

Mechanically induced chemiluminescence of xanthene-modified 1,2-dioxetane in polymers

Yanbing Shen,^{a,b} Yuan Yuan,^{*c} Xiaonan Ma,^b Wensheng Yang^{a,b} and

Yulan Chen^{*a,b,c}

a. Institute of Molecular Plus, Tianjin University, Tianjin, 300072, P. R. China,

b. State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University,

Changchun, 130012, P. R. China. E-mail: yulanchen@jlu.edu.cn

c. Department of Chemistry, Tianjin Key Laboratory of Molecular Optoelectronic Science, Tianjin University,

Tianjin, 300354, P. R. China. E-mail: yyuan@tju.edu.cn

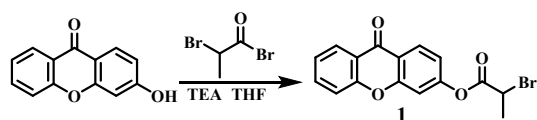
1. General Experimental Details

Materials. Unless otherwise noted, all chemicals were purchased from Sigma-Aldrich, Acros or Adamas and used without further purification. Tetrahydrofuran (THF) was distilled over sodium and benzophenone. Methyl acrylate was filtered through a plug of basic alumina just before use to remove the inhibitor. All reactions were performed under Argon atmosphere unless otherwise specified, and all glassware was oven dried before use. Thin layer chromatography (TLC) was conducted on silica gel 60 F₂₅₄ (Merck, 0.2 mm). Column chromatography was carried out on silica gel, basic alumina, or neutral alumina (0.063-0.2 mm). Photoinitiated polymerizations were performed using a Philips PL-S 10 UV-light source, connected to a timer.

Characterization methods. ¹H NMR (400 MHz) and ¹³C NMR (101 MHz) spectra were recorded on a Bruker AVANCE III-400 NMR spectrometer under 25 °C by using CDCl₃ as the solvent. High-resolution mass analyses were performed on a LTQ Orbitrap XL (Thermo Scientific) mass spectrometer. Gel permeation chromatography (GPC) was performed on a Shimadzu LC10-AT using polystyrene as the standard, using THF as an eluent at a flow rate of 1.0 mL/min. The thermal-induced chemiluminescence spectra were performed on a spectrometer of QE65 Pro of OceanInsight as a power detector. The 365 nm irradiation of solution was realized by a 500 W high-pressure mercury lamp (CEL-M500) with 365 nm optical filter.

Optomechanical testing. Tensile experiments were carried out on a TA Rheometrics, DHR-2 equipped with an Xpansion Instruments, SER3, extensional fixture. The two rotating drums of the fixture are colored black by permanent marker to eliminate reflecting light. The pco.edge 5.5 camera equipped with a Nikon AF NIKKOR 50 mm 1:1.4D lens was used to record videos in darkness. All the videos were recorded in the rolling shutter color mode with a shooting rate of 200 fps and exposure time of 5.00 ms. The frames of the resulting video were exported as separate monochrome TIF-files and light intensity was analyzed with a homemade program in MATLAB as literature¹. The total intensity for a dark image as the noisy signal was subtracted from all film intensities. The dimension of the strips used for tensile tests was 30 × 5.3 × (0.50 ± 0.03) mm.

2. Synthesis and sample preparation

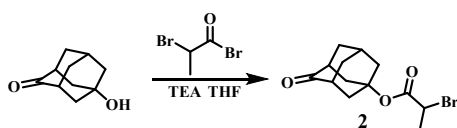


Synthesis of 1

3-hydroxy-9H-xanthen-9-one (14.14 mmol, 3.0 g) and anhydrous triethylamine (TEA, 42.41 mmol, 4.29 g) were dissolved in 50 mL dry THF under N₂ atmosphere. Then, 2-bromopropanoyl bromide (28.27 mmol, 6.10 g) was added to the mixture dropwise at 0 °C. Then the reaction system was stirred vigorously overnight at room temperature. After stirring at room temperature for 12 h, the solution was poured into water (100 mL) and extracted with diethyl ether (3×50 mL). The combined organic layer was washed with water (50 mL), dried over anhydrous MgSO₄ and evaporated under reduced pressure. The residue was purified by silica flash chromatography (DCM as eluent). The product was obtained as white solid (4.6 g, 94 % yield).

¹H NMR (400 MHz, CDCl₃) δ 8.36 (d, *J* = 8.7 Hz, 1H), 8.33 – 8.29 (m, 1H), 7.71 (ddd, *J* = 8.7, 7.1, 1.7 Hz, 1H), 7.46 (dd, *J* = 8.5, 0.6 Hz, 1H), 7.38 (ddd, *J* = 8.1, 7.2, 1.0 Hz, 1H), 7.33 (d, *J* = 2.1 Hz, 1H), 7.15 (dd, *J* = 8.7, 2.2 Hz, 1H), 4.63 (q, *J* = 6.9 Hz, 1H), 1.97 (d, *J* = 6.9 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 176.27, 167.96, 156.69, 156.20, 155.09, 135.00, 128.38, 126.69, 124.28, 121.66, 119.93, 117.90, 117.58, 110.51, 39.24, 21.32.



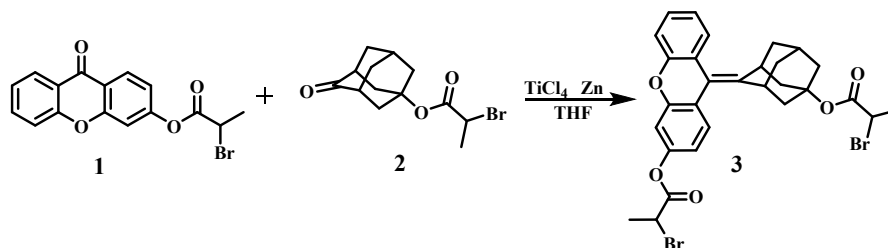
Synthesis of 2

5-hydroxyadamantan-2-one (18.05 mmol, 3.0 g) and anhydrous triethylamine (TEA, 54.15 mmol, 5.48 g) were dissolved in 50 mL dry THF under N₂ atmosphere. Then, 2-bromopropanoyl bromide (36.10 mmol, 7.79 g) was added to the mixture dropwise at 0 °C. Then the reaction system was stirred vigorously overnight at room temperature. After stirring at room temperature for 12 h, the solution was poured into water (100 mL) and extracted with diethyl ether (3×50 mL). The combined organic layer was washed with water (50 mL), dried over anhydrous MgSO₄ and evaporated under

reduced pressure. The residue was purified by silica flash chromatography (PE/EtOAc = 9:1 as eluent). The product was obtained as yellow oil (4.7 g, 86 % yield).

^1H NMR (400 MHz, CDCl_3) δ 4.26 (q, $J = 6.9$ Hz, 1H), 2.65 (s, 2H), 2.46 – 2.28 (m, 8H), 2.03 (d, $J = 11.9$ Hz, 2H), 1.94 (d, $J = 12.9$ Hz, 2H), 1.76 (d, $J = 6.9$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 169.12, 79.33, 67.67, 46.91, 44.68, 43.81, 41.37, 40.85, 39.93, 39.39, 38.17, 29.79, 21.61.



Synthesis of 3

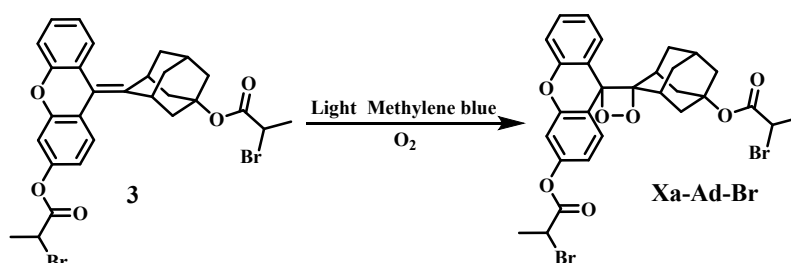
Under a nitrogen atmosphere, TiCl_4 (35.14 mmol, 6.67 g) was added to a suspension of zinc powder (77.77 mmol, 5.08 g) in anhydrous THF (100 mL) at 0 °C, and the suspension was stirred for 10 min under reflux. A solution of 4-oxoadamantan-1-yl 2-bromopropanoate 2 (5.76 mmol, 1.74 g) and 9-oxo-9H-xanthen-3-yl 2-bromopropanoate 1 (5.76 mmol, 2.00 g) in dry THF (20 mL) was added dropwise over a period of 30 min. The reaction mixture was refluxed for 45 minutes. Then, it was cooled to room temperature, quenched with water and extracted with AcOEt (3 x 30 mL). The combined organic layers were dried over anhydrous MgSO_4 and evaporated under vacuum. The crude product was purified by flash chromatography on silica gel (PE/EtOAc = 95:5 as eluent). The product was obtained as yellow solid (1.20 g, 34 % yield).

^1H NMR (400 MHz, CDCl_3) δ 7.28 – 7.24 (m, 2H), 7.23 – 7.14 (m, 2H), 7.13 – 7.06 (m, 1H), 6.99 (dd, $J = 18.9, 2.3$ Hz, 1H), 6.87 (ddd, $J = 18.6, 8.4, 2.3$ Hz, 1H), 3.68 (d, $J = 12.9$ Hz, 2H), 2.58 (q, $J = 7.5$ Hz, 1H), 2.33 (s, 1H), 2.28 – 2.19 (m, 4H), 2.15 (d, $J = 11.0$ Hz, 1H), 1.92 (dd, $J = 8.4, 6.0$ Hz, 2H), 1.84 (t, $J = 14.1$ Hz, 3H), 1.30 – 1.21 (m, 3H), 1.07 (t, $J = 7.5$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 173.73, 172.86, 168.67, 155.45, 154.79, 149.62, 149.25, 143.52, 143.20, 127.82, 127.68, 127.41, 126.02, 124.38, 123.84, 123.10, 122.99, 117.01, 116.90, 116.62, 116.04, 115.45, 110.30, 109.84, 78.98, 42.18, 40.51, 39.59,

38.24, 34.36, 30.66, 28.83, 27.77, 21.44, 9.27, 9.10.

HR-MS (m/z): $[M+Na]^+$ $C_{29}H_{28}Br_2O_5Na^+$ calculated 637.0201; found $[M+Na]^+$ 637.0206.

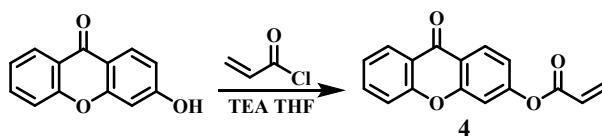


Synthesis of Xa-Ad-Br

To a solution of 3-((2-bromopropanoyl)oxy)-9H-xanthen-9-ylidene)adamantan-1-yl 2-bromopropanoate **3** (0.2 g, 0.32 mmol) in DCM (60 mL) was added methylene blue (30 mg). Oxygen was bubbled through the mixture while irradiating with a 600 Watt high pressure sodium lamp. The irradiation was continued until the starting material disappeared (usually 6 h of irradiation), and the conversion was monitored by 1H NMR. The product **Xa-Ad-Br** was purified by a rapid filtration on a 5 mm layer of silica gel, using DCM as eluent, and the filtered solution was evaporated under vacuum at 0 °C. The product was obtained as yellow solid (80 mg, 38 % yield).

1H NMR (400 MHz, $CDCl_3$) δ 8.35 (dd, $J = 13.1, 5.1$ Hz, 2H), 7.74 (tt, $J = 6.1, 3.0$ Hz, 1H), 7.50 (d, $J = 8.4$ Hz, 1H), 7.41 (t, $J = 7.5$ Hz, 1H), 7.33 (d, $J = 2.1$ Hz, 1H), 7.14 (dd, $J = 8.7, 2.1$ Hz, 1H), 4.09 (t, $J = 6.4$ Hz, 1H), 3.57 (t, $J = 6.6$ Hz, 2H), 3.48 – 3.39 (m, 2H), 2.25 (dd, $J = 9.5, 5.5$ Hz, 10H), 1.64 (s, 3H), 1.25 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.46, 173.66, 172.11, 156.82, 156.31, 155.65, 151.65, 134.90, 130.21, 128.90, 128.22, 126.76, 124.20, 123.62, 121.79, 121.17, 119.61, 118.83, 118.21, 117.94, 116.89, 116.21, 110.83, 109.77, 95.26, 70.30, 69.97, 64.15, 63.46, 47.04, 45.02, 41.32, 39.88, 39.13, 38.20, 35.73, 35.35, 31.44, 29.82, 29.55, 29.17, 28.67, 27.85, 27.61, 27.09, 26.25, 25.55.

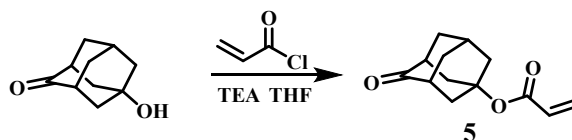


Synthesis of 4

3-hydroxy-9H-xanthen-9-one (14.14 mmol, 3.0 g) and anhydrous triethylamine (TEA, 42.41 mmol, 4.29 g) were dissolved in 50 mL dry THF under N₂ atmosphere. Then, acryloyl chloride (28.27 mmol, 2.56 g) was added to the mixture dropwise at 0 °C. Then the reaction system was stirred vigorously overnight at room temperature. After stirring at room temperature for 12 h, the solution was poured into water (100 mL) and extracted with diethyl ether (3×50 mL). The combined organic layer was washed with water (50 mL), dried over anhydrous MgSO₄ and evaporated under reduced pressure. The residue was purified by silica flash chromatography (DCM as eluent). The product was obtained as white solid (4.6 g, 94 % yield).

¹H NMR (400 MHz, CD₂Cl₂) δ 6.34 (d, *J* = 8.7 Hz, 1H), 6.30 (dd, *J* = 8.0, 1.6 Hz, 1H), 5.69 (ddd, *J* = 8.7, 7.1, 1.7 Hz, 1H), 5.45 (dd, *J* = 8.4, 0.6 Hz, 1H), 5.35 (ddd, *J* = 10.0, 5.5, 1.6 Hz, 2H), 5.14 (dd, *J* = 8.7, 2.2 Hz, 1H), 4.64 (dd, *J* = 17.3, 1.1 Hz, 1H), 4.32 (dd, *J* = 17.3, 10.5 Hz, 1H), 4.06 (dd, *J* = 10.5, 1.1 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 176.43, 163.61, 156.82, 156.32, 155.44, 134.91, 133.73, 128.28, 127.39, 126.77, 124.22, 121.81, 119.74, 118.13, 117.95, 110.84.



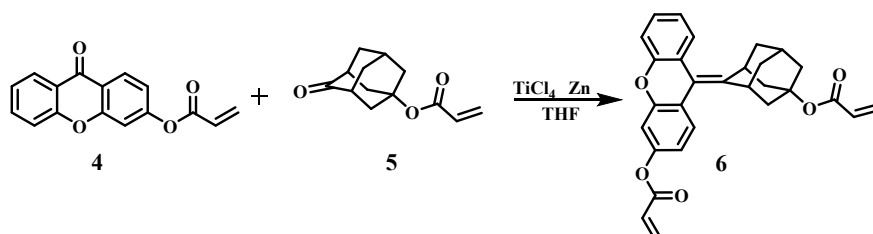
Synthesis of 5

5-hydroxyadamantan-2-one (18.05 mmol, 3.0 g) and anhydrous triethylamine (TEA, 54.15 mmol, 5.48 g) were dissolved in 50 mL dry THF under N₂ atmosphere. Then, acryloyl chloride (36.10 mmol, 3.25 g) was added to the mixture dropwise at 0 °C. Then the reaction system was stirred vigorously overnight at room temperature. After stirring at room temperature for 12 h, the solution was poured into water (100 mL) and extracted with diethyl ether (3×50 mL). The combined organic layer was washed with water (50 mL), dried over anhydrous MgSO₄ and evaporated under reduced pressure. The residue was purified by silica flash chromatography (PE/EtOAc = 9:1 as eluent). The product was obtained as white solid (3.0 g, 86 % yield).

¹H NMR (400 MHz, CDCl₃) δ 6.31 (dd, *J* = 17.3, 1.5 Hz, 1H), 6.02 (dd, *J* = 17.3, 10.4

Hz, 1H), 5.76 (dd, $J = 10.4, 1.5$ Hz, 1H), 2.65 (s, 2H), 2.50 – 2.28 (m, 7H), 2.08 – 1.99 (m, 2H), 1.96 (s, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 215.54, 165.10, 130.25, 129.70, 77.87, 47.02, 41.26, 39.87, 38.18, 29.84.



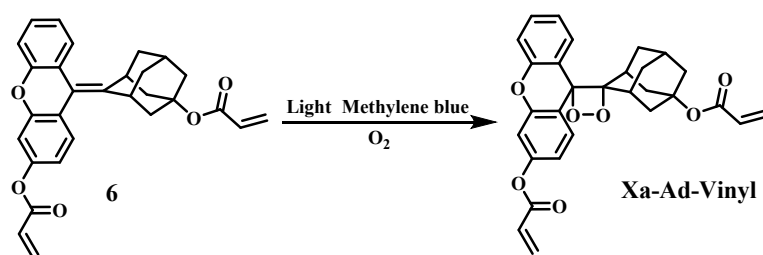
Synthesis of 6

Under a nitrogen atmosphere, TiCl_4 (45.82 mmol, 8.69 g) was added to a suspension of zinc powder (101.41 mmol, 6.63 g) in anhydrous THF (80 mL) at 0 °C, and the suspension was stirred for 10 min under reflux. A solution of 4-oxoadamantan-1-yl acrylate **4** (7.51 mmol, 1.74 g) and 9-oxo-9H-xanthen-3-yl acrylate **5** (7.51 mmol, 2.00 g) in dry THF (30 mL) was added dropwise over a period of 30 min. The reaction mixture was refluxed for 45 minutes. Then, it was cooled to room temperature, quenched with water and extracted with AcOEt (3 x 50 mL). The combined organic layers were dried over anhydrous MgSO_4 and evaporated under vacuum. The crude product was purified by flash chromatography on silica gel (PE/EtOAc = 95:5 as eluent). The product was obtained as yellow oil (1.30 g, 38 % yield).

^1H NMR (400 MHz, CDCl_3) δ 8.42 – 8.28 (m, 1H), 7.73 (ddd, $J = 8.7, 7.1, 1.7$ Hz, 1H), 7.49 (dd, $J = 8.4, 0.6$ Hz, 1H), 7.39 (ddd, $J = 10.5, 5.7, 1.6$ Hz, 1H), 7.18 (dd, $J = 8.7, 2.2$ Hz, 1H), 6.68 (dd, $J = 17.3, 1.1$ Hz, 1H), 6.34 (ddd, $J = 17.3, 14.7, 6.0$ Hz, 1H), 6.07 (ddd, $J = 27.7, 13.9, 5.7$ Hz, 1H), 5.83 – 5.72 (m, 1H), 2.66 (s, 1H), 2.52 – 2.29 (m, 5H), 2.01 (dt, $J = 37.6, 7.6$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 215.70, 176.48, 165.15, 163.64, 156.81, 156.32, 155.43, 134.95, 133.80, 130.33, 129.69, 128.29, 127.37, 126.77, 124.24, 121.79, 119.73, 118.16, 117.96, 110.86, 47.03, 41.26, 39.86, 38.19, 29.84.

HR-MS (m/z): $[\text{M}+\text{Na}]^+$ $\text{C}_{29}\text{H}_{26}\text{O}_5\text{Na}^+$ calculated 477.1678; found $[\text{M}+\text{Na}]^+$ 477.1682.

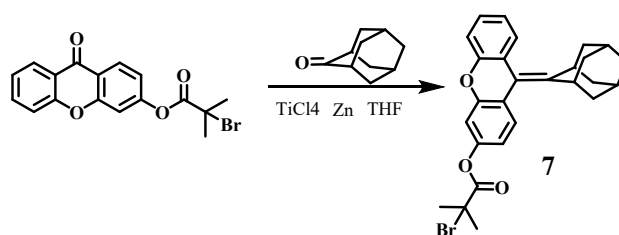


Synthesis of Xa-Ad-Vinyl

To a solution of (1S,3R,5S,7S)-4-((Z)-3-(acryloyloxy)-9H-xanthen-9-ylidene)adamantan-1-yl acrylate **6** (0.2 g, 0.44 mmol) in DCM (60 mL) was added methylene blue (30 mg). Oxygen was bubbled through the mixture while irradiating with a 600 Watt high pressure sodium lamp. The irradiation was continued until the starting material disappeared (usually 6 h of irradiation), and the conversion was monitored by ^1H NMR. The product **Xa-Ad-Vinyl** was purified by a rapid filtration on a 5 mm layer of silica gel, using DCM as eluent, and the filtered solution was evaporated under vacuum at 0 °C. The product was obtained as yellow solid (85 mg, 40 % yield).

^1H NMR (400 MHz, CDCl_3) δ 8.20 – 8.11 (m, 2H), 7.46 – 7.36 (m, 1H), 7.35 – 7.28 (m, 1H), 7.20 (qd, $J = 8.9, 1.6$ Hz, 1H), 7.14 – 7.06 (m, 2H), 6.67 – 6.60 (m, 1H), 6.35 – 6.27 (m, 2H), 6.09 – 6.01 (m, 2H), 5.79 – 5.74 (m, 1H), 4.19 (dd, $J = 9.7, 3.7$ Hz, 1H), 3.57 (dt, $J = 12.0, 5.8$ Hz, 2H), 3.43 (t, $J = 6.2$ Hz, 1H), 2.70 – 2.56 (m, 3H), 2.49 – 2.31 (m, 7H)..

^{13}C NMR (101 MHz, CDCl_3) δ 165.14, 164.06, 151.69, 151.13, 133.21, 130.88, 130.32, 130.25, 129.98, 129.81, 129.69, 128.96, 128.37, 128.13, 127.64, 123.67, 121.12, 119.00, 116.86, 116.75, 116.23, 109.76, 95.22, 84.05, 63.70, 47.03, 45.02, 44.49, 41.26, 39.85, 39.56, 39.36, 39.13, 38.19, 35.75, 35.36, 34.98, 34.82, 34.69, 33.65, 31.44, 30.49, 29.84, 29.72, 29.54, 29.15, 28.18, 27.85, 27.08, 26.24, 26.06, 25.53.



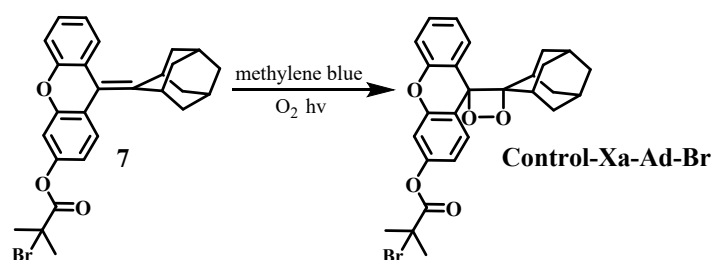
Synthesis of 7

Under a nitrogen atmosphere, TiCl_4 (33.78 mmol, 6.41 g) was added to a suspension of zinc powder (74.75 mmol, 4.89 g) in anhydrous THF (80 mL) at 0 °C, and the suspension was stirred for 10 min under reflux. A solution of adamantan-2-one (5.54 mmol, 0.83 g) and 9-oxo-9H-xanthen-3-yl 2-bromo-2-methylpropanoate (5.54 mmol, 2.00 g) in dry THF (30 mL) was added dropwise over a period of 30 min. The reaction mixture was refluxed for 45 minutes. Then, it was cooled to room temperature, quenched with water and extracted with AcOEt (3 x 50 mL). The combined organic layers were dried over anhydrous MgSO_4 and evaporated under vacuum. The crude product was purified by flash chromatography on silica gel (PE/EtOAc = 95:5 as eluent). The product was obtained as yellow oil (1.20 g, 45 % yield).

^1H NMR (400 MHz, CDCl_3) δ 7.29 – 7.21 (m, 2H), 7.20 – 7.12 (m, 2H), 7.11 – 7.04 (m, 1H), 6.98 – 6.93 (m, 1H), 6.82 (ddd, $J = 7.3, 4.3, 2.5$ Hz, 1H), 3.50 (t, $J = 11.9$ Hz, 2H), 2.87 – 2.71 (m, 1H), 2.06 – 1.97 (m, 2H), 1.95 – 1.81 (m, 10H), 1.30 (dd, $J = 7.0, 2.2$ Hz, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 175.54, 155.56, 154.92, 149.49, 146.85, 127.75, 127.53, 126.97, 126.57, 124.30, 122.82, 116.51, 115.83, 115.78, 110.12, 39.47, 36.99, 34.20, 32.60, 32.57, 29.73, 27.87, 18.95.

HR-MS (m/z): $[\text{M}+\text{Na}]^+$ $\text{C}_{27}\text{H}_{27}\text{BrO}_3\text{Na}^+$ calculated 501.1041; found $[\text{M}+\text{Na}]^+$ 501.1046.



Synthesis of Control-Xa-Ad-Br

To a solution of 9-((1r,3r,5R,7S)-adamantan-2-ylidene)-9H-xanthen-3-yl 2-bromo-2-methylpropanoate 7 (0.2 g, 0.42 mmol) in DCM (60 mL) was added methylene blue (30 mg). Oxygen was bubbled through the mixture while irradiating with a 600 Watt high pressure sodium lamp. The irradiation was continued until the starting material

disappeared (usually 6 h of irradiation), and the conversion was monitored by ^1H NMR. The product **Control-Xa-Ad-Br** was purified by a rapid filtration on a 5 mm layer of silica gel, using DCM as eluent, and the filtered solution was evaporated under vacuum at 0 °C. The product was obtained as yellow solid (90 mg, 42 % yield).

^1H NMR (400 MHz, CDCl_3) δ 8.38 – 8.31 (m, 1H), 8.16 (d, $J = 8.6$ Hz, 1H), 7.73 (ddd, $J = 8.7, 7.2, 1.7$ Hz, 1H), 7.48 (d, $J = 8.4$ Hz, 1H), 7.42 – 7.37 (m, 1H), 7.31 (dd, $J = 4.8, 1.6$ Hz, 1H), 7.20 – 7.10 (m, 1H), 7.05 – 6.99 (m, 1H), 2.90 – 2.77 (m, 1H), 2.54 (s, 2H), 2.41 (s, 1H), 2.03 (ddd, $J = 34.3, 14.2, 7.6$ Hz, 11H), 1.83 (d, $J = 12.6$ Hz, 2H), 1.34 (dd, $J = 6.1, 2.0$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 176.48, 174.78, 156.83, 156.31, 155.83, 151.88, 151.68, 151.17, 134.89, 129.96, 129.03, 128.29, 128.20, 126.77, 124.19, 123.35, 121.80, 121.44, 119.59, 119.07, 118.20, 117.94, 116.60, 116.08, 110.81, 109.61, 97.02, 84.70, 46.99, 39.27, 36.31, 35.98, 34.31, 34.22, 33.11, 32.76, 31.72, 29.73, 27.45, 25.50, 25.29, 18.92, 18.87.

Preparation of liner PMAs

As a representative procedure, a 25 mL flame-dried Schlenk flask equipped with a stir bar was charged with initiator (compound **Xa-Ad-Br**) (20.0 mg, 0.031 mmol), DMSO (1.5 mL), methyl acrylate (3.00 mL, 33.3 mmol) and Me_6TREN (16.0 μL , 0.60 mmol). The flask was sealed, the solution was degassed via four freeze-pump-thaw cycles, and then backfilled with nitrogen and warmed to room temperature. After that, 5 cm of Cu(0) wire wrapped around a Teflon-coated stirring bar was loaded under argon. When the solution became viscous, THF was added to the solution to stop the reaction. The polymerization mixture was dissolved in 15 mL THF, passed through a small neutral Al_2O_3 chromatographic column to remove unreacted Cu(0) catalyst and Cu(II) residues, and the resulting solution was concentrated and precipitated twice in cold methanol with stirring. Methanol was removed by decantation and the final colorless polymer was dried under vacuum. The M_n and M_w/M_n values were determined by GPC with THF as the solvent and PS as the standards, $M_n = 88$ kDa, $PDI = 1.03$.

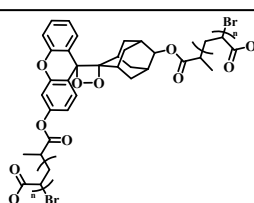
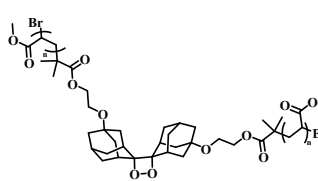
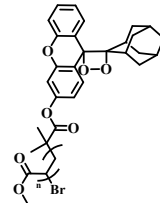
Preparation of Cross-Xa-Ad-PMA

Methyl acrylate (2 mL), **Xa-Ad-Vinyl** (54 mg) and benzoin (3.5 mg) was well mixed before added to a Teflon mold (2.5 cm×4.5 cm×5 mm) with a glass plate covering on it. Polymerization took place by UV irradiation under an N₂ atmosphere for 30 minutes at room temperature. The low molecular weight substances remaining in the samples after polymerization were extracted with THF (200 mL) at room temperature, which was exchanged for three times during 24 h. The film was then dried under vacuum.

Preparation of crosslinked PMA mixed with **Xa-Ad-Br**

Methyl acrylate (2 mL), ethane-1,2-diyl diacrylate (19 mg), **Xa-Ad-Br** (772 mg) and benzoin (3.5 mg) was well mixed before added to a Teflon mold (2.5 cm×4.5 cm×5 mm) with a glass plate covering on it. Polymerization took place by UV irradiation under an N₂ atmosphere for 30 minutes at room temperature. The film was then dried under vacuum.

Table S1: Structural parameters of polymers

Polymer	Structure	Mn (KDa) ^[a]	<i>D</i> ^[a]
Xa-Ad-PMA		88	1.03
Ad-Ad-PMA		83	1.15
Control-Xa-Ad-PMA		102	1.39

[a] Determined from GPC.

3. Sonication experiments

Sonication experiments were conducted with a Sonics VCX 500 W Ultrasonic processor purchased from Sonics and Materials Inc, and a 13 mm extender probe was

used at a frequency of 20 kHz, at 40% of the maximum amplitude. The distance between the titanium tip and the bottom of the Suslick cell was 4 cm. The Suslick cells were made by Beijing Synthware Glass. The solutions were thoroughly degassed before sonication and exposed in argon atmosphere during the whole sonication process. Polymer was dissolved in anhydrous THF (10 mg/mL), and it was then transferred to a dried glass tube, equipped with sonication probe. The sonication sequence was set as 1.0 s on / 1.0 s off. Sonication was carried out on polymer solutions in -5 °C. Samples were taken during the sonication experiment and analyzed by spectrophotometer. Aliquots (1.2 mL) at given times were removed from the cell for GPC tests. The sonication time mentioned in this work represented the total duration of each sonication experiment, including on and off time.

For GPC Analyses

Aliquots of ultrasonicated polymer solutions were diluted in THF to afford a 3 mg/mL solution, filtered through a 0.45 μm PTFE syringe filter, and analyzed by SEC. The rate constants of polymer cleavage (k) for polymers were calculated from the slope of the least squares linear regression of the data according to the method of Kryger et al. using Supplementary Equation 1,³ where M_t is the number average molecular weight (M_n) of the sonicated sample at time t , M_0 is the initial number average molecular weight of the polymer, and k is the rate constant of polymer cleavage adjusted for the molecular weight of the monomer unit, M ($k=k'/M$).

$$\frac{1}{M_t} - \frac{1}{M_0} = kt \quad (1)$$

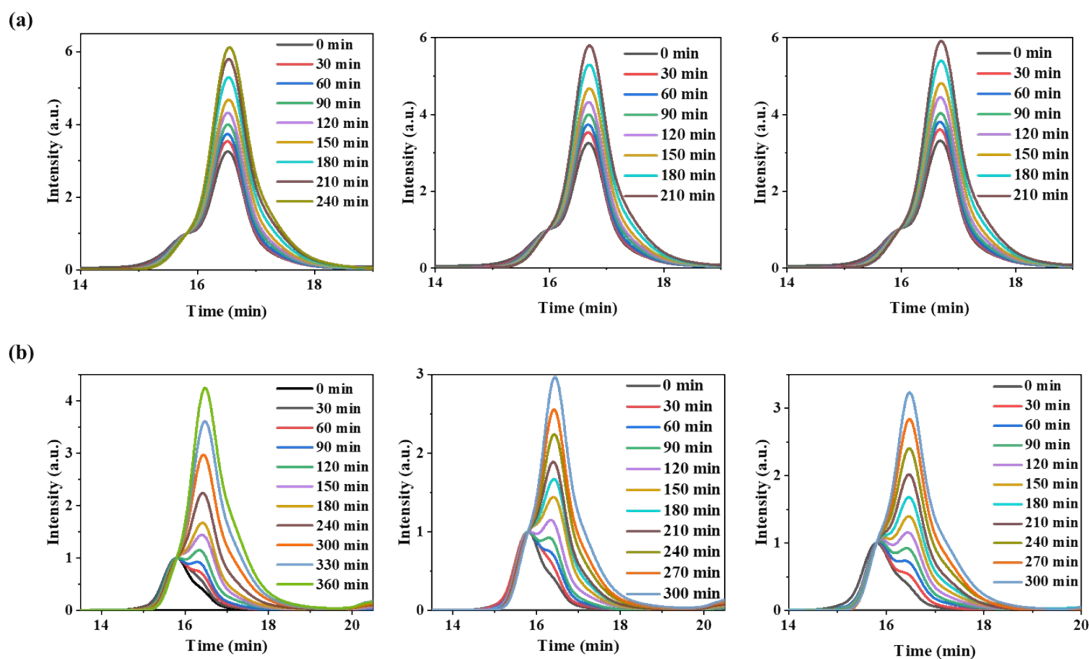


Figure S1 Representative GPC traces (RI) and molecular weight data for **Xa-Ad-PMA** (a) and **Ad-Ad-PMA** (b) taken during the sonication experiment (10 mg/mL in THF).

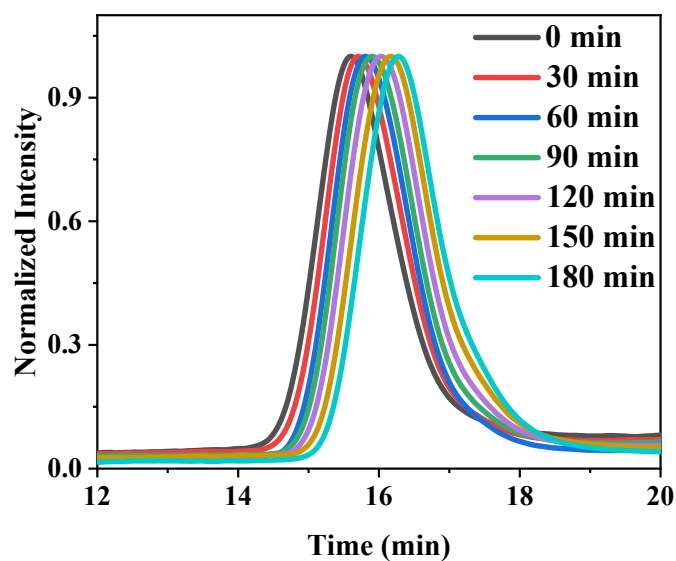


Figure S2 Representative GPC traces (RI) and molecular weight data for **Control-Xa-Ad-PMA** taken during the sonication experiment (10 mg/mL in THF).

4. CoGEF calculation

The stretched structure evolution of three model compounds were explored with Gaussian 09 B3LYP function was employed to describe the system, along with the 6-31 (d) basis sets for all atoms. Solvent effects (THF) were included using the SMD

implicit solvation model. CoGEF method proposed by Beyer *et al.* was used to model the contour length². Briefly, the end-to-end distance of the model compound was fixed to specific values to mimic the imposed force, meanwhile all other geometric coordinates were allowed to fully relax. Then equilibrium geometry was determined at iteratively increased end-to-end distance until the good separation between molecular segments after chain scission.

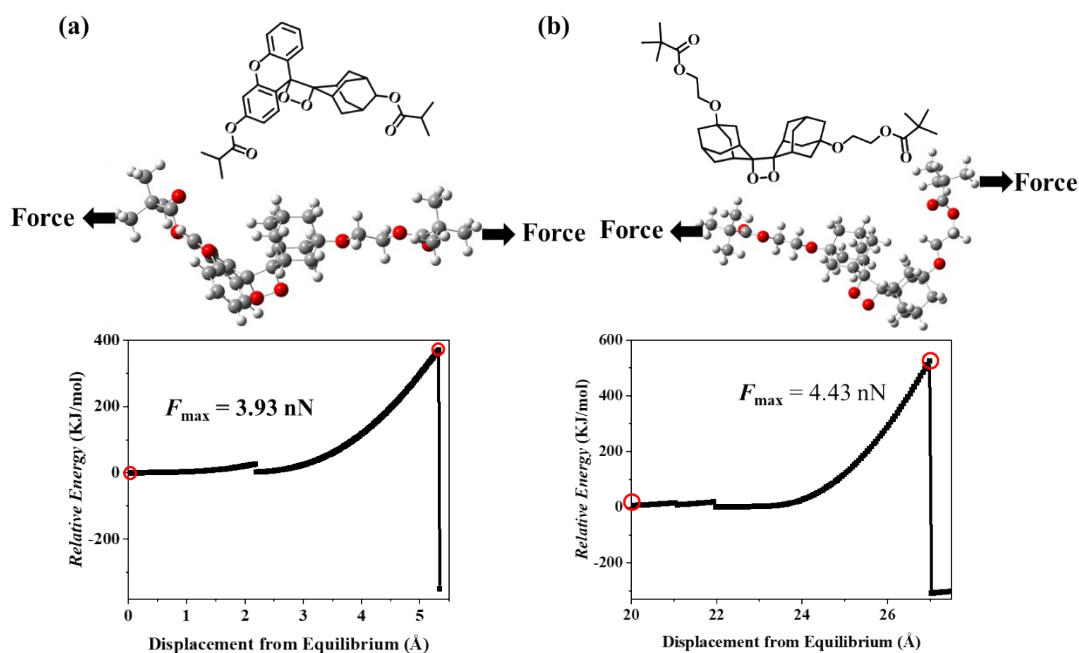


Figure S3 (a) **M-Xa-Ad** and (b) **M-Ad-Ad** of the truncated mechanophore and roducts resulting upon stepwise mechanical elongation predicted at the B3LYP/6-31G* level of theory. CoGEF analysis of **M-Xa-Ad** and **M-Ad-Ad** with the corresponding 3D structures at relax state, at F_{\max} , and after bond cleavage.

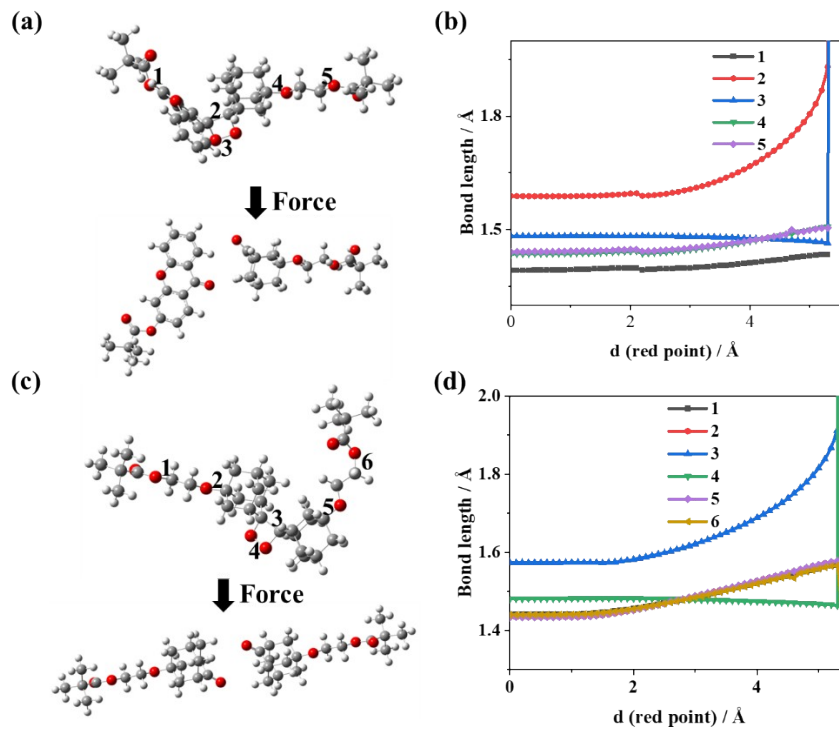


Figure S4 The chemical structure of (a) **Xa-Ad** and (c) **Ad-Ad** used in the calculation; (b) The change of bond length under different extensions for (b) **Xa-Ad** and (d) **Ad-Ad**.

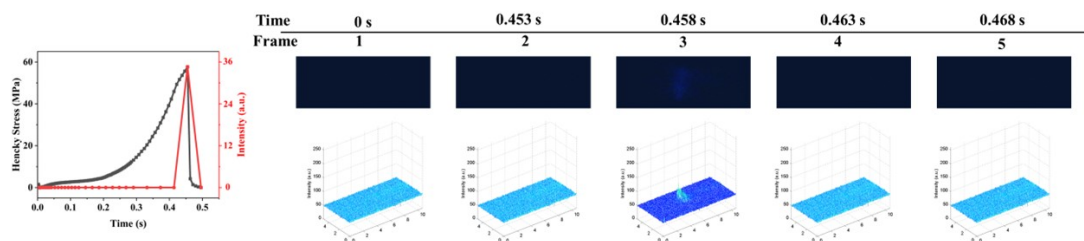


Figure S5 Hencky Stress and light intensity versus time during stretching of bulk films. Graphs of Hencky Stress and light intensity versus time (left) and optical images and intensity analysis of the sample during stretching (right) of (a) crosslinked polymers **Cross-Ad-Ad-PMA**.

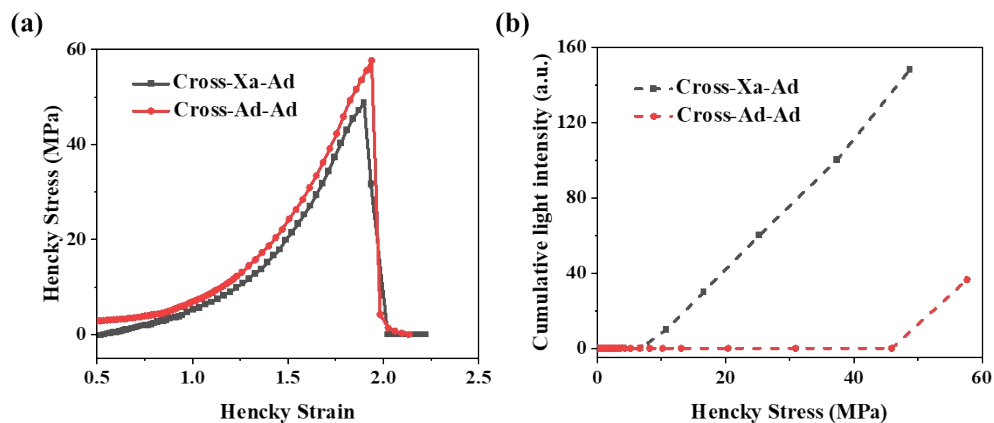
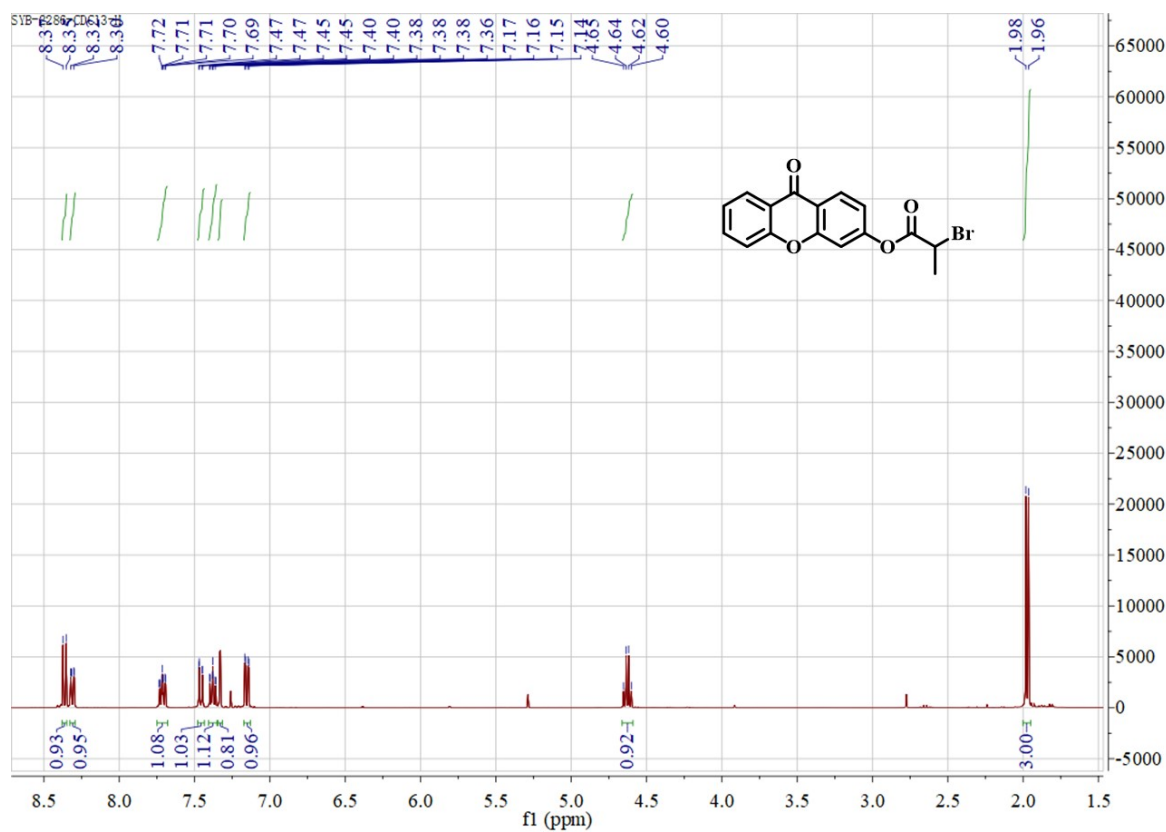
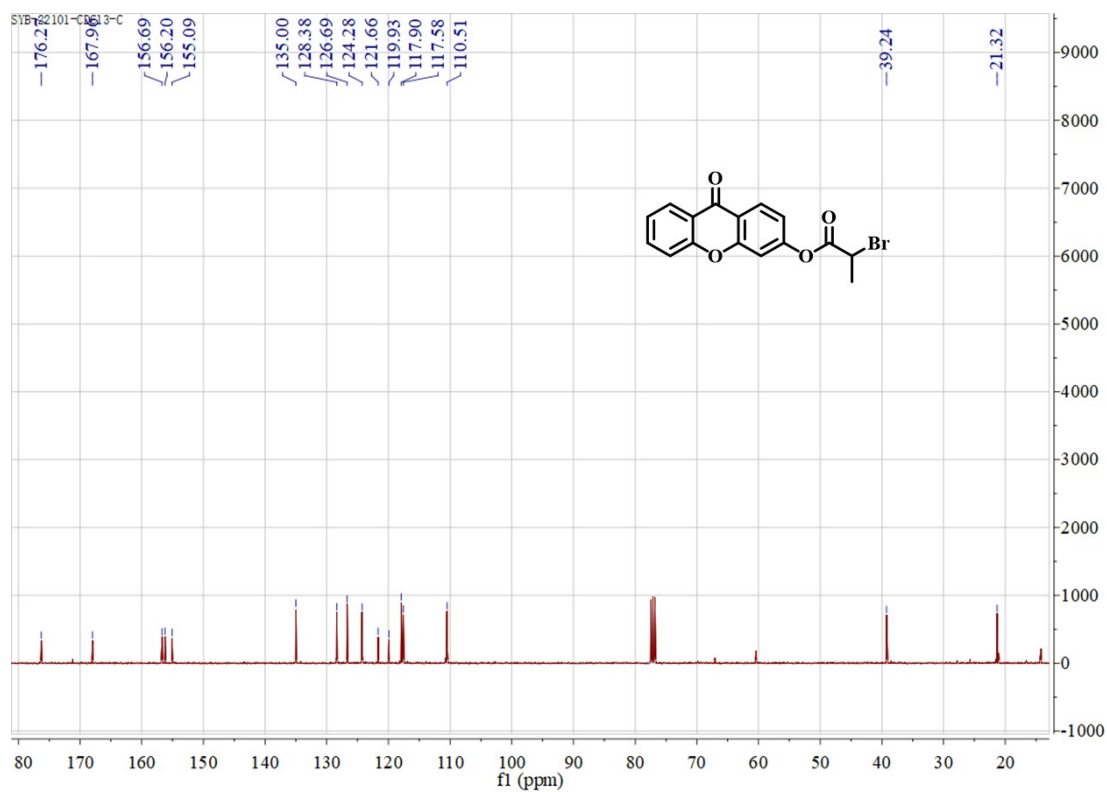


Figure S6 (a) Hencky Stress versus Hencky Strain and (b) light intensity versus Hencky Stress during stretching of crosslinked polymers **Cross-Xa-Ad-PMA** (Black line) and **Cross-Ad-Ad-PMA** (Red line).

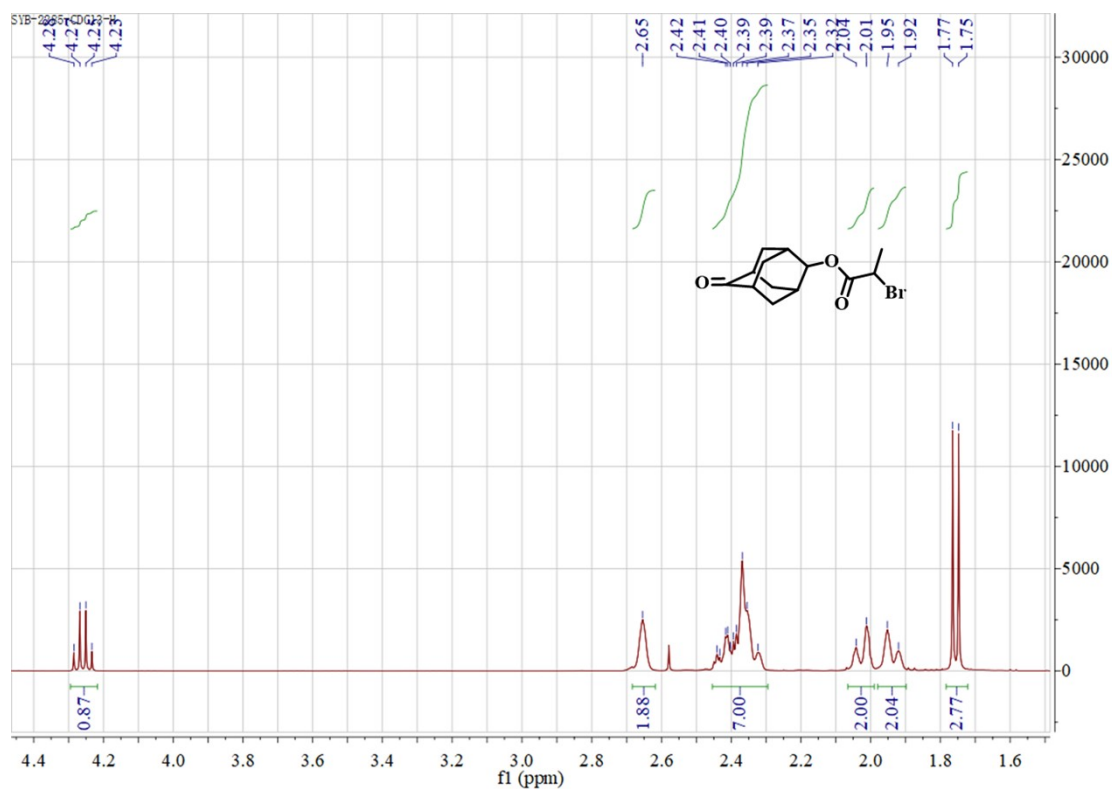
5. NMR Spectra



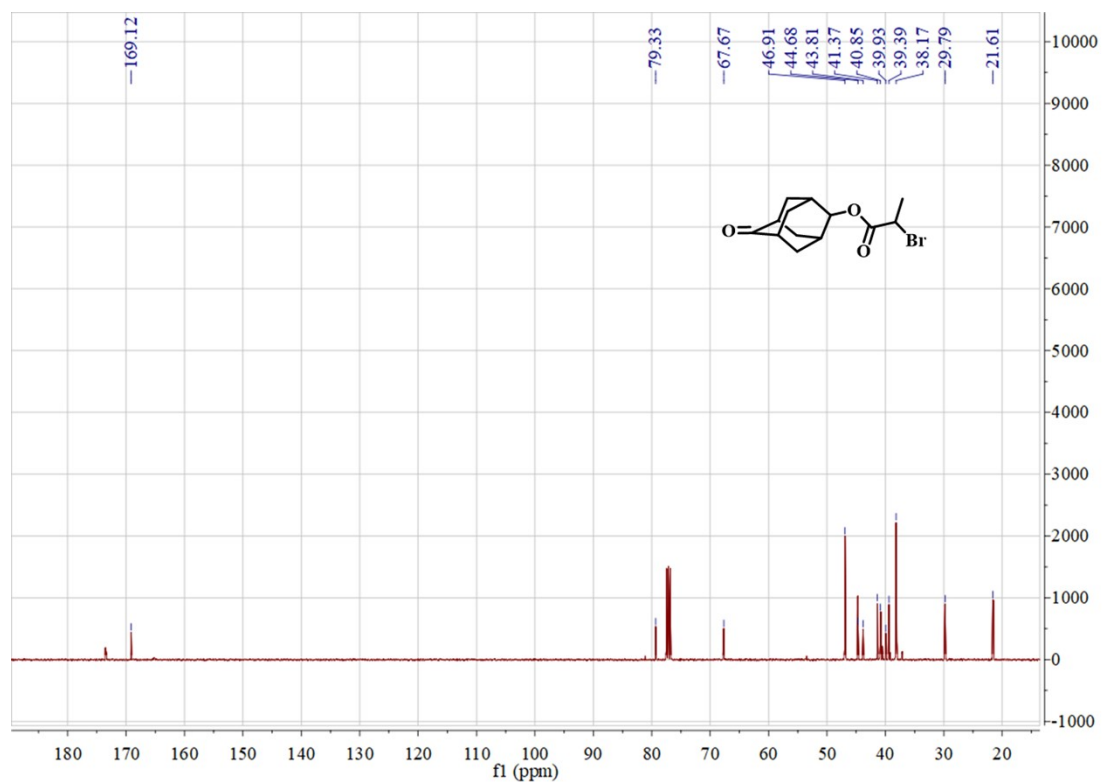
¹H NMR spectrum of compound **1** in CDCl₃.



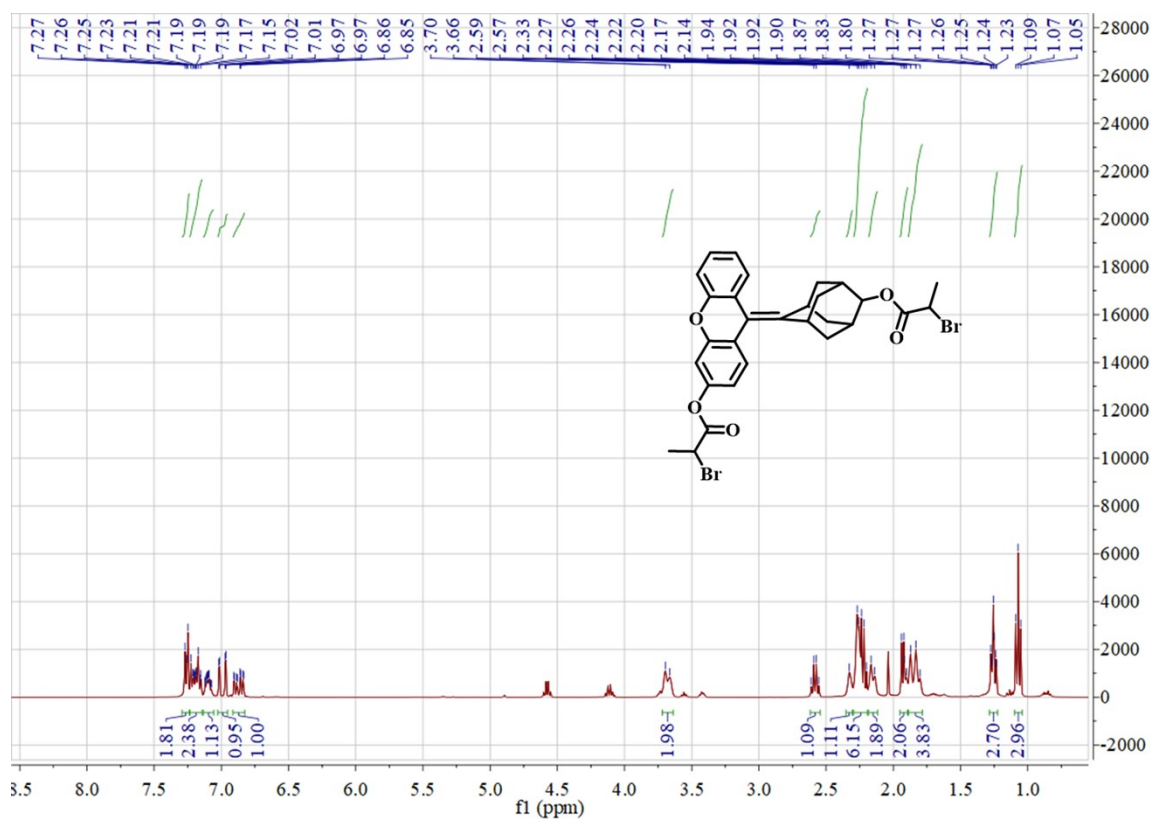
¹³C NMR spectrum of compound **1** in CDCl₃.



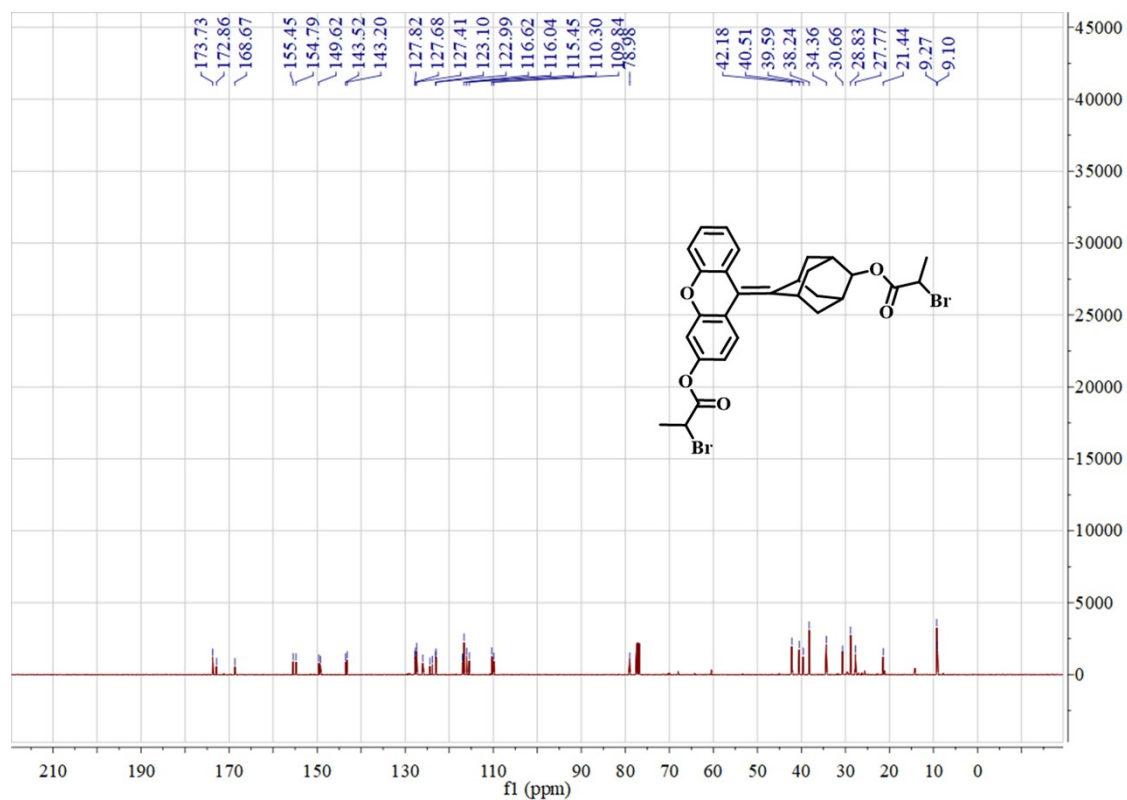
¹H NMR spectrum of compound **2** in CDCl₃.



^{13}C NMR spectrum of compound **2** in CDCl_3 .



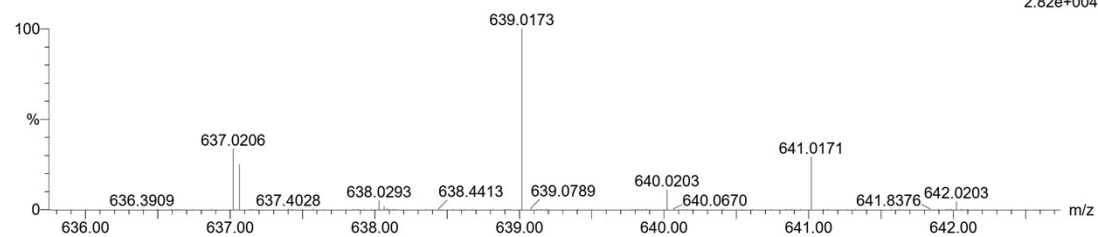
^1H NMR spectrum of compound **3** in CDCl_3 .



¹³C NMR spectrum of compound **3** in CDCl₃.

16
230809-3-1 20 (0.229)

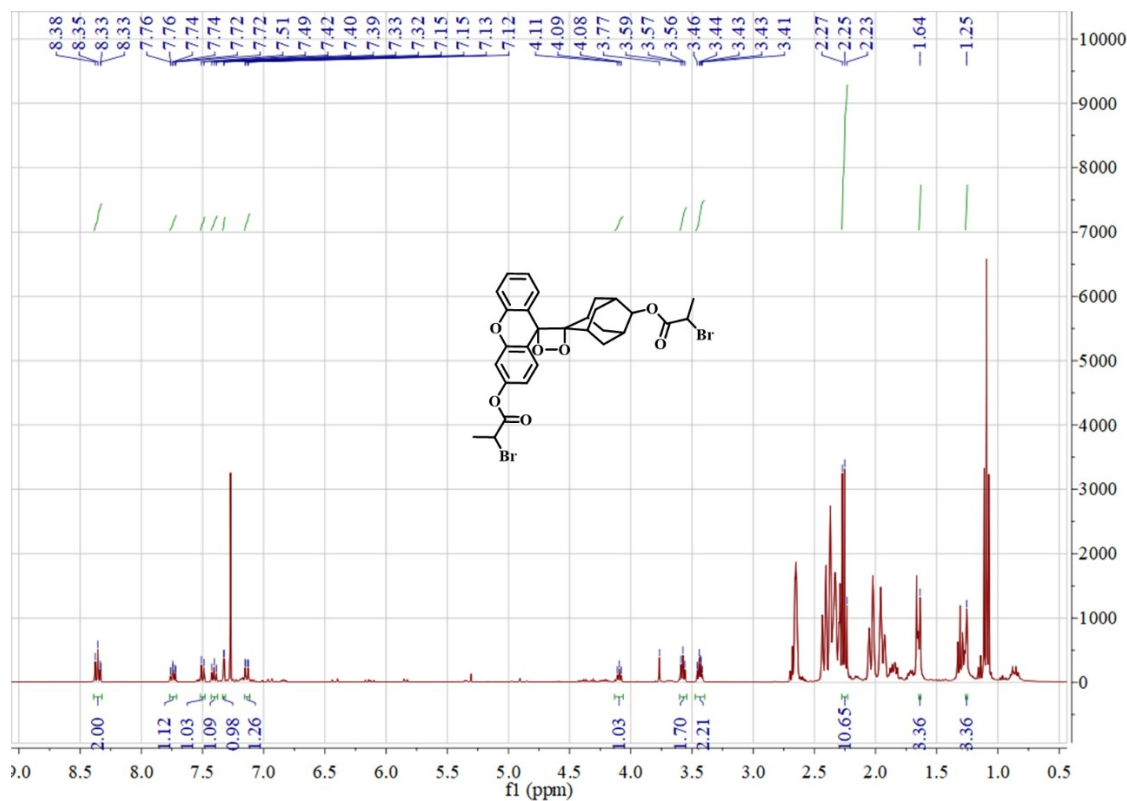
1: TOF MS ES+
2.82e+004



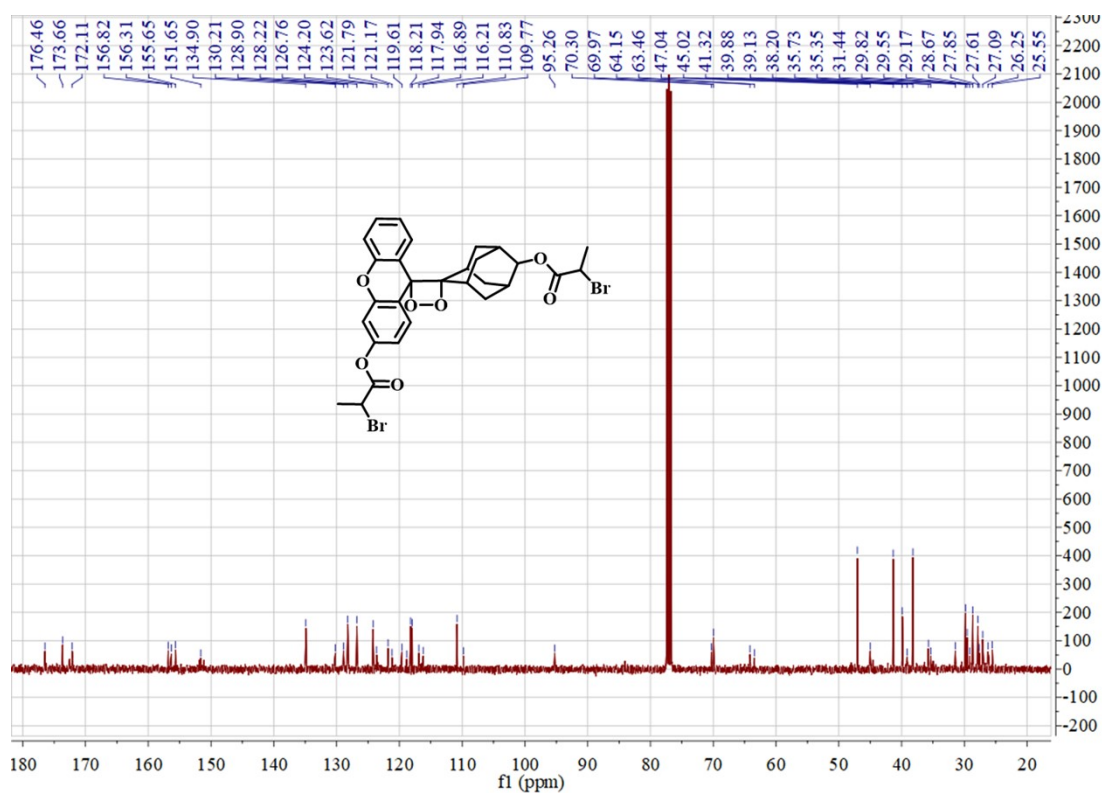
Minimum: -1.5
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
637.0206	637.0201	0.5	0.8	14.5	288.4	n/a	n/a	C ₂₉ H ₂₈ O ₅ NaBr ₂

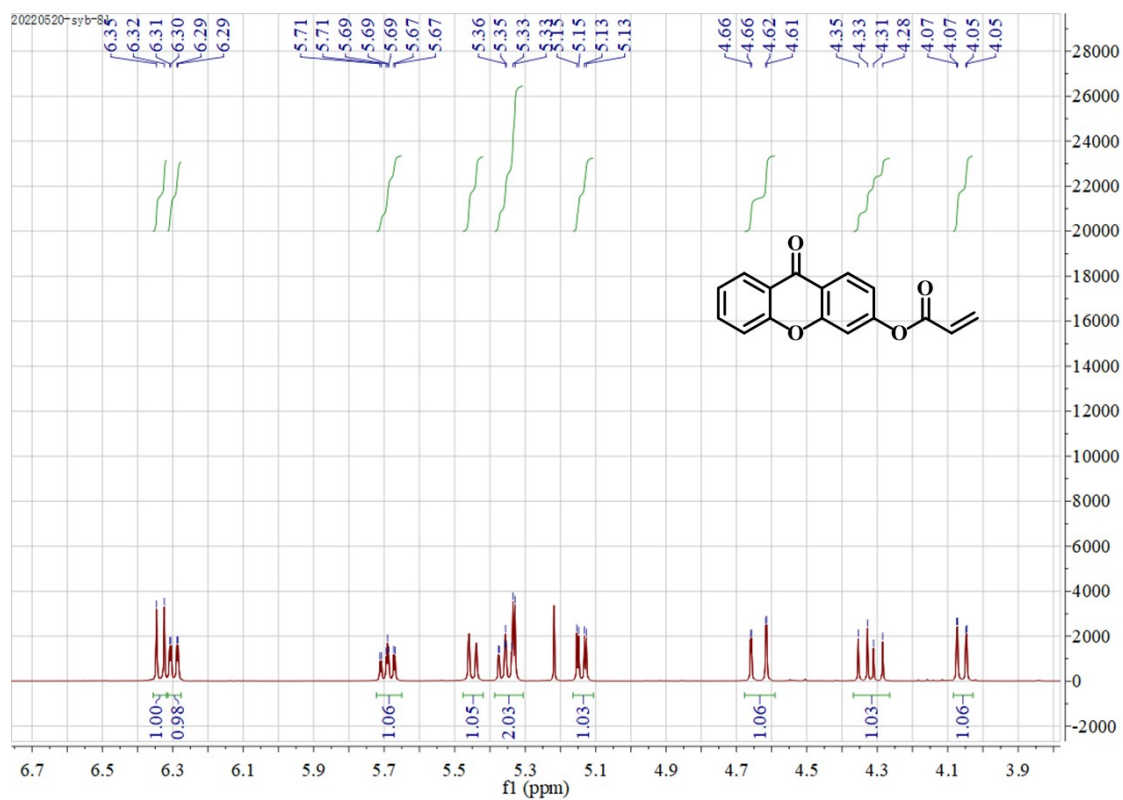
Mass spectrum of compound **3**.



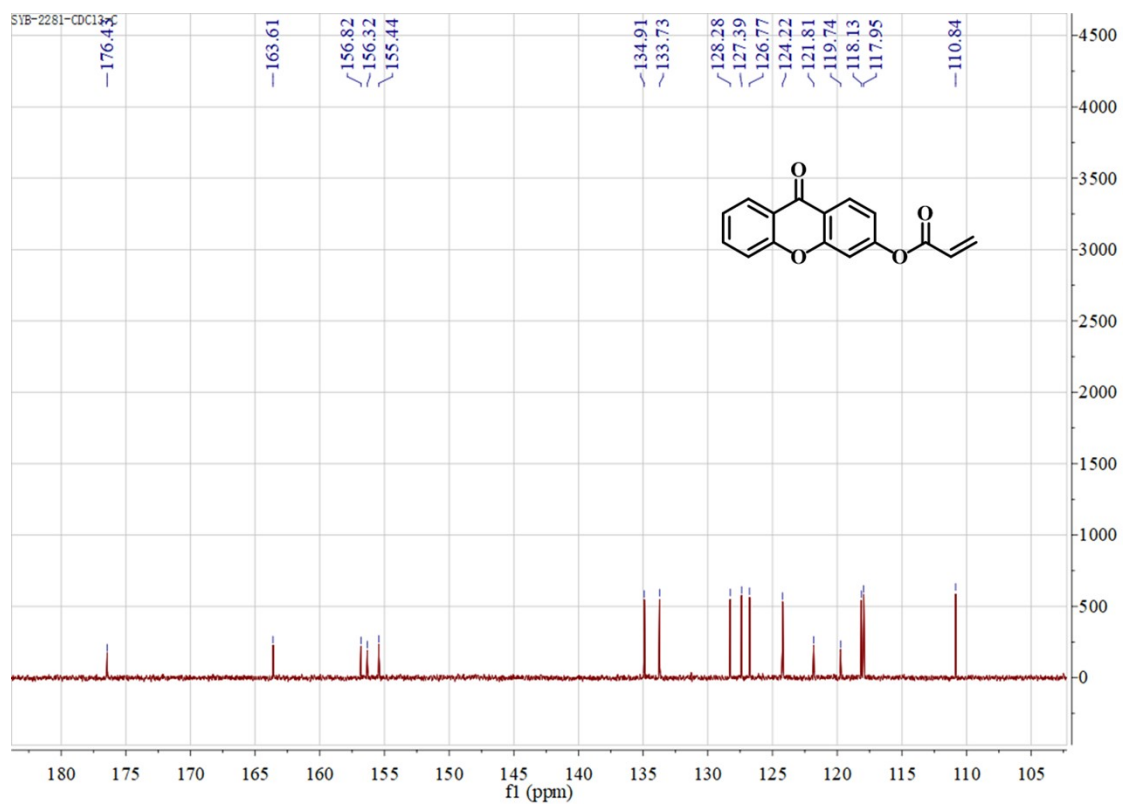
¹H NMR spectrum of compound **Xa-Ad-Br** in CDCl₃.



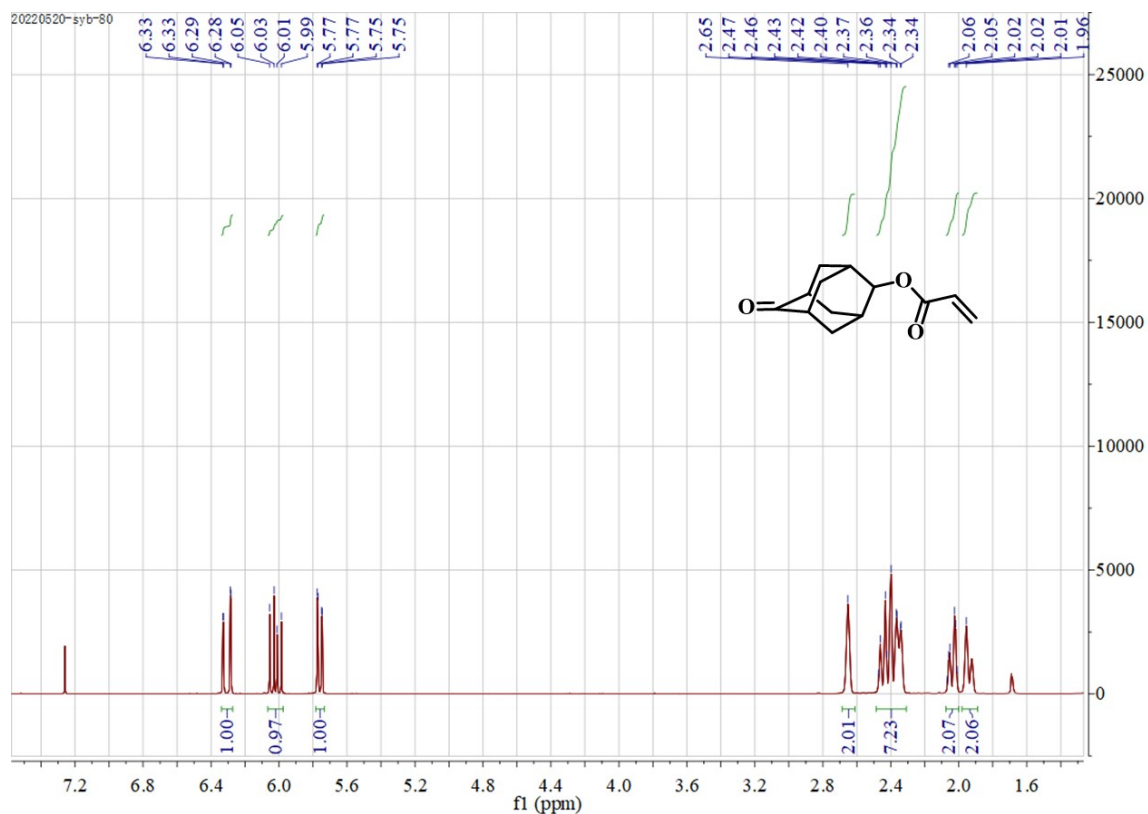
¹³C NMR spectrum of compound **Xa-Ad-Br** in CDCl₃.



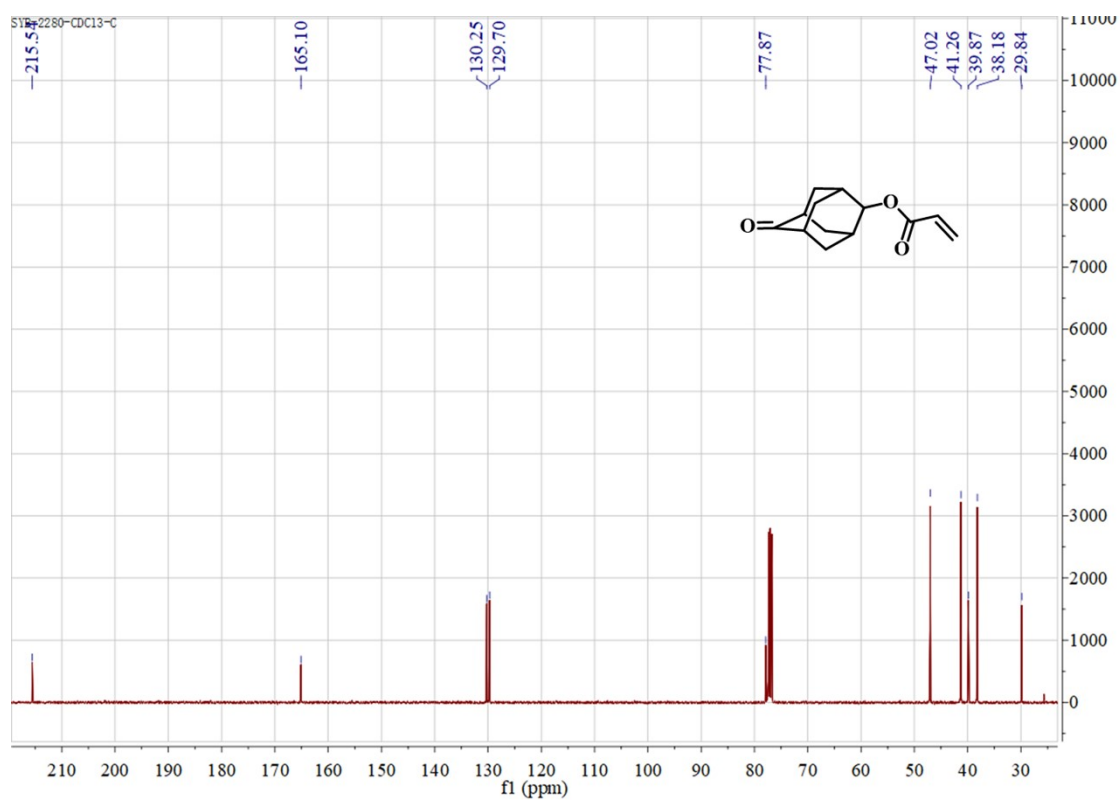
^1H NMR spectrum of compound **4** in CDCl_3 .



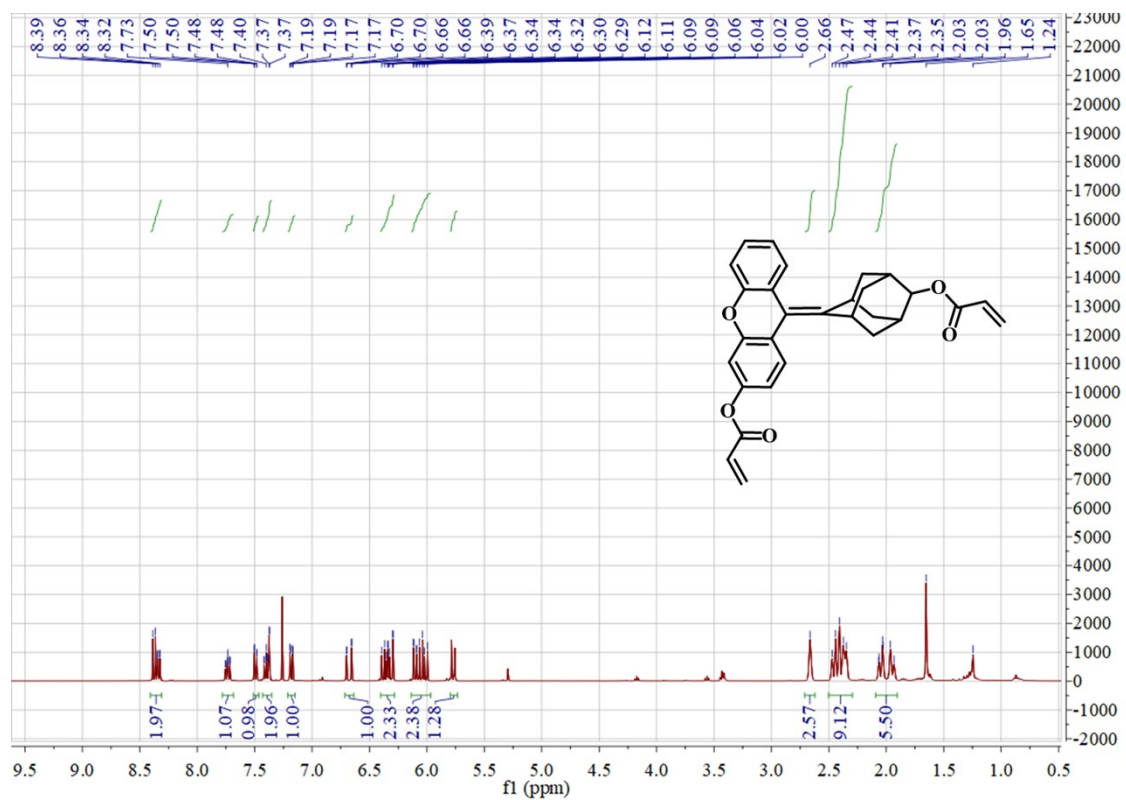
^{13}C NMR spectrum of compound **4** in CDCl_3 .



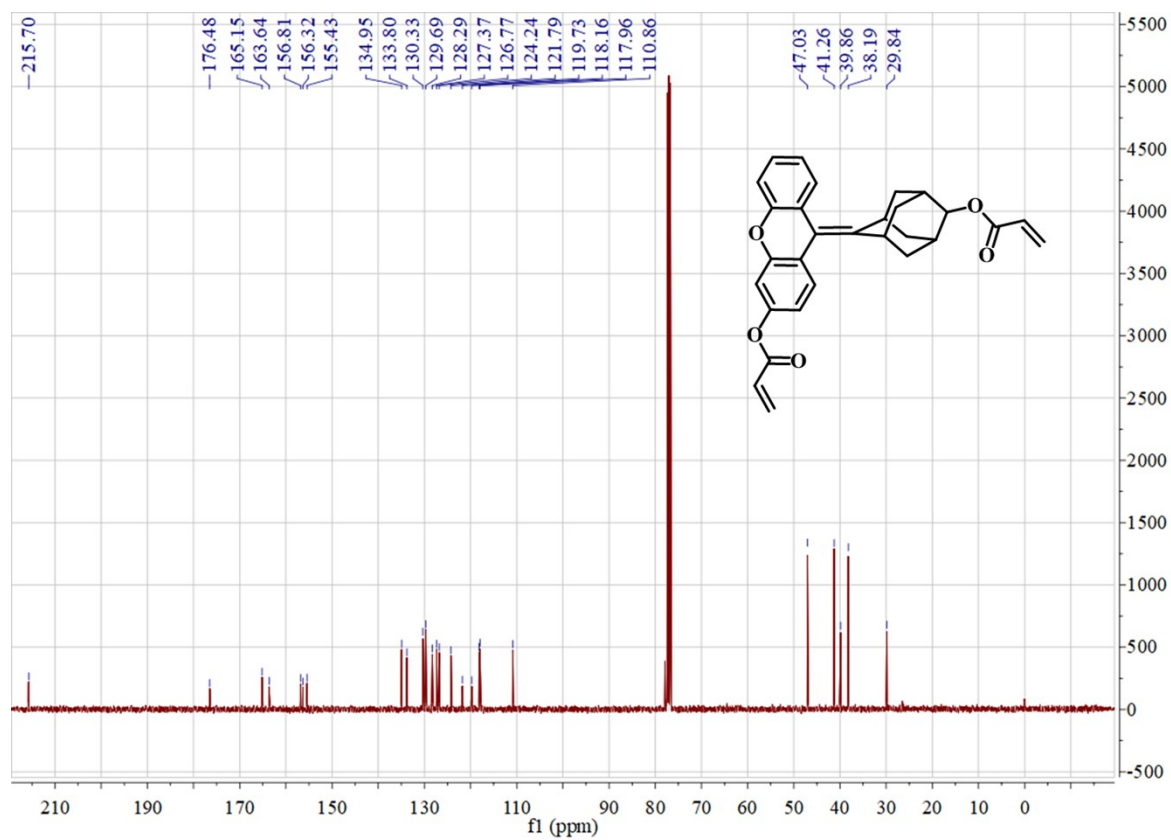
^1H NMR spectrum of compound **5** in CDCl_3 .



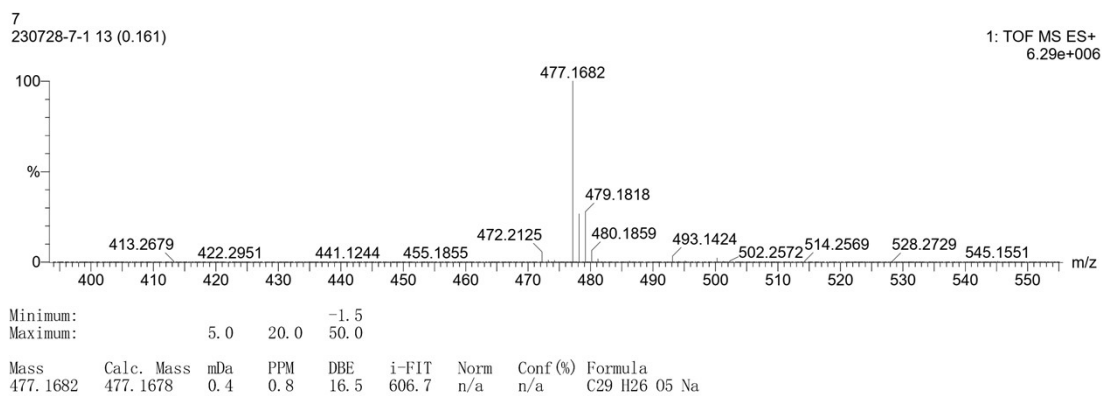
^{13}C NMR spectrum of compound **5** in CDCl_3 .



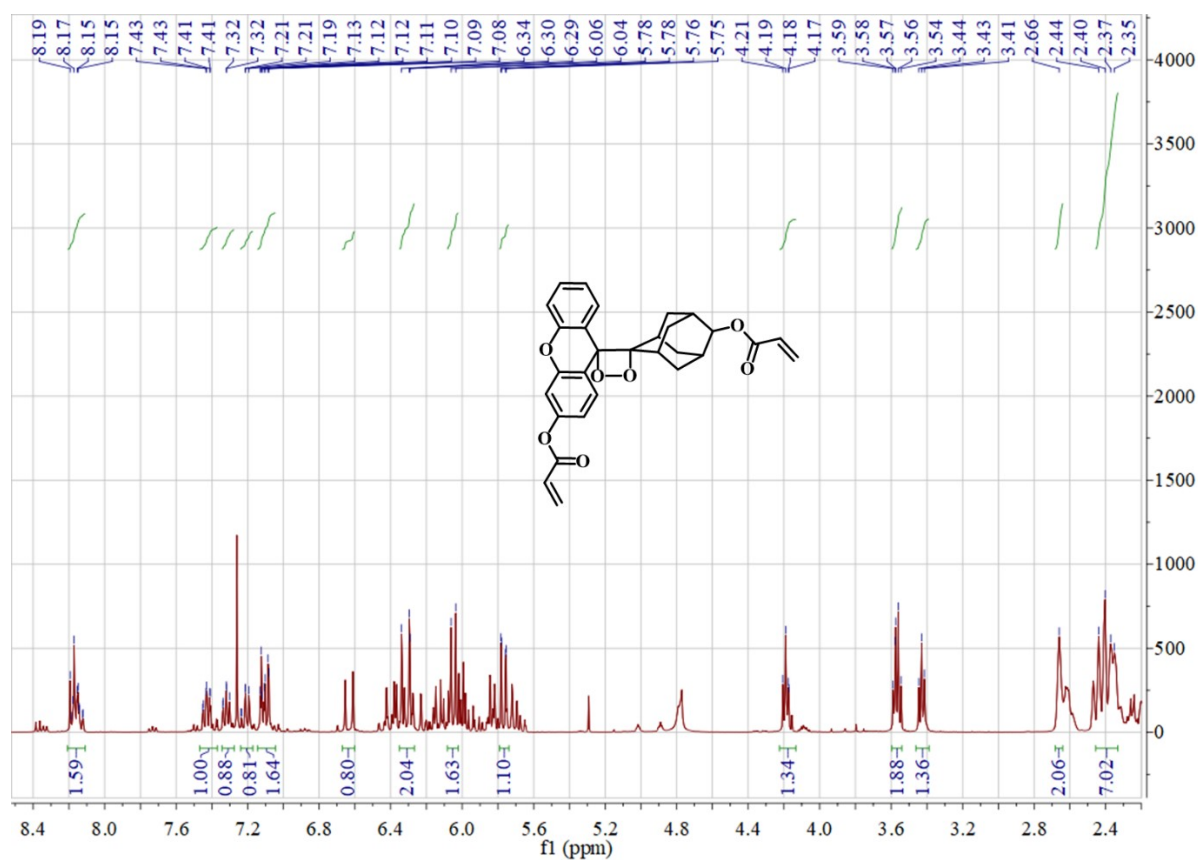
¹H NMR spectrum of compound 6 in CDCl₃.



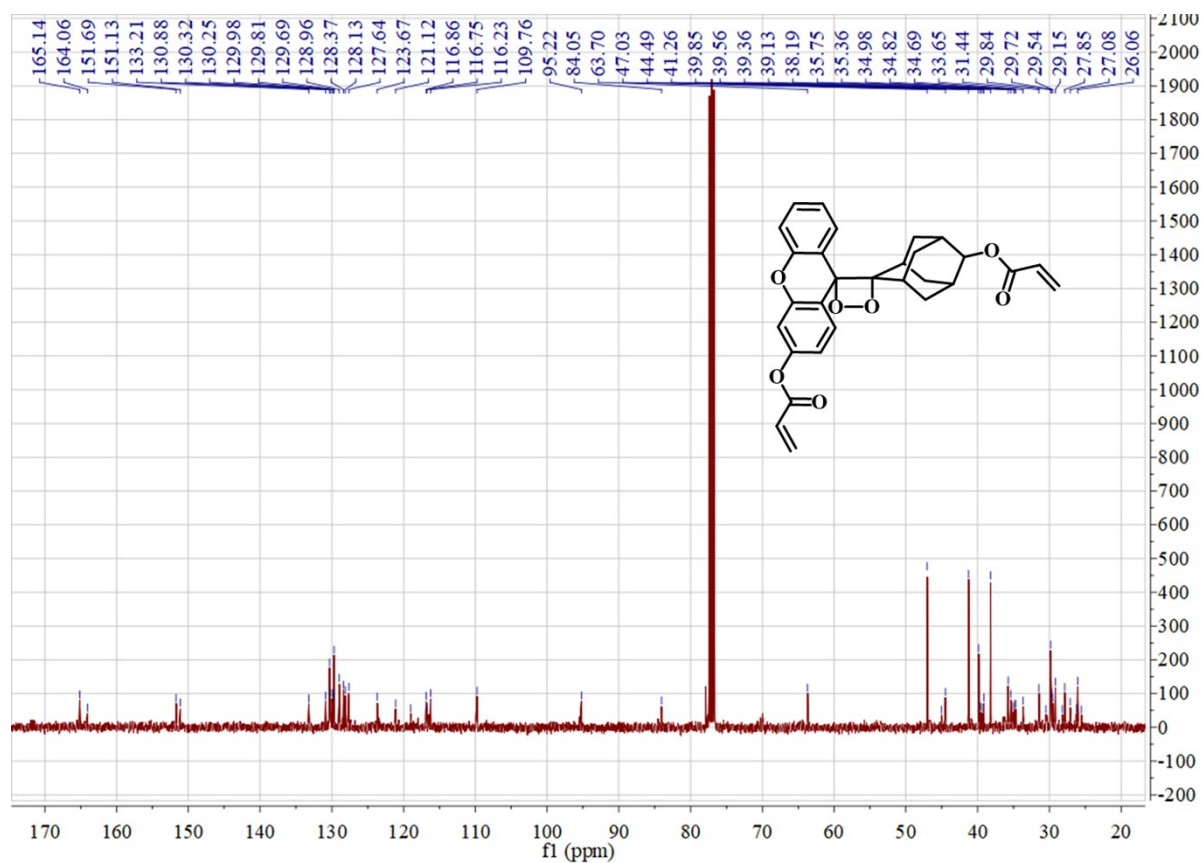
¹³C NMR spectrum of compound 6 in CDCl₃.



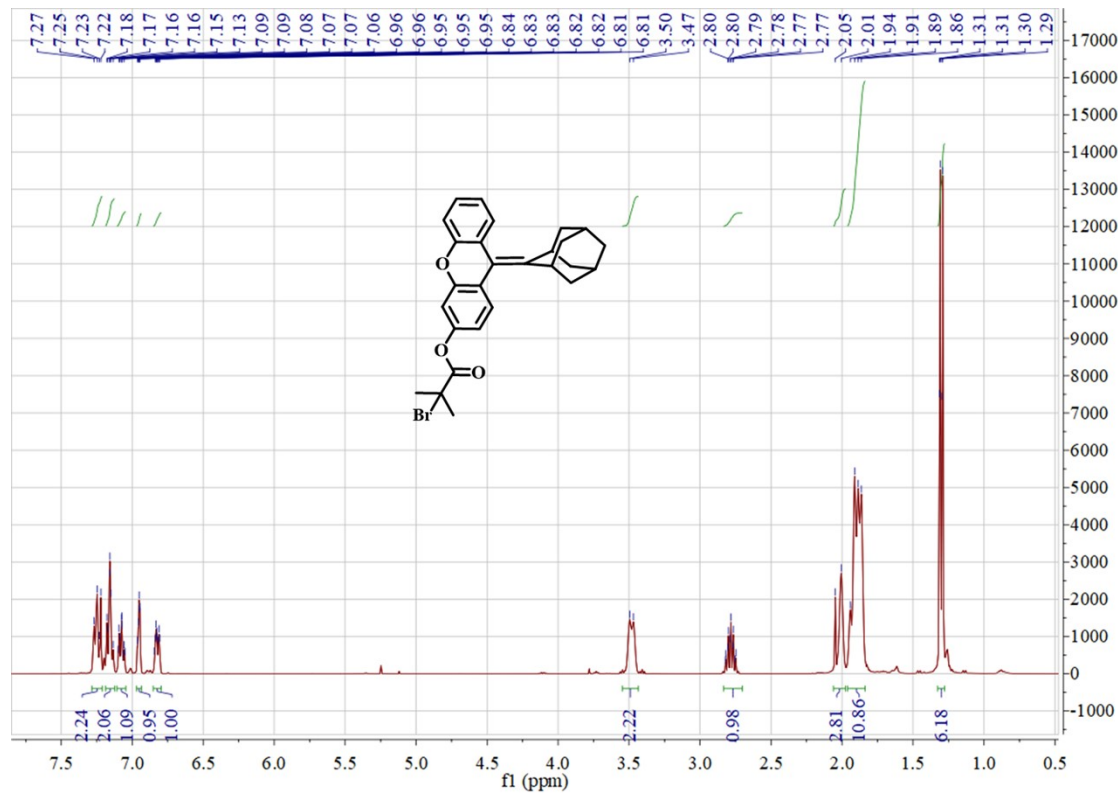
Mass spectrum of compound 6.



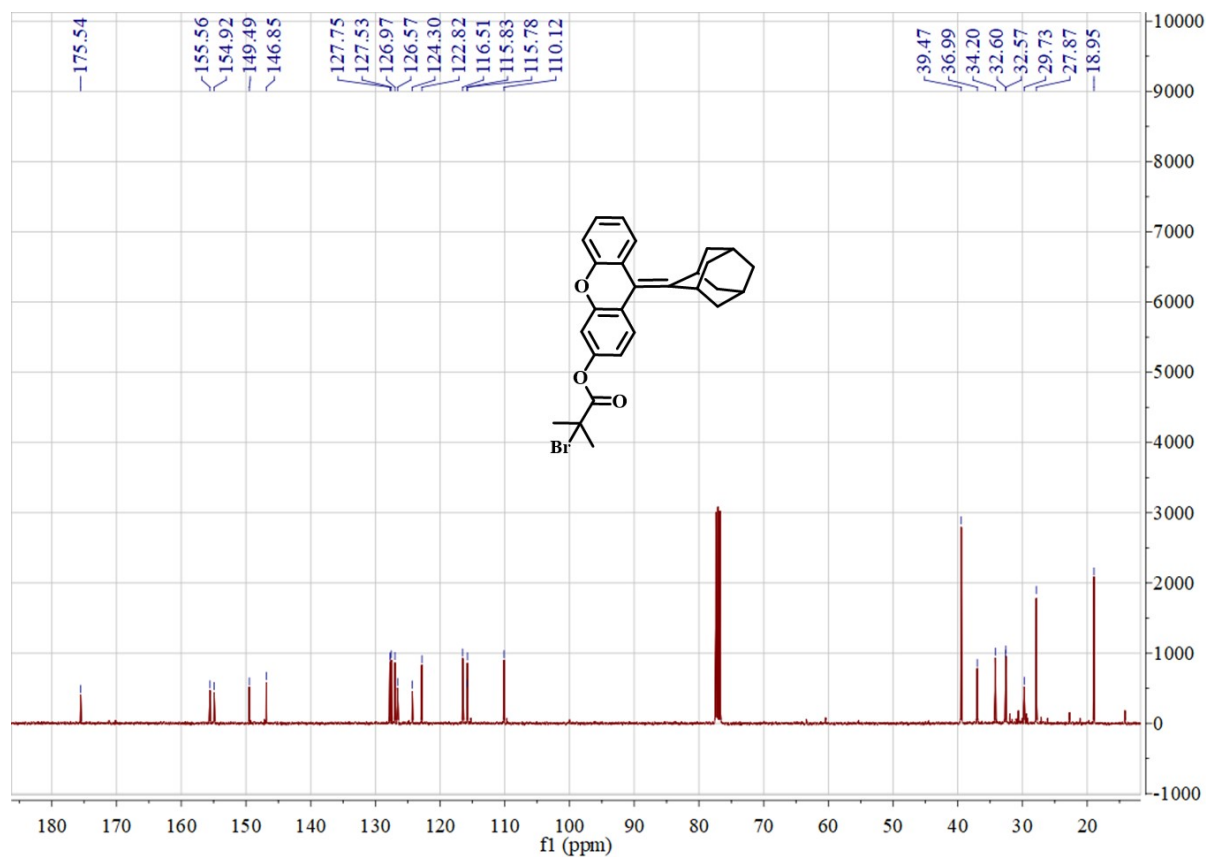
¹H NMR spectrum of compound **Xa-Ad-Vintl** in CDCl₃.



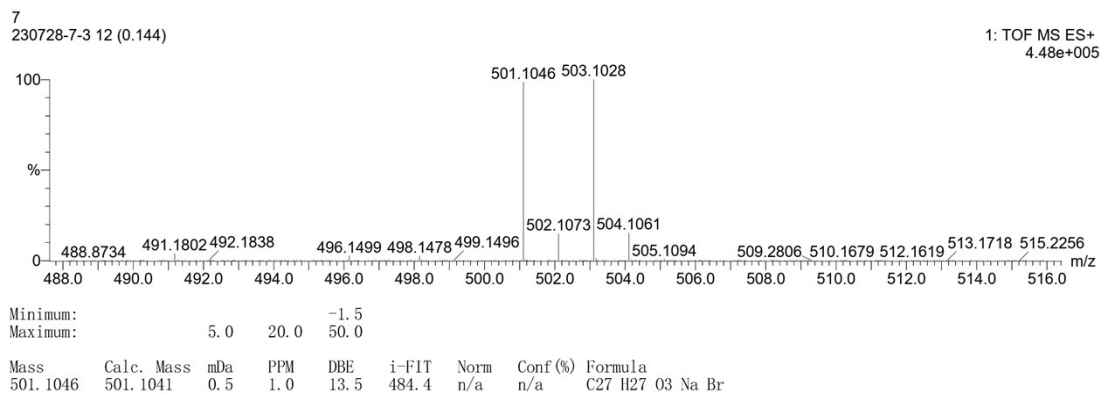
¹³C NMR spectrum of compound **Xa-Ad-Vintl** in CDCl₃.



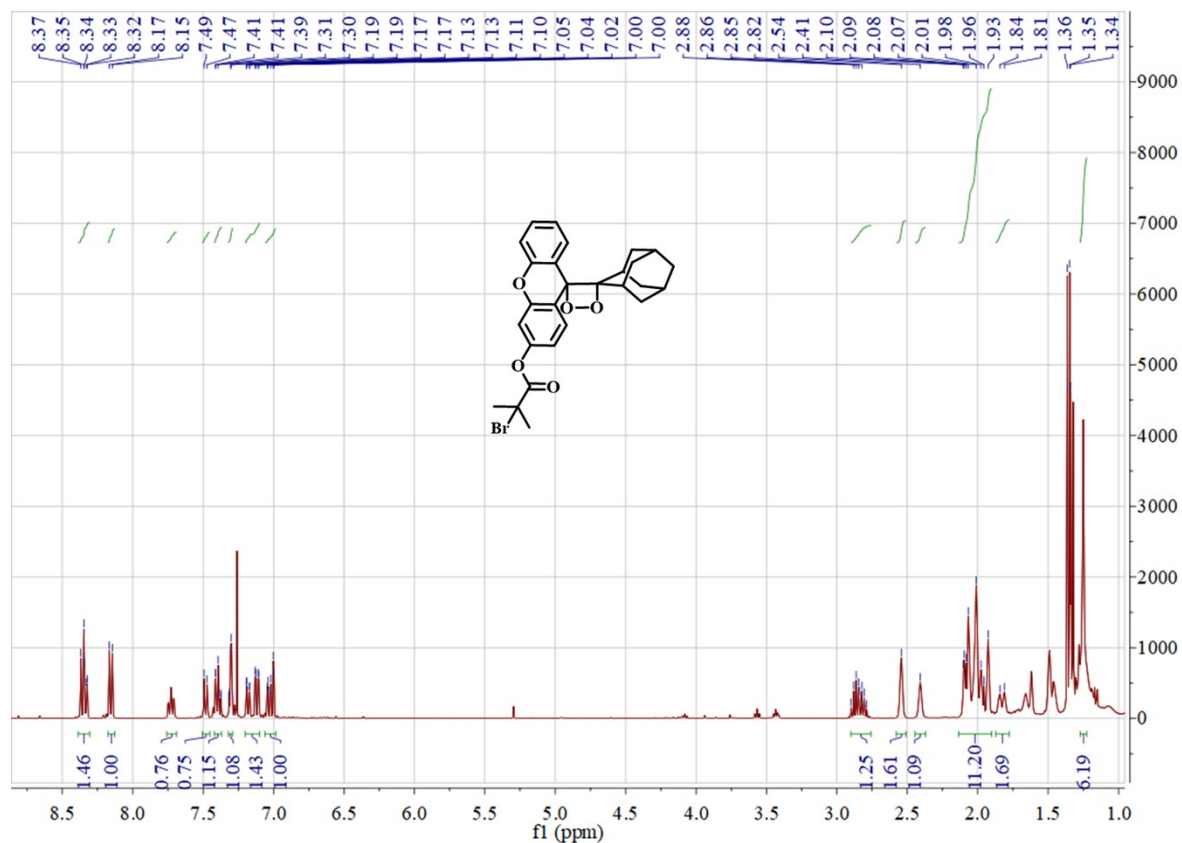
¹H NMR spectrum of compound **7** in CDCl₃.



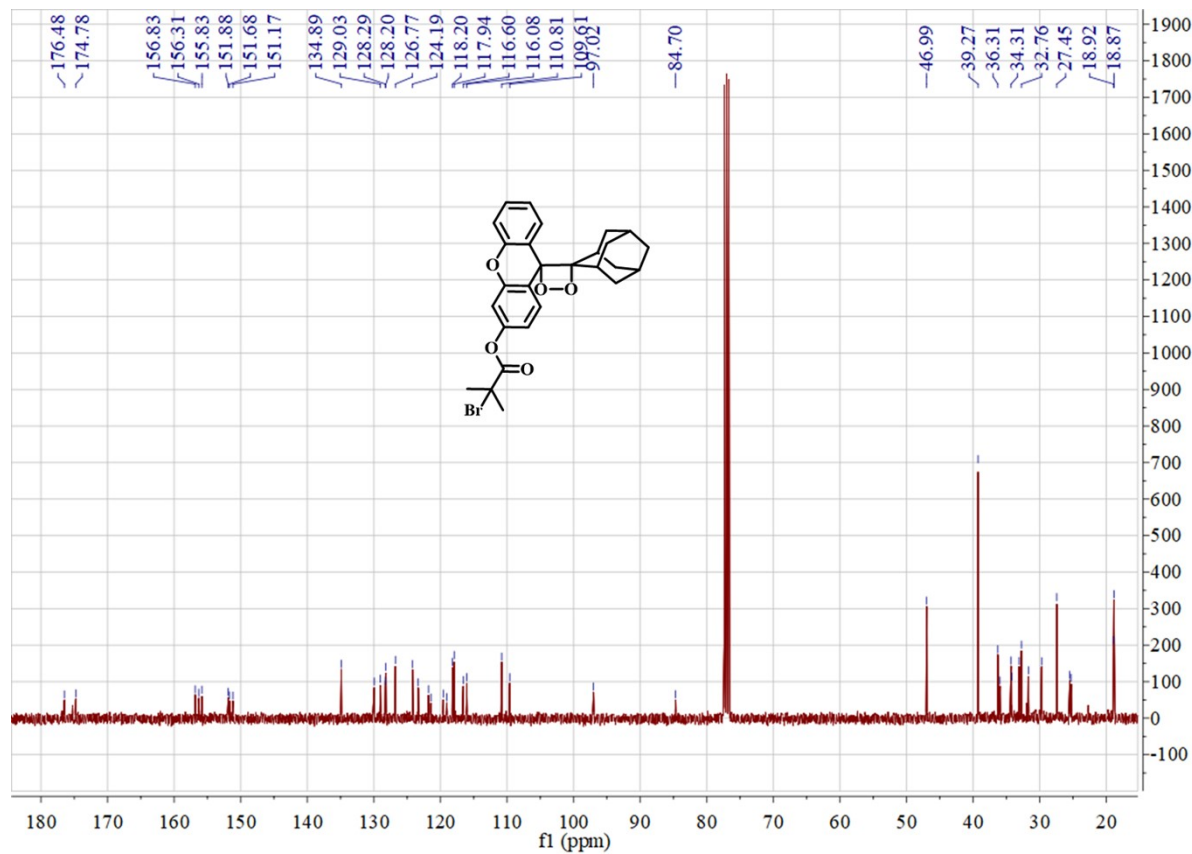
¹³C NMR spectrum of compound 7 in CDCl₃.



Mass spectrum of compound 7.



¹H NMR spectrum of compound Control-Xa-Ad-Br in CDCl₃.



¹³C NMR spectrum of compound Control-Xa-Ad-Br in CDCl₃.

6. Reference

1. Y. Chen and R. P. Sijbesma, *Macromolecules*, 2014, **47**, 3797-3805.
2. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J Chem Phys*, 2010, **132**, 154104.
3. M. J. Kryger, A. M Munaretto and J. S. Moore, *J. Am. Chem. Soc.* 2011, **133**, 18992–18998.