Electronic Supplementary Data

A One-Pot Fluorogenic Cascade Cyclization Reaction *via* BF$_3$-Sensing

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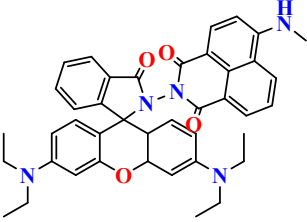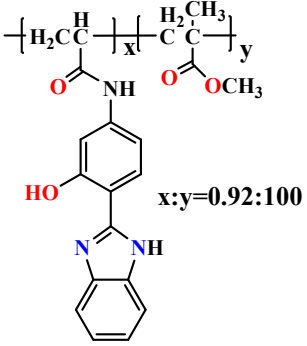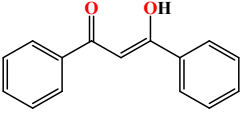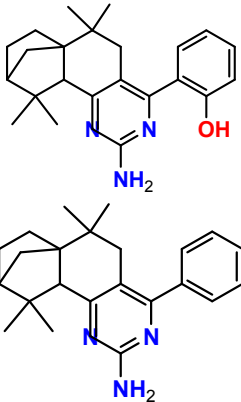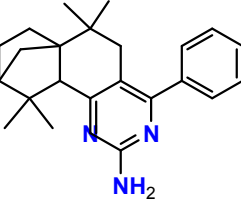
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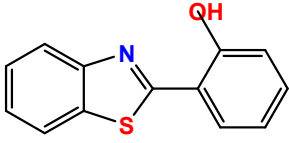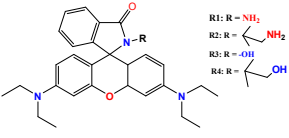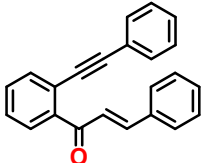*correspondence Address: Email: akmahapatra@chem.iiests.ac.in
                            Email: akar@chem.iiests.ac.in

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1. Table S1. Comparison of the recently reported BF$_3$ sensor with the current work.

Sl. No	Probe structure	Solvent	Mode of sensing	LOD	Application	Reference
1.		Ethanol	FRET	2.7×10^{-5} M	TLC based test strip	Liu et al. *Sens. Actuat. B-Chem*. 243 ,**2017**, 940–945
2.		Acetonitrile	ESIPT	8.7×10^{-8} M	Whatma-n filter paper test strip	Choi et al. *Sensors and Actuators B*. 17, **2017**, 30921-8
3.		-	Thin-films	<1ppm	-	Banet et al. *Sens. Actuat. B-Chem*. 130, **2008**,1–8
4.		Acetonitrile	Turn-On	13.4nM	Logical gate and TLC based test strip	Wang et al. *Sens. Actuat. B-Chem*.: 304, **2020**, 127-083
		Acetonitrile	Ratiometric	68.5nM	Logical gate and TLC based test strip	

5.		Acetonitrile	ESIPT	8.7×10^{-8}M	TLC based test strip	Chang et.al *Sens. Actuat. B-Chem.*: 251, **2017**, 713–719
6.		Acetonitrile	Ring Opening	1.4×10^{-9}M	TLC based test strip	Liu ei. Al *Sens. Actuat. B-Chem.*: 276, **2018**, 166–172
7.		Acetonitrile	Chemod osimeter	6.36×10^{-10} M	TLC based test strip	Our work

2. Experimental Section

2.1. Materials and Instrumentation

All solvents were dried by distillation prior to use whereas commercial reagents (**1**, phenylacetylene, BF$_3$•Et$_2$O) were used without any further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Jeol (500 MHz) spectrometer using a deuterated solvent as the lock and residual protiated solvent as internal reference (CDCl$_3$: δ_H 7.26 ppm, δ_C 77.0 ppm). The following abbreviations were used to define NMR peak patterns: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, ddd = doublet of doublets of doublets, td = triplet of doublets, br = broad, m= multiplet. The coupling constants are given in Hertz (Hz) and, wherever possible, assignment of protons is made. The carbons in the molecular skeletons were not necessarily numbered following the IUPAC nomenclature rules; numeration was exclusively done for assigning NMR signals. All electrospray ionization (ESI-MS) spectra were recorded on a Thermo-Quest LCQ deca and the theoretical isotopic distributions of the mass signals were calculated using IsoPro 3.0 software. Melting points of compounds were measured on a BÜCHI 510 instrument and are not corrected. Infrared spectra were recorded on a Varian 1000 FT-IR instrument. Elemental analysis was performed using the EA-3000 CHNS analyzer. UV-vis spectra were recorded on Cary Win 50 (298 K) spectrometer. Column chromatography was performed either on silica gel (60-400 mesh) or neutral alumina (Fluka, 0.05-0.15 mm,

Brockmann Activity 1). Merck silica gel (60 F254) or neutral alumina (150 F254) sheets were used for thin layer chromatography (TLC). Compounds **2**[1] and **3**[2] were synthesized according to literature known procedures.

## 2.2. General Method of UV-vis and Fluorescence Titrations

For UV-visible and fluorescence titration, a stock solution of the chemosensor **4** (1×10^{-5} M) and the stock solution of the analyte, $BF_3 \cdot OEt_2$ (1×10^{-4} M) were prepared in acetonitrile solution. Same concentration will be pursued for other intrusive ordinary Lewis acids. Titrations were executed by filling 2 ml of the probe solution in a quartz cell having 1 cm optical path length.

3. Synthesis and characterization of Probe
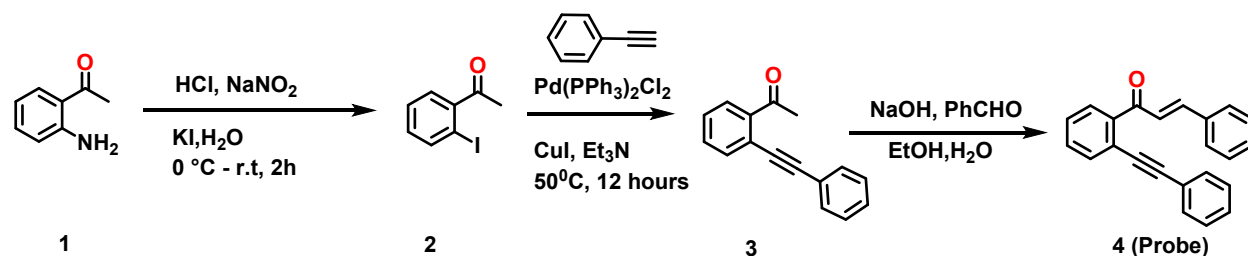
Scheme S1. Synthetic scheme for the preparation of Probe **4**

[(E)-3-phenyl-1-(2-(phenylethynyl) phenyl) prop-2-en-1-one] (4)
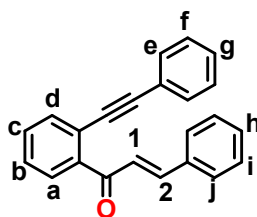

To a solution of compound **3** (220 mg, 1.0 mmol) and Benzaldehyde (106 mg, 1.0 mmol) in Methanol (50 mL) was added 5 mL solution of NaOH (1 M in in H_2O) at 0 °C. After stirring for 1 h at this temperature its was subjected to stir at room temperature for 2 h. After the starting materials had been consumed, the mixture was extracted with ethyl acetate, washed with brine

and dried over anhydrous Na_2SO_4. The solvent was evaporated, and the residue was purified by column chromatography (silica gel, EtOAc/Hexane = 1:7) to afford 210 mg (680 µmol, 68%) of the desired product 4 as yellow oil. **IR (KBr):** $\widetilde{\nu}$ = 755, 811, 852, 915, 963, 997, 1031, 1069, 1096, 1159, 1185, 1278, 1310, 1383, 1442, 1491, 1570, 1599, 1623, 1697, 1954, 2216, 3058, 3200 cm^{-1}. **^{1}H NMR (500 MHz, CDCl$_3$, 298K):** δ = 7.18-7.23 (m, 1H, i-H), 7.26-7.27 (m, 1H, h-H), 7.34-7.39 (m, 4H, f, g-H), 7.44 (ddd, ^3J = 7.8 Hz, ^4J = 1.0 Hz, 1H, c-H), 7.50 (ddd, ^3J = 7.8 Hz, ^3J = 3.2 Hz, ^4J = 1.0 Hz, 1H, b-H), 7.57 (d, ^3J = 15.8 Hz, 1H, 2-H), 7.58-7.62 (m, 2H, e, j-H), 7.65 (ddd, ^3J = 7.8 Hz, ^4J = 1.2 Hz, ^5J = 0.2 Hz, 1H, b-H), 7.69 (ddd, ^3J = 7.8 Hz, ^4J = 1.2 Hz, ^5J = 0.2 Hz, 1H, a-H), 7.70 (d, ^3J = 15.8 Hz, 1H, 1-H) ppm. **^{13}C NMR (125 MHz, CDCl$_3$, 298K):** δ = 87.9, 95.4, 121.6, 122.6, 128.2, 128.3, 128.5, 128.6, 128.7, 128.8, 128.9, 130.5, 130.8, 131.5, 133.1, 134.9, 141.9, 144.4, 193.7 ppm. **ESI-MS: m/z (%)** = 309.4 (100) [4+H]$^+$; **Elemental analysis: Calcd. for** $C_{23}H_{16}O$: C, 89.58; H, 5.23; **Found**: C, 89.39; H, 5.12;

4. Synthesis and characterization of Product
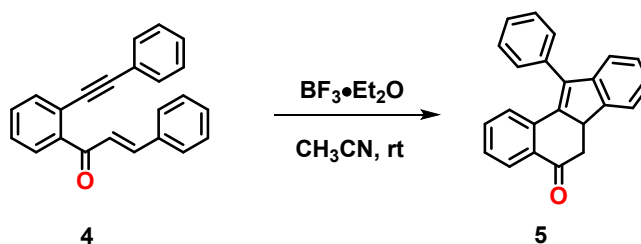
Scheme S2. Synthetic scheme for the preparation of compound 5
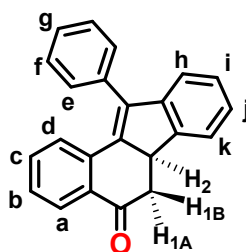
Compound 4 (100 mg, 324 µmol) was loaded into an oven-dried 100 mL round bottom flask and charged with BF$_3$•Et$_2$O (3.95 µL, 3.24 µmol) at room temperature and subjected to stir for 30 min. After completion of reaction (monitored by TLC), the mixture was extracted with ethyl acetate, washed with brine and dried over anhydrous Na_2SO_4. The solvent was evaporated, and the residue was purified by column chromatography (silica gel, EtOAc/Hexane = 1:3) to afford 84 mg (275 µmol, 85%) of the desired product 5 as reddish soid. **IR (KBr)**: $\widetilde{\nu}$ = 662, 678, 737,

790, 852, 881, 980, 1030, 1141, 1167, 1380, 1422, 1440, 1490, 1510, 1535, 1566, 1604, 1789 2161, 2911 cm^{-1}; **^{1}H NMR (500 MHz, CDCl$_3$, 298K):** δ = 2.50 (dd, ^3J = 16 Hz, ^3J = 14 Hz, 1H, 2-H), 3.52 (dd, ^4J = 16.0 Hz, ^3J = 5.5 Hz, 1H, 1$_A$-H), 4.17 (dd, ^4J = 16.0 Hz, ^3J = 5.5 Hz, 1H, 1$_B$-H), 7.16-7.19 (m, 1H, d-H), 7.23-7.26 (m, 1H, c-H), 7.28-7.32 (m, 1H, [e, i, k, b -H), 7.41-7.53 (m, 1H, [f, g, h, i] -H) ppm. **^{13}C NMR (125 MHz, CDCl$_3$, 298K):** δ = 42.9, 48.9, 121.4, 122.8, 126.0, 127.5, 127.7, 127.8, 128.0, 128.9, 129.0, 130.9, 133.3, 134.7, 137.2, 138.0, 139.5, 145.8, 146.4 ppm. **ESI-MS:** *m/z* (%) = 309.1 (100) [**5**+H]$^+$; **Elemental analysis:** Calcd. for C$_{23}$H$_{16}$O: C, 89.58; H, 5.23; Found: C, 89.62; H, 5.20.

5. Solid State BF$_3$ Sensing

A small piece of TLC sticks is supposed to be a solid-state platform for the detection of BF$_3$. The TLC strips were dipped into the probe solution (1 × 10^{-5} M) followed by drying in air. Different concentrations of BF$_3$ solutions (10, 20, 30, 40, 50 and 60 µL) were prepared in acetonitrile solution in a glass screw top container. The probe coated TLC strips were exposed in various concentrations of BF$_3$ solution for 5 minutes. After 5 minutes. photographs will be taken to scrutinize the sensing performance.

6. Computational Method

For the determination of the electronic behavior of the product, we as well executed quantum chemical DFT calculation by using the Gaussian 09 program with the assist of the Gauss View visualization program. The probe and the product were optimized by using the B3LYP/6-311G+(d, p) basis set.

Table S2: The vertical main orbital transition of product calculated by TDDFT method

Energy (eV)	Wave length (nm)	Osc.strength (f)	Transition
3.3875	366.01	0.1867	HOMO→LUMO

3.5128	352.95	0.0622	HOMO-1→LUMO
4.0365	307.16	0.1706	HOMO→LUMO+1

Table S3: The vertical main orbital transition of probe calculated by TDDFT method

Energy (eV)	Wave length (nm	Osc.strength (f)	Transition
3.1385	395.04	0.0005	HOMO-2 →LUMO
3.2178	385.31	0.0800	HOMO→LUMO
3.7849	327.57	0.1861	HOMO-1 →LUMO

7. Calculation of Limit of Detection (LOD)

The detection limit is obtained from a plot of fluorescence intensity at 449 nm vs function of BF_3 concentration. The S/N ration is determined by the 10 times measurable emission intensity of the probe without the addition of BF_3. Afterward the standard deviation of blank measurements is calculated. The LOD value of probe for BF_3 was determined by the following equation:

$$LOD = K \times \delta / m \tag{1}$$

Where K= 2 or 3

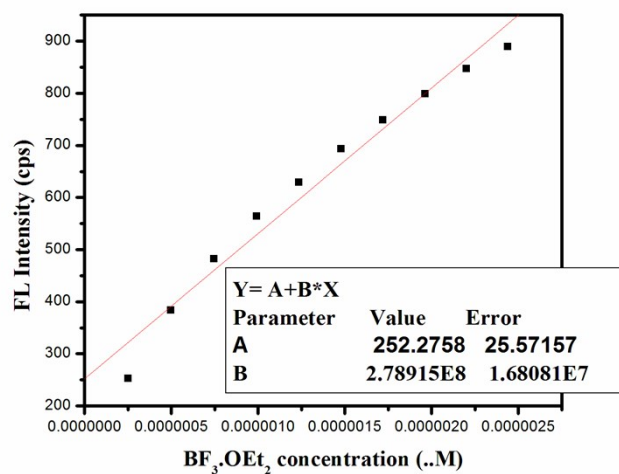(δ is the standard deviation of the blank solution and m is the slope the calibration curve.

Figure S1. Calibration curve of the probe at 449 nm depending on BF_3 concentration

$$So, \ LOD = 6.36 \times 10^{-10} \ (M) \ (R^2 = 0.98578).$$

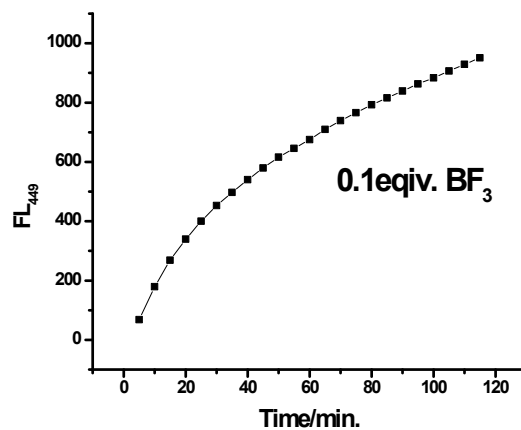## 8. Determination of the response time of probe towards the product

Figure S2. Time periods (0–130 mins) of fluorescence enhancement of probe (1×10^{-5} M) in acetonitrile solution upon addition of 0.1 equivalent of BF_3 (λ_{ex} = 370 nm; λ_{em} = 449 nm).

9. Calculation of first order rate constant (k')

First order rate constant was calculated by the following equation:

$$\ln[(F_{max} - F_t)/ \ F_{max}] = - \ k't \tag{2}$$

Where, F_t and F_{max} symbolize the fluorescence intensities at 449 nm at time t and maximum value acquired upon the completion of the reaction and k' is the monitored first order rate constant.
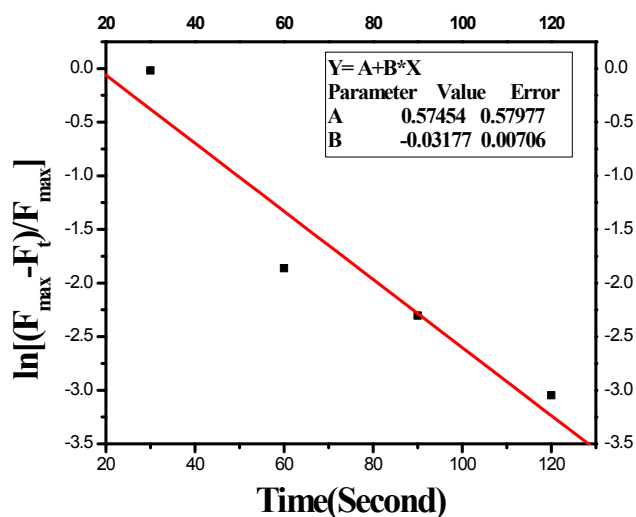

Figure S3. First order kinetic plot of probe (1×10^{-5} M) in the presence of 5 equivalent of 1×10^{-4} (M) BF$_3$ solution (λ_{ex}= 370 nm, λ_{em} = 449 nm).

First order rate constant $k' = 0.031$ s^{-1}.

10. Determination of fluorescence quantum yield of 5.

The fluorescence quantum yield is calculated by the following equation:

$$\varphi_S = \varphi_A \times F_A/F_S \times A_A/A_S \times \eta_A^2/\eta_S^2 \qquad (3)$$

Where F_A and F_S are the integrated fluorescence intensity of **5** and Anthracene (reference) respectively.

A_A and A_S are the absorbance of the **5** and Anthracene (reference) respectively at same excitation wavelength.

η_A and η_S are the refractive indices of respective solvents employed as Acetonitrile and Ethanol.

So, quantum yeild = 0.27 (27%)
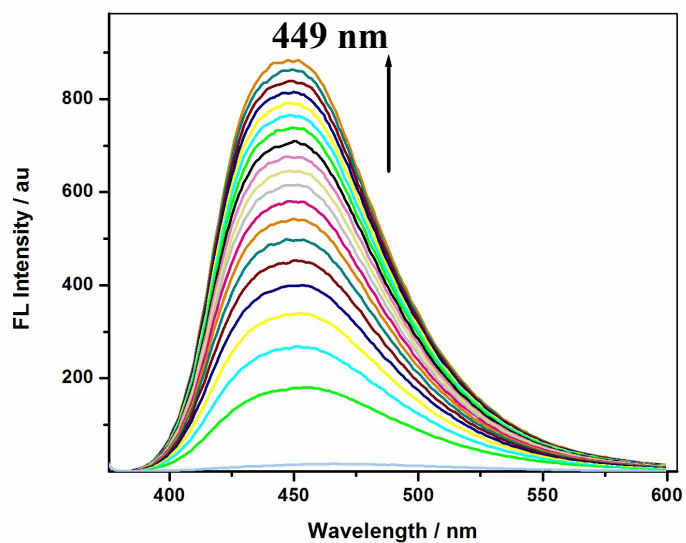
11. Emission spectra of probe

Figure S4: Emission spectra of probe (1×10^{-5} M) upon steady addition of $BF_3 \cdot OEt_2$(0 to 50 μM): (λ_{ex}= 326 nm, λ_{em} = 449 nm).

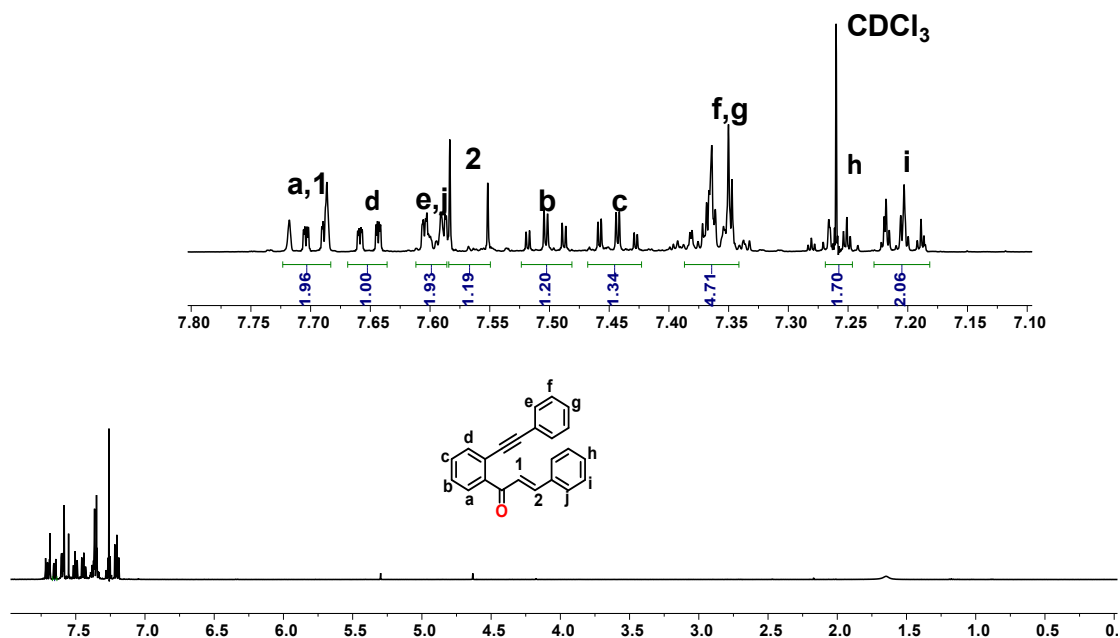## 12. NMR spectra: ^{1}H NMR, ^{1}H-^{1}H COSY, ^{13}C NMR,

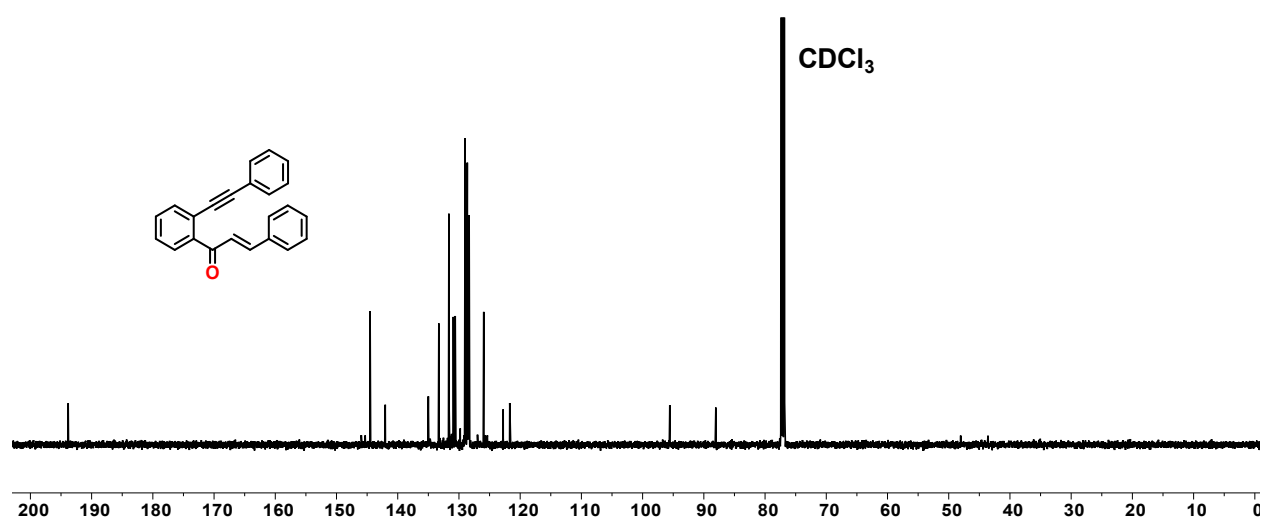**Figure S5.** ^{1}H NMR spectrum of **4** in CDCl$_3$ (500 MHz, 298 K).

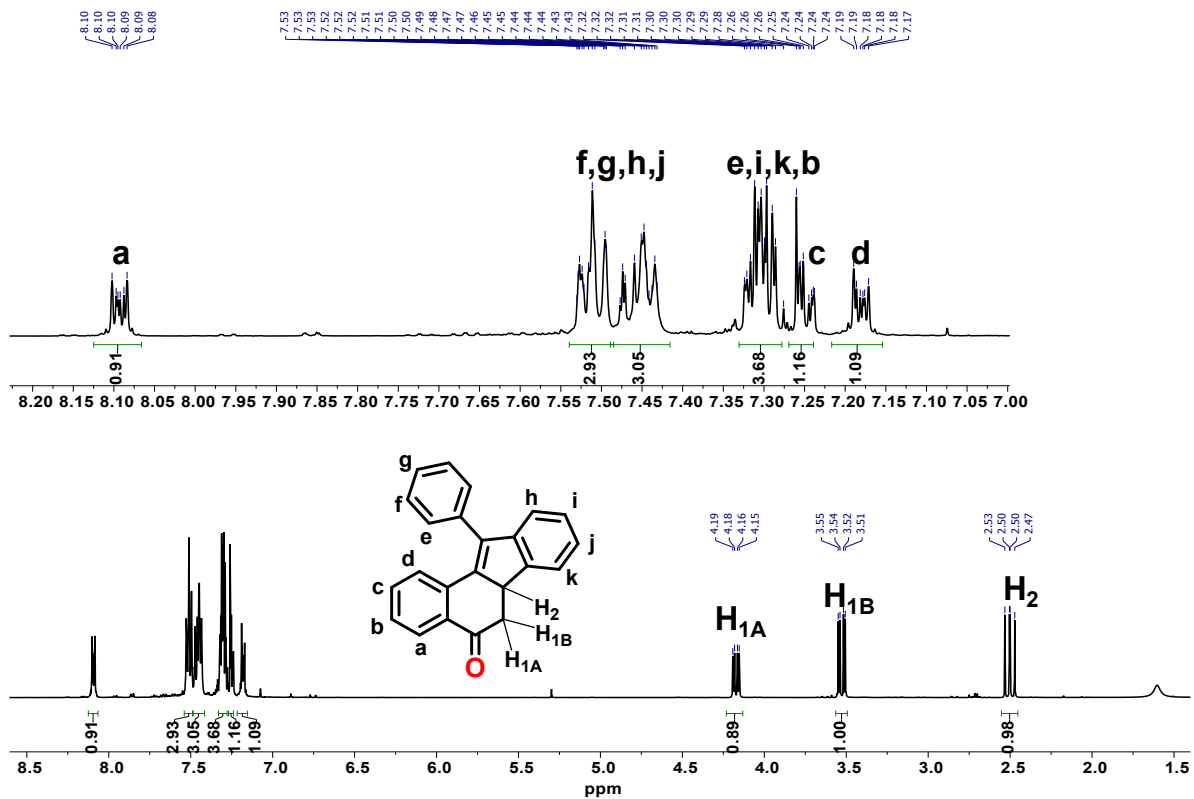**Figure S6**. ^{13}C NMR spectrum of **4** in CDCl$_3$ (500 MHz, 298 K).

Figure S7. ^{1}H NMR spectrum of **5** in CDCl$_3$ (500 MHz, 298 K).
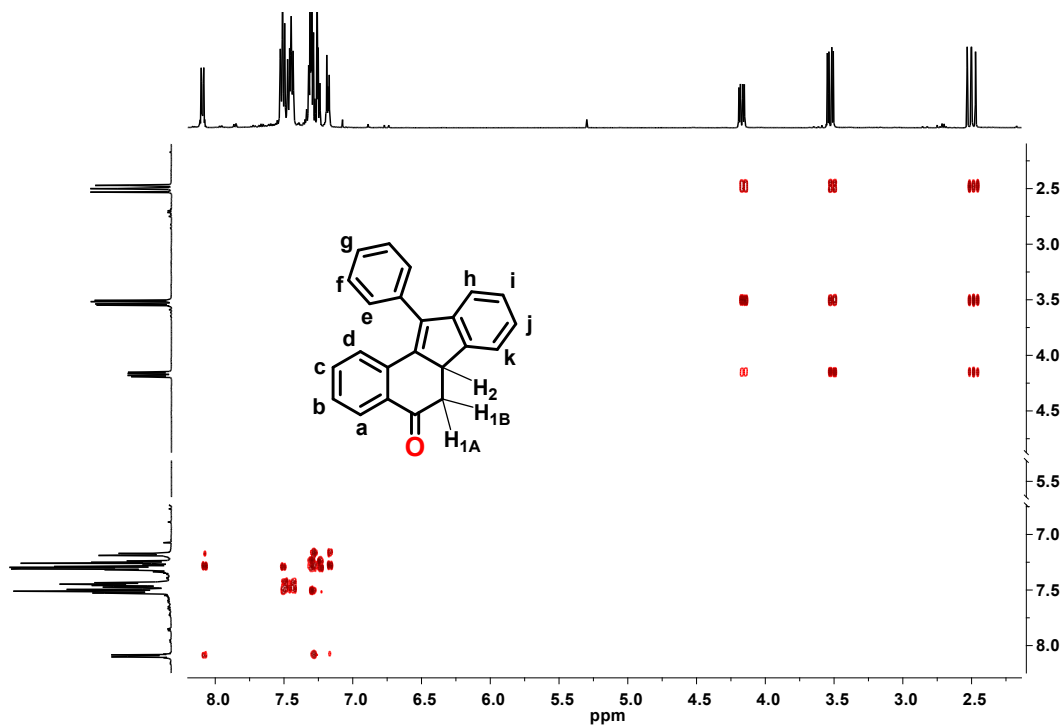

Figure S8. ^{1}H-^{1}H COSY NMR spectrum of **5** in CDCl$_3$ (500 MHz, 298 K).
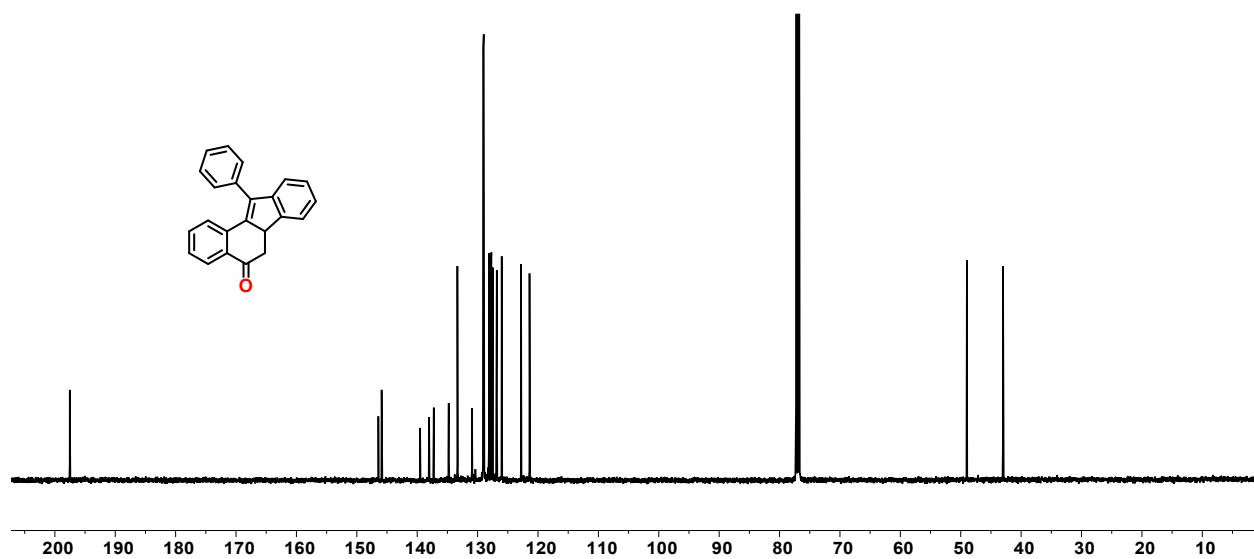
Figure S9. ^{13}C COSY NMR spectrum of **5** in CDCl$_3$ (500 MHz, 298 K).
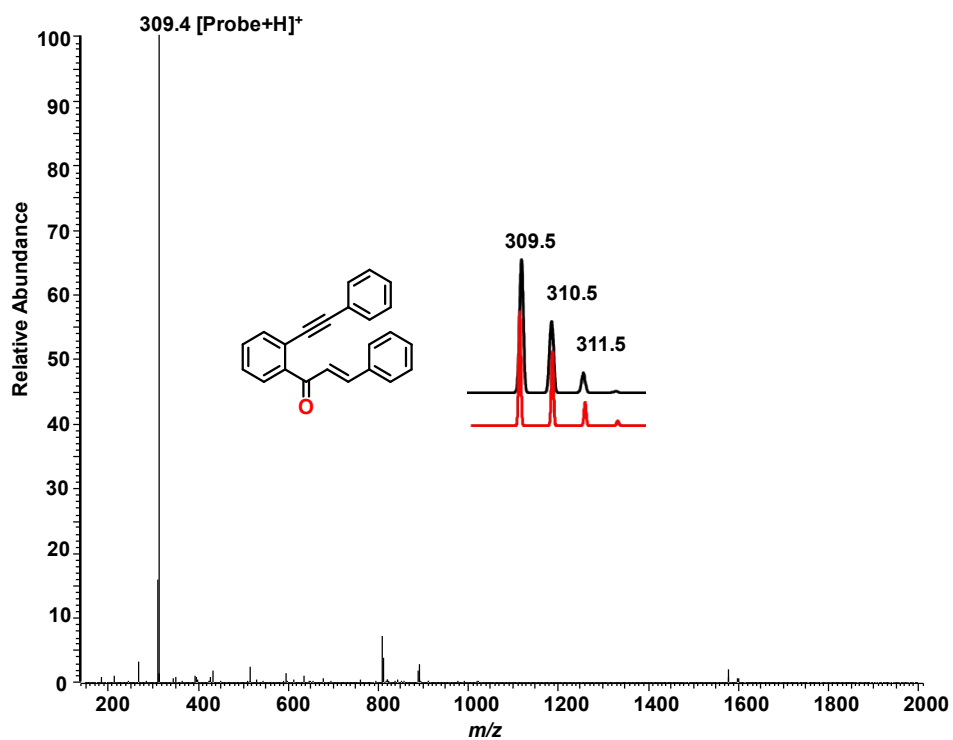
13. ESI-MS Spectra

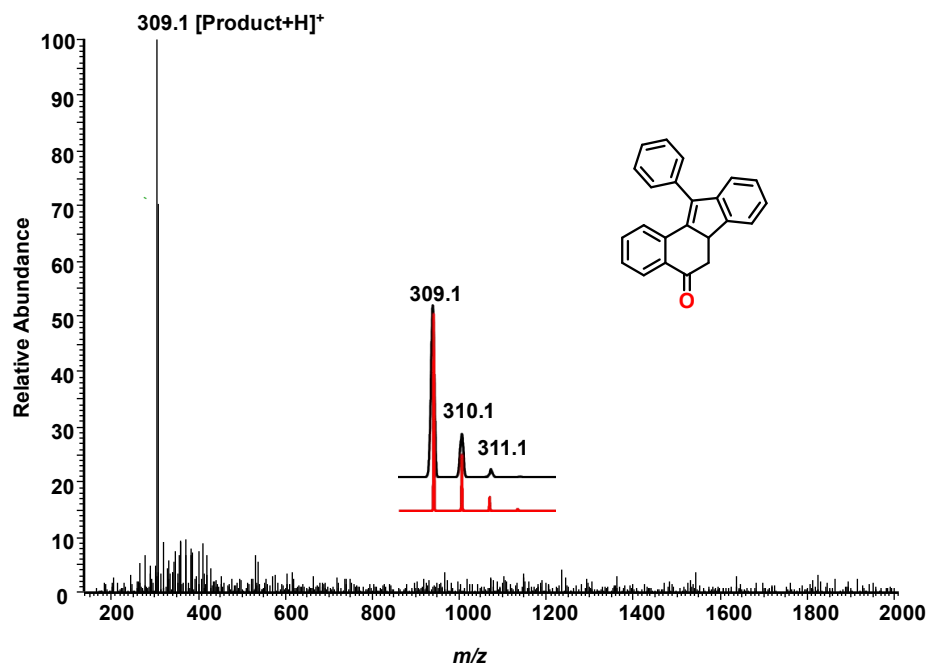**Figure S10.** ESI-MS of **4** after protonation.

Figure S11. ESI-MS of **5** after protonation.

References:

1. Q. Li, J. Liu, Y. Wei, and M. Shi, *J. Org. Chem.,* 2020, **85**, 2438-2455
2. L. Zheng, B. Zhou, Hongwei Jin, T. Li, and Y. Liu, *Org. Lett*., 2018, **20**, 7053-7056