Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for:

A Mechanistically-distinct Approach to Fluorescence Visualization of Singlet Oxygen.

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1. General Notes.

All reagents used for reactions were reagent grade and use without further purification.

Dry solvent was obtained by filtration of reagent-grade solvent through an Innovative Technologies solvent drying system.

Column chromatographic purification was performed with Merck silica gel 60 (particle size 0.040-0.063mm); the eluting solvent for each purification was determined by thin-layer chromatography (TLC). Analytical TLC was performed with Merck TLC silica gel 60 F254 or Macherey-Nagel POLYGRAM ALOX N/UV254.

^{1}H-NMR chemical shifts are reported in parts per million relative to the residual solvent peak(s) ($CDCl_3$: 7.26 ppm; DMSO-d_6: 2.50 ppm). Multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), or m (multiplet).

^{13}C-NMR chemical shifts are reported in parts per million relative to the residual solvent peaks ($CDCl_3$: 77.10 ppm; DMSO-d_6: 39.60 ppm).

MS data were acquired on Agilent Technologies 6230 TOF LC/MS with ESI source.

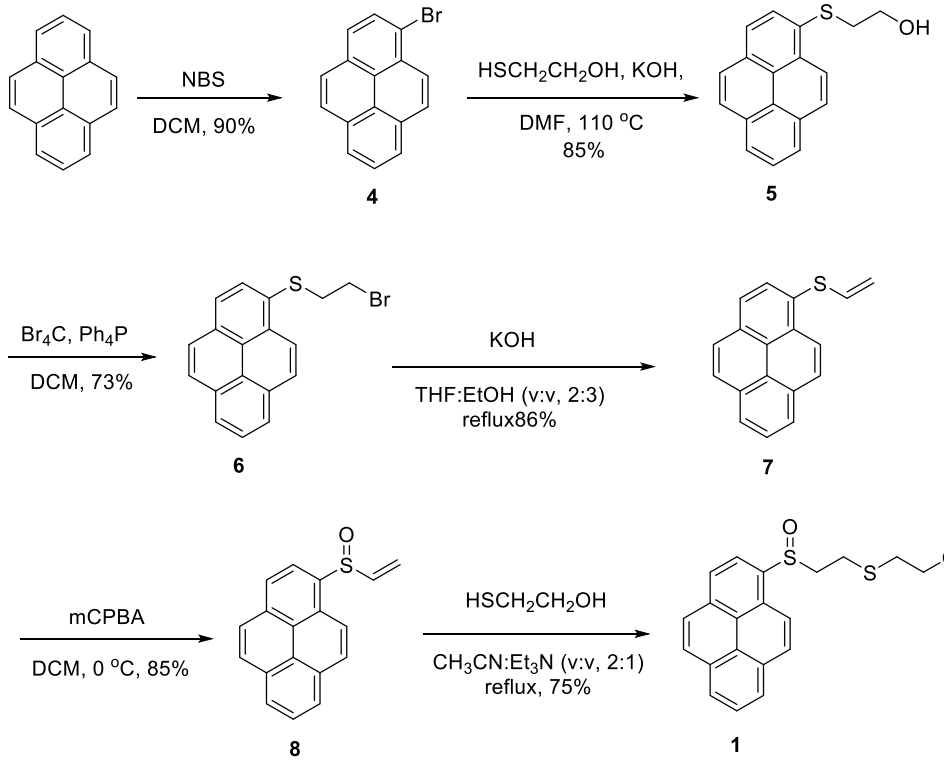
HPLC measurements were carried out on a Shimadzu HPLC LC-20AT, SPD-20A UV/VIS detector, and CTO-20A column oven. Due do only minor differences in molar absorptivity, HPLC analyses were not corrected.

Fluorescence measurements were carried on Edinburgh FLS980 spectrophotometer, using 450W Xenon lamp. Emission spectra were obtained by exciting at the longest wavelength excitation maximum. Absolute quantum yields were measured using an integrating sphere detector from Edinburgh Instruments..

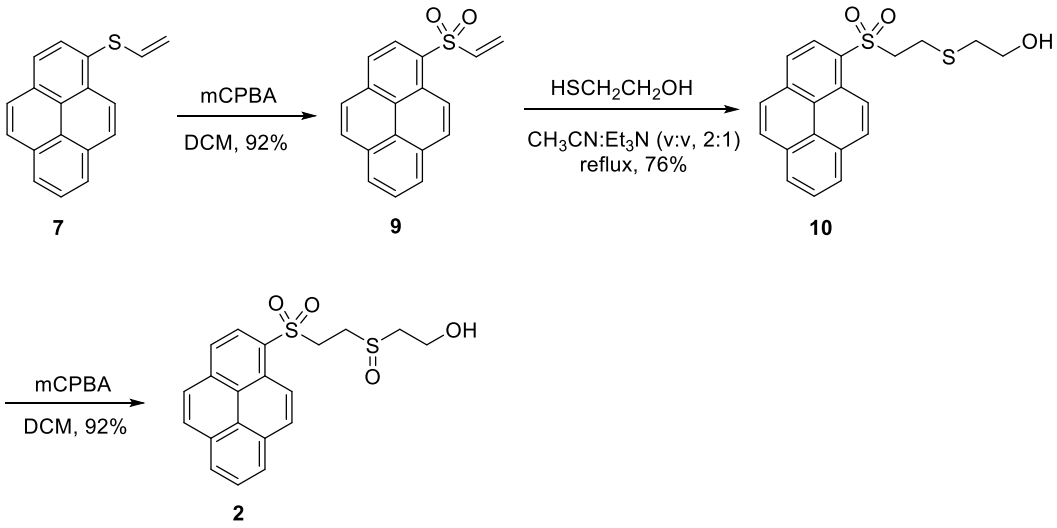
UV measurements were carried out on HITACHI U-3900 Spectrophotometer.

The TLC plate pictures were taken with illumination by a Blak-Ray B-100A/R high-intensity UV Lamp at 365 nm excitation.

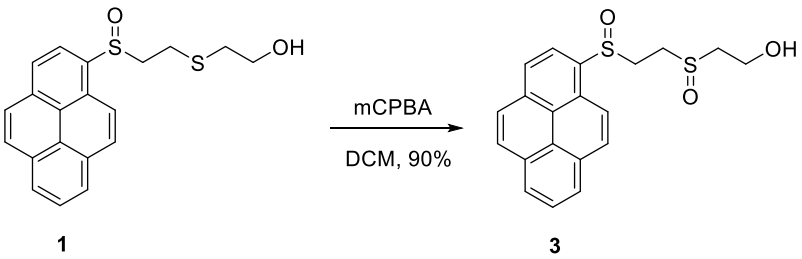
2. Synthetic schemes.



Scheme S1. Synthesis of **1**, **4**-**8**.

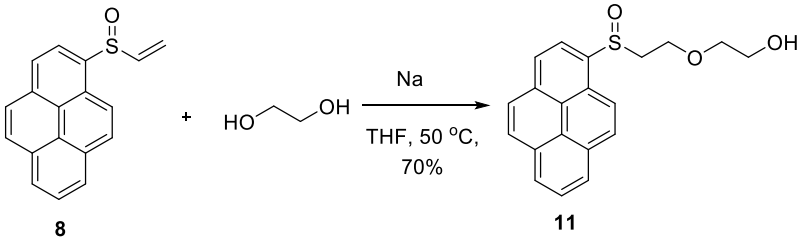


Scheme S2. Synthesis of **2**, **9**, and **10.**

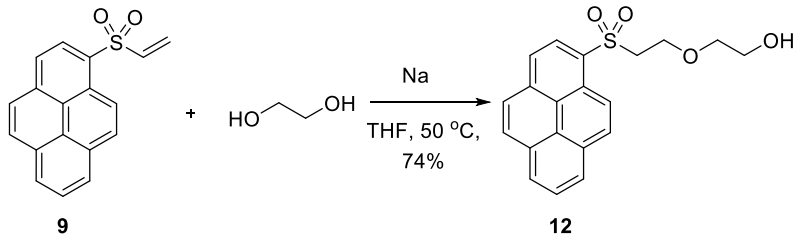


1 3

Scheme S3. Synthesis of **3**.



8 11



9 12

Scheme S4. Synthesis of **11** and **12**.

3. Synthetic procedure and tabulated spectroscopic data.

DCM: Dichloromethane

DMF: *N,N*-Dimethylformamide

THF: Tetrahydrofuran

EtOH: Ethanol

Et_3N: Triethylamine

mCPBA: *m*-Chloroperbenzoic acid

NBS: *N*-Bromosuccinimide

EtOAc: Ethyl acetate

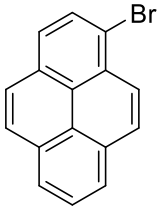
Pet: Petroleum ether

MeOH: Methanol

TPP: 5,10,15,20-Tetraphenylporphyrin

PPh_3: Triphenylphosphine

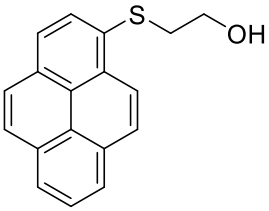
1-Bromopyrene (4)[1]**.**



NBS (2.34 g, 13.2 mmol, 1.05 eq) was added to the solution of pyrene (2.54 g, 12,6 mmol, 1 eq) in DCM (50 mL). The resulting mixture was stirred at room temperature for 2 hours and diluted with DCM (50 mL). The solution was washed with water (50 mL) and brine (50 mL). The organic layer was dried over Na_2SO_4 and concentrated in vacuo. Purified by column chromatography (silica; Hexane) gave **4** (90%).

^{1}H-NMR (400 MHz; $CDCl_3$); δ: 8.40-8.38 (d, J = 9.2 Hz, 1H), 8.21-8.11 (m, 4H), 8.06-7.95 (m, 4H) was consistent with reported literature data.

2-(Pyren-1-ylthio)ethanol (5)[2].



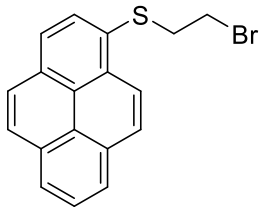
2-Mercaptoethanol (1.91 mL, 2.12 g, 27.1 mmol, 2 eq) and KOH (1.52 g, 27.1 mmol, 2 eq) was dissolved in DMF (dry, 47 mL). The resulting mixture was stirred at room temperature until all KOH was dissolved. 1-Bromopyrene (**4**; 3.81 g, 13.6 mmol, 1 eq) in dry DMF (54 mL) was added to the previous solution. The resulting mixture was kept at 110 ^{o}C for 1 hour and cooled to room temperature before diluted with diethyl ether (350 mL). The mixture was washed by water (150 mL) and brine (150 mL). The organic layer was dried over Na_2SO_4 and concentrated in vacuo. The product was purified by column chromatography (silica; DCM) gave **5** (85%).

^{1}HNMR (400 MHz; $CDCl_3$); δ: 8.63-8.60 (d, J = 9.2 Hz, 1H), 8.09-8.07 (d, J = 7.6 Hz, 2H), 8.04-8.00 (m, 2H), 7.95-7.89 (m, 3H), 7.86-7.84 (d, J = 8.8 Hz, 1H), 3.71-3.67 (m, 2H), 3.19-3.16 (t, J = 6.2 Hz, 2H), 2.87-2.84 (t, J = 5.8 Hz, 1H).

^{13}CNMR (400 MHz; $CDCl_3$); δ: 131.32, 130.98, 130.60, 130.44, 129.69, 128.88, 127.94, 127.42, 126.91, 125.99, 125.20, 125.18, 124.89, 124.60, 124.11, 124.08, 60.45, 38.30.

MS-ESI: calculated for $C_{18}H_{15}OS$ $[M+H]^+$: 279.0844, found 279.0829.

(2-Bromoethyl)(pyren-1-yl)sulfide (6).



To a solution of 2-(pyren-1-ylthio)ethanol (**5**; 1.5 g, 5.4 mmol, 1 eq) and CBr_4 (2.144 g, 6.5 mmol, 1.2 eq) in dry DCM (36 mL), PPh_3 (2.195 g, 6.5 mmol, 1.2 eq) was added. The resulting mixture was stirred at room temperature for 3 hours. The solvent was evaporated and the crude residue was purified by column chromatography (silica; Hexane) to give **6** (73%).

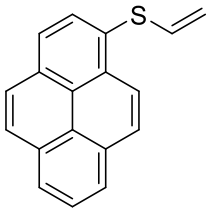
^{1}HNMR (400 MHz; $CDCl_3$); δ: 8.66-8.64 (d, J = 9.2 Hz, 1H), 8.16-8.08 (m, 4H), 8.01-7.96 (m, 3H), 7.92-7.90 (m, J = 8 Hz, 1H), 3.50-3.40 (m, 4H).

^{13}CNMR (400MHz; $CDCl_3$); δ: 132.02, 131.02, 130.95, 130.79, 130.58, 128.20, 127.82, 127.73, 126.89, 126.09, 125.41, 125.38, 124.97, 124.70, 124.26, 124.08,

37.74, 30.30.

MS-ESI: calculated for $C_{18}H_{14}BrS$ $[M+H]^+$: 341.0000, 342.9979, found 340.9998, 342.9968.

Pyren-1-yl(vinyl)sulfide (7).

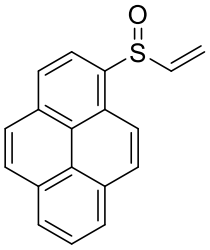


To a solution of (2-bromoethyl)(pyren-1-yl)sulfane (**6**; 1.0236 g, 3 mmol, 1 eq) in THF: EtOH (2:3, 15 mL), KOH (181.8 mg, 3.3 mmol, 1.1 eq) was added. The resulting mixture was kept at reflux for 1 hour, cooled to room temperature and diluted with DCM (90 mL). The solution was washed with water (40 mL) and brine (40 mL). The organic layers were dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography (silica, Hexane) gave **7** (86%).

^{1}HNMR (400 MHz; $CDCl_3$); δ: 8.59-8.56 (d, J = 9.2 Hz, 1H), 8.19-7.97 (m, 8H), 6.71-6.64 (m, 1H), 5.38-5.33 (d, J = 18 Hz, 1H), 5.17-5.13 (d, J = 16.4 Hz, 1H).

MS-ESI: calculated for $C_{18}H_{13}S$ $[M+H]^+$: 261.0738, found 261.0700.

1-(Vinylsulfinyl)pyrene (8).



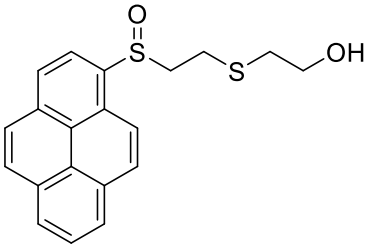
m-CPBA (**7**; 909 mg, 85% assay, 4.4 mmol, 0.9 eq) was added to the solution of pyren-1-yl(vinyl)sulfane (1.2747 g, 4.9 mmol, 1 eq) in DCM (228 mL) at 0 °C. The mixture was kept at room temperature for 2 hours before quenched by saturated $Na_2S_2O_3$ (200 mL) water solution, and the resulting mixture was kept at room temperature for another 30 minutes. The organic layer was separated and washed by water (200 mL) , brine (200 mL) and dried over $MgSO_4$. The solvent was distilled. **8** was purified by column chromatography (silica, Hexane, 85%)

^{1}HNMR (400 MHz; $CDCl_3$); δ: 8.44-8.42 (d, J = 8 Hz, 1H), 8.29-8.27 (m, 1H), 8.24-8.16 (m, 3H), 8.10-7.96 (m, 4H), 6.75-6.68 (m, 1H), 6.35-6.31 (d, J = 16.4 Hz, 1H), 5.86-5.84 (d, J = 9.6 Hz, 1H).

^{13}CNMR (400 MHz; $CDCl_3$); δ: 142.12, 135.12, 133.08, 130.91, 130.18, 129.16, 129.05, 127.81, 127.04, 126.49, 126.37, 126.24, 125.47, 124.33, 124.05, 121.41, 120.50, 119.93.

MS-ESI: calculated for $C_{18}H_{13}OS$ $[M+H]^+$: 277.0687, found 277.1322.

2-((2-(Pyren-1-ylsulfinyl)ethyl)thio)ethanol (1).



Under N_2 protection, 2-mercaptoethanol (70.0 mg, 63.1 µL, 0.9 mmol, 1.1 eq) was added to the solution of 1-(vinylsulfinyl)pyrene (**8**; 225 mg, 0.81 mmol, 1 eq) in CH_3CN: Et_3N (2:1, dry, 36 mL). The resulting mixture was kept at reflux overnight and concentrated in vacuo. 2-((2-(pyren-1-ylsulfinyl)ethyl)thio)ethanol was given by column chromatography (silica, DCM: EtOAc = 2:1, 75%).

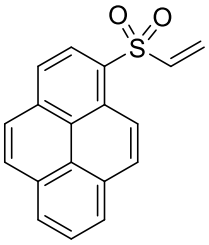
^{1}HNMR (400 MHz; DMSO-d_6); δ: 8.51-8.46 (m, 2H), 8.38-8.10 (m, 7H), 4.81 (s, 1H), 3.51-3.48 (t, *J* = 6.4 Hz, 2H), 3.39-3.31 (m, 1H), 3.19-3.12 (m, 1H), 3.02-2.95 (m, 1H), 2.73-2.67 (m, 1H), 2.61-2.58 (t, *J* = 6.6 Hz, 2H).

^{13}CNMR (400 MHz; DMSO-d_6); δ: 136.17, 132.59, 130.70, 129.99, 129.31, 128.99, 127.31, 126.98, 126.81, 126.61, 126.50, 125.40, 123.58, 123.47, 121.46, 120.61, 60.84, 56.02, 34.14, 24.49.

MS-ESI: calculated for $C_{20}H_{19}O_2S_2$ $[M+H]^+$: 355.0826, found 355.0851.

1 was determined to be >99% pure by HPLC analysis. (See Section 5 for conditions.)

1-(Vinylsulfonyl)pyrene (9).



m-CPBA (447 mg, 85% assay, 2.2 mmol, 2.2 eq) was added to **7** (260 mg, 1 mmol, 1 eq) in DCM (30 mL) at 0 °C. The resulting mixture was kept at room temperature for 1 hour before it was quenched by saturated $Na_2S_2O_3$ water solution (30 mL). The mixture was kept at room temperature for another 30 minutes and washed by water (20 mL) and brine (20 mL). The organic layer was dried over Na_2SO_4 and concentrated in vacuo and purified by column chromatography (silica, Pet :EtOAc =5:1, 92%) gave **9**.

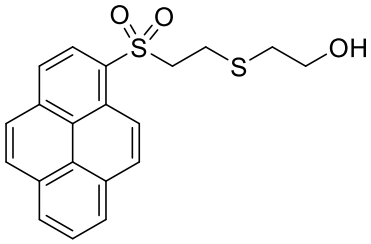
^{1}HNMR (400 MHz; $CDCl_3$); δ: 8.93-8.91 (d, *J* = 9.2 Hz, 1H), 8.76-8.74 (d, *J* = 8Hz, 1H), 8.32-8.19 (m, 5H), 8.11-8.06 (m, 2H), 6.90-6.84 (m, 1H), 6.65-6.61

(d, J = 16.4 Hz, 1H), 6.09-6.06 (d, J = 10 Hz, 1H).

^{13}CNMR (400 MHz; $CDCl_3$); δ: 139.02, 135.75, 133.92, 130.87, 130.80, 130.45, 130.28, 130.02, 129.89, 129.08, 128.35, 127.36, 127.30, 127.22, 127.06, 126.95, 124.40, 122.75.

MS-ESI: calculated for $C_{18}H_{13}O_2S$ $[M+H]^+$: 293.0636, found 293.0634.

2-((2-(Pyren-1-ylsulfonyl)ethyl)thio)ethan-1-ol (10).



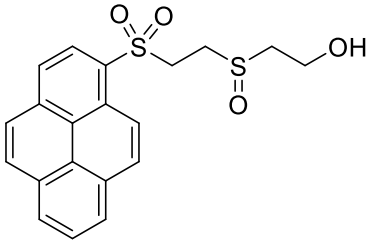
2-Mercaptoethanol (117 mg, 1.5 mmol, 1.5 eq) was added to the solution of **9** (292 mg, 1 mmol, 1 eq) in CH_3CN: Et_3N (2:1, dry, 12 mL) under nitrogen protection. The resulting mixture was kept at reflux for 4 hours. The mixture was concentrated in vacuo and purified by column chromatography gave**10** (silica, Pet: EtOAc = 2:1, 76%).

^{1}HNMR (400 MHz; $CDCl_3$); δ: 9.01-8.99 (d, J = 9.2 Hz, 1H), 8.67-8.65 (d, J = 8.4 Hz, 1H), 8.32-8.29 (t, J = 7.2 Hz, 3H), 8.23-8.20 (m, 2H), 8.12-8.06 (m, 2H), 3.67-3.60 (m, 4H), 2.87-2.83 (m, 2H), 2.62-2.59 (t, J = 5.8 Hz, 2H).

^{13}CNMR (400 MHz; $CDCl_3$); δ: 134.11, 130.94, 130.90, 129.99, 129.60, 129.19, 127.81, 127.47, 127.32, 127.06, 127.04, 125.14, 124.24, 123.94, 122.36, 60.88, 56.60, 35.19, 24.54.

MS-ESI: calculated for $C_{20}H_{19}O_3S_2$ $[M+H]^+$: 371.0776, found 371.0791.

2-((2-(Pyren-1-ylsulfonyl)ethyl)sulfinyl)ethan-1-ol (2).



m-CPBA (97 mg, 85% assay, 0.48 mmol, 0.9 eq) was added to **10** (197 mg, 0.53 mmol, 1 eq) in DCM (30 mL) at 0 °C. The resulting mixture was kept at room temperature for 1 hour before it was quenched by saturated $Na_2S_2O_3$ water solution (30 mL). The resulting solution was kept at room temperature for another 30 minutes and washed by water

(30 mL) and brine (30 mL). The organic layer was dried by Na_2SO_4 and concentrated in vacuo. **2** was gotten by column chromatography (silica, DCM: EtOAc =1:1, 92%)

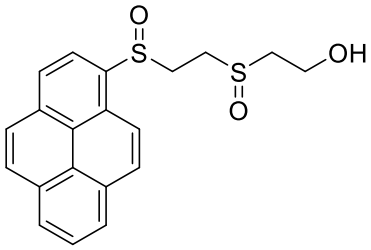
^{1}HNMR (400 MHz; DMSO-d_6); δ: 9.00-8.97 (d, *J* = 9.6 Hz, 1H), 8.67-8.65 (d, *J* = 8.4 Hz, 1H), 8.57-8.46 (m, 5H), 8.36-8.34 (d, *J* = 9.2 Hz, 1H), 8.27-8.24 (t, *J* = 7.6 Hz, 1H), 4.96-4.94 (t, *J* = 5.0 Hz, 1H), 3.99-3.85 (m, 2H), 3.70-3.59 (m, 2H), 3.24-3.17 (m, 1H), 3.03-2.96 (m, 1H), 2.91-2.84 (m, 1H), 2.79-2.73 (m, 1H).

^{13}CNMR (400 MHz; DMSO-d_6); δ: 135.31, 130.97, 130.81, 130.55, 129.80, 129.63, 128.49, 127.75, 127.70, 127.48, 127.22, 124.64, 124.30, 123.16, 122.41, 54.15, 53.88, 48.83, 43.31.

MS-ESI: calculated for $C_{20}H_{19}O_4S_2$ $[M+H]^+$: 387.0725, found 387.0746.

2 was determined to be >99% pure by HPLC analysis. (See Section 5 for conditions.)

2-((2-(Pyren-1-ylsulfinyl)ethyl)sulfinyl)ethan-1-ol (3).



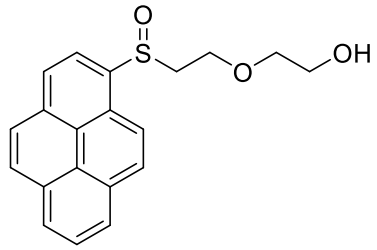
m-CPBA (36 mg, 85% assay, 0.18 mmol, 0.9 eq,) was added to the solution of 2-((2-(pyren-1-ylsulfinyl)ethyl)thio)ethanol (69.1 mg, 0.2 mmol, 1 eq) in DCM : DMF (5:1, 6 mL) at 0 °C. The resulting mixture was kept at room temperature for 2 hours and quenched by saturated $Na_2S_2O_3$ water solution (6 mL). The resulting solution was kept at room temperature for another 30 minutes before it was washed by water (6 mL) and brine (6 mL). The organic layer was dried over Na_2SO_4 and concentrated in vacuo. **3** was purified by column chromatography (silica, DCM: MeOH = 20:1, 90%).

^{1}HNMR (400 MHz; $CDCl_3$); δ: 8.57-8.55 (d, *J* = 8 Hz, 1H), 8.38-8.36 (d, *J* = 8 Hz, 1H), 8.32-8.29 (m, 2H), 8.25-8.18 (m, 3H), 8.14-8.08 (m, 2H), 4.12-4.07, (m, 2H), 3.67-3.59 (m, 1H), 3.46-3.25 (m, 2H), 3.01-2.73 (m, 4H).

^{13}CNMR (400 MHz; DMSO-d_6); δ: 135.67, 133.00, 130.92, 130.21, 129.65, 129.33, 127.55, 127.25, 127.01, 126.91, 126.81, 125.57, 123.88, 123.68, 121.79, 120.90, 54.75, 54.29, 47.81, 43.09.

MS-ESI: calculated for $C_{20}H_{19}O_3S_2$ $[M+H]^+$: 371.0776, found 371.0781.

2-(2-(Pyren-1-ylsulfinyl)ethoxy)ethan-1-ol (11).



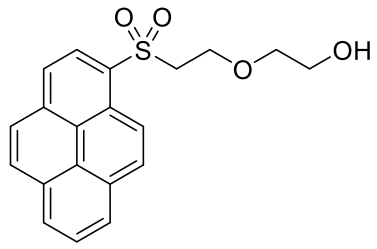
A piece of sodium was added to Ethylene glycol (3 mL) and kept stirring at 0°C until the sodium solid disappeared. The resulting mixture was added to the solution of **8** (138 mg, 0.5 mmol, 1 eq) in THF (dry, 3 mL), and the mixture was kept at 50°C overnight. The solvent was diluted by DCM (10 mL), and washed by water (6 mL) and brine (6 mL). The organic layer was dried over Na_2SO_4 and concentrated in vacuo. **11** was purified by column chromatography (silica, DCM:MeOH = 30:1, 70%).

^{1}HNMR (400 MHz; $CDCl_3$); δ: 8.56-8.54 (d, J = 8 Hz, 1H), 8.26-8.24 (d, J = 8.4 Hz, 1H), 8.19-7.98 (m, 7H), 4.08-4.02 (m, 1H), 3.79-3.74 (m, 3H), 3.62-3.58 (m, 2H), 3.29-3.23 (m, 4H), 3.25-3.07 (m, 2H).

^{13}CNMR (400 MHz; $CDCl_3$); δ: 135.85, 133.16, 131.03, 130.26, 129.20, 129.03, 127.41, 127.16, 126.58, 125.44, 126.30, 125.40, 124.24, 124.15, 121.05, 120.35, 72.62, 64.16, 61.62, 57.19.

MS-ESI: calculated for $C_{19}H_{20}O_3S$ $[M+H]^+$: 339.1055, found 339.1071.

2-(2-(Pyren-1-ylsulfonyl)ethoxy)ethan-1-ol (12).



A piece of sodium was added to Ethylene glycol (3 mL) and kept stirring at at 0°C until the sodium solid disappeared. The resulting mixture was added to the solution of **9** (146 mg, 0.5 mmol, 1 eq) in THF (dry, 3 mL), and the mixture was kept at 50°C overnight. The solvent was diluted by DCM (10 mL), and washed by water (6 mL) and brine (6 mL). The organic layer was dried over Na_2SO_4 and concentrated in vacuo. **12** was purified by column chromatography (silica, DCM:MeOH = 40:1, 74%).

^{1}HNMR (400 MHz; $CDCl_3$); δ: 8.93-8.91 (d, J = 9.6 Hz, 1H), 8.62-8.60 (d, J = 8.4 Hz, 1H), 8.20-7.92 (m,7H), 3.85-3.82 (t, J = 6 Hz, 2H), 3.67-3.64 (t, J = 5.8 Hz, 2H), 3.41-3.32 (m, 4H), 2.32 (s, 1H).

^{13}CNMR (400 MHz; DMSO-d_6); δ: 135.21, 130.81, 130.64, 130.54, 130.10, 129.60, 128.48, 127.70, 127.57, 127.38, 127.36, 127.19, 124.61, 124.24, 123.16, 122.51, 60.74, 56.28, 34.06, 24.44.

MS-ESI: calculated for $C_{20}H_{29}O_4S$ $[M+H]^+$: 355.1004, found 355.1031.

4. Optical data and spectra.

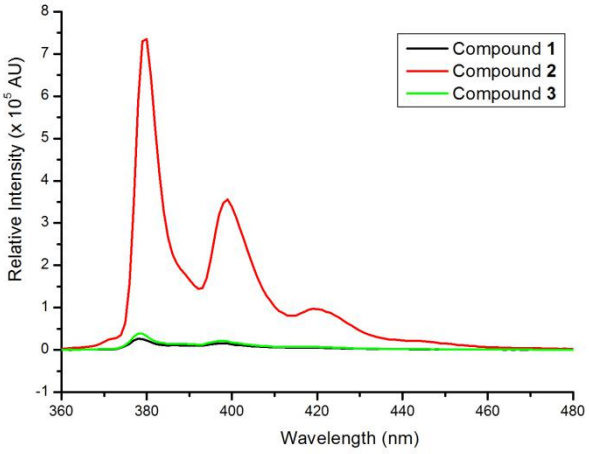


Figure S1. Emission spectra of **1**, **2** and **3**.
In THF at 10^{-6} M; excitation wavelength 350 nm.

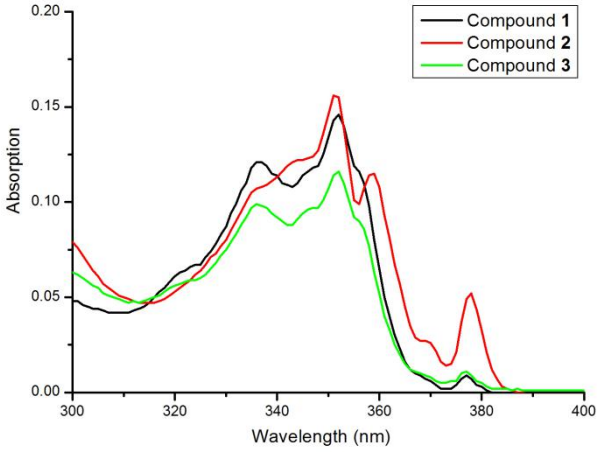


Figure S2. UV spectra of **1**, **2**, and **3.**
In THF at 10^{-6} M.

Table S1. Quantum yields of **1**, **2**, and **3**.[a]

	Compound **1**	Compound **2**	Compound **3**
ϕ	0.01	0.55	0.01

[a] In THF at 10^{-6} M.

5. Photochemical studies.

HPLC conditions: Symmetry C18 - 3.5 µm column (4.6 mm × 150 mm). 35% acetonitrile: 65% water eluent, 1 mL/min flow rate. Retention times of the **1**, **2**, and **3** were 21.67, 10.71 and 6.48 minutes, respectively. Identical conditions were used for determining the purity of **1**–**3**.

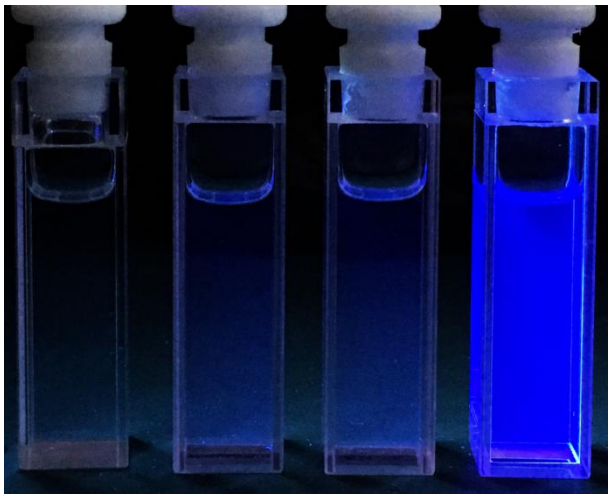


Figure S1. Emission from **1**, **2** and **3** excited at 365 nm.
Left to right: THF, **1**, **3**, and **2**. In THF at 10^{-6} M.

5.1 Effect of solvent composition on the photooxidation of 1.

1 was dissolved in differing ratios of MeOH:THF to provide 10^{-5} M solutions. TPP was added at 0.05 mg/mL. The mixtures were placed under a pure oxygen atmosphere and irradiated by sodium lamp for 5 hours. The resulting mixture was analyzed by TLC and HPLC.

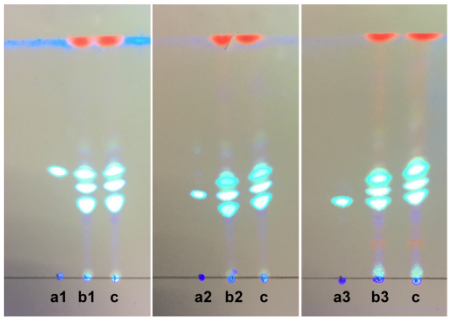


Figure S2. TLC analysis for photooxidation reactions of **3** in 90% MeOH:10% THF, eluting with DCM:MeOH = 25:2. Lanes a1, a2, a3 are **1**, **3**, and **2**, respectively. Lanes b1, b2, b3 are cospot lanes. Lanes c are the reaction mixtures. The red band at the solvent front is the sensitizer, TPP.

Table S2. Proportions of **2** and **3** as a function of solvent composition**.**

Solvent MeOH: THF	Percentage of compound **2**	Percentage of compound **3**
1:9	6%	94%
3:7	14%	86%
5:5	33%	67%
7:3	33%	67%
9:1	52%	48%

5.2. Evaluation of concentration effects in the photooxidation of 3.

1 was dissolved in THF:MeOH (7:3) to obtain solutions of different concentration: 10^{-4} M, 10^{-5} M, 10^{-6} M, 10^{-7} M. TPP was added at 0.05mg/mL. The resulting mixture was kept at 24 °C under oxygen and sodium lamp irradiation for 5 hours. The resulting solution of concentration 10^{-4} M was analyzed by HPLC directly. Solutions of at 10^{-5} M, 10^{-6} M, and 10^{-7} M were concentrated in vacuo prior to HPLC analysis.

Table S3. Percentage formation of **2** and **3** as a function of concentration.[a]

Concentration	Percentage of **2**	Percentage **3**
10^{-4} M	17%	83%
10^{-5} M	27%	73%
10^{-6} M	33%	67%
10^{-7} M	48%	52%

[a] All reactions reached complete conversion, with no detectable products other than **2** and **3**.

5.3 Peroxide byproduct detection.

Driven by curiosity, we tested for the formation of hydrogen peroxide and/or THF peroxides under our standard photolysis conditions. A sensitizer blank (0.05 mg/mL) in 7:3 THF:MeOH was compared with an identical solution containing compound **1** at 10^{-4} M. After photolysis, the resulting solutions were analyzed with enzymatic

peroxide test strips (Figure S3). As can be seen, in the presence of sulfide **1** is there clear formation of some peroxide byproduct(s). This is consistent with the idea that the excited state of the sensitizer could be reduced by sulfide **1**, forming the sensitizer radical anion. This is turn could reduce oxygen (especially $^1O_2$) to form superoxide, which could then lead to H_2O_2 production.[S3] However, the oxidation of sulfides with H_2O_2 at RT is slow in the absence of a catalyst, and the oxidation of sulfoxides even more so. We believe that H_2O_2 production may be a good indication of TPP bleaching, but is not relevant to the formation of **2** or **3** under our standard reaction conditions.

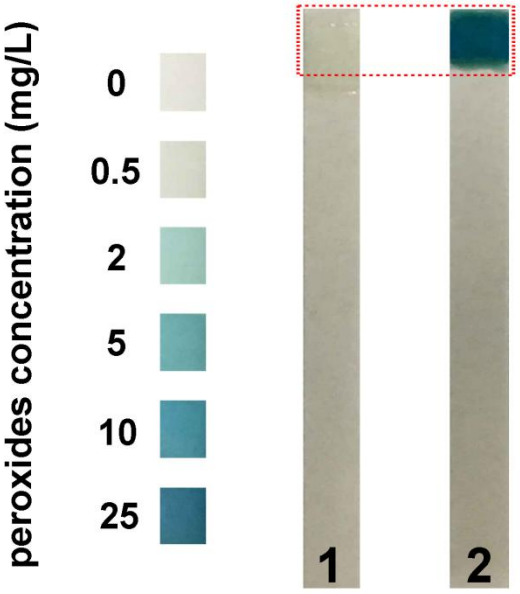


Figure S3. Peroxide content analysis of blank photooxidation and photoxidation of **1**.

5.4 The presence of a sulfide is essential for "$^1O_2$ capture."

Compound **11** was dissolved in THF:MeOH (7:3) to obtain a 10^{-4} M solution. TPP was added at 0.05mg/mL. The resulting mixture was photolyzed under pure oxygen with sodium lamp for 5 hours. The resulting mixture was analyzed by TLC and compared with compound **12**. There is no evidence for photooxidation of **11** to **12**, consistent with the intermediacy of a persulfoxide intermediate in the conversion of **1** to **2**.

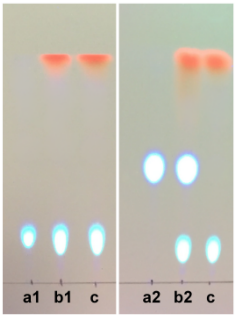


Figure S4. The TLC plate of resulting mixture by using compound **11** as the starting material. **a1** and **a2** are **11** and **12**, respectively. **b1, b2** are mixed points. **c** are the reaction mixtures. The left TLC plate was eluted with DCM:EtOAc = 2:3, and the right with DCM:EtOAc = 1:1.

6.1. On the partitioning between 2 and 3 upon photooxidation of 1.

Our observations regarding the increased formation of **2** relative to **3** in the presence of hydroxylic solvents are unexpected. It has been established that the presence of even small amounts of hydroxylic solvent stabilize peroxysulfide intermediates relative to direct decomposition to sulfide and $^3O_2$.[S4] In methanol, the peroxysulfide derived from Et_2S persists for ca. 5 μs, and partitions roughly 9:1 between oxidation and regeneration of $^3O_2$.[S5] (In comparison, the partitioning in benzene is 1:9, favoring re-formation of $^3O_2$.)

However, this does not explain why further increases in the proportion of CH_3OH should favor the formation of intramolecular product **2** vs. intermolecular product **3** (roughly linearly; Table 1 of manuscript). As noted in the manuscript (ref. 19) this is in direct contrast to the literature precedent for intra/intermolecular partitioning in 1,4-dithiane.

One possible explanation is that, because we chose a hydroxyethyl fragment as a solubilizing group, we may have opened an alternative reaction pathway involving a sulfurane intermediate (Figure S5).[S7] Such intermediates are known to form in intramolecular systems, and would clearly possess distinct reactivity, and have been proposed to be relevant in systems involving hydroxylic solvents.[S7] However, the equilibrium formation of a 4-membered ring sulfurane would almost certainly not favor the cyclic sulfurane. An alternative explanation for the influence of CH_3OH follows in the next section.

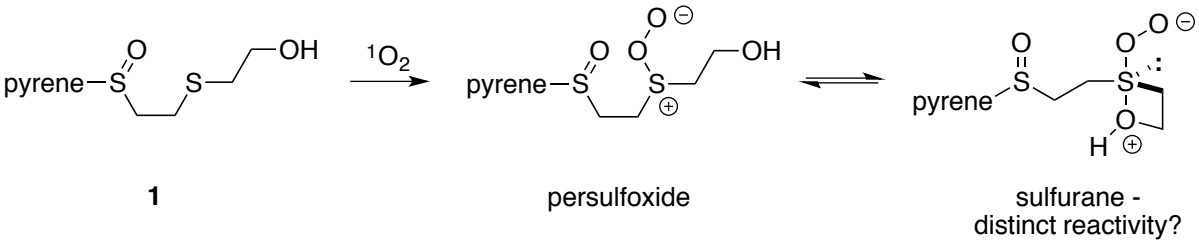


Figure S5. A possible a sulfurane intermediate with reactivity distinct from the persulfoxide precursor.

6.2. On the kinetics of the photooxidation of 1.

Here we present what we can only refer to as “qualitative” kinetic data. True, quantitative data would be particularly difficult to obtain. Among the reasons for this are:

- It is not easy to measure, or consistently maintain, [$^1O_2$].
- We worry about consistent TPP dissolution above 70:30 CH_3OH:THF.
- We worry about [TTP] because we use only catalytic amounts. We do use

stock solutions, but they are so dilute that there's a lot of room for error from solution to solution, because of initial weighing error.

- The rate-limiting step appears to change as a function of solvent composition. The rate of reaction is definitely solvent dependent: The reaction slows down as % CH_3OH increases, but in a non-linear way.
- We don't know how much we need to worry about TPP bleaching as a function of time or solvent composition. This in turn means that we do not know how much superoxide we might generating by electron transfer from the TPP excited state to $^1O_2$.

These concerns expressed, the kinetic data we have acquired are informative. Beyond the general observation that the reaction slows with increased [CH_3OH], there is clear variation in the depletion of **1** as a function of solvent composition (Figure S6).

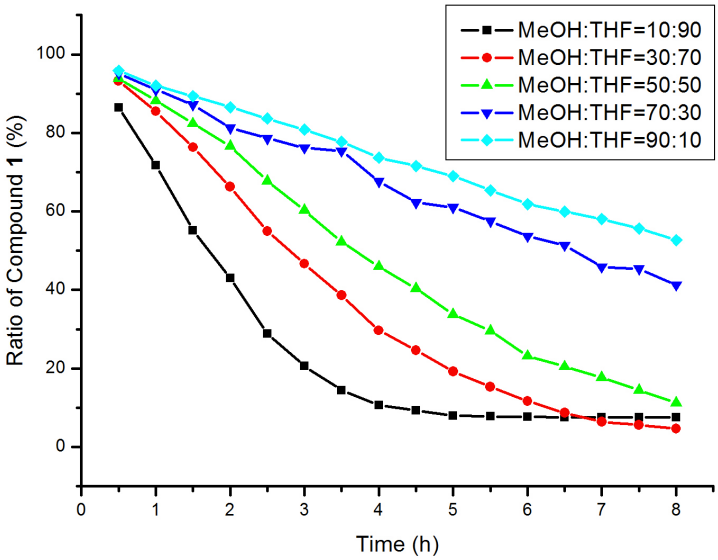


Figure S6. Decay of % **1** as a function of solvent composition (Initial [**1**] = 10^{-4} M).

Inspecting the above, the most striking feature is that at the lowest [CH_3OH] there is a distinct curvature to the plot, whereas it becomes almost linear at the highest [CH_3OH]. At first one might be tempted to explain this as a shift from bimolecular to unimolecular kinetic behavior, as expected for a shift from bimolecular to unimolecular oxygen atom transfer. (That is, a shift from **3** to **2** as the major product.)

However, this cannot be the case – even at the highest [CH_3OH], the product ratio is ~ 1:1 **3**:**2**. An alternative explanation is that the data reflect a change in rate-determining step, such that at low [CH_3OH], oxygen atom transfer is rate-limiting, while at high [CH_3OH], some step before oxygen atom transfer becomes rate-limiting. The only viable candidate for a rate-limiting step that precedes oxygen atom transfer

is the formation of the persulfoxide intermediate itself. (The rate of $^1O_2$ is essentially solvent-independent.)

This would be consistent with the formation of a CH_3OH adduct with the persulfoxide intermediate that is either unreactive, or substantially less reactive that the free persulfoxide. Reversible formation of such an intermediate could lead to a situation in which the liberation of free persulfoxide is the rate-limiting step in the overall oxidative process (Scheme S7). While the $^1O_2$ reaction of sulfides in alcohol solvents is surprisingly complex, such an explanation is neither unreasonable nor wholly unprecedented.[S4,S7]

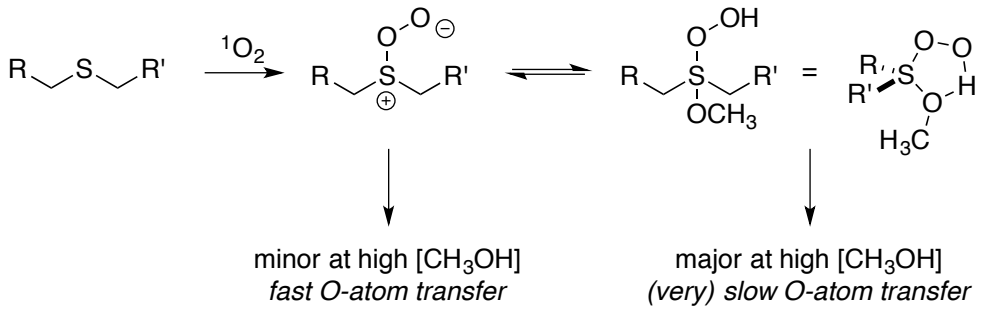


Figure S7. A plausible scenario explaining a change in rate-determining step as a function of [CH_3OH]. Sulfide substituents abbreviated as R/R' for simplicity.

7. References

S1. Xu Q, Ma H, Yip H, Jen AKY. Nanotechnology. 2008; 19: 135605.

S2. Sipila K, Hase T. Syn. Comm. 1997; 27: 1391-1393.

S3. Clennan, EL. Personal communication.

S4. a. Clennan EL, Greer A. Effects of alcohols on the photooxidative behavior of diethylsulfide. J. Org. Chem. 1996; 61: 4783–4797. b. Bonesi SM, Albini A. Effect of protic cosolvents on the photooxygenation of diethyl sulfide. J. Org. Chem. 2000; 65: 4532–4536. See also manuscript ref. 2.

S5. Gu CL, Foote, CS. J. Am. Chem. Soc. 1982; 104: 6060–6063.

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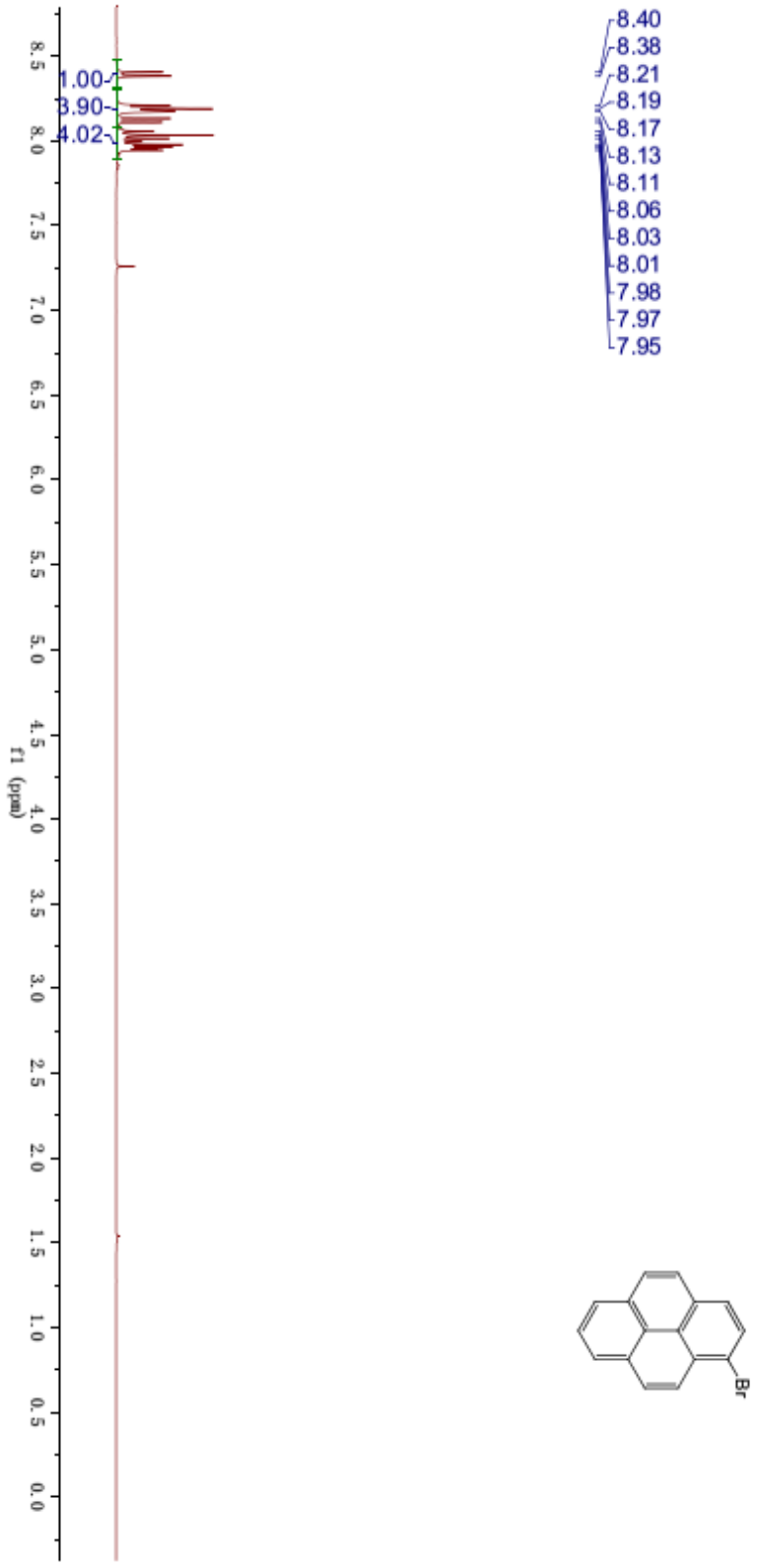
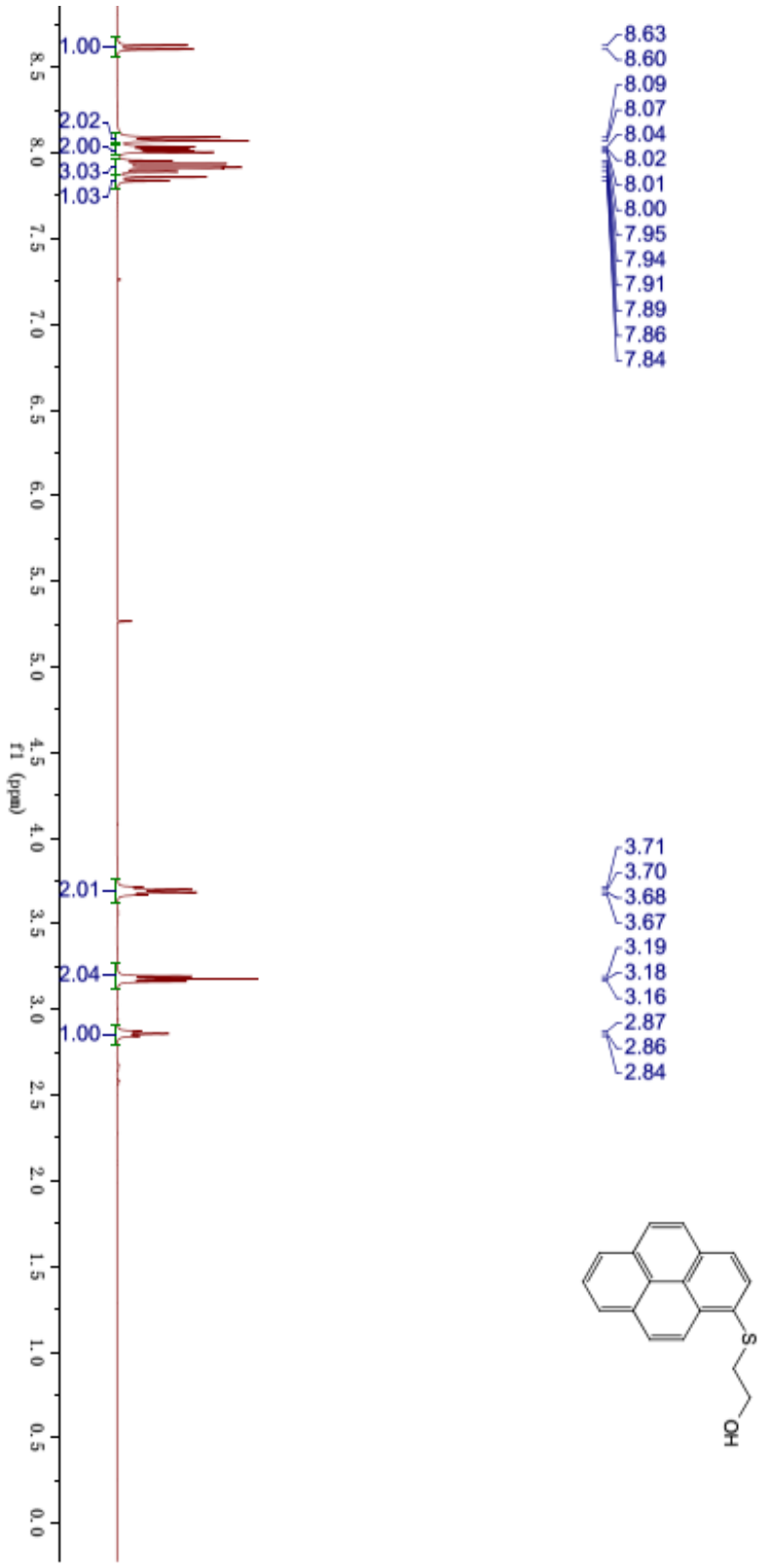
S7. Clennan EL. New Mechanistic and Synthetic Aspects of Singlet Oxygen Chemistry Tetrahedron. 2009; 56: 9151–9179. See also manuscript ref. 6.

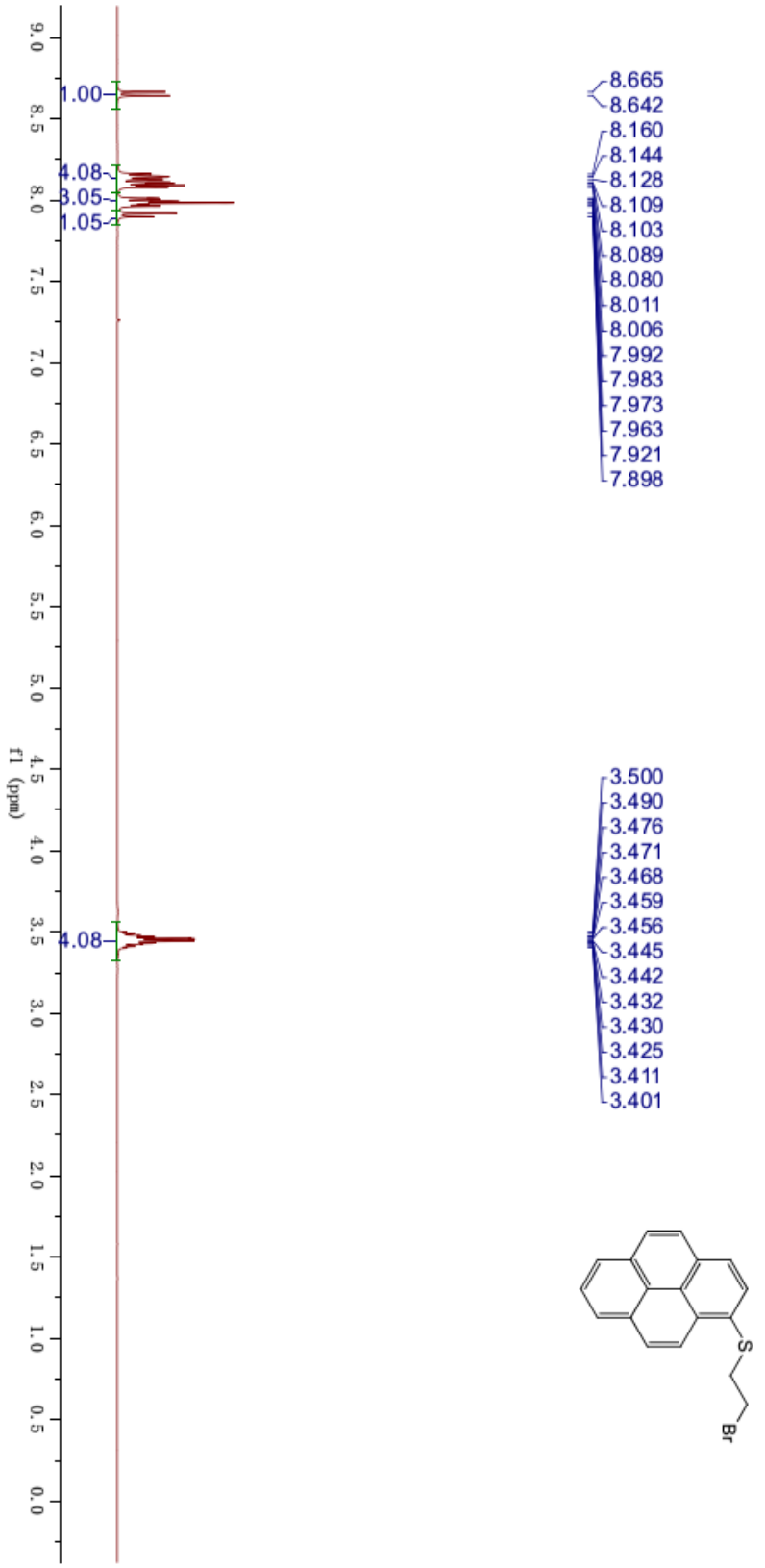
8. NMR and MS spectrum.



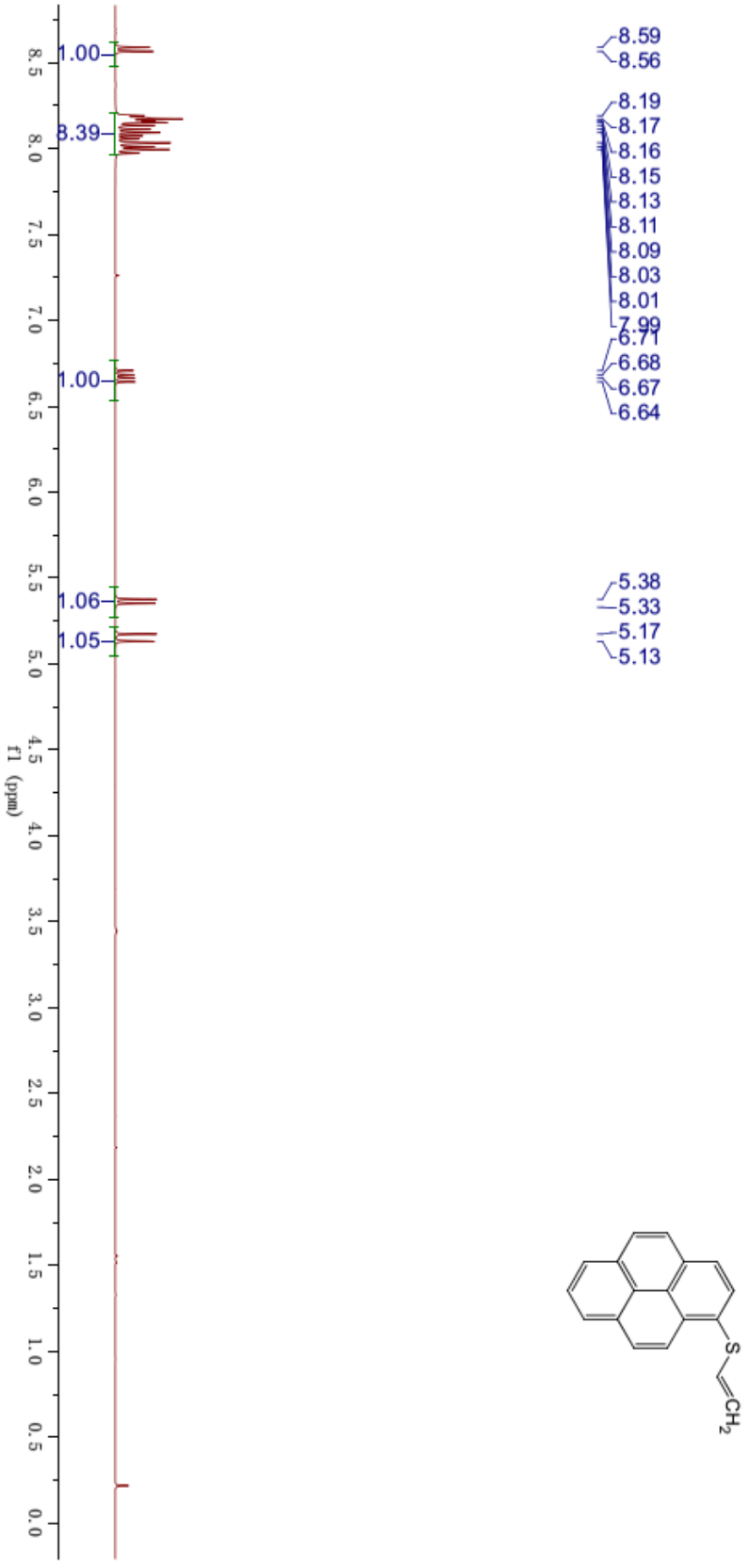
^{1}H-NMR spectrum of **4** (in $CDCl_3$)



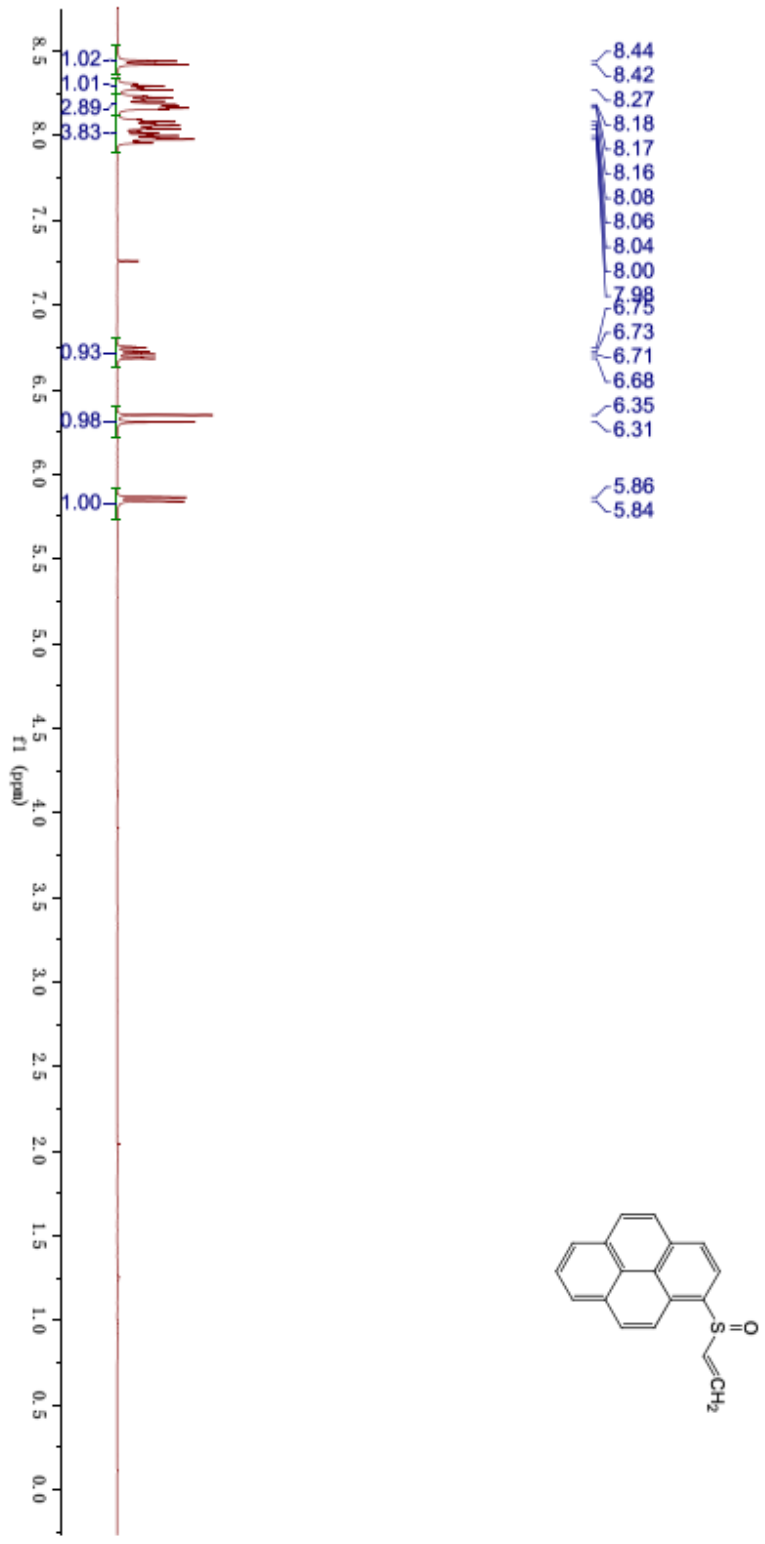
^{1}H-NMR spectrum of **5** (in $CDCl_3$)



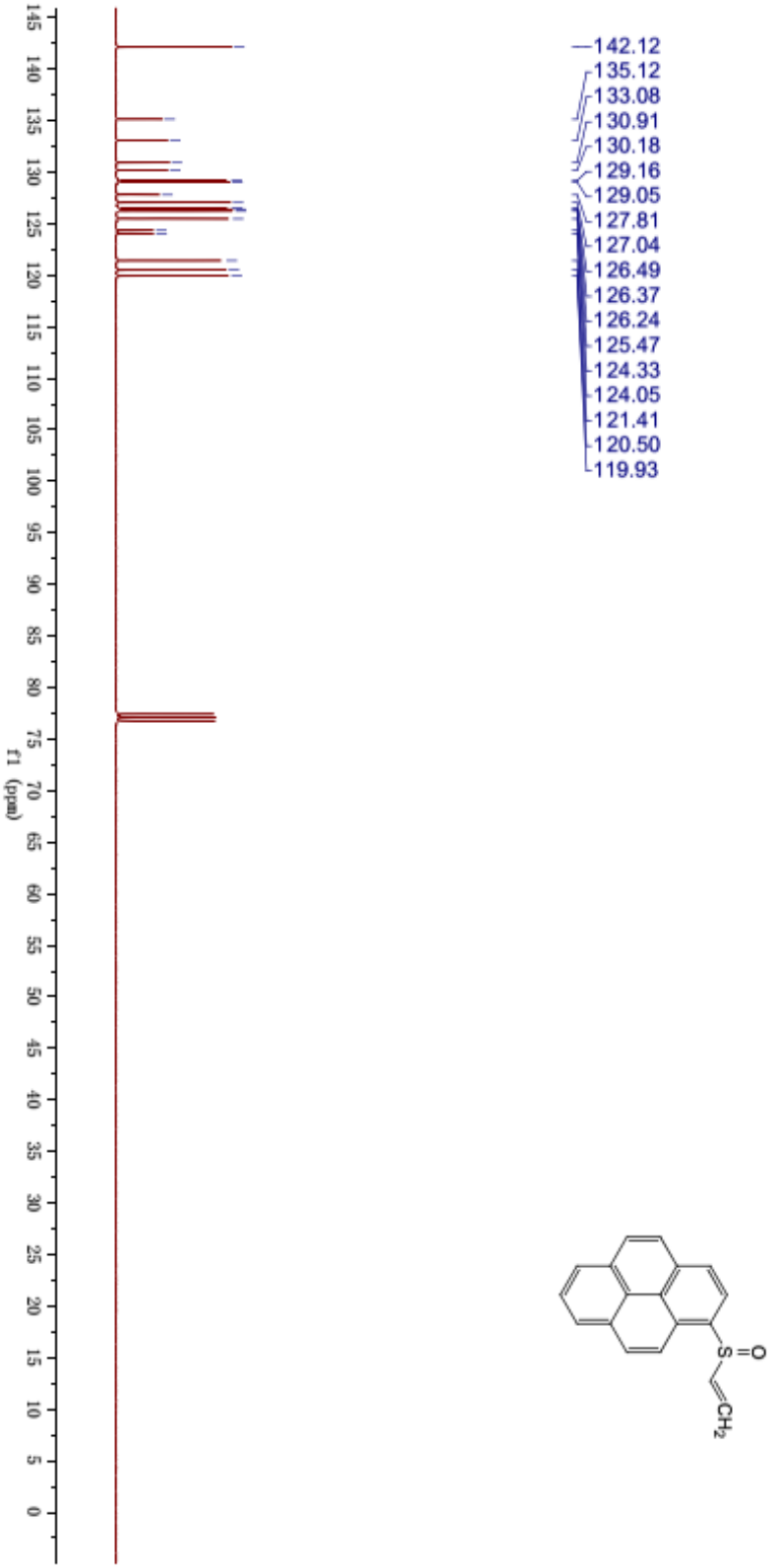
^{1}H-NMR spectrum of **6** (in $CDCl_3$)



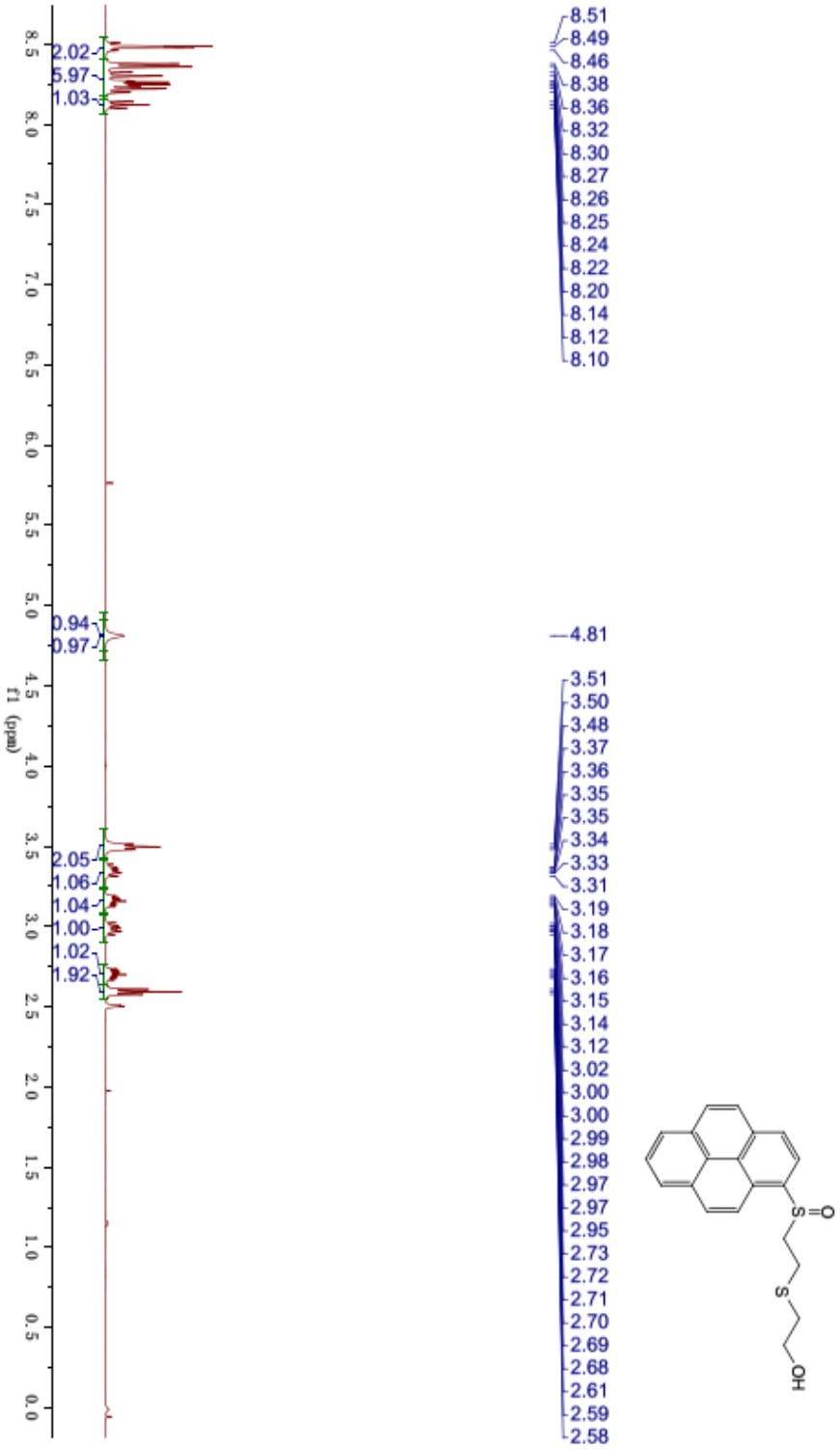
^{1}H-NMR spectrum of **7** (in $CDCl_3$)



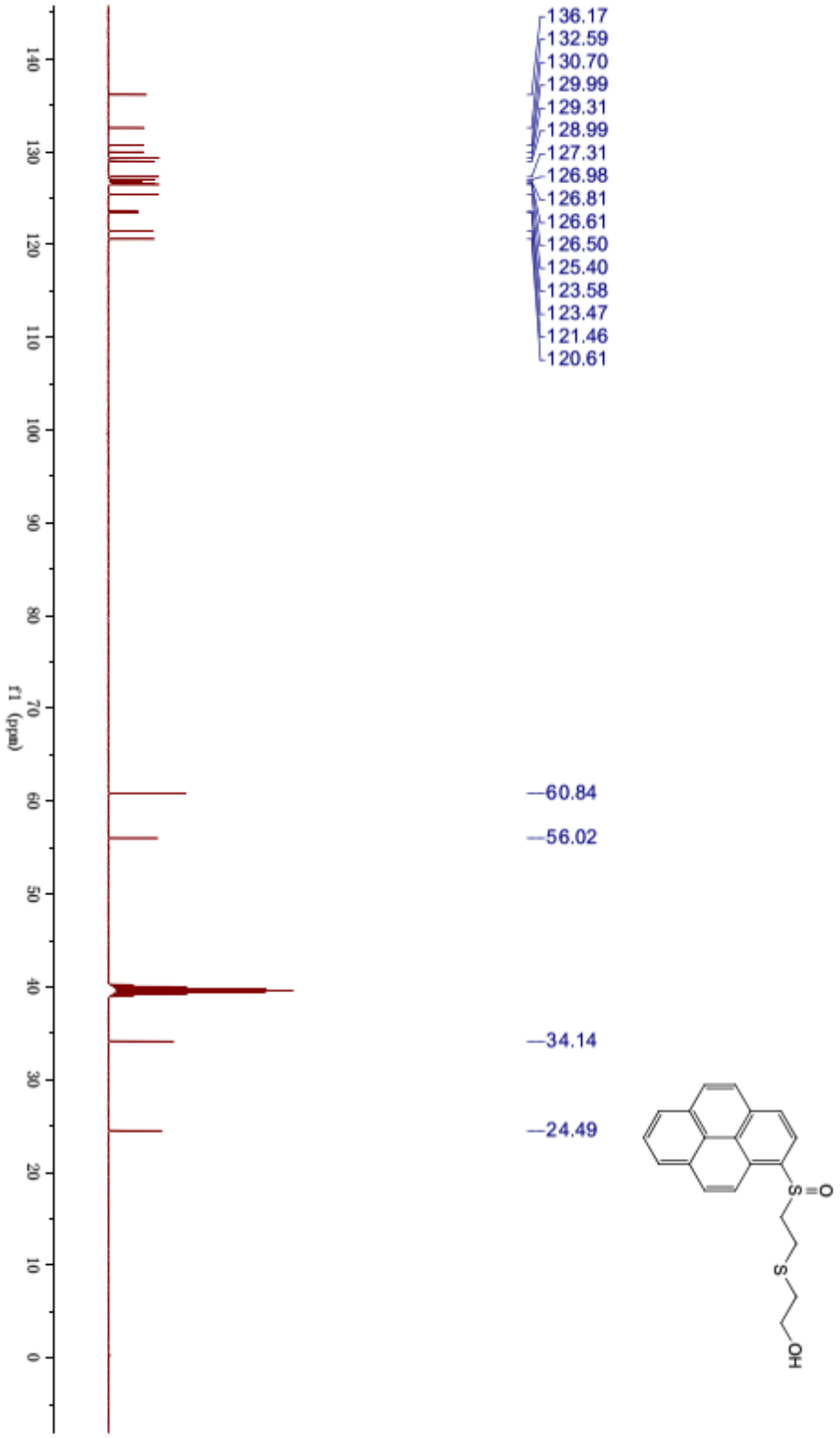
^{1}H-NMR spectrum of **8** (in $CDCl_3$)



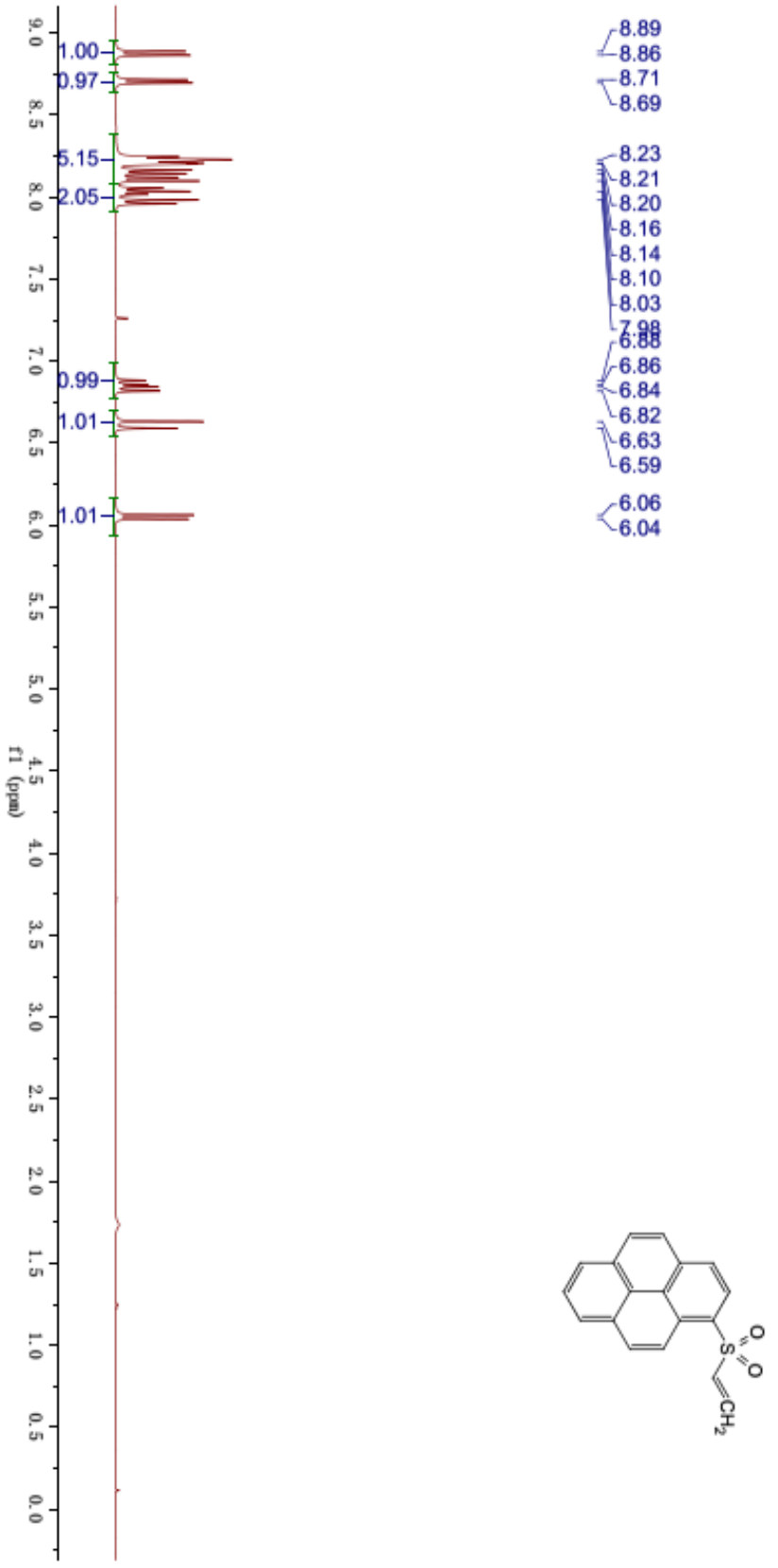
^{13}C-NMR spectrum of **8** (in $CDCl_3$)



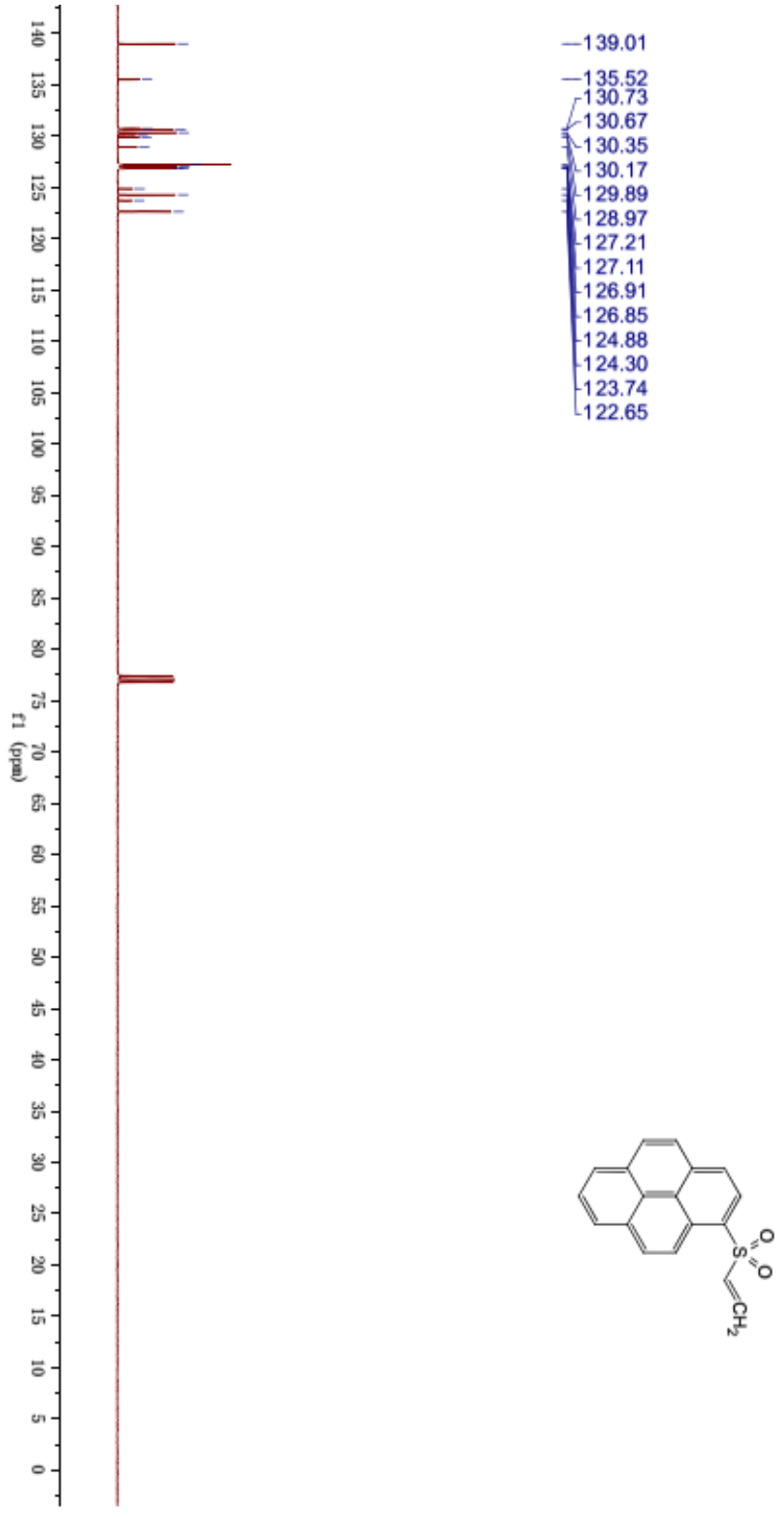
^{1}H-NMR spectrum of **1** (in DMSO-d_6)



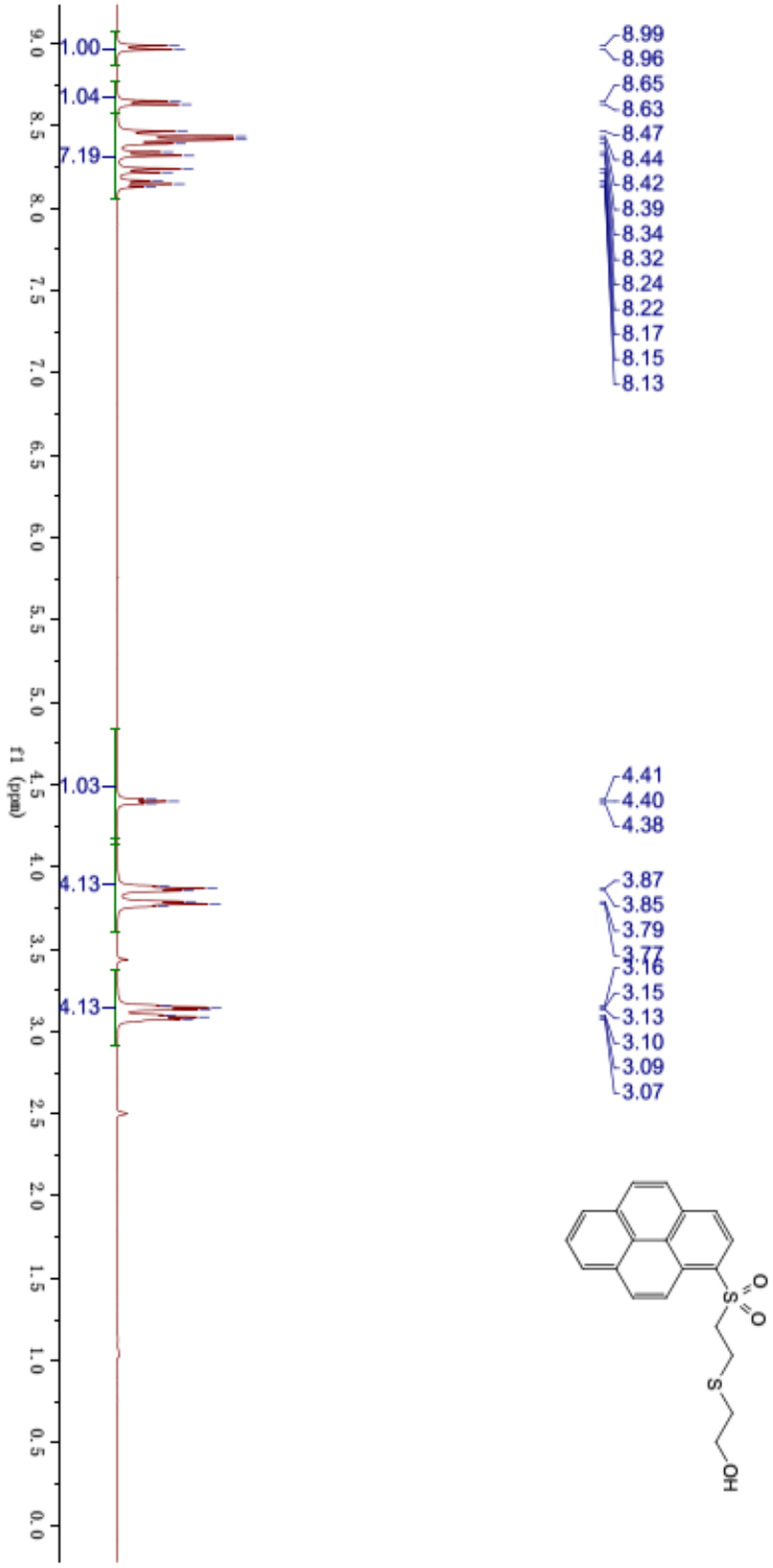
^{13}C-NMR spectrum of **1** (in DMSO-d_6)



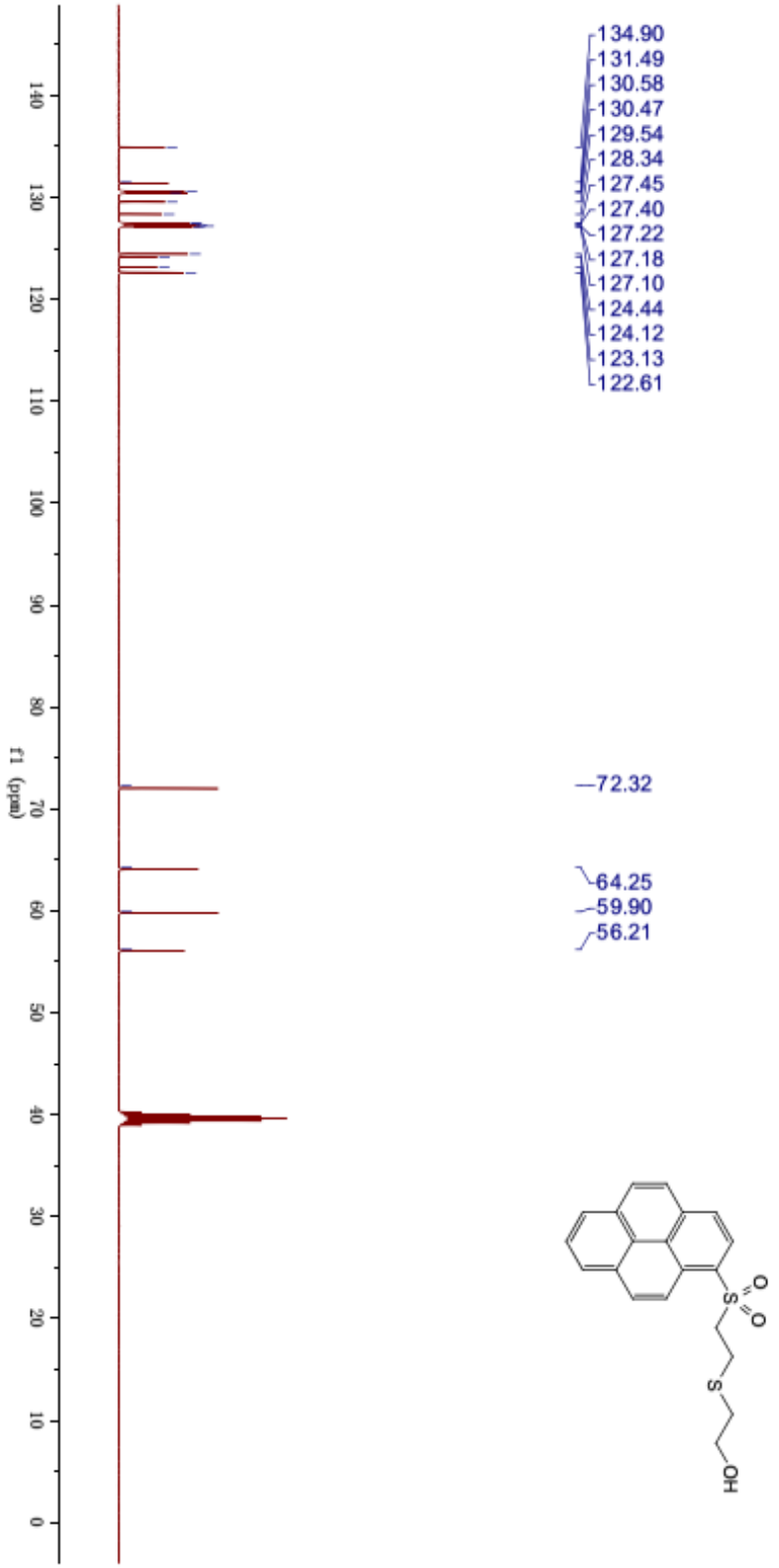
^{1}H-NMR spectrum of **9** (in $CDCl_3$)



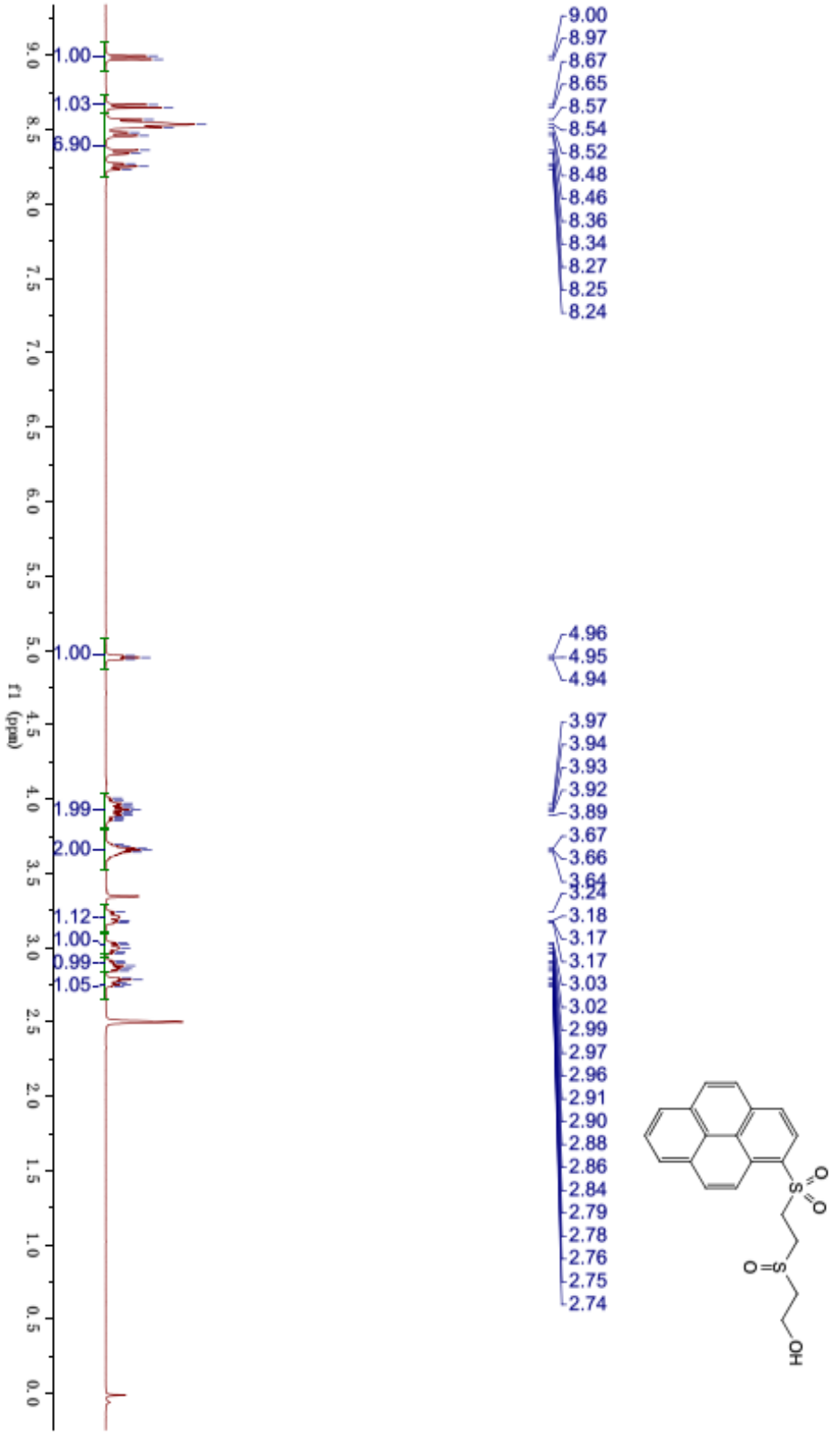
^{13}C-NMR spectrum of **9** (in $CDCl_3$)



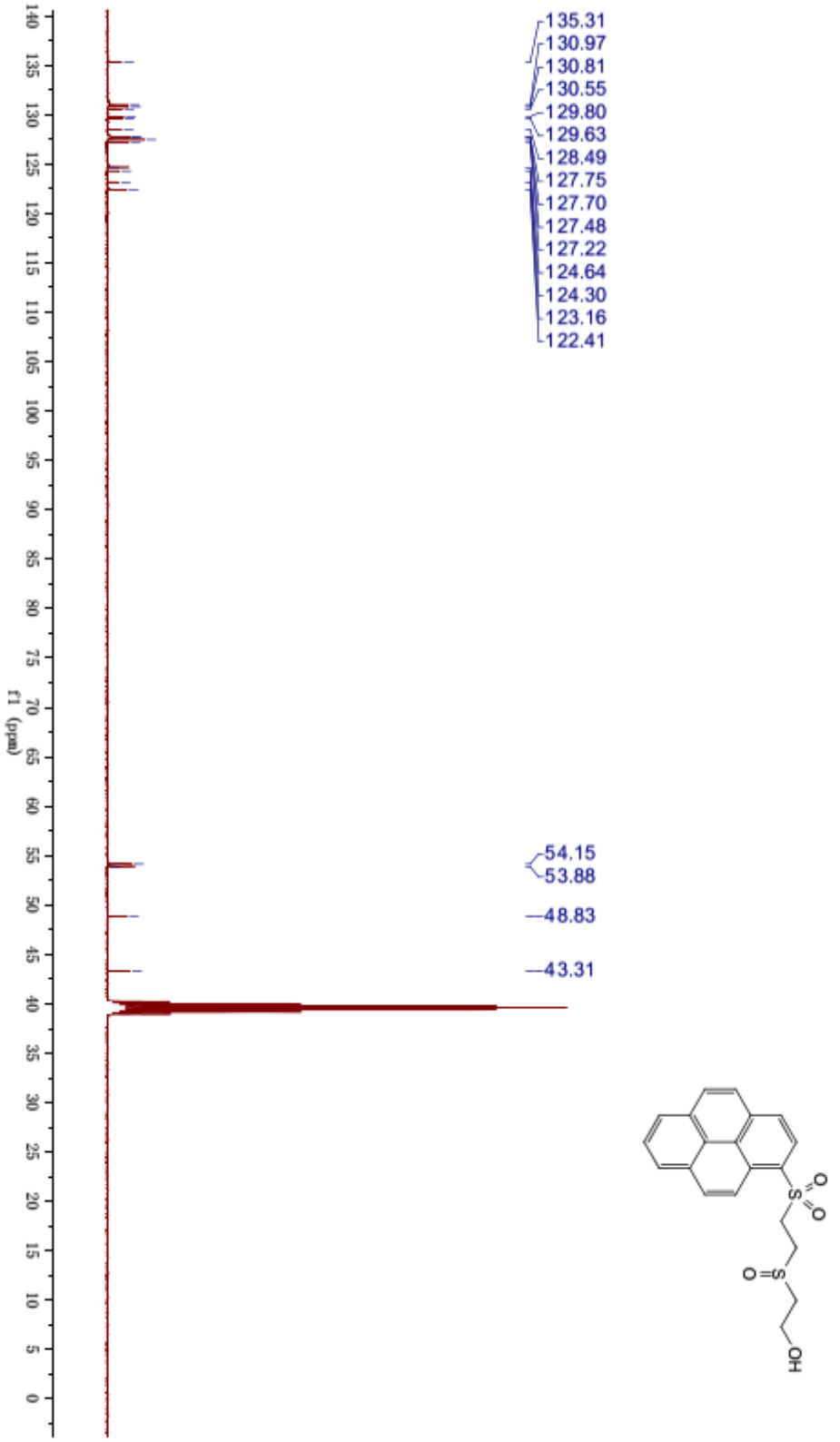
^{1}H-NMR spectrum of **10** (in DMSO-d_6)



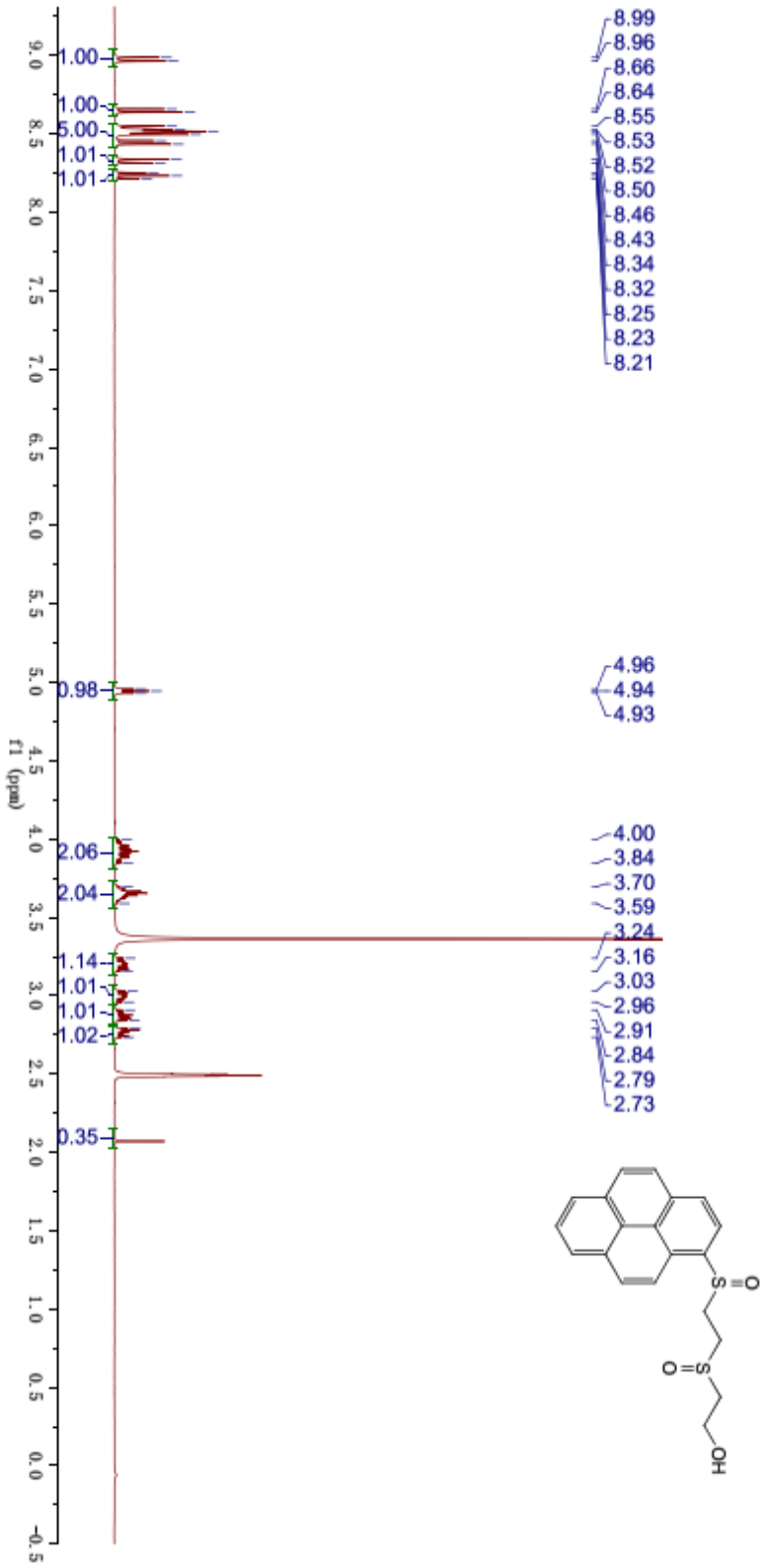
^{13}C-NMR spectrum of **10** (in DMSO-d_6)



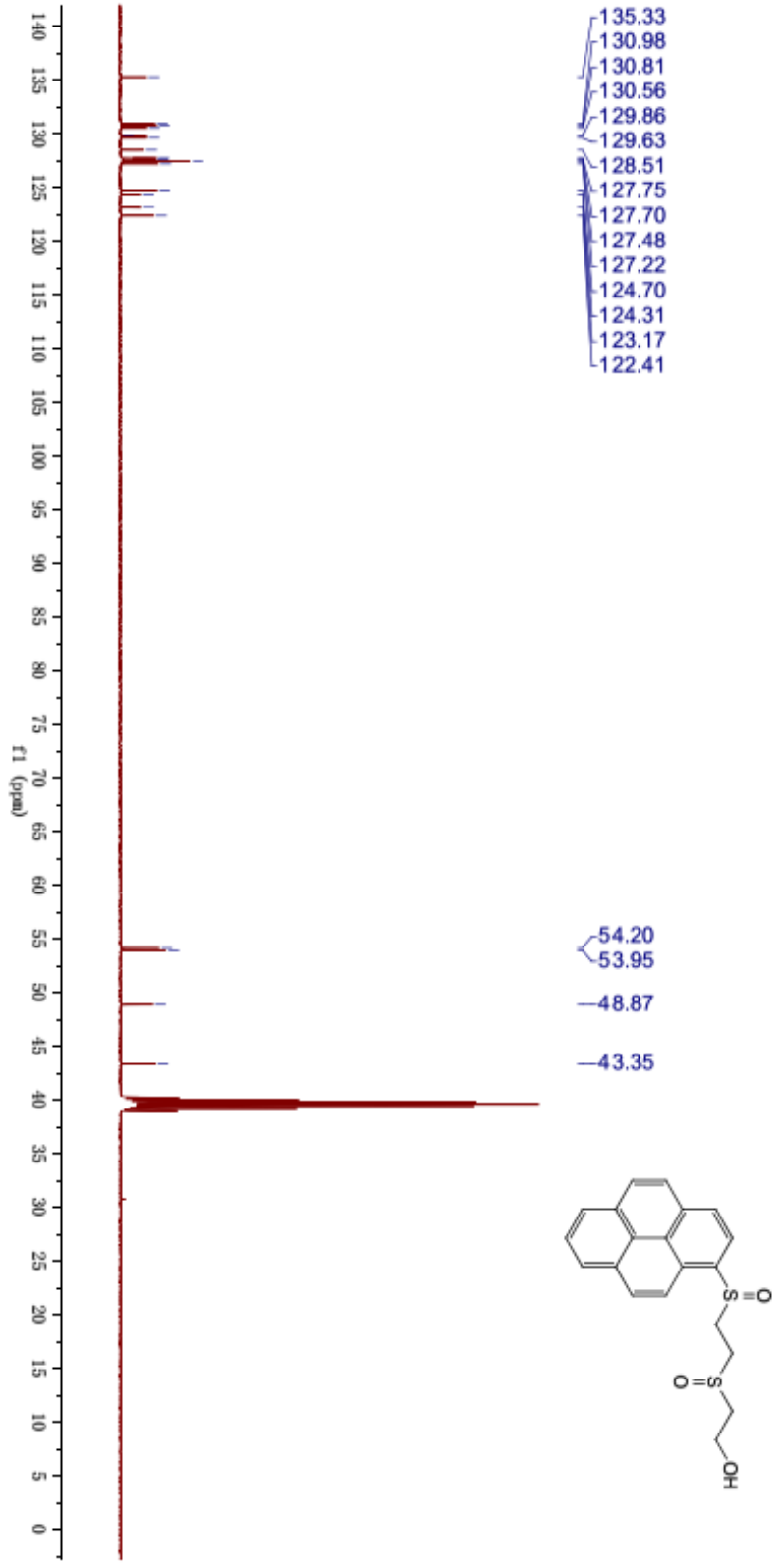
^{1}H-NMR spectrum of **2** (in DMSO-d_6)



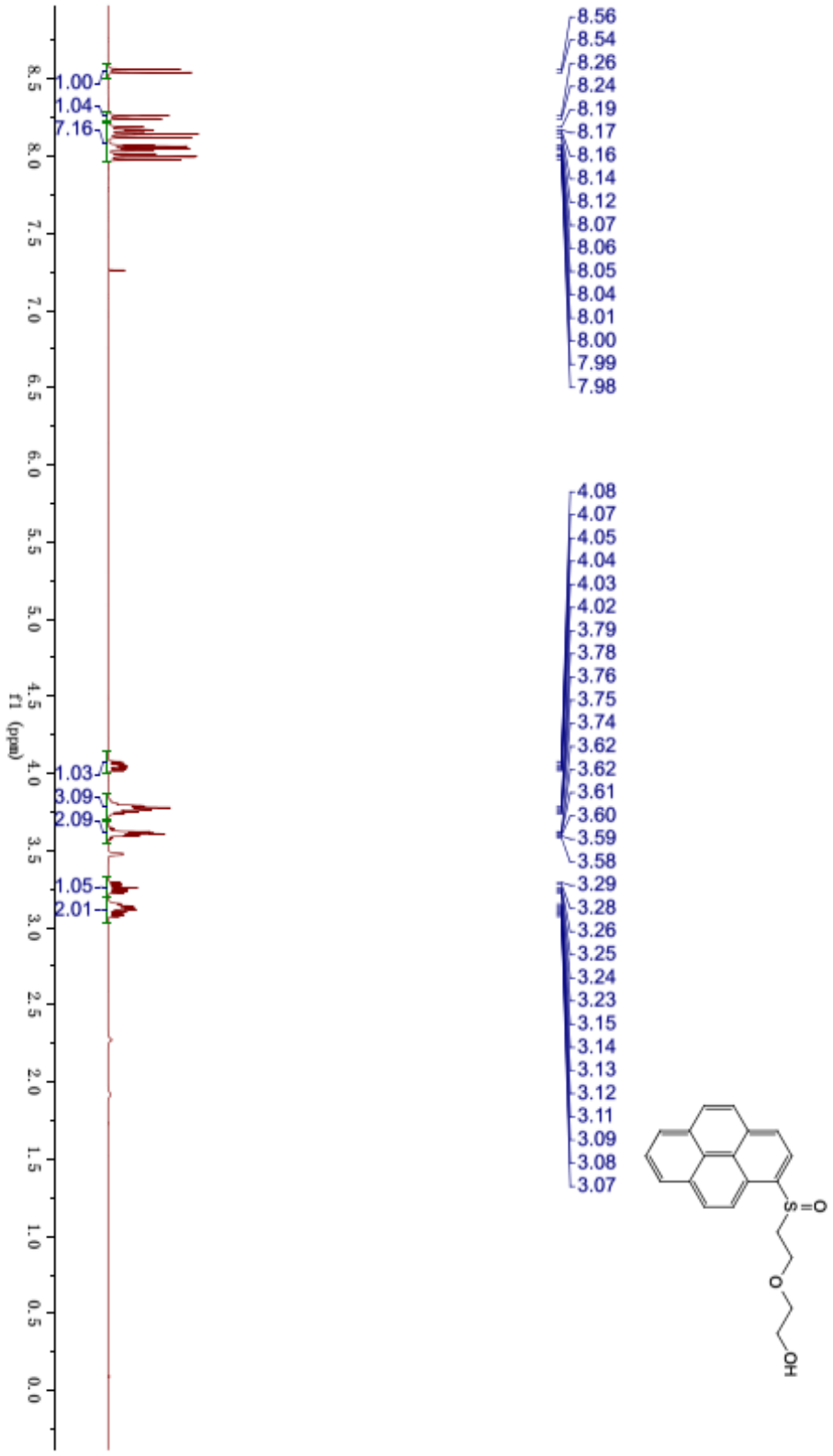
^{13}C-NMR spectrum of **2** (in DMSO-d_6)



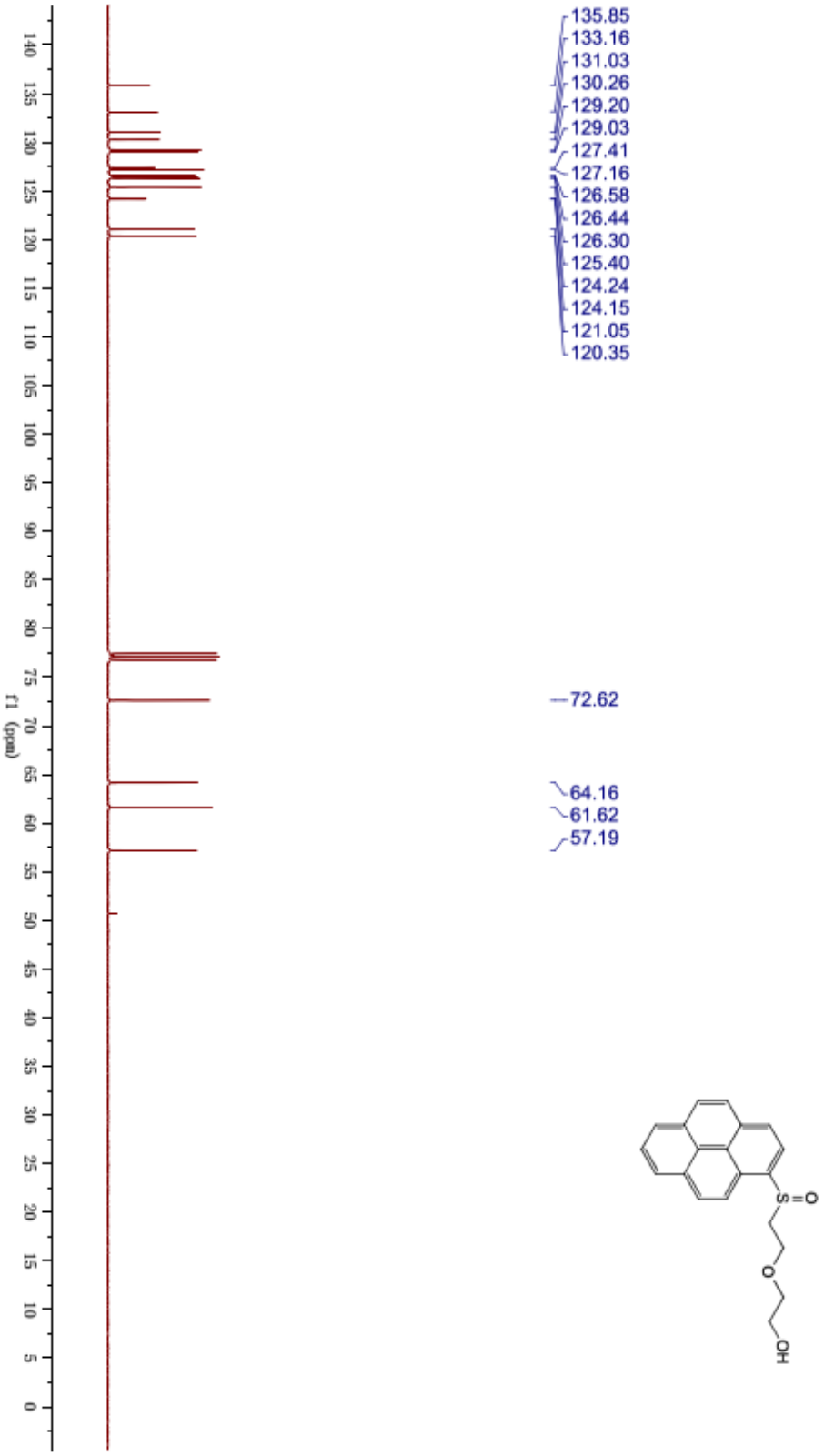
^{1}H-NMR spectrum of **3** (in DMSO-d_6)



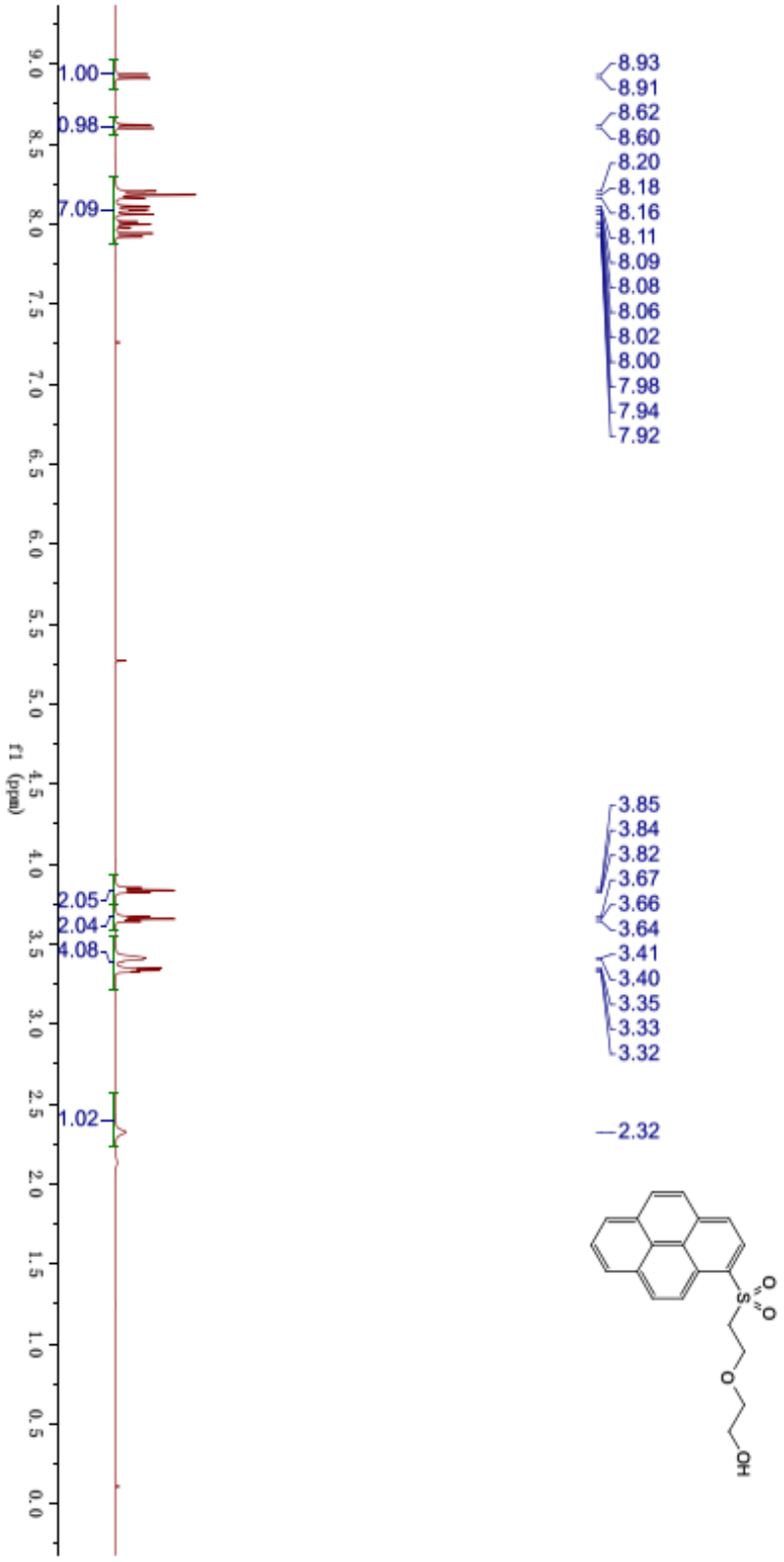
^{13}C-NMR spectrum of **3** (in DMSO-d_6)



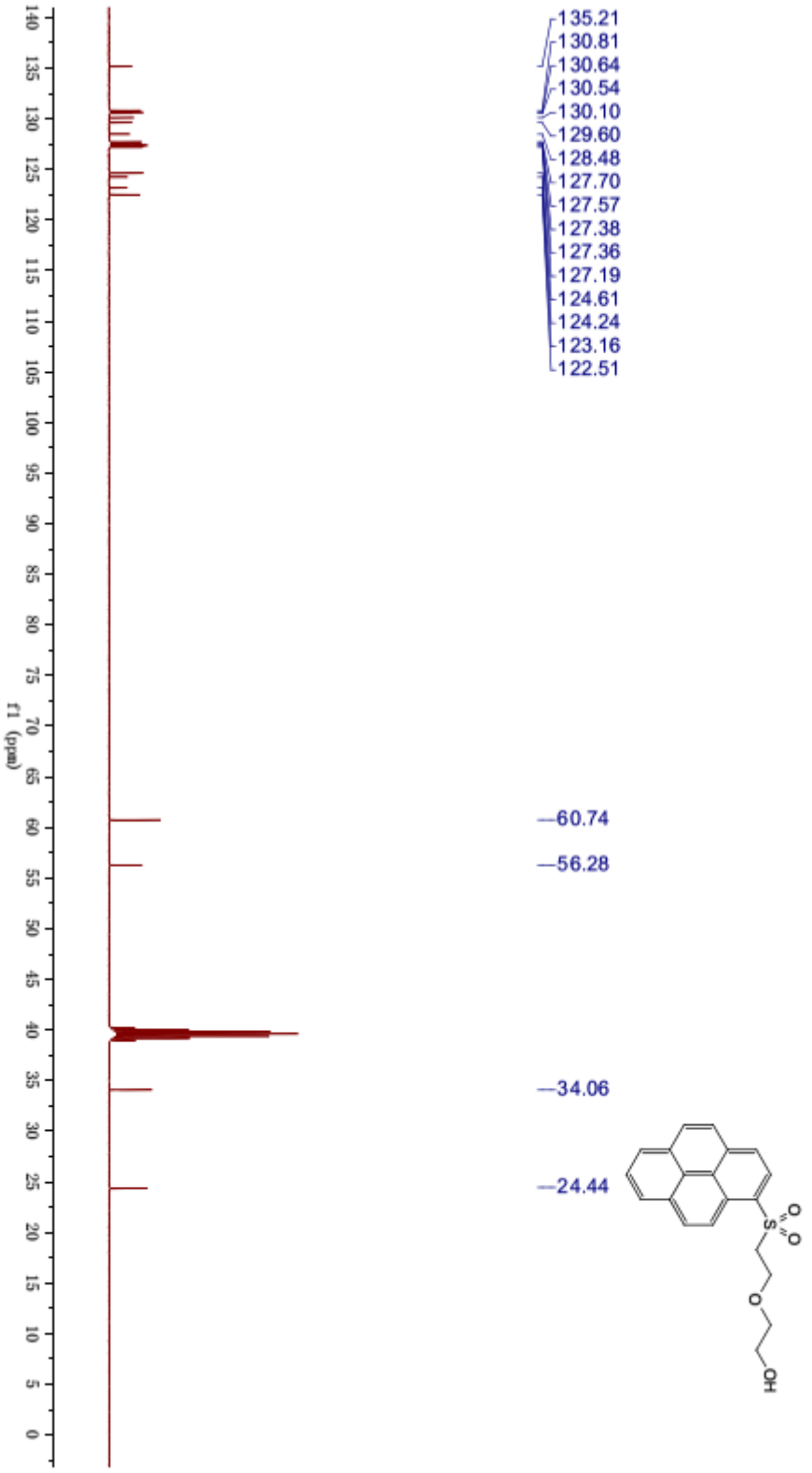
^{1}H-NMR spectrum of **11** (in $CDCl_3$)



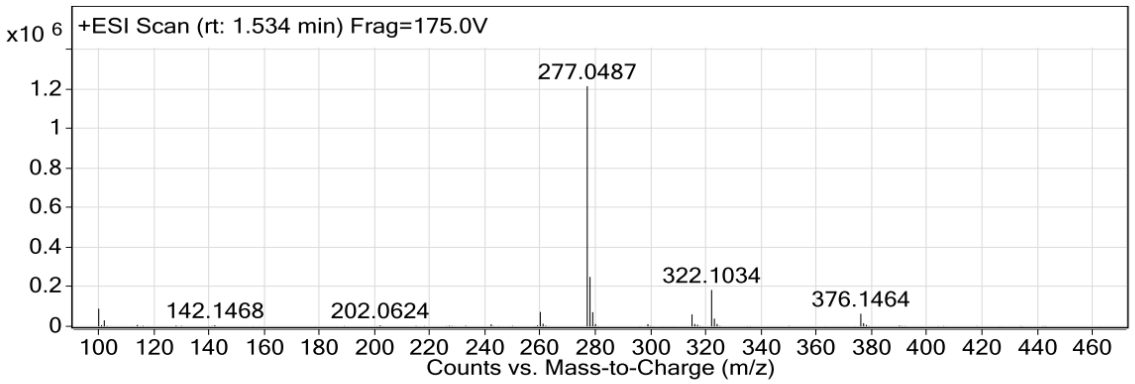
^{13}C-NMR spectrum of **11** (in $CDCl_3$)



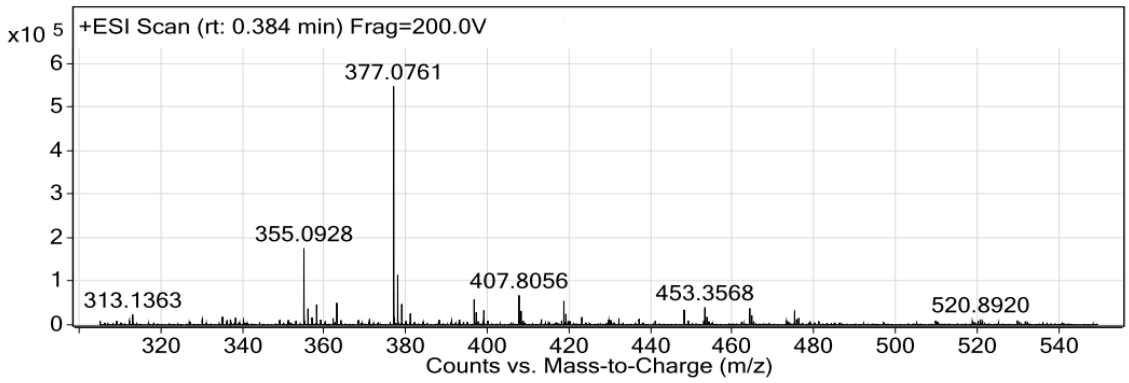
^{1}H-NMR spectrum of **12** (in $CDCl_3$)



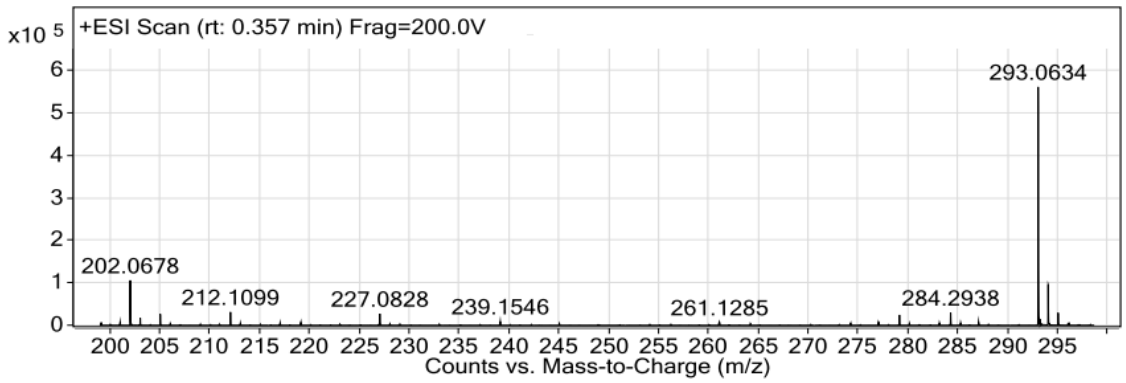
^{13}C-NMR spectrum of **12** (in DMSO-d_6)



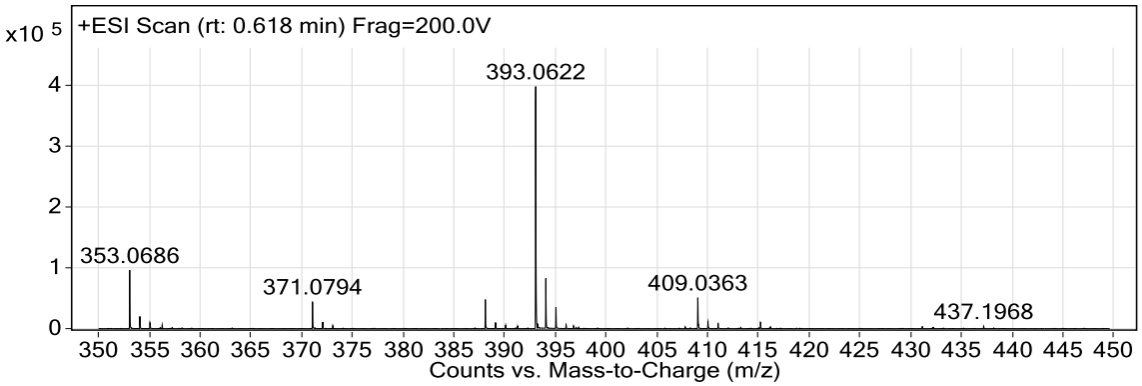
MS spectrum of **8**. MS(ESI): m/z 277.0487 $[M+H]^+$.



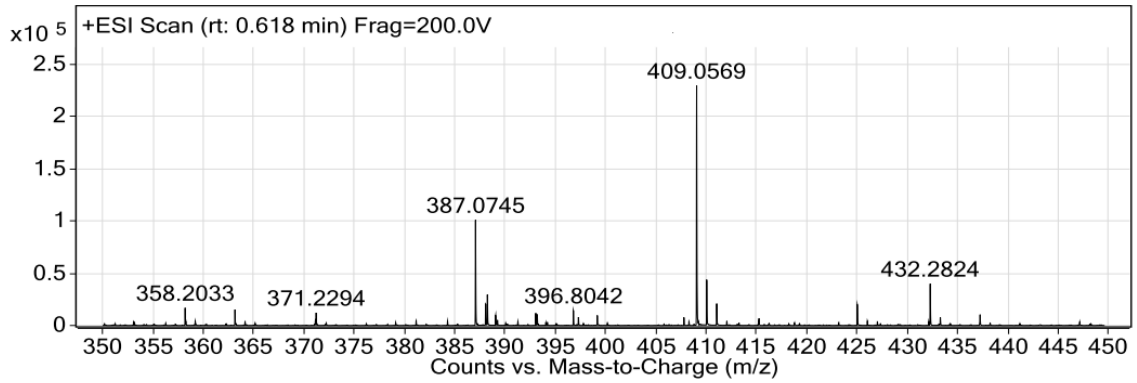
MS spectrum of **1.** MS(ESI): m/z 355.0928 $[M+H]^+$; m/z 377.0761 $[M+Na]^+$.



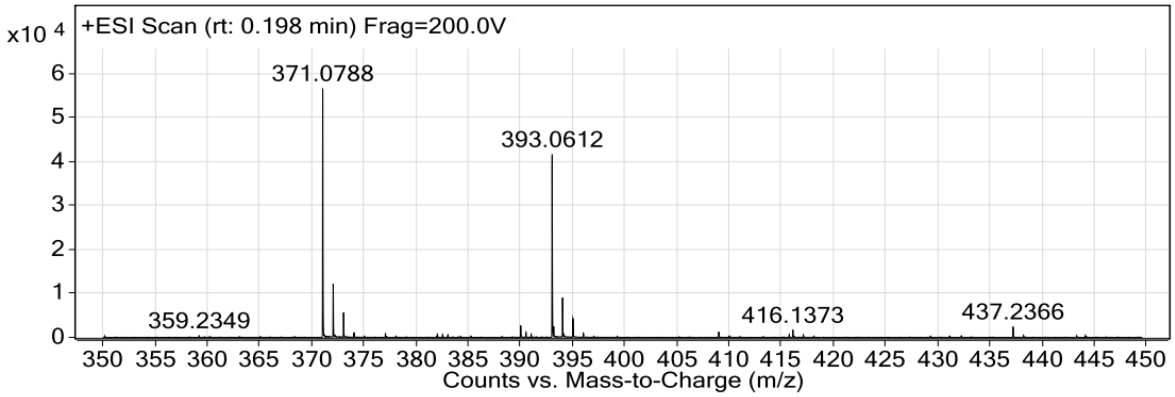
MS spectrum of **9.** MS(ESI): m/z 293.0634 $[M+H]^+$



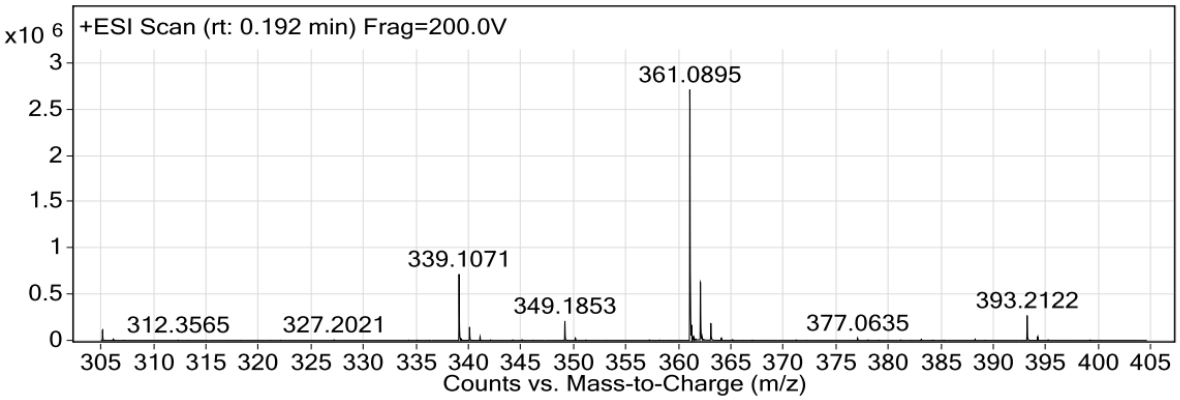
MS spectrum of **10**. MS(ESI): m/z 371.0794 $[M+H]^+$; m/z 393.0622 $[M+Na]^+$.



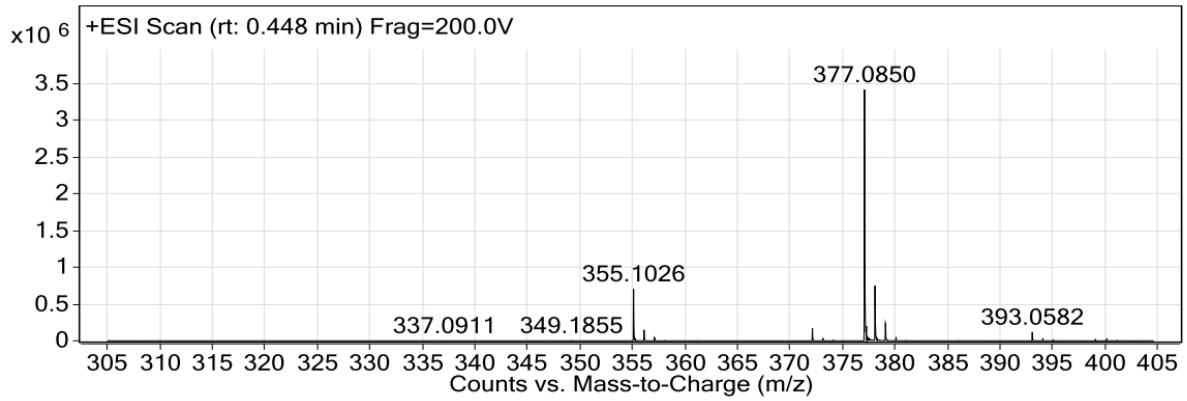
MS spectrum of **2**. MS(ESI): m/z 387.0745 $[M+H]^+$; m/z 409.0569 $[M+Na]^+$.



MS spectrum of **3**. MS(ESI): m/z 371.0788 $[M+H]^+$; m/z 393.0612 $[M+Na]^+$.



MS spectrum of **11**. MS(ESI): m/z 339.1071 $[M+H]^+$; m/z 361.0895 $[M+Na]^+$.



MS spectrum of **12**. MS(ESI): m/z 355.1026 $[M+H]^+$; m/z 377.0850 $[M+Na]^+$.