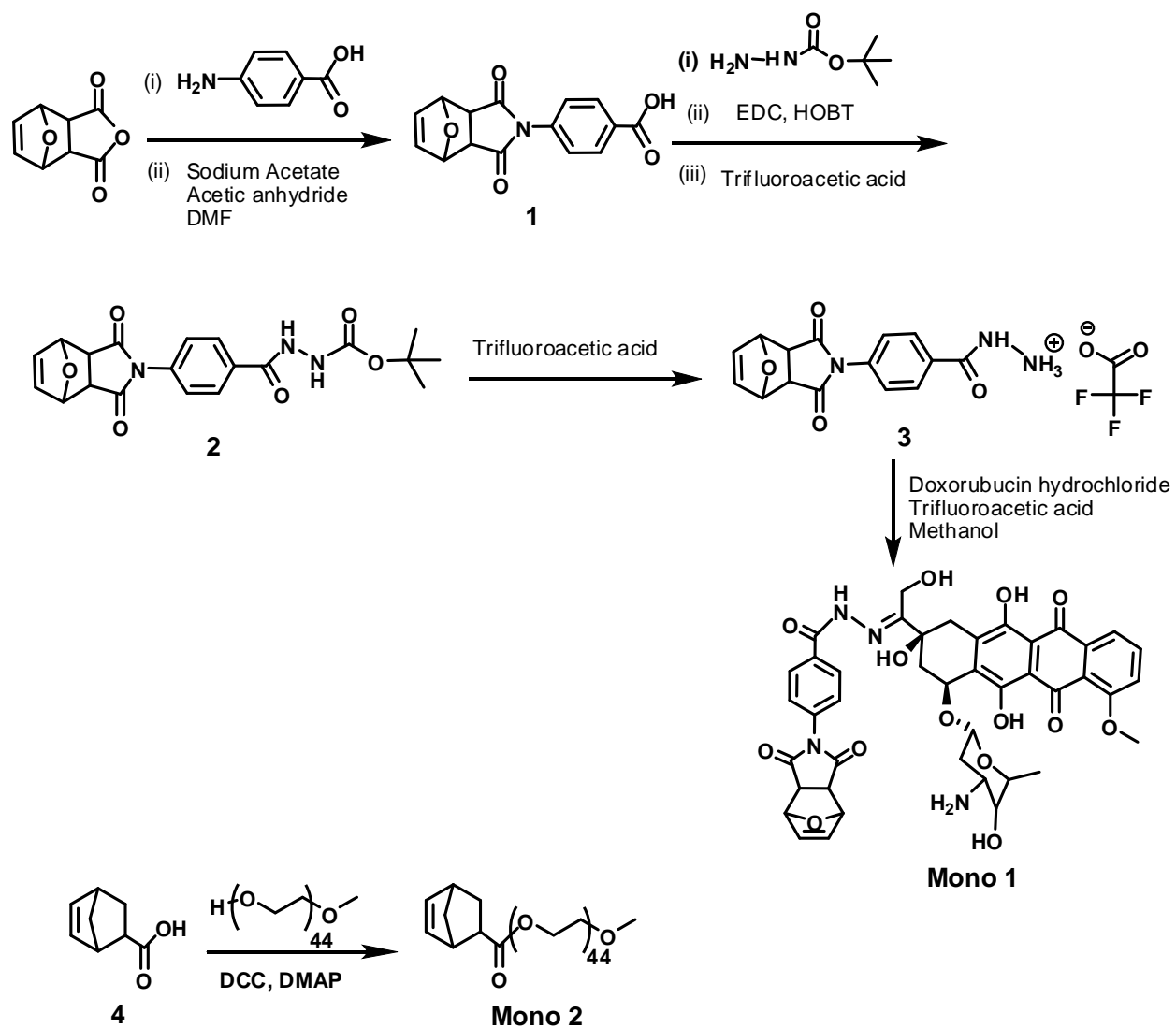


Supporting Information

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Synthesis scheme and procedure:



Scheme 1: Synthesis of monomer **1** and monomer **2**.

Synthesis of compound 1 (SI Scheme 1): Exo - oxabicyclo- [2.2.1] hept-5-ene-2, 3 - dicarboxylic anhydride¹, 1.914 g (11.5 mmol) was charged in 4 neck reaction flask. Charged 35 ml of acetone and heated until it became clear solution. To this solution, charged para amino benzoic acid 1.605 g (11.5 mmol) with stirring. After fifteen minutes heating was stopped and reaction mixture was allowed to stir for about 30 minutes. The solid was filtered and dried under oven at 55 °C under vacuum. The dried intermediate was then dissolved in 30 ml of dimethyl formamide and heated to 50 °C. Acetic anhydride 15 ml (158.97 mmol) and sodium acetate 0.635 g (7.743 mmol) were charged under stirring. The reaction mixture was allowed to stir for three hours at 55 °C. After 3 h the reaction mixture was poured into 500 ml of water acidified by addition of 5 ml concentrated HCl. White colour solid was precipitated immediately and filtered the solid and washed with water and dried at 90 °C, under vacuum (80 % yield). ¹H NMR (DMSO-D₆, 400 MHz): δ 13.1 (bs, 1H), 8.0 - 8.2 (m, 2H), 7.4 - 7.5 (m, 2H), 6.6 (s, 2H), 3.1 (s, 2H). ¹³C NMR (DMSO-D₆, 400 MHz): δ 175.43, 166.59, 136.65, 135.78, 130.0, 126.79, 80.86, 47.58. IR (KBr, cm⁻¹): 3236, 2635, 2073, 1954, 1826, 1780, 1729, 1698, 1607, 1515, 1418, 1218, 1144, 1125, 1020, 975, 950, 912, 883, 878, 804, 726, 672, 633, 598, 541, 521. MS (ESI) calculated for C₈H₁₀O₂Na [M + H]⁺ : 285.05 ; observed 284.95

Synthesis of compound 2 (SI Scheme 1): 1 g (6.92 mmol) of compound 1 was Charged into 10 ml of dimethyl formamide. 0.85 g (4.46 moml) of N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC) and 1-hydroxybenzotriazole (HOBT) 0.62 g (4.46 mmol) in to the reaction mixture. Reaction mixture allowed to stir for 15 h at room temperature. Reaction mixture was cooled to 0-5 °C. Tertiary butyl carbazate was dissolved in dimethyl formamide and this solution was added to the reaction mixture at 0-5 °C. Reaction mixture was stirred for another 30 minutes at 0-5 °C. Charged ethyl acetate followed by water to the reaction mixture. Organic layer was washed with 2 x 10 ml of water followed by sodium bicarbonate wash. Finally organic layer was washed with brine solution. Organic layer concentrated under vacuum to yield a white colour solid (700 mg, 70% yield). ¹H NMR (DMSO-D₆, 400 MHz): δ 10.30 (bs, 1H), 8.96 (s, 1H), 7.8 - 7.9 (m, 2H), 7.2 - 7.26 (m, 2H), 6.60 (s, 2H), 5.34 (s, 2H), 3.11 (s, 2H), 1.26 (s, 9H). ¹³C NMR (CDCl₃, 400 MHz): δ 175.48, 165.39, 155.42, 136.64, 134.80,

128.03, 126.67, 80.85, 79.27, 47.58, 28.08. IR (KBr, cm^{-1}): 3456, 3367, 3277, 2999, 1786, 1747, 1729, 1660, 1630, 1541, 1516, 1390, 1261, 1014, 946, 912, 875, 867, 781, 722. MS (ESI) calculated for $\text{C}_8\text{H}_{10}\text{O}_2\text{Na}$ $[\text{M} + \text{H}]^+$: 399.40 ; observed 399.14

Synthesis of compound 3 (SI Scheme 1): 500 mg (1.754 mmol) of compound **2** was dissolved in 5 ml of dichloromethane at room temperature. Trifluoroacetic acid 6 ml was charged in to the reaction mixture. Reaction mixture allowed to stirred for 1 h at room temperature. Reaction mixture concentrated to pasty mass, and charged diethyl ether resultant white product was collected by suction filtration, washed with 10 ml diethyl ether and dried at 40 $^{\circ}\text{C}$ under vacuum (420 mg, 84 % yield). ^1H NMR ($\text{DMSO}-\text{D}_6$, 400 MHz): δ 11.43 (bs, 1H), 7.8 - 7.9 (m, 2H), 7.33 - 7.40 (m, 2H), 6.6 (s, 2H), 5.25 (s, 2H), 3.11 (s, 2H), 1.8 - 1.9 (m, 3H); IR (KBr, cm^{-1}): 3481, 2975, 1785, 1717, 1512, 1393, 1304, 1207, 1172, 1070, 880, 726. ^{13}C NMR (CDCl_3 , 400 MHz): δ 175.48, 165.39, 155.42, 136.64, 134.80, 128.03, 126.67, 80.85, 79.27, 47.58. MS (ESI) calculated for $\text{C}_8\text{H}_{10}\text{O}_2\text{Na}$ $[\text{M} + \text{H}]^+$: 299.28 observed 299.98

Isolation of compound 4: 25 g (0.18 mmols) of exo-5-norbornene-2-carboxylic acid was separated from the commercially available mixture of endo and exo 5-norbornene-2-carboxylic acid by the iodolactonization method of Ver Nooy and Rondestvedt² (5 g, 20% yield). ^1H NMR ($\text{DMSO}-\text{D}_6$, 400 MHz): δ 1.13 - 1.17 (m, 2H), 1.28 - 1.29 (d, $J = 8.5$ Hz, 1H), 1.66 - 1.71 (m, 1H), 1.97 - 2.05 (dt, $J = 12.7$ Hz, 1H), 2.76 (s, 1H), 2.9 (s, 1H), 6.03-6.05 (m, 2H), 12.00 (br, 1H). ^{13}C NMR (CDCl_3 , 500 MHz): 182.7, 138.1, 135.7, 46.7, 46.4, 43.2, 41.7, 30.3. IR (KBr, cm^{-1}): 2919, 2852, 1700, 1421, 1218, 909, 766. MS (ESI) calculated for $\text{C}_8\text{H}_{10}\text{O}_2\text{Na}$ $[\text{M} + \text{H}]^+$; 138.07; observed 138.09.

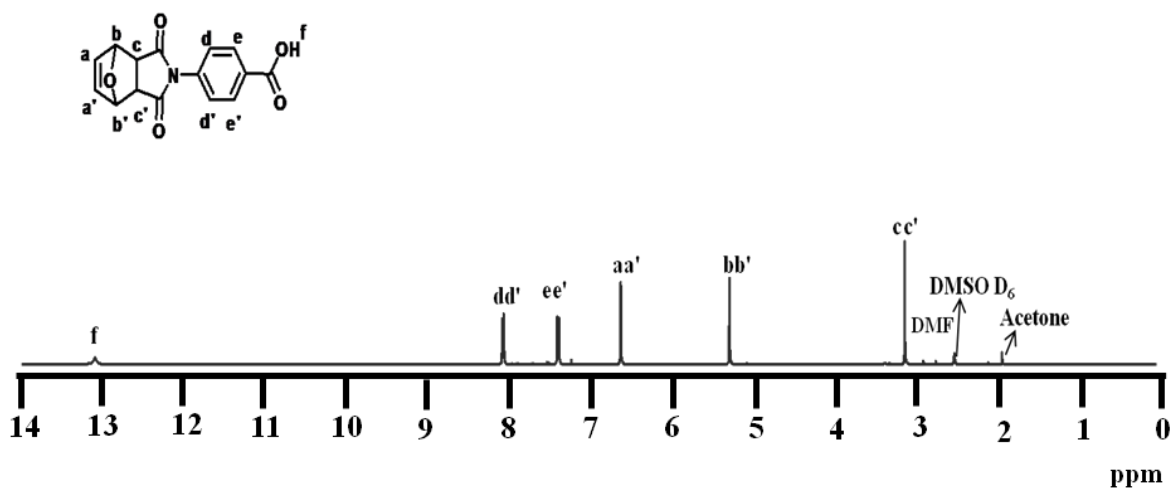


Figure S1. ^1H NMR spectrum of compound **1** in DMSO- d_6 .

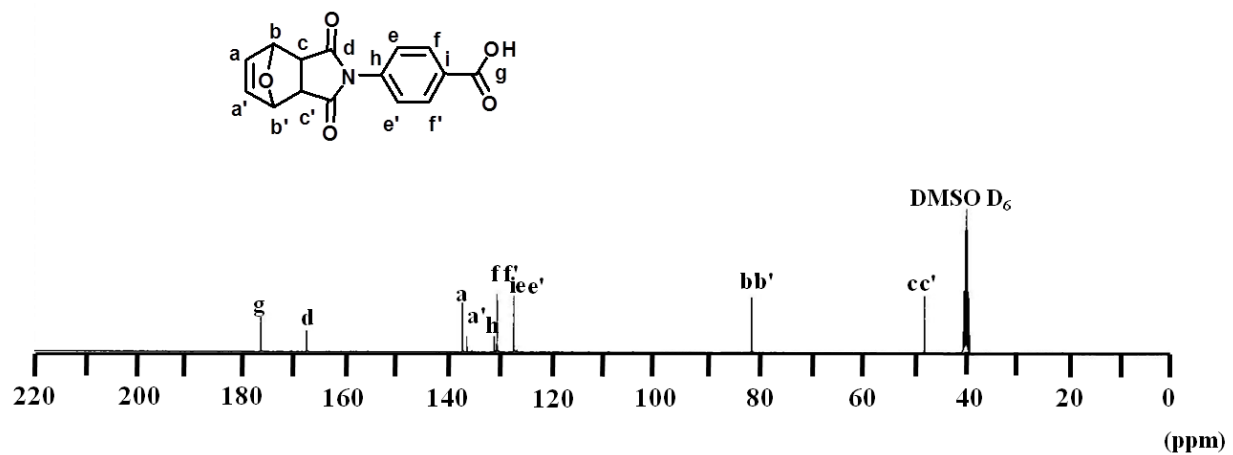


Figure S2. ^{13}C NMR spectrum of compound **1** in DMSO- d_6 .

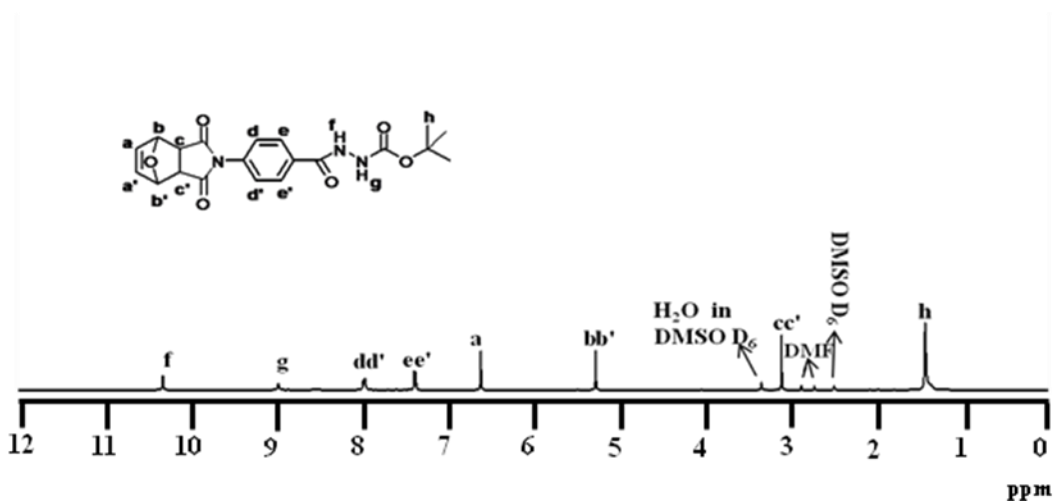


Figure S3. ^1H NMR spectrum of compound **2** in DMSO- d_6 .

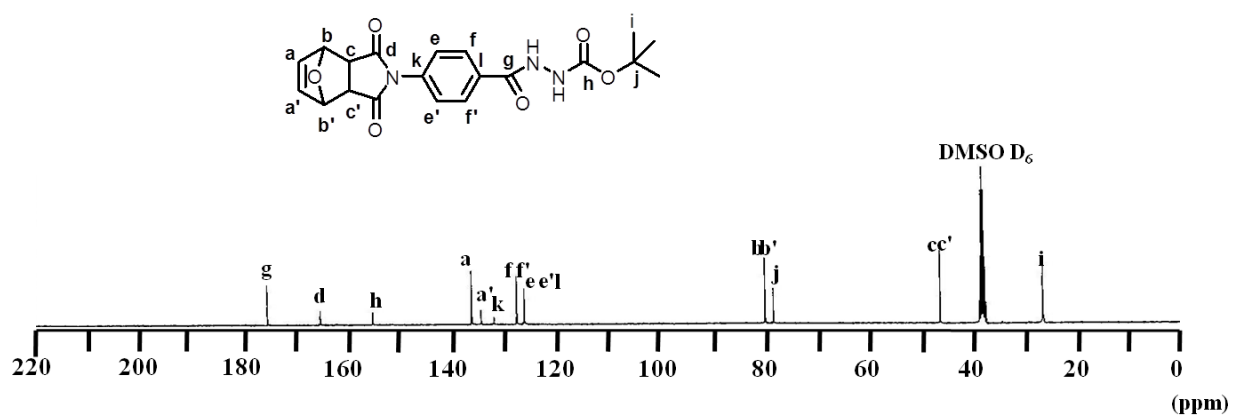


Figure S4. ^{13}C NMR spectrum of compound **2** in DMSO- d_6 .

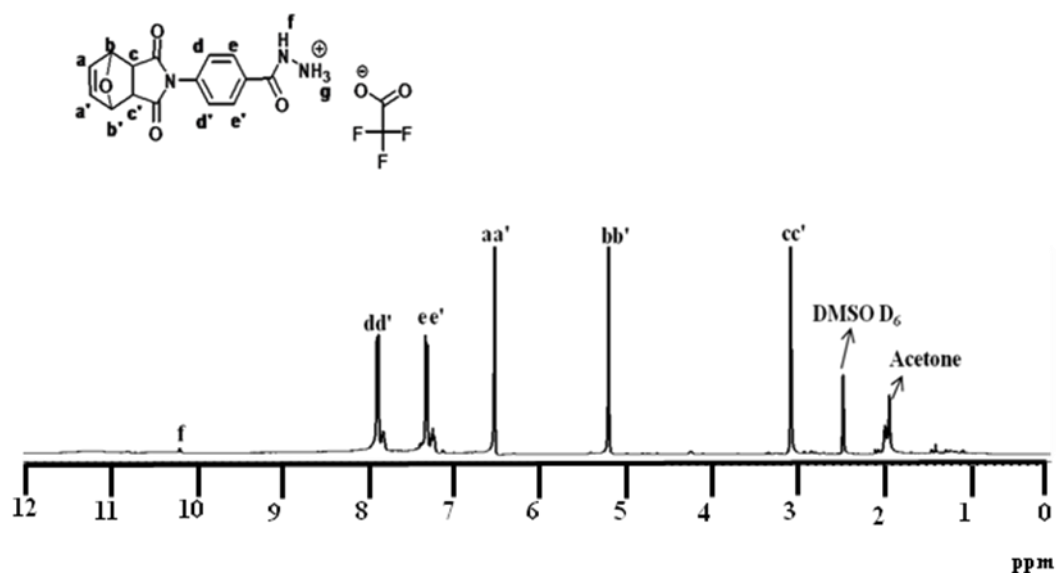


Figure S5. ¹H NMR spectrum of compound **3** in DMSO-d₆.

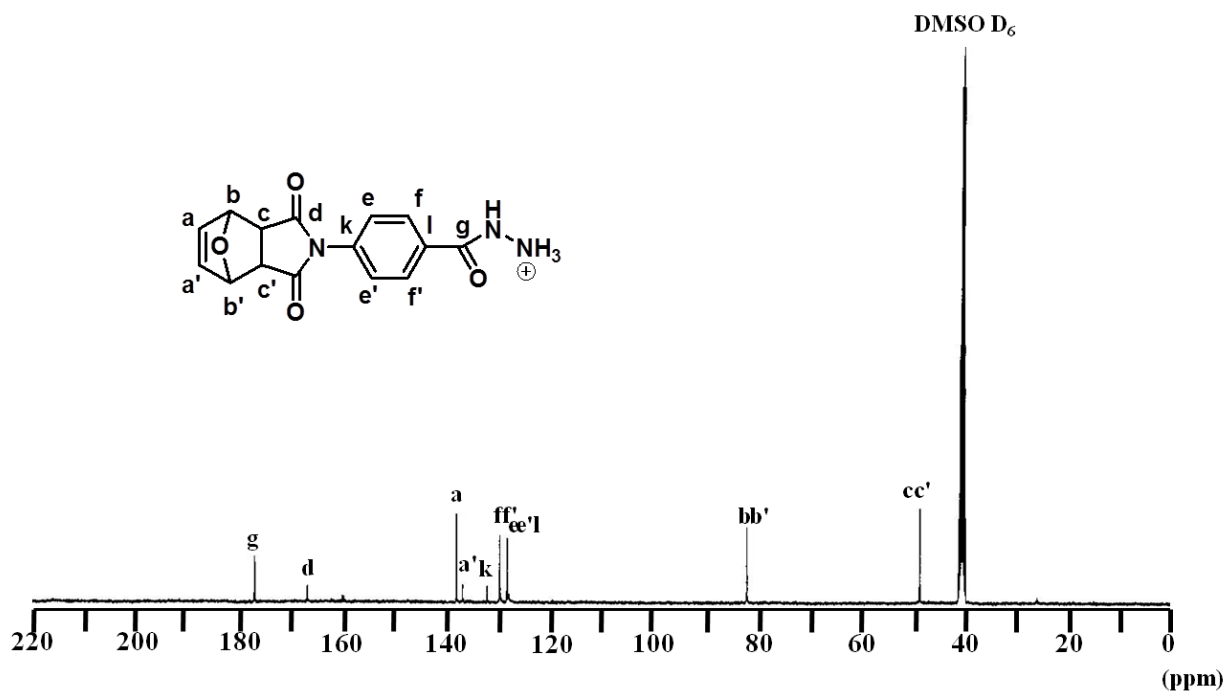


Figure S6. ¹³C NMR spectrum of compound **3** in DMSO-d₆.

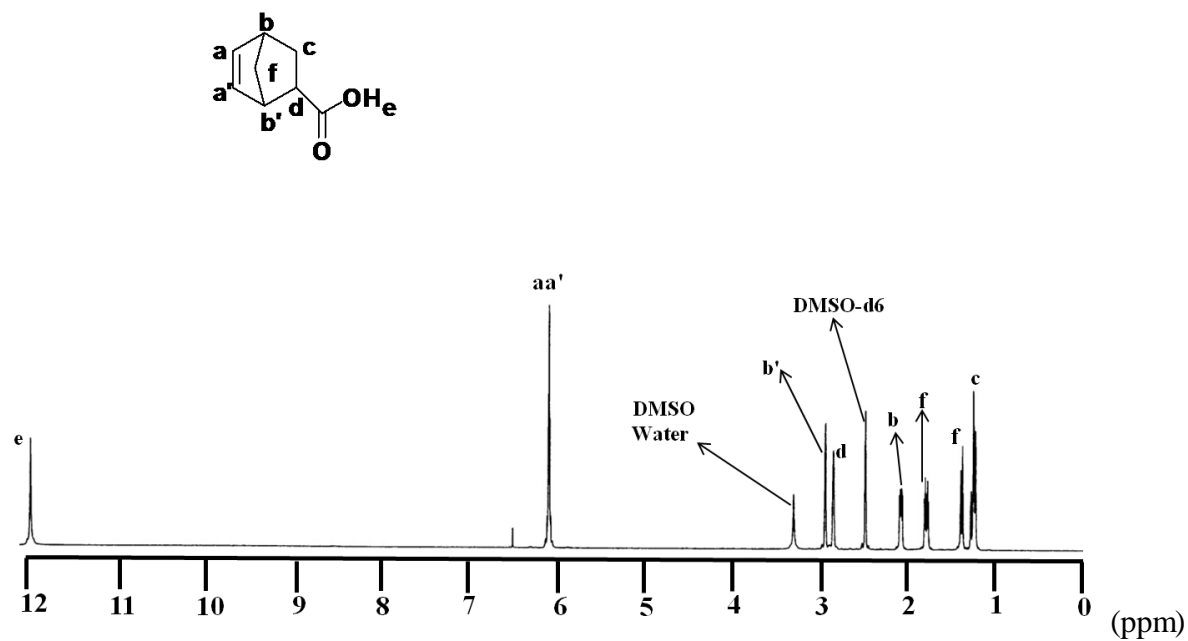


Figure S7. ^1H NMR spectrum of compound **4** in DMSO-d_6 .

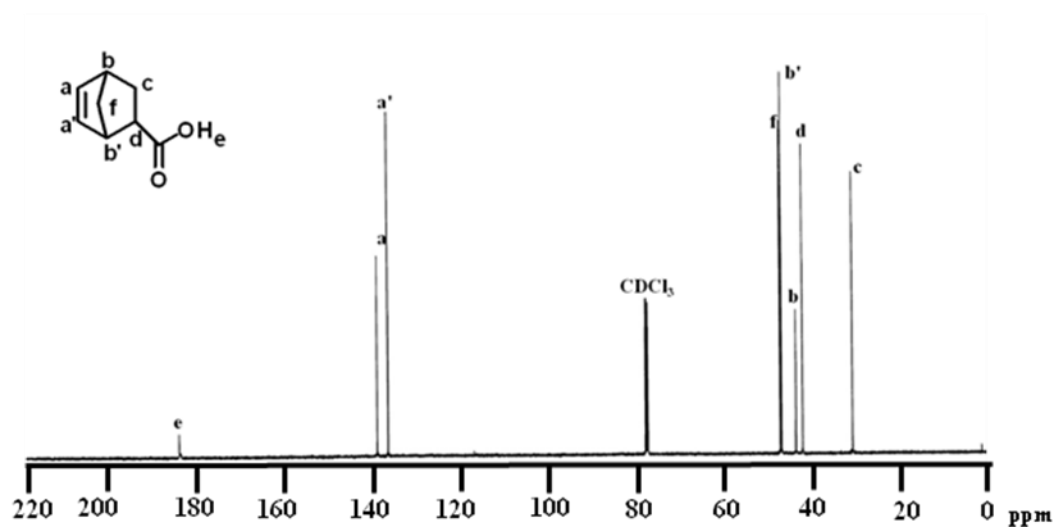


Figure S8. ^{13}C NMR spectrum of compound **4** in CDCl_3 .

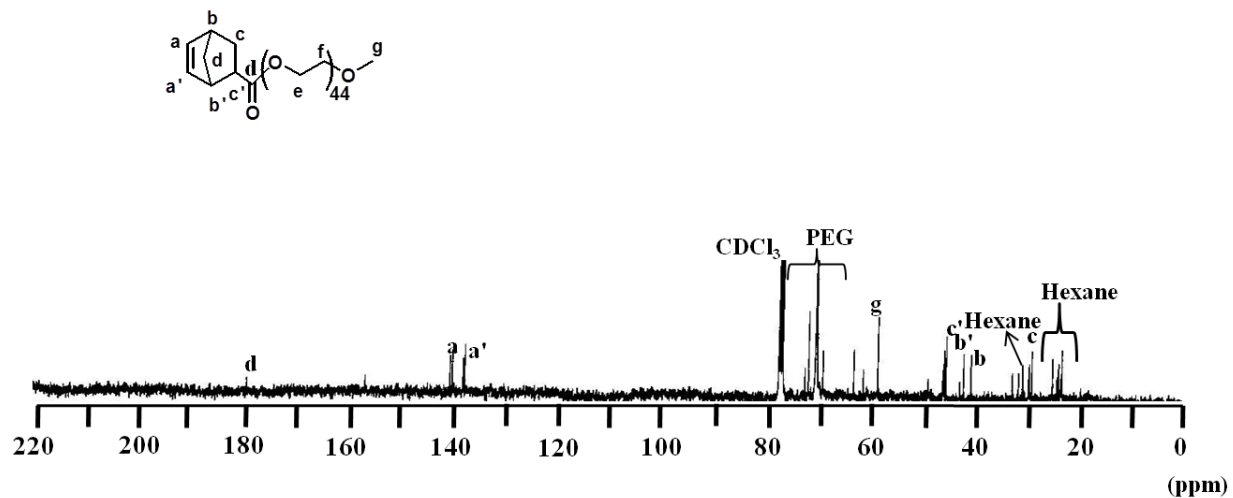


Figure S9. ^{13}C NMR spectrum of **mono 2** in CDCl₃.

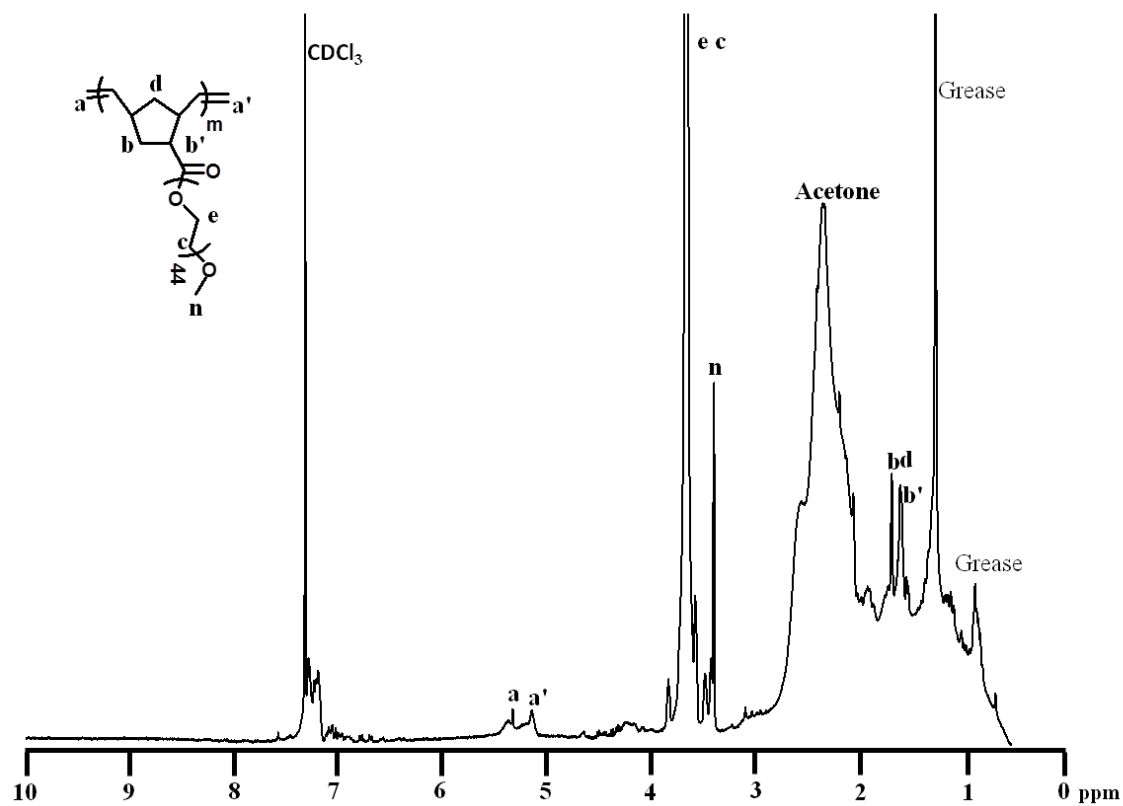


Figure S10. ^1H NMR spectrum of **poly 2** in CDCl₃.

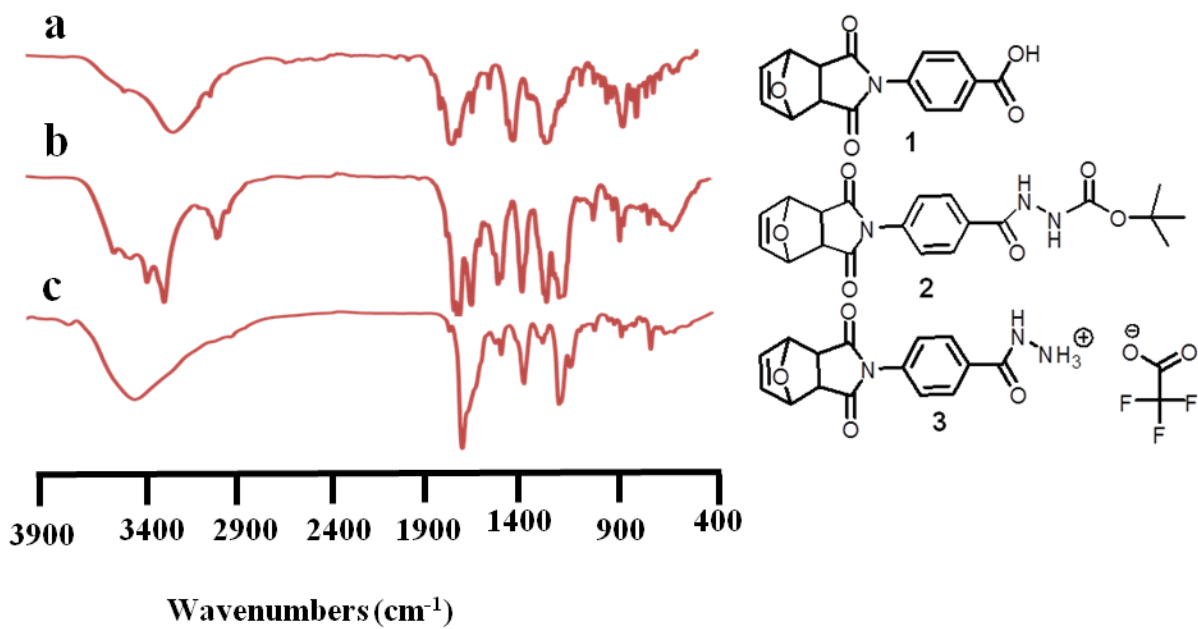


Figure S11. FT-IR spectra of (a) compound 1 (b) compound 2 (c) compound 3.

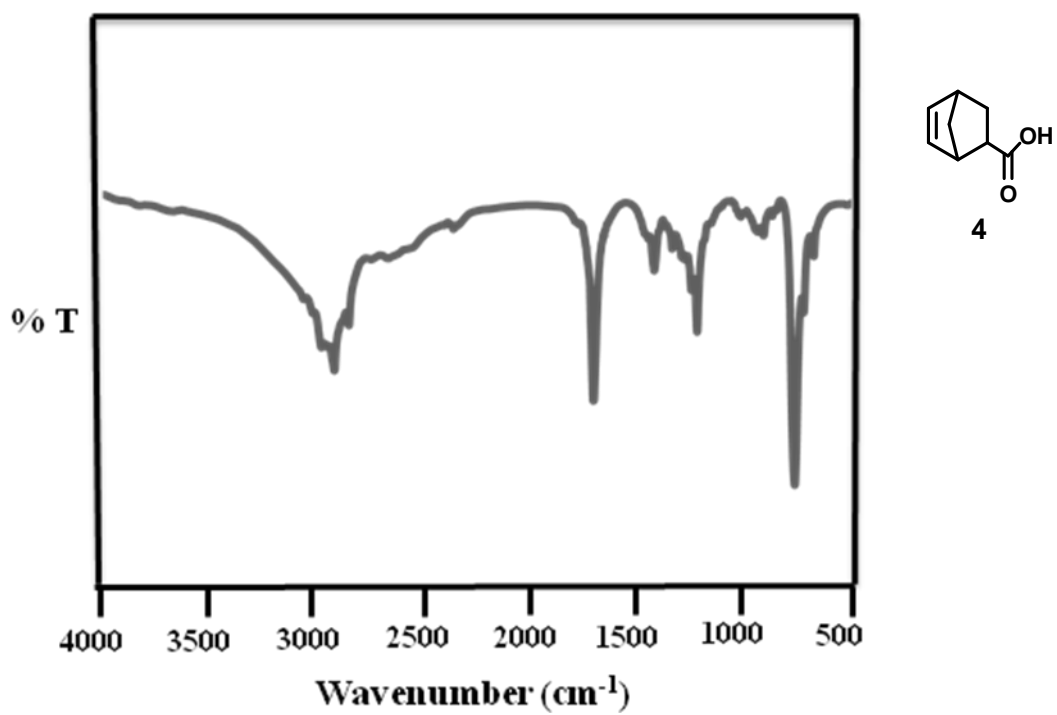


Figure S12. FT-IR spectrum of compound 4.

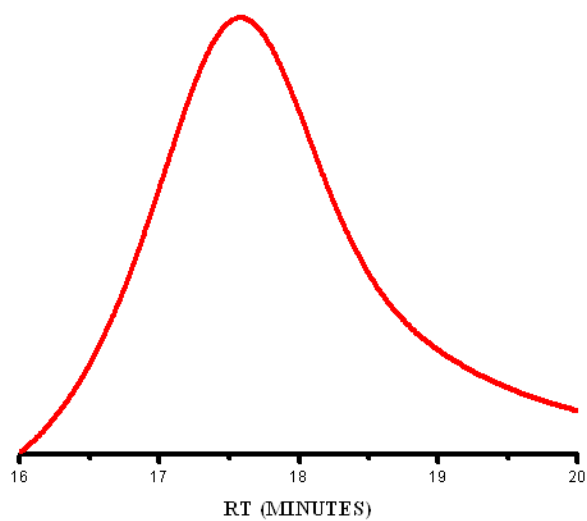


Figure S13. Gel permeation chromatogram (GPC) of **poly 1**. The observed $M_n = 17400$ and $PDI = 1.17$ suggested the controlled polymerization of **mono 1**.

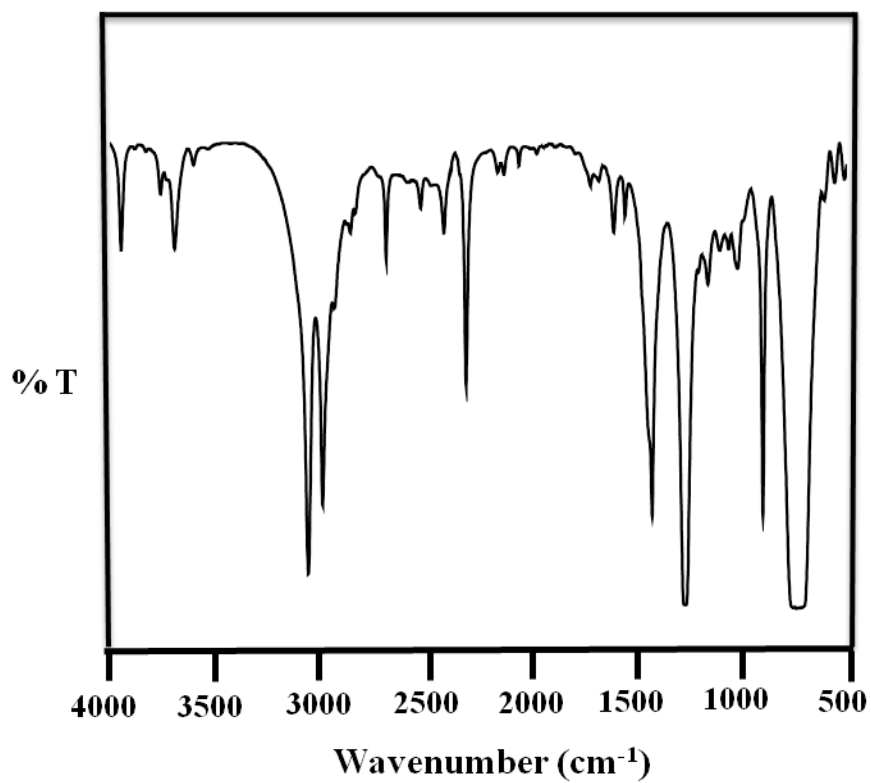


Figure S14. FT-IR spectrum of Poly 1.

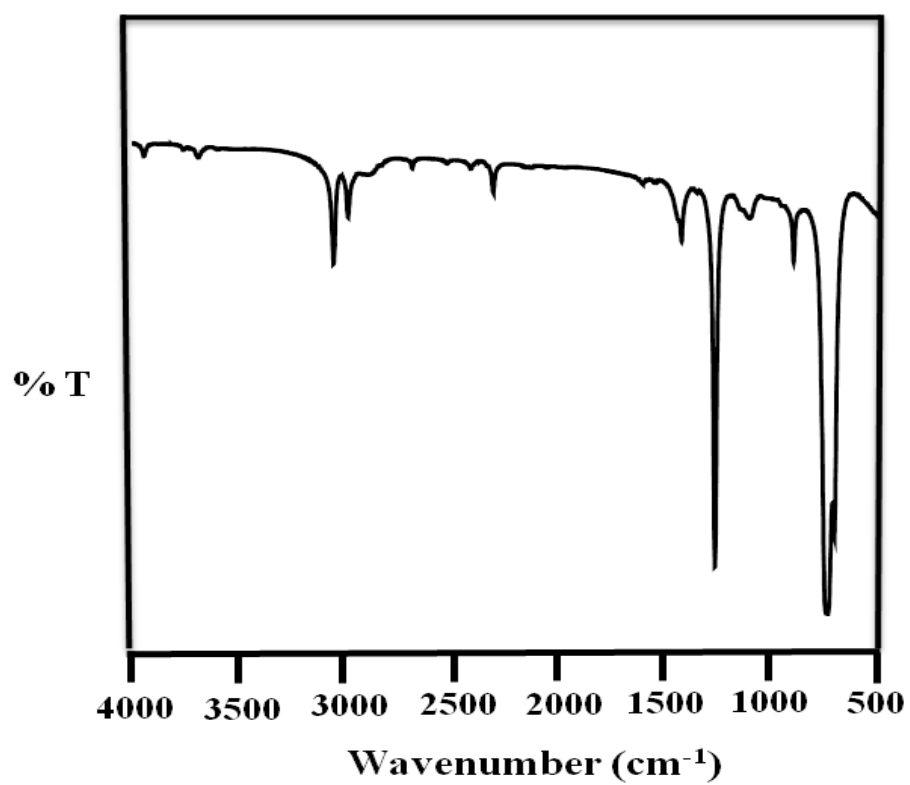


Figure S15. FT-IR spectrum of Poly 2.

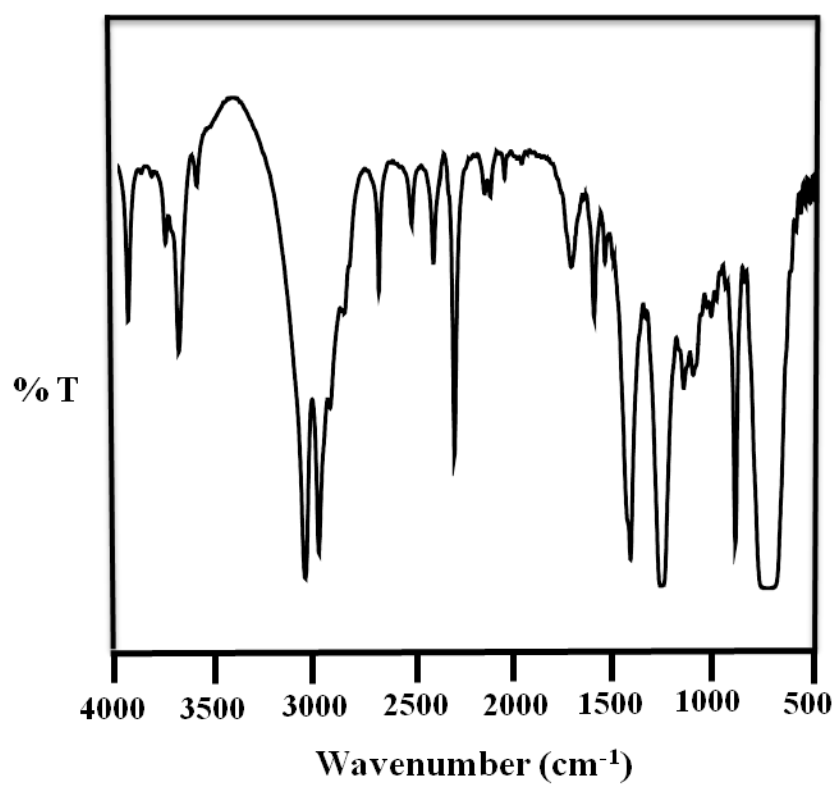


Figure S16. FT-IR spectrum of COPY-DOX.

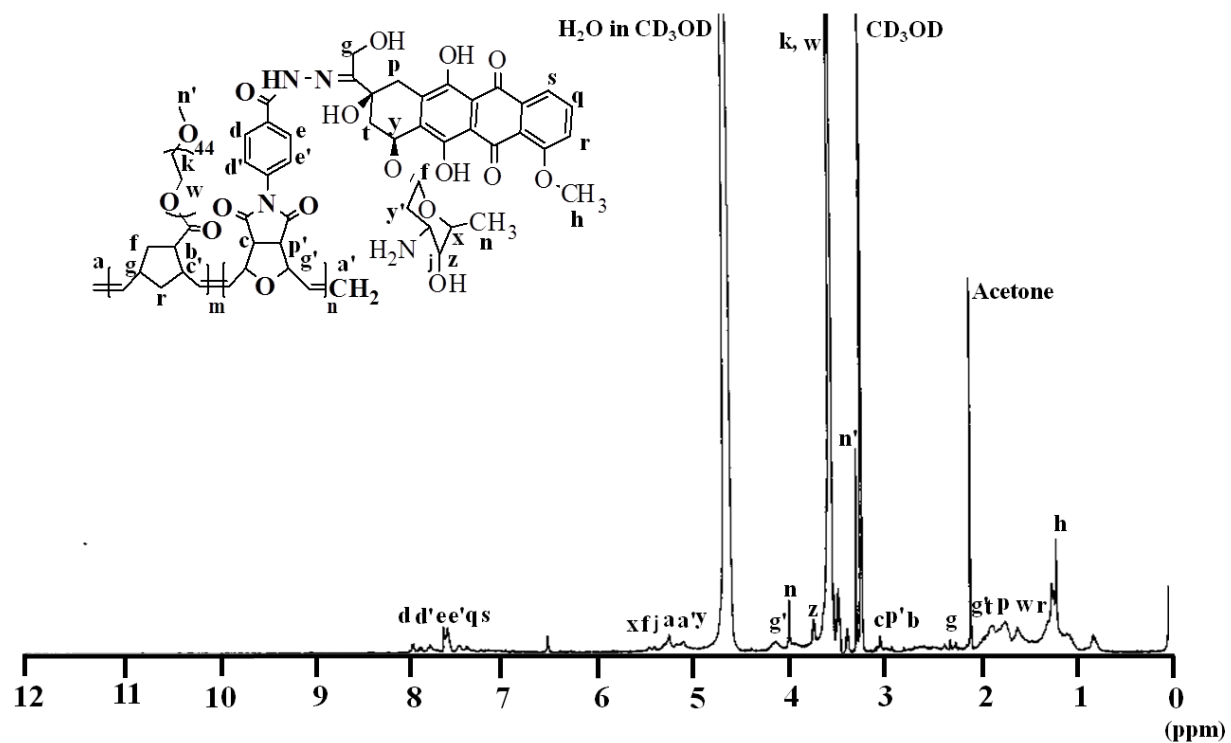


Figure S17. ^1H NMR spectrum of **mono 1**.

References:

1. Alfred, S. F.; Al-Badri, Z. M.; Madkour, A. E.; Lienkamp, K.; Tew, G. N. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, 46, 2640.
2. Ver Nooy, C. C.; Rondestvedt, C. S. *J. Am. Chem. Soc.*, **1955**, 77, 3583.