Electronic Supplementary Material (ESI) for Analytical Methods.

A novel intramolecular cyclization-induced fluorescent "turn-on" probe for detection of Pd^{2+} based on Tsuji-Trost reaction

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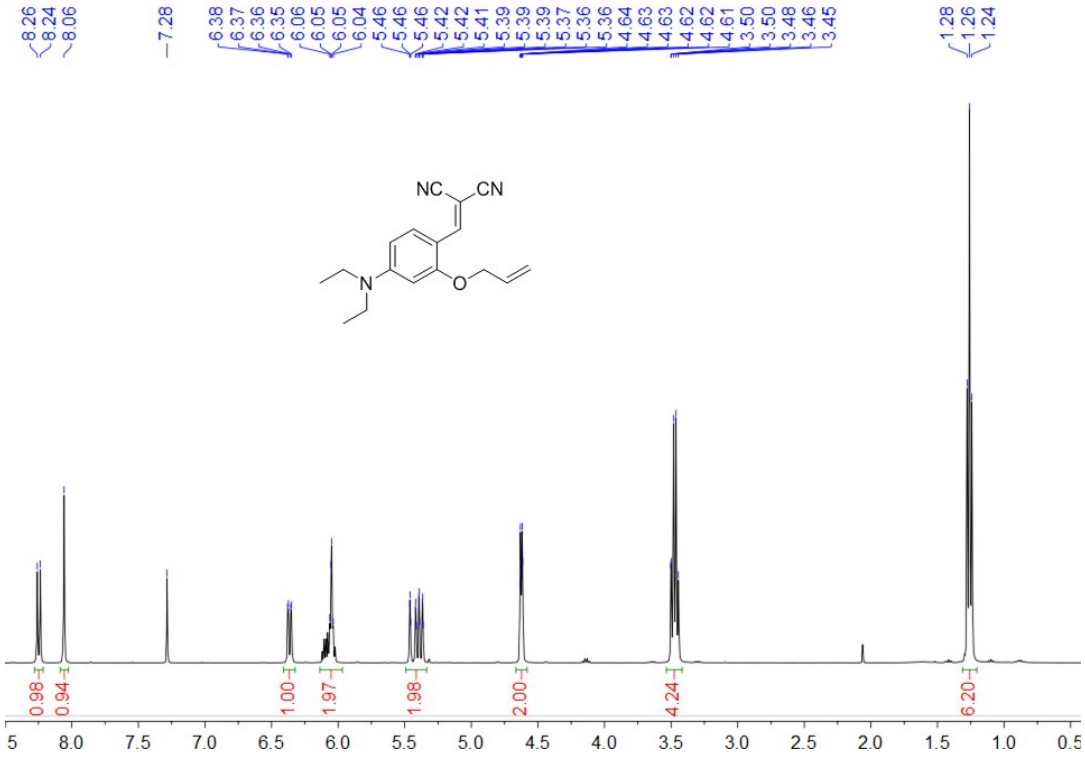

Fig. S1 The [1]H NMR spectrum of **CM480**

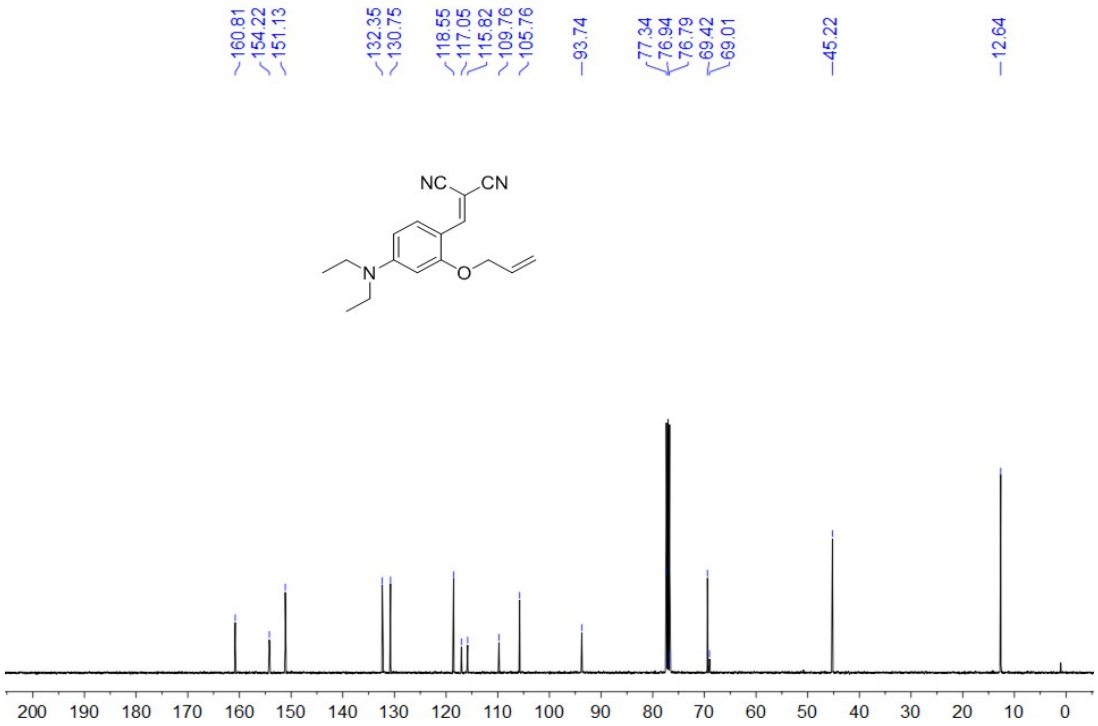

Fig. S2 The [13]C NMR spectrum of **CM480**

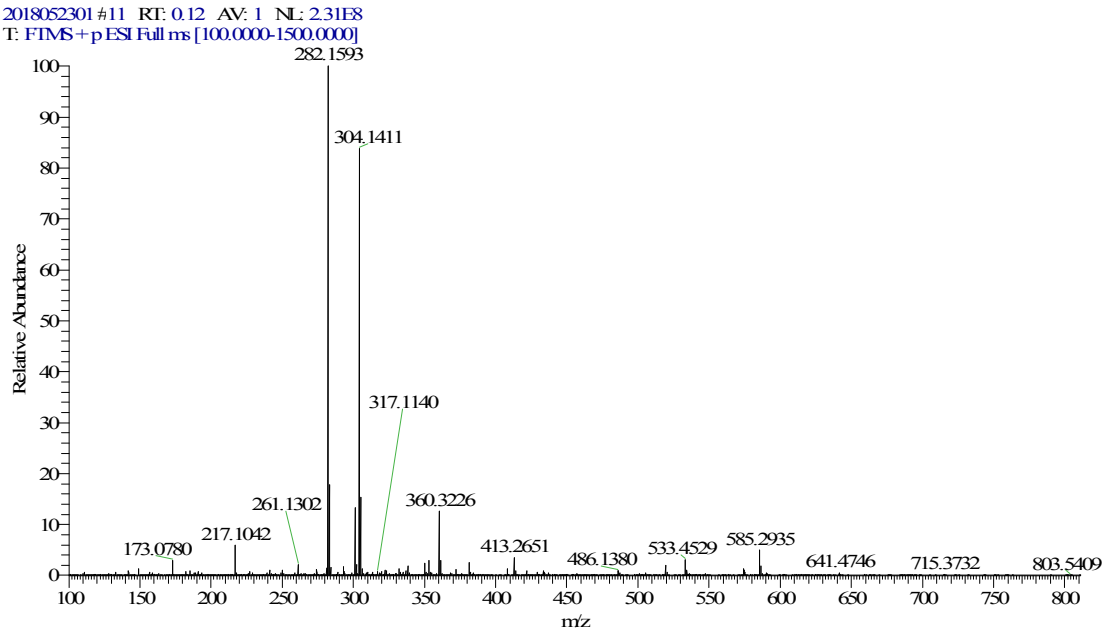

Fig. S3 The mass spectrum of **CM480**

Synthesis of the coumarin derivative

To a solution of 1 (96 mg, 0.5 mmol) and malononitrile (40 mg, 0.6 mmol) in EtOH (8 mL) and water (2 mL) was added Na_2CO_3 (106 mg, 1.0 mmol), the mixture was stirred for 1 h at 25℃. The mixture solution was extracted with DCM, dried over Mg_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by Prep-TLC (EA/DCM=1/1 as eluent) to afford **coumarin derivative** as a yellow solid (84 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.56 (s, 1H), 7.15-7.13 (d, *J*=8.0 Hz, 1H), 6.49-6.47 (m, 1H), 6.32 (s, 1H), 3.46-3.41 (m, 4H), 1.25-1.22 (t, *J*=6.0 Hz, 6H). ESI-HRMS: calcd for $C_{14}H_{15}N_3O$ $[M - H]^-$, 240.2940; found 240.1139.

Determination of quantum yields

The fluorescence quantum yields of **CM480** and **CM480** + Pd^{2+} were determined using the equation [S1] as followed.

$$\frac{\Phi_u}{\Phi_s} = \frac{(FA_u)(A_s)(\lambda_{exs})\eta_u^2}{(FA_s)(A_u)(\lambda_{exu})\eta_s^2}$$

In this equation, Φ is the fluorescence quantum yield; FA is integrated area under the corrected emission spectrum; A is the absorbance at the excitation wavelength; ex is the excitation wavelength; η is the refractive index of the solution; and the subscripts

'u' and 's' refer to the unknown and the standard, respectively. Rhodamine B is chosen as the standard, which has a fluorescence quantum yield of 0.49 in ethanol[S2].

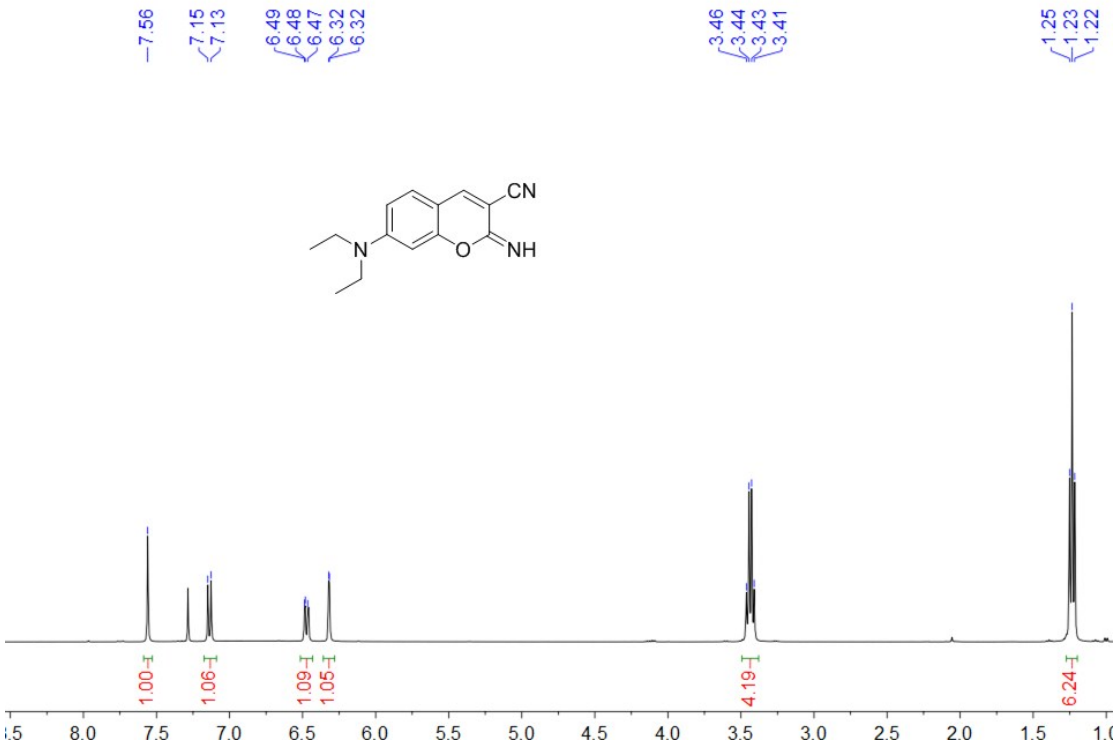

Fig. S4 The ^{1}H NMR spectrum of coumarin derivative

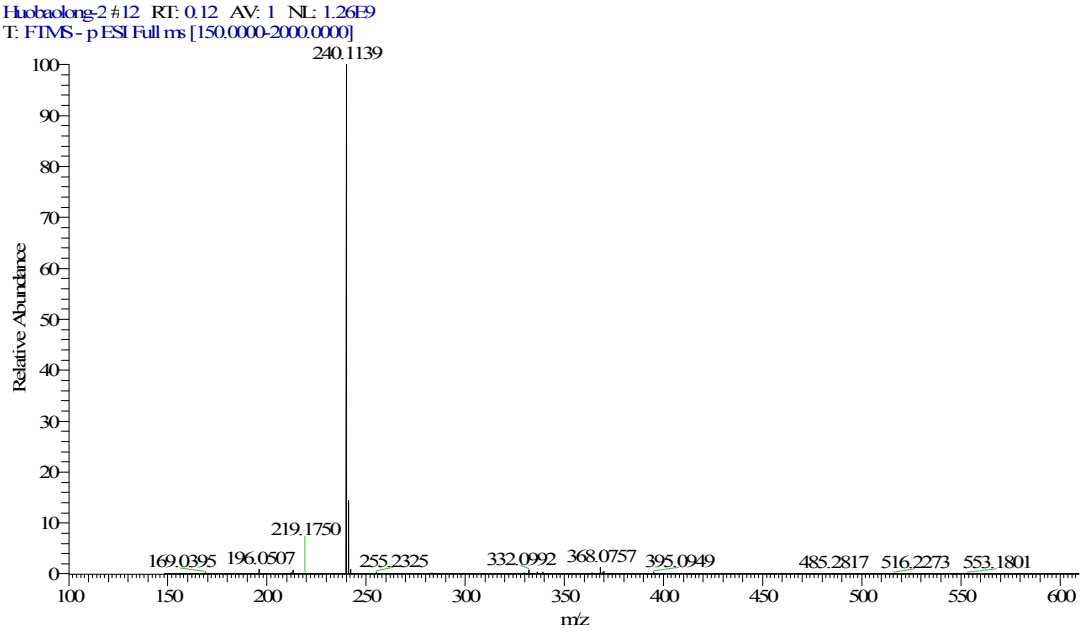

Fig. S5 The mass spectrum of coumarin derivative

Separation of the generated fluorescent substance

To a solution of CM480 (20 mg, 0.07 mmol) and PPh_3 (149 mg, 0.56 mmol) in PBS buffer (pH 7.0, 20% DMSO) (20 mL) was added a solution of $PdCl_2$ (12.5 mg, 0.07 mmol) in DMSO (5 mL) at room temperature. After stirring for 5 minutes, The mixture solution was extracted with DCM, dried over Mg_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by Prep-TLC (EA/DCM=1/1 as eluent) to afford the generated fluorescent substance.

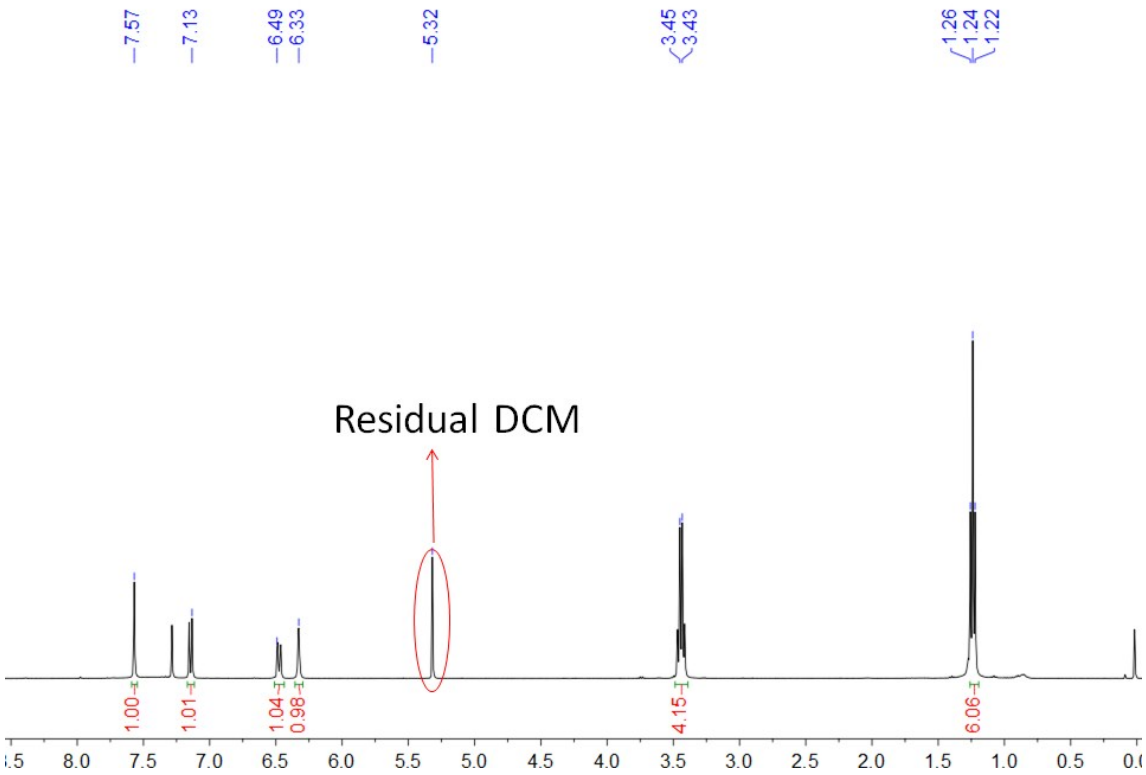

Fig. S6 The ^1H NMR spectrum of the generated fluorescent substance

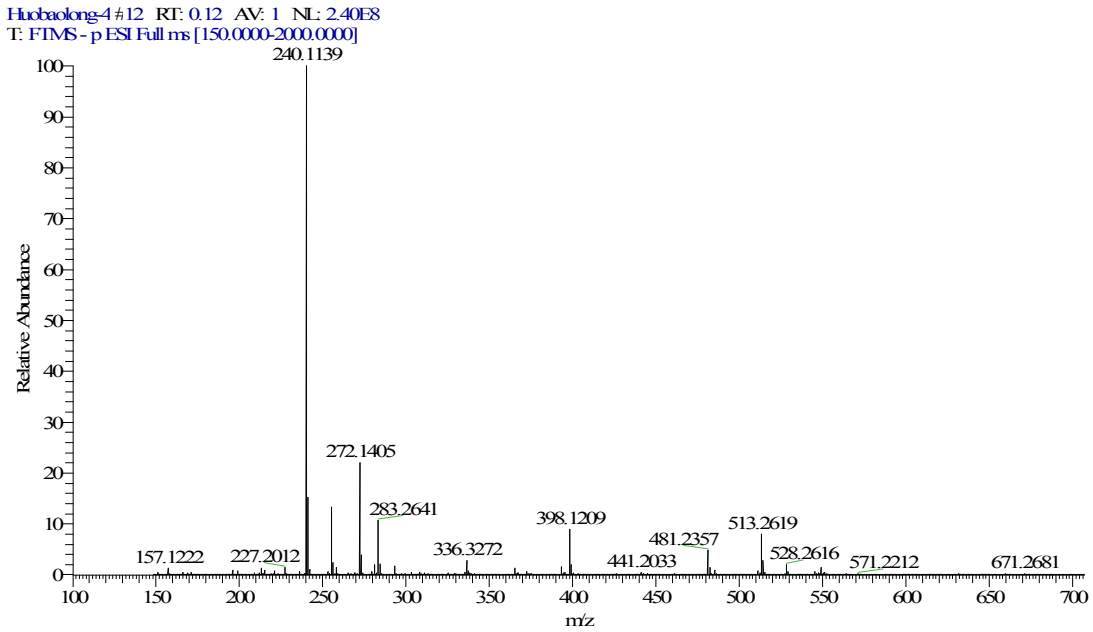

Fig. S7 The mass spectrum of the generated fluorescent substance

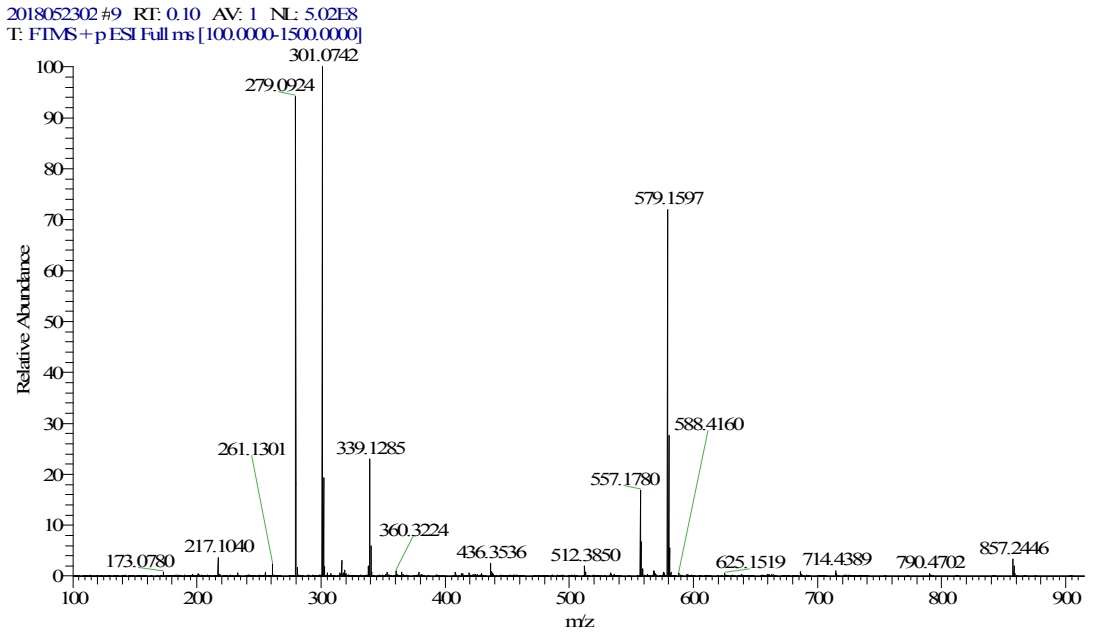

Fig. S8 The mass spectrum of the generated substance between Pd^{2+} and PPh_3

References

[S1] T. Karstens and K. Kobs, *J. Phys. Chem.* 1980, **84**, 1871.

[S2] K. G. Casey and E. L. Quitevis, *J. Phys. Chem.* 1988, **92**, 6590.