Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Supporting Information

A Fluorescence-activatable Tumor-reporting Probe for Precise Photodynamic Therapy

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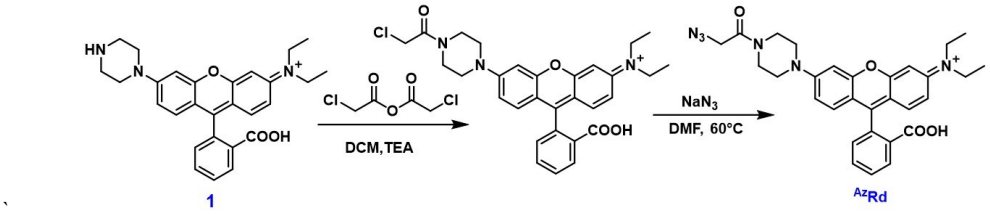
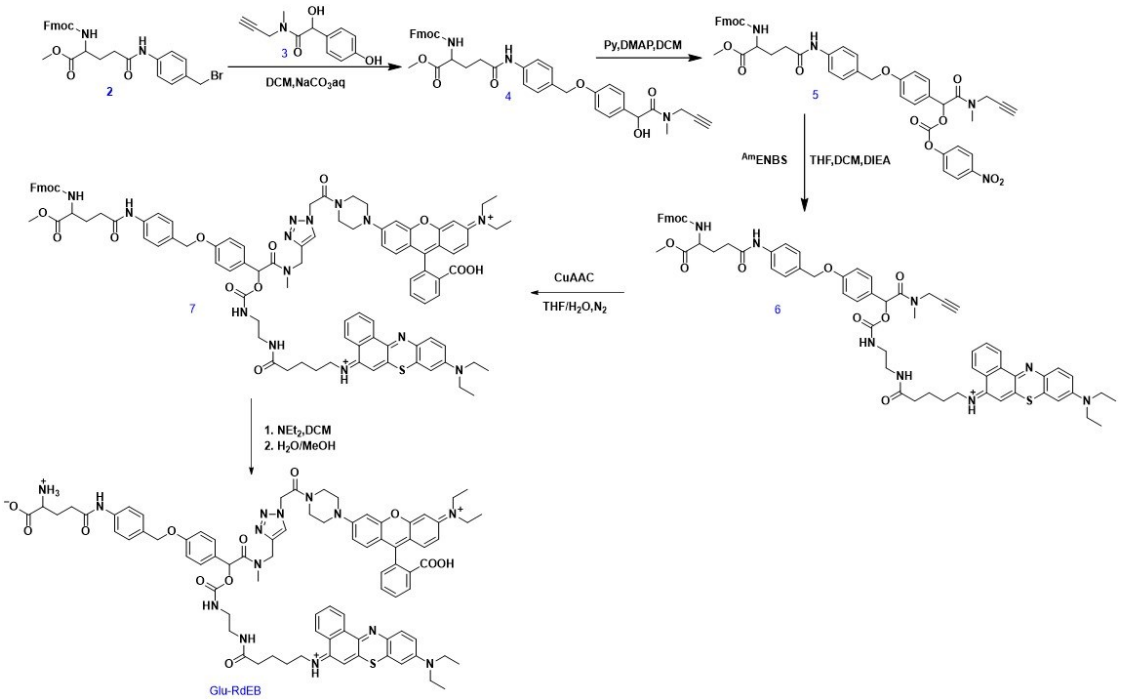
Synthesis of compounds



Scheme S1. Synthetic route for ^{Az}Rd.



Scheme S2. Synthetic route for Glu-RdEB.

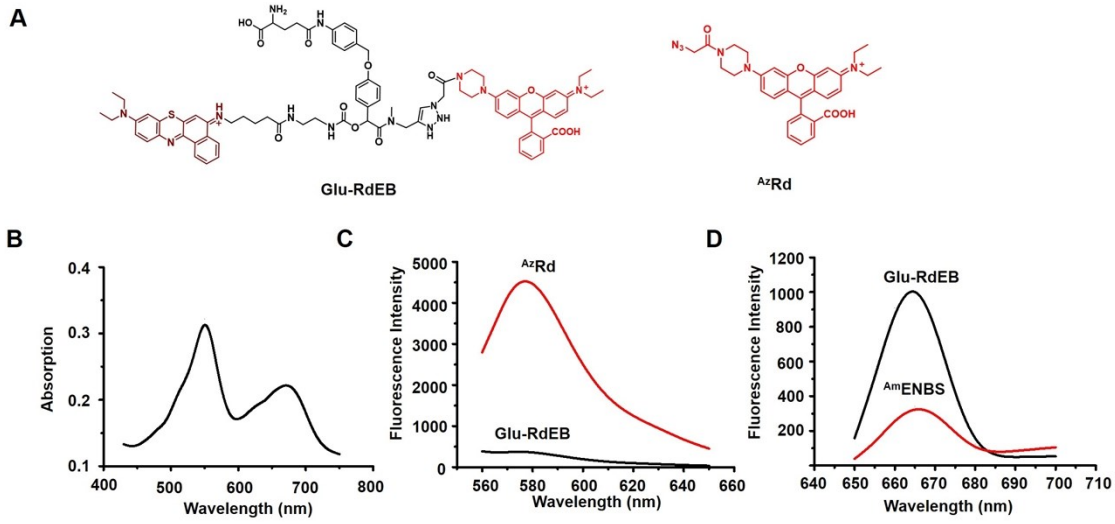


Fig. S1 Optical property of Glu-RdEB. (A) Chemical structures of Glu-RdEB and ^{Az}Rd. (B) UV-Vis absorption of Glu-RdEB. (C) Rd fluorescence emission of Glu-RdEB (10 μM), ^{Az}Rd (10 μM) in PBS (pH 7.4). The fluorescence emission

was measured using λ_{ex} = 540 nm. (D) Rd fluorescence emission of Glu-RdEB (10 μM), ^{Am}ENBS (10 μM) in sodium phosphate buffer (pH 7.4). The fluorescence emission was measured using λ_{ex} = 660 nm.

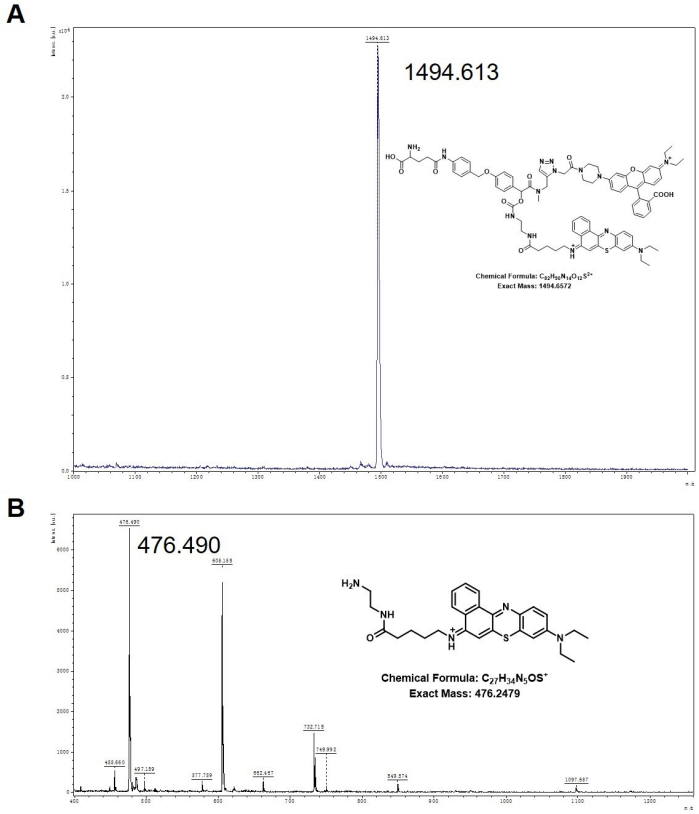


Fig. S2 MALDI-TOFMS analysis of Glu-RdEB solution spiked with GGT. (A) MALDI-TOFMS of Glu-RdEB. (B) MALDI-TOFMS of GGT inactivation by Glu-RdEB, Glu-RdEB (10 μM) was incubated for 16 h in PBS (pH 7.4) with GGT (80 Units) at 37 ℃.

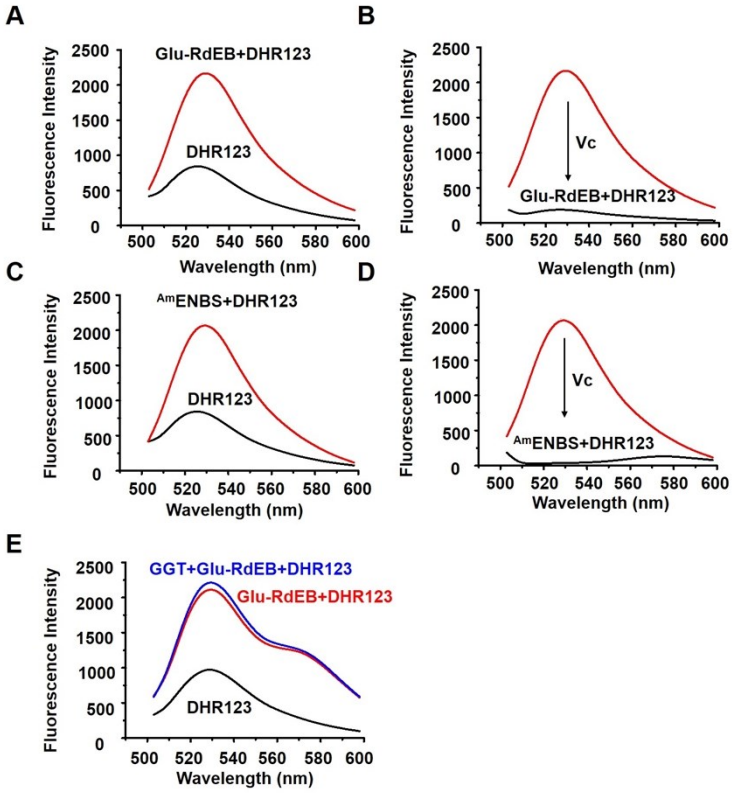


Fig. S3 Fluorescence spectra for $O_2^{-\bullet}$ using DHR123 as fluorescence probe. (A) The solution of Glu-RdEB (10 μM) containing DHR 123 (10 μM) were exposed to light illumination for 6 min before analysis for fluorescence emission. (B) $O_2^{-\bullet}$ quenching experiment, 0.5 mM Vc was added to the above (Glu-RdEB+DHR123) aqueous solution before light irradiation. (C) The solution of ^{Am}ENBS (10 μM) containing DHR 123 (10 μM) were exposed to light illumination for 6 min before analysis for fluorescence emission. (D) $O_2^{-\bullet}$ quenching experiment, 0.5 mM Vc was added to the above (^{Am}ENBS+DHR123) aqueous solution before light irradiation. (E) The solutions of Glu-RdEB (10 μM) containing DHR 123 (10 μM) containing GGT (0, or 80 units/L) were incubated for 16 h and then exposed to light illumination for 6 min before analysis for fluorescence emission. As control, DHR123 aqueous solution without photosensitizers was subjected to irradiation.

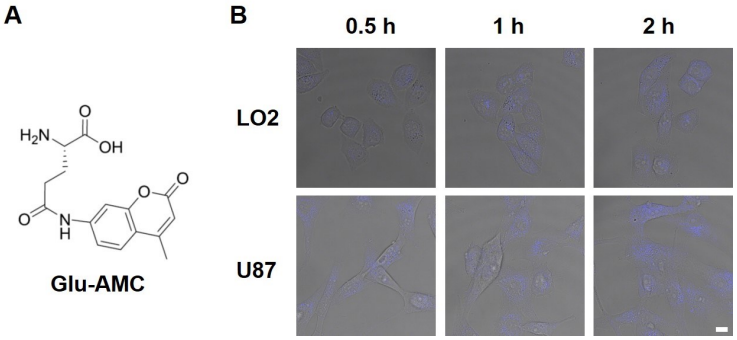


Fig. S4 (A) The chemical structure of commercial fluorescence probe (AMC-Glu). (B) GGT activity detection of U87 and LO2 with AMC-Glu based on fluorescence imaging. LO2 cells and U87 cells are incubated with AMC-Glu (10 μM) for 0.5，1，2 h. Scale bars: 10 μm.

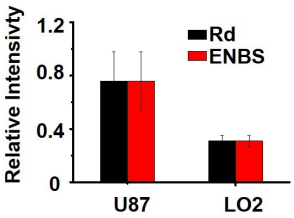


Fig. S5 preferred probe uptake and turnover in U87 cells over LO2 cells. U87 cells and LO2 cells pre-labeled with blue or green fluorescein were cocultured in DMEM for 16 h and then exposed to Glu-RdEB (20 μM) for 2 h before confocal microscopic analysis. The columns showed the intracellular rhodamine and ENBS fluorescence relative intensity (average of three areas) of U87 and LO2 cells in 3B.

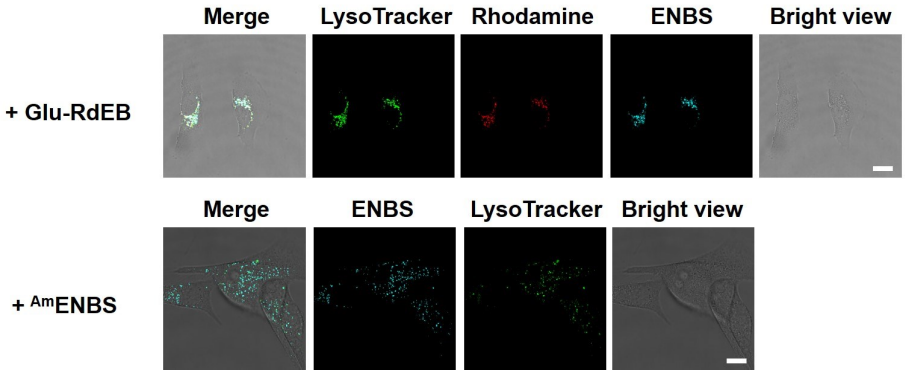


Fig. S6 Subcellular location of Glu-RdEB and ^{Am}ENBS in live cells. U87 cells were incubated for 2 h with Glu-RdEB (10 μM), ^{Am}ENBS (1 μM), and then with Lysotracker Green DND 26 (1 μM) for 30 min before confocal microscopic analysis. Scale bars: 10 μm.

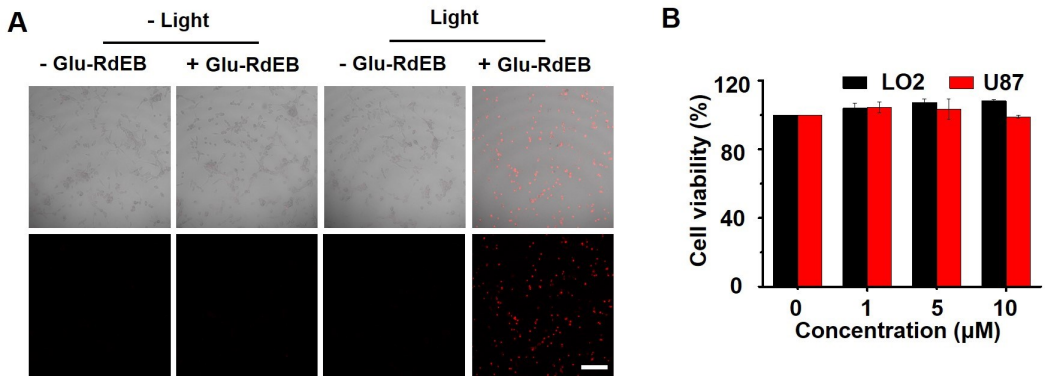


Fig. S7 (A) Photo-induced cytotoxicity of Glu-RdEB. U87 cells were incubated with Glu-RdEB (0.4 μM) for 2 h, then irradiate upon 660 nm light for 20 min, and then cultured in DMEM at 37 ℃ for 16 h, Dead cell staining assays using propidium iodide (20 μM, 0.5 h) as fluorescence probes. (λ_{ex}: 552 nm). Scale bars: 100 μm. (B) None dark toxicity of Glu-RdEB in live cell. U87 or LO2 cells were incubated with Glu-RdEB for 2 h, and then cell viability was determined by CCK-8 Kit.

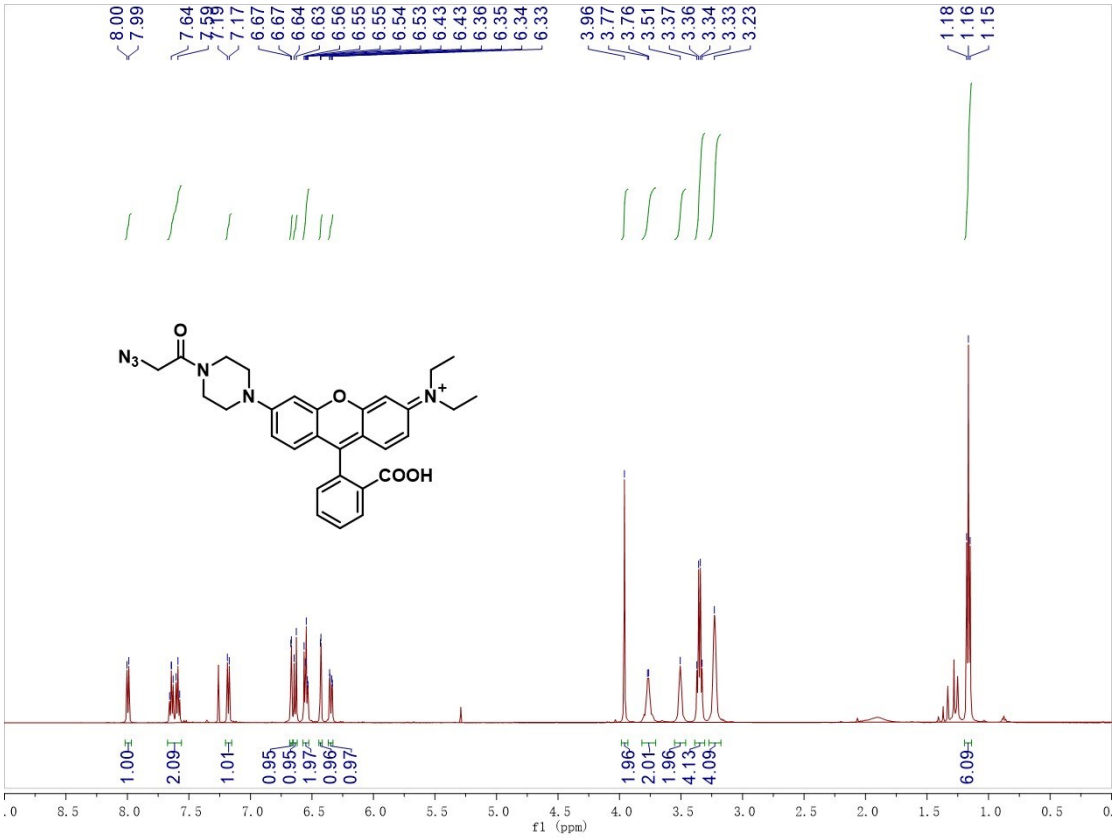


Fig. S8 ^{1}H-NMR Spectrum of ^{Az}Rd.

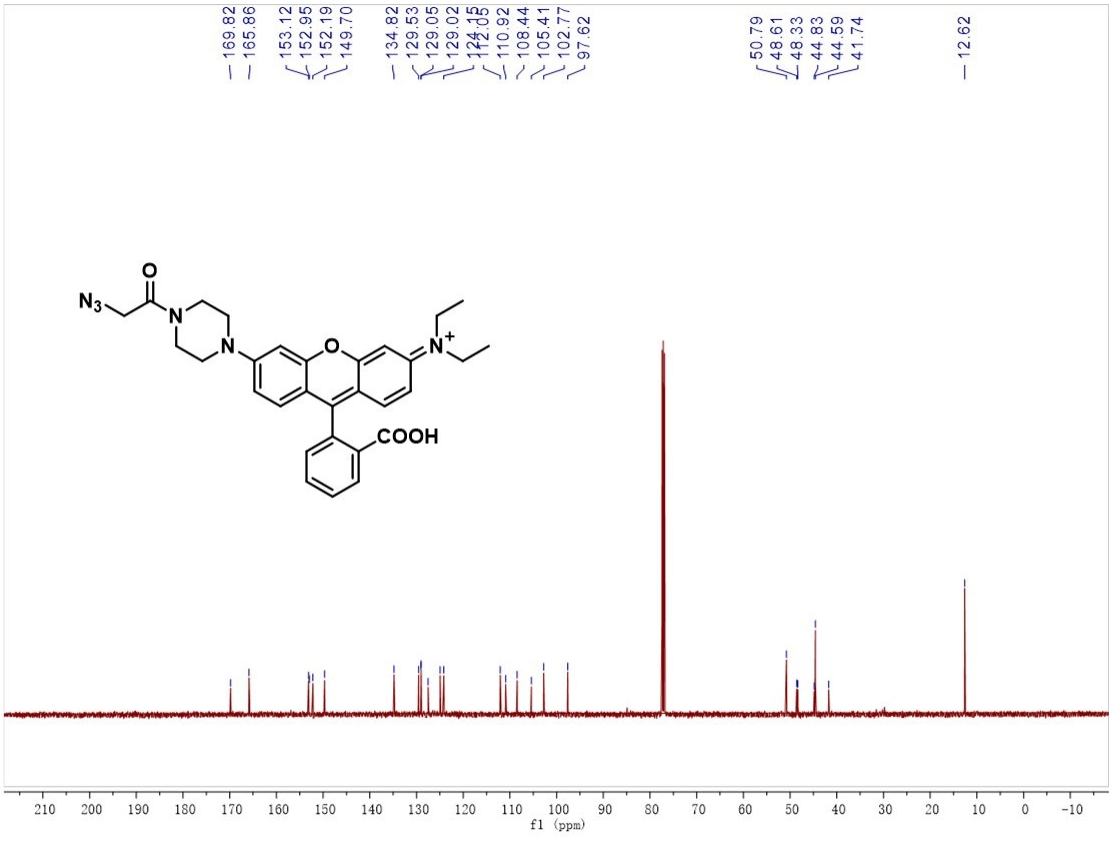


Fig. S9 ^{13}C-NMR Spectrum of ^{Az}Rd.

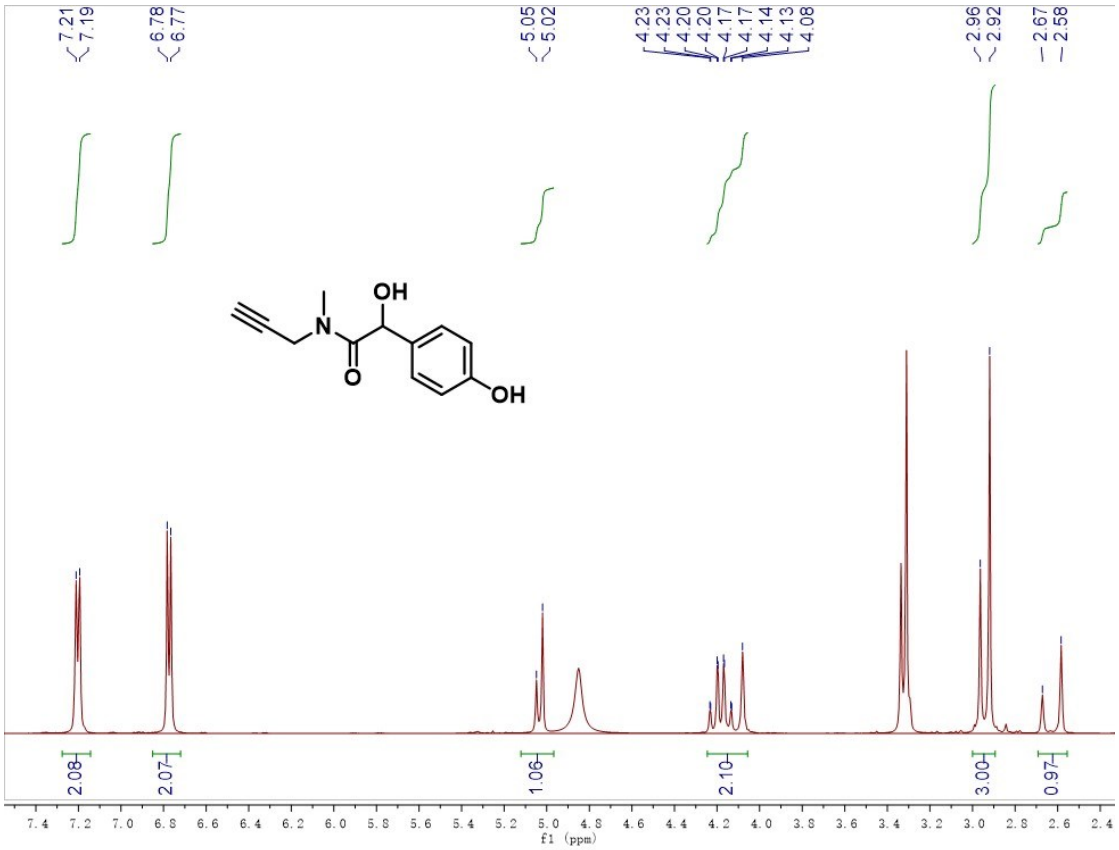


Fig. S10 ^{1}H-NMR Spectrum of compound **3**.

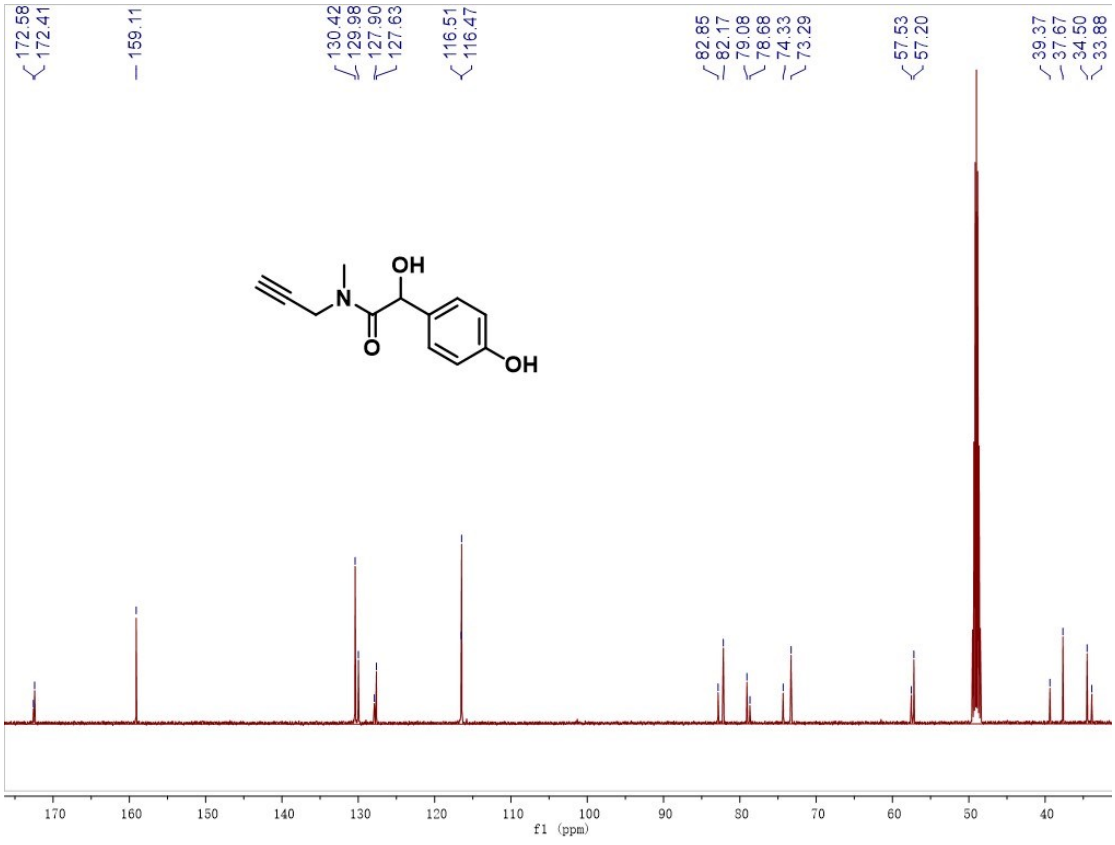


Fig. S11 ^{13}C-NMR Spectrum of compound **3**.

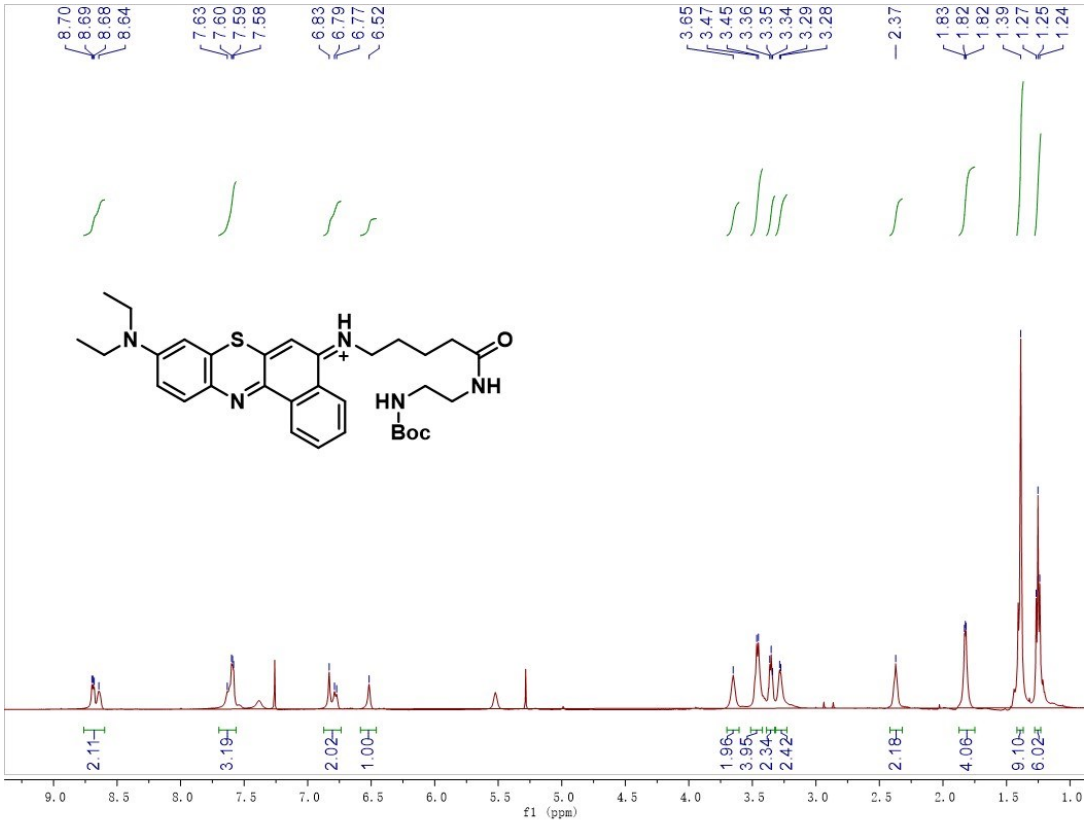


Fig. S12 ^{1}H-NMR Spectrum of ^{Am}ENBS-Boc.

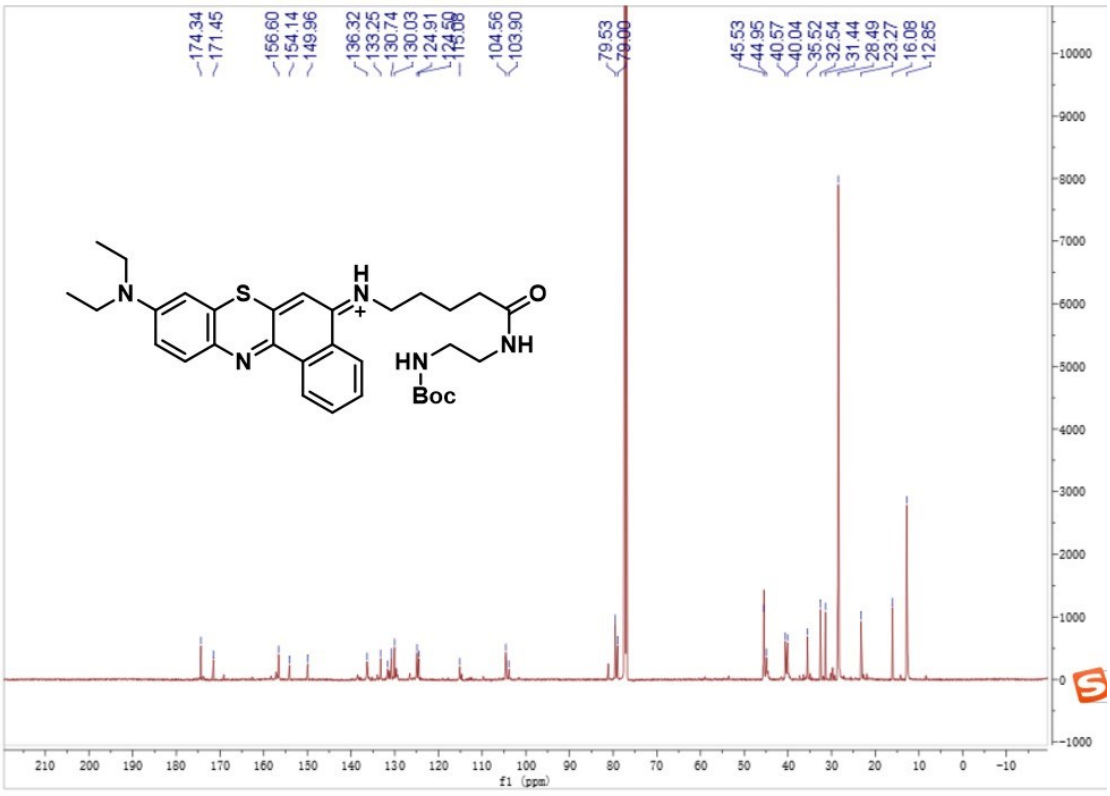


Fig. S13 ^{13}C-NMR Spectrum of ^{Am}ENBS-Boc.

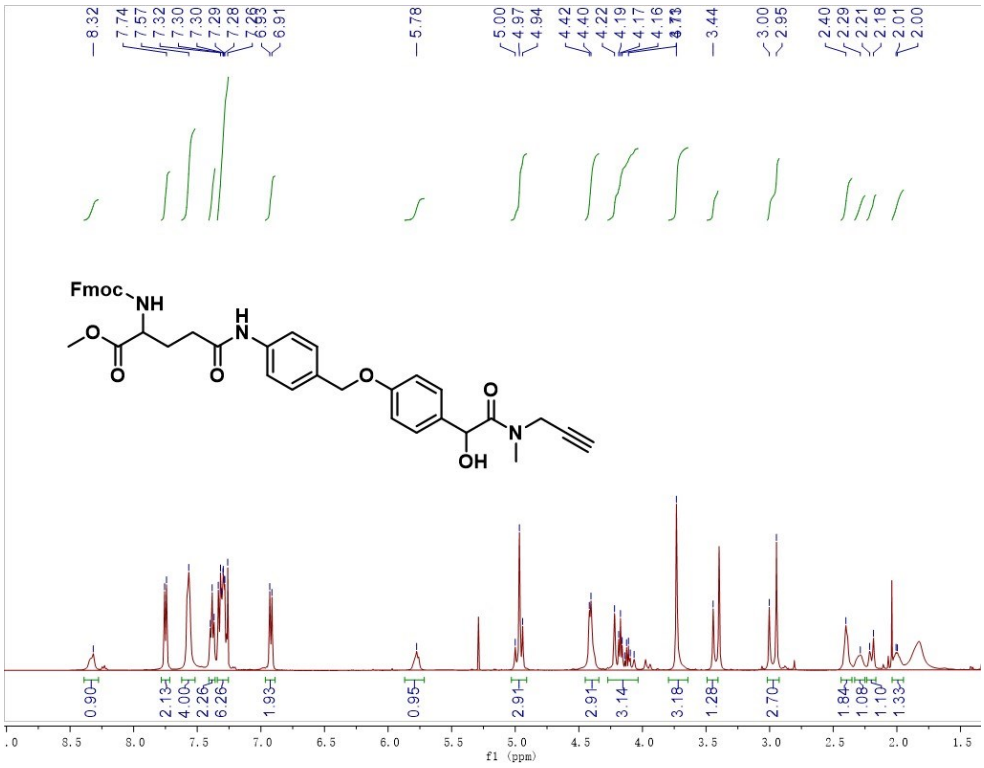


Fig. S14 ^{1}H-NMR Spectrum of compound compound **4**.

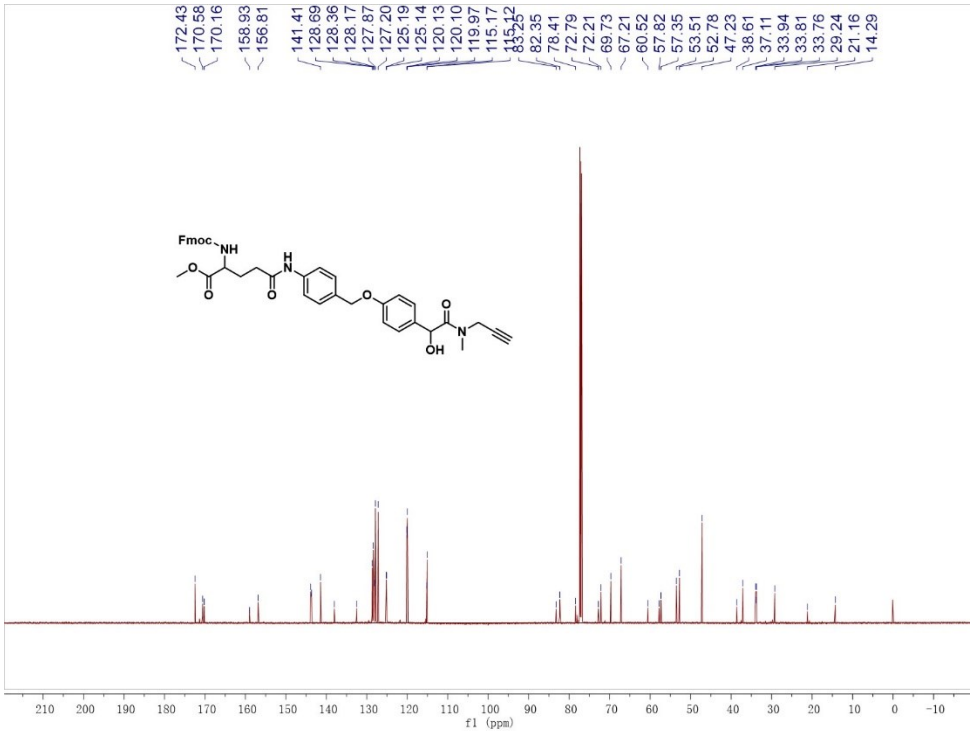


Fig. S15 ^{13}C-NMR Spectrum of compound **4**.

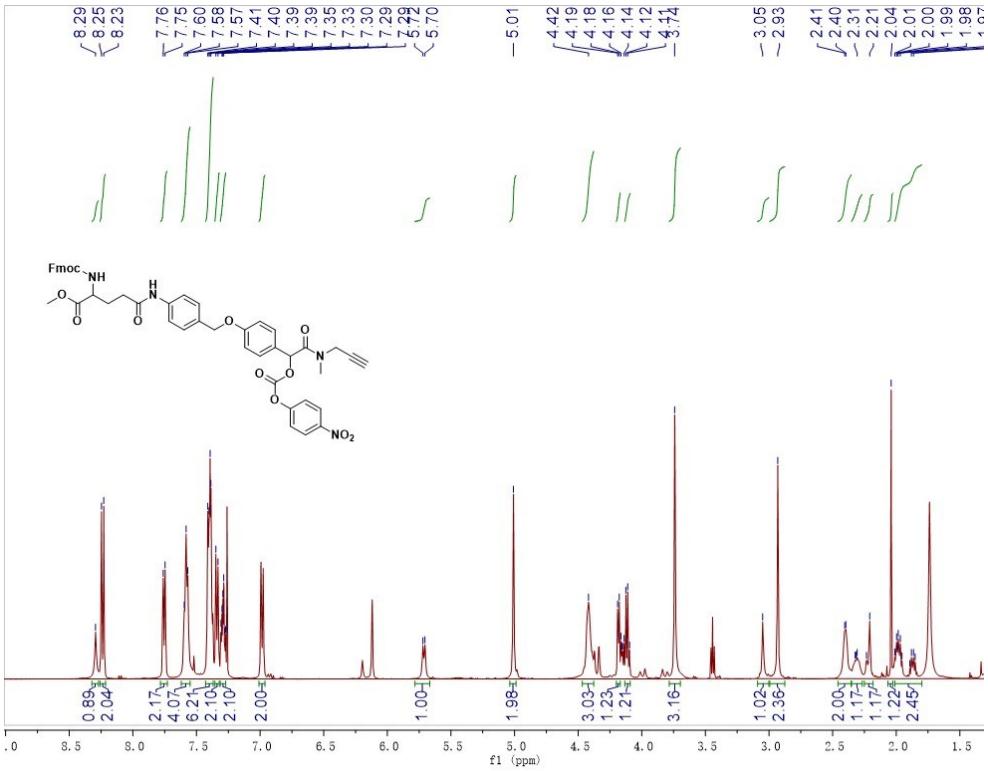


Fig. S16 ^{1}H-NMR Spectrum of compound compound **5**.

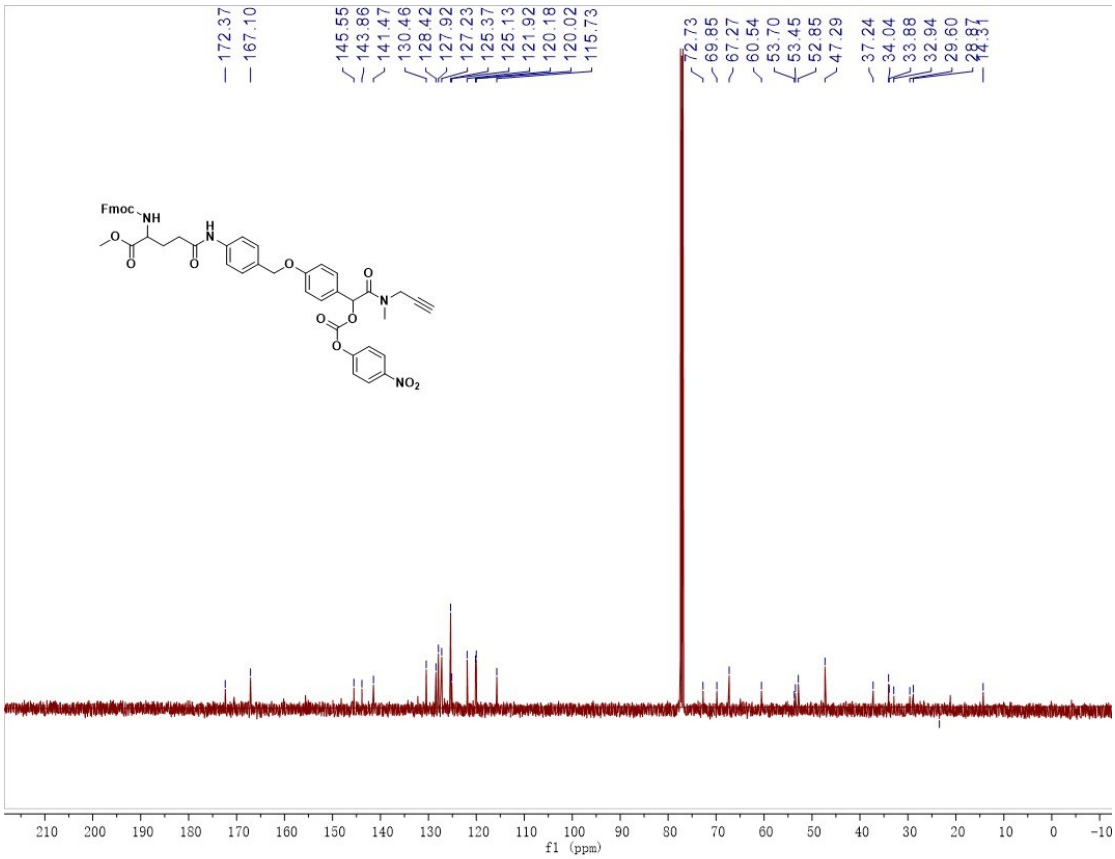


Fig. S17 ^{13}C-NMR Spectrum of compound compound **5**.

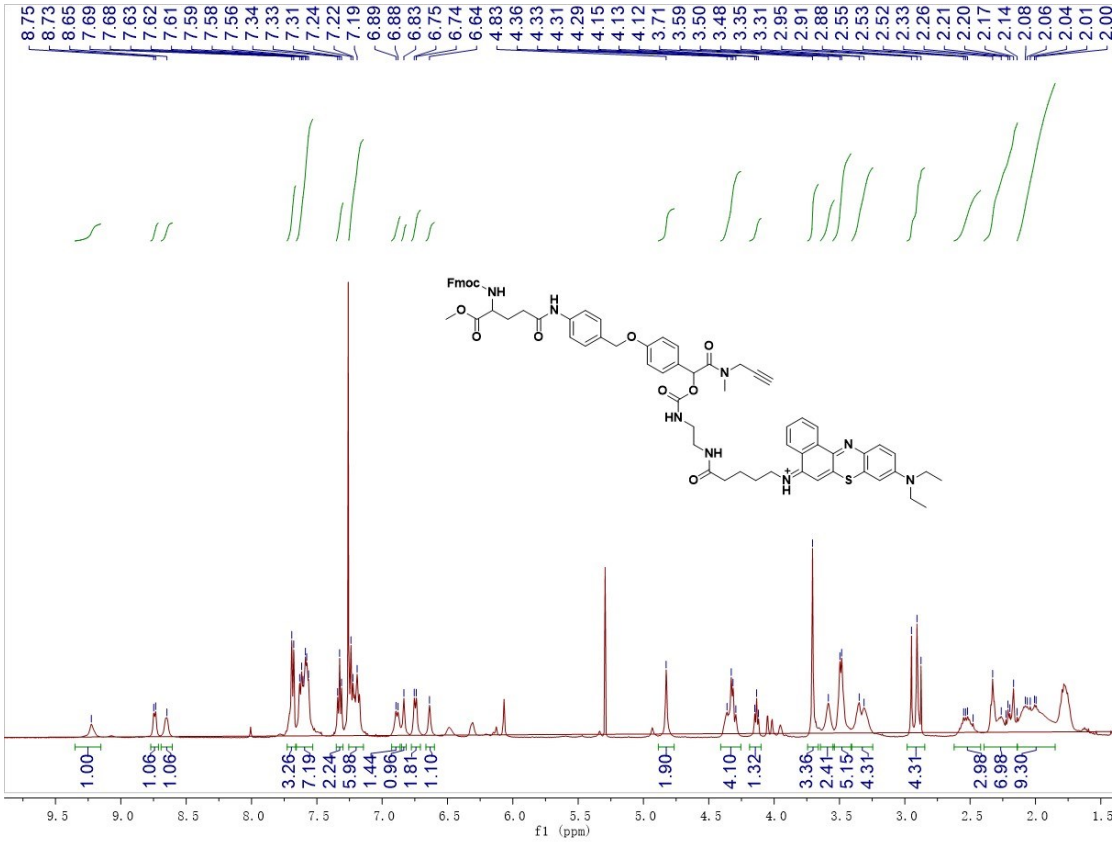


Fig. S18 [1]H-NMR Spectrum of compound compound **6**.

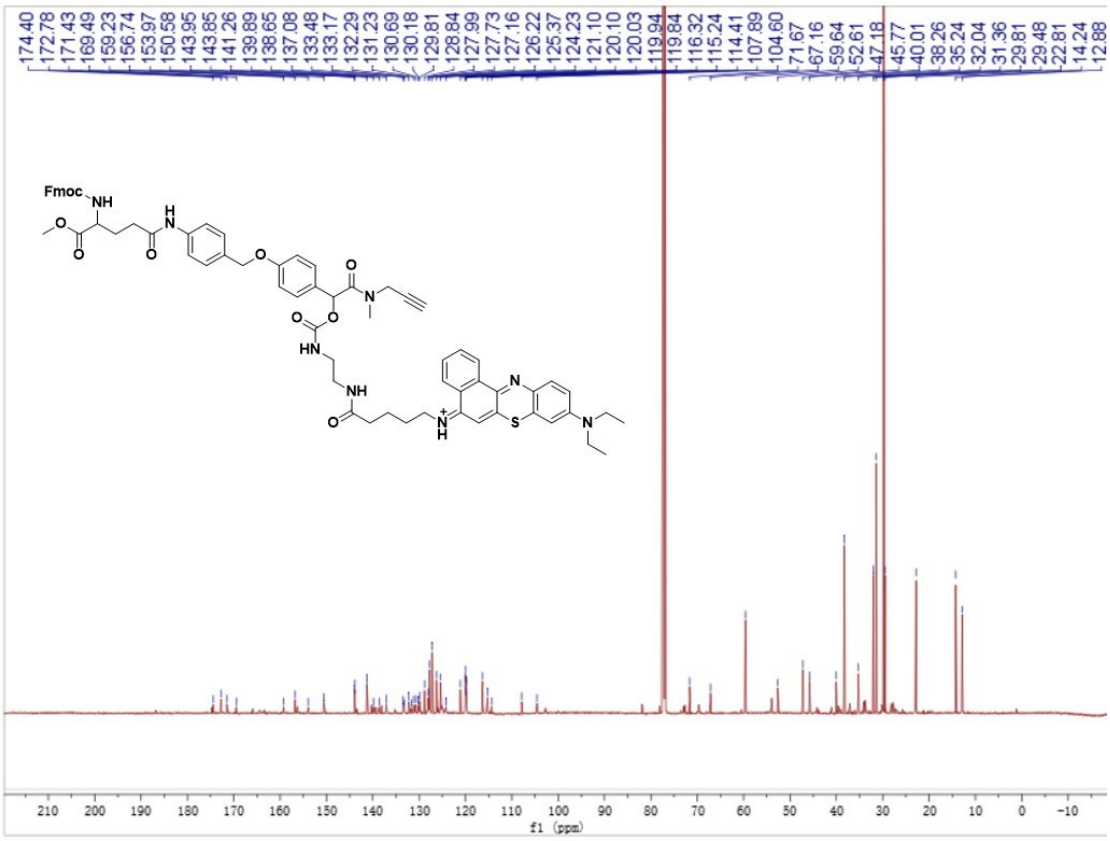


Fig. S19 [13]C-NMR Spectrum of compound compound **6**.

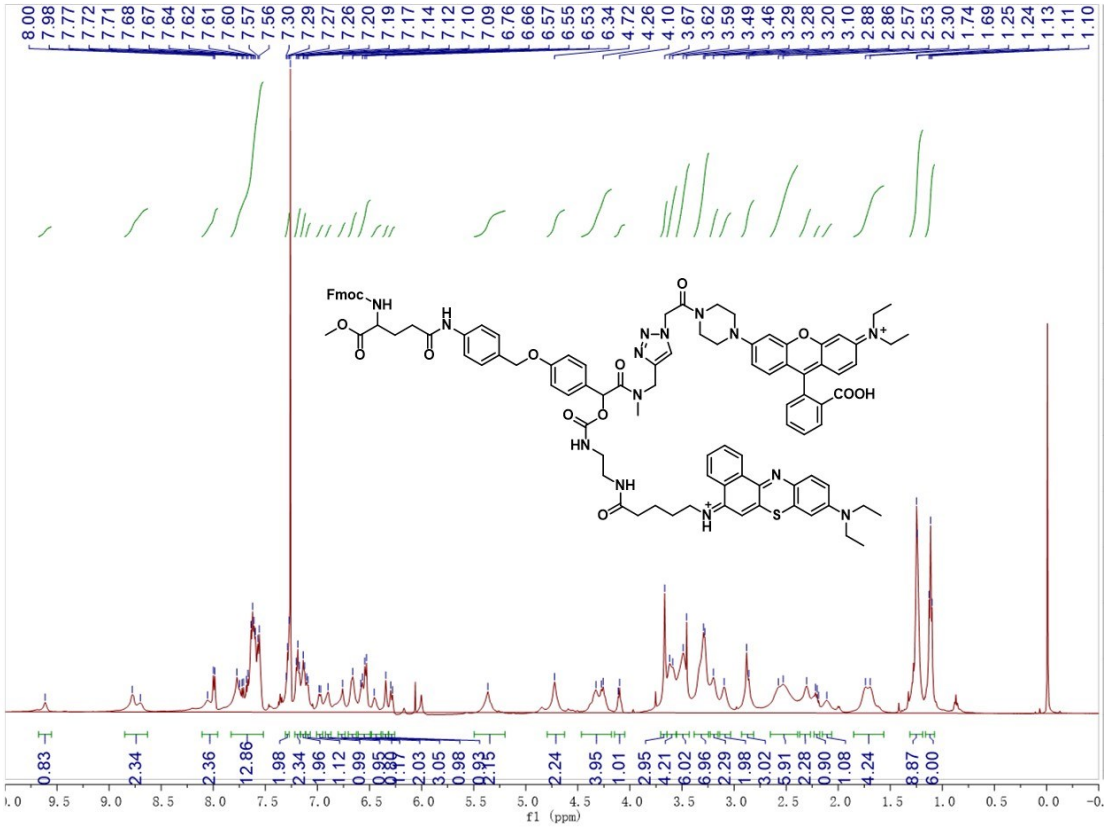


Fig. S20 ^{1}H-NMR Spectrum of compound **7**.

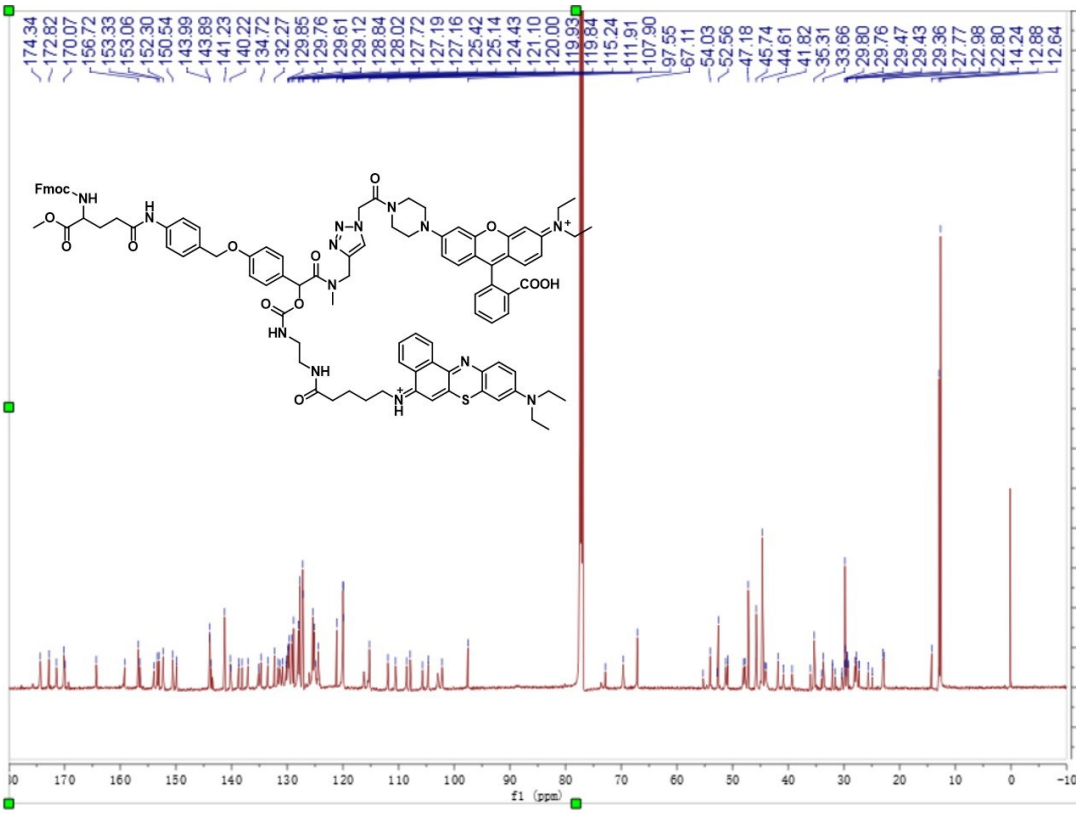


Fig. S21 ^{13}C-NMR Spectrum of compound **7**.

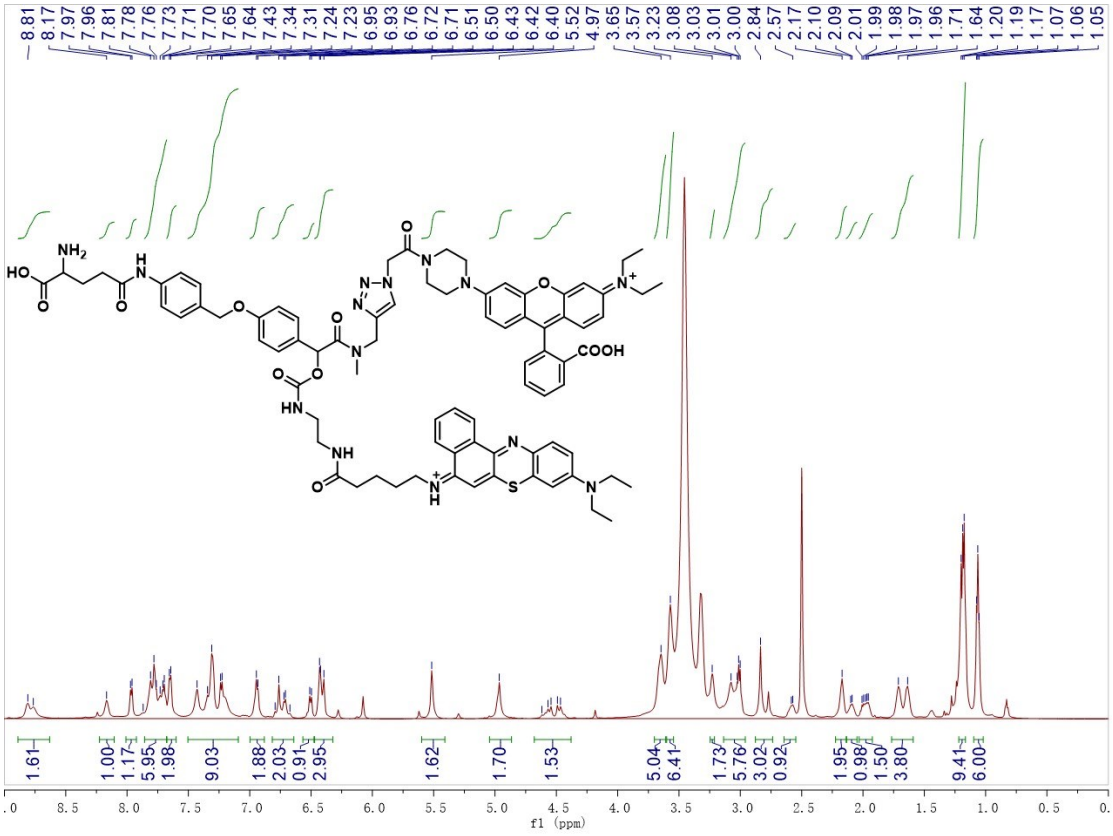


Fig. S22 [1]H-NMR Spectrum of compound Glu-RdEB.

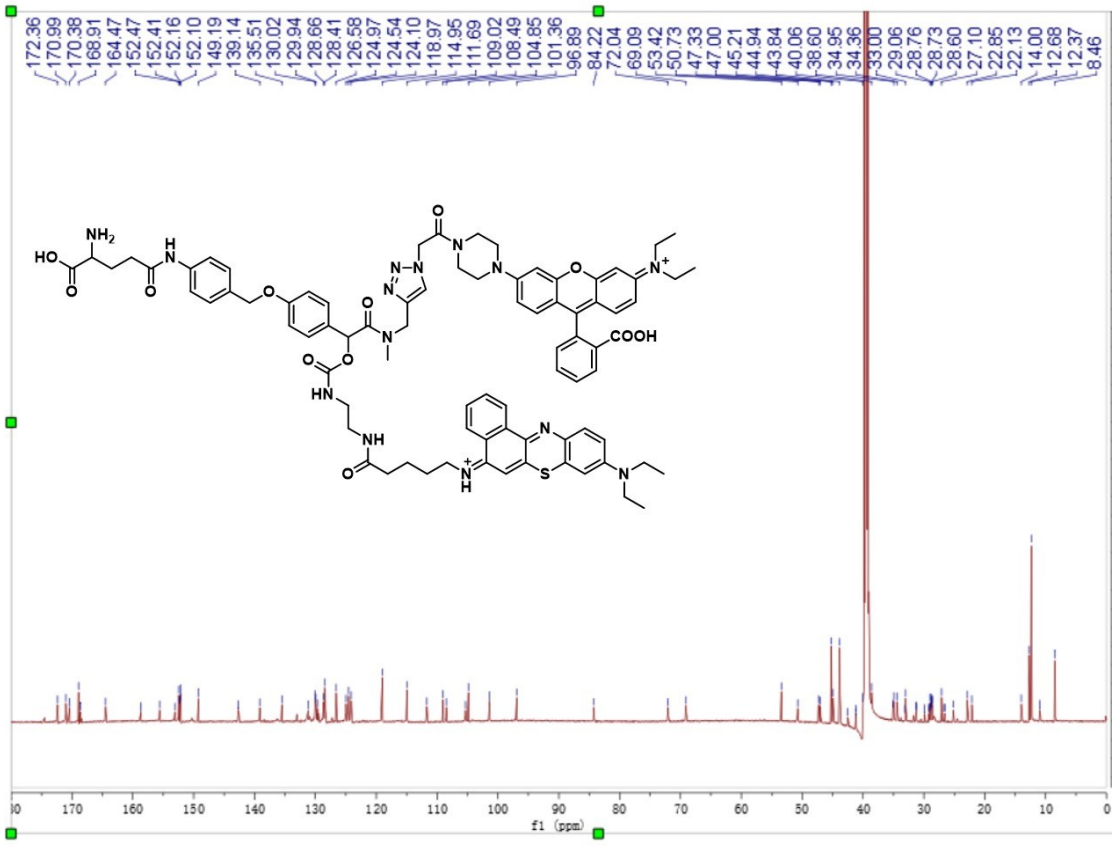


Fig. S23 [13]C-NMR Spectrum of compound Glu-RdEB.