Electronic Supplementary Material (ESI) for Soft Matter.

Self-assembly of an alkynylpyrene derivative for multi-responsive fluorescence behavior and photoswitching performance

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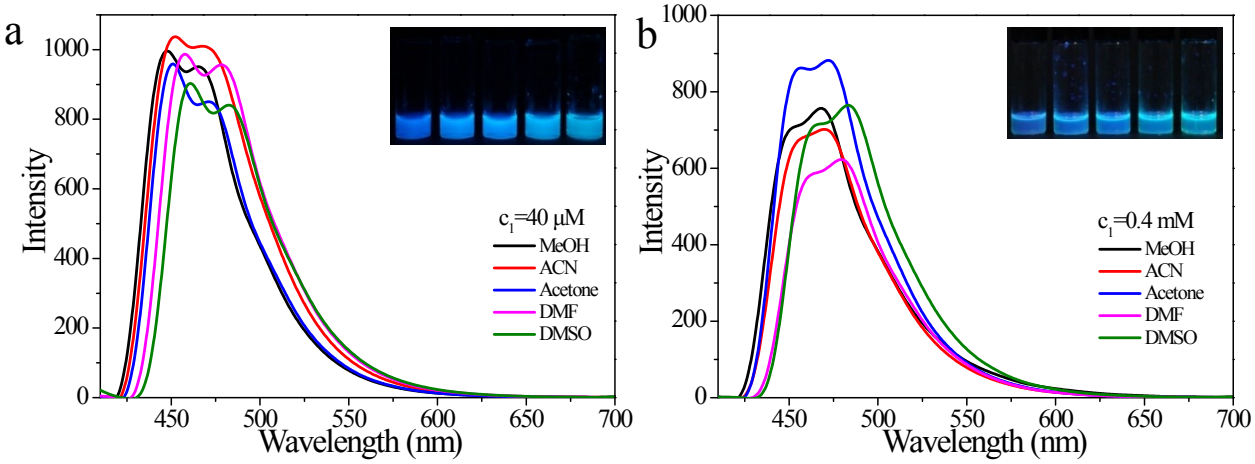


Fig. S1. Fluorescence spectra of **1** in different solvents with the concentration of 40μM (a) and 0.4 mM (b), and the samples were excited at 390 nm. The inset photographs are the **1** for 40 μM, 0.4 mM in different solvents (from left to right are MeOH, ACN, Acetone, DMF and DMSO, respectively) under 365 nm UV irradiation.

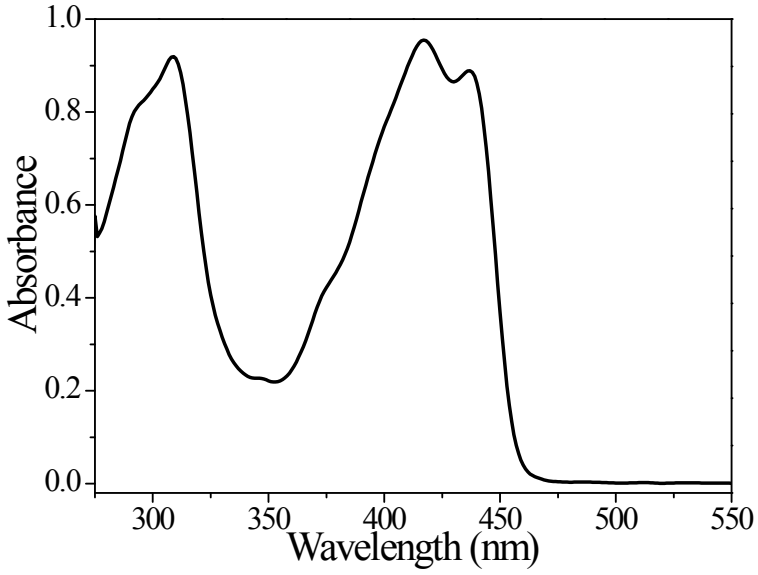


Fig. S2. UV−vis absorption of 40 μM **1** in DMSO after diluted 3-fold.

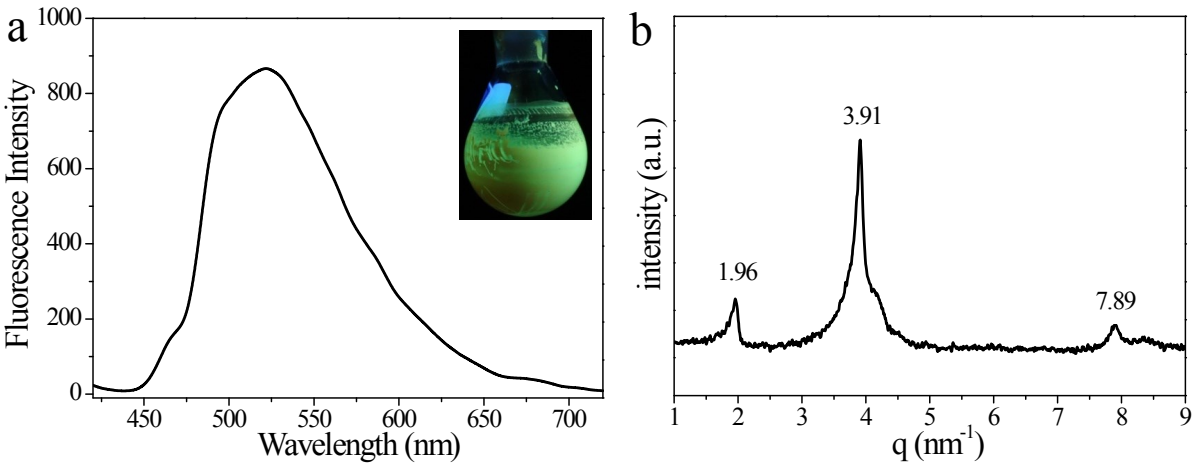


Fig. S3. (a) Emission spectrum of **1** in solid state at an excitation wavelength of 390 nm, inset is the photograph of **1** under 365 nm UV irradiation. (b) SAXS patterns of the superstructures for **1** in solid state.

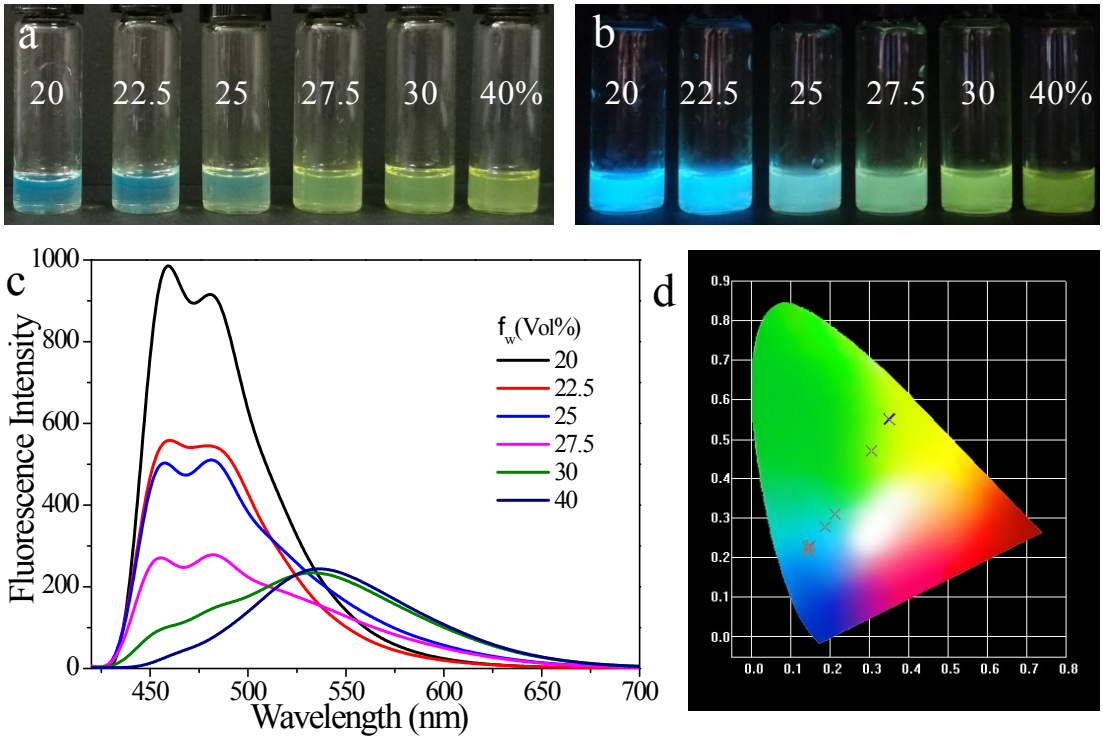


Fig. S4. Sample photographs of **1** under daylight (a) and 365 nm UV-light (b) at various f_w. (c) Fluorescence spectra and (d) the corresponding CIE diagram of **1** at 390 nm excitation in varied f_w in the mixed solvent ($f_w = V_{water}/V_{DMSO+water}$). The concentration of **1** in all experiments fixed at 40 μM.

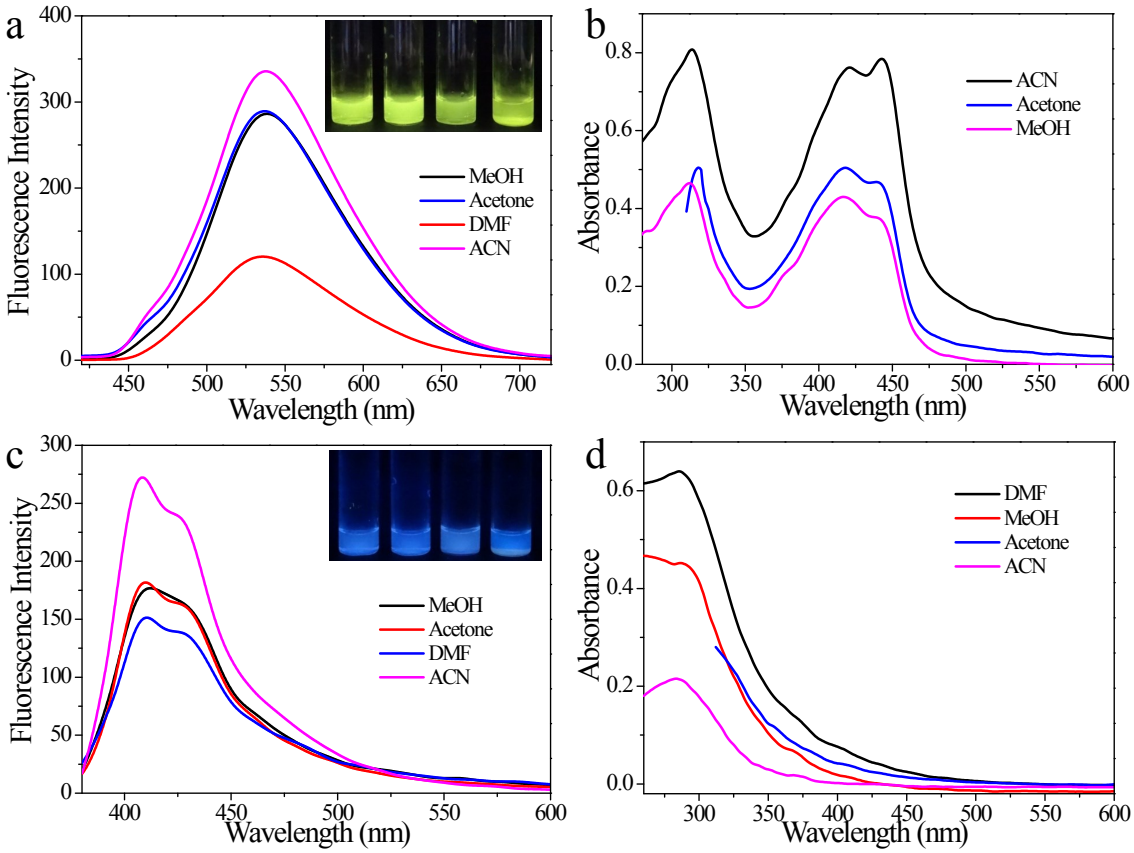


Fig. S5. (a) Fluorescence spectra (λ_{ex} = 390 nm) and (b) UV-vis spectra of **1** (40μM) in 20% different solvents and 80% H_2O systems. (c) Fluorescence spectra (λ_{ex} = 360 nm) and (d) UV-vis spectra of samples in (a) after irradiated 2 hours with 420 nm LED lamp. The inset photographs of (a) and (c) are the corresponding samples before and after irradiation (from left to right are MeOH, Acetone, DMF and ACN, respectively) under 365 nm UV-light.

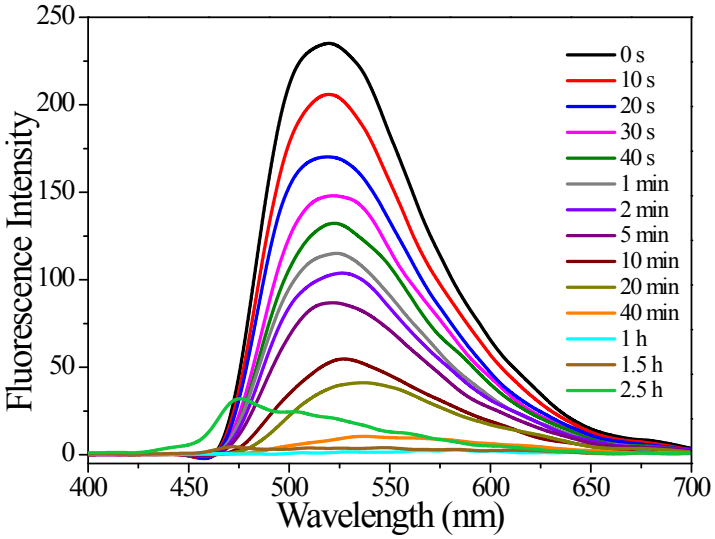


Fig. S6. Fluorescence spectra of **1** in MeOH with the concentration of 4 mM excited at 390 nm upon successive 420 nm photo irradiation.

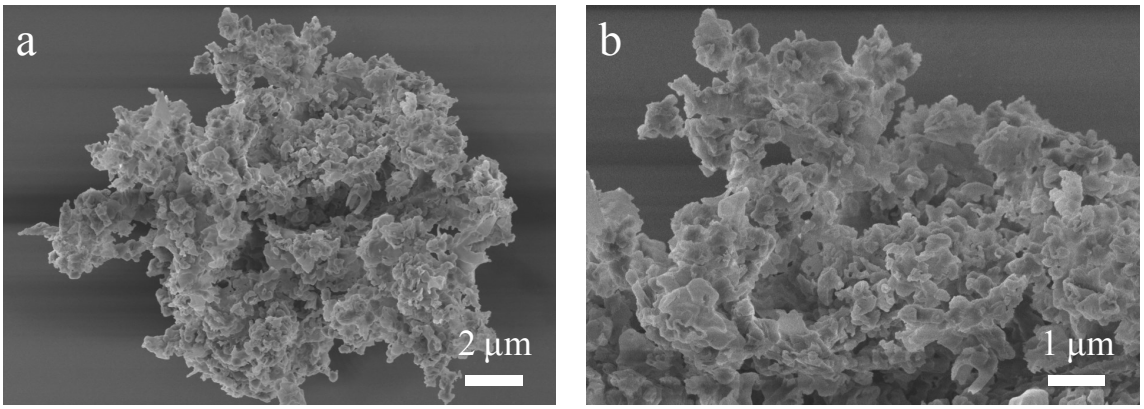


Fig. S7. SEM images of 4 mM **1** in MeOH solution after irradiation with 420 nm LED lamp.

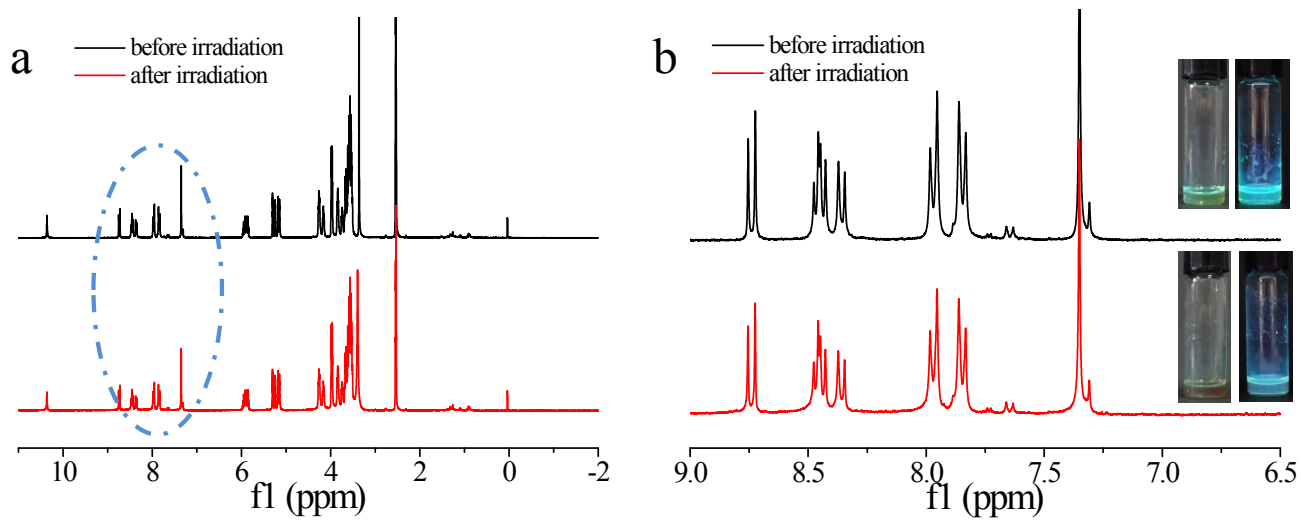
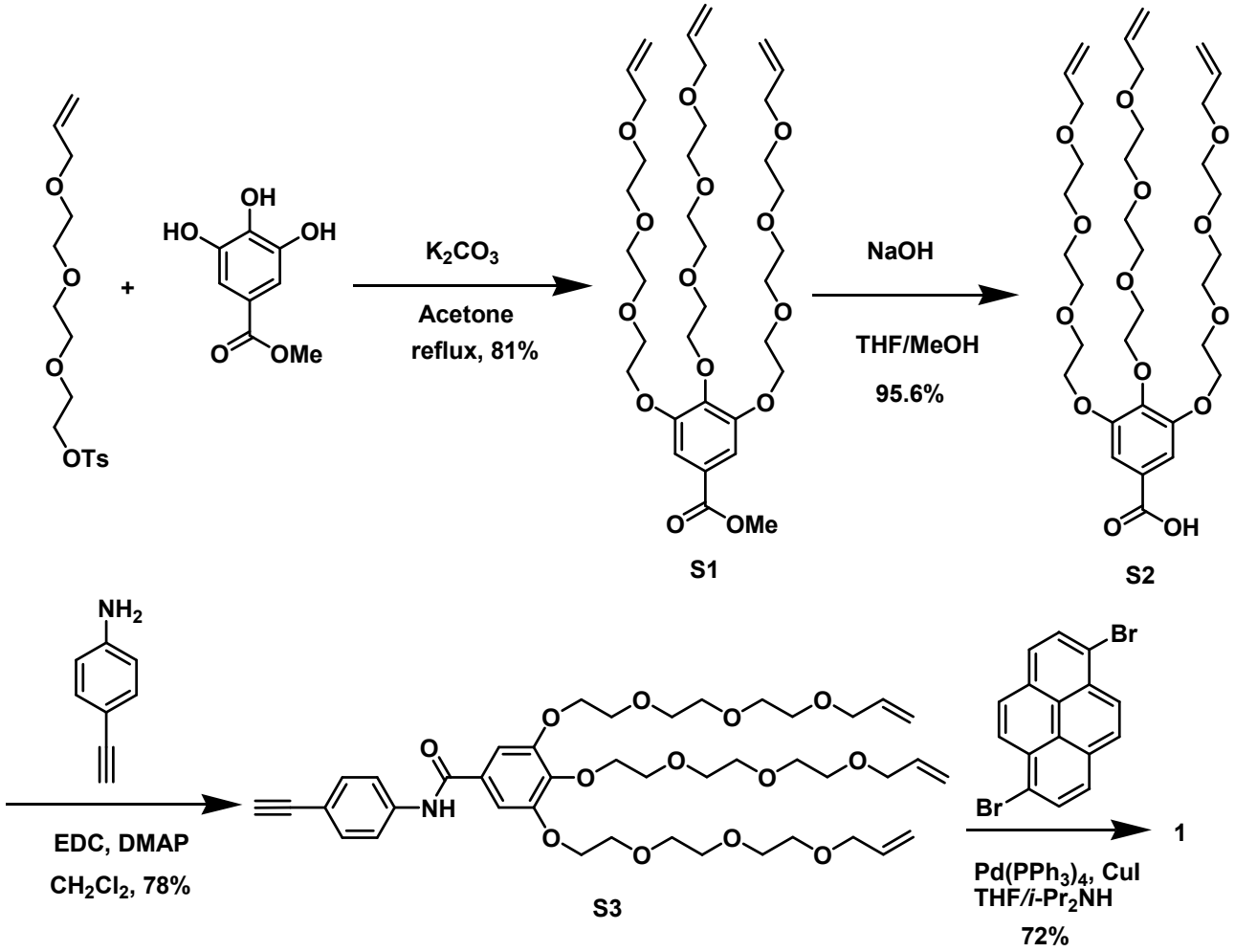


Fig. S8. Partial ^{1}H NMR spectra of **1** (298 K, 4 mM) in DMSO-d_6 solvent before and after photo irradiation.



Scheme S1. Synthesis route of compound **1**.

Synthesis of compound S2: Methyl 3,4,5-trihydroxybenzoate (0.47 g, 2.54 mmol) and K_2CO_3 (2.11 g, 6.0 eq) were dissolved in acetone (50 mL) in a 250 mL round-bottom flask. p-toluenesulfonate (3.50 g, 10.16 mmol) was added to the solution and the reaction mixture was stirred under argon-atmosphere overnight at 85 °C. After the reaction control via TLC showed the consumption of the starting material, the suspension was filtered off and the solvent of the filtrate was removed under reduced pressure. The residue was partitioned between water (40 mL) and CH_2Cl_2 (80 mL). The aqueous layer was extracted with CH_2Cl_2 (3×60 mL), and the combined organic layer was dried over anhydrous Na_2SO_4. After evaporating the solvent, the residue was purified by column chromatography (eluent: CH_2Cl_2/MeOH, 12/1, v/v) to afford ester compound as a colorless liquid (1.30 g, 72.6%). To a solution of ester (3.50 g, 4.99 mmol) in THF/methanol (20 ml/20 ml) was added NaOH (0.20 g) and refluxed for 3 h. After concentration, the residue was extracted with chloroform and water. To the aqueous layer was added 1 M HCl aq and the precipitate was extracted with chloroform. After drying the organic layer over anhydrous Na_2SO_4 and concentration, the compound **S3** was obtained as a yellow oil (3.50 g, 99%). ^{1}H NMR (400 MHz, $CDCl_3$): 7.35 (s, 2H), 5.96-5.86 (m, 3H), 5.29-5.16 (m, 6H), 4.24-4.19 (m, 6H), 4.03-4.01 (m, 6H), 3.88-3.86 (m, 4H), 3.82-3.79 (m, 2H), 3.75-3.59 (m, 24H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 170.47, 152.34, 143.27, 134.77, 124.01, 117.15, 109.61, 76.72, 72.48, 72.25, 70.86, 70.74, 70.69, 70.65, 70.61, 70.58, 69.67, 69.44, 68.91. ESI-MS m/z: $[M+H]^+$, calculated 687.3592, found 687.3581; $[M+Na]^+$, calculated 709.3411, found 709.3407.

Synthesis of compound S1: Benzoic acid **S3** (3.50 g, 5.10 mmol), 4-aminophenylacetylene (597 mg, 5.10 mmol), EDC•HCl (970 mg, 5.10 mmol) and DMAP (310 mg, 2.55 mmol) were dissolved in CH_2Cl_2 and stirred at room temperature for 24 h. The reaction mixture was then extracted with

H_2O/CH_2Cl_2, washed with brine and the solvent was removed with a rotary evaporator. The residue was purified by flash column chromatograph (CH_2Cl_2/CH_3OH, 10:1) to afford compound **S1** as a pale yellow liquid (2.80 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): 8.46 (s, 1H), 7.66 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 7.22 (s, 2H), 5.94-5.80 (m, 3H), 5.25-5.15 (m, 6H), 4.23-4.20 (m, 6H), 4.02-3.95 (m, 6H), 3.84-3.78 (m, 6H), 3.72-3.54 (m, 24H), 3.05 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 165.58, 152.15, 141.43, 138.96, 134.48, 134.33, 132.47, 129.59, 120.06, 117.19, 116.98, 116.86, 107.42, 83.37, 72.13, 71.93, 70.42, 70.37, 70.36, 70.31, 70.29, 70.26, 69.50, 69.19, 69.13, 68.77. ESI-MS m/z: $[M+H]^+$, calculated 786.4065; found 786.4053; $[M+Na]^+$, calculated 808.3884; found 808.3879.

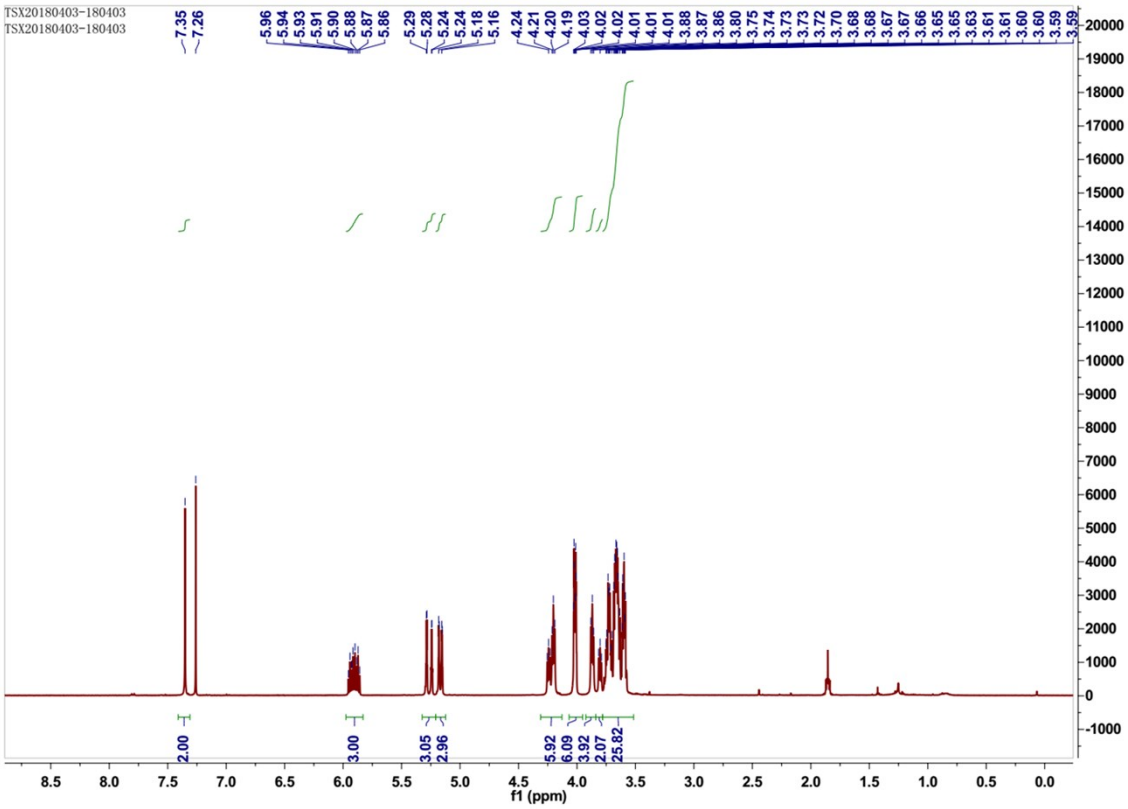


Fig. S9. ^{1}H NMR spectrum of compound **S3** in $CDCl_3$ (400 MHz) at 25 ^{o}C.

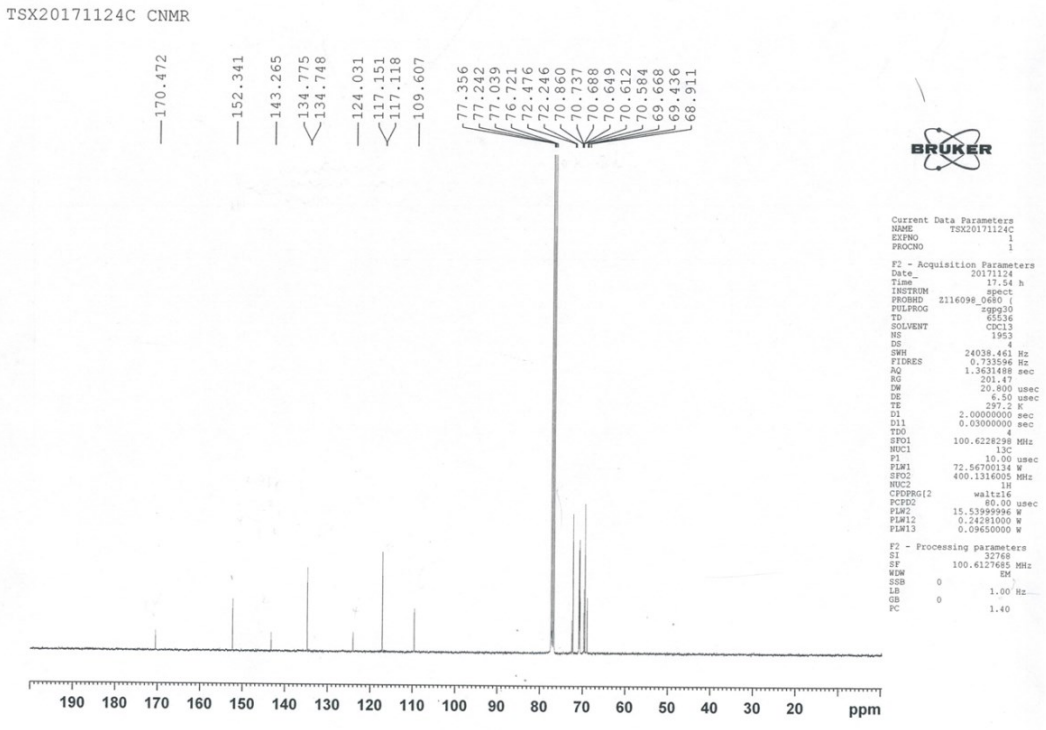


Fig. S10. ^{13}C NMR spectrum of compound **S3** in $CDCl_3$ (100 MHz) at 25 ^{o}C.

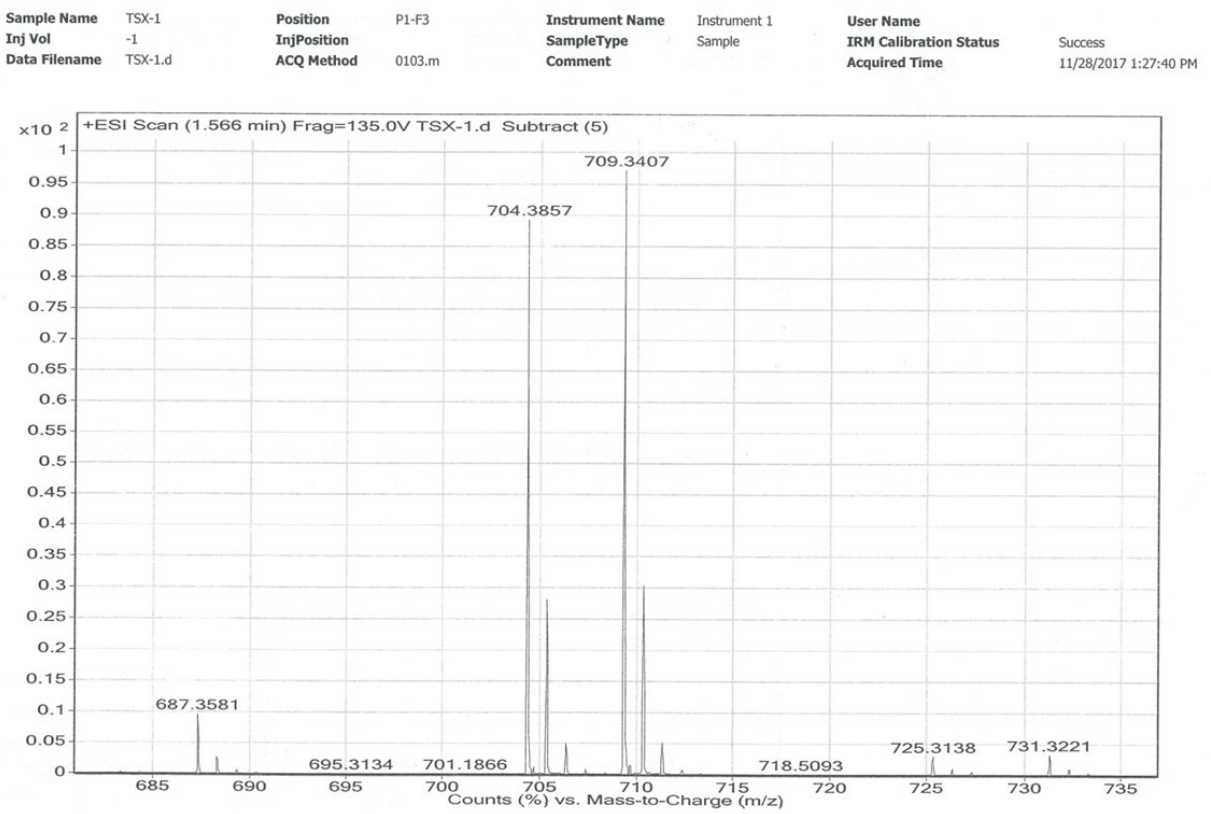


Fig. S11. HR-ESI-MS spectra of compound **S3**.

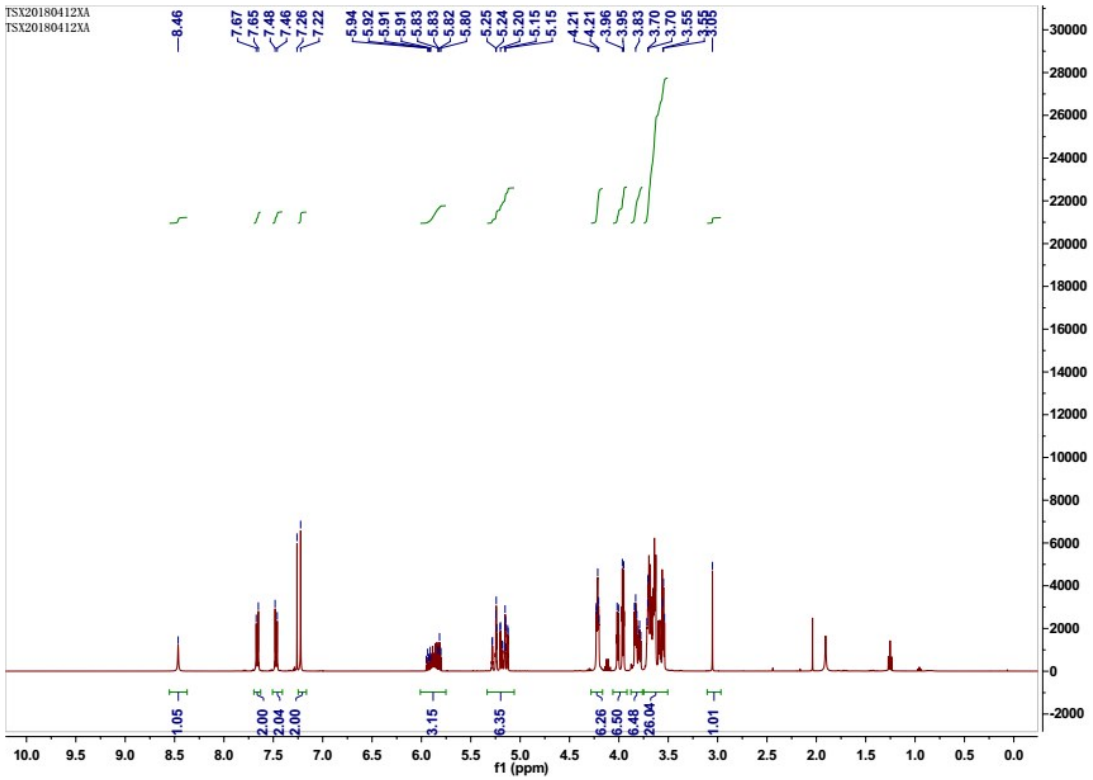


Fig. S12. ^{1}H NMR spectrum of compound **S1** in $CDCl_3$ (400 MHz) at 25 °C.

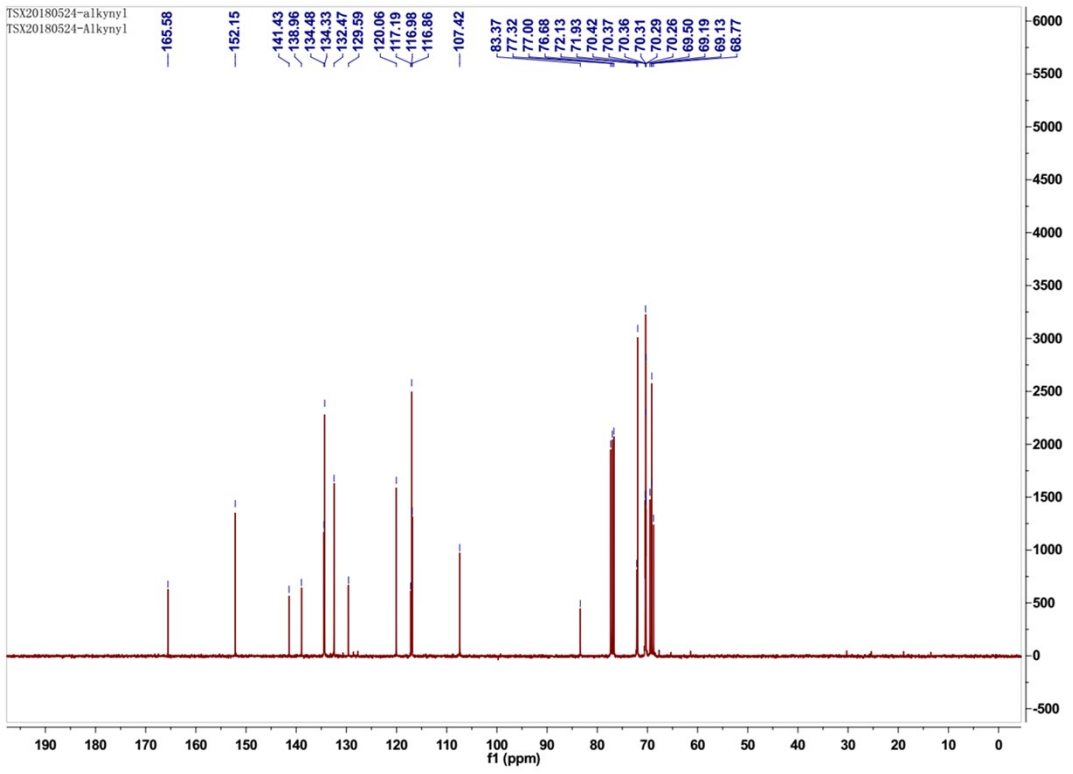


Fig. S13. ^{13}C NMR spectrum of compound **S1** in $CDCl_3$ (100 MHz) at 25 °C.

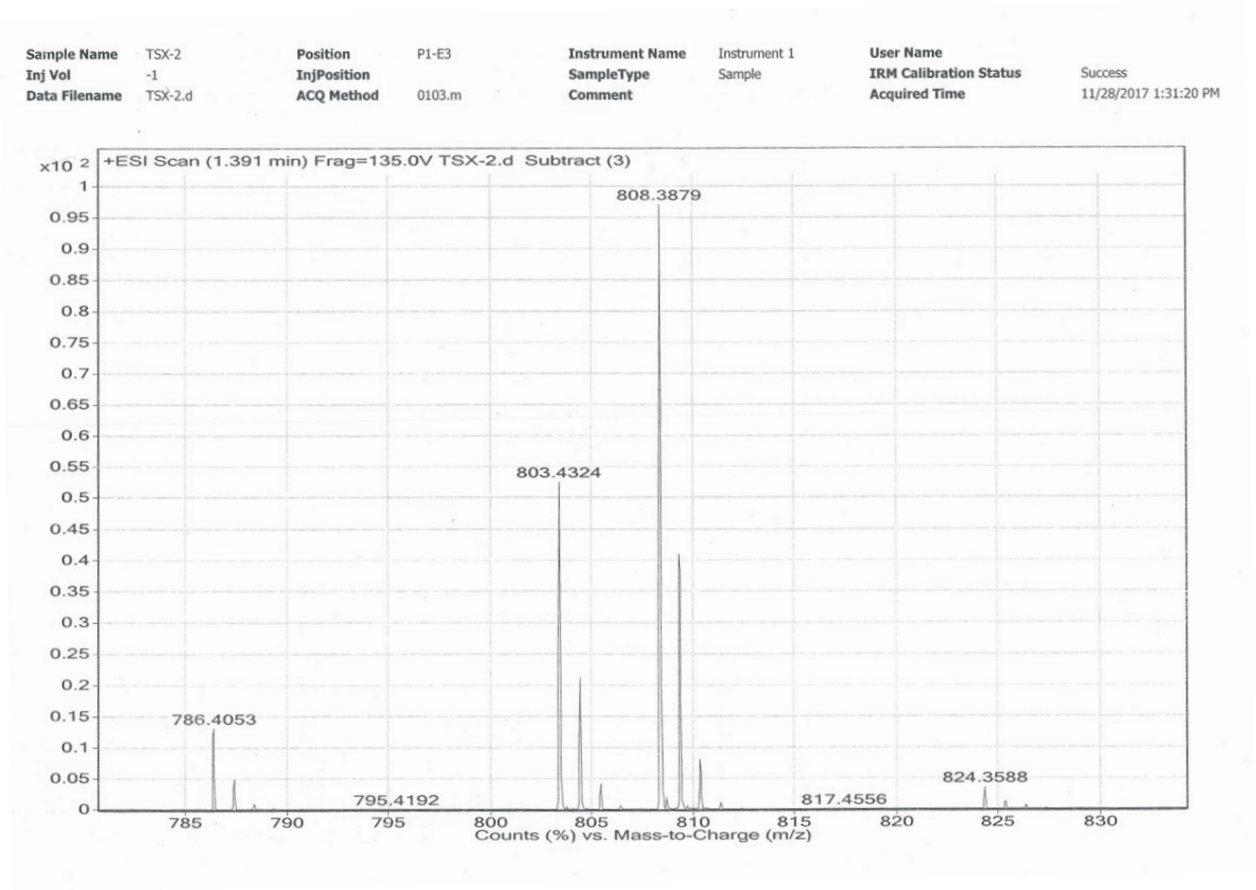


Fig. S14. HR-ESI-MS spectra of compound **S1**.

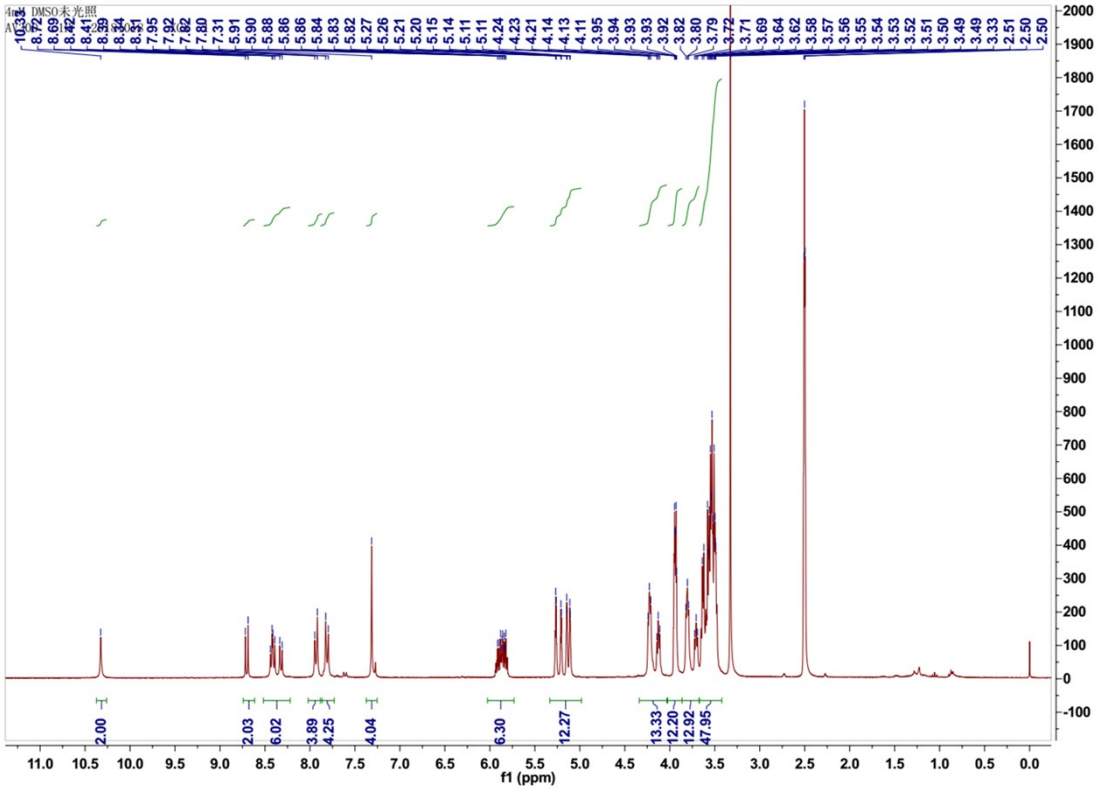


Fig. S15. ^{1}H NMR spectrum of compound **1** in DMSO-d_6 (400 MHz) at 25 °C.

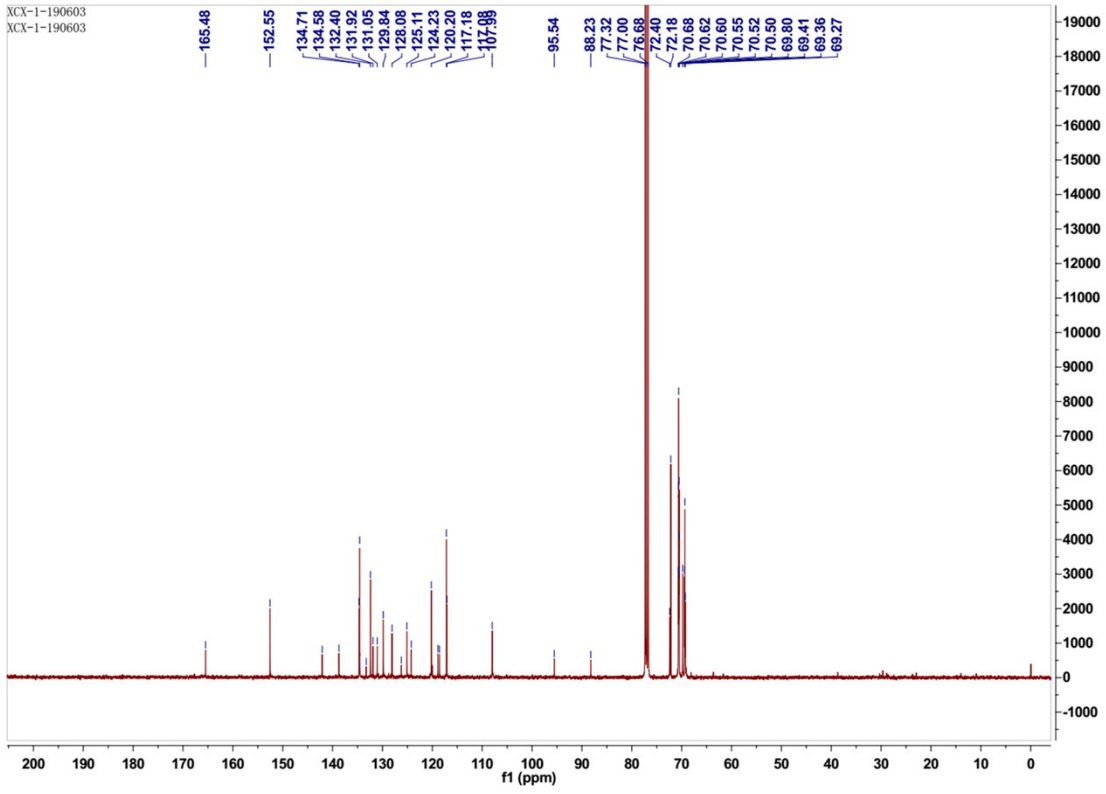


Fig. S16. ^{13}C NMR spectrum of compound **1** in $CDCl_3$ (100 MHz) at 25 °C.

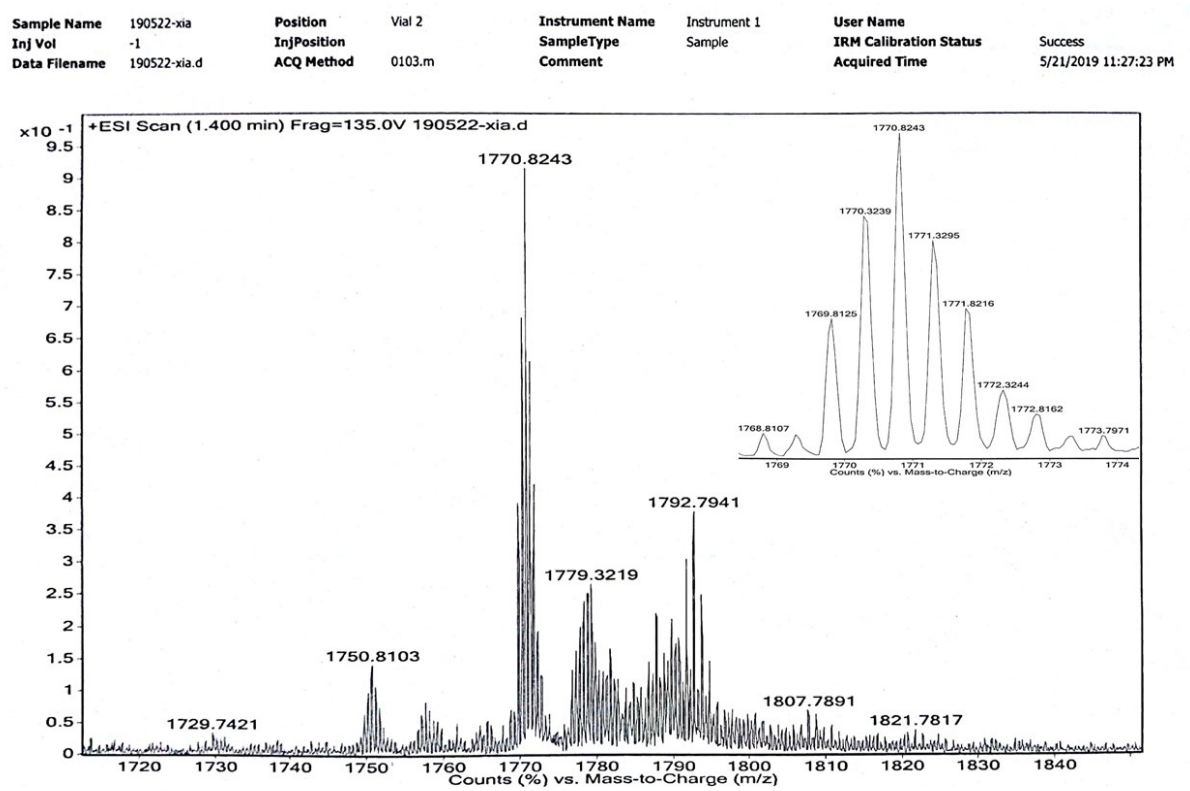


Fig. S17. HR-ESI-MS spectra of compound **1**.