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Ring-Opening (co)Polymerization of Six-Membered Substituted δ -Valerolactones with Alkali Metal Alkoxides

This manuscript is a tribute to the 50 year anniversary of the French Polymer Group (Groupe Français des Polymères - GFP)

Valérie Hardouin Duparc,^a Rama M. Shakaroun,^a (ORCID 0000-0001-5983-8746) Martine Slawinsky,^b Jean-François Carpentier,^{a,*} (ORCID 0000-0002-9160-7662) and Sophie M. Guillaume^{a,*} (ORCID 0000-0003-2917-8657)

^a Univ. Rennes, CNRS, Institut des Sciences Chimiques de Rennes, UMR 6226, F-35042 Rennes, France. E-mail: jean-francois.carpentier@univ-rennes1.fr, sophie.guillaume@univ-rennes1.fr

^b Total Petrochemicals Research Feluy, Zone Industrielle Feluy C, B-7181

Abstract

The ring-opening polymerization (ROP) of bio-derived six-membered (substituted) δ -valerolactones, including the 5-Me substituted δ -valerolactone (aka δ -hexalactone (HL)), 2-ethylidene-6-hepten-5-olide (EVL), 2-ethylheptane-5-olide (EHO) and the novel 2-ethylidene-6-heptan-5-olide (MH), is investigated. In comparison to the ubiquitous unsubstituted δ -valerolactone (VL), the presence of a substituent on the lactone ring appears to significantly affect the polymerizability of the monomer, whichever the catalyst/initiator system or the operating conditions. Typical Brønsted acids, organocatalysts or Lewis acidic metal complexes revealed hardly active in the ROP of HL, most likely originating from polymerization/depolymerization issues. Better efficiency was achieved from alkali metal complexes, especially using NaOMe (1–2.5 mol%) from which high-to-quantitative HL conversion was reached within 18 h at 60 °C. Oligomers ($\bar{M}_{n,NMR} \leq 3800 \text{ g}\cdot\text{mol}^{-1}$, $D_M = 1.22\text{--}1.36$) were thus synthesized from ROP, as supported by NMR spectroscopy, SEC and MALDI-ToF mass spectrometry analyses. P(HL-*co*-VL) random copolymers incorporating up to 44 mol% of HL into PVL were next synthesized from the simultaneous HL/VL copolymerization mediated by NaOMe ($\bar{M}_{n,NMR}$ up to 9700 $\text{g}\cdot\text{mol}^{-1}$, $D_M = 1.21\text{--}1.40$). The ROP of the sustainable CO₂/butadiene-derived EVL, EHO or MH –the original semi-hydrogenated parent lactone–, remained unsuccessful, regardless of the catalytic system.

Keywords: δ -hexalactone; δ -valerolactone; ring-opening polymerization (ROP); copolymer; alkali metal catalyst

Introduction

Ring-opening polymerization (ROP) of cyclic esters (lactones, lactides or cyclic carbonates) is a commonly used method to synthesize polyesters with controlled molar masses, narrow dispersities and tailored macromolecular structures.[1,2,3,4,5,6,7,8,9,10,11,12] Homo- and co-polyesters have shown great potential for biomedical applications and as materials for the plastic industry as alternatives to regular polyolefins.[13,14,15] Metal- and organo-based ROP catalysts need to be appropriately chosen for each specific monomer type to achieve the best compromise between the rate and the control of the polymerization. The use of a bio-sourced lactone monomer, associated with a simple and cheap catalytic polymerization method, adds significantly to the interest in the corresponding polyester-based materials due to their renewability and sustainability.

Among the large variety of cyclic esters that have been investigated in ROP, the 5-Me substituted δ -valerolactone, often referred to as δ -hexalactone (HL) (Figure 1), is a biosourced six-membered monomer that can be derived from pineapple and used as a food additive,[16,17] which has been less commonly explored than the related ubiquitous (unsubstituted) δ -valerolactone (VL). The ROP of HL using “lanthanum trisopropoxide” was reported in 2002; performed in dichloromethane/toluene (70:30 v/v) solution at 21 °C, it did not reach full conversion even after a long reaction time (77% in 18 h) and returned oligomers ($\bar{M}_{n,SEC} = 5200 \text{ g}\cdot\text{mol}^{-1}$) with a moderate control over molar mass distribution ($D_M = 1.3$).[18] A better activity was reported recently with strontium bisopropoxide as catalyst/initiator using *n*-dodecanol as co-initiator.[19] In toluene solution at 23 °C, poly(HL)s (PHLs) were obtained within short reaction times (82% conv. in 15 min, $\bar{M}_{n,SEC} < 5000 \text{ g}\cdot\text{mol}^{-1}$) and with a fair dispersity ($D_M = 1.16\text{--}1.30$); noteworthy, the ROP hardly proceeded in the absence of the co-initiator (6% conv. in 15 min). Furthermore, the ROP of HL using the diphenyl phosphate (DPP) organic acid was reported independently in 2015-2016 by Hadjichristidis and Hillmyer.[20,21] At high monomer concentration ($[\text{HL}]_0 = 3.5 \text{ M}$) and room temperature in toluene, DPP allowed a chain extension ROP with a high HL conversion (89%), a controlled molar mass ($\bar{M}_{n,NMR} = 11,400 \text{ g}\cdot\text{mol}^{-1}$ vs. $\bar{M}_{n,theo} = 10,900 \text{ g}\cdot\text{mol}^{-1}$) and a narrow dispersity ($D_M = 1.09$) of the resulting PHL end-capped with DPP.[20] Thermodynamic investigations also revealed that HL shows, in bulk or in solution, a much higher reactivity (polymerization rate) and a slightly higher equilibrium conversion than analogous 5-alkyl- δ -valerolactones with longer alkyl substituents (i.e., 5-butyl- δ -lactone and 5-pentyl- δ -valerolactone,

also known as δ -nonalactone and δ -decalactone, respectively).[20,21,22] Besides, the ROP of HL ($\Delta H_p^\circ = -19.3 \pm 0.5 \text{ kJ.mol}^{-1}$; $\Delta S_p^\circ = -62 \pm 2 \text{ J.mol}^{-1}\text{K}^{-1}$) was shown to be more exothermic and entropically unfavored as compared to VL ($\Delta H_p^\circ = -10.5 \text{ kJ.mol}^{-1}$; $\Delta S_p^\circ = -15 \text{ J.mol}^{-1}\text{K}^{-1}$).[18,21,22]

The ring-opening copolymerization (ROCOP) of HL with various comonomers has also been investigated.[23,24,25] The simultaneous copolymerization of HL with its structural isomer ϵ -caprolactone (CL) catalyzed by DPP at 100 °C in bulk can serve as an effective method to regulate the properties of poly(CL) (PCL); it typically returns random copolymers with reduced crystallinity and enhanced enzymatic degradability with HL content as low as 5mol%.[23] Also, the ROCOP of HL with ethylene brassylate (EB) using BiPh₃ as catalyst gave copolyesters incorporating up to 90mol% of EB (bulk monomers, 3 to 6 days, 130 °C), with reduced crystallization capability, higher degradation rate, improved flexibility and good thermal stability in comparison to PCL.[24] Likewise, a new kind of low glass transition random copolyesters that showed a decreased crystalline fraction, a lower stiffness, and an improved biodegradability in comparison to PCL, was developed by copolymerization of ω -pentadecalactone (PDL) with HL using also BiPh₃ as catalyst under the same conditions.[25] The PDL content ranged from 39 to 82 mol%, and the resulting materials revealed non cytotoxic, and thus suitable for potential use in the biomedical field.

In addition, the related disubstituted δ -valerolactones, such as 2-ethylidene-6-hepten-5-olide (EVL) and 2-ethylheptane-5-olide (EHO) (Figure 1), which can be readily produced by a telomerization reaction of CO₂ with 1,3-butadiene – an economical large-volume chemical that can also be derived from top biomass platform chemicals –, and subsequent hydrogenation, respectively, have attracted a growing interest as new potential renewable monomers.[26,27,28,29,30] EVL was even produced at a miniscale plant.[31] However, the very few literature reports on the polymerizability of EVL indicate that, so far, only the radical homopolymerization of this monomer is operative. When initiated by 2,2'-azobis(isobutyronitrile) (AIBN) in the presence of ZnCl₂ (100 °C, 24 h), the polymerization provides a butadiene/CO₂ copolymer incorporating small amounts of alkenes ($\overline{M}_{n,SEC}$ up to 85,0000 g.mol⁻¹, $D_M = 1.1-1.5$).[32,33,34,35] Alternatively, simple additive-/solvent-free heating of EVL in the presence

of O₂ gave a full monomer conversion, thereby providing a convenient avenue toward CO₂-based polymers.[36]

Herein, we report new results on the polymerizability of these little-studied 6-membered δ -valerolactones, namely HL, EVL, EHO, and MH in comparison to VL. Various readily available organic and metal-based catalytic systems have been investigated for the (co)polymerization of these substituted δ -valerolactones.

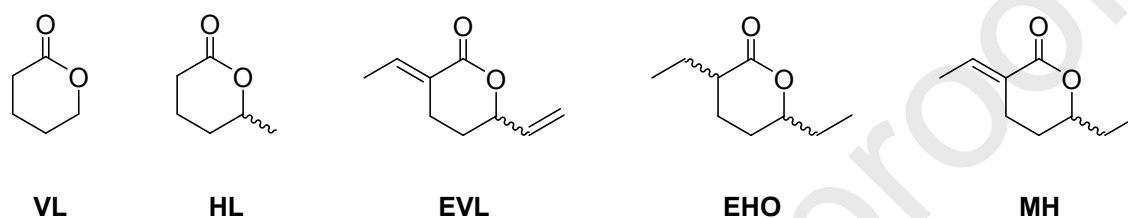


Figure 1. Six-membered ring (substituted) δ -valerolactones explored in the present study.

Experimental section

Materials

All catalytic experiments were performed under an inert argon atmosphere using standard Schlenk line and glovebox techniques. KO^tBu (Strem Chemicals, 98%), La(N(TMS)₂)₃ (Sigma Aldrich, 98%) and Y(OTf)₃ (Sigma Aldrich, 98%) were used as received. Benzyl alcohol (Acros, 98%) was distilled over Mg turnings under argon atmosphere and stored over 3–4 Å activated molecular sieves. NaOMe, NaO^tBu and KOMe were prepared from the corresponding metal and alcohol, respectively. 2-*tert*-Butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (BEMP; Aldrich, 98%), δ -valerolactone (VL; TCI, 98%) and 5-Me substituted δ -valerolactone (δ -hexalactone (HL); Alfa Aesar, 98%) were distilled from CaH₂ and stored under argon. 2-Ethylidene-6-hepten-5-olide (EVL) was synthesized from 1,3-butadiene and CO₂ according to the literature procedure, and similarly distilled from CaH₂ and stored under argon.[26,27,28,29,30]

Instrumentation and measurements

^1H (400 MHz) and $^{13}\text{C}\{^1\text{H}\}$ (100 MHz) NMR spectra were recorded on Bruker Avance AM Ascend 400 spectrometer in CDCl_3 at 25 °C, and referenced internally relative to SiMe_4 (δ 0 ppm) using the residual solvent resonances.

Number-average molar mass ($\overline{M}_{n,\text{SEC}}$) and dispersity ($D_M = \overline{M}_w/\overline{M}_n$) values of the (co)polymers were determined by size exclusion chromatography (SEC) in THF at 30 °C (flow rate = 1.0 mL min^{-1}) on a Polymer Laboratories PL50 apparatus equipped with a refractive index detector and a set of two ResiPore PLgel 3 μm MIXED-D 300 \times 7.5 mm columns. The polymer samples were dissolved in THF (2 mg mL^{-1}). All elution curves were calibrated with polystyrene standards; the reported $\overline{M}_{n,\text{SEC}}$ values of the copolymers are uncorrected for the difference in hydrodynamic radius vs. polystyrene.

Monomer conversions were calculated from ^1H NMR spectra of the crude polymer samples in CDCl_3 by using the integration (Int.) ratio $\text{Int.}_{\text{Polymer}}/[\text{Int.}_{\text{Polymer}} + \text{Int.}_{\text{Monomer}}]$ of the COO-CH_2 methylene (δ_{PVL} 4.11 ppm, δ_{VL} 4.37 ppm) or COO-CH methine (δ_{PHL} 4.93 ppm, δ_{HL} 4.45 ppm), in the polymer and residual monomer, respectively. The molar mass values of copolymer samples were determined by ^1H NMR analysis in CDCl_3 , from the relative intensities of the signals of the main-chain methylene OC(O)CH_2 (δ_{CH_2} 2.30 ppm) relative to the chain-end OMe signals (δ_{CH_3} 3.68 ppm).

Mass spectra were recorded at CRMPO-ScanMAT (Rennes, France). ESI mass spectra were recorded on an orbitrap type Thermo Fisher Scientific Q-Exactive instrument with an ESI source in positive or negative mode by direct introduction at 5–10 $\mu\text{g mL}^{-1}$. Samples were prepared in CH_2Cl_2 at 10 $\mu\text{g mL}^{-1}$. High resolution MALDI-ToF mass spectra were recorded using an ULTRAFLEX III TOF/TOF spectrometer (Bruker Daltonik GmbH, Bremen, Germany) in positive and/or negative ionization mode. Spectra were recorded using reflectron mode and an accelerating voltage of 25 kV. A mixture of a freshly prepared solution of the polymer in THF or CH_2Cl_2 (HPLC grade, 10 mg mL^{-1}) and DCTB (*trans*-2-(3-(4-*tert*-butylphenyl)-2methyl-2-propenyldene) malononitrile, and a MeOH solution of the cationizing agent (NaI, 10 mg mL^{-1}) were prepared. The solutions were combined in a 1:1:1 v/v/v ratio of matrix-to-sample-to-cationizing agent - if added. The resulting solution (0.25–0.5 mL) was deposited onto the sample target (Prespotted AnchorChip PAC II 384 / 96 HCCA) and air or vacuum dried.

Synthesis of 2-ethylheptane-5-olide (EHO). EVL (1.50 g, 10.0 mmol), THF (20 mL) and Pd/C (37.5 mg) were added in a 50 mL stainless steel autoclave under argon. 20 bar of H₂ was introduced in the reactor and then the suspension was stirred magnetically at 60 °C for 1 h. After depressurization of the reactor at room temperature, volatiles were removed under vacuum and the crude product was purified by fractional distillation to recover 2-ethylheptane-5-olide (EHO) as a colorless liquid (1.30 g, 85%). ESI-MS: 157.12 ([M+H]⁺). ¹H NMR (CDCl₃, 400 MHz, 23 °C) (Figure S12): δ 4.22 (m, 1H, CHCOO), 2.39 (m, 1H, COO-CH), 1.5–2.2 (m, 8H, CH₃CH₂CHCH₂CH₂CHCH₂CH₃), 1.01 (m, 6H, CH₃). ¹³C{¹H} NMR (CDCl₃, 100 MHz, 23 °C) (Figure S13) (data in parentheses refer to the second minor diastereomer): δ 175.69 (173.84) (COO), 79.29 (82.53) (COOCH), 39.70 (42.10) (CHCOO), 28.29 (29.15) (CH₃CH₂CHCO), 26.24 (24.87) (CH₂CH), 23.85 (22.88) (CHCH₂), 11.59 (11.05) (CH₃CH₂CHO), 9.58 (9.24) (CH₃CH₂CHCO).

Synthesis of 2-ethylidene-6-heptan-5-olide (MH). In a typical procedure, EVL (1.50 g, 10.0 mmol), THF (20 mL) and Ni-Raney (75 mg) were added in a 50 mL stainless steel autoclave under argon. 20 bar of H₂ was introduced in the reactor and the suspension was stirred with a magnetic bar at room temperature for 1 h. After depressurization of the reactor, volatiles were removed under vacuum and the crude product was purified by column chromatography (Hexanes/AcOEt 4:1 v/v) to recover the desired product (MH) as a colorless liquid (1.15 g, 75%). ESI-MS: 155.11 ([M+H]⁺). ¹H NMR (CDCl₃, 400 MHz, 23 °C) (Figure S14): δ 7.12 (q, ³J = 8.0 Hz, 1H, CH₃CH), 4.15 (m, 1H, CHCH₂CH₃), 2.37–2.60 (m, 2H, CH₂CH₂), 1.63–1.95 (m, 4H), 1.78 (d, ³J = 8.0 Hz, 3H, CH₃CH), 1.00 (m, 3H, CH₂CH₃). ¹³C{¹H} NMR (CDCl₃, 100 MHz, 23 °C) (Figure S15): δ 166.97 (COO), 140.67 (CH₃CH), 126.25 (CH₃CH=C), 80.52 (CHCH₂CH₃), 28.28, 26.96, 22.57, 14.07 (CH₃CH), 9.34 (CHCH₂).

General procedure for the ring-opening (co)polymerization of six-membered δ-valerolactones. In a typical experiment, a Schlenk flask placed under argon was charged with the Na (pre)catalyst/initiator (NaOMe, 4.75 mg, 0.088 mmol, 1 equiv.) (Table 2, entry 14). Then, the monomer (HL, 100 mg, 0.88 mmol, 10 equiv.) was added in using a syringe and the reaction mixture was magnetically stirred at the desired temperature using an oil bath. After a given period (reaction times were not systematically optimized), the reaction was quenched upon addition of acetic acid (a few drops of a 6 M toluene solution), and volatiles were removed under vacuum at

low temperature (for the residual monomer not to evaporate). After determination of the monomer conversion by ^1H NMR analysis of the crude product, when some polymer was formed, the resulting crude residue was dissolved in CH_2Cl_2 (0.5 mL) and the polymer was precipitated in cold hexane (1 mL, 0 °C), filtered and dried under vacuum. The recovered polymer was then analyzed by NMR and SEC.

H-PHL-OMe: ^1H NMR (CDCl_3 , 400 MHz, 23 °C) (Figure S1): δ 4.93 (m, 1H, COOCH), 3.68 (s, OMe terminal group), 2.30 (m, 2H, CHCH₂), 1.64 (3, 4H, CHCH₂CH₂CH₂), 1.42 (d, 3H, $J = 7$ Hz, CH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz, 23 °C) (Figure S2): δ 172.91 (COO), 70.41 (COOCH), 51.55 (OMe terminal group), 35.24 (CHCH₂CH₂CH₂), 34.21 (CHCH₂CH₂CH₂), 20.84 (CHCH₂CH₂CH₂), 19.91 (CH₃).

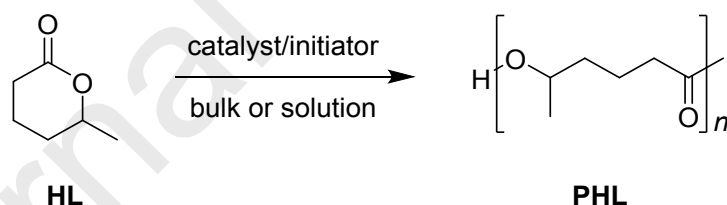
H-P(HL-co-VL)-OMe: ^1H NMR (CDCl_3 , 400 MHz, 23 °C) (Figures S4,S6,S8): δ 4.89 (COOCH HL), 4.09 (COOCH₂ VL), 3.69 (s, OMe terminal group), 2.35 (CHCH₂ HL and COOCH₂CH₂ VL), 1.69 (COOCH₂CH₂CH₂ HL and VL), 1.22 (CH₃ HL). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz, 23 °C) (Figures S5,S7,S9): δ 173.23 (COO VL), 172.83 (COO HL), 70.38 (COOCH HL), 63.90 (COOCH₂ VL), 35.23 (CHCH₂CH₂CH₂ HL), 34.03 (CHCH₂CH₂CH₂ HL), 33.66 (COOCH₂CH₂ VL), 28.08 (COOCH₂CH₂CH₂ VL), 21.42 (COOCH₂CH₂CH₂CH₂ VL), 20.77 (CHCH₂CH₂CH₂ HL), 19.00 (CH₃ HL).

Results and Discussion

Homopolymerization of HL

The polymerization performances of different ubiquitous catalytic systems regularly employed with success in the ROP of lactones were investigated towards HL (Scheme 1, Table 1). Preliminary experiments, all performed in bulk (i.e., neat, solvent-free) conditions with the aim to enhance reaction rates and to reach high monomer conversions, established the complete inability of sebacic and decanoic Brønsted acids to produce polymers at temperatures as high as 230 °C (Table 1, entries 1–2).[37] Only a poor activity was observed with BEMP, a usually most effective ROP organocatalyst, especially with monomers that are reluctant to polymerize such as β -lactones or δ -valerolactones:[3,38,39,40,41] at 60 °C, HL homopolymerization only reached 15% conversion in 2 h, without any further reaction overnight (Table 1, entries 3–4), while no reaction

proceeded at room temperature. Similarly, reactions performed at room temperature using the strong Lewis acidic “Y(OTf)₃” combined with benzyl alcohol (BnOH) as co-initiator, a catalytic system effective in the ROP of even touchy cyclic esters such as β-lactones,[42,43] failed to consume any monomer (Table 1, entry 5). At 60 °C, progress of the reaction remained slow with only 27% conversion after 72 h. At 100 °C also, the reaction reached a plateau around 30% HL conversion (Table 1, entries 6–9), possibly suggesting a polymerization/depolymerization equilibrium.[18,44] The La(N(TMS)₂)₃/BnOH catalytic system, which proved quite effective even towards ROP-reluctant 5-membered γ-lactones and at quite low temperatures to avoid depolymerisation,[45,46,47] showed also no activity towards HL at room temperature (Table 1, entry 10).[48] ROP of HL with this catalytic system proceeded at best, yet slowly, at 60 °C, giving a 44% maximum conversion after 72 h (Table 1, entries 11 and 12). At 100 °C, a plateau was reached within less than 2 h at ca. 30% HL conversion (Table 1, entries 13 and 14), a value comparable to that observed with “Y(OTf)₃” under similar conditions. Raising further the temperature up to 160 °C proved ineffective, as no monomer consumption was then detected (Table 1, entry 15). These observations also suggest a possible polymerization/depolymerization issue.[18]



Scheme 1. Ring-opening polymerization of HL towards PHL.

Table 1. ROP of HL mediated by organo- or metal-based catalyst systems.

Entry	(Pre)catalyst	$[\text{HL}]_0/[\text{Cat.}]_0$ $/[\text{BnOH}]_0$ [a]	Reaction temp. [°C]	Reaction time [b] [h]	HL conv. [c] [%]
1	decanoic acid	100:5:0	230	6	0
2	sebacic acid	100:5:0	230	6	0
3	BEMP	100:1:2	60	2	14
4	“	100:1:2	60	18	18

5	Y(OTf) ₃	100:1:3	21	18	0
6	“	100:1:3	60	2	16
7	“	100:1:3	60	72	26
8	“	100:1:3	100	2	31
9	“	100:1:3	100	72	27
10	La(N(TMS) ₂) ₃	100:1:3	21	18	0
11	“	100:1:3	60	2	26
12	“	100:1:3	60	72	44
13	“	100:1:3	100	2	32
14	“	100:1:3	100	72	30
15	“	100:1:3	160	18	0

^[a] All reactions were performed in bulk conditions (neat monomer). ^[b] Reaction times were not necessarily optimized. ^[c] As determined by ¹H NMR analysis of the crude reaction mixture.

In order to reach higher conversion of HL with an straightforward process and a cheap and easily available catalyst, different alkali metal alkoxides were then investigated as ROP initiator.^[49,50,51,52,53,54] The activity of KO*t*Bu (10 mol%) was first evaluated with HL, at room or higher temperature, in bulk or in toluene solution (Table 2, entries 1–10). In toluene solution, the HL conversion reached a plateau at ca. 30%, both at room temperature and at 60 °C (Table 2, entries 1–4). Under bulk conditions, as anticipated, the HL conversion reached higher values, which were slightly (and negatively) affected by the temperature: 78% at room temperature, 68% at 60 °C, and 61–64% at 100 °C (Table 2, entries 5–10). Interestingly, the ROP of HL using NaOMe proved more efficient, as full conversions could be achieved under different conditions (Table 2, entries 11–17). The reaction was rather sluggish at room temperature and required 10 mol% to reach full monomer conversion. Raising the temperature to 60 or 100 °C successfully enabled to convert > 90% of HL within 2 h with 10 mol% of NaOMe (Table 2, entries 13–15) and within 18 h with “only” 3 mol% (Table 2, entries 18–21).

Table 2. ROP of HL mediated by alkali metal alkoxides.

Entry	Catalyst	[HL] ₀ /[Cat.] ₀	[HL] ₀ ^[a]	Reaction temp. [°C]	Reaction time ^[b] [h]	HL conv. ^[c] [%]
1	KO <i>t</i> Bu	10:1	1M	21	2	28

2	“	10:1	“	21	18	25
3	“	10:1	“	60	2	30
4	“	10:1	“	60	18	30
5	“	10:1	bulk	21	2	52
6	“	10:1	“	21	18	78
7	“	10:1	“	60	2	50
8	“	10:1	“	60	18	68
9	“	10:1	“	100	2	64
10	“	10:1	“	100	18	61
11	NaOMe	10:1	“	21	2	82
12	“	10:1	“	21	18	100
13	“	10:1	“	60	2	90
14	“	10:1	“	60	18	100
15	“	10:1	“	100	8	96
16	“	33:1	“	21	2	29
17	“	33:1	“	21	18	35
18	“	33:1	“	60	2	47
19	“	33:1	“	60	18	100
20	“	33:1	“	100	2	46
21	“	33:1	“	100	18	100
22	NaOtBu	10:1	“	21	2	63
23	“	10:1	“	21	18	88
24	KOMe	10:1	“	21	2	60
25	“	10:1	“	21	18	85

^[a] All reactions were performed with $[\text{HL}]_0 = 1 \text{ M}$ in toluene or in bulk (neat monomer, no solvent). ^[b] Reaction times were not necessarily optimized. ^[c] As determined by ¹H NMR analysis of the crude reaction mixture.

To explore the influence of the alkali metal salt and of the alkoxide initiator on the reaction rate, comparative experiments were conducted with NaOtBu and KOMe (Table 2, entries 22–25), while KOMe proved less effective than NaOMe (Table 2, entries 11,12 vs. 24,25). NaOtBu proved somehow more effective than KOtBu (Table 2, entries 5,6 vs. 22,23). Overall, the best reactivity was obtained with sodium salts and with the methoxide group. This can be tentatively rationalized by a higher Lewis acidity of the cationic metal center (Na^+ vs. K^+) and the lower steric hindrance of the initiator (OMe vs. OtBu).

NaOMe, as the most efficient initiator for the ROP of HL, was hence selected to further investigate the influence of the polymerization temperature and of the $[\text{HL}]_0/[\text{NaOMe}]_0$ ratio on

the ROP of HL (Table 3); in parallel, the microstructure and molar mass control of the PHL formed were studied. As revealed by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy (Fig. S1–S2) and as further supported by MALDI-ToF mass spectrometry (MS) analyses (Fig. S3), polymers with a major distribution of macromolecules end-capped by a methoxycarbonyl and a hydroxyl groups $(\text{C}_6\text{H}_{10}\text{O}_2)_n(\text{CH}_4\text{O})$ were observed ($m/z = 114n + \text{M}(\text{CH}_4\text{O}) + \text{M}(\text{Na}^+)$) (for instance, for $n = 4$, $m/z_{\text{obs}} = 511.2878$ vs. $m/z_{\text{calcd}} = 511.2883$). Besides, other lower intensity peaks were observed that originate from different side-reactions, which in turn may explain the slightly broadened dispersities observed (*vide infra*). A minor series was assigned to cyclic oligomers $(\text{C}_6\text{H}_{10}\text{O}_2)_n$ with $m/z = 114n + \text{M}(\text{Na}^+)$ (for instance, for $n = 6$, $m/z_{\text{obs}} = 707.3975$ vs. $m/z_{\text{calcd}} = 707.3977$), that results from intramolecular transesterification. Another minor population with hydroxy-terminated chains $(\text{C}_6\text{H}_{10}\text{O}_2)_n(\text{H}_2\text{O})$, $m/z = 114n + \text{M}(\text{H}_2\text{O}) + \text{M}(\text{Na}^+)$ (for instance, for $n = 6$, $m/z_{\text{obs}} = 725.4080$ vs. $m/z_{\text{calcd}} = 725.4088$) was also observed. Hydrolytic work-up with acetic acid (refer to the Experimental section), adventitious presence of traces of water during the reaction or hydrolysis of cyclic oligomers with water under MS conditions, are possible explanations for the observation of these hydroxy end-capped polymers.

Table 3. Characteristics of PHL obtained from the ROP of HL initiated by NaOMe.

Entry	$[\text{HL}]_0 / [\text{NaOMe}]_0$ [a]	Reaction temp. [°C]	HL conv. [b]	$\overline{M}_{n,\text{theo}}$ [c]	$\overline{M}_{n,\text{NMR}}$ [d]	$\overline{M}_{n,\text{SEC}}$ [e]	D_M [f]
1	10:1	21	90	1100	1700	1600	1.21
2	10:1	60	100	1200	1400	950	1.47
3	10:1	100	96	1100	1600	1000	2.03
4	20:1	21	95	2200	2500	3250	1.20
5	20:1	60	100	2300	2900	2300	1.22
6	33:1	21	61	2300	2000	2700	1.20
7	33:1	60	92	3500	3050	3500	1.36
8	33:1	100	96	3600	3800	3700	1.74
9	100:1	21	21	2400	2200	2500	1.17
10	100:1	60	53	6100	3450	2100	1.25
11	100:1	100	82	9400	2700	2300	1.35

[a] All reactions were performed in bulk conditions (neat monomer) over 18 h; the reaction time was not optimized. [b] Experimental molar mass as determined by ^1H NMR analysis of the crude reaction mixture.

[c] Theoretical molar mass calculated from the relation: $[\text{HL}]_0 / [\text{NaOMe}]_0 \times \text{Conv.}_{\delta\text{-HL}} \times M_{\delta\text{-HL}} + M_{\text{MeOH}}$

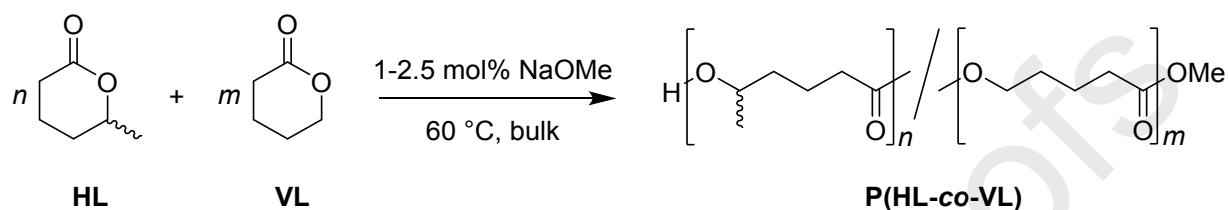
($M_{\text{HL}} = 114 \text{ g.mol}^{-1}$; $M_{\text{MeOH}} = 32 \text{ g.mol}^{-1}$). ^[d] Experimental molar mass value determined by ^1H NMR analysis of the isolated polymer, from ^1H NMR resonances of the methoxy terminal group. ^[e] Experimental, uncorrected number-average molar mass value determined by SEC in THF at 20 °C versus polystyrene standards. ^[f] Dispersity ($D_M = \bar{M}_w/\bar{M}_n$) as determined by SEC using PS standards.

All HL oligomers produced using 1–5 mol% of NaOMe as initiator at room temperature (Table 3, entries 4, 6 and 9) showed a fairly good match between the molar mass values measured by NMR analysis (on the basis of the methoxy chain end-group observed at δ 3.68 ppm) and the corresponding theoretical values calculated on the basis of HL conversion ($\bar{M}_{n,\text{theo}}$); noteworthy, the PHL produced at 21 °C with 10 mol% of NaOMe (Table 3, entry 1) showed a somewhat higher value than the theoretical one, possibly pointing out an incomplete initiation efficiency. Also, the dispersity values of all the polymers produced at room temperature were moderately narrow ($D_M = 1.17$ – 1.21) hinting at some limited transesterification side reactions. Raising the temperature to 60 °C resulted, as anticipated, in slightly higher dispersity values ($D_M = 1.22$ – 1.47). The experimental $\bar{M}_{n,\text{NMR}}$ values of PHL produced at this temperature with 5 or 10 mol% of initiator were in line with the ones calculated (Table 3, entries 2,5), but distinctly lower than the ones calculated when lower amounts of initiator were used (1 and 3 mol%; Table 3, entries 7,10). These trends were even more pronounced at 100 °C: the dispersity broadened in the range 1.35–2.03 and the $\bar{M}_{n,\text{NMR}}$ values, although in good line when using 3–10 mol% of initiator (Table 3, entries 3,8), significantly dropped below the theoretical value when only 1 mol% of NaOMe was used (Table 3, entry 11). Overall, these observations indicate a relatively fast and quantitative initiation and limited undesirable side reactions when operating at a relatively low temperature (21–60°C) with 1–5 mol% of NaOMe. On the other hand, only partial initiation takes place when excessive loading of NaOMe (10 mol%) is used and detrimental side reactions (especially transesterification i.e. reshuffling, backbiting) – typical of cyclic esters ROP reactions –, occur to a significant extent at 100 °C. Typically, oligomers with $\bar{M}_{n,\text{NMR}} \leq 3800 \text{ g.mol}^{-1}$ were recovered under these operating conditions.

Copolymerization of HL with VL

Random ring-opening copolymerization (ROCOP) of HL with its unsubstituted parent monomer, VL, was targeted to explore the influence of the monomer substituent on the control of the

polymerization and the relative monomer reactivity (Scheme 2). The reactions were performed using various monomer-to-initiator ratios under the above optimized conditions, namely at 60 °C with 1 or 2.5 mol% NaOMe, over a non-optimized 24 h time period (Table 4).



Scheme 2. Simultaneous ring-opening copolymerization of HL with VL.

Three different monomers feeds were used (i.e. $[\text{HL}]_0/[\text{VL}]_0 = 1:1; 1:3$ and $3:1$), coupled to two different catalytic loadings ($[\text{NaOMe}]_0 = 1$ or 2.5 mol%). In each case, high conversion of both comonomers was observed, as monitored by ^1H NMR analysis: 72–87% for HL and 91–98% for VL, the latter lactone which revealed more reactive than its substituted analogue whatever the conditions, as expected from their respective homopolymerization behavior. As revealed by ^1H and ^{13}C NMR spectroscopy (Fig. S4,S6,S8), the random copolymers displayed, besides the repeating unit typical signals, a methoxycarbonyl chain-end group observed at ca. δ 3.65 ppm. The P(HL-co-VL) molar mass values recorded up to $\bar{M}_{n,\text{NMR}} = 9700$ g.mol $^{-1}$ (Table 4) typically remained lower than those of the HL/CL, HL/PDL or HL/EB copolymers.[23,24,25] The copolymers recovered from the experiments conducted with 2.5 mol% of NaOMe showed $\bar{M}_{n,\text{NMR}}$ values that matched well the $\bar{M}_{n,\text{theo}}$ data based on HL and VL conversion, no matter of the initial ratio of comonomers (Table 4, entries 1–3). This was not necessarily the case in the polymerizations performed with 1 mol% of NaOMe ratio, with the aim to increase the copolymer molar masses (Table 4, entries 4–6). Indeed, with an equimolar mixture of comonomers or with an excess of HL, the copolymerization process was not well-controlled, that is $\bar{M}_{n,\text{NMR}}$ values $\ll \bar{M}_{n,\text{theo}}$; on the other hand, a copolymer with a predictable molar mass was obtained when using an excess of VL, the monomer most readily to polymerize. These results indicate that an excess of HL leads to a loss of control of the polymerization at a catalytic loading of 1 mol%. Long polymeric chains do not seem

to be accessible for HL with this catalyst system.[55] Chain-transfer or cyclization side-reactions could explain the reduced experimental average molar mass of the final copolymer.

Table 4. Simultaneous ring-opening copolymerization of HL and VL.

Entry	$\frac{[\text{HL}]_0/[\text{VL}]_0}{[\text{NaOMe}]_0}$ ^[a]	HL conv. ^[b] [%]	VL conv. ^[b] [%]	$\overline{M}_{n,\text{theo}}$ ^[c] [g mol ⁻¹]	$\overline{M}_{n,\text{NMR}}$ ^[d] [g mol ⁻¹]	$\overline{M}_{n,\text{SEC}}$ ^[e] [g mol ⁻¹]	D_M ^[f]
1	20:20:1	87	98	4000	4600	3500	1.28
2	10:30:1	76	95	3700	3300	3750	1.38
3	30:10:1	88	97	4000	3900	3600	1.32
4	50:50:1	72	91	8700	3700	3000	1.25
5	25:75:1	82	96	9600	9700	9150	1.21
6	75:25:1	83	91	9400	2400	2600	1.40

^[a] Reactions conditions: bulk (neat monomers), 60 °C, 24 h (reaction time was not optimized).

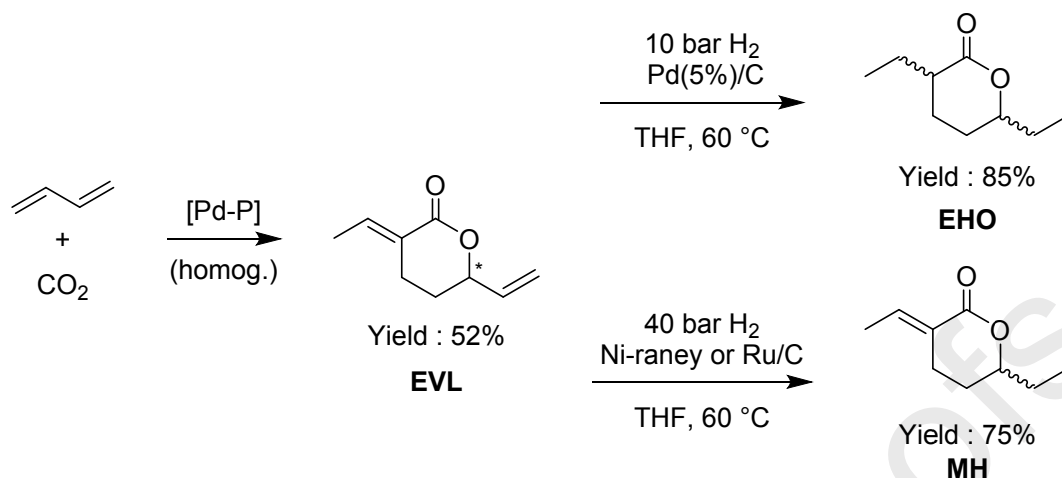
^[b] As determined by ¹H NMR analysis of the crude reaction mixture. ^[c] Theoretical molar mass value calculated from the relation: $([\text{HL}]_0/[\text{NaOMe}]_0 \times \text{Conv.}_{\text{HL}} \times M_{\text{HL}}) + ([\text{VL}]_0/[\text{NaOMe}]_0 \times \text{Conv.}_{\text{VL}} \times M_{\text{VL}}) + M_{\text{MeOH}}$ ($M_{\text{HL}} = 114 \text{ g}\cdot\text{mol}^{-1}$; $M_{\text{VL}} = 100 \text{ g}\cdot\text{mol}^{-1}$; $M_{\text{MeOH}} = 32 \text{ g}\cdot\text{mol}^{-1}$).

^[d] Experimental molar mass value determined by ¹H NMR analysis of the isolated polymer, from ¹H resonances of the methoxy terminal group.

^[e] Experimental, uncorrected number-average molar mass value determined by SEC in THF at 20 °C versus polystyrene standards. ^[f] Dispersity ($\overline{M}_w/\overline{M}_n$) as determined by SEC.

Attempted ROP of disubstituted δ -valerolactones

Ethylidene-6-hepten-5-olide (EVL) is an interesting disubstituted δ -valerolactone that can be efficiently obtained from the telomerization of butadiene with CO₂ via palladium catalysis (selectivity over 90%) (Scheme 3).[26,27,28,29,30] As briefly reported by Behr et al.,[27] its hydrogenation, also performed by Pd catalysis, leads readily to 2-ethylheptane-5-olide (EHO); in our hands, this latter saturated disubstituted δ -valerolactone is typically recovered as a diastereomeric mixture (63:37, as determined by ¹³C{¹H} NMR analysis using the methine signal at δ 40 ppm; refer to the Experimental section and Fig. S12,S13). While optimizing the latter EHO synthesis, we observed that the previously unreported disubstituted, semi-hydrogenated δ -valerolactone MH can also be selectively and straightforwardly synthesized in high yields (up to 75%) using either Ni-Raney, Ru/C, Crabtree's catalyst or Wilkinson's catalyst under mild conditions (Table S1; Fig. S14,S15).



Scheme 3. Access to the disubstituted δ -valerolactones EVL, EHO and MH, from CO_2 and butadiene and subsequent (semi)hydrogenation.

We were therefore interested in exploring whether these six-membered disubstituted δ -lactones obtained from sustainable chemical reactants and processes can undergo ROP to access original polyester materials.

Disappointingly, all our attempts to ring-open polymerize EHO and MH with different catalytic systems (Chart S1) under a variety of reaction conditions, failed. None of these catalysts was effective in the 20–180 °C temperature range, the monomer remains unreacted.[48] This may be due to a low ceiling temperature of EHO and MH. Note also that no polymerization occurred when using the $\text{La}(\text{N}(\text{TMS})_2)_3/\text{BnOH}$ catalytic system effective towards ROP-reluctant 5-membered γ -lactones (–40 °C, toluene, 18 h).[45,46,47] Similarly, the attempted ring-opening copolymerization of EVL, MH or EHO with VL or HL all remained unsuccessful, even in the presence of an excess of VL or HL. These results are reminiscent of EVL for which no successful ROP has been reported in the literature to date.

Conclusion

Typical examples of Brønsted acids, organocatalysts or Lewis acidic metal complexes remain poorly active in the ROP of HL under a range of reaction conditions. On the other hand, alkali metal alkoxides successfully homopolymerize HL under optimized mild operating conditions (1–2.5 mol% NaOMe, solvent-free, 60 °C, 18 h). In particular, the readily available sodium

methoxide promoted the ROP of HL to afford PHL oligomers ($\bar{M}_{n,NMR}$ up to ca. 4000 g.mol⁻¹, $D_M < 1.36$). The results showed the occurrence of some –yet limited– transesterification side-reactions. Further copolymerization of HL with the unsubstituted alike VL mediated by NaOMe showed a good-to-high conversion (72–98%) of both comonomers, the latter unsubstituted lactone showing a slightly higher reactivity. Random copolymers with a predictable molar mass ($\bar{M}_{n,NMR}$ up to ca. 10,000 g.mol⁻¹, $D_M < 1.40$) were thus recovered. Overall, the formation of high molar mass copolymers of HL/VL seems to be impeded by chain-transfer and/or cyclization side-reactions. This is the first report of the successful RO(CO)P of HL promoted by the readily available sodium methoxide. Finally, HL showed a significantly better reactivity than the analogous 1,5-alkyl 6-membered δ -valerolactones EHO, EVL and MH, which unfortunately remained inaccessible to ROP under the experimental conditions we investigated and regardless of the catalyst/initiator used. These results shine new lights on the ring-opening polymerizability of substituted δ -valerolactones, of which the alkyl substituent on the 1- and/or 5- position on the cyclic ester ring play a major detrimental role in their ROP.

Acknowledgements

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Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to legal or ethical reasons.

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Supporting Information

Figure S1. ^1H NMR spectrum (CDCl_3 , 400 MHz, 23 °C) of a PHL sample obtained from the ROP of HL using NaOMe at 60 °C (Table 3, entry 3).

Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 100 MHz, 23 °C) of a PHL sample obtained from the ROP of HL using NaOMe at 60 °C (Table 3, entry 3).

Figure S3. MALDI-ToF mass spectrum of a PHL sample obtained from the ROP of HL using NaOMe as initiator (Table 3, entry 2).

Figure S4. ^1H NMR spectrum (CDCl_3 , 400 MHz, 23 °C) of a P(VL-*co*-HL) sample obtained from the ROCOP of VL and HL (1:1) using NaOMe at 60 °C (Table 4, entry 1).

Figure S5. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 100 MHz, 23 °C) of a P(VL-*co*-HL) sample obtained from the ROCOP of VL with HL (1:1) using NaOMe at 60 °C (Table 4, entry 1).

Figure S6. ^1H NMR spectrum (CDCl_3 , 400 MHz, 23 °C) of a P(VL-*co*-HL) sample obtained from the ROCOP of VL and HL (1:3) using NaOMe at 60 °C (Table 4, entry 2).

Figure S7. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 100 MHz, 23 °C) of a P(VL-*co*-HL) sample obtained from the ROCOP of VL and HL (1:3) using NaOMe at 60 °C (Table 4, entry 2).

Figure S8. ^1H NMR spectrum (CDCl_3 , 400 MHz, 23 °C) of a P(VL-*co*-HL) sample obtained from the ROCOP of VL and HL (3:1) using NaOMe at 60 °C (Table 4, entry 3).

Figure S9. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 100 MHz, 23 °C) of a P(VL-*co*-HL) sample obtained from ROCOP of VL and HL (3:1) using NaOMe at 60 °C (Table 4, entry 3).

Figure S10. ^1H NMR spectrum (CDCl_3 , 400 MHz, 23 °C) of EVL.

Figure S11. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 100 MHz, 23 °C) of EVL.

Figure S12. ^1H NMR spectrum (CDCl_3 , 400 MHz, 23 °C) of EHO.

Figure S13. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 100 MHz, 23 °C) of EHO.

Figure S14. ^1H NMR spectrum (CDCl_3 , 400 MHz, 23 °C) of MH.

Figure S15. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 100 MHz, 23 °C) of MH.

Table S1. Hydrogenation systems for selective hydrogenation of EVL into MH.

Chart S1. Various catalysts assessed in the attempted ROP of EHO.

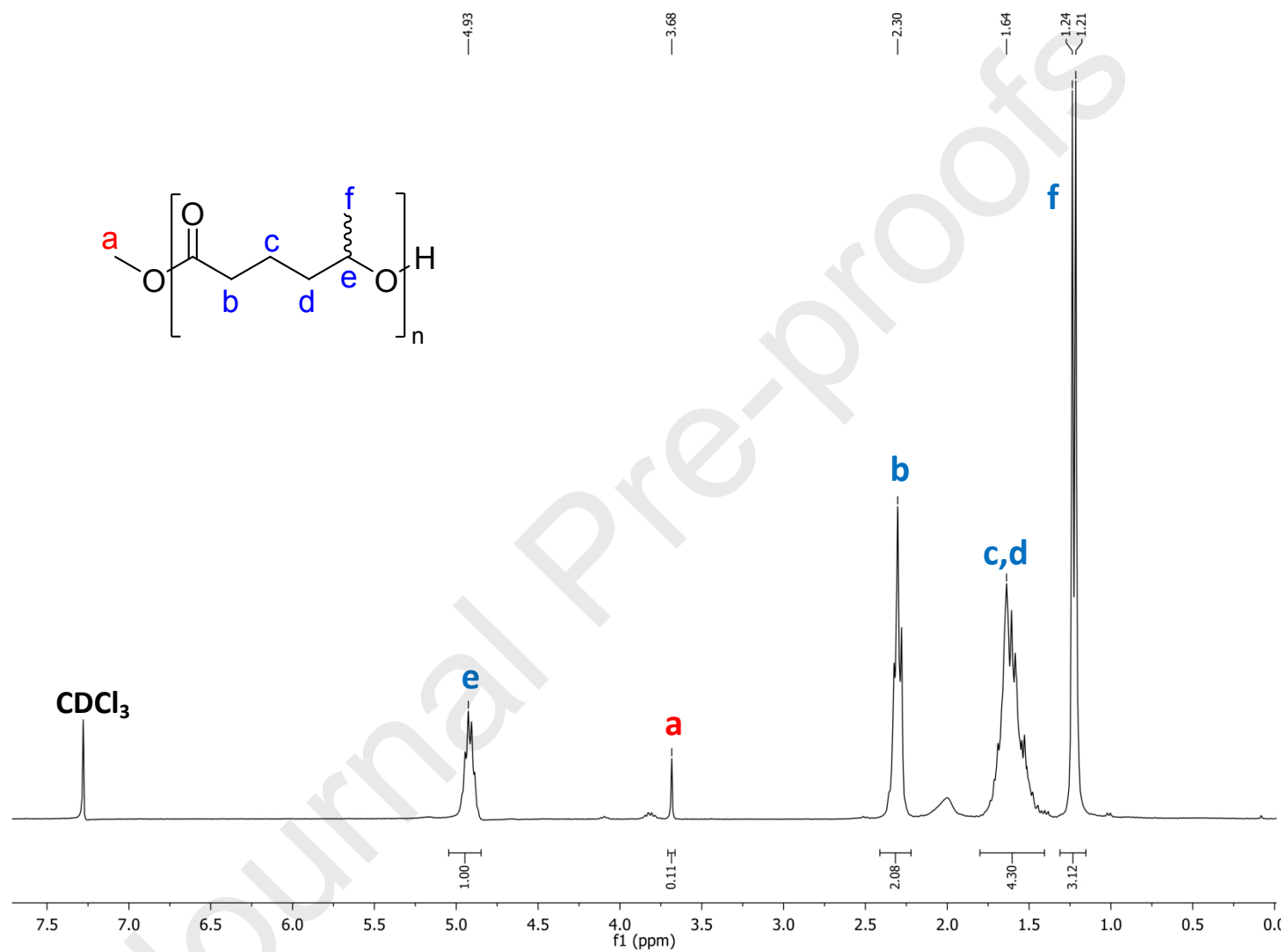


Figure S1. ^1H NMR spectrum (CDCl_3 , 400 MHz, 23 $^\circ\text{C}$) of a PHL sample obtained from the ROP of HL using NaOMe at 60 $^\circ\text{C}$ (Table 3, entry 3).

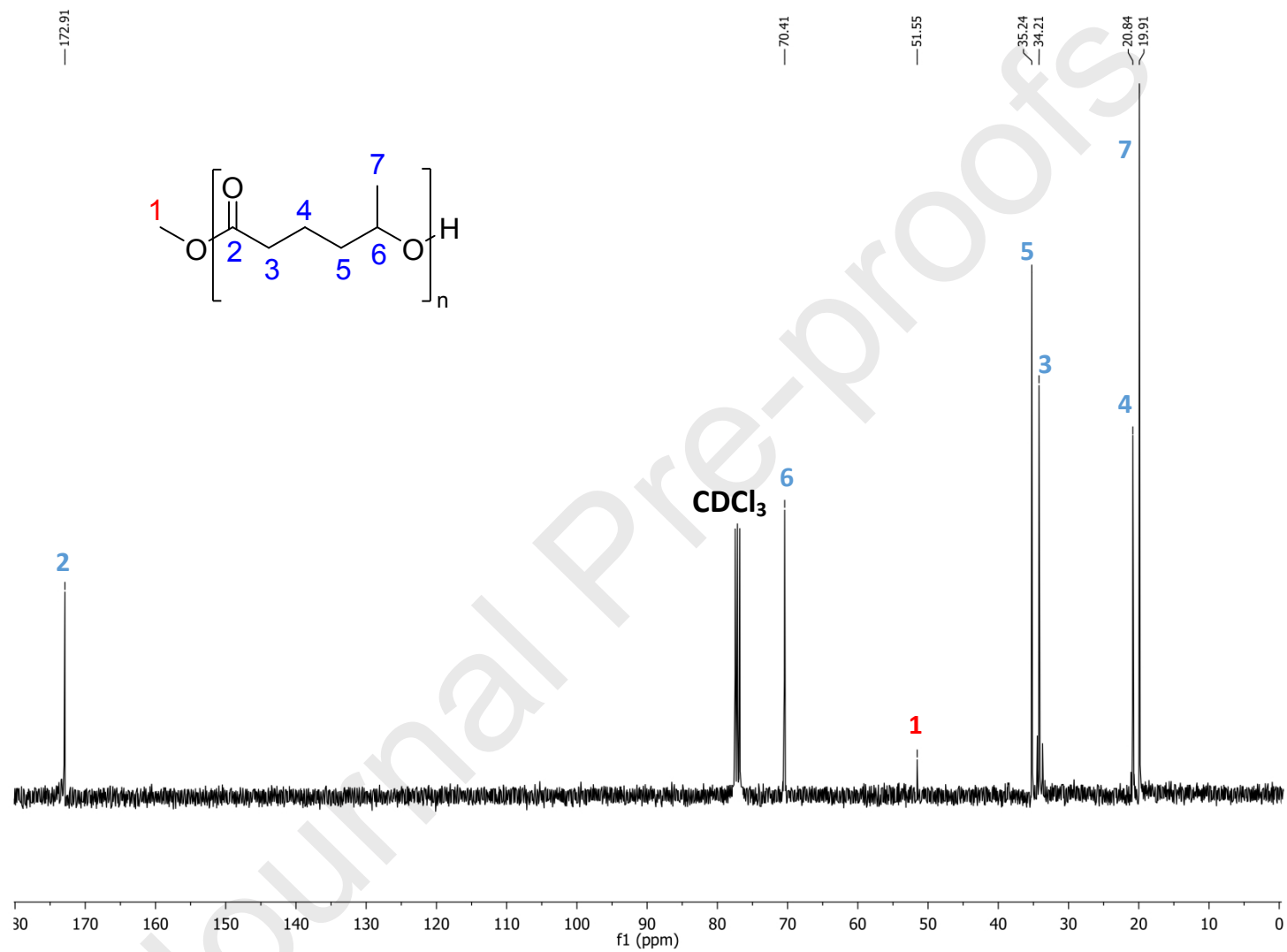


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 100 MHz, 23 °C) of a PHL sample obtained from the ROP of HL using NaOMe at 60 °C (Table 3, entry 3).

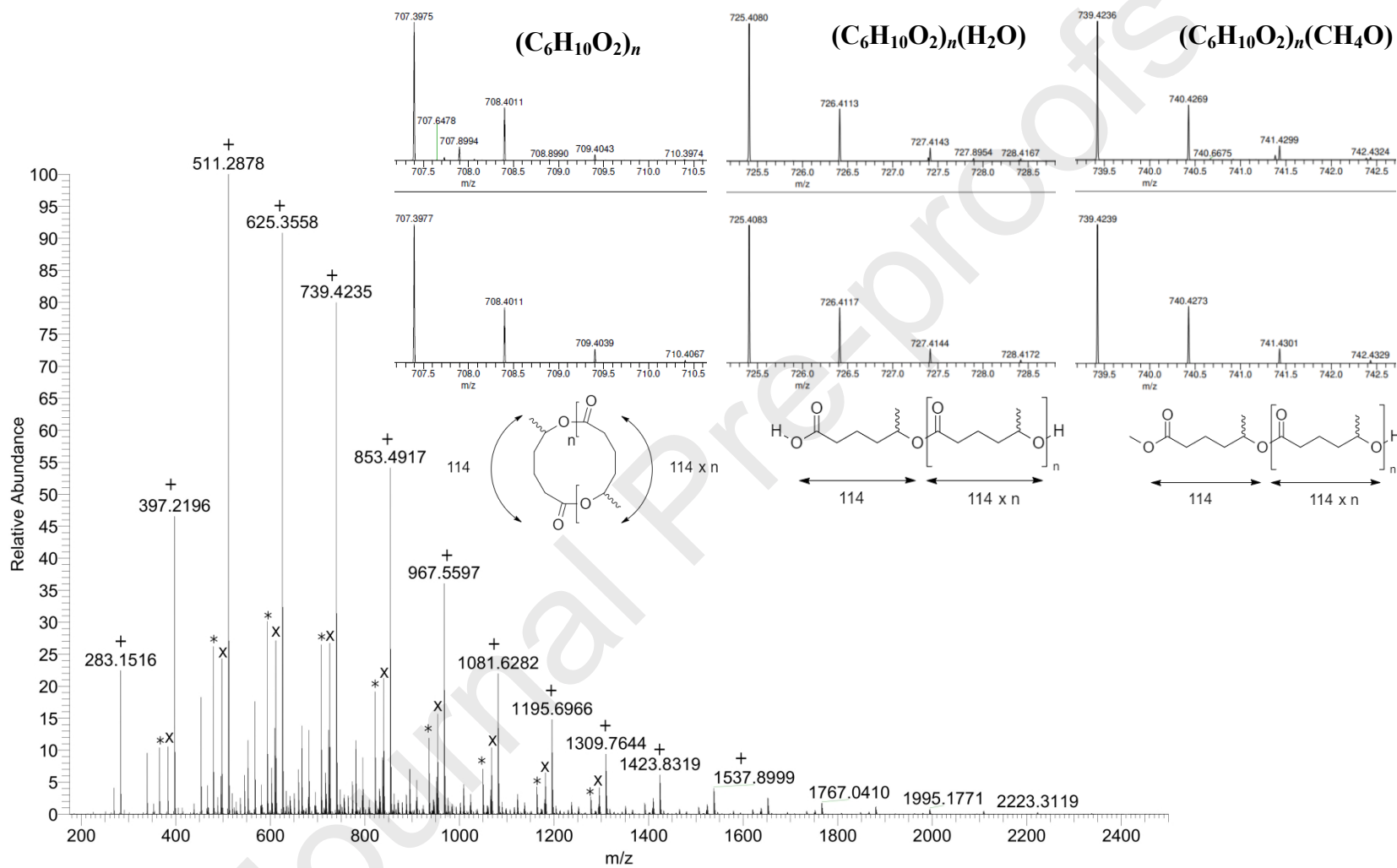


Figure S3. MALDI-ToF mass spectrum of a PHL sample obtained from the ROP of HL using NaOMe as initiator (Table 3, entry 2). +, X and * refer to methoxy-terminated chains $(C_6H_{10}O_2)_n(CH_4O)$, hydroxy-terminated chains $(C_6H_{10}O_2)_n(H_2O)$, and cyclic oligomers $(C_6H_{10}O_2)_n$, respectively.

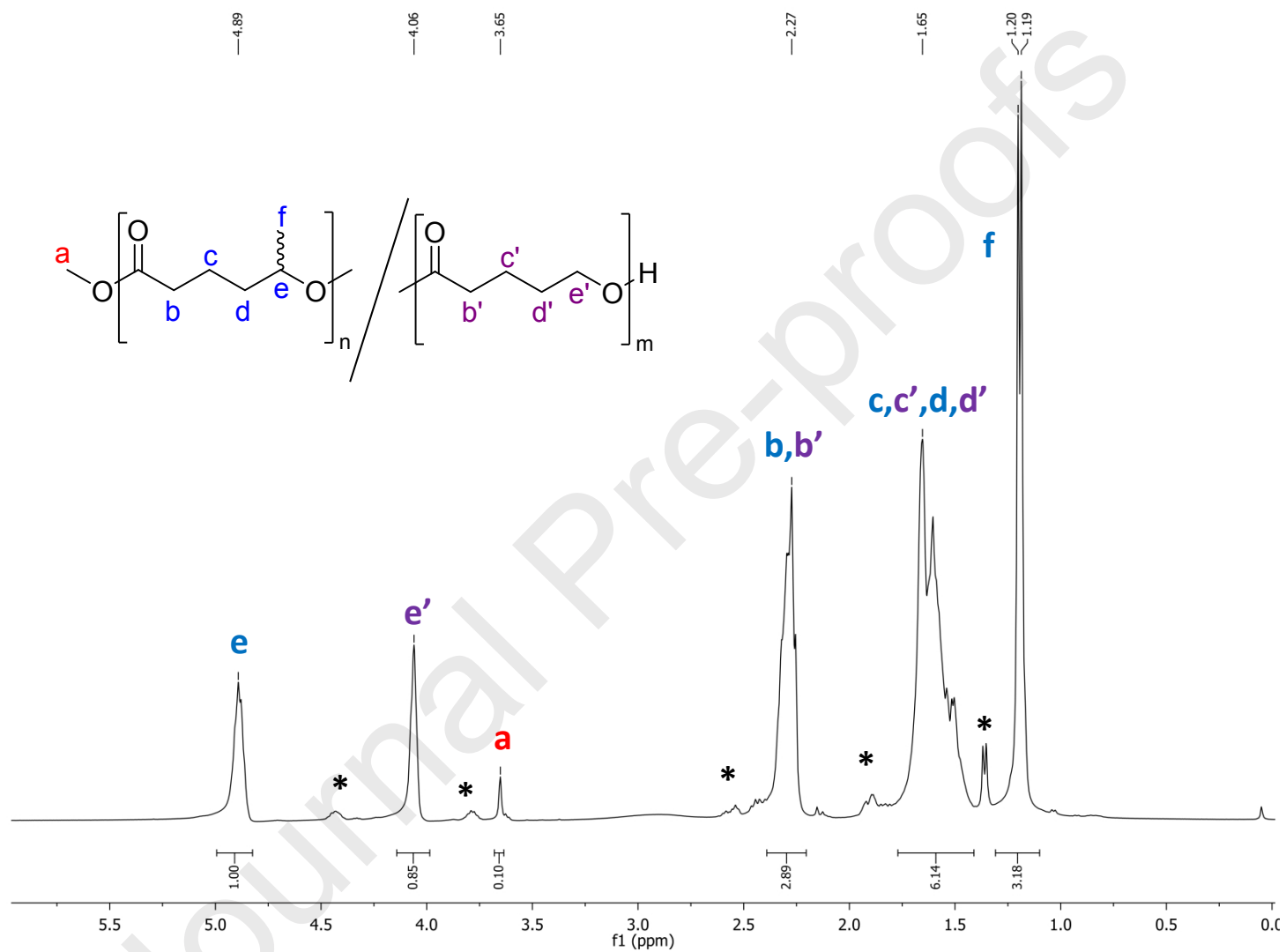


Figure S4. ¹H NMR spectrum (CDCl₃, 400 MHz, 23 °C) of a P(VL-co-HL) sample obtained from the ROCOP of VL and HL (1:1) using NaOMe at 60 °C (Table 4, entry 1). *stands for residual monomers trapped in the oligomers.

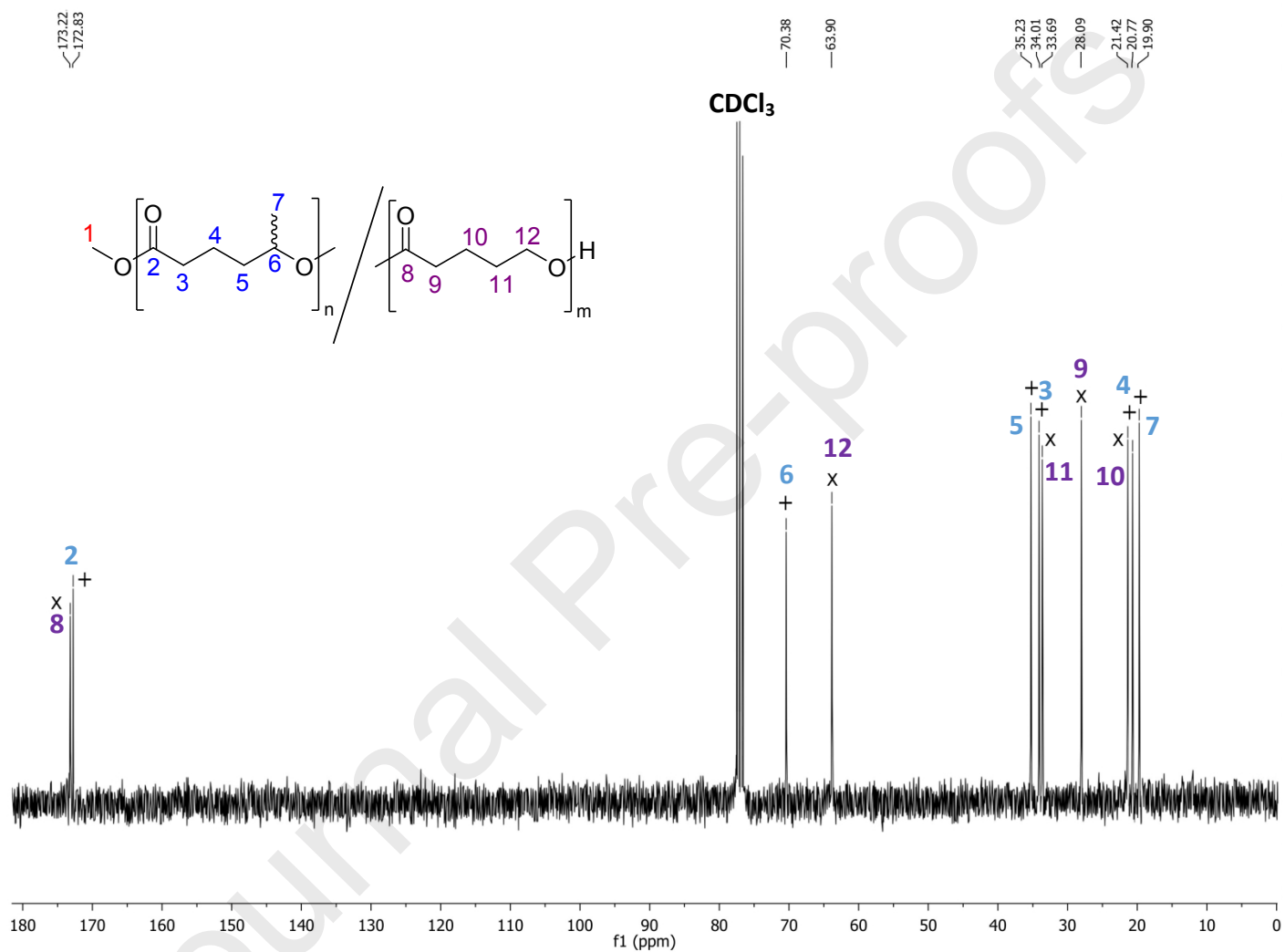


Figure S5. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 100 MHz, 23 °C) of a P (VL-*co*-HL) sample obtained from the ROCOP of VL and HL (1:1) using NaOMe at 60 °C (Table 4, entry 1). The signal for the terminal OMe group (1) was not observed due to its low intensity; × and + refer to VL and HL signals, respectively.

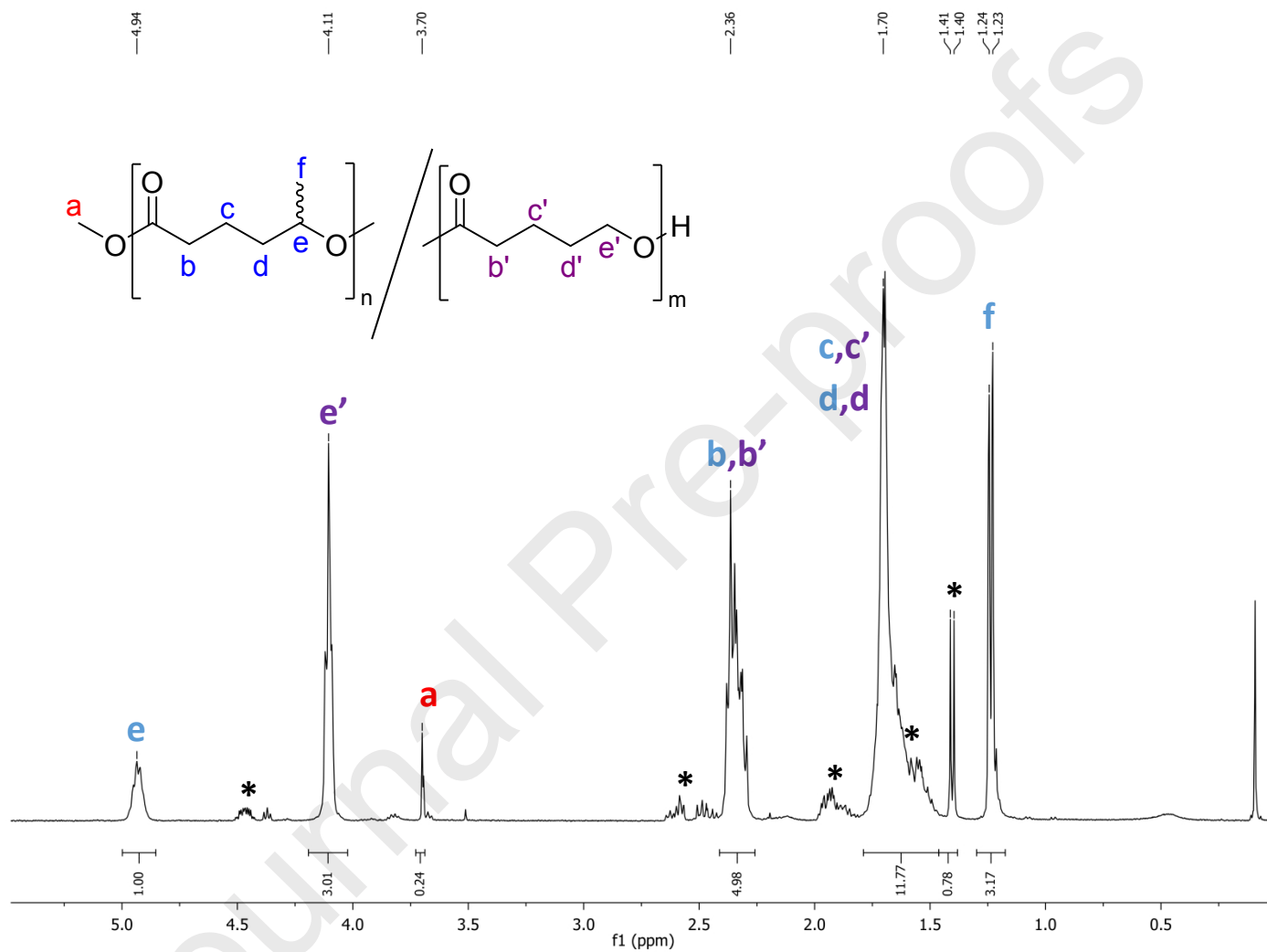


Figure S6. ^1H NMR spectrum (CDCl_3 , 400 MHz, 23 $^\circ\text{C}$) of a P(VL-co-HL) sample obtained from the ROCOP of VL and HL (1:3) using NaOMe at 60 $^\circ\text{C}$ (Table 4, entry 2). *stands for residual monomers trapped in the oligomers.

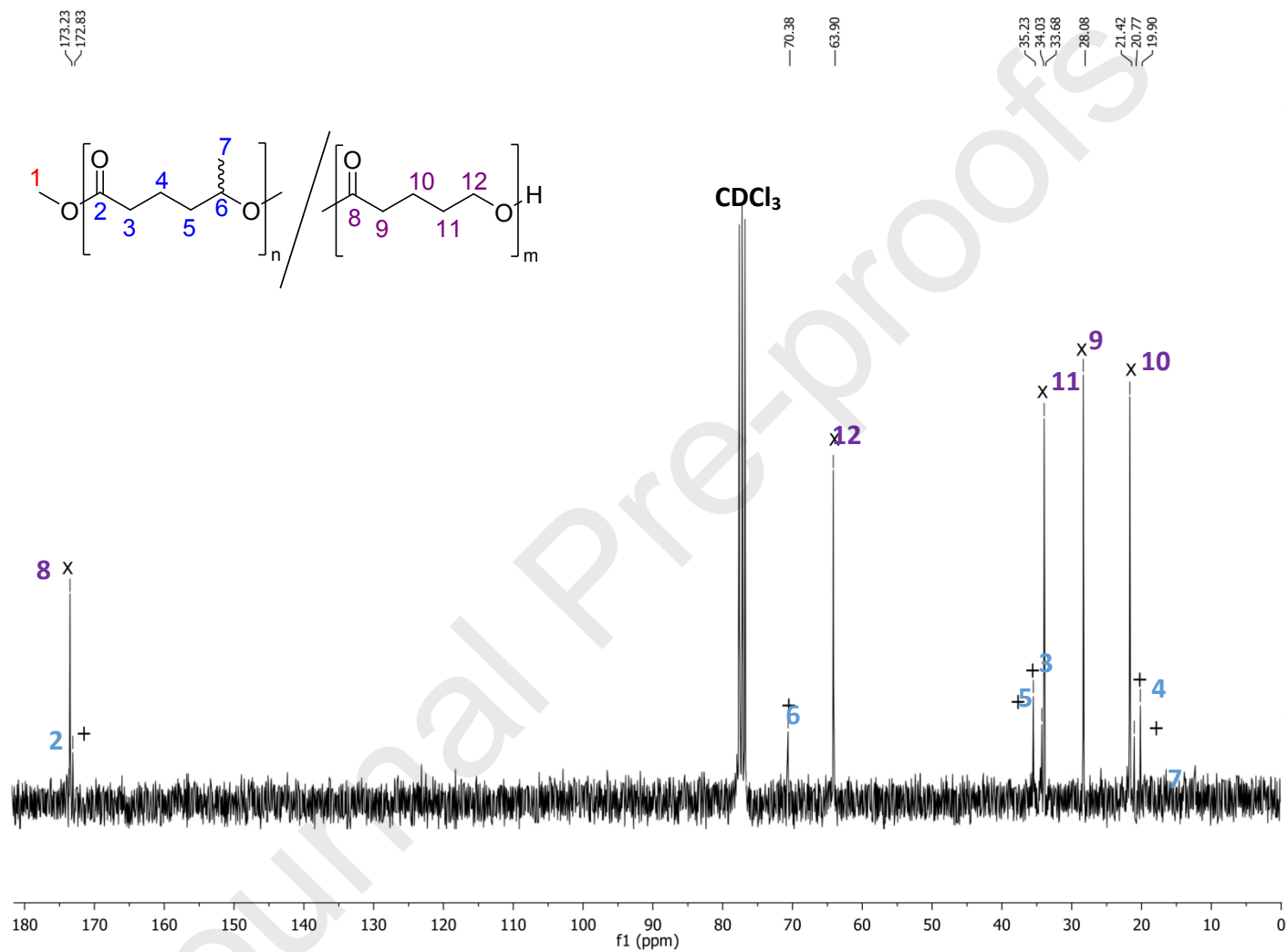


Figure S7. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 100 MHz, 23 °C) of a P(VL-co-HL) sample obtained from the ROCOP of VL and HL (1:3) using NaOMe at 60 °C (Table 4, entry 2). The signal for the terminal OMe group (1) was not observed due to its low intensity; × and + refer to VL and HL signals, respectively.

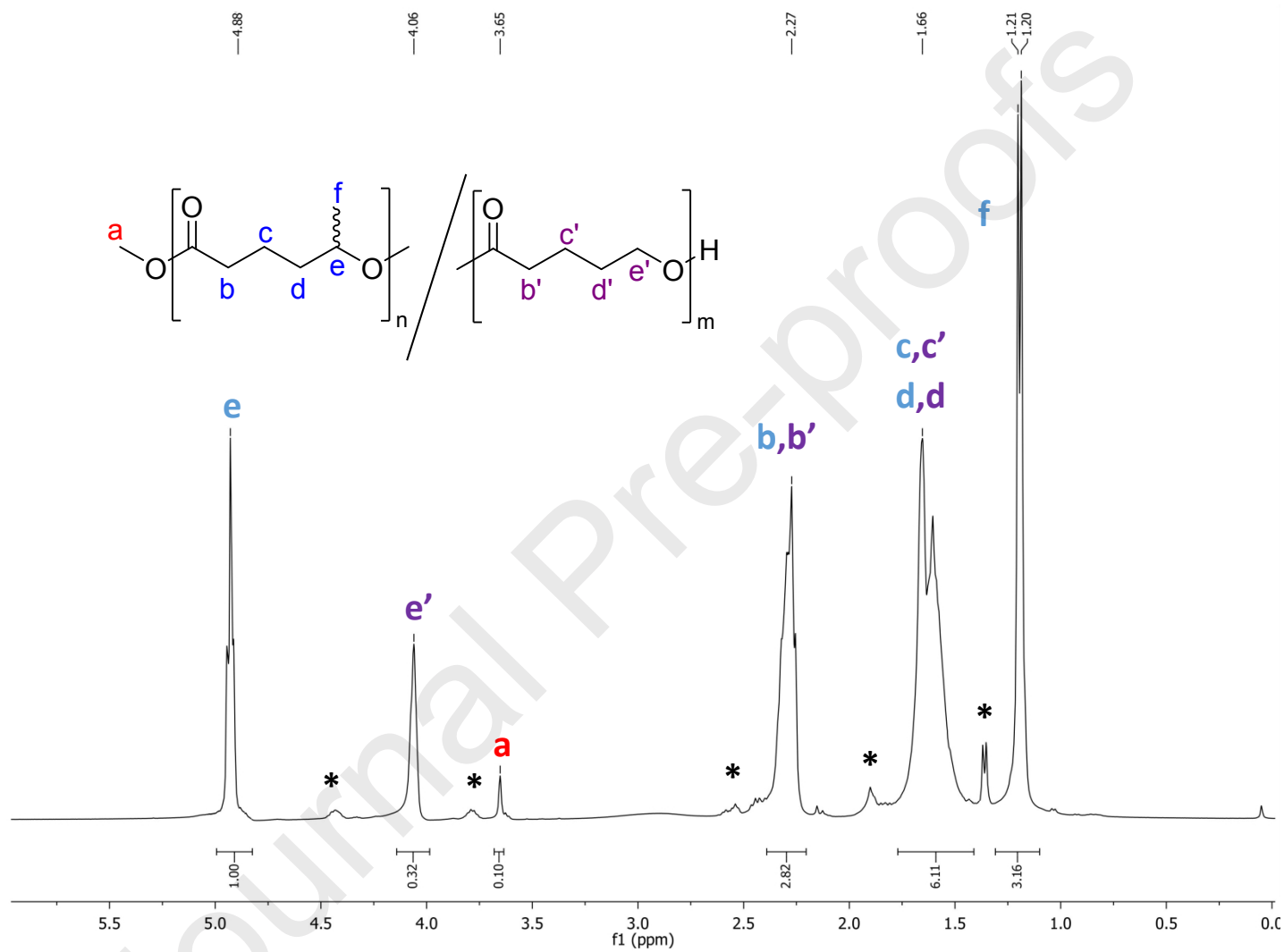


Figure S8. ^1H NMR spectrum (CDCl_3 , 400 MHz, 23 $^\circ\text{C}$) of a P(VL-*co*-HL) sample obtained from the ROCOP of VL and HL (3:1) using NaOMe at 60 $^\circ\text{C}$ (Table 4, entry 3). *stands for residual monomers trapped in the oligomers

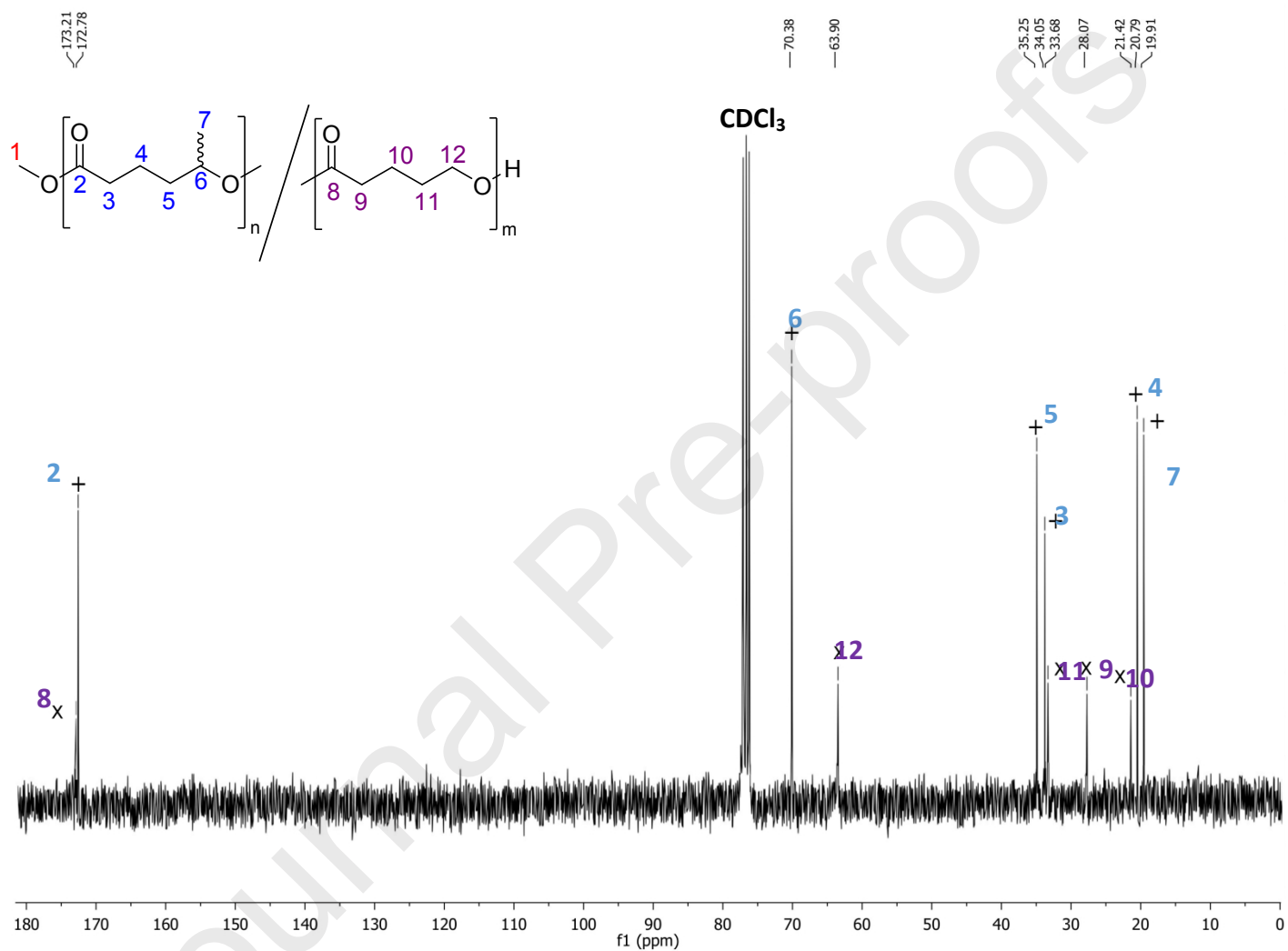


Figure S9. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 100 MHz, 23 °C) of a P(VL-co-HL) sample obtained from ROCOP of VL with HL (3:1) using NaOMe at 60 °C (Table 4, entry 3). The signal for the terminal OMe group (1) was not observed due to its low intensity; × and + refer to VL and HL signals, respectively.

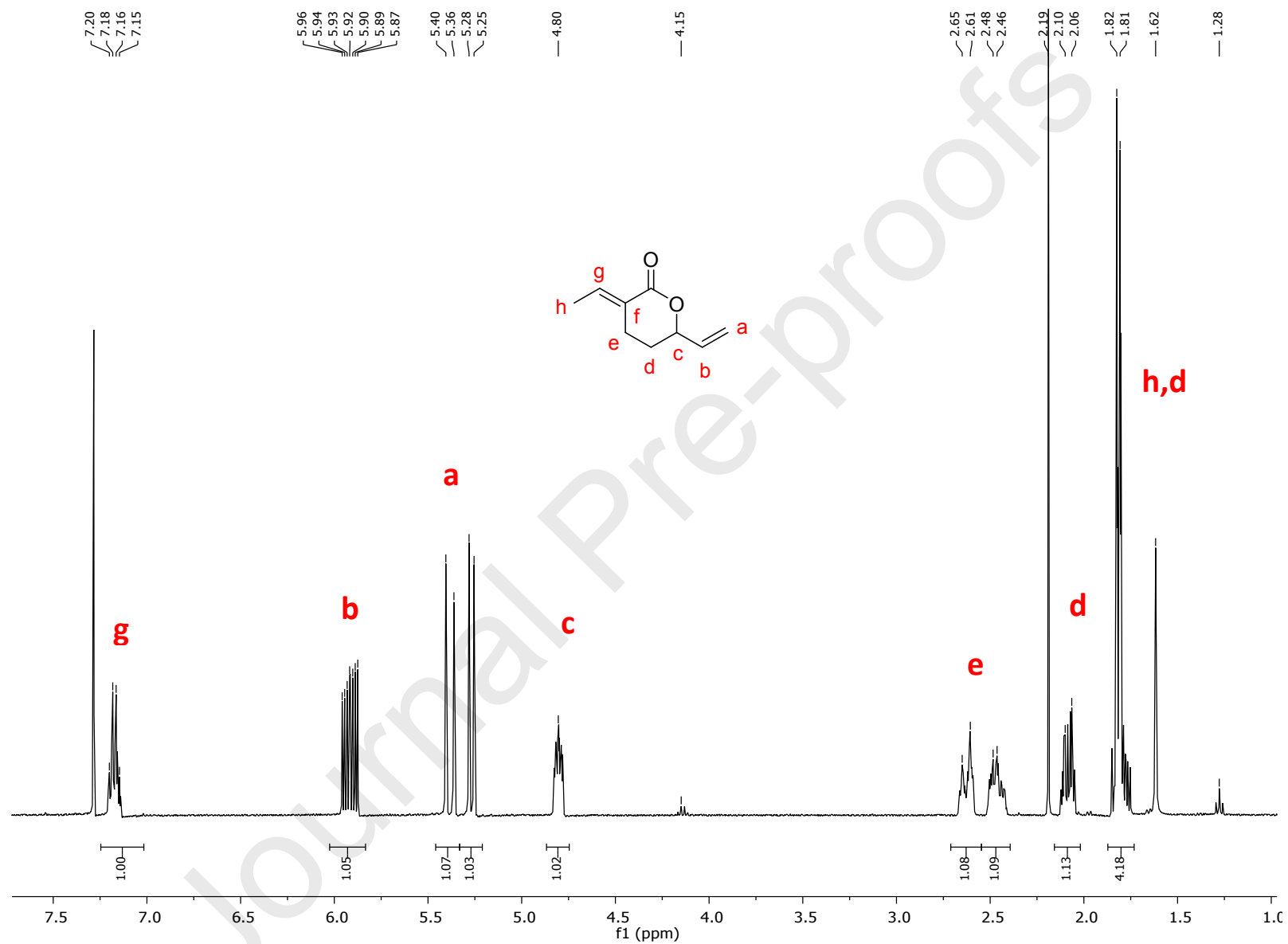


Figure S10. ^1H NMR spectrum (CDCl_3 , 400 MHz, 23 $^\circ\text{C}$) of EVL (2-ethylidene-6-hepten-5-olide).

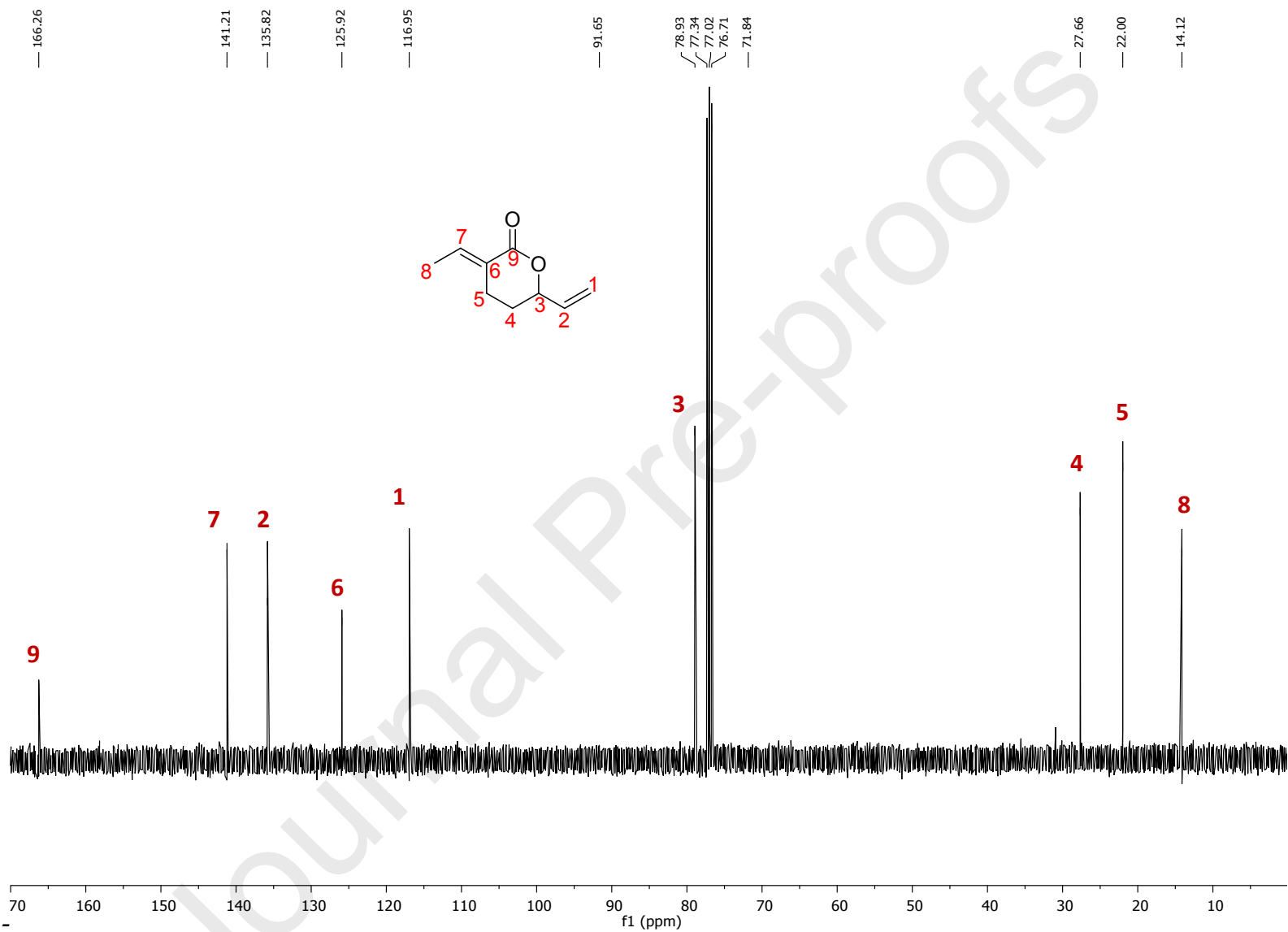


Figure S11. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 100 MHz, 23 °C) of EVL (2-ethylidene-6-hepten-5-olide).

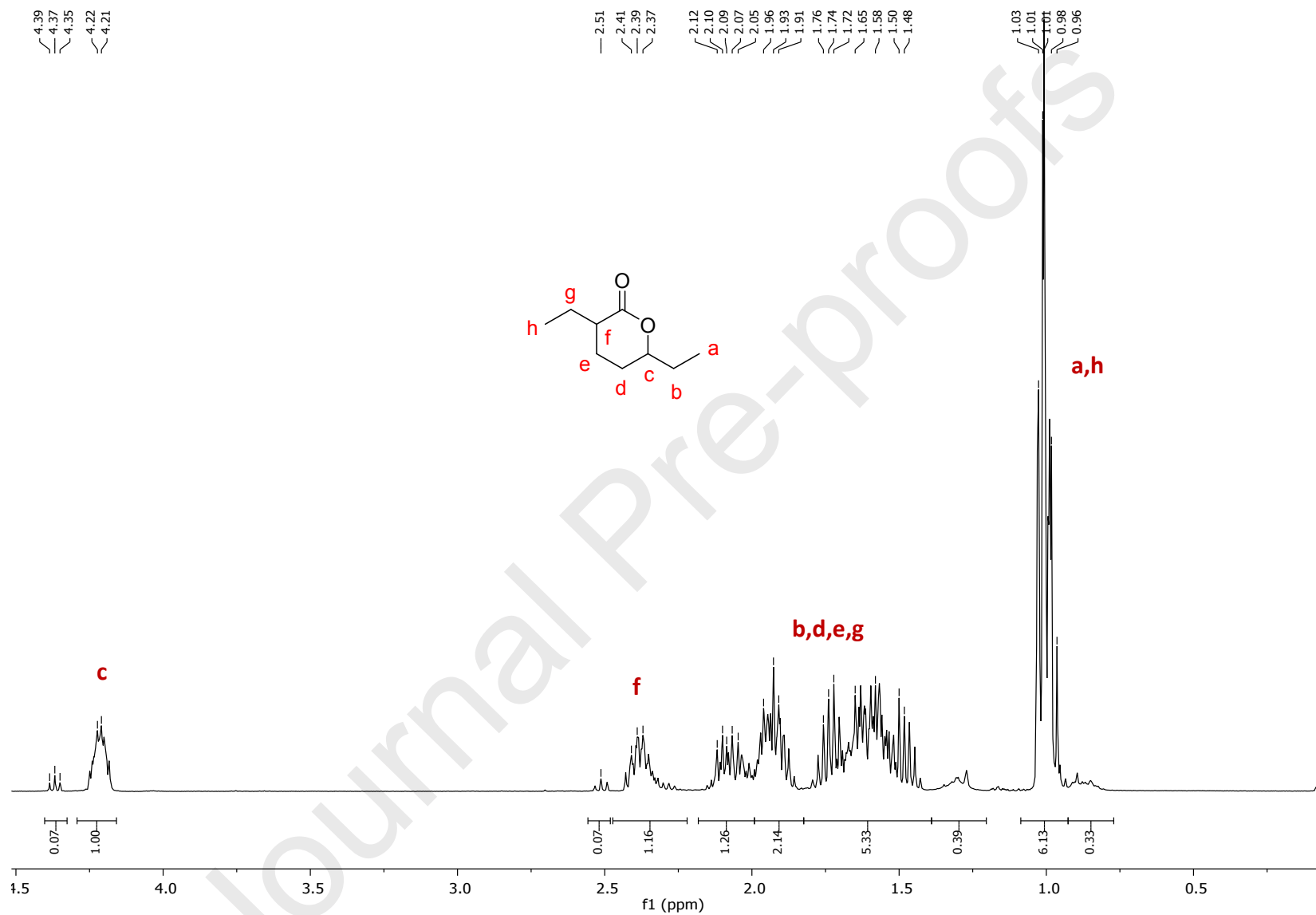


Figure S12. ^1H NMR spectrum (CDCl_3 , 400 MHz, 23 $^\circ\text{C}$) of EHO (2-ethylheptane-5-olide) (as a 63:37 diastereomeric mixture).

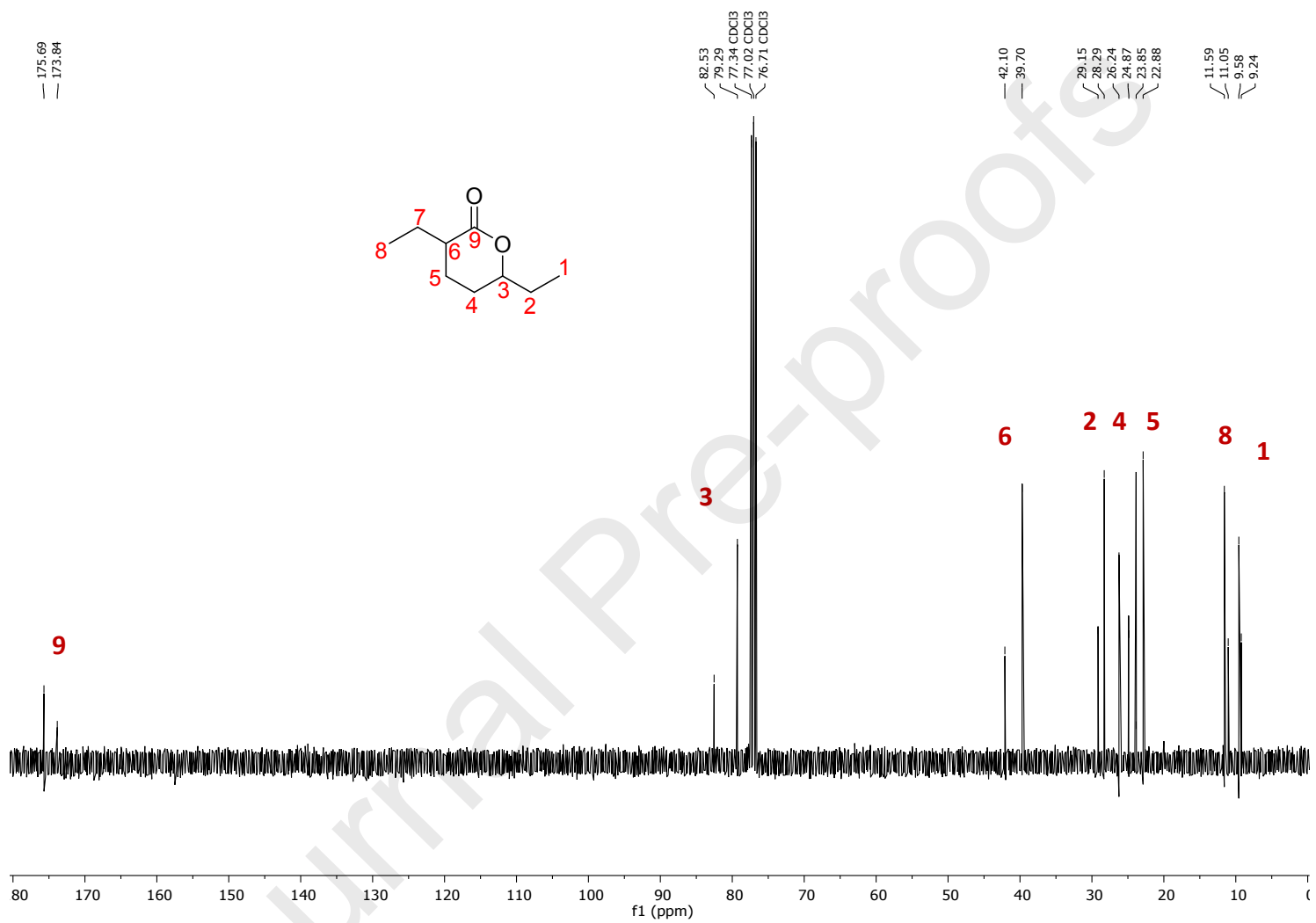


Figure S13. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 100 MHz, 23 °C) of EHO (2-ethylheptane-5-olide) (as a 63:37 diastereomeric mixture).

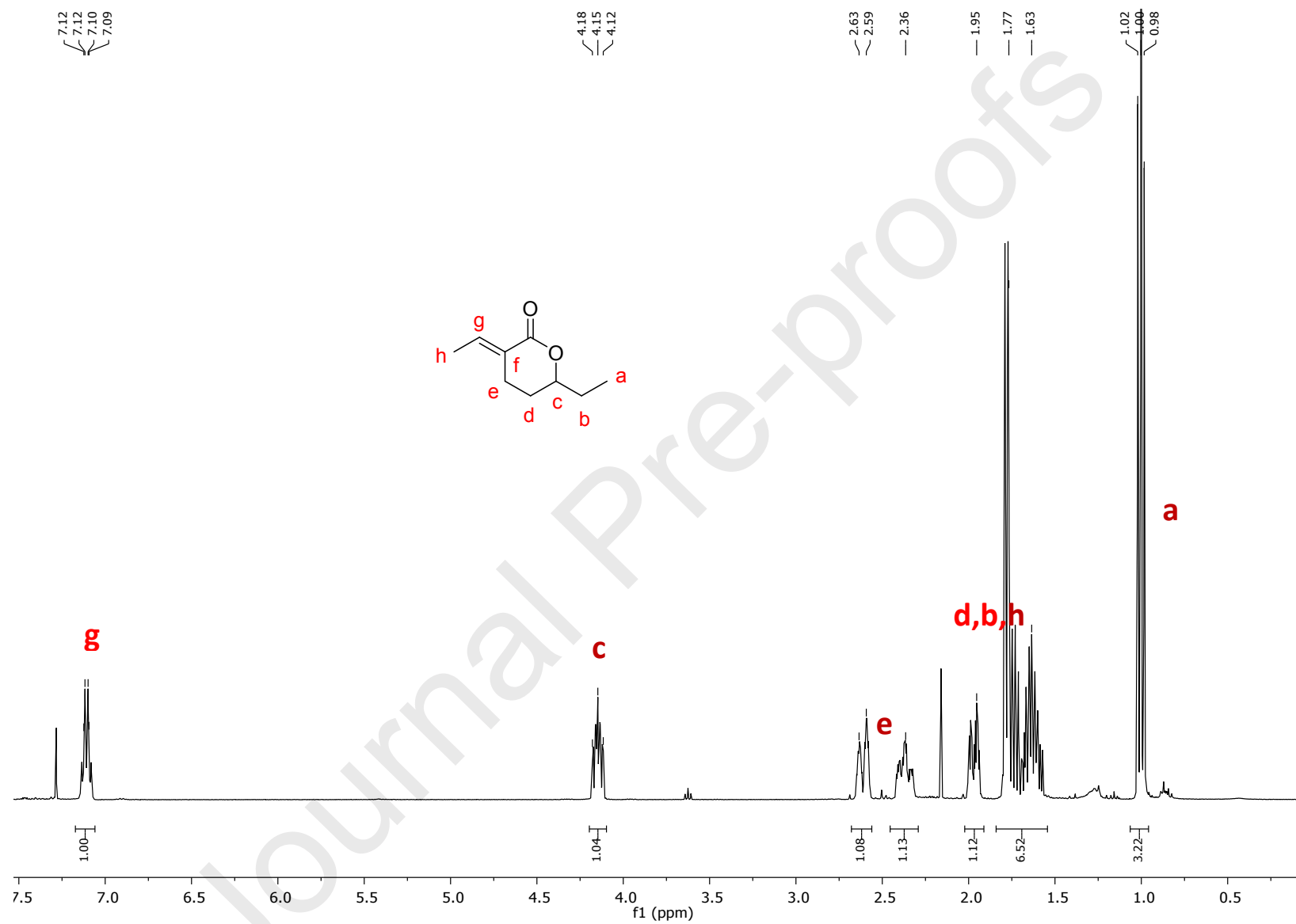


Figure S14. ¹H NMR spectrum (CDCl₃, 400 MHz, 23 °C) of MH (2-ethylidene-6-heptan-5-olide).

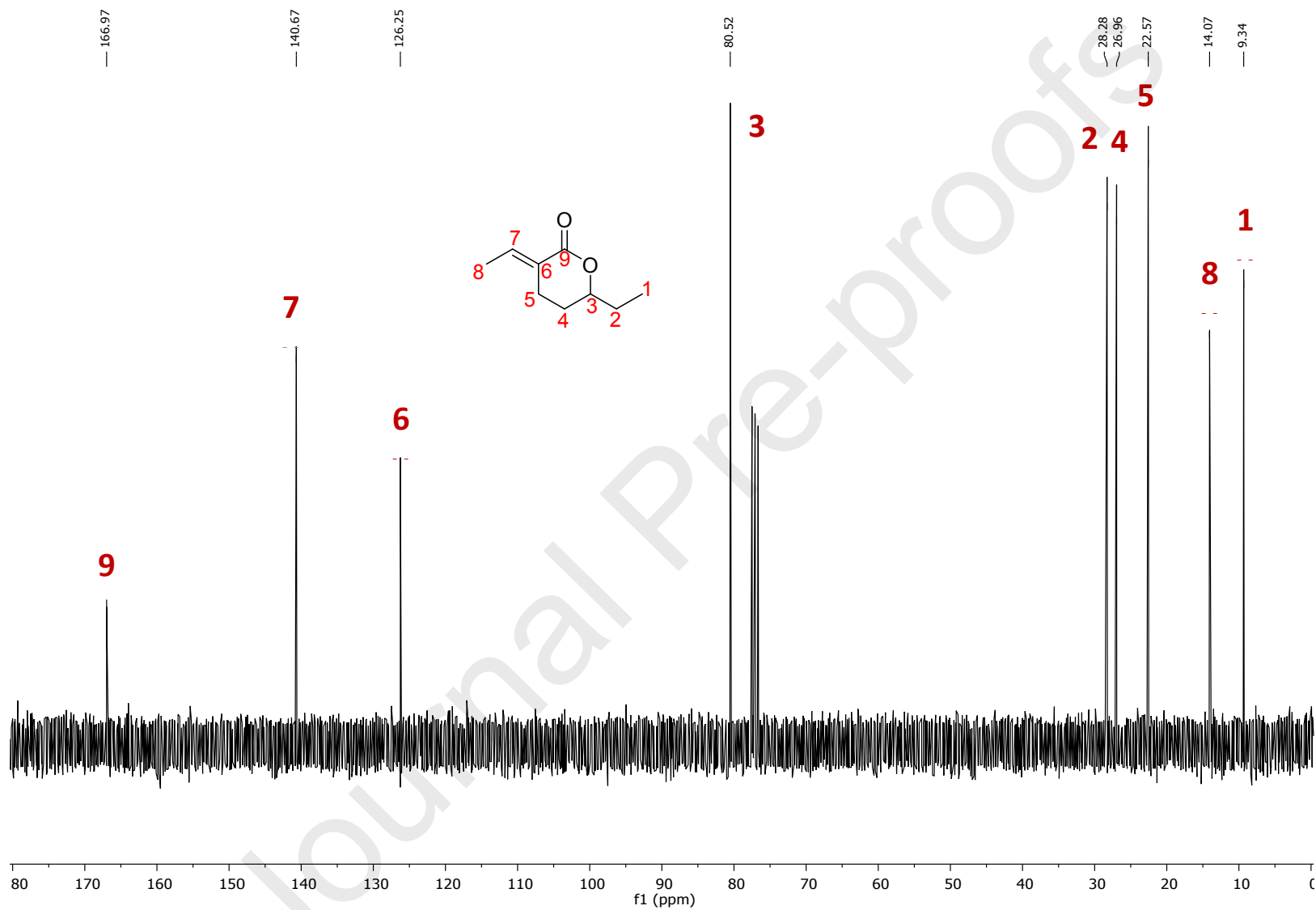
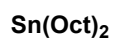


Figure S15. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 100 MHz, 23 °C) of MH (2-ethylidene-6-heptan-5-olide).

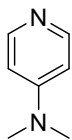
Table S1. Hydrogenation systems successfully used for the selective and quantitative hydrogenation of EVL into MH.

	Catalytic system	Reaction temperature [°C]	Amount of catalyst [mol%]	Conversion of EVL into MH [%]
1	Ni-Raney, THF	60	10	100
2	Ru/C, THF	60	3.5	100
3	RhCl(PPh ₃) ₃ , Benzene	21	1	100
4	RuCl ₃ /(<i>S</i>)-BINAP, Benzene	50	1	100
5	IrCODPyPCy ₃ , THF	21	2.5	100

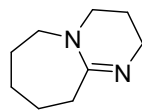
Metal salts :



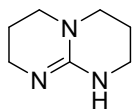
Organocatalysts :



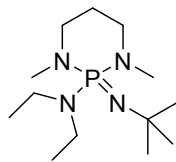
DMAP



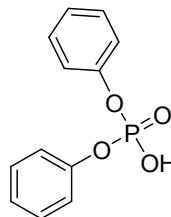
DBU



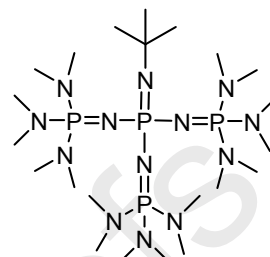
TBD



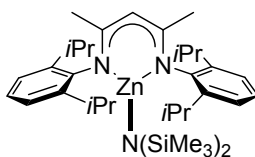
BEMP



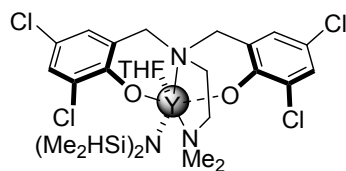
DPP

^tBu-P₄

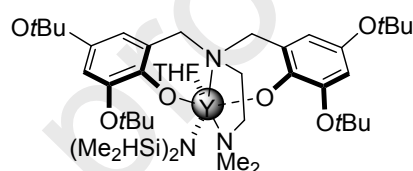
Metal complexes :



Zn-DBI



Y-complex 1



Y-complex 2

Chart S2. Various catalysts assessed in the attempted ROP of EHO (all proved unsuccessful).

Highlights

The ring-opening polymerization (ROP) of some original bio-derived six-membered (substituted) δ -valerolactones is investigated

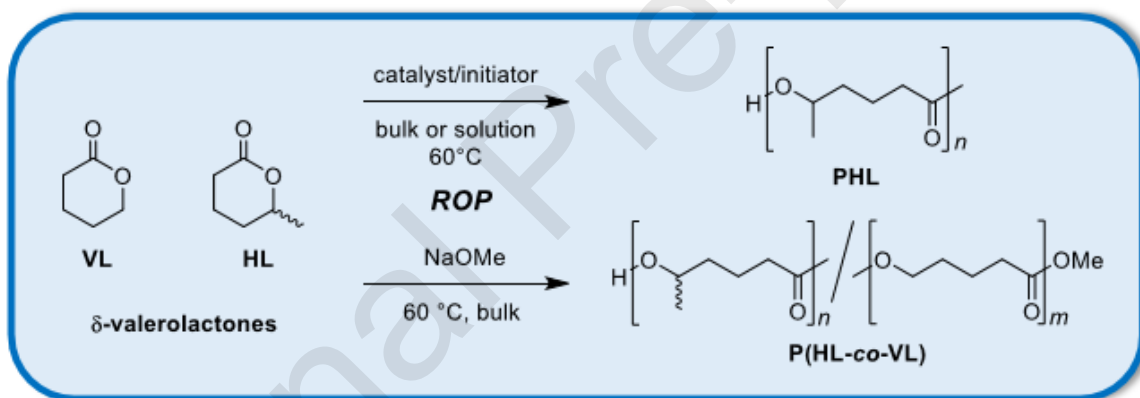
Alkali metal alkoxides successfully homopolymerize for the first time the 5-Me substituted δ -valerolactone (aka δ -hexalactone (HL))

Well-defined PHL oligomers and P(HL-co- δ -valerolactone) random copolymers are thus recovered

HL shows a significantly better reactivity than the analogous 1,5-alkyl 6-membered δ -valerolactones

The alkyl substituent at the 1- and/or 5- position on the cyclic ester ring significantly affects its ring-opening polymerizability of substituted δ -valerolactones

Graphical abstract



AUTHOR STATEMENT

Ring-Opening (co)Polymerization of Six-Membered Substituted δ -Valerolactones with Alkali Metal Alkoxides

Valérie Hardouin Duparc ^a: Experimental work, Data curation,

Rama M. Shakaroun ^a: Experimental work

Martine Slawinsky ^b: Conceptualization, Funding acquisition

Jean-François Carpentier, ^a Sophie M. Guillaume ^a: Conceptualization, Methodology, Supervision,
Data curation, Writing- Reviewing and Editing,

The authors declare no conflict of interest.