

Supporting Information

A novel amino-pillar[5]arene as a fluorescent probe for highly selective detection of Au³⁺ ions

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1. Materials

1,4-Diethoxybenzene, paraformaldehyde, 1,2-dichloroethane, boron trifluoride etherate, chloroform, boron tribromide, ethanol, potassium carbonate, anhydrous acetonitrile, methyl chloroacetate, dichloromethane, anhydrous sodium sulphate, methanol, ethylenediamine, *n*-hexane, and hydrochloric acid were obtained from Aladdin Reagent Co. Ltd. Ag⁺, Al³⁺, Ba²⁺, Bi⁺, Ca²⁺, Cd²⁺, Co³⁺, Cs⁺, Cu²⁺, Fe²⁺, Fe³⁺, Hg²⁺, K⁺, Li⁺, Mg²⁺, Na⁺, Pb²⁺, Sb²⁺, Sn²⁺, Sr²⁺, Ni²⁺, Au³⁺, Br⁻, I⁻, PO₄³⁻, HPO₄²⁻, Cl⁻, HSO₃⁻, CO₃²⁻, HCO₃⁻, SO₄²⁻, NO₃⁻, NO₂⁻, F⁻ (AgNO₃, Al(NO₃)₃·9H₂O, BaCl₂·2H₂O, Bi(NO₃)₃·5H₂O, CaCl₂, CdCl₂, CoCl₂·6H₂O, Cs₂CO₃, CuSO₄·5H₂O, FeSO₄·7H₂O, FeCl₃·6H₂O, HgCl₂, KCl, LiF, MgSO₄·7H₂O, Na₂SO₄, Pb(NO₃)₂, SbCl₃, SnCl₂·2H₂O, SrCl₂·6H₂O, NiCl₂·6H₂O, HAuCl₄, NaBr, NaI, Na₃PO₄, Na₂HPO₄, NaCl, NaHSO₃, Na₂CO₃, NaHCO₃, Na₂SO₄, NaNO₃, NaNO₂, and NaF) metal ions were purchased from Sinopharm Chemical Reagent Co. Ltd. Deionized water was used throughout all experiments.

2. Synthesis of probe APA

The synthetic route to fluorescent probe **E** is depicted in Figure S1. First, compound **B** was obtained in one step by a Lewis acid-catalyzed condensation reaction of commercial starting material **A** and paraformaldehyde. Subsequently, deprotection of compound **B** with boron tribromide in chloroform produced compound **C**, which was further applied in the substitution reaction with methyl chloroacetate to achieve compound **D**. Finally, the desired product **E** was obtained via amidation of compound **D** with ethylenediamine.

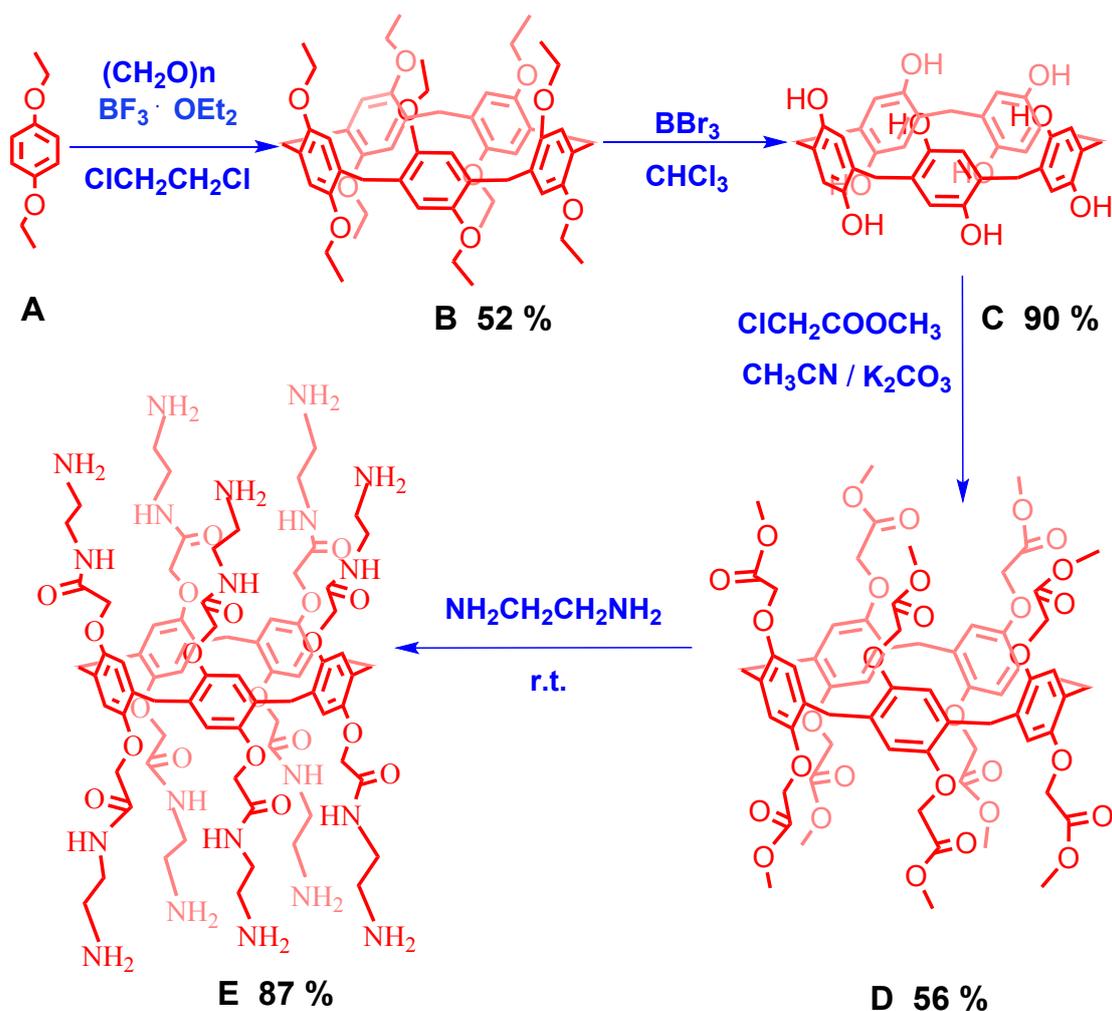


Figure S1 Synthetic route of fluorescent probe **E** from **A-D**.

2.1 Synthesis of compound B

Paraformaldehyde (2.8 g, 0.09 mol) was added to a solution of 1,4-diethoxybenzene (5.0 g, 0.03 mol) in dry $\text{ClCH}_2\text{CH}_2\text{Cl}$ (150 mL) under a nitrogen atmosphere at 25°C. Next, $\text{BF}_3 \cdot \text{OEt}_2$ (4.2 mL) was added to the mixture, and the reaction was then stirred at 25°C for 90 min. The mixture was then quenched with ethanol (20 mL). After stirring for 7 min, the filtrate was collected. The filtrate was extracted 3 times with deionized water, and the organic phase was combined and dried by anhydrous sodium sulfate. After removal of the solvent, the obtained solid was dissolved in CH_2Cl_2 (30 mL) and precipitated in EtOAc. The solid was recrystallized from CH_2Cl_2 and *n*-hexane to obtain a white solid **B** (2.8 g, **Yield**: 52%). ^1H NMR (400 MHz,

CDCl₃) δ (ppm): 6.74 (s, 10H), 3.86 (q, $J=6.8$ Hz, 20H), 3.77 (s, 10H), 1.28 (t, $J=6.8$ Hz, 30H).

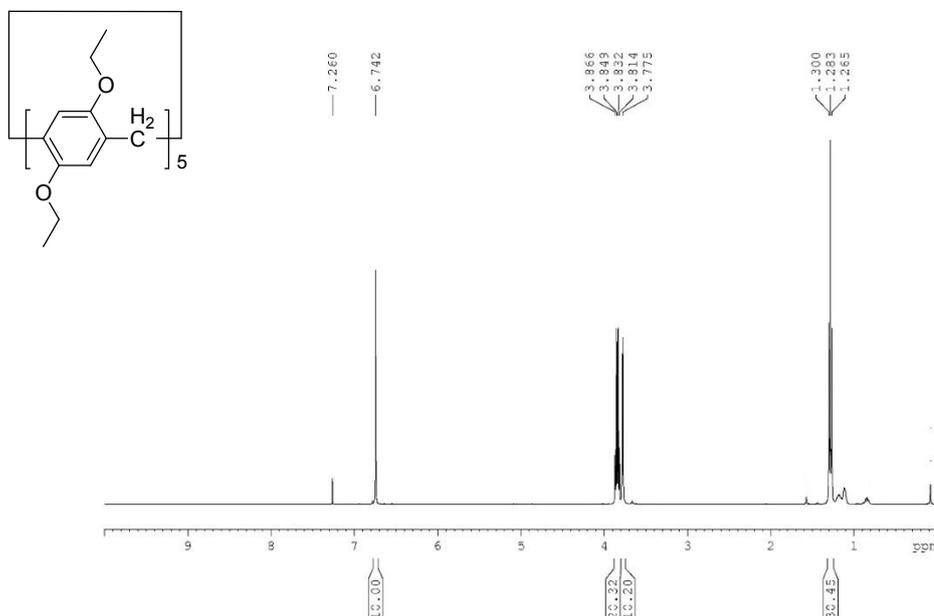


Figure S2 The ¹H NMR spectrum (400 MHz, CDCl₃, 293 K) of **B**.

2.2 Synthesis of compound C

Boron tribromide (4.5 mL, 0.044 mol) was slowly added to a solution of compound **B** (2.0 g, 0.022 mol) in CHCl₃ (100 mL) under a nitrogen atmosphere at -12 °C. The reaction was then stirred at 25°C for 24 h. The mixture was then quenched by ice water (50 mL) and stirred for 30 min. Finally, the solid was collected by filtration and was washed by hydrochloric acid (36%). Then, the samples were washed three times with CHCl₃ and dried to get a white solid **C** (1.42 g, **Yield:** 90%). ¹H NMR (400 MHz, DMSO) δ (ppm): 8.44 (s, 10H), 6.57 (s, 10H), 3.43 (s, 10H). ¹³C NMR (100 MHz, DMSO) δ (ppm): 146.5, 126.8, 117.7, 29.5.

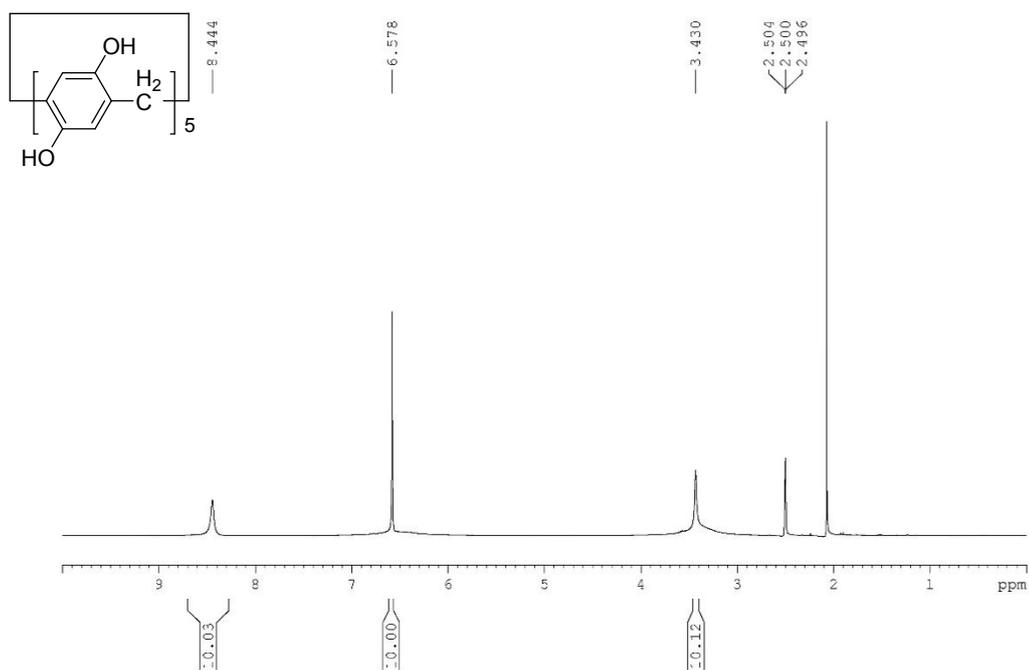


Figure S3 The ^1H NMR spectrum (400 MHz, DMSO, 293 K) of C.

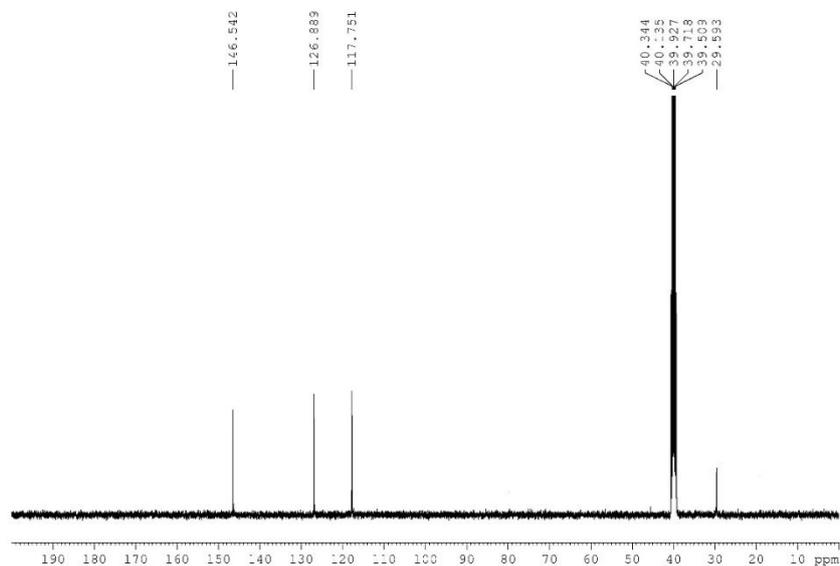


Figure S4 The ^{13}C NMR spectrum (400 MHz, DMSO, 293 K) of C.

2.3 Synthesis of compound D

potassium carbonate (10 g, 0.1 mol) and methyl chloroacetate (10 mL, 0.1 mol) was sequentially added to a solution of compound C (1.5 g, 0.0025 mol) in anhydrous

CH₃CN (60 mL) under a nitrogen atmosphere. The reaction was stirred at 85 °C for 36 h. After washing with dichloromethane, the filtrate was collected. Then, the solvent was removed, and the solid was recrystallized from CH₂Cl₂ and MeOH to obtain a white solid **D** (1.87 g, **Yield:** 56%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 6.98 (s, 10H), 4.55 (s, 20H), 3.85 (s, 10H), 3.53 (s, 30H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 169.7, 148.8, 128.4, 114.4, 65.4, 51.9, 29.2.

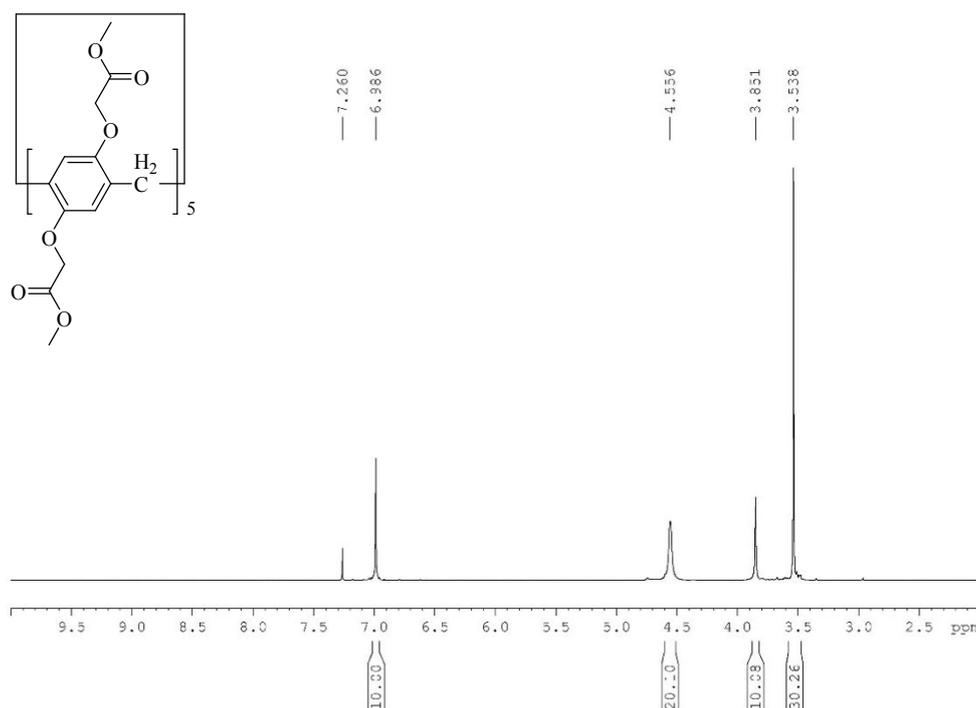


Figure S5 The ¹H NMR spectrum (400 MHz, CDCl₃, 293 K) of **D**.

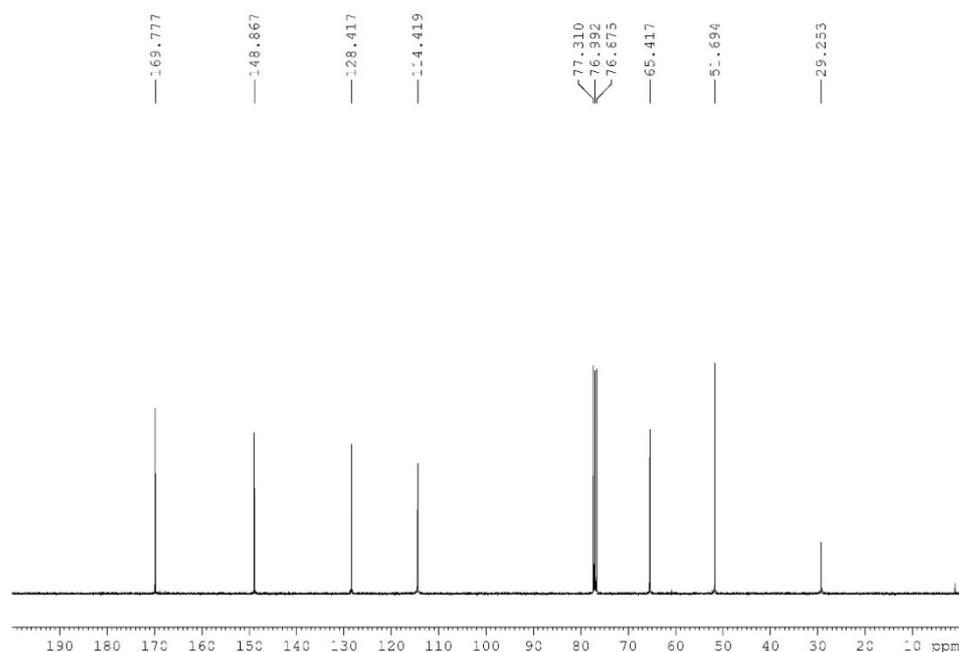


Figure S6 The ^{13}C NMR spectrum (400 MHz, CDCl_3 , 293 K) of **D**.

2.4 Synthesis of compound E

Compound **D** (1.33 g, 0.001 mol) was dissolved in ethylenediamine (5 mL) under a nitrogen atmosphere. The reaction was stirred at 110 °C for 12 h. Then, the solvent was removed, and the residue was dissolved in deionized water (15 mL) and finally extracted three times with CHCl_3 . The combined organic phase was washed with water, brined, dried by Na_2SO_4 , filtered, and concentrated under reduced pressure to get a light-yellow solid **E** (1.4 g, **Yield**: 87%). Mp: 126-127 °C. IR ν_{max} (cm^{-1}): 3,357, 2,931, 1,666, 1,541, 1,496, 1,438, 1,403, 1,206, 1,062, 934, 582. ^1H NMR (400 MHz, D_2O) δ (ppm): 6.88 (s, 10H), 4.54 (s, 20H), 3.88 (s, 10H), 3.53-3.16 (m, 20H), 2.97-2.40 (m, 20H). ^{13}C NMR (100 MHz, DMSO) δ (ppm): 168.3, 149.4, 128.4, 115.1, 68.2, 42.0, 41.2, 29.3. HRMS (ESI) m/z calcd for $\text{C}_{75}\text{H}_{111}\text{N}_{20}\text{O}_{20}$ $[\text{M}+\text{H}]^+$ 1611.8278; found 1611. 8277.

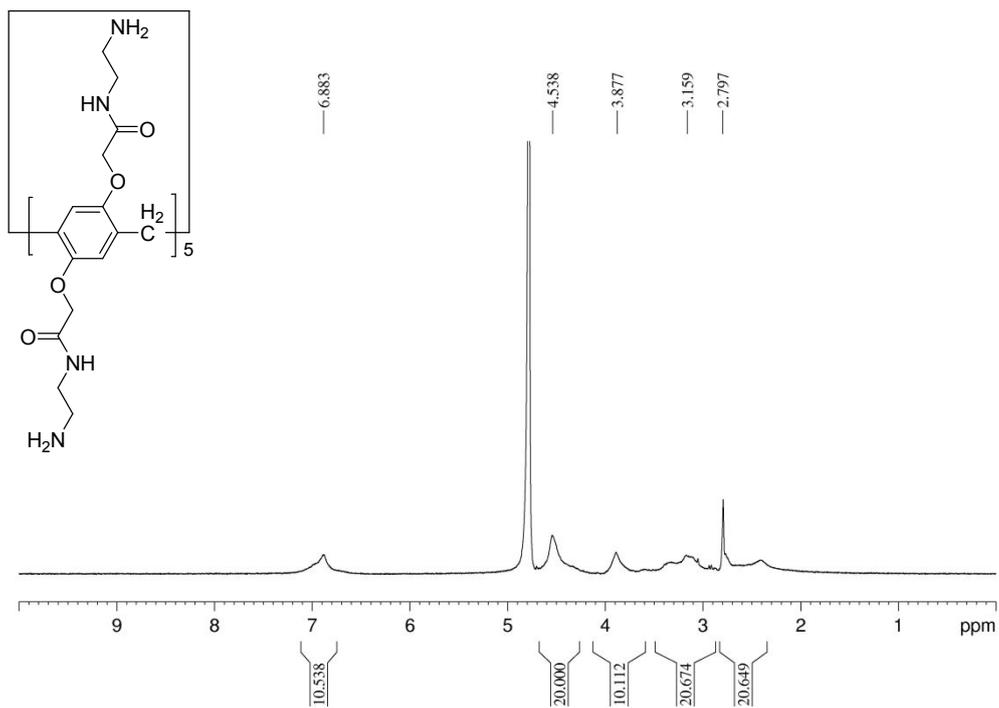


Figure S7 The ^1H NMR spectrum (400 MHz, D_2O , 293 K) of **E**.

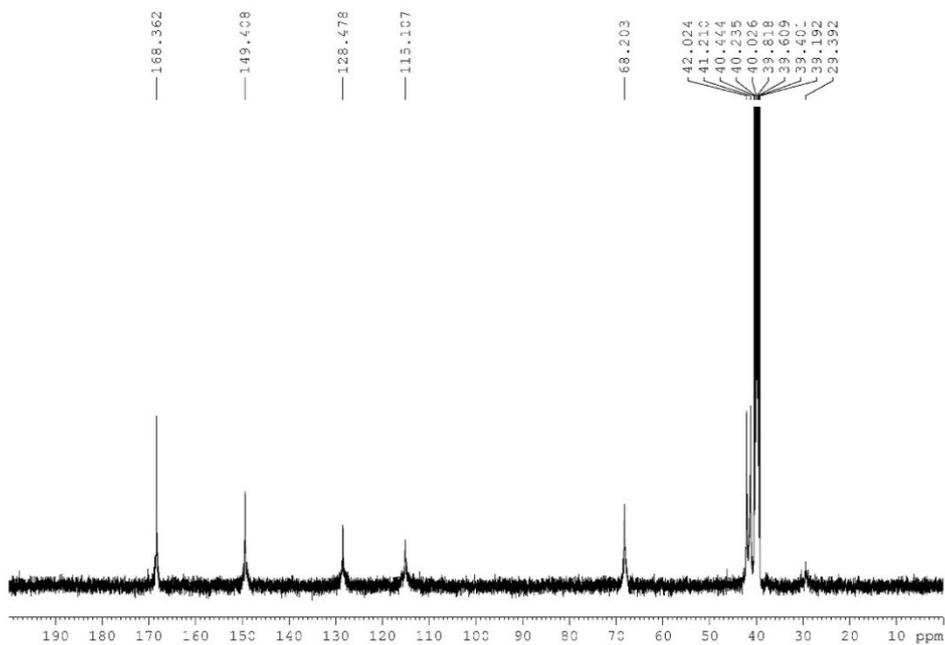


Figure S8 The ^{13}C NMR spectrum (400 MHz, DMSO, 293 K) of **E**.

MS Formula Results: + Scan (0.2130 min) Sub (xyp-3+++d)

m/z	Ion	Formula	Abundance
1611.8277	(M+H) ⁺	C ₇₅ H ₁₁₁ N ₂₀ O ₂₀	26772

Best	Formula (M)	Ion Formula	Score	Cross Score	Calc m/z	Diff (ppm)	Mass Match	Abund Match	Spacing Match
<input checked="" type="checkbox"/>	C ₇₅ H ₁₁₀ N ₂₀ O ₂₀	C ₇₅ H ₁₁₁ N ₂₀ O ₂₀	99.16		1611.8278	-0.19	99.92	97.85	99.21

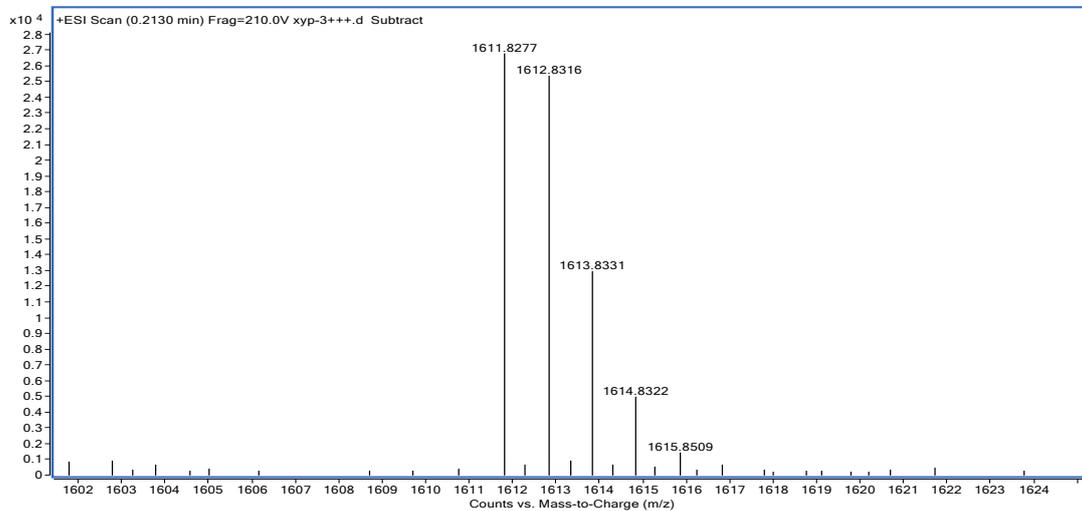


Figure S9 The mass spectrum of E.

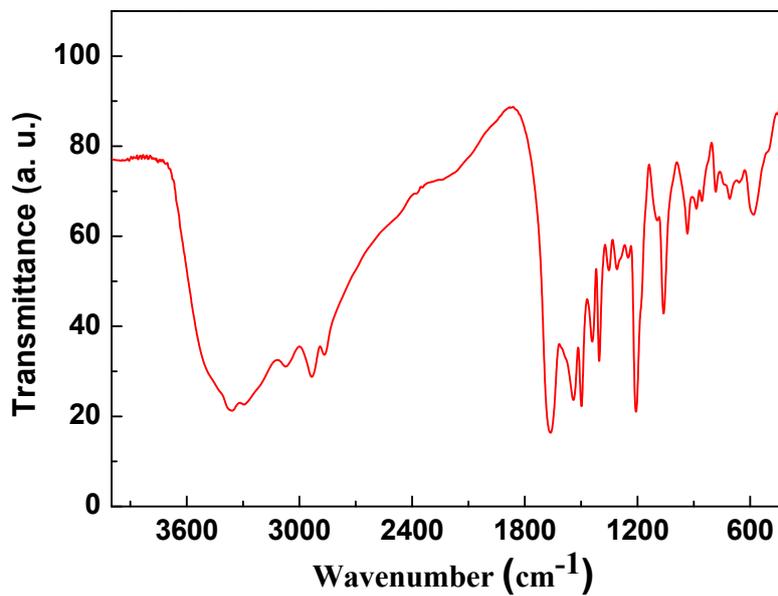


Figure S10 The infrared spectrum of E.