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Electronic Supplementary Information

Adamantyl-terminated dendronized molecules: synthesis and interaction with *β*-cyclodextrin functionalized poly(dimethylsiloxane) Interface

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Abstract . This supplementary information provides all the additional information and a more detailed discussion of the current study.

Study on the photophysical properties of compound 6. The compound 3-azido-7-hydroxy coumarin, which shows diminished fluorescence because of the existence of the electron-rich azide group on its 3-position, is used as fluorogenic substrate. This azide is 'clicked' into compound **5** to synthesize compound **6** via triazole ring formation, simultaneously accompanying the appearance of strong fluorescence. The photophysical properties of compound **6** are shown in Figs. S1-3.

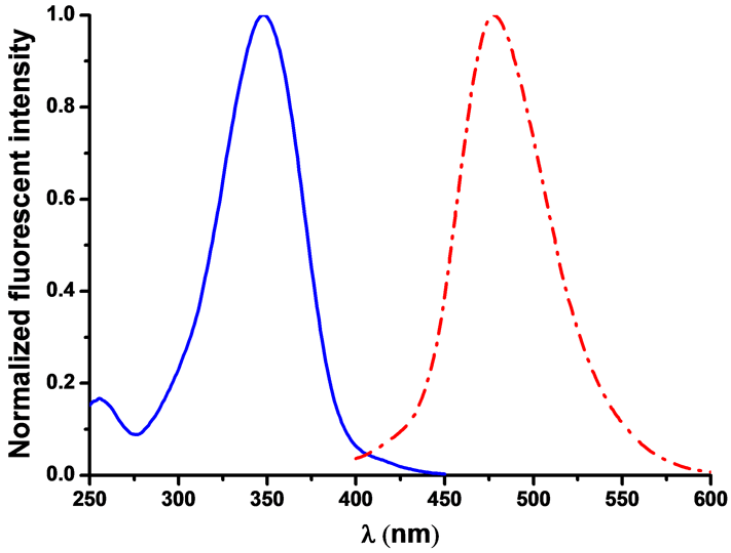


Fig. S1. Normalized excitation ($\lambda_{Ex.\ max}$ = 348 nm) and emission ($\lambda_{Em.\ max}$ = 478 nm) spectra of the aqueous solution of compound **6.**

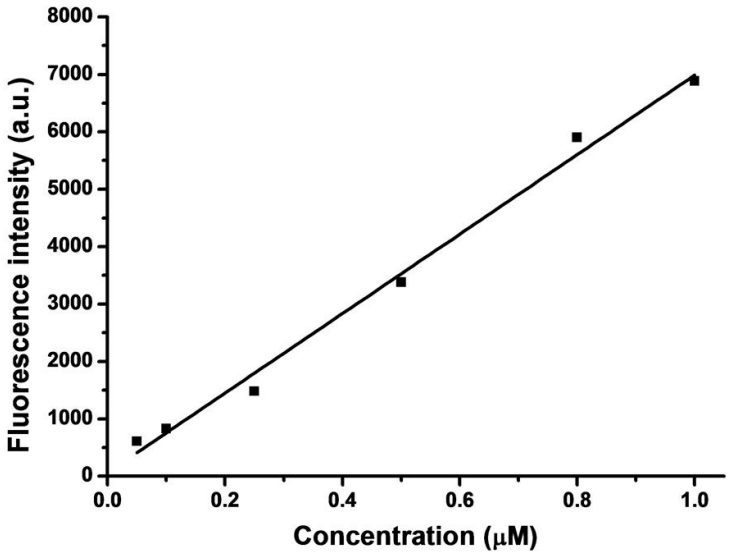


Fig. S2: Relationship between the fluorescence intensity of compound **6** aqueous solution, which was excited at 348 nm, and its various concentrations, showing a linear correlation (r = 0.99) in the concentration range of 0.05 μM to 1.0 μM.

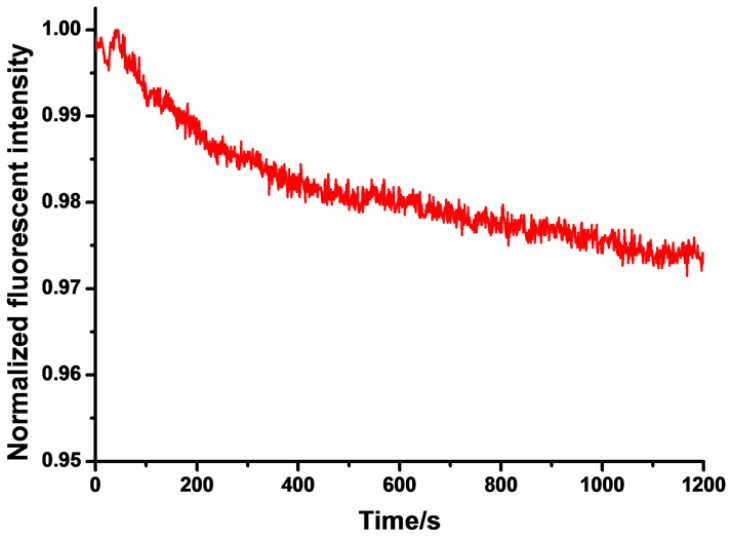
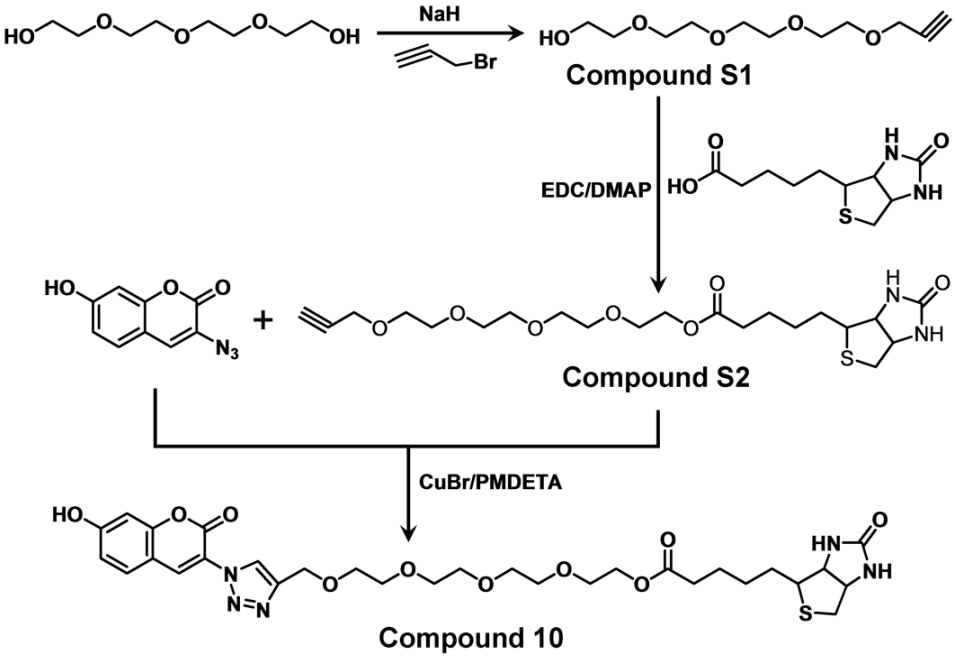


Fig. S3. Photostability of compound **6** in aqueous solution.

Synthesis of fluorescent biotin (compound **10**)



Scheme S1. Synthetic route for compound **10.**

Compound **S1** was synthesized following previously reported methods (Y.R. Zhang, et al. *Anal. Chem*. **2011**, *83*, 9651–9659; J. Diot, et al. *Org. Biomol. Chem*. **2009**, *7*, 357–363), ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.16 (d, 2H, *J* = 2.4 Hz), 3.70 to 3.50 (m, 16H), 2.89 (br, 1H), and 2.41 (t, 1H, *J* = 2.4 Hz).

Compound **S2** was synthesized as follows: a solution of 4-DMAP (0.064 g, 0.5 mmol) in 2 mL of DMF was first added drop-wise to an ice-cooled mixture solution of compound **S1** (0.116 g, 0.5 mmol) and D-biotin (0.122 g, 0.5 mmol) in 15 mL DMF. After stirring for 10 min at room temperature, EDC (0.115 g, 0.6 mmol) was added upon stirring of the reaction mixture. The reaction mixture was kept in an ice-water bath for another 10 min and was stirred overnight at room temperature. DMF was removed under vacuum, the residue was resolved in CH_2Cl_2 and washed with 1 M HCl to get rid of 4-DMAP. After drying on anhydrous Na_2SO_4, the organic layer was purified through silica gel column chromatography (eluent: CH_2Cl_2/CH_3OH, 10:1, v/v) to give compound **S2** (174.1 mg, 76%). MS (ESI): $[M+Na]^+$ calcd for $C_{21}H_{34}N_2O_7SNa$, 481.21, found 481.13; ^1H NMR (500 MHz, $CDCl_3$): δ 5.74 (s, 1H), 5.13 (s, 1H), 4.52 (br, 1H), 4.32 (br, 1H), 4.25 to 4.20 (m, 4H), 3.71 to 3.65 (m, 14H), 3.16 (br, 1H), 2.92 (d, *J* = 12.5 Hz, 1H), 2.74 (d, *J* = 12.5 Hz, 1H), 2.45 (s, 1H), 2.38 (t, *J* = 7.0 Hz, 2H), 1.69 (br, 4H), and 1.45 (br, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): 173.72, 163.84, 79.67, 74.62, 70.59, 70.57, 70.50, 70.39. 69.14, 69.10, 63.43, 61.94, 60.11, 58.39, 55.61, 40.55, 33.78, 28.33, 28.22, and 24.74.

Compound **10** was synthesized as follows: compound **S2** (137.5 mg, 0.3 mmol), 3-azido-7-hydroxy couramin (0.3 mmol, 61.0 mg), PMDETA (0.03 mmol, 7.0 μL) were added sequentially to a Schlenk tube equipped with a magnetic stirring bar, and then, 5 mL of DMF was added. The resulting mixture was degassed via three freeze-thaw cycles, and CuBr (9.0 mg, 0.06 mmol) was added under nitrogen atmosphere. The mixture was stirred at room temperature for 24 h. DMF was removed under vacuum. The residue was dissolved in 20 mL of CH_2Cl_2; the organic phase was washed with EDTA [1% (w/v), 15 mL × 2] and water successively, and dried by anhydrous Na_2SO_4. The crude product was purified through column chromatography (eluent: CH_2Cl_2/CH_3OH, 8:1, v/v) to give compound **S10** (168.6 mg, 85%). MS (ESI): $[M+Na]^+$ calcd for $C_{30}H_{39}N_5O_{10}SNa$, 684.24, found 684.12; ^1H NMR (500 MHz, $CDCl_3$): δ 8.54 (s, 1H), 8.38 (s, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 6.87 to 6.83 (m, 2H), 6.06 (br, 1H), 5.55 (br, 1H), 4.55 (br, 1H), 4.35 (br, 1H), 4.28 (br, 1H), 4.23 (br, 1H), 4.16 (br,

2H), 3.75 to 3.63 (m, 14H), 3.16 (br, 1H), 2.91 (d, *J* = 10.5 Hz, 1H), 2.76 (d, *J* = 13.0 Hz, 1H), 2.37 (s, 1H), 2.31 (s, 2H), 1.63 to 1.61 (m, 4H), and 1.42 (br, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): 173.62, 163.83, 162.53, 156.30, 154.71, 134.31, 130.21, 119.30, 115.08, 110.53, 103.06, 70.64, 70.58, 70.54, 70.44, 69.83, 69.10, 64.45, 63.45, 62.12, 60.29, 58.93, 55.53, 40.49, 33.67, 29.70, 28.29, 28.20, and 24.69.

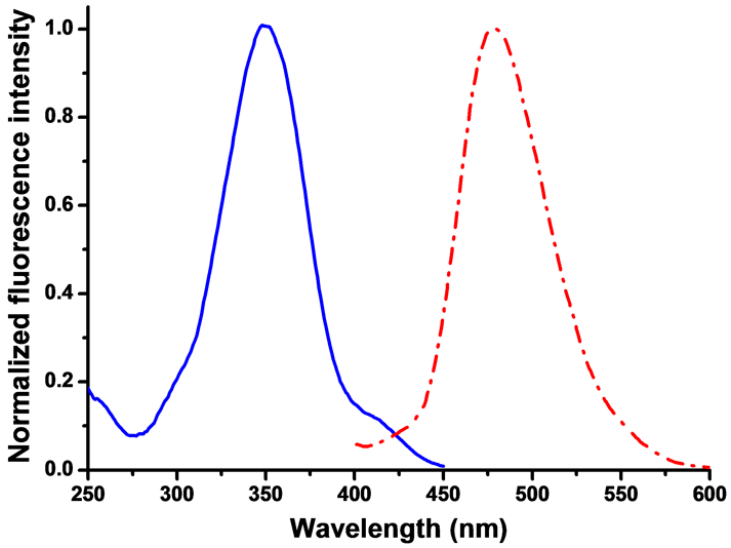
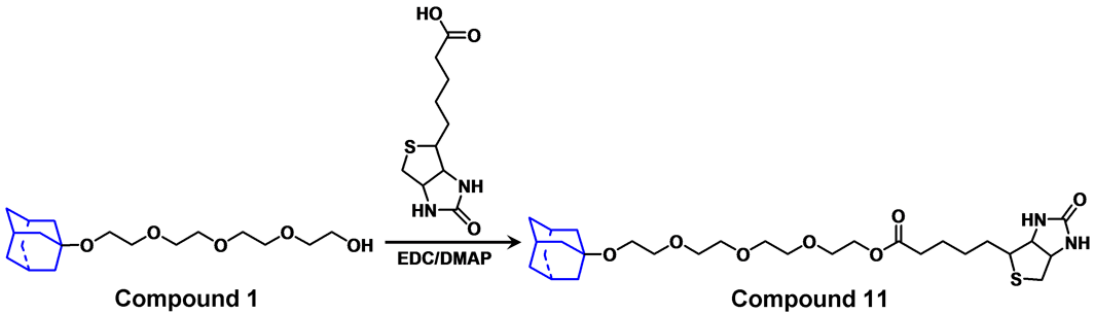


Fig. S4. Normalized excitation ($\lambda_{Ex.\ max}$ = 350 nm) and emission ($\lambda_{Em.\ max}$ = 480 nm) scan of compound **10.**

Synthesis of biotinylated monoadamantyl-terminated molecule (compound **11**)



Scheme S2. Synthetic route for compound **11.**

A solution of 4-DMAP (49.0 mg, 0.4 mmol) in 2 mL of DMF was first added drop-wise to an ice-cooled mixture solution of compound **1** (131.4 mg, 0.4 mmol) and D-biotin (97.8 mg, 0.4 mmol) in 15 mL of DMF. After stirring for 5 min at room temperature, EDC (92.0 mg, 0.48 mmol) was added upon stirring of the reaction mixture. The reaction mixture was kept in

an ice-water bath for another 10 min and was stirred overnight at room temperature. DMF was removed under vacuum, and the residue was resolved in CH_2Cl_2 and washed with 1 M HCl to get rid of 4-DMAP. After drying on anhydrous Na_2SO_4, the organic layer was purified through silica gel column chromatography (eluent: CH_2Cl_2/CH_3OH, 30:1, v/v) to obtain compound **11** (197.3 mg, 89%). MS (ESI): $[M+Na]^+$ calcd for $C_{28}H_{46}N_2O_7SNa$, 577.30, found 577.26; ^1H NMR (500 MHz, $CDCl_3$): δ 6.51 (s, 1H), 6.07 (s, 1H), 4.36 to 4.30 (m, 1H), 4.16 to 4.10 (m, 1H), 4.10 to 4.05 (m, 2H), 3.60 to 3.40 (m, 14H), 3.02 to 2.95 (m, 1H), 2.76 to 2.70 (m, 1H), 2.62 to 2.58 (m, 1H), 2.22 (t, *J* = 5.70 Hz, 2H), 1.99 (s, 3H), 1.60 to 1.40 (m, 16H), and 1.33 to 1.25 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): 173.52, 164.11, 72.06, 71.11, 70.46, 70.42, 70.40, 70.37, 68.99, 63.28, 61.85, 60.05, 59.13, 55.61, 41.34, 36.33, 33.67, 30.35, 28.27, 28.10, and 24.62.

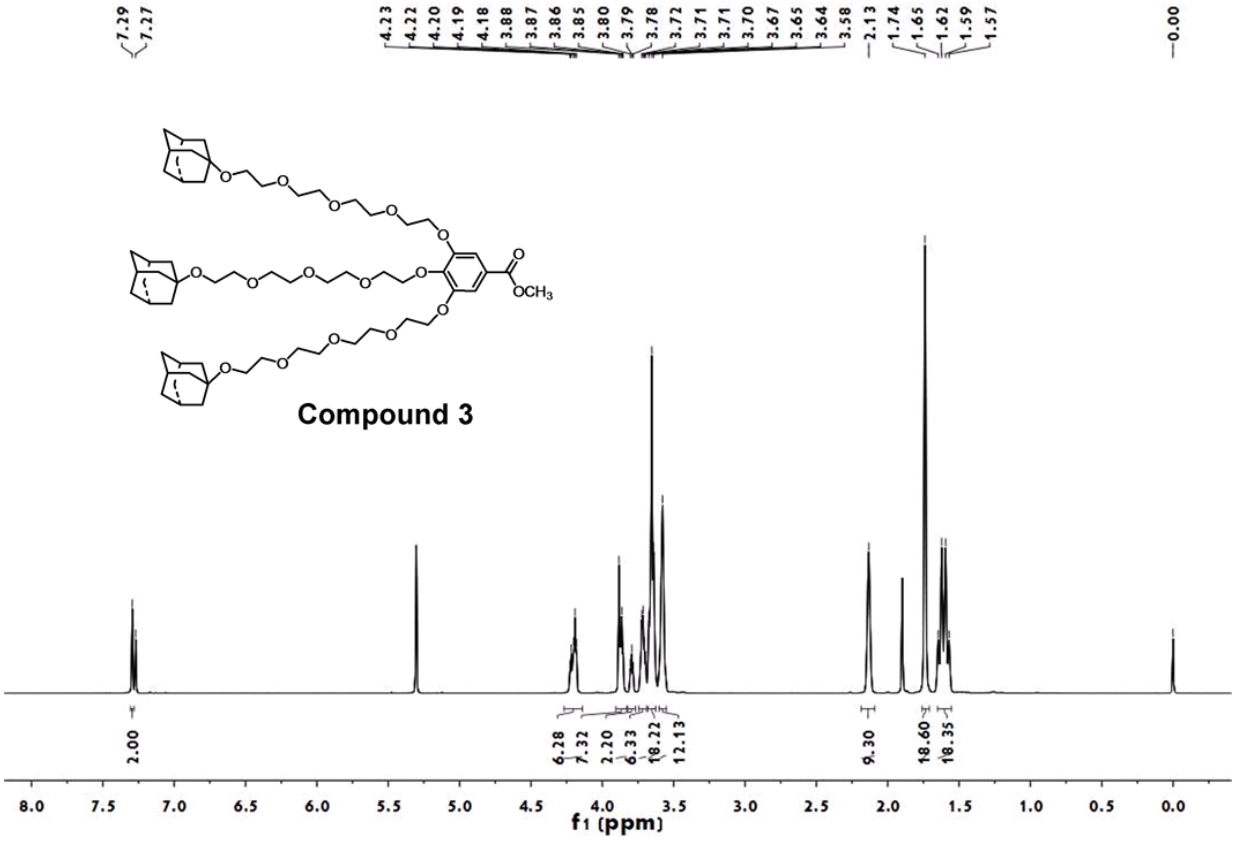


Fig. S5. ^1H NMR spectrum of compound **3** in $CDCl_3$.

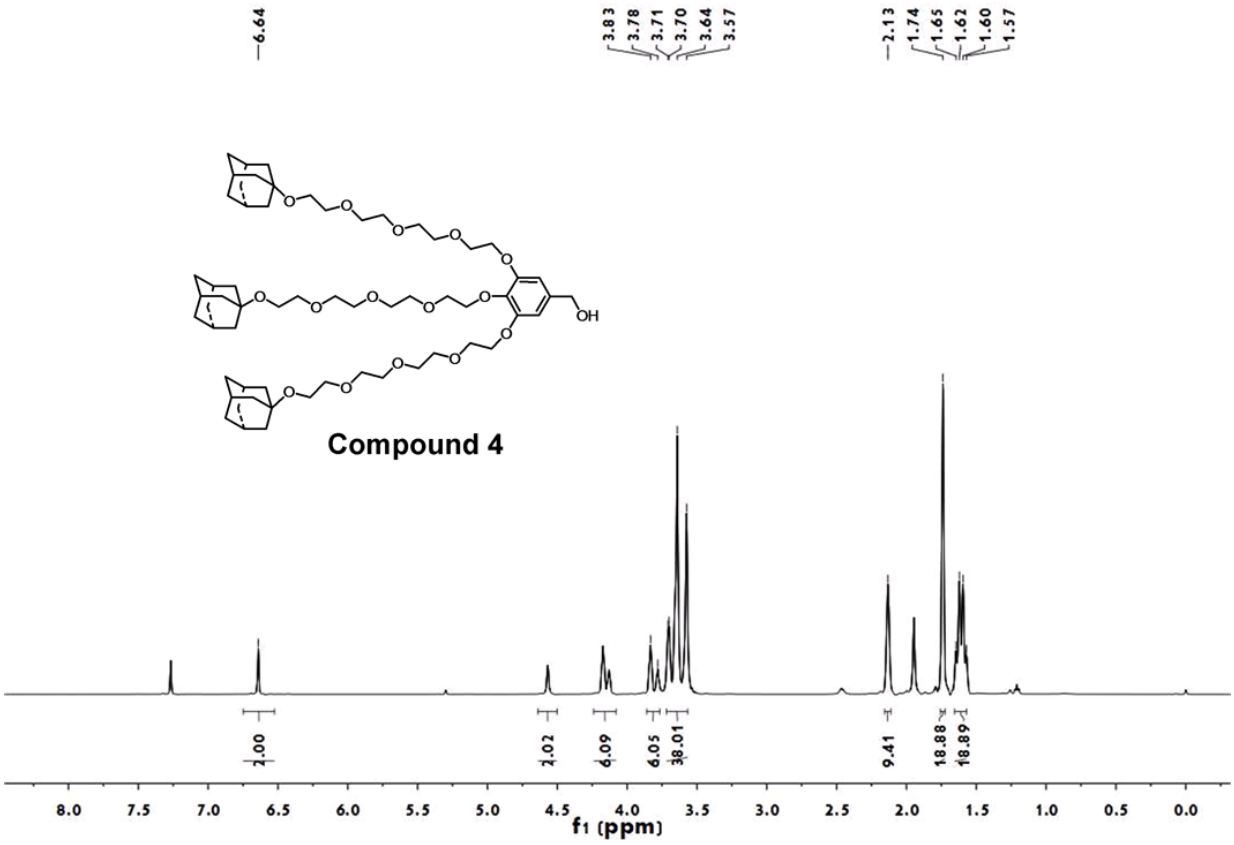


Fig. S6. ^{1}H NMR spectrum of compound **4** in $CDCl_3$.

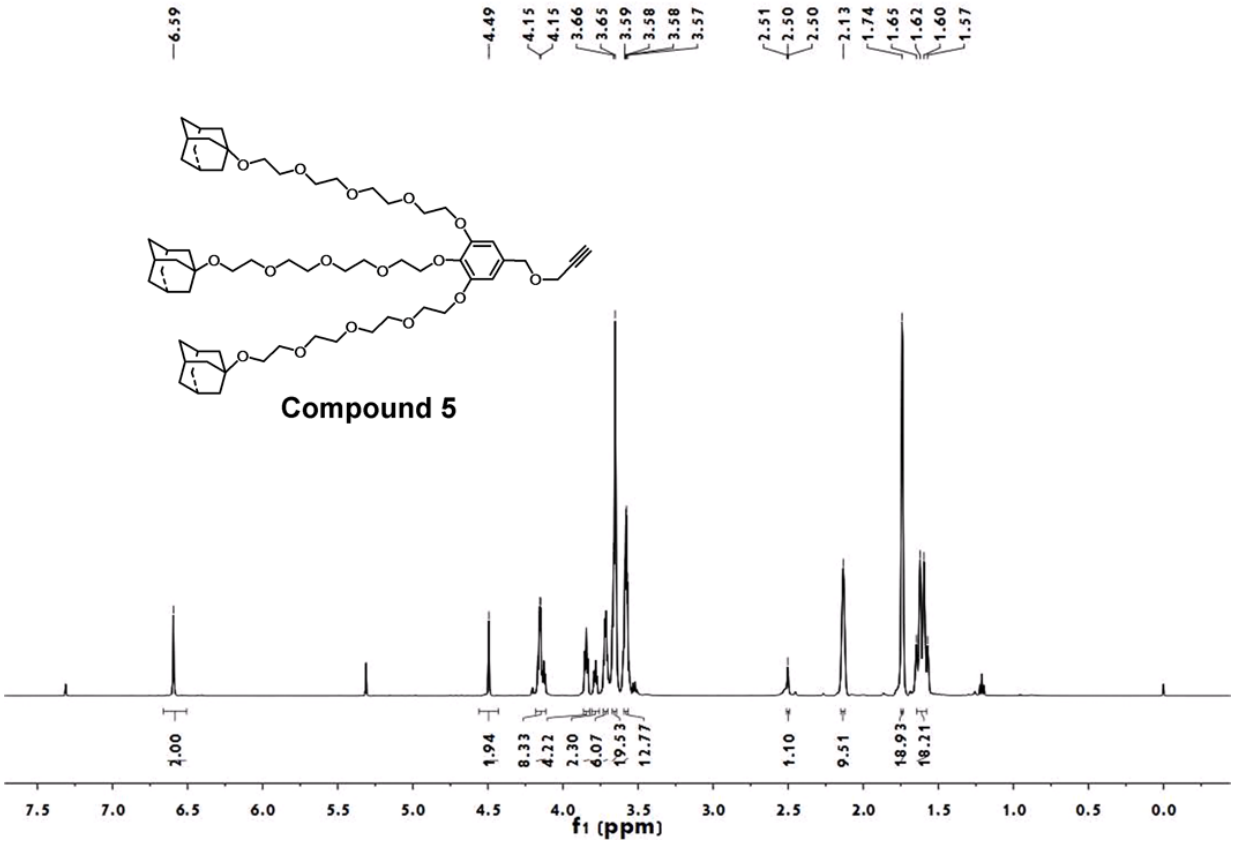


Fig. S7. ^{1}H NMR spectrum of compound **5** in $CDCl_3$.

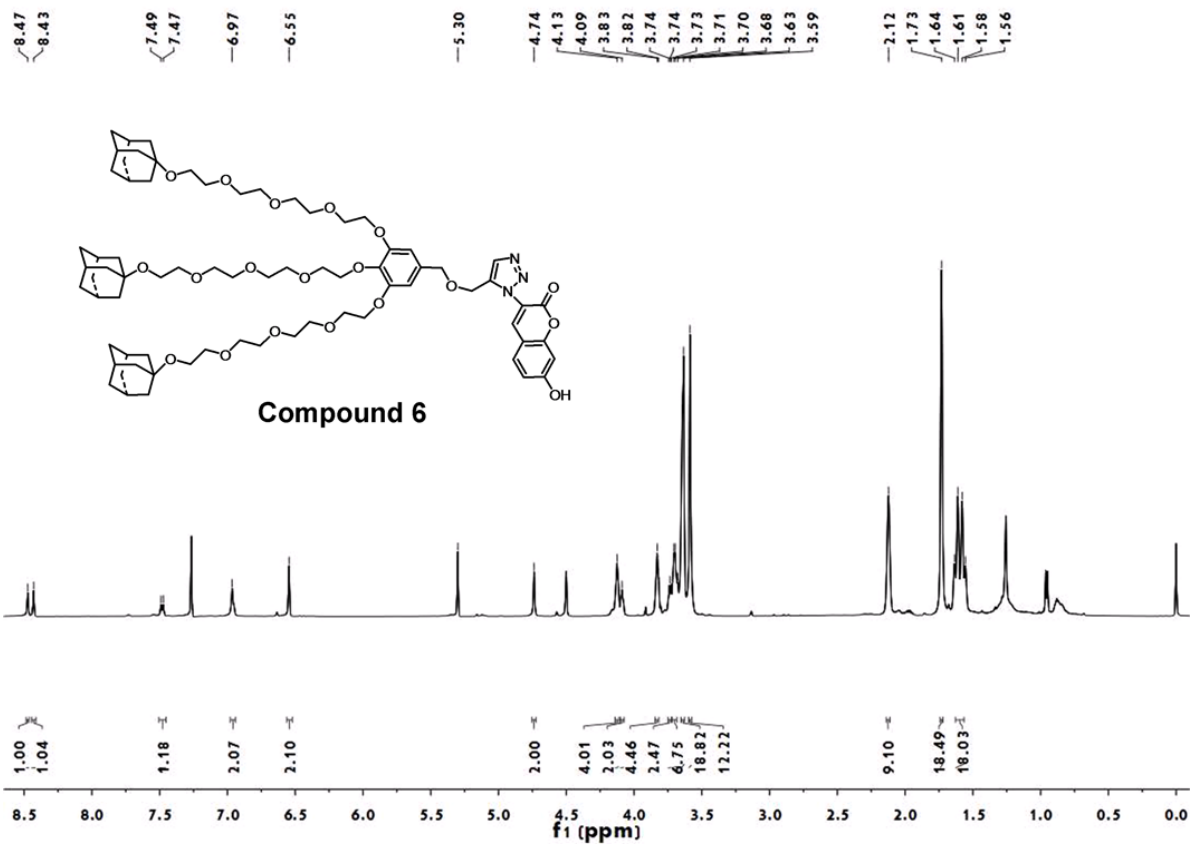


Fig. S8. ^{1}H NMR spectrum of compound **6** in $CDCl_3$.

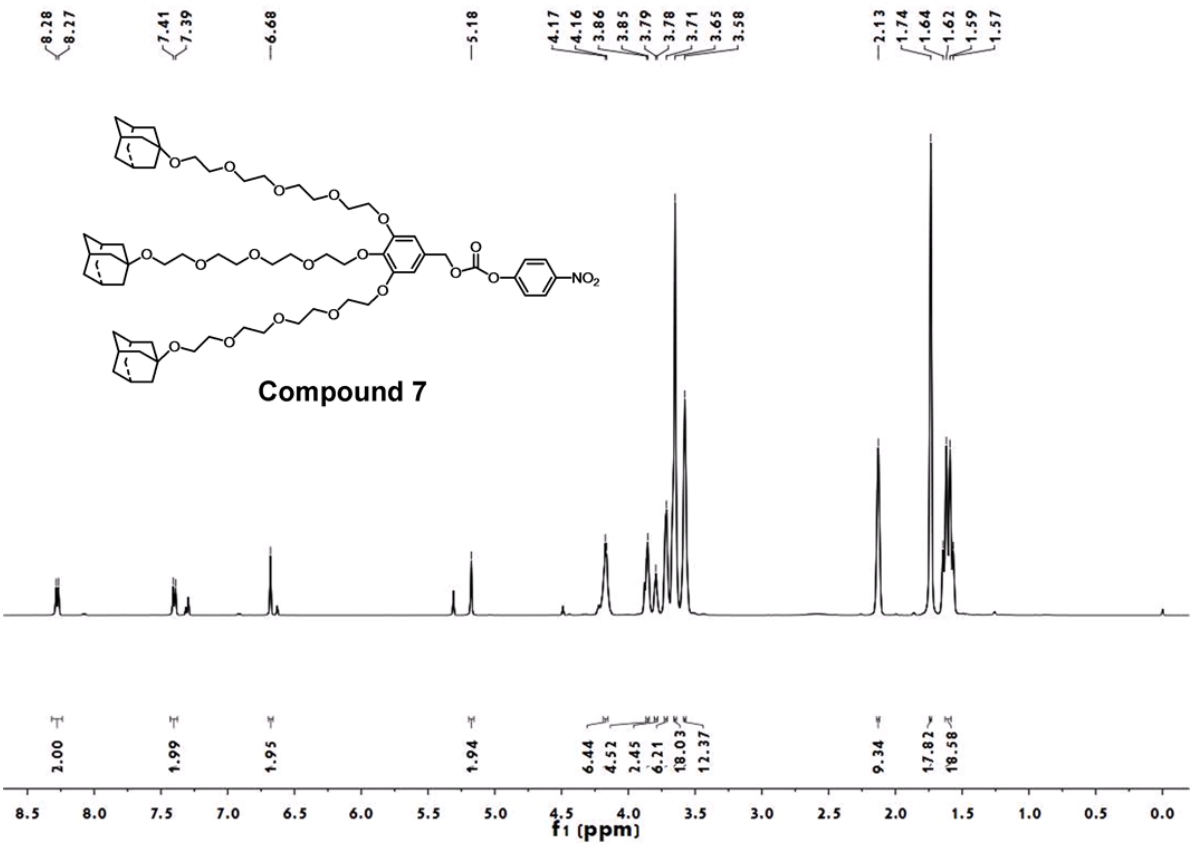


Fig. S9. ^{1}H NMR spectrum of compound **7** in $CDCl_3$.

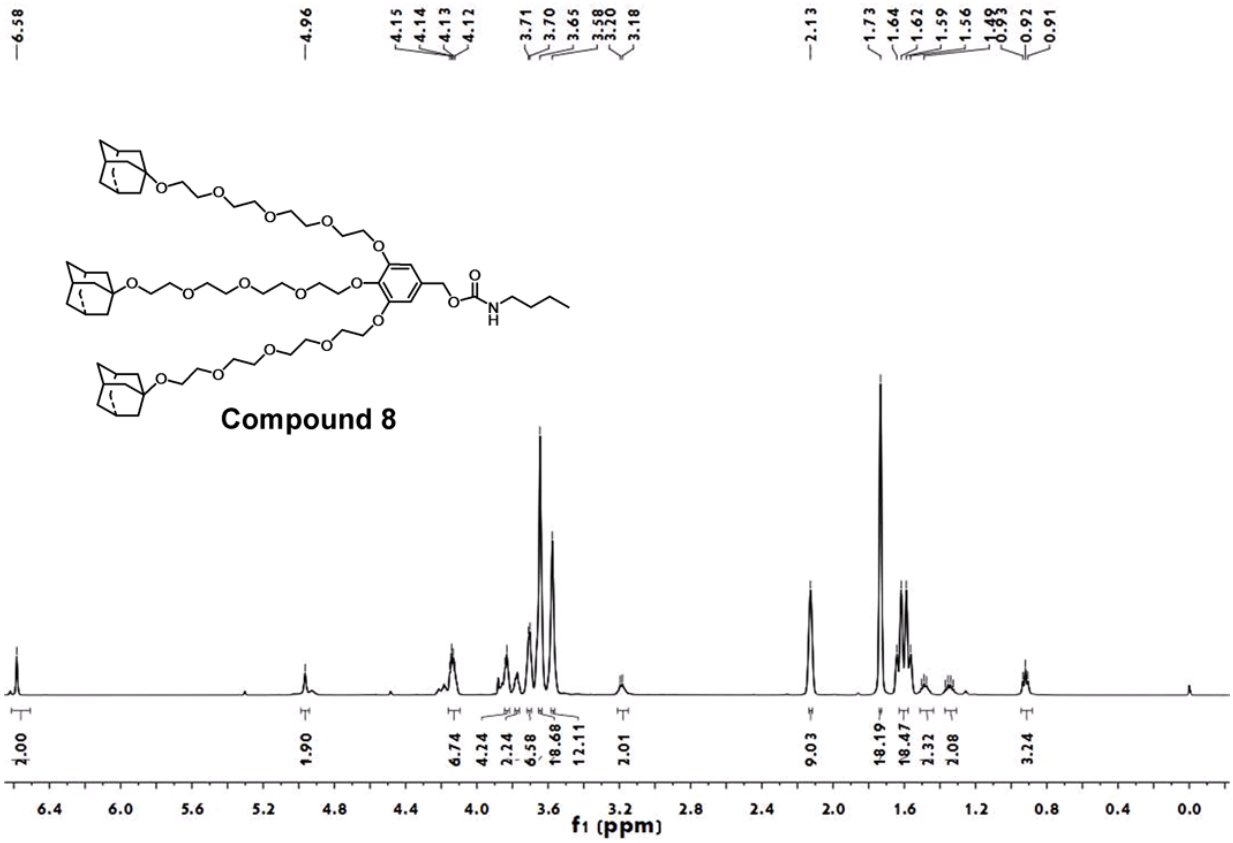


Fig. S10. ^{1}H NMR spectrum of compound **8** in $CDCl_3$.

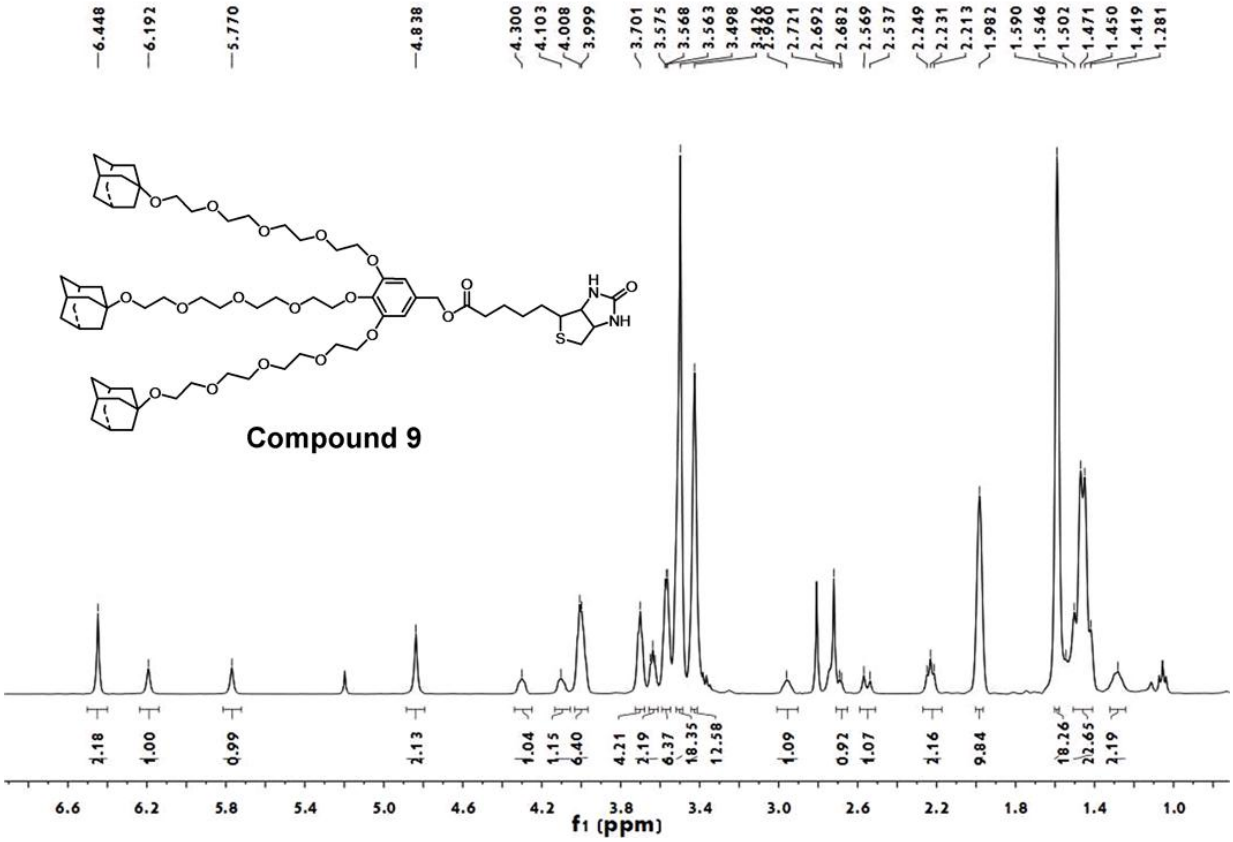


Fig. S11. ^{1}H NMR spectrum of compound **9** in $CDCl_3$.

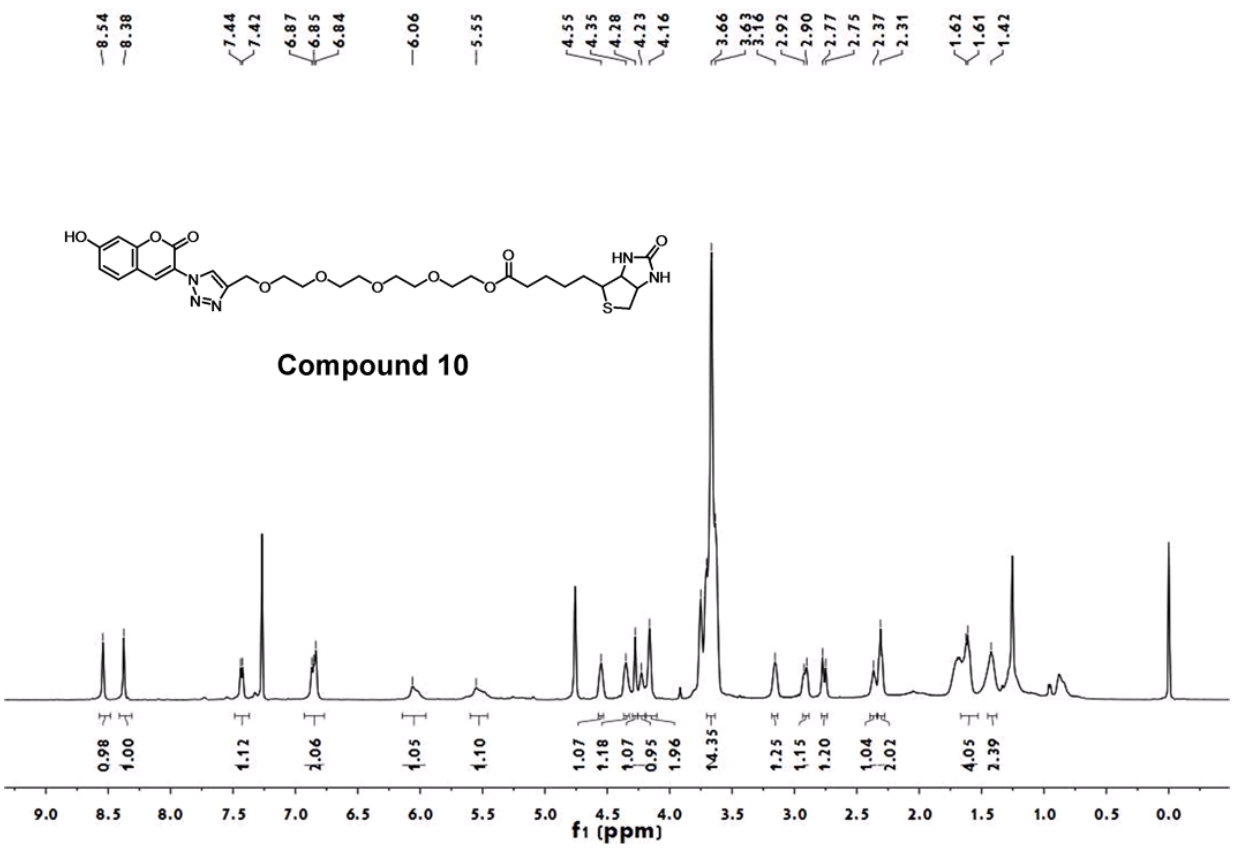


Fig. S12. ^{1}H NMR spectrum of compound **10** in $CDCl_3$.

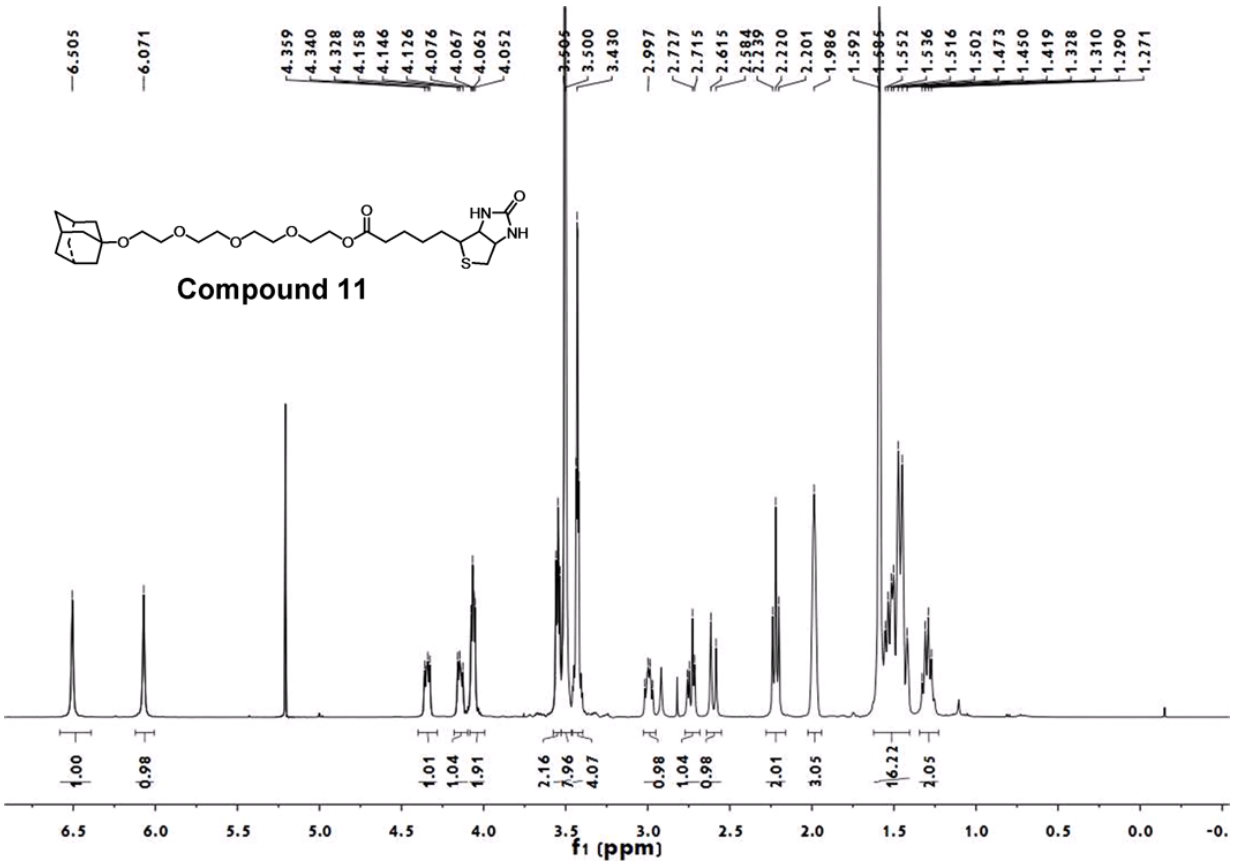


Fig. S13. ^{1}H NMR spectrum of compound **11** in $CDCl_3$.

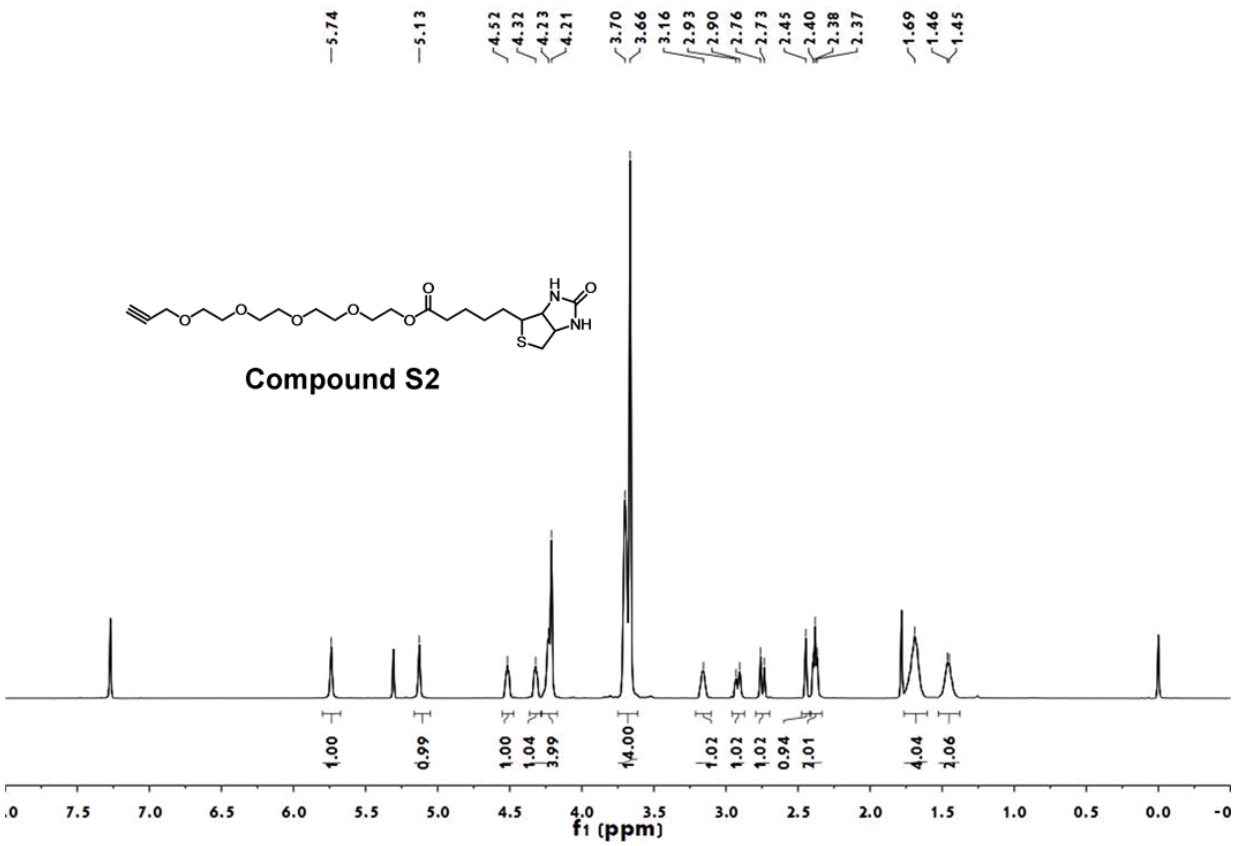


Fig. S14. ^{1}H NMR spectrum of compound **S2** in $CDCl_3$.