Electronic Supporting Information

Dewar Lactone as a Modular Platform to a New Class of Substituted Poly(acetylene)s

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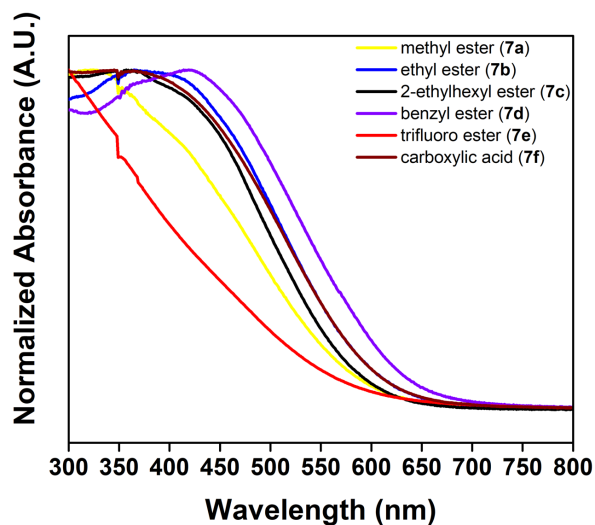
[c] Department of Energy Engineering, Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, Republic of Korea. Email: bielawski@unist.ac.kr.

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UV-vis Spectroscopy Data

Figure S1. (a) UV-vis absorption spectra recorded for THF solutions of **7a-e** or a MeOH solution of **7f** ($[7]_0 = 1.3 \times 10^{-2}$ mg mL^{-1} in terms of polymer repeat unit) at ambient temperature.
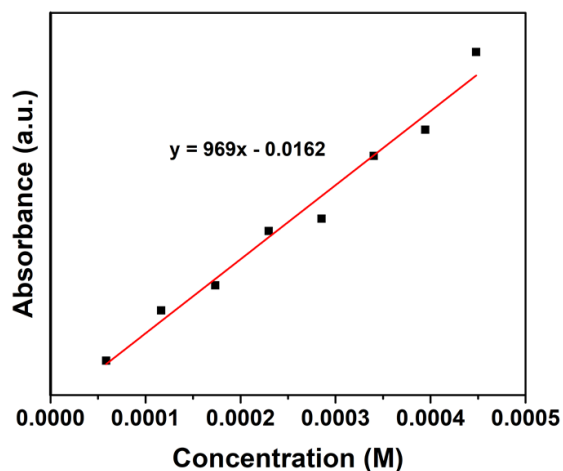
Table S1. Electronic properties of **7a-e** in THF and **7f** in MeOH.[a]

Polymer (side group)	λ$_{max}$ (nm)	HOMO-LUMO (eV)[c]	Absorption Onset (nm)
7a (methyl ester)	322	2.03	611
7b (ethyl ester)	365	1.98	626
7c (2-ethylhexyl ester)	357	2.02	614
7d (benzyl ester)	414	1.91	663
7e (2,2,2-trifluoroethyl ester)	n/a[b]	2.08	597
7f (carboxylic acid)	395	1.90	654

[a] The λ$_{max}$ and HOMO-LUMO gap values recorded for **7a-e** were measured in THF and those recorded for **7f** were measured in MeOH. $[7]_0 = 1.3 \times 10^{-2}$ mg mL^{-1} in terms of polymer repeat unit at ambient temperature. [b] The λ$_{max}$ of **7e** appears to be before the solvent UV cutoff value. [c] The HOMO-LUMO gaps were determined from the onsets of the absorption signals.
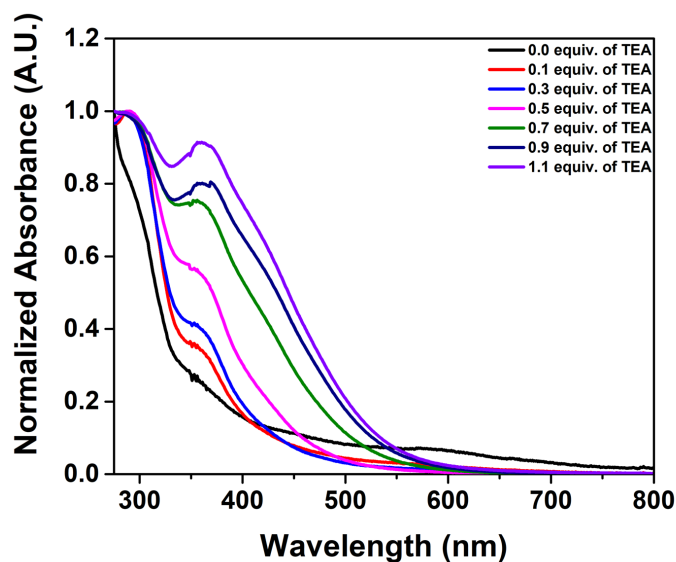
Figure S2. UV-vis absorption spectra recorded for poly(**1c**) as a function of added TEA per repeat unit of poly(**1c**) (indicated) in THF ([poly(**1c**)]$_0$ = 1.1 × 10^{-2} mg mL^{-1} in terms of polymer repeat unit) at ambient temperature.

| Concentration in Methanol (M)	Absorbance at 395 nm
5.86 x 10^{-5}	0.045
1.16 x 10^{-4}	0.111
1.73 x 10^{-4}	0.144
2.30 x 10^{-4}	0.215
2.85 x 10^{-4}	0.231
3.40 x 10^{-4}	0.313
3.94 x 10^{-4}	0.347
4.48 x 10^{-4}	0.449
ε = 969 M^{-1}cm^{-1}	

$y = 969x - 0.0162$

Figure S3. A plot of absorbance versus molar concentration (M) of **7g** and the calculated extinction coefficient (ε as determined by the UV-vis absorbance value measured at 395 nm. Note: the molar concentration (M) were calculated using the repeat unit of **7g** in MeOH. Measurements were taken in a quartz cuvette with a 1 cm path length.

Table S2. The polymerization of **1c** in the presence of a variety of pyridine derivatives.[a]

Pyridine Derivative	Predicted pKa[b]	Experimental pKa	Polymerization Observed
2-nitro	-7.64	n/a	Yes
2-cyano	0.98	-0.26[d]	Yes
2-fluoro	-0.92	0.44[c]	Yes
2-chloro	1.13	0.49[c]	No[g]
2-bromo	1.47	0.7[c]	No[g]
4-nitro	1.06	1.6[e]	No
2-iodo	1.65	1.82[c]	No
3-bromo	3.45	2.84[c]	No
4-bromo	4.01	3.96[f]	No
2-*t*-butyl	5.29	n/a	No
2-isopropyl	5.46	n/a	No
lutidine	6.54	6.60[c]	No

[a] The polymerization reaction was conducted with **1c** (0.2 M in CD_2Cl_2) in the presence of HG2 catalyst ([**1c**]$_0$/[HG2]$_0$ = 82) and the pyridine indicated ([HG2]/[pyr.] = 0.5) for 12 h under a nitrogen atmosphere at ambient temperature. [b] Predicted pKa values were calculated using MarvinSketch v. 19.13. [c] pKa values were taken from reference 1. [d] pKa values were taken from reference 2. [e] pKa values were taken from the CRC Handbook of Chemistry and Physics, 91st Ed. [f] pKa values were taken from reference 3. [g] Although broad ^{1}H NMR signals consistent with poly(**1c**) were observed, signals that corresponded to **1c** were also present, indicating that monomer consumption was incomplete.
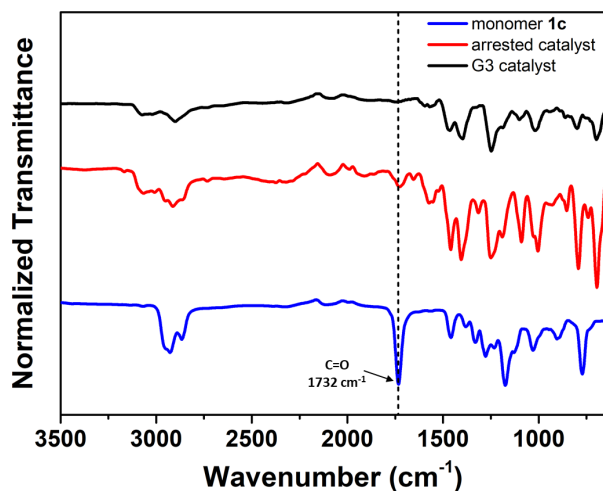
Infrared and Raman Spectra
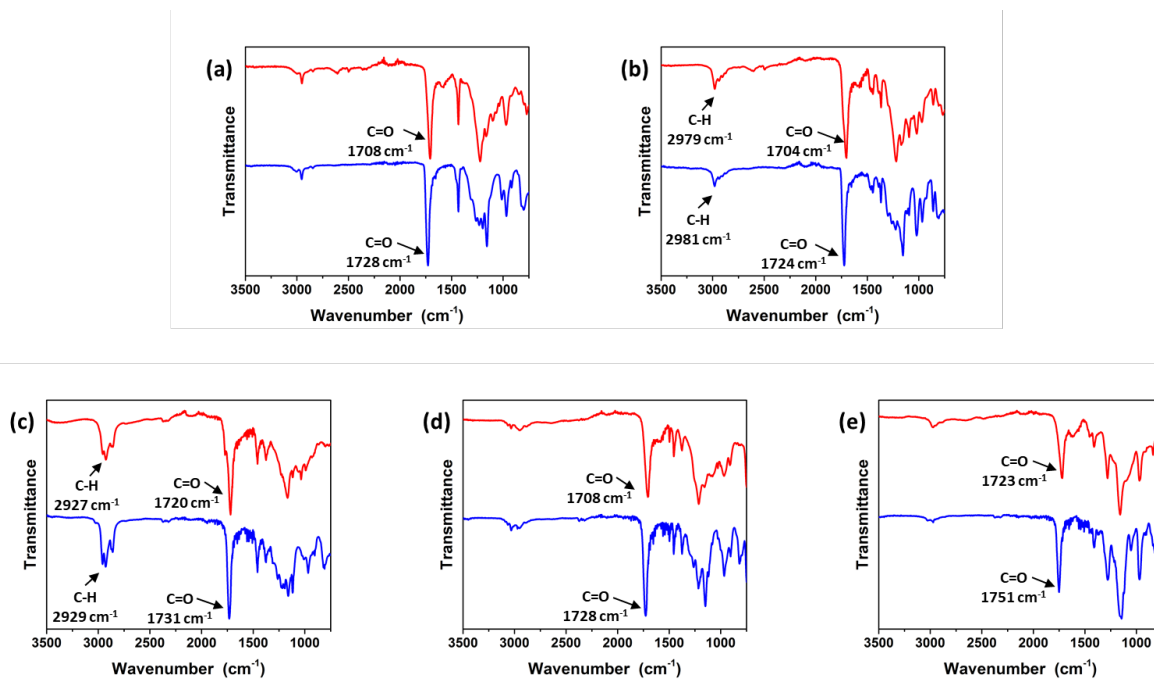
Figure S4. Infrared spectra recorded for poly(**1a-e**) (blue) and their corresponding products **7a-e** (red) formed through elimination.
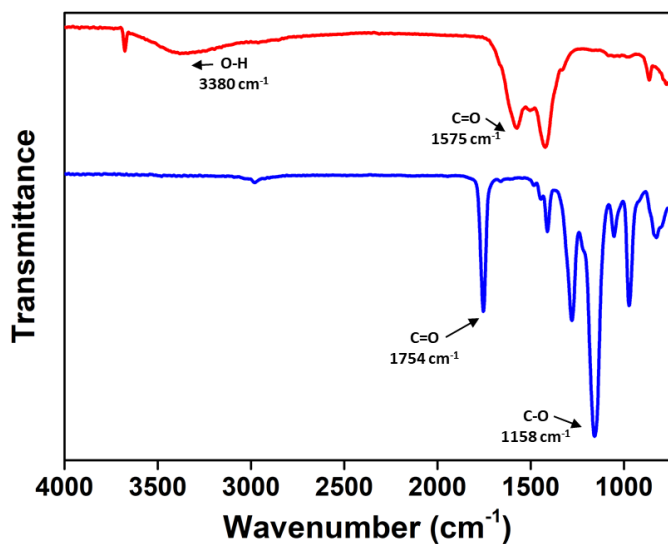
Figure S5. Infrared spectra recorded for poly(**1e**) (blue) and the water-soluble poly(acetylene) derivative **7f** formed from a concurrent elimination/hydrolysis reaction using LiOH (red).

Figure S6. Infrared spectra recorded for G3 (black), an arrested catalyst (red) and monomer **1c** (blue). Conditions: $[1c]_0/[G3]_0 = 1.0$; $[3\text{-bromopyridine}]_0/[G3]_0 = 10$; $[1c]_0 = 0.2$ M in CH_2Cl_2. The vertical black dotted line is centered at 1732 cm^{-1}.
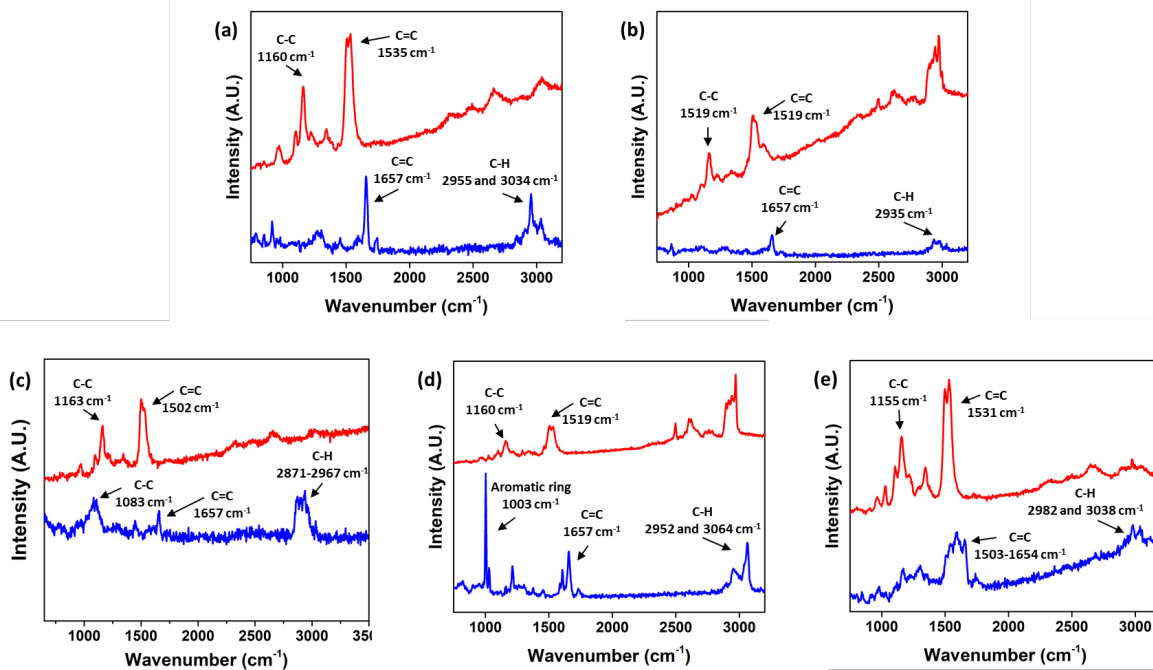
Figure S7. Raman spectra recorded before (blue) and after (red) elimination for (a) poly(**1a**), (b) poly(**1b**), (c) poly(**1c**), (d) poly(**1d**) and (e) poly(**1e**).

Additional X-Ray Photoelectron Spectroscopy Measurement Details and Data

XPS survey spectra were recorded using a Thermo Fisher Scientific Escalab 250Xi. The measurement was taken over a spot size of 500 μm at an angle normal to the surface with charge compensation using a combined/flood gun operating at a current of 50 μA and an ion voltage of 2 V. Following previously reported procedures,[4] survey spectra were initially calibrated by recording the gold $4f_{7/2}$ spectrum of a gold foil. The spectrum was then shifted such that the peak position of the gold $4f_{7/2}$ spectrum was equal to 84.0 eV. The shifted value was then applied to all subsequent XPS spectra. Survey spectra were taken at a pass energy of 100 eV (5 scans).
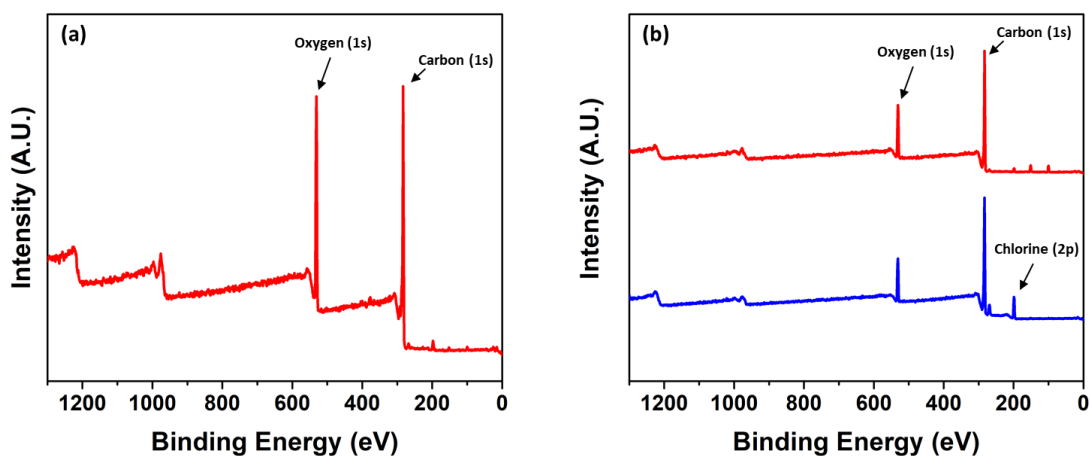
Figure S8. (a) XPS survey spectra recorded for (a) **7f** as well as (b) poly(**1c**) (blue) and **7c** (red). Note: Relatively weak chlorine 2p signals (ca. 200 eV) were recorded during the analyses of **7f** and **7c**.

Table S3. Elemental analysis data recorded for **7f**.

	Carbon	Hydrogen	Nitrogen	Sulfur
Weight (%) (Experimental)	54.3	4.3	0.0	0.0
Atomic (%) (Experimental)	4.5	4.3	0.0	0.0
Weight (%) (Theoretical)	60.0	4.0	0.0	0.0
Atomic (%) (Theoretical)	5.0	4.0	0.0	0.0

TGA and DSC Data
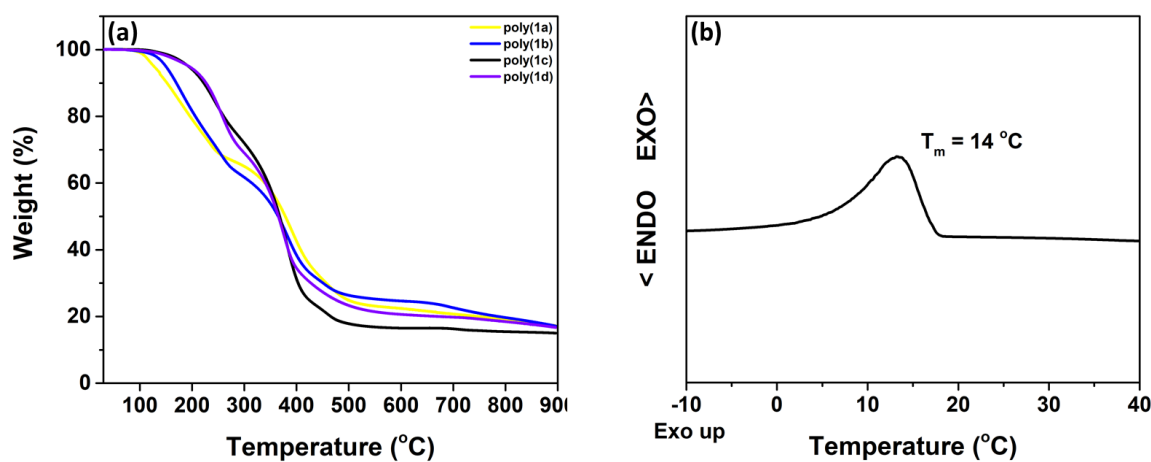
Figure S9. (a) TGA data recorded for poly(**1a-d**) as obtained under an atmosphere of nitrogen and at a heating rate of 10 °C min^{-1}. (b) DSC data recorded for **7c** as obtained under an atmosphere of nitrogen and at a heating and cooling rate of 20 °C min^{-1}. Measurements for poly(**1e**) were not conducted due to the presence of fluorine in the material.

GPC Data
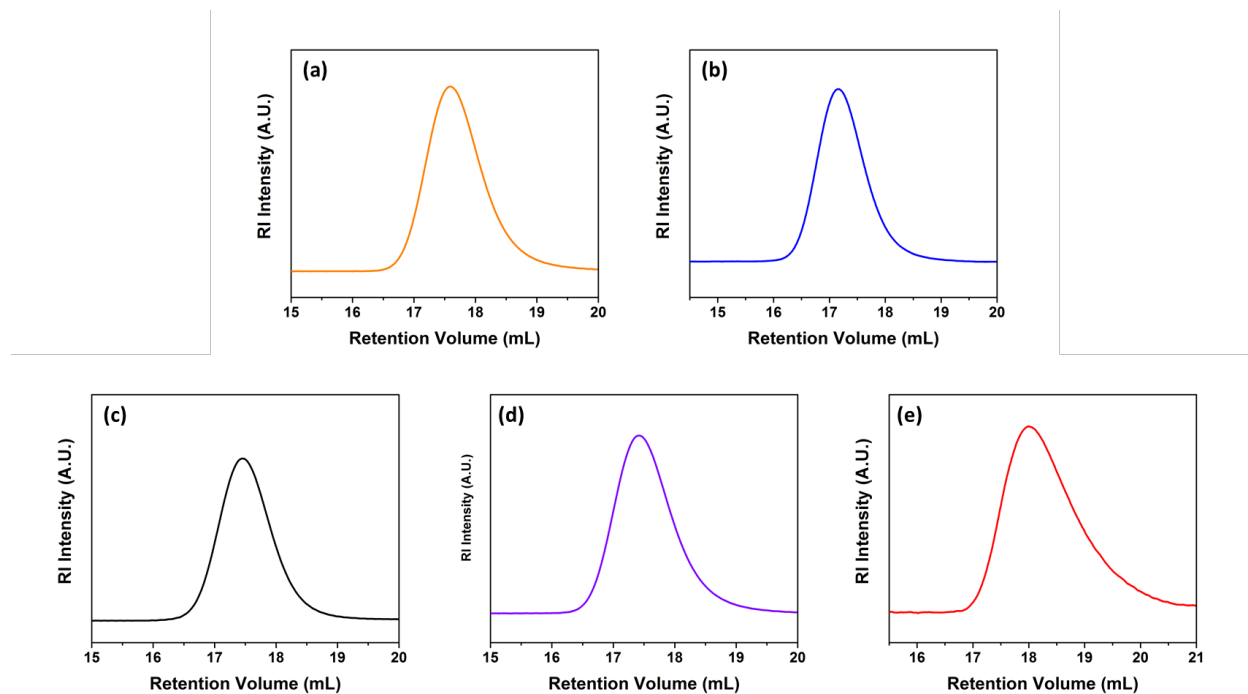
Figure S10. GPC data for poly(**1a-e**). Conditions and data: polymerizations were performed using HG2 as a catalyst and CH_2Cl_2 as a solvent under an atmosphere of nitrogen at 25 °C. Polymerizations were conducted for 60 min under an atmosphere of nitrogen and monitored for completion by thin-layer chromatography. GPC data are reported against poly(styrene) standards in THF. (a) $[\textbf{1a}]_0$ / $[\text{Ru}]_0$ = 27; M_n = 15.7 kDa, $Đ$ = 1.24 (yellow); 71% yield. (b) $[\textbf{1b}]_0$ / $[\text{Ru}]_0$ = 125; M_n = 21.5 kDa, $Đ$ = 1.18 (blue); 79% yield. (c) $[\textbf{1c}]_0$ / $[\text{Ru}]_0$ = 82; M_n = 24.9 kDa, $Đ$ = 1.17 (black); 88% yield. (d) $[\textbf{1d}]_0$ / $[\text{Ru}]_0$ = 90; M_n = 24.2 kDa, $Đ$ = 1.20 (violet); 93% yield. (e) $[\textbf{1e}]_0$ / $[\text{Ru}]_0$ = 15; M_n = 7.3 kDa, $Đ$ = 1.64 (red); 90% yield.

NMR Spectra

(a) HG2 (0.3 equiv.) + 1c (1.0 equiv.) + 3-bromopyridine (0.6 equiv.)

(b) HG2 (1.0 equiv.) + 1c (1.0 equiv.)

1:1 mixture of (a) and (b)
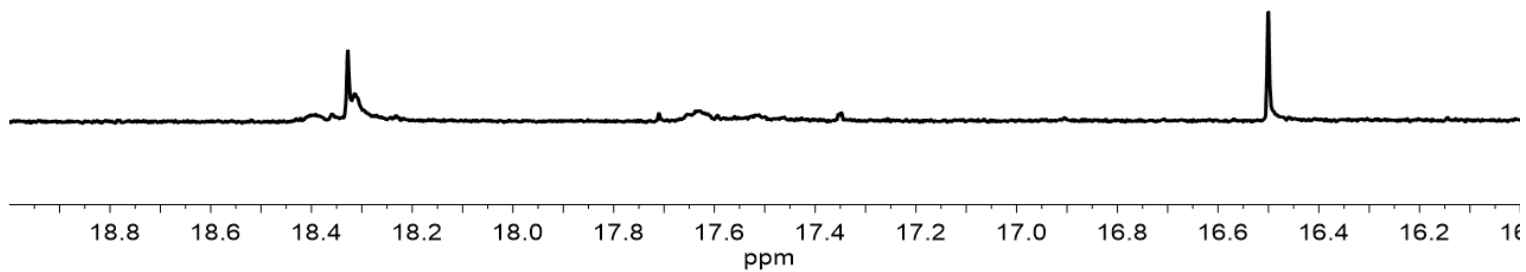
Figure S11. ^{1}H NMR spectra recorded in CD_2Cl_2 for various mixtures (indicated).
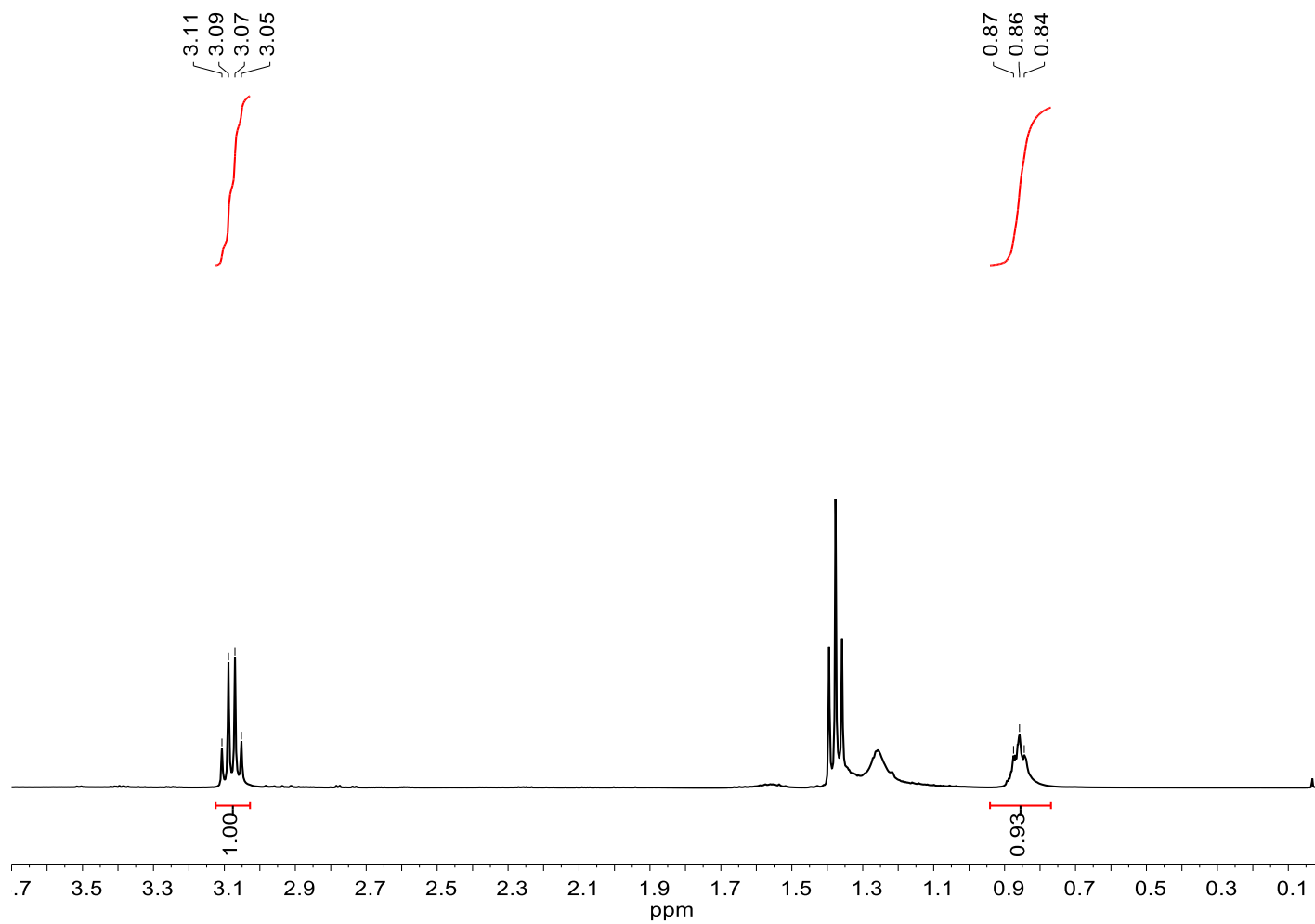
Figure S12. ^{1}H NMR spectrum recorded for a mixture of poly(**1c**) and TEA (1 : 1 equiv. in terms of polymer repeat unit of poly(**1c**)) at 25 °C in CD_2Cl_2.
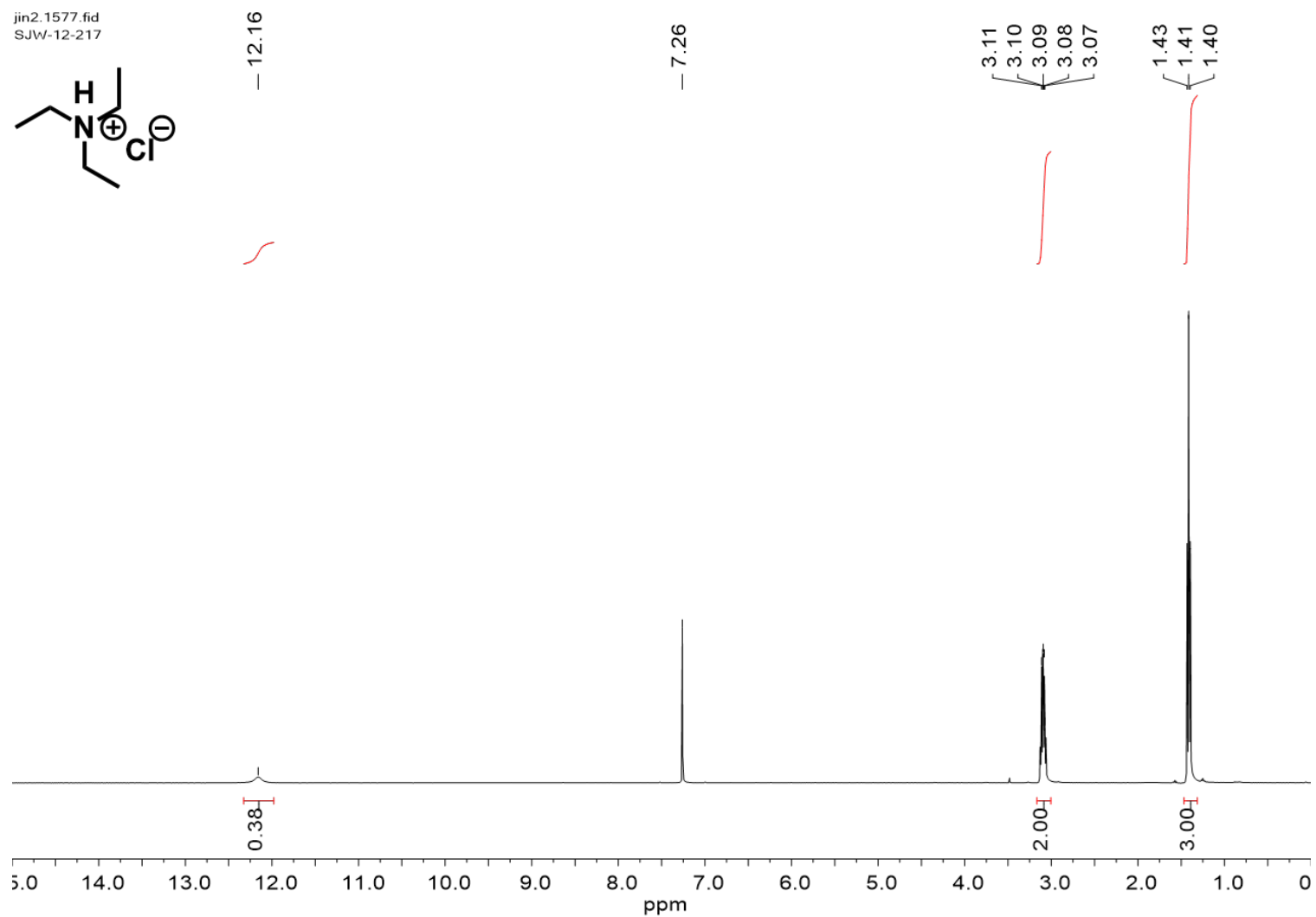
Figure S13. ^{1}H NMR spectrum recorded for triethylammonium chloride (Et$_3$NH$^+$Cl$^-$) at 25 °C in CDCl$_3$. The salt was isolated via filtration from the elimination reaction of poly(**1c**) using TEA (10 equiv. based on the repeat unit of the polymer).

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SJW-8-89

7.5203
7.5151
7.5127
7.5074
7.5027
7.4999
7.3772
7.3717
7.3613
7.3543
7.3480
7.3376
7.3321
6.3332
6.3096
6.2677
6.2520
6.2371

— 5.3201

1.00
1.04

1.00
1.00
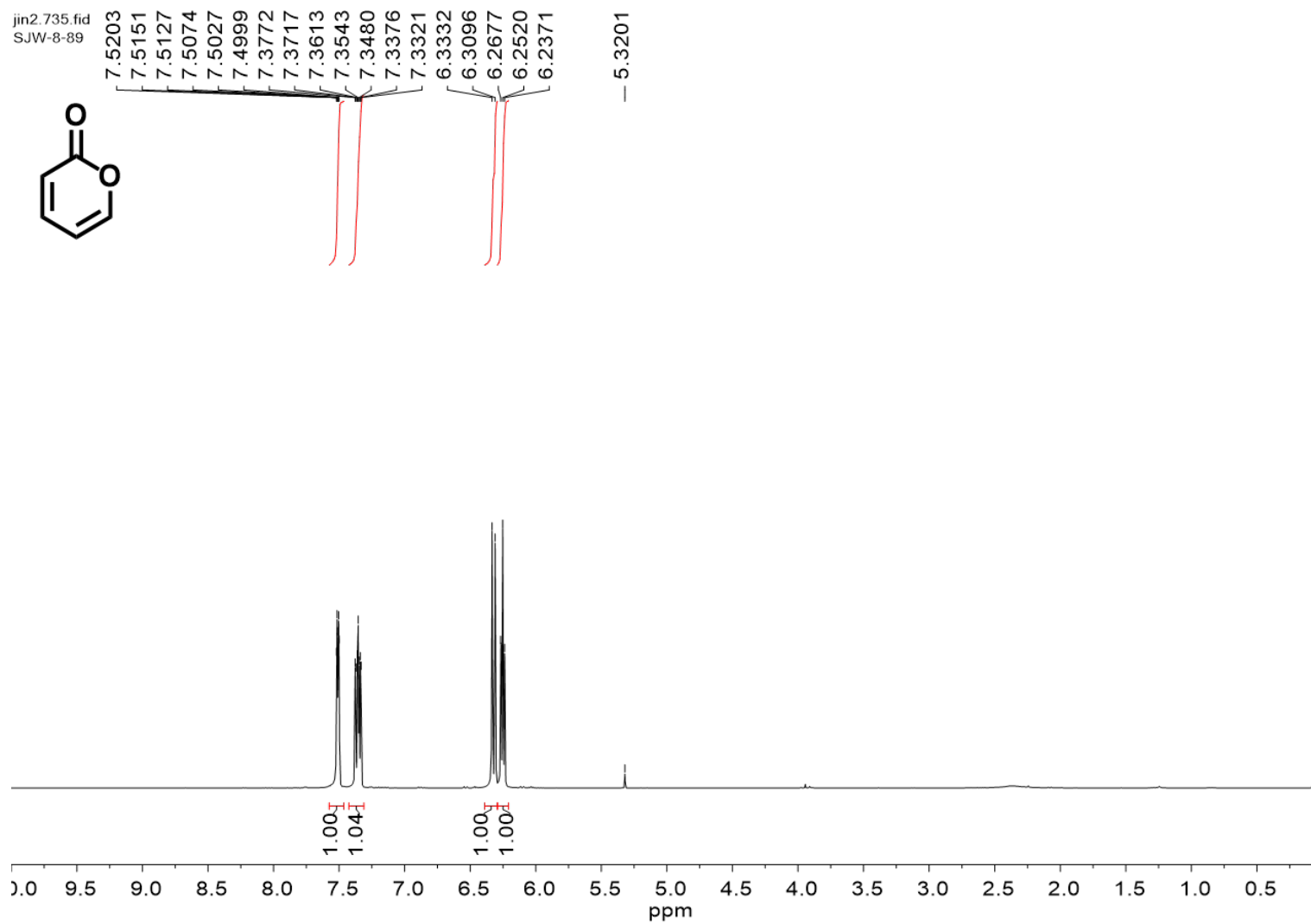
Figure S14. ^{1}H NMR spectrum recorded for **3** at 25 °C in CD$_2$Cl$_2$.
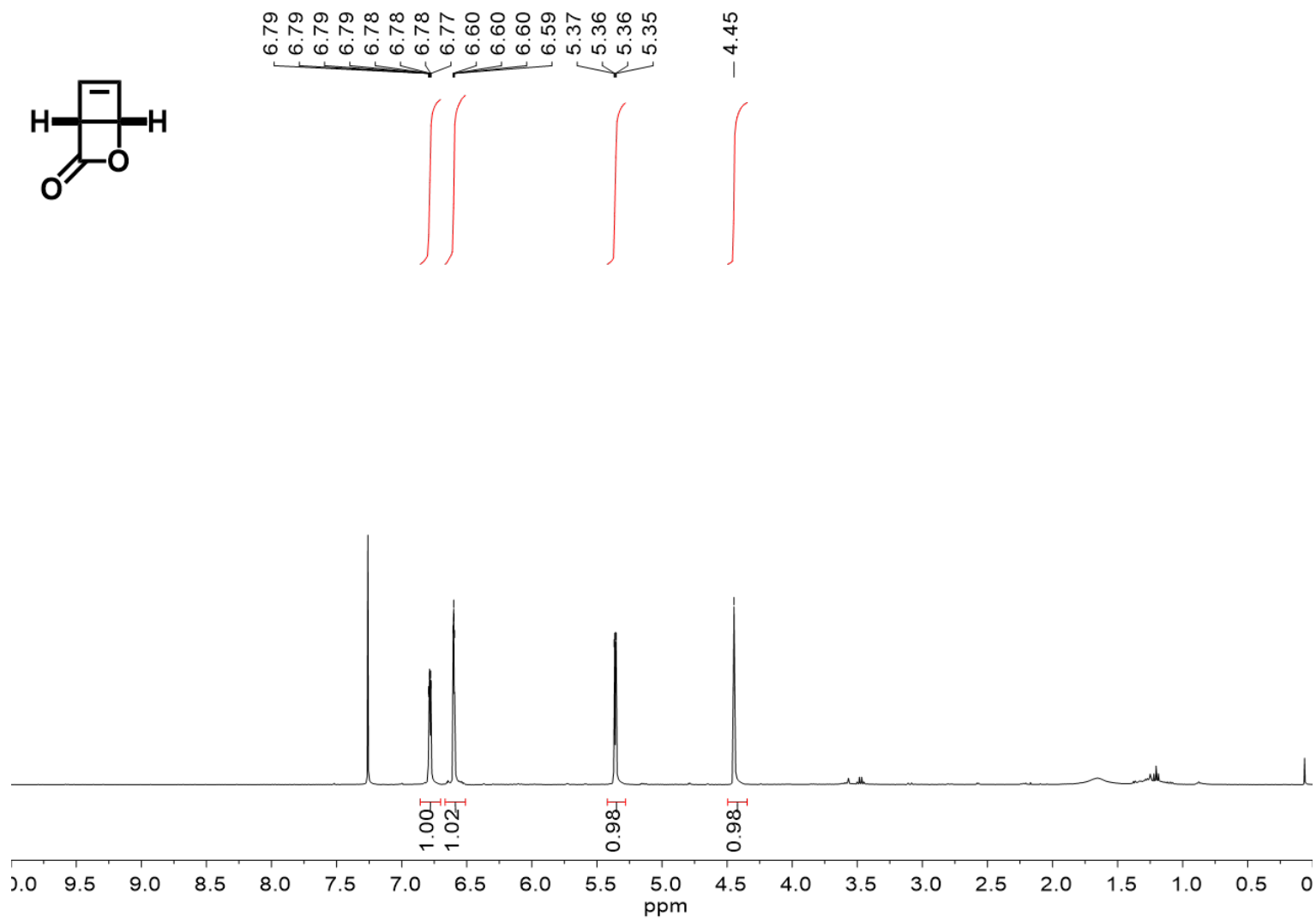
Figure S15. ^{1}H NMR spectrum recorded for **4** at 25 °C in CDCl$_3$.
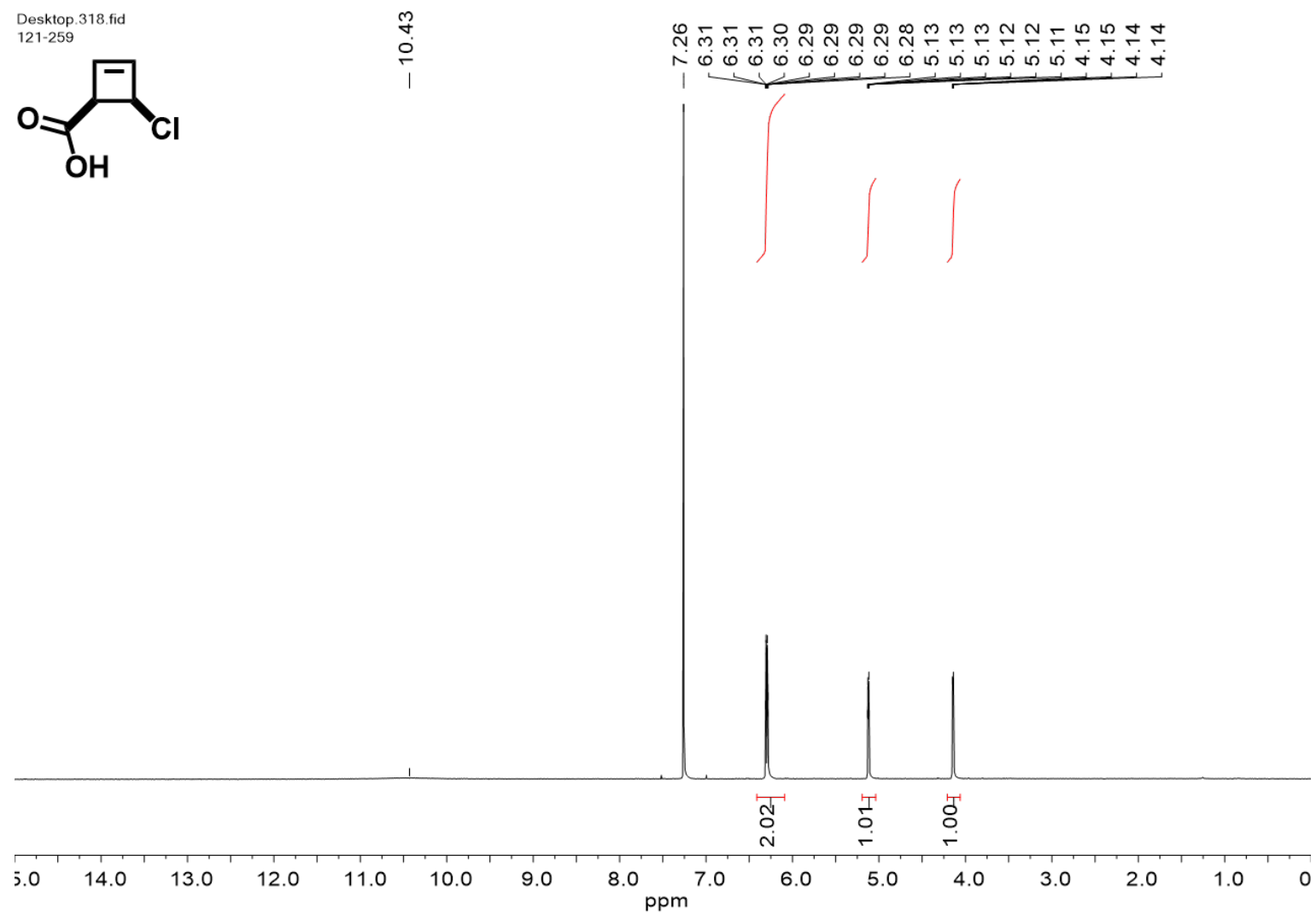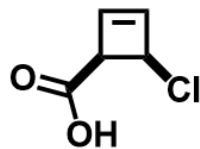
Figure S16. ^{1}H NMR spectrum recorded for **5** at 25 °C in CDCl$_3$.
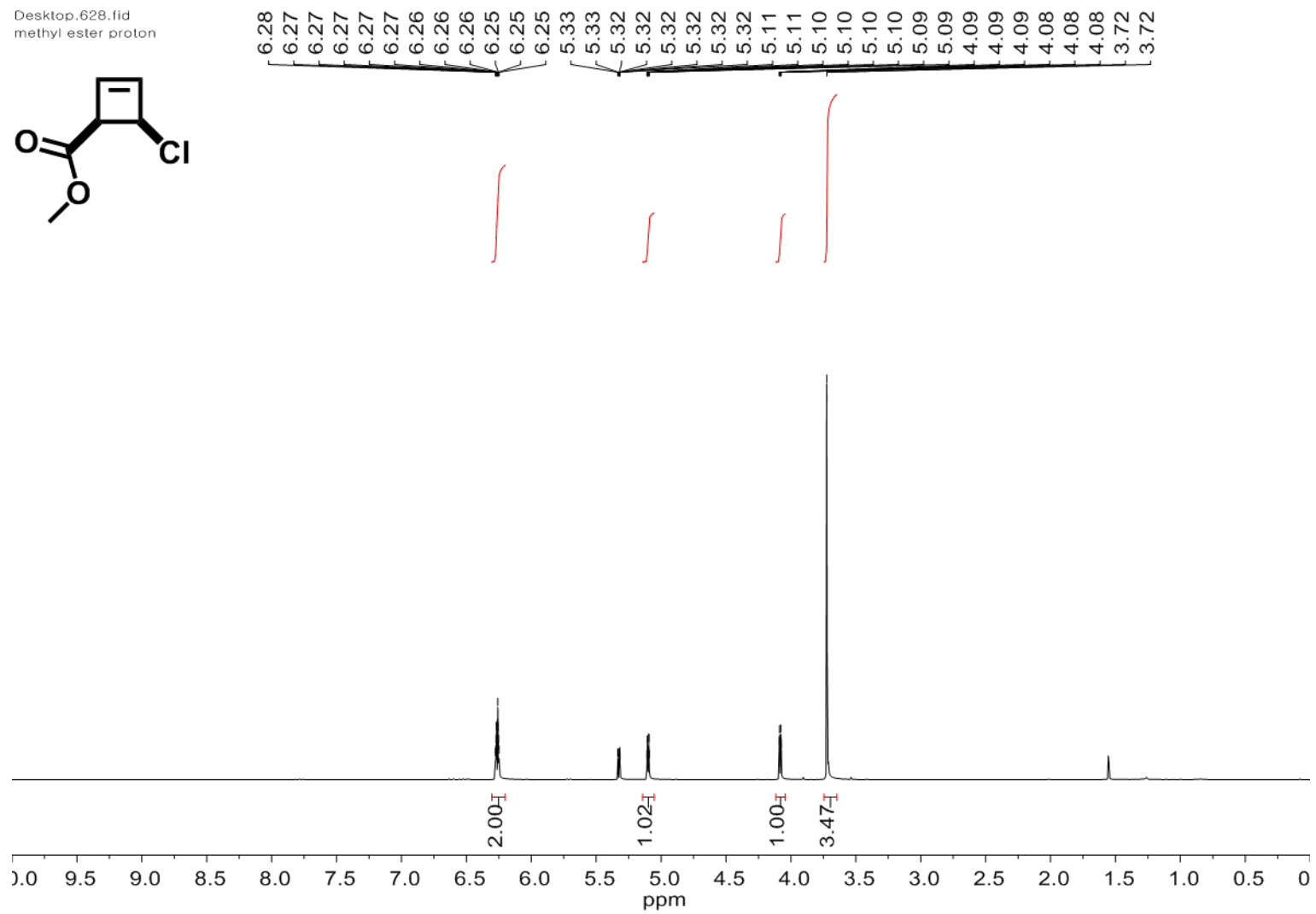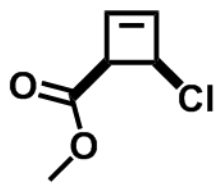
Figure S17. ^{1}H NMR spectrum recorded for **1a** at 25 °C in CD$_2$Cl$_2$.

S17

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methyl ester carbon nmr

— 170.64
— 140.78
— 137.27
— 57.10
— 54.59
— 52.36
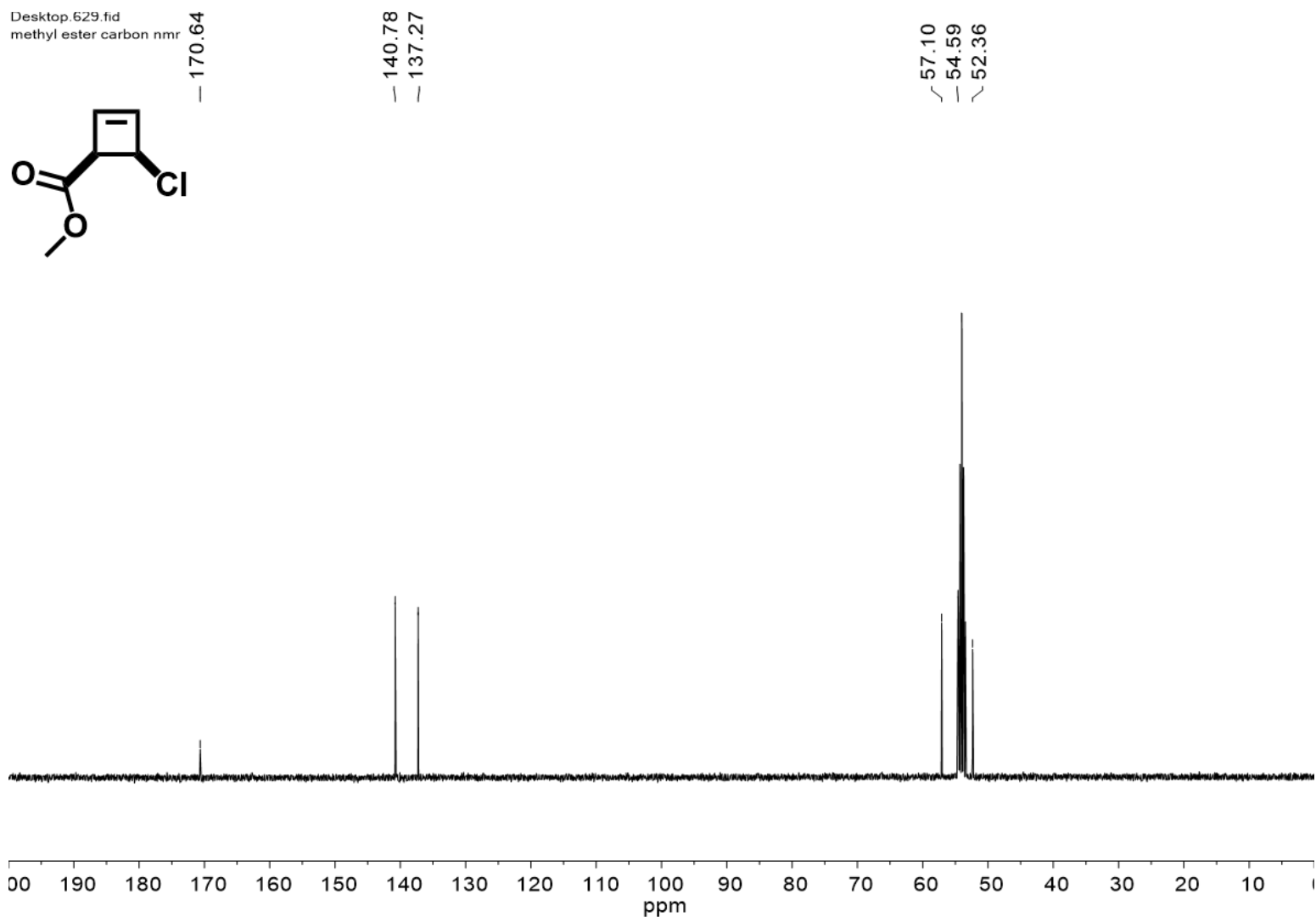
Figure S18. ^{13}C NMR spectrum recorded for **1a** at 25 °C in CD_2Cl_2.

Figure S19. ^{1}H NMR spectrum recorded for **1b** at 25 °C in CD$_2$Cl$_2$.
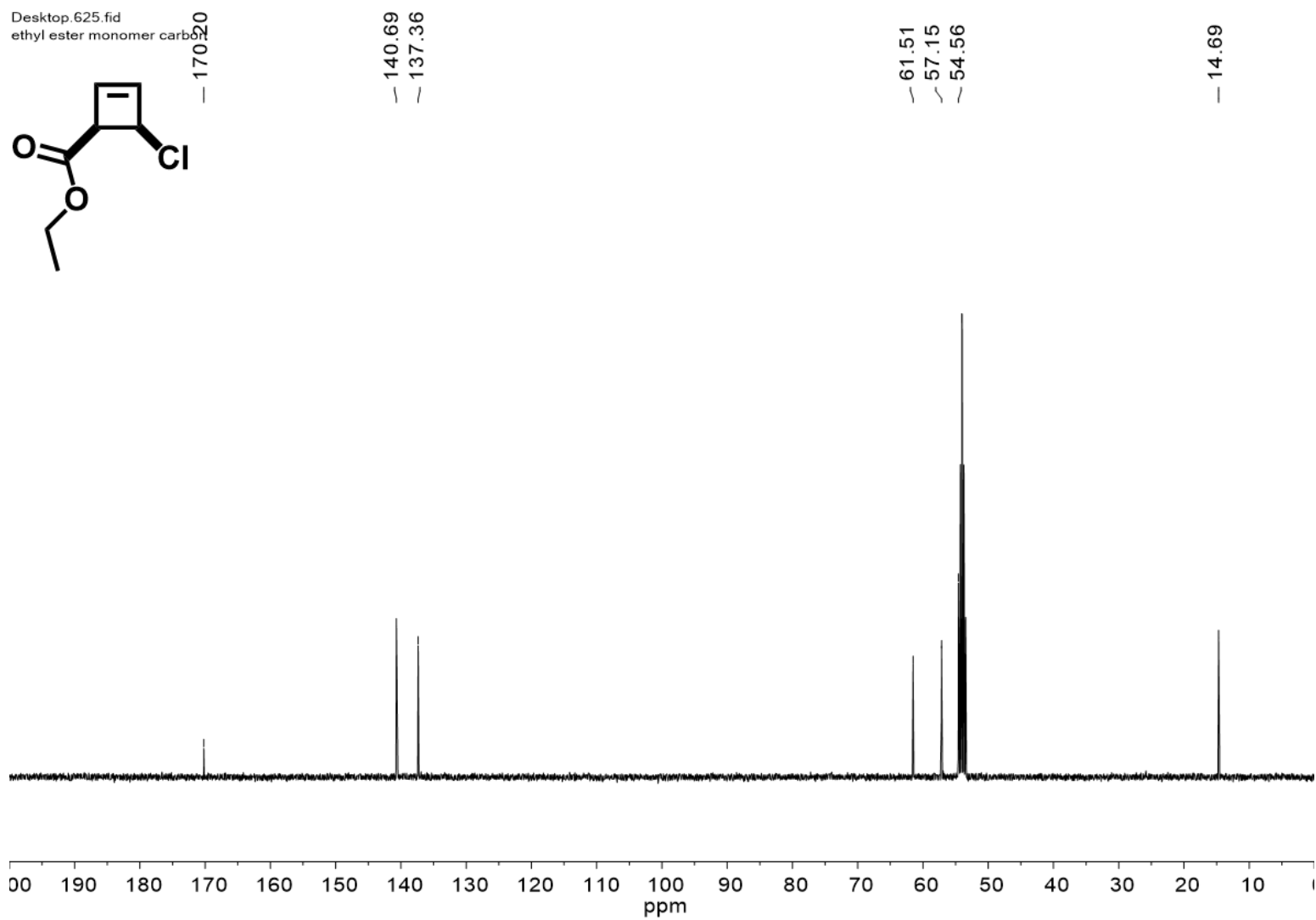
Figure S20. ^{13}C NMR spectrum recorded for **1b** at 25 °C in CD_2Cl_2.

Figure S21. ^{1}H NMR spectrum recorded for **1c** at 25 °C in CD$_2$Cl.

Figure S22. ^{13}C NMR spectrum recorded for **1c** at 25 °C in CD$_2$Cl$_2$.
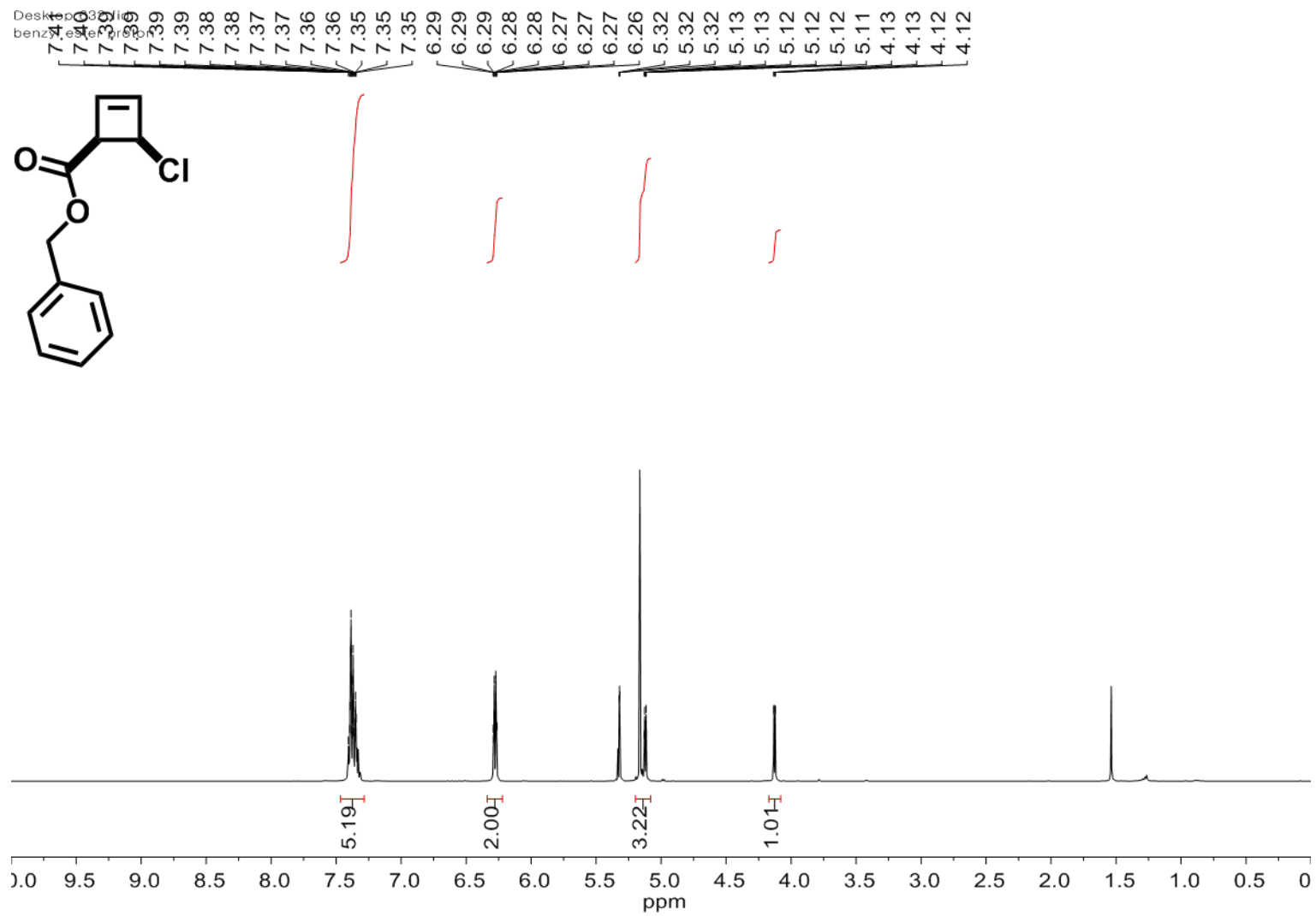
Figure S23. ^{1}H NMR spectrum recorded for **1d** at 25 °C in CD$_2$Cl$_2$.
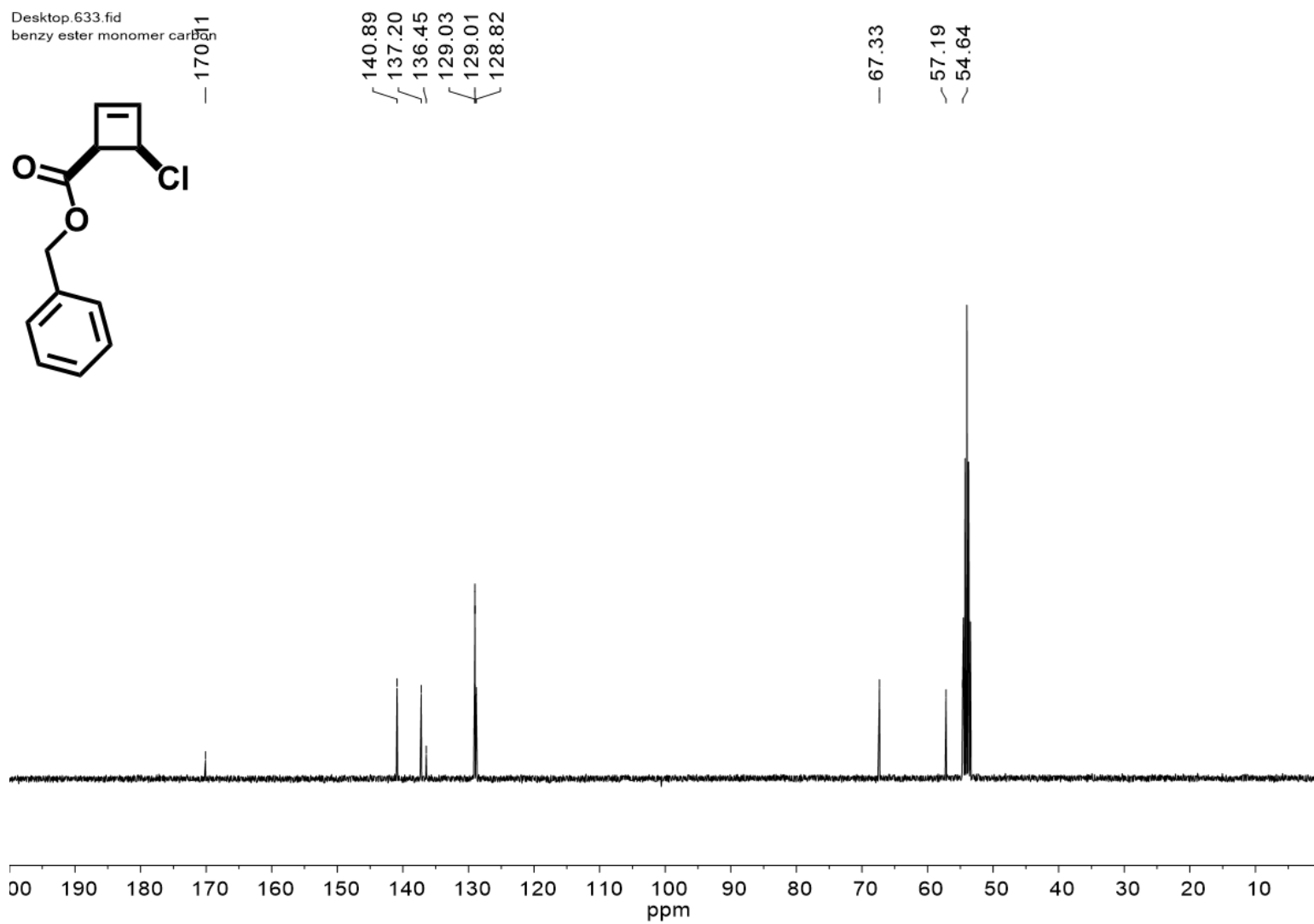
Figure S24. ^{13}C NMR spectrum recorded for **1d** at 25 °C in CD_2Cl_2.

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trifluoro ethyl ester monomer proton

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1.00 0.52 1.13 0.53
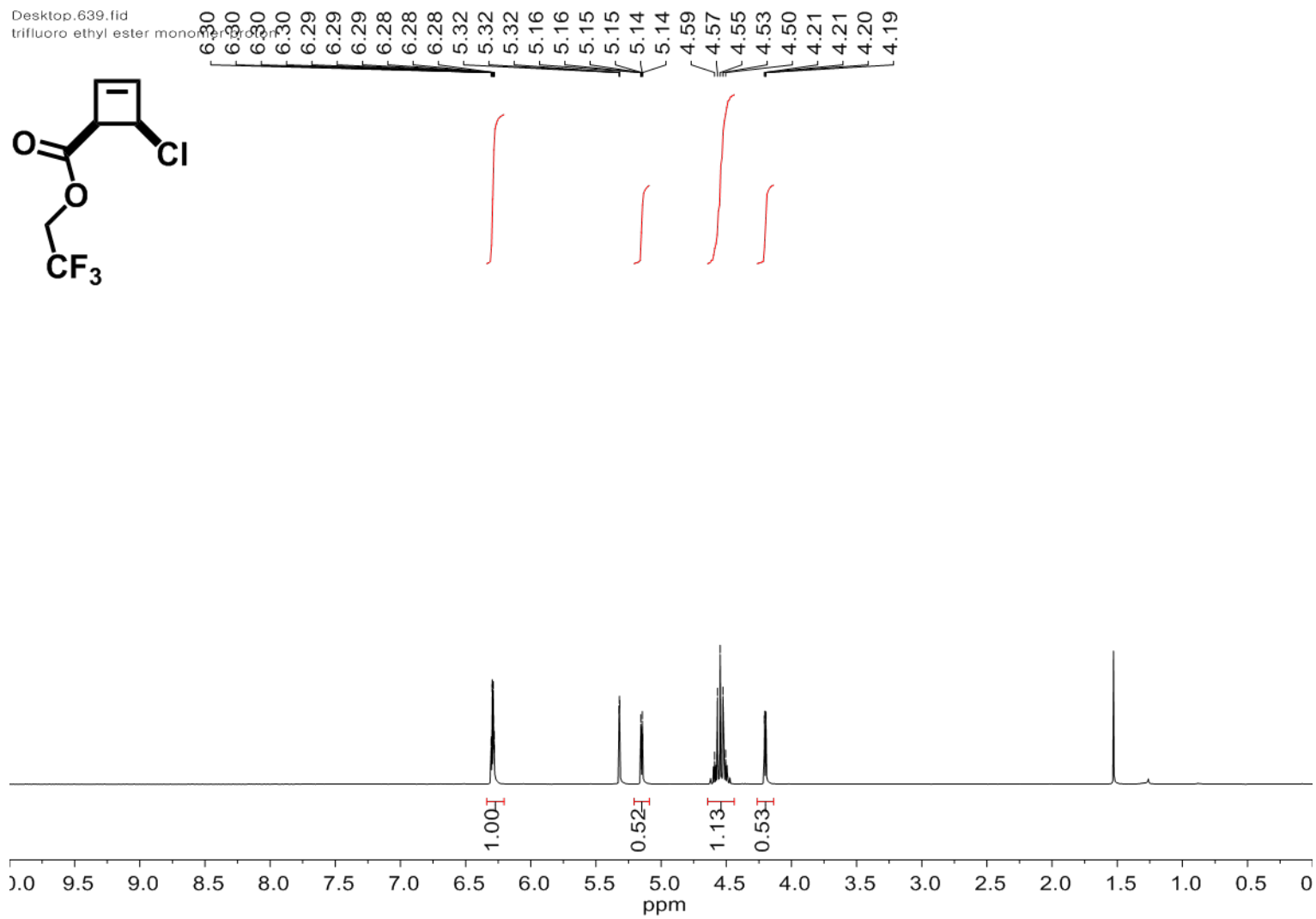
Figure S25. ^{1}H NMR spectrum recorded for **1e** at 25 °C in CD$_2$Cl$_2$.

S25

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trifluoro ethyl ester monomer carbon

168.80

141.49
136.45

125.01
122.26

61.73
61.36
61.00
60.64
56.76
54.00
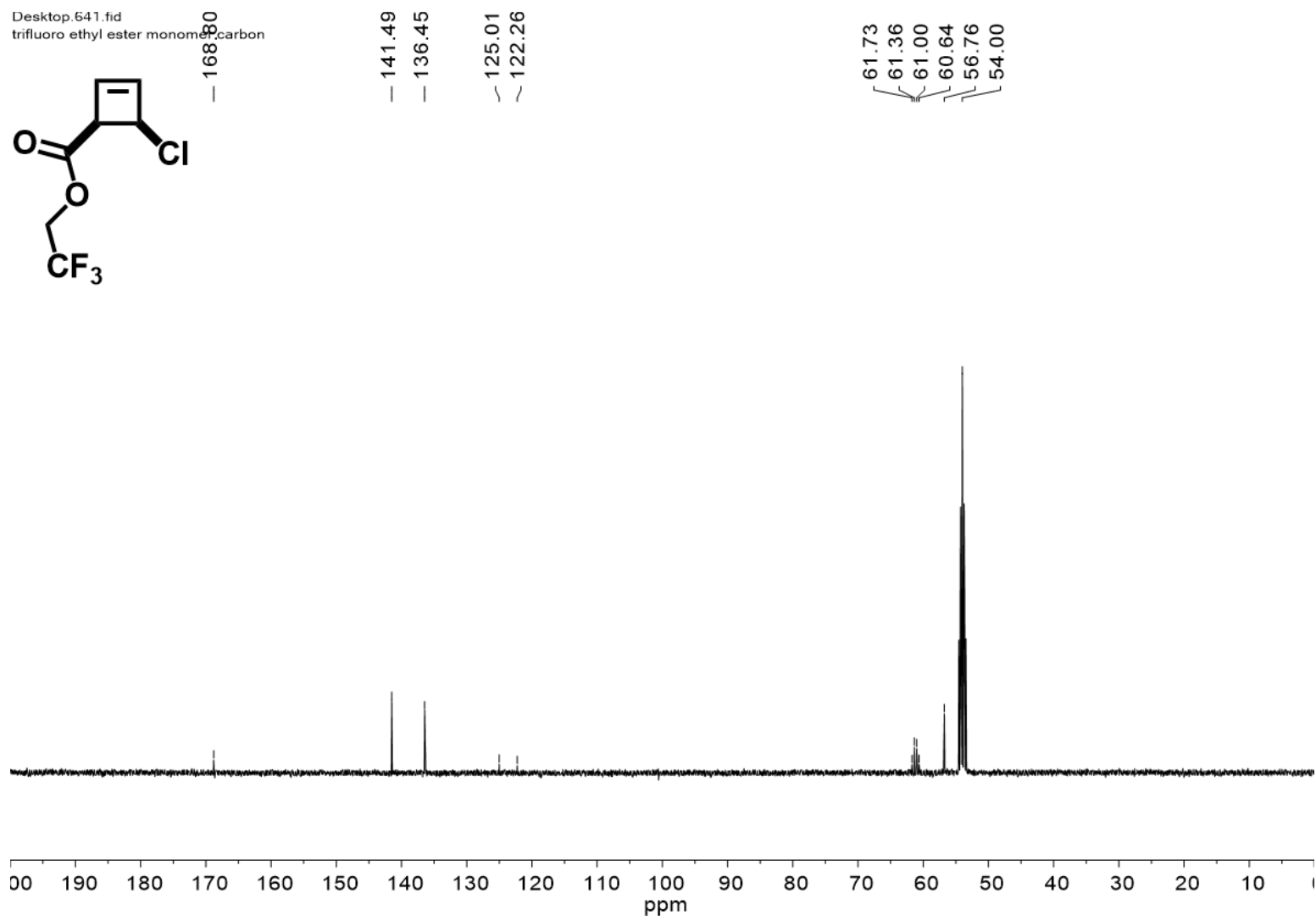
Figure S26. ^{13}C NMR spectrum recorded for **1e** at 25 °C in CD$_2$Cl$_2$.
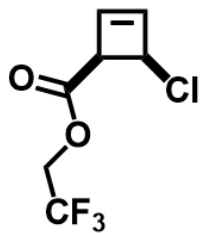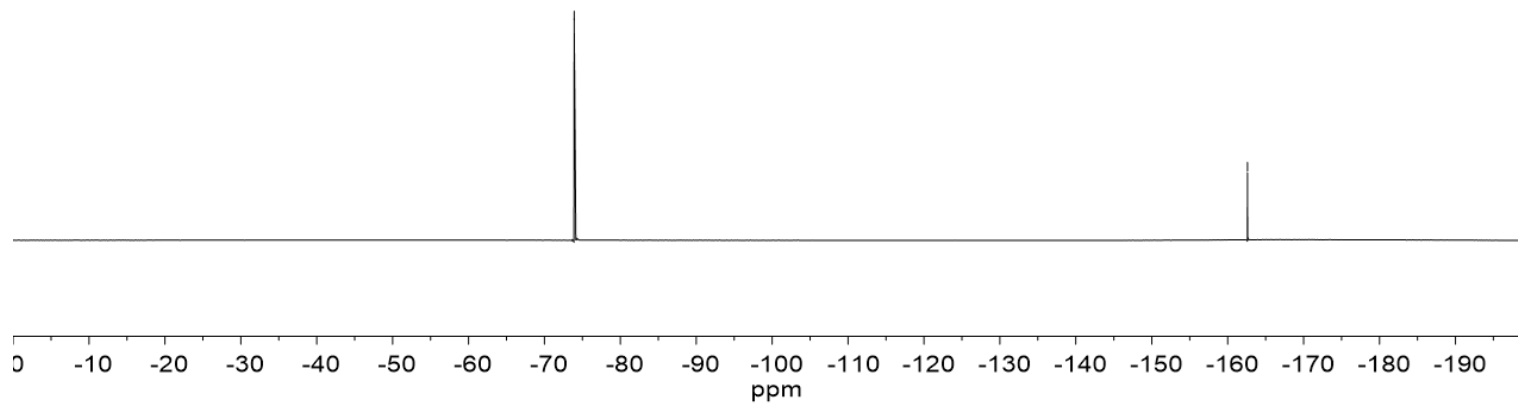
Figure S27. ^{19}F NMR spectrum recorded for **1e** at 25 °C in CD$_2$Cl$_2$.
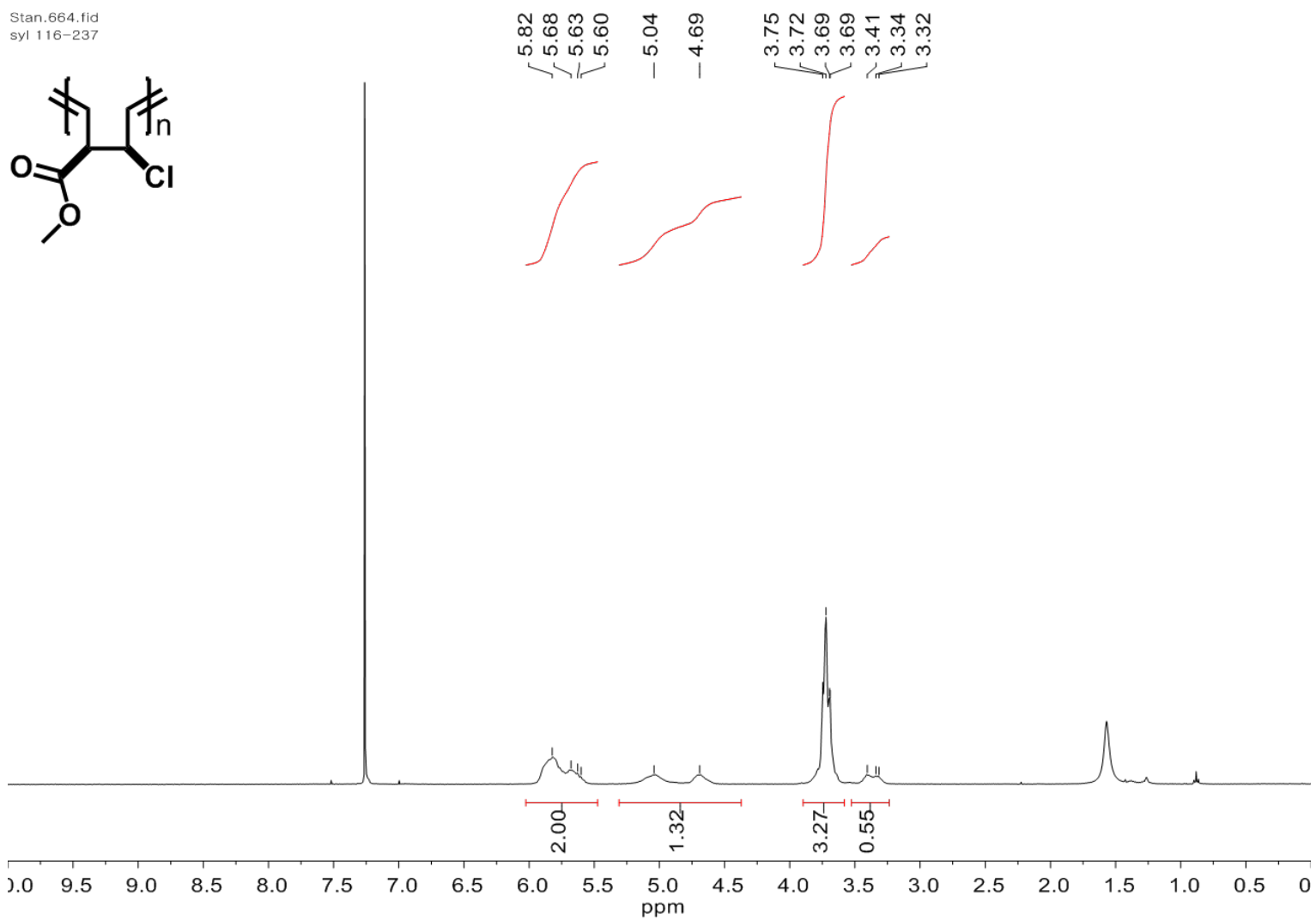
Figure S28. ^{1}H NMR spectrum recorded for poly(**1a**) at 25 °C in CDCl$_3$.
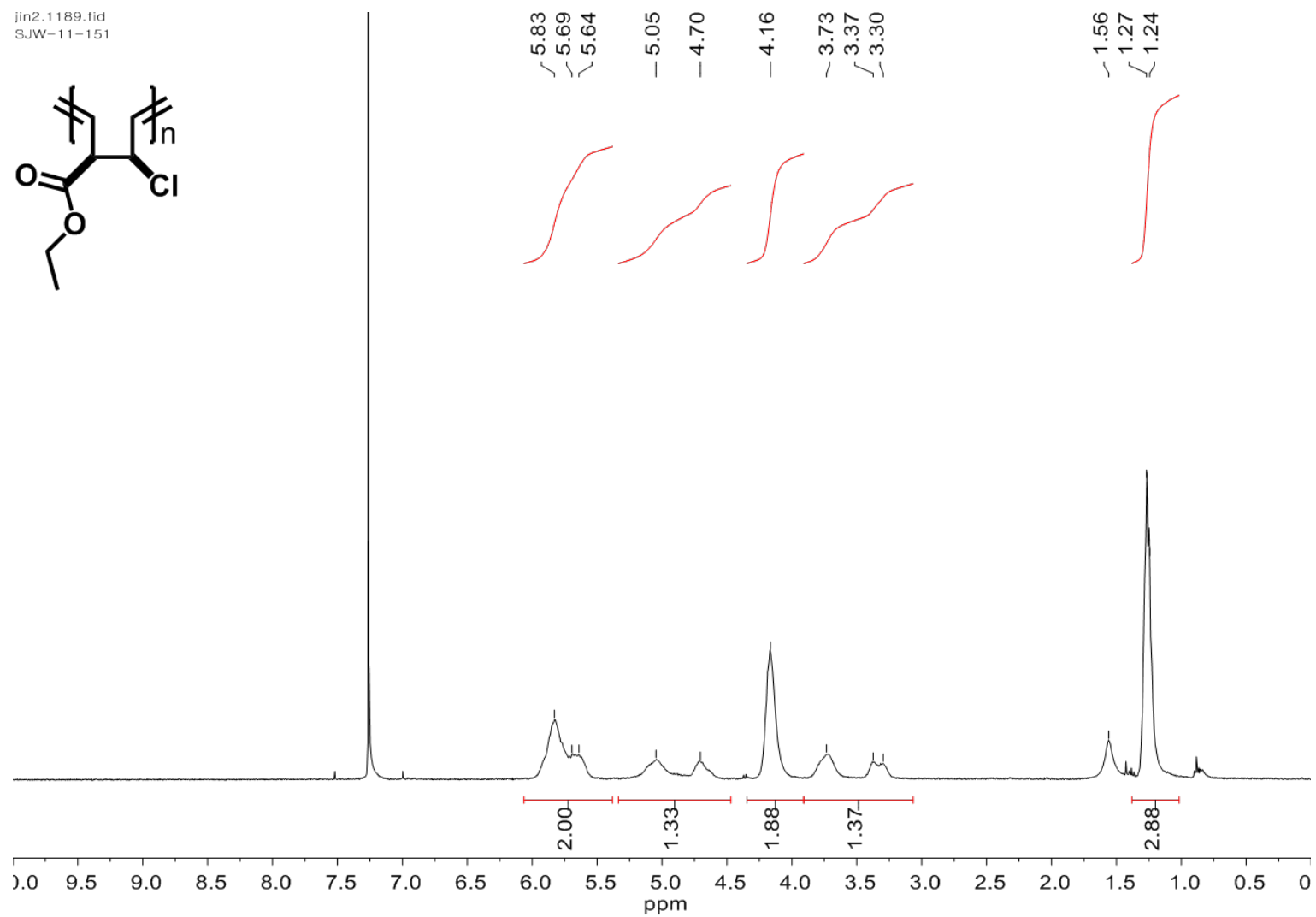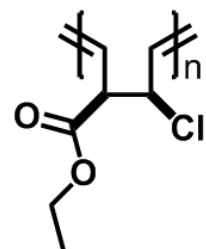
Figure S29. ^{1}H NMR spectrum recorded for poly(**1b**) at 25 °C in CDCl$_3$.
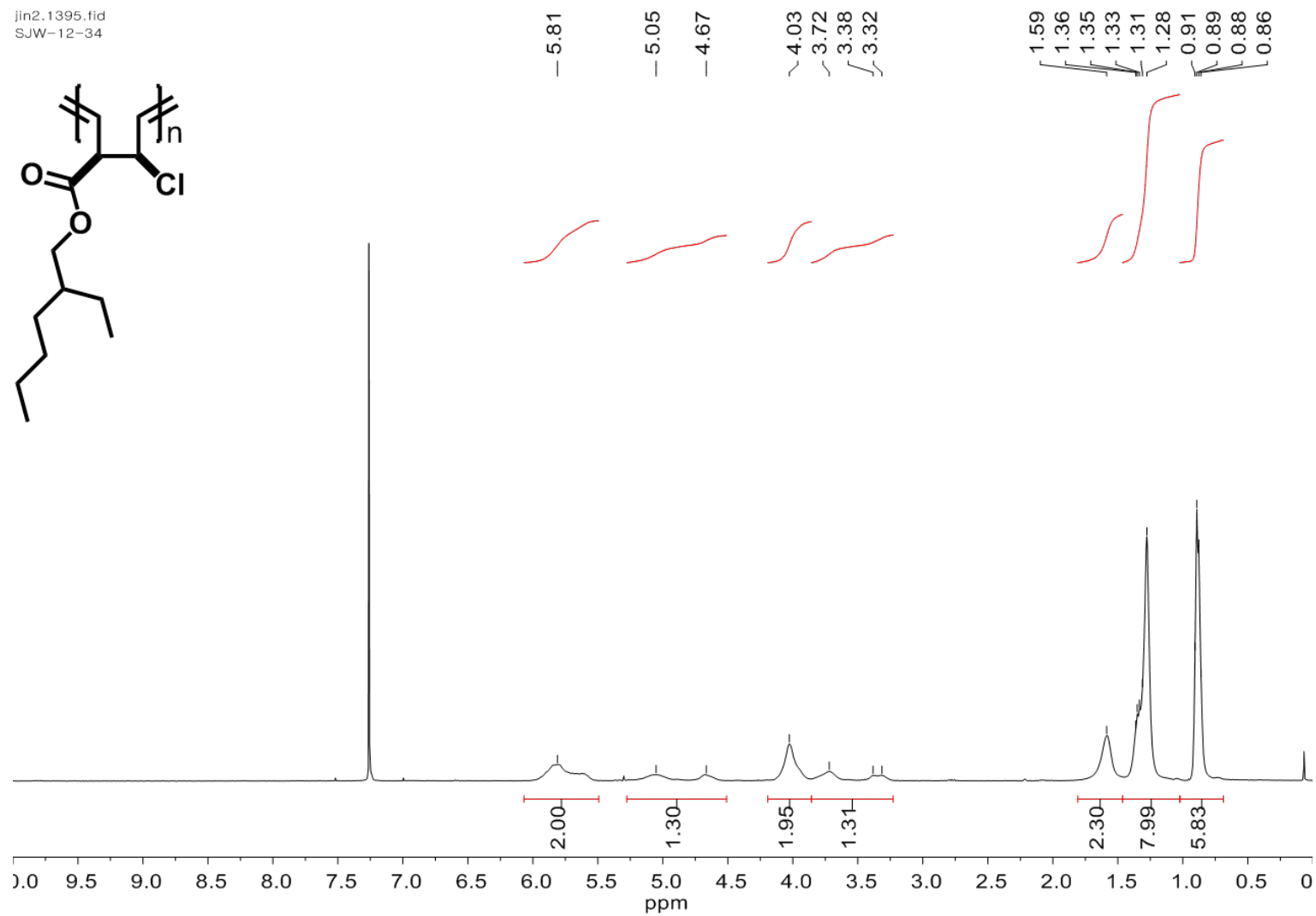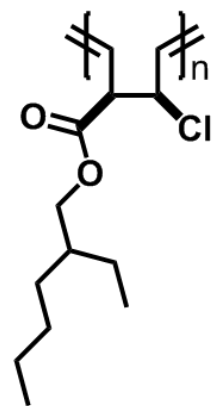
Figure S30. ^{1}H NMR spectrum recorded for poly(**1c**) at 25 °C in CDCl$_3$.
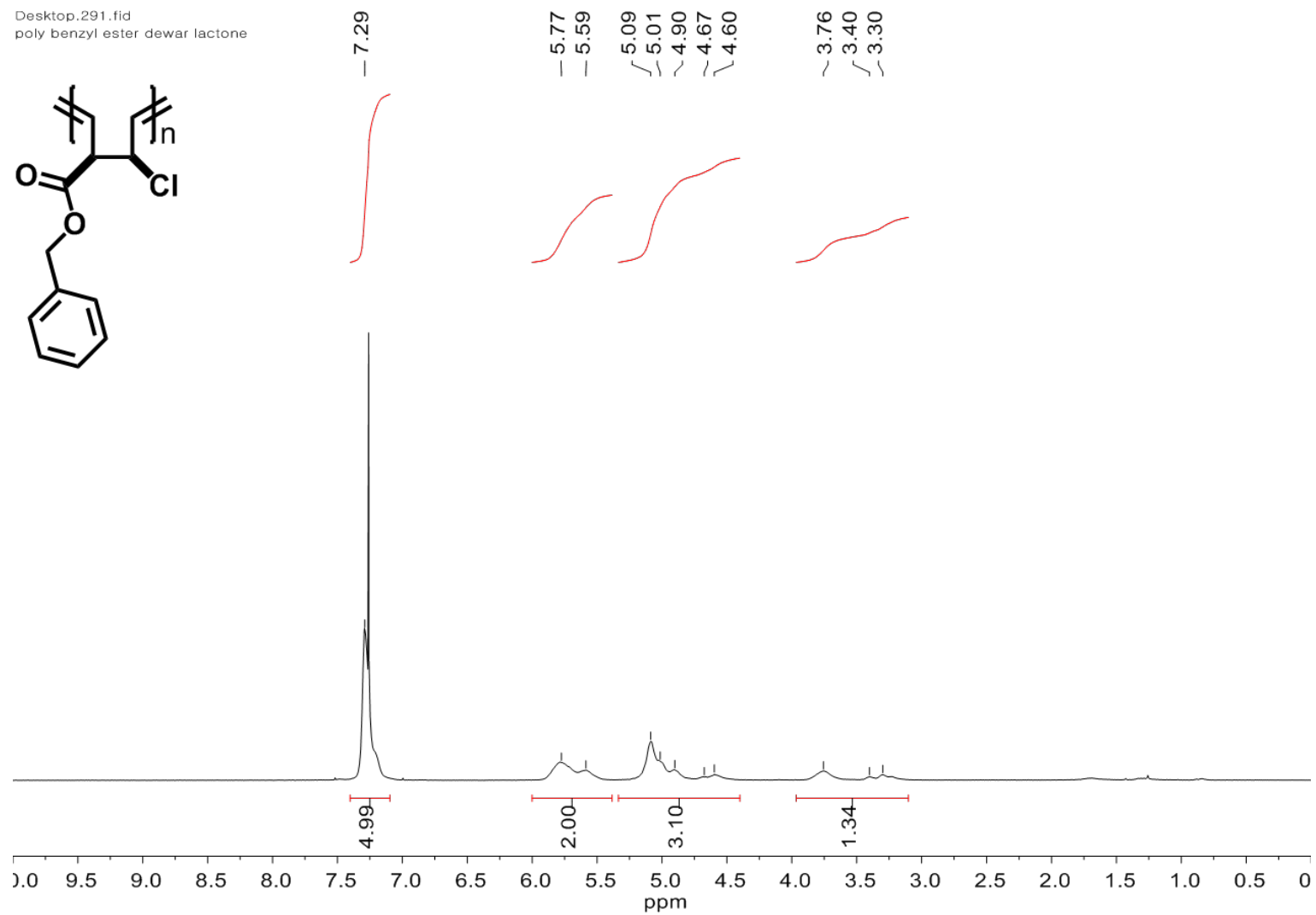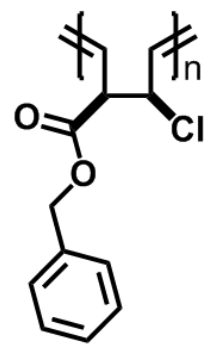
Figure S31. ^{1}H NMR spectrum recorded for poly(**1d**) at 25 °C in CDCl$_3$.
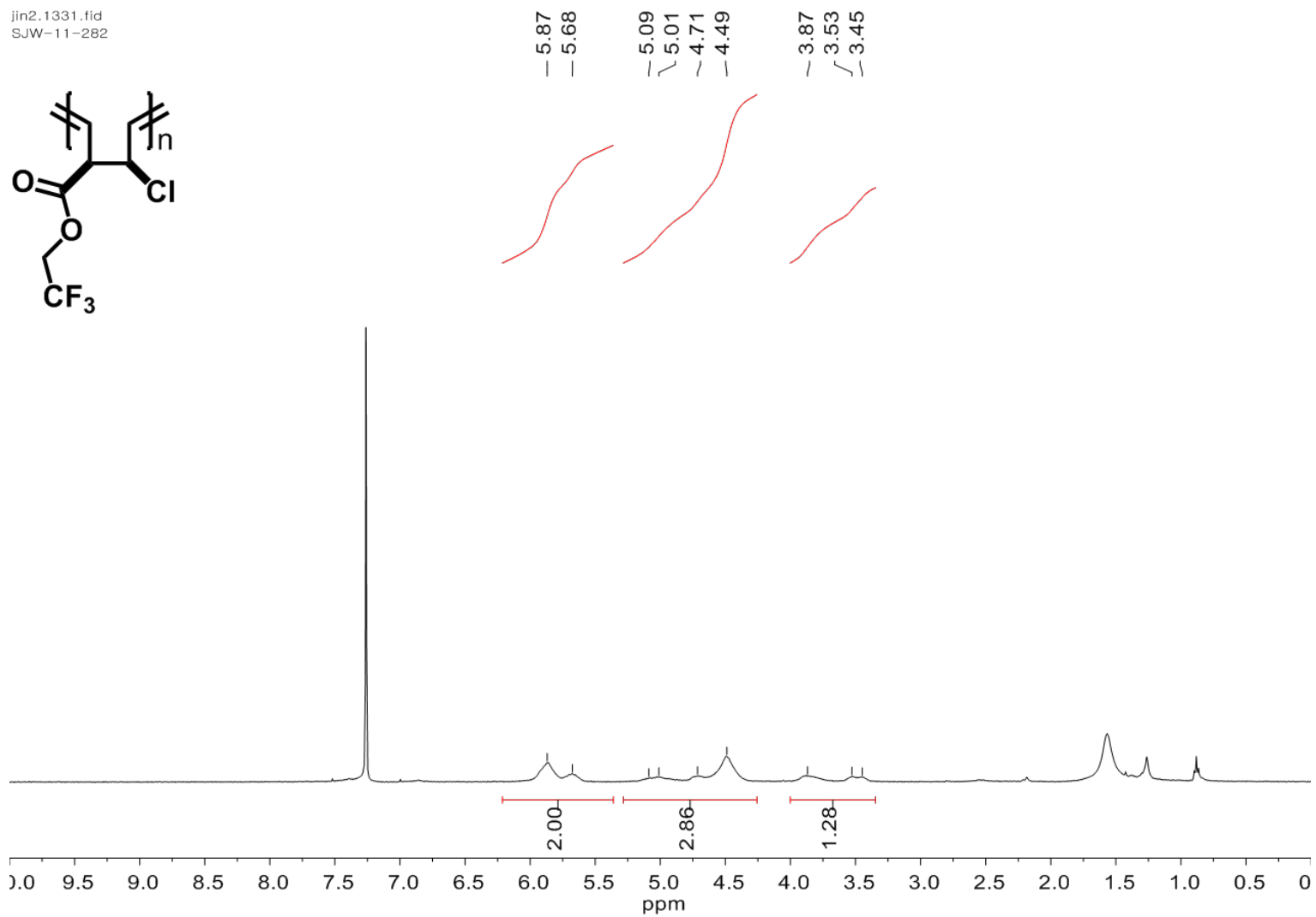
Figure S32. ^{1}H NMR spectrum recorded for poly(**1e**) at 25 °C in CDCl$_3$.
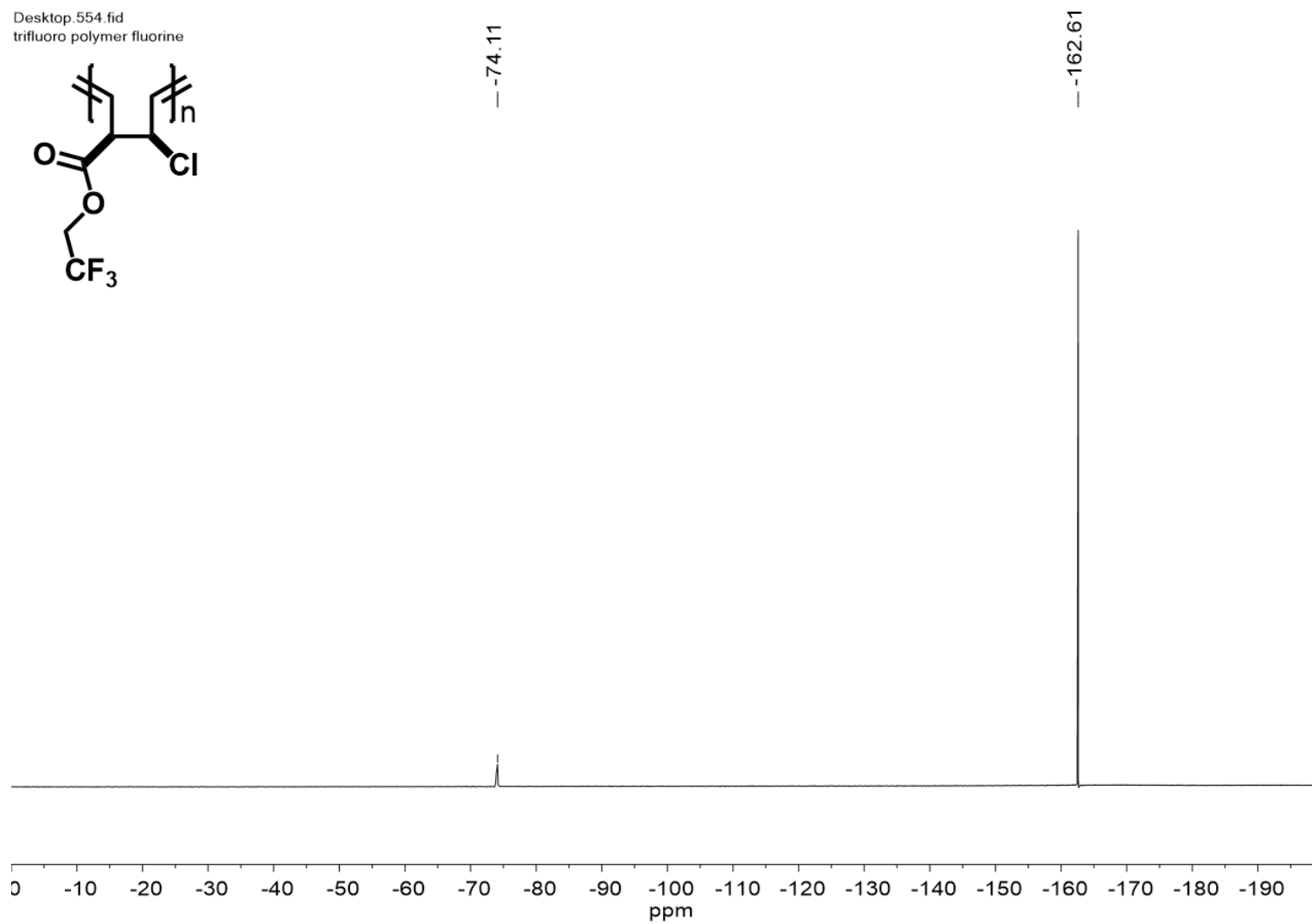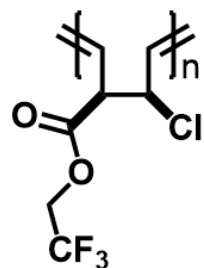
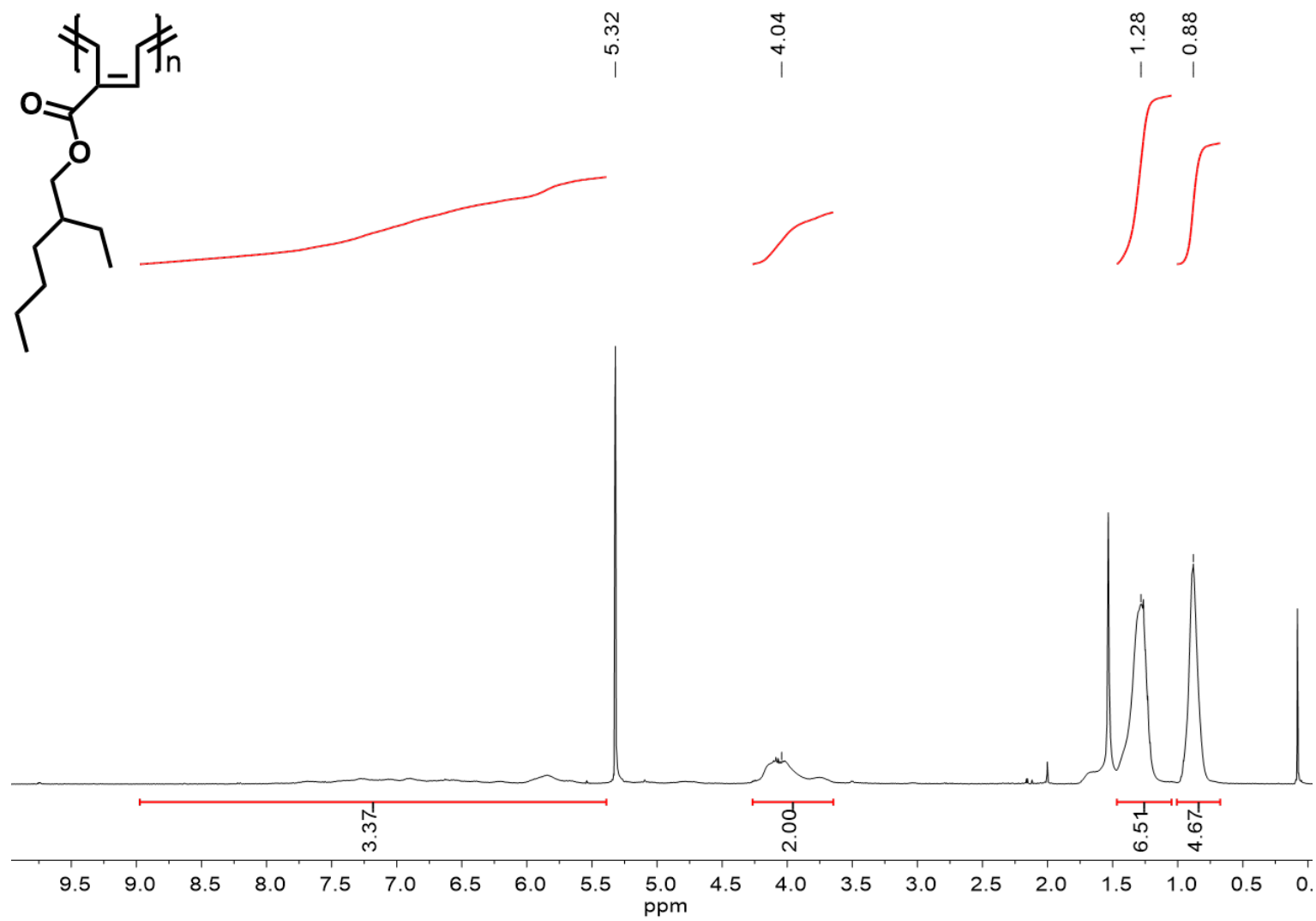**Figure S33.** ^{19}F NMR spectrum recorded for poly(**1e**) at 25 °C in CD_2Cl_2.
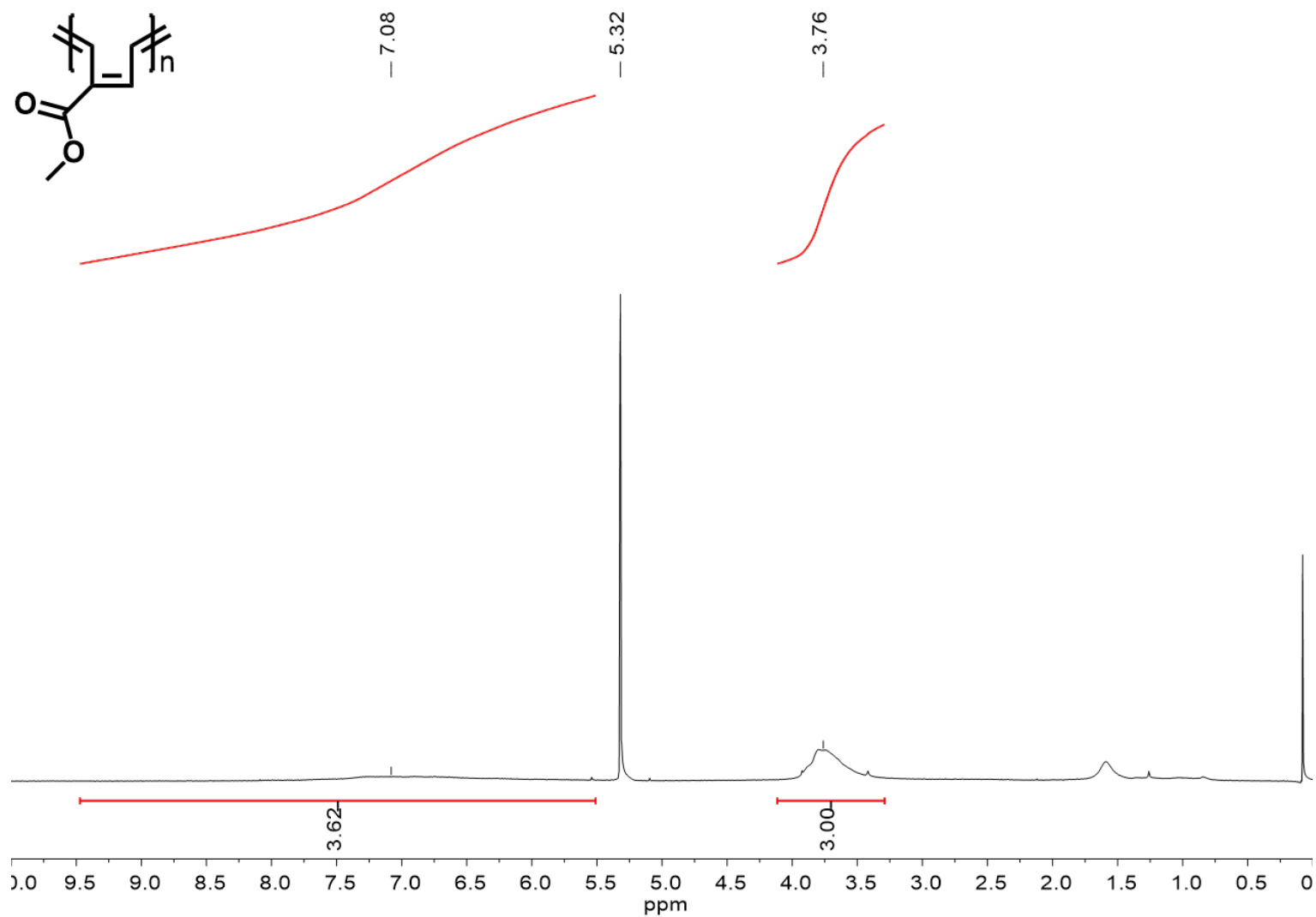
Figure S34. ^{1}H NMR spectrum recorded for **7a** at 25 °C in CD$_2$Cl$_2$.
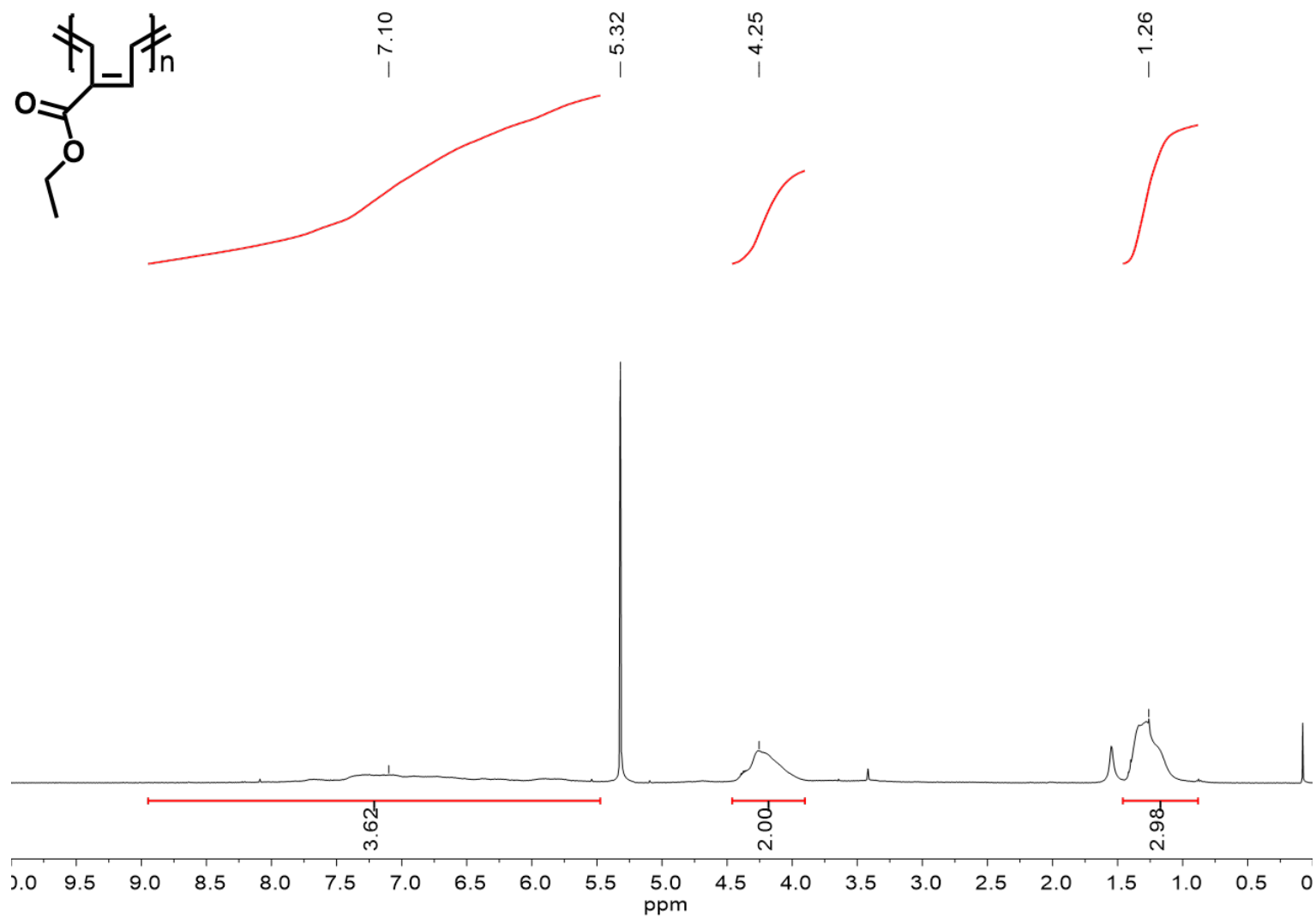
Figure S35. ^{1}H NMR spectrum recorded for **7b** at 25 °C in CD$_2$Cl$_2$.
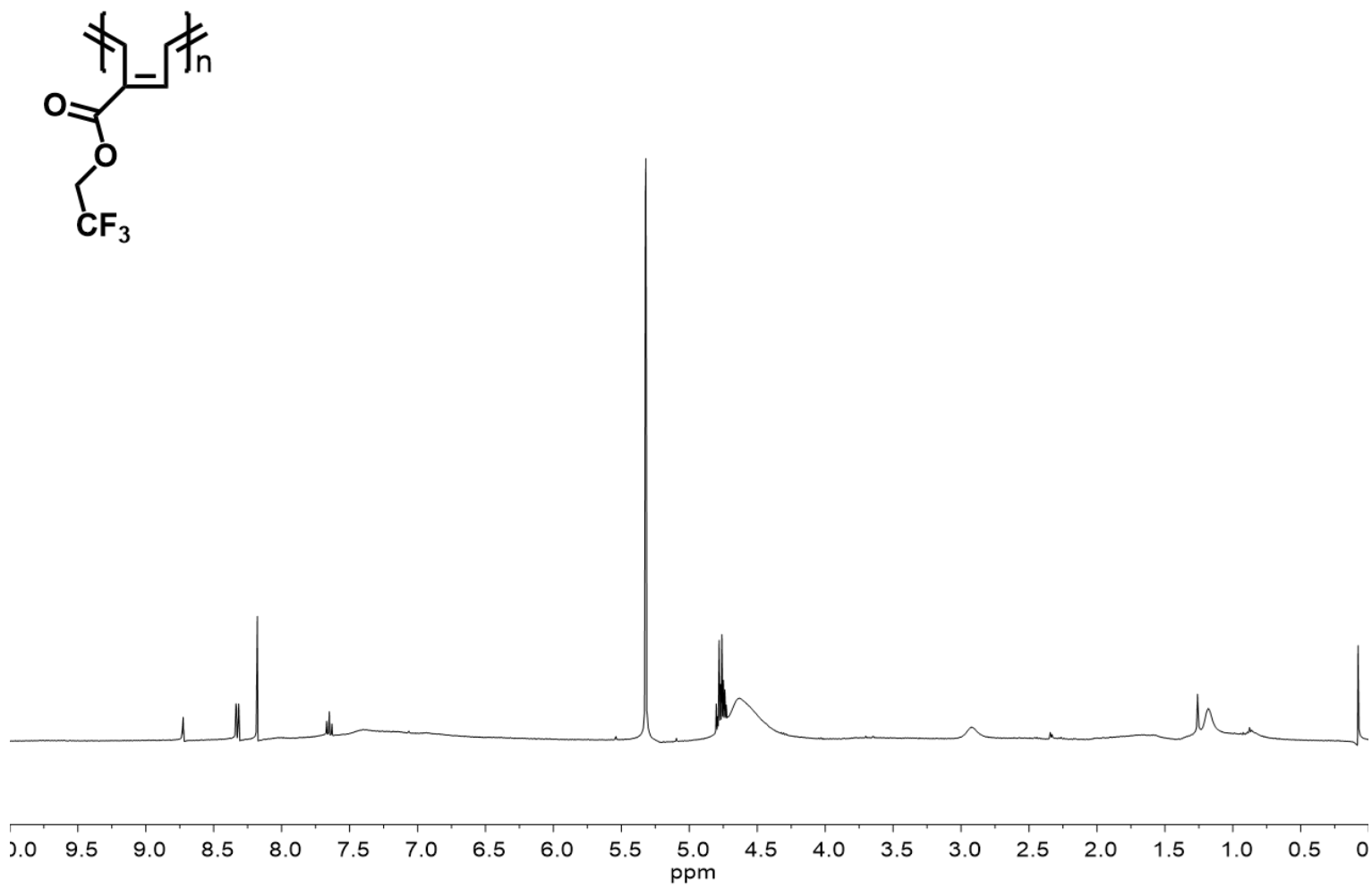
Figure S36. ^{1}H NMR spectrum recorded for **7c** at 25 °C in CD$_2$Cl$_2$.

S36
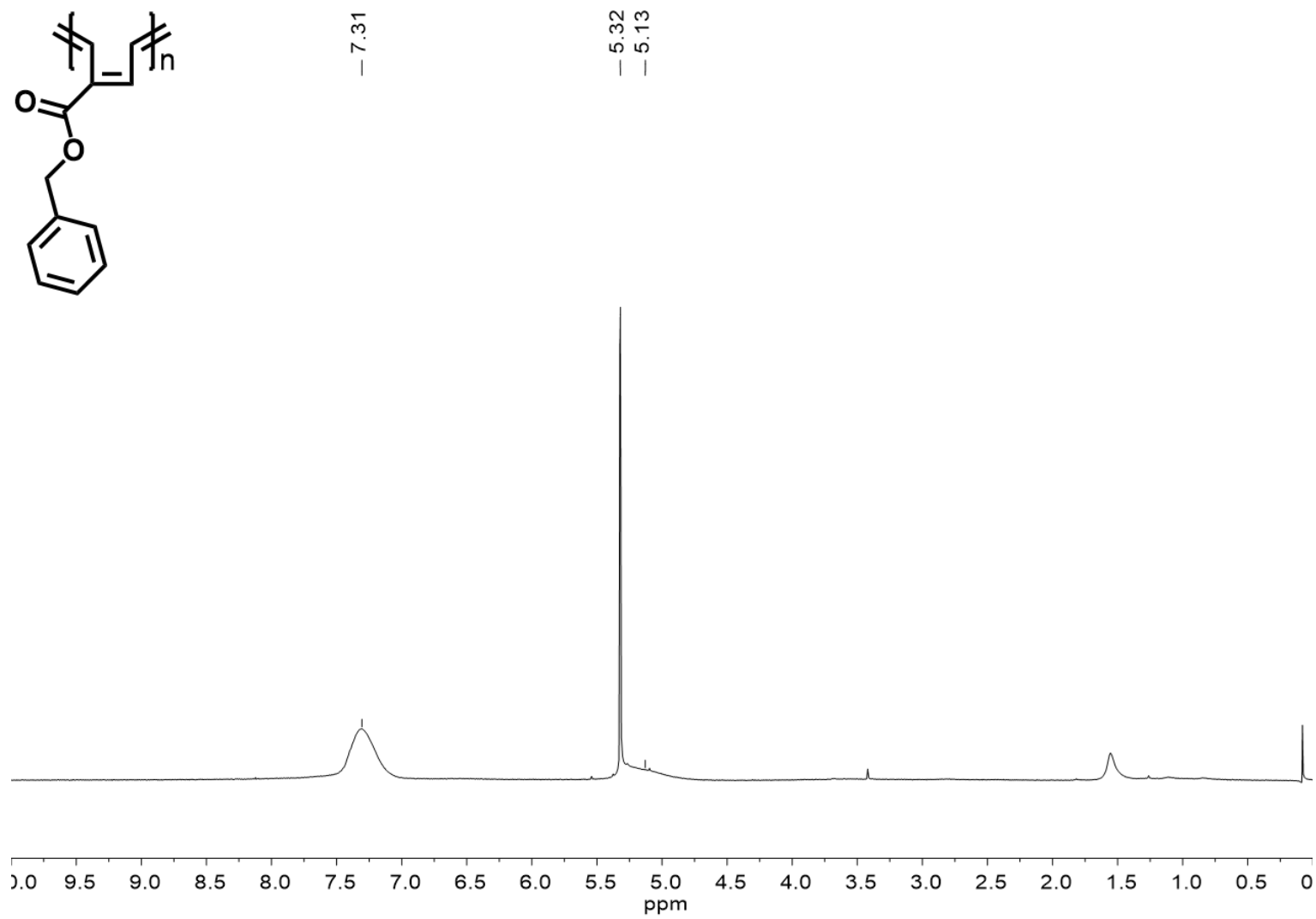
Figure S37. ^{1}H NMR spectrum recorded for **7d** at 25 °C in CD$_2$Cl$_2$.

Figure S38. ^{1}H NMR spectrum recorded for **7e** at 25 °C in CD_2Cl_2.
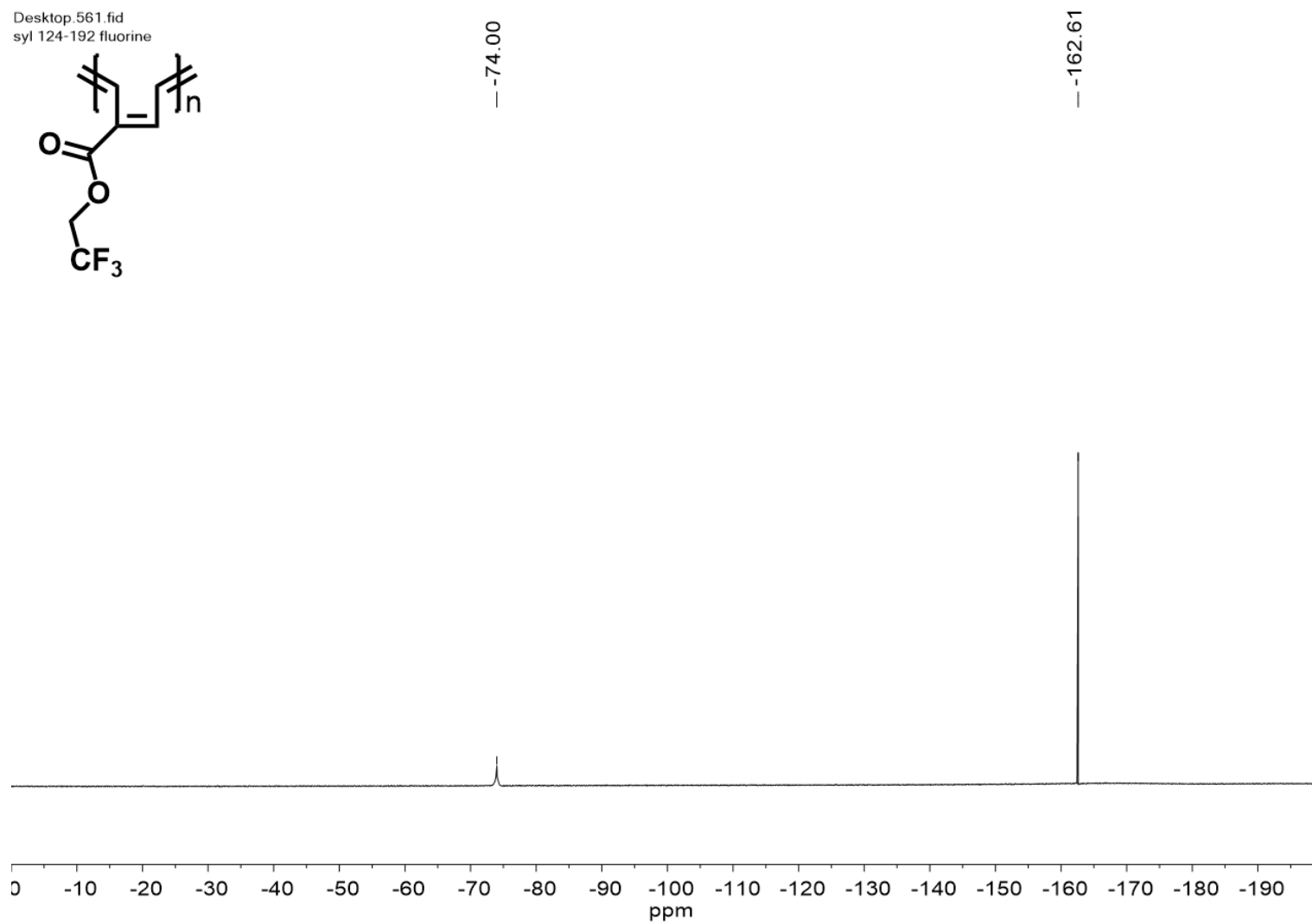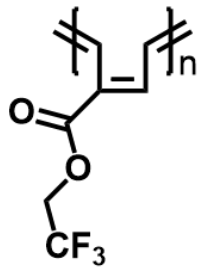
Figure S39. ^{19}F NMR spectrum recorded for **7e** at 25 °C in CD$_2$Cl$_2$.
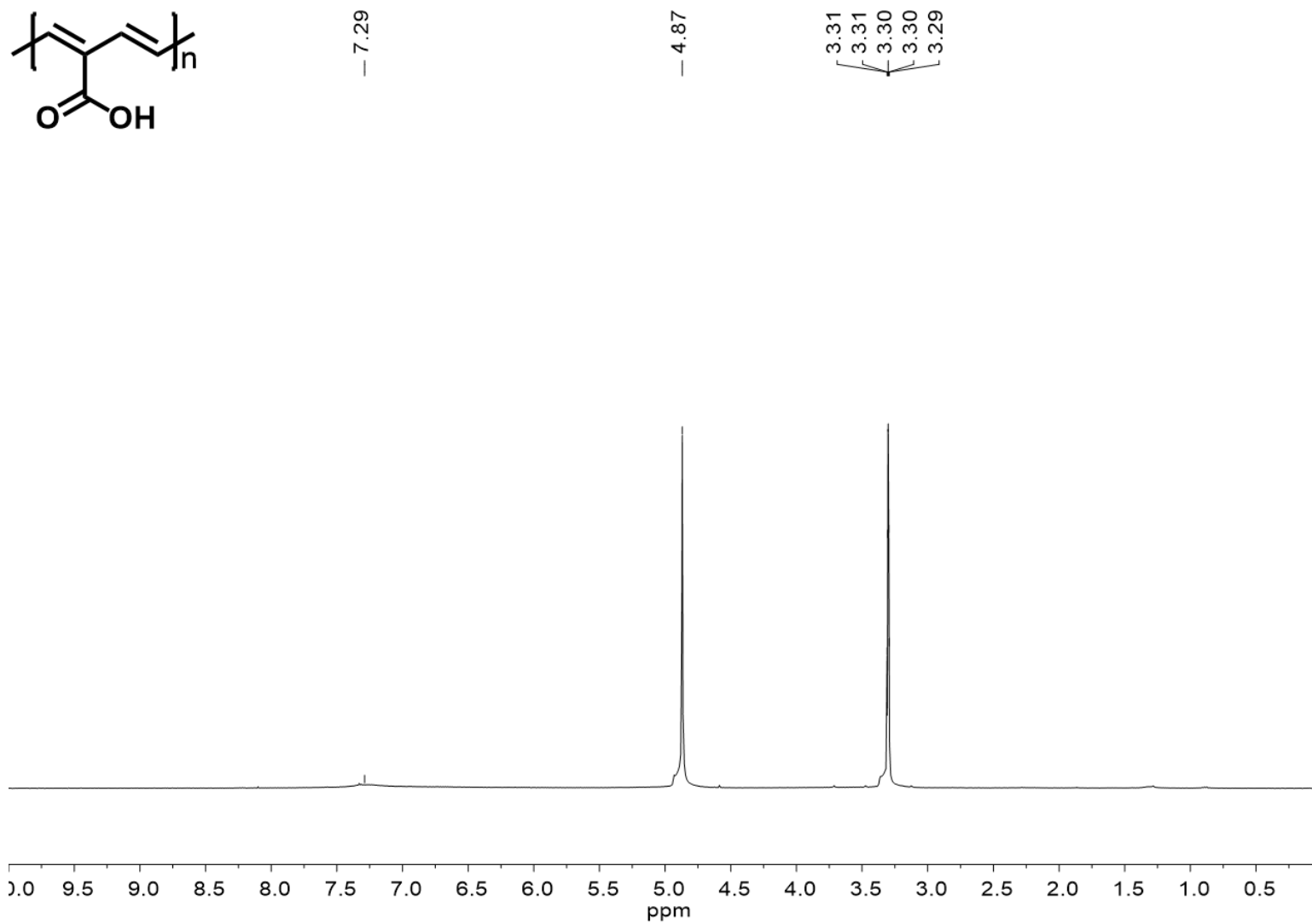
Figure S40. ^{1}H NMR spectrum recorded for **7f** at 25 °C in CD₃OD.

High Resolution Mass Spectrometry Data
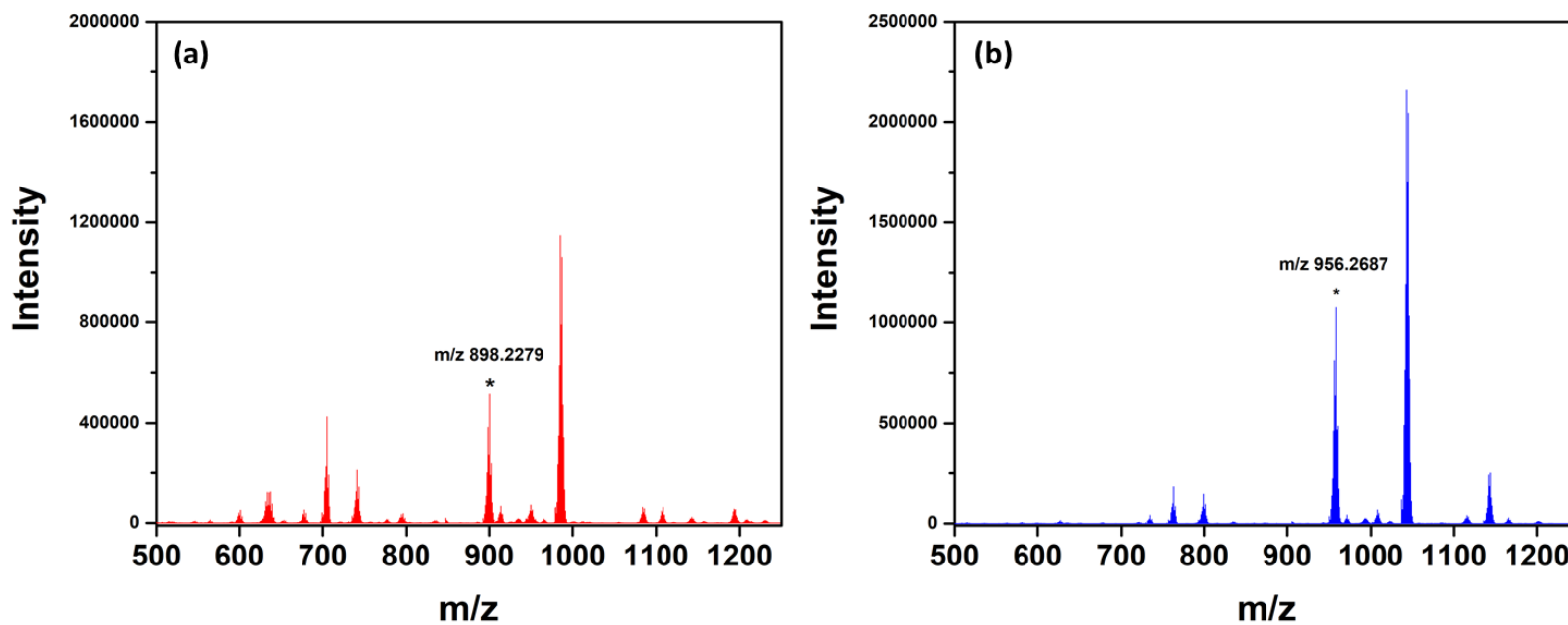

Figure S41. HR-MS spectroscopy data as recorded in the ESI mode upon analysis of reaction mixtures containing (a) **1c** (3.0 equiv.), G3 (1.0 equiv.) and 3-bromopyridine (10 equiv.) in CH_2Cl_2 (red) and (b) **1c** (3.0 equiv.), HG2 (1.0 equiv.) and 3-bromopyridine (2.0 equiv.) in CH_2Cl_2 (blue). Conditions: $[1c]_0 = 0.2$ M in CH_2Cl_2 room temperature, 12 h under nitrogen atmosphere.

References

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3. A. Fischer, W. J. Galloway and J. Vaughan, *J. Chem. Soc.*, 1964, 3591-3596.

4. M. T. Anthony and M. P. Seah, *Surf. Interface Anal.*, 1984, **6**, 107-115.