Supporting Information

Regio- and diastereoselective synthesis of cyclobutylated phenothiazines *via* [2+2] photocycloaddition: demonstrating wavelength-gated cycloreversion inside live cell[#]

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1. General Experimental Details

All the reactions were carried out in a thoroughly oven-dried borosilicate round bottom flask equipped with a magnetic stirrer bar. As an optimized light source, 240 W Blue LEDs were used. Naphthoquinone and 2-amino-benzenethiol were purchased from Spectrochem and Sigma Aldrich and used without further purifying. Commercially available styrene derivatives and solvents were purchased from various suppliers (Sigma-Aldrich, TCI, Alfa Aesar, or Spectrochem) and were directly utilized without further purification or distillation. Styrene derivatives of commercial drugs (ibuprofen, flurbiprofen, gemfibrozil, clofibric acid, and fenbufen) were synthesized following the literature procedures.[1] All the light-driven reactions were performed using borosilicate glassware (25/50 mL RBF) under the Blue LED bulb (240 W) setup (*vide infra*). The progress of the reactions was monitored by performing the thin-layer chromatography (TLC) technique using TLC plates purchased from Merck (Silica gel 60 F_{254}). Column chromatography was performed using glass columns loaded with silica gel of mesh size 230-400 (purchased from RANKEM Pvt. Ltd. India) to purify the product using the solvent mixture of EtOAc/ hexane, CH_2Cl_2/ hexane or EtOAc/ CH_2Cl_2. ^1H, ^{13}C, and ^{19}F NMR data were obtained on a Bruker 400/ 500 MHz spectrometer using $CDCl_3$ as the solvent. ^1H NMR spectra were reported as chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. Whereas ^{13}C NMR spectra were reported like chemical shift (δ ppm) and multiplicity. Multiplicity was correctly indicated using the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet) and m (multiplet). High-resolution mass spectroscopic (HRMS) analysis was executed on quadrupole-time-of-flight Bruker MicroTOF-Q II mass spectrometer equipped with an electrospray ionization (ESI +ve/−ve) or atmospheric pressure chemical ionization (APCI) source. Mass analysis for the radical trapping experiment was performed on the Agilent 6546 HRLC-QTOF ESI instrument coupled with the 1290 Infinity II LC System. The UV-visible study was performed on Agilent Technologies Cary (5000) series UV-Vis-NIR spectrophotometer. All the fluorescence measurements were carried out using a HORIBA Jobin Yvon fluorimeter by taking the solution in a 1 cm path-length quartz cuvette. Single crystal X-ray data for the synthesized angular phenothiazines were collected on a Bruker D8 VENTURE diffractometer equipped with CMOS Photon 100 detector and Mo$K\alpha$ (λ = 0.71073 Å) and Cu$K\alpha$ (λ = 1.54178) radiations were used, computed with Bruker APEX2. Corresponding melting points of the products were evaluated using an electro-thermal melting point apparatus by taking them within capillary tubes.

Note 1. It is worth mentioning that the reaction yield greatly depends upon the quality of styrene used. We have always observed that styrenes from freshly opened bottles or freshly prepared/distilled styrenes provide much better conversion (yield).

Note 2. All column chromatographies were performed in low-light conditions and covered with aluminum foil when required. Similar precautions were taken while acquiring the characterization data.

2. Experimental Set-up for the Photocatalytic Reaction

Gesto® 5050 SMD LEDS with 200 tri-chip royal-blue LED strips were manually installed on the inner surface of a rectangular cardboard box, and the overall setup was settled on a magnetic stirrer (Figure S1). The blue LED light with 240 W has a λ_{max} of 457 nm (Figure S2). The reaction vessels were placed approximately 5-6 cm away from the LED strips, and the temperature inside the vessel was around 28 °C.

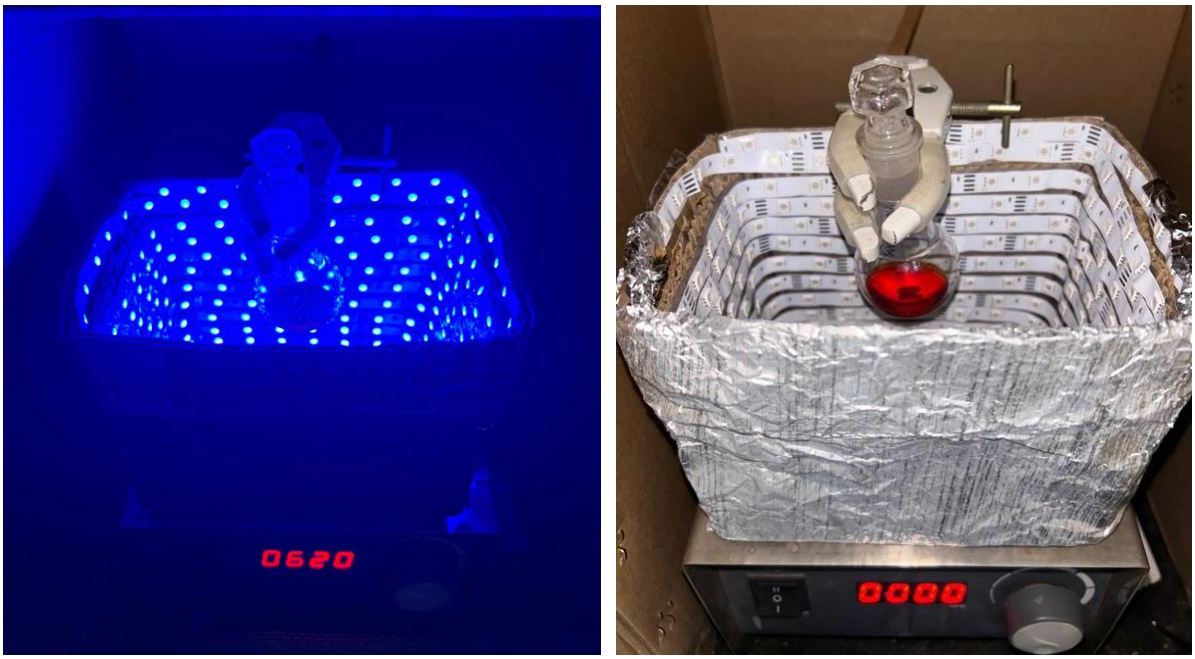


Figure S1. Reaction set up: box equipped with blue LEDs on a magnetic stirrer (a) with blue light on (Left), (b) with blue light off (Right)

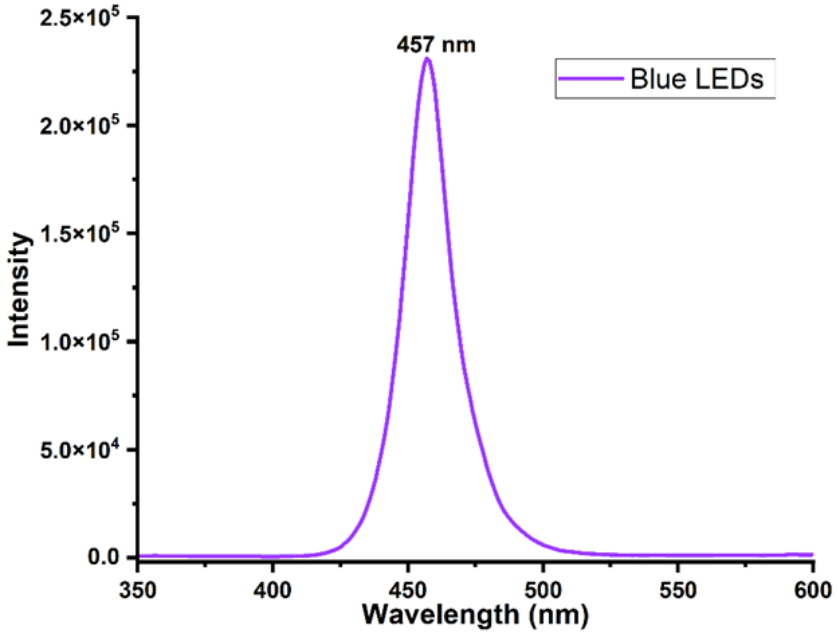


Figure S2. Emission plot of blue LEDs light used as a light source in the reaction

3. External Light Source of 405 nm

The [2+2] cycloreversion phenomenon from cyclobutylated angular phenothiazines into its precursors was performed by using an external laser light source of 405 nm (power: 5 mW, illuminance ~ 88 lx, measured with a lux meter) (Figure S3).

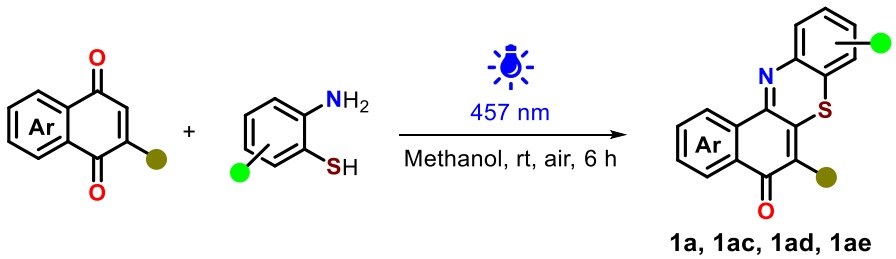
Figure S3. Image of the external laser source of 405 nm

4. Lux Meter

The dependency of the rate of the [2+2] photocycloaddition reaction on the intensity of incident light has been measured using a Lutron LX-101 LUX METER (Figure S4). The original incident light intensity of the blue LEDs on the reaction vessel was around 900 lx.

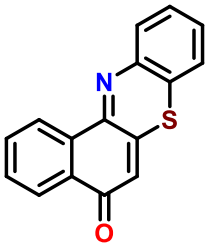
Figure S4. Image of lux meter LX-101 (taken under the lab lights)

5. Synthesis of Angular Phenothiazines

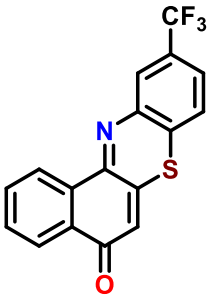


Scheme S1. Visible light-irradiated synthesis of the angular phenothiazines

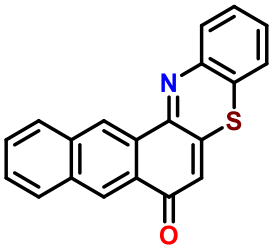
Synthetic protocol: Quinone (200 mg, 1 equiv) and *ortho*-aminobenzenethiol (2 equiv) were mixed in methanol (5 mL) and stirred under blue light irradiation (240 W) at room temperature for 6 h within the open-air atmosphere. Then methanol was evaporated under reduced pressure, and the reaction mixture was directly subjected to column chromatography using silica gel of mesh size 230-400 and solvent mixture ranging from 10% EtOAc/hexane up to 4% EtOAc/CH_2Cl_2 solvent to obtain the desired angular phenothiazines **1a**, **1ac**, **1ad**, **1ae**.



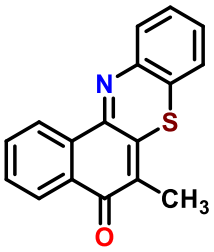
5*H*-Benzo[*a*]phenothiazin-5-one (**1a**). Reddish orange solid. Yield 3.6 g (55% at 26 mmol or 4 g scale), mp: 148-150 °C (reported 164-165 °C).[2] Purified using EtOAc/CH_2Cl_2 (15:85) as eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.87 – 8.82 (m, 1H), 8.31 – 8.24 (m, 1H), 7.94 – 7.89 (m, 1H), 7.79 – 7.70 (m, 2H), 7.48 – 7.43 (m, 1H), 7.42 – 7.36 (m, 2H), 6.82 (s, 1H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 180.2, 144.8, 138.6, 137.8, 134.2, 133.4, 132.6, 131.6, 131.3, 130.0, 127.8, 125.8, 125.6, 124.7, 122.9, 120.3; **HRMS (ESI)** m/z: $[M]^+$ calcd for $C_{16}H_9NO_2S$, 279. 0349, found 279. 0377.



10-(Trifluoromethyl)-5*H*-benzo[*a*]phenothiazin-5-one (**1ac**). Yellowish orange solid. Yield 160 mg (37% at 1.3 mmol scale), mp: 162 – 163 °C. Purified using EtOAc/CH_2Cl_2 (15:85) as eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.87 – 8.75 (m, 1H), 8.26 (dd, J = 6.7, 2.5 Hz, 1H), 8.13 (d, J = 2.0 Hz, 1H), 7.81 – 7.73 (m, 2H), 7.61 (dd, J = 8.3, 2.0 Hz, 1H), 7.49 (d, J = 8.3 Hz, 1H), 6.83 (s, 1H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 180.2, 146.3, 138.6, 136.5, 133.8, 132.6, 132.0 (d, J = 8.1 Hz), 130.1 – 129.9 (m), 126.9, 126.0, 125.9 (d, J = 3.8 Hz), 125.8, 125.4, 121.5; **^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$)** δ -62.73; **HRLCMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{17}H_9F_3NOS$, 332.0351, found 332.0371.



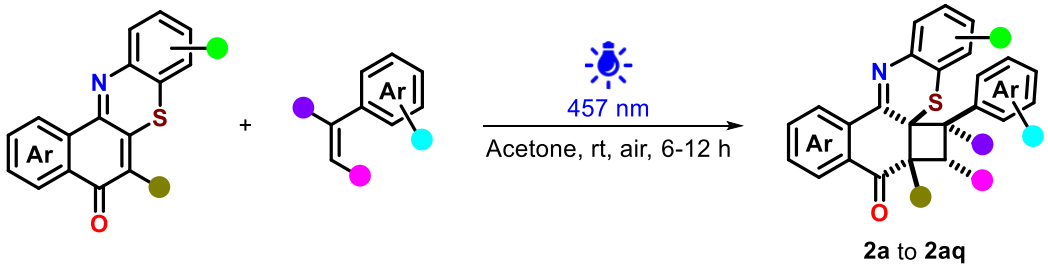
7*H*-naphtho[2,3-*a*] phenothiazin-7-one (1ad). The product could not be thoroughly purified and characterized; therefore, we proceeded with the next [2+2] cycloaddition reaction with styrene (*vide infra*) without any further purification (crude weight = 160 mg).



6-Methyl-5*H*-benzo[*a*]phenothiazin-5-one (1ae). The product could not be thoroughly purified and characterized; therefore, we proceeded with the next [2+2] cycloaddition reaction with styrene (*vide infra*) without any further purification (crude weight = 150 mg).

6. Synthesis of Cyclobutylated Phenothiazines *via* Light-Irradiated Two- and Three-Component Couplings

6.1. Synthesis of Cyclobutylated Phenothiazines *via* Intermolecular [2+2] Photo-cycloaddition

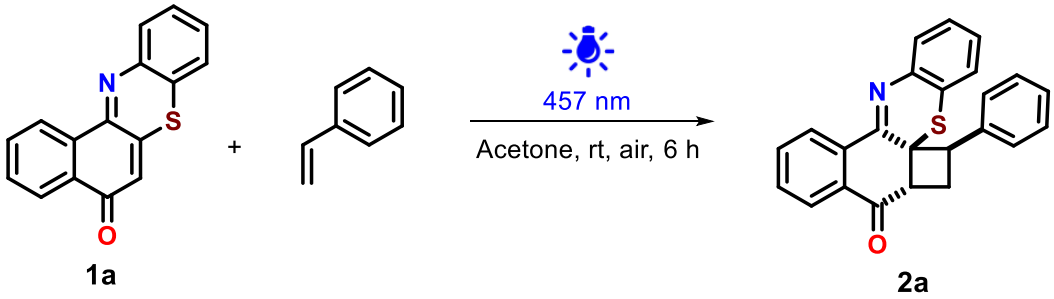


Scheme S2. Synthesis of cyclobutylated phenothiazines

Synthetic protocol: Angular phenothiazine precursor **1a** (0.76 mmol, 200 mg, 1 equiv) with styrene (2.28 mmol, 260 μL, 3 equiv) in a round bottom flask (10ml) in the open-air atmosphere at room temperature for 6-12 h under blue-light irradiation. Reaction progress was analyzed

through the thin layer chromatography. Upon the completion of the reaction, the solvent was evaporated and purified by flash chromatography, which provided the desired cyclobutylated angular phenothiazine.

Table S1. Additional Reaction Conditions Optimization [a]



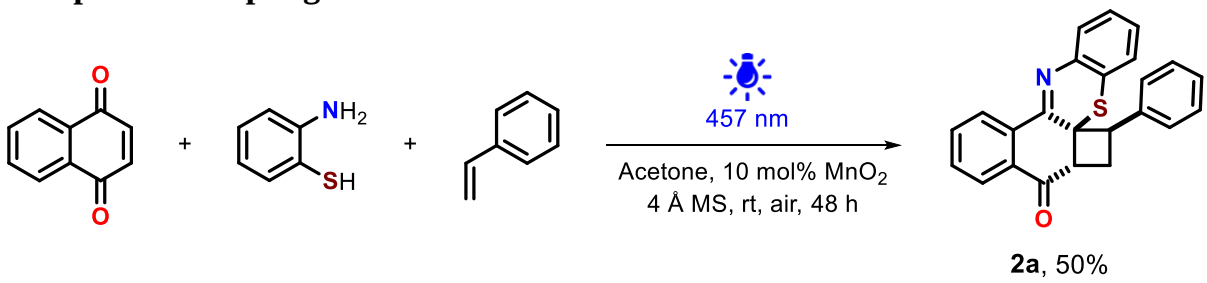
Entry	Deviation from the standard condition	Yield (%) [b]
1	**--**	**99 (96)[c]**
2	CH_3CN	98
3	CH_2Cl_2	96
4	Toluene	66
5	rt at dark	N.R.[d]
6	55 °C, at dark	N.R.
7	N_2	98
8	O_2	96
9	Sunlight	98

[a] Standard conditions: angular phenothiazine **1a (**10 mg, 0.038 mmol, 1 equiv) and styrene (13 µL, 0.114 mmol, 3 equiv) mixed in 200 µL of acetone solvent at room temperature, under air atmosphere, inside a blue-LEDs box and irradiated for 6h; [b] NMR yield; [c] Isolated yield; [d] After 12 h

Here, we have listed the extra reaction optimization conditions, which have been performed to reach the final optimized condition for [2+2] cycloaddition. The reaction conditions were optimized at a 0.038 mmol scale. Firstly, the reaction was performed with an acetone solvent

and open-air conditions under blue light irradiation. The crude reaction mixture was subjected to NMR analysis, showing 99% conversion into desired cyclobutylated phenothiazine **2a** (entry 1, Table S1), and upon column purification, desired cyclobutylated phenothiazine **2a** was obtained in 96% yield. Next, we screened different solvents in place of acetone under standard reaction conditions (entries 2-4, Table S1). When polar solvents, namely acetonitrile or dichloromethane, were used, the yield of **2a** was comparable to the best yield we got using acetone (entries 2 and 3). However, nonpolar solvents like toluene provided only 66% conversion to the product (entry 4). To gain more insight into the reaction mechanism, we executed dark reactions at both room and elevated temperatures (entries 5 and 6). In both cases, no product formation was observed. Further, we performed the reaction under strict inert conditions (entry 7) and a strict oxygen atmosphere (entry 8), both provided a comparable conversion to the desired product **2a**. Finally, we ventured for sunlight instead of blue-LEDs, keeping other reaction conditions the same as the standard condition, and observed 98% conversion to the desired cycloadduct within 6 h (entry 9).

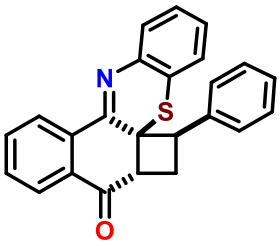
6.2. Synthesis of Cyclobutylated Phenothiazine 2a *via* Light-Irradiated Three-Component Coupling



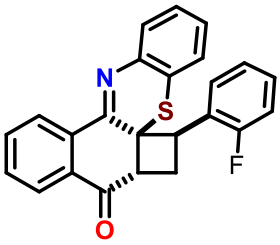
Scheme S3. Visible light-irradiated synthesis of cyclobutylated phenothiazine **2a** *via* a three-component coupling reaction between naphthoquinone, 2-aminothiophenol, and styrene

For the three-component reaction, at first the 1,4-naphthoquinone (10 mg, 0.06 mmol, 1 equiv), 2-aminothiophenol (19 μL, 0.18 mmol, 3 equiv) and styrene (28 μL, 0.24 mmol, 4 equiv) were taken in a glass vial (3mL) equipped with magnetic stirrer and irradiated under blue-LEDs in air atmosphere at room temperature. After 24 h, only ~5% conversion to the desired cyclobutylated phenothiazine **2a** was observed. Next, we performed the same reaction in the presence of a catalytic amount of Na_2EosinY photocatalysts (10 mol %); however, no enhancement was observed in the product yield. After realizing that the initial step of the

reaction likely involves an oxidative dehydrogenative coupling of C-H and S-H bonds of 1,4-naphthoquinone and 2-aminothiophenol, we hypothesized that peroxides or some other reactive oxygen species might be generated in the reaction mixture as side products, which might impede the second step. Consequently, we envisioned quenching the *in situ* generated side products, which may facilitate the second step. In pursuit of this, we added a catalytic amount of MnO_2 along with molecular sieves in the reaction mixture, keeping other reaction conditions unaltered. Pleasingly, by adopting this condition, we could obtain around 50% yield of the desired cyclobutylated phenothiazine **2a** from a one-pot-three-component coupling reaction.

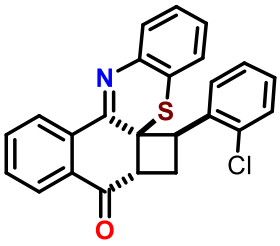


6-Phenyl-7,7a-dihydrobenzo[*a*]cyclobuta[*d*]phenothiazin-8(6*H*)-one (**2a**). Yellow solid. Yield 266 mg (96% at 0.76 mmol scale), m.p. 133-135 °C. Purified using EtOAc/hexane (20:80) as eluent. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.72 (d, J = 8.1 Hz, 1H), 8.19 (dd, J = 7.8, 1.4 Hz, 1H), 7.82 – 7.77 (m, 1H), 7.70 – 7.64 (m, 1H), 7.36 (dd, J = 7.8, 1.3 Hz, 1H), 7.07 – 7.04 (m, 1H), 6.98 – 6.91 (m, 5H), 6.73 – 6.68 (m, 1H), 6.64 (dd, J = 7.8, 1.5 Hz, 1H), 3.91 (t, J = 9.2 Hz, 1H), 3.26 (dd, J = 10.9, 3.7 Hz, 1H), 3.17 – 3.10 (m, 1H), 2.60 – 2.54 (m, 1H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.8, 153.6, 144.2, 137.5, 135.9, 134.8, 132.5, 131.6, 128.2, 127.6, 127.37, 127.36, 127.2, 127.1, 127.0, 126.8, 126.4, 122.6, 49.9, 48.1, 45.3, 27.9; **HRMS (ESI)** *m/z*: $[M+Na]^+$ calcd for $C_{24}H_{17}NOSNa$, 390. 0923, found 390. 0961.

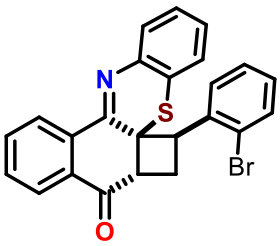


6-(2-Fluorophenyl)-7,7a-dihydrobenzo[*a*]cyclobuta[*d*]phenothiazin-8(6*H*)-one (2b). Pale **y**ellow solid. Yield 275 mg (94% at 0.76 mmol scale), mp: 80 – 84 °C. It was purified using EtOAc/hexane (20:80) as eluent. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.71 (d, J = 8.0 Hz, 1H), 8.18 (dd, J = 8.0, 1.5 Hz, 1H), 7.82 – 7.76 (m, 1H), 7.70 – 7.64 (m, 1H), 7.41 (dd, J = 7.9, 1.2 Hz,

1H), 7.37 – 7.31 (m, 1H), 7.09 – 7.03 (m, 1H), 7.01 – 6.94 (m, 1H), 6.94 – 6.89 (m, 1H), 6.73 – 6.60 (m, 2H), 6.51 – 6.34 (m, 1H), 4.27 (t, *J* = 9.5 Hz, 1H), 3.30 – 3.20 (m, 1H), 3.15 (q, *J* = 10.8 Hz, 1H), 2.58 – 2.50 (m, 1H); **^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$)** δ 196.7, 161.5, 159.5, 153.1, 144.1, 136.0, 134.9, 132.6, 131.5, 129.1 (d, *J* = 3.7 Hz), 128.8 (d, *J* = 8.4 Hz), 127.7, 127.6, 127.3, 126.8, 126.6, 126.5, 125.3, 125.2, 122.8 (d, *J* = 3.5 Hz), 122.2, 113.9, 113.7, 48.0, 45.3, 41.8 (d, *J* = 2.9 Hz), 27.1; **^{19}F{^{1}H} NMR (471 MHz, CDCl$_3$)** δ -116.3; **HRLCMS (ESI)** *m/z*: $[M+H]^+$ calcd for $C_{24}H_{17}FNOS$, 386.1009, found 386.0990.

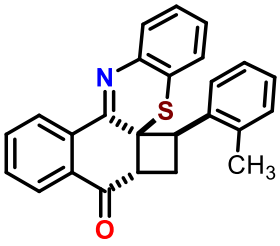


6-(2-Chlorophenyl)-7,7a-dihydrobenzo[*a*]cyclobuta[*d*]phenothiazin-8(6*H*)-one (**2c**). Brownish-yellow solid. Yield 268 mg (88% at 0.76 mmol scale), mp: 123 – 124 °C. Purified using EtOAc/hexane (20:80) as eluent. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.71 (d, *J* = 8.0 Hz, 1H), 8.19 (d, *J* = 7.9 Hz, 1H), 7.79 (t, *J* = 7.6 Hz, 1H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.41 (d, *J* = 7.9 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.04 (dd, *J* = 8.3, 4.2 Hz, 1H), 6.86 (t, *J* = 7.7 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.65 (d, *J* = 4.5 Hz, 2H), 4.55 (t, *J* = 9.5 Hz, 1H), 3.20 (d, *J* = 11.0 Hz, 1H), 3.12 (q, *J* = 10.8 Hz, 1H), 2.55 (t, *J* = 10.4 Hz, 1H); **^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$)** δ 196.9, 153.0, 144.0, 136.1, 135.4, 134.9, 134.3, 132.7, 131.5, 129.1, 128.3, 128.2, 127.8, 127.7, 127.2, 126.7, 126.43, 126.39, 125.5, 122.1, 48.3, 45.3, 44.9, 28.0; **HRLCMS (APCI)** *m/z*: $[M+H]^+$ calcd for $C_{24}H_{17}ClNOS$, 402.0714, found 402.0727.

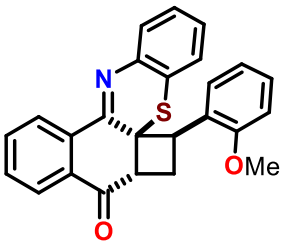


6-(2-Bromophenyl)-7,7a-dihydrobenzo[*a*]cyclobuta[*d*]phenothiazin-8(6*H*)-one (**2d**). Light brown solid. Yield 280 mg (83% at 0.76 mmol scale), mp: 68 – 70 °C. Purified using EtOAc/hexane (20:80) as eluent. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.71 (d, *J* = 8.0 Hz, 1H), 8.20 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.82 – 7.77 (m, 1H), 7.70 – 7.65 (m, 1H), 7.53 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.42 (d, *J* = 7.9 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.05 – 7.00 (m, 1H), 6.97 (dd, *J* = 7.9,

1.3 Hz, 1H), 6.81 – 6.76 (m, 1H), 6.66 (d, *J* = 4.2 Hz, 2H), 4.55 (t, *J* = 9.6 Hz, 1H), 3.22 – 3.15 (m, 1H), 3.10 (q, *J* = 10.9 Hz, 1H), 2.58 – 2.52 (m, 1H); **$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)** δ 196.9, 153.0, 144.0, 137.0, 136.1, 134.9, 132.7, 131.7, 131.5, 129.3, 128.5, 127.9, 127.7, 127.2, 126.8, 126.4, 126.1, 125.3, 122.1, 48.3, 47.4, 45.3, 28.4; **HRMS (ESI)** *m/z*: $[M-H]^+$ calcd for $C_{24}H_{15}BrNOS$, 444.0052, found 444.0044.

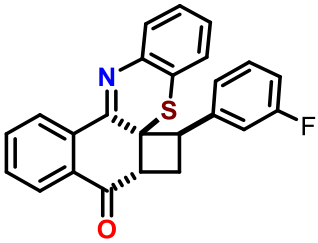


6-(*o*-Tolyl)-7,7a-dihydrobenzo[*a*]cyclobuta[*d*]phenothiazin-8(6*H*)-one (**2e**). Brown solid. Yield 275 mg (95% at 0.76 mmol scale), mp: 125 – 128 °C. Purified using EtOAc/hexane (20:80) as eluent. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.70 (d, *J* = 8.1 Hz, 1H), 8.20 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.82 – 7.77 (m, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.03 – 6.98 (m, 1H), 6.86 – 6.82 (m, 1H), 6.67 (d, *J* = 4.3 Hz, 2H), 6.58 (d, *J* = 7.5 Hz, 1H), 4.23 (t, *J* = 9.4 Hz, 1H), 3.24 – 3.12 (m, 2H), 2.56 – 2.50 (m, 1H), 1.82 (s, 3H); **$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)** δ 197.1, 154.0, 143.8, 136.2, 136.0, 134.8, 132.8, 131.6, 129.2, 127.7, 127.6, 127.3, 127.1, 127.0, 126.9, 126.8, 126.3, 124.8, 122.8, 48.5, 45.3, 45.0, 28.6, 19.2; **HRLCMS (ESI)** *m/z*: $[M+H]^+$ calcd for $C_{25}H_{20}NOS$, 382.1260, found 382.1250.

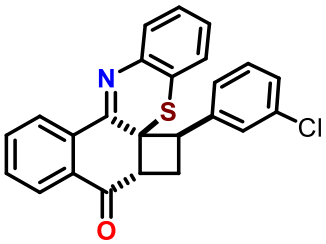


6-(2-Methoxyphenyl)-7,7a-dihydrobenzo[*a*]cyclobuta[*d*]phenothiazin-8(6*H*)-one (2f). Yellow solid. Yield 256 mg (85% at 0.76 mmol scale), mp: 128 – 130 °C. Purified using EtOAc/hexane (20:80) as eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.80 (d, *J* = 8.1 Hz, 1H), 8.22 (d, *J* = 7.8 Hz, 1H), 7.83 (t, *J* = 7.7 Hz, 1H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 7.5 Hz, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.95 (t, *J* = 7.7 Hz, 1H), 6.86 (t, *J* = 7.4 Hz, 1H), 6.70 (d, *J* = 8.5 Hz, 2H), 6.23 (d, *J* = 8.1 Hz, 1H), 4.52 (t, *J* = 9.5 Hz, 1H), 3.39 (s, 3H), 3.23 (d, *J* = 10.9 Hz, 1H), 3.20 – 3.11 (m, 1H), 2.49 (t, *J* = 10.2 Hz, 1H); **$^{13}C\{^{1}H\}$ NMR (126**

MHz, $CDCl_3$) δ 197.2, 156.9, 154.1, 143.8, 134.7, 132.9, 131.6, 128.4, 128.3, 127.8, 127.3, 127.1, 126.9, 126.7, 126.4, 126.0, 122.7, 119.1, 108.2, 54.5, 48.9, 45.7, 42.5, 27.1; **HRLCMS (ESI)** *m/z*: $[M+H]^+$ calcd for $C_{25}H_{20}NO_2S$, 398.1185, found 398.1209.

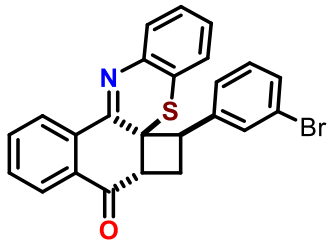


6-(3-Fluorophenyl)-7,7a-dihydrobenzo[*a*]cyclobuta[*d*]phenothiazin-8(6*H*)-one (**2g**). Brown solid. Yield 248 mg (85% at 0.76 mmol scale), mp: 114 – 116 °C. Purified using EtOAc/hexane (20:80) as eluent. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.71 (d, *J* = 8.0 Hz, 1H), 8.19 (d, *J* = 7.8 Hz, 1H), 7.80 (t, *J* = 7.7 Hz, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.37 (d, *J* = 7.9 Hz, 1H), 7.11 – 7.05 (m, 1H), 6.89 (q, *J* = 7.5 Hz, 1H), 6.77 – 6.64 (m, 5H), 3.90 (t, *J* = 9.3 Hz, 1H), 3.24 (dd, *J* = 10.8, 3.4 Hz, 1H), 3.13 – 3.05 (m, 1H), 2.60 – 2.53 (m, 1H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.5, 163.1, 161.1, 153.3, 144.2, 140.1 (d, *J* = 7.3 Hz), 135.8, 134.9, 132.5, 131.7, 128.3 (d, *J* = 8.3 Hz), 127.6, 127.44, 127.38, 127.1, 127.0, 126.7, 124.0 (d, *J* = 2.8 Hz), 122.3, 115.2, 115.0, 114.1, 114.0, 49.6 (d, *J* = 1.9 Hz), 48.0, 45.2, 27.9; **HRLCMS (APCI)** *m/z*: $[M+H]^+$ calcd for $C_{24}H_{17}FNOS$, 386.1009, found 386.0980.

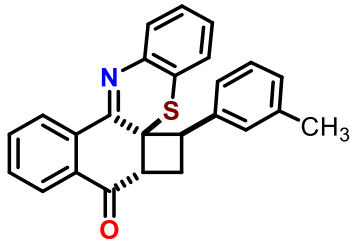


6-(3-Chlorophenyl)-7,7a-dihydrobenzo[*a*]cyclobuta[*d*]phenothiazin-8(6*H*)-one (**2h**). Pale yellow solid. Yield 286 mg (94% at 0.76 mmol scale), mp: 129 – 131 °C. Purified using EtOAc/hexane (20:80) as eluent. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.71 (d, *J* = 8.0 Hz, 1H), 8.18 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 7.9 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.96 – 6.86 (m, 3H), 6.82 (d, *J* = 7.6 Hz, 1H), 6.76 (t, *J* = 7.5 Hz, 1H), 6.71 (d, *J* = 7.7 Hz, 1H), 3.87 (t, *J* = 9.3 Hz, 1H), 3.23 (dd, *J* = 10.6, 3.4 Hz, 1H), 3.10 (q, *J* = 10.5 Hz, 1H), 2.60 – 2.53 (m, 1H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.5, 153.4, 144.2, 139.5, 135.7, 134.9, 133.2, 132.5, 131.7, 128.4, 128.1, 127.6, 127.40, 127.38, 127.3, 127.1,

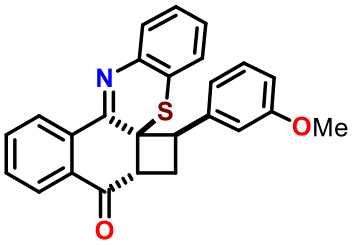
127.0, 126.9, 126.3, 122.2, 49.5, 48.0, 45.1, 27.8; **HRLCMS (ESI)** *m/z*: $[M+H]^+$ calcd for $C_{24}H_{17}ClNOS$, 402.0714, found 402.0700.



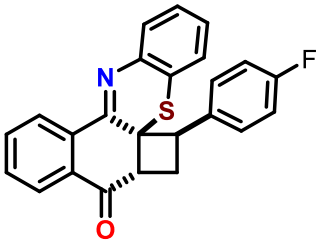
6-(3-Bromophenyl)-7,7a-dihydrobenzo[*a*]cyclobuta[*d*]phenothiazin-8(6*H*)-one (**2i**). Greyish brown solid. Yield 284 mg (84% at 0.76 mmol scale), mp: 138 – 140 °C. Purified using EtOAc/hexane (20:80) as eluent. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.73 (d, J = 8.0 Hz, 1H), 8.21 (d, J = 7.7 Hz, 1H), 7.83 (t, J = 7.6 Hz, 1H), 7.71 (t, J = 7.5 Hz, 1H), 7.41 (d, J = 7.9 Hz, 1H), 7.16 – 7.06 (m, 3H), 6.80 (t, J = 7.5 Hz, 1H), 6.75 (d, J = 7.6 Hz, 1H), 3.89 (t, J = 9.3 Hz, 1H), 3.26 (dd, J = 10.5, 2.7 Hz, 1H), 3.12 (q, J = 10.4 Hz, 1H), 2.59 (ddd, J = 12.1, 8.8, 3.4 Hz, 1H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.5, 153.4, 144.2, 139.8, 135.7, 134.9, 132.5, 131.7, 131.4, 130.3, 128.4, 127.6, 127.41, 127.38, 127.1, 127.05, 126.95, 126.8, 122.2, 121.5, 49.5, 48.0, 45.1, 27.8; **HRLCMS (ESI)** *m/z*: $[M+H]^+$ calcd for $C_{24}H_{17}BrNOS$, 446.0209, found 446.0182.



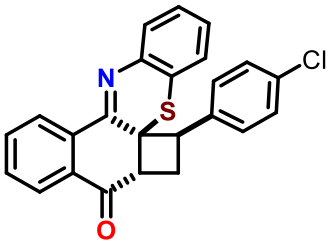
6-(*m*-Tolyl)-7,7a-dihydrobenzo[*a*]cyclobuta[*d*]phenothiazin-8(6*H*)-one (**2j**). Bright yellow solid. Yield 237 m*g* (82% at 0.76 mmol scale), mp: 100 – 102 °C. Purified using EtOAc/hexane (20:80) as eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.73 (d, J = 8.0 Hz, 1H), 8.19 (d, J = 7.7 Hz, 1H), 7.80 (t, J = 7.5 Hz, 1H), 7.67 (t, J = 7.4 Hz, 1H), 7.39 (d, J = 7.8 Hz, 1H), 7.06 (t, J = 7.4 Hz, 1H), 6.92 (t, J = 7.4 Hz, 1H), 6.84 – 6.71 (m, 3H), 6.67 (d, J = 7.7 Hz, 1H), 6.61 (s, 1H), 3.88 (t, J = 9.0 Hz, 1H), 3.30 – 3.23 (m, 1H), 3.17 – 3.08 (m, 1H), 2.60 – 2.51 (m, 1H), 2.08 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 196.8, 153.8, 144.3, 137.4, 136.7, 135.9, 134.8, 132.5, 131.6, 129.4, 127.9, 127.6, 127.4, 127.3, 127.1, 127.0, 126.8, 126.4, 125.0, 122.7, 50.0, 48.0, 45.3, 27.8, 21.1; **HRLCMS (ESI)** *m/z*: $[M+H]^+$ calcd for $C_{25}H_{20}NOS$, 382.1266, found 382.1260.



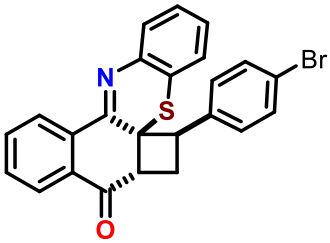
6-(*m*-Tolyl)-7,7a-dihydrobenzo[*a*]cyclobuta[*d*]phenothiazin-8(6*H*)-one (**2k**). Bright orange solid. Yield 293 mg (97% at 0.76 mmol scale), mp: 84 – 86 °C. Purified using EtOAc/hexane (20:80) as eluent. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.72 (d, J = 8.0 Hz, 1H), 8.18 (dd, J = 7.9, 1.4 Hz, 1H), 7.82 – 7.78 (m, 1H), 7.70 – 7.65 (m, 1H), 7.38 (d, J = 7.9 Hz, 1H), 7.09 – 7.05 (m, 1H), 6.92 (t, J = 7.9 Hz, 1H), 6.77 – 6.73 (m, 1H), 6.71 (dd, J = 7.8, 1.6 Hz, 1H), 6.58 (d, J = 7.5 Hz, 1H), 6.53 (dd, J = 8.2, 2.6 Hz, 1H), 6.40 (t, J = 2.2 Hz, 1H), 3.88 (t, J = 9.2 Hz, 1H), 3.62 (s, 3H), 3.26 (dd, J = 10.7, 3.7 Hz, 1H), 3.14 – 3.07 (m, 1H), 2.59 – 2.53 (m, 1H); **^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$)** δ 196.7, 158.7, 139.1, 134.8, 132.5, 131.6, 128.0, 127.6, 127.3, 127.1, 126.9, 126.4, 120.8, 113.7, 113.2, 55.1, 50.0, 48.0, 45.3, 27.95; **HRLCMS (ESI)** *m/z*: $[M+H]^+$ calcd for $C_{25}H_{20}NO_2S$, 398.1209, found 398.1182.



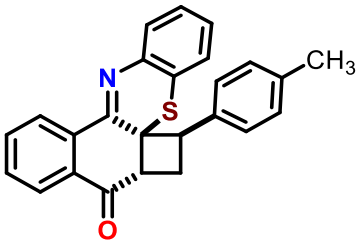
6-(4-Fluorophenyl)-7,7a-dihydrobenzo[*a*]cyclobuta[*d*]phenothiazin-8(6*H*)-one (**2l**). Light brown solid. Yield 278 mg (95% at 0.76 mmol scale), mp: 110 – 111 °C. Purified using EtOAc/hexane (20:80) as eluent. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.70 (d, J = 8.0 Hz, 1H), 8.18 (d, J = 7.8 Hz, 1H), 7.79 (t, J = 7.8 Hz, 1H), 7.67 (t, J = 7.6 Hz, 1H), 7.34 (d, J = 7.8 Hz, 1H), 7.07 (t, J = 7.7 Hz, 1H), 6.92 – 6.85 (m, 2H), 6.76 (t, J = 7.7 Hz, 1H), 6.68 – 6.59 (m, 3H), 3.89 (t, J = 9.5 Hz, 1H), 3.21 (dd, J = 10.7, 3.5 Hz, 1H), 3.08 (q, J = 10.9 Hz, 1H), 2.60 – 2.53 (m, 1H); **^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$)** δ 196.6, 162.9, 160.9, 153.6, 144.1, 135.8, 134.8, 133.2 (d, J = 3.1 Hz), 132.6, 131.7, 129.7 (d, J = 8.2 Hz), 127.5, 127.4 (d, J = 2.2 Hz), 127.1, 126.8, 126.6, 122.5, 113.9, 113.7, 49.2, 48.2, 45.1, 28.1; **^{19}F{^{1}H} NMR (471 MHz, CDCl$_3$)** δ -115.61; **HRMS (ESI)** *m/z*: $[M+Na]^+$ calcd for $C_{24}H_{16}FNOSNa$, 408.0829, found 408.0836.



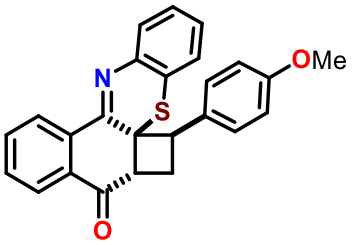
6-(4-Chlorophenyl)-7,7a-dihydrobenzo[*a*]cyclobuta[*d*]phenothiazin-8(6*H*)-one (**2m**). Orange solid. Yield 290 mg (95% at 0.76 mmol scale), mp: 108 – 110 °C. Purified using EtOAc/hexane (20:80) as eluent. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.70 (dd, *J* = 8.1, 1.2 Hz, 1H), 8.18 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.82 – 7.78 (m, 1H), 7.70 – 7.65 (m, 1H), 7.34 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.12 – 7.07 (m, 1H), 6.92 – 6.87 (m, 2H), 6.86 – 6.82 (m, 2H), 6.81 – 6.77 (m, 1H), 6.65 (dd, *J* = 7.8, 1.4 Hz, 1H), 3.88 (t, *J* = 9.3 Hz, 1H), 3.25 – 3.19 (m, 1H), 3.12 – 3.05 (m, 1H), 2.59 – 2.54 (m, 1H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.6, 153.6, 144.1, 135.9, 135.8, 134.9, 133.01, 132.5, 131.7, 129.4, 127.5, 127.4, 127.3, 127.2, 127.0, 126.7, 126.6, 122.4, 49.3, 48.2, 45.1, 27.8; **HRMS (APCI)** *m/z*: $[M+H]^+$ calcd for $C_{24}H_{17}ClNOS$, 402.0714, found 402.0697.



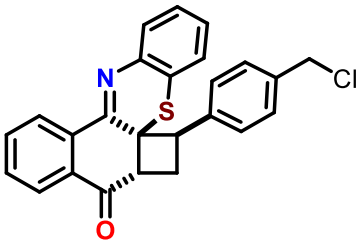
6-(4-Bromophenyl)-7,7a-dihydrobenzo[*a*]cyclobuta[*d*]phenothiazin-8(6*H*)-one (**2n**). Brown solid. Yield 298 mg (88% at 0.76 mmol scale), mp: 121 – 123 °C. Purified using EtOAc/hexane (20:80) as eluent. **^{1}H NMR (500 MHz, $CDCl_3$)** δ ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (d, *J* = 8.0 Hz, 1H), 8.18 (d, *J* = 7.9 Hz, 1H), 7.79 (t, *J* = 7.6 Hz, 1H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.10 (t, *J* = 7.7 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.78 (t, *J* = 8.0 Hz, 3H), 6.64 (d, *J* = 7.7 Hz, 1H), 3.86 (t, *J* = 9.3 Hz, 1H), 3.22 (dd, *J* = 10.8, 3.4 Hz, 1H), 3.08 (q, *J* = 10.9 Hz, 1H), 2.62 – 2.51 (m, 1H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.6, 153.5, 144.1, 136.4, 135.8, 134.9, 132.5, 131.7, 130.0, 129.7, 127.5, 127.4, 127.3, 127.2, 126.7, 126.6, 122.4, 121.4, 49.3, 48.1, 45.1, 27.7; **HRMS (ESI)** *m/z*: $[M+Na]^+$ calcd for $C_{24}H_{16}BrNOSNa$, 468.0028, found 468.0012.



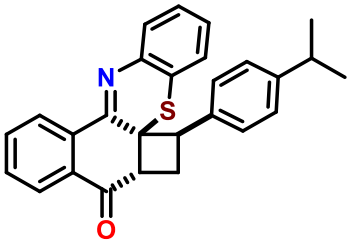
6-(*p*-Tolyl)-7,7a-dihydrobenzo[*a*]cyclobuta[*d*]phenothiazin-8(6*H*)-one (**2o**). Dirty yellow solid. Yield 272 mg (94% at 0.76 mmol scale), mp: 117 – 119 °C. Purified using EtOAc/hexane (20:80) as eluent. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.71 (d, J = 8.0 Hz, 1H), 8.18 (d, J = 7.8 Hz, 1H), 7.79 (t, J = 7.6 Hz, 1H), 7.67 (t, J = 7.5 Hz, 1H), 7.35 (d, J = 7.9 Hz, 1H), 7.06 (t, J = 7.6 Hz, 1H), 6.81 – 6.70 (m, 5H), 6.63 (d, J = 7.8 Hz, 1H), 3.87 (t, J = 9.2 Hz, 1H), 3.25 (dd, J = 10.7, 3.7 Hz, 1H), 3.14 – 3.06 (m, 1H), 2.59 – 2.52 (m, 1H), 2.16 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.9, 153.8, 144.2, 136.7, 136.0, 134.7, 134.4, 132.5, 131.6, 128.0, 127.7, 127.5, 127.33, 127.29, 127.1, 126.4, 126.3, 122.7, 49.6, 48.3, 45.3, 28.0, 20.9; **HRMS (APCI)** *m/z*: $[M]^+$ calcd for $C_{25}H_{19}NOS$, 381.1182, found 381.1197.



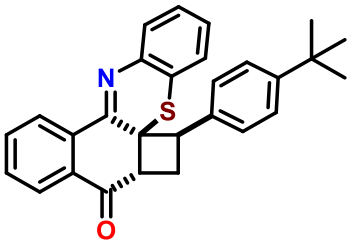
6-(4-Methoxyphenyl)-7,7a-dihydrobenzo[*a*]cyclobuta[*d*]phenothiazin-8(6*H*)-one (**2p**). Orange solid. Yield 290 mg (96% at 0.76 mmol scale), mp: 127 – 129 °C. Purified using EtOAc/hexane (20:80) as eluent. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.71 (d, J = 8.1 Hz, 1H), 8.18 (d, J = 7.9 Hz, 1H), 7.79 (t, J = 7.7 Hz, 1H), 7.67 (t, J = 7.6 Hz, 1H), 7.35 (d, J = 8.0 Hz, 1H), 7.06 (t, J = 7.6 Hz, 1H), 6.84 (d, J = 8.3 Hz, 2H), 6.77 – 6.65 (m, 2H), 6.49 (d, J = 8.2 Hz, 2H), 3.86 (t, J = 9.3 Hz, 1H), 3.69 (s, 3H), 3.28 – 3.17 (m, 1H), 3.08 (q, J = 10.9 Hz, 1H), 2.61 – 2.50 (m, 1H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.9, 158.6, 153.8, 144.2, 135.9, 134.8, 132.5, 131.6, 129.8, 129.2, 127.5, 127.3, 127.1, 126.6, 126.4, 122.8, 112.5, 55.2, 49.3, 48.4, 45.1, 28.2; **HRLCMS (APCI)** *m/z*: $[M-H]^+$ calcd for $C_{25}H_{18}NO_2S$, 396.1053, found 396.1083.



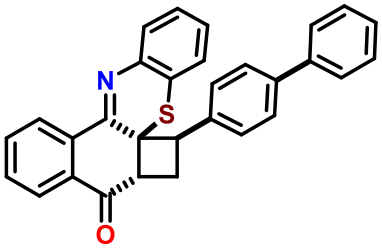
6-(4-(Chloromethyl)phenyl)-7,7a-dihydrobenzo[*a*]cyclobuta[*d*]phenothiazin-8(6*H*)-one (**2q**). Bright yellow solid. Yield 300 mg (95% at 0.76 mmol scale), mp: 121 – 123 °C. Purified using EtOAc/hexane (20:80) as eluent. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.71 (dd, J = 8.1, 1.3 Hz, 1H), 8.19 (dd, J = 7.9, 1.5 Hz, 1H), 7.82 – 7.78 (m, 1H), 7.70 – 7.65 (m, 1H), 7.34 (dd, J = 8.0, 1.4 Hz, 1H), 7.07 – 7.04 (m, 1H), 6.96 (d, J = 8.1 Hz, 2H), 6.91 (d, J = 8.3 Hz, 2H), 6.73 – 6.69 (m, 1H), 6.61 (dd, J = 7.8, 1.4 Hz, 1H), 4.40 (s, 2H), 3.91 (t, J = 9.3 Hz, 1H), 3.26 – 3.21 (m, 1H), 3.17 – 3.10 (m, 1H), 2.59 – 2.53 (m, 1H); **^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$)** δ 196.7, 153.6, 144.1, 137.8, 136.0, 135.8, 134.8, 132.5, 131.6, 128.5, 127.5, 127.4, 127.3, 127.23, 127.17, 126.5, 122.4, 49.6, 48.1, 46.0, 45.1, 27.7; **HRLCMS (ESI)** *m/z*: $[M+H]^+$ calcd for $C_{25}H_{19}ClNOS$, 416.0870, found 416.0857.



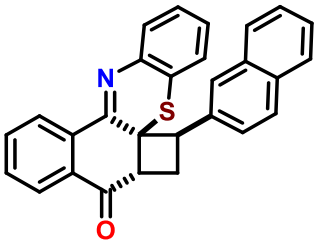
6-(4-*Iso*propylphenyl)-7,7a-dihydrobenzo[*a*]cyclobuta[*d*]phenothiazin-8(6*H*)-one (**2r**). Red solid. Yield 295 mg (95% at 0.76 mmol scale), mp: 100 – 102 °C. Purified using EtOAc/hexane (20:80) as eluent. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.71 (d, J = 8.0 Hz, 1H), 8.19 (d, J = 7.7 Hz, 1H), 7.79 (t, J = 7.6 Hz, 1H), 7.67 (t, J = 7.5 Hz, 1H), 7.33 (d, J = 7.9 Hz, 1H), 7.02 (t, J = 7.5 Hz, 1H), 6.86 (d, J = 8.0 Hz, 2H), 6.79 (d, J = 7.9 Hz, 2H), 6.63 (dd, J = 16.2, 7.4 Hz, 2H), 3.90 (t, J = 9.2 Hz, 1H), 3.21 (dd, J = 10.6, 2.4 Hz, 1H), 3.14 (q, J = 10.5 Hz, 1H), 2.76 – 2.66 (m, 1H), 2.57 – 2.50 (m, 1H), 1.12 (d, J = 6.9 Hz, 6H); **^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$)** δ 197.0, 153.7, 147.6, 144.2, 135.9, 134.8, 134.76, 132.6, 131.5, 128.1, 127.5, 127.3, 127.0, 126.8, 126.2, 125.0, 122.8, 49.7, 48.3, 45.2, 33.7, 27.9, 23.9, 23.7; **HRLCMS (ESI)** *m/z*: $[M+H]^+$ calcd for $C_{27}H_{24}NOS$, 410.1573, found 410.1561.



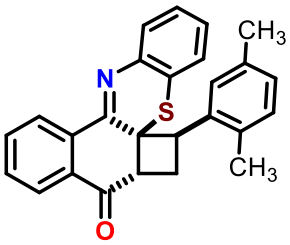
6-(4-(*Tert*-butyl) phenyl)-7,7a-dihydrobenzo[*a*]cyclobuta[*d*]phenothiazin-8(6*H*)-one (**2s**). Greenish solid. Yield 299 mg (93% at 0.76 mmol scale), mp: 131 – 133 °C. Purified using EtOAc/hexane (20:80) as eluent. **^{1}H NMR (500 MHz, CDCl$_3$)** δ ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (d, *J* = 8.0 Hz, 1H), 8.19 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 7.3 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 7.9 Hz, 1H), 7.01 (d, *J* = 7.0 Hz, 1H), 6.95 (d, *J* = 8.2 Hz, 2H), 6.87 (d, *J* = 8.2 Hz, 2H), 6.62 (dd, *J* = 14.9, 7.3 Hz, 2H), 3.90 (d, *J* = 8.7 Hz, 1H), 3.22 – 3.12 (m, 2H), 2.53 (s, 1H), 1.19 (s, 9H); **^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$)** δ 197.0, 153.7, 149.7, 144.3, 135.9, 134.8, 134.4, 132.7, 131.6, 127.9, 127.5, 127.3, 127.0, 126.8, 126.2, 123.8, 122.8, 49.6, 48.4, 45.2, 34.3, 31.1, 27.8; **HRLCMS (ESI)** *m/z*: $[M+Na]^+$ calcd for $C_{28}H_{25}NOSNa$, 446.1549, found 446.1535.



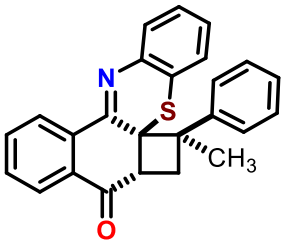
6-([1,1'-Biphenyl]-4-yl)-7,7a-dihydrobenzo[*a*]cyclobuta[*d*]phenothiazin-8(6*H*)-one (**2t**). Orange solid. Yield 316 mg (94% at 0.76 mmol scale), mp: 123 – 125 °C. Purified using EtOAc/hexane (20:80) as eluent. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.73 (d, *J* = 8.0 Hz, 1H), 8.21 (d, *J* = 7.8 Hz, 1H), 7.83 – 7.78 (m, 1H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 4.4 Hz, 4H), 7.38 – 7.31 (m, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 7.09 – 7.04 (m, 1H), 6.99 (d, *J* = 7.9 Hz, 2H), 6.68 – 6.58 (m, 2H), 3.97 (t, *J* = 9.2 Hz, 1H), 3.26 (dd, *J* = 10.7, 2.9 Hz, 1H), 3.23 – 3.16 (m, 1H), 2.64 – 2.56 (m, 1H); **^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$)** δ 196.8, 153.8, 144.3, 141.0, 139.9, 136.5, 135.9, 134.8, 132.6, 131.6, 128.7, 128.5, 127.6, 127.4, 127.3, 127.2, 127.1, 127.0, 126.5, 126.4, 125.7, 122.7, 49.7, 48.5, 45.2, 27.8; **HRLCMS (ESI)** *m/z*: $[M+H]^+$ calcd for $C_{30}H_{22}NOS$, 444.1417, found 444.1398.



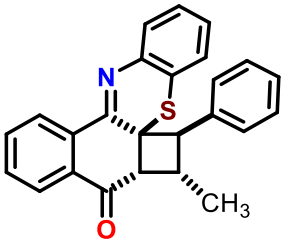
6-(Naphthalen-2-yl)-7,7a-dihydrobenzo[*a*]cyclobuta[*d*]phenothiazin-8(6*H*)-one (**2u**). Greenish-yellow solid. Yield 269 mg (85% at 0.76 mmol scale), mp: 121 – 123 °C. Purified using EtOAc/hexane (20:80) as eluent.; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.75 (dd, J = 8.1, 1.3 Hz, 1H), 8.21 (dd, J = 7.9, 1.4 Hz, 1H), 7.85 – 7.79 (m, 1H), 7.72 – 7.61 (m, 3H), 7.45 (d, J = 1.8 Hz, 1H), 7.41 – 7.32 (m, 4H), 6.94 – 6.87 (m, 2H), 6.41 – 6.34 (m, 2H), 4.08 (t, J = 8.7 Hz, 1H), 3.35 – 3.23 (m, 2H), 2.71 – 2.62 (m, 1H); **^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$)** δ 196.8, 153.8, 144.1, 135.9, 134.9, 134.8, 132.6, 132.5, 132.48, 131.6, 127.8, 127.6, 127.4, 127.2, 127.1, 126.9, 126.5, 126.4, 126.3, 125.6, 122.4, 50.1, 48.4, 45.3, 27.8; **HRLCMS (ESI)** *m/z*: $[M+Na]^+$ calcd for $C_{28}H_{19}NOSNa$, 440.1080, found 440.1071.



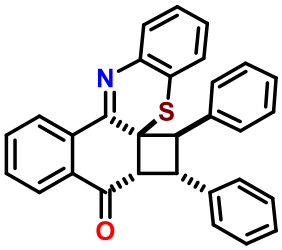
6-(2,5-Dimethylphenyl)-7,7a-dihydrobenzo[*a*]cyclobuta[*d*]phenothiazin-8(6*H*)-one (**2v**). Pinkish brown solid. Yield 249 mg (83% at 0.76 mmol scale), mp: 148 – 150 °C. Purified using EtOAc/hexane (20:80) as eluent. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.69 (dd, J = 8.1, 1.3 Hz, 1H), 8.20 (dd, J = 7.8, 1.4 Hz, 1H), 7.81 – 7.77 (m, 1H), 7.70 – 7.66 (m, 1H), 7.34 – 7.31 (m, 1H), 7.28 (d, J = 1.8 Hz, 1H), 7.03 – 6.98 (m, 1H), 6.71 – 6.63 (m, 3H), 6.46 (d, J = 7.6 Hz, 1H), 4.19 (t, J = 9.4 Hz, 1H), 3.24 – 3.20 (m, 1H), 3.17 – 3.10 (m, 1H), 2.55 – 2.50 (m, 1H), 2.35 (s, 3H), 1.76 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$)** δ 197.2, 154.0, 143.9, 136.0, 135.6, 134.8, 134.0, 133.0, 132.8, 131.6, 129.1, 128.3, 127.64, 127.58, 127.3, 127.1, 126.9, 126.7, 126.3, 122.8, 48.4, 45.4, 44.9, 28.7, 21.2, 18.7; **HRLCMS (ESI)** *m/z*: $[M+H]^+$ calcd for $C_{26}H_{22}NOS$, 396.1417, found 396.1391.



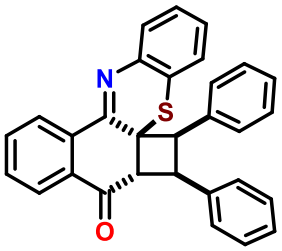
6-Methyl-6-phenyl-7,7a-dihydrobenzo[*a*]cyclobuta[*d*]phenothiazin-8(6*H*)-one (**2w**). Orange solid. Yield 156 mg (54% at 0.76 mmol scale), mp: 128 – 130 °C. Purified using EtOAc/hexane (20:80) as eluent. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.71 (d, J = 8.0 Hz, 1H), 8.15 (d, J = 7.8 Hz, 1H), 7.78 (t, J = 7.7 Hz, 1H), 7.66 (t, J = 7.5 Hz, 1H), 7.48 (d, J = 7.9 Hz, 1H), 7.18 (t, J = 7.6 Hz, 1H), 7.05 – 7.01 (m, 3H), 6.93 – 6.89 (m, 2H), 6.79 (t, J = 7.5 Hz, 1H), 6.62 (d, J = 7.7 Hz, 1H), 3.42 (t, J = 11.6 Hz, 1H), 3.29 (dd, J = 10.9, 5.3 Hz, 1H), 2.28 (dd, J = 12.4, 5.3 Hz, 1H), 1.43 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 197.0, 151.8, 144.7, 142.1, 137.5, 134.6, 132.3, 131.5, 127.32, 127.30, 126.94, 126.92, 126.91, 126.7, 126.6, 122.8, 52.1, 49.5, 44.0, 35.6, 25.8; **HRMS (ESI)** *m/z*: $[M-H]^+$ calcd for $C_{25}H_{18}NOS$, 380.1104, found 380.1101.



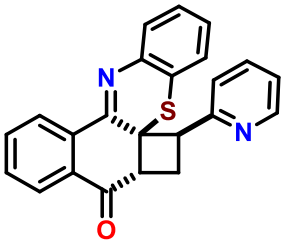
7-Methyl-6-phenyl-7,7a-dihydrobenzo[*a*]cyclobuta[*d*]phenothiazin-8(6*H*)-one (**2x**). Orange solid. Yield 168 mg (58% at 0.76 mmol scale), mp: 92 – 94 °C. Purified using EtOAc/hexane (20:80) as eluent. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.77 (dd, J = 8.1, 1.3 Hz, 1H), 8.24 (dd, J = 7.9, 1.4 Hz, 1H), 7.82 – 7.78 (m, 1H), 7.70 – 7.65 (m, 1H), 7.33 (dd, J = 7.9, 1.4 Hz, 1H), 7.04 – 7.00 (m, 1H), 6.98 – 6.94 (m, 5H), 6.70 – 6.66 (m, 1H), 6.62 (dd, J = 7.8, 1.5 Hz, 1H), 3.52 – 3.46 (m, 2H), 3.33 – 3.27 (m, 1H), 1.10 – 1.05 (m, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 194.4, 154.2, 143.9, 137.0, 135.8, 134.8, 133.3, 131.5, 128.2, 127.7, 127.6, 127.2, 127.1, 127.0, 126.9, 126.8, 126.3, 122.7, 58.3, 49.4, 45.1, 34.5, 16.4; **HRLCMS (ESI)** *m/z*: $[M+H]^+$ calcd for $C_{25}H_{20}NOS$, 382.1260, found 382.1235.



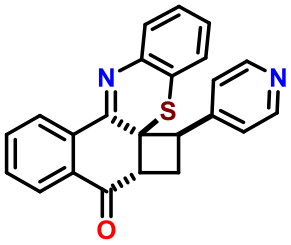
6,7-Diphenyl-7,7a-dihydrobenzo[*a*]cyclobuta[*d*]phenothiazin-8(6*H*)-one (2y). Brown solid. Yield 101 mg (30% at 0.76 mmol scale), mp: 150 – 152 °C. Purified using EtOAc/hexane (20:80) as eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.83 (s, 1H), 8.05 (s, 1H), 7.83 (s, 1H), 7.65 (s, 1H), 7.40 (s, 1H), 7.24 (s, 3H), 7.15 (s, 2H), 7.07 (s, 3H), 6.96 (s, 3H), 6.73 (s, 2H), 4.72 (s, 1H), 4.36 (d, J = 11.4 Hz, 1H), 3.67 (d, J = 11.3 Hz, 1H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 192.9, 153.9, 143.7, 136.5, 136.4, 135.7, 134.7, 133.6, 131.6, 128.4, 128.2, 128.1, 128.0, 127.7, 127.41, 127.37, 127.2, 127.1, 126.8, 126.5, 122.5, 54.9, 52.1, 45.2, 44.0; **HRLCMS (ESI)** *m/z*: $[M+H]^+$ calcd for $C_{30}H_{22}NOS$, 444.1395, found 444.1417.



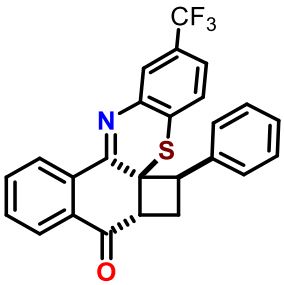
6,7-Diphenyl-7,7a-dihydrobenzo[*a*]cyclobuta[*d*]phenothiazin-8(6*H*)-one (2z). Trace amount realized. **HRLCMS (ESI)** *m/z*: $[M+H]^+$ calcd for $C_{30}H_{22}NOS$, 444.1392, found 444.1417.



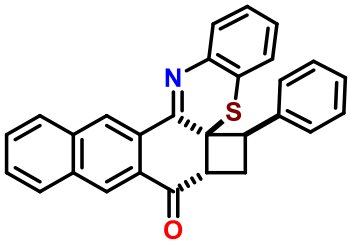
6-(Pyridin-2-yl)-7,7a-dihydrobenzo[*a*]cyclobuta[*d*]phenothiazin-8(6*H*)-one (**2aa**). Orange solid, trace amount of compound. **HRLCMS (ESI)** *m/z*: $[M+H]^+$ calcd for $C_{23}H_{17}N_2OS$, 369.1056, found 369.1030.



6-(Pyridin-4-yl)-7,7a-dihydrobenzo[*a*]cyclobuta[*d*]phenothiazin-8(6*H*)-one (**2ab**). Orange solid, trace amount of compound. **HRLCMS (ESI)** *m/z*: $[M+H]^+$ calcd for $C_{23}H_{17}N_2OS$, 369.1056, found 369.1048.

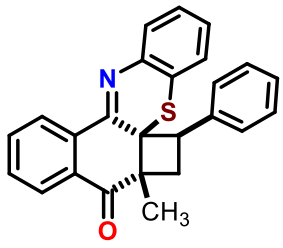


6-Phenyl-2-(trifluoromethyl)-7,7a-dihydrobenzo[*a*]cyclobuta[*d*]phenothiazin-8(6*H*)-one (2ac). Yellow solid. Yield 237 mg (90% at 0.60 mmol scale), mp: 86 – 88 °C. Purified using EtOAc/hexane (20:80) as eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.70 (d, J = 8.1 Hz, 1H), 8.21 (d, J = 7.9 Hz, 1H), 7.82 (t, J = 7.6 Hz, 1H), 7.71 (t, J = 7.5 Hz, 1H), 7.59 (s, 1H), 7.00 – 6.88 (m, 6H), 6.74 (d, J = 8.2 Hz, 1H), 3.94 (t, J = 9.2 Hz, 1H), 3.27 – 3.12 (m, 2H), 2.56 (t, J = 10.2 Hz, 1H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 196.3, 155.2, 144.2, 137.0, 135.3, 134.9, 132.8, 132.2, 128.9, 128.6, 128.2, 127.7, 127.6, 127.4 (d, J = 5.5 Hz), 127.1, 125.2, 123.9 (d, J = 3.9 Hz), 122.7 (d, J = 4.0 Hz), 122.5, 50.1, 48.3, 45.0, 27.5; **^{19}F NMR (471 MHz, $CDCl_3$)** δ -62.64; **HRLCMS (ESI)** *m/z*: $[M+H]^+$ calcd for $C_{25}H_{17}F_3NOS$, 436.0977, found 436.0970.

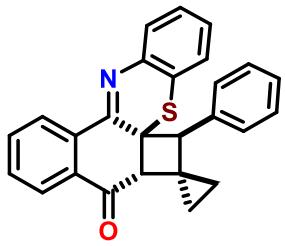


6-Phenyl-7,7a-dihydrocyclobuta[*d*]naphtho[2,3-a]phenothiazin-8(6*H*)-one (**2ad**). Pale yellow solid. Yield 184 mg (69% at 0.64 mmol scale), mp: 140 – 142 °C. Purified using EtOAc/hexane (15:85) as eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.24 (s, 1H), 8.76 (s, 1H),

8.08 (t, *J* = 8.1 Hz, 2H), 7.70 – 7.61 (m, 2H), 7.44 (d, *J* = 7.9 Hz, 1H), 7.11 – 7.06 (m, 1H), 7.00 – 6.92 (m, 5H), 6.73 (t, *J* = 7.6 Hz, 1H), 6.69 – 6.63 (m, 1H), 3.93 (t, *J* = 9.1 Hz, 1H), 3.36 (dd, *J* = 10.8, 4.0 Hz, 1H), 3.20 – 3.11 (m, 1H), 2.65 – 2.57 (m, 1H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 197.0, 154.0, 144.3, 137.6, 136.2, 134.0, 131.2, 130.0, 129.45, 129.38, 129.36, 129.3, 128.5, 128.4, 128.2, 127.2, 127.17, 127.1, 127.06, 126.6, 126.4, 122.6, 50.0, 48.3, 45.6, 28.0; **HRLCMS (ESI)** *m/z*: $[M+H]^+$ calcd for $C_{28}H_{20}NOS$, 418.1260, found 418.1250.

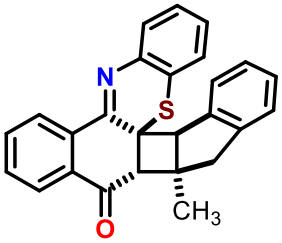


7a-Methyl-6-phenyl-7,7a-dihydrobenzo[*a*]cyclobuta[*d*]phenothiazin-8(6*H*)-one (2ae). Yellow solid. Yield 58 mg (20% at 0.76 mmol scale), mp: 142 – 144 °C. Purified using EtOAc/hexane (20:80) as eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.78 (d, *J* = 8.1 Hz, 1H), 8.19 (d, *J* = 7.8 Hz, 1H), 7.85 (t, *J* = 7.6 Hz, 1H), 7.73 (t, *J* = 7.5 Hz, 1H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.03 (q, *J* = 4.1 Hz, 1H), 6.98 (s, 2H), 6.95 – 6.89 (m, 3H), 6.68 (d, *J* = 4.3 Hz, 2H), 3.79 – 3.73 (m, 1H), 2.83 (t, *J* = 11.3 Hz, 1H), 2.77 – 2.72 (m, 1H), 1.50 (d, *J* = 1.4 Hz, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 200.8, 153.0, 143.0, 136.8, 134.9, 134.8, 132.4, 132.1, 128.2, 128.0, 127.7, 127.5, 127.2, 127.13, 127.06, 126.9, 126.3, 123.1, 54.1, 49.2, 48.5, 33.6, 21.0; **HRLCMS (ESI)** *m/z*: $[M+H]^+$ calcd for $C_{25}H_{20}NOS$, 382.1248, found 382.1260.

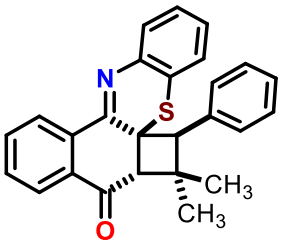


6-Phenyl-6*H*-spiro[benzo[*a*]cyclobuta[*d*]phenothiazine-7,1'-cyclopropan]-8(7a*H*)-one (2af). Greenish-yellow solid. Yield 149 mg (50% at 0.76 mmol scale), mp: 130 – 132 °C. Purified using EtOAc/hexane (20:80) as eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.88 (d, *J* = 8.0 Hz, 1H), 8.18 (d, *J* = 7.8 Hz, 1H), 7.85 (t, *J* = 7.6 Hz, 1H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 6.7 Hz, 3H), 6.89 (d, *J* = 6.9 Hz, 2H), 6.81 (t, *J* = 7.6 Hz, 1H), 6.63 (d, *J* = 7.8 Hz, 1H), 3.74 (s, 1H), 3.69 (s, 1H), 0.90 – 0.85 (m, 1H), 0.72 – 0.64 (m, 2H), 0.45 – 0.39 (m, 1H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 193.3,

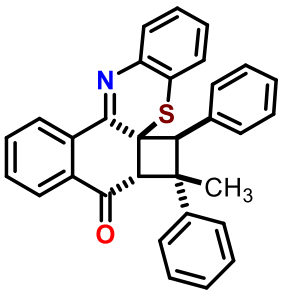
155.8, 143.7, 137.0, 134.9, 134.8, 132.2, 130.1, 128.1, 127.32, 127.27, 127.03, 127.00, 126.9, 126.8, 126.7, 122.7, 58.0, 51.4, 44.3, 24.7, 11.3, 10.8; **HRLCMS (ESI)** *m/z*: $[M+H]^+$ calcd for $C_{26}H_{20}NOS$, 394.1258, found 394.1260.



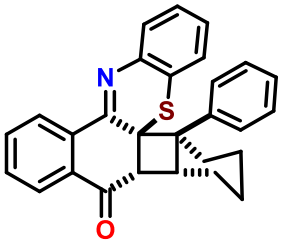
10b-Methyl-10a,10b,11,15b-tetrahydro-10*H*-benzo[*a*]indeno[1',2':3,4]cyclobuta[1,2-*d*]phenothiazin-10-one (2ag). Yellow solid. Yield 45 mg (15% at 0.76 mmol scale), mp: 130 – 132 °C. Purified using EtOAc/hexane (20:80) as eluent. **^{1}H NMR (700 MHz, $CDCl_3$)** δ 8.84 – 8.77 (m, 1H), 8.19 (d, *J* = 7.7 Hz, 1H), 7.83 – 7.68 (m, 3H), 7.39 (s, 1H), 7.26 (d, *J* = 7.4 Hz, 2H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 1H), 7.01 (t, *J* = 7.3 Hz, 1H), 5.95 (d, *J* = 7.6 Hz, 1H), 3.58 (s, 1H), 3.44 (d, *J* = 16.7 Hz, 1H), 3.36 (s, 1H), 2.98 (d, *J* = 16.7 Hz, 1H), 1.21 (s, 3H); **^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$)** δ 194.2, 153.8, 144.3, 143.8, 139.6, 135.7, 134.8, 132.9, 132.0, 128.2, 127.9, 127.6, 127.4, 127.0, 126.88, 126.86, 126.2, 124.9, 123.0, 62.1, 55.4, 50.3, 46.6, 43.5, 22.5; **HRLCMS (ESI)** *m/z*: $[M+H]^+$ calcd for $C_{26}H_{20}NOS$, 394.1280, found 394.1260.



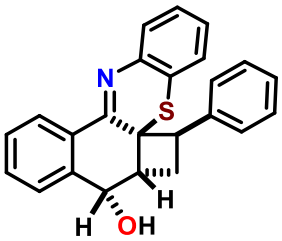
7,7-Dimethyl-6-phenyl-7,7a-dihydrobenzo[*a*]cyclobuta[*d*]phenothiazin-8(6*H*)-one (2ah). Trace amount realized. **HRLCMS (APCI)** *m/z*: $[M+H]^+$ calcd for $C_{26}H_{22}NOS$, 396.1443, found 396.1417.



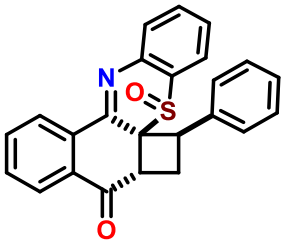
7-Methyl-6,7-diphenyl-7,7a-dihydrobenzo[*a*]cyclobuta[*d*]phenothiazin-8(6*H*)-one (2ai). Trace amount realized. **HRLCMS (ESI)** *m/z*: $[M-H]^+$ calcd for $C_{31}H_{22}NOS$, 456.1412, found 456.1417.



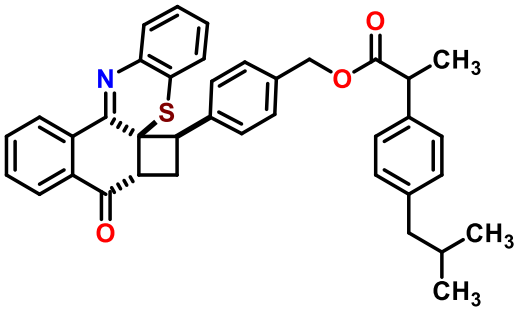
5b-Phenyl-6,7,8,9,9a,9b-hexahydrobenzo[*a*]benzo[3,4]cyclobuta[1,2-*d*]phenothiazin-10(5b*H*)-one (2aj). Trace amount realized. **HRLCMS (ESI-QTOF)** *m/z*: $[M+H]^+$ calcd for $C_{28}H_{24}NOS$, 422.1573, found 422.1572.



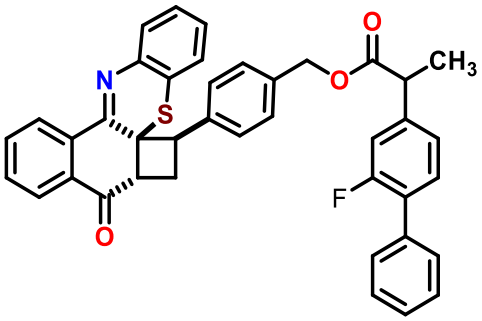
6-Phenyl-6,7,7a,8-tetrahydrobenzo[*a*]cyclobuta[*d*]phenothiazin-8-ol (**2ak**). Pink solid. Yield 249 mg (89% at 0.76 mmol scale), mp: 123 – 125 °C. Purified using EtOAc/hexane (35:65) as eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.57 (d, J = 7.8 Hz, 1H), 7.77 (d, J = 7.7 Hz, 1H), 7.61 (t, J = 7.5 Hz, 1H), 7.54 (dd, J = 14.0, 7.8 Hz, 2H), 7.23 (t, J = 7.5 Hz, 1H), 7.16 (d, J = 6.6 Hz, 3H), 6.95 (t, J = 7.5 Hz, 1H), 6.80 – 6.71 (m, 3H), 5.11 (d, J = 5.4 Hz, 1H), 3.40 – 3.30 (m, 2H), 2.38 – 2.30 (m, 1H), 2.23 (t, J = 11.2 Hz, 1H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 157.6, 143.7, 139.8, 138.7, 131.6, 131.2, 128.7, 127.9, 127.7, 127.3, 127.2, 126.9, 126.3, 125.4, 122.3, 66.3, 49.4, 45.2, 40.5, 22.3; **HRLCMS (ESI)** *m/z*: $[M+H]^+$ calcd for $C_{24}H_{20}NOS$, 370.1260, found 370.1268.



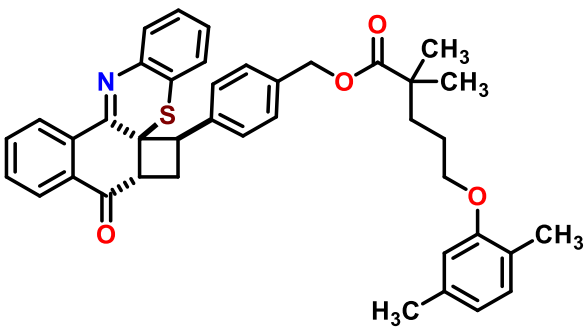
6-Phenyl-7,7a-dihydrobenzo[*a*]cyclobuta[*d*]phenothiazin-8(6*H*)-one 5-oxide (**2al**). Light yellow solid. Yield 227 mg (78% at 0.76 mmol scale), mp: 173 – 175 °C. Purified by precipitation technique using pentane. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.80 (d, J = 8.2 Hz, 1H), 8.22 (d, J = 7.8 Hz, 1H), 7.81 (t, J = 7.9 Hz, 1H), 7.71 (t, J = 7.5 Hz, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.46 (s, 1H), 6.93 (s, 5H), 6.81 (d, J = 7.1 Hz, 2H), 4.18 – 4.02 (m, 2H), 3.53 (d, J = 11.4 Hz, 1H), 2.79 (t, J = 10.7 Hz, 1H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.2, 156.9, 140.7, 137.1, 135.8, 134.8, 134.0, 132.7, 132.5, 130.5, 128.5, 128.4, 127.9, 127.8, 127.4, 127.2, 127.0, 123.6, 62.6, 48.9, 40.2, 27.7; **HRLCMS (ESI)** *m/z*: $[M+Na]^+$ calcd for $C_{24}H_{17}NO_2SNa$, 406.0872, found 406.0895.



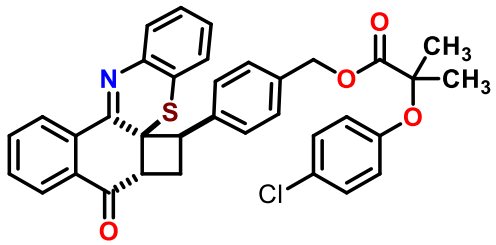
4-(8-Oxo-6,7,7a,8-tetrahydrobenzo[*a*]cyclobuta[*d*]phenothiazin-6-yl) benzyl 2-(4-isobutyl- phenyl) propanoate (**2am**). Ibuprofen coupled cyclobutylated phenothiazine **2ae** was prepared by the [2+2] photo-cycloaddition reaction between **1a** and 4-vinylbenzyl 2-(4-isobutylphenyl) propanoate (synthesized by following reported procedure)[1a] using standard reaction conditions. Brownish thick liquid. Yield 289 mg (65% at 0.76 mmol scale), mp: 101 – 103 °C. Purified using CH_2Cl_2 solvent as eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.71 (d, J = 8.0 Hz, 1H), 8.19 (dd, J = 7.9, 1.4 Hz, 1H), 7.82 – 7.76 (m, 1H), 7.69 – 7.64 (m, 1H), 7.34 – 7.30 (m, 1H), 7.24 – 7.20 (m, 2H), 7.12 (dd, J = 8.2, 2.1 Hz, 2H), 7.00 (q, J = 7.3 Hz, 1H), 6.87 – 6.79 (m, 4H), 6.62 – 6.57 (m, 1H), 6.54 – 6.49 (m, 1H), 4.92 (d, J = 2.5 Hz, 2H), 3.89 (t, J = 9.3 Hz, 1H), 3.78 – 3.71 (m, 1H), 3.23 (dd, J = 10.6, 3.4 Hz, 1H), 3.15 – 3.06 (m, 1H), 2.59 – 2.51 (m, 1H), 2.47 (dd, J = 7.2, 1.9 Hz, 2H), 1.92 – 1.81 (m, 1H), 1.52 (d, J = 7.2 Hz, 3H), 0.92 (dd, J = 6.6, 2.0 Hz, 6H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 196.7, 174.4, 153.7, 144.2, 140.7, 137.7, 137.6, 137.3, 135.9, 134.9, 134.8, 132.5, 131.6, 129.4, 128.2, 127.6, 127.4, 127.2, 127.1, 126.7, 126.4, 126.3, 122.5, 65.9, 49.6, 48.2, 45.3, 45.2, 45.1, 30.2, 27.8, 22.4, 18.6, 18.5; **HRLCMS (ESI)** *m/z*: $[M+H]^+$ calcd for $C_{38}H_{36}NO_3S$, 586.2410, found 586.2418.



4-(8-Oxo-6,7,7a,8-tetrahydrobenzo[*a*]cyclobuta[*d*]phenothiazin-6-yl) benzyl 2-(2-fluoro-[1,1'-biphenyl]-4-yl) propanoate (**2an**). Flurbiprofen coupled cyclobutylated phenothiazine **2af** was prepared by the [2+2] photo-cycloaddition reaction between **1a** and 4-vinylbenzyl 2-(2-fluoro-[1,1'-biphenyl]-4-yl) propanoate (synthesized following reported procedure)[1b] following standard reaction protocol along with 10 mol % Na_2EosinY photocatalyst as without the catalyst the yield of the desired product was very less. Brownish sticky solid. Yield 228 mg (50% at 0.76 mmol scale), mp: 107 – 109 °C. Purified using CH_2Cl_2 solvent as eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.72 (dd, J = 8.1, 1.3 Hz, 1H), 8.19 (dd, J = 7.9, 1.5 Hz, 1H), 7.82 – 7.77 (m, 1H), 7.69 – 7.65 (m, 1H), 7.57 – 7.53 (m, 2H), 7.48 – 7.40 (m, 3H), 7.40 – 7.37 (m, 1H), 7.36 – 7.32 (m, 1H), 7.19 – 7.12 (m, 2H), 7.05 – 6.99 (m, 1H), 6.91 – 6.84 (m, 4H), 6.66 – 6.60 (m, 1H), 6.58 – 6.53 (m, 1H), 4.97 (d, J = 3.6 Hz, 2H), 3.90 (t, J = 9.3 Hz, 1H), 3.84 – 3.77 (m, 1H), 3.27 – 3.20 (m, 1H), 3.16 – 3.07 (m, 1H), 2.59 – 2.52 (m, 1H), 1.57 (d, J = 7.1 Hz, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 196.6, 173.7, 160.7, 158.7, 153.6, 144.2, 141.7 (d, J = 7.5 Hz), 137.6, 135.8, 135.5, 134.8, 134.6 (d, J = 3.2 Hz), 132.5, 131.6, 130.8 (d, J = 4.0 Hz), 129.0 (d, J = 2.9 Hz), 128.5, 128.3, 128.0, 127.9, 127.8, 127.6, 127.4, 127.3, 127.1, 126.7, 126.5, 126.4, 123.6 (d, J = 3.4 Hz), 122.6, 115.4, 115.2, 66.3 (d, J = 2.6 Hz), 49.6, 48.1, 45.2, 45.1 (d, J = 7.3 Hz), 27.8 (d, J = 1.9 Hz), 18.4 (d, J = 11.1 Hz); **^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$)** δ -117.50; **HRLCMS (APCI)** *m/z*: $[M+H]^+$ calcd for $C_{40}H_{31}FNO_3S$, 624.2003, found 624.1987.

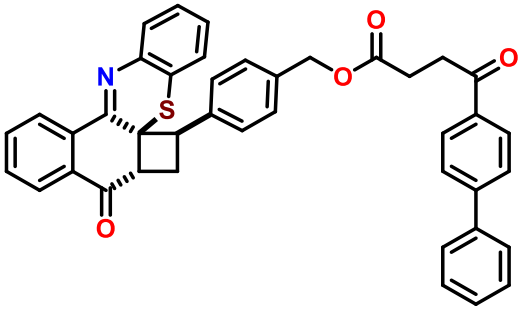


4-(8-Oxo-6,7,7a,8-tetrahydrobenzo[*a*]cyclobuta[*d*]phenothiazin-6-yl) benzyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (**2ao**). Gemfibrozil coupled cyclobutylated phenothiazine **2ag** was prepared by the [2+2] photo-cycloaddition reaction between **1a** and 4-vinylbenzyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (synthesized following reported procedure)[1b] using standard reaction conditions. Orangish sticky solid. Yield 297 mg (62% at 0.76 mmol scale), mp: 86 – 88 °C. Purified using EtOAc/CH_2Cl_2 (20:80) as eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.72 (dd, *J* = 8.1, 1.3 Hz, 1H), 8.19 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.83 – 7.78 (m, 1H), 7.70 – 7.65 (m, 1H), 7.35 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.07 – 7.02 (m, 1H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.95 – 6.88 (m, 4H), 6.72 – 6.65 (m, 2H), 6.62 – 6.58 (m, 2H), 4.93 (d, *J* = 1.7 Hz, 2H), 3.93 – 3.86 (m, 3H), 3.27 – 3.22 (m, 1H), 3.16 – 3.07 (m, 1H), 2.59 – 2.52 (m, 1H), 2.31 (s, 3H), 2.17 (s, 3H), 1.74 (s, 4H), 1.25 (s, 6H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 196.7, 177.5, 156.9, 153.6, 144.2, 137.4, 136.5, 135.9, 135.1, 134.8, 132.5, 131.6, 130.3, 128.3, 127.6, 127.4, 127.1, 126.6, 126.44, 126.4, 123.6, 122.6, 120.8, 111.9, 67.9, 65.7, 49.6, 48.1, 45.2, 42.2, 37.1, 29.7, 27.8, 25.21, 25.17, 21.5, 15.8; **HRLCMS (ESI)** *m/z*: $[M+Na]^+$ calcd for $C_{40}H_{39}NO_4SNa$, 652.2492, found 652.2501.



4-(8-Oxo-6,7,7a,8-tetrahydrobenzo[*a*]cyclobuta[*d*]phenothiazin-6-yl) benzyl 2-(4-chlorophenoxy)-2-methylpropanoate (**2ap**). Clofibric acid coupled cyclobutylated phenothiazine **2ah** was prepared by the [2+2] photo-cycloaddition reaction between **1a** and 4-vinylbenzyl 2-(4-chlorophenoxy)-2-methylpropanoate (synthesized following reported procedure)[1b] using standard reaction conditions. Yellow sticky solid. Yield 325 mg (72% at 0.76 mmol scale), mp: 109 – 111 °C. Purified using EtOAc/CH_2Cl_2 (20:80) as eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.71 (dd, *J* = 8.2, 1.3 Hz, 1H), 8.18 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.82 – 7.76 (m, 1H), 7.70 – 7.64 (m, 1H), 7.33 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.17 – 7.11 (m, 2H), 7.04 – 6.99 (m, 1H), 6.86 (q, *J* = 8.1 Hz, 4H), 6.75 – 6.70 (m, 2H), 6.68 – 6.63 (m, 1H), 6.55 (dd, *J* = 7.8, 1.4 Hz, 1H), 4.99 (s, 2H), 3.90 (t, *J* = 9.2 Hz, 1H), 3.28 – 3.21 (m, 1H), 3.17 – 3.07 (m, 1H), 2.60 – 2.53 (m, 1H), 1.58 (s, 6H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 196.6, 173.7, 154.0,

153.6, 144.1, 137.8, 135.8, 134.8, 134.0, 132.5, 131.7, 129.1, 128.4, 127.6, 127.37, 127.35, 127.3, 127.1, 126.9, 126.7, 126.4, 122.5, 120.5, 79.5, 66.8, 49.6, 48.1, 45.2, 27.8, 25.4, 25.3; **HRLCMS (ESI)** *m/z*: $[M+Na]^+$ calcd for $C_{35}H_{28}ClNO_4SNa$, 616.1320, found 616.1290.



4-(8-Oxo-6,7,7a,8-tetrahydrobenzo[*a*]cyclobuta[*d*]phenothiazin-6-yl) benzyl 4-([1,1'-biphenyl]-4-yl)-4-oxobutanoate (**2aq**). Fenbufen-coupled cyclobutylated phenothiazine **2ai** was prepared by the [2+2] photo-cycloaddition reaction between **1a** and 4-vinylbenzyl 4-([1,1'-biphenyl]-4-yl)-4-oxobutanoate (synthesized following reported procedure)[1b] using standard reaction conditions. Orangish sticky solid. Yield 328 mg (68% at 0.76 mmol scale), mp: 88 – 90 °C. Purified using EtOAc/CH_2Cl_2 (10:90) as eluent and did a column for a prolonged time. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.72 (dd, J = 8.1, 1.3 Hz, 1H), 8.19 (dd, J = 7.9, 1.4 Hz, 1H), 8.09 – 8.05 (m, 2H), 7.82 – 7.78 (m, 1H), 7.72 – 7.66 (m, 3H), 7.65 – 7.61 (m, 2H), 7.50 – 7.45 (m, 2H), 7.43 – 7.39 (m, 1H), 7.34 (dd, J = 8.0, 1.3 Hz, 1H), 7.07 – 7.03 (m, 1H), 6.96 – 6.89 (m, 4H), 6.72 – 6.67 (m, 1H), 6.61 (dd, J = 7.8, 1.4 Hz, 1H), 4.97 (s, 2H), 3.91 (t, J = 9.2 Hz, 1H), 3.37 (t, J = 6.6 Hz, 2H), 3.27 – 3.21 (m, 1H), 3.17 – 3.08 (m, 1H), 2.84 (t, J = 6.6 Hz, 2H), 2.59 – 2.52 (m, 1H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 197.6, 196.7, 172.7, 153.6, 146.0, 144.1, 139.8, 137.5, 135.8, 135.2, 134.8, 134.7, 132.5, 131.6, 129.0, 128.7, 128.34, 128.3, 127.6, 127.4, 127.31, 127.29, 127.2, 126.8, 126.7, 126.5, 122.5, 66.1, 49.6, 48.2, 45.2, 33.4, 28.3, 27.8; **HRLCMS (ESI)** *m/z*: $[M+Na]^+$ calcd for $C_{41}H_{31}NO_4SNa$, 656.1866, found 656.1897.

7. Photophysical Studies Regarding the [2+2] Cycloaddition Reaction

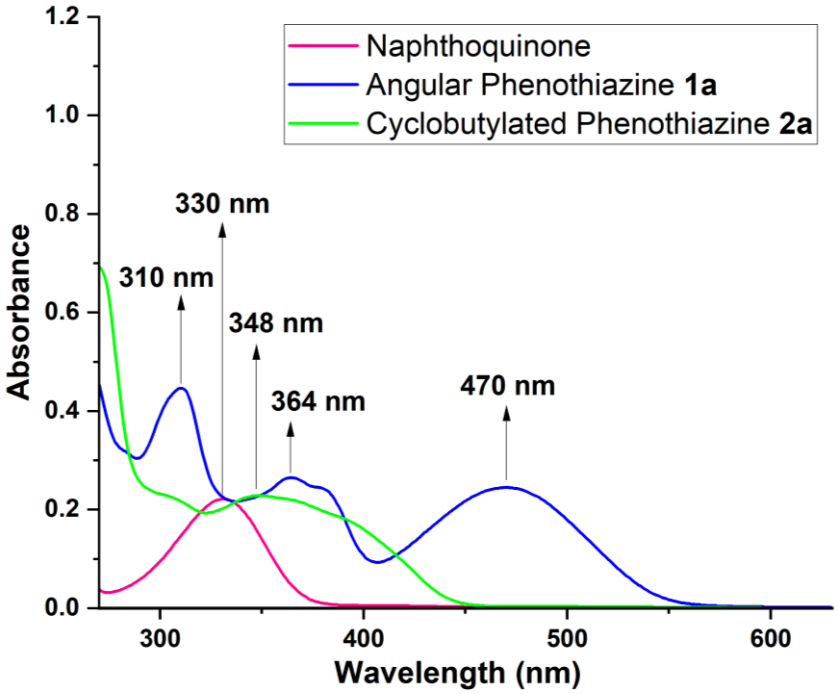


Figure S5. Absorption spectra of angular phenothiazine **1a** (60 μM), cyclobutylated phenothiazine **2a** (60 μM), and naphthoquinone (60 μM) in acetonitrile

Next, the electronic absorption spectra of angular phenothiazine **1a** in various solvents were investigated (Figure S6). The normalized absorption spectra revealed consistent maxima around 468-478 nm, with no significant shift observed in different solvents. In water, an elevation in absorption intensity above the baseline was observed, and the broad spectrum indicated the formation of soluble aggregates (Figure S6a). Furthermore, the normalized solvent-dependent emission spectra of **1a** revealed that solvent polarity did not attribute any role to the shift in emission maxima (λ_{max} = 605 - 618 nm, Figure S6b). Cuvette images revealed that, in most of the solvents the angular phenothiazine **1a** exhibited orange emission, in water almost non-emissive, however, in acetone and methanol it exhibited red emission (Figure S6c).

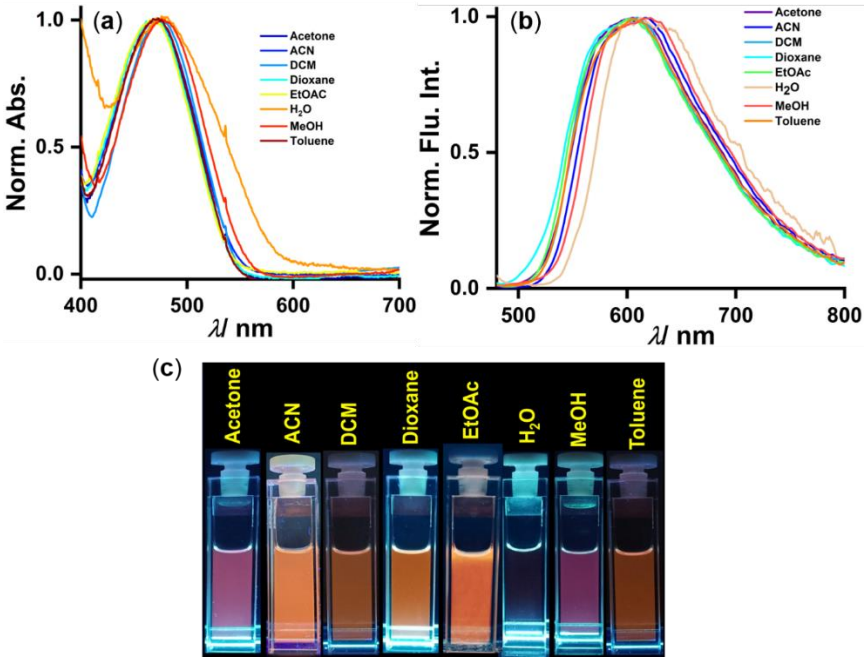


Figure S6. (a) UV–Visible absorption spectra of the angular phenothiazine **1a** (10 μM) in different solvents, (b) emission spectra of **1a** (10 μM) in different solvents, (c) cuvette images in different solvents under 365 nm excitation by a hand-held UV lamp

Kinetic Studies

The blue light irradiated (λ_{max} = 457 nm) reaction mixture of angular phenothiazine **1a** and styrene, in acetonitrile was studied by UV−visible spectroscopy at different time intervals. Initially, the absorption spectra of the reaction mixture were recorded by taking 10 μL of aliquot from the reaction vessel before exposing it to light irradiation. Next, the reaction mixture was irradiated with blue light (λ_{max} = 457 nm), and the same amount (10μL) of the aliquot of the reaction mixture was screened over different time intervals. The spectra of the time-based UV-visible study have been pasted in the main manuscript (Figure 3). The absorption spectrum of the reaction mixture suggests that after 6 hours of light exposure, there was no further decrement in absorbance of the angular phenothiazine **1a** was realized; in other words, the peak at 470 nm gets saturated after 6 hours of light irradiation (λ_{max} = 457 nm), which means the reaction finished after 6 hours.

Further, the rate of the [2+2] cycloaddition reaction was also studied by the UV-visible experiment. The reaction shows first-order kinetics with respect to both reactants individually, with a rate constant of (6.6 ± 0.4) x 10^{-3} min^{-1} (Figure 3c, main manuscript). Moreover, the

initial reaction rate was calculated from the respective rate constants for the first 240 minutes using the first-order rate law. It suggests that the initial rate of the reaction for [2+2] cycloaddition was observed as 0.26 μM min^{-1} within 240 min of the reaction (*vide infra*).

$$\text{Rate of reaction} = -\frac{\Delta(\text{Angular Phenothiazine})}{\Delta\text{time}}$$

$$\text{Rate for the formation of } \mathbf{2a} = -\frac{\Delta(\text{Angular Phenothiazine})}{\Delta\text{time}}$$

$$= -\frac{(17.54-80.0)\ \mu\text{M}}{(240-0)\ \text{min}} = 0.26\ \mu\text{M min}^{-1}$$

Rate (v_o): 0.26 μM min^{-1} (experiments have been repeated triplicate).

Dependency of the Rate of [2+2] Photocycloaddition Reaction on the Intensity of Incident Light

To investigate whether the rate of the [2+2] photocycloaddition reaction has any dependency on the incident light intensity, we conducted the reaction between angular phenothiazine **1a** and styrene under optimized reaction conditions, at variable light intensities. The reactions were carried out up to saturation and the rate of each reaction was monitored for up to 240 mins (Figure S7). At the optimal light intensity of 900 lx, the reaction rate was at its maximum (0.26 μM min^{-1}), with a rate constant of (6.6 ± 0.4)×10^{-3} min^{-1}. As the incident photon concentration decreased, the reaction rate also gradually declined. At 400 lx, the rate was 0.12 μM min^{-1} with a rate constant of (1.9 ± 0.04)×10^{-3} min^{-1}, and at 70 lx, the rate was 0.097 μM min^{-1} with a rate constant of (1.5 ± 0.1)×10^{-3} min^{-1}. These results are suggestive of the dependency of rate law on the intensity of incident light.

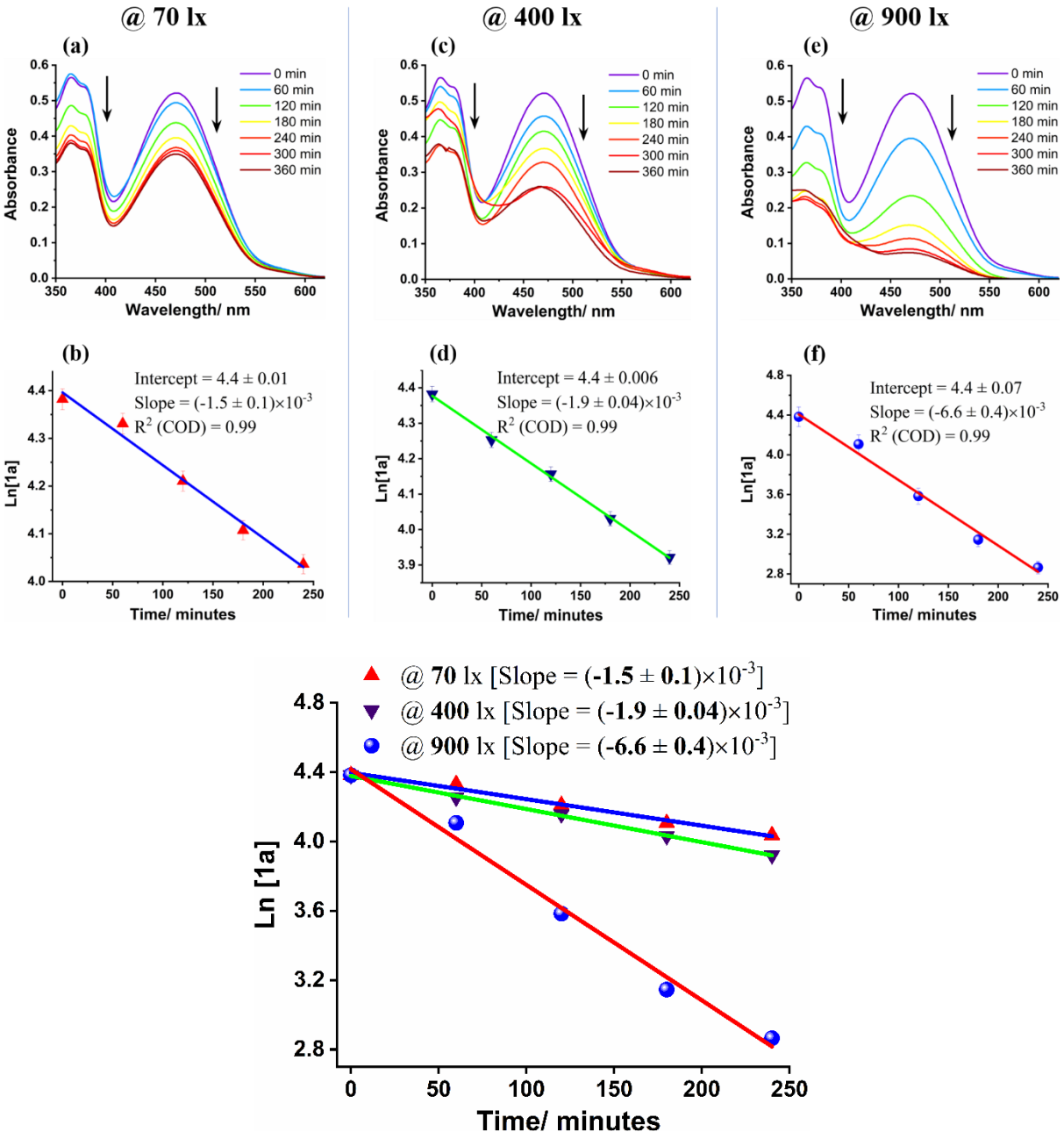


Figure S7. Dependence of rate of the [2+2] photocycloaddition reaction at different incident light intensities. (a) time-dependent absorption spectra of the [2+2] cycloaddition reaction at 70 lx; (b) plot of ln[**1a**] with respect to time for determining the rate of reaction at 70 lx; (c) time-dependent absorption spectra of the [2+2] cycloaddition reaction at 400 lx; (d) plot of ln[**1a**] with respect to time for determining the rate of reaction at 400 lx; (e) time-dependent absorption spectra of the [2+2] cycloaddition reaction at 900 lx; (f) plot of ln[**1a**] with respect to time for determining the rate of reaction at 900 lx; (g)) plot of ln[**1a**] with respect to time at different incident light intensities for determining the rate differences of the cycloaddition reaction.

Emission Studies

As a part of the kinetic experiment of the [2+2] photocycloaddition reaction, the time-dependent emission spectra of the blue light irradiated (λ_{max} = 457 nm) reaction mixture of angular phenothiazine **1a** and styrene was measured at room temperature in acetonitrile solvent. Following a similar trend as absorption spectroscopy, in emission spectra also the maximum emission at 611 nm corresponding to the precursor angular phenothiazine **1a** got saturated within 360 minutes, indicating the completion of the cycloaddition reaction (Figure S8).

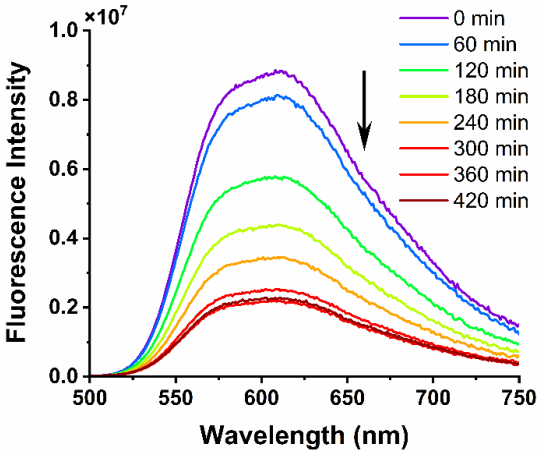
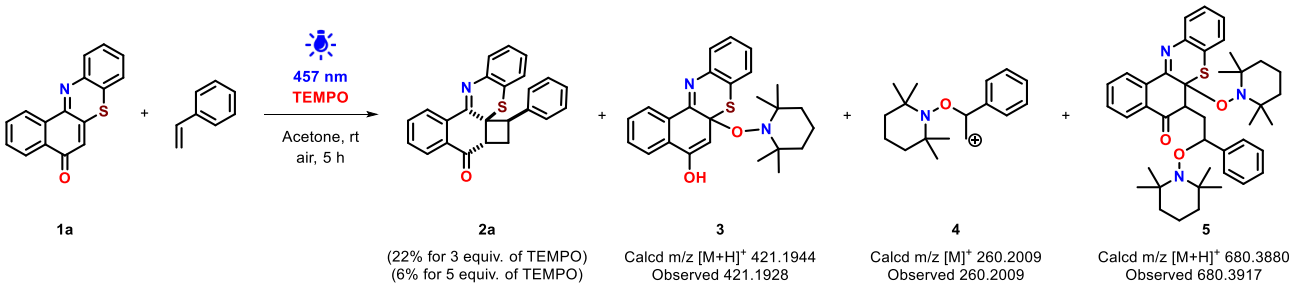


Figure S8. Time-dependent emission spectra of the [2+2] photocycloaddition reaction

8. Mechanistic Investigations

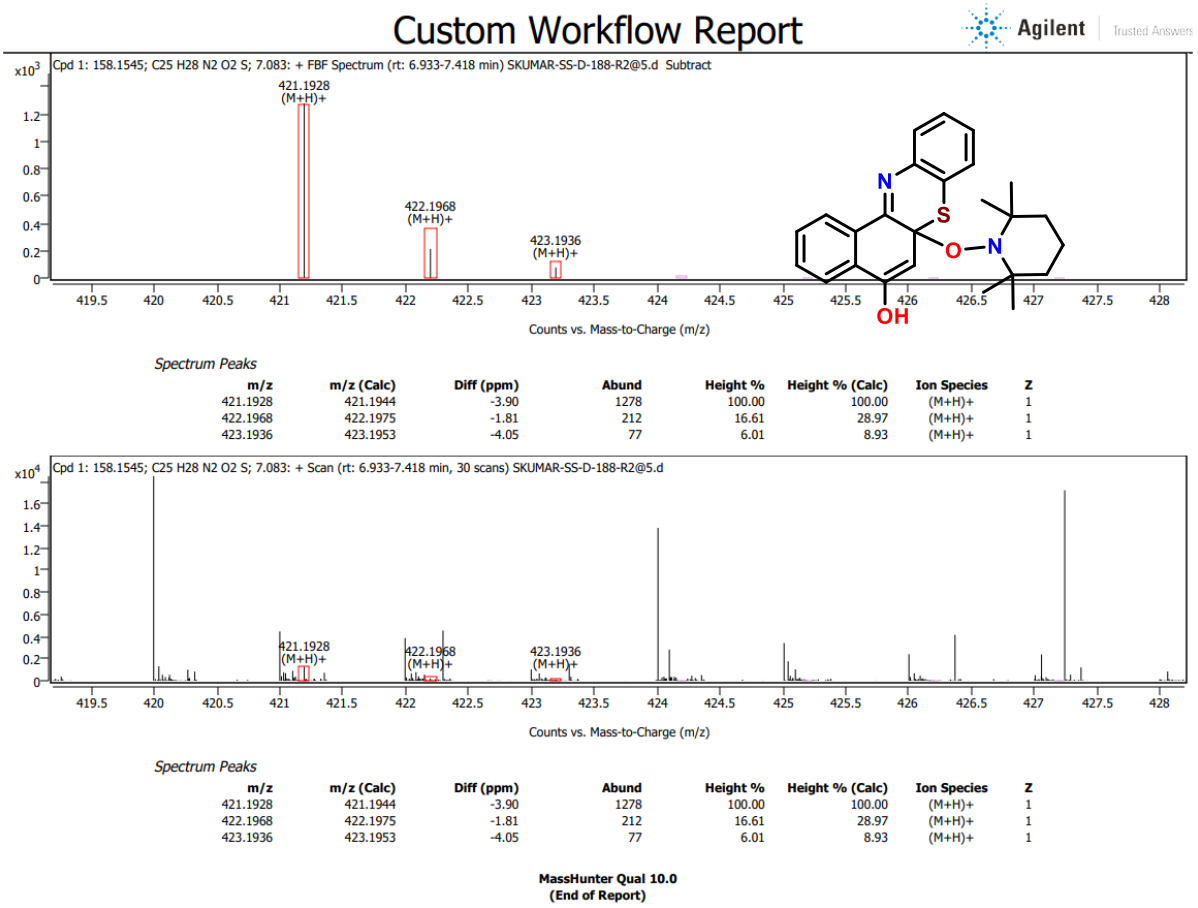
Radical Trapping Experiment

When the reaction was carried out in the presence of a radical trapping agent (TEMPO), a drastic decrement in the yield of the desired cyclobutylated phenothiazine **2a** was observed. We have also varied the loading of TEMPO, and we observed that when 3 and 5 equivalents of TEMPO were used, **2a** was obtained in 22% and 6%. When the reaction mixture was subjected for HRMS analysis; along with the desired product **2a**, it showed the formation of the following TEMPO adducts **3**, **4**, and **5**. A reduced form of phenothiazinyl-TEMPO adduct **3** exhibited calculated m/z $[M+H]^+$ = 421.1944, observed 421.1928; an oxidized form of styrenyl-TEMPO adduct **4** exhibited calculated m/z $[M]^+$ = 260.2009, observed 260.2009; and a phenothiazinyl-styrenyl-TEMPO adduct **5** had calculated m/z $[M+H]^+$ = 680.3880, observed 680.3917.



Scheme S4. Control experiment: radical trapping experiment with TEMPO

<u>Mass Spectrum for the reduced form of phenothiazinyl-TEMPO adduct **3**</u>

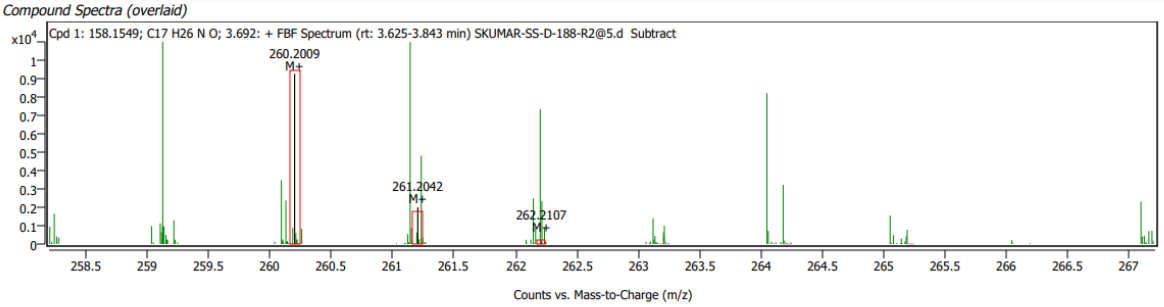


Mass Spectrum for oxidized form of styrenyl-TEMPO adduct **4**

Custom Workflow Report

Agilent Trusted Answers

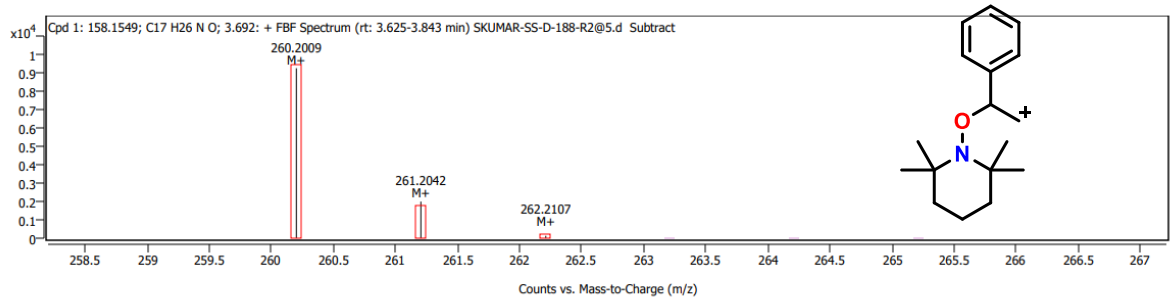
Compound Spectra (overlaid)



Spectrum Peaks

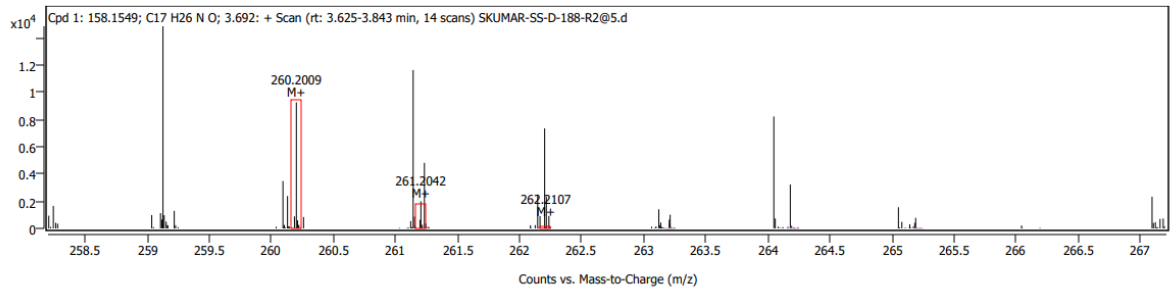
m/z	Z	Abund	Diff (ppm)	Height %	Height % (Calc)	Ion Species	Formula
260.2009	1	9248	0.19	100.00	100.00	M+	C17H26NO
261.2042	1	1992	0.01	21.54	19.09	M+	C17H26NO
262.2107	1	127	13.23	1.38	1.93	M+	C17H26NO

Compound Spectra



Spectrum Peaks

m/z	m/z (Calc)	Diff (ppm)	Abund	Height %	Height % (Calc)	Ion Species	Z
260.2009	260.2009	0.19	9248	100.00	100.00	M+	1
261.2042	261.2042	0.01	1992	21.54	19.09	M+	1
262.2107	262.2072	13.23	127	1.38	1.93	M+	1

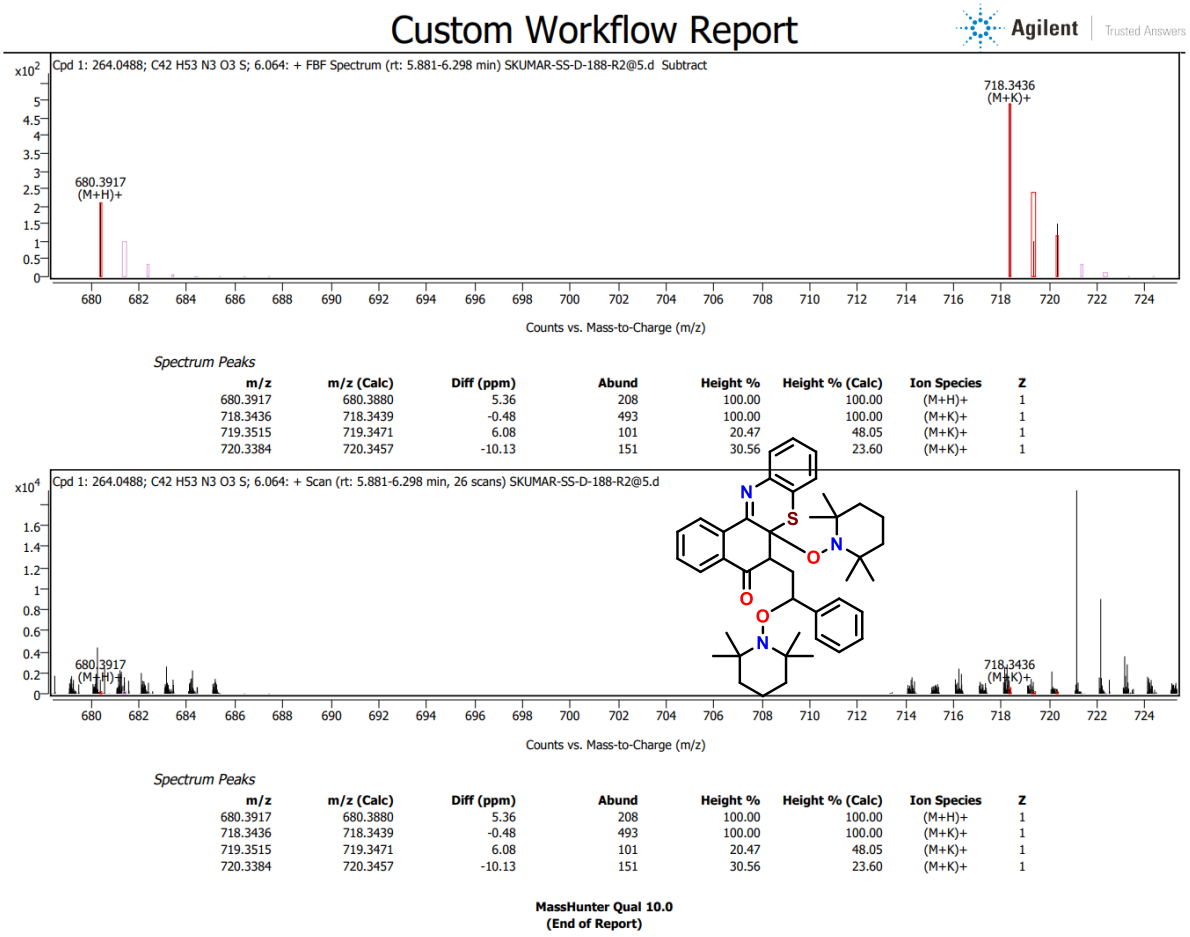


Spectrum Peaks

m/z	m/z (Calc)	Diff (ppm)	Abund	Height %	Height % (Calc)	Ion Species	Z
260.2009	260.2009	0.19	9248	100.00	100.00	M+	1
261.2042	261.2042	0.01	1992	21.54	19.09	M+	1
262.2107	262.2072	13.23	127	1.38	1.93	M+	1

MassHunter Qual 10.0
(End of Report)

Mass Spectrum for phenothiazinyl-styrenyl-TEMPO adduct **5**



Calculation of the Rehm-Weller equation for understanding the feasibility of the [2+2] cycloaddition reaction

The Rehm-Weller equation for the calculation of the excited state potential of the electron acceptor is given by the equation: $E_{1/2}^{*Red}(A) = E_{1/2}^{Red}(A) + E_{00}(A)$ where, $E_{1/2}^{*Red}(A)$ = excited-state redox potential of the acceptor, $E_{1/2}^{Red}(A)$ = ground-state redox potential of the acceptor (known by CV experiment) and $E_{00}(A)$ = mean photon energy of the emission spectra of the acceptor in eV.

Now, $E_{1/2}^{Red}(A)$ = –0.875 V [vs Ag/AgCl in acetonitrile, Figure S6 (a)]; $E_{00}(A)$ = 2.64 eV (for 470 nm). Therefore, from the Rehm and Weller equation, the $E_{1/2}^{*Red}(A)$ = (–0.875 + 2.64) = + 1.765 V (for 470 nm). On the other hand, the one-electron oxidation potential of styrene $E_{1/2}^{Ox}(D)$= +1.1 V. Therefore, the more positive excited-state redox potential $E_{1/2}^{*Red}(A)$ value of

angular phenothiazine **1a** (+1.765 V) in comparison to the ground-state one-electron oxidation potential of styrene [$E^{Ox}_{1/2}$(D) = +1.1 V] strongly suggested that angular phenothiazine **1a** in the excited state is capable of oxidizing styrene.

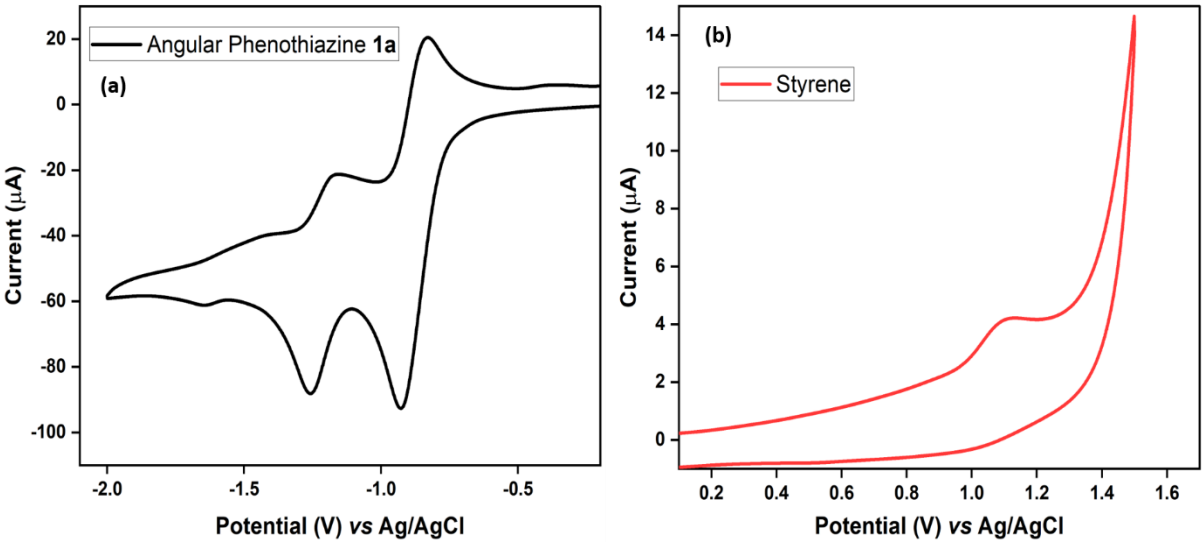


Figure S9. CV plots of angular phenothiazine **1a** and styrene. Glassy carbon, Ag/AgCl, and Pt electrode are used as the working, reference, and counter electrodes, respectively, using $^{n}Bu_4NPF_6$ as a supporting electrolyte in acetonitrile solvent within the range of ~1.3 to -2.0 V.

Further, the feasibility of the electron transfer process was calculated by the Rehm-Weller Equation where $\Delta G_{ET} = E^{Ox}_{1/2}(D) - E^{Red}_{1/2}(A) - E_{00}(A) + \Delta E_{Coulombic}$

Neglecting the very small $\Delta E_{Coulombic}$ value and putting all other values we get,

$\Delta G_{ET} = 1.1 - (-0.875) - (+2.64)$

$= -0.665$ V

$= -64.16$ kJ/mol

which indicates the high feasibility of the photo-induced-electron-transfer (PET) process for the developed [2+2] cycloaddition reaction between angular phenothiazine **1a** and styrene.

9. DFT Studies for [2+2] Photo-Cycloaddition Reaction

All computational studies were performed with the Gaussian 09 Revision A.02 program suite with the DFT method of Becke's three-parameter hybrid Hartree-Fock procedure with the LeeYang-Parr correlation function (B3LYP). The geometry optimization and energy calculations of the reactants, intermediates, and transition state were fully optimized by the DFT/B3LYP method with the 6311+g(d,p) basis set in the solution phase using CPCM (Conductor-like Polarizable Continuum Model) model in acetone solvent. The electron density of radical intermediates was also analyzed. Energy obtained from computation is listed in Hartree and converted to kcal/mol.

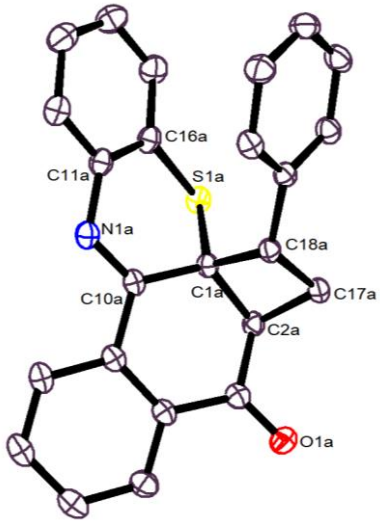
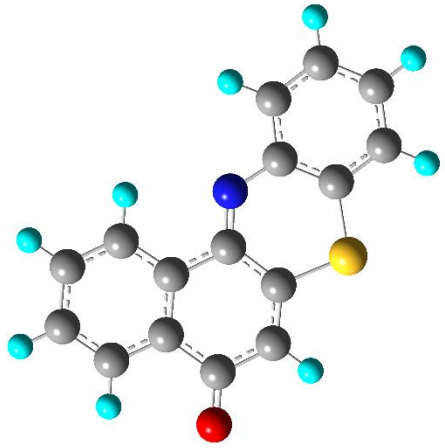


Table S2. Comparison of bond lengths and bond angles of the experimentally obtained structure of **2a** and calculated structure using DFT/B3LYP/6-311+g(d,p)

Atoms	Experimental	Calculated	% Error
S1a-C1a	1.804	1.832	1.55
N1a-C10a	1.287	1.288	0.07
C1a-C18a	1.591	1.600	0.56
C2a-C17a	1.548	1.558	0.64
C10a-N1a-C11a	120.67	123.06	1.98
C1a-S1a-C16a	97.46	98.99	1.57
C2a-C17a-C18a	88.72	89.63	1.02

In the experiment, **2a** crystallizes in neat $CHCl_3$. The relative error presented here is calculated as (|calculated–experimental|/|experimental|) × 100.

Tetracyclic Angular Phenothiazine 1a



Gibbs free energy: -1143.348964

Correction to Gibbs free energy: 0.162676

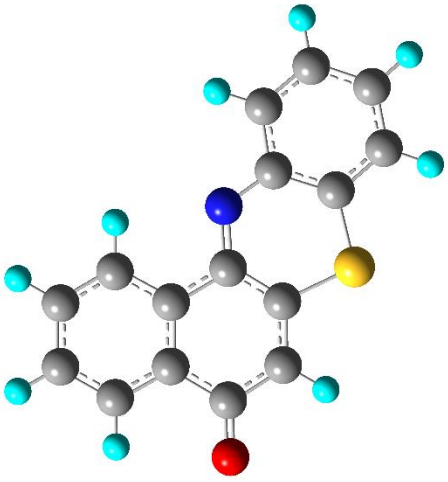
Zero-point correction: 0.204152

Imaginary vibration frequency: 0

Symbol	Coordinates (Å)		
	X	Y	Z
C	-3.185386	2.565786	-0.000081
C	-1.882386	2.089261	0.000032
C	-1.626618	0.708218	0.000032
C	-2.715299	-0.187216	-0.000031
C	-4.026120	0.306930	-0.000171
C	-4.264031	1.673558	-0.000214
H	-3.366040	3.634519	-0.000070
H	-1.045770	2.774540	0.000108
C	-0.235425	0.205176	0.000009
C	-2.490107	-1.655917	0.000188
H	-4.844353	-0.402090	-0.000228
H	-5.280632	2.049146	-0.000343
C	-1.115643	-2.111264	0.000052
C	-0.056755	-1.254834	-0.000040

H	-0.964088	-3.185019	0.000079
O	-3.433754	-2.457215	0.000477
N	0.721335	1.080510	0.000035
S	1.557762	-1.941887	-0.000284
C	2.066300	0.777475	0.000018
C	2.600054	-0.529395	-0.000089
C	2.963844	1.866210	0.000177
C	3.984310	-0.732488	-0.000065
C	4.332313	1.664010	0.000190
H	2.541452	2.863765	0.000271
C	4.842913	0.358699	0.000063
H	4.383522	-1.740232	-0.000142
H	5.006994	2.511300	0.000297
H	5.913626	0.193150	0.000082

Excited State Tetracyclic Angular Phenothiazine (I)



Gibb's free energy: -1143.299412

Correction to Gibb's free energy: 0.159642

Zero-point correction: 0.201948

Imaginary vibration frequency: 0

Symbol	Coordinates (Å)		
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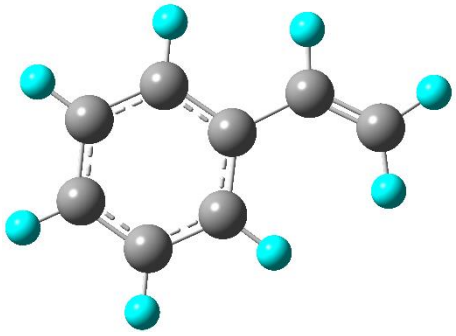
C	-3.182735	2.560716	0.000143
C	-1.882090	2.083286	-0.000087
C	-1.621239	0.697198	-0.000088
C	-2.722377	-0.198775	0.000058
C	-4.032269	0.304783	0.000306
C	-4.266319	1.670716	0.000373
H	-3.361596	3.629936	0.000139
H	-1.044009	2.766025	-0.000225
C	-0.246270	0.203287	-0.000170
C	-2.496820	-1.651781	-0.000109
H	-4.854713	-0.399768	0.000465
H	-5.281812	2.049188	0.000627
C	-1.128329	-2.092826	0.000343
C	-0.053590	-1.184043	0.000058
H	-0.949959	-3.162234	0.000758
O	-3.431829	-2.487181	-0.000718
N	0.749746	1.144971	-0.000400
S	1.539918	-1.927940	0.000078
C	2.049965	0.802966	-0.000152
C	2.586952	-0.533680	0.000134
C	3.003067	1.866424	-0.000254
C	3.971883	-0.761927	0.000272
C	4.355828	1.625909	-0.000109
H	2.611219	2.876165	-0.000432
C	4.852981	0.302821	0.000179
H	4.345953	-1.779463	0.000451
H	5.050322	2.457880	-0.000166
H	5.920472	0.121523	0.000292

Styrene



Gibbs free energy: -309.633005

Correction to Gibbs free energy: 0.101493

Zero-point correction: 0.132793

Imaginary vibration frequency: 0

Symbol	Coordinates (Å)		
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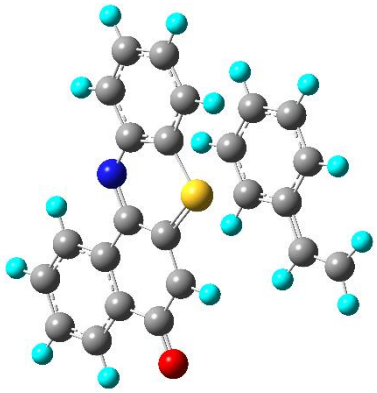
C	0.009281	1.092136	0.000032
C	-1.361198	1.328681	0.000009
C	-2.263644	0.261441	-0.000018
C	-1.779672	-1.045656	-0.000013
H	-0.036093	-2.301481	0.000001
H	0.689685	1.935688	0.000065
H	-1.729200	2.348710	0.000012
H	-3.331185	0.449892	-0.000036
H	-2.469592	-1.882092	-0.000031
C	1.954802	-0.529976	0.000025
H	2.186790	-1.592872	0.000130
C	2.974595	0.336077	-0.000044
H	2.834422	1.411517	-0.000123
H	3.998846	-0.017477	-0.000009

Radical Ion Pair II



Gibbs free energy: -1452.922080

Correction to Gibbs free energy: 0.271952

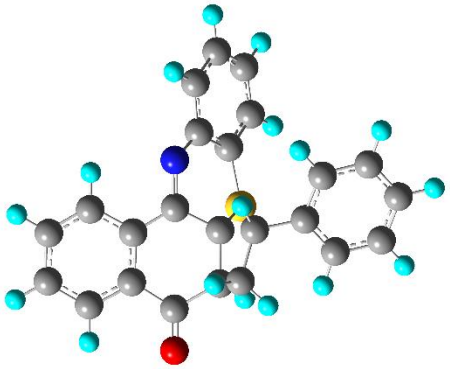
Zero-point correction: 0.334703

Imaginary vibration frequency: 0

Symbol	Coordinates (Å)		
	X	Y	Z
S	-0.798707	1.290740	-2.167449
O	3.800111	-0.676985	-2.249672
N	0.017135	1.951904	0.825685
C	0.699523	0.942640	-1.315596
C	1.672314	0.274417	-2.082813
C	2.954853	-0.082318	-1.539621
C	3.203915	0.284760	-0.137550
C	4.433926	-0.031534	0.459664
H	5.178735	-0.544887	-0.135705
C	4.688287	0.305471	1.779620
H	5.641476	0.056584	2.231272
C	3.706438	0.970432	2.527900
H	3.901650	1.235853	3.560713
C	2.485861	1.291625	1.956417
H	1.726432	1.804291	2.529924
C	2.205969	0.958080	0.614832

C	0.915958	1.301451	0.020841
C	-1.195183	2.324636	0.379713
C	-2.049308	3.001690	1.302415
H	-1.660893	3.166842	2.299914
C	-3.306110	3.427775	0.946369
H	-3.926814	3.939215	1.672797
C	-3.799688	3.206825	-0.359534
H	-4.790954	3.546527	-0.632387
C	-3.012830	2.554575	-1.289863
H	-3.384334	2.381225	-2.293647
C	-1.727323	2.111686	-0.941752
C	-0.461926	-4.448600	-1.981702
6	-0.251385	-4.062293	-0.718181
H	0.743596	-4.199636	-0.300453
C	-1.224303	-3.458175	0.208601
C	-0.812284	-3.149965	1.515262
H	0.210500	-3.360621	1.810531
C	-1.692078	-2.580644	2.434574
H	-1.349479	-2.351797	3.437548
C	-3.007686	-2.307463	2.064564
H	-3.695792	-1.864921	2.775762
C	-3.433456	-2.607588	0.767470
H	-4.455114	-2.397038	0.471151
C	-2.554687	-3.175308	-0.148777
H	-2.907313	-3.398175	-1.149220
H	1.477019	0.006274	-3.115135
H	-1.422850	-4.349900	-2.475073
H	0.339822	-4.882164	-2.568354

1,4–Biradical Intermediate (III)



Gibbs free energy: -1452.944876

Correction to Gibbs free energy: 0.292393

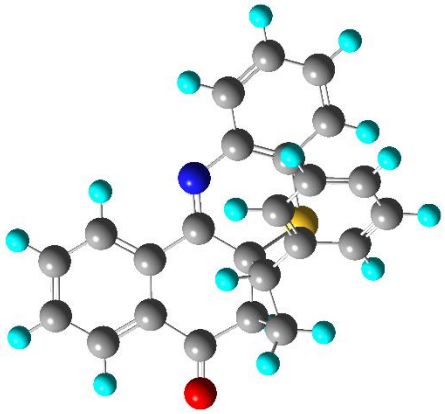
Zero-point correction: 0.342527

Imaginary vibration frequency: 0

Symbol	Coordinates (Å)		
	X	Y	Z
S	0.645573	0.190950	1.580085
O	-2.892292	-2.953916	1.143164
N	-0.564916	1.658342	-0.927185
C	-0.225373	-0.551059	0.097243
C	-0.895711	-1.904787	0.405583
H	-0.406083	-2.423560	1.231343
C	-2.387165	-1.954445	0.633309
C	-3.178147	-0.802351	0.179384
C	-4.575430	-0.862911	0.249958
H	-5.026919	-1.761605	0.652480
C	-5.366664	0.189465	-0.187072
H	-6.446295	0.123508	-0.127630
C	-4.754872	1.341647	-0.723053
H	-5.370868	2.160959	-1.076577
C	-3.383553	1.435539	-0.808834

H	-2.919102	2.316051	-1.232811
C	-2.540850	0.375202	-0.351020
C	-1.138178	0.499944	-0.410629
C	0.431195	2.260458	-0.293977
C	0.935983	3.492646	-0.843022
H	0.490431	3.836472	-1.768763
C	1.899316	4.219867	-0.196489
H	2.244724	5.158653	-0.612660
C	2.449475	3.747128	1.018852
H	3.214103	4.322983	1.526080
C	2.040891	2.530538	1.553559
H	2.505993	2.158261	2.459249
C	1.054919	1.768541	0.924551
C	-0.356485	-2.437742	-0.961603
H	-1.104053	-2.382745	-1.753599
H	0.063723	-3.441912	-0.938276
C	0.652624	-1.253617	-1.041817
H	0.594410	-0.691385	-1.973251
C	2.102943	-1.543387	-0.747496
C	3.087938	-0.738303	-1.335703
H	2.790271	0.064596	-2.002114
C	4.441836	-0.956499	-1.085067
H	5.185332	-0.322744	-1.555546
C	4.837795	-1.991166	-0.238324
H	5.889743	-2.166412	-0.043462
C	3.869123	-2.804317	0.349867
H	4.165710	-3.615548	1.005356
C	2.516116	-2.582697	0.096859
H	1.786123	-3.234000	0.563452

[2+2] Cycloaddition Product: Pentacyclic Cyclobutylated Angular Phenothiazine 2a



Gibbs free energy: -1452.944872

Correction to Gibbs free energy: 0.292397

Zero-point correction: 0.342529

Imaginary vibration frequency: 0

Symbol	Coordinates (Å)		
	X	Y	Z
S	0.679147	-0.018942	2.015083
O	-3.615294	-2.419026	0.970961
N	-0.326995	1.829751	-0.228121
C	-0.453045	-0.477280	0.648903
C	-1.424243	-1.567708	1.179743
H	-1.450691	-1.670330	2.267756
C	-2.864575	-1.484876	0.726736
C	-3.332928	-0.273188	0.009146
C	-4.688417	-0.207768	-0.351570
H	-5.328635	-1.041521	-0.093121
C	-5.193634	0.895735	-1.019136
H	-6.241213	0.935828	-1.292921
C	-4.339387	1.958119	-1.337564
H	-4.724868	2.824830	-1.862174
C	-2.998852	1.908874	-0.986498

H	-2.336402	2.727573	-1.231648
C	-2.467532	0.798622	-0.307916
C	-1.027723	0.785168	0.050523
C	1.007878	1.972010	0.146651
C	1.757824	2.978787	-0.485479
H	1.286806	3.536859	-1.286450
C	3.058007	3.259302	-0.087927
H	3.621978	4.036053	-0.590702
C	3.629092	2.551034	0.973940
H	4.638022	2.774936	1.300288
C	2.907661	1.545493	1.611108
H	3.356340	0.984592	2.423156
C	1.610034	1.240269	1.192357
C	-0.591525	-2.658826	0.442208
H	-1.154144	-3.410334	-0.111205
H	0.090145	-3.160959	1.127154
C	0.089468	-1.553186	-0.403512
H	-0.497851	-1.396182	-1.313140
C	1.539665	-1.641630	-0.793277
C	1.958651	-1.094961	-2.015039
H	1.229173	-0.619564	-2.662875
C	3.292474	-1.157496	-2.412396
H	3.592480	-0.729766	-3.362584
C	4.236987	-1.776302	-1.592738
H	5.275180	-1.831134	-1.900355
C	3.833629	-2.331791	-0.379145
H	4.558703	-2.821172	0.261728
C	2.497552	-2.265860	0.016461
H	2.207580	-2.707926	0.961463

Molecular Orbital Picture of Optimized Structures

To get more insight into the mechanistic pathway of [2+2] photo-cycloaddition between angular phenothiazine **1a** and styrene, we have also looked into the SOMO, HOMO, and LUMO pictures of the reactants, intermediates, and product.

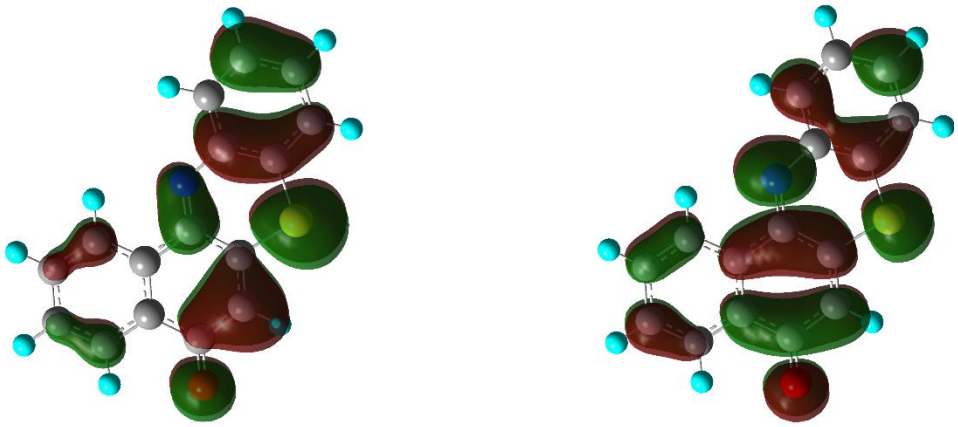


Figure S10. HOMO (left) and LUMO (right) pictures of the **angular phenothiazine 1a**

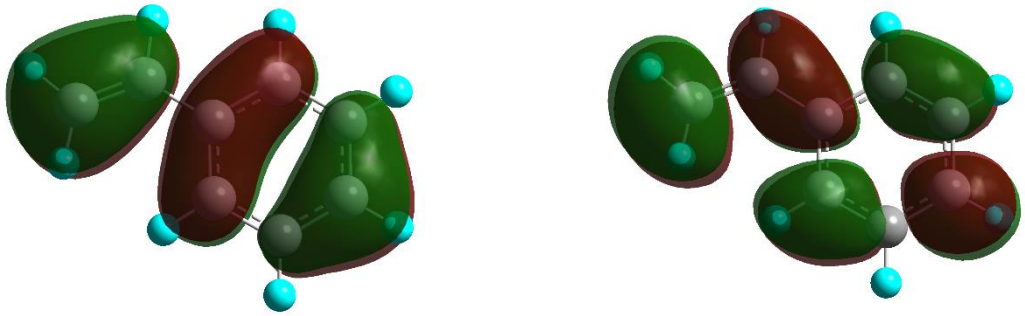


Figure S11. HOMO (left) and LUMO (right) pictures of **styrene**

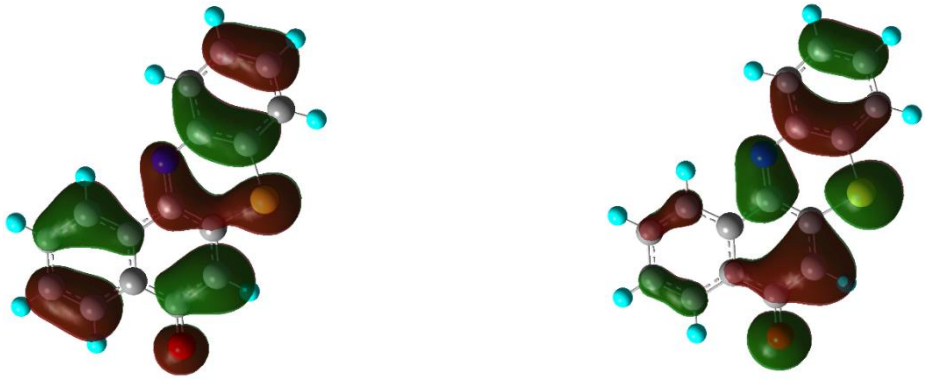
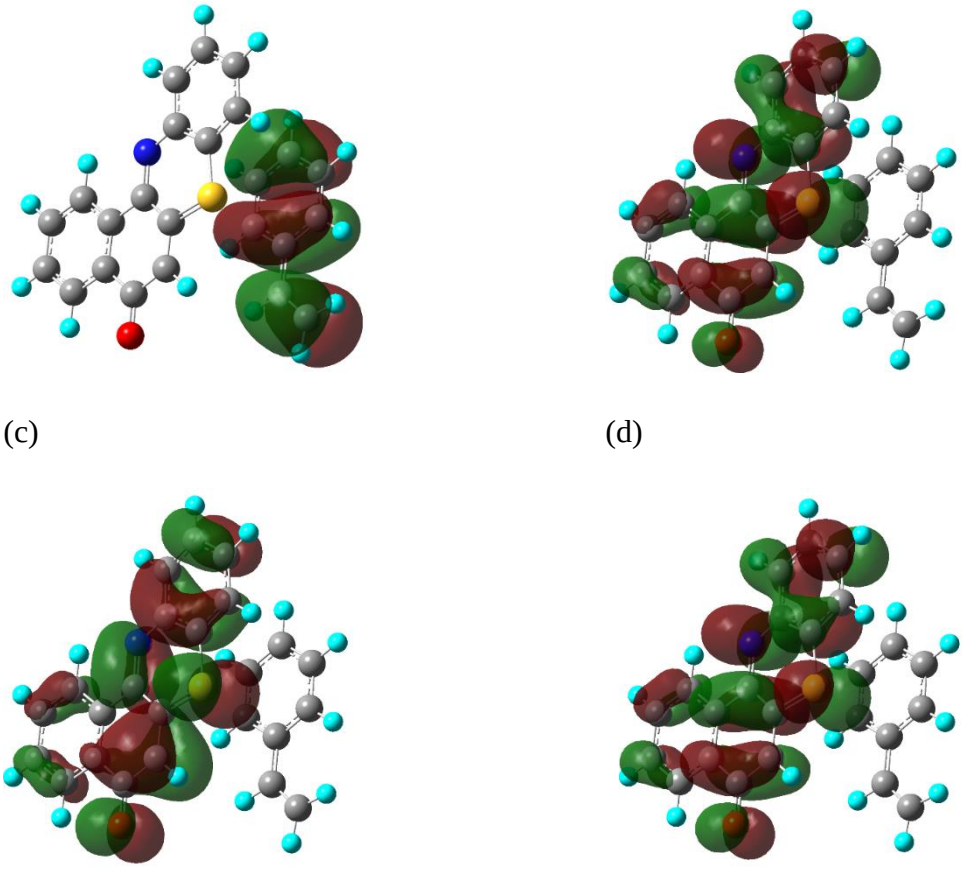


Figure S12. SOMO (left) and LUMO (right) pictures of **excited state angular phenothiazine** (**I**)

This pictorial view of the singly occupied molecular orbital (SOMO) of excited state angular phenothiazine (**I**) indicates that electrons lie more on the carbon atom adjacent to sulfur, and HOMO of styrene lies on the whole molecule. The energy difference between the SOMO of excited state angular phenothiazine (**I**) and the HOMO of styrene is 6.11 kcal/mol (0.27 eV), which is highly favorable for electron transfer.

(a) (b)



(c) (d)

Figure S13. (a) SOMO, (b) SOMO + 1, (c) LUMO, and (d) LUMO + 1 pictures of **radical-ion pair II**

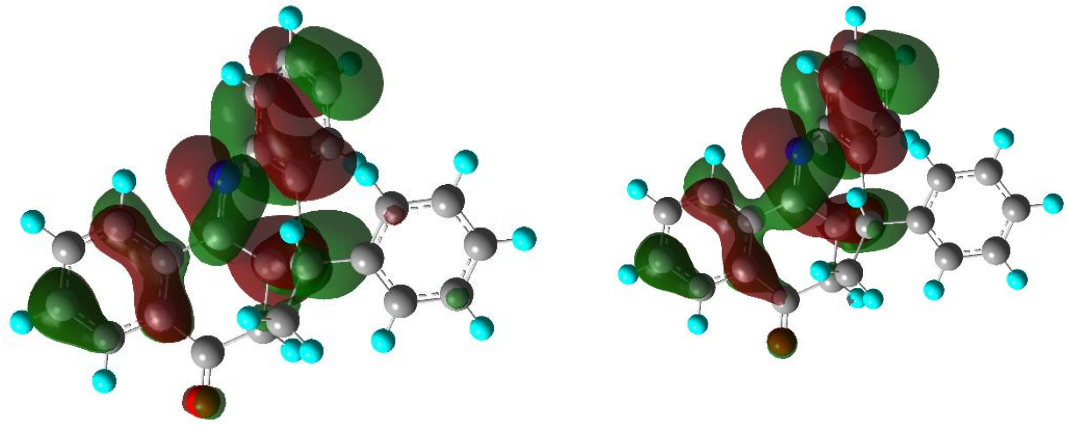


Figure S14. SOMO (left) and LUMO (right) pictures of the proposed **1,4-biradical intermediate** (**III**)

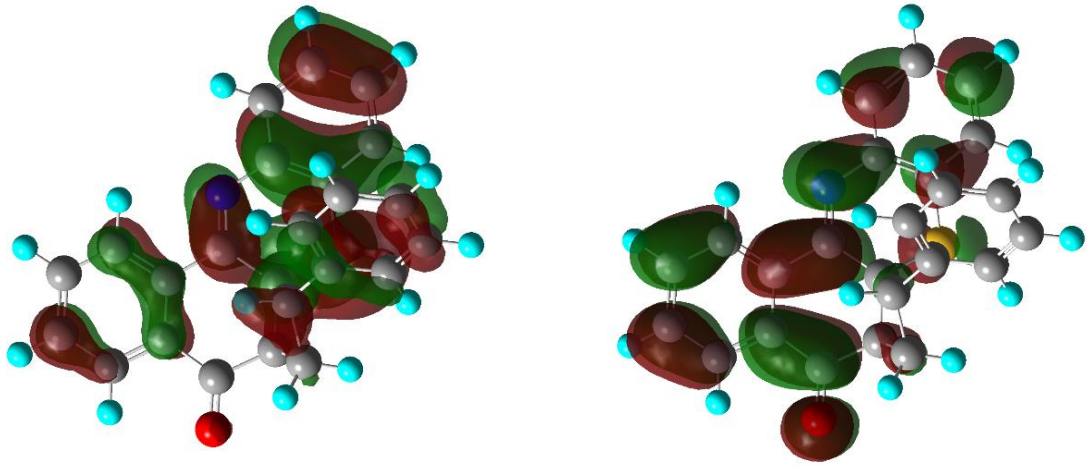


Figure S15. HOMO (left) and LUMO (right) pictures of the **[2+2] cycloadduct**: **cyclobutylated phenothiazine 2a**

Spin Density Profile for Radical Intermediates

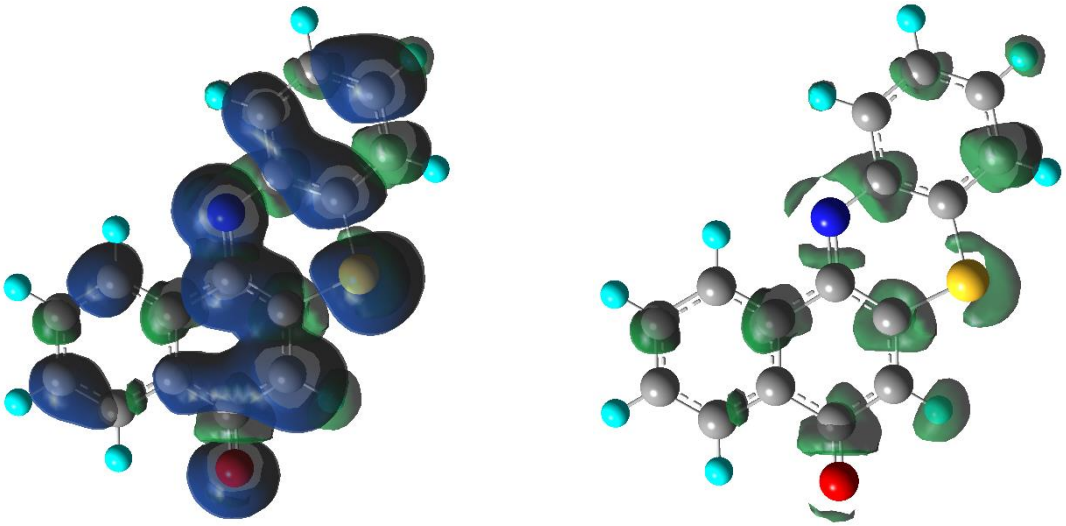


Figure S16. Spin density profile of **excited state angular phenothiazine** (**I**) with (a) total electron density, and (b) negative electron density.

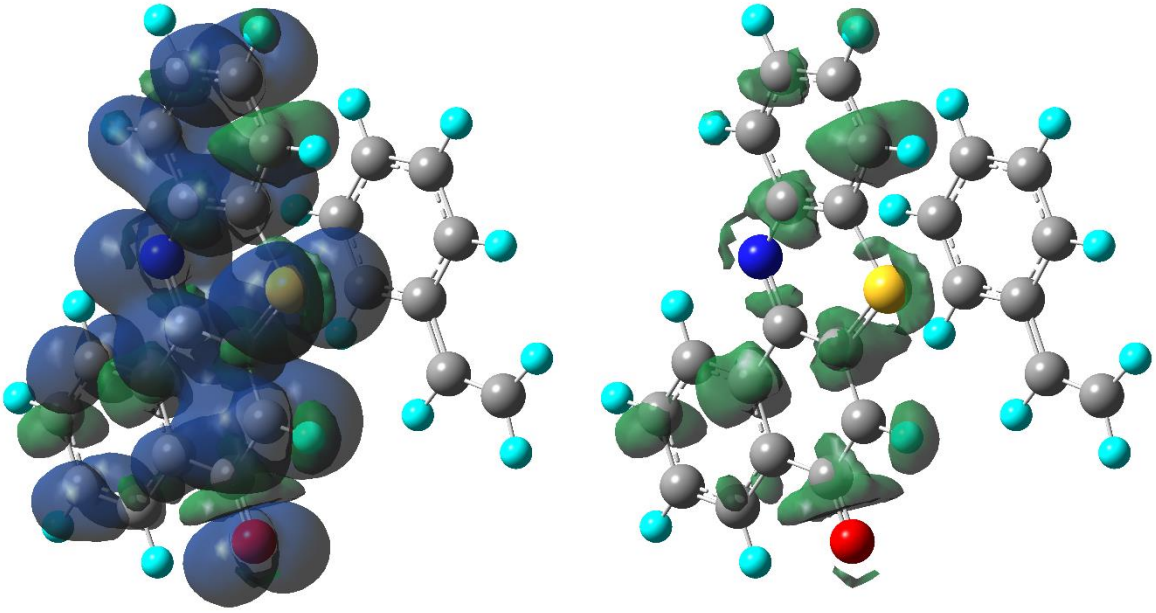


Figure S17. Spin density profile of **radical-ion pair (II)** with (a) total electron density, and (b) negative electron density.

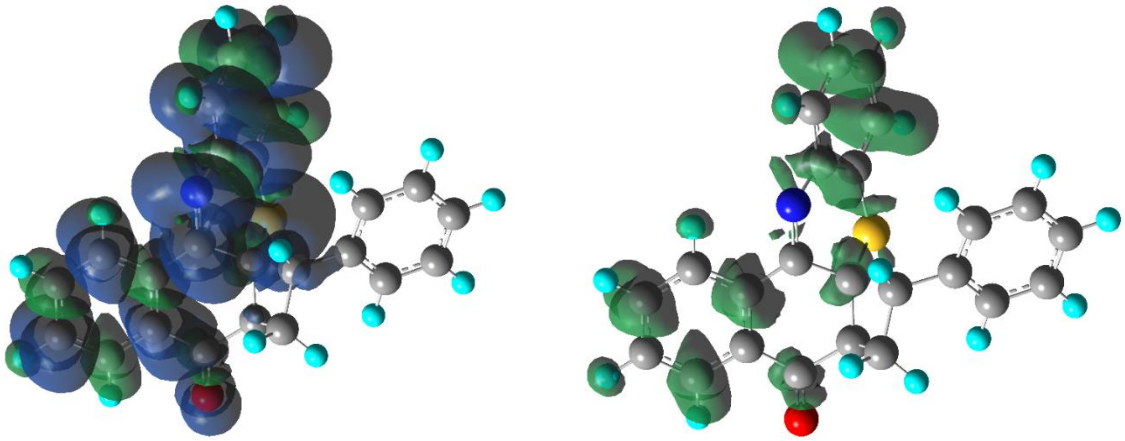
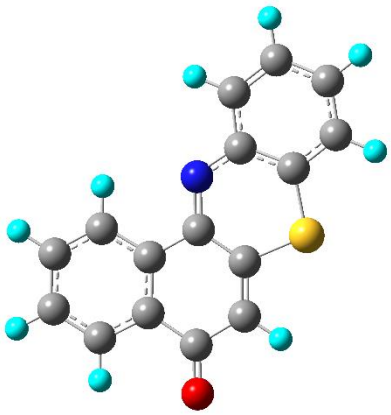


Figure S18. Spin density profile of proposed **1,4-biradical intermediate** (**III**) with (a) total electron density, and (b) negative electron density.

Calculation for Lowest Excited Sate Phenothiazine

We have performed TD-DFT to get the energies of the lowest lying singlet and triplet state of phenothiazine molecule using B3LYP/6-311+g(d,p) level of theory with N = 10 states and acetone solvent.

Lowest Excited Singlet State Phenothiazine



Electronic + Thermal Free Energies: -1143.267953

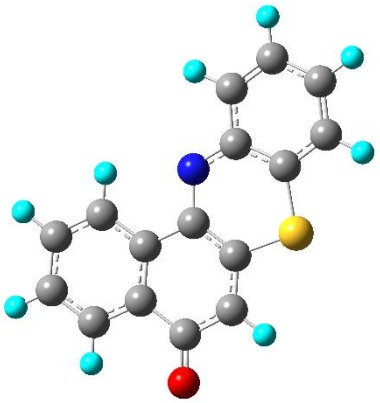
Correction to Gibb's free energy: 0.160120

Zero-point correction: 0.201577

Imaginary vibration frequency: 0

Symbol	Coordinates (Angstroms)		
	X	Y	Z
C	-3.207955	2.549335	-0.000053
C	-1.902631	2.085773	-0.000033
C	-1.620783	0.701859	-0.000030
C	-2.718220	-0.207641	-0.000050
C	-4.036464	0.288921	-0.000070
C	-4.287489	1.649147	-0.000072
H	-3.395855	3.617233	-0.000055
H	-1.073099	2.779730	-0.000019
C	-0.246362	0.233370	-0.000006
C	-2.497820	-1.654952	-0.000047
H	-4.850004	-0.426301	-0.000083
H	-5.306209	2.018238	-0.000086
C	-1.105379	-2.085219	-0.000029
C	-0.052438	-1.174371	-0.000004
H	-0.916035	-3.152821	-0.000034
O	-3.413900	-2.500210	-0.000075
N	0.750639	1.153464	0.000014
S	1.531729	-1.905343	0.000030
C	2.055688	0.813581	0.000040
C	2.589224	-0.529424	0.000049
C	3.012727	1.862629	0.000057
C	3.972066	-0.771452	0.000074
C	4.370353	1.609912	0.000081
H	2.634490	2.877597	0.000050
C	4.862712	0.287338	0.000090
H	4.335867	-1.792865	0.000080
H	5.067651	2.439591	0.000094
H	5.928892	0.099678	0.000108

Lowest Excited Triplet State Phenothiazine



Electronic + Thermal Free Energies: -1143.307452

Correction to Gibb's free energy: 0.158881

Zero-point correction: 0.200670

Imaginary vibration frequency: 0

Symbol	Coordinates (Angstroms)		
	X	Y	Z
C	-3.175225	2.564122	-0.000067
C	-1.875721	2.079375	-0.000030
C	-1.625239	0.692529	-0.000011
C	-2.732644	-0.194434	-0.000027
C	-4.038438	0.312800	-0.000069
C	-4.263141	1.682035	-0.000087
H	-3.347834	3.634282	-0.000082
H	-1.033256	2.756065	-0.000018
C	-0.252898	0.186045	0.000018
C	-2.502221	-1.645984	0.000011
H	-4.866223	-0.385412	-0.000081
H	-5.276230	2.066587	-0.000115
C	-1.137454	-2.094828	-0.000017
C	-0.052096	-1.188187	-0.000000
H	-0.968576	-3.165608	-0.000041
O	-3.433279	-2.485186	-0.000083
N	0.751260	1.154811	0.000028

S	1.546144	-1.947014	-0.000009
C	2.048919	0.802356	0.000050
C	2.588762	-0.531684	0.000041
C	3.003869	1.867946	0.000068
C	3.971552	-0.753922	0.000058
C	4.357665	1.633109	0.000086
H	2.608937	2.876719	0.000070
C	4.856178	0.312137	0.000083
H	4.348453	-1.770705	0.000051
H	5.049049	2.467842	0.000103
H	5.923575	0.129776	0.000097

Molecular Orbital Pictures of Lowest Excited Angular Phenothiazine

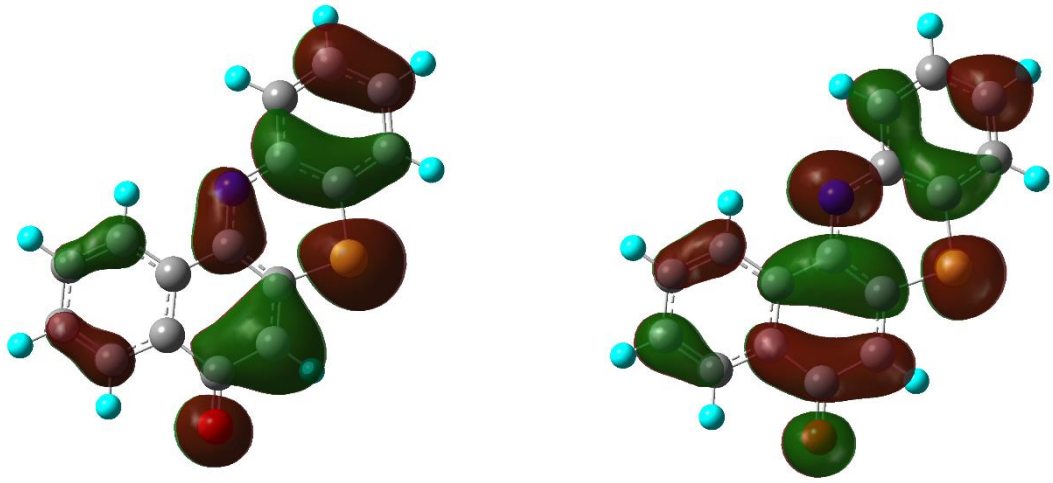


Figure S19. HOMO (left) and LUMO (right) pictures of the **lowest excited singlet state angular phenothiazine 1a**

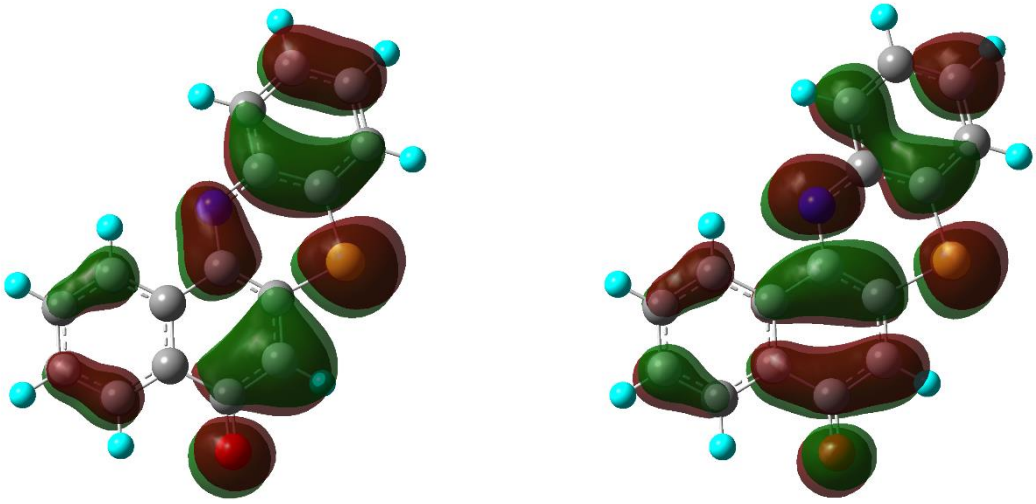
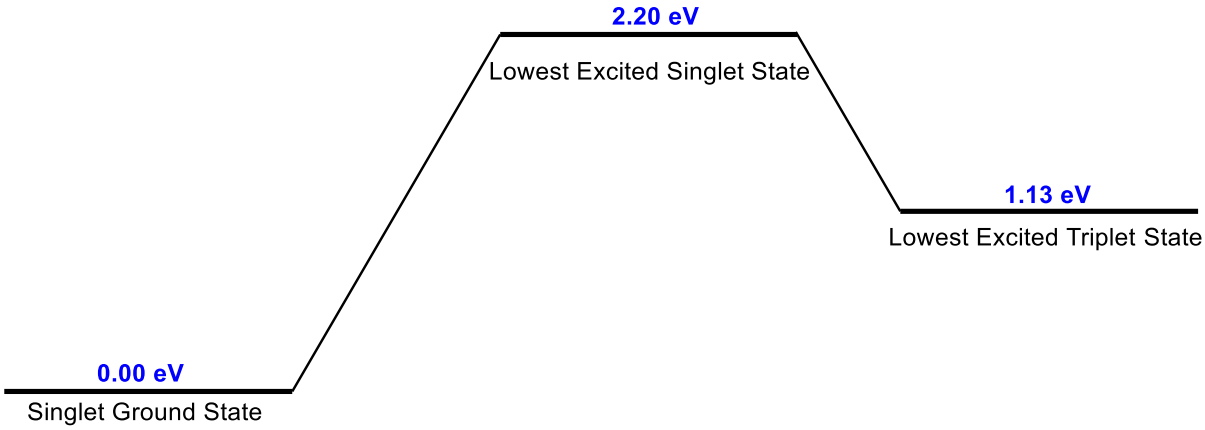


Figure S20. HOMO (left) and LUMO (right) pictures of the **lowest excited triplet state angular phenothiazine 1a**

Through these calculations, we found the following energy details:

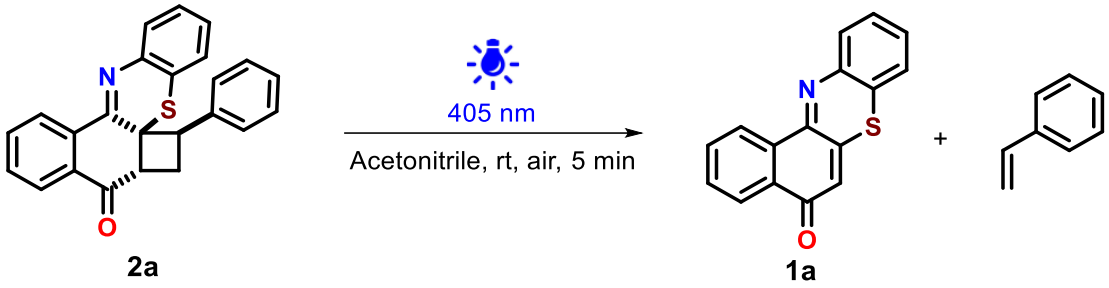
State of Phenothiazine	Electronic + Thermal Free Energies	Relative Free Energy (eV)
Singlet Excited State	-1143.267953	2.20
Triplet Excited State	-1143.307452	1.13
Singlet Ground State	-1143.348964	0.0

Based on our computational studies, we observed that the energy difference between the singlet ground state and singlet excited state of angular phenothiazine **1a** is 2.20 eV, which is well corroborated with the experimental result which we have observed through the emission study as angular phenothiazine molecule is emitting at 613 nm (~2.02 eV). Further, the lowest singlet excited state angular phenothiazine having n,π* character gets relieved by 1.1 eV to the lowest triplet excited state angular phenothiazine having n,π* character through the intersystem crossing, as the energy gap is sufficiently small which allows them to the intersystem crossing from S1 (n,π*) to T1 (n,π*). A similar phenomenon was also reported by Kochi and co-workers, where they have explored the photoexcited singlet quinones and their ultrafast electron transfer *vs* intersystem crossing (ISC) rates.[3]



Scheme S5. Energy profile diagram of ground and lowest excited state of angular phenothiazine **1a**.

10. HPLC Experiment for Light-irradiated [2+2] Cyclo-reversion Reaction:



Scheme S6. Light-irradiated (405 nm external laser source (*vide supra*)) [2+2] cycloreversion of cyclobutylated phenothiazine **2a** into its precursors: angular phenothiazine **1a** and styrene

The HPLC experiments were performed in Waters Alliance e2695 separation module equipped with 2998 PDA detector. The chromatography was performed in reverse phase, in gradient mode, with Water: Acetonitrile (95:5 to 5:95) mobile phase for 15 minutes. The samples were passed through a C18 silica column with a flow rate of 1 ml/min. The peaks were observed and extracted at 254 nm. The working solutions of compounds namely, angular phenothiazine **1a** and cyclobutylated phenothiazine **2a** were 10 μM in acetonitrile (Figure S21). Irradiation was achieved with the 405 nm external light source.

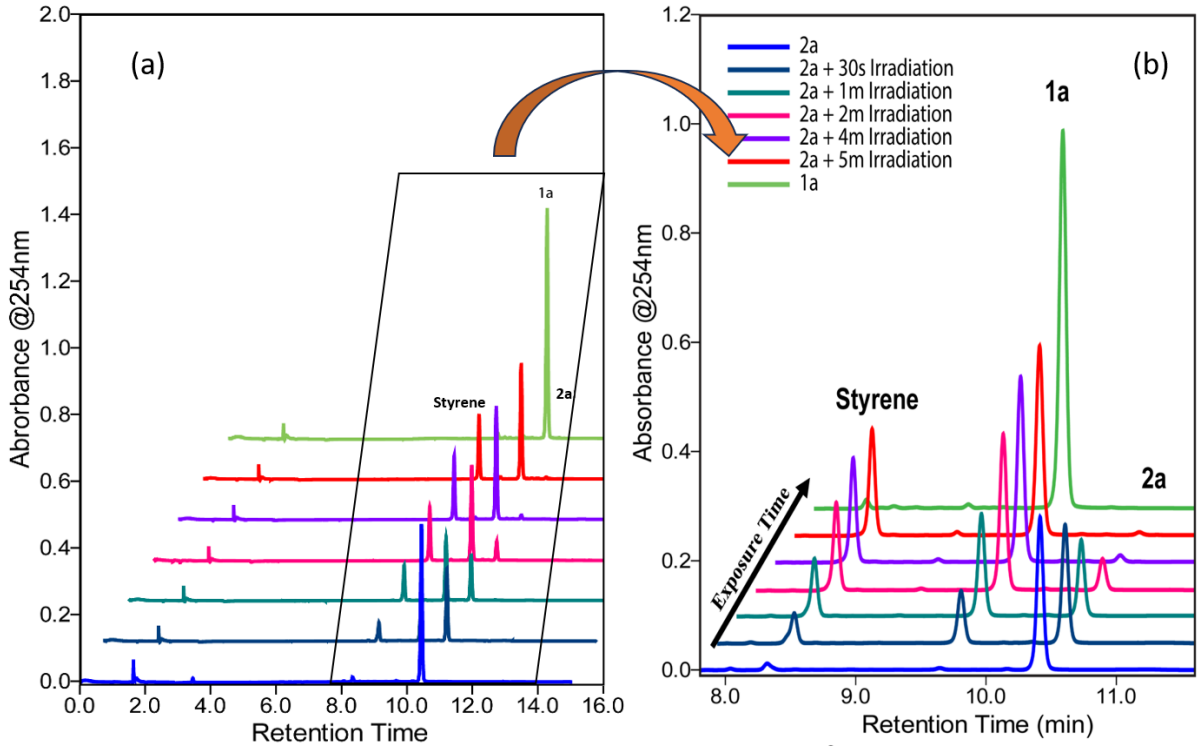


Figure S21. Time-dependent HPLC spectra for light-irradiated [2+2] cyclo-reversion Reaction reaction: (a) Full spectra of the run-time, (b) Zoomed-in Image

11. Structure-activity Relationship:

To gain a thorough understanding of the compound's structure-activity relationship i.e., the relation between the molecular structure and its cycloreversion as well as imaging activity, we have conducted a series of experiments involving substituted cyclobutylated phenothiazines to investigate the rate of their [2+2] cycloreversion reactions. Firstly, we monitored the time-dependent [2+2] cycloreversion reactions of *ortho*-fluoro, *meta*-fluoro, and *para*-fluoro substituted cyclobutylated phenothiazines **2b**, **2g** and **2l** to investigate the effect of the fluoro-substitution at *ortho*, *meta* and *para* positions, on the compound's [2+2] cycloreversion activity (Figure 22a). All the experiments were conducted by monitoring the time-dependent UV-absorption spectra of the cycloreversion reactions (5 μM solution of each compound in acetonitrile solvent), under 405 nm light irradiation from an external laser source. Then the corresponding rates of the reaction have been calculated and compared (Figure 22a). Similarly, bromo (**2d**, **2i**, **2n**), methyl (**2e**, **2j**, **2o**), and methoxy substitutions (**2f**, **2k**, **2p**) at *ortho*-, *meta*- and *para*- positions of cyclobutylated phenothiazines were investigated (Figures 22b, 22c, 22d), respectively. We observed that in all cases, the *ortho*-substituted cyclobutylated phenothiazines are providing the highest rates (Figures 22a-22d). While the *meta*- substituents are the slowest and p*ara*-substituted products exhibited rates in between *ortho*- and *meta*- ones.

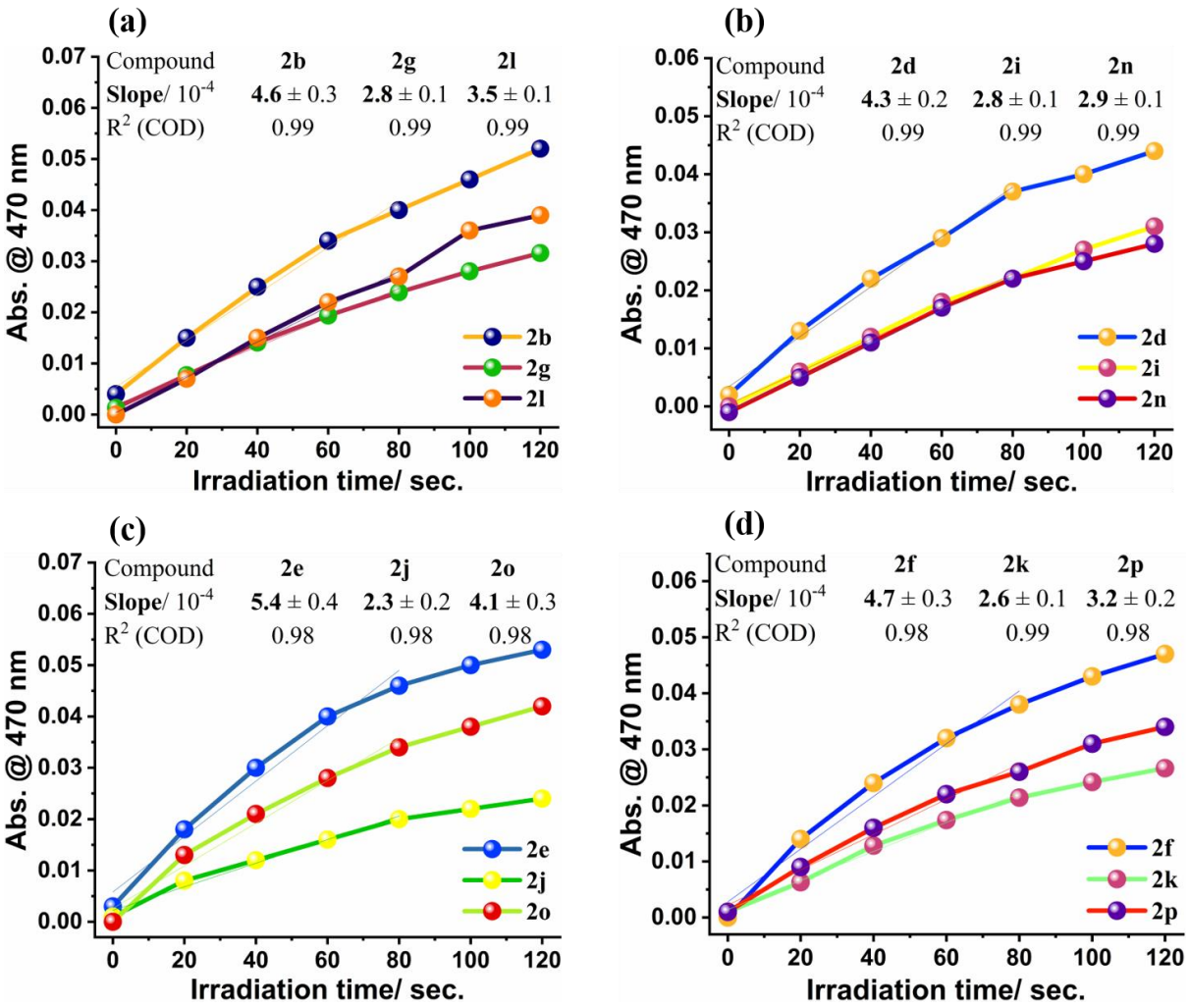


Figure S22. Rate of the [2+2] photocycloreversion reaction of variously substituted cyclobutylated phenothiazines. (a) *ortho*-, *meta*-, and *para*-fluoro substituted cyclobutylated phenothiazines **2b**, **2g**, **2l**; (b) *ortho*-, *meta*-, and *para*-bromo substituted cyclobutylated phenothiazines **2d**, **2i**, **2n**; (c) *ortho*-, *meta*-, and *para*-methyl substituted cyclobutylated phenothiazines **2e**, **2j**, **2o**; (d) *ortho*-, *meta*-, and *para*-methoxy substituted cyclobutylated phenothiazines **2f**, **2k**, **2p**.

The slope values reveal the rate constants of the reactions, showing that the *ortho*-methyl substituted cyclobutylated phenothiazine (**2e**) exhibits the highest rate of cycloreversion among the halogenated, methylated, and methoxylated compounds, whereas the *meta*-methyl substituted cyclobutylated phenothiazine (**2j**) displays the slowest rate.

Subsequently, we compared the rate of the photocycloreversion reaction of many other substituted-cyclobutylated phenothiazines (**2x**, **2v**, **2w**, **2q**, **2u**, **2ae**, **2s**, **2t**, **2af**, and **2y**) with respect to **2e** and **2j** (Figure 23).

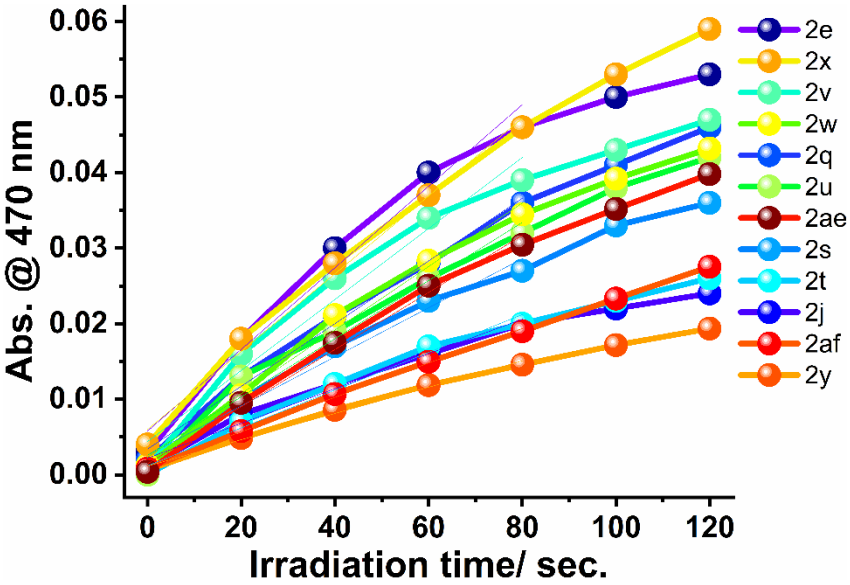


Figure S23. Comparison of the rate of [2+2] photocycloreversion of variously substituted-cyclobutylated phenothiazine with respect to **2e** and **2j**

Corresponding rate constants (slope) and R^2 values from Figure 23 are given below:

Compound	**Slope**/ 10^{-4}	**R^2** (COD)
2e	5.4 ± 0.4	0.98
2x	5.15 ± 0.3	0.99
2v	4.7 ± 0.5	0.96
2w	4.21 ± 0.3	0.99
2q	4.15 ± 0.2	0.99
2u	3.85 ± 0.4	0.97
2ae	3.8 ± 0.2	0.99
2s	3.25 ±0.2	0.98
2t	2.5 ± 0.2	0.98
2j	2.3 ± 0.2	0.98
2af	2.28 ± 0.1	0.99
2y	1.7 ± 0.1	0.99
Where, COD = Coefficient of Determination		

Here, it has been observed that *ortho*-methyl substituted cyclobutylated phenothiazine **2e** is exhibiting the highest rate of photocycloreversion with a rate constant of $(5.4 \pm 0.4) \times 10^{-4}$ sec^{-1} and rate of 0.049 μM sec^{-1}. In contrast, the *trans*-stilbene fused cyclobutylated phenothiazine **2y** exhibited the slowest rate among all variants, with a rate constant of $(1.7 \pm 0.1) \times 10^{-4}$ sec^{-1} and rate of 0.016 μM sec^{-1}. The photocycloreversion rates for both **2e** and **2y** were calculated over the initial 80 seconds of irradiation.

$$\text{Rate of reaction} = -\frac{\Delta(\text{Angular Phenothiazine})}{\Delta\text{time}}$$

$$\text{Rate of photocycloreversion of } \mathbf{2e} = -\frac{\Delta(\text{Angular Phenothiazine})}{\Delta\text{time}}$$

$$= -\frac{(3.9-0.0)\ \mu\text{M}}{(80-0)\ \text{sec}} = -0.049\ \mu\text{M sec}^{-1}$$

Rate (v_o) of formation of the angular phenothiazine by the [2+2] photocycloreversion of **2e** is: 0.049 μM sec^{-1} (experiments have been repeated triplicate).

$$\text{Rate of photocycloreversion of } \mathbf{2y} = -\frac{\Delta(\text{Angular Phenothiazine})}{\Delta\text{time}}$$

$$= -\frac{(1.24-0.0)\ \mu\text{M}}{(80-0)\ \text{sec}} = -0.016\ \mu\text{M sec}^{-1}$$

Rate (v_o) of formation of the angular phenothiazine by the [2+2] photocycloreversion of **2e** is: 0.016 μM sec^{-1} (experiments have been repeated triplicate).

Subsequently, we proceed to explore the structure-activity relationship in live HeLa cells. When the HeLa cells were treated with **2e**, no signal was detected from the cells prior to irradiation (Figure 24a). However, after 1 minute of irradiation, a significant enhancement in signal intensity was observed throughout the cells, which was visible in the FITC channel (Figure 24b). On the other hand, when the cells were incubated with **2y** and subjected to photo-irradiation, no distinguishable signal was observed in the FITC channel after 1 minute of irradiation (Figure 25a). Even after 5 minutes of irradiation, only a very weak emission signal was detected in the FITC channel (Figure 25b), suggesting that the stilbene-derived **2y** undergoes cycloreversion at a slower rate than *ortho*-methylated **2e** and takes longer time for cell imaging. Therefore, the cellular experimental observations were corroborated well with the corresponding spectroscopic evidence, demonstrating the structure-activity relationship.

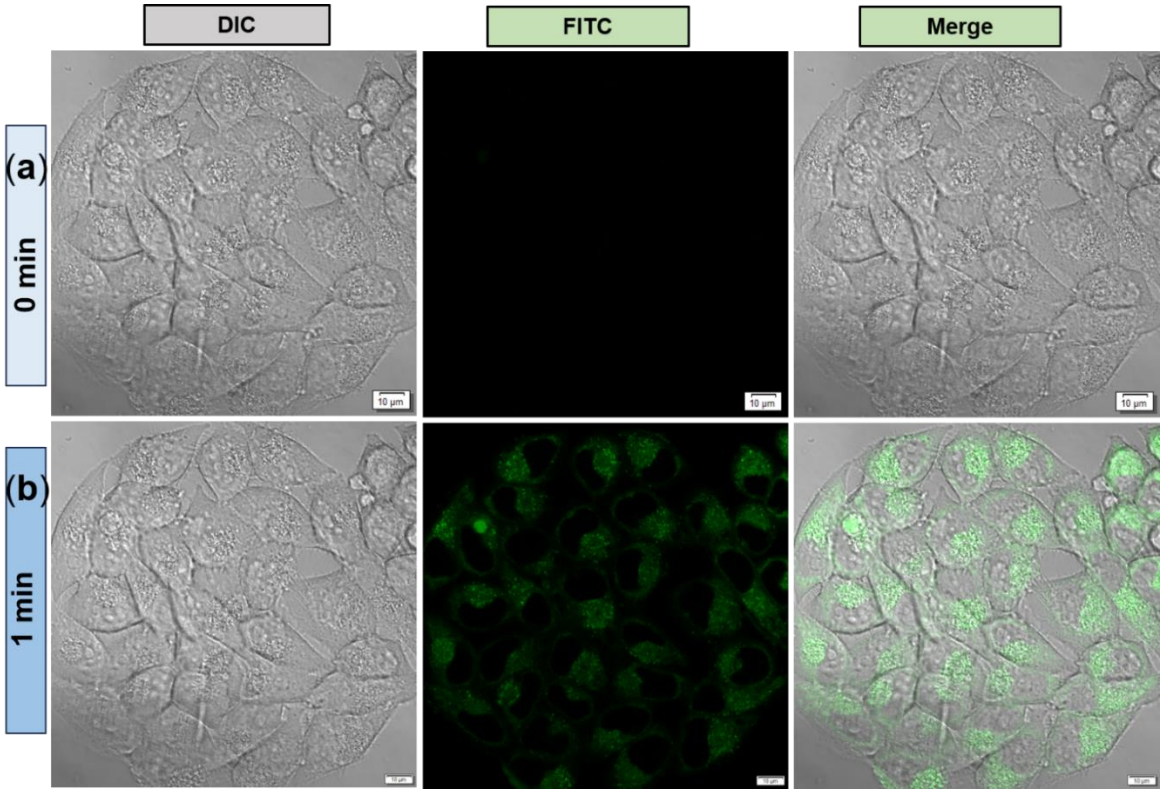


Figure S24. Confocal laser scanning microscopy (CLSM) images of HeLa cells after treatment with 5 μM of probe **2e** upon without irradiation (upper panel) and with irradiation (lower panel)

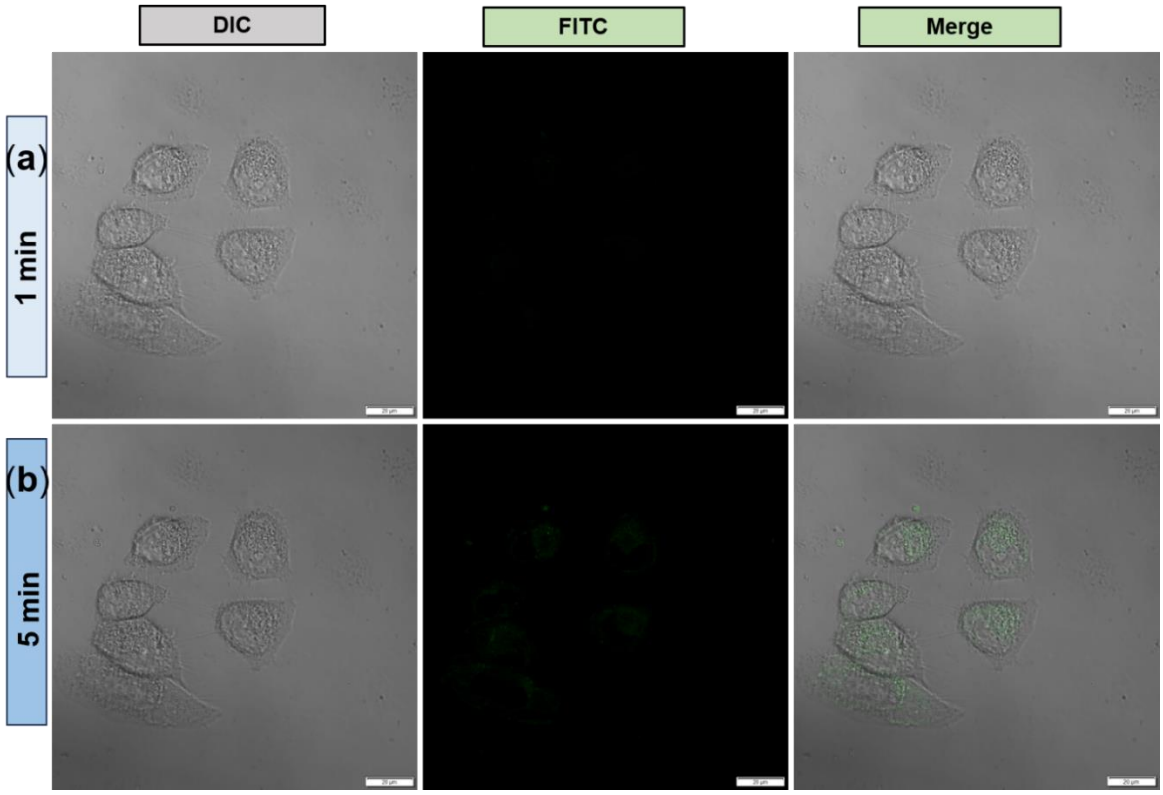


Figure S25. Confocal laser scanning microscopy (CLSM) images of HeLa cells after treatment with 5 μM of probe **2y** upon 1 min irradiation (upper panel) and 5 min irradiation (lower panel).

12. Cell Culture, Imaging and Spectroscopy:

Materials:

Dulbecco's modified Eagle's medium (DMEM) was purchased from Sigma-Aldrich (USA). Fetal bovine serum (FBS) and antibiotic cocktails were purchased from HiMedia (USA). The 35 mm glass-bottom imaging dishes were purchased from Ibidi (Germany). The image was processed with the help of cellSens Dimension software v3.2 (Olympus).

Culture Method:

HeLa cell lines were obtained from the National Center for Cell Science, Pune, India, and were cultured in DMEM containing 10% (v/v) FBS and 1% (v/v) antibiotic cocktail in 5% CO_2 at 310 K (37 °C) in the incubator. For imaging, cells were grown in the 35 mm glass-bottom imaging dish for 24 h with 75 – 80% confluency.

Cytotoxicity Assay:

Around 5,000 cells per well were seeded in a 96-well plate and grown for 24 h in 5% CO_2 at 310 K (37 °C) in the incubator. After that, cells were stained with the angular phenothiazine **1a** and the cyclobutylated phenothiazine **2a** from stock solution in DMSO (1 mM). The added amount of DMSO was not more than 2 μL. After 24 h of incubation, 20 μL of MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium bromide) dye solution (from a stock of 5 mg/ mL in PBS 7.4 buffer) was added to each well and incubated for 4 h. The media was removed gently from each well, and 100 μL DMSO was added to each well to dissolve the purple-colored crystal. The absorbance at 570 nm was recorded in a Synergy H1 Hybrid multi-mode microplate reader from Biotek.

Sample Preparation for Cell Imaging:

For Cellular Localization of the Angular Phenothiazine 1a and **Cyclobutylated Phenothiazines 2a:** From 1 *m*M DMSO stock solution of the angular phenothiazine **1a** or the cyclobutylated phenothiazine **2a**, 5 μL was taken, and added to 1 mL of phosphate-buffered saline (PBS 1X, pH 7.4) in a 1.5 mL Eppendorf tube. From these, 500 μL solution was added to a 35 mm glass-bottom imaging dish containing HeLa cells (the final concentration of both the probes in the incubating solution = 5 μM). The cells were then incubated for 15 min at 37 °C, thereafter, the cells were washed with PBS 1X (pH 7.4) twice before imaging. The imaging

was performed in 1X PBS (pH 7.4) supplemented with 5 mM $MgCl_2$. The rest of the procedure for imaging study is the same as above.

For Intracellular [2+2] Photocycloreversion Reaction:

This experiment was done by using the cyclobutylated phenothiazine probe **2a** in HeLa cells. After staining the cells with 5 μM of the same probe, a particular field of view (FOV) was selected, and cells were imaged. Thereafter, a 405 nm external laser source (*vide supra*) was used to irradiate the cells for the required period and imaged accordingly. The imaging dish was not disturbed and therefore, the FOV was kept the same throughout the experiment.

For Endocytosis Study:

HeLa cells were cultured for 24 h, and then, the cells were pre-treated at 37 °C (control group) and 4 °C for 2 h. After washing two times with PBS solution, the cells were incubated with 5 μM of the angular phenothiazine **1a** in DMEM media for 15 minutes, followed by washing. For the cellular uptake mechanism, five inhibitors were applied to block the endocytic pathway. HeLa cells were pre-treated at 37 °C with the DMEM media containing 100 μM chloroquine, 30 μM chlorpromazine, 500 μm MβCD and 200 μm amiloride for 2 h, and 5 μm cytochalasin-D for 15 minutes, washed two times with PBS solution. Further cells with 5 μM of the angular phenothiazine **1a** in DMEM media for 15 minutes followed via washing with PBS solution and then imaged under the microscope.

Confocal Microscopy:

All the confocal imaging was performed with an Olympus FV3000 confocal laser scanning microscope (CLSM). For both the angular phenothiazine **1a** and cyclobutylated phenothiazine **2a**, 488 nm excitation lasers were used with 1% laser (max. power = 20 *m*W). The confocal aperture was kept at 1 Airy Disk (AU) unit, while the dwell time was 8 μs/pixel. The image acquisition was performed in a sequential scanning mode to eliminate the possibility of crosstalk and bleed-through between different imaging channels.

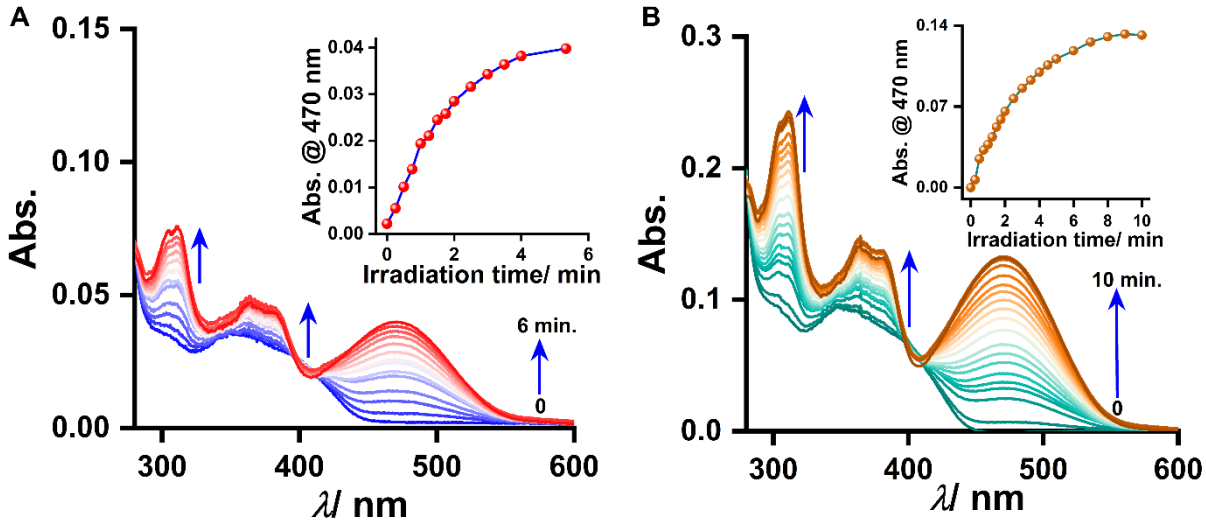


Figure S26. Time-dependent UV-Vis absorption spectra in acetonitrile upon irradiation with visible light at different times, (A) for 5 μM concentration; (B) for 20 μM concentration of the cyclobutylated phenothiazine **2a**

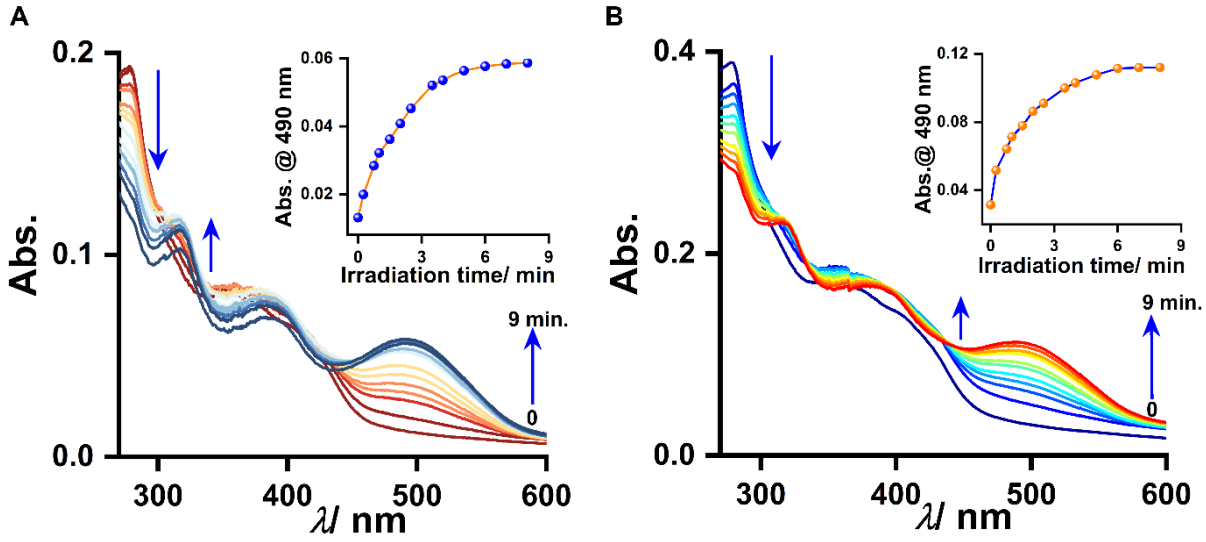


Figure S27. Time-dependent UV-visible absorption spectra in PBS solution (pH 7.4) upon irradiation with visible light at different times, (A) for 10 μM concentration; (B) for 20 μM concentration of the cyclobutylated phenothiazine **2a**

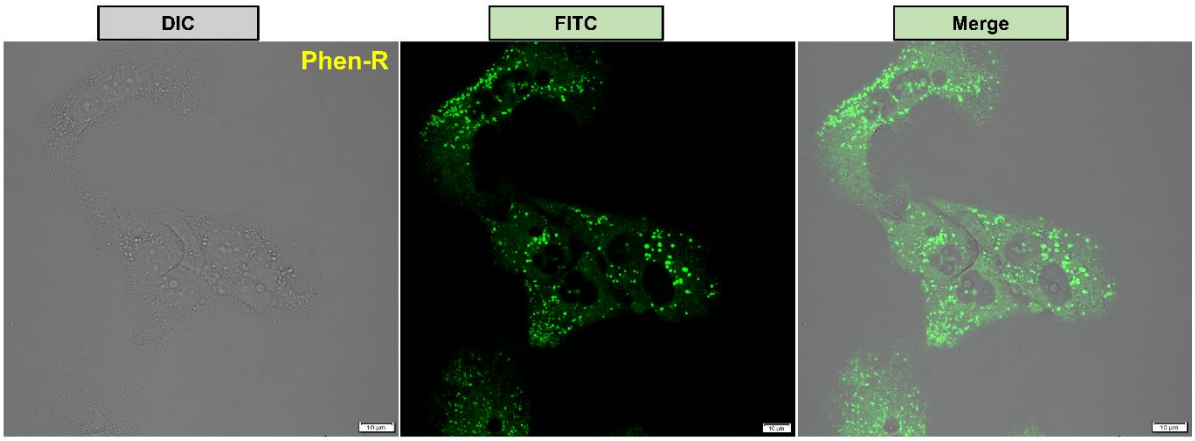


Figure S28. Confocal laser scanning microscopy (CLSM) images of HeLa cells after treatment with 5 μM of the angular phenothiazine probe **1a**, Scale bar = 10 μm

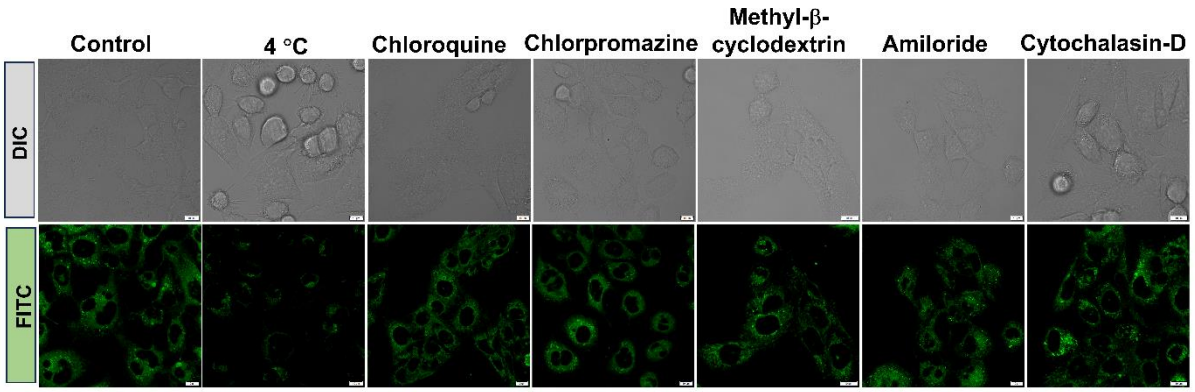


Figure S29. Effects of temperature and different endocytosis inhibitors (100 μm chloroquine, 30 μm chlorpromazine, 500 μm MβCD, 200 μm amiloride, and 5 μm cytochalasin-D) with 5 μM of the angular phenothiazine probe **1a** in HeLa cells were analysed by confocal microscopys

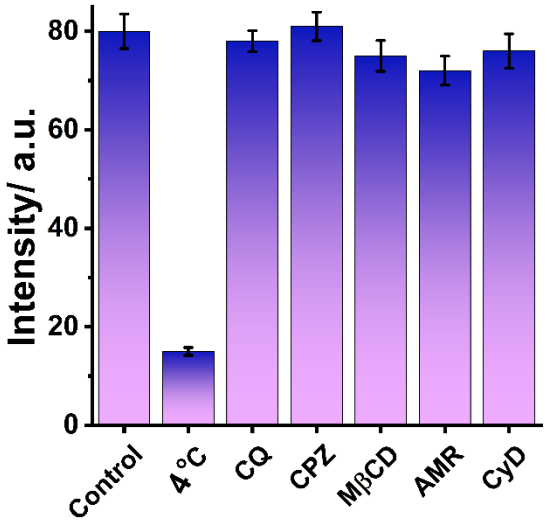


Figure S30. The bar plot shows the average fluorescence intensities in HeLa cells in the control set, incubated at low temperature, and when treated with different endocytosis inhibitors

UV-Vis Spectra of the Ibuprofen-Coupled Cyclobutylated Phenothiazine 2am

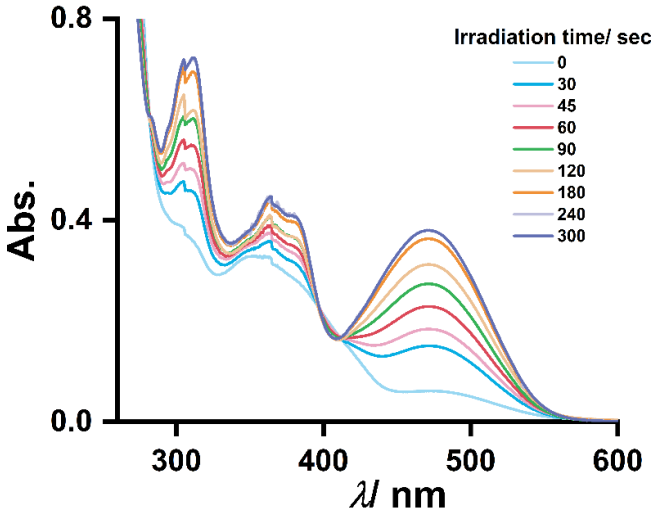


Figure S31. Time-dependent UV-vis absorption spectra of 10 μM **2am** in acetonitrile upon irradiation with a 405 nm external laser source

Prior to any light exposure, the ibuprofen-coupled cyclobutylated phenothiazine **2am** displays featureless, broad absorption spectra spanning from 322 nm to 455 nm, with minimal absorbance in longer wavelength regions. Upon being subjected to an external laser source of 405 nm for 30 seconds, the absorbance values gradually increase beyond 455 nm and within

the range of 290 nm to 455 nm. Further exposure to the same light, generates a well-defined vibronic feature, with an absorption band peaking at 470 nm, perfectly mirroring the absorption spectrum of its precursor namely, angular phenothiazine **1a** in acetonitrile (Figure S31). After 5 minutes of light exposure, the spectrum becomes saturated, and no further change in absorbance values was observed.

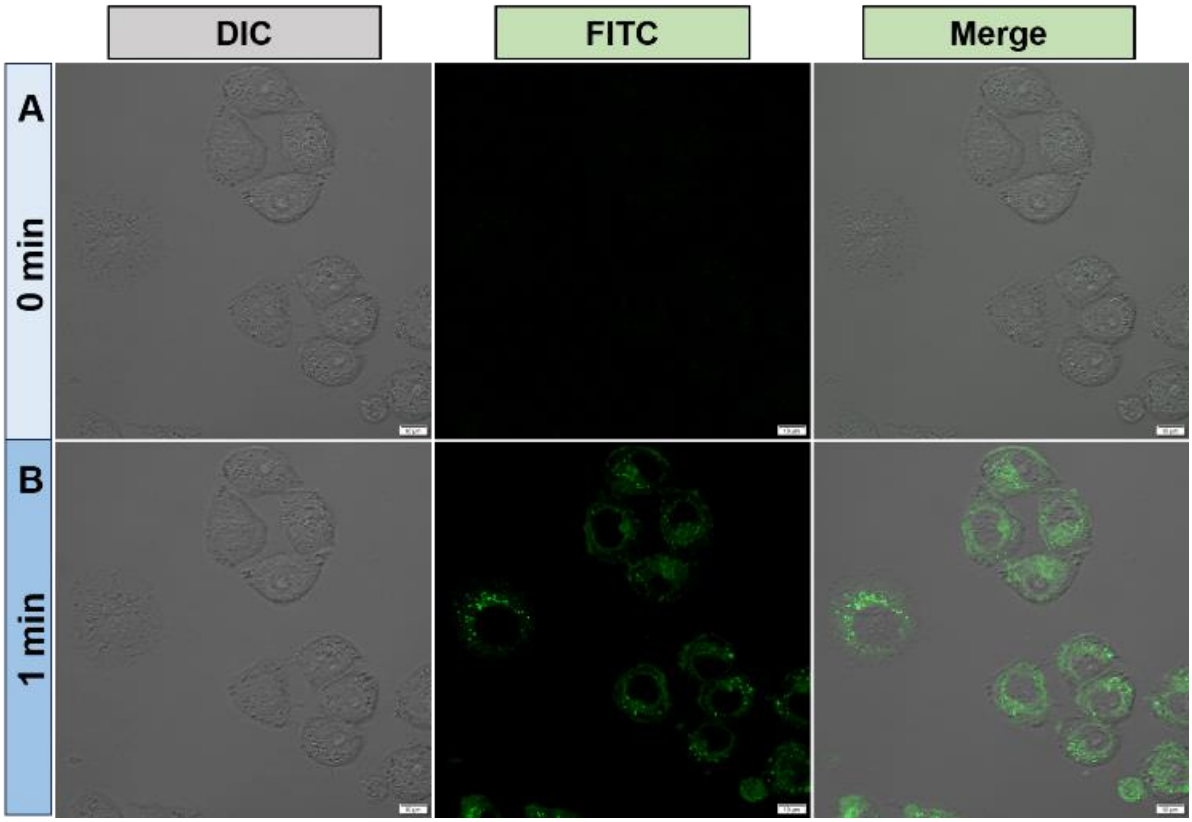
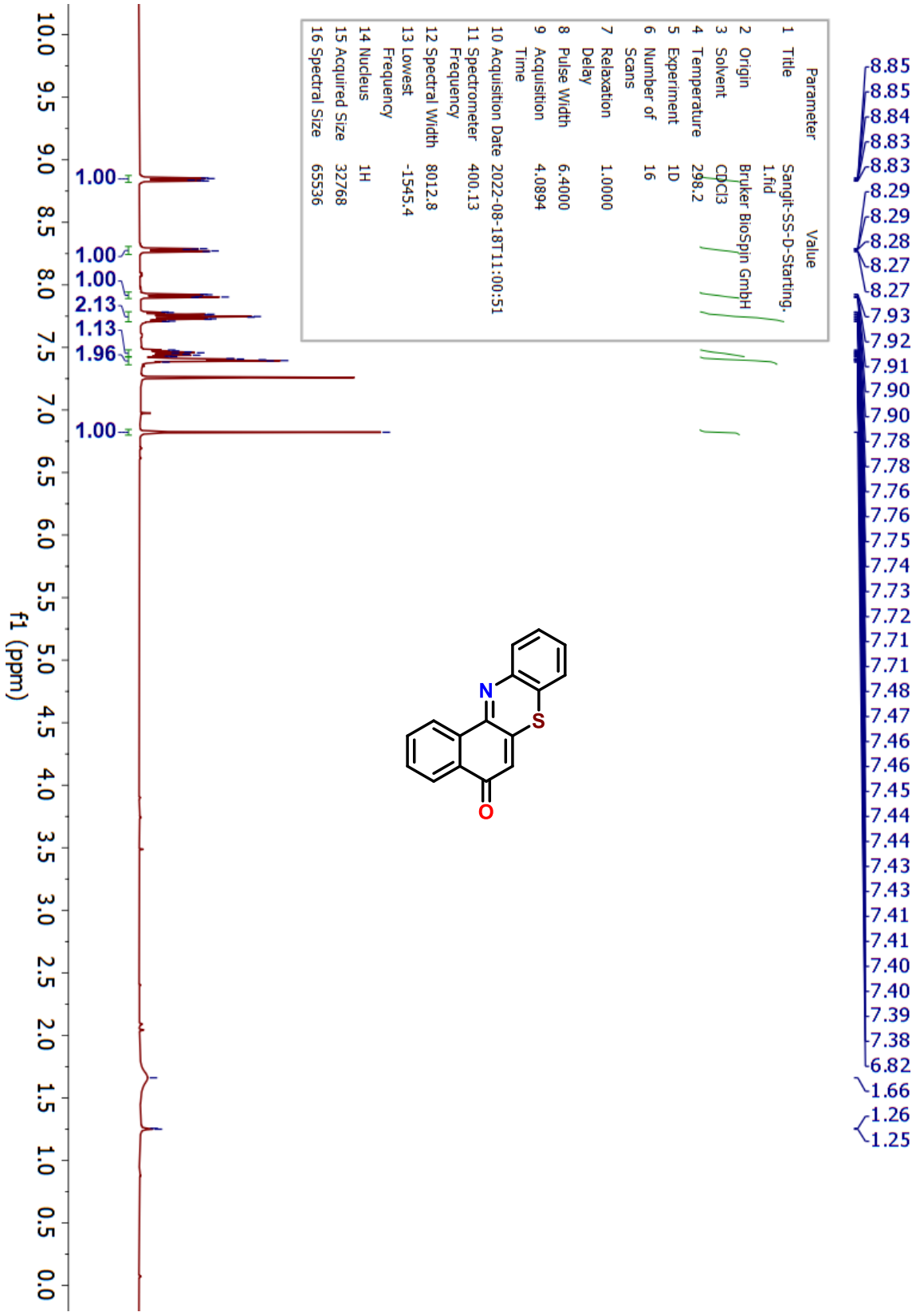


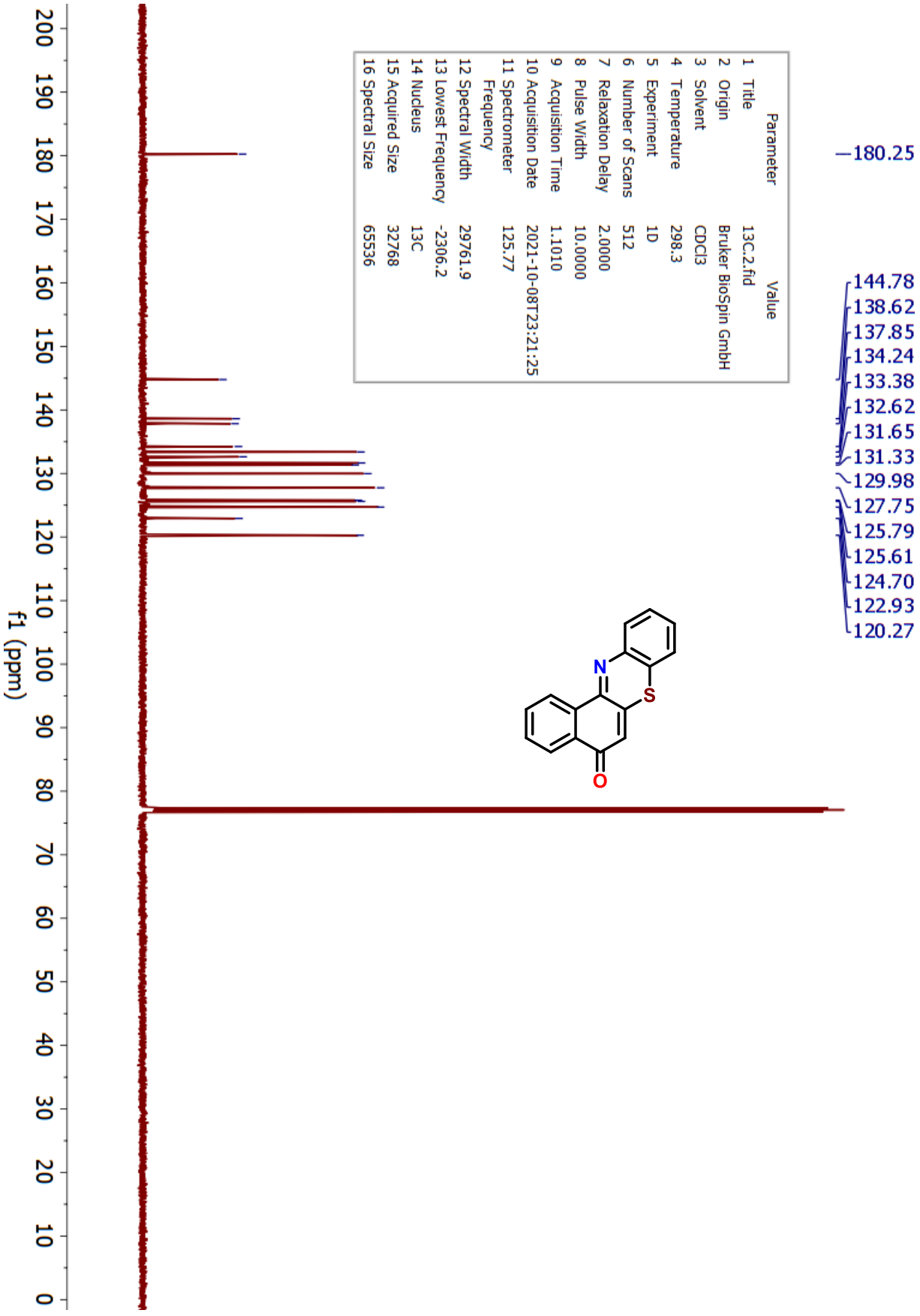
Figure S32. Confocal laser scanning microscopy (CLSM) images of HeLa cells after treatment with 5 μM of the ibuprofen-coupled cyclobutylated phenothiazine derivative **2am** upon irradiation without (upper panel: A) and with (lower panel: B) light. Scale bar = 10 μm

13. Spectroscopic Characterization of Synthesized Compounds using NMR Analysis:

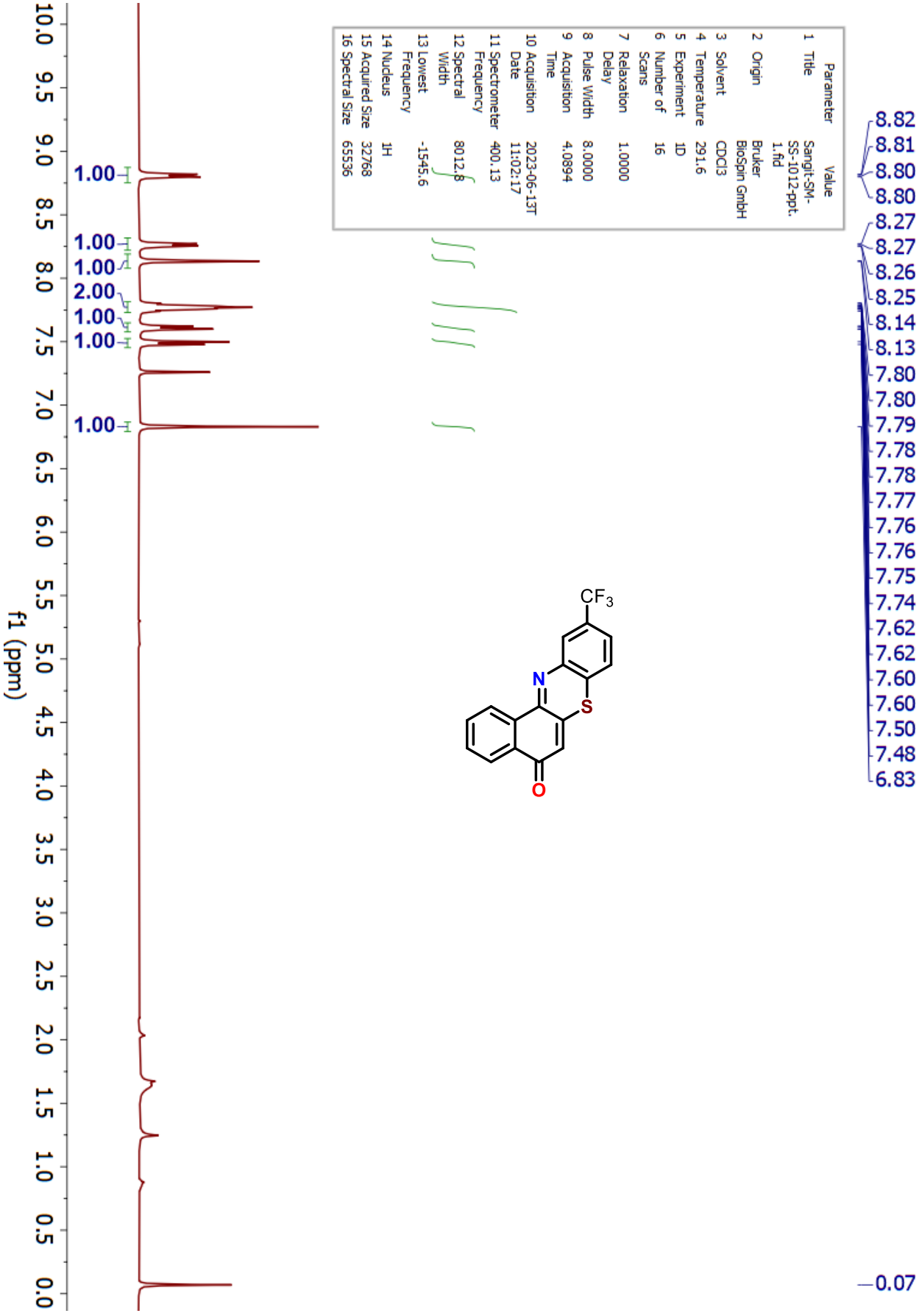
^{1}H NMR spectra of **1a**



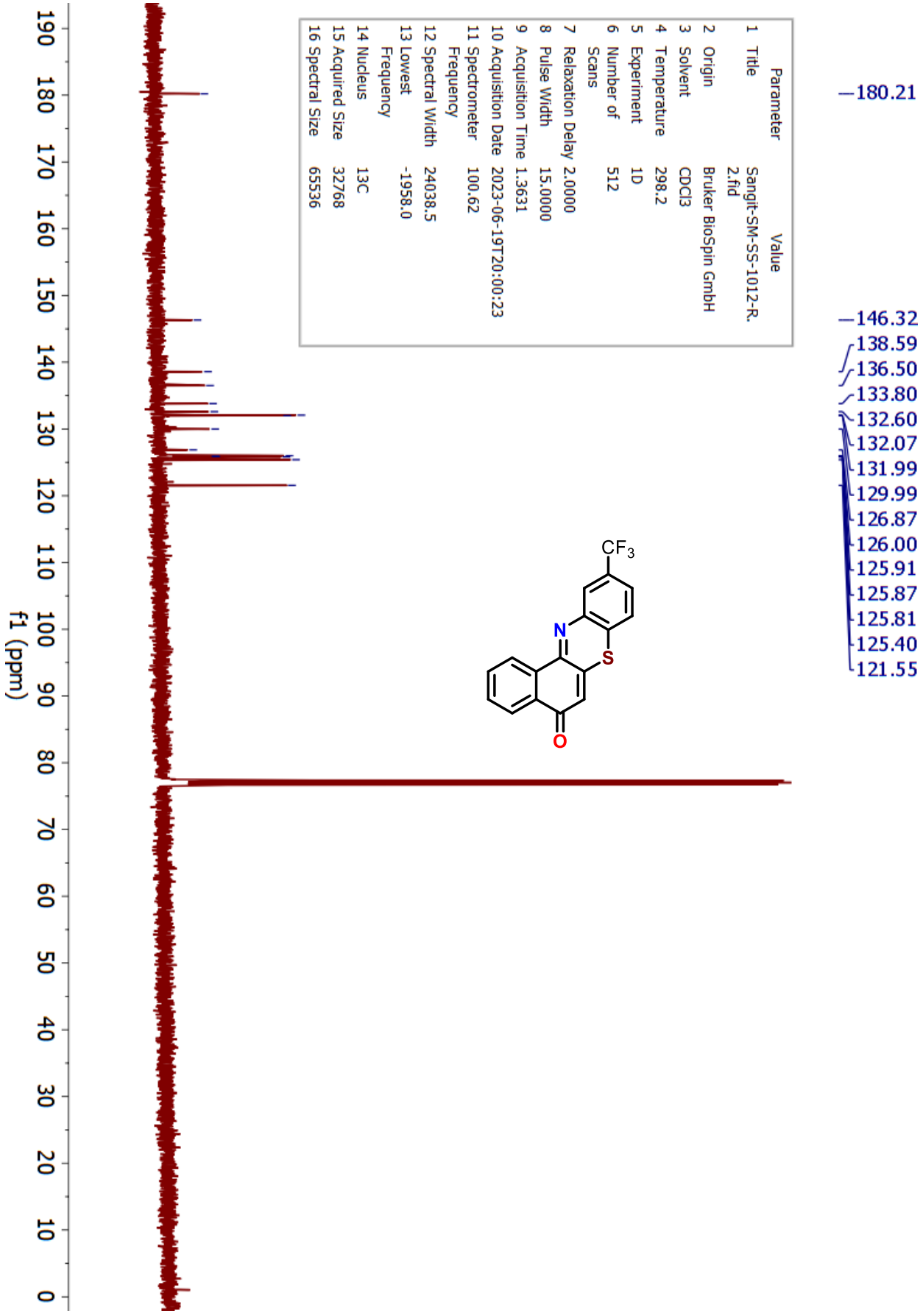
$^{13}C\{^{1}H\}$ NMR spectra of **1a**



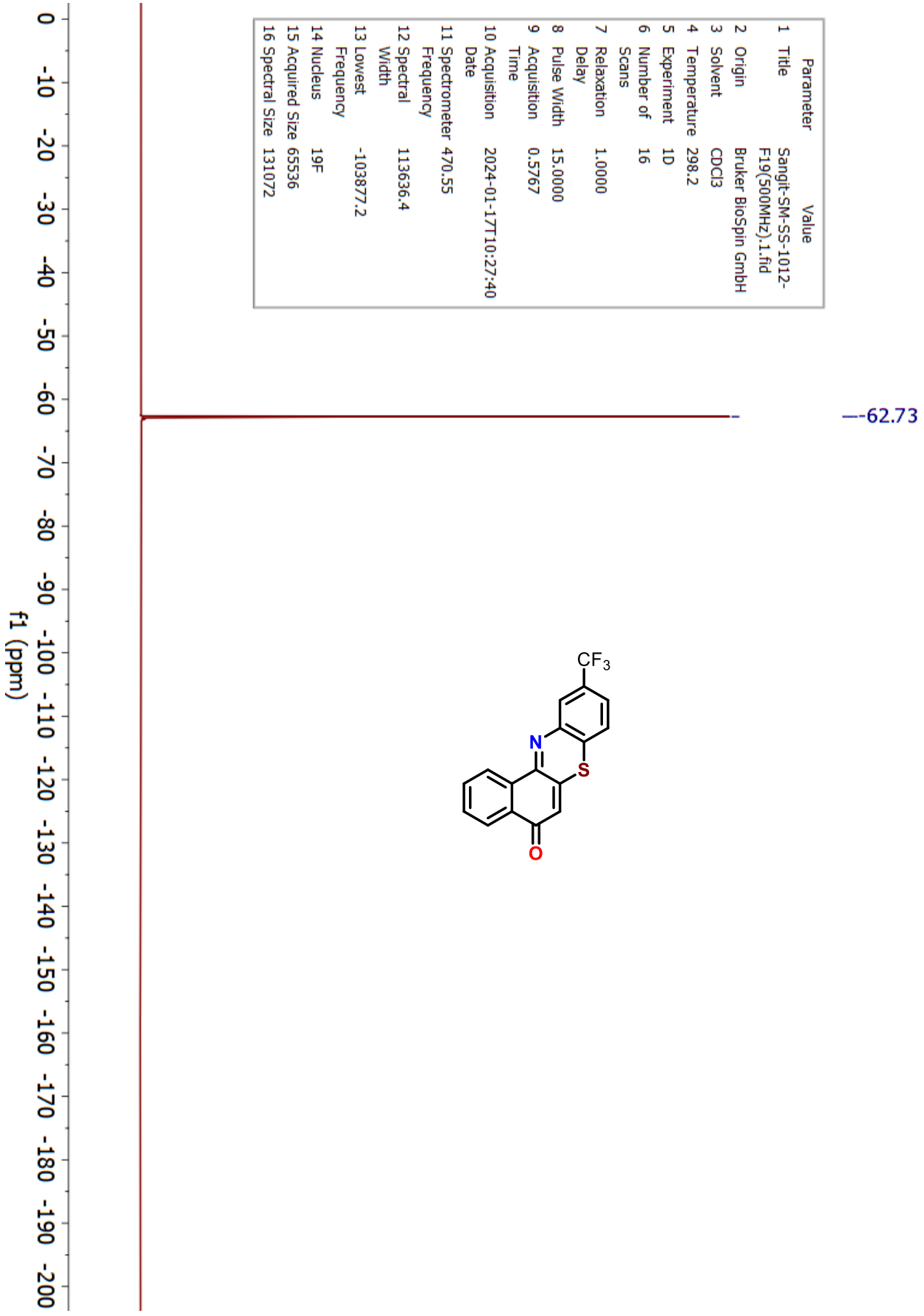
^{1}H NMR spectra of **1ac**



$^{13}C\{^{1}H\}$ NMR spectra of **1ac**



$^{19}F\{^{1}H\}$ NMR spectra **1ac**



	Parameter	Value
1	Title	Sangit-SM-SS-1012-F19(500MHz).1.fid
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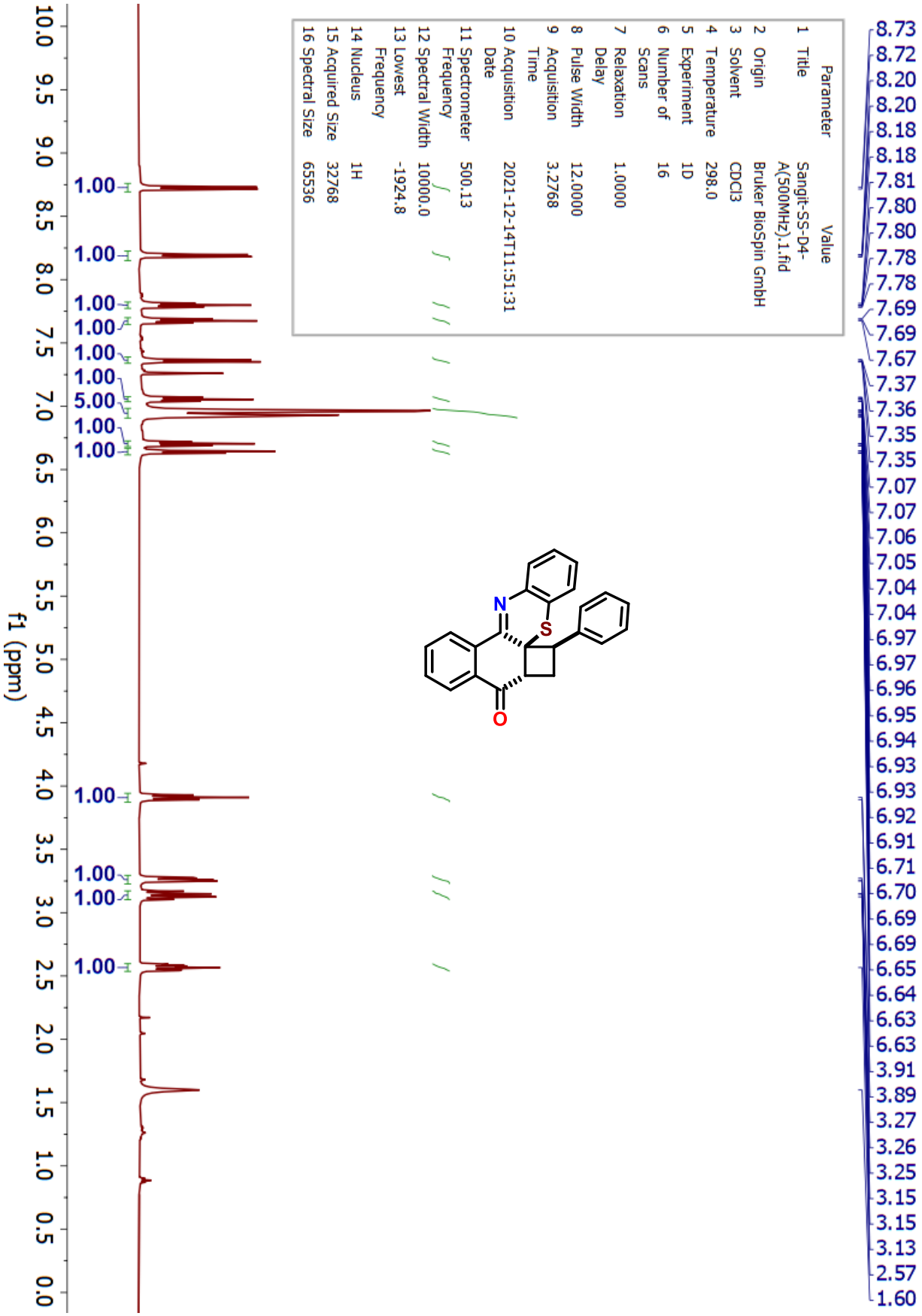
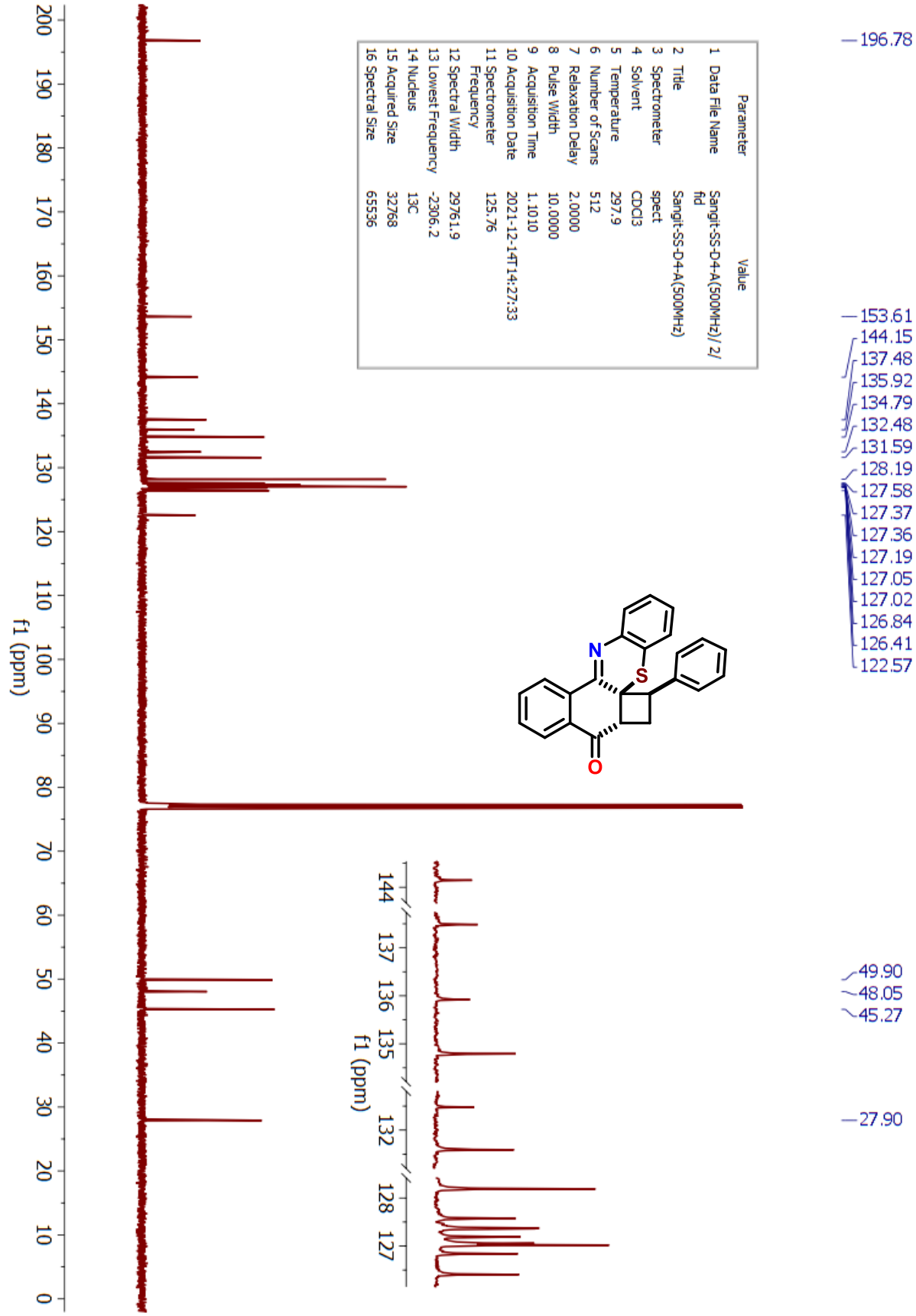
3	Solvent	CDCl3
4	Temperature	298.2
5	Experiment	1D
6	Number of Scans	16
7	Relaxation Delay	1.0000
8	Pulse Width	15.0000
9	Acquisition Time	0.5767
10	Acquisition Date	2024-01-17T10:27:40
11	Spectrometer Frequency	470.55
12	Spectral Width	113636.4
13	Lowest Frequency	-103877.2
14	Nucleus	19F
15	Acquired Size	65536
16	Spectral Size	131072

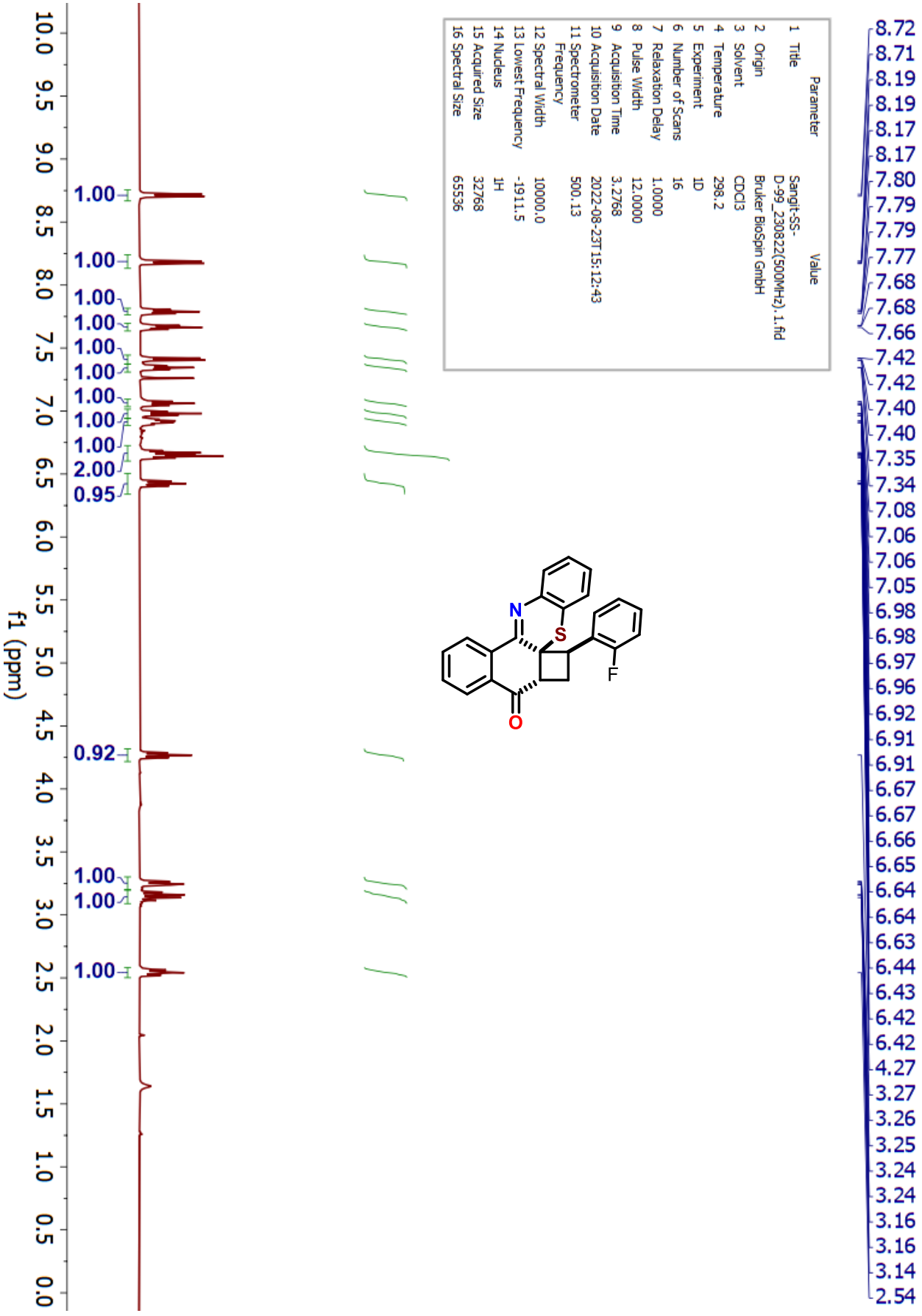
^{1}H NMR spectra of **2a**



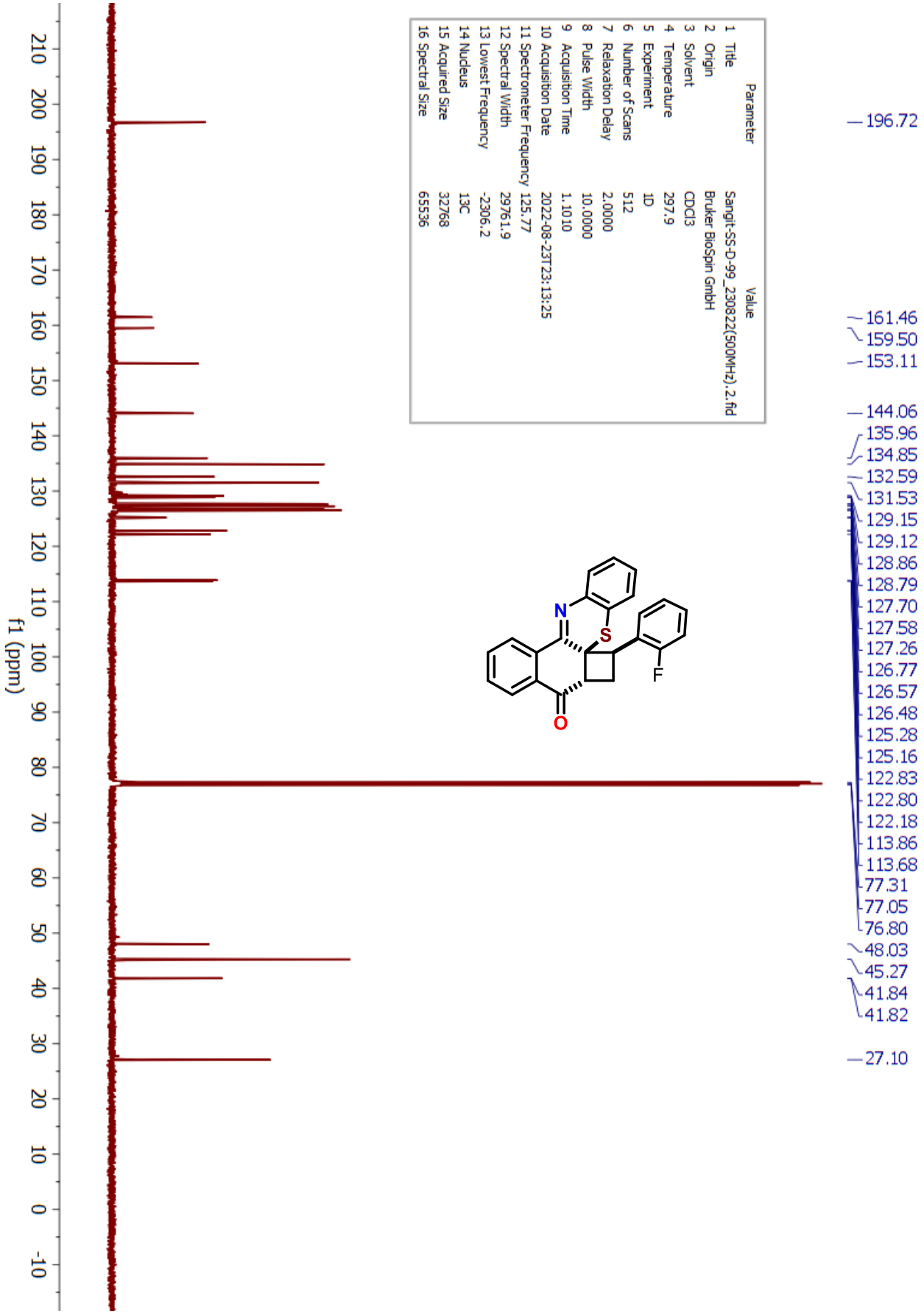
$^{13}C\{^{1}H\}$ NMR spectra of **2a**



^{1}H NMR spectra of **2b**



$^{13}C\{^{1}H\}$ NMR spectra of **2b**



$^{19}F\{^{1}H\}$ NMR spectra of **2b**

	Parameter	Value
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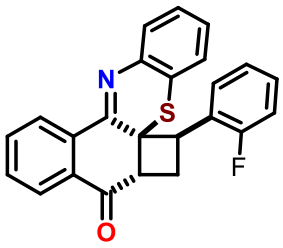
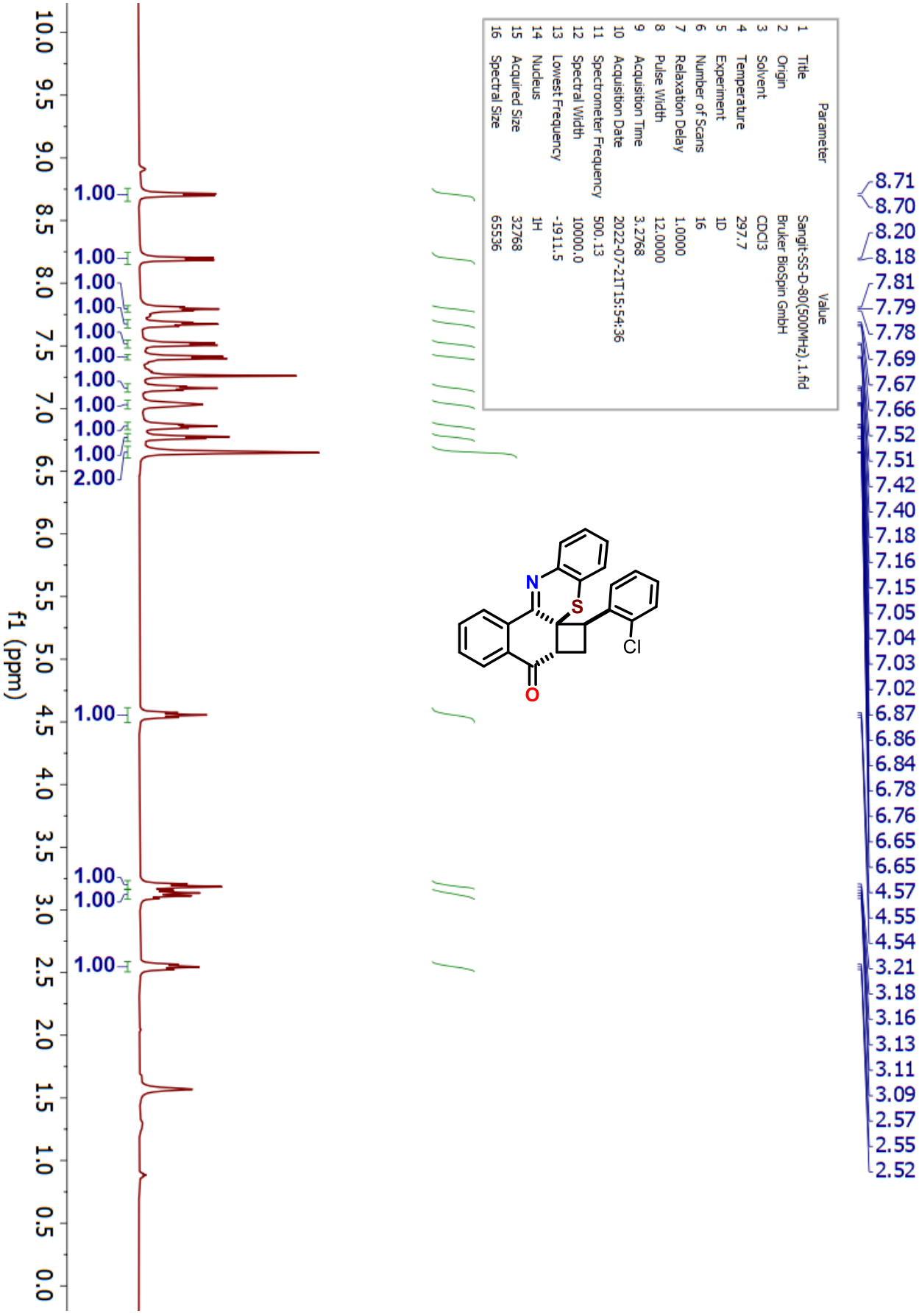
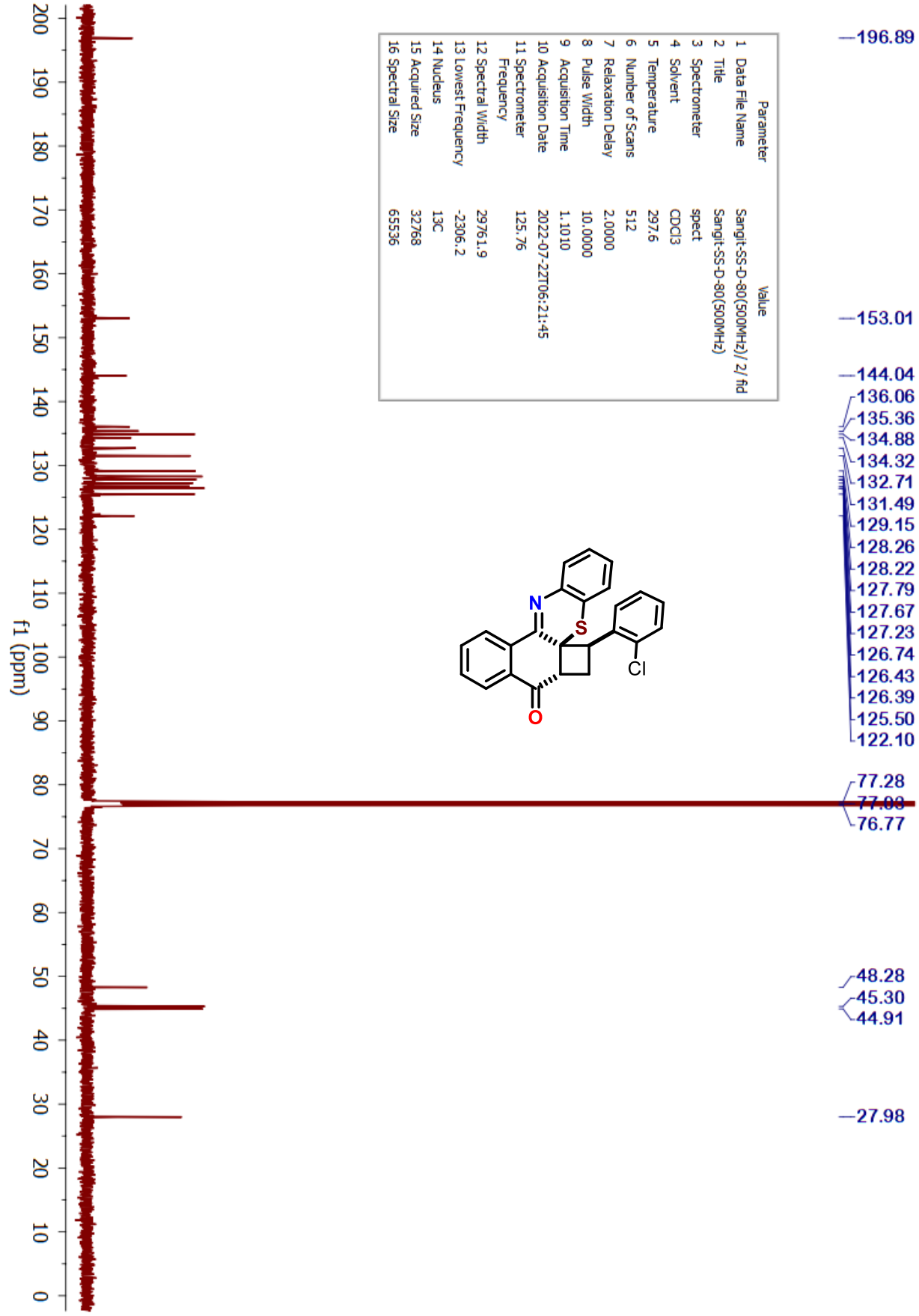
3	Solvent	CDCl3
4	Temperature	297.7
5	Experiment	1D
6	Number of Scans	16
7	Relaxation Delay	1.0000
8	Pulse Width	15.0000
9	Acquisition Time	0.5767
10	Acquisition Date	2024-01-12T12:41:39
11	Spectrometer Frequency	470.55
12	Spectral Width	113636.4
13	Lowest Frequency	-103877.2
14	Nucleus	19F
15	Acquired Size	65536
16	Spectral Size	131072



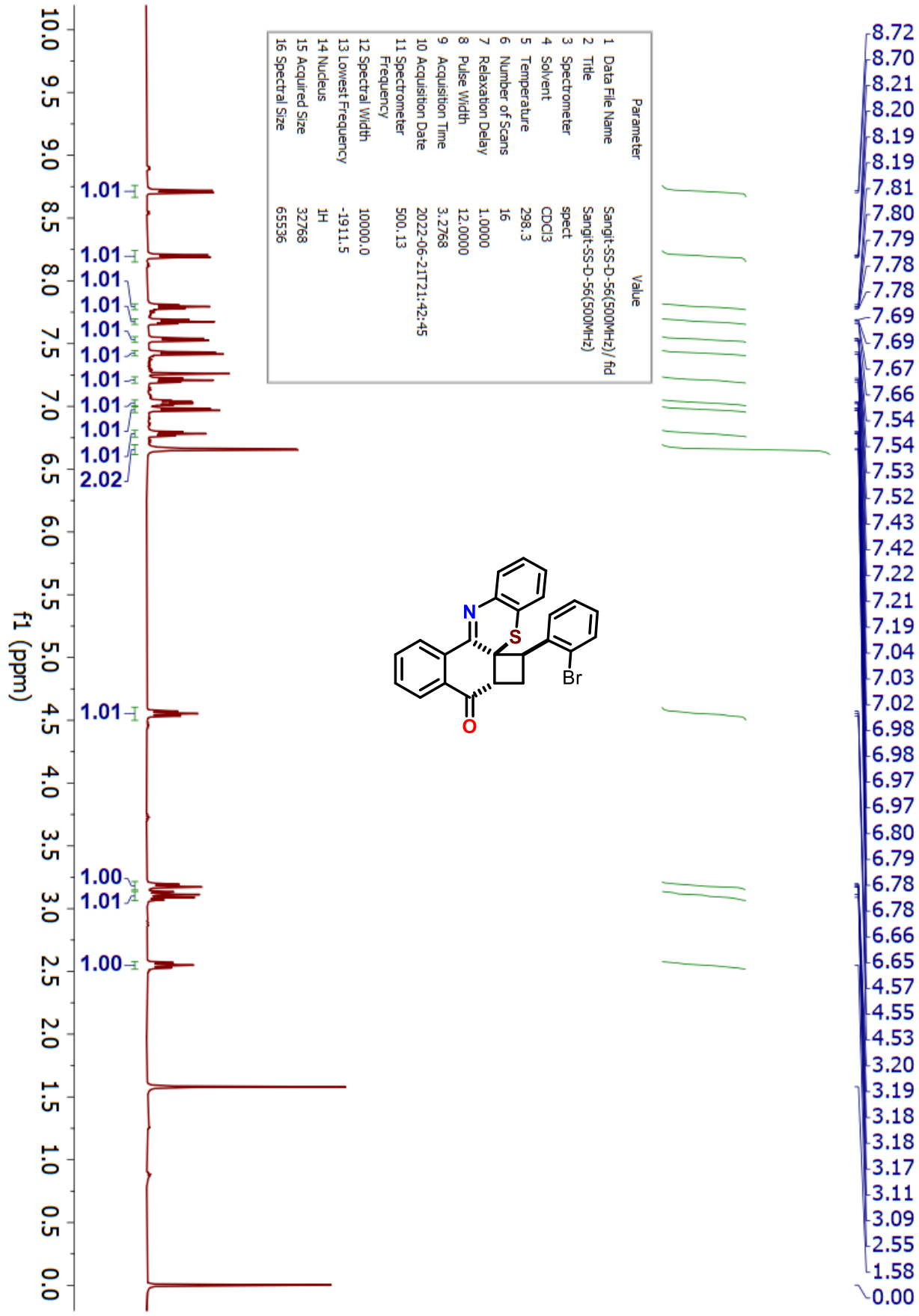
^{1}H NMR spectra of **2c**



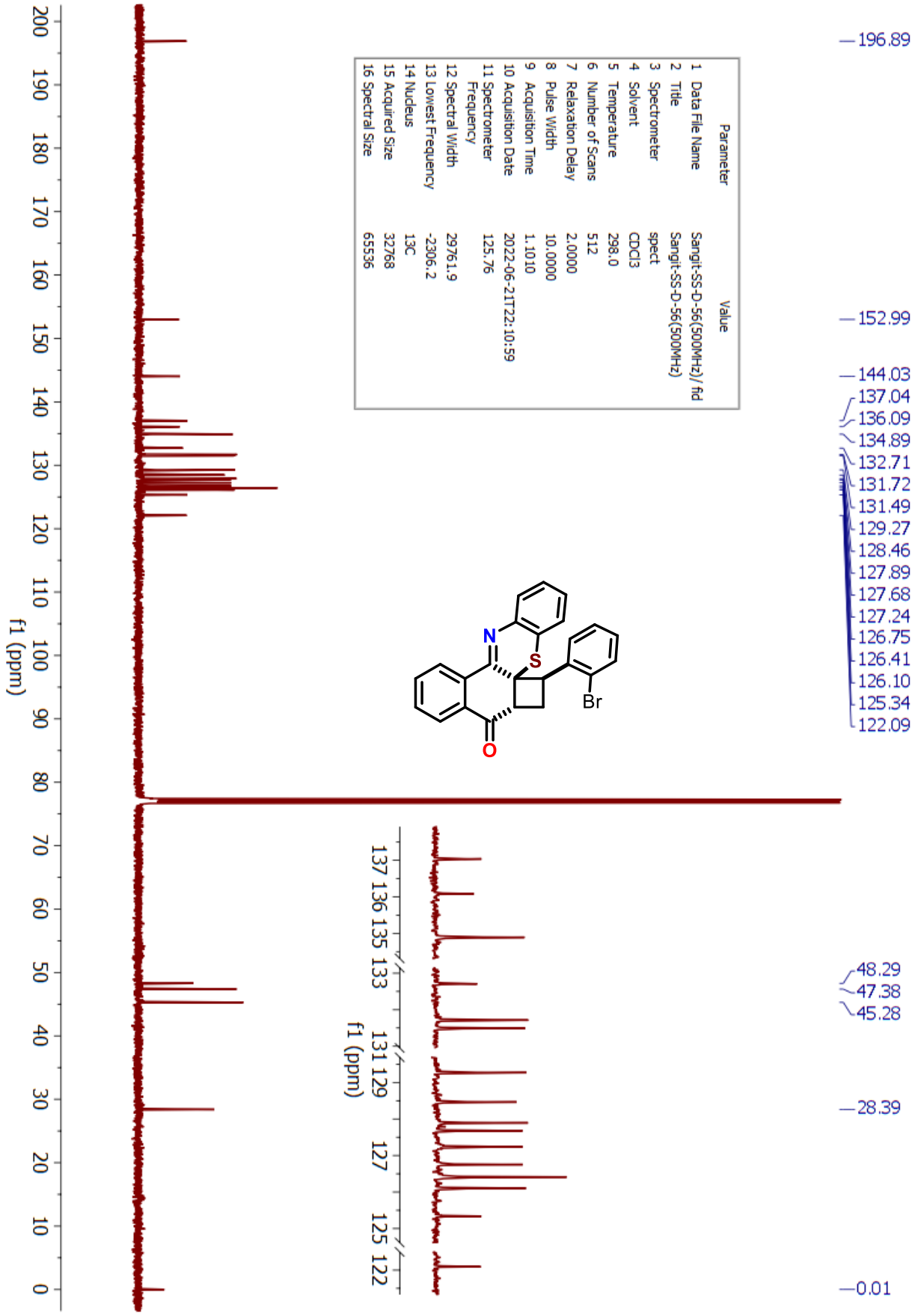
$^{13}C\{^{1}H\}$ NMR spectra of **2c**



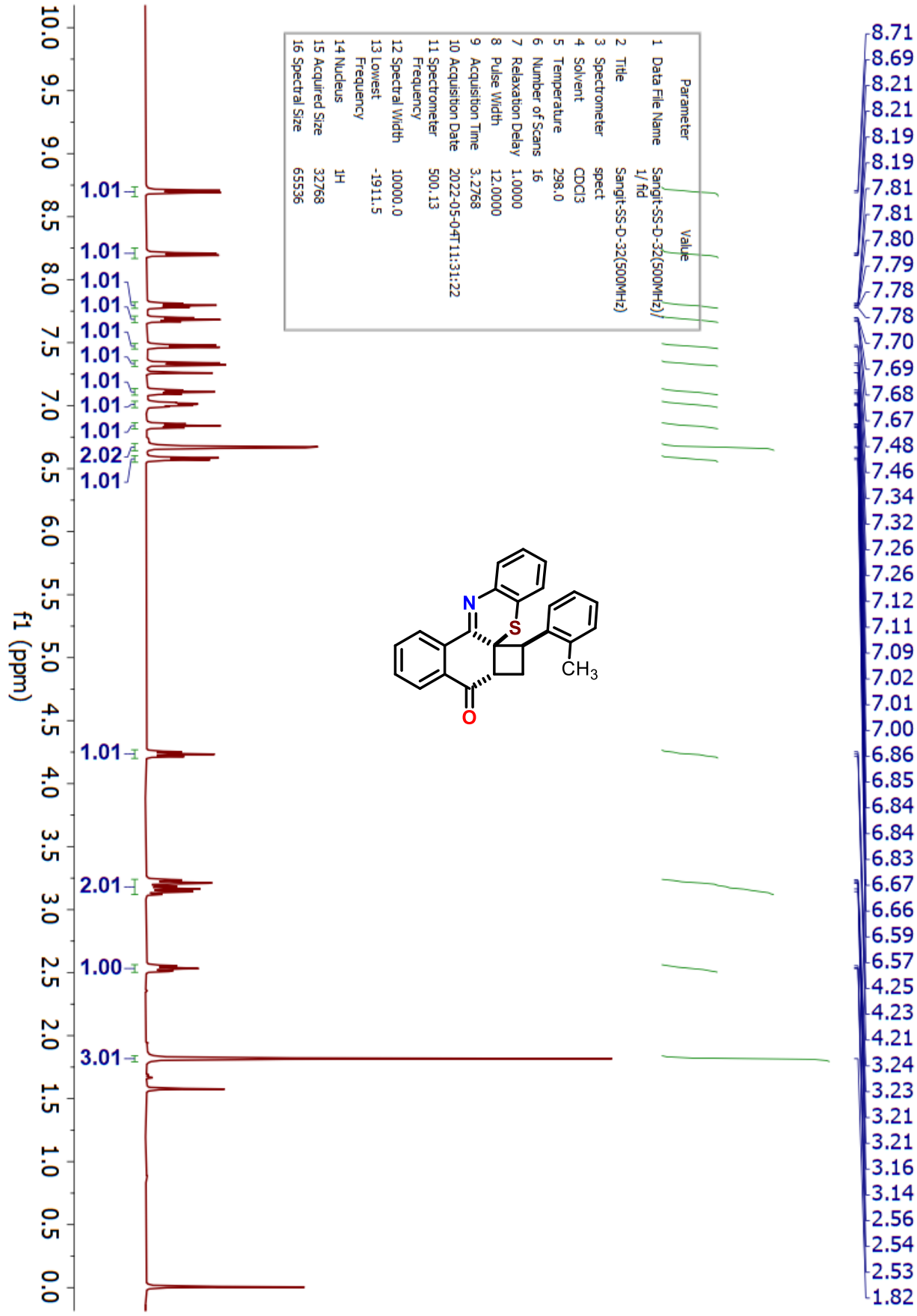
^{1}H NMR spectra of **2d**



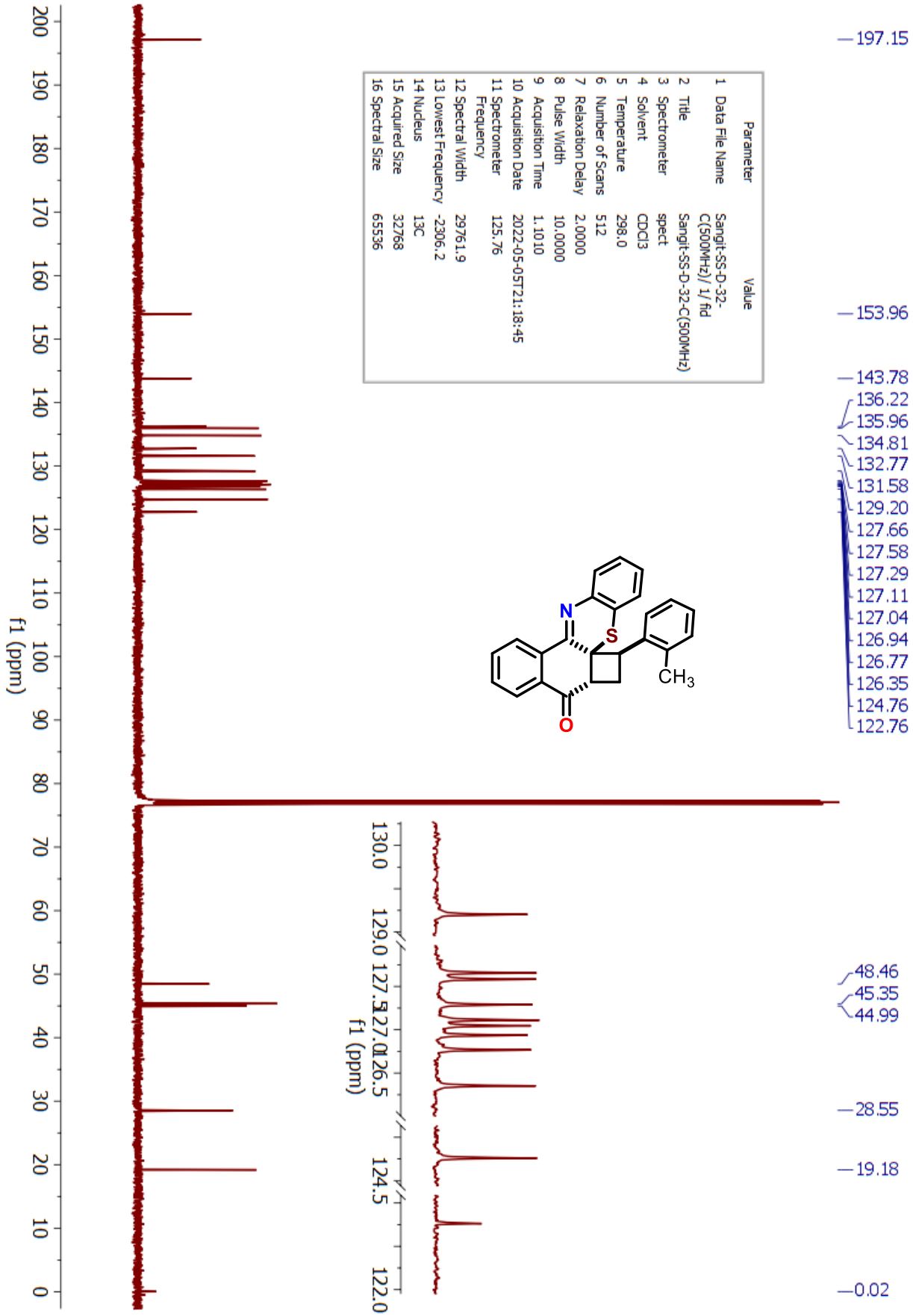
$^{13}C\{^{1}H\}$ NMR spectra of **2d**



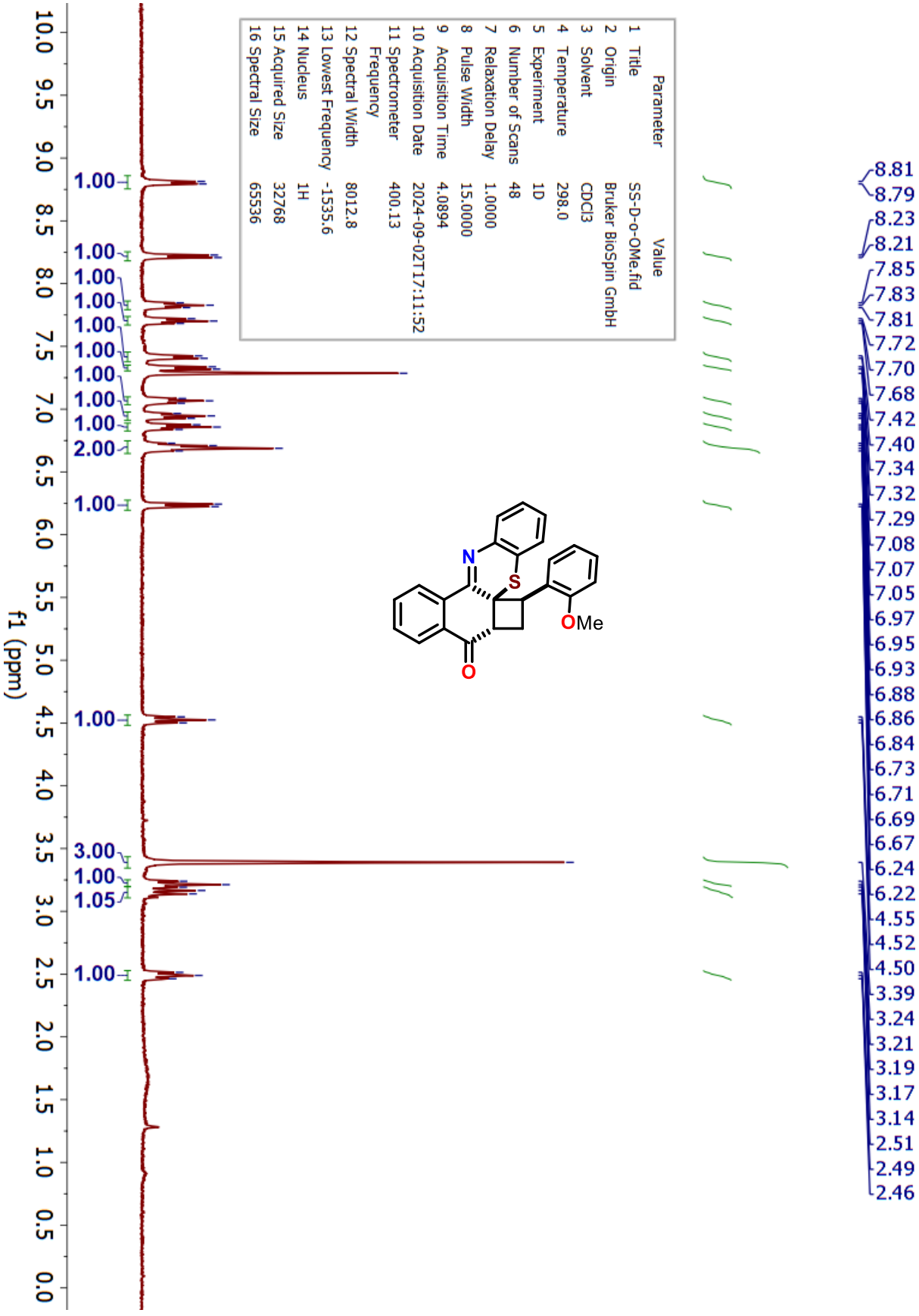
^{1}H NMR spectra of **2e**



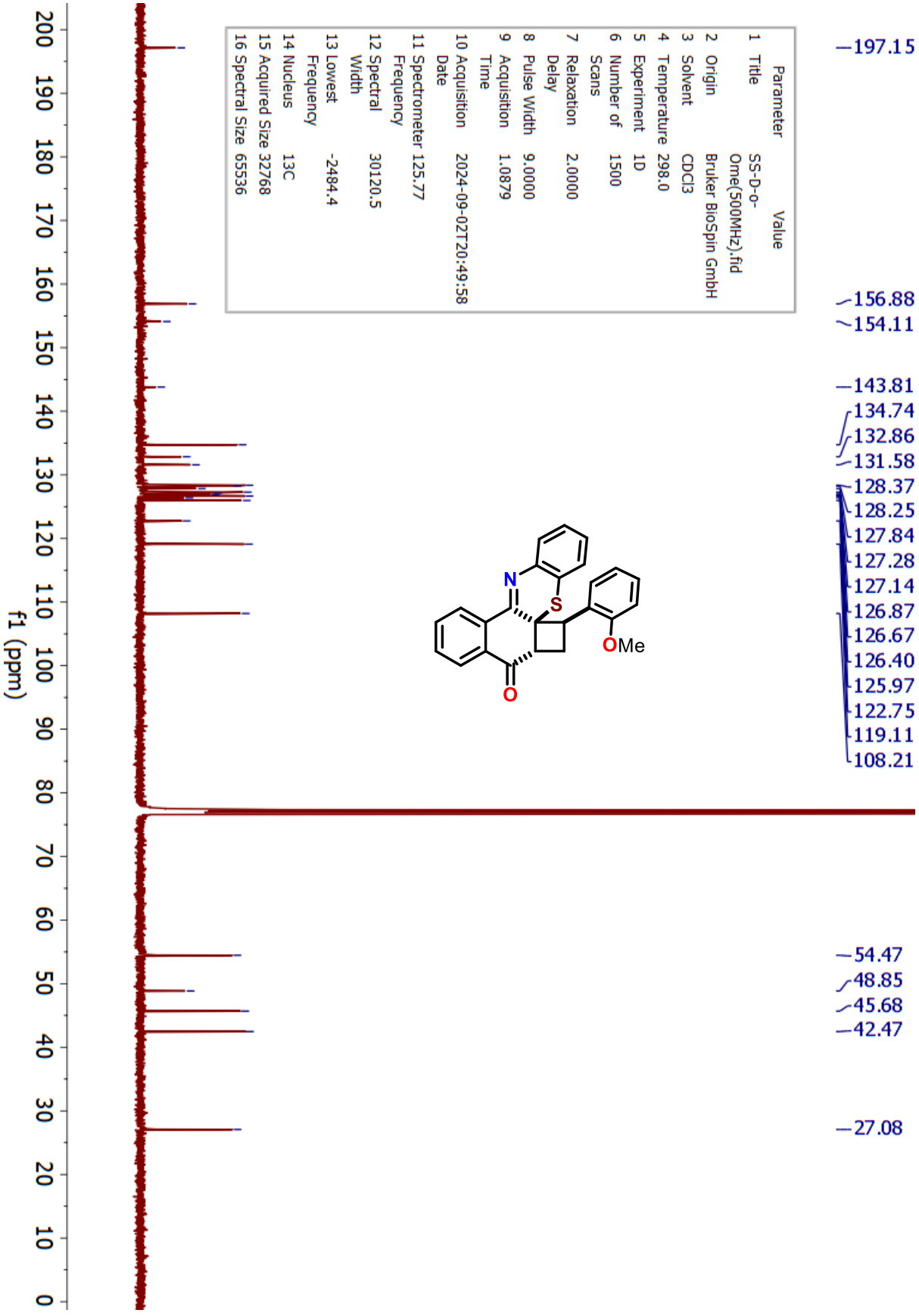
$^{13}C\{^{1}H\}$ NMR spectra of **2e**



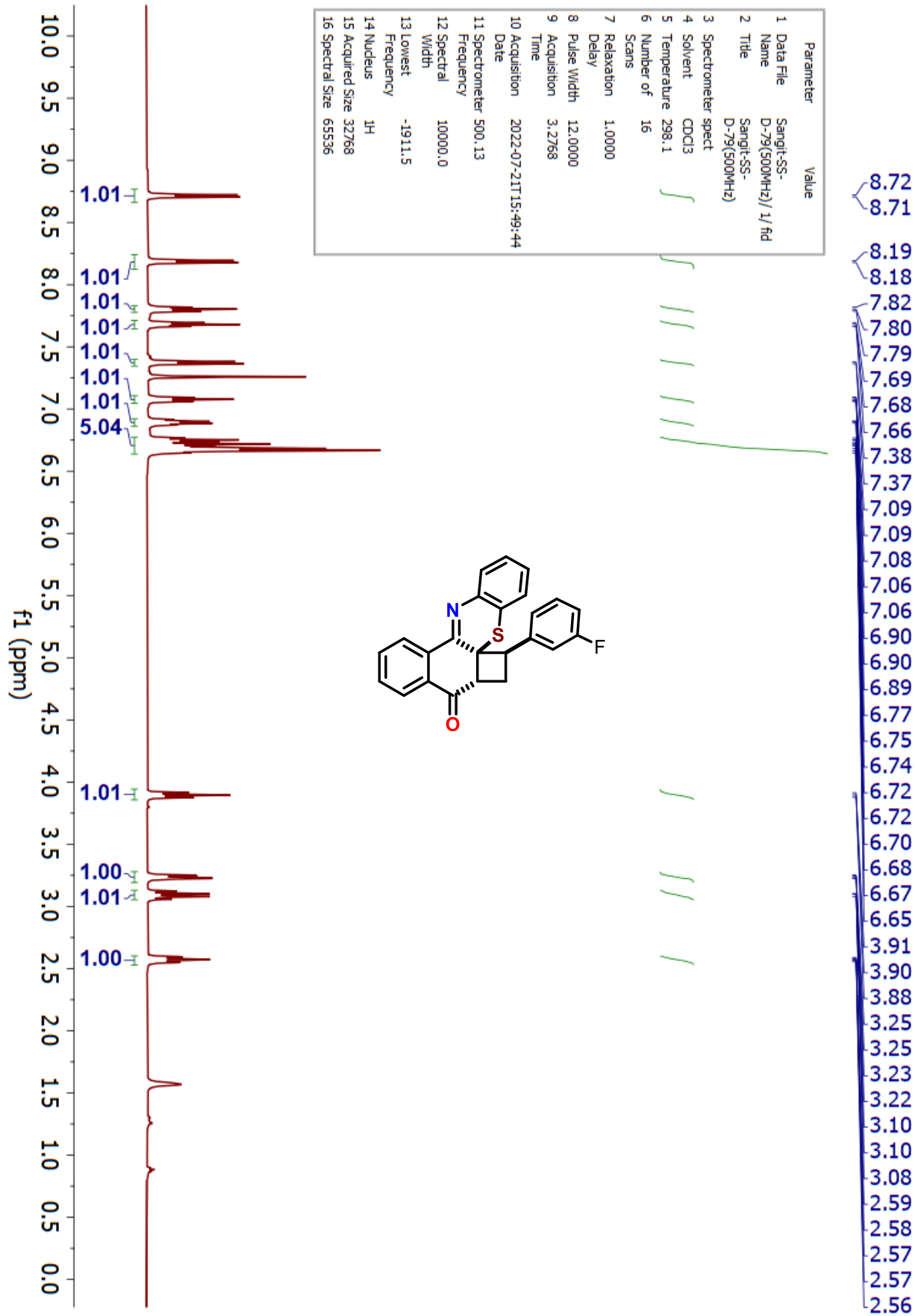
^{1}H NMR spectra of **2f**



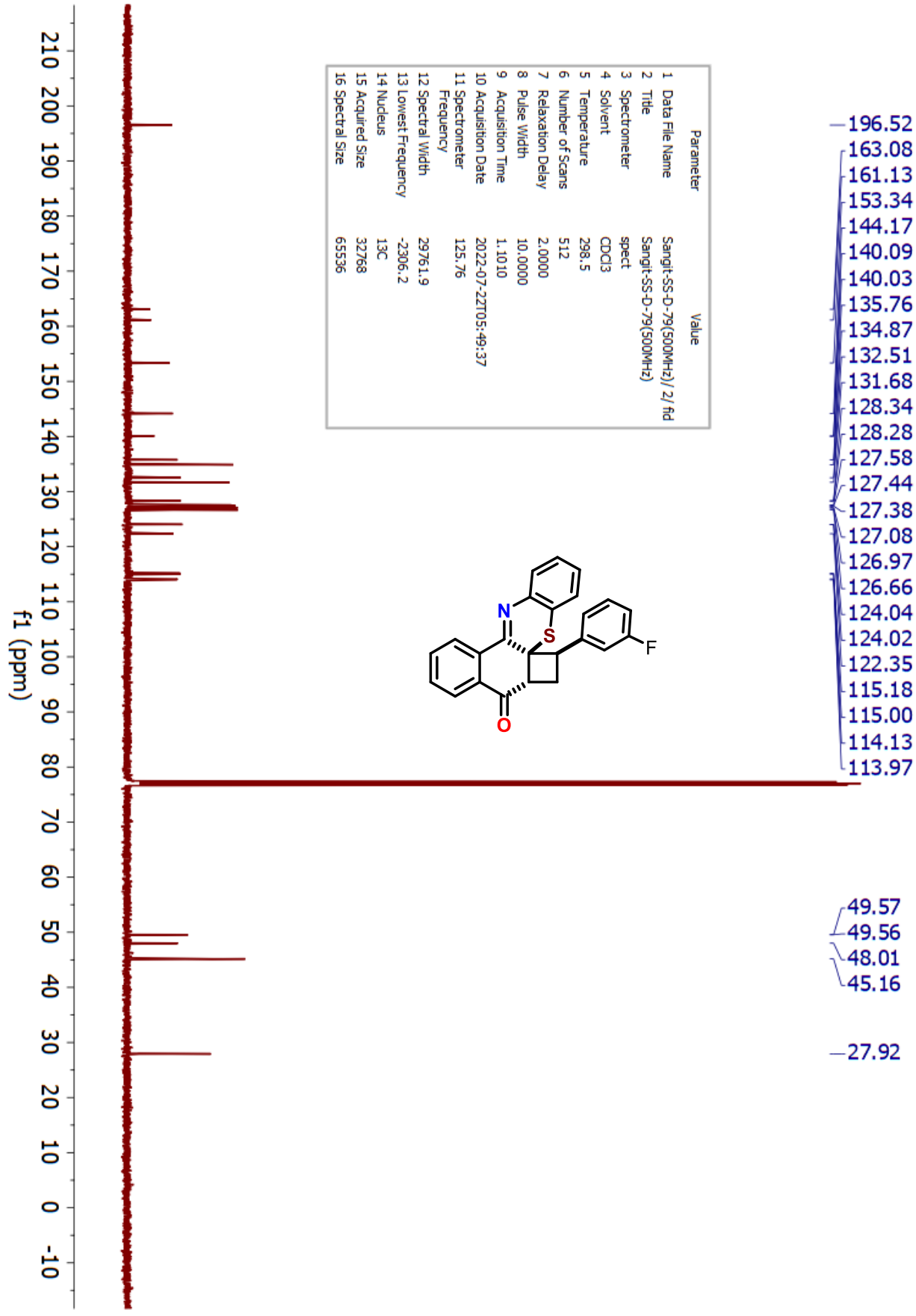
$^{13}C\{^{1}H\}$ NMR spectra of **2f**



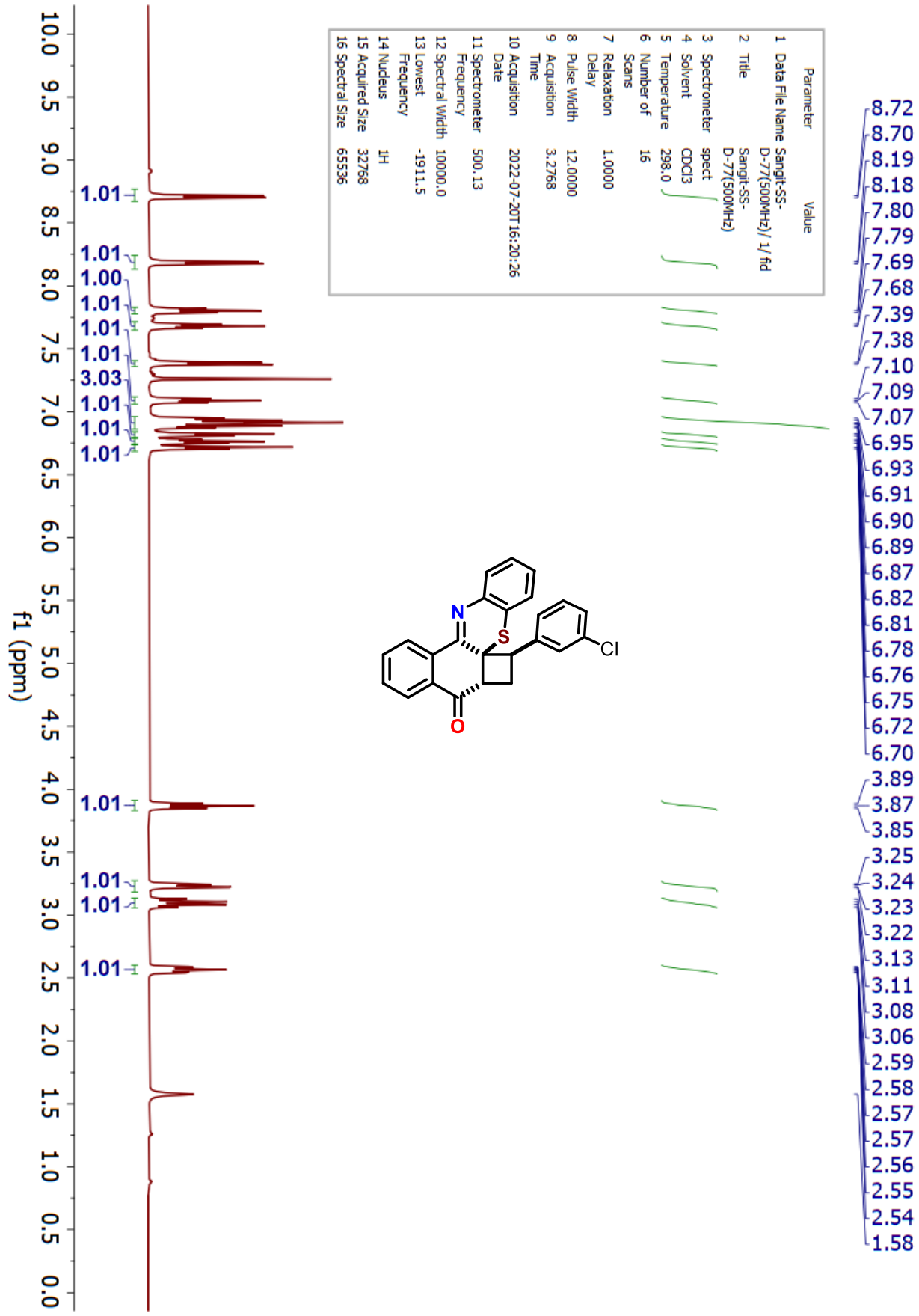
^{1}H NMR spectra of **2g**



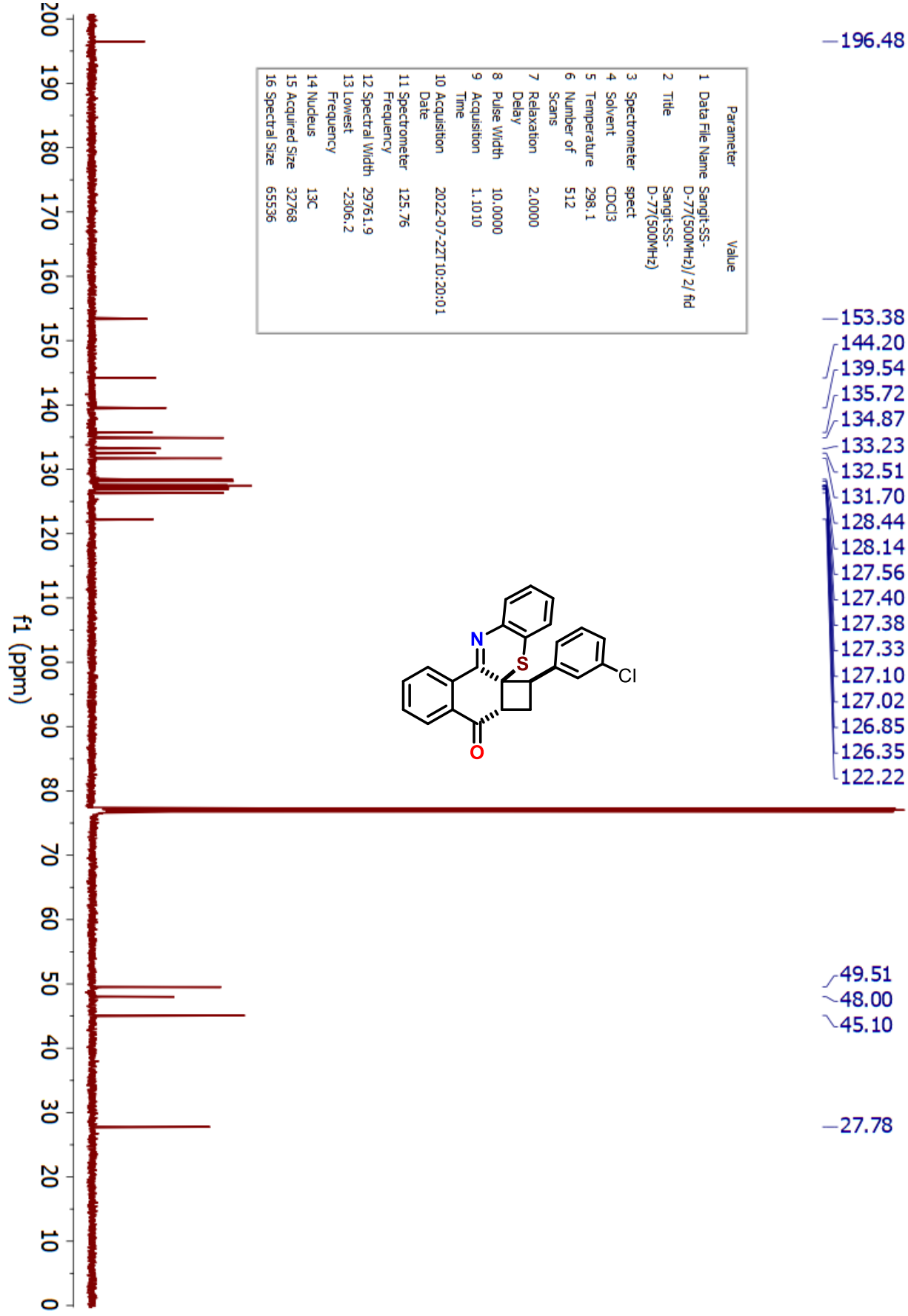
$^{13}C\{^{1}H\}$ NMR spectra of **2g**



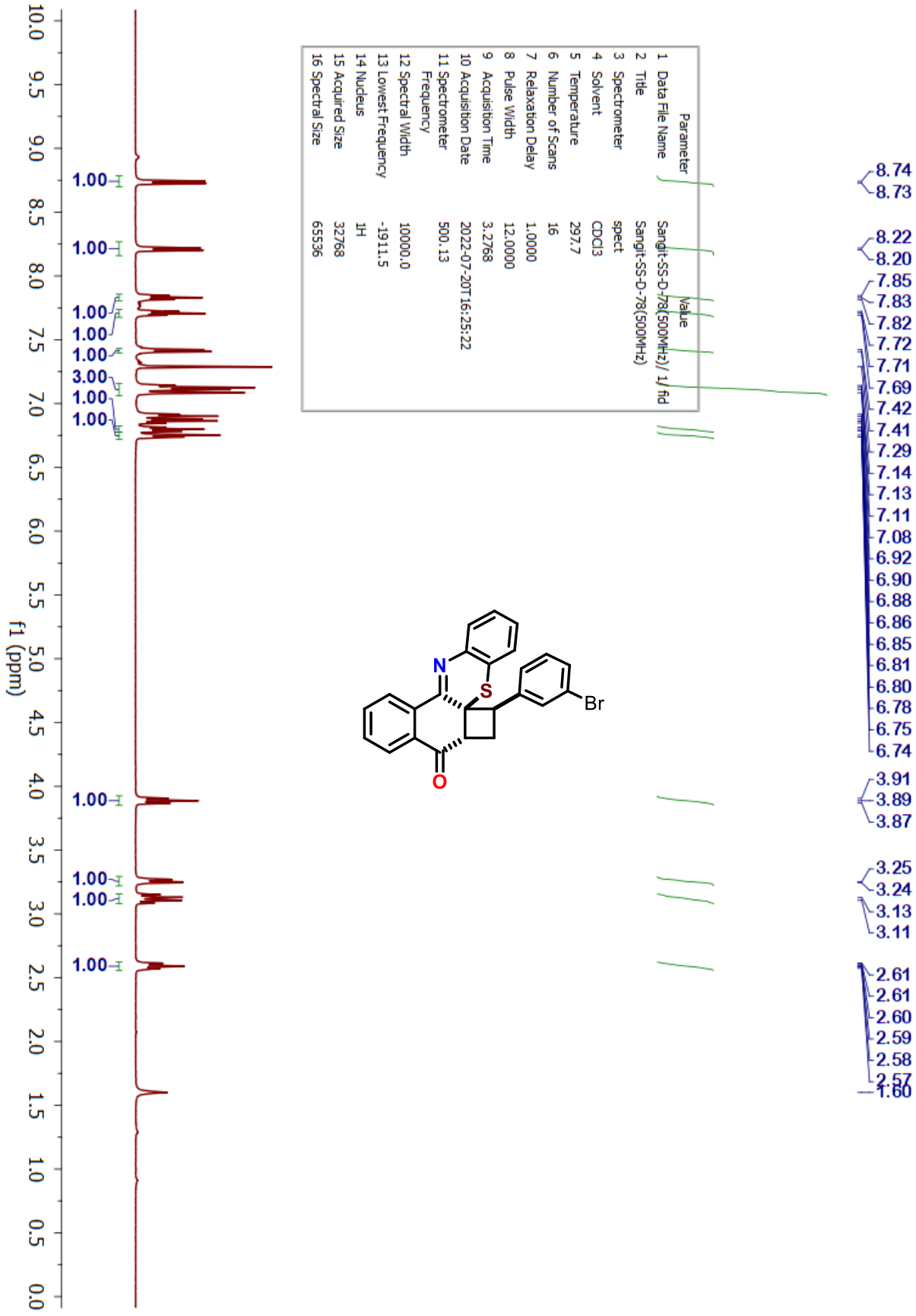
^{1}H NMR spectra of **2h**



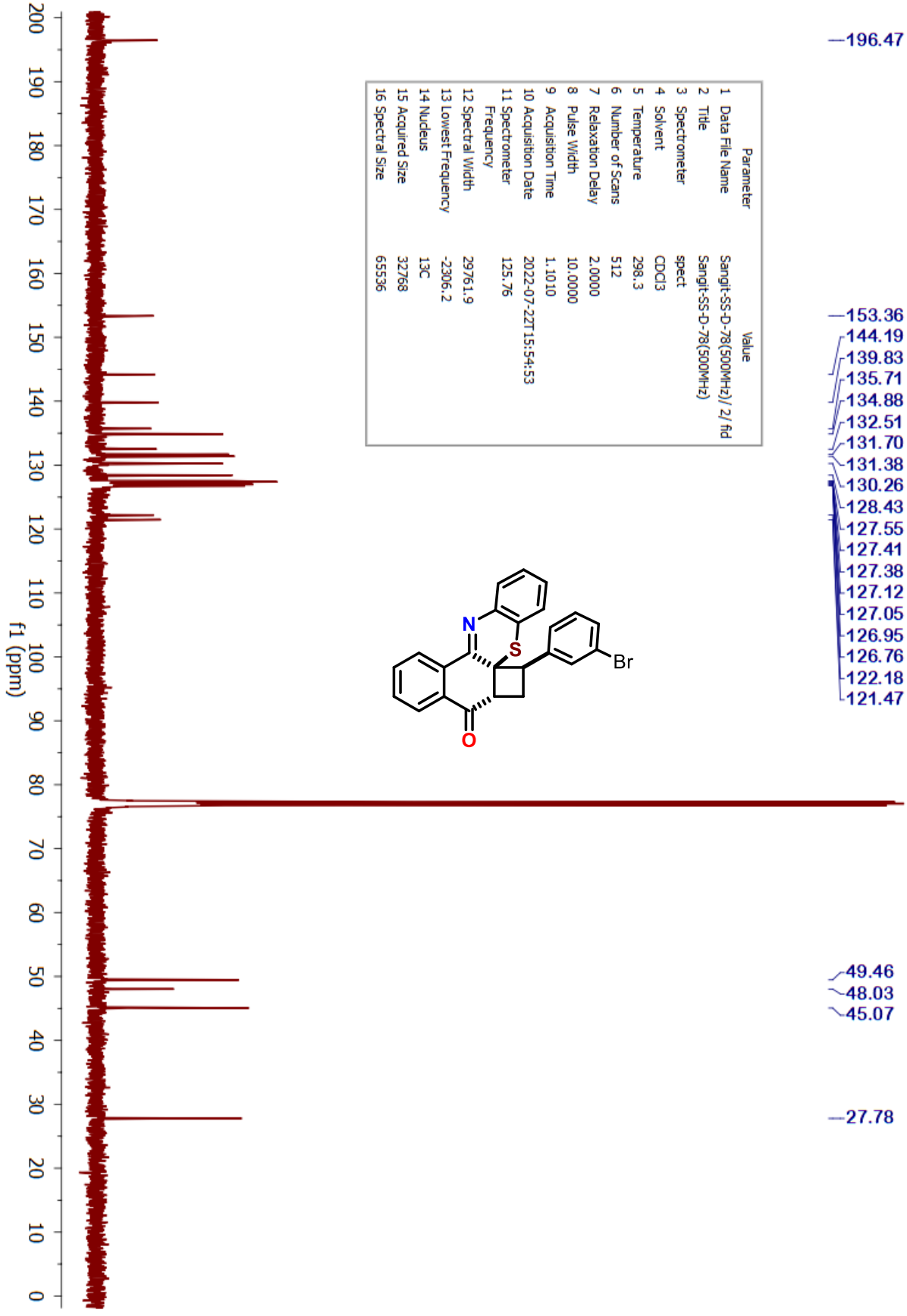
$^{13}C\{^{1}H\}$ NMR spectra of **2h**



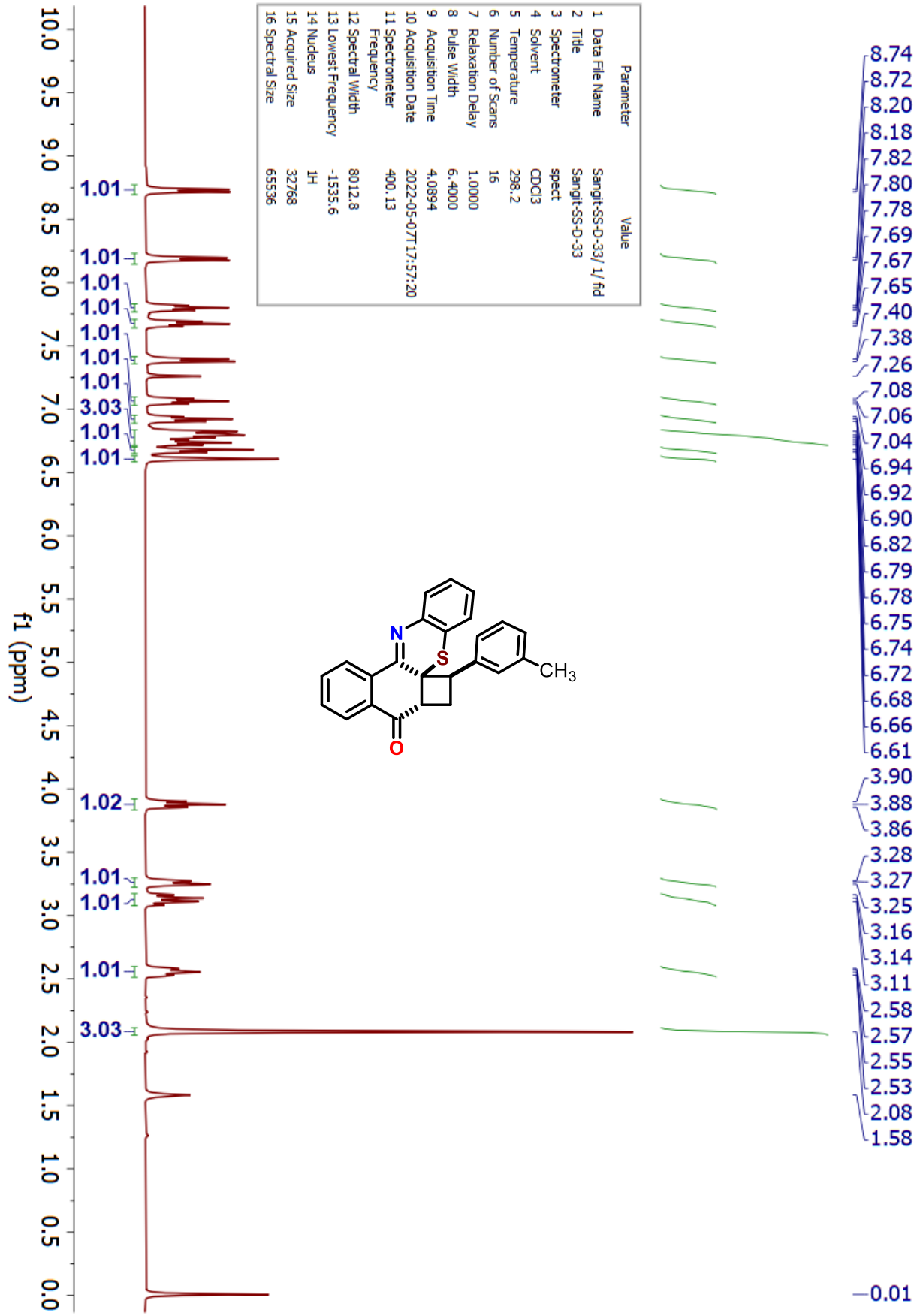
^{1}H NMR spectra of **2i**



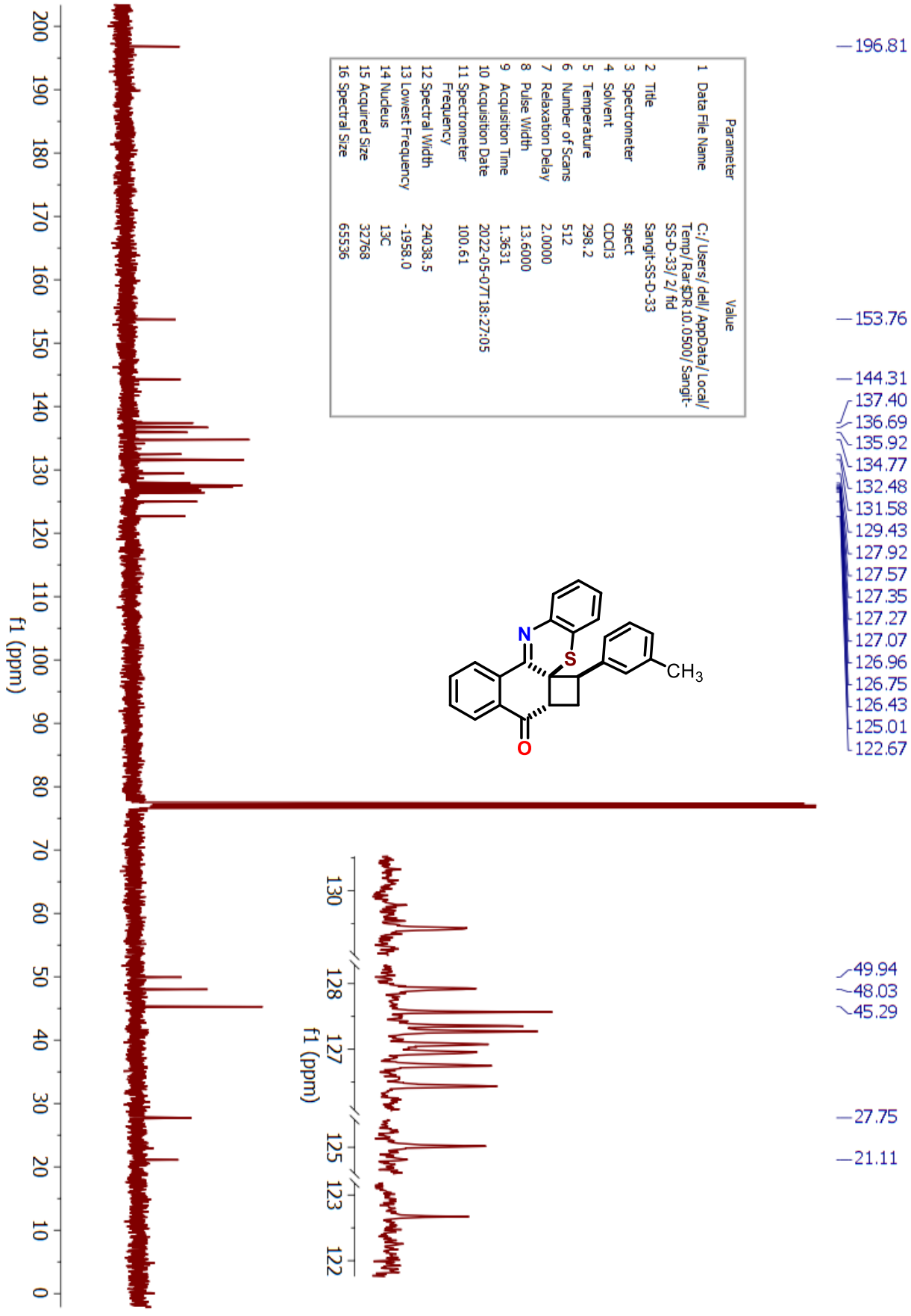
$^{13}C\{^{1}H\}$ NMR spectra of **2i**



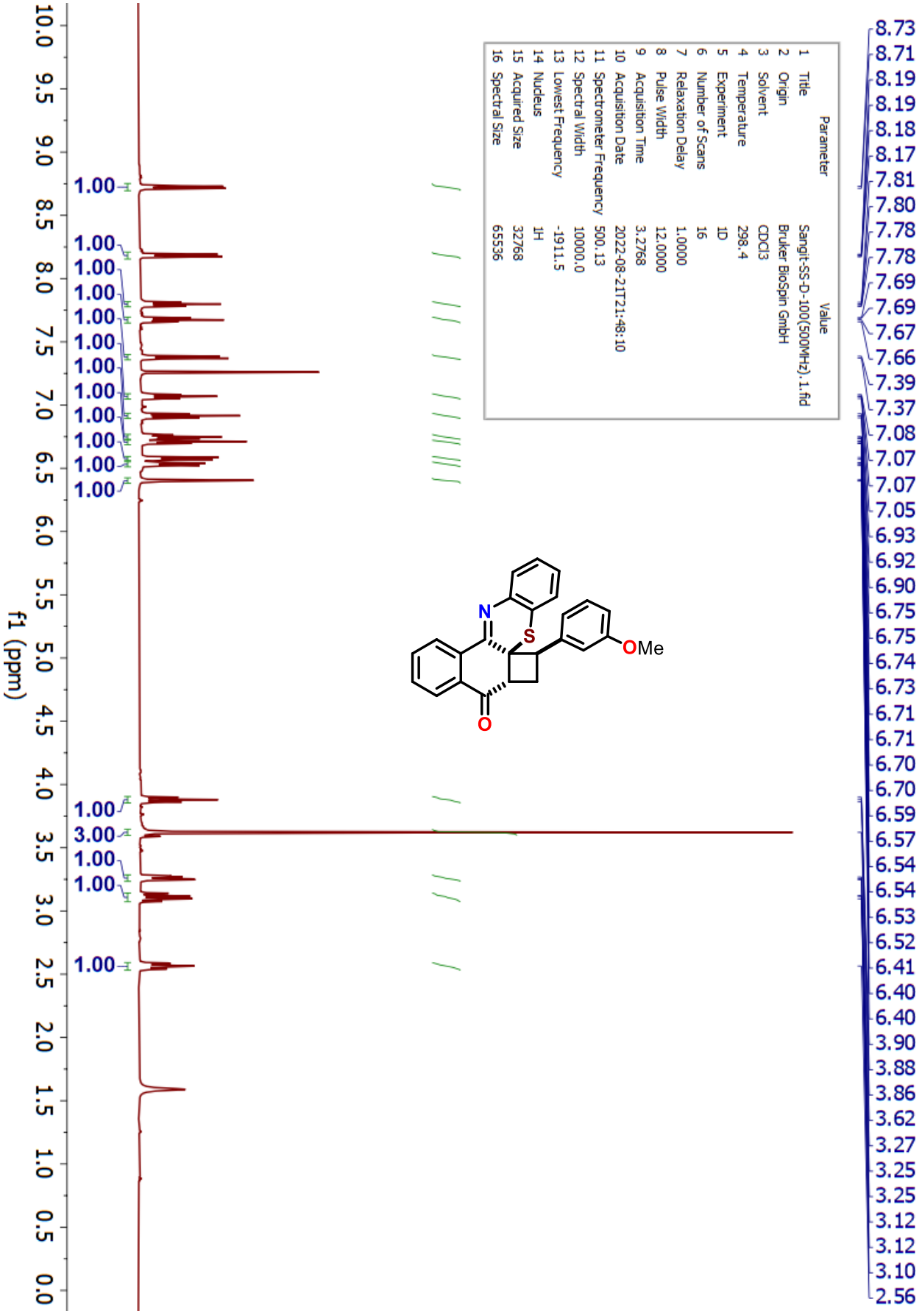
^{1}H NMR spectra of **2j**



$^{13}C\{^{1}H\}$ NMR spectra of **2j**



^{1}H NMR spectra of **2k**



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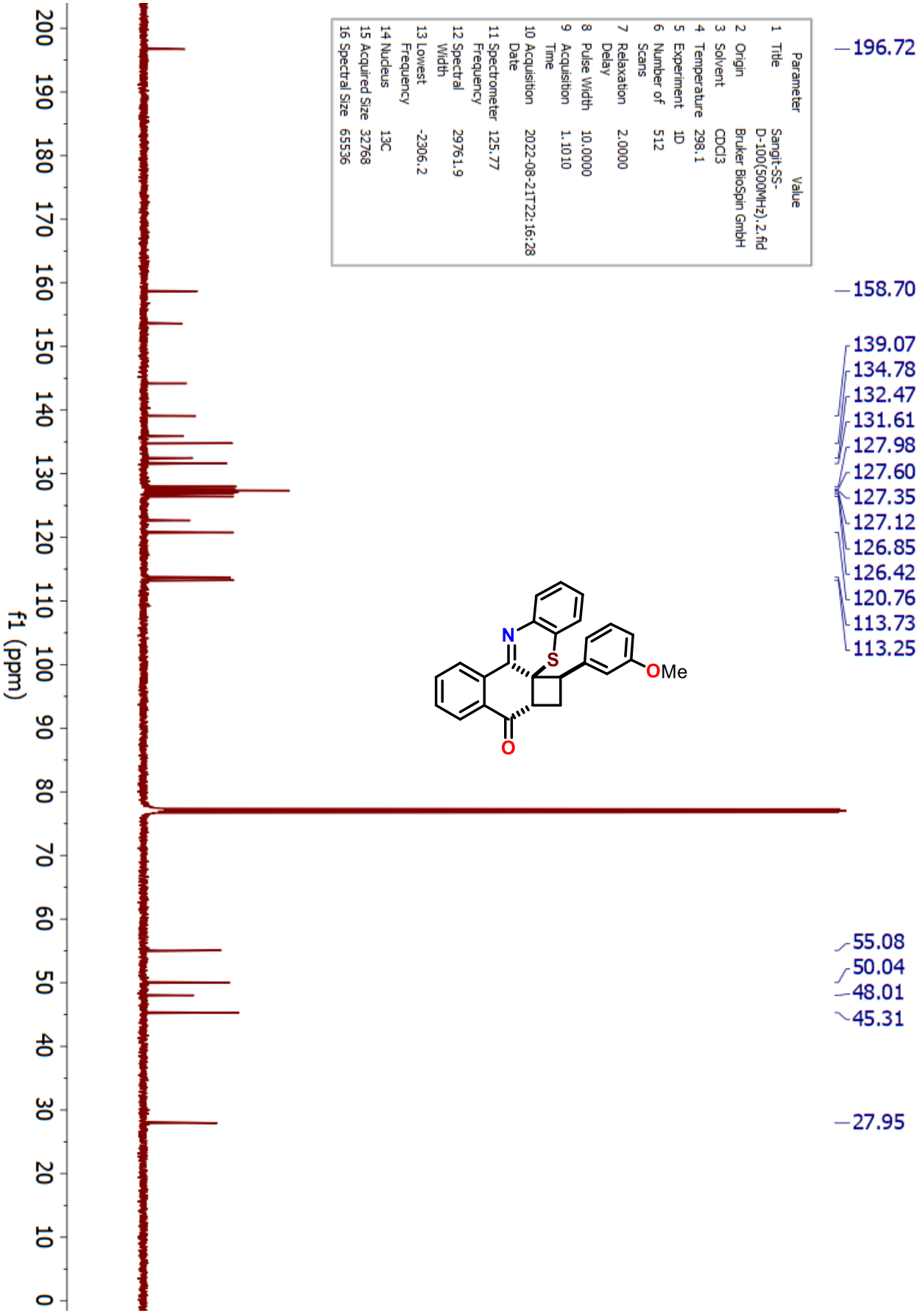
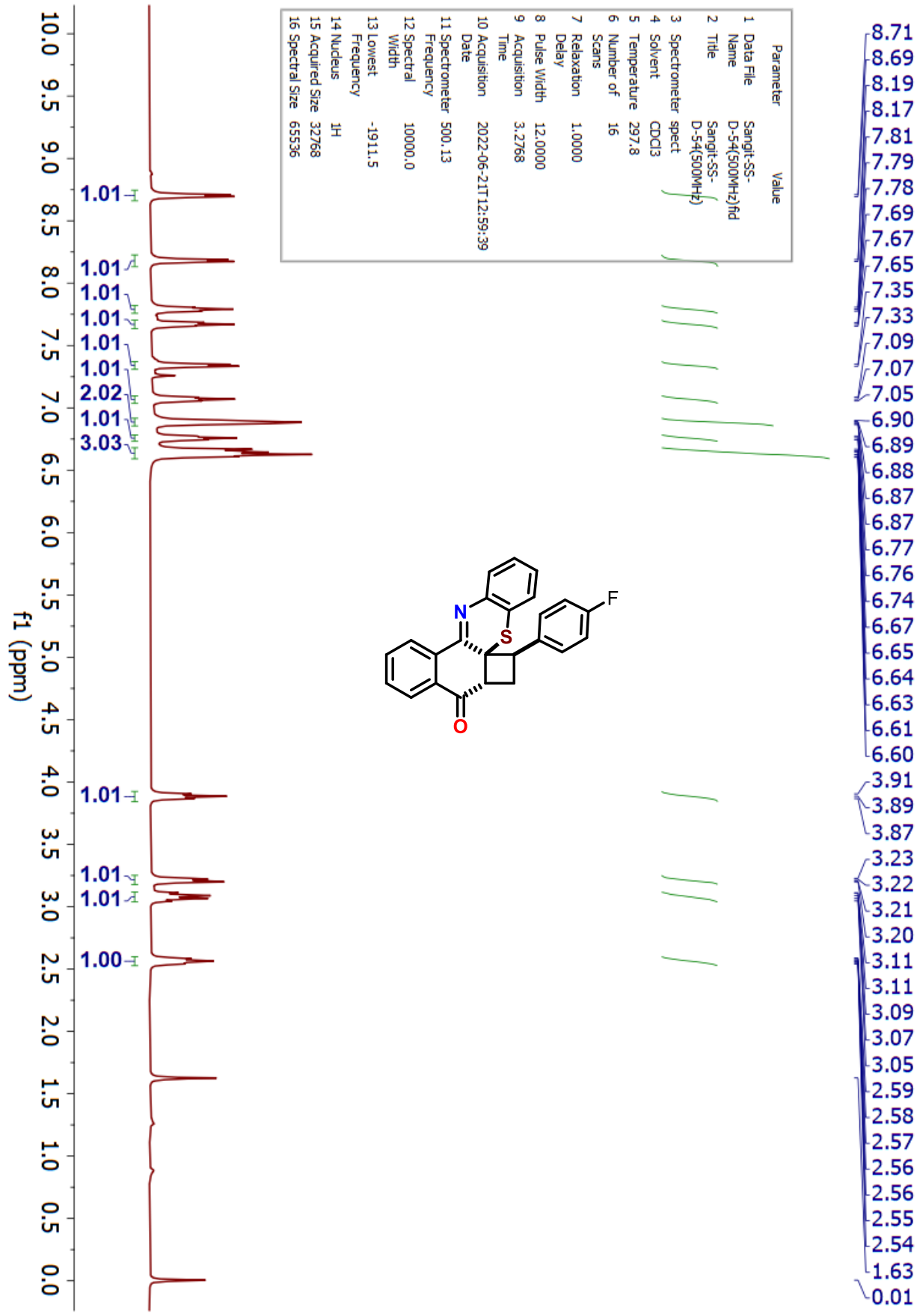
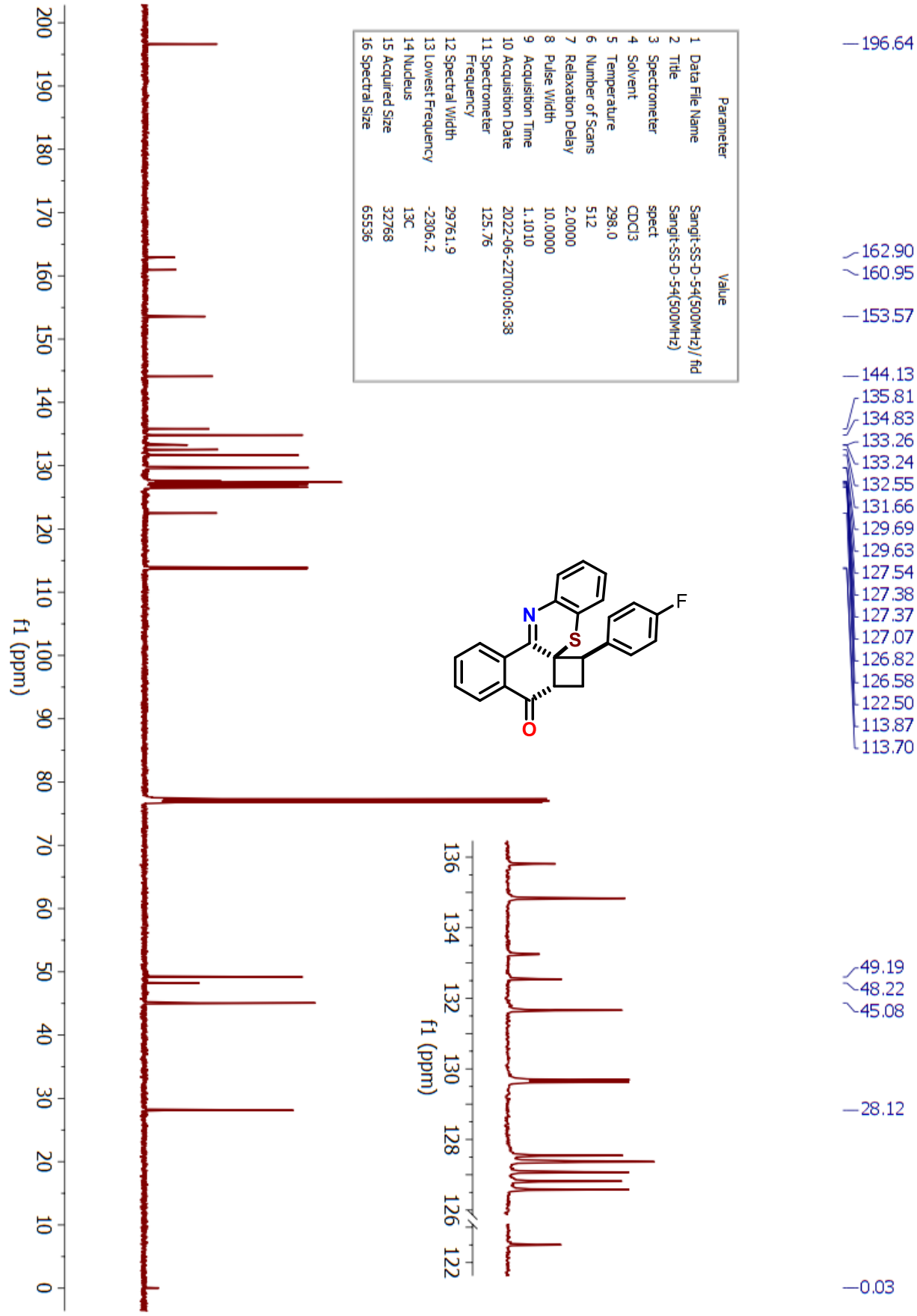


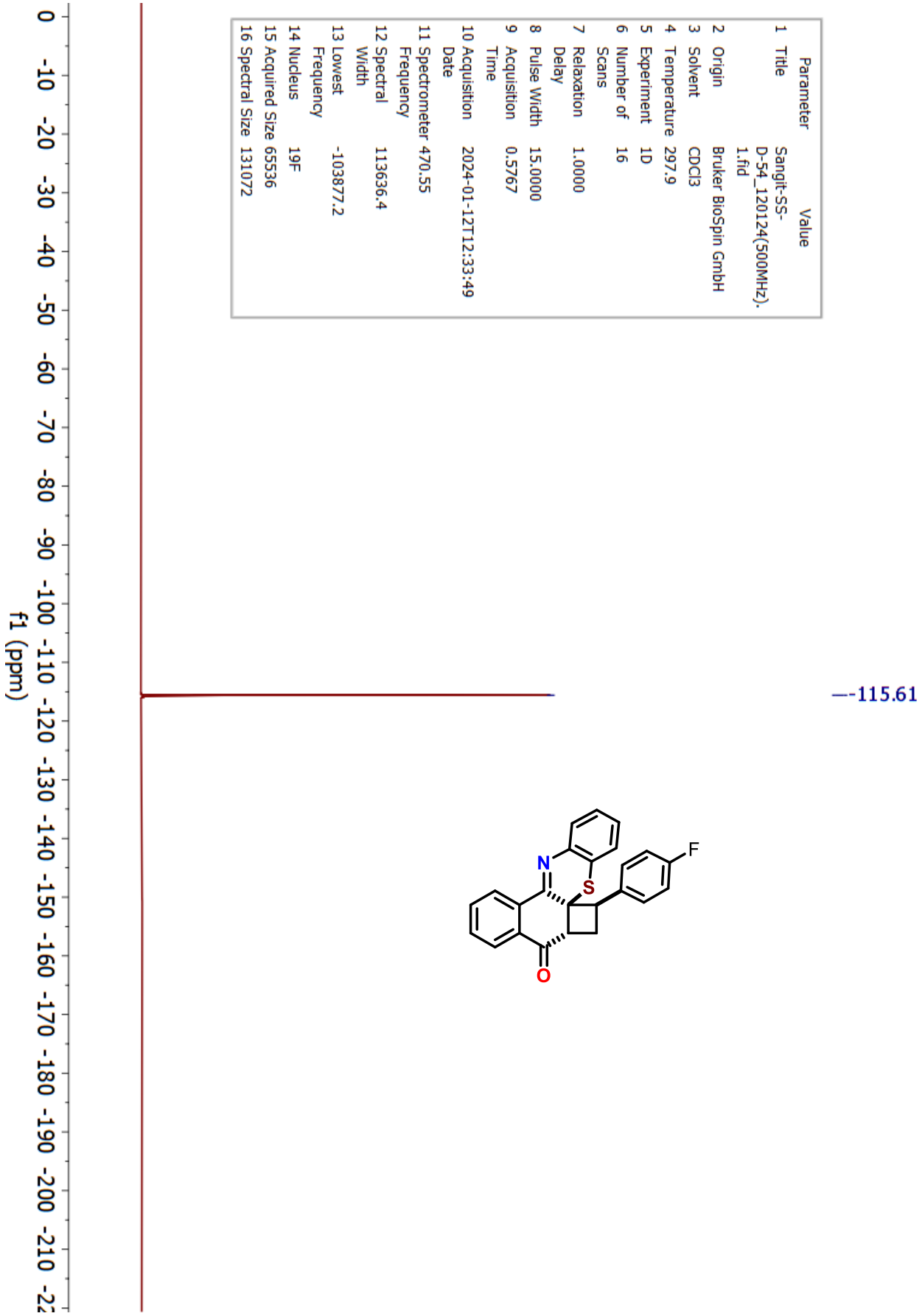
^{1}H NMR spectra of **2l**



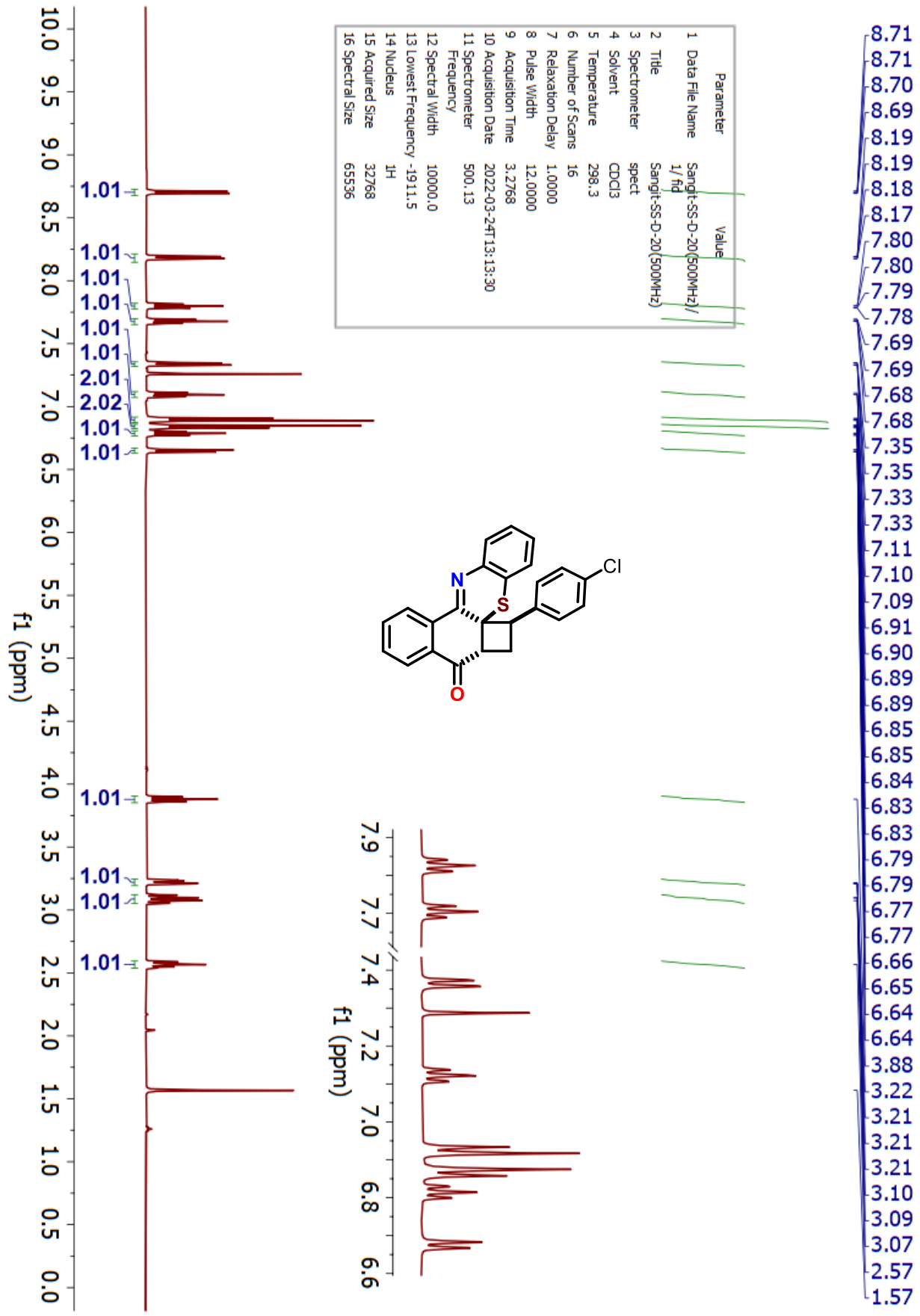
$^{13}C\{^{1}H\}$ NMR spectra of **2l**



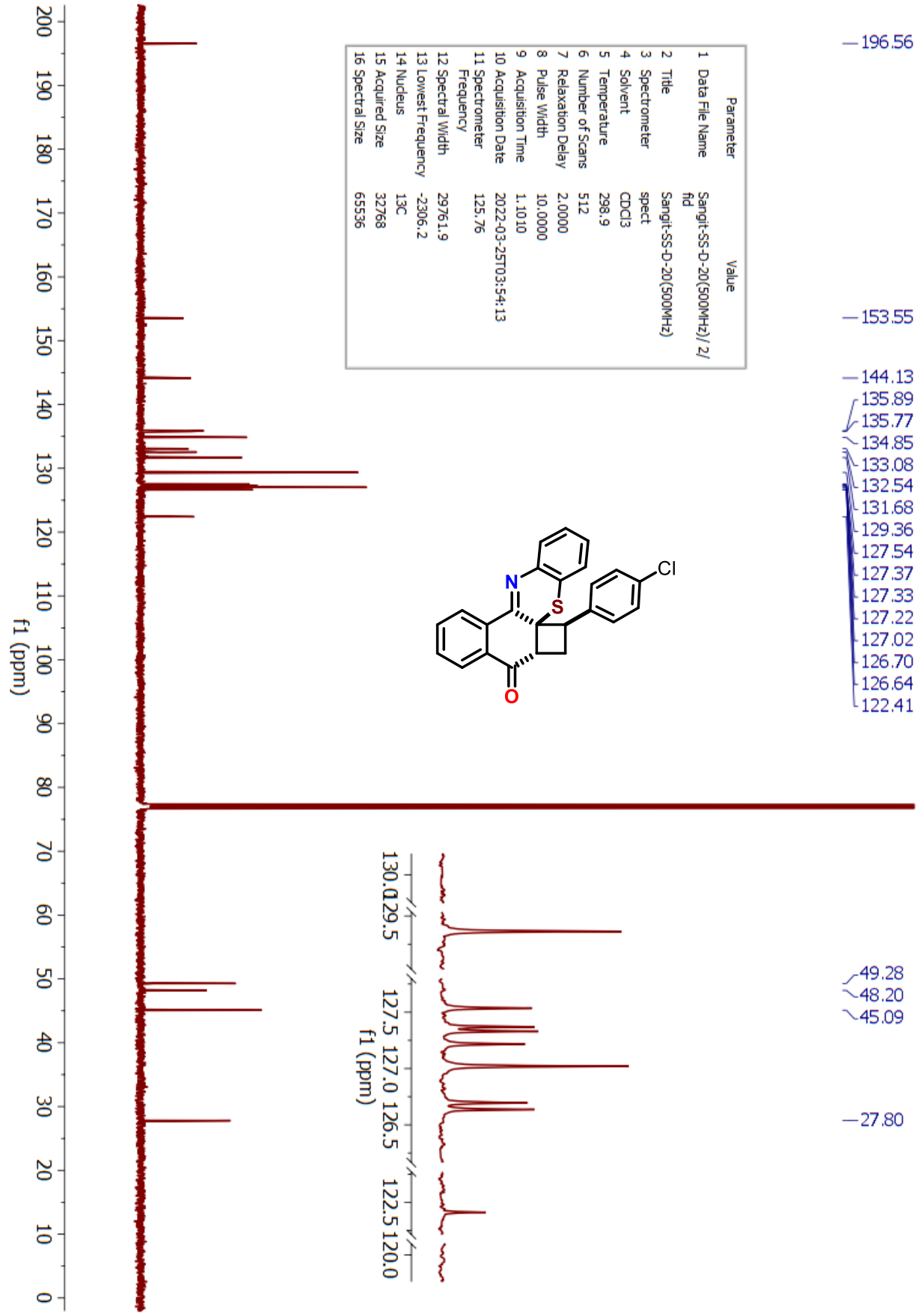
$^{19}F\{^{1}H\}$ NMR spectra of **2l**



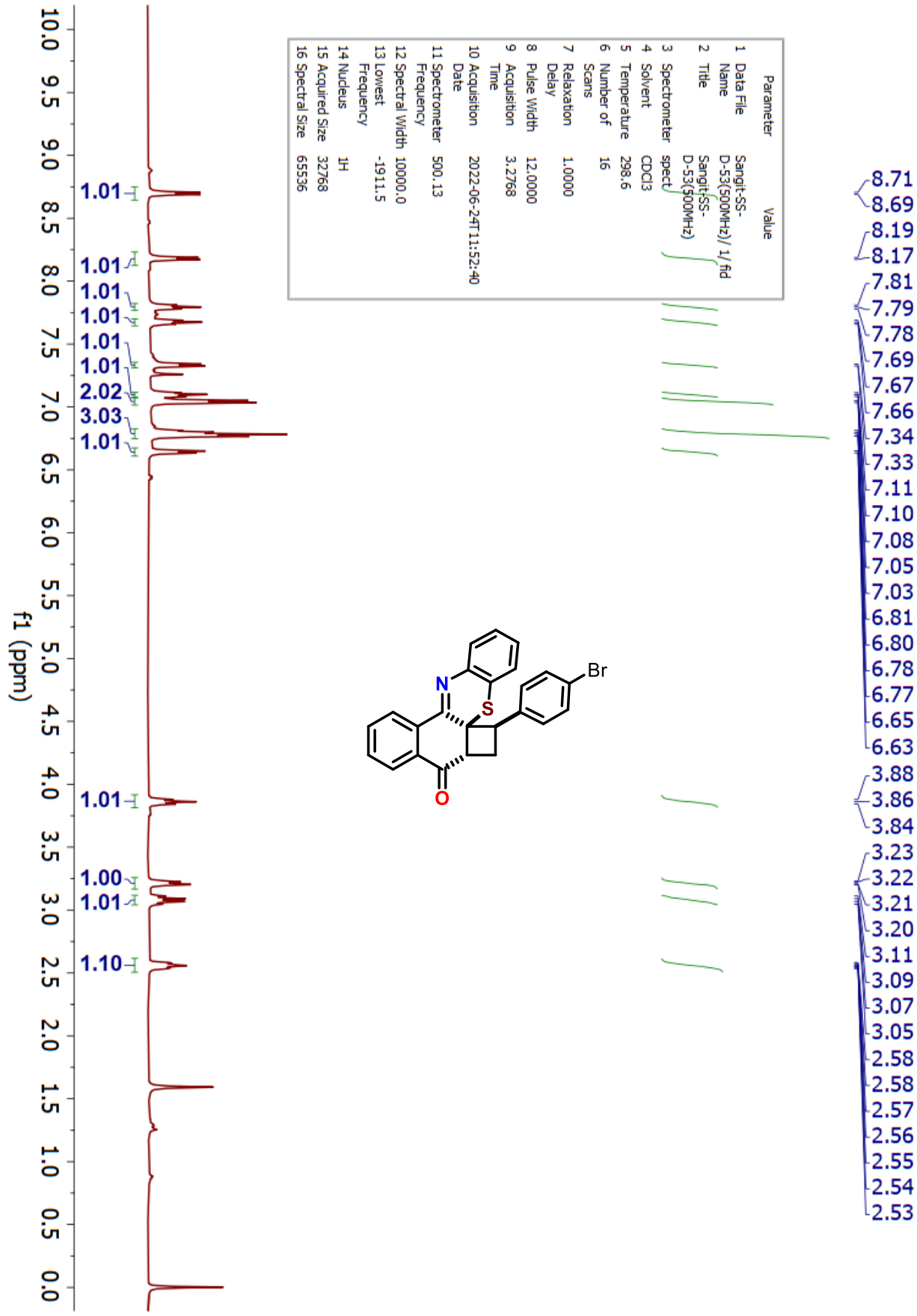
^{1}H NMR spectra of **2m**



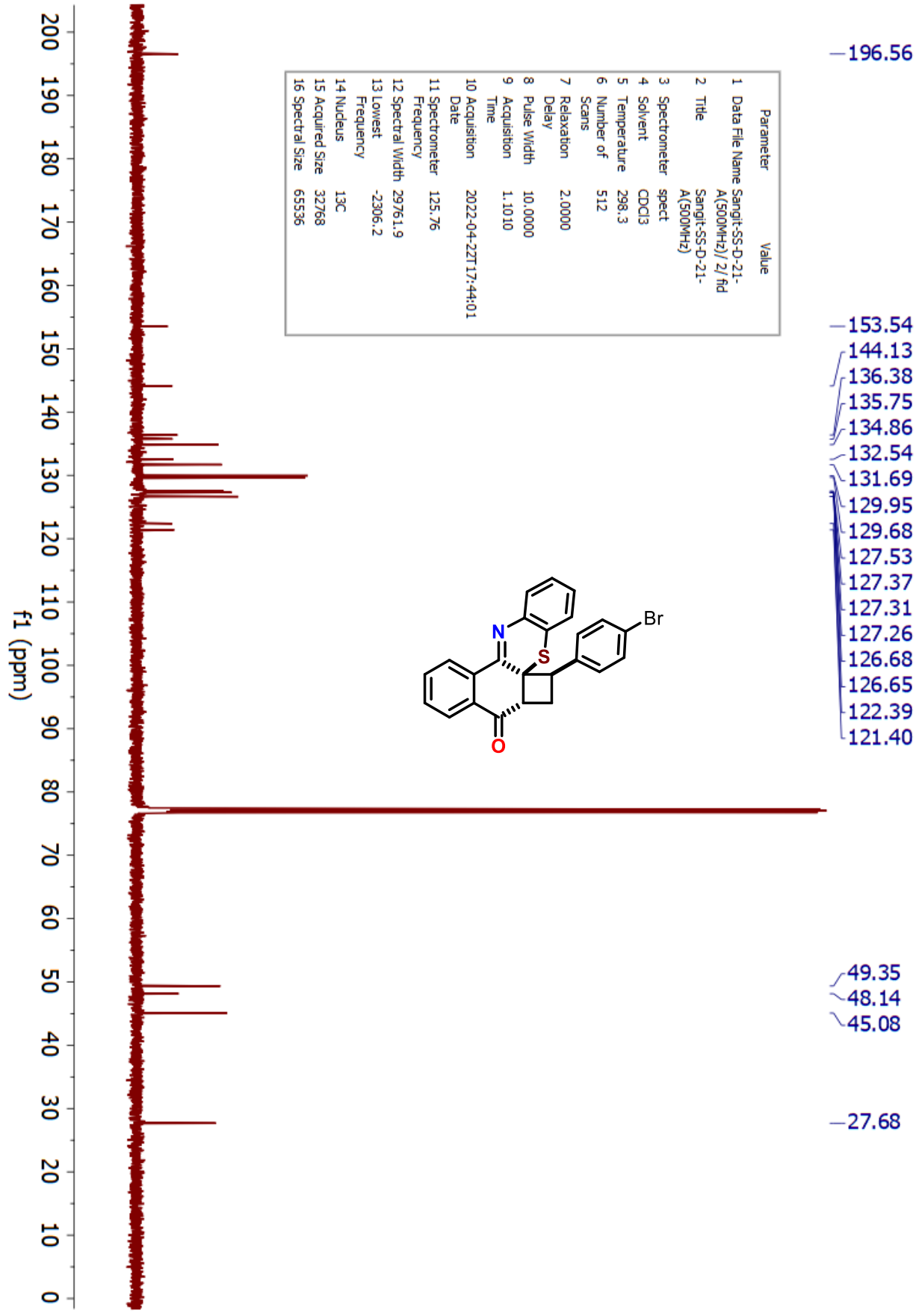
$^{13}C\{^{1}H\}$ NMR spectra of **2m**



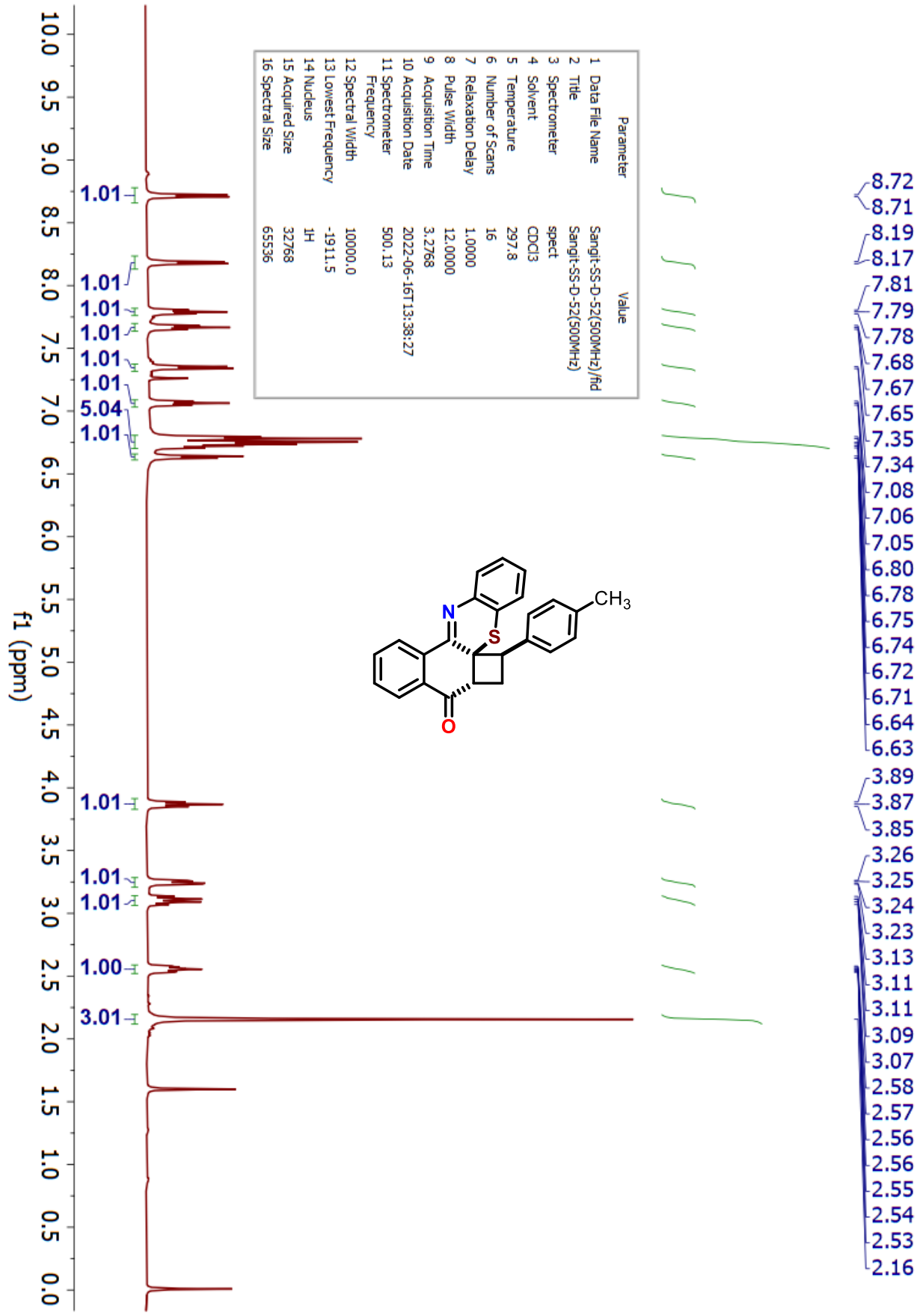
^{1}H NMR spectra of **2n**



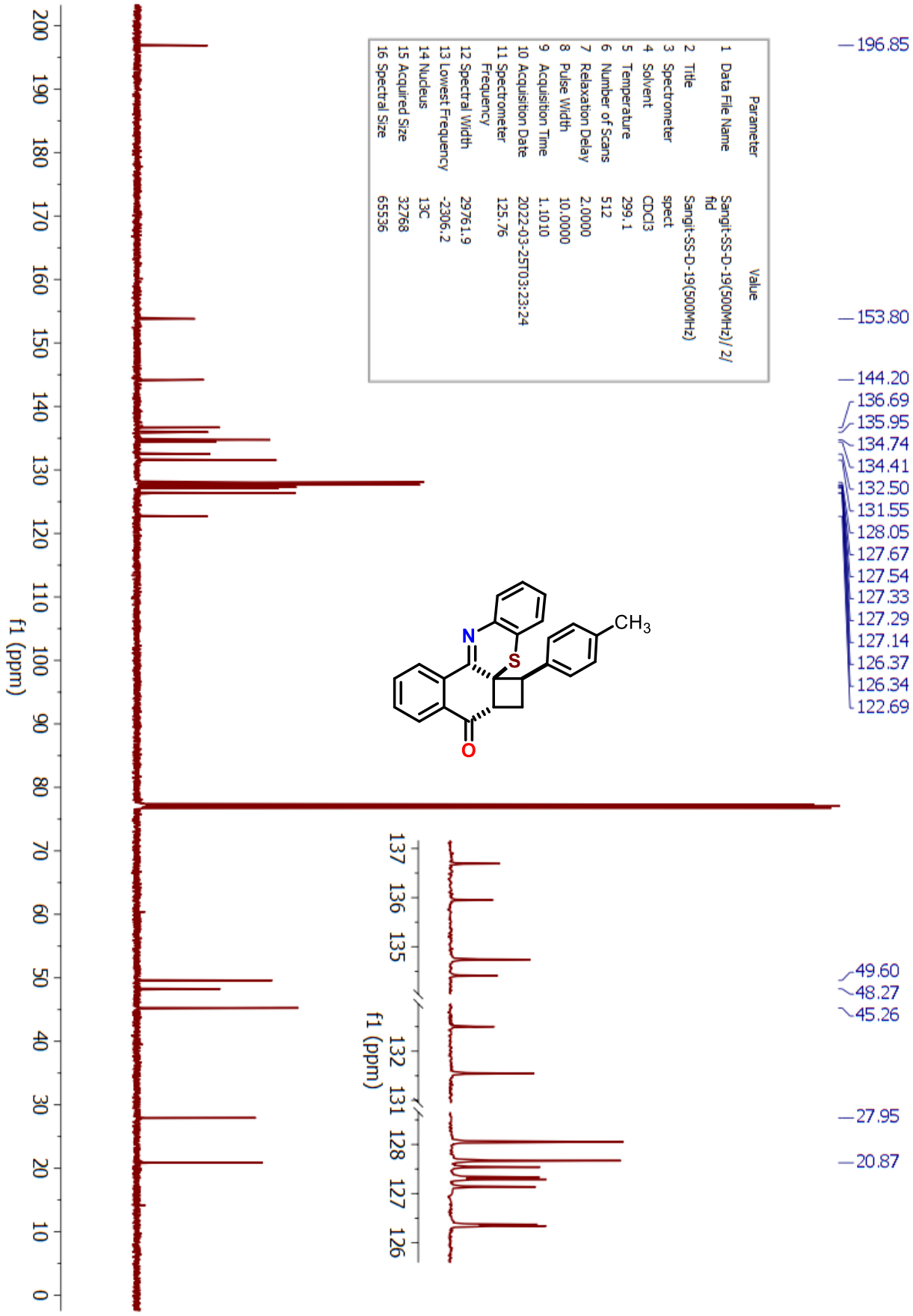
$^{13}C\{^{1}H\}$ NMR spectra of **2n**



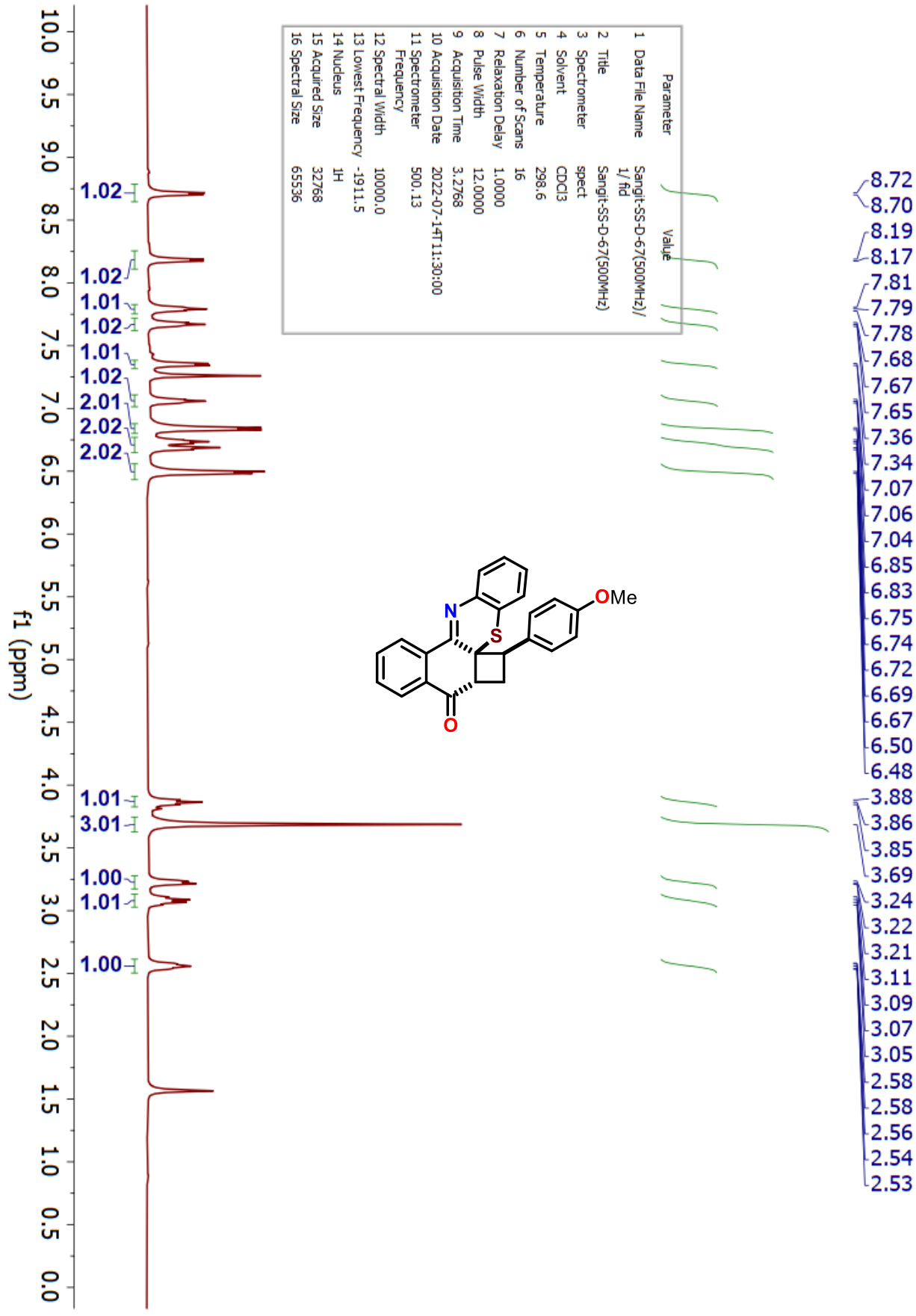
^{1}H NMR spectra of **2o**



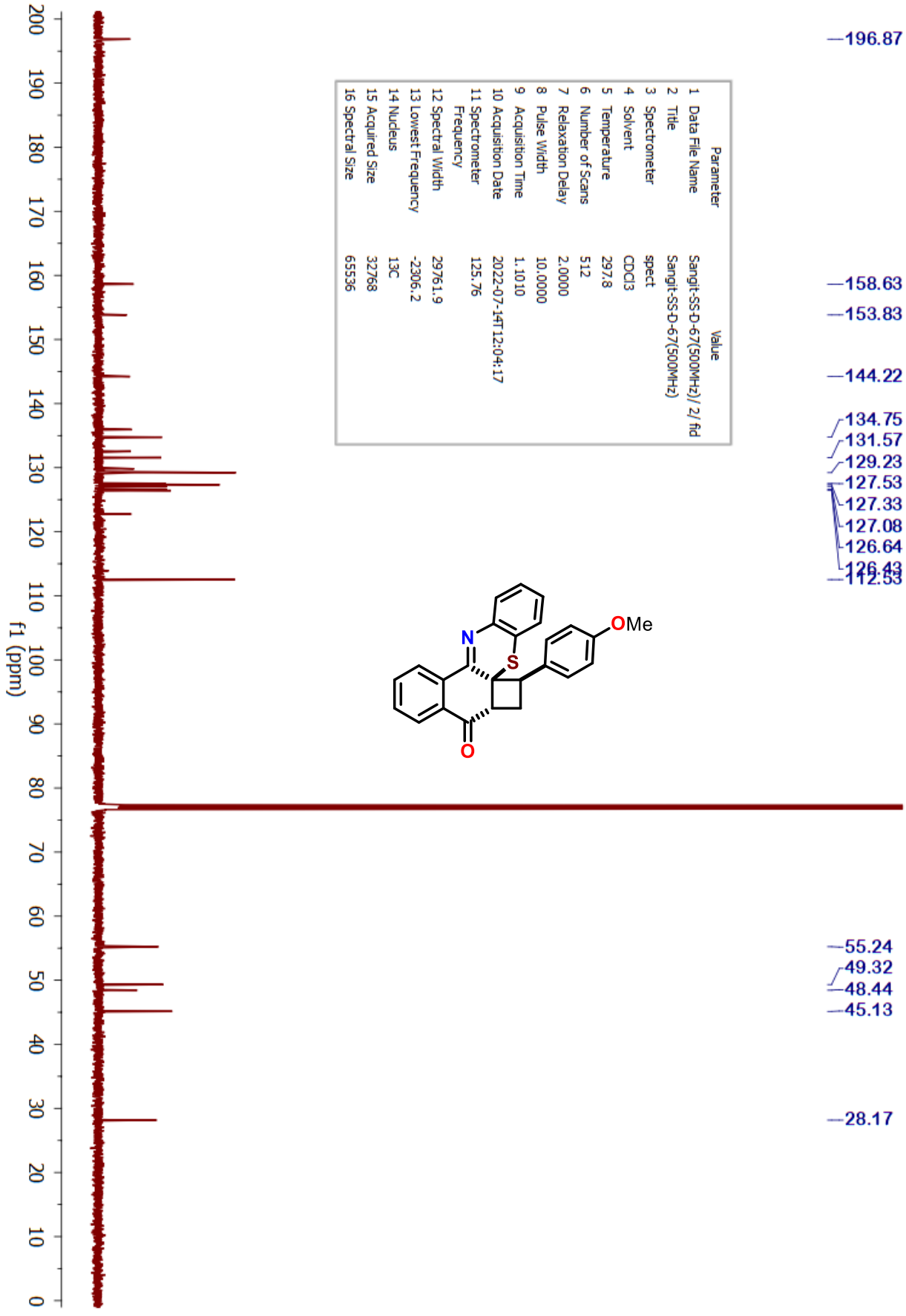
$^{13}C\{^{1}H\}$ NMR spectra of **2o**



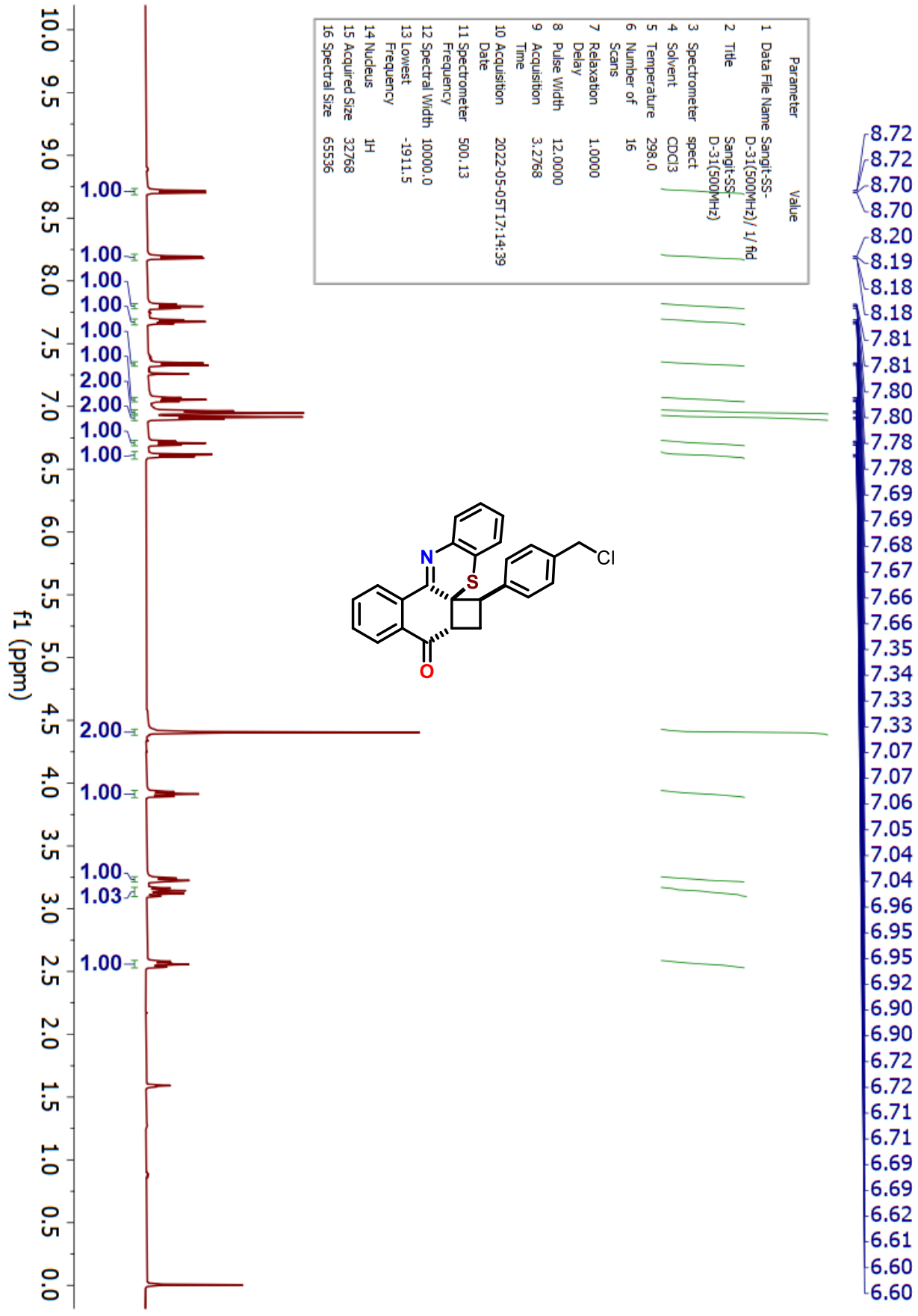
^{1}H NMR spectra of **2p**



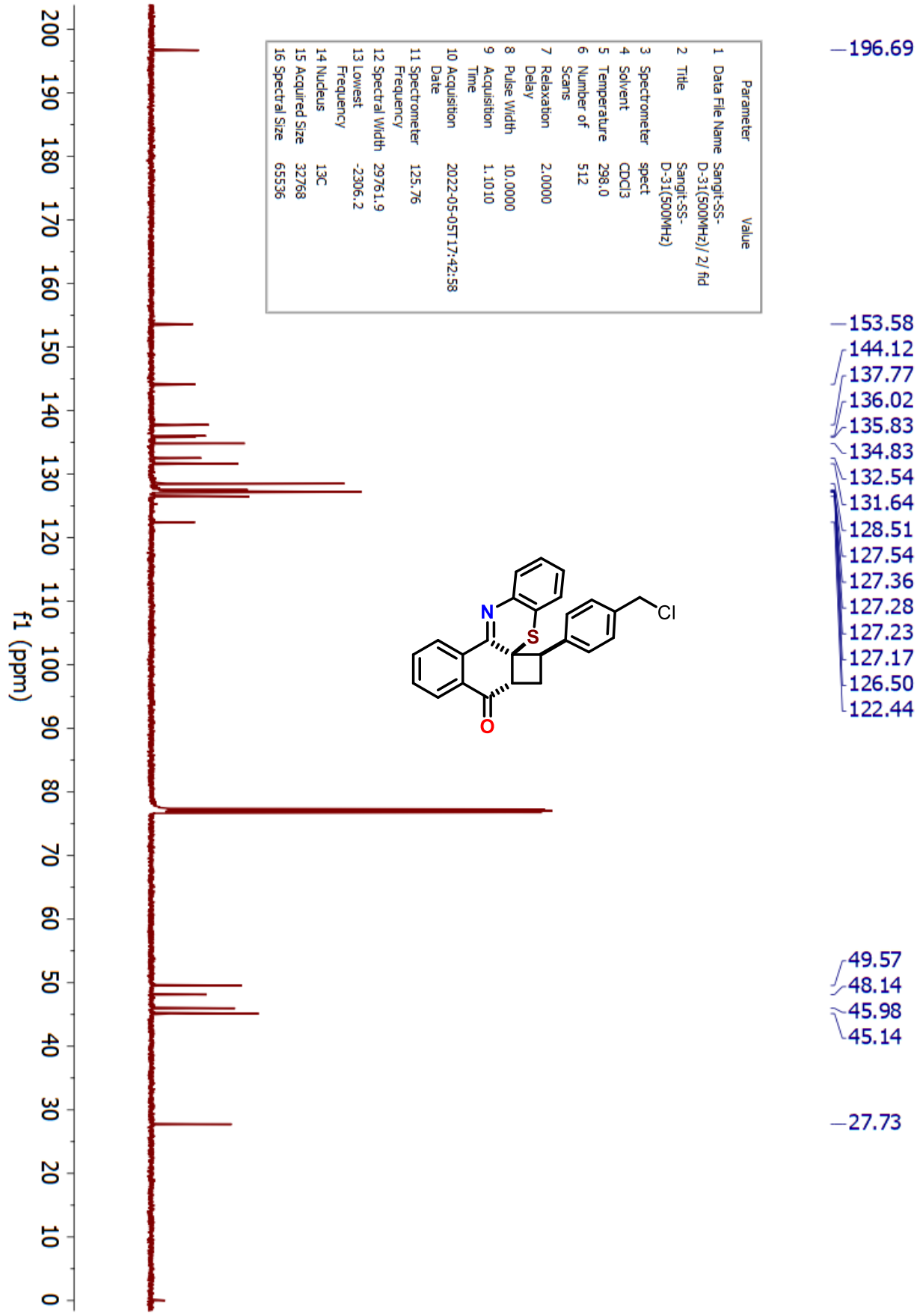
$^{13}C\{^{1}H\}$ NMR spectra of **2p**



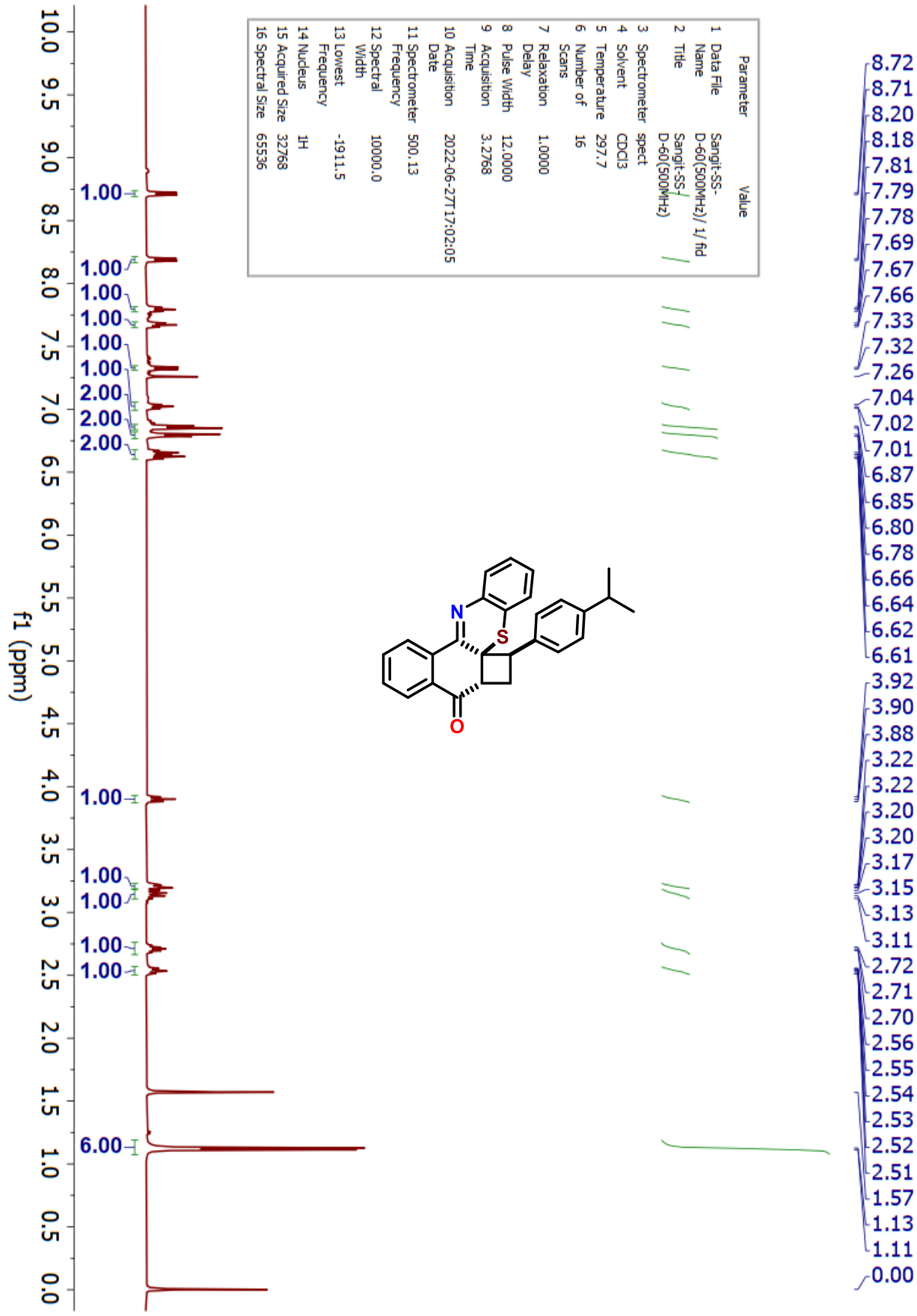
^{1}H NMR spectra of **2q**



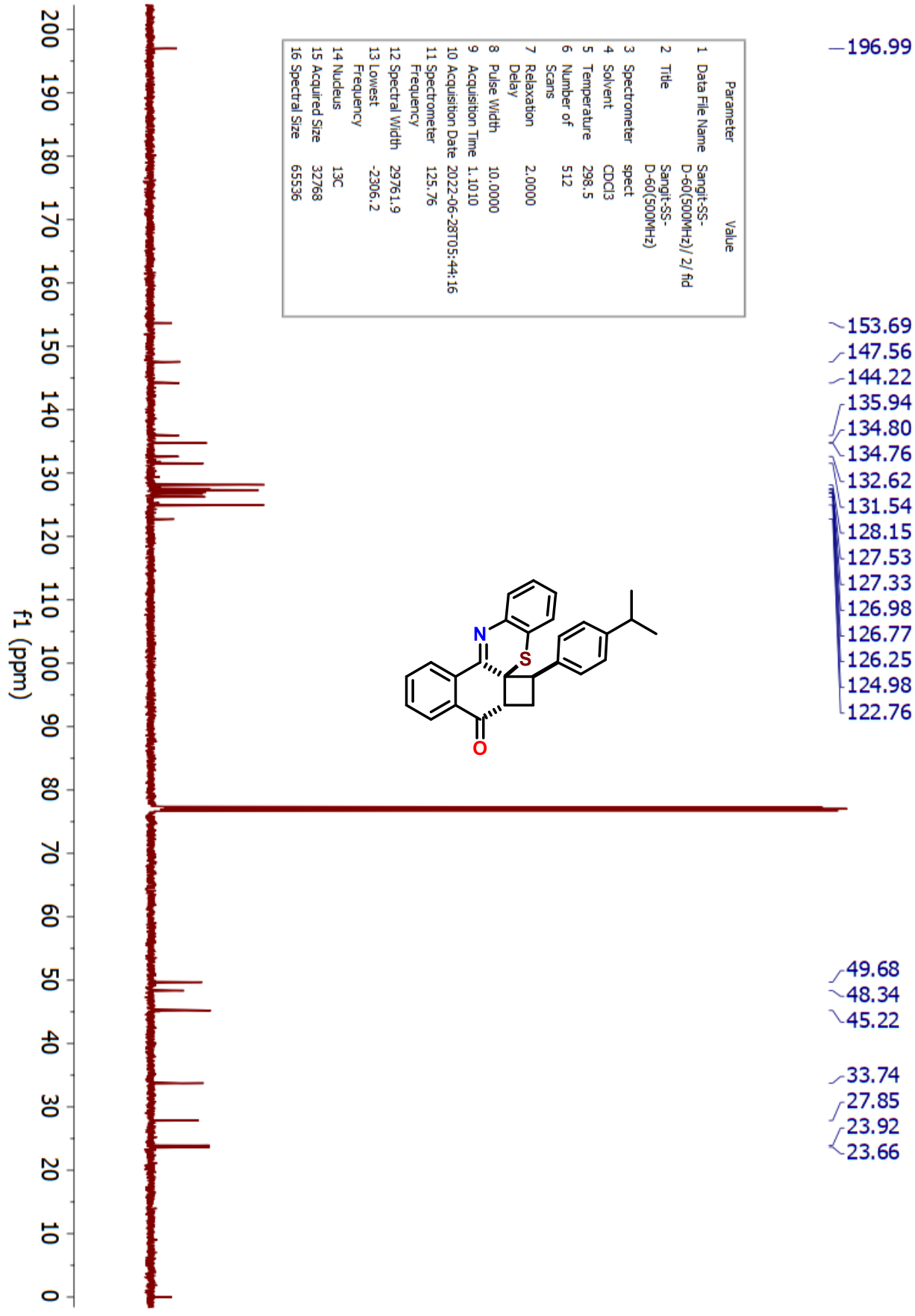
$^{13}C\{^{1}H\}$ NMR spectra of **2q**



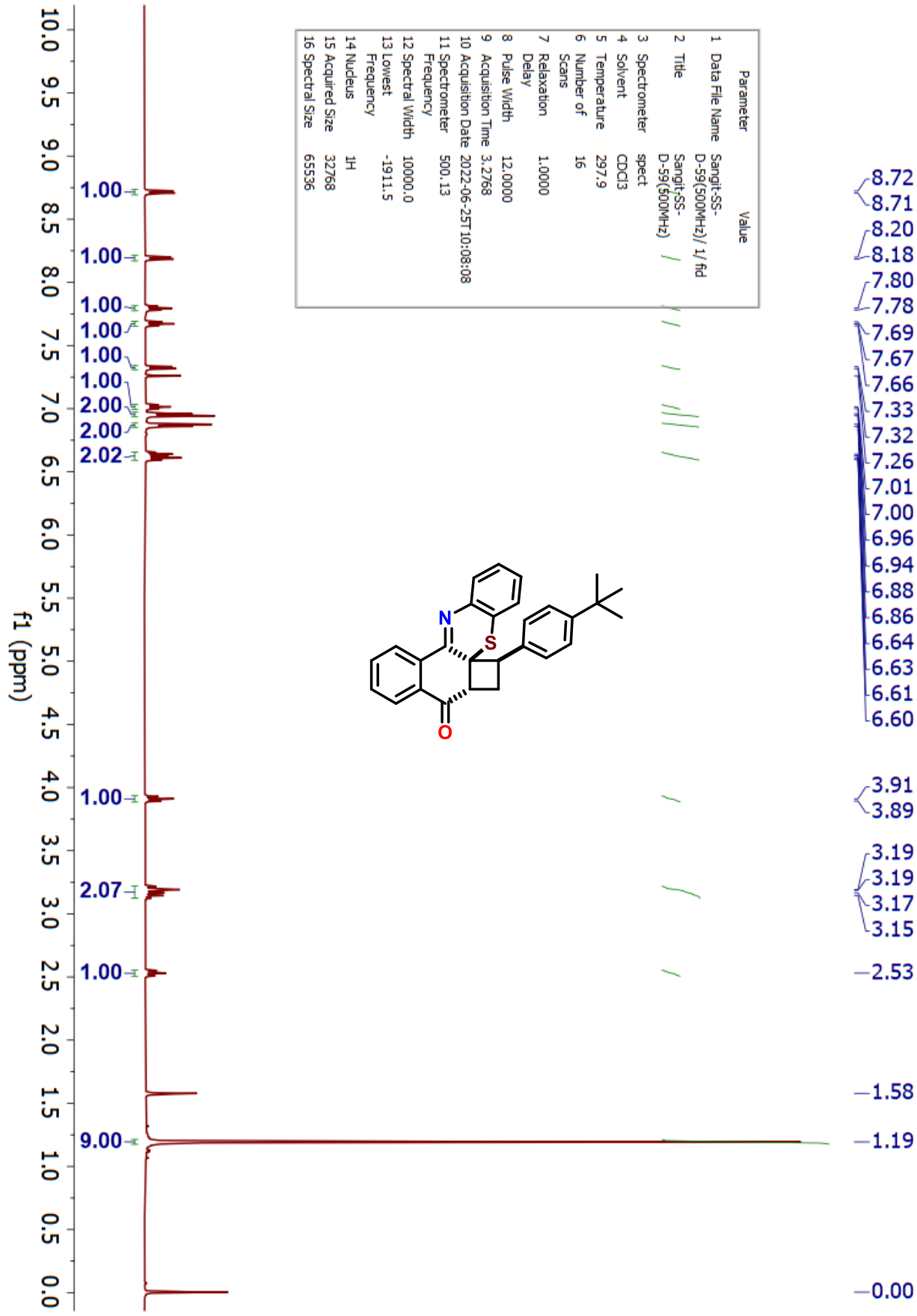
^{1}H NMR spectra of **2r**



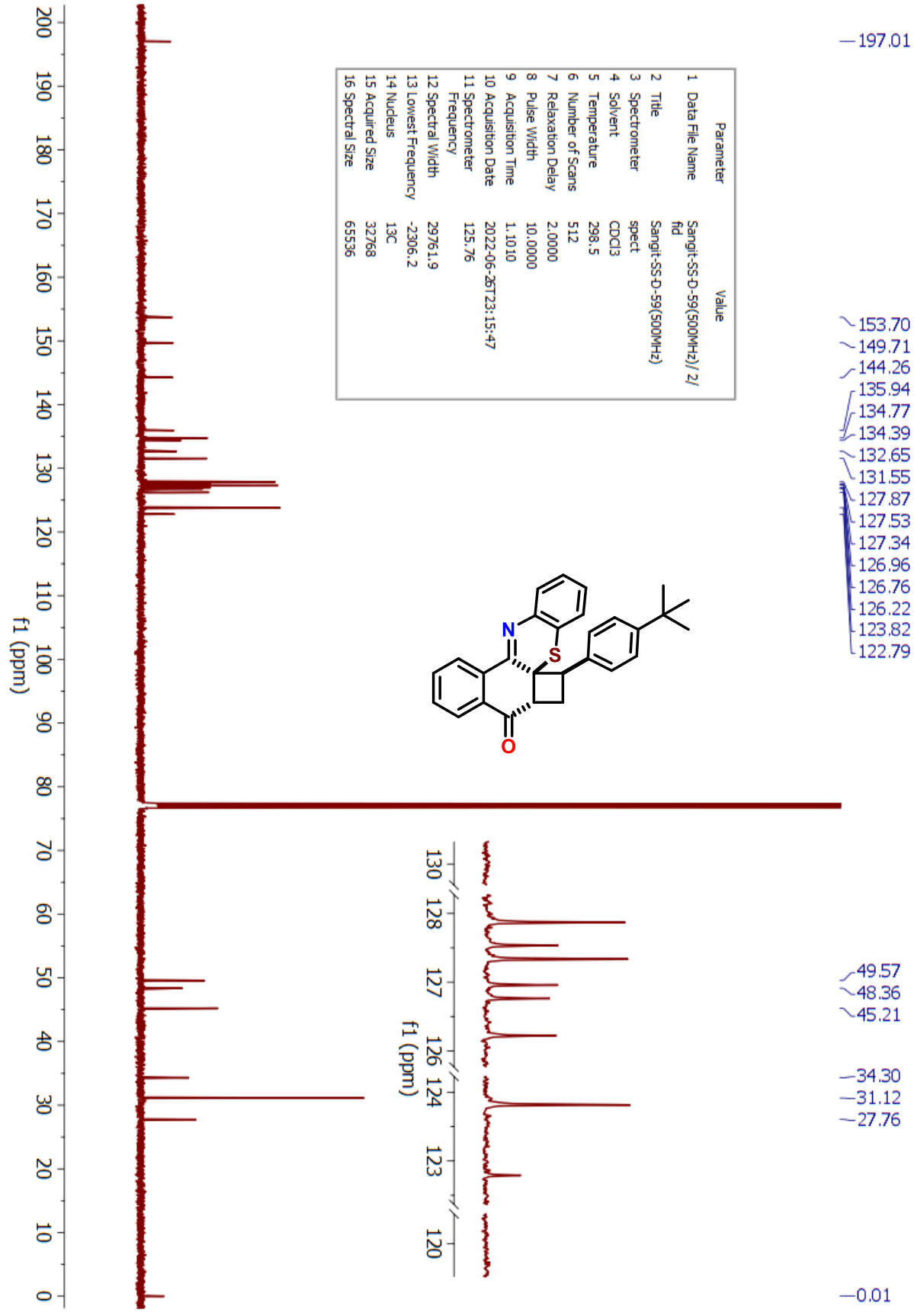
$^{13}C\{^{1}H\}$ NMR spectra of **2r**



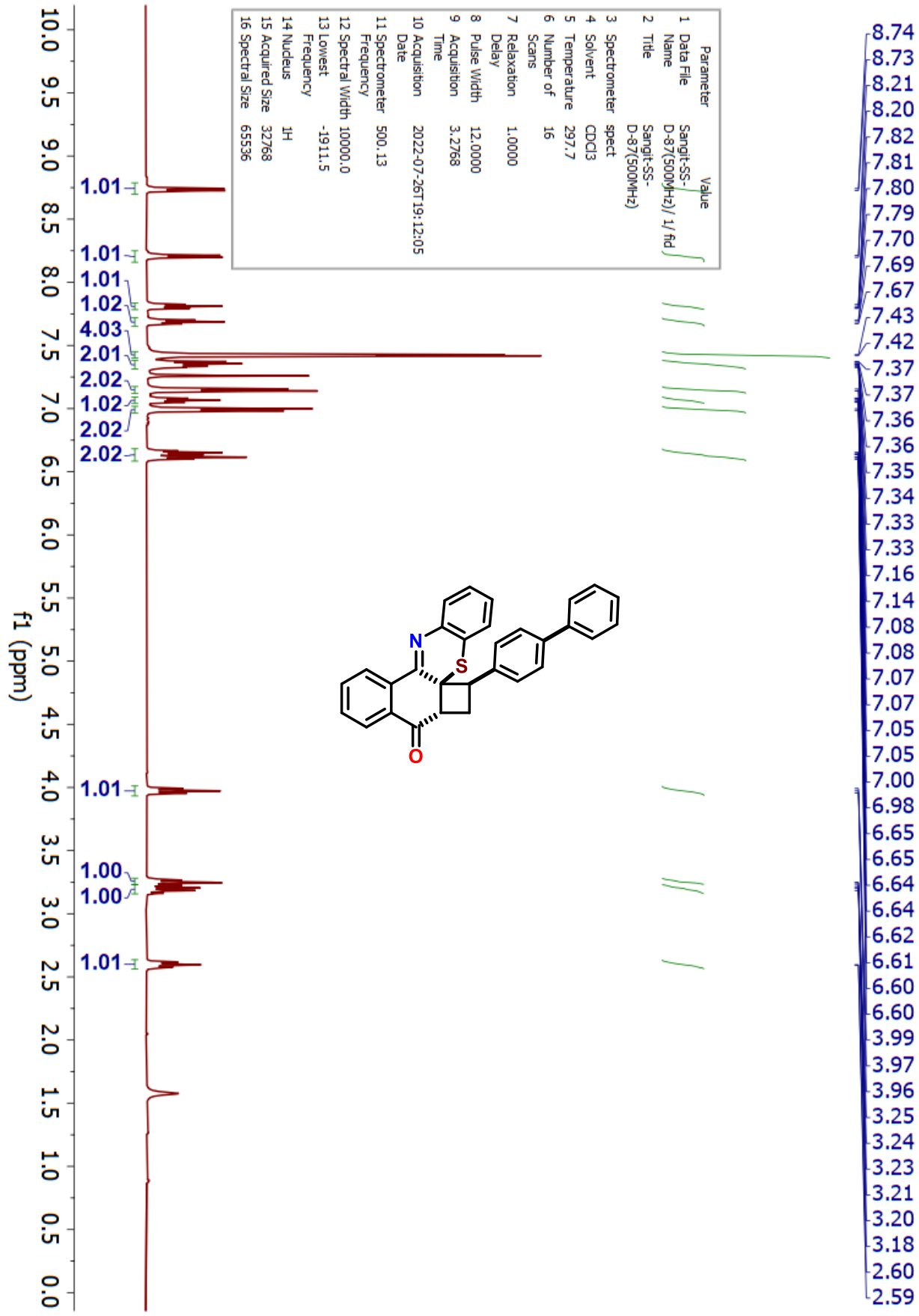
^{1}H NMR spectra of **2s**



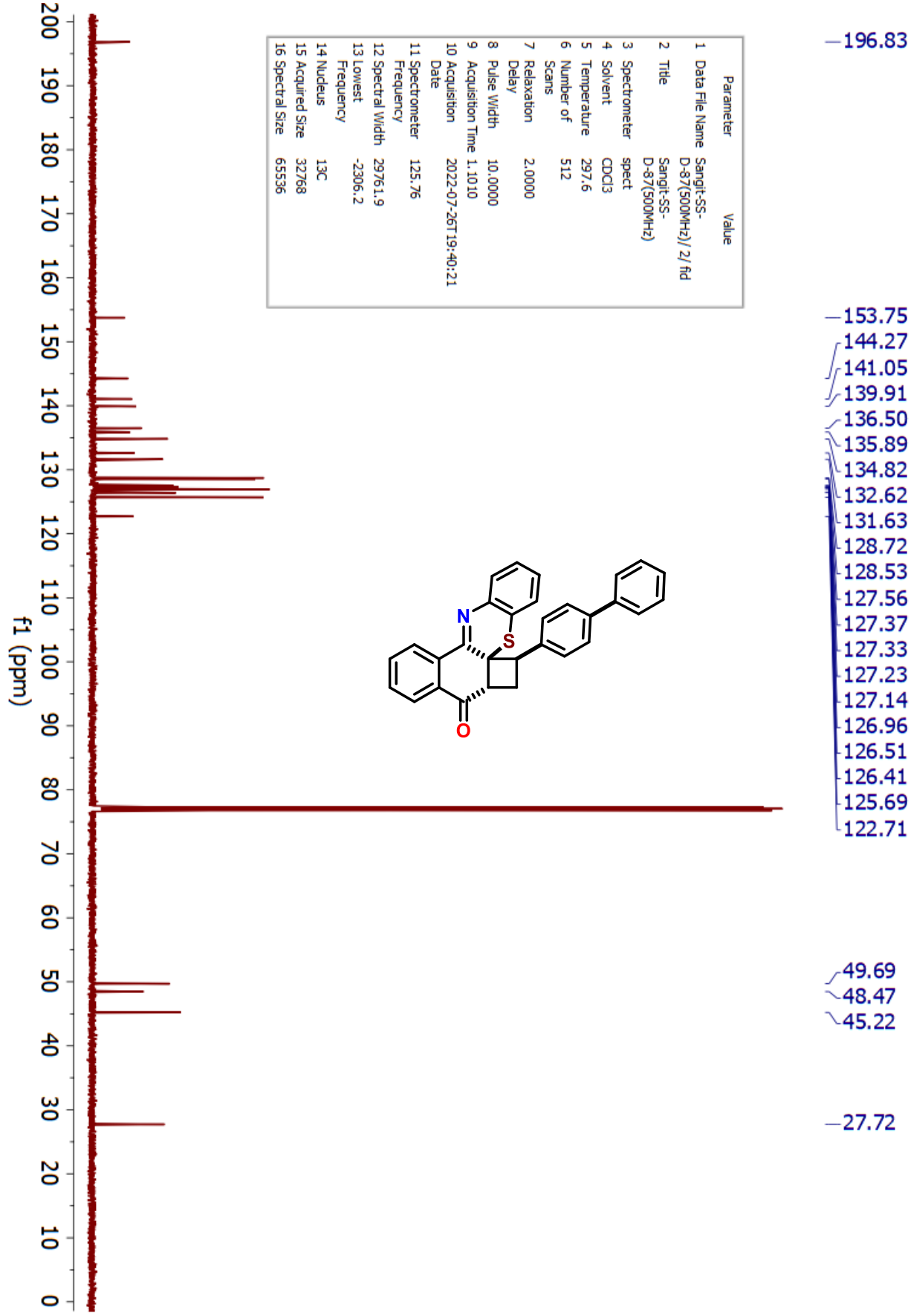
$^{13}C\{^{1}H\}$ NMR spectra of **2s**



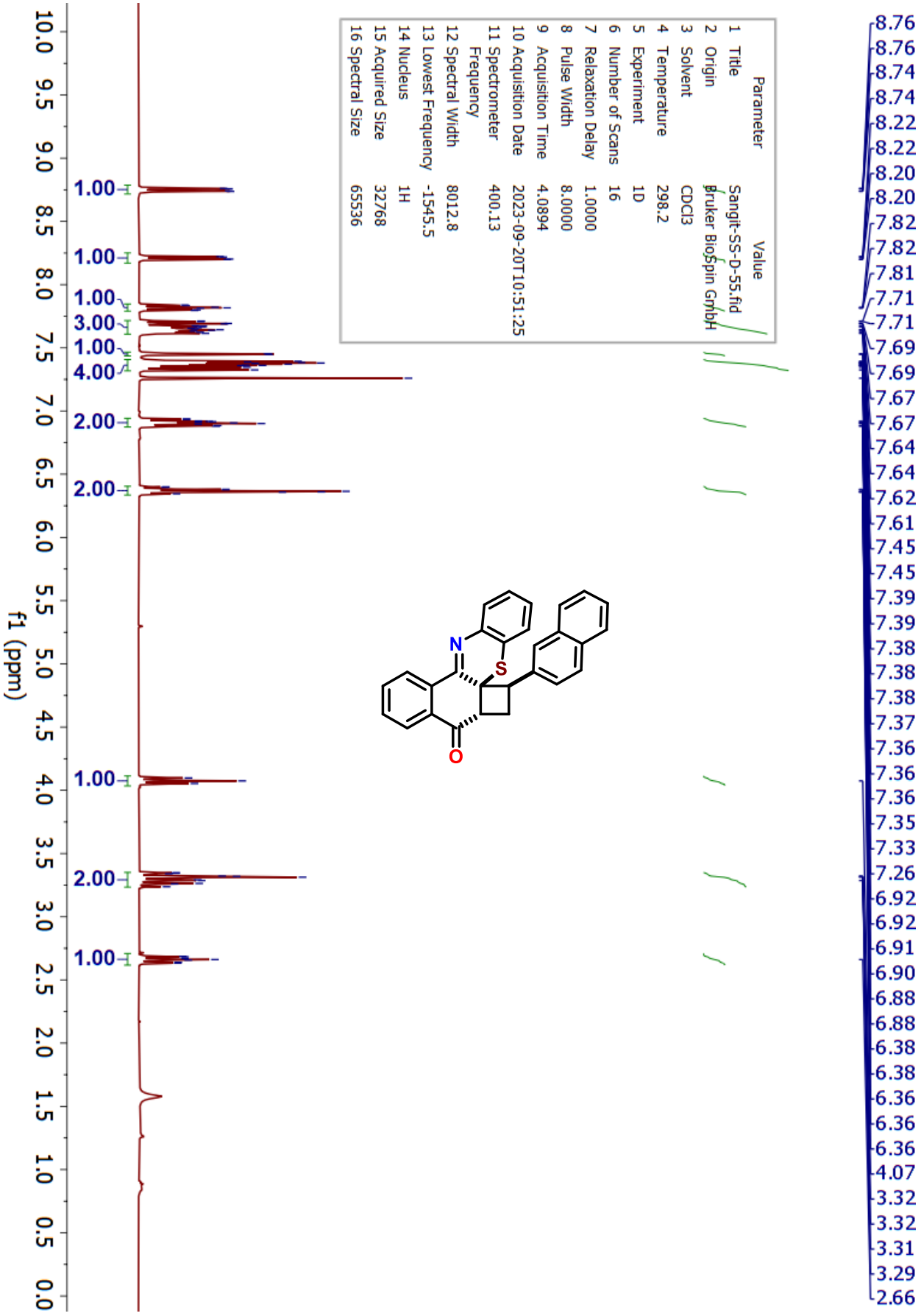
^{1}H NMR spectra of **2t**



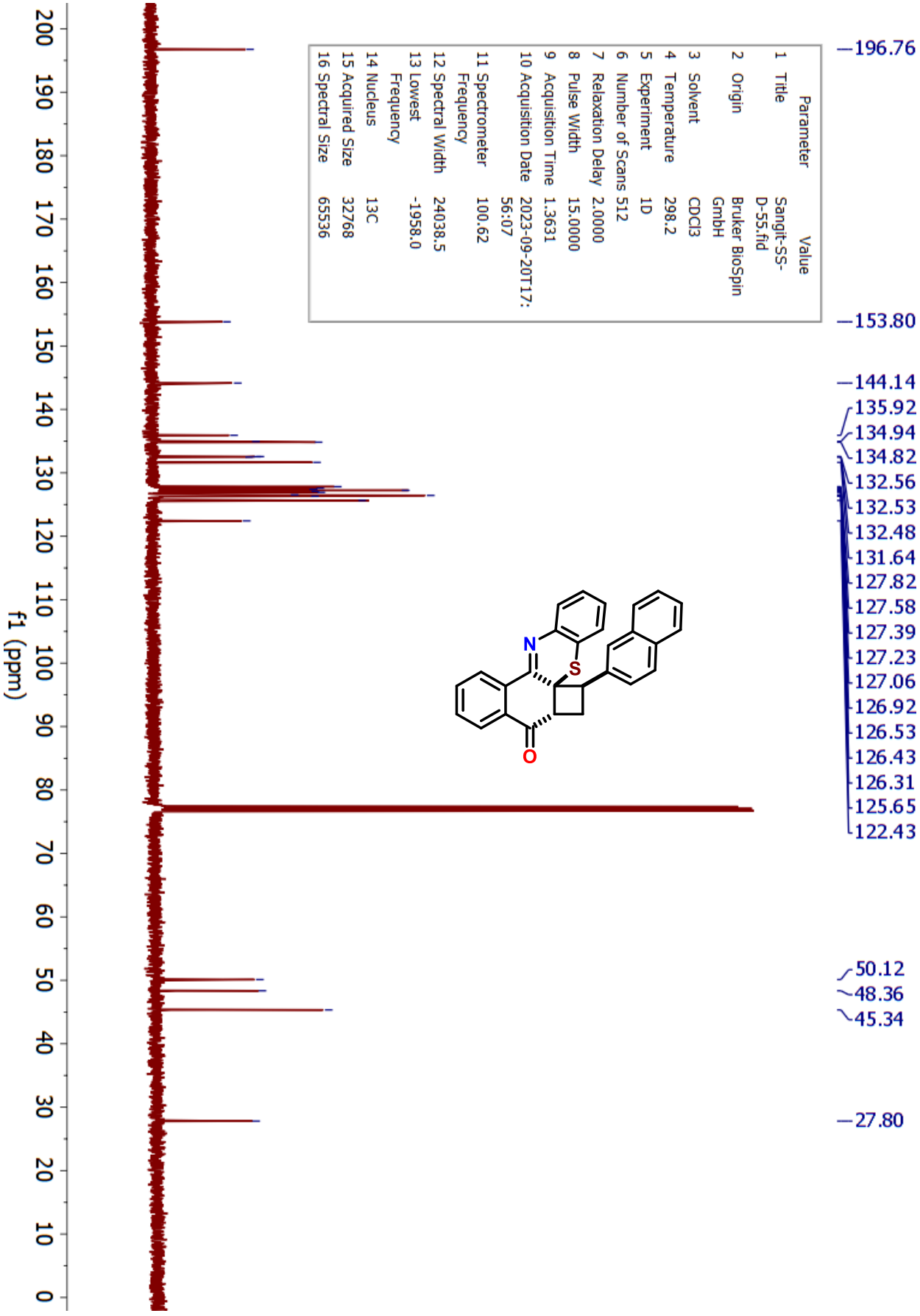
$^{13}C\{^{1}H\}$ NMR spectra of **2t**



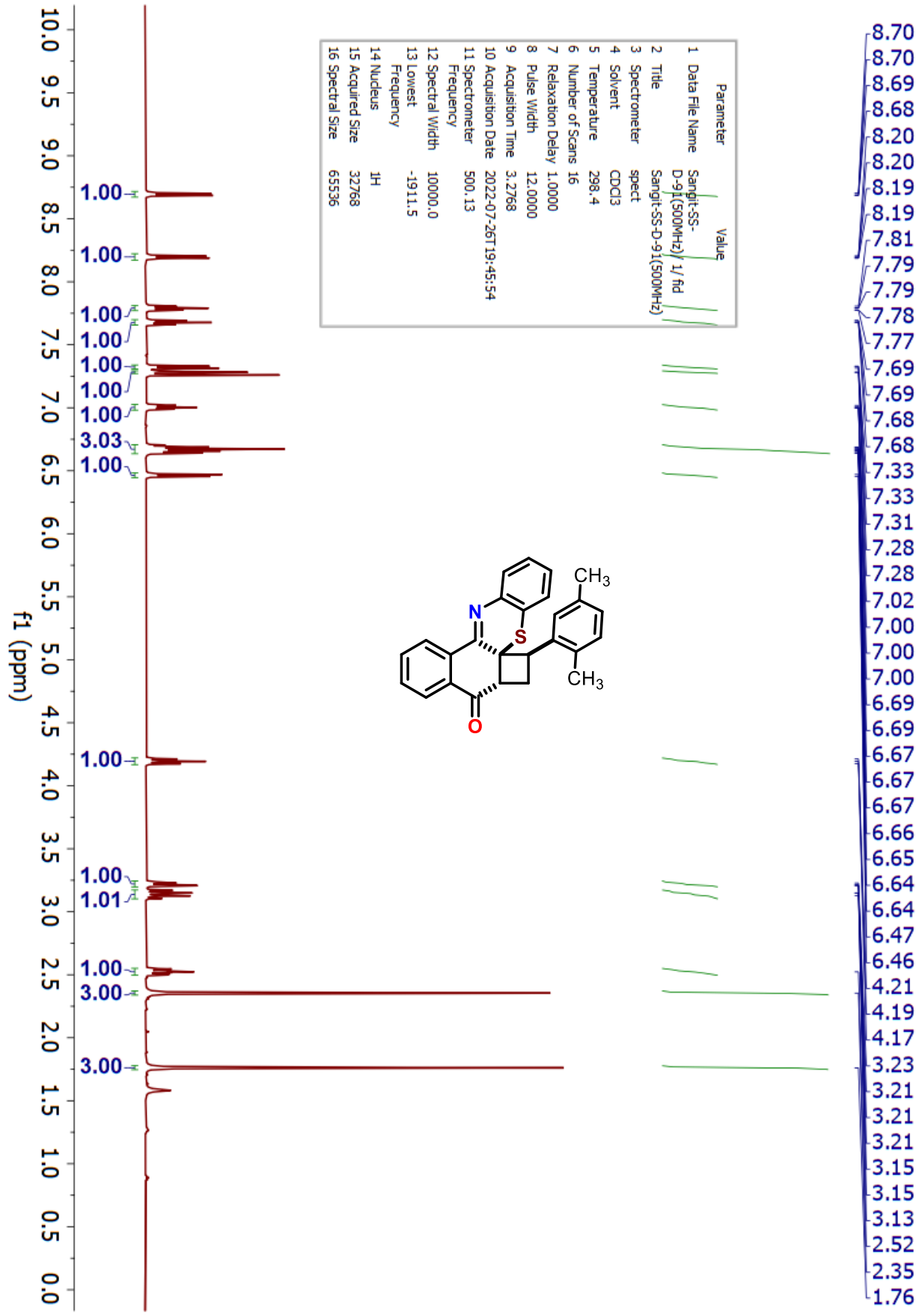
^{1}H NMR spectra of **2u**



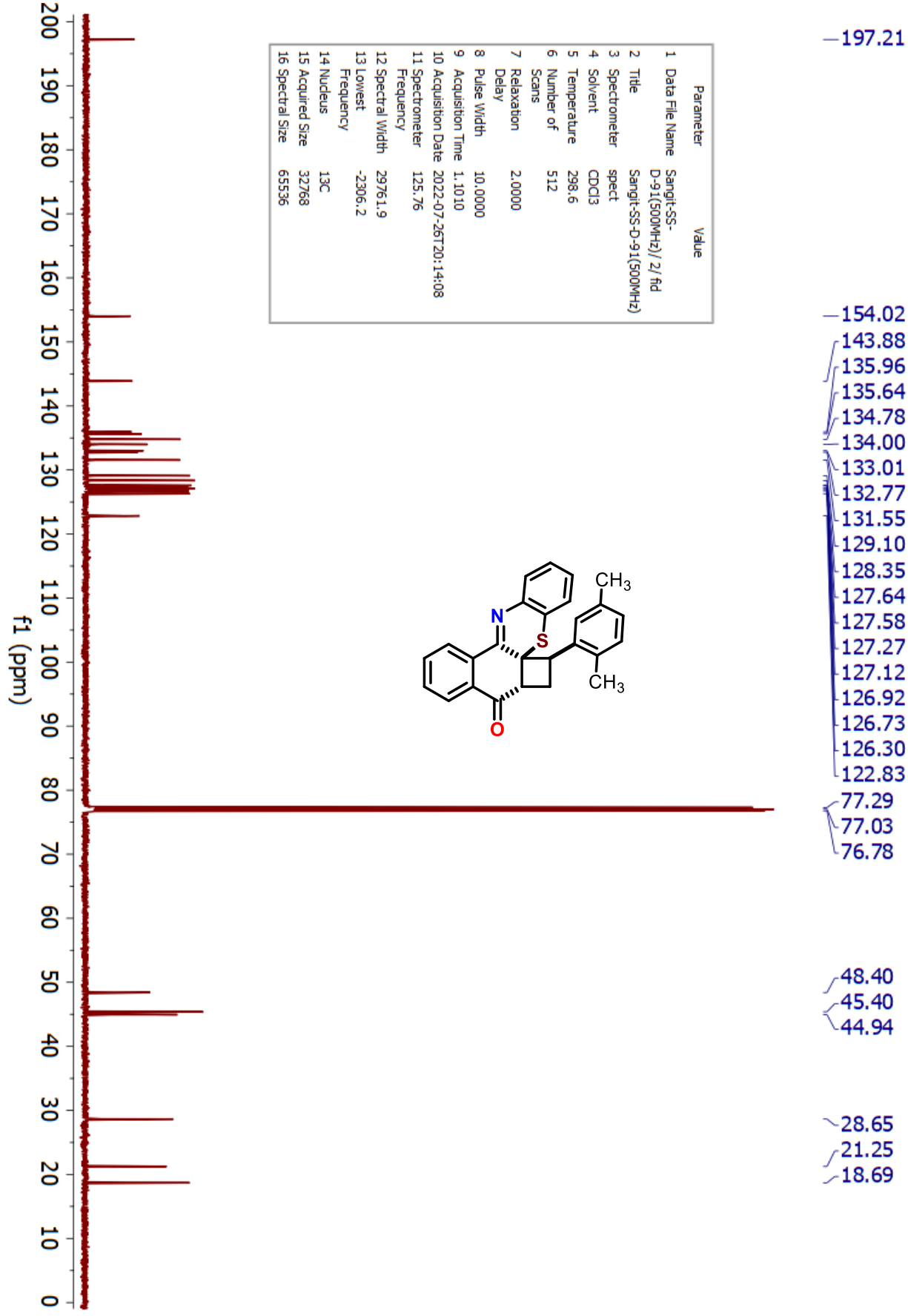
$^{13}C\{^{1}H\}$ NMR spectra of **2u**



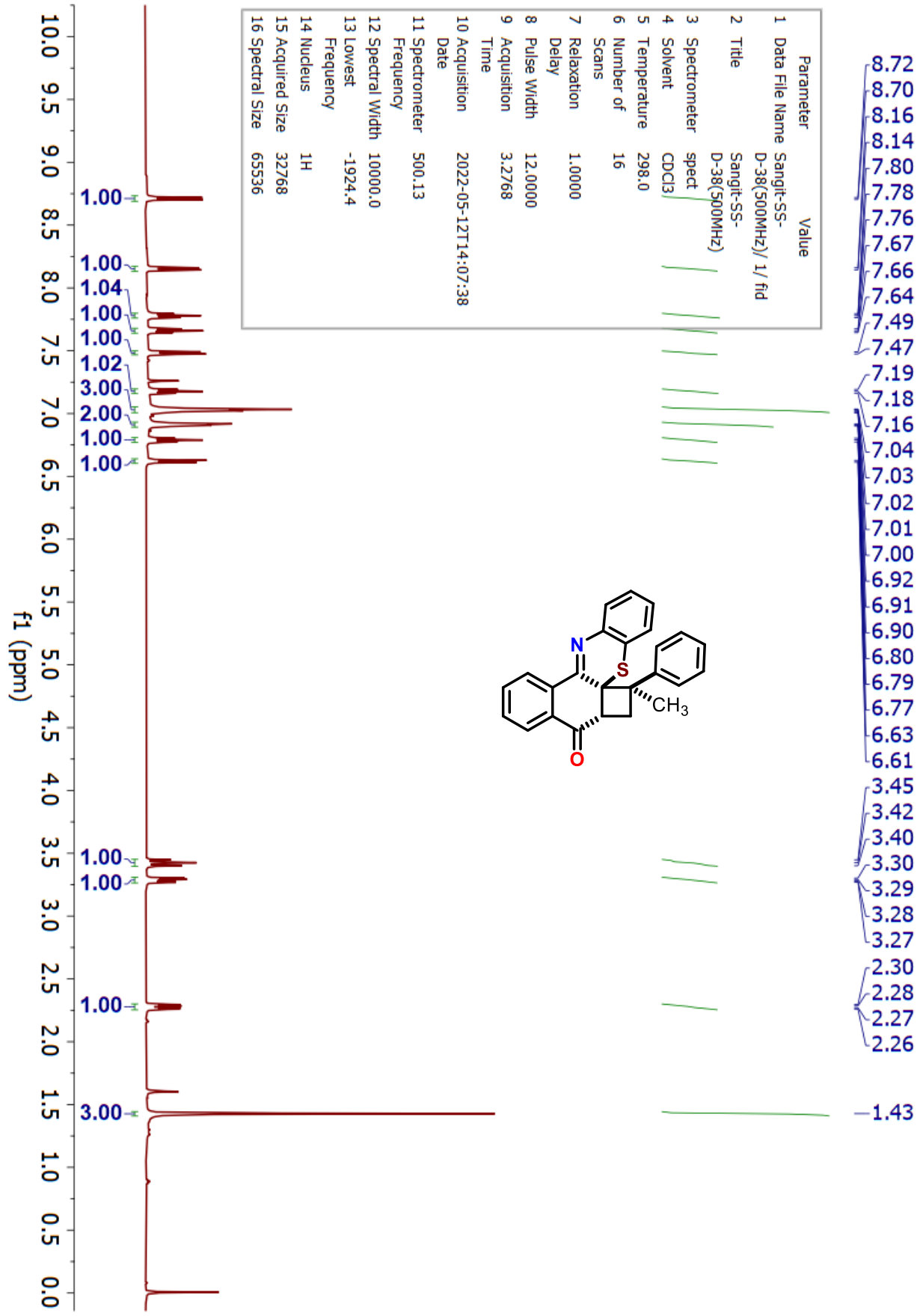
^{1}H NMR spectra of **2v**



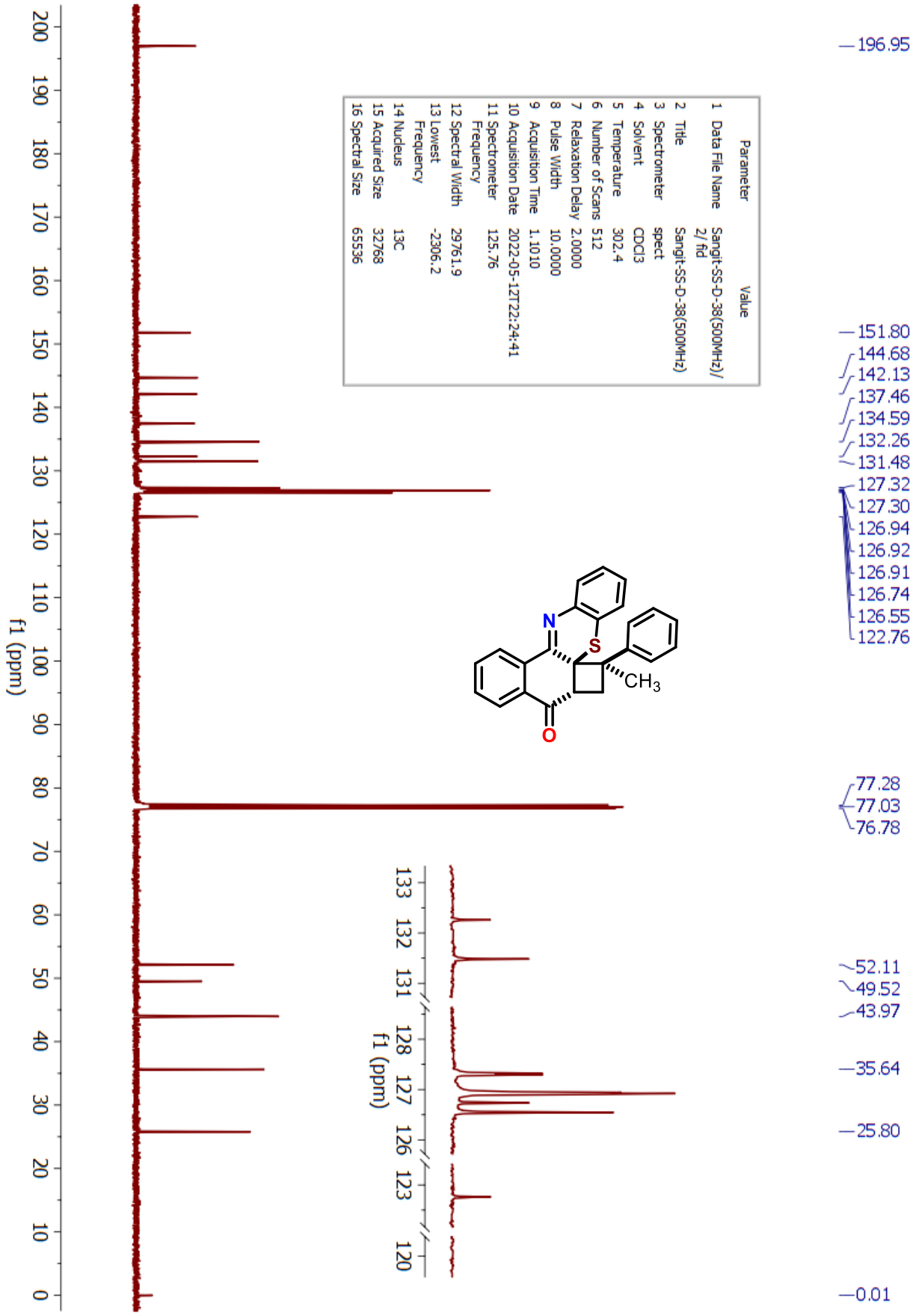
$^{13}C\{^{1}H\}$ NMR spectra of **2v**



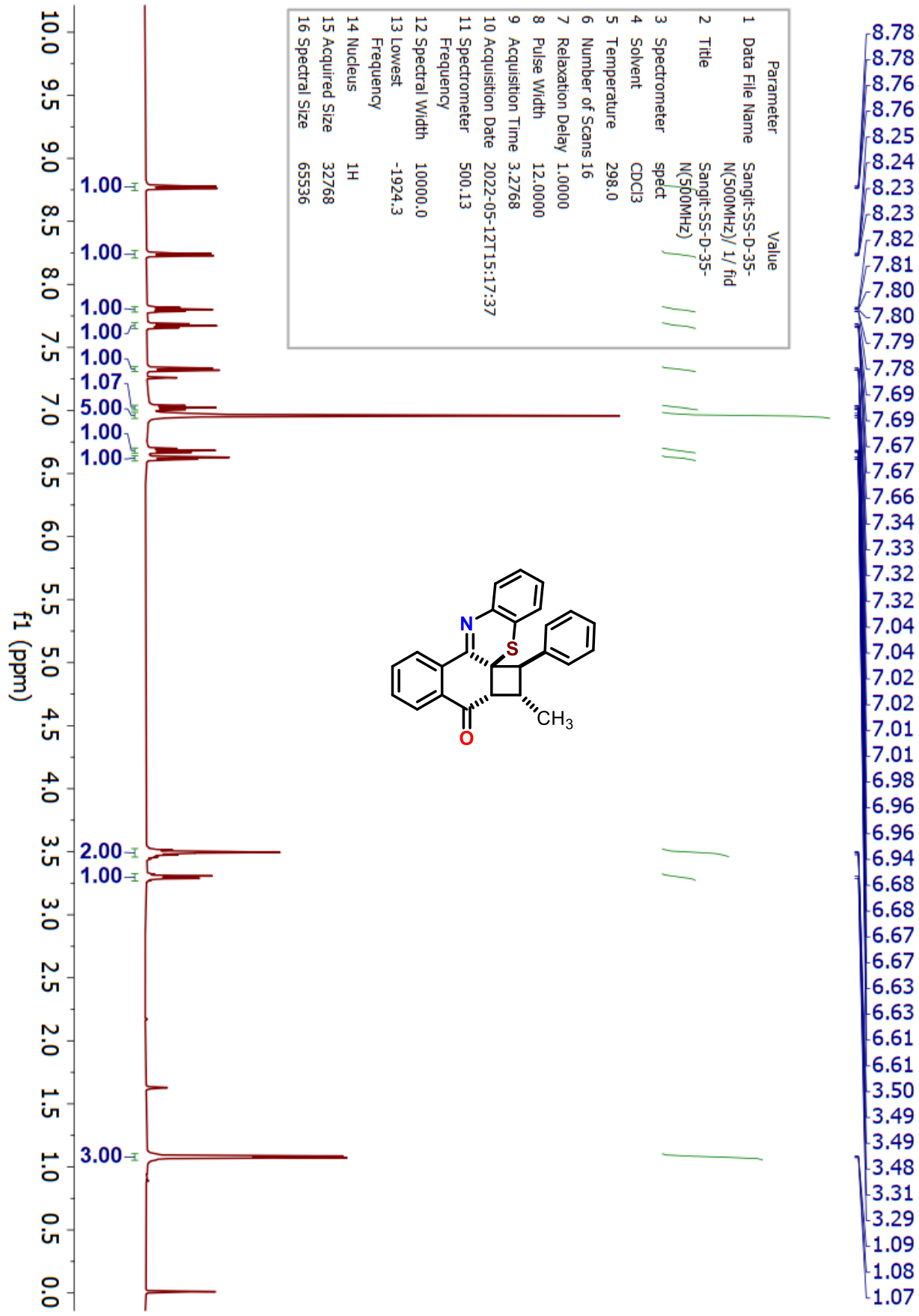
^{1}H NMR spectra of **2w**



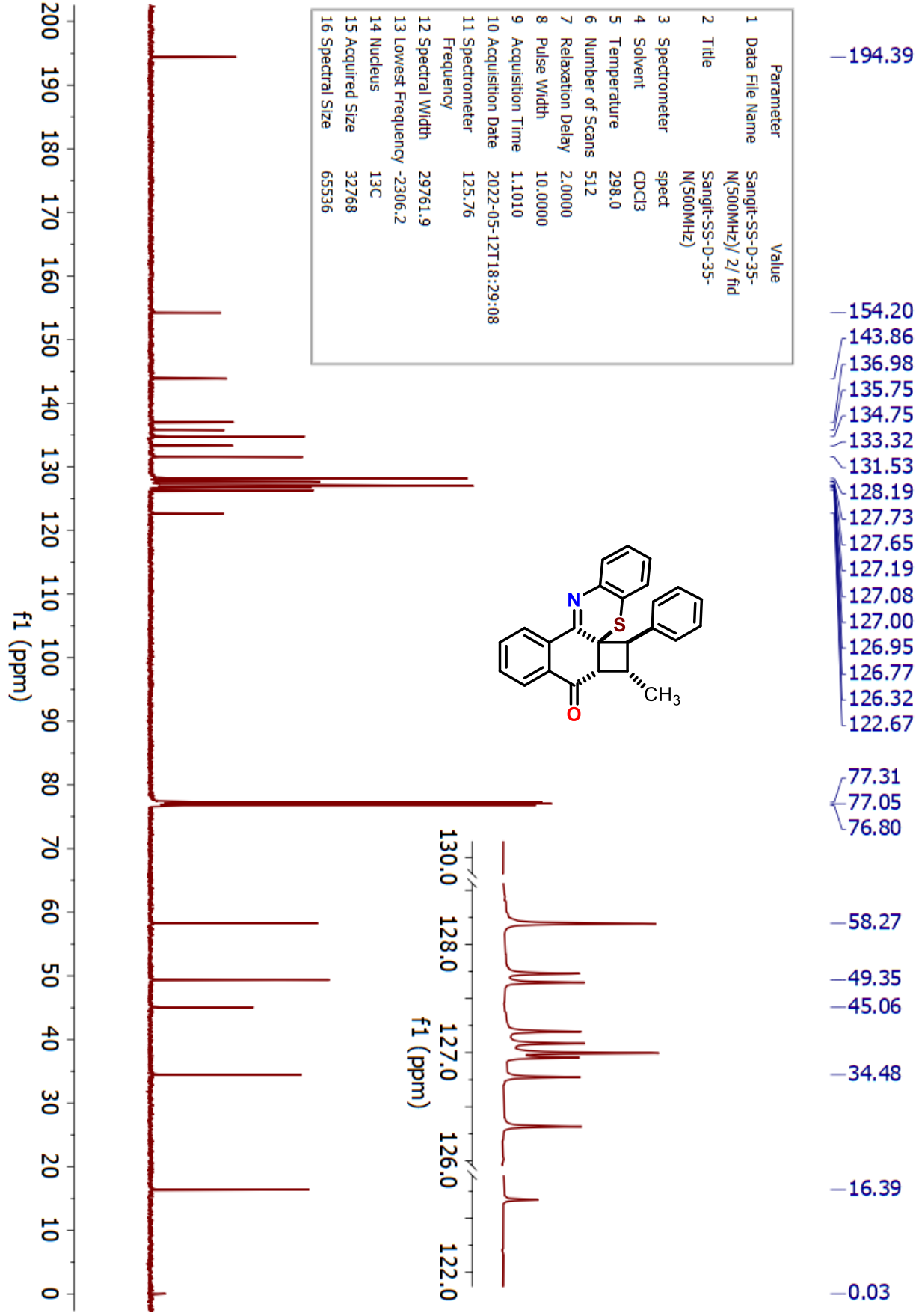
$^{13}C\{^{1}H\}$ NMR spectra of **2w**



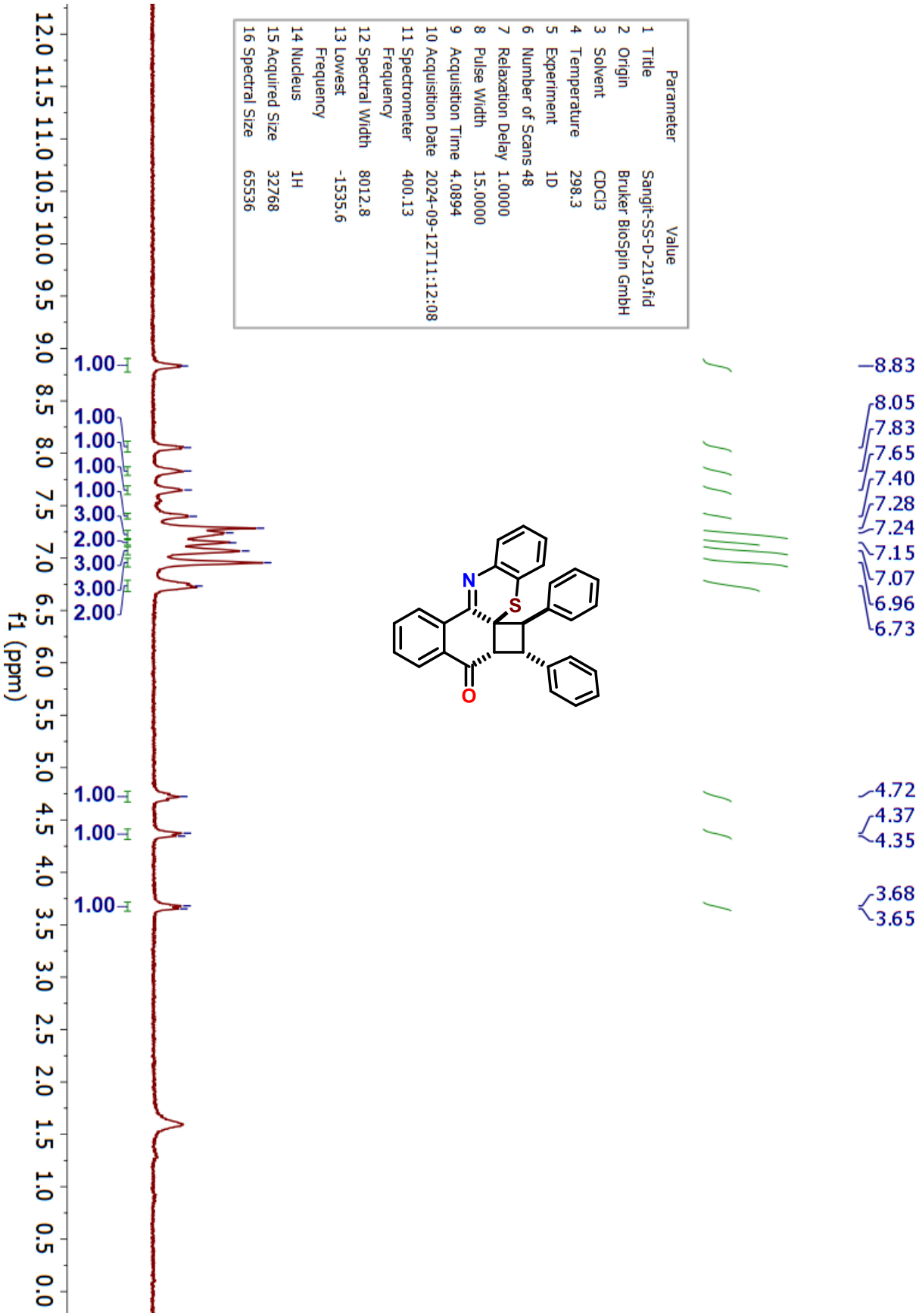
^{1}H NMR spectra of **2x**



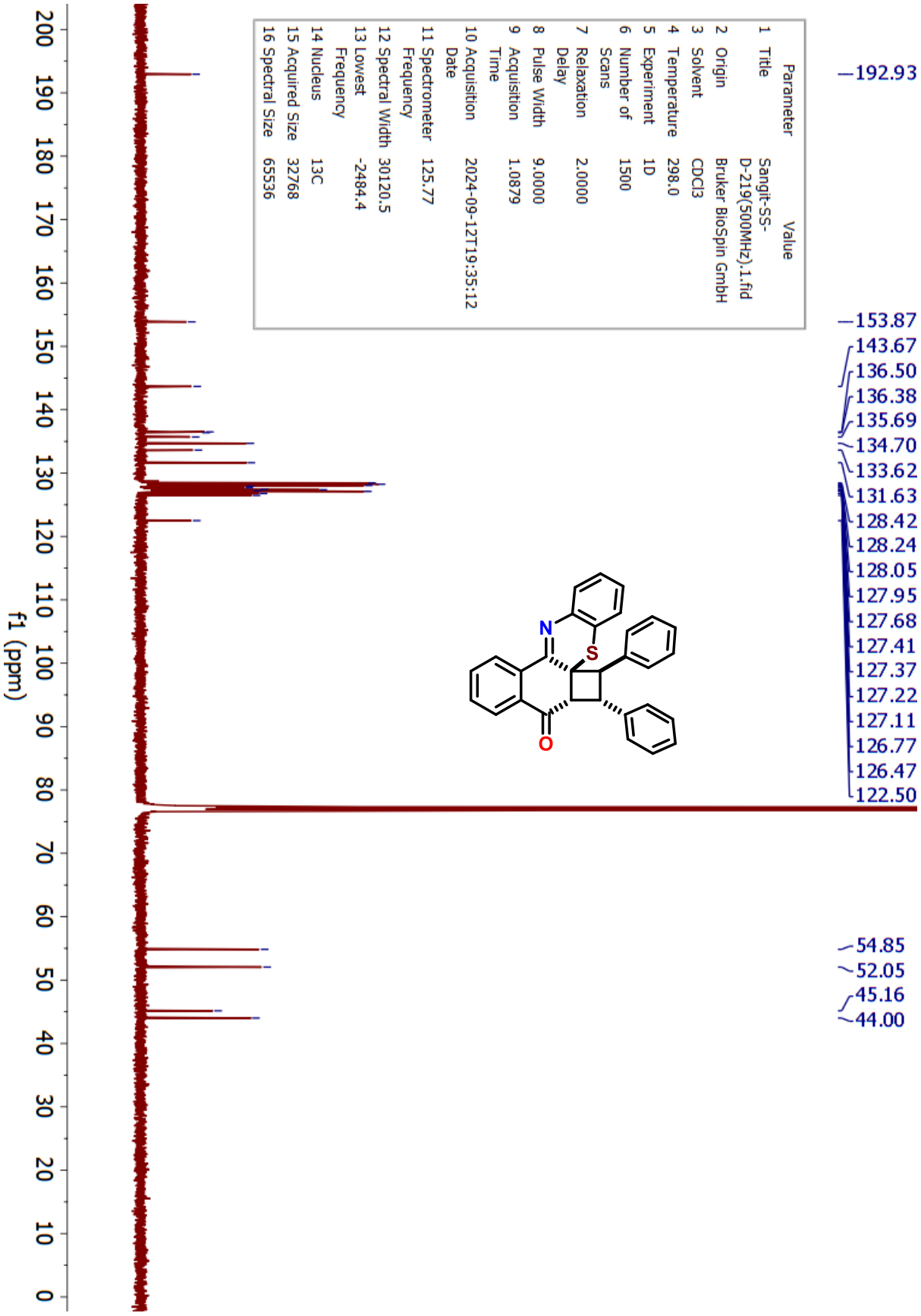
$^{13}C\{^{1}H\}$ NMR spectra of **2x**



^{1}H NMR spectra of **2y**



$^{13}C\{^{1}H\}$ NMR spectra of **2y**



Mass Spectrum of **2z**

Display Report

Analysis Info

Analysis Name	D:\Data\USER DATA 2024\Sept-2024\09-sept-24\Prof.S.Kumar-SS-D-218_1-A,8_01_5258.d	Acquisition Date	09-09-2024 14:35:05
Method	HRLCMS-20 APR23.m	Operator	Bruker
Sample Name	Prof.S.Kumar-SS-D-218	Instrument	micrOTOF-Q 10330
Comment			

Acquisition Parameter

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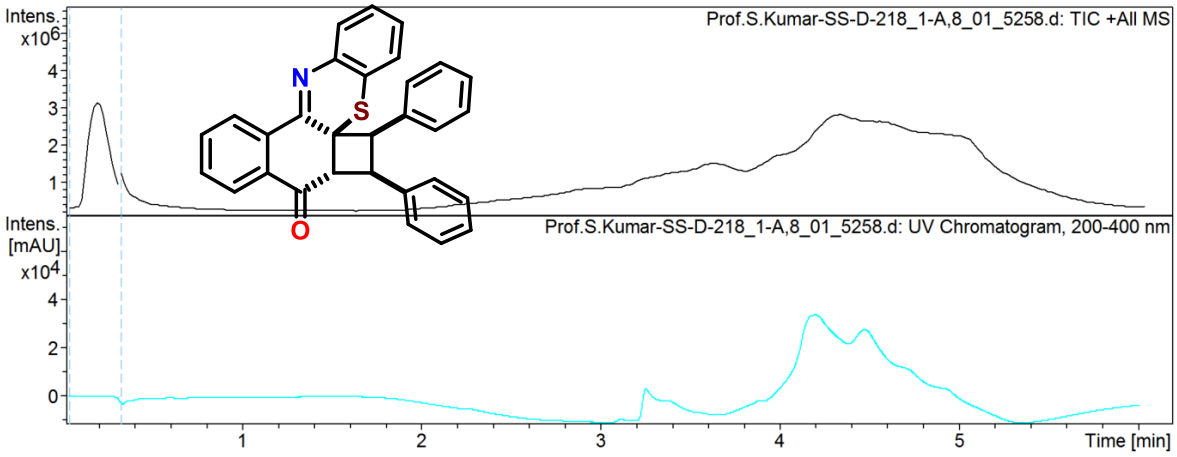

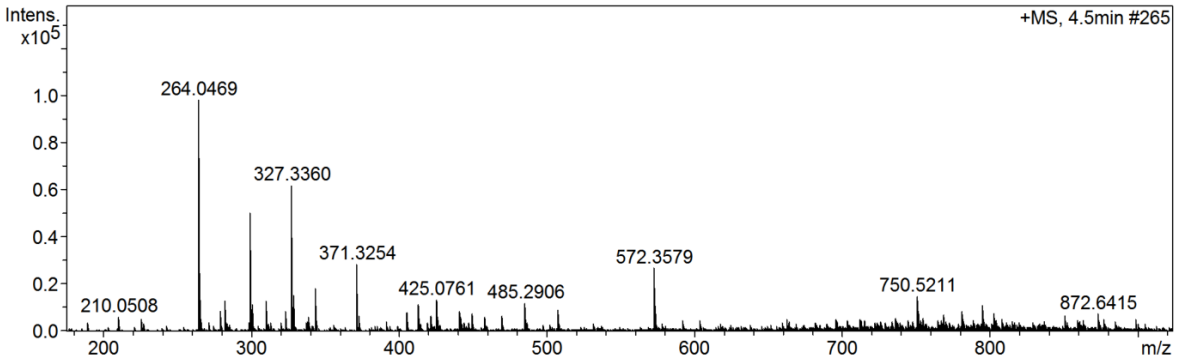

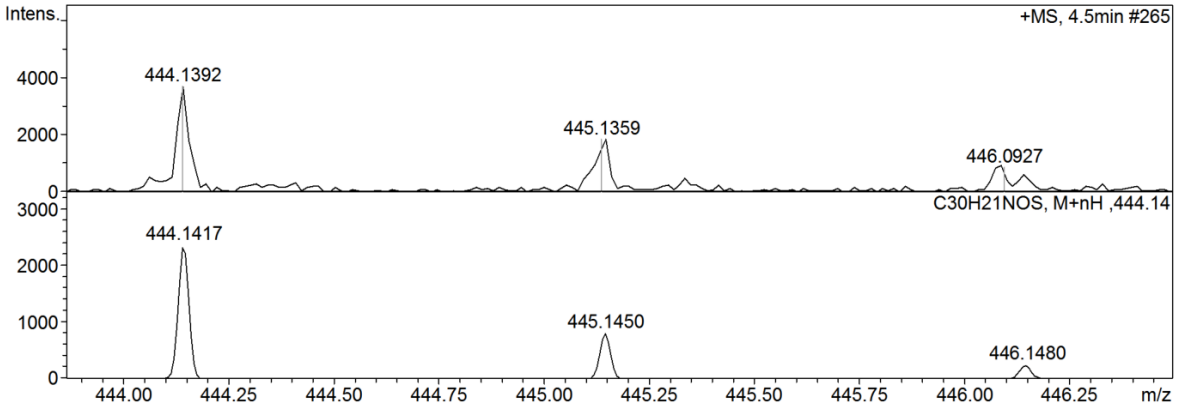

Mass Spectrum of **2aa**

Display Report

Analysis Info

Analysis Name	D:\Data\USER DATA 2022\JULY2022\19-07-22\Dr.S.Kumar-SS_D_75.d	Acquisition Date	19-07-2022 15:47:42
Method	tune_wide.m	Operator	Bruker
Sample Name	SS_D_75	Instrument	micrOTOF-Q 10330
Comment			

Acquisition Parameter

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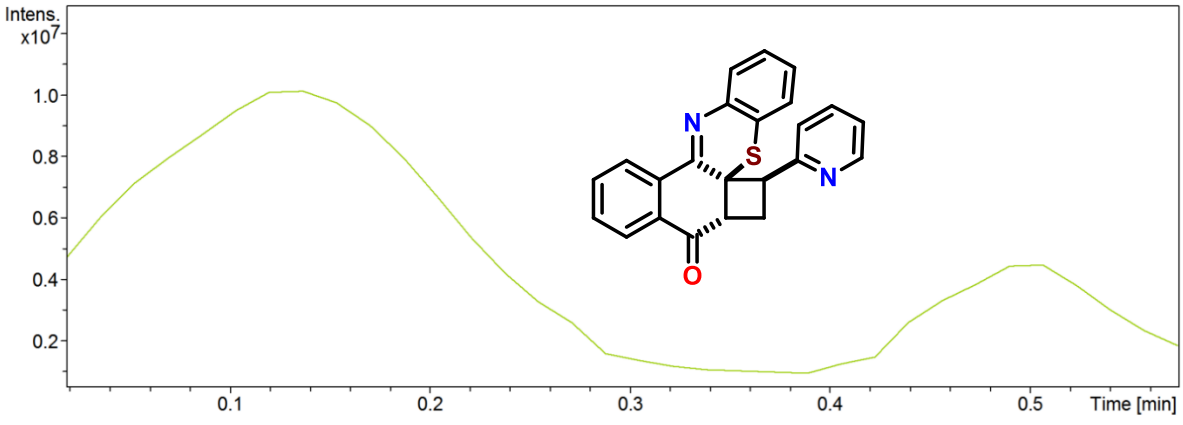
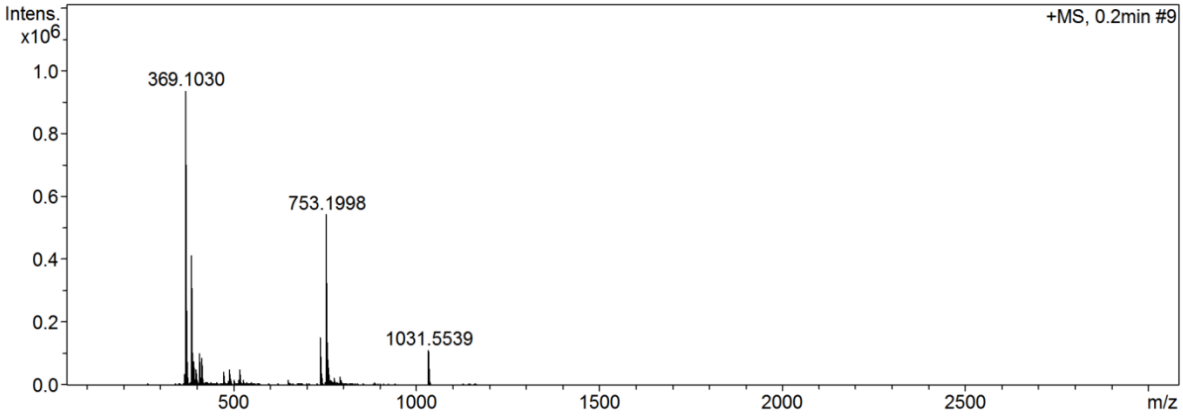
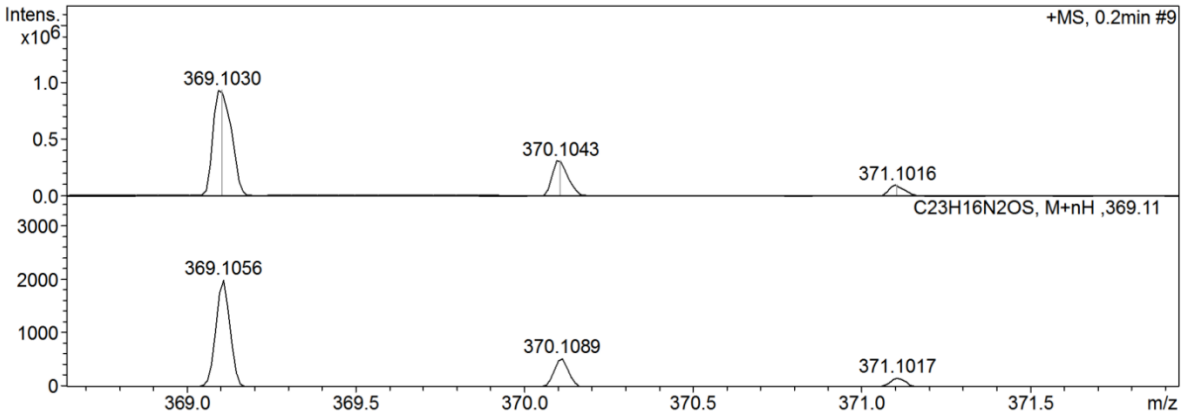


TIC +All MS





Mass Spectrum of **2ab**

Display Report

Analysis Info

Analysis Name	D:\Data\USER DATA 2022\JULY2022\18-07-22\Prof.S.Kumar-SS_D_70.d	Acquisition Date	18-07-2022 14:57:47
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Sample Name	SS_D_70	Instrument	micrOTOF-Q 10330
Comment			

Acquisition Parameter

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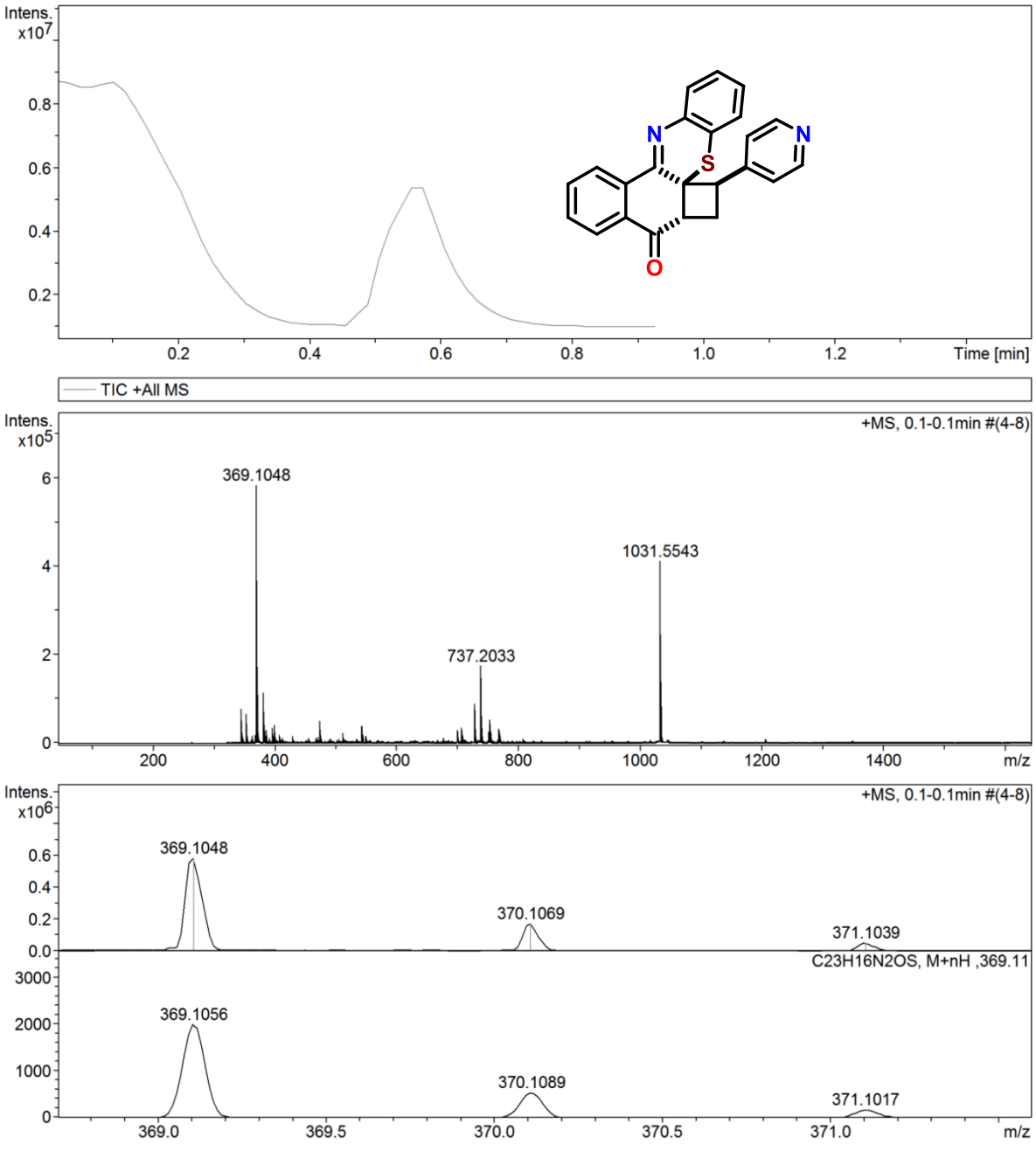
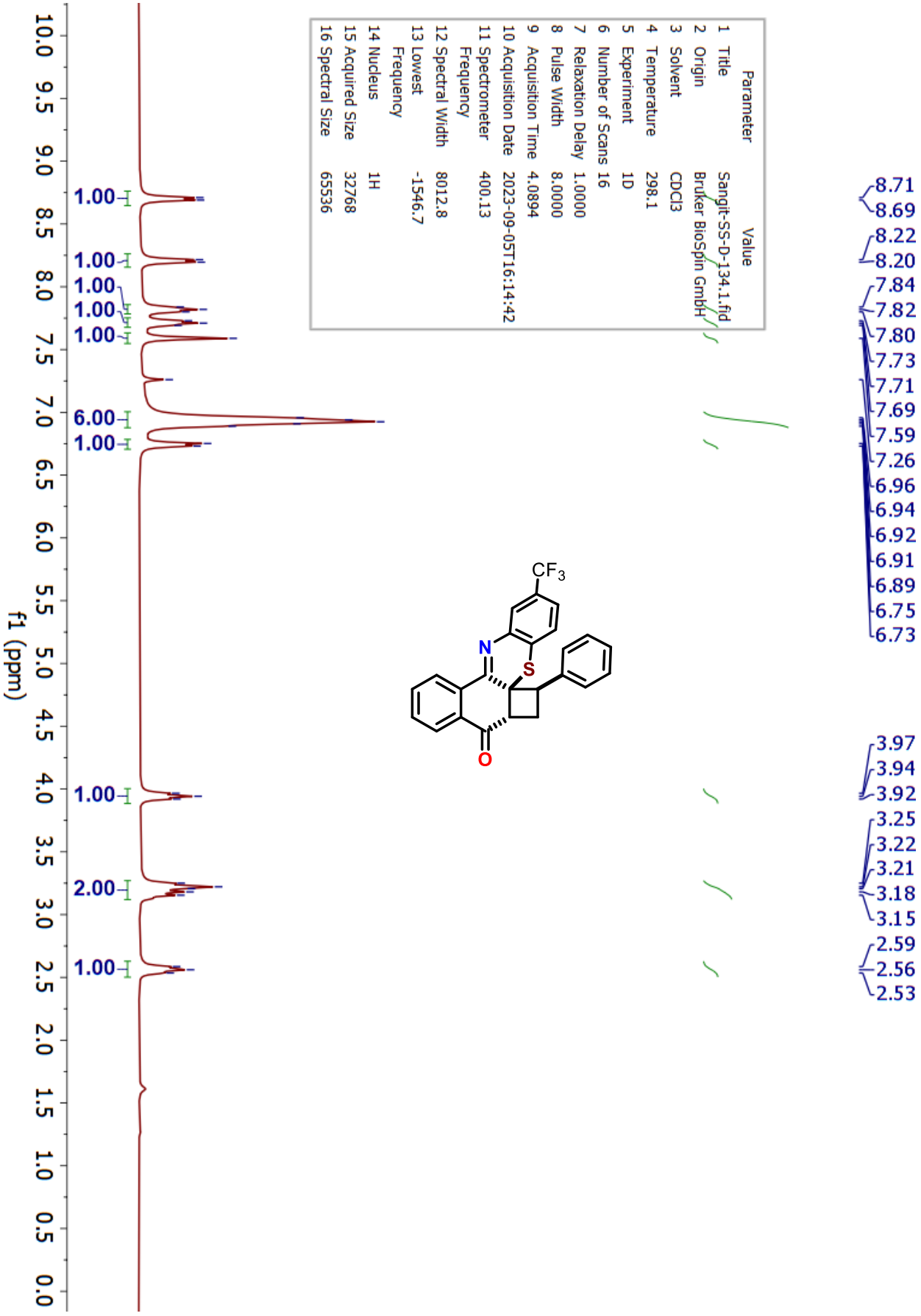
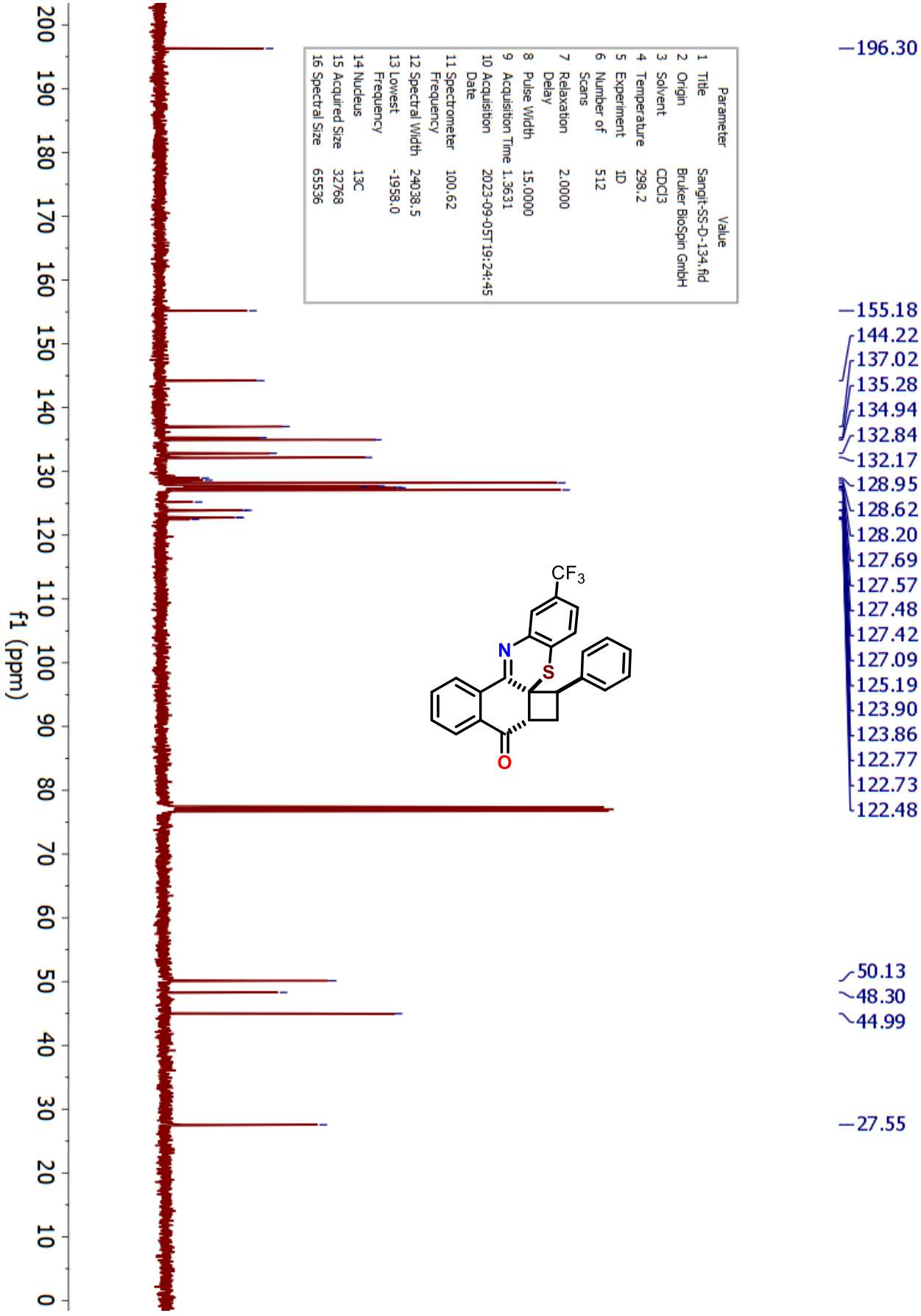


Bruker Compass DataAnalysis 4.0 printed: 18-07-2022 14:59:24 Page 1 of 1

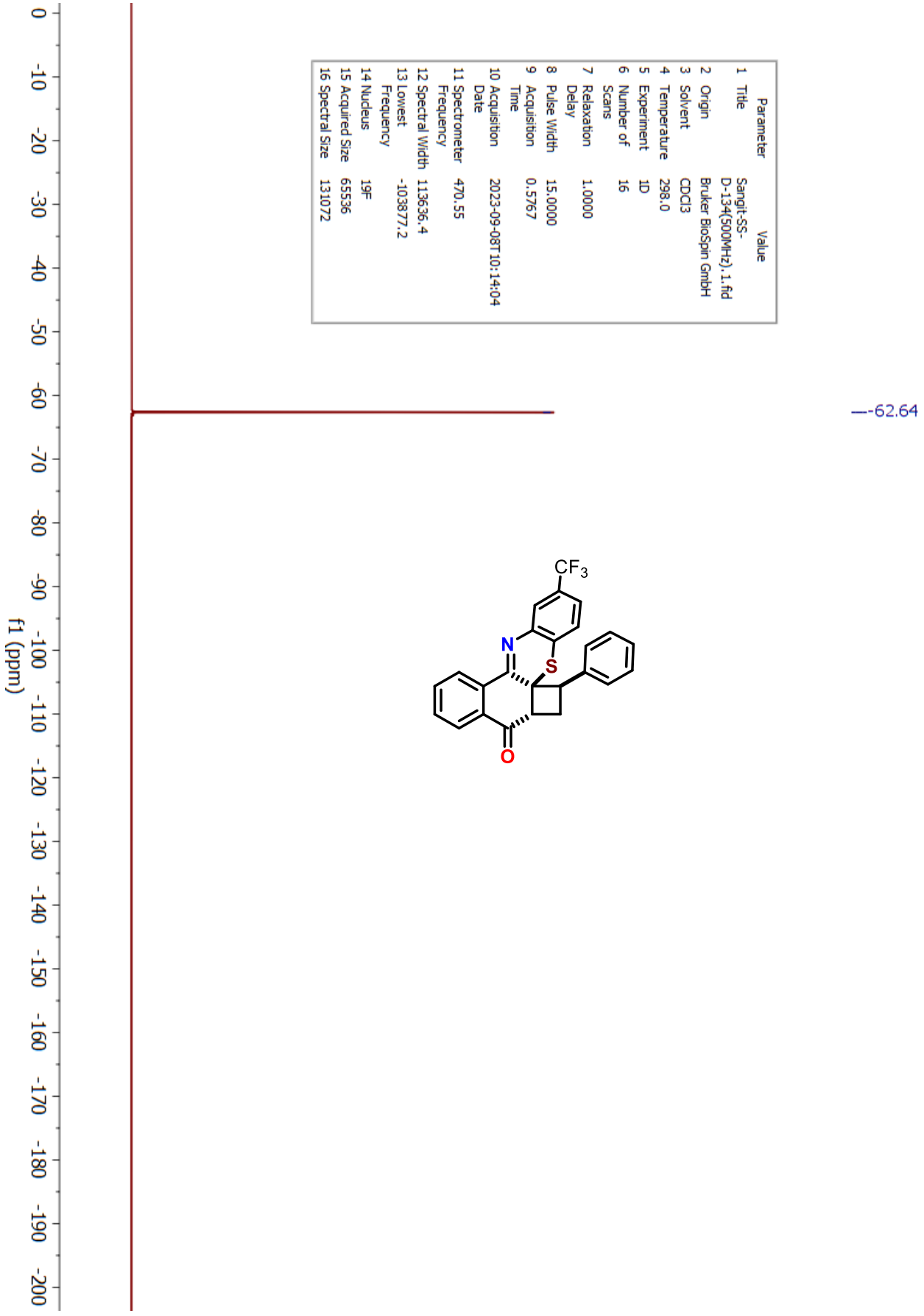
^{1}H NMR spectra of **2ac**



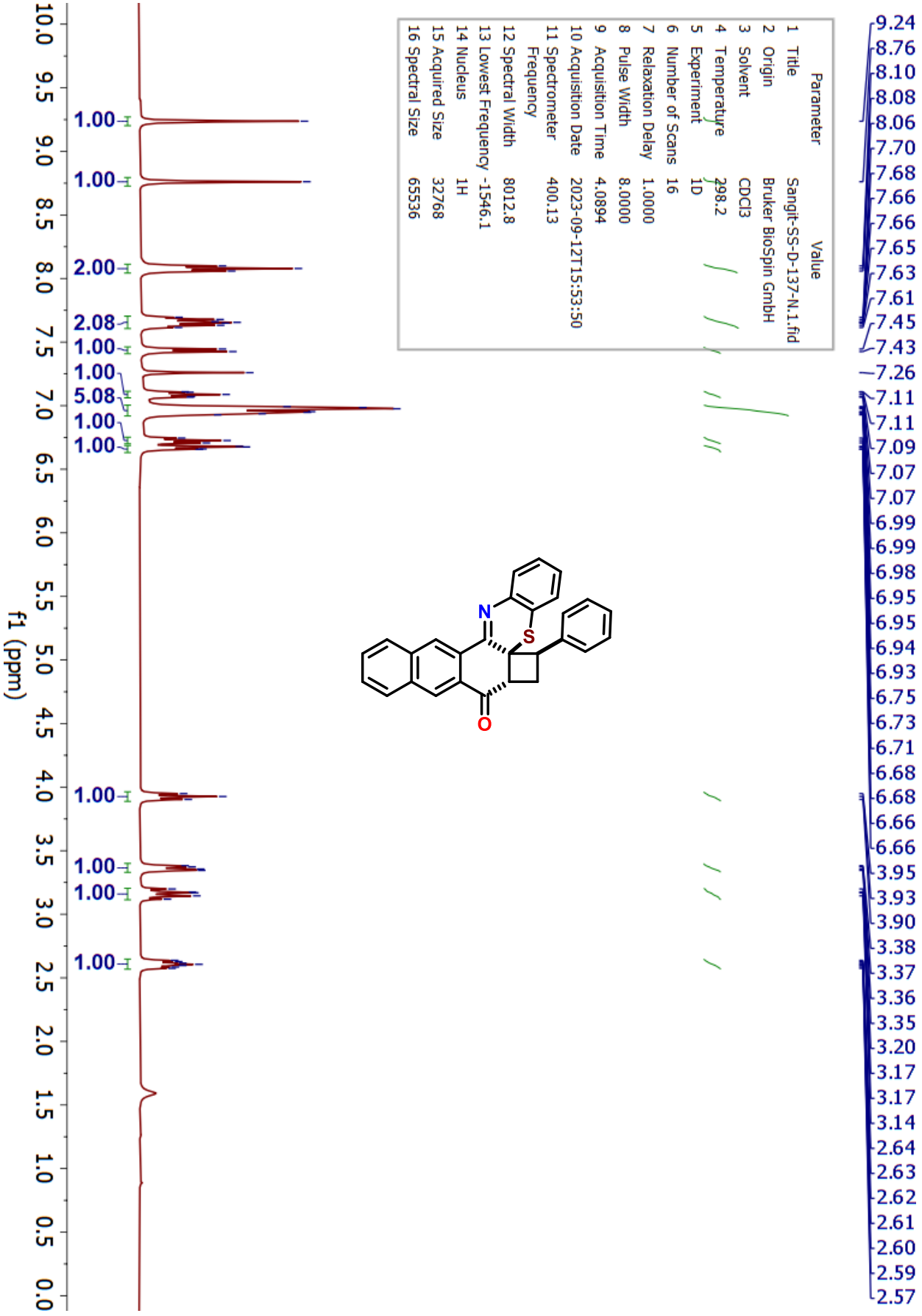
$^{13}C\{^{1}H\}$ NMR spectra of **2ac**



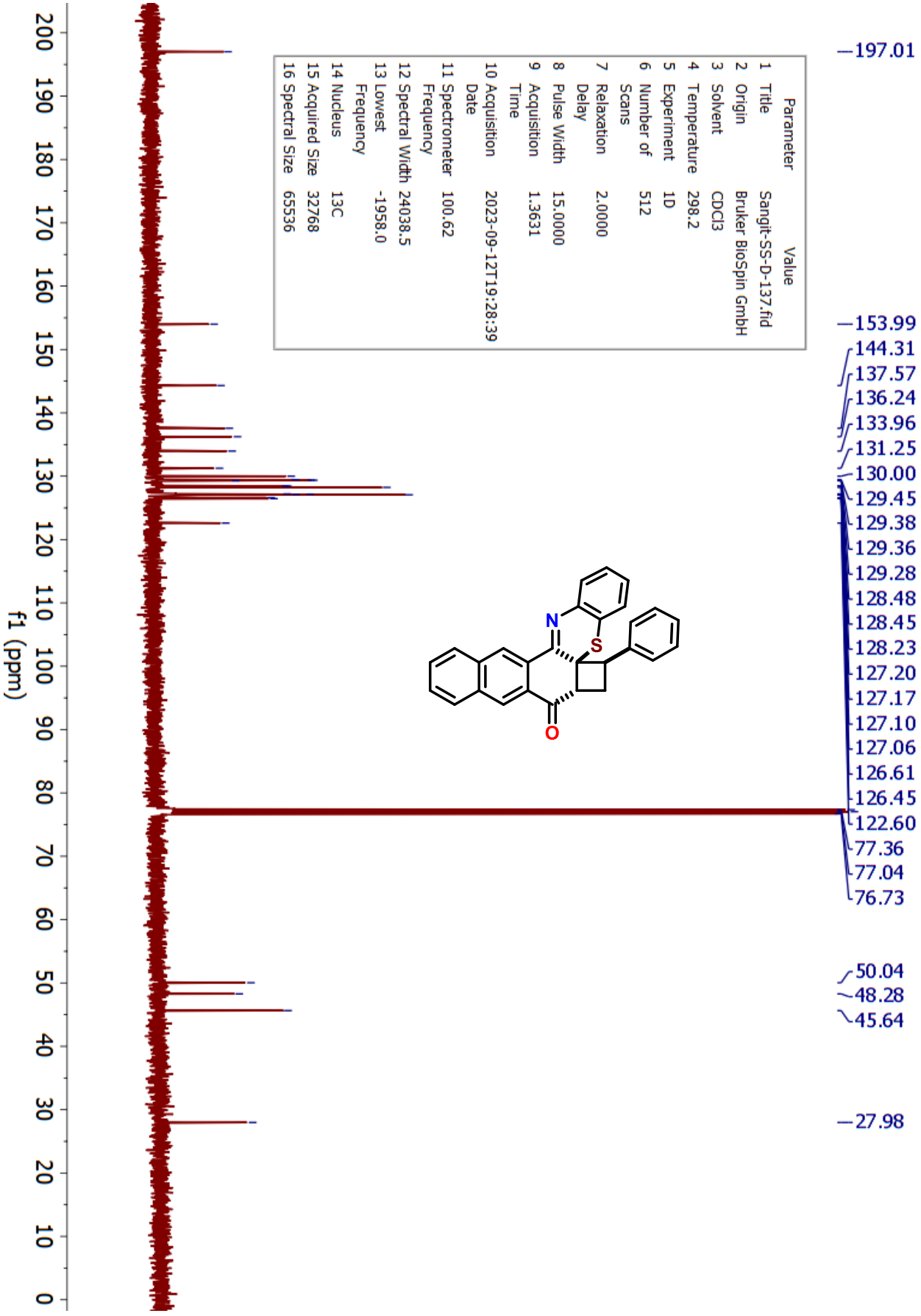
$^{19}F\{^{1}H\}$ NMR spectra of **2ac**



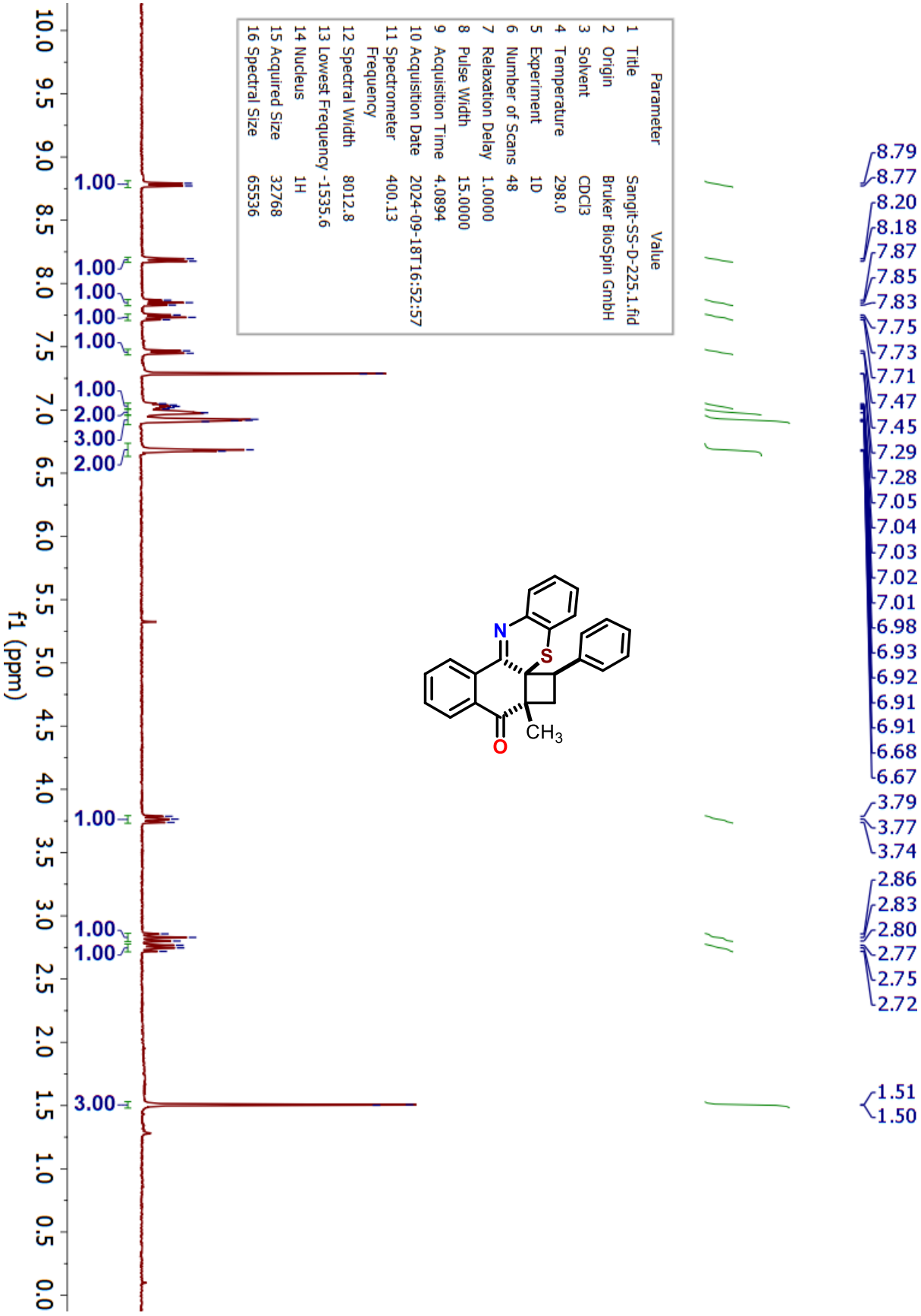
^{1}H NMR spectra of **2ad**



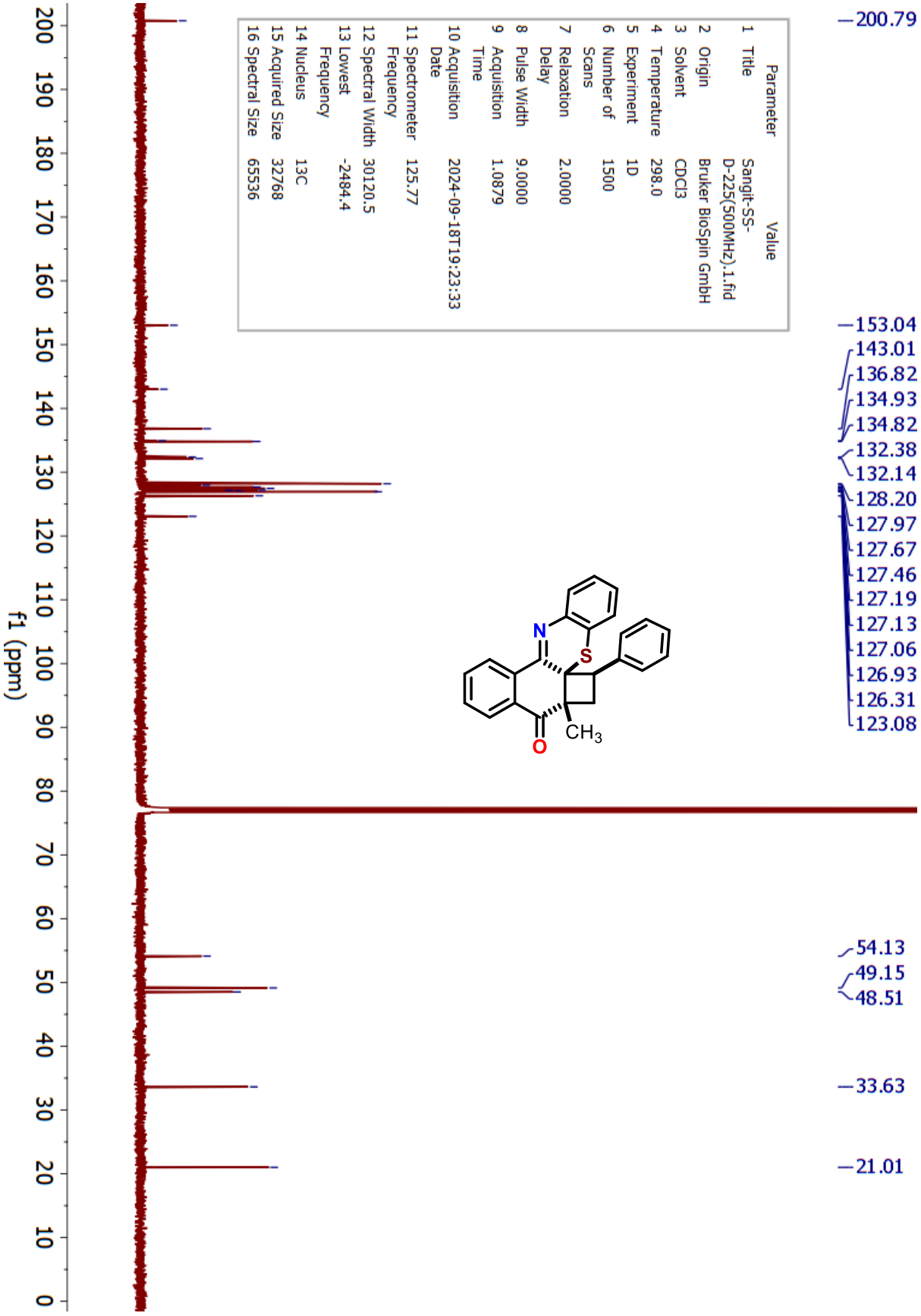
$^{13}C\{^{1}H\}$ NMR spectra of **2ad**



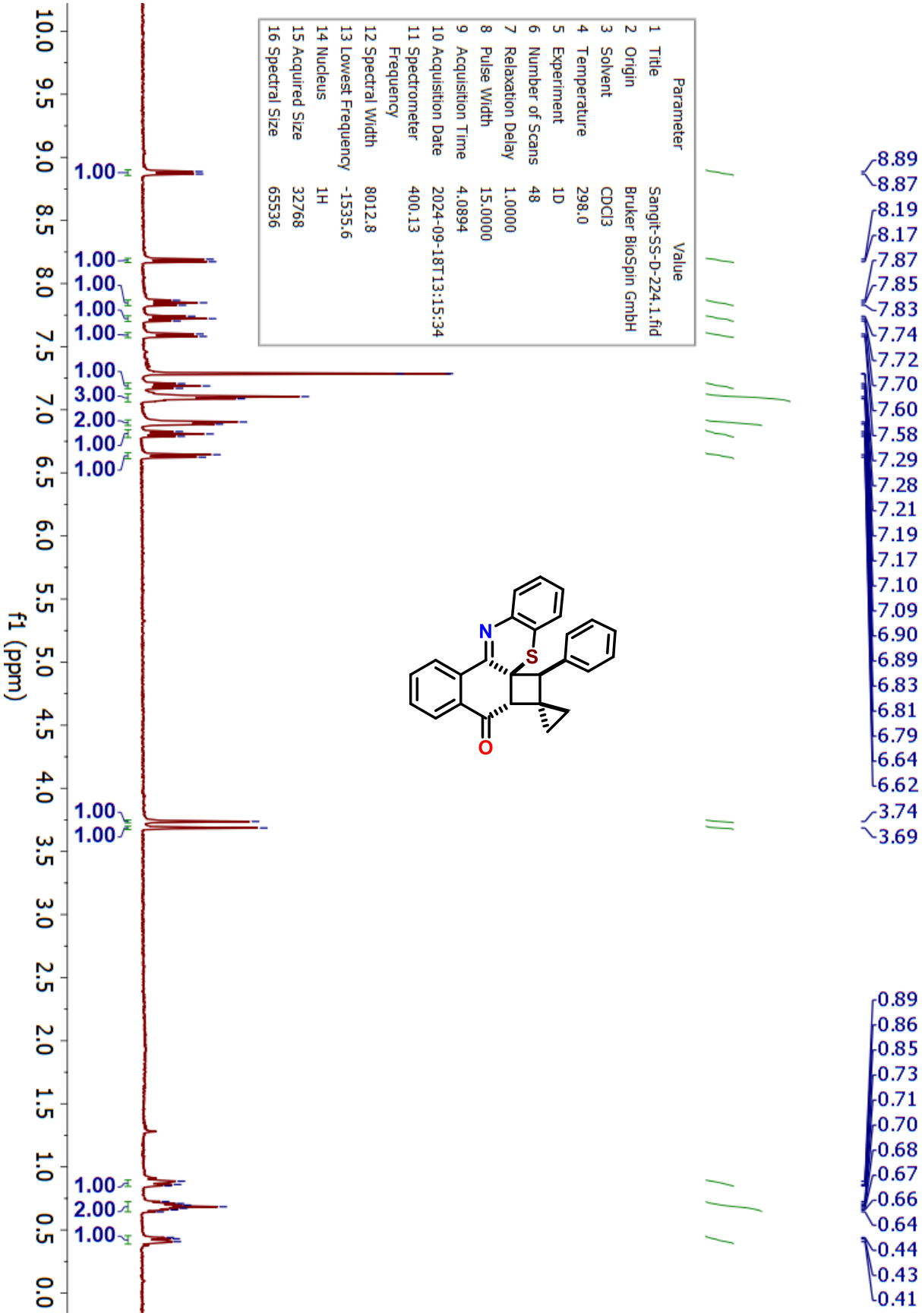
^{1}H NMR spectra of **2ae**



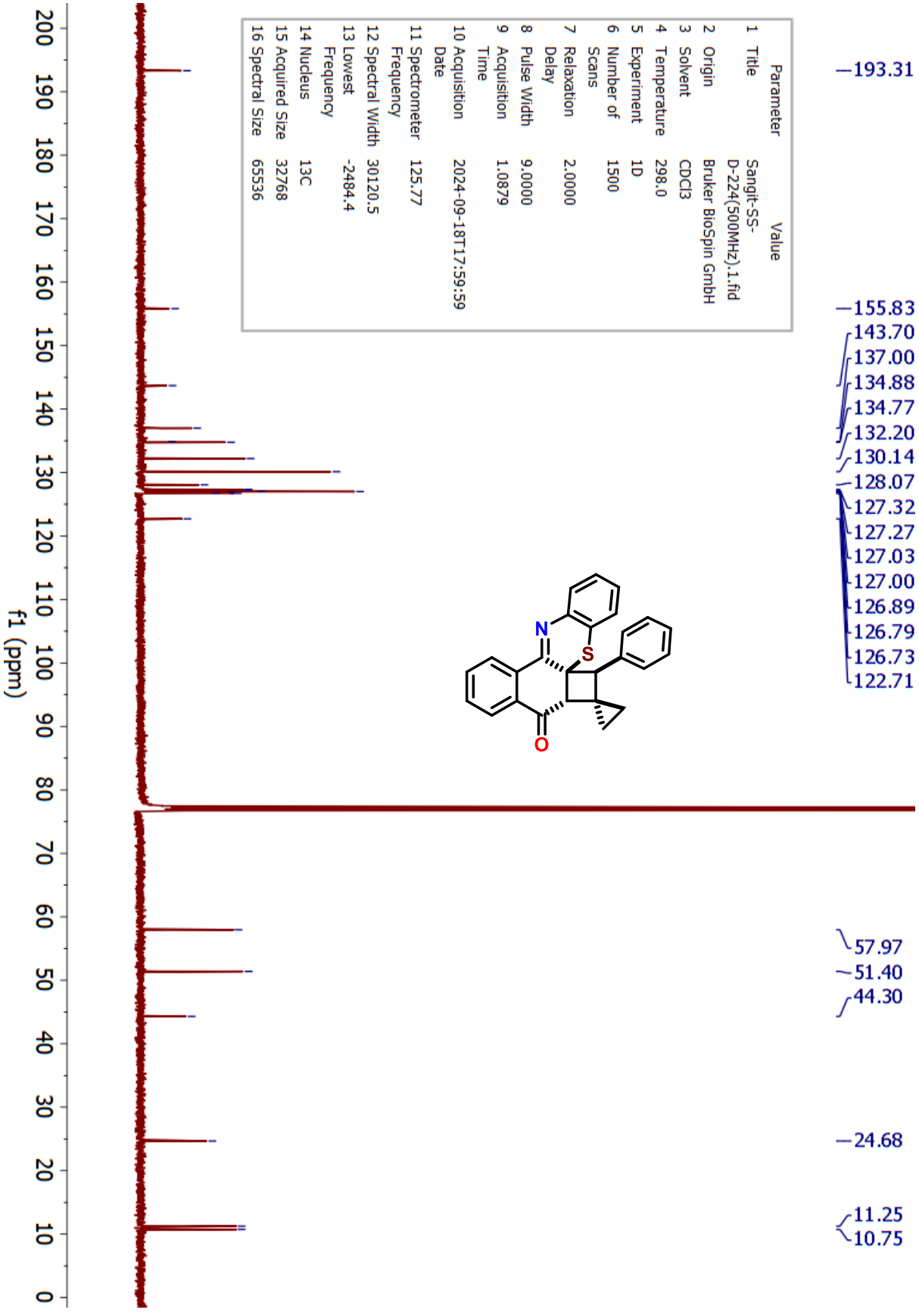
$^{13}C\{^{1}H\}$ NMR spectra of **2ae**



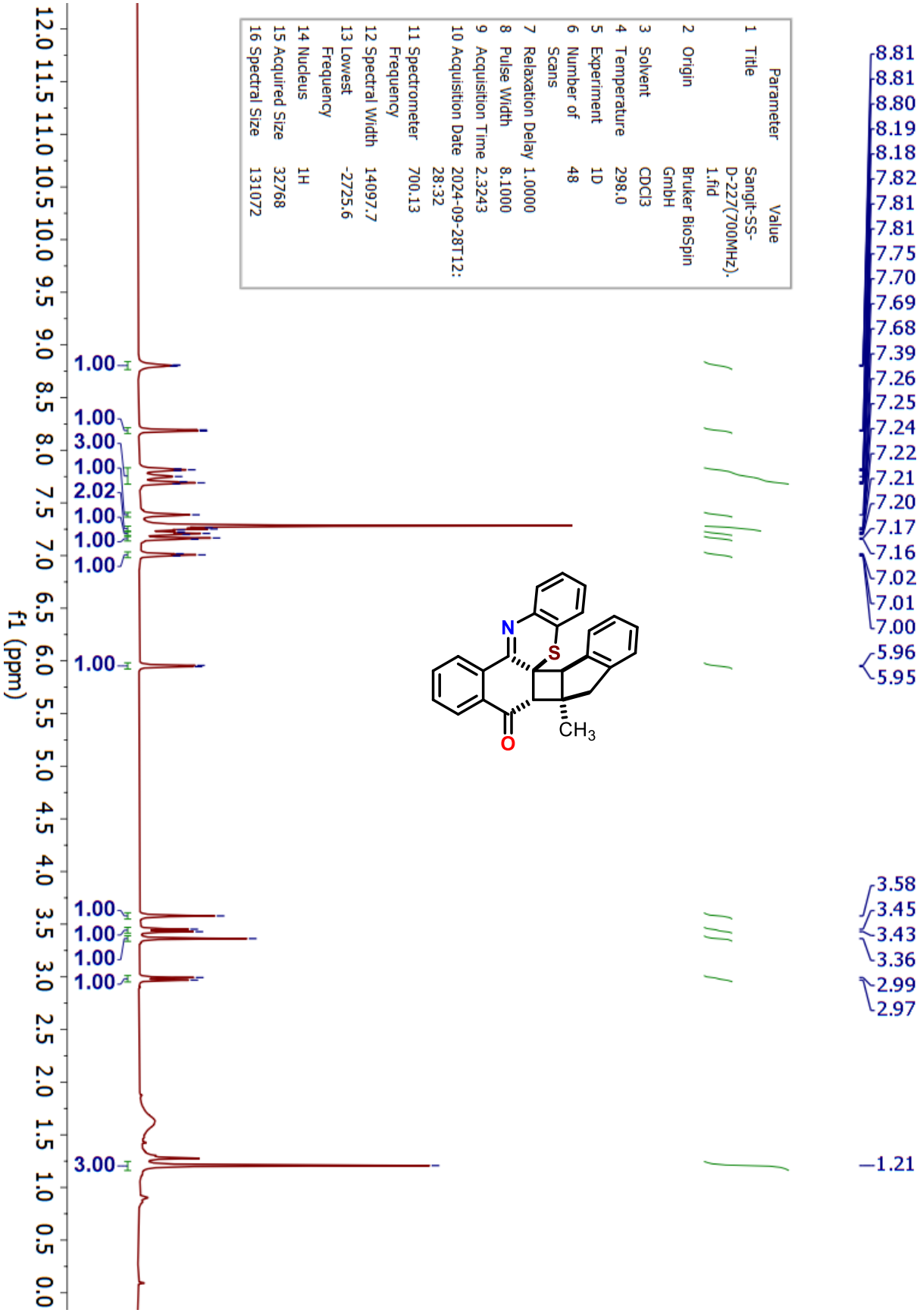
^{1}H NMR spectra of **2af**



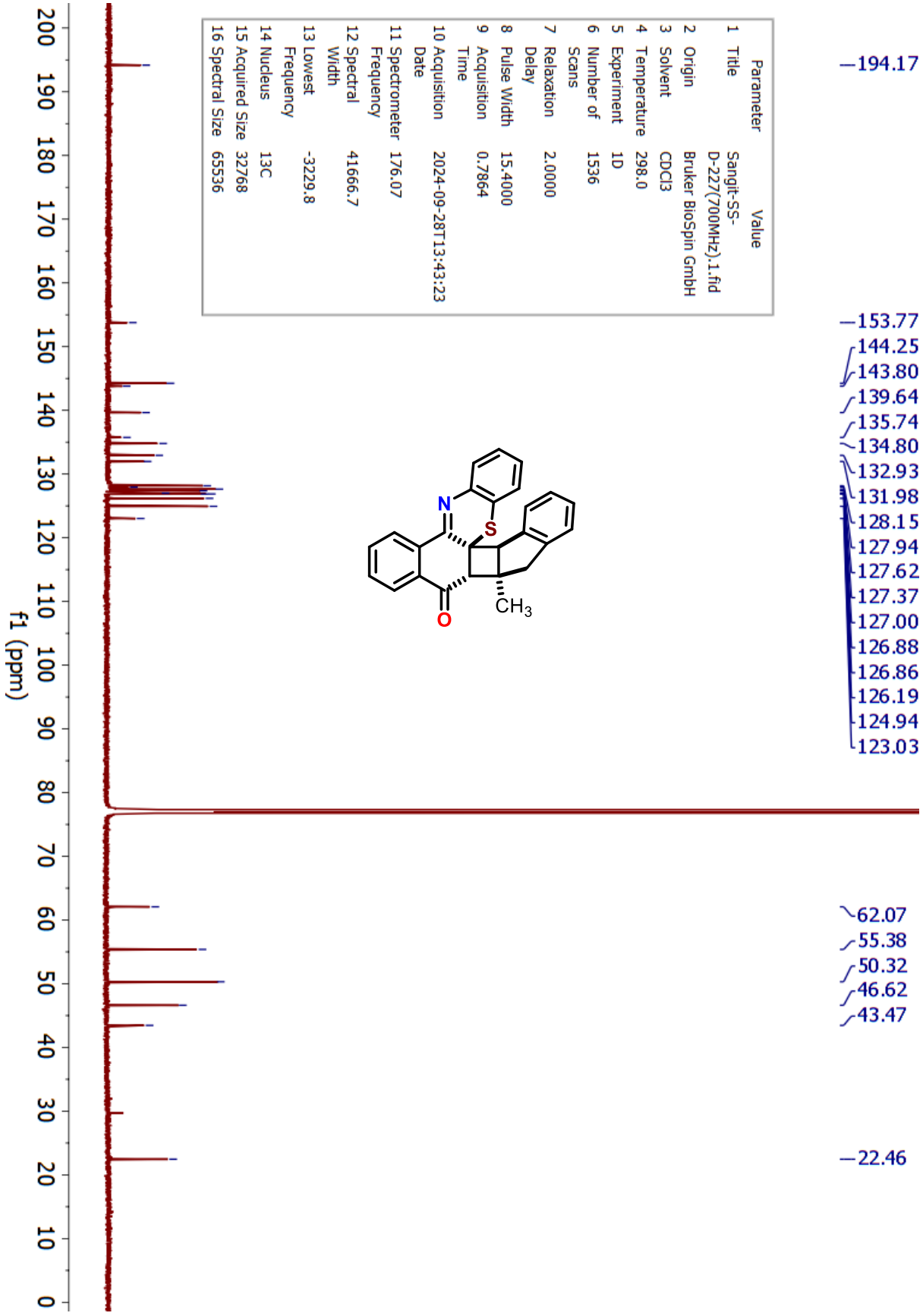
$^{13}C\{^{1}H\}$ NMR spectra of **2af**



^{1}H NMR spectra of **2ag**



$^{13}C\{^{1}H\}$ NMR spectra of **2ag**



Mass Spectrum of **2ah**

Display Report

Analysis Info

Analysis Name	D:\Data\USER DATA 2024\Aug-2024\29-aug\Dr.S.Kumar-SD-214-1.d	Acquisition Date	29-08-2024 16:07:14
Method	tune_wide _APCI_23.06.m	Operator	Bruker
Sample Name	SD-214-1	Instrument	micrOTOF-Q 10330
Comment			

Acquisition Parameter

Source Type	Multi Mode	Ion Polarity	Positive	Set Nebulizer	29.0 psi
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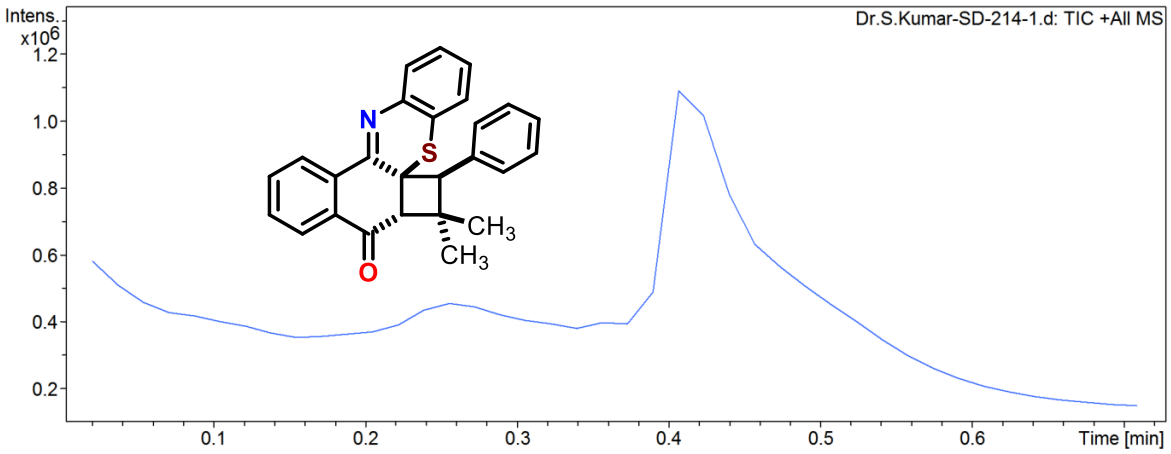
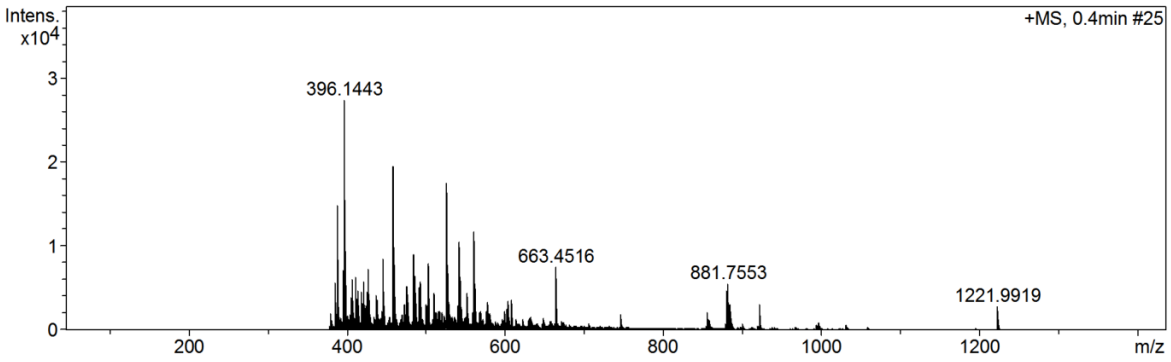
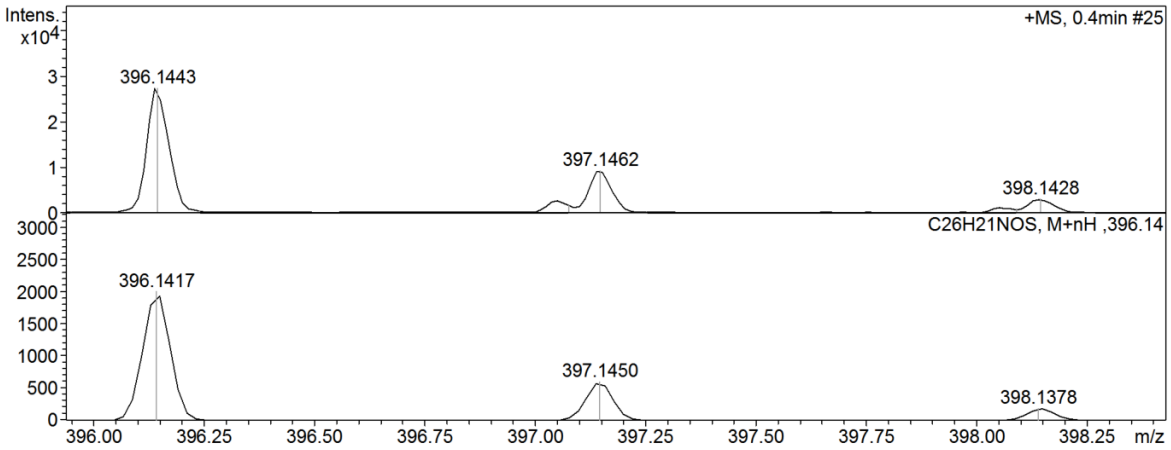
Scan End	3000 m/z	Set Collision Cell RF	750.0 Vpp	Set Divert Valve	Waste







Mass Spectrum of **2ai**

Display Report

Analysis Info

Analysis Name	D:\Data\USER DATA 2024\Sept-2024\18-sept-24\Prof.S.Kumar-SS-D-226.d	Acquisition Date	18-09-2024 14:18:12
Method	tune_low.m	Operator	Bruker
Sample Name	SS-D-226	Instrument	micrOTOF-Q 10330
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	7.3 psi
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
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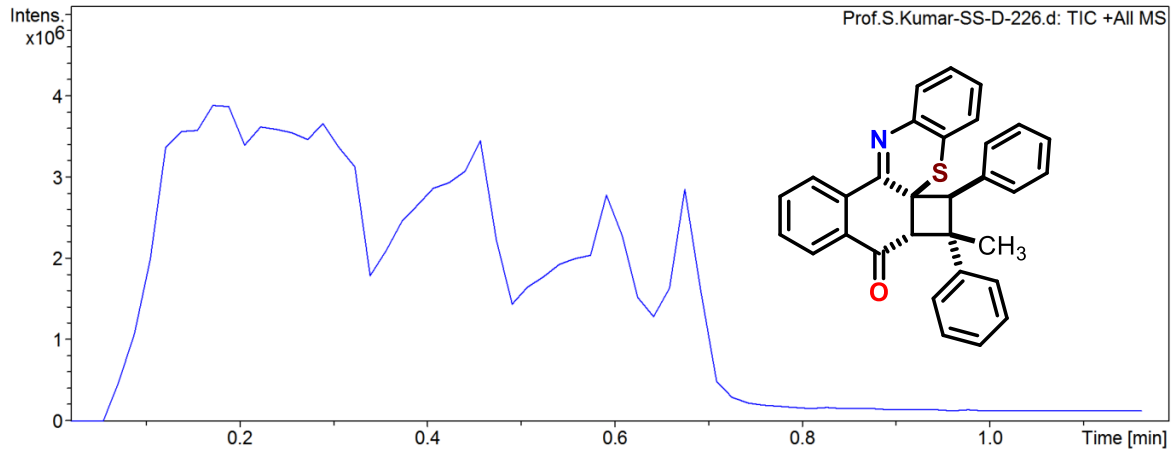
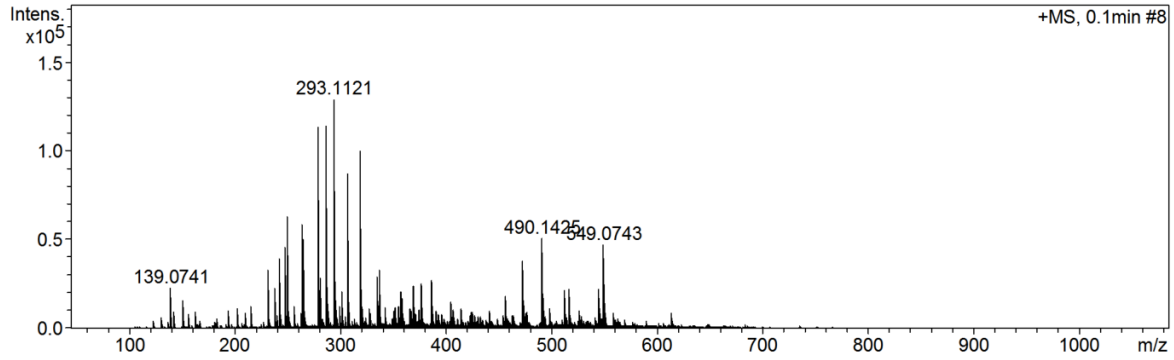
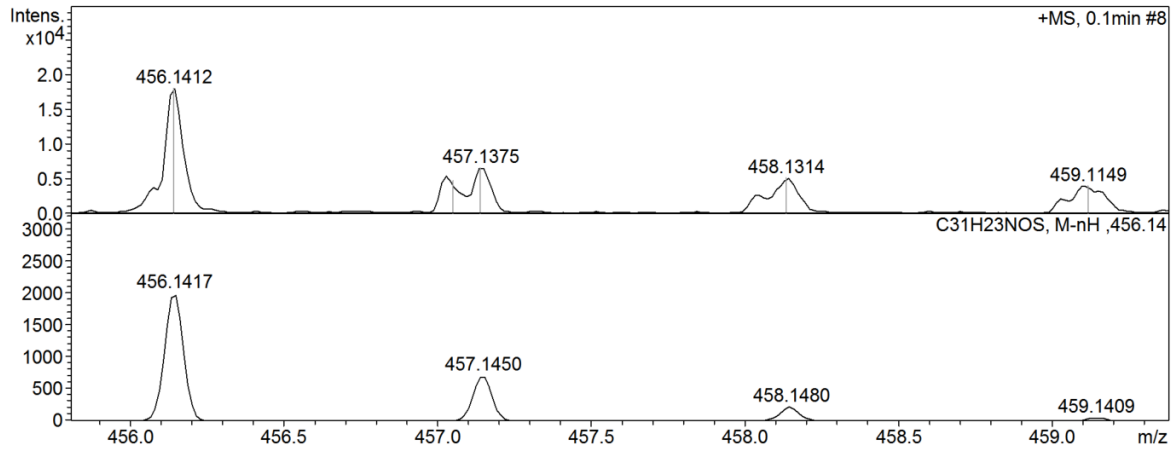
Scan End	3000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste







Mass Spectrum of **2aj**

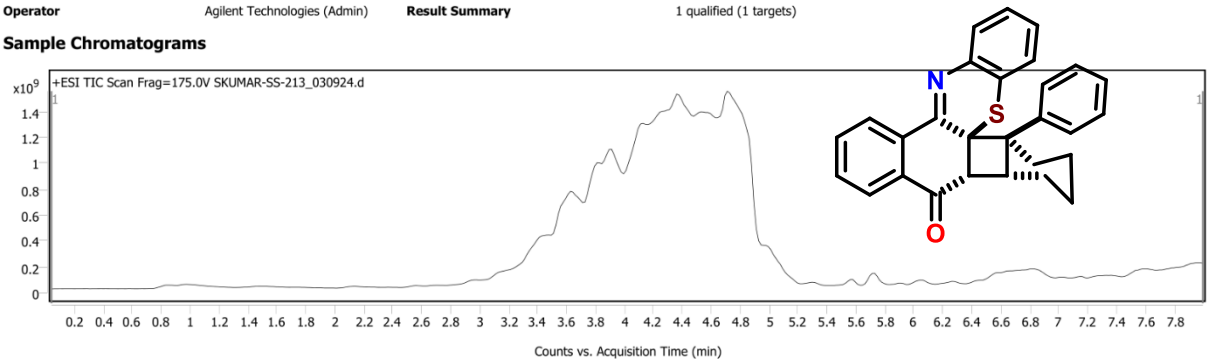
Custom Workflow Report

Agilent | Trusted Answers

Sample Information

Name	SKUMAR-SS-213_030924	**Data File Path**	D:\Projects\small molecules\2024\SEPTEMBER 2024\03 sep\SKUMAR-SS-213_030924.d
Sample ID		**Acq. Time (Local)**	9/3/2024 3:22:43 PM (UTC+05:30)
Instrument	Agilent LCQTOF	**Method Path (Acq)**	D:\Projects\SmallMolecule_Coloumn_21122022\Methods\PRINCI_250724.m
MS Type	QTOF	**Version (Acq SW)**	6200 series TOF/6500 series Q-TOF (11.0.221.1)
Inj. Vol. (ul)	1	**IRM Status**	Success
Position	P2-A5	**Method Path (DA)**	
Plate Pos.		**Target Source Path**	
Operator	Agilent Technologies (Admin)	**Result Summary**	1 qualified (1 targets)

Sample Chromatograms



Compound Summary

Cpd	Name	Formula	RT	Mass	CAS	ID Source	Score	Score (Lib)	Score (DB)	Score (MFG)	Algorithm
1		C28 H23 N O S	3.811	421.1497		FBF	88.72				FBF

Compound Details

Cpd. 1: C28 H23 N O S

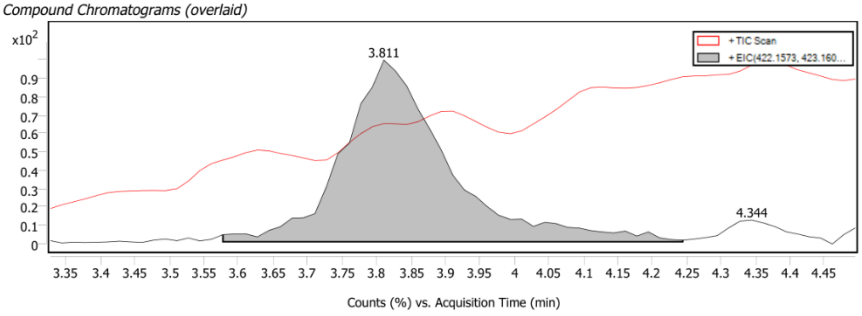
Name	Formula	RT	RI	Mass	Score	Algorithm	Lib/DB
	C28 H23 N O S	3.811		421.1497	88.72	FBF	

Species	m/z	Score (Lib)	Num Spectra	Score (DB)	Score (MFG)	Score (RT)
(M+H)+	422.1572					

Compound ID Table

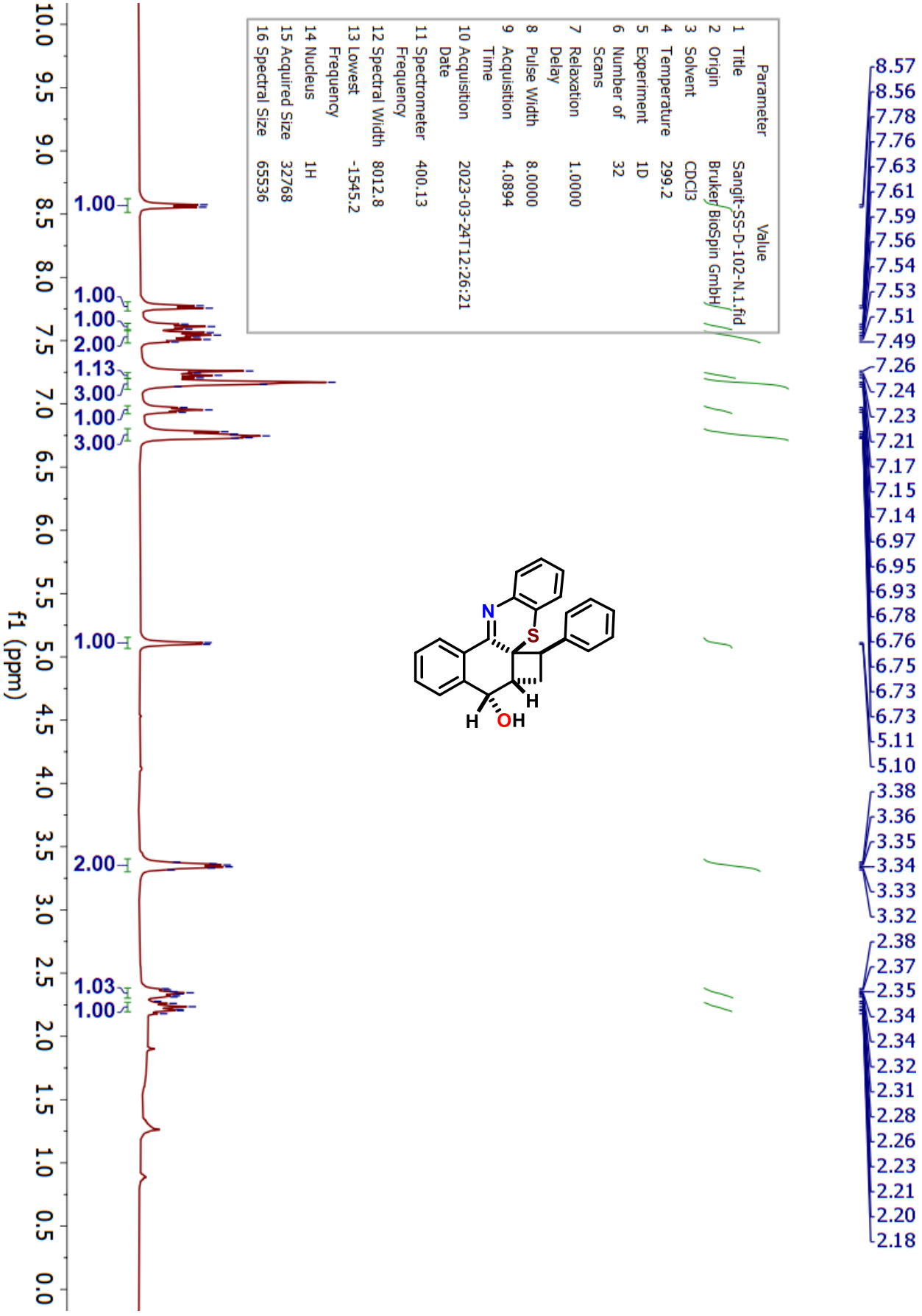
Name	Formula	Species	RT	RT Diff	Mass	CAS	ID Source	Score	Score (DB)	Score (MFG)
	C28 H23 N O S	(M+H)+	3.811		421.1497		FBF	88.72		

Compound Chromatograms (overlaid)

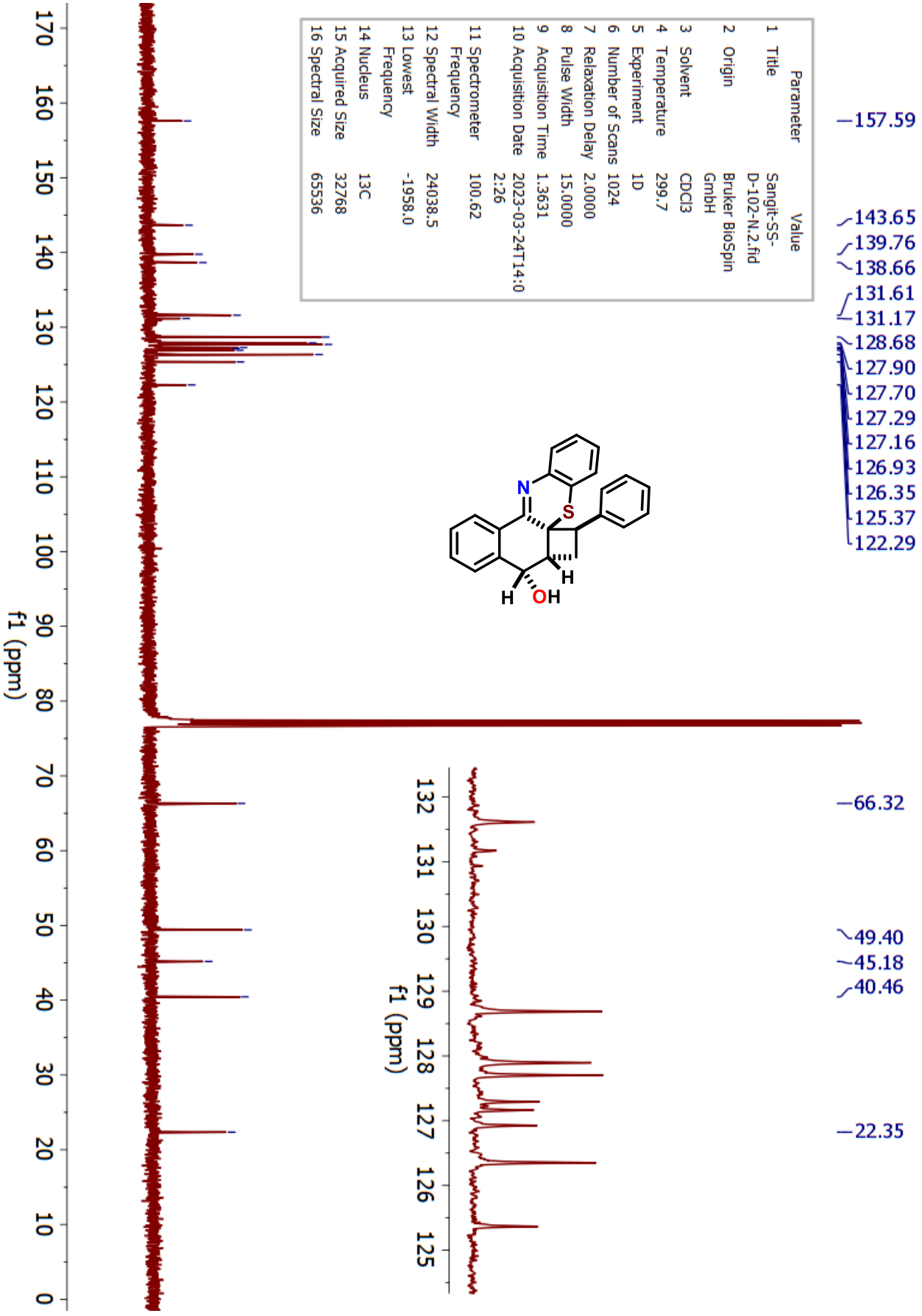


Structure

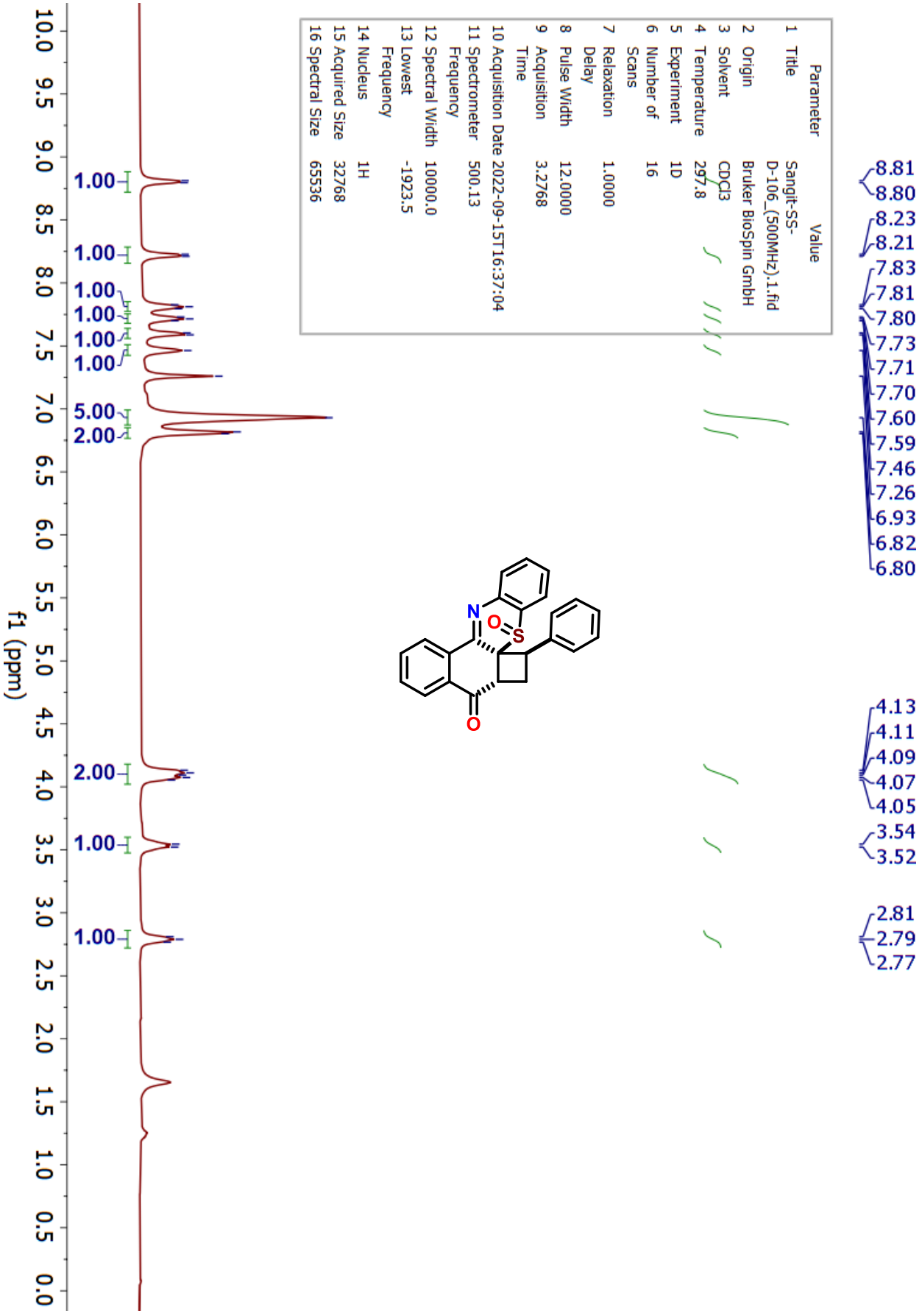
^{1}H NMR spectra of **2ak**



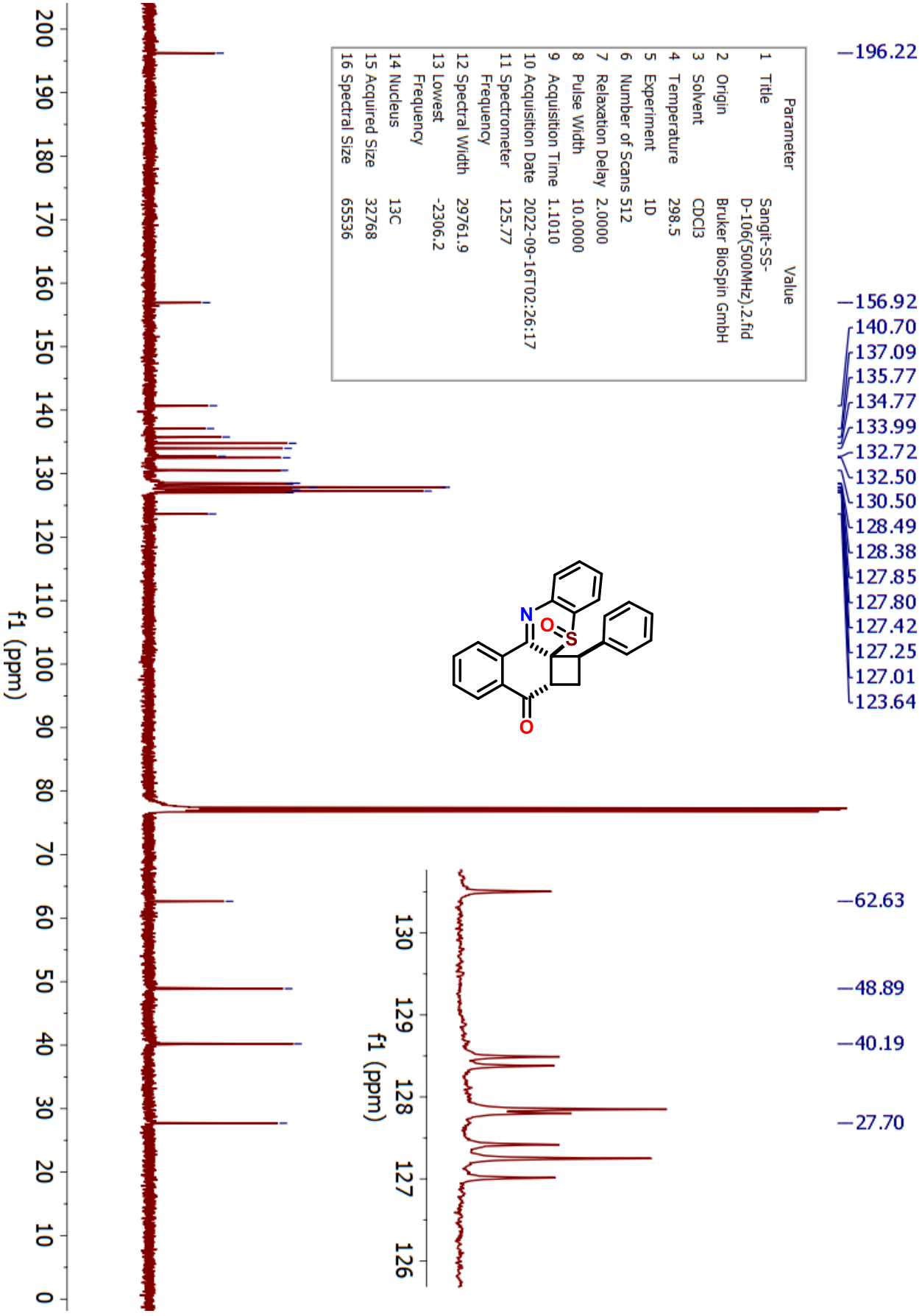
$^{13}C\{^{1}H\}$ NMR spectra of **2ak**



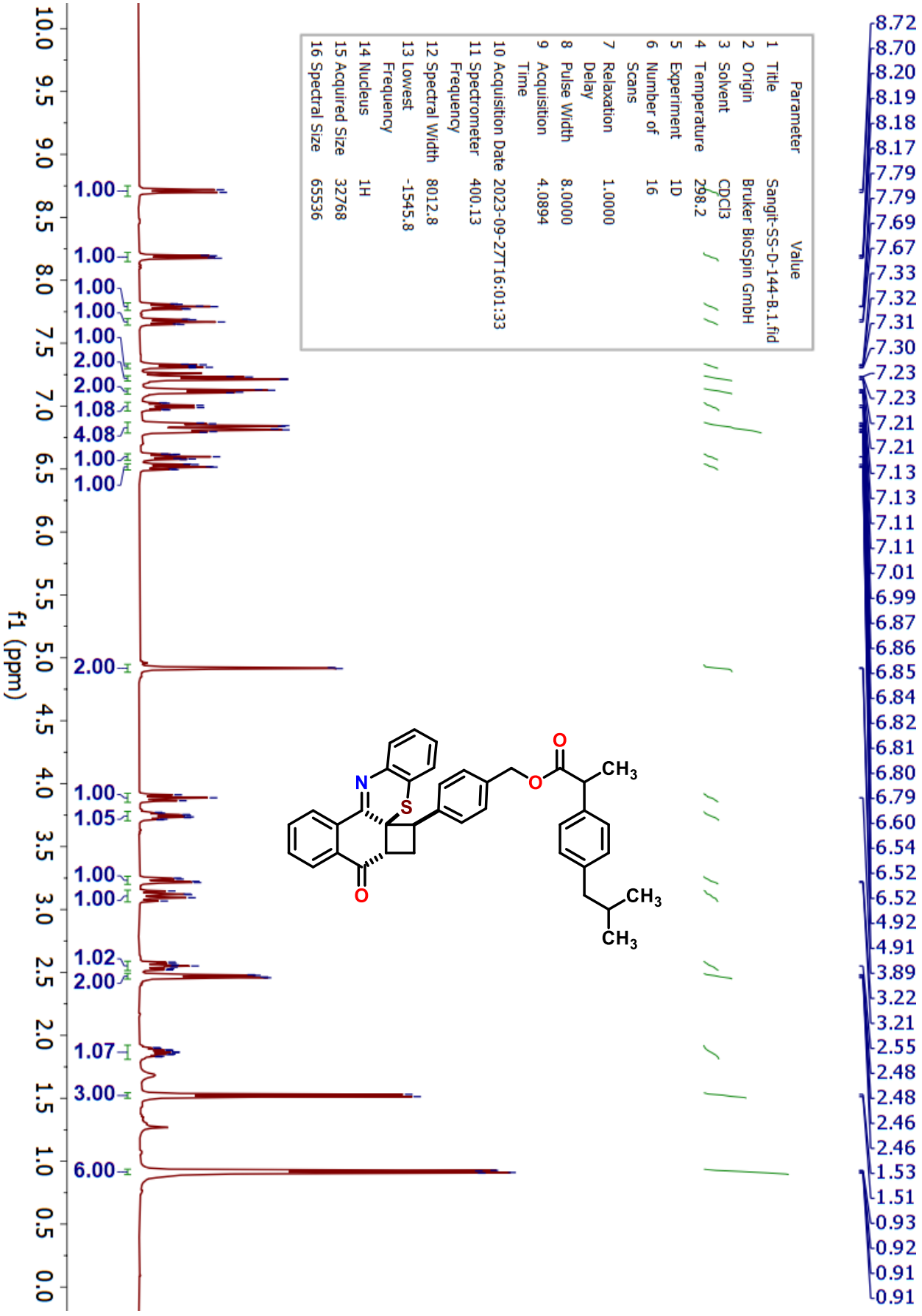
^{1}H NMR spectra of **2al**



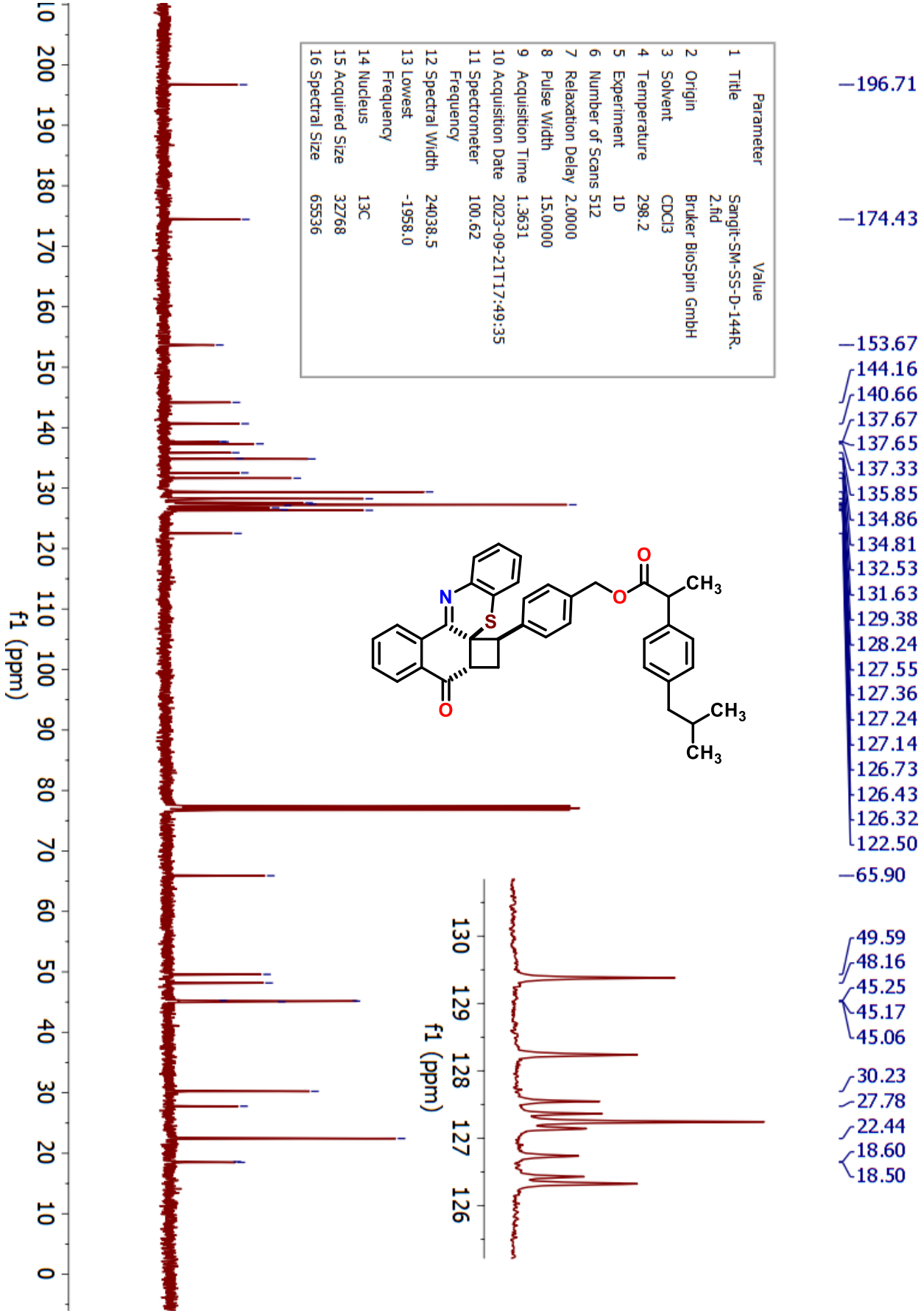
$^{13}C\{^{1}H\}$ NMR spectra of **2al**



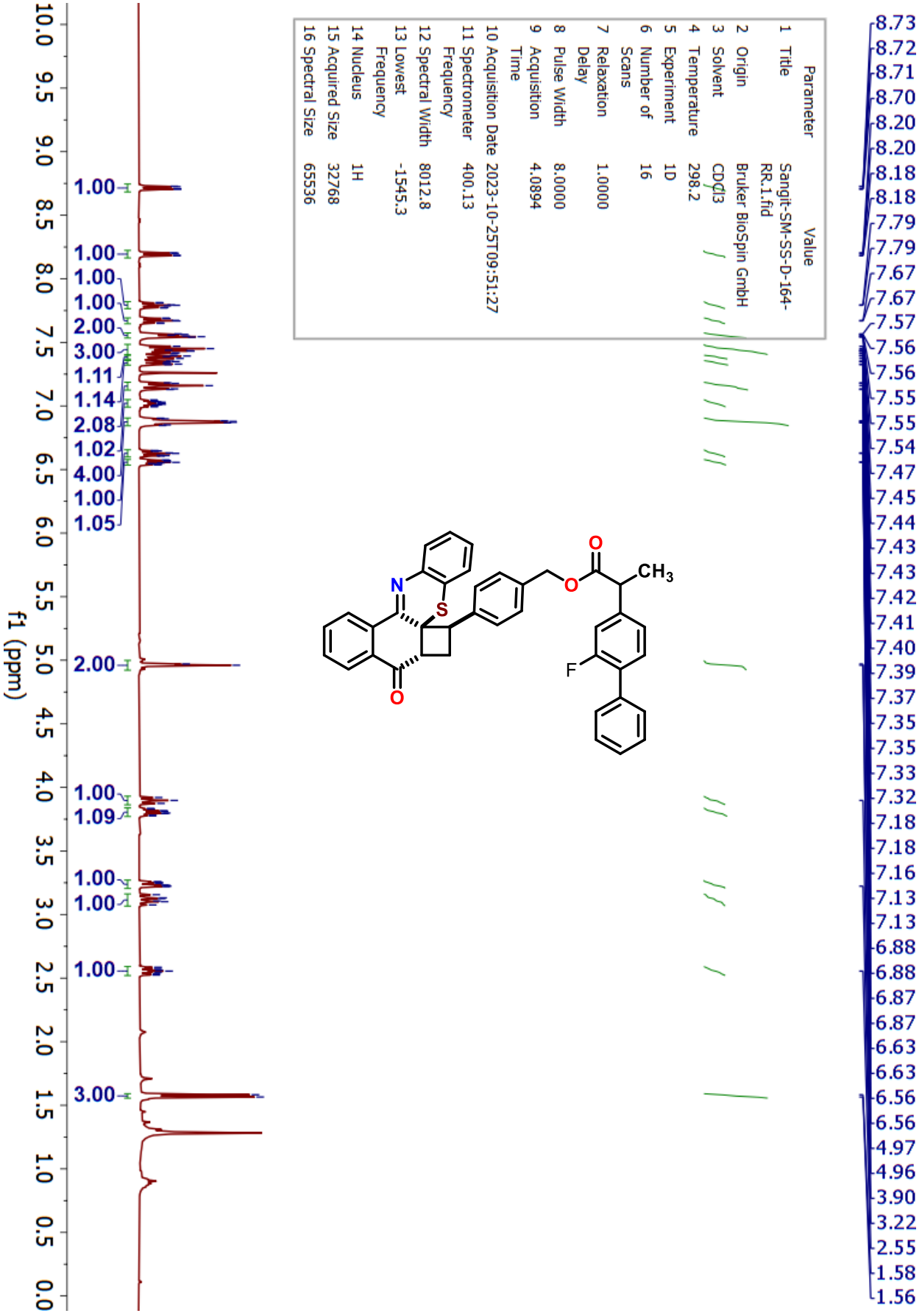
^{1}H NMR spectra of **2am**



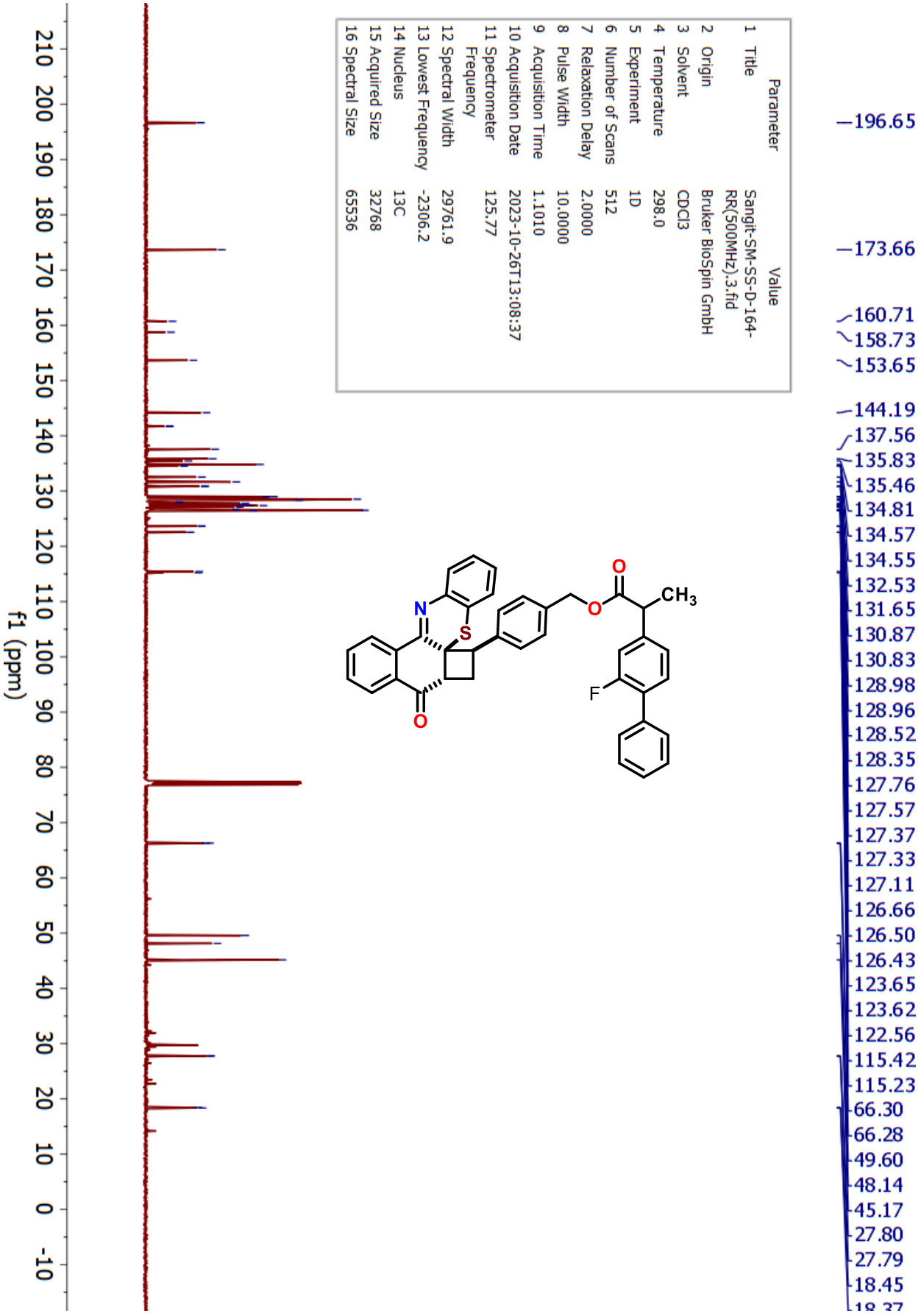
$^{13}C\{^{1}H\}$ NMR spectra of **2am**



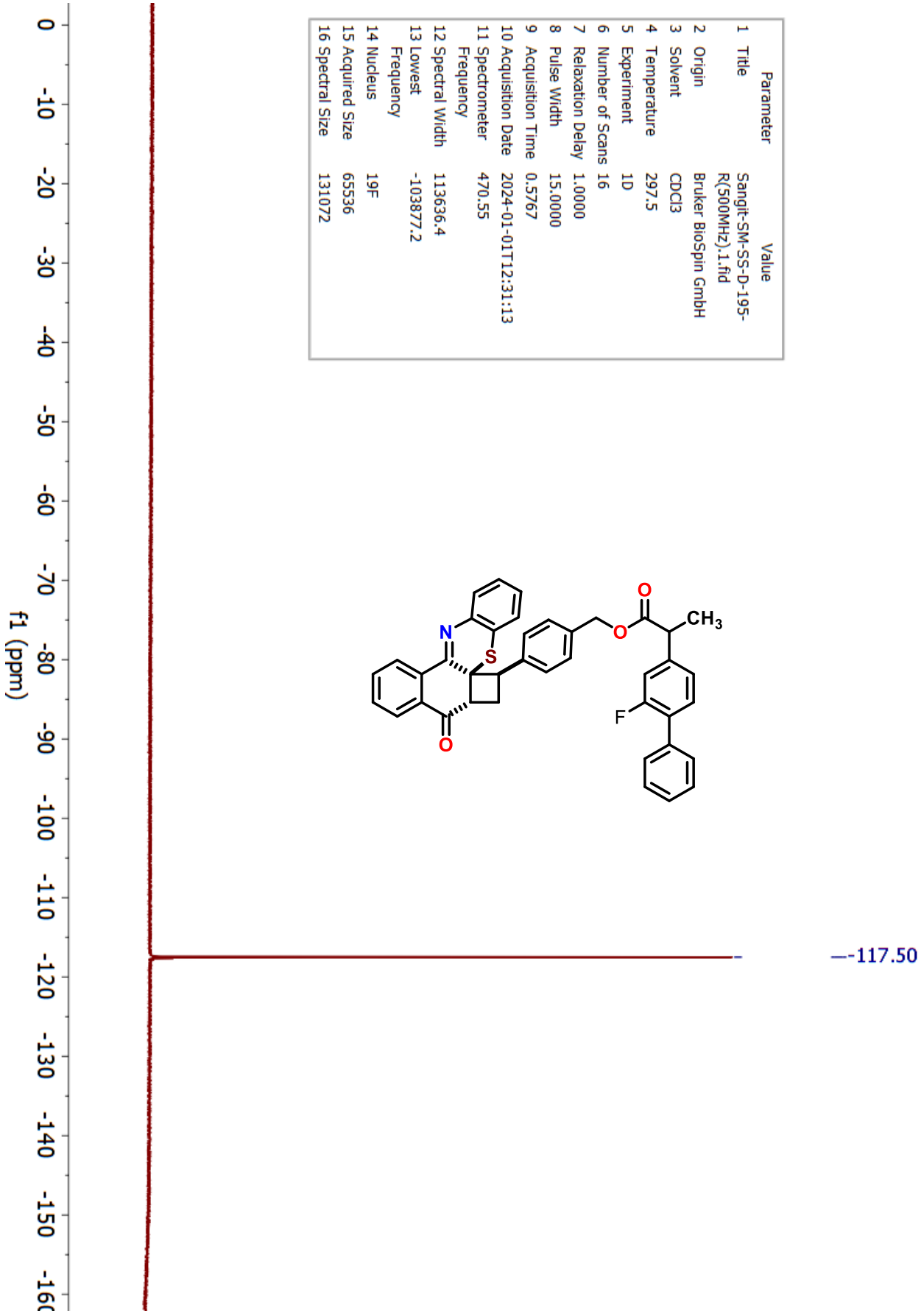
^{1}H NMR spectra of **2an**



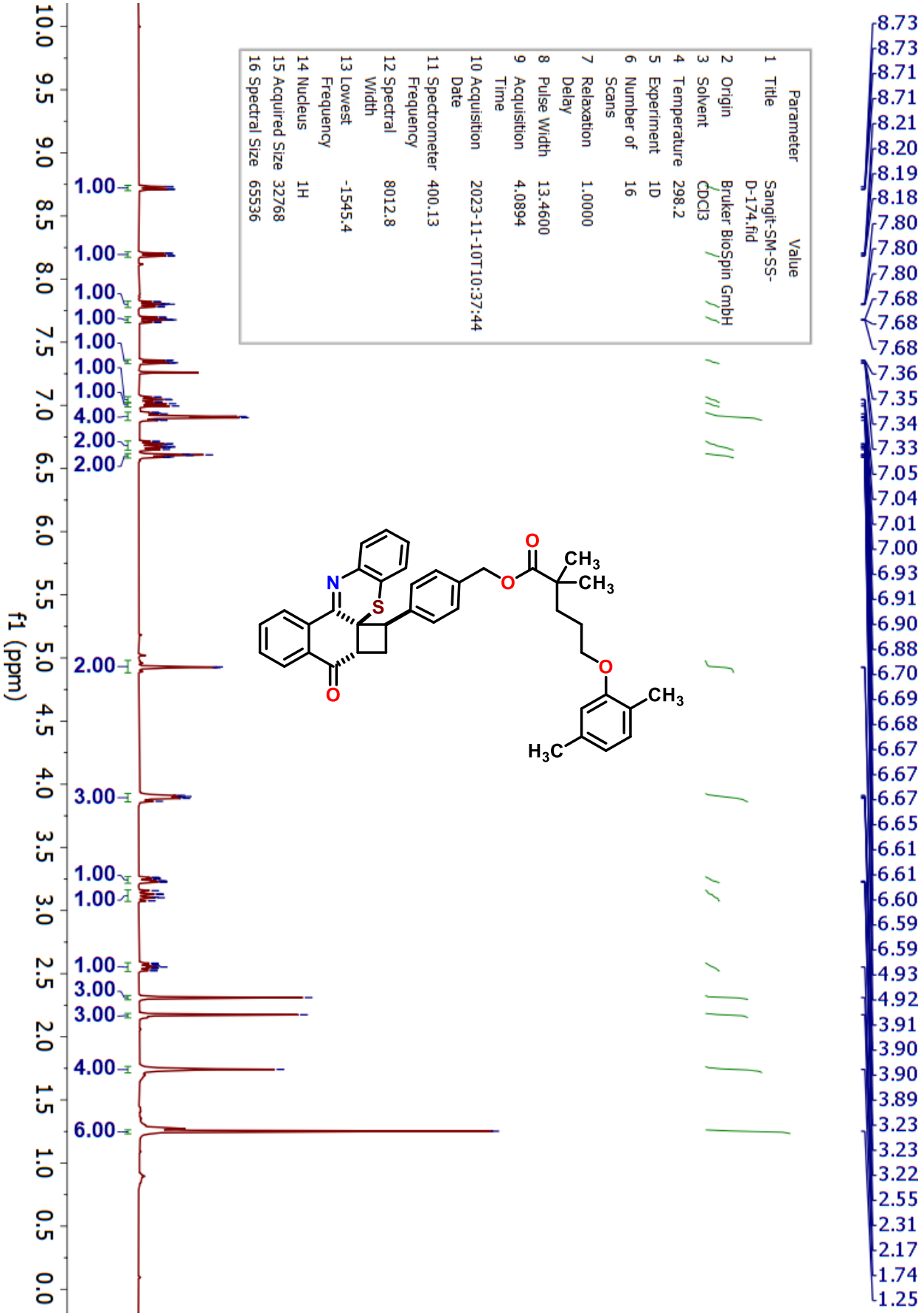
$^{13}C\{^{1}H\}$ NMR spectra of **2an**



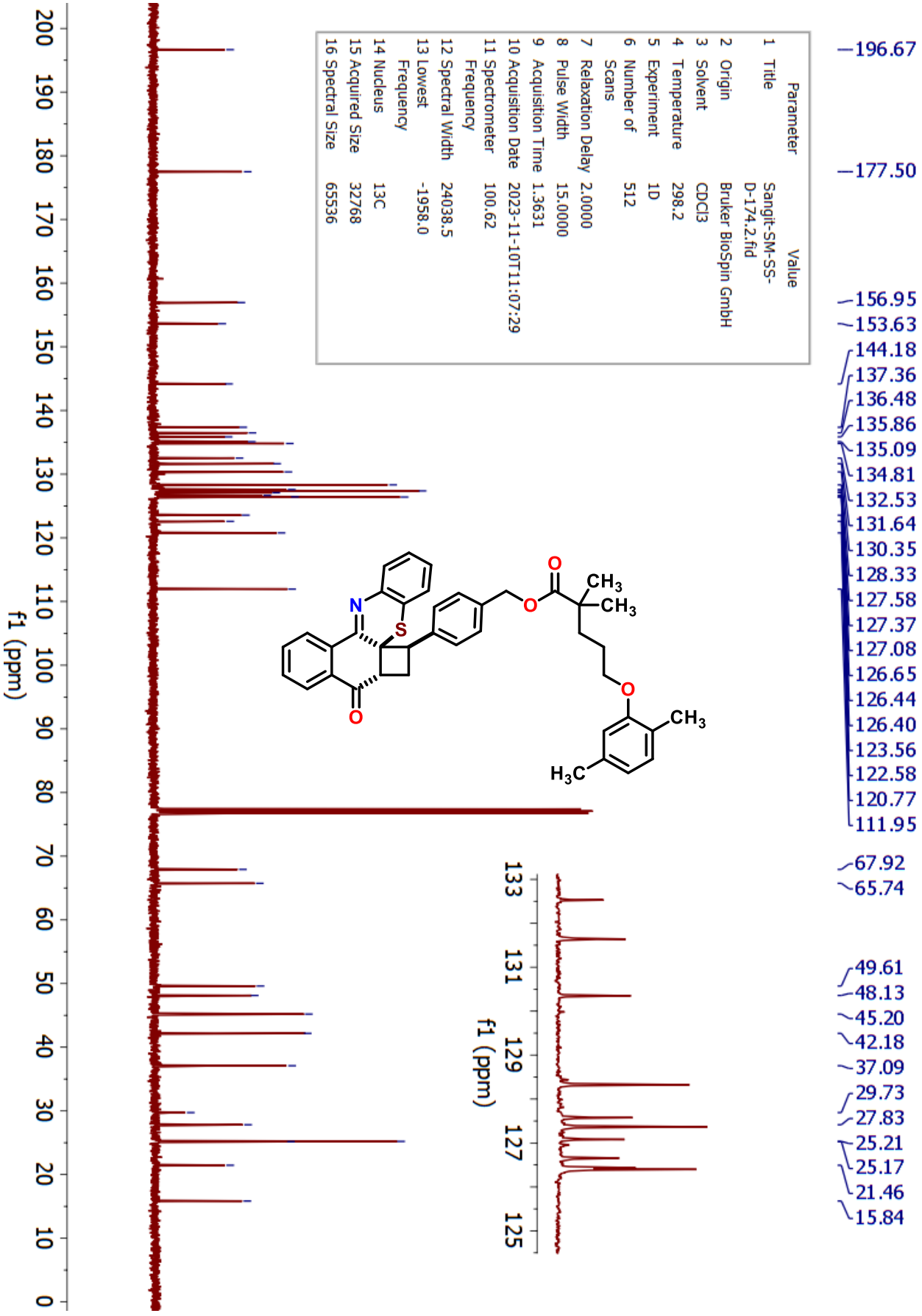
$^{19}F\{^{1}H\}$ NMR spectra of **2an**



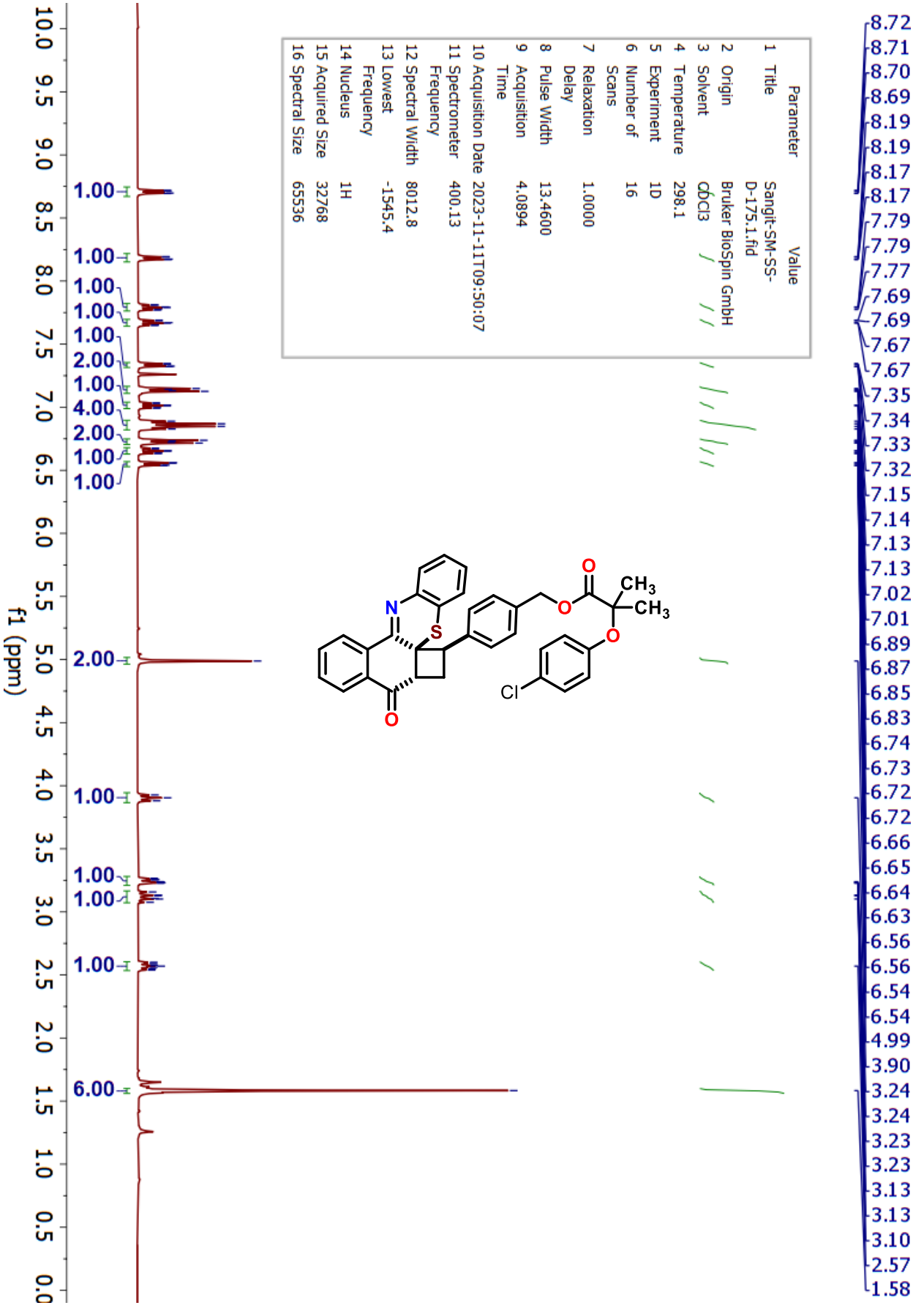
^{1}H NMR spectra of **2ao**



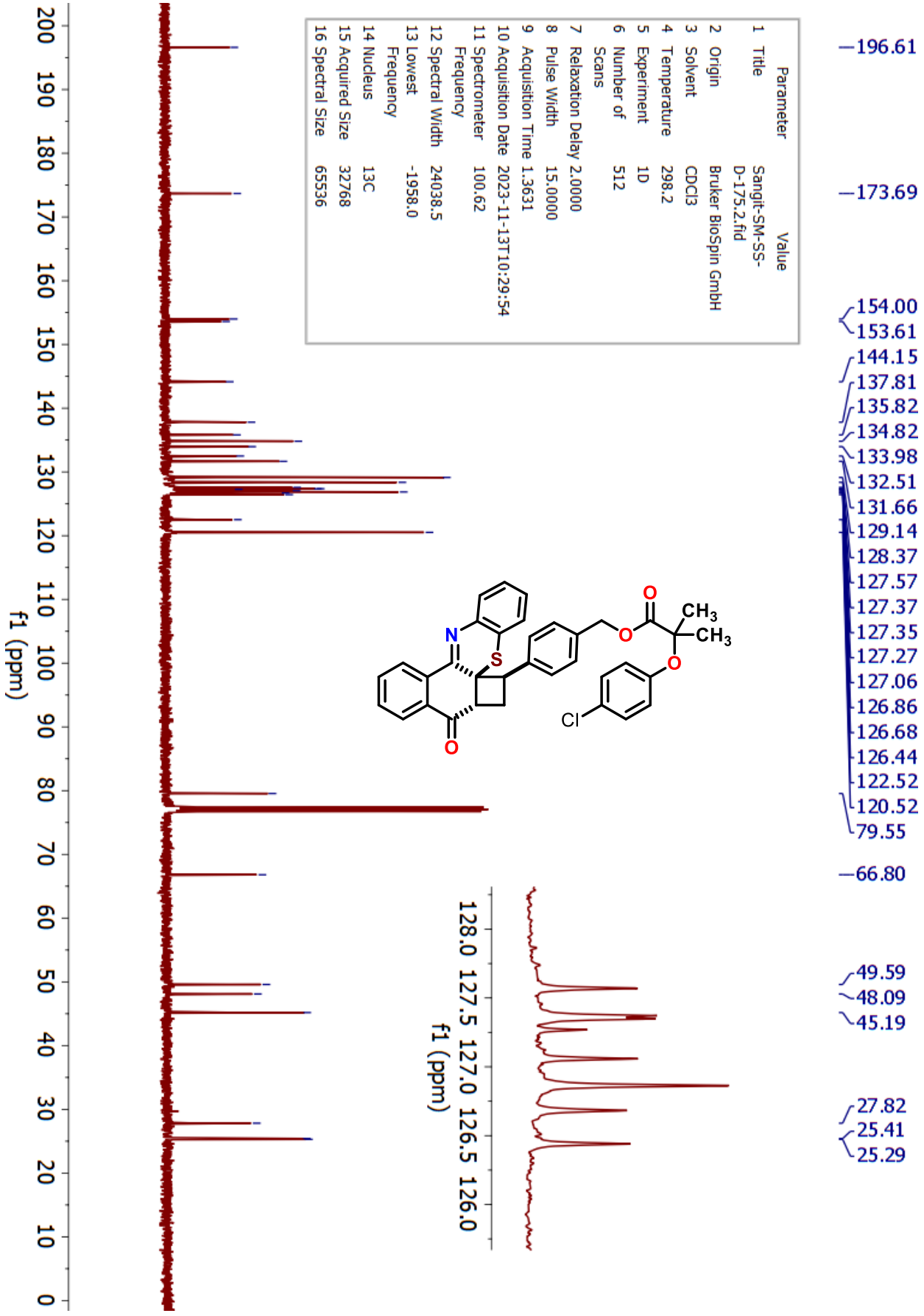
$^{13}C\{^{1}H\}$ NMR spectra of **2ao**



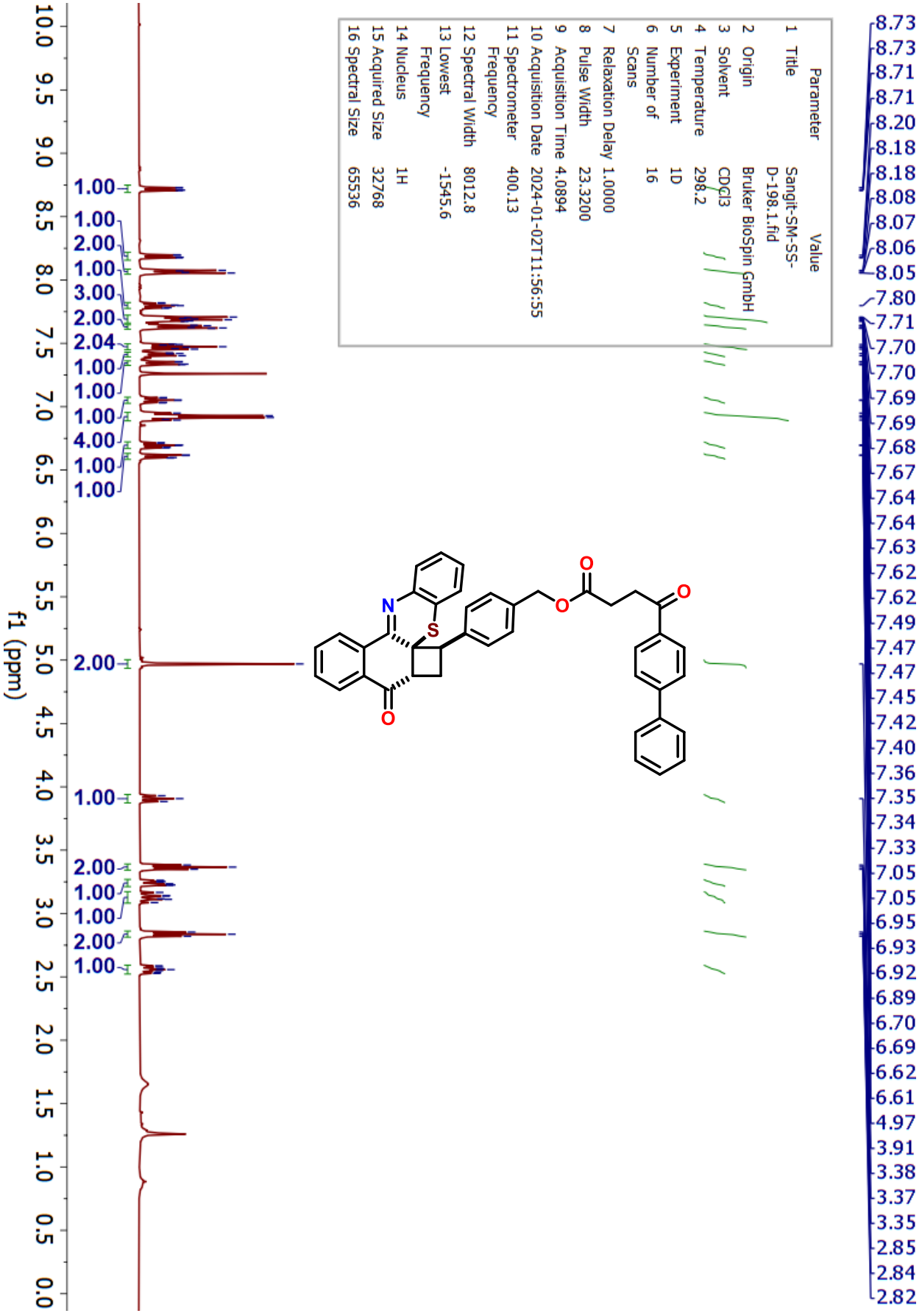
^{1}H NMR spectra of **2ap**



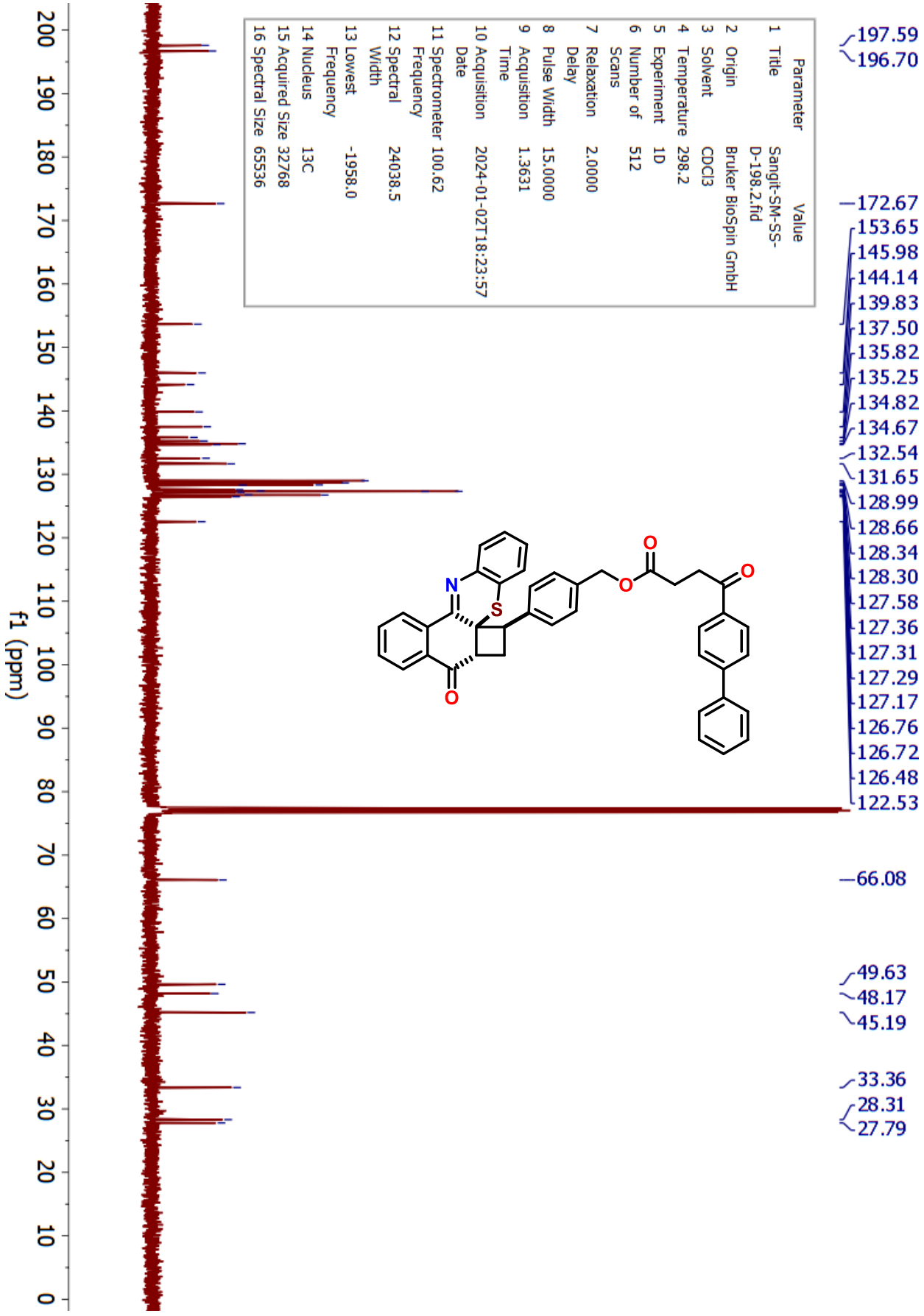
$^{13}C\{^{1}H\}$ NMR spectra of **2ap**



^{1}H NMR spectra of **2aq**



$^{13}C\{^{1}H\}$ NMR spectra of **2aq**



14. Details X-ray Single-crystal Data of 2a, 2o, 2x, 2y, 2ad, 2af, 2ak and 2al

The structures of cyclobutylated phenothiazines **2a** (CCDC: 2332714), **2o** (CCDC: 2332712), **2x** (CCDC: 2403401), **2y** (CCDC: 2403402), **2ad** (CCDC: 2332711), **2af** (CCDC: 2403403), **2ak** (CCDC: 2332713), and **2al** (CCDC: 2403404) were confirmed by X-ray structure analysis. We isolated the suitable single crystals by the slow evaporation method of the solvents, namely, chloroform and dichloromethane. The cyclobutylated phenothiazine **2a** crystallizes in a monoclinic crystal system with a $P2_1/n$ space group. Its crystal structure analysis further revealed that the plane of the cyclobutane ring in **2a** is almost perpendicular to the plane of the 1,4-thiazine ring, with a dihedral angle (θ) of 82° and also to the plane of the iminoquinone ring (θ = 95.8°). This arranges the cyclobutane ring and the 1,4-thiazine ring in a spiro-like orientation containing a quaternary C-centre (**C1**) in between. The *para*-methylated-styrene coupled cyclobutylated phenothiazine **2o** crystallizes in a monoclinic crystal system with a $P2_1/n$ space group as well. Cyclobutylated phenothiazines **2x** snd **2y** crystallize in a monoclinic crystal system having $P2_1/c$ and $P2_1$ space groups, respectively. The cyclobutylated hexacyclic phenothiazine **2ad** crystallizes in a monoclinic crystal system with a $P2_1/c$ space group. Cyclobutylated phenothiazines **2af** having cyclopropyl ring crystalizes in a monoclinic crystal system with $P2_1/n$ space group. The reduced form of **2a,** where the carbonyl group was reduced to its corresponding alcohol **2ak**, was crystallized in a trigonal crystal system with an R-3 space group. The oxidized form of **2a,** where the thio group was oxidized to its corresponding sulfoxide **2al**, was crystallized in an orthorhombic crystal system with a $P2_12_12_1$ space group. Interestingly, crystal structure analysis revealed that there is a strong $\pi - \pi$ interaction between the plane of the phenyl ring of styrene and the phenyl ring of benzothiazine in all of the synthesized cyclobutylated angular phenothiazines.

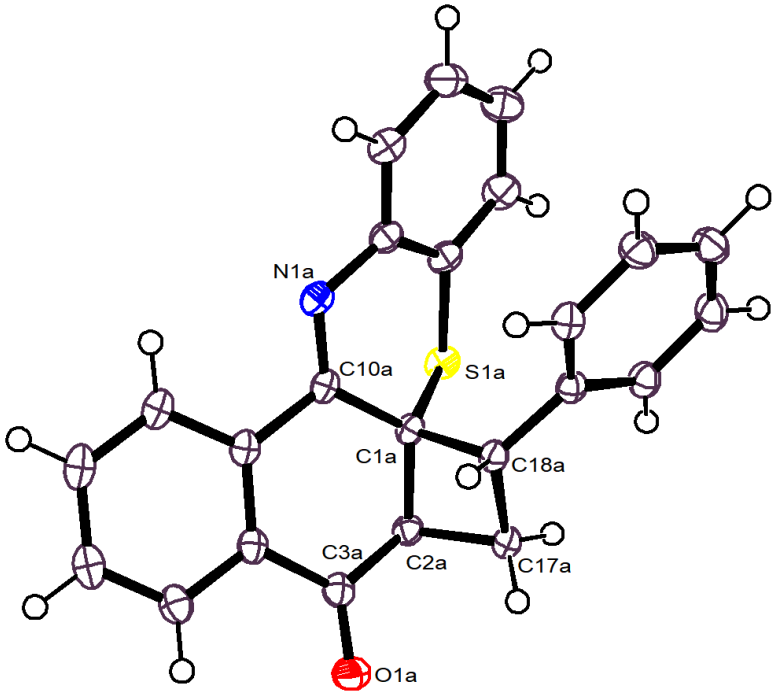


Table S3. Crystal Data and Structure Refinement for 2a.

Identification code	**2a**
CCDC Noumber	**2332714**
Empirical formula	$C_{48}H_{34}N_2O_2S_2$
Formula weight	734.89
Temperature/K	139(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.7018(7)
b/Å	13.6726(8)
c/Å	21.9850(14)
α/°	90
β/°	91.133(3)
γ/°	90
Volume/Å^3	3516.8(4)
Z	4
ρ_{calc}g/cm^3	1.388
μ/mm^{-1}	0.198

F(000)	1536.0
Crystal size/mm^3	0.051 × 0.042 × 0.034
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.912 to 61.038
Index ranges	$-15 \leq h \leq 16$, $-19 \leq k \leq 19$, $-31 \leq l \leq 31$
Reflections collected	92403
Independent reflections	10722 [R_{int} = 0.0739, R_{sigma} = 0.0418]
Data/restraints/parameters	10722/0/487
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0458, wR_2 = 0.1164
Final R indexes [all data]	R_1 = 0.0656, wR_2 = 0.1310
Largest diff. peak/hole / e $Å^{-3}$	0.90/-0.25

Table S4. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 2a. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	10559.6(3)	5741.6(2)	2562.5(2)	18.20(8)
O1	8745.3(9)	7912.5(8)	932.5(5)	25.1(2)
N1	8087.7(9)	5004.9(8)	2565.0(5)	19.4(2)
C1	9316.6(10)	6384.6(9)	2273.7(6)	15.6(2)
C2	9668.1(11)	7053.8(10)	1739.2(6)	18.4(3)
C3	8774.1(11)	7172.0(10)	1240.3(6)	18.3(3)
C4	7977.5(11)	6347.8(10)	1126.1(6)	19.3(3)
C5	7394.5(13)	6307.8(11)	563.4(7)	25.2(3)
C6	6661.2(13)	5540.6(12)	428.7(7)	27.4(3)
C7	6494.4(12)	4807.3(11)	858.2(7)	24.5(3)
C8	7059.7(11)	4840.4(10)	1417.1(7)	20.2(3)
C9	7805.3(11)	5614.6(10)	1562.8(6)	17.9(3)
C10	8391.7(11)	5636.5(9)	2165.0(6)	16.7(2)

Table S4. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 2a. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C11	8724.4(11)	4897.4(10)	3109.6(6)	18.8(3)
C12	8200.1(13)	4428.3(11)	3596.5(7)	24.8(3)
C13	8803.7(14)	4222.6(12)	4126.4(7)	30.4(3)
C14	9962.3(14)	4460.9(12)	4175.8(8)	30.1(3)
C15	10498.1(12)	4921.0(11)	3699.2(7)	24.3(3)
C16	9886.7(11)	5152.9(9)	3166.9(6)	18.6(3)
C17	9736.4(13)	7932.2(10)	2181.5(6)	23.3(3)
C18	9019.8(11)	7349.4(9)	2642.9(6)	17.7(3)
C19	9301.7(11)	7395.2(10)	3311.9(6)	18.1(3)
C20	8504.8(12)	7065.0(11)	3730.5(7)	23.8(3)
C21	8773.1(15)	7043.4(12)	4347.8(7)	29.8(3)
C22	9826.0(15)	7377.9(12)	4561.7(7)	31.0(3)
C23	10618.1(14)	7717.9(11)	4152.4(7)	26.6(3)
C24	10362.7(12)	7724.2(10)	3532.8(6)	20.6(3)
S1A	9379.1(3)	12612.5(3)	2404.8(2)	20.00(9)
O1A	11159.6(9)	10429.0(8)	4038.7(5)	27.2(2)
N1A	11834.9(10)	13403.3(8)	2443.6(5)	20.1(2)
C1A	10623.3(10)	11999.5(10)	2717.1(6)	16.4(2)
C2A	10250.4(11)	11323.2(10)	3241.9(6)	18.1(3)
C3A	11154.3(11)	11173.3(10)	3735.5(6)	19.5(3)
C4A	11996.2(11)	11968.8(10)	3846.5(6)	18.6(3)
C5A	12644.4(12)	11942.6(11)	4388.3(7)	23.2(3)
C6A	13414.5(13)	12682.6(12)	4526.2(7)	26.3(3)
C7A	13536.4(12)	13464.3(11)	4124.9(7)	25.4(3)
C8A	12914.8(11)	13488.7(10)	3582.6(7)	21.4(3)

Table S4. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 2a. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C9A	12146.4(11)	12735.8(10)	3429.5(6)	18.3(3)
C10A	11535.5(11)	12756.2(9)	2834.8(6)	17.2(2)
C11A	11212.1(11)	13523.7(10)	1895.0(6)	19.6(3)
C12A	11738.2(13)	14039.1(11)	1429.1(7)	24.2(3)
C13A	11140.1(14)	14270.4(11)	897.9(7)	28.8(3)
C14A	9997.7(14)	13996.7(12)	829.0(8)	31.3(3)
C15A	9464.3(12)	13480.2(11)	1284.3(7)	25.8(3)
C16A	10062.4(11)	13236.0(10)	1817.5(7)	20.1(3)
C17A	10185.4(12)	10459.3(10)	2787.2(6)	21.4(3)
C18A	10972.7(11)	11040.3(9)	2360.3(6)	17.1(2)
C19A	10824.6(11)	11005.6(9)	1682.5(6)	17.6(3)
C20A	9790.4(12)	10742.6(10)	1398.5(7)	21.5(3)
C21A	9669.0(13)	10776.3(11)	770.1(7)	26.1(3)
C22A	10578.3(14)	11069.0(11)	414.0(7)	26.9(3)
C23A	11607.7(13)	11324.6(11)	691.5(7)	25.7(3)
C24A	11731.9(12)	11292.3(10)	1319.7(7)	21.5(3)

Table S5. Anisotropic Displacement Parameters (Å^2×10^3) for 2a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	13.83(14)	18.50(16)	22.33(17)	0.18(12)	1.68(12)	1.60(11)
O1	28.3(5)	23.7(5)	23.1(5)	4.6(4)	-0.8(4)	-1.9(4)
N1	17.2(5)	17.7(5)	23.4(6)	0.7(4)	-0.5(4)	-1.5(4)
C1	13.2(5)	16.5(6)	17.2(6)	-0.7(5)	0.1(4)	-0.7(4)
C2	17.4(6)	19.1(6)	18.8(6)	0.9(5)	-0.1(5)	-3.1(5)

Table S5. Anisotropic Displacement Parameters ($Å^2×10^3$) for 2a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C3	17.5(6)	20.2(6)	17.2(6)	-1.0(5)	2.5(5)	-0.4(5)
C4	17.9(6)	21.2(6)	18.8(6)	-2.6(5)	0.3(5)	0.7(5)
C5	26.3(7)	29.5(8)	19.6(7)	-1.5(6)	-2.5(5)	-1.4(6)
C6	26.8(7)	32.7(8)	22.5(7)	-7.4(6)	-4.8(6)	-1.5(6)
C7	20.4(6)	24.9(7)	27.9(8)	-9.4(6)	-2.9(5)	-1.9(5)
C8	17.7(6)	18.5(6)	24.3(7)	-3.8(5)	0.6(5)	-0.8(5)
C9	14.9(5)	18.7(6)	20.1(6)	-3.9(5)	0.4(5)	0.6(5)
C10	14.6(5)	15.5(6)	19.9(6)	-1.5(5)	0.3(5)	0.4(4)
C11	19.3(6)	15.8(6)	21.2(7)	0.5(5)	-0.4(5)	-0.3(5)
C12	22.7(7)	23.3(7)	28.5(8)	5.8(6)	1.1(6)	-2.1(5)
C13	32.5(8)	32.1(8)	26.7(8)	11.4(6)	2.3(6)	-2.4(6)
C14	31.1(8)	29.9(8)	29.2(8)	9.2(6)	-5.4(6)	1.0(6)
C15	21.4(6)	22.5(7)	28.7(8)	2.8(6)	-4.4(6)	2.7(5)
C16	18.5(6)	14.9(6)	22.5(7)	0.4(5)	0.6(5)	1.8(5)
C17	32.2(7)	17.9(6)	19.7(7)	1.1(5)	-3.1(6)	-7.0(6)
C18	17.0(6)	14.9(6)	21.0(6)	-1.6(5)	-1.9(5)	0.2(4)
C19	18.2(6)	15.2(6)	21.0(7)	-1.7(5)	0.9(5)	2.6(5)
C20	22.8(6)	20.5(7)	28.3(8)	-2.6(6)	5.6(6)	1.8(5)
C21	39.0(8)	25.5(8)	25.4(8)	0.8(6)	12.1(6)	3.3(6)
C22	47.4(10)	25.4(8)	20.2(7)	0.3(6)	-1.0(7)	6.8(7)
C23	30.5(7)	25.1(7)	23.8(7)	-1.7(6)	-6.8(6)	3.2(6)
C24	20.2(6)	20.2(6)	21.3(7)	-1.6(5)	-0.3(5)	0.9(5)
S1A	13.64(15)	19.58(17)	26.84(19)	0.85(13)	1.91(12)	1.93(11)
O1A	29.4(5)	25.1(5)	26.8(6)	5.7(4)	-2.5(4)	-4.3(4)
N1A	18.0(5)	18.0(5)	24.4(6)	-0.5(4)	1.2(4)	-1.4(4)
C1A	13.7(5)	16.4(6)	19.3(6)	-0.9(5)	0.7(4)	-0.7(4)

Table S5. Anisotropic Displacement Parameters ($Å^2×10^3$) for 2a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C2A	16.3(6)	18.5(6)	19.4(6)	0.2(5)	1.5(5)	-3.0(5)
C3A	18.8(6)	22.0(7)	17.8(6)	-2.1(5)	3.3(5)	-1.2(5)
C4A	16.6(6)	20.5(6)	18.8(6)	-3.9(5)	1.9(5)	-0.5(5)
C5A	22.1(6)	26.8(7)	20.7(7)	-2.5(5)	0.6(5)	-0.1(5)
C6A	23.4(7)	32.3(8)	23.1(7)	-8.1(6)	-2.3(6)	-0.7(6)
C7A	19.6(6)	26.1(7)	30.4(8)	-9.6(6)	-1.2(6)	-2.4(5)
C8A	16.9(6)	19.3(6)	27.9(7)	-5.6(5)	1.8(5)	-1.0(5)
C9A	15.3(6)	18.7(6)	21.1(7)	-4.3(5)	1.0(5)	1.1(5)
C10A	14.7(5)	16.2(6)	20.8(6)	-3.3(5)	1.3(5)	-0.8(4)
C11A	20.1(6)	15.4(6)	23.4(7)	-0.4(5)	1.8(5)	1.6(5)
C12A	23.6(7)	20.9(7)	28.2(8)	1.1(6)	2.5(6)	-1.2(5)
C13A	34.5(8)	25.8(8)	26.4(8)	5.4(6)	4.1(6)	1.2(6)
C14A	35.2(8)	28.1(8)	30.4(8)	7.1(6)	-4.8(7)	4.4(7)
C15A	21.6(7)	23.5(7)	32.3(8)	2.9(6)	-3.6(6)	3.2(5)
C16A	19.5(6)	15.1(6)	25.6(7)	0.4(5)	2.0(5)	2.9(5)
C17A	26.7(7)	18.4(6)	19.0(6)	-1.0(5)	-0.9(5)	-5.8(5)
C18A	16.9(6)	15.4(6)	19.1(6)	-1.7(5)	-0.9(5)	0.3(5)
C19A	17.7(6)	15.2(6)	20.0(6)	-1.3(5)	-1.2(5)	2.4(5)
C20A	19.1(6)	21.1(7)	24.2(7)	-1.7(5)	-2.1(5)	0.1(5)
C21A	26.9(7)	24.2(7)	26.9(8)	-3.0(6)	-9.3(6)	1.6(6)
C22A	36.0(8)	24.1(7)	20.4(7)	-0.2(6)	-3.8(6)	5.3(6)
C23A	28.7(7)	26.2(7)	22.3(7)	0.0(6)	5.0(6)	0.0(6)
C24A	19.7(6)	21.0(7)	23.8(7)	-3.2(5)	-1.1(5)	0.4(5)

Table S6. Bond Lengths for 2a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C1	1.8042(13)	S1A	C1A	1.8039(13)
S1	C16	1.7536(14)	S1A	C16A	1.7532(15)
O1	C3	1.2177(17)	O1A	C3A	1.2165(17)
N1	C10	1.2876(17)	N1A	C10A	1.2873(18)
N1	C11	1.4054(17)	N1A	C11A	1.4065(17)
C1	C2	1.5512(18)	C1A	C2A	1.5481(18)
C1	C10	1.5048(17)	C1A	C10A	1.5053(17)
C1	C18	1.5907(18)	C1A	C18A	1.5859(18)
C2	C3	1.5095(18)	C2A	C3A	1.5141(18)
C2	C17	1.5464(19)	C2A	C17A	1.5483(19)
C3	C4	1.4808(18)	C3A	C4A	1.4844(18)
C4	C5	1.4020(18)	C4A	C5A	1.3998(18)
C4	C9	1.4052(19)	C4A	C9A	1.4063(19)
C5	C6	1.384(2)	C5A	C6A	1.385(2)
C6	C7	1.394(2)	C6A	C7A	1.395(2)
C7	C8	1.3846(19)	C7A	C8A	1.385(2)
C8	C9	1.4048(18)	C8A	C9A	1.4034(18)
C9	C10	1.4794(18)	C9A	C10A	1.4778(18)
C11	C12	1.400(2)	C11A	C12A	1.396(2)
C11	C16	1.4074(18)	C11A	C16A	1.4088(18)
C12	C13	1.379(2)	C12A	C13A	1.386(2)
C13	C14	1.397(2)	C13A	C14A	1.394(2)
C14	C15	1.383(2)	C14A	C15A	1.384(2)
C15	C16	1.3960(19)	C15A	C16A	1.394(2)
C17	C18	1.549(2)	C17A	C18A	1.547(2)
C18	C19	1.5023(19)	C18A	C19A	1.4976(18)

Table S6. Bond Lengths for 2a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C19	C20	1.398(2)	C19A	C20A	1.3978(18)
C19	C24	1.3986(18)	C19A	C24A	1.397(2)
C20	C21	1.387(2)	C20A	C21A	1.387(2)
C21	C22	1.388(2)	C21A	C22A	1.392(2)
C22	C23	1.385(2)	C22A	C23A	1.384(2)
C23	C24	1.389(2)	C23A	C24A	1.386(2)

Table S7. Bond Angles for 2a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C16	S1	C1	96.85(6)	C16A	S1A	C1A	97.46(6)
C10	N1	C11	120.20(11)	C10A	N1A	C11A	120.67(11)
C2	C1	S1	109.26(9)	C2A	C1A	S1A	108.91(9)
C2	C1	C18	87.78(10)	C2A	C1A	C18A	87.35(10)
C10	C1	S1	107.27(9)	C10A	C1A	S1A	108.08(9)
C10	C1	C2	118.77(11)	C10A	C1A	C2A	119.46(11)
C10	C1	C18	118.76(10)	C10A	C1A	C18A	117.68(10)
C18	C1	S1	114.03(8)	C18A	C1A	S1A	114.20(9)
C3	C2	C1	115.04(11)	C1A	C2A	C17A	89.16(10)
C3	C2	C17	113.59(11)	C3A	C2A	C1A	114.31(11)
C17	C2	C1	89.60(10)	C3A	C2A	C17A	112.60(11)
O1	C3	C2	120.26(12)	O1A	C3A	C2A	120.12(12)
O1	C3	C4	121.88(12)	O1A	C3A	C4A	121.78(12)
C4	C3	C2	117.81(12)	C4A	C3A	C2A	118.08(12)
C5	C4	C3	118.22(13)	C5A	C4A	C3A	117.90(13)
C5	C4	C9	120.08(13)	C5A	C4A	C9A	120.08(12)
C9	C4	C3	121.69(12)	C9A	C4A	C3A	122.02(12)

Table S7. Bond Angles for 2a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C6	C5	C4	120.48(14)	C6A	C5A	C4A	120.47(14)
C5	C6	C7	119.67(13)	C5A	C6A	C7A	119.71(13)
C8	C7	C6	120.45(13)	C8A	C7A	C6A	120.30(13)
C7	C8	C9	120.71(13)	C7A	C8A	C9A	120.80(14)
C4	C9	C10	121.78(12)	C4A	C9A	C10A	121.76(12)
C8	C9	C4	118.58(12)	C8A	C9A	C4A	118.58(12)
C8	C9	C10	119.63(12)	C8A	C9A	C10A	119.65(13)
N1	C10	C1	123.71(12)	N1A	C10A	C1A	123.98(12)
N1	C10	C9	117.91(12)	N1A	C10A	C9A	118.08(12)
C9	C10	C1	118.38(11)	C9A	C10A	C1A	117.91(12)
N1	C11	C16	123.05(12)	N1A	C11A	C16A	123.26(13)
C12	C11	N1	117.80(12)	C12A	C11A	N1A	117.36(12)
C12	C11	C16	118.86(13)	C12A	C11A	C16A	119.08(13)
C13	C12	C11	120.95(14)	C13A	C12A	C11A	120.71(14)
C12	C13	C14	119.89(14)	C12A	C13A	C14A	119.84(15)
C15	C14	C13	120.07(14)	C15A	C14A	C13A	120.26(14)
C14	C15	C16	120.39(13)	C14A	C15A	C16A	120.29(14)
C11	C16	S1	119.58(10)	C11A	C16A	S1A	119.68(11)
C15	C16	S1	120.61(10)	C15A	C16A	S1A	120.47(11)
C15	C16	C11	119.80(13)	C15A	C16A	C11A	119.82(13)
C2	C17	C18	89.44(10)	C18A	C17A	C2A	88.72(10)
C17	C18	C1	88.05(10)	C17A	C18A	C1A	87.83(10)
C19	C18	C1	119.22(10)	C19A	C18A	C1A	119.51(11)
C19	C18	C17	120.55(11)	C19A	C18A	C17A	121.91(11)
C20	C19	C18	119.65(12)	C20A	C19A	C18A	122.33(12)
C20	C19	C24	118.32(13)	C24A	C19A	C18A	119.02(11)

Table S7. Bond Angles for 2a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C24	C19	C18	121.98(12)	C24A	C19A	C20A	118.57(13)
C21	C20	C19	120.66(14)	C21A	C20A	C19A	120.48(14)
C20	C21	C22	120.45(15)	C20A	C21A	C22A	120.36(13)
C23	C22	C21	119.45(14)	C23A	C22A	C21A	119.52(14)
C22	C23	C24	120.37(14)	C22A	C23A	C24A	120.28(14)
C23	C24	C19	120.73(14)	C23A	C24A	C19A	120.79(13)

Table S8. Hydrogen Bonds for 2a.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
C12	H12	O1[1]	0.95	2.55	3.2623(18)	132.2
C18	H18	S1A[1]	1.00	3.01	3.9929(14)	166.4
C12A	H12A	O1A[2]	0.95	2.54	3.2896(19)	136.3

[1]3/2-X,-1/2+Y,1/2-Z; [2]5/2-X,1/2+Y,1/2-Z

Table S9. Torsion Angles for 2a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S1	C1	C2	C3	146.19(10)	S1A	C1A	C2A	C3A	-150.36(10)
S1	C1	C2	C17	-97.81(10)	S1A	C1A	C2A	C17A	95.11(10)
S1	C1	C10	N1	50.97(15)	S1A	C1A	C10A	N1A	-48.83(16)
S1	C1	C10	C9	-128.27(10)	S1A	C1A	C10A	C9A	133.00(10)
S1	C1	C18	C17	93.25(10)	S1A	C1A	C18A	C17A	-89.95(10)
S1	C1	C18	C19	-31.06(15)	S1A	C1A	C18A	C19A	35.95(15)
O1	C3	C4	C5	17.1(2)	O1A	C3A	C4A	C5A	-13.4(2)
O1	C3	C4	C9	-163.39(13)	O1A	C3A	C4A	C9A	167.08(14)
N1	C11	C12	C13	174.41(14)	N1A	C11A	C12A	C13A	-173.65(13)
N1	C11	C16	S1	6.35(19)	N1A	C11A	C16A	S1A	-5.00(19)

Table S9. Torsion Angles for 2a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N1	C11	C16	C15	-172.54(13)	N1A	C11A	C16A	C15A	172.65(13)
C1	S1	C16	C11	30.97(12)	C1A	S1A	C16A	C11A	-30.51(12)
C1	S1	C16	C15	-150.15(12)	C1A	S1A	C16A	C15A	151.86(12)
C1	C2	C3	O1	152.33(13)	C1A	C2A	C3A	O1A	-153.11(13)
C1	C2	C3	C4	-30.08(17)	C1A	C2A	C3A	C4A	28.77(17)
C1	C2	C17	C18	-17.36(10)	C1A	C2A	C17A	C18A	20.08(10)
C1	C18	C19	C20	-88.63(15)	C1A	C18A	C19A	C20A	-85.38(16)
C1	C18	C19	C24	88.76(15)	C1A	C18A	C19A	C24A	91.34(15)
C2	C1	C10	N1	175.37(12)	C2A	C1A	C10A	N1A	-174.00(12)
C2	C1	C10	C9	-3.88(17)	C2A	C1A	C10A	C9A	7.84(17)
C2	C1	C18	C17	-16.88(9)	C2A	C1A	C18A	C17A	19.62(9)
C2	C1	C18	C19	-141.20(12)	C2A	C1A	C18A	C19A	145.52(12)
C2	C3	C4	C5	-160.49(13)	C2A	C3A	C4A	C5A	164.68(12)
C2	C3	C4	C9	19.06(19)	C2A	C3A	C4A	C9A	-14.84(19)
C2	C17	C18	C1	16.92(10)	C2A	C17A	C18A	C1A	-19.60(9)
C2	C17	C18	C19	140.09(12)	C2A	C17A	C18A	C19A	-143.45(12)
C3	C2	C17	C18	99.95(12)	C3A	C2A	C17A	C18A	-96.02(12)
C3	C4	C5	C6	178.48(14)	C3A	C4A	C5A	C6A	-177.76(13)
C3	C4	C9	C8	-178.32(12)	C3A	C4A	C9A	C8A	176.57(12)
C3	C4	C9	C10	1.3(2)	C3A	C4A	C9A	C10A	-4.6(2)
C4	C5	C6	C7	0.6(2)	C4A	C5A	C6A	C7A	0.6(2)
C4	C9	C10	N1	171.92(13)	C4A	C9A	C10A	N1A	-170.33(13)
C4	C9	C10	C1	-8.79(18)	C4A	C9A	C10A	C1A	7.95(18)
C5	C4	C9	C8	1.2(2)	C5A	C4A	C9A	C8A	-2.9(2)
C5	C4	C9	C10	-179.18(13)	C5A	C4A	C9A	C10A	175.89(12)
C5	C6	C7	C8	-0.2(2)	C5A	C6A	C7A	C8A	-1.8(2)

Table S9. Torsion Angles for 2a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C6	C7	C8	C9	0.4(2)	C6A	C7A	C8A	C9A	0.6(2)
C7	C8	C9	C4	-0.9(2)	C7A	C8A	C9A	C4A	1.8(2)
C7	C8	C9	C10	179.52(12)	C7A	C8A	C9A	C10A	-177.07(13)
C8	C9	C10	N1	-8.49(19)	C8A	C9A	C10A	N1A	8.49(19)
C8	C9	C10	C1	170.80(12)	C8A	C9A	C10A	C1A	-173.23(12)
C9	C4	C5	C6	-1.1(2)	C9A	C4A	C5A	C6A	1.8(2)
C10	N1	C11	C12	161.76(13)	C10A	N1A	C11A	C12A	-163.46(13)
C10	N1	C11	C16	-24.5(2)	C10A	N1A	C11A	C16A	22.9(2)
C10	C1	C2	C3	22.77(17)	C10A	C1A	C2A	C3A	-25.59(17)
C10	C1	C2	C17	138.77(12)	C10A	C1A	C2A	C17A	-140.12(12)
C10	C1	C18	C17	-138.76(12)	C10A	C1A	C18A	C17A	141.74(12)
C10	C1	C18	C19	96.93(14)	C10A	C1A	C18A	C19A	-92.37(14)
C11	N1	C10	C1	-8.6(2)	C11A	N1A	C10A	C1A	8.3(2)
C11	N1	C10	C9	170.64(12)	C11A	N1A	C10A	C9A	-173.57(12)
C11	C12	C13	C14	-1.7(2)	C11A	C12A	C13A	C14A	0.7(2)
C12	C11	C16	S1	-179.97(11)	C12A	C11A	C16A	S1A	-178.57(11)
C12	C11	C16	C15	1.1(2)	C12A	C11A	C16A	C15A	-0.9(2)
C12	C13	C14	C15	1.4(3)	C12A	C13A	C14A	C15A	-1.1(2)
C13	C14	C15	C16	0.2(2)	C13A	C14A	C15A	C16A	0.5(2)
C14	C15	C16	S1	179.69(12)	C14A	C15A	C16A	S1A	178.16(12)
C14	C15	C16	C11	-1.4(2)	C14A	C15A	C16A	C11A	0.5(2)
C16	S1	C1	C2	176.18(9)	C16A	S1A	C1A	C2A	-176.78(9)
C16	S1	C1	C10	-53.84(10)	C16A	S1A	C1A	C10A	52.02(10)
C16	S1	C1	C18	79.81(10)	C16A	S1A	C1A	C18A	-81.02(10)
C16	C11	C12	C13	0.4(2)	C16A	C11A	C12A	C13A	0.3(2)
C17	C2	C3	O1	51.06(18)	C17A	C2A	C3A	O1A	-53.28(18)

Table S9. Torsion Angles for 2a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C17	C2	C3	C4	-131.35(13)	C17A	C2A	C3A	C4A	128.60(13)
C17	C18	C19	C20	164.82(13)	C17A	C18A	C19A	C20A	22.15(19)
C17	C18	C19	C24	-17.79(19)	C17A	C18A	C19A	C24A	-161.13(13)
C18	C1	C2	C3	-99.10(12)	C18A	C1A	C2A	C3A	94.94(12)
C18	C1	C2	C17	16.91(10)	C18A	C1A	C2A	C17A	-19.59(9)
C18	C1	C10	N1	-80.10(16)	C18A	C1A	C10A	N1A	82.33(16)
C18	C1	C10	C9	100.65(14)	C18A	C1A	C10A	C9A	-95.84(14)
C18	C19	C20	C21	175.96(13)	C18A	C19A	C20A	C21A	176.11(13)
C18	C19	C24	C23	-177.12(13)	C18A	C19A	C24A	C23A	-176.25(13)
C19	C20	C21	C22	2.0(2)	C19A	C20A	C21A	C22A	0.3(2)
C20	C19	C24	C23	0.3(2)	C20A	C19A	C24A	C23A	0.6(2)
C20	C21	C22	C23	-1.2(2)	C20A	C21A	C22A	C23A	0.1(2)
C21	C22	C23	C24	0.0(2)	C21A	C22A	C23A	C24A	-0.2(2)
C22	C23	C24	C19	0.5(2)	C22A	C23A	C24A	C19A	-0.2(2)
C24	C19	C20	C21	-1.5(2)	C24A	C19A	C20A	C21A	-0.6(2)

Table S10. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2a.

Atom	*x*	*y*	*z*	U(eq)
H2	10432.59	6875.02	1576.86	22
H5	7503.8	6811.19	272.44	30
H6	6273.29	5513.86	45.41	33
H7	5989.31	4281.12	766.91	29
H8	6942.1	4334.06	1705.03	24
H12	7417.22	4248.99	3561.53	30
H13	8431.93	3919.38	4457.13	37
H14	10382.91	4306.67	4537.18	36

Table S10. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2a.

Atom	*x*	*y*	*z*	U(eq)
H15	11286.9	5080.17	3734.28	29
H17A	9350.93	8528.09	2024.56	28
H17B	10521.89	8081.72	2329.1	28
H18	8192.73	7509.03	2576.46	21
H20	7772.15	6853.41	3590.91	29
H21	8232.33	6797.86	4625.96	36
H22	10002.03	7373.67	4985.35	37
H23	11340.13	7948.05	4296.26	32
H24	10914.91	7954.47	3256.05	25
H2A	9488.35	11503.47	3406.68	22
H5A	12555.33	11413.31	4663.25	28
H6A	13857.96	12658.19	4892.54	32
H7A	14048.17	13982.28	4224.07	30
H8A	13009.66	14021.53	3310.86	26
H12A	12514.3	14233.22	1476.69	29
H13A	11508.1	14614.73	581.6	35
H14A	9583.56	14165.34	468.1	38
H15A	8687.06	13291.19	1233.22	31
H17C	10529.7	9846.33	2945.32	26
H17D	9409.53	10340.97	2615.02	26
H18A	11785.48	10879.27	2467.7	21
H20A	9166.16	10539.4	1637.63	26
H21A	8961.52	10598.79	581.59	31
H22A	10493	11093.06	-16.39	32
H23A	12231.58	11522.98	450.58	31
H24A	12442.63	11467.27	1505.5	26

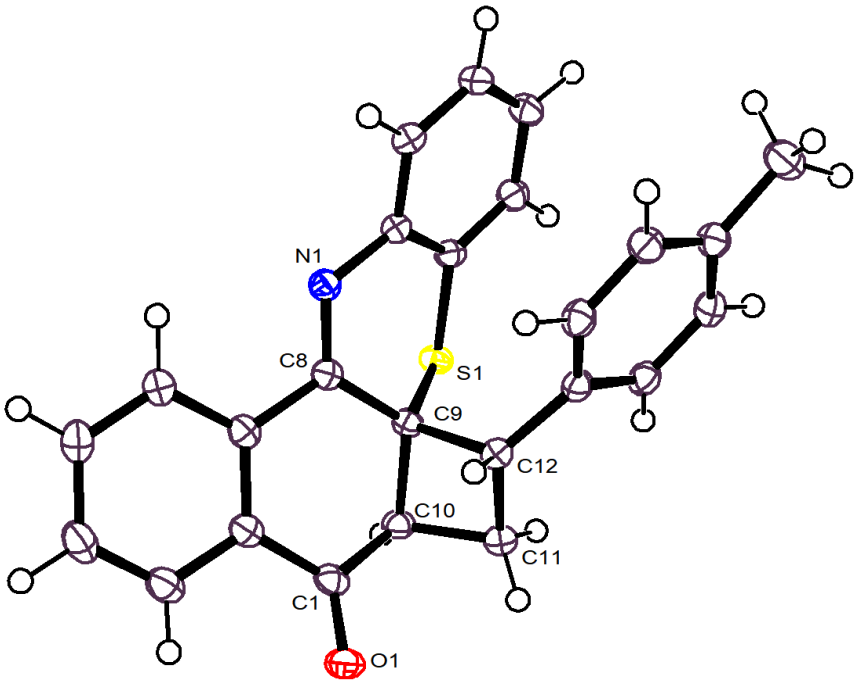


Table S11. Crystal data and structure refinement for 2o.

Identification code	**2o**
CCDC Number	**2332712**
Empirical formula	$C_{25}H_{19}NOS$
Formula weight	381.47
Temperature/K	140(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.381(2)
b/Å	20.496(7)
c/Å	11.336(4)
α/°	90
β/°	105.075(7)
γ/°	90
Volume/Å^3	1880.3(10)

Z	4
ρ_{calc}g/cm^3	1.348
μ/mm^{-1}	0.188
F(000)	800.0
Crystal size/mm^3	0.0151 × 0.0134 × 0.0123
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.412 to 53.864
Index ranges	-10 ≤ h ≤ 8, -25 ≤ k ≤ 26, -13 ≤ l ≤ 14
Reflections collected	15251
Independent reflections	4046 [R_{int} = 0.0415, R_{sigma} = 0.0389]
Data/restraints/parameters	4046/0/329
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0397, wR_2 = 0.0973
Final R indexes [all data]	R_1 = 0.0447, wR_2 = 0.1008
Largest diff. peak/hole / e Å^{-3}	0.68/-0.20

Table S12. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 2o. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	7780.5(5)	3092.0(2)	6551.0(3)	19.05(11)
O1	9619.4(15)	4670.7(5)	3652.5(11)	25.5(3)
N1	4545.9(16)	3261.3(6)	4524.0(11)	18.7(3)
C1	8561(2)	4437.4(7)	4101.3(14)	20.1(3)
C2	6812(2)	4665.6(7)	3742.0(14)	20.1(3)
C3	6473(2)	5286.2(8)	3197.5(15)	25.4(3)
C4	4871(2)	5523.3(8)	2853.4(16)	28.2(4)
C5	3570(2)	5141.6(8)	3041.3(15)	25.8(3)
C6	3877(2)	4526.6(7)	3573.7(14)	21.6(3)

Table S12. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 2o. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C7	5501.0(19)	4279.4(7)	3933.4(13)	18.8(3)
C8	5814.0(18)	3622.1(7)	4505.9(13)	17.1(3)
C9	7593.5(18)	3416.6(7)	5029.0(13)	17.0(3)
C10	9012.0(19)	3916.0(7)	5086.7(14)	19.5(3)
C11	10094(2)	3360.3(8)	4777.1(16)	22.9(3)
C12	8477.7(19)	2970.8(7)	4229.3(14)	19.3(3)
C13	8359.7(19)	2238.1(7)	4321.9(14)	20.0(3)
C14	9456(2)	1869.8(8)	5215.6(15)	22.2(3)
C15	9179(2)	1202.7(8)	5346.2(15)	23.9(3)
C16	7802(2)	889.5(8)	4593.2(15)	23.6(3)
C17	6717(2)	1260.8(8)	3694.4(15)	24.1(3)
C18	6997(2)	1919.8(8)	3551.0(15)	22.8(3)
C19	7461(3)	172.4(9)	4748.7(18)	31.8(4)
C20	6153.0(18)	2516.5(7)	6136.5(13)	17.8(3)
C21	6257(2)	1923.5(7)	6764.7(14)	21.4(3)
C22	4983(2)	1467.2(8)	6410.2(15)	24.0(3)
C23	3615(2)	1600.6(8)	5438.8(16)	23.6(3)
C24	3491.7(19)	2197.9(8)	4832.5(15)	21.3(3)
C25	4768.6(19)	2661.1(7)	5160.8(14)	18.3(3)

Table S13. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 2o. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	18.2(2)	20.07(19)	17.57(19)	0.81(13)	2.33(14)	-3.00(14)
O1	27.9(6)	22.8(6)	29.5(6)	-1.0(5)	13.9(5)	-6.2(5)
N1	17.1(6)	18.1(6)	20.1(6)	0.8(5)	3.5(5)	-0.5(5)

Table S13. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 2o. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	24.7(8)	15.9(7)	20.7(7)	-4.5(6)	7.5(6)	-4.7(6)
C2	25.1(8)	18.1(7)	18.1(7)	-1.0(6)	7.4(6)	-1.6(6)
C3	32.7(9)	20.7(8)	25.1(8)	2.0(6)	11.6(7)	-1.9(7)
C4	38.7(10)	19.5(8)	27.4(8)	4.8(6)	10.6(7)	4.3(7)
C5	28.1(9)	23.8(8)	25.2(8)	1.9(6)	6.2(7)	7.4(7)
C6	23.4(8)	19.6(7)	21.4(7)	0.1(6)	5.3(6)	1.8(6)
C7	23.1(8)	17.1(7)	16.4(7)	-1.4(5)	5.5(6)	-0.1(6)
C8	18.5(7)	17.3(7)	15.7(7)	-1.2(5)	4.8(6)	-0.7(5)
C9	17.4(7)	15.8(7)	17.5(7)	-0.4(5)	3.7(6)	-2.6(5)
C10	17.5(8)	19.0(7)	21.8(8)	-1.5(6)	5.0(6)	-3.9(6)
C11	18.7(8)	20.8(8)	29.9(9)	0.3(6)	7.7(7)	-1.8(6)
C12	17.7(8)	19.7(7)	20.9(7)	0.0(6)	6.0(6)	0.2(6)
C13	18.8(8)	19.6(7)	23.4(8)	-3.5(6)	8.7(6)	0.3(6)
C14	16.4(8)	23.3(8)	26.2(8)	-2.5(6)	4.4(6)	0.5(6)
C15	21.5(8)	23.4(8)	26.7(8)	0.9(6)	6.0(7)	4.7(6)
C16	26.3(9)	20.3(7)	27.1(8)	-3.0(6)	12.4(7)	-0.7(6)
C17	22.3(8)	23.4(8)	26.5(8)	-6.9(6)	5.9(7)	-2.8(6)
C18	22.0(8)	23.4(8)	22.6(8)	-3.4(6)	5.1(6)	1.8(6)
C19	36.6(10)	23.0(8)	36.1(10)	0.8(7)	10.2(8)	-3.2(7)
C20	17.1(7)	18.6(7)	18.6(7)	-0.6(5)	6.2(6)	-1.8(6)
C21	21.1(8)	21.5(7)	21.9(8)	2.1(6)	5.8(6)	0.9(6)
C22	27.1(9)	19.7(7)	27.3(8)	4.8(6)	10.7(7)	-0.4(6)
C23	20.6(8)	19.7(7)	32.2(9)	-1.2(6)	10.1(7)	-4.3(6)
C24	16.3(8)	22.8(8)	24.7(8)	0.1(6)	5.3(6)	-0.8(6)
C25	17.5(7)	17.5(7)	20.8(7)	0.6(6)	6.7(6)	0.3(6)

Table S14. Bond Lengths for 2o.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C9	1.8175(16)	C10	C11	1.552(2)
S1	C20	1.7718(16)	C11	C12	1.556(2)
O1	C1	1.2284(19)	C12	C13	1.510(2)
N1	C8	1.2993(19)	C13	C14	1.398(2)
N1	C25	1.4139(19)	C13	C18	1.405(2)
C1	C2	1.491(2)	C14	C15	1.401(2)
C1	C10	1.521(2)	C15	C16	1.400(2)
C2	C3	1.410(2)	C16	C17	1.401(2)
C2	C7	1.416(2)	C16	C19	1.516(2)
C3	C4	1.386(3)	C17	C18	1.388(2)
C4	C5	1.403(2)	C20	C21	1.400(2)
C5	C6	1.392(2)	C20	C25	1.411(2)
C6	C7	1.410(2)	C21	C22	1.397(2)
C7	C8	1.489(2)	C22	C23	1.394(2)
C8	C9	1.514(2)	C23	C24	1.394(2)
C9	C10	1.557(2)	C24	C25	1.406(2)
C9	C12	1.599(2)			

Table S15. Bond Angles for 2o.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C20	S1	C9	96.98(7)	C11	C10	C9	89.59(11)
C8	N1	C25	120.22(13)	C10	C11	C12	88.11(12)
O1	C1	C2	121.96(14)	C11	C12	C9	87.97(11)
O1	C1	C10	120.63(15)	C13	C12	C9	118.72(12)
C2	C1	C10	117.38(12)	C13	C12	C11	123.25(13)
C3	C2	C1	118.31(14)	C14	C13	C12	122.98(14)

Table S15. Bond Angles for 2o.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C3	C2	C7	119.71(15)	C14	C13	C18	118.32(14)
C7	C2	C1	121.99(13)	C18	C13	C12	118.41(14)
C4	C3	C2	120.64(15)	C13	C14	C15	120.52(15)
C3	C4	C5	119.77(15)	C16	C15	C14	121.05(15)
C6	C5	C4	120.49(16)	C15	C16	C17	118.08(15)
C5	C6	C7	120.44(15)	C15	C16	C19	121.60(16)
C2	C7	C8	121.13(14)	C17	C16	C19	120.31(16)
C6	C7	C2	118.96(14)	C18	C17	C16	121.07(16)
C6	C7	C8	119.92(13)	C17	C18	C13	120.95(15)
N1	C8	C7	118.02(14)	C21	C20	S1	120.10(12)
N1	C8	C9	124.19(13)	C21	C20	C25	120.71(14)
C7	C8	C9	117.79(12)	C25	C20	S1	119.18(11)
C8	C9	S1	107.85(10)	C22	C21	C20	119.54(15)
C8	C9	C10	119.81(12)	C23	C22	C21	120.36(14)
C8	C9	C12	119.44(12)	C22	C23	C24	120.13(15)
C10	C9	S1	108.92(10)	C23	C24	C25	120.55(15)
C10	C9	C12	86.45(11)	C20	C25	N1	123.75(13)
C12	C9	S1	113.01(10)	C24	C25	N1	117.51(14)
C1	C10	C9	112.95(13)	C24	C25	C20	118.67(13)
C1	C10	C11	113.43(13)				

Table S16. Hydrogen Bonds for 2o.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
C10	H10	O1[1]	0.98(2)	2.571(19)	3.301(2)	131.1(14)
C21	H21	N1[2]	0.99(2)	2.64(2)	3.611(2)	166.3(15)

[1]2-X,1-Y,1-Z; [2]1/2+X,1/2-Y,1/2+Z

Table S17. Torsion Angles for 2o.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S1	C9	C10	C1	-152.35(10)	C8	C9	C12	C13	-89.39(17)
S1	C9	C10	C11	92.25(11)	C9	S1	C20	C21	146.77(12)
S1	C9	C12	C11	-88.23(11)	C9	S1	C20	C25	-32.51(13)
S1	C9	C12	C13	39.07(17)	C9	C10	C11	C12	21.44(11)
S1	C20	C21	C22	-178.50(12)	C9	C12	C13	C14	-86.12(19)
S1	C20	C25	N1	-3.8(2)	C9	C12	C13	C18	87.62(18)
S1	C20	C25	C24	179.40(11)	C10	C1	C2	C3	157.17(14)
O1	C1	C2	C3	-20.7(2)	C10	C1	C2	C7	-22.8(2)
O1	C1	C2	C7	159.34(14)	C10	C9	C12	C11	20.83(11)
O1	C1	C10	C9	-147.11(14)	C10	C9	C12	C13	148.14(14)
O1	C1	C10	C11	-47.03(19)	C10	C11	C12	C9	-20.87(11)
N1	C8	C9	S1	-48.03(17)	C10	C11	C12	C13	-144.35(14)
N1	C8	C9	C10	-173.28(13)	C11	C12	C13	C14	22.0(2)
N1	C8	C9	C12	82.75(18)	C11	C12	C13	C18	-164.27(14)
C1	C2	C3	C4	-179.59(14)	C12	C9	C10	C1	94.53(13)
C1	C2	C7	C6	179.85(13)	C12	C9	C10	C11	-20.87(11)
C1	C2	C7	C8	-0.1(2)	C12	C13	C14	C15	172.72(14)
C1	C10	C11	C12	-93.51(14)	C12	C13	C18	C17	-172.14(14)
C2	C1	C10	C9	34.95(18)	C13	C14	C15	C16	-0.3(2)
C2	C1	C10	C11	135.04(14)	C14	C13	C18	C17	1.9(2)
C2	C3	C4	C5	-0.4(2)	C14	C15	C16	C17	0.7(2)
C2	C7	C8	N1	-171.97(13)	C14	C15	C16	C19	-178.19(15)
C2	C7	C8	C9	7.9(2)	C15	C16	C17	C18	0.1(2)
C3	C2	C7	C6	-0.1(2)	C16	C17	C18	C13	-1.5(2)
C3	C2	C7	C8	-179.99(13)	C18	C13	C14	C15	-1.0(2)
C3	C4	C5	C6	0.2(3)	C19	C16	C17	C18	179.08(15)

Table S17. Torsion Angles for 2o.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C4	C5	C6	C7	0.1(2)	C20	S1	C9	C8	53.06(11)
C5	C6	C7	C2	-0.1(2)	C20	S1	C9	C10	-175.46(10)
C5	C6	C7	C8	179.77(14)	C20	S1	C9	C12	-81.19(11)
C6	C7	C8	N1	8.1(2)	C20	C21	C22	C23	-0.1(2)
C6	C7	C8	C9	-171.97(13)	C21	C20	C25	N1	176.95(13)
C7	C2	C3	C4	0.3(2)	C21	C20	C25	C24	0.1(2)
C7	C8	C9	S1	132.06(11)	C21	C22	C23	C24	-1.5(2)
C7	C8	C9	C10	6.81(19)	C22	C23	C24	C25	2.5(2)
C7	C8	C9	C12	-97.15(15)	C23	C24	C25	N1	-178.76(13)
C8	N1	C25	C20	23.9(2)	C23	C24	C25	C20	-1.7(2)
C8	N1	C25	C24	-159.28(14)	C25	N1	C8	C7	-173.78(12)
C8	C9	C10	C1	-27.61(18)	C25	N1	C8	C9	6.3(2)
C8	C9	C10	C11	-143.01(13)	C25	C20	C21	C22	0.8(2)
C8	C9	C12	C11	143.30(13)					

Table S18. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2o.

Atom	*x*	*y*	*z*	U(eq)
H3	7390(20)	5540(9)	3100(17)	28(5)
H4	4650(20)	5965(10)	2506(17)	31(5)
H5	2450(20)	5293(9)	2801(17)	28(5)
H6	2940(20)	4253(9)	3710(17)	28(5)
H10	9440(20)	4142(9)	5869(18)	29(5)
H11A	10770(20)	3170(9)	5496(18)	26(5)
H11B	10800(20)	3470(9)	4244(17)	25(5)
H12	7990(20)	3106(8)	3352(17)	21(4)
H14	10390(20)	2078(9)	5761(18)	29(5)

Table S18. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2o.

Atom	*x*	*y*	*z*	U(eq)
H15	9950(20)	959(9)	5980(18)	31(5)
H17	5730(30)	1037(9)	3198(18)	31(5)
H18	6200(20)	2193(9)	2919(18)	29(5)
H19A	6580(30)	112(11)	5160(20)	52(7)
H19B	8490(30)	-80(12)	5200(20)	58(7)
H19C	7020(30)	-50(13)	3920(30)	69(8)
H21	7270(20)	1834(9)	7431(18)	25(5)
H22	5110(20)	1052(9)	6825(18)	30(5)
H23	2750(20)	1285(9)	5171(18)	31(5)
H24	2500(20)	2292(9)	4164(17)	24(5)

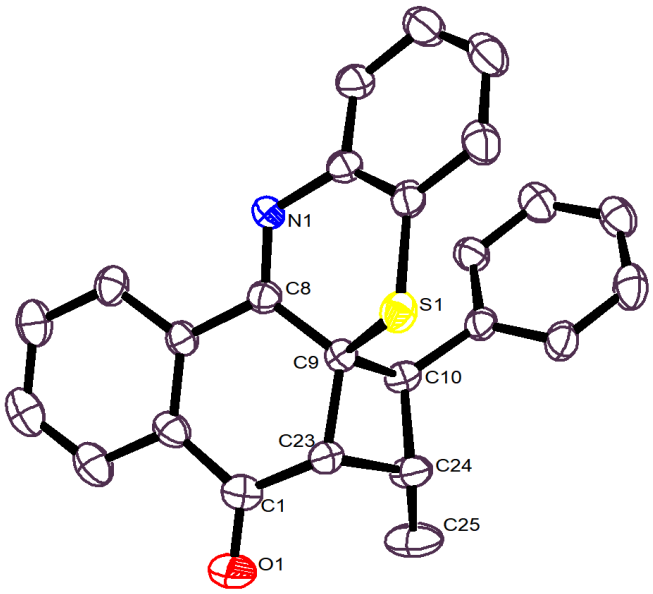


Table S19. Crystal data and structure refinement for 2x.

Identification code	**2x**
CCDC Number	**2403401**
Empirical formula	$C_{50}N_2O_2S_2$
Formula weight	724.64
Temperature/K	140.0

Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	23.545(2)
b/Å	7.4959(7)
c/Å	24.005(2)
α/°	90
β/°	117.294(4)
γ/°	90
Volume/Å^3	3764.9(6)
Z	4
ρ_{calc}g/cm^3	1.278
μ/mm^{-1}	0.185
F(000)	1448.0
Crystal size/mm^3	0.02 × 0.01 × 0.008
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.014 to 60.178
Index ranges	-32 ≤ h ≤ 33, -10 ≤ k ≤ 10, -33 ≤ l ≤ 33
Reflections collected	58260
Independent reflections	11018 [R_{int} = 0.1528, R_{sigma} = 0.1161]
Data/restraints/parameters	11018/0/505
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0912, wR_2 = 0.2367
Final R indexes [all data]	R_1 = 0.1572, wR_2 = 0.2903
Largest diff. peak/hole / e Å^{-3}	0.77/-0.36

Table S20. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 2x. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S001	-3967.6(4)	-5326.3(12)	-7776.0(4)	28.0(2)
S1	-1096.0(4)	-4983.7(12)	-2385.8(5)	28.0(2)

Table S20. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 2x. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O003	-3090.7(14)	-3371(5)	-5553.7(13)	48.2(8)
N004	-2774.3(13)	-3393(4)	-7669.2(13)	24.8(6)
N1	-2336.9(14)	-6656(4)	-2512.6(13)	25.3(6)
O1	-262.5(16)	-7439(6)	-216.0(14)	62.1(11)
C007	-2420.9(16)	-2967(5)	-6029.2(16)	25.2(7)
C008	-1741.4(17)	-2719(4)	-6532.6(17)	26.4(7)
C009	-2347.8(15)	-3030(4)	-6576.5(16)	22.8(7)
C00A	-2885.9(16)	-3378(4)	-7195.6(16)	23.7(7)
C00B	-1219.3(17)	-2366(5)	-5953.0(18)	30.8(8)
C6	-2522.9(18)	-7060(5)	-1467.2(18)	28.2(8)
C00D	-4370.7(17)	-1151(5)	-7988.6(16)	25.0(7)
C9	-1163.1(16)	-6789(5)	-1927.6(16)	23.6(7)
C11	-979.9(16)	-9137(5)	-2668.8(16)	24.2(7)
C00G	-3605.3(17)	-3856(5)	-6632.5(17)	27.6(7)
C7	-1905.0(16)	-7064(4)	-1421.0(16)	23.3(7)
C2	-1379.4(18)	-7287(5)	-826.7(17)	28.5(8)
C00J	-3036.1(17)	-3376(5)	-6028.1(17)	30.0(8)
C00K	-1896.1(19)	-2553(5)	-5450.7(18)	32.3(8)
C00L	-3540.5(15)	-3562(5)	-7239.1(16)	22.8(7)
C8	-1829.4(16)	-6806(4)	-1989.3(16)	23.6(7)
C5	-2604(2)	-7214(5)	-932.4(19)	34.1(9)
C00O	-3822.6(17)	-4678(5)	-8397.2(18)	27.8(8)
C23	-581.5(17)	-6725(5)	-1266.7(17)	27.1(7)
C00Q	-3153.9(18)	-3203(5)	-8774.8(18)	31.4(8)
C10	-908.1(16)	-8642(5)	-2031.1(17)	25.3(7)
C00S	-3262.9(17)	-3746(5)	-8277.3(17)	27.2(7)
C00T	-1305.6(18)	-2247(5)	-5418.1(18)	32.4(8)

Table S20. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 2x. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C16	-1531.2(18)	-10021(5)	-3087.4(17)	28.9(8)
C21	-2837.0(19)	-6690(5)	-3631.5(18)	32.6(8)
C15	-1635(2)	-10379(5)	-3690.5(19)	35.8(9)
C00X	-4255.3(19)	-5112(6)	-9009.1(19)	35.8(9)
C4	-2077(2)	-7433(5)	-347(2)	38.7(10)
C00Z	-5009.5(18)	-1597(5)	-8276.5(18)	31.9(8)
C010	-3925.0(16)	-1754(5)	-7334.0(16)	25.0(7)
C011	-4119.3(19)	-210(5)	-8324.7(18)	31.8(8)
C22	-2301.5(17)	-6293(5)	-3068.7(17)	26.3(7)
C3	-1475(2)	-7489(5)	-300.3(19)	36.2(9)
C1	-707.4(19)	-7219(6)	-726.3(18)	35.5(9)
C015	-4160.8(17)	-2453(5)	-6874.4(17)	29.4(8)
C24	-247.2(17)	-8163(5)	-1485.4(18)	31.2(8)
C17	-1780.2(18)	-5447(5)	-3083.3(17)	26.6(7)
C018	-5144(2)	-223(6)	-9238.7(18)	37.8(9)
C019	-5404.6(19)	-1140(6)	-8907.6(18)	38.8(10)
C14	-1184(2)	-9881(5)	-3884.3(19)	34.5(9)
C18	-1810(2)	-4938(5)	-3653.7(19)	34.0(9)
C13	-632(2)	-9041(5)	-3464(2)	36.1(9)
C12	-529.3(18)	-8648(5)	-2860.8(19)	31.9(8)
C20	-2865(2)	-6189(6)	-4197.1(19)	41.1(10)
C01F	-3582(2)	-3629(6)	-9384.9(19)	39.6(10)
C01G	-4506(2)	249(6)	-8949(2)	37.9(9)
C01H	-4122(2)	-4602(6)	-9501(2)	41.5(10)
C19	-2352(2)	-5274(6)	-4206(2)	40.2(10)
C01J	-4211(2)	-1152(6)	-6416(2)	38.5(9)
C25	136(2)	-9680(6)	-1058(2)	50.3(13)

Table S21. Anisotropic Displacement Parameters ($Å^2×10^3$) for 2x. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S001	22.1(4)	30.3(5)	29.8(5)	1.4(4)	10.4(4)	-2.7(3)
S1	28.4(5)	27.0(4)	32.4(5)	3.4(4)	17.3(4)	0.2(3)
O003	35.2(16)	85(2)	27.8(15)	13.7(16)	17.3(13)	10.6(16)
N004	19.6(14)	29.8(15)	22.0(14)	1.8(12)	6.9(12)	1.6(12)
N1	24.5(15)	32.3(15)	20.0(14)	3.7(12)	10.9(12)	2.7(12)
O1	35.1(18)	115(3)	26.3(16)	11.4(18)	5.7(14)	14.6(19)
C007	20.9(16)	29.2(17)	22.5(17)	2.9(14)	7.5(13)	2.0(13)
C008	24.3(18)	20.8(15)	31.3(19)	-1.3(14)	10.4(15)	-1.8(13)
C009	18.0(16)	21.4(15)	25.9(17)	1.1(13)	7.4(13)	-0.6(12)
C00A	21.6(17)	23.4(16)	26.6(17)	3.6(13)	11.4(14)	2.0(13)
C00B	25.2(19)	29.3(18)	29.4(19)	-1.2(15)	5.2(15)	-2.8(14)
C6	30.1(19)	26.8(17)	32.8(19)	3.3(15)	18.7(16)	1.2(14)
C00D	23.3(17)	27.6(17)	22.2(17)	0.6(13)	8.8(14)	5.0(13)
C9	21.4(16)	27.0(16)	22.3(16)	1.4(13)	10.0(13)	0.7(13)
C11	23.7(17)	24.3(16)	25.7(17)	3.7(13)	12.4(14)	4.9(13)
C00G	20.6(17)	35.3(19)	27.0(18)	6.7(15)	10.9(14)	4.3(14)
C7	25.6(17)	23.3(15)	23.2(17)	0.9(13)	12.9(14)	-1.5(13)
C2	34(2)	28.5(17)	22.0(17)	3.9(14)	11.8(15)	2.2(15)
C00J	26.7(19)	39(2)	22.4(18)	8.6(15)	9.6(15)	7.8(15)
C00K	31(2)	35.1(19)	25.3(19)	2.8(15)	7.7(16)	-0.8(16)
C00L	17.1(16)	26.8(16)	23.0(16)	5.0(13)	8.0(13)	2.5(13)
C8	23.3(17)	23.8(16)	23.6(17)	4.0(13)	10.8(14)	3.2(13)
C5	44(2)	30.5(19)	39(2)	0.7(16)	28.0(19)	-4.6(16)
C00O	19.0(17)	32.4(18)	28.1(18)	-0.5(15)	7.5(14)	2.0(14)
C23	21.7(17)	32.8(18)	24.3(17)	-2.5(14)	8.5(14)	1.9(14)
C00Q	29.4(19)	40(2)	23.6(18)	1.6(16)	11.2(15)	4.5(16)
C10	21.4(17)	24.6(16)	26.7(18)	2.2(14)	8.2(14)	1.9(13)

Table S21. Anisotropic Displacement Parameters ($Å^2×10^3$) for 2x. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C00S	21.2(17)	34.2(18)	25.9(18)	-2.2(15)	10.6(14)	0.7(14)
C00T	26.5(19)	33.5(19)	26.5(19)	1.4(15)	3.0(15)	-3.9(15)
C16	28.9(19)	31.6(18)	24.5(18)	-1.3(14)	10.7(15)	-2.0(15)
C21	32(2)	37(2)	26.5(19)	3.3(16)	10.7(16)	11.2(16)
C15	43(2)	34(2)	31(2)	-0.7(16)	18.5(18)	1.7(17)
C00X	24.3(19)	44(2)	27.8(19)	-1.9(17)	2.6(15)	-0.8(16)
C4	58(3)	31.4(19)	34(2)	-1.3(16)	28(2)	-3.5(18)
C00Z	23.8(18)	40(2)	27.5(19)	-0.9(16)	8.3(15)	3.6(16)
C010	20.0(16)	29.9(17)	24.9(17)	2.9(14)	10.1(14)	3.4(13)
C011	36(2)	31.5(19)	25.0(19)	4.5(15)	10.9(16)	1.0(15)
C22	25.7(18)	27.2(17)	24.6(17)	4.0(14)	10.2(14)	7.9(14)
C3	49(3)	34(2)	29(2)	3.1(16)	20.4(19)	1.2(18)
C1	31(2)	44(2)	26.6(19)	1.7(17)	8.9(16)	4.2(17)
C015	22.8(18)	40(2)	27.3(18)	6.7(15)	13.1(15)	5.7(15)
C24	23.4(18)	30.7(18)	30.1(19)	-4.6(15)	4.0(15)	4.5(15)
C17	30.0(19)	26.1(16)	27.4(18)	7.5(14)	16.3(15)	10.0(14)
C018	35(2)	46(2)	24.1(19)	1.6(17)	6.1(17)	8.3(18)
C019	33(2)	53(3)	24.4(19)	-1.1(18)	7.5(16)	8.1(18)
C14	46(2)	29.6(19)	31(2)	1.7(16)	20.7(18)	6.5(17)
C18	45(2)	31.6(19)	33(2)	9.9(16)	23.7(18)	13.2(17)
C13	44(2)	34(2)	42(2)	0.7(17)	29(2)	7.7(17)
C12	30(2)	34.7(19)	35(2)	3.3(16)	19.3(17)	6.6(16)
C20	49(3)	47(2)	26(2)	2.8(18)	15.5(19)	16(2)
C01F	34(2)	54(3)	26(2)	4.3(18)	9.9(17)	1.1(19)
C01G	36(2)	44(2)	32(2)	4.5(18)	14.2(18)	3.1(18)
C01H	29(2)	60(3)	28(2)	-1.5(19)	6.7(17)	2.7(19)
C19	56(3)	40(2)	28(2)	9.1(17)	23(2)	19(2)
C01J	37(2)	48(2)	35(2)	1.1(18)	20.1(18)	10.7(18)

Table S21. Anisotropic Displacement Parameters ($Å^2×10^3$) for 2x. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C25	39(3)	41(2)	44(3)	3(2)	-3(2)	12.6(19)

Table S22. Bond Lengths for 2x.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S001	C00L	1.798(4)	C7	C8	1.467(5)
S001	C00O	1.744(4)	C2	C3	1.389(5)
S1	C9	1.796(3)	C2	C1	1.488(5)
S1	C17	1.745(4)	C00K	C00T	1.376(6)
O003	C00J	1.203(4)	C00L	C010	1.587(5)
N004	C00A	1.279(4)	C5	C4	1.394(6)
N004	C00S	1.409(4)	C00O	C00S	1.400(5)
N1	C8	1.281(4)	C00O	C00X	1.389(5)
N1	C22	1.402(4)	C23	C1	1.504(5)
O1	C1	1.203(5)	C23	C24	1.560(5)
C007	C009	1.402(5)	C00Q	C00S	1.392(5)
C007	C00J	1.482(5)	C00Q	C01F	1.382(5)
C007	C00K	1.406(5)	C10	C24	1.548(5)
C008	C009	1.402(5)	C16	C15	1.379(5)
C008	C00B	1.396(5)	C21	C22	1.393(5)
C009	C00A	1.468(5)	C21	C20	1.381(6)
C00A	C00L	1.503(5)	C15	C14	1.392(6)
C00B	C00T	1.392(6)	C00X	C01H	1.406(6)
C6	C7	1.407(5)	C4	C3	1.370(6)
C6	C5	1.387(5)	C00Z	C019	1.409(5)
C00D	C00Z	1.378(5)	C010	C015	1.537(5)
C00D	C010	1.504(5)	C011	C01G	1.394(5)
C00D	C011	1.392(5)	C22	C17	1.396(5)
C9	C8	1.507(5)	C015	C01J	1.515(6)

Table S22. Bond Lengths for 2x.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C9	C23	1.550(5)	C24	C25	1.520(6)
C9	C10	1.578(5)	C17	C18	1.391(5)
C11	C10	1.507(5)	C018	C019	1.389(6)
C11	C16	1.392(5)	C018	C01G	1.381(6)
C11	C12	1.386(5)	C14	C13	1.379(6)
C00G	C00J	1.499(5)	C18	C19	1.377(6)
C00G	C00L	1.548(5)	C13	C12	1.387(6)
C00G	C015	1.568(5)	C20	C19	1.397(7)
C7	C2	1.405(5)	C01F	C01H	1.379(6)

Table S23. Bond Angles for 2x.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C00O	S001	C00L	98.24(17)	C00S	C00O	S001	119.9(3)
C17	S1	C9	97.81(17)	C00X	C00O	S001	120.2(3)
C00A	N004	C00S	121.3(3)	C00X	C00O	C00S	119.9(4)
C8	N1	C22	121.0(3)	C9	C23	C24	88.8(3)
C009	C007	C00J	122.3(3)	C1	C23	C9	116.4(3)
C009	C007	C00K	120.2(3)	C1	C23	C24	116.7(3)
C00K	C007	C00J	117.4(3)	C01F	C00Q	C00S	120.6(4)
C00B	C008	C009	120.5(3)	C11	C10	C9	120.2(3)
C007	C009	C008	118.8(3)	C11	C10	C24	121.2(3)
C007	C009	C00A	122.3(3)	C24	C10	C9	88.3(3)
C008	C009	C00A	118.8(3)	C00O	C00S	N004	123.5(3)
N004	C00A	C009	117.9(3)	C00Q	C00S	N004	116.7(3)
N004	C00A	C00L	124.0(3)	C00Q	C00S	C00O	119.7(3)
C009	C00A	C00L	117.9(3)	C00K	C00T	C00B	120.5(4)
C00T	C00B	C008	119.8(3)	C15	C16	C11	120.5(4)
C5	C6	C7	120.2(4)	C20	C21	C22	120.6(4)
C00Z	C00D	C010	122.0(3)	C16	C15	C14	120.2(4)

Table S23. Bond Angles for 2x.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C00Z	C00D	C011	119.3(3)	C00O	C00X	C01H	119.1(4)
C011	C00D	C010	118.6(3)	C3	C4	C5	119.7(4)
C8	C9	S1	109.0(2)	C00D	C00Z	C019	120.7(4)
C8	C9	C23	119.5(3)	C00D	C010	C00L	119.1(3)
C8	C9	C10	115.6(3)	C00D	C010	C015	122.9(3)
C23	C9	S1	108.6(2)	C015	C010	C00L	88.6(3)
C23	C9	C10	88.1(2)	C00D	C011	C01G	120.5(4)
C10	C9	S1	114.9(2)	C21	C22	N1	117.3(3)
C16	C11	C10	118.9(3)	C21	C22	C17	119.2(3)
C12	C11	C10	121.8(3)	C17	C22	N1	123.3(3)
C12	C11	C16	119.2(3)	C4	C3	C2	121.0(4)
C00J	C00G	C00L	116.5(3)	O1	C1	C2	121.6(4)
C00J	C00G	C015	114.9(3)	O1	C1	C23	119.2(4)
C00L	C00G	C015	88.9(3)	C2	C1	C23	119.0(3)
C6	C7	C8	119.2(3)	C010	C015	C00G	88.8(3)
C2	C7	C6	118.5(3)	C01J	C015	C00G	119.5(3)
C2	C7	C8	122.3(3)	C01J	C015	C010	118.5(3)
C7	C2	C1	122.4(3)	C10	C24	C23	88.8(3)
C3	C2	C7	120.1(4)	C25	C24	C23	121.6(4)
C3	C2	C1	117.4(3)	C25	C24	C10	116.9(3)
O003	C00J	C007	122.0(3)	C22	C17	S1	120.1(3)
O003	C00J	C00G	118.7(3)	C18	C17	S1	119.8(3)
C007	C00J	C00G	119.2(3)	C18	C17	C22	120.0(4)
C00T	C00K	C007	120.0(4)	C01G	C018	C019	120.2(4)
C00A	C00L	S001	109.6(2)	C018	C019	C00Z	119.2(4)
C00A	C00L	C00G	119.2(3)	C13	C14	C15	119.1(4)
C00A	C00L	C010	115.5(3)	C19	C18	C17	120.2(4)
C00G	C00L	S001	107.8(2)	C14	C13	C12	120.9(4)
C00G	C00L	C010	87.8(3)	C11	C12	C13	119.9(4)

Table S23. Bond Angles for 2x.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C010	C00L	S001	115.5(2)	C21	C20	C19	119.8(4)
N1	C8	C9	123.8(3)	C01H	C01F	C00Q	119.6(4)
N1	C8	C7	117.8(3)	C018	C01G	C011	120.0(4)
C7	C8	C9	118.3(3)	C01F	C01H	C00X	120.9(4)
C6	C5	C4	120.4(4)	C18	C19	C20	120.0(4)

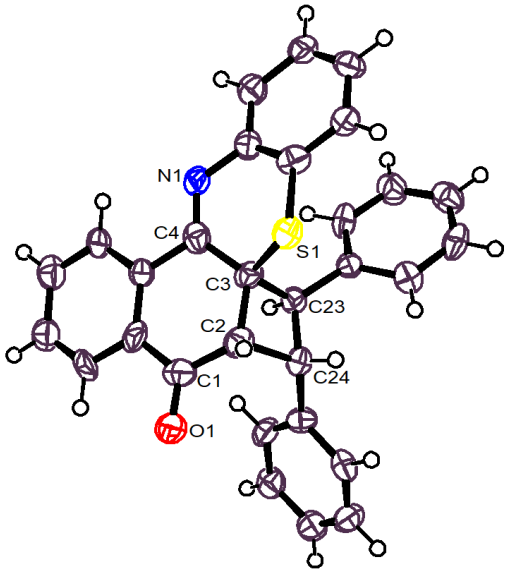


Table S24. Crystal data and structure refinement for 2y.

Identification code	**2y**
CCDC Number	**2403402**
Empirical formula	$C_{60}H_{42}N_2O_2S_2$
Formula weight	887.07
Temperature/K	120.0
Crystal system	monoclinic
Space group	$P2_1$
a/Å	5.9514(19)
b/Å	16.600(5)
c/Å	22.163(7)
α/°	90

β/°	90.368(14)
γ/°	90
Volume/Å^3	2189.5(12)
Z	2
ρ_{calc}g/cm^3	1.346
μ/mm^{-1}	0.172
F(000)	928.0
Crystal size/mm^3	0.02 × 0.01 × 0.008
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.42 to 59.148
Index ranges	-8 ≤ h ≤ 8, -23 ≤ k ≤ 23, -30 ≤ l ≤ 30
Reflections collected	75484
Independent reflections	12259 [R_{int} = 0.2866, R_{sigma} = 0.2275]
Data/restraints/parameters	12259/1/596
Goodness-of-fit on F^2	1.024
Final R indexes [I>=2σ (I)]	R_1 = 0.1177, wR_2 = 0.2794
Final R indexes [all data]	R_1 = 0.2350, wR_2 = 0.3453
Largest diff. peak/hole / e Å^{-3}	0.65/-0.50
Flack parameter	0.08(10)

Table S25. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 2y. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	3425(5)	4562.6(16)	8517.3(14)	37.5(7)
S1A	5292(5)	4770.7(18)	3375.1(14)	41.5(8)
O1	4828(17)	4077(5)	10718(4)	52(2)
N1	8142(17)	3836(5)	8431(4)	35(2)
O1A	6507(16)	4554(6)	5549(4)	55(2)
N1A	928(17)	3874(6)	3654(4)	38(2)
C22	6629(19)	6086(6)	8793(5)	30(2)

Table S25. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 2y. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C25	5143(18)	5882(7)	10360(5)	33(2)
C23	6448(19)	5439(6)	9272(5)	31(2)
C16A	3160(20)	4541(7)	2859(5)	39(3)
C1A	5110(20)	4491(7)	5150(6)	41(3)
C1	5600(20)	4069(7)	10207(5)	41(3)
C24A	4575(19)	5894(6)	4643(5)	34(3)
C22A	2100(20)	6249(6)	3670(5)	33(2)
C13	8040(20)	4688(7)	6885(5)	44(3)
C16	5234(18)	4616(7)	7887(5)	37(3)
C17A	60(20)	6156(7)	3374(5)	39(3)
C30A	2120(20)	6042(7)	5570(5)	39(3)
C12	8700(20)	4272(7)	7424(5)	39(3)
C18	8720(20)	6697(8)	7995(6)	46(3)
C6A	3160(20)	3964(7)	5187(5)	40(3)
C5	8460(20)	3530(6)	9474(5)	33(2)
C10	10380(20)	3074(6)	9378(5)	35(3)
C5A	1680(20)	3816(6)	4710(5)	37(3)
C11A	1230(20)	4162(7)	3066(6)	41(3)
C14	5940(20)	5054(7)	6866(5)	44(3)
C7	8760(20)	3207(7)	10540(6)	46(3)
C4	7360(20)	3969(6)	8948(6)	36(3)
C19	7030(20)	7241(8)	7880(6)	45(3)
C9	11470(20)	2695(7)	9845(6)	47(3)
C10A	-160(20)	3298(7)	4778(6)	40(3)
C3A	3670(20)	4851(7)	4039(5)	39(3)
C29A	1670(20)	6402(7)	6132(6)	45(3)
C3	5542(19)	4563(7)	9099(5)	34(2)

Table S25. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 2y. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C23A	2600(20)	5709(7)	4203(5)	37(3)
C17	8590(20)	6137(7)	8441(6)	45(3)
C20A	3040(20)	7300(9)	2947(6)	53(4)
C30	7140(20)	5768(7)	10689(6)	40(3)
C4A	2106(19)	4162(7)	4098(6)	40(3)
C11	7320(20)	4252(6)	7924(5)	36(3)
C2	4420(20)	4549(7)	9712(5)	41(3)
C8	10610(20)	2777(7)	10435(6)	47(3)
C15	4500(20)	5017(7)	7367(5)	39(3)
C2A	5410(20)	4978(7)	4582(5)	42(3)
C6	7600(20)	3594(6)	10072(6)	39(3)
C27A	5100(30)	7122(8)	6078(6)	55(4)
C24	4650(20)	5493(6)	9766(5)	38(3)
C29	7520(20)	6150(7)	11222(6)	41(3)
C21	4860(20)	6659(7)	8691(6)	46(3)
C21A	3520(20)	6838(7)	3450(6)	42(3)
C26	3570(20)	6412(6)	10619(5)	36(3)
C25A	4040(20)	6238(6)	5240(6)	41(3)
C19A	1000(30)	7160(7)	2649(6)	50(3)
C15A	3370(20)	4780(7)	2247(6)	48(3)
C26A	5570(20)	6785(7)	5512(6)	45(3)
C7A	2750(30)	3611(7)	5751(6)	51(3)
C12A	-440(20)	3968(7)	2632(5)	40(3)
C9A	-510(30)	2951(7)	5334(6)	48(3)
C20	5130(20)	7209(7)	8231(6)	45(3)
C13A	-270(20)	4212(8)	2043(6)	45(3)
C18A	-560(30)	6585(8)	2860(6)	48(3)

Table S25. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 2y. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C28	5930(20)	6672(7)	11462(6)	46(3)
C28A	3190(30)	6932(7)	6393(6)	55(4)
C8A	900(30)	3102(8)	5816(7)	55(4)
C27	3950(20)	6794(7)	11156(6)	48(3)
C14A	1560(20)	4582(9)	1847(6)	56(4)

Table S26. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 2y. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	35.7(14)	32.0(14)	44.9(17)	-2.9(13)	0.0(12)	-0.6(12)
S1A	43.1(16)	40.9(16)	40.6(17)	-6.2(13)	7.4(13)	0.8(13)
O1	84(7)	30(4)	42(5)	-2(4)	14(5)	-3(4)
N1	46(6)	25(4)	35(6)	-4(4)	-6(4)	2(4)
O1A	63(6)	53(5)	49(5)	-2(5)	-14(5)	12(5)
N1A	52(6)	29(5)	33(5)	-1(4)	1(5)	0(4)
C22	39(6)	25(5)	26(6)	-3(4)	-5(5)	-1(4)
C25	32(6)	36(6)	30(6)	-5(5)	2(5)	-5(5)
C23	35(6)	29(5)	29(6)	0(4)	-3(5)	2(4)
C16A	49(7)	35(6)	33(6)	-7(5)	8(5)	0(6)
C1A	50(7)	34(6)	39(7)	1(5)	4(6)	12(6)
C1	60(8)	28(5)	35(7)	-6(5)	13(6)	-18(5)
C24A	38(6)	30(5)	34(6)	-10(5)	-1(5)	-7(5)
C22A	46(7)	29(5)	25(6)	-1(4)	-2(5)	-3(5)
C13	66(8)	30(6)	36(7)	-4(5)	6(6)	0(6)
C16	36(6)	36(6)	40(6)	-4(5)	12(5)	-12(5)
C17A	46(7)	36(6)	36(7)	-1(5)	5(6)	3(5)
C30A	45(7)	38(6)	36(7)	-6(5)	-6(5)	1(5)

Table S26. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 2y. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C12	44(7)	32(6)	41(7)	-1(5)	-2(5)	-5(5)
C18	47(7)	45(7)	45(8)	9(6)	6(6)	0(6)
C6A	41(6)	42(6)	35(7)	-3(5)	-4(5)	6(5)
C5	45(7)	21(5)	33(6)	1(4)	4(5)	-7(5)
C10	45(7)	22(5)	38(6)	3(5)	2(5)	-5(5)
C5A	53(7)	28(5)	31(6)	-1(5)	-5(5)	5(5)
C11A	39(6)	31(6)	53(8)	-5(5)	8(6)	-2(5)
C14	71(9)	37(6)	26(6)	0(5)	-2(6)	-5(6)
C7	80(10)	23(5)	34(7)	11(5)	0(6)	-10(6)
C4	40(6)	27(5)	41(7)	2(5)	-5(5)	-6(5)
C19	56(8)	40(6)	40(7)	6(5)	-2(6)	-13(6)
C9	53(8)	35(6)	52(8)	4(6)	-5(7)	-1(6)
C10A	51(7)	30(6)	38(7)	1(5)	-2(6)	9(5)
C3A	59(7)	27(5)	29(6)	2(5)	0(5)	9(5)
C29A	56(8)	44(7)	35(7)	6(5)	8(6)	2(6)
C3	44(6)	25(5)	32(6)	-6(5)	4(5)	-6(5)
C23A	44(7)	29(5)	38(7)	-10(5)	-4(5)	0(5)
C17	42(7)	34(6)	57(8)	5(6)	-5(6)	14(5)
C20A	58(9)	60(8)	40(8)	17(6)	18(7)	13(7)
C30	47(7)	26(5)	46(7)	-4(5)	12(6)	5(5)
C4A	33(6)	39(6)	49(8)	-6(5)	5(5)	-6(5)
C11	41(6)	30(5)	36(7)	-3(5)	-11(5)	2(5)
C2	47(7)	33(5)	42(7)	-5(5)	2(5)	0(5)
C8	62(9)	34(6)	44(8)	1(5)	-7(7)	3(6)
C15	43(7)	36(6)	37(7)	-3(5)	-2(5)	7(5)
C2A	50(7)	40(6)	37(7)	-6(5)	-1(6)	4(5)
C6	49(7)	18(5)	48(7)	-5(5)	2(6)	0(5)
C27A	86(11)	42(7)	36(7)	-9(6)	-14(7)	-14(7)

Table S26. Anisotropic Displacement Parameters ($Å^2×10^3$) for 2y. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C24	53(8)	24(5)	37(7)	0(5)	2(6)	3(5)
C29	50(7)	29(6)	43(7)	-1(5)	-3(6)	-7(5)
C21	54(8)	41(7)	41(8)	6(6)	0(6)	4(6)
C21A	46(7)	40(6)	41(7)	-1(5)	9(6)	7(6)
C26	41(7)	31(5)	35(6)	7(5)	-9(5)	-3(5)
C25A	61(8)	24(5)	37(7)	-2(5)	-4(6)	2(5)
C19A	79(10)	35(6)	36(7)	-8(5)	10(7)	5(6)
C15A	63(8)	33(6)	47(7)	-8(6)	23(6)	6(6)
C26A	62(8)	31(6)	40(7)	-9(5)	-7(6)	1(6)
C7A	83(10)	29(6)	40(8)	-4(5)	-4(7)	-2(6)
C12A	52(7)	29(5)	39(7)	-7(5)	-3(6)	0(5)
C9A	72(9)	25(6)	48(8)	-3(5)	3(7)	-6(6)
C20	49(7)	24(5)	63(9)	-7(5)	-5(7)	4(5)
C13A	50(8)	51(7)	35(7)	-19(6)	1(6)	14(6)
C18A	67(9)	39(7)	39(7)	8(6)	-5(7)	7(6)
C28	67(9)	34(6)	35(7)	-4(5)	-4(6)	-2(6)
C28A	95(11)	33(6)	36(7)	-13(5)	4(8)	3(7)
C8A	67(9)	36(7)	61(9)	-3(6)	12(8)	0(7)
C27	59(8)	36(6)	49(8)	-2(6)	21(7)	7(6)
C14A	61(8)	69(9)	38(7)	-15(7)	-6(6)	23(8)

Table S27. Bond Lengths for 2y.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C16	1.772(11)	C18	C17	1.360(18)
S1	C3	1.797(12)	C6A	C5A	1.396(17)
S1A	C16A	1.745(12)	C6A	C7A	1.404(18)
S1A	C3A	1.771(12)	C5	C10	1.388(16)
O1	C1	1.225(14)	C5	C4	1.519(16)

Table S27. Bond Lengths for 2y.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N1	C4	1.258(15)	C5	C6	1.428(16)
N1	C11	1.406(15)	C10	C9	1.371(17)
O1A	C1A	1.217(15)	C5A	C10A	1.400(17)
N1A	C11A	1.401(16)	C5A	C4A	1.496(17)
N1A	C4A	1.297(15)	C11A	C12A	1.417(18)
C22	C23	1.514(15)	C14	C15	1.411(17)
C22	C17	1.411(17)	C7	C8	1.330(19)
C22	C21	1.434(17)	C7	C6	1.399(17)
C25	C30	1.402(17)	C4	C3	1.503(16)
C25	C24	1.494(15)	C19	C20	1.377(18)
C25	C26	1.407(16)	C9	C8	1.414(19)
C23	C3	1.597(15)	C10A	C9A	1.377(17)
C23	C24	1.539(16)	C3A	C23A	1.602(15)
C16A	C11A	1.389(16)	C3A	C4A	1.480(17)
C16A	C15A	1.420(17)	C3A	C2A	1.599(18)
C1A	C6A	1.451(18)	C29A	C28A	1.39(2)
C1A	C2A	1.508(17)	C3	C2	1.519(15)
C1	C2	1.522(18)	C20A	C21A	1.382(18)
C1	C6	1.463(17)	C20A	C19A	1.40(2)
C24A	C23A	1.551(16)	C30	C29	1.358(17)
C24A	C2A	1.606(16)	C2	C24	1.578(16)
C24A	C25A	1.480(16)	C27A	C26A	1.403(18)
C22A	C17A	1.387(17)	C27A	C28A	1.37(2)
C22A	C23A	1.511(16)	C29	C28	1.392(18)
C22A	C21A	1.384(17)	C21	C20	1.379(18)
C13	C12	1.434(17)	C26	C27	1.367(18)
C13	C14	1.387(19)	C25A	C26A	1.417(17)
C16	C11	1.381(16)	C19A	C18A	1.41(2)
C16	C15	1.398(17)	C15A	C14A	1.426(19)

Table S27. Bond Lengths for 2y.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C17A	C18A	1.391(17)	C7A	C8A	1.40(2)
C30A	C29A	1.410(17)	C12A	C13A	1.373(18)
C30A	C25A	1.400(18)	C9A	C8A	1.38(2)
C12	C11	1.385(17)	C13A	C14A	1.33(2)
C18	C19	1.375(18)	C28	C27	1.37(2)

Table S28. Bond Angles for 2y.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C16	S1	C3	98.0(5)	C4A	C3A	C23A	114.7(10)
C16A	S1A	C3A	99.4(6)	C4A	C3A	C2A	116.1(10)
C4	N1	C11	120.8(10)	C2A	C3A	S1A	106.3(8)
C4A	N1A	C11A	120.6(10)	C2A	C3A	C23A	88.2(8)
C17	C22	C23	119.5(10)	C28A	C29A	C30A	120.6(13)
C17	C22	C21	118.8(10)	C23	C3	S1	114.0(8)
C21	C22	C23	121.7(10)	C4	C3	S1	110.0(8)
C30	C25	C24	124.0(10)	C4	C3	C23	114.1(9)
C30	C25	C26	115.8(10)	C4	C3	C2	120.7(10)
C26	C25	C24	120.1(10)	C2	C3	S1	109.3(8)
C22	C23	C3	120.2(9)	C2	C3	C23	87.1(8)
C22	C23	C24	120.7(9)	C24A	C23A	C3A	91.1(9)
C24	C23	C3	89.3(8)	C22A	C23A	C24A	121.3(10)
C11A	C16A	S1A	118.8(9)	C22A	C23A	C3A	115.3(9)
C11A	C16A	C15A	121.2(12)	C18	C17	C22	119.5(11)
C15A	C16A	S1A	119.9(10)	C21A	C20A	C19A	117.8(13)
O1A	C1A	C6A	123.6(11)	C29	C30	C25	121.6(11)
O1A	C1A	C2A	118.3(12)	N1A	C4A	C5A	116.9(10)
C6A	C1A	C2A	118.1(11)	N1A	C4A	C3A	123.7(11)
O1	C1	C2	119.2(12)	C3A	C4A	C5A	119.2(11)
O1	C1	C6	120.2(12)	C16	C11	N1	124.8(11)

Table S28. Bond Angles for 2y.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C6	C1	C2	120.5(10)	C16	C11	C12	118.7(11)
C23A	C24A	C2A	89.7(8)	C12	C11	N1	116.5(10)
C25A	C24A	C23A	118.2(10)	C1	C2	C24	115.2(10)
C25A	C24A	C2A	120.6(10)	C3	C2	C1	116.7(10)
C17A	C22A	C23A	118.1(10)	C3	C2	C24	90.8(9)
C21A	C22A	C17A	116.7(11)	C7	C8	C9	121.1(12)
C21A	C22A	C23A	125.2(11)	C16	C15	C14	118.6(11)
C14	C13	C12	118.6(11)	C1A	C2A	C24A	113.5(9)
C11	C16	S1	118.7(9)	C1A	C2A	C3A	118.4(10)
C11	C16	C15	122.3(10)	C3A	C2A	C24A	89.2(9)
C15	C16	S1	118.9(9)	C5	C6	C1	121.7(11)
C22A	C17A	C18A	123.7(12)	C7	C6	C1	119.8(11)
C25A	C30A	C29A	121.5(12)	C7	C6	C5	118.4(11)
C11	C12	C13	121.1(12)	C28A	C27A	C26A	122.1(13)
C17	C18	C19	122.6(12)	C25	C24	C23	121.3(10)
C5A	C6A	C1A	124.3(11)	C25	C24	C2	120.9(9)
C5A	C6A	C7A	119.2(12)	C23	C24	C2	87.1(8)
C7A	C6A	C1A	116.4(11)	C30	C29	C28	120.9(12)
C10	C5	C4	119.7(10)	C20	C21	C22	117.9(12)
C10	C5	C6	118.8(11)	C20A	C21A	C22A	123.3(13)
C6	C5	C4	121.5(10)	C27	C26	C25	122.6(11)
C9	C10	C5	121.3(11)	C30A	C25A	C24A	124.0(11)
C6A	C5A	C10A	121.2(11)	C30A	C25A	C26A	116.9(11)
C6A	C5A	C4A	120.5(11)	C26A	C25A	C24A	119.1(12)
C10A	C5A	C4A	118.1(11)	C20A	C19A	C18A	121.7(13)
N1A	C11A	C12A	117.3(10)	C16A	C15A	C14A	117.4(12)
C16A	C11A	N1A	125.0(11)	C27A	C26A	C25A	120.4(13)
C16A	C11A	C12A	117.3(11)	C8A	C7A	C6A	119.0(13)
C13	C14	C15	120.7(12)	C13A	C12A	C11A	121.4(12)

Table S28. Bond Angles for 2y.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C8	C7	C6	121.4(12)	C8A	C9A	C10A	121.5(13)
N1	C4	C5	117.0(10)	C19	C20	C21	122.8(12)
N1	C4	C3	126.1(11)	C14A	C13A	C12A	121.0(13)
C3	C4	C5	116.8(10)	C17A	C18A	C19A	116.6(13)
C18	C19	C20	118.2(12)	C27	C28	C29	119.1(12)
C10	C9	C8	118.9(12)	C27A	C28A	C29A	118.4(12)
C9A	C10A	C5A	118.4(12)	C9A	C8A	C7A	120.5(13)
C23A	C3A	S1A	118.3(8)	C26	C27	C28	119.9(12)
C4A	C3A	S1A	111.2(8)	C13A	C14A	C15A	121.4(13)

Table S29. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2y.

Atom	*x*	*y*	*z*	U(eq)
H23	7950.69	5378.9	9471.11	37
H24A	5673.76	6254.35	4435.7	41
H13	9012.12	4712.49	6547.24	53
H17A	-984.2	5778.41	3532.34	47
H30A	1088.85	5657.48	5410.26	47
H12	10114.24	4006.23	7439.12	47
H18	10030.7	6714.46	7753.33	55
H10	10949.56	3023.89	8980.53	42
H14	5479.56	5333.49	6512.77	53
H7	8227.75	3253.68	10941.53	55
H19	7161.73	7627.62	7565.94	54
H9	12775.82	2383.13	9773.67	56
H10A	-1139.75	3188.02	4448.02	48
H29A	304.64	6280.93	6334.82	54
H23A	1196.76	5626.67	4439.93	45
H17	9811.65	5780.98	8514.42	54

Table S29. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2y.

Atom	*x*	*y*	*z*	U(eq)
H20A	4055.26	7698.79	2808.74	63
H30	8252.89	5415.1	10534.73	48
H2	2804.63	4387.16	9674.44	49
H8	11356.79	2520.19	10762.47	56
H15	3050.23	5259.3	7352.06	47
H2A	6999.59	4950.48	4437.9	51
H27A	6136.9	7494.73	6248.88	66
H24	3272.91	5747.2	9589.71	46
H29	8887.27	6058.54	11433.61	49
H21	3548.63	6658.46	8931.9	55
H21A	4907	6930.41	3655.82	51
H26	2197.28	6507.8	10410.75	43
H19A	655.07	7458.96	2295.31	60
H15A	4654.92	5060.98	2108.66	57
H26A	6917.34	6923.26	5310.35	54
H7A	3721.69	3716.11	6084.51	61
H12A	-1713.03	3661.83	2752.48	48
H9A	-1756.11	2600.04	5385.83	58
H20	3952.83	7582.99	8153.19	54
H13A	-1477.64	4113.75	1770.65	54
H18A	-1951.89	6495.42	2660.36	58
H28	6211.55	6941.18	11833.33	55
H28A	2923.88	7157.3	6779.51	66
H8A	604.51	2858.69	6195.42	66
H27	2836.63	7142.5	11317.56	57
H14A	1672.28	4719.19	1432.2	67

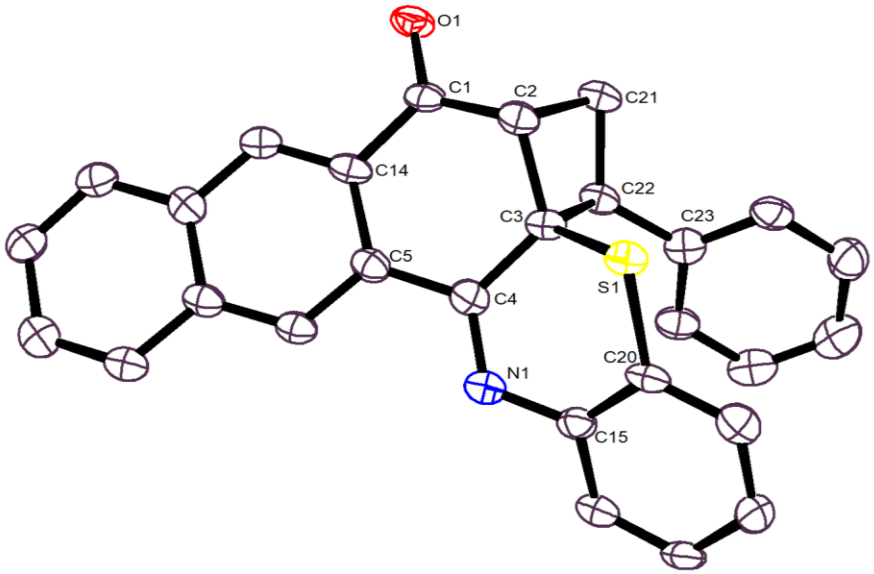


Table S30. Crystal data and structure refinement for 2ad.

Identification code	**2ad**
CCDC Number	**2332711**
Empirical formula	$C_{28}H_{19}NOS$
Formula weight	417.50
Temperature/K	110.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	20.812(7)
b/Å	7.486(3)
c/Å	13.413(4)
α/°	90
β/°	105.313(7)
γ/°	90
Volume/Å^3	2015.5(11)

Z	4
ρ_{calc}g/cm^3	1.376
μ/mm^{-1}	0.182
F(000)	872.0
Crystal size/mm^3	0.20 × 0.12 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.288 to 59.364
Index ranges	-28 ≤ h ≤ 28, -9 ≤ k ≤ 9, -17 ≤ l ≤ 15
Reflections collected	13296
Independent reflections	4465 [R_{int} = 0.1749, R_{sigma} = 0.2108]
Data/restraints/parameters	4465/0/281
Goodness-of-fit on F^2	1.024
Final R indexes [I>=2σ (I)]	R_1 = 0.0915, wR_2 = 0.2075
Final R indexes [all data]	R_1 = 0.1384, wR_2 = 0.2539
Largest diff. peak/hole / e Å^{-3}	0.56/-0.47

Table S31. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 2ad. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	2095.6(5)	2166.8(13)	6023.2(8)	24.7(3)
O1	3973.1(14)	4542(4)	4589(2)	30.1(7)
N1	2923.0(17)	4294(4)	7887(3)	26.0(8)

Table S31. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 2ad. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C4	3150(2)	4031(5)	7084(3)	24.3(9)
C3	2714.8(19)	3847(5)	6002(3)	23.2(8)
C20	1800(2)	3121(5)	7018(3)	25.4(9)
C9	6107(2)	3845(5)	9595(3)	28.4(9)
C14	4174(2)	4101(5)	6395(3)	24.2(9)
C22	2415(2)	5603(5)	5392(3)	24.3(9)
C15	2235.4(19)	4141(5)	7787(3)	24.3(9)
C5	3882(2)	3954(5)	7250(3)	24.0(9)
C12	5279(2)	4101(5)	7571(3)	24.7(9)
C16	1982(2)	4954(6)	8542(3)	27.2(9)
C19	1140(2)	2879(5)	7034(3)	28.4(9)
C23	1741(2)	6310(5)	5412(3)	27.6(9)
C1	3752(2)	4105(5)	5317(3)	23.5(9)
C13	4855(2)	4207(5)	6573(3)	25.6(9)
C2	3041(2)	3469(5)	5113(3)	25.9(9)
C21	2540(2)	4768(6)	4408(3)	29.1(9)
C10	6381(2)	4185(5)	8751(3)	27.1(9)
C7	4996(2)	3835(5)	8418(3)	24.8(9)
C11	5982(2)	4283(5)	7760(3)	27.0(9)

Table S31. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 2ad. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C28	1692(2)	7472(5)	6198(3)	29.8(10)
C8	5433(2)	3664(5)	9425(3)	26.9(9)
C17	1326(2)	4735(6)	8553(3)	28.8(9)
C6	4302(2)	3794(5)	8228(3)	25.4(9)
C24	1165(2)	5791(6)	4671(3)	29.2(10)
C27	1068(2)	8073(6)	6254(4)	35.4(10)
C18	908(2)	3684(6)	7799(3)	30.0(10)
C26	496(2)	7586(6)	5507(4)	40.0(12)
C25	549(2)	6437(6)	4716(3)	36.1(11)

Table S32. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 2ad. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	32.1(6)	22.2(5)	21.0(6)	-1.5(4)	9.0(4)	-1.5(4)
O1	36.9(17)	37.7(17)	17.4(16)	1.6(12)	10.1(12)	-4.9(12)
N1	32.7(19)	25.9(17)	20.1(19)	0.5(13)	8.1(14)	-0.5(14)
C4	29(2)	20.9(18)	23(2)	1.5(15)	7.1(16)	-4.9(15)
C3	32(2)	20.5(19)	19(2)	-0.2(15)	9.8(16)	1.6(15)
C20	37(2)	26(2)	14(2)	1.1(15)	8.2(15)	3.2(16)
C9	34(2)	19.1(18)	30(2)	-2.6(16)	4.7(17)	0.1(15)

Table S32. Anisotropic Displacement Parameters ($Å^2×10^3$) for 2ad. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C14	37(2)	18.6(18)	17(2)	-2.8(15)	8.3(16)	-2.0(15)
C22	33(2)	22.9(19)	18(2)	1.8(15)	7.1(16)	0.0(15)
C15	29(2)	27(2)	19(2)	3.9(15)	8.5(15)	1.5(15)
C5	31(2)	20.1(18)	20(2)	-1.5(15)	5.1(15)	2.0(15)
C12	30(2)	17.5(18)	25(2)	-1.1(15)	4.7(16)	1.5(15)
C16	38(2)	27(2)	17(2)	1.2(16)	6.7(16)	2.8(17)
C19	35(2)	23(2)	26(2)	3.9(16)	6.0(17)	-2.9(16)
C23	35(2)	21(2)	28(2)	2.7(16)	11.1(17)	0.8(16)
C1	33(2)	20.1(18)	19(2)	-5.2(15)	9.4(16)	2.9(15)
C13	33(2)	25(2)	22(2)	-2.9(15)	11.0(16)	-1.0(15)
C2	33(2)	23.1(19)	21(2)	-4.0(15)	7.3(16)	-1.2(16)
C21	37(2)	34(2)	16(2)	1.2(17)	7.6(16)	-0.1(18)
C10	30(2)	21.6(19)	31(2)	-4.2(16)	10.5(17)	0.2(15)
C7	36(2)	18.9(18)	20(2)	1.7(15)	8.1(16)	3.5(15)
C11	33(2)	25(2)	27(2)	-1.1(16)	13.1(17)	1.8(16)
C28	42(2)	26(2)	24(2)	5.0(16)	12.4(18)	-1.7(16)
C8	37(2)	24(2)	21(2)	0.3(16)	9.4(16)	-0.7(16)
C17	38(2)	35(2)	16(2)	1.8(17)	11.6(16)	6.2(18)
C6	33(2)	25(2)	19(2)	-3.9(16)	7.8(16)	0.2(16)
C24	38(2)	31(2)	20(2)	6.1(17)	10.0(17)	-2.4(17)

Table S32. Anisotropic Displacement Parameters ($Å^2×10^3$) for 2ad. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C27	51(3)	25(2)	36(3)	3.0(18)	21(2)	5.7(19)
C18	26(2)	37(2)	28(2)	4.5(18)	8.6(17)	1.2(17)
C26	43(3)	34(2)	48(3)	12(2)	20(2)	13(2)
C25	32(2)	41(3)	35(3)	7(2)	7.5(18)	1.8(19)

Table S33. Bond Lengths for 2ad.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C3	1.806(4)	C5	C6	1.377(5)
S1	C20	1.762(4)	C12	C13	1.397(5)
O1	C1	1.230(5)	C12	C7	1.424(6)
N1	C4	1.300(5)	C12	C11	1.424(5)
N1	C15	1.406(5)	C16	C17	1.381(6)
C4	C3	1.501(5)	C19	C18	1.383(6)
C4	C5	1.481(5)	C23	C28	1.391(6)
C3	C22	1.586(5)	C23	C24	1.395(6)
C3	C2	1.545(5)	C1	C2	1.509(5)
C20	C15	1.405(5)	C2	C21	1.551(5)
C20	C19	1.390(6)	C10	C11	1.370(6)
C9	C10	1.418(6)	C7	C8	1.421(5)
C9	C8	1.367(6)	C7	C6	1.400(6)

Table S33. Bond Lengths for 2ad.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C14	C5	1.436(6)	C28	C27	1.395(6)
C14	C1	1.480(5)	C17	C18	1.391(6)
C14	C13	1.376(6)	C24	C25	1.387(6)
C22	C23	1.507(6)	C27	C26	1.388(7)
C22	C21	1.543(5)	C26	C25	1.392(7)
C15	C16	1.398(6)			

Table S34. Bond Angles for 2ad.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C20	S1	C3	97.07(19)	C7	C12	C11	119.5(4)
C4	N1	C15	119.5(3)	C17	C16	C15	121.3(4)
N1	C4	C3	123.8(4)	C18	C19	C20	119.7(4)
N1	C4	C5	117.7(3)	C28	C23	C22	119.2(4)
C5	C4	C3	118.4(3)	C28	C23	C24	119.6(4)
C4	C3	S1	107.4(3)	C24	C23	C22	121.2(4)
C4	C3	C22	118.5(3)	O1	C1	C14	121.8(4)
C4	C3	C2	119.2(3)	O1	C1	C2	119.7(3)
C22	C3	S1	113.6(3)	C14	C1	C2	118.5(3)
C2	C3	S1	110.2(3)	C14	C13	C12	121.6(4)
C2	C3	C22	86.9(3)	C3	C2	C21	89.7(3)
C15	C20	S1	119.3(3)	C1	C2	C3	114.3(3)

Table S34. Bond Angles for 2ad.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C19	C20	S1	120.2(3)	C1	C2	C21	112.4(3)
C19	C20	C15	120.5(4)	C22	C21	C2	88.3(3)
C8	C9	C10	119.7(4)	C11	C10	C9	121.0(4)
C5	C14	C1	120.9(4)	C8	C7	C12	118.4(4)
C13	C14	C5	120.0(3)	C6	C7	C12	118.8(3)
C13	C14	C1	119.2(3)	C6	C7	C8	122.8(4)
C23	C22	C3	121.5(3)	C10	C11	C12	119.9(4)
C23	C22	C21	121.7(3)	C23	C28	C27	119.8(4)
C21	C22	C3	88.5(3)	C9	C8	C7	121.4(4)
C20	C15	N1	123.8(4)	C16	C17	C18	119.3(4)
C16	C15	N1	117.7(3)	C5	C6	C7	122.5(4)
C16	C15	C20	118.3(4)	C25	C24	C23	120.2(4)
C14	C5	C4	120.8(3)	C26	C27	C28	120.6(4)
C6	C5	C4	121.0(4)	C19	C18	C17	120.8(4)
C6	C5	C14	118.1(4)	C27	C26	C25	119.2(4)
C13	C12	C7	118.9(4)	C24	C25	C26	120.5(4)
C13	C12	C11	121.6(4)				

Table S35. Torsion Angles for 2ad.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S1	C3	C22	C23	35.4(5)	C15	C20	C19	C18	1.5(6)
S1	C3	C22	C21	-91.5(3)	C15	C16	C17	C18	0.1(6)
S1	C3	C2	C1	-150.5(3)	C5	C4	C3	S1	129.9(3)
S1	C3	C2	C21	94.9(3)	C5	C4	C3	C22	-99.7(4)
S1	C20	C15	N1	-7.5(5)	C5	C4	C3	C2	3.8(5)
S1	C20	C15	C16	177.1(3)	C5	C14	C1	O1	166.9(4)
S1	C20	C19	C18	-177.9(3)	C5	C14	C1	C2	-16.1(5)
O1	C1	C2	C3	-151.1(3)	C5	C14	C13	C12	2.7(6)
O1	C1	C2	C21	-50.8(5)	C12	C7	C8	C9	3.5(6)
N1	C4	C3	S1	-51.7(4)	C12	C7	C6	C5	1.8(6)
N1	C4	C3	C22	78.7(5)	C16	C17	C18	C19	-0.9(6)
N1	C4	C3	C2	-177.8(4)	C19	C20	C15	N1	173.1(4)
N1	C4	C5	C14	-164.9(4)	C19	C20	C15	C16	-2.3(6)
N1	C4	C5	C6	13.2(5)	C23	C22	C21	C2	-145.9(4)
N1	C15	C16	C17	-174.2(4)	C23	C28	C27	C26	-2.8(6)
C4	N1	C15	C20	24.3(6)	C23	C24	C25	C26	-1.0(7)
C4	N1	C15	C16	-160.3(4)	C1	C14	C5	C4	-7.7(5)
C4	C3	C22	C23	-92.1(4)	C1	C14	C5	C6	174.2(3)
C4	C3	C22	C21	141.0(4)	C1	C14	C13	C12	-176.1(3)
C4	C3	C2	C1	-25.7(5)	C1	C2	C21	C22	-96.6(3)
C4	C3	C2	C21	-140.3(3)	C13	C14	C5	C4	173.5(4)

Table S35. Torsion Angles for 2ad.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C4	C5	C6	C7	-175.7(3)	C13	C14	C5	C6	-4.6(5)
C3	S1	C20	C15	-29.7(4)	C13	C14	C1	O1	-14.3(6)
C3	S1	C20	C19	149.7(3)	C13	C14	C1	C2	162.7(4)
C3	C4	C5	C14	13.7(5)	C13	C12	C7	C8	177.7(4)
C3	C4	C5	C6	-168.3(3)	C13	C12	C7	C6	-3.8(5)
C3	C22	C23	C28	87.7(5)	C13	C12	C11	C10	179.5(4)
C3	C22	C23	C24	-91.0(5)	C2	C3	C22	C23	146.1(4)
C3	C22	C21	C2	-19.1(3)	C2	C3	C22	C21	19.2(3)
C3	C2	C21	C22	19.7(3)	C21	C22	C23	C28	-162.3(4)
C20	S1	C3	C4	53.4(3)	C21	C22	C23	C24	19.0(6)
C20	S1	C3	C22	-79.7(3)	C10	C9	C8	C7	-0.9(6)
C20	S1	C3	C2	-175.3(3)	C7	C12	C13	C14	1.6(6)
C20	C15	C16	C17	1.5(6)	C7	C12	C11	C10	0.6(6)
C20	C19	C18	C17	0.1(6)	C11	C12	C13	C14	-177.4(4)
C9	C10	C11	C12	2.1(6)	C11	C12	C7	C8	-3.3(5)
C14	C5	C6	C7	2.4(6)	C11	C12	C7	C6	175.2(3)
C14	C1	C2	C3	31.8(5)	C28	C23	C24	C25	0.4(6)
C14	C1	C2	C21	132.1(3)	C28	C27	C26	C25	2.1(7)
C22	C3	C2	C1	95.5(3)	C8	C9	C10	C11	-1.9(6)
C22	C3	C2	C21	-19.1(3)	C8	C7	C6	C5	-179.8(4)
C22	C23	C28	C27	-177.1(4)	C6	C7	C8	C9	-174.9(4)

Table S35. Torsion Angles for 2ad.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C22	C23	C24	C25	179.0(4)	C24	C23	C28	C27	1.6(6)
C15	N1	C4	C3	9.9(5)	C27	C26	C25	C24	-0.2(7)
C15	N1	C4	C5	-171.7(3)					

Table S36. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2ad.

Atom	*x*	*y*	*z*	U(eq)
H9	6390.83	3744.2	10275.16	34
H22	2746.6	6585.98	5622.7	29
H16	2268.09	5670.96	9057.21	33
H19	850.82	2165.15	6521.7	34
H13	5040.93	4355.11	6003.53	31
H2	2981.56	2203.82	4866.38	31
H21A	2746.35	5596.46	4007.1	35
H21B	2144.59	4170.75	3956.53	35
H10	6847.92	4346.86	8873.87	33
H11	6173.82	4471.66	7200.34	32
H28	2083.1	7854.55	6695.84	36
H8	5253.19	3418.23	9991.59	32
H17	1160.82	5297.63	9070.9	35
H6	4113.77	3650.03	8795.91	31

Table S36. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2ad.

Atom	*x*	*y*	*z*	U(eq)
H24	1195.06	4992.56	4134.83	35
H27	1034.82	8823.11	6809.6	42
H18	457.58	3515.63	7810.02	36
H26	73.71	8030.02	5534.49	48
H25	159.47	6094.12	4202.21	43

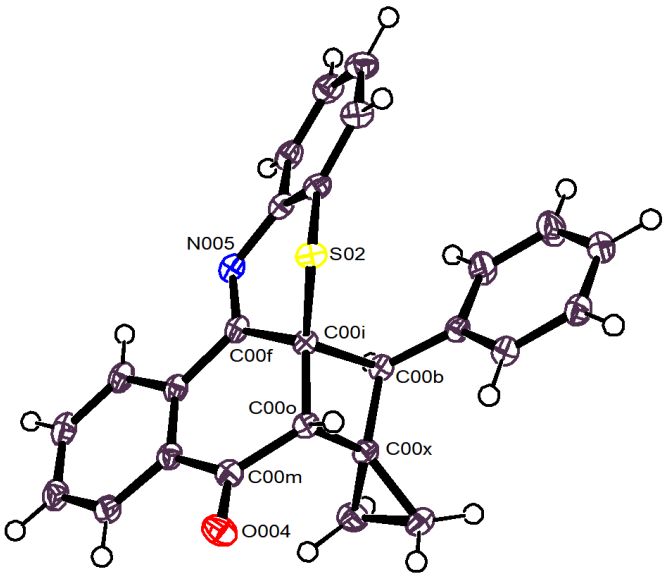


Table S37. Crystal data and structure refinement for 2af.

Identification code	**2af**
CCDC Number	**2403403**
Empirical formula	$C_{52}H_{38}N_2O_2S_2$
Formula weight	786.96
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.2581(6)

b/Å	25.0852(11)
c/Å	12.7705(6)
α/°	90
β/°	95.524(2)
γ/°	90
Volume/Å^3	3908.7(3)
Z	4
ρ_{calc}g/cm^3	1.337
μ/mm^{-1}	0.183
F(000)	1648.0
Crystal size/mm^3	0.02 × 0.016 × 0.012
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.4 to 60.066
Index ranges	-16 ≤ h ≤ 17, -35 ≤ k ≤ 35, -17 ≤ l ≤ 17
Reflections collected	93193
Independent reflections	11369 [R_{int} = 0.0575, R_{sigma} = 0.0319]
Data/restraints/parameters	11369/0/523
Goodness-of-fit on F^2	1.022
Final R indexes [I>=2σ (I)]	R_1 = 0.0389, wR_2 = 0.1032
Final R indexes [all data]	R_1 = 0.0447, wR_2 = 0.1088
Largest diff. peak/hole / e Å^{-3}	0.46/-0.29

Table S38. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 2af. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S01	1934.3(2)	4242.3(2)	3667.7(2)	15.67(6)
S02	3445.6(2)	4137.1(2)	6725.0(2)	16.72(6)
O003	3709.8(7)	2732.1(3)	5314.5(6)	21.80(16)

Table S38. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 2af. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O004	5648.9(7)	2767.4(3)	8338.6(7)	24.13(17)
N005	3313.9(7)	4567.1(4)	8950.3(7)	17.52(17)
N006	4244.8(7)	4615.6(4)	3298.1(7)	17.08(17)
C007	2574.3(9)	4783.2(4)	8157.6(8)	17.09(19)
C008	4878.7(9)	3446.9(4)	4958.7(8)	17.19(19)
C009	3375.9(8)	4873.7(4)	2717.9(8)	15.99(18)
C00A	3074.0(8)	3829.4(4)	3388.6(8)	14.17(17)
C00B	2255.3(8)	3456.5(4)	8085.7(8)	15.37(18)
C00C	4101.8(8)	4149.3(4)	3684.3(8)	15.22(18)
C00D	1402.3(8)	3439.6(4)	7158.7(8)	16.11(18)
C00E	1763.9(9)	4002.1(4)	836.5(8)	17.85(19)
C00F	3753.8(8)	4108.8(4)	8820.7(8)	15.38(18)
C00G	4985.4(8)	3933.4(4)	4432.7(8)	17.06(19)
C00H	3869.5(9)	3121.4(4)	4773.6(8)	16.72(19)
C00I	3376.8(8)	3750.3(4)	7905.0(8)	14.24(17)
C00J	2603.0(9)	4657.6(4)	7085.9(8)	17.51(19)
C00K	3054.9(8)	3580.1(4)	2238.2(8)	15.27(18)
C00L	2270.3(8)	4778.6(4)	2874.9(8)	15.42(18)
C00M	5030.9(8)	3127.0(4)	8537.9(8)	16.86(19)
C00N	1962.7(8)	3602.7(4)	1592.6(8)	15.89(18)
C00O	3961.4(8)	3204.0(4)	7885.0(8)	15.03(18)
C00P	1119.4(9)	3245.9(4)	1753.7(9)	19.2(2)
C00Q	1459.0(9)	3089.9(4)	6317.2(8)	18.10(19)
C00R	1453.9(9)	5109.1(4)	2401.6(9)	18.9(2)
C00S	1869.0(9)	5189.9(4)	8433.3(9)	20.7(2)

Table S38. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 2af. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C00T	4648.8(8)	3934.9(4)	9611.8(8)	16.39(18)
C00U	3367.7(9)	3052.0(4)	2792.7(8)	16.44(19)
C00V	5268.6(8)	3474.4(4)	9471.7(8)	17.00(19)
C00W	3628.3(9)	5284.2(4)	2038.6(9)	19.9(2)
C00X	2954.0(8)	2958.6(4)	8341.3(8)	16.52(18)
C00Y	3064.4(8)	3261.6(4)	3859.2(8)	15.46(18)
C00Z	666.1(9)	3102.8(4)	5459.5(9)	20.6(2)
C010	6144.3(9)	3339.2(5)	10210.2(9)	21.4(2)
C011	1722.7(10)	5514.6(5)	1735.6(9)	23.4(2)
C012	5719.9(9)	3271.3(5)	5698.6(9)	21.7(2)
C013	4915.0(9)	4251.2(4)	10506.3(9)	19.9(2)
C014	1974.6(10)	4948.8(4)	6317.6(9)	21.9(2)
C015	747.2(10)	4044.2(5)	254.4(9)	21.5(2)
C016	5931.3(10)	4238.8(5)	4669.3(10)	23.7(2)
C017	2971.5(10)	2662.6(5)	9366.7(9)	23.7(2)
C018	5762.6(10)	4106.4(5)	11246.3(9)	23.7(2)
C019	532.2(10)	3798.6(5)	7121.0(10)	25.1(2)
C01A	108.4(9)	3283.4(4)	1164.4(9)	22.0(2)
C01B	2809.4(10)	5595.8(5)	1535.7(9)	23.4(2)
C01C	1290.5(10)	5352.2(5)	6609.2(10)	24.2(2)
C01D	1224.8(10)	5467.7(4)	7670.0(10)	23.9(2)
C01E	6384.3(10)	3651.7(5)	11098.7(9)	24.8(2)
C01F	2627.8(10)	2384.5(5)	8335.5(10)	24.3(2)
C01G	4371.5(10)	2726.9(5)	2635.7(9)	23.4(2)
C01H	3242.7(10)	2494.1(4)	2387.7(9)	23.7(2)

Table S38. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 2af. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C01I	6652.5(10)	3578.3(5)	5919.0(10)	27.1(2)
C01J	-196.6(10)	3463.0(5)	5433.0(10)	25.2(2)
C01K	-78.9(10)	3681.2(5)	411.0(9)	23.1(2)
C01L	6754.2(10)	4062.3(5)	5404.1(11)	28.9(3)
C01M	-256.1(11)	3810.7(5)	6268.5(12)	31.6(3)

Table S39. Anisotropic Displacement Parameters (Å^2×10^3) for 2af. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S01	15.81(12)	15.93(12)	16.03(12)	1.26(8)	5.51(9)	1.18(8)
S02	20.51(13)	15.86(12)	14.67(12)	0.26(8)	6.18(9)	1.82(8)
O003	25.8(4)	19.9(4)	20.4(4)	6.5(3)	5.8(3)	2.7(3)
O004	23.4(4)	25.9(4)	23.1(4)	-1.4(3)	2.6(3)	8.1(3)
N005	18.2(4)	17.0(4)	18.1(4)	-2.6(3)	5.3(3)	-2.3(3)
N006	15.9(4)	16.4(4)	18.9(4)	1.4(3)	1.8(3)	0.2(3)
C007	17.9(5)	14.1(4)	19.9(5)	-2.3(4)	5.2(4)	-2.3(3)
C008	18.8(5)	17.8(5)	15.3(4)	0.2(4)	3.6(3)	3.3(4)
C009	17.0(4)	13.9(4)	17.0(4)	-0.1(3)	1.5(3)	-0.4(3)
C00A	14.8(4)	13.9(4)	14.4(4)	0.4(3)	4.3(3)	0.6(3)
C00B	15.4(4)	15.7(4)	15.4(4)	-1.5(3)	3.8(3)	-0.4(3)
C00C	14.5(4)	16.0(4)	15.4(4)	-0.5(3)	3.3(3)	0.8(3)
C00D	14.9(4)	15.7(4)	18.0(4)	-1.2(4)	3.3(3)	-1.2(3)
C00E	22.6(5)	17.6(5)	13.9(4)	0.2(4)	4.6(4)	-2.0(4)
C00F	16.3(4)	16.5(4)	14.1(4)	-1.8(3)	5.1(3)	-3.5(3)
C00G	16.5(4)	17.7(5)	17.1(4)	0.6(4)	2.1(3)	2.7(4)
C00H	19.4(5)	16.6(4)	14.9(4)	0.8(4)	5.5(3)	3.4(4)

Table S39. Anisotropic Displacement Parameters ($Å^2×10^3$) for 2af. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C00I	15.3(4)	14.5(4)	13.2(4)	-1.0(3)	3.3(3)	-0.5(3)
C00J	19.2(5)	14.4(4)	19.7(5)	-0.8(4)	6.1(4)	-0.6(3)
C00K	17.6(4)	15.4(4)	13.5(4)	0.3(3)	5.0(3)	-1.1(3)
C00L	17.5(4)	14.1(4)	14.9(4)	-0.3(3)	2.8(3)	0.1(3)
C00M	17.2(4)	18.5(5)	15.3(4)	1.6(4)	4.1(3)	-0.8(4)
C00N	19.2(5)	15.3(4)	13.5(4)	-1.4(3)	3.6(3)	-1.1(3)
C00O	16.2(4)	14.6(4)	14.7(4)	-1.2(3)	3.7(3)	0.6(3)
C00P	22.6(5)	16.1(4)	19.2(5)	1.3(4)	2.9(4)	-3.1(4)
C00Q	17.1(4)	18.4(5)	19.1(5)	-2.5(4)	3.8(4)	-0.5(4)
C00R	16.5(4)	18.8(5)	21.5(5)	1.6(4)	2.8(4)	1.4(4)
C00S	20.8(5)	16.9(5)	25.3(5)	-5.0(4)	7.1(4)	-1.4(4)
C00T	16.7(4)	18.6(5)	14.3(4)	0.0(4)	4.0(3)	-4.4(4)
C00U	19.2(5)	15.1(4)	15.6(4)	0.3(3)	4.5(3)	0.7(3)
C00V	17.1(4)	18.3(5)	15.8(4)	1.7(4)	2.9(3)	-3.6(3)
C00W	19.0(5)	18.5(5)	22.3(5)	3.4(4)	3.0(4)	-2.5(4)
C00X	16.8(4)	15.7(4)	17.3(4)	0.4(4)	3.1(3)	-1.2(3)
C00Y	17.6(4)	14.3(4)	15.1(4)	1.9(3)	4.6(3)	0.2(3)
C00Z	22.3(5)	20.8(5)	18.7(5)	-2.8(4)	2.3(4)	-4.0(4)
C010	21.2(5)	20.6(5)	21.9(5)	4.6(4)	-0.5(4)	-4.0(4)
C011	21.9(5)	21.6(5)	26.2(5)	6.8(4)	-0.7(4)	2.3(4)
C012	24.1(5)	20.7(5)	20.0(5)	2.4(4)	0.2(4)	5.3(4)
C013	21.9(5)	21.5(5)	16.8(5)	-2.1(4)	5.2(4)	-6.7(4)
C014	25.8(5)	19.1(5)	21.2(5)	1.8(4)	5.3(4)	2.0(4)
C015	26.4(5)	21.3(5)	16.4(5)	1.1(4)	0.6(4)	1.2(4)
C016	20.6(5)	20.2(5)	29.3(6)	3.1(4)	-3.2(4)	-0.1(4)
C017	23.0(5)	25.6(5)	22.8(5)	7.4(4)	4.1(4)	-1.5(4)

Table S39. Anisotropic Displacement Parameters ($Å^2×10^3$) for 2af. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C018	26.2(6)	28.2(6)	16.4(5)	-0.8(4)	1.5(4)	-11.8(4)
C019	21.7(5)	23.7(5)	29.1(6)	-10.1(4)	-1.8(4)	4.6(4)
C01A	22.1(5)	19.0(5)	24.7(5)	-1.7(4)	1.5(4)	-4.1(4)
C01B	24.1(5)	20.7(5)	25.2(5)	8.2(4)	1.9(4)	-1.2(4)
C01C	24.9(5)	19.1(5)	29.1(6)	3.1(4)	4.6(4)	3.5(4)
C01D	22.0(5)	17.5(5)	33.2(6)	-3.1(4)	7.4(4)	2.0(4)
C01E	25.5(5)	27.7(6)	20.0(5)	5.4(4)	-4.2(4)	-9.1(4)
C01F	23.9(5)	16.6(5)	32.1(6)	2.3(4)	0.9(4)	-3.7(4)
C01G	25.5(5)	22.5(5)	22.9(5)	-1.3(4)	6.6(4)	6.1(4)
C01H	32.0(6)	15.7(5)	23.3(5)	-2.5(4)	2.5(4)	1.0(4)
C01I	25.4(6)	26.0(6)	28.2(6)	1.6(5)	-6.3(4)	5.4(4)
C01J	24.5(5)	22.5(5)	27.0(6)	-1.4(4)	-5.9(4)	-0.3(4)
C01K	24.1(5)	24.4(5)	20.0(5)	-2.5(4)	-1.7(4)	-0.8(4)
C01L	22.5(5)	25.5(6)	36.4(7)	1.8(5)	-8.4(5)	-0.5(4)
C01M	25.1(6)	26.6(6)	40.6(7)	-10.4(5)	-9.6(5)	9.0(5)

Table S40. Bond Lengths for 2af.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S01	C00A	1.8022(10)	C00K	C00U	1.5333(14)
S01	C00L	1.7563(10)	C00L	C00R	1.3919(14)
S02	C00I	1.8012(10)	C00M	C00O	1.4969(14)
S02	C00J	1.7539(11)	C00M	C00V	1.4831(15)
O003	C00H	1.2227(13)	C00N	C00P	1.3975(14)
O004	C00M	1.2205(13)	C00O	C00X	1.5435(14)
N005	C007	1.4014(14)	C00P	C01A	1.3898(15)
N005	C00F	1.2872(13)	C00Q	C00Z	1.3930(15)

Table S40. Bond Lengths for 2af.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N006	C009	1.3967(13)	C00R	C011	1.3858(15)
N006	C00C	1.2879(13)	C00S	C01D	1.3825(17)
C007	C00J	1.4081(15)	C00T	C00V	1.4036(15)
C007	C00S	1.4037(14)	C00T	C013	1.4031(14)
C008	C00G	1.4053(14)	C00U	C00Y	1.5386(14)
C008	C00H	1.4822(15)	C00U	C01G	1.5055(15)
C008	C012	1.4009(15)	C00U	C01H	1.4947(15)
C009	C00L	1.4094(14)	C00V	C010	1.4007(15)
C009	C00W	1.4002(14)	C00W	C01B	1.3809(15)
C00A	C00C	1.5107(14)	C00X	C017	1.5037(15)
C00A	C00K	1.5948(14)	C00X	C01F	1.4945(15)
C00A	C00Y	1.5463(14)	C00Z	C01J	1.3888(16)
C00B	C00D	1.5028(14)	C010	C01E	1.3872(16)
C00B	C00I	1.5960(14)	C011	C01B	1.3953(17)
C00B	C00X	1.5318(14)	C012	C01I	1.3847(17)
C00C	C00G	1.4766(14)	C013	C018	1.3840(16)
C00D	C00Q	1.3941(14)	C014	C01C	1.3878(16)
C00D	C019	1.3932(15)	C015	C01K	1.3905(16)
C00E	C00N	1.3966(14)	C016	C01L	1.3827(16)
C00E	C015	1.3922(15)	C017	C01F	1.5138(17)
C00F	C00I	1.5120(14)	C018	C01E	1.3946(18)
C00F	C00T	1.4836(14)	C019	C01M	1.3846(17)
C00G	C016	1.3984(15)	C01A	C01K	1.3898(16)
C00H	C00Y	1.4965(14)	C01C	C01D	1.3951(17)
C00I	C00O	1.5477(14)	C01G	C01H	1.5072(17)
C00J	C014	1.3943(15)	C01I	C01L	1.3922(18)

Table S40. Bond Lengths for 2af.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C00K	C00N	1.5043(14)	C01J	C01M	1.3855(18)

Table S41. Bond Angles for 2af.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C00L	S01	C00A	95.56(5)	C00E	C00N	C00K	119.53(9)
C00J	S02	C00I	96.03(5)	C00E	C00N	C00P	118.62(10)
C00F	N005	C007	120.17(9)	C00P	C00N	C00K	121.81(9)
C00C	N006	C009	119.95(9)	C00M	C00O	C00I	119.15(8)
N005	C007	C00J	122.72(9)	C00M	C00O	C00X	115.33(8)
N005	C007	C00S	118.11(10)	C00X	C00O	C00I	87.61(7)
C00S	C007	C00J	118.68(10)	C01A	C00P	C00N	120.70(10)
C00G	C008	C00H	121.12(9)	C00Z	C00Q	C00D	120.57(10)
C012	C008	C00G	119.95(10)	C011	C00R	C00L	120.02(10)
C012	C008	C00H	118.89(10)	C01D	C00S	C007	120.88(11)
N006	C009	C00L	122.73(9)	C00V	C00T	C00F	121.94(9)
N006	C009	C00W	117.84(9)	C013	C00T	C00F	119.14(10)
C00W	C009	C00L	119.05(9)	C013	C00T	C00V	118.87(10)
C00C	C00A	S01	106.80(7)	C00K	C00U	C00Y	92.43(8)
C00C	C00A	C00K	112.12(8)	C01G	C00U	C00K	125.29(9)
C00C	C00A	C00Y	115.43(8)	C01G	C00U	C00Y	124.98(9)
C00K	C00A	S01	117.69(7)	C01H	C00U	C00K	129.52(9)
C00Y	C00A	S01	114.67(7)	C01H	C00U	C00Y	126.93(9)
C00Y	C00A	C00K	89.82(7)	C01H	C00U	C01G	60.31(8)
C00D	C00B	C00I	116.29(8)	C00T	C00V	C00M	121.29(9)
C00D	C00B	C00X	118.50(9)	C010	C00V	C00M	118.53(10)
C00X	C00B	C00I	86.31(7)	C010	C00V	C00T	120.17(10)

Table S41. Bond Angles for 2af.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N006	C00C	C00A	121.84(9)	C01B	C00W	C009	120.68(10)
N006	C00C	C00G	117.56(9)	C00B	C00X	C00O	92.61(8)
C00G	C00C	C00A	120.60(9)	C017	C00X	C00B	123.30(9)
C00Q	C00D	C00B	122.85(9)	C017	C00X	C00O	125.51(9)
C019	C00D	C00B	118.77(9)	C01F	C00X	C00B	129.87(9)
C019	C00D	C00Q	118.35(10)	C01F	C00X	C00O	127.29(9)
C015	C00E	C00N	120.74(10)	C01F	C00X	C017	60.65(8)
N005	C00F	C00I	122.01(9)	C00H	C00Y	C00A	119.39(9)
N005	C00F	C00T	117.81(9)	C00H	C00Y	C00U	114.39(8)
C00T	C00F	C00I	120.18(9)	C00U	C00Y	C00A	87.67(7)
C008	C00G	C00C	122.12(9)	C01J	C00Z	C00Q	120.42(10)
C016	C00G	C008	119.07(10)	C01E	C010	C00V	120.16(11)
C016	C00G	C00C	118.70(9)	C00R	C011	C01B	120.47(10)
O003	C00H	C008	121.76(10)	C01I	C012	C008	120.12(11)
O003	C00H	C00Y	119.95(10)	C018	C013	C00T	120.53(11)
C008	C00H	C00Y	118.20(9)	C01C	C014	C00J	120.02(11)
C00B	C00I	S02	118.69(7)	C01K	C015	C00E	120.03(10)
C00F	C00I	S02	106.93(7)	C01L	C016	C00G	120.45(11)
C00F	C00I	C00B	111.48(8)	C00X	C017	C01F	59.38(7)
C00F	C00I	C00O	115.59(8)	C013	C018	C01E	120.43(11)
C00O	C00I	S02	113.84(7)	C01M	C019	C00D	121.02(11)
C00O	C00I	C00B	90.02(7)	C00P	C01A	C01K	120.19(10)
C007	C00J	S02	119.50(8)	C00W	C01B	C011	119.76(10)
C014	C00J	S02	120.30(8)	C014	C01C	C01D	120.31(11)
C014	C00J	C007	120.20(10)	C00S	C01D	C01C	119.84(10)
C00N	C00K	C00A	115.05(8)	C010	C01E	C018	119.81(11)

Table S41. Bond Angles for 2af.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C00N	C00K	C00U	117.10(9)	C00X	C01F	C017	59.98(7)
C00U	C00K	C00A	86.13(7)	C00U	C01G	C01H	59.49(7)
C009	C00L	S01	119.59(8)	C00U	C01H	C01G	60.20(7)
C00R	C00L	S01	120.52(8)	C012	C01I	C01L	119.92(11)
C00R	C00L	C009	119.89(9)	C01M	C01J	C00Z	119.15(11)
O004	C00M	C00O	120.47(10)	C01A	C01K	C015	119.71(11)
O004	C00M	C00V	121.61(10)	C016	C01L	C01I	120.48(11)
C00V	C00M	C00O	117.76(9)	C019	C01M	C01J	120.48(11)

Table S42. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2af.

Atom	*x*	*y*	*z*	U(eq)
H00B	1941.75	3595.73	8726.6	18
H00E	2328.64	4247.91	718	21
H00K	3659.76	3722.49	1845.83	18
H00O	4010.56	3081.74	7145.66	18
H00P	1238.51	2974.76	2271.52	23
H00Q	2043.56	2840.69	6328.7	22
H00R	712.4	5056.71	2535.24	23
H00S	1833.84	5275.26	9153.98	25
H00W	4370.68	5349.14	1922.54	24
H00Y	2304.84	3151.69	3988.87	19
H00Z	715.69	2863.76	4889.15	25
H010	6574.9	3032.72	10102.43	26
H011	1163.01	5738.81	1412.89	28
H012	5650.41	2940.89	6049.74	26
H013	4510.25	4567.19	10604.72	24

Table S42. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2af.

Atom	*x*	*y*	*z*	U(eq)
H014	2014.85	4871.09	5594.3	26
H015	617.9	4320.94	-250.05	26
H016	6009.08	4569.87	4322.87	28
H01G	2394.88	2747.08	9832.97	28
H01H	3694.25	2570.09	9735.29	28
H018	5921.88	4318.07	11858.73	28
H019	478.81	4038.76	7688.96	30
H01A	-456.2	3036.5	1276.89	26
H01B	2985.3	5864.42	1055.26	28
H01J	864.81	5550.64	6084.02	29
H01M	738.67	5736.56	7867.25	29
H01N	6970.5	3556.27	11605.24	30
H01O	3140.38	2121.37	8076.03	29
H01P	1841.53	2298.3	8173.68	29
H01C	4818.21	2595.04	3269.99	28
H01D	4792.48	2821.1	2038.22	28
H01E	2973.44	2444.57	1638.07	28
H01F	2999.16	2218.61	2869.25	28
H01I	7222.26	3458.77	6421.03	33
H01Q	-739	3470.85	4849.38	30
H01K	-768.29	3704.96	4.72	28
H01L	7393.58	4272.91	5558.69	35
H01R	-841.89	4059.27	6256.39	38

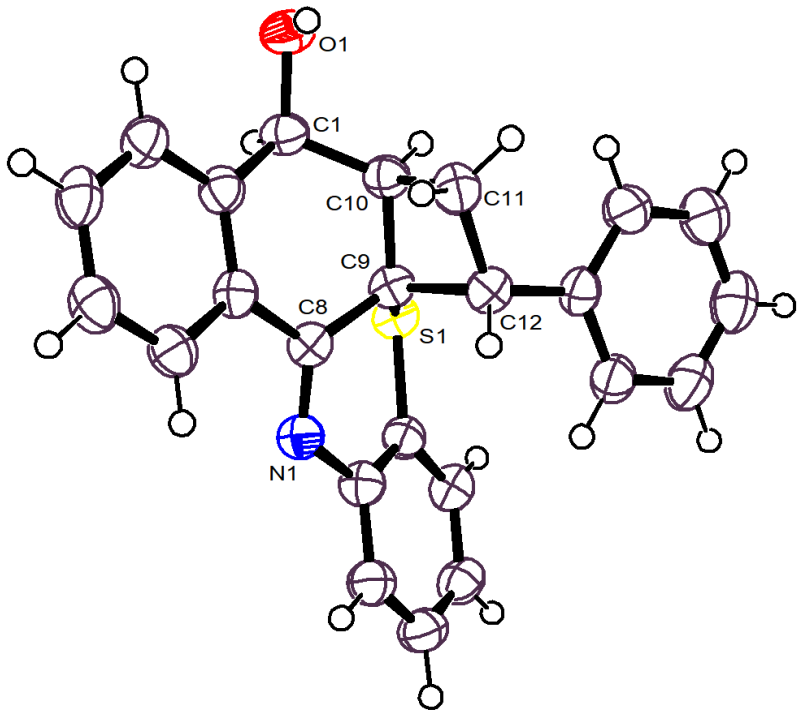


Table S43. Crystal data and structure refinement for 2ak.

Identification code	**2ak**
CCDC Number	**2332713**
Empirical formula	$C_{24}H_{19}NOS$
Formula weight	369.46
Temperature/K	140(2)
Crystal system	trigonal
Space group	R-3
a/Å	32.1279(14)
b/Å	32.1279(14)
c/Å	9.3505(5)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	8358.5(9)
Z	18

ρ_{calc}g/cm^3	1.321
μ/mm^{-1}	1.640
F(000)	3492.0
Crystal size/mm^3	0.051 × 0.042 × 0.034
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	9.536 to 149.55
Index ranges	-40 ≤ h ≤ 39, -40 ≤ k ≤ 37, -11 ≤ l ≤ 11
Reflections collected	27501
Independent reflections	3782 [R_{int} = 0.1192, R_{sigma} = 0.0710]
Data/restraints/parameters	3782/0/246
Goodness-of-fit on F^2	1.146
Final R indexes [I>=2σ (I)]	R_1 = 0.0713, wR_2 = 0.2071
Final R indexes [all data]	R_1 = 0.0895, wR_2 = 0.2249
Largest diff. peak/hole / e Å^{-3}	0.41/-0.57

Table S44. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 2ak. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	1857.2(2)	4143.5(2)	4697.9(7)	34.9(3)
O1	2768.1(7)	5842.4(7)	5998(2)	53.5(6)
N1	1223.9(8)	4425.0(7)	2983(2)	34.8(5)
C1	2442.2(9)	5458.3(9)	5121(3)	36.8(6)
C2	2171.8(9)	5604.9(9)	4113(3)	36.2(6)
C3	2353.1(10)	6083.6(9)	3727(3)	42.2(7)
C4	2109.3(11)	6211.8(10)	2763(3)	45.2(7)
C5	1676.7(10)	5865.6(10)	2192(3)	43.4(7)
C6	1490.9(10)	5388.6(9)	2553(3)	39.3(6)
C7	1736.2(9)	5251.6(9)	3515(3)	33.2(6)

Table S44. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 2ak. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C8	1537.8(9)	4734.1(8)	3841(3)	31.8(6)
C9	1703.9(9)	4594.6(9)	5182(3)	32.6(6)
C10	2100.2(9)	5024.1(9)	6013(3)	34.5(6)
C11	1704.2(10)	5030.7(9)	6934(3)	38.7(6)
C12	1349.9(9)	4503.4(8)	6482(3)	34.6(6)
C13	1287.6(9)	4105.8(9)	7485(3)	36.3(6)
C14	1568.5(10)	4184.8(11)	8690(3)	47.0(7)
C15	1500.6(12)	3802.5(11)	9548(3)	57.7(9)
C16	1152.9(12)	3337.2(11)	9219(4)	58.2(9)
C17	871.2(11)	3255.0(11)	8022(3)	51.9(8)
C18	935.9(10)	3636.6(9)	7167(3)	41.6(7)
C19	1309.7(9)	3747.1(9)	3865(3)	34.2(6)
C20	1045.0(9)	3930.3(9)	3183(3)	35.4(6)
C21	603.3(9)	3613.5(10)	2565(3)	41.1(7)
C22	422.6(10)	3121.6(10)	2635(3)	43.8(7)
C23	688.8(10)	2942.8(9)	3289(3)	42.6(7)
C24	1128.9(9)	3251.9(9)	3903(3)	38.4(6)

Table S45. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 2ak. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	33.0(4)	32.4(4)	42.5(5)	-1.2(2)	-1.2(2)	18.9(3)
O1	57.5(13)	32.9(11)	51.9(13)	-4.7(9)	-12.5(10)	8.8(9)
N1	34.8(11)	32.7(11)	38.0(12)	-0.7(9)	-2.3(9)	17.6(9)
C1	35.5(14)	30.8(13)	40.7(14)	-4.0(11)	-4.0(11)	14.2(11)

Table S45. Anisotropic Displacement Parameters ($Å^2×10^3$) for 2ak. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C2	40.6(14)	33.1(13)	35.7(14)	1.0(11)	1.0(11)	19.1(12)
C3	48.0(16)	33.0(14)	40.3(15)	3.6(11)	2.1(12)	16.3(12)
C4	60.0(18)	35.8(14)	42.0(15)	8.5(12)	9.0(13)	25.7(14)
C5	54.7(17)	41.0(15)	42.6(15)	5.0(12)	-1.6(13)	29.9(14)
C6	43.5(15)	41.2(15)	37.3(14)	1.3(11)	-1.0(12)	24.3(12)
C7	37.9(14)	31.3(13)	34.2(13)	2.2(10)	3.4(10)	20.1(11)
C8	30.3(13)	31.5(13)	37.0(13)	0.7(10)	1.4(10)	18.1(11)
C9	32.2(13)	29.9(12)	37.7(13)	-0.8(10)	-0.5(10)	17.0(11)
C10	34.2(13)	33.2(13)	36.8(13)	-1.4(10)	-3.3(11)	17.5(11)
C11	49.5(16)	34.4(14)	36.3(14)	-0.9(11)	2.7(12)	24.1(13)
C12	32.7(13)	35.1(14)	38.5(14)	0.3(11)	2.2(11)	18.9(11)
C13	33.4(14)	39.0(14)	36.6(14)	5.9(11)	7.1(11)	18.1(12)
C14	46.7(16)	45.1(16)	45.0(16)	5.5(13)	-5.7(13)	19.9(14)
C15	64(2)	58(2)	48.8(18)	14.4(15)	-2.6(15)	28.7(17)
C16	67(2)	48.9(18)	57(2)	16.7(15)	12.9(17)	27.7(17)
C17	53.7(18)	38.8(16)	56.2(18)	6.2(14)	13.0(15)	17.9(14)
C18	40.0(15)	40.5(15)	40.4(15)	2.5(12)	5.2(12)	17.3(13)
C19	36.5(14)	32.1(13)	33.9(13)	-2.2(10)	1.2(10)	16.9(11)
C20	37.3(14)	32.7(13)	38.3(14)	-1.2(11)	-1.0(11)	19.1(11)
C21	38.2(14)	40.4(15)	42.4(15)	-0.6(12)	-2.8(12)	18.0(12)
C22	37.2(15)	38.8(15)	47.6(16)	-4.3(12)	-2.4(12)	13.3(12)
C23	43.3(15)	31.3(14)	47.5(16)	-4.5(12)	4.6(13)	14.3(12)
C24	40.1(14)	35.0(14)	43.2(15)	0.6(11)	4.4(11)	21.0(12)

Table S46. Bond Lengths for 2ak.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C9	1.806(2)	C9	C12	1.589(3)
S1	C19	1.756(3)	C10	C11	1.545(3)
O1	C1	1.414(3)	C11	C12	1.554(3)
N1	C8	1.283(3)	C12	C13	1.515(3)
N1	C20	1.406(3)	C13	C14	1.386(4)
C1	C2	1.508(4)	C13	C18	1.391(4)
C1	C10	1.522(3)	C14	C15	1.390(4)
C2	C3	1.392(3)	C15	C16	1.381(4)
C2	C7	1.404(4)	C16	C17	1.379(5)
C3	C4	1.385(4)	C17	C18	1.389(4)
C4	C5	1.381(4)	C19	C20	1.406(3)
C5	C6	1.380(3)	C19	C24	1.395(3)
C6	C7	1.404(3)	C20	C21	1.392(4)
C7	C8	1.484(3)	C21	C22	1.386(4)
C8	C9	1.515(3)	C22	C23	1.388(4)
C9	C10	1.540(3)	C23	C24	1.382(4)

Table S47. Bond Angles for 2ak.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C19	S1	C9	96.72(11)	C1	C10	C11	121.0(2)
C8	N1	C20	120.7(2)	C9	C10	C11	88.62(18)
O1	C1	C2	112.4(2)	C10	C11	C12	89.61(18)
O1	C1	C10	111.2(2)	C11	C12	C9	86.56(18)
C2	C1	C10	111.4(2)	C13	C12	C9	114.2(2)
C3	C2	C1	121.2(2)	C13	C12	C11	117.9(2)
C3	C2	C7	119.2(2)	C14	C13	C12	123.3(2)

Table S47. Bond Angles for 2ak.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C7	C2	C1	119.6(2)	C14	C13	C18	118.3(3)
C4	C3	C2	120.7(3)	C18	C13	C12	118.4(2)
C5	C4	C3	120.2(2)	C13	C14	C15	120.5(3)
C6	C5	C4	120.1(3)	C16	C15	C14	120.8(3)
C5	C6	C7	120.4(3)	C17	C16	C15	119.1(3)
C2	C7	C6	119.4(2)	C16	C17	C18	120.2(3)
C2	C7	C8	121.3(2)	C17	C18	C13	121.0(3)
C6	C7	C8	119.3(2)	C20	C19	S1	119.60(19)
N1	C8	C7	118.0(2)	C24	C19	S1	120.7(2)
N1	C8	C9	123.0(2)	C24	C19	C20	119.7(2)
C7	C8	C9	118.9(2)	C19	C20	N1	122.8(2)
C8	C9	S1	107.91(16)	C21	C20	N1	117.5(2)
C8	C9	C10	114.1(2)	C21	C20	C19	119.4(2)
C8	C9	C12	111.25(19)	C22	C21	C20	120.4(3)
C10	C9	S1	114.24(17)	C21	C22	C23	119.9(3)
C10	C9	C12	88.50(18)	C24	C23	C22	120.4(2)
C12	C9	S1	120.06(17)	C23	C24	C19	120.1(2)
C1	C10	C9	116.0(2)				

Table S48. Hydrogen Bonds for 2ak.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O1	H1	O1[1]	0.84	1.85	2.658(2)	159.7

[1]-1/3+Y,1/3-X+Y,4/3-Z

Table S49. Torsion Angles for 2ak.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S1	C9	C10	C1	93.9(2)	C8	C9	C10	C11	93.3(2)
S1	C9	C10	C11	-141.88(18)	C8	C9	C12	C11	-96.1(2)
S1	C9	C12	C11	136.61(19)	C8	C9	C12	C13	144.8(2)
S1	C9	C12	C13	17.5(3)	C9	S1	C19	C20	30.4(2)
S1	C19	C20	N1	7.7(4)	C9	S1	C19	C24	-148.0(2)
S1	C19	C20	C21	-177.9(2)	C9	C10	C11	C12	19.80(19)
S1	C19	C24	C23	177.6(2)	C9	C12	C13	C14	91.8(3)
O1	C1	C2	C3	22.7(3)	C9	C12	C13	C18	-87.2(3)
O1	C1	C2	C7	-159.3(2)	C10	C1	C2	C3	148.3(2)
O1	C1	C10	C9	175.8(2)	C10	C1	C2	C7	-33.7(3)
O1	C1	C10	C11	70.5(3)	C10	C9	C12	C11	19.27(18)
N1	C8	C9	S1	49.2(3)	C10	C9	C12	C13	-99.8(2)
N1	C8	C9	C10	177.3(2)	C10	C11	C12	C9	-19.20(18)
N1	C8	C9	C12	-84.5(3)	C10	C11	C12	C13	96.4(2)
N1	C20	C21	C22	175.5(2)	C11	C12	C13	C14	-7.6(4)
C1	C2	C3	C4	177.8(3)	C11	C12	C13	C18	173.4(2)
C1	C2	C7	C6	-178.6(2)	C12	C9	C10	C1	-143.5(2)
C1	C2	C7	C8	-0.8(4)	C12	C9	C10	C11	-19.36(18)
C1	C10	C11	C12	139.7(2)	C12	C13	C14	C15	-178.4(3)
C2	C1	C10	C9	49.6(3)	C12	C13	C18	C17	178.1(2)
C2	C1	C10	C11	-55.6(3)	C13	C14	C15	C16	0.0(5)
C2	C3	C4	C5	1.2(4)	C14	C13	C18	C17	-0.9(4)
C2	C7	C8	N1	-160.5(2)	C14	C15	C16	C17	0.0(5)
C2	C7	C8	C9	21.1(3)	C15	C16	C17	C18	-0.4(5)
C3	C2	C7	C6	-0.6(4)	C16	C17	C18	C13	0.9(4)
C3	C2	C7	C8	177.3(2)	C18	C13	C14	C15	0.5(4)

Table S49. Torsion Angles for 2ak.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C3	C4	C5	C6	-1.5(4)	C19	S1	C9	C8	-53.53(19)
C4	C5	C6	C7	0.8(4)	C19	S1	C9	C10	178.46(18)
C5	C6	C7	C2	0.2(4)	C19	S1	C9	C12	75.3(2)
C5	C6	C7	C8	-177.6(2)	C19	C20	C21	C22	0.8(4)
C6	C7	C8	N1	17.3(3)	C20	N1	C8	C7	175.9(2)
C6	C7	C8	C9	-161.1(2)	C20	N1	C8	C9	-5.7(4)
C7	C2	C3	C4	-0.2(4)	C20	C19	C24	C23	-0.8(4)
C7	C8	C9	S1	-132.45(19)	C20	C21	C22	C23	-1.8(4)
C7	C8	C9	C10	-4.3(3)	C21	C22	C23	C24	1.5(4)
C7	C8	C9	C12	93.9(3)	C22	C23	C24	C19	-0.2(4)
C8	N1	C20	C19	-27.1(4)	C24	C19	C20	N1	-173.8(2)
C8	N1	C20	C21	158.4(2)	C24	C19	C20	C21	0.6(4)
C8	C9	C10	C1	-30.9(3)					

Table S50. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2ak.

Atom	*x*	*y*	*z*	U(eq)
H1	2621.03	5959.22	6431.63	80
H1A	2635.89	5359.63	4520.6	44
H3	2647.31	6324.81	4128.29	51
H4	2239.94	6538.84	2494.08	54
H5	1506.73	5956.14	1549.67	52
H6	1195.31	5151.47	2147.45	47
H10	2287.34	4915.57	6605.41	41
H11A	1608.63	5263.2	6598.44	46
H11B	1777.45	5069.8	7969.71	46
H12	1034.24	4459.91	6155.46	41

Table S50. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2ak.

Atom	*x*	*y*	*z*	U(eq)
H14	1809.21	4502.72	8932.43	56
H15	1695.9	3862	10371.14	69
H16	1108.31	3077.32	9808.49	70
H17	632.06	2936.34	7781.13	62
H18	736.67	3576.02	6353.11	50
H21	424.65	3735.26	2092.03	49
H22	116.9	2907.04	2234.95	53
H23	567.64	2605.84	3315.87	51
H24	1308.61	3126.89	4351.68	46

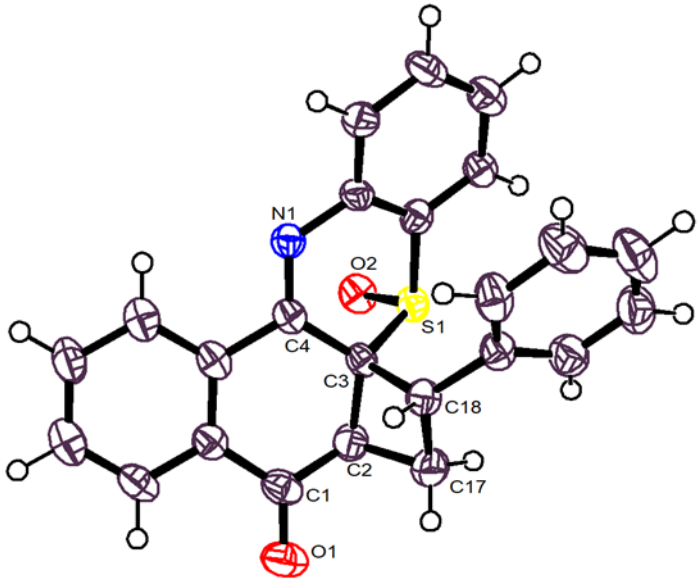


Table S51. Crystal data and structure refinement for 2al.

Identification code	**2al**
CCDC Number	**2403404**
Empirical formula	$C_{24}H_{17}NO_2S$
Formula weight	383.47
Temperature/K	140.0
Crystal system	orthorhombic

Space group	$P2_12_12_1$
a/Å	7.3105(8)
b/Å	9.5818(10)
c/Å	26.479(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1854.8(3)
Z	4
ρ_{calc}g/cm^3	1.3732
μ/mm^{-1}	0.195
F(000)	800.8
Crystal size/mm^3	0.02 × 0.015 × 0.012
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.52 to 60.34
Index ranges	$-10 \leq h \leq 10$, $-13 \leq k \leq 13$, $-37 \leq l \leq 34$
Reflections collected	28021
Independent reflections	5461 [R_{int} = 0.1912, R_{sigma} = 0.1939]
Data/restraints/parameters	5461/0/253
Goodness-of-fit on F^2	0.994
Final R indexes [I>=2σ (I)]	R_1 = 0.0689, wR_2 = 0.1323
Final R indexes [all data]	R_1 = 0.1755, wR_2 = 0.1729
Largest diff. peak/hole / e Å^{-3}	0.68/-0.74
Flack parameter	0.2(2)

Table S52. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 2al. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	713.0(14)	7639.3(10)	3253.6(4)	32.0(3)
O2	780(4)	9082(3)	3041.4(9)	37.1(7)

Table S52. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 2al. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
N1	4844(4)	7821(3)	3525.9(11)	29.3(8)
O1	415(5)	9426(3)	5059.6(11)	51.3(9)
C11	4324(6)	6856(4)	3150.4(13)	30.0(9)
C4	3644(5)	8279(4)	3843.7(14)	28.3(9)
C3	1717(5)	7762(4)	3881.5(13)	26.8(9)
C16	2539(6)	6666(4)	2991.2(15)	30.2(9)
C12	5702(6)	6114(4)	2916.8(15)	36.3(10)
C19	1159(6)	4994(4)	3950.0(15)	33.3(10)
C5	4216(6)	9396(4)	4194.7(14)	30.4(9)
C18	1229(6)	6414(4)	4198.6(15)	32.1(10)
C15	2103(6)	5718(4)	2608.9(14)	32.2(10)
C6	3129(6)	9848(4)	4590.9(15)	32.4(10)
C14	3495(6)	4963(5)	2383.8(16)	41.5(11)
C2	384(6)	8562(4)	4223.9(15)	35.9(10)
C20	2760(7)	4218(4)	3921.5(16)	41.3(12)
C1	1259(6)	9285(4)	4664.0(15)	37.4(11)
C10	5946(6)	10008(4)	4138.7(16)	39.8(11)
C7	3747(7)	10842(4)	4932.6(15)	38.7(11)
C13	5309(6)	5157(5)	2533.9(17)	43.7(12)
C17	-557(7)	7182(4)	4360.2(16)	45.1(11)
C8	5460(7)	11418(4)	4872.3(17)	43.6(11)
C24	-426(7)	4448(5)	3746.7(16)	45.8(12)
C23	-407(8)	3151(5)	3511.8(17)	51.8(13)
C9	6539(7)	11016(4)	4475.2(17)	44.9(12)
C21	2768(8)	2926(5)	3682.2(16)	53.4(14)
C22	1172(8)	2406(5)	3477.0(17)	59.1(14)

Table S53. Anisotropic Displacement Parameters ($Å^2×10^3$) for 2al. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S1	30.7(5)	28.5(5)	36.9(5)	0.1(5)	-2.2(5)	-2.0(4)
O2	45.0(18)	27.0(15)	39.3(15)	6.2(15)	-4.9(14)	6.1(12)
N1	30.7(18)	27.6(18)	29.7(16)	-0.3(15)	0.5(14)	-0.0(15)
O1	52(2)	61(2)	41.3(18)	3.3(18)	11.0(16)	-12.5(16)
C11	38(2)	22.1(18)	30(2)	0.3(19)	7(2)	-0.6(16)
C4	34(2)	26(2)	25(2)	1.0(18)	-4.1(18)	1.4(16)
C3	32(2)	21.1(18)	27(2)	1.2(17)	-2.2(16)	-0.8(17)
C16	30(2)	27(2)	33(2)	-0.2(18)	0.1(18)	3.7(19)
C12	34(2)	33(2)	42(2)	1(2)	6(2)	-3.9(19)
C19	42(3)	27(2)	31(2)	-2(2)	-1.5(19)	5.2(18)
C5	39(2)	23.1(18)	30(2)	4(2)	-7(2)	1.2(16)
C18	38(3)	23.9(19)	34(2)	1.1(18)	1.4(19)	3.3(17)
C15	36(3)	26(2)	34(2)	2(2)	-1.4(19)	1.3(19)
C6	40(3)	28(2)	29(2)	1(2)	-1.8(19)	0.3(18)
C14	52(3)	39(3)	34(3)	0(2)	-2(2)	-7(2)
C2	33(3)	33(2)	41(2)	0(2)	1(2)	-0.9(19)
C20	55(3)	29(2)	40(3)	-4(2)	-11(2)	7(2)
C1	49(3)	30(2)	33(2)	8(2)	2(2)	-1.6(19)
C10	41(3)	33(2)	45(3)	0(2)	-8(2)	-3.9(19)
C7	60(3)	29(2)	28(2)	3(2)	-1(2)	-3.5(18)
C13	48(3)	42(3)	42(3)	5(2)	5(2)	-18(2)
C17	51(3)	34(2)	51(3)	-6(2)	14(2)	-3(2)
C8	51(3)	33(2)	47(3)	1(2)	-12(2)	-7(2)
C24	59(3)	38(3)	40(2)	-5(3)	2(2)	1(2)
C23	69(4)	38(3)	48(3)	-13(3)	-3(3)	1(2)
C9	44(3)	37(3)	54(3)	-5(2)	-8(2)	-13(2)
C21	76(4)	38(3)	46(3)	8(3)	-5(3)	-2(2)
C22	101(4)	32(3)	45(3)	-4(3)	-9(3)	-5(2)

Table S54. Bond Lengths for 2al.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	O2	1.493(3)	C5	C6	1.385(6)
S1	C3	1.821(4)	C5	C10	1.402(6)
S1	C16	1.770(4)	C18	C17	1.559(6)
N1	C11	1.410(5)	C15	C14	1.384(6)
N1	C4	1.292(5)	C6	C1	1.482(6)
O1	C1	1.223(5)	C6	C7	1.389(5)
C11	C16	1.383(6)	C14	C13	1.397(6)
C11	C12	1.380(5)	C2	C1	1.499(6)
C4	C3	1.497(5)	C2	C17	1.534(5)
C4	C5	1.477(5)	C20	C21	1.391(6)
C3	C18	1.581(5)	C10	C9	1.384(6)
C3	C2	1.536(5)	C7	C8	1.378(6)
C16	C15	1.397(5)	C8	C9	1.370(6)
C12	C13	1.397(6)	C24	C23	1.389(6)
C19	C18	1.512(5)	C23	C22	1.361(7)
C19	C20	1.389(6)	C21	C22	1.380(7)
C19	C24	1.380(6)			

Table S55. Bond Angles for 2al.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C3	S1	O2	105.70(16)	C19	C18	C3	120.8(3)
C16	S1	O2	108.37(18)	C17	C18	C3	87.1(3)
C16	S1	C3	95.06(18)	C17	C18	C19	121.1(4)
C4	N1	C11	120.0(3)	C14	C15	C16	118.9(4)
C16	C11	N1	123.7(3)	C1	C6	C5	120.9(4)
C12	C11	N1	117.2(4)	C7	C6	C5	121.4(4)
C12	C11	C16	119.0(4)	C7	C6	C1	117.7(4)
C3	C4	N1	124.7(3)	C13	C14	C15	120.4(4)

Table S55. Bond Angles for 2al.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C5	C4	N1	117.6(4)	C1	C2	C3	114.8(4)
C5	C4	C3	117.6(4)	C17	C2	C3	89.6(3)
C4	C3	S1	109.9(3)	C17	C2	C1	114.0(4)
C18	C3	S1	109.9(3)	C21	C20	C19	120.3(5)
C18	C3	C4	121.2(3)	C6	C1	O1	122.5(4)
C2	C3	S1	108.4(3)	C2	C1	O1	120.1(4)
C2	C3	C4	118.1(3)	C2	C1	C6	117.4(4)
C2	C3	C18	87.2(3)	C9	C10	C5	120.4(4)
C11	C16	S1	121.5(3)	C8	C7	C6	119.7(4)
C15	C16	S1	117.0(3)	C14	C13	C12	119.3(4)
C15	C16	C11	121.5(4)	C2	C17	C18	88.1(3)
C13	C12	C11	120.9(4)	C9	C8	C7	120.0(4)
C20	C19	C18	118.4(4)	C23	C24	C19	120.3(5)
C24	C19	C18	122.6(4)	C22	C23	C24	120.5(5)
C24	C19	C20	118.9(4)	C8	C9	C10	120.7(5)
C6	C5	C4	122.7(4)	C22	C21	C20	119.9(5)
C10	C5	C4	119.4(4)	C21	C22	C23	120.0(4)
C10	C5	C6	117.8(4)				

Table S56. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2al.

Atom	*x*	*y*	*z*	U(eq)
H12	6936(6)	6255(4)	3017.8(15)	43.6(12)
H18	2067(6)	6363(4)	4496.4(15)	38.5(12)
H15	869(6)	5594(4)	2505.0(14)	38.6(12)
H14	3215(6)	4309(5)	2125.6(16)	49.8(14)
H2	-436(6)	9198(4)	4027.9(15)	43.1(12)
H20	3856(7)	4572(4)	4066.0(16)	49.6(14)
H10	6716(6)	9729(4)	3867.8(16)	47.8(13)

Table S56. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2al.

Atom	*x*	*y*	*z*	U(eq)
H7	2992(7)	11124(4)	5206.3(15)	46.4(13)
H13	6265(6)	4644(5)	2377.2(17)	52.5(15)
H17a	-1631(7)	6960(4)	4146.9(16)	54.1(14)
H17b	-853(7)	7086(4)	4723.4(16)	54.1(14)
H8	5893(7)	12095(4)	5105.9(17)	52.3(14)
H24	-1535(7)	4961(5)	3767.5(16)	55.0(14)
H23	-1505(8)	2782(5)	3374.3(17)	62.2(16)
H9	7707(7)	11432(4)	4430.5(17)	53.8(15)
H21	3869(8)	2403(5)	3660.1(16)	64.0(17)
H22	1177(8)	1526(5)	3311.3(17)	71.0(17)

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