Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Unsaturated Sulfur-Containing Polymers from Modular Alcohol Click Chemistry

Ziheng Liu, [a]Chengjian Zhang* [a] and Xinghong Zhang*[a, b, c]

a, MOE Key Laboratory of Macromolecular Synthesis and Functionalization, International Research Center for X Polymers, Department of Polymer Science and Engineering, Zhejiang University
Hangzhou 310027 (China)
E-mail: chengjian.zhang@zju.edu.cn (C. Zhang); xhzhang@zju.edu.cn (X. Zhang)
b, Center of Chemistry for Frontier Technologies, Zhejiang University
Hangzhou 310027 (China)
c, Shanxi-Zheda Institute of Advanced Materials and Chemical Engineering
Hangzhou 310027 (China)

Corresponding authors (*): chengjian.zhang@zju.edu.cn (Chengjian Zhang);

xhzhang@zju.edu.cn (Xinghong Zhang)

Table of Contents

Materials and methods

Materials

COS(APK(Shanghai) Gas Co., Ltd) was used as received. Methyl propiolate, ethyl propiolate, 3-butyn-2-one, 4-phenyl-3-butyn-2-one, 2-propynenitrile, methanol, ethanol, 1-propanol, isopropanol, and tert-butanol, N-Boc-4-piperidinemethanol, ethyl glycolate, 4-bromophenethyl alcohol, furfuryl alcohol, m-anisyl alcohol, 2-methyl-1,3-butanediol, 1,4-butanediol, 3-methyl-1,5-pentanediol, 1,6-hexanediol, 2-ethyl-1,3-hexanediol, 1,2-cyclohexanediol, 1,4-cyclohexanedimethanol, 1,4-benzenedimethanol, 1,10-decanediol, 1,5-diazabicyclo(5,4,0)undec-5-ene(DBU), 4-dimethylaminopyridine (DMAP), N,N,N',N'-tetraethylethylenediamine (TEEDA), tetrabutylammonium chloride (TBACl), bis(triphenylphosphine)iminium chloride (PPNCl), potassium tert-butoxide (t-BuOK), tri-tert-butylphosphine (t-Bu_3P) and tributylphosphine (n-Bu_3P) were bought from Tokyo Chemical Industry Co., Ltd and were used as received. 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) was bought from Sigma-Aldrich LLC and used as received.

Experimental details for the reaction of alcohols, COS and ynes

All syntheses were carried out in an argon-filled glovebox. A 10 mL reaction vessel with a magnetic stirrer was dried in an oven at 120 °C overnight and transferred into the glovebox immediately. The reaction below is taken from **1** as an example. Methyl propiolate 0.36 mL (4.05 mmol), methanol 0.16 mL (3.95 mmol) and 12 μL DBU (0.0821 mmol) were added to the reaction tube successively, then filled with COS 260-280 mg (4.33-4.67 mmol). The COS gas is inflated into vessels through the gas cylinder. Since the pressure of COS is not obvious on the pressure gauge with a range of 1-5 MPa, and in order to accurately control the amount of COS, we use the method of weighing the vessels before and after inflation to add a certain amount of COS gas. In order to avoid the direct reaction of methanol and methyl propiolate, methanol and DBU were firstly add in a 2 mL spawn bottle, after the COS was added, shake and rotate the vessel to mix the reactant. The reaction vessel was stirred at 25 °C for 2h. After reaction, the crude product was purified through a silica gel column without eluent. The obtained precipitate was collected and dried under vacuum.

Experimental details for the synthesis of HDP

4.73 g of 1,6-hexanediol (40.0 mmol), 0.138g of p-toluenesulfonic acid (0.801 mmol), 6.40 g of propynoic acid (91.3 mmol), and 100 mL of toluene were successively added to a 250 mL round-bottom flask. The mixture was refluxed with a Dean-Stark trap and a Allihn condenser at 120 °C for 8 hours. Afterward, the toluene was removed by rotary evaporation to obtain crude product. The crude product was first washed with water and then dried over anhydrous magnesium sulfate. Subsequently, it was purified through a silica gel column using ethyl acetate: n-hexane = 1:10 as the eluent. Finally, the eluent was removed by rotary evaporation to obtain HDP 8.17 g (91.9%).

Experimental details for the synthesis of EHDP

5.85 g of 2-ethyl-1,3-hexanediol (40.0 mmol), 0.138g of p-toluenesulfonic acid (0.801 mmol), 6.40 g of propynoic acid (91.3 mmol), and 100ml of toluene were successively added to a 250 mL round-bottom flask. The mixture was refluxed with a Dean-Stark trap and a Allihn condenser at 120 ℃ for 8 hours. Afterward, the toluene was removed by rotary evaporation to obtain crude product. The crude product was first washed with water and then dried over anhydrous magnesium sulfate. Subsequently, it was purified through a silica gel column using ethyl acetate: n-hexane = 1:20 as the eluent. Finally, the eluent was removed by rotary evaporation to obtain EHDP 7.31 g (73.0%).

Experimental details for the copolymerization of diols, COS and dipropiolates

All syntheses were carried out in an argon-filled glovebox. A 10 mL reaction vessel with a magnetic stirrer was dried in an oven at 120 °C overnight and transferred into the glovebox immediately. The copolymerization below is taken from **P4** as an example. **HDP** (4.10 mmol), 1,6-Hexanediol (4.01 mmol), MeCN (1 mL) and DBU (0.0821 mmol) were added to the reaction tube successively, then filled with COS (8.15 mmol). The reaction vessel was stirred at 60 °C for 12 h. After polymerization, the crude product was dissolved in dichloromethane and precipitated into ethanol three times. The obtained precipitate was collected and dried under vacuum.

Characterization methods

The molecular weights and molecular weight distributions of polymers were determined with a PL-GPC220 chromatograph (Polymer Laboratories Ltd) equipped with an HP 1100pump from Agilent Technologies. The GPC columns were eluted with THF at 1.0 ml/min at 35 °C. The sample concentration was 0.4 wt. % and the injection volume was 50 μL. Calibration was performed using monodisperse polystyrene standards covering the molecular weight range from 580 to 460 000 Da.

^1H and ^{13}C NMR spectra of the products were obtained on a Bruker Advance DMX 400 MHz spectrometer. Chemical shift values were referenced to $CHCl_3$ as internal standard at 7.26 ppm or TMS as internal standard at 0 ppm for ^1H NMR (400 MHz) and against $CDCl_3$ at 77.16 ppm for ^{13}C NMR (100 MHz).

The decomposition temperature (T_d) of the polymers were determined by using TA Q50 instrument. The sample was heated from 40 to 400 °C at a rate of 10 °C/min under nitrogen atmosphere. Temperature when the mass loss is five percent was taken as $T_{d,5\%}$.

Differential scanning calorimetry (DSC) was taken on a DSCQ200 equipped with a liquid nitrogen cooling system. 3~5 mg of samples was placed in aluminum pans. The cooling and heating rates were 10 °C/min.

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometric measurements (MALDI-TOF-MS) were performed on a Bruker Ultraflex MALDI TOF mass spectrometer, equipped with a nitrogen laser delivering 3 ns laser pulses at 337nm. 2,5-dihydroxy benzoic acid (DHB) was used as matrix. Sodium trifluoroacetate was added for ion formation.

General Procedure for DBU-Catalyzed Alcohol-COS-Alkyne Reactions

The general procedure for **1** was followed using methyl propiolate (0.36 mL, 4.05 mmol, 1.0 equiv), methanol (0.16 ml, 3.95 mmol, 1.0 equiv), COS (260 mg, 4.3 mmol, 1.1 equiv), DBU (12 μL, 0.08 mmol, 0.02 equiv) at 25 °C for 2 h. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, J = 16.1 Hz, 1H), 7.69 (d, J = 10.2 Hz, 1H), 6.07 (d, J = 10.2 Hz, 1H), 6.06 (d, J = 16.1 Hz, 1H), 3.89 (s, 3H), 3.73 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.77, 166.45, 166.23, 164.26, 139.97, 139.13, 119.51, 116.48, 60.72, 54.90.

The general procedure for **2** was followed using methyl propiolate (0.36 mL, 4.05 mmol, 1.0 equiv), ethanol (0.24 ml, 4.11 mmol, 1.0 equiv), COS (260 mg, 4.3 mmol, 1.1 equiv), DBU (12 μL, 0.08 mmol, 0.02 equiv) at 25 °C for 2 h. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, J = 16.1 Hz, 1H), 7.71 (d, J = 10.2 Hz, 1H), 6.10 (d, J = 10.2 Hz, 1H), 6.09 (d, J = 16.1 Hz, 1H), 4.37 (q, J = 7.1 Hz, 2H), 3.77 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.16, 166.88, 140.75, 139.98, 118.90, 115.99, 65.19, 64.79, 51.92, 14.39.

The general procedure for **3** was followed using methyl propiolate (0.36 mL, 4.05 mmol, 1.0 equiv),1-propanol (0.30 ml, 4.11 mmol, 1.0 equiv), COS (260 mg, 4.3 mmol, 1.1 equiv), DBU (12 μL, 0.08 mmol, 0.02 equiv) at 25 °C for 2 h. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, J = 16.1 Hz, 1H), 7.62 (d, J = 10.2 Hz, 1H), 6.01 (d, J = 10.2 Hz, 1H), 6.00 (d, J = 16.1 Hz, 1H), 4.19 (t, J = 6.6 Hz, 2H), 3.67 (s, 3H), 1.65 (tq, J_1 = 6.6 Hz, J_2 = 7.4 Hz 2H), 0.87 (t, J = 7.4 Hz, 3H) ; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.90, 166.56, 165.64, 164.64, 140.50, 139.71, 118.63, 115.73, 70.35, 69.94, 51.60, 21.92, 10.06.

The general procedure for **4** was followed using methyl propiolate (0.36 mL, 4.05 mmol, 1.0 equiv), 2-propanol (0.31 ml, 4.08 mmol, 1.0 equiv), COS (260 mg, 4.3 mmol, 1.1 equiv), DBU (12 μL, 0.08 mmol, 0.02 equiv) at 25 °C for 2 h. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, J = 16.1 Hz, 1H), 7.67 (d, J = 10.2 Hz, 1H), 6.04 (d, J = 10.2 Hz, 1H), 6.02 (d, J = 16.1 Hz, 1H), 5.16 (sept, J = 6.3 Hz, 1H), 3.72 (s, 3H), 1.28 (d, J = 6.3 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.33, 166.72, 165.10, 164.87, 140.81, 118.52, 115.70, 73.75, 73.19, 51.74, 21.81..

The general procedure for **5** was followed using ethyl propiolate (0.41 mL, 4.05 mmol, 1.0 equiv), methanol (0.16 ml, 3.95 mmol, 1.0 equiv), COS (260 mg, 4.3 mmol, 1.1 equiv), DBU (12 μL, 0.08 mmol, 0.02 equiv) at 25 °C for 2 h. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 16.1 Hz, 1H), 7.63 (d, *J* = 10.2 Hz, 1H), 6.01 (d, *J* = 10.2 Hz, 1H), 6.00 (d, *J* = 16.1 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 3H), 1.24 (q, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.73, 166.43, 166.26, 164.28, 139.95, 139.03, 119.49, 116.47, 60.77, 54.90, 14.21.

The general procedure for **6** was followed using ethyl propiolate (0.41 mL, 4.05 mmol, 1.0 equiv), ethanol (0.24 ml, 4.11 mmol, 1.0 equiv), COS (260 mg, 4.3 mmol, 1.1 equiv), DBU (12 μL, 0.08 mmol, 0.02 equiv) at 25 °C for 2 h. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 16.1 Hz, 1H), 7.71 (d, *J* = 10.2 Hz, 1H), 6.08 (d, *J* = 10.2 Hz, 1H), 6.07 (d, *J* = 16.1 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 4.16 (q, *J* = 7.2 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.31 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.99, 166.21, 165.72, 164.29, 140.12, 139.31, 119.21, 116.26, 64.96, 64.53, 60.68, 14.19.

The general procedure for **7** was followed using ethyl propiolate (0.41 mL, 4.05 mmol, 1.0 equiv), 1-propanol (0.30 ml, 4.11 mmol, 1.0 equiv), COS (260 mg, 4.3 mmol, 1.1 equiv), DBU (12 μL, 0.08 mmol, 0.02 equiv) at 25 °C for 2 h. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 16.1 Hz, 1H), 7.69 (d, *J* = 10.2 Hz, 1H), 6.03 (d, *J* = 10.2 Hz, 1H), 6.02 (d, *J* = 16.1 Hz, 1H), 4.22 (t, *J* = 6.6 Hz, 2H), 4.16 (q, *J* = 7.2 Hz, 2H), 1.65 (tq, J_1 = 6.6 Hz, J_2 = 7.4 Hz 2H), 1.24 (t, *J* = 7.2 Hz, 3H) 0.91 (t, *J* = 7.4 Hz, 3H) ; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.09, 166.23, 165.82, 164.29, 140.17, 139.37, 119.20, 116.25, 70.36, 69.96, 62.25, 60.63, 21.97, 14.19, 10.13.

The general procedure for **8** was followed using ethyl propiolate (0.41 mL, 4.05 mmol, 1.0 equiv), 2-propanol (0.31 ml, 4.08 mmol, 1.0 equiv), COS (260 mg, 4.3 mmol, 1.1 equiv), DBU (12 μL, 0.08 mmol, 0.02 equiv) at 25 °C for 2 h. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 16.1 Hz, 1H), 7.69 (d, *J* = 10.2 Hz, 1H), 6.05 (d, *J* = 10.2 Hz, 1H), 6.04 (d, *J* = 16.1 Hz, 1H), 5.20 (sept, *J* = 6.3 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 1.30 (d, *J* = 6.3 Hz, 6H), 1.26 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.54, 166.40, 165.31, 164.54, 140.49, 139.81, 119.13, 116.26, 73.78, 73.21, 60.82, 21.90, 14.36.

The general procedure for **9** was followed using 3-butyn-2-one (0.31 mL, 4.0 mmol, 1.0 equiv), methanol (0.16 ml, 3.95 mmol, 1.0 equiv), COS (260 mg, 4.3 mmol, 1.1 equiv), DBU (12 μL, 0.08 mmol, 0.02 equiv) at 25 °C for 2 h. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 16.5 Hz, 1H), 7.69 (d, *J* = 9.8 Hz, 1H), 6.53 (d, *J* = 9.8 Hz, 1H), 6.35 (d, *J* = 16.5 Hz, 1H), 3.91 (s, 3H), 2.28 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.40, 195.16, 169.98, 166.61, 138.99, 122.57, 55.43, 55.00, 30.39.

The general procedure for **10** was followed using 3-butyn-2-one (0.31 mL, 4.0 mmol, 1.0 equiv), ethanol (0.24 ml, 4.11 mmol, 1.0 equiv), COS (260 mg, 4.3 mmol, 1.1 equiv), DBU (12 μL, 0.08 mmol, 0.02 equiv) at 25 °C for 2 h. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, J = 16.5 Hz, 1H), 7.66 (d, J = 9.8 Hz, 1H), 6.50 (d, J = 9.8 Hz, 1H), 6.31 (d, J = 16.5 Hz, 1H), 4.33 (q, J = 7.1 Hz, 2H), 2.26 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.37, 195.24, 169.26, 165.94, 139.52, 139.23, 128.29, 122.43, 65.28, 64.65, 30.39, 27.04, 14.34.

The general procedure for **11** was followed using 3-butyn-2-one (0.31 mL, 4.0 mmol, 1.0 equiv), 1-propanol (0.30 ml, 4.11 mmol, 1.0 equiv), COS (260 mg, 4.3 mmol, 1.1 equiv), DBU (12 μL, 0.08 mmol, 0.02 equiv) at 25 °C for 2 h. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, J = 16.5 Hz, 1H), 7.67 (d, J = 9.8 Hz, 1H), 6.51 (d, J = 9.8 Hz, 1H), 6.33 (d, J = 16.5 Hz, 1H), 4.25 (t, J = 6.6 Hz, 2H), 2.26 (s, 3H), 1.63 (tq, J_1 = 6.6 Hz, J_2 = 7.4 Hz 2H), 0.94 (t, J = 7.4 Hz, 3H) ; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.35, 195.19, 169.32, 166.02, 139.24, 128.27, 122.41, 70.66, 70.07, 30.37, 27.02, 22.08, 10.28.

The general procedure for **12** was followed using 3-butyn-2-one (0.31 mL, 4.0 mmol, 1.0 equiv), 2-propanol (0.31 ml, 4.08 mmol, 1.0 equiv), COS (260 mg, 4.3 mmol, 1.1 equiv), DBU (12 μL, 0.08 mmol, 0.02 equiv) at 25 °C for 2 h. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, J = 16.5 Hz, 1H), 7.69 (d, J = 9.8 Hz, 1H), 6.51 (d, J = 9.8 Hz, 1H), 6.33 (d, J = 16.5 Hz, 1H), 5.19 (sept, J = 6.3 Hz, 1H), 2.26 (s, 3H), 1.32 (t, J = 6.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.27, 168.50, 139.82, 139.40, 128.04, 122.19, 73.93, 73.08, 30.31, 21.79.

The general procedure for **13** was followed using 4-phenyl-3-butyn-2-one (0.58 mL, 4.0 mmol, 1.0 equiv), methanol (0.16 ml, 3.95 mmol, 1.0 equiv), COS (260 mg, 4.3 mmol, 1.1 equiv), DBU (12 μL, 0.08 mmol, 0.02 equiv) at 25 °C for 2 h. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56-7.38 (Ar, 5H), 6.75 (s, 1H), 3.73 (s, 3H), 3.65 (s, 3H), 2.34 (s, 3H),1.88 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.45, 196.54, 167.34, 167.26, 145.12, 144.21, 139.90, 137.20, 54.62, 54.52, 31.11, 30.17.

The general procedure for **14** was followed using 4-phenyl-3-butyn-2-one (0.58 ml, 4.0 mmol, 1.0 equiv), ethanol (0.24 ml, 4.11 mmol, 1.0 equiv), COS (260 mg, 4.3 mmol, 1.1 equiv), DBU (12 μL, 0.08 mmol, 0.02 equiv) at 25 °C for 2 h. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56-

7.38 (Ar, 5H), 6.75 (s, 1H), 4.19 (q, J = 7.0 Hz, 2H), 4.10 (q, J = 7.1 Hz, 2H), 2.36 (s, 3H),1.88 (s, 3H), 1.23(t, J = 7.0 Hz, 3H), 1.13(t, J = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.52, 196.54, 166.62, 145.61, 144.62, 140.11, 137.32, 134.62, 64.15, 31.10, 14.01.

The general procedure for **15** was followed using 4-phenyl-3-butyn-2-one (0.58 ml, 4.0 mmol, 1.0 equiv), 1-propanol (0.30 ml, 4.11 mmol, 1.0 equiv), COS (260 mg, 4.3 mmol, 1.1 equiv), DBU (12 µL, 0.08 mmol, 0.02 equiv) at 25 °C for 2 h. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56-7.38 (Ar, 5H), 6.75 (s, 1H), 4.08 (t, J = 6.6 Hz, 2H), 4.00 (t, J = 6.6 Hz, 2H), 2.36 (s, 3H),1.88 (s, 3H),2.26 (s, 3H), 1.58 (tq, J_1 = 6.6 Hz, J_2 = 7.4 Hz, 2H), 1.51 (tq, J_1 = 6.6 Hz, J_2 = 7.4 Hz, 2H), 0.86 (t, J = 7.4 Hz, 3H), 0.83 (t, J = 7.4 Hz, 3H) ; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.52, 196.55, 166.73, 145.58, 144.60, 140.09, 137.33, 134.66, 69.80, 69.63, 31.11, 30.18, 21.86, 10.16.

The general procedure for **16** was followed using 4-phenyl-3-butyn-2-one (0.58 ml, 4.0 mmol, 1.0 equiv), 2-propanol (0.31 ml, 4.08 mmol, 1.0 equiv), COS (260 mg, 4.3 mmol, 1.1 equiv), DBU (12 µL, 0.08 mmol, 0.02 equiv) at 25 °C for 2 h. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56-7.38 (Ar, 5H), 6.73 (s, 1H), 6.71 (s, 1H), 4.98 (sept, J = 6.3 Hz, 1H), 4.87 (sept, J = 6.3, Hz, 1H), 2.35 (s, 3H),1.88 (s, 3H),2.26 (s, 3H), 1.16 (d, J = 6.3 Hz, 6H), 1.08 (d, J = 6.3 Hz, 6H) ; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.61, 196.54, 166.05, 146.14, 145.08, 140.34, 137.47, 134.27, 72.93, 72.64, 31.12, 30.20, 21.65, 21.54.

The general procedure for **17** was followed using 4-phenyl-3-butyn-2-one (0.509 g, 4.0 mmol, 1.0 equiv), methanol (0.16 ml, 3.95 mmol, 1.0 equiv), COS (260 mg, 4.3 mmol, 1.1 equiv), DBU (12 µL, 0.08 mmol, 0.02 equiv) at 25 °C for 2 h. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97-7.39 (Ar, 5H), 6.07 (s, 1H), 3.80 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.73, 152.50, 136.82, 115.76, 105.58, 55.37.

The general procedure for **18** was followed using 4-phenyl-3-butyn-2-one (0.509 g, 4.0 mmol, 1.0 equiv), ethanol (0.24 ml, 4.11 mmol, 1.0 equiv), COS (260 mg, 4.3 mmol, 1.1 equiv), DBU (12 µL, 0.08 mmol, 0.02 equiv) at 25 °C for 2 h. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97-7.39 (Ar, 5H), 6.04 (s, 1H), 4.22 (q, J = 7.1 Hz, 2H), 1.23 (t J = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.96, 152.82, 136.93, 131.19, 128.94, 127.43, 115.78, 105.14, 65.17, 14.09.

The general procedure for **19** was followed using 4-phenyl-3-butyn-2-one (0.509 g, 4.0 mmol, 1.0 equiv), 1-propanol (0.30 ml, 4.11 mmol, 1.0 equiv), COS (260 mg, 4.3 mmol, 1.1

equiv), DBU (12 μL, 0.08 mmol, 0.02 equiv) at 25 °C for 2 h. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97-7.39 (Ar, 5H), 6.04 (s, 1H), 4.14 (t, J = 6.6 Hz, 2H), 1.60 (tq, J_1 = 6.6 Hz, J_2 = 7.4 Hz, 2H), 0.88 (t, J = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.13, 152.90, 137.00, 131.25, 129.00, 127.48, 115.82, 105.18, 70.66, 21.96, 10.20.

The general procedure for **20** was followed using 4-phenyl-3-butyn-2-one (0.509 g, 4.0 mmol, 1.0 equiv), 2-propanol (0.31 ml, 4.08 mmol, 1.0 equiv), COS (260 mg, 4.3 mmol, 1.1 equiv), DBU (12 μL, 0.08 mmol, 0.02 equiv) at 25 °C for 2 h. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97-7.39 (Ar, 5H), 6.01 (s, 1H), 5.13 (sept, J = 6.3 Hz, 1H), 5.01 (sept, J = 6.3 Hz, 1H), 1.29 (d, J = 6.3 Hz, 6H), 1.19 (d, J = 6.3 Hz, 6H).

The general procedure for **21** was followed using 4-phenyl-3-butyn-2-one (0.509 g, 4.0 mmol, 1.0 equiv), *tert*-butanol (0.38 ml, 3.97 mmol, 1.0 equiv), COS (260 mg, 4.3 mmol, 1.1 equiv), DBU (12 μL, 0.08 mmol, 0.02 equiv) at 25 °C for 2 h. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97-7.39 (Ar, 5H), 6.00 (s, 1H), 1.38 (s, 9H).

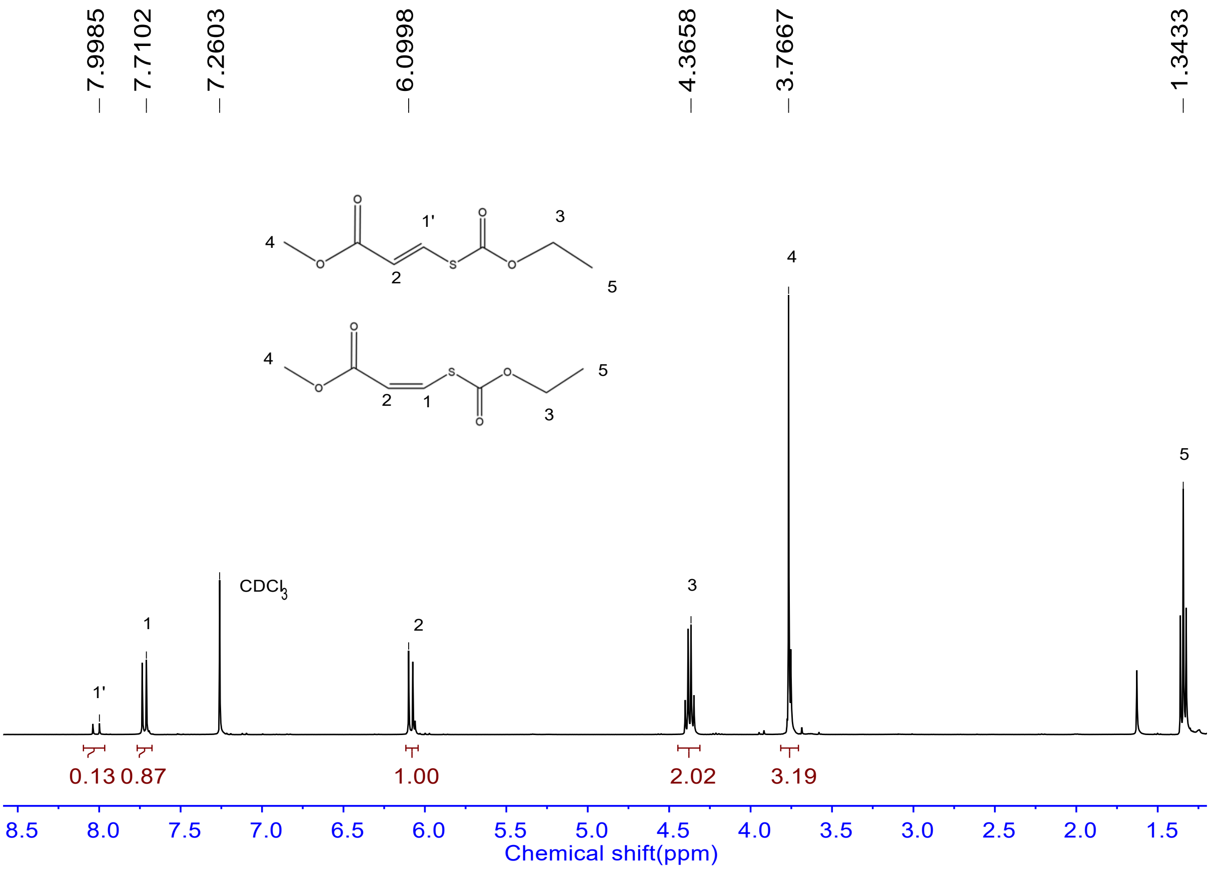

Figure S1. ^{1}H NMR spectrum of the purified **2** (in **Figure 2**).

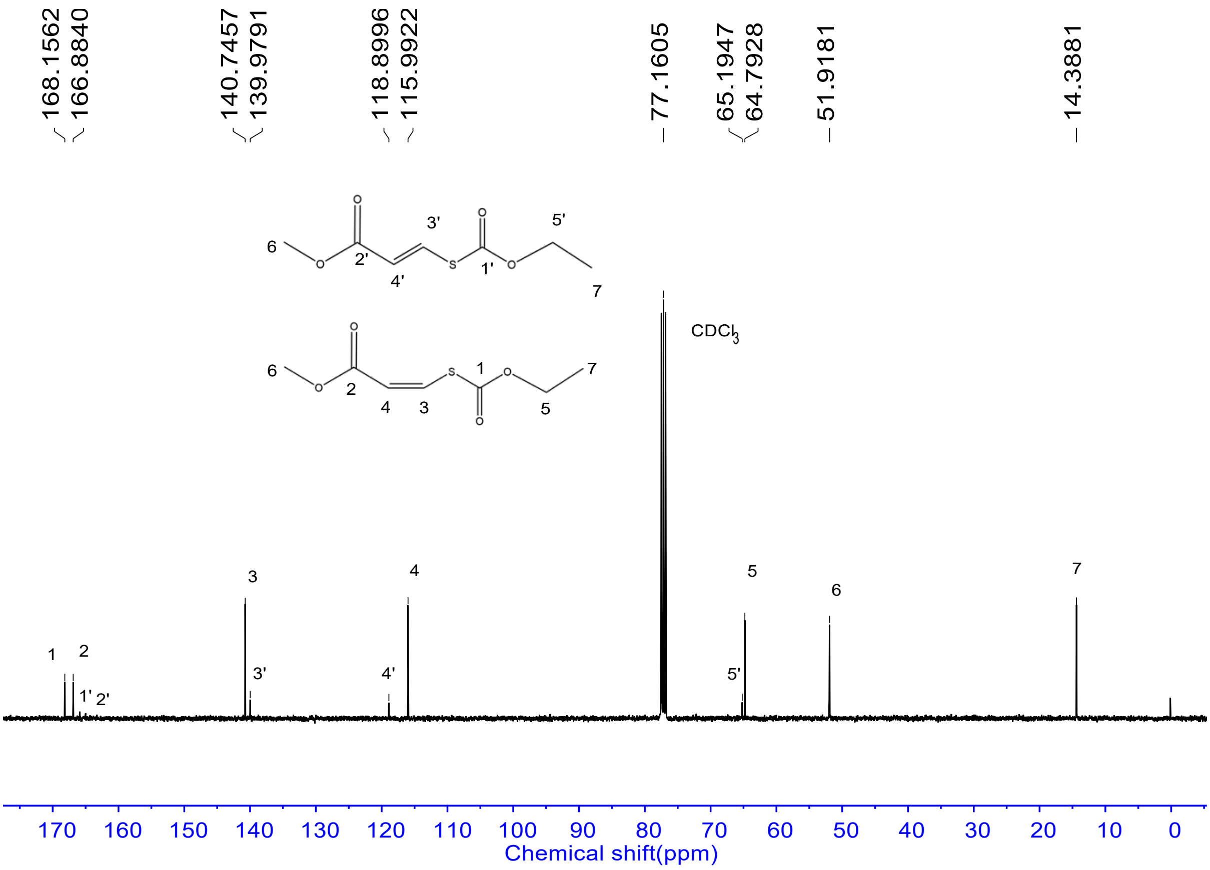

Figure S2. ^{13}C NMR spectrum of the purified **2** (in **Figure 2**).

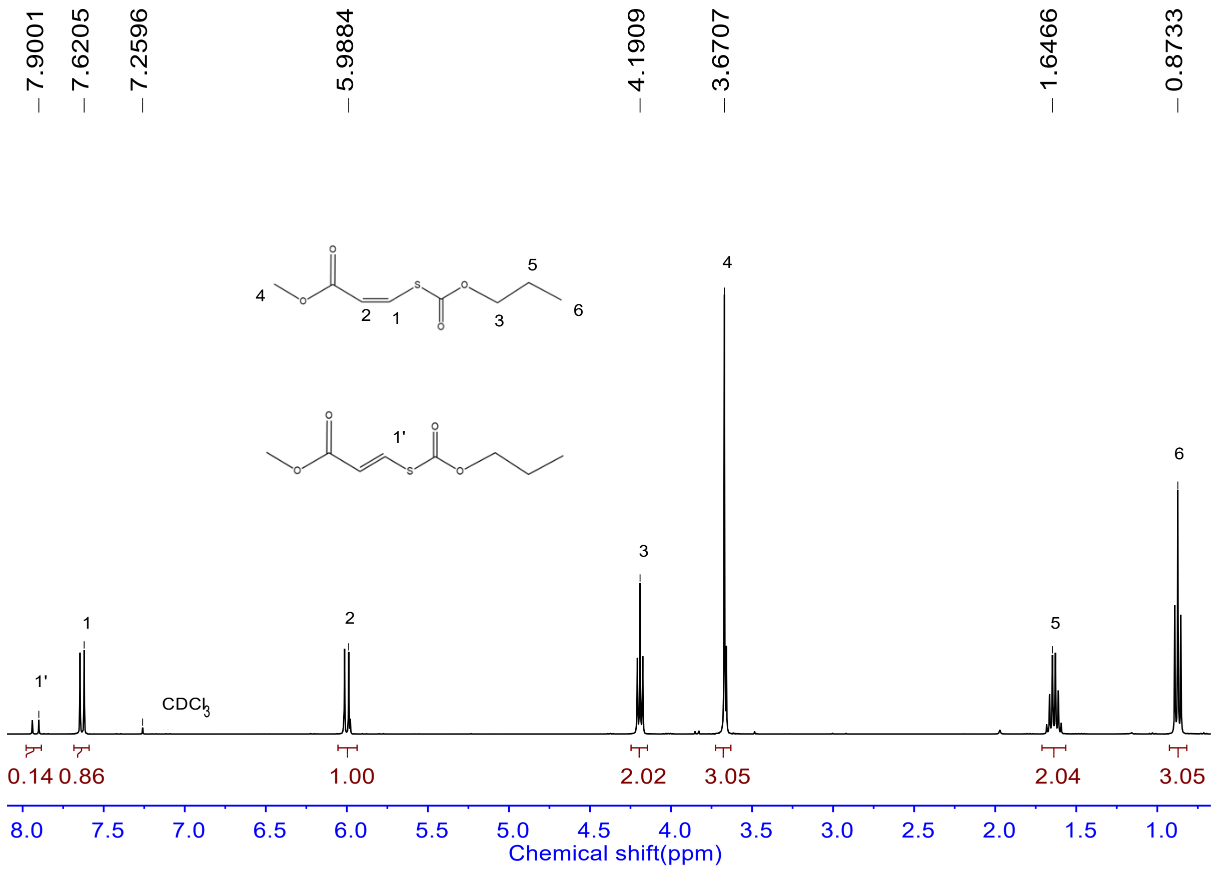

Figure S3. ^{1}H NMR spectrum of the purified **3** (in **Figure 2**).

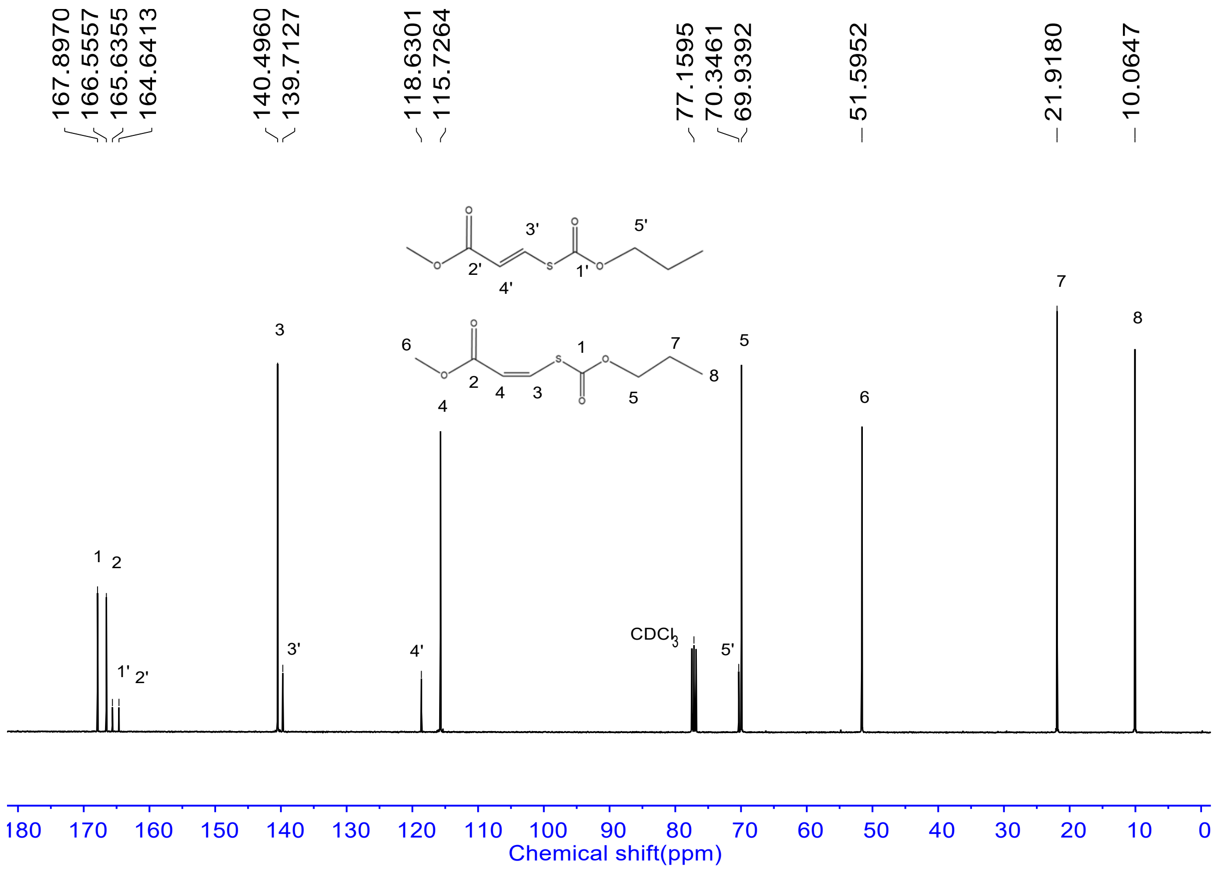

Figure S4. ^{13}C NMR spectrum of the purified **3** (in **Figure 2**).

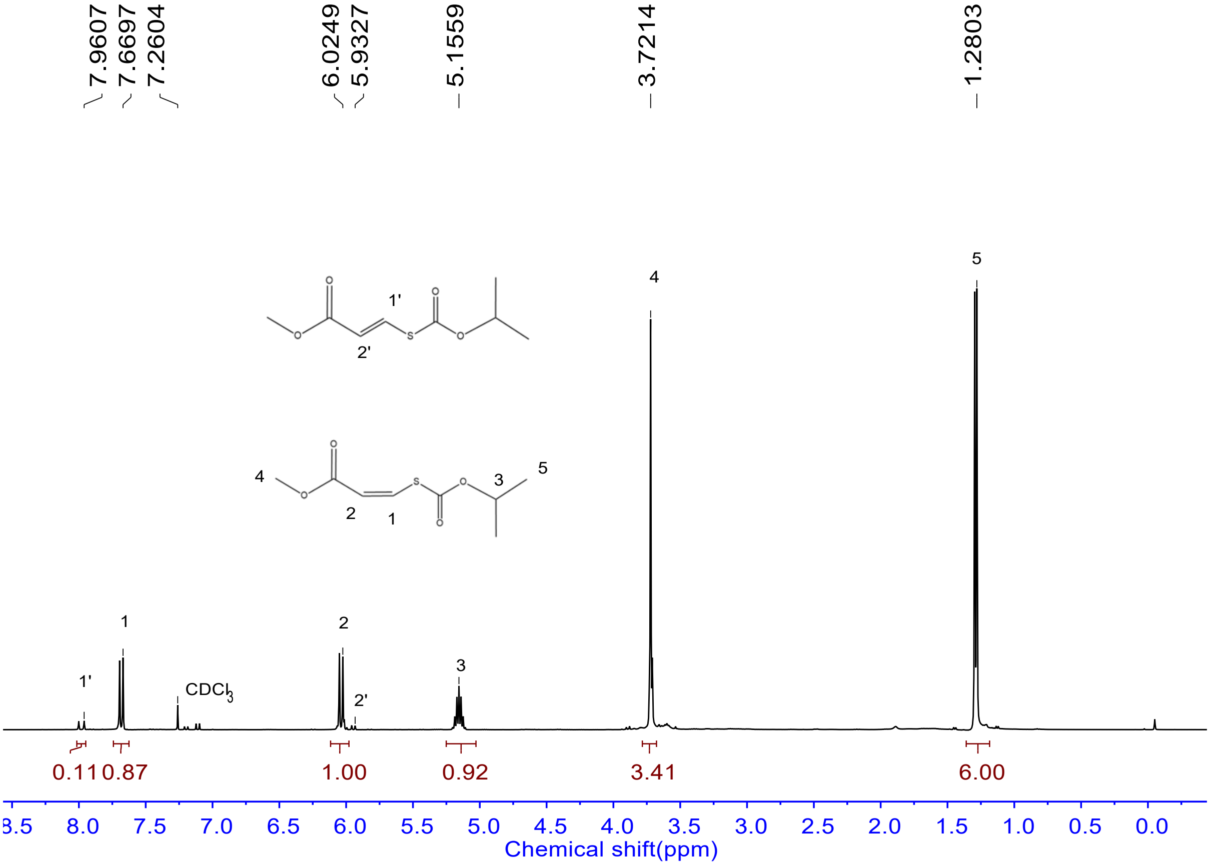

Figure S5. ^{1}H NMR spectrum of the purified **4** (in **Figure 2**).

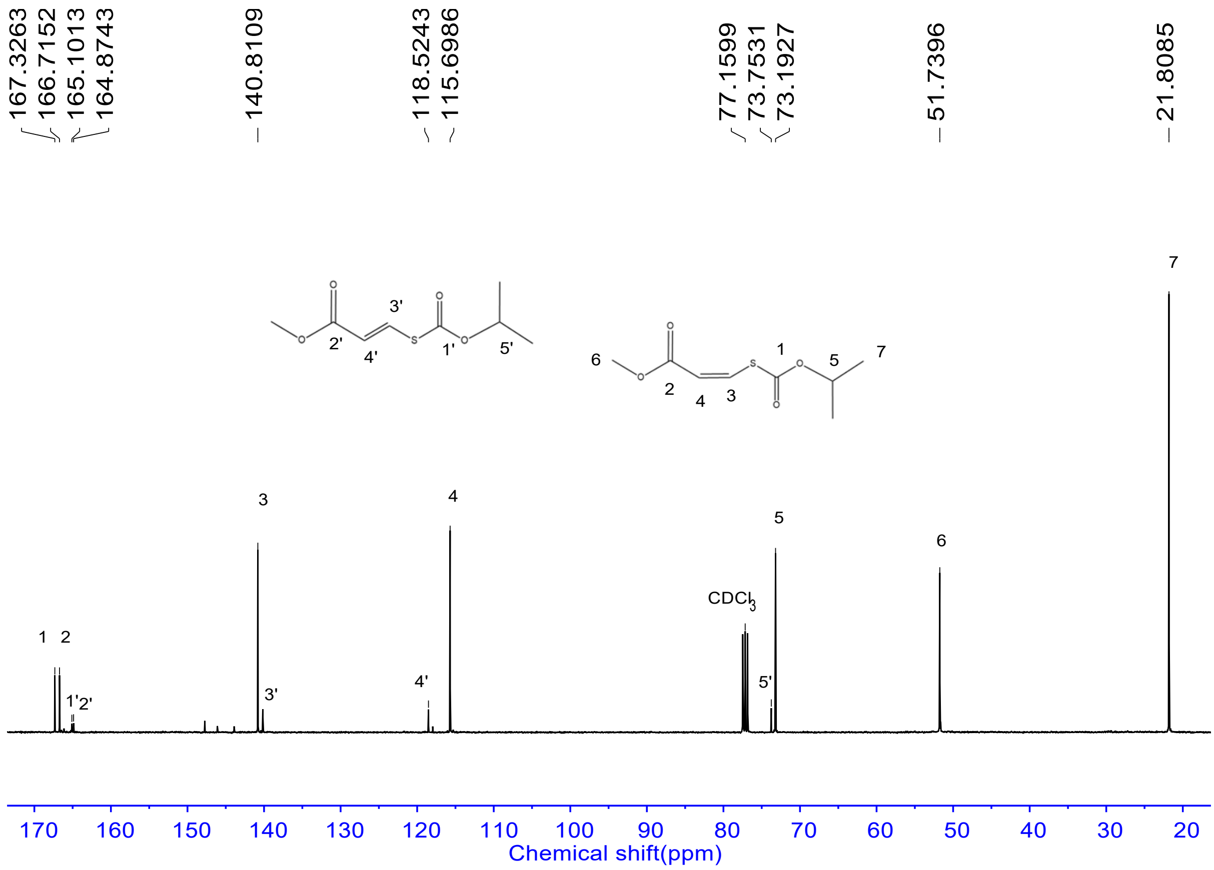

Figure S6. ^{13}C NMR spectrum of the purified **4** (in **Figure 2**).

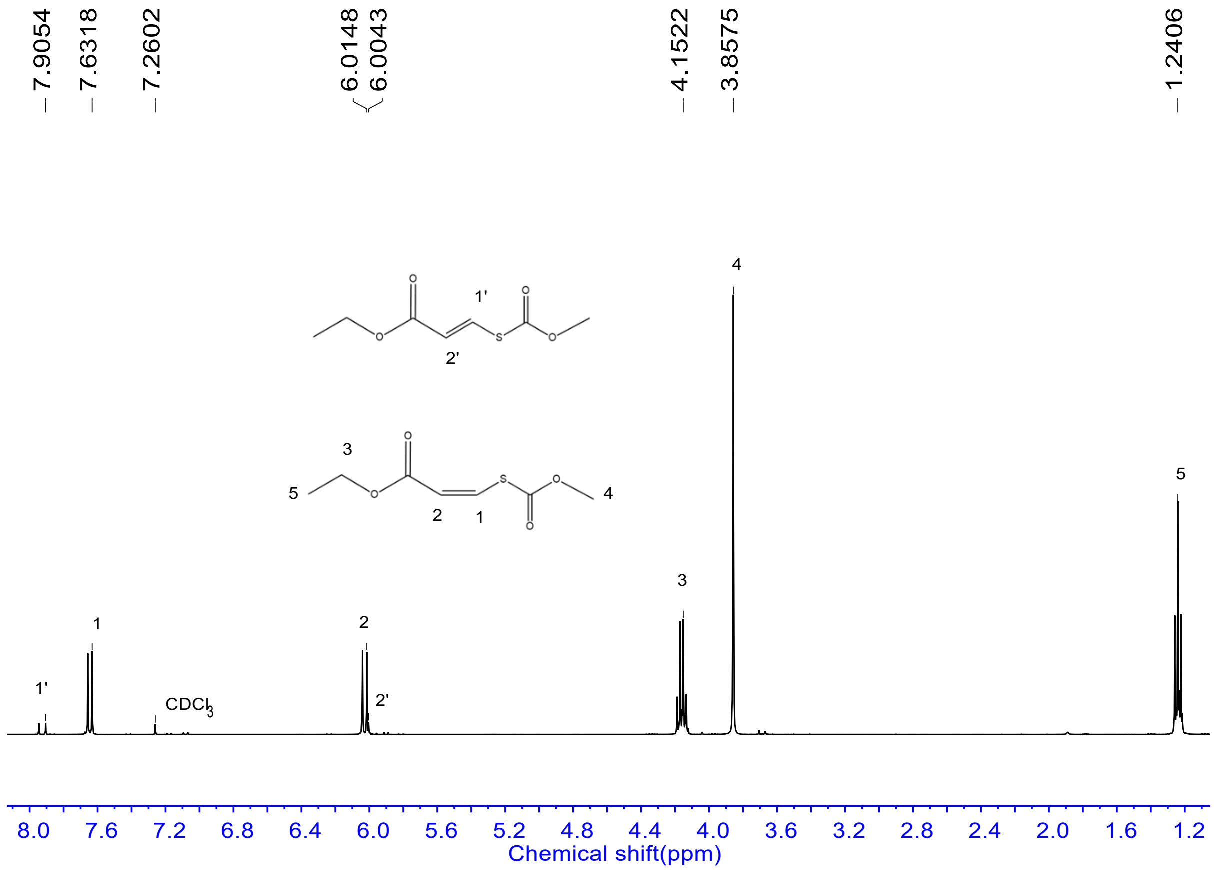

Figure S7. ^{1}H NMR spectrum of the purified **5** (in **Figure 2**).

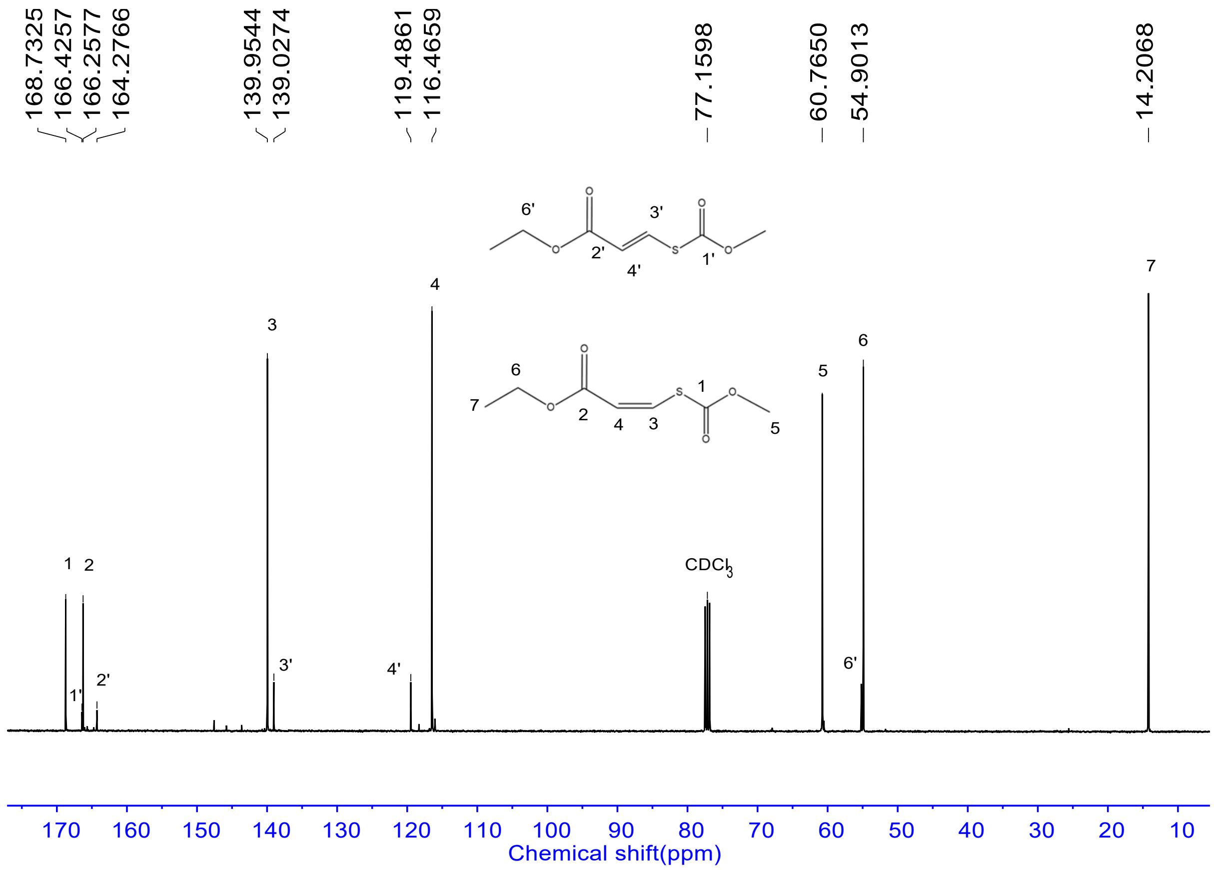

Figure S8. ^{13}C NMR spectrum of the purified **5** (in **Figure 2**).

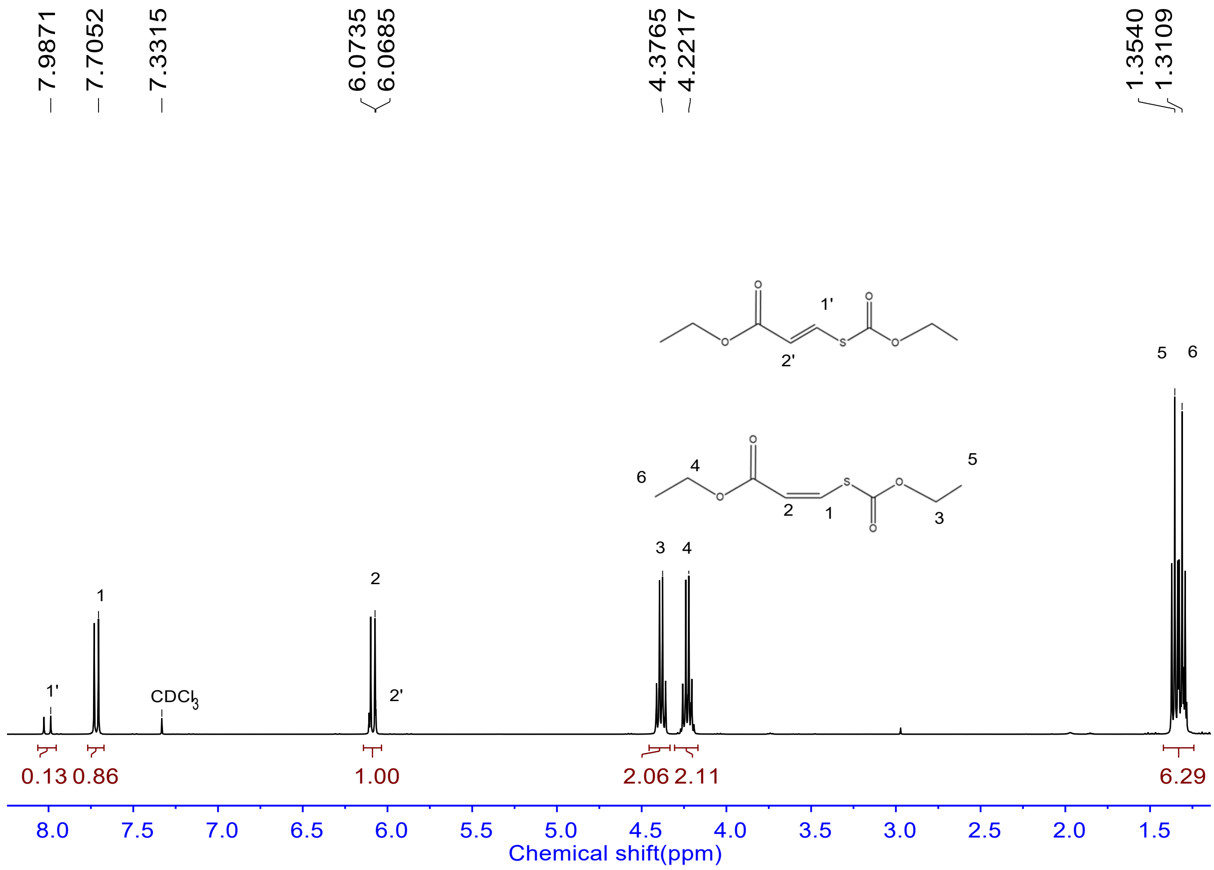

Figure S9. ^{1}H NMR spectrum of the purified **6** (in **Figure 2**).

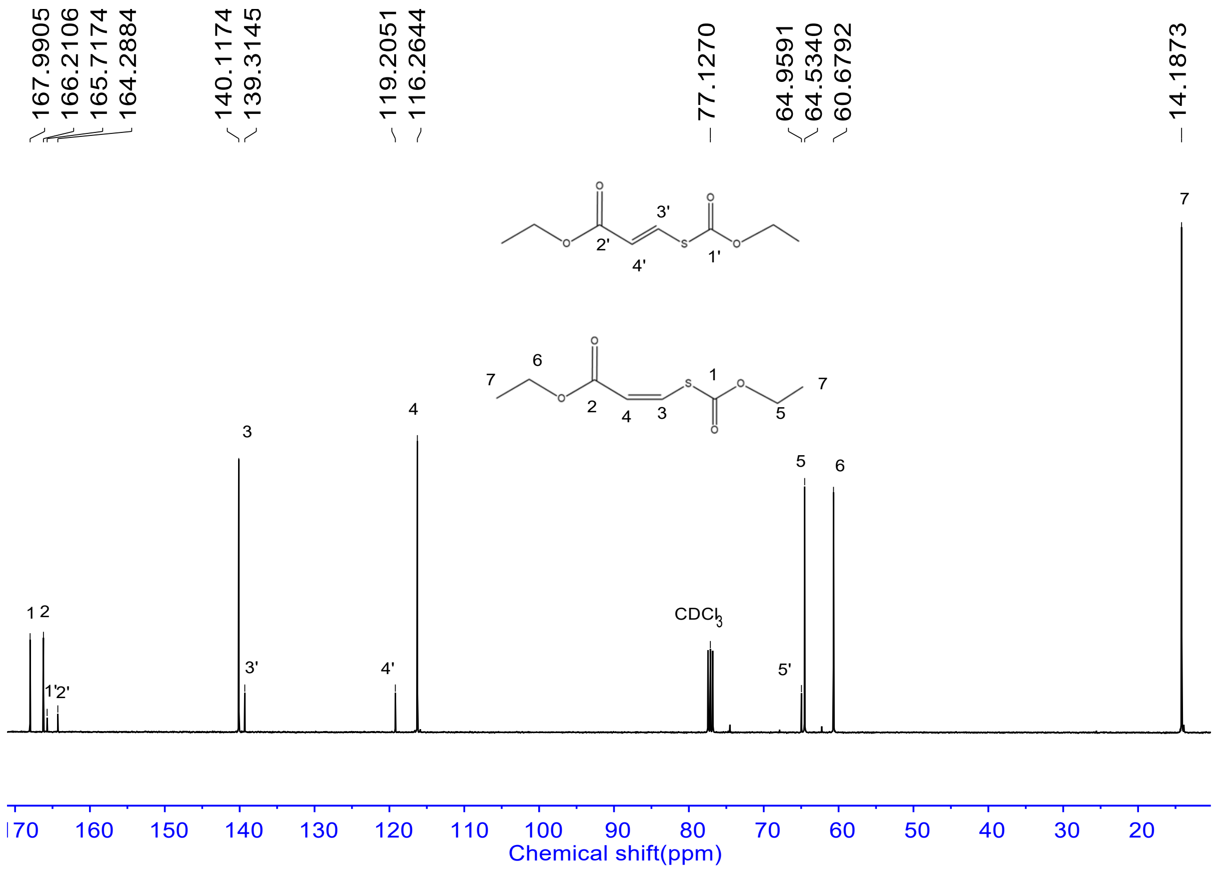

Figure S10. ^{13}C NMR spectrum of the purified **6** (in **Figure 2**).

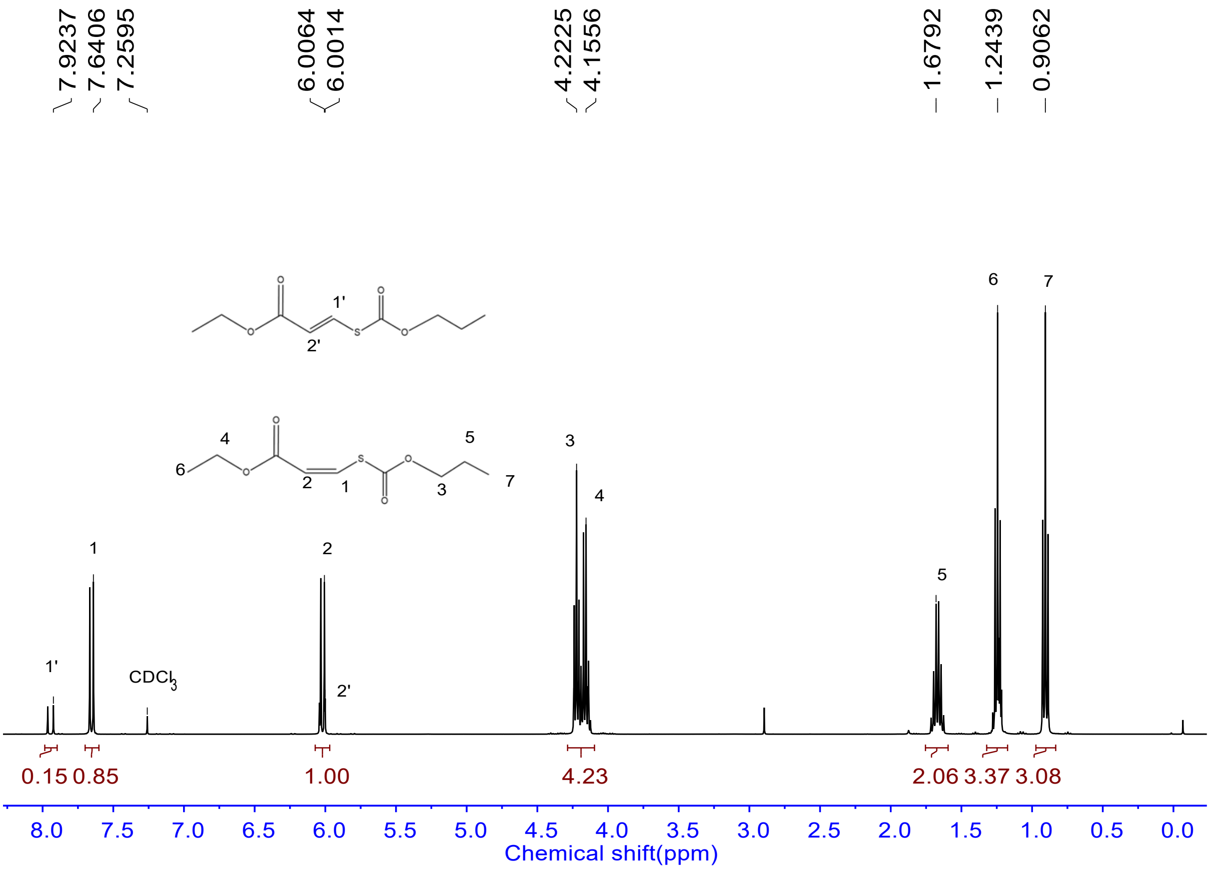

Figure S11. ^{1}H NMR spectrum of the purified **7** (in **Figure 2**).

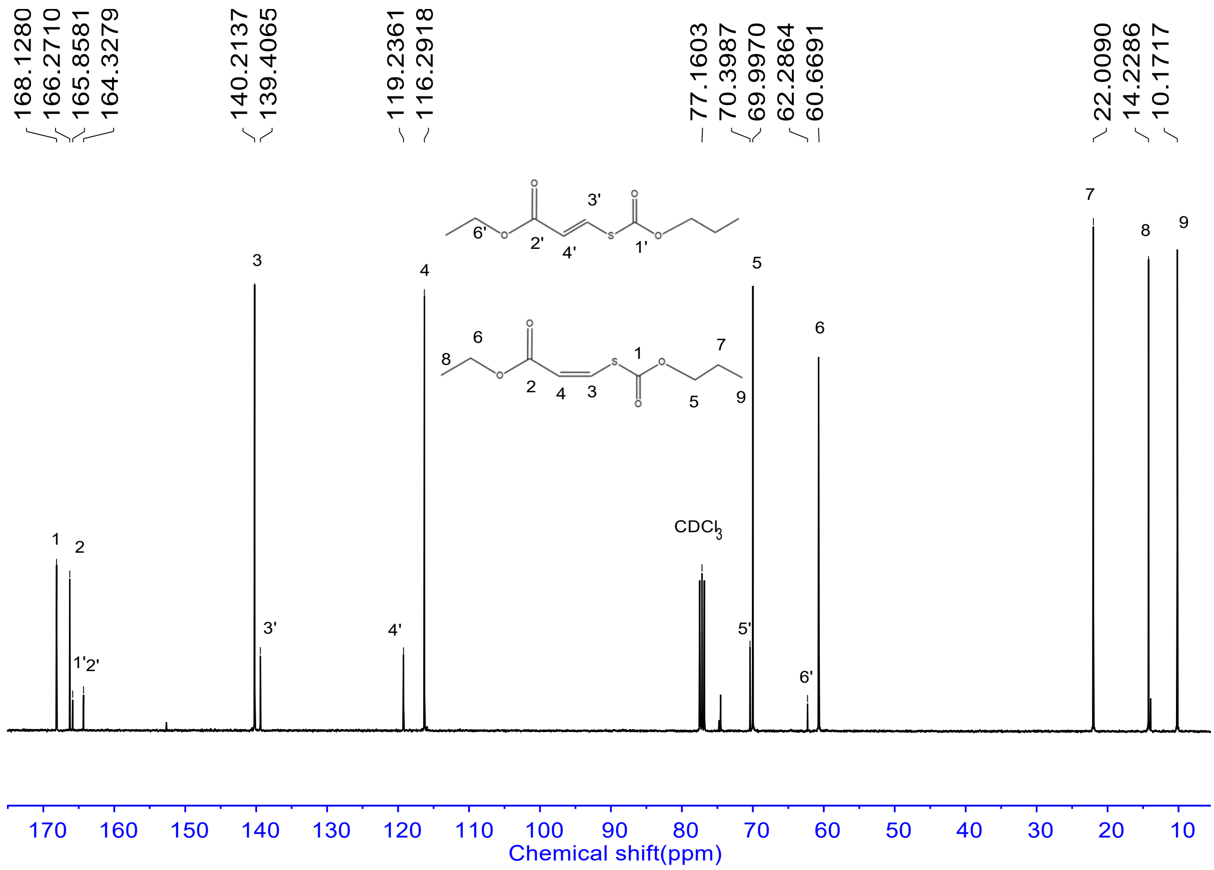

Figure S12. ^{1}H NMR spectrum of the purified **7** (in **Figure 2**).

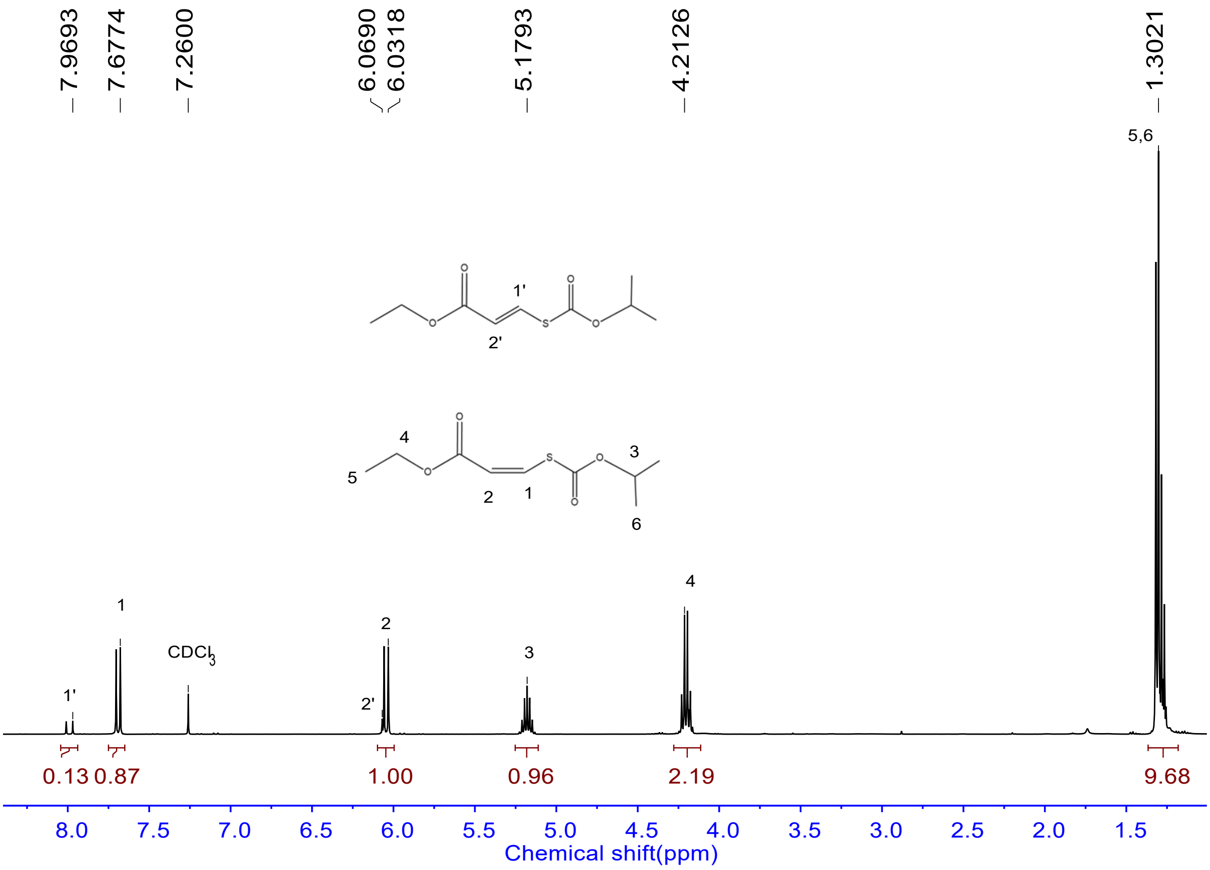

Figure S13. ^{1}H NMR spectrum of the purified **8** (in **Figure 2**).

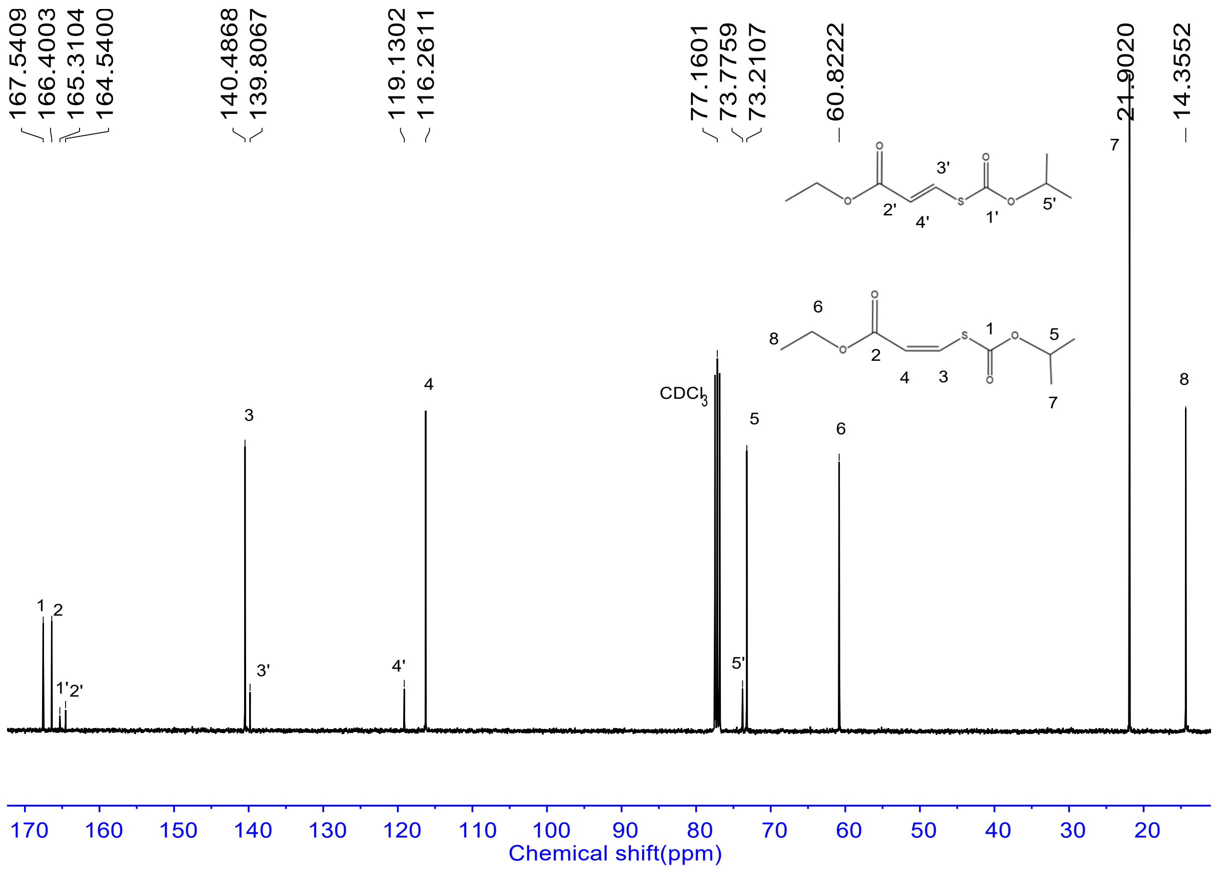

Figure S14. ^{13}C NMR spectrum of the purified **8** (in **Figure 2**).

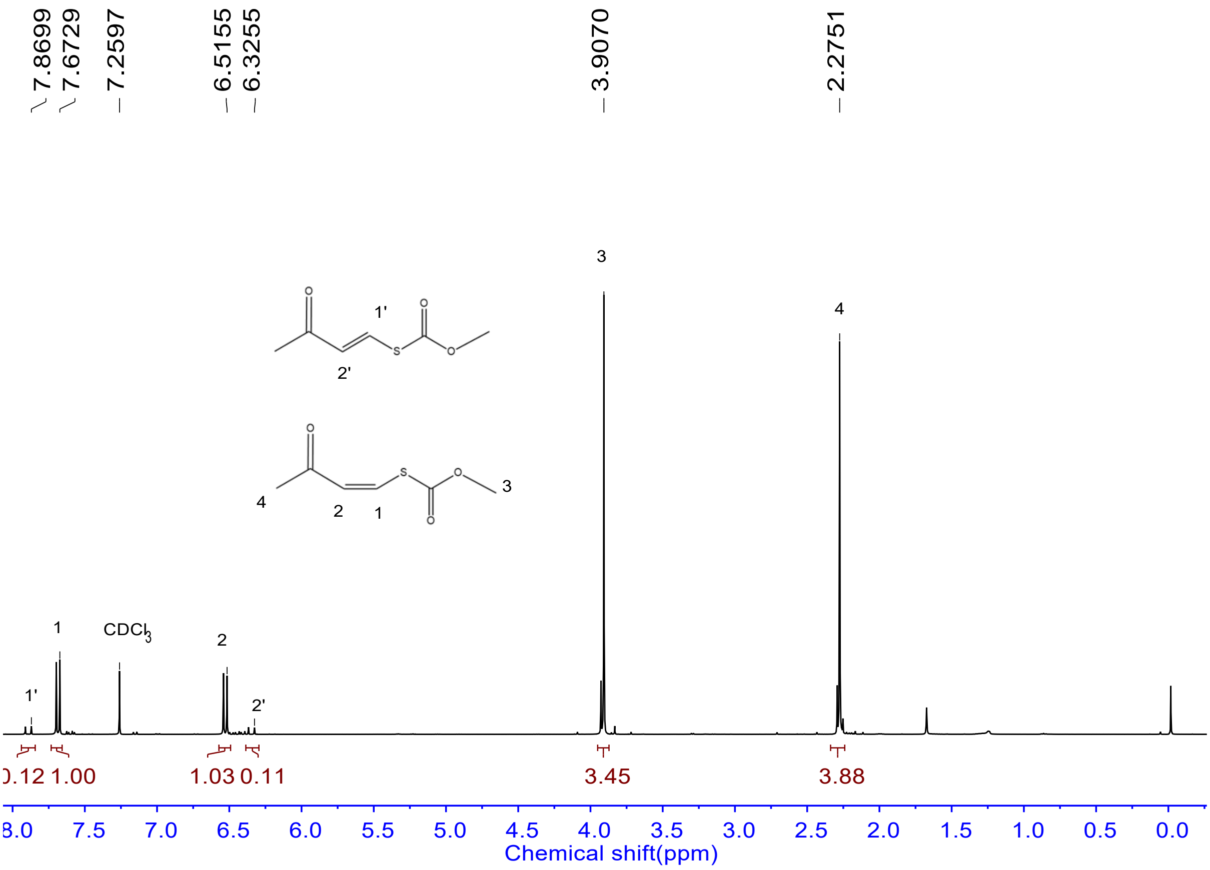

Figure S15. ^{1}H NMR spectrum of the purified **9** (in **Figure 2**).

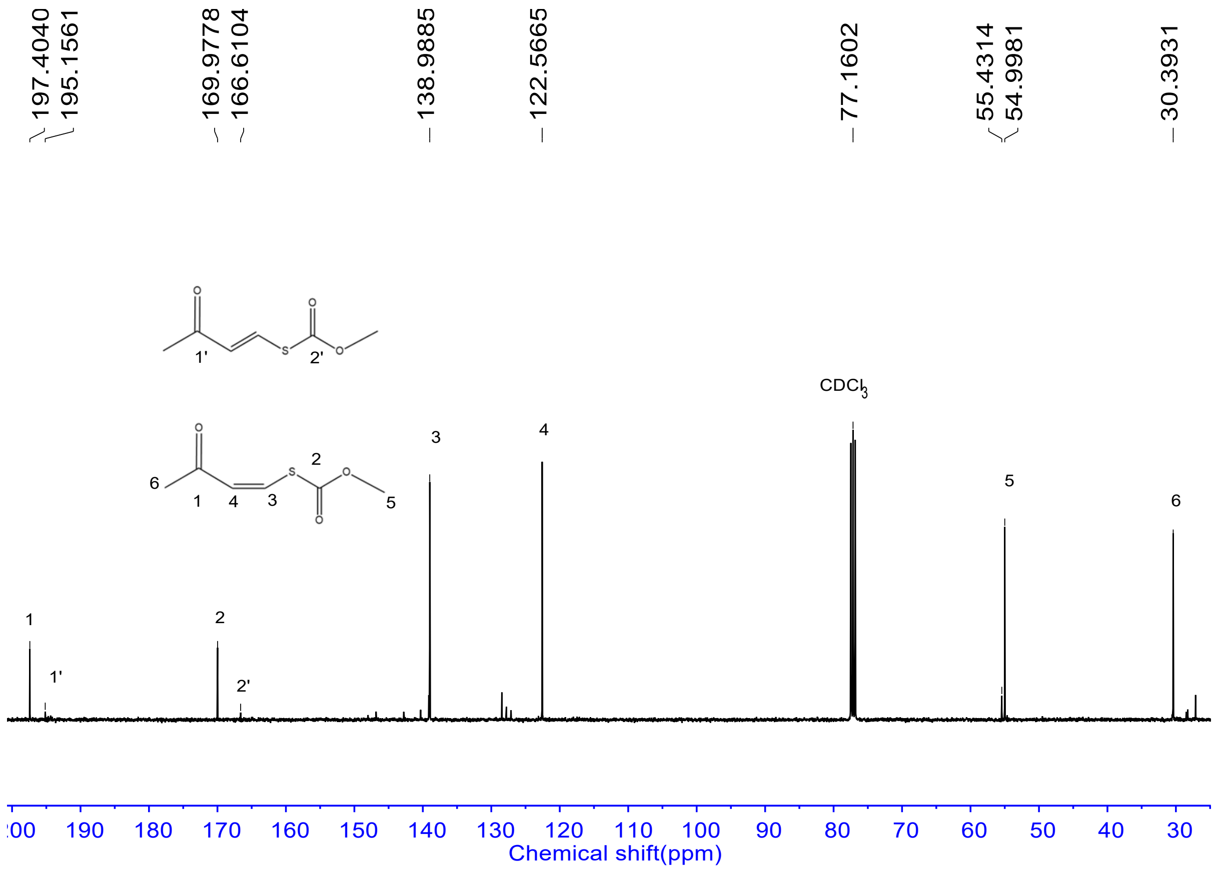

Figure S16. ^{13}C NMR spectrum of the purified **9** (in **Figure 2**).

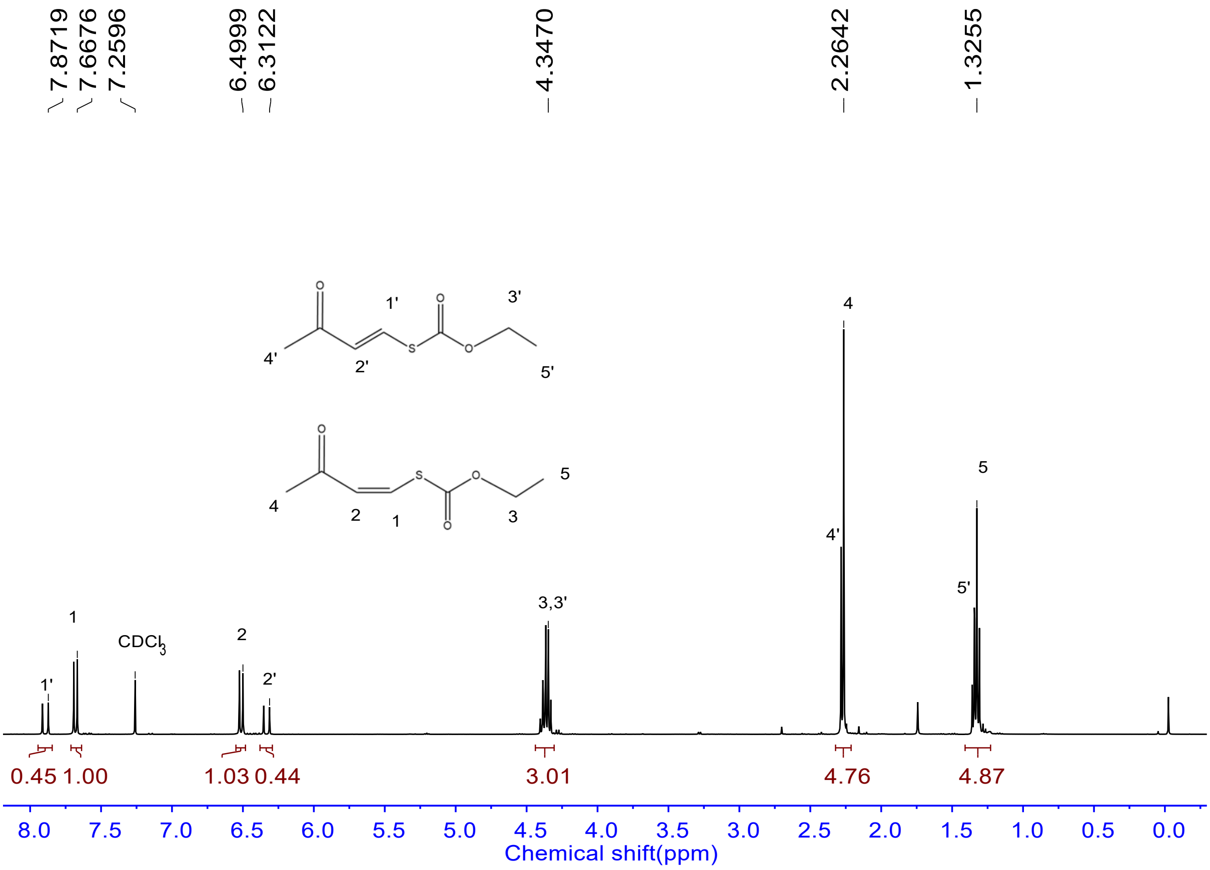

Figure S17. ^{1}H NMR spectrum of the purified **10** (in **Figure 2**).

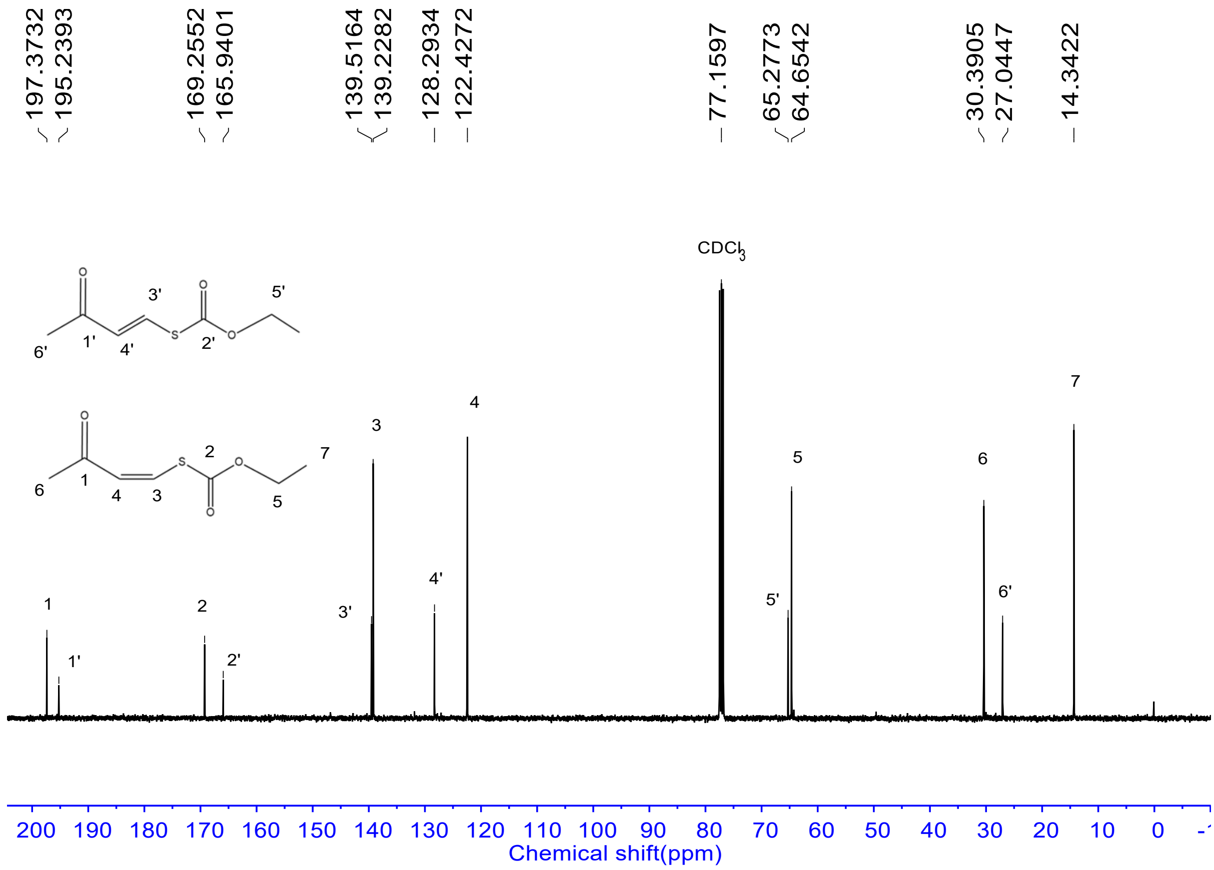

Figure S18. ^{13}C NMR spectrum of the purified **10** (in **Figure 2**).

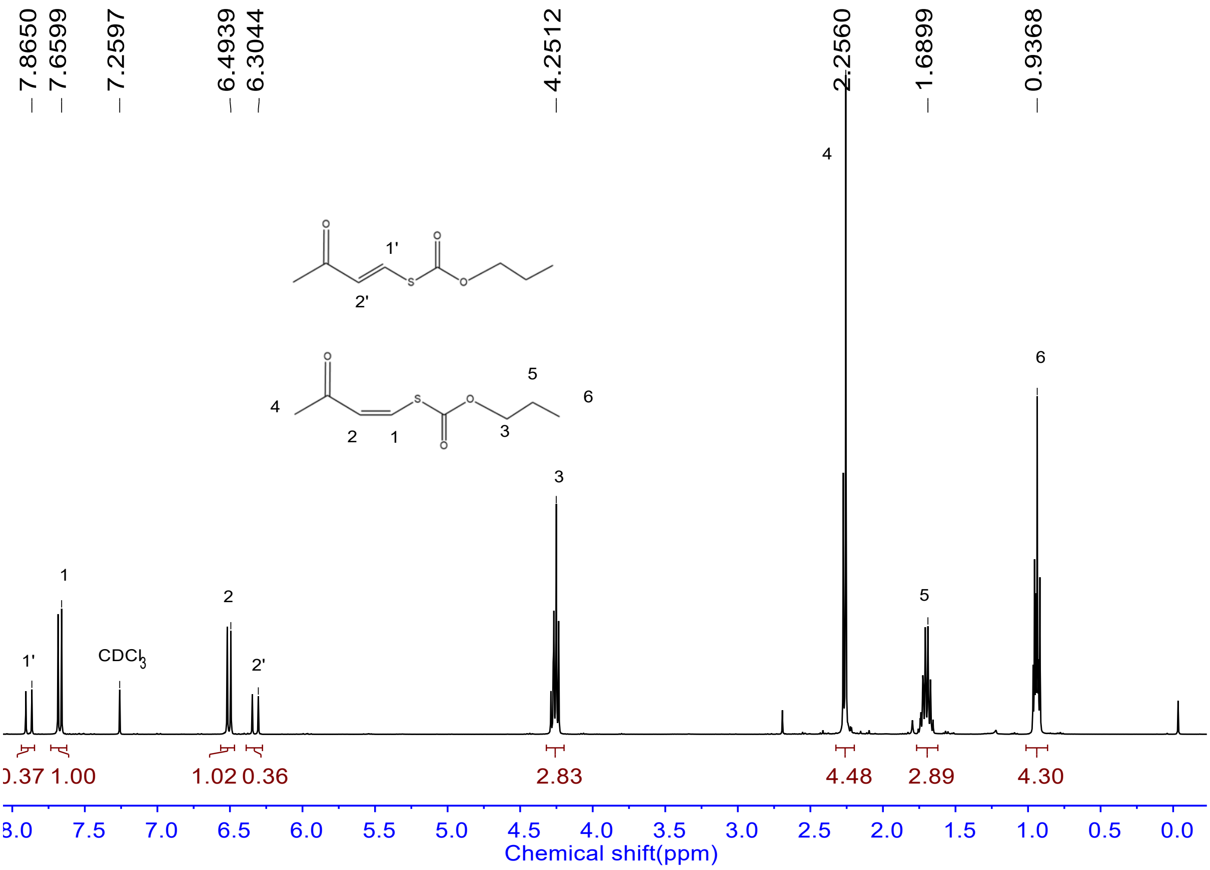

Figure S19. ^{1}H NMR spectrum of the purified **11** (in **Figure 2**).

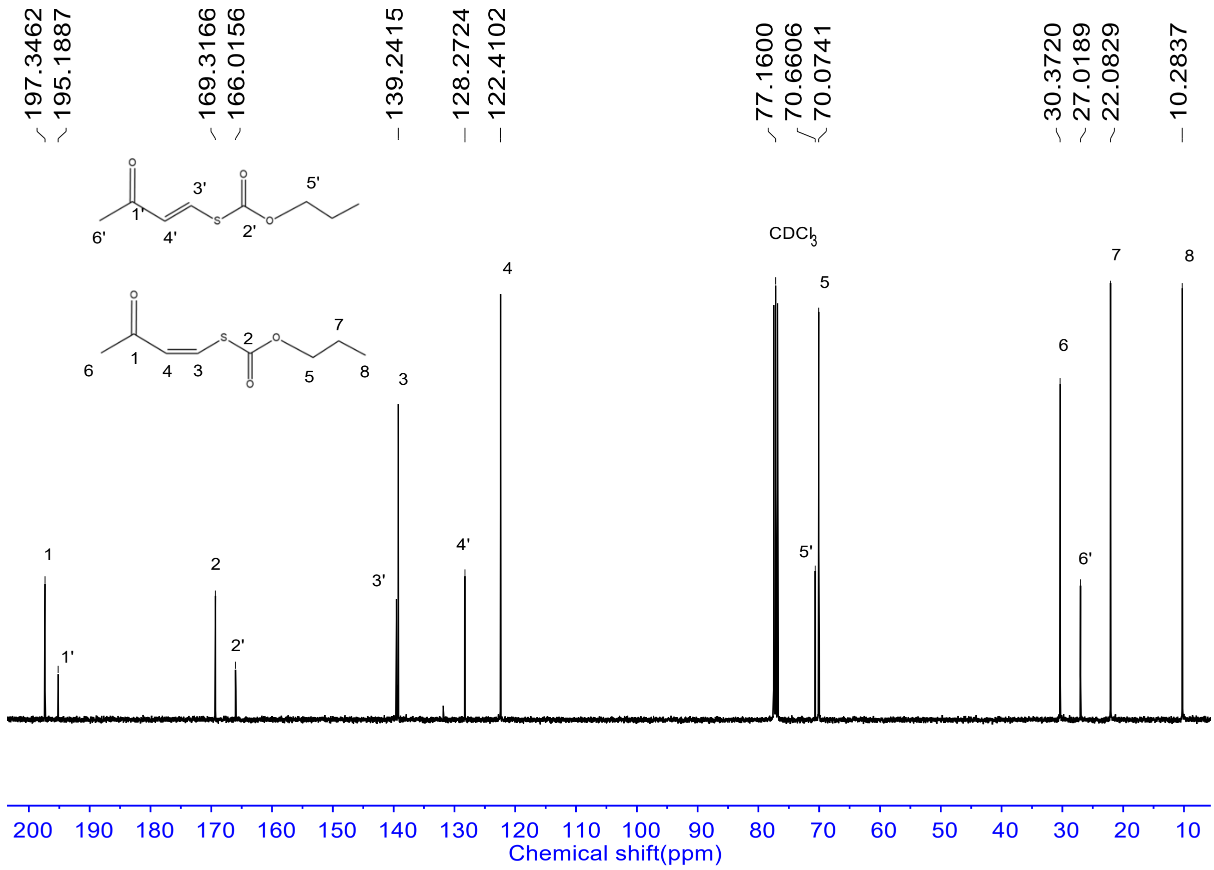

Figure S20. ^{13}C NMR spectrum of the purified **11** (in **Figure 2**).

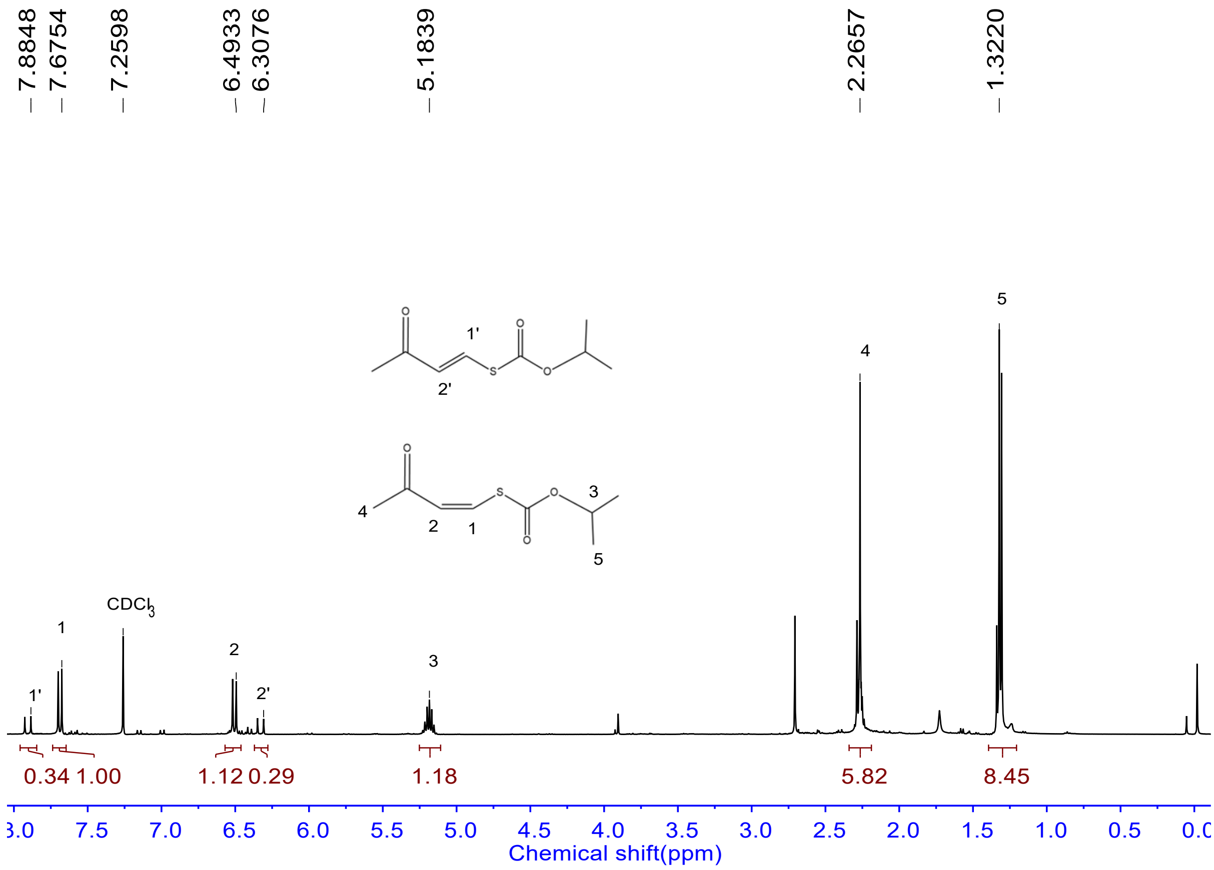

Figure S21. ^{1}H NMR spectrum of the purified **12** (in **Figure 2**).

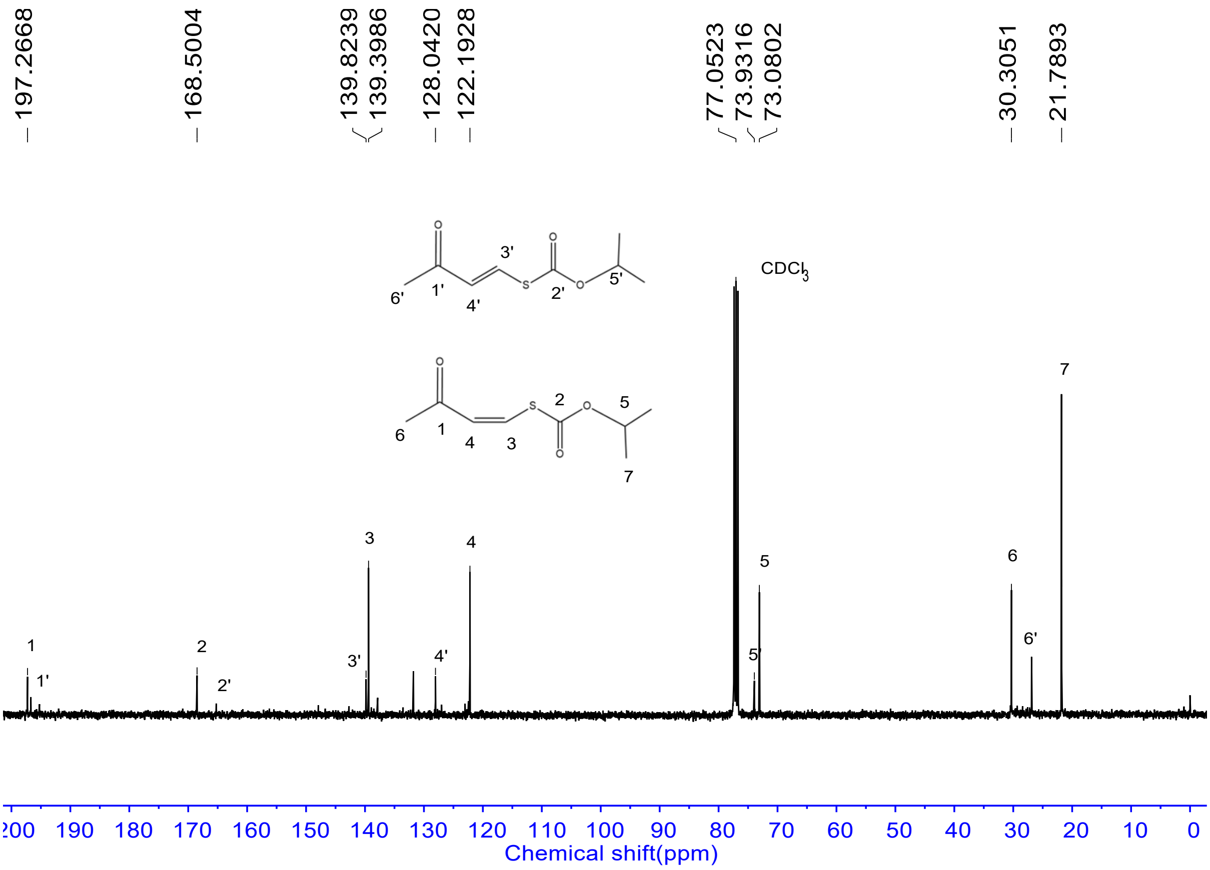

Figure S22. ^{13}C NMR spectrum of the purified **12** (in **Figure 2**).

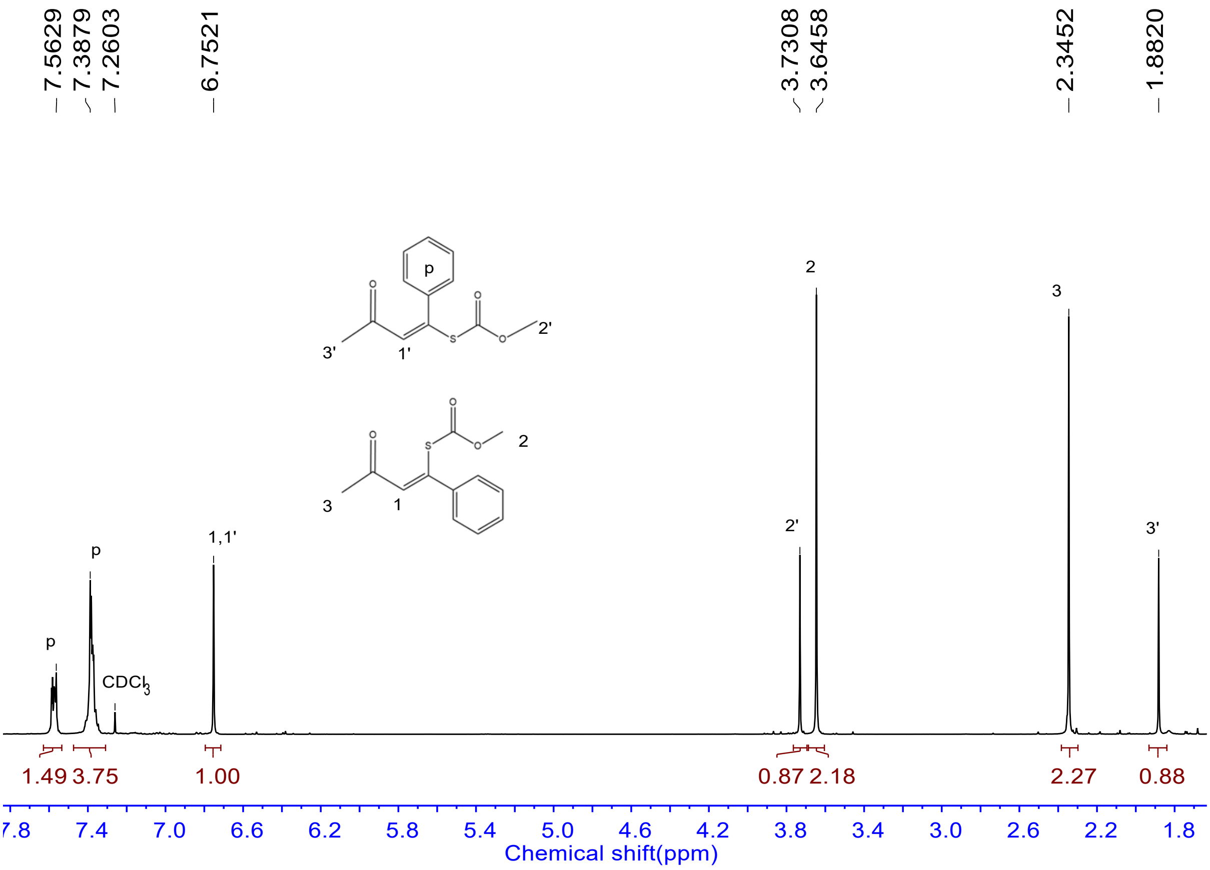

Figure S23. ^{1}H NMR spectrum of the purified **13** (in **Figure 2**).

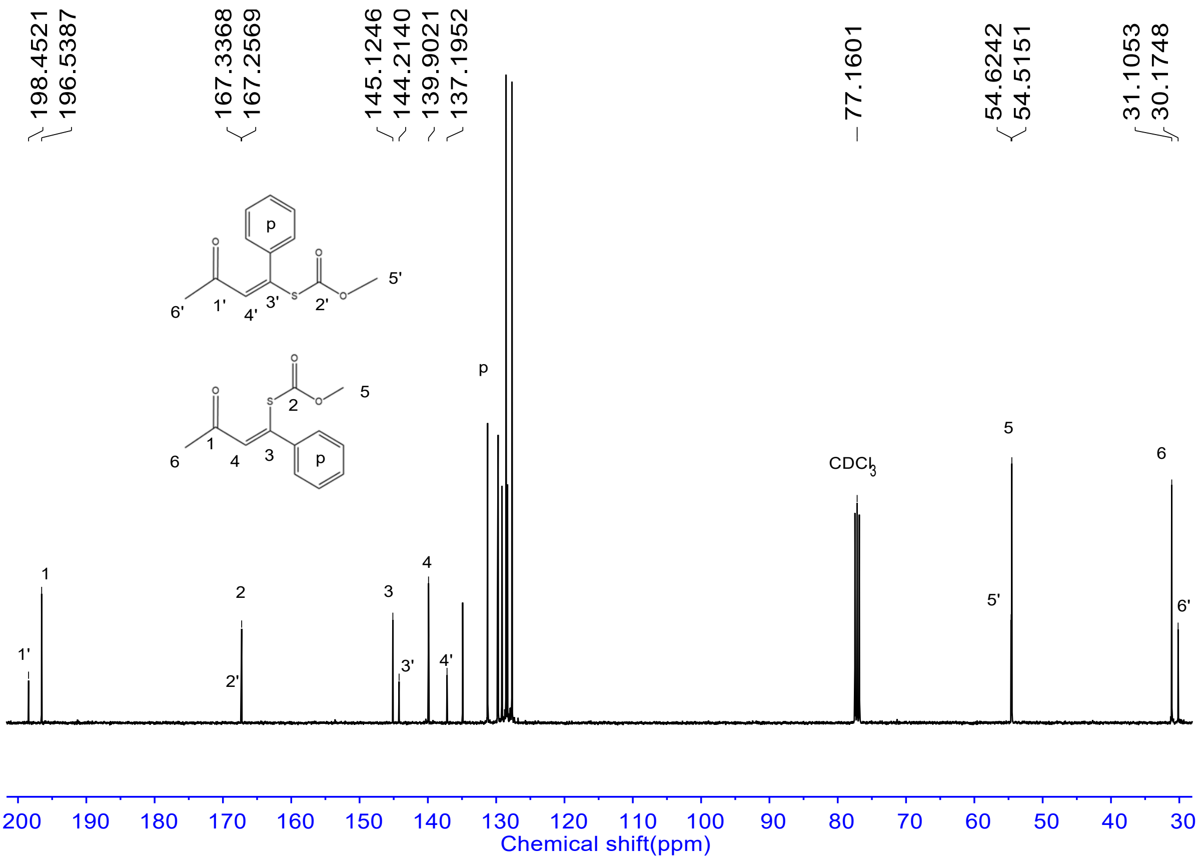

Figure S24. ^{13}C NMR spectrum of the purified **13** (in **Figure 2**).

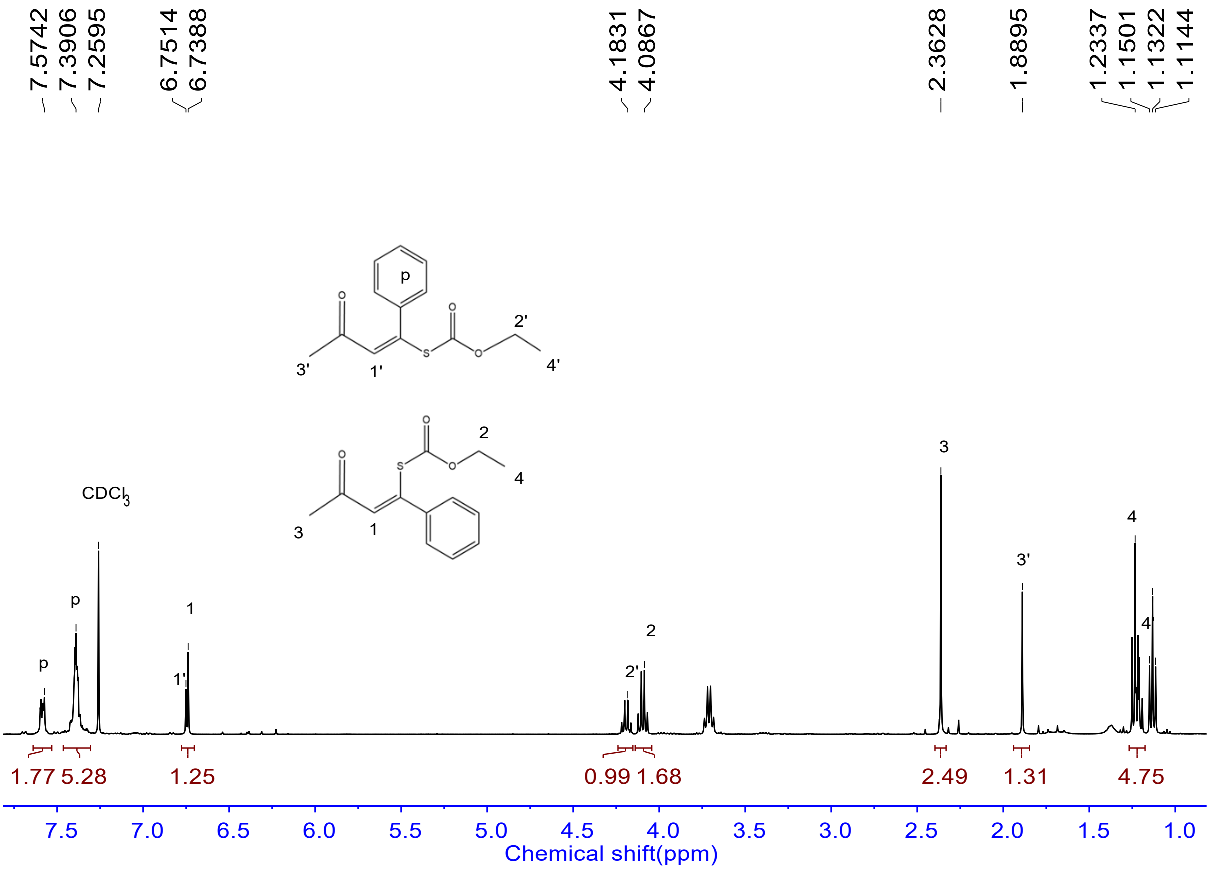

Figure S25. ^{1}H NMR spectrum of the purified **14** (in **Figure 2**).

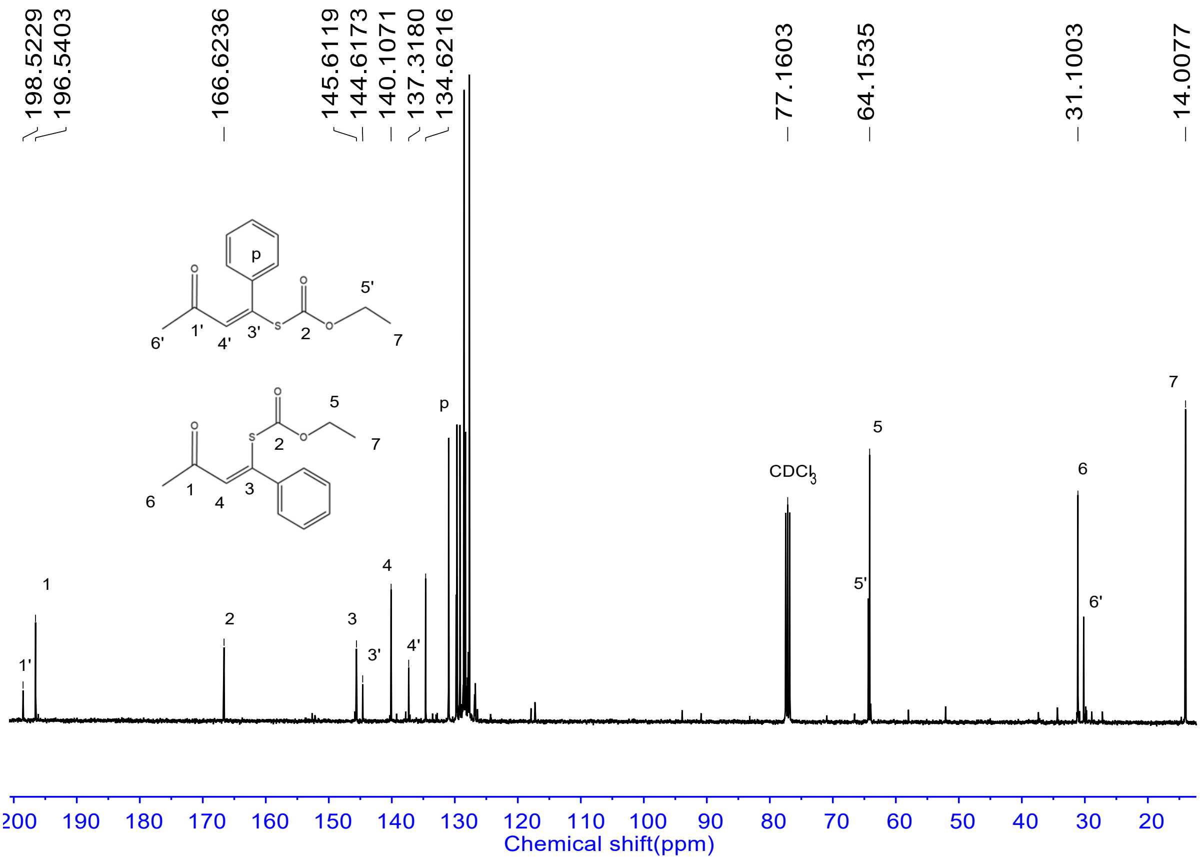

Figure S26. ^{13}C NMR spectrum of the purified **14** (in **Figure 2**).

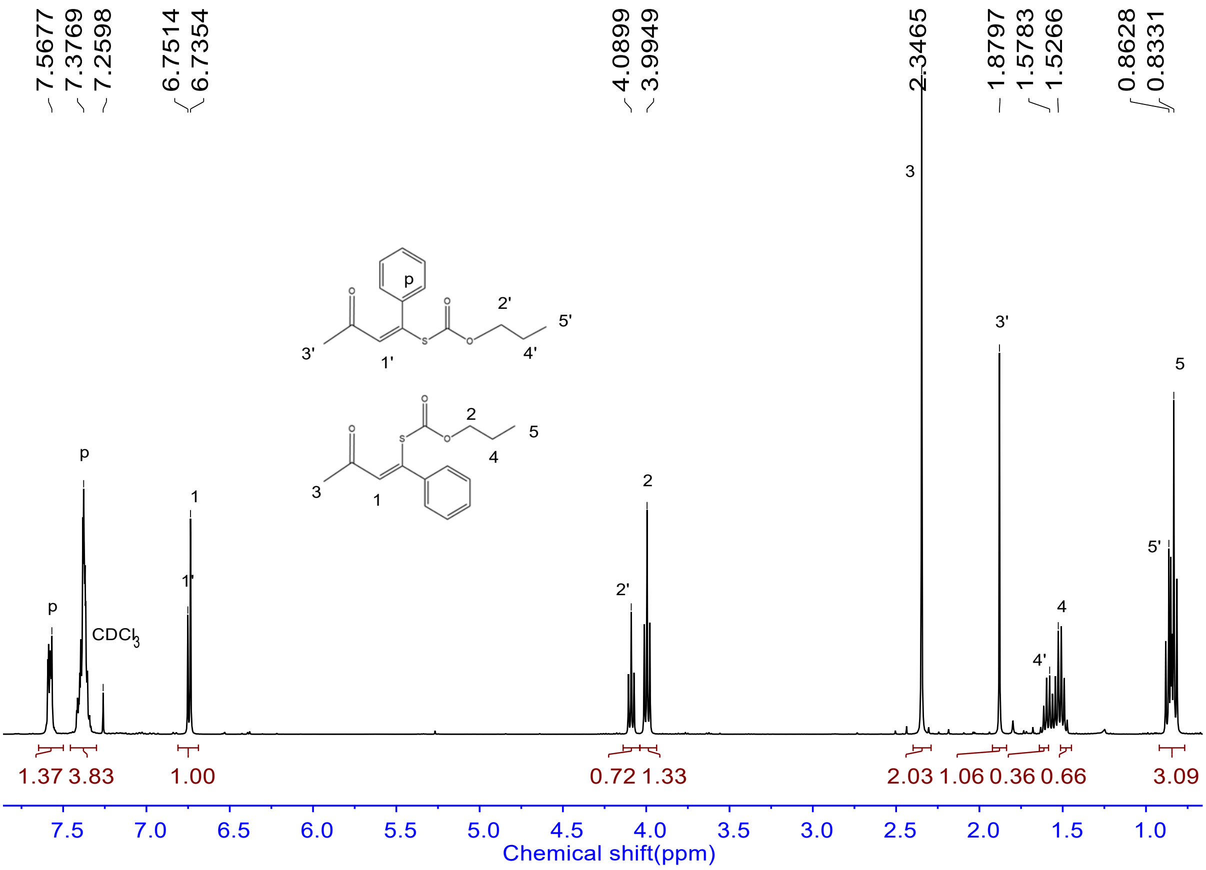

Figure S27. ^{1}H NMR spectrum of the purified **15** (in **Figure 2**).

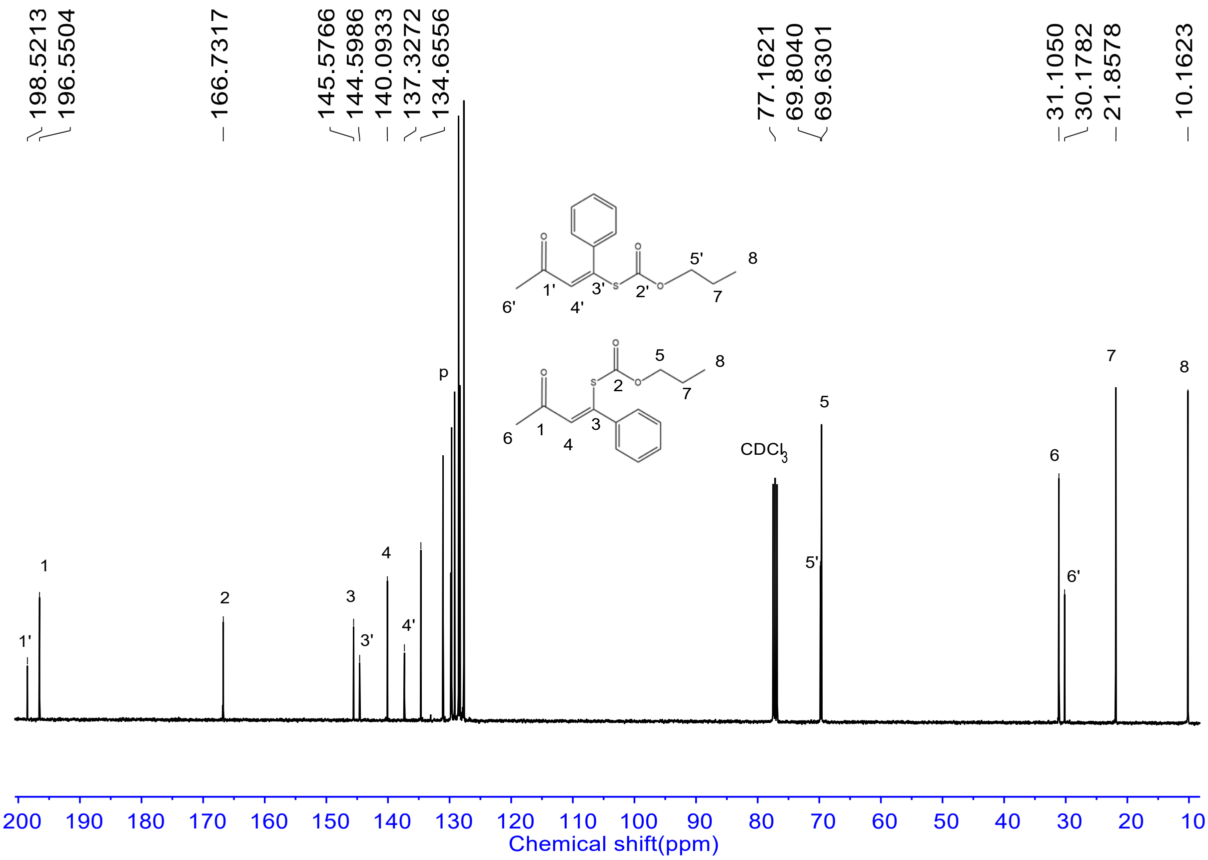

Figure S28. ^{13}C NMR spectrum of the purified **15** (in **Figure 2**).

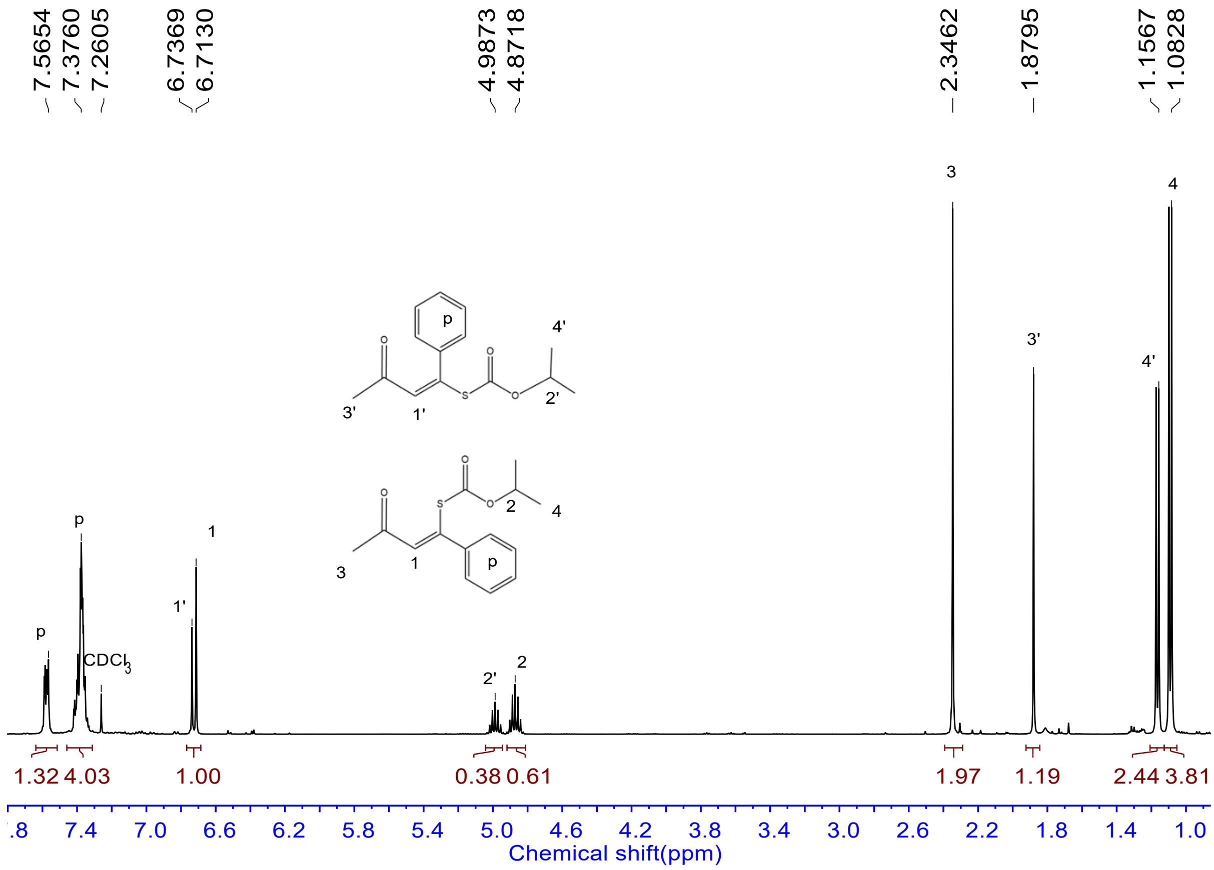

Figure S29. ^{1}H NMR spectrum of the purified **16** (in **Figure 2**).

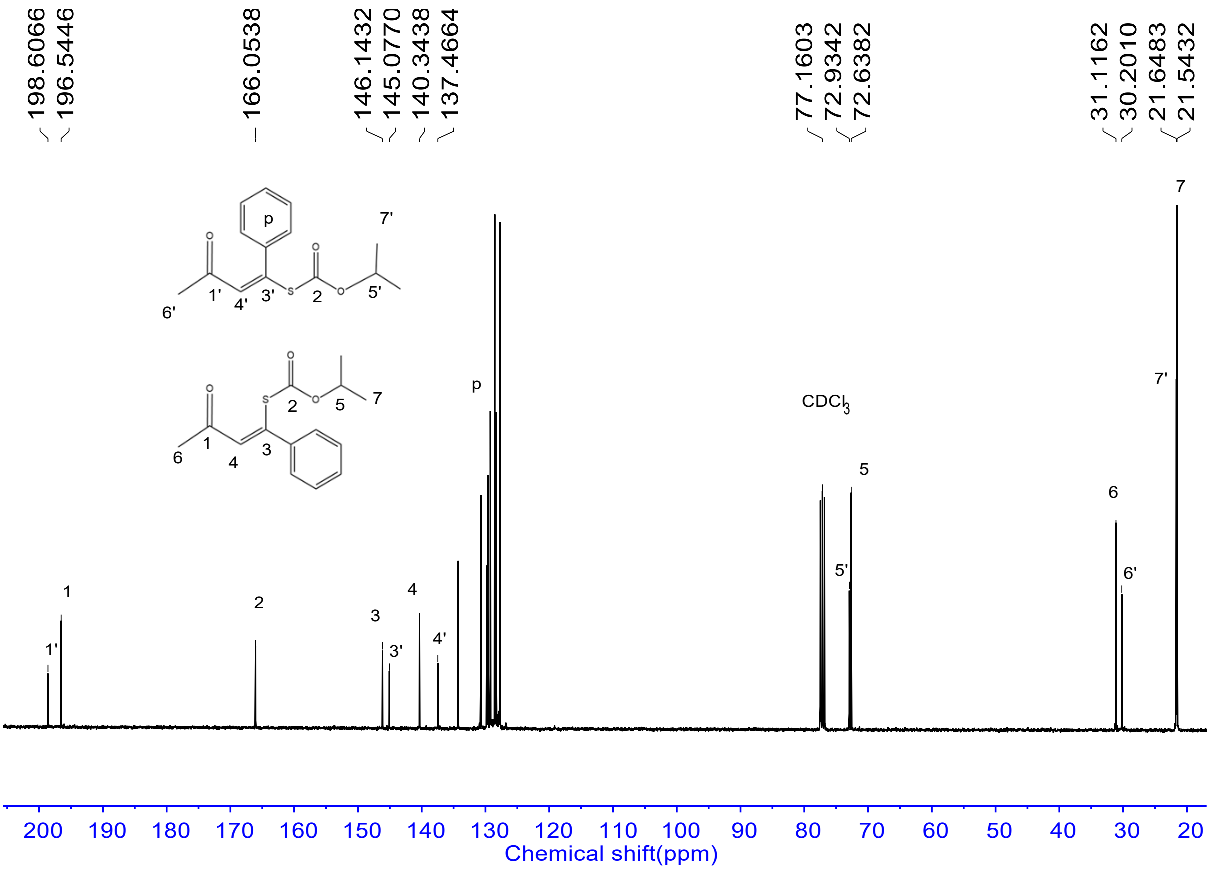

Figure S30. ^{13}C NMR spectrum of the purified **16** (in **Figure 2**).

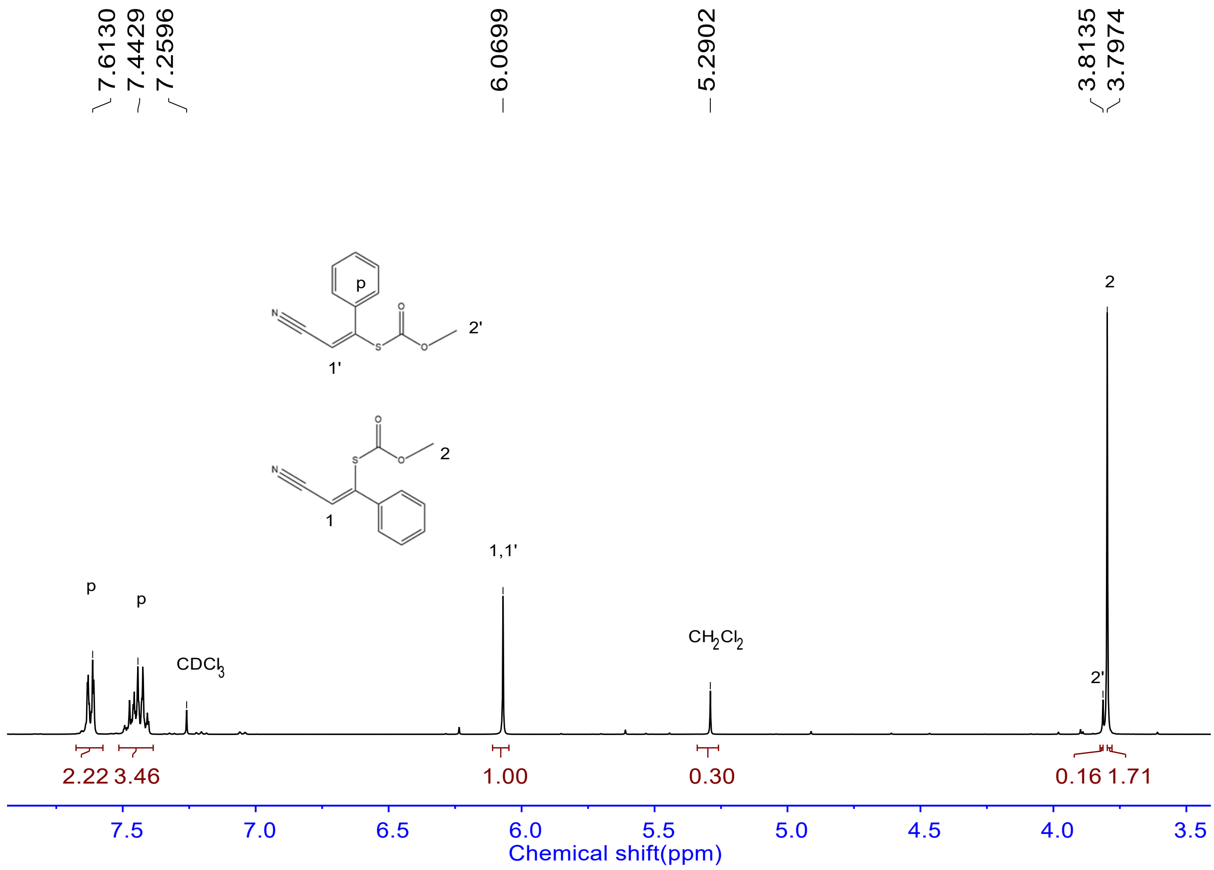

Figure S31. [1]H NMR spectrum of the purified **17** (in **Figure 2**).

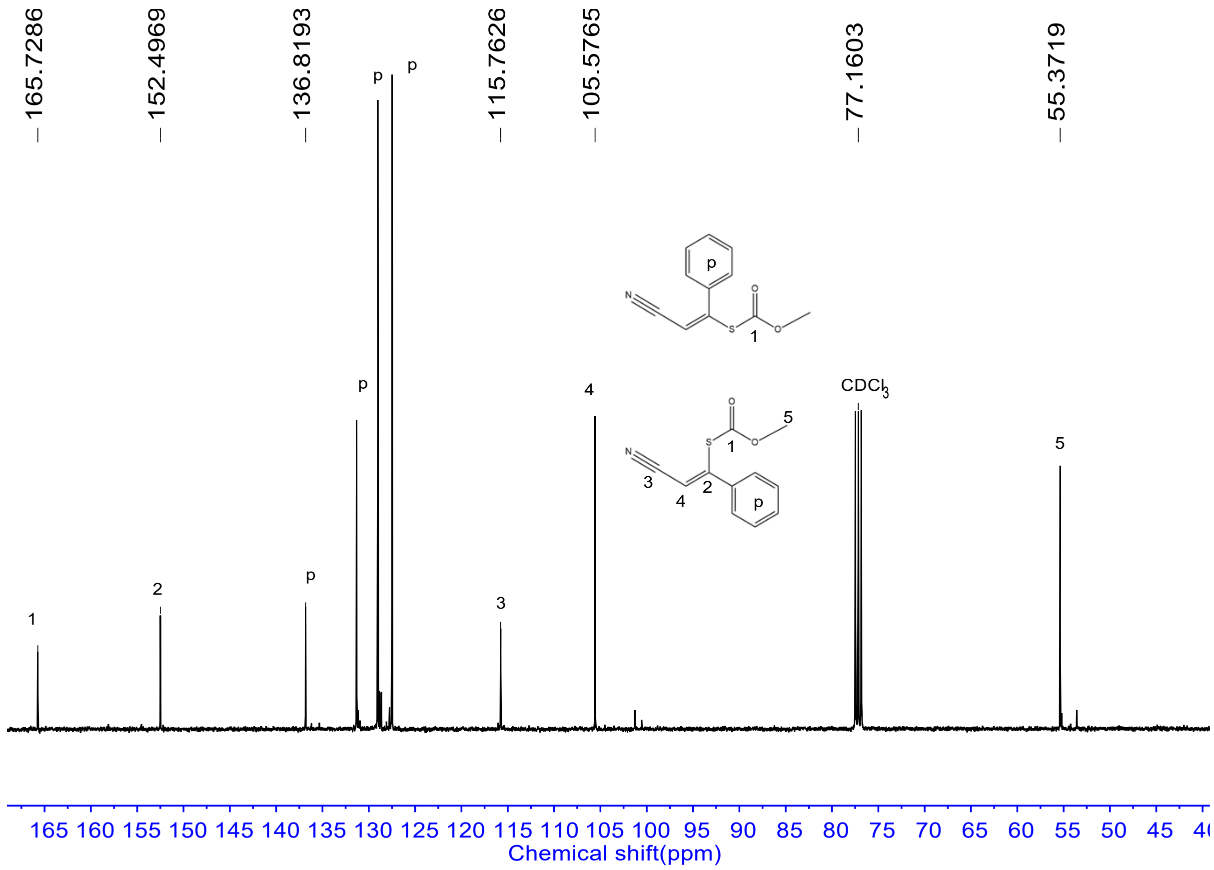

Figure S32. ^{13}C NMR spectrum of the purified **17** (in **Figure 2**).

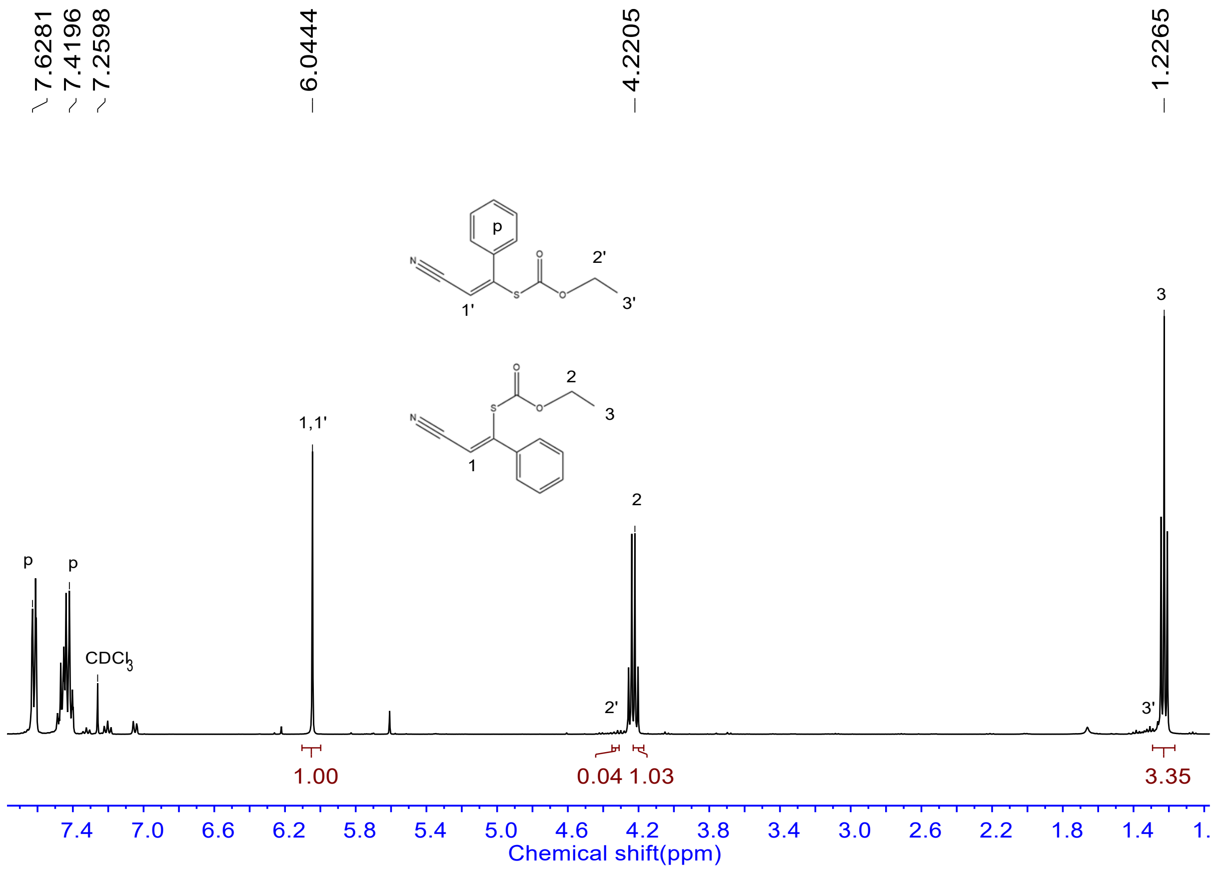

Figure S33. ^{1}H NMR spectrum of the purified **18** (in **Figure 2**).

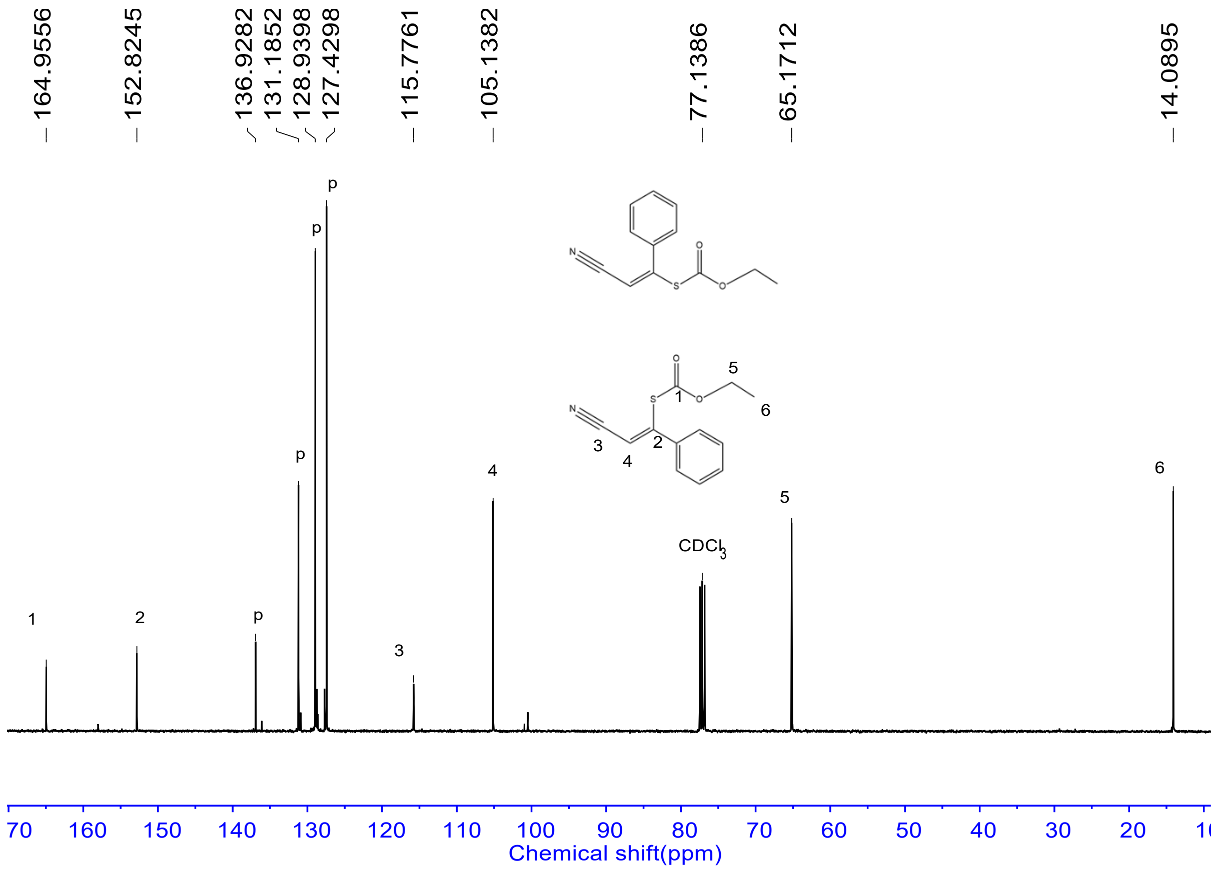

Figure S34. ^{13}C NMR spectrum of the purified **18** (in **Figure 2**).

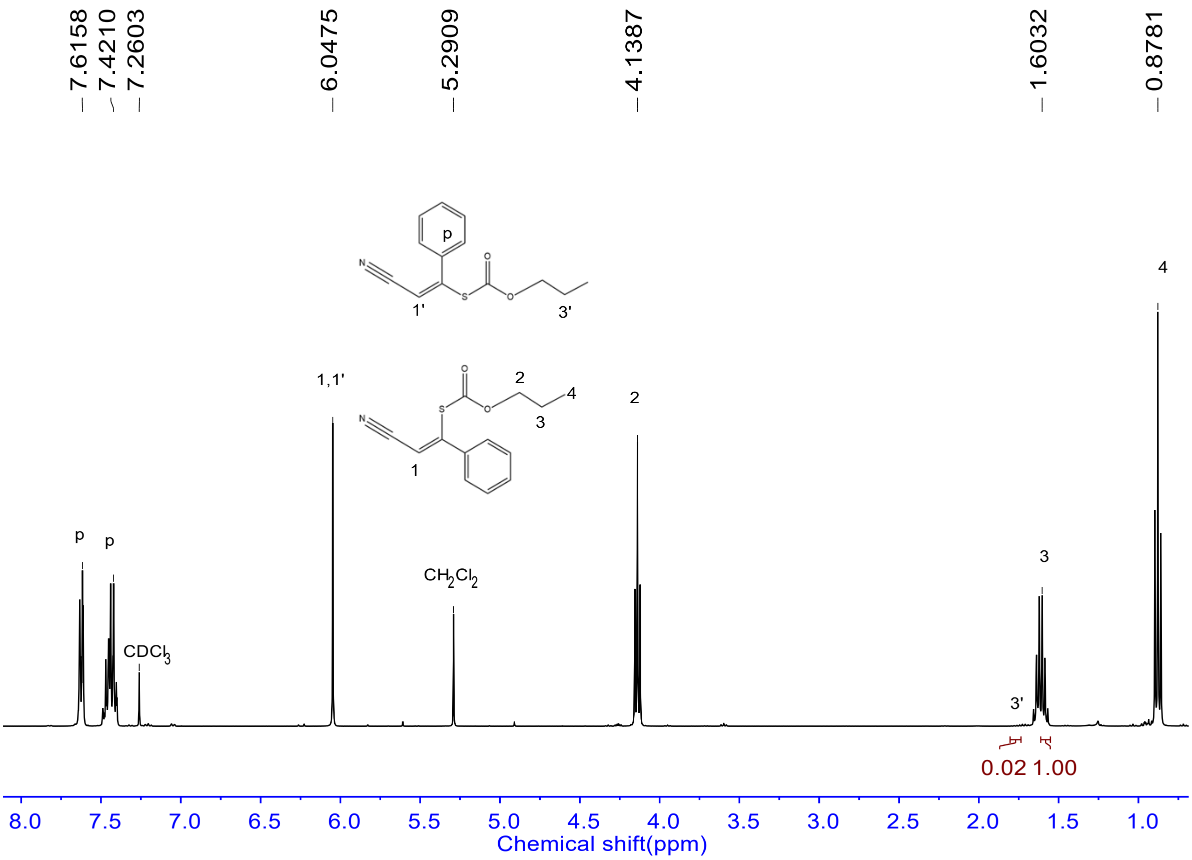

Figure S35. ^{1}H NMR spectrum of the purified **19** (in **Figure 2**).

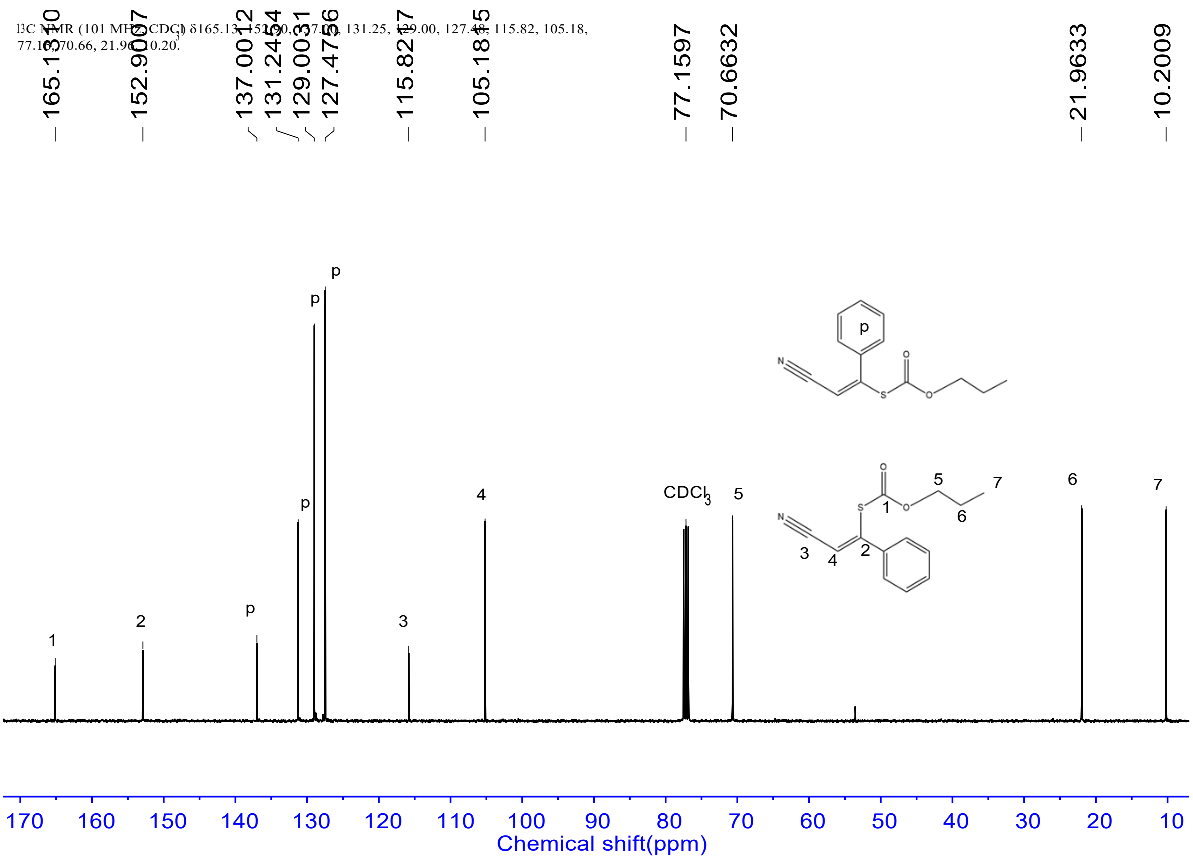

Figure S36. ^{13}C NMR spectrum of the purified **19** (in **Figure 2**).

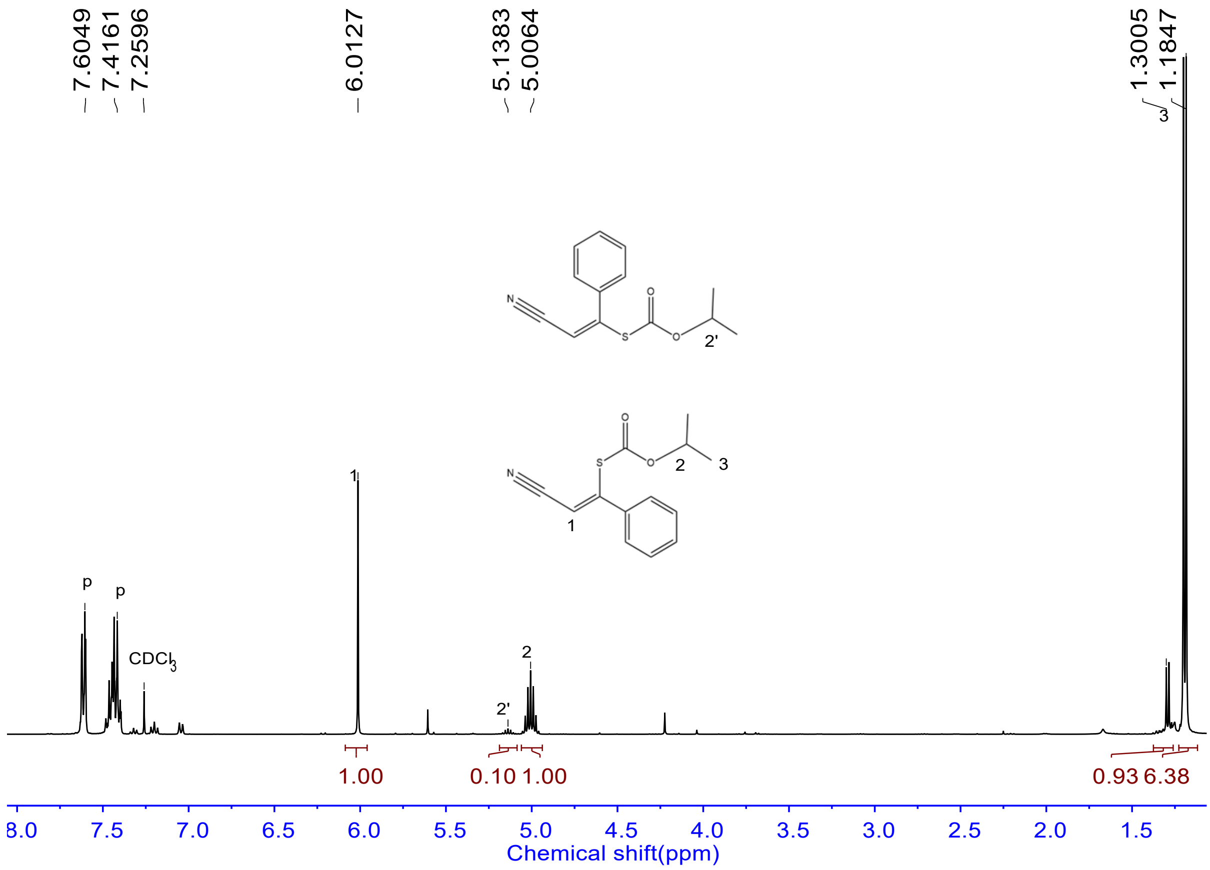

Figure S37. ^{1}H NMR spectrum of the purified **20** (in **Figure 2**).

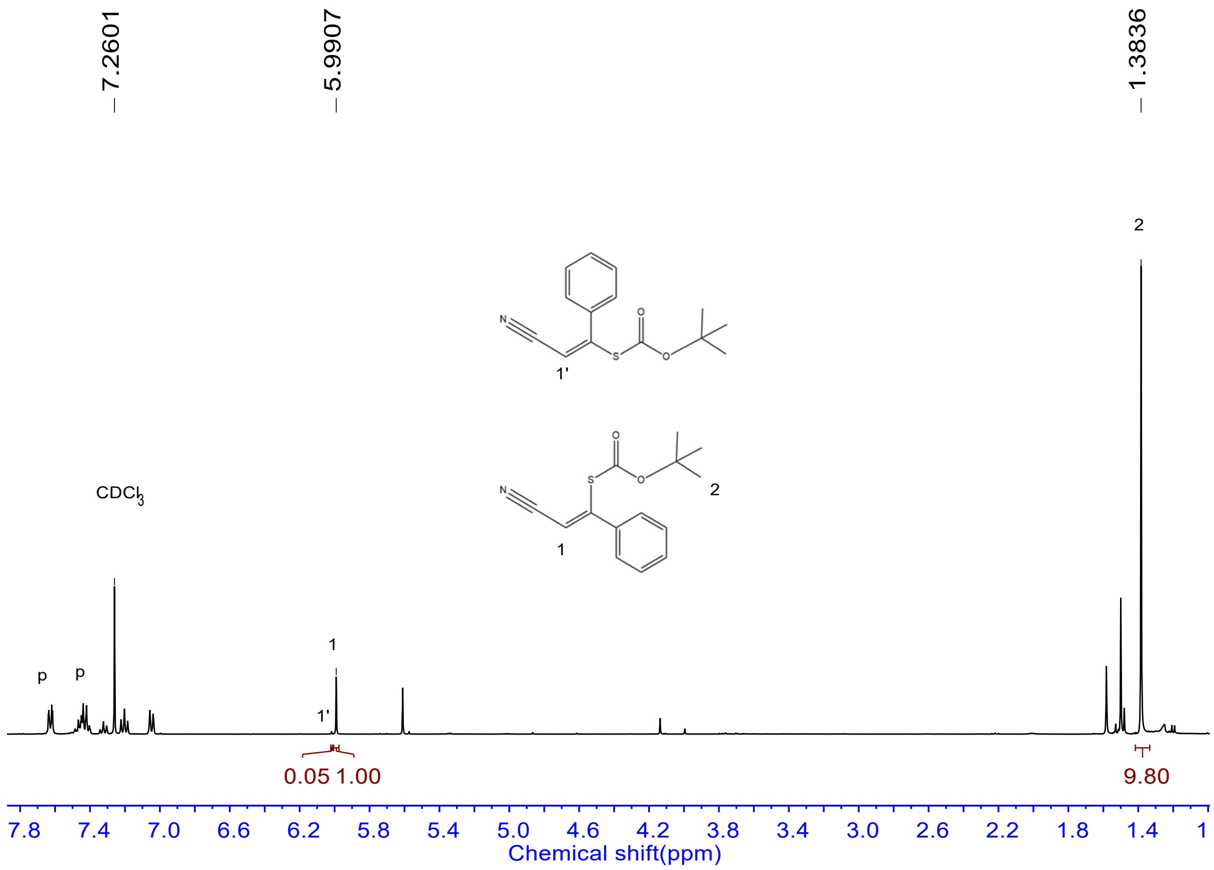

Figure S38. ^{1}H NMR spectrum of **21** (in **Figure 2**).

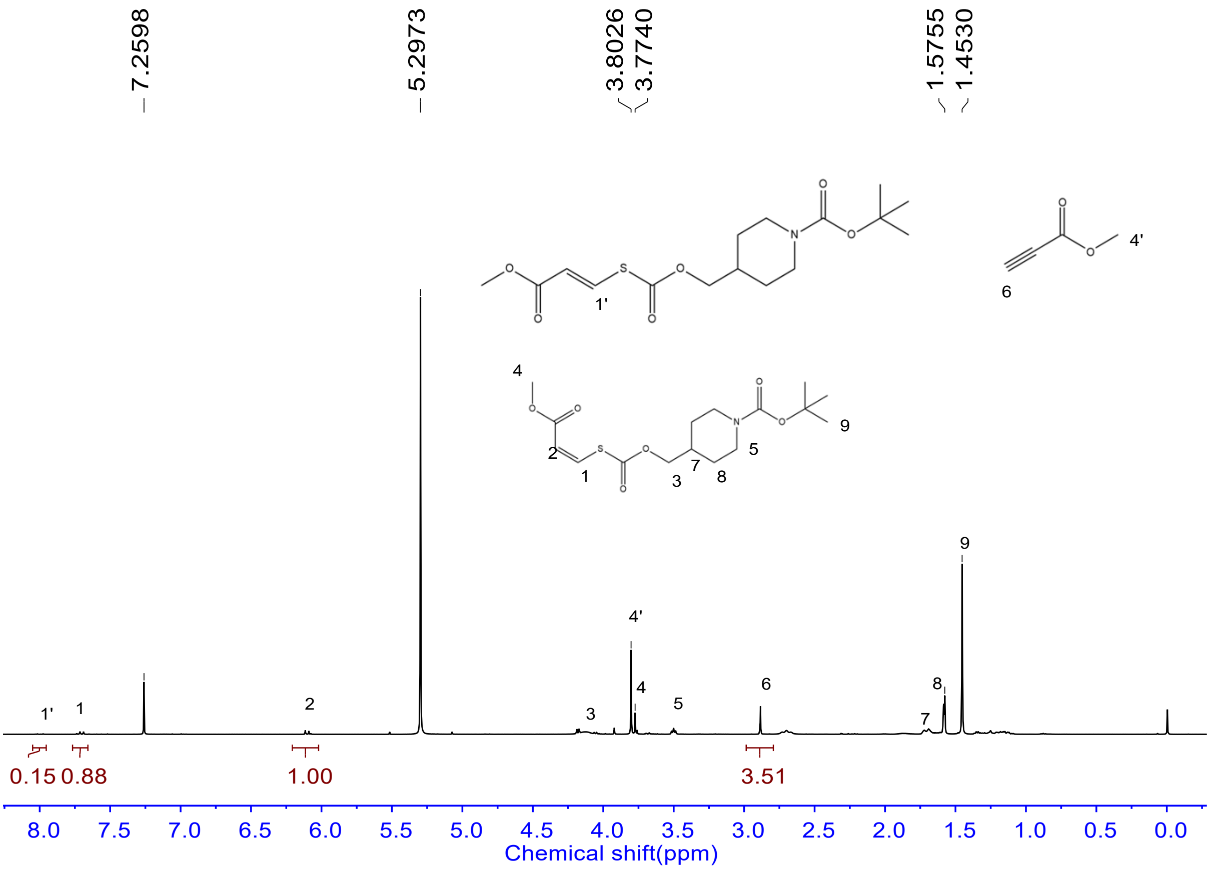

Figure S39. ^1H NMR spectrum of the product of methyl propiolate, N-Boc-4-piperidinemethanol and COS.

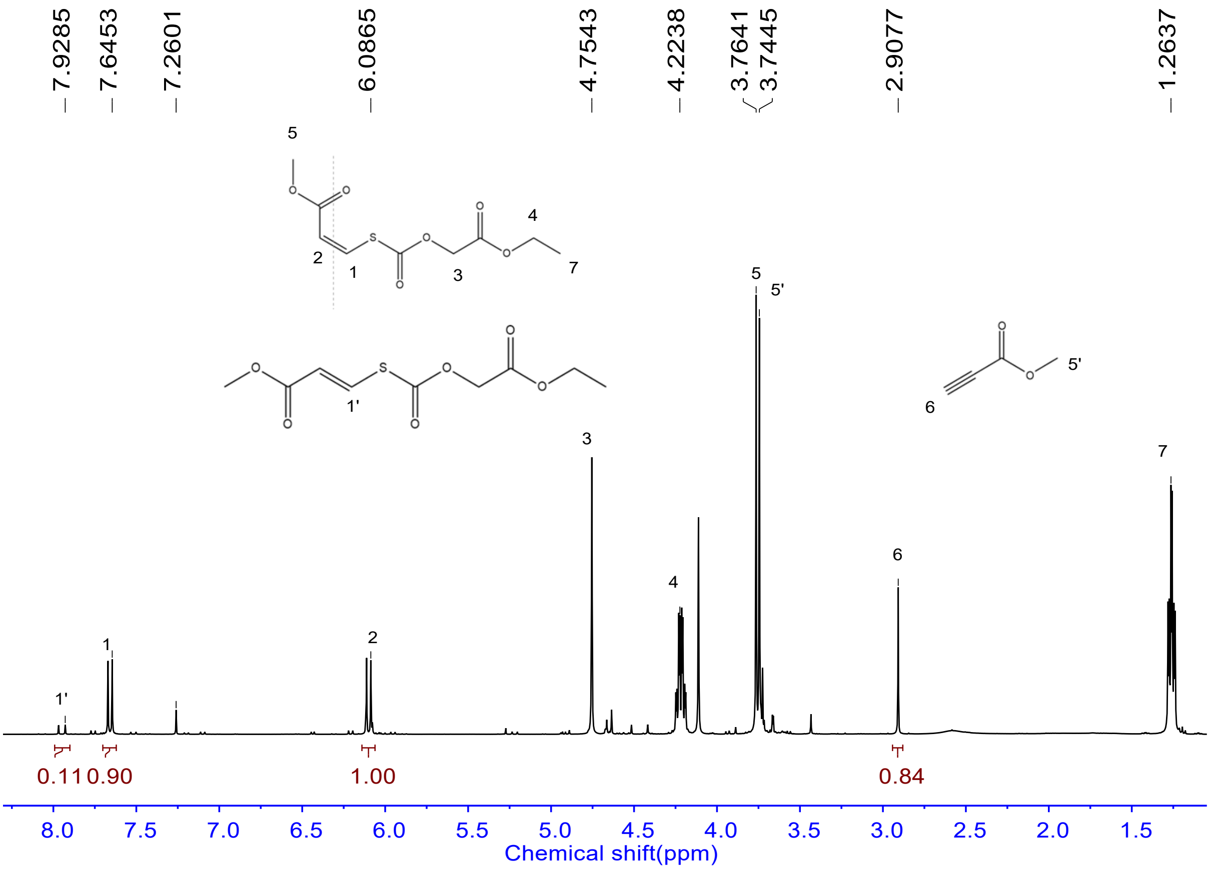

Figure S40. [1]H NMR spectrum of the product of methyl propiolate, ethyl glycolate and COS.

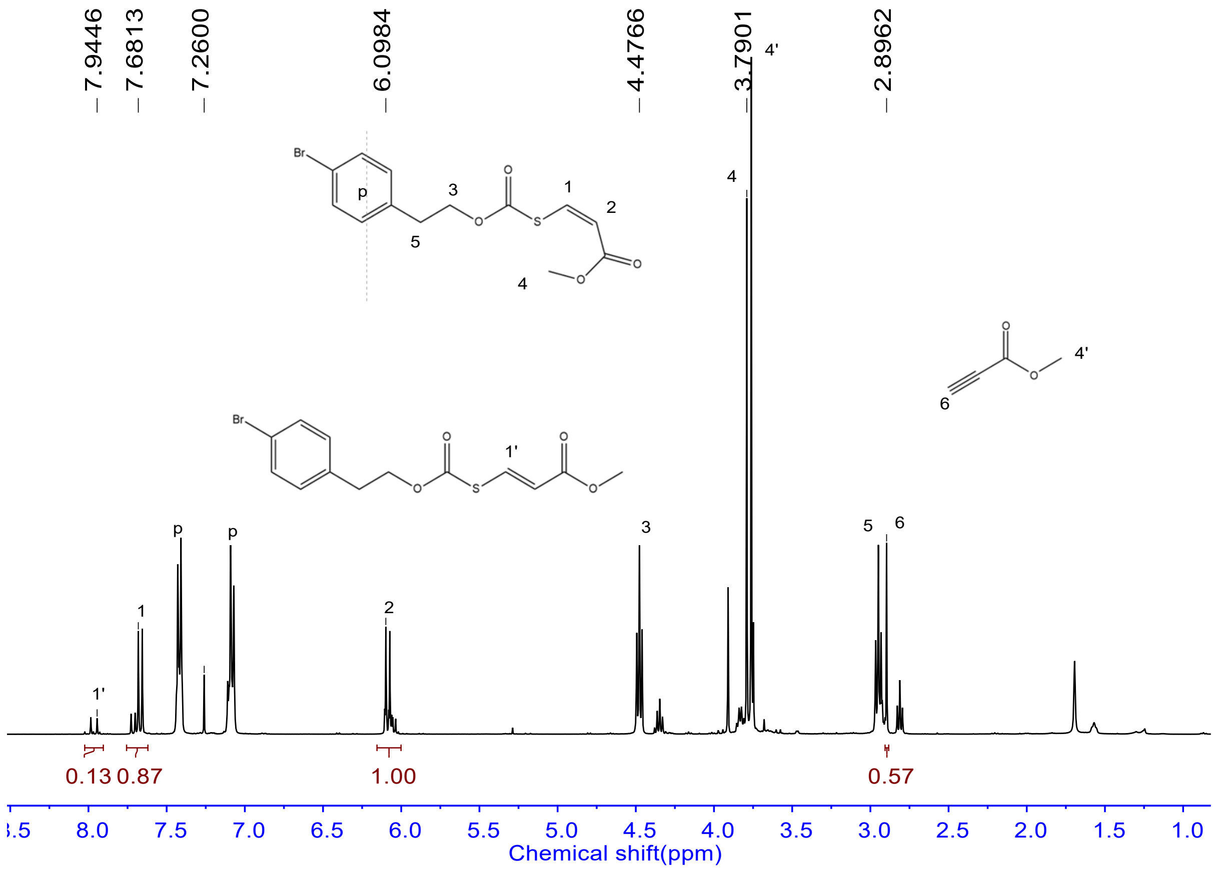

Figure S41. ^{1}H NMR spectrum of the product of methyl propiolate, 4-bromophenethyl alcohol and COS.

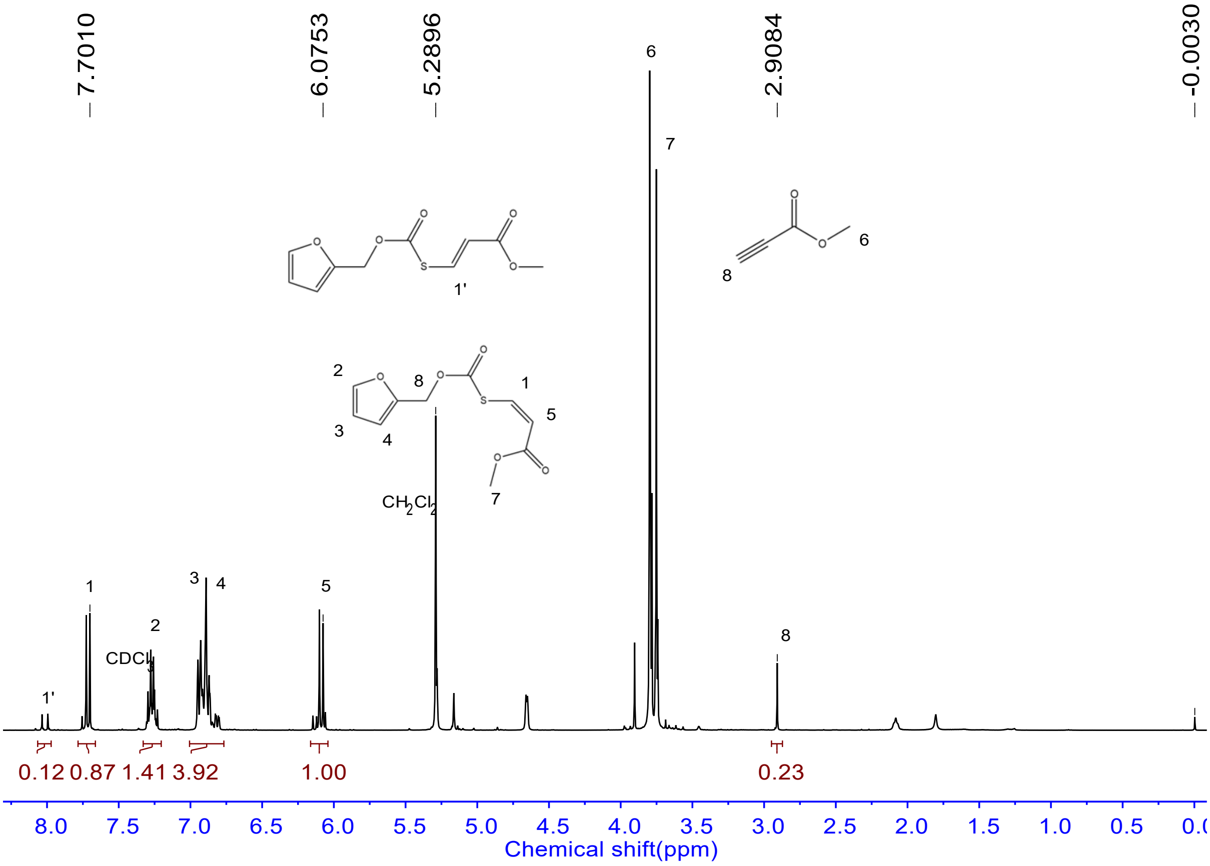

Figure S42. ^{1}H NMR spectrum of the product of methyl propiolate, furfuryl alcohol and COS.

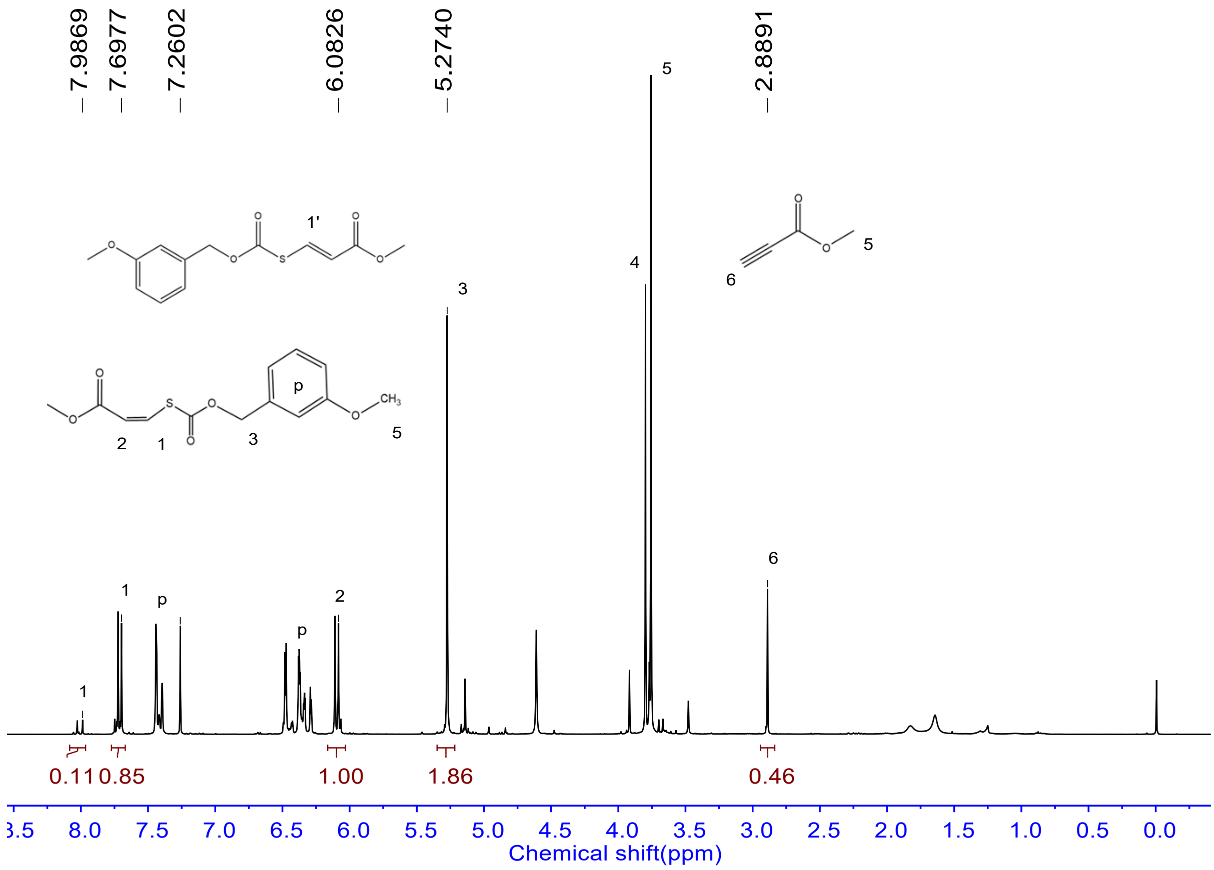

Figure S43. ^{1}H NMR spectrum of the product of methyl propiolate, m-anisyl alcohol and COS.

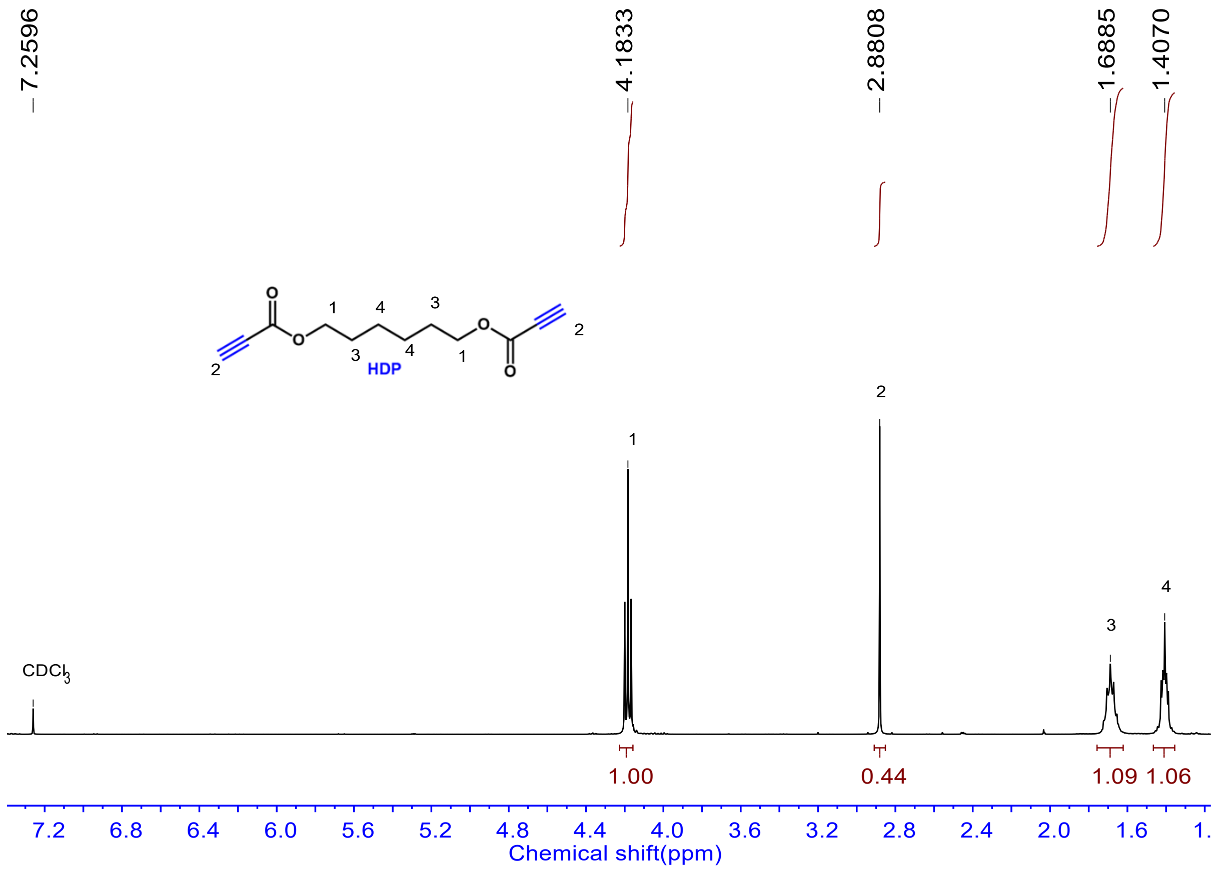

Figure S44. ^{1}H NMR spectrum of HDP.

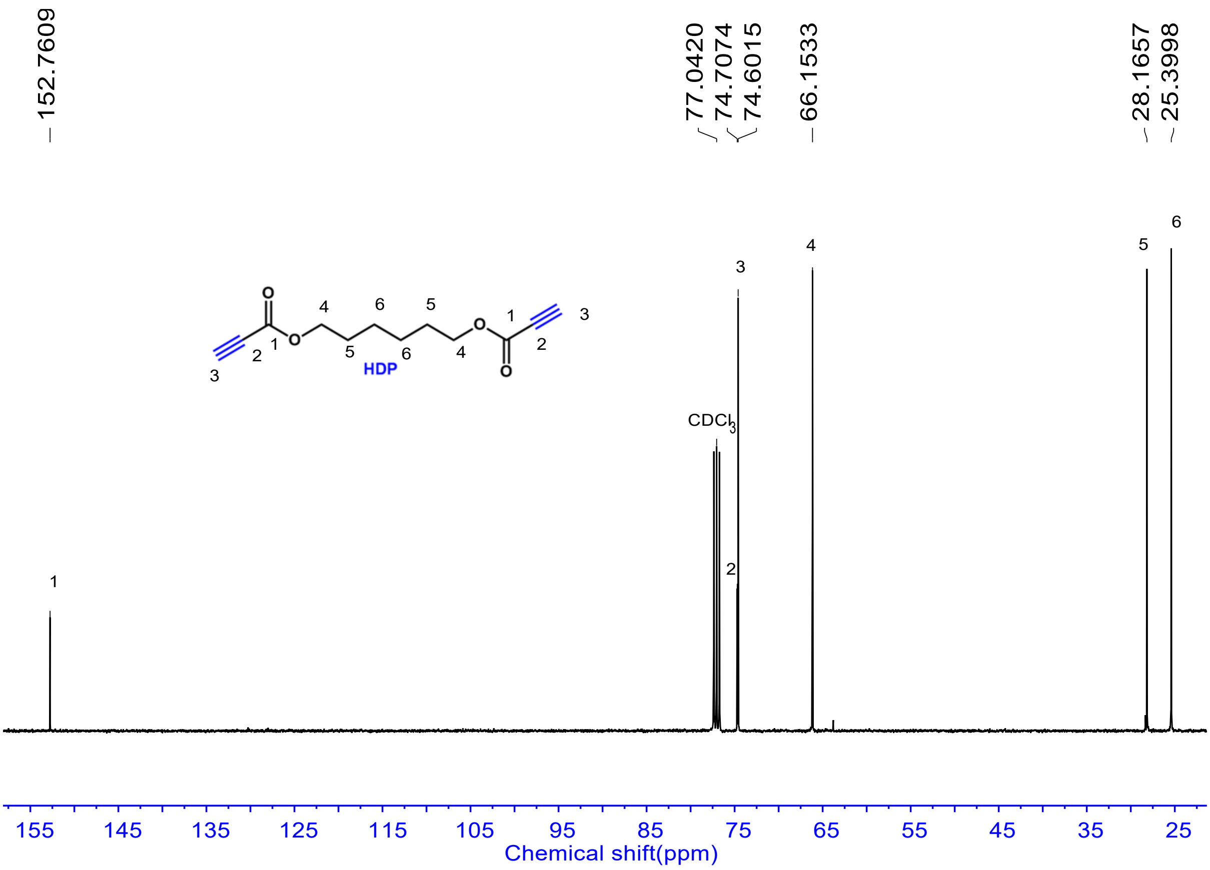

Figure S45. ^{13}C NMR spectrum of HDP.

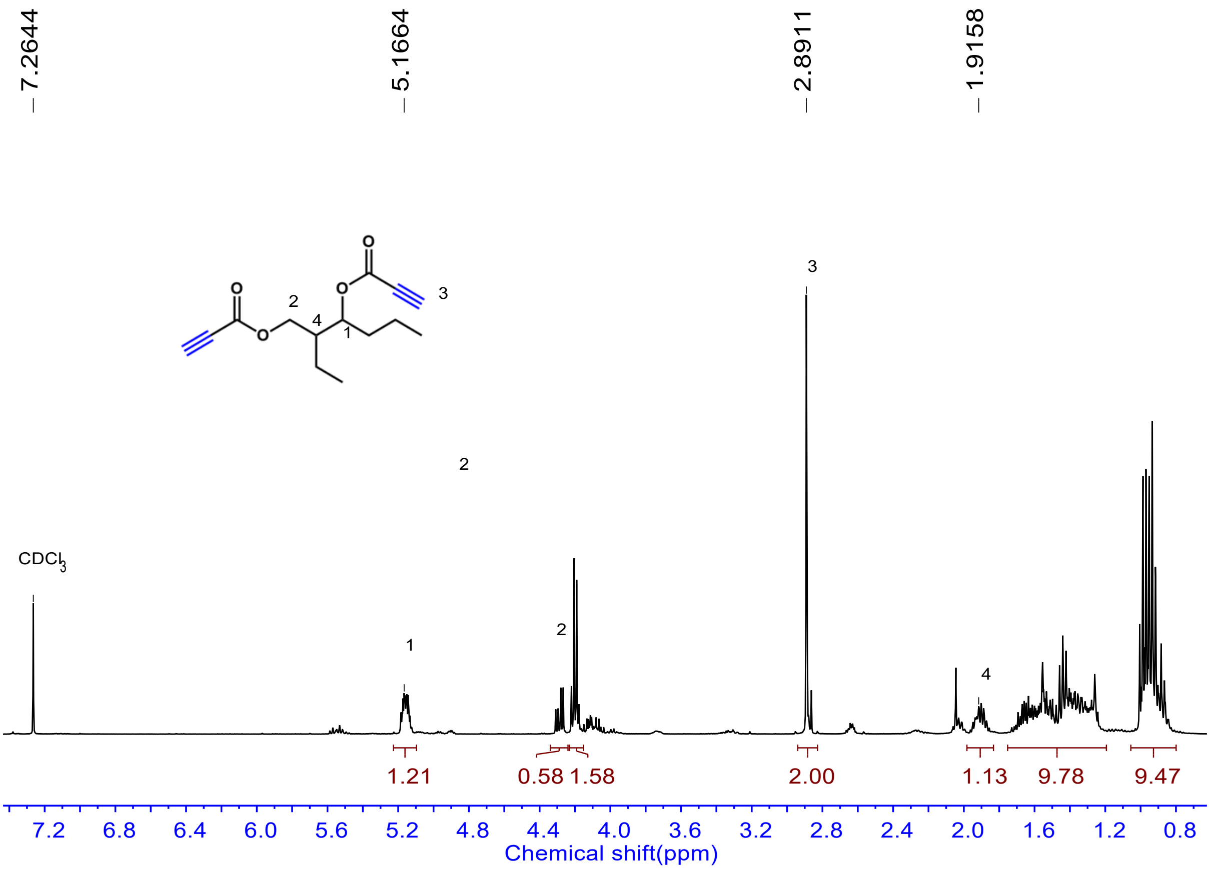

Figure S46. ^{1}H NMR spectrum of EHDP.

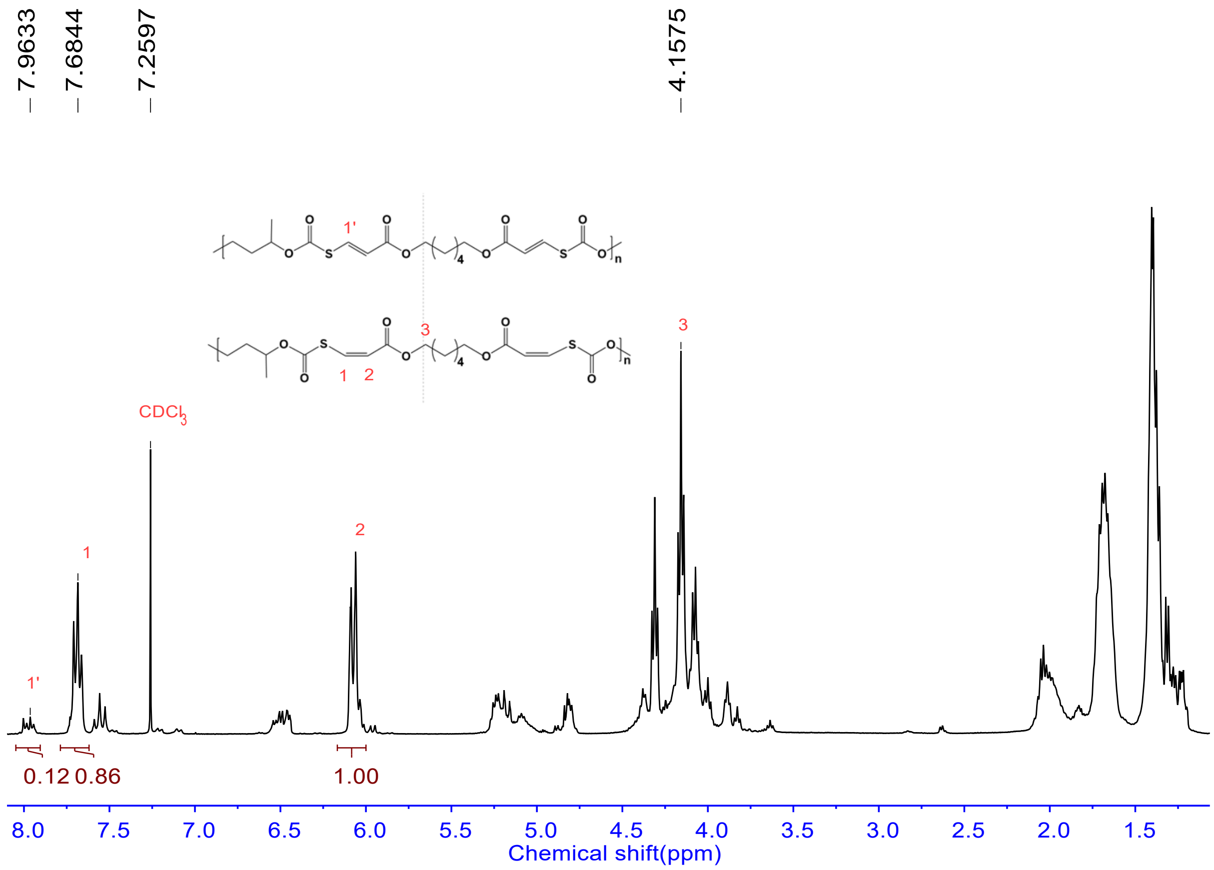

Figure S47. ^{1}H NMR spectrum of the **P1** (in **Figure 5**).

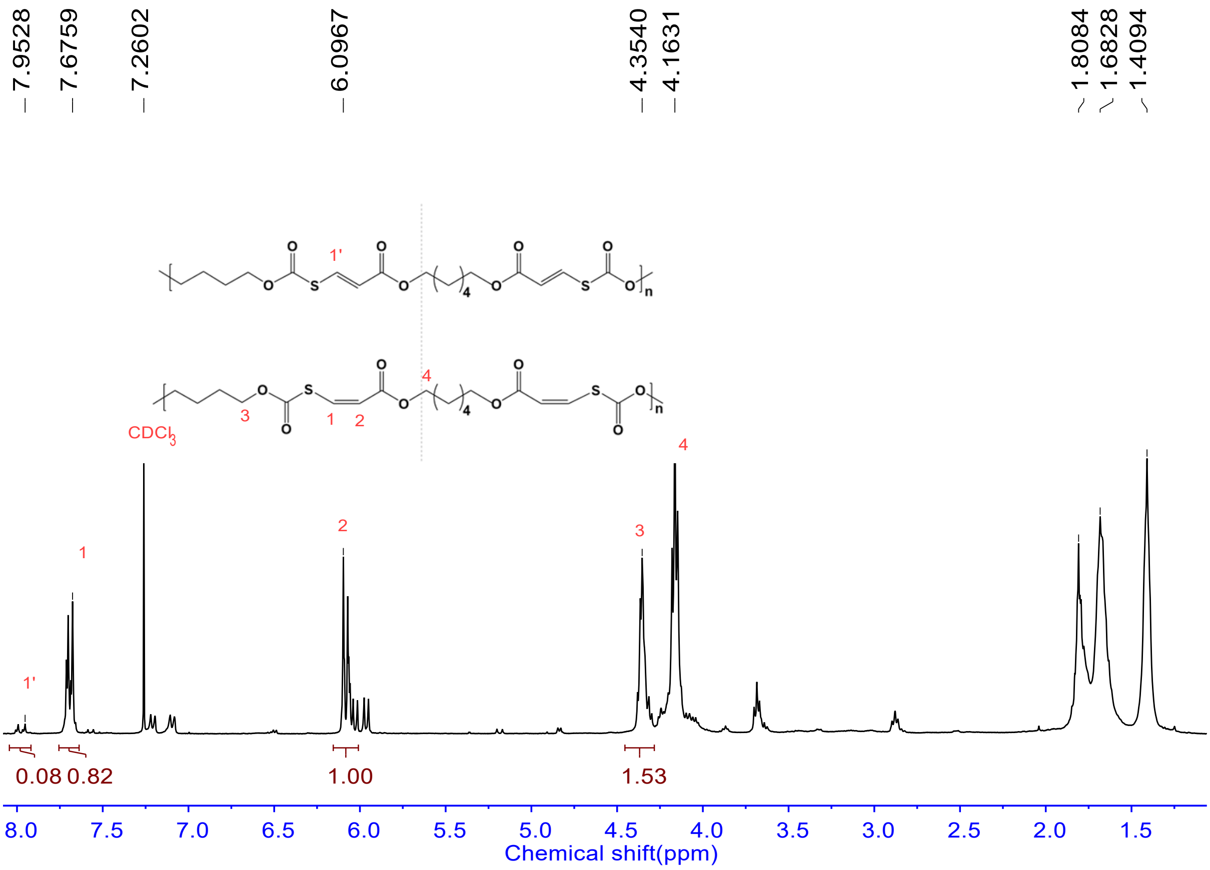

Figure S48. ^{1}H NMR spectrum of the **P2** (in **Figure 5**).

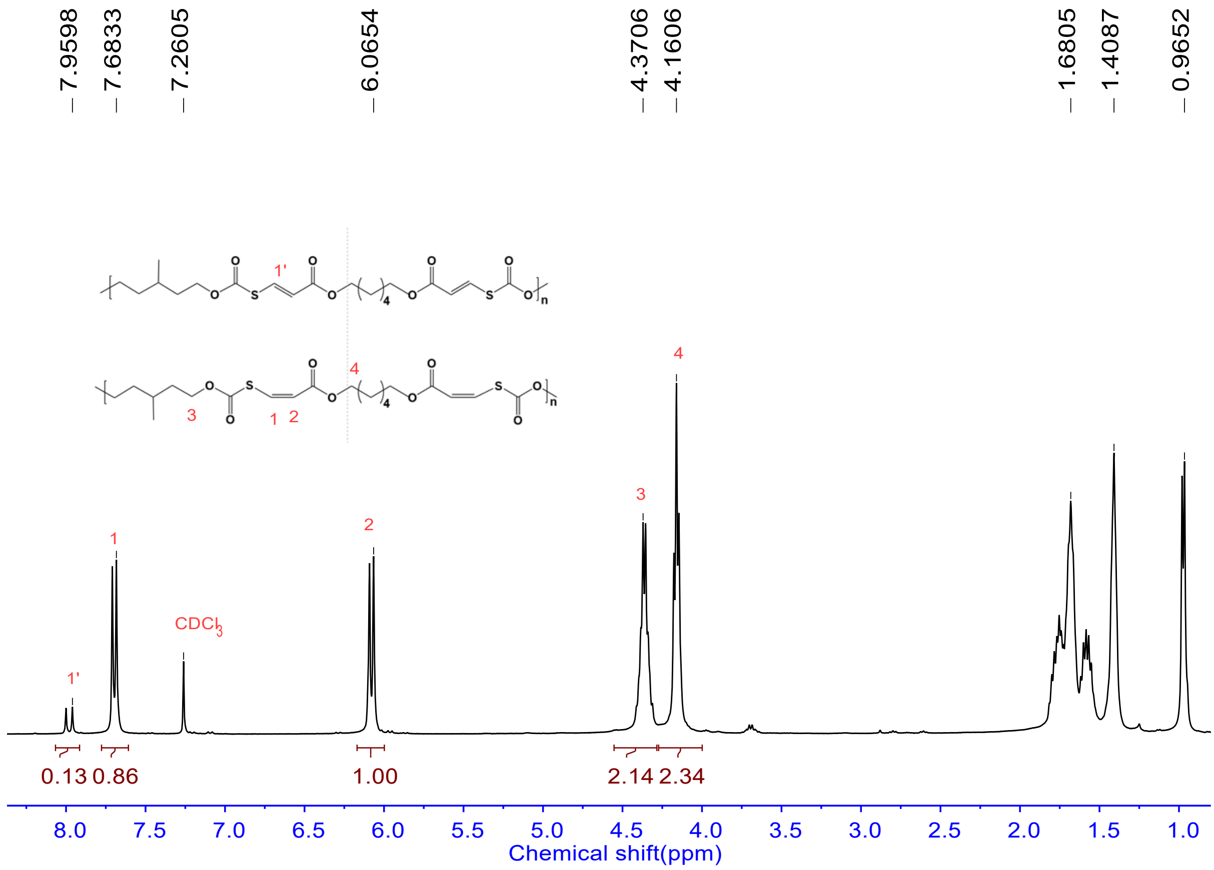

Figure S49. ^{1}H NMR spectrum of the **P3** (in **Figure 5**).

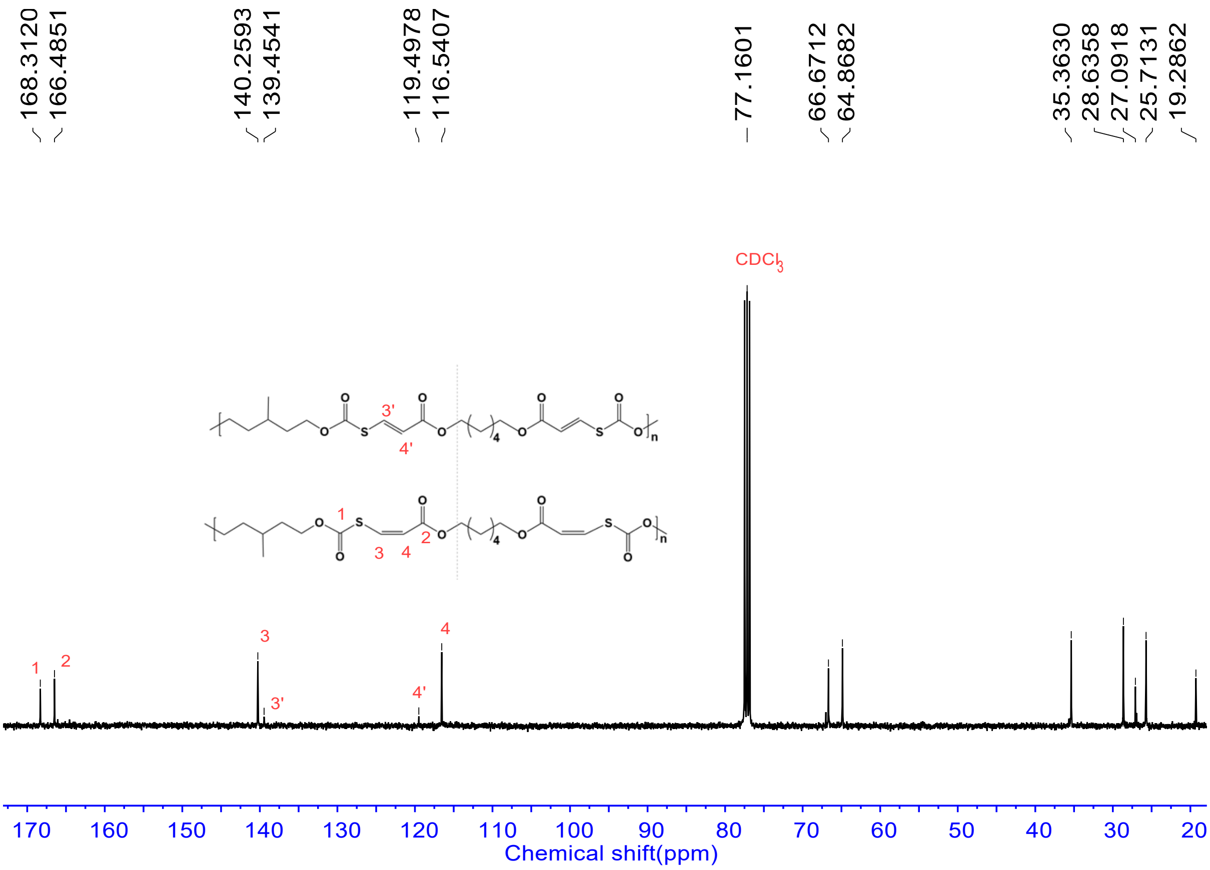

Figure S50. ^{13}C NMR spectrum of the **P3** (in **Figure 5**).

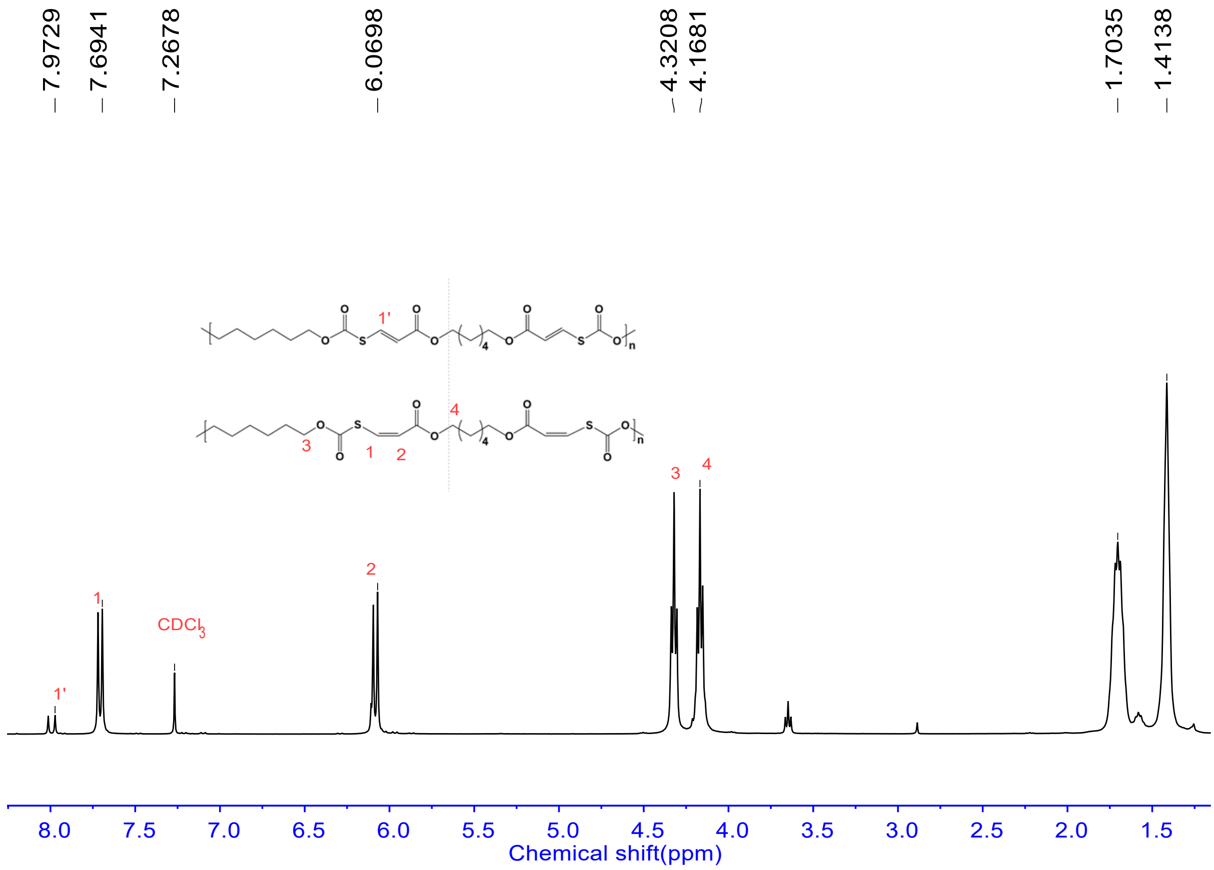

Figure S51. ^{1}H NMR spectrum of the **P4** (in **Figure 5**).

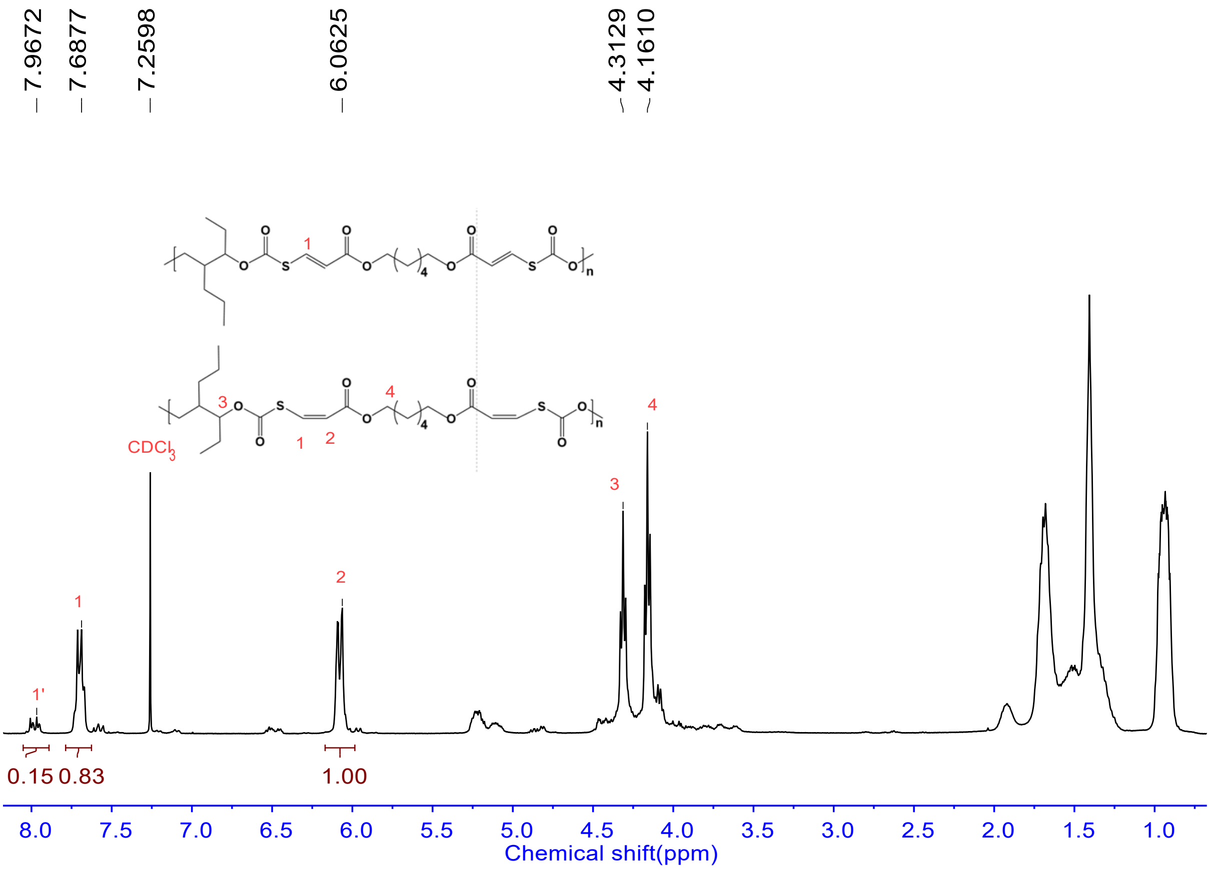

Figure S52. ^{1}H NMR spectrum of the **P5** (in **Figure 5**).

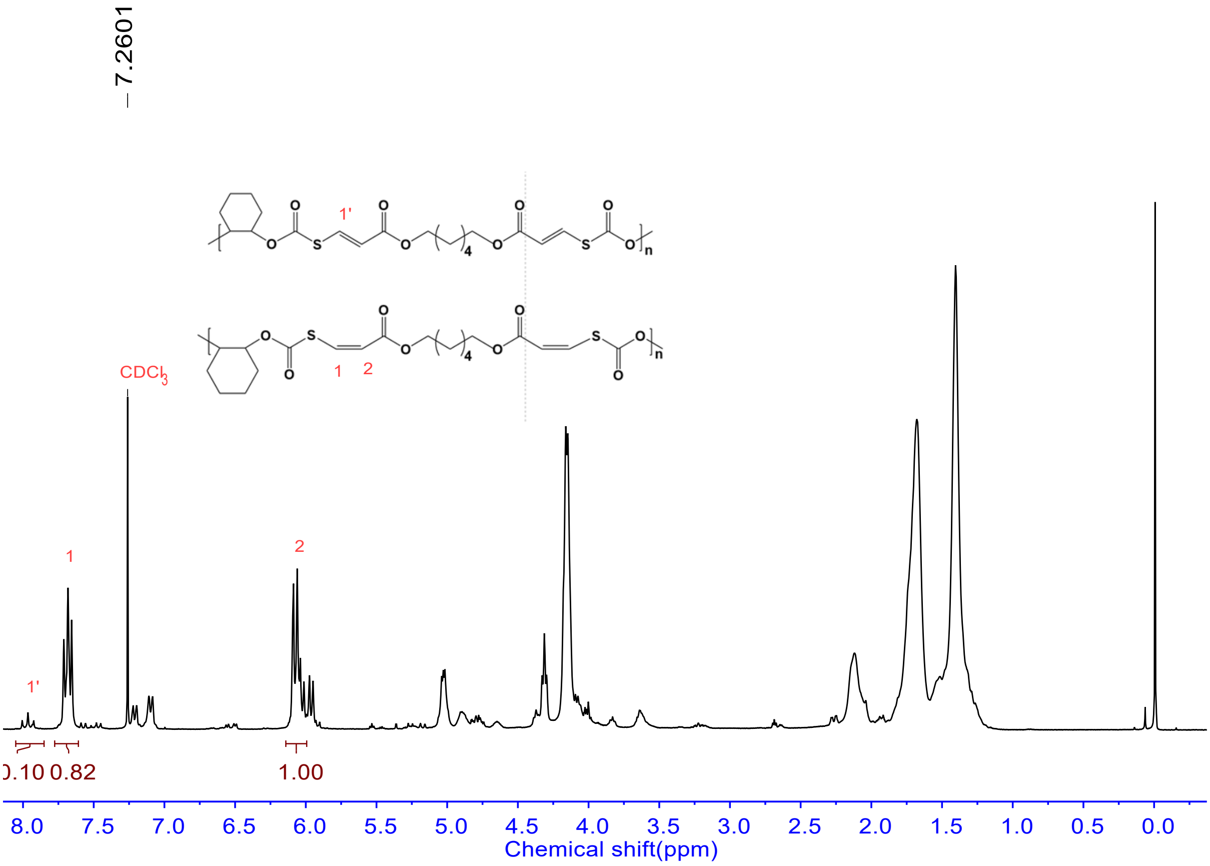

Figure S53. ^{1}H NMR spectrum of the **P6** (in **Figure 5**).

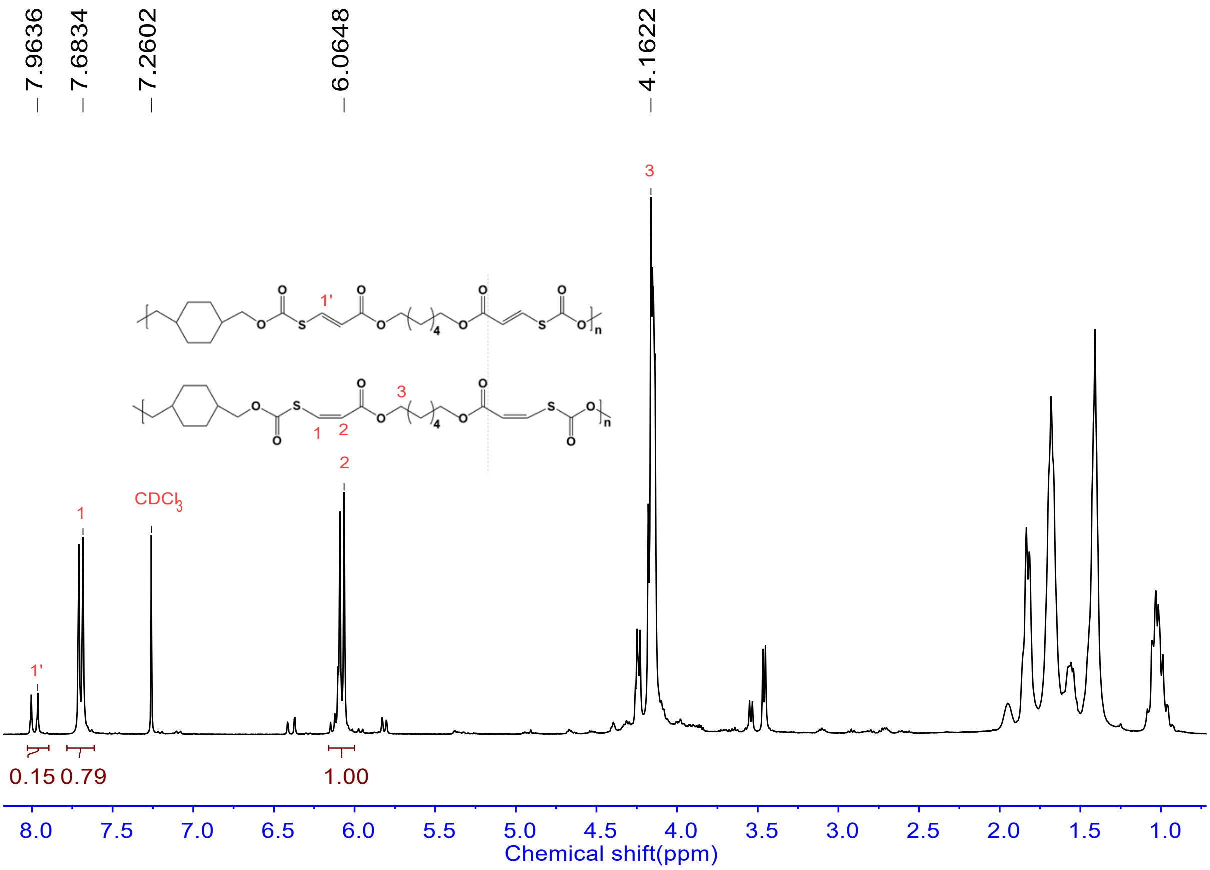

Figure S54. ^{1}H NMR spectrum of the **P7** (in **Figure 5**).

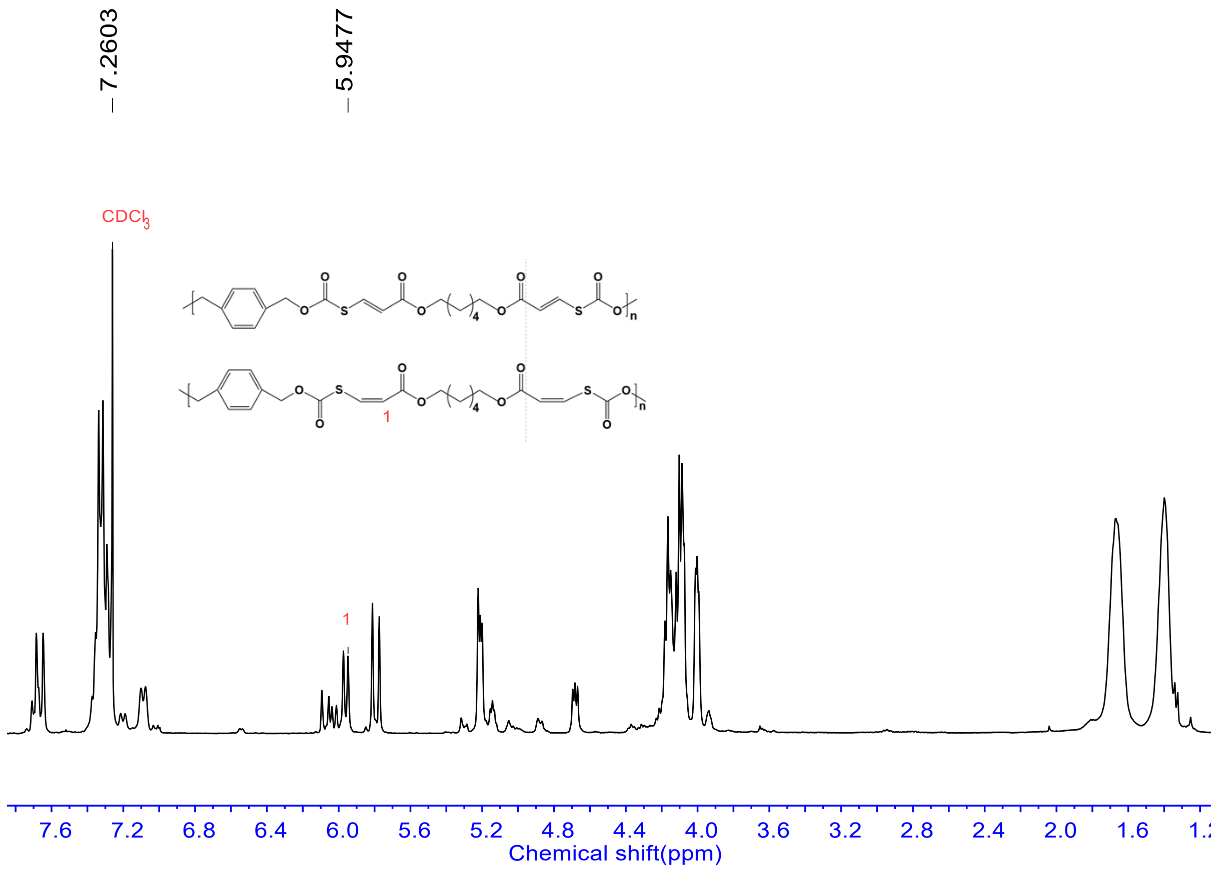

Figure S55. ^{1}H NMR spectrum of the **P8** (in **Figure 5**).

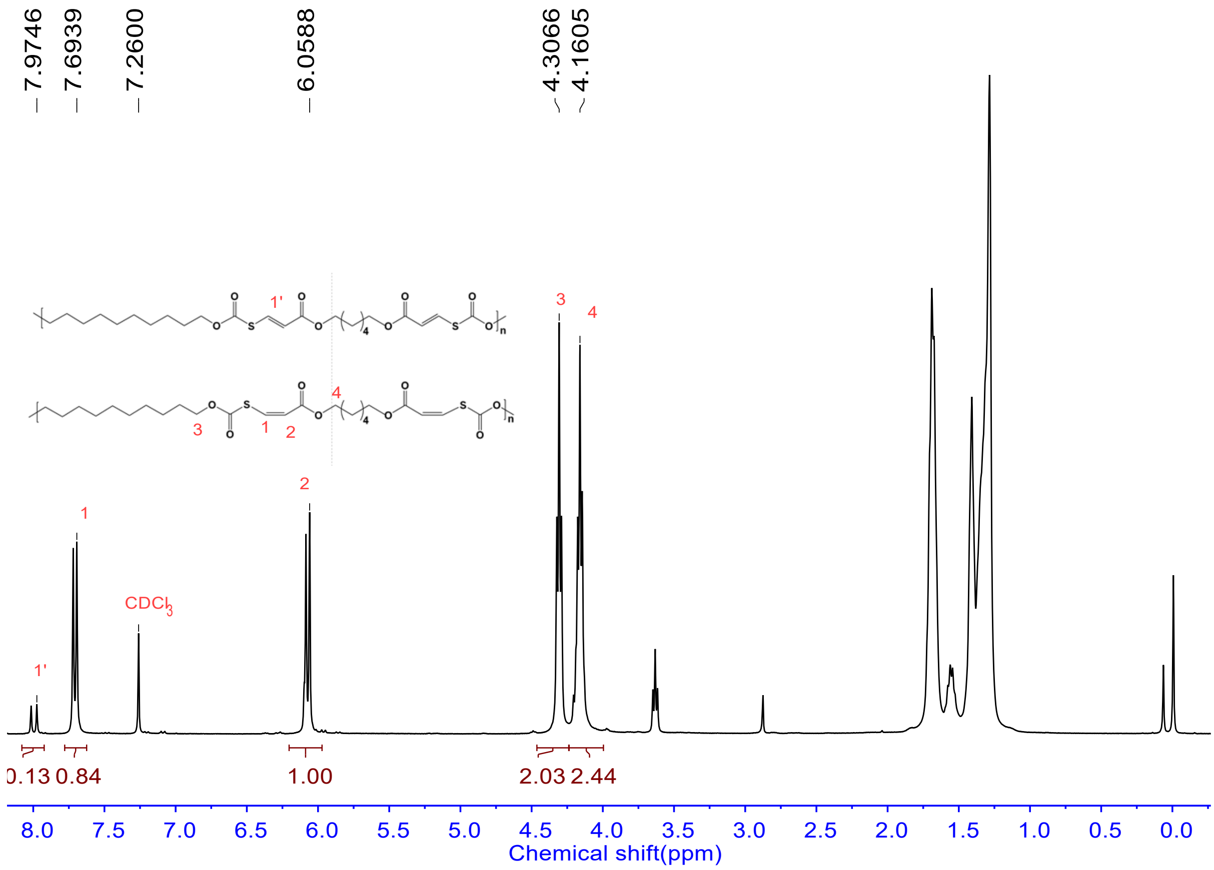

Figure S56. [1]H NMR spectrum of the **P9** (in **Figure 5**).

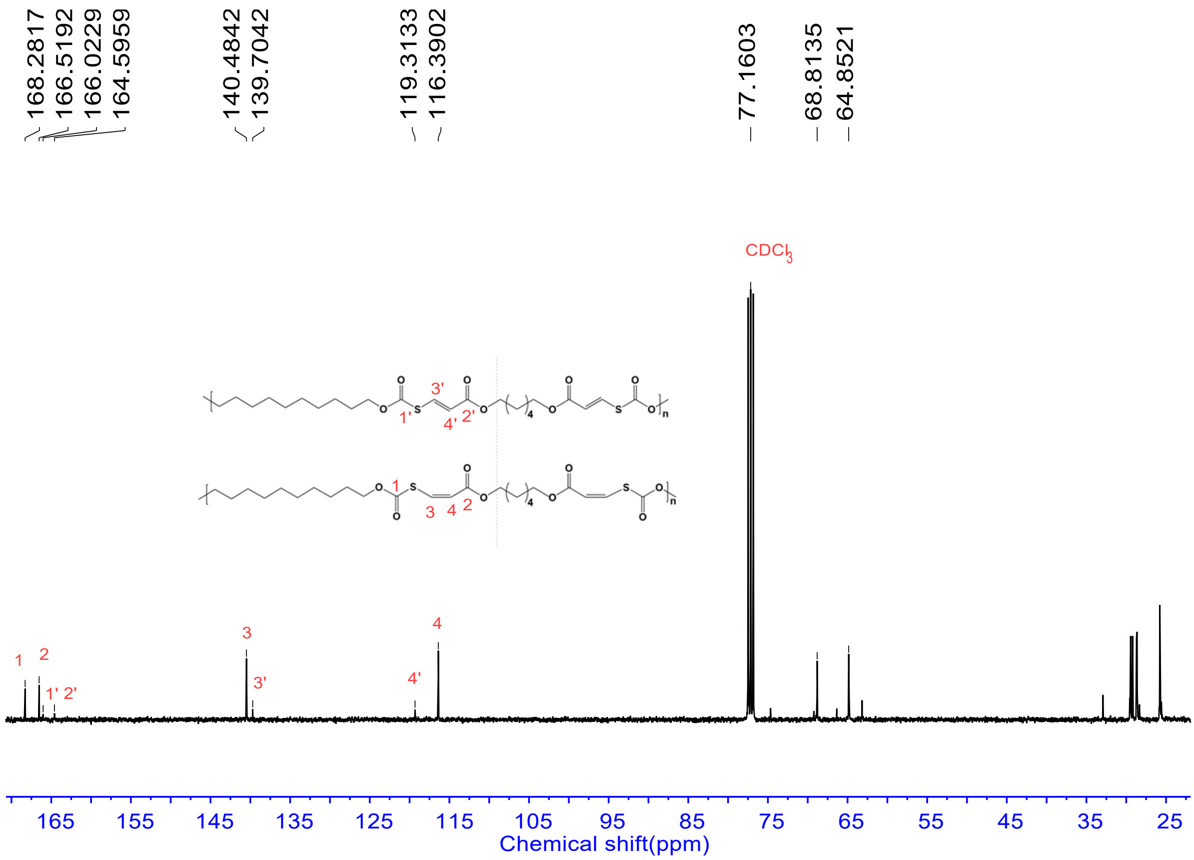

Figure S57. ^{13}C NMR spectrum of the **P9** (in **Figure 5**).

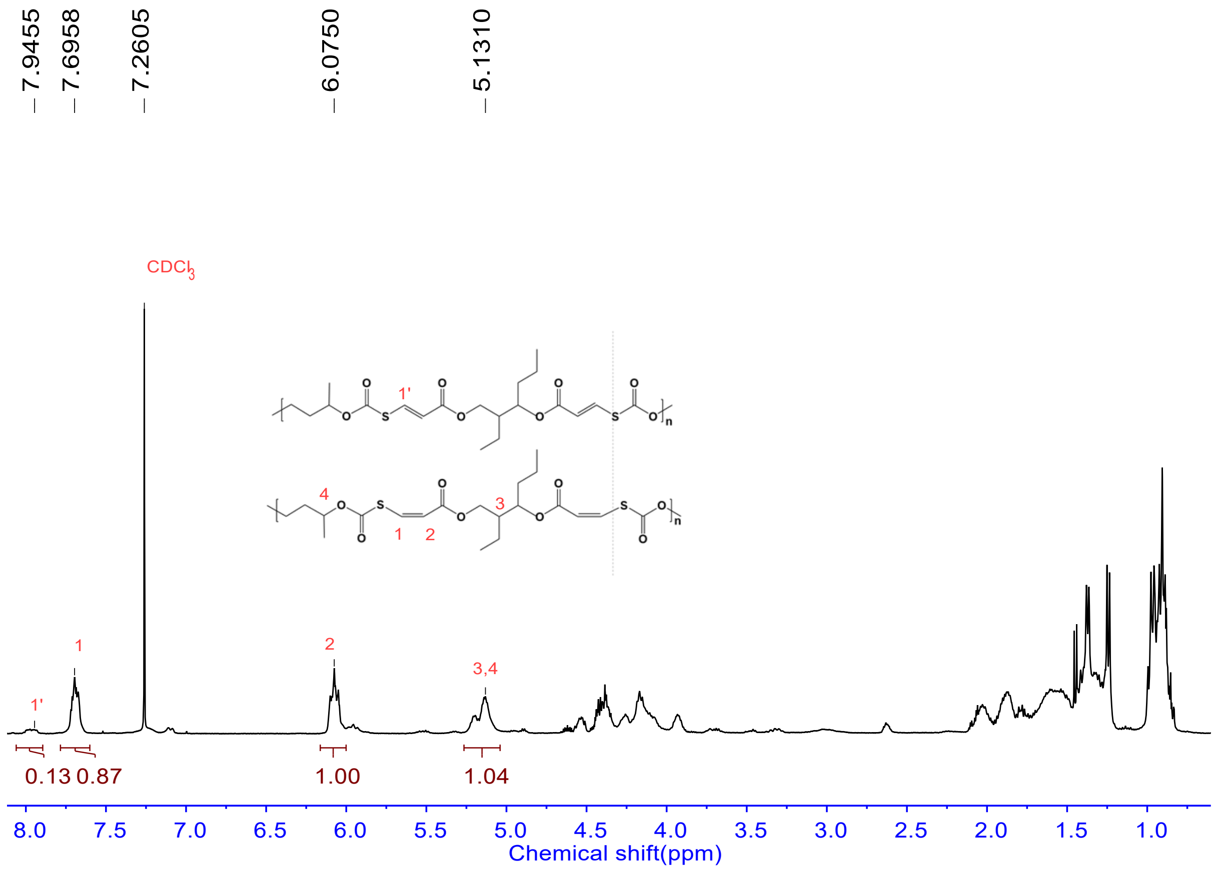

Figure S58. ^{1}H NMR spectrum of the **P10** (in **Figure 5**).

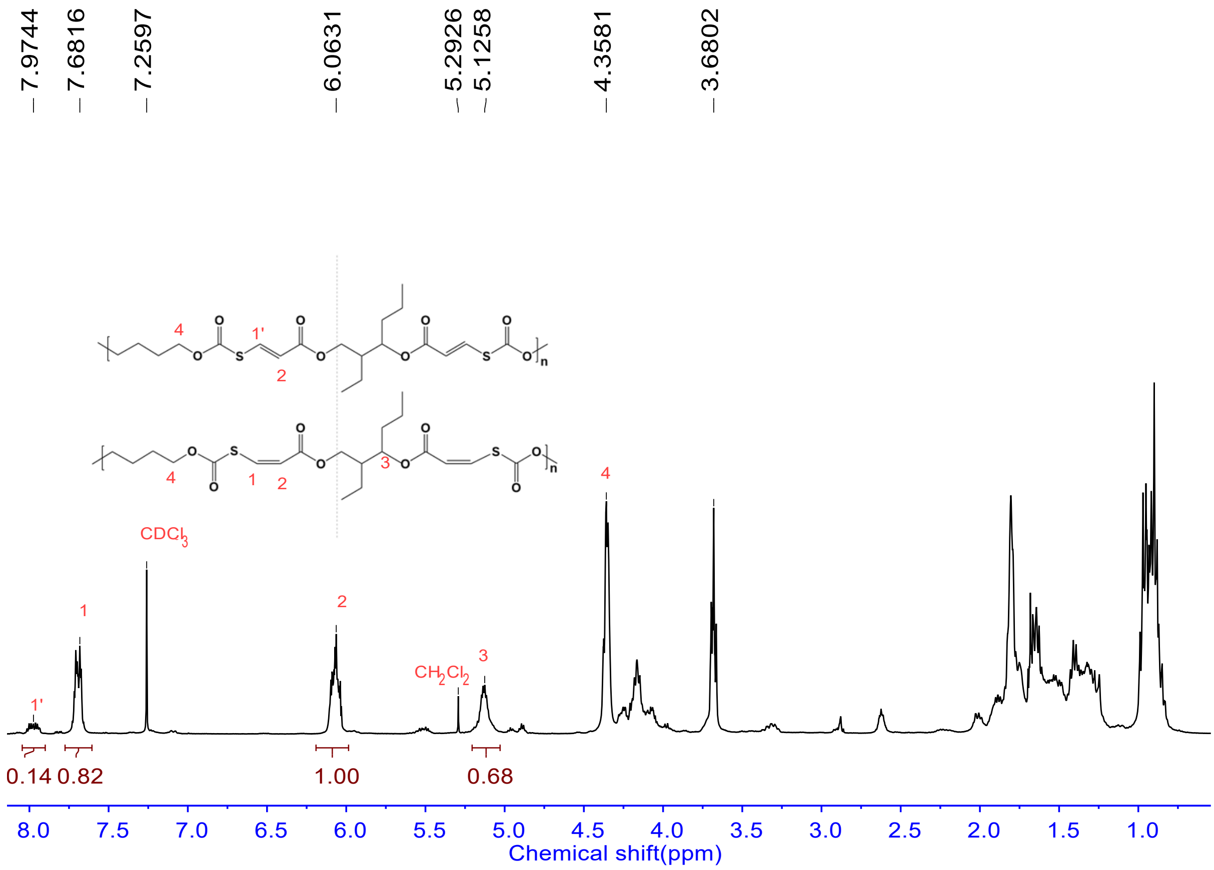

Figure S59. ^{1}H NMR spectrum of the **P11** (in **Figure 5**).

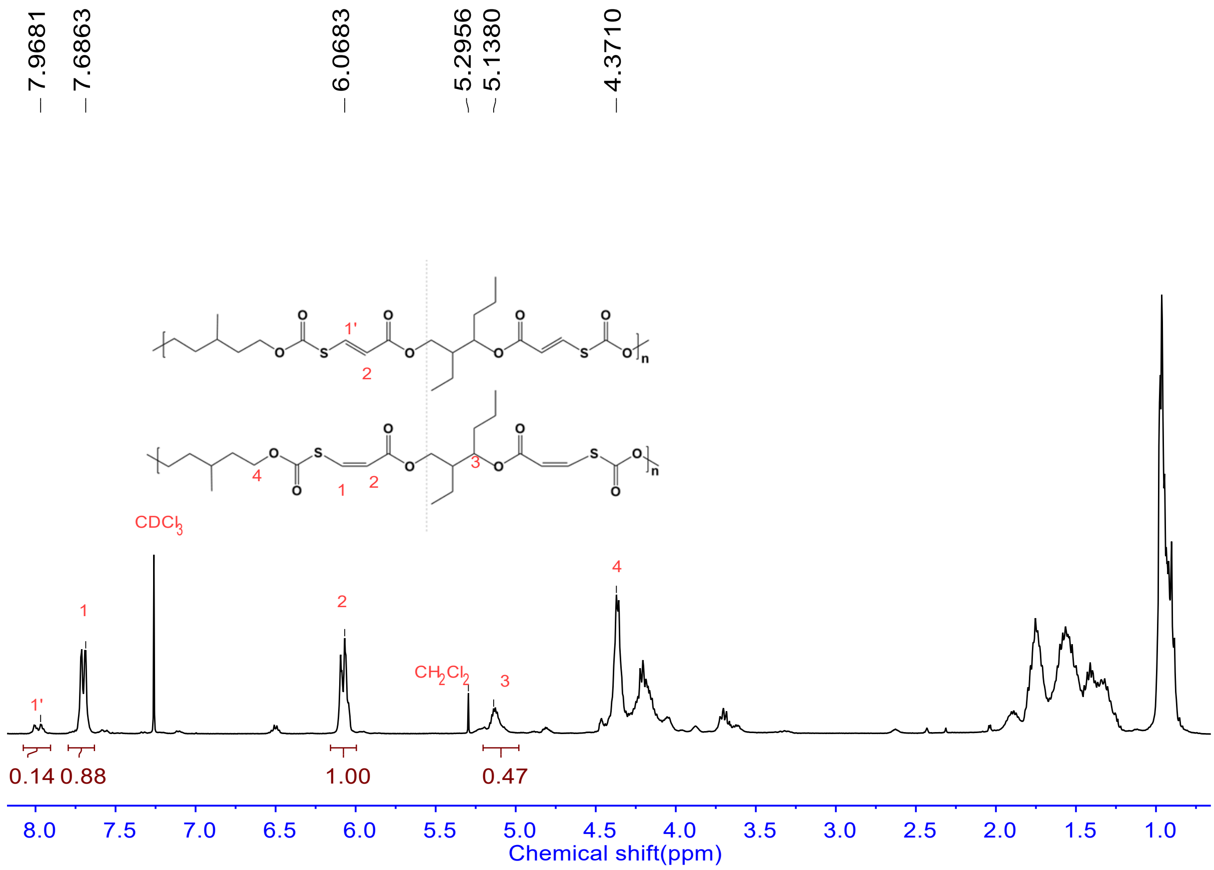

Figure S60. ^{1}H NMR spectrum of the **P12** (in **Figure 5**).

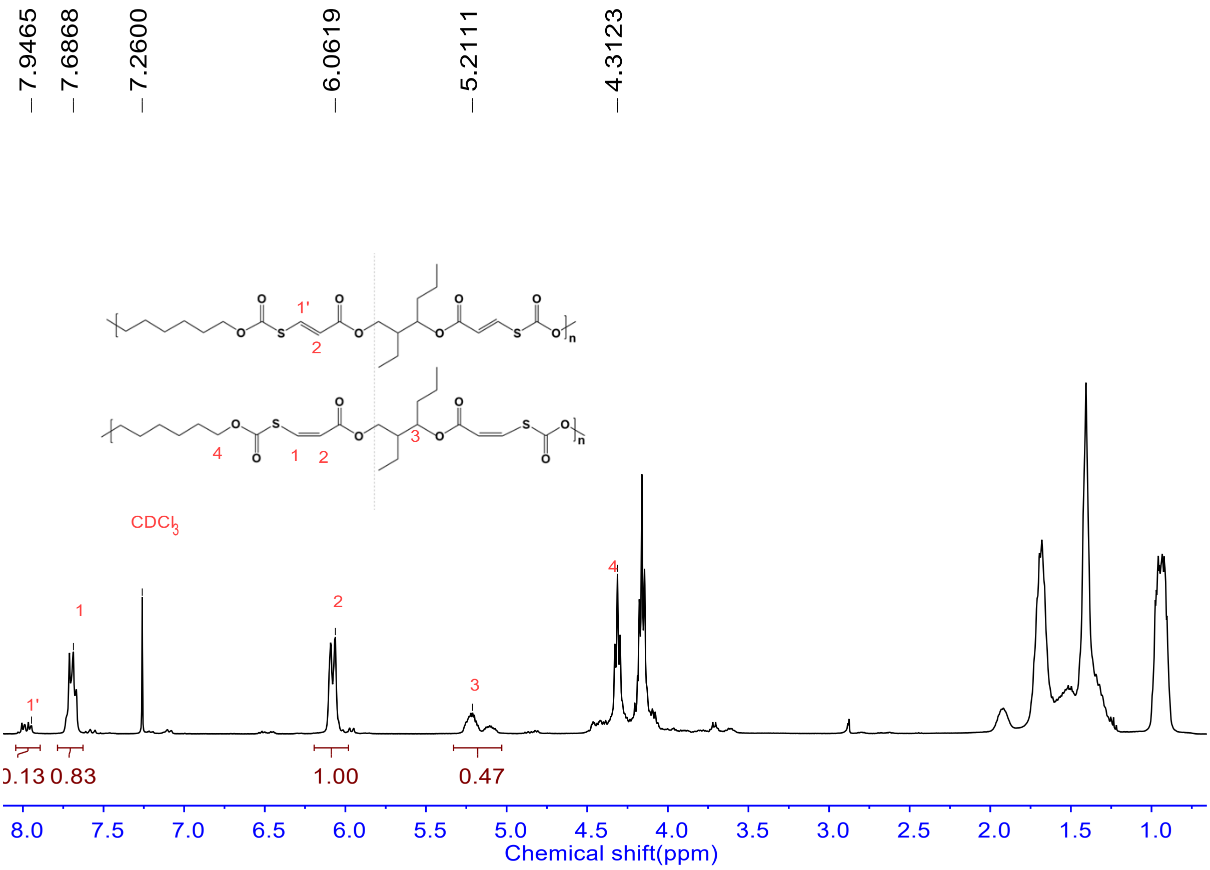

Figure S61. ^{1}H NMR spectrum of the **P13** (in **Figure 5**).

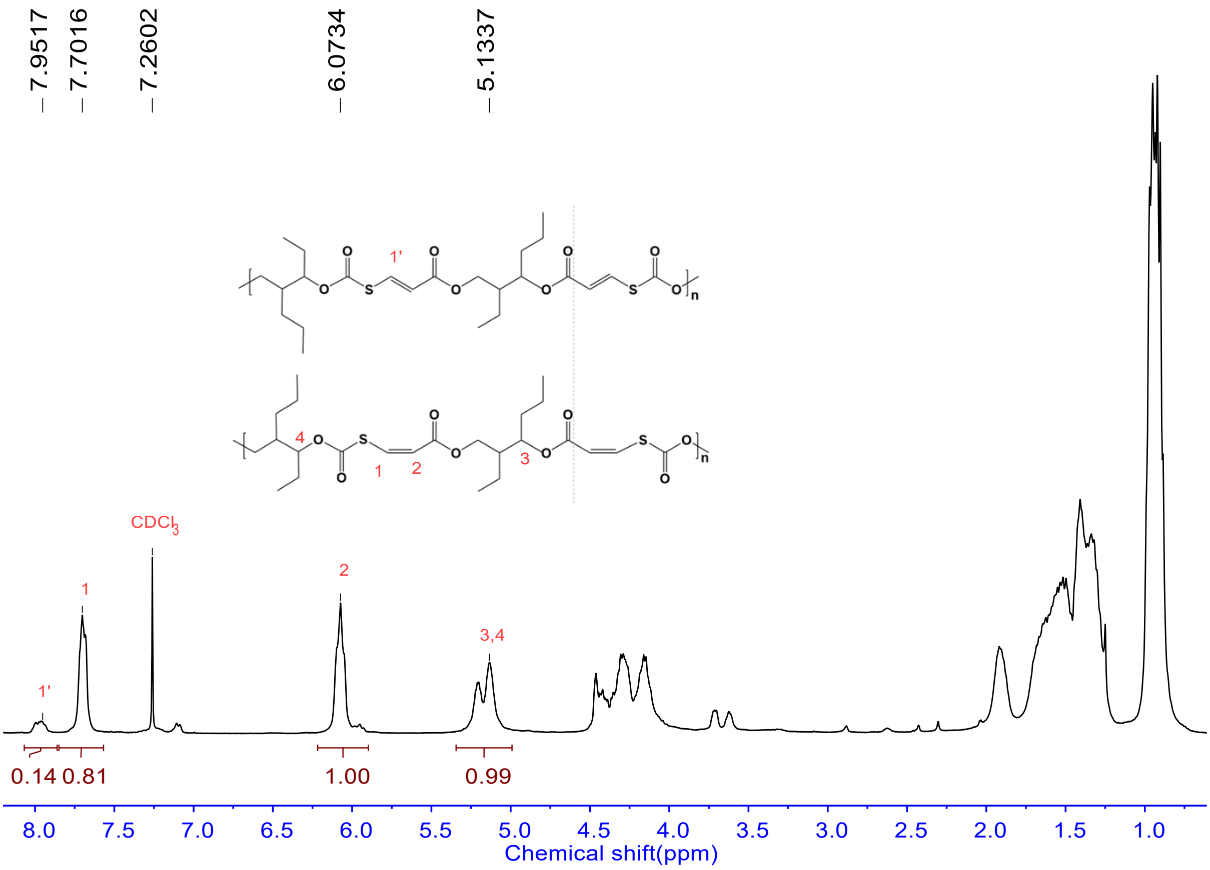

Figure S62. ^{1}H NMR spectrum of the **P14** (in **Figure 5**).

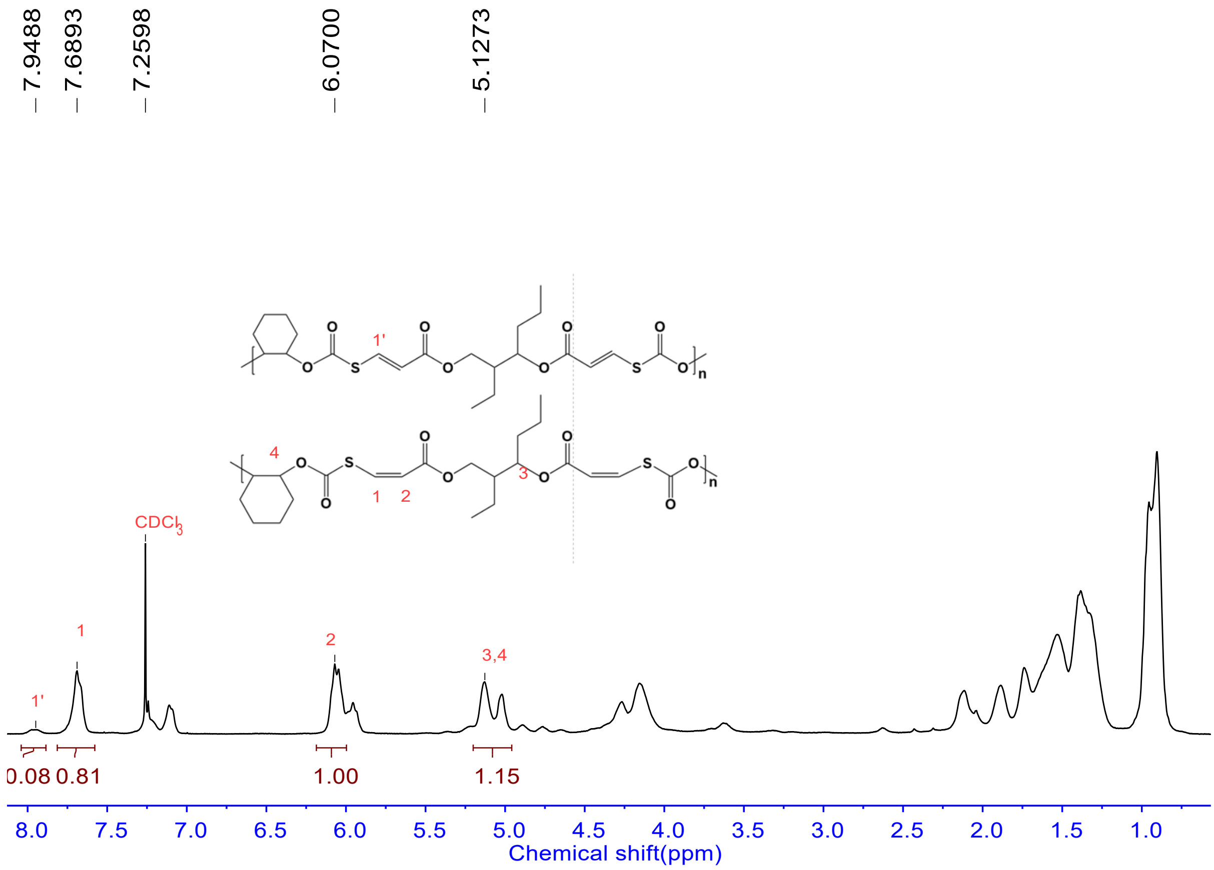

Figure S63. ^{1}H NMR spectrum of the **P15** (in **Figure 5**).

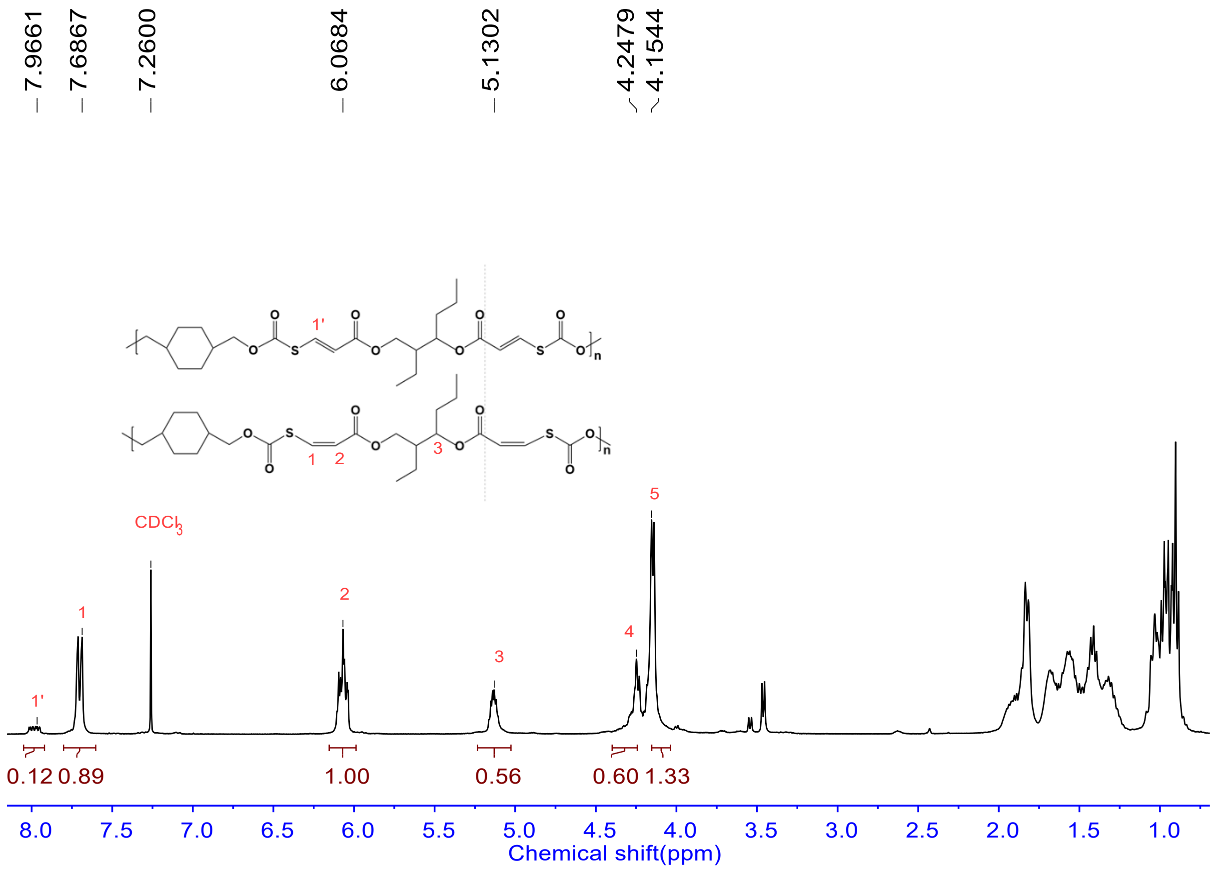

Figure S64. ^{1}H NMR spectrum of the **P16** (in **Figure 5**).

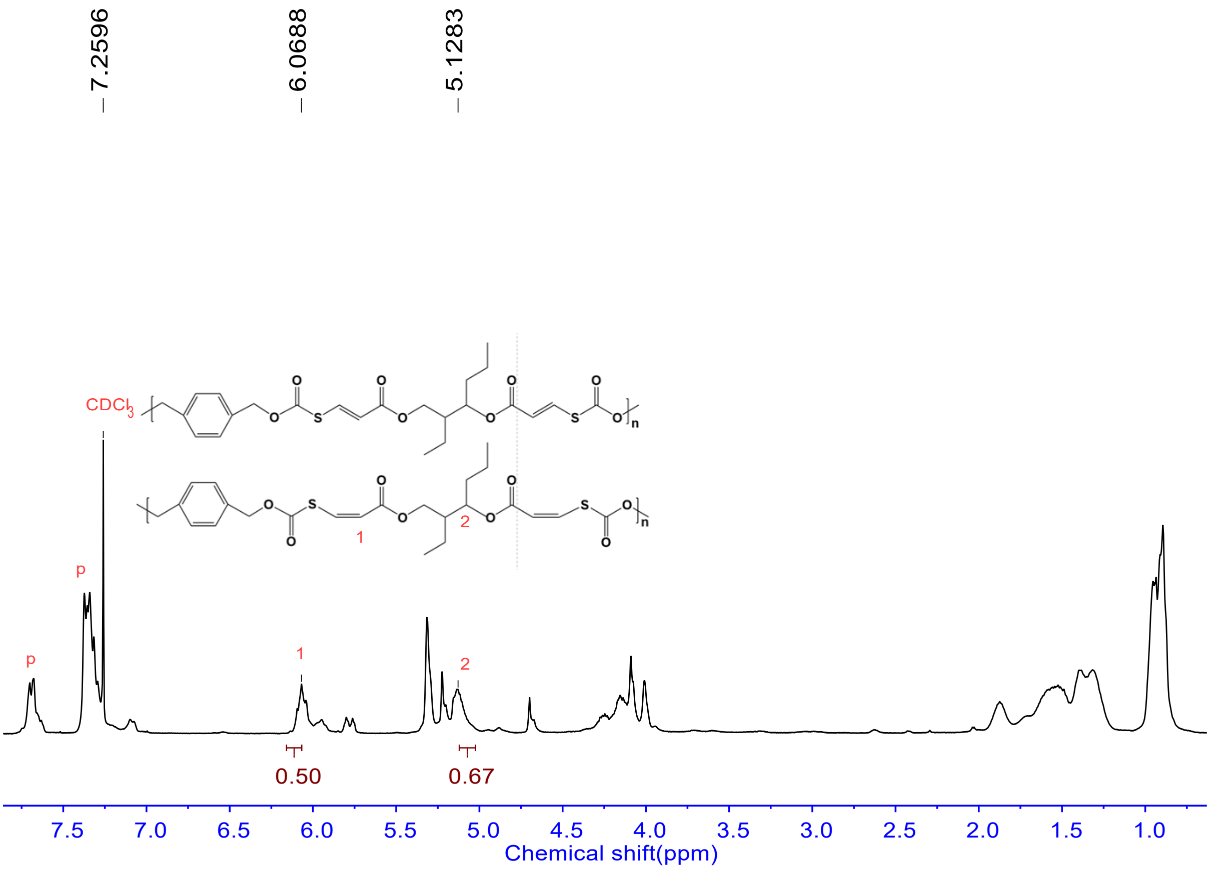

Figure S65. ^{1}H NMR spectrum of the **P17** (in **Figure 5**).

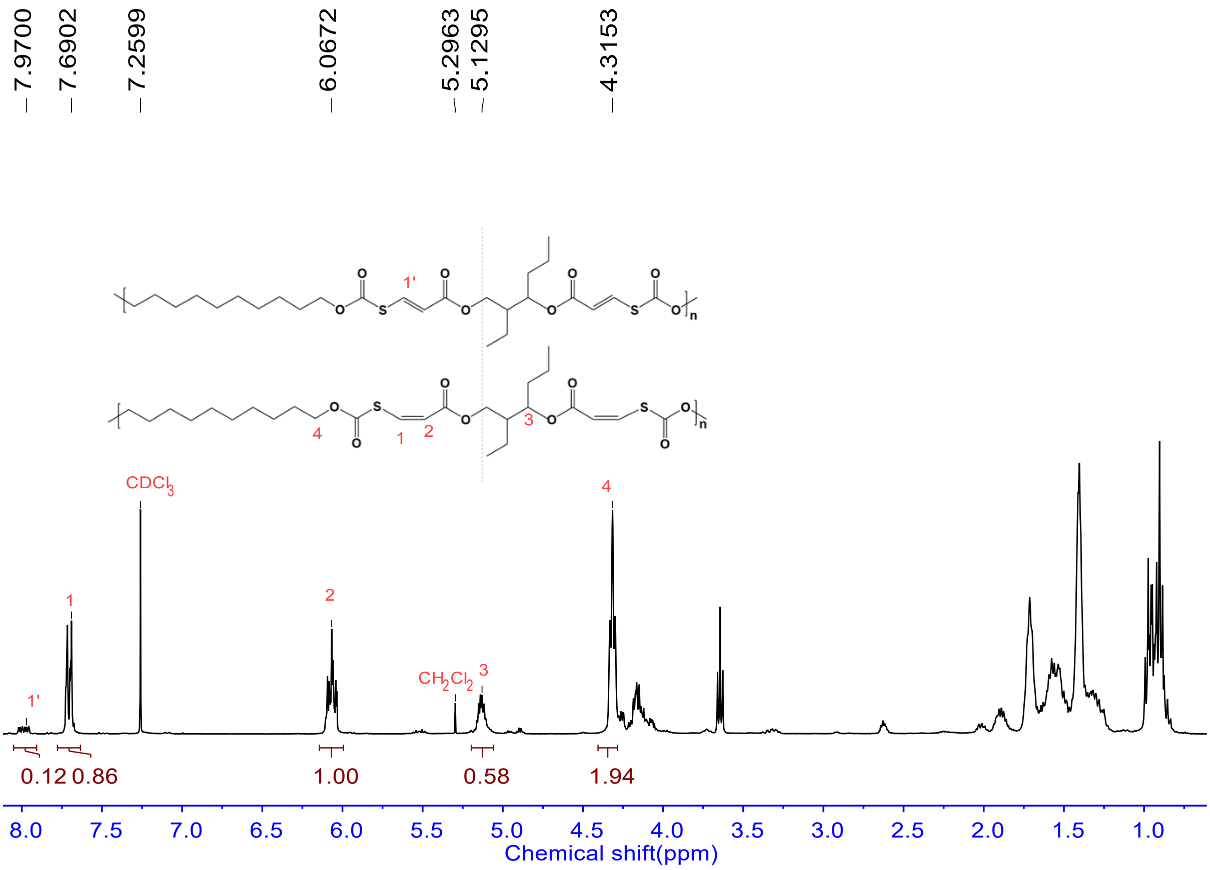

Figure S66. ^{1}H NMR spectrum of the **P18** (in **Figure 5**).

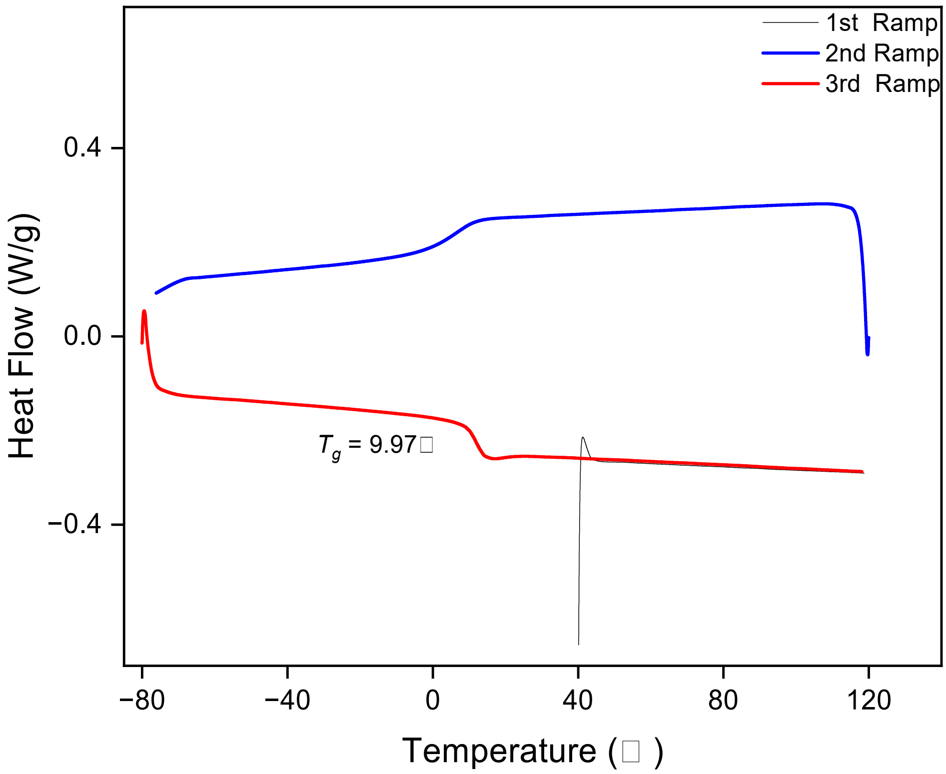

Figure S67. DSC curve of the **P1** (in **Figure 5**).

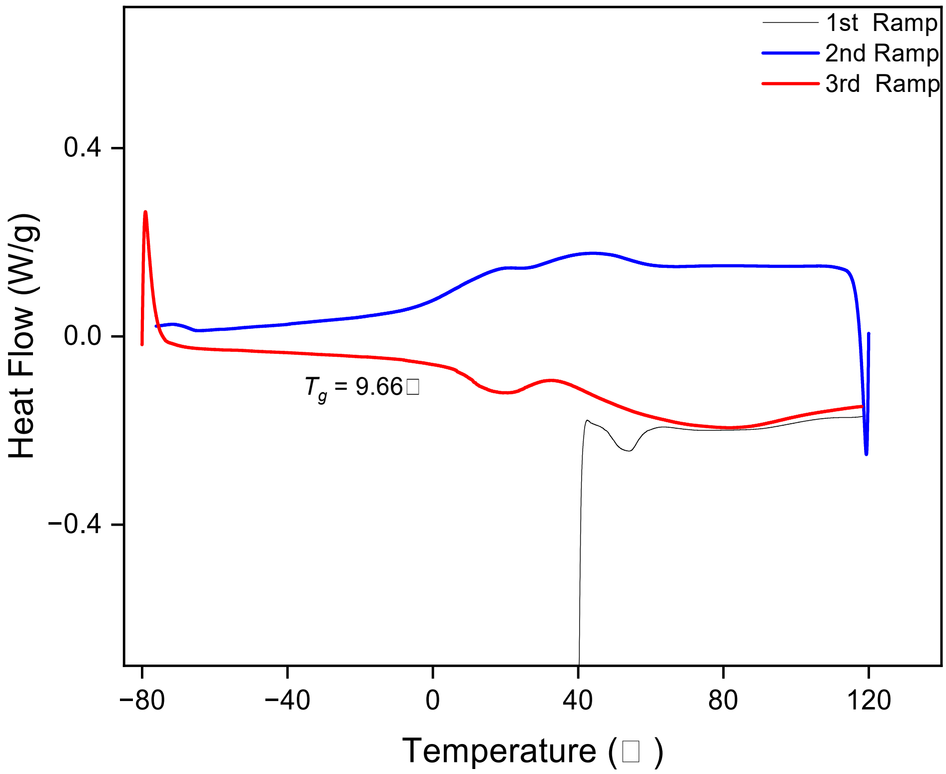

Figure S68. DSC curve of the **P2** (in **Figure 5**).

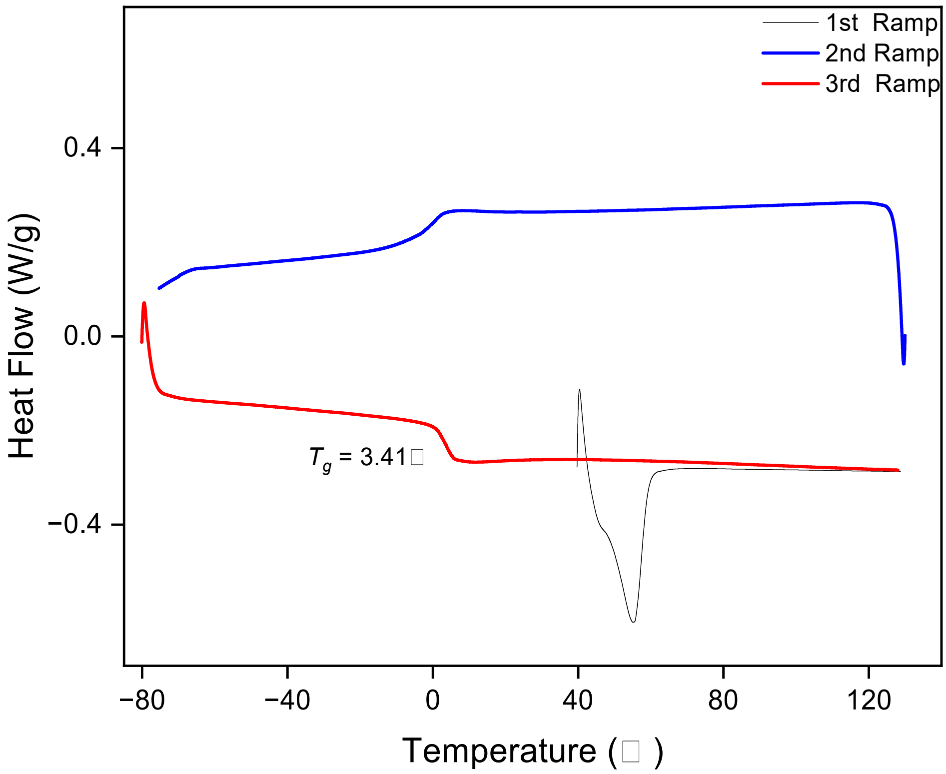

Figure S69. DSC curve of the **P3** (in **Figure 5**).

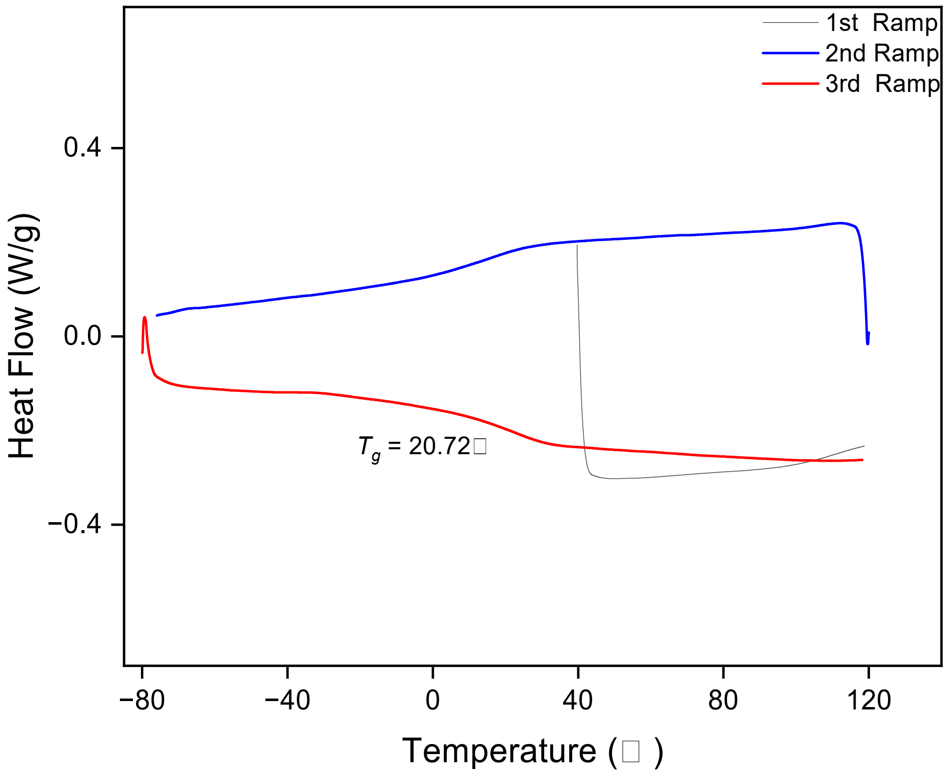

Figure S70. DSC curve of the **P4** (in **Figure 5**).

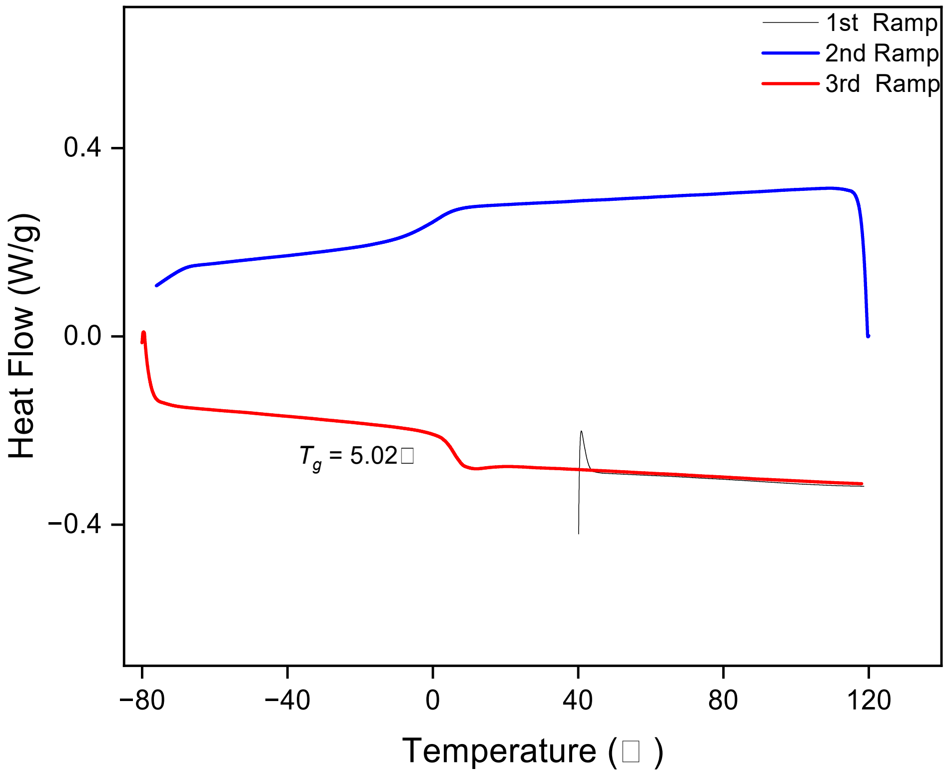

Figure S71. DSC curve of the **P5** (in **Figure 5**).

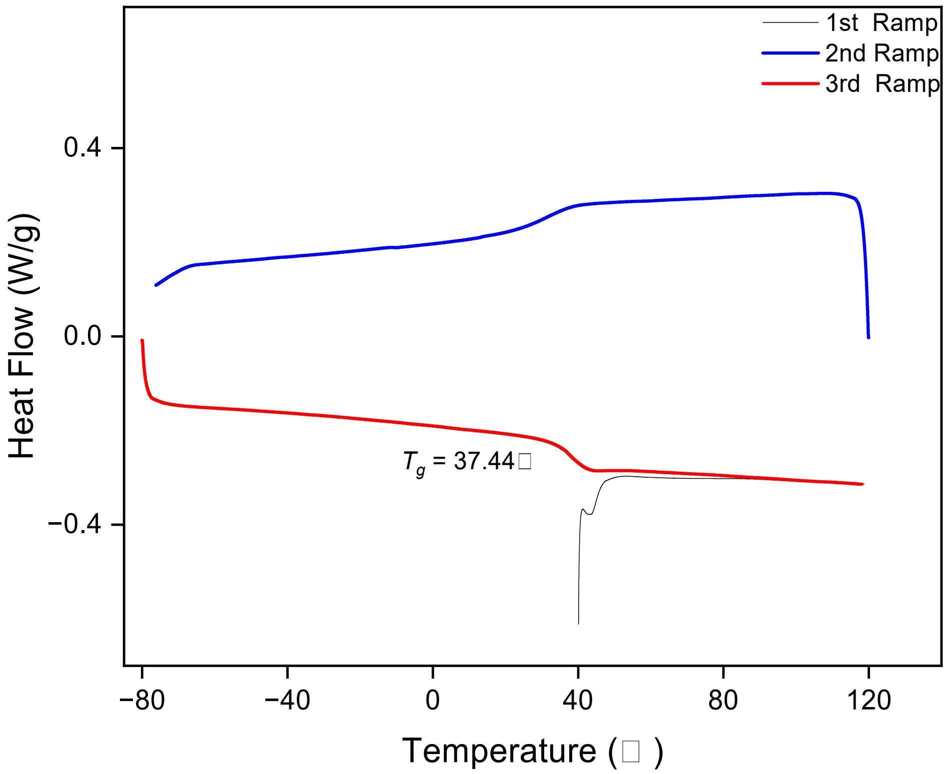

Figure S72. DSC curve of the **P6** (in **Figure 5**).

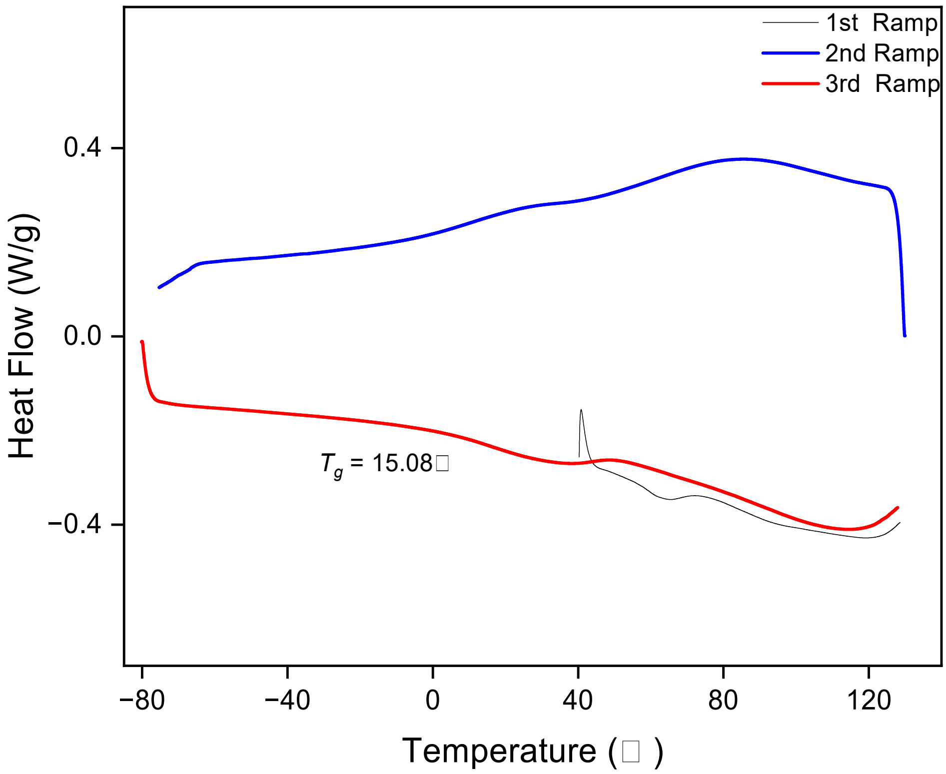

Figure S73. DSC curve of the **P7** (in **Figure 5**).

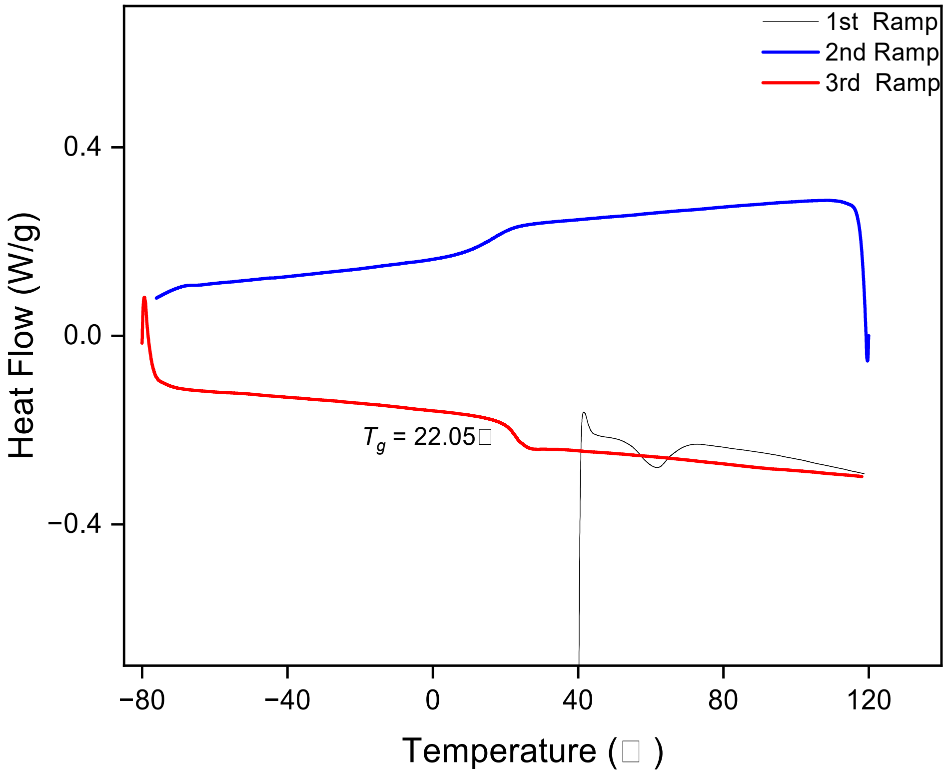

Figure S74. DSC curve of the **P8** (in **Figure 5**).

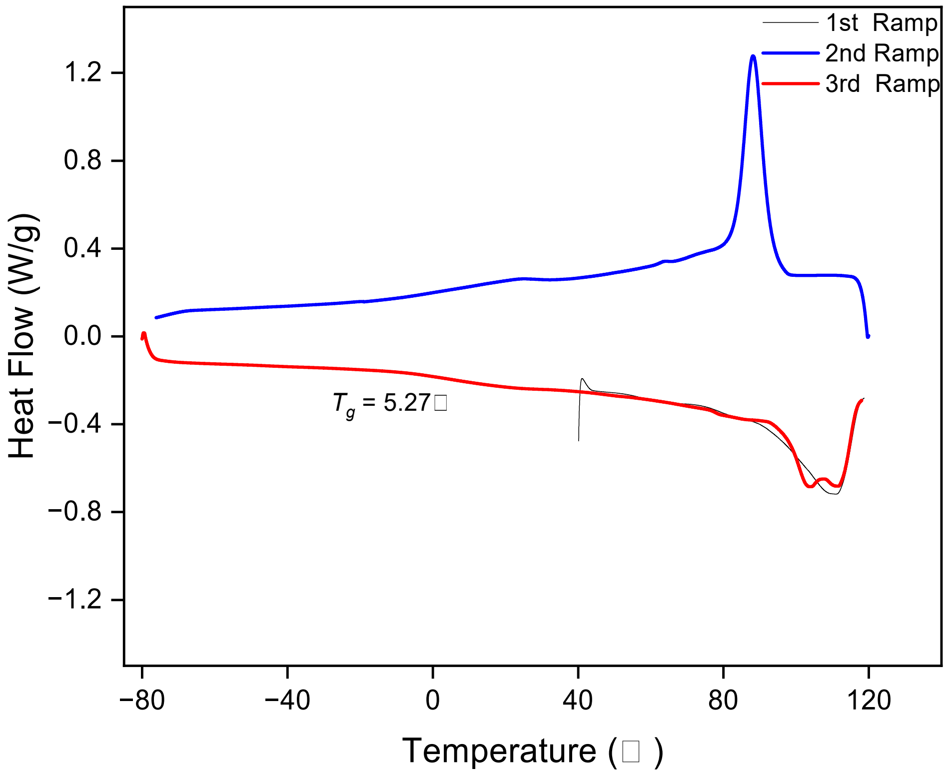

Figure S75. DSC curve of the **P9** (in **Figure 5**).

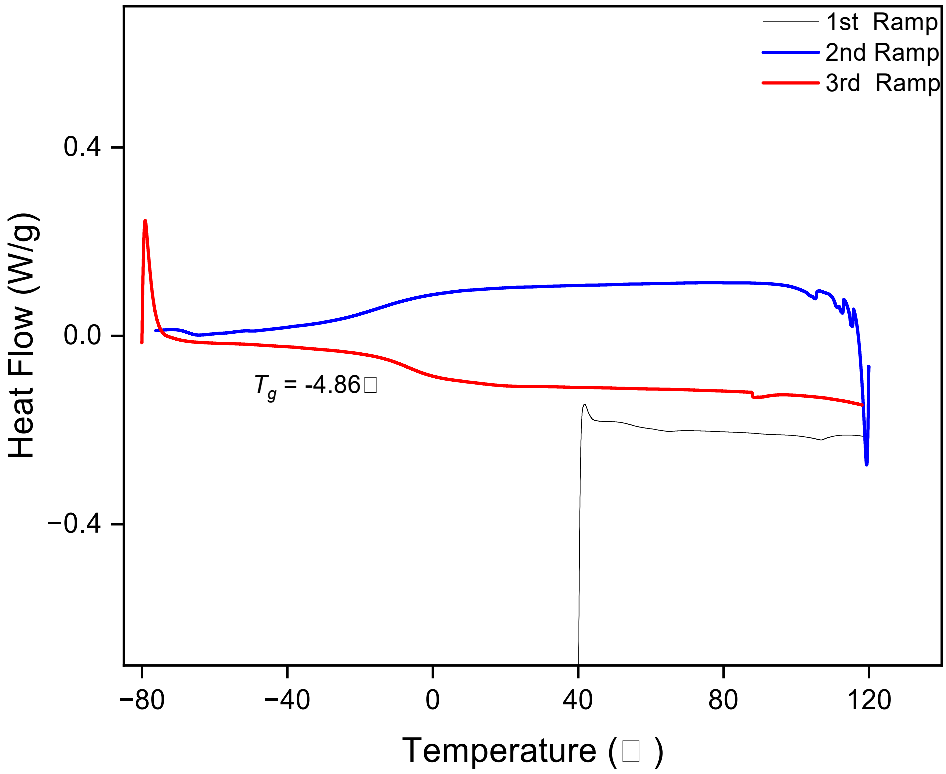

Figure S76. DSC curve of the **P10** (in **Figure 5**).

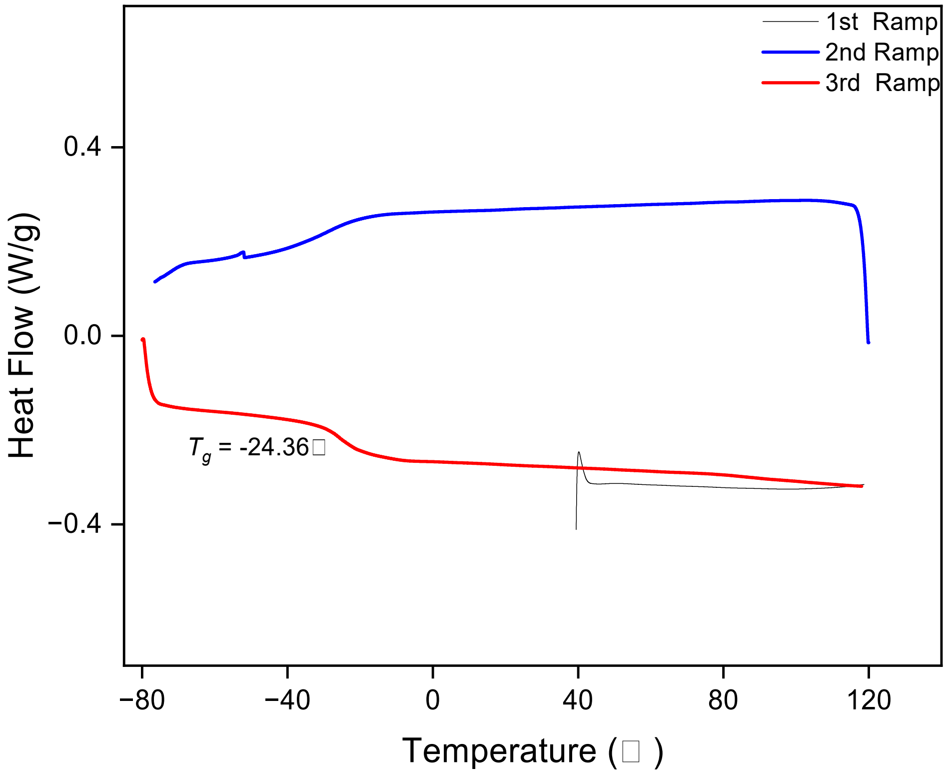

Figure S77. DSC curve of the **P11** (in **Figure 5**).

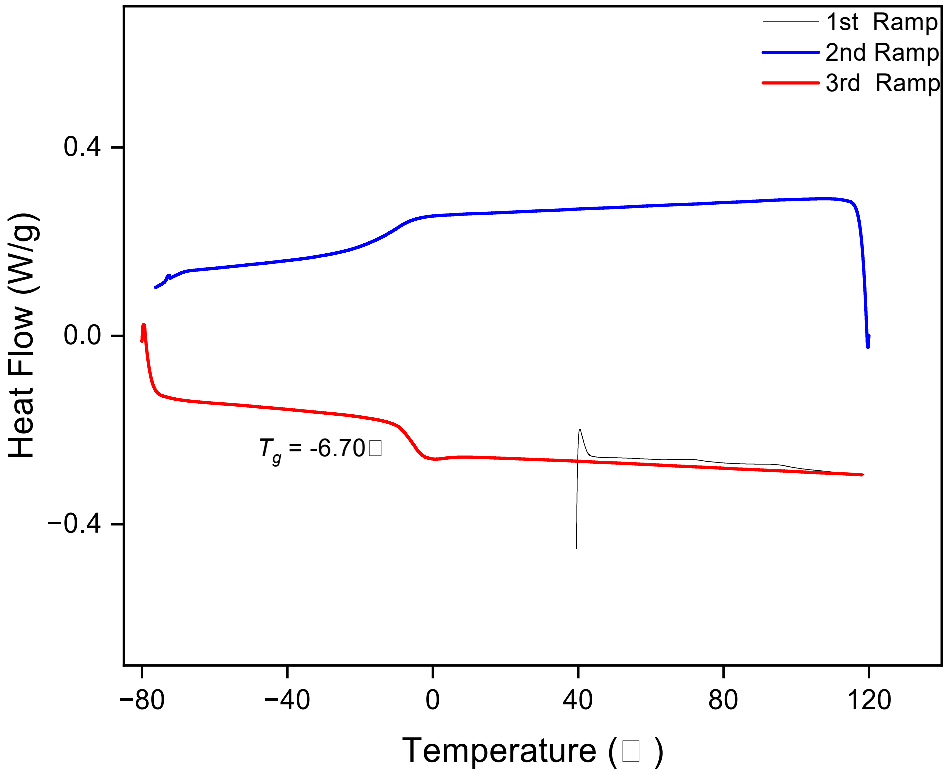

Figure S78. DSC curve of the **P12** (in **Figure 5**).

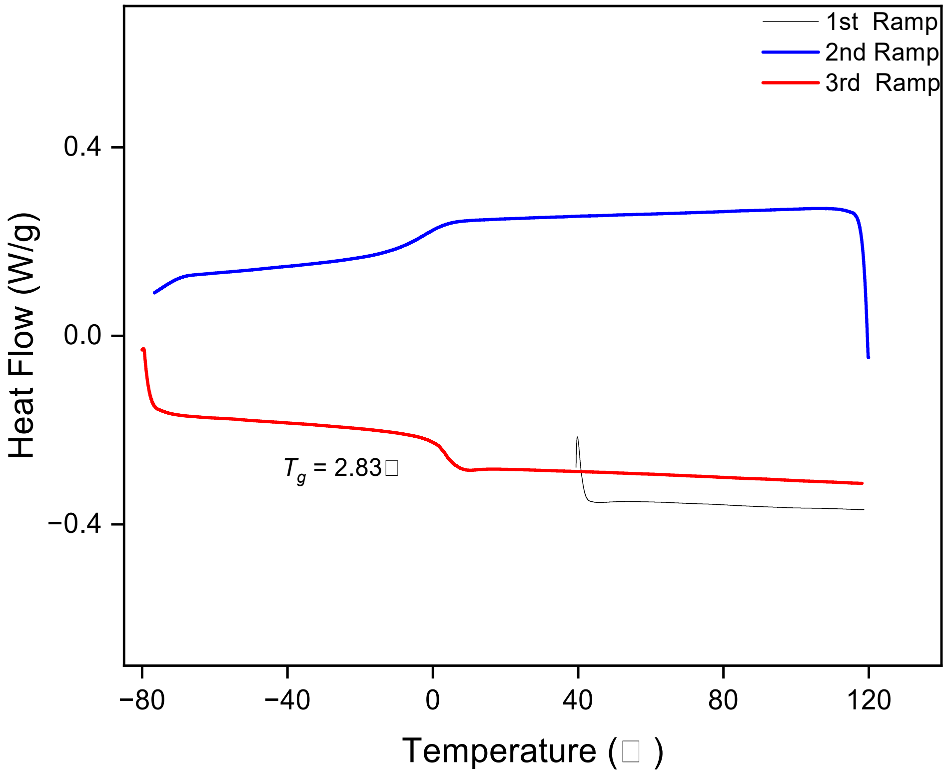

Figure S79. DSC curve of the **P13** (in **Figure 5**).

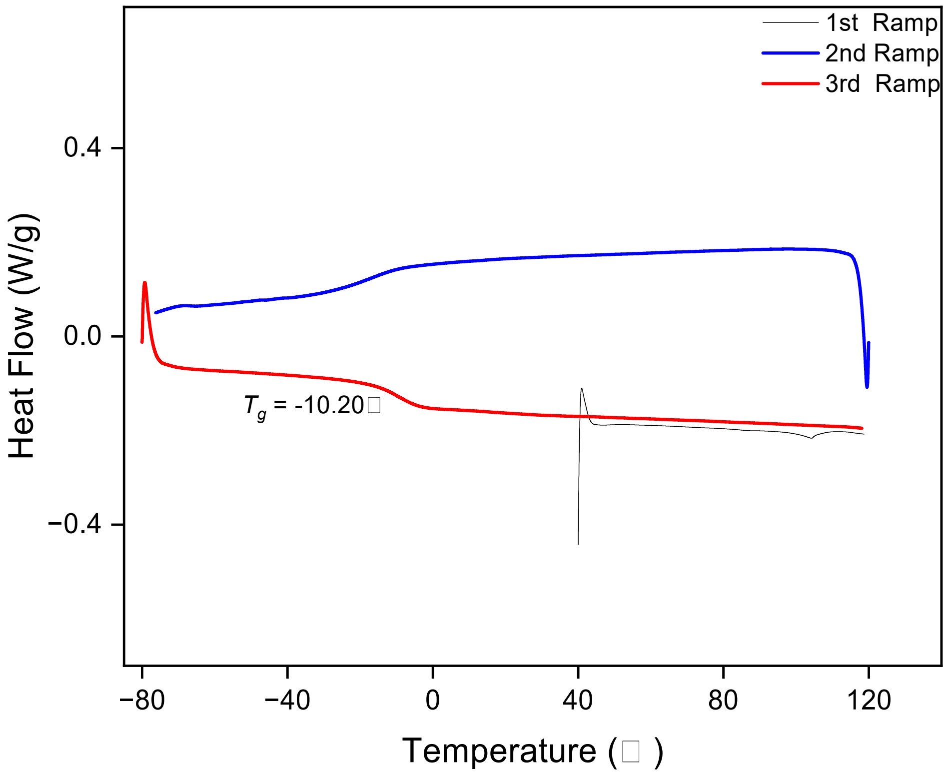

Figure S80. DSC curve of the **P14** (in **Figure 5**).

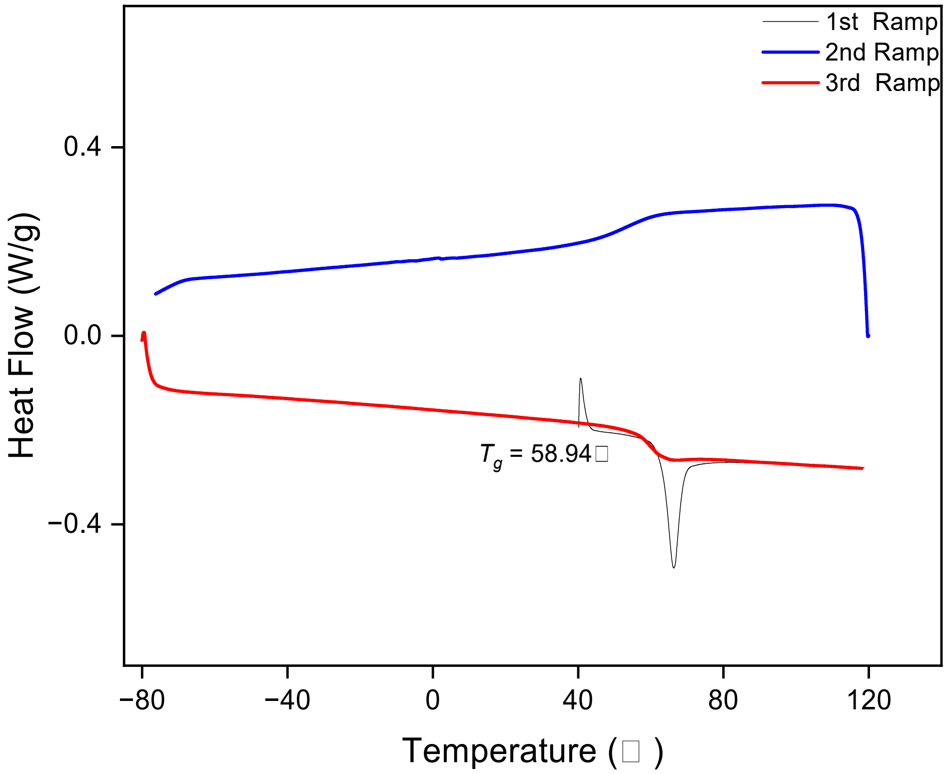

Figure S81. DSC curve of the **P15** (in **Figure 5**).

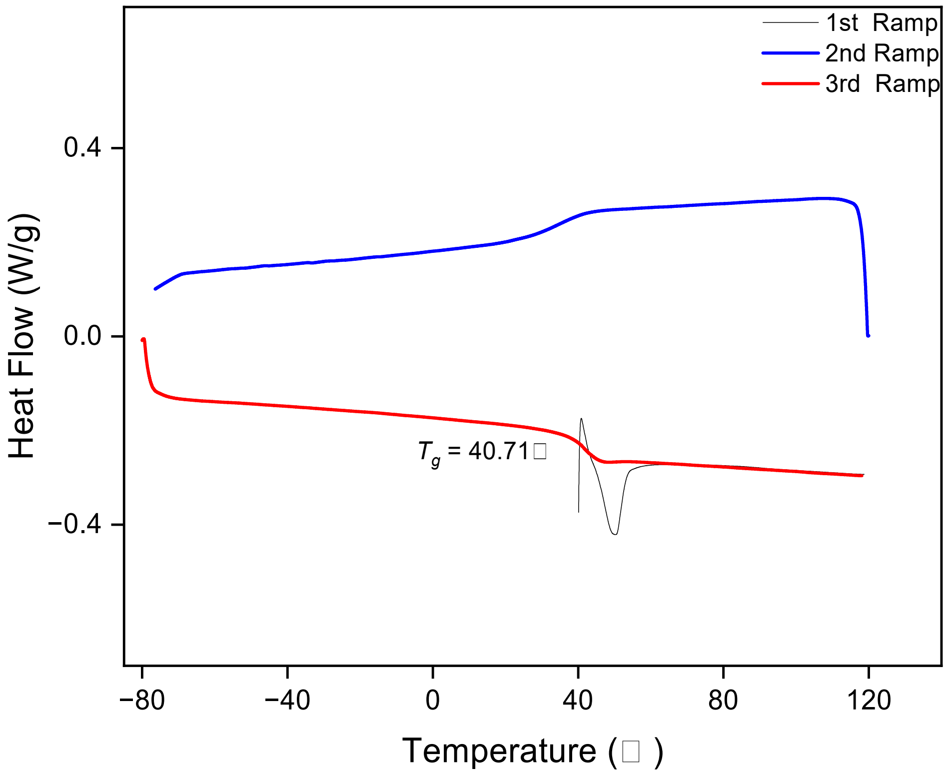

Figure S82. DSC curve of the **P16** (in **Figure 5**).

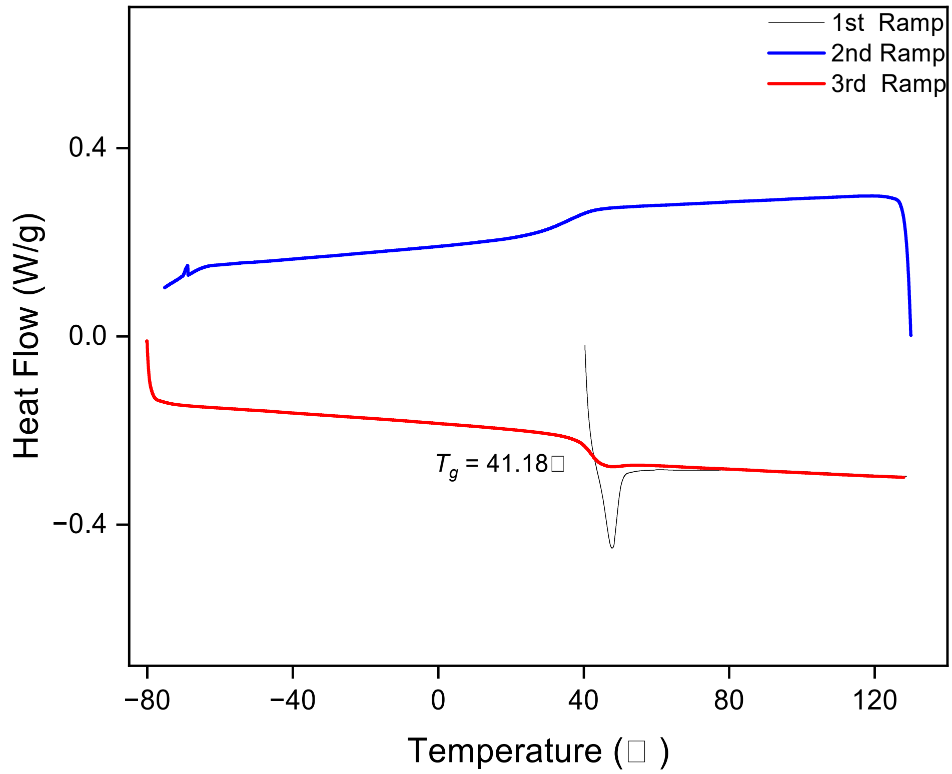

Figure S83. DSC curve of the **P17** (in **Figure 5**).

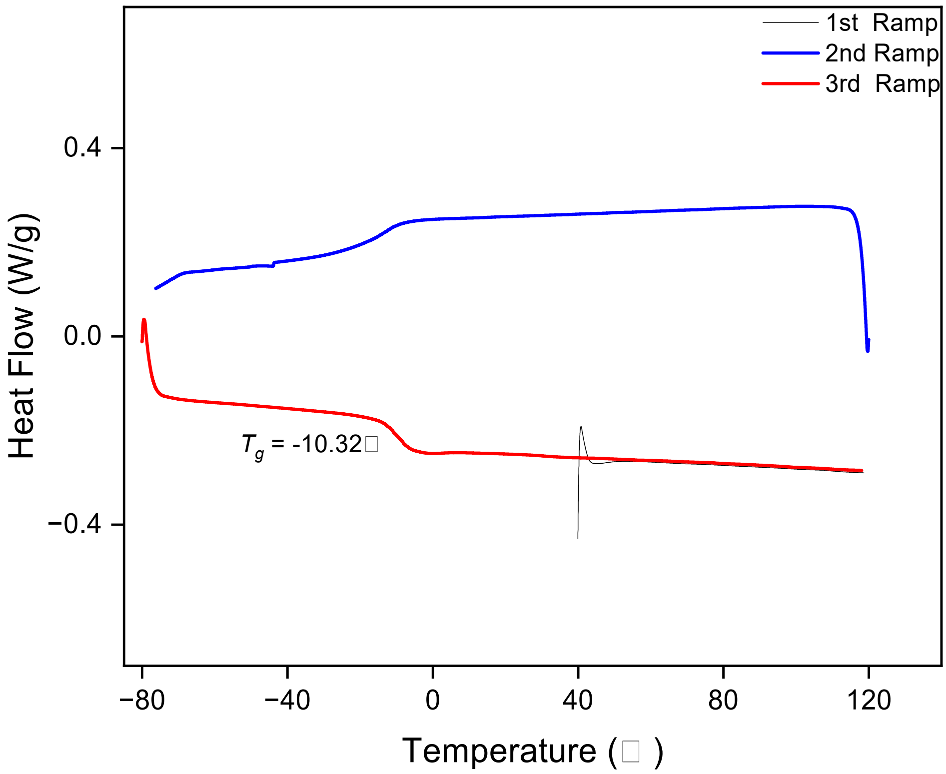

Figure S84. DSC curve of the **P18** (in **Figure 5**).

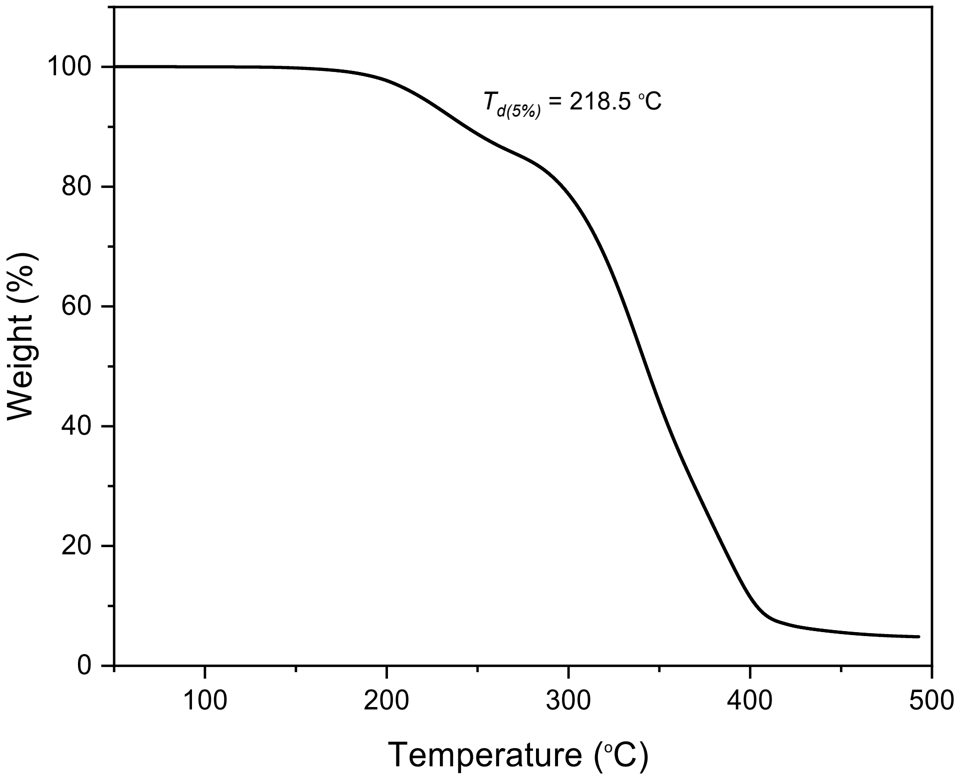

Figure S85. TGA curve of the **P1** (in **Figure 5**).

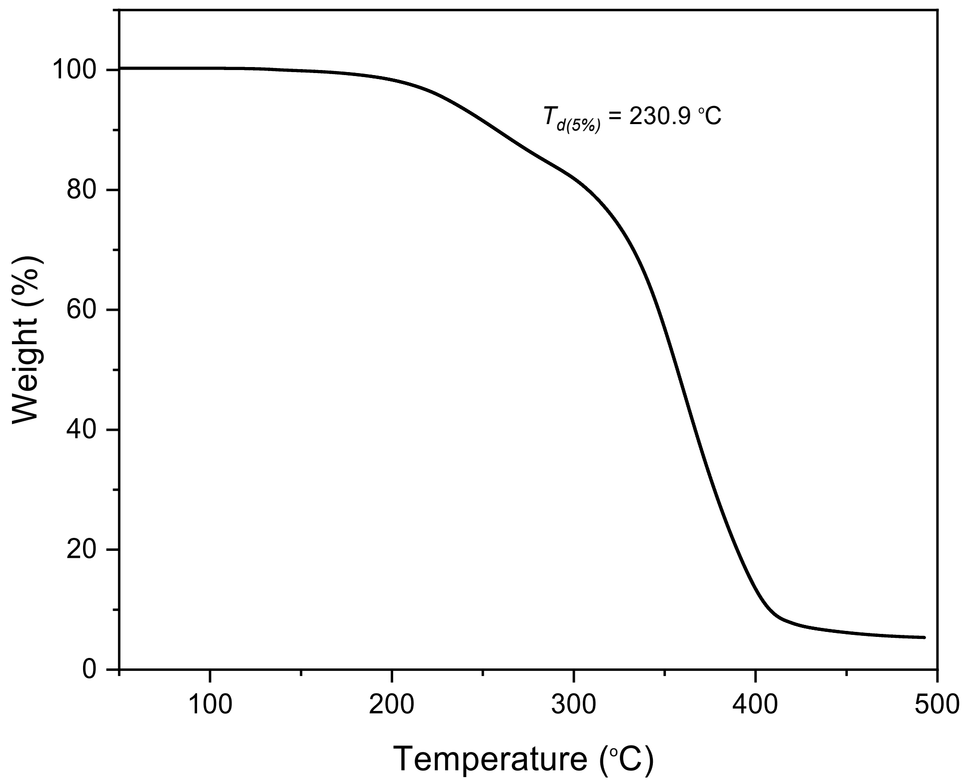

Figure S86. TGA curve of the **P2** (in **Figure 5**).

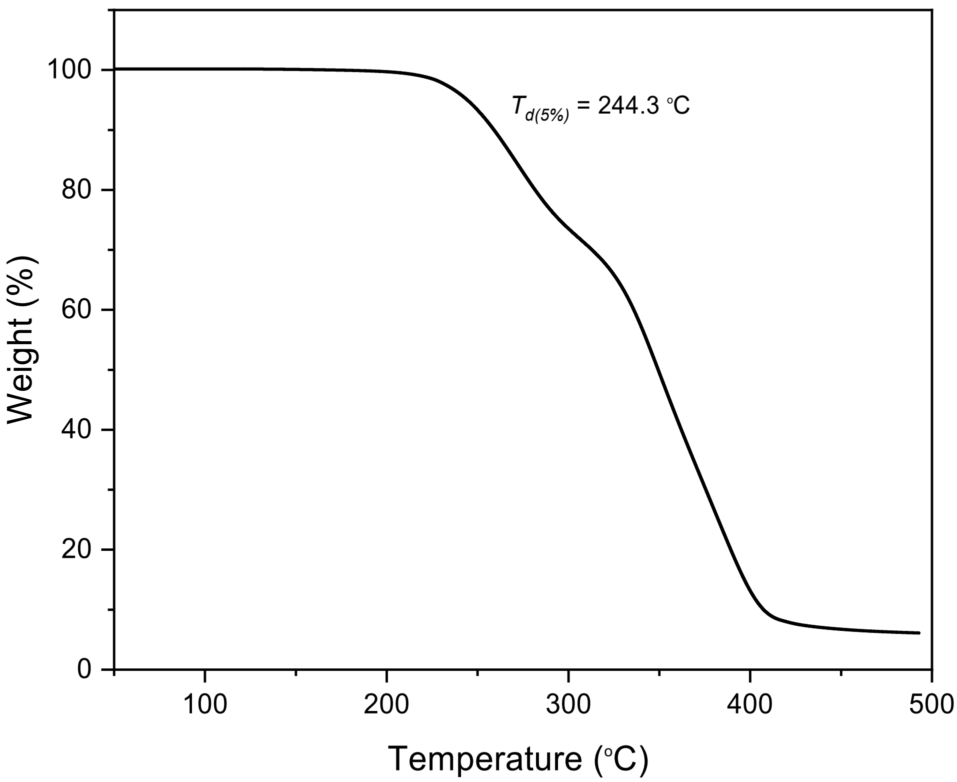

Figure S87. TGA curve of the **P3** (in **Figure 5**).

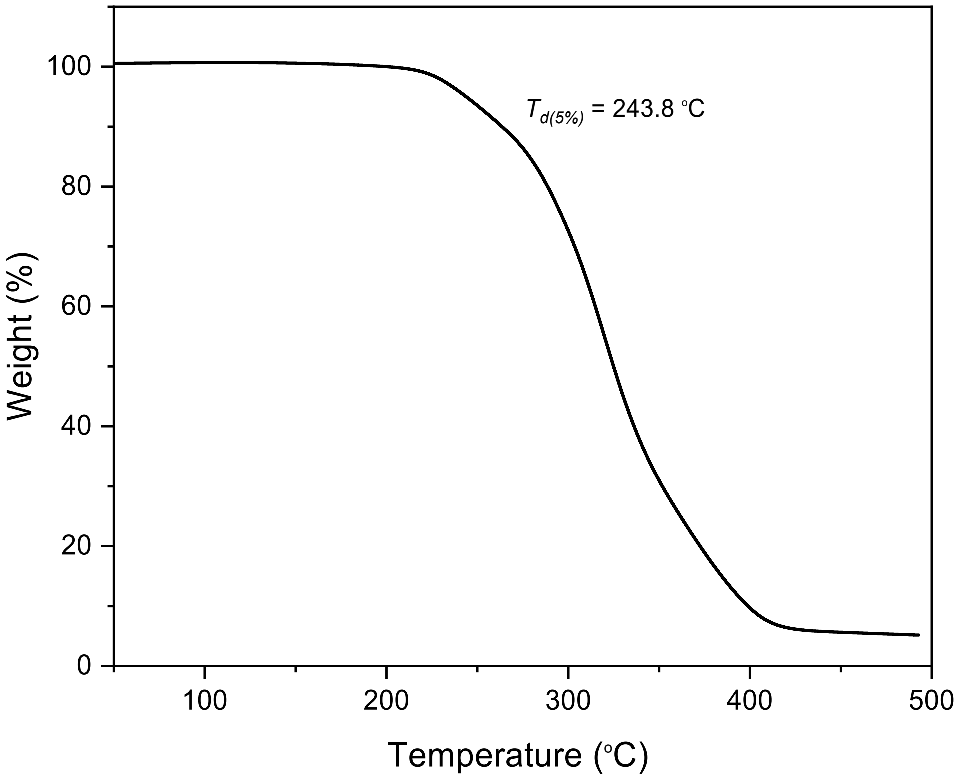

Figure S88. TGA curve of the **P4** (in **Figure 5**).

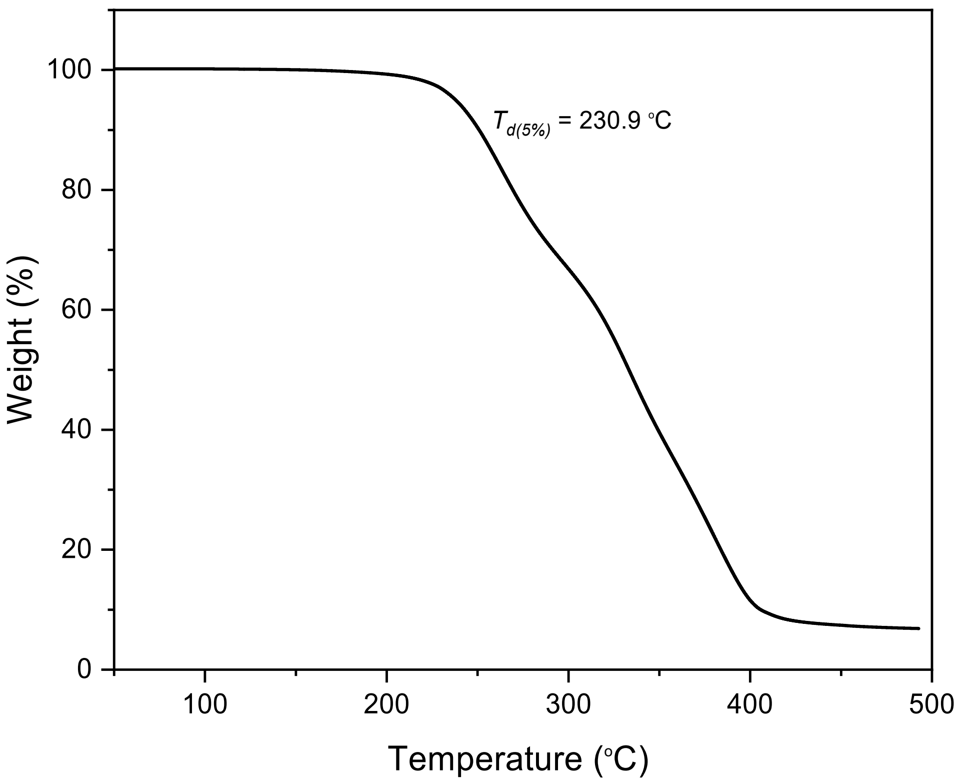

Figure S89. TGA curve of the **P5** (in **Figure 5**).

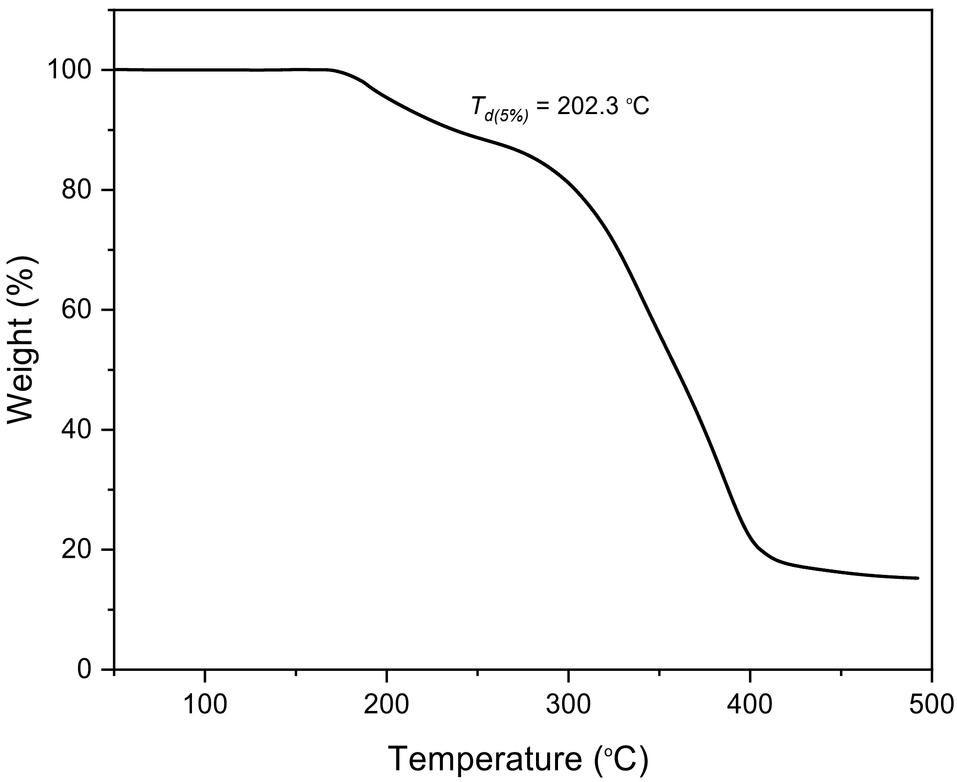

Figure S90. TGA curve of the **P6** (in **Figure 5**).

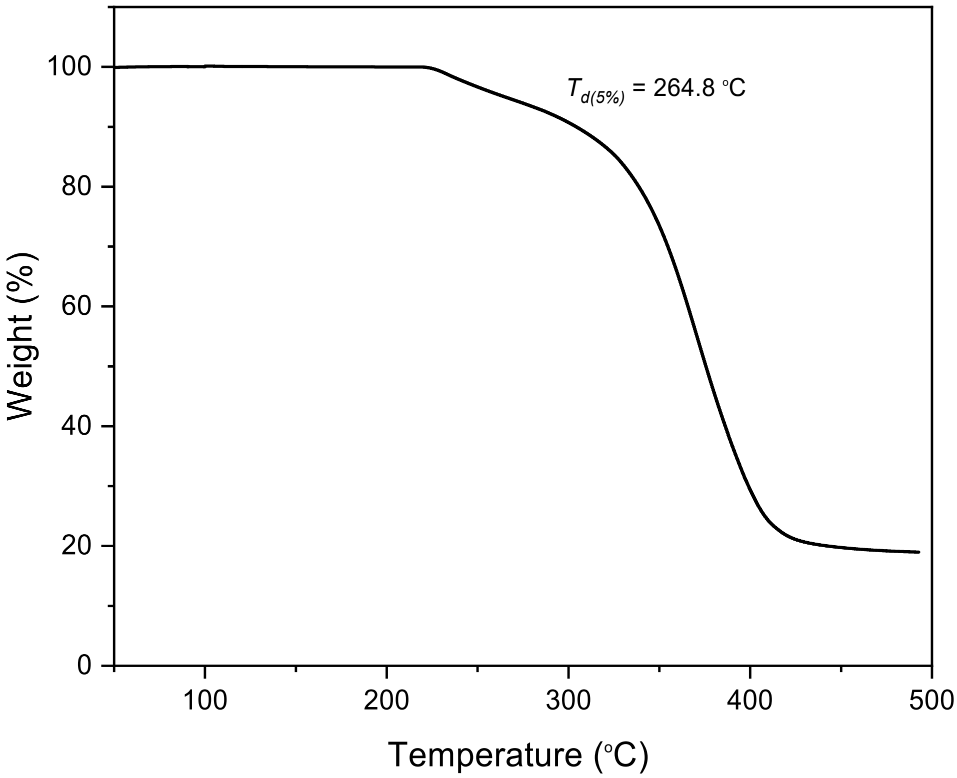

Figure S91. TGA curve of the **P7** (in **Figure 5**).

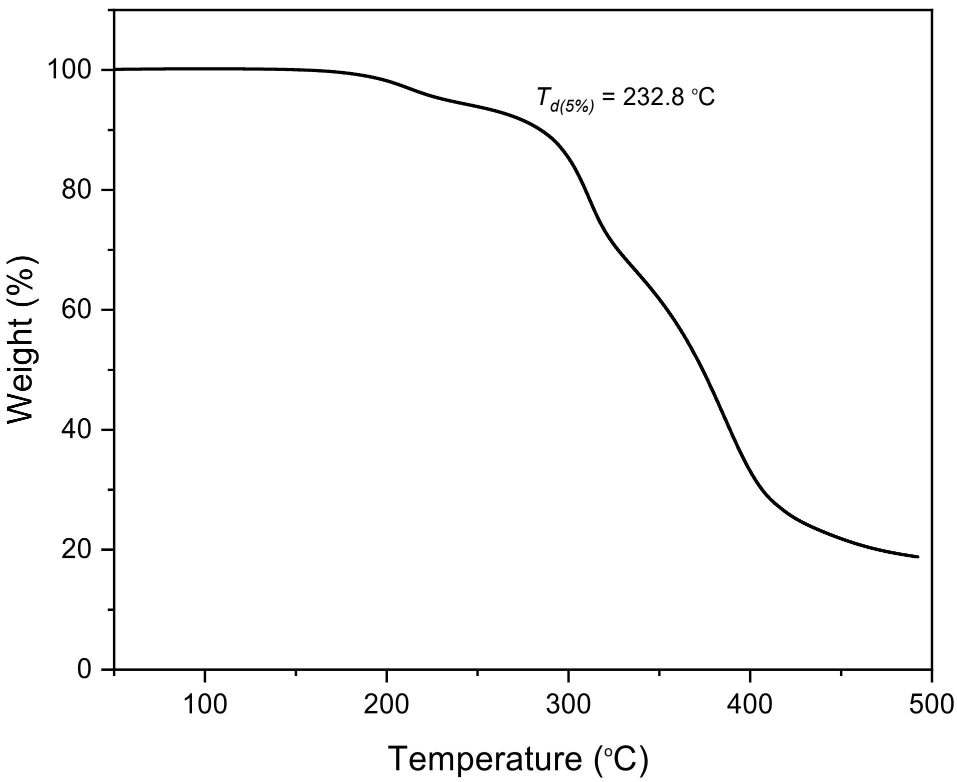

Figure S92. TGA curve of the **P8** (in **Figure 5**).

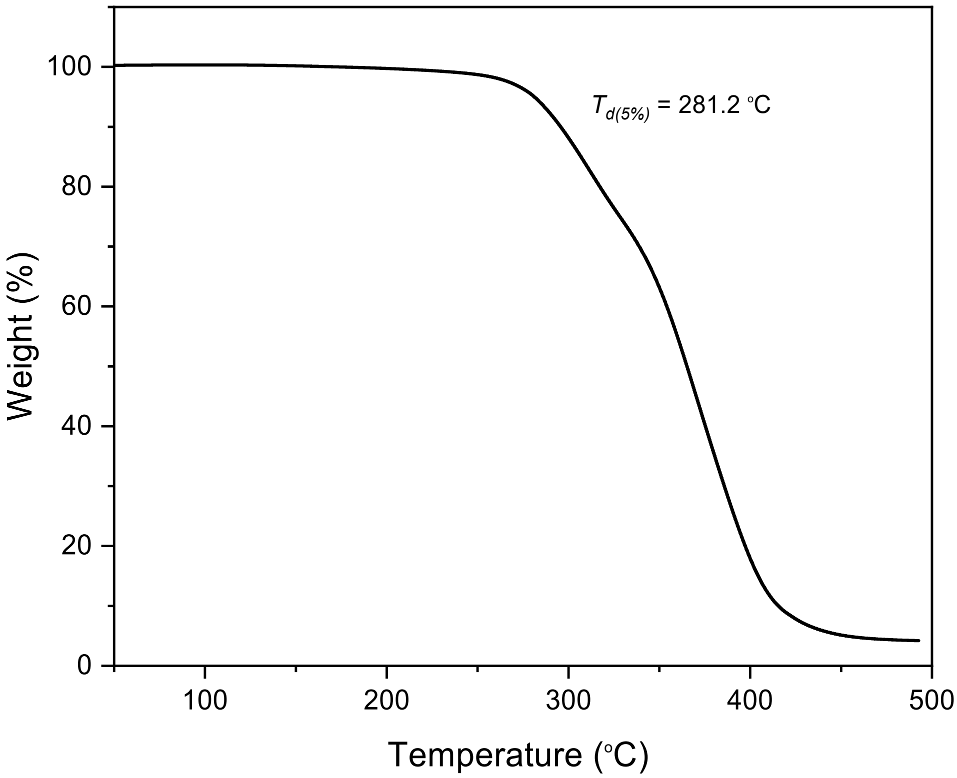

Figure S93. TGA curve of the **P9** (in **Figure 5**).

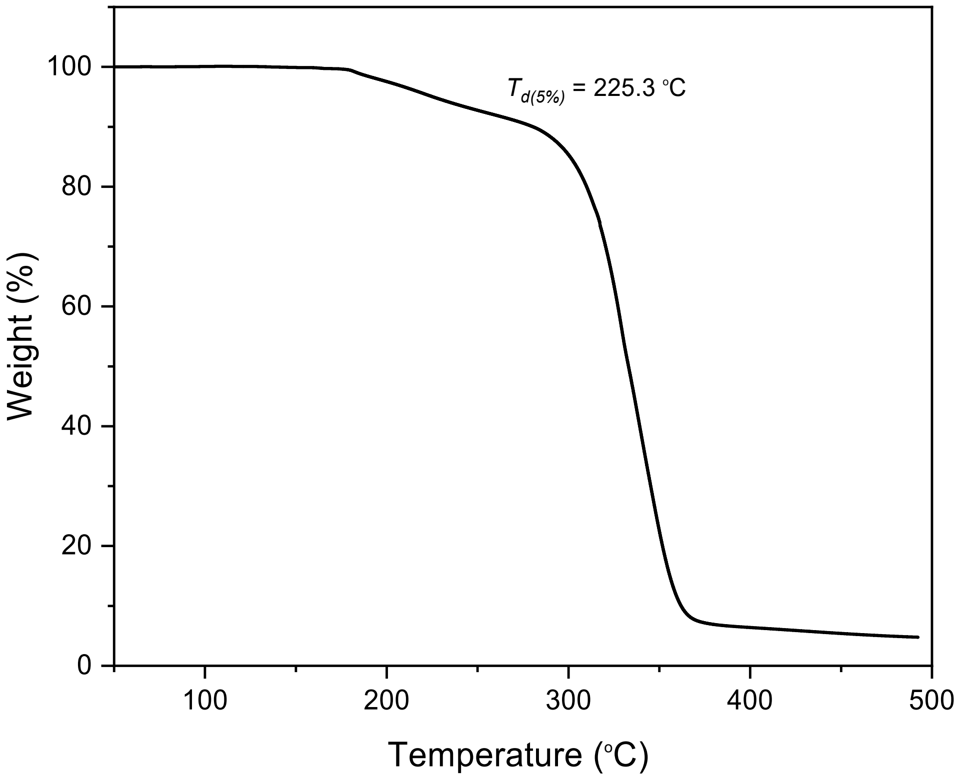

Figure S94. TGA curve of the **P10** (in **Figure 5**).

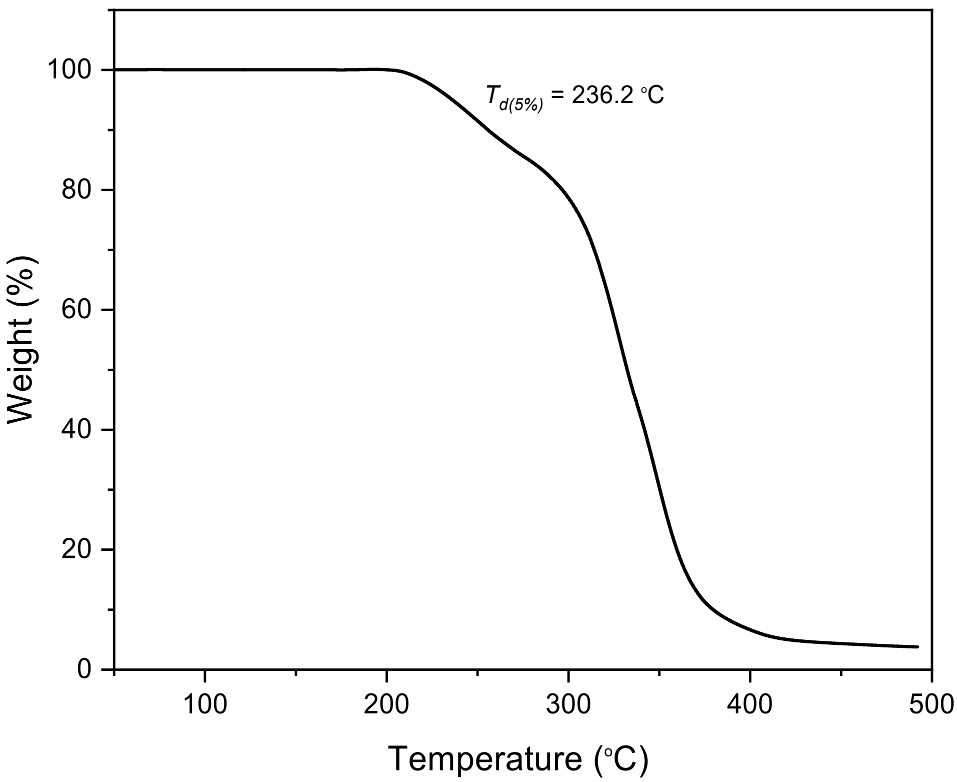

Figure S95. TGA curve of the **P11** (in **Figure 5**).

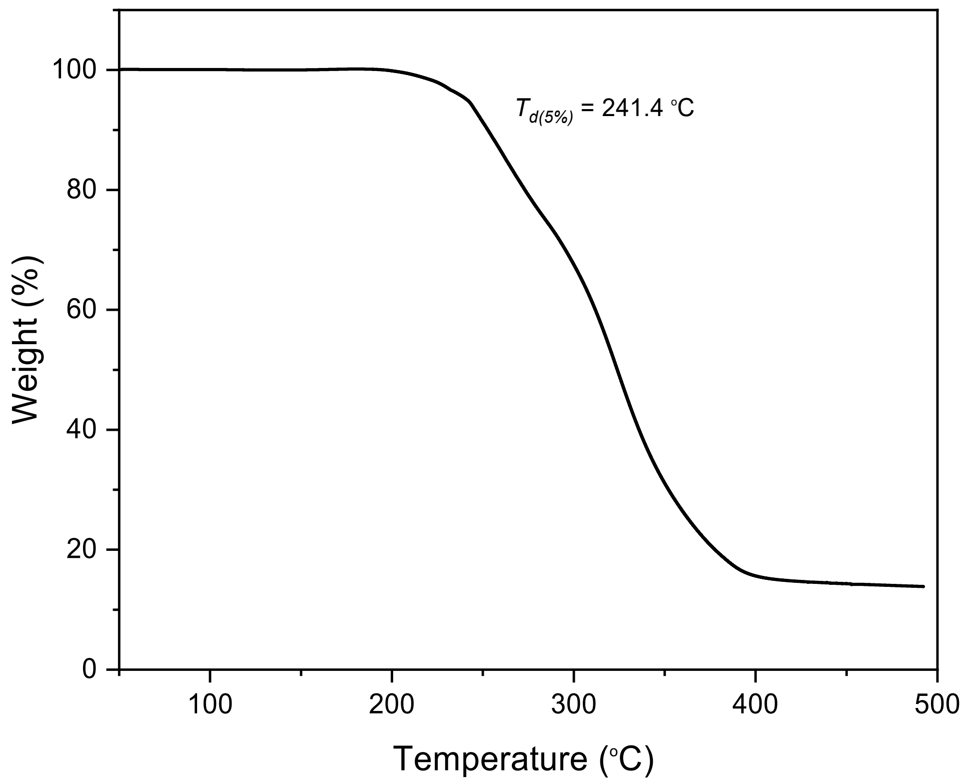

Figure S96. TGA curve of the **P12** (in **Figure 5**).

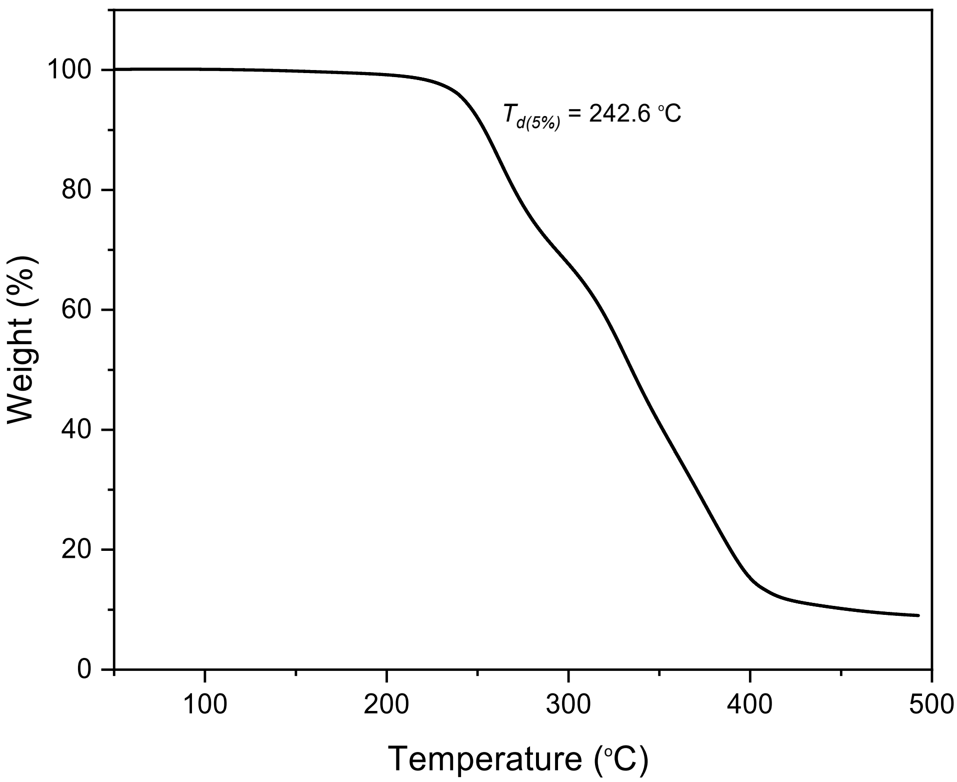

Figure S97. TGA curve of the **P13** (in **Figure 5**).

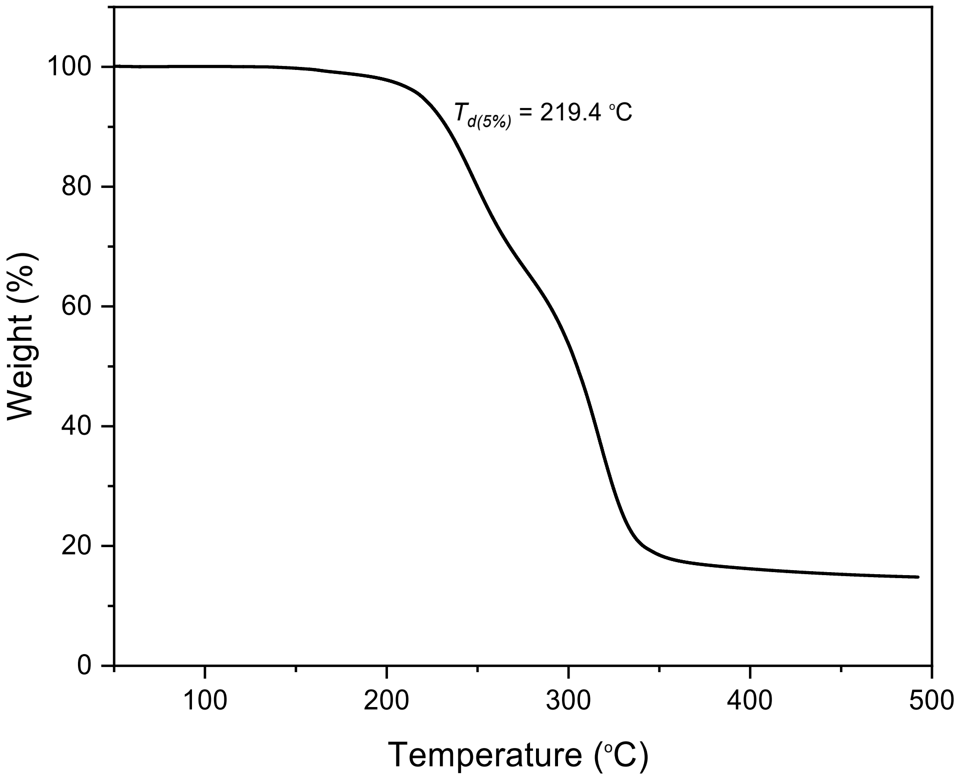

Figure S98. TGA curve of the **P14** (in **Figure 5**).

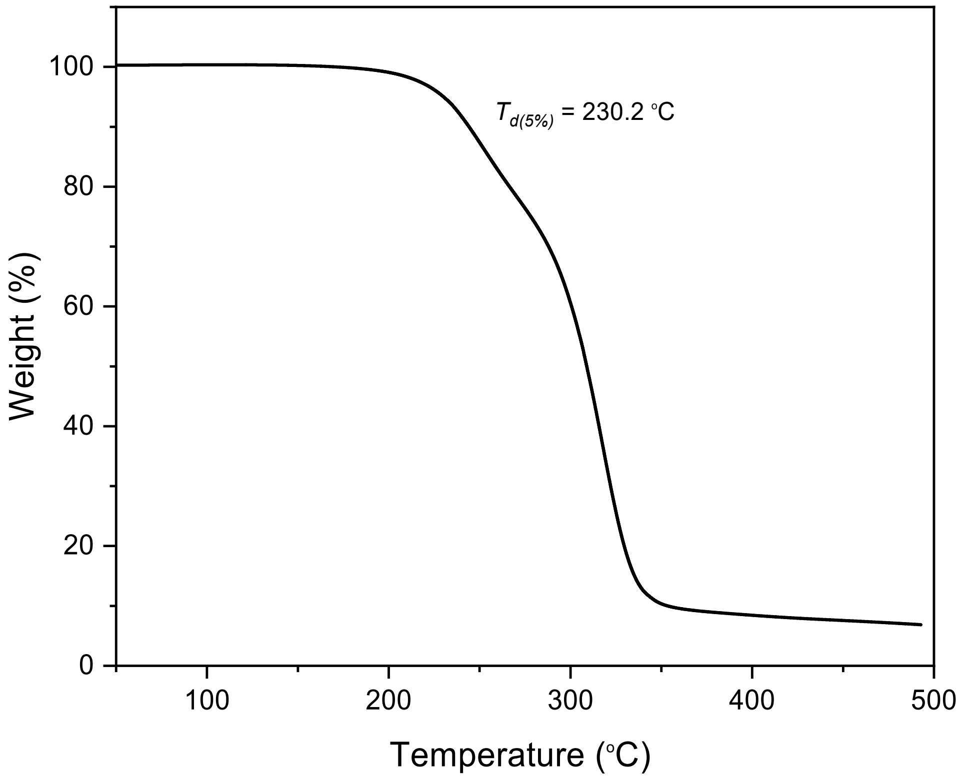

Figure S99. TGA curve of the **P15** (in **Figure 5**).

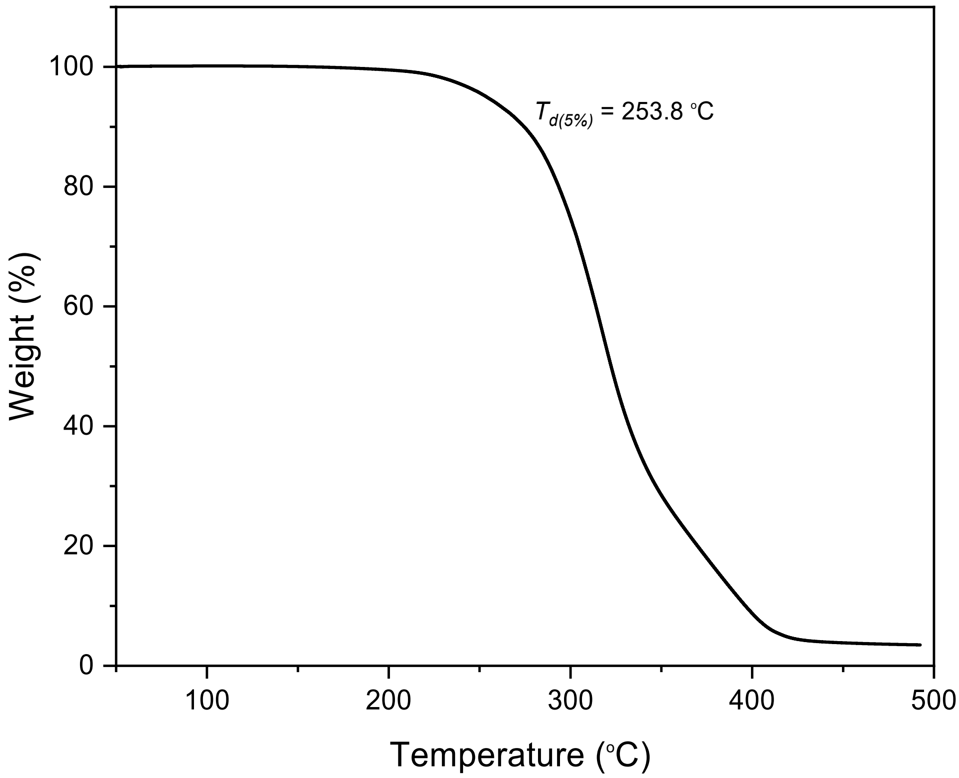

Figure S100. TGA curve of the **P16** (in **Figure 5**).

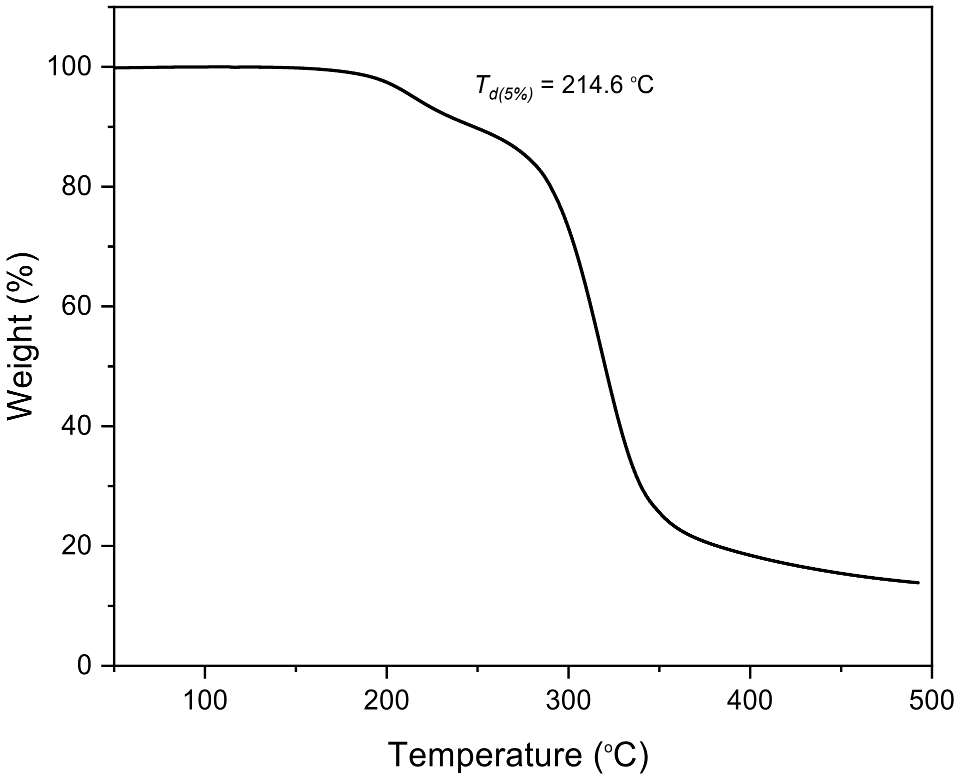

Figure S101. TGA curve of the **P17** (in **Figure 5**).

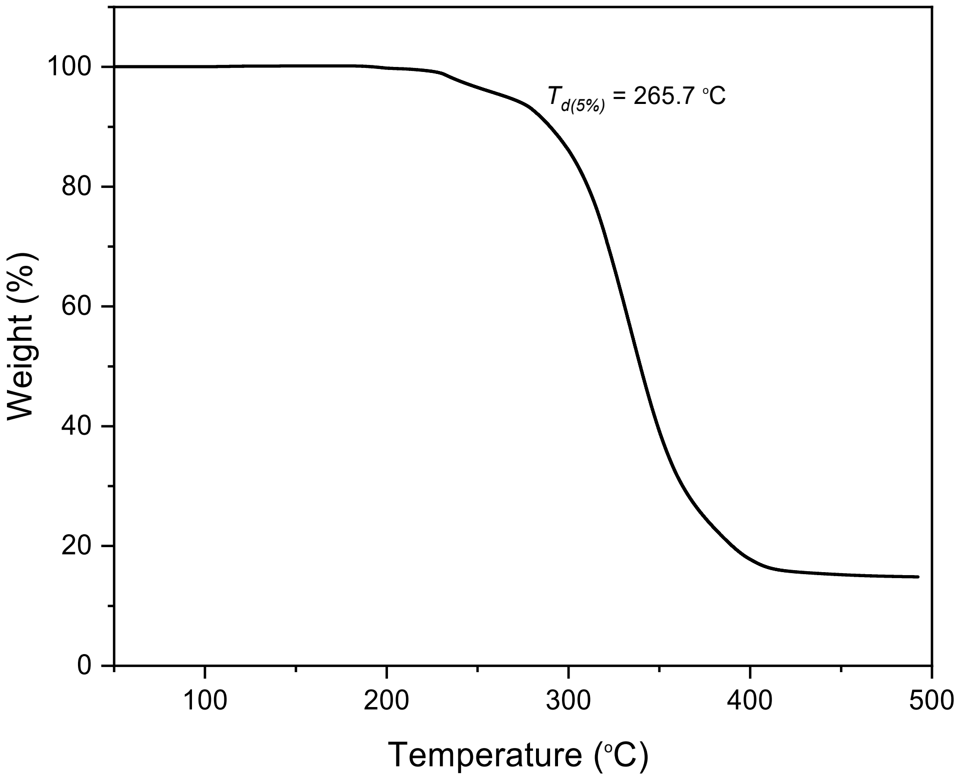

Figure S102. TGA curve of the **P18** (in **Figure 5**).

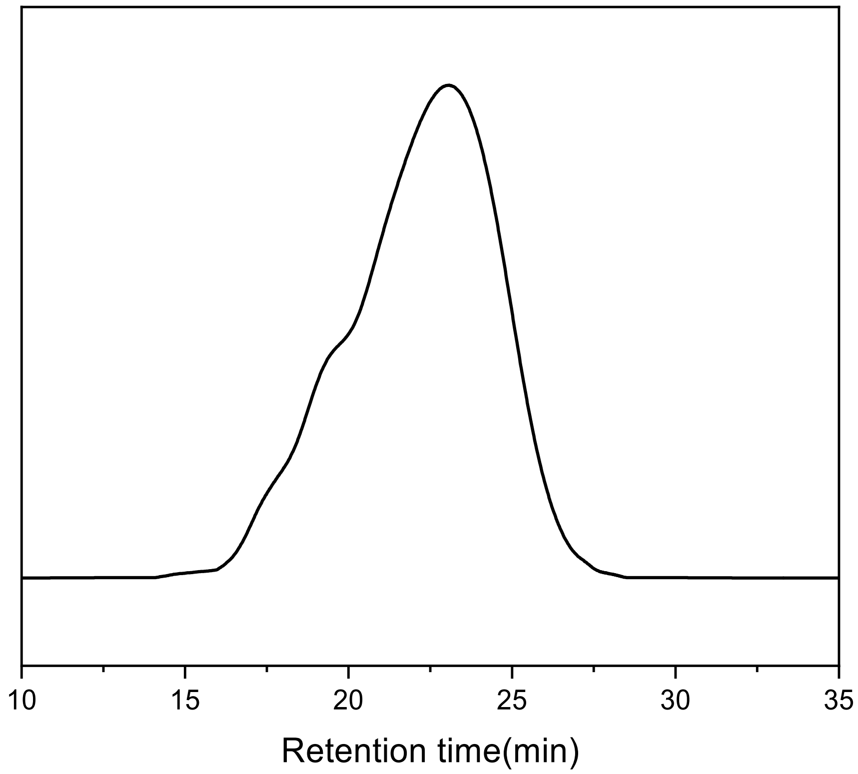

Figure S103. GPC curve of the **P1** (in **Figure 5**).

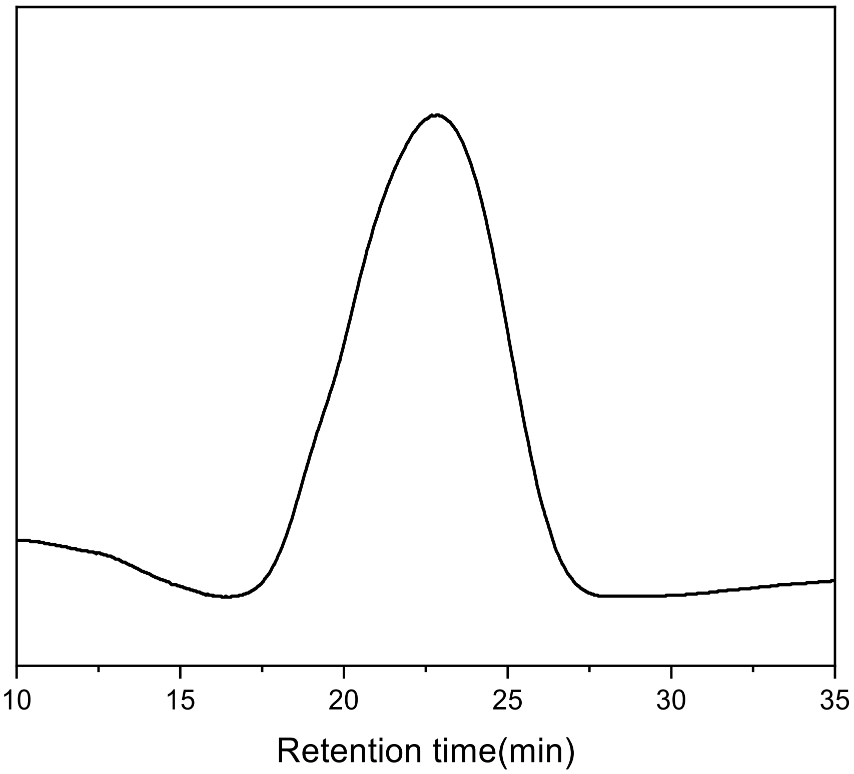

Figure S104. GPC curve of the **P2** (in **Figure 5**).

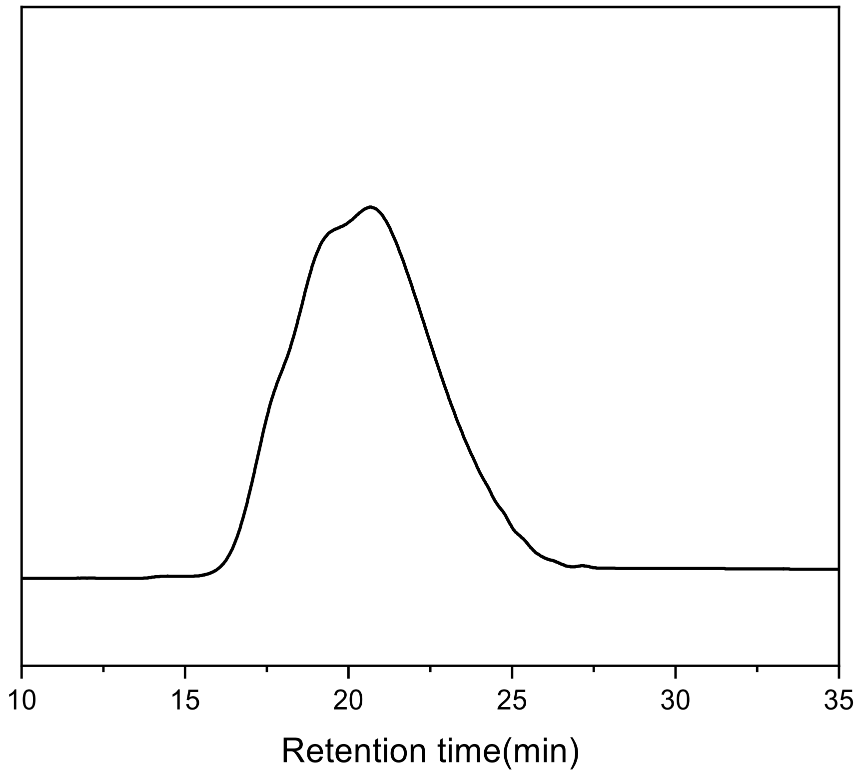

Figure S105. GPC curve of the **P3** (in **Figure 5**).

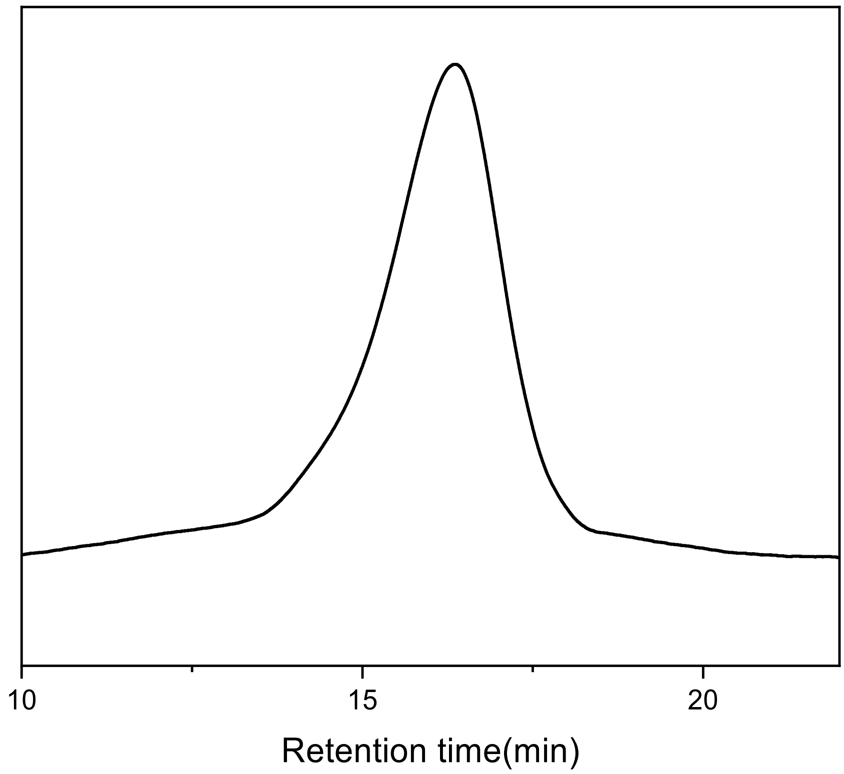

Figure S106. GPC curve of the **P4** (in **Figure 5**).

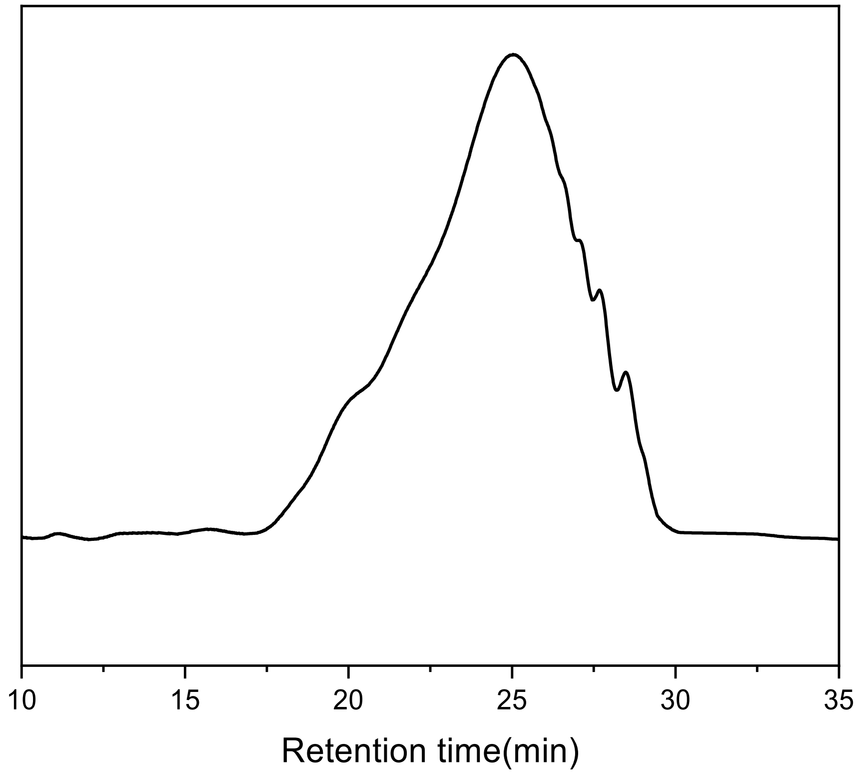

Figure S107. GPC curve of the **P5** (in **Figure 5**).

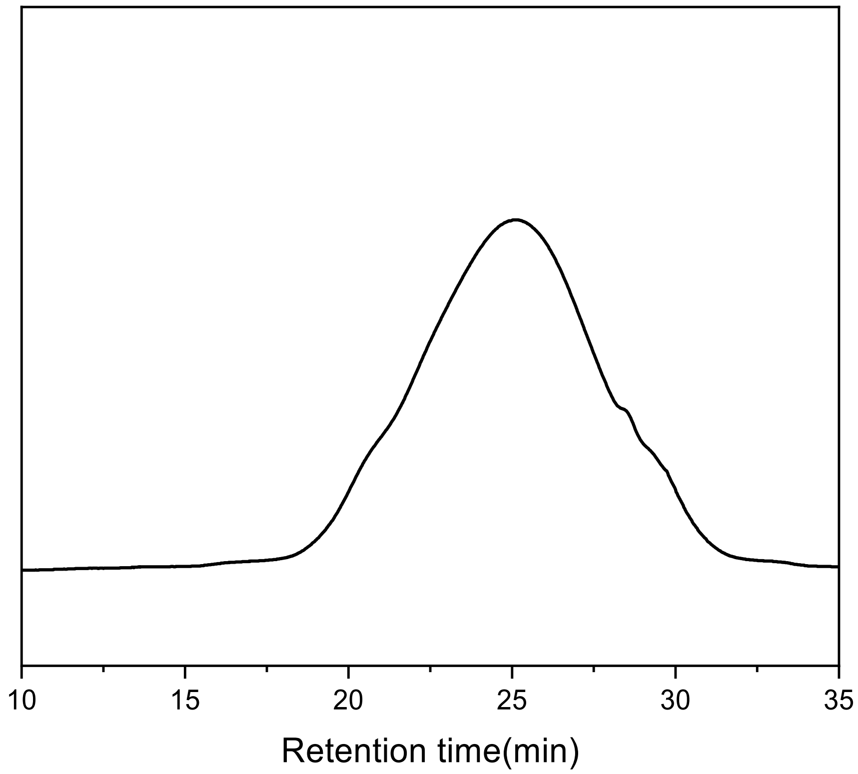

Figure S108. GPC curve of the **P6** (in **Figure 5**).

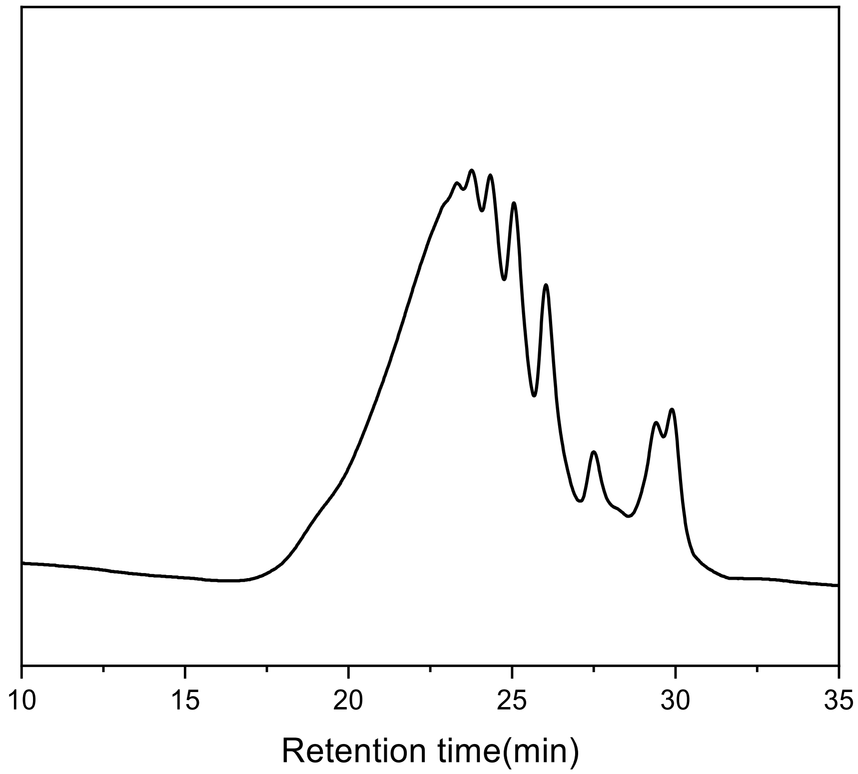

Figure S109. GPC curve of the **P7** (in **Figure 5**).

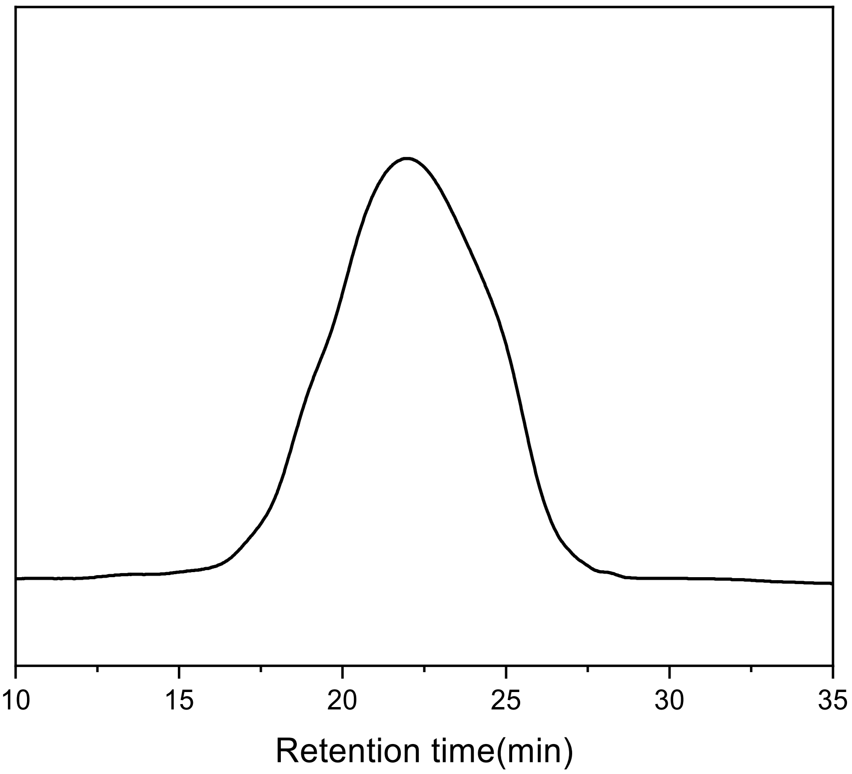

Figure S110. GPC curve of the **P8** (in **Figure 5**).

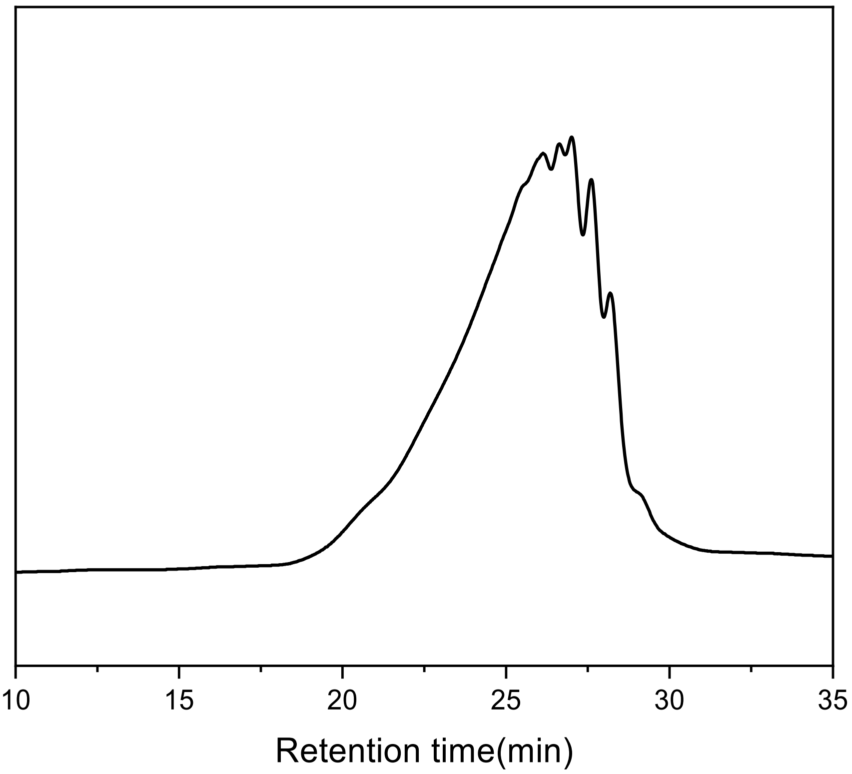

Figure S111. GPC curve of the **P9** (in **Figure 5**).

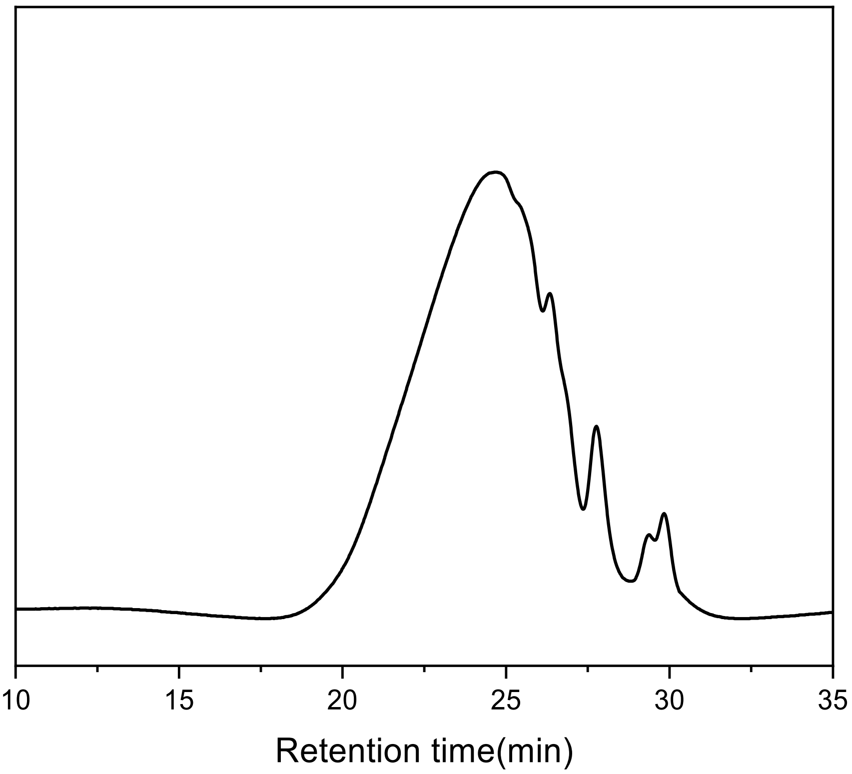

Figure S112. GPC curve of the **P10** (in **Figure 5**).

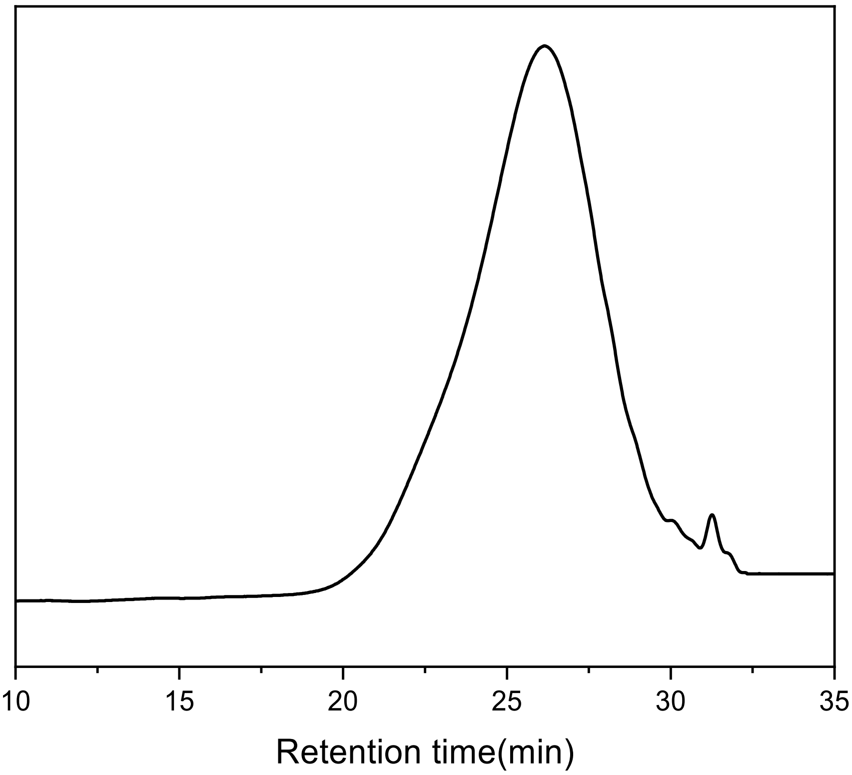

Figure S113. GPC curve of the **P11** (in **Figure 5**).

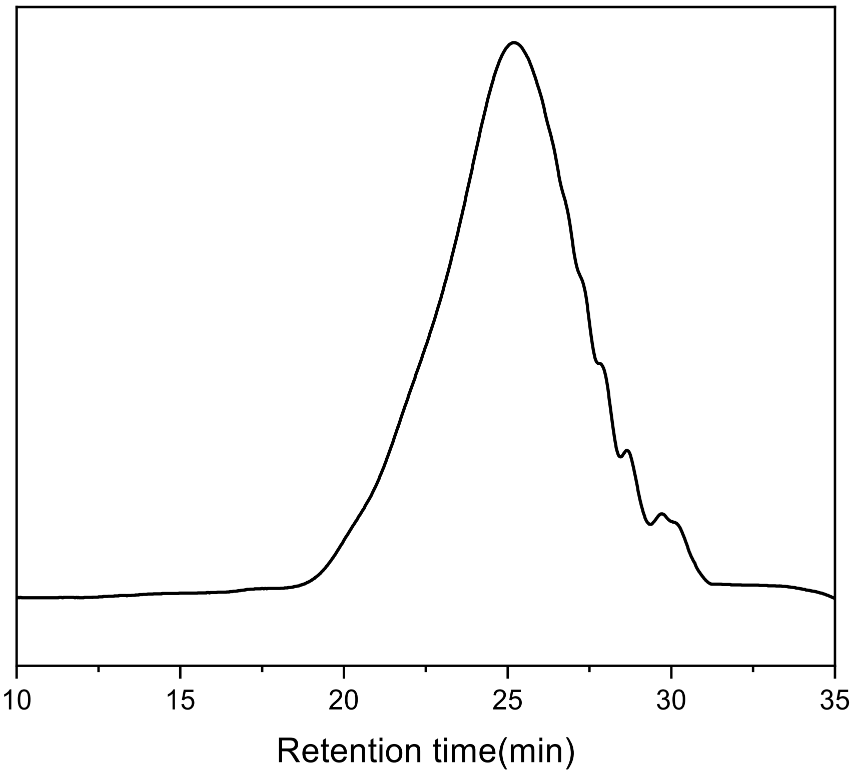

Figure S114. GPC curve of the **P12** (in **Figure 5**).

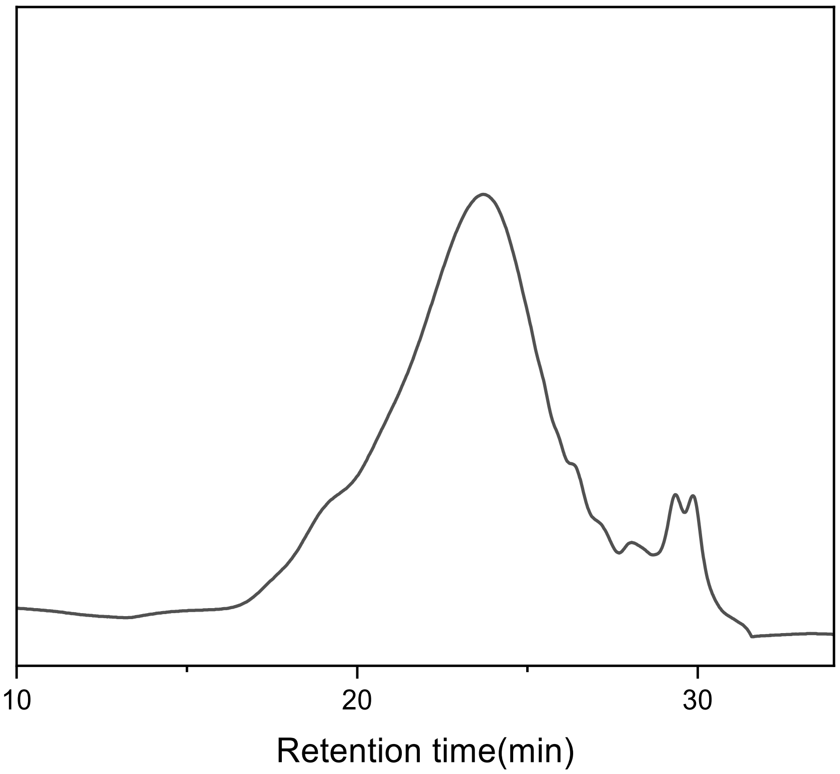

Figure S115. GPC curve of the **P13** (in **Figure 5**).

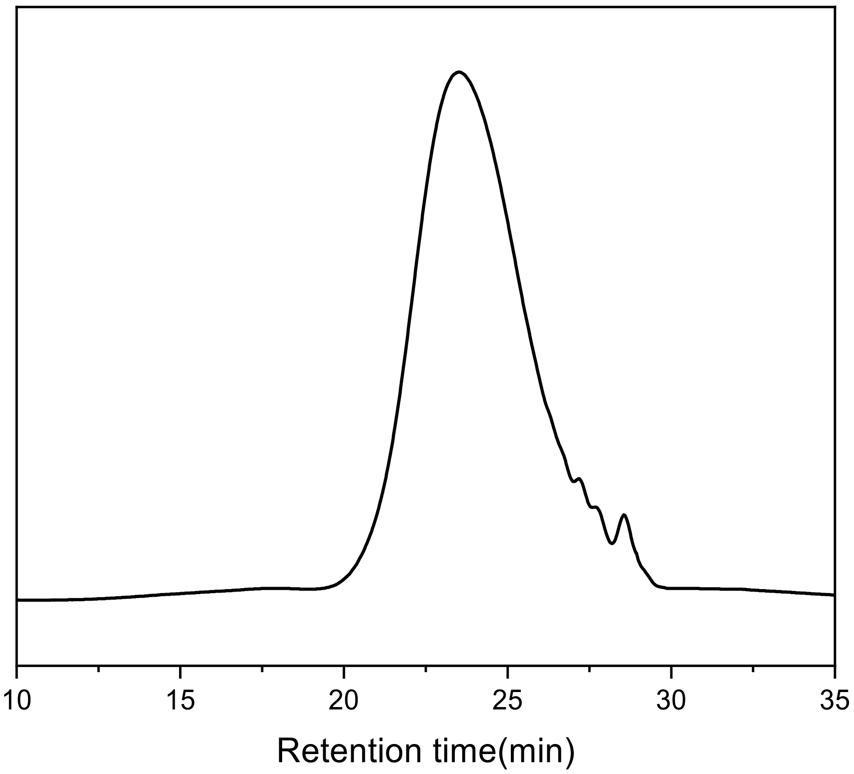

Figure S116. GPC curve of the **P14** (in **Figure 5**).

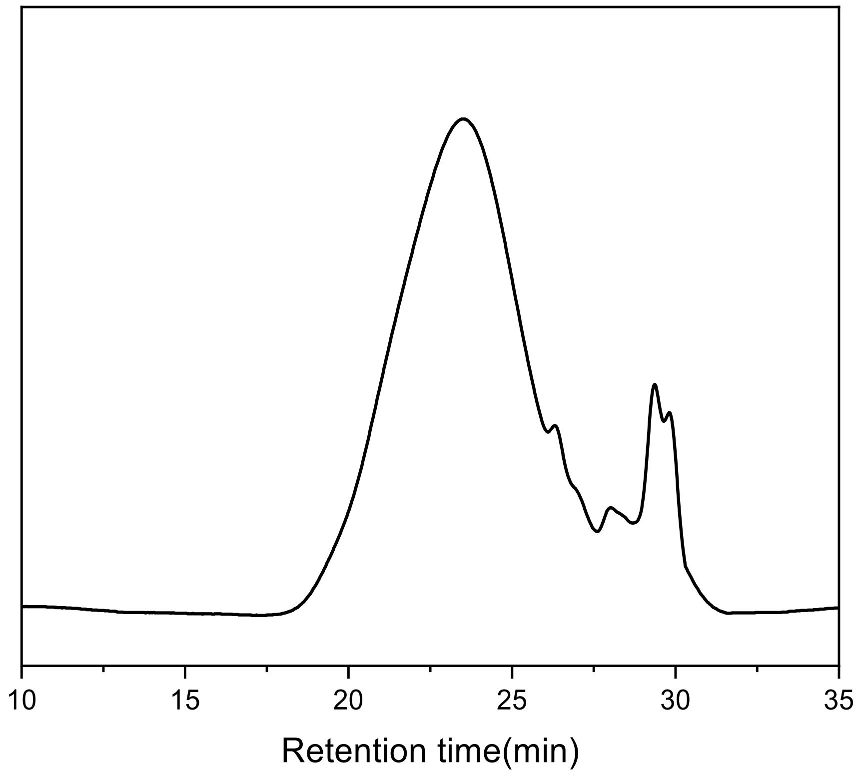

Figure S117. GPC curve of the **P15** (in **Figure 5**).

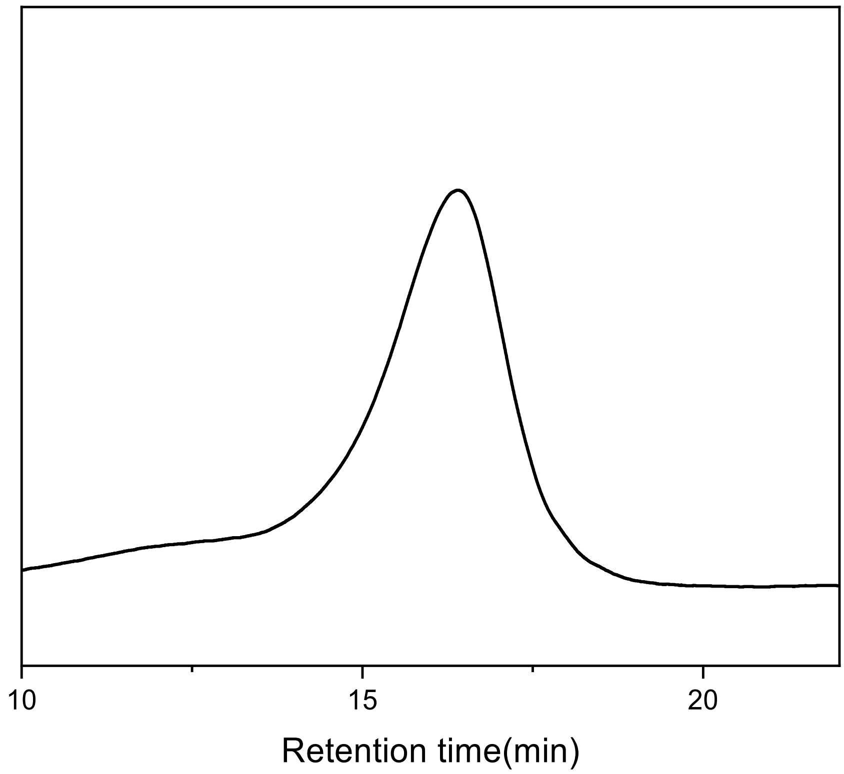

Figure S118. GPC curve of the **P16** (in **Figure 5**).

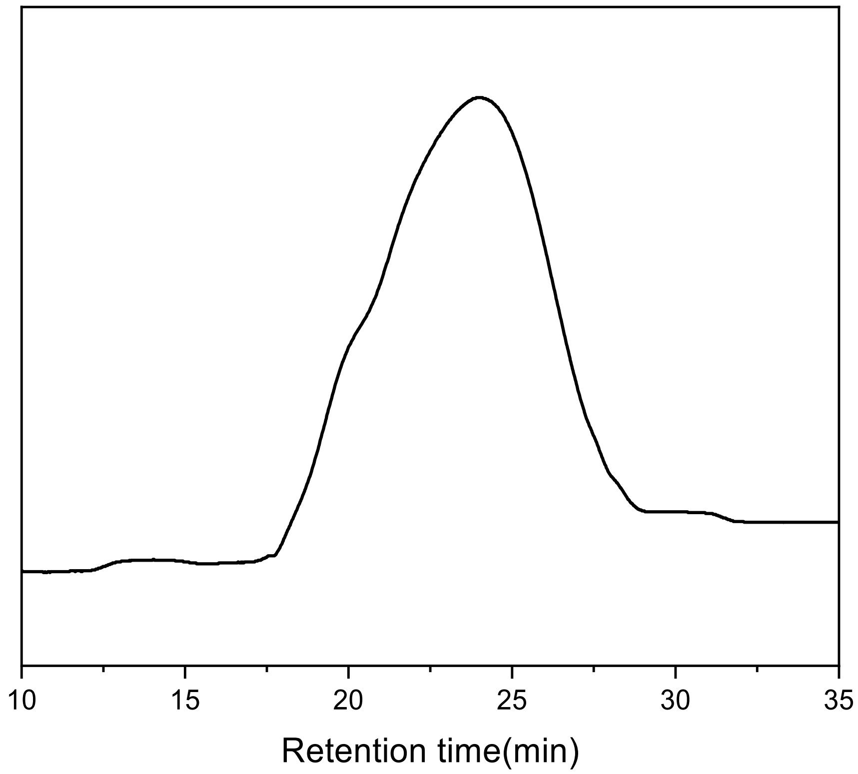

Figure S119. GPC curve of the **P17** (in **Figure 5**).

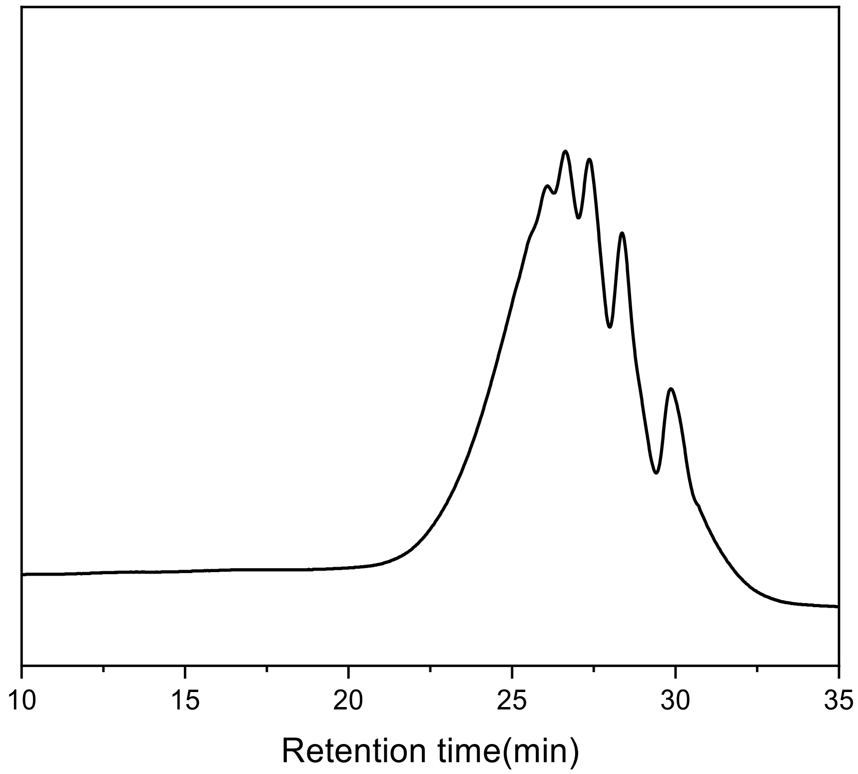

Figure S120. GPC curve of the **P18** (in **Figure 5**).

Computational Details

All DFT calculations were performed using Gaussian 16 program.[1] Calculations were performed using the M06-2X[2]/6-311++G(d,p) level of theory and the ultrafine integration grid which has been shown successful to describe thermodynamics of the reaction for methyl propiolate, ethanol and COS. All reactants and intermediates were subjected to geometry optimizations and stationary points were characterized as minima (0 imaginary frequencies for ground states and 1 imaginary for transition state). The effects of solvation (MeCN) were included using the SMD implicit solvent model.[3] Thermodynamic data were generated by Shermo.[4] The 3D diagrams of molecules were generated by Multiwfn[5] and CYLView .[6]

Cartesian coordinates of the calculated species

COS

S	0.00000000	0.00000000	1.03633800
C	0.00000000	0.00000000	-0.52777700
O	0.00000000	0.00000000	-1.67684300

DBU

C	-0.85234400	1.49808900	-0.01484300
C	-2.09521800	0.98751300	-0.73221600
C	-0.92624900	-1.54368900	-0.12155700
C	-2.91492800	0.01062800	0.11189300
C	-2.01840800	-1.01319000	0.80966100
H	-1.09620700	1.75472400	1.02546700
H	-1.31861900	-1.63802100	-1.14022000
H	-1.79565600	0.52923300	-1.67916200

H	-3.63360300	-0.50631000	-0.53161100
H	-0.53003400	2.42521200	-0.49781700
H	-2.70881400	1.85462500	-0.98884000
H	-0.61686300	-2.54414800	0.17947100
H	-3.49279200	0.56405700	0.85831400
H	-2.62315000	-1.84884300	1.16919400
H	-1.55353900	-0.56422600	1.69358500
C	2.69753100	-0.69241100	-0.41810100
H	2.82514300	-0.29891200	-1.43680900
H	3.52402600	-1.38194800	-0.23486900
C	2.71809300	0.46658400	0.56802800
H	2.60908600	0.07487300	1.58376800
H	3.65413100	1.02618700	0.51846600
C	1.55841600	1.38261900	0.23045900
H	1.35238200	2.06720800	1.05966800
H	1.79552800	1.99393900	-0.64810900
N	0.32892000	0.62438500	-0.03872900
N	1.44602900	-1.43165800	-0.32234800
C	0.36383000	-0.73893300	-0.16715100

[DBUH]$^+$

C	-0.90826100	1.51319100	0.04974500
C	-2.12554500	1.00372200	-0.70822300
C	-0.92983200	-1.53095000	-0.12906500
C	-2.95049400	-0.01164100	0.08172100
C	-2.05913200	-1.03887000	0.77822400
H	-1.14606100	1.71652800	1.09888600
H	-1.27757700	-1.63410600	-1.16226100
H	-1.79558300	0.58338700	-1.66270200
H	-3.63901800	-0.52048700	-0.59886100

H	-0.57906000	2.45169500	-0.39847500
H	-2.74185300	1.87214100	-0.95069700
H	-0.59970800	-2.52160400	0.18735900
H	-3.55795600	0.50626400	0.82895700
H	-2.65286300	-1.90089600	1.08694000
H	-1.62983900	-0.61411200	1.69050900
C	2.76611300	-0.67222800	-0.34549400
H	3.00133000	-0.38758200	-1.37445800
H	3.50137200	-1.39919500	-0.00540400
C	2.71181000	0.54789400	0.55396400
H	2.58561600	0.23252000	1.59247800
H	3.63508300	1.12162000	0.47602900
C	1.54727000	1.41847500	0.12743300
H	1.36096600	2.20130200	0.86375100
H	1.74145800	1.89549300	-0.83739100
N	0.29227800	0.64625200	0.00618900
N	1.45491100	-1.31297700	-0.30160400
C	0.30738900	-0.66542600	-0.14174800
H	1.40745800	-2.32089800	-0.36608800

EtOH

C	0.00000000	0.55296200	0.00000000
H	0.03293100	1.19621400	0.88638700
H	0.03293100	1.19621400	-0.88638700
C	1.17467600	-0.39936000	0.00000000
H	1.15142900	-1.03658500	0.88717000
H	2.11344500	0.15904500	0.00000000
H	1.15142900	-1.03658500	-0.88717000
O	-1.19768300	-0.22239800	0.00000000
H	-1.94875500	0.37926400	0.00000000

[EtO]⁻

C	0.00000000	0.53070700	0.00000000
H	0.27302700	1.16879900	0.88046600
H	0.27302700	1.16879900	-0.88046600
C	1.01110800	-0.63267300	0.00000000
H	0.85772100	-1.26038000	0.88471700
H	2.05171000	-0.28358600	0.00000000
H	0.85772100	-1.26038000	-0.88471700
O	-1.29748200	0.13481800	0.00000000

DBU-EtOH

C	-2.47583900	0.68547700	0.54022200
C	-3.21994700	-0.34013300	-0.30430700
C	-0.56803700	-1.24023400	-0.85831700
C	-2.86781800	-1.78403900	0.05641200
C	-1.35947400	-1.96233400	0.23400600
H	-2.48141400	0.38277000	1.59588500
H	-1.09761100	-1.31014700	-1.81460800
H	-3.02114400	-0.14180900	-1.36148200
H	-3.22773500	-2.45053100	-0.73345200
H	-3.01187900	1.63725000	0.48348800
H	-4.28981800	-0.17503300	-0.15509000
H	0.39968400	-1.72019700	-1.00962200
H	-3.38363000	-2.06991000	0.97803600
H	-1.10633100	-3.02503400	0.21860300
H	-1.05018800	-1.58408100	1.21393700
C	1.27503100	2.01494400	-0.81308500
H	0.80035600	2.66360100	-1.56188400
H	2.35580900	2.10696000	-0.94463800
C	0.84628200	2.45399000	0.57928500

H	1.34081000	1.82066400	1.32283300
H	1.11754600	3.49201500	0.77983700
C	-0.65810500	2.29370100	0.67194500
H	-0.99043200	2.34736400	1.71315700
H	-1.16515800	3.09505000	0.12242000
N	-1.09749900	0.99828200	0.13429200
N	0.90337400	0.62509300	-1.04294700
C	-0.24071100	0.21868400	-0.58321800
C	2.38222700	-1.59497100	1.35558900
H	1.39778800	-1.12831500	1.26324900
H	2.69659900	-1.52418200	2.40094200
H	2.28850700	-2.65254500	1.09357200
C	3.39305700	-0.91094500	0.44633200
H	4.38276700	-1.35159000	0.59472600
H	3.46862900	0.15269200	0.71269600
O	3.07757600	-1.05411400	-0.92656000
H	2.27512300	-0.50053700	-1.08871600

Methyl propiolate

C	-2.62557200	-0.41104600	0.00009300
C	-1.46347600	-0.11417900	-0.00000900
C	-0.06941700	0.30338300	-0.00013400
O	0.27759500	1.45586600	0.00000200
H	-3.66126800	-0.67857200	0.00037300
C	2.15405000	-0.43242900	0.00019600
H	2.41165300	0.13543900	0.89409900
H	2.65987100	-1.39384900	-0.00006500
H	2.41218400	0.13617800	-0.89308100
O	0.74791100	-0.74006200	-0.00027600

S2

C	1.69850500	-0.46672300	-0.52265400
H	1.73694100	0.21418400	-1.37367500
O	0.32938100	-0.80334800	-0.25416600
C	-0.53763100	0.24824100	-0.15459100
O	-0.13104700	1.38319600	-0.33919400
S	-2.16164800	-0.23322500	0.23444600
H	2.14962200	-1.41390200	-0.81627000
C	2.40365900	0.12767600	0.69982300
H	3.20346700	-0.52527400	1.05381200
H	2.83167500	1.10659400	0.47943600
H	1.69078900	0.25603900	1.51697200

TS1

C	0.94225400	1.28799200	-0.23350000
H	0.09648900	1.90702100	-0.47810500
C	2.18167900	1.17218800	-0.17467700
C	4.85536900	-1.24129300	-0.54037400
H	5.70992000	-0.64817200	-0.21184300
H	4.59954600	-1.97052900	0.22926600
H	5.08893900	-1.74920800	-1.47339900
O	3.77649000	0.28802700	1.31176400
O	3.73708700	-0.39714700	-0.82972400
C	3.27467600	0.33607600	0.20420000
S	-0.45101200	-0.48398400	0.40786500
O	-2.06705300	1.46223000	-0.38169900
C	-1.95188900	0.31013800	-0.01049200
C	-4.30168700	0.08273100	-0.20210400
H	-4.47207600	0.94295200	0.44883000
H	-4.28384200	0.43276400	-1.23630700

O	-3.02232900	-0.49897000	0.11724800
C	-5.34599900	-0.98856200	0.00518500
H	-5.34889600	-1.33245200	1.04148100
H	-6.33364600	-0.58439100	-0.22708500
H	-5.16021500	-1.84298100	-0.64880700

S3

C	-3.88457900	0.33632000	-0.33102300
H	-4.22966300	-0.45949600	0.32921400
O	-2.57320100	-0.01308500	-0.83765500
C	-1.70389600	-0.51254000	0.04322900
O	-1.94714800	-0.74675200	1.19779500
S	-0.14678000	-0.79267100	-0.76209800
C	0.80622300	-1.50647700	0.62934100
C	2.06840900	-1.20161300	0.89124700
C	2.78029300	-0.22503100	0.10280100
O	3.44320400	-0.44383300	-0.90134800
H	0.21165200	-2.24830800	1.15503900
H	-4.51320100	0.36248100	-1.21945500
C	3.48660100	2.02585700	-0.03052200
H	3.12909200	2.15988500	-1.05298600
H	3.33705600	2.94276100	0.53672000
H	4.54762400	1.77086800	-0.05126900
O	2.73372000	1.02088600	0.64619600
C	-3.85507700	1.67858900	0.36713000
H	-4.86626600	1.94042700	0.68690200
H	-3.21158200	1.65066500	1.24791500
H	-3.49667600	2.45509900	-0.31162800

S4

C	4.20498300	-0.46533500	-0.37317500
H	4.36557800	0.39829200	-1.01826700
O	2.78332700	-0.77681800	-0.36669200
C	1.94984000	0.24163500	-0.25286200
O	2.23952700	1.40285100	-0.20092600
S	0.28136300	-0.44003200	-0.19752600
C	-0.59085300	1.07050500	-0.06853000
C	-1.91728500	1.20279600	0.03081600
C	-2.83114000	0.05065500	0.04581000
O	-2.48173400	-1.10580700	-0.04524900
H	-2.34772600	2.19329600	0.10664500
H	0.04873900	1.94703800	-0.07358900
H	4.66099100	-1.34381400	-0.82473700
C	-5.07212900	-0.63051000	0.20200700
H	-4.88374900	-1.29217500	1.04792100
H	-6.03771600	-0.14336600	0.31031000
H	-5.03648500	-1.20000400	-0.72706400
O	-4.10466200	0.42758000	0.17405500
C	4.70712700	-0.23228600	1.03357600
H	5.78495700	-0.05883200	1.00134800
H	4.23177600	0.64017300	1.48465300
H	4.51691200	-1.10730500	1.65783400

S6

O	-3.73826700	-1.23836600	-0.33583300
C	-3.07074700	-0.22804200	-0.22357000
C	-2.11191100	-1.18468400	1.74115900
H	-3.06378800	-1.32021800	2.26102200
H	-1.90092300	-2.09818200	1.17935800

S	-3.03545400	1.14257800	-1.30073000
H	-0.81626100	1.32678700	-0.56827900
N	0.15196900	1.43219700	-0.24716100
C	0.54093100	2.70311900	0.34801400
C	0.94907100	0.38250600	-0.33736300
H	0.35551400	2.67742900	1.42631900
H	-0.08278200	3.47987500	-0.09326700
C	2.01459000	2.92026300	0.06000200
C	0.33170500	-0.85103700	-0.95217300
N	2.20431100	0.44393100	0.08421700
H	2.16147200	3.04713500	-1.01540700
H	2.37893700	3.81411500	0.56625400
C	2.79127500	1.71568600	0.55465000
C	1.28517500	-1.70361000	-1.79163400
H	-0.10576300	-1.44479700	-0.14259900
H	-0.50307600	-0.49777200	-1.56026200
C	3.16324000	-0.68020300	0.15910700
H	3.81829300	1.74295900	0.18698900
H	2.82160100	1.68812000	1.64785000
C	2.06247200	-2.70212100	-0.93403800
H	0.70266300	-2.23373700	-2.54720100
H	1.97477000	-1.04922400	-2.33335600
C	2.55864900	-2.06216400	0.36238400
H	3.79966000	-0.65304600	-0.73193200
H	3.79469400	-0.44085700	1.01628800
H	1.42263800	-3.55517000	-0.69009800
H	2.91197200	-3.08805100	-1.50443100
H	1.75152000	-1.98897500	1.09776400
H	3.33034200	-2.69071700	0.81240000
O	-2.22076800	-0.08064000	0.83161600

C	-0.99325300	-0.85279400	2.70305700
H	-1.21781900	0.06119100	3.25724100
H	-0.86407300	-1.66819900	3.41817800
H	-0.05119400	-0.71226800	2.16562200

TS2

C	3.44385100	-1.38716800	0.27914800
H	4.38023200	-0.86224400	0.33395000
C	2.73228200	-2.29540000	0.76167800
C	0.09993000	-4.48755400	-0.42606700
H	-0.64872800	-3.77240600	-0.76993500
H	0.24823700	-5.26233900	-1.17486600
H	-0.22444900	-4.93192600	0.51571700
O	0.44953300	-2.51587900	1.28431600
O	1.37258400	-3.85111100	-0.27100600
C	1.42140800	-2.85667900	0.63666400
O	3.86895400	1.63934800	0.06632100
C	2.89888500	1.39193400	-0.61608800
C	2.03453600	3.54574000	-0.12462200
H	2.22557600	3.36324100	0.93496800
H	2.89071900	4.08119600	-0.54137300
S	2.59661500	-0.12574600	-1.45023300
H	0.35581500	0.11944300	-0.54341000
N	-0.29109900	0.39477400	0.19379300
C	0.28967000	0.77044500	1.47677100
C	-1.58491300	0.29048100	-0.04918300
H	0.45616800	1.85149700	1.50279000
H	1.25181900	0.26184000	1.55825800
C	-0.67056000	0.34099900	2.56955400
C	-1.94521800	-0.18291500	-1.43788200

N	-2.47611600	0.57373200	0.88822700
H	-0.70461400	-0.74946000	2.60281000
H	-0.33889000	0.71463200	3.53845500
C	-2.04618500	0.90029100	2.26290500
C	-3.19958200	-1.05568300	-1.51530900
H	-2.04346600	0.69626300	-2.08293000
H	-1.07729600	-0.73746700	-1.79869200
C	-3.94459000	0.63266000	0.72022900
H	-2.79290100	0.47366400	2.93409500
H	-2.06799600	1.98857900	2.37567300
C	-4.47456600	-0.21973800	-1.62374800
H	-3.11056900	-1.71546000	-2.38022200
H	-3.24224800	-1.70263500	-0.63371900
C	-4.44476100	0.97820200	-0.67510400
H	-4.37038100	-0.31341300	1.07134700
H	-4.26633900	1.41115500	1.41367600
H	-4.59394600	0.13961200	-2.64990300
H	-5.34063700	-0.84827200	-1.39843400
H	-3.82757900	1.78460100	-1.08207600
H	-5.45201200	1.38631700	-0.56541000
C	0.74169200	4.29670800	-0.33869800
H	0.79260600	5.26386100	0.16572200
H	0.56417700	4.46995700	-1.40199000
H	-0.10159600	3.73549500	0.07167000
O	1.90289200	2.27923300	-0.80063800

S7

C	3.22993100	-2.11773700	-0.63451500
H	4.22996600	-2.28956400	-1.02082200
C	2.60757600	-2.87946600	0.25099700

C	-1.00825700	-3.09799600	0.60584800
H	-1.29097300	-2.08211000	0.88464700
H	-1.68766400	-3.48744100	-0.15025300
H	-1.04279200	-3.73085100	1.49586900
O	1.04569300	-1.95419100	1.77906900
O	0.29402900	-3.13496300	0.02099400
C	1.29290900	-2.57220900	0.75249500
O	3.99223600	0.58853700	0.36034300
C	3.12381600	0.67546200	-0.46360800
C	2.89087200	2.99472800	-0.07716900
H	2.76755300	2.81199900	0.99219200
H	3.94667800	3.18078700	-0.28204300
S	2.46308800	-0.66057600	-1.44651900
H	0.26075900	-0.03646200	-0.51864500
N	-0.36388900	0.44694000	0.11928300
C	0.21370200	1.03860400	1.32194300
C	-1.66356800	0.36742200	-0.12666800
H	0.38323000	2.10730700	1.16100800
H	1.16582100	0.54156300	1.50587100
C	-0.76157800	0.80442900	2.45969400
C	-2.03755800	-0.34079400	-1.40846900
N	-2.54167400	0.85363100	0.73304400
H	-0.82182900	-0.26880800	2.65582100
H	-0.42549000	1.30935200	3.36538700
C	-2.11730100	1.35058800	2.05866500
C	-3.37144200	-1.08814200	-1.37296300
H	-2.02332700	0.39399100	-2.22028100
H	-1.22354200	-1.04108300	-1.61038100
C	-3.99771000	1.00282200	0.51234200
H	-2.88645400	1.03828600	2.76686100

H	-2.10973700	2.44382400	2.02255300
C	-4.55398400	-0.17065900	-1.67899400
H	-3.32976400	-1.90216000	-2.09913700
H	-3.49644400	-1.55396800	-0.39075500
C	-4.43458800	1.16035500	-0.93699800
H	-4.50728600	0.16210900	0.99432800
H	-4.26421400	1.90500500	1.06513200
H	-4.60583900	0.02053700	-2.75460400
H	-5.48330400	-0.67144000	-1.39376000
H	-3.73465100	1.83034300	-1.44521500
H	-5.40067700	1.66970200	-0.93194000
C	2.01285200	4.12050500	-0.56419100
H	2.28219200	5.03926900	-0.03934600
H	2.14708200	4.28196900	-1.63539800
H	0.96045100	3.90499900	-0.36745400
O	2.48876200	1.80069000	-0.79316700

S8

C	1.89670400	-1.81240100	-0.44188100
H	2.79707500	-2.28694900	-0.04881700
C	0.64374400	-2.24378900	-0.35228800
C	0.07198400	-5.80504600	0.21765600
H	-0.95633200	-5.76018700	0.58028400
H	0.16110200	-6.56817000	-0.55313600
H	0.73823600	-6.03763600	1.04970300
O	0.06635200	-3.54662100	1.55325100
O	0.44403100	-4.57504900	-0.40610000
C	0.38872200	-3.46868600	0.37801900
O	3.52719300	0.18489100	0.90311700
C	3.25926400	0.56171100	-0.20723700

C	4.46472900	2.56482900	0.11295700
H	3.88825300	2.79411000	1.01111100
H	5.36163000	2.01443200	0.40210700
S	2.27379000	-0.32631400	-1.39140200
H	-0.44957800	-0.63505300	-0.12673400
N	-0.77869900	0.27322200	0.26225600
C	0.12629400	0.97815200	1.15980300
C	-2.01920100	0.65528300	0.02029700
H	0.66778500	1.75276500	0.60632300
H	0.84897000	0.25083200	1.53166700
C	-0.69899500	1.59617200	2.27359100
C	-2.79321600	-0.22573600	-0.93225500
N	-2.52621000	1.73498900	0.59969000
H	-1.14819200	0.80432200	2.87820700
H	-0.07572900	2.21403400	2.92021100
C	-1.78089800	2.45704800	1.65139700
C	-4.29307800	-0.32814100	-0.65022100
H	-2.61375000	0.13717200	-1.94968500
H	-2.32676400	-1.21023900	-0.87087600
C	-3.83194900	2.36367500	0.30282400
H	-2.51296900	2.76033900	2.40170000
H	-1.35638500	3.36120000	1.20510400
C	-5.07756300	0.81541000	-1.29259900
H	-4.65314100	-1.28664300	-1.02831200
H	-4.45616700	-0.33972600	0.43174700
C	-4.36788700	2.15634800	-1.10655700
H	-4.55521600	2.03070700	1.05496900
H	-3.66412700	3.42993500	0.46386900
H	-5.20336300	0.62201300	-2.36183000
H	-6.07781000	0.86207400	-0.85291400

H	-3.54346400	2.26485200	-1.81734500
H	-5.06266000	2.97355000	-1.31289600
C	4.79578300	3.80674200	-0.67676600
H	5.40492800	4.47149300	-0.06095400
H	5.36048900	3.55551600	-1.57651300
H	3.88688600	4.33846500	-0.96459600
O	3.66085000	1.71439400	-0.74077100

S9

C	-4.37392600	-0.20434900	-0.38387000
H	-4.18711700	-0.91313800	-1.19033600
O	-3.19255400	0.63397900	-0.22739000
C	-2.02362700	0.02388800	-0.25392500
O	-1.81715300	-1.14072100	-0.43498400
S	-0.75671400	1.27159700	0.02429400
C	0.66193400	0.25718500	-0.06660300
C	1.89807200	0.72720200	0.10299300
H	0.47585000	-0.79305700	-0.27263600
H	-5.14827000	0.49595400	-0.68935200
C	-4.71803800	-0.89079300	0.91797400
H	-5.63884100	-1.46249400	0.78346300
H	-3.92838000	-1.57820000	1.22532000
H	-4.88110700	-0.15511000	1.70768300
C	3.03721800	-0.21057100	0.00564400
O	2.95571600	-1.39388800	-0.22662900
O	4.19635900	0.42093900	0.21086900
C	5.37547300	-0.39183100	0.14109300
H	5.46824000	-0.83941300	-0.84879900
H	6.20790500	0.28065200	0.33150400
H	5.33998300	-1.17539400	0.89845000

H	2.11759400	1.76779000	0.31124900

References

[1]. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian 16, Revision B.01; Gaussian, Inc., Wallingford CT, 2016.

[2]. Y. Zhao, D. G. Truhlar, Theor. Chem. Acc. ***2008***, 120, 215–241.

[3]. Aleksandr V. Marenich, Christopher J. Cramer, and Donald G. Truhlar.The Journal of Physical Chemistry B ***2009*** 113 (18), 6378-6396.

[4]. Tian Lu, Qinxue Chen. Comput. Theor. Chem. ***2021***, 1200, 113249.

[5]. Tian Lu, Feiwu Chen. J. Comput. Chem. ***2012***, 33, 580-592.

[6]. Legault, C. Y. CYLview, 1.0b; Université de Sherbrooke, ***2009*** (http://www.cylview.org).