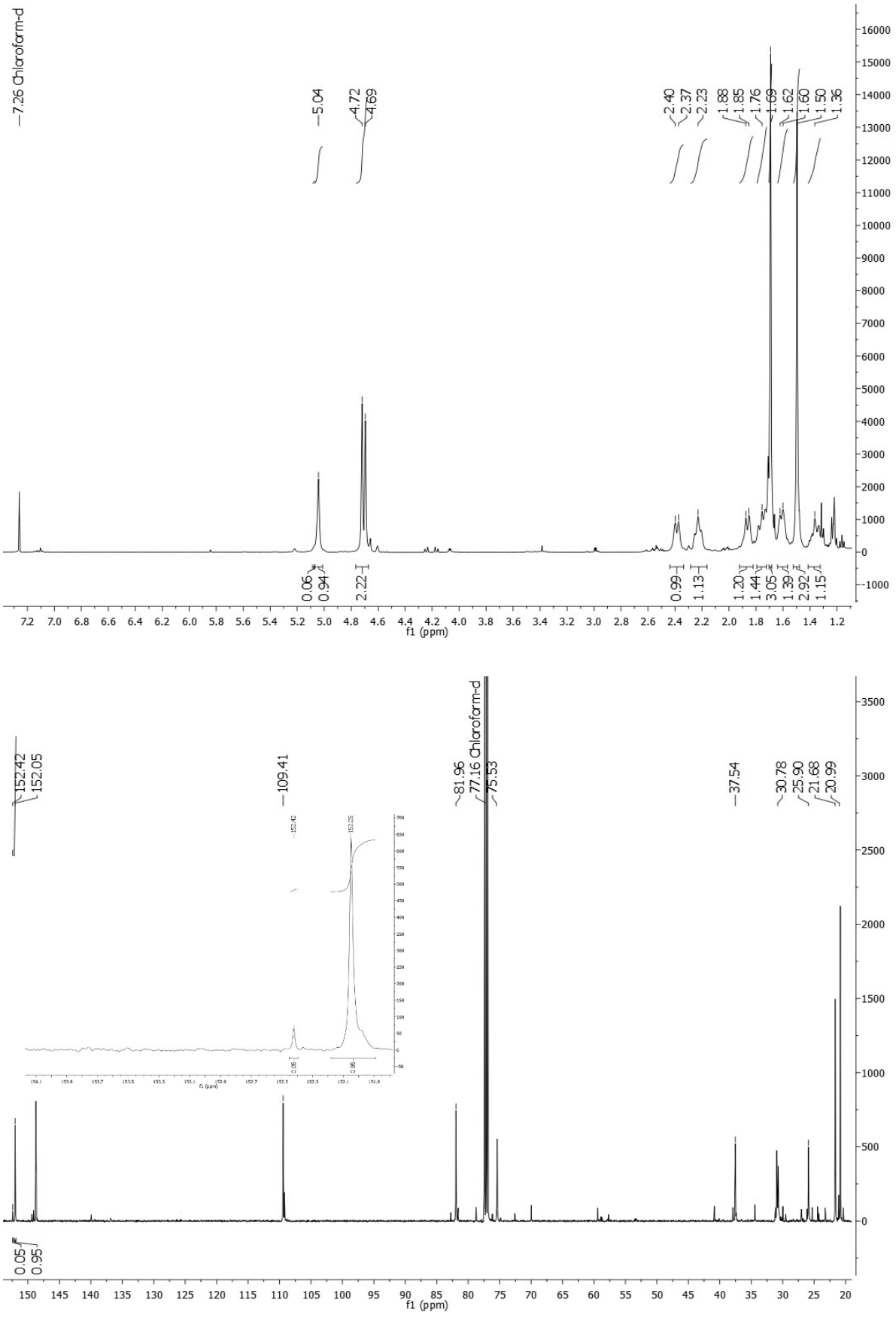


Figure S28. ^{1}H and ^{13}C NMR spectra of Poly(limonene carbonate), Table 3, Entry 10.

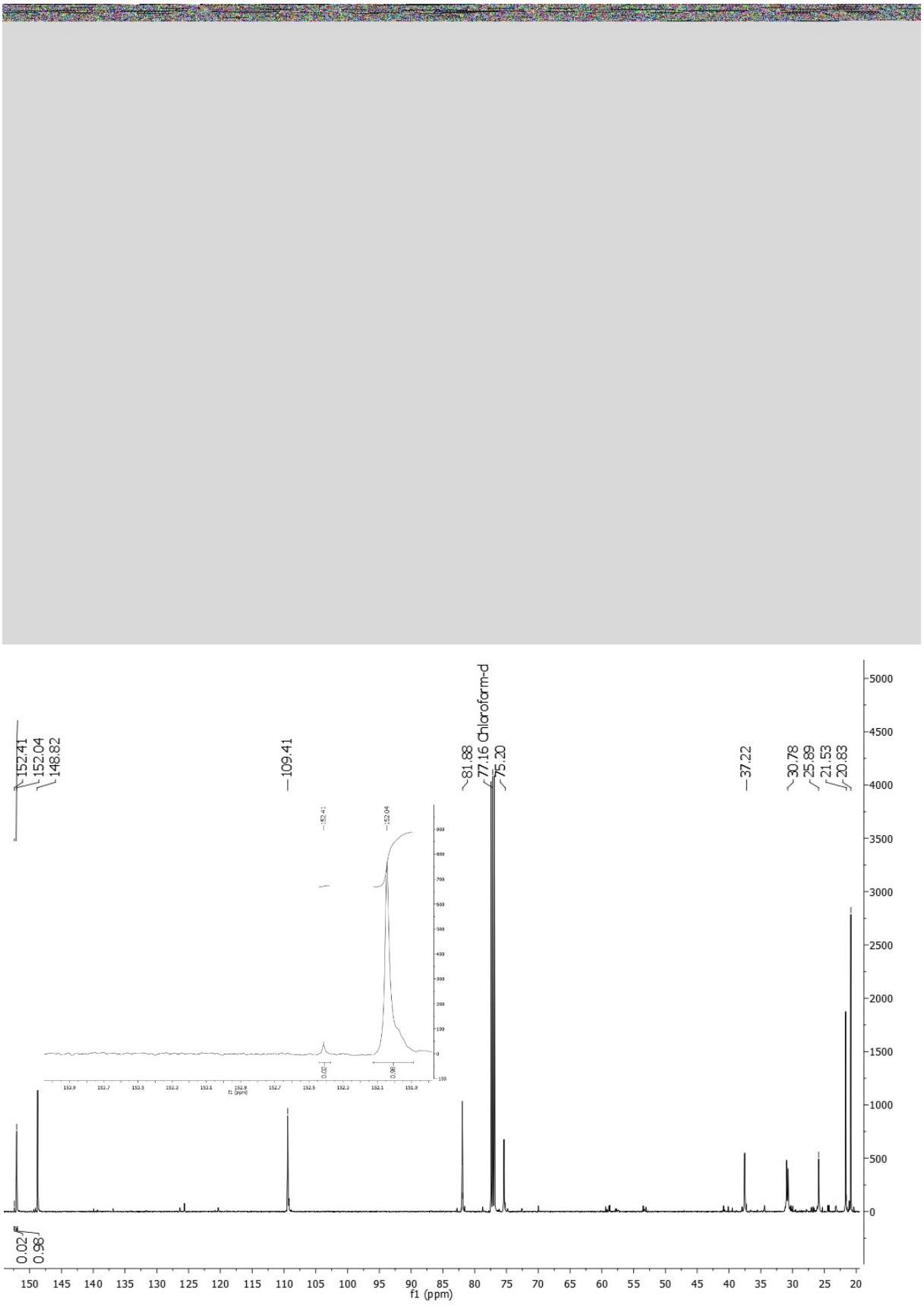


Figure S29. ^{1}H and ^{13}C NMR spectra of Poly(limonene carbonate), Table 3, Entry 13.

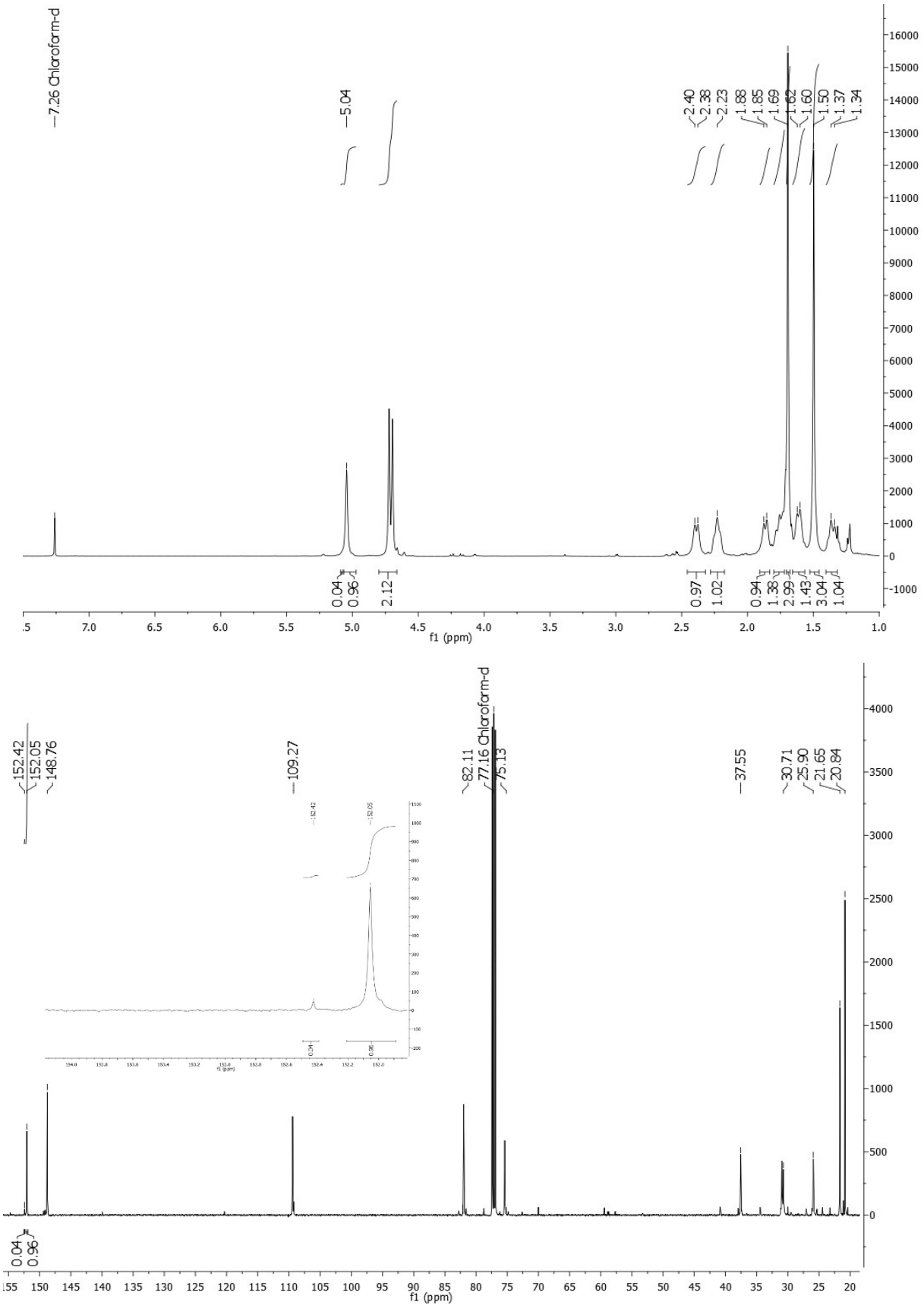


Figure S30. ^{1}H and ^{13}C NMR spectra of Poly(limonene carbonate), Table 3, Entry 14.

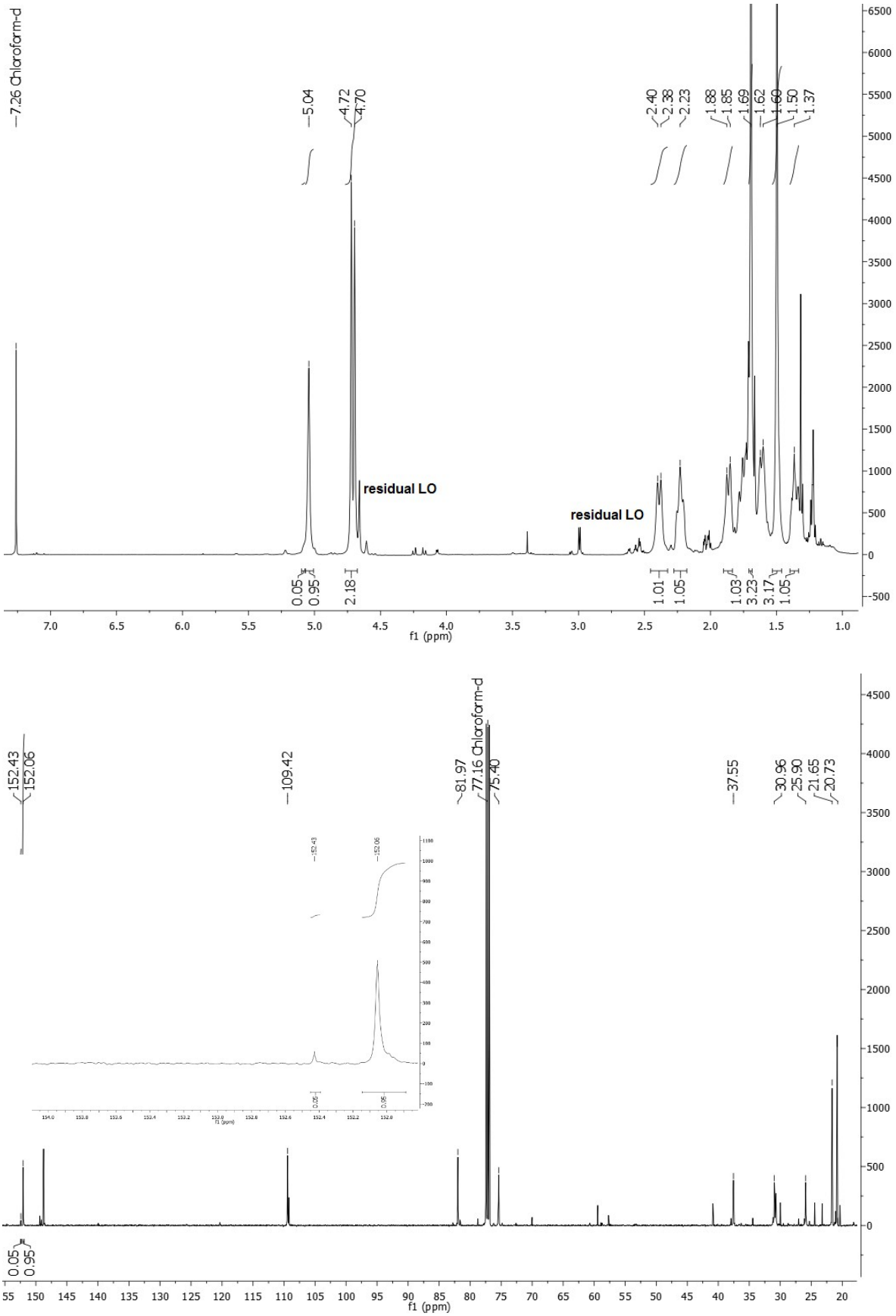


Figure S31. ^{1}H and ^{13}C NMR spectra of Poly(limonene carbonate), Table 3, Entry 15.

10. Single Crystal X-Ray Determination

General

Data were collected on a single crystal X-ray diffractometer equipped with a CCD detector (APEX II, *κ*-CCD), a fine-focus sealed tube with MoK_α radiation (λ = 0.71073 Å) and a Triumph monochromator using the APEX II software package (**1**) or with a CMOS detector (APEX III, *κ*-CMOS), an IMS microsource with MoK_α radiation (λ = 0.71073 Å) and a Helios optic using the APEX III software package (**2**).[1,2] The crystals were fixed on the top of a kapton micro sampler with perfluorinated ether, transferred to the diffractometer and frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorentz and polarization effects, scan speed, and background using SAINT.[3] Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS.[3] Space group assignments were based upon systematic absences, *E* statistics, and successful refinement of the structures. Structures were solved using SHELXT with the aid of successive difference Fourier maps, and were refined against all data using the APEX III software in conjunction SHELXL-2014 and SHELXLE.[4] [2] [5] [6] Hydrogen atoms were calculated in ideal positions as follows: Methyl hydrogen atoms were refined as part of rigid rotating groups, with a C–H distance of 0.98 Å and $U_{iso(H)} = 1.5 \cdot U_{eq(C)}$. Other H atoms were placed in calculated positions and refined using a riding model with methylene and aromatic C–H distances of 0.99 Å and 0.95 Å, respectively, other C–H distances of 1.00 Å and $U_{iso(H)} = 1.2 \cdot U_{eq(C)}$. Non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2-F_c^2)^2$ with the SHELXL-97 weighting scheme.[5] Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*.[7]. **2** contains four disordered molecules of toluene in the unit cell which were treated as a diffuse contribution to the overall scattering without specific atom positions using the PLATON/SQUEEZE procedure.[8] Images were created with PLATON.[9]

References

[1] Bruker, *APEX suite of crystallographic software, APEX 2 Version 2014-9.0*, Bruker AXS Inc., Madison, Wisconsin, USA, **2014**.

[2] Bruker, *APEX suite of crystallographic software, APEX 3 Version 2015-5.2*, Bruker AXS Inc., Madison, Wisconsin, USA, **2015**.

[3] Bruker, *SAINT, Version 8.34A and SADABS, Version 2014/5*, Bruker AXS Inc., Madison, Wisconsin, USA, **2014**.

[4] G. M. Sheldrick, *Acta Cryst. A* **2015**, *71*, 3–8.

[5] G. M. Sheldrick, *Acta Cryst. C* **2015**, *71*, 3–8.

[6] C. B. Huebschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Cryst.* **2011**, *44*, 1281–1284.

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Compound 1 (CCDC 1508590)

Diffractometer operator C. Jandl
scanspeed 10 s per frame
dx 80 mm
7296 frames measured in 21 data sets
phi-scans with delta_phi = 0.5
omega-scans with delta_omega = 0.5

Crystal data

$C_{31}H_{45}F_6N_3Si_2Zn$	$F(000)$ = 728
M_r = 695.27	
Triclinic, *P*-1	D_x = 1.325 Mg m^{-3}
Hall symbol: -P 1	Melting point: ? K
a = 10.5225 (11) Å	Mo *K*α radiation, λ = 0.71073 Å
b = 11.8495 (13) Å	Cell parameters from 9867 reflections
c = 16.4988 (18) Å	θ = 2.2–28.3°
α = 91.643 (5)°	μ = 0.83 mm^{-1}
β = 107.641 (5)°	*T* = 100 K
γ = 115.266 (4)°	Fragment, yellow
V = 1742.8 (3) Å^3	0.44 × 0.26 × 0.23 mm
Z = 2	

Data collection

Apex II CCD diffractometer	7111 independent reflections
Radiation source: fine-focus sealed tube	6403 reflections with $I > 2\sigma(I)$
Triumph monochromator	R_{int} = 0.030
Detector resolution: 16 pixels mm^{-1}	θ_{max} = 26.4°, θ_{min} = 1.9°
phi– and ω–rotation scans	*h* = −13 13
Absorption correction: multi-scan *SADABS* 2014/5, Bruker, 2014	*k* = −14 14
T_{min} = 0.673, T_{max} = 0.746	*l* = −20 20
41885 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.036	H-atom parameters constrained
$wR(F^2)$ = 0.099	$W = 1/[\Sigma^2(FO^2) + (0.0479P)^2 + 2.1134P]$ WHERE $P = (FO^2 + 2FC^2)/3$
S = 1.05	$(\Delta/\sigma)_{max}$ = 0.001
7111 reflections	$\Delta\rho_{max}$ = 1.21 e Å^{-3}
398 parameters	$\Delta\rho_{min}$ = −0.39 e Å^{-3}
0 restraints	Extinction correction: none
0 constraints	Extinction coefficient: -
Primary atom site location: intrinsic phasing	

Compound 2 (CCDC 1508589)

Diffractometer operator C. Jandl
scanspeed 10 s per frame
dx 50 mm
3249 frames measured in 7 data sets
phi-scans with delta_phi = 0.5
omega-scans with delta_omega = 0.5
shutterless mode

Crystal data

$C_{56}H_{72}F_{12}N_4O_2Si_2Zn_2$	
M_r = 1248.14	D_x = 1.200 Mg m^{-3}
Monoclinic, $P2_1/c$	Melting point: ? K
Hall symbol: -P 2ybc	Mo $K\alpha$ radiation, λ = 0.71073 Å
a = 11.3281 (6) Å	Cell parameters from 9241 reflections
b = 24.0698 (13) Å	θ = 2.3–27.5°
c = 13.5639 (6) Å	μ = 0.80 mm^{-1}
β = 110.910 (2)°	T = 100 K
V = 3454.8 (3) Å^3	Fragment, light yellow
Z = 2	0.44 × 0.39 × 0.17 mm
F(000) = 1296	

Data collection

Bruker Photon CMOS diffractometer	7623 independent reflections
Radiation source: IMS microsource	7048 reflections with $I > 2\sigma(I)$
Helios optic monochromator	R_{int} = 0.030
Detector resolution: 16 pixels mm^{-1}	θ_{max} = 27.1°, θ_{min} = 2.2°
phi– and ω–rotation scans	h = −14 14
Absorption correction: multi-scan *SADABS* 2014/5, Bruker, 2014	k = −30 30
T_{min} = 0.674, T_{max} = 0.746	l = −14 17
139559 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.028$	H-atom parameters constrained
$wR(F^2) = 0.071$	$W = 1/[\Sigma^2(FO^2) + (0.031P)^2 + 2.6115P]$ WHERE $P = (FO^2 + 2FC^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} = 0.002$
7623 reflections	$\Delta\rho_{max} = 0.40$ e Å^{-3}
416 parameters	$\Delta\rho_{min} = -0.39$ e Å^{-3}
165 restraints	Extinction correction: none
0 constraints	Extinction coefficient: -
Primary atom site location: intrinsic phasing	