Supporting Information
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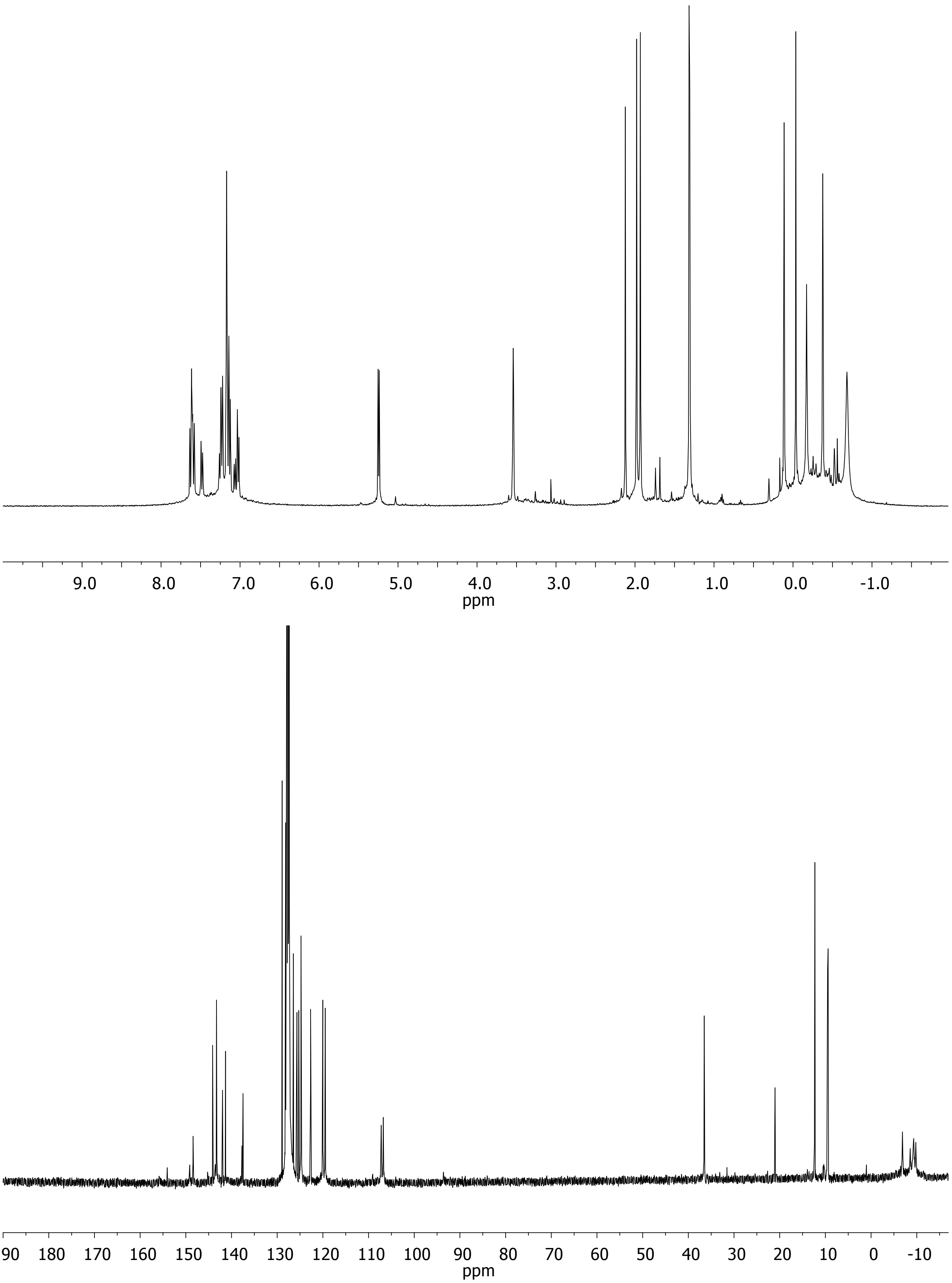
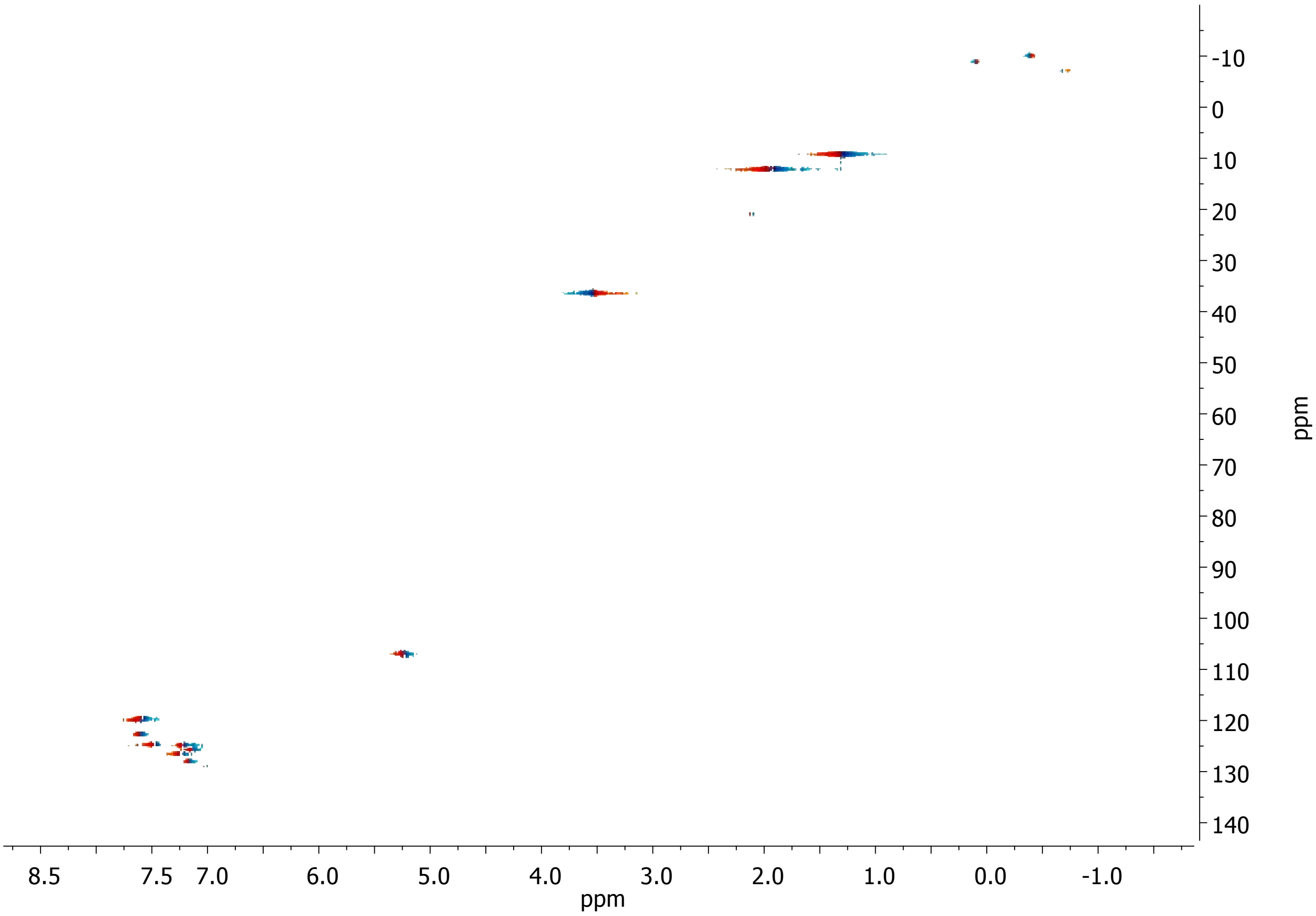
Synthesis of Helical Aluminium Catalysts for Cyclic Carbonate Formation

Figure S1. NMR Spectra for complex **7** in C_6D_6

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ppm

Crystallographic data and selected interatomic distances and angles for compound 1

Table S1. Crystal data and structure refinement for **1**

Compound	**1**
Formula	$C_{40}H_{49}Al_2N_5S$
M	685.86
CCDC	1884536
Crystal System	Monoclinic
Space group	$P2_1/c$
T [K]	100
a [Å]	16.119(5)
b [Å]	24.785(5)
c [Å]	21.326(4)
α [deg]	90
β [deg]	115.151(16)
γ [deg]	90
V [Å^3]	7712(3)
Z	8
Density [gcm^{-3}]	1.181
μ [mm^{-1}]	0.164
Observed reflections	39723
R_{int}	0.0636
R1^b / wR2^c [I>2σ(I)]	0.0842 / 0.2258
R1^b / wR2^c (all data)	0.1092 / 0.2461
GoF	1.106
Largest diff. pk and hole [eÅ^{-3}]	0.995 and -0.554

$^a S = [\Sigma w(F_0^2 - F_c^2)^2 / (N_{obs} - N_{para}m)]^{1/2}$. $^b R_1 = \Sigma||F_0|-|F_c|| / \Sigma|F_0|$.

$^c wR_2 = [\Sigma w(F_0^2 - F_c^2)^2 / \Sigma wF_0^2]^{1/2}$ $w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$ where $P = (\max(F_0^2,0) + 2F_c^2)/3$

Table S2. **Selected interatomic distances and angles for compound 1**

Bond distances (Å)		Bond angles (º)	
S(1A)–Al(1)	2.295(2)	Al(1)–S(1A)–C(14A)	97.9(2)
S(1A)–C(14A)	1.775(5)	S(1A)–Al(1) –N(1A)	95.0(1)
Al(1)–N(1A)	1.957(6)	S(1A)–Al(1)–C(1A)	118.3(2)
Al(1)–C(1A)	1.970(6)	S(1A)–Al(1)–C(2A)	105.5(2)
Al(1)–C(2A)	1.955(7)	N(1A)–Al(1)–C(1A)	107.3(2)
Al(2)–N(4A)	1.966(4)	N(1A)–Al(1)–C(2A)	112.2(2)
Al(2)–N(5A)	1.897(5)	C(1A)–Al(1)–C(2A)	116.6(3)
Al(2)–C(1AA)	1.969(5)	N(4A)–Al(2)–N(5A)	92.5(2)
Al(2)–C(2AA)	1.957(7)	N(4A)–Al(2)–C(1AA)	110.5(2)
N(1A)–N(2A)	1.384(6)	N(4A)–Al(2)–C(2AA)	108.5(2)
N(1A)–C(4A)	1.345(7)	N(5A)–Al(2)–C(1AA)	110.9(2)
N(2A)–C(6A)	1.350(8)	N(5A)–Al(2)–C(2AA)	113.9(2)
N(2A)–C(13A)	1.432(6)	C(1AA)–Al(2)–C(2AA)	117.7(2)
N(3A)–N(4A)	1.386(5)	Al(1)–N(1A)–N(2A)	118.4(3)
N(3A)–C(9A)	1.371(6)	Al(1)–N(1A)–C(4A)	132.7(4)
N(3A)–C(13A)	1.429(6)	N(2A)–N(1A)–C(4A)	106.1(4)
N(4A)–C(11A)	1.345(6)	N(1A)–N(2A)–C(6A)	110.2(4)
N(5A)–C(14A)	1.369(5)	N(1A)–N(2A)–C(13A)	121.9(4)
N(5A)–C(15A)	1.421(7)	C(6A)–N(2A)–C(13A)	127.6(4)
		N(4A)–N(3A)–C(9A)	109.7(4)
		N(4A)–N(3A)–C(13A)	121.5(4)
		C(9A)–N(3A)–C(13A)	128.8(4)
		Al(2)–N(4A)–N(3A)	117.6(3)
		Al(2)–N(4A)–C(11A)	133.6(4)
		N(3A)–N(4A)–C(11A)	106.7(4)
		Al(2)–N(5A)–C(14A)	117.8(3)
		A(l2)–N(5A)–C(15A)	120.2(4)
		C(14A)–N(5A)–C(15A)	120.3(4)

Figure S2. *M* (left) and *P* (right) enantiomers of compound **1** in the unit cell.

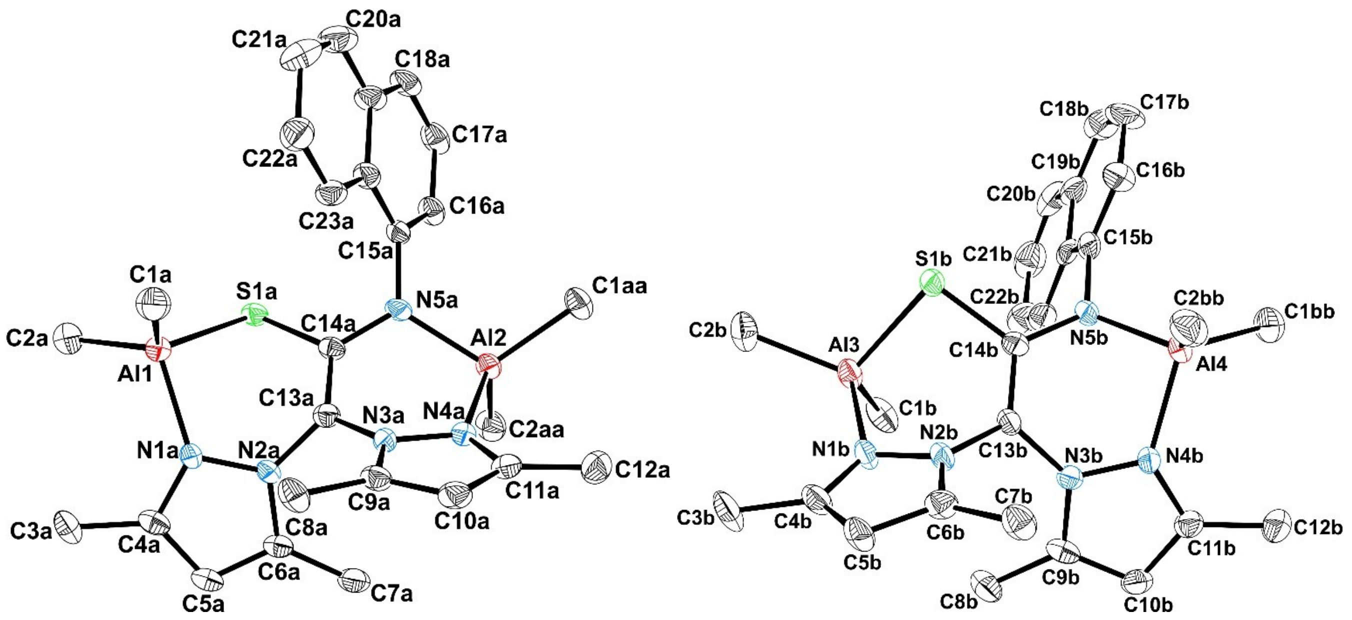


Table S3. Non-covalent interactions found in complex **1**. *β* is the angle formed by H–centroid and H–plane lines in the case of the CH···π interaction. *α* is the dihedral angle formed by the plane of the two rings of the π–π stacking.

CH···*π* interactions			
Groups	**d(H···centroid) Å**	**d(H···plane) Å**	***β*** **°**
(C7)H7A2···ph(C15B-C24B)	3.3	3.2	16.5
ph(C15A-C24A)···(C7)H7B2	3.3	3.2	9.9
***π*–*π* stacking**			
Groups	**d(Ct···Ct) Å**	**d(Ct···plane) Å**	***α*** **°**
pz(N1A-N2A)···ph(C19B-C24B)	3.9	3.6	4.6
ph(C19A-C24A)··· pz(N1B-N2B)-	3.9	3.5	4.9

General procedures for cyclic carbonates synthesis and polyether-polycarbonates

General procedure for synthesis of cyclic carbonates at 1 bar pressure

An epoxide **9a–j** (1.7 mmol), complex **2** (46.3 mg, 83.0 μmol) and Bu_4NBr (26.7 mg, 83.0 μmol) were placed in a sample vial fitted with a magnetic stirrer bar and placed in a large conical flask. Cardice pellets were added to the conical flask which was fitted with a rubber stopper pierced by a deflated balloon. The reaction mixture was stirred for 24 h at 25 °C for epoxides **9a–e**,**h–j** or 50 °C for epoxides **9f,g**. The conversion of epoxide into cyclic carbonate was then determined by analysis of a sample by ^{1}H-NMR spectroscopy. The remaining sample was filtered through a plug of silica, eluting with CH_2Cl_2 to remove the catalyst. The eluent was evaporated *in vacuo* to give either the pure cyclic carbonate or a mixture of cyclic carbonate and unreacted epoxide. In the latter case, the mixture was purified by flash chromatography using a solvent system of first hexane, then hexane-EtOAc (9:1), then hexane-EtOAc (3:1), then EtOAc to give the pure cyclic carbonate. Cyclic carbonates **10a**–**j** are all known compounds and the spectroscopic data for samples prepared using complex **2** were consistent with those reported in the literature.[1]

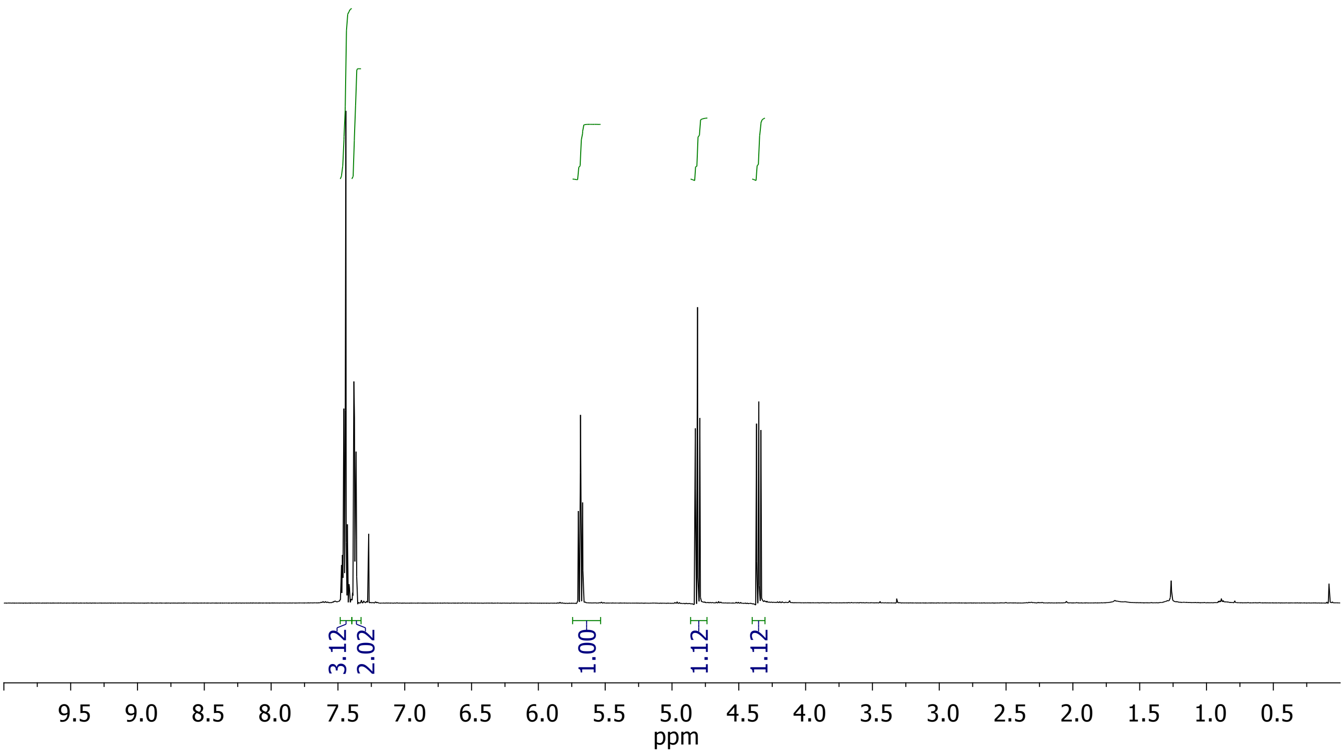
General procedure for synthesis of cyclic carbonates at 10 bar pressure

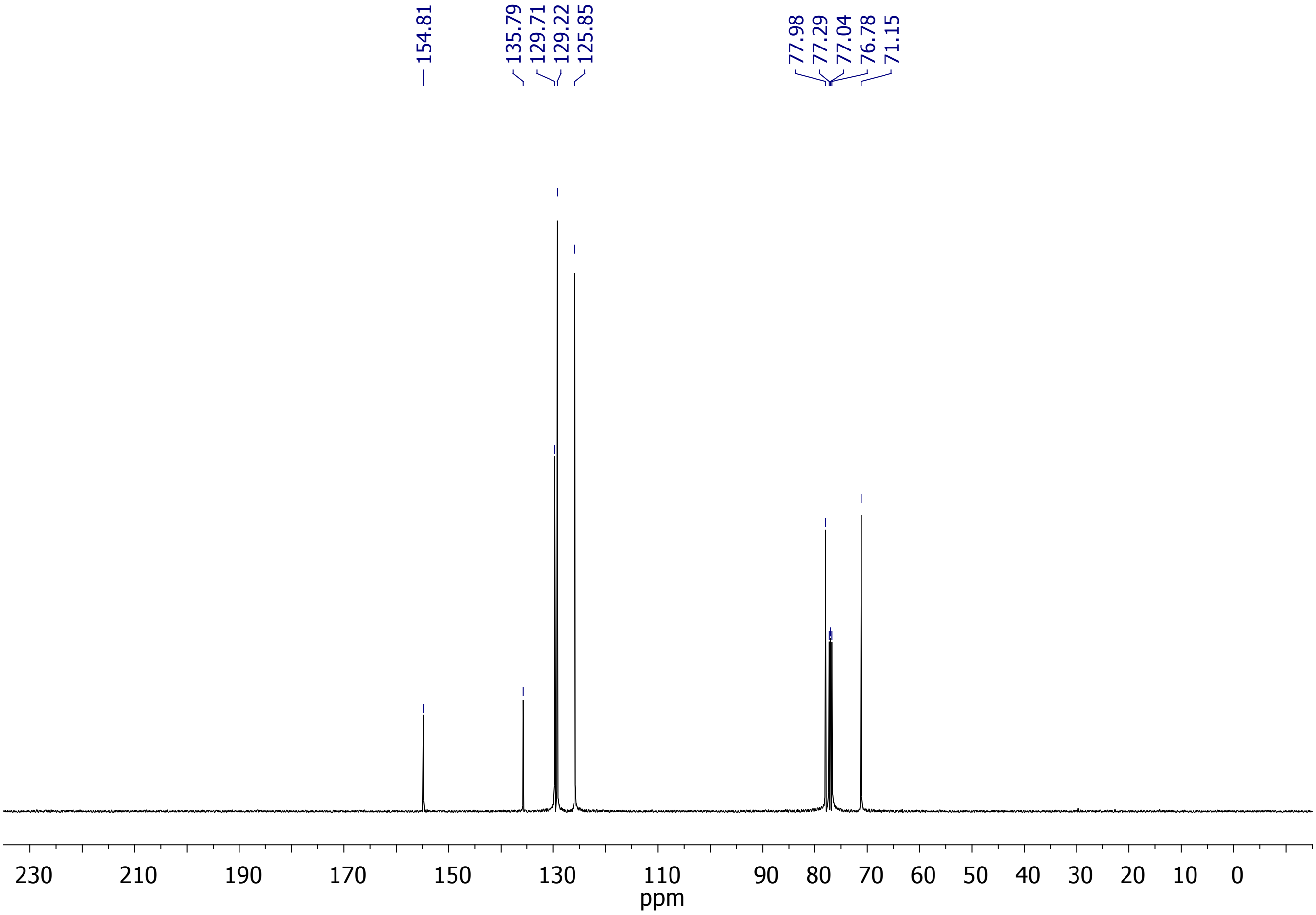
An epoxide **11a**–**e** (1.7 mmol), complex **2** (9.3 mg, 17.0 μmol) and Bu_4NBr (5.3 mg, 17.0 μmol) were placed in a stainless steel pressure reactor with a magnetic stirrer bar. The reactor was pressurised to 10 bar of carbon dioxide and the reaction mixture was stirred 50–90 °C for 16 h. Then the conversion of epoxide into cyclic carbonate **11a**–**e** was determined by analysis of a sample by ^{1}H-NMR spectroscopy. The remaining sample was filtered through a plug of silica, eluting with CH_2Cl_2 to remove the catalyst. The eluent was evaporated *in vacuo* to give a mixture of cyclic carbonate and unreacted epoxide. The mixture was purified by flash chromatography using a solvent system of first hexane, then hexane-EtOAc (9:1), then hexane-EtOAc (3:1), then EtOAc to give the pure cyclic carbonate. Cyclic carbonates **12a**–**e** are all known compounds and the spectroscopic data for samples prepared using complex **2** were consistent with those reported in the literature.[1]

General procedure for synthesis of polyether-polycarbonate

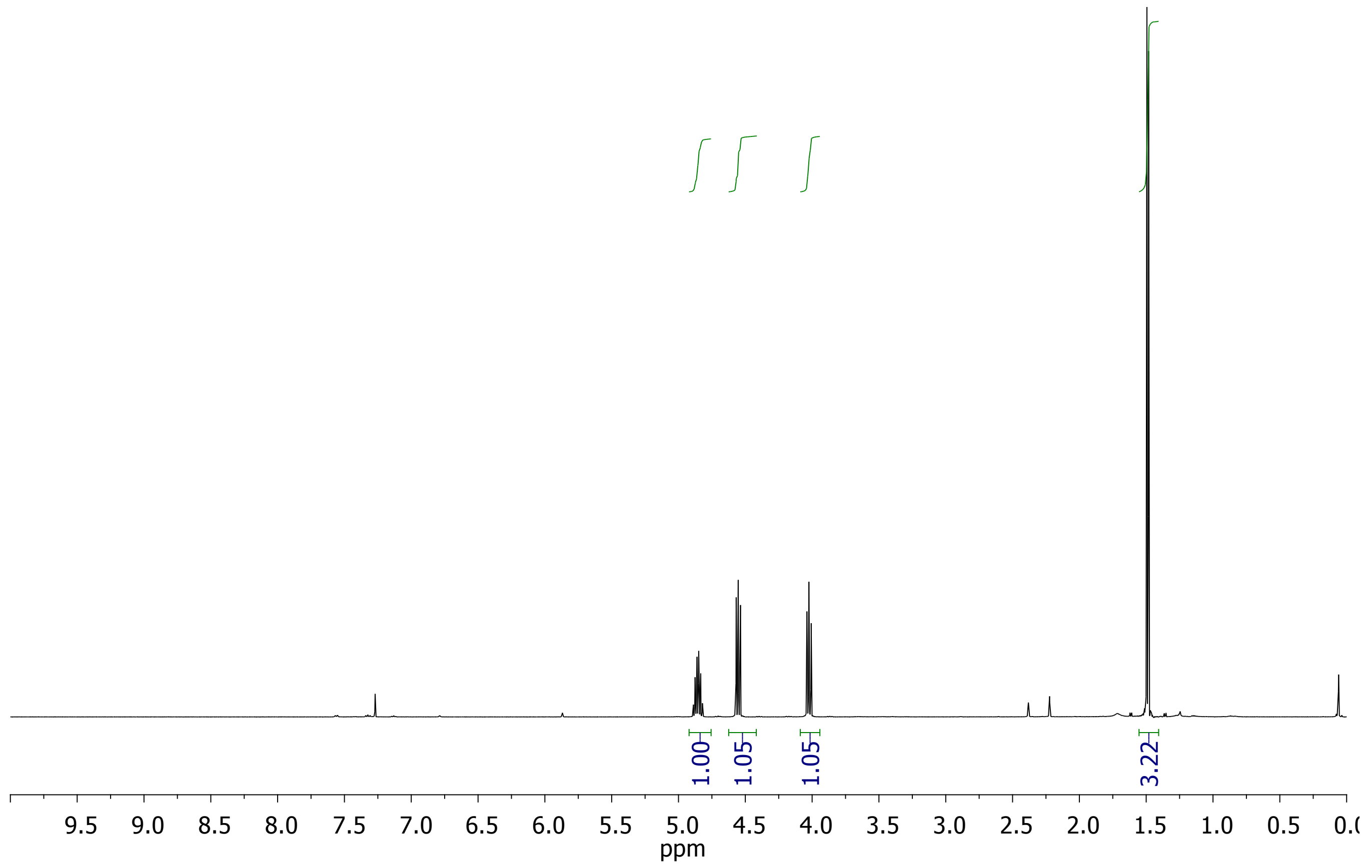
Cyclohexene oxide (0.98 g, 10.0 mmol), complex **2** (0.0–55.7 mg, 0.0–0.1 mmol) and Bu_4NBr (0.0–96.7 mg, 0.0–0.3 mmol) were placed in a stainless steel reactor with a magnetic stirrer bar. The autoclave was sealed, pressurised to 5 bar with CO_2, heated to the desired temperature and then pressurised to 10-40 bar with CO_2. The reaction mixture was subsequently stirred at 50–90 °C for 24 h. The conversion of cyclohexene oxide into cyclohexene carbonate **12f**, polyether or polyether-polycarbonate was determined by analysis of a sample by ^{1}H NMR spectroscopy.[1]

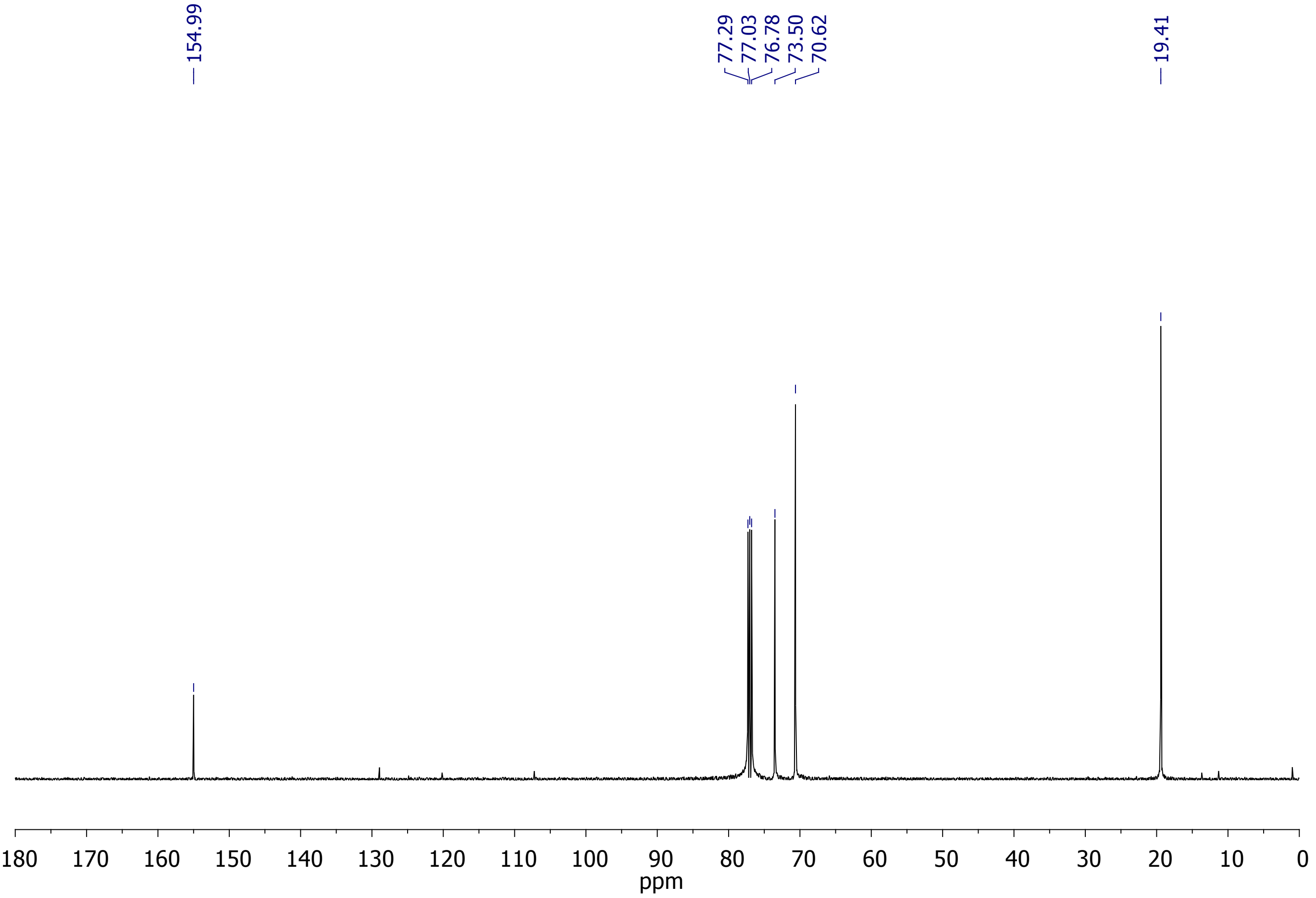
NMR Spectra for styrene carbonate **10a** in $CDCl_3$



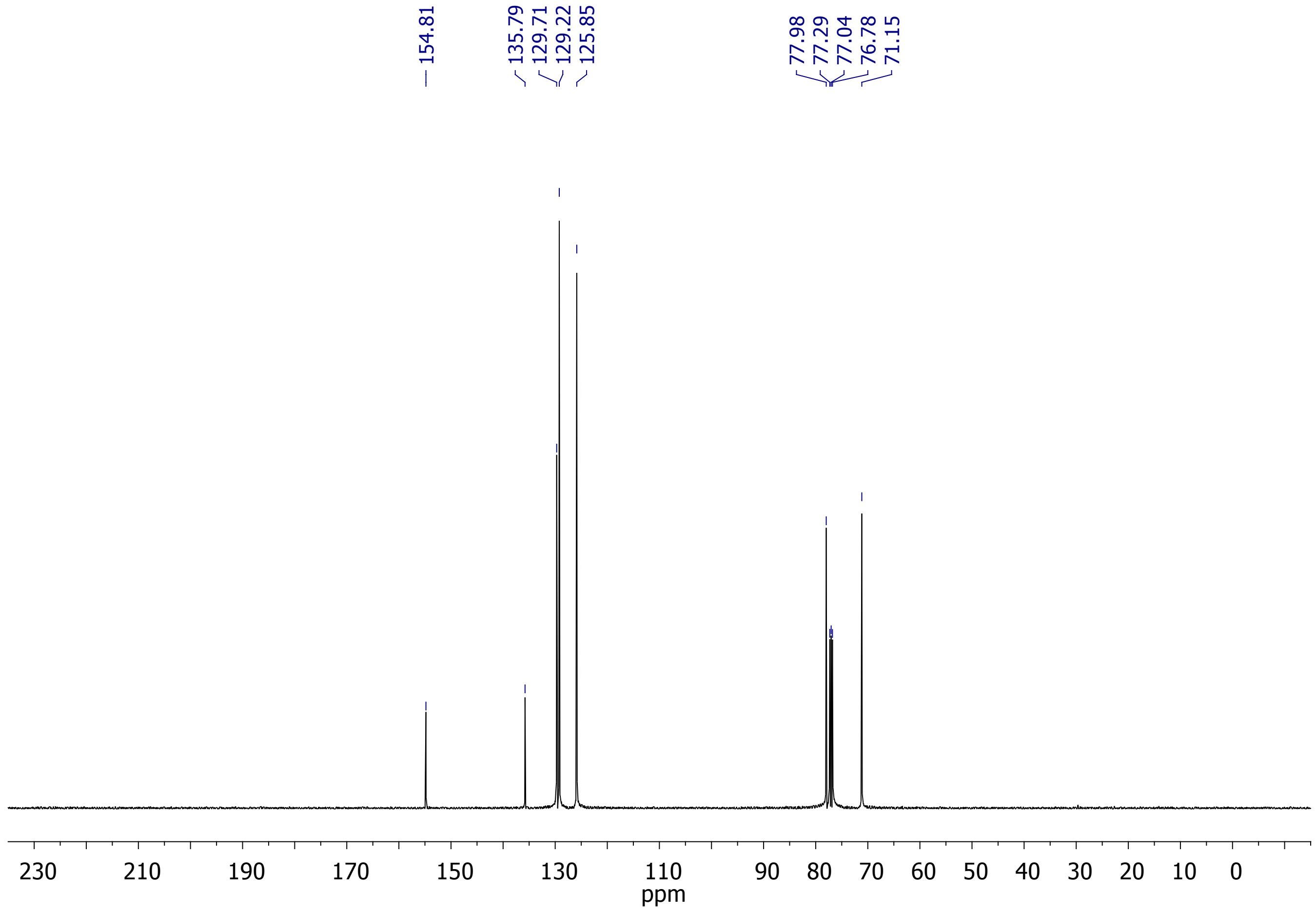


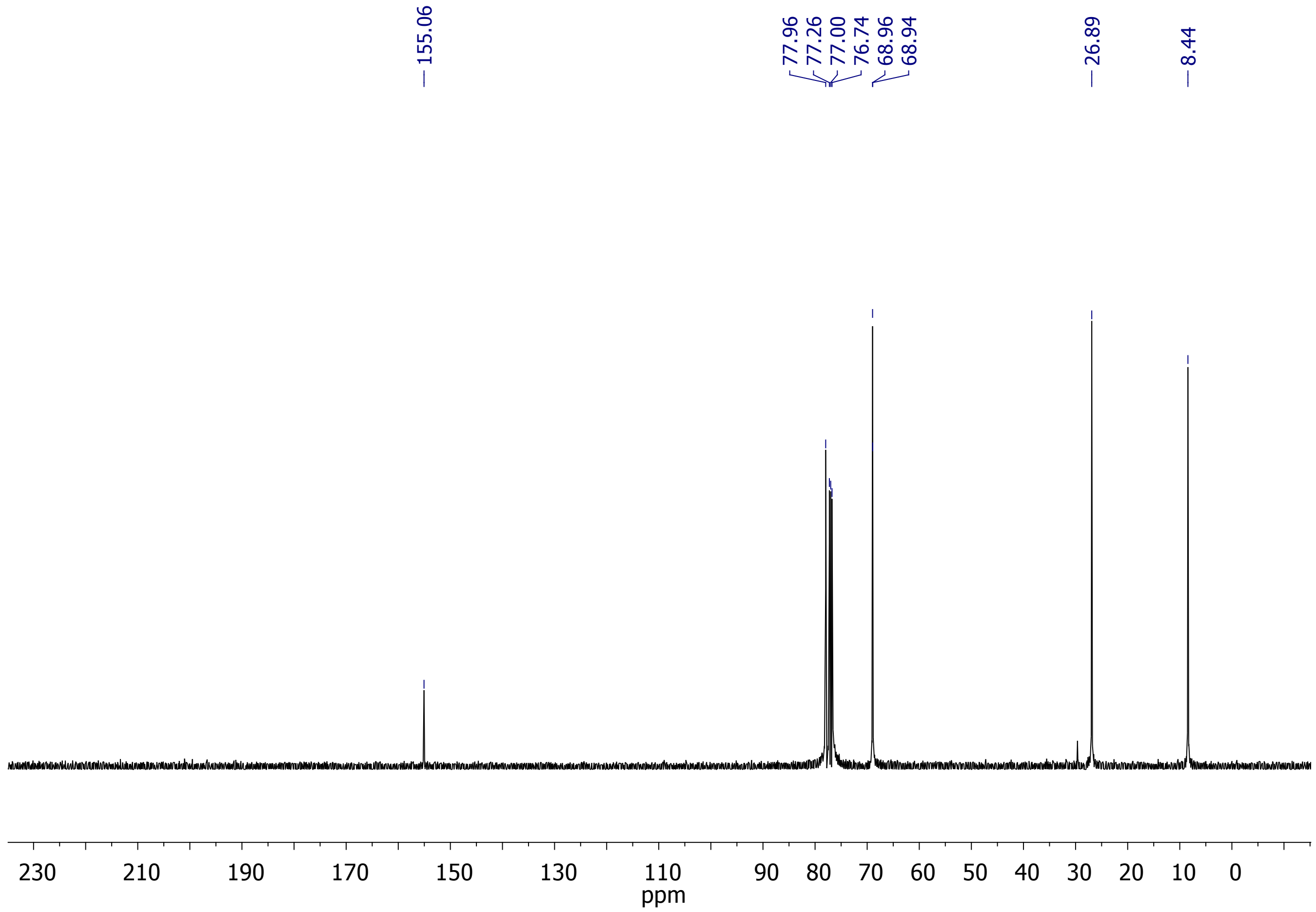
NMR Spectra for propylene carbonate **10b** in $CDCl_3$



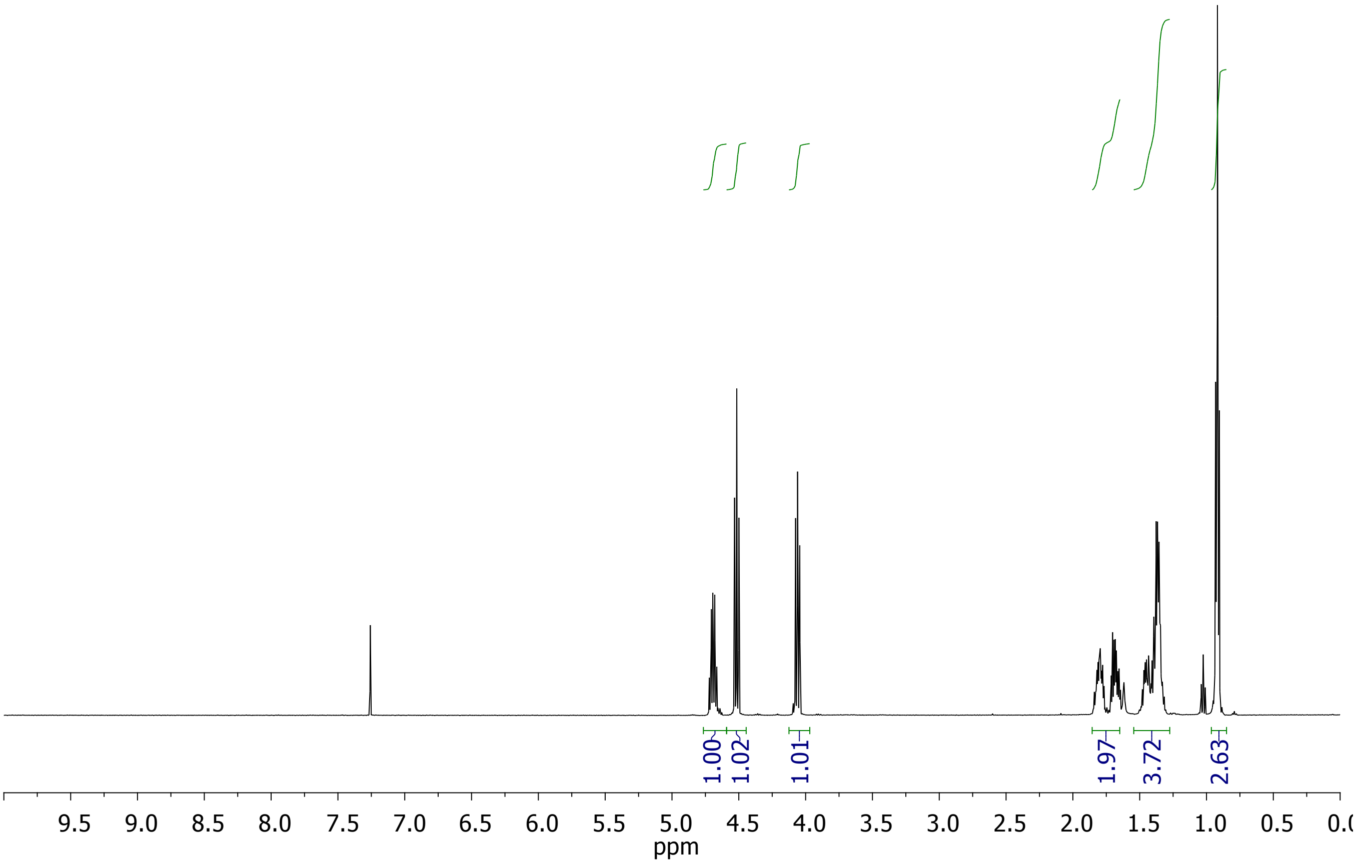


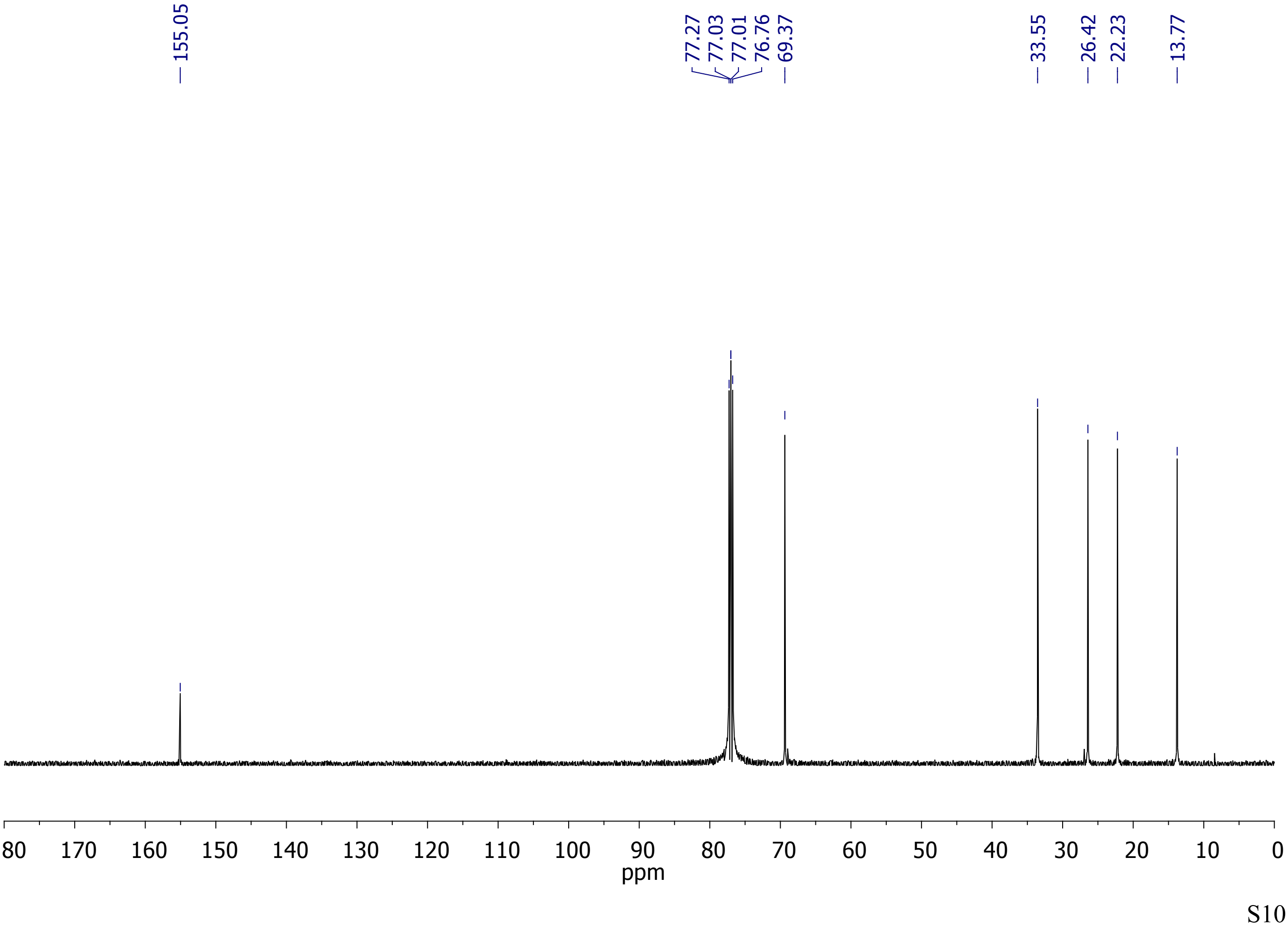
NMR Spectra for 1,2-butylene carbonate **10c** in $CDCl_3$



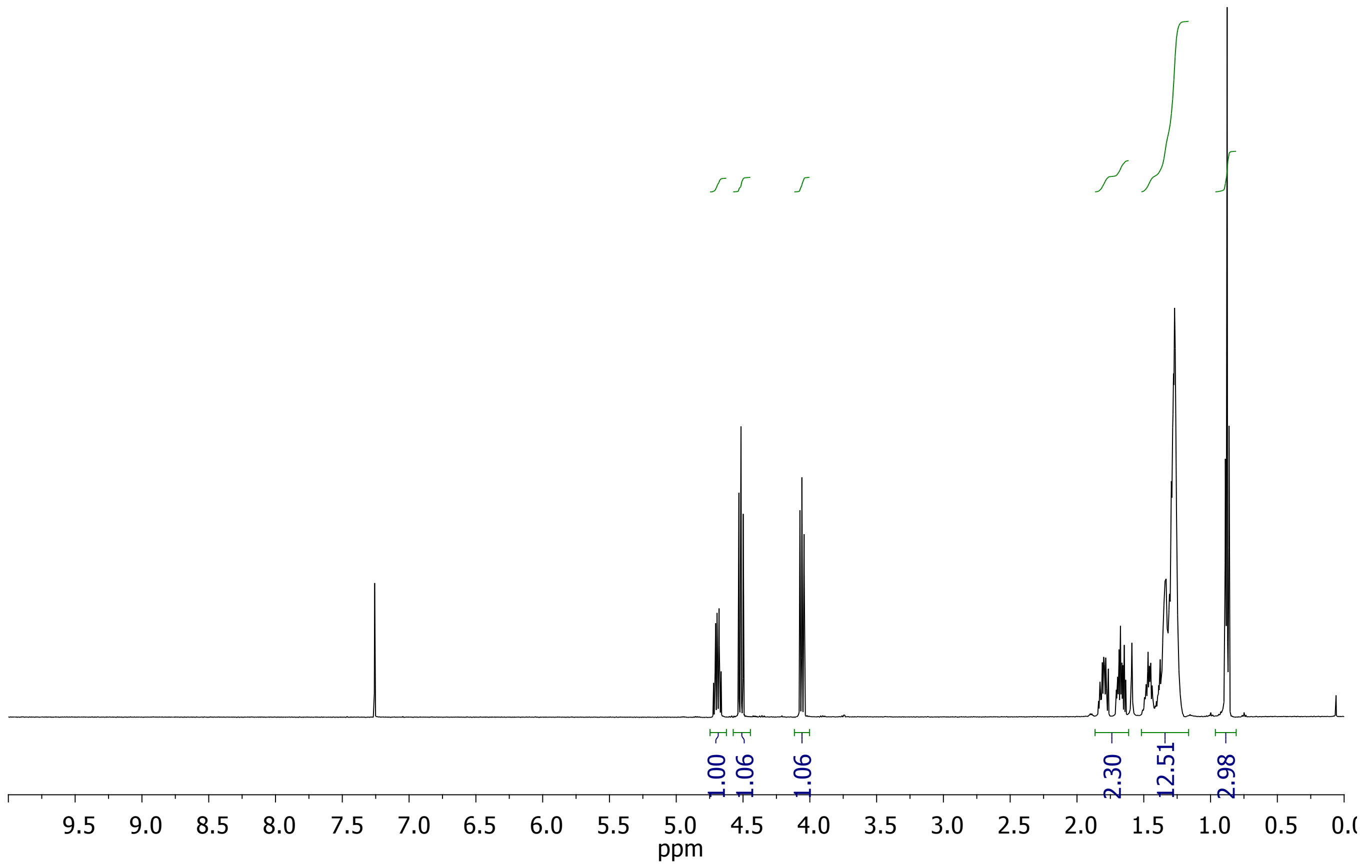


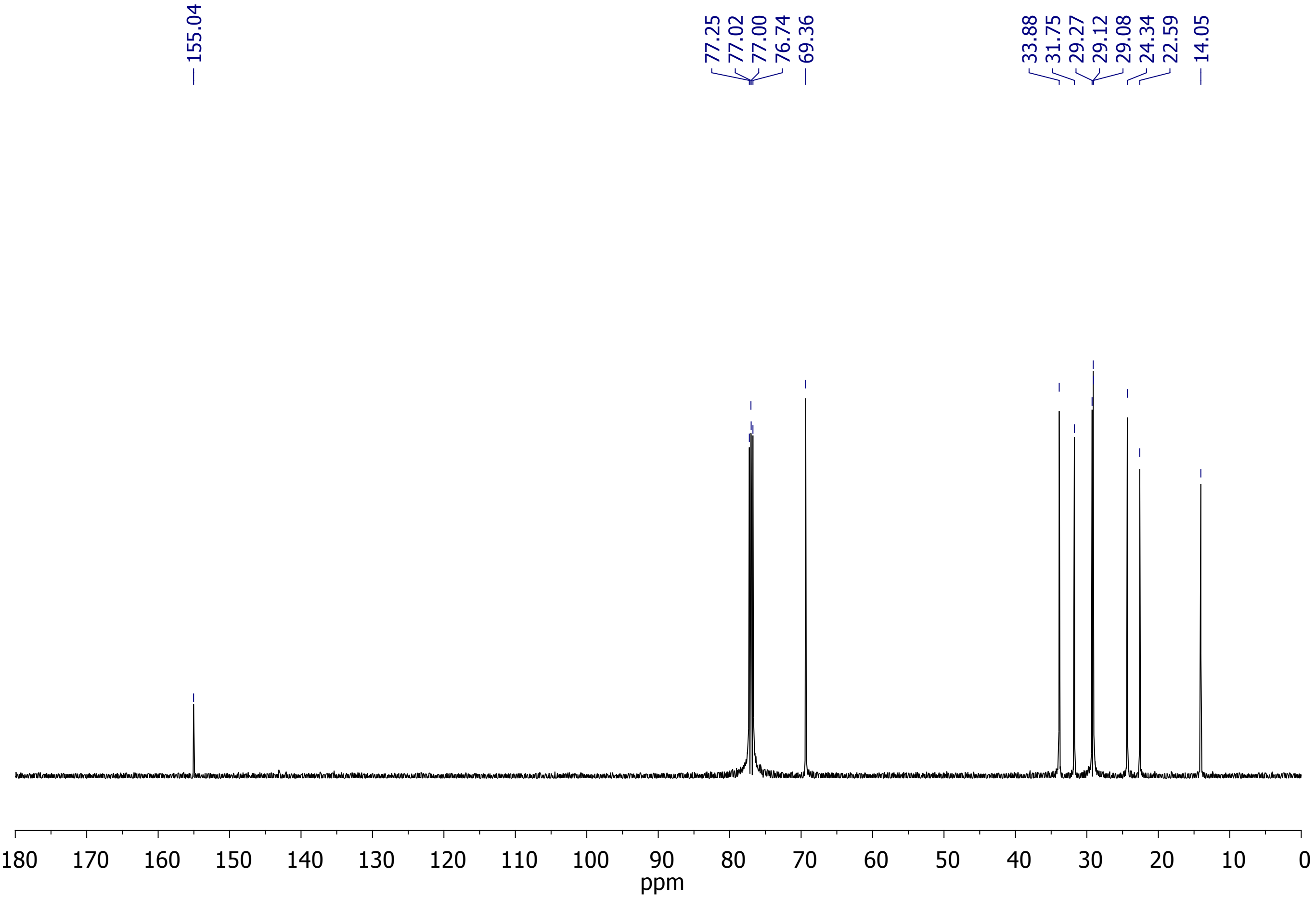
NMR Spectra for 1,2-hexylene carbonate **10d** in $CDCl_3$



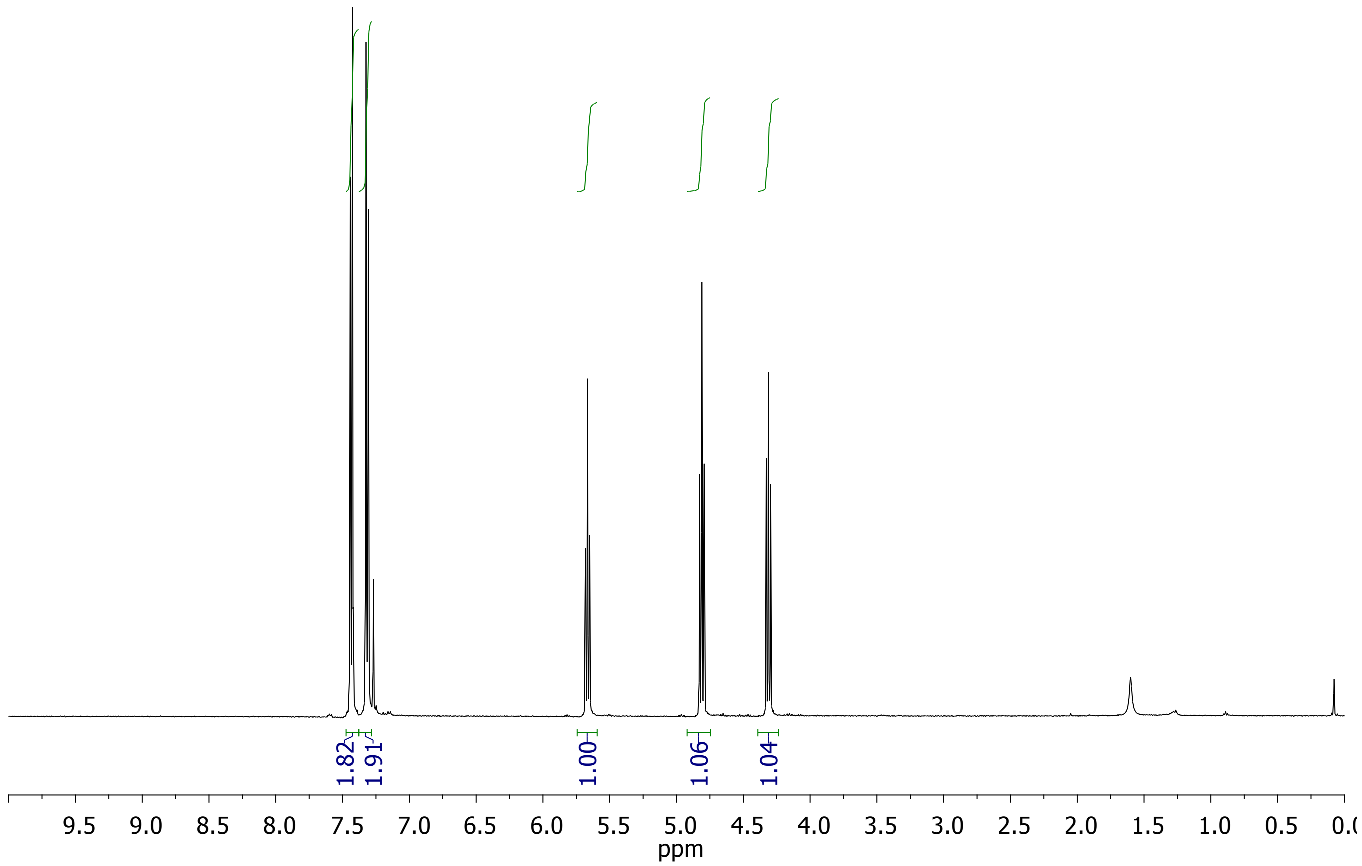


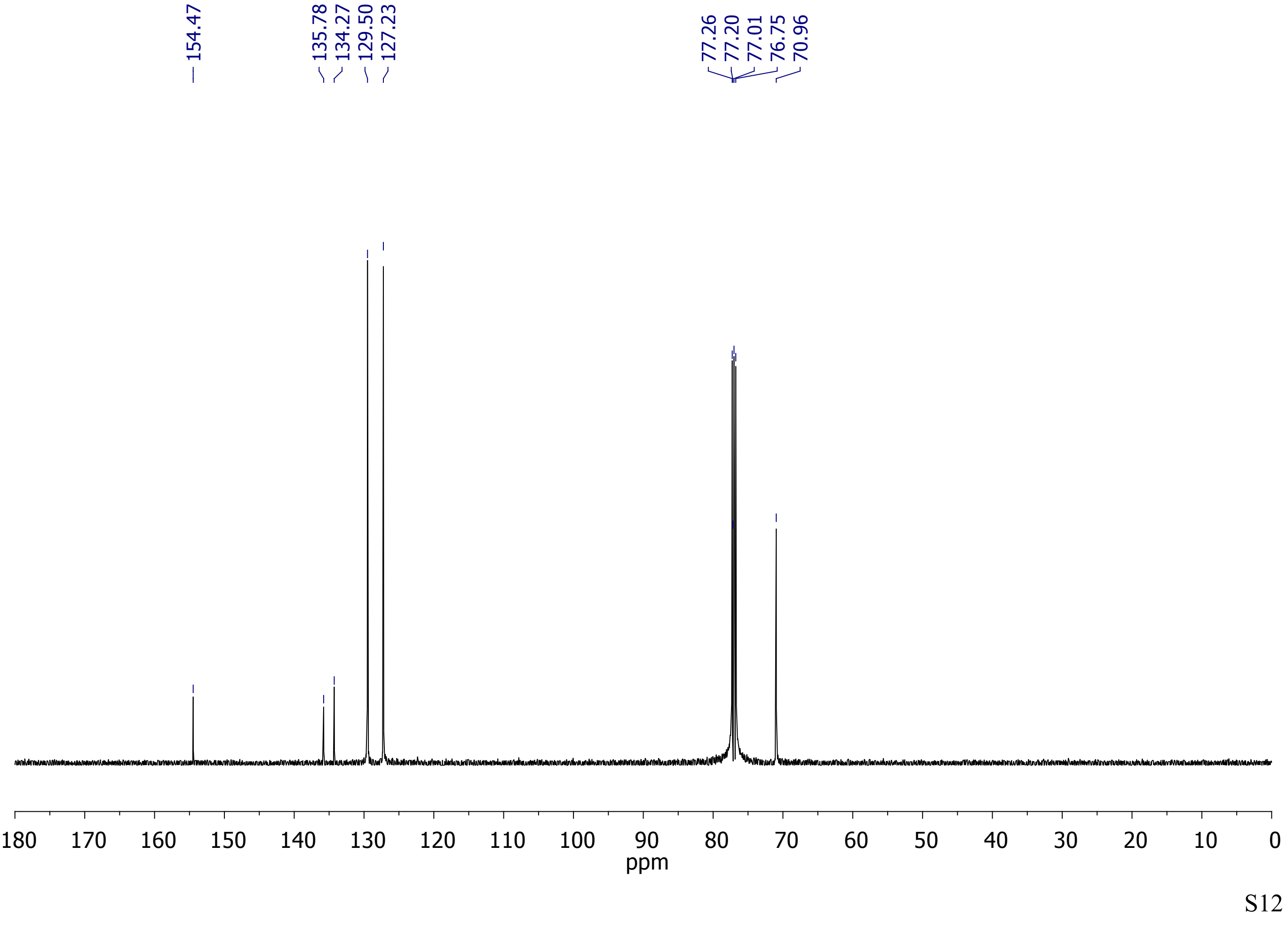
NMR Spectra for 1,2-decylene carbonate **10e** in $CDCl_3$



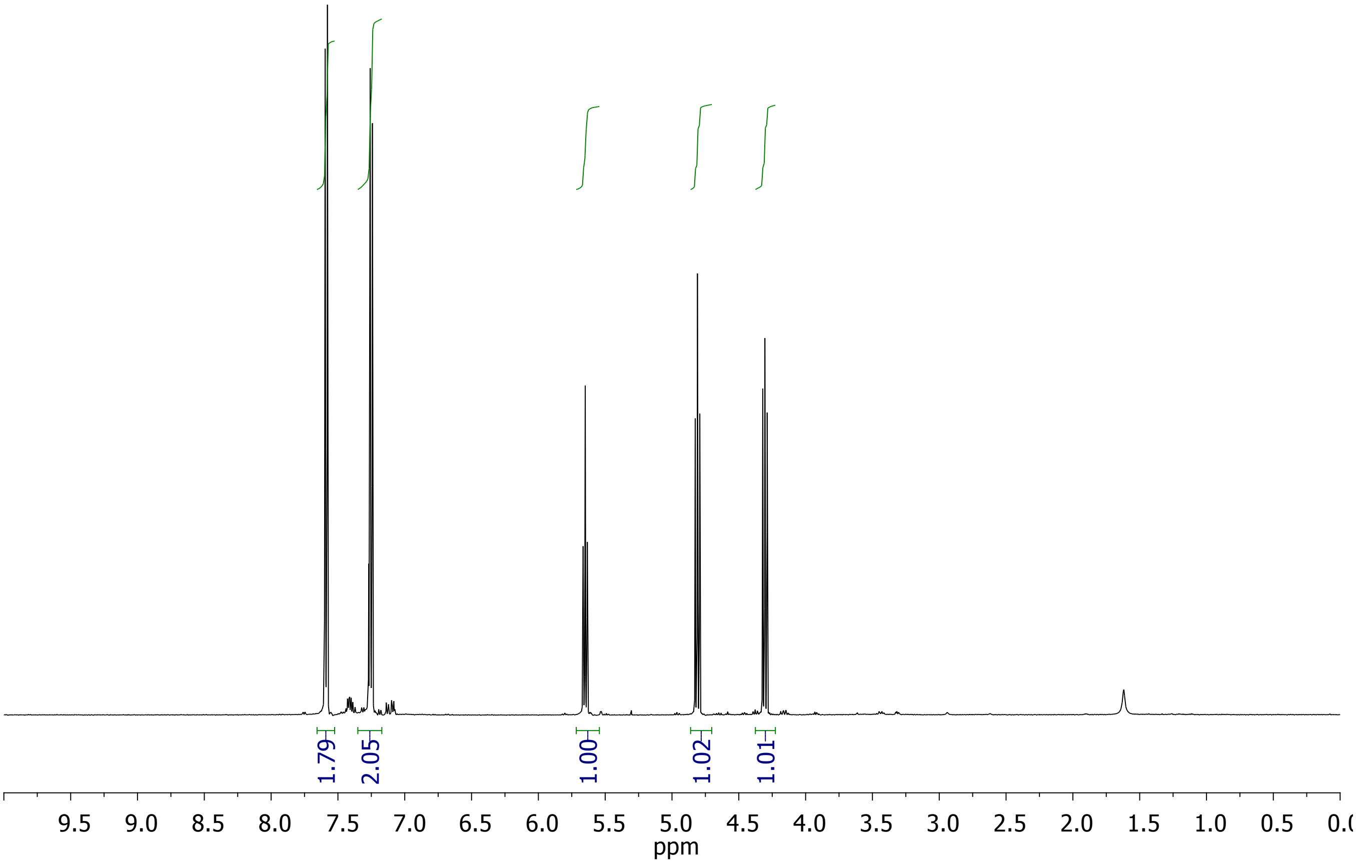


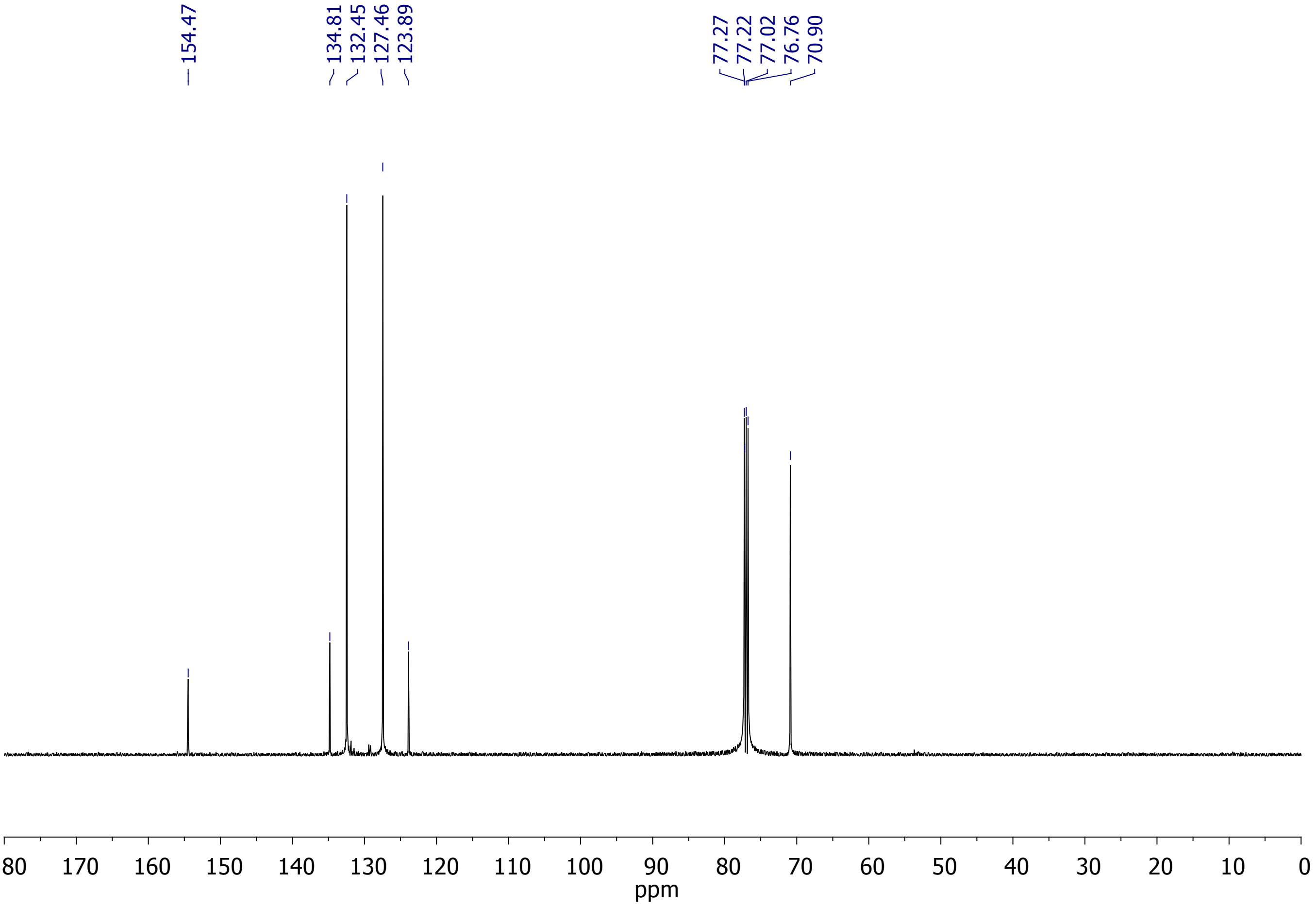
NMR Spectra for 4-chlorostyrene carbonate **10f** in $CDCl_3$



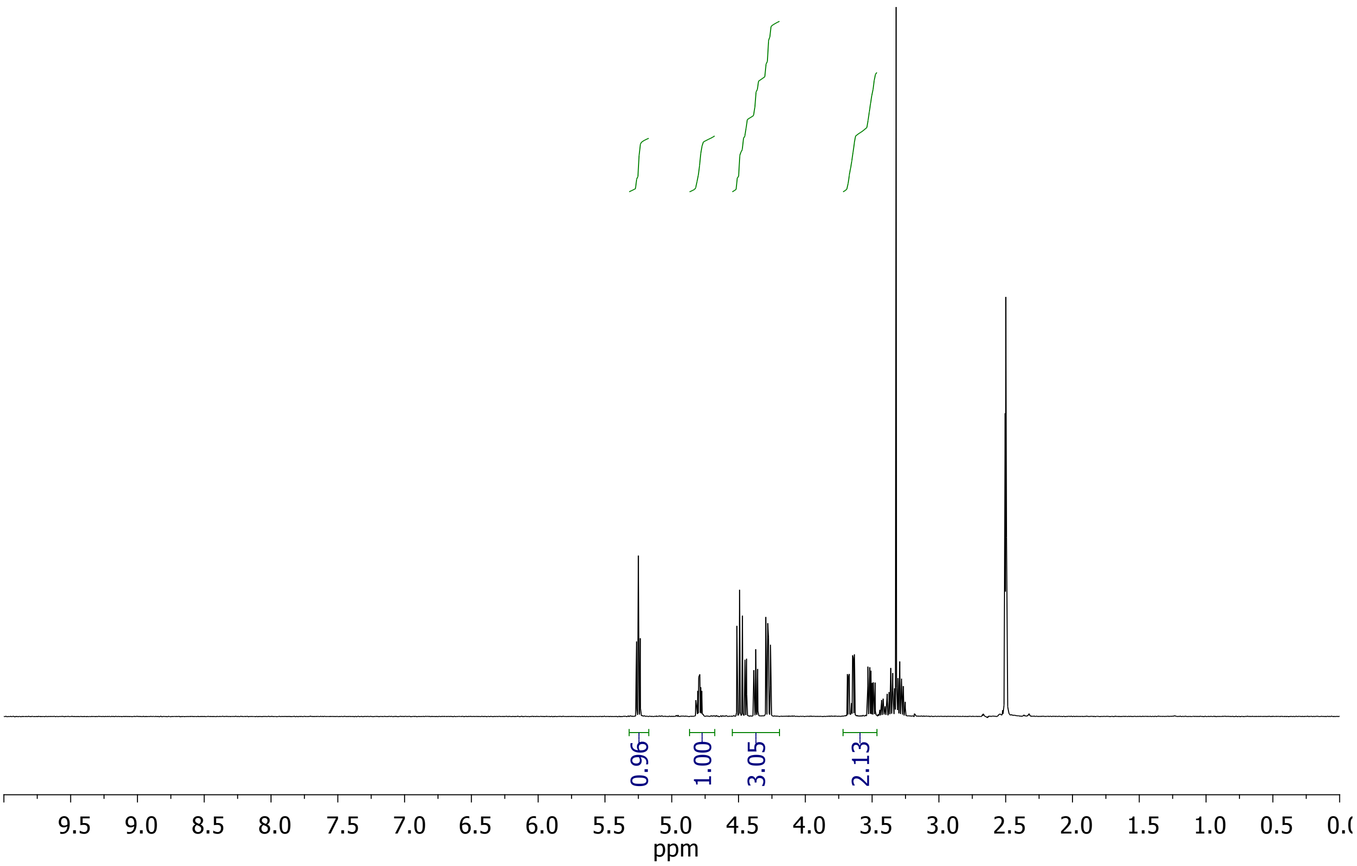


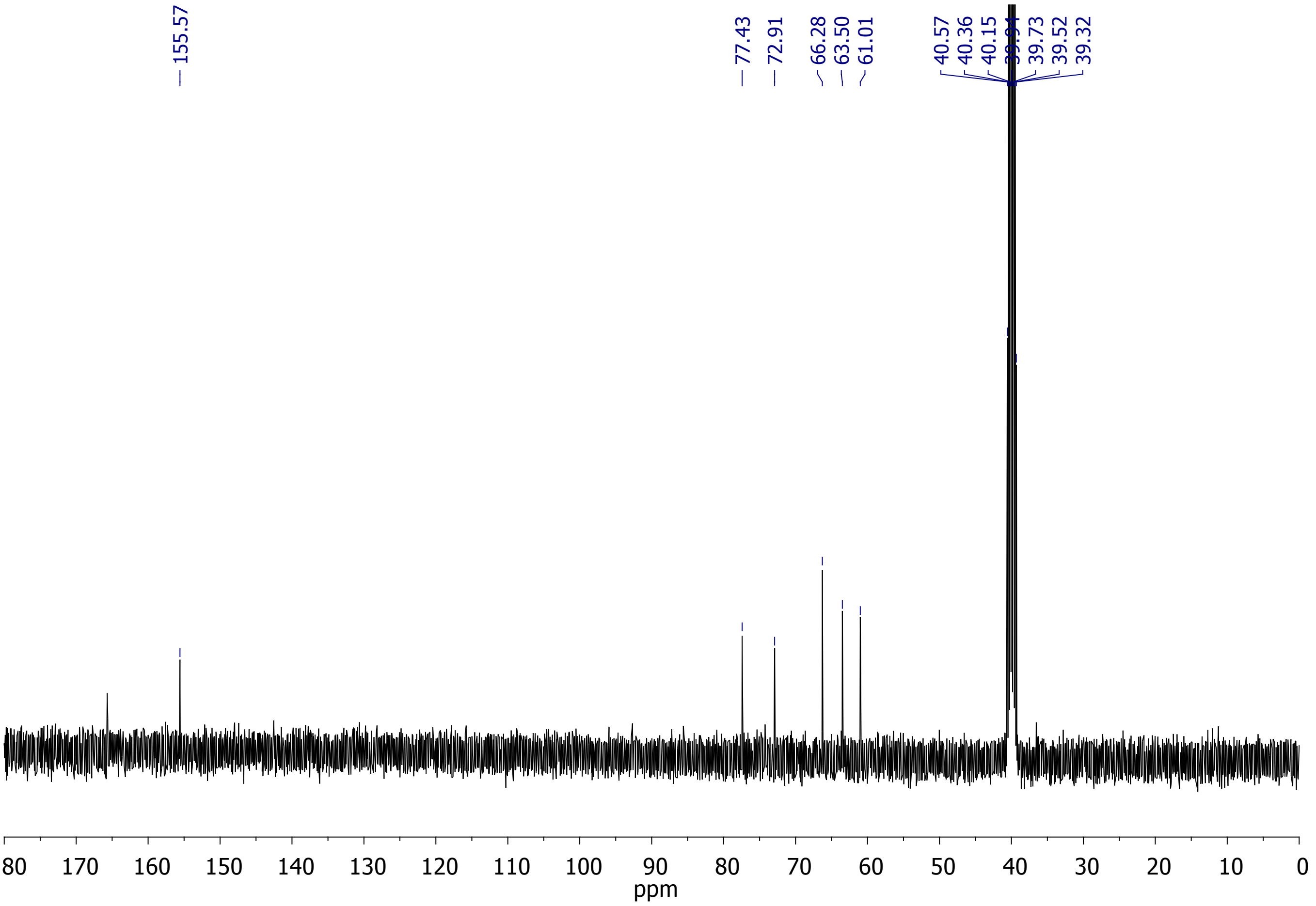
NMR Spectra for 4-bromostyrene carbonate **10g** in $CDCl_3$



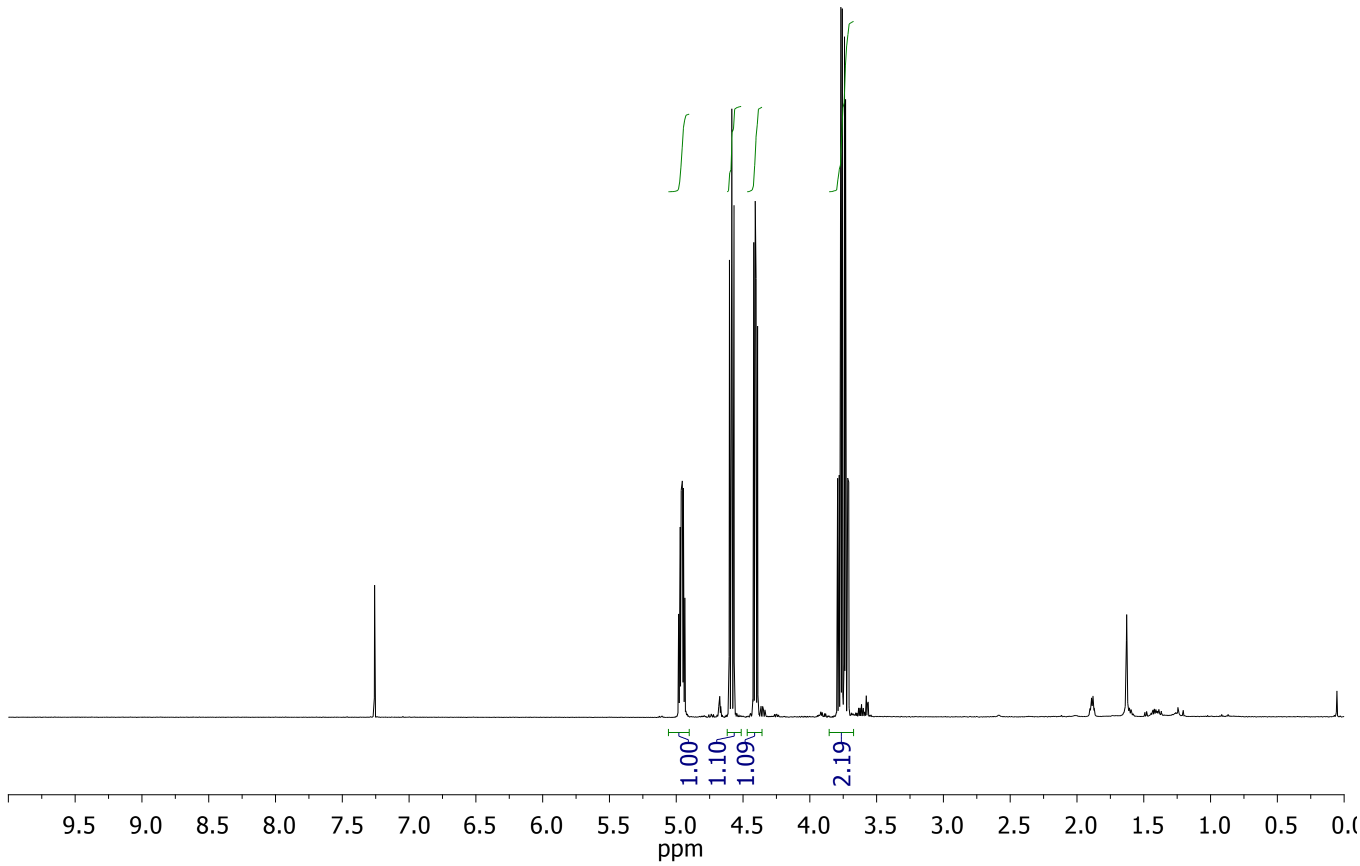


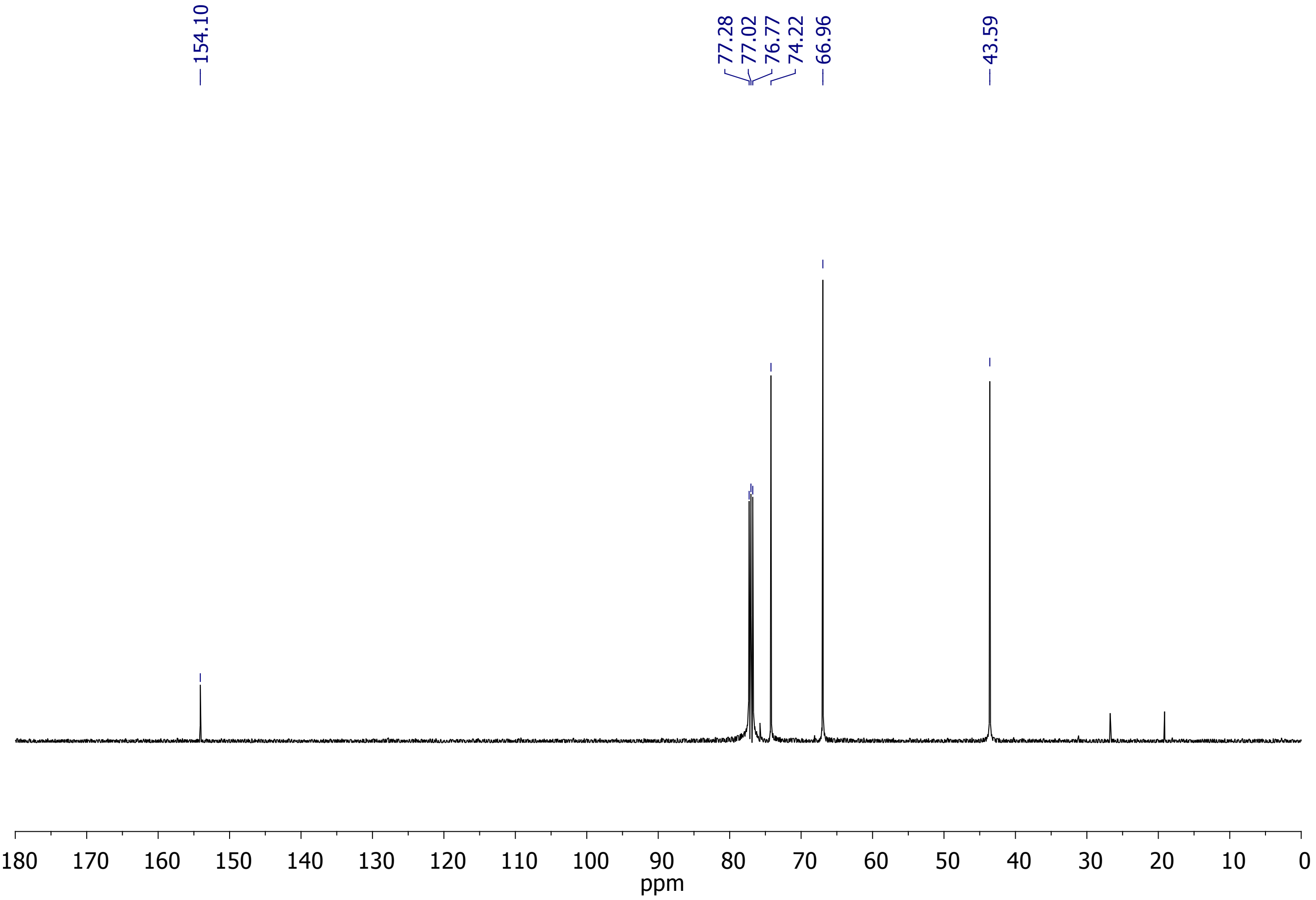
NMR Spectra for glycerol carbonate **10h** in DMSO-d_6



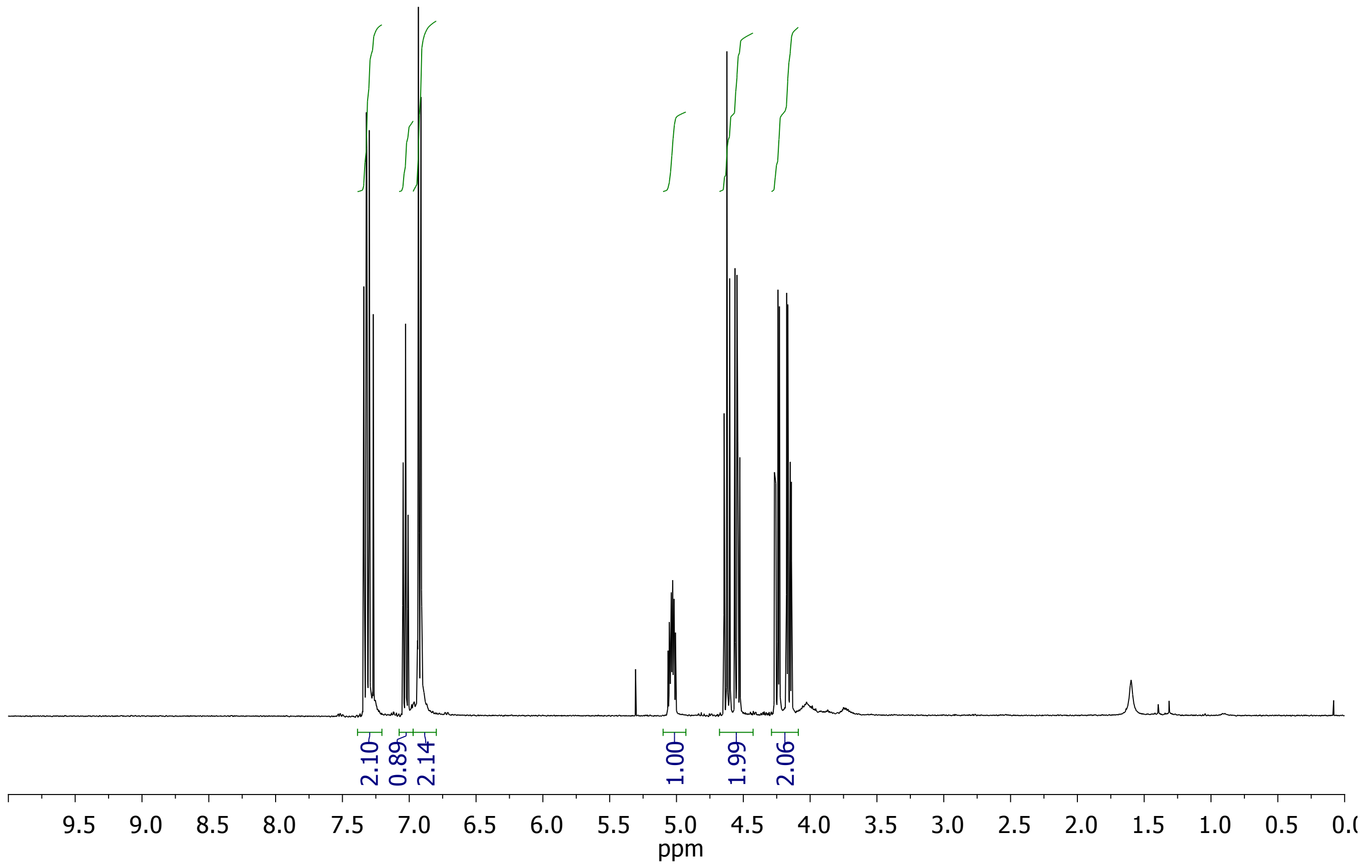


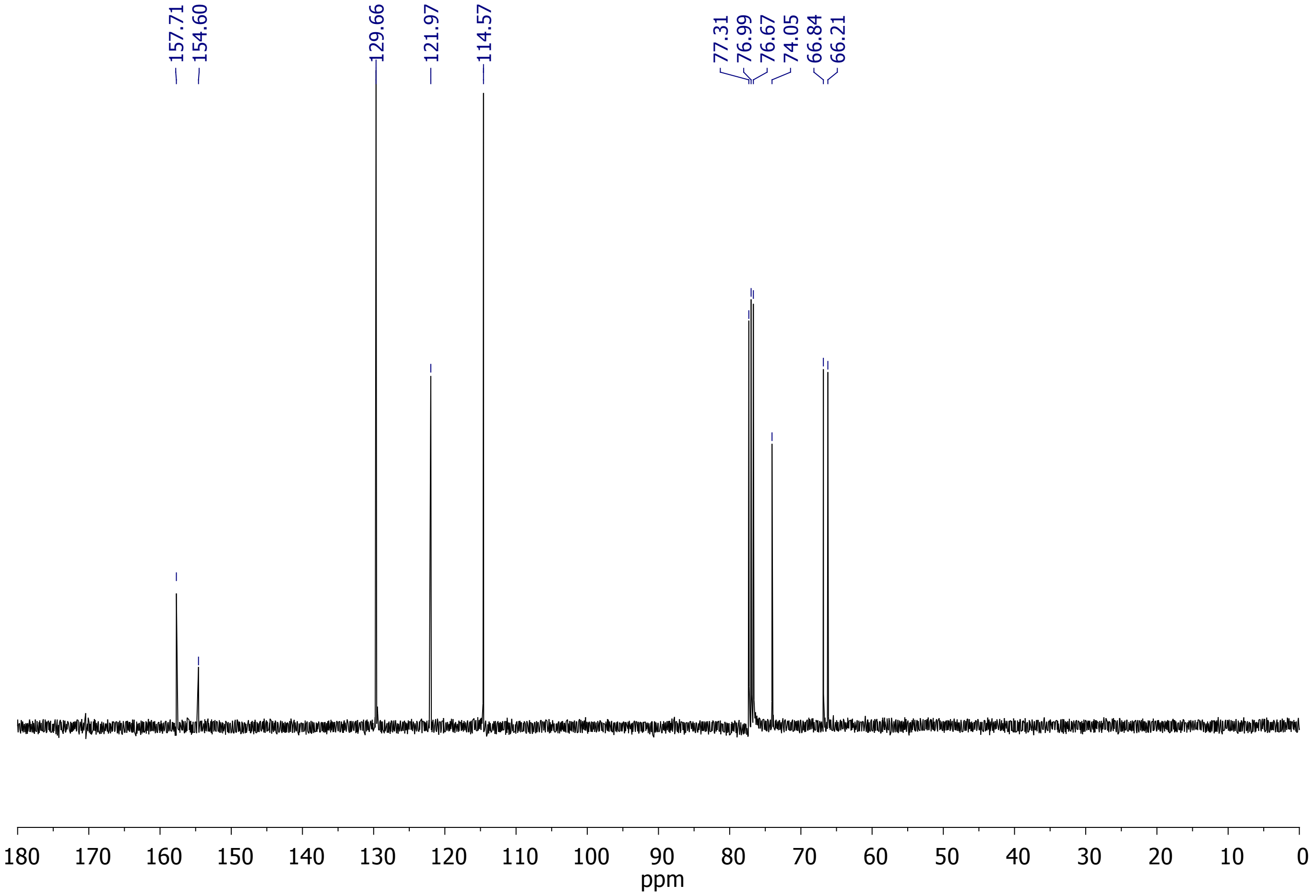
NMR Spectra for 3-chloropropylene carbonate **10i** in $CDCl_3$



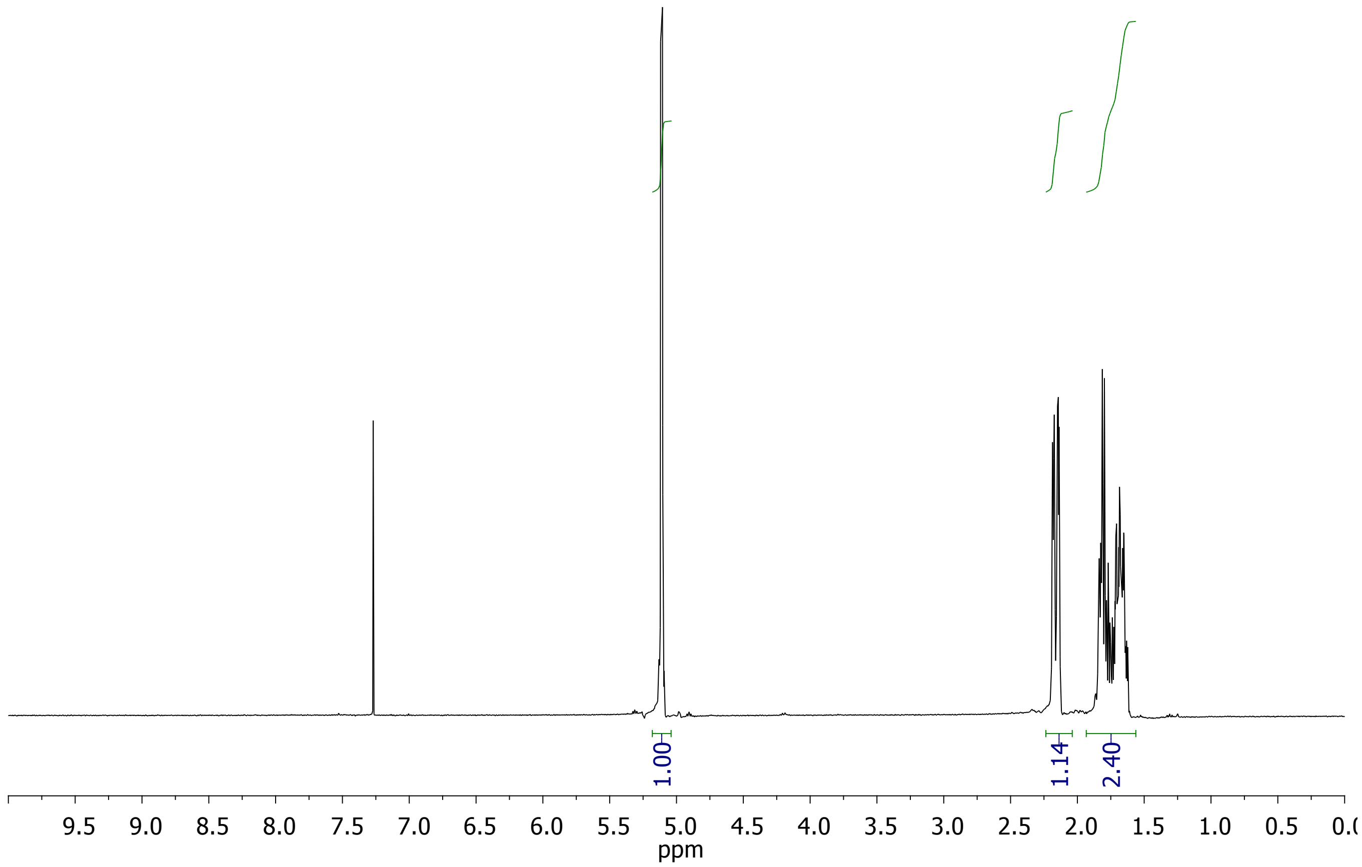


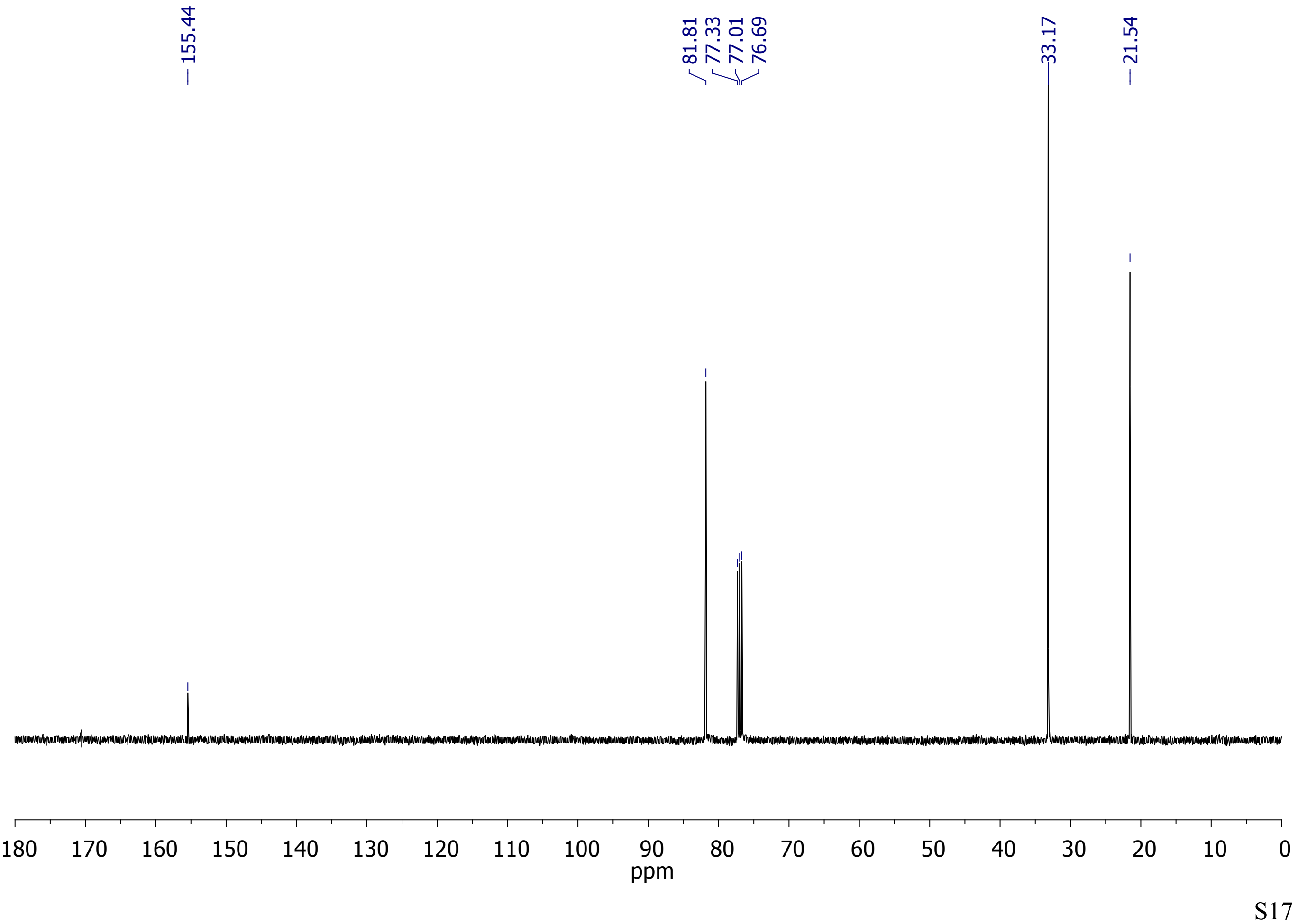
NMR Spectra for 3-phenoxypropylene carbonate **10j** in $CDCl_3$



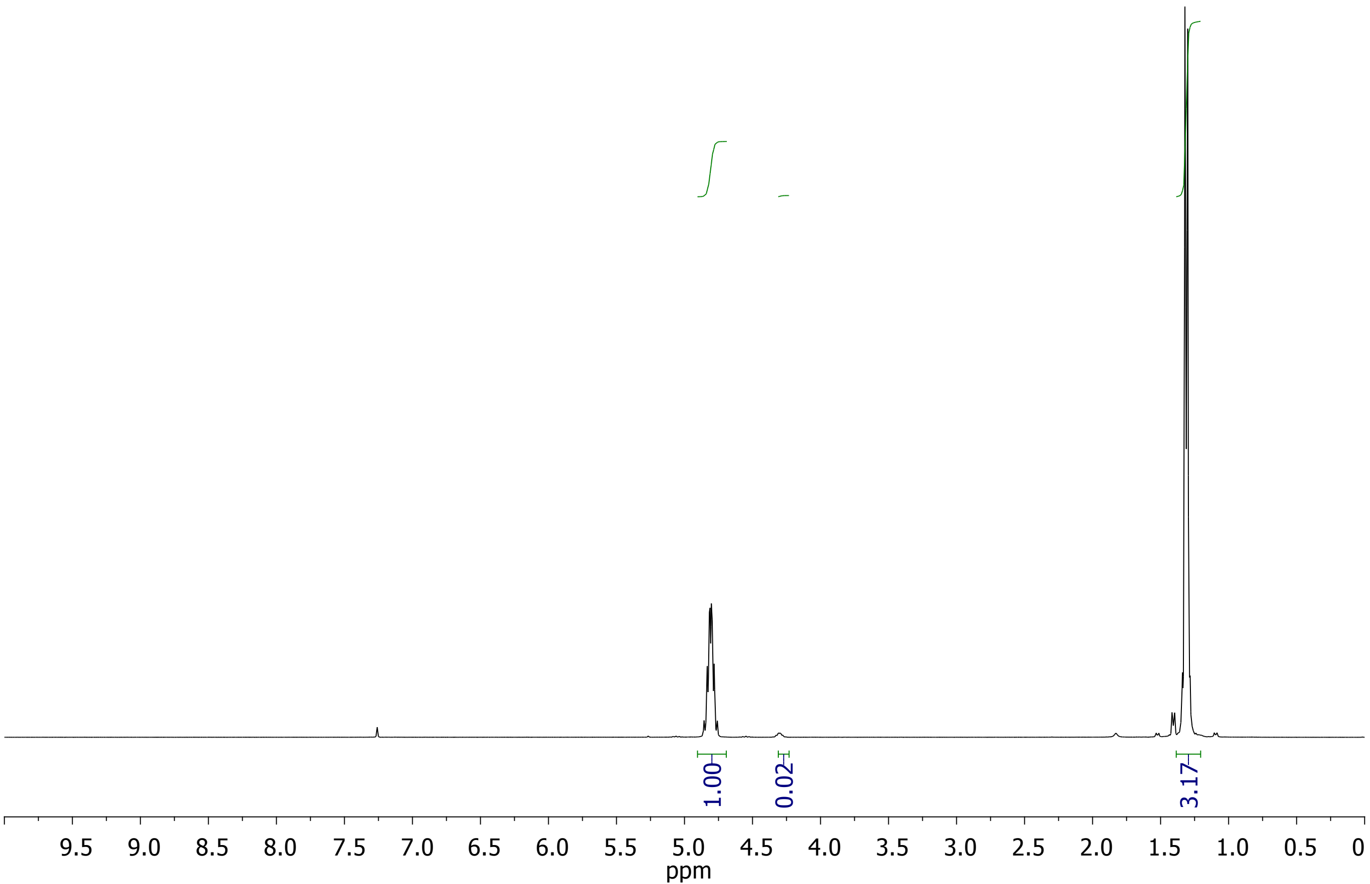


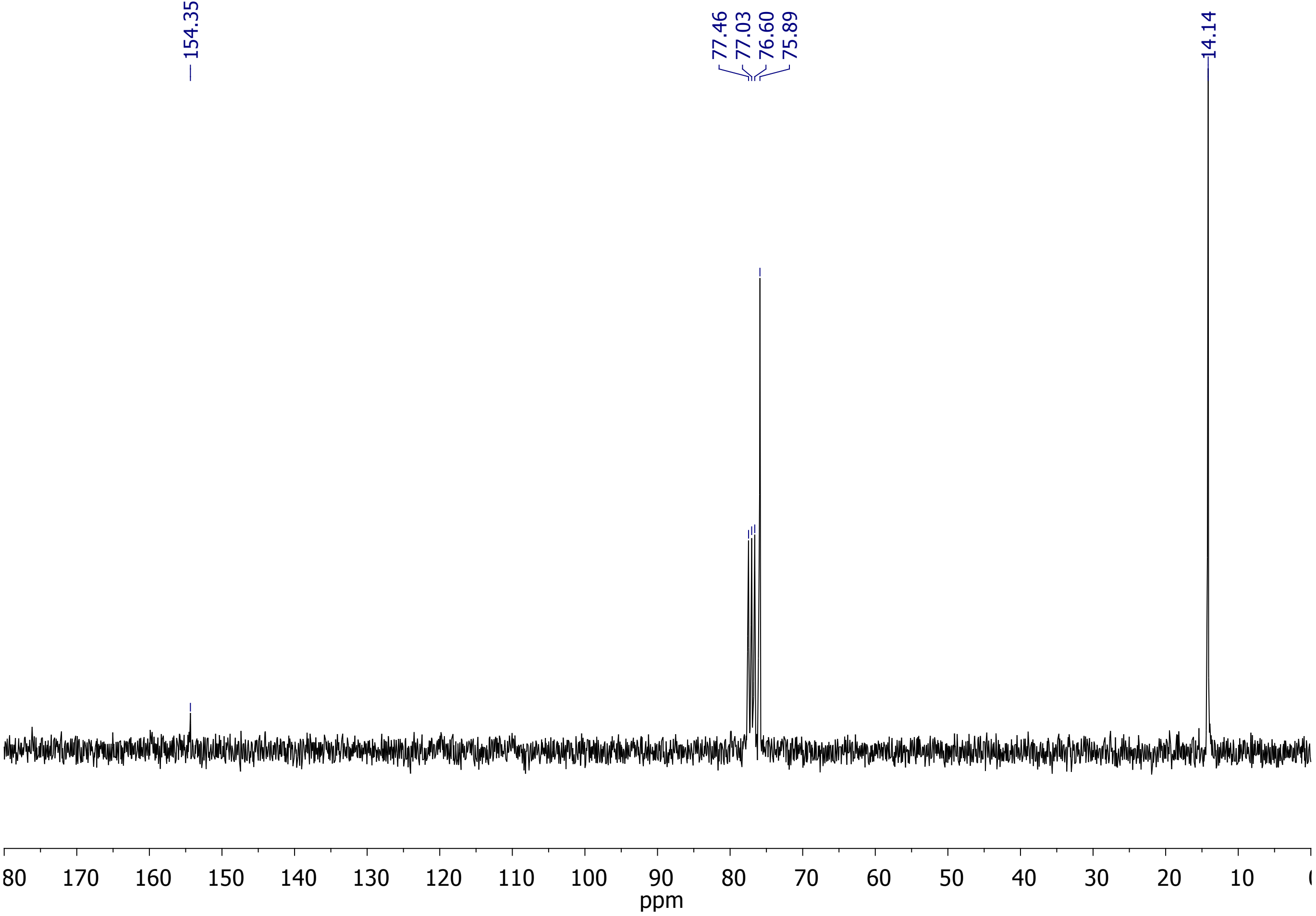
NMR Spectra for cyclopentene carbonate **12a** in $CDCl_3$



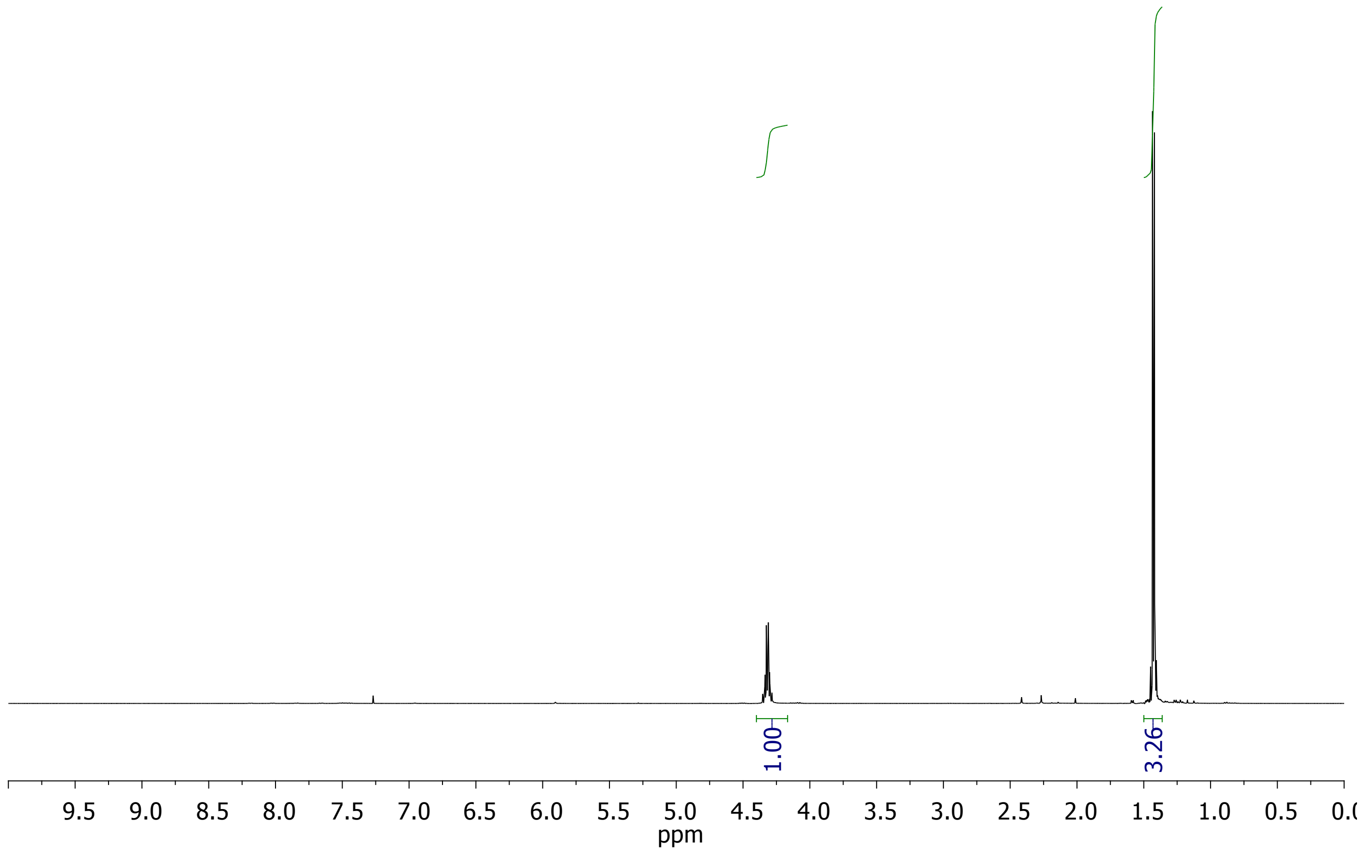


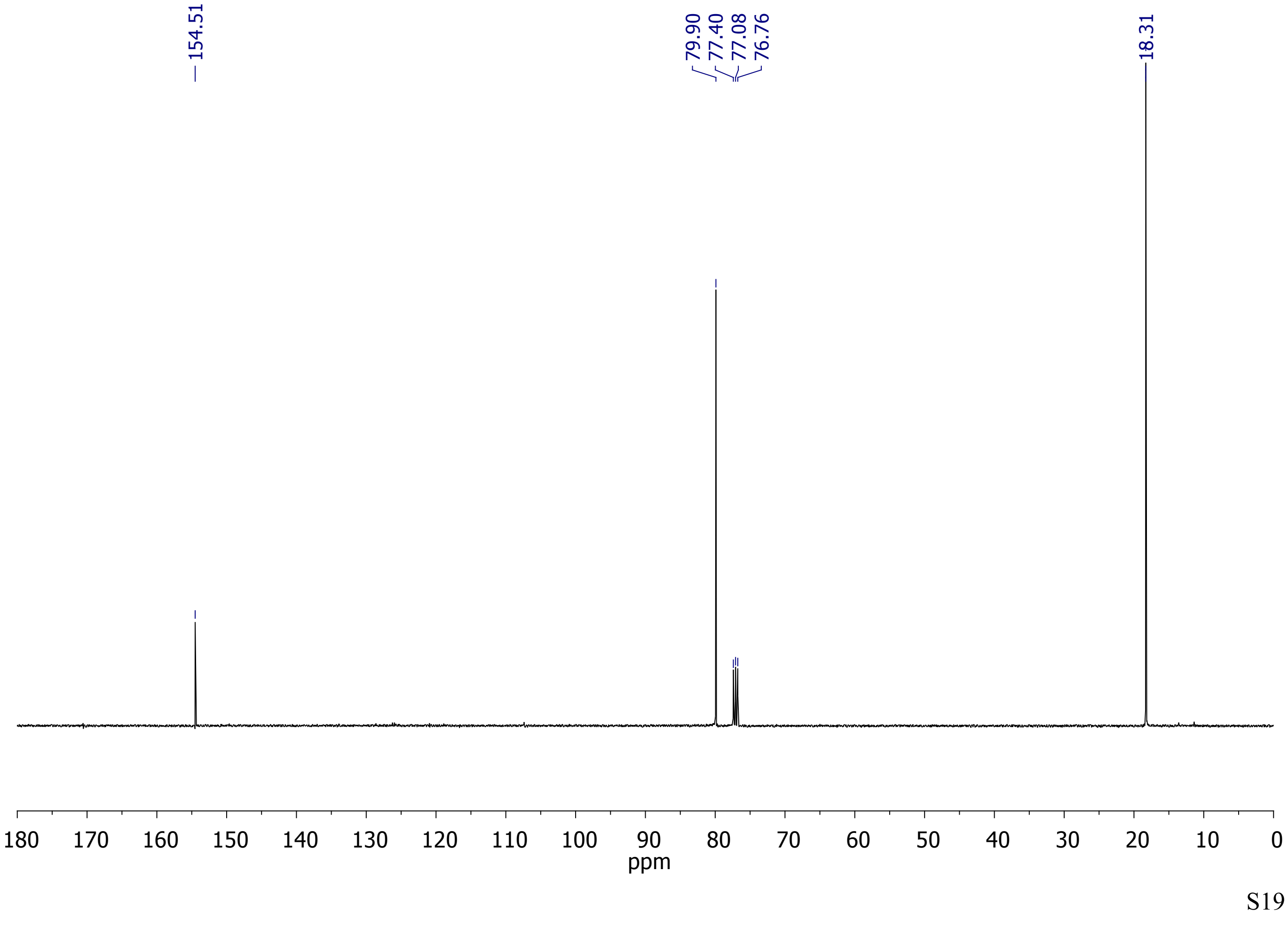
NMR Spectra for *cis*-2,3-butene carbonate **12b** in $CDCl_3$



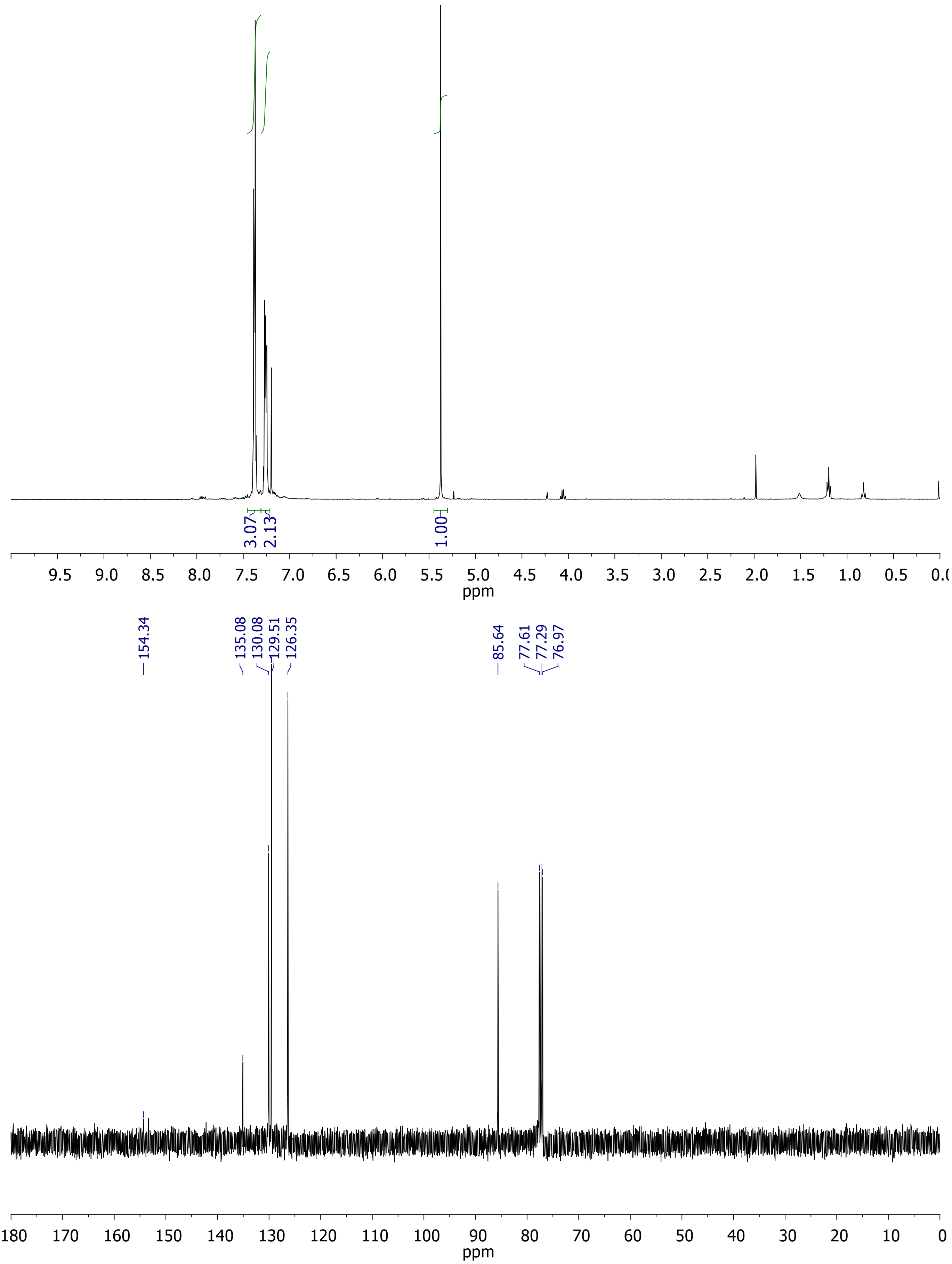


NMR Spectra for *trans*-2,3-butene carbonate **12c** in $CDCl_3$

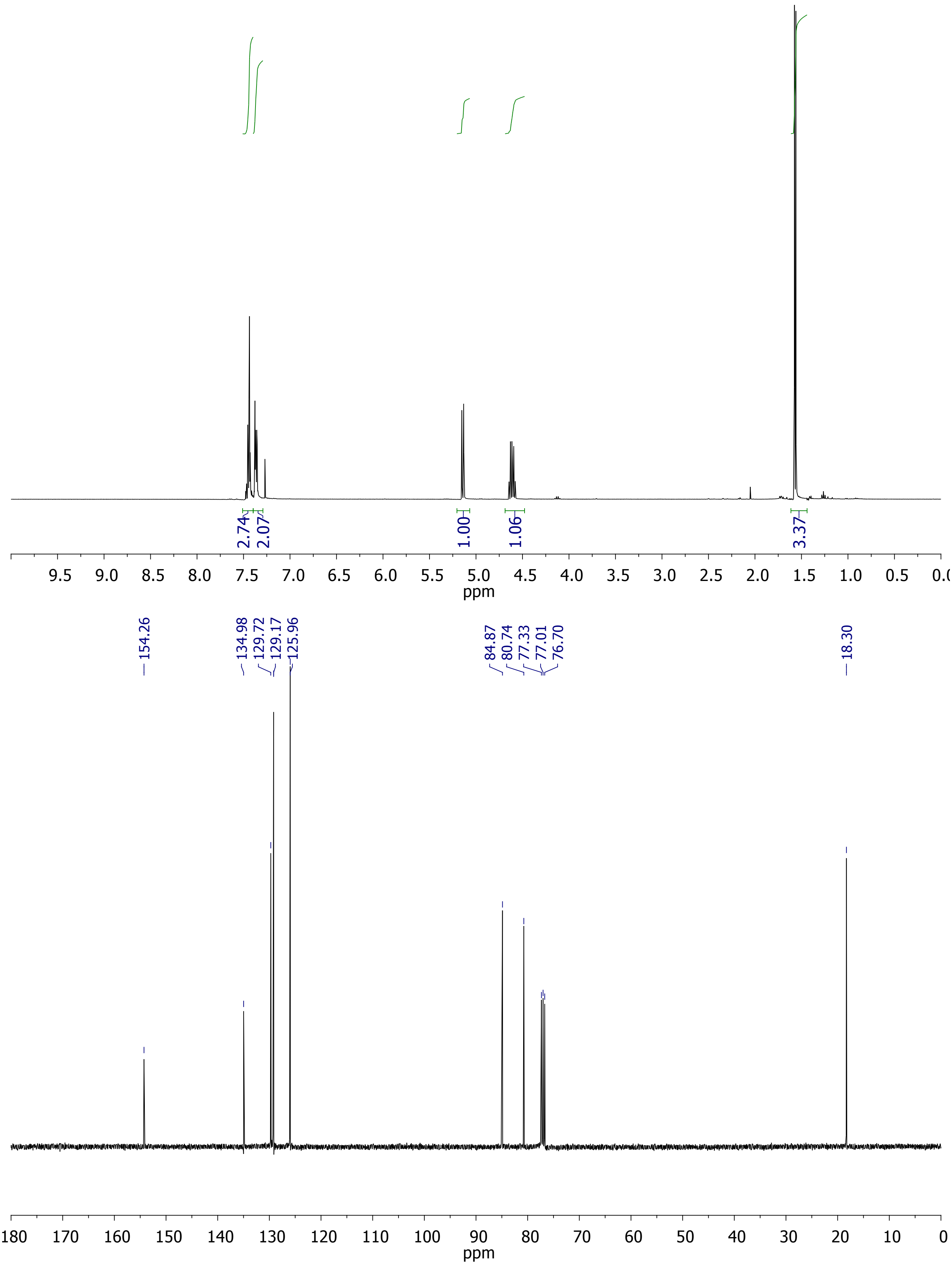




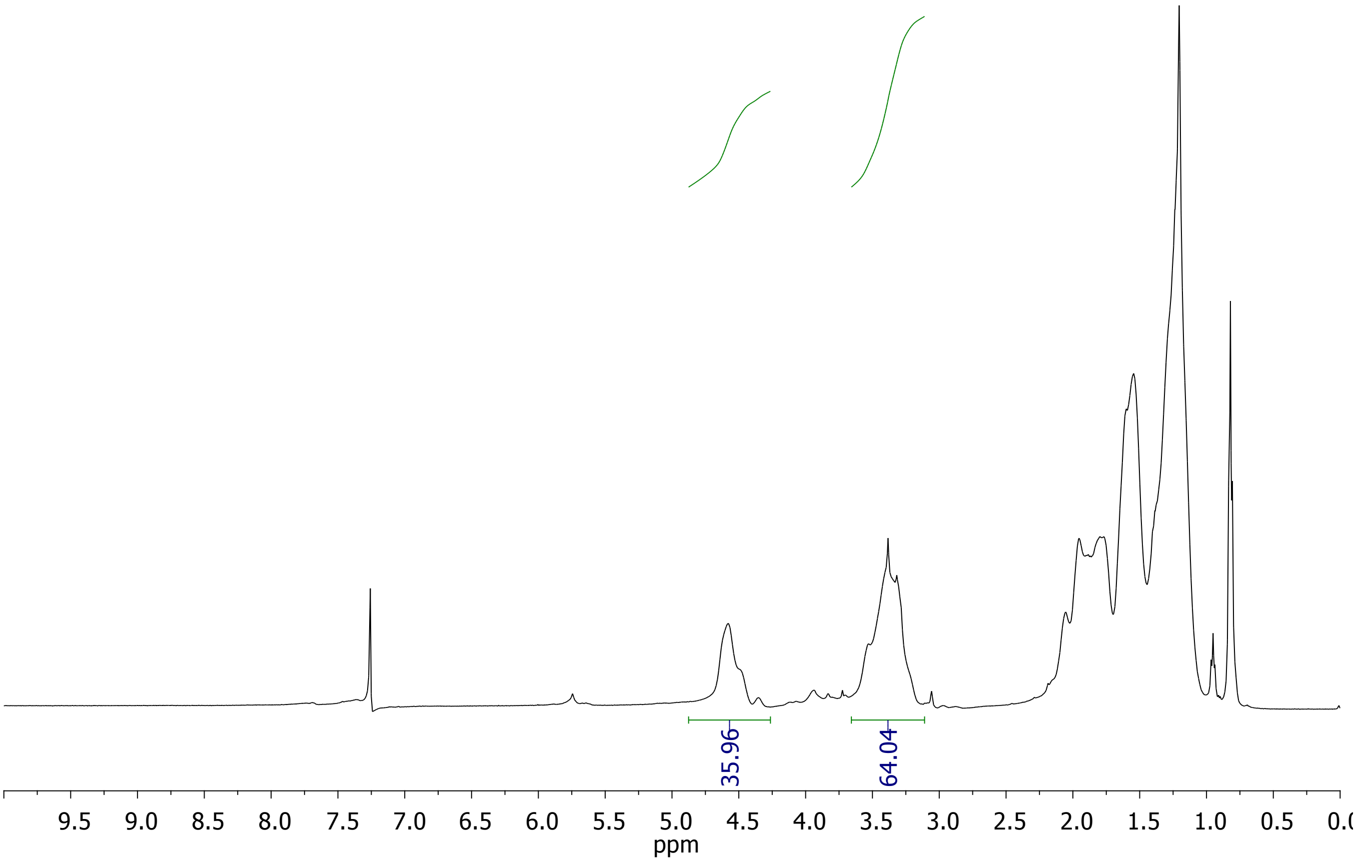
NMR Spectra for *trans*-1,2-diphenylethylene carbonate **12d** in $CDCl_3$



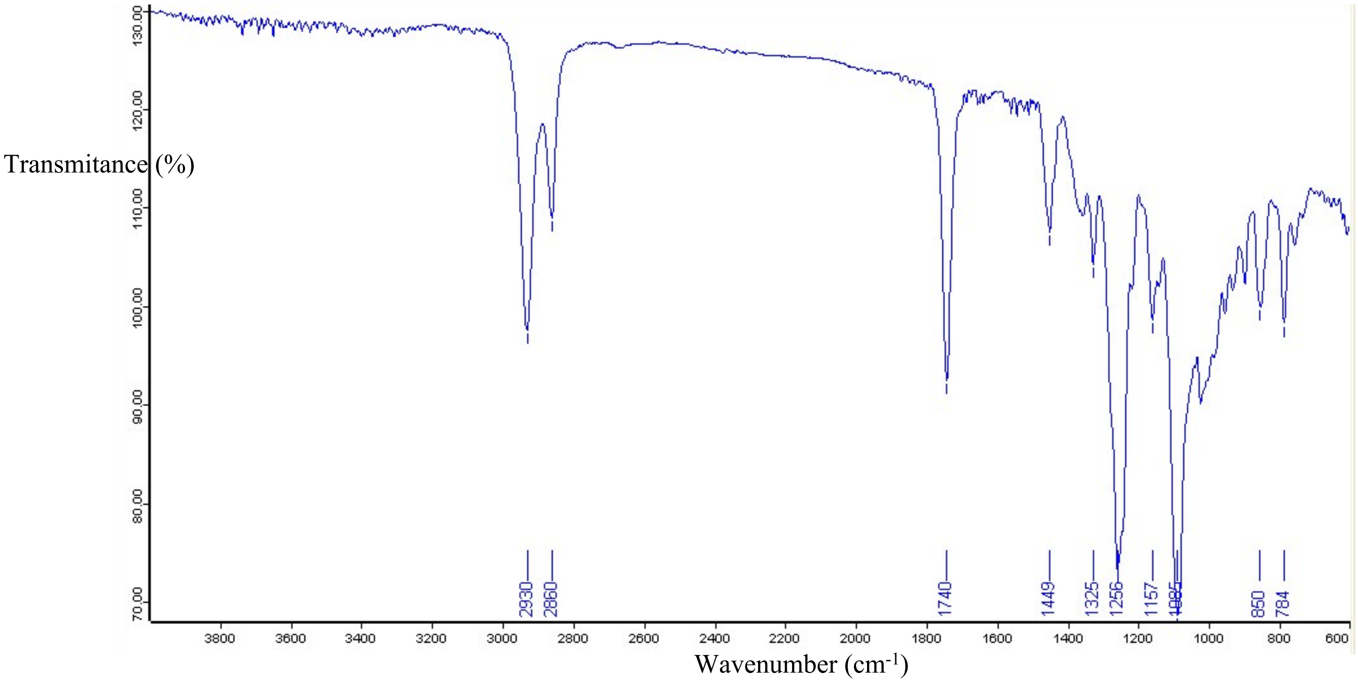
NMR Spectra for *trans*-1-phenyl-2-methylethylene carbonate **12e** in $CDCl_3$



^{1}H NMR spectrum for polyether-polycarbonate **12f** derived from CHO and CO_2 in $CDCl_3$



IR NMR spectrum for polyether-polycarbonate **12f** derived from CHO and CO_2



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1. (a) J. A. Castro-Osma, C. Alonso-Moreno, A. Lara-Sánchez, J. Martínez, M. North and A. Otero, *Catal. Sci. Technol.*, 2014, **4**, 1674; (b) J. Martínez, J. A. Castro-Osma, A. Earlam, C. Alonso-Moreno, A. Otero, A. Lara-Sánchez, M. North and A. Rodríguez-Diéguez, *Chem. Eur. J.*, 2015, **21**, 9850; (c) J. Martínez, J. A. Castro-Osma, C. Alonso-Moreno, A. Rodríguez-Diéguez, M. North, A. Otero and A. Lara-Sánchez, *ChemSusChem*, 2017, **10**, 1175; (d) D. O. Meléndez, A. Lara-Sánchez, J. Martínez, X. Wu, A. Otero, J. A. Castro-Osma, M. North and R. S. Rojas, *ChemCatChem*, 2018, **10**, 2271; (e) F. de la Cruz-Martínez, J. Martínez, M. A. Gaona, J. Fernández-Baeza, L. F. Sánchez-Barba, A. M. Rodríguez, J. A. Castro-Osma, A. Otero and A. Lara-Sánchez, *ACS Sustain. Chem. Eng.*, 2018, **6**, 5322.