

# Supplementary Materials

## Fine-tuning the molecular conformation and packing structures of coumarin-based luminogens to achieve distinct piezochromic properties upon mechanical grinding and hydrostatic pressure

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## Materials and instruments

All the chemicals and solvents were purchased and used from commercial suppliers without further purification. The solvents used for UV-vis absorption and fluorescence measurements were in analytical grade.  $^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra were recorded on a Bruker Avance 400 MHz spectrometer. The triple quadrupole mass spectra were measured with an atmospheric chemical ionization (APCI) equipment with Mass Hunter software. UV-vis absorption spectra were recorded using a TU-1901 spectrometer from Beijing Purkinje General Instrument Co., Ltd with samples in a quartz cuvette (path length 1 cm). Fluorescence spectra were obtained on a Hitachi FL-7000 (Hitachi high technologies corporation Tokyo Japan). The absolute photoluminescence quantum yield in the solid state was measured on a HORIBA FluoroMax-4P spectrofluorometer using an integrating sphere (HORIBA Scientific, F-3092 integrating sphere). The single-crystal X-ray diffraction measurements were performed on a STOE STADIVARI X-ray diffractometer using graphite-monochromated CuK $\alpha$  radiation, the data was analyzed by X-area software, and the structure was resolved by Olex2 software, respectively. The powder X-ray diffraction measurements were performed on a Rigaku SmartLab X-ray diffractometer. The theoretical calculation was carried out with Gaussian 09 program package at B3LYP/6-311G\*\* level with empirical dispersion correction considered.<sup>1</sup>

For the hydrostatic pressure experiments, the samples were placed in the holes of a T301 steel gasket with diameter of 200  $\mu\text{m}$ . A small ruby chip was inserted into the sample compartment for in-situ pressure calibration according to the R1 ruby fluorescence method. A 4:1 mixture of methanol and ethanol was used as a pressure transmitting medium (PTM). The pressure on the sample was determined by monitoring the widths and separation of the R1 and R2 lines. The photoluminescence measurements under high pressure were performed on a QuantaMaster 40 spectrometer in the reflection mode. The 405 nm line of a violet diode laser with a spot size of 20  $\mu\text{m}$  and a power of 100 mW was used as the excitation source. The diamond anvil cell (DAC) containing the sample was put on a Nikon fluorescence microscope to focus the laser on the sample. The emission spectra were recorded with a monochromator equipped with a photomultiplier. All experiments were conducted at room temperature. The time-correlated single photon counting (TCSPC) experiments were performed on a Horiba Fluoro max plus with time resolution of 25 ps.

## Synthesis of the target molecules

Compound **5** and **4-CPOMe** were synthesized following literature reported methods.<sup>2,3</sup>

### Compound **6**

To a 100 mL three-necked flask, compound **5** (893.08 mg, 4 mmol) was added, the system was degassed 3 times with nitrogen, then Et<sub>3</sub>N (809.52 mg, 8 mmol) was added. The solution was cooled down to 0°C, and trifluoromethanesulfonic anhydride was added in dropwise (1467.1 mg, 5.2 mmol). After 2 hours, ice water was added to the reaction to quench the reaction. The resulted solution was extracted by CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 mL), and the organic layer was separated, dried with anhydrous Mg<sub>2</sub>SO<sub>4</sub>. The solvents were evaporated to get the crude product, which was further purified by column chromatography (petroleum ether : EtOAc = 3 : 1, v/v). The target compound was obtained as bright yellow powder, 1.18 g, yield 81%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ : 1.20 (t, *J* = 7.1 Hz, 6H), 3.41 (q, *J* = 7.1 Hz, 4H), 6.01 (d, *J* = 2.5 Hz, 1H), 6.48 (d, *J* = 2.5 Hz, 1H), 6.63 (dd, *J* = 9.1, 2.5 Hz, 1H), 7.39 (d, *J* = 9.1 Hz, 1H).

### Compound **3-CPOMe**

Under N<sub>2</sub> atmosphere, 4-(diethylamino) salicylaldehyde (2.90 g, 15 mmol) was added to a 100 mL three-necked flask, then 4-methoxybenzyl cyanide (2.21 g, 15 mmol), piperidine (638.63 mg, 7.5 mmol), acetic acid (5 mL) and DMF (25 mL) were added successively. The mixture was heated to reflux for 12 hours. After that, the solution was filtered as it is hot to get the precipitate, which is rinsed with acetic acid. The precipitate was collected as the crude product, and was further purified by recrystallization with ethanol, to get the pure target compound as a yellow green solid, 3.87 g, yield 80%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ : 1.21 (t, *J* = 7.1 Hz, 6H), 3.41 (q, *J* = 7.1 Hz, 4H), 3.83 (s, 3H), 6.52 (d, *J* = 2.5 Hz, 1H), 6.58 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.91 – 6.97 (m, 2H), 7.29 (d, *J* = 8.7 Hz, 1H), 7.63 (dd, *J* = 6.5, 2.4 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm) δ: 161.05, 156.66, 151.28, 141.83, 140.55, 132.08, 129.49, 128.63, 119.00, 118.25, 110.86, 109.33, 108.76, 97.02, 44.97, 12.46. **3-CPOMe**: *m/z* ([M+H]<sup>+</sup>) calcd: 324.1584, found = 324.1521.

### Compound **3-CPCN**

**3-CPCN** was synthesized following a similar procedure with **3-CPOMe** with 4-(diethylamino)

salicylaldehyde (2.90 g, 15 mmol), 4-cyanophenylacetonitrile (2.13 g, 15 mmol), piperidine (638.63 mg, 7.5 mmol), acetic acid (5 mL) and DMF (25 mL) as yellow solid, 3.77 g, yield 79%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ : 1.22 (t, *J* = 7.1 Hz, 6H), 3.43 (q, *J* = 7.1 Hz, 4H), 6.51 (d, *J* = 2.5 Hz, 1H), 6.61 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.32 (d, *J* = 8.8 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.76 (s, 1H), 7.83 (d, *J* = 8.6 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm) δ: 161.05, 156.66, 141.83, 140.55, 132.08, 129.49, 128.64, 119.00, 118.25, 109.33, 108.76, 97.01, 44.97, 12.46. **3-CPCN**: *m/z* ([M+H]<sup>+</sup>) calcd: 319.1368, found = 319.1432.

#### Compound **4-CPCN**

Under N<sub>2</sub> atmosphere, in a 3-necked flask, 4-cyanophenylboronic acid (1.83 g, 5 mmol) was added to a mixed solution of triflate **6** (1.83 g, 5 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (288.89 mg, 0.25 mmol, 2 mol%), K<sub>2</sub>CO<sub>3</sub> (829.20 mg, 6 mmol) in toluene (30 mL). The reaction mixture was refluxed for 1 h, then cooled down to room temperature. The solvent was evaporated to get the crude product, which was further purified by column chromatography (petroleum ether : EtOAc = 3 : 1, v/v) to get the pure product as yellow green solid, 796 mg, yield 50%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ : 1.21 (t, *J* = 7.1 Hz, 6H), 3.42 (q, *J* = 7.1 Hz, 4H), 5.97 (s, 1H), 6.48 – 6.60 (m, 2H), 7.07 (d, *J* = 9.0 Hz, 1H), 7.52 – 7.58 (m, 2H), 7.79 (d, *J* = 8.1 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm) δ: 161.56, 156.92, 154.03, 151.01, 140.97, 132.59, 129.27, 127.33, 108.80 (d, *J* = 14.0 Hz), 98.09, 44.94, 12.50. **4-CPCN**: *m/z* ([M+H]<sup>+</sup>) calcd: 319.1368, found = 319.1432.

## Figures, spectra & tables

### Solvatochromic properties

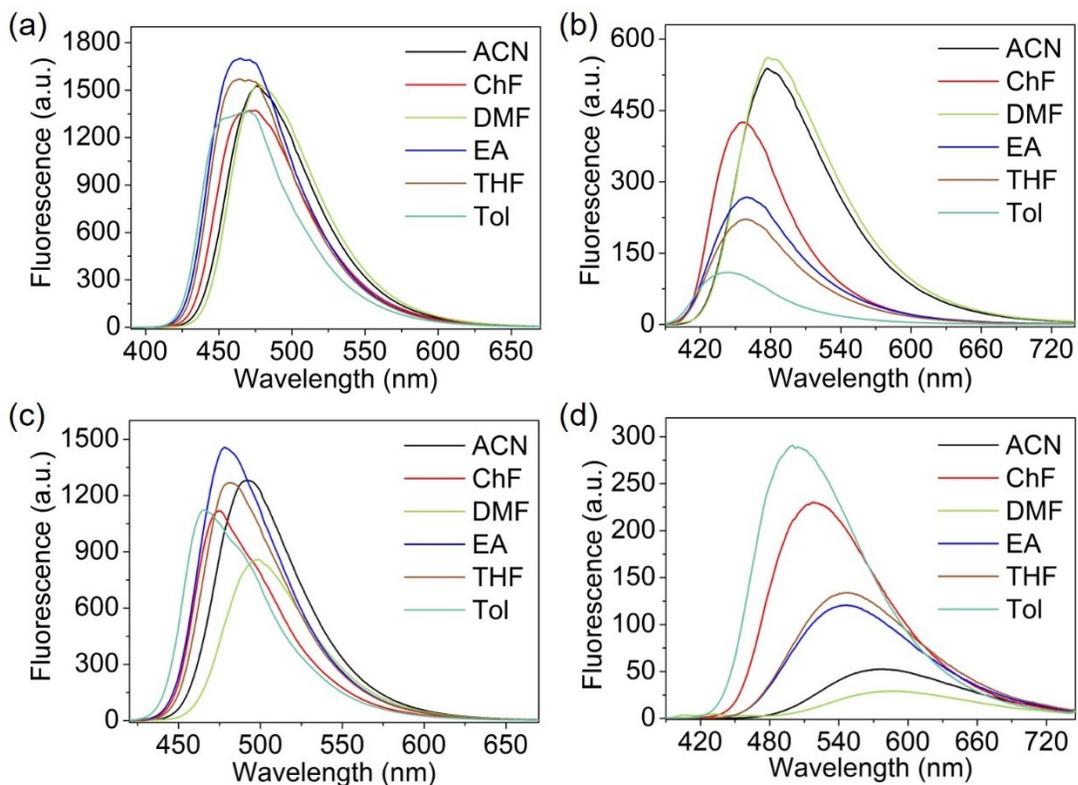


Fig. S1 PL spectra of the compounds in various organic solvents.

## AIE properties

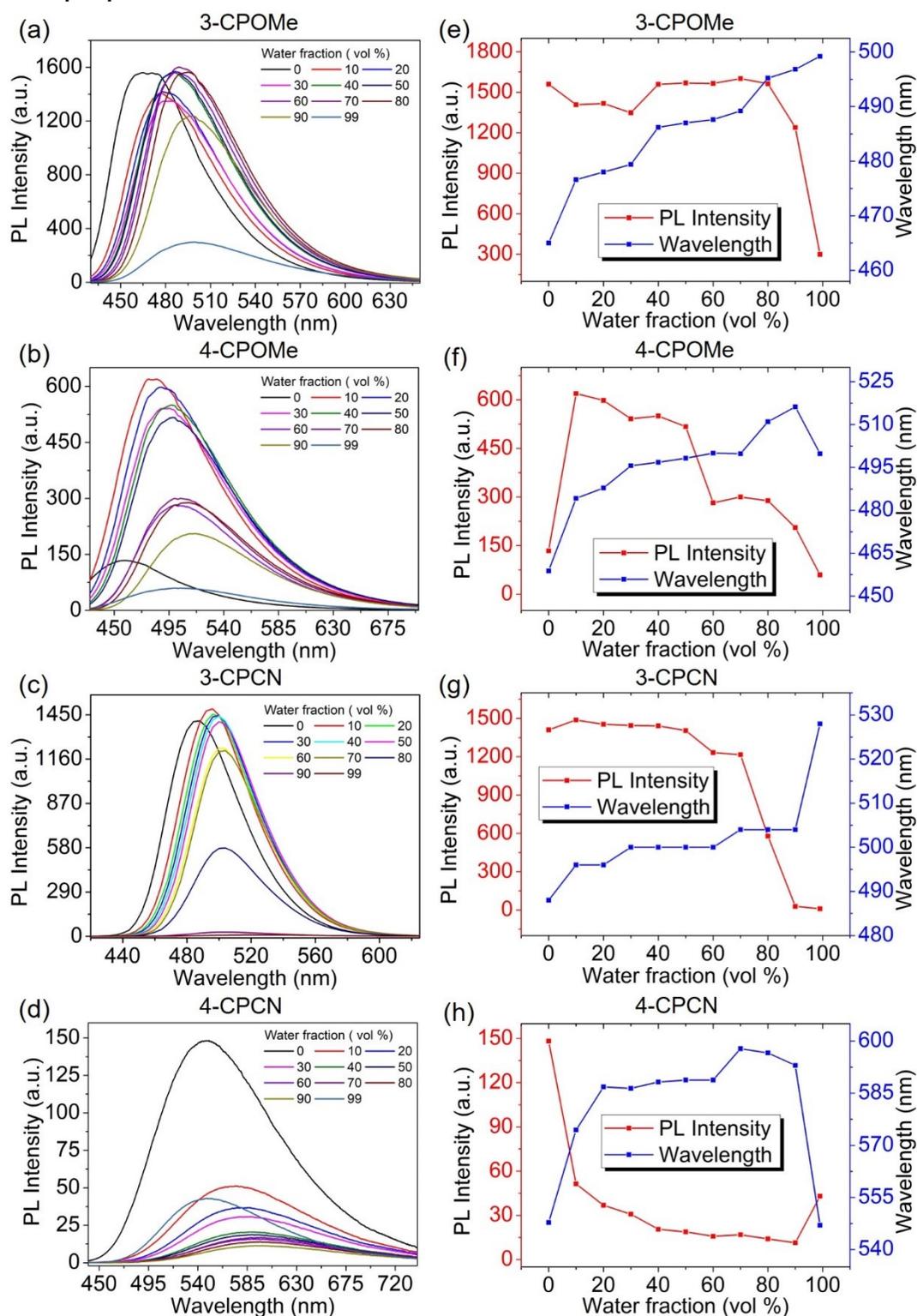


Fig. S2 The AIE properties of the four materials in THF/H<sub>2</sub>O mixed solutions; (a-d) show the PL spectra with different H<sub>2</sub>O fractions, (e-h) represent the corresponding changes of emission wavelengths and intensities as the increase of H<sub>2</sub>O fractions.

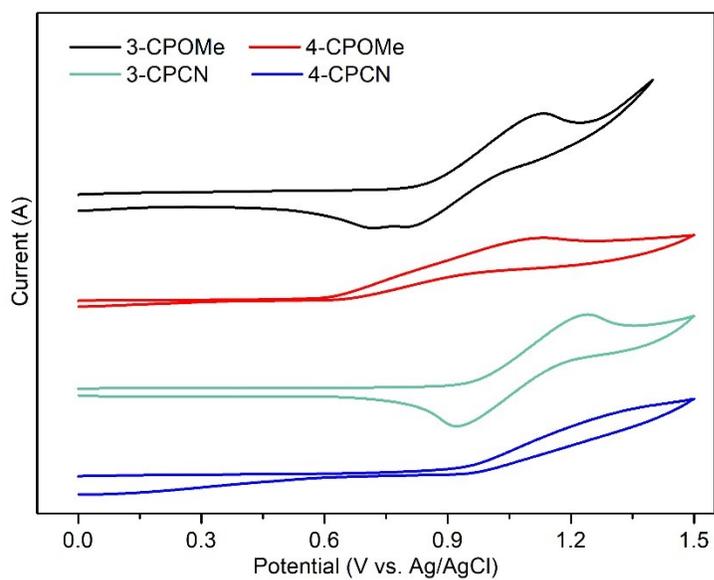


Fig. S3 The cyclic voltammograms of the compounds in THF (Ag/AgCl as the reference electrode, Pt as working electrode and  $\text{Bu}_4\text{NPF}_6$  as electrolyte, scanning speed 100 mV/s).

Table S1 The single-crystal data of the four compounds.

Compound	<b>3-CPOMe</b>	<b>4-CPOMe</b>	<b>3-CPCN</b>	<b>4-CPCN</b>
Empirical formula	C <sub>20</sub> H <sub>21</sub> NO <sub>3</sub>	C <sub>20</sub> H <sub>21</sub> NO <sub>3</sub>	C <sub>20</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub>	C <sub>20</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub>
Formula weight	323.38	323.38	318.36	318.36
Temperature/K	150	120	120.00	120
Crystal system	monoclinic	triclinic	triclinic	monoclinic
Space group	P2 <sub>1</sub> /n	P-1	P-1	P2 <sub>1</sub> /c
a/Å	6.4917(18)	9.2173(14)	6.6330(6)	11.4430(8)
b/Å	19.911(6)	9.4972(11)	7.5002(7)	13.2770(8)
c/Å	12.759(4)	9.5809(10)	17.4918(16)	10.8931(8)
α/°	90	88.263(9)	79.488(7)	90
β/°	90.73(2)	82.367(10)	81.308(7)	99.297(6)
γ/°	90	85.479(11)	64.528(7)	90
Volume/Å <sup>3</sup>	1649.0(8)	828.51(18)	769.83(13)	1633.23(19)
Z	4	2	2	4
ρ <sub>calc</sub> /g/cm <sup>3</sup>	1.303	1.296	1.373	1.295
μ/mm <sup>-1</sup>	0.703	0.699	0.718	0.677
F(000)	688.0	344.0	336.0	672.0
Crystal size/mm <sup>3</sup>	0.5 × 0.3 × 0.1	0.5 × 0.3 × 0.1	0.5 × 0.3 × 0.3	0.5 × 0.3 × 0.1
Radiation	Cu Kα (λ = 1.54186)	Cu Kα (λ = 1.54186)	CuKα (λ = 1.54186)	Cu Kα (λ = 1.54186)
2θ range for data collection/°	8.232 to 136.584	12.556 to 138.662	10.322 to 127.992	10.588 to 138.832
Index ranges	-5 ≤ h ≤ 7, - 23 ≤ k ≤ 23, -15 ≤ l ≤ 12	-11 ≤ h ≤ 4, -11 ≤ k ≤ 10, -11 ≤ l ≤ 10	-7 ≤ h ≤ 7, -8 ≤ k ≤ 8, -7 ≤ l ≤ 20	-13 ≤ h ≤ 9, -15 ≤ k ≤ 6, -13 ≤ l ≤ 12
Reflections collected	14629	5757	2488	6618
Independent reflections	2958 [R <sub>int</sub> = 0.0273, R <sub>sigma</sub> = 0.0238]	2933 [R <sub>int</sub> = 0.0272, R <sub>sigma</sub> = 0.0307]	2488 [R <sub>int</sub> = 0.0317, R <sub>sigma</sub> = 0.0327]	2935 [R <sub>int</sub> = 0.0197, R <sub>sigma</sub> = 0.0232]
Data/restraints/parameters	2958/0/220	2933/0/220	2488/0/220	2935/0/219
Goodness-of-fit on F <sup>2</sup>	1.017	1.094	1.202	1.049
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0343, wR <sub>2</sub> = 0.0788	R <sub>1</sub> = 0.0416, wR <sub>2</sub> = 0.1143	R <sub>1</sub> = 0.0894, wR <sub>2</sub> = 0.2840	R <sub>1</sub> = 0.0342, wR <sub>2</sub> = 0.0920
Final R indexes [all data]	R <sub>1</sub> = 0.0517, wR <sub>2</sub> = 0.0857	R <sub>1</sub> = 0.0518, wR <sub>2</sub> = 0.1225	R <sub>1</sub> = 0.0993, wR <sub>2</sub> = 0.2880	R <sub>1</sub> = 0.0407, wR <sub>2</sub> = 0.0954
Largest diff. peak/hole / e Å <sup>-3</sup>	0.13/-0.17	0.18/-0.26	0.42/-0.37	0.16/-0.24

# NMR spectra

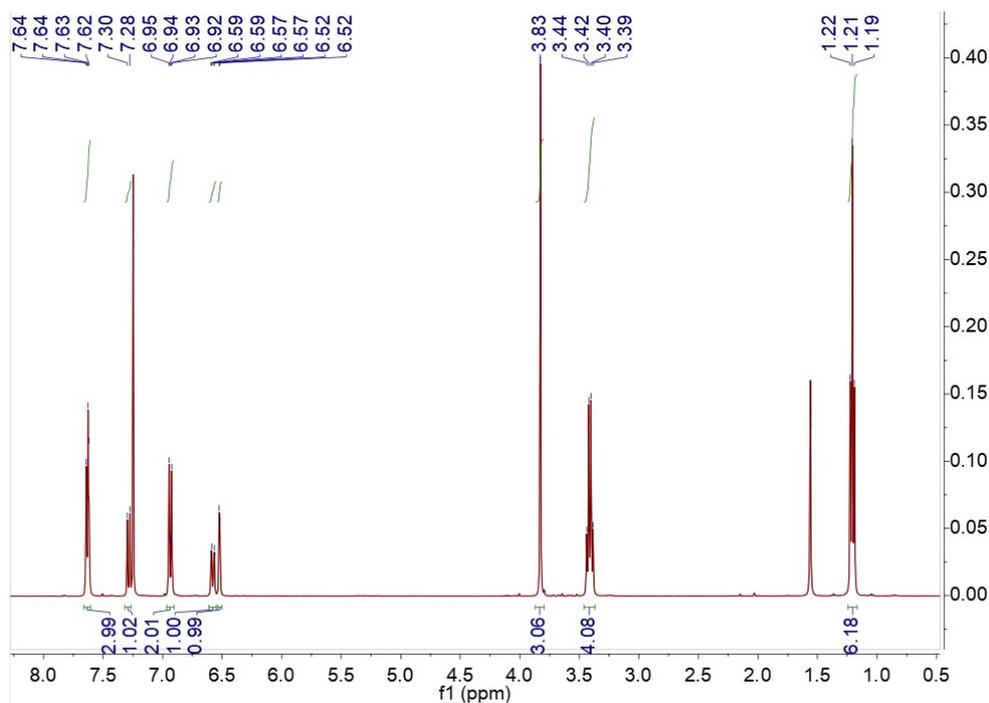


Fig. S4 <sup>1</sup>H NMR spectrum of 3-CPOMe.

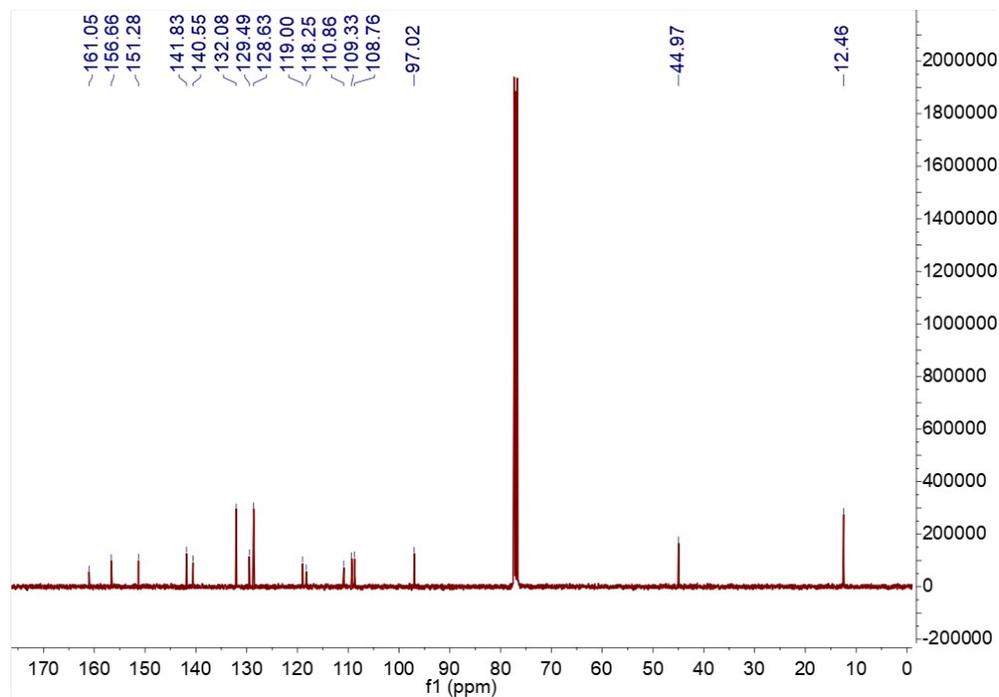


Fig. S5 <sup>13</sup>C NMR spectrum of 3-CPOMe.

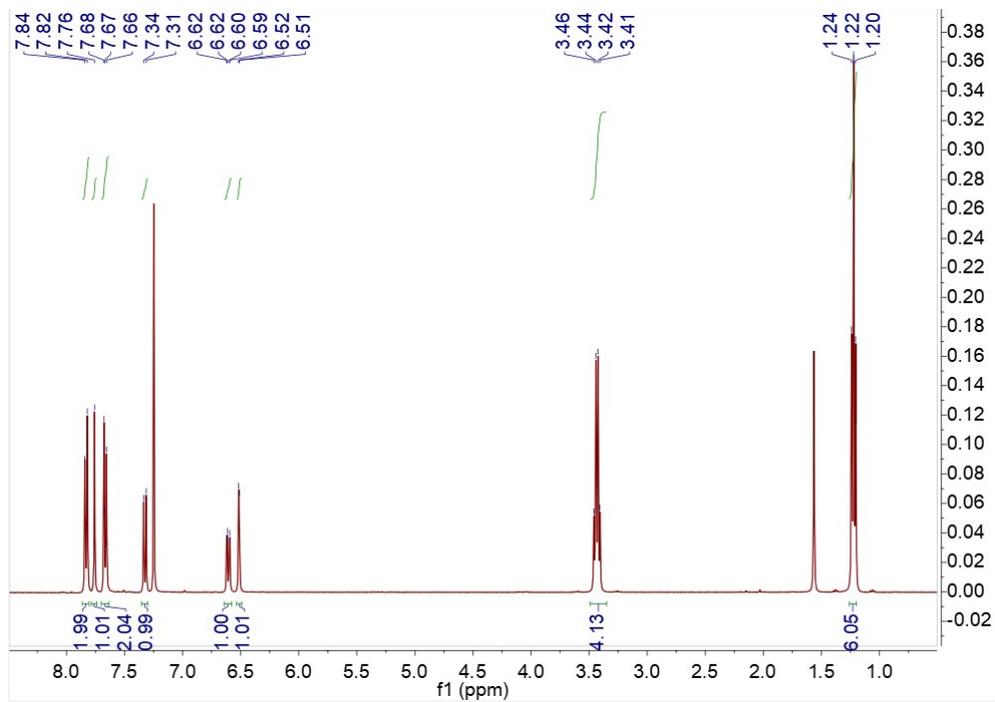


Fig. S6  $^1\text{H}$  NMR spectrum of **3-CPCN**.

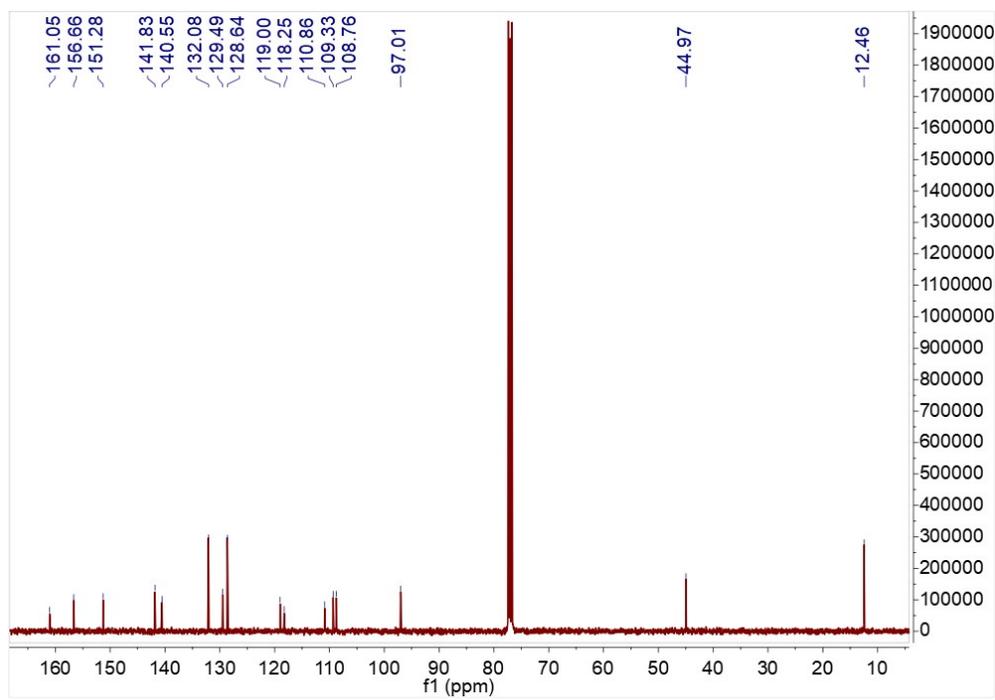


Fig. S7  $^{13}\text{C}$  NMR spectrum of **3-CPCN**.

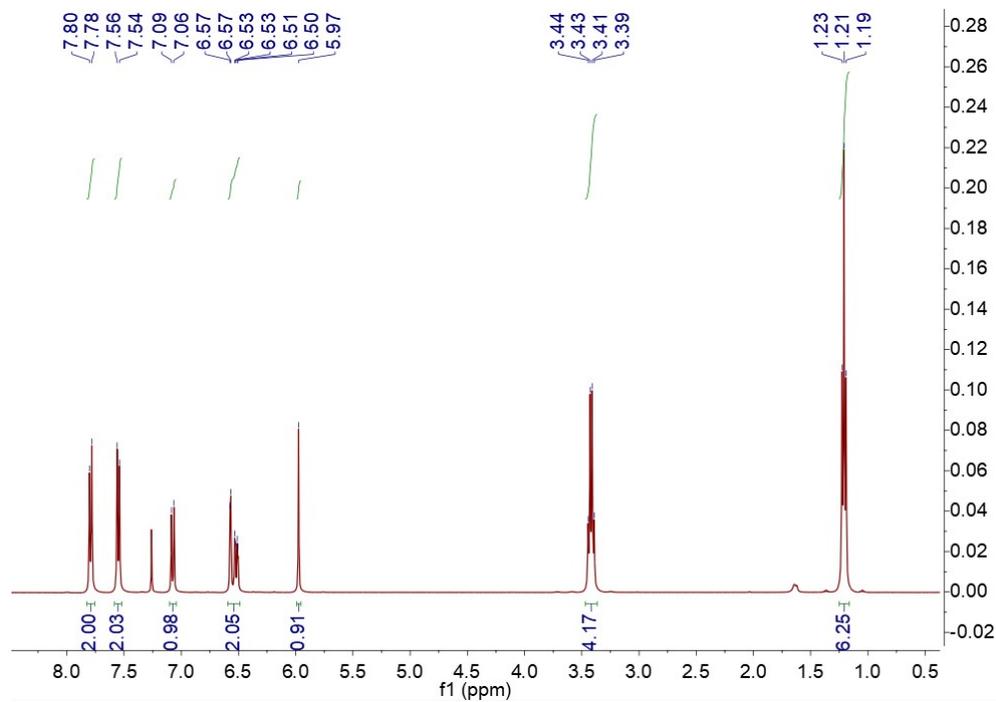


Fig. S8  $^1\text{H}$  NMR spectrum of 4-CPCN.

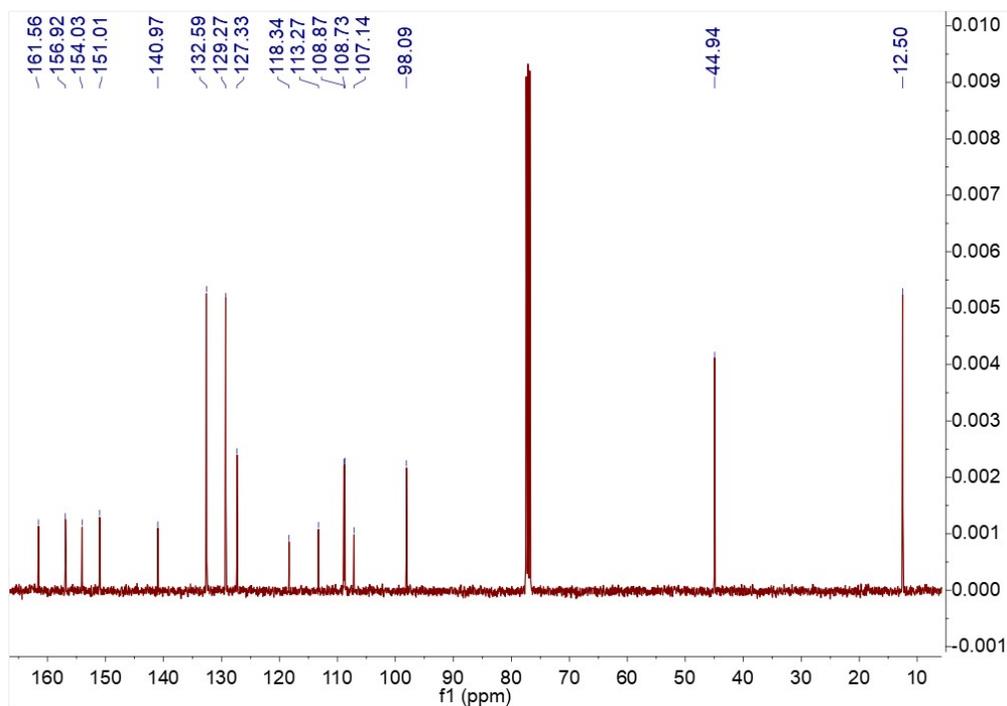


Fig. S9  $^{13}\text{C}$  NMR spectrum of 4-CPCN.

# MS spectra

T: FTMS + c ESI Full ms [100.00-1000.00]

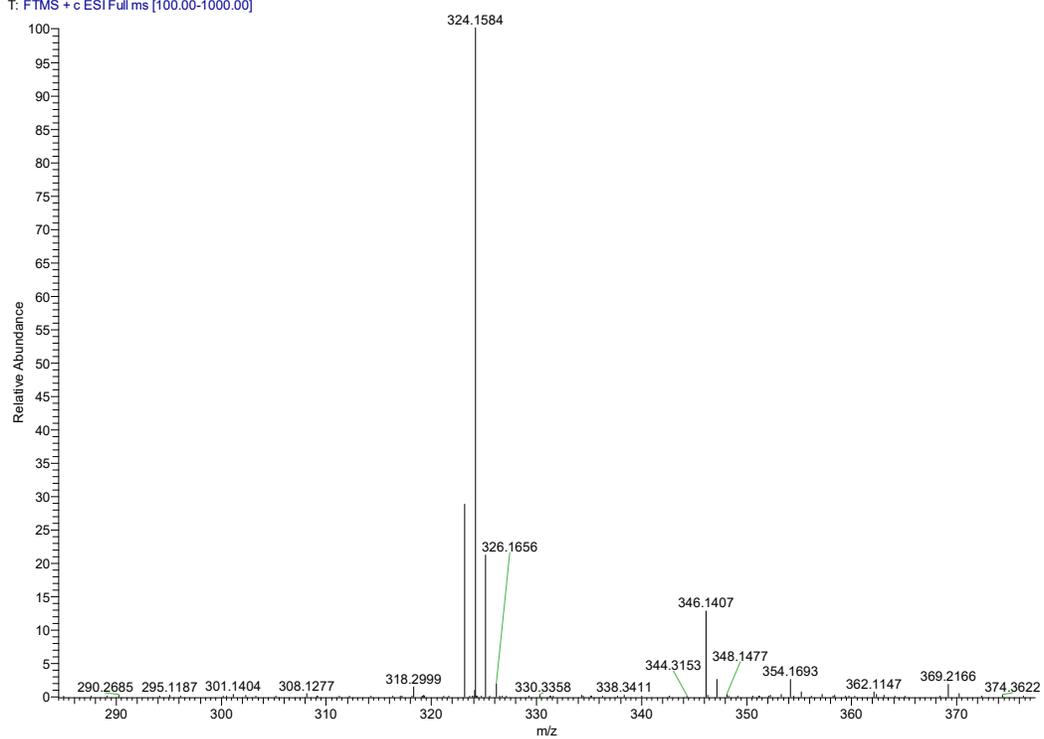


Fig. S10 ESI-MS spectra of 3-CPOMe.

T: FTMS + c ESI Full ms [100.00-1000.00]

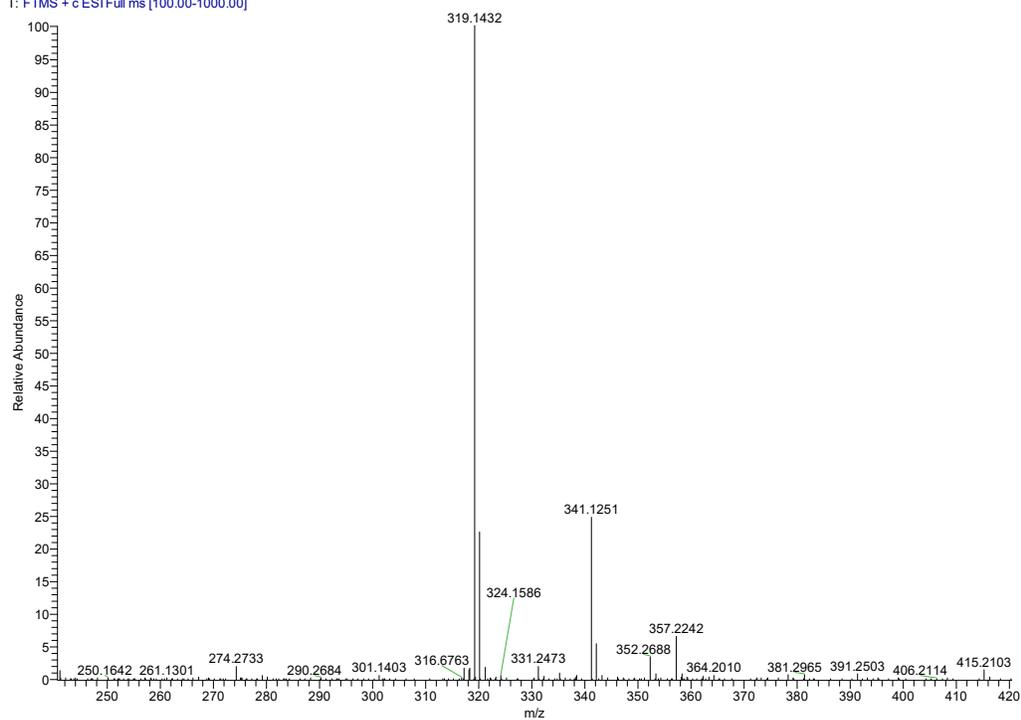


Fig. S11. ESI-MS spectra of 3-CPCN.

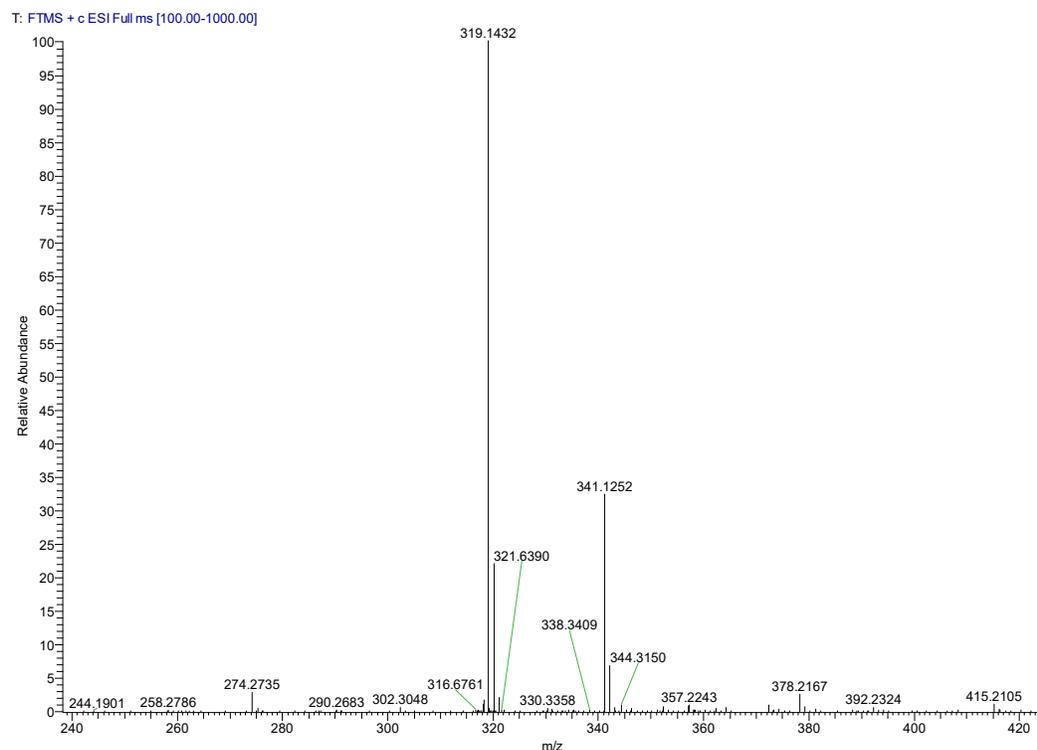


Fig. S12. ESI-MS spectra of **4-CPCN**.

## References

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