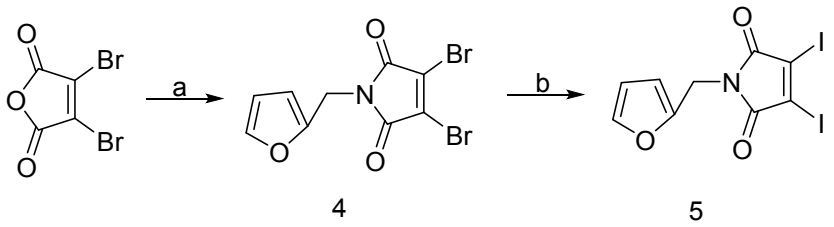
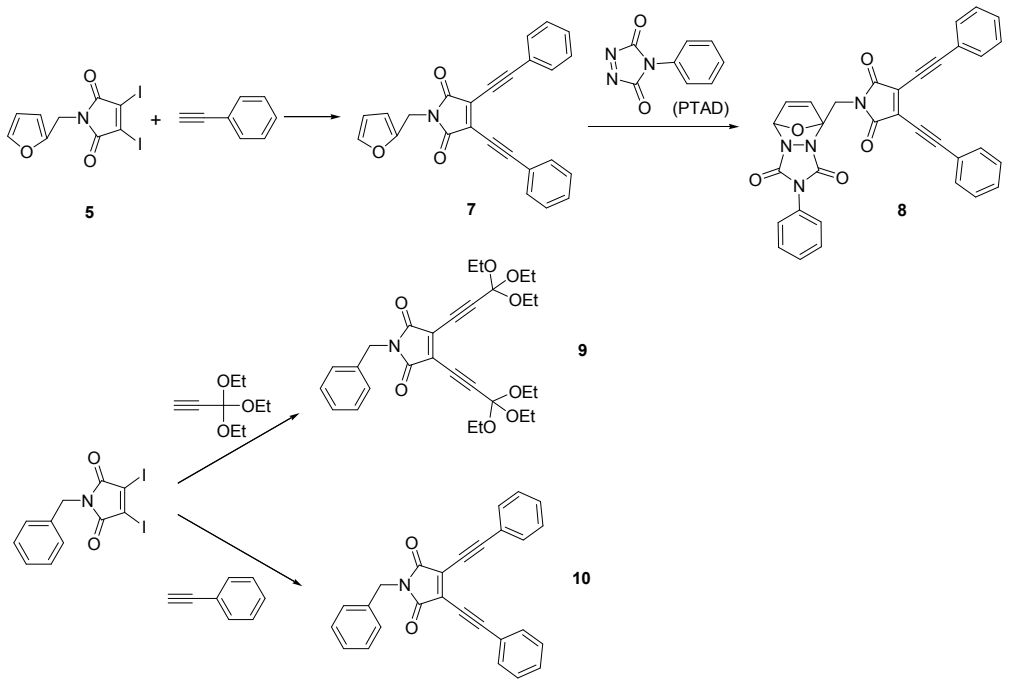
Synthesis



Scheme S1. Synthesis of compound 4 and 5. (a) furfurylamine, acetic acid, 22 h; (b) KI, acetic acid, 5 h.

3,4-dibromo-1-(furan-2-ylmethyl)-1H-pyrrole-2,5-dione (Compound 4). 3,4-dibromomaleic anhydride (6.14 g, 24.3 mmol) was dissolved in acetic acid (60 mL) with slowly addition of furfurylamine (2.748 g, 28.3 mmol), the solution was stirred at room temperature until the white smoke disappeared, then the system was heated at 120 ºC for 22 h. After removal of solvent, the crude residue was separated by column chromatography on silica gel (hexane/ethyl acetate = 15/1) to give compound **4** as a light yellow solid (5.645 g, 70.1 %). ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): 7.33-7.32 (d, -O-C*H*=CH, 1H), 6.35-6.34 (m, -CH=C*H*-, 1H), 6.30-6.29 (d, -C=C*H*-, 1H), 4.75 (s, -N-CH_2-, 2H). ^{13}C NMR (DMSO-d_6, 100MHz, ppm): 163.1, 148.0, 142.7, 129.5, 110.5, 109.4, 35.6.

3,4-diiodo-1-(furan-2-ylmethyl)-1H-pyrrole-2,5-dione (Compound 5). A solution of compound **4** (3.723 g, 11.18 mmol) and potassium iodide (7.427 g, 44.74 mmol) in 50 mL acetic acid was heated at 120 ºC and stirred for 5 h. After removal of acetic acid, the crude residue was separated by column chromatography on silica gel (hexane/ethyl acetate = 10/1) to give compound **5** as a light yellow solid (3.03 g, 63.2 %). ^{1}H NMR (DMSO-d_6, 400MHz, ppm): 7.27-7.20 (d, -O-C*H*=, 1H), 6.28 (m, -CH=C*H*-, 1H), 6.24-6.23 (d, -C=C*H*-, 1H), 4.72 (s, -N-CH_2-, 2H). ^{13}C NMR (DMSO-d_6, 100MHz, ppm): 166.6, 148.9, 142.7, 119.2, 110.6, 108.3, 35.7. HRMS (ESI): m/z cald. for $C_9H_5I_2NO_3Na$ $(M+Na)^+$: 451.8256; found: 451.8254.



Scheme S2. Synthesis of fluorescent enediyne compounds.

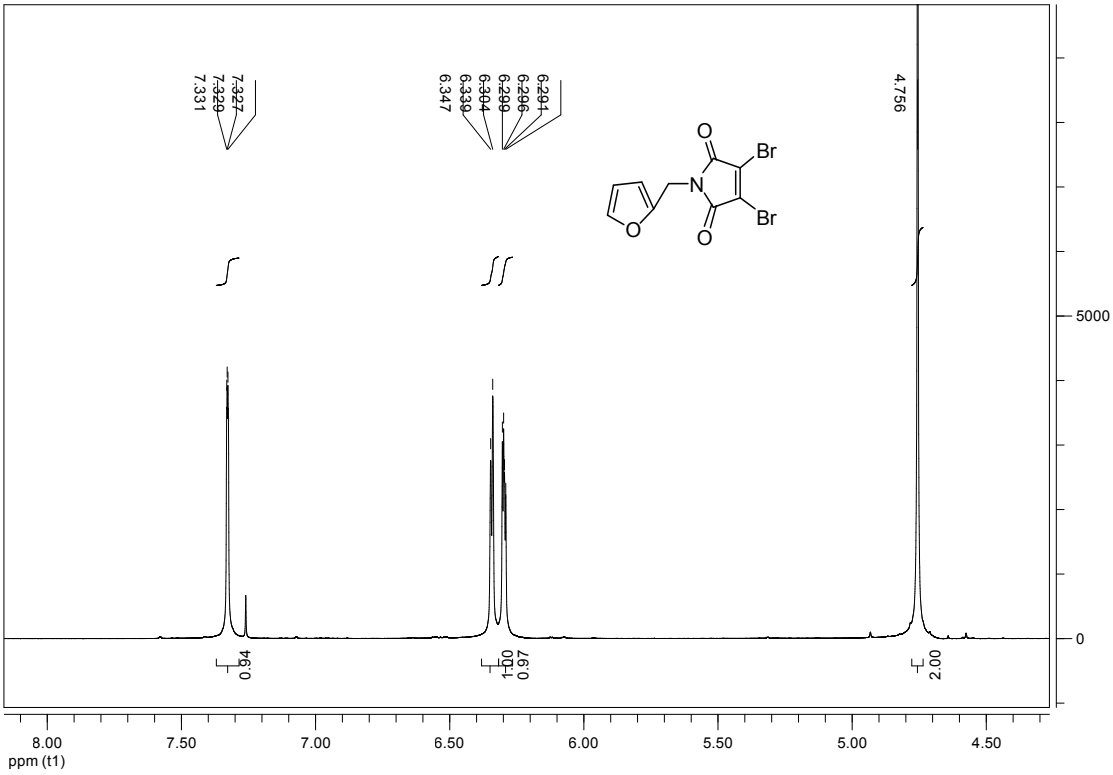


Figure S1. ^{1}H NMR spectrum of compound 4

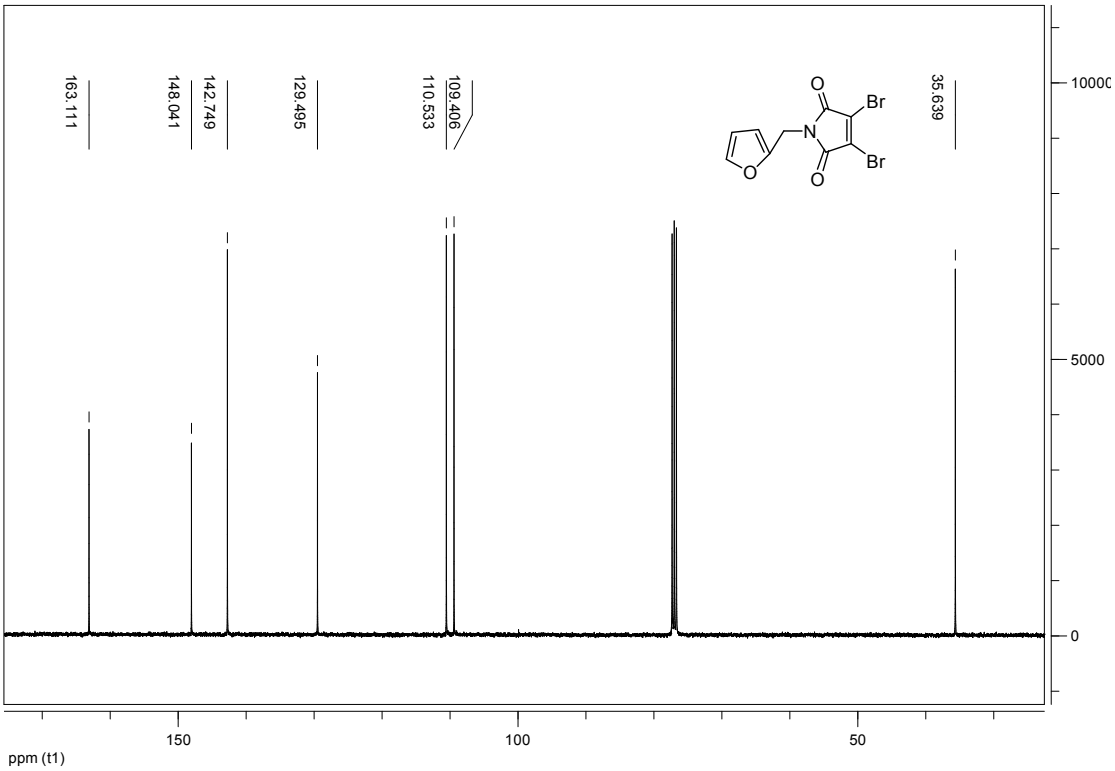


Figure S2. ^{13}C NMR spectrum of compound 4

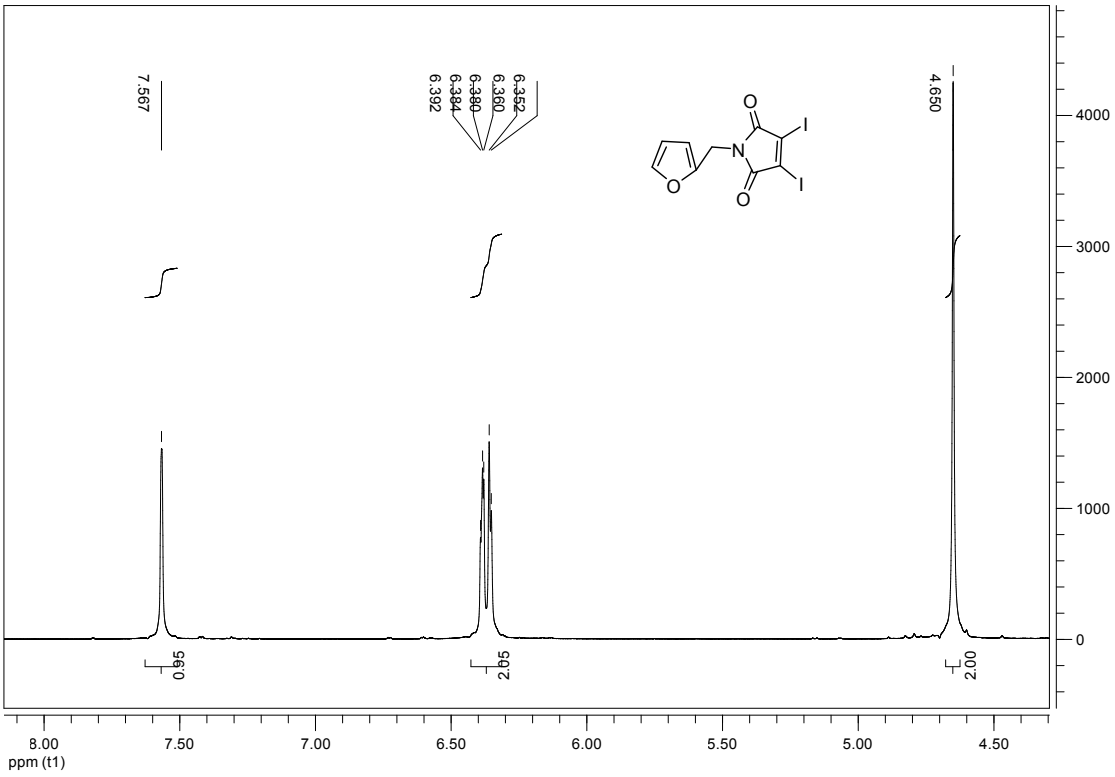


Figure S3. ^{1}H NMR spectrum of compound 5

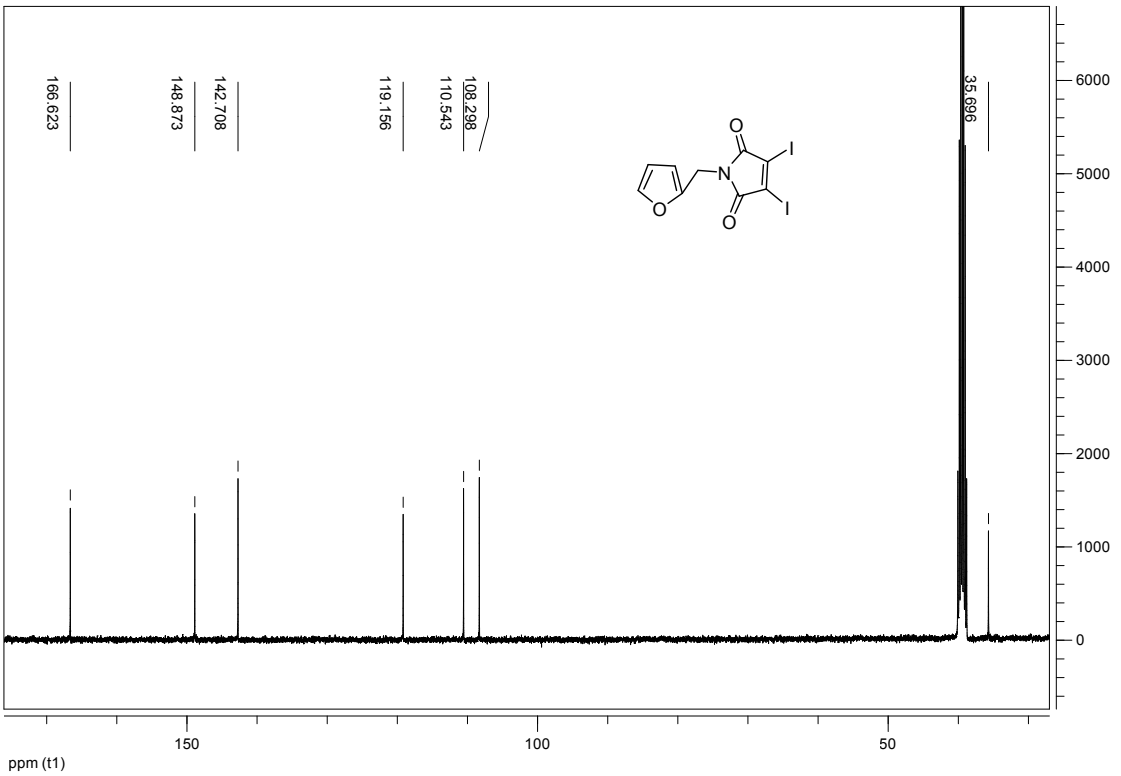


Figure S4. ^{13}C NMR spectrum of compound 5

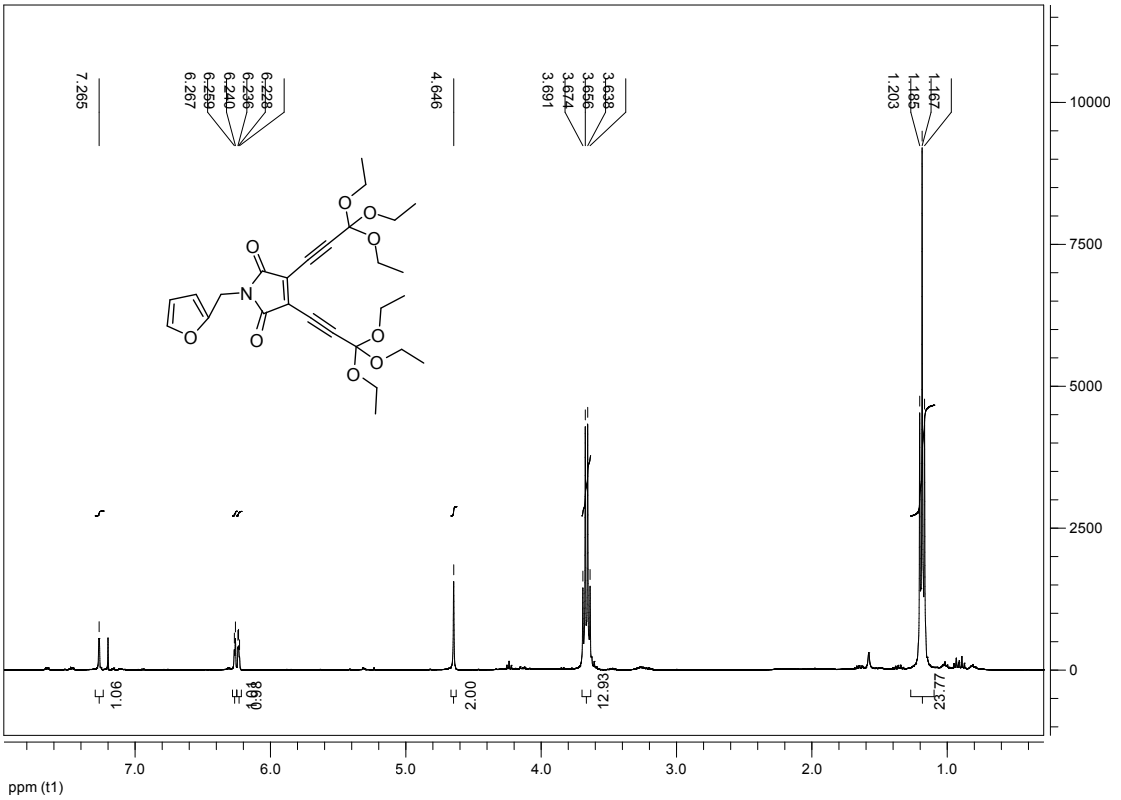


Figure S5. ^{1}H NMR spectrum of enediyne 1

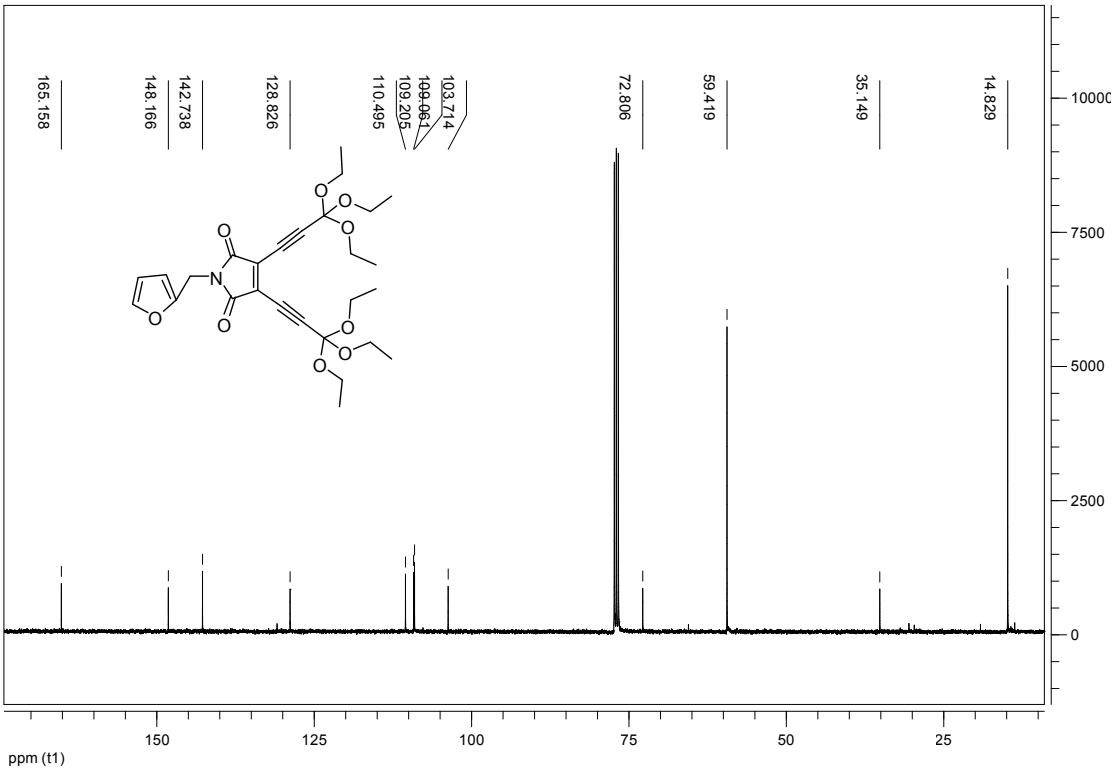


Figure S6. ^{13}C NMR spectrum of enediyne 1

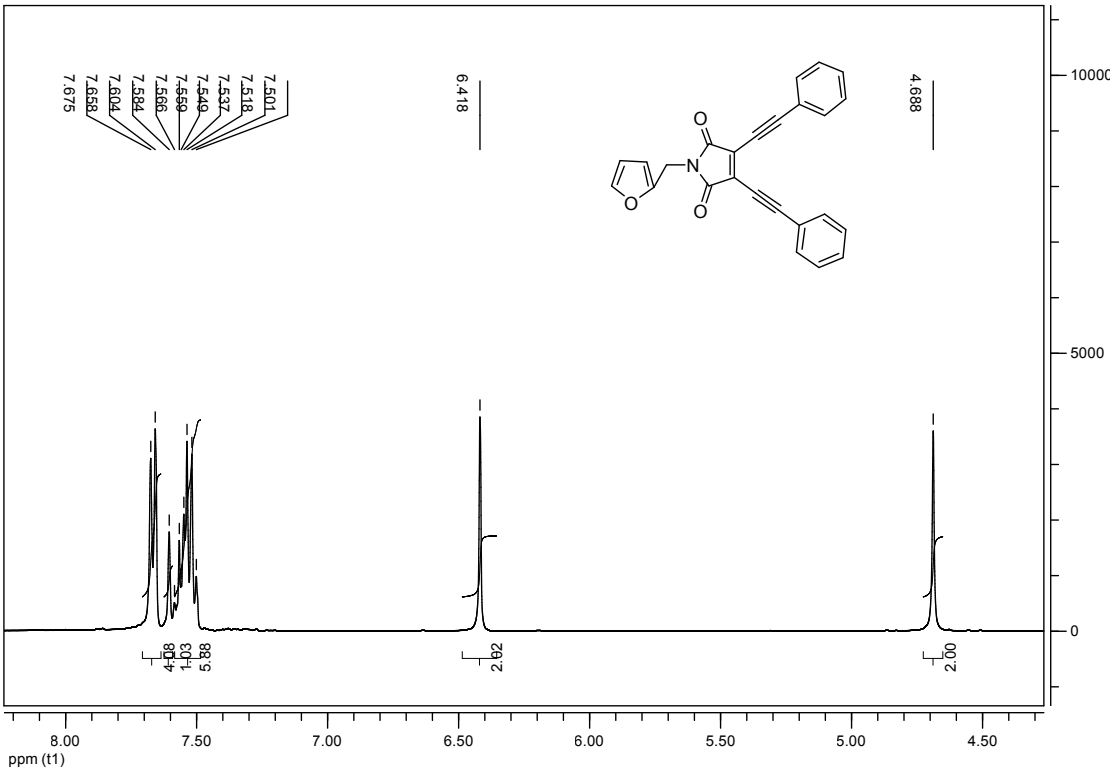


Figure S7. ^{1}H NMR spectrum of enediyne 7

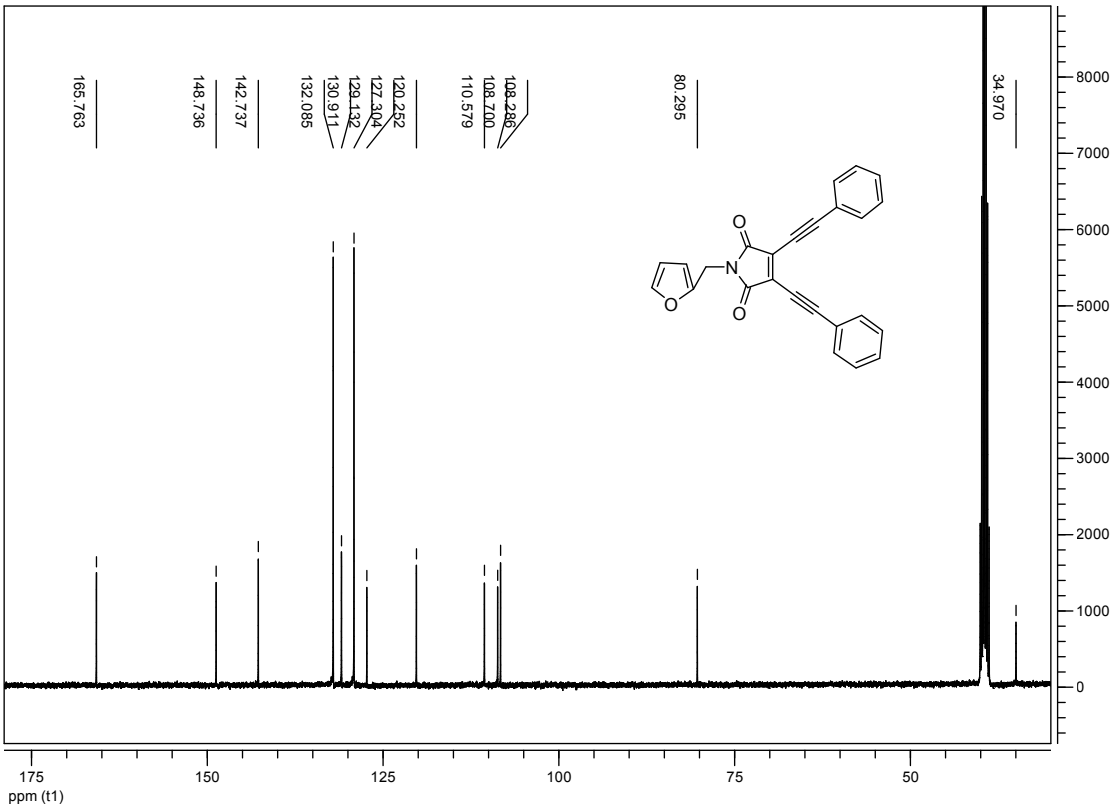


Figure S8. ^{13}C NMR spectrum of enediyne 7

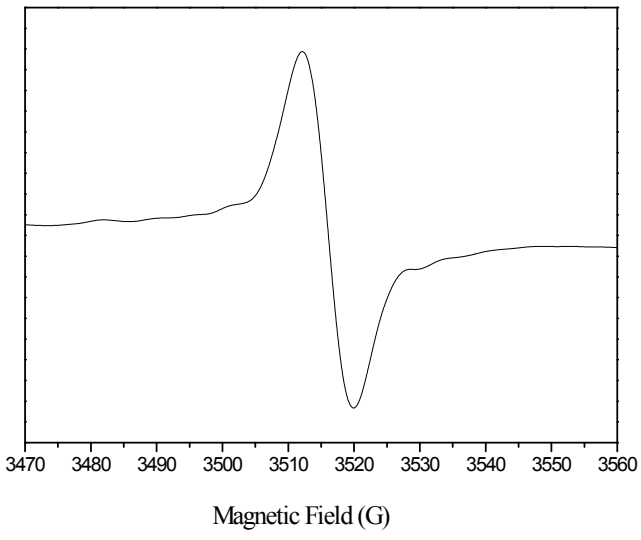


Figure S9. EPR spectrum of DA-product (enediyne **2)** in $CHCl_3$. Enediyne **2** was dissolved in $CHCl_3$ with the addition of one drop of TFA.

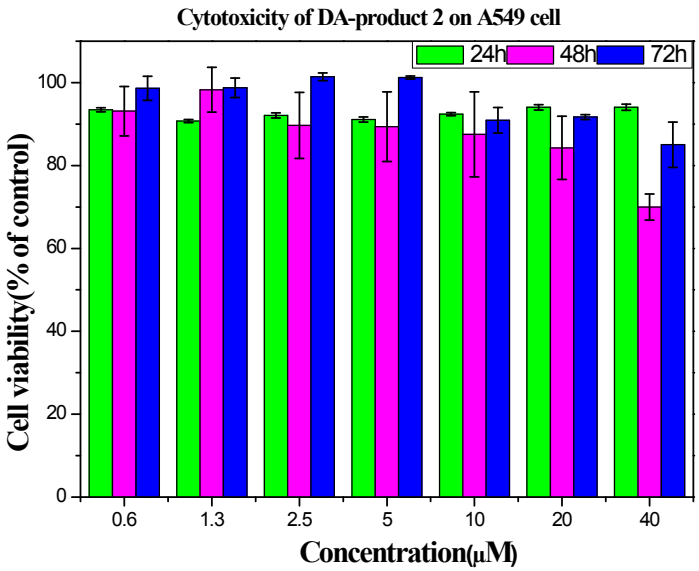


Figure S10.Effect of DA-product (enediyne **2)** on cell viability of tumor model cell lines A549 cells

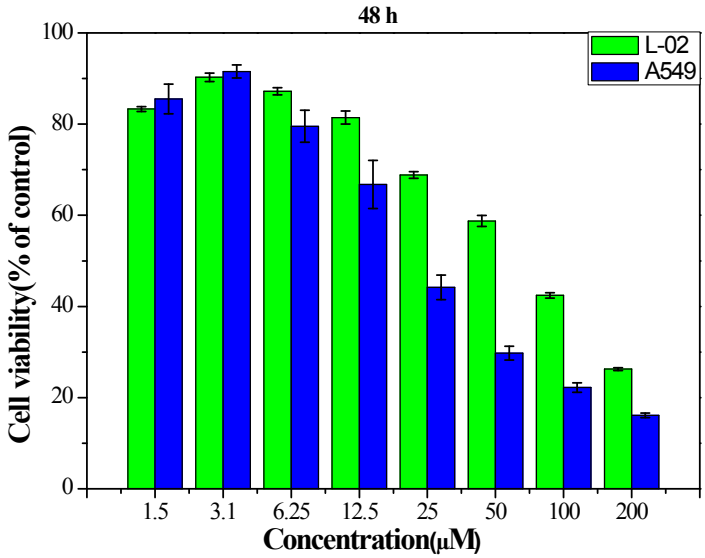


Figure S11. Effect of enediyne **1** on cell viability of tumor model cell lines A549 cells and normal model cell lines L-02 cells. Cells were incubated with enediyne **1** for 48 h and cell viability was determined and analyzed by MTT assay.

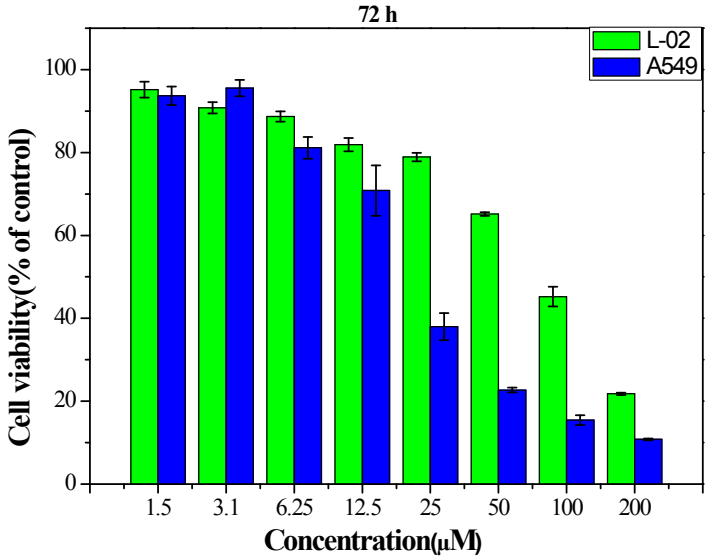


Figure S12. Effect of enediyne **1** on cell viability of tumor model cell lines A549 cells and normal model cell lines L-02 cells. Cells were incubated with enediyne **1** for 72 h and cell viability was determined and analyzed by MTT assay.

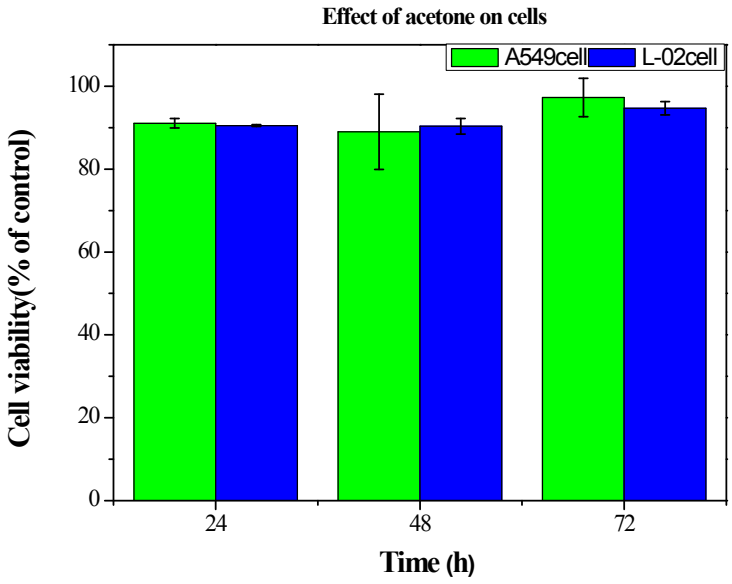


Figure S13. Effects of 0.1% acetone on cell viability of tumor and normal cells. The cells were incubated with acetone for 24 h, 48 h, and 72 h respectively. Cell viability was determined and analyzed by MTT assay.

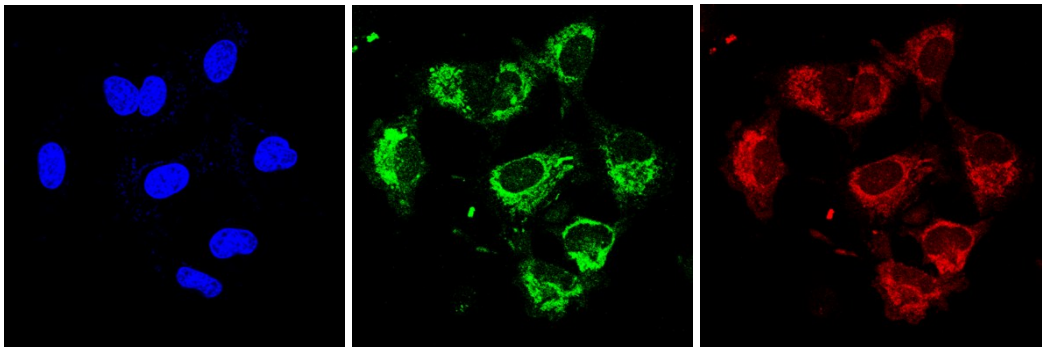


Figure. S14. Cellular distribution of enediyne **7** entering in A549 cell at 12 h observed by CLSM. Blue-nucleus; green-enediyne; red-lysosome.

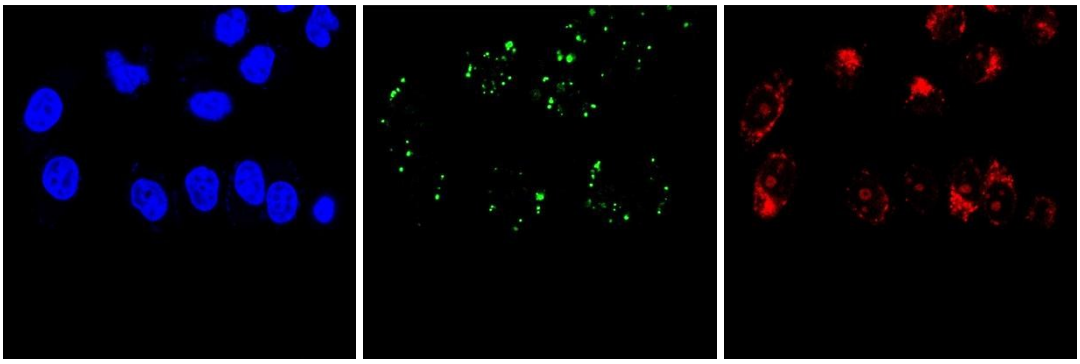


Figure. S15. Cellular distribution of enediyne **8** in A549 cell at 12 h observed by CLSM. Blue-nucleus; green-enediyne; red-lysosome.

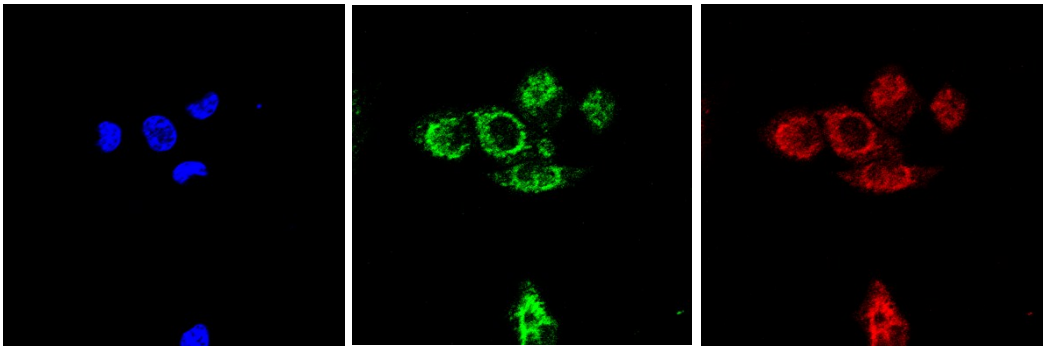


Figure. S16. Cellular distribution of enediyne **10** entering in A549 cell at 12 h observed by CLSM. Blue-nucleus; green-enediyne; red-lysosome.