Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Mechanical activation of polymers containing two adjacent mechanophores

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2 General Experimental Details

Unless otherwise stated, all reagents and solvents were purchased from commercial suppliers and used without further purification. Cu(0) wire (diameter: 0.25 mm, purity 99.9%) was purchased from Sigma-Aldrich. Me_6TREN was purchased from Alfa Aesar. Compound **S1** was prepared according to literature procedure.[S1]

Initial molecular weight of polymers were analysed using gel permeation chromatography (GPC) in THF solution (~0.6 mg/mL) at 35 °C on an Agilent 1260 Infinity II system equipped with 2 × PL gel 10 µm mixed-B columns and refractive index detector. All sonication analyses were performed using either the Agilent system or a Malvern Viscotek GPCmax VE2001 solvent/sample module with 2 × PL gel 10 µm mixed-B and a PL gel 500 Å column, and equipped with a Viscotek VE3580 refractive index detector. Narrow polydispersity polystyrene standards (Agilent or Malvern Panalytical) were employed as calibration references. Samples were filtered through a Whatman Puradisc 4 mm syringe filter with 0.45 µm PTFE membrane before injection to equipment, and experiments were carried out with injection volume of 100 µL, flow rate of 1 mL/min. Results were analysed using Agilent GPC/SEC Software or Malvern OmniSEC 5.12 software using *n*-dodecane as an internal marker. Whilst different GPC systems were used to analyse polymer degradation, we do not anticipate that this will affect the rates of cleavage calculated.

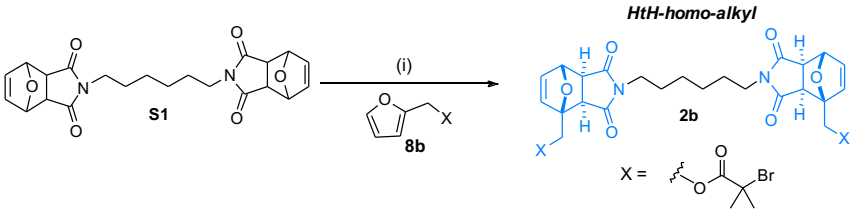
Ultrasound experiments were performed using a Sonics VCX 500 ultrasonic processor equipped with a 13 mm diameter removable-tip probe. The distance between the titanium tip and the bottom of the Suslick cell was 2 cm. The ultrasonic intensity was calibrated using the method outlined by Hickenboth *et al*.[S2] The Suslick cells were fabricated by the School of Chemistry glass workshop at the University of Manchester.

Analytical TLC was performed on precoated silica gel plates (0.25 mm thick, 60 F254, Merck, Germany) and observed under UV light or stained with a potassium permanganate solution. Preparative TLC was performed on precoated silica gel plates: 2 mm, UNIPLATE GF, Analtech Inc., DE, USA. Flash column chromatography was performed with silica gel 60 (230-400 mesh) from Sigma-Aldrich. ^{1}H and ^{13}C NMR spectra were obtained using either a Bruker Avance III 500 MHz Prodigy instrument or a Bruker Avance III 400 MHz Prodigy instrument at the University of Manchester. Chemical shifts are reported in parts per million (ppm) from high to low frequency and referenced to the residual solvent resonance. Coupling constants (*J*) are reported in Hertz (Hz) and splitting patterns are designated as follows: b = broad, s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet. Mass spectra were obtained through the Mass Spectrometry services in the School of Chemistry at the University of Manchester.

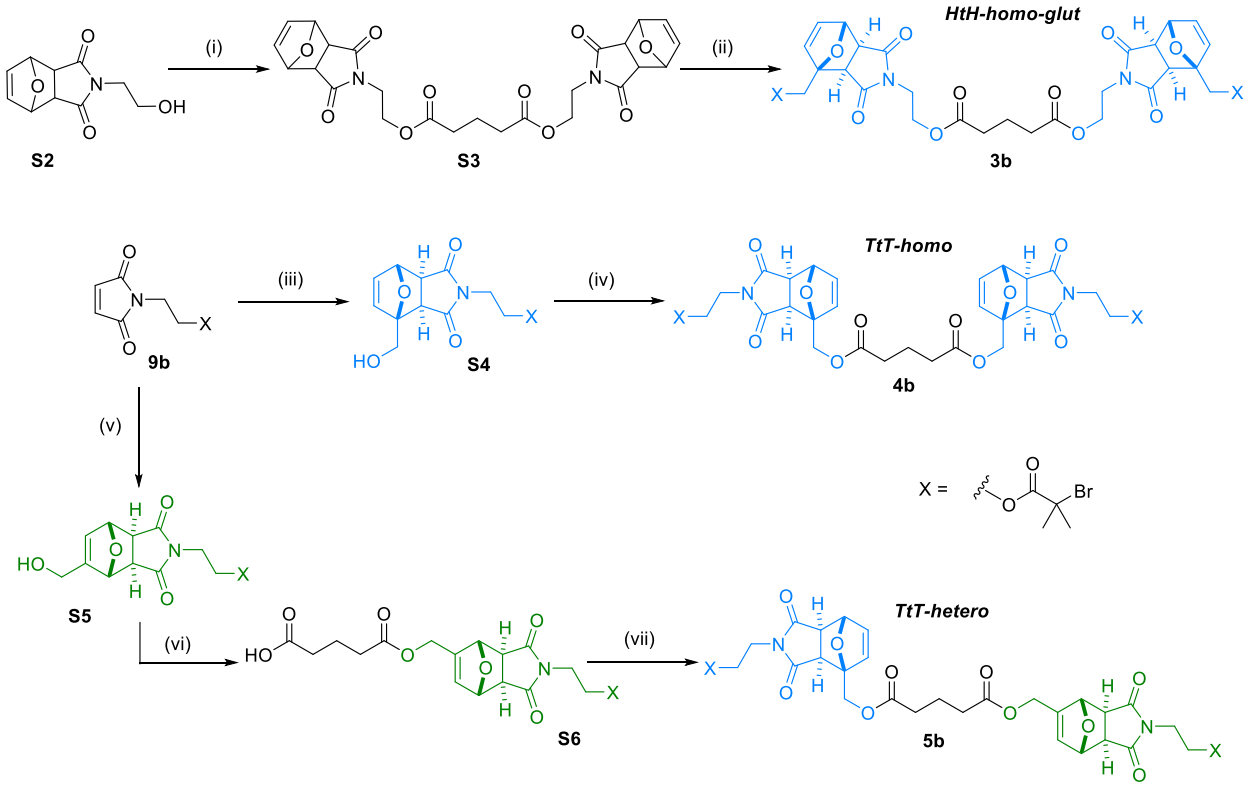
Abbreviations: DCM: dichloromethane; DMAP: 4-(*N*,*N*-dimethylamino)pyridine; EDCI: 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide; ESI: electrospray ionization; EtOAC: ethyl acetate; 2-HBMP: 2-hydroxyethyl 2-bromo-2-methylpropionate; HRMS: high resolution mass spectrometry; MeOH: methanol; MS: mass spectrometry; PE: petroleum ether; TLC: thin layer chromatography.

3 Synthesis of Diels-Alder adducts and reference compounds

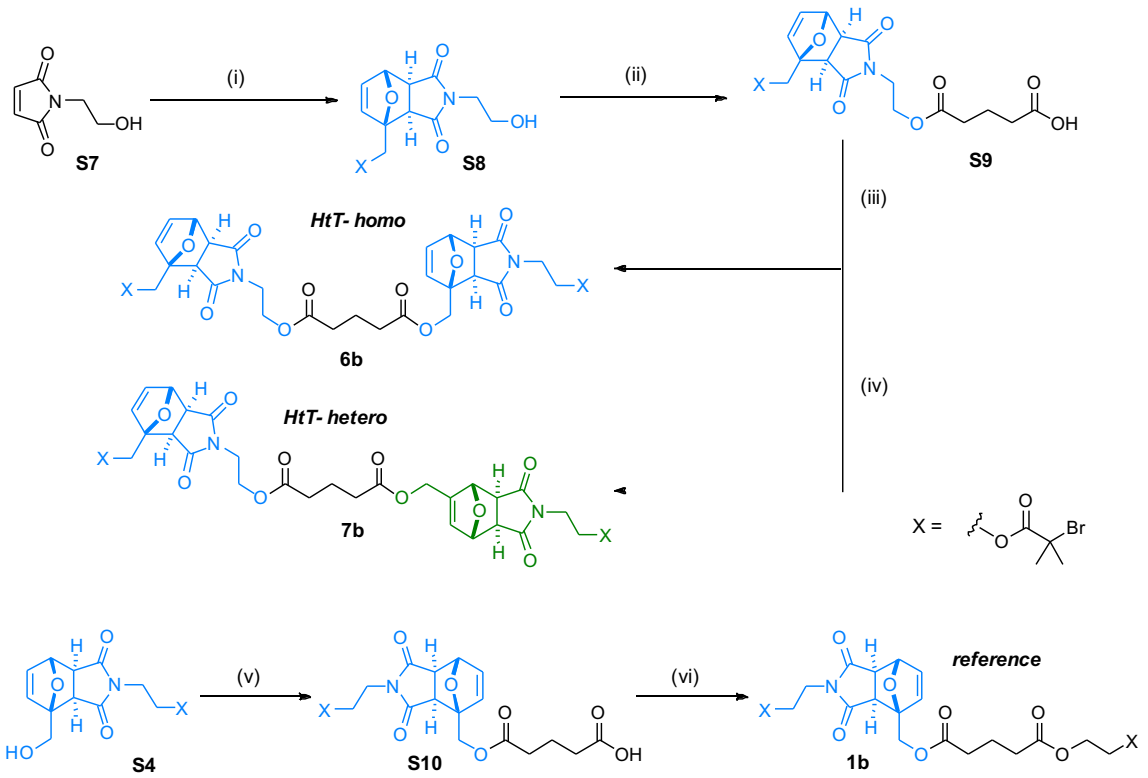
3.1 Outline of syntheses



Scheme S1. Outline of the preparation of HtH-alkyl-linked mechanophore. Reaction conditions: (i) [1] toluene, 105°C, overnight [2] toluene, 70°C, 9 d, 34%.

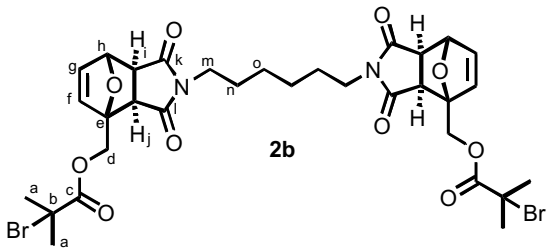


Scheme S2. (Top) Synthesis of HtH-homo-dimer **3b**. Reaction conditions: (i) glutaryl chloride, DMAP, Et_3N, DCM, 30°C, 18 h, 40%; (ii) [1] toluene, 108°C, overnight [2] **8b**, toluene, 75°C, 27.5 h, 53%. (Bottom) Synthesis of TtT-homo-dimer **4b** and TtT-hetero-dimer **5b**. Reaction conditions: (iii) furfuryl alcohol, toluene, DMF, 75°C, 24 h, 58%; (iv) glutaryl chloride, DMAP, Et_3N, DCM, 32°C, 24 h, 56%; (v) 3-furanmethanol, toluene, 75°C, overnight, 53%; (vi) glutaric anhydride, DMAP, Et_3N, DCM, RT, 22 h, 35%; (vii) **S4**, EDCI, DMAP, DCM, DMF, RT, 25 h, 30%.



Scheme S3. (Top) Synthesis of HtT-homo-dimer **6b** and HtT-hetero-dimer **7b**. Reaction conditions: (i) **8a**, toluene, 75°C, overnight, 36%; (ii) glutaric anhydride, DMAP, Et_3N, DCM, RT, 1.5 d, 50%; (iii) **S4**, EDCI.HCl, DMAP, DCM, RT, 23 h, 42%; (iv) **S5**, EDCI.HCl, DMAP, DCM, RT, 23 h, 29%. (Bottom) Synthesis of the reference mechanophore **1b**. Reaction conditions: (v) glutaric anhydride, DMAP, Et_3N, DCM, RT, 24 h, 55%; (vi) 2-HBMP, EDCI·HCl, DMAP, DCM, RT, 25 h, 30%.

3.2 Synthesis of 2b



A solution of **S1** (200 mg, 0.48 mmol, 1.0 eq.) in toluene (1.94 mL) was heated to 105°C for 1 d. The solution was then cooled to 70°C and **8b** added (240 mg, 0.96 mmol, 2.0 eq.). After 3.5 d the solution was cooled to room temperature and solvent removed. The crude was purified by preparative TLC (2:3 PE:EtOAc, 2 elutions) yielding **2b** (R_f = 0.65) as a white powder (128 mg, 0.17 mmol, 34% yield).

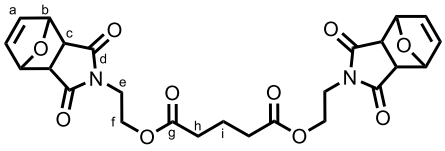
^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.56 (dd, *J* = 5.7, 1.7 Hz, 2H, H_g), 6.47 (d, *J* = 5.7 Hz, 2H, H_f), 5.27 (d, *J* = 1.7 Hz, 2H, H_h), 4.96 (d, *J* = 12.6 Hz, 2H, H_d), 4.56 (d, *J* = 12.6 Hz, 2H, $H_{d'}$), 3.45 (t, *J* = 7.2 Hz, 4H, H_m), 2.97 (d, *J* = 6.4 Hz, 2H, H_i), 2.92 (d, *J* = 6.4 Hz, 2H, H_j), 1.94 (d, *J* = 8.1 Hz, 12H, H_a), 1.53 (t, *J* = 6.9 Hz, 4H, H_n), 1.30 – 1.26 (m, 4H, H_o).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 175.77 (C_k or C_l), 174.32 (C_k or C_l), 171.22 (C_c), 137.56 (C_g), 137.05 (C_f), 89.43 (C_e), 81.25 (C_h), 62.76 (C_d), 55.56 (C_b), 49.94 (C_i), 48.45 (C_j), 38.96 (C_m), 30.92 (C_a), 30.86 ($C_{a'}$), 27.43 (C_n), 26.13 (C_o).

MS-ESI(+): *m/z* = 791.2 (35, $[M+Na]^+$), 793.2 (100, $[M+Na]^+$), 795.2 (50, $[M+Na]^+$);

HRMS-ESI(+): *m/z* = 791.0778 $[M+Na]^+$, calculated for $C_{32}H_{38}O_{10}N_2Br_2Na^+$: 791.0785

3.3 Synthesis of S3

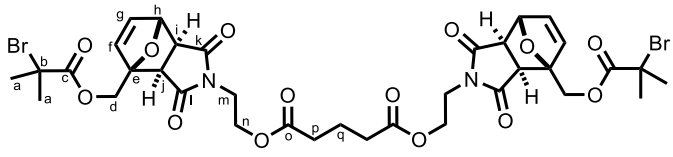


S3

To a dry flask containing **S2** (1.11 g, 5.33 mmol, 2.00 eq.) and DCM (50 mL) was added a solution of DMAP (16 mg, 0.13 mmol, 0.05 eq.) in Et_3N (0.82 mL, 5.86 mmol, 2.20 eq.) and DCM (3.3 mL). The solution was cooled in an ice bath before the dropwise addition of glutaryl chloride (0.34 mL, 2.66 mmol, 1.00 eq.). The solution was heated to 30°C for 18 h before being quenched with water and extracted into DCM (3x150 mL). The organic fraction was dried over Na_2SO_4, filtered and the solvent removed *in vacuo*. The crude was purified by flash column chromatography (1.5% MeOH in DCM) to yield the product as a white powder (543 mg, 1.06 mmol, 40%).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.52 (d, *J* = 1.1 Hz, 4H, H_a), 5.27 (d, *J* = 1.2 Hz, 4H, H_b), 4.22 (t, *J* = 5.3 Hz, 4H, H_f), 3.74 (t, *J* = 5.4 Hz, 4H, H_e), 2.87 (s, 4H, H_c), 2.31 (t, *J* = 7.3 Hz, 4H, H_h), 1.86 (p, *J* = 7.5 Hz, 2H, H_i).
^{13}C NMR (126 MHz, $CDCl_3$) δ = 176.17 (C_d), 172.79 (C_g), 136.71 (C_a), 81.09 (C_b), 60.74 (C_f), 47.63 (C_c), 38.01 (C_e), 33.10 (C_h), 19.71 (C_i).
MS-ESI(+): *m/z* = 537.2 (100, $[M+Na]^+$), 538.2 (15, $[M+Na]^+$).
HRMS-ESI(+): *m/z* = 537.1458 $[M+Na]^+$, calculated for $C_{25}H_{26}O_{10}N_2Na^+$: 537.1480.

3.4 Synthesis of 3b

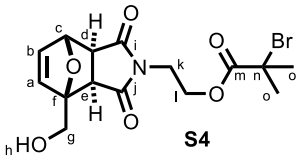


3b

A solution of **S3** (400 mg, 0.78 mmol, 1.00 eq.) in toluene (1.6 mL) was heated to 108°C overnight. The solvent was removed and the crude product used directly in the next step without purification.
The crude product and **8b** (392 mg, 1.58 mmol, 2.02 eq.) were dissolved in toluene (1 mL) and the reaction solution heated to 75°C for 27.5 h. The solvent was removed and the crude split into 75 mg aliquots. A single aliquot was purified by preparative TLC (1:1 PE:EtOAc, 4 elutions) yielding the product as a colourless sticky solid which dries to a white powder under vacuum (39.5 mg, 0.045 mmol, 53% representative yield of the aliquot).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.57 (dd, *J* = 5.7, 1.7 Hz, 2H, H_g), 6.48 (d, *J* = 5.7 Hz, 2H, H_f), 5.28 (d, *J* = 1.7 Hz, 2H, H_h), 4.94 (dd, *J* = 12.7, 1.2 Hz, 2H, H_d), 4.57 (d, *J* = 12.6 Hz, 2H, $H_{d'}$), 4.22 (ddt, *J* = 36.3, 11.4, 5.3 Hz, 4H, H_n), 3.74 (t, *J* = 5.3 Hz, 4H, H_m), 3.02 (d, *J* = 6.4 Hz, 2H, H_i), 2.96 (dd, *J* = 6.5, 1.3 Hz, 2H, H_j), 2.32 (t, *J* = 7.3 Hz, 4H, H_p), 1.94 (d, *J* = 7.5 Hz, 12H, H_a), 1.86 (p, *J* = 7.3 Hz, 2H, H_q).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 175.56 (C_k), 174.13 (C_l), 172.81 (C_o), 171.18 (C_c), 137.56 (C_g), 137.08 (C_f), 89.47 (C_e), 81.24 (C_h), 62.66 (C_d), 60.68 (C_n), 55.51 (C_b), 50.02 (C_i), 48.54 (C_j), 38.14 (C_m), 33.03 (C_p + C_r), 30.89 (C_a), 30.84 ($C_{a'}$), 19.71 (C_q).
MS-ESI(+): *m/z* = 893.2 (25, $[M+Na]^+$), 895.2 (100, $[M+Na]^+$), 897.2 (40, $[M+Na]^+$).
HRMS-ESI(+): *m/z* = 893.0718 $[M+Na]^+$, calculated for $C_{35}H_{40}O_{14}N_2Br_2Na^+$: 893.0739.

3.5 Synthesis of S4

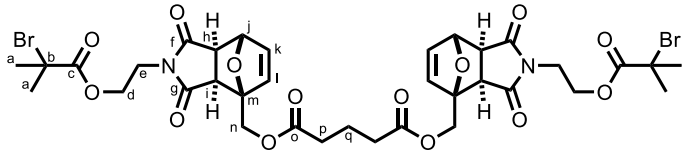


S4

A solution of **9b** (400 mg, 1.40 mmol, 1.0 eq.) and furfuryl alcohol (0.12 mL, 1.40 mmol, 1.0 eq.) in a mixture of toluene (2.5 mL) and DMF (0.25 mL) was heated to 75°C for 24 h. The solvent was then removed *in vacuo* and the crude purified by flash column chromatography (1% MeOH in DCM) to yield **S4** as a colourless viscous liquid (310 mg, 0.80 mmol, 58%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.61 (d, *J* = 5.7 Hz, 1H, H_a), 6.56 – 6.51 (m, 1H, H_b), 5.24 (d, *J* = 1.7 Hz, 1H, H_c), 4.44 – 4.25 (m, 2H, H_k), 4.13 – 4.07 (m, 2H, H_g), 3.83 (qdd, *J* = 14.3, 6.3, 4.0 Hz, 2H, H_l), 3.02 (d, *J* = 6.6 Hz, 1H, H_d), 2.98 (d, *J* = 6.5 Hz, 1H, H_e), 2.69 (t, *J* = 7.2 Hz, 1H, H_h), 1.89 (d, *J* = 2.8 Hz, 6H, H_o).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 175.83 (C_i or C_j), 175.75 (C_i or C_j), 171.56 (C_m), 138.47 (C_a), 137.11 (C_b), 91.52 (C_f), 80.97 (C_c), 80.90 ($C_{c'}$), 62.21 (C_k), 60.84 (C_g), 55.72 (C_m), 50.15 (C_d), 48.27 (C_e), 37.91 (C_l), 30.70 (C_o).
MS-ESI(+): *m*/*z* = 410.0 (80, $[M+Na]^+$), 411.0 (10, $[M+Na]^+$) 412.0 (100, $[M+Na]^+$), 413.0 (10, $[M+Na]^+$); 797.1 (10, $[2M+Na]^+$), 799.1 (20, $[2M+Na]^+$), 801.1 (10, $[2M+Na]^+$).
HRMS-ESI(+): *m*/*z* = 410.0206 $[M+Na]^+$, calculated for $C_{15}H_{18}O_6NBrNa^+$: 410.0210.

3.6 Synthesis of 4b

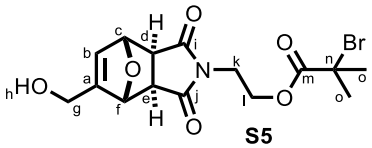


4b

To a dry microwave vial containing **S4** (225 mg, 0.58 mmol, 2.00 eq.) and DCM (4.8 mL) was added a solution of DMAP (1.8 mg, 14 µmol, 0.05 eq.) in Et_3N (89 µL, 0.64 mmol, 2.20 eq.) and DCM (1 mL). The solution was cooled in an ice bath before the dropwise addition of glutaryl chloride (41 µL, 0.30 mmol, 1.10 eq.). The solution was heated to 32°C for 24 h before being quenched with water and extracted into DCM (3x40 mL). The organic fraction was dried over Na_2SO_4, filtered and the solvent removed *in vacuo*. The crude was purified by flash column chromatography (1% MeOH in DCM) to yield the product as a white powder (142 mg, 0.16 mmol, 56%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.56 (d, *J* = 5.8 Hz, 2H, H_k), 6.42 (d, *J* = 5.7 Hz, 2H, H_l), 5.26 (s, 2H, H_j), 4.93 (d, *J* = 12.8 Hz, 2H, H_n), 4.46 (d, *J* = 12.9 Hz, 2H, $H_{n'}$), 4.39 – 4.27 (m, 4H, H_d), 3.89 – 3.74 (m, 4H, H_e), 3.01 (d, *J* = 6.5 Hz, 2H, H_h), 2.92 (d, *J* = 6.3 Hz, 2H, H_i), 2.43 (t, *J* = 7.3 Hz, 4H, H_p), 1.96 (p, *J* = 7.4 Hz, 2H, H_q), 1.89 (s, 12H, H_a).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 175.46 (C_f or C_g), 174.01 (C_f or C_g), 172.43 (C_o), 171.57 (C_c), 137.68 (C_k), 137.22 (C_l), 89.61 (C_m), 81.09 (C_j), 62.26 (C_d), 61.41 (C_n), 55.80 (C_b), 50.14 (C_h), 48.49 (C_i), 37.90 (C_e), 33.00 (C_p), 30.69 (C_a), 20.10 (C_q).
MS-ESI(+): *m*/*z* = 893.1 (50, $[M+Na]^+$), 894.1 (20, $[M+Na]^+$), 895.2 (100, $[M+Na]^+$), 896.1 (40, $[M+Na]^+$), 897.2 (50, $[M+Na]^+$), 898.1 (20, $[M+Na]^+$).
HRMS-ESI(+): *m*/*z* = 893.0728 $[M+Na]^+$, calculated for $C_{35}H_{40}O_{14}N_2Br_2Na^+$: 893.0739.

3.7 Synthesis of S5

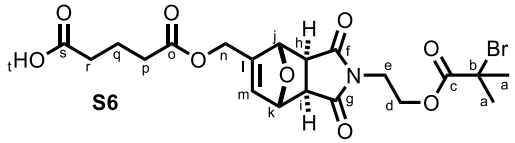


S5

A solution of **9b** (200 mg, 0.70 mmol, 1.0 eq.) and 3-furanmethanol (60 µL, 0.70 mmol, 1.0 eq.) in toluene (1.4 mL) was heated to 75°C for overnight. The solvent was then removed *in vacuo* and the crude purified by preparative TLC (1% MeOH in DCM, 3 elutions) to yield the product (R_f = 0.24) as a light orange viscous liquid (143 mg, 0.38 mmol, 53%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.29 (t, *J* = 1.6 Hz, 1H, H_b), 5.25 (s, 1H, H_c), 5.20 (s, 1H, H_f), 4.46 – 4.36 (m, 2H, H_g), 4.33 (t, *J* = 5.2 Hz, 2H, H_l), 3.82 (t, *J* = 5.2 Hz, 2H, H_k), 2.95 (s, 2H, H_d + H_e), 1.89 (s, 6H, H_o), 1.71 (t, *J* = 5.5 Hz, 1H, H_h).
^{13}C NMR (126 MHz, $CDCl_3$) δ = 176.00 (C_i or C_j), 175.90 (C_i or C_j), 171.57 (C_m), 151.18 (C_a), 130.15 (C_b), 81.79 (C_c), 81.47 (C_f), 62.32 (C_l), 58.55 (C_g), 55.83 (C_n), 49.00 (C_d or C_e), 47.54 (C_d or C_e), 37.79 (C_k), 30.74 (C_o).
MS-ESI(+): *m/z* = 410.0 (70, $[M+Na]^+$), 411.0 (10, $[M+Na]^+$) 412.0 (100, $[M+Na]^+$), 413.0 (10, $[M+Na]^+$); 797.2 (30, $[2M+Na]^+$), 799.2 (40, $[2M+Na]^+$), 801.2 (30, $[2M+Na]^+$).
HRMS-ESI(+): *m/z* = 410.0203 $[M+Na]^+$, calculated for $C_{15}H_{18}O_6NBrNa^+$: 410.0210.

3.8 Synthesis of S6

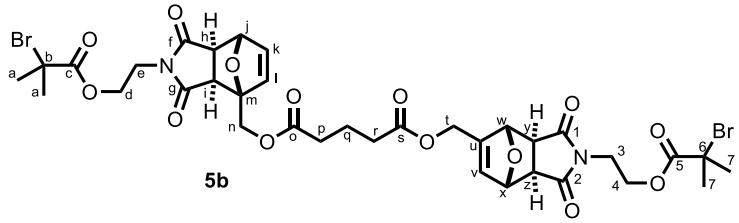


S6

To a dry microwave vial containing **S5** (77.6 mg, 0.20 mmol, 1.00 eq.) and dry DCM (2 mL) was added a solution of DMAP (1.2 mg, 10 µmol, 0.05 eq.) in Et_3N (33 µL, 0.24 mmol, 1.20 eq.) and dry DCM (1 mL). This was followed by the addition of a solution of glutaric anhydride (27.4 mg, 0.24 mmol, 1.20 eq.) in dry DCM (1 mL). The solution was stirred at room temperature for 22 h and the reaction solvent removed *in vacuo*. The crude was purified by preparative TLC (2% MeOH in DCM, 2 elutions) yielding the product (R_f = 0.23) as a clear sticky solid (35.4 mg, 71 µmol, 35%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.34 (s, 1H, H_m), 5.25 (s, 1H, H_k), 5.18 (s, 1H, H_j), 4.84 – 4.71 (m, 2H, H_n), 4.32 (t, *J* = 5.3 Hz, 2H, H_d), 3.81 (t, *J* = 5.3 Hz, 2H, H_e), 2.99 (d, *J* = 6.6 Hz, 1H, H_h), 2.94 (d, *J* = 6.4 Hz, 1H, H_i), 2.43 (dt, *J* = 13.3, 7.2 Hz, 4H, H_p + H_r), 1.94 (q, *J* = 7.7 Hz, 2H, H_q), 1.88 (s, 6H, H_a).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 176.27 (C_f), 175.72 (C_g), 172.72 (C_o + C_s), 171.57 (C_c), 146.44 (C_l), 132.81 (C_m), 81.75 (C_k), 81.58 (C_j), 62.29 (C_d), 59.43 (C_n), 55.81 (C_b), 48.66 (C_i), 47.36 (C_h), 37.86 (C_e), 33.03 (C_p + C_r), 30.72 (C_a), 20.03 (C_q).
MS-ESI(-): *m/z* = 500.1 (75, $[M-H]^-$), 502.1 (100, $[M-H]^-$).
HRMS-ESI(-): *m/z* = 500.0559 $[M+H]^-$, calculated for $C_{20}H_{23}O_9N^-$: 500.0562.

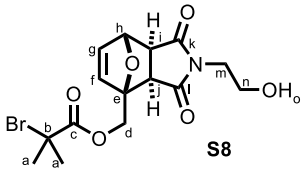
3.9 Synthesis of 5b



A dry microwave vial was containing **S6** (35.4 mg, 71 µmol, 1.05 eq.), **S4** (26.0 mg, 67 µmol, 1.00 eq.), DMAP (1.6 mg, 13 µmol, 0.20 eq.) and dry DCM (0.67 mL) was cooled in an ice bath. EDCI (19.3 mg, 0.100 mmol, 1.5 eq.) in DCM (0.2 mL) and a few drops of DMF was added and the reaction mixture stirred at room temperature for 25 h. The solvent was removed and the crude purified by preparative TLC (3% MeOH in DCM, 3 elutions) to yield the **5b** as a clear sticky solid (17.2 mg, 20 µmol, 30%).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.56 (d, *J* = 5.7 Hz, 1H, H_k), 6.42 (d, *J* = 5.7 Hz, 1H, H_l), 6.32 (s, 1H, H_v), 5.26 (s, 1H, H_j), 5.24 (s, 1H, H_x), 5.16 (s, 1H, H_w), 4.93 (d, *J* = 12.8 Hz, 1H, H_n), 4.81 – 4.71 (m, 2H, H_t), 4.47 (d, *J* = 12.8 Hz, 1H, $H_{n'}$), 4.38 – 4.27 (m, 4H, H_d + H_4), 3.88 – 3.75 (m, 4H, H_e + H_3) 3.01 (d, *J* = 6.5 Hz, 1H, H_h or H_i), 2.93 (dd, *J* = 9.9, 5.6 Hz, 3H, [H_h or H_i] + H_y + H_z), 2.44 (t, *J* = 7.3 Hz, 4H, H_p + H_r), 1.97 (p, *J* = 7.2 Hz, 2H, H_q), 1.92 – 1.86 (m, 12H, H_a + H_7).
^{13}C NMR (126 MHz, $CDCl_3$) δ = 175.74 (C_f or C_g or C_1 or C_2), 175.67 (C_f or C_g or C_1 or C_2), 175.41 (C_f or C_g or C_1 or C_2), 174.00 (C_f or C_g or C_1 or C_2), 172.45 (C_o or C_s), 172.31 (C_o or C_s), 171.57 (C_c or C_5), 171.55 (C_c or C_5), 146.48 (C_u), 137.70 (C_k), 137.25 (C_l), 132.67 (C_v), 89.62 (C_m), 81.76 (C_x), 81.71 ($C_{x'}$), 81.56 (C_w), 81.51 ($C_{w'}$), 81.15 (C_j), 81.10 ($C_{j'}$), 62.30 (C_d or C_4), 62.26 (C_d or C_4), 61.49 (C_n), 59.30 (C_t), 55.81 (C_b or C_6), 55.80 (C_b or C_6), 50.18 (C_h or C_i), 48.65 (C_y or C_z), 48.52 (C_h or C_i), 47.35 (C_y or C_z), 37.93 (C_e or C_3), 37.82 (C_e or C_3), 33.03 (C_p or C_r), 33.00 (C_p or C_r), 30.74 (C_a + C_7), 20.09 (C_q).
MS-ESI(+): *m/z* = 893.2 (25, $[M+Na]^+$), 895.2 (100, $[M+Na]^+$), 896.2 (25, $[M+Na]^+$), 897.1 (45, $[M+Na]^+$).
HRMS-ESI(+): *m/z* = 893.0745 $[M+Na]^+$, calculated for $C_{35}H_{40}O_{14}N_2Br_2Na^+$: 893.0739.

3.10 Synthesis of S8

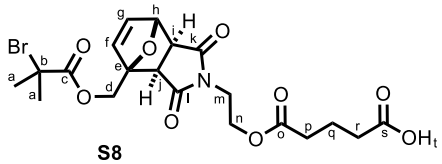


A solution of **S7** (115 mg, 0.815 mmol, 1.0 eq.) and **8b** (200 mg, 0.815 mmol, 1.0 eq.) in toluene (1.7 mL) was heated to 75°C for overnight. The solvent was then removed *in vacuo* and the crude purified by preparative TLC (1% MeOH in DCM, 2 elutions, R_f = 0.23) yielding a mixture of *endo* and *exo* isomers. A second purification by preparative TLC (10:15:3 PE:EtOAc:MeOH, 2 elutions) gave **S8** (R_f = 0.48) as a light orange viscous liquid (114 mg, 0.294 mmol, 36%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.58 (dd, *J* = 5.7, 1.7 Hz, 1H, H_g), 6.49 (d, *J* = 5.7 Hz, 1H, H_f), 5.30 (d, *J* = 1.7 Hz, 1H, H_h), 4.95 (d, *J* = 12.6 Hz, 1H, H_d), 4.60 (d, *J* = 12.7 Hz, 1H, $H_{d'}$), 3.80 – 3.74 (m, 2H, H_n), 3.73 – 3.68 (m, 2H, H_m), 3.04 (d, *J* = 6.4 Hz, 1H, H_i), 2.98 (d, *J* = 6.4 Hz, 1H, H_j), 2.10 (t, *J* = 5.7 Hz, 1H, H_o), 1.94 (d, *J* = 6.4 Hz, 6H, H_a).
^{13}C NMR (126 MHz, $CDCl_3$) δ = 176.28 (C_k or C_l), 174.82 (C_k or C_l), 171.24 (C_c), 137.54 (C_g), 137.11 (C_f), 89.54 (C_e), 81.34 (C_h), 62.63 (C_d), 60.42 (C_n), 55.46 (C_b), 50.04 (C_i), 48.59 (C_j), 41.93 (C_m), 30.89 (C_a), 30.84 ($C_{a'}$).

MS-ESI(+): *m/z* = 410.0 (100, $[M+Na]^+$), 412.0 (95, $[M+Na]^+$).
HRMS-ESI(+): *m/z* = 410.0195 $[M+Na]^+$, calculated for $C_{15}H_{18}O_6NBrNa^+$: 410.0210.

3.11 Synthesis of S9

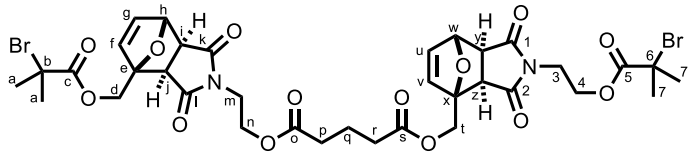


S8

To a dry microwave vial containing **S8** (68.0 mg, 0.18 mmol, 1.00 eq.) was added a solution of DMAP (1.1 mg, 9.0 µmol, 0.05 eq.) in dry DCM (1.0 mL). This was followed by the addition of a solution of glutaric anhydride (24.0 mg, 0.21 mmol, 1.17 eq.) in Et_3N (29 µL, 0.21 mmol, 1.17 eq.) and dry DCM (2.5 mL). The solution was stirred at room temperature for 1.5 d and the reaction solvent removed *in vacuo*. The crude was purified by preparative TLC (3% MeOH in DCM, 2 elutions) yielding the product as a clear sticky solid (44.2 mg, 88 µmol, 50%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.57 (dd, *J* = 5.7, 1.6 Hz, 1H, H_g), 6.49 (d, *J* = 5.7 Hz, 1H, H_f), 5.28 (d, *J* = 1.7 Hz, 1H, H_h), 4.94 (d, *J* = 12.6 Hz, 1H, H_d), 4.57 (d, *J* = 12.6 Hz, 1H, $H_{d'}$), 4.32 – 4.15 (m, 2H, H_n), 3.82 – 3.70 (m, 2H, H_m), 3.02 (d, *J* = 6.5 Hz, 1H, H_i), 2.96 (d, *J* = 6.5 Hz, 1H, H_j), 2.42 (t, *J* = 7.3 Hz, 2H, H_p or H_r), 2.36 (t, *J* = 7.3 Hz, 2H, H_p or H_r), 1.97 – 1.87 (m, 8H, H_a + H_q).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 175.69 (C_k or C_l), 174.19 (C_k or C_l), 172.83 (C_o + C_s), 171.25 (C_c), 137.57 (C_g), 137.09 (C_f), 89.48 (C_e), 81.27 (C_h), 62.69 (C_d), 60.83 (C_n), 55.50 (C_b), 50.03 (C_i), 48.56 (C_j), 38.20 (C_m), 33.01 (C_p + C_r), 30.88 (C_a), 30.84 ($C_{a'}$), 19.76 (C_q).
MS-ESI(+): *m/z* = 524.1 (100, $[M+Na]^+$), 525.1 (20, $[M+Na]^+$), 526.0 (95, $[M+Na]^+$), 527.1 (20, $[M+Na]^+$).
HRMS-ESI(+): *m/z* = 524.0506 $[M+Na]^+$, calculated for $C_{20}H_{24}O_9NBrNa^+$: 524.0527.

3.12 Synthesis of 6b



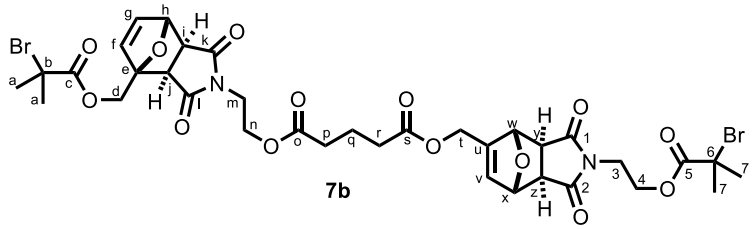
6b

A dry microwave vial containing **S9** (30.0 mg, 59.7 µmol, 1.00 eq.), **S8** (24.3 mg, 62.7 µmol, 1.05 eq.), DMAP (1.5 mg, 12.5 µmol, 0.20 eq.) and dry DCM (0.63 mL) was cooled in an ice bath. EDCI.HCl (18.0 mg, 94.1 µmol, 1.50 eq.) was added and the reaction mixture stirred at room temperature for 23 h. The solvent was removed and the crude purified by preparative TLC (2% MeOH in DCM, 2 elutions) to yield the product as a clear sticky solid (22.7 mg, 26.0 µmol, 42%).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.56 (ddd, *J* = 6.5, 4.5, 1.7 Hz, 2H, H_g + H_u), 6.48 (d, *J* = 5.7 Hz, 1H, H_f), 6.43 (d, *J* = 5.7 Hz, 1H, H_v), 5.26 (dd, *J* = 8.0, 1.7 Hz, 2H, H_h + H_w), 4.95 – 4.93 (m, 1H, H_d), 4.93 – 4.90 (m, 1H, H_t), 4.57 (d, *J* = 12.6 Hz, 1H, $H_{d'}$), 4.45 (d, *J* = 12.8 Hz, 1H, $H_{t'}$), 4.37 – 4.22 (m, 3H, H_n + H_4), 4.21 – 4.15 (m, 1H, $H_{n'}$), 3.86 – 3.76 (m, 2H, H_3), 3.74 (t, *J* = 5.3 Hz, 2H, H_m), 3.03 – 2.99 (m, 2H, H_i + H_y), 2.95 (dd, *J* = 6.4, 2.9 Hz, 1H, H_j or H_z), 2.92 (dd, *J* = 6.5, 2.8 Hz, 1H, H_j or H_z), 2.41 (td, *J* = 7.4, 1.4 Hz, 2H, H_r), 2.34 (t, *J* = 7.3 Hz, 2H, H_p), 1.96 – 1.90 (m, 8H, H_a + H_q), 1.89 (d, *J* = 1.9 Hz, 6H, H_7).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 175.56 (C_l or C_z), 175.47 (C_k or C_1), 174.12 (C_l or C_z), 174.01 (C_k or C_1), 172.75 (C_o), 172.48 (C_s), 171.57 (C_5), 171.19 (C_c), 137.60 (C_g + C_u), 137.33 (C_v), 137.10 (C_f), 89.67 (C_x), 89.48 (C_e), 81.28 (C_h or C_w), 81.23 (C_h or C_w), 81.14 ($C_{h'}$ or $C_{w'}$), 81.09 ($C_{h'}$ or $C_{w'}$), 62.66 (C_d or C_t), 62.27 (C_4), 61.39 (C_d or C_t), 60.76 (C_n), 55.81 (C_6), 55.50 (C_b), 50.19 (C_i or C_y), 50.02 (C_i or C_y), 48.55 (C_j + C_z), 38.15 (C_m or C_4), 37.91 (C_m or C_4), 33.02 (C_p + C_r), 30.89 (C_a), 30.85 ($C_{a'}$), 30.73 (C_7), 19.93 (C_q).
MS-ESI(+): *m/z* = 893.2 (50, $[M+Na]^+$), 894.2 (10, $[M+Na]^+$), 895.2 (100, $[M+Na]^+$), 896.2 (20, $[M+Na]^+$), 897.2 (55, $[M+Na]^+$).
HRMS-ESI(+): *m/z* = 893.0723 $[M+Na]^+$, calculated for $C_{35}H_{40}O_{14}N_2Br_2Na^+$: 893.0739.

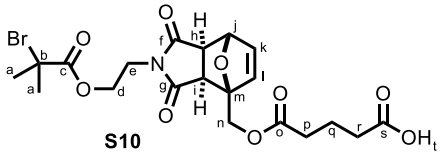
3.13 Synthesis of 7b



A dry microwave vial containing **S9** (30.0 mg, 59.7 µmol, 1.00 eq.), **S5** (24.3 mg, 62.7 µmol, 1.05 eq.), DMAP (1.5 mg, 12.5 µmol, 0.20 eq.) and dry DCM (0.63 mL) was cooled in an ice bath. EDCI.HCl (18.0 mg, 94.1 µmol, 1.50 eq.) was added and the reaction mixture stirred at room temperature for 23 h. The solvent was removed and the crude purified by preparative TLC (2% MeOH:DCM, 2 elutions) to yield the product as a clear sticky solid (15.6 mg, 17.9 µmol, 29%).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.58 – 6.55 (m, 1H, H_g), 6.48 (d, *J* = 5.7 Hz, 1H, H_f), 6.33 (q, *J* = 1.7 Hz, 1H, H_v), 5.28 (d, *J* = 1.7 Hz, 1H, H_h), 5.24 (d, *J* = 1.7 Hz, 1H, H_x), 5.17 (s, 1H, H_w), 4.94 (dd, *J* = 12.6, 2.5 Hz, 1H, H_d), 4.77 (dd, *J* = 3.9, 1.6 Hz, 2H, H_t), 4.57 (d, *J* = 12.6 Hz, 1H, $H_{d'}$), 4.32 (t, *J* = 5.3 Hz, 2H, H_4), 4.30 – 4.24 (m, 1H, H_n), 4.21 – 4.15 (m, 1H, $H_{n'}$), 3.81 (t, *J* = 5.3 Hz, 2H, H_3), 3.75 (ddd, *J* = 6.4, 4.7, 2.1 Hz, 2H, H_m), 3.02 (dd, *J* = 6.5, 1.2 Hz, 1H, H_i), 2.98 – 2.92 (m, 3H, H_j + H_y + H_z), 2.42 (t, *J* = 7.4 Hz, 2H, H_r), 2.34 (t, *J* = 7.2 Hz, 2H, H_p), 1.93 (dd, *J* = 7.2, 3.0 Hz, 8H, H_a + H_q), 1.89 (s, 6H, H_7).
^{13}C NMR (126 MHz, $CDCl_3$) δ = 175.77 (C_1 or C_2), 175.74 (C_1 or C_2), 175.59 (C_k or C_l), 174.16 (C_k or C_l), 172.68 (C_o), 172.56 (C_s), 171.55 (C_5), 171.20 (C_c), 146.56 (C_u), 137.56 (C_g), 137.12 (C_f), 132.63 (C_v), 89.49 (C_e), 81.77 (C_x), 81.73 ($C_{x'}$), 81.60 (C_w), 81.55 ($C_{w'}$), 81.29 (C_h), 81.24 ($C_{h'}$), 62.68 (C_d), 62.32 (C_4), 60.87 (C_n), 59.27 (C_t), 55.81 (C_6), 55.50 (C_b), 50.03 (C_i), 48.68 (C_y), 48.56 (C_j), 47.36 (C_z), 38.18 (C_m or C_4), 37.80, 33.04 (C_p + C_r), 30.89 (C_a), 30.85 ($C_{a'}$), 30.74 (C_7), 19.87 (C_q).
MS-ESI(+): *m/z* = 893.2 (45, $[M+Na]^+$), 894.2 (10, $[M+Na]^+$), 895.2 (100, $[M+Na]^+$), 896.2 (35, $[M+Na]^+$), 897.2 (45, $[M+Na]^+$), 898.2 (10, $[M+Na]^+$).
HRMS-ESI(+): *m/z* = 893.0723 $[M+Na]^+$, calculated for $C_{35}H_{40}O_{14}N_2Br_2Na^+$: 893.0739.

3.14 Synthesis of S10

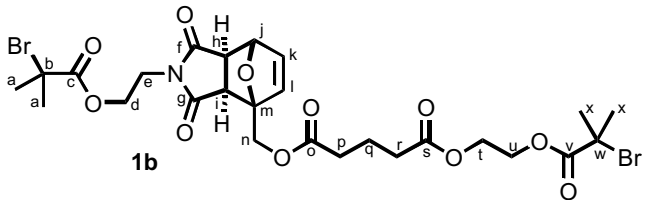


To a dry microwave vial containing **S4** (60.0 mg, 0.155 mmol, 1.00 eq.) and dry DCM (1.5 mL) was added a solution of DMAP (1.0 mg, 8 µmol, 0.05 eq.) in Et_3N (26 µL, 0.185 mmol, 1.20 eq.) and dry DCM (0.5 mL). This was followed by the addition of a solution of glutaric anhydride (21.2 mg, 0.185

mmol, 1.20 eq.) in dry DCM (1.1 mL). The solution was stirred at room temperature for 24 h and the reaction solvent removed *in vacuo*. The crude was purified by preparative TLC (2% MeOH in DCM, 2 elutions) yielding the product as a clear sticky solid (42.3 mg, 0.084 mmol, 55%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.58 – 6.54 (m, 1H, H_k), 6.42 (d, *J* = 5.7 Hz, 1H, H_l), 5.26 (d, *J* = 1.5 Hz, 1H, H_j), 4.92 (d, *J* = 12.8 Hz, 1H, H_n), 4.46 (d, *J* = 12.8 Hz, 1H, $H_{n'}$), 4.39 – 4.25 (m, 2H, H_d), 3.88 – 3.74 (m, 2H, H_e), 3.01 (d, *J* = 6.4 Hz, 1H, H_h), 2.93 (d, *J* = 6.5 Hz, 1H, H_i), 2.43 (dt, *J* = 12.3, 7.1 Hz, 4H, H_p + H_r), 1.96 (q, *J* = 7.2 Hz, 2H, H_q), 1.88 (d, *J* = 1.4 Hz, 6H, H_a).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 175.48 (C_f), 174.14 (C_g), 172.56 (C_o + C_s), 171.59 (C_c), 137.68 (C_k), 137.26 (C_l), 89.62 (C_m), 81.13 (C_j), 62.27 (C_d), 61.48 (C_n), 55.80 (C_b), 50.20 (C_h), 48.51 (C_i), 37.94 (C_e), 33.08 (C_p + C_r), 30.73 (C_a), 20.06 (C_q).
MS-ESI(-): *m/z* = 500.1 (100, $[M-H]^-$), 501.1 (20, $[M-H]^-$), 502.1 (50, $[M-H]^-$) 503.1 (15, $[M-H]^-$).
HRMS-ESI(-): *m/z* = 500.0567 $[M+H]^-$, calculated for $C_{20}H_{23}O_9N^-$: 500.0562.

3.15 Synthesis of 1b



A dry microwave vial containing **S10** (35.4 mg, 70 µmol, 1.05 eq.), 2-HBMP (26.0 mg, 67 µmol, 1.00 eq.), DMAP (1.6 mg, 13 µmol, 0.20 eq.) and dry DCM (0.67 mL) was cooled in an ice bath. EDCI (19.3 mg, 100 µmol, 1.50 eq.) in DCM (0.2 mL) and a few drops of DMF was added and the reaction mixture stirred at room temperature for 25 h. The solvent was removed and the crude purified by preparative TLC (2% MeOH:DCM, 2 elutions) to yield the product as a clear sticky solid (17.2 mg, 20 µmol, 30%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.56 (ddd, *J* = 5.6, 1.8, 0.7 Hz, 1H, H_k), 6.42 (d, *J* = 5.7 Hz, 1H, H_l), 5.26 (d, *J* = 1.7 Hz, 1H, H_j), 4.93 (d, *J* = 12.8 Hz, 1H, H_n), 4.46 (dd, *J* = 12.8, 0.9 Hz, 1H, $H_{n'}$), 4.40 – 4.27 (m, 6H, H_d + H_t + H_u), 3.88 – 3.74 (m, 2H, H_e), 3.00 (d, *J* = 6.5 Hz, 1H, H_h), 2.91 (d, *J* = 6.5 Hz, 1H, H_i), 2.42 (dt, *J* = 11.1, 7.3 Hz, 4H, H_p + H_r), 2.00 – 1.91 (m, 8H, H_q + H_a or H_x), 1.89 (d, *J* = 1.4 Hz, 6H, H_a or H_x).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 175.42 (C_f or C_g), 173.98 (C_f or C_g), 172.68 (C_s), 172.39 (C_o), 171.60 (C_c or C_v), 171.57 (C_c or C_v), 137.67 (C_k), 137.27 (C_l), 89.66 (C_m), 81.12 (C_j), 63.66 (C_u), 62.27 (C_d or C_t), 61.85 (C_d or C_t), 61.43 (C_n), 55.79 (C_b or C_w), 55.55, 50.19 (C_h), 48.52 (C_i), 37.94 (C_e), 33.13 (C_p + C_r), 30.82 (C_a or C_x), 30.74 (C_a or C_x), 20.10 (C_q).
MS-ESI(+): *m/z* = 716.1 (30, $[M+Na]^+$), 718.1 (100, $[M+Na]^+$), 720.1 (50, $[M+Na]^+$).
HRMS-ESI(+): *m/z* = 716.0293 $[M+Na]^+$, calculated for $C_{26}H_{33}O_{11}NBr_2Na^+$: 716.0313.

4 Polymers

4.1 Representative Procedure for the Synthesis of Mechanophore-Linked PMA

Methyl acrylate was filtered through basic alumina to remove the inhibitor prior to use. A stock solution of Me_6TREN (16 µL, 0.060 mmol) and $CuBr_2$ (5.6 mg, 0.025 mmol) in dry DMSO (1 mL) was prepared. To a 15 mL vial was added initiator-functionalised Diels-Alder adduct (27 mg, 0.05 mmol, 1.0 eq.), 200 µL of catalytic solution (Me_6TREN: 0.012 mmol, 0.24 eq.; $CuBr_2$: 0.005 mmol, 0.1 eq.), methyl acylate (4.51 mL, 50.1 mmol, 1000 eq.) and dry DMSO (3.90 mL). This solution was degassed by bubbling with N_2 for 10 min. A Cu(0) wire (~2 cm, ~20 mg, 0.315 mmol, ~6.3 eq. cleaned in HCl_{conc} for 10 min) wrapped around a stirrer bar was added and the solution degassed for a further 2 min before being allowed to stir for 45 min. The solution was then precipitated out in stirring methanol, recovered and dried under a high vacuum for several days yielding a white polymer (1.80 g, M_n = 60.0 kDa). Molecular weight and polydispersity indices were recorded using an analytical GPC that had been calibrated with polystyrene standards.

4.2 List of polymers synthesised

The following polymers were synthesised using the method outlined above. The molecular weights for mechanophore-centred polymers range from 51.1 kDa to 58.6 kDa with polydispersities (*Đ*) ranging from 1.16 to 1.29. Molecular weight and polydispersity determined using an Agilent 1260 Infinity II system equipped with 2 × PL gel 10 µm mixed-B columns and refractive index detector.

Table S1. M_n and *Đ* values for polymers **1-7c**.

Polymer	M_n (kDa)	*Đ*
1c	58.6	1.14
2c	51.1	1.22
3c	52.7	1.16
4c	53.8	1.18
5c	54.1	1.19
6c	55.8	1.19
7c	53.4	1.29

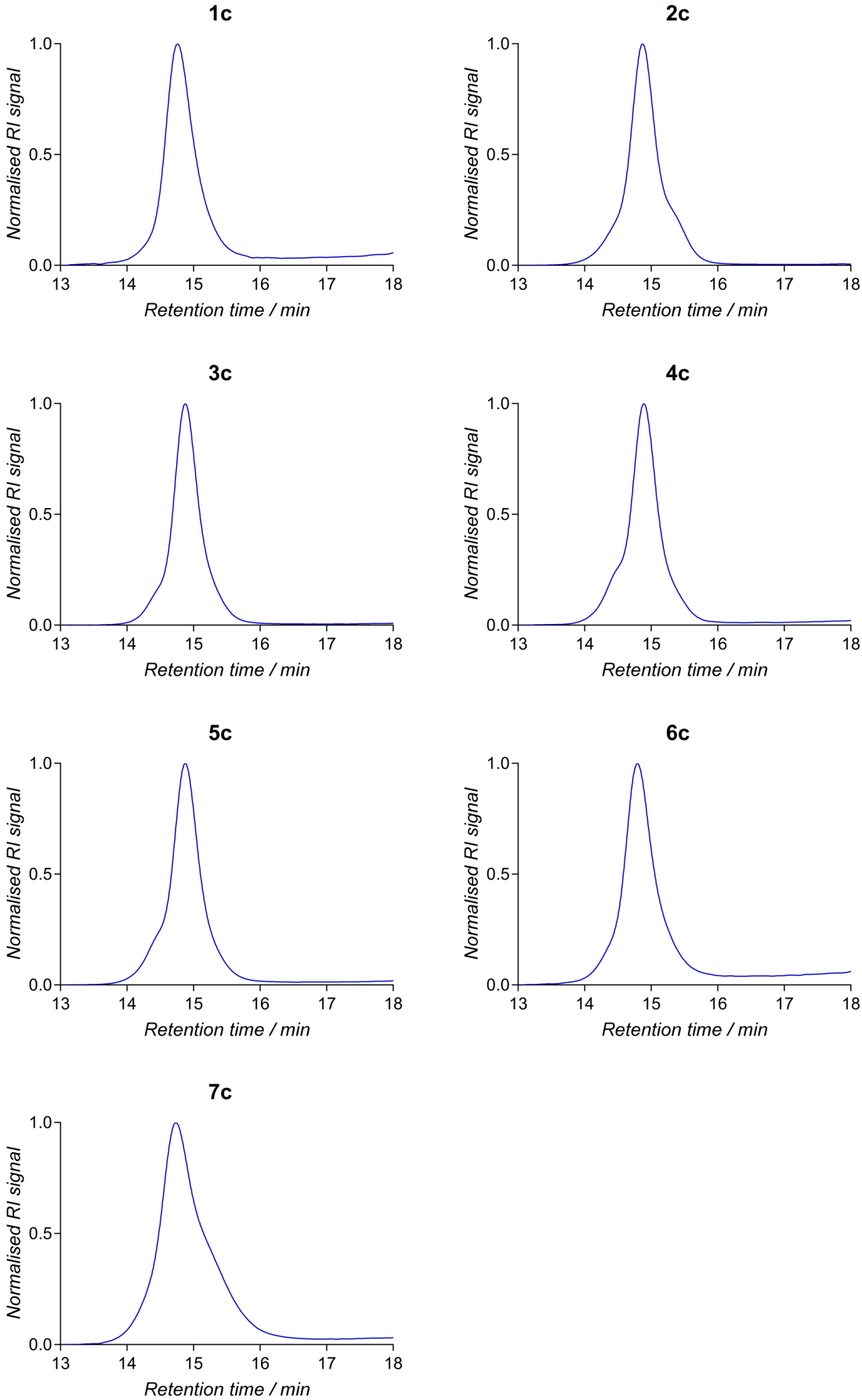
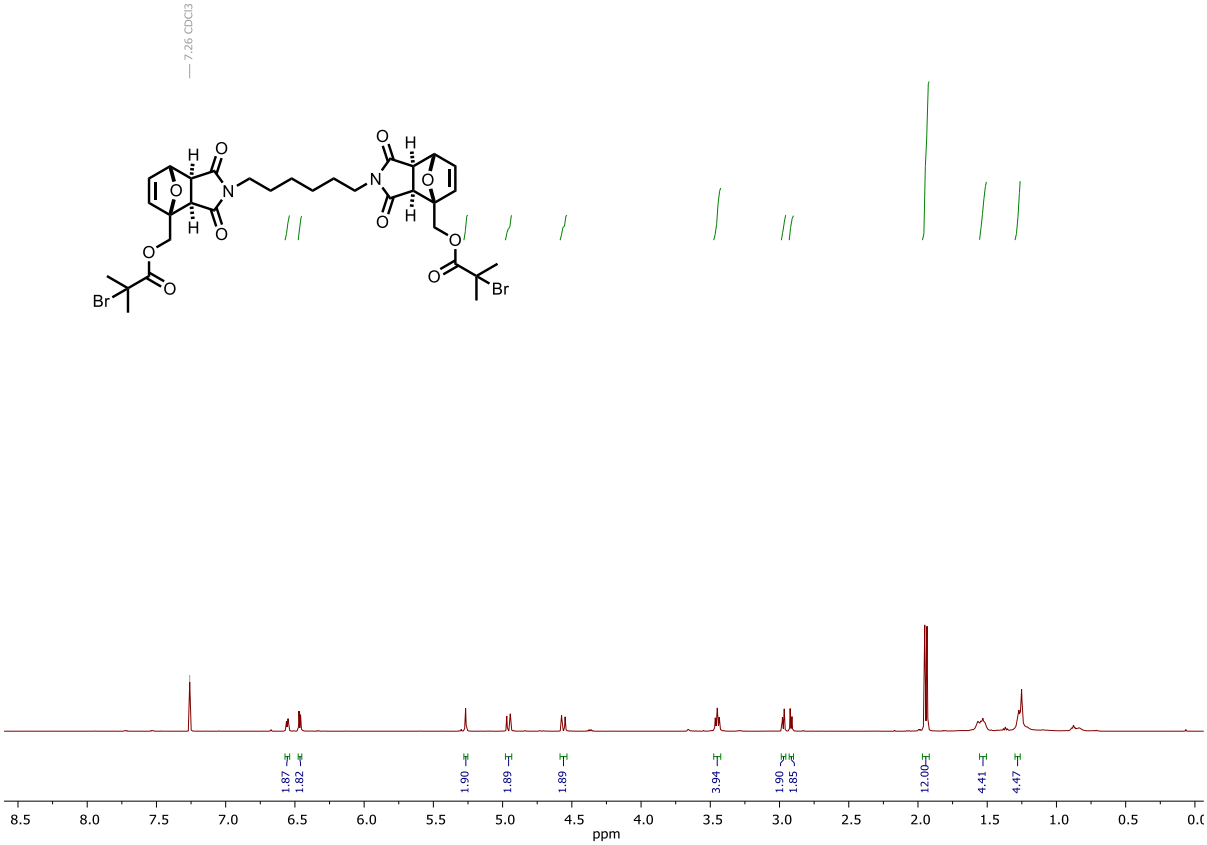


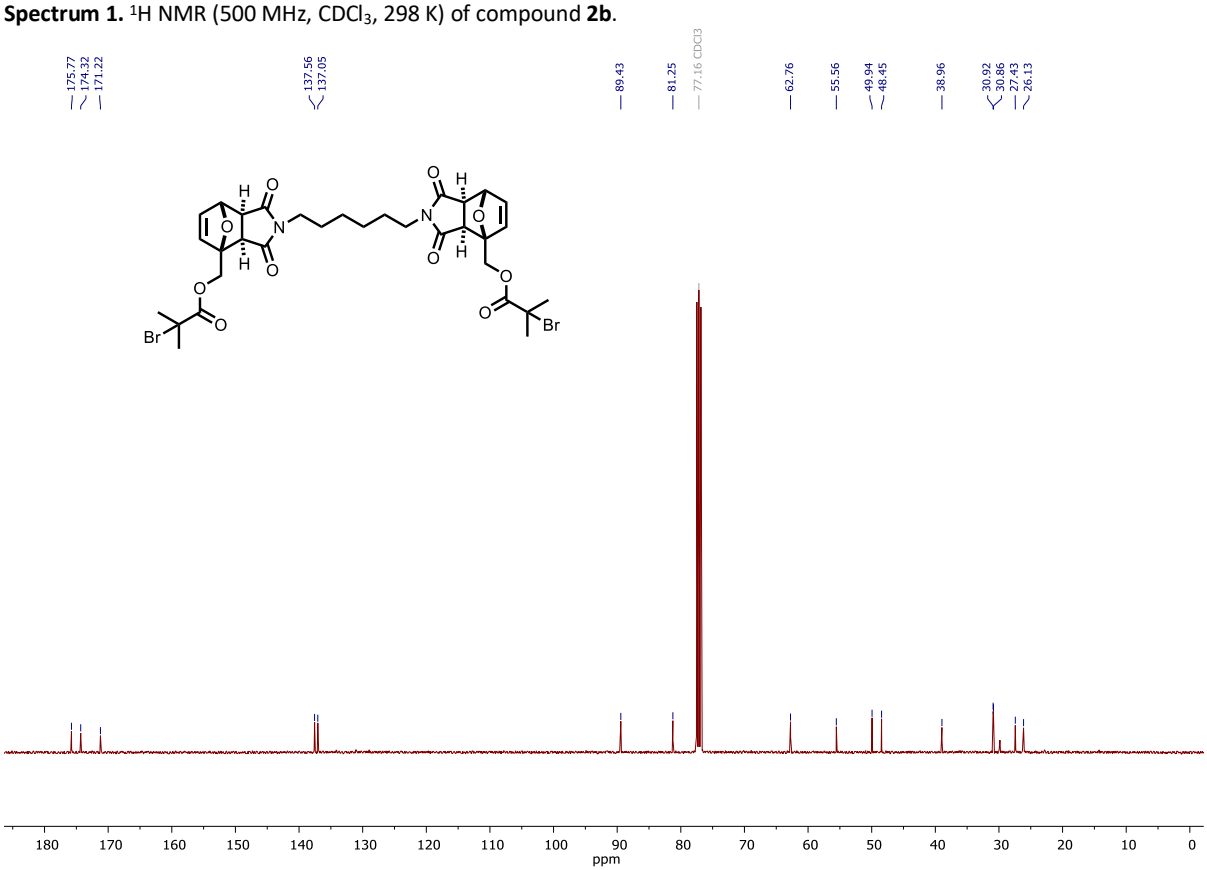
Figure S1. GPC traces of polymers **1-7c**.

5 NMR Spectra

5.1 Spectra of 2b

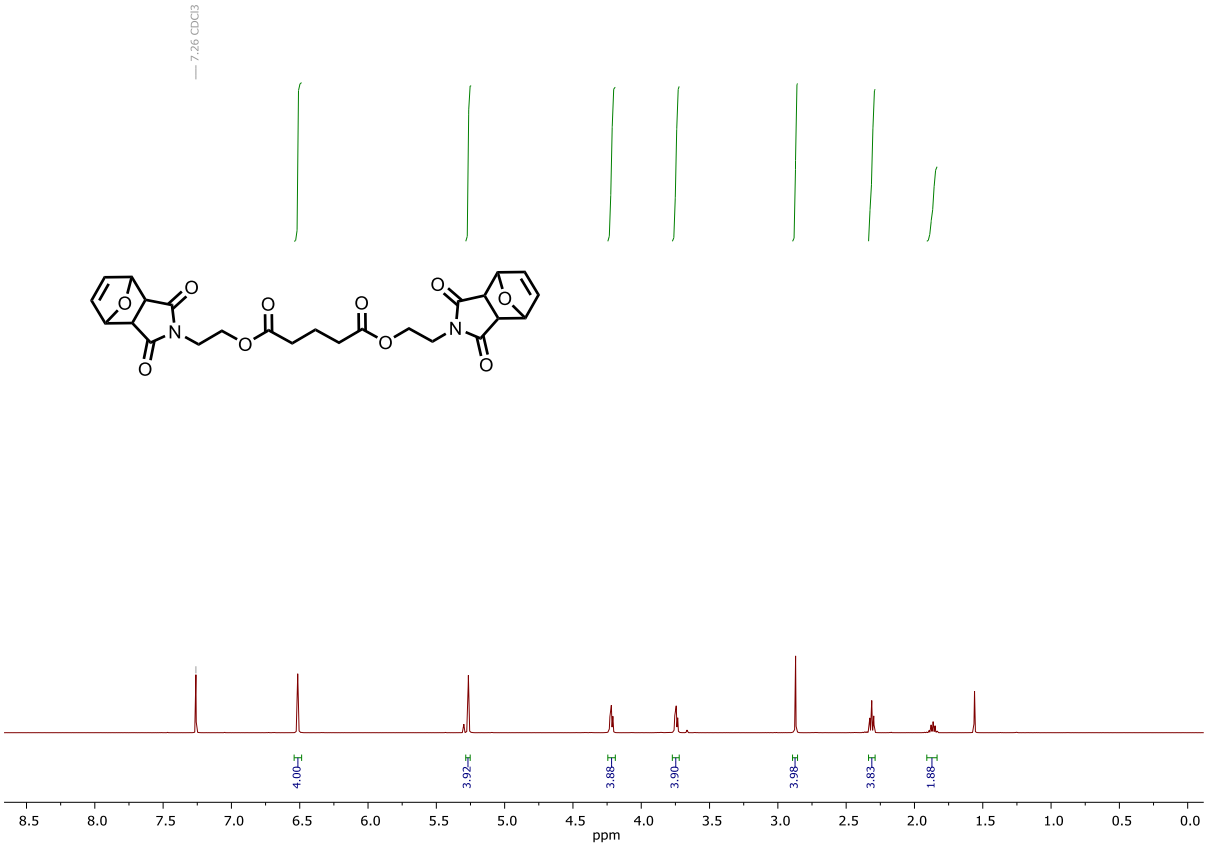


Spectrum 1. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) of compound **2b**.

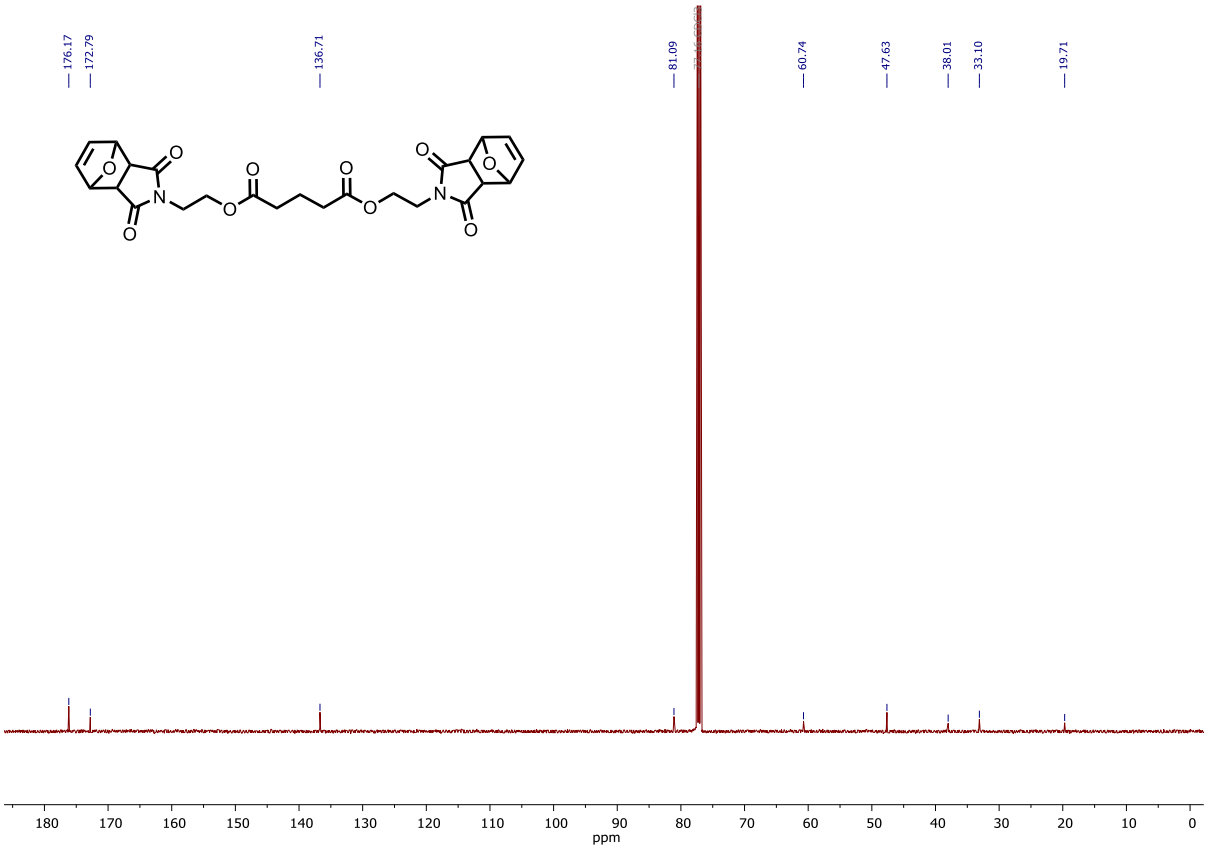


Spectrum 2. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) of compound **2b**.

5.2 Spectra of S3

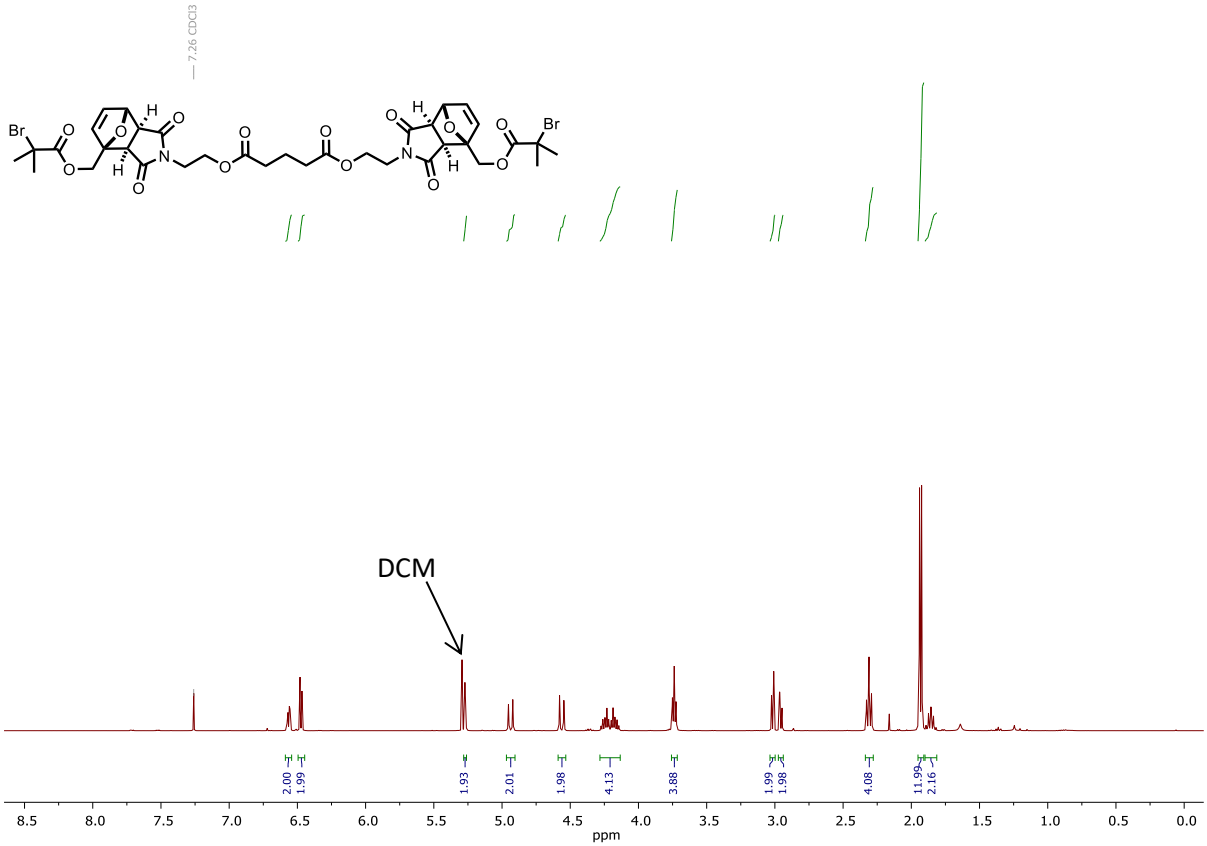


Spectrum 3. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) of compound **S3**.

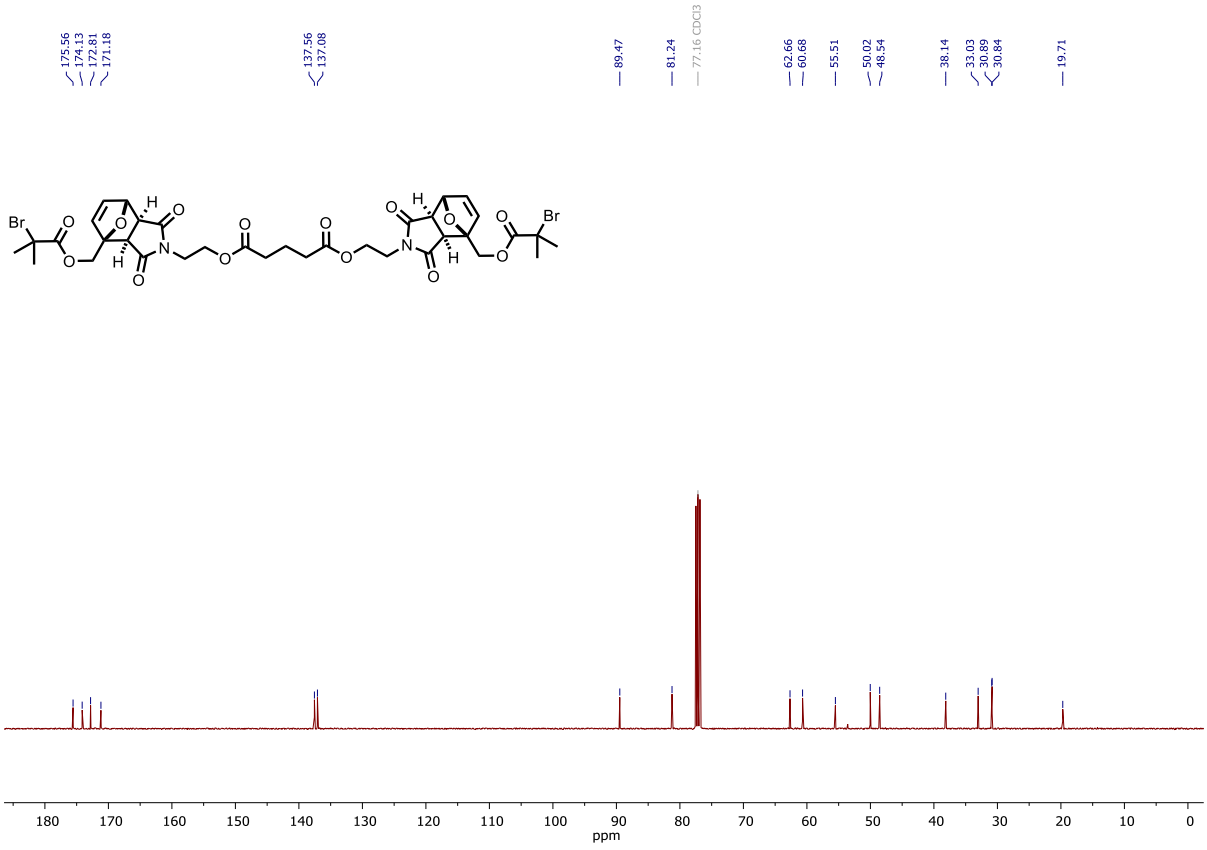


Spectrum 4. ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) of compound **S3**.

5.3 Spectra of 3b

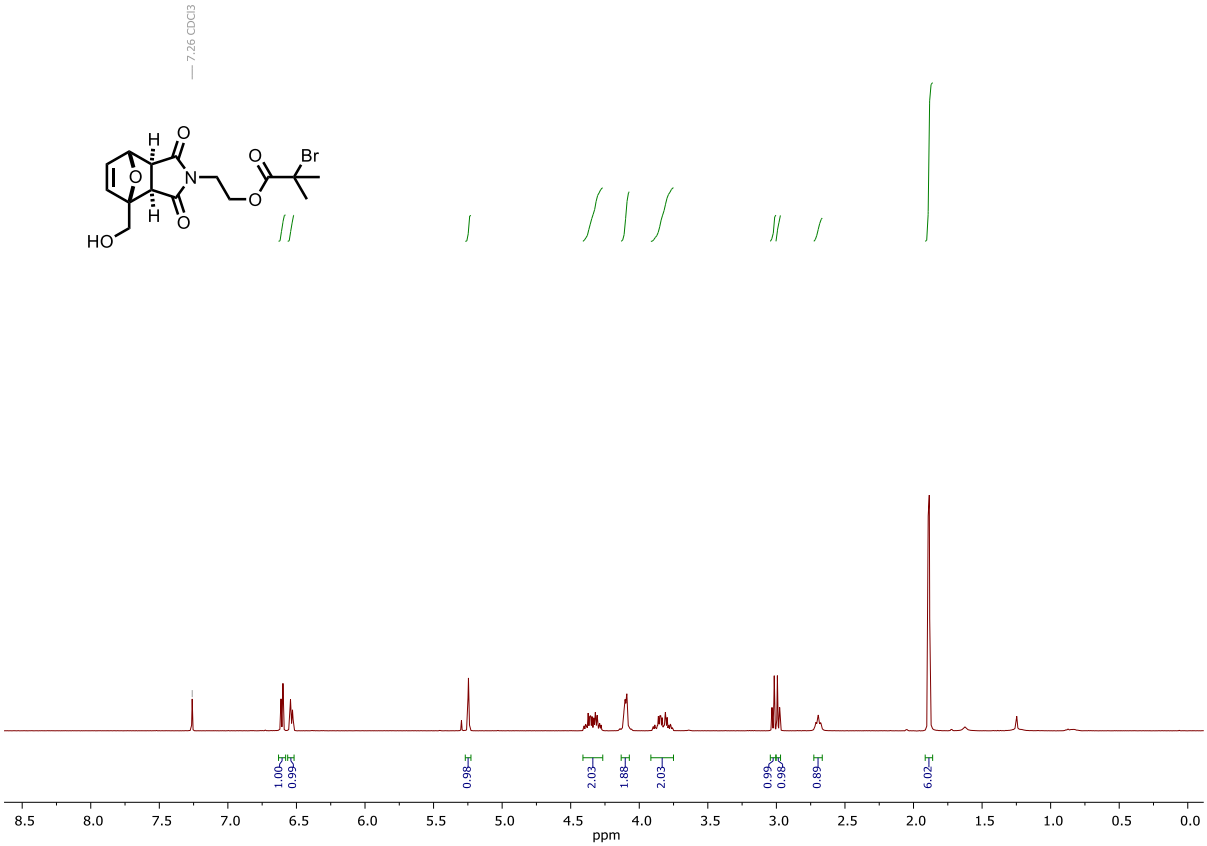


Spectrum 5. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) of compound **3b**.

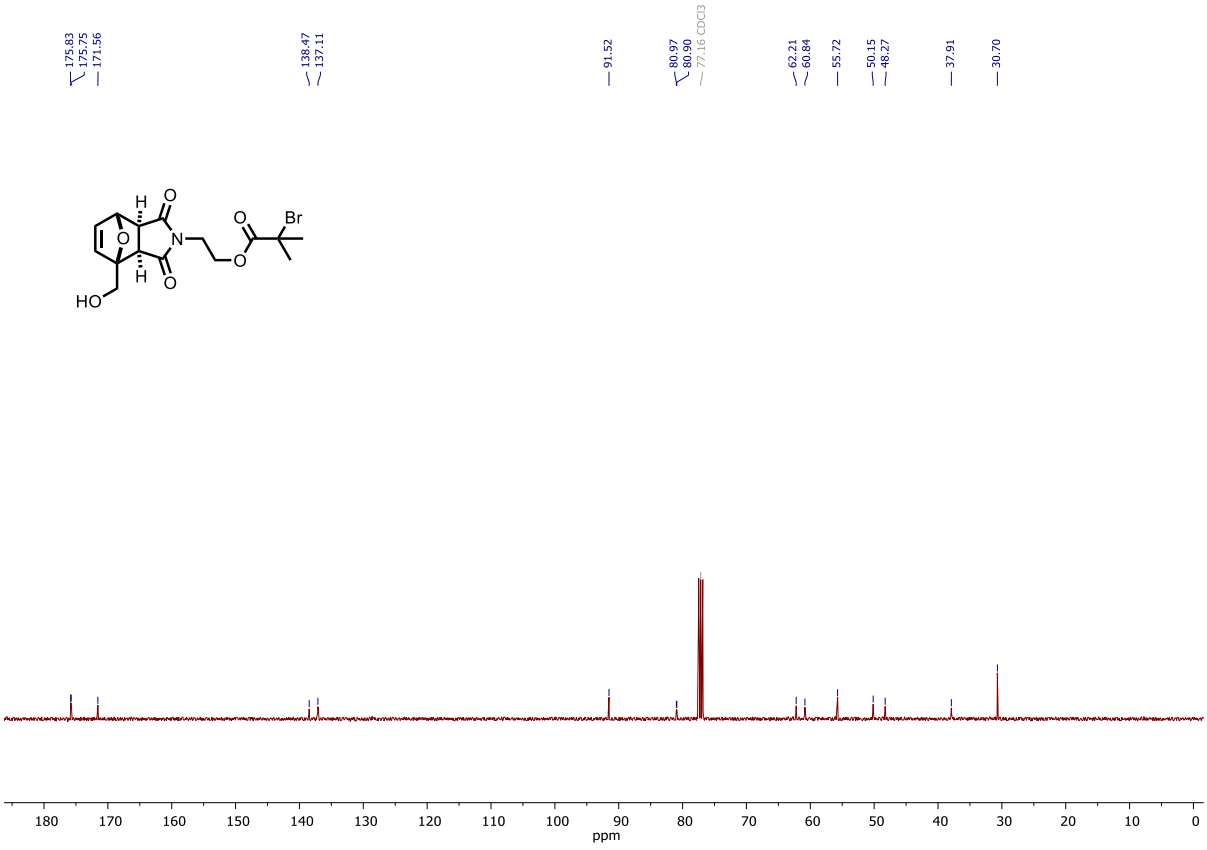


Spectrum 6. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) of compound **3b**.

5.4 Spectra of S4

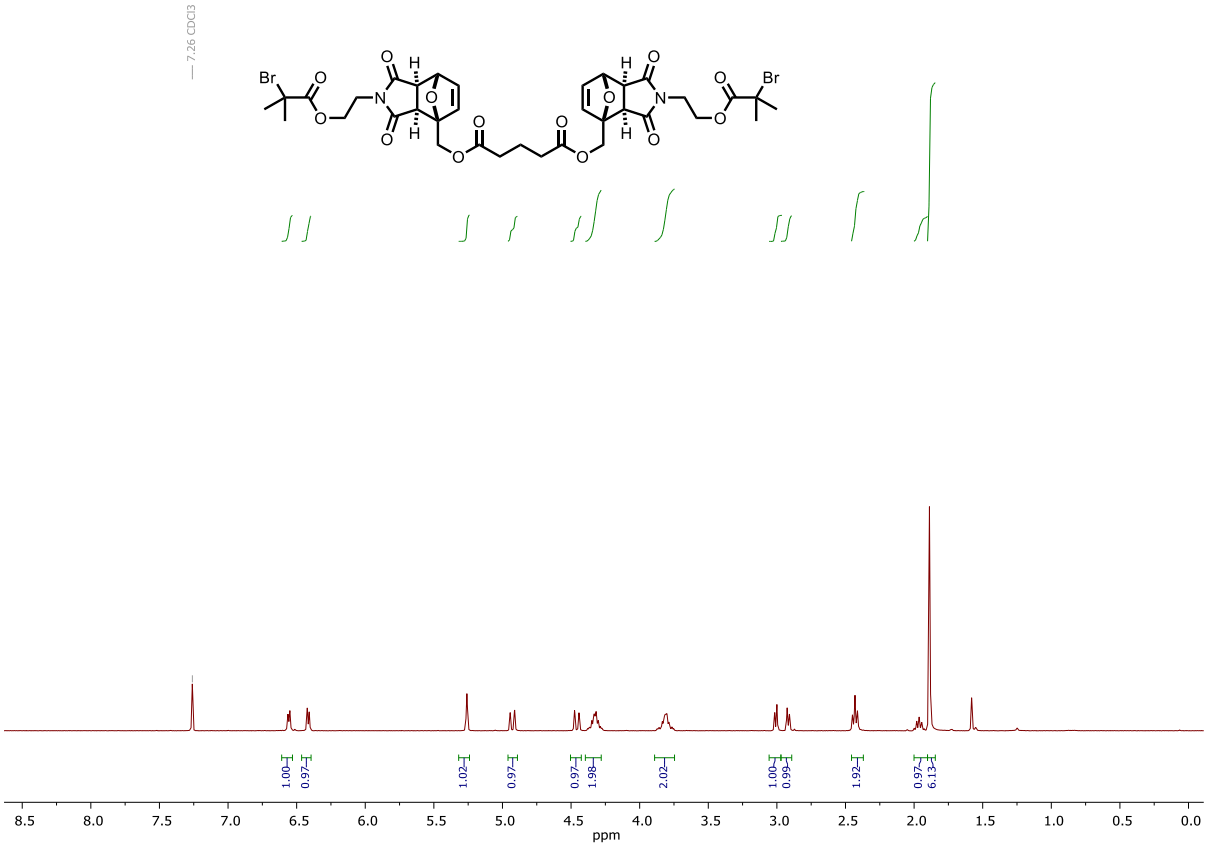


Spectrum 7. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of compound **S4**.

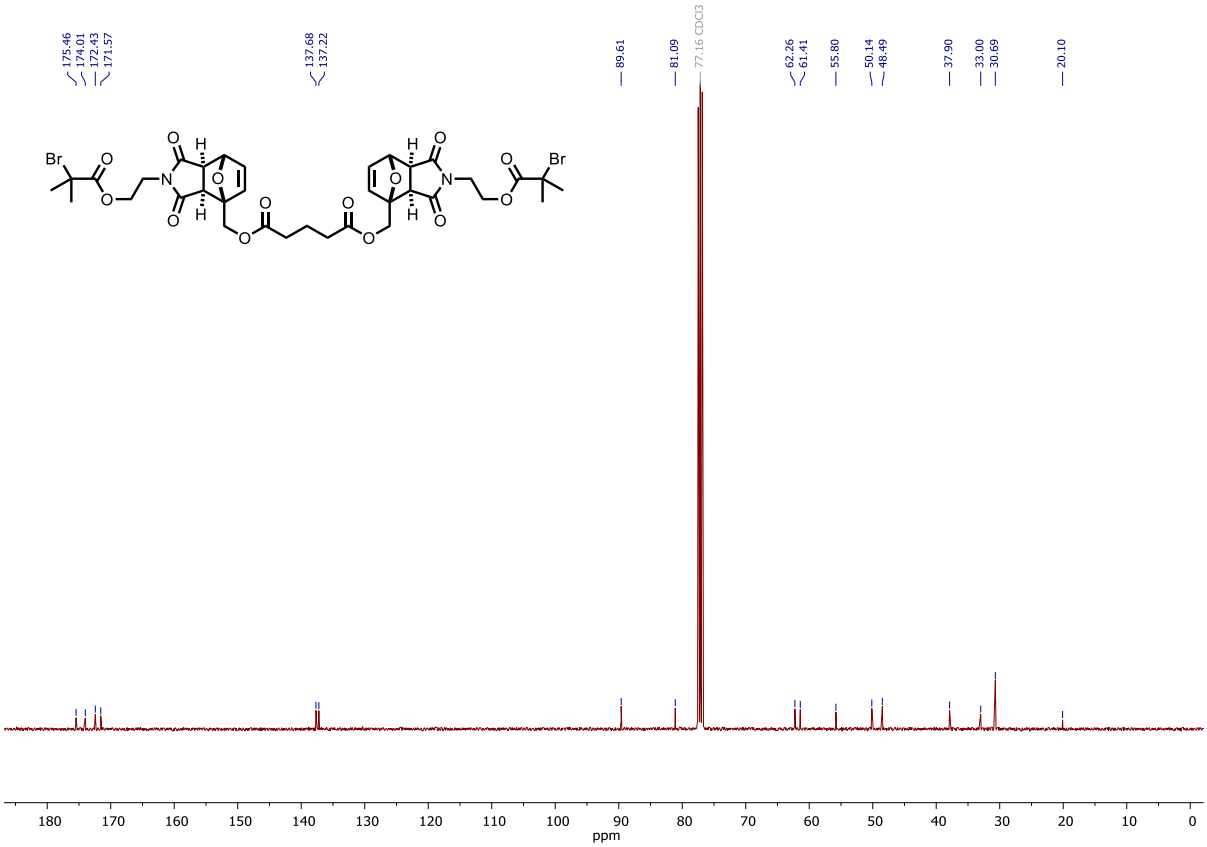


Spectrum 8. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) of compound **S4**.

5.5 Spectra of 4b

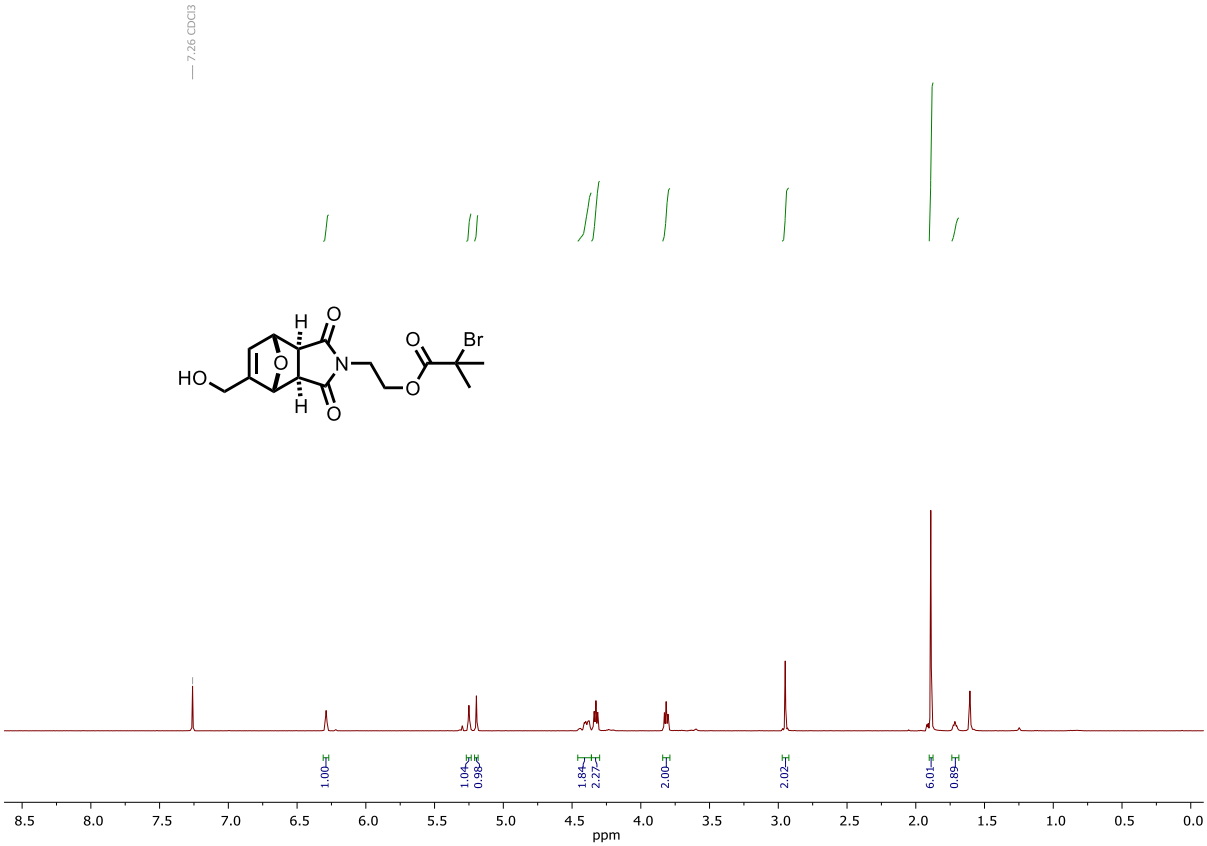


Spectrum 9. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of compound **4b**.

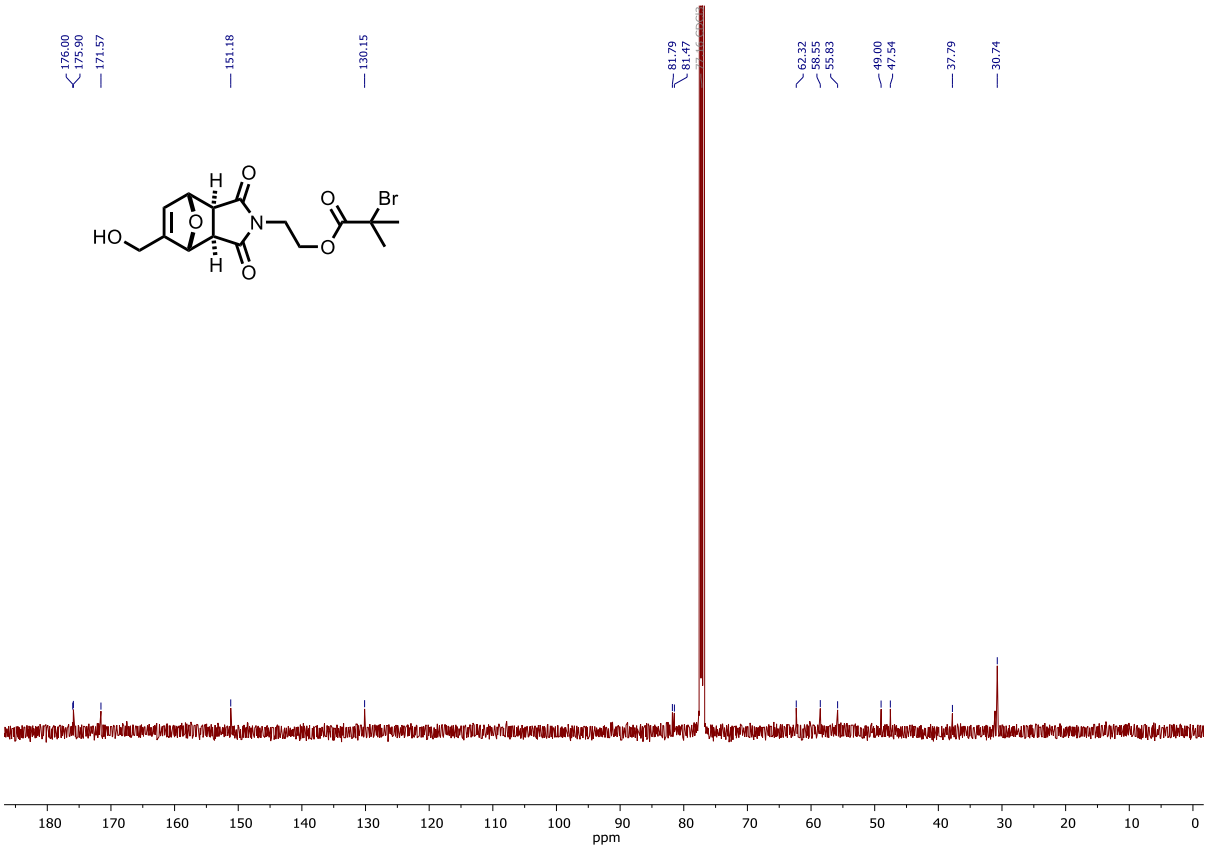


Spectrum 10. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) of compound **4b**.

5.6 Spectra of S5

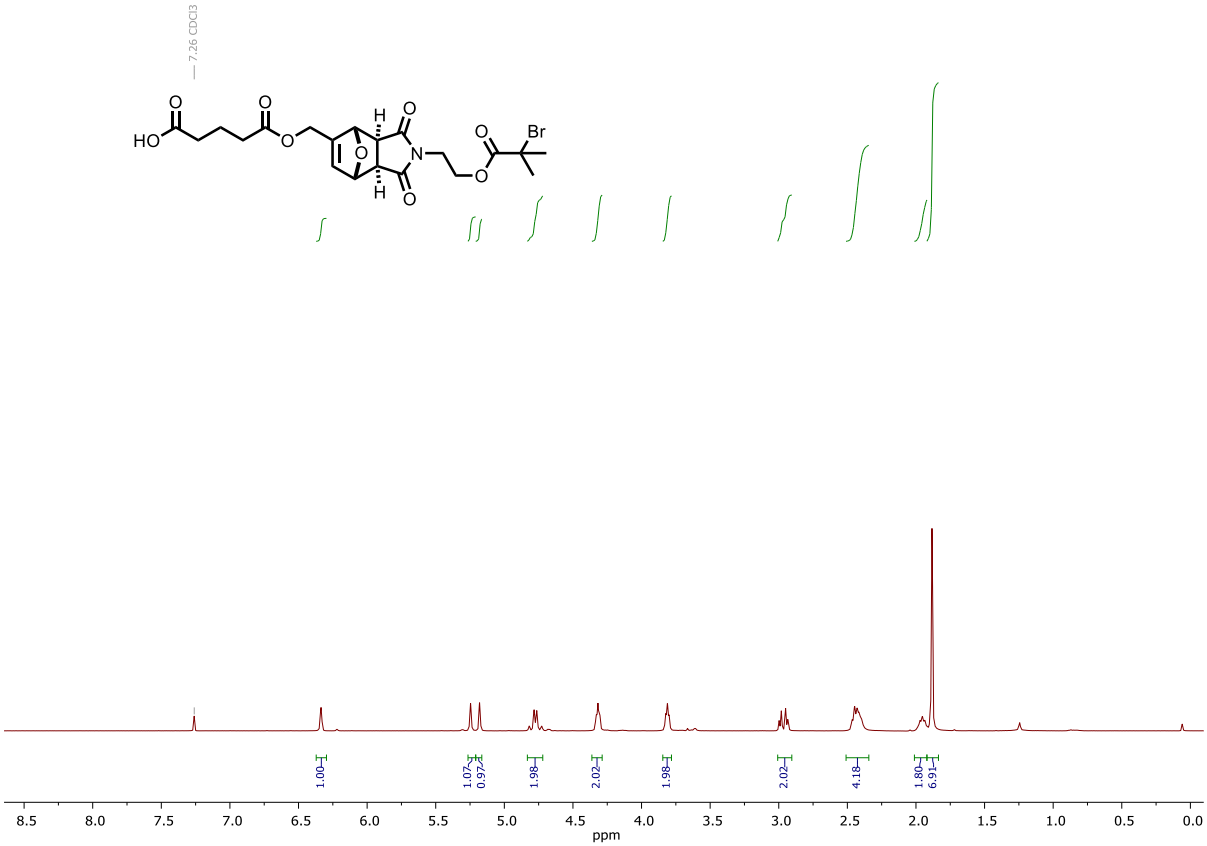


Spectrum 11. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of compound **S5**.

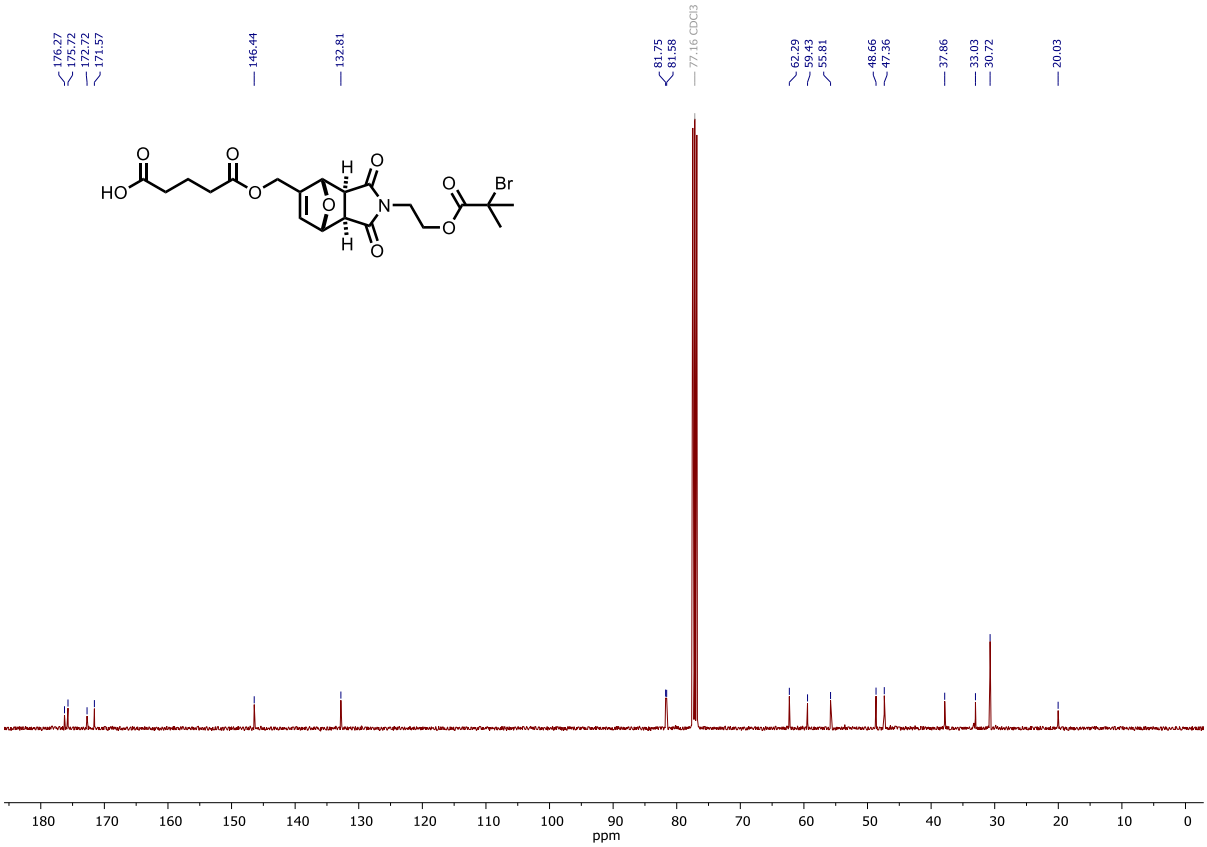


Spectrum 12. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) of compound **S5**.

5.7 Spectra of S6

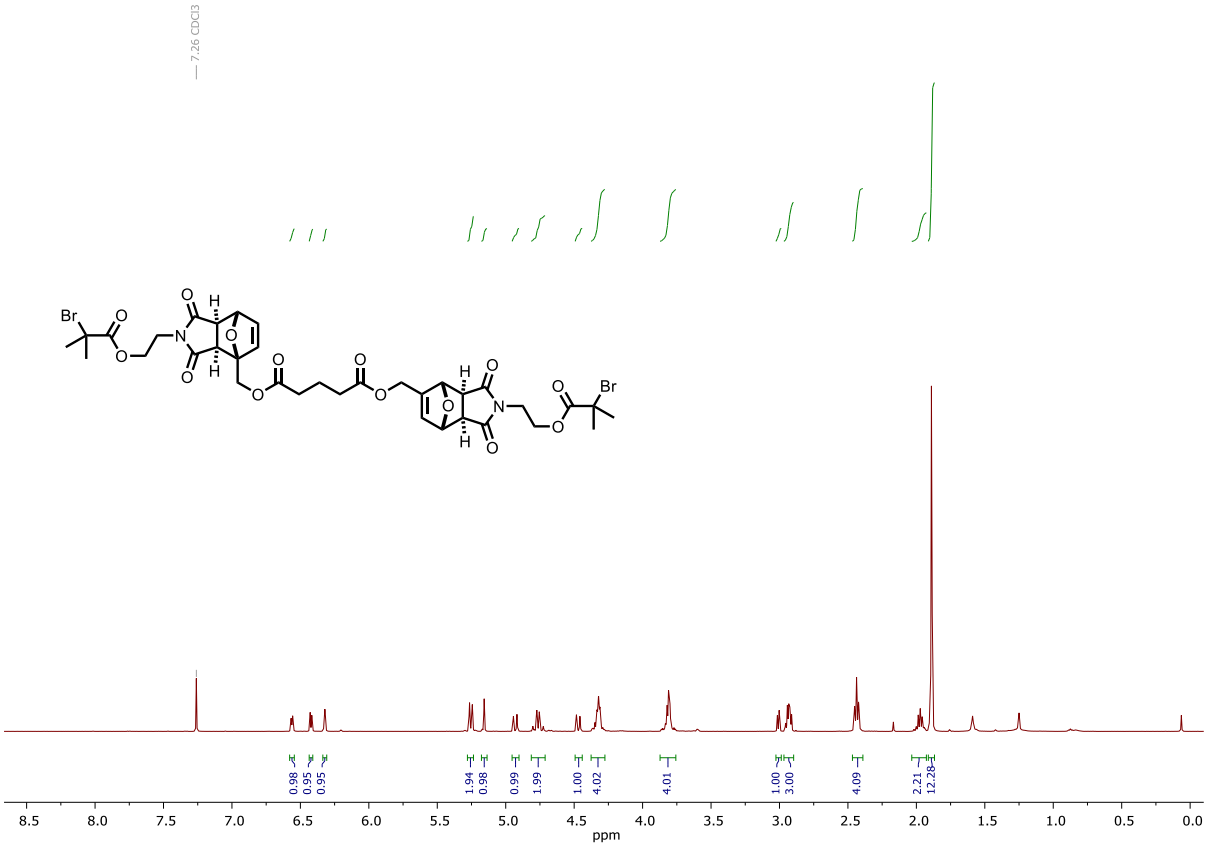


Spectrum 13. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of compound **S6**.

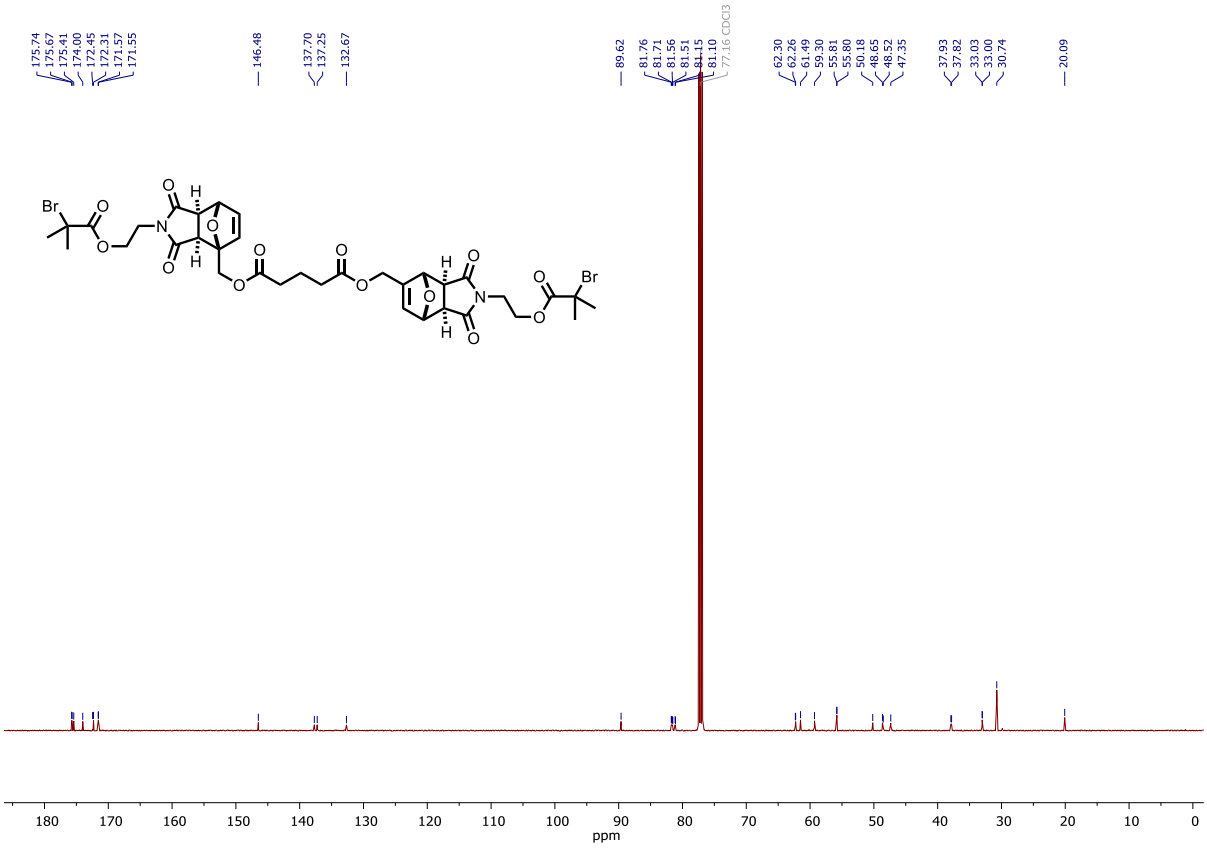


Spectrum 14. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) of compound **S6**.

5.8 Spectra of 5b

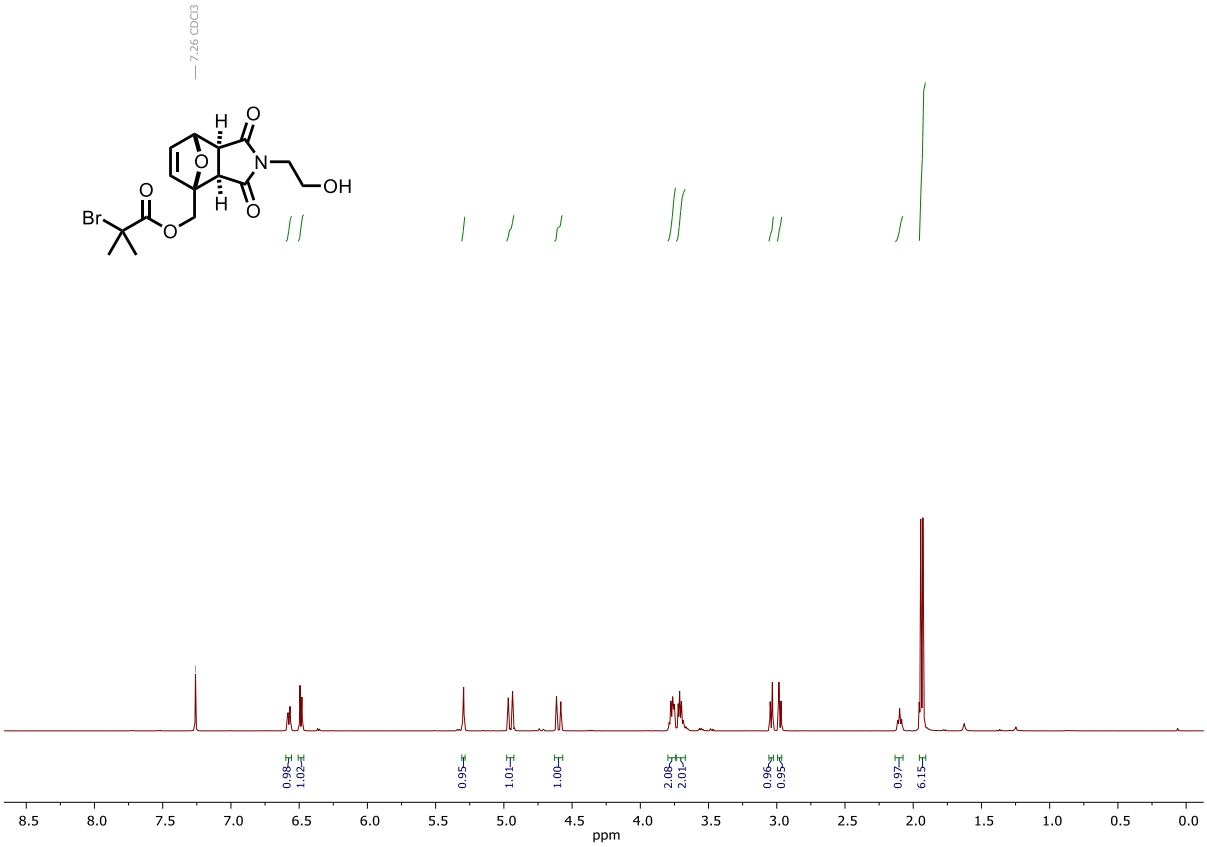


Spectrum 15. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) of compound **5b**.

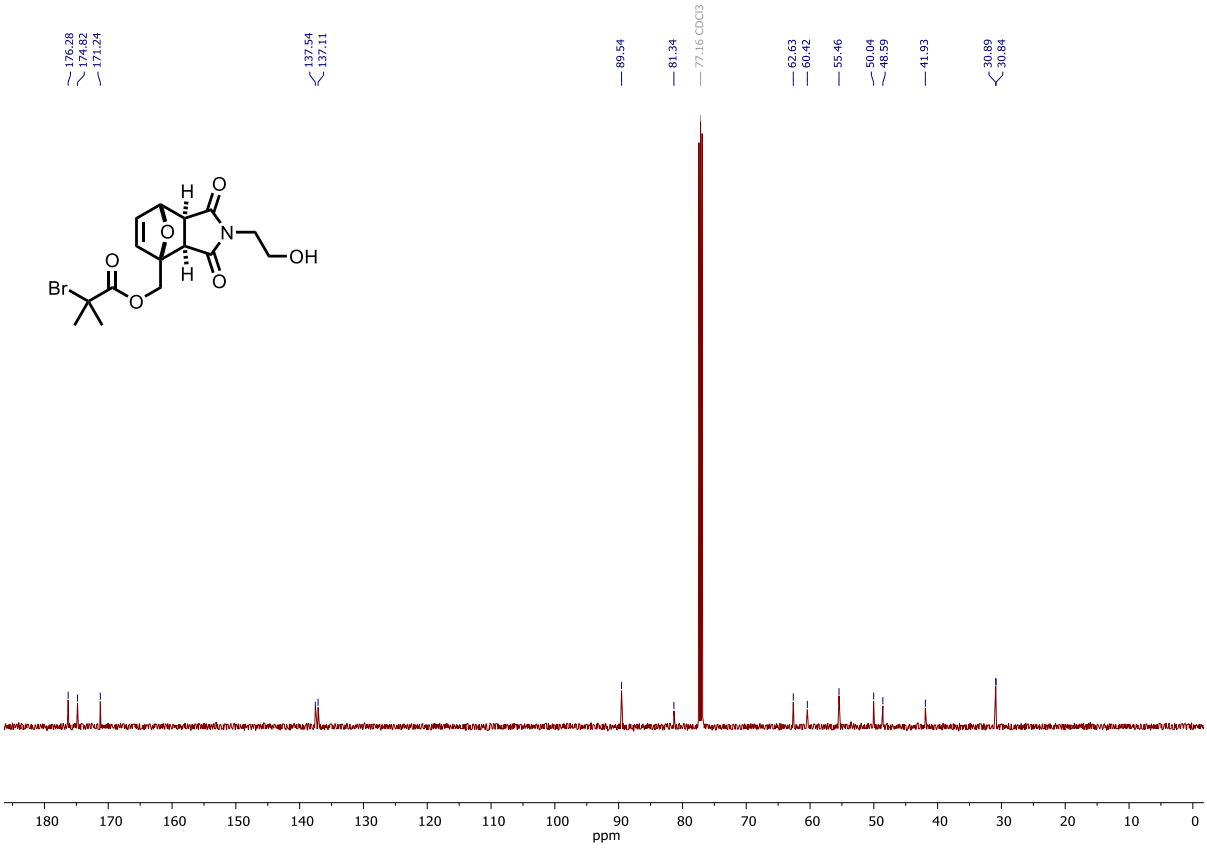


Spectrum 16. ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) of compound **5b**.

5.9 Spectra of S8

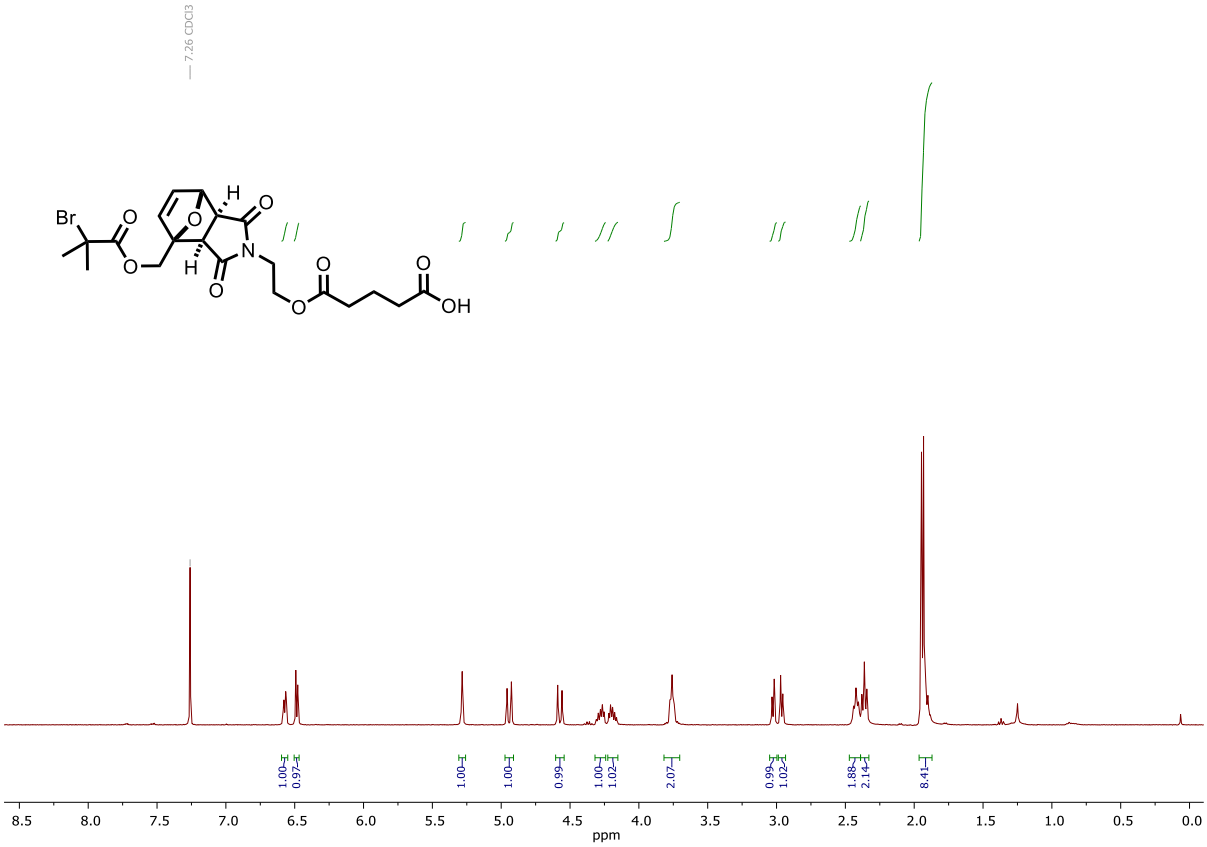


Spectrum 17. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of compound **S8**.

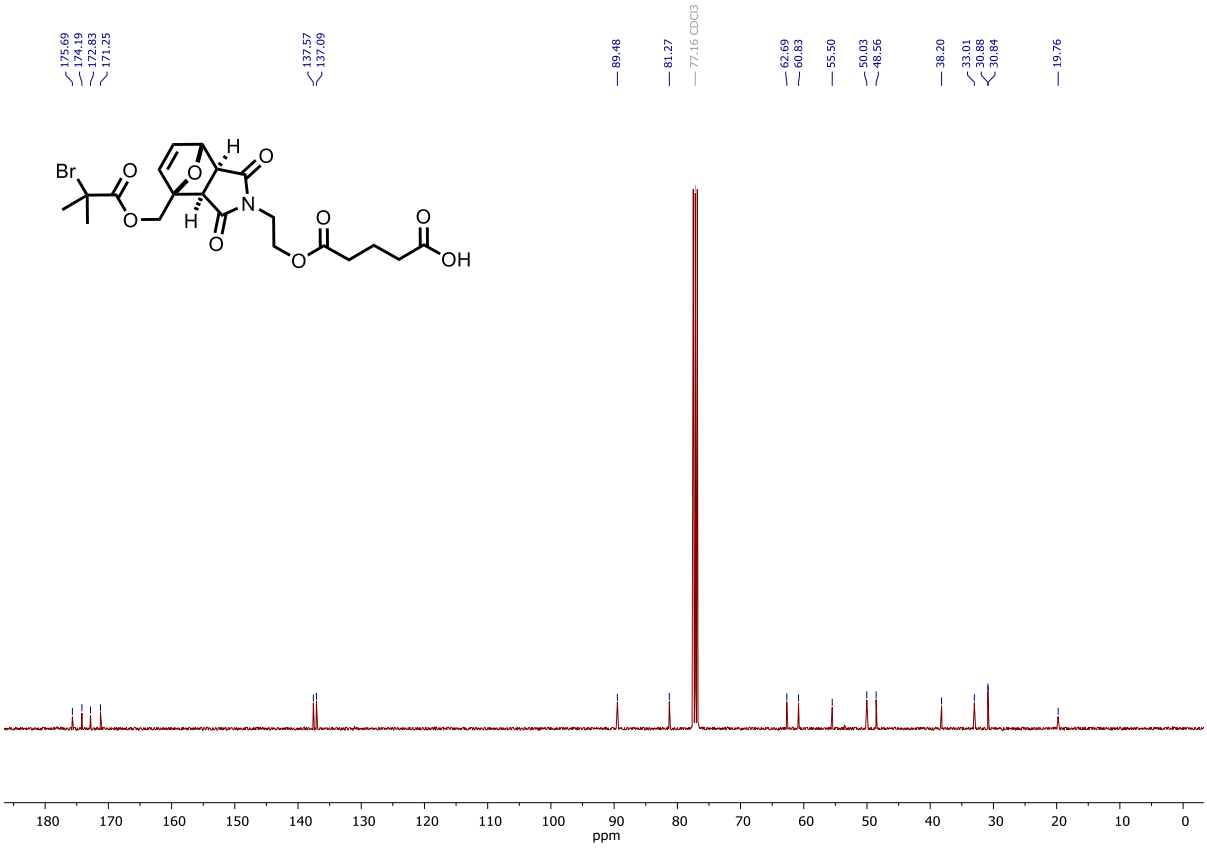


Spectrum 18. ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) of compound **S8**.

5.10 Spectra of S9

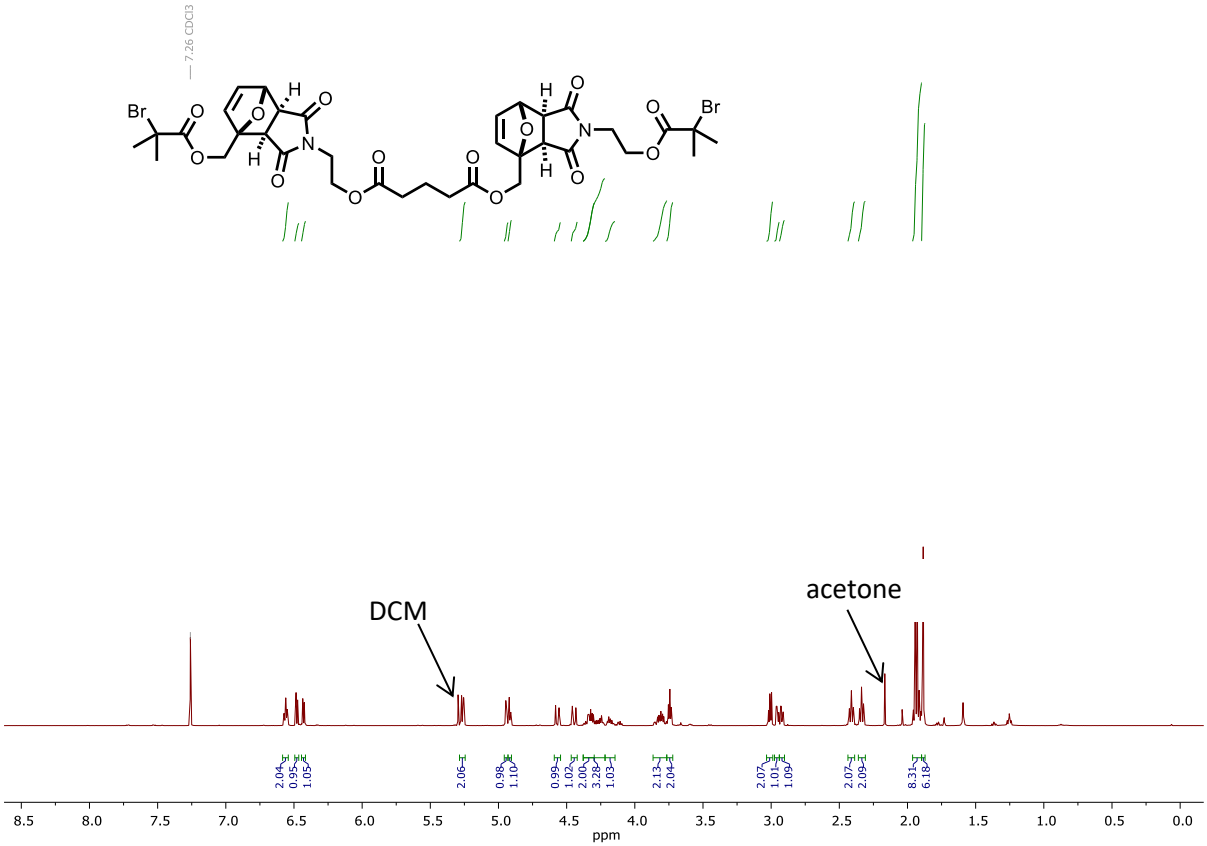


Spectrum 19. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of compound **S9**.

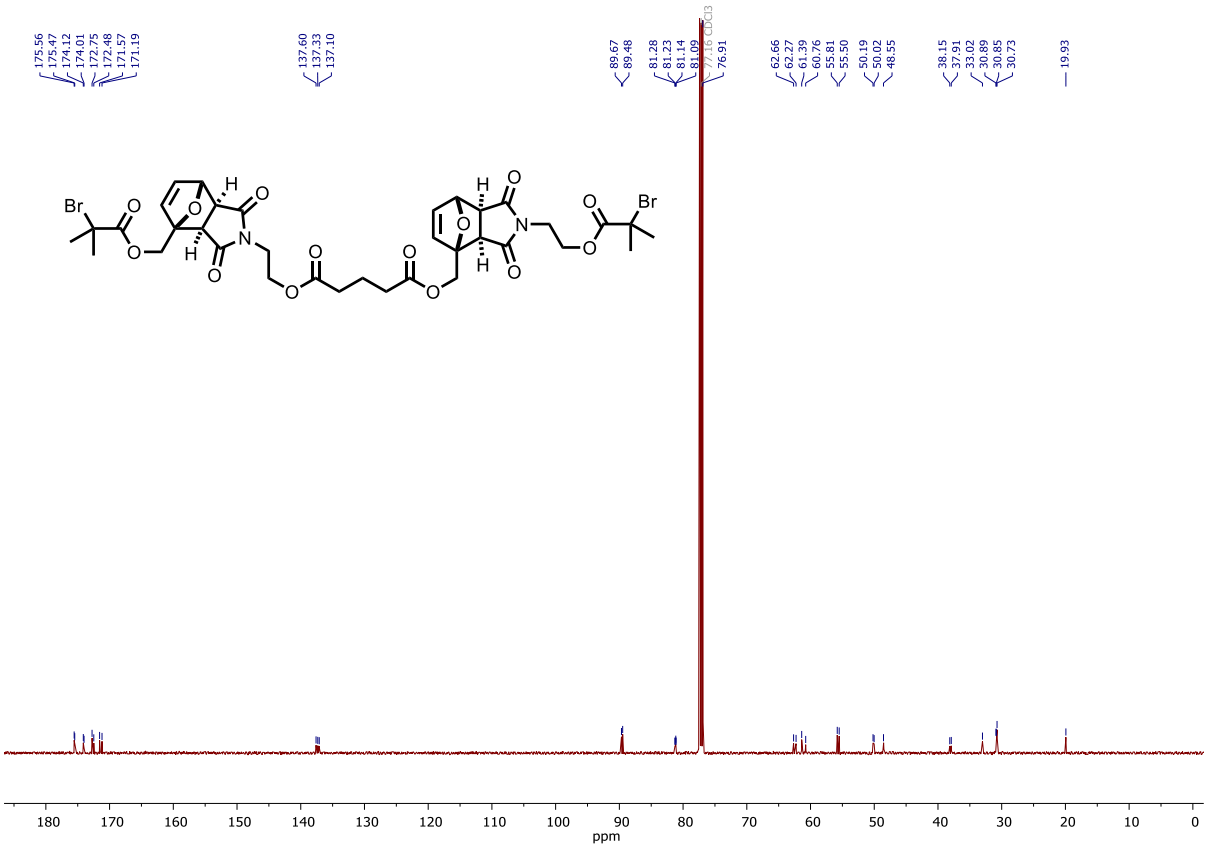


Spectrum 20. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) of compound **S9**.

5.11 Spectra of 6b

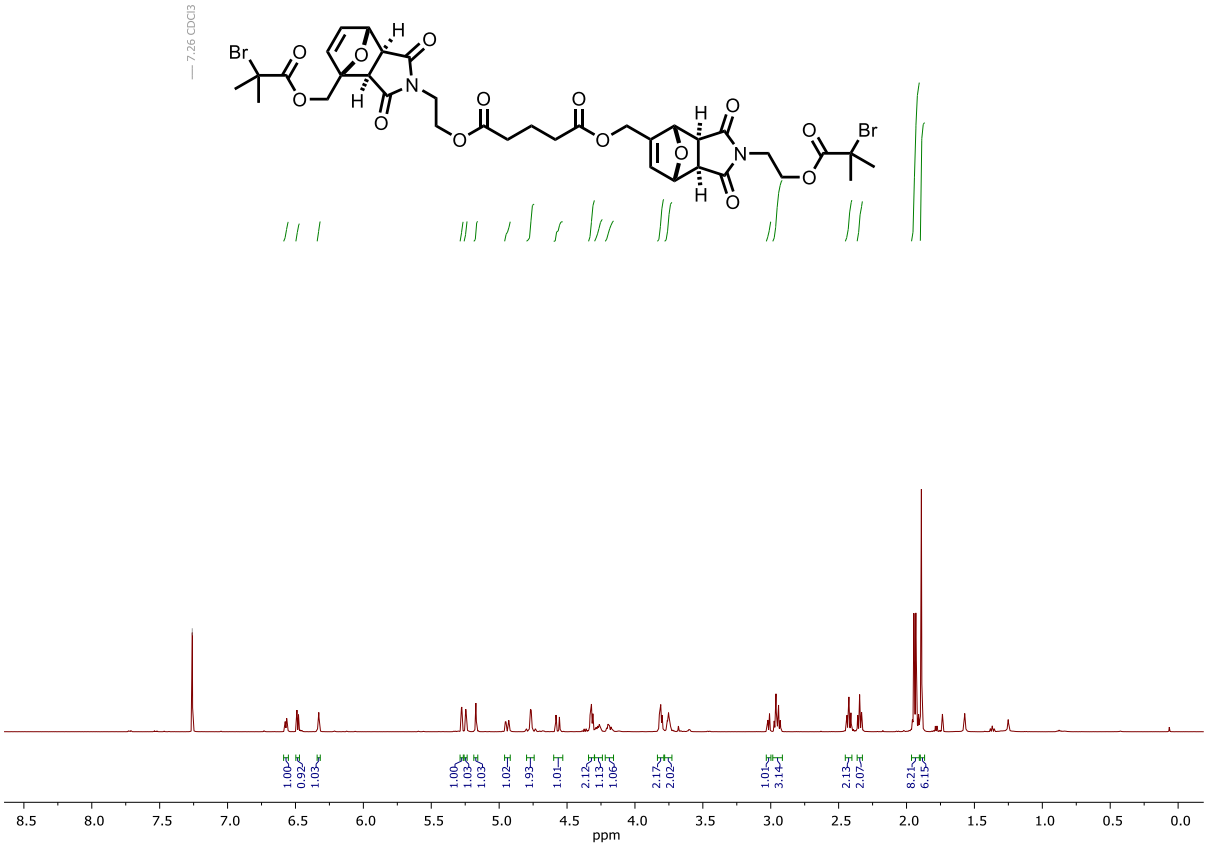


Spectrum 21. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) of compound **6b**.

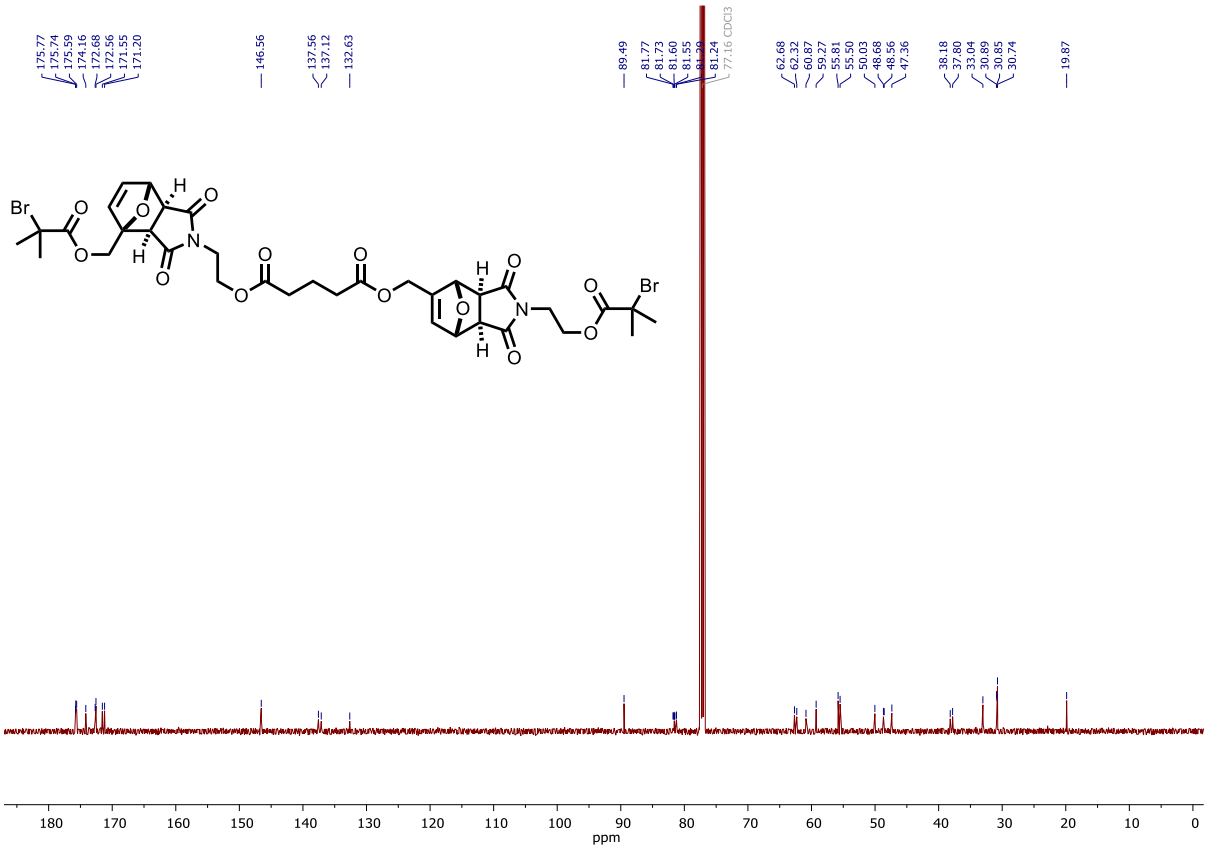


Spectrum 22. ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) of compound **6b**.

5.12 Spectra of 7b

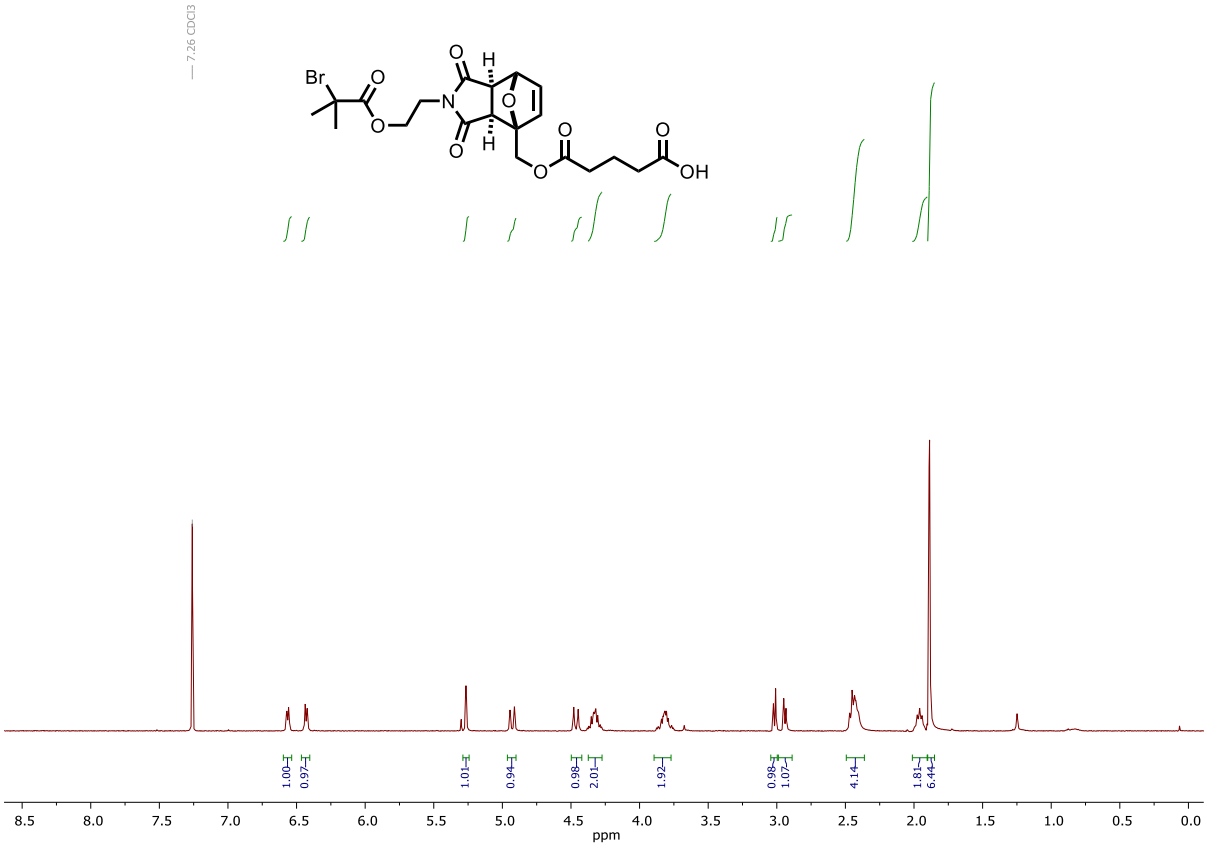


Spectrum 23. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) of compound **7b**.

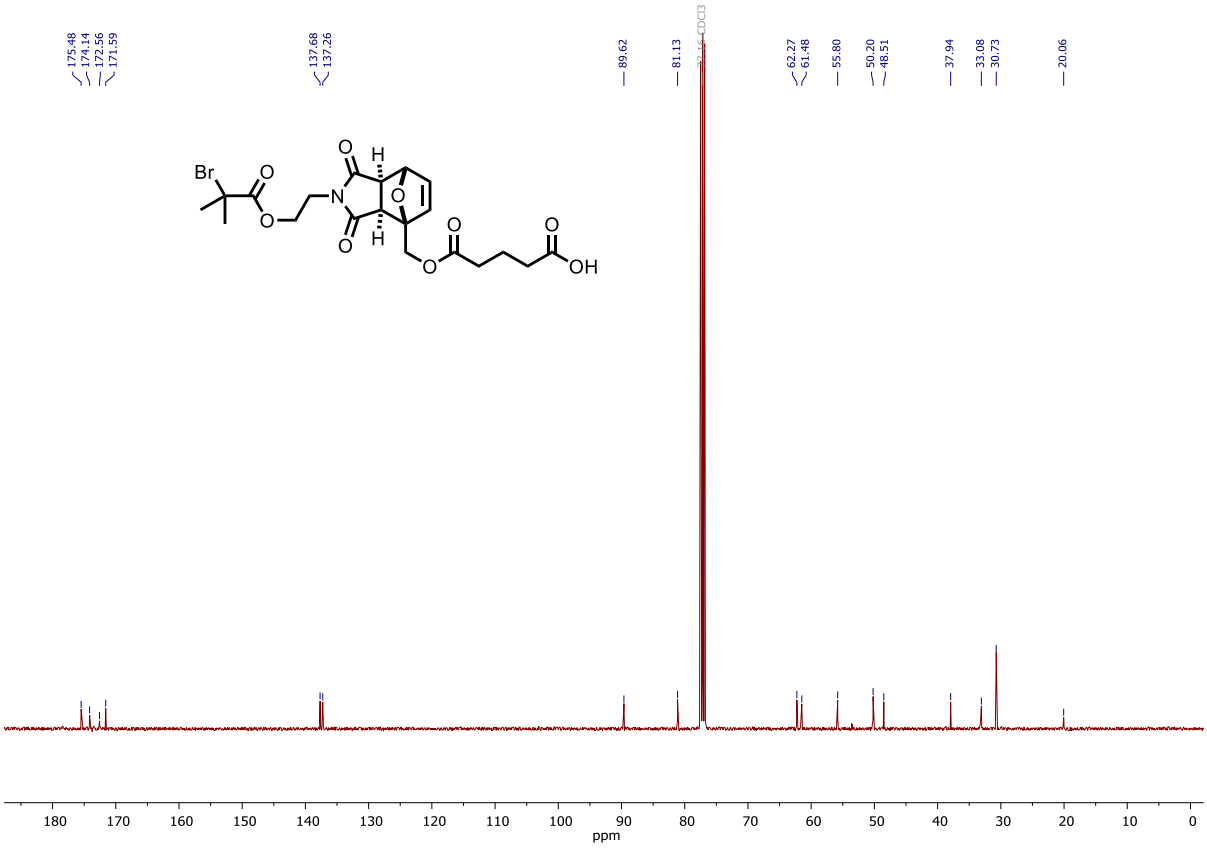


Spectrum 24. ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) of compound **7b**.

5.13 Spectra of S10

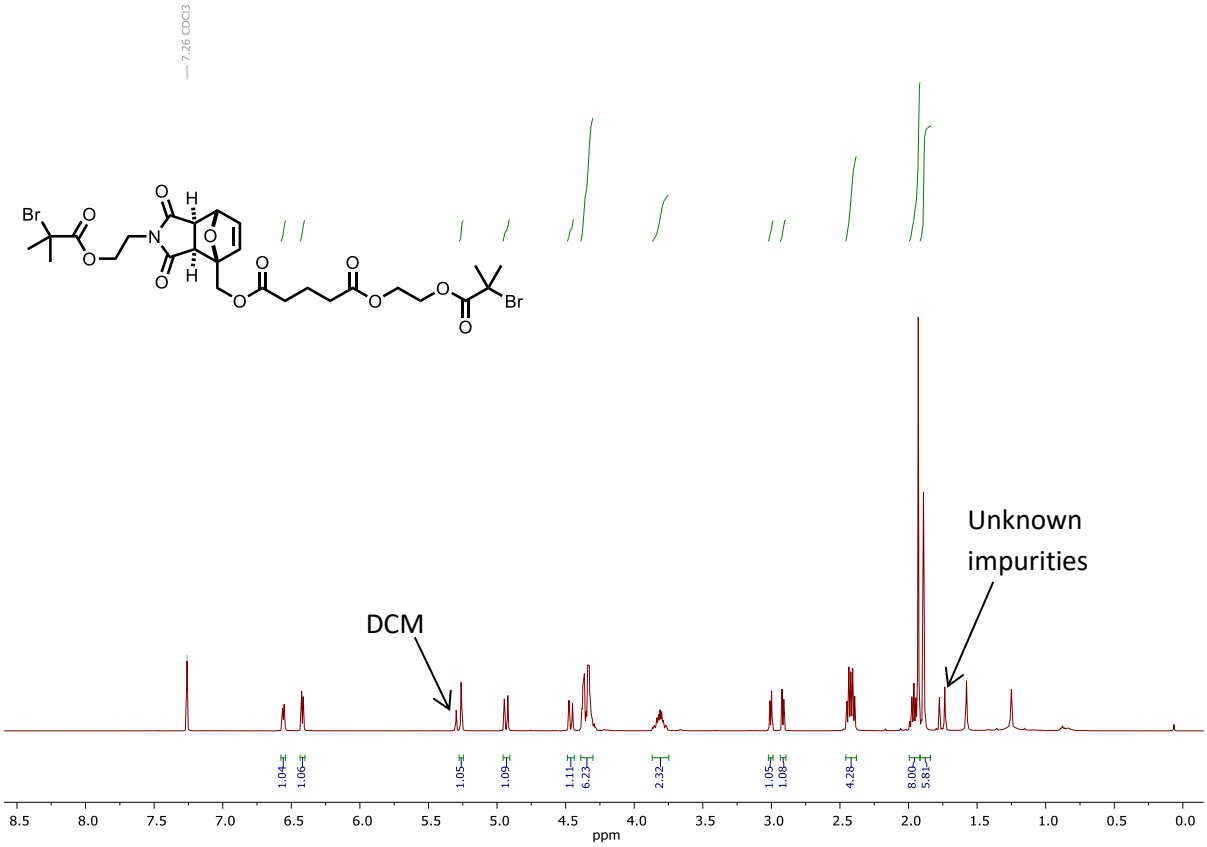


Spectrum 25. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of compound **S10**.

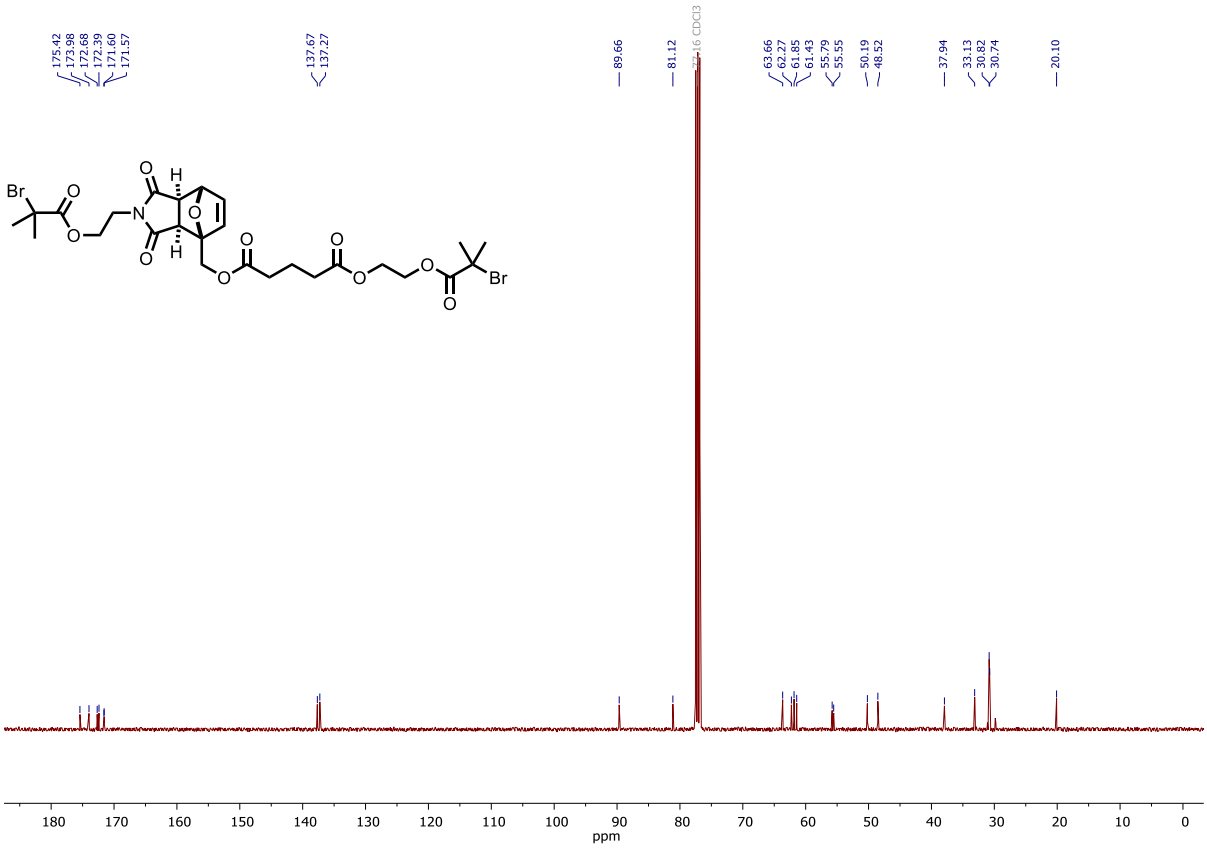


Spectrum 26. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) of compound **S10**.

5.14 Spectra of 1b

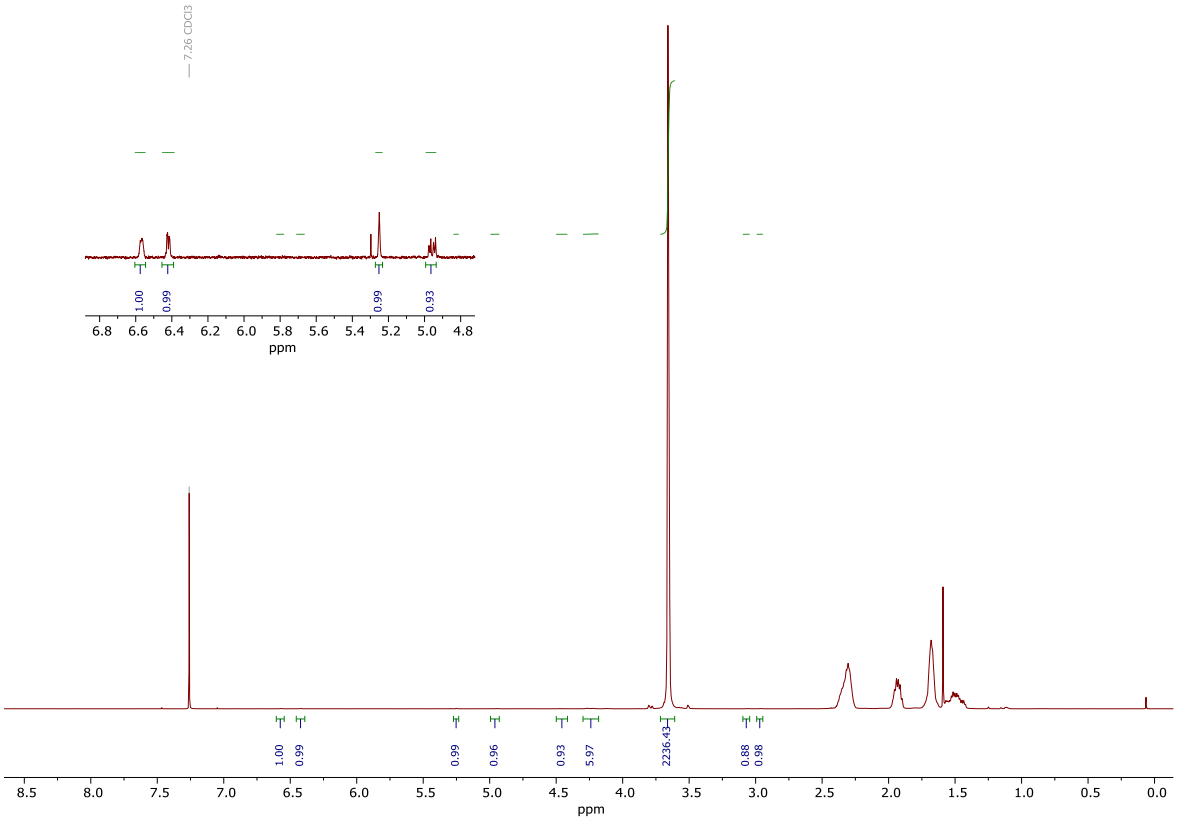


Spectrum 27. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of compound **1b**.



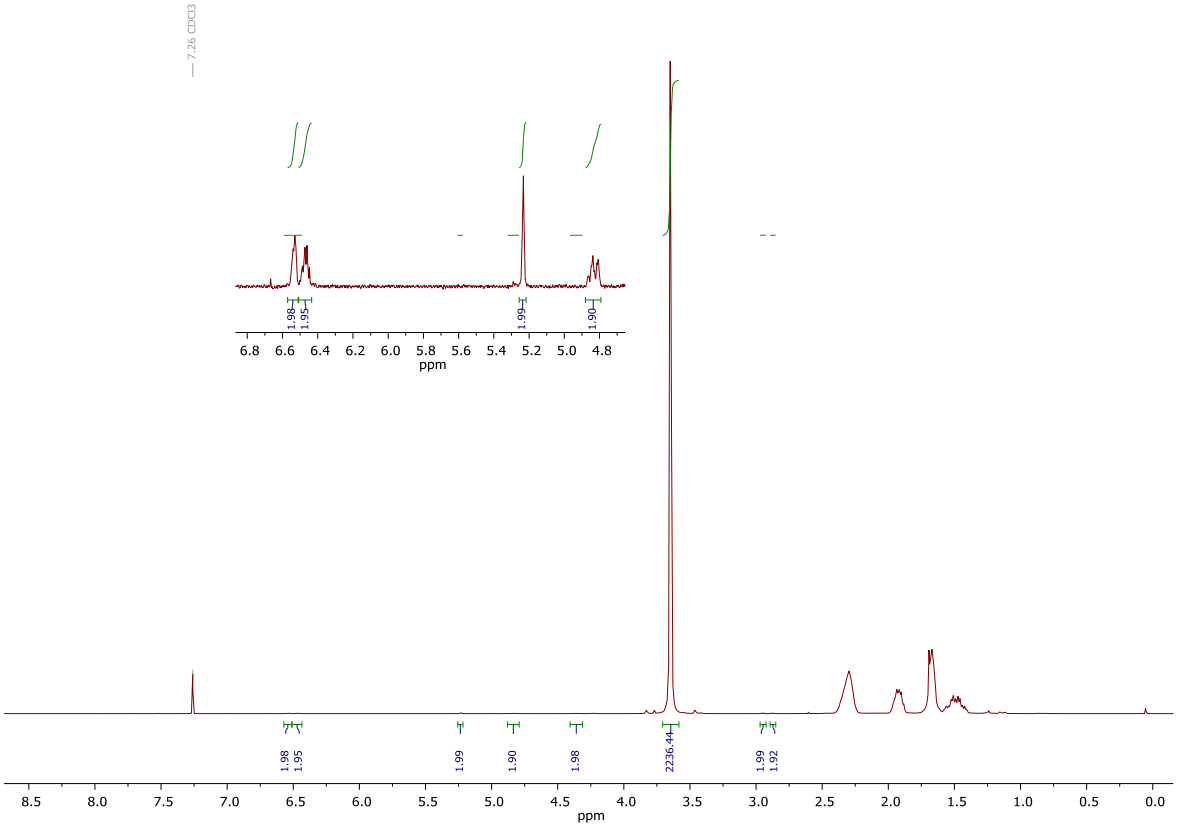
Spectrum 28. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) of compound **1b**.

5.15 Spectrum of polymer 1c (58.6 kDa)



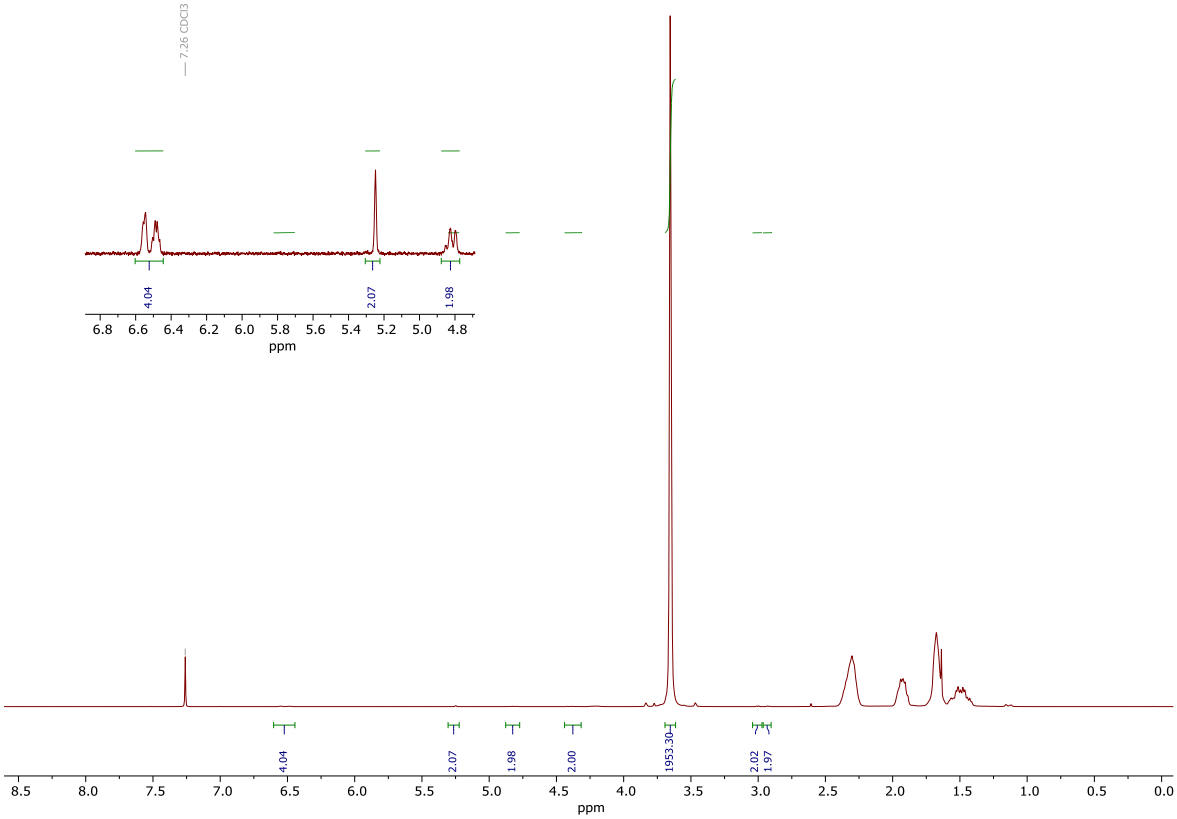
Spectrum 29. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of polymer **1c**.

5.16 Spectrum of polymer 2c (51.1 kDa)



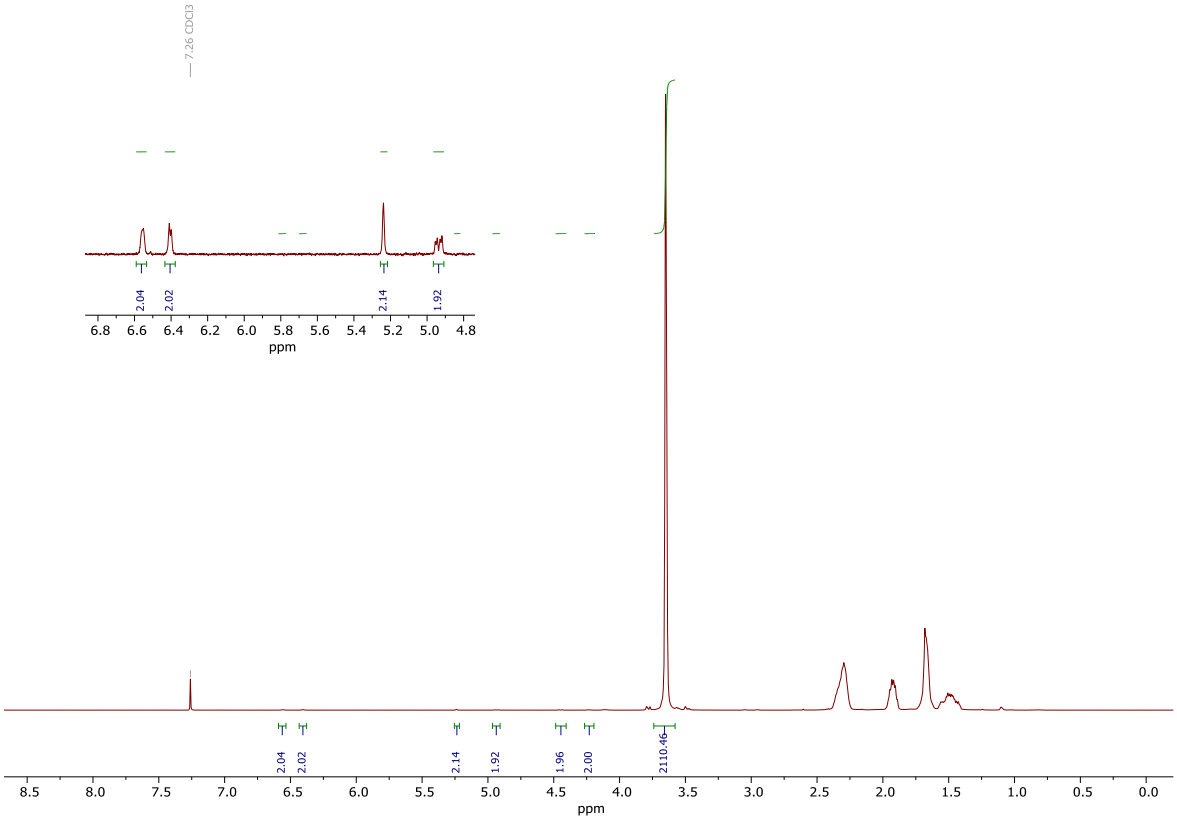
Spectrum 30. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of polymer **2c**.

5.17 Spectrum of polymer 3c (52.7 kDa)



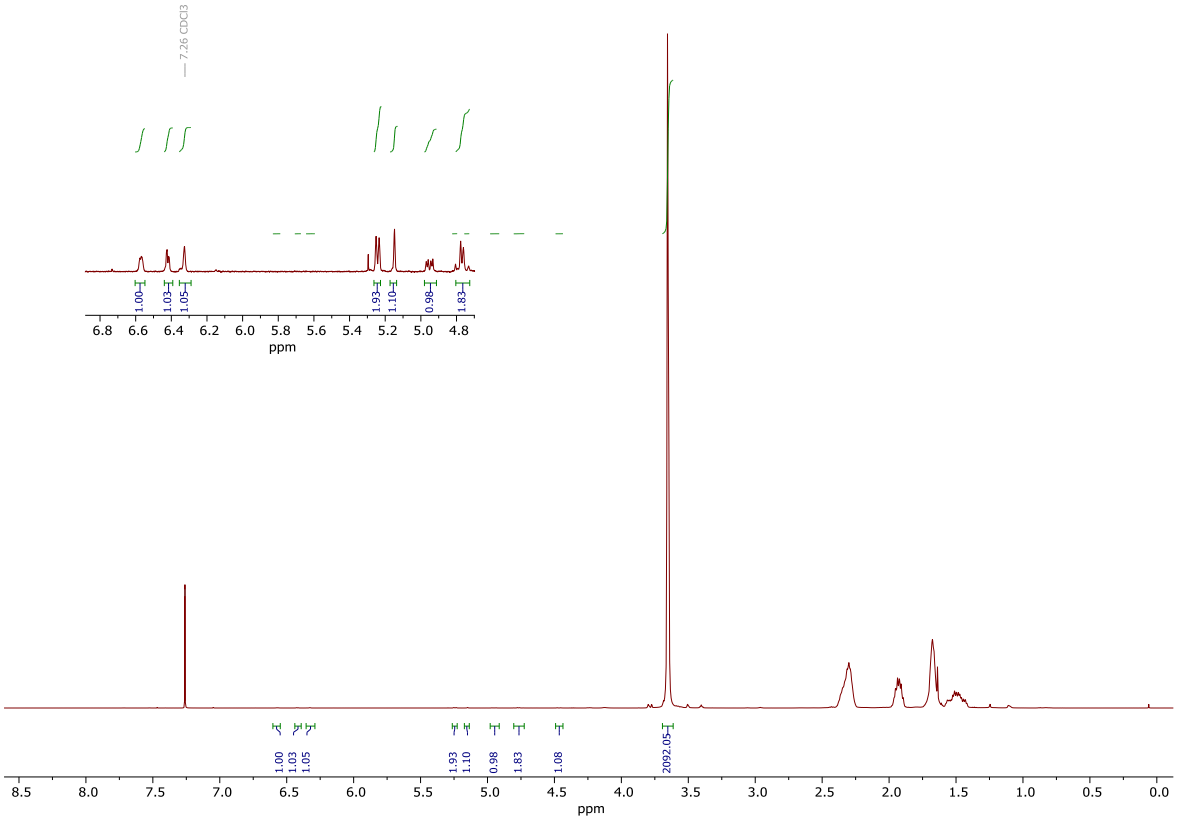
Spectrum 31. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of polymer **3c**.

5.18 Spectrum of polymer 4c (53.8 kDa)



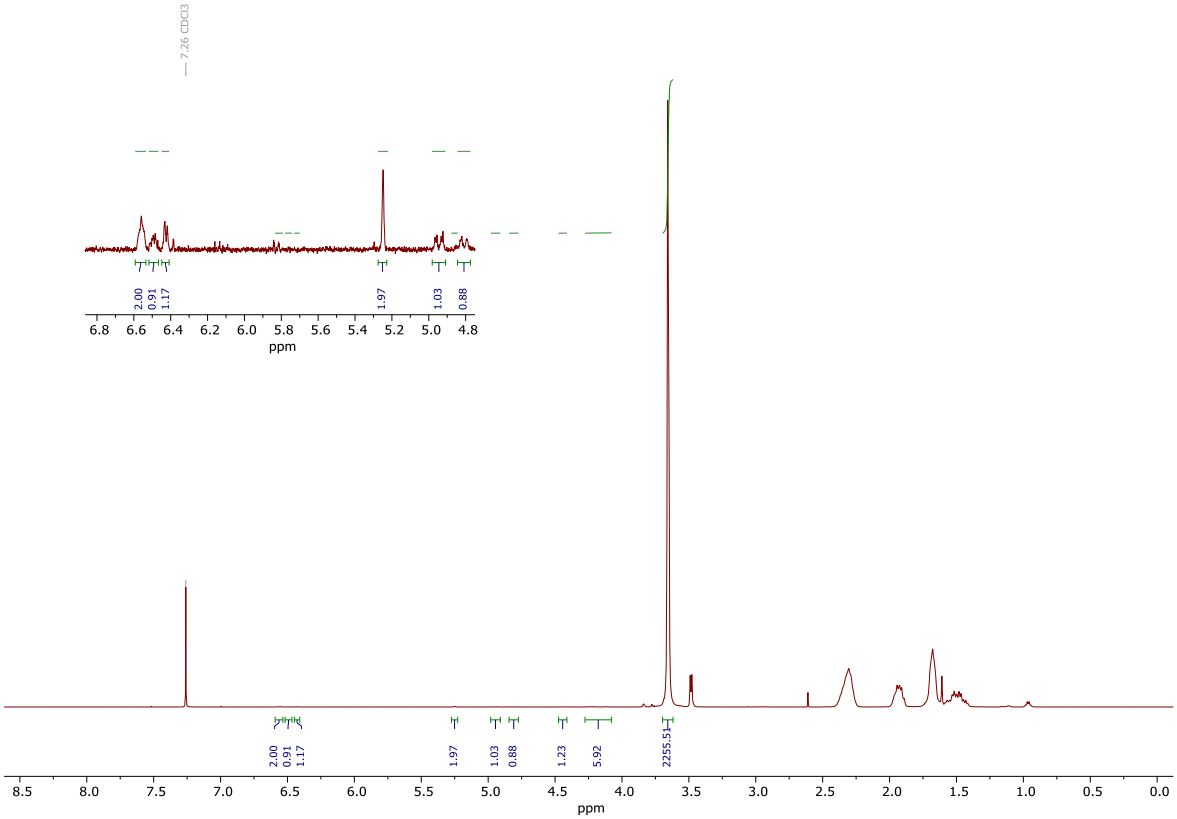
Spectrum 32. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of polymer **4c**.

5.19 Spectrum of polymer 5c (54.1 kDa)



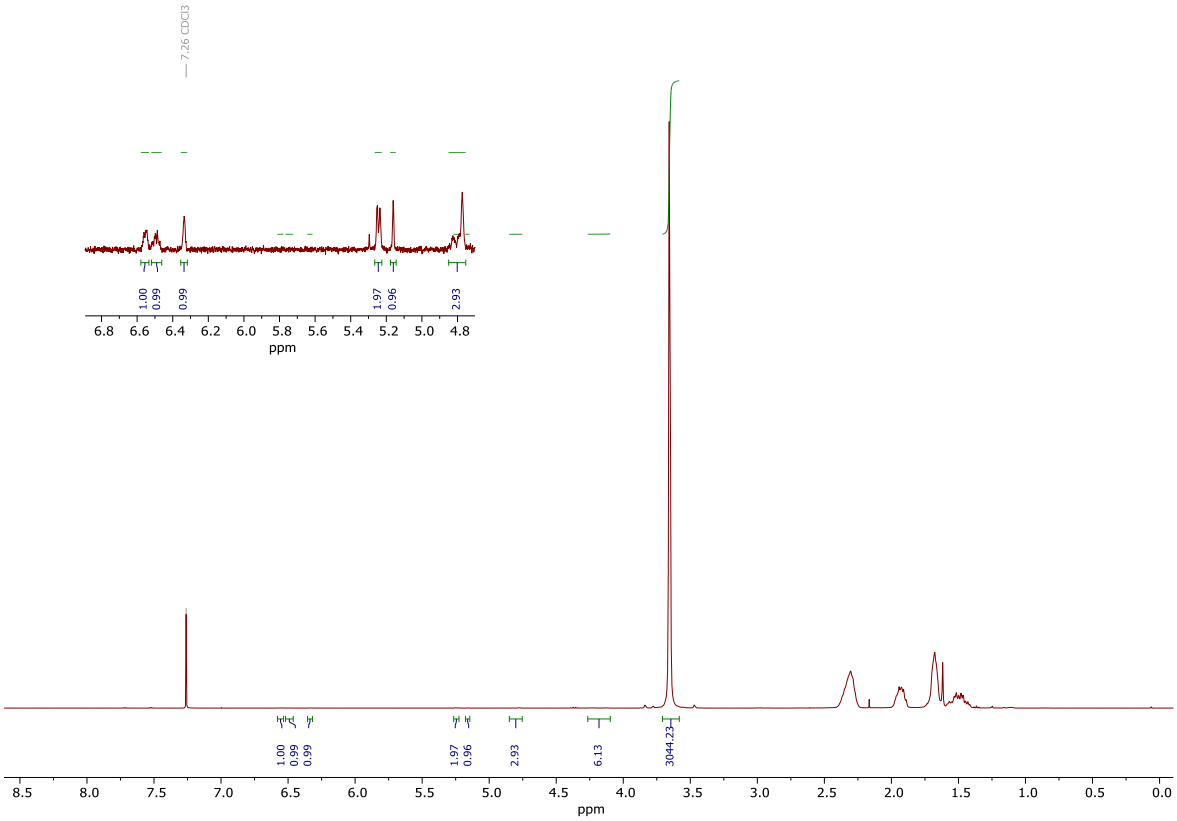
Spectrum 33. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of polymer **5c**.

5.20 Spectrum of polymer 6c (55.8 kDa)



Spectrum 34. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of polymer **6c**.

5.21 Spectrum of polymer 7c (53.4 kDa)



Spectrum 35. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of polymer **7c**.

6 Sonication Setup and Procedures

6.1 General Procedure for Sonication Experiments

Mechanophore-centred polymer (15 mg) was added to the Suslick cell and dissolved in dry acetonitrile (15 mL). The solution was degassed with N_2 for a minimum of 10 min prior to sonication starting and bubbling maintained throughout the experiment. The three arms of the Suslick cell were sealed with screw cap septa. The Suslick cell was cooled with an ice bath throughout the duration of the sonication to maintain a temperature of 5-10°C. Pulsed ultrasound was applied to the system (1.0 s on, 2.0 s off, 25% amplitude (11.7 W cm^{-2}), 20 kHz). Aliquots of 300 µL were taken at intervals of 30 min sonication time, solvent evaporated and residue redissolved in 500 µL of THF. The sample was filtered through a syringe filter (PTFE, 0.45 µm pore size) and analysed by GPC.

6.2 Experimental k* values for the mechanochemical rDA of polymers 1-7c

Table S2. M_n and k^* values for polymers **1-7c**.

Polymer	M_n (kDa)	k^* ($min^{-1}.kDa^{-1}.10^5$)					
		Run 1	Run 2	Run 3	Run 4	Run 5	Ave
1c	58.6	6.47	6.49	6.73	6.33	6.02	6.41
2c	51.1	7.43	6.69	7.25	5.31	6.29	6.59
3c	52.7	6.38	5.87	7.19	6.43	5.80	6.33
4c	53.8	5.87	5.59	5.81	4.64	5.05	5.39
5c	54.1	6.85	5.32	5.34	5.33	5.40	5.65
6c	55.8	6.43	5.82	6.86	5.89	6.53	6.31
7c	53.4	6.60	7.00	5.15	5.57	5.16	5.90

6.3 Comparison of Molecular Weight Range in Mechanophores in Close Proximity

The molecular weight and polydispersity of polymers **1-7c** display a small degree of variety and so we wanted to confirm that any difference in rate of mechanical cleavage is not due to this variation. The relative rate constants for each polymer were plotted against their respective M_n, M_w and M_p. There appears to be no correlation between any of the three molecular weight values and the relative rates of cleavage. Thus, we can be satisfied that the polymers synthesised can be directly compared and our statistical analysis is valid.

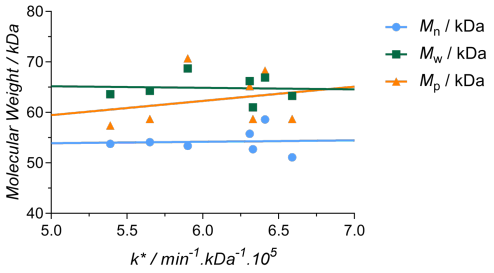


Figure S2. Comparison of different molecular weight values with relative rate of cleavage k^* for polymers **1-7c**. Solid lines correspond to a linear fit (R^2 = 2.62x10^{-3}, 2.76x10^{-3} and 5.28x10^{-2} for M_n, M_w and M_p respectively. Lack of correlation between molecular weight and k^* confirms differences in polymer cleavage are not due to variation of polymer molecular weight.

6.4 Representative Examples of Sonication Experiments

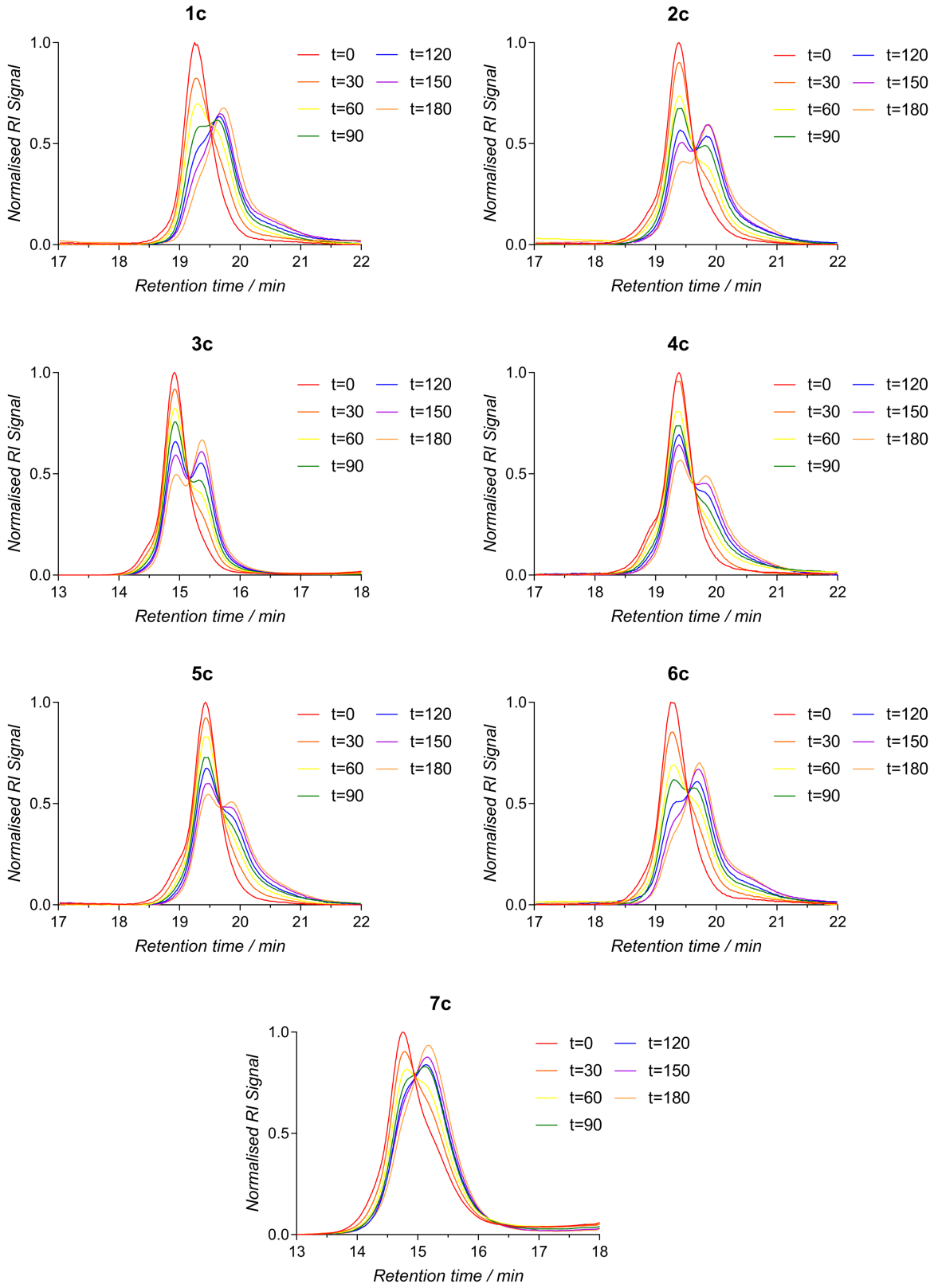
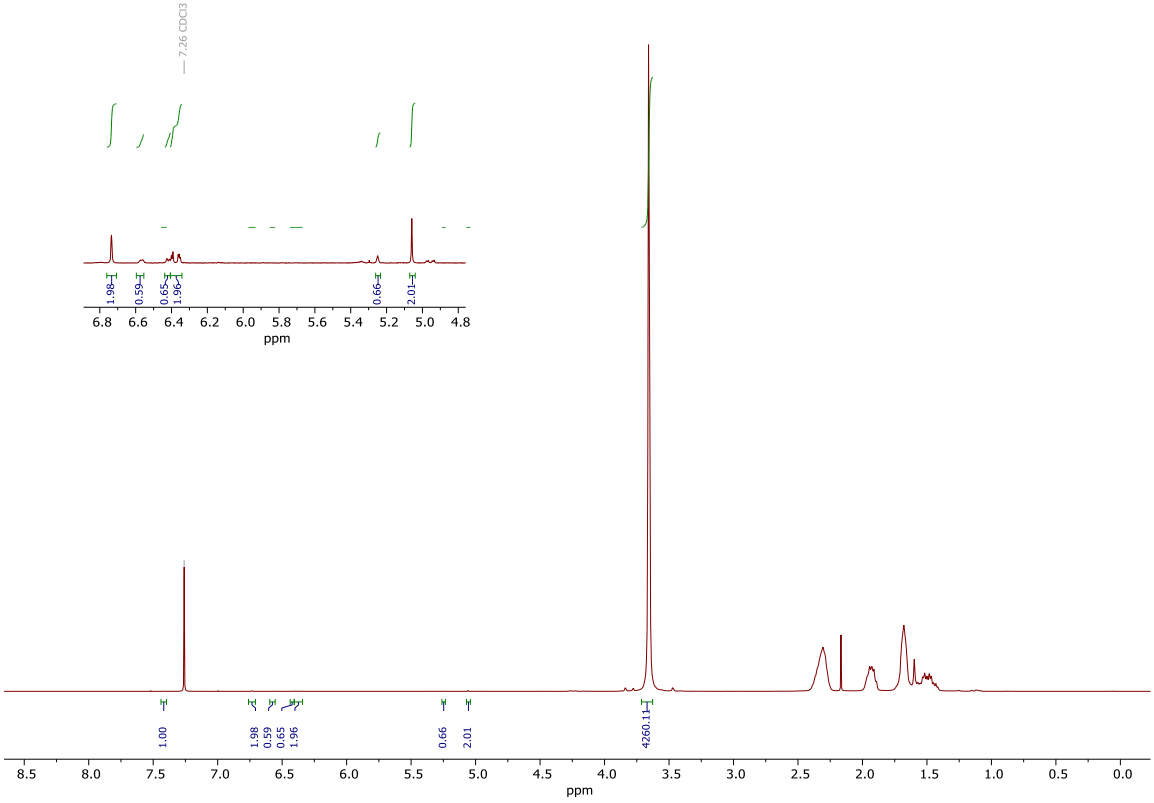


Figure S3. Representative examples of polymer cleavage by sonication for polymers **1-7c**. GPC traces show disappearance of peak corresponding to the mechanophore-centred polymer and the appearance of a peak corresponding to half the initial M_n (M_0).

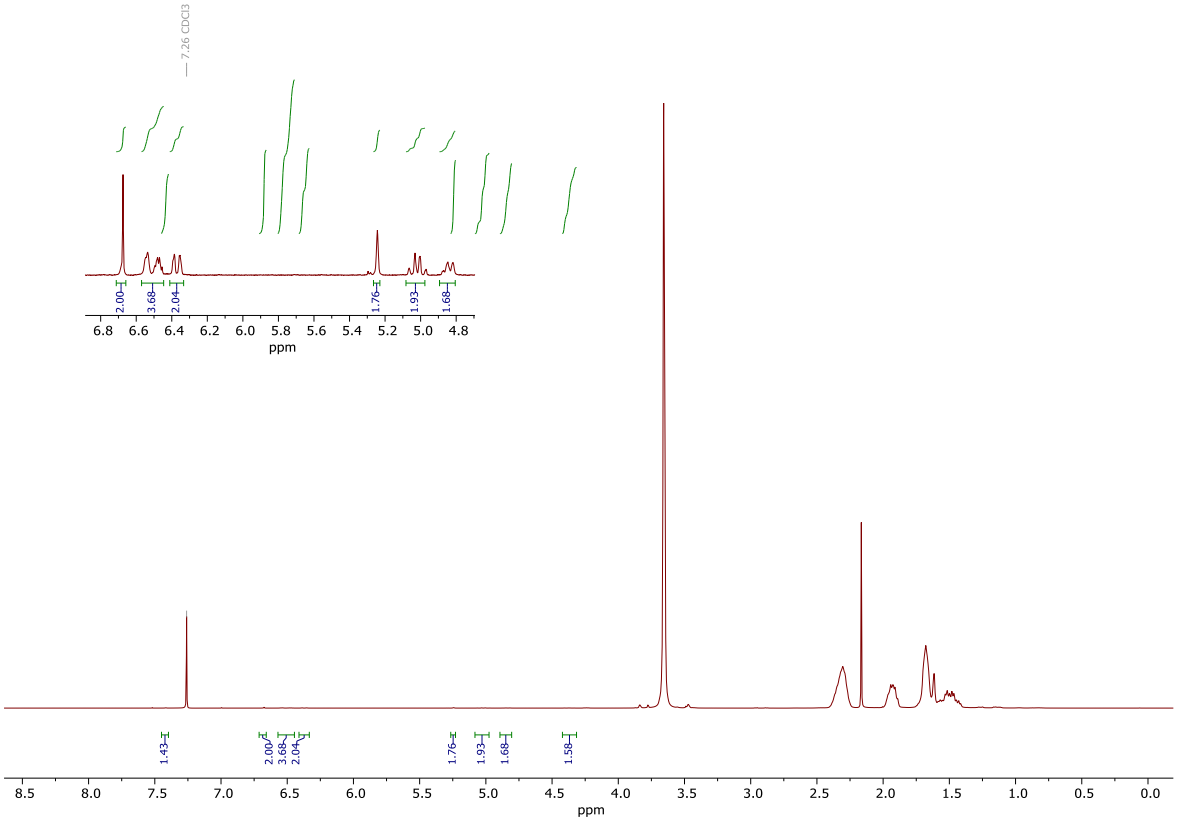
6.5 NMR of sonicated polymers

6.5.1 Post-sonication ^{1}H NMR of polymer 1c



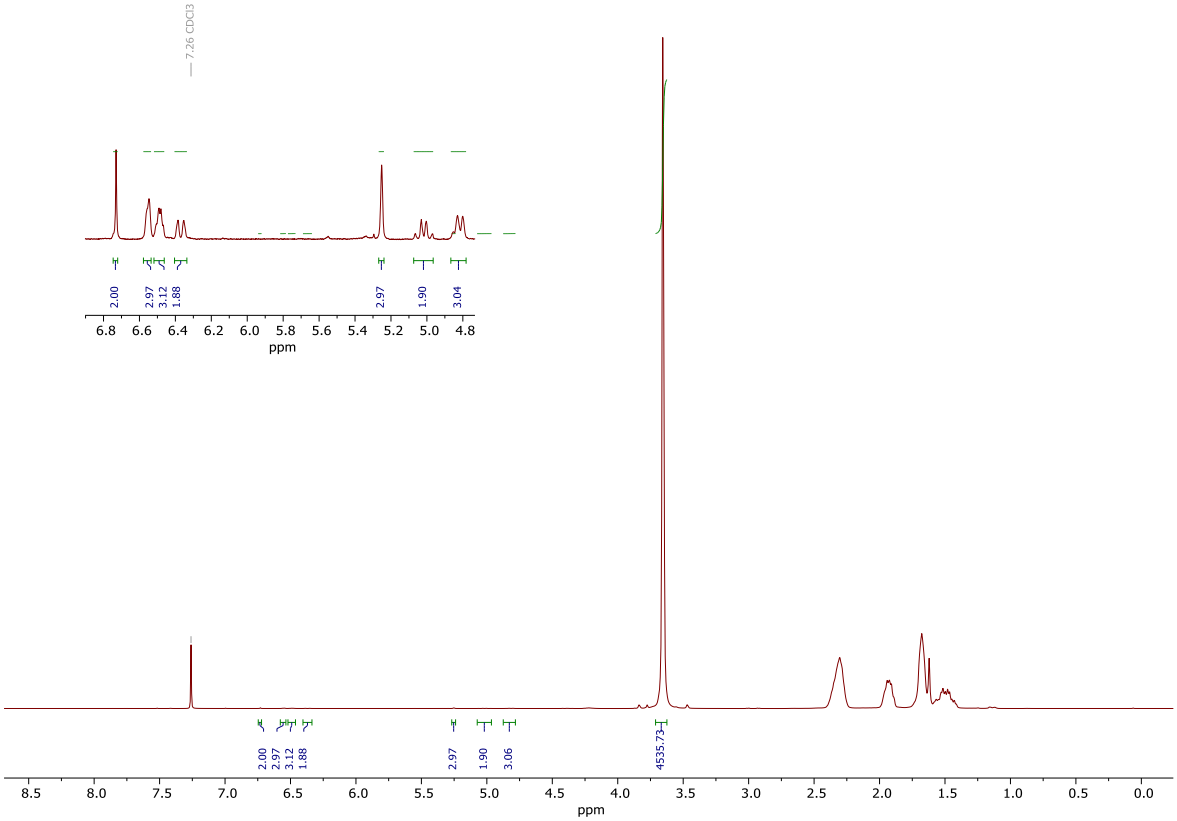
Spectrum 36. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of polymer **1c** after 240 min of sonication.

6.5.2 Post-sonication ^{1}H NMR of polymer 2c



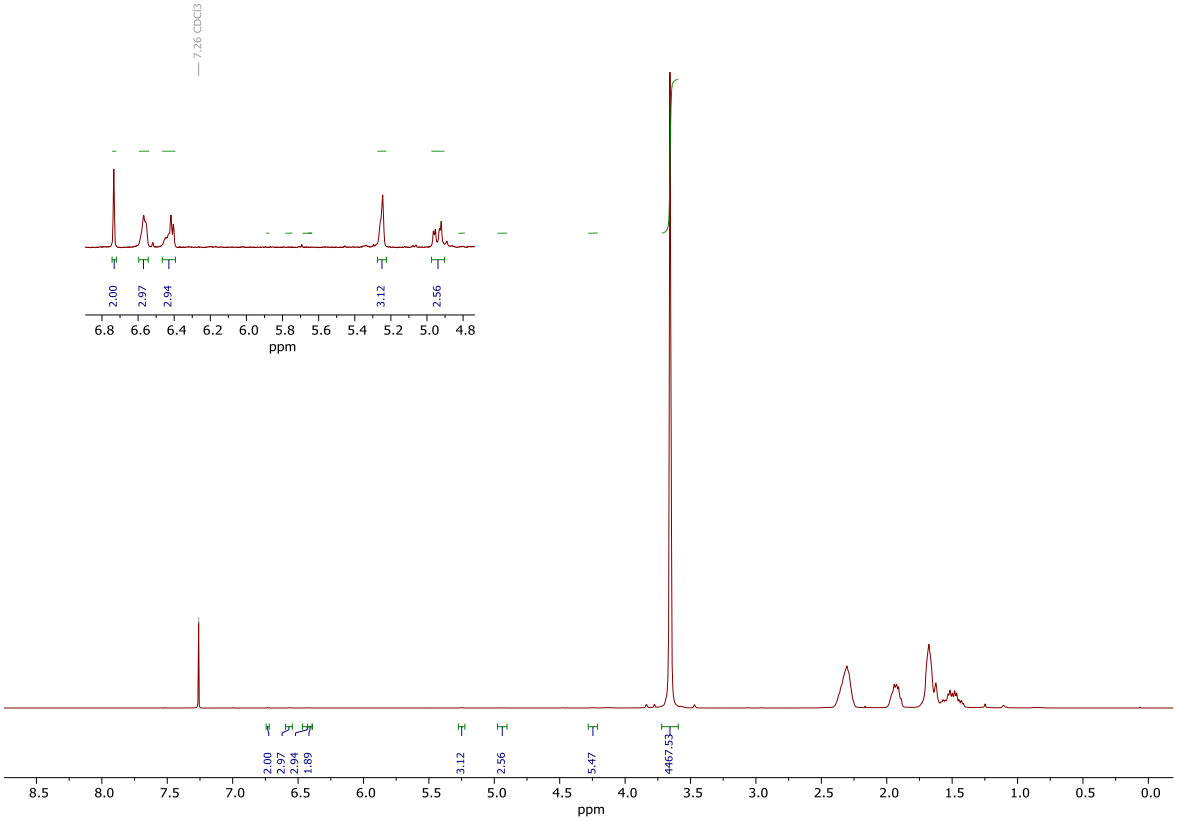
Spectrum 37. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of polymer **2c** after 240 min of sonication.

6.5.3 Post-sonication ^{1}H NMR of polymer 3c



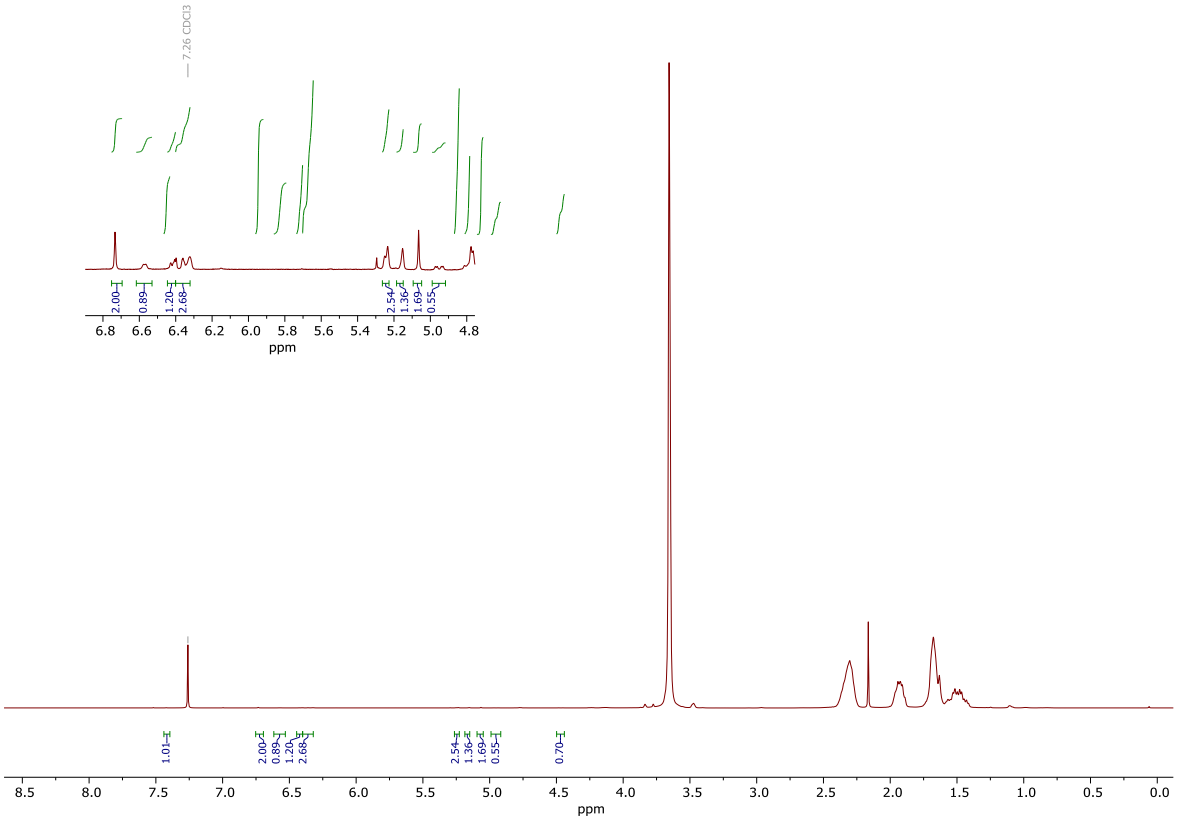
Spectrum 38. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of polymer **3c** after 240 min of sonication.

6.5.4 Post-sonication ^{1}H NMR of polymer 4c



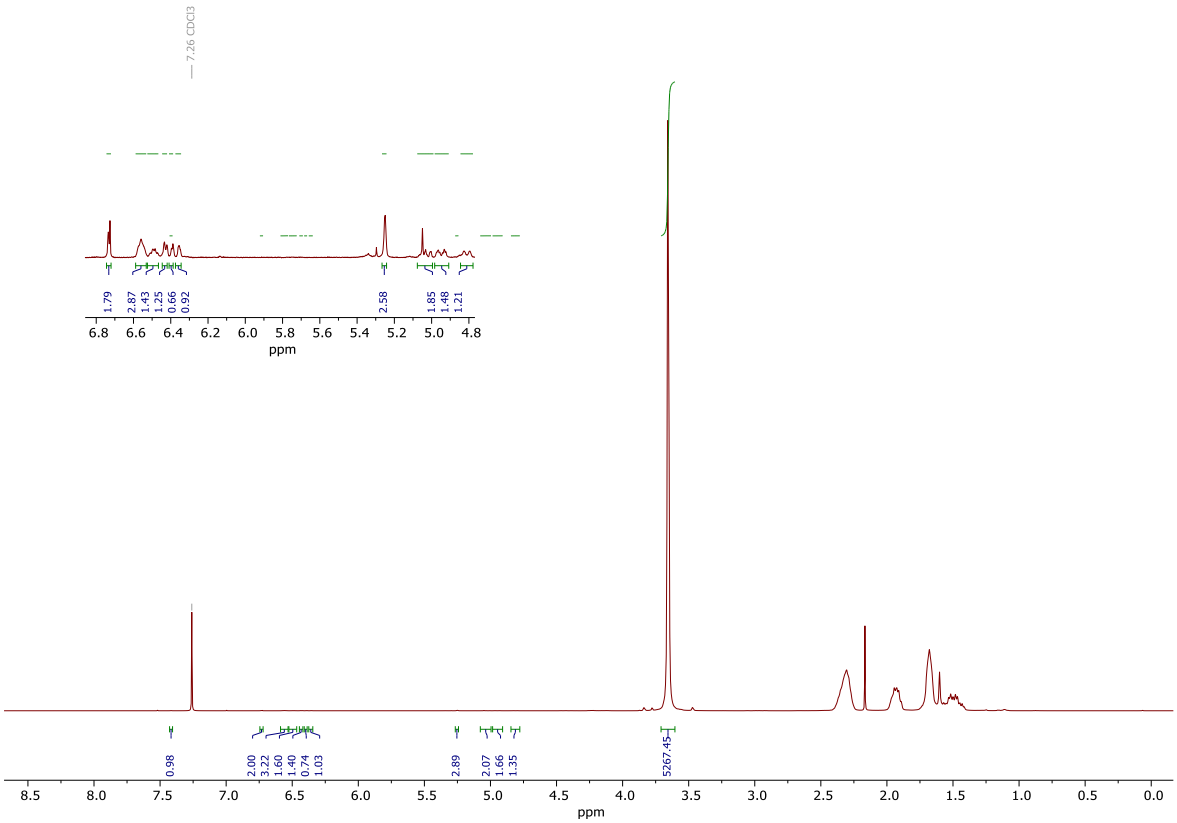
Spectrum 39. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of polymer **4c** after 240 min of sonication.

6.5.5 Post-sonication ^{1}H NMR of polymer 5c



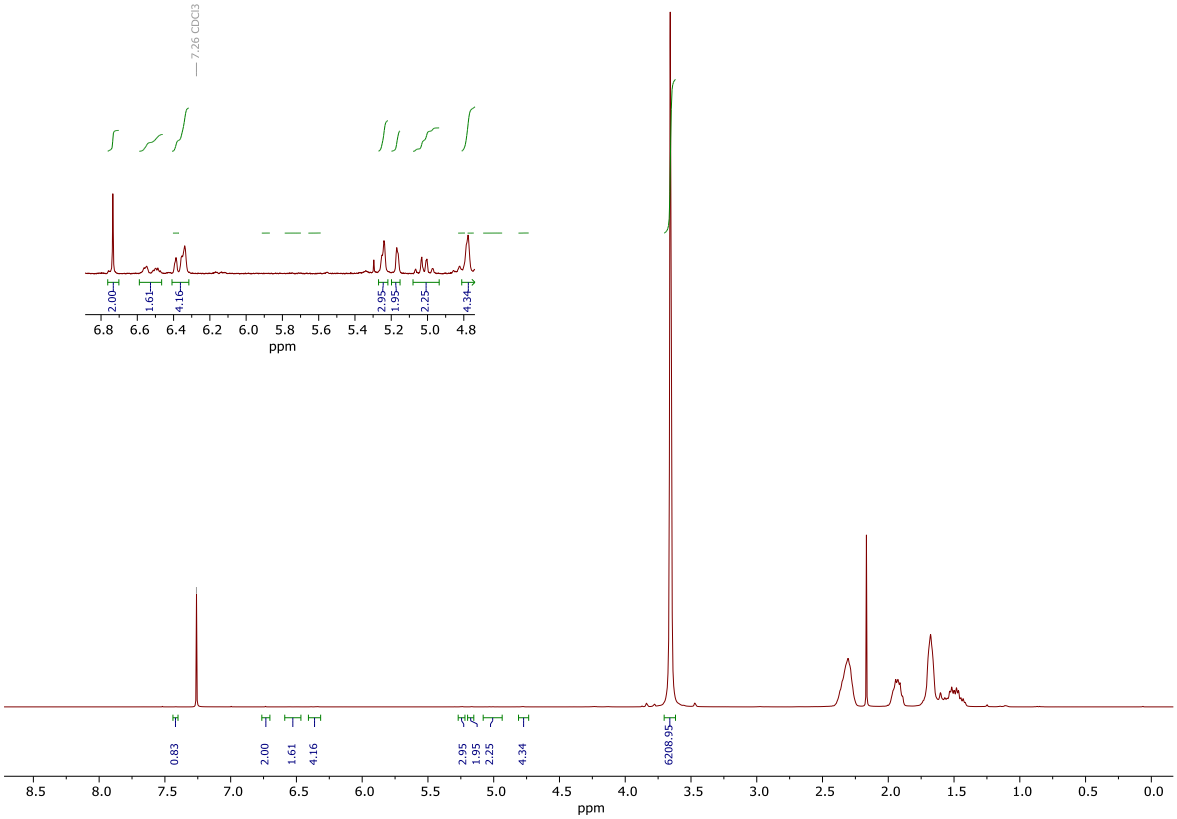
Spectrum 40. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of polymer **5c** after 240 min of sonication.

6.5.6 Post-sonication ^{1}H NMR of polymer 6c



Spectrum 41. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of polymer **6c** after 240 min of sonication.

6.5.7 Post-sonication ^{1}H NMR of polymer 7c



Spectrum 42. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of polymer **7c** after 240 min of sonication.

7 CoGEF Analysis

7.1 Analysis

CoGEF calculations were performed on Spartan '14 following Beyer's method.[S3] The structure of each mechanophore was built in Spartan '14 and minimized using molecular mechanics (MMFF). The distance between the methyl groups of each terminal pivaloyl ester was constrained and increased in increments of 0.05Å and the energy was minimized by molecular mechanics (MMFF) then DFT (B3LYP/6-31G*). The relative energy of each intermediate was determined by setting the energy of the initial state at 0 kJ/mol. Upon fragmentation all mechanophores cleave by retro-Diels-Alder. F_{max} values were determined from the slope of the final 40% of the energy/elongation curve (i.e. from 0.6 E_{max} to E_{max}). The enthalpic stretch is defined as the section of the elongation profile where ⍰d is repeatedly ≥0.001.

7.2 Structures

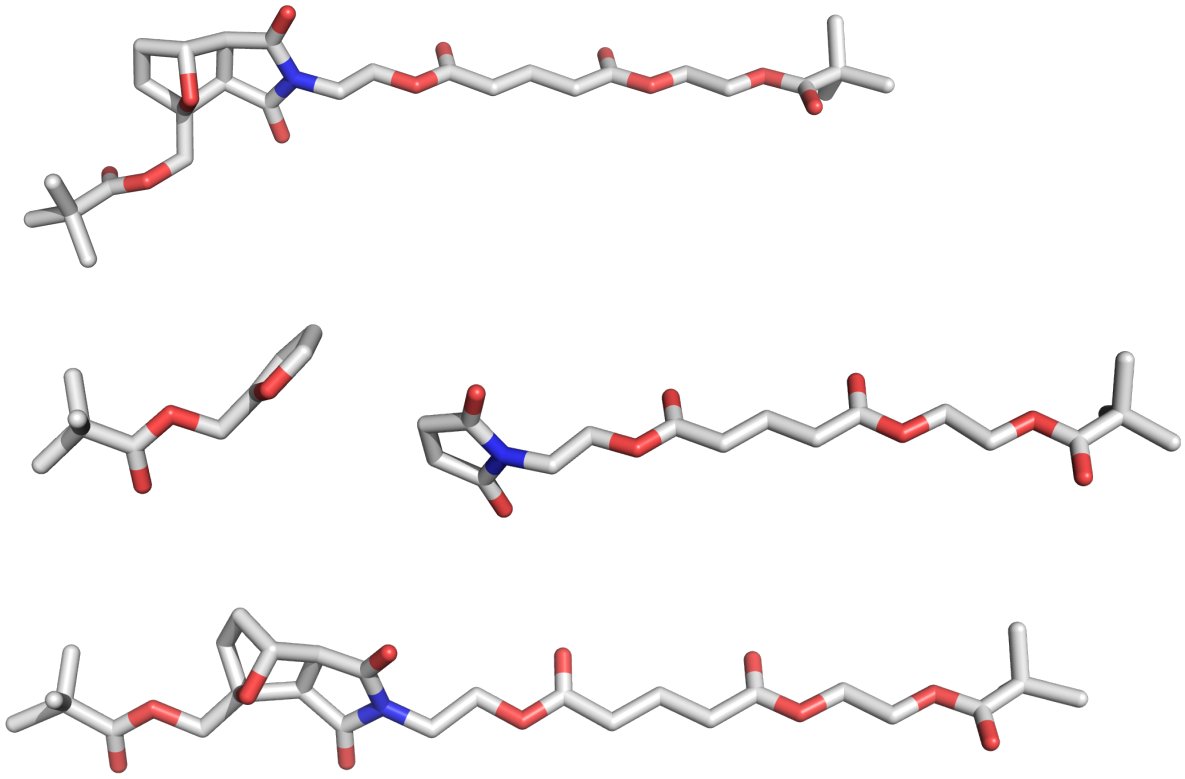


Figure S4. CoGEF structures of adduct **1a** at E_0 (top), E_{max} (middle), and after scission (bottom).

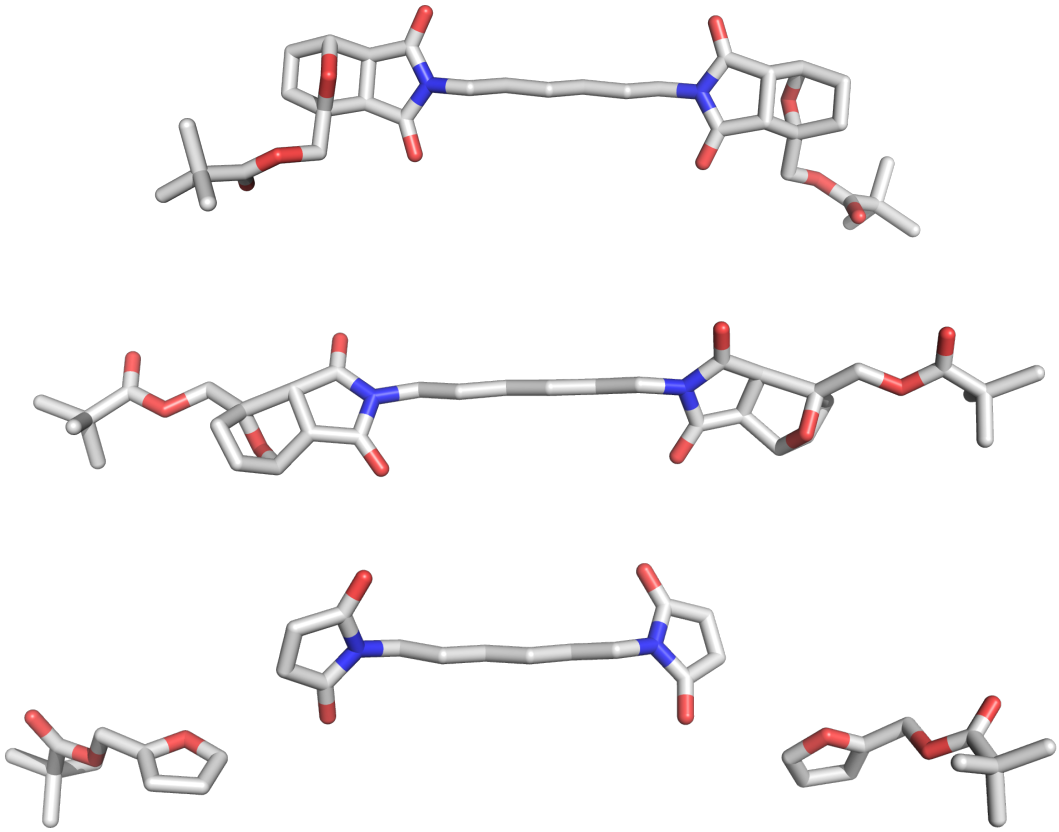


Figure S5. CoGEF structures of adduct **2a** at E_0 (top), E_{max} (middle), and after scission (bottom).

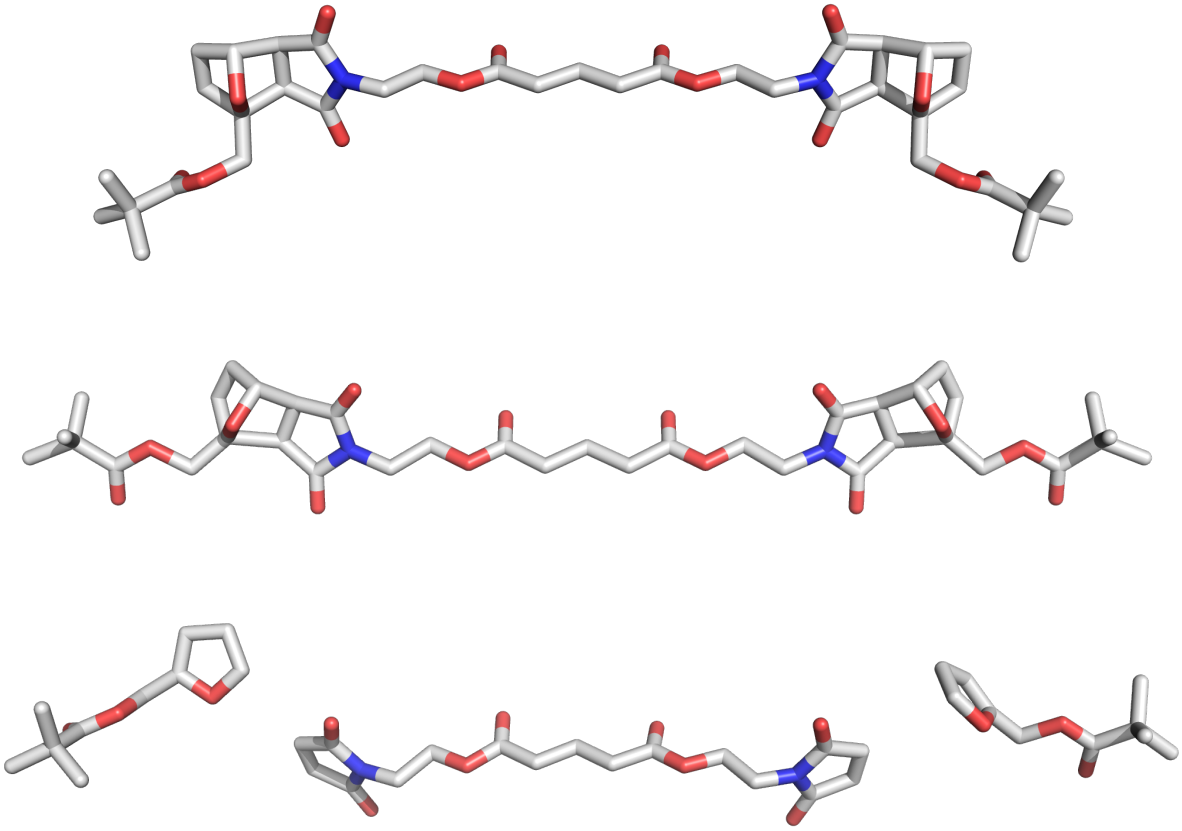


Figure S6. CoGEF structures of adduct **3a** at E_0 (top), E_{max} (middle), and after scission (bottom).

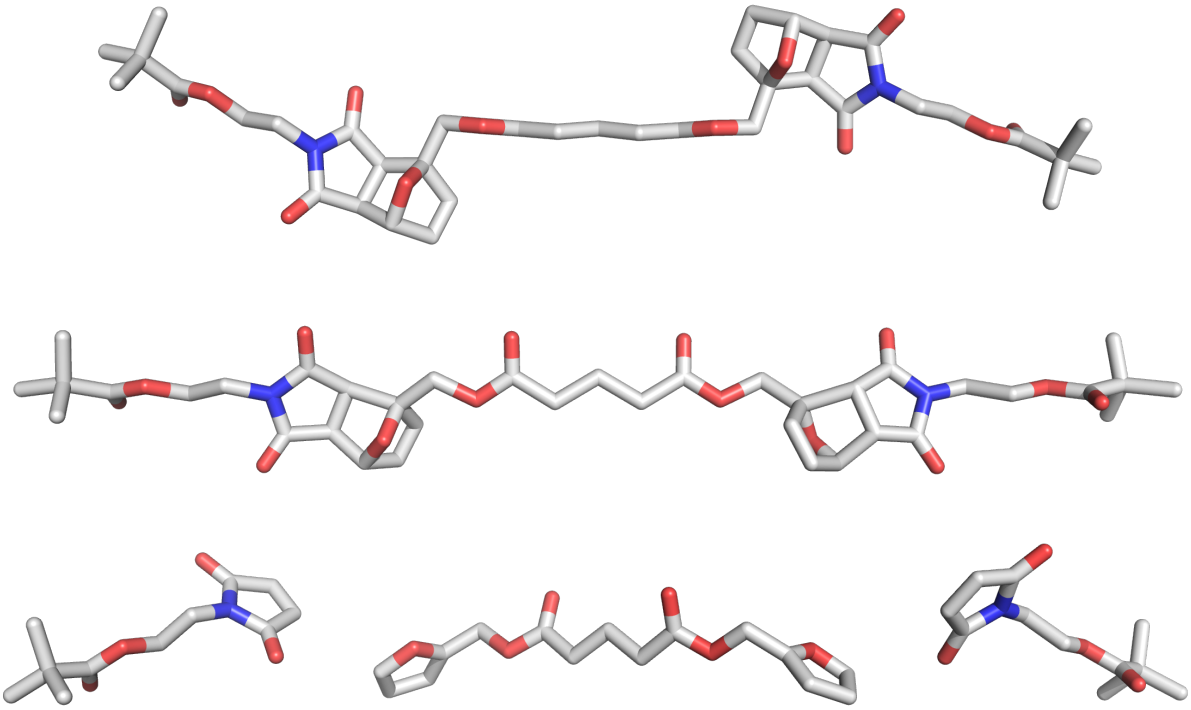


Figure S7. CoGEF structures of adduct **4a** at E_0 (top), E_{max} (middle), and after scission (bottom).

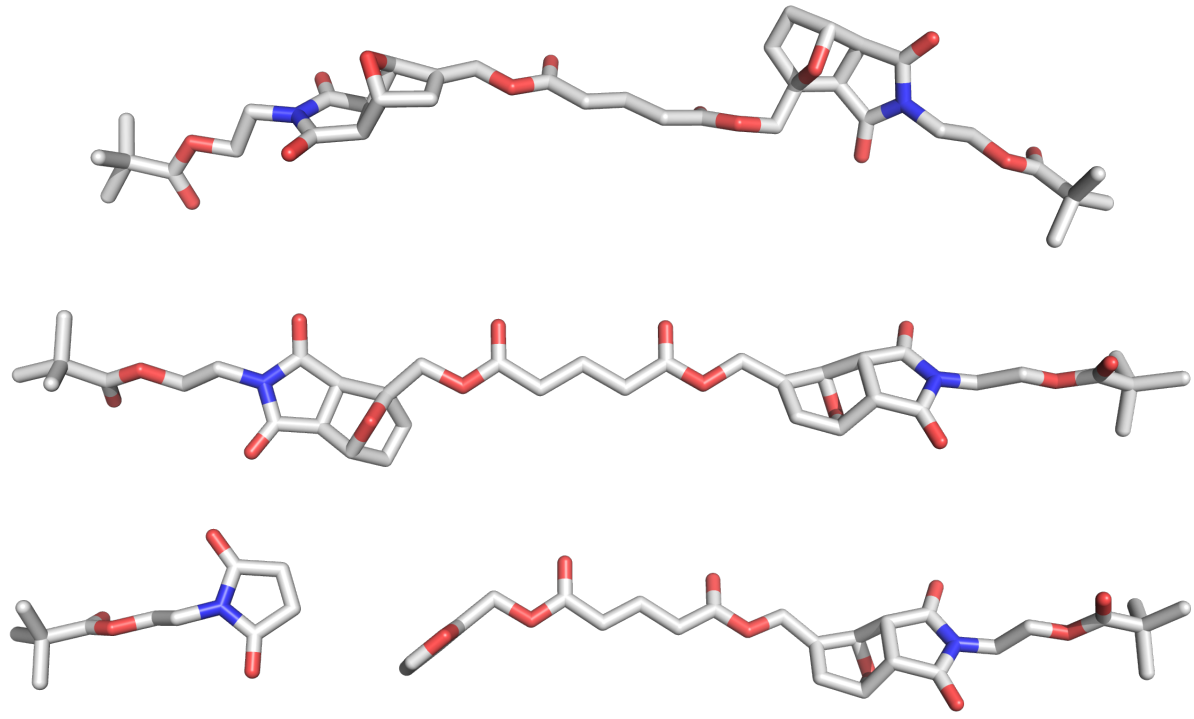


Figure S8. CoGEF structures of adduct **5a** at E_0 (top), E_{max} (middle), and after scission (bottom).

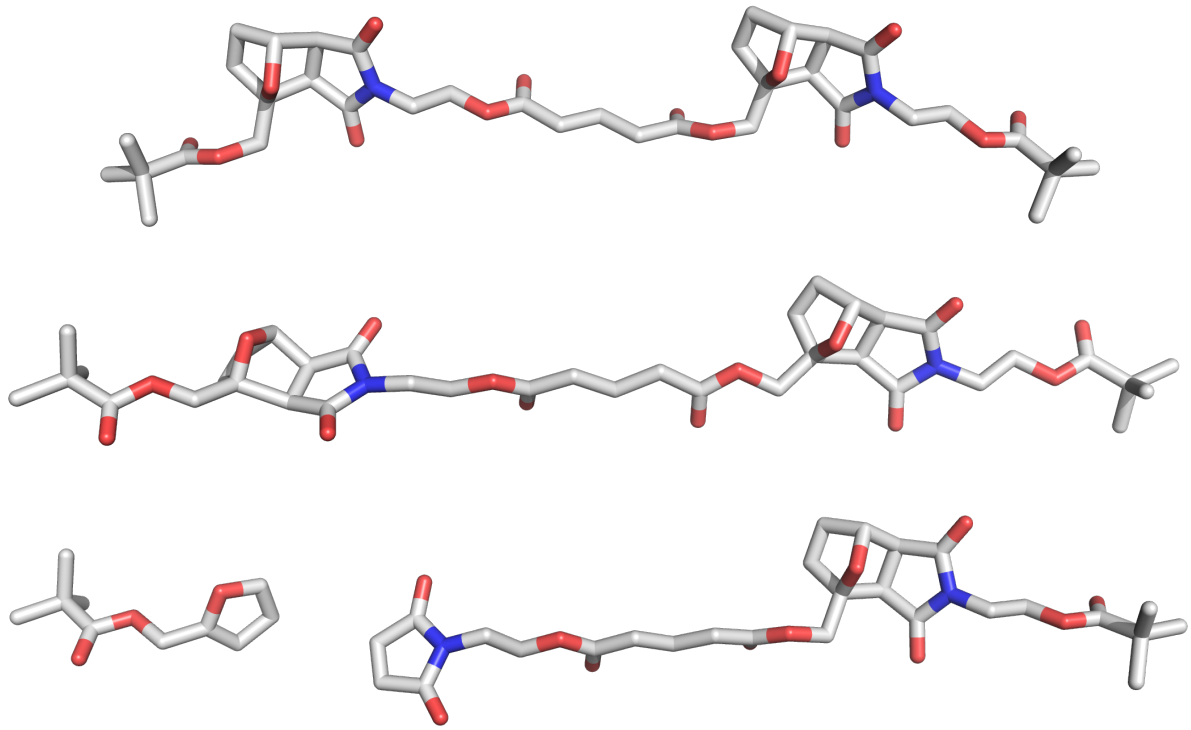


Figure S9. CoGEF structures of adduct **6a** at E_0 (top), E_{max} (middle), and after scission (bottom).

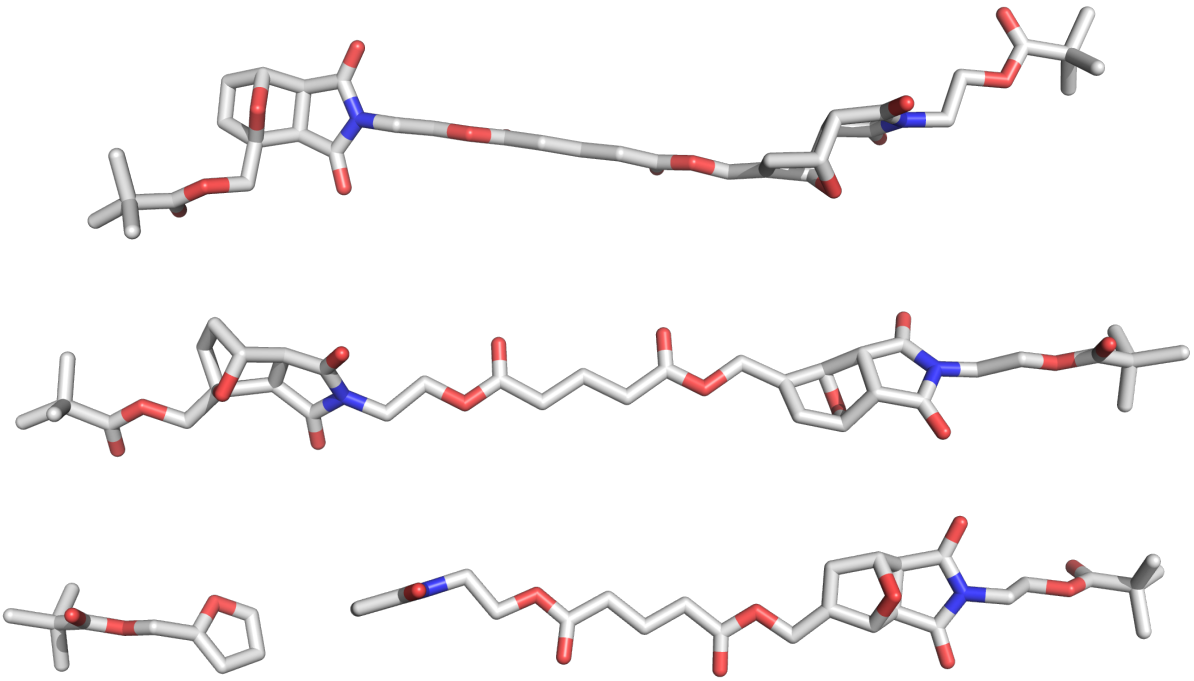


Figure S10. CoGEF structures of adduct **7a** at E_0 (top), E_{max} (middle), and after scission (bottom).

8 Statistical Analysis Data

Comparison of the elevations from the kinetic runs of polymers **1-7c** shows no clear correlation between rate of cleavage and structure of linked-mechanophores. Comparisons were made at the 95% confidence level. However, only one pair (**5c** vs **7c**) would be considered significantly different at the 90% confidence level that is not considered significantly different at 95%. This paring would have no overall effect on the conclusions drawn here.

Table S3. Pairwise comparison of elevations calculated using one-way ANOVA on Graphpad Prism. Listed are the pairwise comparisons as to whether elevation differences are considered statistically significant (Y) or not statistically significant (N). *P*-values are shown in parentheses and compared at the 95% confidence level.

	1c	**2c**	**3c**	**4c**	**5c**	**6c**	**7c**
1c	-	-	-	-	-	-	-
2c	N (0.9703)	-	-	-	-	-	-
3c	Y (0.0007)	Y (0.0138)	-	-	-	-	-
4c	Y (0.0136)	N (0.1551)	N (0.9710)	-	-	-	-
5c	N (0.9479)	N (>0.9999)	Y (0.0187)	N (0.1942)	-	-	-
6c	N (0.1455)	N (0.6788)	N (0.5053)	N (0.9750)	N (0.7475)	-	-
7c	N (0.9957)	N (>0.9999)	Y (0.0062)	N (0.0838)	N (>0.9999)	N (0.4953)	-

9 References

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(S2) Hickenboth, C. R.; Moore, J. S.; White, S. R.; Sottos, N. R.; Baudry, J.; Wilson, S. R. Biasing Reaction Pathways with Mechanical Force. *Nature* **2007**, *446* (7134), 423–427.

(S3) Beyer, M. The Mechanical Strength of a Covalent Bond Calculated by Density Functional Theory. *J. Chem. Phys.* **2000**, *112* (17), 7307–7312.