Electronic Supplementary Material (ESI) for Polymer Chemistry.

Synthesis and Characterization of Light-Degradable Bromocoumarin functionalized Polycarbonates

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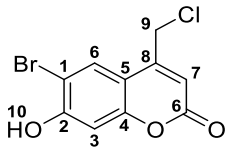
Supporting Information

Synthesis of compounds 2-5 (Scheme 1)

Synthesis of bromo-4-(chloromethyl)-7-hydroxycoumarin (2)

Compound **2** was synthesized according to the literature.[1] 4-Bromoresorcinol (**1**, 10.00 g, 52.9 mmol, 1 equiv.) was dissolved in methanesulfonic acid (80 mL). Methyl 4-chloroacetoacetate (9.20 mL, 79.4 mmol, 1.5 equiv.) was added and the solution was stirred for 2 h at room temperature. The reaction mixture was poured into ice-water (250 mL) and stirred for 30 min, before a white solid was obtained via filtration. The raw product was washed with ice-water (3x5 mL) and recrystallized from ethyl acetate/*n*-hexane (6: 7). A white solid (12.10 g, 41.9 mmol) was obtained (Yield: 79%).



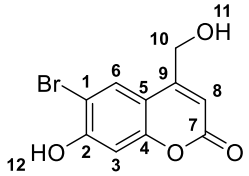
^{1}H-NMR (500 MHz, DMSO-*d*$_6$): δ(ppm)= 4.99 (s, 2 H, H^{9}), 6.47 (s, 1 H, H^{7}), 6.92 (s, 1 H, H^{3}), 7.99 (s, 1 H, H^{6}), 11.51 (s, 1 H, H^{10})

^{13}C-NMR (125 MHz, DMSO-*d*$_6$): δ(ppm)= 41.3 (s, 1 C, C^{9}), 103.4 (s, 1 C, C^{3}), 106.3 (s, 1 C, C^{1}), 110.8 (s, 1 C, C^{5}), 112.2 (s, 1 C, C^{7}), 129.2 (s, 1 C, C^{6}), 150.3 (s, 1 C, C^{4}), 154.2 (s, 1 C, C^{2}), 157.6 (s, 1 C, C^{8}), 159.8 (s, 1 C, C^{6})

Melting temperature (T_m)=250-255 °C

Synthesis of 6-bromo-7-hydroxymethylcoumarin (3)

Compound **3** was synthesized according to the literature.[1] **2** (6.10 g, 21.1 mmol) was suspended in water (1.5 L) and stirred for 11 d under reflux. After cooling to room temperature, the brown solid was filtered off to afford dark brown crystals (5.20 g, 19.2 mmol) (Yield: 99%).



^{1}H-NMR (500 MHz, DMSO-*d*$_6$): δ(ppm)= 4.69 (s, 2 H, H^{10}), 5,58 (b, 1 H, H^{11}), 6.27 (s, 1 H, H^{8}), 6.89 (s, 1 H, H^{3}), 7.83 (s, 1 H, H^{6}), 11.35 (s, 1 H, H^{12})

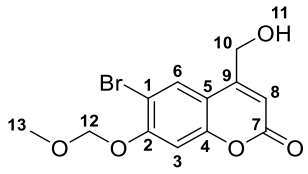
^{13}C-NMR (125 MHz, DMSO-*d*$_6$): δ(ppm)= 59.2 (s, 1 C, C^{10}), 103.2 (s, 1 C, C^{3}), 106.1 (s,

1 C, C^1), 107.8 (s, 1 C, C^8), 111.1 (s, 1 C, C^5), 128.3 (s, 1 C, C^6), 153.8 (s, 1 C, C^4), 156.1 (s, 1 C, C^9), 157.2 (s, 1 C, C^2), 160.2 (s, 1 C, C^7)

Melting temperature (T_m)=258-259 °C

Synthesis of 6-bromo-7-*O*-(methoxymethyl)-4-hydroxymethylcoumarin (4)

Compound **4** was synthesized according to the literature.[1] Under argon atmosphere **3** (4.70 g, 17.3 mmol, 1 equiv.) was dissolved in dry DCM (108 mL). DIPEA (3.32 mL, 19.1 mmol, 1.1 equiv.) was added at 0 °C as well as MOMCl (1.44 mL, 19.1 mmol, 1.1 equiv.). The reaction was conducted for 2 h at 0 °C. The brown suspension was mixed with 0.5 M citric acid (110 mL) and extracted three times with chloroform (3x100 mL). The combined organic layer was washed with brine (100 mL), dried over magnesium sulfate and the solvent was removed under reduced pressure. The crude product was stirred in *n*-hexane and filtered off to give a brown powder (5.16 g, 16.4 mmol) (Yield: 95 %).



^{1}H-NMR (500 MHz, DMSO-d_6): δ(ppm)= 3.42 (s, 3 H, H^{13}), 4.72 (dd, 2 H, $^3J_{HH}$=5.6 Hz, $^4J_{HH}$=1.3 Hz. H^{10}), 5.41 (s, 2 H, H^{12}), 5.64 (t, 1 H, $^3J_{HH}$=5.5 Hz, H^{11}), 6.36 (t, 1 H, $^4J_{HH}$=1.3 Hz, H^8), 7.24 (s, 1 H, H^3), 7.93 (s, 1 H, H^6)

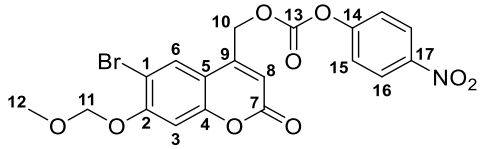
^{13}C-NMR (125 MHz, DMSO-d_6): δ(ppm)= 56.3 (s, 1 C, C^{13}), 59.2 (s, 1 C, C^{10}), 95.0 (s, 1 C, C^{12}), 103.6 (s, 1 C, C^3), 107.6 (s, 1 C, C^1), 109.1 (s, 1 C, C^8), 112.9 (s, 1 C, C^5), 128.3 (s, 1 C, C^6), 153.6 (s, 1 C, C^4), 155.3 (s, 1 C, C^2), 155.8 (s, 1 C, C^9), 160.0 (s, 1 C, C^7)

Decomposition temperature (T_D)=170-178 °C.

Synthesis of (6-bromo-7-(methoxymethoxy)-2-oxo-2H-chromen-4-yl)methyl-(4-nitrophenyl)carbonate (5)

Compound **5** was synthesized according to the literature.[2] Under argon atmosphere **4** (5.16 g, 16.4 mmol, 1 equiv.) and 4-nitrophenyl chloroformate (16.46 g, 81.9 mmol,

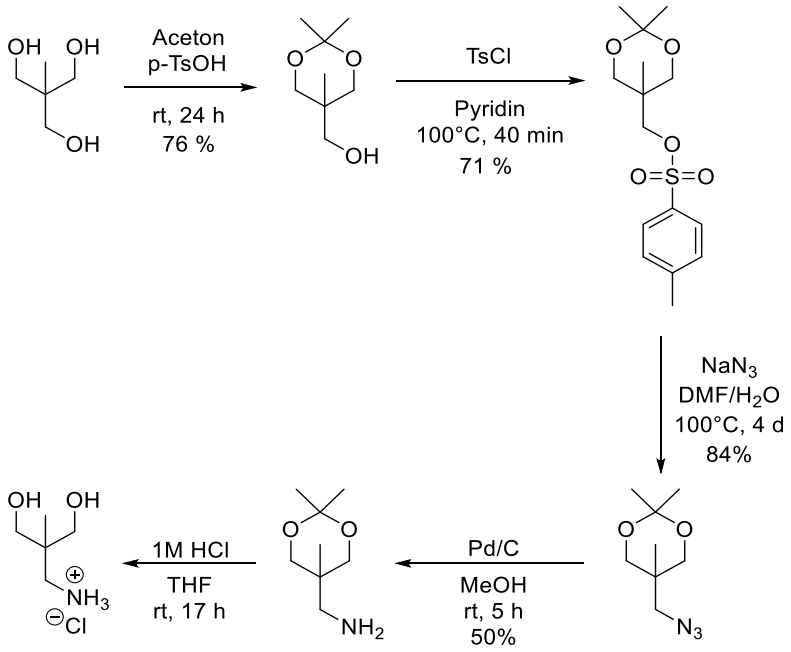
5 equiv.) were dissolved in dry DCM (160 mL). The reaction mixture was cooled to 0 °C before adding DIPEA (14.24 mL, 81.9 mmol, 5 equiv.) and then stirred for 3 h at room temperature. The resulting red solution was washed three times with 0.1 M hydrochloric acid (3x120 mL) and once with brine (160 mL). The solution was dried over magnesium sulfate, filtered off and the solvent was removed under reduced pressure. The crude product was recrystallized from diethyl ether/*n*-hexane and acetone, respectively, to give a white solid (6.76 g, 14.1 mmol) (Yield: 86%).



^{1}H-NMR (500 MHz, DMSO-*d*$_6$): δ(ppm)= 3.43 (s, 3 H, H^{12}), 5.44 (s, 2 H, H^{11}), 5.58 (d, 2 H, $^{4}J_{HH}$= 1.1 Hz, H^{10}), 6.49 (t, 1 H, $^{4}J_{HH}$=1.1 Hz, H^{8}), 7.29 (s, 1 H, H^{3}), 7.64 (d, 2 H, $^{3}J_{HH}$=9.3 Hz, H^{15}), 8.09 (s, 1 H, H^{6}), 8.34 (d, 2 H, $^{3}J_{HH}$=9.3 Hz, H^{16})

^{13}C-NMR (125 MHz, DMSO-*d*$_6$): δ(ppm)= 56.4 (s, 1 C, C^{12}), 65.8 (s, 1 C, C^{10}), 95.0 (s, 1 C, C^{11}), 103.8 (s, 1 C, C^{3}), 107.9 (s, 1 C, C^{1}), 111.9 (s, 1 C, C^{8}), 112.3 (s, 1 C, C^{5}), 122.7 (s, 2 C, C^{15}), 125.5 (s, 2 C, C^{16}), 128.9 (s, 1 C, C^{6}), 145.4 (s, 1 C, C^{17}), 148.0 (s, 1 C, C^{9}), 151.5 (s, 1 C, C^{13}), 153.9 (s, 1 C, C^{4}), 155.3 (s, 1 C, C^{14}), 155.7 (s, 1 C, C^{2}), 159.4 (s, 1 C, C^{7})

Decomposition temperature (T_D)=192-195 °C.



Scheme S1. Synthesis route of 3-(hydroxy)-2-(hydroxymethyl)-2-methylpropan-1-ammonium chloride (**8**)[3-6]

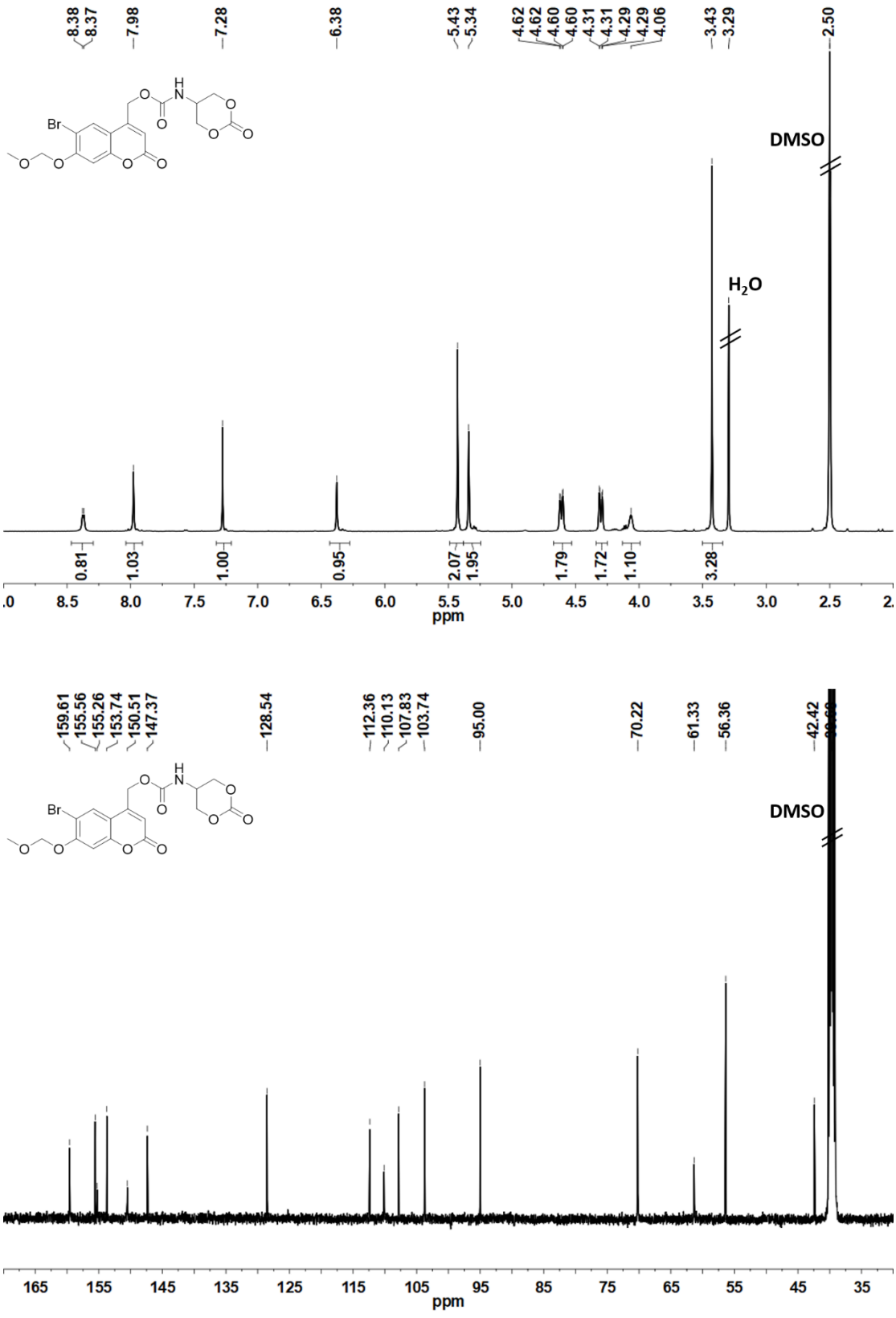


Figure S1. ^{1}H and ^{13}C NMR spectra of compound **7a**.

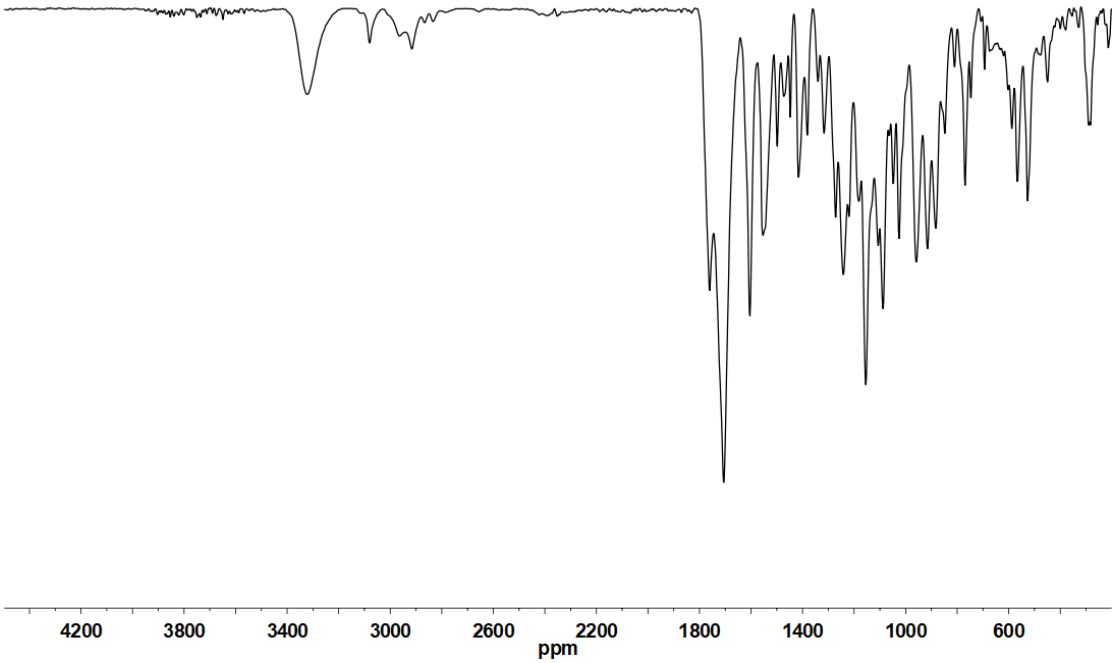


Figure S2. FTIR spectrum of compound **7a**.

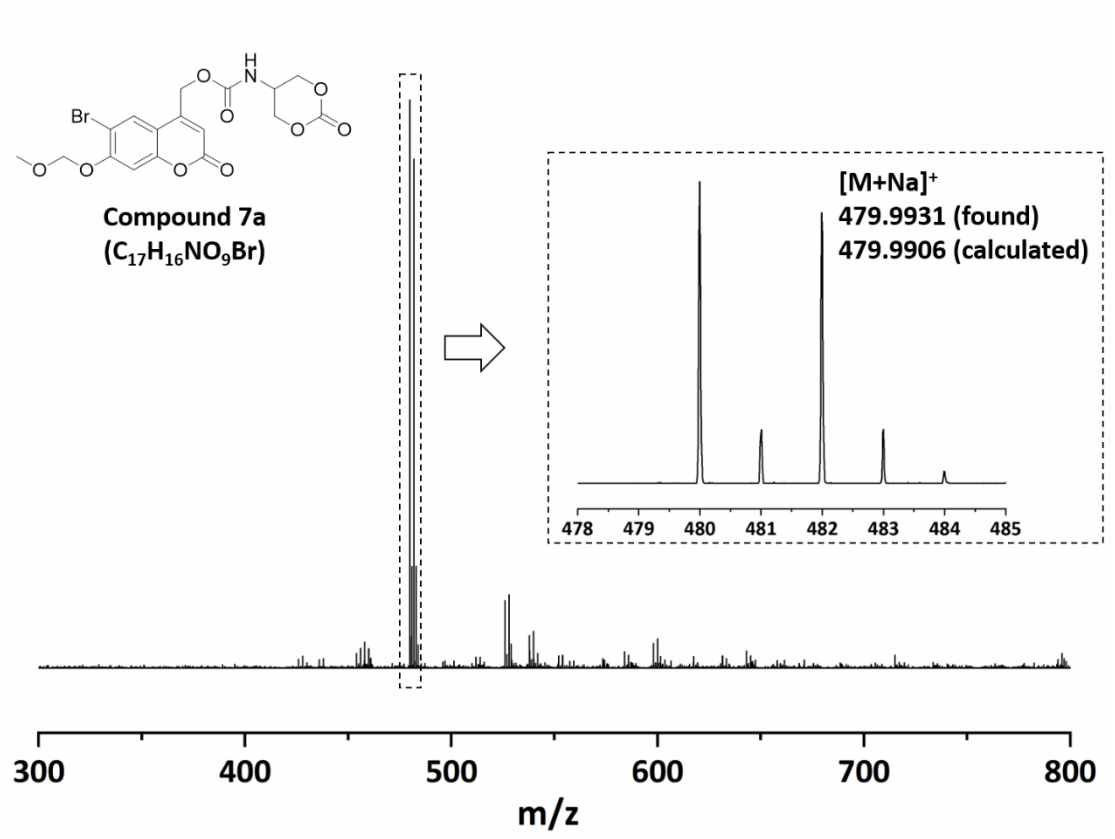


Figure S3. ESI-ToF mass spectrum of compound **7a**.

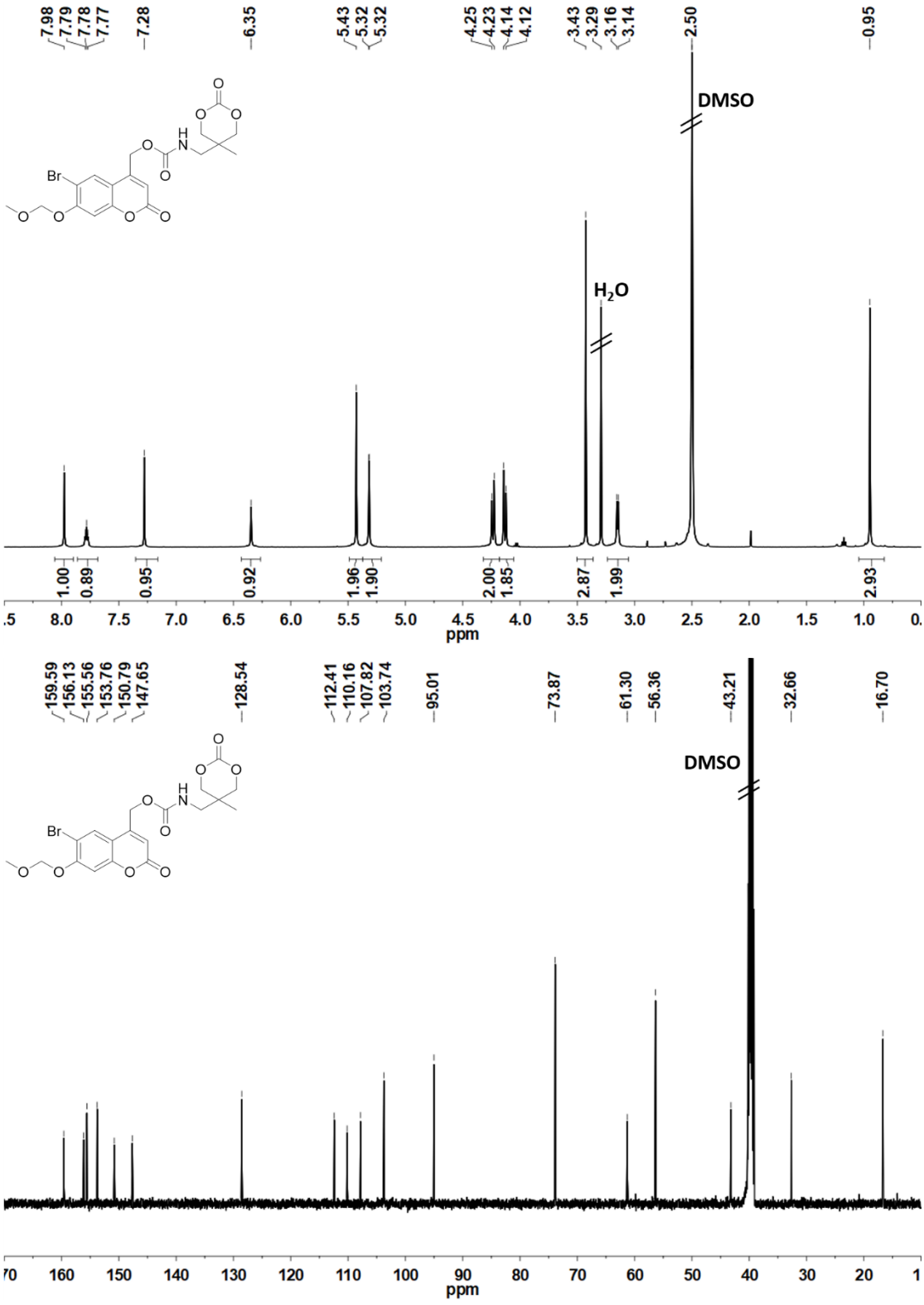


Figure S4. ^{1}H and ^{13}C NMR spectra of compound **7b**.

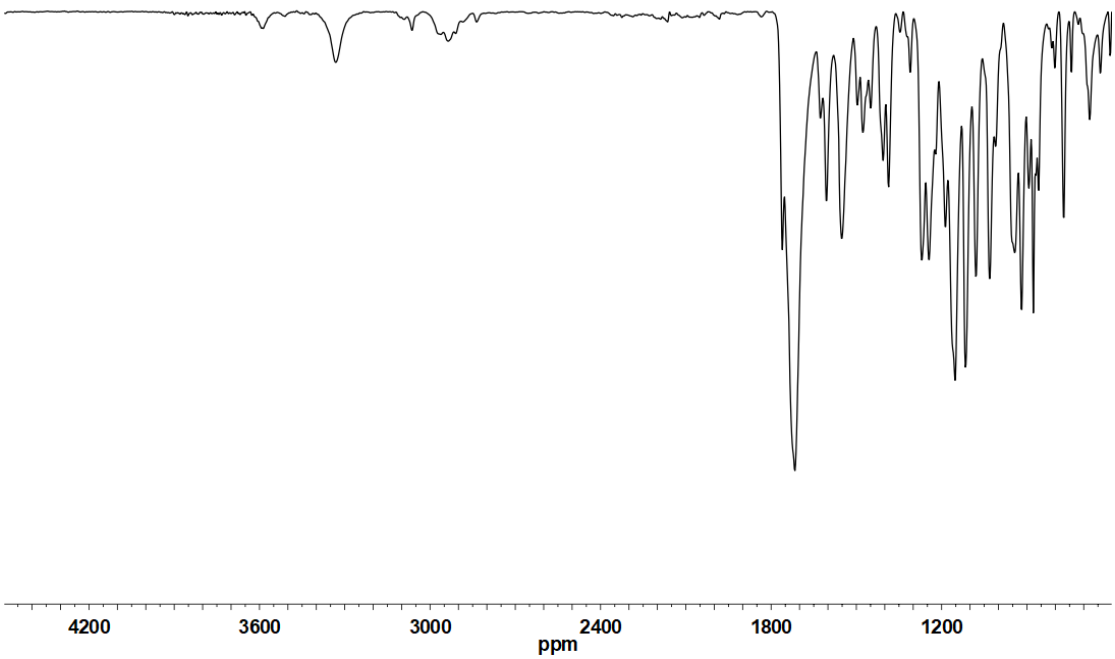


Figure S5. FTIR spectrum of compound **7b**.

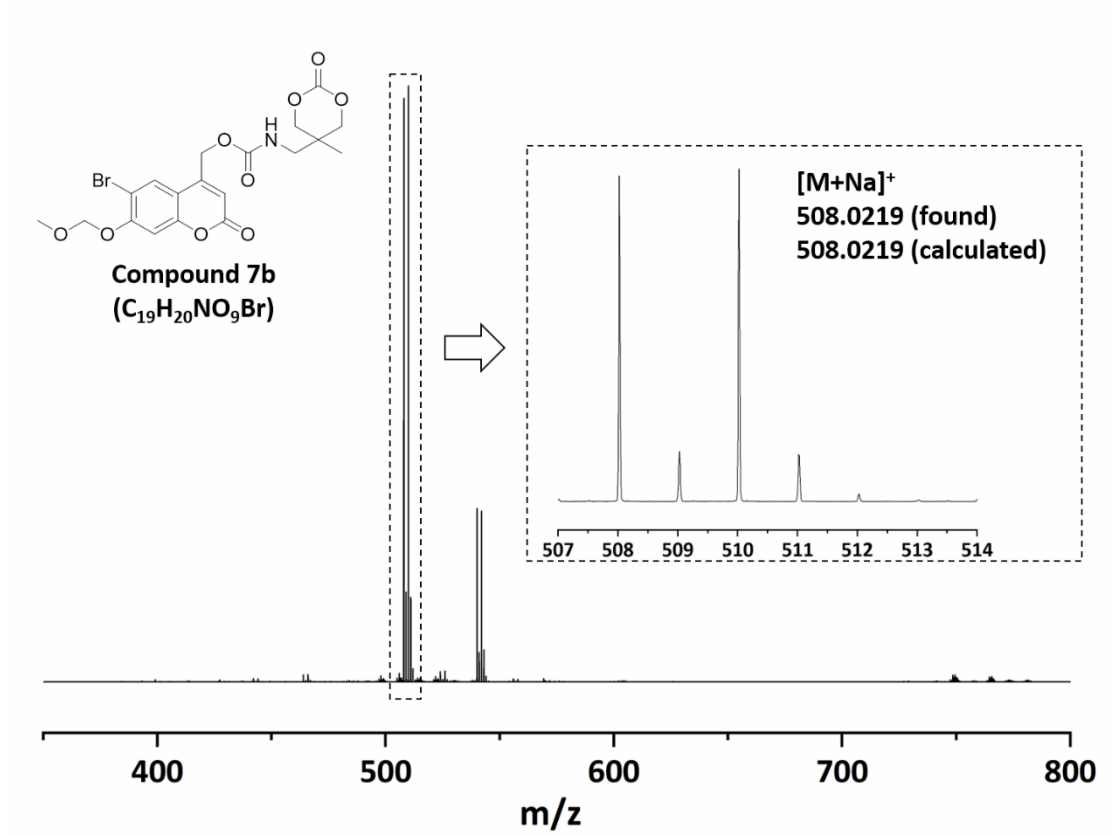
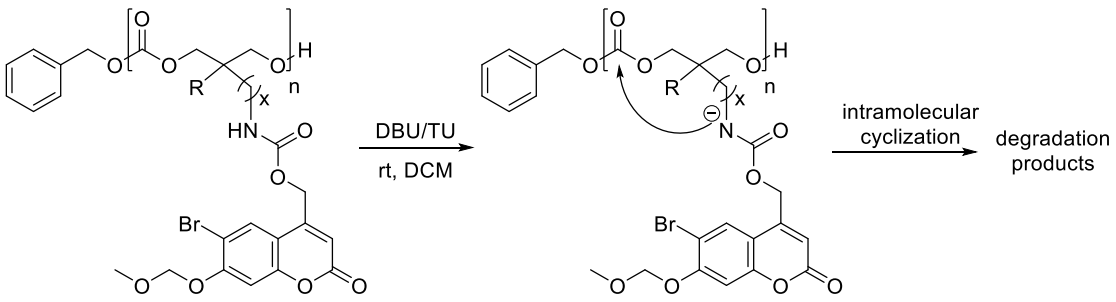
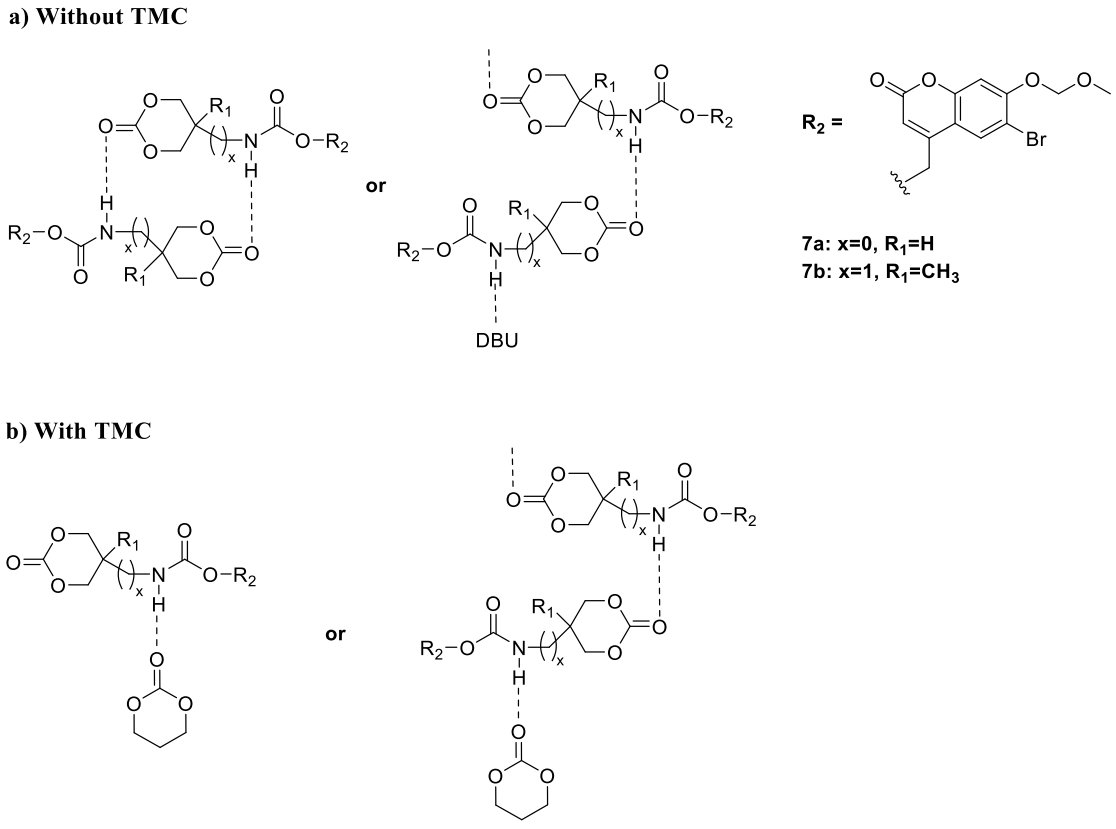


Figure S6. ESI-ToF mass spectrum of compound **7b**.



CouPC1: x=0, R=H
CouPC2: x=1, R=CH_3

Scheme S2. Possible mechanism of the DBU-catalyzed intramolecular transcarbamation of homopolymers.



Scheme S3. Possible intermolecular hydrogen bonding between carbamate containing cyclic carbonates and DBU without (a) or with (b) TMC

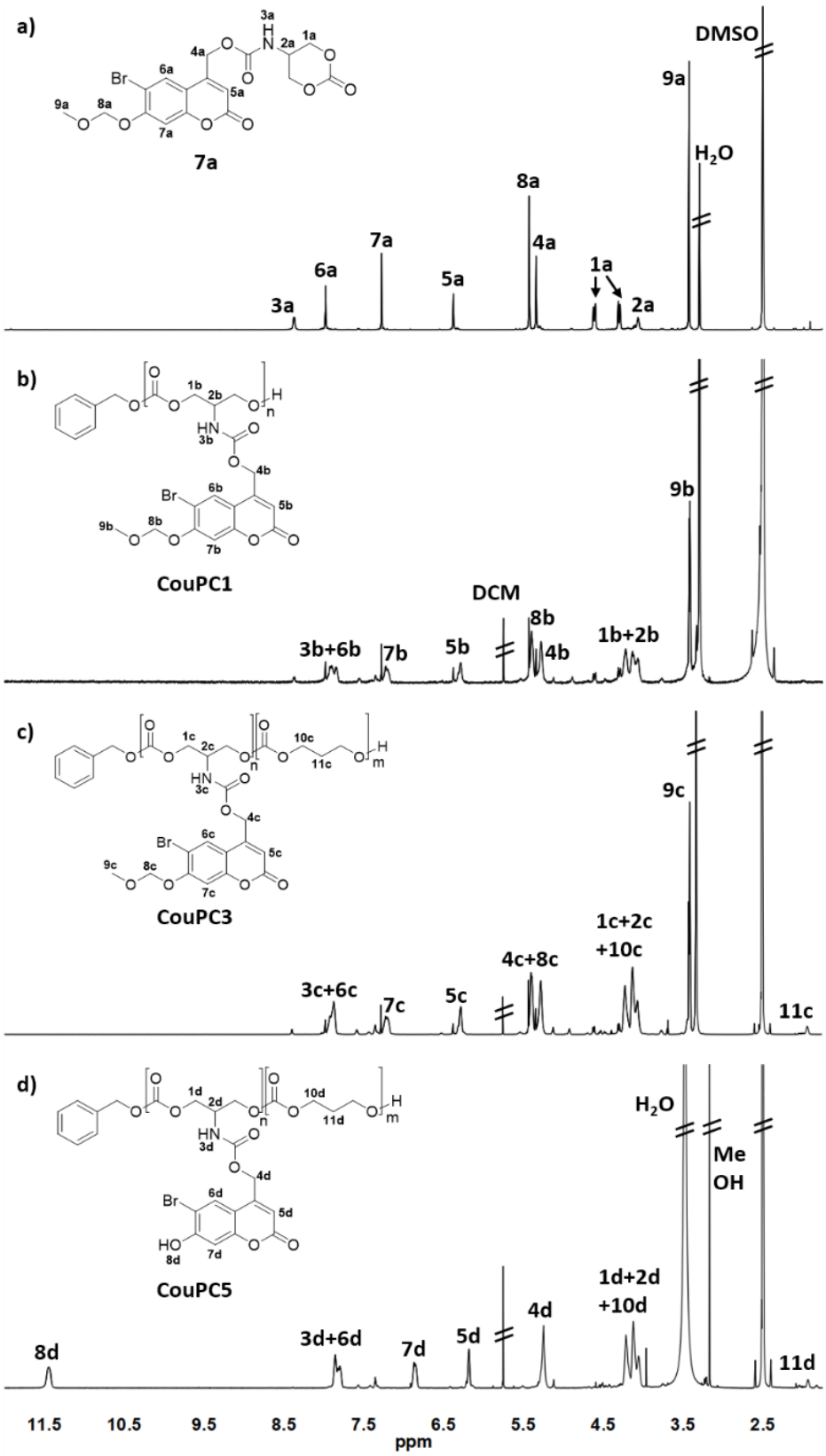


Figure S7. ^{1}H NMR spectra of monomer **7a**, homopolymer **CouPC1** and copolymers **CouPC3** and **CouPC5**.

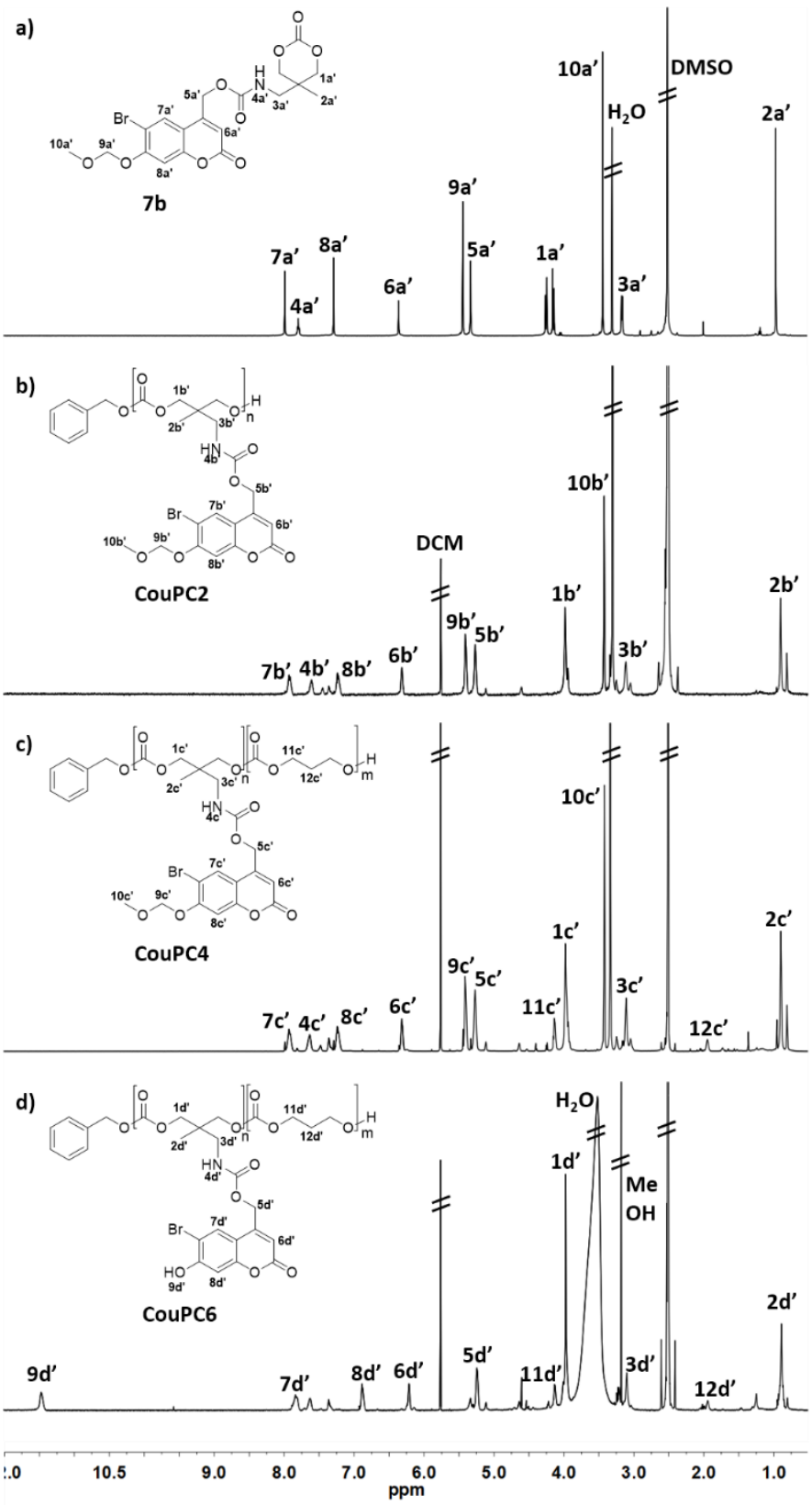


Figure S8. ^{1}H NMR spectra of monomer **7b**, homopolymer **CouPC2** and copolymers **CouPC4** and **CouPC6**.

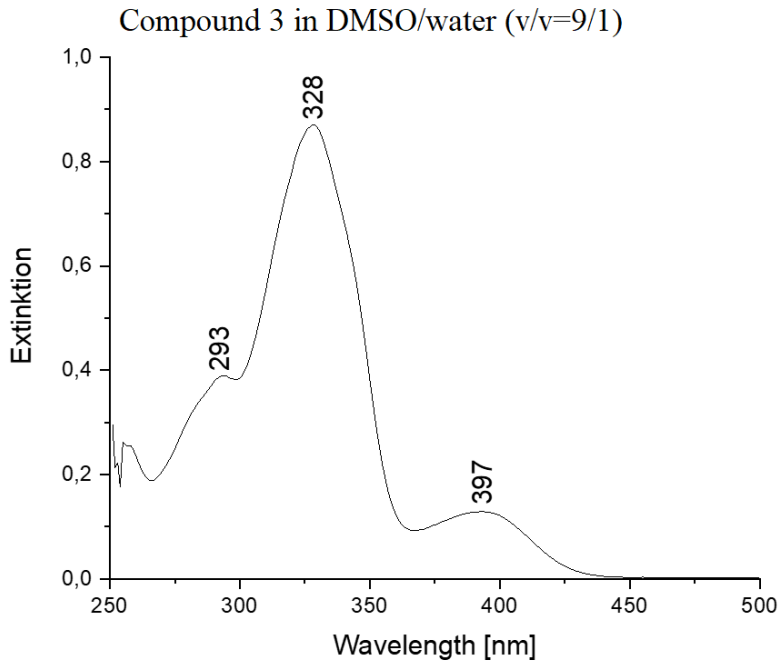


Figure S9. UV/vis spectrum of compound **3** in DMSO/H_2O (v/v=9/1).

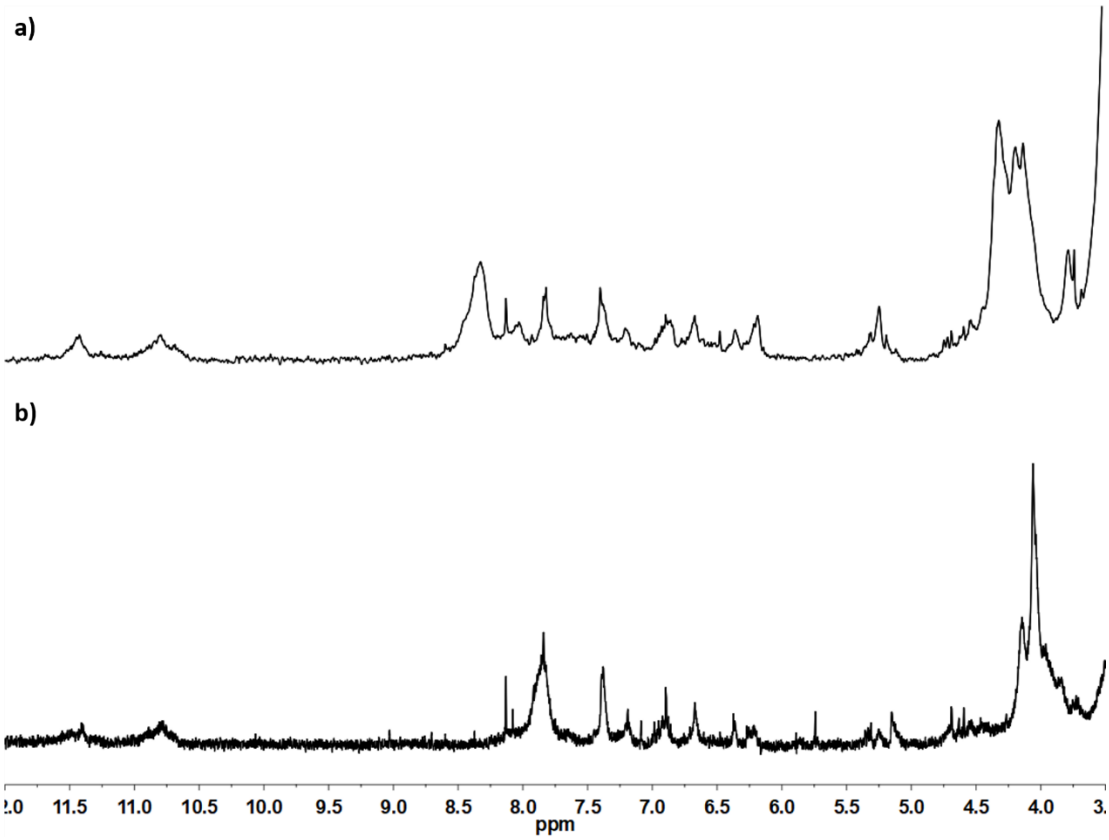


Figure S10. NMR spectra of **CouPC5** (a) and **CouPC6** (b) in DMSO-d_6 after irradiation.

- **Additional NMR, IR and ESI-ToF-MS spectra of small molecules and polymers**

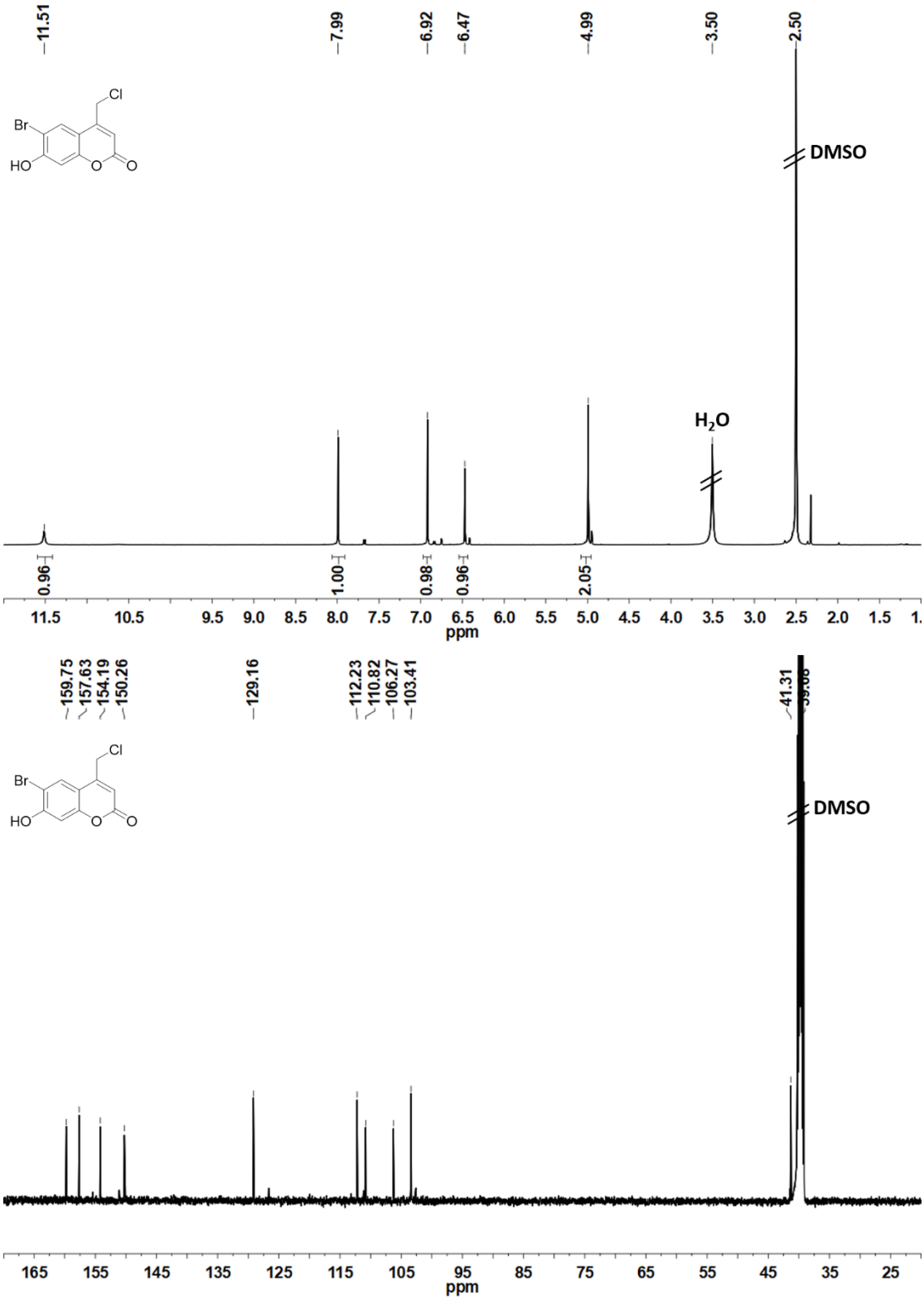


Figure S11. ^{1}H and ^{13}C NMR spectra of compound **2**.

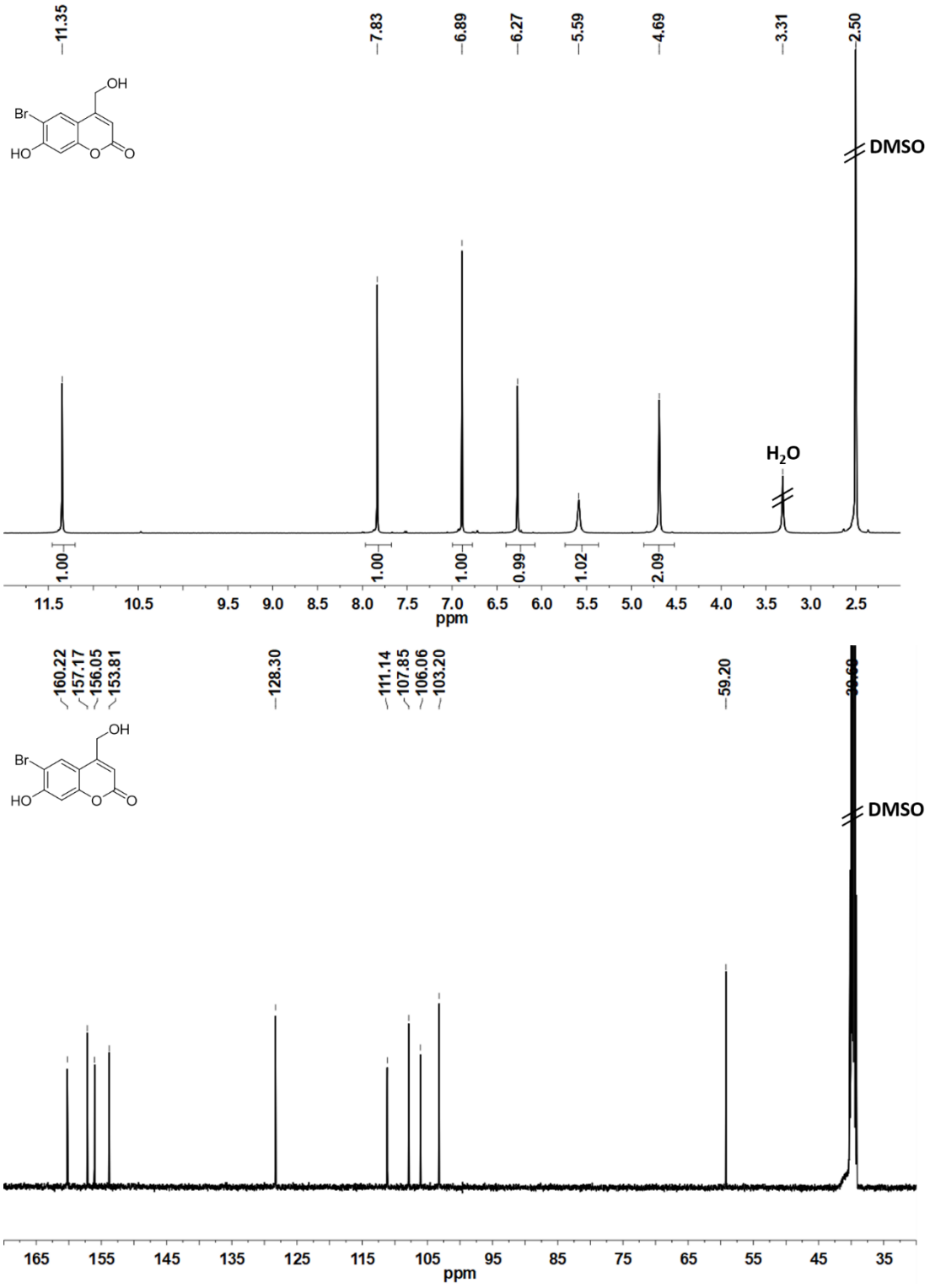


Figure S12. ^{1}H and ^{13}C NMR spectra of compound **3**.

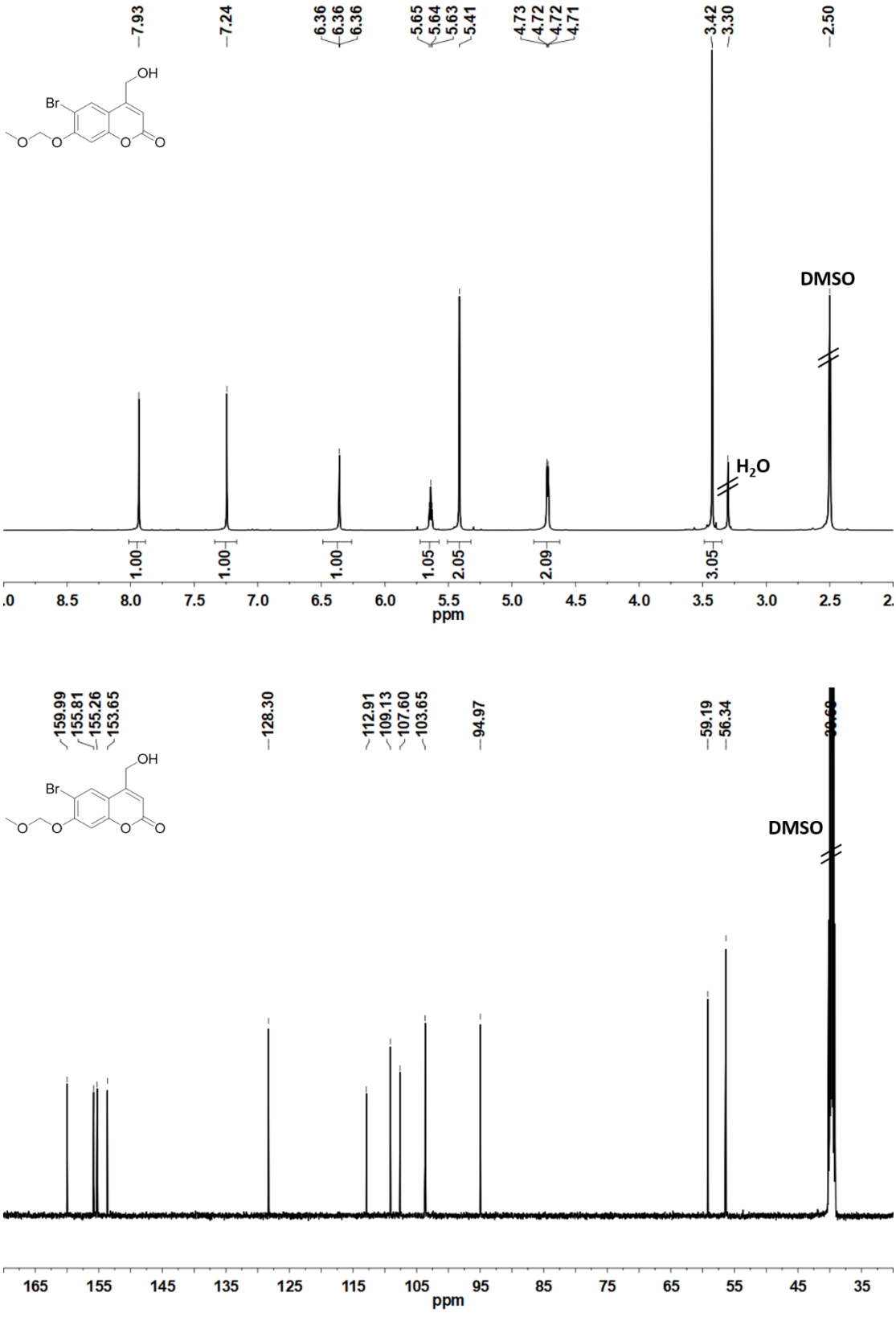


Figure S13. ^{1}H and ^{13}C NMR spectra of compound **4**.

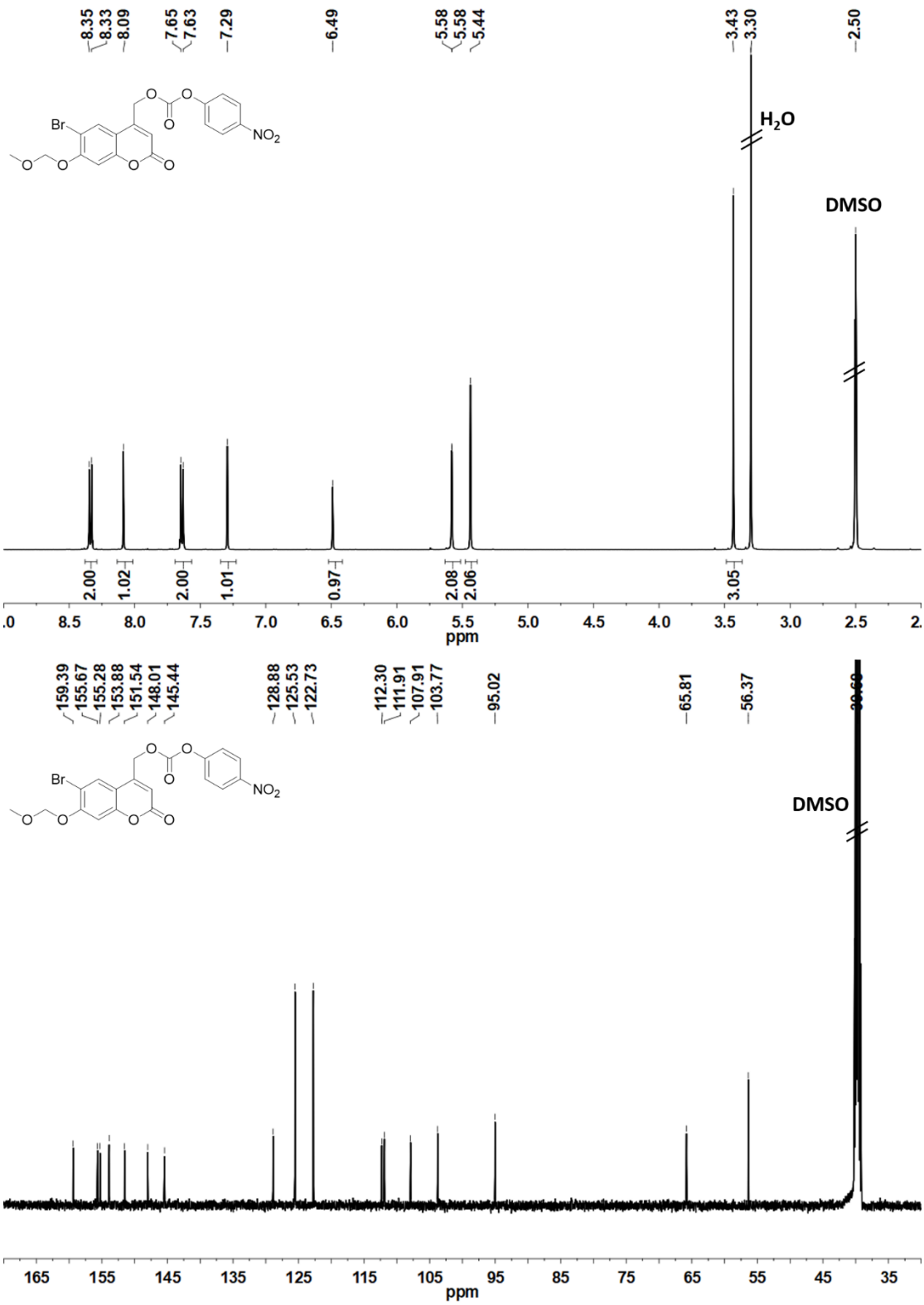


Figure S14. ^{1}H and ^{13}C NMR spectra of compound **5**.

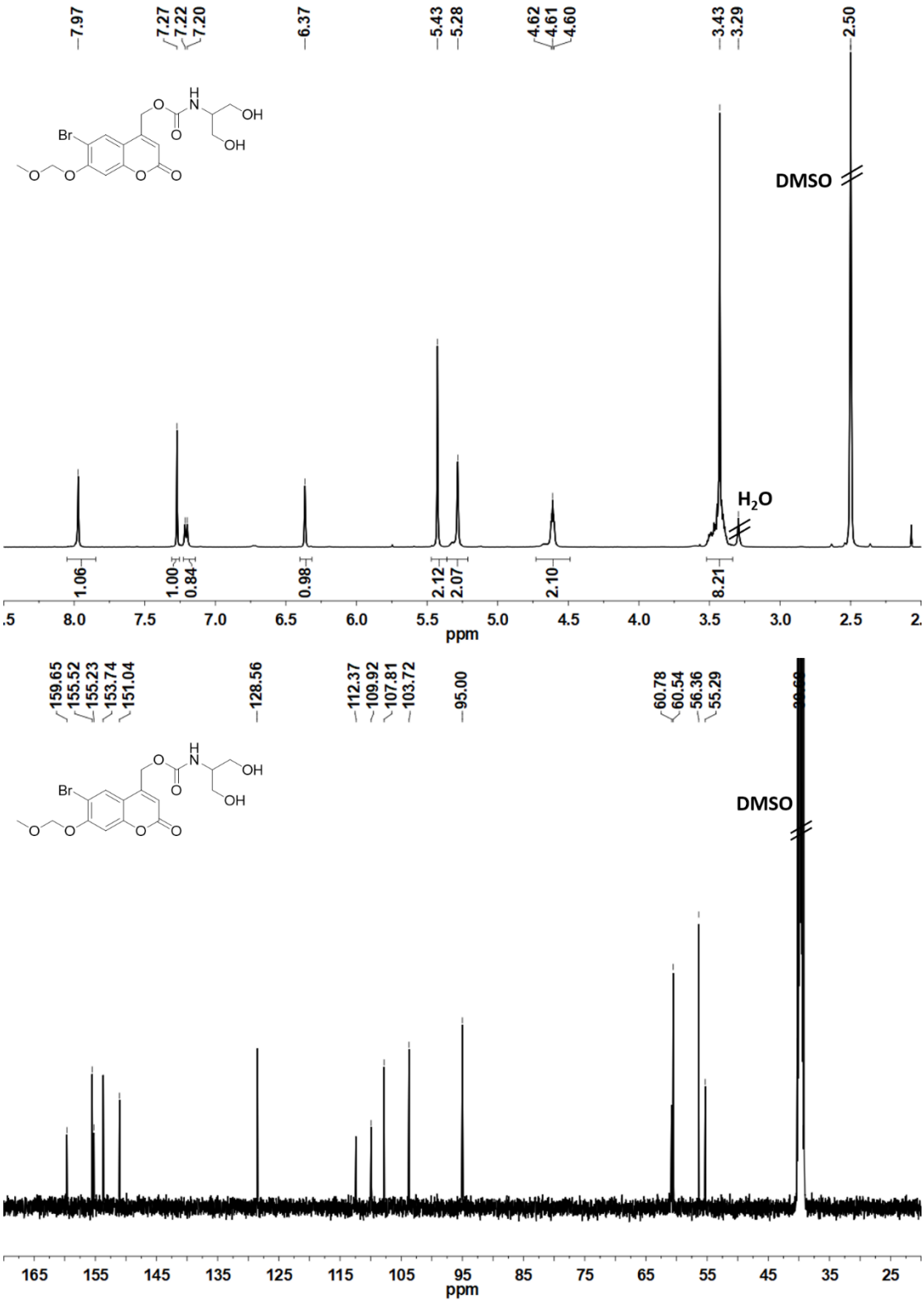


Figure S15. ^{1}H and ^{13}C NMR spectra of compound **6a**.

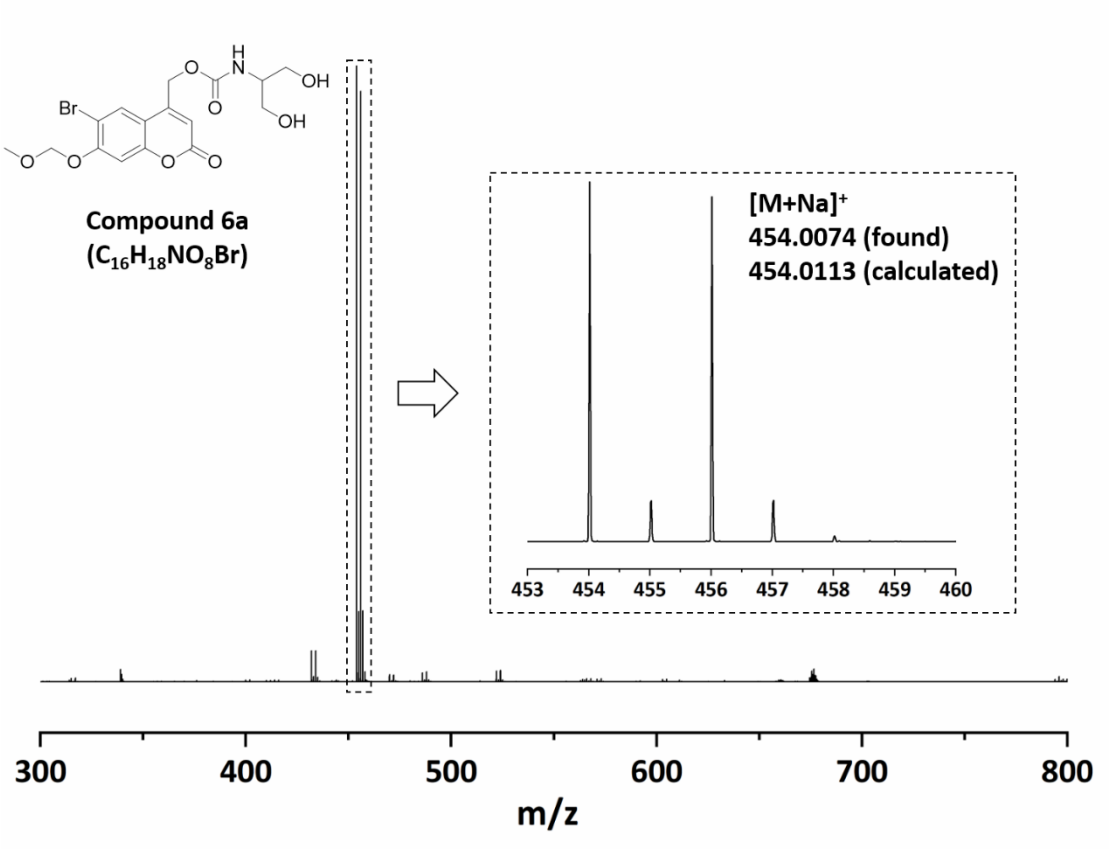


Figure S16. ESI-ToF mass spectrum of compound **6a**.

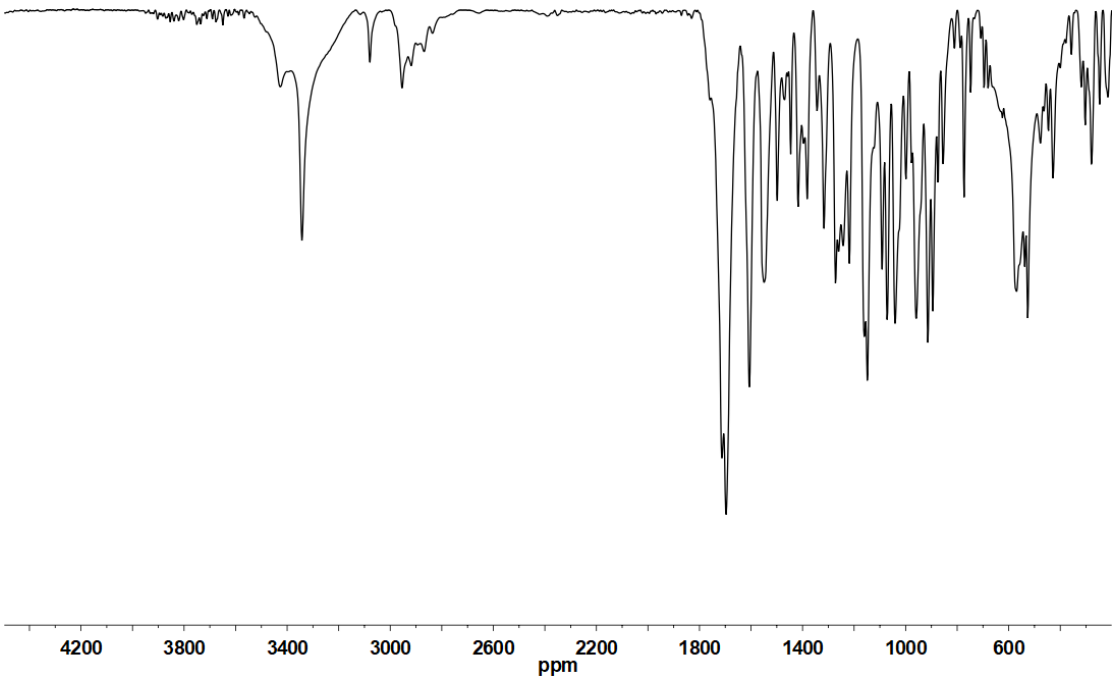


Figure S17. FTIR spectrum of compound **6a**.

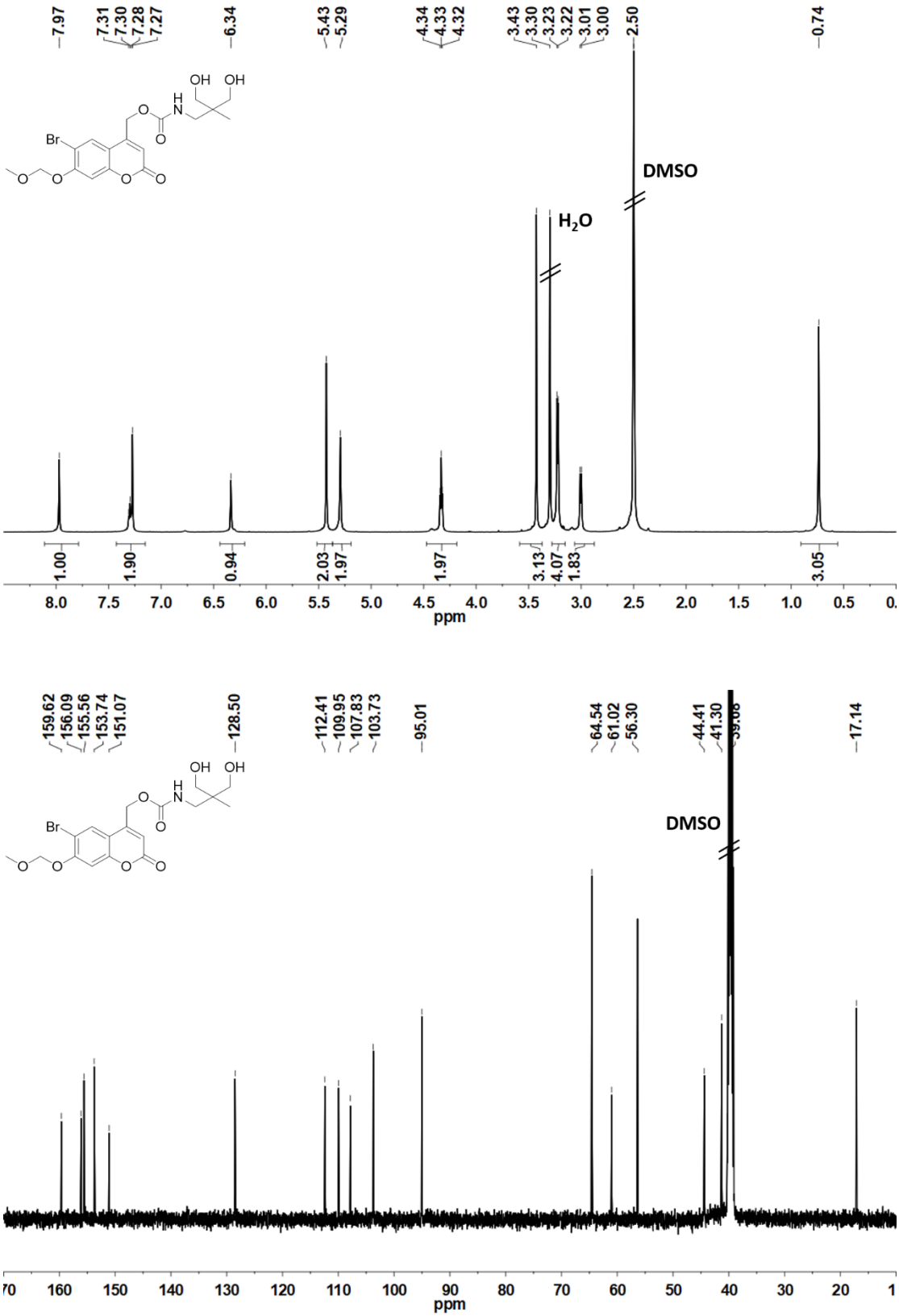


Figure S18. ^{1}H and ^{13}C NMR spectra of compound **6b**.

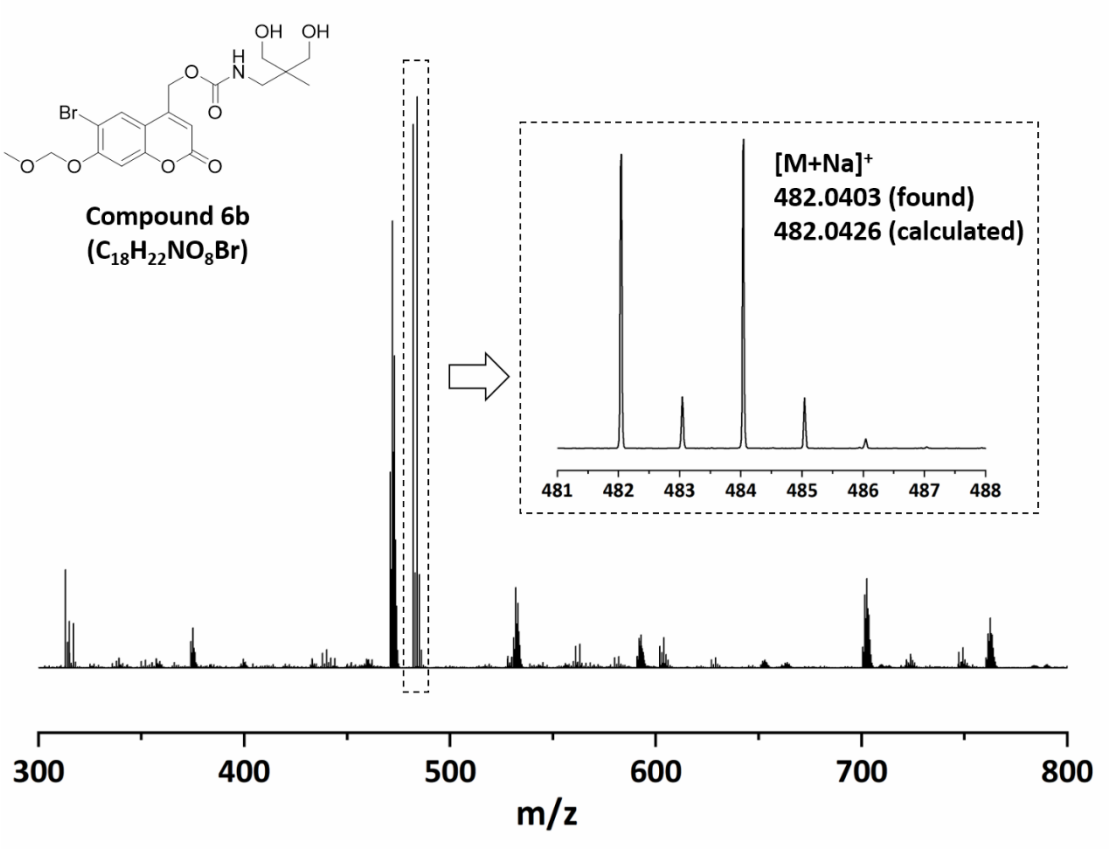


Figure S19. ESI-ToF mass spectrum of compound **6b**.

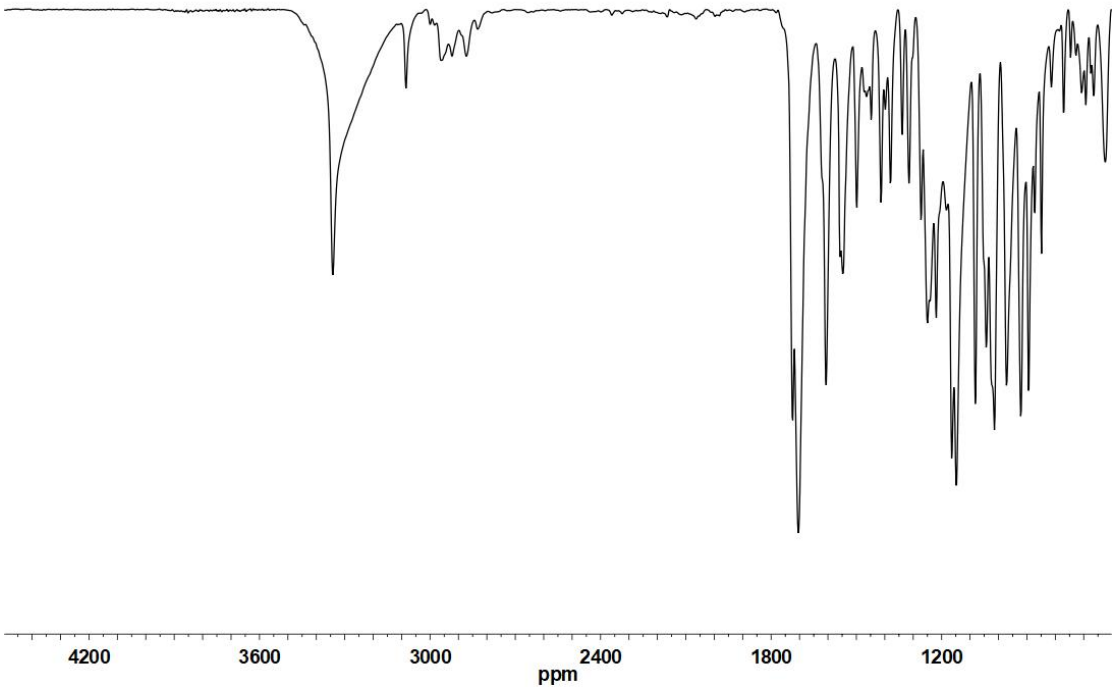


Figure S20. FTIR spectrum of compound **6b**.

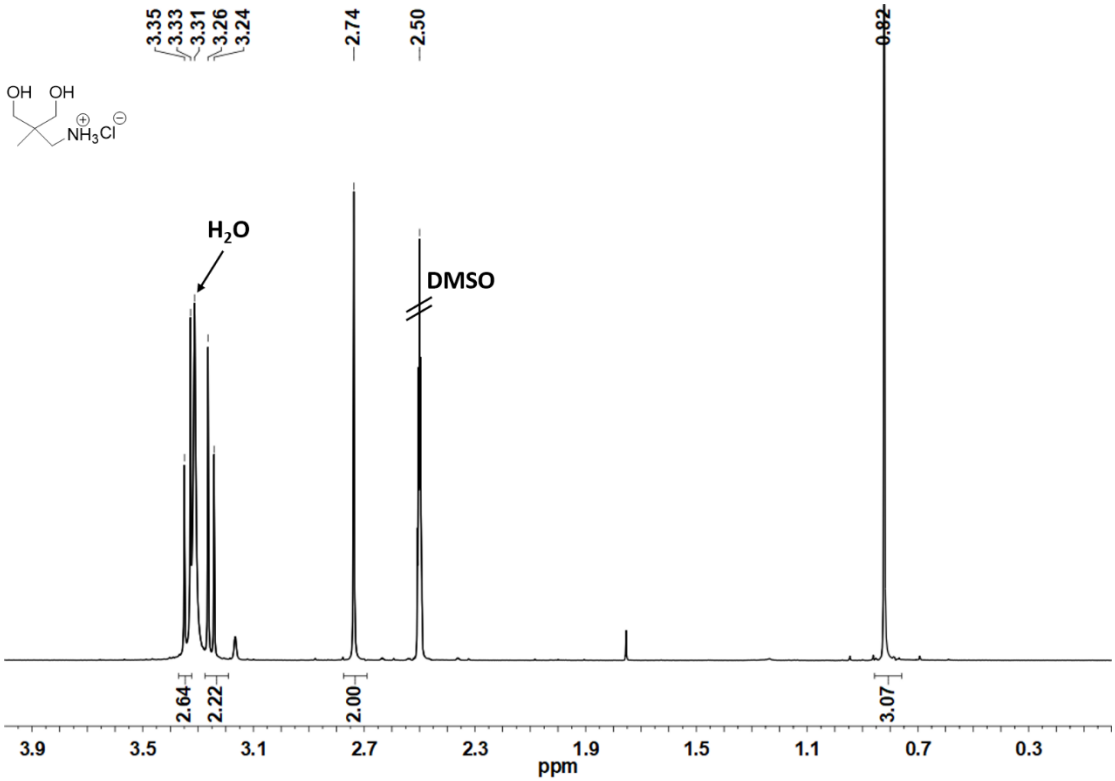


Figure S21. [1]H-NMR spectrum of compound **8**.

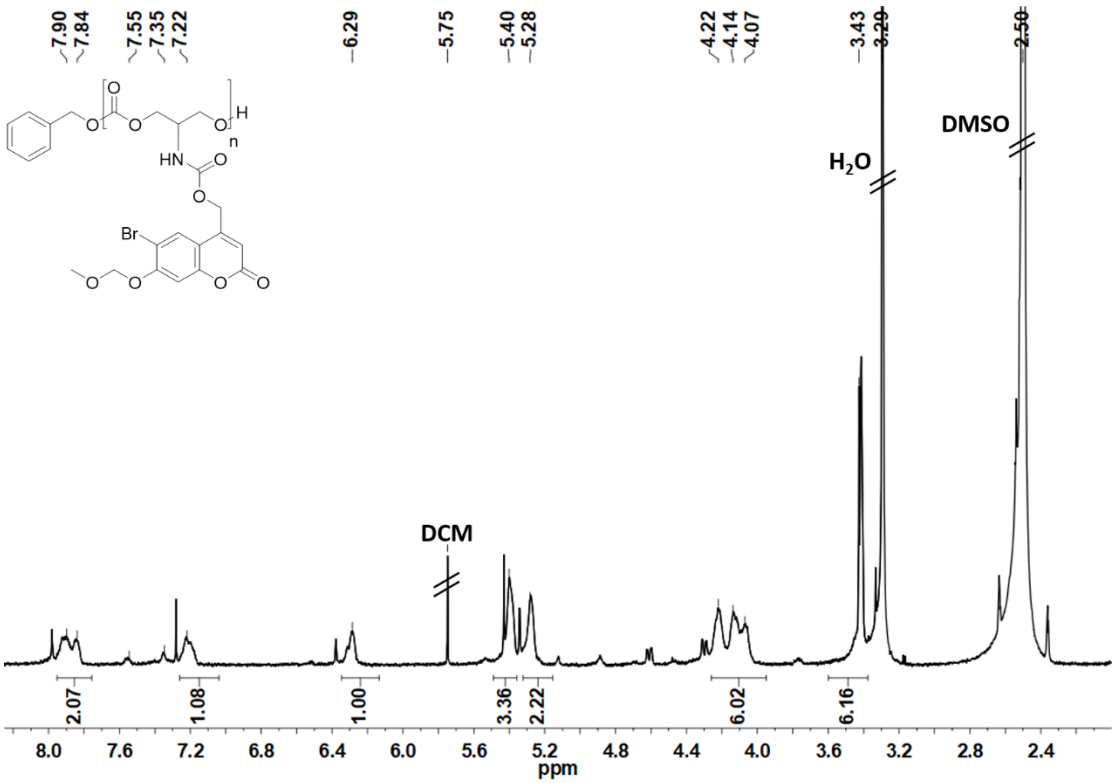


Figure S22. [1]H-NMR spectrum of **CouPC1**.

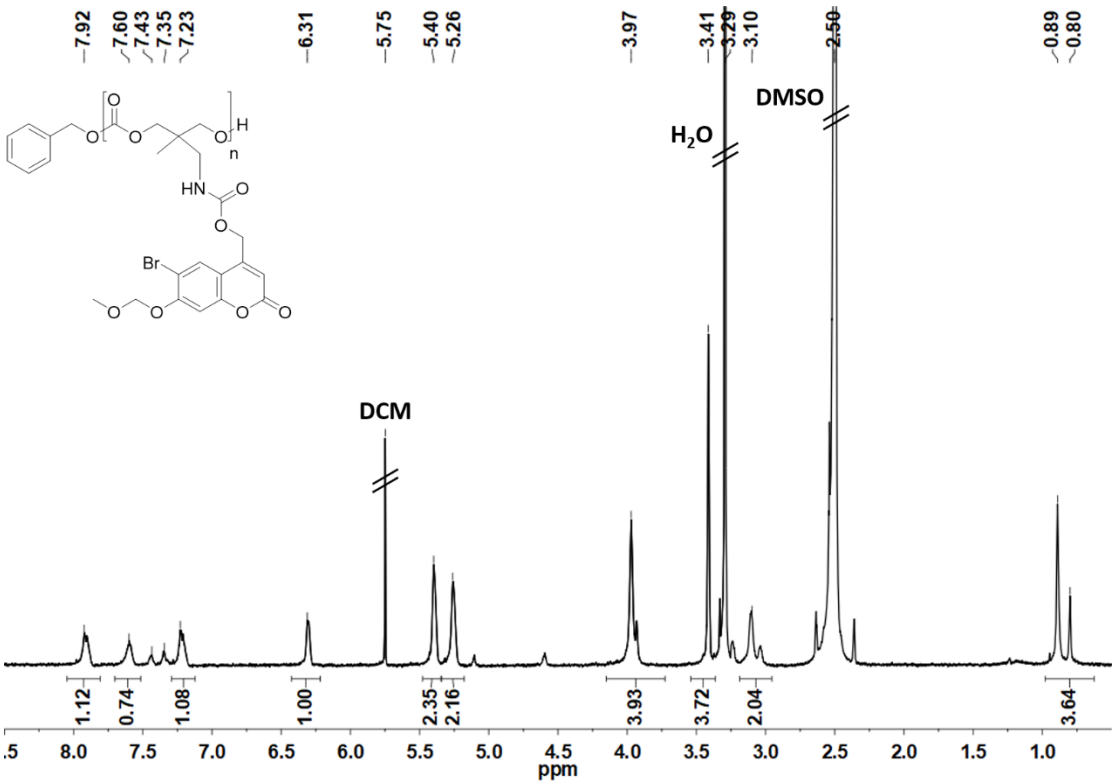


Figure S23. ^{1}H-NMR spectrum of **CouPC2**.

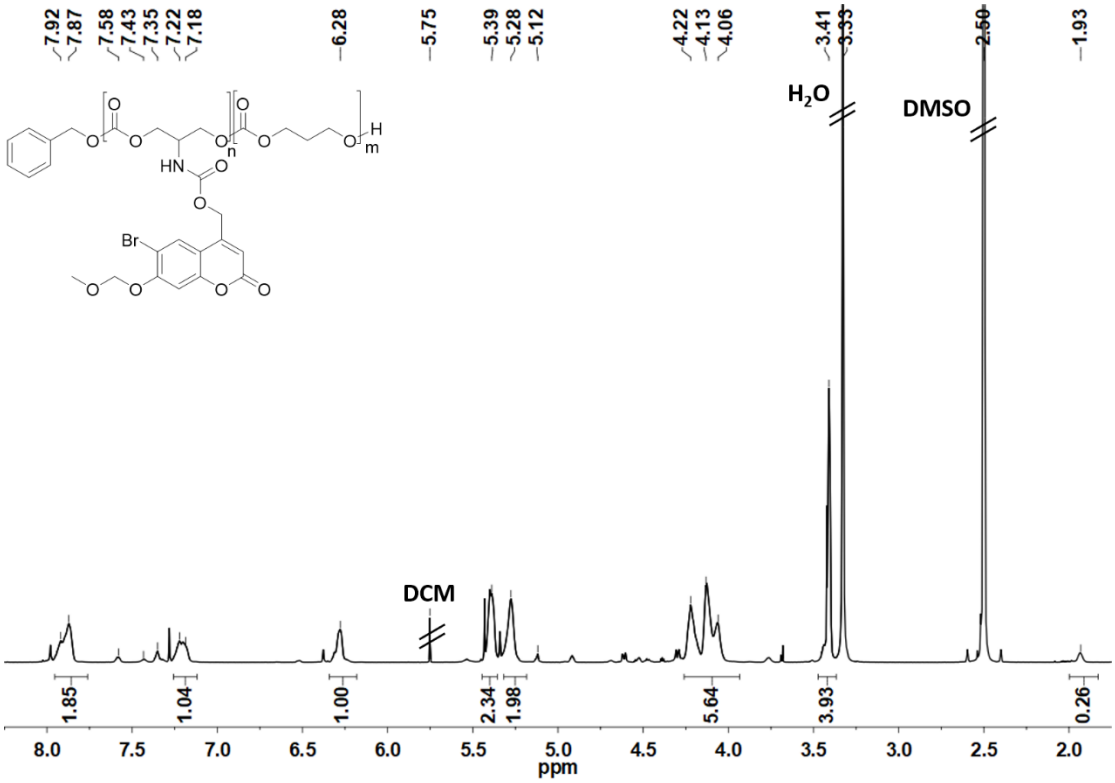


Figure S24. ^{1}H spectrum of **CouPC3**.

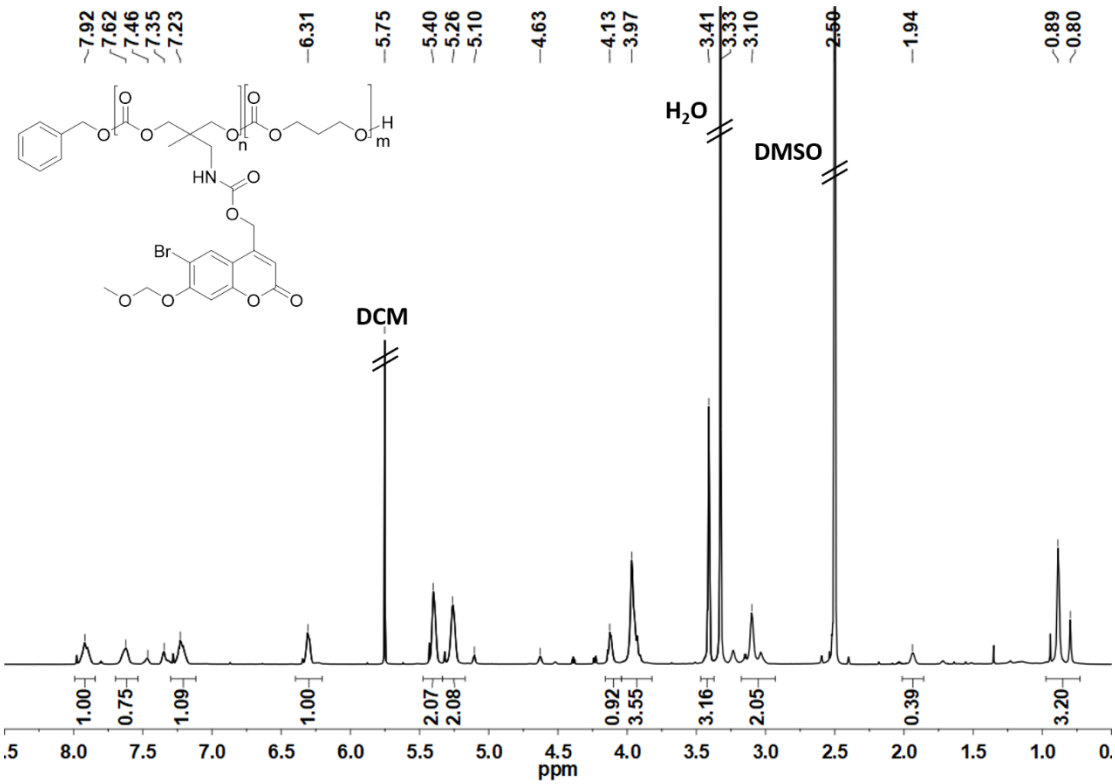


Figure S25. ^{1}H NMR spectrum of **CouPC4**.

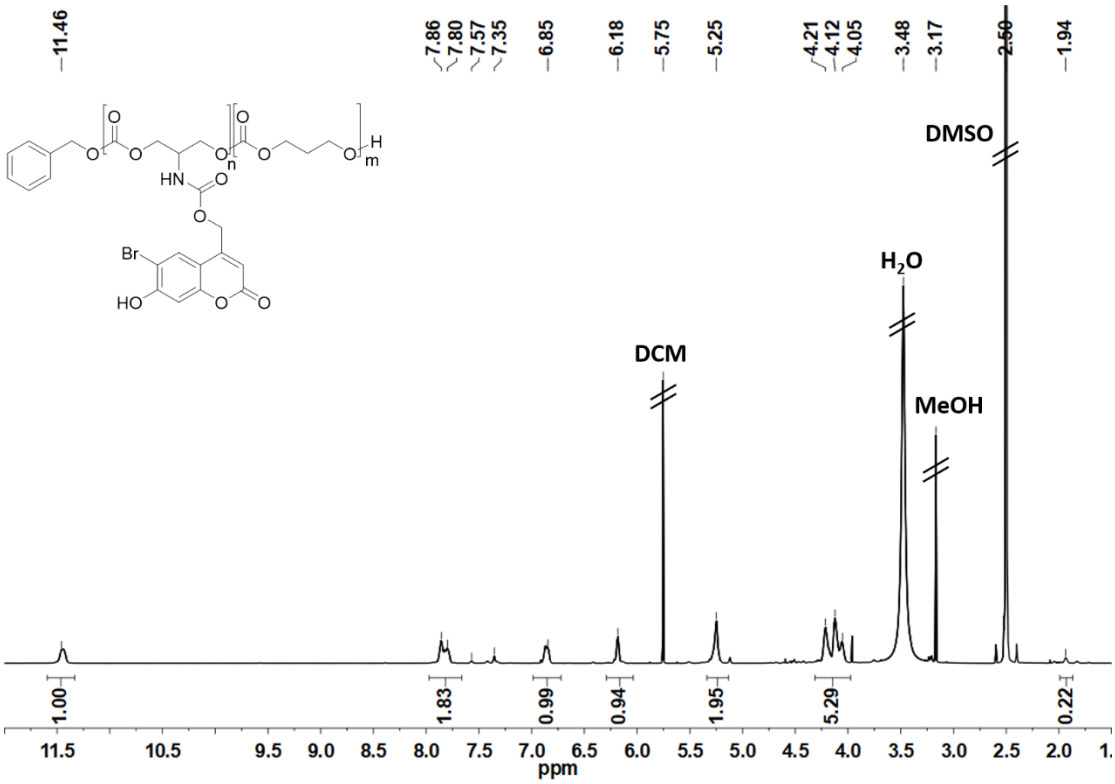


Figure S26. ^{1}H NMR spectrum of **CouPC5**.

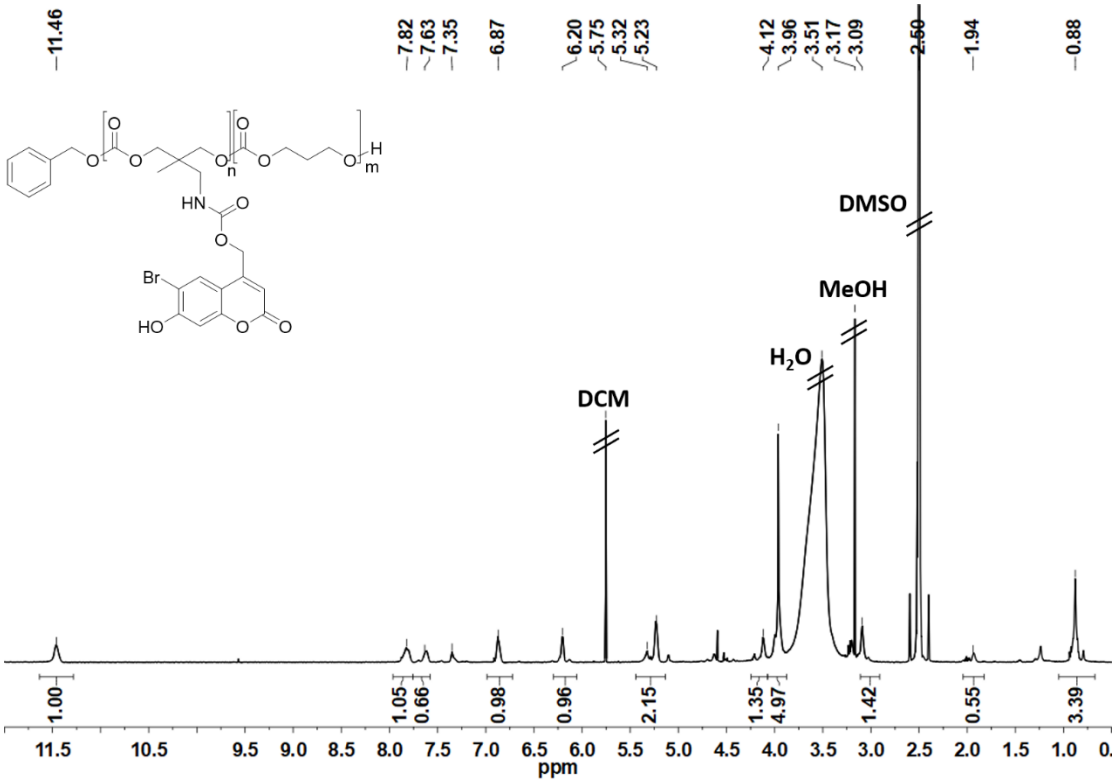


Figure S27. ^{1}H NMR spectrum of **CouPC6**.

Reference

1. Y. A. Kim, D. M. C. Ramirez, W. J. Costain, L. J. Johnstonb and R. Bittman, *Chem. Commun.*, 2011, **47**, 9236-9238.
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3. Z. Jia, D. E. Lonsdale, J. Kulis and M. J. Monteiro, *ACS Macro Lett.*, 2012, **1**, 780-783.
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