Electronic Supplementary Information

for

Herbaceous Plants-derived Hydroxycinnamic Units for Constructing Recyclable and Controllable Copolyesters

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1. General Information

Materials: All commercially available compounds were used as received, unless otherwise noted. Miscanthus, sorghum stem, cornstalk, and corncob were harvested from Beijing, China, all biomass feedstocks were crushed before dried at 60 °C for 24 h. Triethylamine, dimethyl sulfoxide, tetrabutyl titanate, butanediol, adipic acid, ferulic acid, and *p*-Coumaric acid were purchased from Energy Chemical. Palladium (II) acetate were purchased from ShanXi KaiDa Chemical Engineering Co,.LTD. Sulfuryl fluoride were purchased from Shanghai Qinba Chemical Co., Ltd. 1,3-bis(diphenylphosphino) propane were purchased from Beijing InnoChem Science & Technology Co., Ltd. Commercial cellulase (Cellic@CTec2, 100FPU mL^{-1}) were provided from Novozymes (Beijing, China).

Gas chromatograph (GC) and gas chromatograph-mass spectrometer (GC-MS): GC and GC-MS were carried out on a Shimadzu Model 2010 plus equipped with a HP-5 column (30 m × 0.25 mm × 0.25 mm) using a flame ionization detector (FID) and a Shimadzu GCMS-QP2010SE equipped with a HP-5MS (30 m × 0.25 mm × 0.25 mm) column, respectively. The injection temperature was 250 °C. The column temperature program was: 50 °C (3 min), 8 °C min^{-1} to 280 °C (5 min). The detection temperature was 200 °C for FID. GC-MS and GC was used for products identification and determination of conversion and yield values.

Nuclear Magnetic Resonance (NMR) spectroscopy: The copolymers NMR spectra (^{1}H, ^{13}C, dept135, 2D HSQC) were acquired on a Bruker Avance 600 MHz spectrometer at room temperature. Other compounds NMR spectra (^{1}H, ^{13}C) were acquired on a Bruker Avance 400 MHz spectrometer. The solvent resonance was used as the internal standard (Chloroform-d: 7.26 for ^{1}H, 77.16 for ^{13}C).

Gel permeation chromatography analysis (GPC): Copolymer samples (10 mg) was dissolved in THF (ca. 2 mg mL^{-1}) and filtered through a Nylon filter (0.22 μm). The average molecular weight was determined on Shimadzu LC-20AD equipped with a PLgel 10 μm Mixed-B 7.5 mm I.D. column (mixed) and UV detection detector (254 nm) at 50 °C, using THF as the solvent (1 mL min^{-1}). The average molecular weight was calibrated with polystyrene standards.

High performance liquid chromatography (HPLC): HPLC analysis was conducted on a Shimadzu LC-20A equipped with an aminex HPX-87H column (300 × 7.8 mm) with 9 μm particle size using a differential refractive index detector (RID-20A). The detection temperature was 60 °C, The velocity of the pump was 0.6 mL min^{-1} (5 mM H_2SO_4).

Thermogravimetric analysis (TGA): TGA was performed on a TA Instruments TGA 550. The detection temperature was 30-600 °C (10 °C min^{-1}) in N_2 (10 mL min^{-1}). The temperatures were recorded when 5 % weight loss ($T_{5\%}$) and maximum rate of mass loss (T_{max}) occurred.

Differential scanning calorimetry analysis (DSC): DSC analysis was conducted on a TA Instruments TA Q2000. In N_2 atmosphere, the sample (5-10 mg) was first raised from room temperature to 200 °C to eliminate the thermal history, then decreased from 200 to -80 °C, and finally raised to 200 °C. The cooling rate and heating rate were both 10 °C min^{-1}, take the second and third paragraphs of the experimental method as the test results for analysis.

Hot-press molding: The hot-press molding of the copolymer was in a vulcanizing press machine (BD-

8820-BE-30T, Dongguan Baoding Precision Instrument Co., Ltd). Typically, the flocculent solid were melted and pressed at 180 °C under 1.0-6.0 MPa for 10 min (degassing steps were simultaneously implemented), then the plates were fast cooled down to 20 °C by water circulation under the same pressure. The obtained film is a square with a length and width of 30 mm and a thickness of about 0.1 mm.

UV-Vis transmission spectrum: The transmission of the copolyester films in the 200-800 nm range were measured with a PERSEE T9 Double Monochromator UV-Vis.

Uniaxial Tensile Test: Tensile properties of the films were measured by an Instron 5900 universal testing machine at room temperature. For each sample, dumbbell shaped specimens with the width of 2 mm and length of 15 mm were tested. The drawing speed was set at 5 mm min^{-1}.

Abbreviations:

*p*CA-Et: ethyl (E)-3-(4-hydroxyphenyl)acrylate

FA-Et: ethyl (E)-3-(4-hydroxy-3-methoxyphenyl)acrylate

*p*CA-Et-SO_2F: ethyl (E)-3-(4-((fluorosulfonyl)oxy)phenyl)acrylate

FA-Et-SO_2F: ethyl (E)-3-(4-((fluorosulfonyl)oxy)-3-methoxyphenyl)acrylate

L_1: ethyl (E)-4-(3-ethoxy-3-oxoprop-1-en-1-yl)benzoate

L_2: ethyl (E)-4-(3-ethoxy-3-oxoprop-1-en-1-yl)-2-methoxybenzoate

BDO: 1,4-butanediol

AA: adipic acid

2. Reductive catalytic fractionation (RCF) of Herbaceous biomass

2.1 Preparation of $ZnMoO_4$/MCM-41 catalyst

$ZnMoO_4$/MCM-41 was prepared as described previously.[1] MCM-41 (1.5 g) in deionized water (10 mL) was added a mixture of $(NH_4)_6Mo_7O_{24}\cdot 4\,H_2O$ (1.1 g) and $Zn(OAc)_2$ (1.2 g) in water (20 mL) slowly under vigorous stirring. After stirring for 12 h at room temperature, the volatiles were removed under vacuum at 120 °C for 10 h. Calcination was conducted in a quartz tube under air atmosphere at 550 °C for 6 h. After cooling to room temperature, a white powder (2.3 g) is collected as $ZnMoO_4$/MCM-41.

2.2 Chemical composition of herbaceous plants

General procedure: Firstly, the herbaceous plants were extracted with toluene/ethanol (2:1, v/v) in a Soxhlet instrument for 12 h, and then dried at 80 °C for 8 hours. The chemical composition was determined followed by National Renewable Energy laboratory's (NREL) standard analytical procedure. The lignocellulose (300 mg) was milled and hydrolyzed at room temperature with 72 wt% sulfuric acid solution (3.0 mL) for 1 h. Deionized water (84.0 mL) was added to dilute sulfuric acid (*ca*. 3%). This mixture was then heated at 120 °C for 1 h in the autoclave. After cooling, the mixture was filtered through a mixed cellulose ester (MCE) membrane filter (0.2μm). The amount of acid insoluble lignin (AIL, Klason lignin) was determined by measurement the weight of residue after drying. The concentration of acid soluble lignin (ASL) was determined by UV spectra by measuring the absorbance of the soluble fraction at 205 nm. The determination of monomeric sugars in the aqueous soluble fraction performed on HPLC system equipped with an aminex HPX-87H column (300 × 7.8 mm) using a differential refractive index detector (RID-20A) by comparison with authentic samples, by comparison with authentic samples. These samples were conducted in triplicate.

Table S1. The composition of different sources of herbaceous plants lignocellulosic biomass[a]

Substrates	AIL[b] (wt%)	ASL[c] (wt%)	TLC[d] (wt%)	Cellulose (wt%)	Hemicellulose (wt%)	Extractive (wt%)	C.B.[e]
Miscanthus	18.3	2.1	20.5	45.7	22.8	1.9	90.9
Sorghum stem	21.0	2.2	23.2	41.1	23.5	3.9	91.7
Cornstalk	14.6	2.8	17.4	39.4	18.2	5.1	80.1
Corncob	12.6	3.3	15.9	37.5	31.5	2.6	87.5
Corncob residue[f]	3.7	2.6	6.3	43.3	35.9	0	

[a] The compositions of biomass were analyzed according to the procedures of the NREL method.

[b] AIL: acid insoluble lignin (klason lignin).

[c] ASL: acid-soluble lignin.

[d] TLC: total lignin content.

[e] C.B.: carbon balance.

[f] Insoluble solids obtained from RCF of corncob

2.3 General procedure of catalytic fragmentation of herbaceous plants

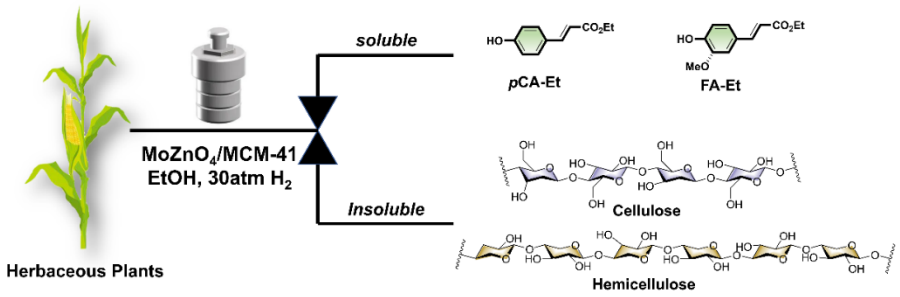


Figure S1. $ZnMoO_4$/MCM-41catalytic fragmentation of herbaceous plants.

Herbaceous plants (500 mg), $ZnMoO_4$/MCM-41 (100 mg), and ethanol (15 mL) were loaded into a 100 mL Parr autoclave (Parr Instruments Co., stainless-steel type 316). After purging with N_2 5 times, the autoclave was pressured to 3 MPa H_2 at room temperature and then heated to the 220 °C with magnetic stirring. After the reaction, the autoclave was cooled and depressurized carefully. The reaction mixture was filtered by 0.22 nm filter, and the insoluble fraction was washed with EtOH. The solution was evaporated and extracted with CH_2Cl_2. The lignin oily products were obtained by the removal of all volatiles under vacuum. An external standard (tetradecane) was added to the lignin oil solution in CH_2Cl_2, and the mixture was subjected to GC-MS and GC with flame ionization detection (FID) for analysis. The identification and quantification of lignin monomers in the oily product were assessed by comparison with authentic samples.

Further column chromatography corncob lignin oil could give a mixture containing *p*CA-Et and FA-Et. Corncob holocellulose residue was separated from the catalyst by sieving, and 386.5 mg was obtained after drying.

Table S2. Products distribution from RCF reaction of herbaceous plants

Substrates	H_2 (atm)	Monomer yield (wt%) [a]			Total (wt%)	Selectivity
		*p*CA-Et	FA-Et	Others		
Miscanthus	30	10.2	3.8	3.6	17.7	79.6
Sorghum stem	30	4.6	2.9	3.7	11.3	66.8
Cornstalk	30	5.1	3.3	4.0	12.5	67.7
Corncob	30	16.6	8.1	1.7	26.4	93.5
Corncob [b]	-	9.0	3.3	1.4	13.6	89.9

[a] Monomer yield (wt%) calculated based on the mass of lignin in the biomass.

[b] The degradation reaction was carried out under N_2 at 30 atm.

Enzymatic hydrolysis of corncob residual solids: 200 mg of corncob residual solid, 10 mL of citric acid buffer (pH = 4.8, 50 mM), and 30μL of cellulase (100 FPU mL^{-1}) were added in the shaking flask, which was placed in an incubator shaker at 50 °C under and shook at 150 rpm. At every few hours intervals, 100 μL of reaction sample was taken out, inactivated enzyme, and filtered with a 0.22 μm filter. The samples were further analyzed using HPLC system. Corncob was also conducted as control enzymatic hydrolysis experiment. This was basically consistent with the previous literature.[2]

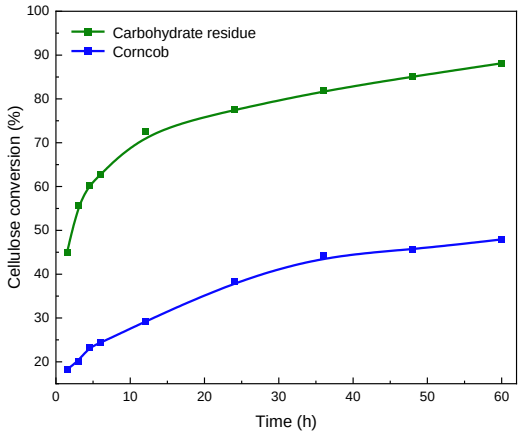


Figure S2. Enzymatical conversion of cellulose.

3. General procedures for phenolic hydroxyl esterification

3.1 Two-step procedure

*Fluorosulfonation reaction: p*CA-Et or FA-Et (40.0 mmol, 1.0 equiv), Et_3N (8.1 g, 80.0 mmol, 2.0 equiv), and CH_2Cl_2 (100 mL) were mixed in an oven-dried Schlenk flask (200 mL). The gas of the flasks was replaced with SO_2F_2. The reaction was carried out at room temperature until the phenol was completely consumed (monitored by TLC). The solution was washed with brine (3×100 mL), dried over anhydrous Na_2SO_4, and concentrated, which afforded pure *p*CA-SO_2F (99%) or FA-SO_2F (99%) as white crystals.

*p*CA-Et-SOF_2, ^{1}H NMR (400 MHz, Chloroform-d): δ 7.66 (d, *J* = 16.2 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 9.0 Hz, 2H), 6.44 (d, *J* = 16.0 Hz, 1H), 4.27 (q, *J* = 7.12 Hz, 2H), 1.34 (t, *J* = 7.08 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 167.3, 149.1, 143.2, 134.3, 131.8, 123.4, 120.6, 60.0, 15.8. MS (EI) found for $C_{11}H_{11}FO_5S$: 273.95.

FA-Et-SOF_2, ^{1}H NMR (400 MHz, Chloroform-d): δ 7.60 (d, *J* = 16.0 Hz, 1H), 7.30 (d, *J* = 8.3 Hz, 1H), 7.14 (s, 1H), 7.12 (d, *J* = 8.3 Hz, 1H), 6.41 (d, *J* = 16.0 Hz, 1H), 4.25 (q, *J* = 7.12 Hz, 2H), 3.95 (s, 3H), 1.32 (t, *J* = 7.12Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 166.3, 151.4, 142.6, 139.8, 136.1, 122.8, 120.7 120.5, 112.2, 60.8, 56.2, 14.2. MS (EI) found for $C_{12}H_{13}FO_6S$: 304.05.

*Carboxylation under ambient CO pressure: p*CA-SO_2F or FA-SO_2F (1.0 mmol, 1.0 equiv), Et_3N (280 μl, 2.0 mmol, 2.0 equiv), $Pd(OAc)_2$ (2.3 mg, 1 mol %), DPPP (4.1 mg, 1 mol %), DMSO (2.0 mL), and ethanol (40 equiv.) were mixed in an oven-dried Schlenk flasks (10 mL). The reaction mixture stirred at 60 ºC for 12 h with continued CO bubbling. After the aryl fluorosulfonate had been completely consumed, the reaction was quenched with 1M HCl (15 mL), which was then extracted with CH_2Cl_2 (3×15 mL). The combined organic layer was washed with brine (3×15 mL), dried over anhydrous Na_2SO_4, and concentrated to dryness. The residue was purified by column chromatography on silica gel (PE: EA=6:1) to afford the **L₁** (92%) or **L₂** (89%).

Carboxylation under 1MPa CO pressure: In a Parr reactor, *p*CA-SO_2F or FA-SO_2F (40.0 mmol, 1.0 equiv), $Pd(OAc)_2$ (89.8mg, 0.4 mmol), DPPP (165.0 mg, 0.4 mmol), Et_3N (8.1 g, 80.0 mmol, 2.0 equiv), DMSO (10 mL) and ethanol (40 mL) were mixed loaded into a Parr reactor. After purging with N_2 5 times, the autoclave was pressured to 1 MPa CO. The reaction was carried out at 60 ºC for 4 h. After the reaction, the autoclave was cooled and depressurized carefully. After the solution was evaporated and extracted, the yellow oily products were dissolved in 100 mL CH_2Cl_2, washed with brine (3×100 mL), dried over anhydrous Na_2SO_4, and evaporated by vacuum. The crystalline diester **L₁** (94%) or **L₂** (91%) was obtained by 80 ºC vacuum sublimation overnight.

L₁ ^{1}H NMR (400 MHz, Chloroform-d): δ 8.04 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 16.0 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 2H), 6.50 (d, *J* = 16.04 Hz, 2H), 4.38 (q, *J* = 7.16 Hz, 2H), 4.36 (q, *J* = 7.08 Hz, 2H), 1.39 (t, *J* = 7.16 Hz, 3H), 1.33 (t, *J* = 7.12 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 166.5, 166.0, 143.2,

138.6, 131.7, 130.0, 127.8, 120.6, 62.2, 60.7, 14.3. MS (EI) found for $C_{14}H_{16}O_4$: 248.10.

L_2 ^{1}H NMR (400 MHz, Chloroform-d): δ 7.76 (d, *J* = 8.2 Hz, 1H), 7.63 (d, *J* = 16.0 Hz, 1H), 7.11 (d, *J* = 7.0 Hz, 1H), 7.10 (s, 1H), 6.51 (d, *J* = 16.00 Hz, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 4.27 (q, *J* = 7.12 Hz, 2H), 3.91 (s, 3H), 1.38 (t, *J* = 7.08 Hz, 3H), 1.33 (t, *J* = 7.16 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 166.0, 165.1, 159., 143.0, 139.0, 131.6, 121.5, 120.2, 119.4, 111.1, 60.5530, 60.3, 55.6, 14.0. MS (EI) found for $C15H_{18}O_5$: 278.10.

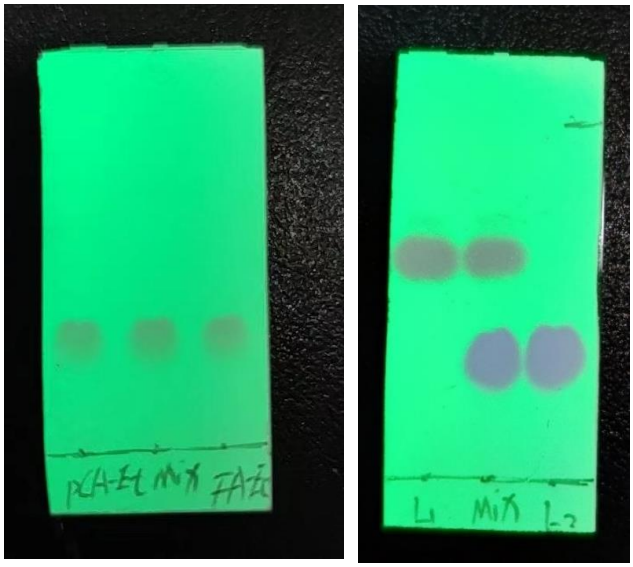
3.2 One-pot procedure

*p*CA-Et or FA-Et (40.0 mmol, 1.0 equiv), Et_3N (16.2 g, 0.16 mol, 4.0 equiv), and DMSO (30.0 mL) were mixed in a Parr reactor equipped with a stirrer bar. The gas was replaced with SO_2F_2 in the reactor equipped with a SO_2F_2 gas balloon. The reaction was carried out at room temperature for 4h. Then $Pd(OAc)_2$ (89.8mg, 0.4 mmol), DPPP (165.0 mg, 0.4 mmol), and the ethanol (23 mL, 0.4 mol, 10 equiv), were added into the reaction mixture. After purging with N_2 5 times, the autoclave was pressured to 1 MPa CO. After carried out at 60 ºC for 4h, the reaction was quenched with 1M HCl (15 mL). Then the mixture extracted with CH_2Cl_2 (3×30 mL), and the combined organic layer was washed with brine (3×50 mL), dried over anhydrous Na_2SO_4, and concentrated to dryness. The residue was purified by column chromatography on silica gel (PE:EA=6:1) to afford the **L_1** (90%) or **L_2** (84%).

Table S3. Screening of reaction equivalents

Entry	Phenol (mmol)	$Pd(OAc)_2$ and DPPP (mmol)	Et_3N (mmol)	CO (atm)	Yield (%)
1	*p*CA-Et (1.0)	0.01	2.0	1.0	92
2	FA-Et (1.0)	0.01	2.0	1.0	89
3	FA-Et (2.0)	0.02	4.0	1.0	52
4	FA-Et (3.0)	0.03	6.0	1.0	38
5	FA-Et (2.0)	0.02	10.0	1.0	61
6	FA-Et (40.0)	0.4	80.0	9.9	91
7	*p*CA-Et (40.0)	0.4	80.0	9.9	94

[a] Step-by-step reaction.

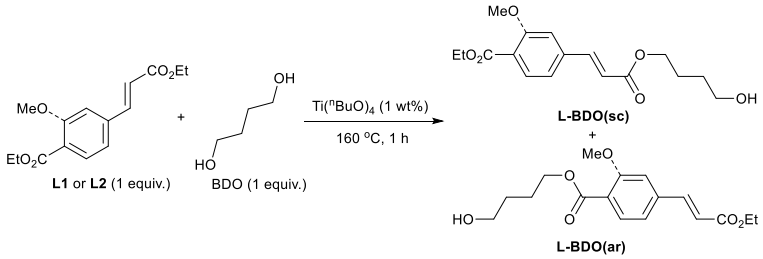


a **b**

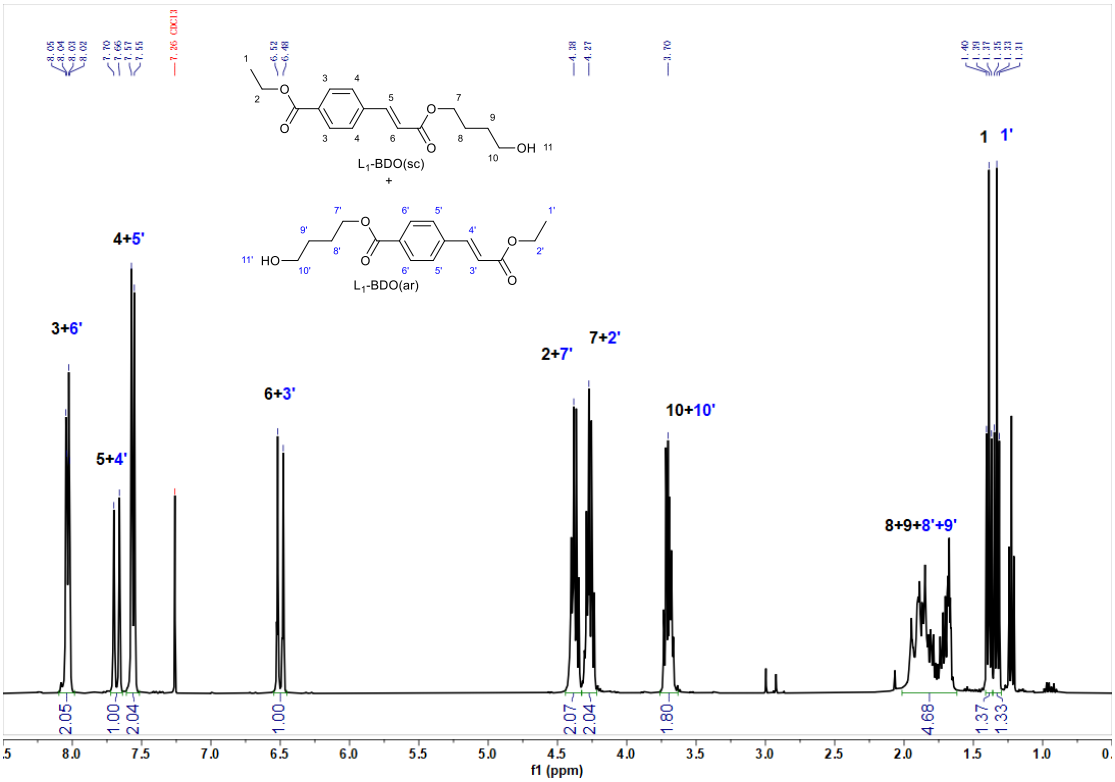
Figure S3. *p*CA-Et and FA-Et have the same Rf value on TLC, **L_1** and **L_2** have significantly different Rf values on TLC (PE : EA=4:1).

Figure S4. Diesters are purified by sublimation separation

3.3 Competitive reaction of L_1 carboxylic esters



L_1 or **L_2**(4 mmol), 1,4-butanediol (0.36 g, 4 mmol), and Ti(^{n}BuO)$_4$ (10 mg) were mixed in a sealed tube, which was then heated at 160 ºC for 1 h. After reaction, the reaction mixture was characterized by ^{1}H NMR, which indicated that L-BDO (sc) and L-BDO (ar) were both generated in a 1:1 molar ratio.



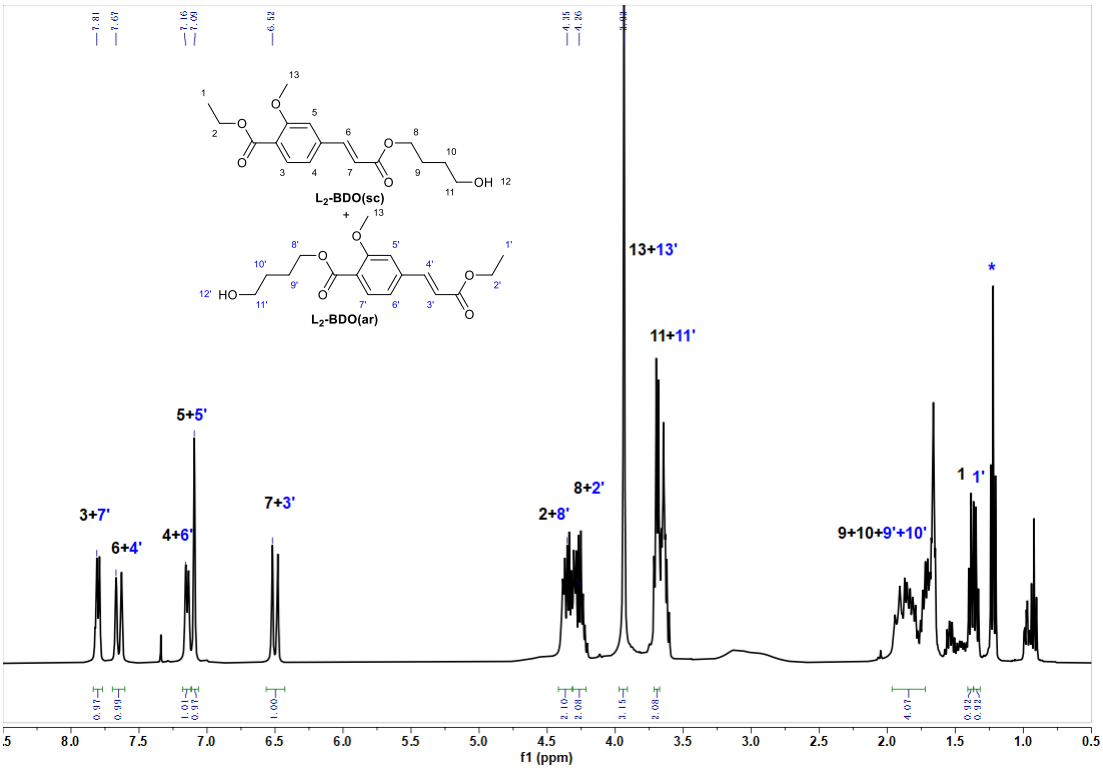


Figure S5 Competitive reaction of L_1 and L_2 carboxylic esters

4. Synthesis of copolyester

4.1 Typical procedure for the synthesis of PBAL

Typical procedure for the synthesis of PBAL$_1$60: Compound **L$_1$** (1.48 g, 6.0 mmol), adipic acid (0.58 g, 4.0 mmol), butanediol (1.442 g, 16.0 mmol), and Ti(^{n}BuO)$_4$ (18 mg, 0.5 wt%) were mixed in an oven-dried Schlenk flask (15 mL) under N_2 atmosphere. The transesterification reaction was initially kept at 180 °C for 2 h under nitrogen atmosphere, which was then carried out at 230 °C for 4 h under 1 torr pressure condition. After reaction, the mixture was dissolved in CH_2Cl_2, which was then dropped in the MeOH. The as-formed white flocculent precipitate was collected as obtained PBAL$_1$60 (1.71g, 75.2 %).

The synthesis of other copolyesters followed the same melt phase polycondensation procedure by using **L$_1$**, **L$_2$**, adipic acid, and butanediol in different molar ratios.

Table S4. Yield and molecular-weight distributions for synthesized copolymer

Substrate	Yield (wt%)	M_w (kDa)	M_n (kDa)	$Đ$
PBA	81.5	nd	nd	nd
PBAL$_1$20	73.9	65.8	33.8	1.9
PBAL$_1$60	78.2	37.8	11.3	3.4
PBAL$_1$80	90.1	29.1	10.6	2.7
PBAL$_1$100	95.8	nd	nd	nd
PBAL$_1$54L$_2$06	80.9	16.6	11.0	1.5
PBAL$_1$48L$_2$12	87.9	24.5	19.0	1.3

Detailed structural analysis of PBAL$_1$

Detailed structural characterization of PBAL$_1$ were performed by ^{1}H, ^{13}C, dept-135 NMR, and 2D NMR. In ^{1}H NMR, the doublet peaks located at 8.05, 7.59, and 6.53 ppm were attributed to aromatic groups and carbon-carbon double bond of **L$_1$.** The peaks located at 4.08-4.51 ppm were attributed to COOC**H**$_2$CH$_2$CH$_2$C**H**$_2$OCO of BDO, which showed multiple-peak revealed the multi-block microstructures. The singlet peaks located at 2.32 ppm were attributed to OCOC**H**$_2$CH$_2$CH$_2$C**H**$_2$COO of adipic acid. The peaks located at 1.68-2.00 ppm were attributed to COOCH$_2$**CH$_2$CH$_2$**CH$_2$OCO of BDO. The singlet peaks located at 1.64 ppm were attributed to OCOCH$_2$**CH$_2$CH$_2$**CH$_2$COO of adipic acid. Although the peaks located at 1.68-2.00 ppm reflected the multi-block microstructures of PBAL$_1$, deconvolution of overlapping peaks were difficult.

Unsymmetrical **L$_1$** aggrandized the complexity of the PBAL$_1$ structure, causing the splitting of BDO units peaks. The electron withdrawing abilities of *ar*-carboxylic esters, *sc*-carboxylic esters, and *aa*-carboxylic esters are arranged in descending order as *ar*-carboxylic esters, *sc*-carboxylic esters, *aa*-carboxylic esters. The peak of protons influenced by stronger electron withdrawing groups move downfield in ^{1}H-NMR. In PBA, BDO unit peaks did not split, because only a dyad sequence, *aa*-*aa*,

existed. In PBL_1, the Unsymmetrical carboxylic esters caused three dyad sequences, *ar-ar, sc-sc, sc-ar* and four proton's microenvironment (6, 7, 8, and 9) form $COOC\underline{\mathbf{H}}_2CH_2CH_2C\underline{\mathbf{H}}_2OCO$ (BDO). In $PBAL_120$ contenting low $\mathbf{L_1}$, BDO unit hardly connected to 1 and 2 at the same time (*ar-ar, sc-sc, sc-ar*). In *aa-ar*, the proton 3 was mainly affected by electron withdrawing from *ar* and less affected by electron withdrawing from *aa*, the proton 2 was mainly affected by electron withdrawing from *aa* and less affected by electron withdrawing from *ar*. In *aa-sc*, the proton 5 was mainly affected by electron withdrawing from *sc* and less affected by electron withdrawing from *aa*, the proton 4 was mainly affected by electron withdrawing from *aa* and less affected by electron withdrawing from *sc*. In $PBAL_160$ and $PBAL_180$, six dyad sequences, *ar-sc*, *ar-ar*, *ar-aa*, *sc-sc*, *sc-aa*, and *aa-aa*, were embody by corresponding nine α-methylene signals from butanediol units. The peaks influenced by electron withdrawing group were arranged as *7*, *9*, *3*, *8*, *6*, *5*, *2*, *4*, *1* from low field to high field.

Integration of α-methylene signals reflected the change of $\mathbf{L_1}$ composition in $PBAL_1$. As $\mathbf{L_1}$ content increased, the integration of 7, 9, 8, 6 gradually increased, the integration of 1 gradually reduced, and the integration of 3, 5, 2, 4 climbed up and then declined.

The block length (L_{nAA} and L_{nL1}) of the adipic acid and $\mathbf{L_1}$ units can be calculated from the molar fractions of six different sequences by means of the following formula[3].

$$L_{nAA} = \frac{(f_2 + f_3 + f_4 + f_5)/_2 + f_1}{(f_2 + f_3 + f_4 + f_5)/_2} \quad (1)$$

$$L_{nL1} = \frac{(f_2 + f_3 + f_4 + f_5)/_2 + f_6 + f_7 + f_8 + f_9}{(f_2 + f_3 + f_4 + f_5)/_2} \quad (2)$$

The degree of randomness (B) can be defined by means of the following formula:

$$B = \frac{1}{L_{nAA}} + \frac{1}{L_{nL1}} \quad (3)$$

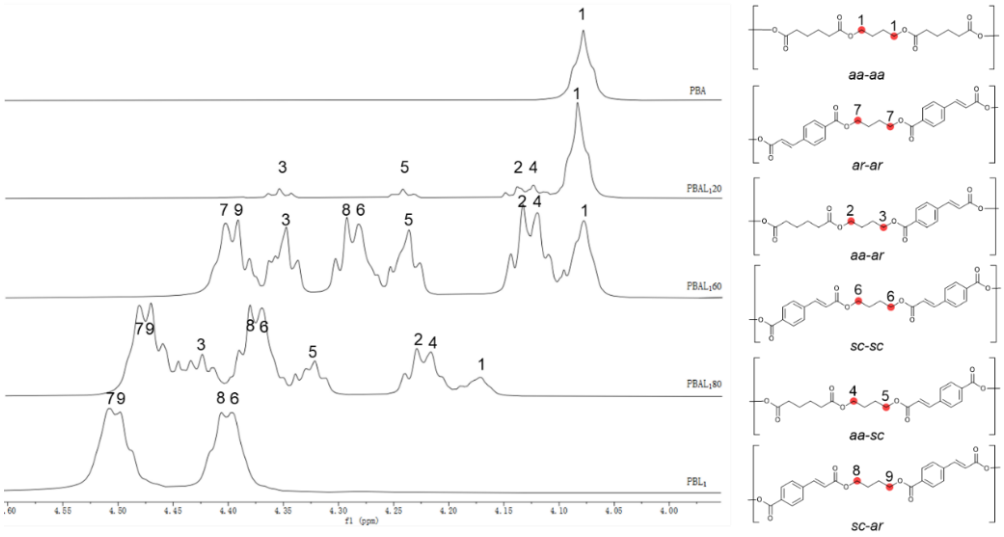


Figure S6. Detailed [1]H-NMR of α-methylene signals from butanediol units (4.0 - 4.6 ppm)

Table S5. Composition and sequence-distribution analysis of copolyesters

Copolymer	Composition molar fraction		Fraction of diads centered in the butylene units									Block lengths		Degree of randomness
	f_{AA}	f_{L1}	f_1	f_2	f_4	f_3	f_7	f_9	f_5	f_8	f_6	L_{nAA}	L_{nL1}	*B*
$PBAL_120$	0.88	0.12	0.66	0.07	0.09	0.07	0.01	0.01	0.06	0.01	0.01	5.6	1.3	0.96
$PBAL_160$	0.46	0.54	0.14	0.12	0.12	0.12	0.10	0.09	0.12	0.09	0.10	1.6	2.6	1.02
PBA L_180	0.20	0.80	0.06	0.08	0.08	0.08	0.16	0.15	0.08	0.15	0.16	1.4	4.9	0.93
PBL_1	-	1	-	-	-	-	0.26	0.24	-	0.26	0.26	-	-	-

5. Properties of copolyester

5.1 Thermal analysis

Thermogravimetric analysis (TGA) of copolymer samples (2-10 mg) was carried out on a thermal gravimetric analyzer (TA Instruments TGA 550) at a heating rate of 10 °C min^{-1} (heat to 600 °C) under a nitrogen atmosphere (flow rate of 10 mL min^{-1}). The temperatures were recorded when 5 % weight loss ($T_{5\%}$) and maximum rate of mass loss (T_{max}) occurred.

Differential scanning calorimetry (DSC) characterization was performed using a thermal analyzer (TA Instruments TA Q2000) to explore the thermal behavior of the copolymer samples. In detail, the sample (5-10 mg) was first raised from room temperature to 200 ºC to eliminate the thermal history, then decreased from 200 to -80 ºC, and finally raised to 200 ºC in an aluminum crucible under a nitrogen atmosphere. The cooling rate and heating rate were both 10 ºC min^{-1}, take the second and third paragraphs of the experimental method as the test results for analysis.

Table S6. Polymer thermal properties

Substrate	T_m (ºC)	T_c (ºC)	ΔT (ºC)	T_g (ºC)	$T_{d,5\%}$ (ºC)	$T_{d,max}$ (ºC)	$Char_{600ºC}$ (wt%)
PBA	50.0	29.9	20.1	-60.3	309.3	341.3	2.9
$PBAL_120$	39.3	13.0	26.3	-42.6	322.3	382.1	4.3
$PBAL_160$	98.8	97.3	1.5	-24.4	333.0	395.4	18.4
$PBAL_180$	127.0	123.4	3.6	-0.3	347.3	395.1	24.7
PBL_1	179.6	164.6	14.4	61.2	351.4	396.4	29.5
$PBAL_154L_206$	74.1	59.5	14.6	-13.0	336.5	388.4	14.9
$PBAL_148L_212$	75.9	38.6	37.3	0.92	341.1	388.8	19.3

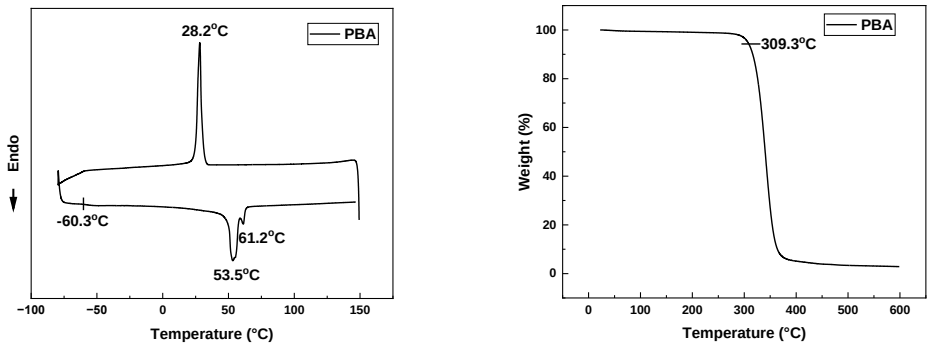


Figure S7. DSC thermogram and TGA plot of PBA

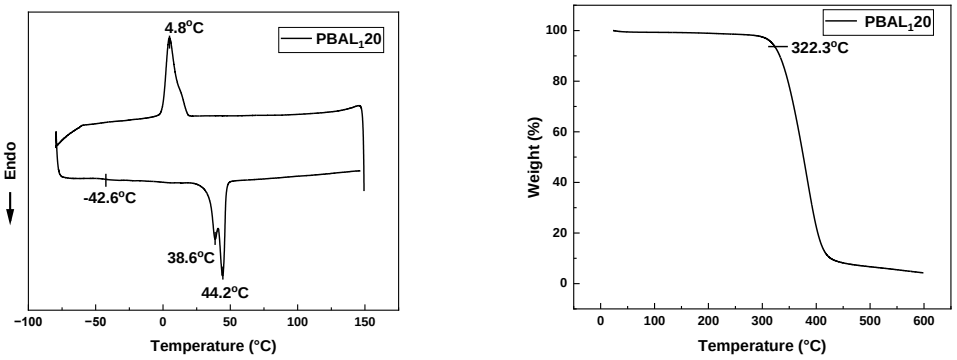


Figure S8. DSC thermogram and TGA plot of PBAL$_1$20

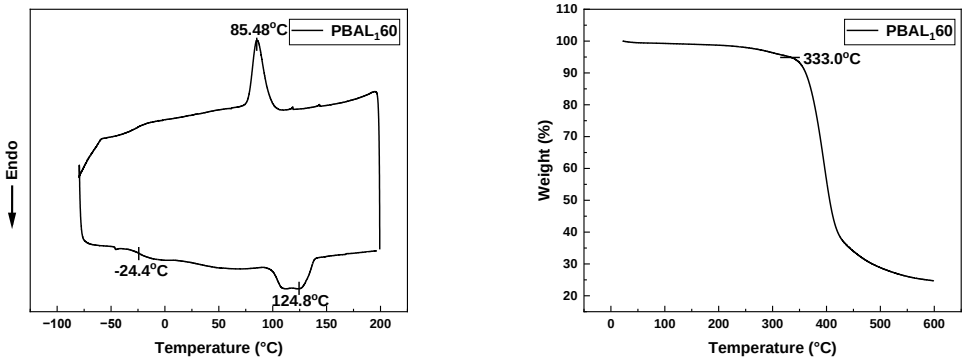


Figure S9. DSC thermogram and TGA plot of PBAL$_1$60

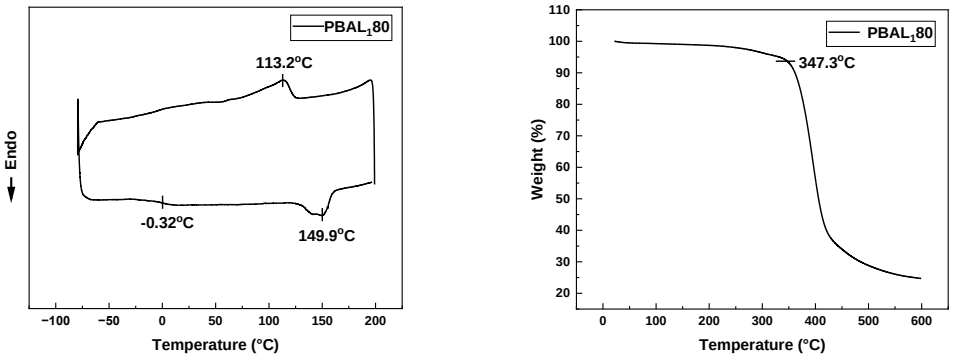


Figure S10. DSC thermogram and TGA plot of PBAL$_1$80

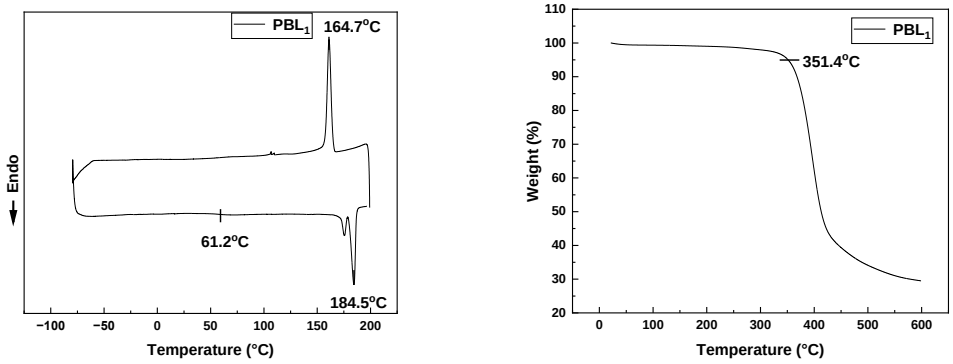


Figure S11. DSC thermogram and TGA plot of PBL_1

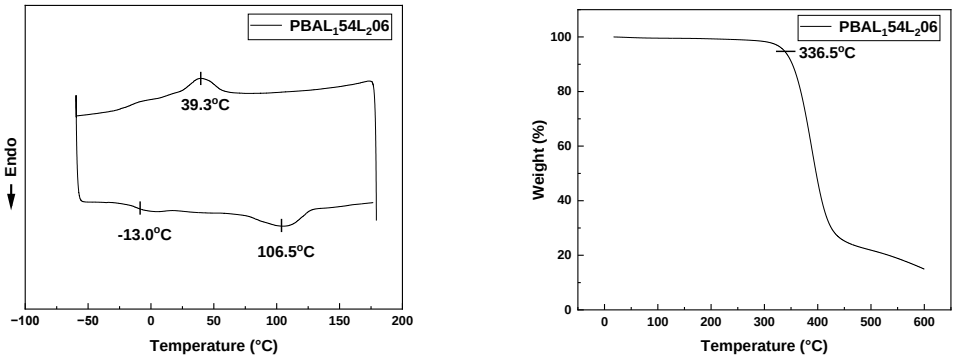


Figure S12. DSC thermogram and TGA plot of $PBAL_154L_206$

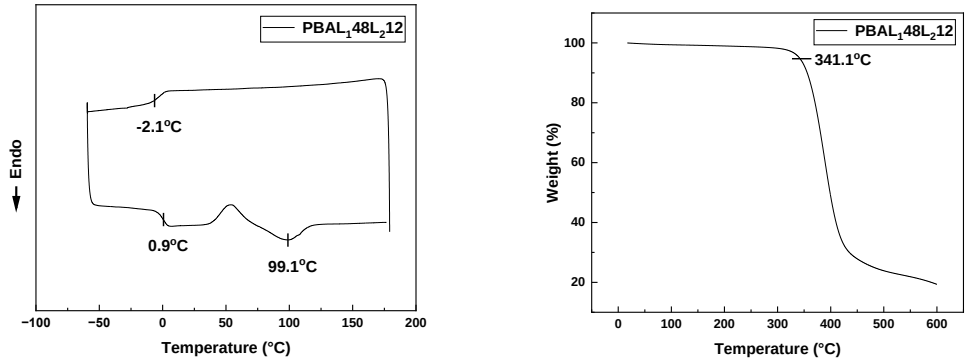


Figure S13. DSC thermogram and TGA plot of $PBAL_148L_212$

5.2 Tensile properties

The copolyester films were prepared by the hot-press molding of the flocculent solid in a vulcanizing press machine (BD-8820-BE-30T, Dongguan Baoding Precision Instrument Co., Ltd). Typically, the copolymer solids were melted and pressed at 180 °C under 1.0-6.5 MPa for 8 min (degassing steps were simultaneously implemented). The plates were cooled down to room temperature by water circulation under the same pressure. The resulting polymer films were a square with a length, width, and thickness of 30mm×30mm×0.1mm.

The tensile properties (such as elongation at break, tensile strength and Young's modulus) of copolyester films with an Instron 5900 universal testing machine at room temperature. The dumbbell-shaped specimens with a size of 2 mm × 15 mm were measured, and the tensile speed employed was 5 mm min^{-1}. Cyclic stress-strain test for PBA $L_1$48$L_2$12 was carried out with a strain rate of 5 mm/min and release rate of 5 mm/min. Strain recovery was determined by a 10% strain step cycle test.

Table S7. Elongation at Break, Ultimate Tensile Strength Values, and Young's modulus

Substrate	Tensile Strength (MPa)	Elongation at Break (%)	Young's modulus (MPa)
PBAP20	6.8±0.3	4.9±0.9	154.8±7.9
PBAP60	6.9±1.4	5.2±2.4	145.9±3.5
PBA$L_1$54$L_2$06	10.8±2.1	22.2±7	138.7±2.6
PBA $L_1$48$L_2$12	6.9±0.2	178.6±21.7	60.8±3.8

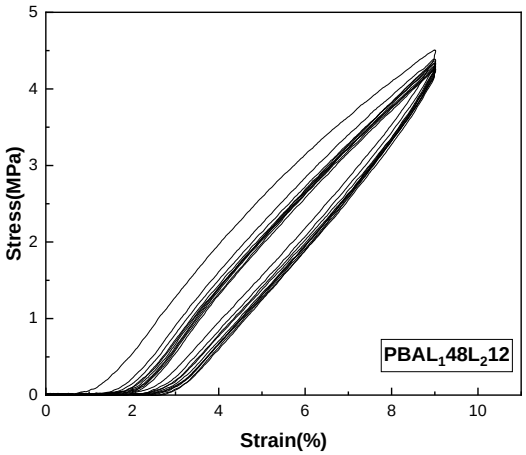


Figure S14. Tensile strength/hysteresis curves of PBA $L_1$48$L_2$12.

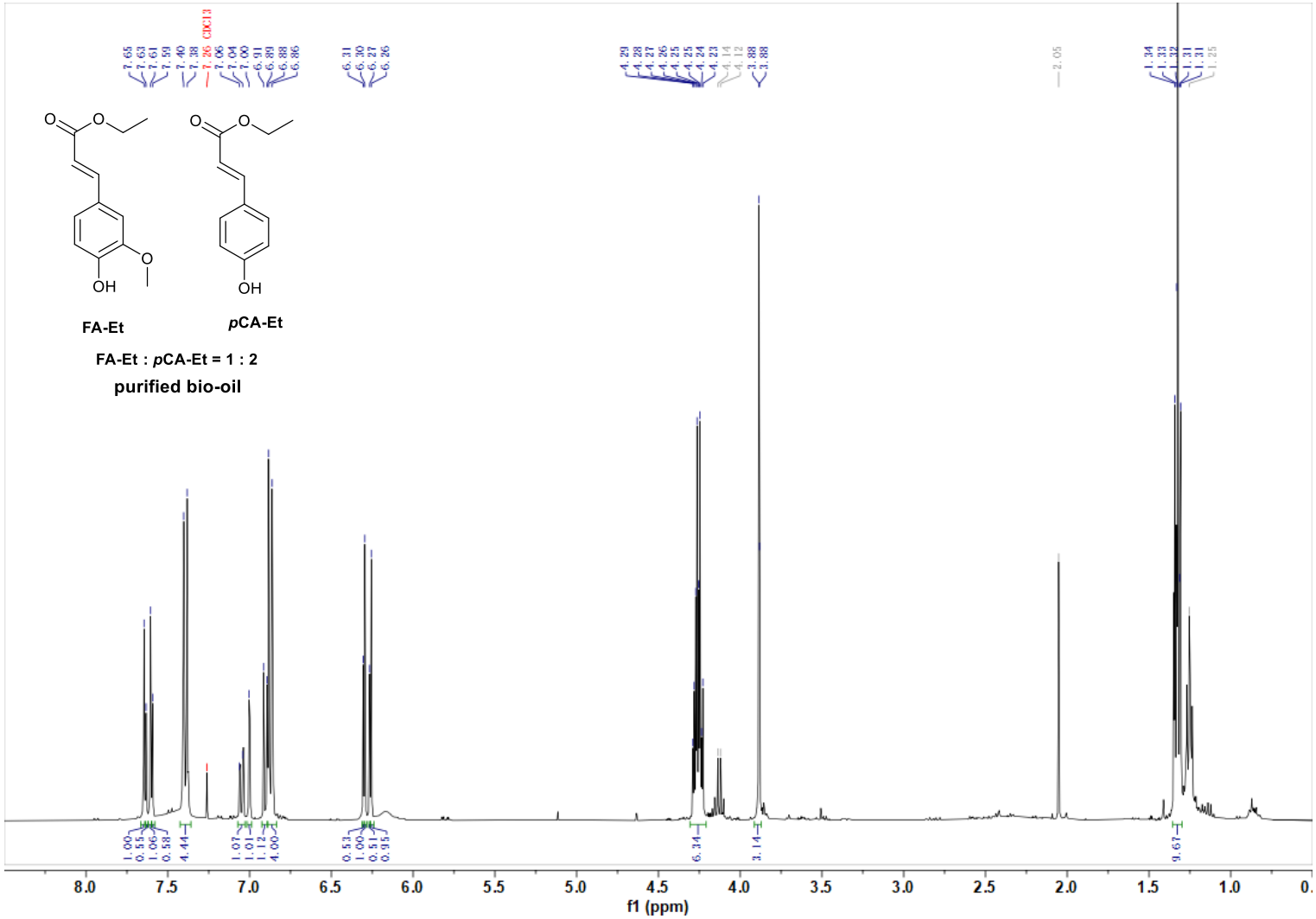
5.3 UV-transmittance

The transmittance (200–800 nm) of UV and visible light for copolymer films (100 μm) were also determined using a spectrophotometer (PERSEE T9 Double Monochromator UV-Vis) under the transmission mode (T %). Prior to UV–vis spectra measurements, the films were tailored into square and then attached to the surface of a quartz plate for further determination.

6. Ethanolysis of copolyester

Ethanolysis at 100 ºC with $Zn(OAc)_2$ (10 wt%): The copolyester PBAL 50 mg, 5mg Zn(OAc)2, diphenyl oxide (51 mg as internal standard) and 10 mL EtOH were mixed in sealed tubes. The mixture was kept 100 ºC for 93 h. At every few hours intervals, 500 μL of reaction sample was taken out, filtered with a 0.22 μm filter. The samples were further evaluated using GC system.

Ethanolysis at 79 ºC with H_2SO_4 (50mM): $PBAL_148L_212$ (50 mg), H_2SO_4 (50 mM), and ethanol (10 mL) were mixed and reflowed for 80 h. At every few hours intervals, 500 μL reaction sample was taken out and mixed with internal standard (2.6mg diphenyl oxide in 500 μL EtOH), filtered with a 0.22 μm filter. The samples were further evaluated using GC system.


FA-Et
pCA-Et
FA-Et : pCA-Et = 1 : 2
purified bio-oil
f1 (ppm)

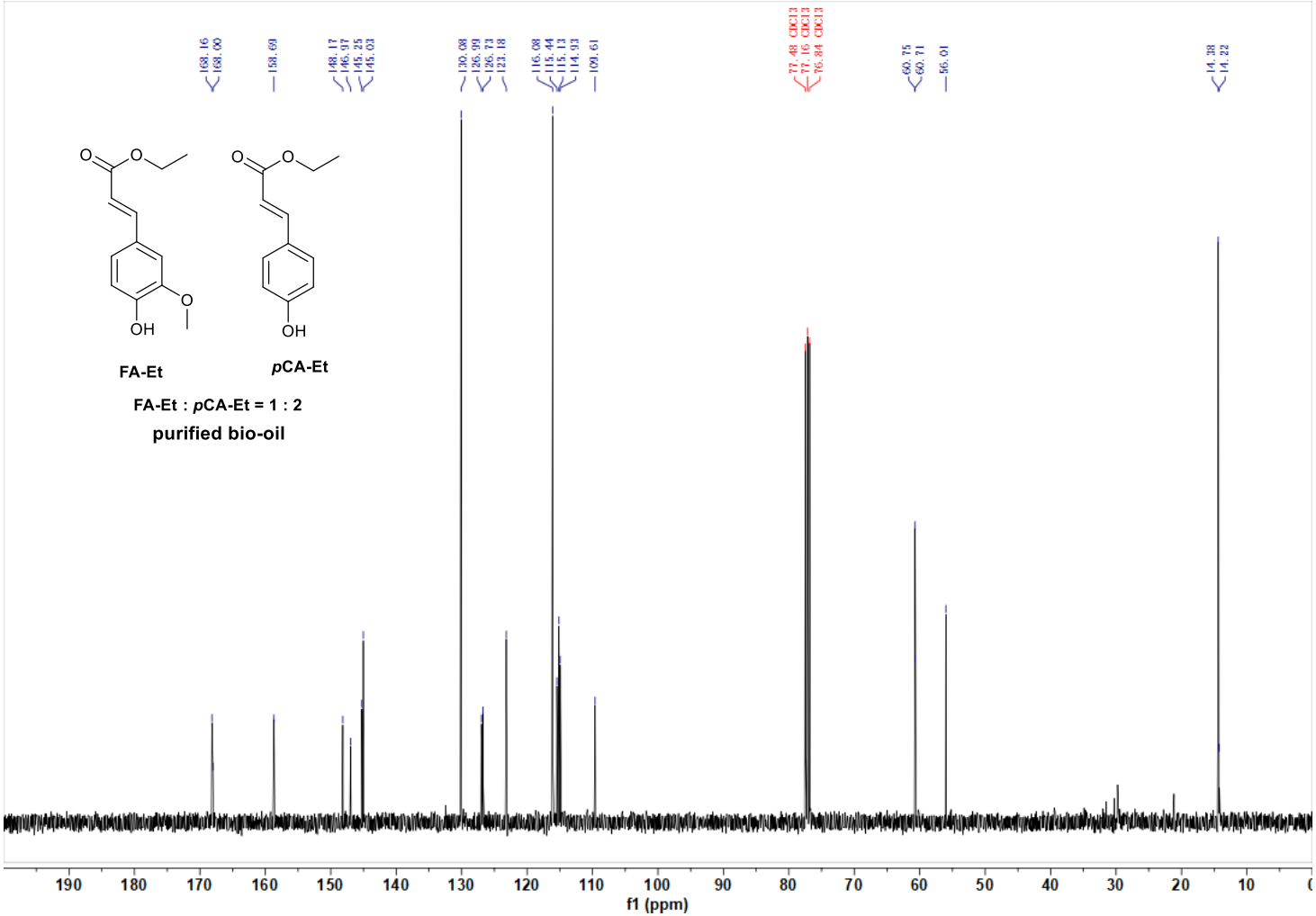
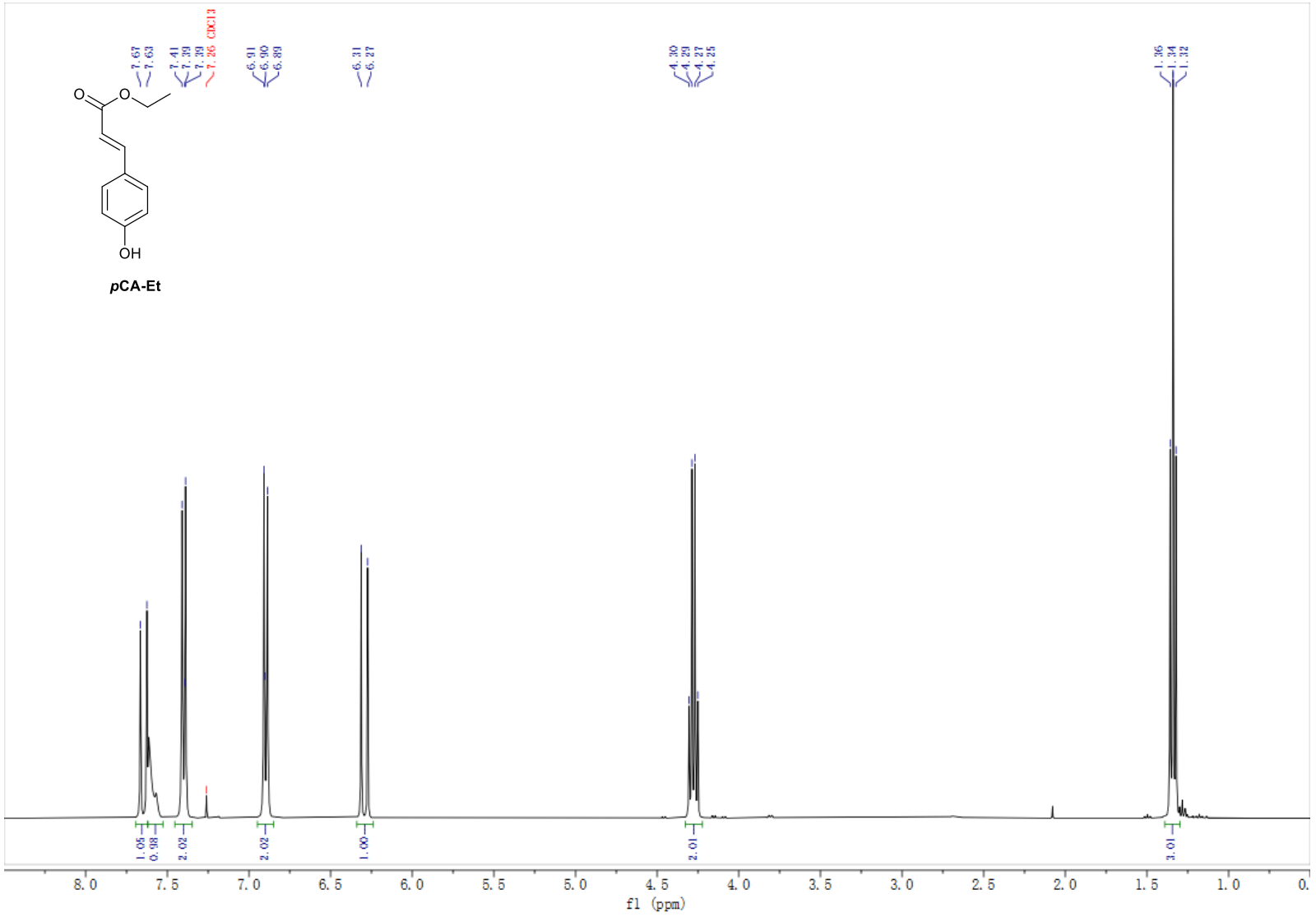


Figure S15. *p*CA-Et and FA-Et isolated from corncob bio-oil.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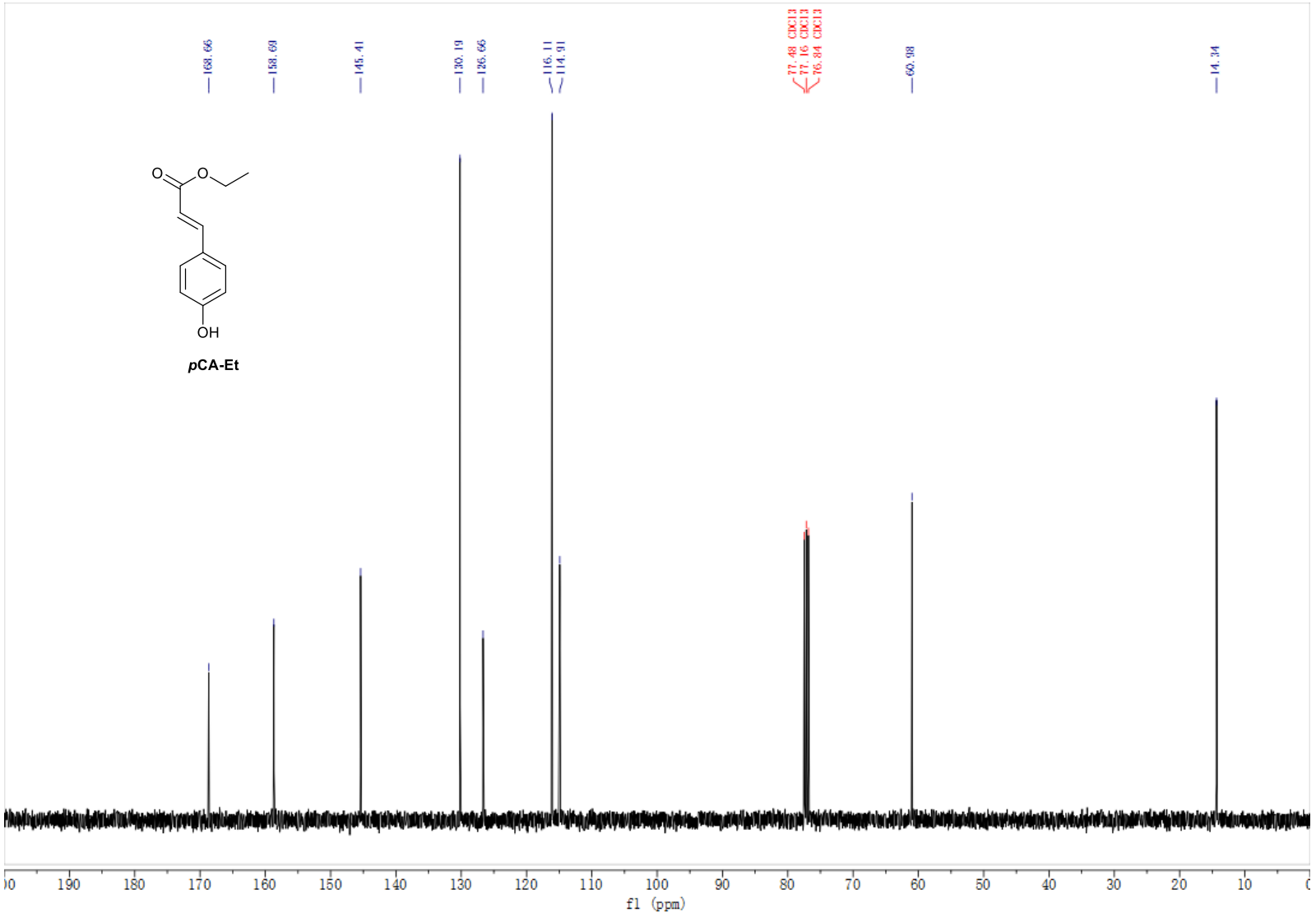
6.90
6.89
6.31
6.27
4.30
4.29
4.27
4.25
1.36
1.34
1.32
O
O
OH
pCA-Ed
1.05
0.98
2.02
2.02
1.00
2.01
3.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.
f1 (ppm)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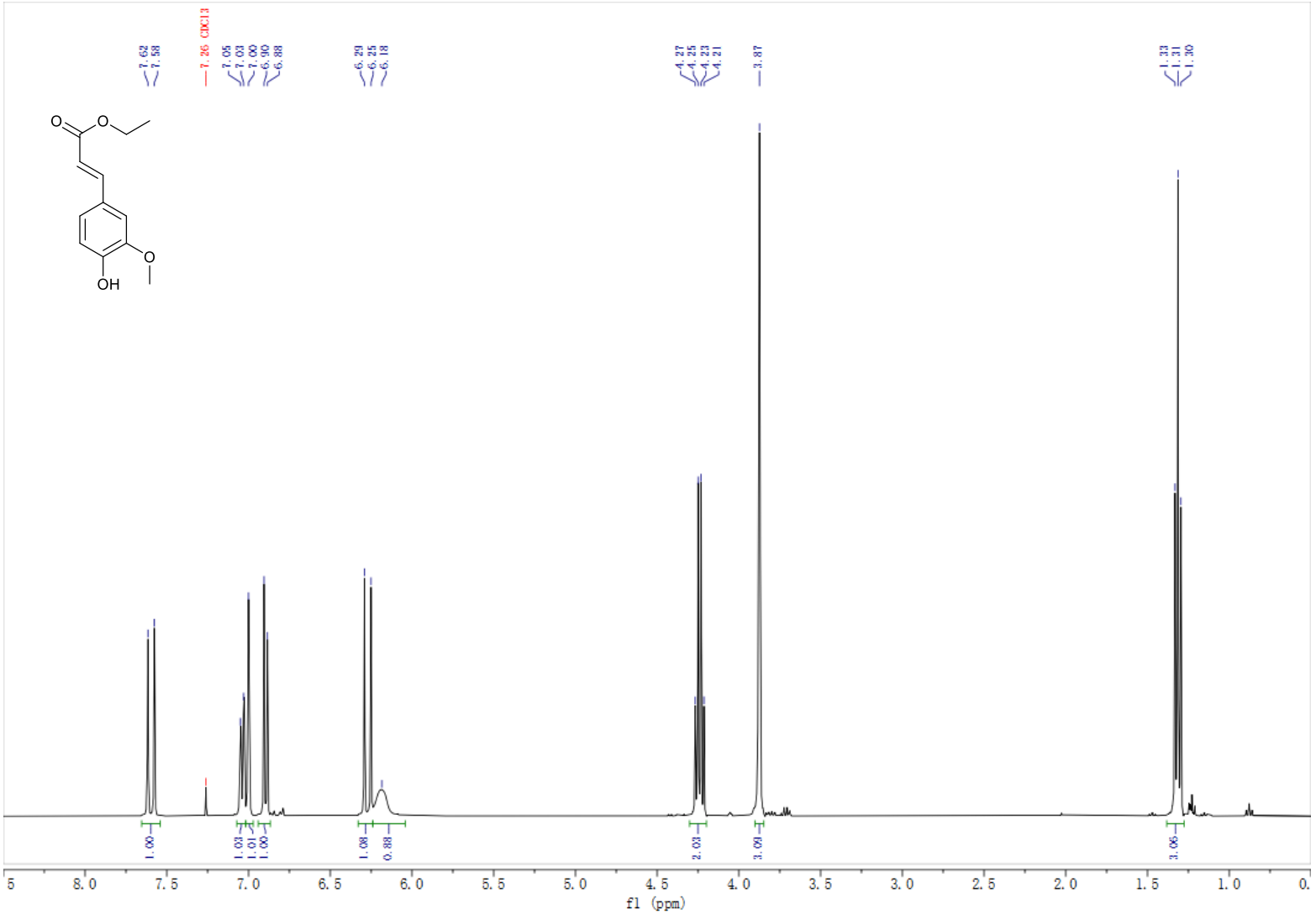
158.69
145.41
130.19
126.66
116.11
114.91
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
60.98
14.34
O
O
OH
pCA-Et
f1 (ppm)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7.03
7.00
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6.88
6.29
6.25
6.18
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4.25
4.23
4.21
3.87
1.33
1.31
1.30
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0.88
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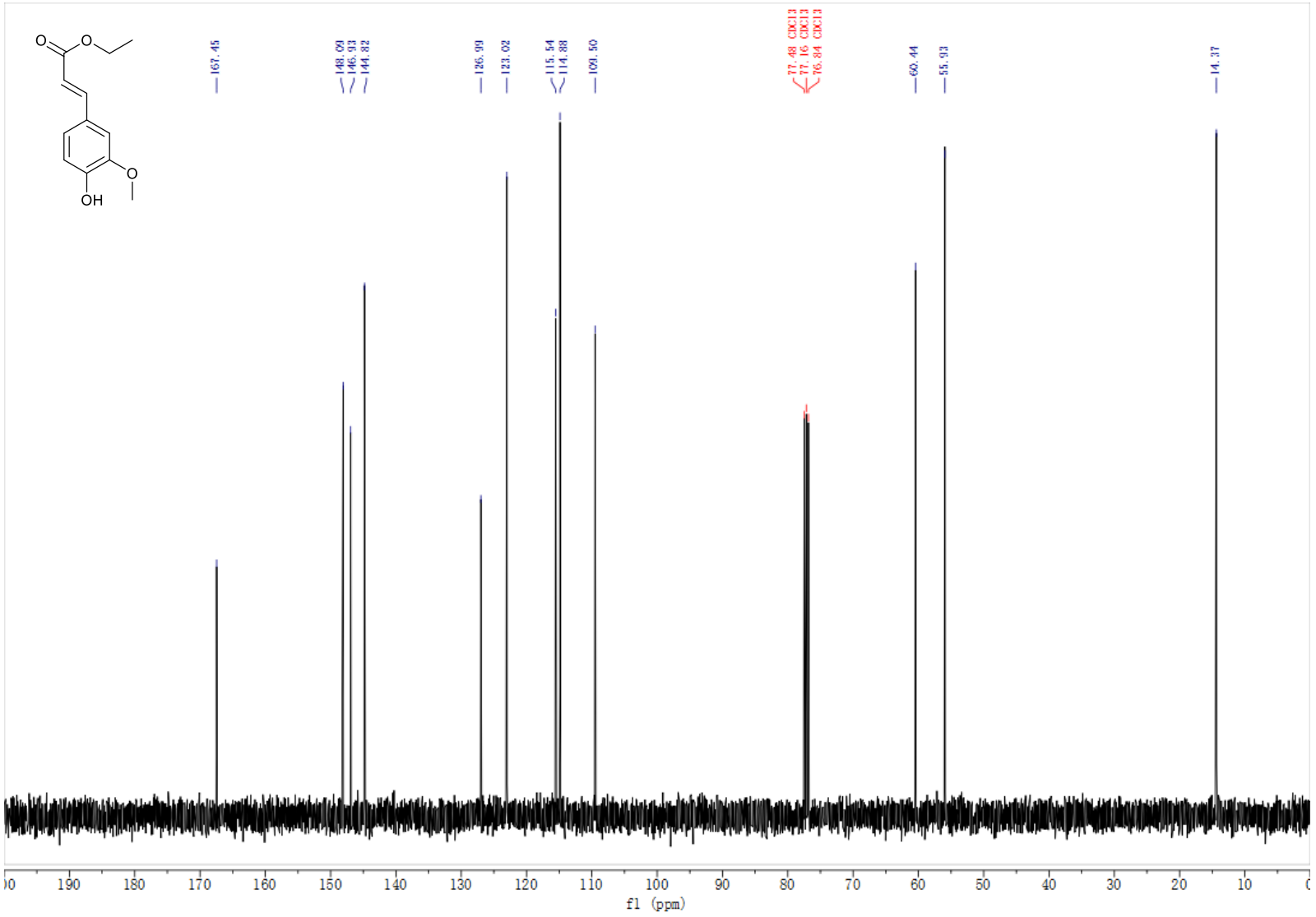
3.06
f1 (ppm)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O
O
OH
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146.93
144.82
126.99
123.02
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114.88
109.50
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77.16 CDCl3
76.84 CDCl3
60.44
55.93
14.37
190
180
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140
130
120
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100
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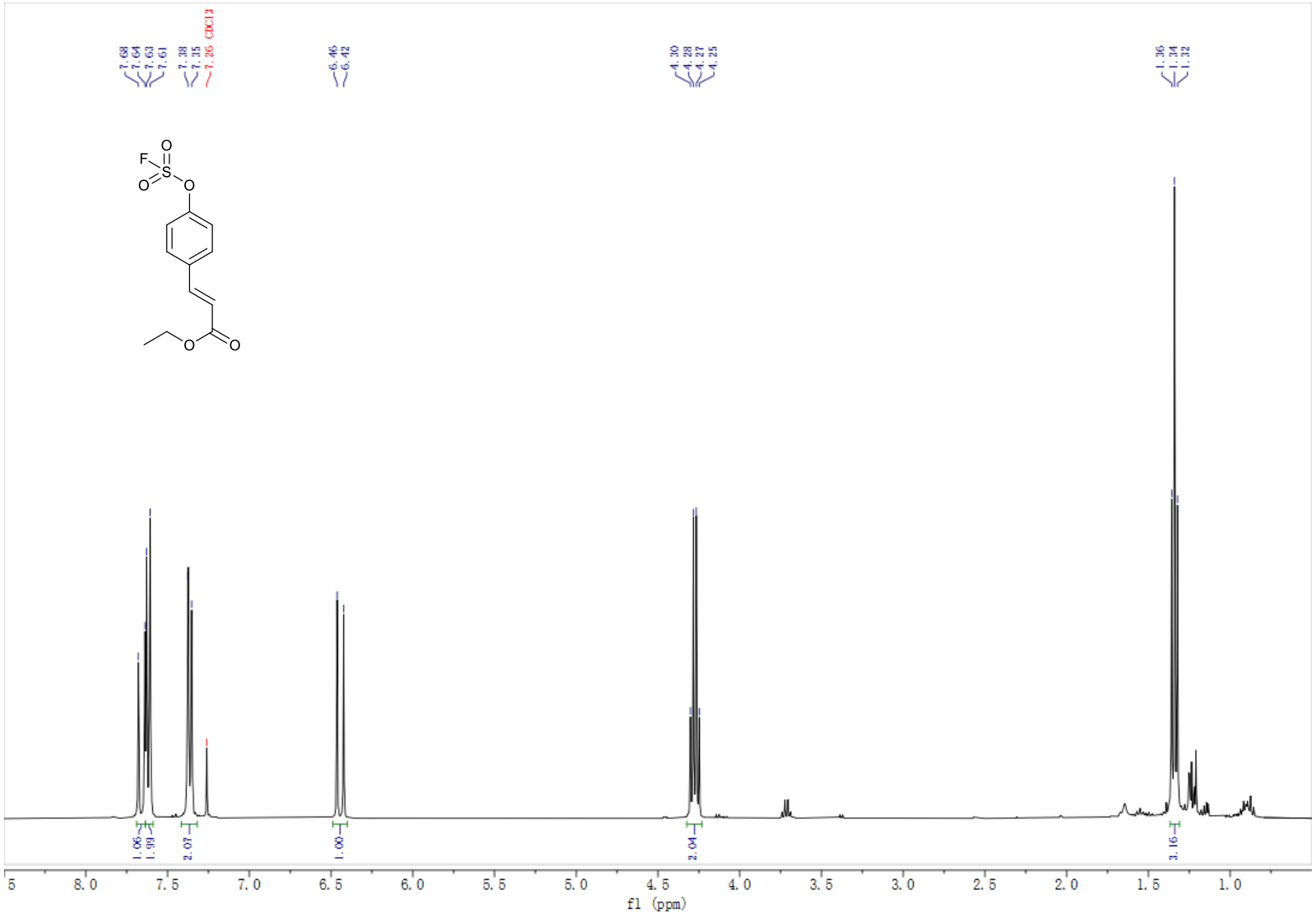
80
70
60
50
40
30
20
10
f1 (ppm)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6.42
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4.28
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1.36
1.34
1.32
F
S
O
O
O
O
O
1.06
1.99
2.07
1.00
2.04
3.16
5
8.0
7.5
7.0
6.5
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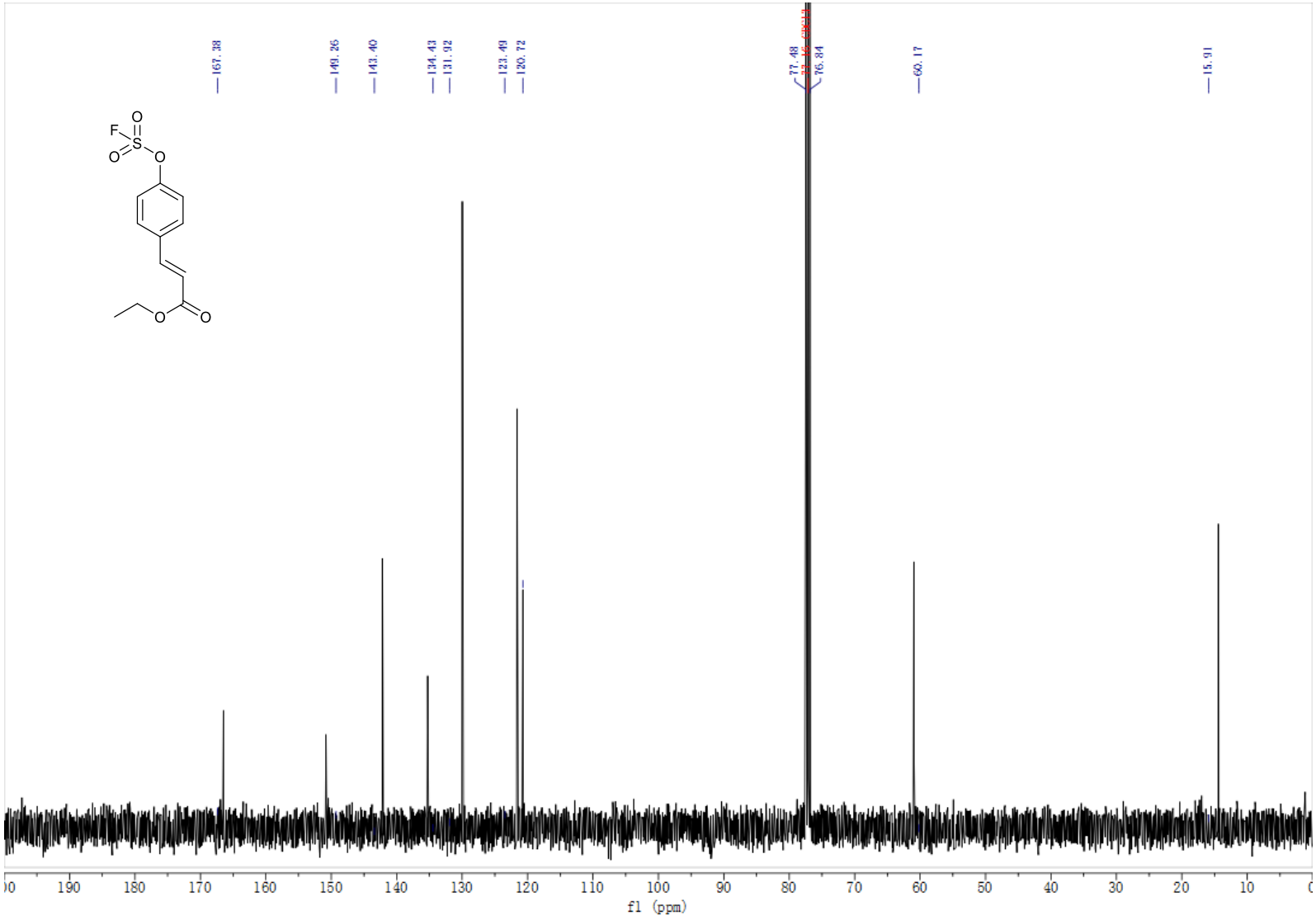
1.0
f1 (ppm)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123.49
120.72
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F
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O
O
O
O
O
190
180
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160
150
140
130
120
110
100
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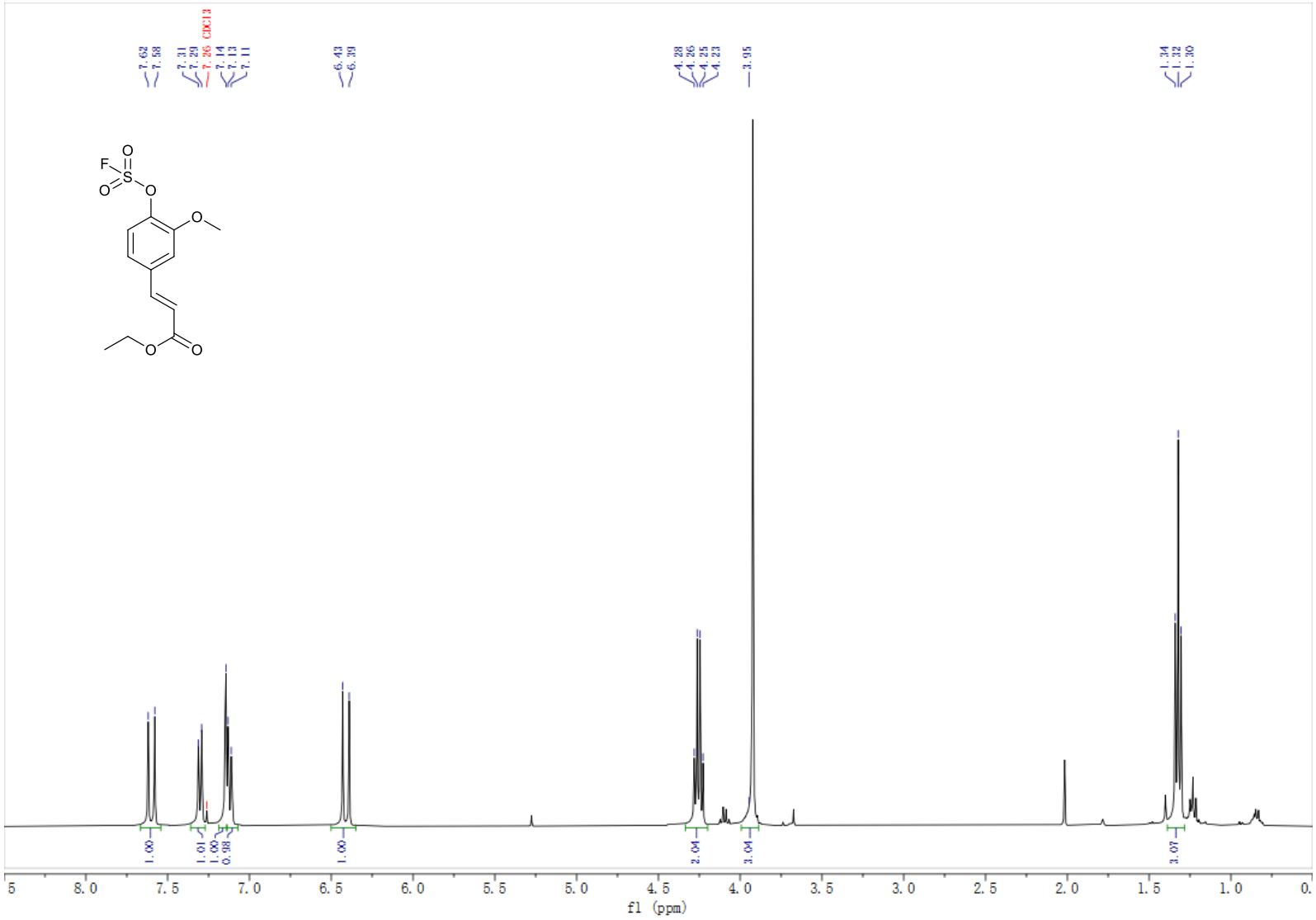
80
70
60
50
40
30
20
10
f1 (ppm)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4.25
4.23
3.95
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1.00
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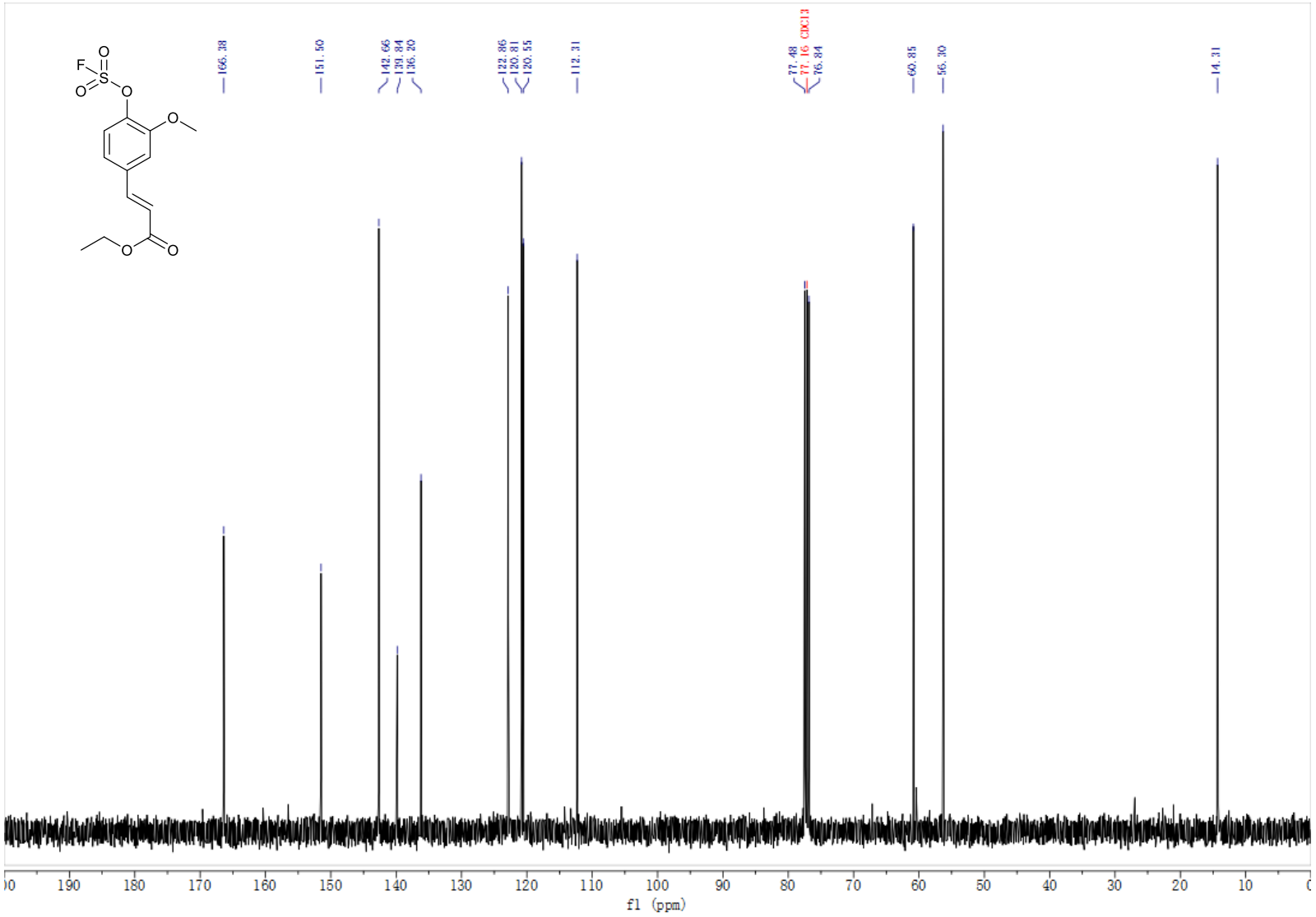
1.00
2.04
3.04
3.07
f1 (ppm)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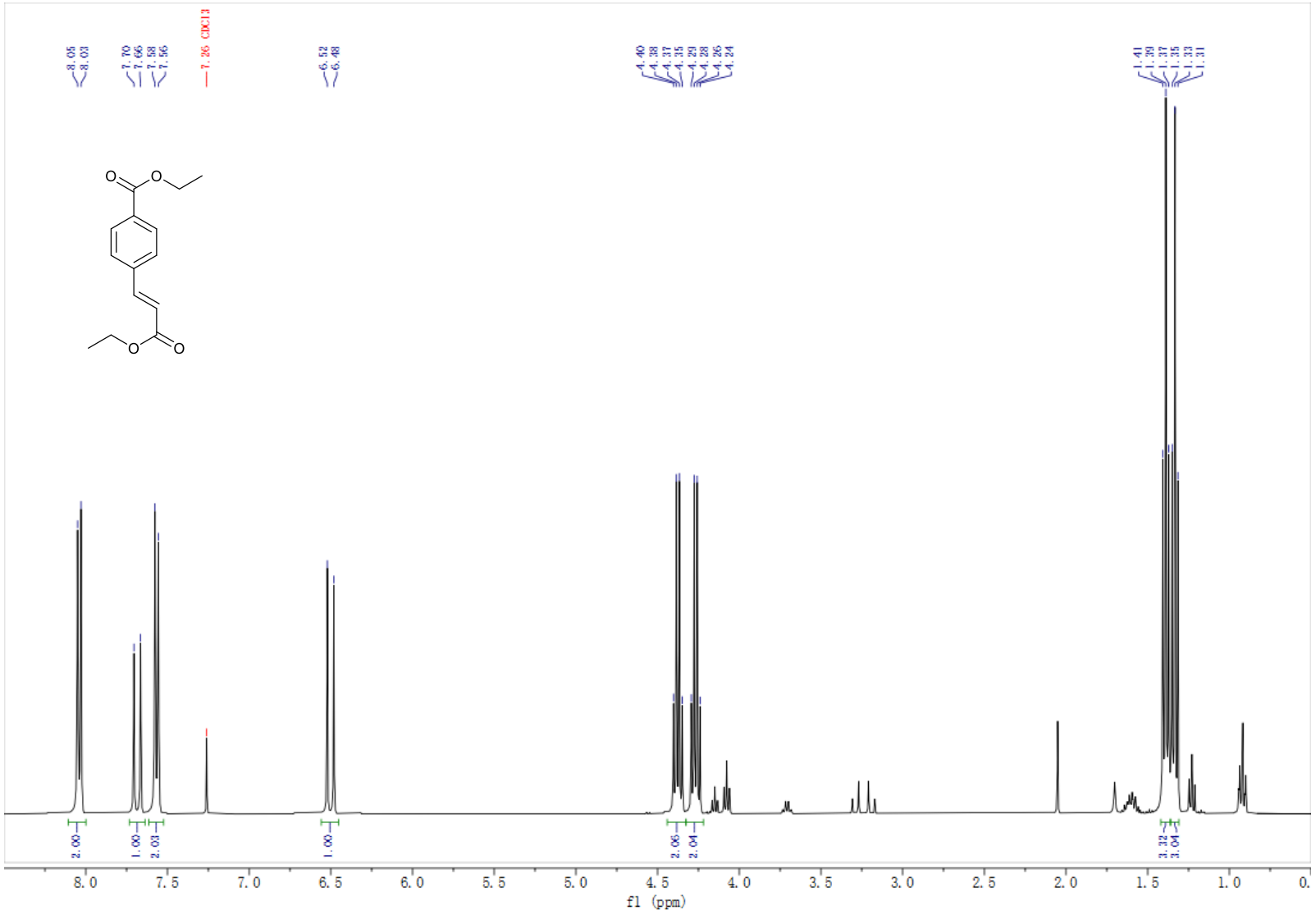
56.30
14.31
f1 (ppm)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4.37
4.35
4.29
4.28
4.26
4.24
1.41
1.39
1.37
1.35
1.33
1.31
2.00
1.00
2.03
1.00
2.06
2.04
3.12
3.04
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7.0
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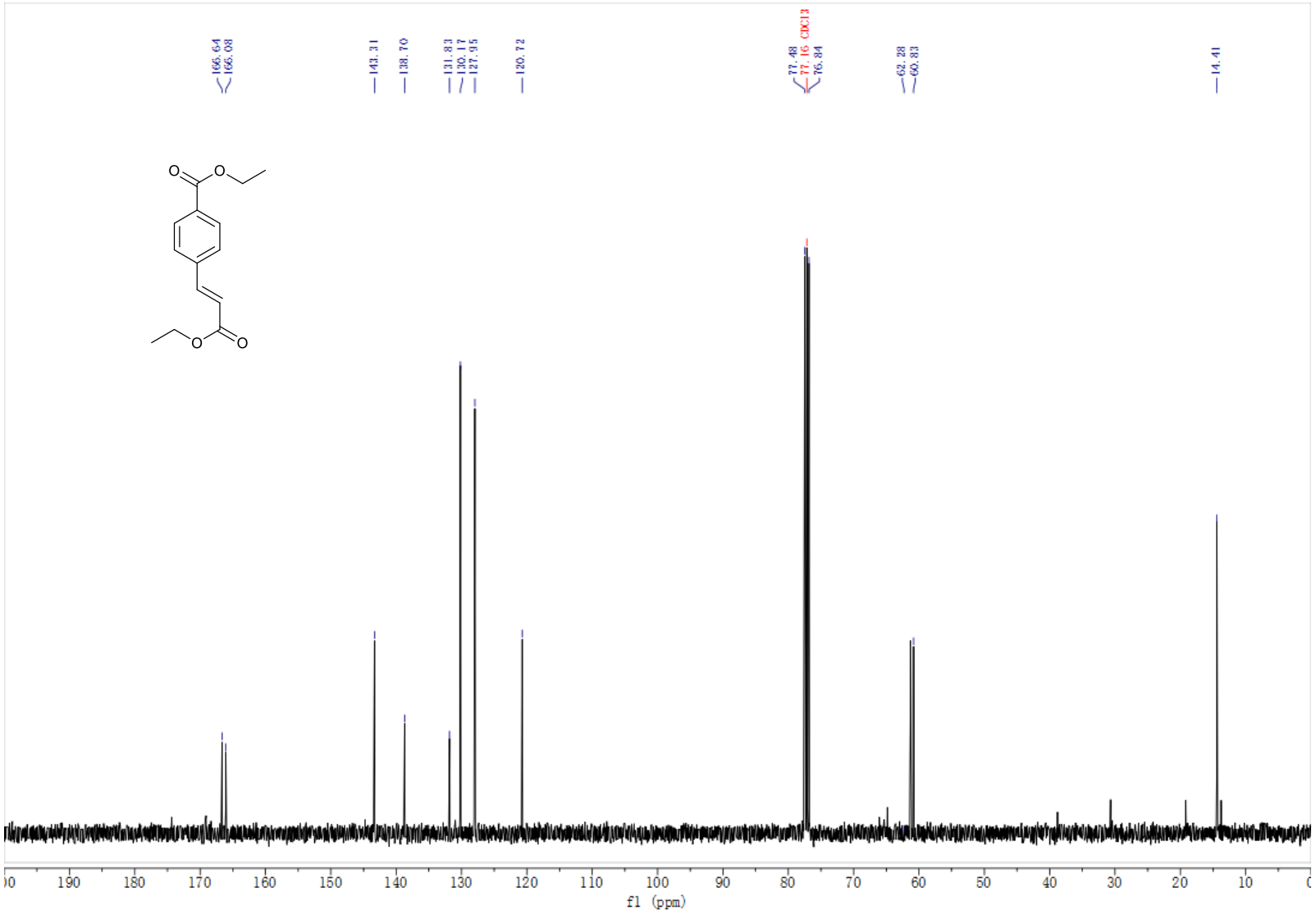
f1 (ppm)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O
O
O
O
190
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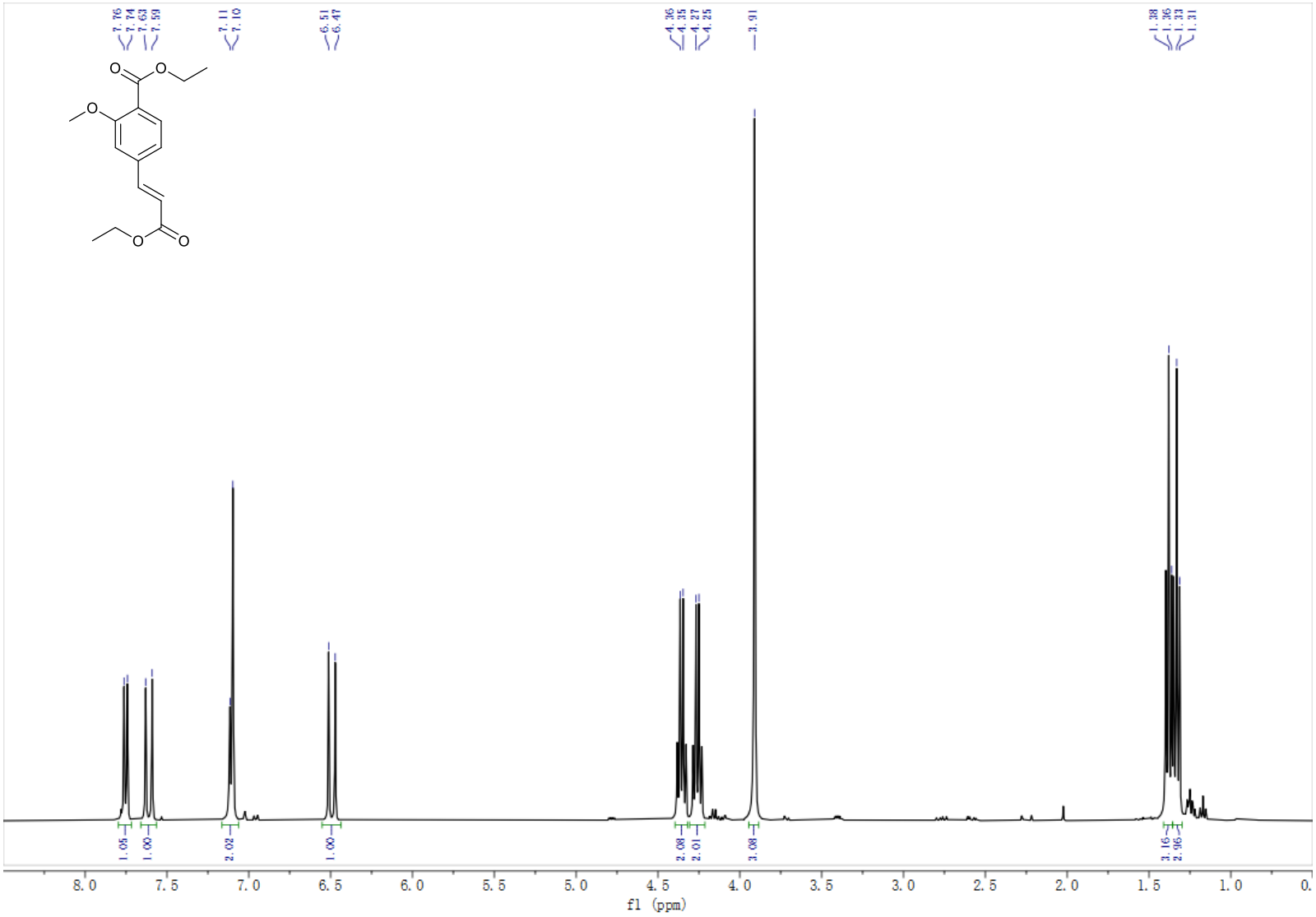
30
20
10
f1 (ppm)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1.05
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1.00
2.08
2.01
3.08
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7.5
7.0
6.5
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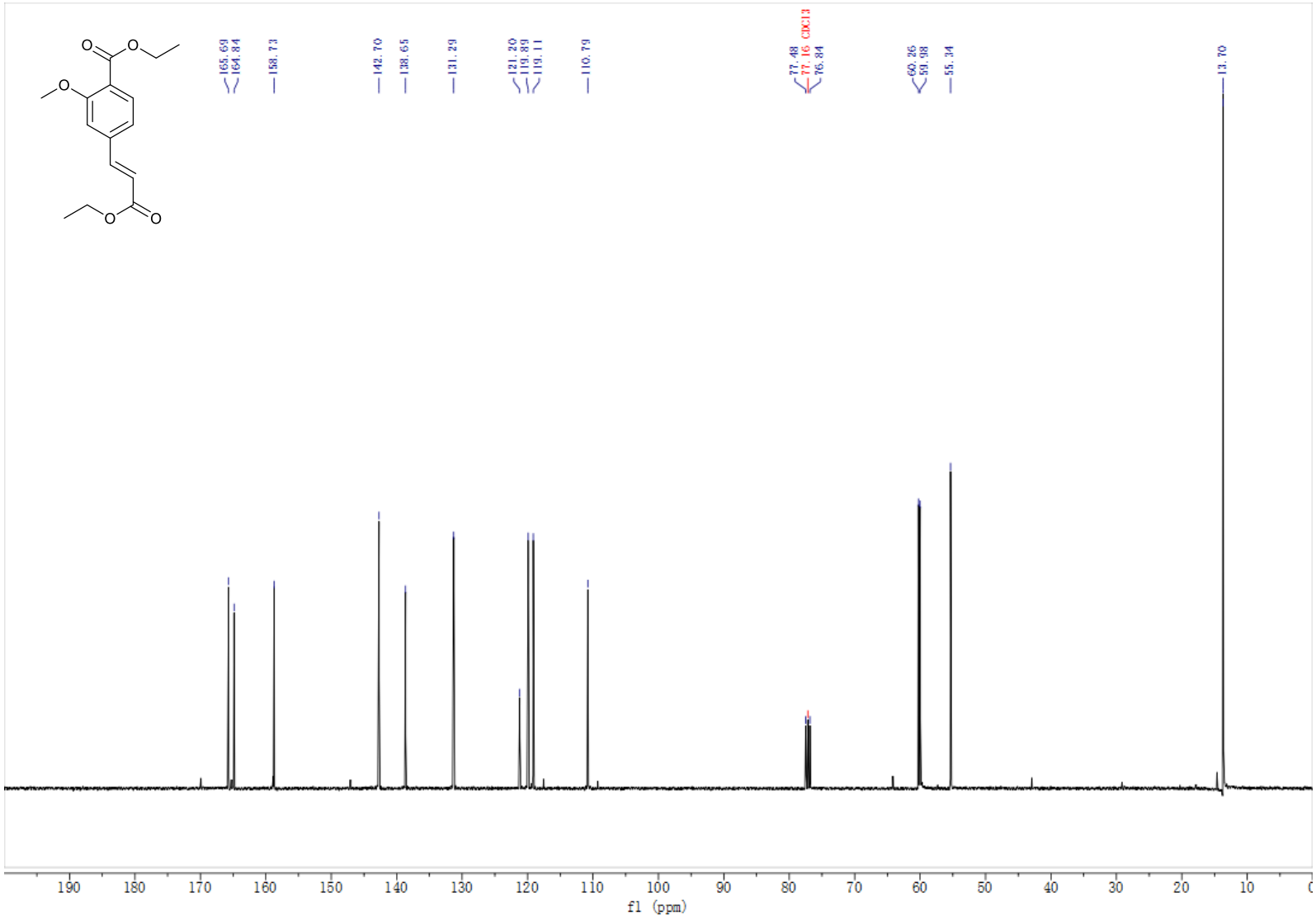
2.0
1.5
1.0
f1 (ppm)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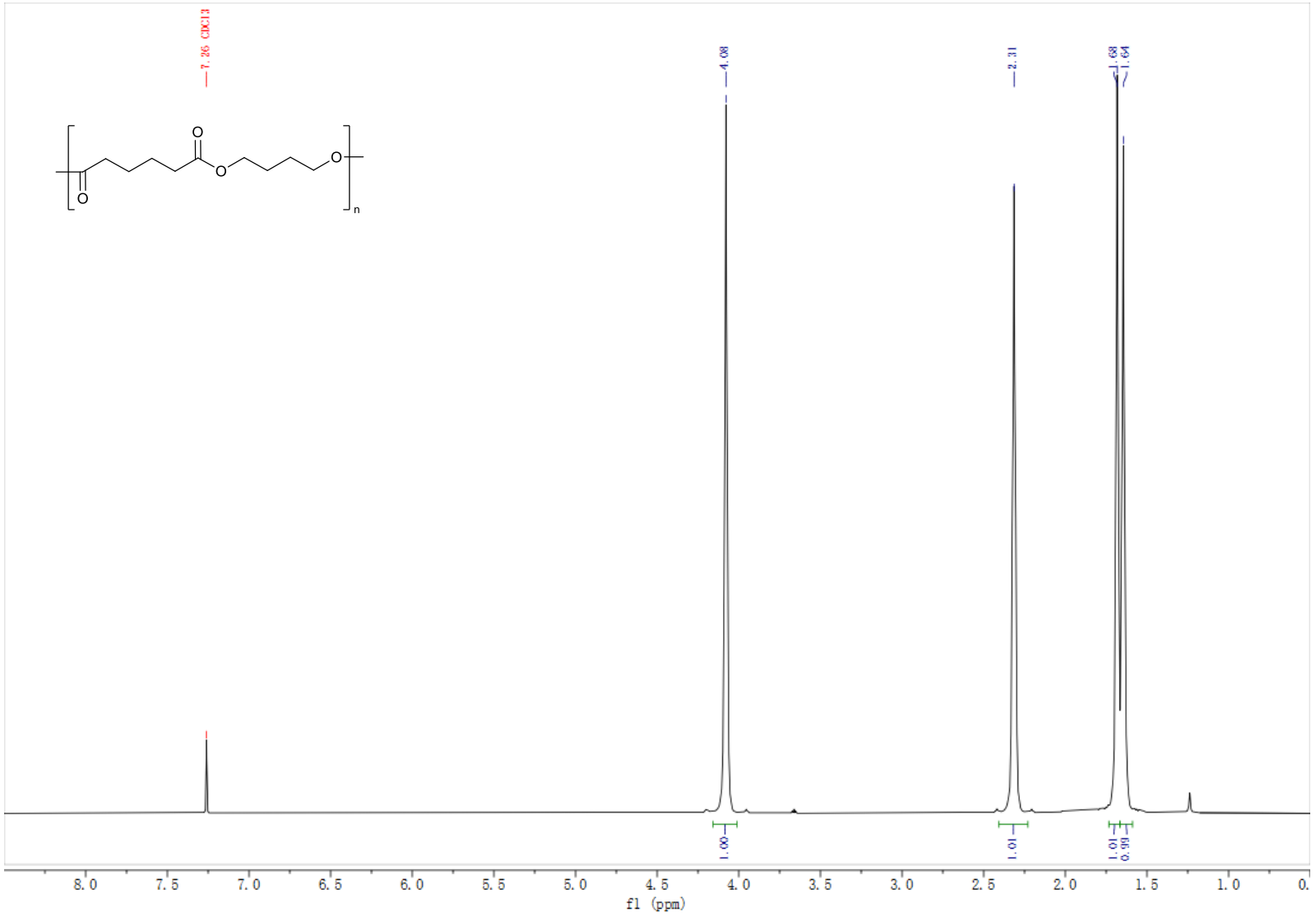
f1 (ppm)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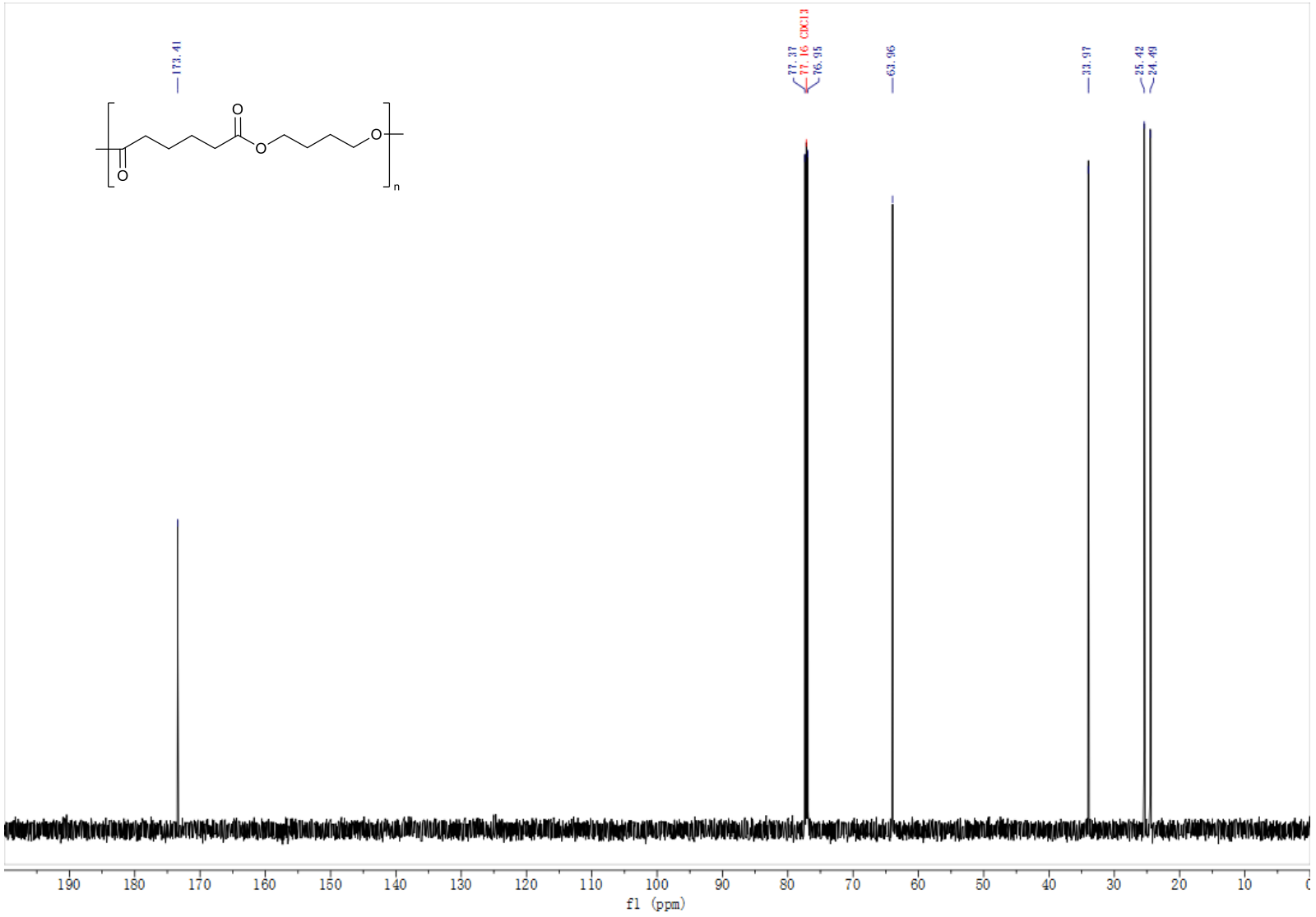
f1 (ppm)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24.49
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O
O
O
n
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180
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140
130
120
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100
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60
50
40
30
20
10
f1 (ppm)

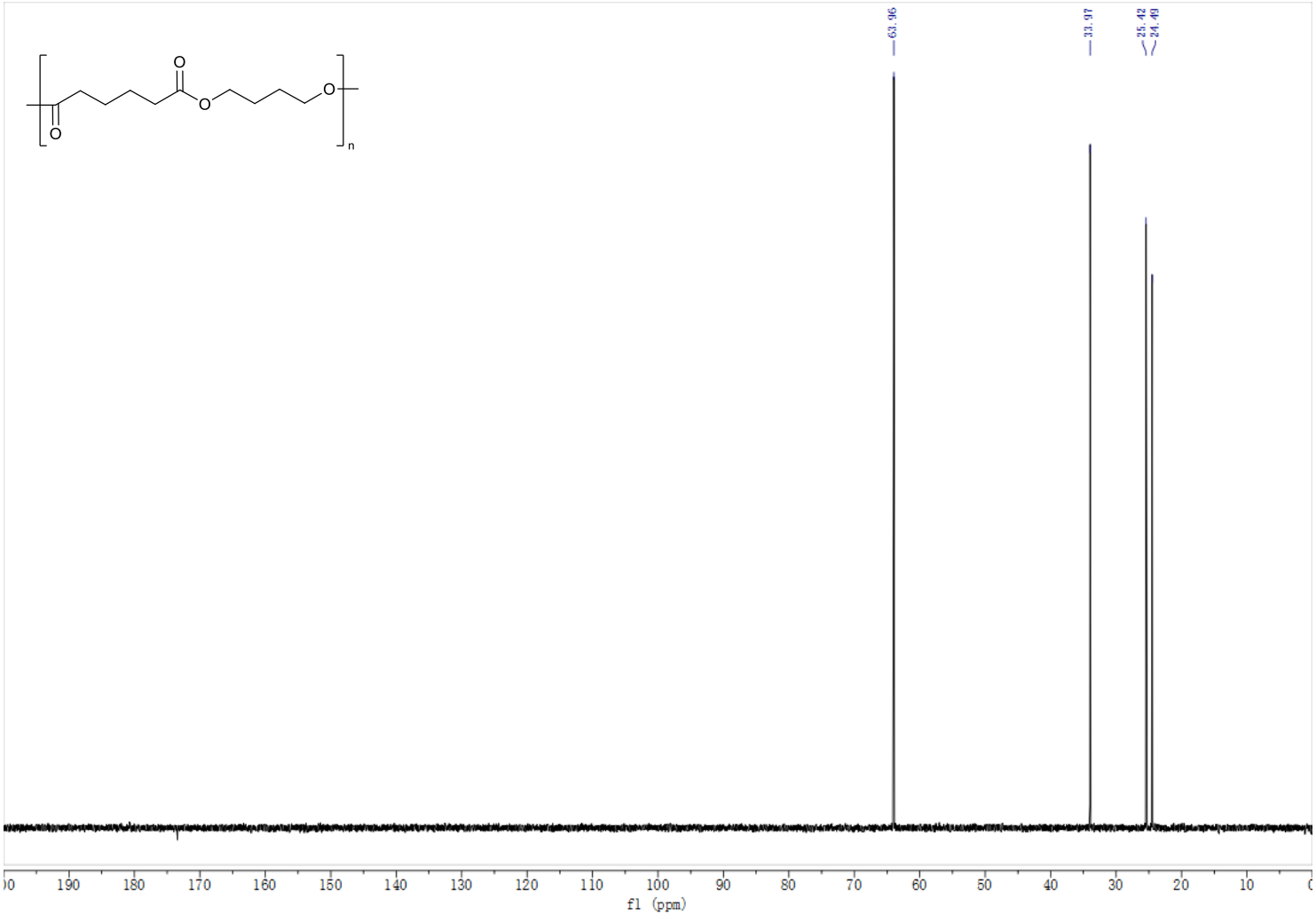
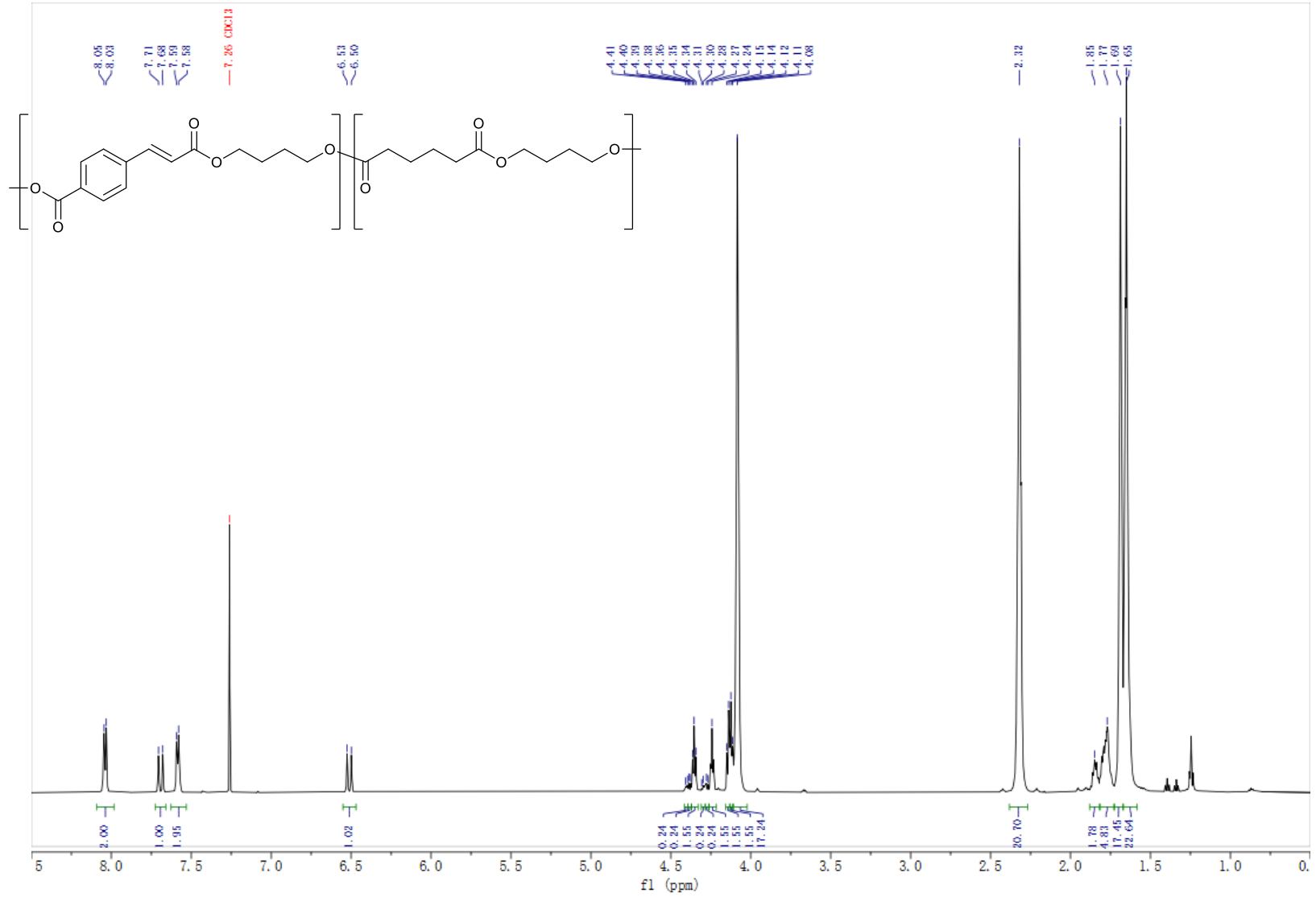


Figure S16. ^{1}H NMR, ^{13}C NMR, and dept 135 NMR spectrum of PBA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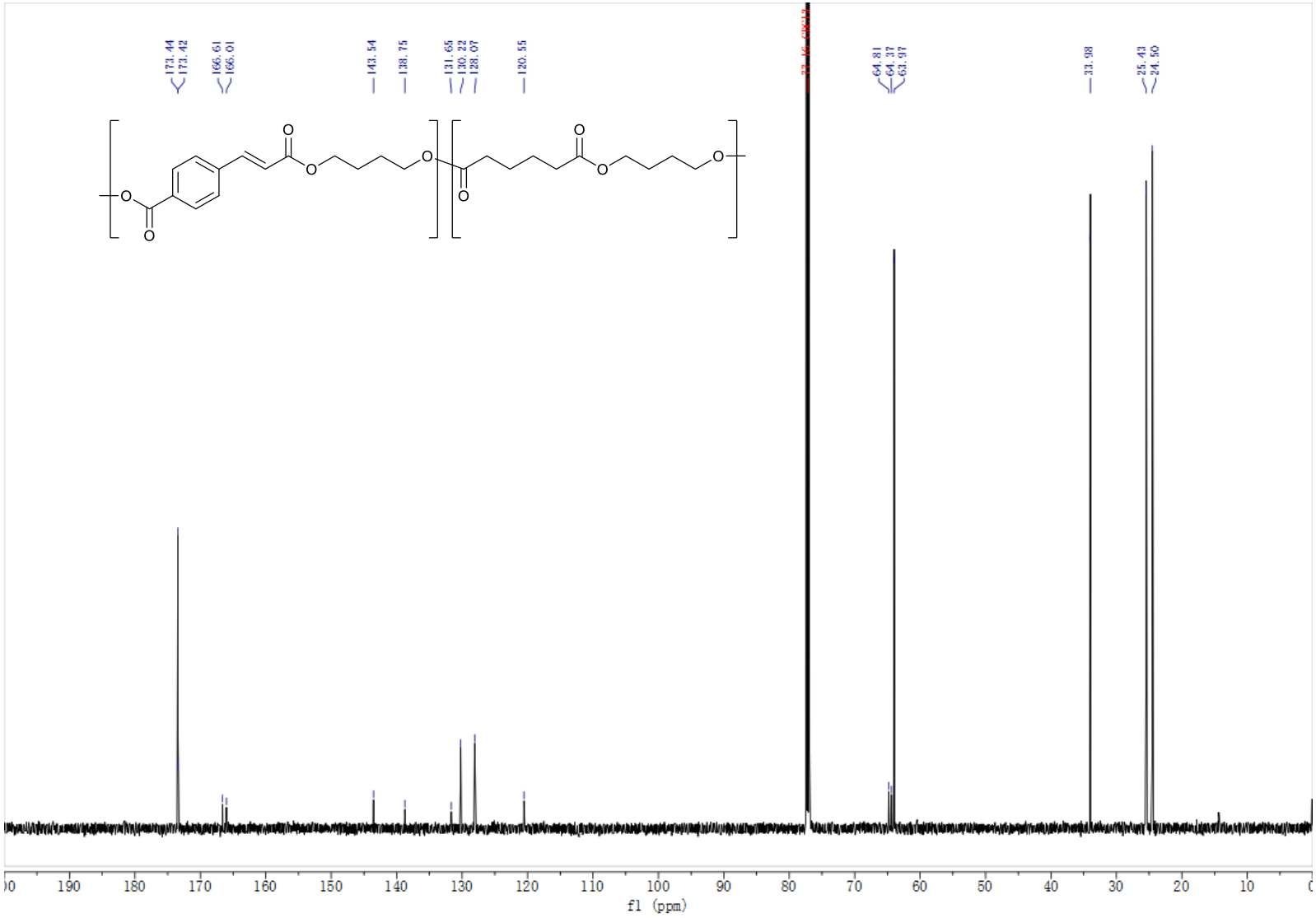
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33.98
25.43
24.50
f1 (ppm)

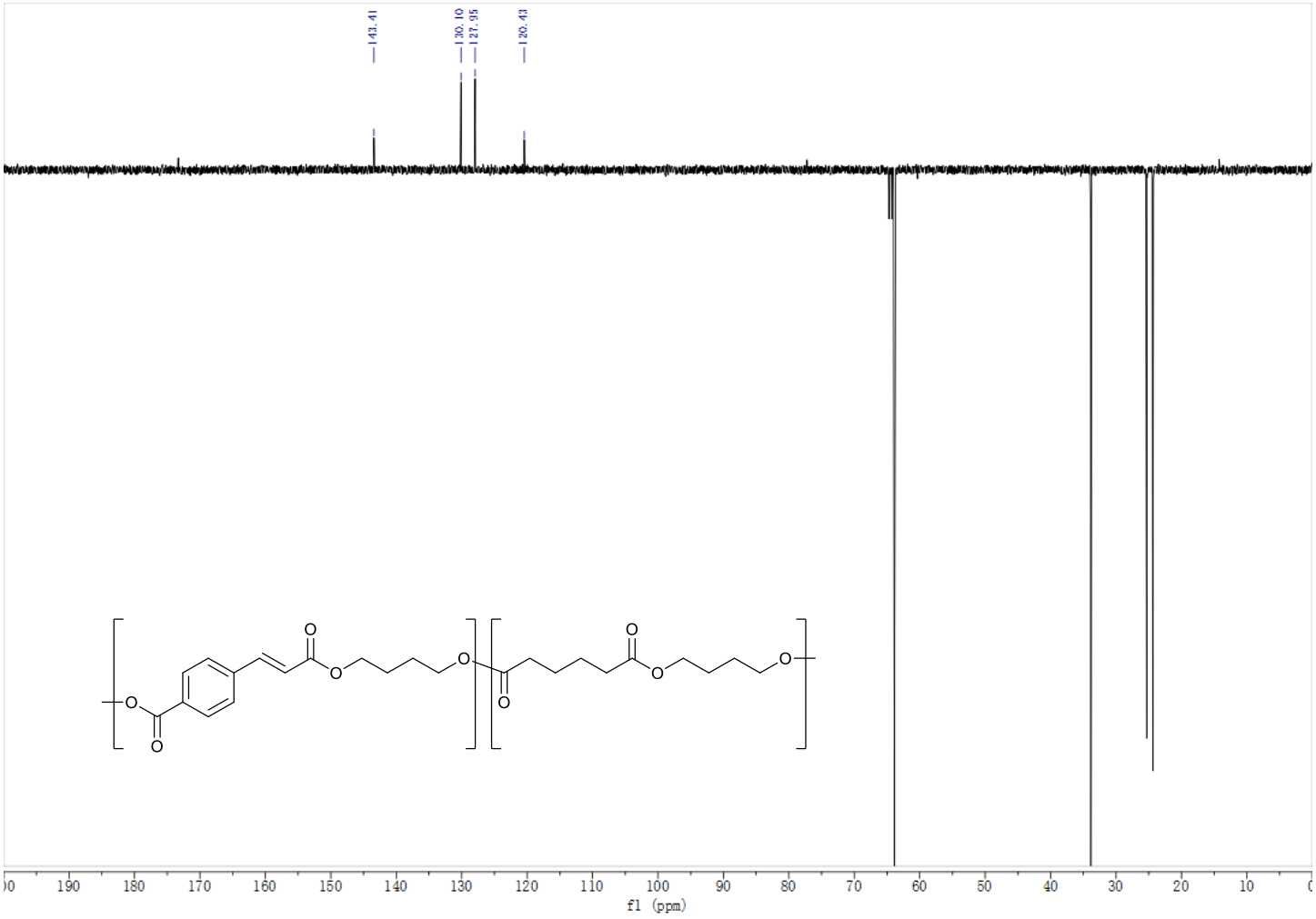
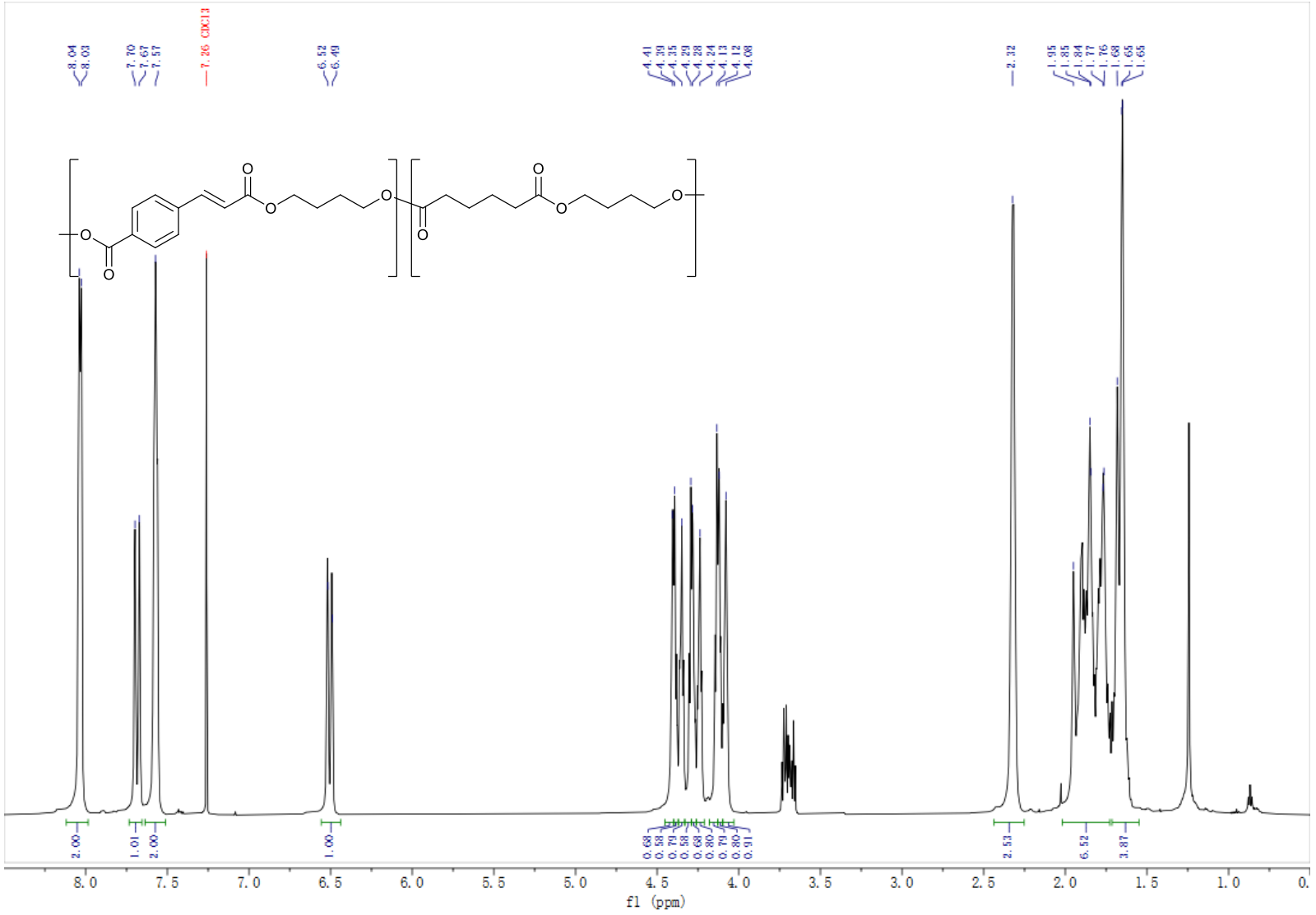
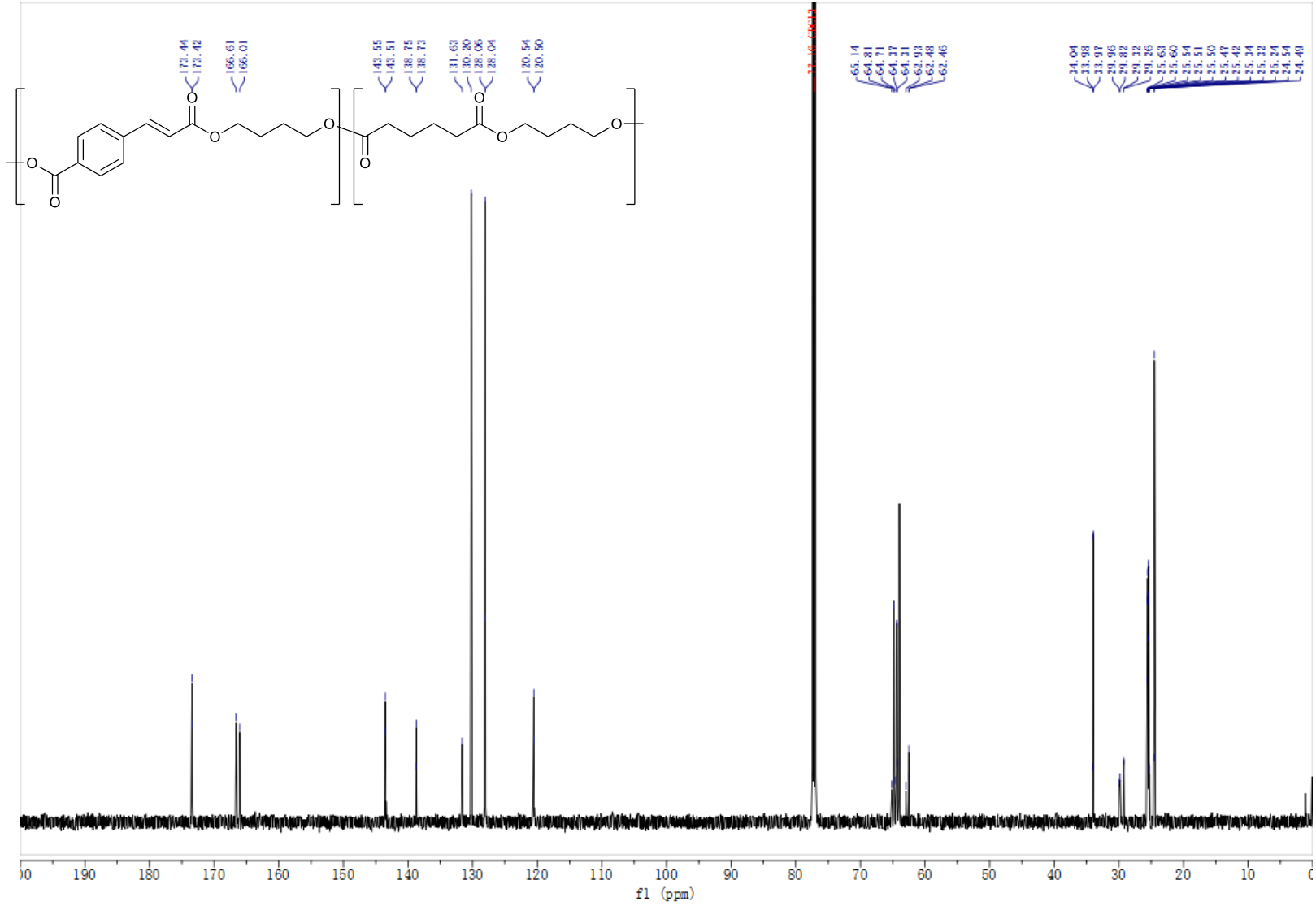
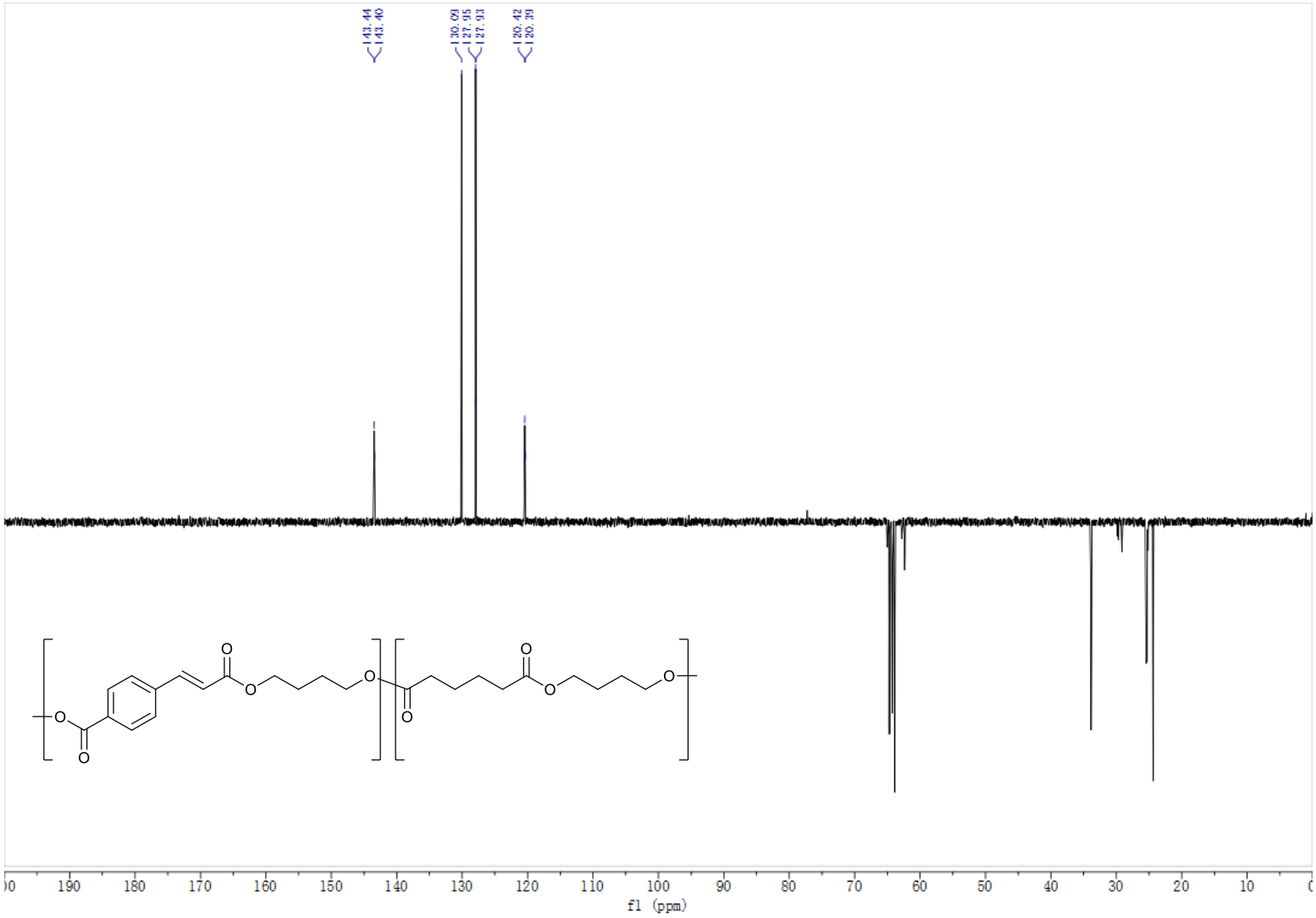


Figure S17. ^{1}H NMR, ^{13}C NMR, and dept 135 NMR spectrum of PBAL$_1$20


8.04
8.03
7.70
7.67
7.57
7.26 CDCl3
6.52
6.49
4.41
4.39
4.35
4.29
4.28
4.24
4.13
4.12
4.08
2.32
1.95
1.85
1.84
1.77
1.76
1.68
1.65
1.65
2.00
1.01
2.00
1.00
0.68
0.58
0.79
0.58
0.68
0.80
0.79
0.89
0.91
2.53
6.52
3.87
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.
f1 (ppm)


173.44
173.42
166.61
166.01
143.55
143.51
138.75
138.73
131.63
130.20
128.06
128.04
120.54
120.50
65.14
64.81
64.71
64.37
64.31
62.93
62.48
62.46
34.04
33.98
33.97
29.96
29.82
29.32
29.26
25.63
25.60
25.54
25.51
25.50
25.47
25.42
25.34
25.32
25.24
24.54
24.49
f1 (ppm)


143.44
143.40
130.09
127.95
127.93
120.42
120.39
O
O
O
O
O
O
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

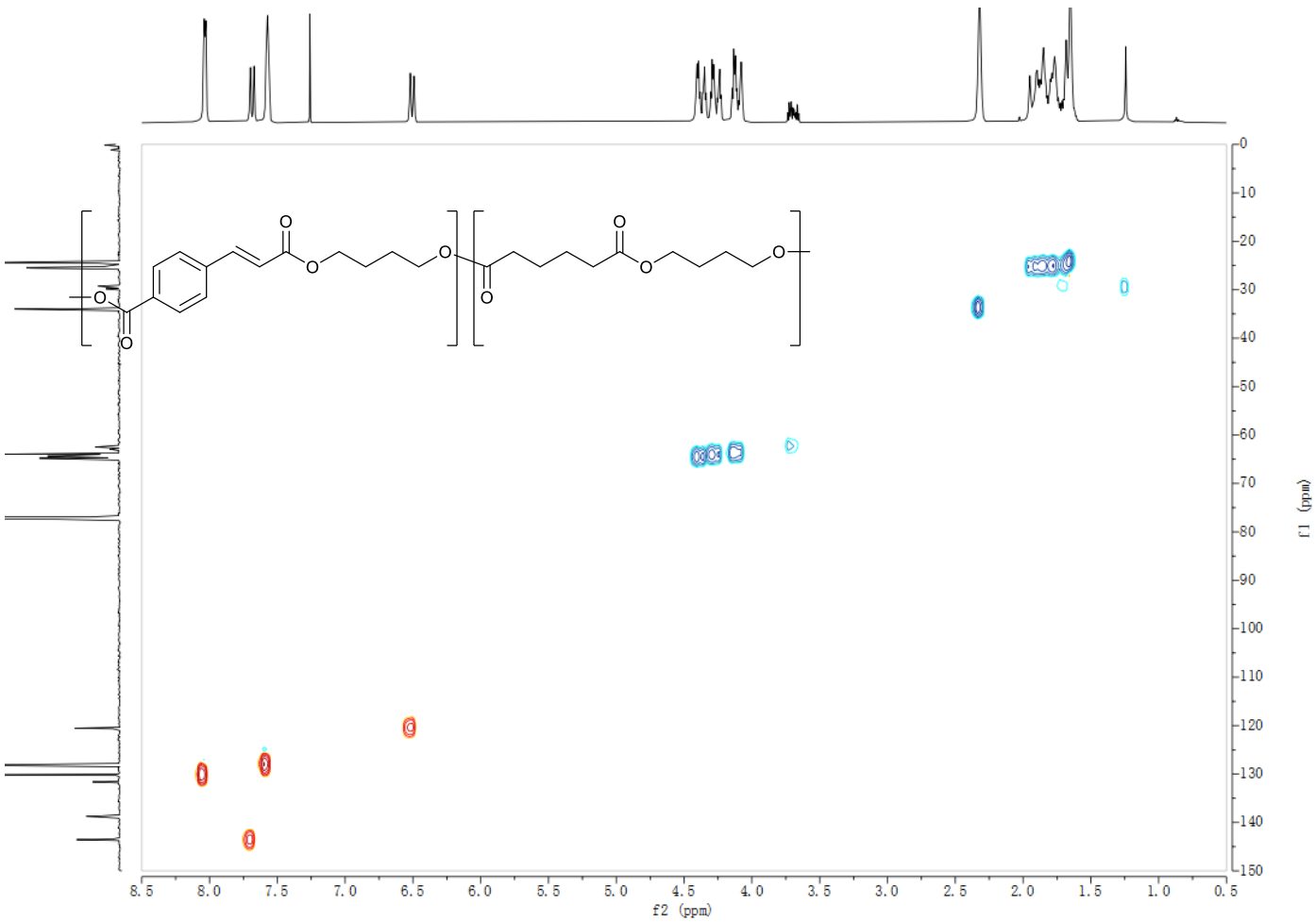
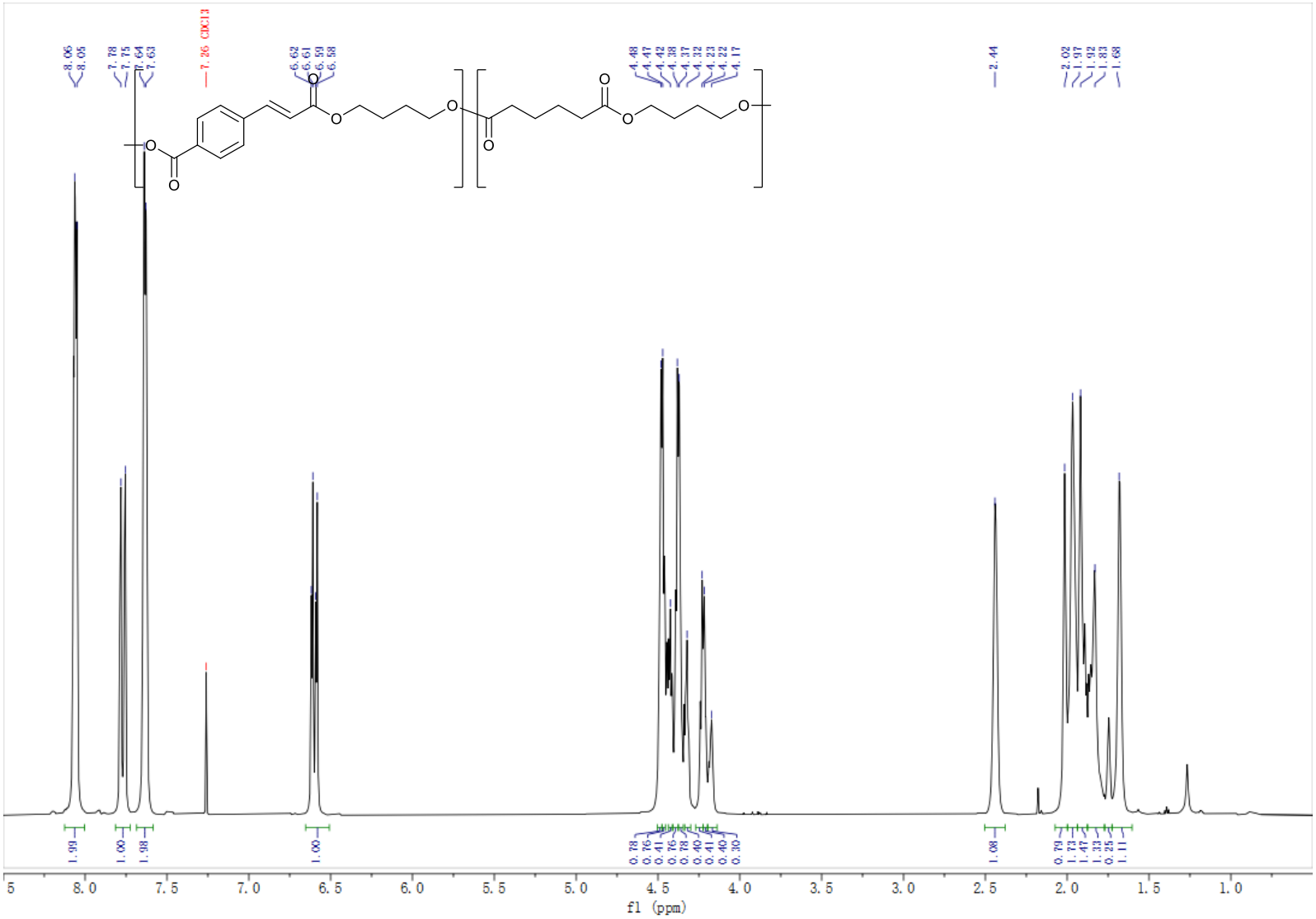


Figure S18. ^{1}H NMR, ^{13}C NMR, dept 135, and 2D HSQC spectrum of PBAL$_1$60


8.06
8.05
7.78
7.75
7.64
7.63
7.26 CDCl3
6.62
6.61
6.59
6.58
4.48
4.47
4.42
4.38
4.37
4.32
4.23
4.22
4.17
2.44
2.02
1.97
1.92
1.83
1.68
1.99
1.00
1.98
1.00
0.78
0.76
0.41
0.76
0.78
0.40
0.41
0.40
0.30
1.08
0.79
1.73
1.47
1.33
0.25
1.11
f1 (ppm)

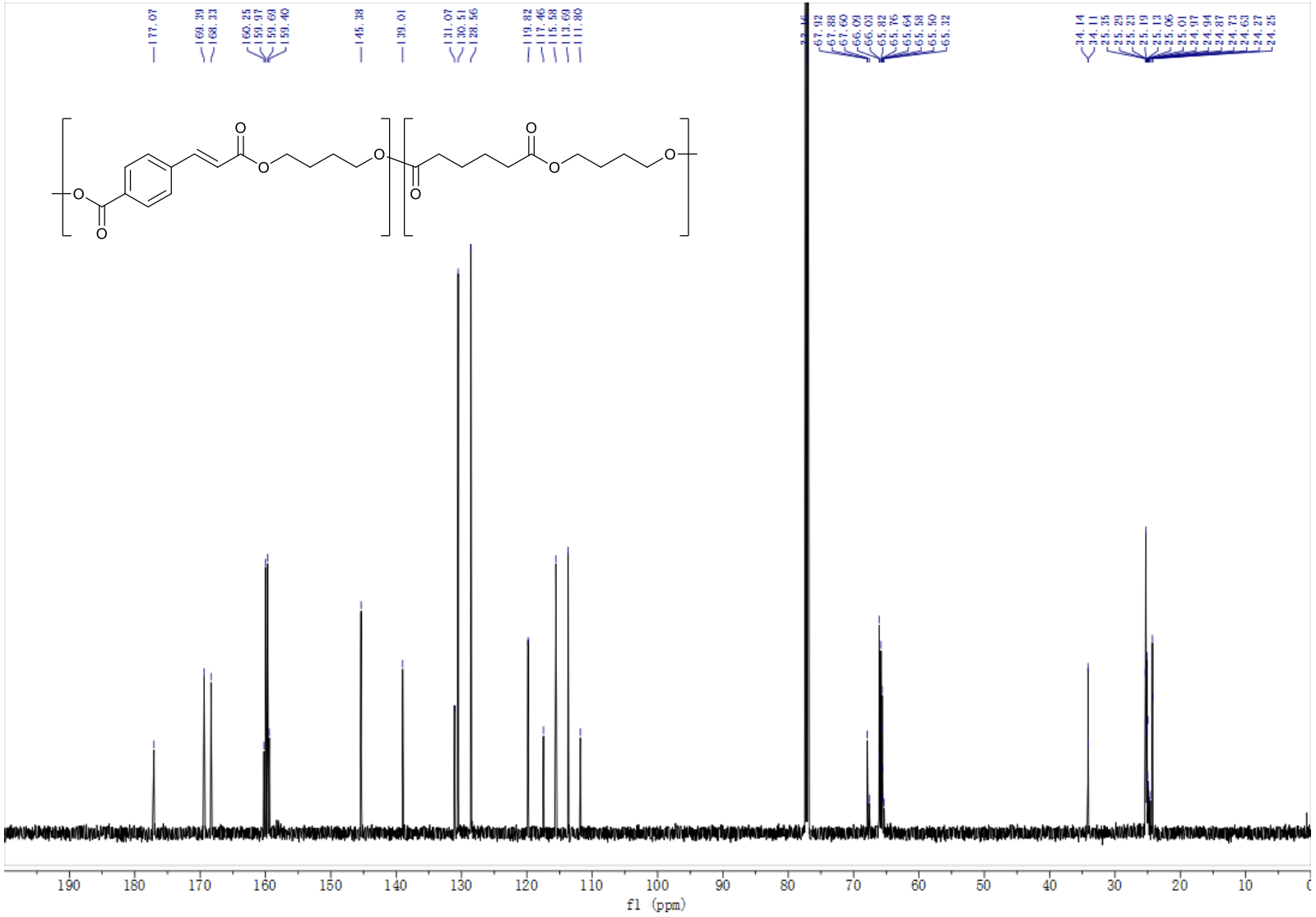
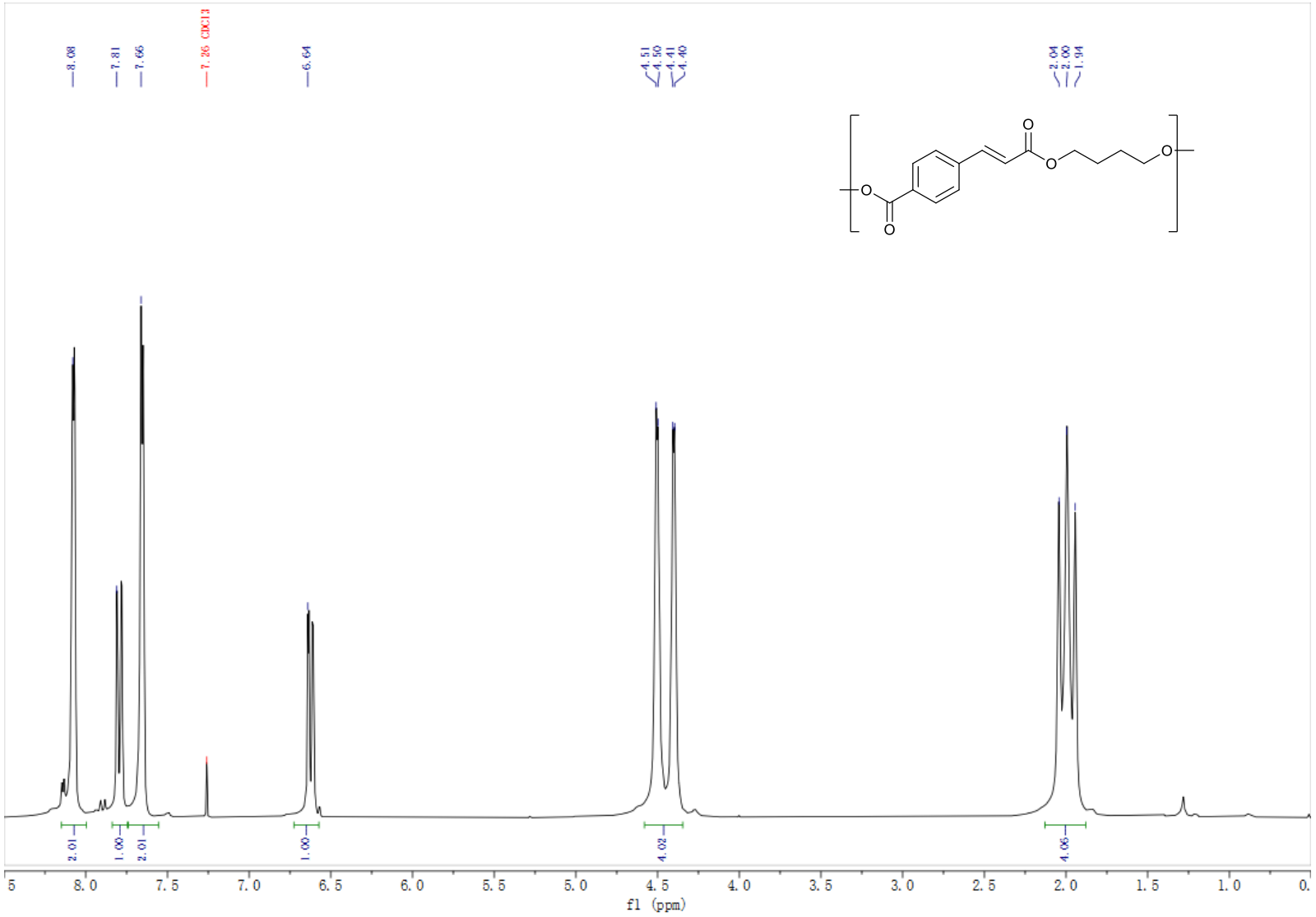
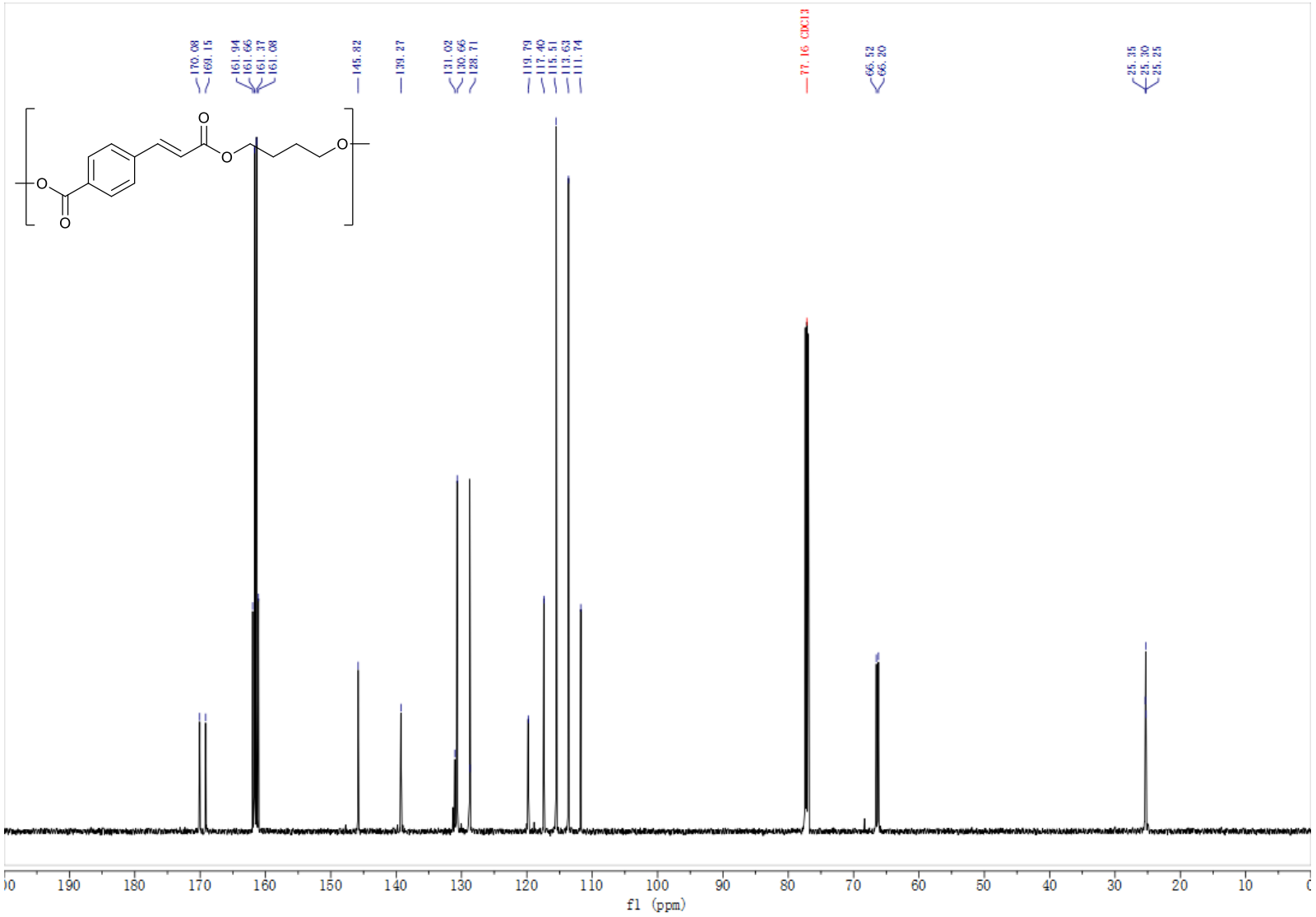

177.07
169.39
168.33
160.25
159.97
159.69
159.40
145.38
139.01
131.07
130.51
128.96
119.82
117.46
115.38
113.69
111.80
67.92
67.88
67.60
66.09
66.03
65.82
65.76
65.64
65.58
65.50
65.32
34.14
34.11
25.35
25.29
25.23
25.19
25.13
25.06
25.01
24.97
24.94
24.87
24.73
24.63
24.27
24.25
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

Figure S19. ^{1}H NMR, ^{13}C NMR, and dept 135 spectrum of PBAL$_1$80


8.08
7.81
7.66
7.26 CDCl3
6.64
4.51
4.50
4.41
4.40
2.04
2.00
1.94
2.01
1.00
2.01
1.00
4.02
4.00
f1 (ppm)


170.08
169.15
161.94
161.66
161.37
161.08
145.82
139.27
131.02
130.66
128.71
119.79
117.40
115.51
113.63
111.74
77.16 CDCl3
66.52
66.20
25.35
25.30
25.25
f1 (ppm)

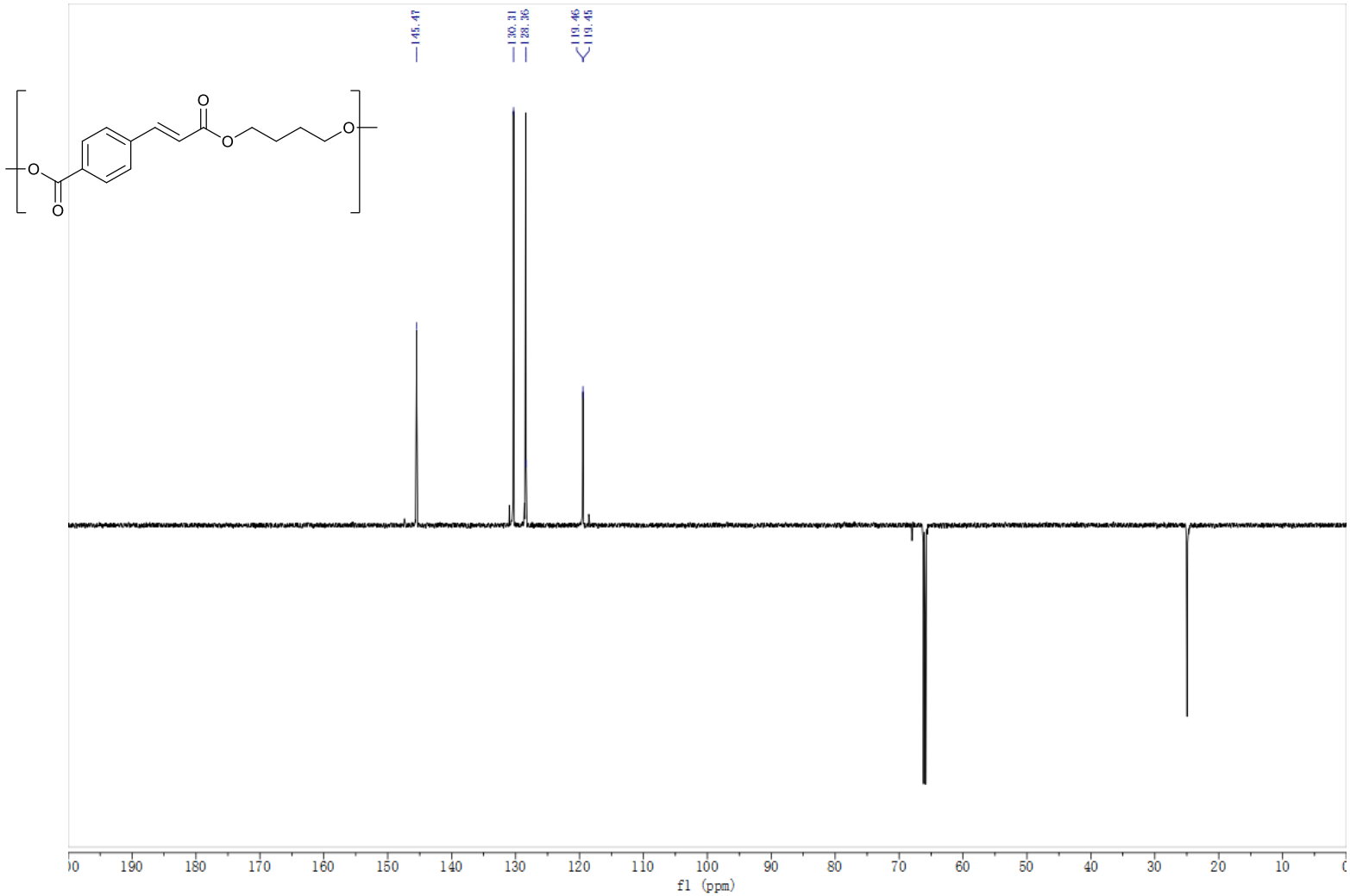
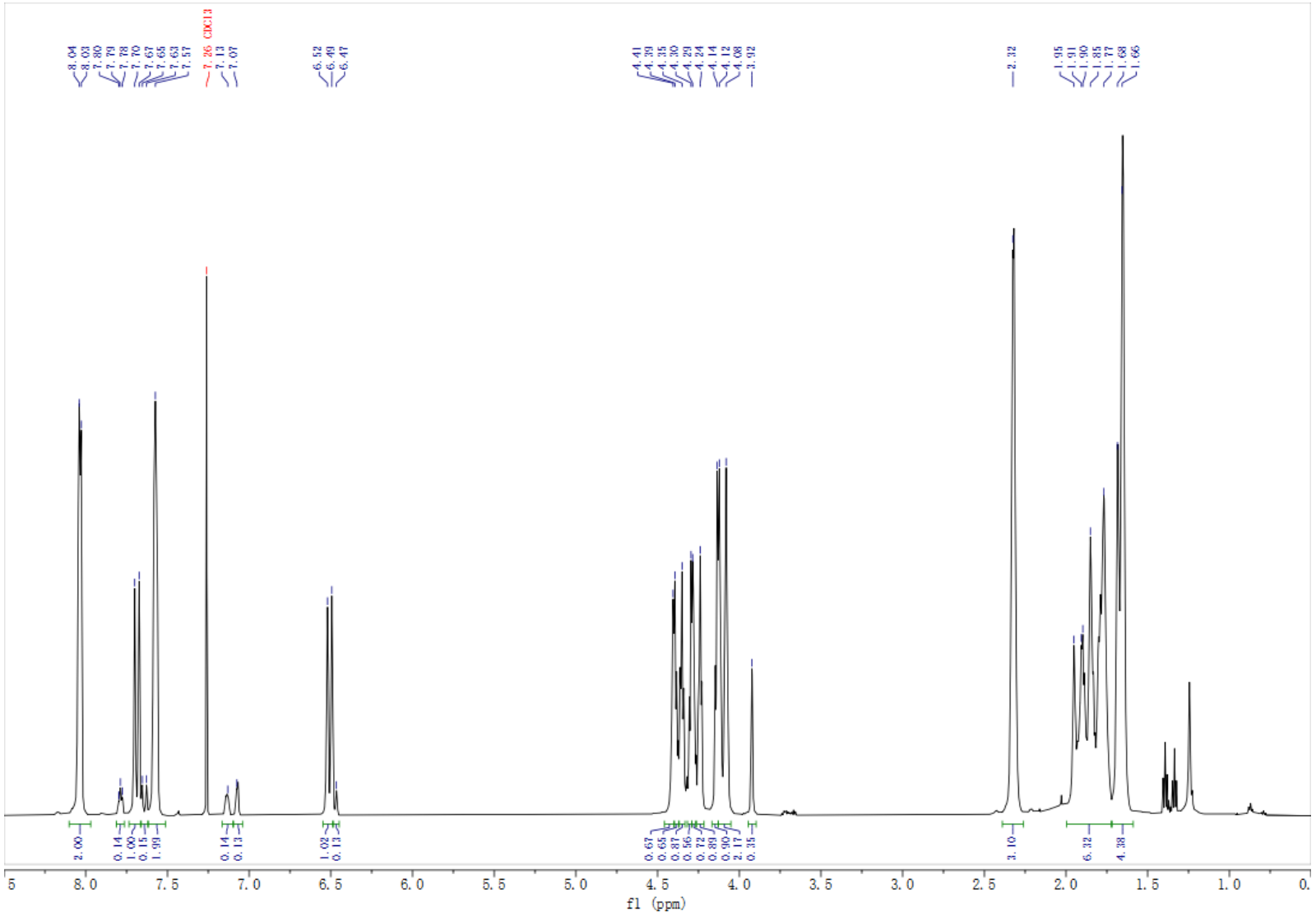
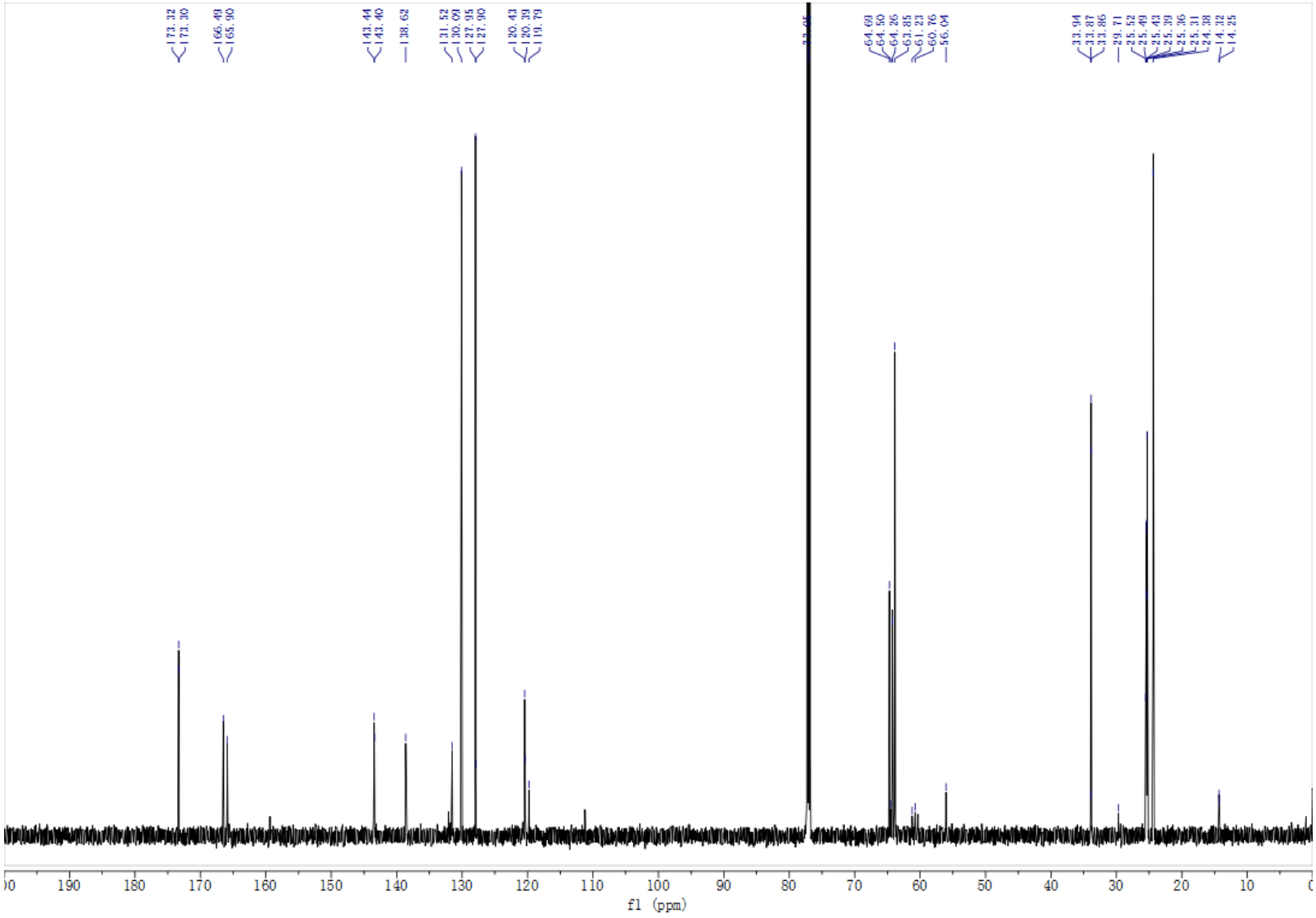


Figure S20. ^{1}H NMR, ^{13}C NMR, and dept 135 spectrum of PBL_1


8.04
8.03
7.80
7.79
7.78
7.70
7.67
7.65
7.63
7.57
7.26 CDCl3
7.13
7.07
6.52
6.49
6.47
4.41
4.39
4.35
4.30
4.29
4.24
4.14
4.12
4.08
3.92
2.32
1.95
1.91
1.90
1.85
1.77
1.68
1.66
2.00
0.14
1.00
0.15
1.99
0.14
0.13
1.02
0.13
0.67
0.65
0.87
0.56
0.72
0.89
0.90
2.17
0.35
3.10
6.32
4.38
f1 (ppm)


173.32
173.20
166.49
165.90
143.44
141.40
138.62
131.52
130.09
127.95
127.90
120.43
120.39
119.79
64.69
64.50
64.26
63.85
61.23
60.76
56.04
33.94
33.87
33.86
29.71
25.52
25.49
25.43
25.39
25.36
25.31
24.38
14.32
14.25
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

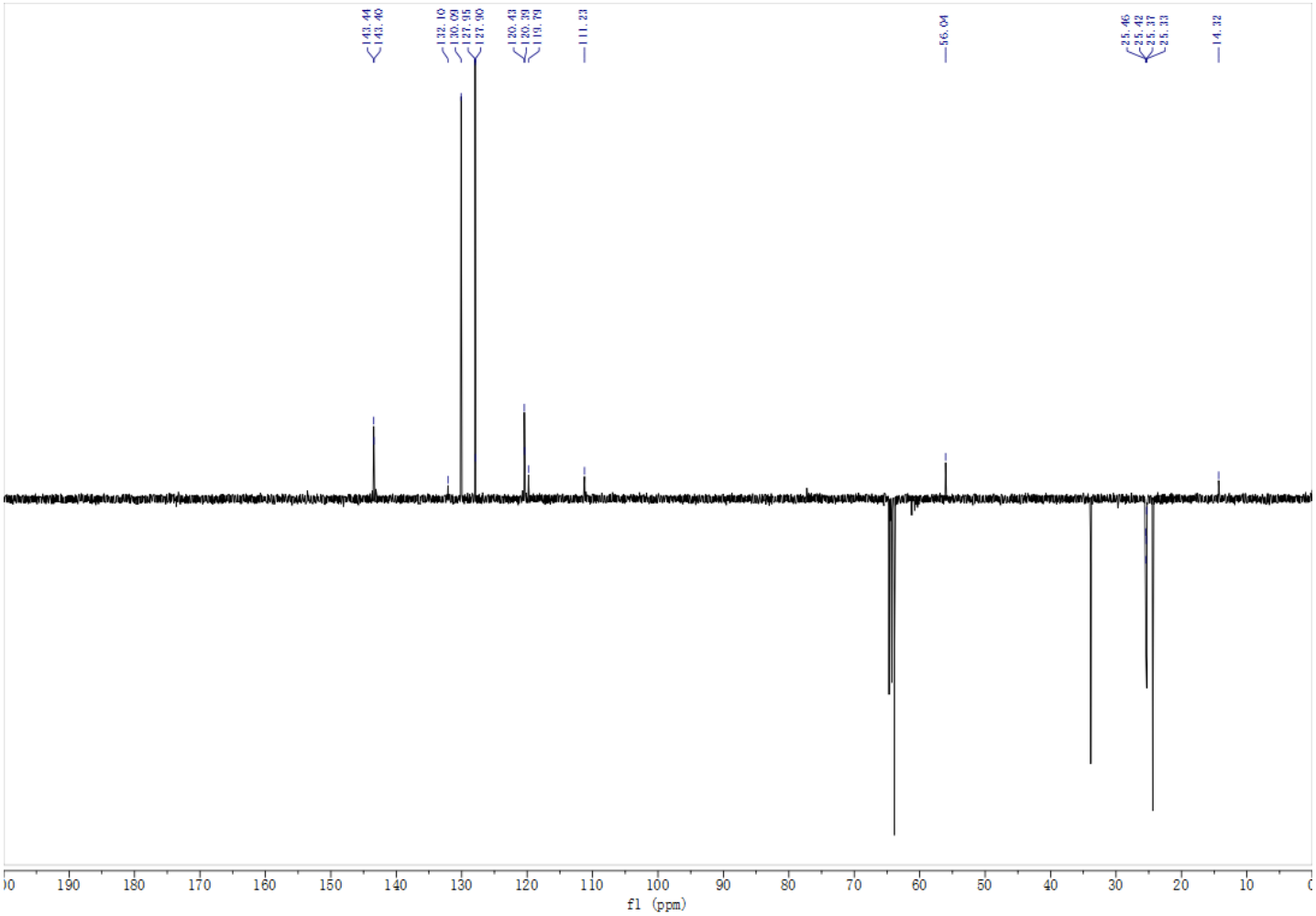
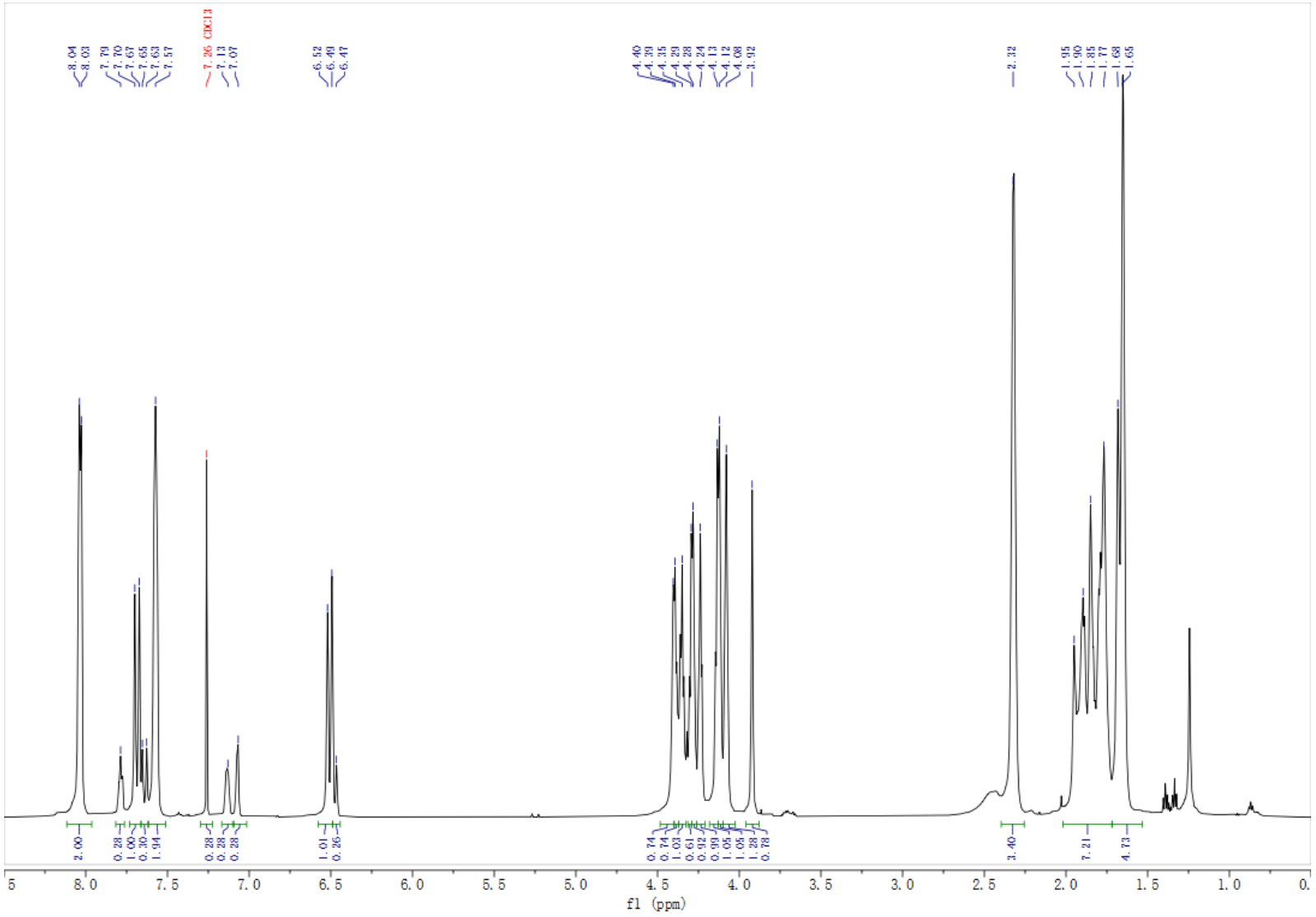
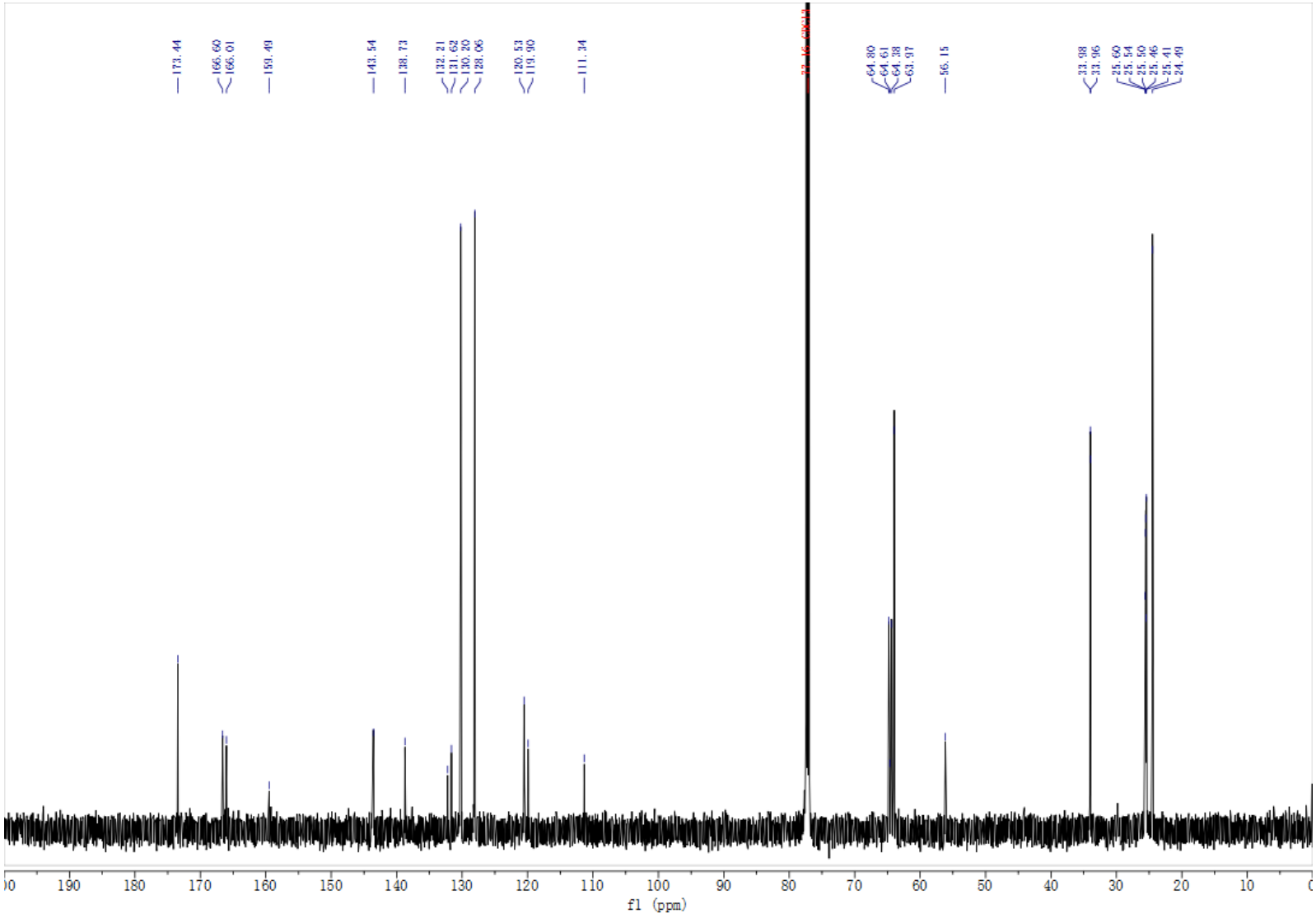
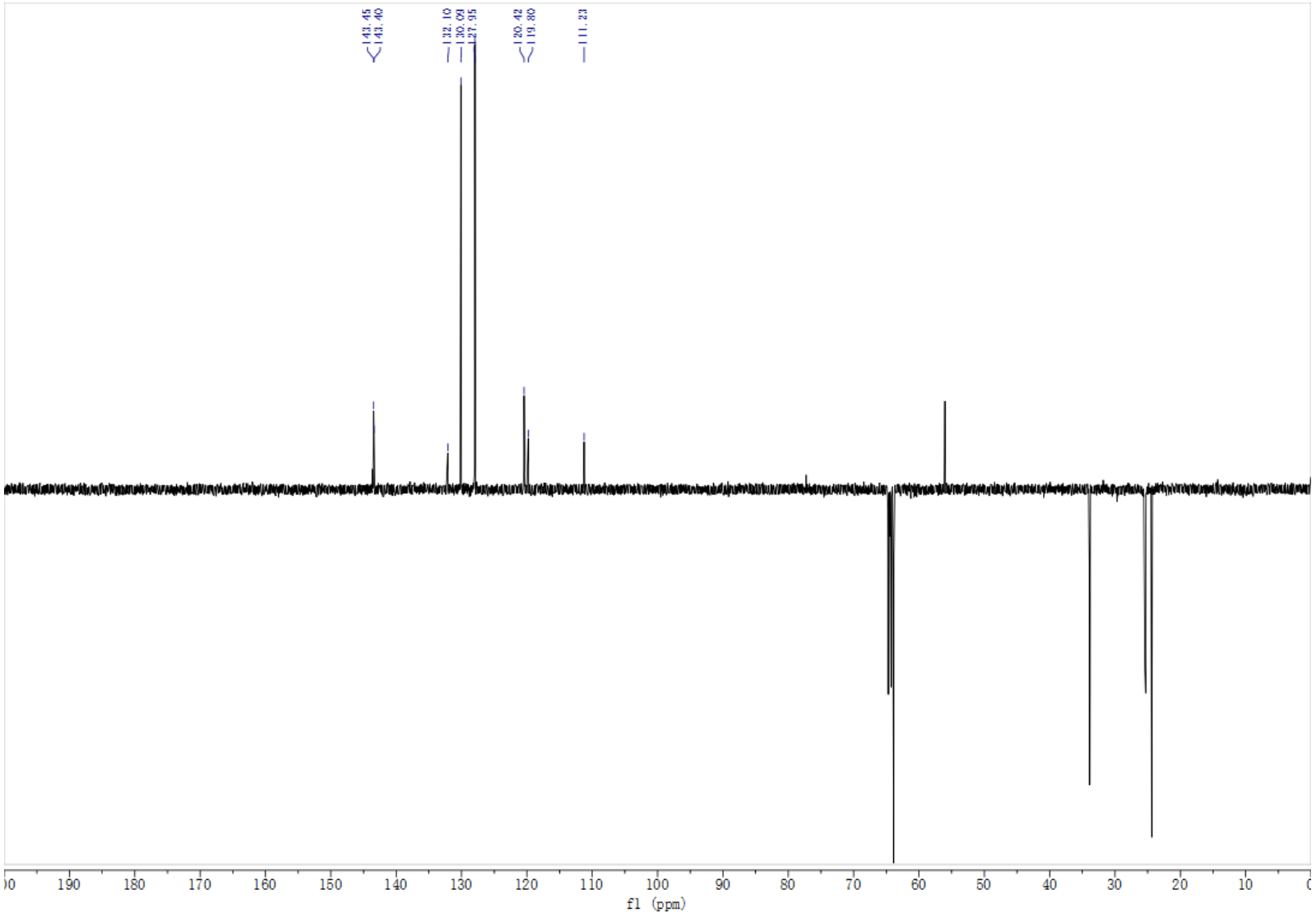


Figure S21. ^{1}H NMR, ^{13}C NMR, and dept 135 spectrum of $PBAL_154L_206$


8.04
8.03
7.79
7.70
7.67
7.65
7.63
7.57
7.26 CDCl3
7.13
7.07
6.52
6.49
6.47
4.40
4.39
4.35
4.29
4.28
4.24
4.13
4.12
4.08
3.92
2.32
1.95
1.90
1.85
1.77
1.68
1.65
2.00
0.28
1.00
0.30
1.94
0.28
0.28
0.28
1.01
0.26
0.74
0.74
1.03
0.61
0.92
0.99
1.05
1.05
1.28
0.78
3.40
7.21
4.73
f1 (ppm)


173.44
166.60
166.01
159.49
143.54
138.73
132.21
131.62
130.20
128.06
120.53
119.90
111.34
64.80
64.61
64.38
63.97
56.15
33.98
33.96
25.69
25.54
25.50
25.46
25.41
24.49
f1 (ppm)


143.45
143.40
132.10
130.04
127.95
120.42
119.80
111.23
f1 (ppm)

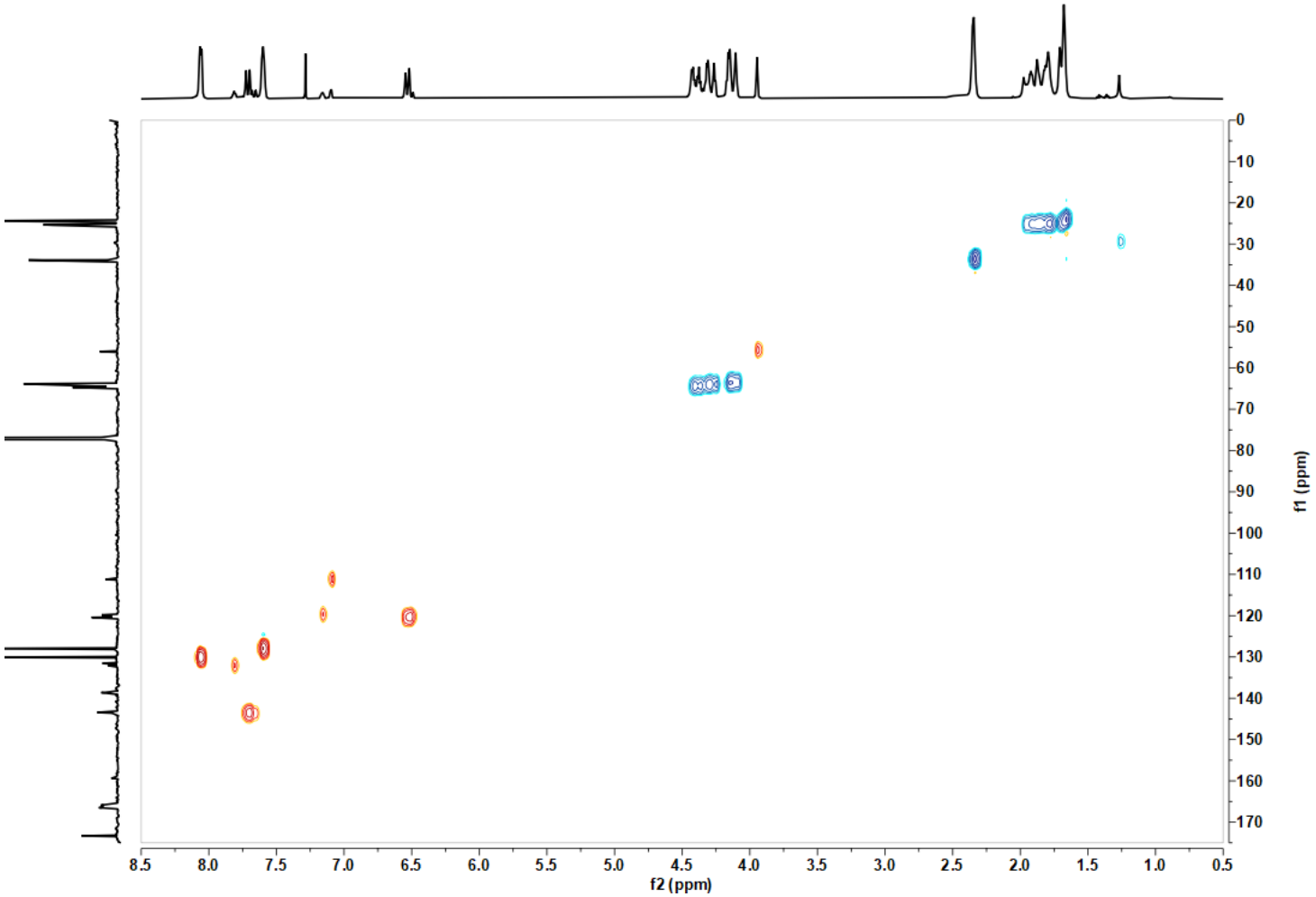


Figure S22. ^{1}H NMR, ^{13}C NMR, dept 135, and 2D HSQC spectrum of $PBAL_148L_212$

1. S. Wang, W. Gao, H. Li, L.-P. Xiao, R.-C. Sun and G. Song, *Chemsuschem*, 2018, **11**, 2114-2123.

2. G. Ji, C. Gao, W. Xiao and L. Han, *Bioresource Technology*, 2016, **205**, 159-165.

3. R. Yamadera and M. Murano, *Journal of Polymer Science Part A-1: Polymer Chemistry*, 1967, **5**, 2259-2268.