Electronic Supplementary Information (ESI) for

A fluorescent probe generating in situ the reactive species for rapid and selective detection of mustard gas

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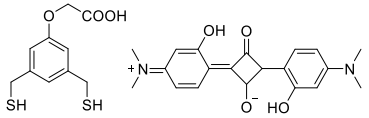
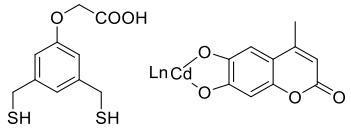
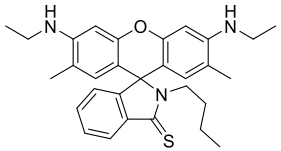
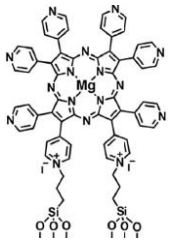
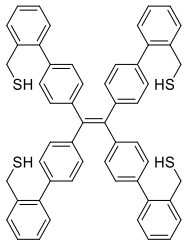
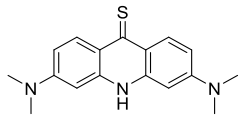
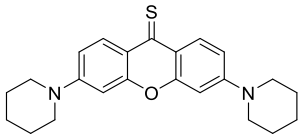
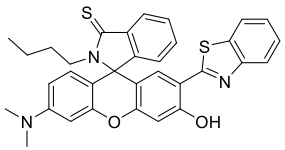
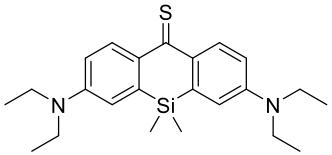
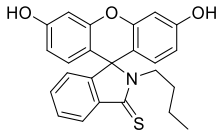
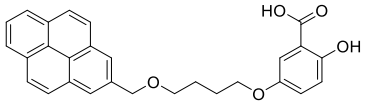
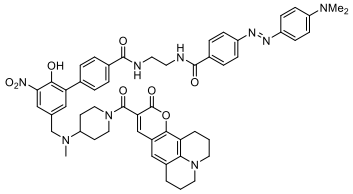
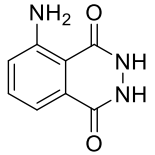
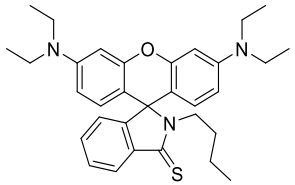
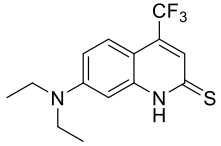
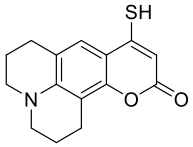
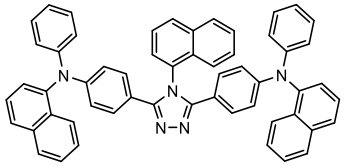
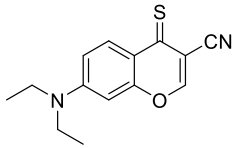
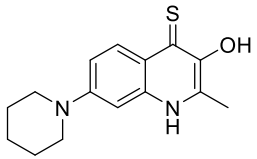
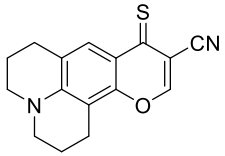
Contents:

1. Table S1. Summary for reported fluorescent probes for sulfur mustard and its simulant

Entry	Structures	Test condition	LOD	Response time (at certain temperature)		References
				Solutions	Gas phase	
1		MeOH+K_2CO_3	10 μM (CEES in solution)	-- (rt) 1 min (80°C, CEES)	/	*Chem. Sci*. **2013**, *4*, 4292.
2		Buffer, pH=9	200 μM (CEES in solution)	-- (rt) 1 min (80°C, CEES)	/	*J. Am. Chem. Soc*. **2013**, *135*, 6338.
3		MeOH/$CHCl_3$ (4:1)	4.75 μM (SM in solution) 6.25 ppm (SM gas)	>1 h (rt, SM) 3 min (60°C, SM)	7 min (50 ppm)	*Chem. Commun.* **2014**, *50*, 12363.
4		$CHCl_3$:CH_3OH, 5:1	< 6.7 ppm (CEES in solution)	-- (rt) 60 min (35°C, CEES)	/	*Anal. Chim. Acta* **2014**, *812*, 222.
5		DMSO/buffer(1:1, pH=9) with $HgCl_2$	1.1 μM (CEES in solution)	-- (rt) 5 min (80°C, CEES)	/	*J. Mater. Chem. C* **2017**, *5*, 11565.

6		MeOH+KOH	7.5 μM (SM in solution)	-- (rt) 1 min (60°C, SM)	/	*Anal. Chem.* **2018**, *90*, 1417.
7		DCM	1.2 μM (CEES in solution) 0.5 ppm (CEES gas)	>1 h (rt, CEES)	1 min (0.5 ppm)	*Anal. Chem.* **2018**, *90*, 5481.
8		MeOH	3.19 μM (CEES in solution)	25 min (rt, CEES) 3 min (60°C, CEES)	30 min (rt) (saturated vapor)	*Talanta* **2018**, *189*, 39.
9		Buffer:CH_3CN, 4:1, pH=7.4	0.8 μM (SM in solution)	10 min (37°C, SM)	/	*ACS Sens.* **2019**, *4*, 2794.
10		Buffer:CH_3CN, 9:1, pH=7.4	1.2 μM (SM in solution)	30 min (37°C, SM)	/	*Sens. Actuator B: Chem.* **2019**, *296*, 126678.
11		DMF+TBAF+ Bu_4NI	/	48 h (40°C, CEES) 2 h (90°C, CEES)	/	*ACS Sens.* **2019**, *4*, 1791.
12		DMSO:H_2O, 9:1	2.3 μM CEES in solution)	2 h (rt, CEES)	/	*Chem. Commun.* **2019**, 55, 8655

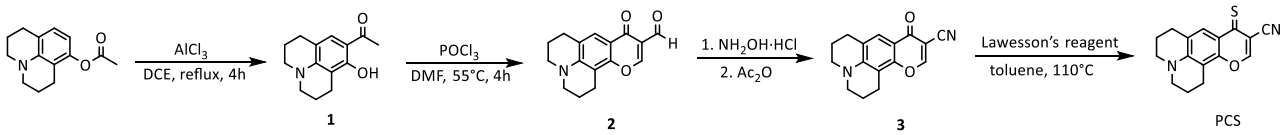
13		[emim][DCA] in buffer, pH 8.5	6 ppm (SM in solution)	1 min (rt, SM)	2 min (--)	*Anal. Chem*. **2021**, *93*,1193.
14		$[BMIm]HSO_4$	3 μM (CEES in solution)	3 min (rt, CEES)	1 min (--)	*Anal. Methods* **2021**, *13*, 484
15		Ethanol+KOH	90 nM (CEES in solution), 50 nM (SM in solution), 20 nM (NH1 in solution) 0.2 ppm (CEES gas)	18 min (rt, CEES) 1 min (CEES), 5 min (SM)(60°C)	4 min (100 ppm CEES), rt	*Anal. Chim. Acta* **2021**, *1159*, 338440
16		Ethanol+TEA	6.6 nM (CEES in solution), 16 nM (SM in solution), 3.6 nM (NH1 in solution) 9 ppb (CEES gas)	50 min (CEES), 90 min (SM) (rt) 1.5 min (CEES), 4 min (SM) (60°C)	3 min (2.5 ppm CEES), rt	*J. Hazard.s Mater*. **2021**, *416*, 125789.
17		DCM	0.55 ppm (CEES gas)	> 34 min (rt, CEES)	5 s (10 ppm)	*ACS Sens*. **2022**, 7, 1946.
18		Ethanol+50 μM KOH	0.28 μM (CEES in solution), 0.20 μM (SM in solution) 7.5 ppm (CEES gas)	15 min (CEES), 35 min (SM) (rt) 0.75 min (CEES), 3 min (SM) (60°C)	3 min (7.5 ppm CEES), rt	*Sens. Actuator B: Chem*. **2022**, 371, 132555.

19		EtOH+DBU	70 nM (SM in EtOH) 5 ppm (CEES gas)	--(rt) 4 min (SM) (60°C)	1 min (7.5-90 ppm CEES)	*Anal. Chem*. **2023**, 95, 1755–1763.
20		Ethanol+80 μM KOH	77 nM (CEES in solution), 41 nM (SM in solution) 5 ppm (CEES gas)	8 min (CEES), 25 min (SM) (rt) 20 s (CEES), 90 s (SM) (60°C)	3 min (5 ppm CEES), rt	This work

"--" Not mentioned

"/" No detection in gas phase or solutions

2. Synthesis and characterization of related compounds



Scheme S1. Synthesis route of the fluorescent probe PCS.

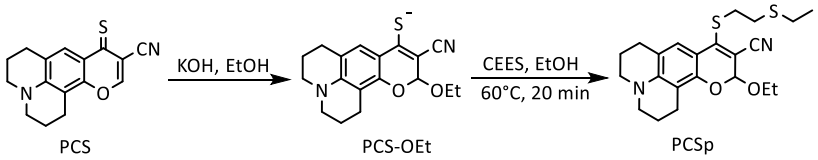
2.1. Synthesis of 1. 8-acetoxyjulolidine (7.75 g, 33.5 mmol) and aluminum chloride (15g, 111.9 mmol) were dissolved in 1,2-dichloroethane (50 mL) and refluxed at 80°C for 1 h. Then the temperature of the reaction was increased to 140 °C for another 4 h. The reaction was quenched by adding 1 M HCl (100 mL) slowly, and the mixture was extracted with DCM (3 × 100 mL). After the solvent was removed, the raw product was purified by using column chromatography (gradient elution from n-hexane to n-hexane/ethyl acetate = 10:1) to get faintly yellow solid (3.64 g, 15.74 mmol, 47% yield). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 13.18 (s, 1H), 7.11 (s, 1H), 4.23 (m, 4H), 2.67 (m, 4H), 2.45 (s, 3H), 1.93(m, 4H) ppm.^{13}C NMR (126 MHz, $CDCl_3$, TMS): δ = 200.0, 160.2, 148.9, 128.4, 112.5, 109.0, 105.5, 50.1, 49.7, 27.5, 25.4, 21.9, 20.8, 19.9 ppm. HRMS (ESI) *m/z* calcd for $C_{14}H_{18}NO_2^+$: 232.1333 $[M+H]^+$, found: 232.1330.

2.2. Synthesis of 2. In a round bottom flask, DMF (20 ml) was taken via syringe under N_2 atmosphere. It was brought at 0ºC, then $POCl_3$ (0.38 ml, 4 mmol) was added dropwise via syringe at the same temperature. It was stirred at room temperature for 20 min and then heated at 55ºC for 30 min. Then it was cooled to 0ºC and a solution of compound **1** (0.23 g, 1 mmol) in DMF (1.20 ml) was added dropwise via syringe over 30 min. It was stirred at room temperature for 30 min and heated at 55ºC for 2 hours (TLC showed complete consumption of starting material). The reaction mixture was again cooled to 0ºC and diluted with ethyl acetate followed by the addition of brine solution dropwise. It was then extracted with ethyl acetate (3 × 80 ml) and brine (60 ml). The organic portions were collected and washed with water. It was dried over with anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was purified by using flash chromatography over silica gel to afford the desired product as yellow solid (126 mg, 0.32 mmol, 32% yield). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 10.37 (s, 1H), 8.38 (s, 1H), 7.66 (s, 1H), 3.31 (m, 4H), 2.84 (m, 4H), 2.00 (m, 4H) ppm.^{13}C NMR (126 MHz, $CDCl_3$, TMS): δ = 190.0, 175.1, 159.2, 153.8, 147.8, 122.8, 121.1, 119.5, 113.2, 106.2, 50.0, 49.5, 27.6, 21.1, 20.3, 20.3 ppm. HRMS (ESI) *m/z* calcd for $C_{16}H_{16}NO_3^+$: 270.1125 $[M+H]^+$, found: 270.1130.

2.3. Synthesis of 3. A suspension of compound **2** (269 mg, 1.00 mmol) and hydroxylamine hydrochloride (76 mg, 1.10 mmol) was stirred in ethanol (3 mL) at 60°C for 1 h. The mixture was concentrated in vacuo, and acetic anhydride (10 mL) was added and stirred at 110°C for 18 h. The mixture was concentrated in vacuo and purified by using flash chromatography over silica gel, affording **3** as a pale yellow solid (134 mg, 0.51 mmol, 51% yield).^{1}H

NMR (500 MHz, $CDCl_3$, TMS): δ = 8.21 (s, 1H), 7.61 (s, 1H), 3.31 (m, 4H), 2.82 (m, 4H), 2.00 (m, 4H) ppm.^{13}C NMR (126 MHz, $CDCl_3$, TMS): δ = 171.2, 167.4, 160.6, 148.1, 122.8, 121.2, 113.4, 111.6, 105.7, 101.2, 50.0, 49.4, 27.6, 21.0, 20.2, 18.0 ppm. HRMS (ESI) *m/z* calcd for $C_{16}H_{15}N_2O_2^+$: 267.1129 $[M+H]^+$, found: 267.1140.

2.4. Synthesis of PCS. Under nitrogen atmosphere, compound **3** (100 mg, 0.41 mmol) and Lawesson's reagent (250 mg, 0.62 mmol) were dissolved in toluene (10 mL), and the reaction mixture was stirred at 110°C for 4 h. After cooling, the mixture was diluted with CH_2Cl_2(20 mL) and washed with $NaHCO_3$ solution for three times (3 × 10 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude mixture was purified by using flash chromatography over silica gel to obtain PCS as a red solid (55 mg, 0.19 mmol, 47% yield).^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 8.00 (s, 1H), 7.99 (s, 1H), 3.35 (m, 4H), 2.82 (m, 4H), 2.00 (m, 4H) ppm.^{13}C NMR (126 MHz, $CDCl_3$, TMS): δ = 171.3, 167.4, 160.6, 148.1, 122.8, 121.2, 113.4, 111.6, 105.7, 101.2, 50.0, 49.4, 27.6, 21.0, 20.2, 18.0 ppm. HRMS (ESI) *m/z* calcd for $C_{16}H_{15}N_2OS^+$: 283.0900 $[M+H]^+$, found: 283.0918.



PCS PCS-OEt PCSp

Scheme S2. The synthesis route of the compound PCSp.

2.5. Synthesis of the PCSp. PCS (50 mg, 0.18 mmol) and KOH (52 mg, 0.92 mmol) were dissolved in absolute ethanol (5 mL), CEES (226 μL, 1.94 mmol) was added and heated at 60°C for 20 min. After cooling, the solvent was evaporated under reduced pressure and then diluted with CH_2Cl_2. Washed with water, the organic layer were dried over Na_2SO_4 and concentrated in vacuo. The crude mixture was purified by using flash chromatography over silica gel to obtain PCSp as a yellow oil (38 mg, 0.092 mmol, 51% yield). ^{1}H NMR (500 MHz, $CDCl_3$,TMS): δ = 7.24 (s, 1H), 5.64 (s, 1H), 3.79 (m, 1H), 3.72 (m, 1H), 3.66 (m, 1H), 3.29 (m, 4H), 3.08 (m, 1H), 2.75 (m, 1H), 2.71 (m, 4H), 2.53 (q, *J*=7.4Hz, 2H) , 2.01 (m, 1H), 1.94(m, 4H) , 1.21 (m, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$,TMS): δ = 148.0, 146.8, 146.8, 125.2, 118.4, 115.6, 108.4, 107.8, 98.3, 95.4, 64.2, 50.0, 49.5, 34.7, 31.3, 27.4, 25.9, 21.6, 20.8, 20.6, 15.0, 14.8 ppm. HRMS (ESI) *m/z* calcd for $C_{16}H_{15}N_2OS^+$: 417.1670 $[M+H]^+$, found: 417.1672.

2.6. Synthesis of the PCS-OEt. PCS (5 mg, 0.018 mmol) and KOH (10 mg, 0.18 mmol) were dissolved in absolute ethanol (5 mL). The mixture was stirred at room temperature for 20 min, and the solvent was removed in vacuo, giving the sulfur enolate anion as a red solid. ^{1}H NMR (400 MHz, DMSO-d_6, TMS): δ = 7.57 (s, 1H), 5.42 (s, 1H), 3.60 (q, *J* = 5.2 Hz, 2H), 3.09 (m, 4H), 2.63 (m, 4H), 1.85 (m, 4H), 1.05 (t, *J* = 5.6 Hz, 3H) ppm. ^{13}C NMR (126 MHz, DMSO-d_6, TMS) δ = 172.8, 146.7, 144.4, 127.4, 124.8, 116.1, 113.7, 106.7, 97.0, 89.3, 62.1, 49.8, 49.3, 27.4, 22.3, 21.6, 21.0, 15.5 ppm. HRMS (ESI) m/z calcd for $C_{18}H_{19}N_2O_2S^-$: 327.1172 $[M^-]$, found: 327.1163.

3. Chemical and photostability of PCS in ethanol solution

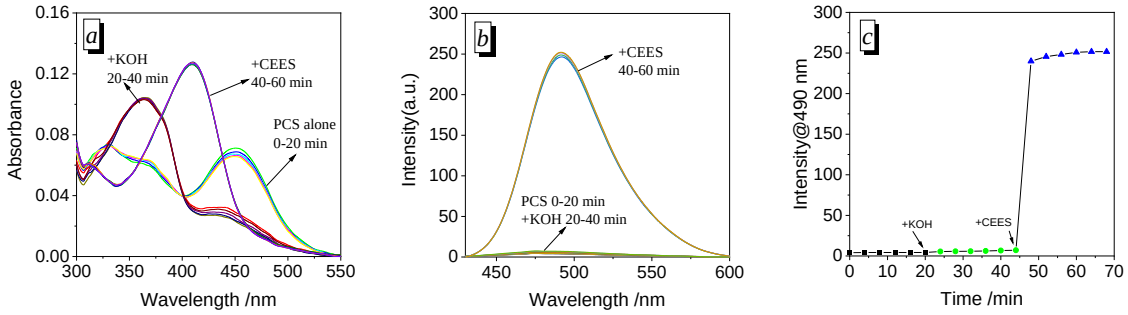


Figure S1. Time-dependent (a) UV-Vis absorption and (b) fluorescence spectra of 10 μM PCS, followed by 80 μM KOH and further addition of 300 μM CEES, monitored for 60 min, excitation at 411 nm. (c) Time-dependent fluorescence intensity at 490 nm of PCS (10 μM) before and after addition of 80 μM KOH and further addition of 300 μM CEES.

4. The UV-Vis absorption response of PCS toward KOH

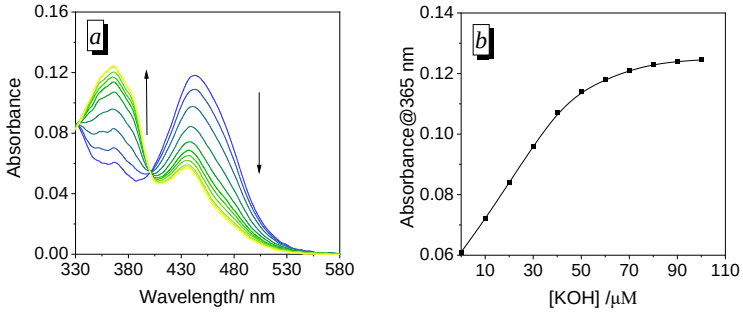


Figure S2. (a) UV-Vis absorption and (b) concentration-dependent absorption at 365 nm of 10 μM PCS upon the addition of 0-100 μM KOH.

5. The spectral response of PCS to CEES at 60°C

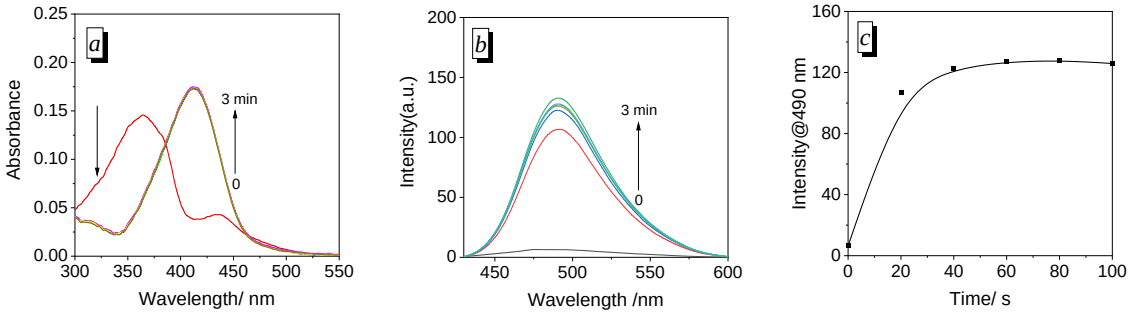


Figure S3. Time-dependent (a) UV-Vis absorption and (b) fluorescence spectra of 10 μM PCS with 80 μM KOH after addition of 300 μM CEES, monitored for 3 min at 60°C, excitation at 411 nm. (c) Time-dependent fluorescence intensity at 490 nm of 10 μM PCS with 80 μM KOH after addition of 300 μM CEES.

6. The spectral response of PCS to SM at 60°C

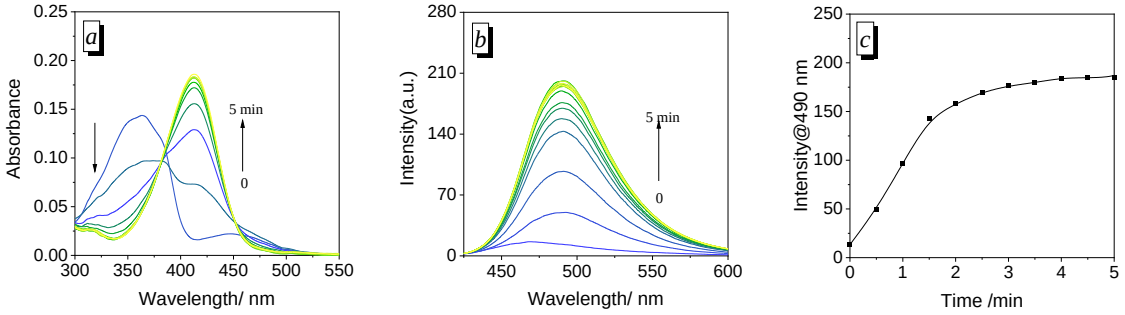


Figure S4. Time-dependent (a) UV-Vis absorption and (b) fluorescence spectra of 10 μM PCS with 80 μM KOH after addition of 300 μM SM, monitored for 5 min at 60°C, excitation at 411 nm. (c) Time-dependent fluorescence intensity at 490 nm of 10 μM PCS with 80 μM KOH after addition of 300 μM SM.

7. Time-dependent fluorescence intensity of PCS toward CEES or SM at room temperature

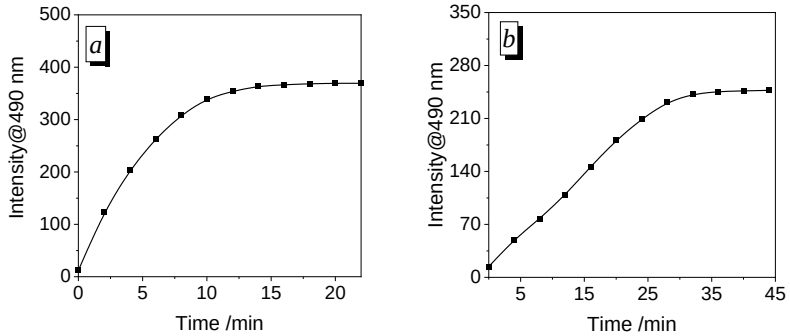


Figure S5. Time-dependent fluorescence intensity at 490 nm of PCS (10 μM) with 80 μM KOH after addition of 300 μM (a) CEES or (b) SM at room temperature.

8. Anti-interference for PCS toward SM

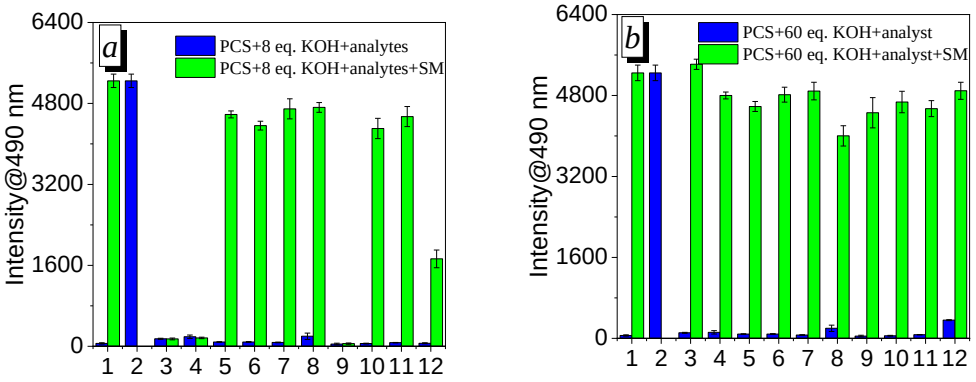


Figure S6. Fluorescence intensity at 490 nm of 10 μM PCS with (a) 80 μM or (b) 600 μM KOH after additions of 300 μM SM or various analytes (blue), or further additions of 300 μM SM in above solutions (green): 1, blank; 2, SM; 3, AC; 4, $POCl_3$; 5, EtI; 6, BCP; 7, BCEE; 8, CEEE; 9, DCP; 10, DCNP; 11, GSH; 12, Met.

9. HRMS spectra of sensing system with SM

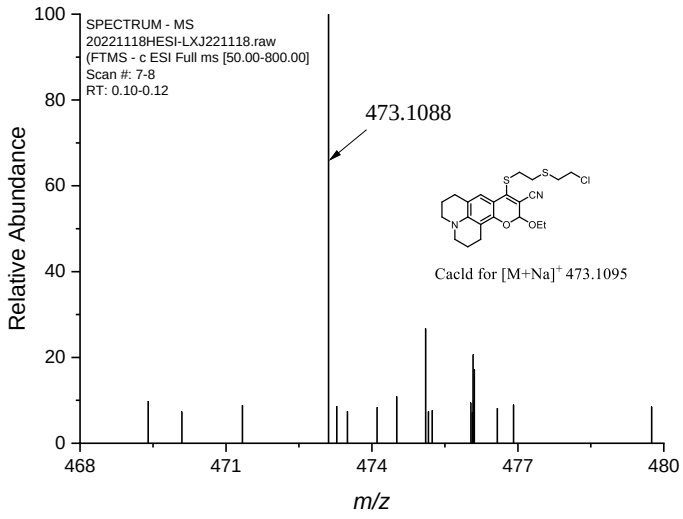


Figure S7. The high-resolution mass spectrum (HRMS) for the mixture of sensing system with SM.

10. Application

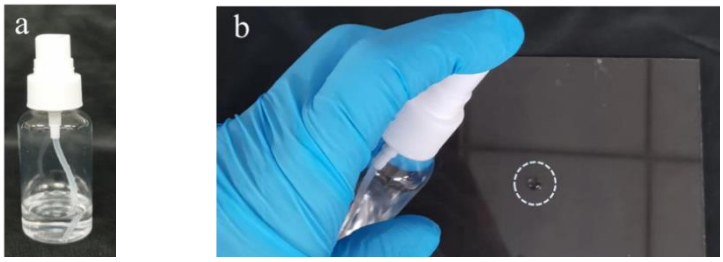


Figure S8. (a) A spray bottle loaded with 0.2 mM PCS and 1.6 mM KOH ethanol solution. (b) Spraying the ethanol solution of PCS and KOH to CEES contaminated surface.

11. NMR spectra for related compounds

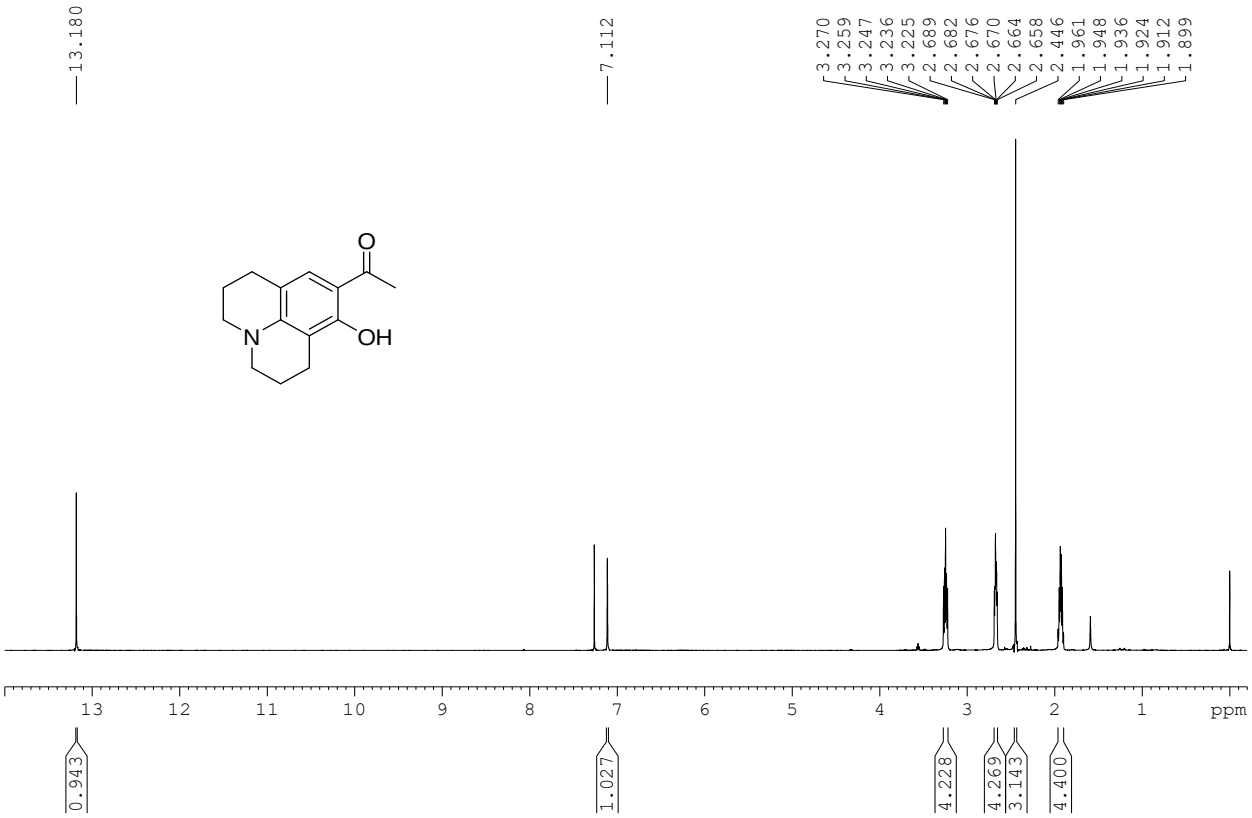


Figure S9. ^{1}H NMR spectrum of compound **1** in $CDCl_3$

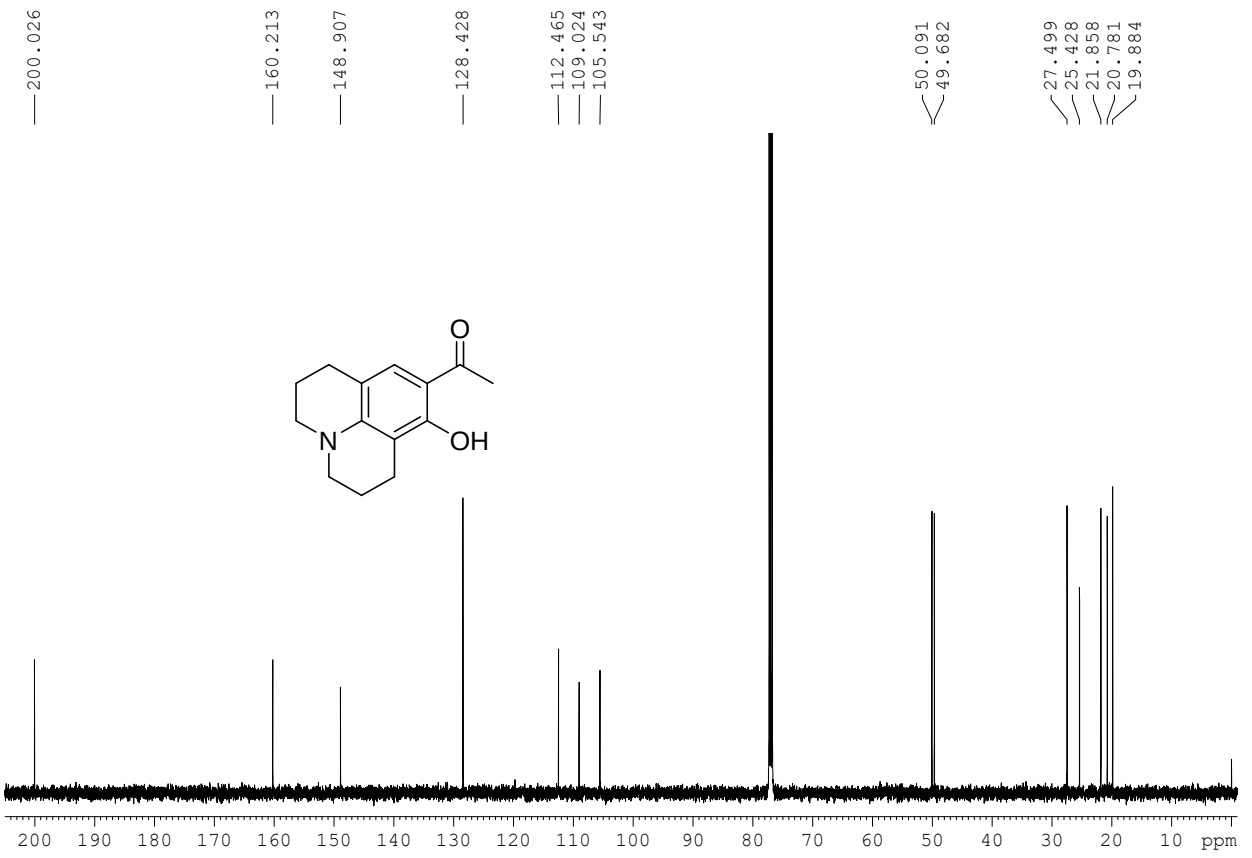


Figure S10. ^{13}C NMR spectrum of compound **1** in $CDCl_3$

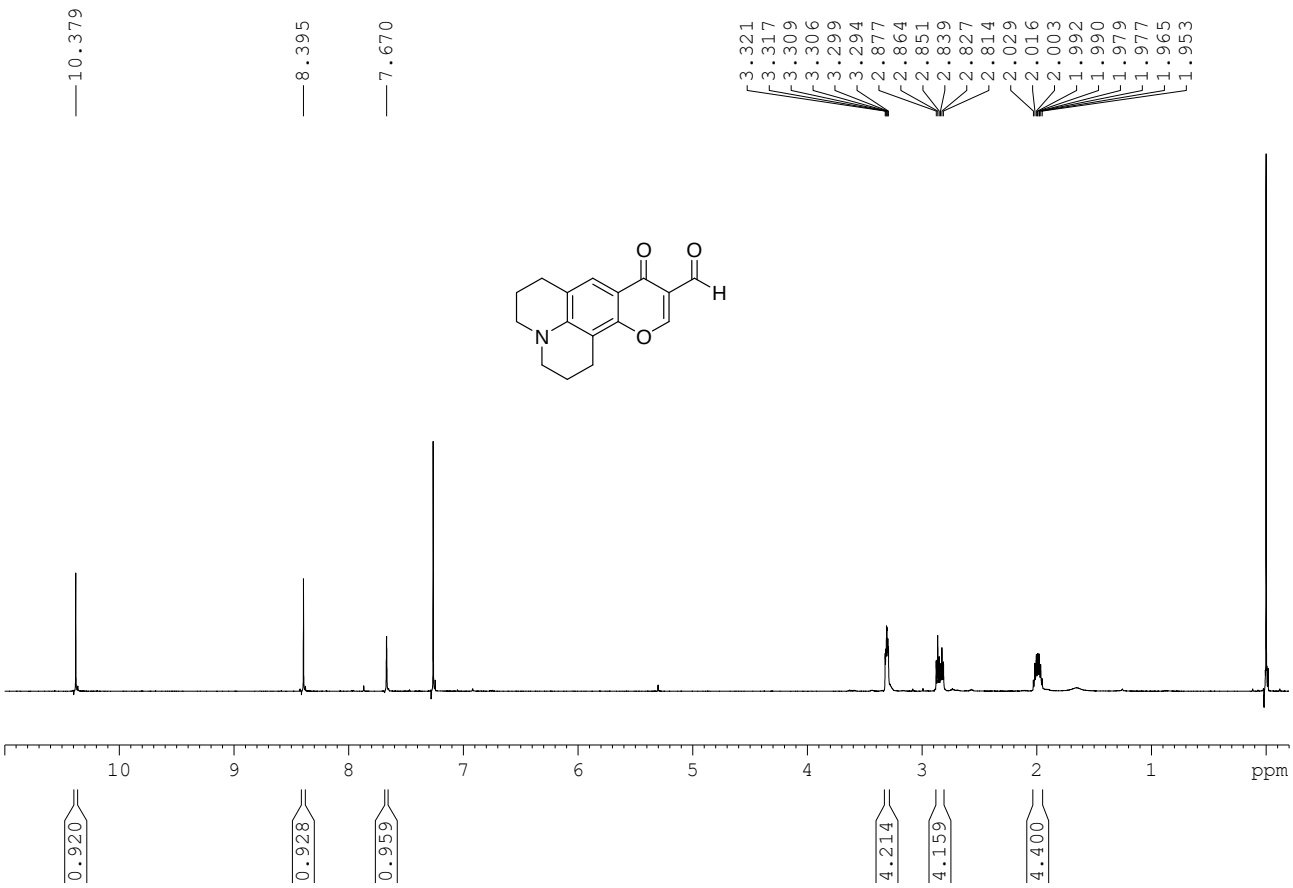


Figure S11. ^{1}H NMR spectrum of compound **2** in $CDCl_3$

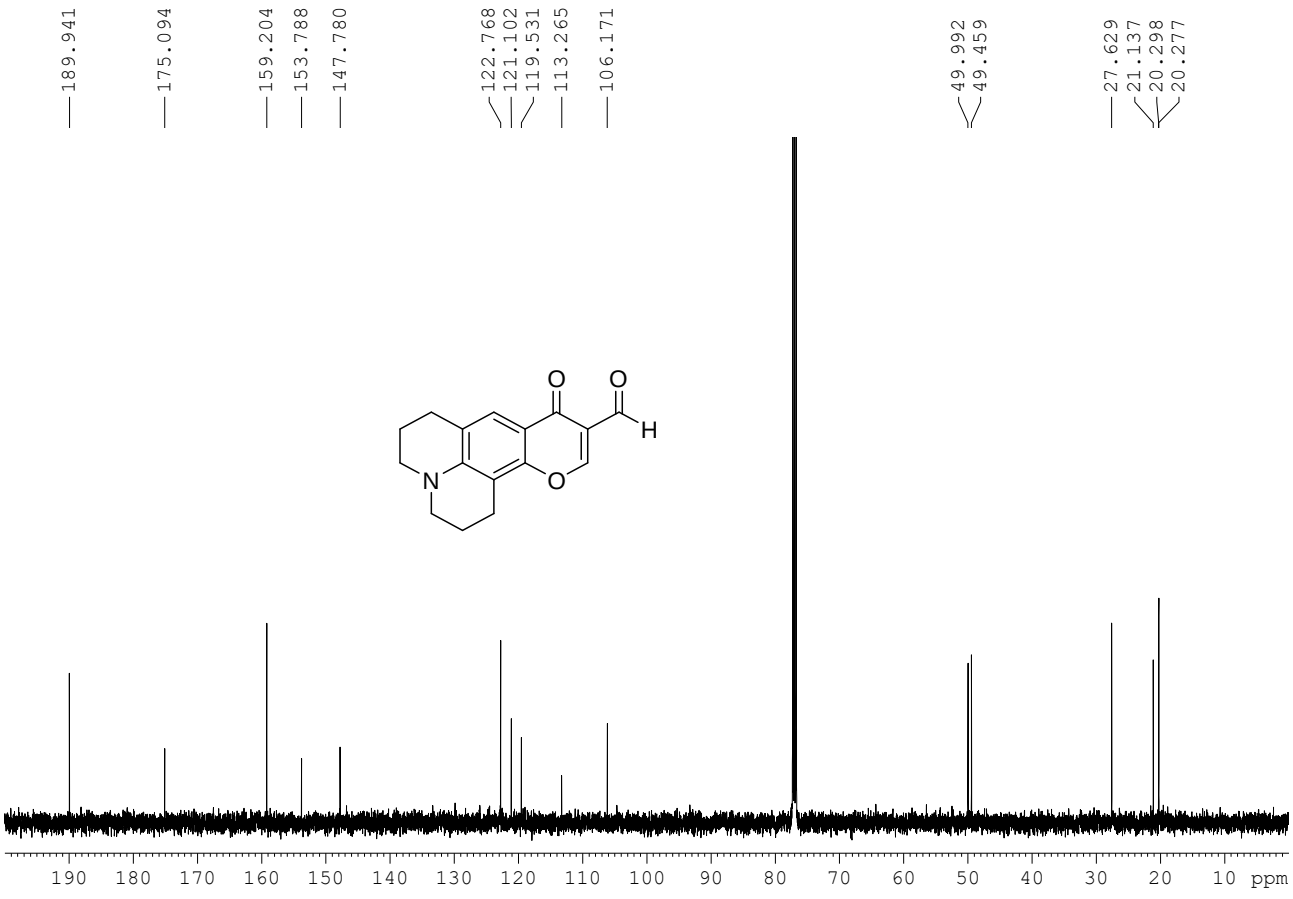


Figure S12. ^{13}C NMR spectrum of compound **2** in $CDCl_3$

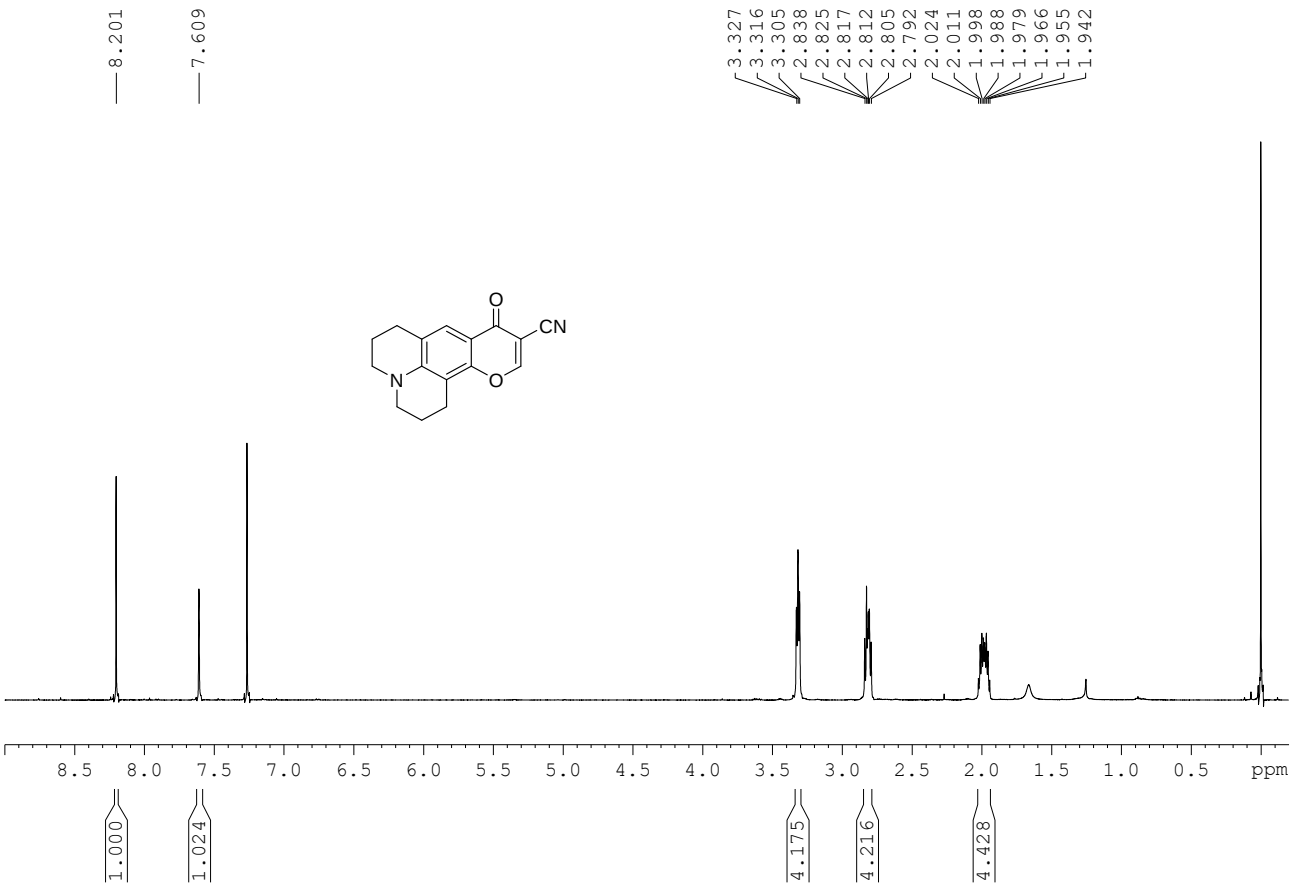


Figure S13. ^{1}H NMR spectrum of compound **3** in $CDCl_3$

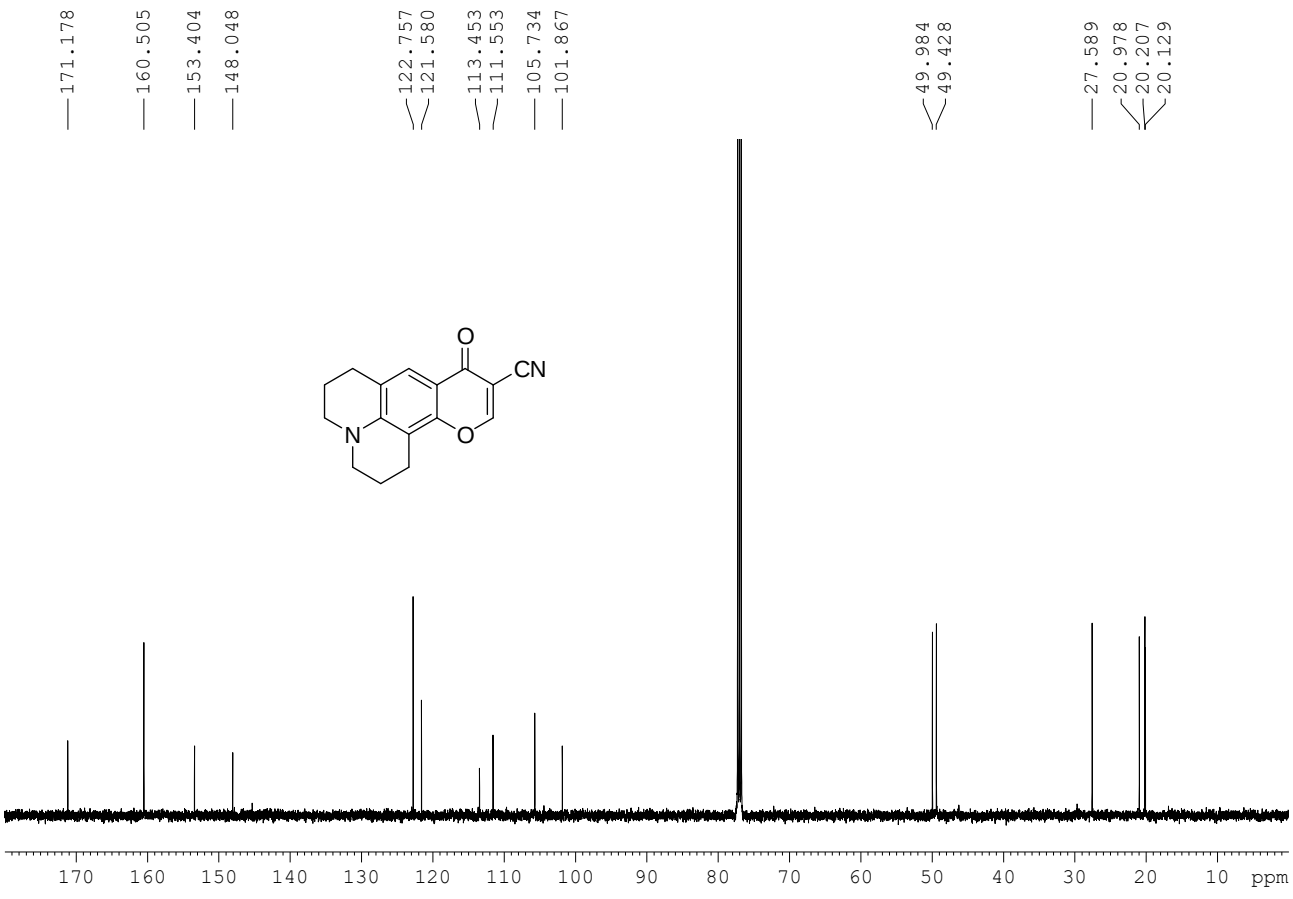


Figure S14. ^{13}C NMR spectrum of compound **3** in $CDCl_3$

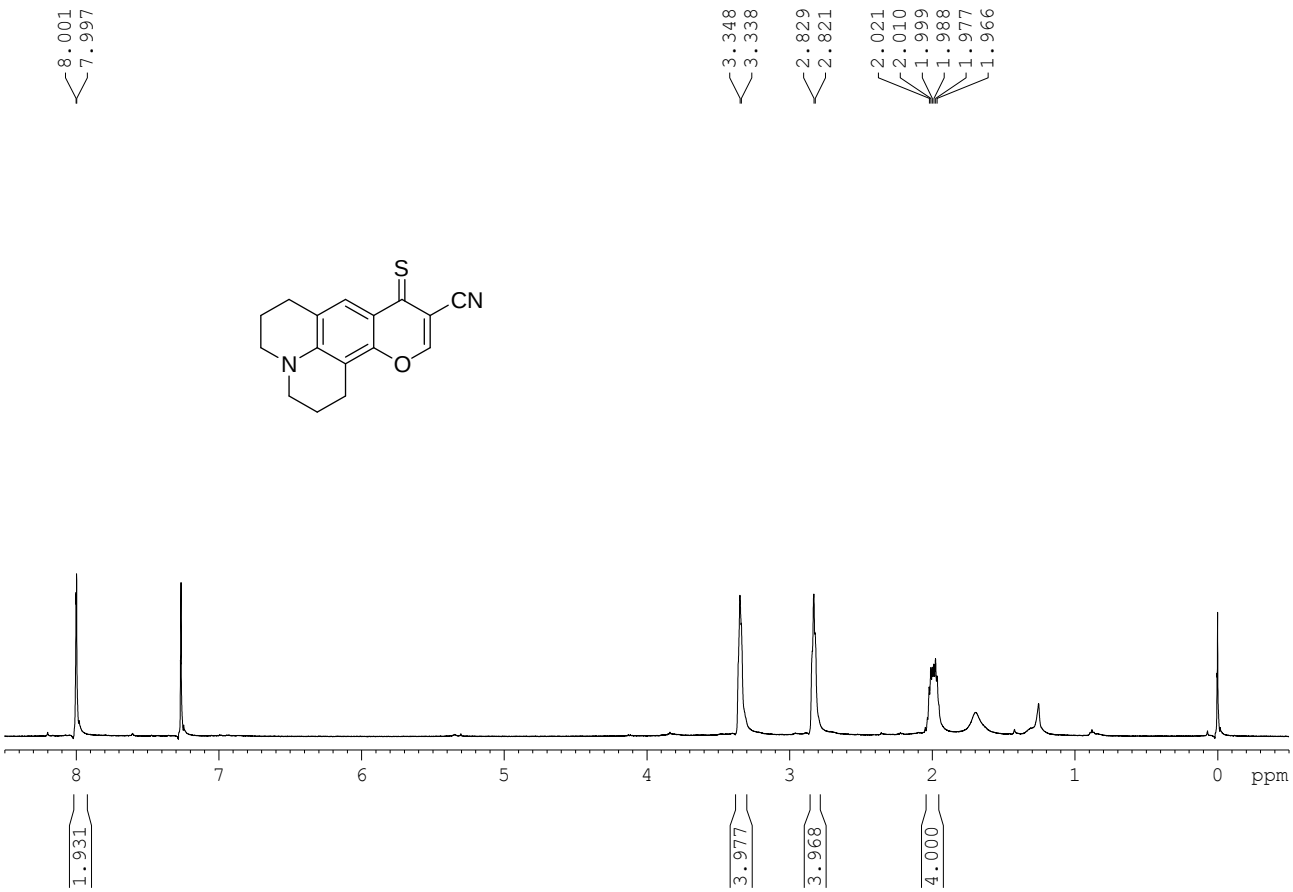


Figure S15. ^{1}H NMR spectrum of compound PCS in $CDCl_3$

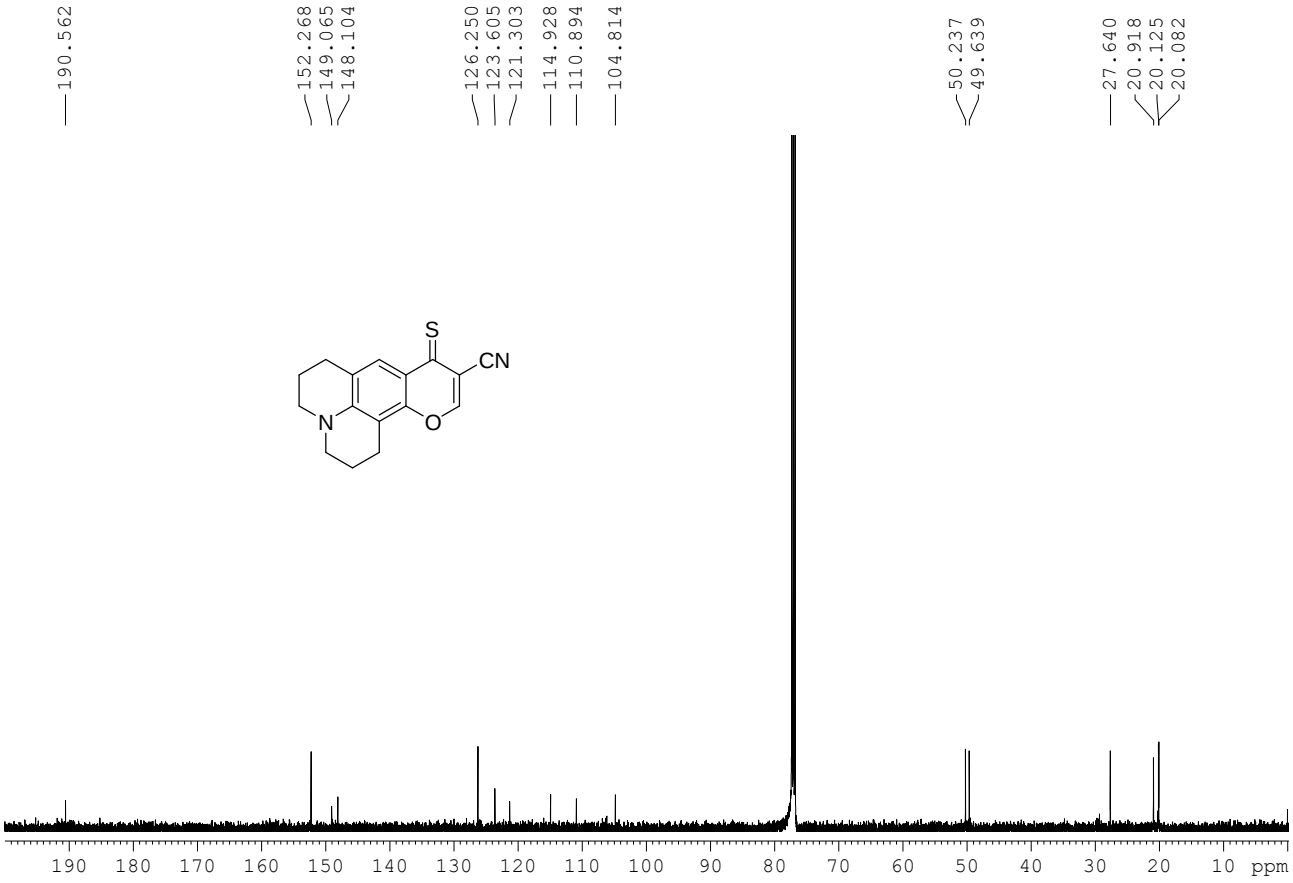


Figure S16. ^{13}C NMR spectrum of compound PCS in $CDCl_3$

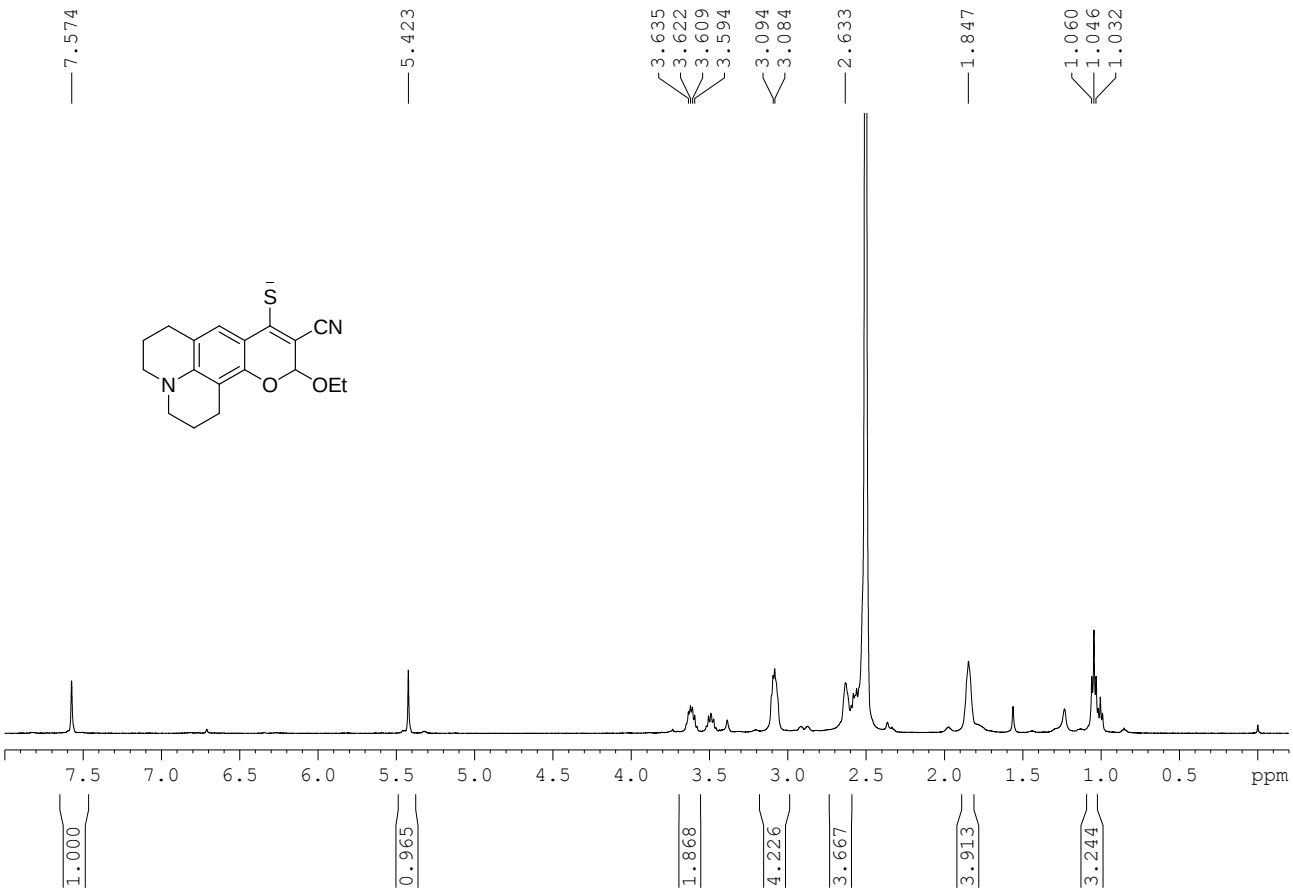


Figure S17. ^{1}H NMR spectrum of compound PCS-OEt in DMSO-d_6.

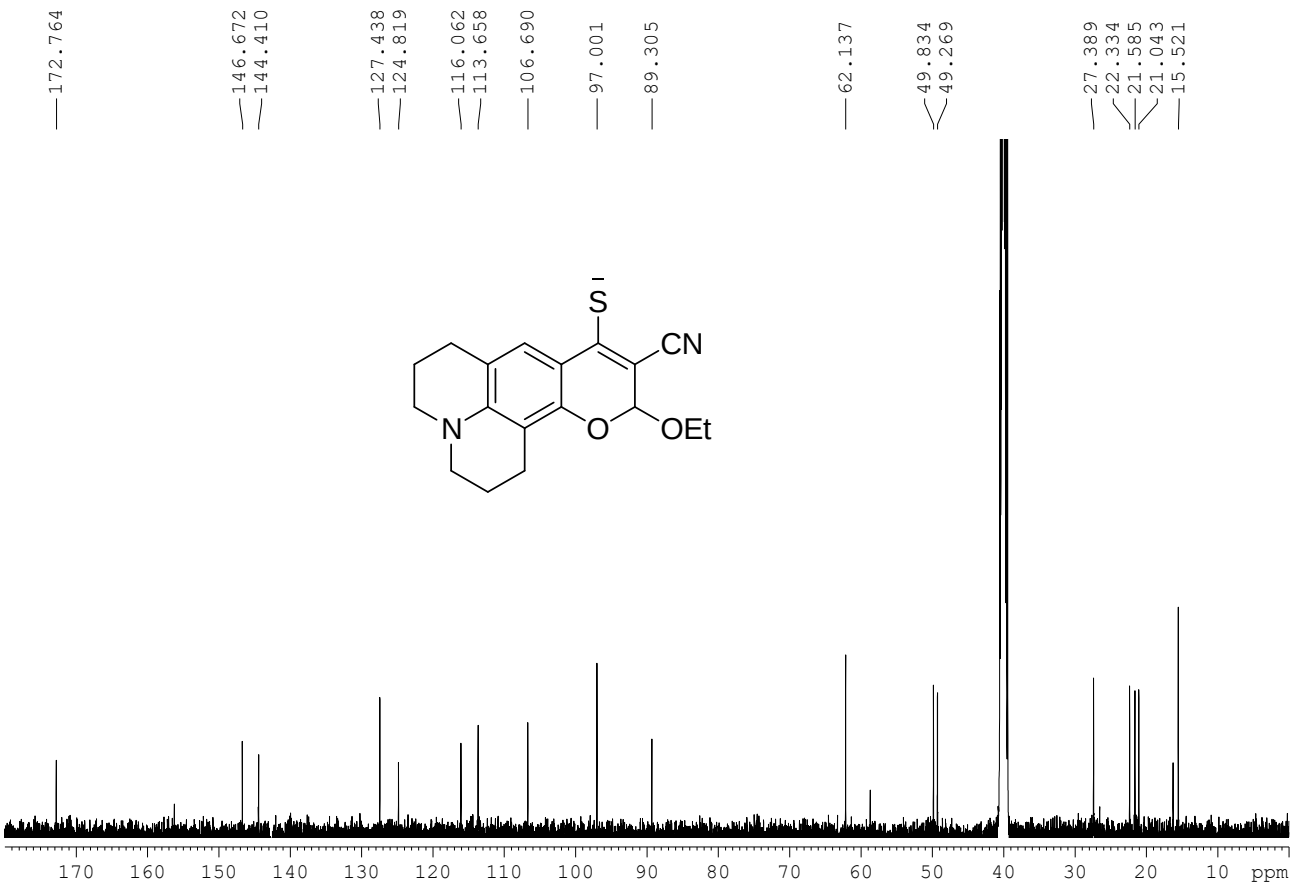


Figure S18. ^{13}C NMR spectrum of compound PCS-OEt in DMSO-d_6.

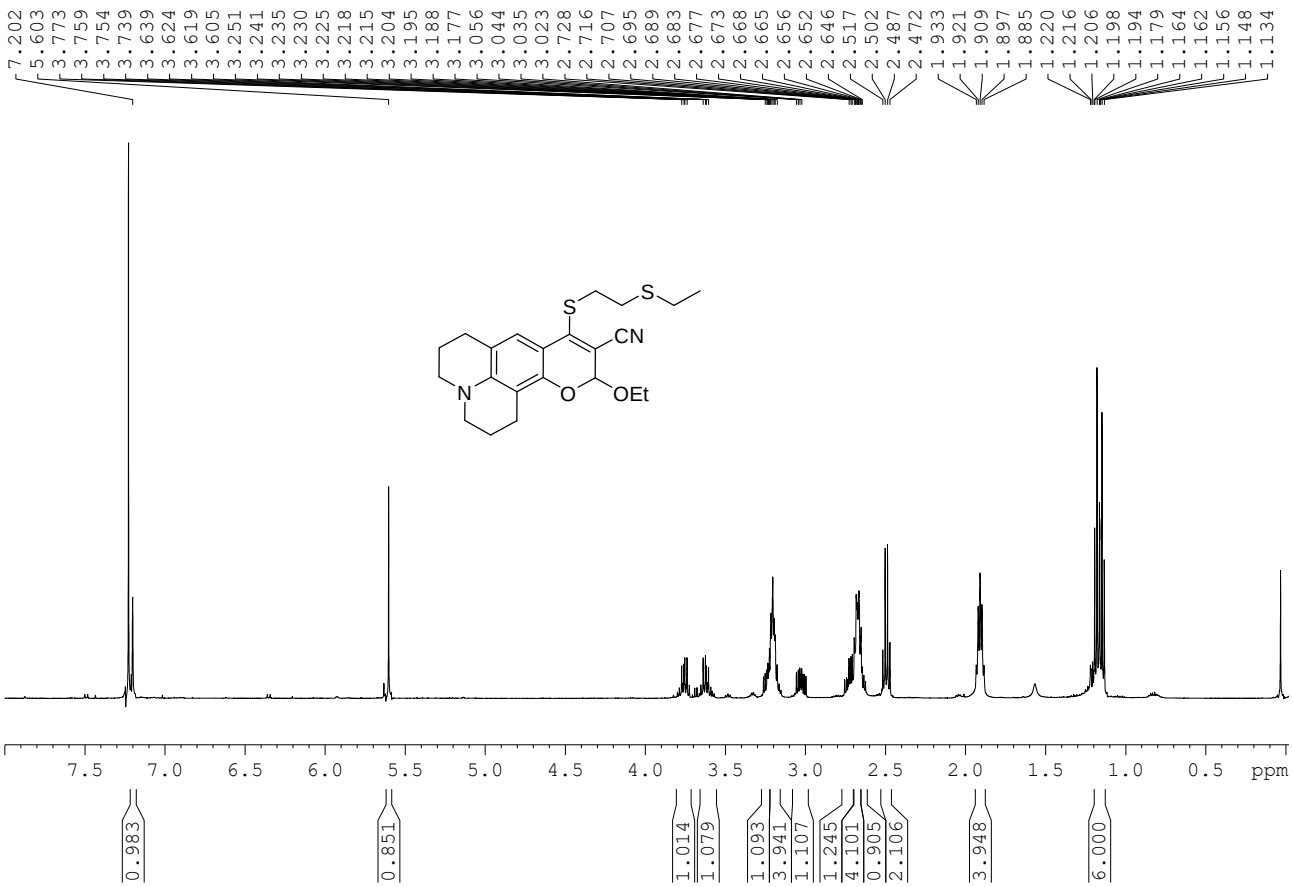


Figure S19. ^{1}H NMR spectrum of compound PCSp in $CDCl_3$

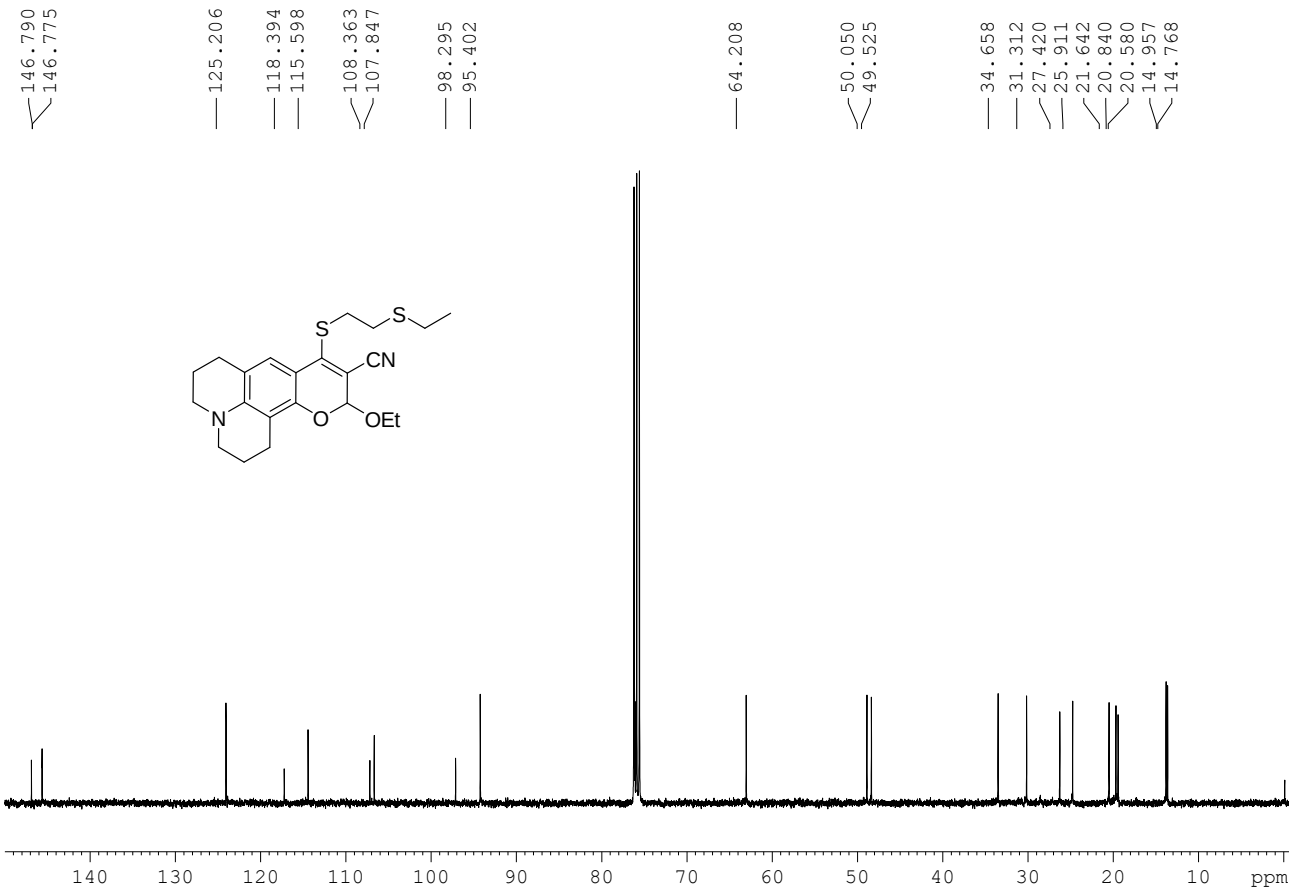


Figure S20. ^{13}C NMR spectrum of compound PCSp in $CDCl_3$