ELECTRONIC SUPPLEMENTARY INFORMATION

Facile Synthesis, Structure and Properties of CO_2-sourced Poly(thioether-*co*-carbonate)s Containing Acetyl Pendants via Thio-Ene Click Polymerization

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1. Synthesis of polymeric monomers

4-Methyl-4-vinyl-5-methylene-1,3-dioxolan-2-one (**2**) was synthesized by the carboxylative cyclization of propargylic alcohol (**1**) with CO_2 according to previous literatures.[1]

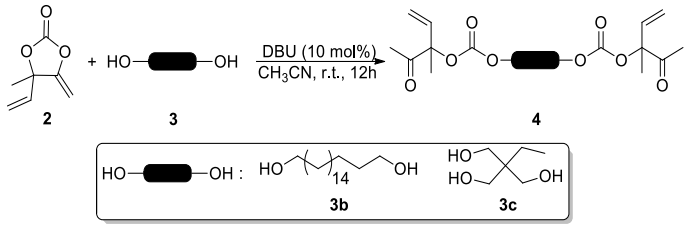


Figure S1. Synthesis of 4-methyl-4-vinyl-5-methylene-1,3-dioxolan-2-one (**2**) with diol **3**.

4-Vinyl substituted *α*CC **2** (10 mmol), 1,18-octadecanediol (**3b**, 5 mmol) and CH_3CN (20.0 mL) were added successively into a 100 mL flask equipped with a magnetic stirrer. Then 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.5 mmol, 10 mol%) was introduced and the mixture was stirred for 12 h at room temperature. After the reaction was over, the solvent was removed by rotary evaporation. The resulting crude mixture was purified by flash column chromatograph on silica gel to afford monomer **4b** (white solid, isolated yield: 75%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 6.01 (dd, *J* = 17.4, 11.0 Hz, 2H), 5.44 (d, *J* = 17.4 Hz, 2H), 5.30 (d, *J* = 11.0 Hz, 2H), 4.14 (d, *J* = 6.7, 2.0 Hz, 4H), 2.14 (s, 6H), 1.70 – 1.64 (m, 4H), 1.60 (s, 6H), 1.38 – 1.21 (m, 28H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 204.2, 153.9, 135.9, 117.0, 87.4, 77.3, 77.1, 76.9, 68.7, 29.8, 29.7, 29.7, 29.6, 29.6, 29.3, 28.7, 25.7, 23.7, 21.3. **IR(KBr)**: ν=3432, 2924, 2853, 1745(C=O), 1728(C=O), 1677, 1633, 1462, 1391, 1370, 1356, 1275, 1181, 1123, 1050, 993, 932, 790, 617 cm^{-1}. **HRMS**: m/z calculated for $C_{32}H_{54}O_8$[M+Na^+]:589.3716; found 589.3690.

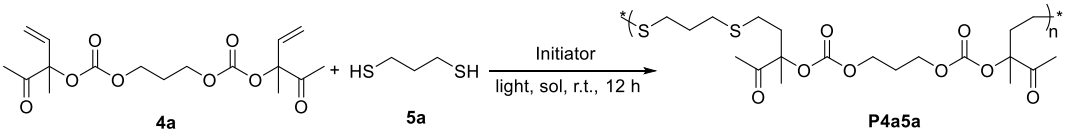
4-Vinyl substituted *α*CC **2** (15 mmol), trimethylolpropane (**3c**, 5 mmol) and CH_3CN (20.0 mL) were added successively into a 100 mL flask equipped with a magnetic stirrer. Then 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.5 mmol, 10 mol%) was introduced and the mixture was stirred for 12 h at room temperature. After the reaction was over, the solvent was removed by rotary evaporation. The resulting crude mixture was purified by flash column chromatograph on silica gel to afford monomer **4c** (coreless oil, isolated yield: 71%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 5.98 (dd, *J* = 17.4, 11.0 Hz, 3H), 5.40 (d, *J* = 17.4 Hz, 3H), 5.29 (d, *J* = 11.0 Hz, 3H), 4.12 (s, 7H), 2.10 (s, 9H), 1.58 (s, 9H), 1.52 (q, *J* = 7.5 Hz, 2H), 0.91 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 203.6, 153.5, 135.6, 117.3, 87.8, 77.3, 77.1, 76.9, 67.0, 41.5, 23.7, 22.4, 21.1, 7.2. **IR(KBr)**:

ν=3435, 2973, 2943, 1747(C=O), 1726(C=O), 1639, 1458, 1393, 1356, 1267, 1180, 1102, 1081, 988, 937, 904, 791, 661 cm^{-1}. **HRMS**: m/z calculated for $C_{27}H_{38}O_{12}$[M+Na^+]:577.2261; found 577.2258.

2. Optimization of polymerization conditions

To a Schlenk tube, 1,3-dimercaptopropane (**5a**, 1.0 mmol), **4a** (1.0 mmol), [Ir (4,4′-^{t}Bu$_2$-bpy)(bpy)$_2$]PF_6 (**[Ir]**, 0.05 mmol, 5.0 mol%), *p*-Toluidine (0.05 mmol, 5.0 mol%) were added, following by the addition of 1-methyl-2-pyrrolidinone (NMP) (1.0 mL). The Schlenk tube was irradiated with a 450 nm LED for 24 h. After that, a small amount of the crude product was taken to determine monomer conversion by ^{1}H NMR spectrum. The remaining product was repeatedly dissolved in CH_2Cl_2, precipitated with cold methanol, isolated by centrifuge, and dried under vacuum at 35 °C for 24 h to afford polymer **P4a5a** (light yellow sticky liquid, 84% yield.).

Table S1. Optimization of reaction conditions for the synthesis of polymers.



Entry	Polymer	Solvent	Initiator (5 mol%)	M_n (g/mol)[e]	Conv. (%)[f]	$Đ$[e]
1[a]	**P4a5a**	THF	DMPA	5900	>99%	2.12
2[b]	**P4a5a**	THF	[Ir]+ *p*-Toluidine	7800	90%	1.46
3	**P4a5a**	DMF	[Ir]+ *p*-Toluidine	5100	>99%	1.37
4	**P4a5a**	NMP	[Ir]+ *p*-Toluidine	7800	>99%	1.37
5[b]	**P4a5a**	NMP	[Ir]+ *p*-Toluidine	10400	>99%	1.43
6[c]	**P4a5a**	NMP	[Ir]+ *p*-Toluidined	5300	>99%	1.45
7[d]	**P4a5a**	NMP	[Ir]+ *p*-Toluidinee	4800	89%	1.32
8	**P4a5a**	NMP	[Ir]	4500	>99%	1.48

[a]. 365 nm. [b]. 24 h. [c].Initiator = 10 mol%. [d]. Initiator = 1 mol%. [e]. Molecular weights were measured by GPC.[f]. Conversions was determined by ^{1}H-NMR spectroscopy on the crude samples. **[Ir]** = [Ir (4,4′-^{t}Bu$_2$-bpy)(bpy)$_2$]PF_6 (^{t}Bu: *tert*-butyl). 2,2-Dimethoxy-2-phenyl acetophenone (DMPA).

3. Synthesis of polymers via thiol-ene click reaction

3.1 Synthesis of polymer **P4a5**

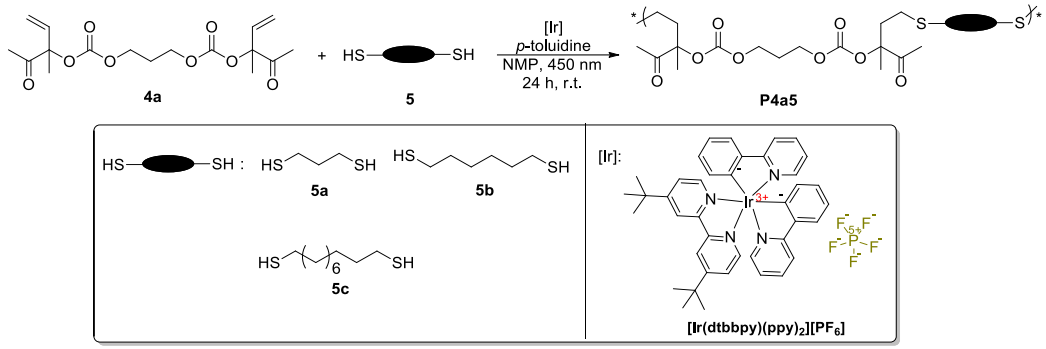
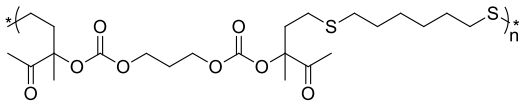
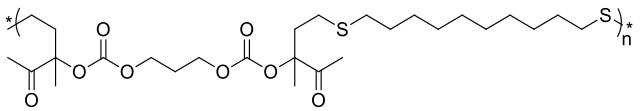


Figure S2. Synthesis of **P4a5** from **4a** and dithiol **5**.

To a Schlenk tube, dithiol (**5**, 1.0 mmol), **4a** (1.0 mmol), [Ir (4,4′-^{t}Bu$_2$-bpy)(bpy)$_2$]PF$_6$ (**[Ir]**, 0.05 mmol, 5.0 mol%), *p*-toluidine (0.05 mmol, 5.0 mol%) were added, following by the addition of 1.0 mL of 1-methyl-2-pyrrolidinone (NMP). The Schlenk tube was irradiated with a 450 nm LED for 24 h. After that, a small amount of the crude product was taken to determine monomer conversion by ^{1}H NMR spectrum. The remaining product was repeatedly dissolved in CH_2Cl_2, precipitated with cold methanol, isolated by centrifuge, and dried under vacuum at 35 °C for 24 h to afford polymer **P4a5**.



P4a5b (light yellow sticky liquid. 82% yield.) M_n = 9300 g/mol. PDI = 1.43. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 4.23 (t, J = 6.1 Hz, 4H), 2.55 – 2.39 (m, 8H), 2.25 – 2.11 (m, 8H), 2.03 (m, 4H), 1.63 – 1.49 (m, 10H), 1.37 (s, 4H). **^{13}C NMR (150 MHz, CDCl$_3$)** δ 205.9, 153.7, 87.4, 77.3, 77.1, 76.9, 64.5, 36.9, 32.2, 29.4, 28.5, 28.2, 25.8, 24.4, 20.5. **IR(KBr)**: ν=2927, 2854, 1746(C=O), 1721(C=O), 1461, 1379, 1360, 1331, 1268, 1165, 1102, 1072, 1032, 913, 791 cm^{-1}.



P4a5c (light yellow sticky liquid. 87% yield.) M_n = 14700 g/mol. PDI = 1.37. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 4.23 (t, J = 6.1 Hz, 4H), 2.58 – 2.38 (m, 8H), 2.23 – 2.12 (m, 8H), 2.03 (m, 4H), 1.54 (d, J = 13.5 Hz, 10H), 1.35 (s, 4H), 1.26 (s, 10H). **^{13}C NMR (150 MHz, CDCl$_3$)** δ 205.9, 153.7, 87.5, 77.4, 77.1, 76.8, 64.5, 36.9, 32.3, 29.6, 29.6, 29.3, 29.0, 28.2, 25.8, 24.4, 20.5. **IR(KBr)**:

ν=3433, 2925, 2853, 1743(C=O), 1715(C=O), 1459, 1399, 1358, 1332, 1265, 1165, 1102, 1071,914,871,792 cm^{-1}.

3.2 Synthesis of polymer **P4b5**

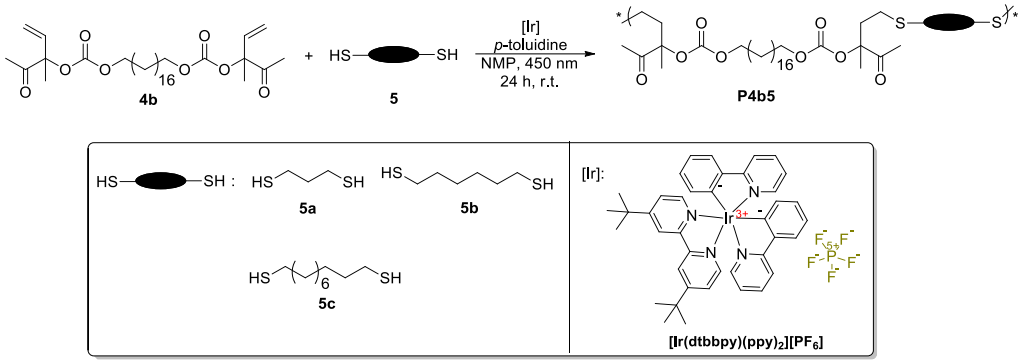
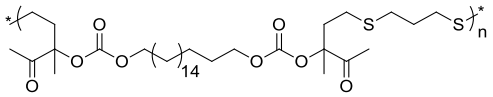
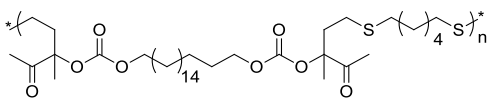


Figure S3. Synthesis of **P4b5** from**4b** and dithiol **5**.

To a Schlenk tube, dithiol (**5**, 1.0 mmol), **4b** (1.0 mmol), [Ir (4,4′-^{t}Bu$_2$-bpy)(bpy)$_2$]PF_6 (**[Ir]**, 0.05 mmol, 5.0 mol%), *p*-toluidine (0.05 mmol, 5.0 mol%) were added, following by the addition of 1.0 mL of 1-methyl-2-pyrrolidinone (NMP). The Schlenk tube was irradiated with a 450 nm LED for 24 h. After that, a small amount of the crude product was taken to determine monomer conversion by ^{1}H NMR spectrum. The remaining product was repeatedly dissolved in CH_2Cl_2, precipitated with cold methanol, isolated by centrifuge, and dried under vacuum at 35 °C for 24 h to afford polymer **P4b5**.

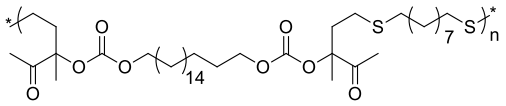


P4b5a (light yellow solid. 85% yield.) M_n = 12500 g/mol. PDI = 1.14. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 4.12 (t, J = 6.8 Hz, 4H), 2.60 (dd, J = 13.8, 6.8 Hz, 4H), 2.50 (m, 4H), 2.23 – 2.11 (m, 10H), 2.03 (m, 2H), 1.73 – 1.62 (m, 4H), 1.54 (s, 6H), 1.25 (s, 28H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 206.2, 153.9, 87.2, 77.3, 77.1, 76.9, 68.6, 36.8, 32.2, 29.8, 29.7, 29.7, 29.6, 29.4, 29.3, 28.76 28.5, 25.8, 25.7, 24.3, 20.4. **IR(KBr)**: ν=3430, 2927, 2853, 1746(C=O), 1720(C=O), 1463, 1394, 1356, 1276, 1166, 1101, 1075, 915, 793 cm^{-1}.



P4b5b (light yellow solid. 81% yield.) M_n = 16700 g/mol. PDI = 1.35. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 4.12 (t, J = 6.4 Hz, 4H), 2.73 – 2.60 (m, 2H), 2.55 – 2.42 (m, 6H), 2.17 (s, 6H), 2.08 –

1.95 (m, 2H), 1.72 – 1.62 (m, 6H), 1.62 – 1.51 (m, 10H), 1.24 (s, 32H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 206.2, 153.9, 87.1, 77.3, 77.1, 76.9, 68.7, 36.8, 32.2, 29.8, 29.7, 29.7, 29.6, 29.4, 29.3, 28.7, 28.5, 25.8, 25.7, 24.3, 20.4. **IR(KBr)**: ν=3425, 2923, 2853, 1743(C=O), 1723(C=O), 1465, 1398, 1358, 1277, 1168, 1130, 1104, 1077, 1029, 917, 792 cm^{-1}.



P4b5c (light yellow solid. 89% yield.) M_n = 23900 g/mol. PDI = 2.15. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 4.12 (t, J = 6.8 Hz, 4H), 2.59 – 2.39 (m, 8H), 2.24 – 2.10 (m, 8H), 2.03 (m, 2H), 1.67 (m, 4H), 1.57 – 1.52 (m, 10H), 1.38 – 1.30 (m, 8H), 1.26 (d, J = 6.5 Hz, 32H), 1.24 – 1.24 (m, 1H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 206.3, 153.9, 87.1, 68.7, 36.8, 32.3, 29.8, 29.8, 29.7, 29.6, 29.6, 29.3, 29.0, 28.7, 25.8, 25.7, 24.3, 20.4. **IR(KBr)**: ν=3428, 2922, 2853, 1744(C=O), 1724(C=O), 1463, 1393, 1356, 1276, 1165, 1073, 916, 793 cm^{-1}.

3.3 Synthesis of polymer **P4c5**

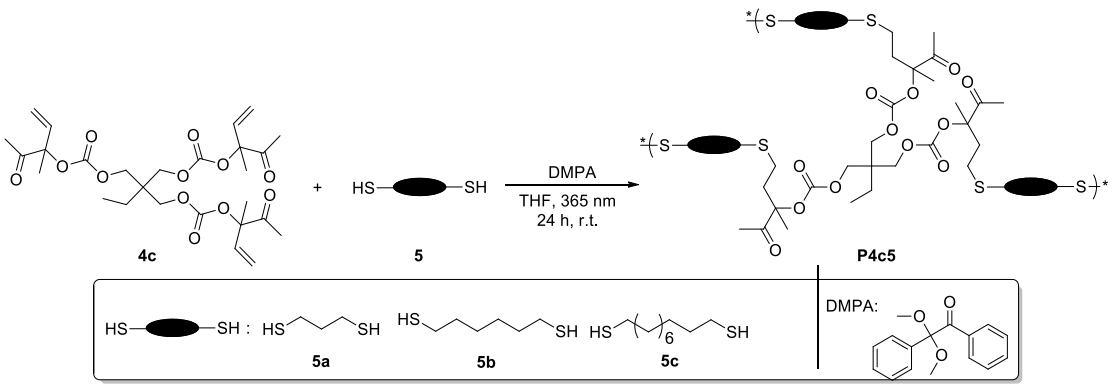
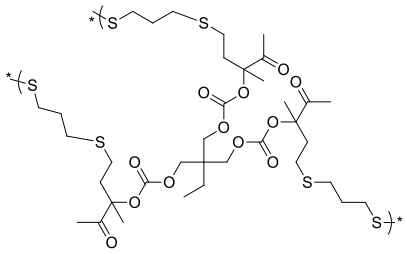
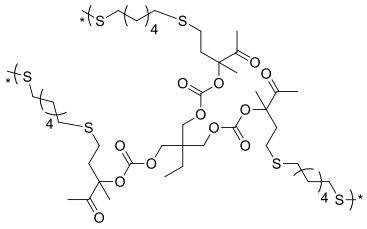


Figure S4. Synthesis of **P4c5** from **4c** and dithiol **5**.

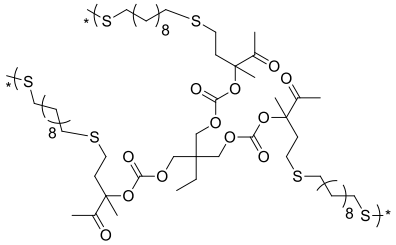
To a Schlenk tube, dithiol (**5**, 1.5 mmol), **4c** (1.0 mmol) and benzoin dimethyl ether (DMPA 0.05 mmol, 5.0 mol%) were added, following by the addition of THF (1.0 mL). The Schlenk tube was irradiated with a 365 nm LED for 24 h. After that, a small amount of the crude product was taken to determine monomer conversion by ^{1}H NMR spectrum. The remaining product was repeatedly dissolved in CH_2Cl_2, precipitated with cold methanol, isolated by centrifuge, and dried under vacuum at 35 °C for 24 h to afford polymer **P4c5**.



P4c5a (colorless sticky liquid. 86% yield.) M_n = 6600g/mol. PDI = 1.83. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 4.12 (s, 6H), 2.69 – 2.56 (m, 8H), 2.56 – 2.41 (m, 6H), 2.17 (d, J = 1.2 Hz, 9H), 2.04 (m, 4H), 1.85 (m, 4H), 1.56 (s, 9H), 1.56 (s, 8H), 1.54 (s, 2H), 0.94 (t, J = 7.5 Hz, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 205.7, 153.6, 87.6, 77.3, 77.1, 76.9, 67.0, 41.6, 36.9, 36.7, 33.3, 31.0, 30.5, 29.0, 25.8, 25.7, 24.5, 23.5, 22.4, 20.5, 20.5, 7.4. **IR(KBr)**: ν=3453, 2972, 2936, 1746 (C=O), 1721 (C=O), 1461, 1380, 1358, 1267, 1165, 1102, 1074, 963, 918, 788 cm^{-1}.



P4c5b (colorless sticky liquid. 82% yield.) M_n = 6300 g/mol. PDI = 2.27. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 4.11 (s, 6H), 2.60 – 2.37 (m, 14H), 2.17 (s, 9H), 2.09 – 1.94 (m, 3H), 1.74 – 1.45 (m, 26H), 1.47 – 1.34 (m, 10H), 0.93 (t, J = 7.5 Hz, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 205.7, 153.6, 87.6, 77.3, 77.1, 76.9, 67.0, 41.6, 36.9, 36.8, 33.9, 32.3, 32.2, 29.4, 29.4, 28.6, 28.3, 28.0, 25.85 25.8, 24.6, 24.4, 22.4, 20.4, 20.4, 7.4. **IR(KBr)**: ν=3474, 2929, 2855, 1804, 1746 (C=O), 1721 (C=O), 1461, 1395, 1357, 1266, 1164, 1102, 1074, 962, 917, 789, 734 cm^{-1}.



P4c5c (colorless sticky liquid. 85% yield.) M_n = 6800 g/mol. PDI = 1.85. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 4.11 (s, 6H), 2.56 – 2.39 (m, 14H), 2.16 (s, 9H), 2.09 – 1.95 (m, 3H), 1.60 (d, J = 5.1 Hz, 6H), 1.58 – 1.48 (m, 18H), 1.43 – 1.20 (m, 31H), 0.92 (t, J = 7.5 Hz, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 205.7, 153.6, 87.6, 77.4, 77.1, 76.8, 66.9, 41.6, 36.9, 34.1, 32.3, 32.3, 29.6, 29.6, 29.5,

29.3, 29.3, 29.1, 29.0, 28.9, 28.4, 25.8, 24.7, 24.3, 22.4, 20.4, 7.4. **IR(KBr)**: ν=3461, 2925, 2853, 1746(C=O), 1723 (C=O), 1462, 1391, 1357, 1266, 1165, 1072, 962, 917, 788 cm^{-1}.

4. Degradation of monomers 4 via cascade reaction

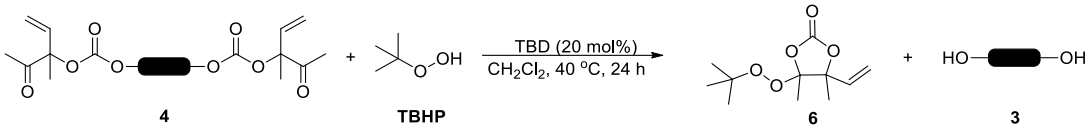
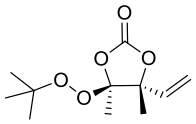
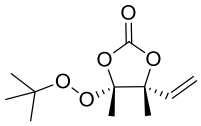


Figure S5. Degradation reaction of monomers **4**.

To a 2 mL high-pressure tube, monomer (**4**, 1.0 mmol), *tert*-butyl hydroperoxide **(**5.5 mmol/mL in decane**)** (TBHP, 2.0 mmol, 2.0 equiv.), 1,5,7-triazabicylo[4.4.0]dec-5-ene (TBD, 20 mol%) and CH_2Cl_2 (0.5 mL) were added. Then the mixture was stirred for 24 h at 40 °C. The reaction solution was cooled to room temperature, and the solvent was removed by rotary evaporation. Two isomers (*E* and *Z*) could be purified and isolated by flash column chromatograph as a colorless oil.



(*E*)-Isomer **6a** (colorless oil, 48% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 5.79 (dd, *J* = 17.1, 10.8 Hz, 1H), 5.42 (d, *J* = 17.1 Hz, 1H), 5.29 (d, *J* = 10.8 Hz, 1H), 1.62 (s, 3H), 1.51 (s, 3H), 1.27 (s, 9H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 153.4, 136.4, 116.1, 110.0, 87.8, 82.3, 26.4, 18.3, 17.9. **IR(KBr)**: ν=2987, 1813(C=O), 1366, 1265, 1195, 1179, 1158, 1141, 1115, 1067, 1025, 1009, 932, 891, 863, 767 cm^{-1}. **HRMS**: m/z calculated for $C_{11}H_{18}O_5$ [M+NH_4^+]: 248.1498; found 248.1492.



(*Z*)-Isomer **6b** (colorless oil, 48% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 6.15 (dd, *J* = 17.5, 11.1 Hz, 1H), 5.43 (d, *J* = 17.5 Hz, 1H), 5.35 (d, *J* = 11.1 Hz, 1H), 1.57 (s, 3H), 1.49 (s, 3H), 1.24 (s, 9H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 153.3, 133.3, 117.9, 110.3, 88.0, 82.1, 26.4, 22.7, 16.6. **IR(KBr)**: ν=2984, 1812(C=O), 1386, 1366, 1263, 1219, 1193, 1108, 1058, 1024, 935 cm^{-1}. **HRMS**: m/z calculated for $C_{11}H_{18}O_5$ [M+NH_4^+]: 248.1498; found 248.1493. All the resonances in ^{1}H and ^{13}C NMR spectra were in good agreement with literature values.[2]

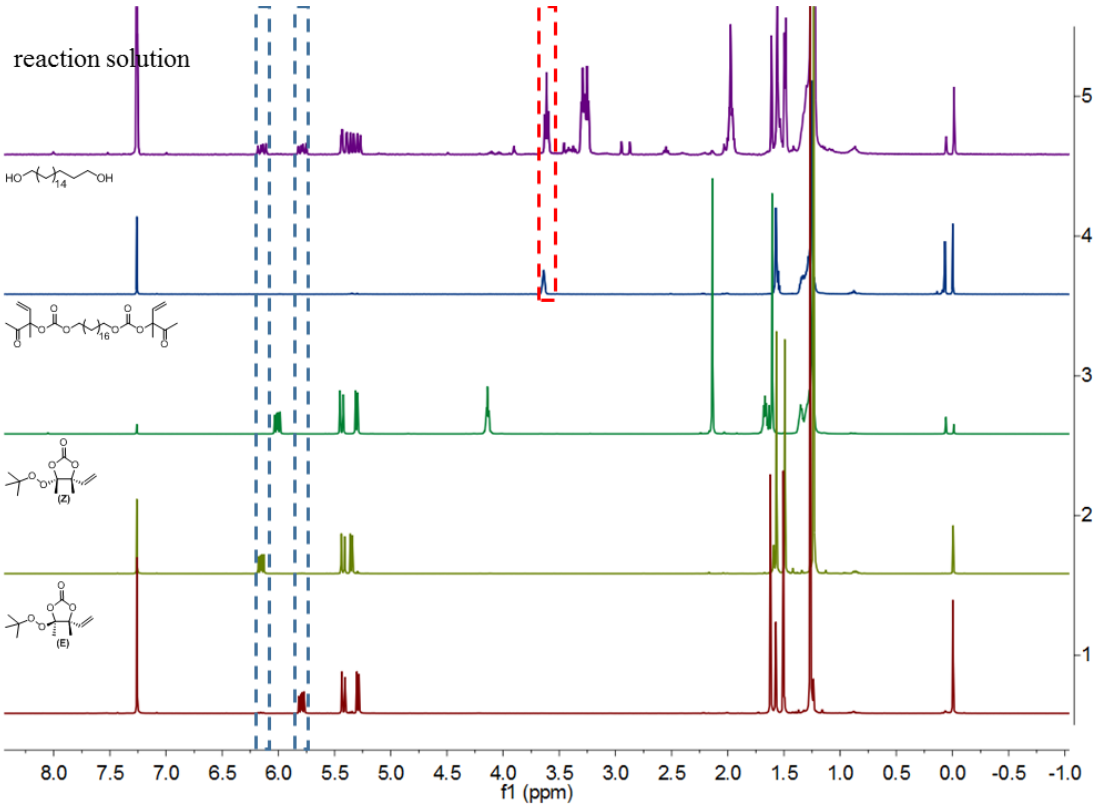


Figure S6. Stacked ^{1}H NMR spectra of the selective depolymerisation of **4b**.

5. *Degradation of polymer P-4b5a via cascade reaction*

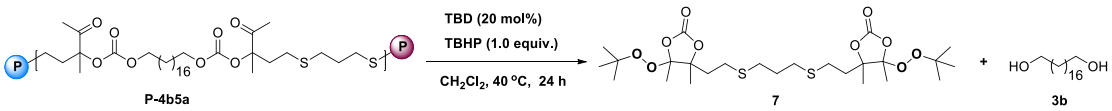


Figure S7. Degradation of polymer **P-4b5a**.

5.1 Degradation of **P4b5a** via cascade reaction

To a 2 mL high-pressure tube, **P4b5a** (175 mg, 0.254 mmol,), *tert*-butyl hydroperoxide (5.5 mmol/mL in decane, 0.508 mmol, 45 mg, 0.1 mL), 1,5,7-triazabicylo[4.4.0]dec-5-ene (TBD, 0.05 mmol, 20 mol%, 6,96 mg) and CH_2Cl_2 (0.5 mL) were added. Then the mixture was stirred for 24 h at 40 °C. The reaction solution was cooled to room temperature. The solution was then evaporated to a minimum amount by evaporation, dissolved with a small amount of CH_2Cl_2 precipitated in hexane, and the product was isolated by centrifuge. Repeated the above steps twice, and vacuum-dried to obtain **3b** (white solid, 65% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 3.64 (d, *J* = 3.6 Hz, 4H), 1.60 – 1.53 (m, 4H), 1.36 – 1.23 (m, 28H), 1.21 (s, 2H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 62.8, 32.8,

29.4, 25.6. All the resonances in ^{1}H and ^{13}C NMR spectra were in good agreement with literature values.[3] Then the filtrate was removed by rotary evaporation. The resulting crude mixture was purified by flash column chromatograph on silica gel to afford **7** (colorless oil, 13% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 2.66 (t, *J* = 7.0 Hz, 4H), 2.64 – 2.56 (m, 4H), 2.38 (m, 2H), 2.18 – 1.94 (m, 4H), 1.94 – 1.84 (m, 2H), 1.56 (s, 6H), 1.40 (s, 6H), 1.26 (s, 19H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 152.9, 110.2, 87.9, 82.3, 77.4, 77.1, 76.8, 33.5, 30.9, 29.0, 26.5, 26.4, 22.5, 17.2. **IR(KBr)**: ν=2924, 1809(C=O), 1630, 1401, 1366, 1248, 1189, 1146, 1045, 1006, 963, 927, 892, 771.05, 729, 519 cm^{-1}. HRMS: m/z calculated for $C_{25}H_{44}O_{10}S_2$ [M+Na^+]: 591.2274; found 591.2283.

5.2 The depolymerization reaction of **P4b5a** were detected by means of In-situ FT-IR

To a 10 mL flask, equipped with a magnetic stir bar, was charged with **P4b5a** (175 mg, 0.254 mmol), *tert*-butyl hydroperoxide (5.5 mmol/mL in decane, 0.1 mL, 2.0 equiv.), 1,5,7-triazabicylo[4.4.0]dec-5-ene (TBD, 0.05 mmol, 20 mol%) and CH_2Cl_2 (0.5 mL), then in-situ FT-IR probe was equipped to check the IR signals. Then the mixture was stirred for 24 h at 40 °C.

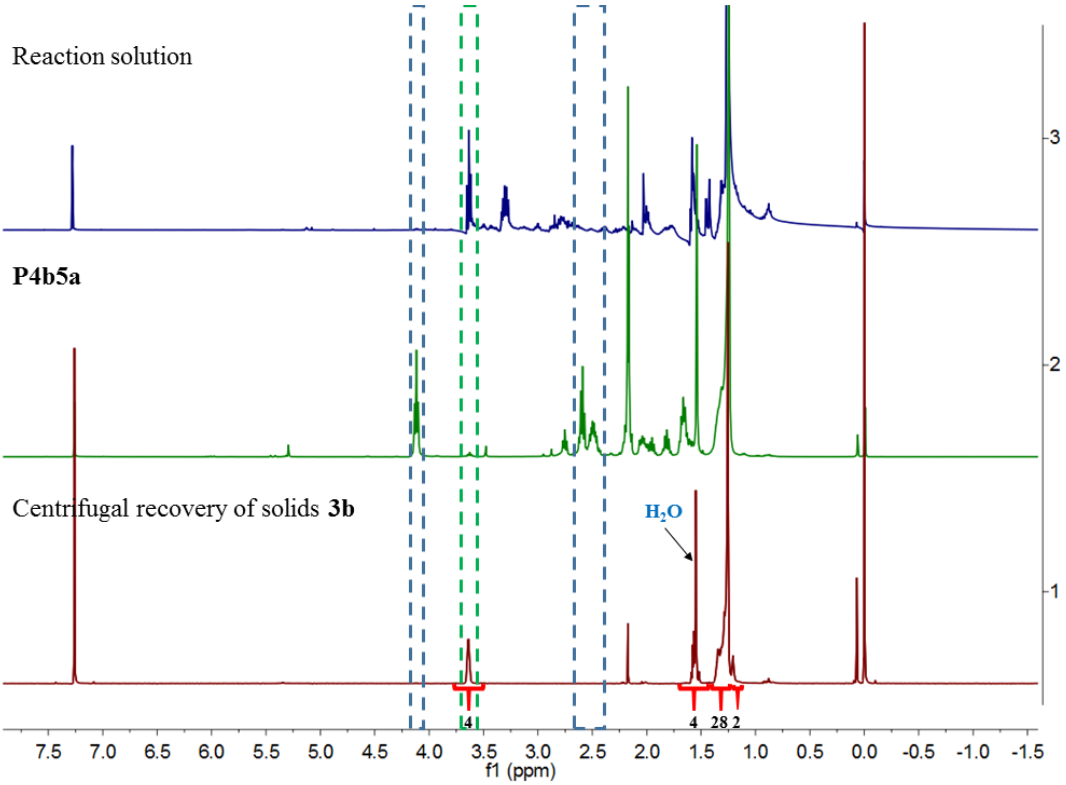


Figure S8. Stacked ^{1}H NMR spectra of the selective depolymerization of **P4b5a**.

6. GPC curves of the polymers P45 and degradable polymer D-P45

Table S2. GPC comparison of polymers **P45** and degradable polymers **D-P45**.

Entry	Polymer	M_n (g/mol)[a]	D-Polymer	M_n' (g/mol)[a]
1	**P4a5a**	10400	**D-P4a5a**	298
2	**P4a5b**	9300	**D-P4a5b**	311
3	**P4a5c**	14700	**D-P4a5c**	626
4	**P4b5a**	12500	**D-P4b5a**	1100
5	**P4b5b**	16700	**D-P4b5b**	1300
6	**P4b5c**	23900	**D-P4b5c**	979
7	**P4c5a**	6600	**D-P4c5a**	417
8	**P4c5b**	6300	**D-P4c5b**	339
9	**P4c5c**	6800	**D-P4c5c**	373

[a]. Number average molecular weights (M_n) were determined by gel permeation chromatography in THF, calibrated with polystyrene.

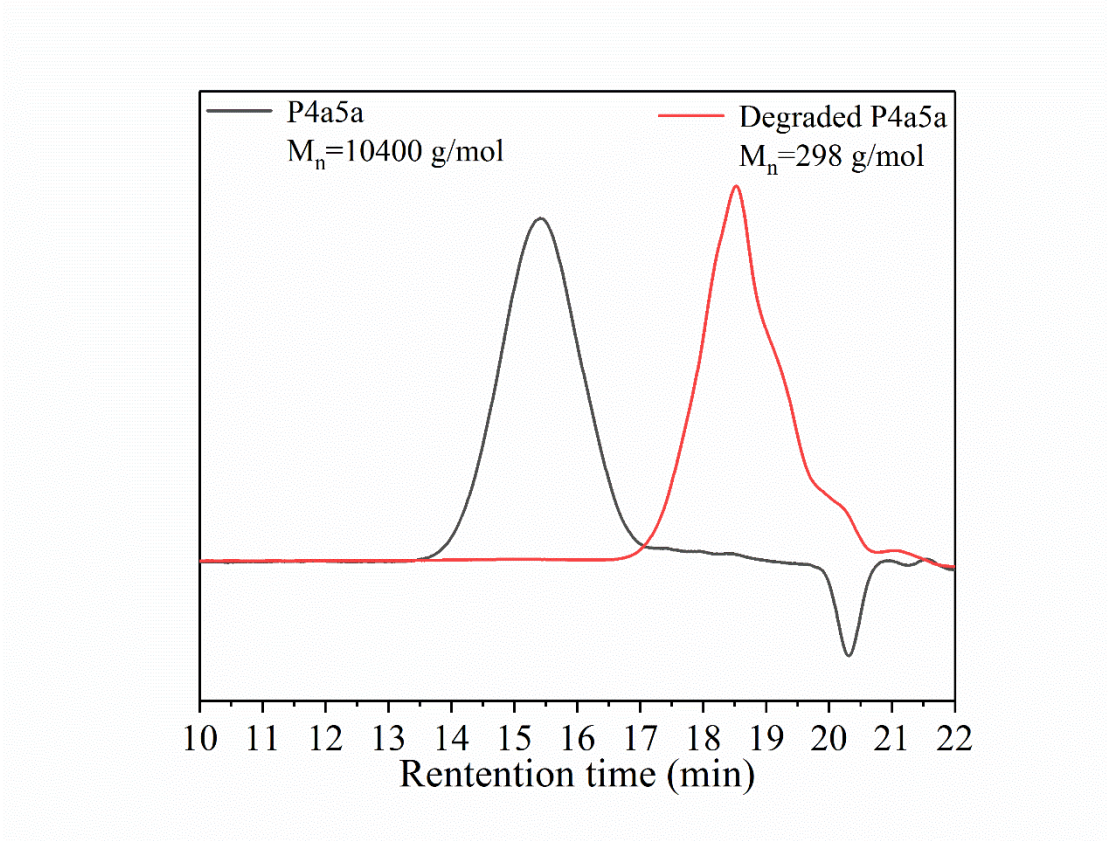


Figure S9. GPC curves of polymer **P-4a5a** and degraded polymer **D-P4a5a**.

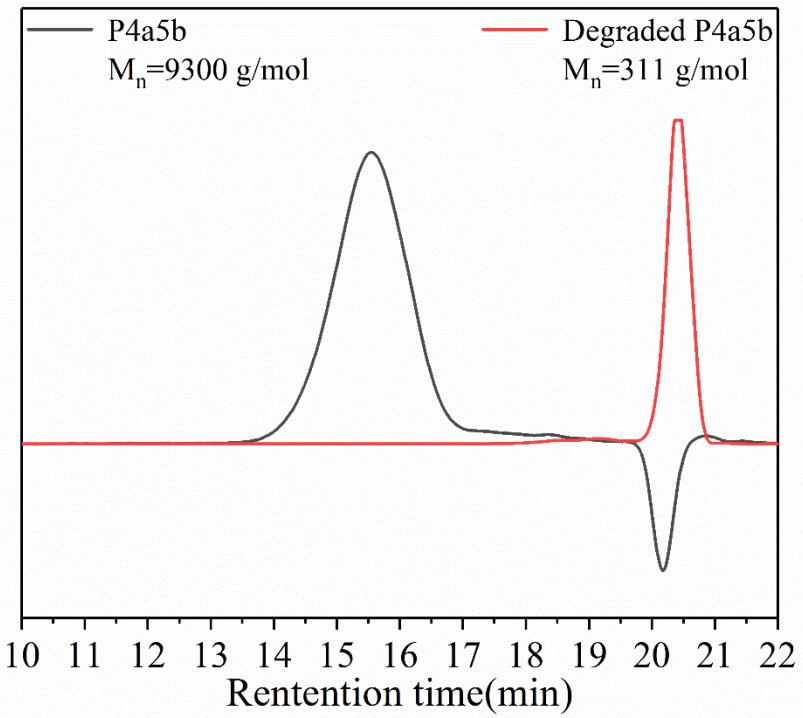


Figure S10. GPC curves of polymer **P-4a5b** and degraded polymer **D-P4a5b**.

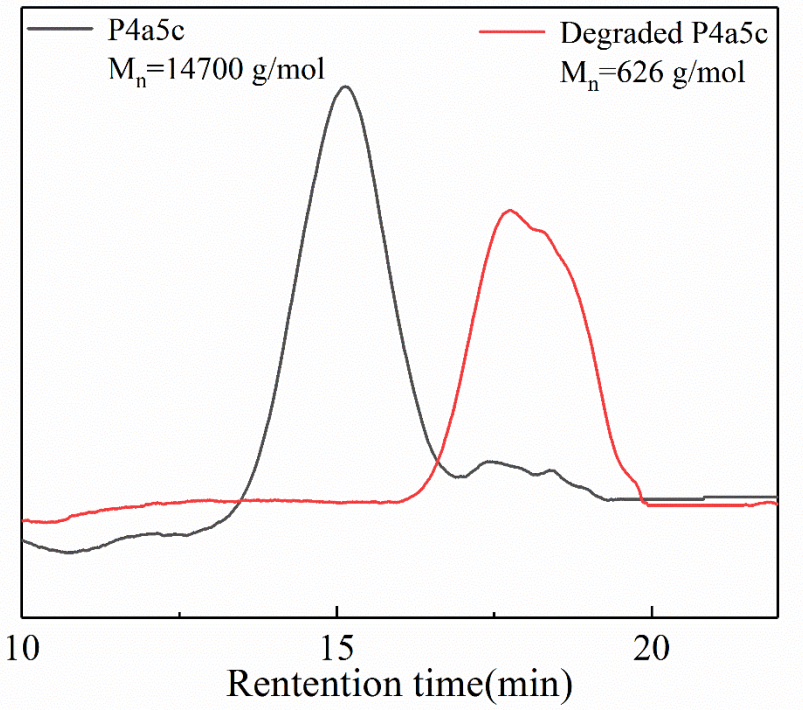


Figure S11. GPC curves of polymer **P-4a5c** and degraded polymer **D-P4a5c**.

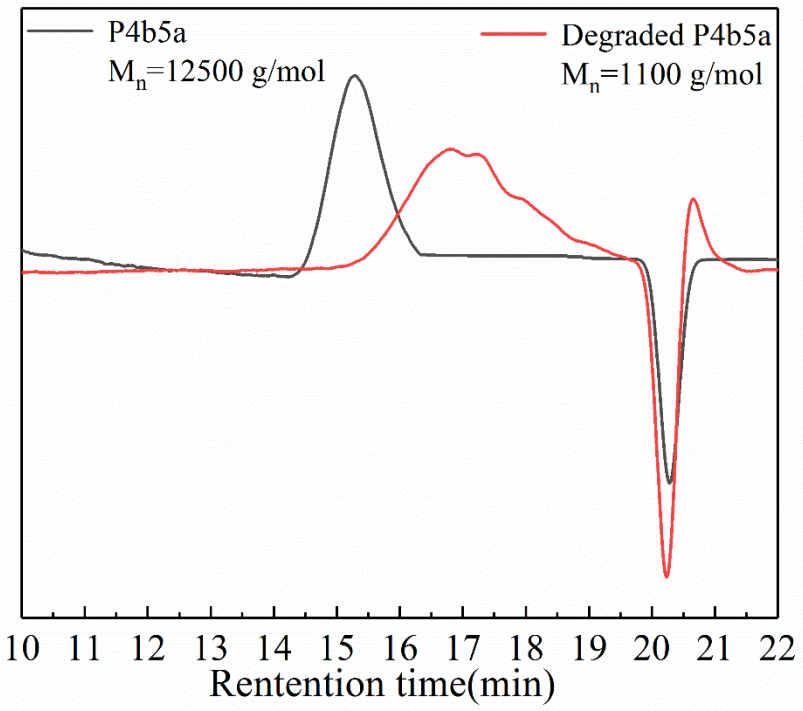


Figure S12. GPC curves of polymer **P-4b5a** and degraded polymer **D-P4b5a**.

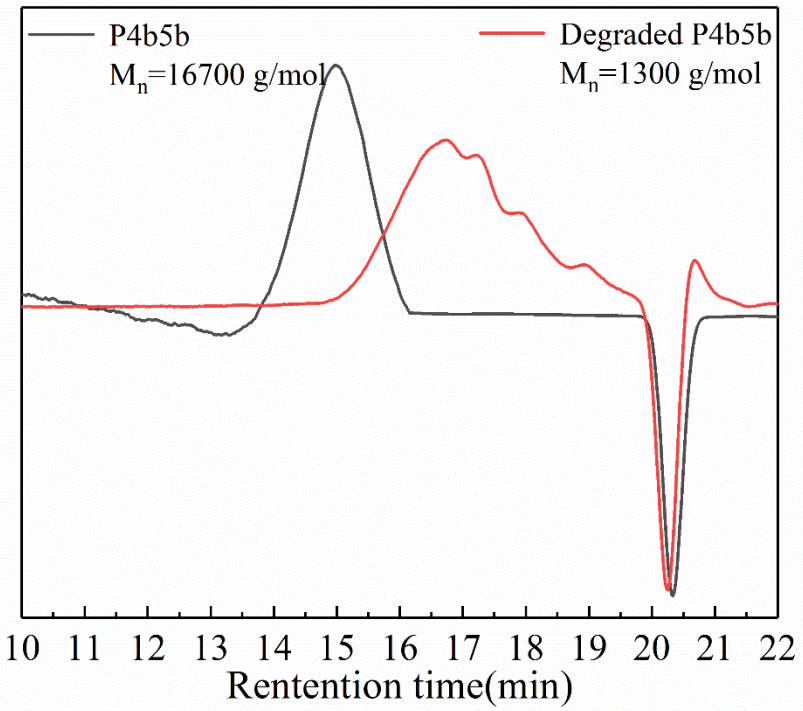


Figure S13. GPC curves of polymer **P-4b5b** and degraded polymer **D-P4b5b**.

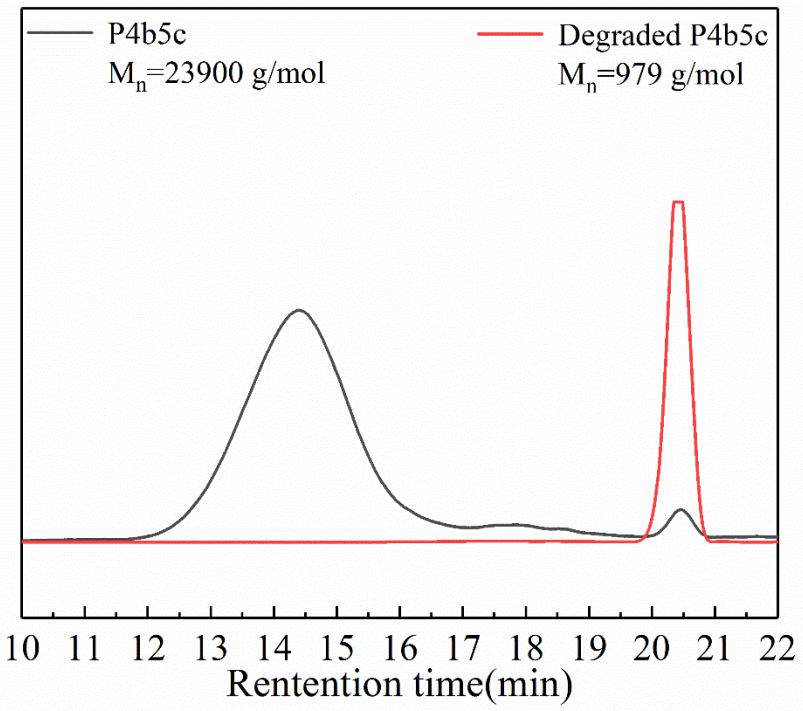


Figure S14. GPC curves of polymer **P-4b5c** and degraded polymer **D-P4b5c**.

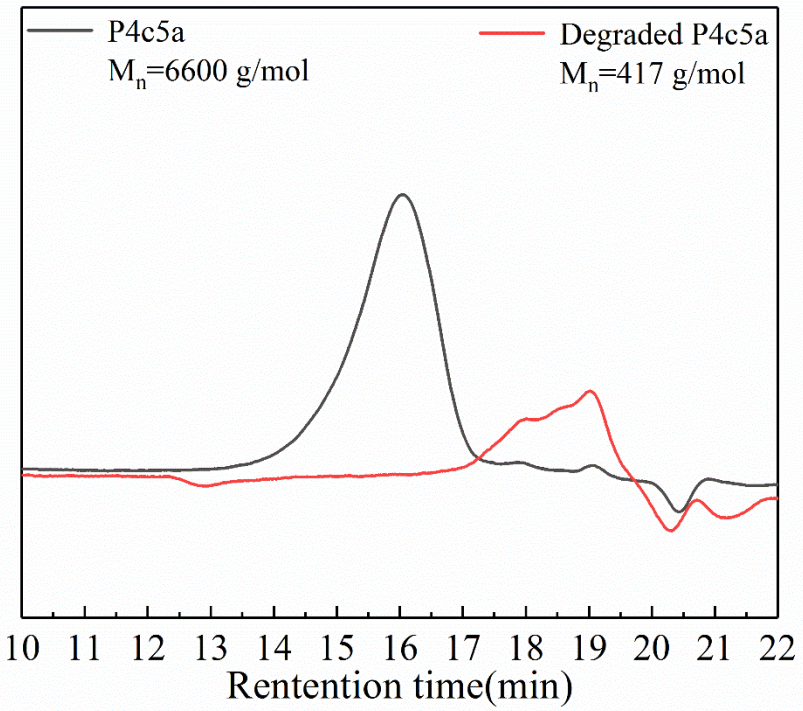


Figure S15. GPC curves of polymer **P-4c5a** and degraded polymer **D-P4c5a**.

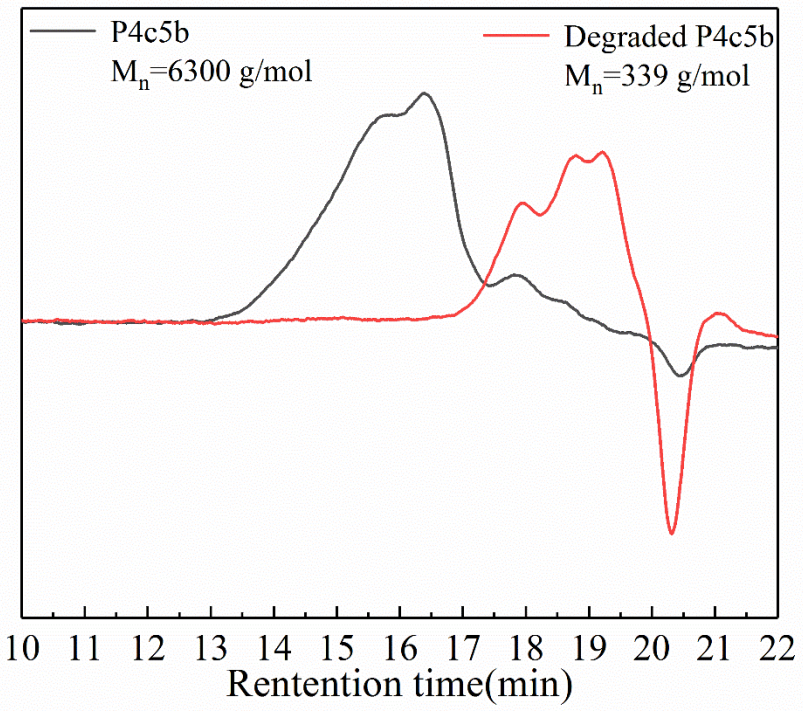


Figure S16. GPC curves of polymer **P-4c5b** and degraded polymer **D-P4c5b**.

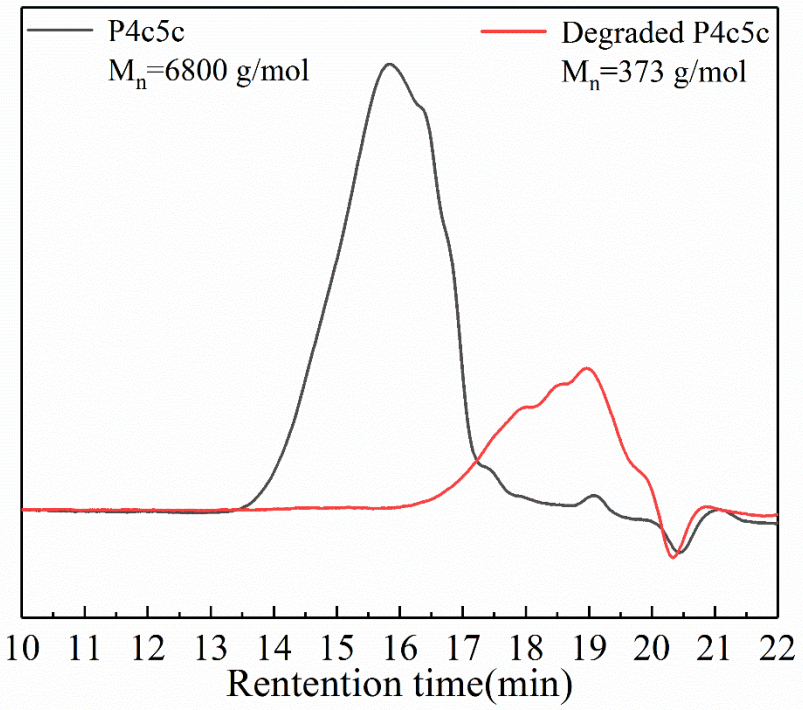


Figure S17. GPC curves of polymer **P-4c5c** and degraded polymer **D-P4c5c**.

8. FT-IR spectra

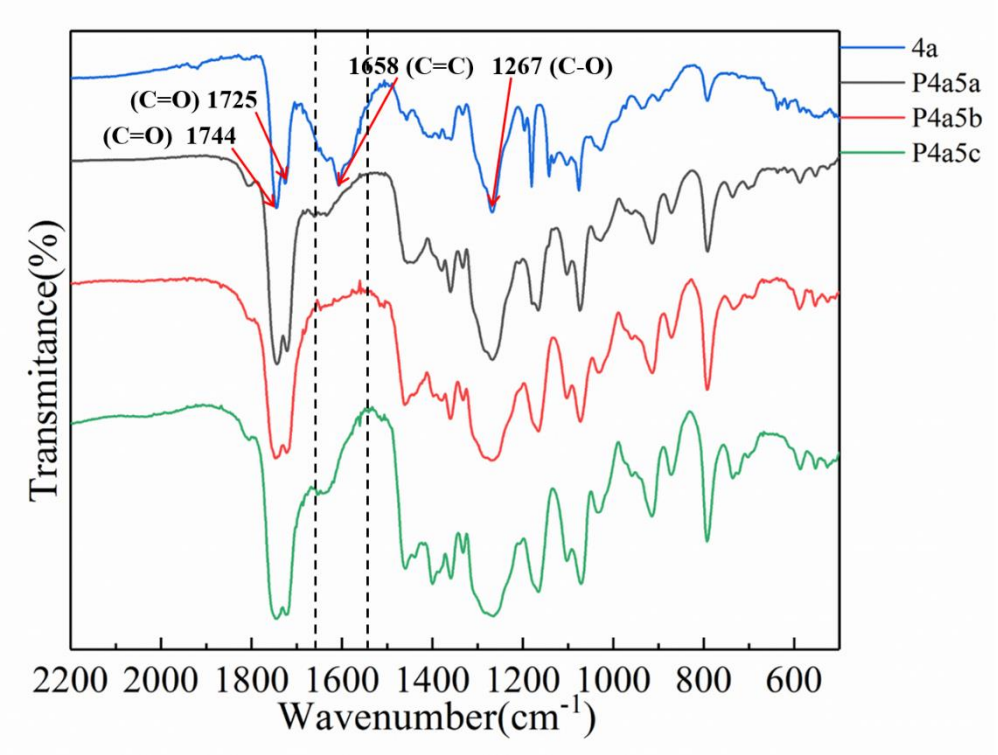


Figure S18. FT-IR spectra of polymers **P4a5**.

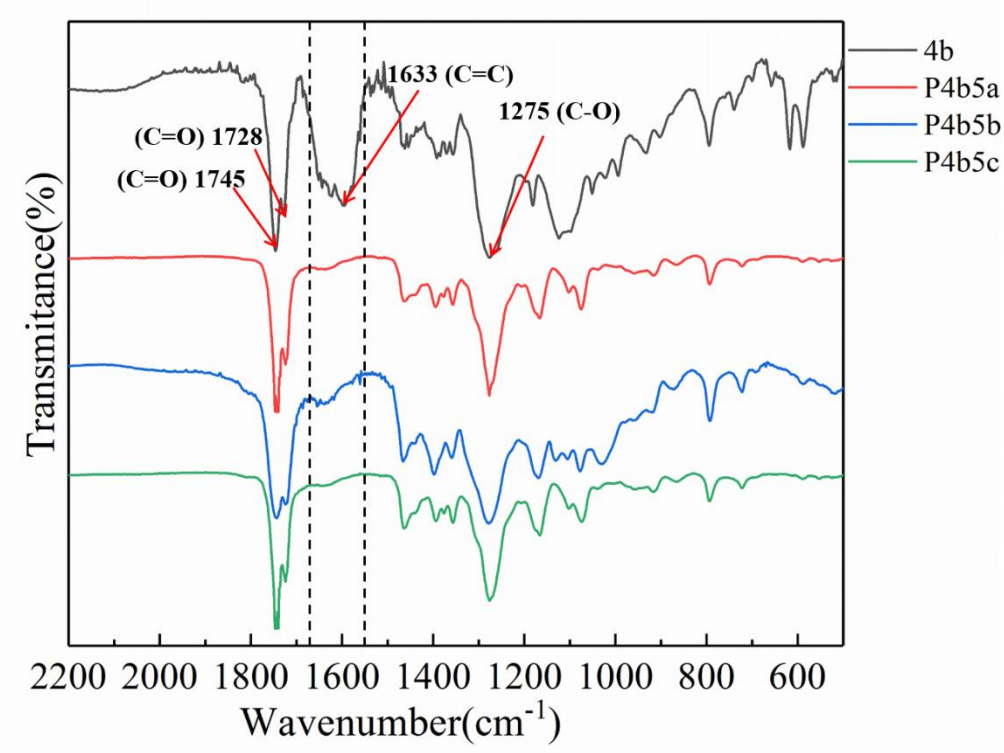


Figure S19. FT-IR spectra of polymers **P4b5**.

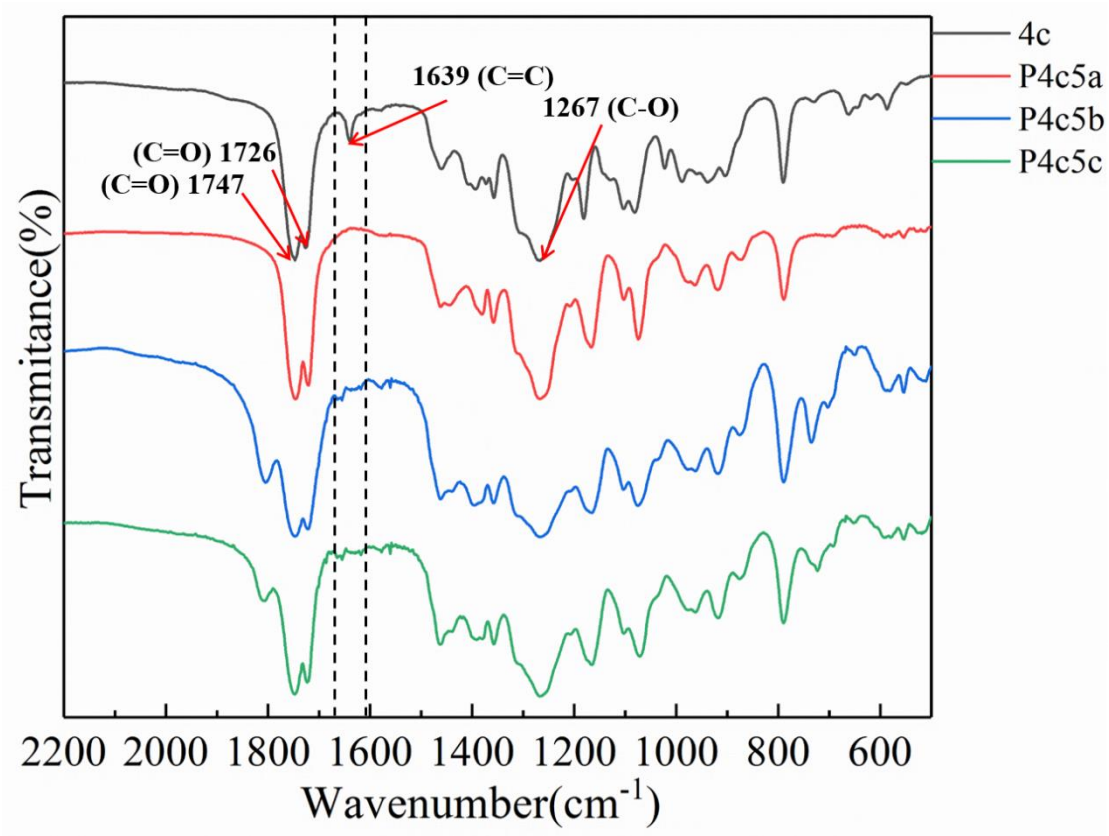


Figure S20. FT-IR spectra of polymers **P4c5**.

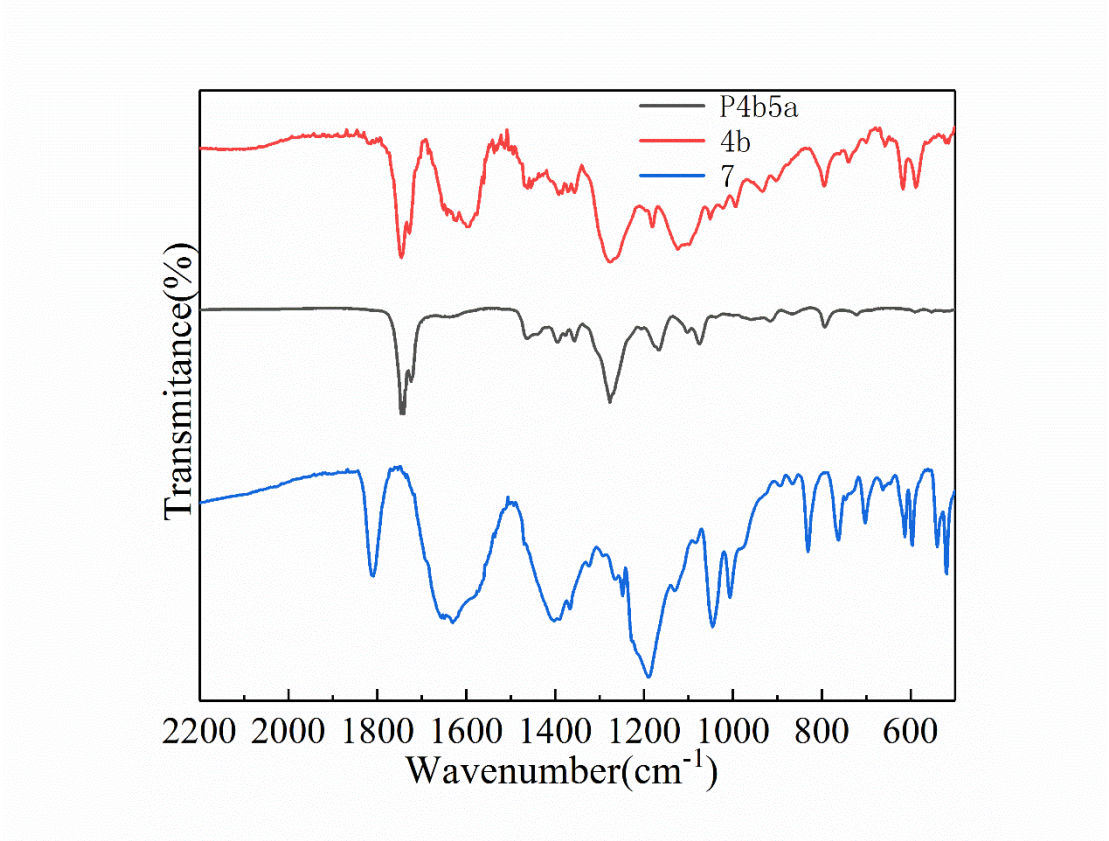


Figure S21. FT-IR spectra of **P4b5a**, **4b** and **7**.

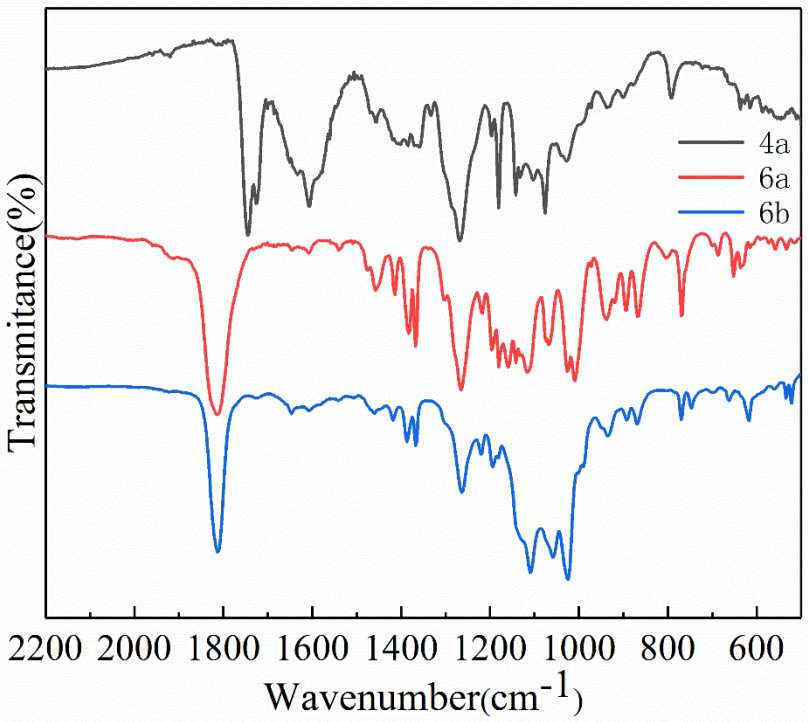


Figure S22. FT-IR spectra of **4a**, **6a** and **6b**.

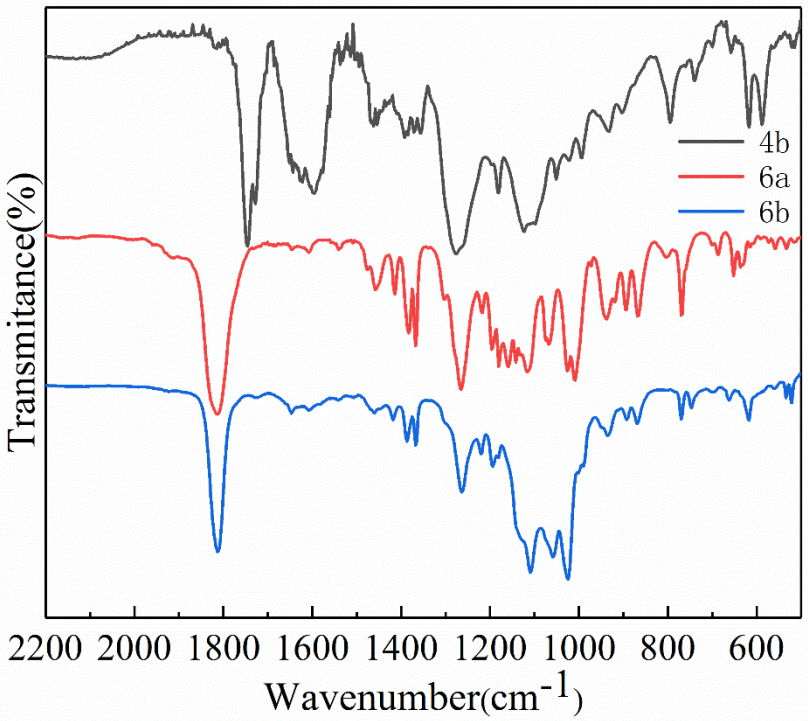


Figure S23. FT-IR spectra of **4b**, **6a** and **6b**.

8. NMR Spectra

8.1 NMR spectra of **4a**

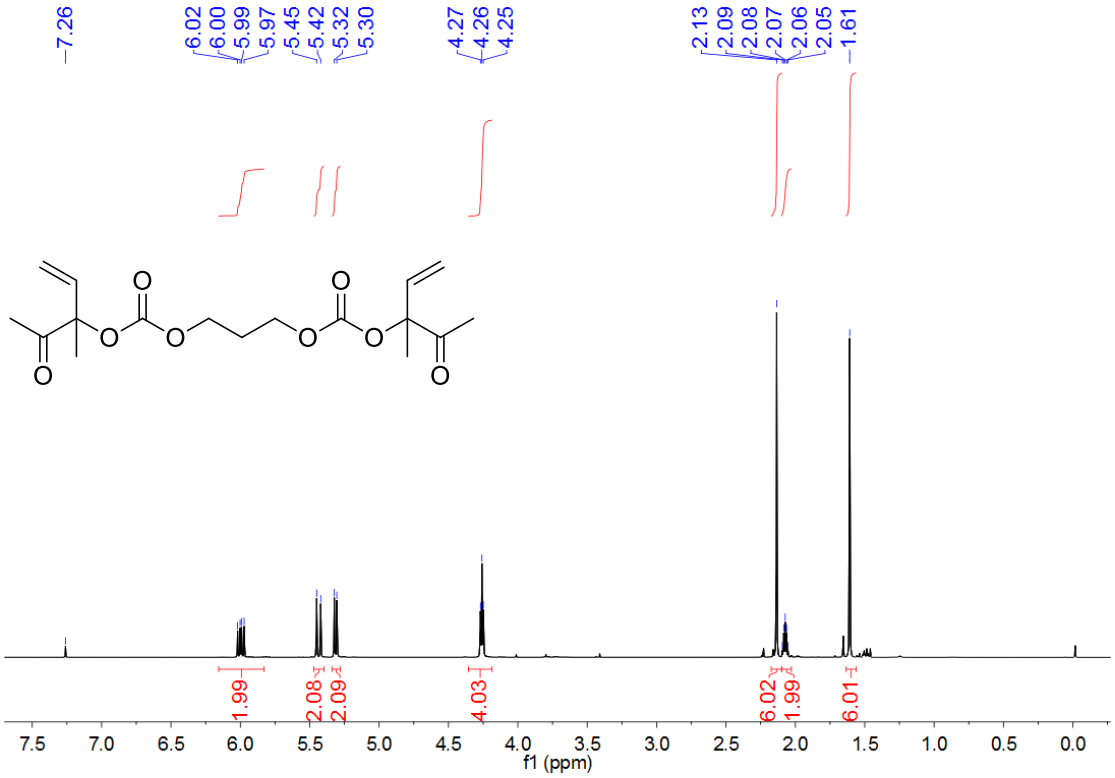


Figure S24. ^{1}H NMR spectrum of **4a**.

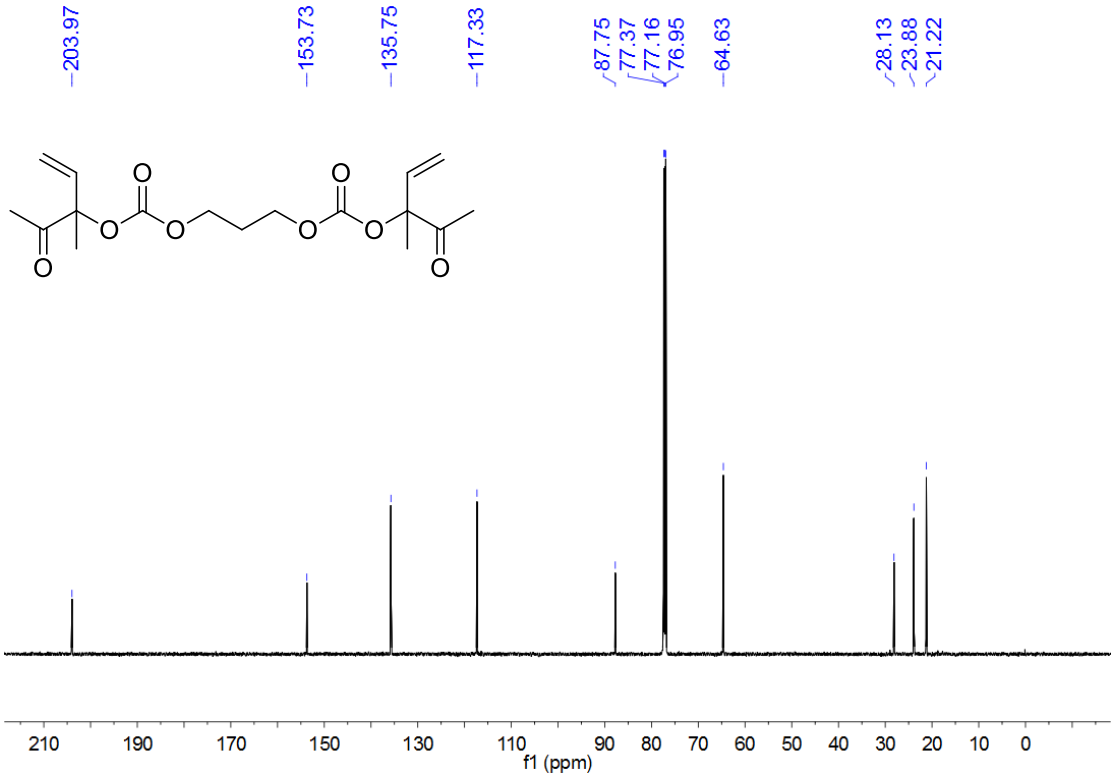


Figure S25. ^{13}C NMR spectrum of **4a**.

8.2 NMR spectra of **4b**

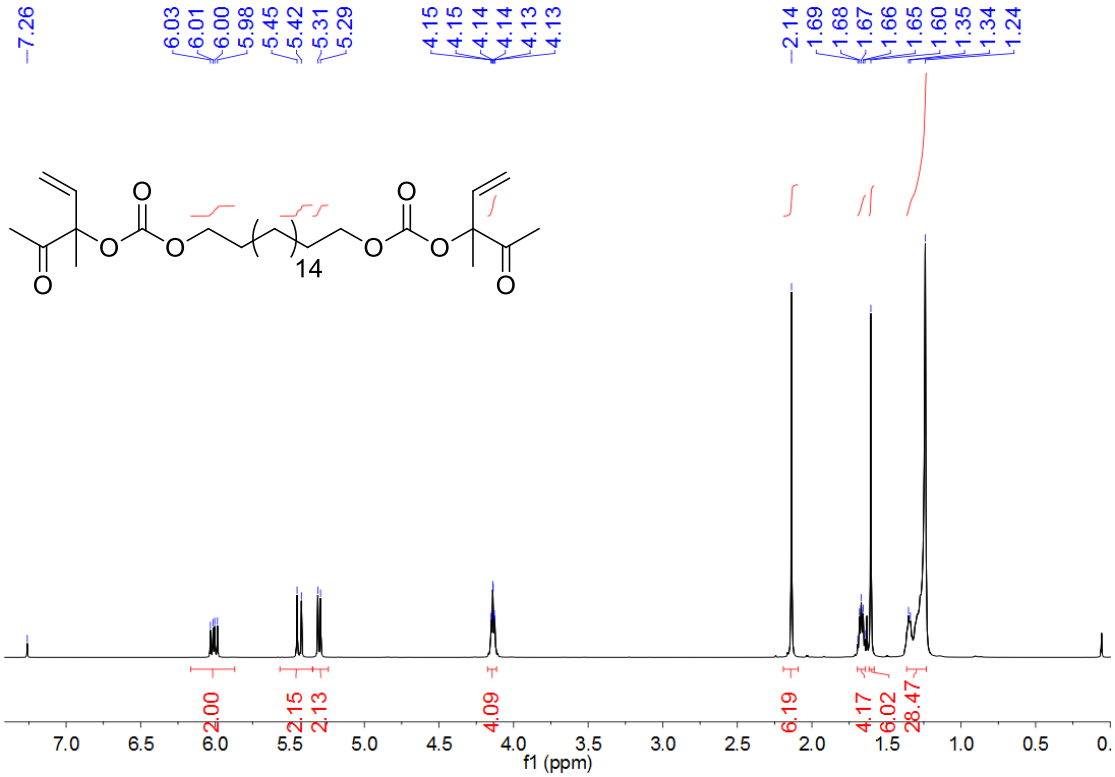


Figure S26. ^{1}H NMR spectrum of **4b**.

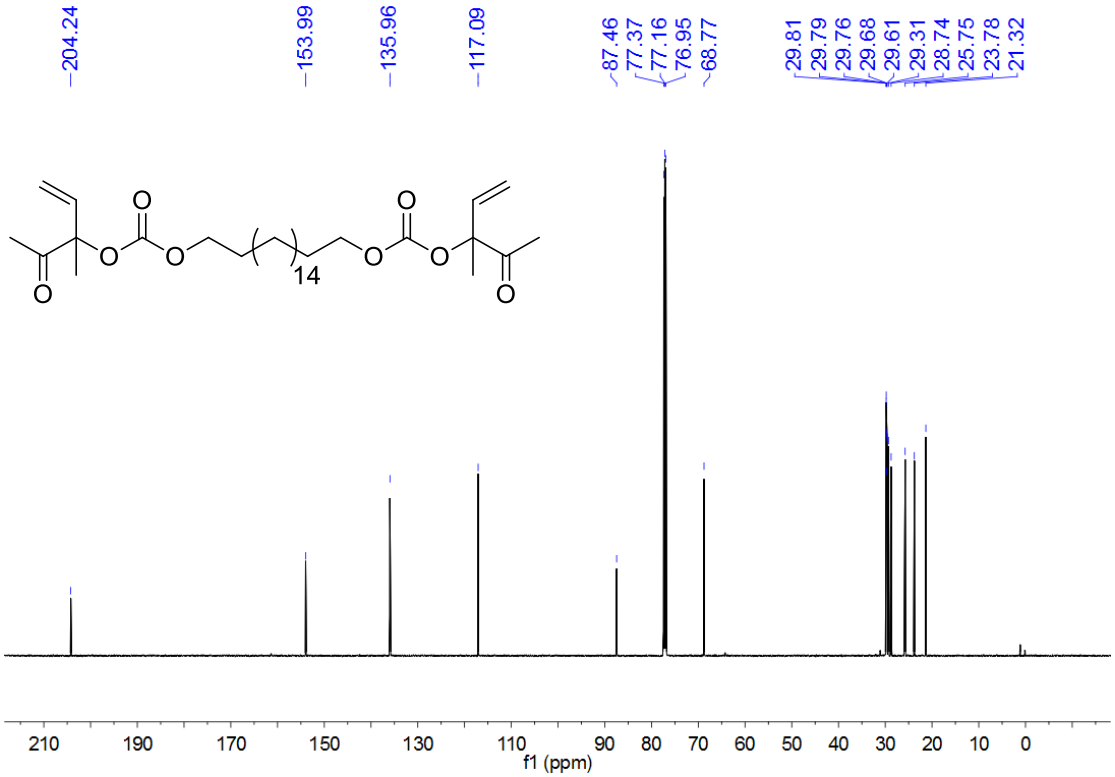


Figure S27. ^{13}C NMR spectrum of **4b**.

8.3 NMR spectra of **4c**

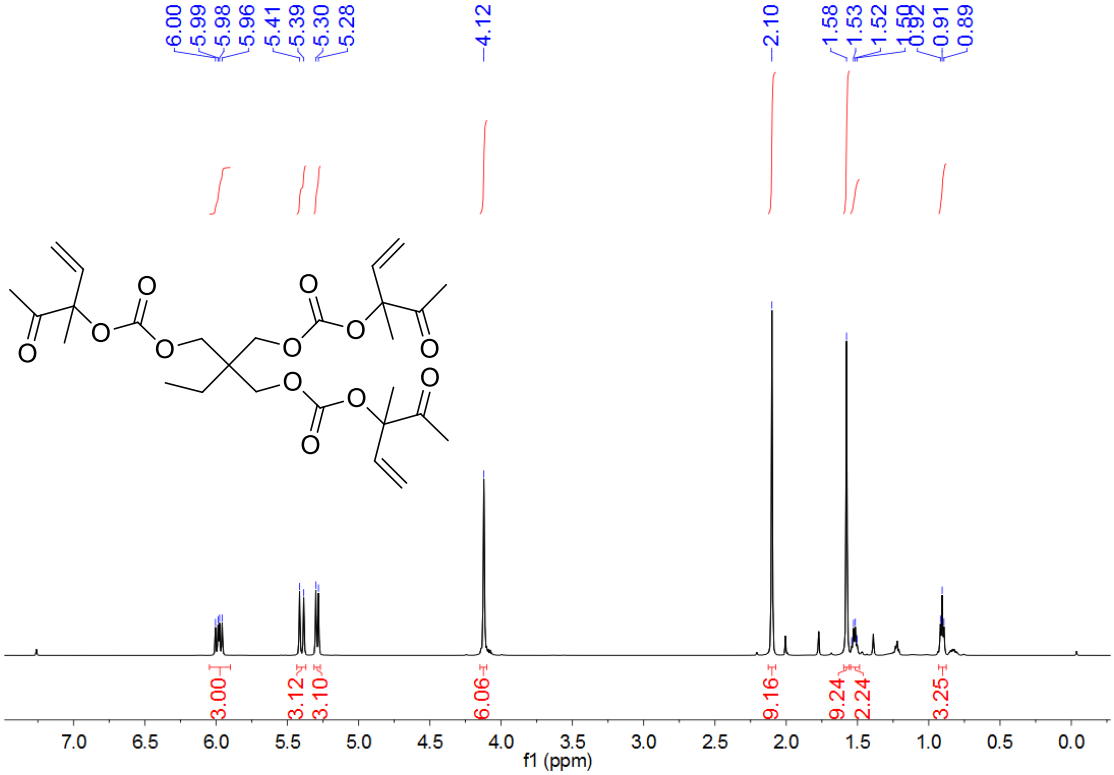


Figure S28. ^{1}H NMR spectrum of **4c**.

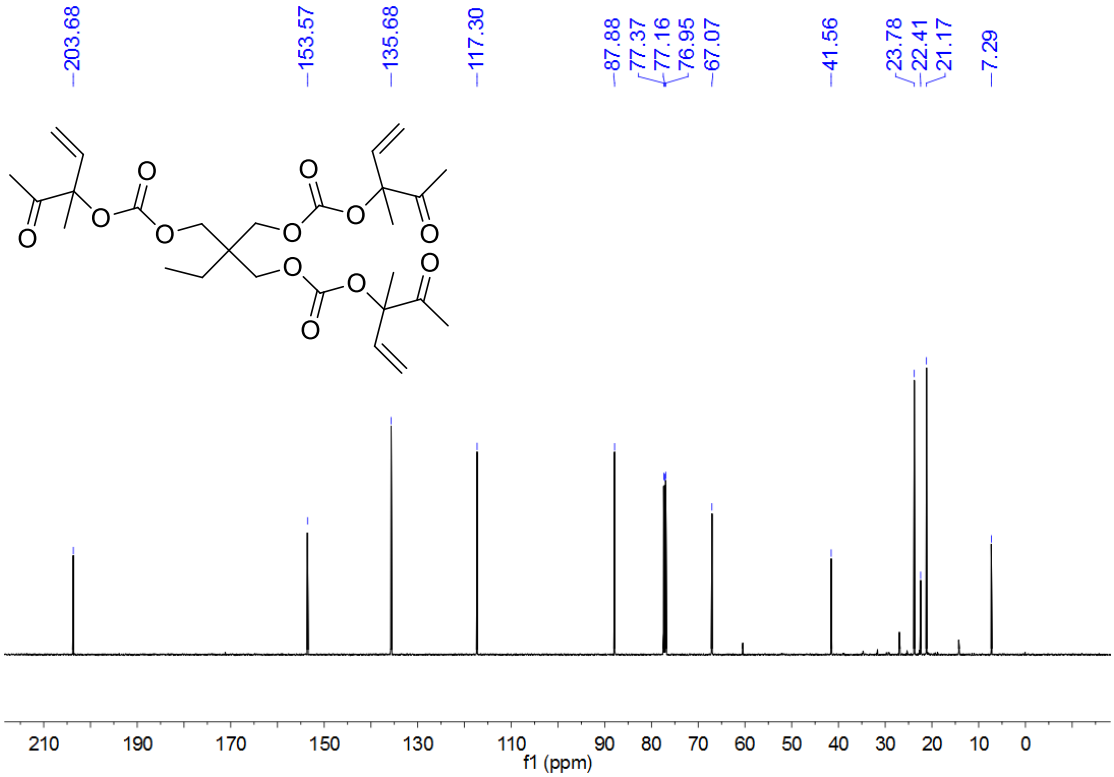


Figure S29. ^{13}C NMR spectrum of **4c**.

8.4 NMR spectra of **P4a5a**

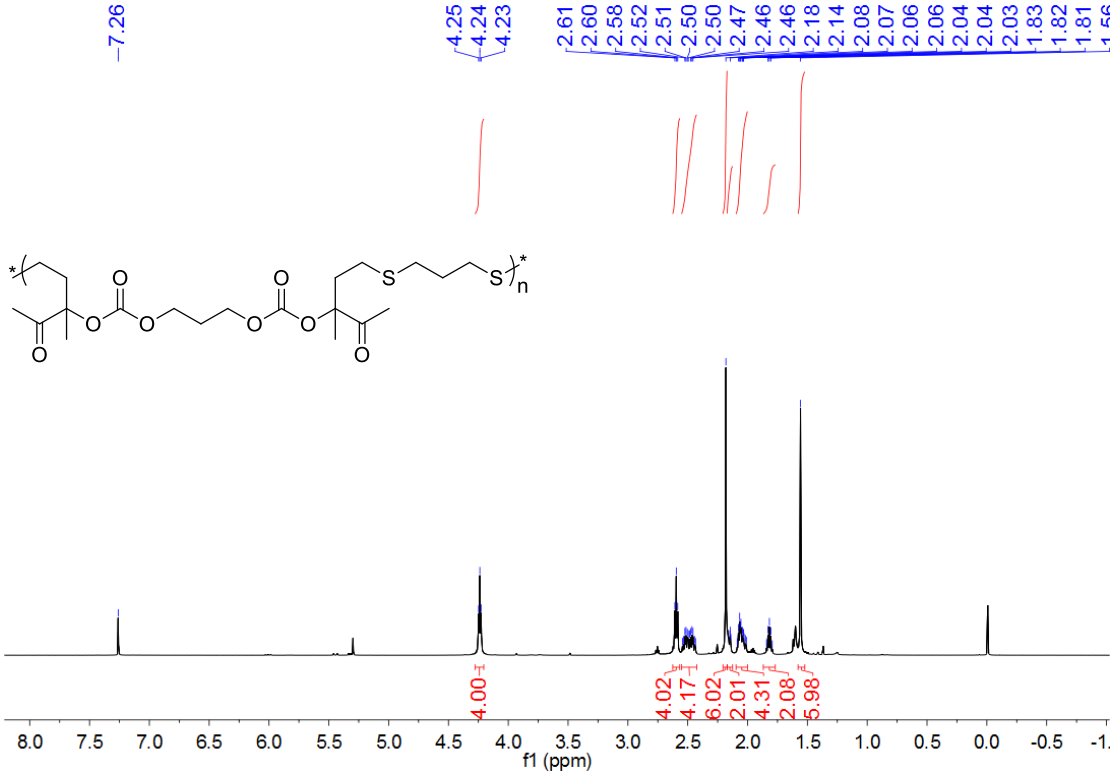


Figure S30. ^{1}H NMR spectrum of **P4a5a**.

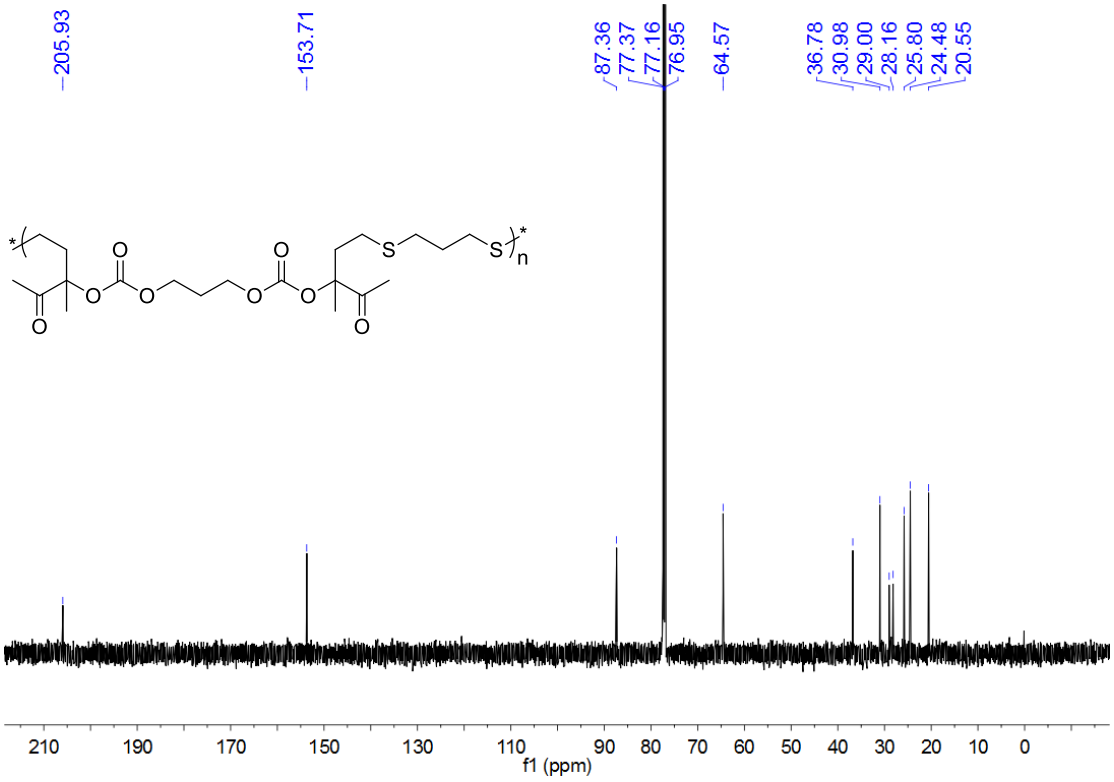


Figure S31. ^{13}C NMR spectrum of **P4a5a**.

8.5 NMR spectra of **P4a5b**

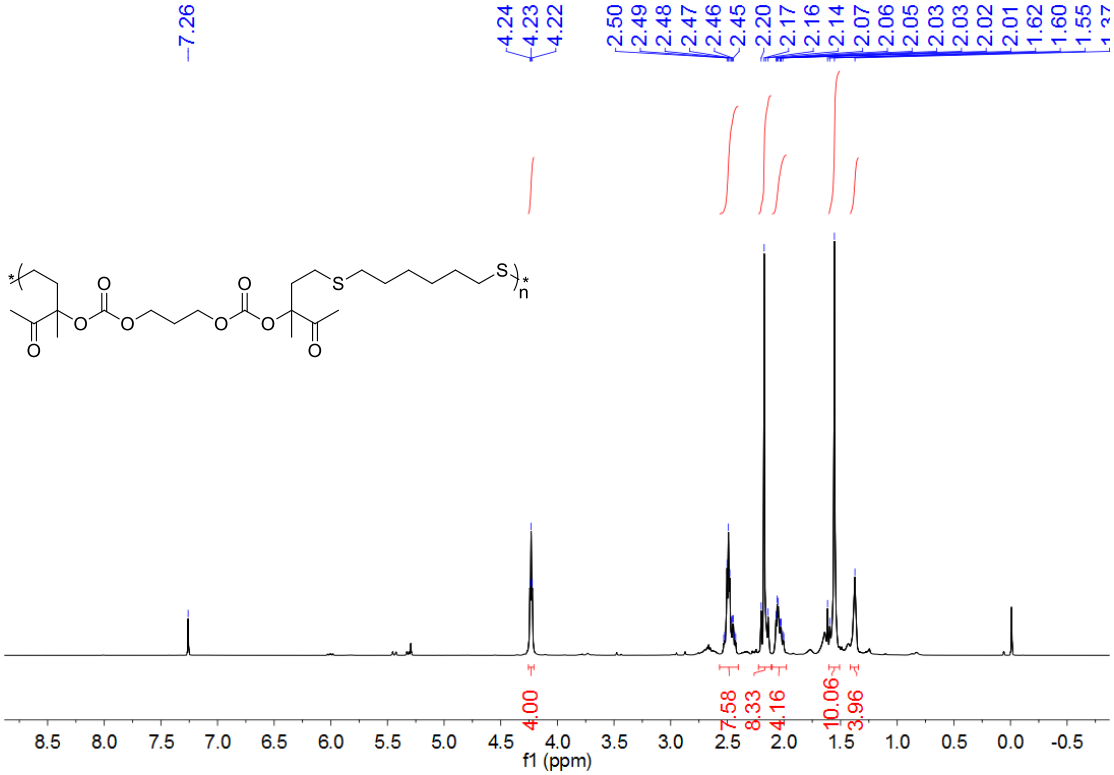


Figure S32. ^{1}H NMR spectrum of **P4a5b**.

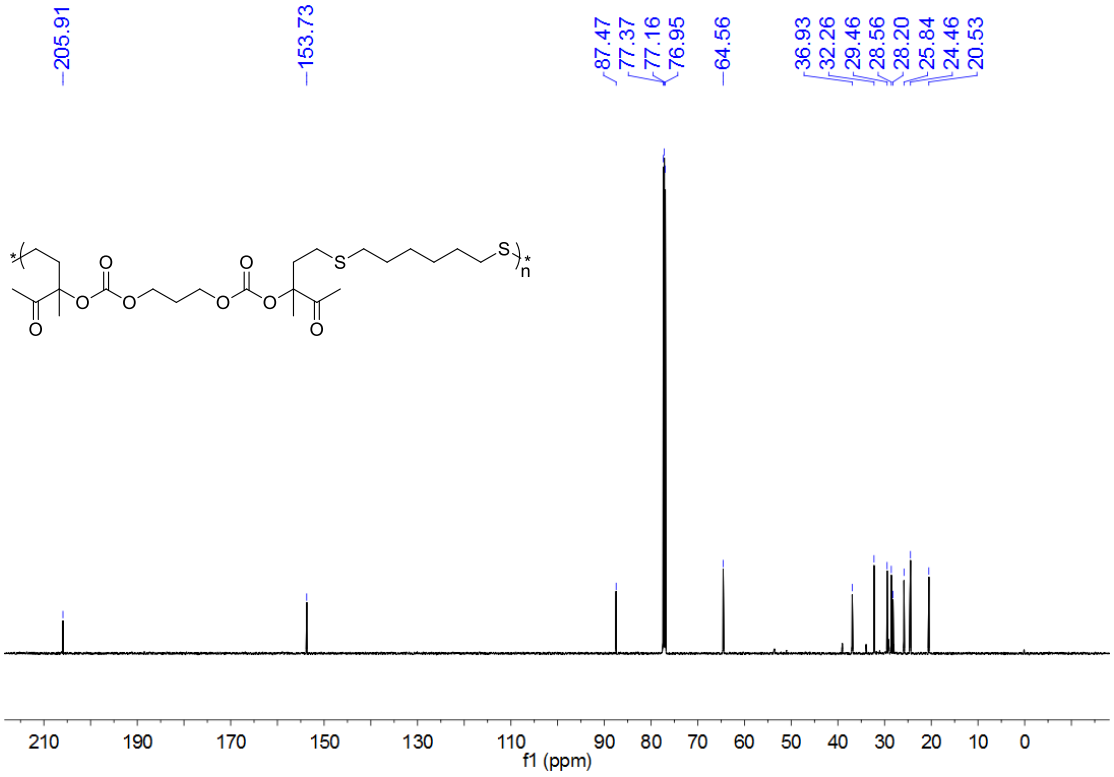


Figure S33. ^{13}C NMR spectrum of **P4a5b**.

8.6 NMR spectra of **P4a5c**

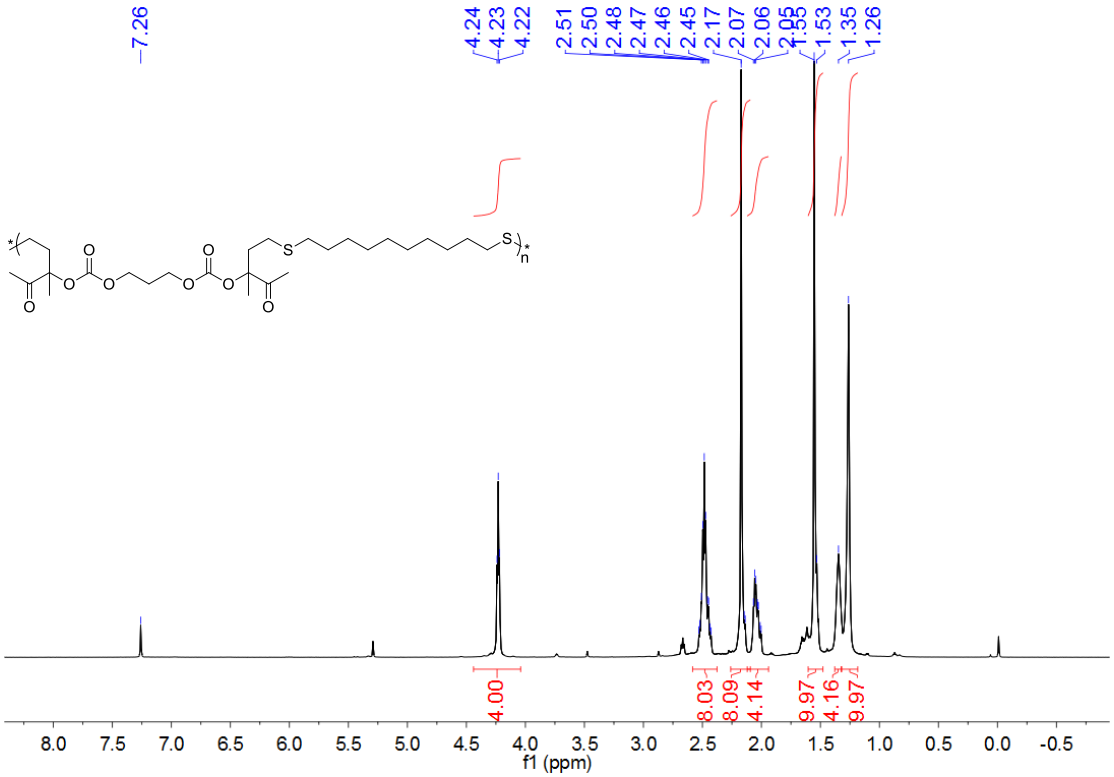


Figure S34 ^{1}H NMR spectrum of **P4a5c**.

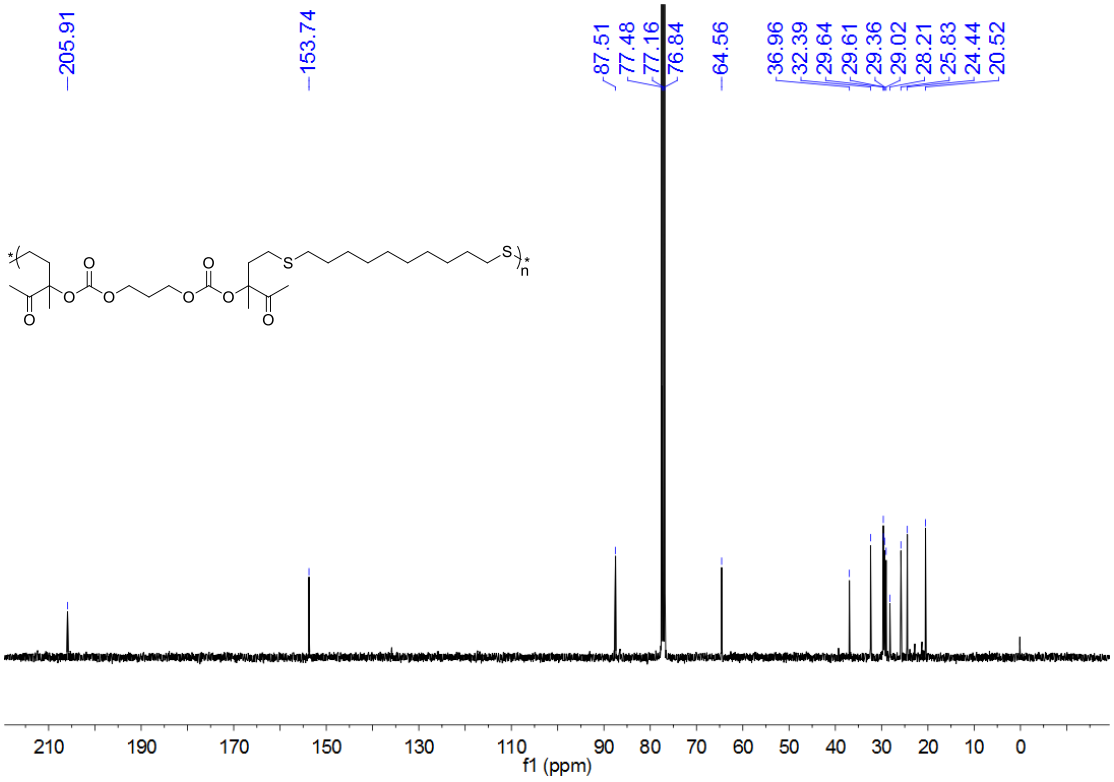


Figure S35. ^{13}C NMR spectrum of **P4a5c**.

8.7 NMR spectra of **P4b5a**

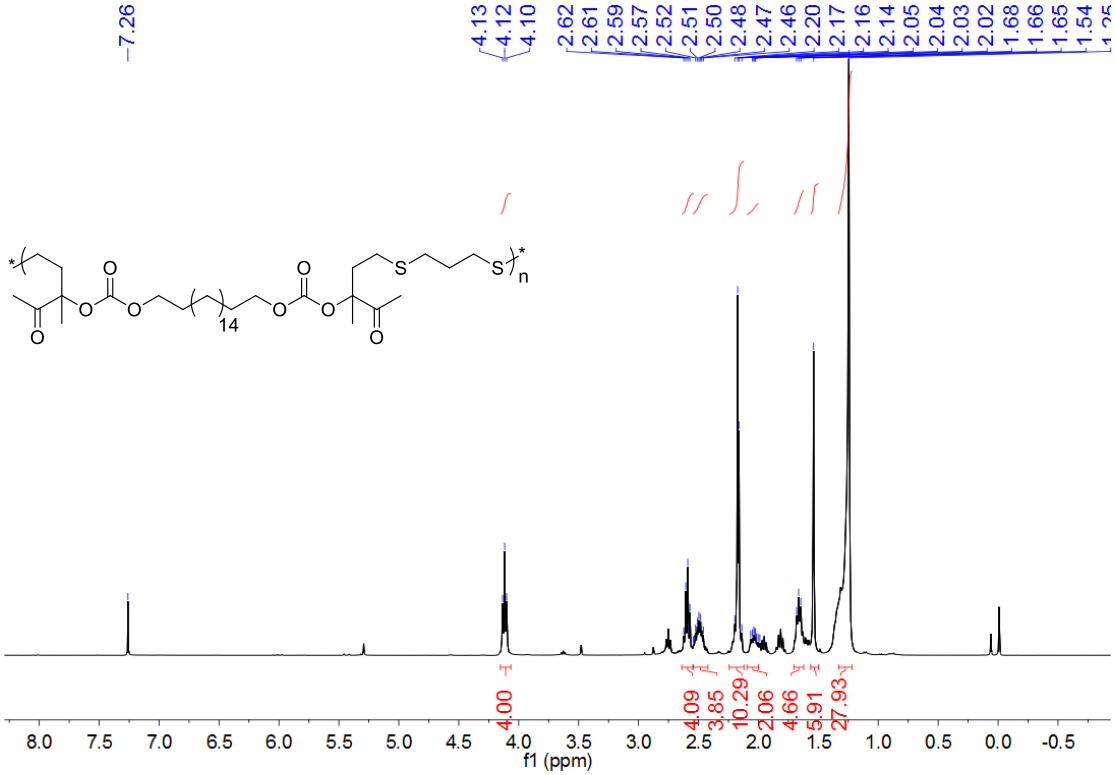


Figure S36. ^{1}H NMR spectrum of **P4b5a**.

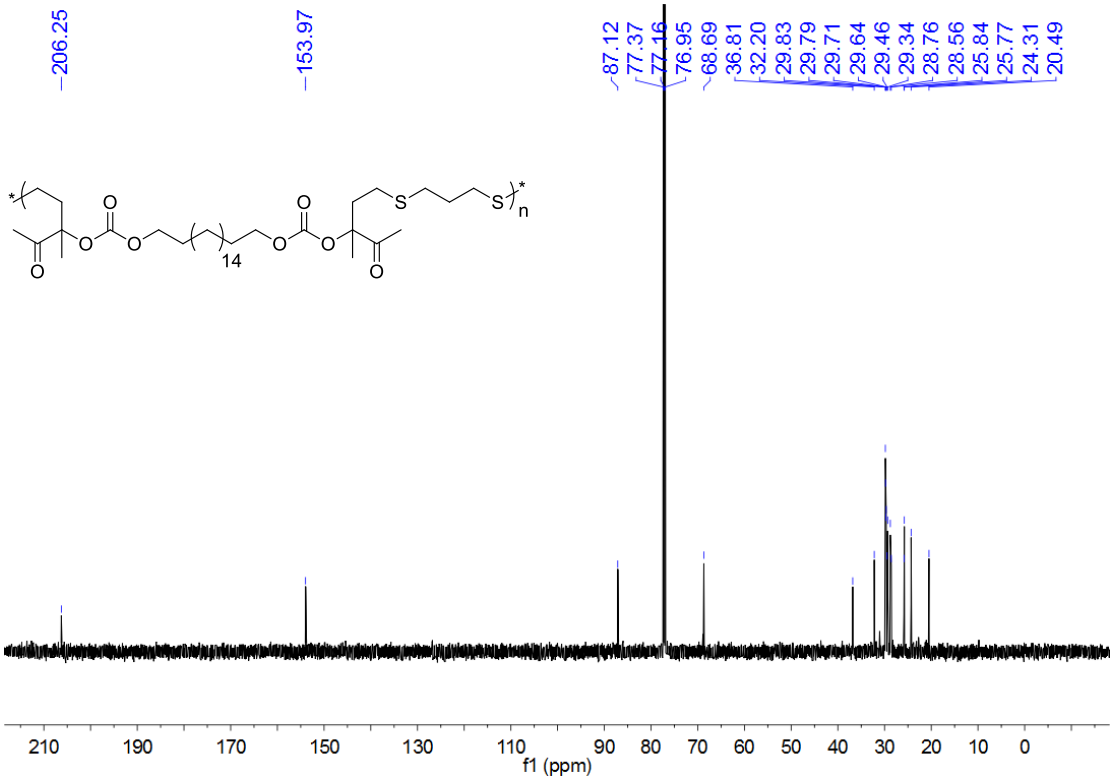


Figure S37. ^{13}C NMR spectrum of **P4b5a**.

8.8 NMR spectra of **P4b5b**

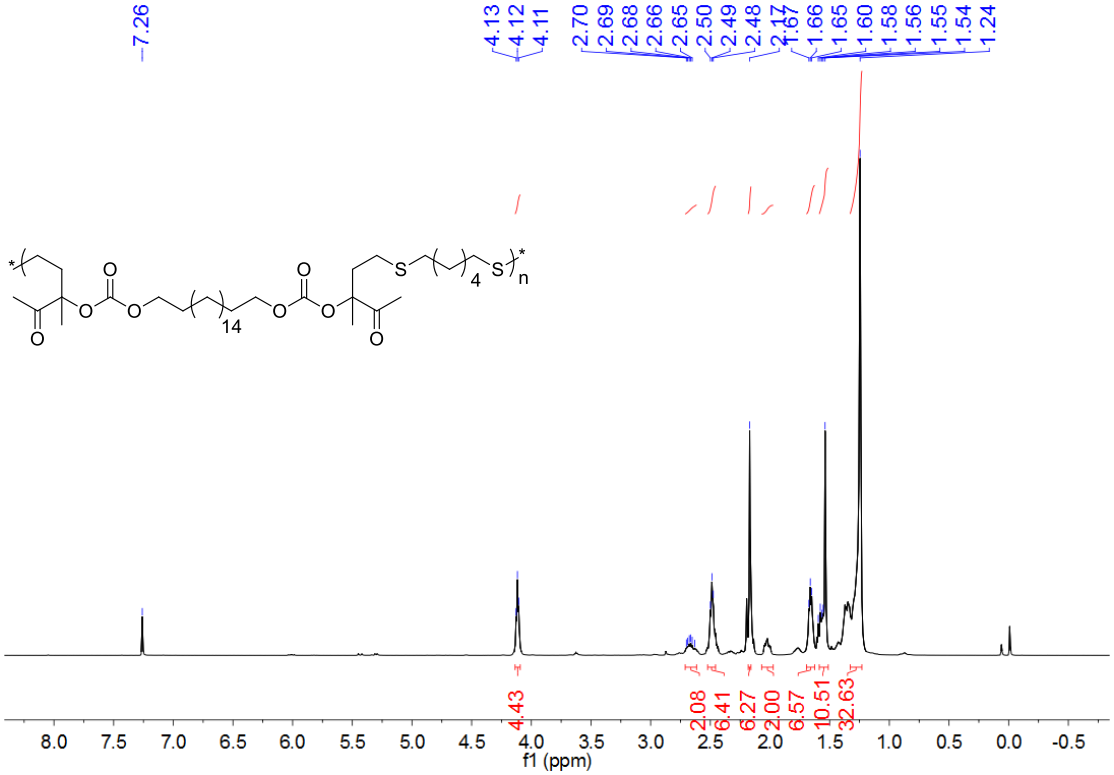


Figure S38. ^{1}H NMR spectrum of **P4b5b**.

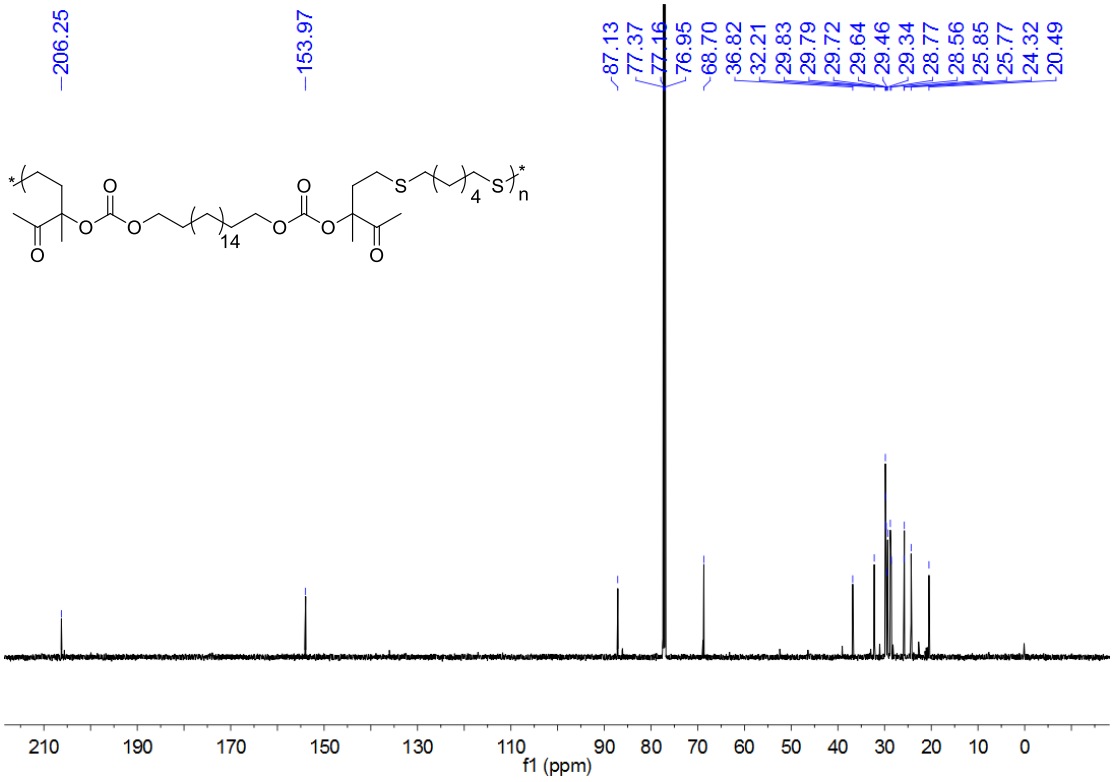


Figure S39. ^{13}C NMR spectrum of **P4b5b**.

8.9 NMR spectra of **P4b5c**

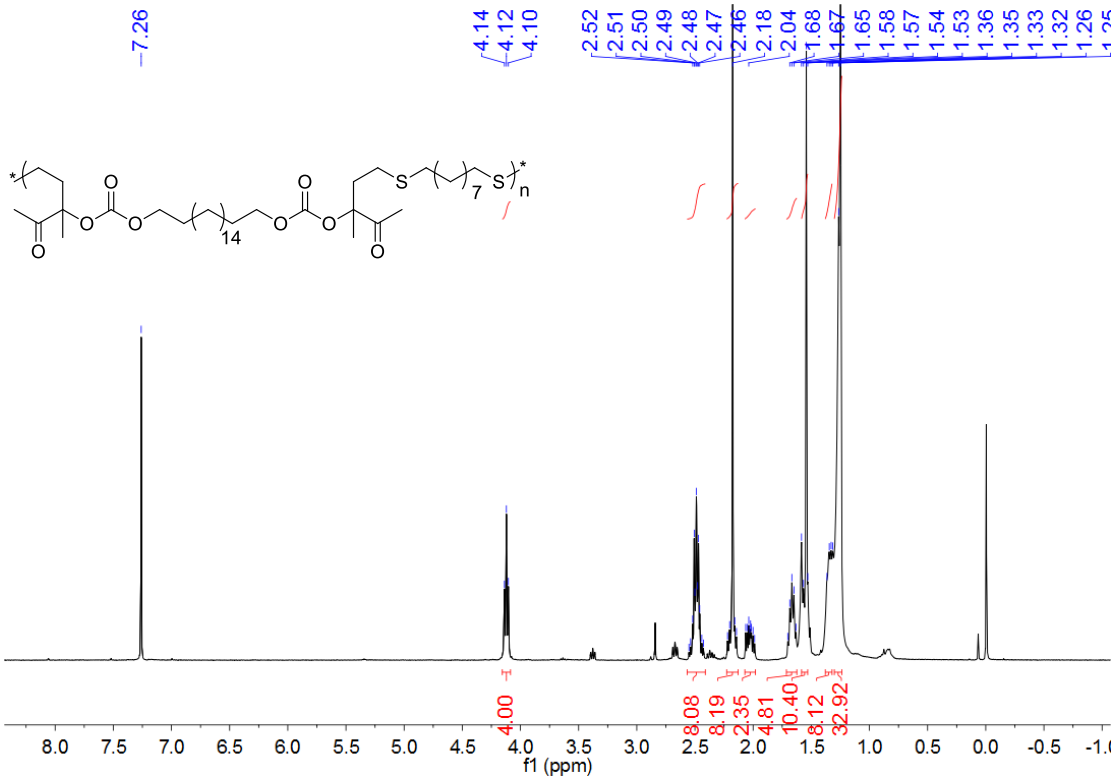


Figure S40. ^{1}H NMR spectrum of **P4b5c**.

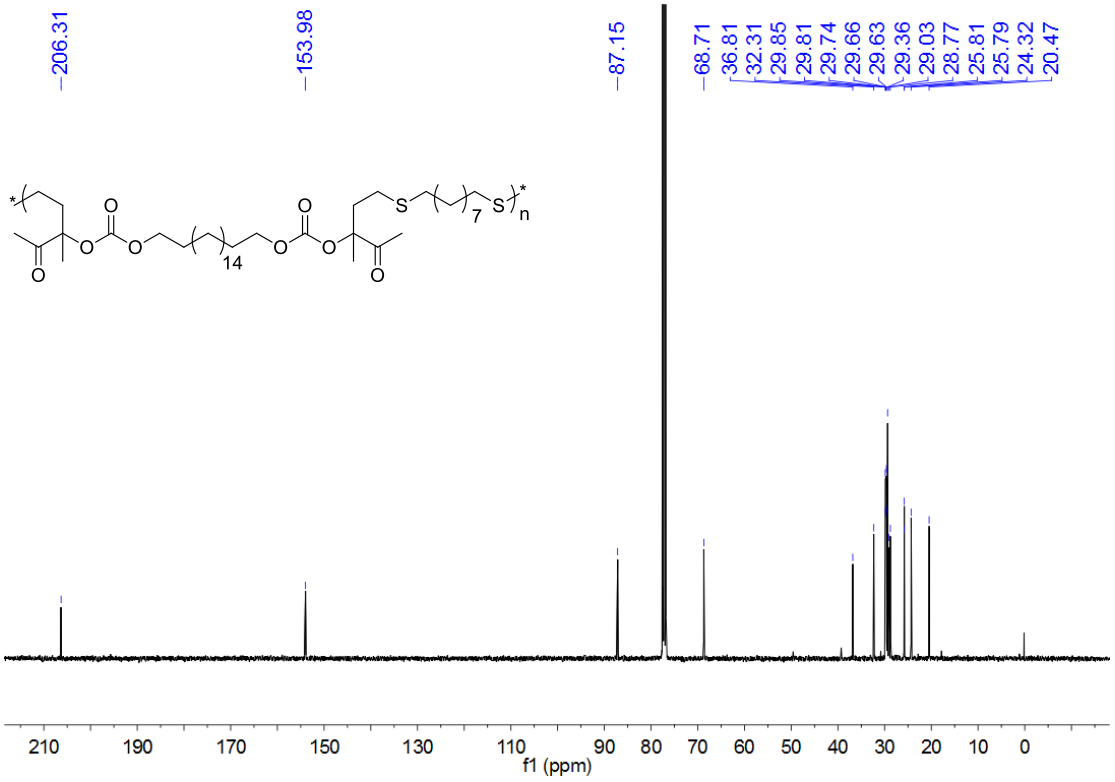


Figure S41. ^{13}C NMR spectrum of **P4b5c**.

8.10 NMR spectra of **P4c5a**

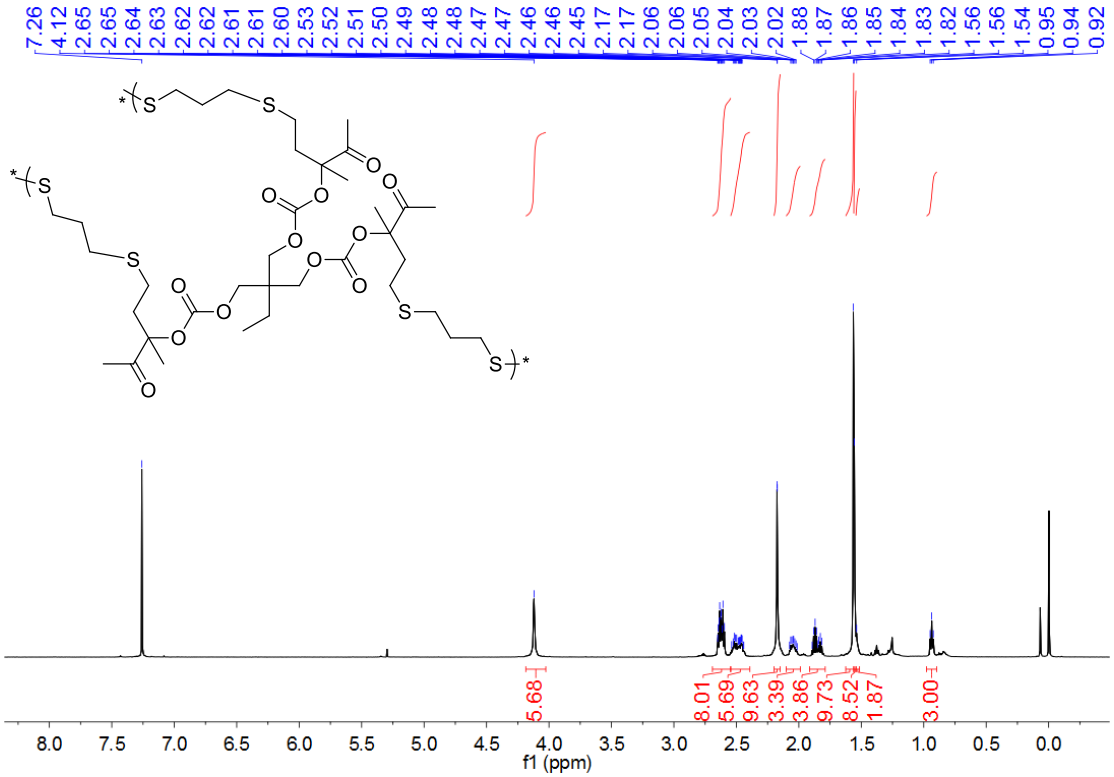


Figure S42. ^{1}H NMR spectrum of **P4c5a**.

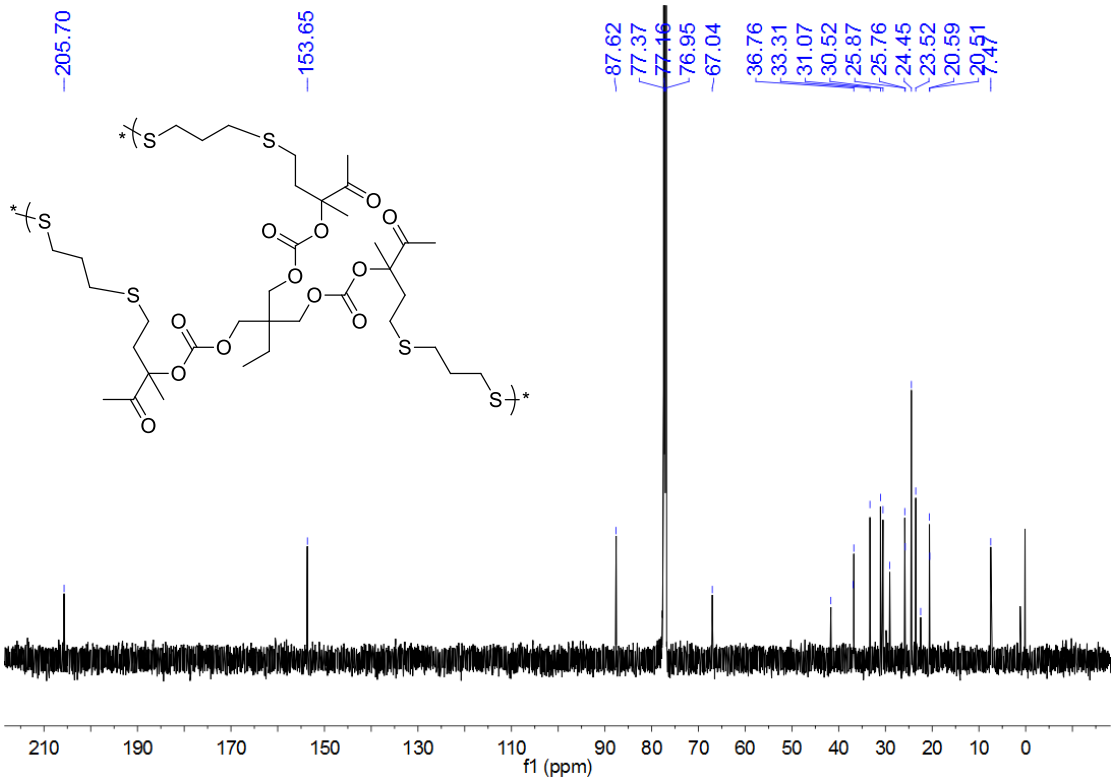


Figure S43. ^{13}C NMR spectrum of **P4c5a**.

8.11 NMR spectra of **P4c5b**

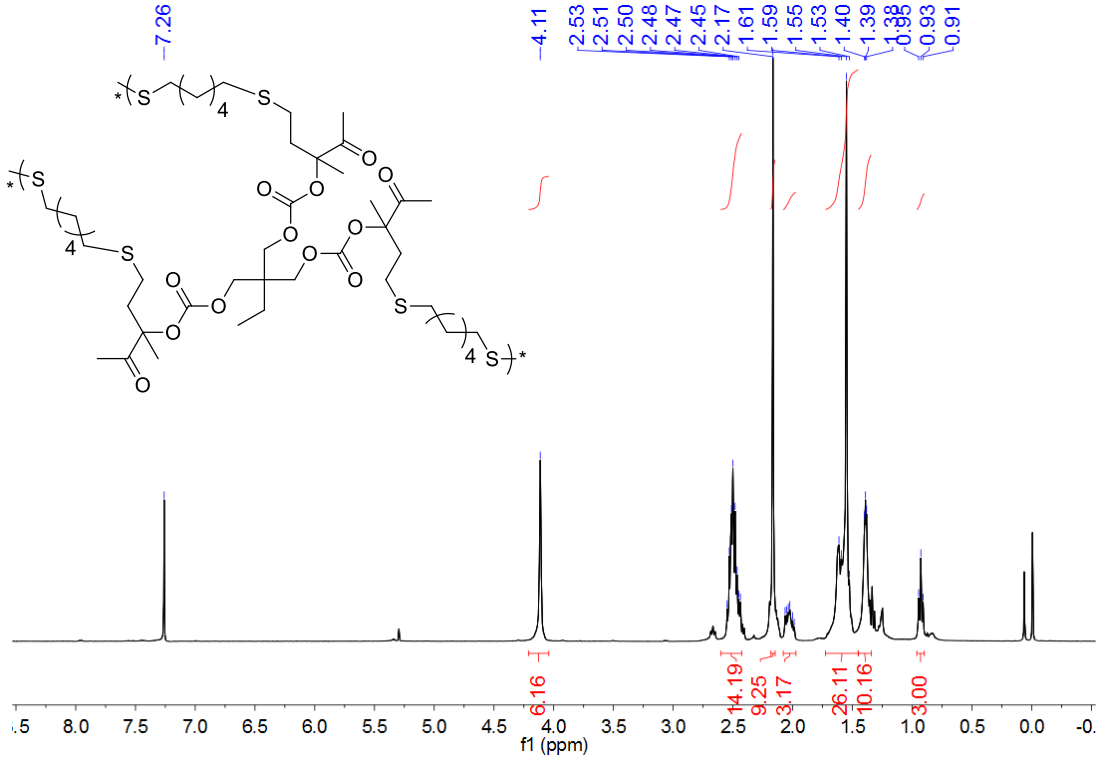


Figure S44. ^{1}H NMR spectrum of **P4c5b**.

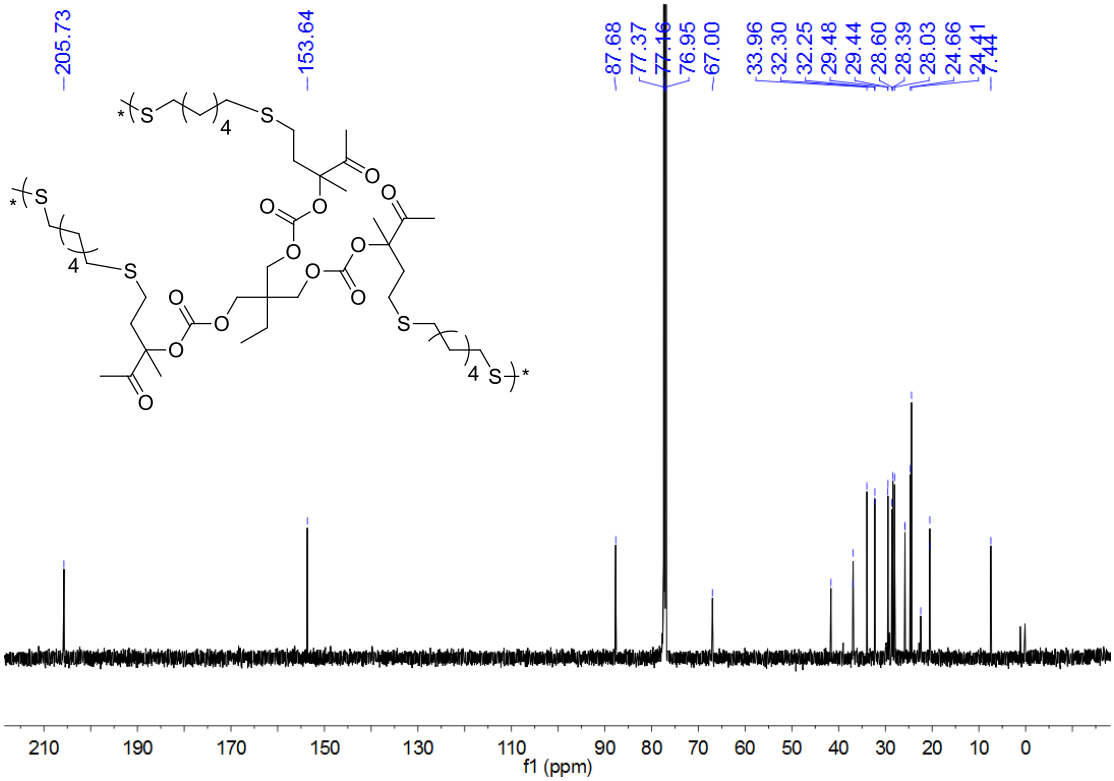


Figure S45. ^{13}C NMR spectrum of **P4c5b**.

8.12 NMR spectra of **P4c5c**

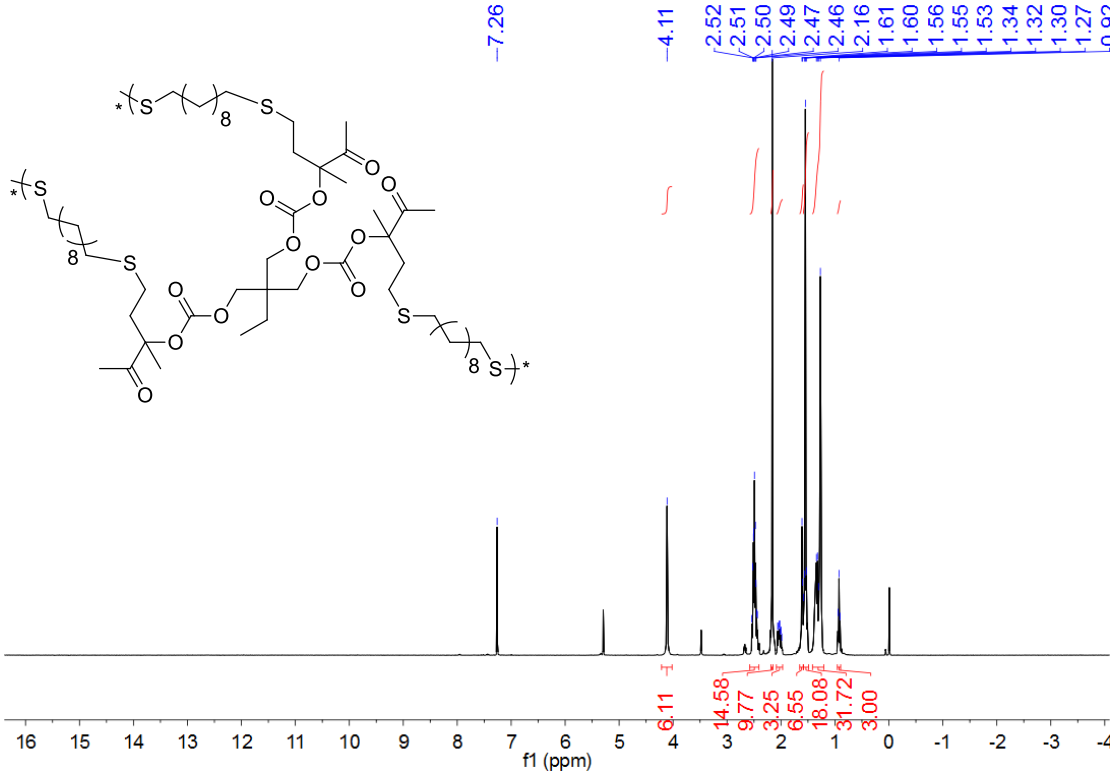


Figure S46. ^{1}H NMR spectrum of **P4c5c**.

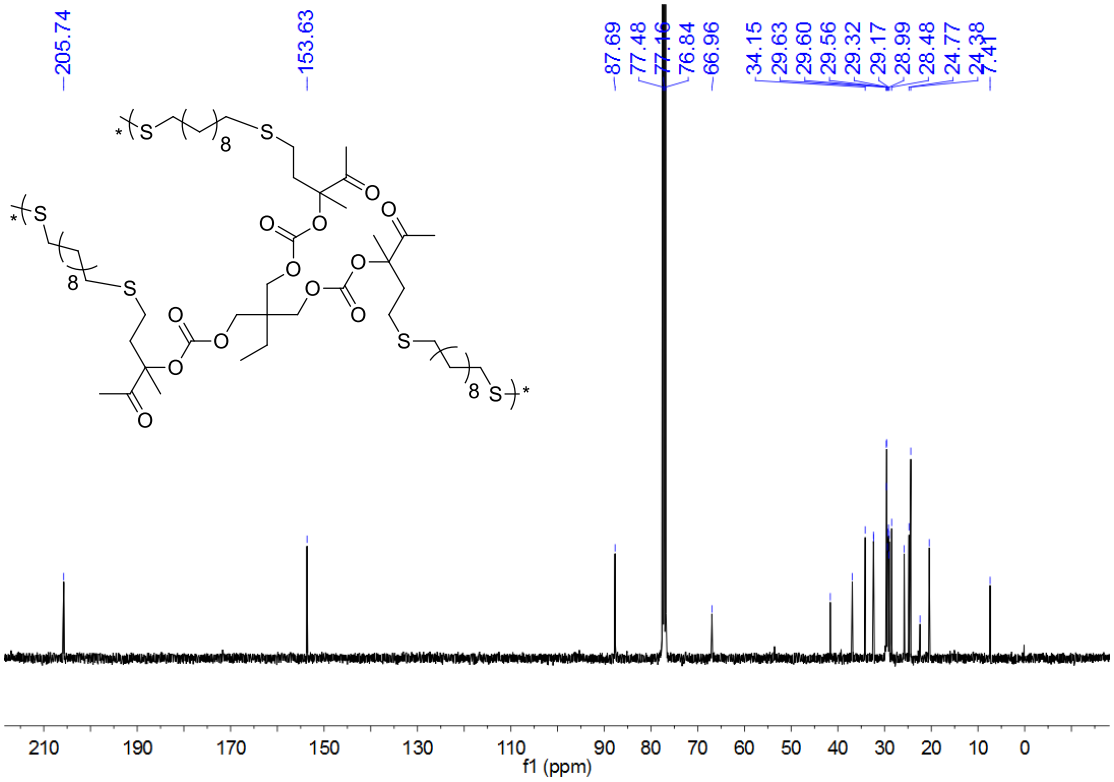


Figure S47. ^{13}C NMR spectrum of **P4c5c**.

8.13 NMR spectra of **6**

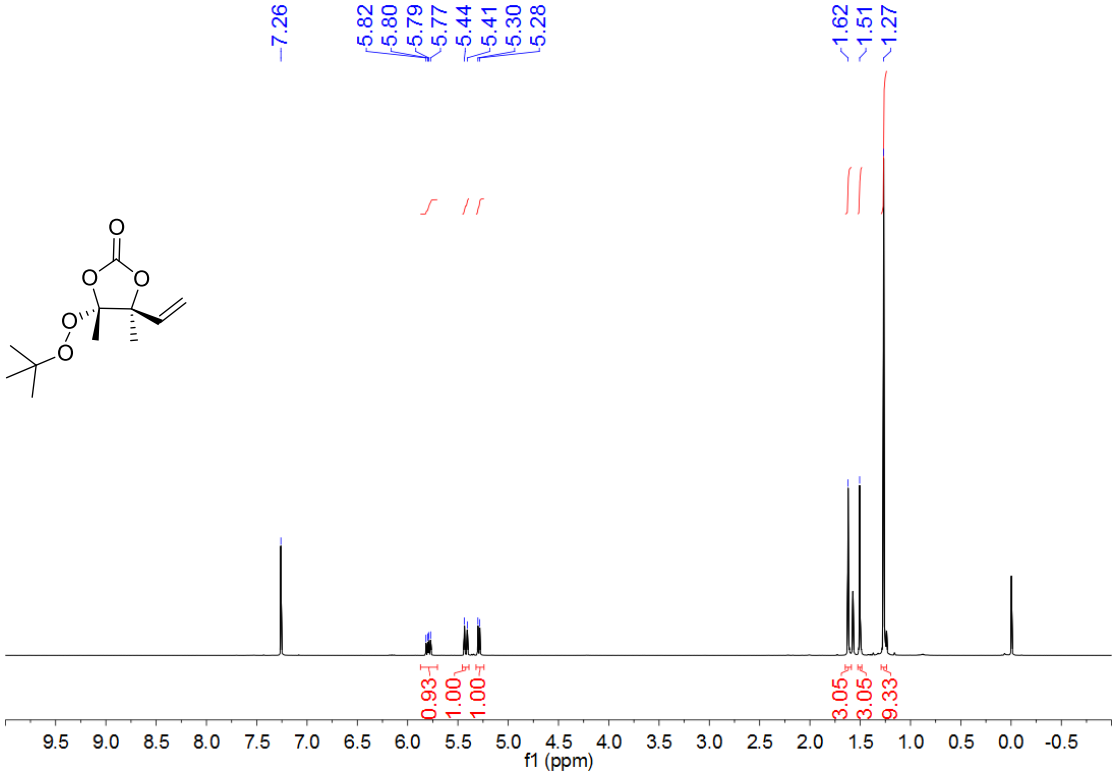


Figure S48. ^{1}H NMR spectrum of **6a**.

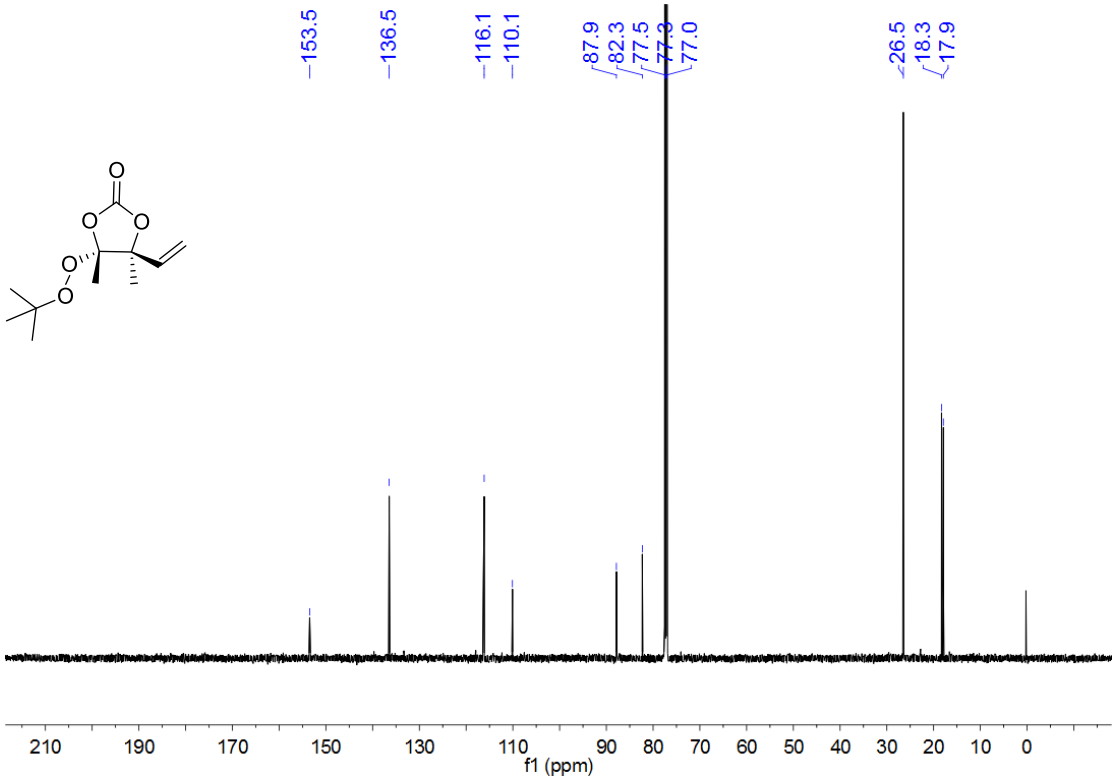


Figure S49. ^{13}C NMR spectrum of **6a**.

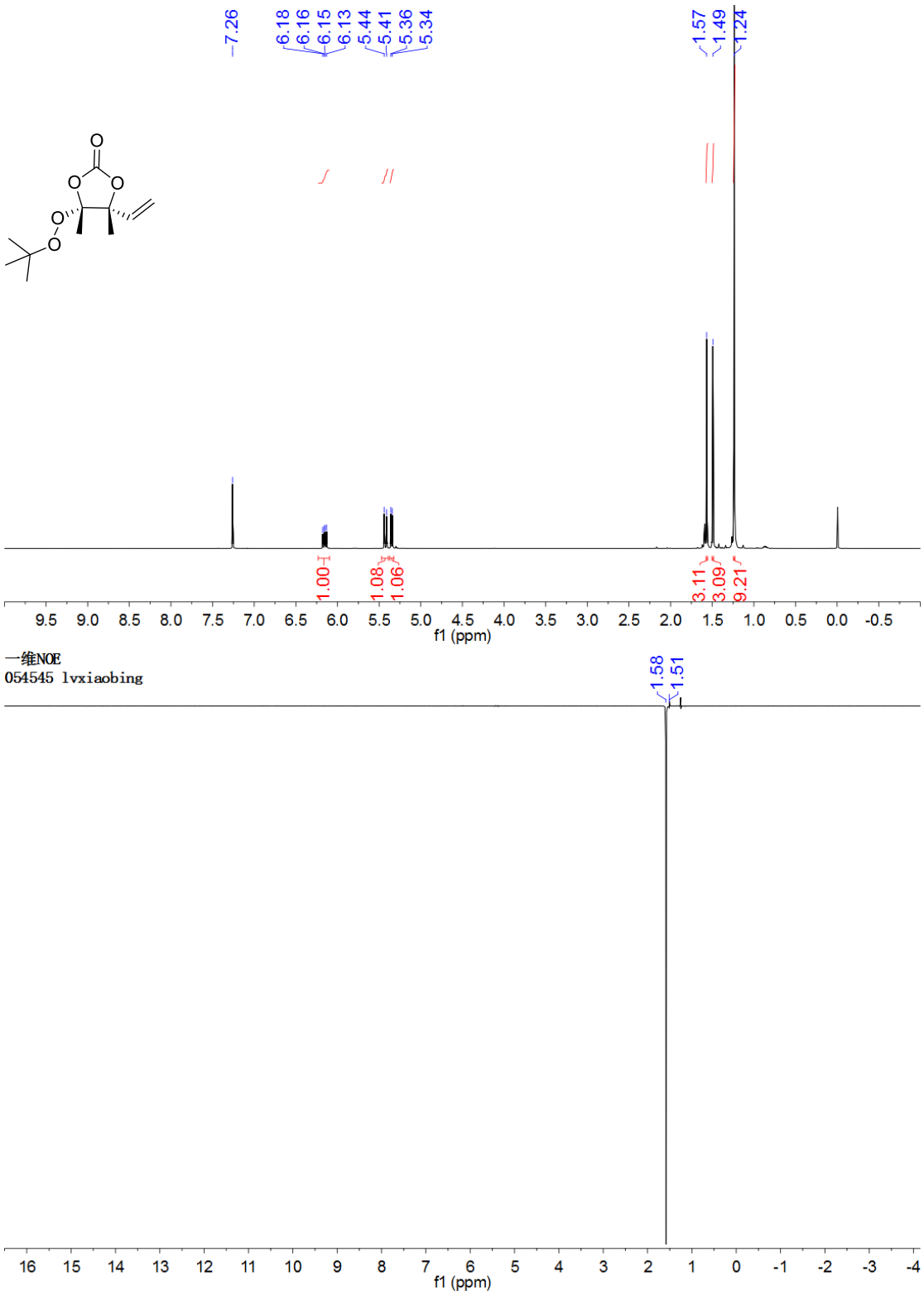


Figure S50. ^{1}H NMR spectrum and NOE spectrum of **6b.**

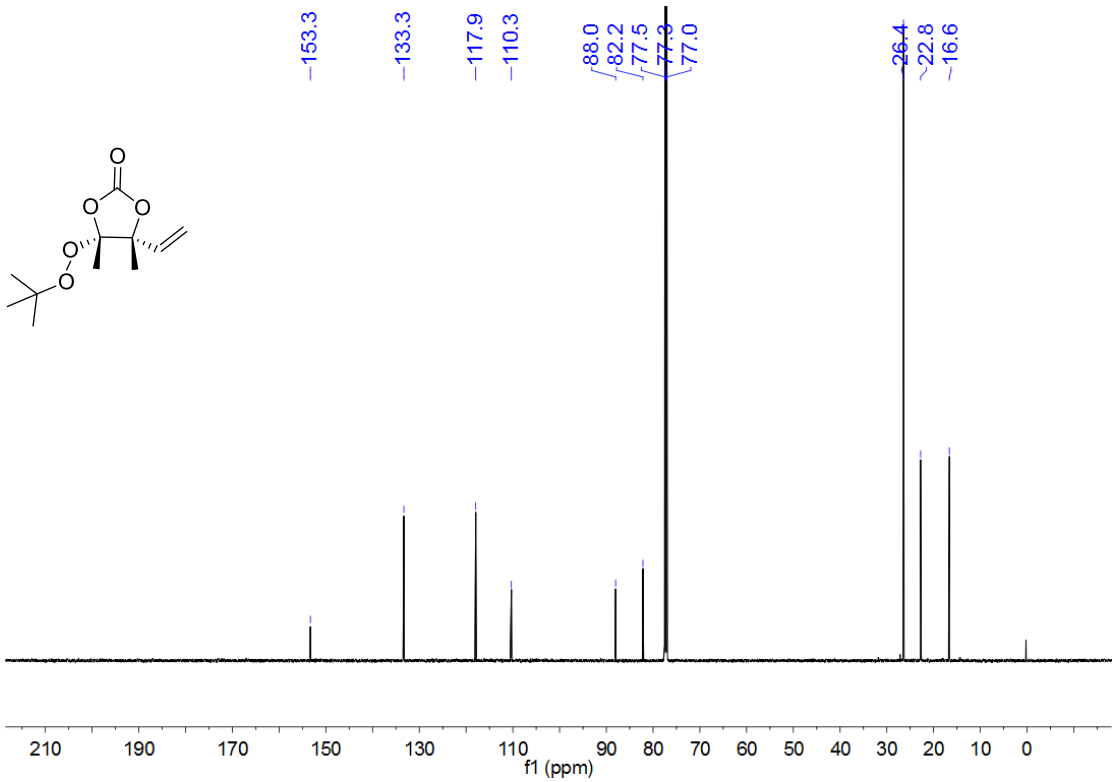


Figure S51. ^{13}C NMR spectrum of **6b**.

8.14 NMR spectra of **7**

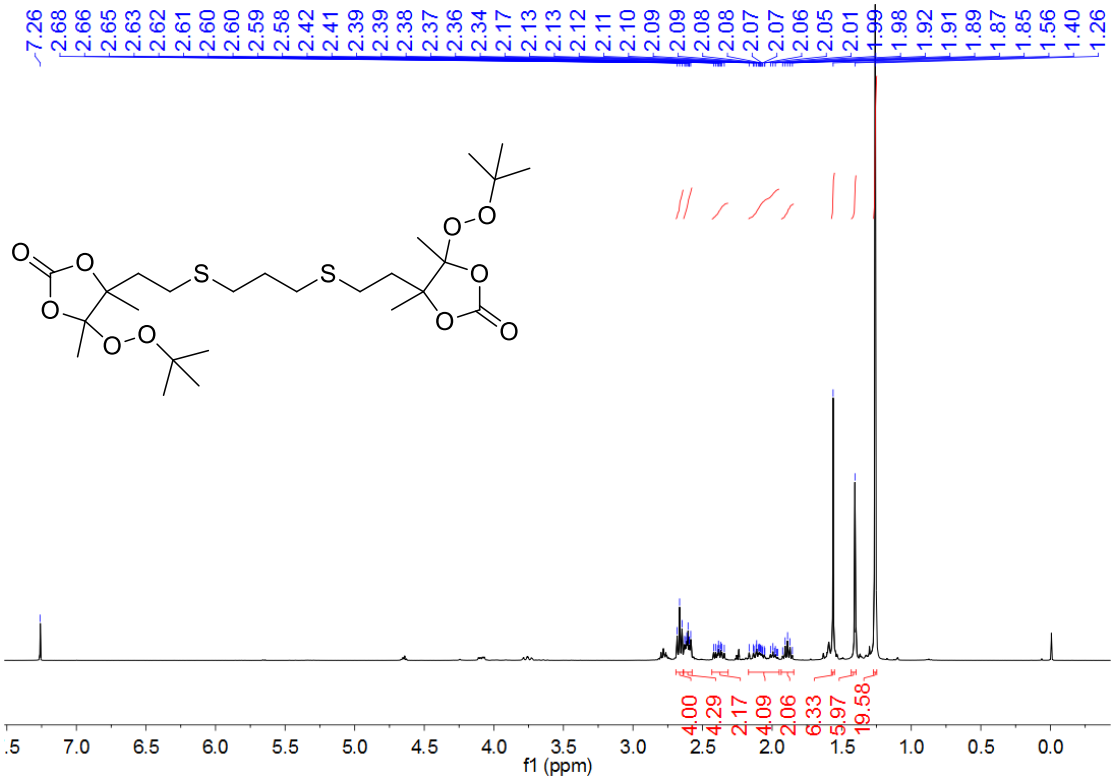


Figure S52. ^{1}H NMR spectrum of **7**.

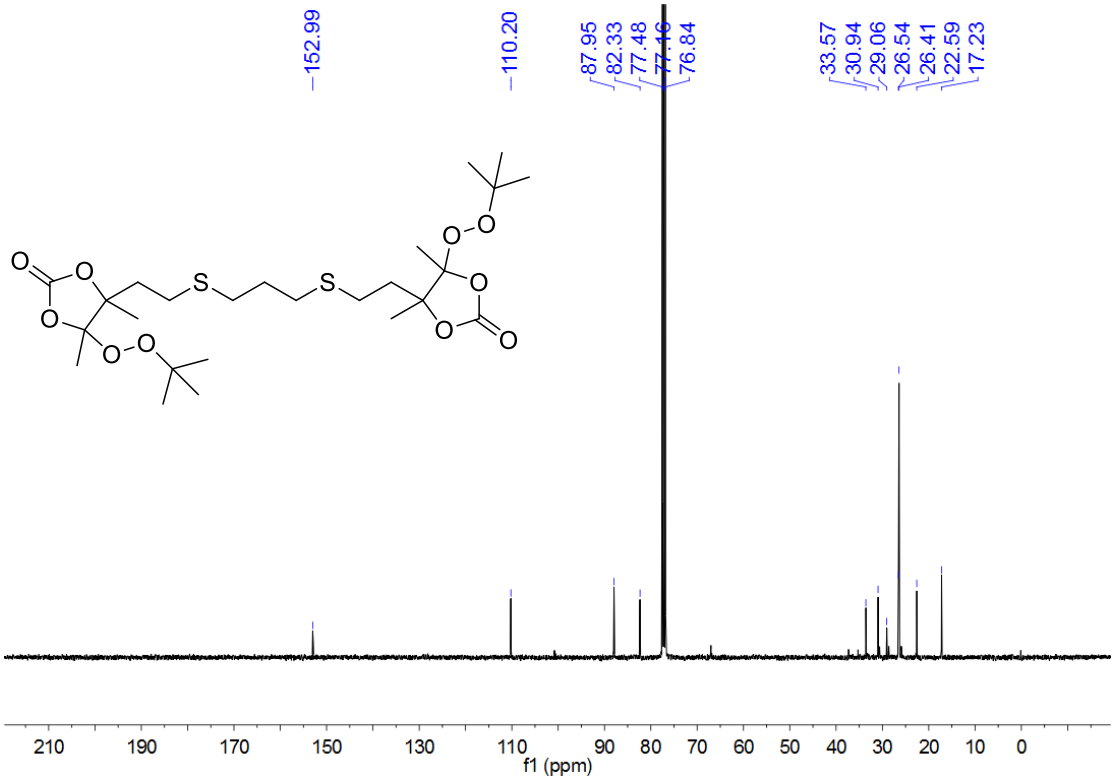


Figure S53. ^{13}C NMR spectrum of **7**.

9. *ESI MS Spectra*

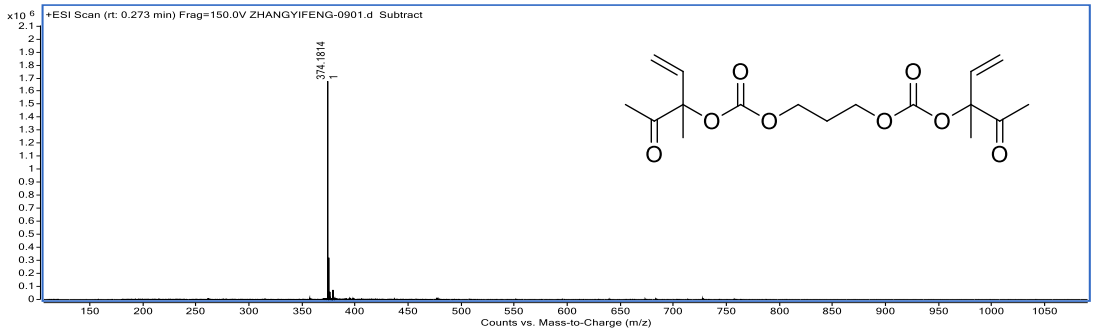


Figure S54. ESI MS spectrum of **4a**.

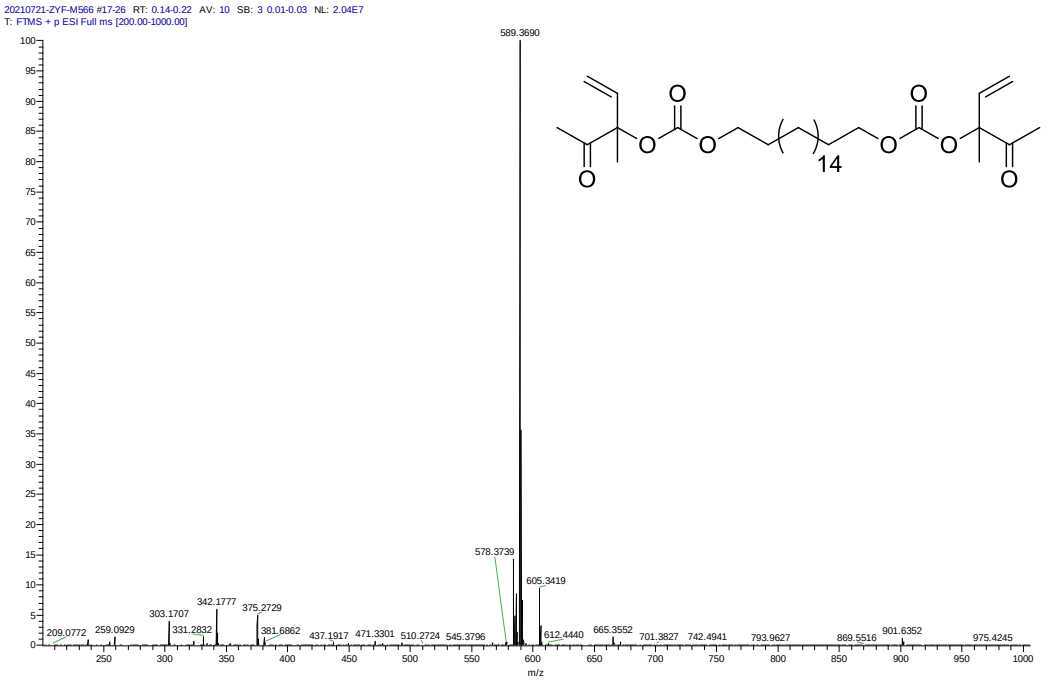


Figure S55. ESI MS spectrum of **4b**.

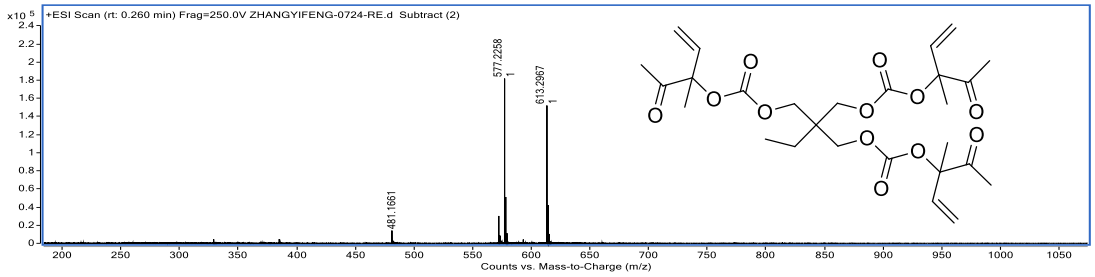


Figure S56. ESI MS spectrum of **4c**.

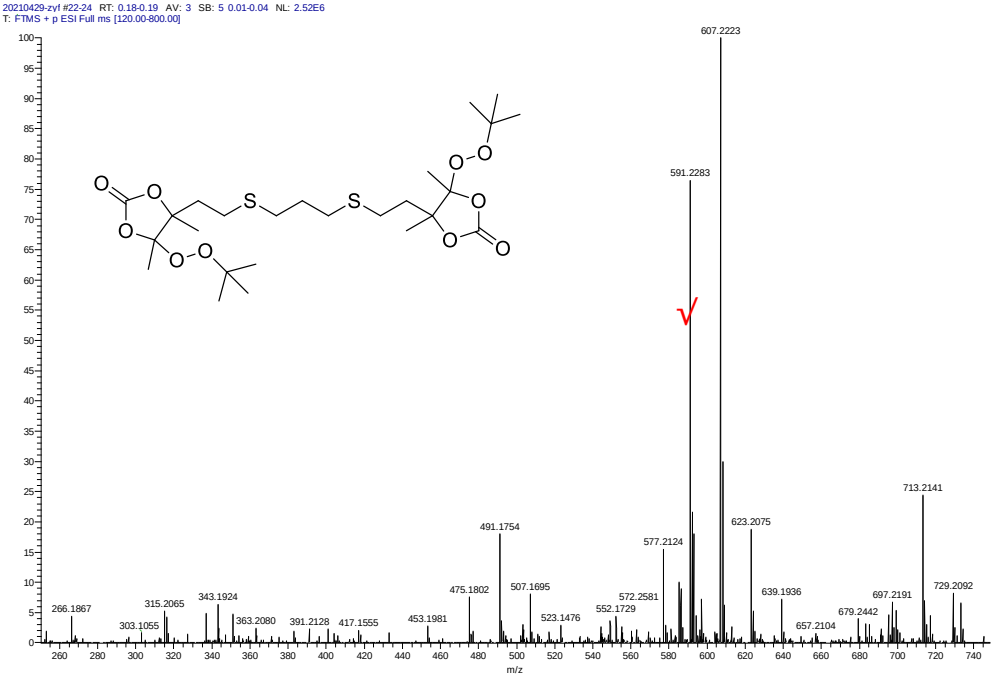


Figure S57. ESI MS spectrum of **7**.

10. Fluorescence spectra of the pure P4c5

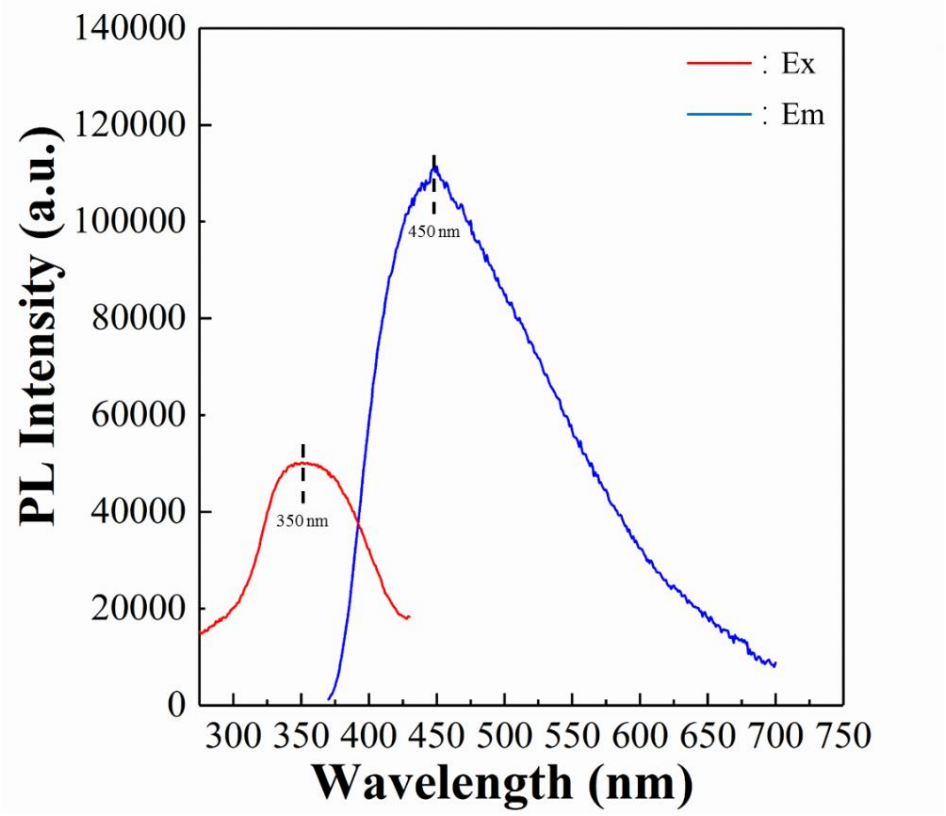


Figure S58. Fluorescence spectra of the pure **P4c5a**.

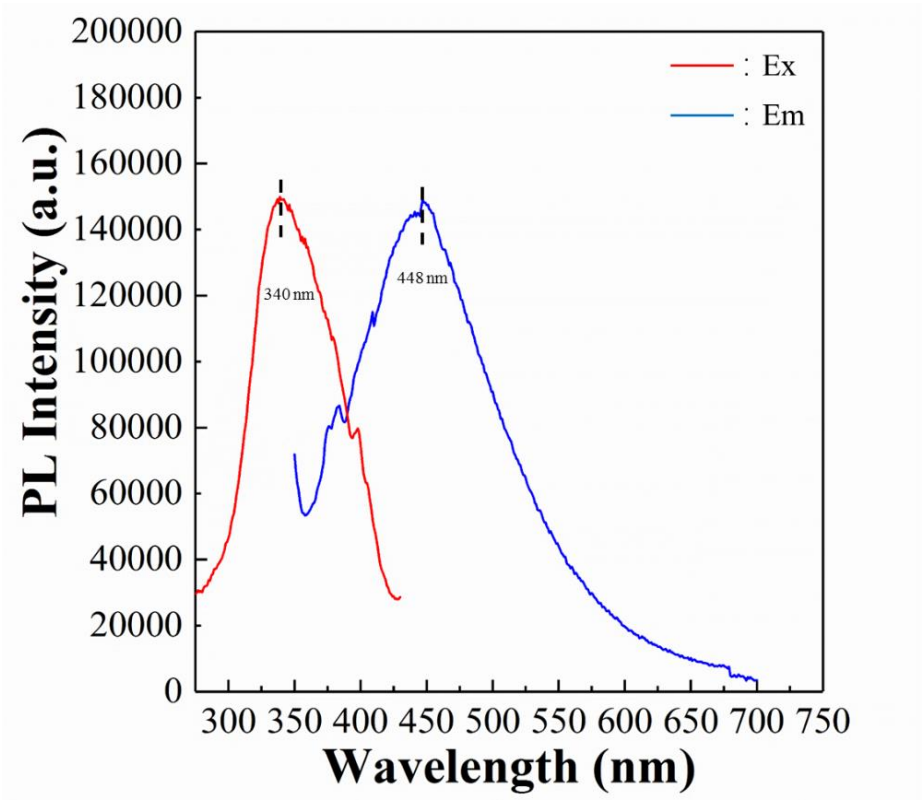


Figure S59. Fluorescence spectra of the pure **P4c5b**.

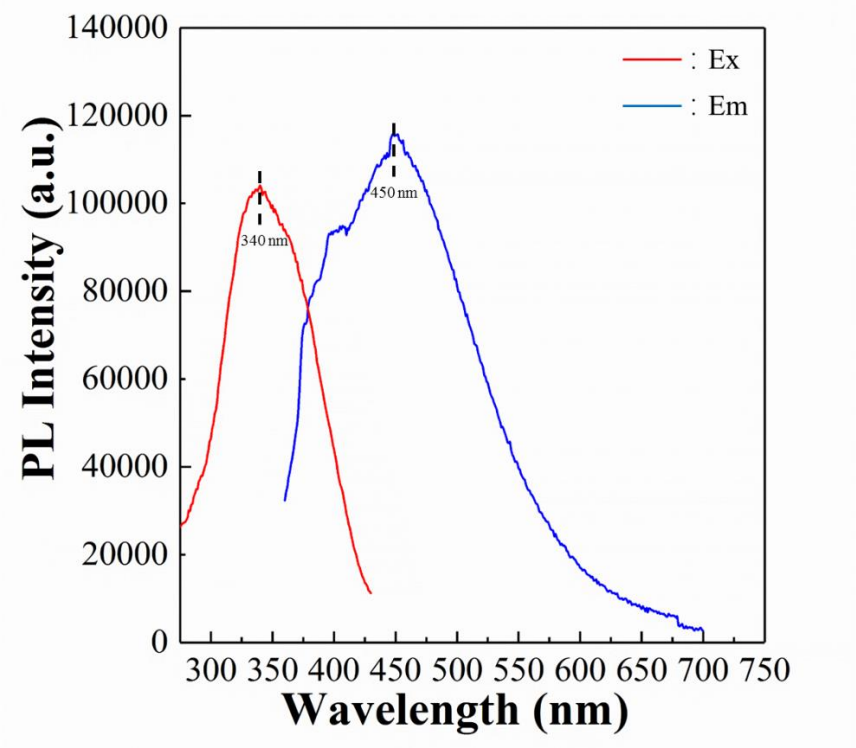


Figure S60. Fluorescence spectra of the pure **P4c5c**.

11. Transient photoluminescence decay curve of the pure P4c5

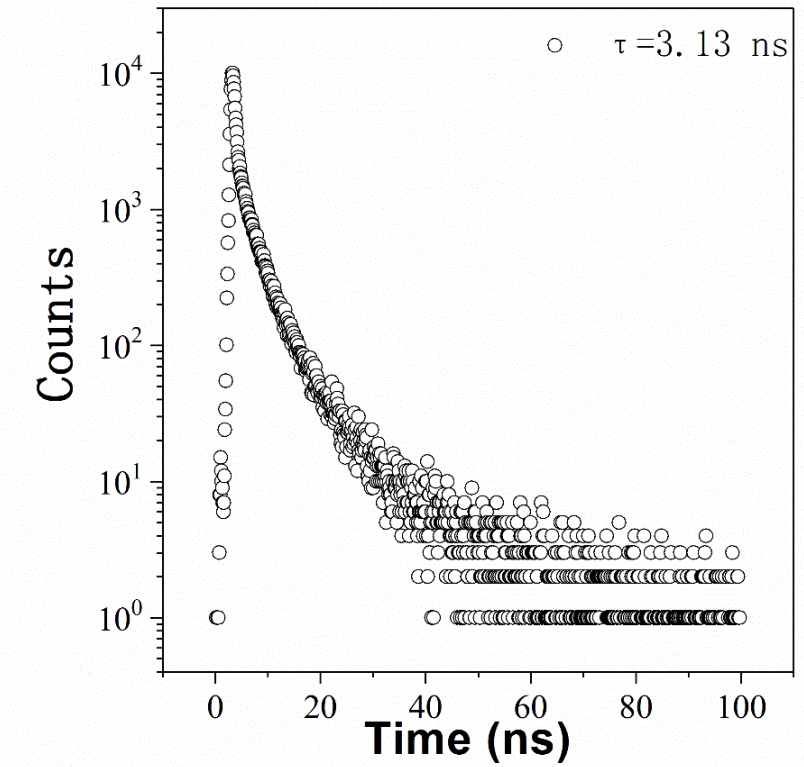


Figure S61. Transient photoluminescence decay curve of the pure **P4c5a** at 450 nm after excited at 350 nm

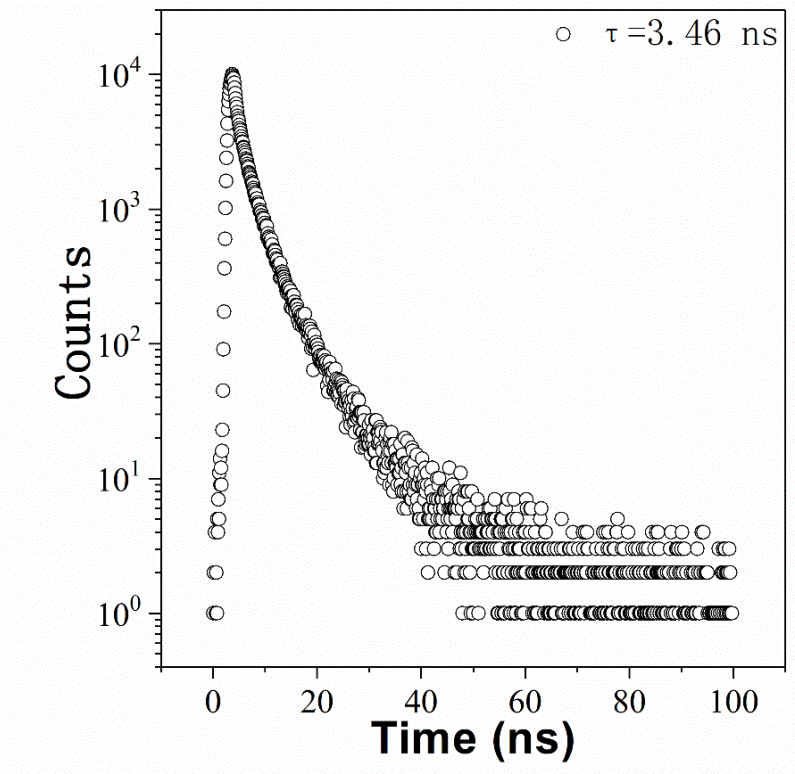


Figure S62. Transient photoluminescence decay curve of the pure **P4c5b** at 448 nm after excited at 340 nm

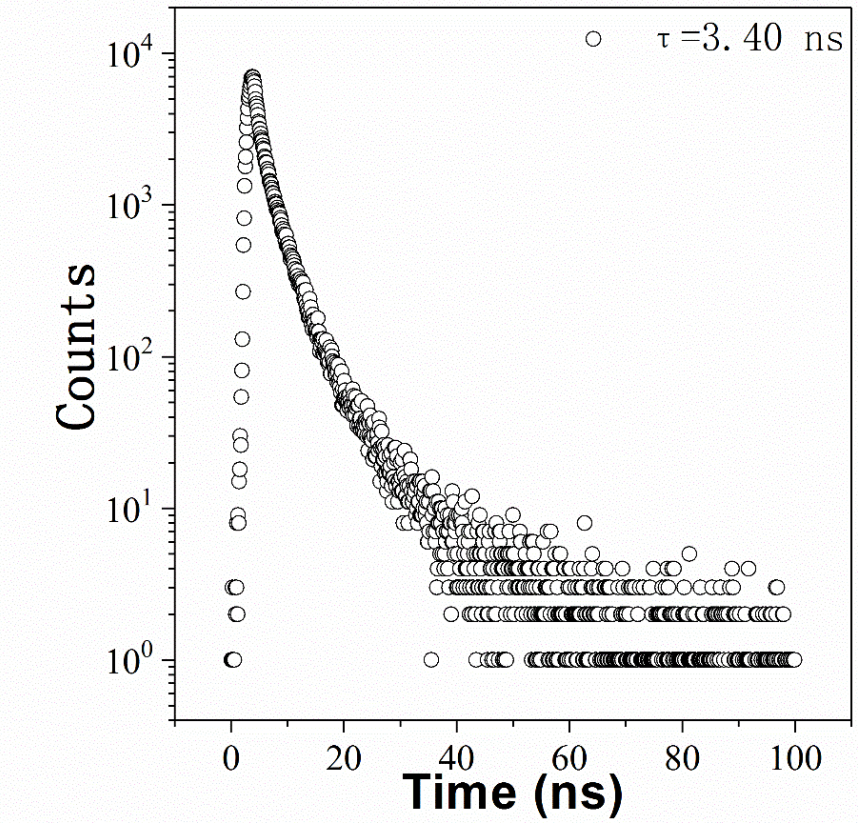


Figure S63. Transient photoluminescence decay curve of the pure **P4c5c** at 450 nm after excited at 340 nm

12. References

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2. H. Zhou, Y.-F. Zhang, W. Chen, W.-Z. Zhang and X.-B. Lu, *Asian J. Org. Chem.*, 2021, DOI: 10.1002/ajoc.202100270.
3. M. Huler, M. Eck, D. Rothauer and S. Mecking, *Nature*, 2021, **590**, 423-427.