

Synthesis and characterization of a potential bifunctional C_{60} - I_h fullerene-based catechol amide ligand

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General materials and methods:

All the organic reagents were purchased from Aladdin. C₆₀-I_h fullerene (99.9%) was purchased from Puyang Yongxin Fullerene Technology Co., Ltd. The solvents were purchased from Chengdu Kelong Chemical Reagents Co. Anhydrous CH₂Cl₂ was distilled prior to use. The 300-400 mesh silica gel was purchased from Qingdao Hailang. ¹H NMR, ¹³C NMR spectra were recorded on Bruker Avance 300, Avance 400 or Avance 600 spectrometer. The FTIR spectra were obtained from Nicolet 380 FT-IR spectrophotometer (Thermo Fisher Nicolet, USA) with a resolution of 4 cm⁻¹ from 400 cm⁻¹ to 4000 cm⁻¹. The UV-Vis spectra were obtained from Evolution 201 UV-Vis spectrophotometer (Thermo Scientific Evolution 201, USA). Mass spectral analysis was conducted using Varian 1200 LC/MS and MALDI-TOF mass spectrometer (Bruker APEX II FT-ICR).

Synthesis Section:

2,3-Dibenzyloxybenzoic acid (2):[1] A solution of 2,3-dihydroxybenzoic acid **1** (10.20 g, 65.9 mmol), benzyl bromide (22.2 g, 130.0 mmol) and K₂CO₃ (18.0 g, 130 mmol) in acetone (220 ml) was refluxed for 24 h. After filtration, the solution was concentrated *in vacuo* to give the crude product as a clear oil. The crude product was dissolved in methanol (200 ml) and LiOH•H₂O (360.0 mmol, 15.10 g) was slowly added. The mixture was refluxed for 3 h. Then the solution was acidified with 3 N HCl to pH 2 and filtered to give the product **2** as a white solid. ¹H NMR (400 MHz, CDCl₃, 300.0 K): δ (ppm) = 7.50-7.10 (m, 12H, Ar-H), 7.03 (t, *J* = 8.0Hz, 1H, Ar-H), 5.12 (s, 2H, O-CH₂-Ar), 5.09 (s, 2H, O-CH₂-Ar). FT-IR (KBr): γ (cm⁻¹) (3100, 2700, 1683, 1035). APCI-MS calculated for C₂₁H₂₂O₄⁻ = 333.4; Found = 333.9.

2,3-Dibenzyloxy-N-(2-hydroxyethyl)benzamide (4a):[2] A solution of 2,3-dibenzyloxybenzoic acid **2** (1.67 g, 5.0 mmol), HOBt (0.12 g, 0.9 mmol) and DCC (1.24 g, 6.0 mmol) in CH₂Cl₂ (50 ml) was stirred for 30 min at room temperature. Ethanolamine (0.34 g, 5.5 mmol) was added dropwise over 3 min and the mixture stirred overnight. The solution was filtered to remove some of the 1,3-dicyclohexylurea (DCU). The filtrate was concentrated *in vacuo* and the residue was purified by flash column chromatography [2:3 acetone/hexane (v/v)] to give the product **4a** as a clear oil (80%). R_f = 0.4 [2:3 acetone/hexane (v/v)]; ¹H NMR (300 MHz, CDCl₃, 298.0 K): δ (ppm) = 8.30 (br s, 1H, CO-NH), 7.71 (m, 1H, Ar-H), 7.50-7.10 (m, 12H, Ar-H), 5.15 (s, 2H, O-CH₂-Ar), 5.10 (s, 2H, O-CH₂-Ar), 3.62 (t, 2H, CH₂), 3.40 (m, 2H, CH₂), 2.87 (br s, 1H, OH). ¹³C NMR (150 MHz, CDCl₃, 298.0 K): δ (ppm) = 165.8 (C=O), 150.9 (ArC), 146.1 (ArC), 135.6 (ArC), 128.1 (ArCH), 128.0 (ArCH), 127.9 (ArCH), 127.5 (ArCH), 126.9 (ArCH), 123.7 (ArCH), 122.5 (ArCH), 116.5 (ArCH), 75.7 (CH₂), 70.5 (CH₂), 61.9 (CH₂), 42.1 (CH₂). FT-IR (KBr): γ (cm⁻¹) (3347, 1625, 1577, 1555, 1498, 1028). APCI-MS calculated for C₂₃H₂₄O₄N⁺ = 378.4; Found = 378.0.

2,3-Dibenzyloxy-N-(3-hydroxypropyl)benzamide (4b):[2] A solution of 2,3-dibenzyloxybenzoic acid **2** (1.67 g, 5.0 mmol), HOBt (0.12 g, 0.9 mmol), and DCC (1.24 g, 6.0 mmol) in CH₂Cl₂ (50 ml) was stirred for 30 min at room temperature. 3-Amino-1-propanol (0.41 g, 5.5 mmol) was added dropwise over 3 min and the mixture stirred overnight. The solution was filtered to remove some of the dicyclohexyl urea (DCU).

The filtrate was concentrated *in vacuo* and the residue purified by flash column chromatography [2:3 acetone/hexane (v/v)] to give the product **4b** as a clear oil (85%). $R_f = 0.5$ [2:3 acetone/hexane (v/v)]; $^1\text{H NMR}$ (300 MHz, CDCl_3 , 298.0 K): δ (ppm) = 8.12 (br s, 1H, CO-NH), 7.72 (m, 1H, Ar-H), 7.50-7.12 (m, 12H, Ar-H), 5.16 (s, 2H, O-CH₂-Ar), 5.09 (s, 2H, O-CH₂-Ar), 3.50 (t, 2H, CH₂), 3.39 (m, 2H, CH₂), 1.52 (m, 2H, CH₂). $^{13}\text{C NMR}$ (150 MHz, CDCl_3 , 298.0 K): δ (ppm) = 165.7 (C=O), 150.9 (ArC), 146.1 (ArC), 135.5 (ArC), 128.0 (ArCH), 127.9 (ArCH), 127.5 (ArCH), 127.0 (ArCH), 123.7 (ArCH), 122.5 (ArCH), 116.4 (ArCH), 75.7 (CH₂), 70.5 (CH₂), 57.9 (CH₂), 34.9 (CH₂), 31.7 (CH₂). FT-IR (KBr): γ (cm^{-1}) (3327, 1635, 1577, 1540, 1452, 1028). APCI-MS calculated for $\text{C}_{24}\text{H}_{26}\text{O}_4\text{N}^+$ = 392.5; Found = 392.0.

2,3-Dibenzyloxy-N-(4-hydroxybutyl)benzamide (4c):[2] A solution of 2,3-dibenzyloxybenzoic acid **2** (1.67 g, 5.0 mmol), HOBT (0.12 g, 0.9 mmol) and DCC (1.24 g, 6.0 mmol) in CH_2Cl_2 (50 ml) was stirred for 30 min at room temperature. 4-Amino-1-butanol (0.49 g, 5.5 mmol) was added dropwise over 3 min and the mixture stirred overnight. The solution was filtered to remove some of the dicyclohexyl urea (DCU). The filtrate was concentrated *in vacuo* and the residue purified by flash column chromatography [2:3 acetone/hexane (v/v)] to give the product **4c** as a clear oil (90%). $R_f = 0.5$ [2:3 acetone/hexane (v/v)]. $^1\text{H NMR}$ (400 MHz, CDCl_3 , 298.0 K): δ (ppm) = 8.01 (br s, 1H, CO-NH), 7.74 (m, 1H, Ar-H), 7.50-7.10 (m, 12H, Ar-H), 5.16 (s, 2H, O-CH₂-Ar), 5.09 (s, 2H, O-CH₂-Ar), 3.58 (m, 2H, CH₂), 3.32 (m, 2H, CH₂), 1.46 (m, 4H, CH₂-CH₂). $^{13}\text{C NMR}$ (150MHz, CDCl_3 , 298.0 K): δ (ppm) = 164.4 (C=O), 150.9 (ArC), 146.0 (ArC), 135.6 (ArC), 127.9 (ArCH), 127.5 (ArCH), 126.9 (ArCH), 123.7 (ArCH), 122.5 (ArCH), 116.1 (ArCH), 75.6 (CH₂), 70.5 (CH₂), 61.5 (CH₂), 38.6 (CH₂), 29.0 (CH₂), 25.1 (CH₂). FT-IR (KBr): γ (cm^{-1}) (3327, 1635, 1577, 1540, 1452, 1033). APCI-MS calculated for $\text{C}_{25}\text{H}_{28}\text{O}_4\text{N}^+$ = 406.5; Found = 406.2.

Bis[2-(2,3-dibenzyloxybenzoylamino)ethyl] malonate (5a): A solution of malonyl dichloride (1.0 mmol) in CH_2Cl_2 (20 ml) was dropped in the solution of compound **4a** (0.75 g, 2.0 mmol), Et_3N (2 ml) in CH_2Cl_2 (20 ml) with icebath. The mixture stirred overnight. After evaporation of solvents and the residue purified by flash column chromatography [1:1 toluene/ethyl acetate (v/v)] to give the product **5a** as a clear oil (90%). $R_f = 0.7$ [1:1 toluene/ethyl acetate (v/v)]; $^1\text{H NMR}$ (300 MHz, CDCl_3 , 298.0 K): δ (ppm) = 8.13 (br s, 2H, CO-NH), 7.69 (m, 2H, Ar-H), 7.50-7.10 (m, 24H, Ar-H), 5.14 (s, 4H, O-CH₂-Ar), 5.06 (s, 4H, O-CH₂-Ar), 4.07 (t, 4H, CH₂), 3.51 (m, 4H, CH₂), 2.99 (s, 2H, CO-CH₂-CO). $^{13}\text{C NMR}$ (150 MHz, CDCl_3 , 298.0 K): δ (ppm) = 166.3 (C=O), 165.6 (C=O), 151.9 (ArC), 146.9 (ArC), 136.5 (ArC), 128.9 (ArCH), 128.8 (ArCH), 128.4 (ArCH), 127.8 (ArCH), 127.3 (ArCH), 124.7 (ArCH), 123.3 (ArCH), 117.2 (ArCH), 76.5 (CH₂), 71.4 (CH₂), 64.3 (CH₂), 40.9 (CH₂), 38.4 (CH₂). FT-IR (KBr): γ (cm^{-1}) (3381, 1753, 1735, 1658, 1576, 1530, 1454, 1027). UV-vis (CH_2Cl_2): λ_{max} (nm) (228, 294). APCI-MS calculated for $\text{C}_{49}\text{H}_{47}\text{O}_{10}\text{N}_2^+$ = 823.9; Found = 823.7.

Bis[3-(2,3-dibenzyloxybenzoylamino)propyl] malonate (5b): A solution of malonyl dichloride (1.0 mmol) in CH_2Cl_2 (20 ml) was dropped in the solution of compound **4b** (0.78 g,

2.0 mmol), Et₃N (2 ml) in CH₂Cl₂ (20 ml) with icebath. The mixture stirred overnight. After evaporation of solvents and the residue purified by flash column chromatography [1:1 toluene/ethyl acetate (v/v)] to give the product **5b** as a clear oil (90%). *R_f* = 0.7 [1:1 toluene/ethyl acetate (v/v)]; ¹H NMR (300 MHz, CDCl₃, 298.0 K): δ (ppm) = 8.00 (br s, 2H, CO-NH), 7.69 (m, 2H, Ar-H), 7.50-7.10 (m, 24H, Ar-H), 5.15 (s, 4H, O-CH₂-Ar), 5.08 (s, 4H, O-CH₂-Ar), 4.06 (t, 4H, CH₂), 3.33 (m, 4H, CH₂), 3.28 (s, 2H, CO-CH₂-CO), 1.68 (m, 4H, CH₂). ¹³C NMR (150 MHz, CDCl₃, 298.0 K): δ (ppm) = 166.6 (C=O), 165.5 (C=O), 151.9 (ArC), 147.0 (ArC), 136.6 (ArC), 129.0 (ArCH), 128.9 (ArCH), 128.4 (ArCH), 127.8 (ArCH), 124.5 (ArCH), 123.4 (ArCH), 117.1 (ArCH), 76.6 (CH₂), 71.5 (CH₂), 63.4 (CH₂), 41.4 (CH₂), 36.6 (CH₂), 28.5 (CH₂). FT-IR (KBr): γ (cm⁻¹) (3387, 1749, 1732, 1656, 1575, 1531, 1454, 1026). UV-vis (CH₂Cl₂): λ_{max} (nm) (228, 294). APCI-MS calculated for C₅₁H₅₁O₁₀N₂⁺ = 852.0; Found = 851.9.

Bis[4-(2,3-dibenzyloxybenzoylamino)butyl] malonate (5c): A solution of malonyl dichloride (1.0 mmol) in CH₂Cl₂ (20 ml) was dropped in the solution of compound **4c** (0.81 g, 2.0 mmol), Et₃N (2 ml) in CH₂Cl₂ (20 ml) with icebath. The mixture stirred overnight. After evaporation of solvents and the residue purified by flash column chromatography [1:1 toluene/ethyl acetate (v/v)] to give the product **5c** as a clear oil (95%). *R_f* = 0.7 [1:1 toluene/ethyl acetate (v/v)]; ¹H NMR (400 MHz, CDCl₃, 298.0 K): δ (ppm) = 7.95 (br s, 2H, CO-NH), 7.72 (m, 2H, Ar-H), 7.50-7.10 (m, 24H, Ar-H), 5.15 (s, 4H, O-CH₂-Ar), 5.08 (s, 4H, O-CH₂-Ar), 4.03 (t, *J* = 6.4, 4H, CH₂), 3.32 (s, 2H, CO-CH₂-CO), 3.26 (m, 4H, CH₂), 1.54 (m, 4H, CH₂), 1.37 (m, 4H, CH₂). ¹³C NMR (150 MHz, CDCl₃, 300.0 K): δ = 166.7 (C=O), 165.4 (C=O), 151.8 (ArC), 146.9 (ArC), 136.6 (ArCH), 128.9 (ArCH), 128.8 (ArCH), 128.4 (ArCH), 127.8 (ArCH), 124.6 (ArCH), 123.4 (ArCH), 117.1 (ArCH), 76.6 (CH₂), 71.4 (CH₂), 65.2 (CH₂), 60.6 (CH₂), 41.6 (CH₂), 39.3 (CH₂), 26.0 (CH₂), 25.9 (CH₂). FT-IR (KBr): γ (cm⁻¹) (3387, 1747, 1731, 1655, 1575, 1531, 1454, 1027). UV-vis (CH₂Cl₂): λ_{max} (nm) (228, 294). APCI-MS calculated for C₅₃H₅₅O₁₀N₂⁺ = 880.0; Found = 880.5.

Bis[2-(2,3-dihydroxybenzoylamino)ethyl] malonate (6a): A mixture of **5a** (0.99 g, 1.2 mmol) and Pd/C (10%) (200 mg) in THF (50 ml) was stirred under H₂ (130 ml/min) flow at 40 °C at atmospheric pressure for 5 h. The resulting mixture was filtered over Celite, evaporated to dryness and dried under vacuum to give **6a** as a clear oil (99%). ¹H NMR (600 MHz, DMSO-*d*₆, 298.0 K): δ = 8.90 (br s, 2H, CO-NH), 7.24 (m, 2H, Ar-H), 6.90 (m, 2H, Ar-H), 6.67 (m, *J* = 7.8Hz, 2H, Ar-H), 4.20 (t, 4H, *J* = 5.7Hz, CH₂), 3.52 (s, 2H, CO-CH₂-CO), 3.44 (m, 4H, CH₂). ¹³C NMR (150 MHz, DMSO-*d*₆, 298.0K): δ = 170.4 (C=O), 166.9 (C=O), 150.0 (ArC), 146.7 (ArC), 119.2 (ArCH), 118.4 (ArCH), 117.8 (ArCH), 115.3 (ArC), 63.6 (CH₂), 41.5 (CH₂), 38.3 (CH₂). FT-IR (KBr): γ (cm⁻¹) (3398, 2957, 2929, 1750, 1731, 1642, 1590, 1546, 1459). UV-vis (CH₂Cl₂): λ_{max} (nm) (251, 313). APCI-MS calculated for C₂₁H₂₃O₁₀N₂⁺ = 463.4; Found = 463.2.

Bis[3-(2,3-dihydroxybenzoylamino)propyl] malonate (6b): A mixture of **5b** (1.02 g, 1.2 mmol) and Pd/C (10%) (200 mg) in THF (50 ml) was stirred under H₂ (130 ml/min) flow for 5 h. The resulting mixture was filtered over Celite, evaporated to dryness and dried under vacuum to give **6b** as a clear oil (99%). ¹H NMR (300 MHz, DMSO-*d*₆, 298.0 K): δ = 12.74

(br s, 2H, Ar-OH), 9.17 (br s, 2H, Ar-OH), 8.82 (br s, 2H, CO-NH), 7.25 (d, 2H, Ar-H), 6.89 (d, 2H, Ar-H), 6.67 (t, $J = 7.9\text{Hz}$, 2H, Ar-H), 4.13 (t, $J = 6.45$, 4H, CH₂), 3.51 (s, 2H, CO-CH₂-CO), 3.34 (m, 4H, CH₂), 1.87 (m, 4H, -CH₂-). ¹³C NMR (150 MHz, DMSO-*d*₆, 298.0K): $\delta = 169.8$ (C=O), 166.5 (C=O), 149.6 (ArC), 146.2 (ArC), 118.8 (ArCH), 117.8 (ArCH), 117.1 (ArCH), 114.9 (ArC), 62.8 (CH₂), 41.2 (CH₂), 35.8 (CH₂), 27.9 (CH₂). FT-IR (KBr): γ (cm⁻¹) (3390, 2956, 1747, 1735, 1641, 1591, 1547, 1459). UV-vis (CH₂Cl₂): λ_{max} (nm) (251, 313). APCI-MS calculated for C₂₃H₂₆O₁₀N₂⁺ = 491.5; Found = 491.1.

Bis[2-(2,3-dihydroxybenzoylamino)butyl] malonate (6c): A mixture of **5c** (1.05 g, 1.2 mmol) and Pd/C (10%) (200 mg) in THF (50 ml) was stirred under H₂ (130 ml/min) flow for 6 h. The resulting mixture was filtered over Celite, evaporated to dryness and dried under vacuum to give **6c** as a clear oil (99%). ¹H NMR (600 MHz, DMSO-*d*₆, 298.0 K): $\delta = 8.80$ (br s, 2H, CO-NH), 7.25 (m, 2H, Ar-H), 6.88 (m, 2H, Ar-H), 6.66 (t, $J = 8.1\text{Hz}$, 2H, Ar-H), 4.09 (t, 4H, $J = 6.3\text{Hz}$, CH₂), 3.50 (s, 2H, CO-CH₂-CO), 3.44 (m, 4H, CH₂), 1.60 (m, 8H, CH₂-CH₂). ¹³C NMR (150 MHz, DMSO-*d*₆, 298.0 K): $\delta = 169.7$ (C=O), 166.6 (C=O), 149.6 (ArC), 146.2 (ArC), 118.7 (ArCH), 117.8 (ArCH), 117.0 (ArCH), 114.9 (ArC), 64.5 (CH₂), 41.1 (CH₂), 38.3 (CH₂), 25.5 (CH₂), 25.2 (CH₂). FT-IR (KBr): γ (cm⁻¹) (3399, 2926, 1745, 1735, 1639, 1594, 1545, 1459). UV-vis (CH₂Cl₂): λ_{max} (nm) (251, 313). APCI-MS calculated for C₂₅H₃₁O₁₀N₂⁺ = 519.5; Found = 519.7.

Bis[2-(2,3-dibenzyloxybenzoylamino)ethyl] 3'H-cyclopropa[1,9](C₆₀-I_h)[5,6]fullerene-3',3'-dicarboxylate (7a): C₆₀ (72 mg, 0.1 mmol) and CBr₄ (49.7 mg, 0.15 mmol) were dissolved in 40 ml of toluene by sonication, followed by the addition of malonate **5a** (82 mg, 0.1 mmol) and DBU (45 μ l, 0.3 mmol). The reaction was complete in 40 min. After conventional workup, the crude reaction mixture was chromatographed on a silica gel column using CS₂ as eluent to remove unreacted C₆₀, followed by [30:1 CH₂Cl₂/ethanol (v/v)] to yield, after evaporation and drying, give the desired product **7a** (50% based on the consumed C₆₀). ¹H NMR (400 MHz, CDCl₃, 298.0 K): $\delta = 8.20$ -7.84 (br m, 2H, CO-NH), 7.72-7.40 (m, 2H, Ar-H), 7.40-6.88 (m, 24H, Ar-H), 5.12-4.80 (m, 8H, 2(O-CH₂-Ar)), 4.47-3.95 (m, 4H, CH₂), 3.69-3.21 (m, 4H, CH₂). ¹³C NMR (100 MHz, CDCl₃, 298.0 K): δ (ppm) = 165.54 (C=O), 163.38 (C=O), 151.8 (ArC), 147.6 (ArC), 146.26 (1C), 145.18 (3C), 145.16 (3C), 145.12 (3C), 145.07 (1C), 145.00 (3C), 144.96 (1C), 144.92 (1C), 144.88 (2C), 144.73 (1C), 144.66 (3C), 144.63 (2C), 144.49 (3C), 143.84 (2C), 143.74 (3C), 143.16 (4C), 143.03 (1C), 142.93 (3C), 142.87 (3C), 142.76 (1C), 142.16 (3C), 141.75 (3C), 140.81 (3C), 138.80 (3C), 136.45 (ArC), 128.92 (ArCH), 128.81 (ArCH), 128.78 (ArCH), 128.72 (ArCH), 128.28 (ArCH), 127.70 (ArCH), 127.63 (ArCH), 124.45 (ArCH), 123.37 (ArCH), 117.08 (ArCH), 76.57 (CH₂), 71.42 (CH₂), 71.30 (2C, *sp*³), 65.66 (CH₂), 40.84 (CH₂), 38.35 (CH₂). FT-IR (KBr): γ (cm⁻¹) (3390, 1741, 1641, 1575, 1538, 1459, 1022, 526). UV-vis (CH₂Cl₂): λ_{max} (nm) (229, 260, 326, 426). MALDI-TOF HRMS calculated for C₁₀₉H₄₅O₁₀N₂⁺ = 1542.3108; Found = 1542.3108.

Bis[3-(2,3-dibenzyloxybenzoylamino)propyl] 3'H-cyclopropa[1,9](C₆₀-I_h)[5,6]fullerene-3',3'-dicarboxylate (7b): C₆₀ (72 mg, 0.1 mmol) and CBr₄ (49.7 mg, 0.15 mmol) were dissolved in 40 ml of toluene by sonication, followed by the addition of malonate **5b** (85 mg, 0.1 mmol) and DBU (45 μ l, 0.3 mmol). The reaction was complete in 40 min. After

conventional workup, the crude reaction mixture was chromatographed on a silica gel column using CS₂ as eluent to remove unreacted C₆₀, followed by [30:1 CH₂Cl₂/ethanol (v/v)] to yield, after evaporation and drying, give the desired product **7b** (52% based on the consumed C₆₀). ¹H NMR (400 MHz, CDCl₃, 298.0 K): δ = 8.31-7.84 (br m, 2H, CO-NH), 7.80-7.5 (m, 2H, Ar-H), 7.50-6.87 (m, 24H, Ar-H), 5.32-4.80 (m, 8H, 2(O-CH₂-Ar)), 4.58-3.90 (m, 4H, CH₂), 3.80-3.30 (m, 4H, CH₂), 2.00-1.00 (m, 4H, CH₂). ¹³C NMR (100 MHz, CDCl₃, 298.0 K): δ (ppm) = 165.47 (C=O), 163.26 (C=O), 151.74 (ArC), 146.74 (ArC), 146.31 (3C), 146.24 (1C), 146.20 (1C), 146.17 (1C), 145.88 (1C), 145.31 (3C), 145.20 (2C), 145.12 (3C), 145.11 (2C), 145.08 (2C), 145.05 (1C), 144.95 (2C), 144.60 (2C), 144.44 (2C), 143.94 (1C), 143.79 (1C), 143.56 (1C), 143.51 (1C), 143.19 (2C), 142.87 (1C), 142.81 (1C), 142.63 (1C), 142.24 (2C), 142.10 (1C), 141.69 (3C), 141.64 (1C), 141.26 (1C), 140.75 (2C), 139.88 (1C), 136.41 (ArC), 128.88 (ArC), 128.86 (ArC), 128.77 (ArC), 128.74 (ArC), 128.71 (ArC), 128.67 (ArC), 128.21 (ArC), 127.61 (ArC), 124.41 (ArC), 123.23 (ArC), 117.03 (ArC), 76.52 (CH₂), 71.18 (CH₂), 71.16 (2C, sp³), 65.34 (CH₂), 38.40 (CH₂), 38.22 (CH₂), 29.69 (CH₂). FT-IR (KBr): γ (cm⁻¹) (3399, 1741, 1640, 1589, 1543, 1453, 1026, 526). UV-vis (CH₂Cl₂): λ_{max} (nm) (229, 254, 322, 428). MALDI-TOF HRMS calculated for C₁₁₁H₄₉O₁₀N₂⁺ = 1570.3421; Found = 1570.3421.

Bis[4-(2,3-dibenzyloxybenzoylamino)butyl] 3'H-cyclopropa[1,9](C₆₀-I_h)[5,6]fullerene-3',3'-dicarboxylate (7c): C₆₀ (72 mg, 0.1 mmol) and CBr₄ (49.7 mg, 0.15 mmol) were dissolved in 40 ml of toluene by sonication, followed by the addition of malonate **5c** (88 mg, 0.1 mmol) and DBU (45 μl, 0.3 mmol). The reaction was complete in 40 min. After conventional workup, the crude reaction mixture was chromatographed on a silica gel column using CS₂ as eluent to remove unreacted C₆₀, followed by [30:1 CH₂Cl₂/ethanol (v/v)] to yield, after evaporation and drying, give the desired product **7c** (55% based on the consumed C₆₀). ¹H NMR (400 MHz, CDCl₃, 298.0 K): δ = 8.11-7.82 (br m, 2H, CO-NH), 7.72-7.58 (m, 2H, Ar-H), 7.50-6.55 (m, 24H, Ar-H), 5.22-4.80 (m, 8H, 2(O-CH₂-Ar)), 4.60-3.83 (m, 4H, CH₂), 3.67-2.94 (m, 4H, CH₂), 2.00-0.91 (m, 8H, CH₂-CH₂). ¹³C NMR (100 MHz, CDCl₃, 298.0 K): δ = 167.9 (C=O), 165.3 (C=O), 151.8 (ArC), 148.5 (ArC), 145.78 (2C), 145.59 (1C), 145.56 (1C), 145.29 (3C), 145.24 (2C), 145.21 (3C), 145.12 (3C), 145.07 (2C), 144.70 (4C), 144.65 (2C), 144.63 (3C), 144.46 (2C), 143.96 (2C), 143.89 (1C), 143.76 (2C), 143.30 (1C), 143.28 (2C), 143.12 (2C), 143.03 (3C), 143.01 (3C), 142.86 (2C), 142.45 (2C), 142.23 (2C), 142.12 (2C), 142.02 (1C), 141.15 (2C), 140.96 (2C), 136.4 (ArC), 128.80 (ArCH), 128.74 (ArCH), 128.67 (ArCH), 128.41 (ArCH), 128.32 (ArCH), 127.69 (ArCH), 127.69 (ArCH), 127.58 (ArCH), 124.52 (ArCH), 117.11 (ArCH), 76.48 (CH₂), 71.69 (CH₂), 71.40 (2C, sp³), 70.63 (CH₂), 65.90 (CH₂), 39.49 (CH₂), 39.11 (CH₂), 26.30 (CH₂), 26.20 (CH₂). FT-IR (KBr): γ (cm⁻¹) (3387, 1731, 1639, 1576, 1541, 1454, 1026, 526). UV-vis (CH₂Cl₂): λ_{max} (nm) (232, 253, 302, 324, 428). MALDI-TOF HRMS calculated for C₁₁₃H₅₃O₁₀N₂⁺ = 1598.3734; Found = 1598.3734.

Bis[2-(2,3-dihydroxybenzoylamino)ethyl] 3'H-cyclopropa[1,9](C₆₀-I_h)[5,6]fullerene-3',3'-dicarboxylate (8a): malonate **6a** (161.8 mg, 0.35 mmol) and NBS (62.0 mg, 0.35 mmol) were dissolved in ethyl acetate, the reaction was complete in 30 min at room temperature. After evaporation, the residue was dissolved in 50 ml of chlorobenzene/DMSO [2:1 (v/v)],

and this was added dropwise to the solution of C₆₀ (250.6 mg, 0.35 mmol) and Gly (182.9 mg, 2.44 mmol) in 250 ml of chlorobenzene/DMSO [2:1 (v/v)], and the mixture was stirred overnight. The reaction mixture was washed with water (300 ml×3), the organic phase was concentrated. The residue was chromatographed on a silica gel column using CS₂ as eluent to remove unreacted C₆₀, followed by [10:1 CH₂Cl₂/ethanol (v/v)] to give the desired product **8a** (40% based on the consumed C₆₀). ¹H NMR (400 MHz, DMSO-*d*₆, 295.1 K): δ = 8.39 (br s, 2H, CO-NH), 6.90-7.69 (m, 6H, Ar-H), 4.16 (4H, CH₂). FT-IR (KBr): γ (cm⁻¹) (3434, 2921, 2851, 1733, 1656, 1636, 1456, 1085, 526). UV-vis (CH₂Cl₂): λ_{max} (nm) (258, 329, 430). MALDI-TOF HRMS calculated for C₈₁H₂₁O₁₀N₂⁺ = 1181.1196; Found = 1181.1196.

Bis[3-(2,3-dihydroxybenzoylamino)propyl] 3'H-cyclopropa[1,9](C₆₀-I_h)[5,6]fullerene-3',3'-dicarboxylate (8b): malonate **6b** (171.7 mg, 0.35 mmol) and NBS (62.0 mg, 0.35 mmol) were dissolved in ethyl acetate, the reaction was complete in 30 min at room temperature. After evaporation, the residue was dissolved in 50 ml of chlorobenzene/DMSO [2:1 (v/v)], and this was added dropwise to the solution of C₆₀ (250.6 mg, 0.35 mmol) and Gly (182.9 mg, 2.44 mmol) in 250 ml of chlorobenzene/DMSO [2:1 (v/v)], and the mixture was stirred overnight. The reaction mixture was washed with water (300 ml×3), the organic phase was concentrated. The residue was chromatographed on a silica gel column using CS₂ as eluent to remove unreacted C₆₀, followed by [10:1 CH₂Cl₂/ethanol (v/v)] to give the desired product **8b** (41% based on the consumed C₆₀). ¹H NMR (600 MHz, DMSO-*d*₆, 358.1 K): δ = 12.44 (br s, 2H, Ar-OH), 8.76 (br s, 2H, Ar-OH), 8.56 (br s, 2H, CO-NH), 7.24 (d, *J* = 7.2Hz, 2H, Ar-H), 6.90 (d, *J* = 7.2Hz, 2H, Ar-H), 6.66 (t, *J* = 7.2Hz, 2H, Ar-H), 4.14 (m, 4H, CH₂), 3.36 (m, 4H, CH₂), 1.89 (m, 4H, CH₂). FT-IR (KBr): γ (cm⁻¹) (3400, 2920, 2848, 1731, 1636, 1576, 1511, 1456, 1036, 526). UV-vis (CH₂Cl₂): λ_{max} (nm) (258, 329, 430). MALDI-TOF HRMS calculated for C₈₃H₂₅O₁₀N₂⁺ = 1209.1509; Found = 1209.1509.

Bis[4-(2,3-dihydroxybenzoylamino)butyl] 3'H-cyclopropa[1,9](C₆₀-I_h)[5,6]fullerene-3',3'-dicarboxylate (8c): malonate **6c** (180.5 mg, 0.35 mmol) and NBS (62.0 mg, 0.35 mmol) were dissolved in ethyl acetate, the reaction was complete in 30 min at room temperature. After evaporation, the residue was dissolved in 50 ml of chlorobenzene/DMSO [2:1 (v/v)], and this was added dropwise to the solution of C₆₀ (250.6 mg, 0.35 mmol) and Gly (182.9 mg, 2.44 mmol) in 250 ml of chlorobenzene/DMSO [2:1 (v/v)], and the mixture was stirred overnight. The reaction mixture was washed with water (300 ml×3), the organic phase was concentrated. The residue was chromatographed on a silica gel column using CS₂ as eluent to remove unreacted C₆₀, followed by [10:1 CH₂Cl₂/ethanol (v/v)] to give the desired product **8c** (42% based on the consumed C₆₀). ¹H NMR (600 MHz, DMSO-*d*₆, 298.0 K): δ = 7.67 (2H, Ar-H), 7.21 (2H, Ar-H), 6.66 (2H, Ar-H), 4.13 (4H, CH₂), 3.48 (4H, CH₂), 1.66 (8H, CH₂-CH₂). FT-IR (KBr): γ (cm⁻¹) (3400, 2925, 2871, 1732, 1657, 1496, 1462, 1026, 528). UV-vis (CH₂Cl₂): λ_{max} (nm) (258, 329, 430). MALDI-TOF HRMS calculated for C₈₅H₂₉O₁₀N₂⁺ = 1238.1466; Found = 1238.1466.

2014-01-07 jinbo-4

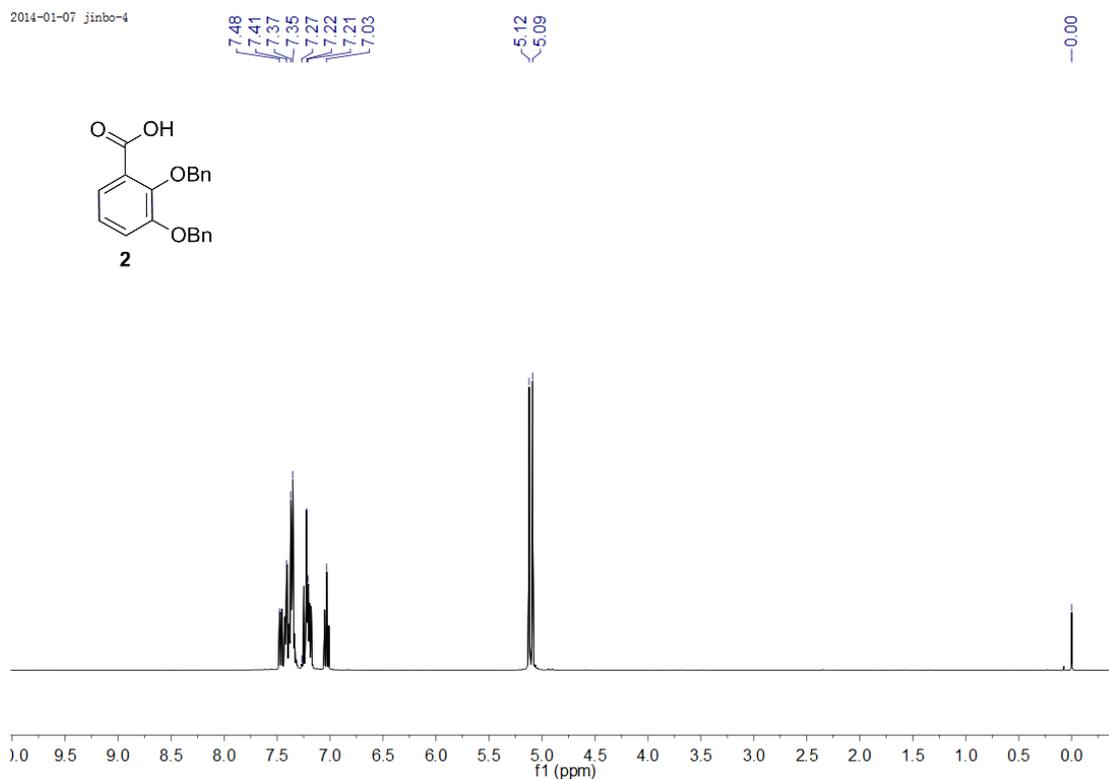


Fig. S1 The ¹H NMR (400 MHz, CDCl₃, 300.0K) spectrum of **2**

2015-11-18 w201311-0843-2

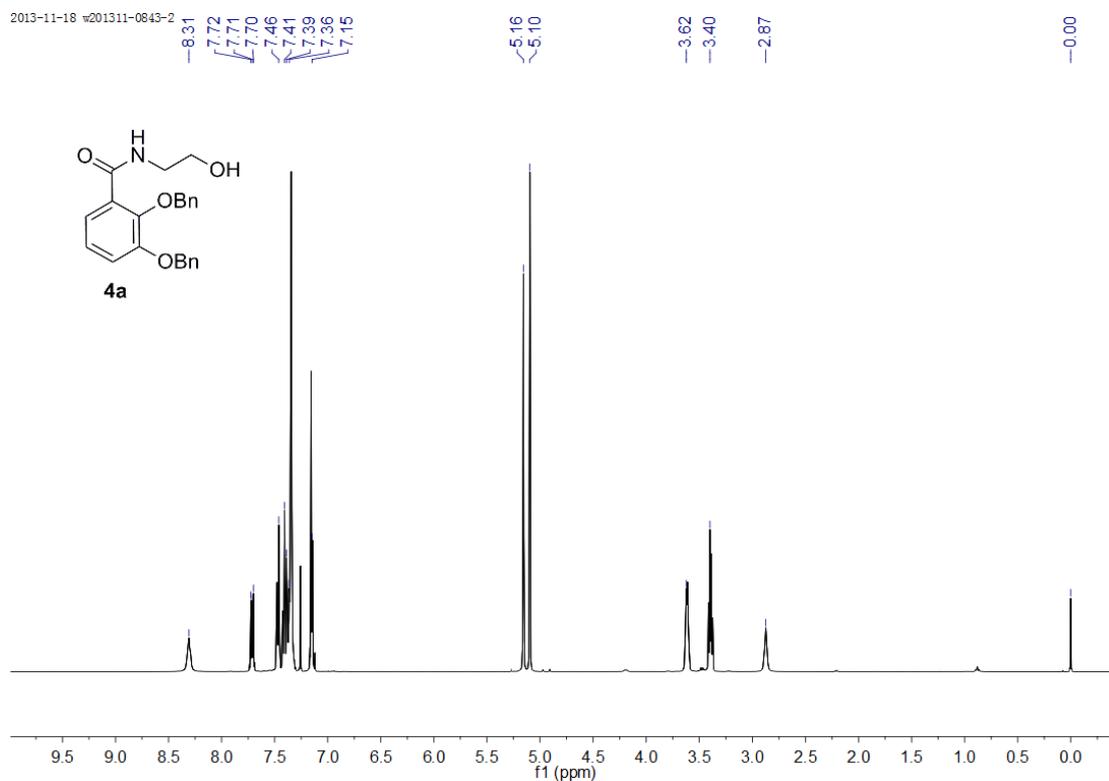


Fig. S2 The ¹H NMR (300MHz, CDCl₃, 298.0K) spectrum of **4a**

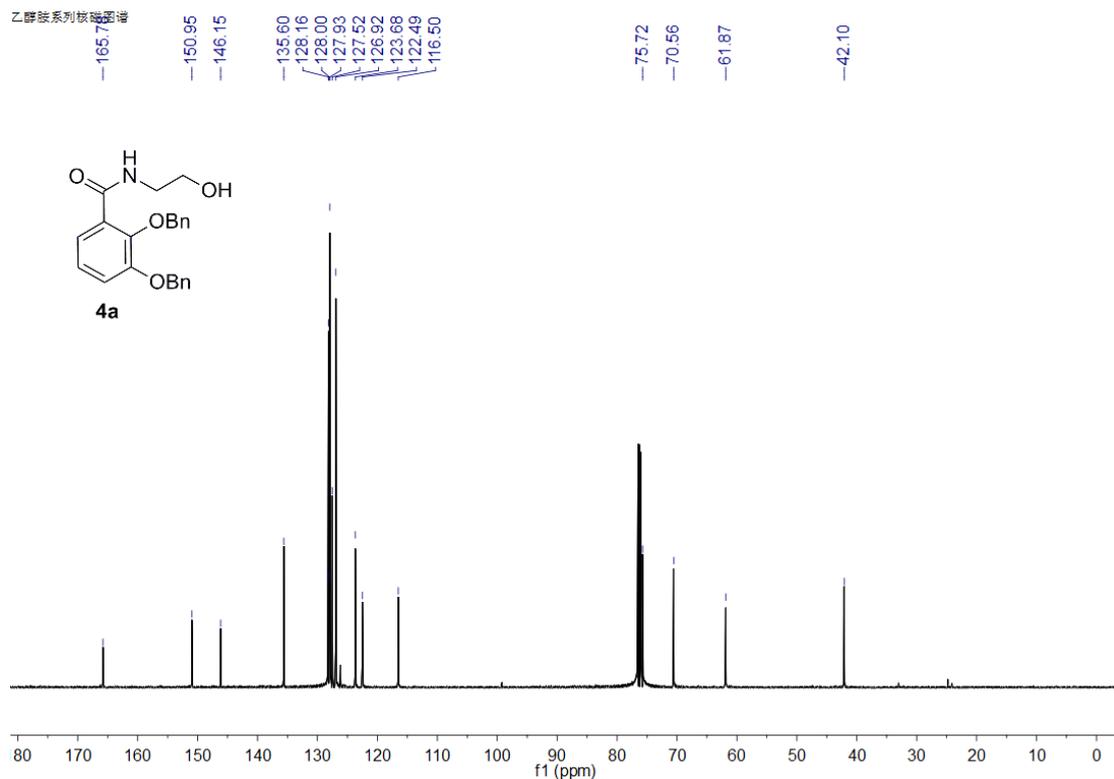


Fig. S3 The ^{13}C NMR (150MHz, CDCl_3 , 298.0K) spectrum of **4a**

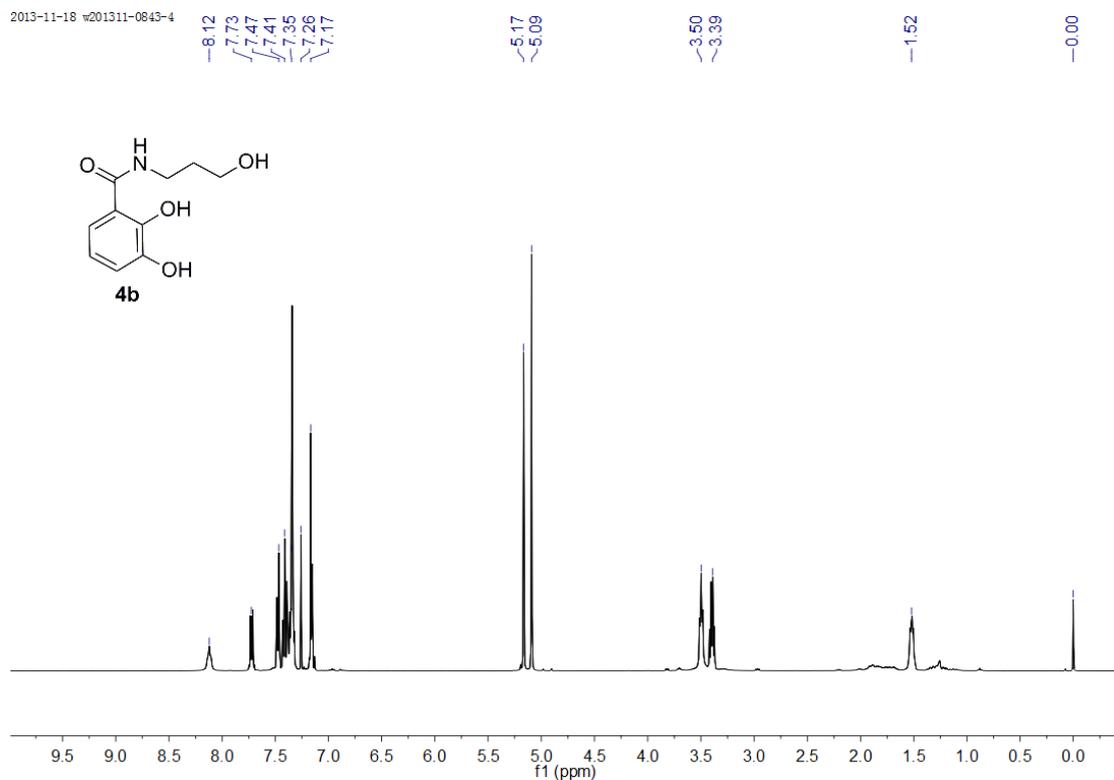


Fig. S4 The ^1H NMR (300MHz, CDCl_3 , 298.0K) spectrum of **4b**

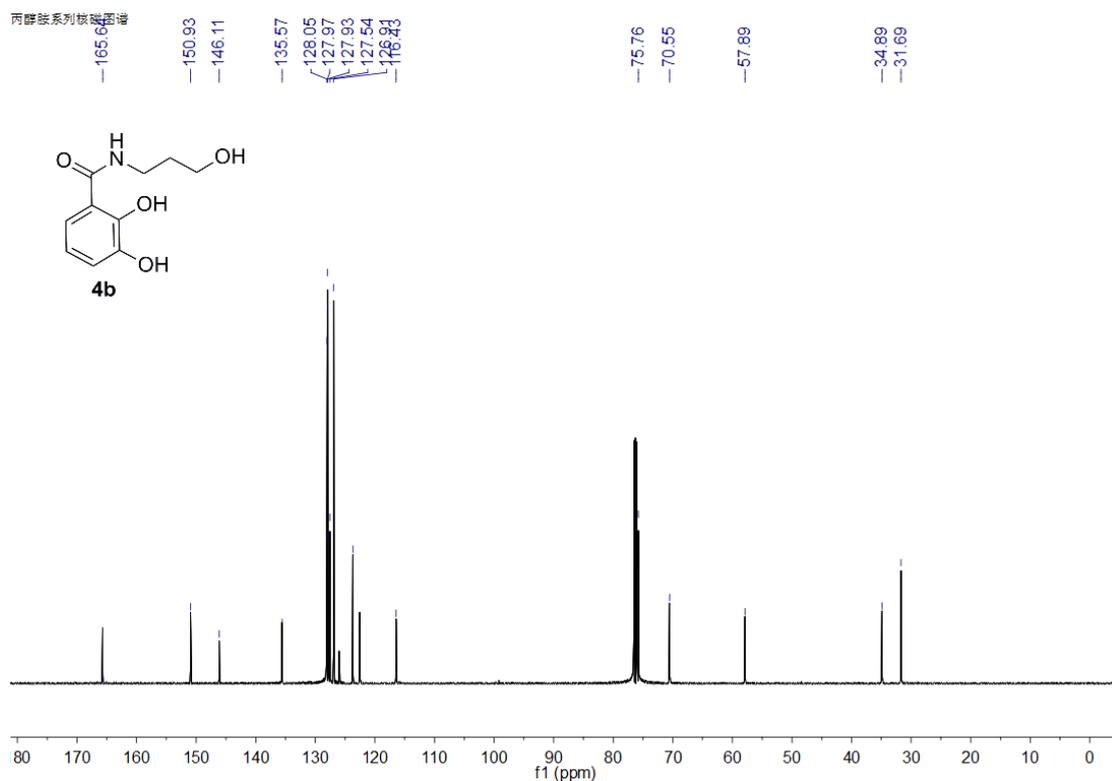


Fig. S5 The ^{13}C NMR (150MHz, CDCl_3 , 298.0K) spectrum of **4b**

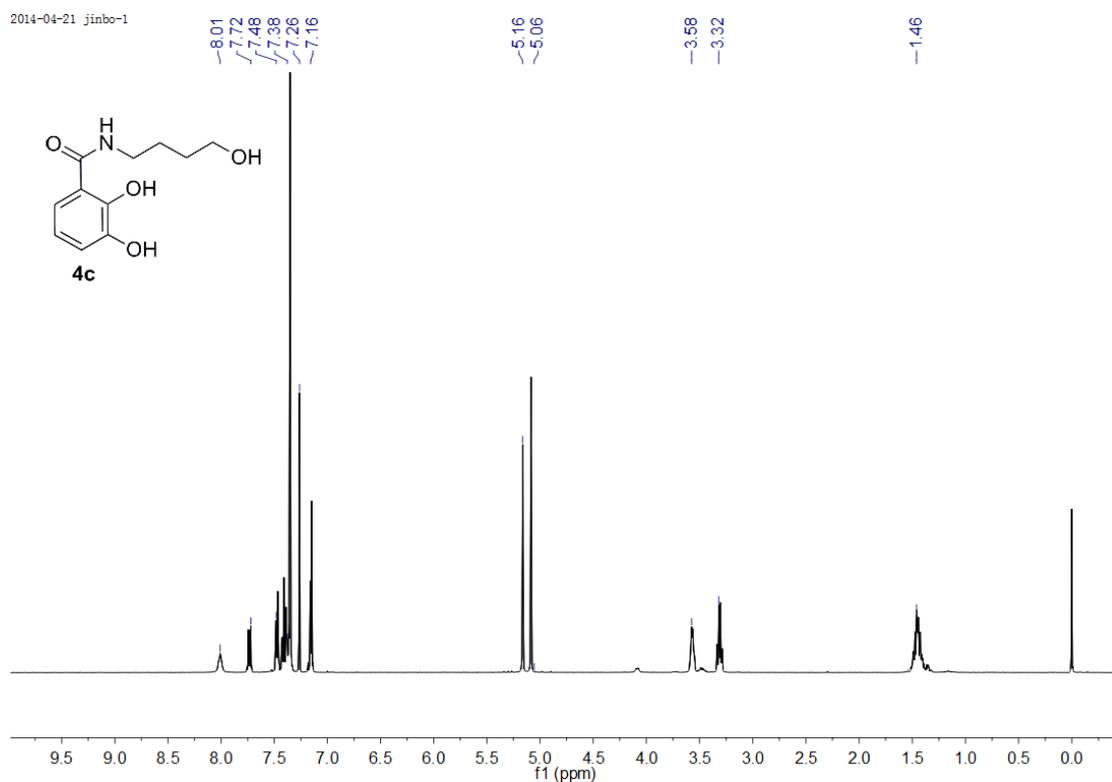


Fig. S6 The ^1H NMR (400MHz, CDCl_3 , 298.0K) spectrum of **4c**

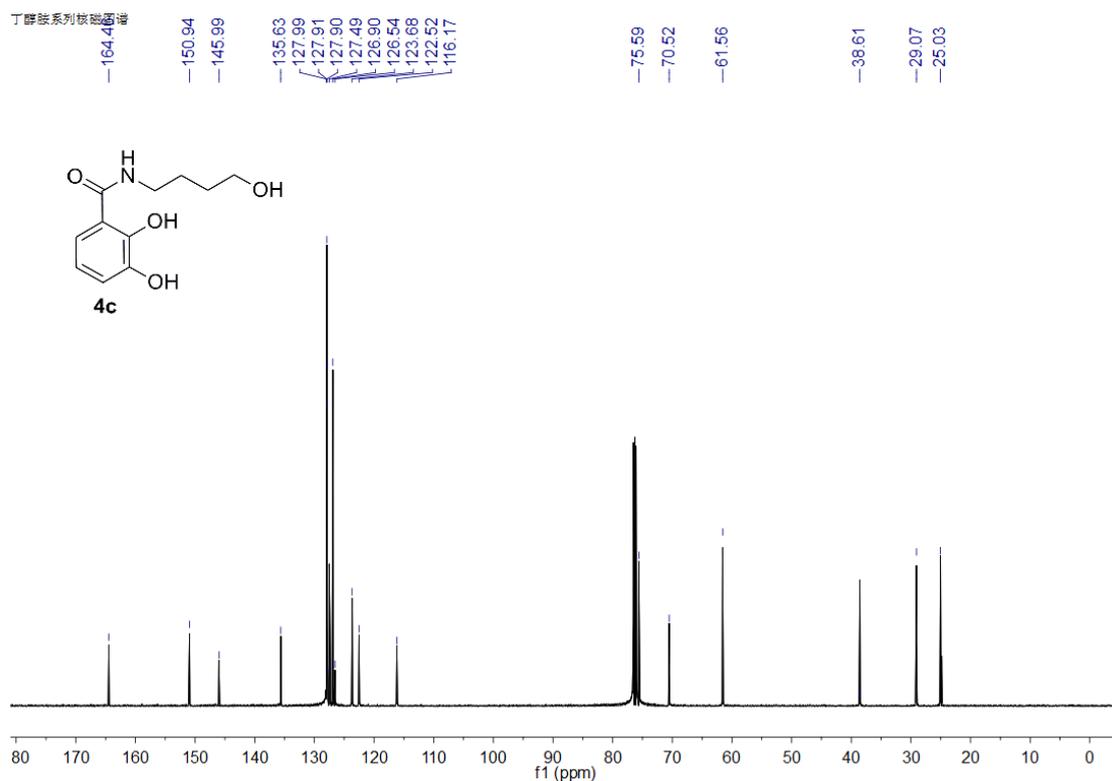


Fig. S7 The ^{13}C NMR (150MHz, CDCl_3 , 298.0K) spectrum of **4c**

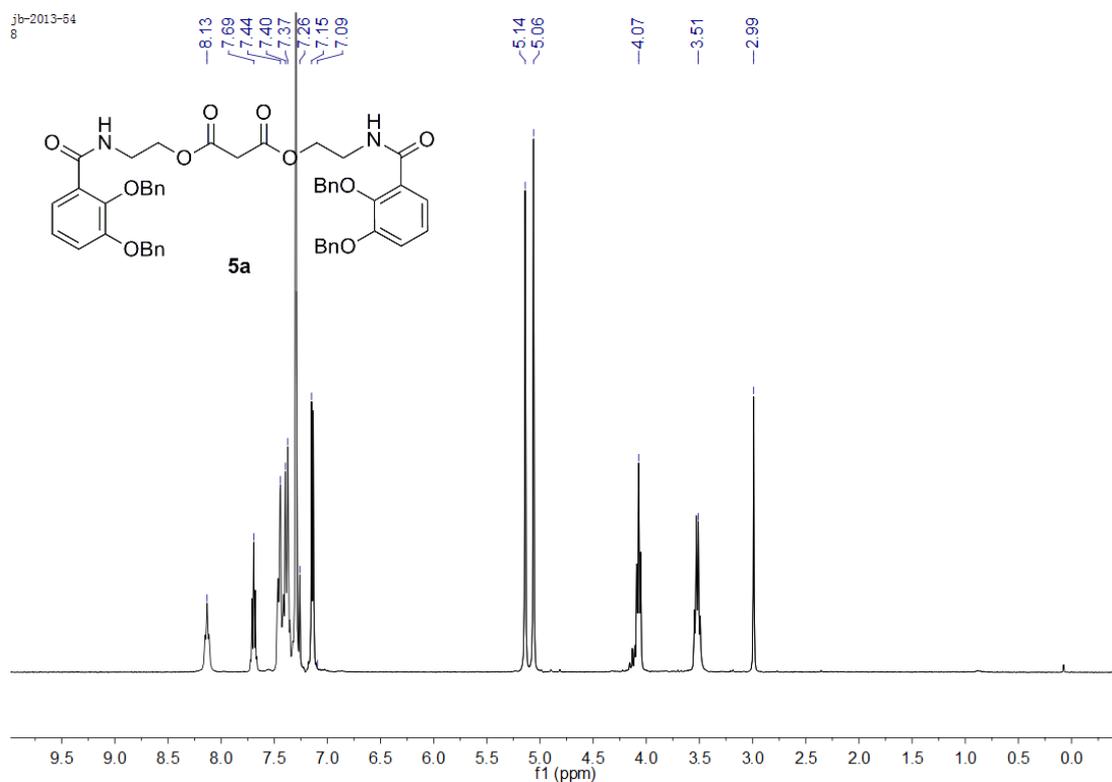


Fig. S8 The ^1H NMR (300MHz, CDCl_3 , 298.0K) spectrum of **5a**

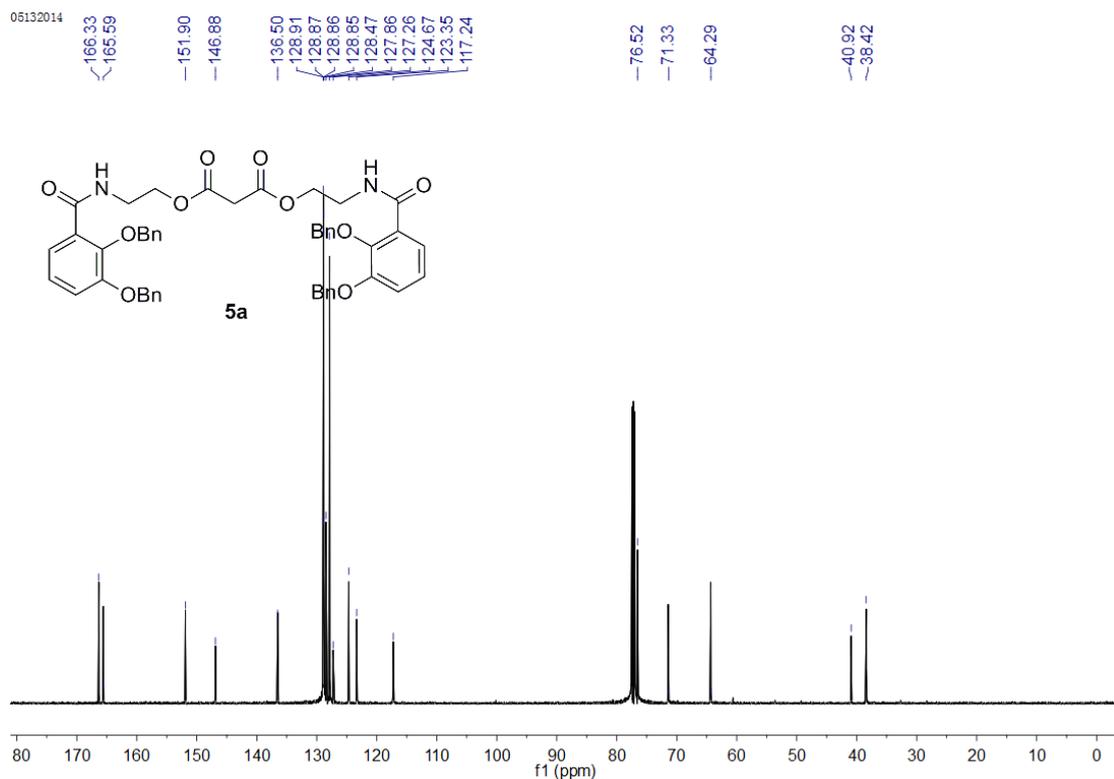


Fig. S9 The ^{13}C NMR (150MHz, CDCl_3 , 298.0K) spectrum of **5a**

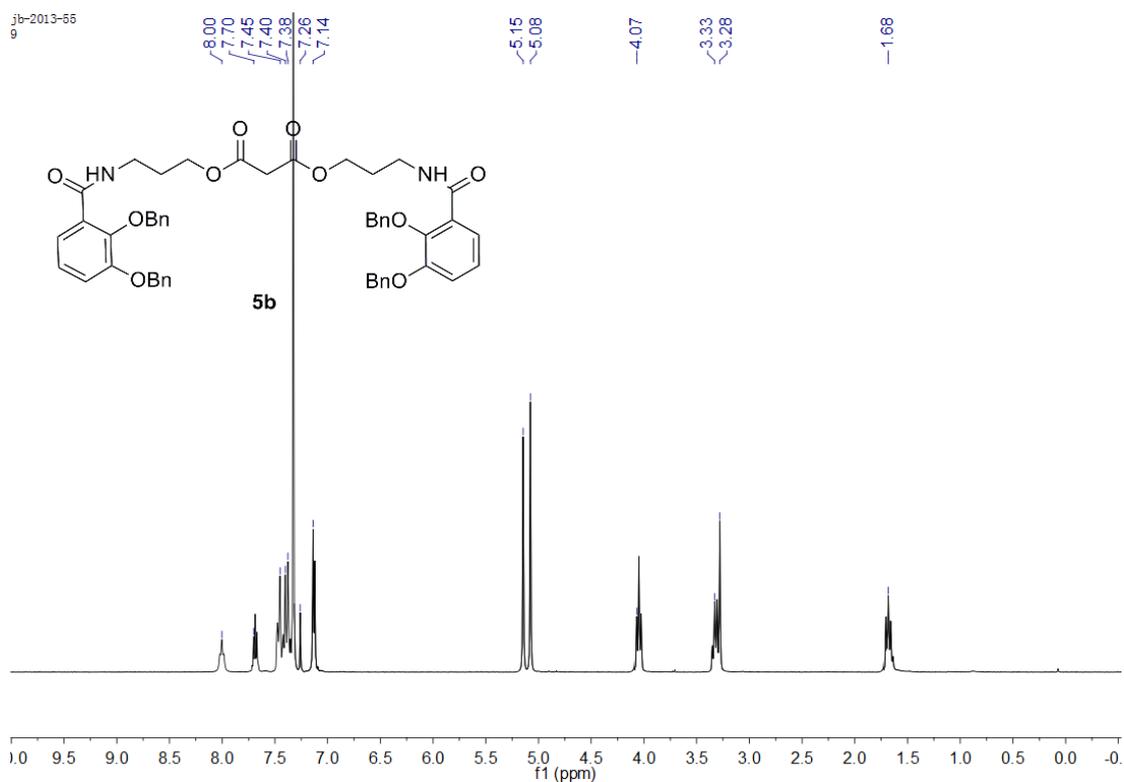


Fig. S10 The ^1H NMR (300MHz, CDCl_3 , 298.0K) spectrum of **5b**

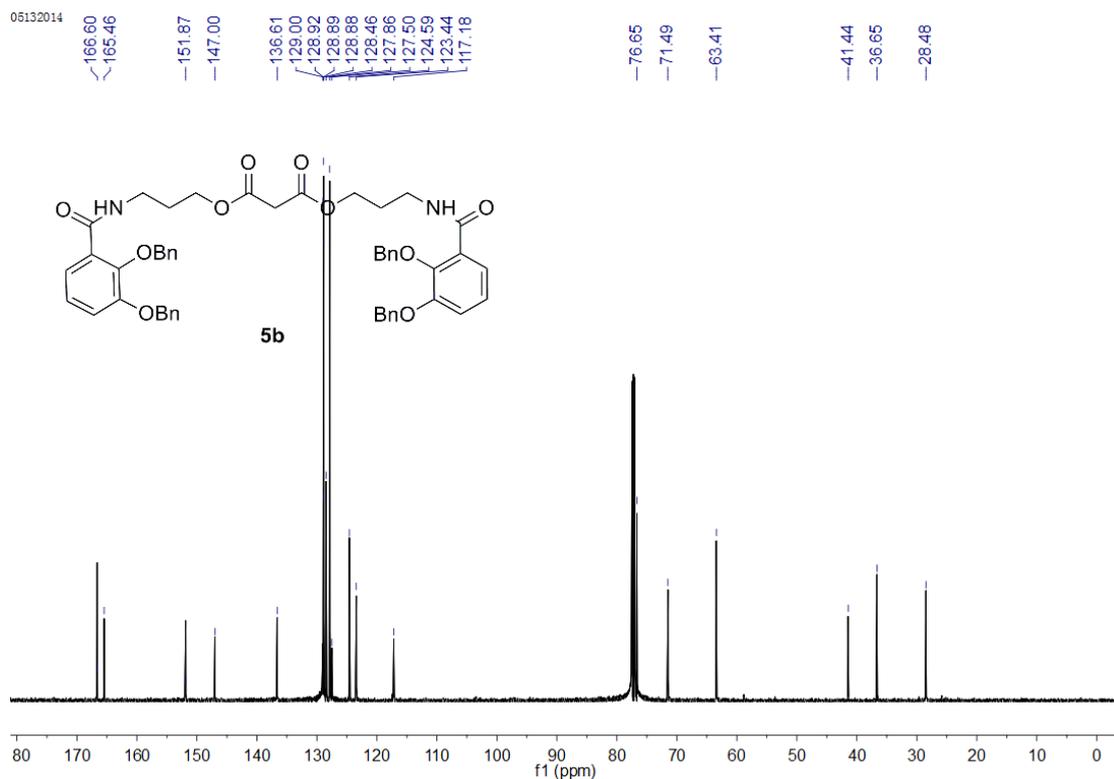


Fig. S11 The ^{13}C NMR (150MHz, CDCl_3 , 298.0K) spectrum of **5b**

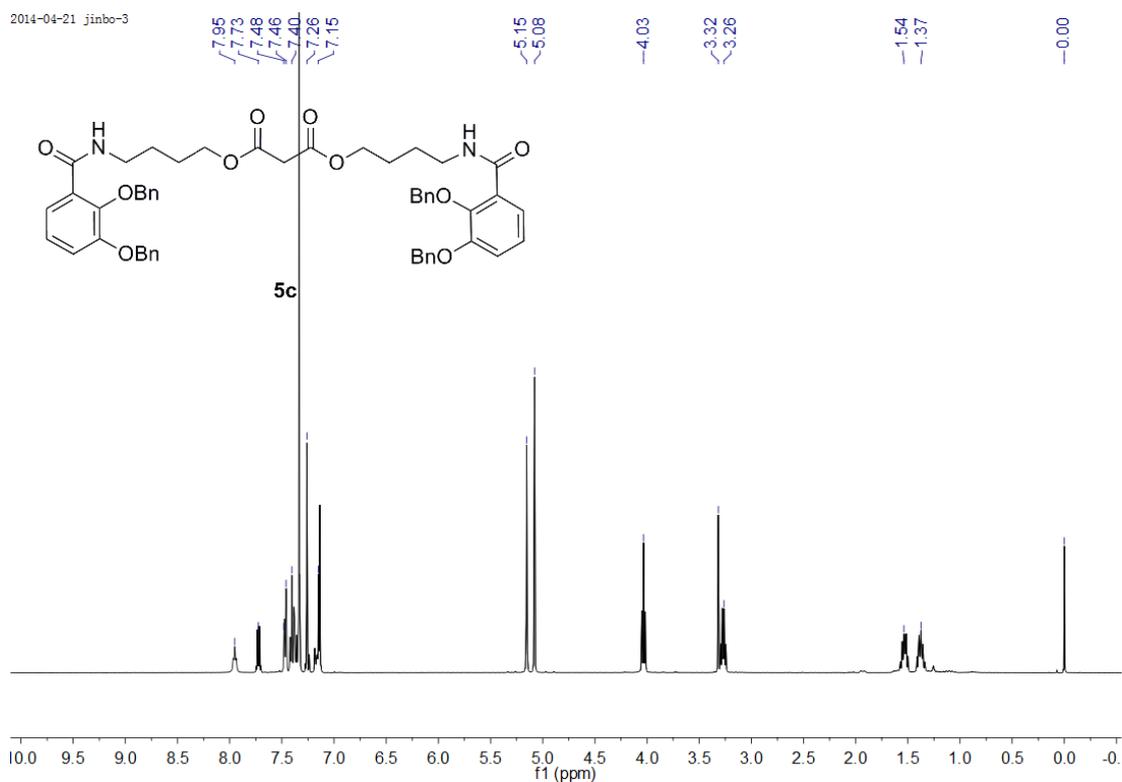


Fig. S12 The ^1H NMR (400MHz, CDCl_3 , 298.0K) spectrum of **5c**

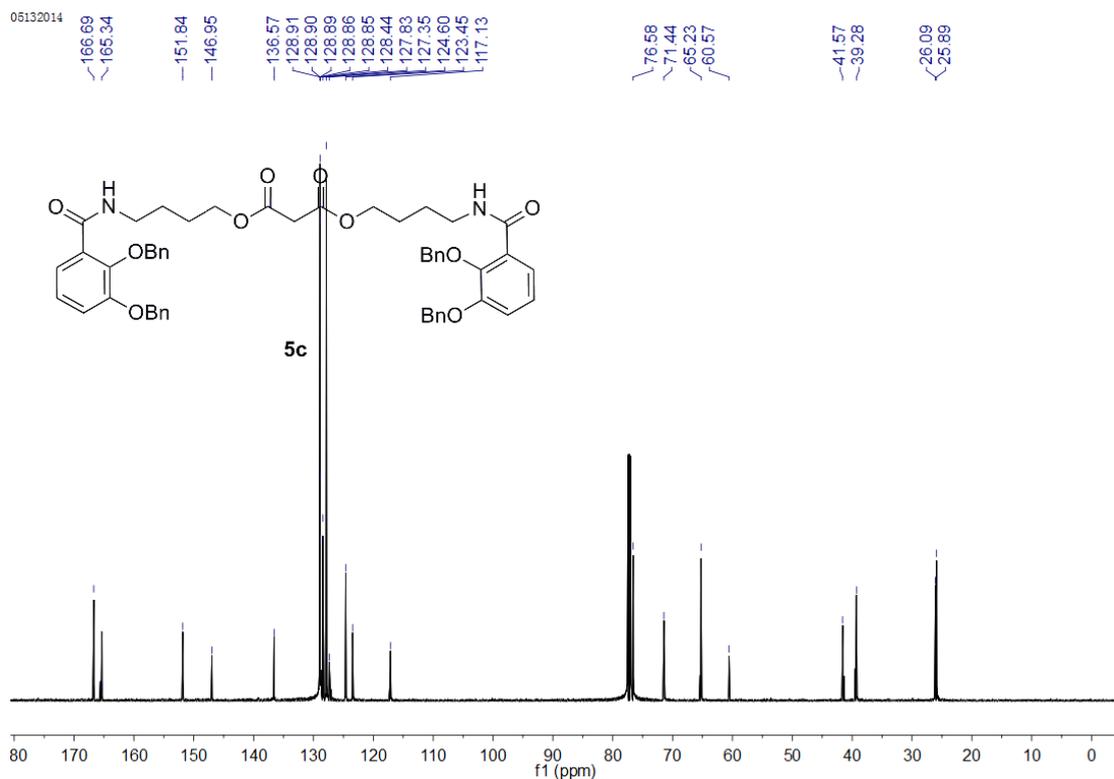


Fig. S13 The ^{13}C NMR (150MHz, CDCl_3 , 298.0K) spectrum of **5c**

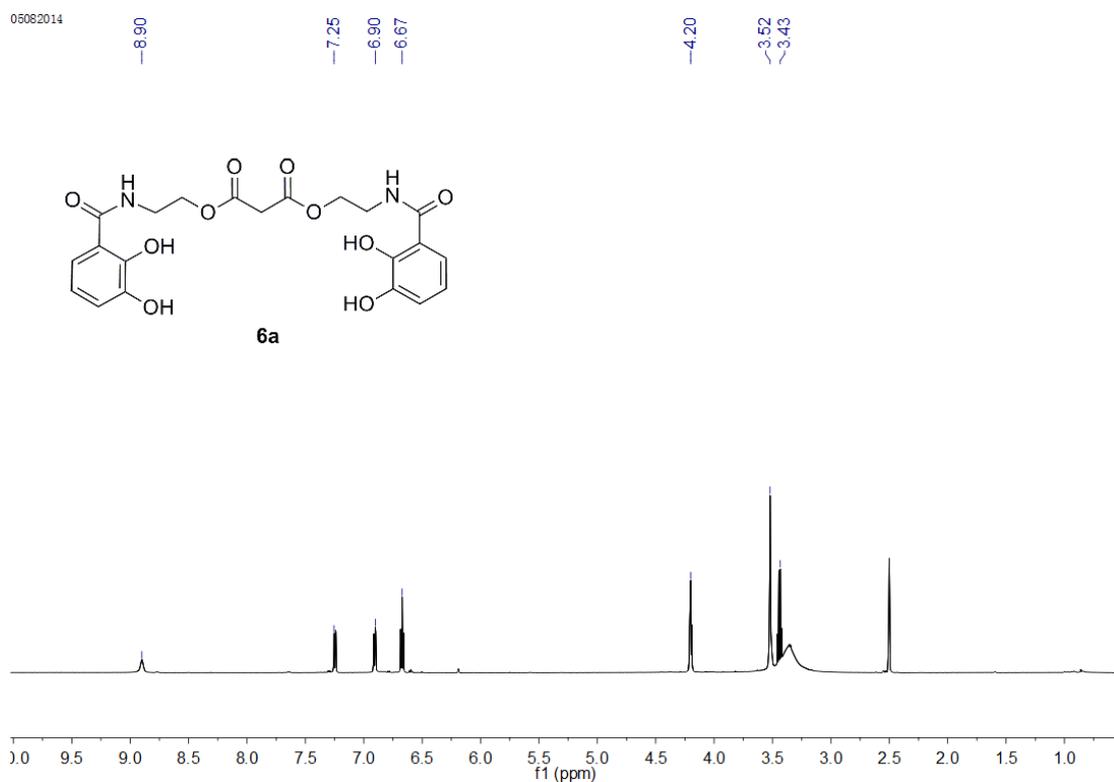


Fig. S14 The ^1H NMR (600MHz, $\text{DMSO}-d_6$, 298.0K) spectrum of **6a**

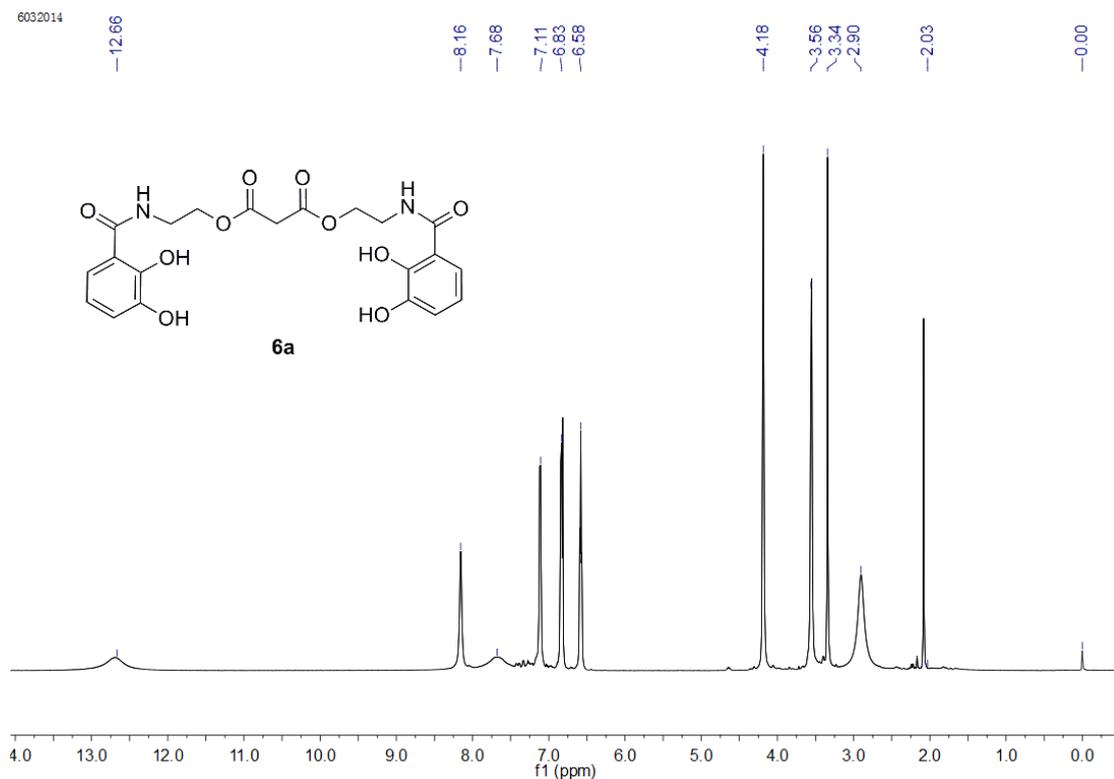


Fig. S15 The ^1H NMR (600MHz, $(\text{CD}_3)_2\text{CO}$, 298.0K) spectrum of **6a**

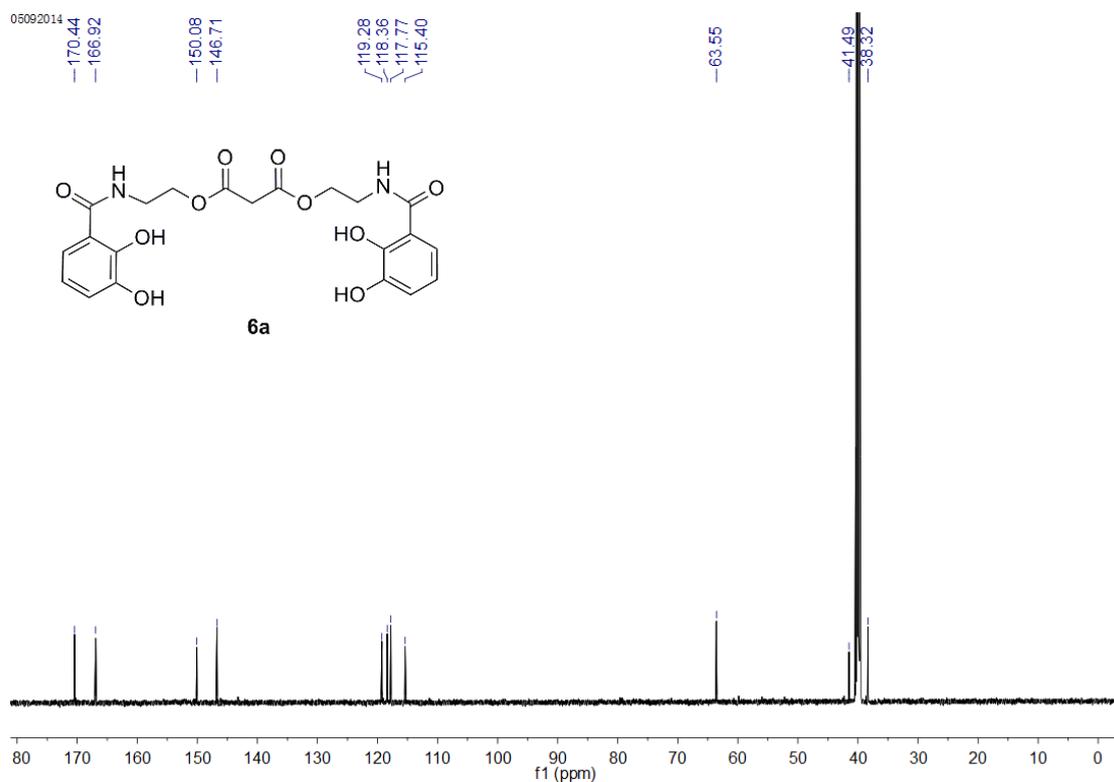


Fig. S16 The ^{13}C NMR (150MHz, $\text{DMSO-}d_6$, 298.0K) spectrum of **6a**

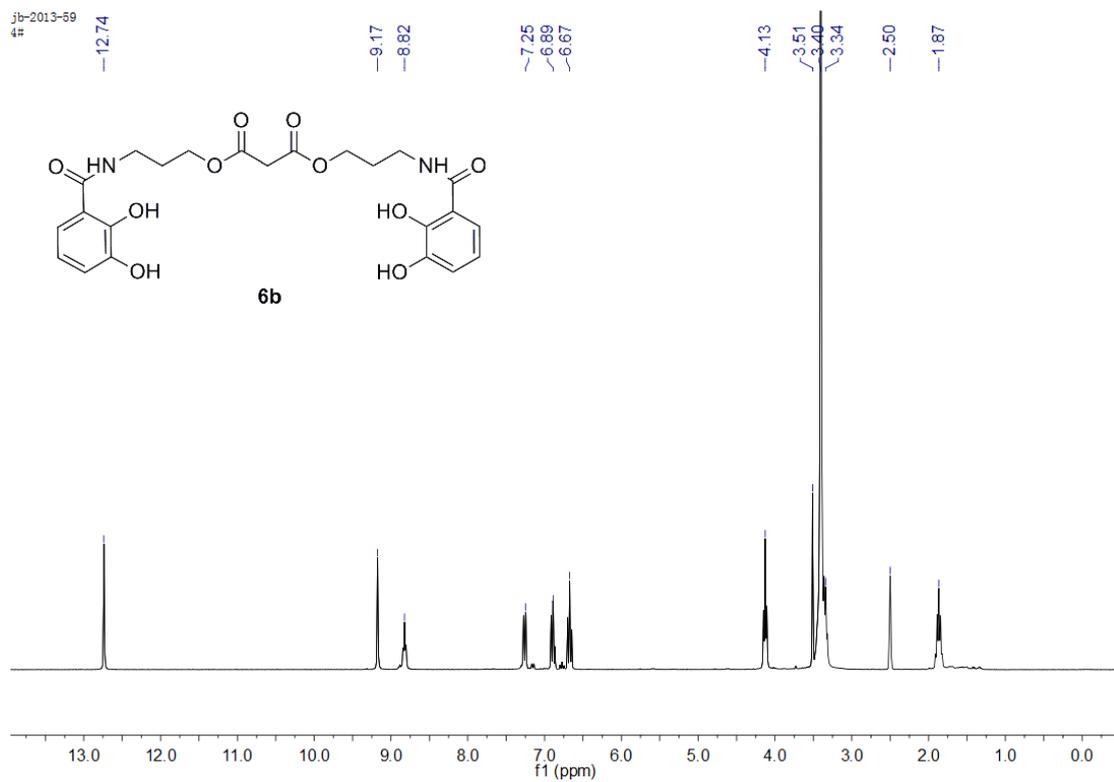


Fig. S17 The ^1H NMR (300MHz, $\text{DMSO-}d_6$, 298.0K) spectrum of **6b**

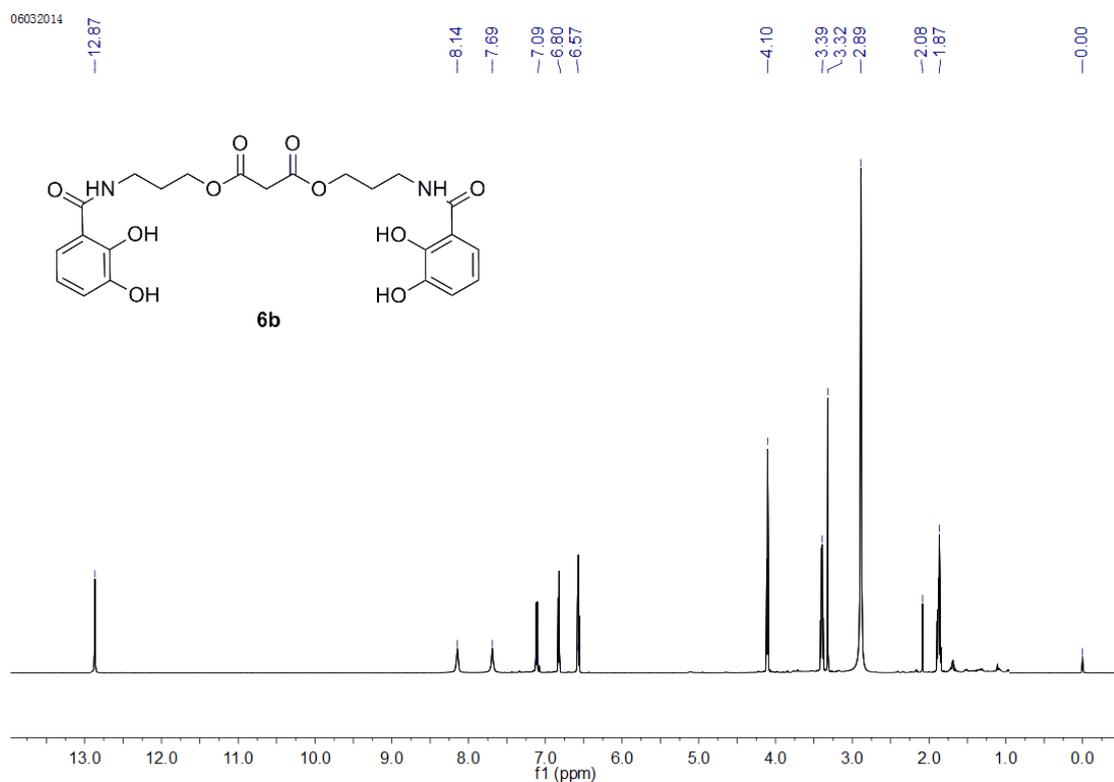


Fig. S18 The ^1H NMR (600MHz, $(\text{CD}_3)_2\text{CO}$, 298.0K) spectrum of **6b**

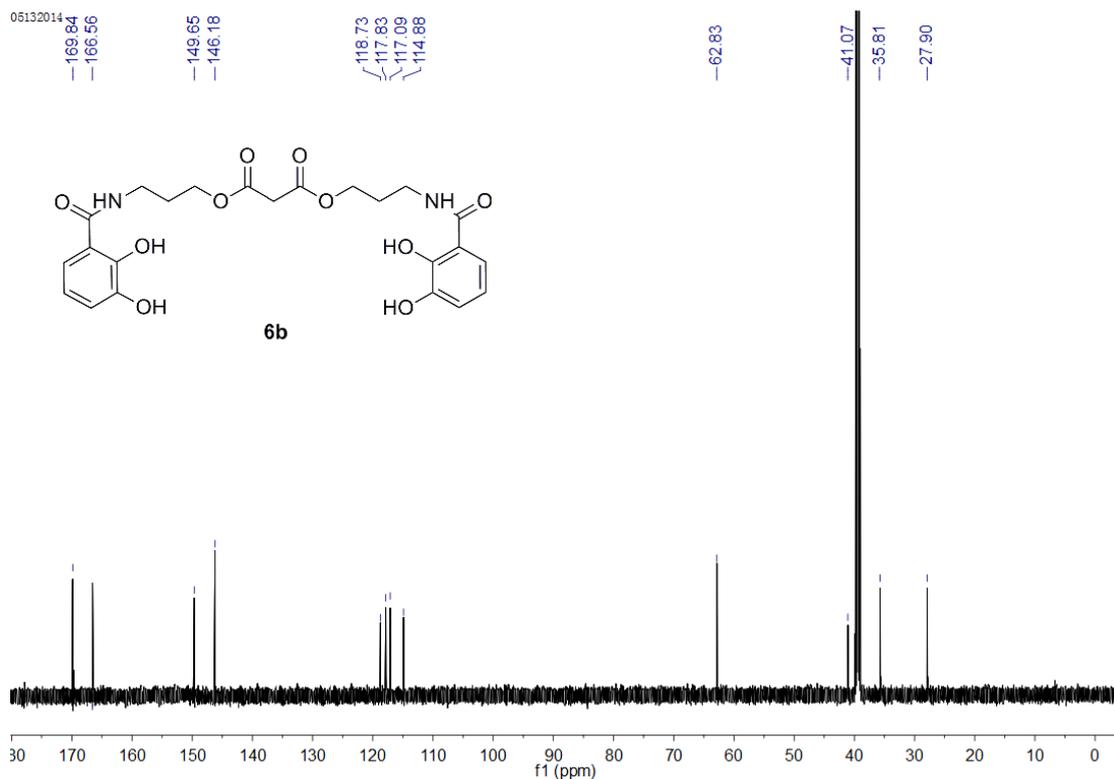


Fig. S19 The ^{13}C NMR (150MHz, $\text{DMSO-}d_6$, 298.0K) spectrum of **6b**

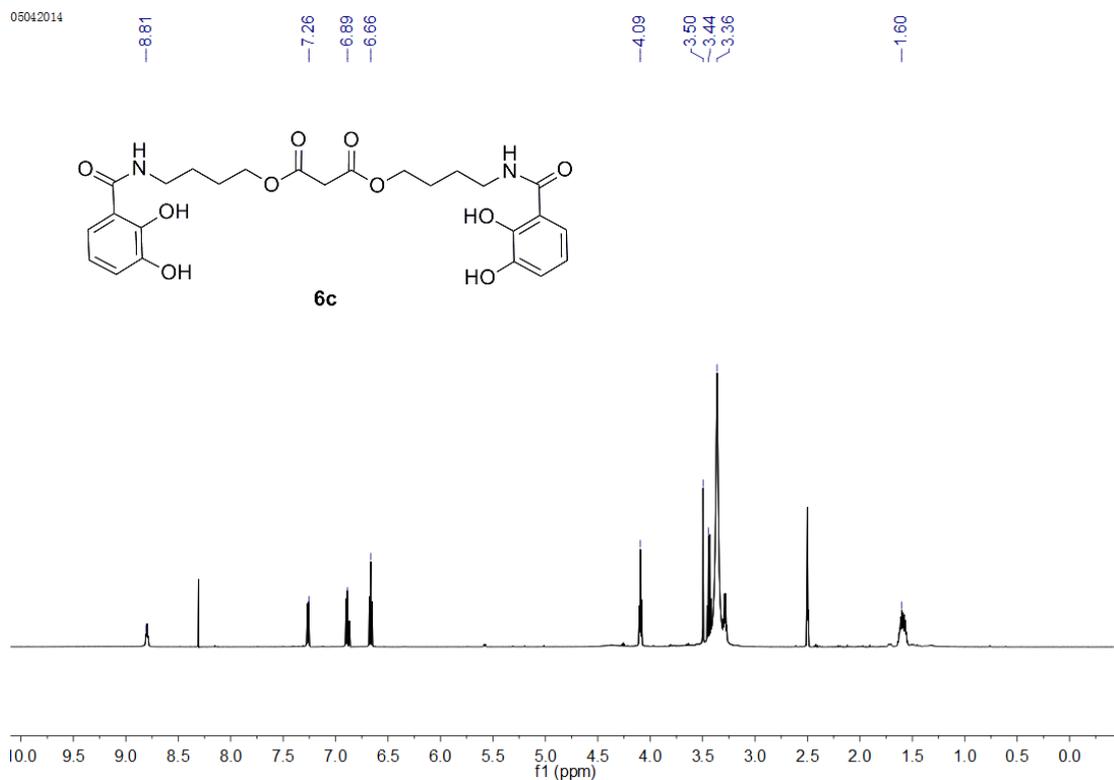


Fig. S20 The ^1H NMR (600MHz, $\text{DMSO-}d_6$, 298.0K) spectrum of **6c**

06032014

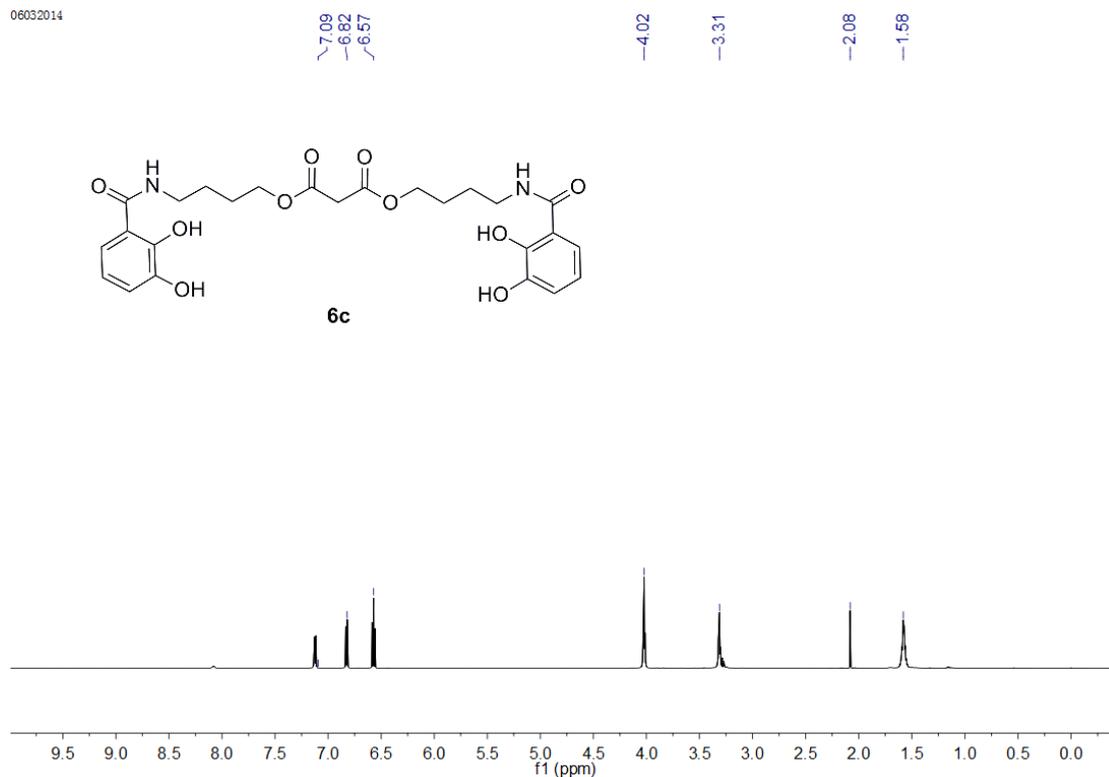


Fig. S21 The ^1H NMR (600MHz, $(\text{CD}_3)_2\text{CO}$, 298.0K) spectrum of **6c**

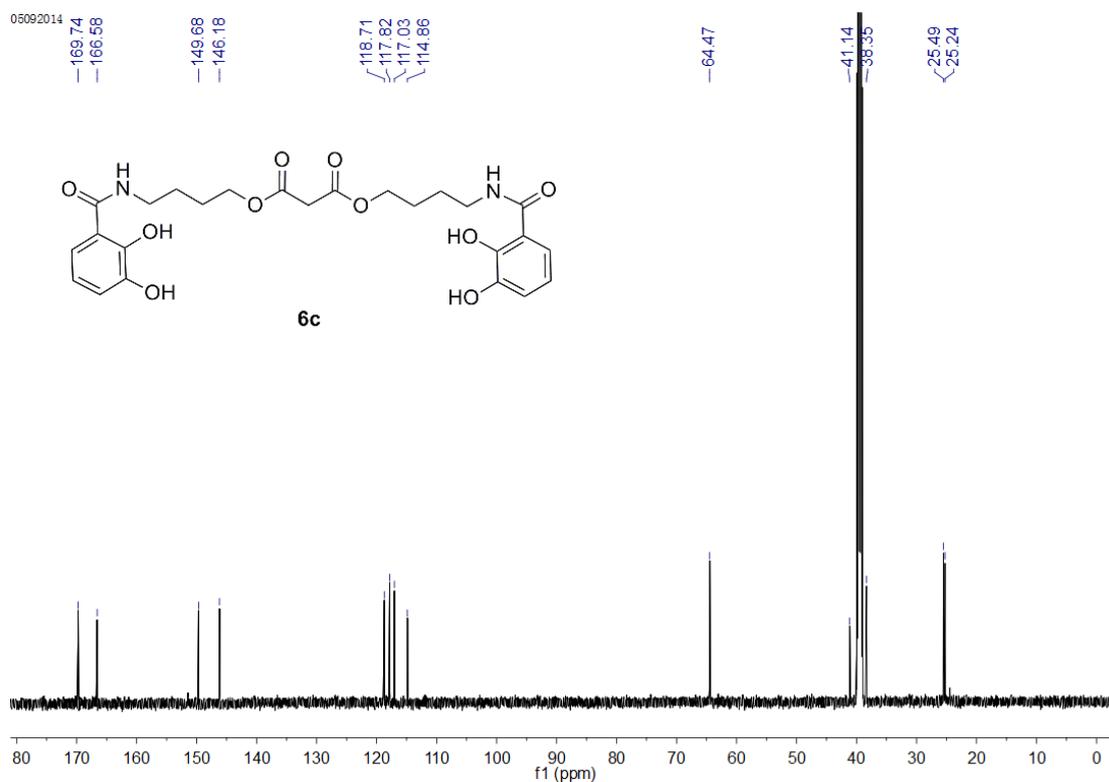


Fig. S22 The ^{13}C NMR (150MHz, $\text{DMSO}-d_6$, 298.0K) spectrum of **6c**

2014-01-07 jinbo-5

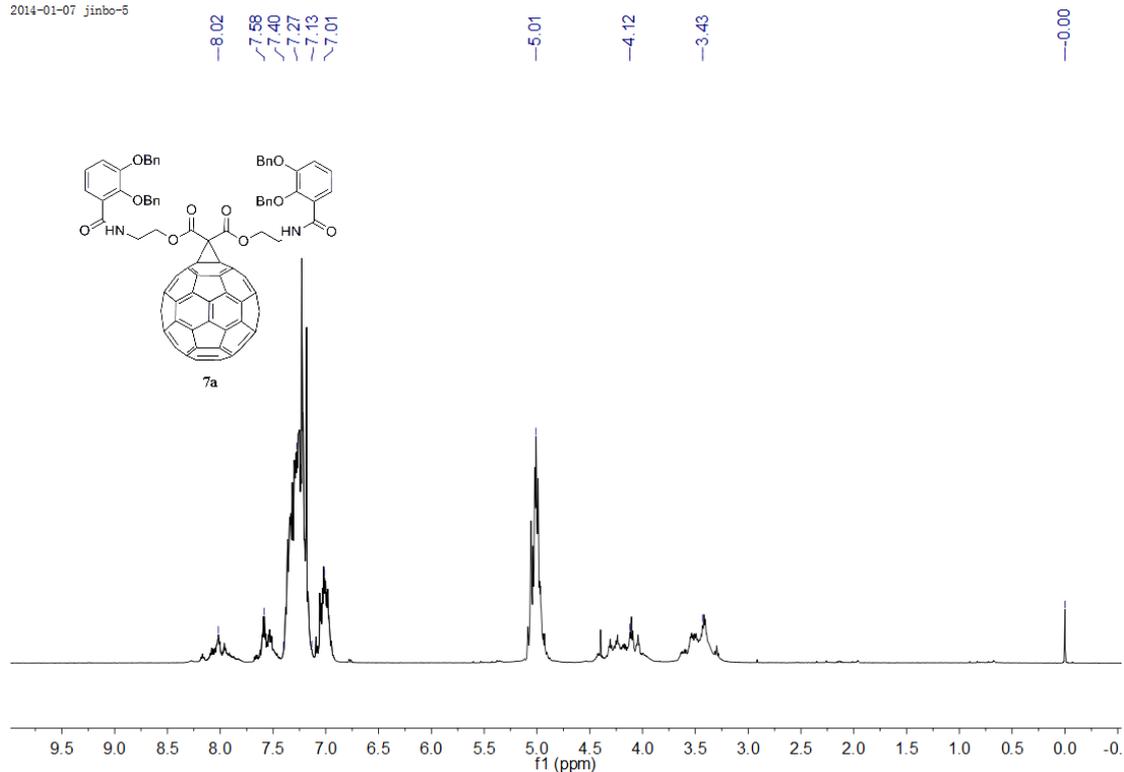


Fig. S23 The ^1H NMR (400MHz, CDCl_3 , 298.0K) spectrum of 7a

2014-06-20 jinbo-1-C

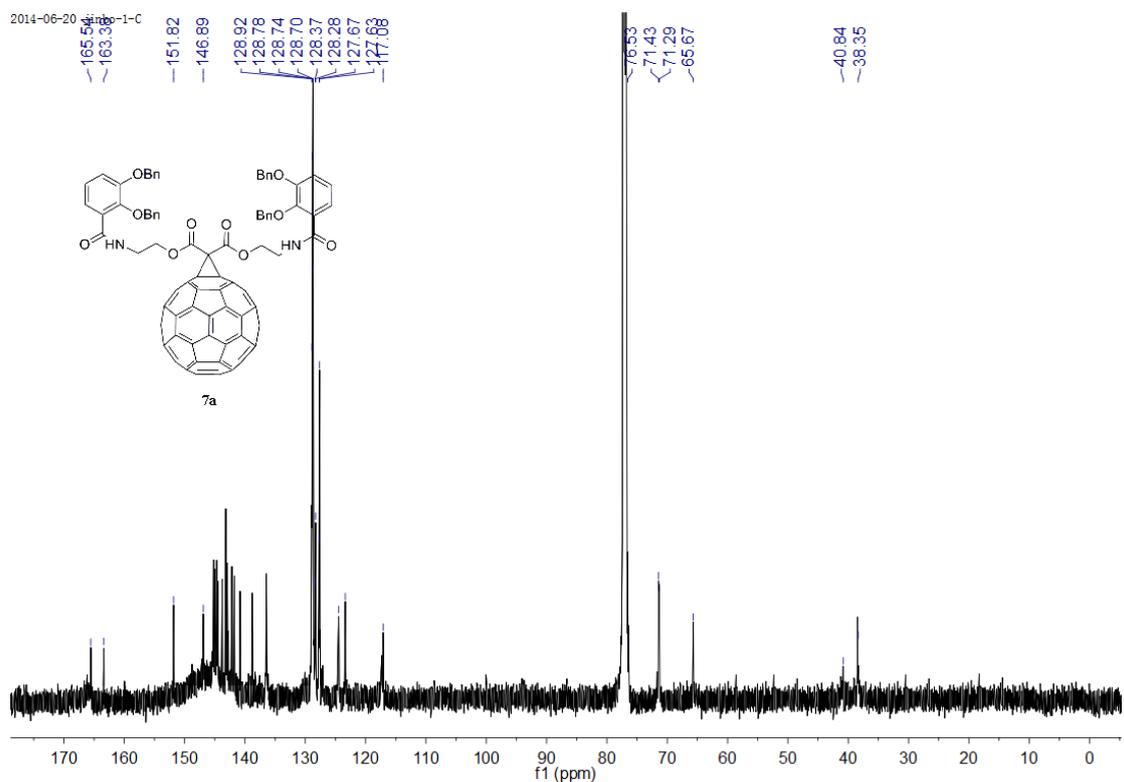


Fig. S24 The ^{13}C NMR (100MHz, CDCl_3 , 298.0K) spectrum of 7a

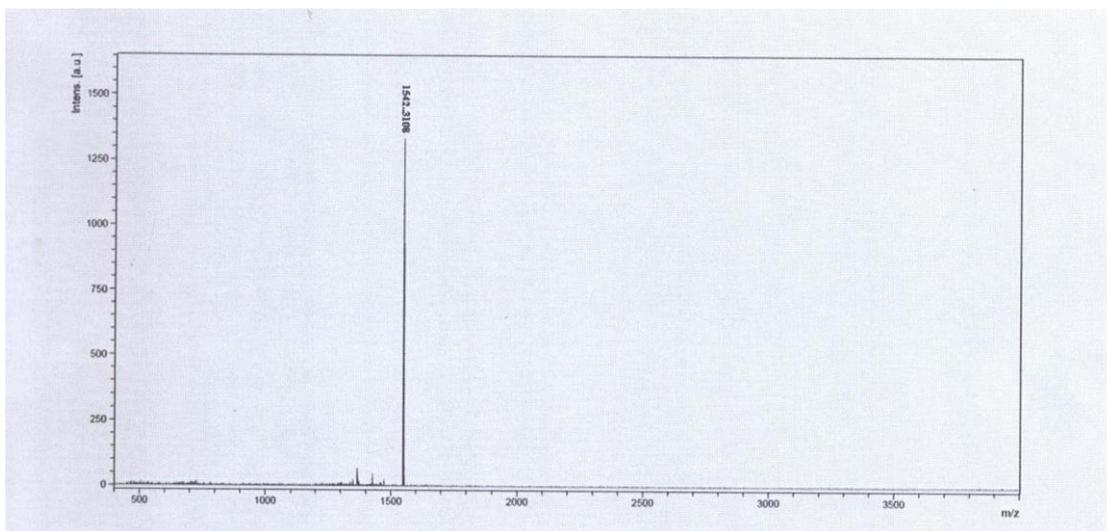


Fig. S25 The MALDI-TOF MS spectrum of **7a**

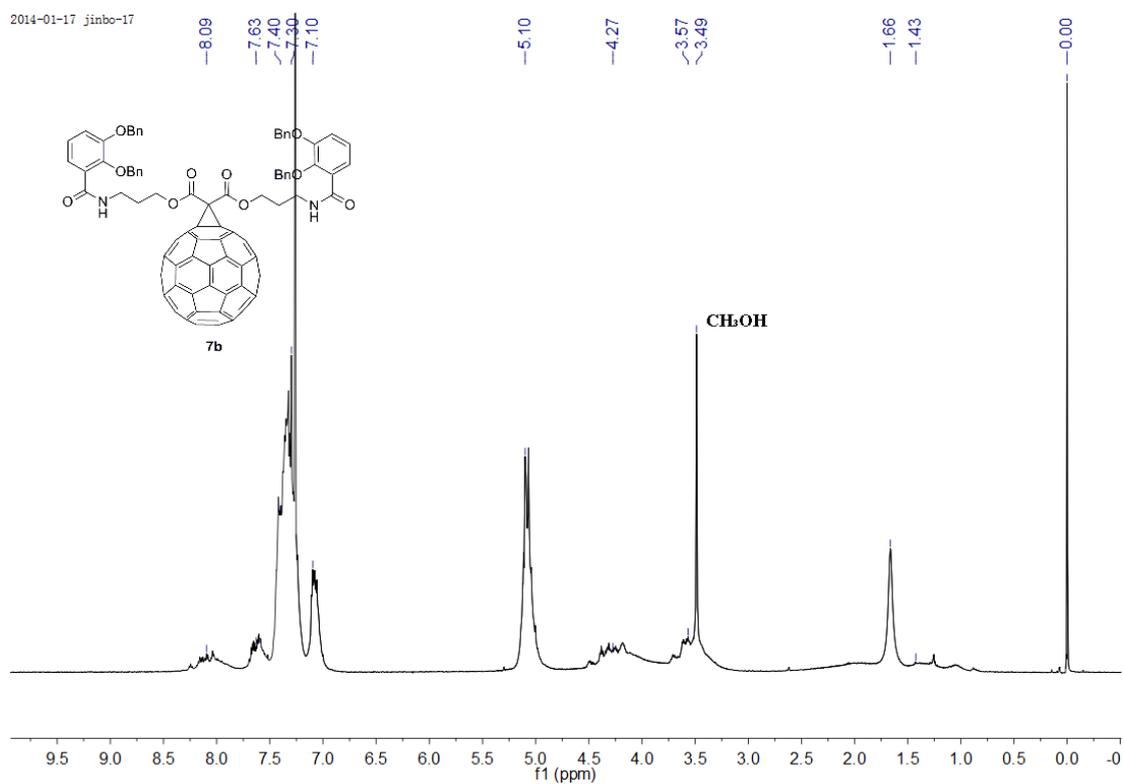


Fig. S26 The ^1H NMR (400MHz, CDCl_3 , 298.0K) spectrum of **7b**

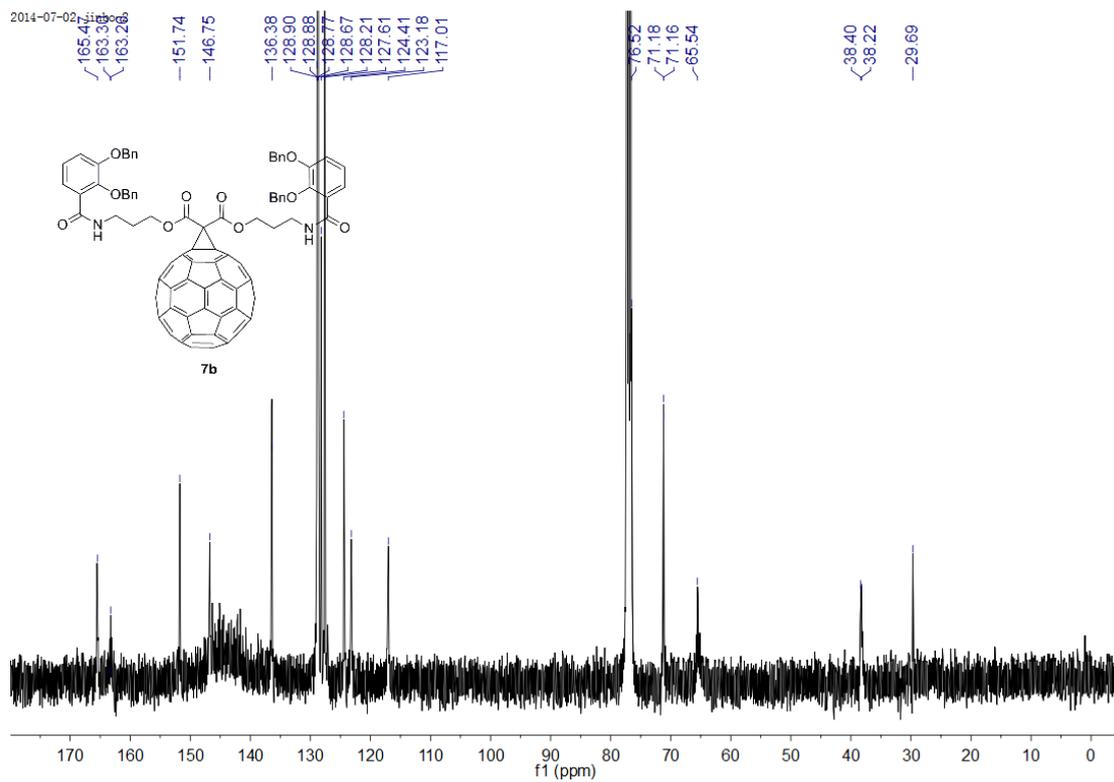


Fig. S27 The ¹³C NMR (100MHz, CDCl₃, 298.0K) spectrum of **7b**

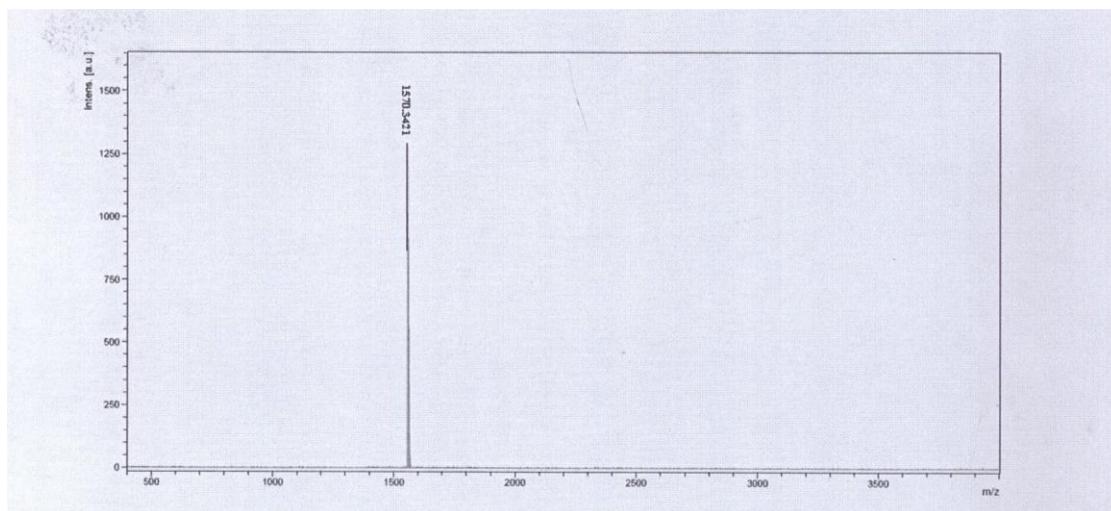


Fig. S28 The MALDI-TOF MS spectrum of **7b**

2014-06-20 jinbo-3

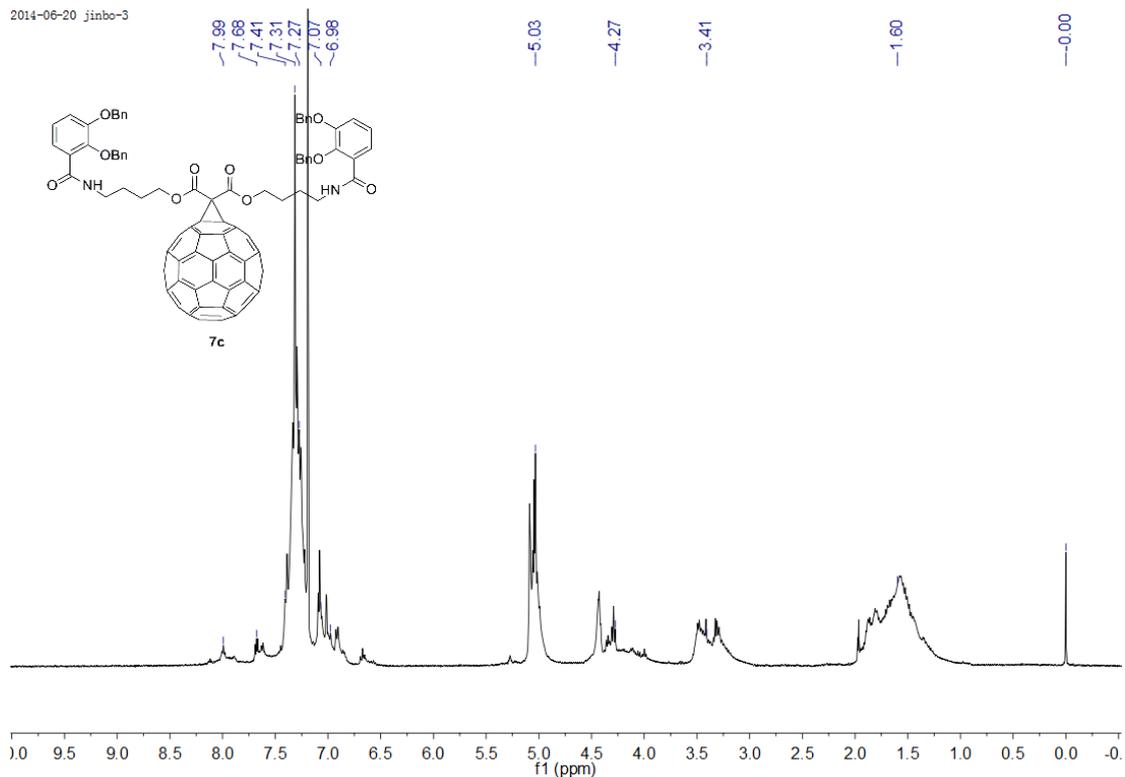


Fig. S29 The ^1H NMR (400MHz, CDCl_3 , 298.0K) spectrum of **7c**

2014-06-20 jinbo-3-C

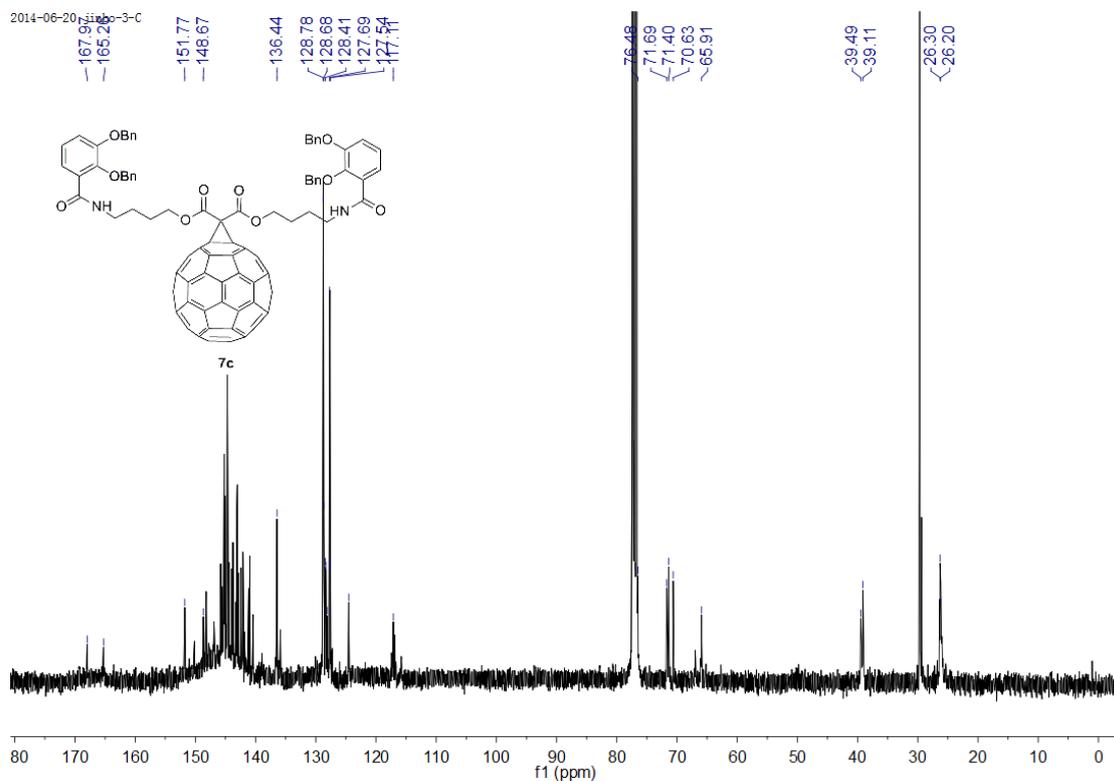


Fig. S30 The ^{13}C NMR (100MHz, CDCl_3 , 298.0K) spectrum of **7c**

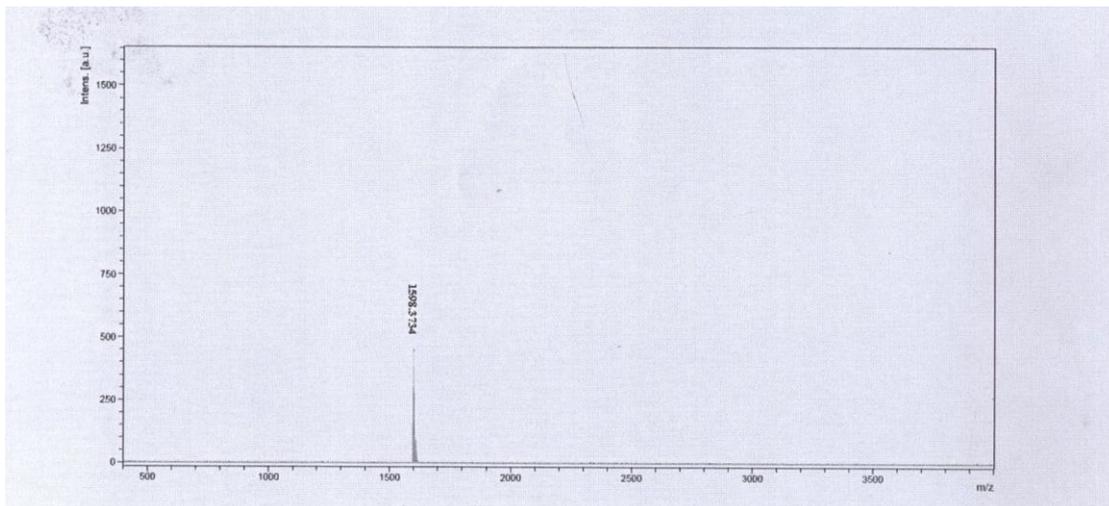


Fig. S31 The MALDI-TOF MS spectrum of **7c**

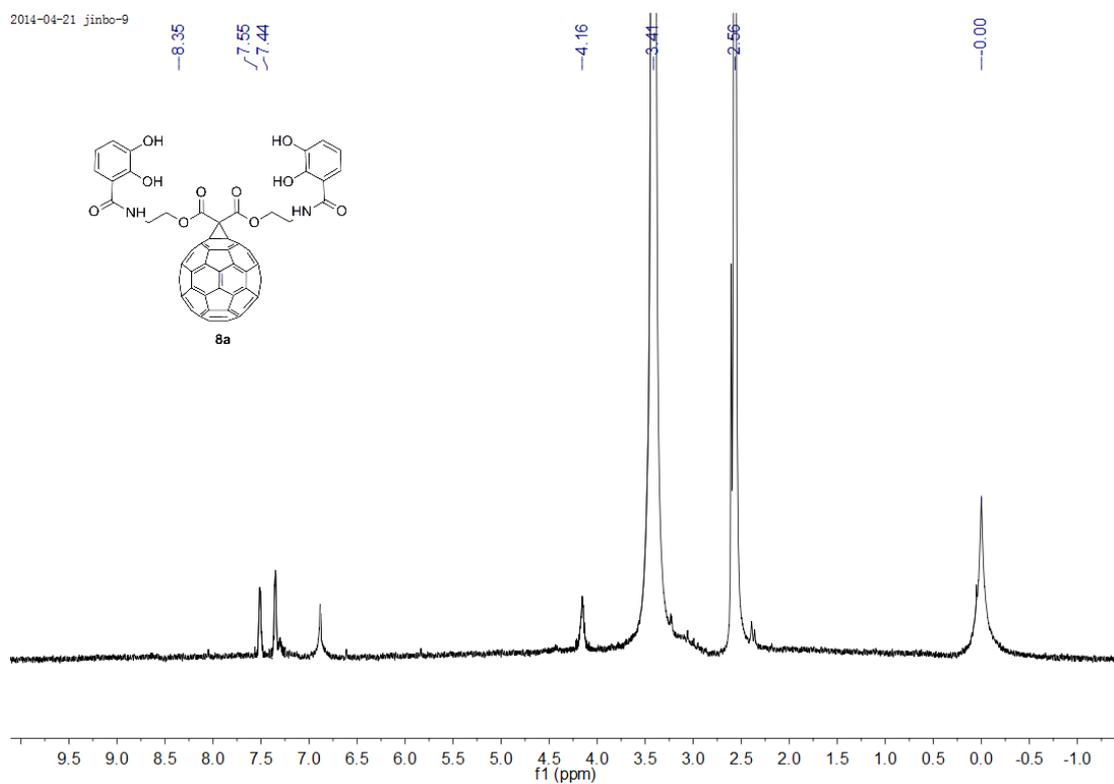


Fig. S32 The ^1H NMR (400MHz, $\text{DMSO-}d_6$, 295.1K) spectrum of **8a**

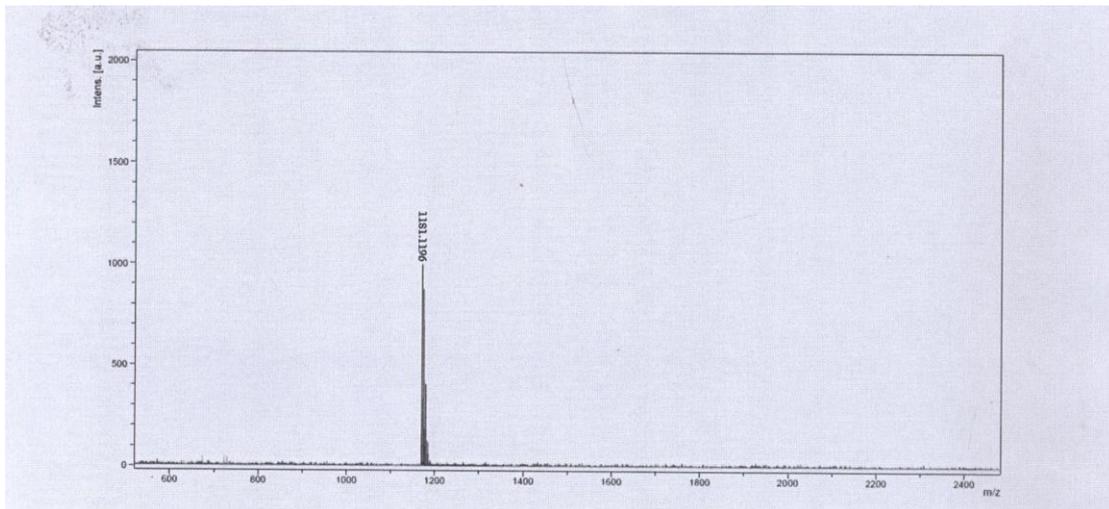


Fig. S33 The MALDI-TOF MS spectrum of **8a**

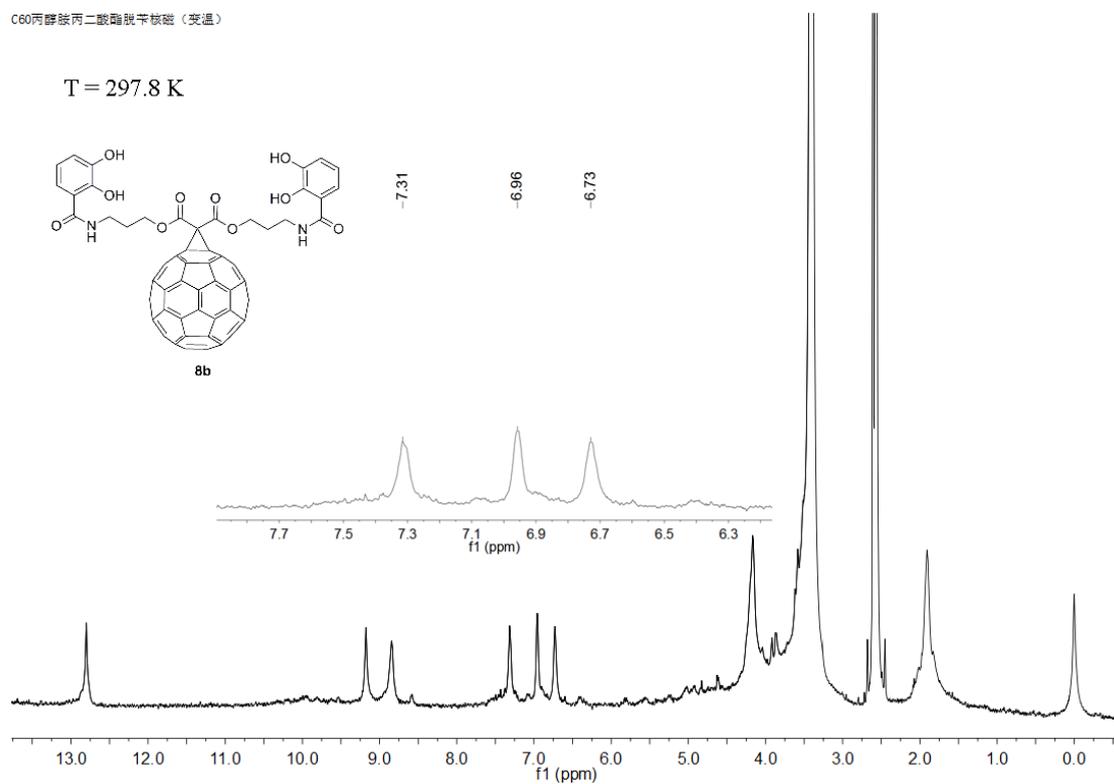


Fig. S34 The ^1H NMR (600MHz, $\text{DMSO-}d_6$, 297.8K, 16 scans) spectrum of **8b**

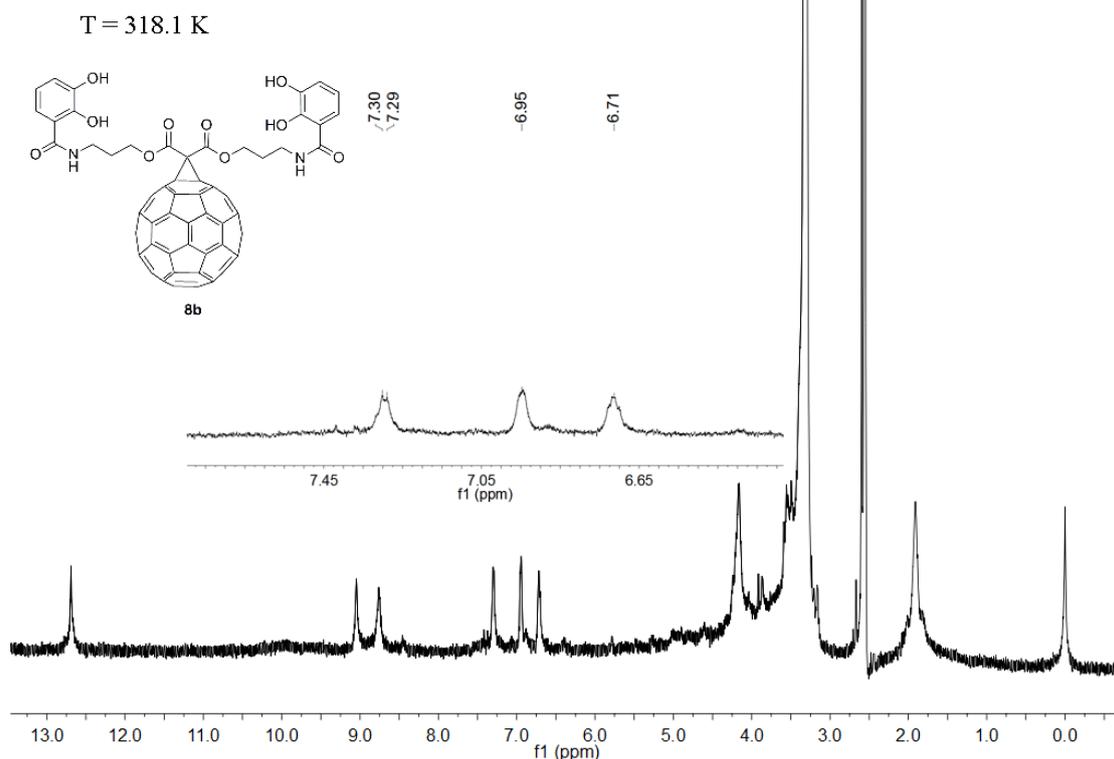


Fig. S35 The ^1H NMR (600MHz, $\text{DMSO-}d_6$, 318.1K, 16 scans) spectrum of **8b**

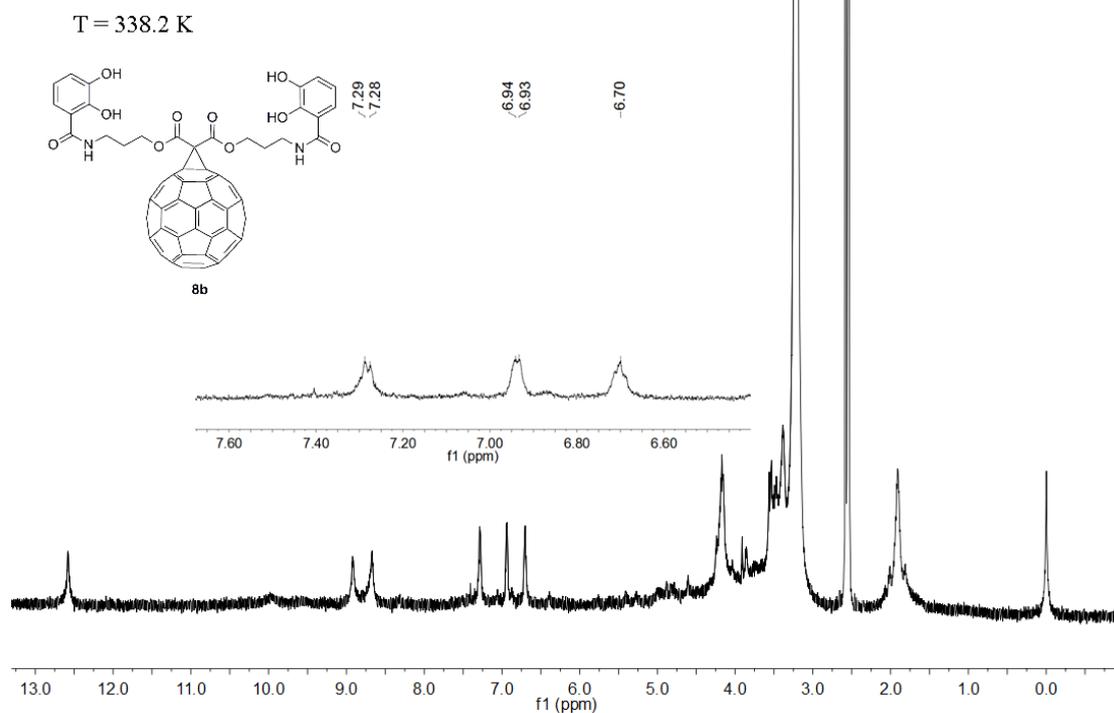


Fig. S36 The ^1H NMR (600MHz, $\text{DMSO-}d_6$, 338.2K, 16 scans) spectrum of **8b**

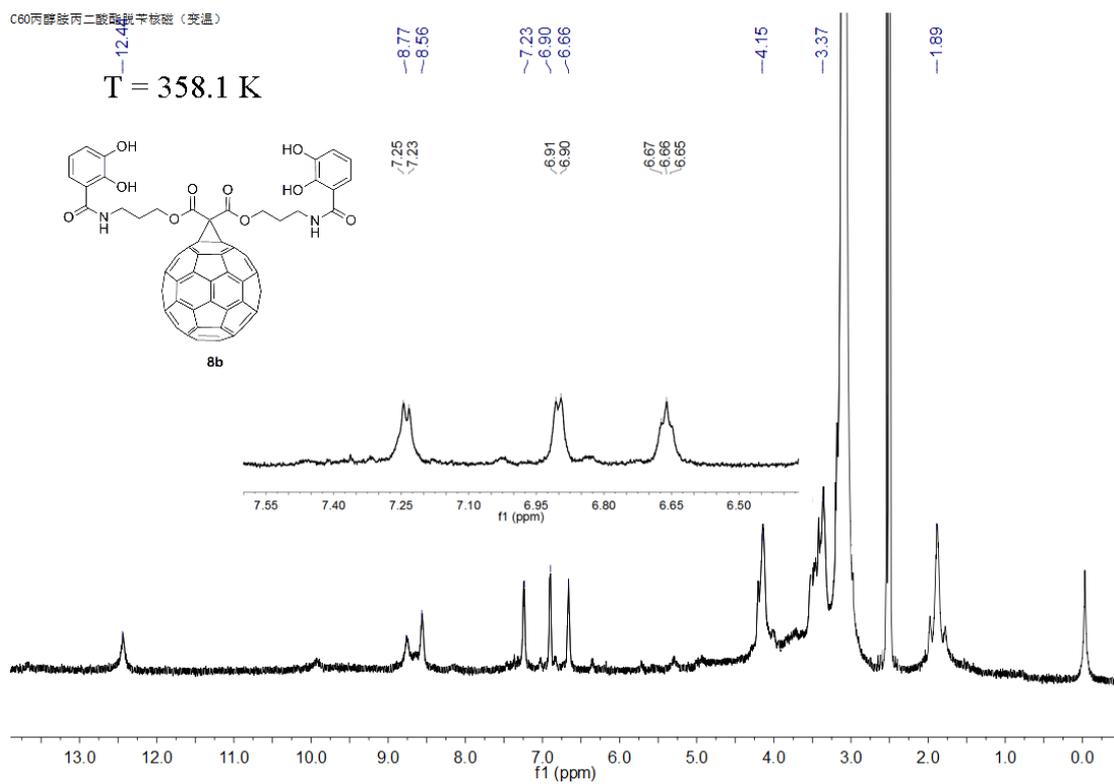


Fig. S37 The ¹H NMR (600MHz, DMSO-d₆, 358.1K, 64 scans) spectrum of **8b**

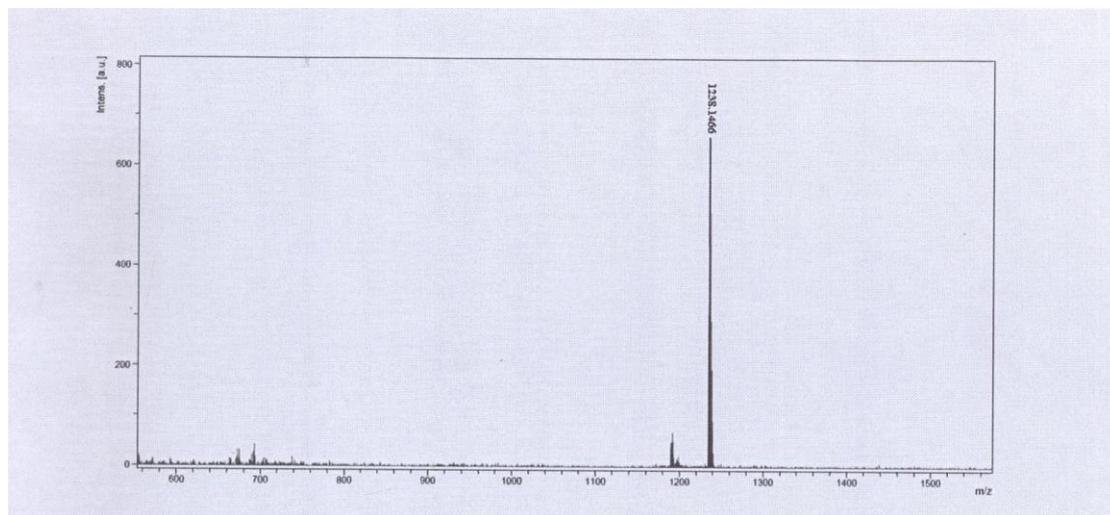


Fig. S38 The MALDI-TOF MS spectrum of **8b**

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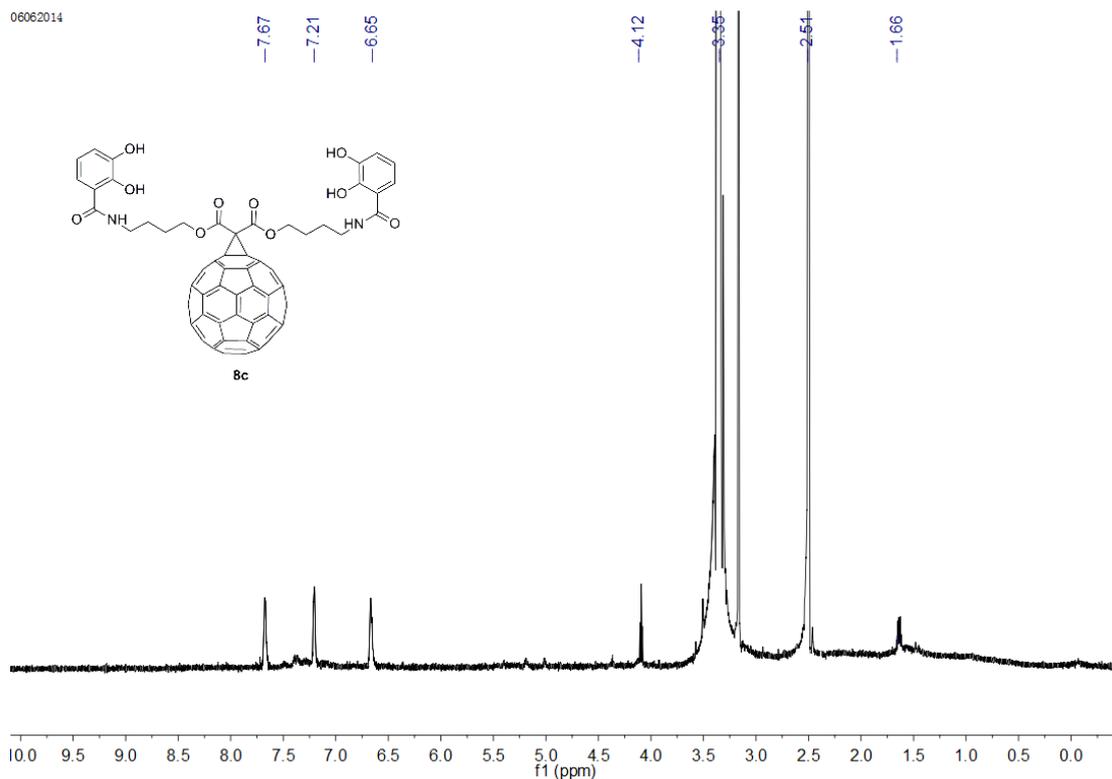


Fig. S39 The ¹H NMR (600MHz, DMSO-d₆, 298.0K) spectrum of **8c**

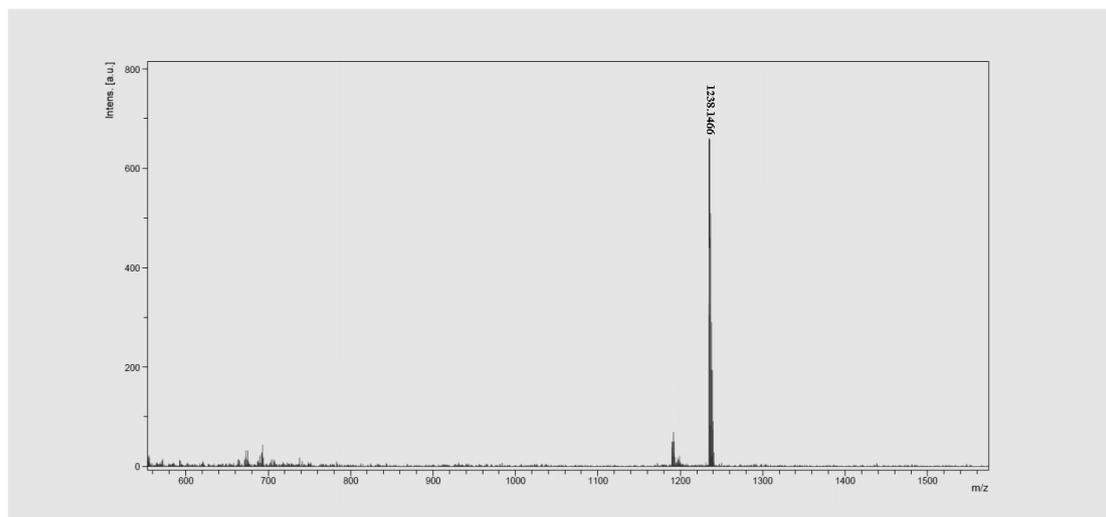


Fig. S40 The MALDI-TOF MS spectrum of **8c**

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