

## **Supporting Information**

**for**

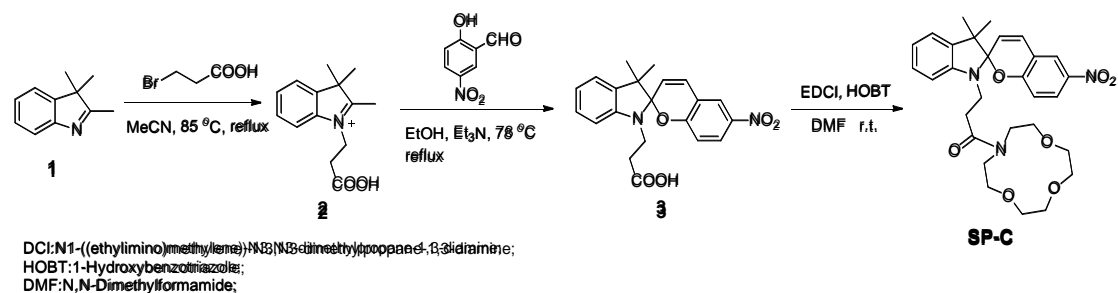
## Section S1: Materials and instruments

2,3,3-trimethylindolenine (>99%), 3-bromopropionic acid (>99%), anhydrous acetonitrile (>99%), diethyl ether (>99%), 5-nitrosalicylaldehyde (>99%), anhydrous ethanol (>99%), triethylamine (>99%), 1-hydroxybenzotriazole (HOBT, >99%), N-(3-dimethylaminopropyl)-N-ethylcarbodiimide hydrochloride (EDCI, >99%), anhydrous N,N-dimethylformamide (DMF, >99%), monoaza-12-crown-4 (>99%), 1,2-dichloroethane (>99%), LiCl (>99%), MgCl<sub>2</sub> (>99%), KCl (>99%), NaCl (>99%) and CaCl<sub>2</sub> (>99%) were purchased from Aladdin. All chemicals were analytical-reagent grade, and were used without further purification. Millipore water (Milli Q, Millipore Corp., 18.2 MΩ·cm) was used for all experiments.

<sup>1</sup>H NMR and <sup>13</sup>C NMR experiments were performed with a Bruker AVANCE-300 MHz and 75 MHz NMR spectrometer, respectively (Bruker, Billerica, MA). ESI determinations were carried out on an LTQ-MS (Thermo) instrument. Ultraviolet-visible (UV-vis) spectra were recorded on an Agilent 8453 UV-vis spectrophotometer. Fluorescence spectra were measured on F-7000 FL Spectrophotometer. A PO-120 quartz cuvette (10 mm) was purchased from Shanghai Huamei Experiment Instrument Plants, China. The concentration of metal ions in aqueous solutions was determined by a flame atomic absorption spectrophotometer (TAS-990, Persee, Beijing, China). The UV (365 nm, 2.6 mW cm<sup>-2</sup>) and light-emitting diode (LED) lamps (10 W) were used as light sources for UV and visible light irradiation, respectively.

## Section S2: Synthesis of SP-C

### Scheme S1. The synthetic route of SP-C.



Scheme S1. Synthesis of SP-C.

#### Synthesis of compound 2

2,3,3-trimethylindolenine (3.18 g, 20 mmol) and 3-bromopropionic acid (6.08 g, 40 mmol) were dissolved in 60 mL anhydrous acetonitrile. The mixed solution was refluxed at 85 °C for 12 h (dark). After the reaction accomplished, the solvent was removed through decompression rotary evaporation. The residue washed by diethyl ether 3 times, then recrystall in solution (DCM:acetone=1:5, v/v), obtained 1-(2-carboxyl)-2,3,3-trimethyl-3-indole bromine (white solid) 1.85 g (yield: 40%).

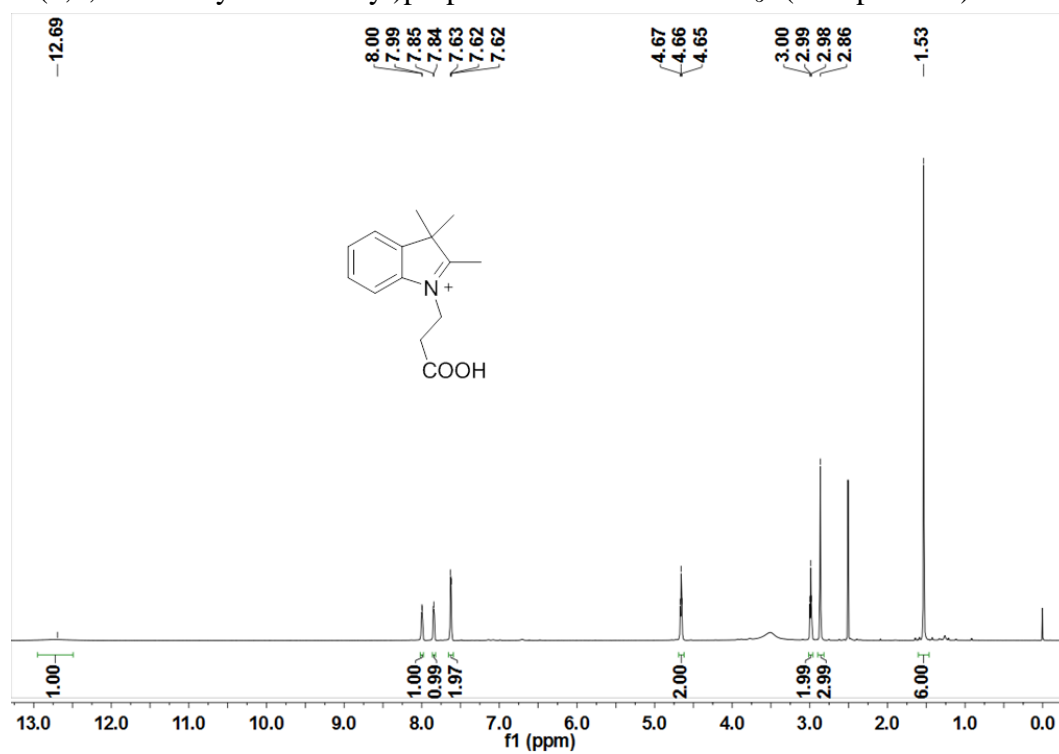
#### Synthesis of compound 3

Compound 2 (3.11 g, 10 mmol) and 5-nitrosalicylaldehyde (1.83 g, 11 mmol) dissolved in 50 mL ethanol, added triethylamine (1.7 mL, 12 mmol) dropwise. The mixture was refluxed in the dark for 6 h. After the reaction, the reactants cooled to room temperature, the precipitation was filtered and washed with ethanol 3 times. The product was dried under vacuum to give a light yellow solid (2.76 g, 60 % yield).

#### Synthesis of SP-C

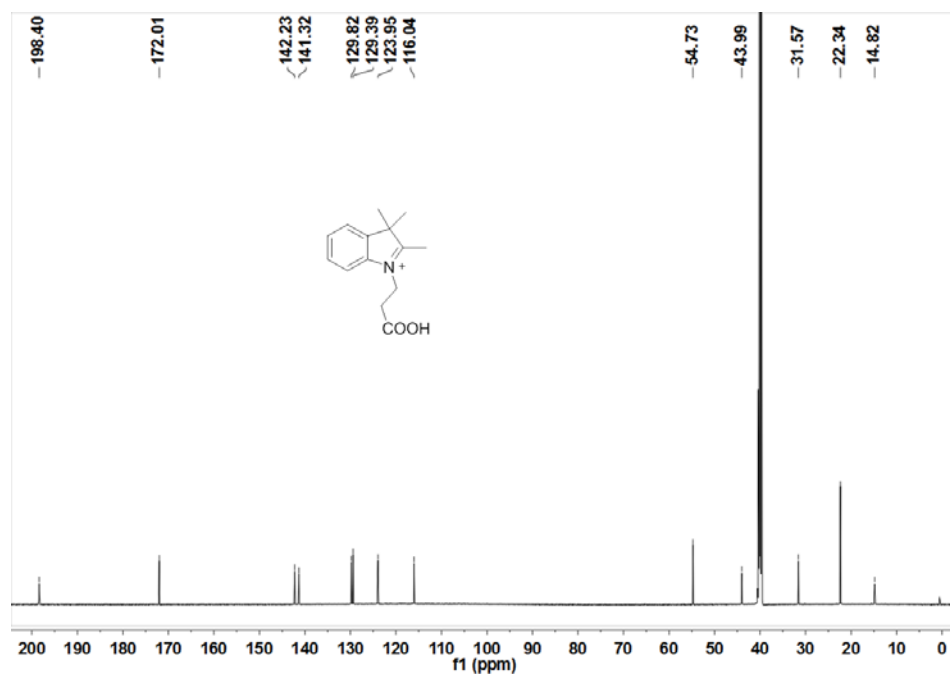
The compound 3 (0.363 g, 1 mmol) and EDCI (0.52 g, 4 mmol), HOBT (0.76 g, 4 mmol), was dissolved in 20 mL anhydrous DMF. Under Ar atmosphere, the reactants were stirred for 30 min (r.t.). After the 30 min, the monoaza-12-crown-4 (0.140 g, 0.8 mmol) and triethylamine 0.6 mL was added. After 24 h stirred in dark and room temperature conditions, the mixture was poured into 200 mL water and the precipitation was filtered and washed with water. The product was dried under vacuum to give a grey solid (0.38 g, 90% yield).

**Figure S1:** The  $^1\text{H}$  NMR (600 MHz) spectra of the 3-(2,3,3-trimethylindolin-1-yl)propanoic acid in  $\text{DMSO-}d_6$ . (Compound 2).



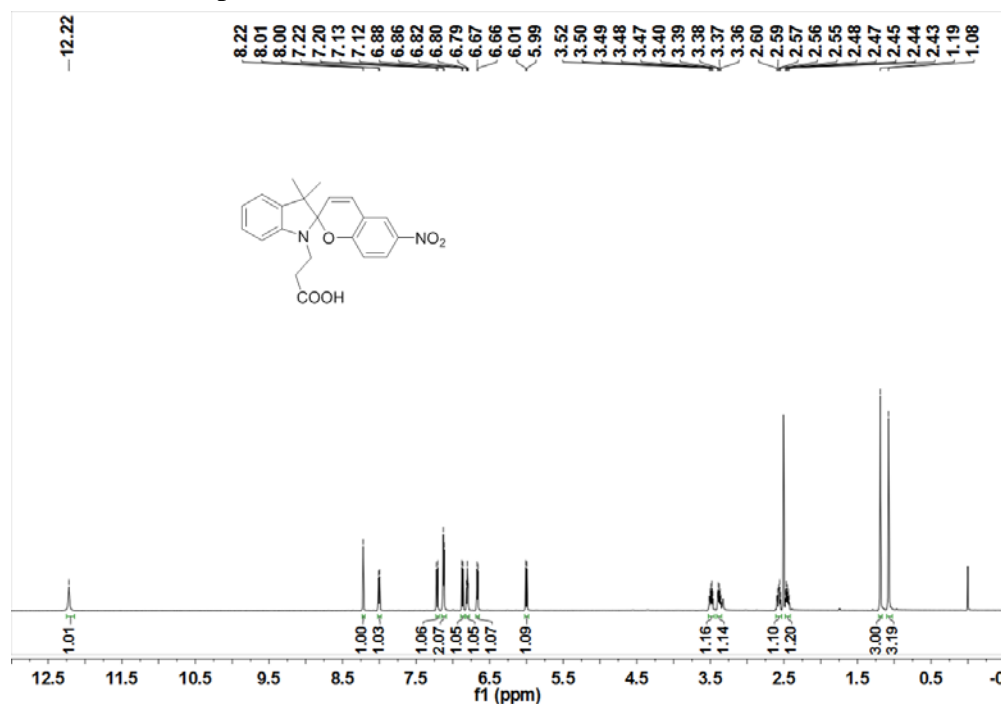
$^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  12.69 (s, 1H), 8.02-7.98 (m, 1H), 7.85 (d,  $J = 4.0$  Hz, 1H), 7.65-7.59 (m, 2H), 4.66 (t,  $J = 6.8$  Hz, 2H), 2.99 (t,  $J = 6.9$  Hz, 2H), 2.86 (s, 3H), 1.53 (s, 6H).

**Figure S2:** The  $^{13}\text{C}$  NMR (600 MHz) spectra of the 3-(2,3,3-trimethylindolin-1-yl)propanoic acid in  $\text{DMSO-}d_6$ . (Compound 2).



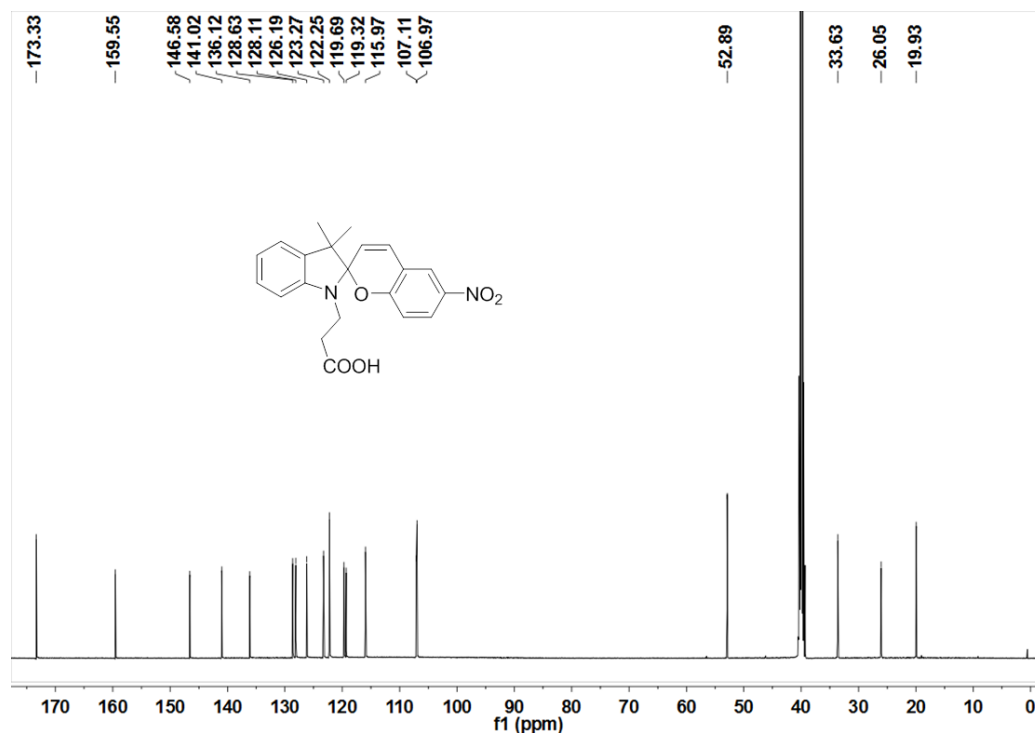
$^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  198.4( $-\text{C}_{\text{C=O}}$ ), 172.0( $-\text{C}_{\text{Ar}}$ ), 142.2( $-\text{C}_{\text{Ar}}$ ), 141.3( $-\text{C}_{\text{Ar}}$ ), 129.8( $-\text{C}_{\text{Ar}}$ ), 129.4( $-\text{C}_{\text{Ar}}$ ), 123.9( $-\text{C}_{\text{Ar}}$ ), 116.0( $-\text{CH}$ ), 54.7( $-\text{C}$ ), 44.0( $-\text{C}_{\text{CH}_2}$ ), 31.6( $-\text{C}_{\text{CH}_2}$ ), 22.3( $-\text{C}_{\text{CH}_3}$ ), 14.82( $-\text{C}_{\text{CH}_3}$ ).

**Figure S3:** The  $^1\text{H}$  NMR (600 MHz) spectra of the 3-(3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-1'-yl)propanoic acid in  $\text{DMSO-}d_6$  (compound 3)



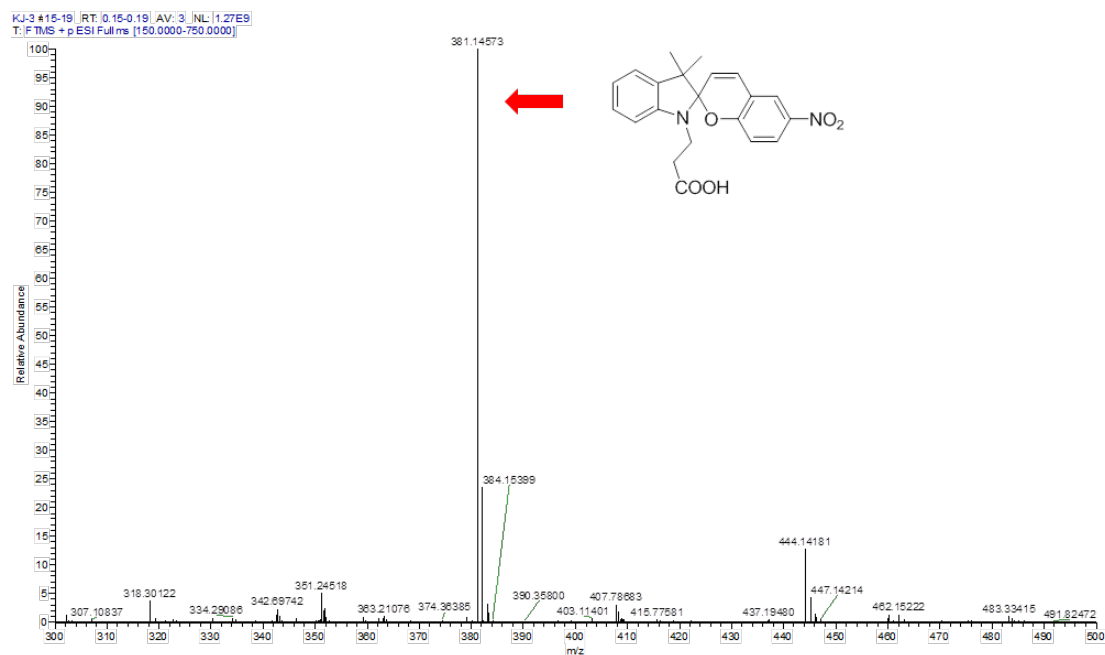
$^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  12.22 (s, 1H), 8.22 (s, 1H), 8.01 (d,  $J = 9.0$  Hz, 1H), 8.00 (d,  $J = 9.0$  Hz, 1H), 7.21 (d,  $J = 10.4$  Hz, 1H), 7.12 (d,  $J = 7.0$  Hz, 2H), 6.87 (d,  $J = 9.0$  Hz, 1H), 6.80 (t,  $J = 7.3$  Hz, 1H), 6.67 (d,  $J = 7.7$  Hz, 1H), 6.00 (d,  $J = 10.4$  Hz, 1H), 3.49 (dt,  $J = 14.8, 7.4$  Hz, 1H), 3.38 (dt,  $J = 14.3, 6.7$  Hz, 1H), 2.57 (dt,  $J = 15.0, 7.2$  Hz, 1H), 2.45 (dt,  $J = 15.2, 6.9$  Hz, 1H), 1.19 (s, 3H), 1.08 (s, 3H).

**Figure S4:** The  $^{13}\text{C}$  NMR (600 MHz) spectra of the 3-(3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-1'-yl)propanoic acid in  $\text{DMSO-}d_6$ . (compound 3)



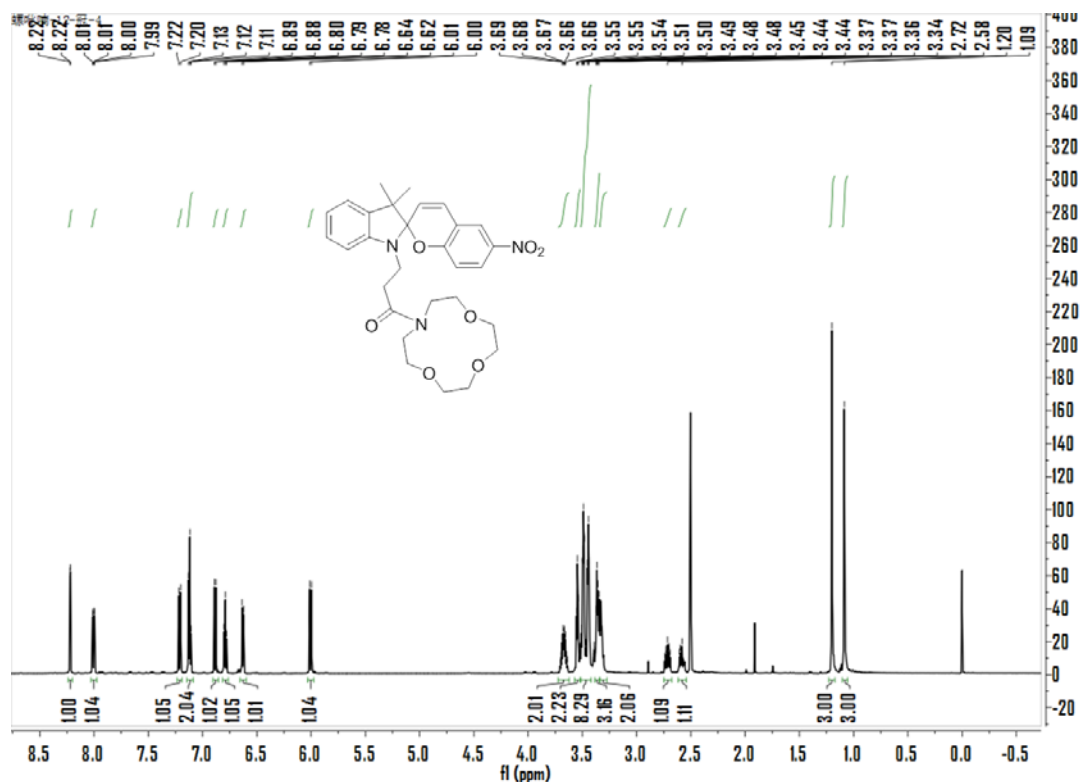
$^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  173.3(- $\text{C}_{\text{C}=\text{O}}$ ), 159.6(- $\text{C}_{\text{Ar}-\text{O}}$ ), 146.6(- $\text{C}_{\text{Ar}-\text{NO}_2}$ ), 141.0(- $\text{C}_{\text{Ar}}$ ), 136.1(- $\text{C}_{\text{Ar}}$ ), 128.6(- $\text{C}_{\text{Ar}}$ ), 128.1(- $\text{C}_{\text{Ar}}$ ), 126.2(- $\text{C}_{\text{Ar}}$ ), 123.3(- $\text{C}_{\text{C}=\text{C}}$ ), 122.3(- $\text{C}_{\text{C}=\text{C}}$ ), 119.7(- $\text{C}_{\text{Ar}}$ ), 119.3(- $\text{C}_{\text{Ar}}$ ), 116.0(- $\text{C}_{\text{Ar}}$ ), 107.1(- $\text{C}_{\text{C}-\text{O}}$ ), 107.0(- $\text{C}$ ), 52.9(- $\text{C}_{\text{CH}_2}$ ), 33.6(- $\text{C}_{\text{CH}_2}$ ), 26.1(- $\text{C}_{\text{CH}_3}$ ), 19.9(- $\text{C}_{\text{CH}_3}$ ). ESI-MS  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for 381.1450, Found 381.1457.

**Figure S5:** ESI-MS of the 3-(3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-1'-yl)propanoic acid m/z:  $[M + H]^+$  Calcd for 381.1450; Found 381.1457. (Compound 3)



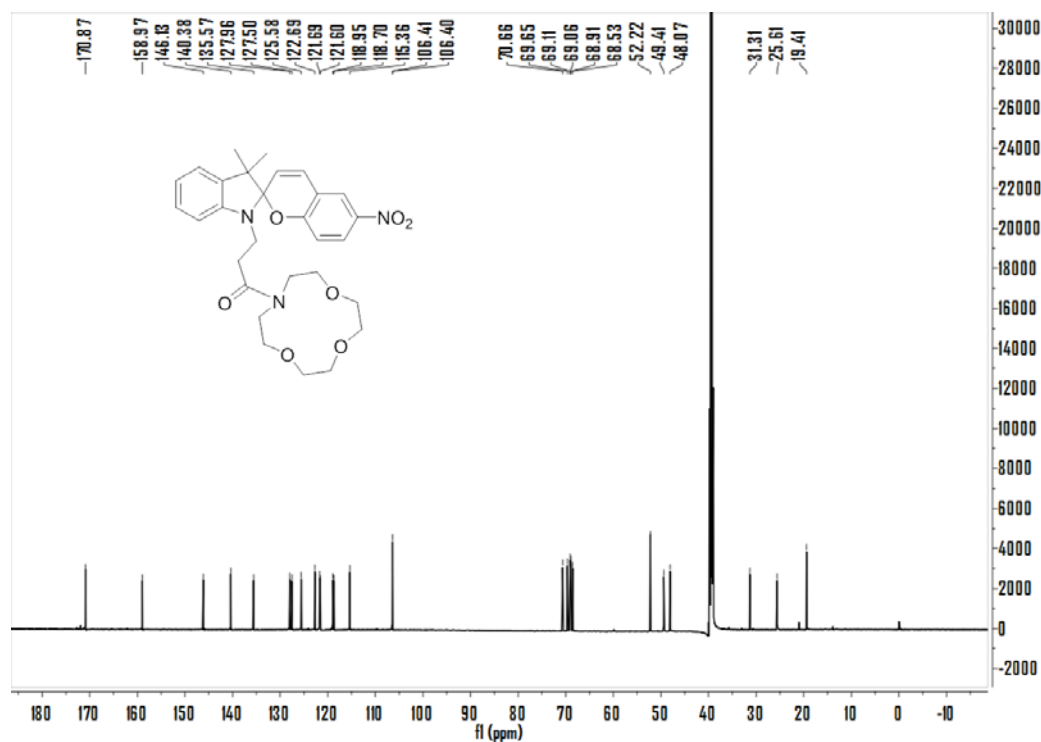


**Figure S6:** The  $^1\text{H}$  NMR (600 MHz) spectra of the 1-(1,4,7-trioxa-10-azacyclododecan-10-yl)-3-(3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-1'-yl)propan-1-one in  $\text{DMSO-}d_6$ .(SP-C)



$^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  8.22 (d,  $J = 2.8$  Hz, 1H), 8.00 (dd,  $J = 9.0, 2.8$  Hz, 1H), 7.21 (d,  $J = 10.4$  Hz, 1H), 7.12 (t,  $J = 7.0$  Hz, 2H), 6.88 (d,  $J = 9.0$  Hz, 1H), 6.79 (t,  $J = 7.3$  Hz, 1H), 6.63 (d,  $J = 7.8$  Hz, 1H), 6.01 (d,  $J = 10.4$  Hz, 1H), 3.67 (qt,  $J = 10.0, 4.5$  Hz, 2H), 3.57-3.52 (m, 2H), 3.51-3.42 (m, 8H), 3.38-3.34 (m, 3H), 3.32 (dt,  $J = 10.2, 4.8$  Hz, 2H), 2.72 (ddd,  $J = 15.4, 8.9, 5.8$  Hz, 1H), 2.59 (dd,  $J = 9.6, 5.6$  Hz, 1H), 1.20 (s, 3H), 1.09 (s, 3H).

**Figure S7:** The  $^{13}\text{C}$  NMR (600 MHz) spectra of the 1-(1,4,7-trioxa-10-azacyclododecan-10-yl)-3-(3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-1'-yl)propan-1-one in  $\text{DMSO-}d_6$ . (SP-C)



$^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  170.9(- $\text{C}_{\text{C}=\text{O}}$ ), 159.0(- $\text{C}_{\text{Ar-O}}$ ), 128.0(- $\text{C}_{\text{Ar-NO}_2}$ ), 127.5(- $\text{C}_{\text{Ar}}$ ), 125.6(- $\text{C}_{\text{Ar}}$ ), 122.7(- $\text{C}_{\text{C}=\text{C}}$ ), 121.7(- $\text{C}_{\text{C}=\text{C}}$ ), 121.6(- $\text{C}_{\text{Ar}}$ ), 119.0(- $\text{C}_{\text{Ar}}$ ), 115.4(- $\text{C}_{\text{Ar}}$ ), 106.4(- $\text{C}_{\text{C-O}}$ ), 106.4(- $\text{C}_{\text{C-O}}$ ), 70.7(- $\text{C}_{\text{C-O}}$ ), 69.7(- $\text{C}_{\text{C-O}}$ ), 69.1(- $\text{C}_{\text{C-O}}$ ), 69.1(- $\text{C}_{\text{C-O}}$ ), 68.9(- $\text{C}_{\text{C-O}}$ ), 68.5(- $\text{C}_{\text{C-O}}$ ), 52.2(- $\text{C}_{\text{C-N}}$ ), 49.4(- $\text{C}_{\text{C-N}}$ ), 48.1(- $\text{C}_{\text{CH}_2}$ ), 31.3(- $\text{C}_{\text{CH}_2}$ ), 25.6(- $\text{C}_{\text{CH}_3}$ ), 19.4(- $\text{C}_{\text{CH}_3}$ ).

### Section 3: Liquid-liquid extraction experiments and analysis of metal ions

The solution of SP-C in 1,2-dichloroethane with concentration 1.0 mM was used as organic phase. The aqueous solution containing metal ions with a certain concentration was considered as aqueous phase. 2 mL of the above organic solution was transferred into one 10 mL transparent tube and was irradiated by UV light ( $\lambda=365$  nm) for 10 min. Then, 4 mL of aqueous solution containing certain metal ions was added into this tube. The tube was vigorously shocked through a homogeneous oscillator for a certain time. After oscillation, the tube stood for several minutes for the formation of two stable liquid layers. Finally, 3 mL of aqueous phase was taken as sample for further ion concentration measurement. It is noted that all the above operations were conducted under UV light to ensure the SP-C is in the form of isomer MC-C.

The concentration of metal ions in aqueous solutions was determined by a flame atomic absorption spectrophotometer. Before the samples test, the calibration curve of  $\text{Li}^+$  or  $\text{Mg}^{2+}$  aqueous solution needs to be conducted first. The extraction quality (mol/mol) is calculated according to:

$$\text{Extraction quality} = \frac{(C_0 - C_t) \cdot V_{aq}}{C_{SP-C} \cdot V_{org}}$$

where  $C_0$  and  $C_t$  is the initial concentration and the concentration at time  $t$  of metal ions in the aqueous phase, respectively.  $C_{SP-C}$  is the concentration of SP-C in 1,2-dichloroethane solution (1.0 mM).  $V_{aq}$  and  $V_{org}$  is the volume of aqueous phase and organic phase, respectively. In this work,  $V_{aq}=4$  mL and  $V_{org}=2$  mL.

#### **Section 4: The recycling of SP-C**

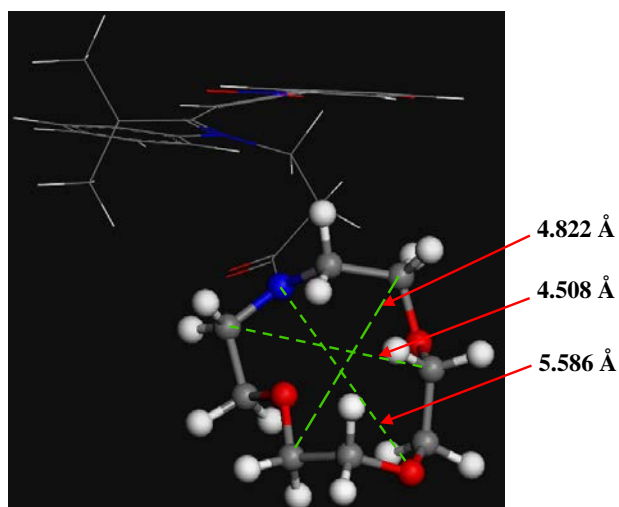
Processing of extraction: The solution of SP-C in 1,2-dichloroethane with concentration 1.0 mM was also used as organic phase. The LiCl aqueous solution with concentration 10 mM was also used as aqueous phase. Firstly, 40 mL of the above organic solution was transferred into one 250 mL erlenmeyer flask and was irradiated by UV light ( $\lambda=365$  nm) for 10 min. Then, 100 mL of above LiCl aqueous solution was added into this flask. The flask was vigorously stirred for 30 min. After stirring, the flask stood for several minutes for the formation of two stable liquid layers. Finally, 3 mL of aqueous phase was taken as sample for further ion concentration measurement.

Processing of reverse extraction: After the above extraction, the aqueous phase was separated carefully by an injector. Then, 10 mL of Millipore water was added into the above erlenmeyer flask. The flask was vigorously stirred for 2 h under visible light irradiation. After stirring, the flask stood for several minutes for the formation of two stable liquid layers. Finally, 3 mL of aqueous phase was taken as sample for further ion concentration measurement. It is noted that all these operations were conducted under visible light to ensure the molecule structure transfer from MC-C to SP-C. The aqueous phase was also separated carefully by an injector, and the left organic phase was used for extraction again in next cycle.

#### **Section 5: Structural optimization of MC-C**

In order to obtain the size of crown ether moiety, the molecular structure of MC-C transformed from SP-C was optimized by DMol<sup>3</sup>. The generalized gradient approximation (GGA) functional and PBE was used for all the calculations in this work. For convergence tolerance, the energy was set to  $2.0 \times 10^{-5}$  Ha, the maximum force was set to 0.004 Ha/Å and maximum displacement was set to 0.005 Å. The maximum iterations were 50 for the calculation. The final molecular structure with the detail value of crown ether moiety size is shown in Figure S1.

**Figure S8: The final optimized molecular structure of MC-C**



**Figure S9: ESI-MS of the 1-(1,4,7-trioxa-10-azacyclododecan-10-yl)-3-(3', 3'-dimethyl- 6 -nitrospiro[chromene-2,2'-indolin]-1'-yl)propan-1-one m/z: [M + H]<sup>+</sup> Calcd for 381.1450; Found 381.1457. (SP-C)**

