Supporting Information

Amphiphilic Dendrons with A Pyrene Functional Group at the Focal Point: Synthesis, Self-Assembly and Generation-Dependent DNA Condensation

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Experimental Section.

Materials. Unless noted otherwise, all chemicals were purchased from Aldrich or Acros and used without further purification. The catalyst precursor $Pd(PPh_3)_4$ was prepared according to the literature[S1] and stored in a Schlenk tube under nitrogen. **PyG0HCl**, *tert*-butyl-3-chloropropylcarbamate (**1**),[S2] 3,5-bis(3-*tert*-butoxy carbonylaminopropoxy) benzoic acid (**3**) [S3] and 3,5-bis{3-[3,5-bis(3-*tert*-butoxy carbonylaminopropoxy)-benzoylamino]propoxy} benzoic acid (**6**)[S3] were prepared according to literatures. Dichloromethane (CH_2Cl_2) was distilled over CaH_2. Tetrahydrofuran (THF) was distilled over sodium and benzophenone. All reactions were performed under an atmosphere of nitrogen and monitored by TLC with silica gel 60 F254 (Merck, 0.2 mm). Column chromatography was carried out on silica gel (200-300 mesh).

Characterization. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV400 spectrometer in $CDCl_3$ or DMSO-d_6. Matrix assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF) was performed on a miorOTOF-QII mass spectrometer (Bruker Daltonics). The electrospray mass spectra (ESI-MS) of lighting products were recorded on a miorOTOF-QII mass spectrometer (Bruker Daltonics). UV-Vis absorption spectra were obtained on a PerkinElmer Lambda 750 UV/VIS/NIR spectrometer. Photoluminescent (PL) spectra were recorded on a Hitachi F-7000 spectrometer. The SEM images were recorded with a field-emission scanning electron microscope (FESEM, JSM-6700F, JEOL) operating at an accelerating voltage of 5 kV.

The TEM images were recorded with transmission electron microscopes (JEOL JEM-1011 operated at 100 kV and Hitachi H-800 operated at 200 kV). Wide-angle X-ray diffraction and small-angel X-ray scattering profiles were collected using monochromated Cu Kα radiation (λ = 1.54056 Å) on a Rigaku D/max-2500 diffractometer. SAXS data were recorded using monochromated Cu Kα radiation (λ = 1.54056 Å) on a Rigaku model RINT Ultima III diffractometer. FT-IR spectra of samples were recorded on a Bruker Tensor 27 spectrometer. AFM images were examined by bruker Multimode 8 SPM. Particle size distribution of aggregates and zeta potential were measured on a Brookhaven ZetaPALS zeta potential analyzer. Gel electrophoresis was photographed by a UV transilluminator and WD-9415B gel documentation system (Beijing Liuyi Instrument Factory, P. R. China).

Sample Preparation. By slowly diffusing of poor solvent (ethanol) into good solvent solution of **PyG1HCl** and **PyG2HCl** (10 mg/μL in water), nanosized aggregation could gradually form on account of their amphiphilic nature. The resulted aggregates were transferred to silicon wafers and copper grids by dip-coating method for SEM and TEM measurements, respectively. At the meantime, the samples were freeze-dried and used for FT-IR, WXRD, SAXS measurements, respectively.

Agarose Gel Electrophoresis. Agarose gels (1%) were prepared by heating agarose (250 mg) in TAE buffer (25 mL; 4.0 x 10^{-2} M Tris, 2.0 x 10^{-2} M acetic acid, 2 x 10^{-3} M ethylenediaminetetraacetic acid from Dingguo Changsheng Biotechnology Co. Ltd.).

Sample solutions containing pBR322 DNA were prepared by adding an appropriate volume of DNA solution into Eppendorf tubes with different compounds, which were then diluted to a total volume of 15 μL. And then the sample solutions were subjected to electrophoresis at 60 V for 40 min and visualized by ethidium bromide staining. The DNA bands were visualized and photographed with a UV transilluminator and gel documentation system

Compound 2. To a solution of **1** (5.0 g, 0.015 mol) in THF (15 mL) was added hydrochloric acid (5 mL, 10 M). The mixture was stirred at room temperature for 12 h. After the addition of ethyl ether (30 mL), the mixture was fiercely shaken, and a large amount of white precipitates were then formed. Filtration and washing with ethyl ether afforded **2** as a colorless solid (3.7 g, 92%). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 8.00 (s, 3H), 7.41 (d, 2H), 6.87 (d, 2H), 4.00 (t, 2H), 2.88 (t, 2H), 1.97 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 157.6, 132.1, 116.8, 112.1, 64.9, 36.1, 26.7. HR-ESI, m/z: calculated for $C_9H_{12}BrNO$ $[M + H]^+$, 230.0175, found: 230.0180.

Compound 4. A mixture of **2** (1.0 g, 3.75 mmol), **3** (875 mg, 1.88 mmol), HOBt (254 mg, 1.88 mmol) and 300 mL of anhydrous CH_2Cl_2 was carefully degassed and charged with N_2. The mixture was cooled to 0–5 ^{o}C in an ice water bath, added Et_3N (5.3 mL) and EDC·HCl (1.1 g, 5.74 mmol), stirred at room temperature for 24 h, and then poured into 100 mL of aqueous $NaHCO_3$. The organic layer was separated, washed with aqueous NaCl and dried over anhydrous Na_2SO_4. After the removal of the solvent, the residue was

purified by chromatography on a silica gel column eluting with ethyl acetate to afford **4** as a colorless solid (820 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.37 (d, 2H), 6.87 (s, 2H), 6.79 (d, 2H), 6.65 (s, 1H), 6.55 (s, 1H), 4.75 (s, 2H), 4.07 (t, 2H), 4.00 (t, 4H), 3.64 (m, 2H), 3.31 (m, 4H), 2.11 (m, 2H), 1.96 (m, 4H), 1.44 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 167.5, 160.2, 157.9, 156.2, 137.0, 132.5, 116.4, 113.3, 105.8, 104.5, 79.5, 66.8, 66.1, 38.1, 38.0, 29.7, 29.1, 28.6. Anal. Calcd for $C_{32}H_{46}BrN_3O_8$: C, 56.47; H, 6.81; N, 6.17; found: C, 56.62; H, 7.06; N, 6.38. MALDI-TOF (m/z), calculated for $C_{32}H_{46}BrN_3O_8$ $[M + Na]^+$, 702.2360; found: 702.4601.

Compound 7. A mixture of **2** (600 mg, 2.25 mmol), **6** (500 mg, 0.43 mmol), HOBt (125 mg, 0.93 mmol) and 200 mL of anhydrous CH_2Cl_2 was carefully degassed and charged with N_2. The mixture was cooled to 0–5 ^{o}C in an ice water bath, added Et_3N (5 mL) and EDC·HCl (500 mg, 2.61 mmol), stirred at room temperature for 24 h, and then poured into 50 mL of aqueous $NaHCO_3$. The organic layer was separated, washed with aqueous NaCl and dried over anhydrous Na_2SO_4. After the removal of the solvent, the residue was purified by chromatography on a silica gel column eluting with ethyl acetate to afford **7** as a colorless solid (378 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.33 (d, 2H), 7.05 (s, 1H), 7.00 (s, 2H), 6.86 (s, 6H), 6.75 (d, 2H), 6.49 (s, 3H), 4.93 (br, 4H), 4.02 (m, 6H), 3.94 (m, 8H), 3.61 (m, 6H), 3.26 (m, 8H), 2.14–2.02 (m, 6H), 1.92 (m, 8H), 1.42 (s, 36H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 167.7, 167.5, 160.1, 160.0, 158.0, 156.3, 136.9, 132.5, 116.5, 113.2, 106.0, 105.9, 104.7, 79.4, 66.6, 66.5, 66.0, 38.0, 37.9, 37.8,

29.9, 29.7, 29.2, 29.1, 28.6. Anal. Calcd for $C_{68}H_{98}BrN_7O_{18}$: C, 59.12; H, 7.15; N, 7.10; found: C, 59.54; H, 7.08; N, 7.15. MALDI-TOF (m/z), calculated for $C_{68}H_{98}BrN_7O_{18}$ [M + Na]$^+$, 1402.6044; found: 1402.9657.

General Procedure for the Synthesis of PyG1Boc and PyG2Boc. A mixture of the precursor (**4**, **7**), **5**, $NaHCO_3$, THF and H_2O was carefully degassed before and after $Pd(PPh_3)_4$ was added. The mixture was heated to reflux and stirred under nitrogen overnight. CH_2Cl_2 and brine was added, and the organic layer was separated and dried over anhydrous Na_2SO_4. After the removal of the solvent, the residue was purified by chromatography on a silica gel column to afford the desired product (**PyG1Boc, PyG2Boc**).

PyG1Boc. 4 (260 mg, 0.382 mmol), **5** (160 mg, 0.485 mmol), $NaHCO_3$ (0.3 g, 3.57 mmol), THF (14 mL), H_2O (6 mL) and $Pd(PPh_3)_4$ (5 mg, 0.004 mmol) were used, and CH_2Cl_2/THF (v/v, 10:1) was used as the eluent to afford **PyG1Boc** as a dark green solid (278 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.20 (m, 4H), 8.09 (s, 2H), 8.02 (d, 2H), 7.96 (d, 1H), 7.56 (d, 2H), 7.12 (d, 2H), 6.94 (s, 2H), 6.70 (s, 1H), 6.57 (s, 1H), 4.69 (br, 2H), 4.25 (m, 2H), 4.04 (m, 4H), 3.74 (m, 2H), 3.31 (m, 4H), 2.21 (m, 2H), 1.96 (m, 4H), 1.41 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 167.5, 160.3, 158.2, 156.2, 137.5, 137.2, 134.2, 131.9, 131.7, 131.2, 130.7, 128.8, 127.9, 127.6, 127.5, 126.2, 125.5, 125.3, 125.2, 124.9, 114.7, 105.9, 104.7, 79.5, 67.0, 66.2, 38.5, 38.1, 29.8, 29.3, 28.6.

Anal. Calcd for $C_{48}H_{55}N_3O_8$: C, 71.89; H, 6.91; N, 5.24; found: C, 71.56; H, 7.06; N, 5.37. MALDI-TOF (m/z), calculated for $C_{48}H_{55}N_3O_8$ $[M\bullet]^+$, 801.3984; found: 801.8178.

PyG2Boc. 7 (200 mg, 0.145 mmol), **5** (75 mg, 0.227 mmol), $NaHCO_3$ (0.3 g, 3.57 mmol), THF (12 mL), H_2O (5 mL) and $Pd(PPh_3)_4$ (3 mg, 0.003 mmol) were used, and CH_2Cl_2/THF (v/v, 5:1) was used as the eluent to afford **PyG2Boc** as a dark green solid (112 mg, 51%). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 8.15 (m, 4H), 8.07 (s, 2H), 7.99 (m, 2H), 7.92 (d, 1H), 7.51 (d, 2H), 7.26 (s, 1H), 7.17 (s, 2H), 7.07 (d, 2H), 6.91 (s, 2H), 6.86 (s, 4H), 6.47 (s, 3H), 4.96 (br, 4H), 4.20 (m, 2H), 4.01 (m, 4H), 3.90 (m, 8H), 3.69 (m, 2H), 3.60 (m, 4H), 3.24 (m, 8H), 2.19 (m, 2H), 2.05 (m, 4H), 1.88 (m, 8H), 1.41 (s, 36H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 167.5, 160.3, 158.2, 156.2, 137.5, 137.2, 134.2, 131.9, 131.7, 131.2, 130.7, 128.8, 127.9, 127.6, 127.5, 126.2, 125.5, 125.3, 125.2, 125.0, 124.9, 114.7, 105.9, 104.7, 79.5, 67.0, 66.2, 38.5, 38.1, 29.8, 29.3, 28.6. Anal. Calcd for $C_{84}H_{107}N_7O_{18}$: C, 67.14; H, 7.18; N, 6.52; found: C, 66.99; H, 7.29; N, 6.61. MALDI-TOF (m/z), calculated for $C_{84}H_{107}N_7O_{18}$ $[M\bullet]^+$, 1501.7667; found: 1502.0160.

General Procedure for the Synthesis of PyG1HCl and PyG2HCl. To the solution of **PyG1Boc** and **PyG2Boc** in THF was added hydrochloric acid. The mixture was stirred at room temperature for 12 h. After the addition of acetone, the mixture was placed in a fridge overnight. A large amount of precipitates were then formed. Filtration and washing with acetone afforded **PyG1HCl** and **PyG2HCl**, respectively.

PyG1HCl. PyG1Boc (150 mg, 0.187 mmol), THF (5 mL), hydrochloric acid (1 mL, 10 M) and acetone (30 mL) were used to afford **PyG1HCl** as a yellow solid (118 mg, 93%). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 8.63 (s, 1H), 8.34–7.95 (m, 14H), 7.94 (d, 1H), 7.50 (d, 2H), 7.12 (d, 2H), 7.05 (s, 2H), 6.64 (s, 1H), 4.07 (m, 6H), 3.43 (m, 2H), 2.89 (m, 4H), 1.98 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 166.1, 159.5, 158.3, 137.1, 136.8, 132.7, 131.6, 131.2, 130.6, 130.0, 127.9, 127.7, 127.6, 127.5, 126.6, 125.5, 125.1, 124.9, 124.4, 124.3, 114.8, 106.2, 104.4, 65.8, 65.3, 36.7, 36.5, 29.1, 26.9. MALDI-TOF (m/z), calculated for $C_{38}H_{39}N_3O_4$ $[M\bullet]^+$, 601.2941; found, 601.3371.

PyG2HCl. PyG2Boc (50 mg, 0.033 mmol), THF (5 mL), hydrochloric acid (1 mL, 10 M) and acetone (30 mL) were used to afford **PyG2HCl** as a yellow solid (38 mg, 92%). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 8.61 (s, 3H), 8.33–7.88 (m, 21H), 7.52 (d, 2H), 7.14 (d, 2H), 7.04 (s, 6H), 6.63 (s, 2H), 6.61 (s, 1H), 4.18–3.93 (m, 14H), 3.50–3.34 (m, 6H), 2.90 (m, 8H), 2.00 (m, 14H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 165. 8, 165.6, 159.6, 159.3, 158.1, 136.9, 136.6, 132.4, 131.4, 131.0, 130.4, 129.8, 127.7, 127.5, 127.4, 127.2, 126.3, 125.2, 124.9, 124.8, 124.7, 124.2, 124.1, 114.6, 106.0, 105.8, 104.1, 103.9, 65.8, 65.6, 65.0, 36.5, 36.4, 36.1, 28.9, 28.7, 26.7. MALDI-TOF (m/z), calculated for $C_{64}H_{75}N_7O_{10}$ $[M + H]^+$, 1102.5648; found, 1102.8004.

Table S1. Zeta potential data (ζ, Δζ) of DNA condensate induced by **PyG0HCl**, **PyG1HCl** and **PyG2HCl**.

	PyG0HCl	PyG1HCl	PyG2HCl[a]	PyG0HCl+DNA	PyG1HCl+DNA	PyG2HCl+DNA
ζ (mV)	+38	+40	--	+24	+18	+17
Δζ(mV)	--	--	--	-14	-22	--

a. Zeta-potential of **PyG2HCl** under such condition was not detected since the corresponding particle size was too small to be measured.

Supporting Figures.

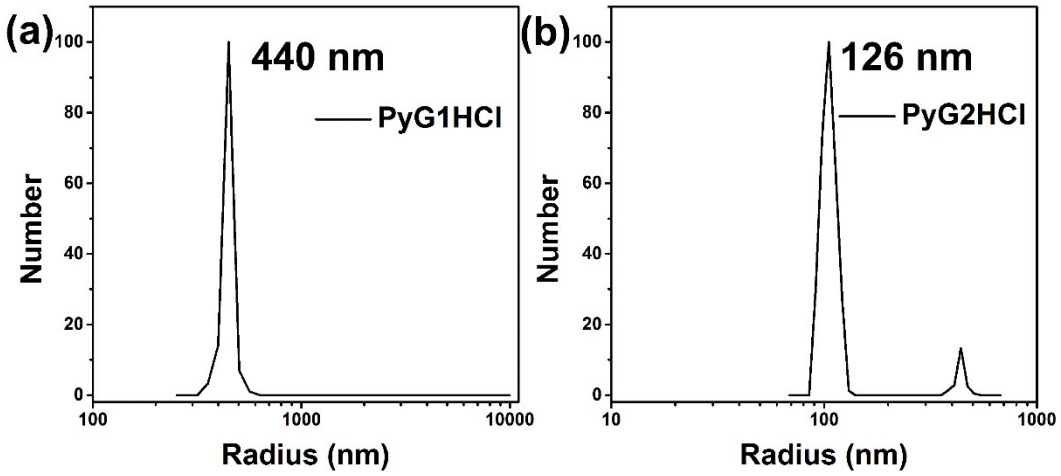

Figure S1. Hydrodynamic radius distribution of (a) **PyG1HCl** in the mixture solution (0.476 mg/ml, water/ethanol = 1:20) and (b) **PyG2HCl** in the mixture solution (0.244 mg/ml, water/ethanol = 1:40).

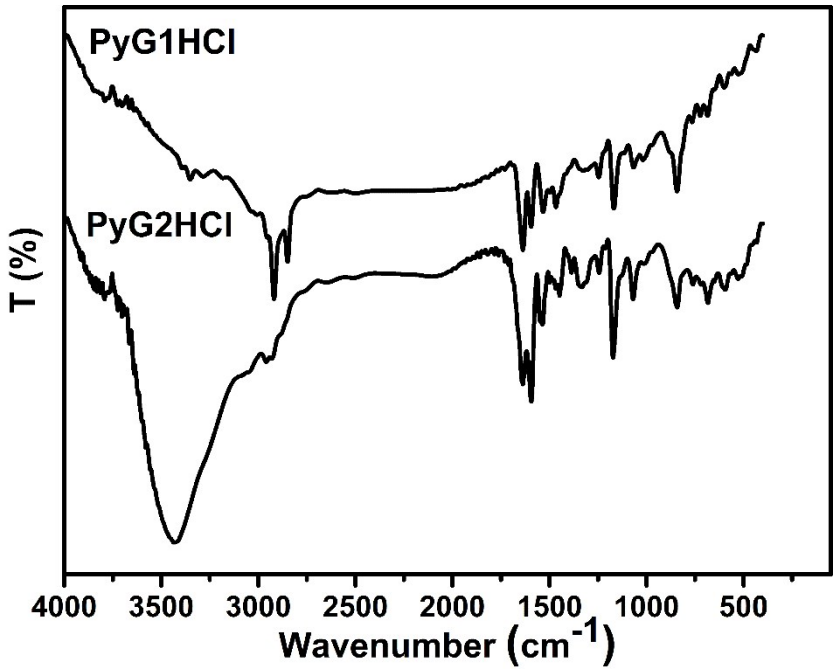

Figure S2. FT-IR spectra of **PyG1HCl** and **PyG2HCl** in their freeze-drying nanostructures.

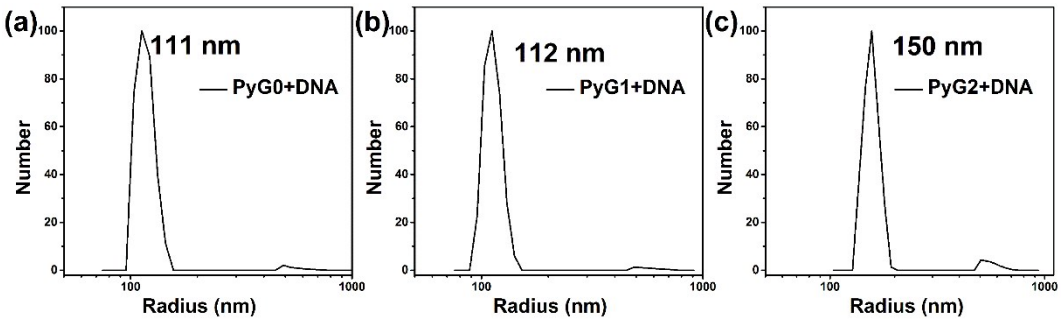

Figure S3. DLS results of DNA condensation induced by (a) **PyG0HCl**, (b) **PyG1HCl** and (c) **PyG2HCl**.

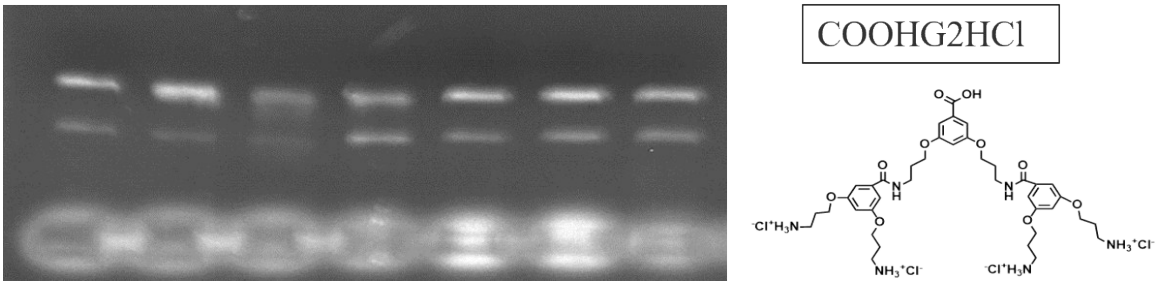

Figure S4. Agarose gel electrophoresis assay to investigate the DNA condensation of **COOHG2HCl**. Lane 1, DNA alone; lanes 2–7, DNA + **COOHG2HCl**. The DNA concentration is 10 ng/μL. The different concentrations of **COOHG2HCl** from lane 2 to lane 7 were 500 μM, 100 μM, 50 μM, 10 μM, 5 μM, 1 μM, respectively.

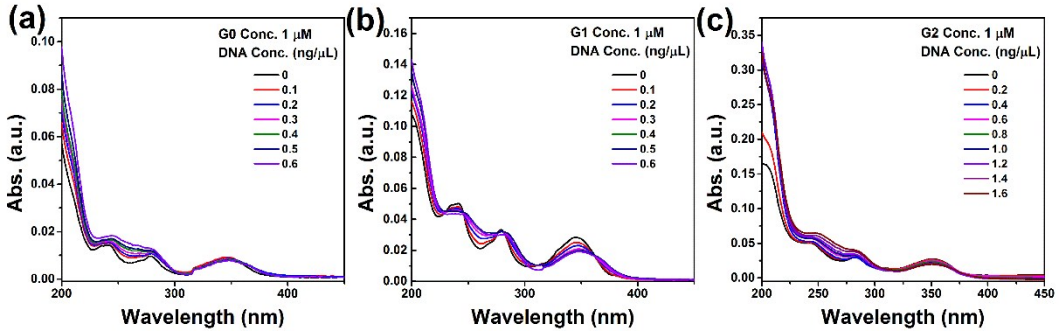

Figure S5. UV-Vis spectra of (a) **PyG0HCl**, (b) **PyG1HCl** and (c) **PyG2HCl** as a function of added DNA (Concentration of **PyG0HCl**, **PyG1HCl** and **PyG2HCl** in water: 1.0 μM).

NMR and Mass Spectra:

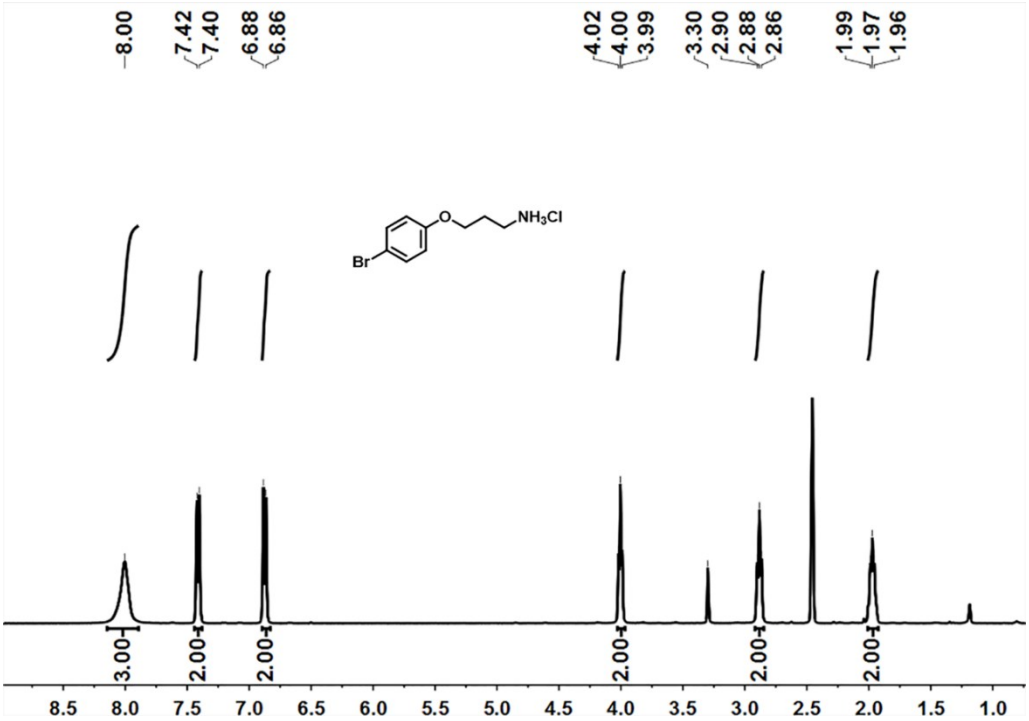

Figure S6. [1]H NMR spectrum of Compound **2** in DMSO-*d*6.

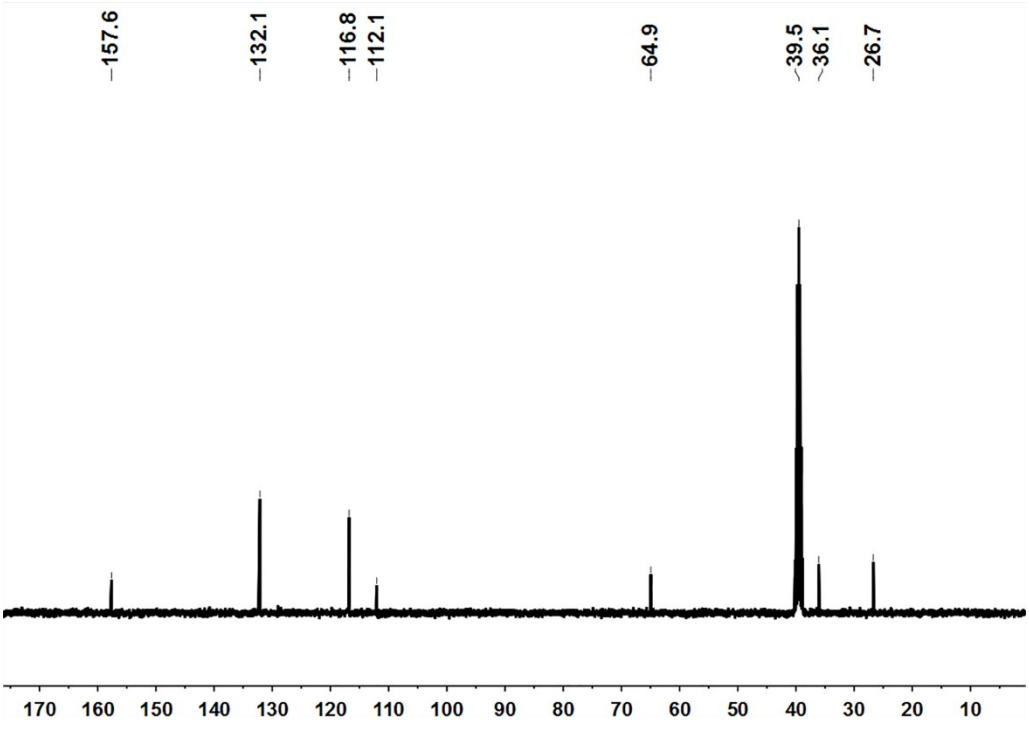

Figure S7. [13]C NMR spectrum of Compound **2** in DMSO-*d*6.

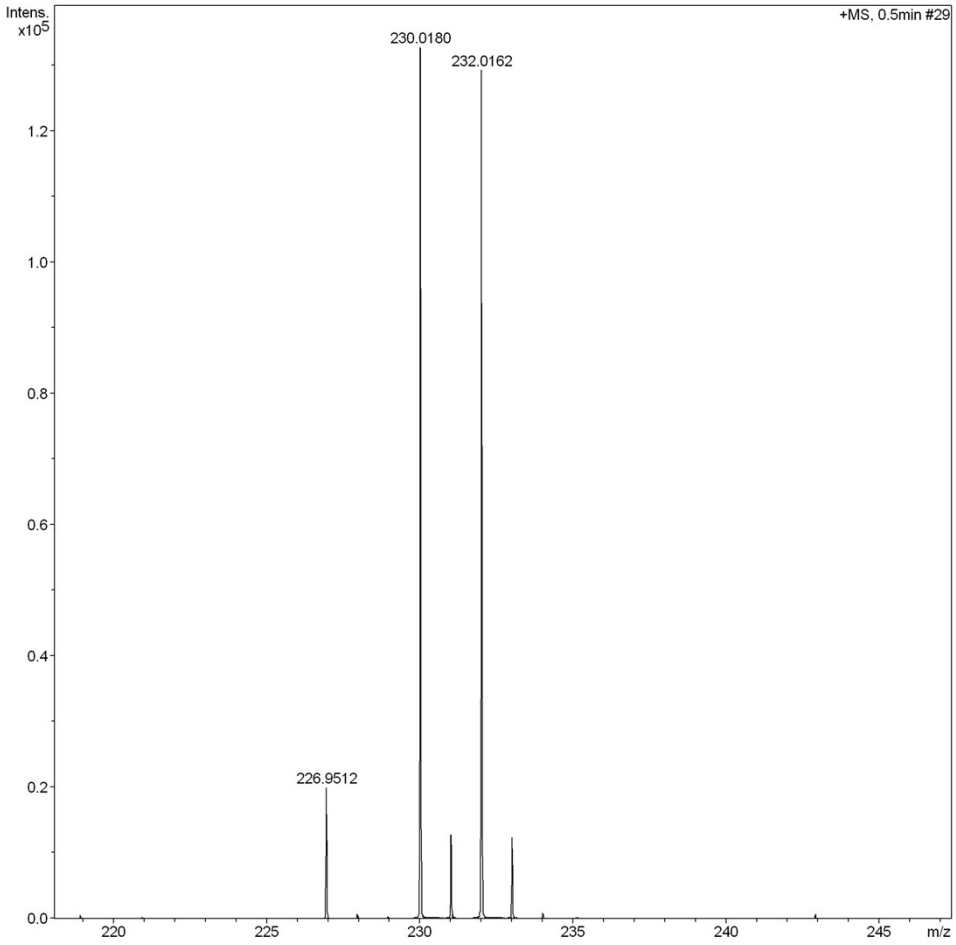

Figure S8. HR-ESI spectrum of Compound **2**.

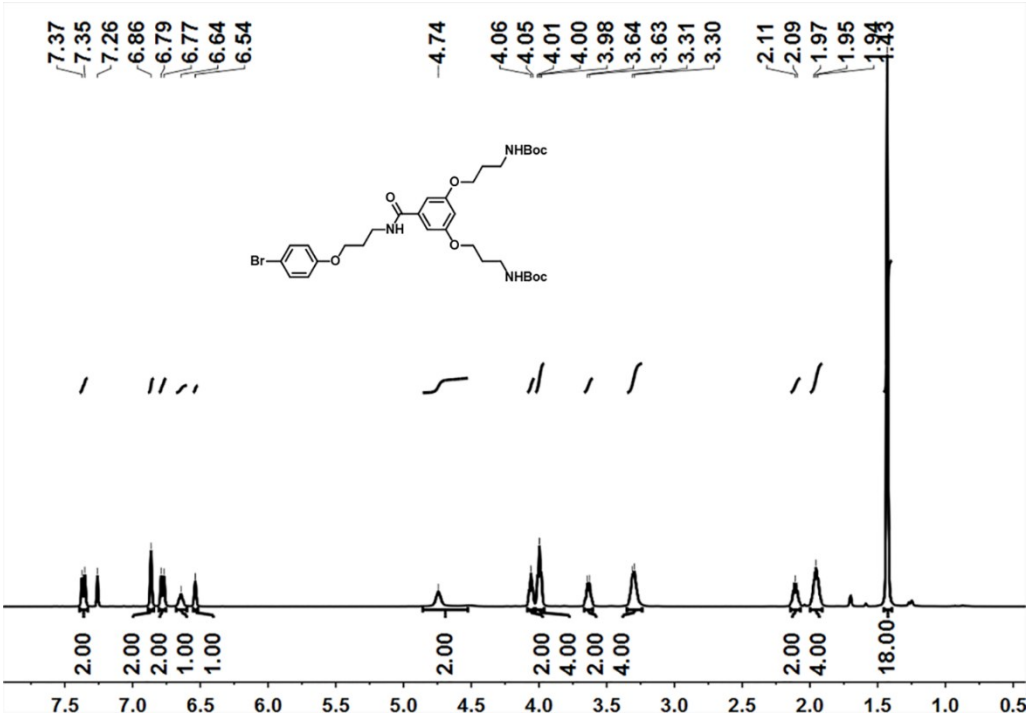

Figure S9. ^{1}H NMR spectrum of Compound **4** in $CDCl_3$.

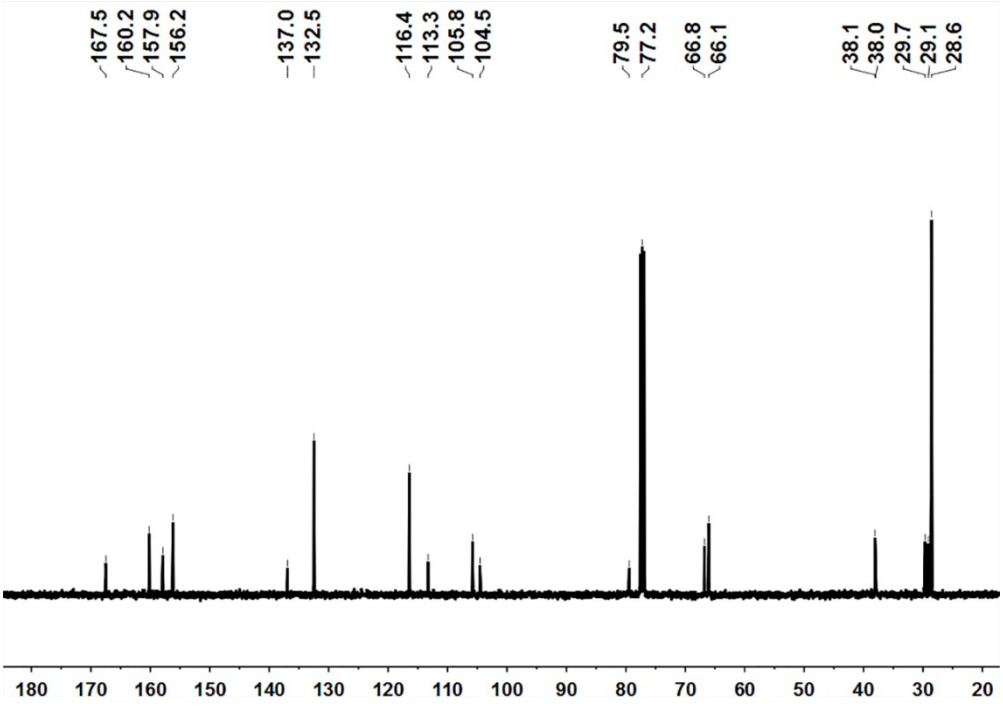

Figure S10. ^{13}C NMR spectrum of Compound **4** in $CDCl_3$.

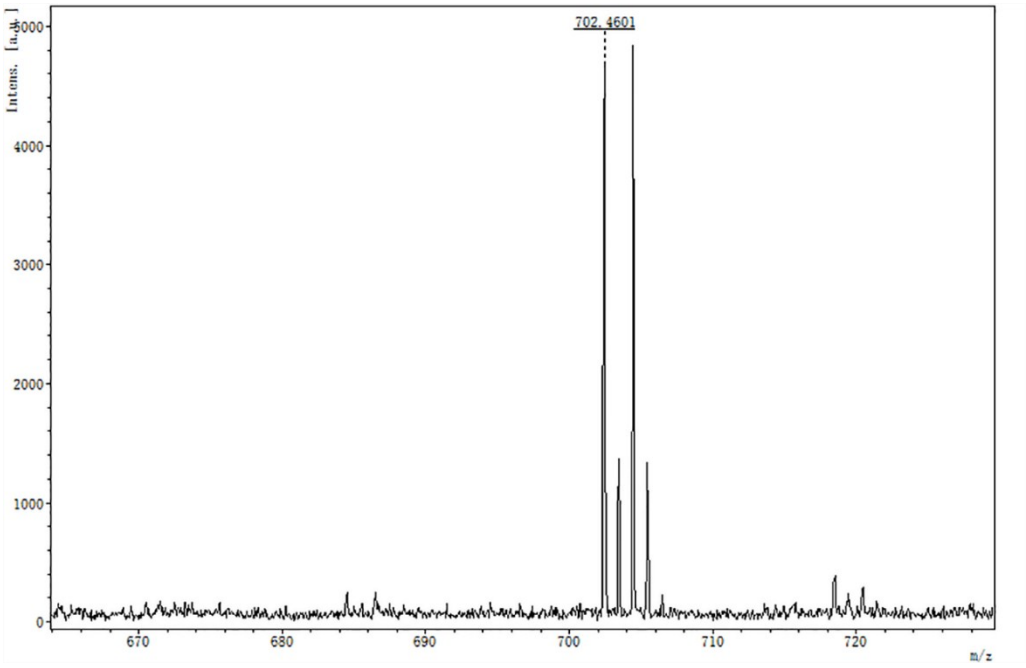

Figure S11. MALDI-TOF spectrum of Compound **4**.

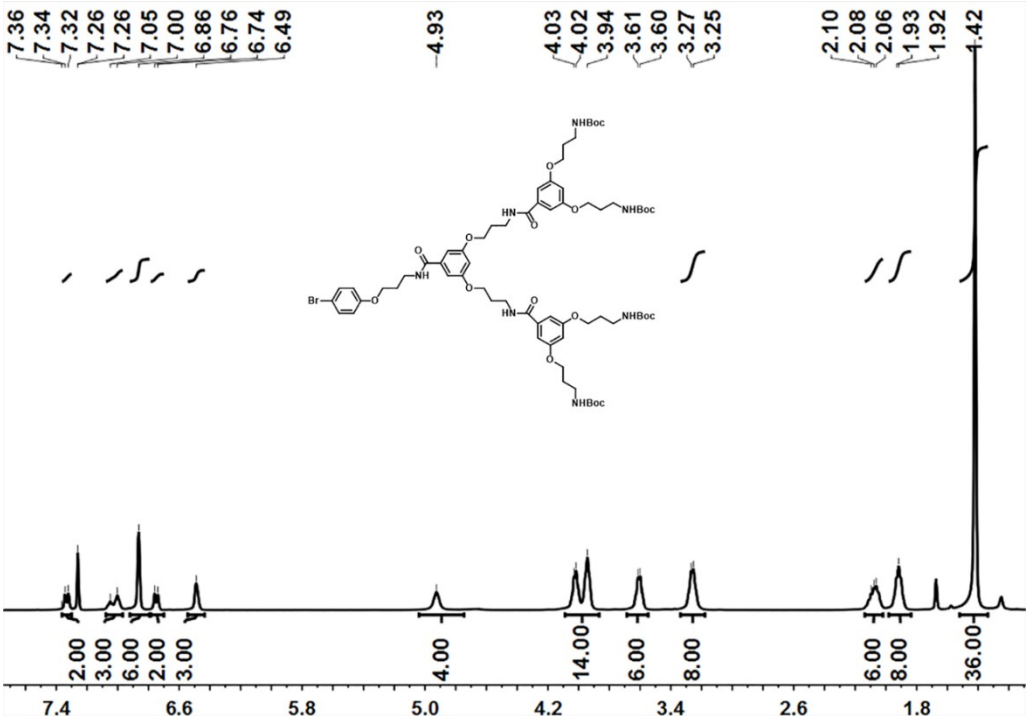

Figure S12. ^{1}H NMR spectrum of Compound **7** in $CDCl_3$.

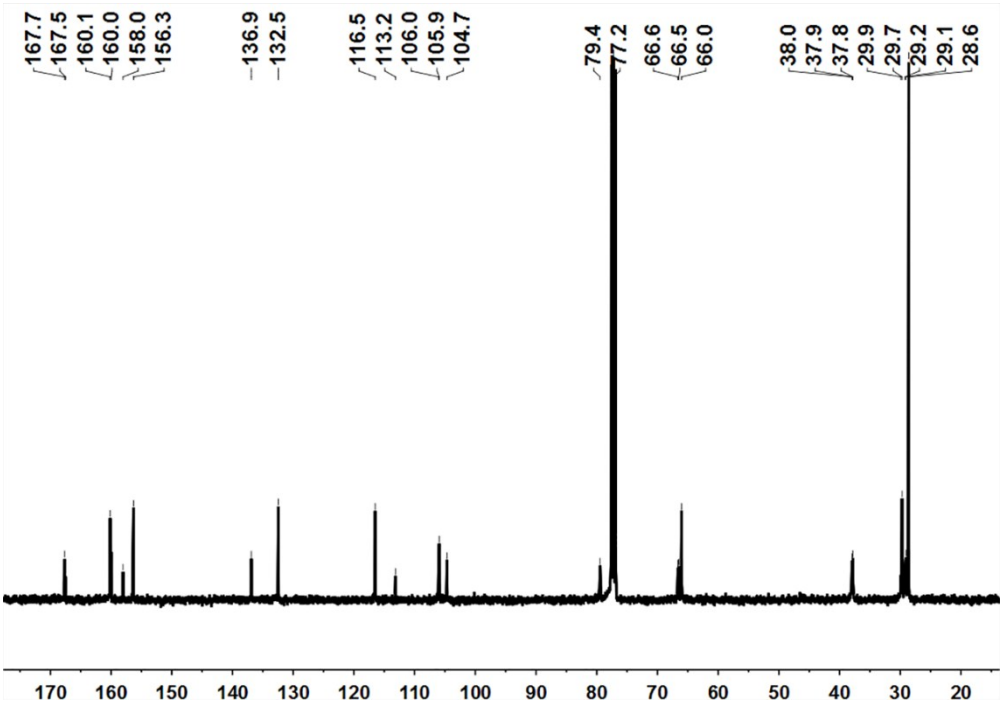

Figure S13. ^{13}C NMR spectrum of Compound **7** in $CDCl_3$.

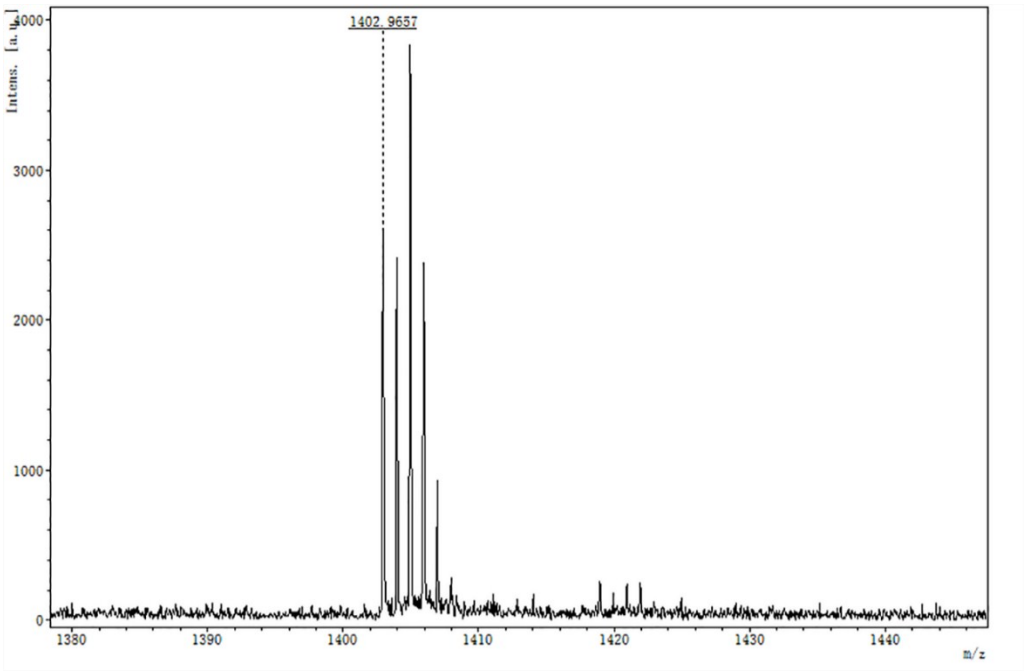

Figure S14. MALDI-TOF spectrum of Compound **7**.

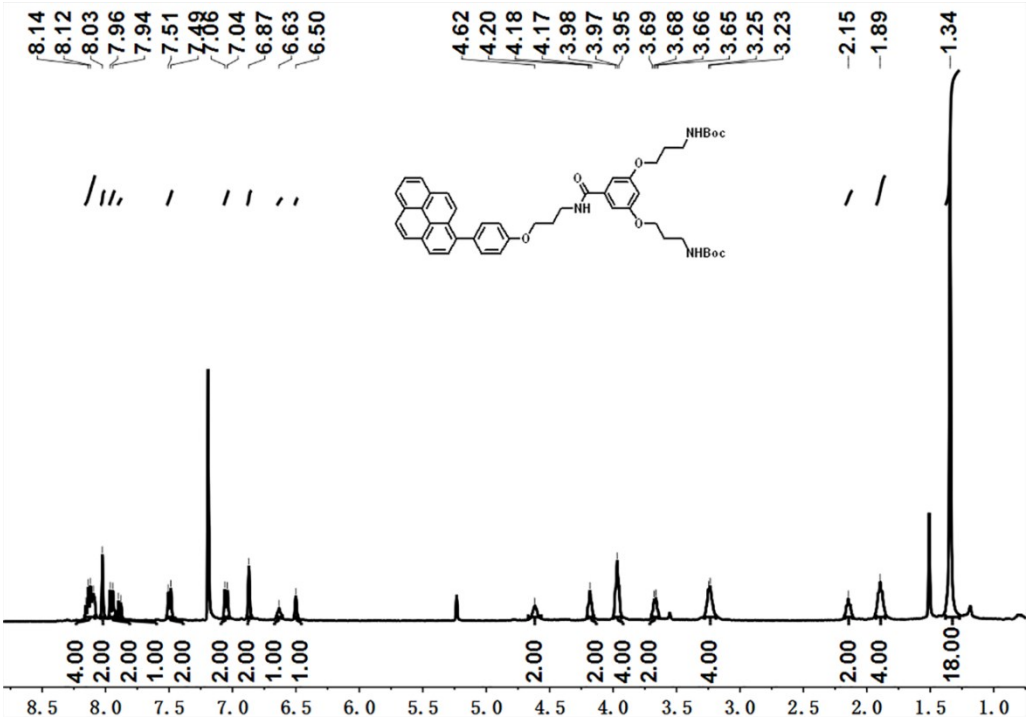

Figure S15. ^{1}H NMR spectrum of **PyG1Boc** in $CDCl_3$.

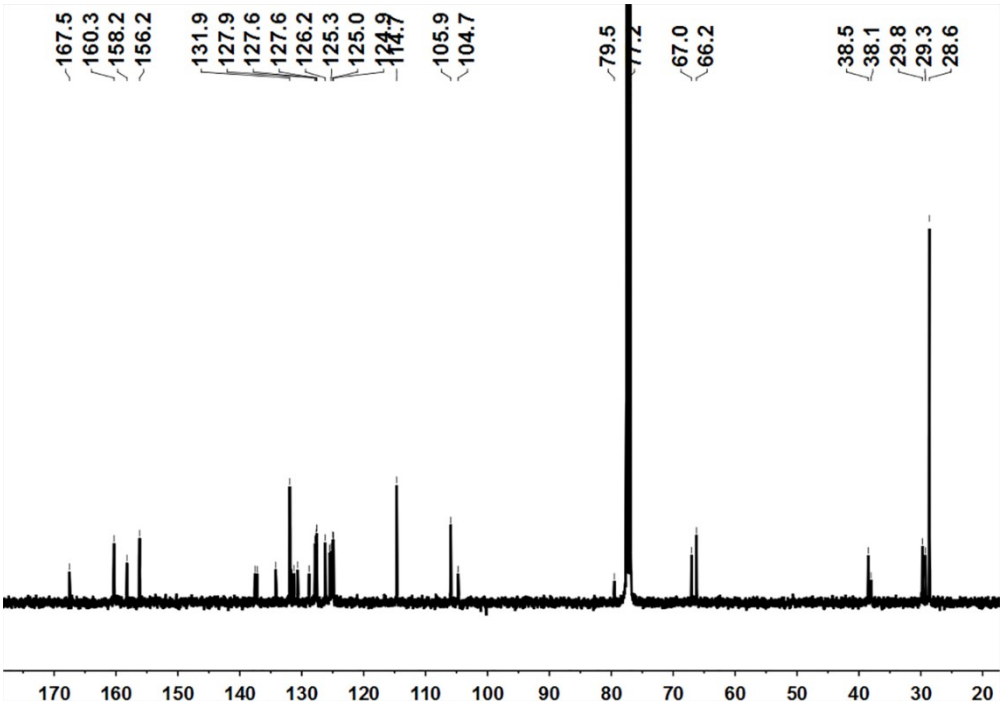

Figure S16. ^{13}C NMR spectrum of **PyG1Boc** in $CDCl_3$.

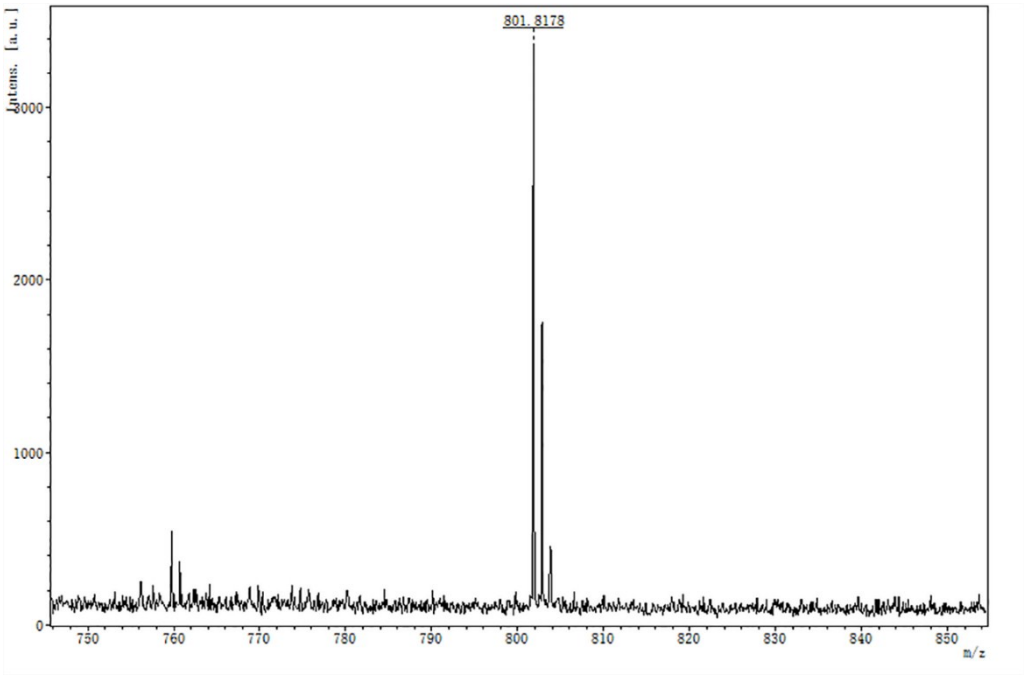

Figure S17. MALDI-TOF spectrum of **PyG1Boc**.

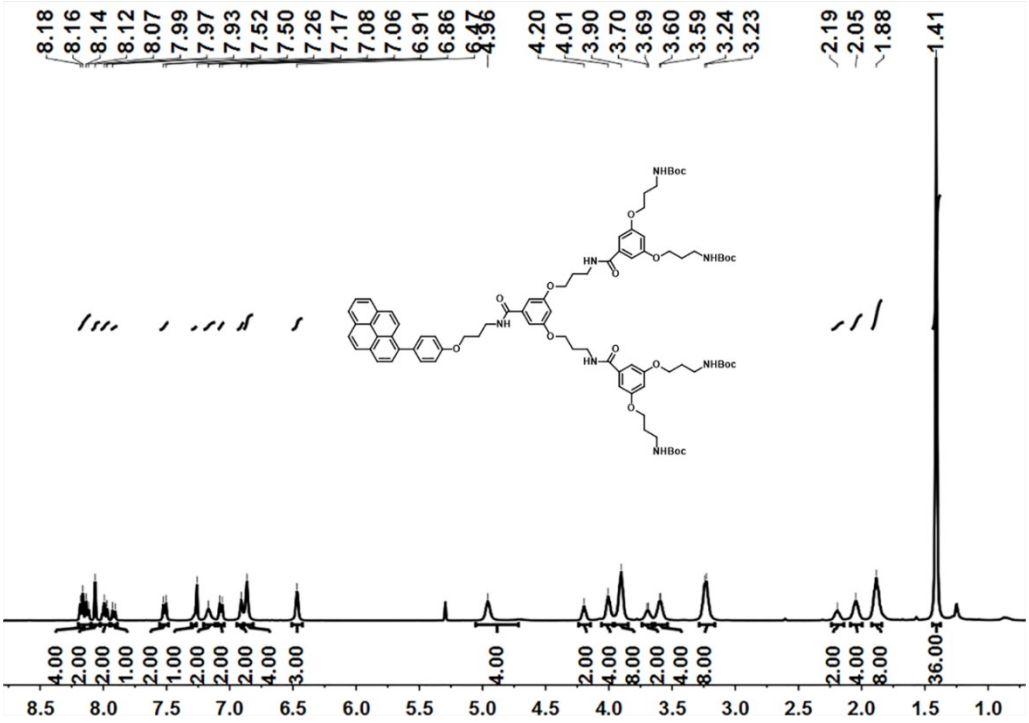

Figure S18. ^{1}H NMR spectrum of **PyG2Boc** in $CDCl_3$.

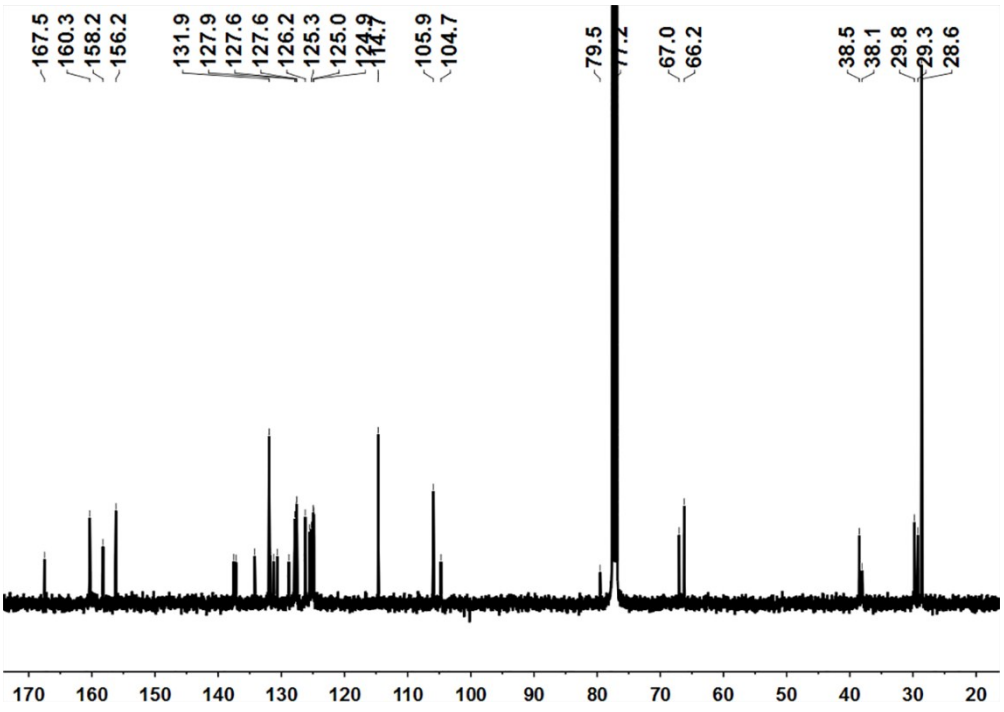

Figure S19. ^{13}C NMR spectrum of **PyG2Boc** in $CDCl_3$.

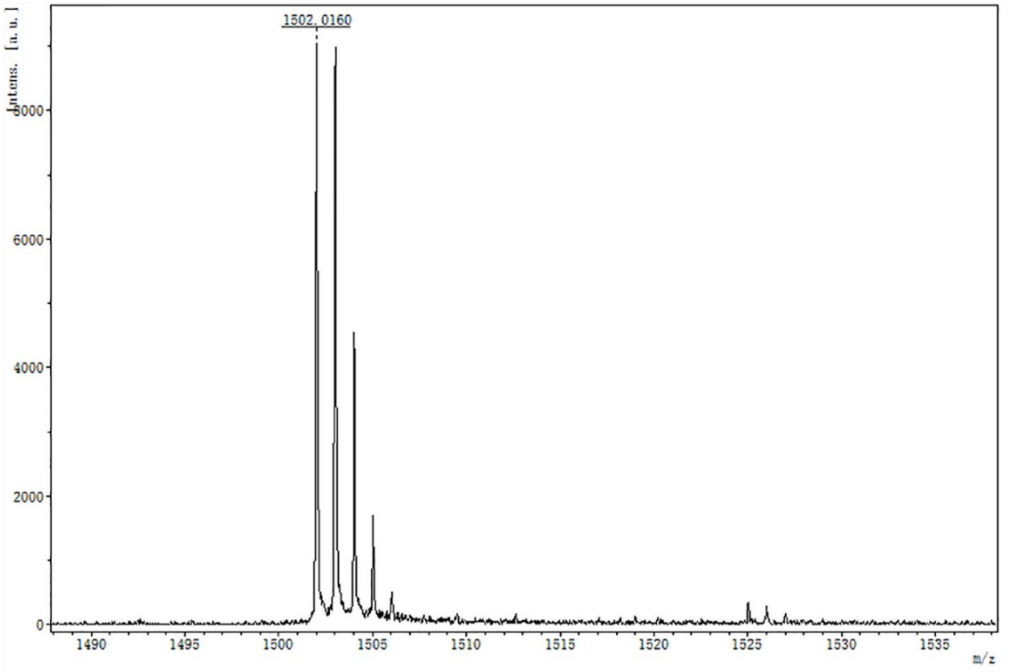

Figure S20. MALDI-TOF spectrum of **PyG2Boc**.

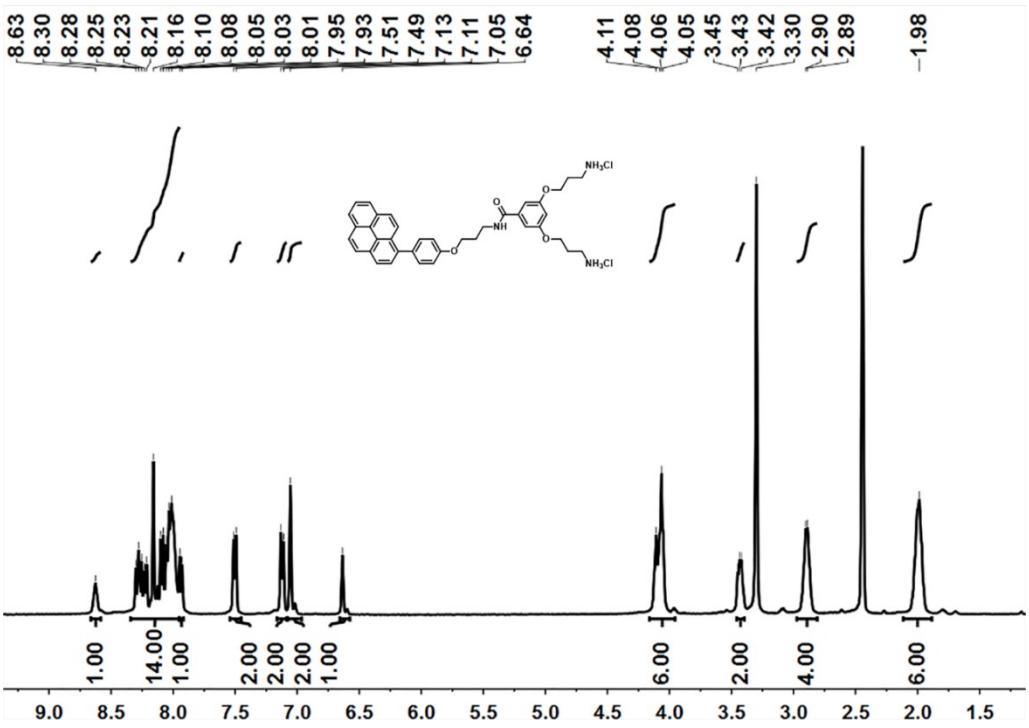

Figure S21. ^{1}H NMR spectrum of **PyG1HCl** in DMSO-*d*$_6$.

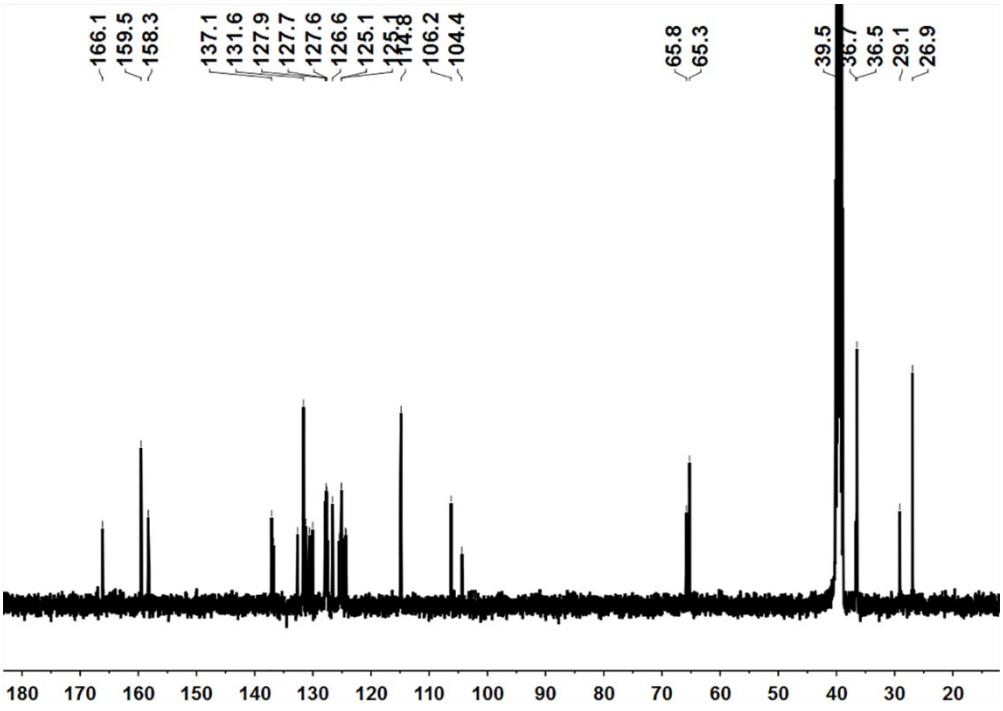

Figure S22. ^{13}C NMR spectrum of **PyG1HCl** in DMSO-*d*$_6$.

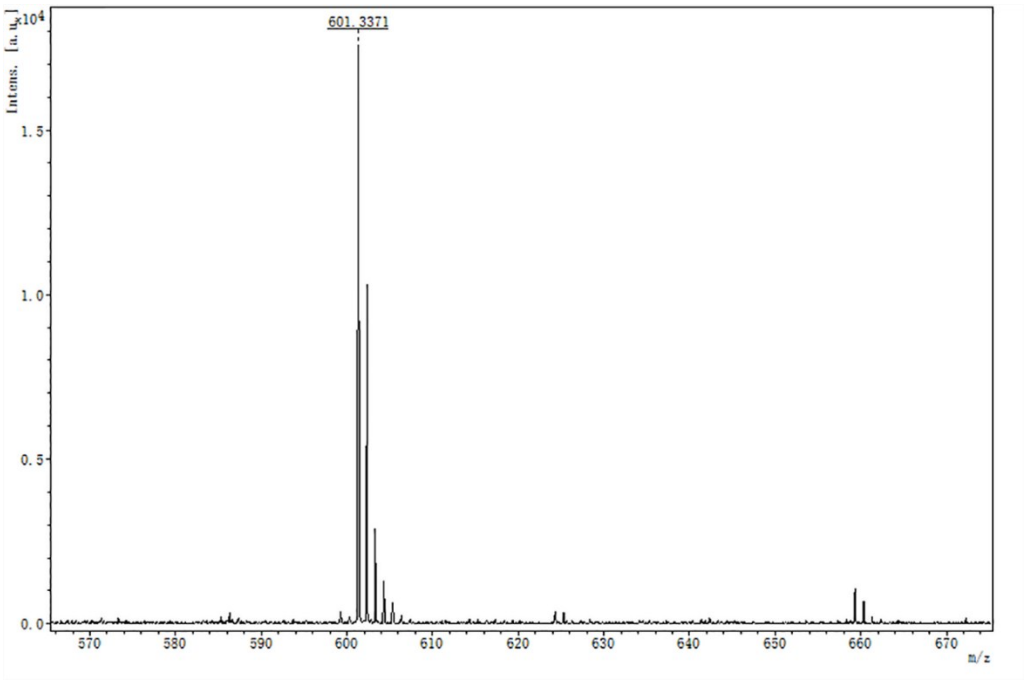

Figure S23. MALDI-TOF spectrum of **PyG1HCl**.

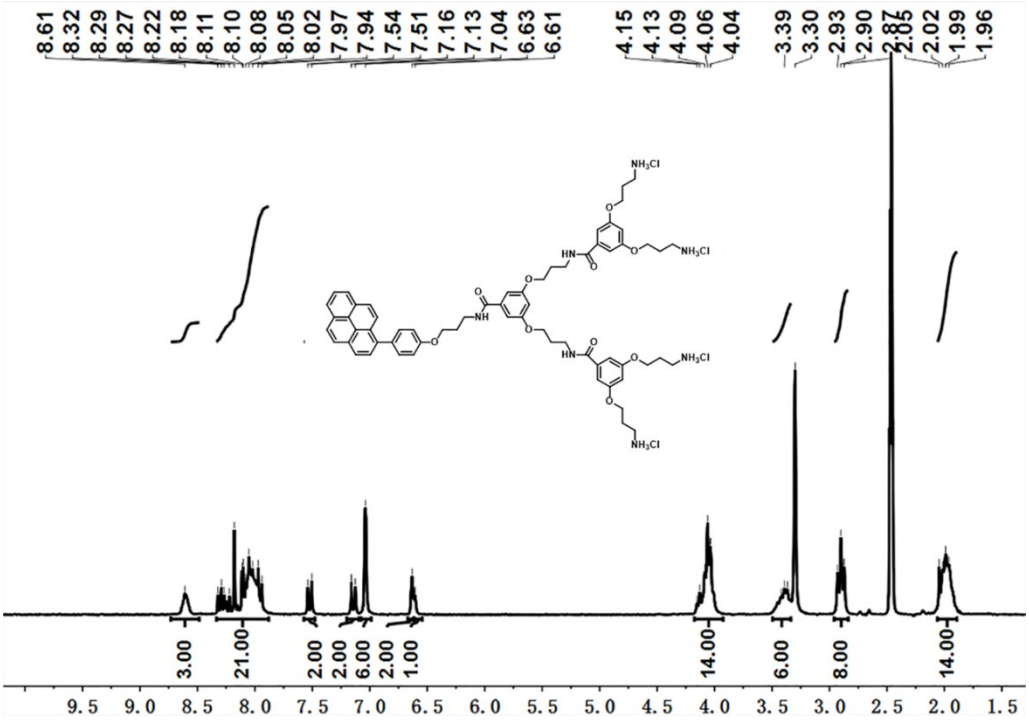

Figure S24. ^{1}H NMR spectrum of **PyG2HCl** in DMSO-*d*$_6$.

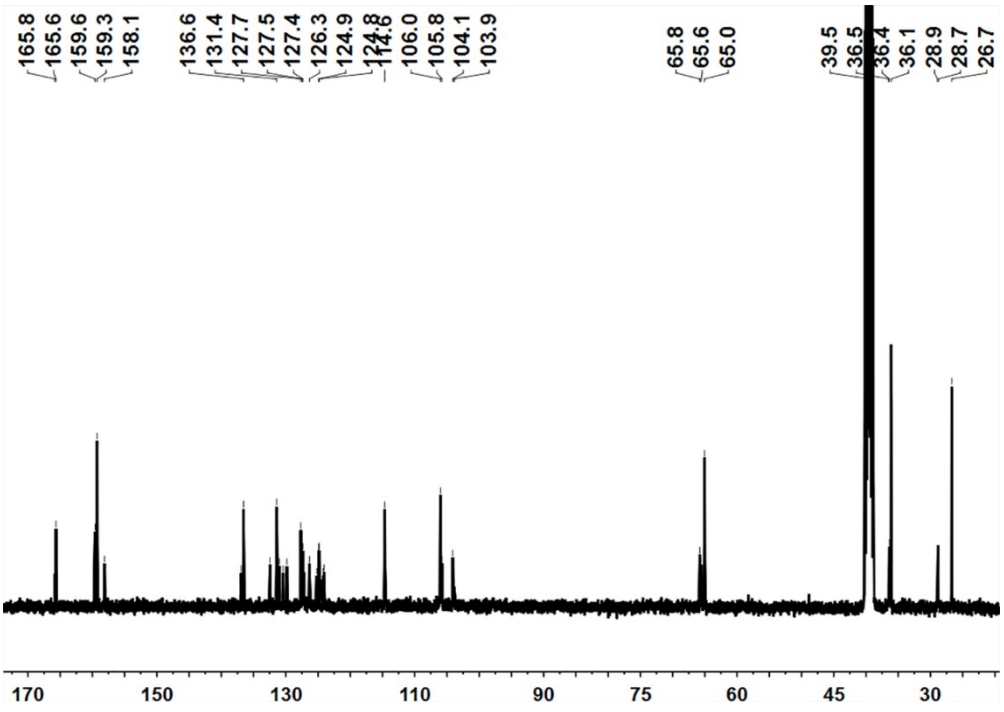

Figure S25. ^{13}C NMR spectrum of **PyG2HCl** in DMSO-*d*6.

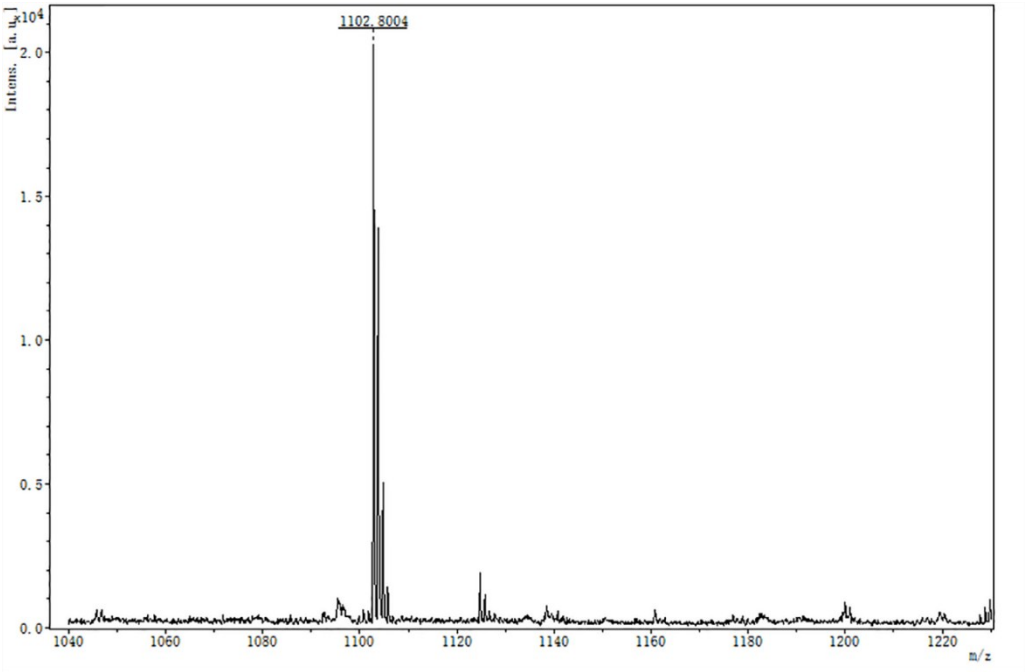

Figure S26. MALDI-TOF spectrum of **PyG2HCl**.

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