Supporting information

A spirooxazine derivative as a highly sensitive cyanide sensor by means of UV-visible difference spectrum

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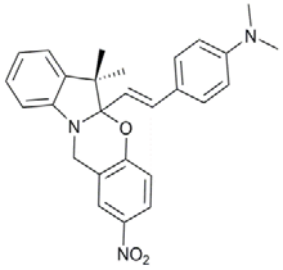
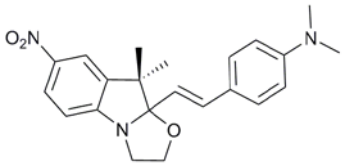
1. Synthesis and characterization of P1, P2 and P3

1-1 Synthesis of 2-nitro-5a-(2-(4-dimethylaminophenyl)-ethylene)-6,6-dimethyl -5a,6-dihydro-12H-indolo[2,1-b] [1,3]benzooxazine (**P1**)



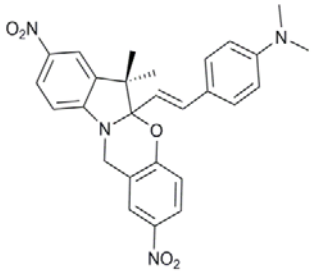
P1 were synthesized according to literature[S1] with improved procedures and higher yield. Detailed procedures were as follows:
1-(2-hydroxy-5-nitrobenzyl)-2,3,3-trimethylindoleninium chloride (0.51 mmol, 176.9 mg) and 4-dimethylaminobenzaldehyde (0.5 mmol, 74.5 mg) were refluxed in 10 ml ethanol solution for 3.5 h. Then the solvent was removed with rotary vacuum evaporator and treated with $NaHCO_3$ aqueous solution. Acetic ether was added to extract the product. Then the organic phase was separated and the solvent was distilled off under reduced pressure. The residue was recrystallized by acetic ether/hexane to get the product, orange solid (196 mg, 89%). ^{1}H NMR (300 MHz, DMSO-d_6): δ=1.35 (6H, s), 2.92 (6H, s), 4.8 (2H, s), 6.39 (1H, d, *J*=18 Hz), 6.67 (2H, d, *J*=9 Hz), 6.84 (1H, m), 6.86 (1H, d, *J*=18 Hz), 6.87 (1H, d, *J*=9 Hz), 6.94 (1H, d, *J*=6 Hz), 7.11 (1H, m), 7.24 (1H, d, *J*=9 Hz), 7.42 (2H, d, *J*=9 Hz), 7.93 (1H, dd, *J*=6 Hz), 8.09 (1H, d, *J*=3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ=40.3,40.6, 49.9, 108.7, 112.1, 117.6, 118.4, 120.1, 120.6, 122.3, 123.2, 123.7, 123.9, 127.5, 127.9, 136.2, 138.4, 140.2, 146.5, 150.7, 159.7. LC-HRMS: *m/z* 442.2121 $[M+H]^+$, calculated 442.2125.

1-2 Synthesis of 10-[2-(4-dimethylaminophenyl)ethylene]-9,9-trimethyl-7-nitro indolino[2,1-b] oxazolidine (**P2**)



P2 was synthesized and purified as described in reference [S2]. Pale yellow solid was gained. ^{1}H NMR (300 MHz, $CDCl_3$) : δ= 1.19 (s, 3H), 1.47 (s, 3H), 2.98 (s, 6H), 3.67 (m, 4H), 5.98 (1H , d, *J* = 16.2 Hz), 6.75 – 6.65 (m, 4H), 7.35 (2H, d, *J* = 8.1 Hz), 7.96 (s, 1H), 8.13 (1H, d, *J* = 7.5 Hz); LC-HRMS: *m/z* 380.1971 $[M+H]^+$, calculated 380.1974. Melting point: 193.3-195.2 ^{o}C.

1-3 Synthesis of 2,8-Nitro-5a-(2-(4-dimethylaminophenyl)-ethylene)-6,6-dimethyl -5a,6-dihydro-12H-indolo[2,1-b] [1,3]benzooxazine (**P3**)



2,8-dinitro-5a,6,6-trimethyl-5a,6-dihydro-12H-indolo-[2,1-b][1,3]benzooxazine (0.7 mmol, 247.8 mg) and 4-(N,N-dimethyl)benzaldehyde (1.4 mmol, 208.6 mg) were refluxed in 10 ml ethanol solution with CH_3SO_3H as catalyst (200 mg) for 12 h under N_2 atmosphere. The solvent was distilled off under reduced pressure. The residue was washed with saturated aqueous Na_2CO_3 solution until the pH of the aqueous solution was neutral, treated with aqueous KOH solution and extracted by ethyl acetate. Then, the organic phase was separated and dried by anhydrous Na_2SO_4. Ethyl acetate was evaporated to get the crude product. The crude product was purified by column chromatography to give **P3** (190 mg, 56%) as a yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ= 1.58 (6H, s), 3.25 (6H, s), 5.76 (2H, s), 6.95 (2H, d, *J*=8 Hz), 7.04 (1H, d, *J*=8 Hz), 7.37 (1H, d, *J*=16 Hz), 7.72 (1H, d, *J*=8 Hz), 8.11 (3H, d, *J*=8 Hz), 8.24 (1H, s), 8.36 (1H, d, *J*=8 Hz), 8.49 (1H, d, *J*=16 Hz), 8.72 (1H, s); ^{13}C NMR (75 MHz, D_6MSO): δ=27.8, 43.9, 54.3, 95.1, 108.8, 113.6, 117.1, 122.1, 123.1, 123.7, 125.7, 128.1, 128.7, 129.1, 130.8, 133.3, 141.2, 144.1, 145.6, 145.9, 155.8, 158.0, 163.5; LC-HRMS: *m/z* 487.1962 $[M+H]^+$, calculated 487.1976. Melt point:128-131^{o}C.

2. Characterization and Solution preparation details

2-1 Characterizations:

NMR spectra (^{1}H and ^{13}C) were obtained using Varian 300M and Varian INOVA 400M spectrometer. Spectra were referenced to the residual proton solvent peaks using shifts reported by Gregory R. Fulmer et al [S3]. LC-HRMS was obtained by Agilent 1290-microTOF Q II. Melting point was determined using a SGW X-4B microscopy melting point apparatus (Shanghai). UV-visible absorption spectra were recorded with a Shimadzu UV-2550 PC double-beam spectrophotometer, path length was 1 cm. pH values were measured with Sartorius PB-21.

2-2 Preparation of NaH_2PO_4/Na_3PO_4 buffer solution

0.2 M aqueous solution of NaH_2PO_4 and Na_3PO_4 were prepared separately. And the two solutions were diluted to 0.02 M with water. The two diluted solutions were mixed and monitored with pH-meter until the pH value got 9.4.

2-3 Preparation of **P1** in buffered CH_3CH_2OH/H_2O (v/v, 2/8) solution

200 μl ethanol solution of **P1** was added into a flask and then 3.8 ml ethanol and 6 ml buffer solution (NaH_2PO_4/Na_3PO_4, pH 9.4) were added into another flask. The two samples were kept at 25 ^{o}C in water bath. After temperature of the samples was stabilized at 25 ^{o}C, they were mixed and shaken to get NaH_2PO_4/Na_3PO_4 buffered CH_3CH_2OH/H_2O (v/v, 2/8).

2-4 Difference UV-Vis absorption spectra measurements:

3 ml above **P1** solution was added to the reference cell and sample cell respectively. UV-visible absorption was measured subsequently to check the base line. Then 15μl or 30 μl tetrabutylammonium cyanide with different concentration in NaH_2PO_4/Na_3PO_4 buffer solution was added to the sample cell and shaken to mix them well. Then UV-Vis absorption spectra were recorded with time until the absorption stabilized. Other measurements with the interference anions were done in the same way.

3. UV-vis absorption spectra of P2 in CH_3CH_2OH/H_2O and in NaH_2PO_4/Na_3PO_4 buffered CH_3CH_2OH/H_2O solution

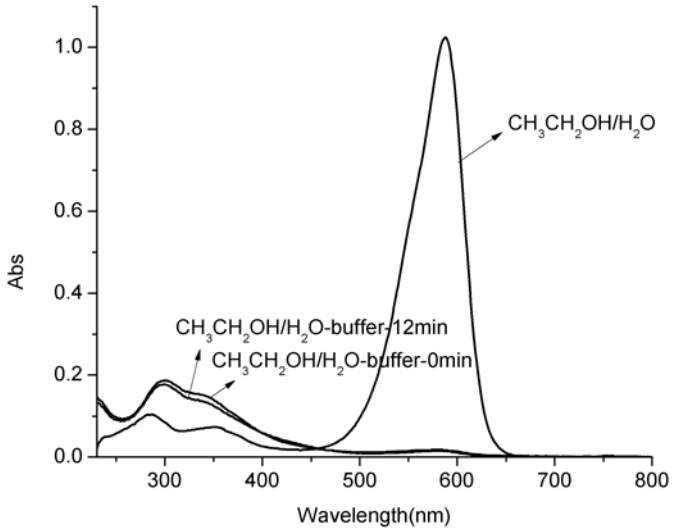


Fig. S1 UV-vis absorption spectra of molecule **P2** (10 μM) in CH_3CH_2OH/H_2O (v/v, 2/8) and buffered CH_3CH_2OH/H_2O mixture (v/v, 2/8; NaH_2PO_4/Na_3PO_4 buffer, pH 9.4). Note: spectra of **P2** in buffered solution were measured soon after it was prepared and we defined the first measurement in buffered CH_3CH_2OH/H_2O as 0 min, and 12 min were relative to this time.

4. UV-vis absorption spectra of P3 in CH_3CH_2OH/H_2O and in NaH_2PO_4/Na_3PO_4 buffered CH_3CH_2OH/H_2O solution

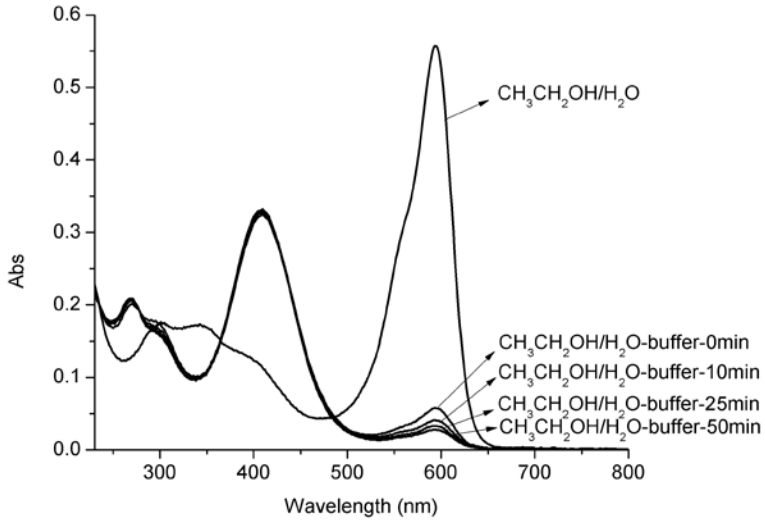


Fig. S2 UV-vis absorption spectra of molecule **P3** (10 μM) in CH_3CH_2OH/H_2O (v/v, 4/6) and buffered CH_3CH_2OH/H_2O mixture (v/v, 2/8; NaH_2PO_4/Na_3PO_4 buffer, pH 9.4). Note: spectra of **P3** in buffered solution were measured soon after it was prepared and we defined the first measurement in buffered CH_3CH_2OH/H_2O as 0 min, and other times were relative to this time.

5. UV-vis difference absorption spectra of P3 in CH_3CH_2OH/H_2O and in NaH_2PO_4/Na_3PO_4 buffered CH_3CH_2OH/H_2O solution for the selectivity to cyanide

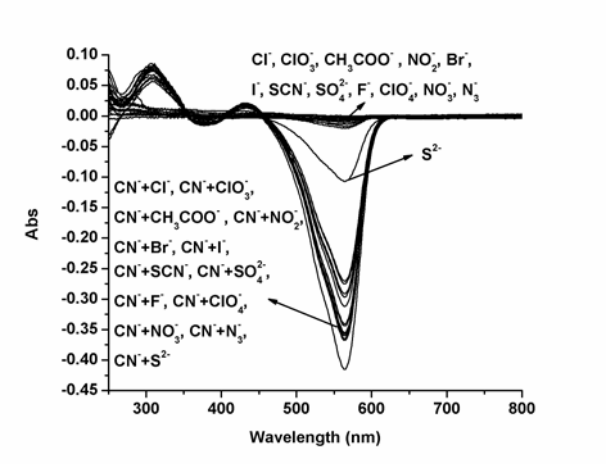
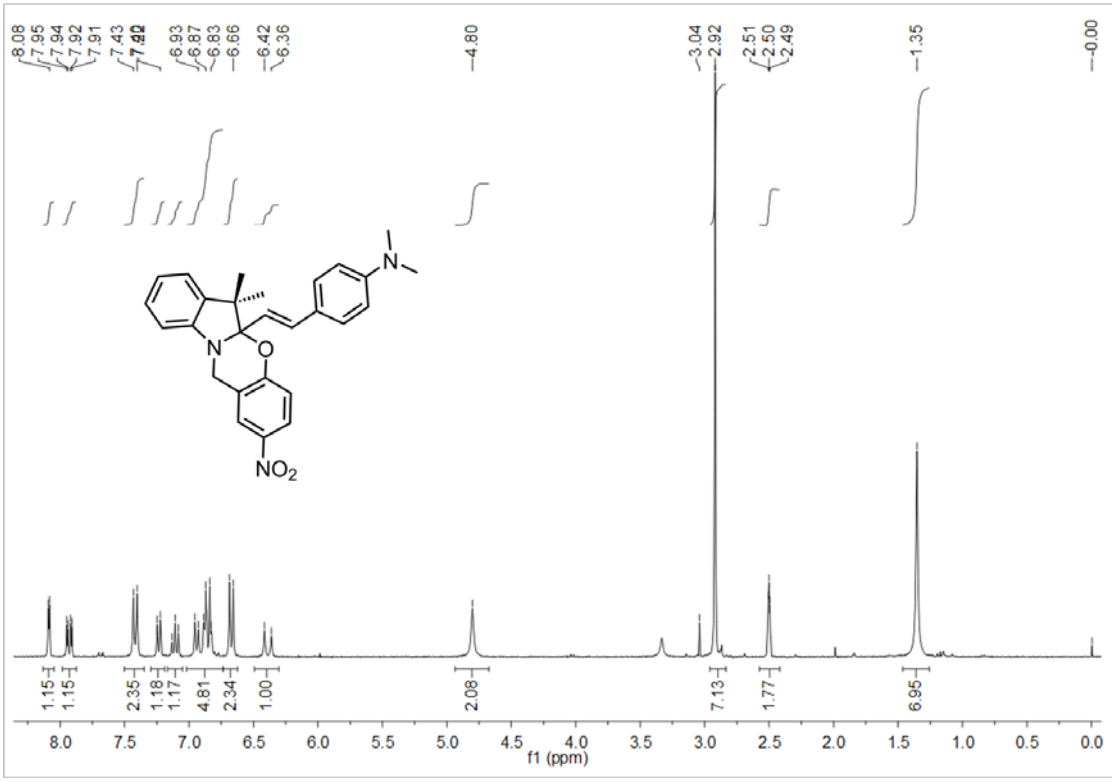


Fig. S3 Absorption spectra of **P1** (10 μM) measured with only interference anions, such as NO_2^-, Cl^-, CH_3COO^-, F^-, NO_3^-, N_3^-, SO_4^{2-}, SCN^-, Br^-, I^-, ClO_4^-, ClO_3^-) (30 equiv) and S^{2-} (3equiv), and CN^- (3 equiv) together with other interference anions (30 equiv or 3equiv). The spectra were obtained after the absorption reached stable state.

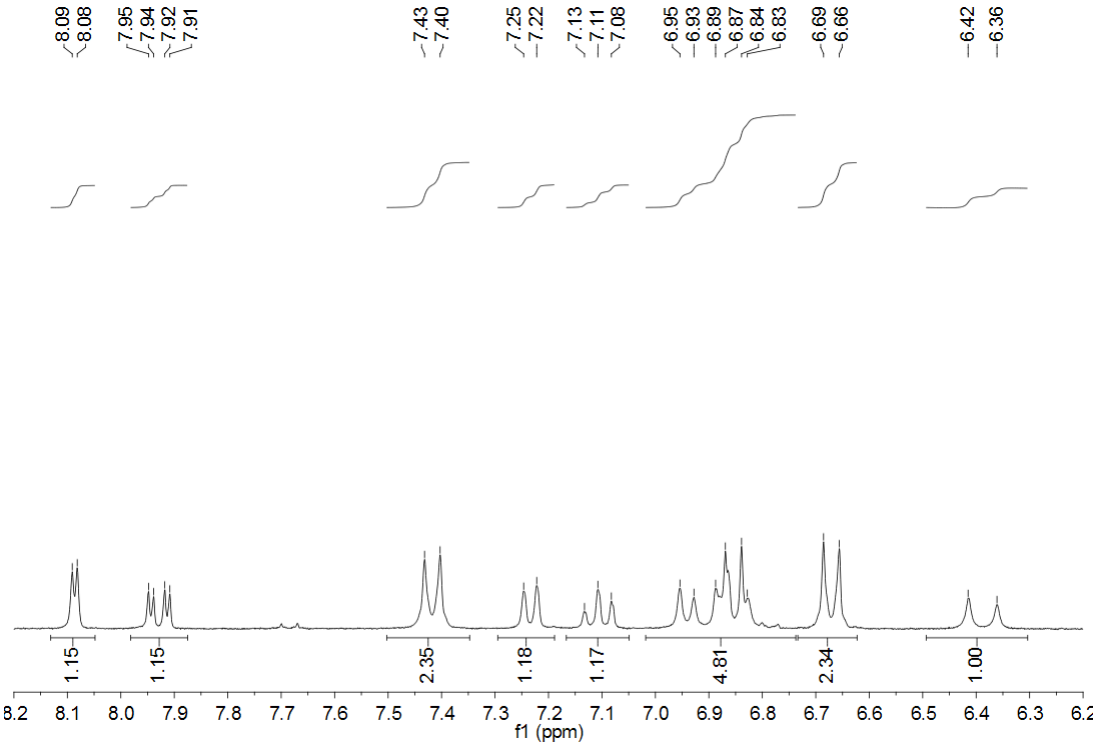
6. ^{1}H NMR spectra and ^{13}C NMR spectra

5-1 ^{1}H NMR spectrum of **P1** (DMSO-d_6)

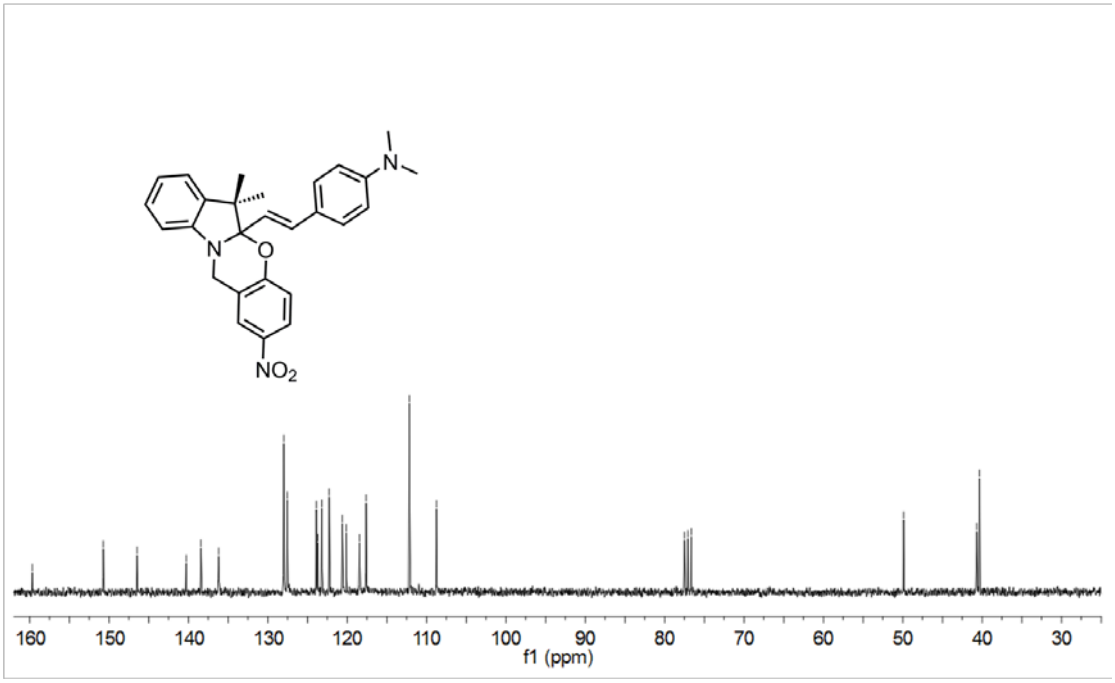
Full spectra



Enlarged view

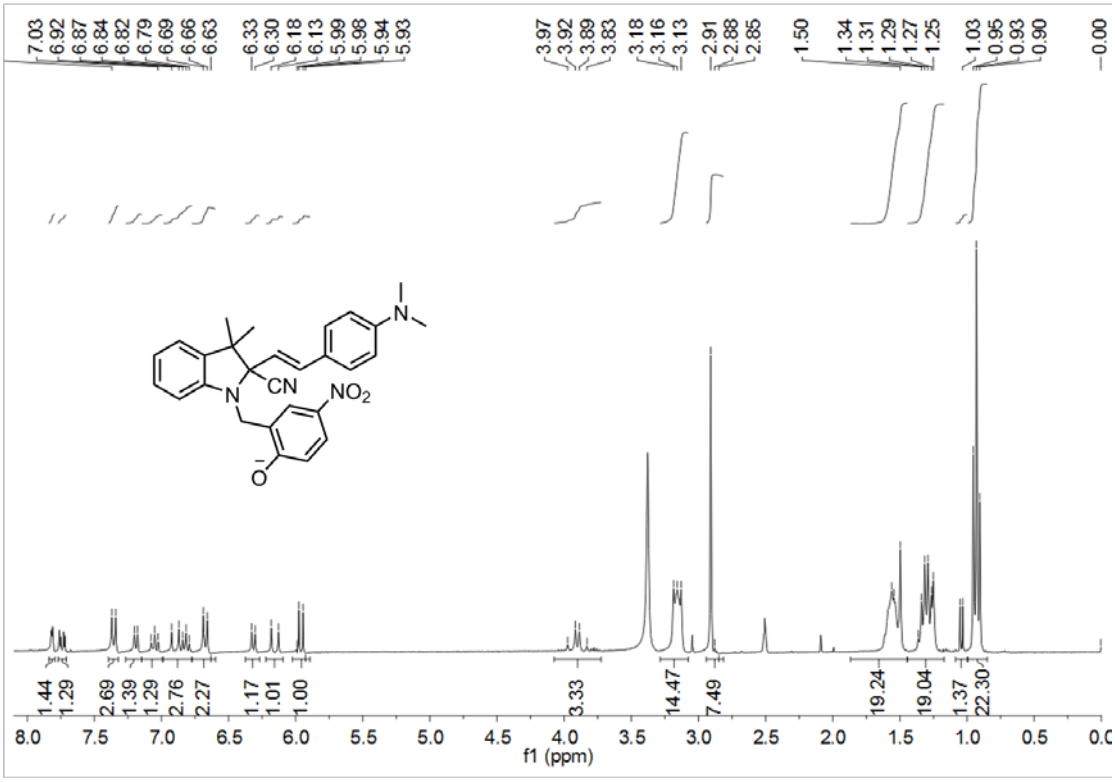


5-2 ^{13}C NMR spectrum of **P1** (DMSO-d_6)

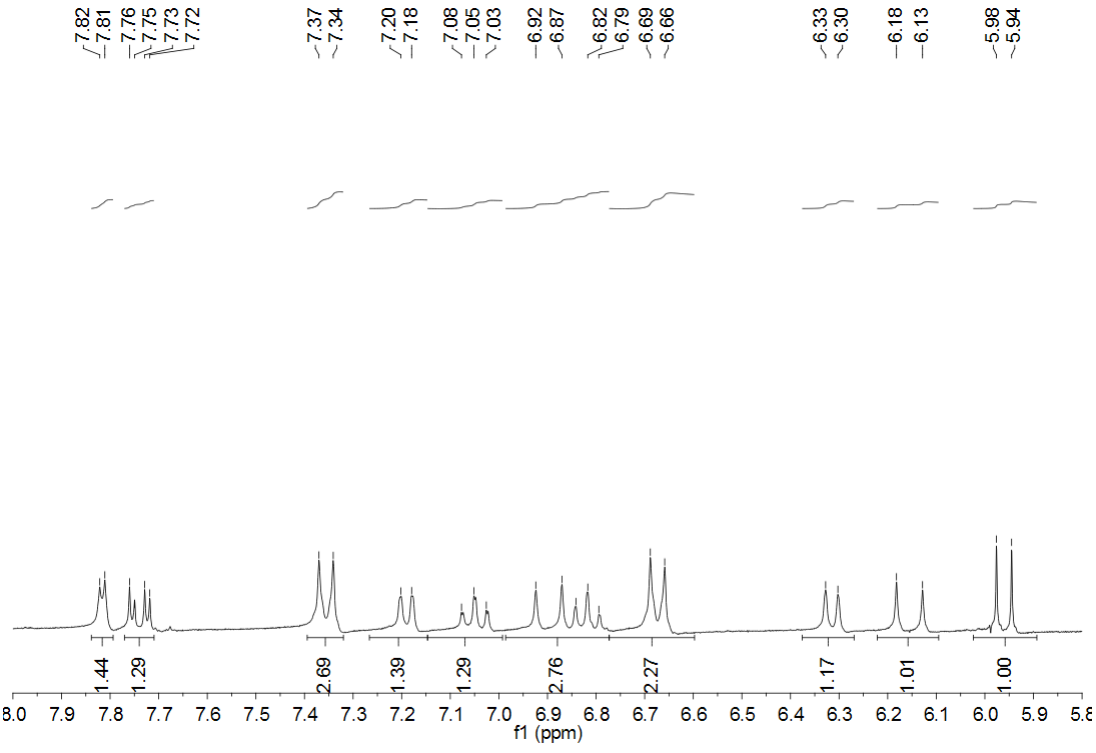


5-3 ^{1}H NMR spectrum of **P1**-CN^{-} (DMSO-d_6)

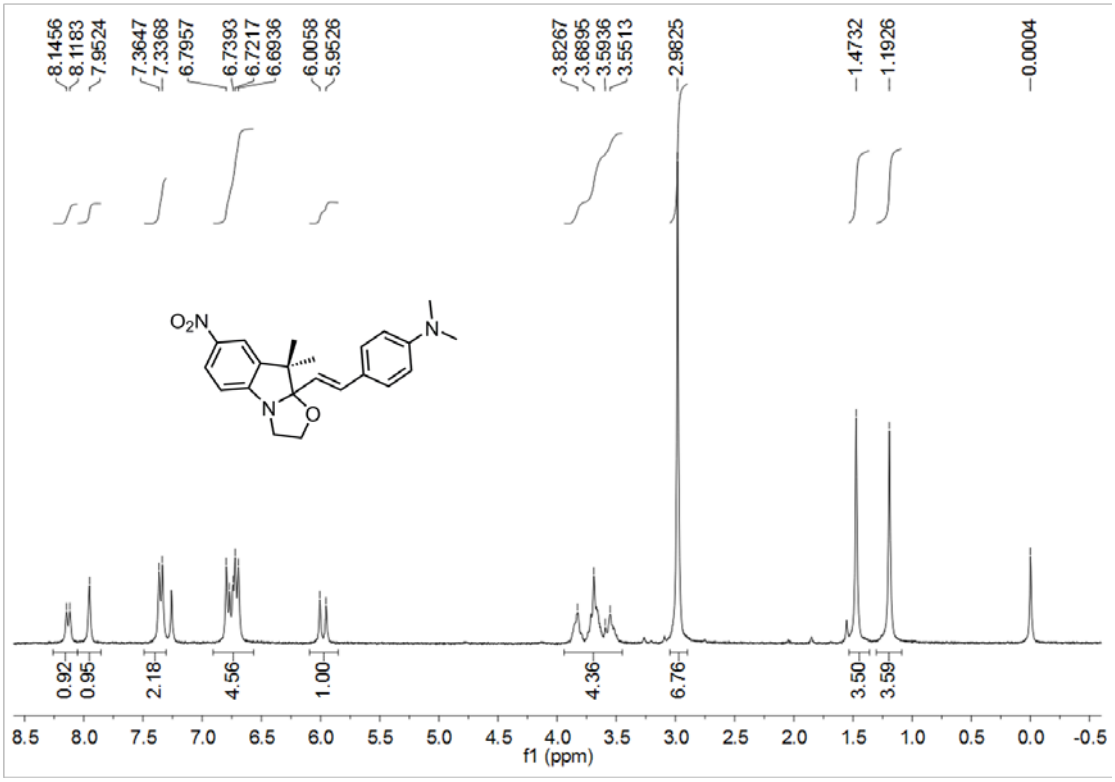
Full spectra



Enlarged view

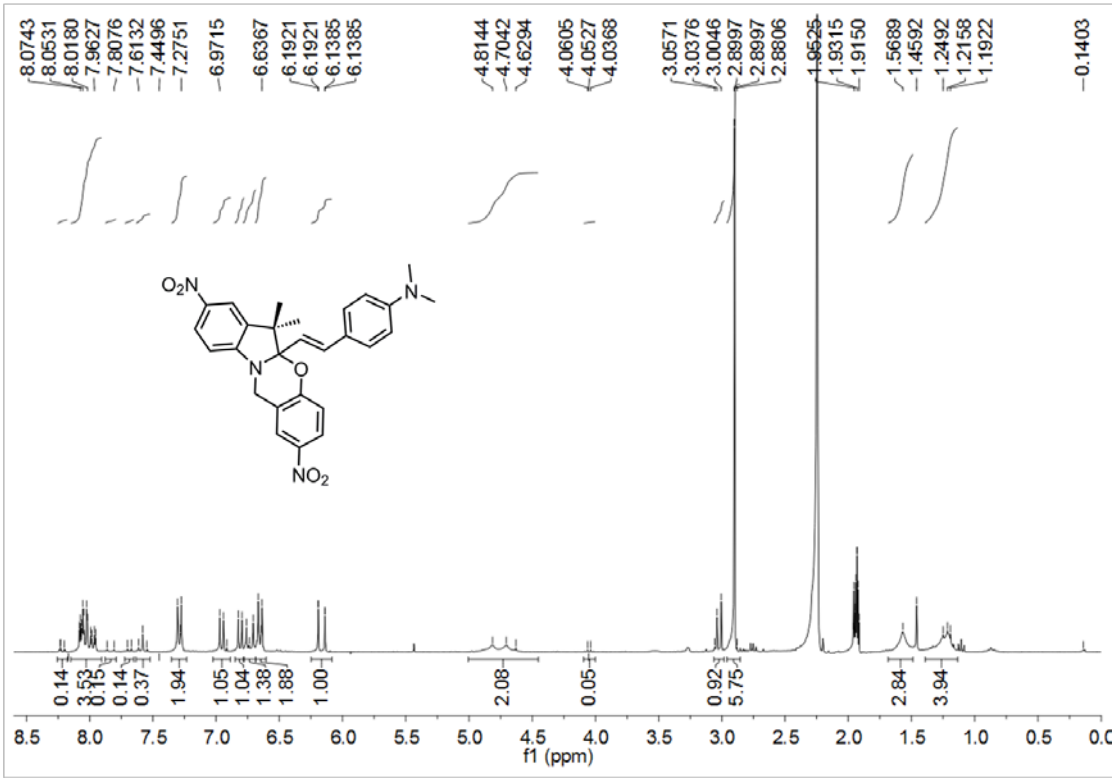


5-4 ^{1}H NMR spectrum of **P2** ($CDCl_3$)

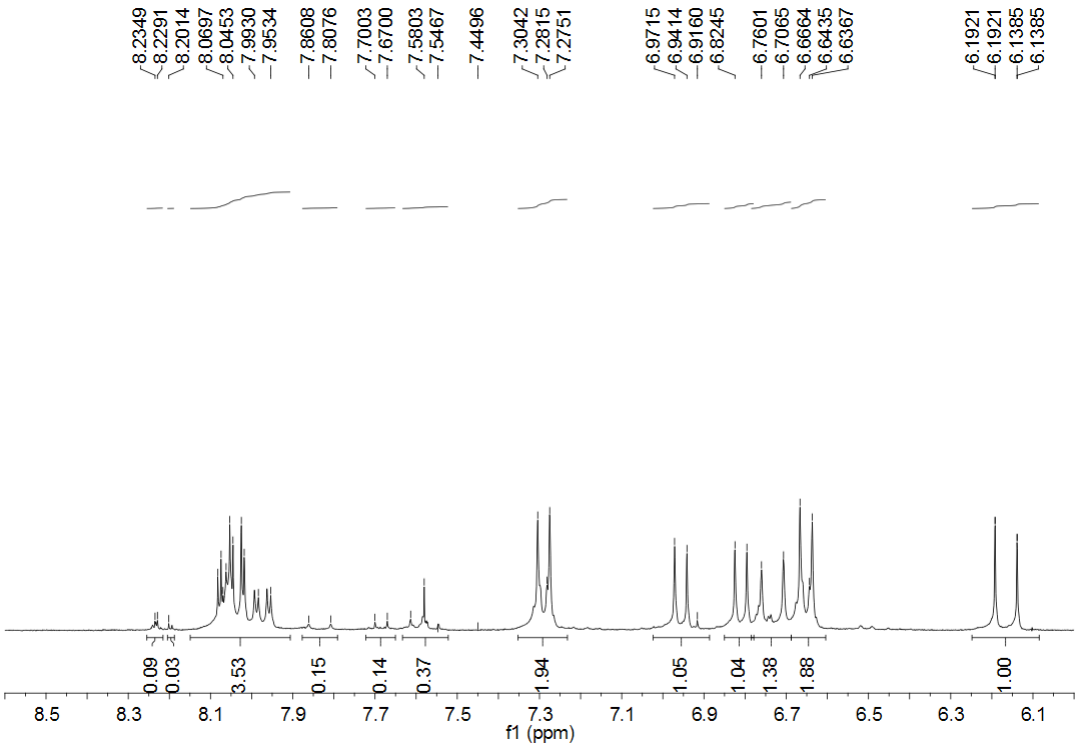


5-5 ^{1}H NMR spectrum of **P3** (CD_3CN)

Full spectra



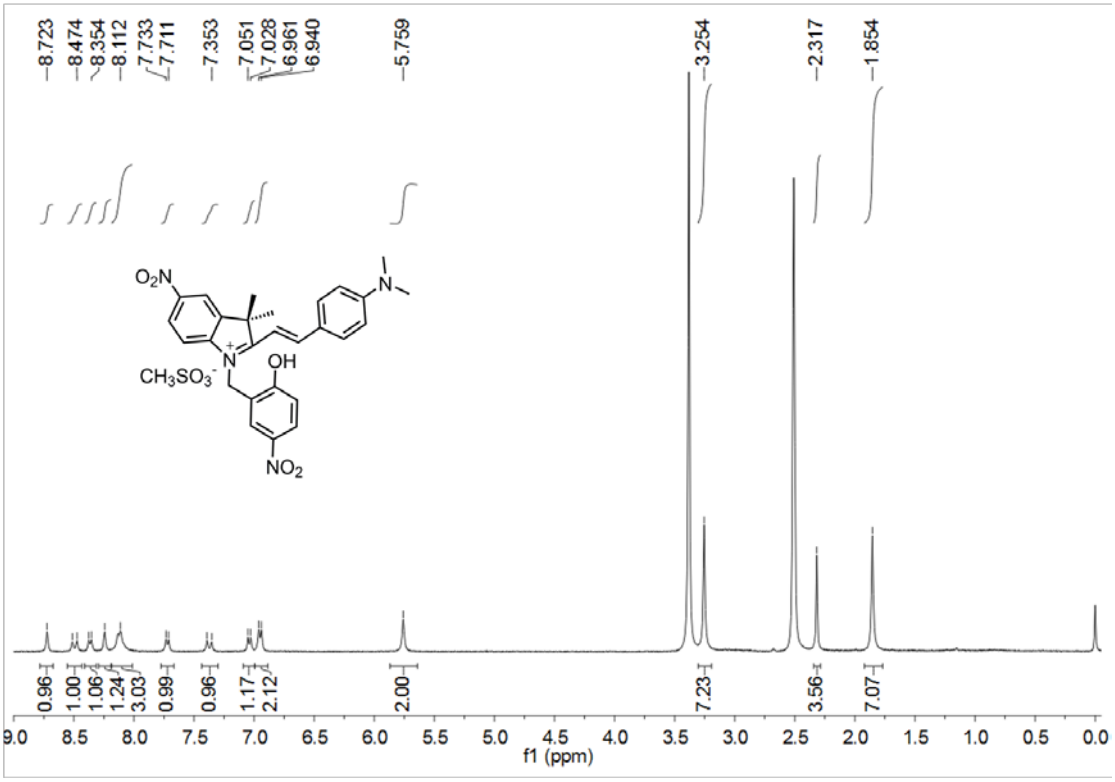
Enlarged view



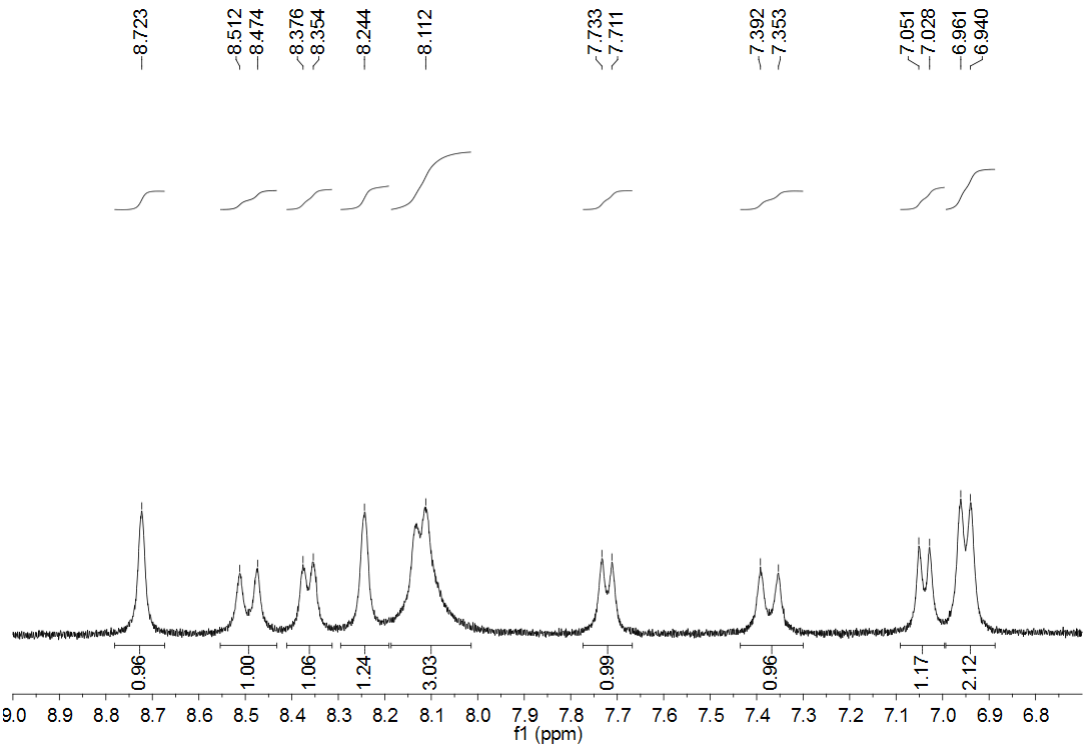
For there are both SP form and MC form of **P3** in CD_3CN, it is hard to resolve the spectra. 5-6 ^{1}H NMR spectrum of **P3 i**n presence of CH_3SO_3H was measured in (DMSO-d_6) as show in 5-6.

5-6 ^{1}H NMR spectrum of [**P3**-$CH_3SO_3^-$](DMSO-d_6)

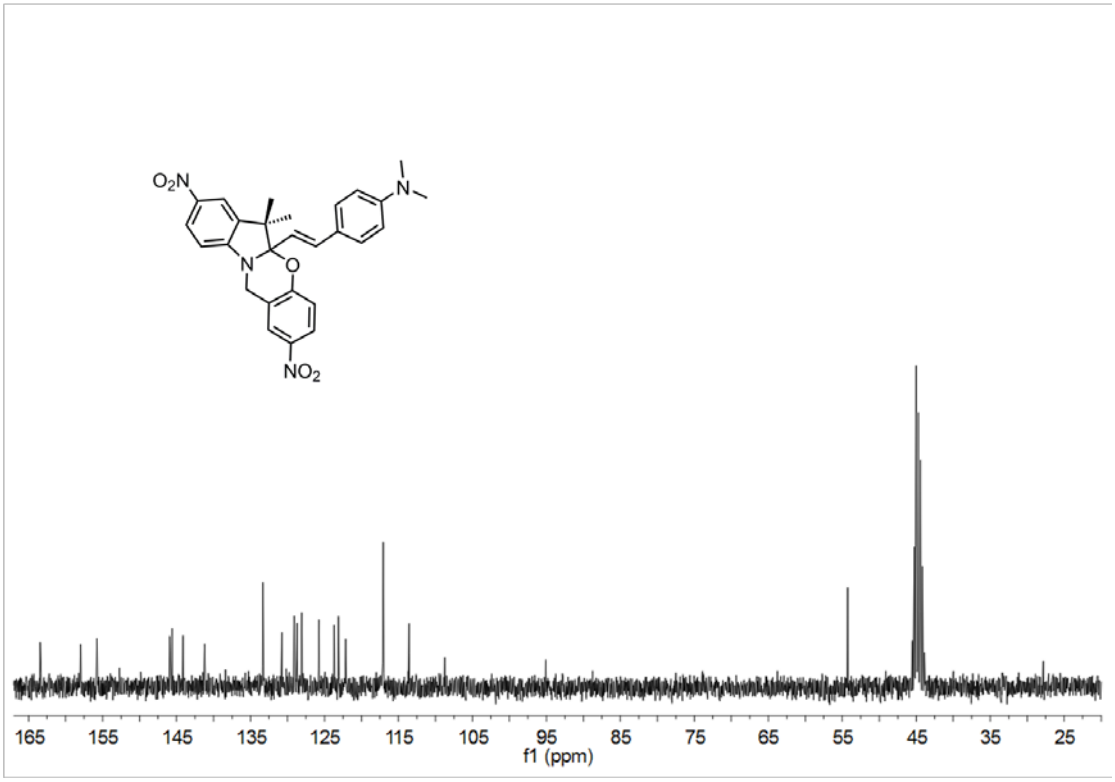
Full spectra



Enlarged view

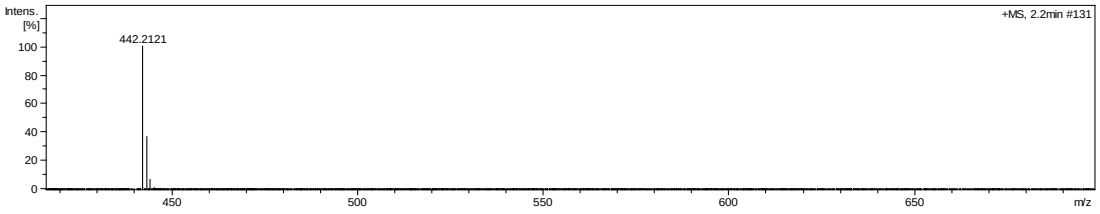


5-7 ^{13}C NMR spectrum of P3 (DMSO-d_6)

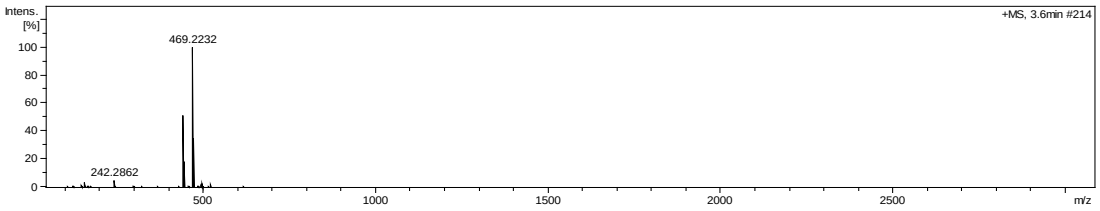


7. LC-HRMS spectra of P1 , P1-CN$^-$, P2 and P3

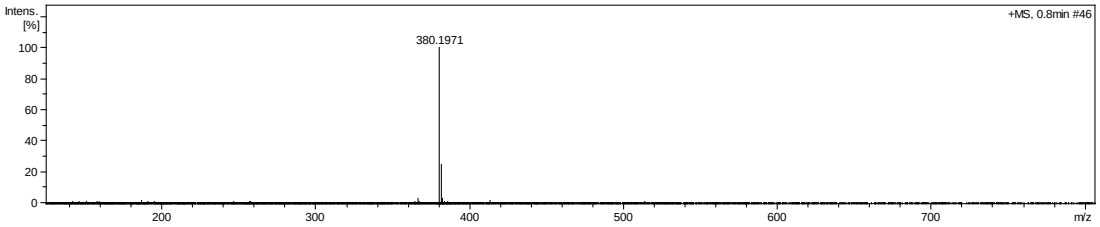
LC-HRMS of **P1**



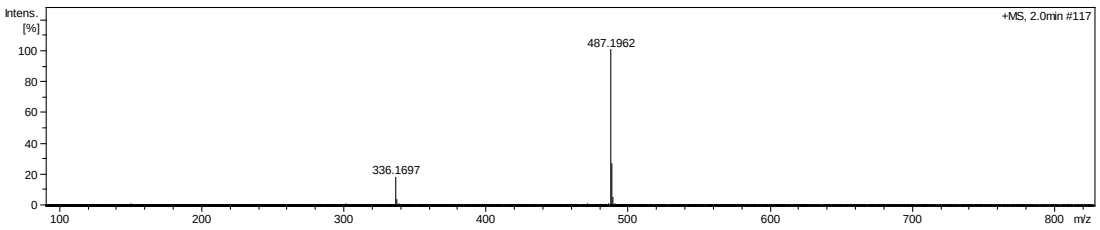
LC-HRMS of **P1**-CN$^-$



LC-HRMS of **P2**



LC-HRMS of **P3**



8. References

S1. E. Deniz, M. Tomasulo, S. Sortino and F. i. M. Raymo, *J. Phys. Chem. C*, 2009, **113**, 8491-8497.

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S3. G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176-2179.