Supplementary Information

Expanding the chemical functionality of levoglucosenone-based monomers for degradable thiol-ene thermosets with high bio-derived content

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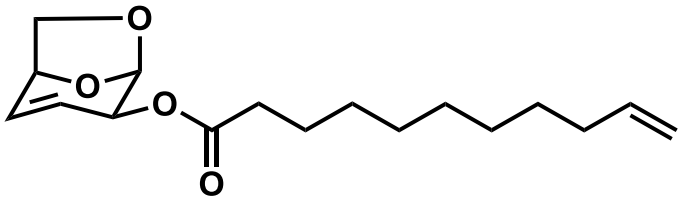
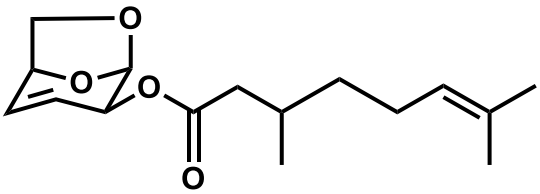
Analytical data of all compounds

Monomer 1



$[\alpha]_D^{23}$ -30.7° (*c* 0.021 molL^{-1} in C_2H_5OH). **IR (film) ν_{max}** 2928, 2856, 1735, 1639, 1356, 1242, 1165, 1123, 1033, 983, 907, 886 cm^{-1}. **^{1}H NMR (600 MHz, $CDCl_3$)**, δ: 6.13 (dd, 1H, *J* =3.6, 3.5 Hz), 5.70-5.77 (m, 1H), 5.54-5.57 (m, 2H), 5.45 (br. s, 1H), 4.85-4.93 (m 2H), 4.62 (t, 1H, *J* =4.1 Hz), 3.91(d, 1H, *J* =6.6 Hz), 3.73 (m, 1H), 2.30-2.33 (td, 2H, *J* =7.6 Hz), 1.96 (q, 2H, *J* =7.1 Hz), 1.57 (m, 2H), 1.21-1.30 (m, 10H). **^{13}C NMR (150 MHz, $CDCl_3$)**, δ: 173.6, 139.2, 132.3, 124.9, 114.1, 99.2, 71.5, 71.4, 71.3, 34.2, 33.7, 30.9, 29.2, 29.1, 29.0, 28.8, 24.8 ppm. **HRMS** calc. for $C_{17}H_{26}O_4$, $[M+Na]^+$: 317.1729, found 317.1731.

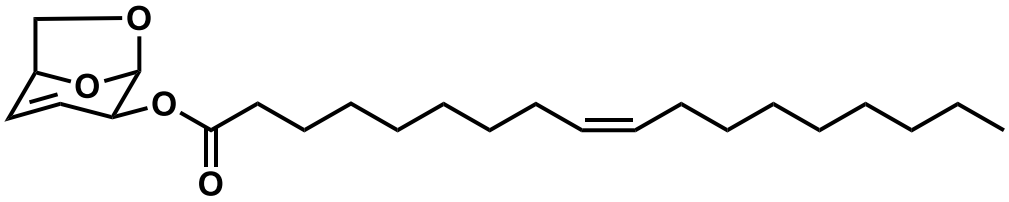
Monomer 2



$[\alpha]_D^{23}$ -30.5° (*c* 0.021 molL^{-1} in C_2H_5OH). **IR (film) ν_{max}** 2966, 2916, 1732, 1458, 1378, 1259, 1164, 1124, 1035, 985, 885, 838, 803 cm^{-1}. **^{1}H NMR (600 MHz, $CDCl_3$)**, δ: 6.12 (dd, 1H, *J* =9.7, 6.0 Hz), 5.54-5.57 (m, 2H), 5.46 (br. s, 1H), 5.01 (t, 1H, *J* =6.3 Hz), 4.62 (s, 1H), 3.91(d, 1H, *J* =6.5 Hz), 3.73 (t, 1H, *J* =4.1 Hz), 2.30-2.35 (m, 1H), 2.11-2.16 (m, 1H), 1.87-1.92 (m, 3H), 1.61 (s, 3H), 1.52 (s, 3H), 1.28 (m, 1H), 1.13-1.19 (m, 1H), 0.90 (d, 3H, *J* =6.2 Hz). **^{13}C NMR (150 MHz, $CDCl_3$)**, δ: 173.0, 172.9, 132.3, 131.5, 124.97, 124.94, 124.2, 99.2, 71.46,

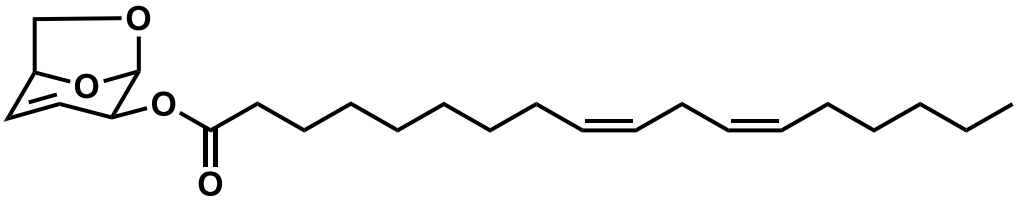
71.41, 71.39, 71.33, 41.62, 36.7, 30.0, 29.9, 25.6, 25.3, 19.5, 17.6 ppm. **HRMS** calc. for $C_{16}H_{24}O_4$, $[M+Na]^+$: 303.1572, found 303.1573.

Monomer 3



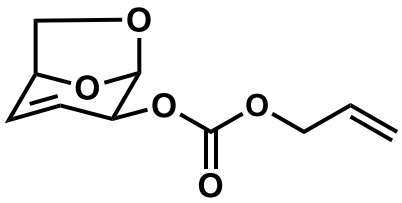
$[\alpha]_D^{23}$ -22.2° (*c* 0.016 molL^{-1} in C_2H_5OH). **IR (film) ν_{max}** 2925, 2855, 1737, 1466, 1361, 1246, 1165, 1124, 1036, 986, 886, 803, 724 cm^{-1}. **^{1}H NMR (600 MHz, $CDCl_3$)**, δ: 6.13 (dd, 1H, *J* =9.7, 5.8 Hz), 5.55-5.57 (m, 2H), 5.45 (br. s, 1H), 5.27 (m, 2H), 4.62 (t, 1H, *J* =4.1 Hz), 3.91(d, 1H, *J* =6.6 Hz), 3.73 (t, 1H, *J* =4.7 Hz), 2.30-2.33 (m, 2H), 1.94 (q, 2H, *J* =6.4 Hz), 1.57 (t, 2H, *J* =6.9), 1.18-1.23 (m, 22H), 0.81 (t, 3H, *J* =6.7 Hz). **^{13}C NMR (150 MHz, $CDCl_3$)**, δ: 173.6, 132.3, 130.0, 129.7, 124.9, 99.2, 71.4, 71.4, 71.3, 34.2, 31.9, 29.7, 29.6, 29.5, 29.3, 29.2, 29.1, 29.1, 29.0, 27.2, 27.1, 24.9, 22.7, 14.1 ppm. **HRMS** calc. for $C_{24}H_{40}O_4$, $[M+Na]^+$: 415.2824, found 415.2844.

Monomer 4



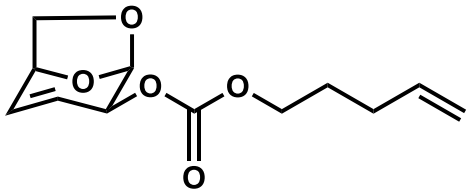
^{1}H NMR (600 MHz, $CDCl_3$), δ: 6.12 (dd, 1H, *J* =9.7, 5.8 Hz), 5.54-5.57 (m, 2H), 5.45 (br. s, 1H), 5.23-5.33 (m, 4H), 4.62 (t, 1H, *J* =4.1 Hz), 3.91(d, 1H, *J* =6.6 Hz), 3.73 (t, 1H, *J* =4.5 Hz), 2.70 (t, 2H, *J* =6.8 Hz), 2.30-2.33 (m, 2H), 1.98 (m, 4H), 1.57 (m, 2H), 1.21-1.30 (m, 14H), 0.82 (t, 3H, *J* =6.7 Hz). **^{13}C NMR (150 MHz, $CDCl_3$)**, δ: 173.6, 132.3, 130.2, 130.0, 128.0, 127.9, 124.9, 99.2, 71.5, 71.4, 71.3, 34.2, 31.5, 29.6, 29.3, 29.2, 29.1, 29.0, 27.2, 25.6, 24.9, 22.5, 14.10 ppm. **HRMS** calc. for $C_{24}H_{38}O_4$, $[M+Na]^+$: 413.2668, found 413.2674.

Monomer 5



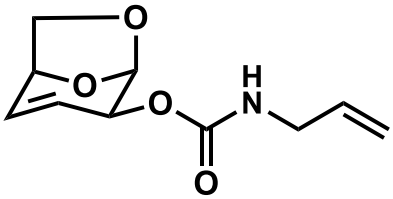
[α]$_D^{23}$ -21.8° (*c* 0.028 molL^{-1} in C_2H_5OH). IR (film) ν_{max} 2964, 2895, 1740, 1370, 1317, 1241, 1124, 1023, 981, 928, 885, 803, 788 cm^{-1}. **^{1}H NMR (600 MHz, $CDCl_3$)**, δ: 6.16 (m, 1H), 5.83-5.89 (m, 1H), 5.64 (t, 1H, *J* =2.1 Hz), 5.61-5.63 (dt, 1H, *J* =2.3, 2.2 Hz), 5.28-5.32 (m, 2H), 5.19-5.21 (dd, 1H, *J* =10.4, 1.1 Hz), 4.63 (t, 1H, *J* =4.2 Hz), 4.58 (d, 2H, *J* =5.8 Hz), 3.91 (d, 1H, *J* =6.6 Hz), 3.74 (m, 1H). **^{13}C NMR (150 MHz, $CDCl_3$)**, δ: 154.6, 133.0, 131.3, 124.1, 119.1, 98.8, 74.6, 71.3, 71.3, 68.8 ppm. **HRMS** calc. for $C_{10}H_{12}O_5$, $[M+Na]^+$: 235.0582, found 235.0586.

Monomer 6



[α]$_D^{23}$ -38.8° (*c* 0.025 molL^{-1} in C_2H_5OH). **IR (film) ν_{max}** 2960, 2894, 1740, 1641, 1389, 1320, 1250, 1124, 1023, 987, 928, 884, 803, 716 cm^{-1}. **^{1}H NMR (600 MHz, $CDCl_3$)**, δ: 6.25 (dd, 1H, *J* =9.5, 4.0 Hz), 5.78-5.84 (m, 1H), 5.70-5.73 (m, 2H), 5.39 (br. s, 1H), 5.05-5.08 (dd, 1H, *J* = 17.1, 1.5 Hz), 5.01-5.03 (dd, 1H, *J* = 10.2, 0.7 Hz), 4.72 (t, 1H, *J* =4.1 Hz), 4.19 (t, 2H, *J* =6.6 Hz), 3.99 (d, 1H, *J* =6.6 Hz), 3.83 (m, 1H), 2.17 (q, 2H, *J* = 7.1 Hz), 1.80 (qun., 2H, *J* =6.7 Hz). **^{13}C NMR (150 MHz, $CDCl_3$)**, δ: 154.8, 137.2, 132.9, 124.2, 115.5, 98.9, 74.4, 71.3, 71.3, 67.7, 29.7, 27.7 ppm. **HRMS** calc. for $C_{12}H_{16}O_5$, $[M+Na]^+$: 263.0895, found 263.0919.

Monomer 7



[α]$_D^{23}$ -29.3° (*c* 0.028 molL^{-1} in C_2H_5OH). **IR (film) ν_{max}** 3338, 2958, 2893, 1701, 1526, 1240, 1122, 1032, 980, 924, 884, 803 cm^{-1}.**^{1}H NMR (600 MHz, $CDCl_3$)**, δ: 6.11 (dd, 1H, *J* =10.3, 4.1 Hz), 5.74-5.80 (m, 1H), 5.59 (m, 2H), 5.40 (br. s, 1H), 5.12-5.15 (d, 1H, *J* =17.1 Hz), 5.07 (d, 1H, *J* =10.3 Hz), 4.88 (br. s, 1H), 4.62 (t, 1H, *J* =4.0 Hz), 3.89 (d, 1H, *J* =6.6 Hz), 3.72-3.75 (m, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)**, δ: 155.5, 134.0, 132.0, 125.3, 116.3, 99.6, 71.8, 71.4, 71.3, 43.5 ppm. **HRMS** calc. for $C_{10}H_{13}NO_4$, $[M+Na]^+$: 234.0742, found 234.0739.

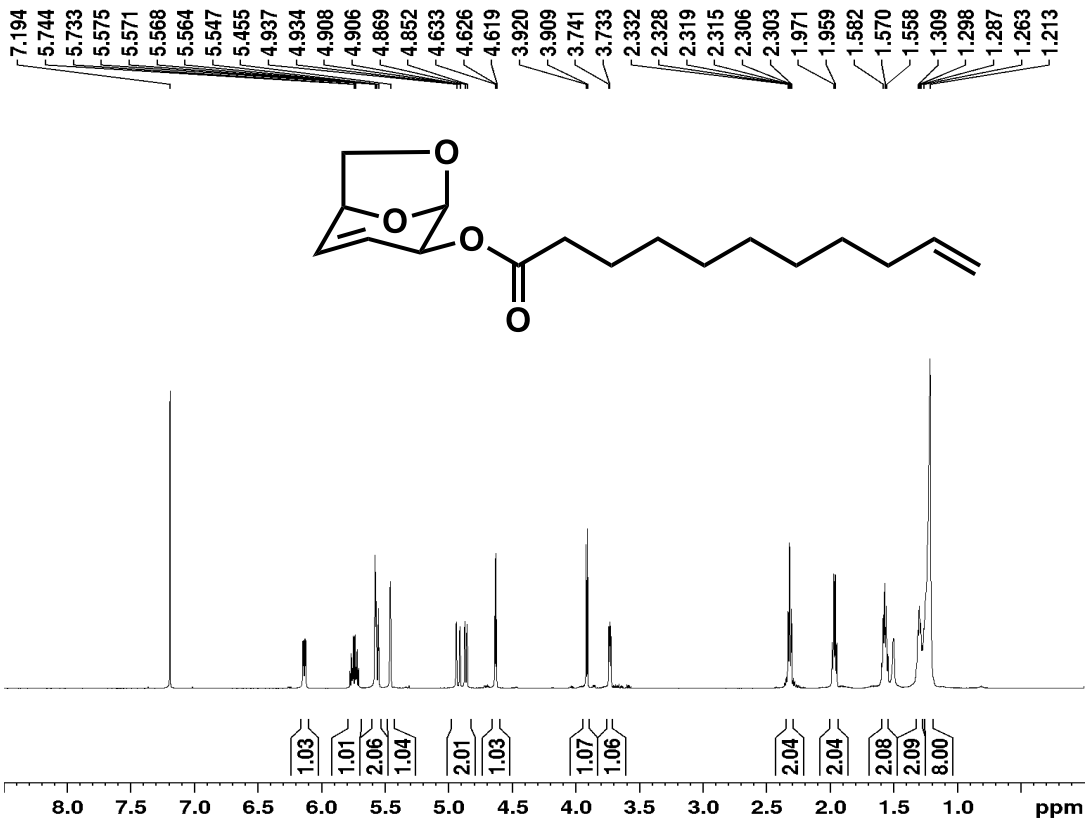


Fig. S1. ^{1}H NMR spectrum of Monomer **1** ($CDCl_3$, 600 MHz)

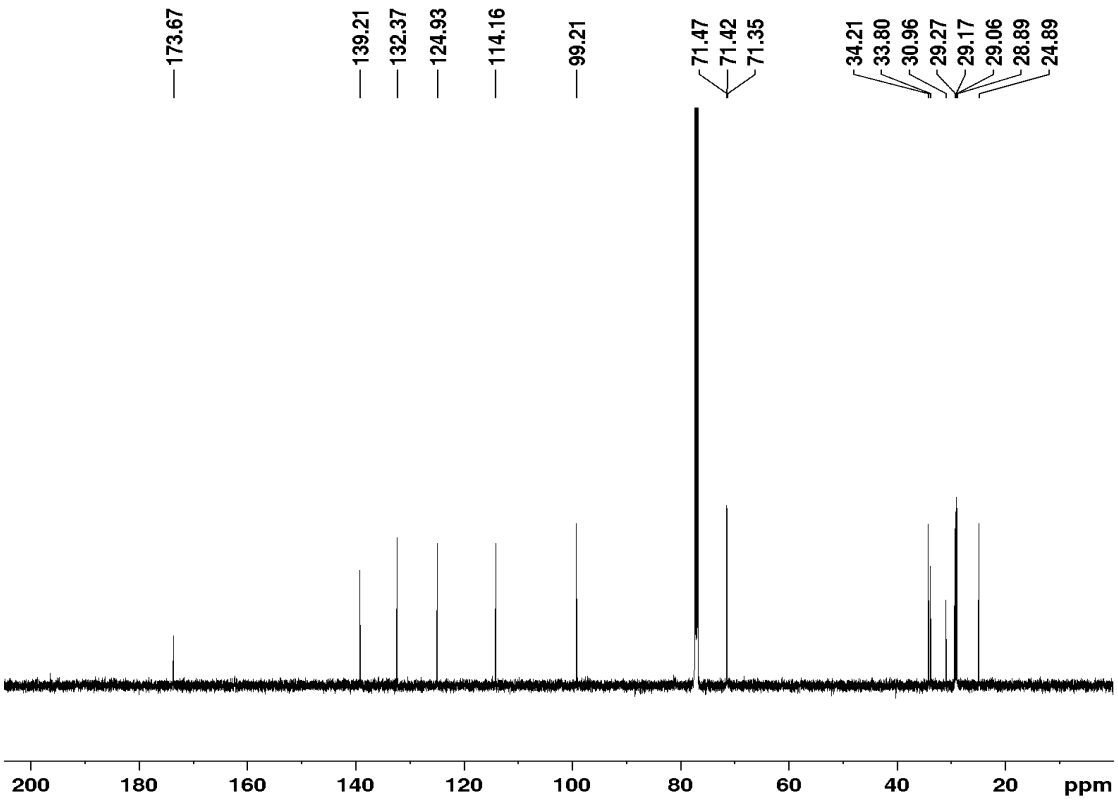


Fig. S2. ^{13}C NMR spectrum of Monomer **1** ($CDCl_3$, 150 MHz)

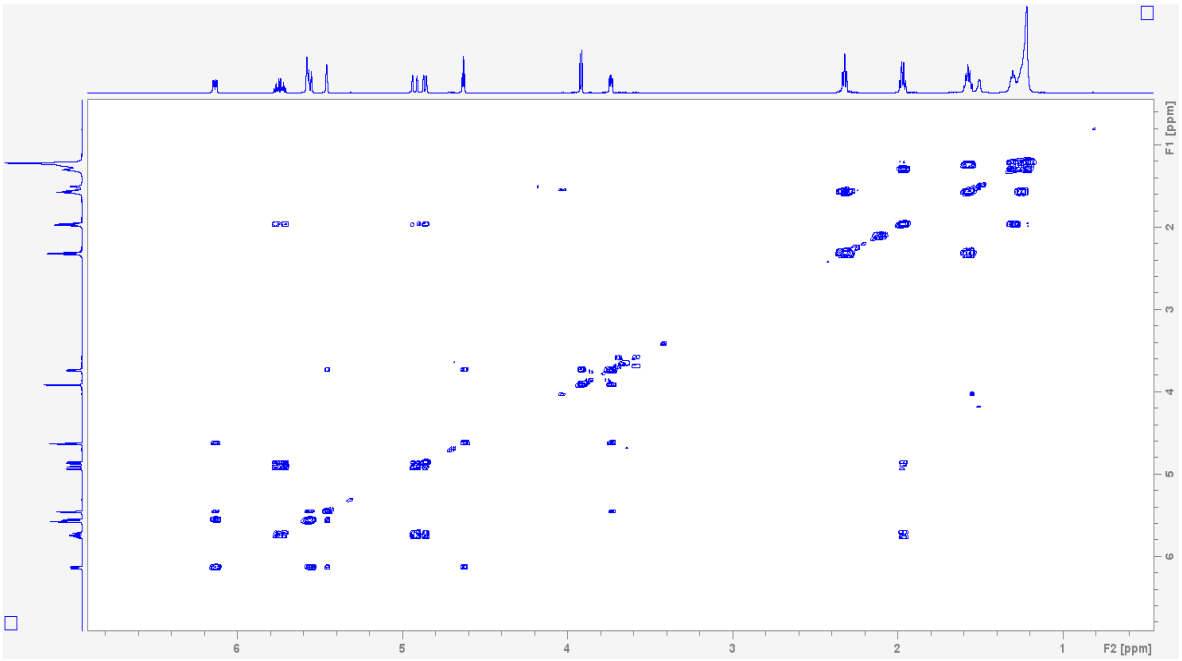


Fig. S3. COSY spectrum of monomer **1** ($CDCl_3$, 600 MHz)

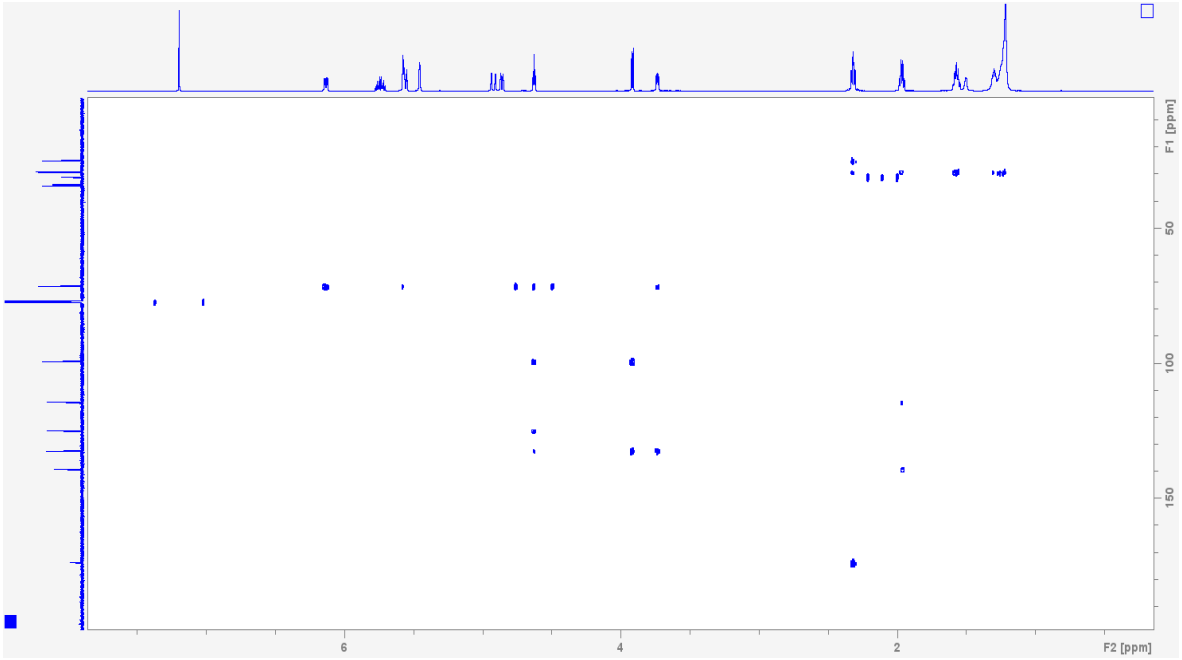


Fig. S4. HBMC spectrum of monomer **1** ($CDCl_3$, 600 MHz)

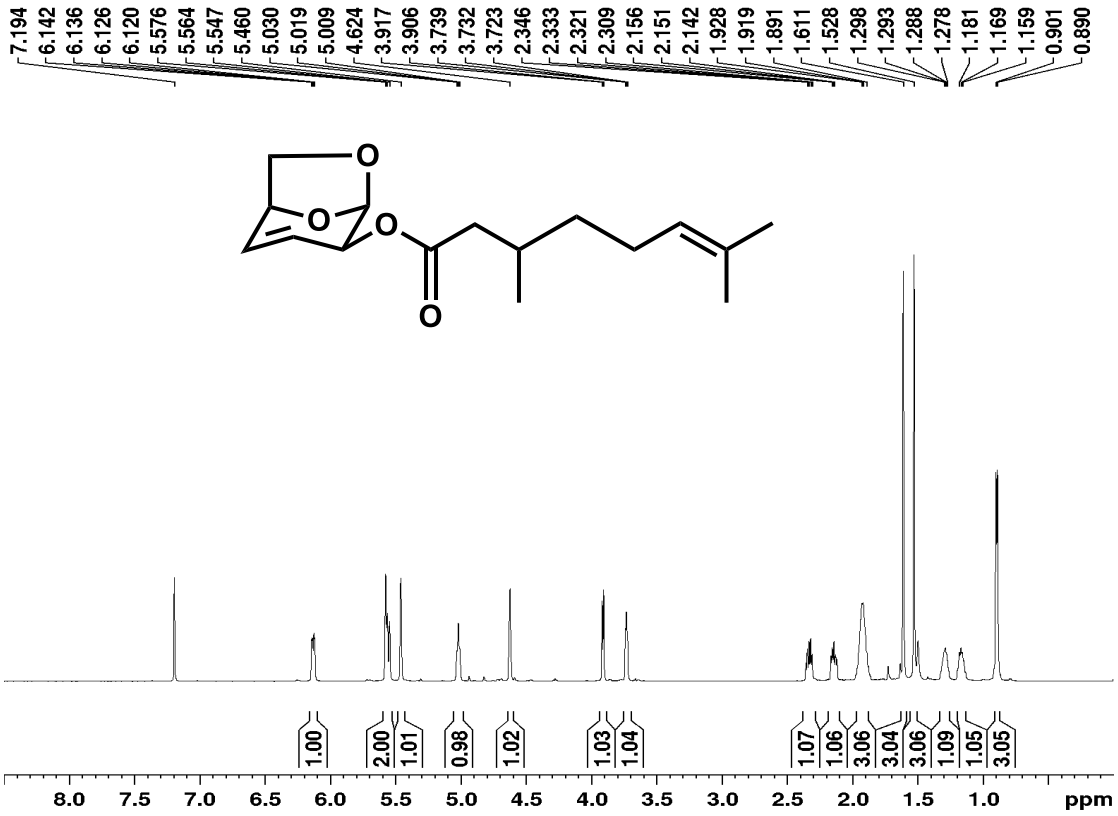


Fig. S5. ^{1}H NMR spectrum of Monomer **2** ($CDCl_3$, 600 MHz)

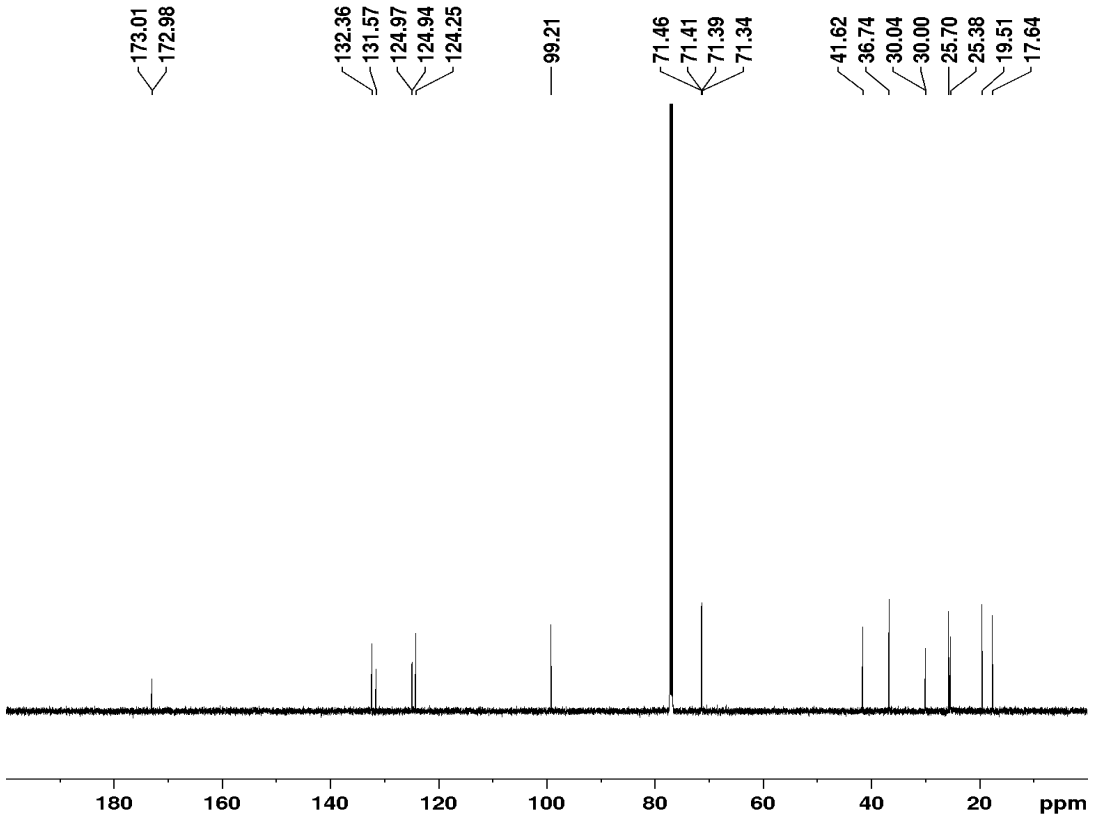


Fig. S6. ^{13}C NMR spectrum of Monomer **2** ($CDCl_3$, 150 MHz)

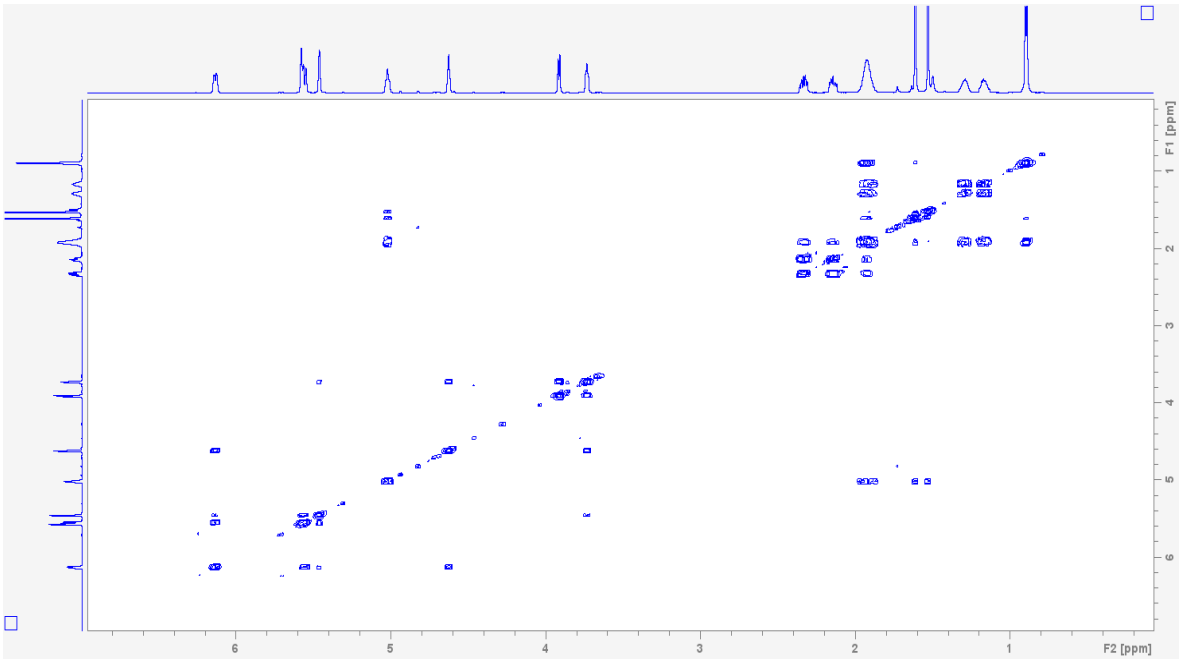


Fig. S7. COSY spectrum of monomer **2** ($CDCl_3$, 600 MHz)

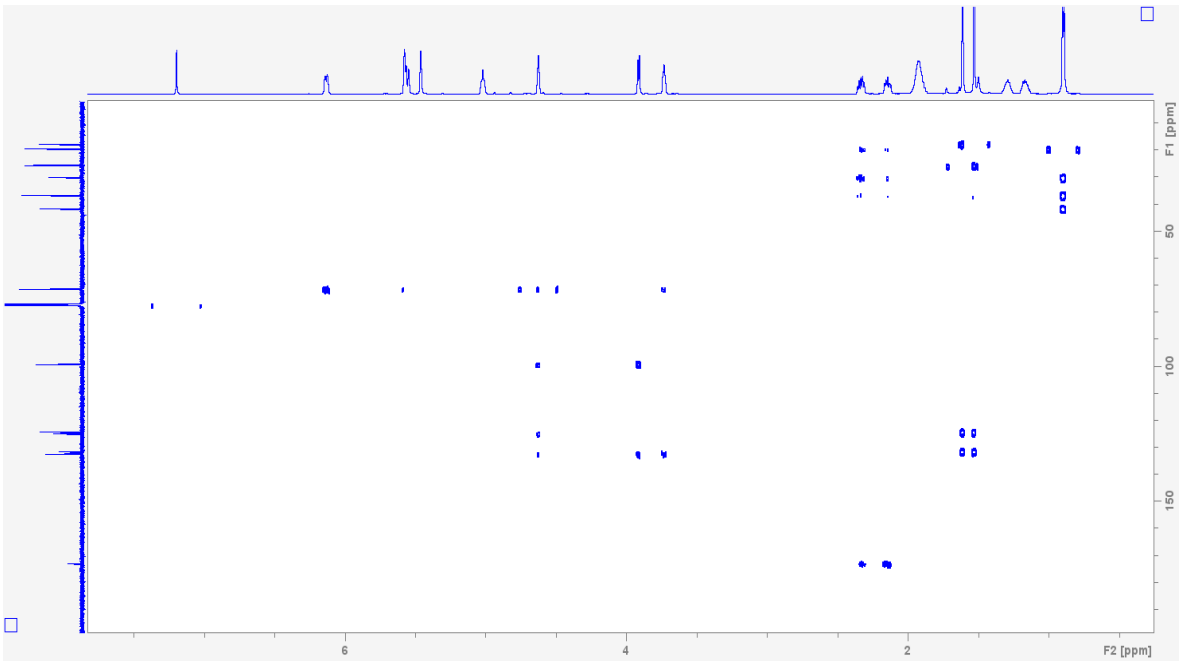


Fig. S8. HBMC spectrum of monomer **2** ($CDCl_3$, 600 MHz)

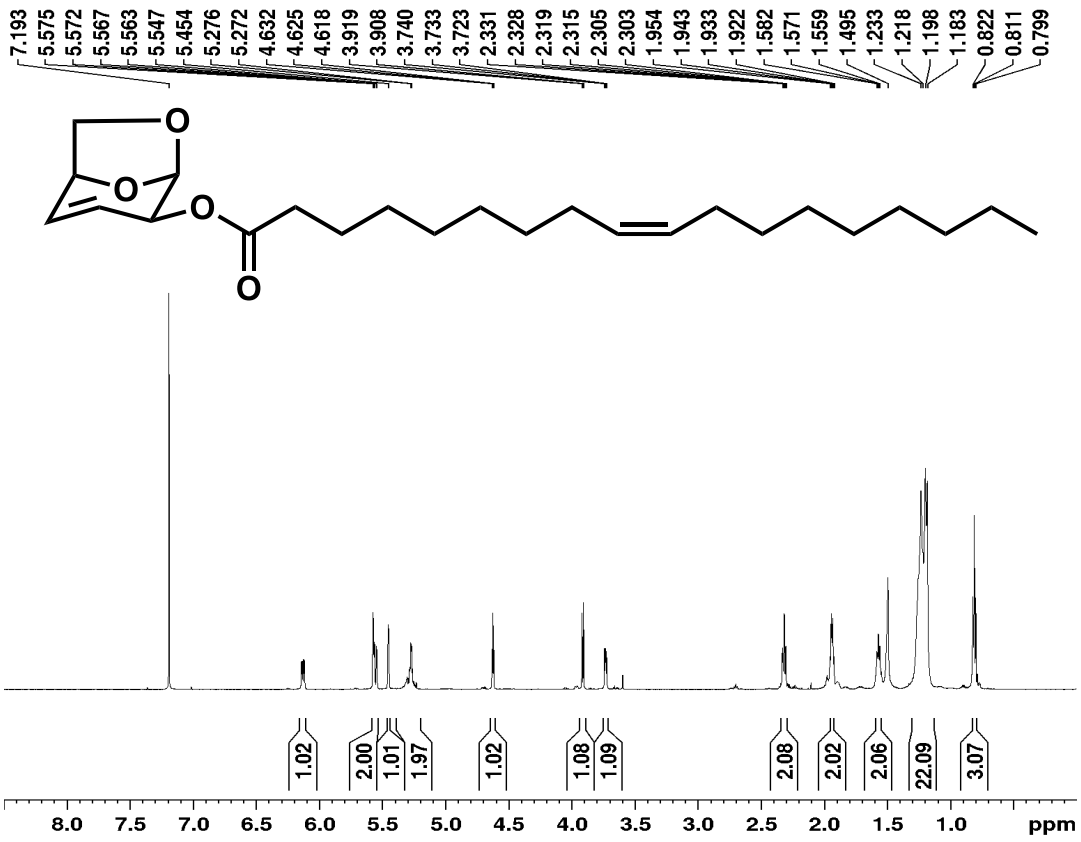


Fig. S9. ^{1}H NMR spectrum of Monomer **3** ($CDCl_3$, 600 MHz)

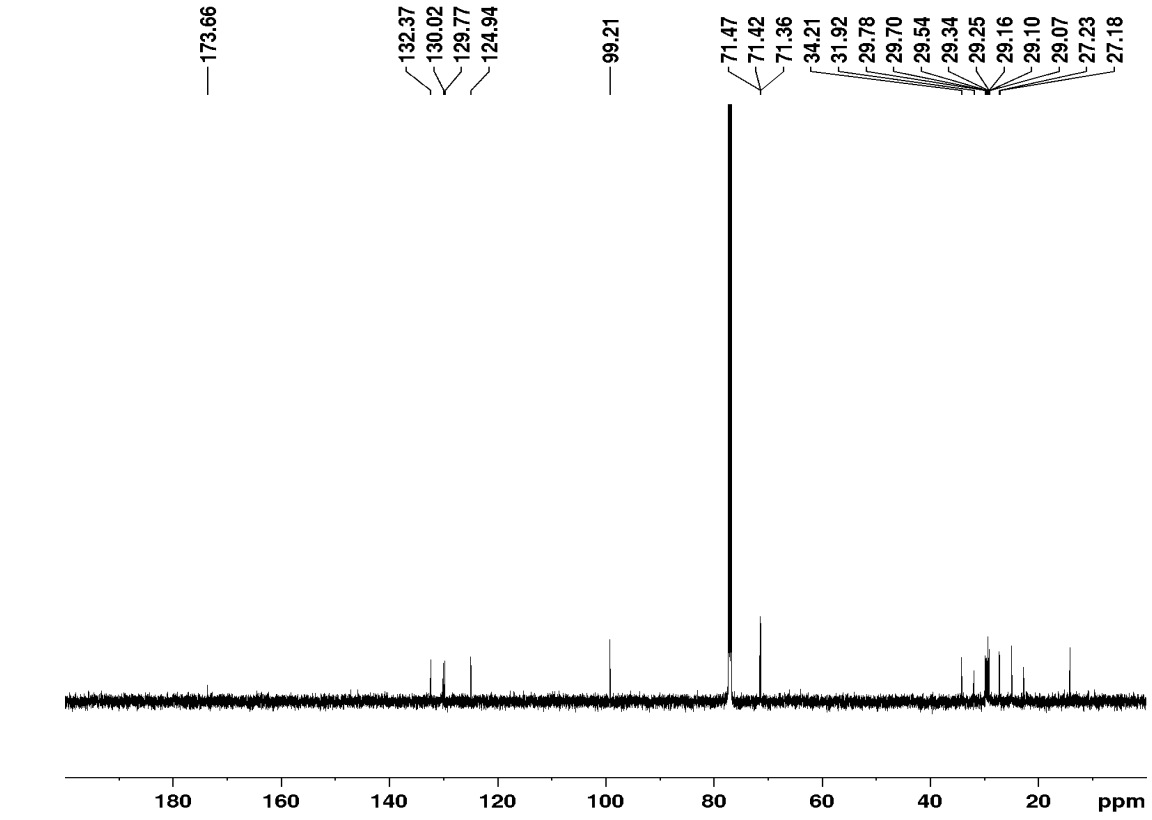


Fig. S10. ^{13}C NMR spectrum of Monomer **3** ($CDCl_3$, 150 MHz)

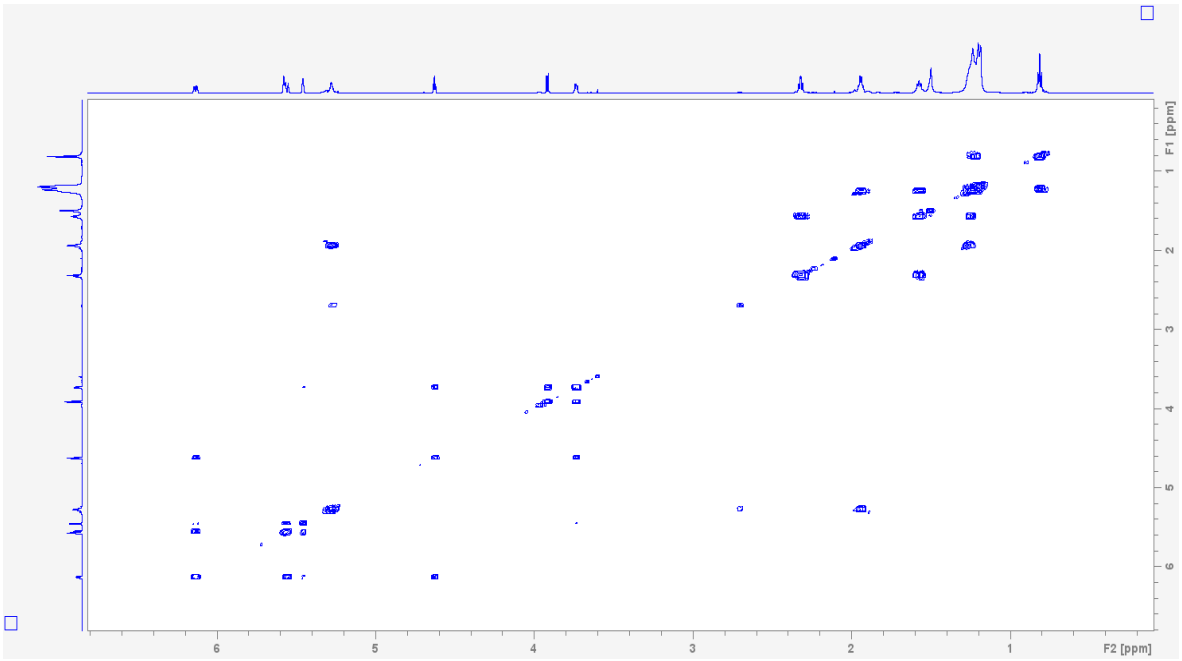


Fig. S11. COSY spectrum of monomer **3** ($CDCl_3$, 600 MHz)

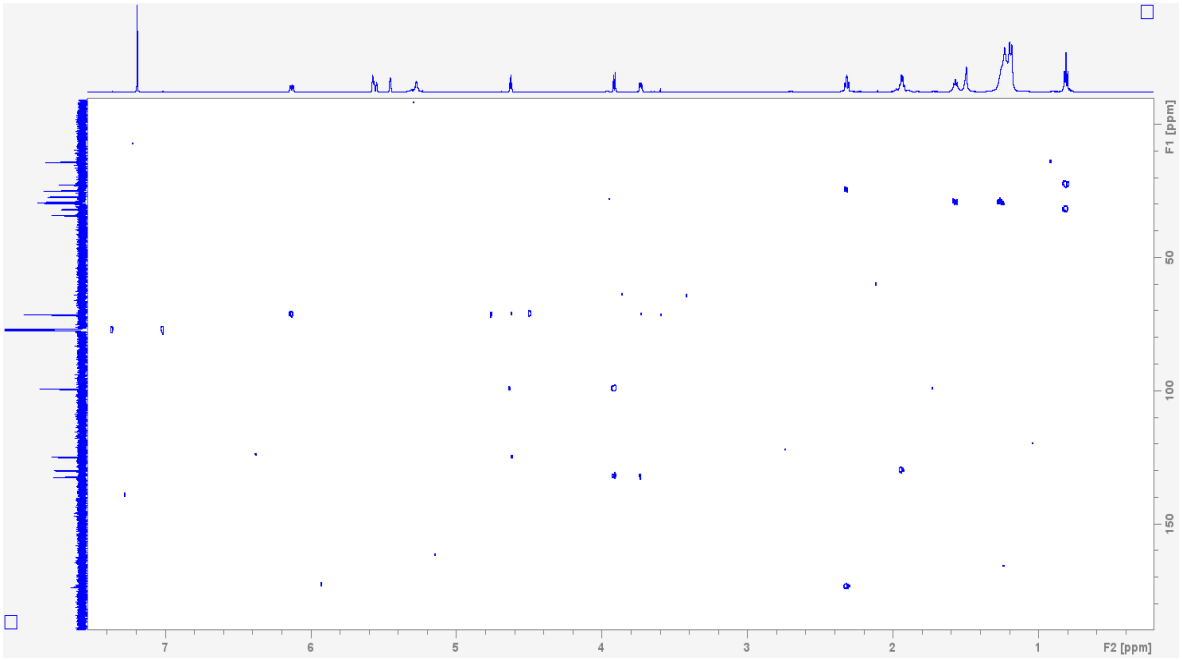


Fig. S12. HMBC spectrum of monomer **3** ($CDCl_3$, 600 MHz)

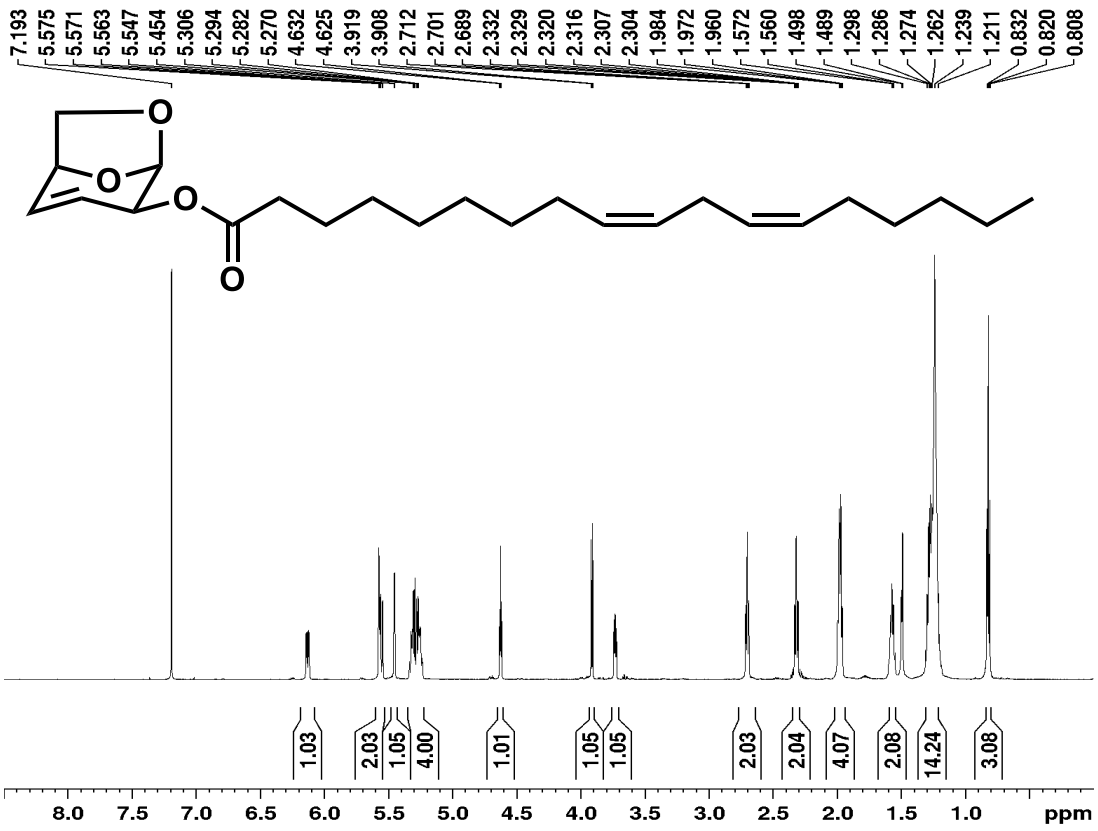


Fig. S13. ^{1}H NMR spectrum of Monomer **4** ($CDCl_3$, 600 MHz)

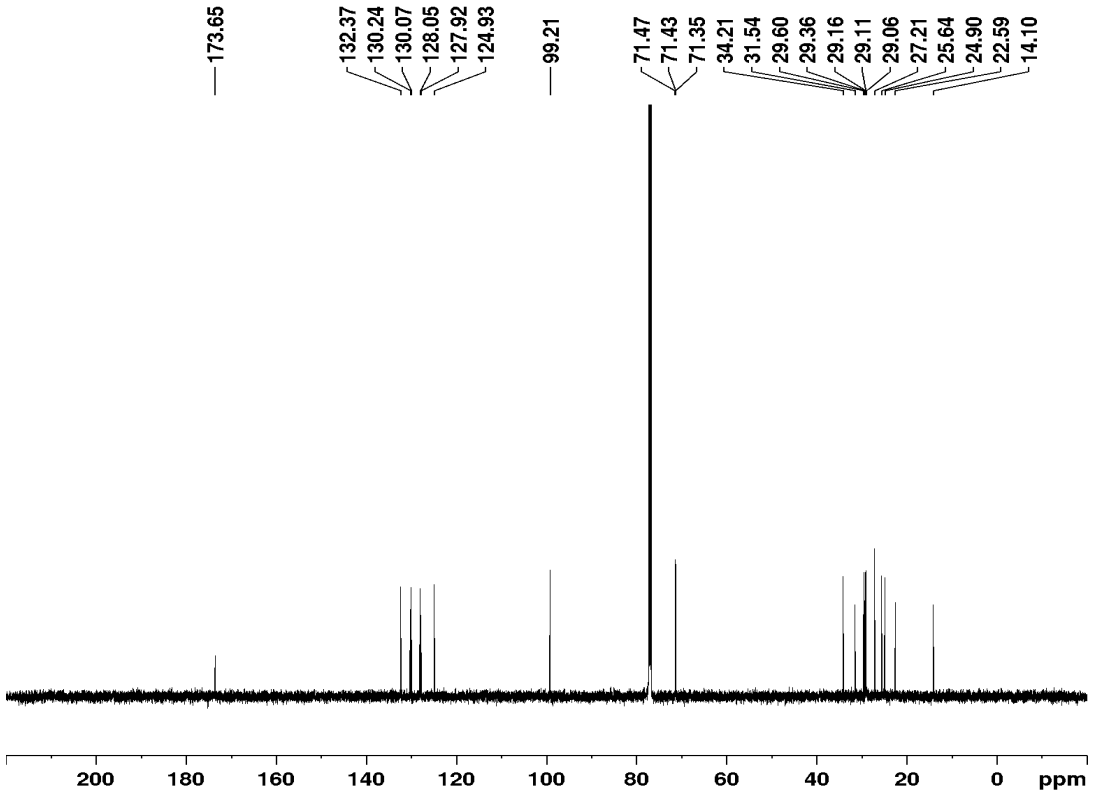


Fig. S14. ^{13}C NMR spectrum of Monomer **4** ($CDCl_3$, 150 MHz)

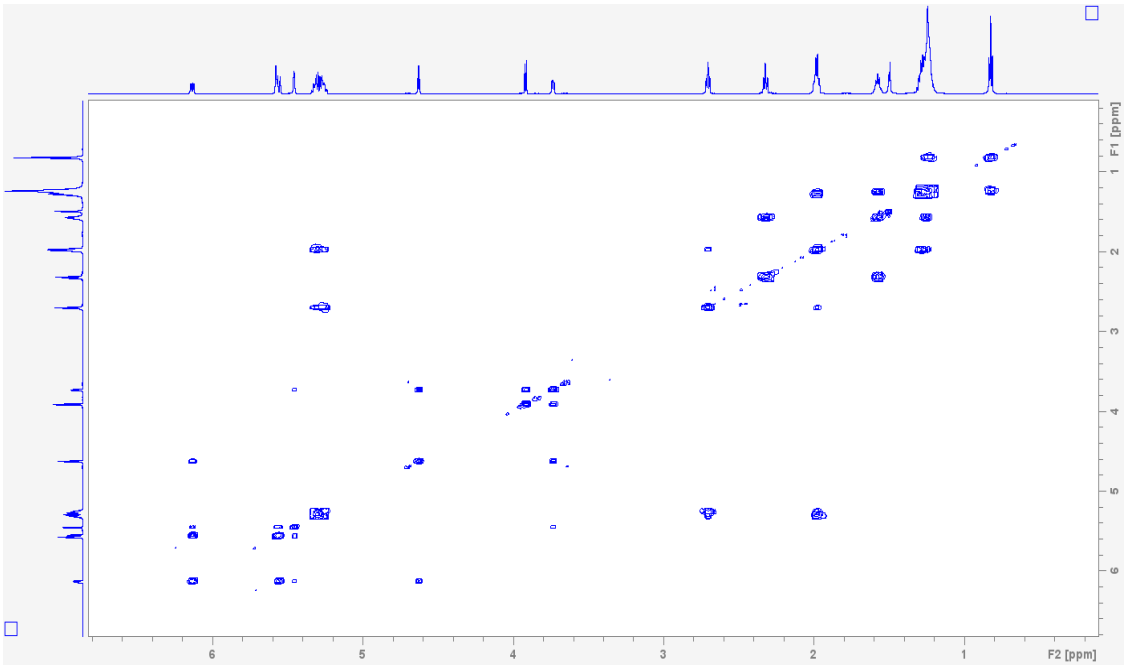


Fig. S15. COSY spectrum of monomer **4** ($CDCl_3$, 600 MHz)

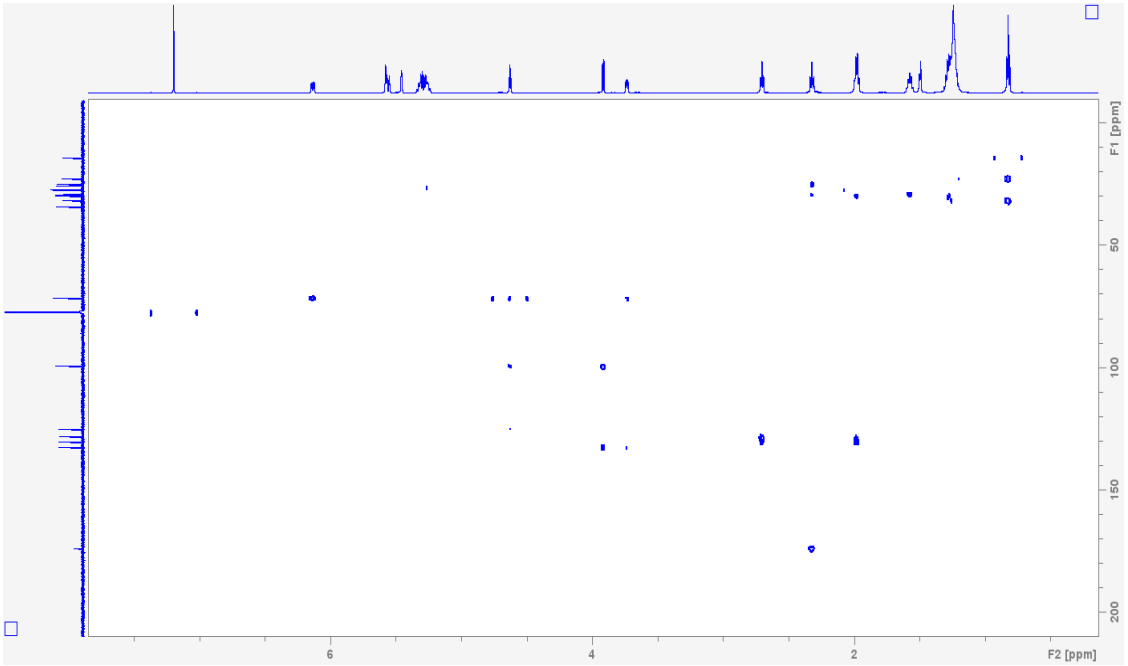


Fig. S16. HMBC spectrum of monomer **4** ($CDCl_3$, 600 MHz)

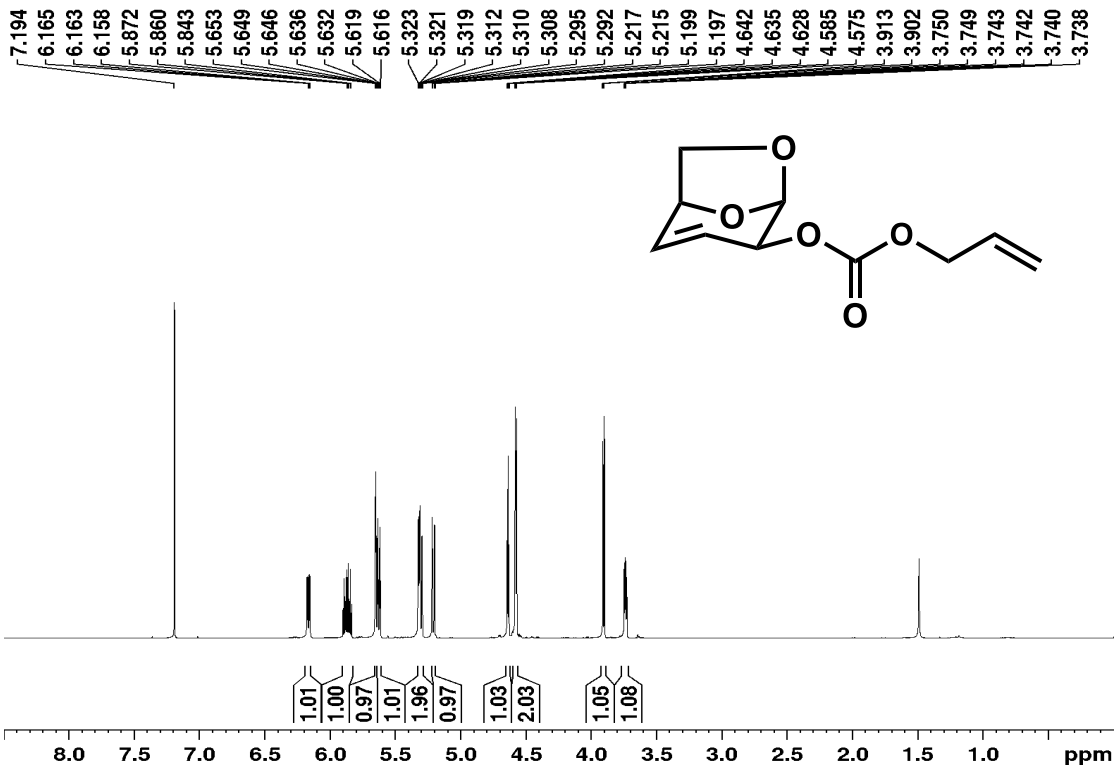


Fig. S17. ^{1}H NMR spectrum of Monomer **5** ($CDCl_3$, 600 MHz)

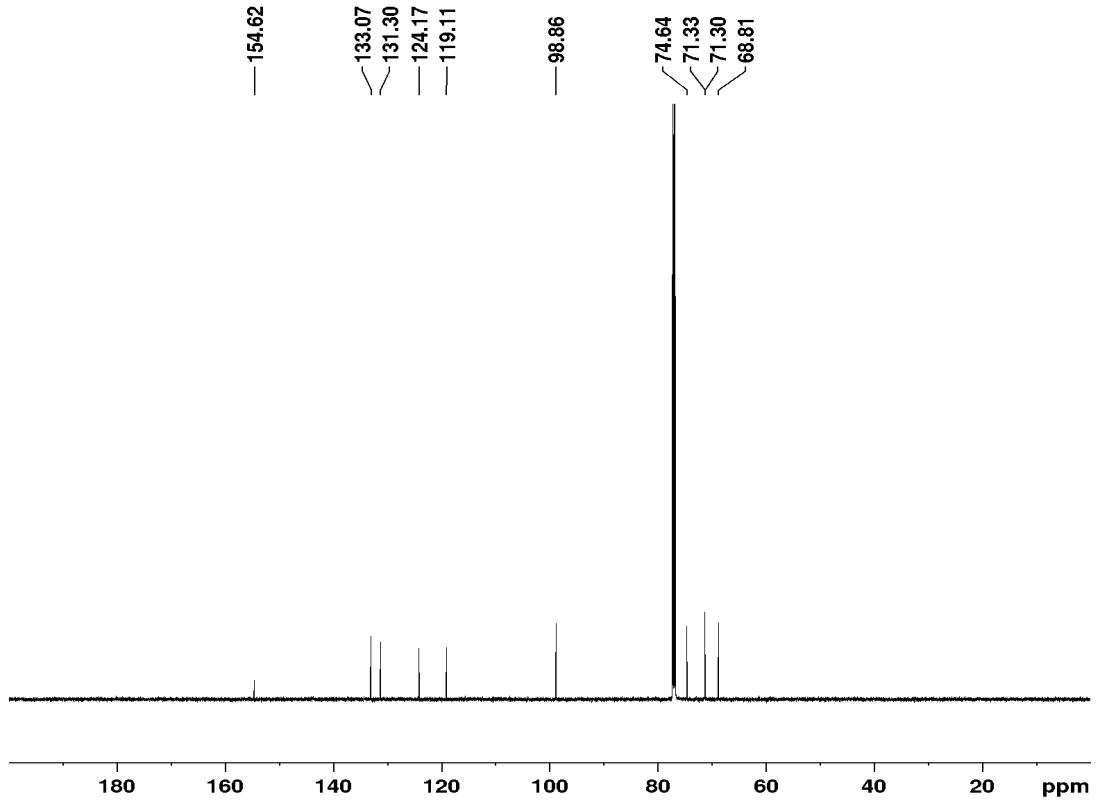


Fig. S18. ^{13}C NMR spectrum of Monomer **5** ($CDCl_3$, 150 MHz)

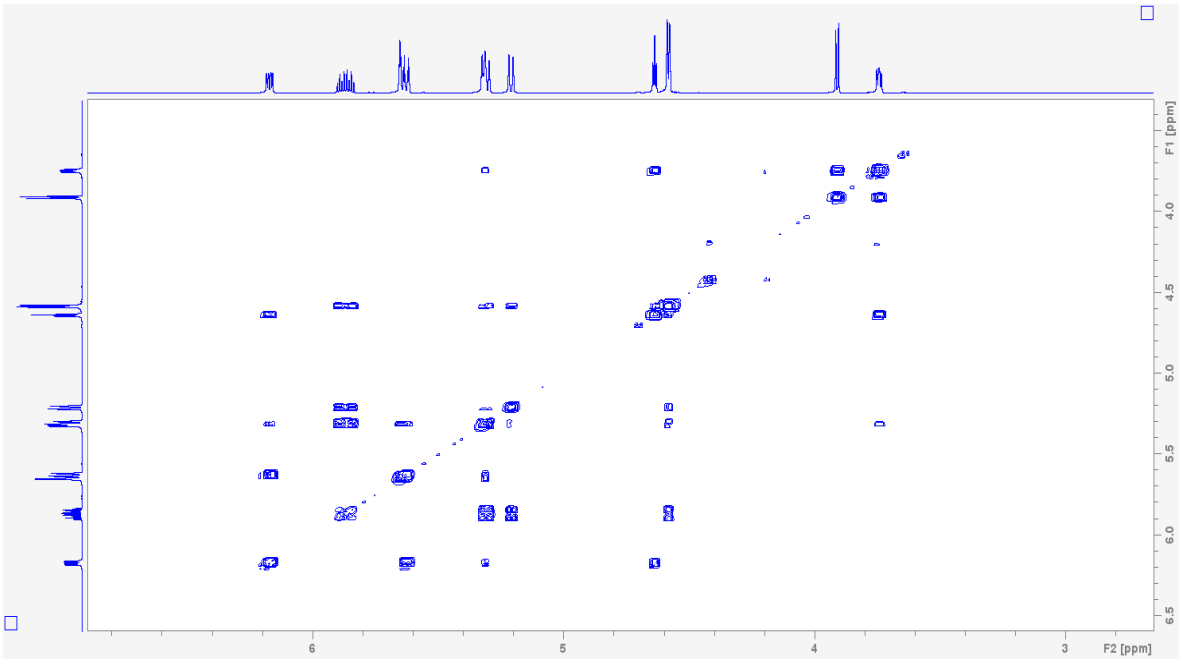


Fig. S19. COSY spectrum of monomer **5** ($CDCl_3$, 600 MHz)

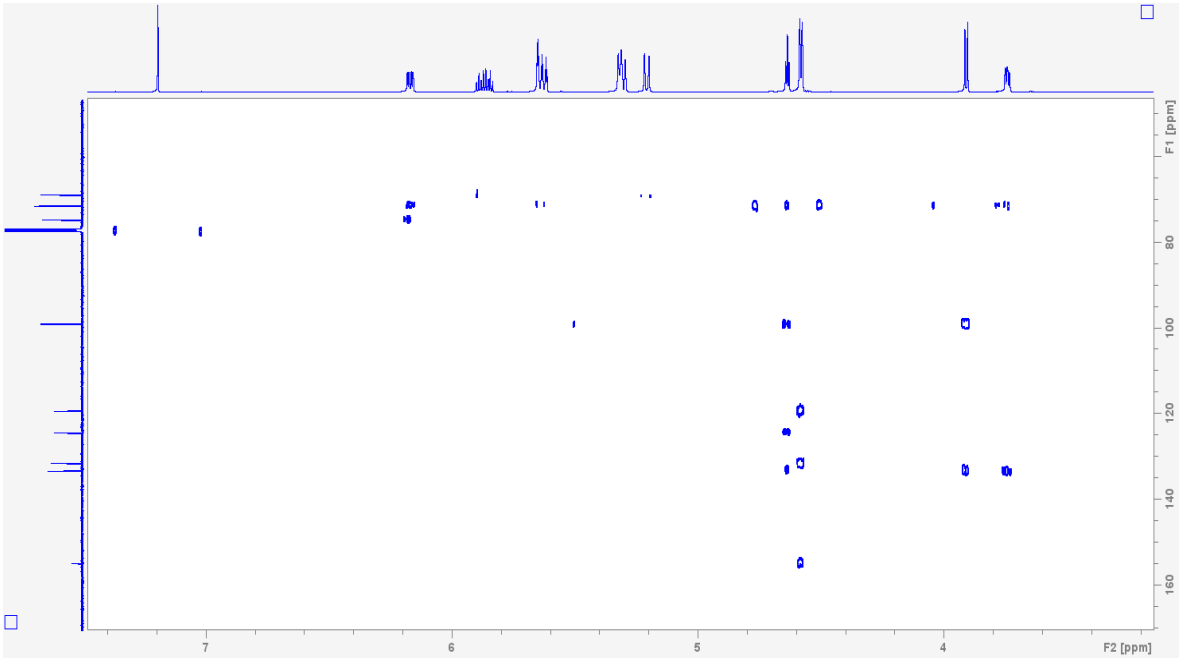


Fig. S20. HMBC spectrum of monomer **5** ($CDCl_3$, 600 MHz)

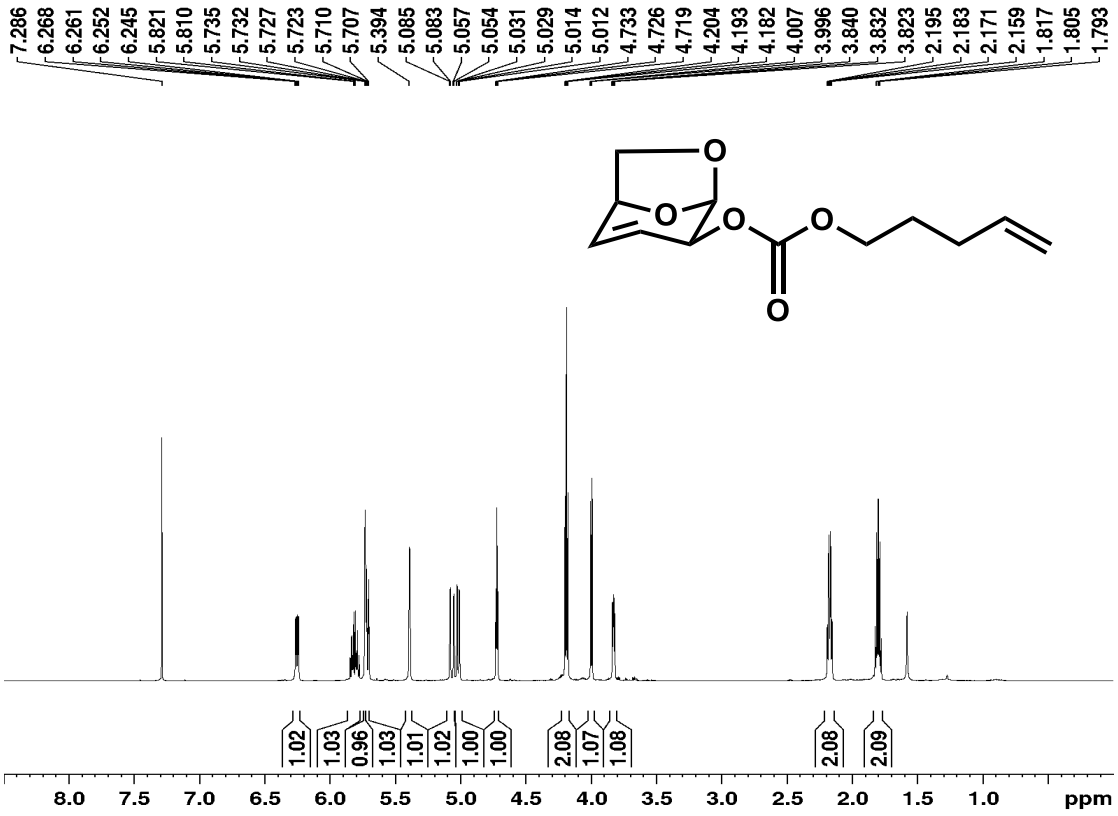


Fig. S21. ^{1}H NMR spectrum of Monomer **6** ($CDCl_3$, 600 MHz)

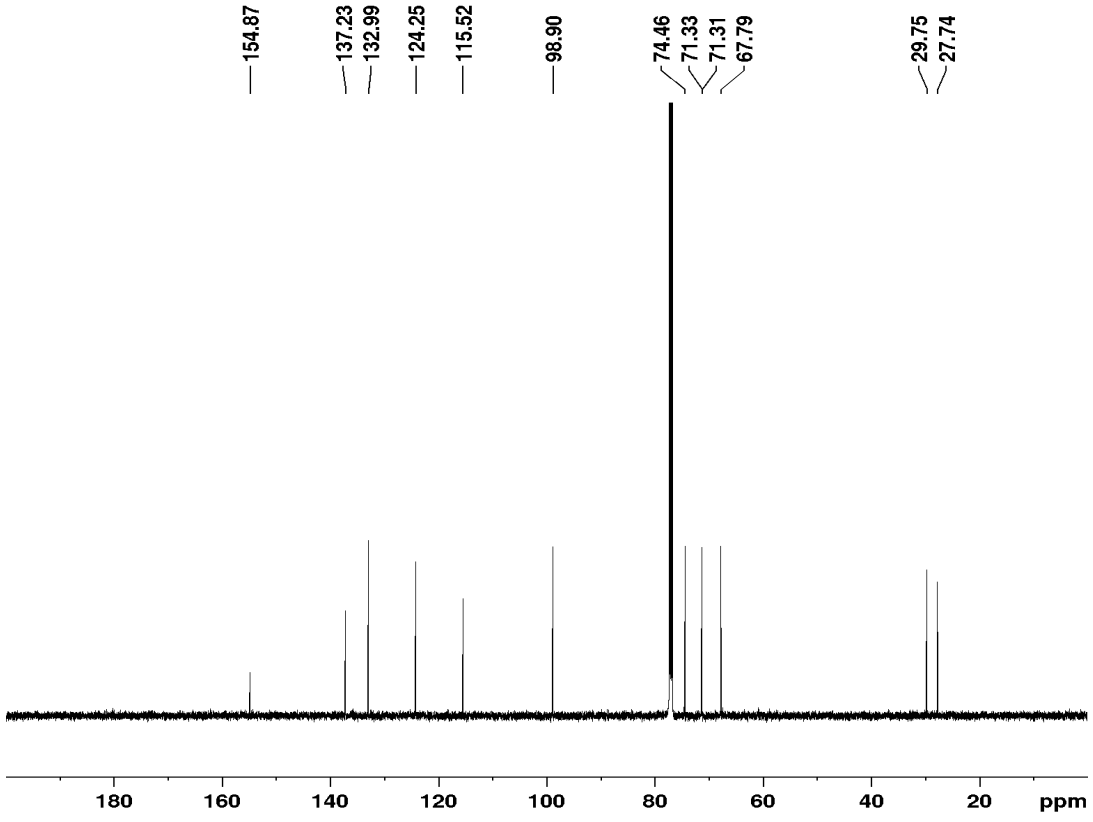


Fig. S22. ^{13}C NMR spectrum of Monomer **6** ($CDCl_3$, 150 MHz)

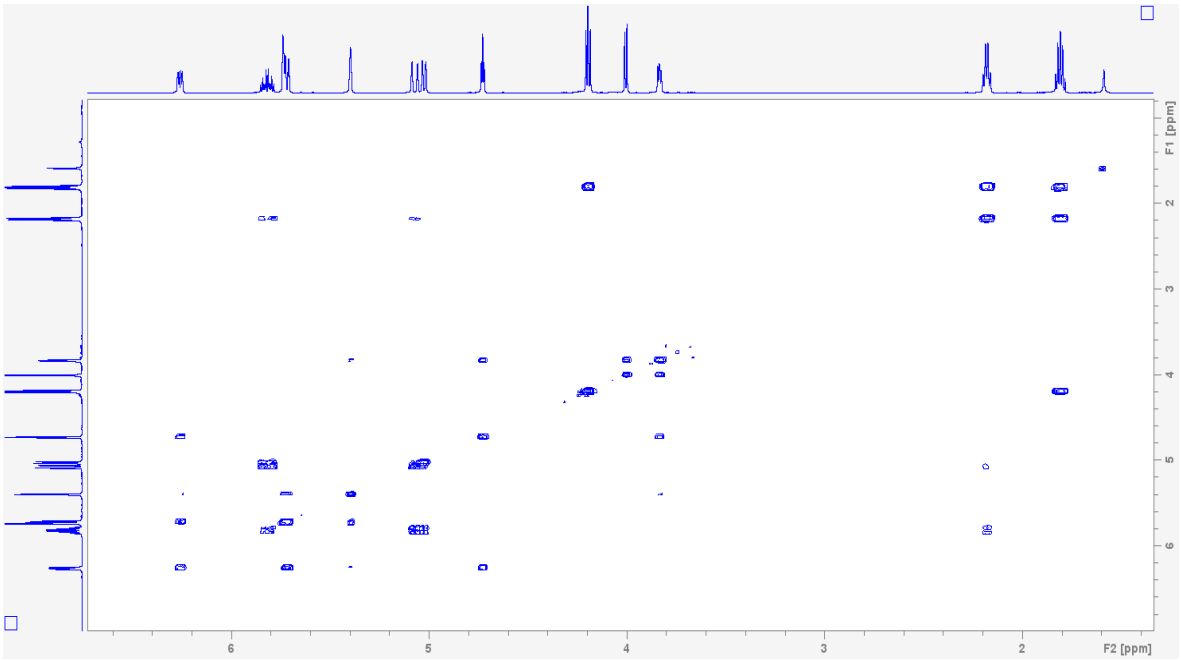


Fig. S23. COSY spectrum of monomer **6** ($CDCl_3$, 600 MHz)

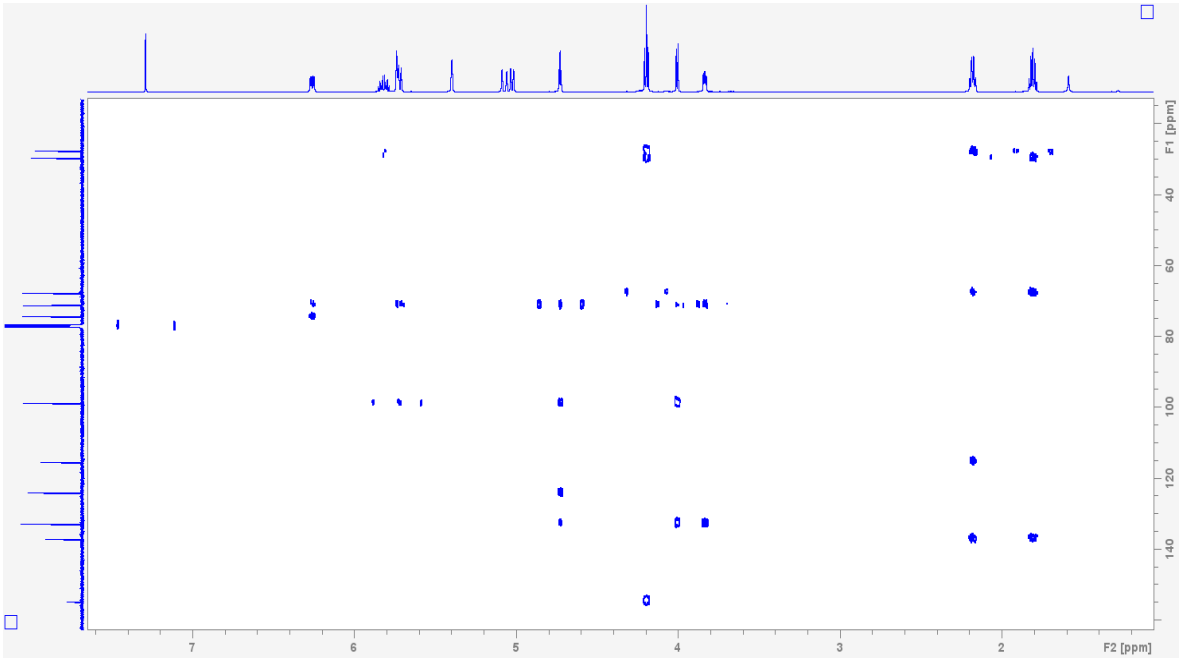


Fig. S24. HMBC spectrum of monomer **6** ($CDCl_3$, 600 MHz)

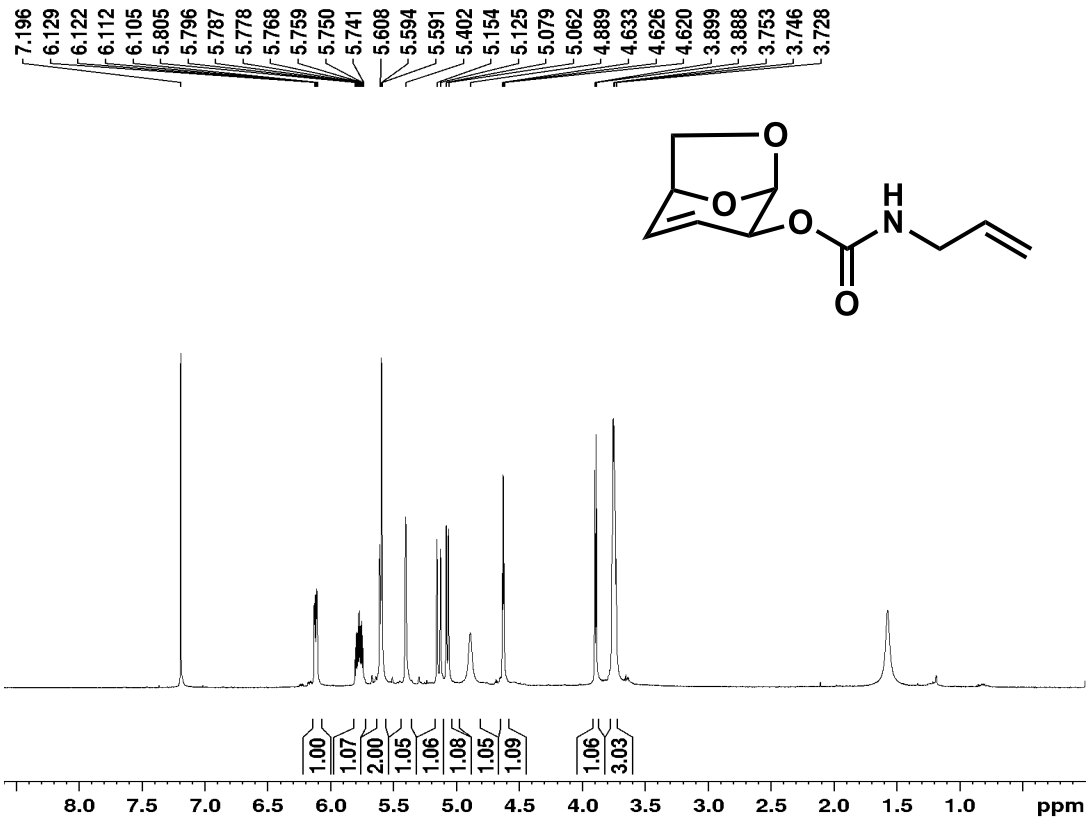


Fig. S25. ^{1}H NMR spectrum of Monomer **7** ($CDCl_3$, 600 MHz)

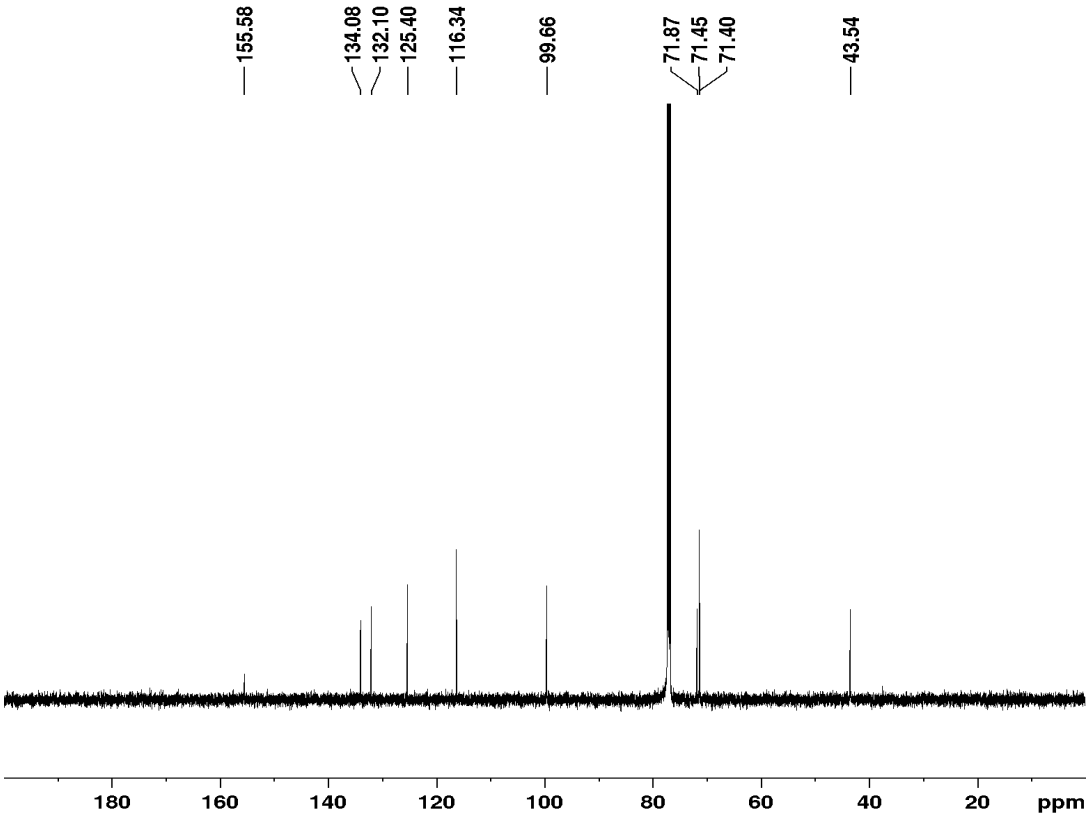


Fig. S26. ^{13}C NMR spectrum of Monomer **7** ($CDCl_3$, 150 MHz)

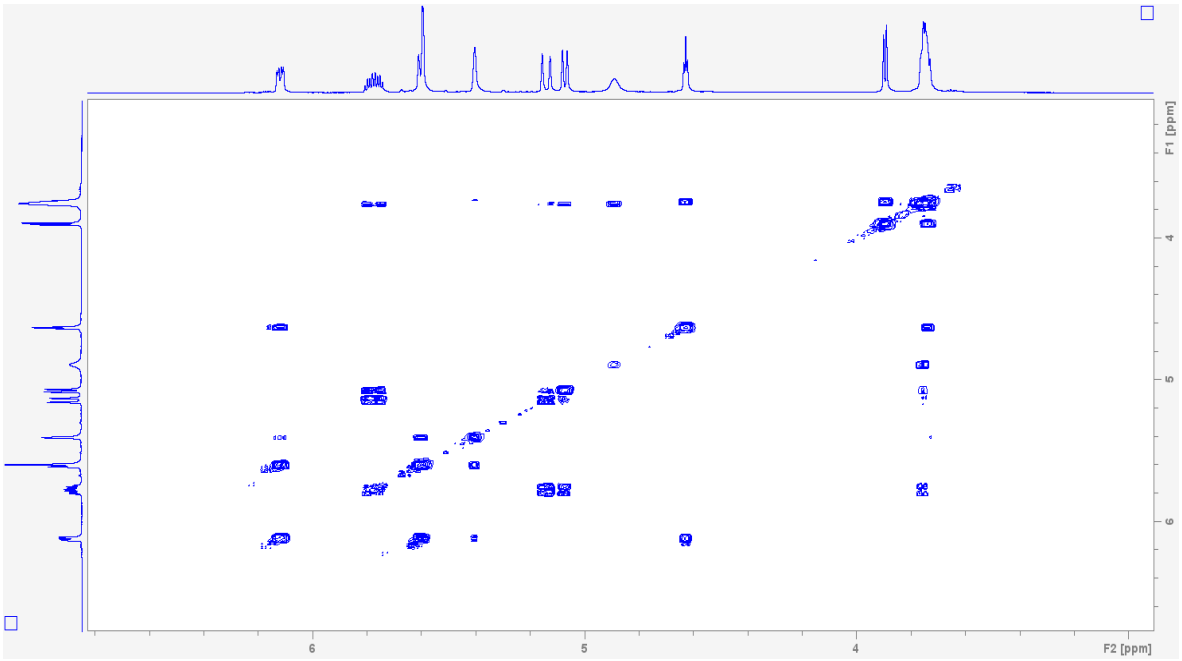


Fig. S27. COSY spectrum of monomer **7** ($CDCl_3$, 600 MHz)

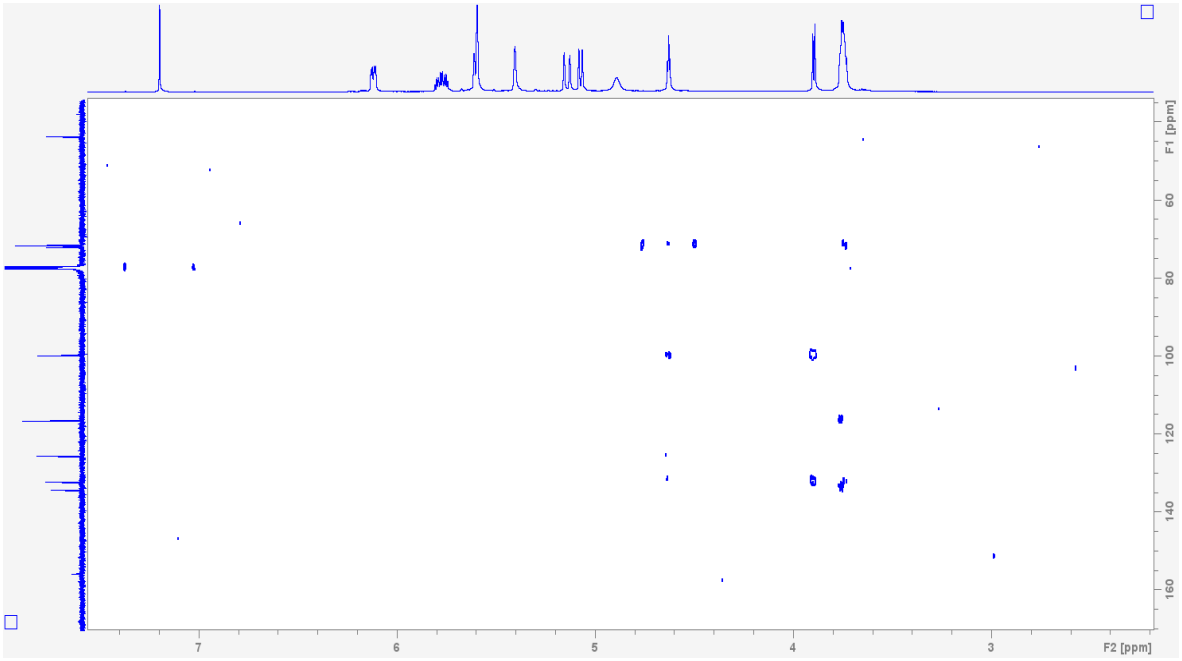


Fig. S28. HMBC spectrum of monomer **7** ($CDCl_3$, 600 MHz)

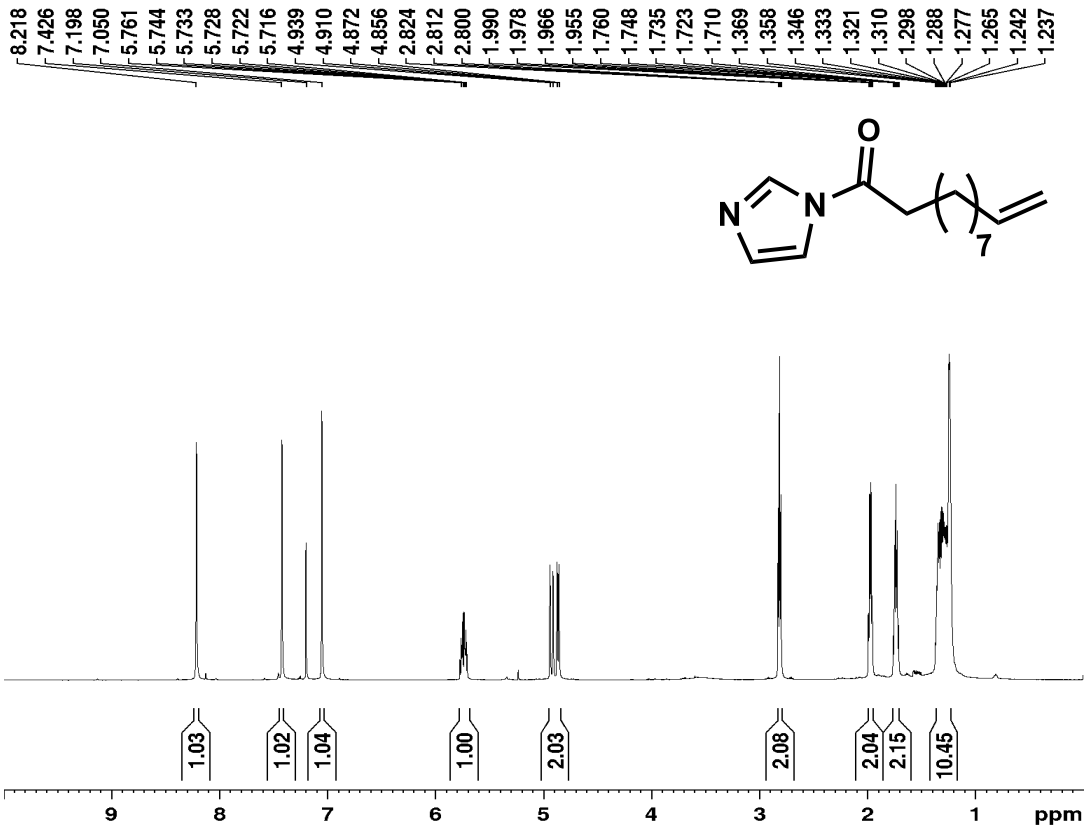


Fig. S29. ^{1}H NMR spectrum of crude intermediate ***a*** ($CDCl_3$, 600 MHz)

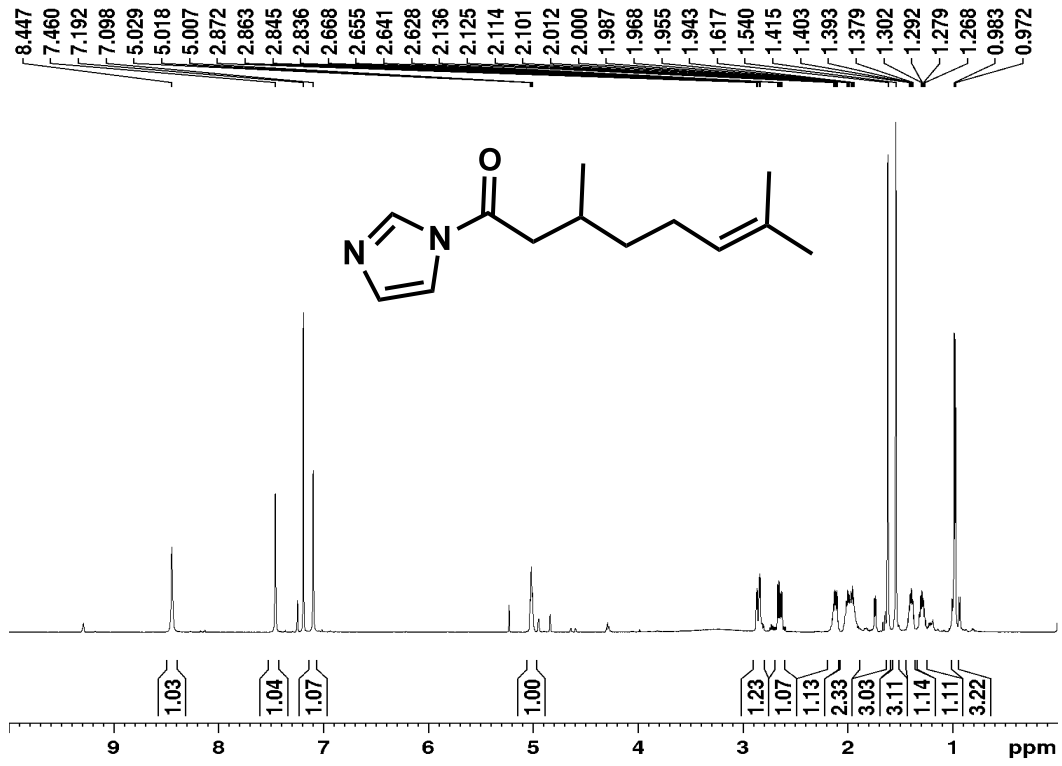


Fig. S30. ^{1}H NMR spectrum of crude intermediate ***b*** ($CDCl_3$, 600 MHz)

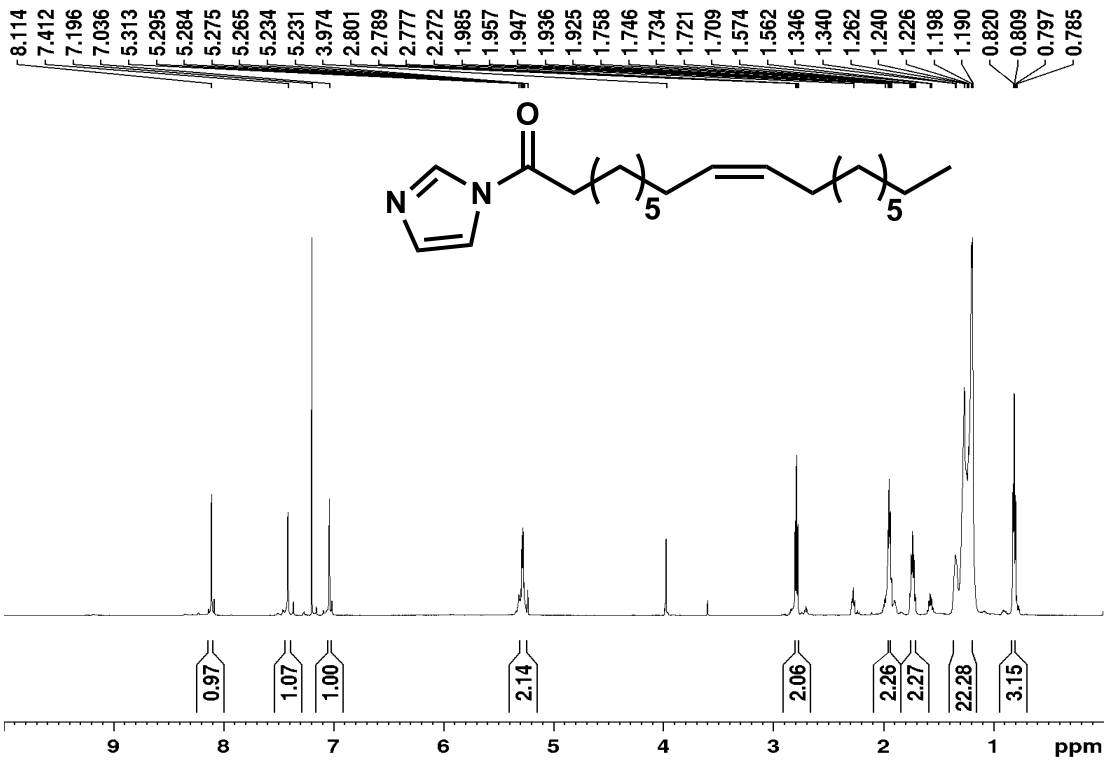


Fig. S31. ^{1}H NMR spectrum of crude intermediate ***c*** ($CDCl_3$, 600 MHz)

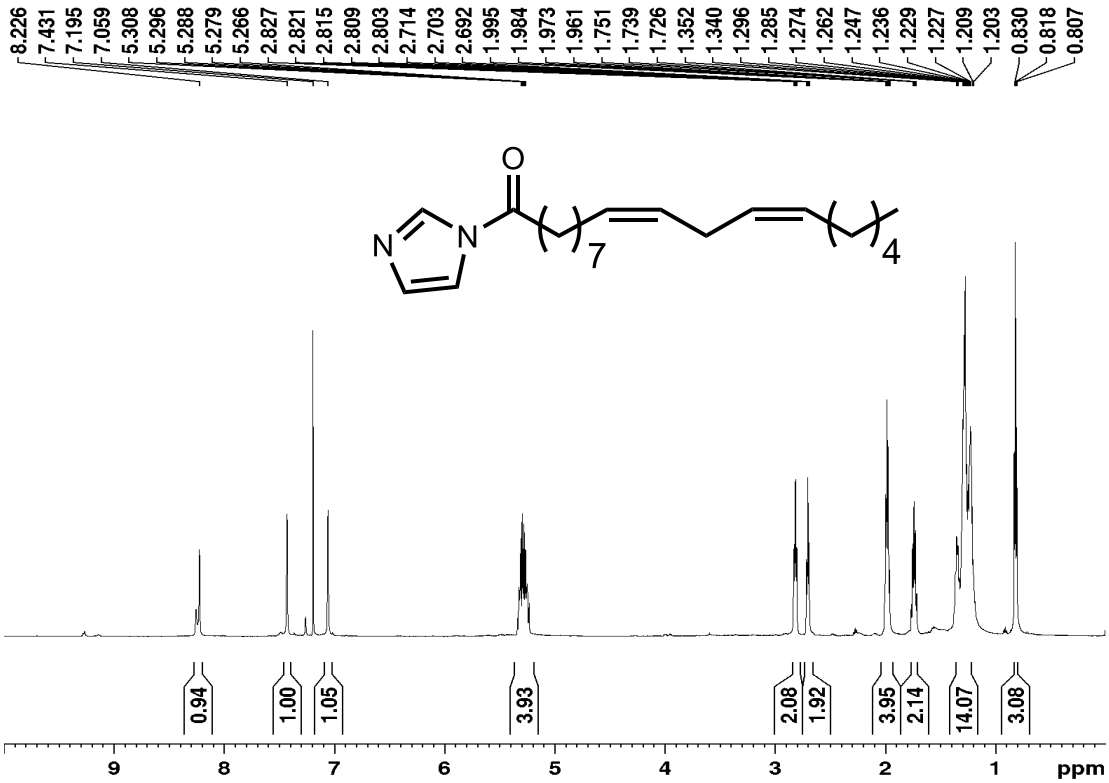


Fig. S32. ^{1}H NMR spectrum of crude intermediate ***d*** ($CDCl_3$, 600 MHz)

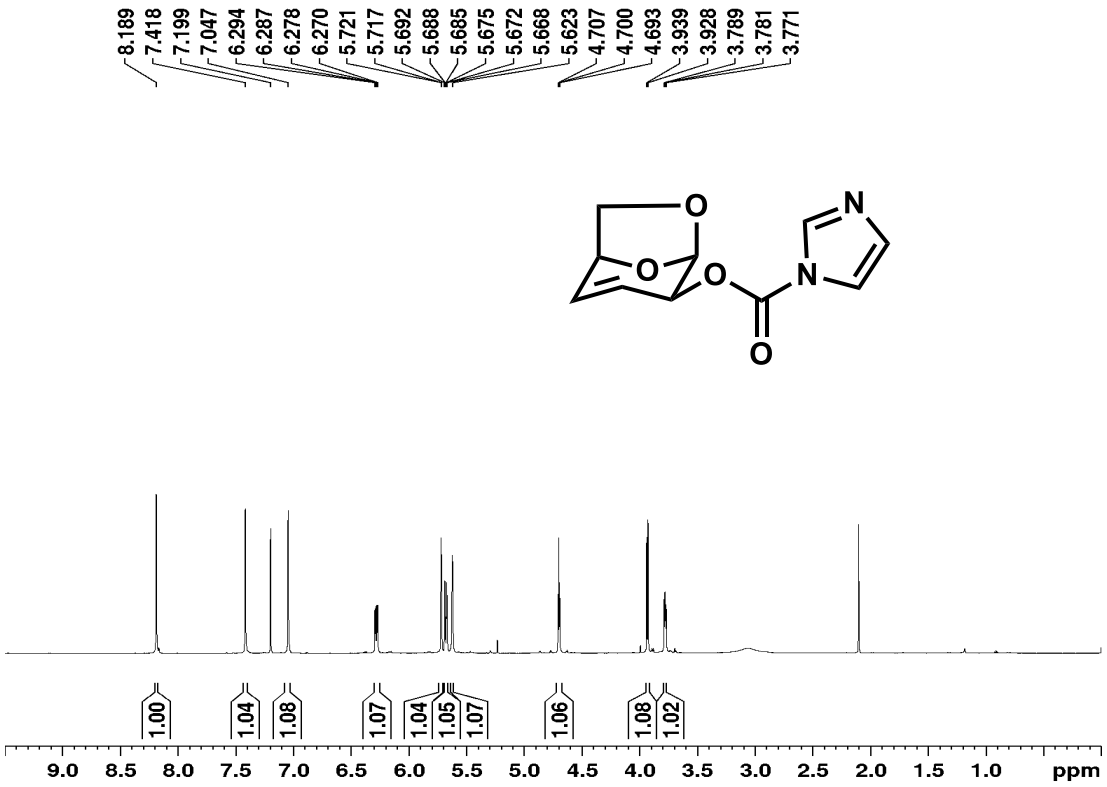


Fig. S33. ^{1}H NMR spectrum of levoglucosenone and CDI intermediate ($CDCl_3$, 600 MHz)

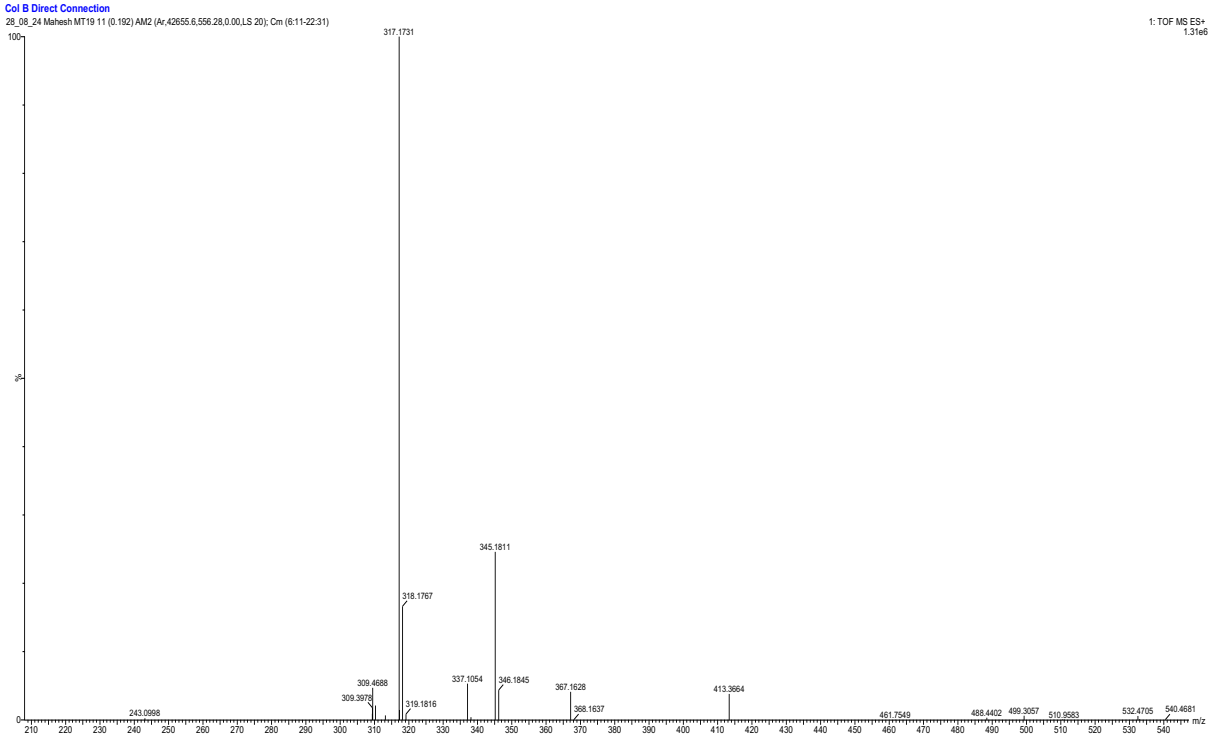


Fig. S34. MS of monomer **1**.

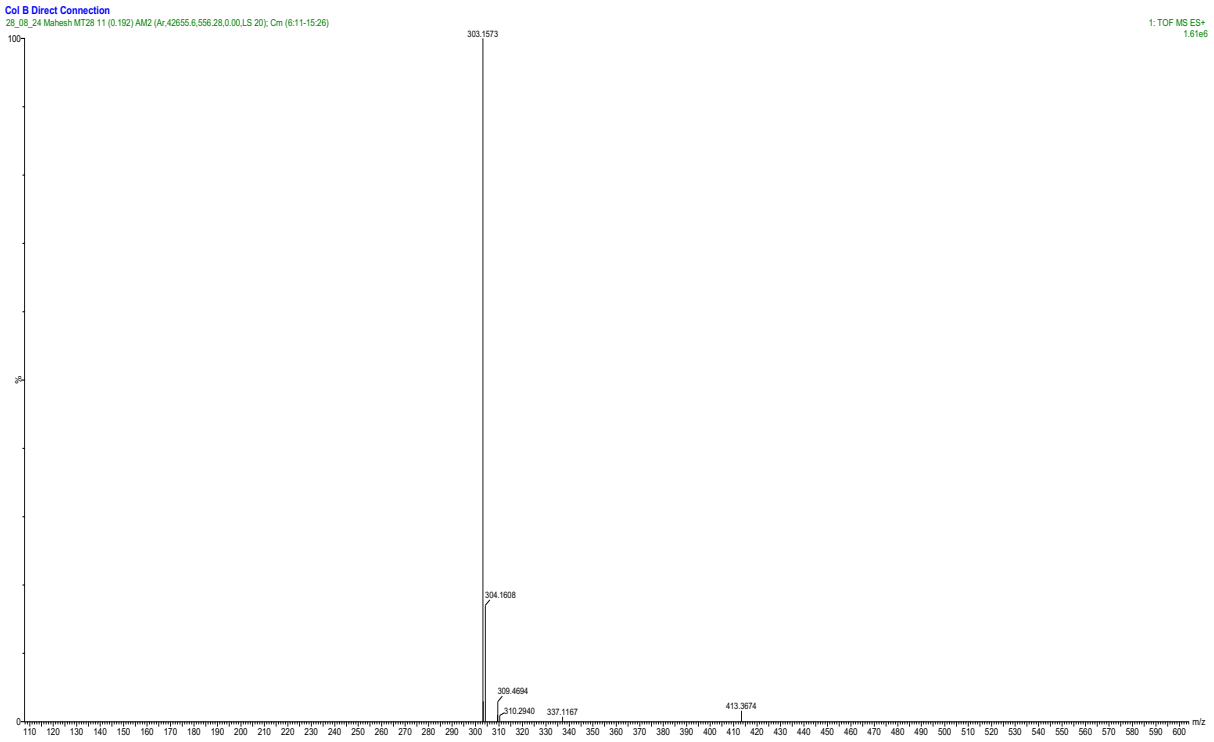


Fig. S35. MS of monomer **2**.

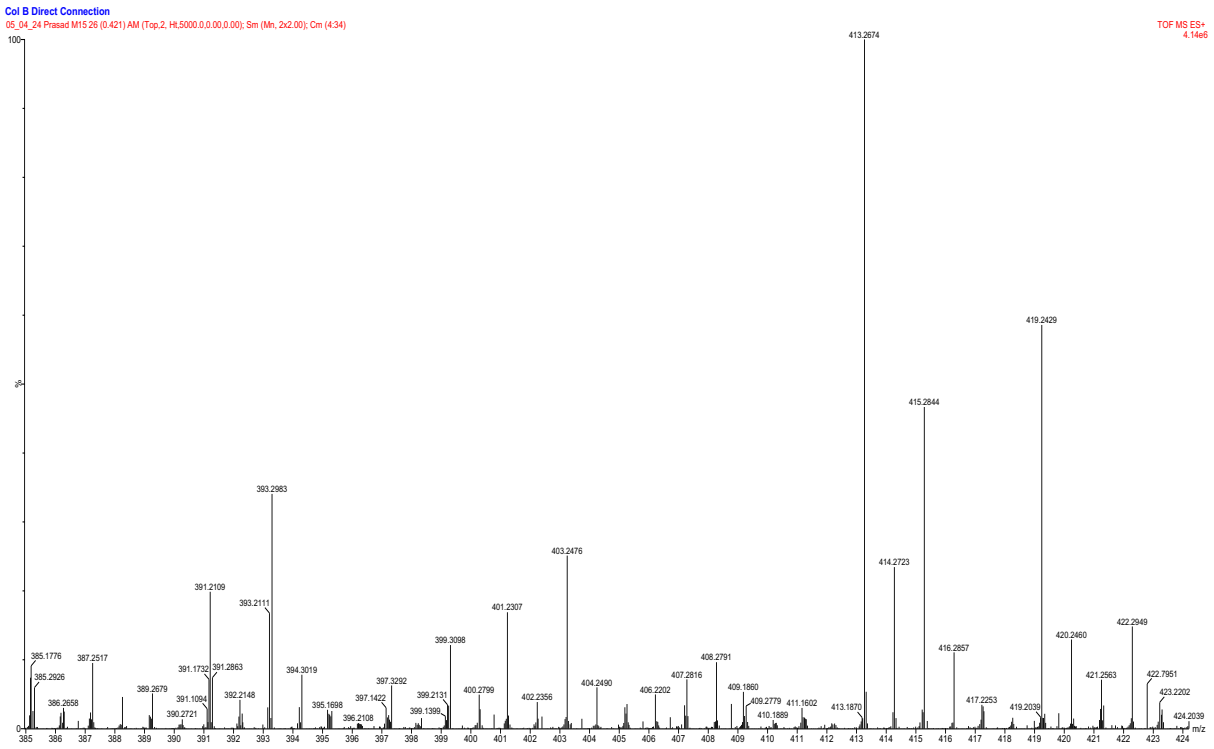


Fig. S36. MS of monomer **3**.

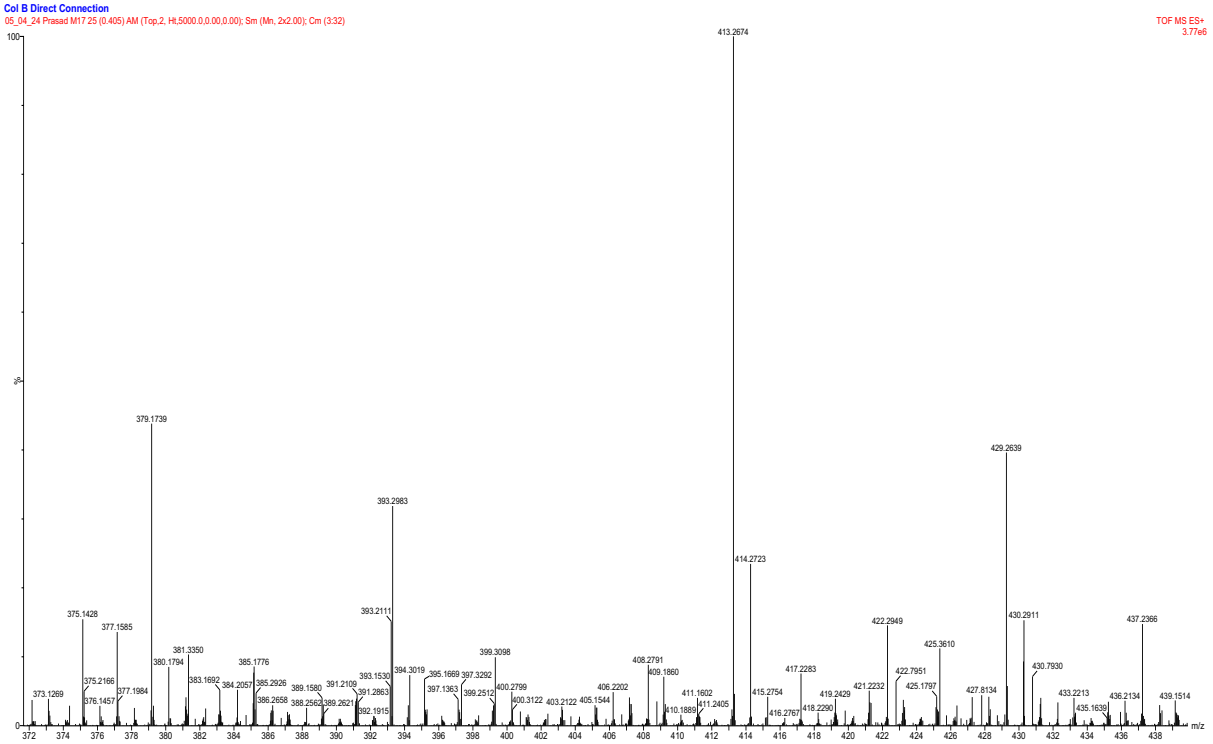


Fig. S37. MS of monomer **4**.

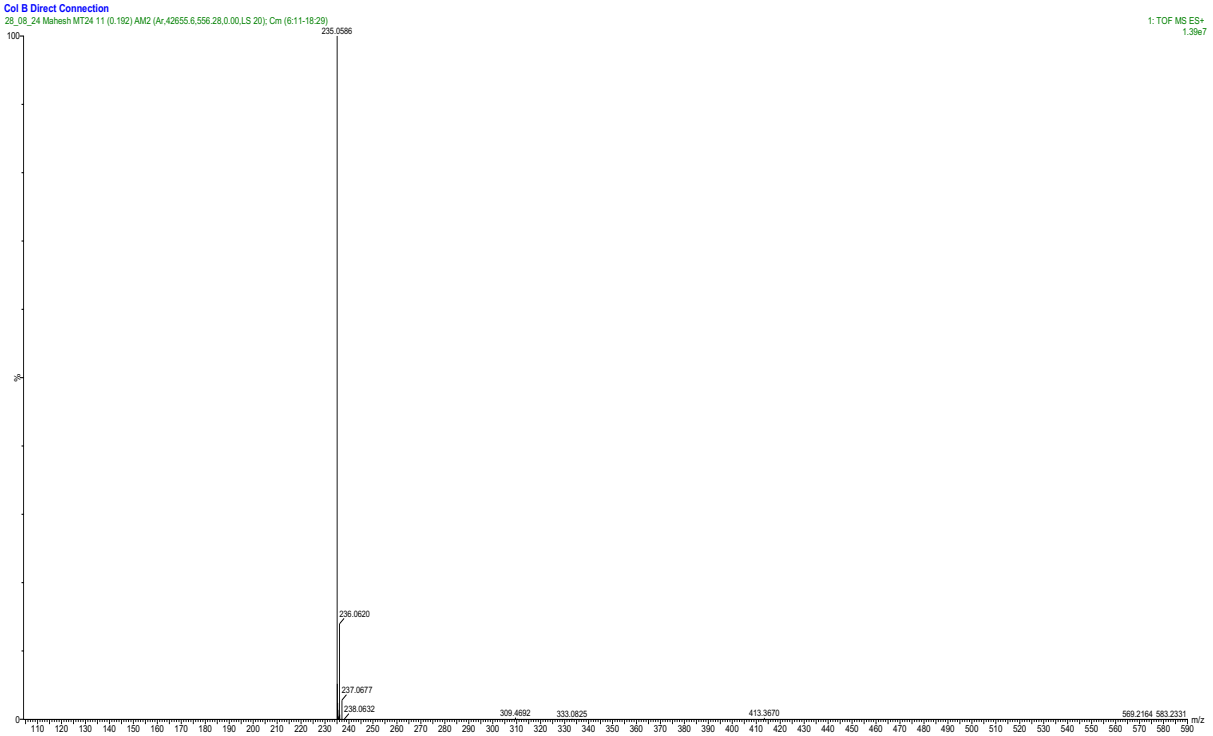


Fig. S38. MS of monomer **5**.

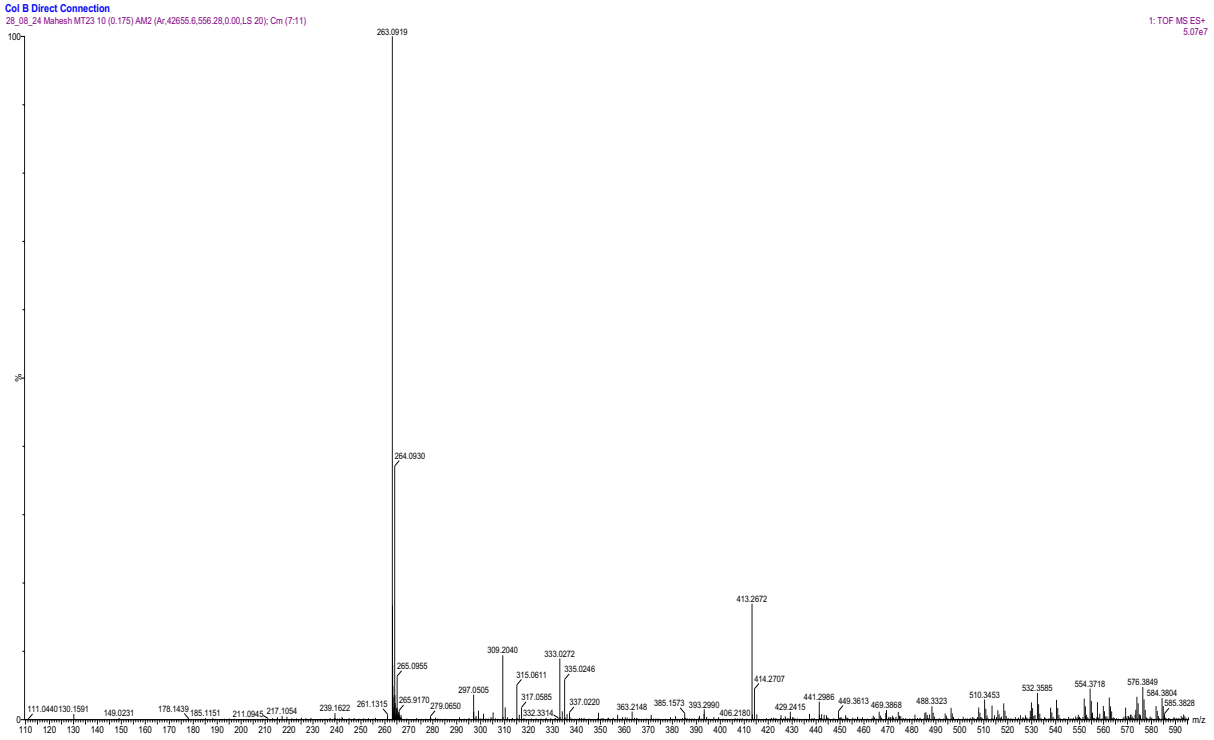


Fig. S39. MS of monomer **6**.

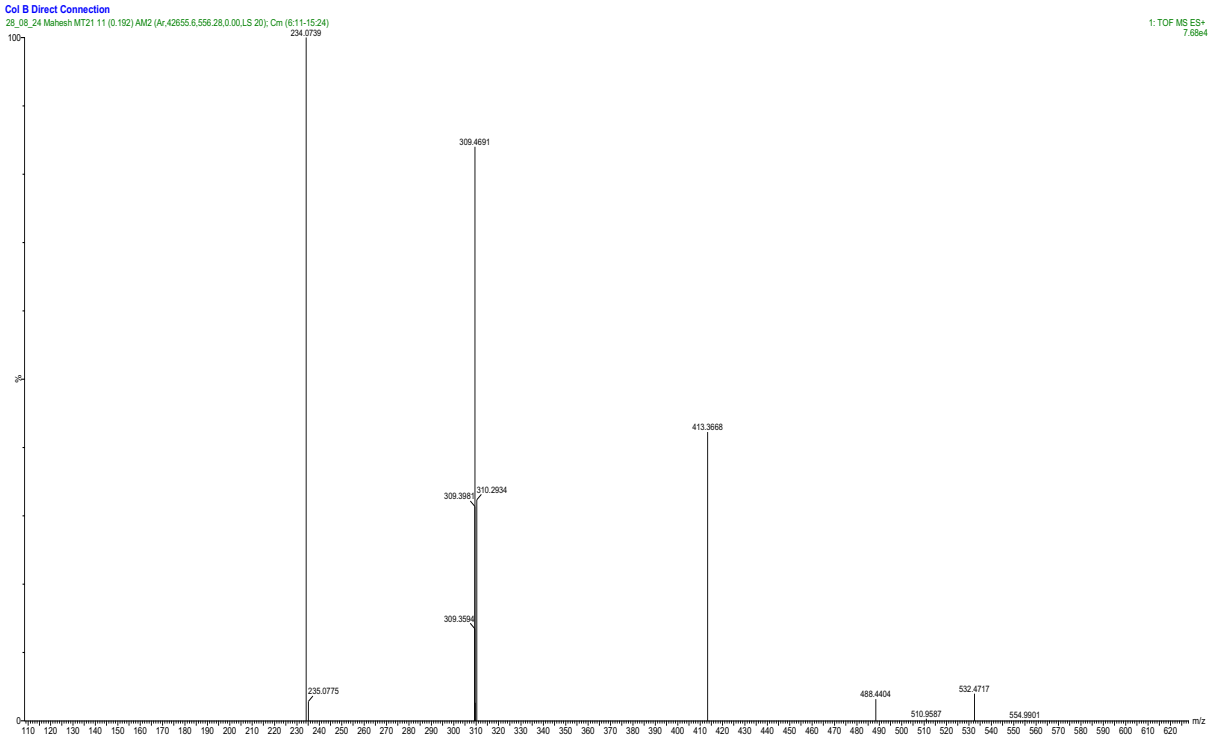


Fig. S40. MS of monomer **7**.

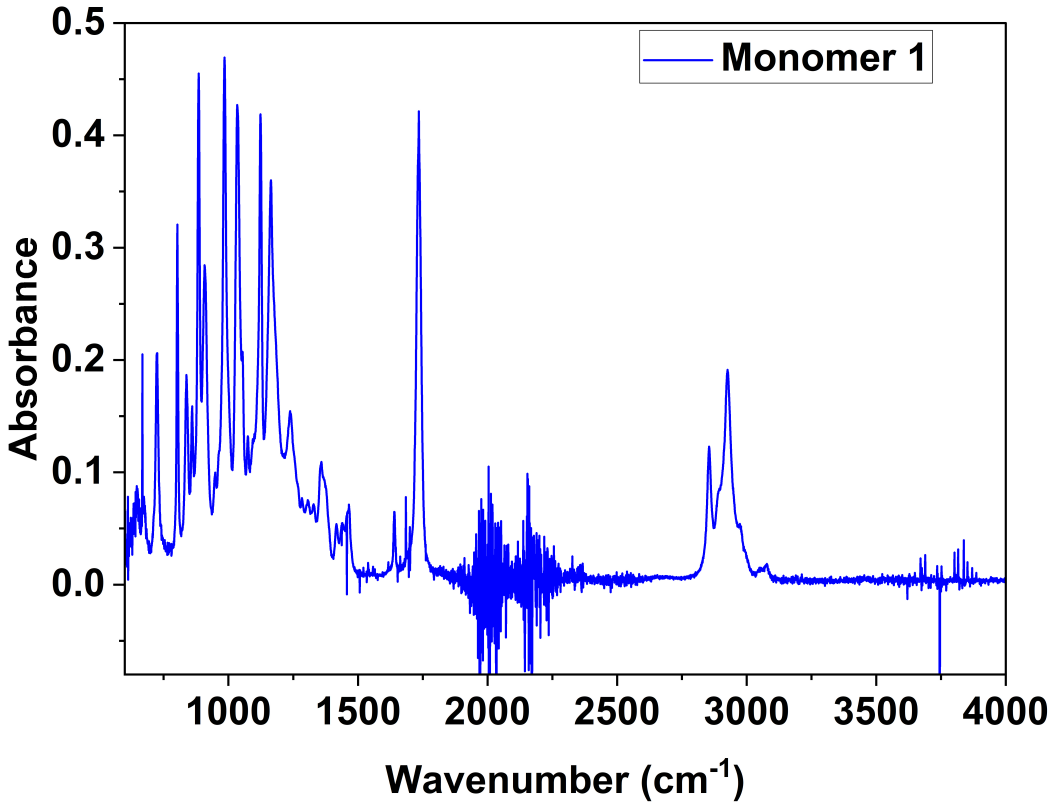


Fig. S41. FTIR of monomer **1**.

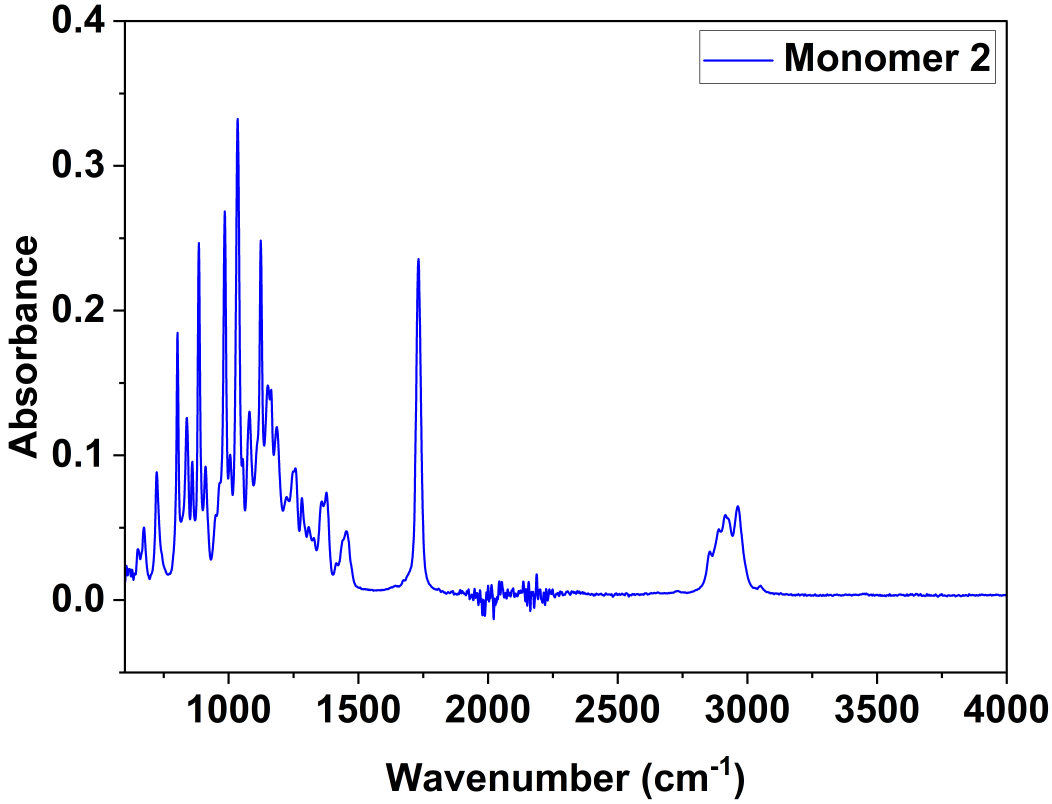


Fig. S42. FTIR of monomer **2.**

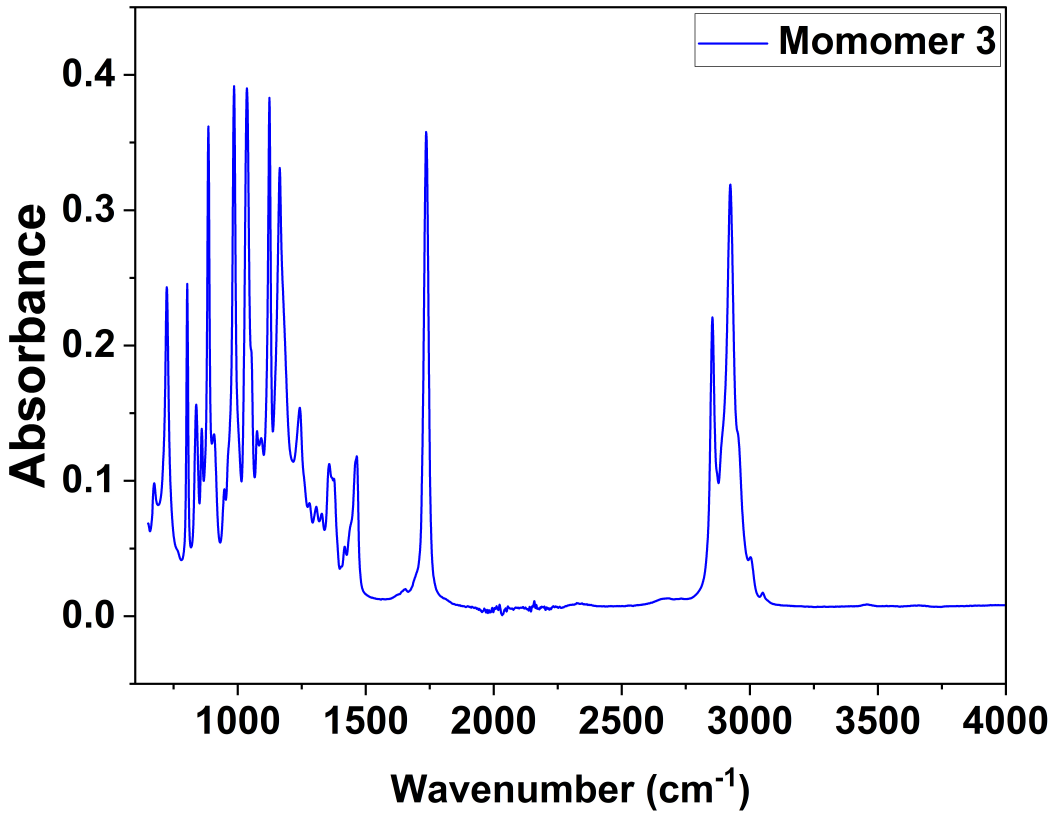


Fig. S43. FTIR of monomer **3.**

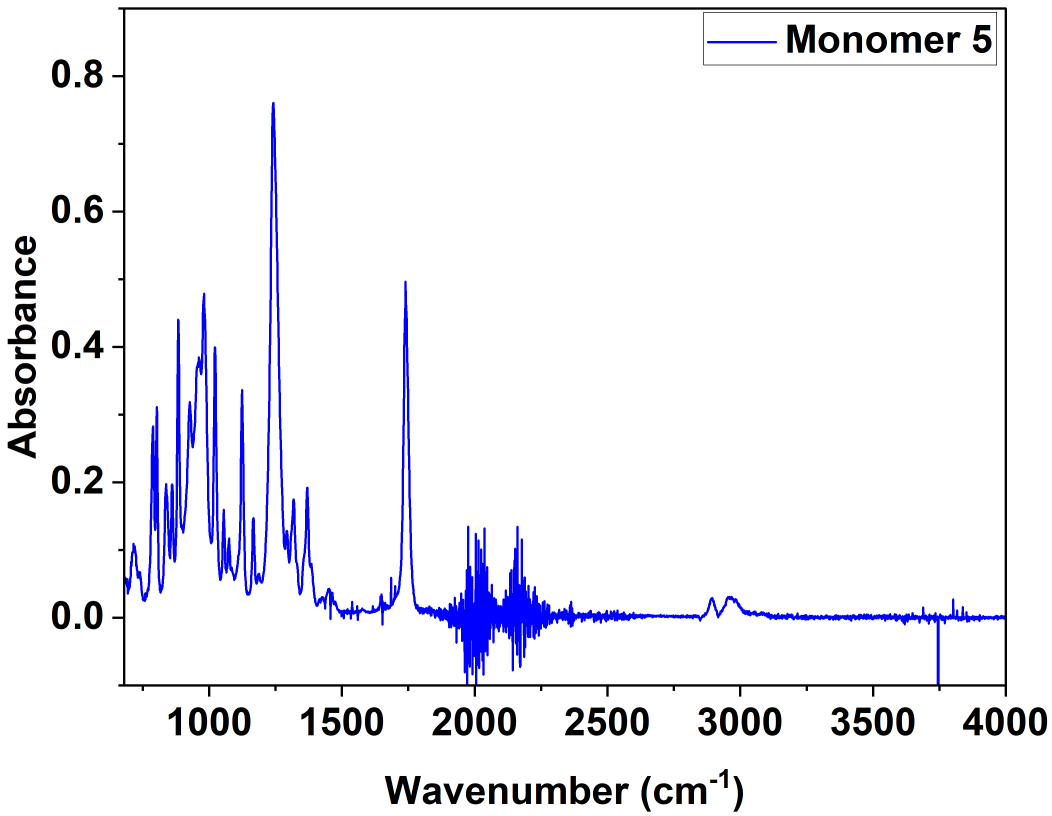


Fig. S44. FTIR of monomer **5.**

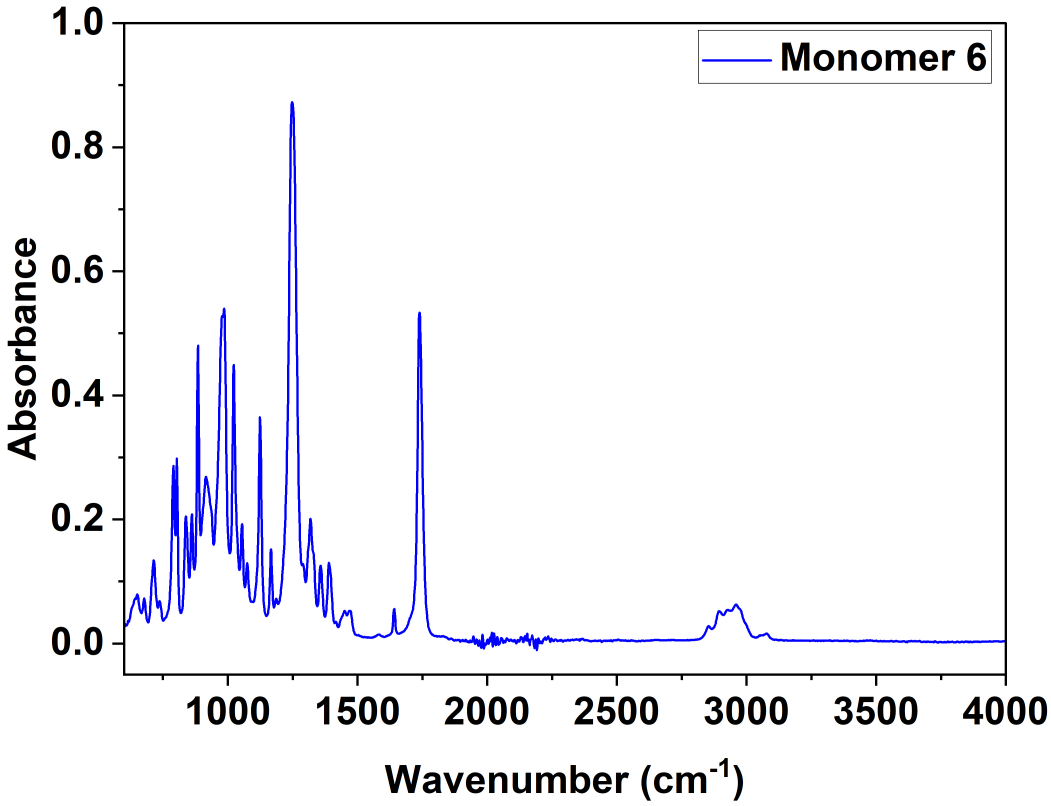


Fig. S45. FTIR of monomer **6.**

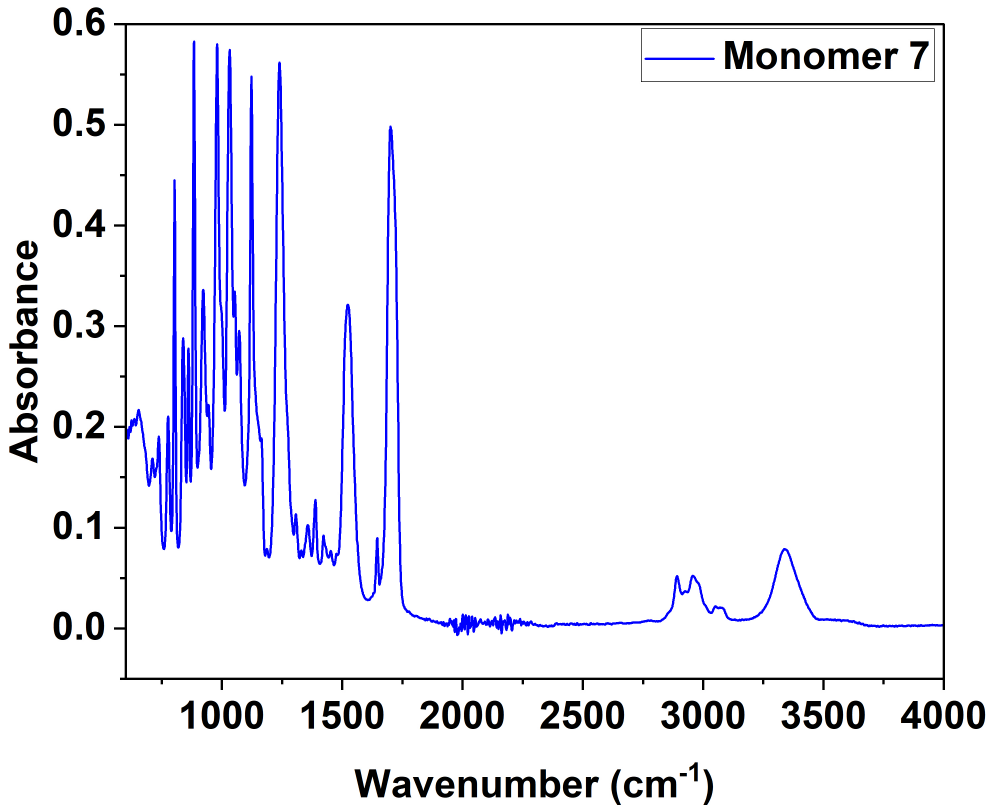


Fig. S46. FTIR of monomer **7.**

Table S1. Preparation of thiol-ene networks.

Monomer	[SH]:[C=C]	Photoinitiator (DPO) (%)	Cure time (s)	Polymer code
1	1:2	0.2	60	Poly(1-co-4SH)
2	1:2	0.2	60	Poly(2-co-4SH)
3	1:2	0.5	480	Poly(3-co-4SH)
5	1:2	0.2	60	Poly(5-co-4SH)
6	1:2	0.2	60	Poly(6-co-4SH)
7	1:2	0.2	60	Poly(7-co-4SH)

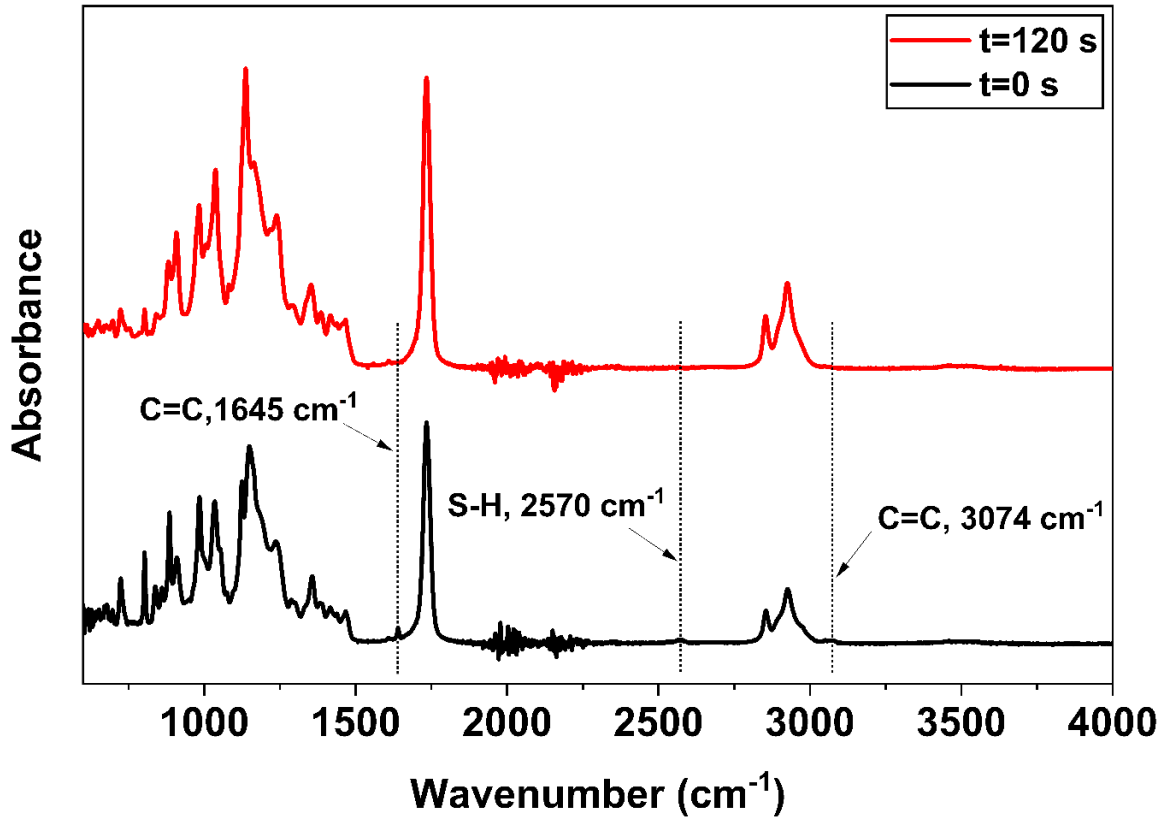


Fig. S47. FTIR of Poly(1-co-4SH) at 0 sec (before UV irradiation) and at 120 sec (after UV irradiation).

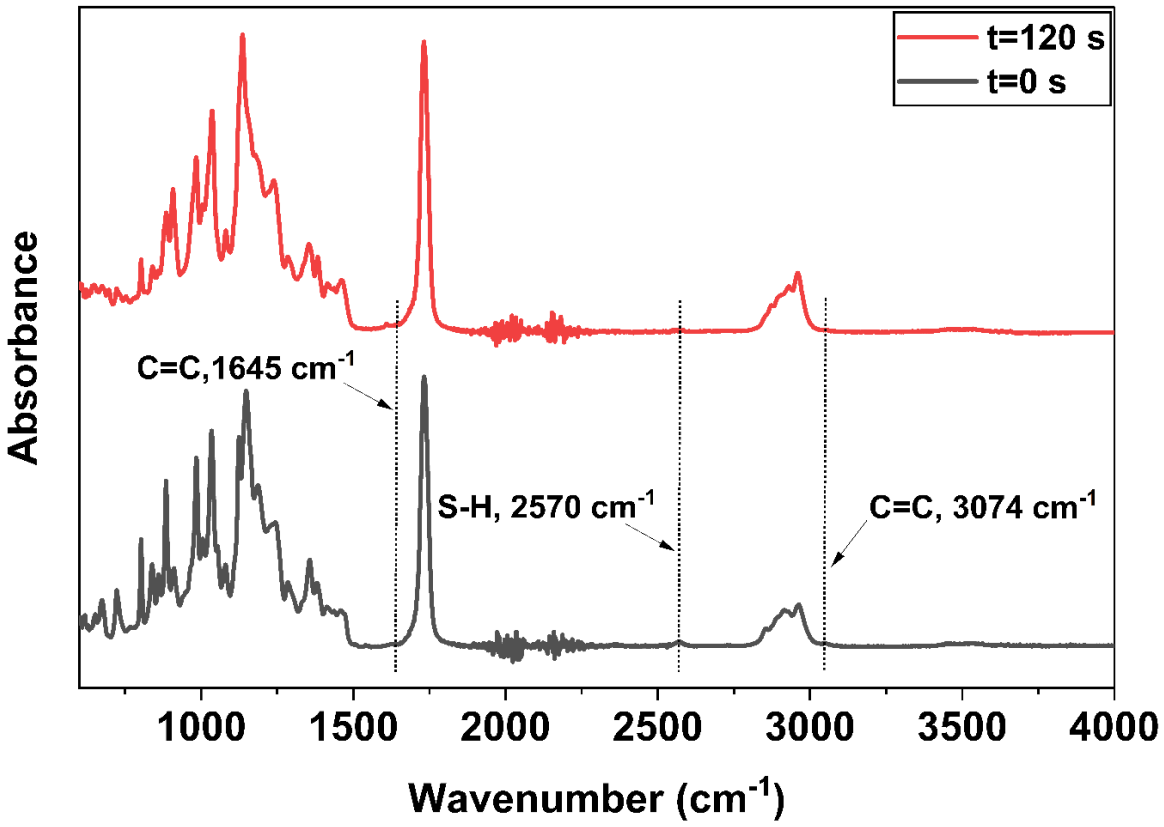


Fig. S48. FTIR of Poly(2-co-4SH) at 0 sec (before UV irradiation) and at 120 sec (after UV irradiation).

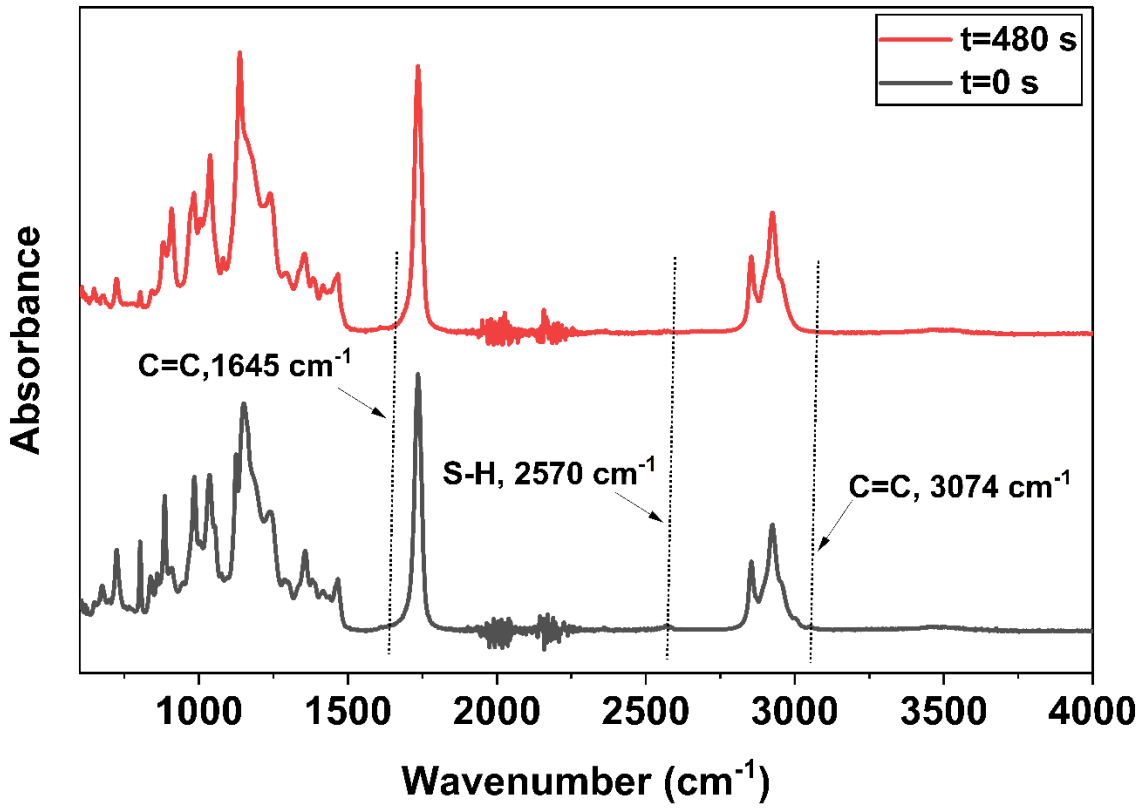


Fig. S49. FTIR of Poly(3-co-4SH) at 0 sec (before UV irradiation) and at 120 sec (after UV irradiation).

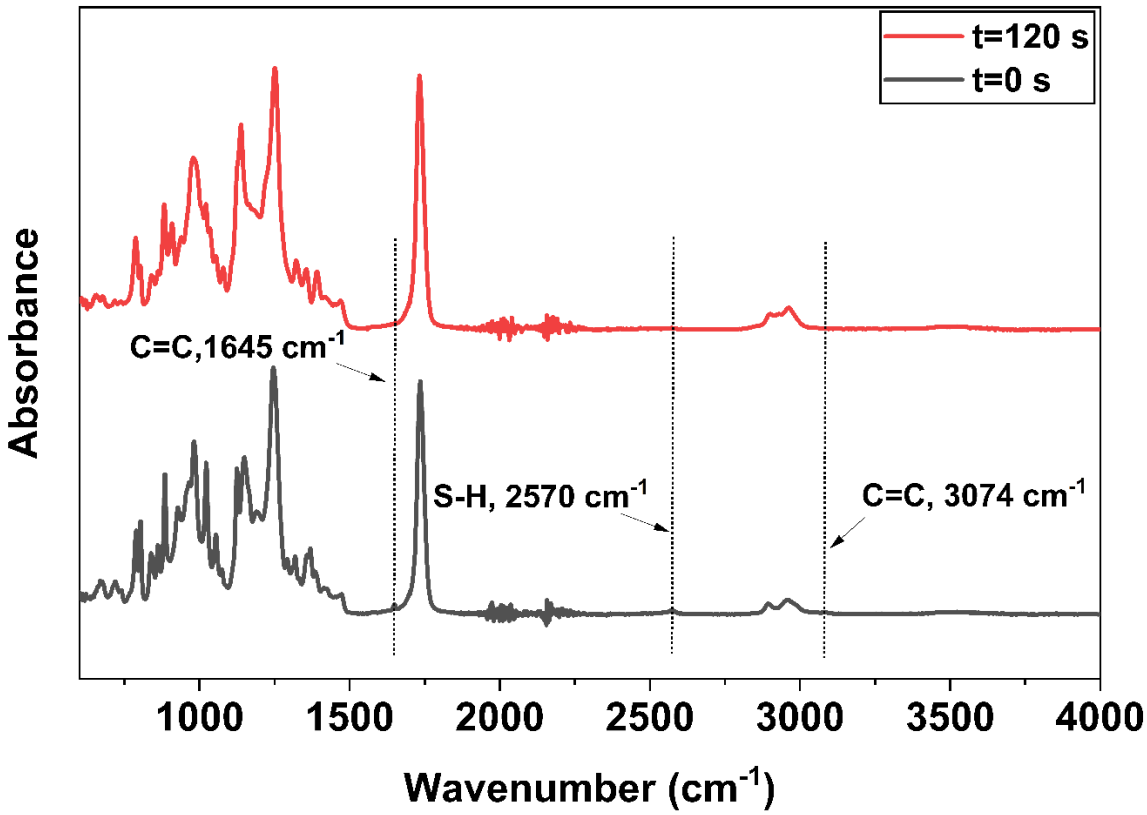


Fig. S50. FTIR of Poly(5-co-4SH) at 0 sec (before UV irradiation) and at 120 sec (after UV irradiation).

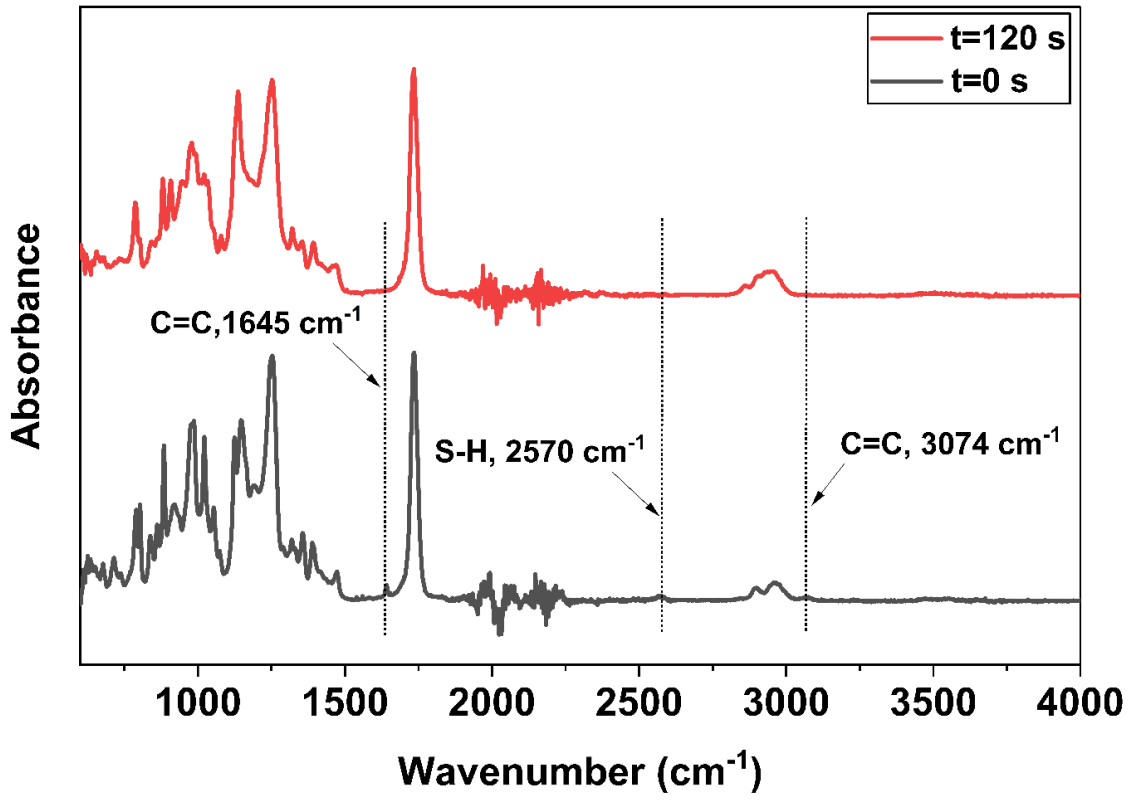


Fig. S51. FTIR of Poly(6-co-4SH) at 0 sec (before UV irradiation) and at 120 sec (after UV irradiation).

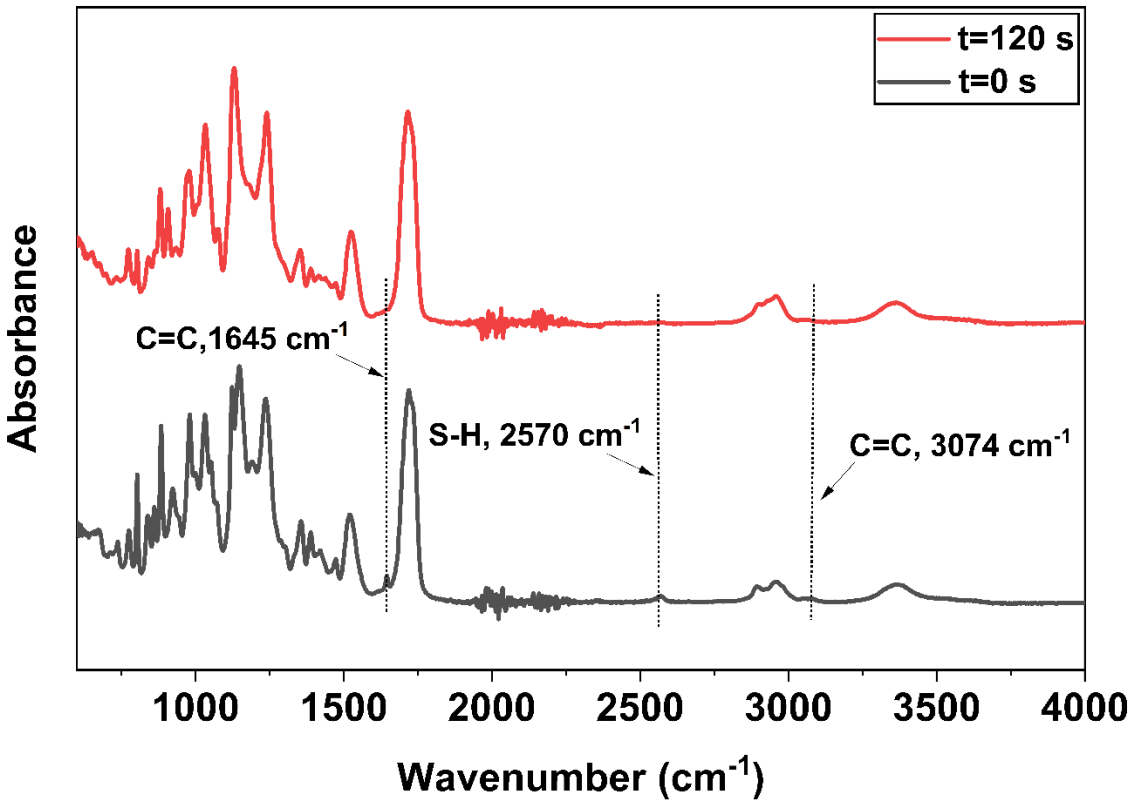


Fig. S52. FTIR of Poly(6-co-4SH) at 0 sec (before UV irradiation) and at 120 sec (after UV irradiation).

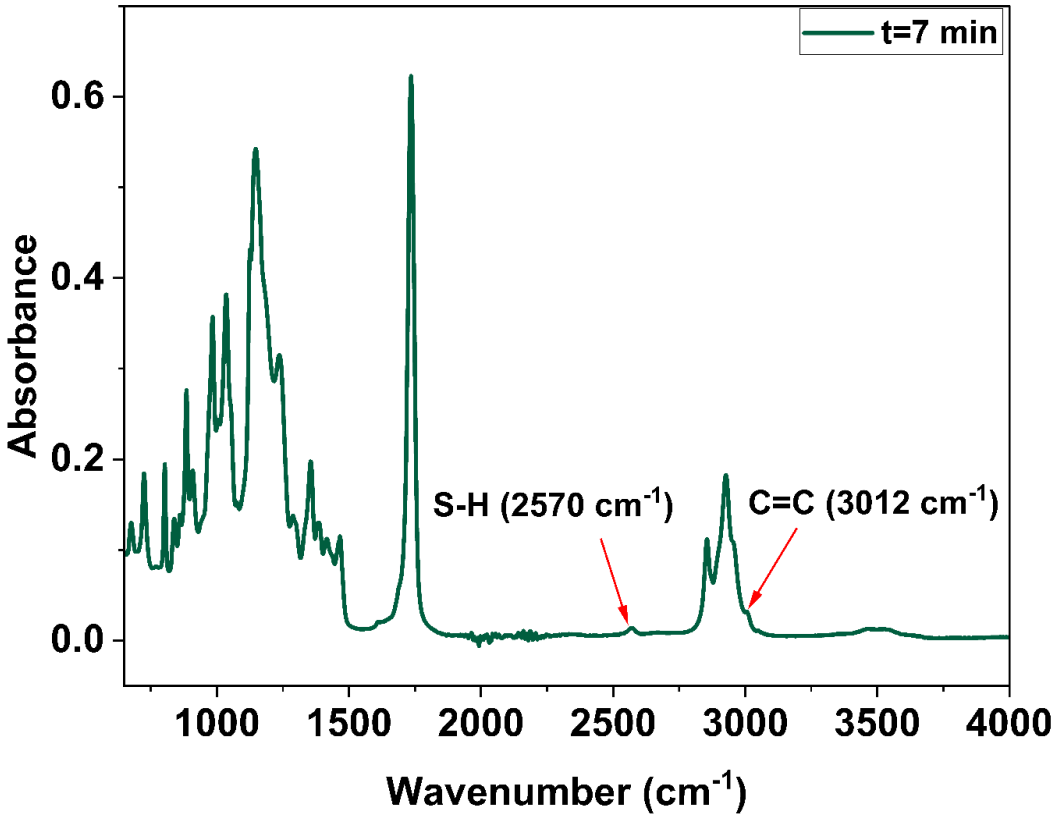


Fig. S53. FTIR of polymerization check (UV cured for 7 minutes) of monomer **4** with tetra-thiol (4SH).

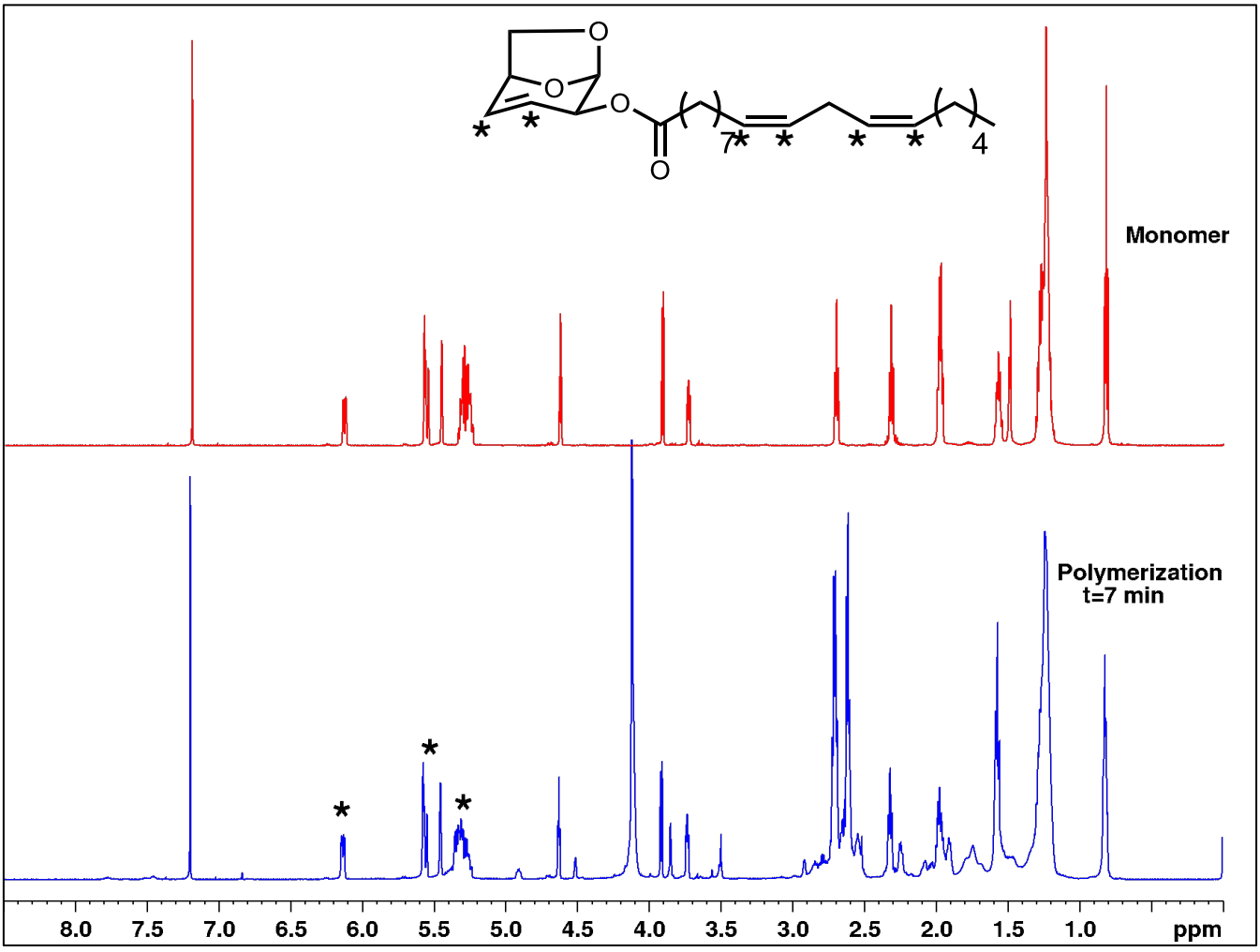


Fig. S54. Comparison of ^{1}H NMR spectrum of Monomer **4** and polymerization check (after UV cured for 7 min) ($CDCl_3$, 600 MHz).

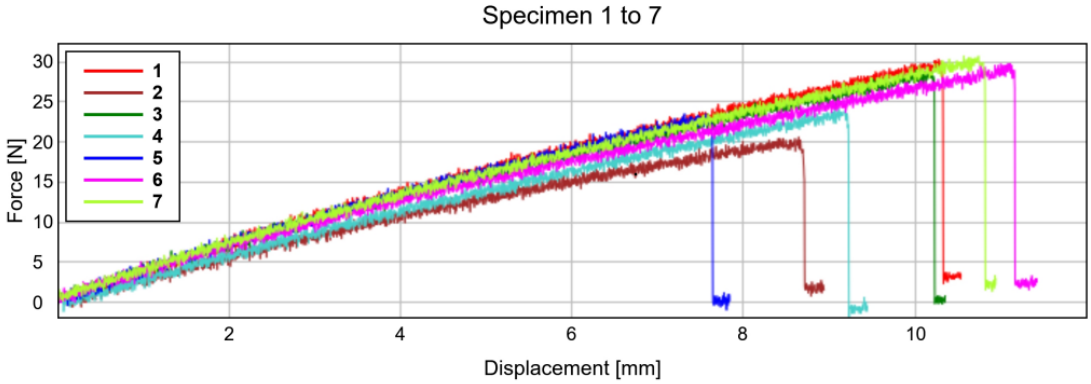


Fig. S55. Stress-strain curve for tensile testing of Poly(1-co-4SH).

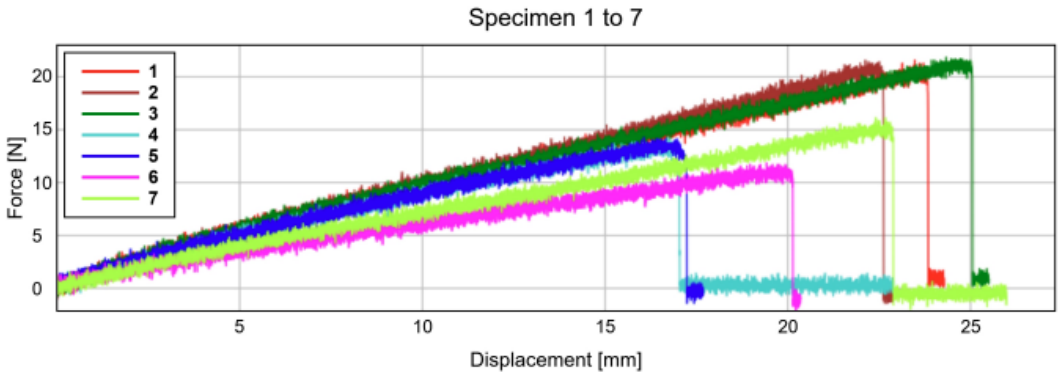


Fig. S56. Stress-strain curve for tensile testing of Poly(2-co-4SH).

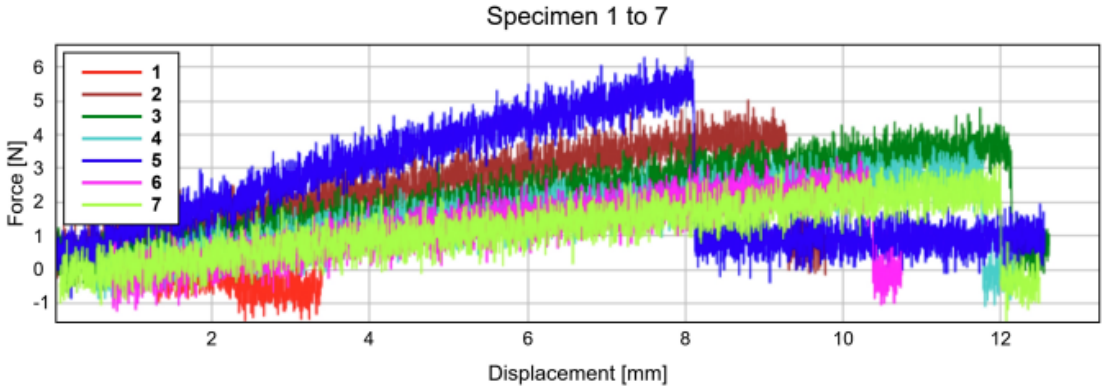


Fig. S57. Stress-strain curve for tensile testing of Poly(3-co-4SH).

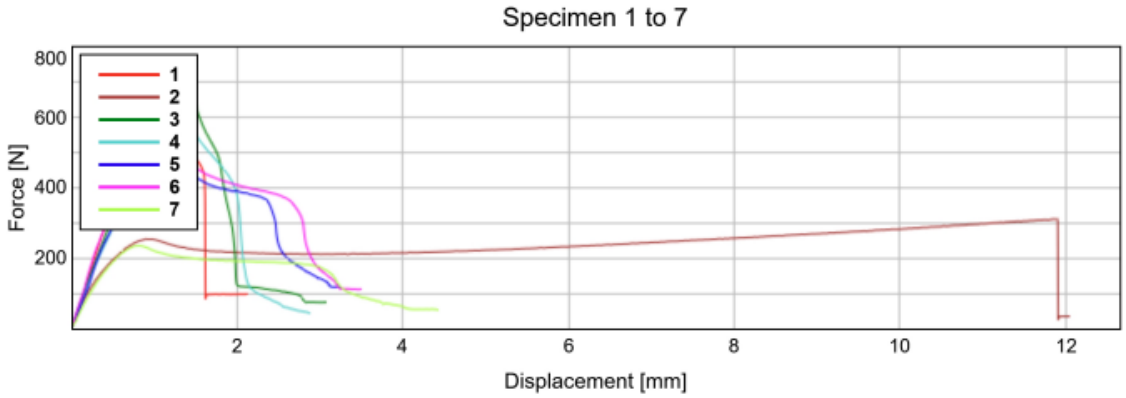


Fig. S58. Stress-strain curve for tensile testing of Poly(5-co-4SH).

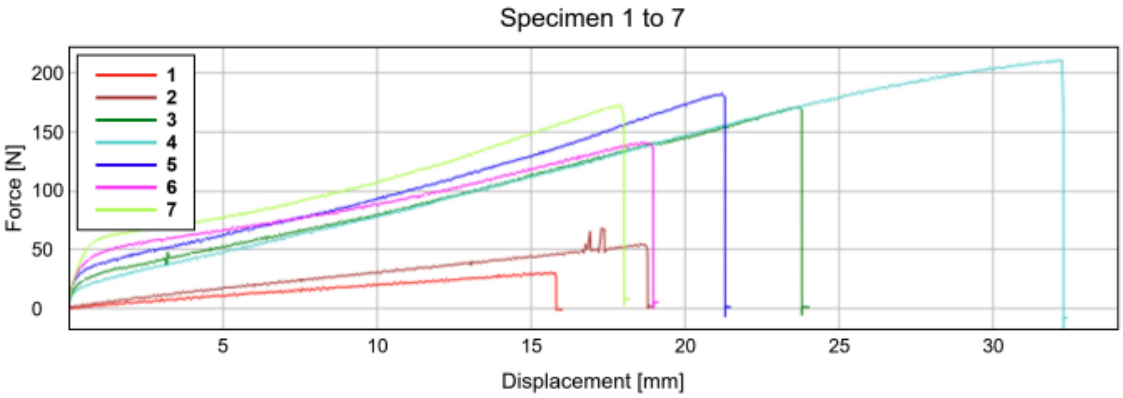


Fig. S59. Stress-strain curve for tensile testing of Poly(6-co-4SH).

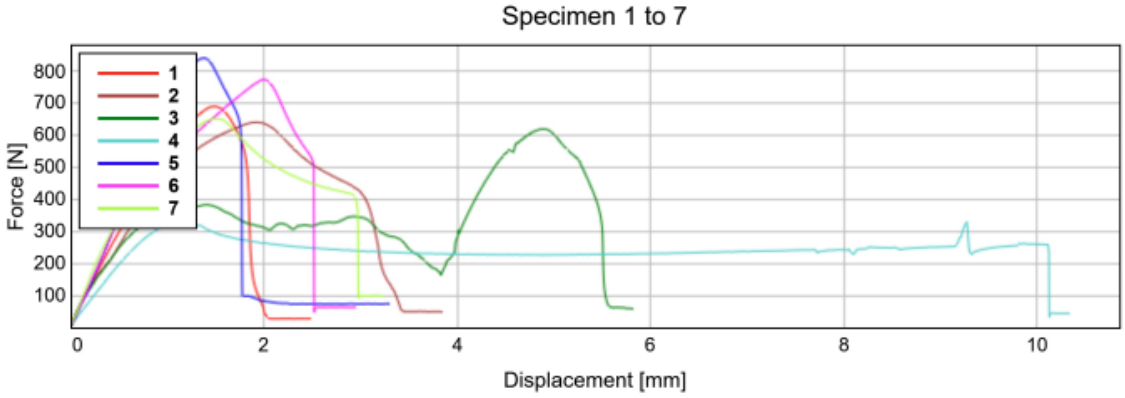


Fig. S60. Stress-strain curve for tensile testing of Poly(7-co-4SH).

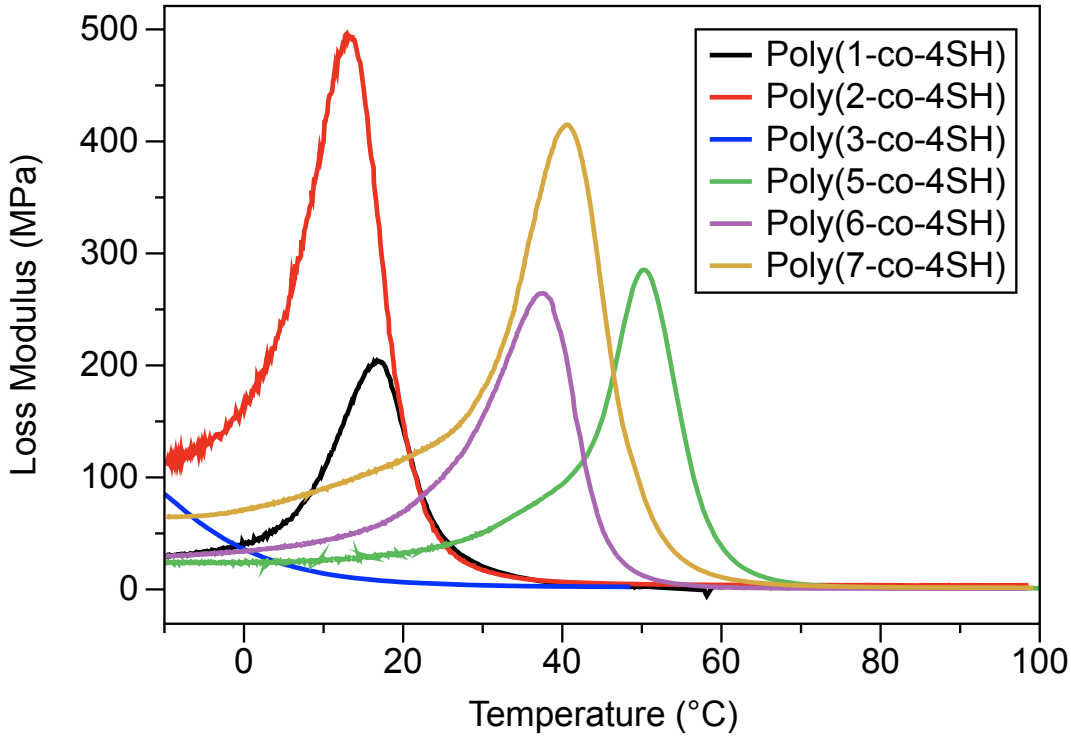


Fig S61. DMA loss modulus data

Table S2. DMA characterisation of thermosets (based on loss modulus data).

Polymer Code	Alternative T_g DMA (°C) [a]
Poly(1-co-4SH)	17.1
Poly(2-co-4SH)	13.5
Poly(3-co-4SH)	n.d.[b]
Poly(5-co-4SH)	50.5
Poly(6-co-4SH)	37.5
Poly(7-co-4SH)	41.1

[a] Based on the temperature at which the loss modulus *E*" passes through a maximum value. no maximum was determined.

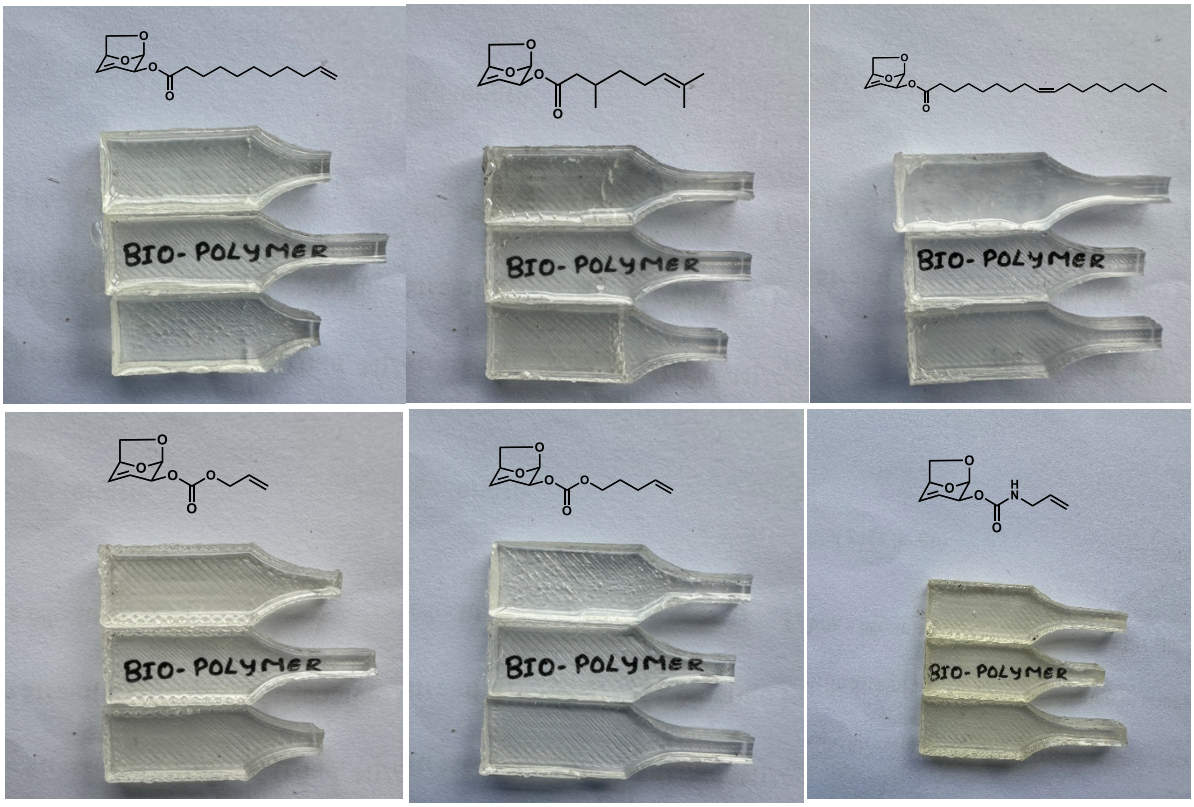


Fig. S62. Polymer samples of each respective monomer showing optical transparency and colour.

Table S3. Degradation analysis of four different thermosets in alkaline medium (1M NaOH).

Time (Days)	Initial and Remaining weight (g)			
	Poly(3-co-4SH)	Poly(5-co-4SH)	Poly(6-co-4SH)	Poly(7-co-4SH)
Initial wt.	0.2166	0.1510	0.1421	0.2609
1	0.0972	0.0162	0.1032	0.0027
2	0.0611	0.0030	0.0909	0.0016
3	0.0356	0.0009	0.0799	0.0009
4	0.0198	0.0005	0.0727	0.0002
5	0.0075	0.0002	0.0669	0

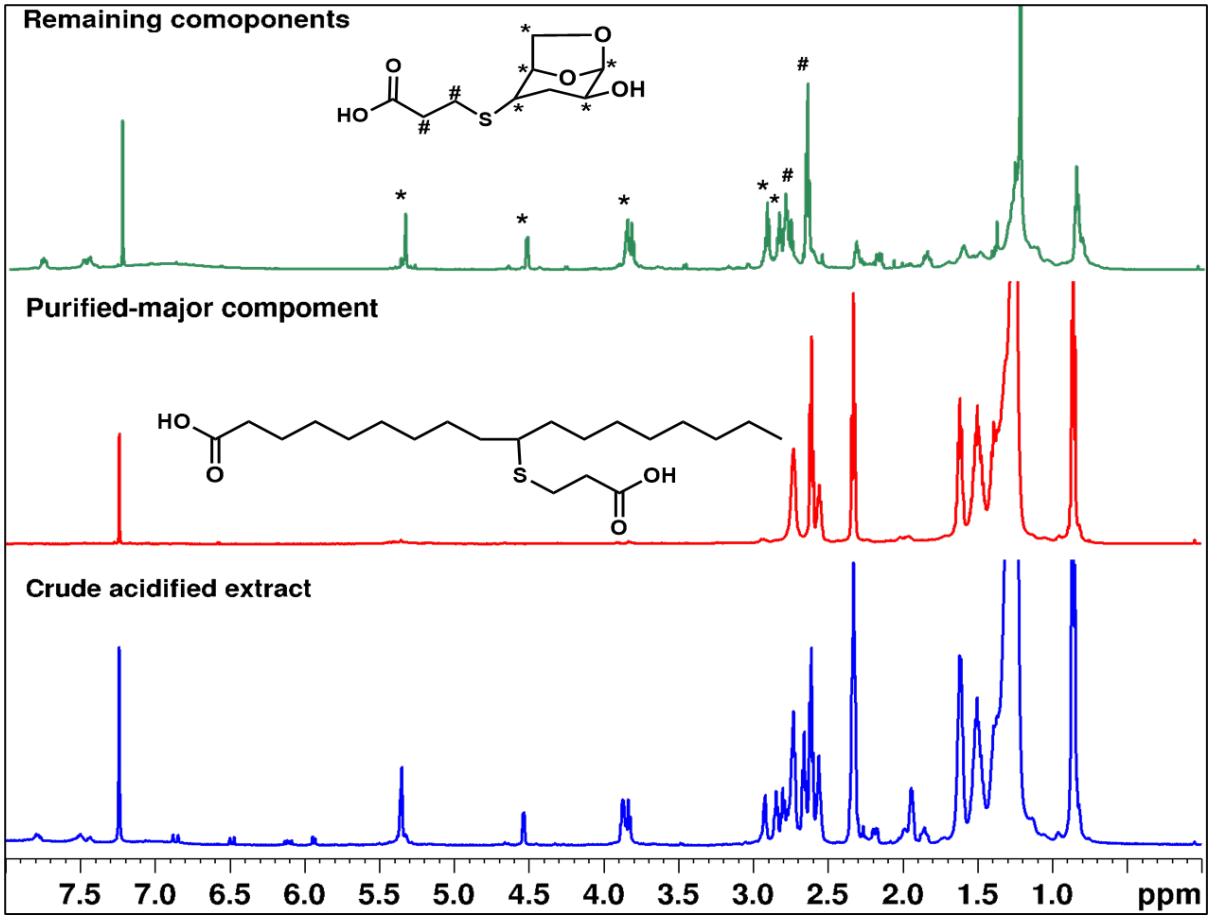


Fig. S63. Comparison of ^{1}H NMR spectra ($CDCl_3$, 600 MHz) of degraded crude acidified extract (extracted with ethyl acetate) with retrieved major fraction and remaining fractions of Poly(3-co-4SH) in 1M NaOH.

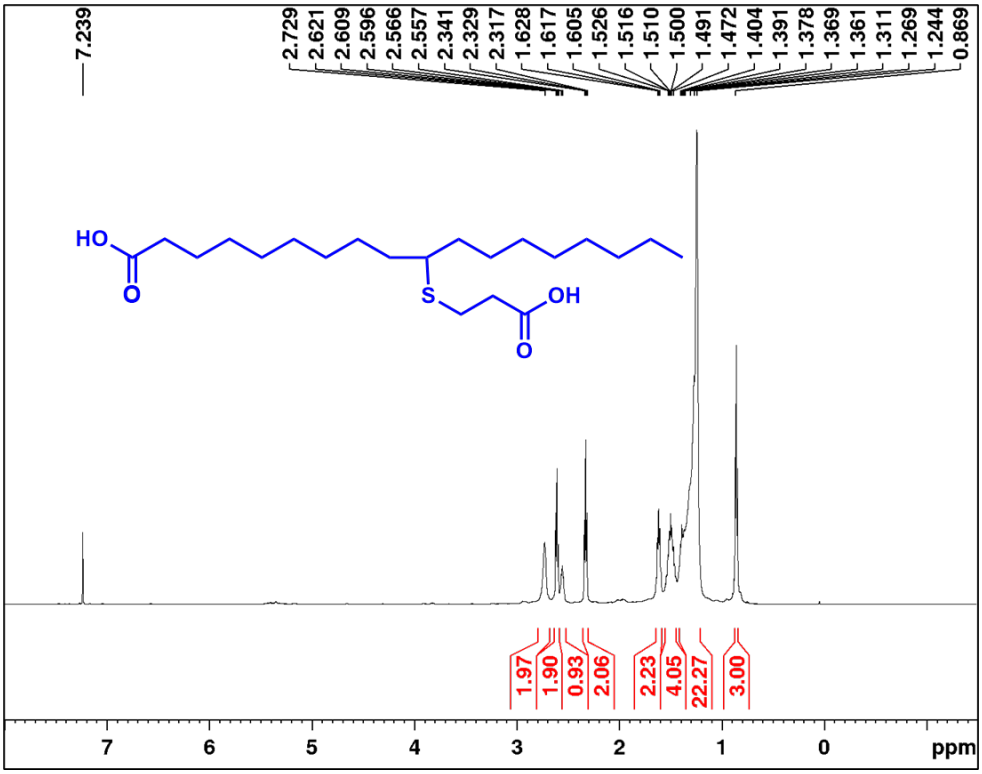


Fig. S64. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of retrieved major fraction of degraded Poly(3-co-4SH) in 1M NaOH.

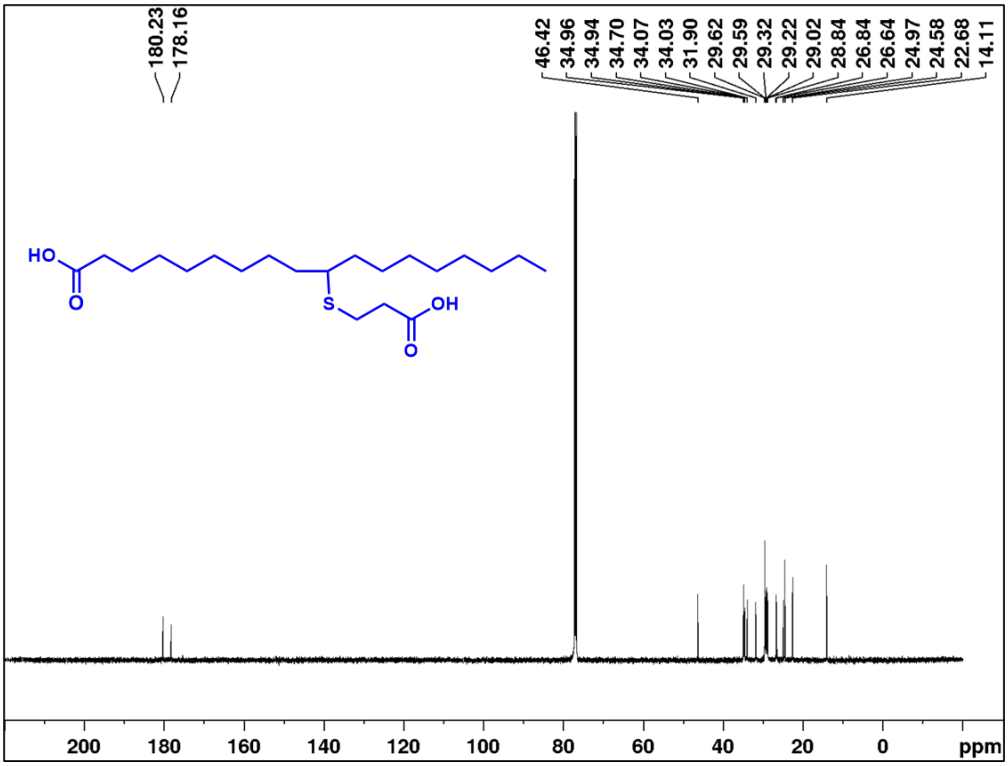


Fig. S65. ^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of retrieved major fraction of degraded Poly(3-co-4SH) in 1M NaOH.

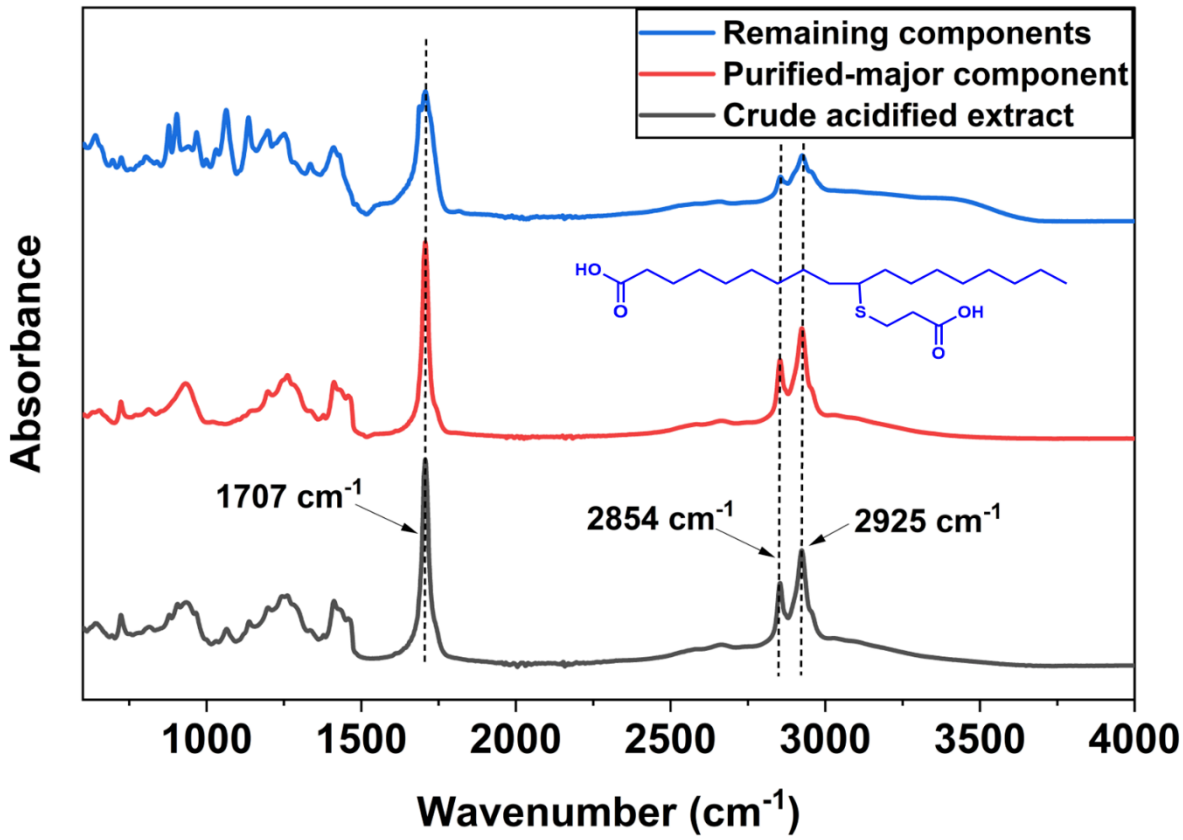


Fig. S66. Comparison of FTIR spectra of degraded crude acidified extract (extracted with ethyl acetate) with retrieved major fraction and remaining fractions of Poly(3-co-4SH) in 1M NaOH.

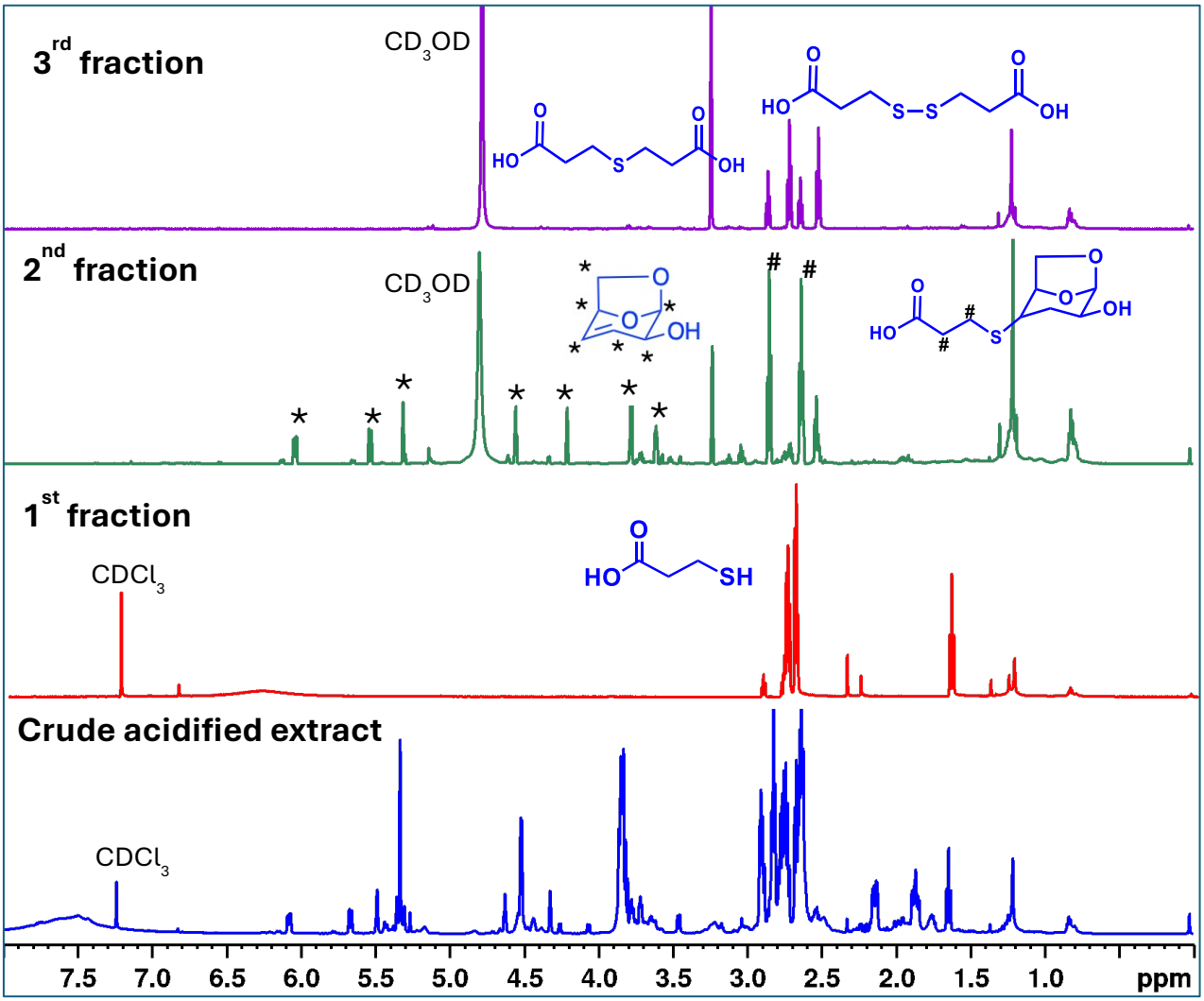


Fig. S67. Comparison of ^{1}H NMR spectra ($CDCl_3$, 600 MHz) of degraded (in 1M NaOH) crude acidified extract (extracted with ethyl acetate) with retrieved all fractions of Poly(7-co-4SH).

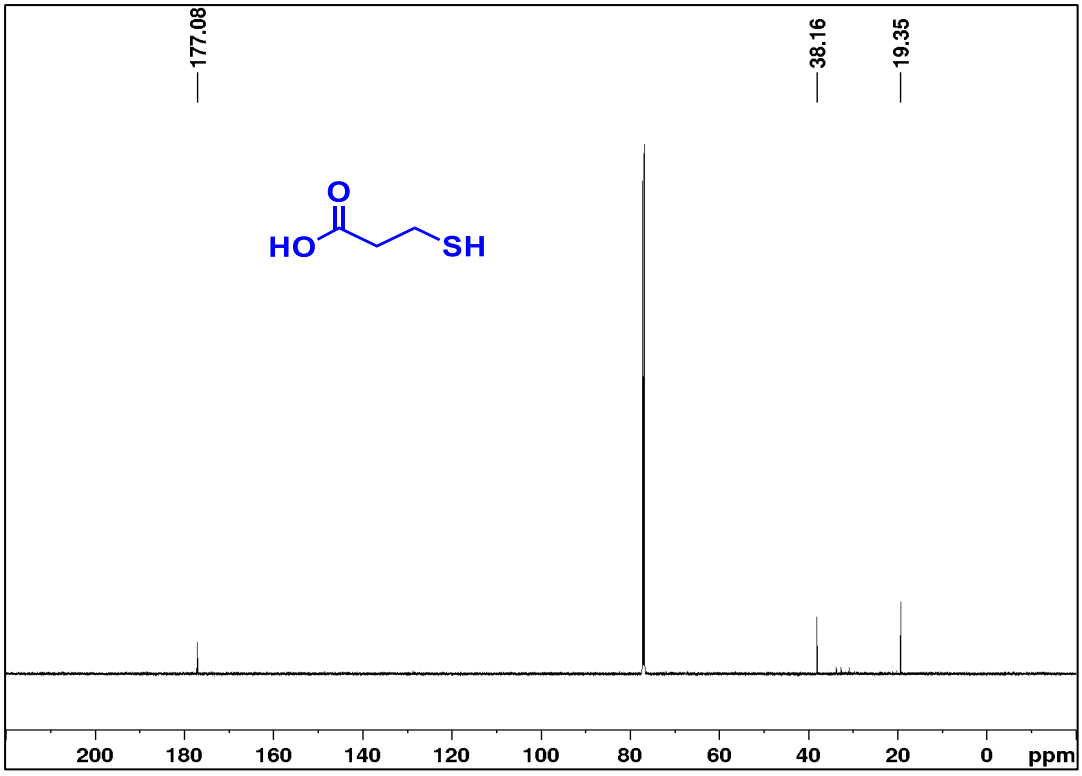


Fig. S68. ^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of retrieved 1st fraction of degraded Poly(7-co-4SH).

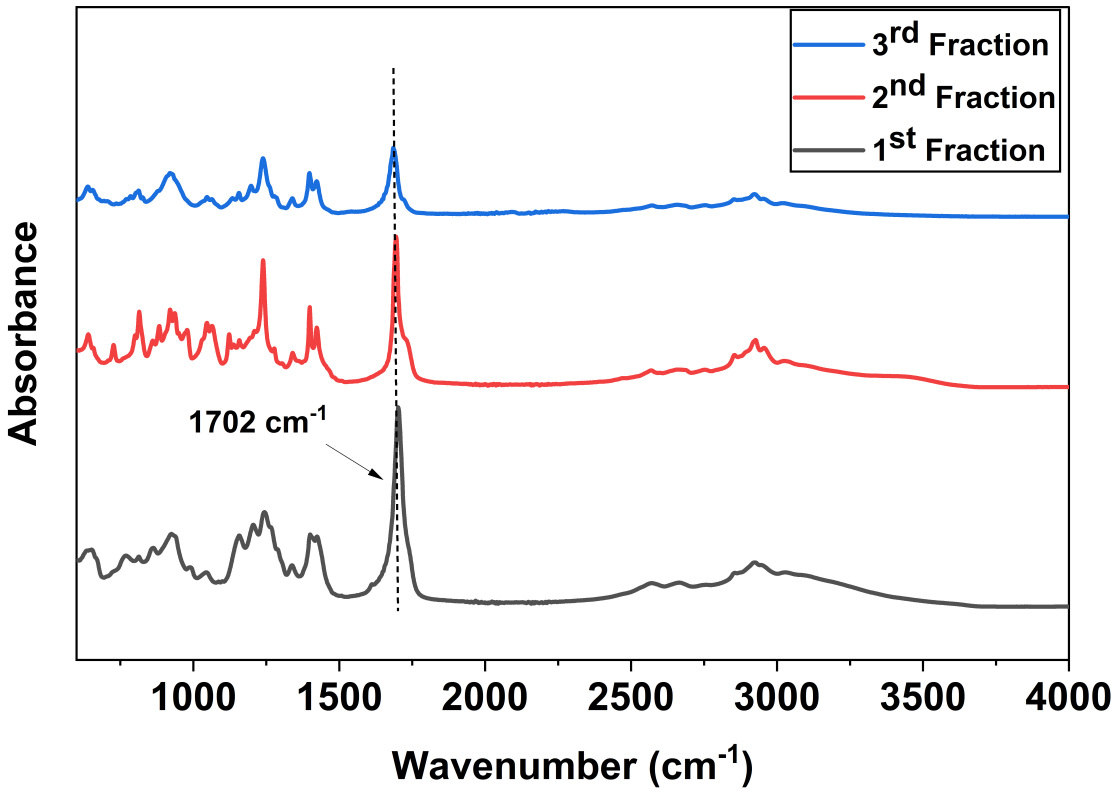


Fig. S69. Comparison of FTIR spectra of degraded crude acidified extracts (extracted with ethyl acetate) of Poly(7-co-4SH).

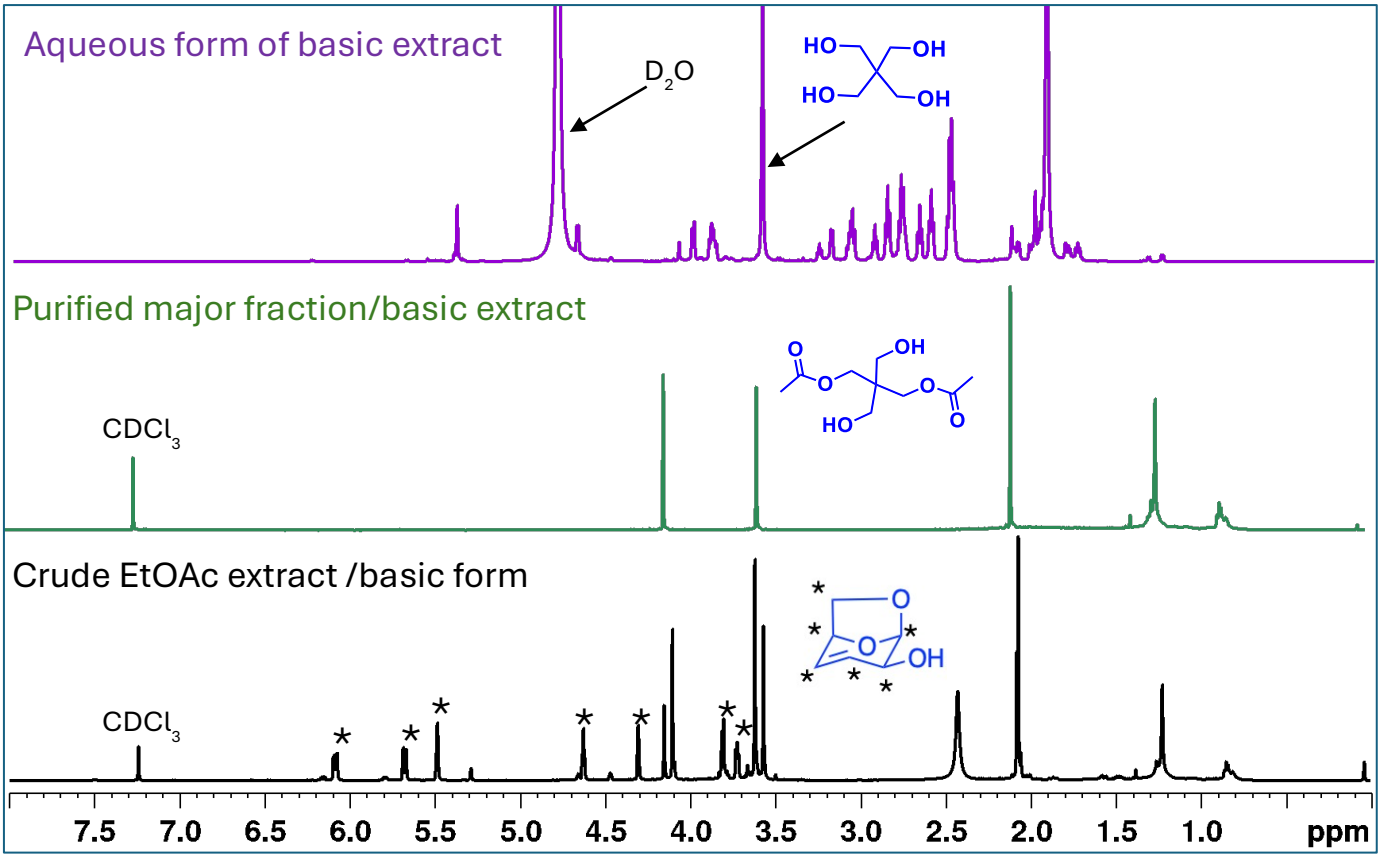


Fig. S70. Comparison of ^{1}H NMR spectrum ($CDCl_3$ and D_2O, 600 MHz) of retrieved fraction (basic form) of degraded Poly(7-co-4SH) in 1M NaOH.

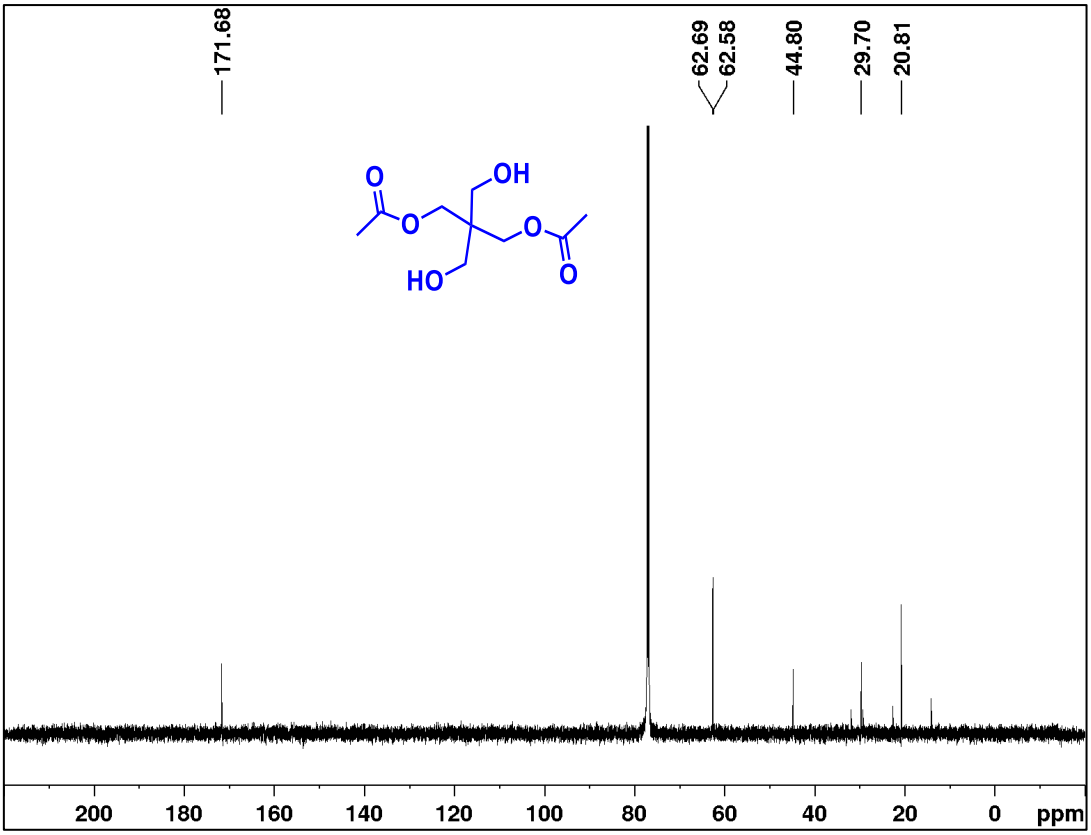


Fig. S71. ^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of retrieved major fraction (basic form-ethyl acetate extract) of degraded Poly(7-co-4SH) in 1M NaOH.