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Supplementary Information

One-step synthesis to polycyclic thianthrenes from unfunctionalized aromatics by thia-APEX reaction

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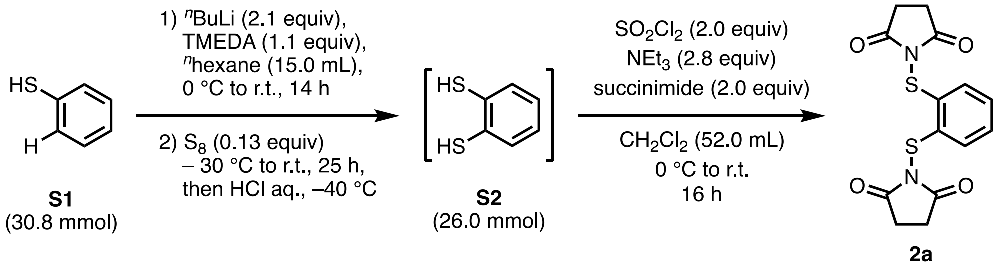
1. General

Unless otherwise noted, all materials including dry solvents were obtained from commercial suppliers and used without further purification. *N*,*N*,*N′*,*N′*-tetramethylethylenediamine (TMEDA), octasulfur, 4-methylbenzenethiol (**S5**), and 1,2-dimethoxybenzene (**1a**) were purchased from Aldrich. CH_2Cl_2, 1,2-dichloroethane, tetrahydrofuran (THF), indole (**S7**), *p*-toluenesulfonyl chloride (TsCl), sodium hydride (40% dispersion in paraffin liquid), and corannulene (**1e**) were purchased from KANTO. Trifluoromethanesulfonic acid (TfOH), a reagent-grade of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), succinimide, benzenethiol (**S1**), 1,2,3,4-tetrafluorobenzene (**S3**), 1,2,3,4-tetramethylbenzene (**1b**) phenanthrene (**1c**), triphenylene (**1f**), and benzo[*b*]thiophene (**1g**) were purchased from TCI. ^{n}BuLi in hexane, SO_2Cl_2, NEt_3, hexane, trifluoroacetic acid (TFA), guaiazulene (**1j**) were purchased from Wako. 2,7-di-*tert*-butylphenanthrene (**1d**) was synthesized by referring literatures.[S1] Flesh bottles of commercially available benzenethiol (**S1**) from TCI and 4-methylbenzenethiol (**S5**) from Aldrich were used. NEt_3 was degassed with argon bubbling before use. *N*-methyldibenzoindole **1i** was prepared according to a literature.[S2] Unless otherwise noted, all reactions were performed with dry solvents under an atmosphere of nitrogen in oven-dried glassware with standard vacuum-line techniques. All work-up and purification procedures were carried out with reagent-grade solvents in air. Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm). The developed chromatogram was analyzed by UV lamp (254 nm and 365 nm). Flash column chromatography was performed with KANTO Silica Gel 60N (spherical, neutral, 40-100 μm) or Biotage Isolera® equipped with a cartridge of Sfär DLV Empty 50‒100 g Column with frit containing KANTO Silica Gel 60N (spherical, neutral, 40-100 μm). Preparative thin-layer chromatography (PTLC) was performed using Wako-gel® B5-F silica coated plates (0.75 mm) prepared in our laboratory. The developed chromatogram was analyzed by UV lamp (254 nm and 365 nm). Gel Permeation Chromatography (GPC) was performed with a LaboACE LC-5060 Series instrument equipped with JAIGEL-2HR columns using chloroform as an eluent. High-resolution mass spectra (HRMS) were obtained from a Thermo Fisher Scientific Exactive Plus (ESI) or JEOL JMS-T100TD (DART). Melting points (m.p.) were measured using an OptiMelt (Stanford Research Systems). Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL Delta ECA-600 (^{1}H 600 MHz, ^{13}C 150 MHz, ^{19}F 560 MHz) spectrometer and a JEOL Delta JNM-ECZ400S/L1 (^{1}H 400 MHz, ^{13}C 100 MHz) and JEOL ECA 600II with Ultra COOL™ probe (^{1}H 600 MHz, ^{13}C 150 MHz). Chemical shifts for ^{1}H NMR are expressed in parts per million (ppm) relative to tetramethylsilane (δ 0.00 ppm) or CD_2Cl_2 (δ 5.32 ppm), or $Cl_2CDCDCl_2$ (δ 6.00 ppm) or acetone-*d*^{6} (δ 2.05 ppm). Chemical shifts for ^{13}C NMR are expressed in ppm relative to $CDCl_3$ (δ 77.16 ppm) or CD_2Cl_2 (δ 53.84 ppm) or $Cl_2CDCDCl_2$ (δ 73.78 ppm). Chemical shifts for ^{19}F NMR are expressed in ppm relative to C_6F_6 as an internal standard (δ –162.00 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublet of doublets, t = triplet, td = triplet of doublets, q = quartet, sep = septet, m = multiplet), coupling constant (Hz), and integration.

2. Material preparation

2-1. Preparation of *S*-diimidated benzenedithiol 2a[S3,S4]

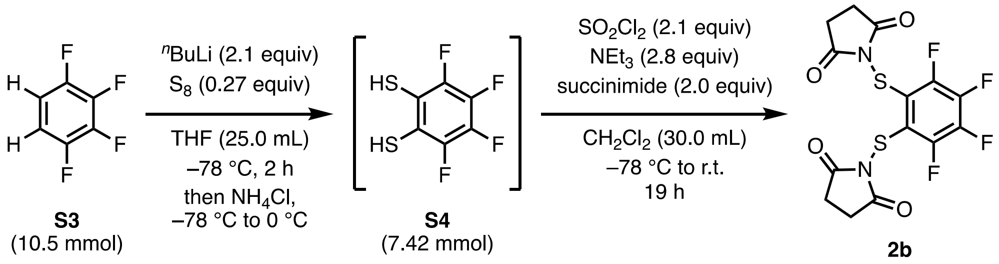


[First step] To a pre-dried three-neck round-bottom flask (300 mL) were added dry hexane (15.0 mL) and TMEDA (3.94 g, 99% purity, 35.6 mmol, 1.09 equiv) under argon atmosphere. This solution was cooled to 0 °C with an ice bath, and 1.6 M ^{n}BuLi in hexane (41.2 mL, 65.9 mmol, 2.14 equiv) was added. To this solution, benzenethiol (**S1**) (3.57 g, 95.0% purity, 30.8 mmol) was added at 0 °C. After 1 h, the ice bath was removed and the stirring continued at room temperature (23 °C) for 14 h. The resulting mixture was cooled to –30 °C with a dry ice/ice/MeOH bath, after which sulfur (1.03 g, 4.00 mmol, 0.130 equiv as S_8 molecule) was slowly added under argon flow. The resulting mixture was stirred at –30 °C for 1 h, and the stirring continued at room temperature (24 °C) for 24 h. After that, the resulting mixture was acidified at –40 °C (dry ice/ice/MeOH bath) using 12 M HCl aq. until the pH became *ca.* 1, under argon flow. After addition of Et_2O and water under argon flow, the organic layers was separated. The aqueous layer was extracted with Et_2O three times. After that, all organic layers were combined, washed with brine. The separated organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* at room temperature to afford 1,2-benzenedithiol (**S2**) as brown oil (3.69 g, 84% crude yield). This product was used for next step without further purifications.

Note: The use of a flesh bottle of commercially available **S1** afforded **2a** in the indicated high yield, otherwise the yield was decreased along with the formation of disulfide and other impurities.

[Second step] To a pre-dried round-bottom flask (100 mL) containing a magnetic stirring bar was added the crude **S2** (3.69 g, assumed ca. 26.0 mmol), and the flask was placed *in vacuo*. After replacing with argon atmosphere, NEt_3 (523.3 mg, 5.17 mmol, 0.199 equiv) and dry CH_2Cl_2 (16.0 mL) were added to the flask. To this mixture, SO_2Cl_2 (7.08 g, 52.6 mmol, 2.02 equiv) was added at 0 °C. After stirring at 0 °C for 15 min., the mixture was warmed to room temperature and stirred for 31 min. After that, the resulting mixture was cooled to 0 °C again. This mixture was transferred via a syringe to a pre-dried two-neck round-bottom flask (300 mL) containing a magnetic stirring bar, succinimide (5.14 g, 51.8 mmol, 2.00 equiv), dry CH_2Cl_2 (46.0 mL), and NEt_3 (6.87 g, 67.9 mmol, 2.61 equiv) at 0 °C. The resulting mixture was warmed and stirred at room temperature (24 °C) for 15 h. After adding water to the mixture, the organic layer was extracted with CH_2Cl_2 three times, and the combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The obtained crude product was purified by flash column chromatography on silica gel (eluents: hexane/AcOEt = 100:0 → 15:85) using Isolera®. The combined fractions containing **2a** was concentrated using a rotary evaporator, and **2a** was solidified. The resulting yellow precipitate was dissolved in a small amount of AcOEt with sonicating. After adding excess amount of hexane and sonicating again, the resulting solid was collected by suction filtration and rinsed with hexane. After drying *in vacuo* at 60 °C, **2a** was obtained as a yellow solid (3.45 g, 9.57 mmol, 93_{wt}% purity, 6.8_{wt}% of **2a′** was contained according to ^{1}H NMR and MS analysis (see compound data of **2a** and **2a′** in Section 4.) in three steps overall 31% yield from **S1**. In the multiple repetition experiments, compound **2a** could be prepared with 88_{wt}%–96_{wt}% purities, and in these purity range, the quality of **2a** did not affect the thia-APEX reaction in terms of yield and reproducibility.

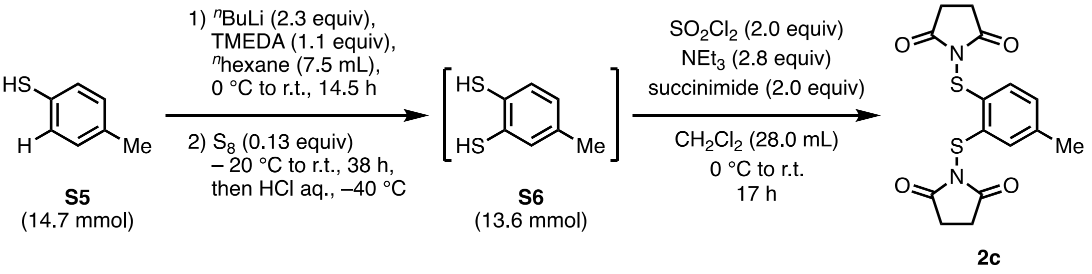
2-2. Preparation of *S*-diimidated tetrafluorobenzenedithiol 2b[S4,S5]



[First step] To a pre-dried three-neck round-bottom flask (200 mL) containing a magnetic stirring bar were added dry THF (15.0 mL) and 1.60 M ^{n}BuLi in hexane (6.75 mL, 10.8 mmol, 1.03 equiv) at –78 °C in dry ice/acetone bath under argon atmosphere. To this solution was added a solution of 1,2,3,4-tetrafluorobenzene (1.57 g, 10.5 mmol) in THF (10.0 mL) at –78 °C over 15 min using a dropping funnel. After that, the mixture was allowed to be stirred for 32 min at –78 °C. Then, powdered octasulfur (359.3 mg, 1.40 mmol, 0.134 equiv) was added portionwise at –78 °C over 10 min under argon flow followed by stirring for 44 min at –78 °C. After that, 1.60 M ^{n}BuLi in hexane (7.25 mL, 11.6 mmol, 1.11 equiv) was added to the reaction mixture at –78 °C. Then, powdered octadulfur (360.9 mg, 1.41 mmol, 0.134 equiv) was added portionwise at –78 °C over 5 min under argon flow, and the resulting mixture was stirred at – 78 °C for 50 min. Then NH_4Cl (ca. 1 g) was added the resulting mixture to quench at –78 °C under argon flow. Next, sat. NH_4Cl aq. (40 mL, degassed by argon bubbling in advance) was added dropwise and the resulting mixture was warmed from –78 °C to 0 °C with stirring, and NH_4Cl (ca. 5 g) was further added until pH = 7. Finally, 1 M HCl aq. was added until pH = 1. The organic layer was extracted using AcOEt three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to afford 3,4,5,6-tatrabenzene-1,2-dithiol (**S4**) as a brown oil (1.59 g, 71% crude yield). This product was used for next step without further purifications.

[Second step] To a pre-dried round-bottom flask (100 mL) containing a magnetic stirring bar was added the crude product **S4** (1.59 g, assumed ca. 7.42 mmol), and the flask was placed *in vacuo*. After replacing with argon atmosphere, NEt_3 (157.4 mg, 1.56 mmol, 0.210 equiv) and dry CH_2Cl_2 (10.0 mL) was added to the flask. To this mixture, SO_2Cl_2 (2.14 g, 15.9 mmol, 2.14 equiv) was added at –78 °C in a dry ice/acetone bath. After stirring at –78 °C for 18 min., the mixture was warmed to room temperature (23 °C) and stirred for 36 min. After that, the resulting mixture was cooled to 0 °C in an ice bath. This mixture was transferred using a syringe and 10.0 mL of dry CH_2Cl_2 to a pre-dried round-bottom flask (200 mL) containing a magnetic stirring bar, succinimide (1.47 g, 14.8 mmol, 2.00 equiv), dry CH_2Cl_2 (10.0 mL), and NEt_3 (1.95 g, 19.3 mmol, 2.60 equiv) at 0 °C. The resulting mixture was warmed and stirred at room temperature (23 °C) for 18.5 h. The resulting mixture was quenched with water (100 mL), and the organic layer was extracted with CH_2Cl_2 (10 mL) three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The obtained crude product was purified by flash column chromatography on silica gel (eluents: hexane/AcOEt = 100:0 → 20:80) using Isolera®. The combined fractions containing **2b** was concentrated using a rotary evaporator, and a crude of **2b** was solidified. The resulting crude **2b** was mixed in small amount of AcOEt with sonicating. After that, the resulting solid was collected by suction filtration and rinsed with hexane. After drying *in vacuo* at 40 °C, **2b** was obtained as a yellow solid (464.0 mg, 1.12 mmol, 11% from **S3**).

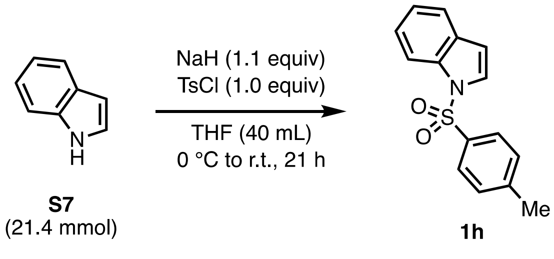
2-3. Preparation of *S*-diimidated toluenedithiol 2c[S3,S4]



[First step] To a pre-dried three-neck round-bottom flask (300 mL) were added dry hexane (15.0 mL) and TMEDA (1.93 g, 99% purity, 16.5 mmol, 1.12 equiv) under argon atmosphere. This solution was cooled to 0 °C with an ice bath and 1.6 M ⁿBuLi in hexane (21.0 mL, 33.6 mmol, 2.28 equiv) was added. To this solution, 4-methylbenzenethiol (**S5**) (1.86 g, 98% purity, 14.7 mmol) was added at 0 °C. After 1 h, the ice bath was removed and the stirring continued at room temperature (24 °C) for 14 h. The resulting mixture was cooled to –36 °C with a dry ice/ice/MeOH bath, after which sulfur (500.7 mg, 1.95 mmol, 0.133 equiv as S_8 molecule) was slowly added under argon flow. The resulting mixture was stirred at –36 to –5 °C for 3 h, and the stirring continued at room temperature (23 °C) for 35 h. After that, the resulting mixture was acidified at –40 °C (dry ice/ice/MeOH bath) using 12 M HCl aq. until the pH became *ca.* 1, under argon flow. After addition of Et_2O and water under argon flow, the organic layer was separated. The aqueous layer was extracted with Et_2O two times. After that, all organic layers were combined, washed with brine. The separated organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* at room temperature to afford 1,2-toluenedithiol (**S6**) as a brown oil (2.09 g, 91% crude yield). This product was used for next step without further purifications.

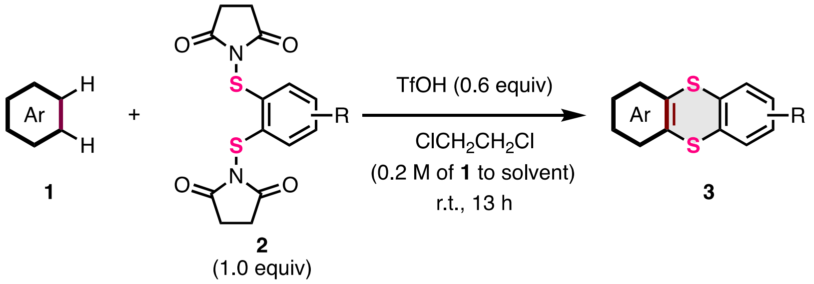
[Second step] To a pre-dried round-bottom flask (100 mL) containing a magnetic stirring bar was added the crude product **S6** (2.09 g, assumed ca. 13.3 mmol), and the flask was placed *in vacuo*. After replacing with argon atmosphere, NEt_3 (266.4 mg, 2.63 mmol, 0.197 equiv) and dry CH_2Cl_2 (8.0 mL) was added to the flask. To this mixture, SO_2Cl_2 (3.62 g, 26.8 mmol, 2.01 equiv) was added at 0 °C. After stirring at 0 °C for 17 min., the mixture was warmed to room temperature (23 °C) and stirred for 28 min. After that, the resulting mixture was cooled to 0 °C again. This mixture was transferred via a syringe to a pre-dried round-bottom flask (300 mL) containing a magnetic stirring bar, succinimide (2.65 g, 26.7 mmol, 2.00 equiv), dry CH_2Cl_2 (20.0 mL), and NEt_3 (3.52 g, 34.8 mmol, 2.61 equiv) at 0 °C. The resulting mixture was warmed and stirred at room temperature (24 °C) for 17 h. The resulting mixture was quenched with water (75 mL), and the organic layer was extracted with CH_2Cl_2 (10 mL) two times. The combined organic layers were washed with brine (100 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The obtained crude product was purified by flash column chromatography on silica gel (eluents: hexane/AcOEt = 80:20 → 50:50 → 20:80 → 0:100) using Isolera®. The combined fractions containing **2c** was concentrated using a rotary evaporator, and viscous crude of **2b** was solidified. The resulting viscous crude product was dissolved in AcOEt with sonicating. Removal of AcOEt by evaporation using a rotary evaporator resulted in the formation of powder, which was dissolved again in a small amount of AcOEt with sonicating. After adding excess amount of hexane and sonicating again with vigorous mixing using a spatula, thus formed solid was collected by suction filtration and rinsed with hexane. After drying *in vacuo* at 60 °C, **2b** was obtained as a yellow solid (1.42 g, 4.04 mmol, 27% from **S5**).

2-3. Preparation of 1-tosyl-1*H*-indole (1h)



To a pre-dried two-neck round-bottom flask (200 mL) were added indole (2.50 g, 21.4 mmol) and dry THF (20.0 mL) under stream of nitrogen. After the solution was cooled to 0 °C with an ice bath, NaH (899.1 mg, 60% purity, 22.5 mmol, 1.05 equiv) was added to the solution in one portion at 0 °C under stream of nitrogen. This reaction solution was stirred at 0 °C to room temperature (23 °C) for 30 min. After that, TsCl (4.21 g, 22.1 mmol, 1.03 equiv) in 20.0 mL of THF was added to the solution at 0 °C. The resulting solution was allowed to warm to room temperature (23 °C) and stirred for 20 h. The reaction mixture was diluted with water at 0 °C and extracted with AcOEt three times. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (hexane/AcOEt = 100:0 to 80:20) to afford **1h** as a colorless oil. This oil was sonicated in a small amount of MeOH for solidification. The resulting solid was collected by suction filtration, and rinsed using hexane and MeOH. After drying *in vacuo* at 50 °C, **1h** was obtained as a white solid (4.24 g, 15.6 mmol, 73%).

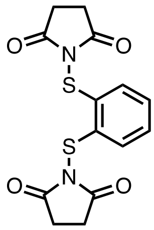
3. General procedure of thia-APEX reaction



To an oven-dried screw-capped tube were added *S*-diimidated arenethiols **2** (1.0 equiv), aromatic substrates **1** (0.20 mmol, 1.0 equiv), and dry 1,2-dichloroethane (1.0 mL: 0.20 M for **1**) under air. After that, TfOH (0.60 equiv) was added to the reaction mixture and the resulting mixture was stirred at room temperature (*ca.* 23 °C) for 13 h. After that, the reaction mixture was diluted with CH_2Cl_2 (4 mL), after which sat. $NaHCO_3$ aq. (4 mL) was added. the organic layer was extracted with CH_2Cl_2 (2 mL) three times. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The obtained crude product was purified by flash column chromatography on silica gel using Isolera®, or PTLC (eluents: hexane/AcOEt) to afford π-extended thianthrene **3**.

4. Compound data

1,1'-(1,2-Phenylenebis(sulfanediyl)-)bis(pyrrolidine-2,5-dione) (2a)



^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.23–7.32 (m, 4H), 2.86 (s, 8H).

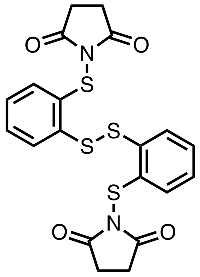
^{13}C NMR (100 MHz, CD_2Cl_2) δ 176.57, 134.82, 131.19, 129.88, 29.19.

HRMS (ESI^{+}) *m/z* calcd for $C_{14}H_{12}N_2O_4S_2Na^{+}$ [M+Na]$^{+}$: 359.0131, found: 359.0130.

M.p.: not determined. **2a** was decomposed over 120 °C.

Note: A collected solid of **1a** included an inseparable byproduct showing *m/z* = 498.9886 for $C_{20}H_{16}N_2O_4S_4Na^{+}$ in ESI analysis, which was considered to correspond to disulfide **2a′** (calcd.: 498.9885 [M+Na]$^{+}$). In addition, a weak singlet peak (0.26 H against to 8.0 H of ethylene protons of succinimide) was observed at 2.90 ppm in ^{1}H NMR spectra of **2a**. This peak was considered to be derived from succinimide moieties of **2a′**. The purity ($_{wt}$%) of resulting **2a** was estimated by accounting the ^{1}H NMR integral ratio of **2a** and **2a′**.

1,1'-((Disulfanediylbis(2,1-phenylene))-bis(sulfanediyl))bis(pyrrolidine-2,5-dione) (2a′)



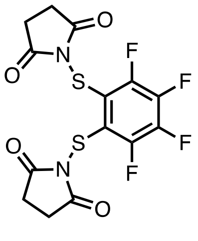
Byproduct **2a′** including a small amount of **2a** and unknown impurities was separated from compound **2a** by GPC using $CHCl_3$ as an eluent.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.52 (dd, *J* = 7.5, 1.6 Hz, 1.78H), 7.20-7.30 (m, 4.45H), 7.09 (dd, *J* = 7.7, 1.4 Hz, 1.77H), 2.90 (s, 8H).

HRMS (ESI^{+}) *m/z* calcd for $C_{20}H_{16}N_2O_4S_4Na^{+}$ [M+Na]$^{+}$: 498.9885, found: 498.9884.

^{13}C NMR (150 MHz, CD_2Cl_2) δ 176.38, 132.52, 129.83, 128.94, 128.20, 29.29. While enough quality of ^{13}C NMR spectrum was not obtained due to the presence of other impurities, the structure of **2a′** was assigned by the results of ^{1}H NMR and HRMS.

1,1'-((Perfluoro-1,2-phenylene)bis(sulfanediyl))bis(pyrrolidine-2,5-dione) (2b)



^{1}H NMR (400 MHz, $CDCl_3$) δ 2.85 (s, 8H).

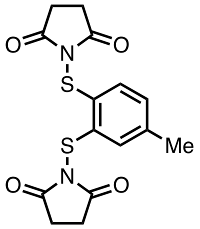
^{13}C NMR (150 MHz, $CDCl_3$) δ 175.67, 147.99 (J_{C-F} = 252.9 Hz), 142.06 (J_{C-F} = 264.4 Hz), 119.57 (d, J_{C-F} = 13.0 Hz), 28.93. $^{2}J_{C-F}$ and $^{3}J_{C-F}$ coupling at 147.99 and 142.06 ppm were difficult to be assigned.

^{19}F NMR (560 MHz, $CDCl_3$) δ –128.22 (d, J_{F-F} = 17.4 Hz), –149.07 (d, J_{F-F} = 17.4 Hz).

HRMS (DART^{+}) *m/z* calcd for $C_{14}H_9F_4N_2O_4S_2^{+}$ [M+H]$^{+}$: 408.99399, found: 408.99252

M.p.: 216.4–222.6 °C. **2b** was decomposed over 223 °C.

1,1'-((4-Methyl-1,2-phenylene)bis-(sulfanediyl))bis(pyrrolidine-2,5-dione) (2c)



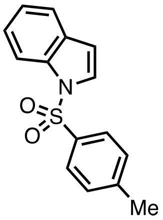
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.7 Hz, 1H), 7.04 (d, *J* = 8.3 Hz, 1H), 7.01 (d, *J* = 0.6 Hz, 1H), 2.91 (s, 4H), 2.85 (s, 4H), 2.29 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 176.35, 176.33, 141.30, 136.30, 133.94, 130.22, 130.18, 129.52, 28.94, 28.89, 21.43.

HRMS (ESI$^+$) *m/z* calcd for $C_{14}H_{12}N_2O_4S_2Na^+$ $[M+Na]^+$: 373.0287, found: 373.0285.

M.p.: ca. 100 °C. **2c** was decomposed over 120 °C.

1-Tosyl-1*H*-indole (1h)



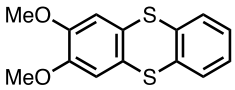
^{1}H NMR (400 MHz, acetone-d^6) δ 8.01 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.87 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 3.6 Hz, 1H), 7.59 (d, *J* = 7.5 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.34 (t, *J* = 8.3 Hz, 1H), 7.24 (t, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 4.0 Hz, 1H), 2.35 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 145.04, 135.36, 134.90, 130.85, 129.97 (2C), 126.91 (2C), 126.43, 124.65, 123.38, 121.48, 113.63, 109.14, 21.67.

HRMS (ESI$^+$) *m/z* calcd for $C_{15}H_{13}NO_2SNa^+$ $[M+Na]^+$: 294.0559, found: 294.0554.

M.p.: 85.8–87.8 °C.

2,3-Dimethoxythianthrene (3aa)



According to the general procedure of thia-APEX reaction, **3aa** was obtained as a white solid (46.5 mg, 0.168 mmol, 83%) from **2a** (78.2 mg, 88_{wt}%, 0.205 mmol, 1.01 equiv), 1,2-dimethoxybenzene (**1a**) (28.2 mg, 99% purity, 0.202 mmol), TfOH (11 μL, 0.125 mmol, 0.62 equiv), and 1,2-dichloroethane (1.0 mL). Eluents of PTLC: hexane/AcOEt = 99:1 → 97:3.

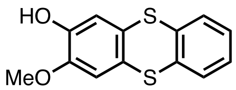
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.50 (dd, *J* = 5.7, 3.4 Hz, 2H), 7.25 (dd, *J* = 5.7, 3.4 Hz, 2H), 7.01 (s, 2H), 3.82 (s, 6H).

^{13}C NMR (100 MHz, CD_2Cl_2) δ 149.58, 136.69, 128.96, 127.95, 126.91, 112.27, 56.44.

HRMS (DART$^+$) *m/z* calcd for $C_{14}H_{13}O_2S_2$ $[M+H]^+$: 277.03570, found: 277.03399.

M.p.: 136.7–137.8 °C

3-Methoxythianthren-2-ol (4)



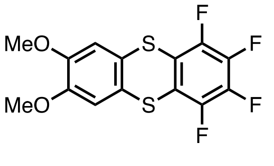
When thia-APEX reaction to obtain **3aa** was conducted, **4** was also isolated from the crude mixture by column chromatography on silica gel (eluents: hexane/AcOEt = 99:1 → 4:1) and following GPC (eluent: $CHCl_3$).

^{1}H NMR (400 MHz, $Cl_2CDCDCl_2$) δ 7.51 (dd, J = 5.7, 3.4 Hz, 2H), 7.27 (dd, J = 5.9, 3.6 Hz, 2H), 7.09 (s, 1H), 7.01 (s, 1H), 5.64 (s, 1H), 3.89 (s, 3H).

^{13}C NMR (150 MHz, $Cl_2CDCDCl_2$) δ 146.39, 145.37, 136.04, 135.97, 128.72, 128.63, 127.60, 127.56, 127.31, 125.75, 114.75, 111.14, 56.25.

HRMS (ESI^{+}) m/z calcd for $C_{13}H_9O_2S_2Na$ $[M–H+Na]^{\cdot+}$: 283.9936, found: 283.9938.

1,2,3,4-Tetrafluoro-7,8-dimethoxythianthrene (3ab)



According to the general procedure of thia-APEX reaction, **3ab** was obtained as a white solid (17.5 mg, 0.0502 mmol, 32%) from **2b** (66.9 mg, 98$_{wt}$%, 0.161 mmol, 1.01 equiv), 1,2-dimethoxybenzene (**1a**) (22.2 mg, 99% purity, 0.159 mmol), TfOH (8.4 µL, 0.095 mmol, 0.60 equiv), and 1,2-dichloroethane (1.0 mL). Eluents of PTLC: hexane/AcOEt = 29:1.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.07 (s, 2H), 3.84 (s, 6H).

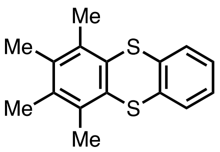
^{13}C NMR (150 MHz, $CDCl_3$) δ 149.78, 144.64 ($J_{C–F}$ = 247.1 Hz), 140.05 ($J_{C–F}$ = 255.8, 15.2, 4.3 Hz), 124.97, 121.64 ($J_{C–F}$ = 17.3 Hz), 112.33, 56.38.

^{19}F NMR (560 MHz, $CDCl_3$) δ –134.60 ($J_{F–F}$ = 17.4 Hz), –155.67 ($J_{F–F}$ = 17.4 Hz).

HRMS (DART^{+}) m/z calcd for $C_{14}H_9F_4O_2S_2$ $[M+H]^{+}$: 348.99801, found: 348.99679.

M.p.: 186.9–188.8 °C

1,2,3,4-Tetramethylthianthrene (3ba)



According to the general procedure of thia-APEX reaction, **3ba** was obtained as a white solid (44.4 mg, 0.163 mmol, 70%) from **2a** (85.6 mg, 93$_{wt}$%, 0.237 mmol, 1.01 equiv), 1,2,3,4-tetramethylbenzene (**1b**) (31.4 mg, 0.234 mmol), TfOH (12 µL, 0.136 mmol, 0.58 equiv), and 1,2-dichloroethane (1.2 mL). Eluents of flash column chromatography on silica gel: hexane/AcOEt = 100:0 → 99:1.

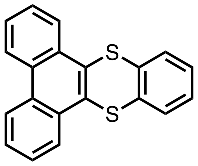
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, J = 5.7, 3.4 Hz, 2H), 7.23 (dd, J = 5.9, 3.2 Hz, 2H), 2.52 (s, 6H), 2.23 (s, 6H).

^{13}C NMR (100 MHz, CD_2Cl_2) δ 137.60, 135.33, 133.60, 132.74, 129.07, 127.85, 18.57, 17.16

HRMS (DART^{+}) m/z calcd for $C_{16}H_{16}S_2$ $[M]^{\cdot+}$: 272.06934, found: 272.06944.

M.p.: 164.8–173.6 °C

Dibenzo[*a,c*]thianthrene (3ca)



According to the general procedure of thia-APEX reaction, crude **3ca** was obtained from **2a** (72.2 mg, 93_{wt}%, 0.200 mmol, 1.00 equiv), phenanthrene (**1c**) (36.0 mg, 0.202 mmol, 1.01 eq), TfOH (10 µL, 0.113 mmol, 0.56 equiv), and 1,2-dichloroethane (1.0 mL). The purification by flash column chromatography on silica gel (eluents: hexane/AcOEt = 100:0 → 99:1 → 97:3) was performed to obtain **3ca** as the semi-pure product. Finally, recrystallization from chloroform/pentane by a vapor diffusion method afforded pure **3ca** as a white solid (13.1 mg, 0.0414 mmol, 21%). GPC purification after flash column chromatography also afforded 3ca in the same yield. The structure was determined by X-ray crystallographic analysis using a single crystal obtained by the same method.

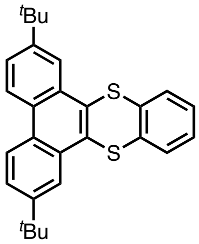
^{1}H NMR (400 MHz, $Cl_2CDCDCl_2$) δ 8.62–8.72 (m, 4H), 7.67–7.76 (m, 6H), 7.36 (dd, *J* = 5.7, 3.4 Hz, 2H).

^{13}C NMR (150 MHz, $Cl_2CDCDCl_2$) δ 136.42, 132.50, 130.17, 129.62, 128.89, 127.95, 127.41, 127.24, 125.17, 123.01.

HRMS (DART$^+$) *m*/*z* calcd for $C_{20}H_{13}S_2$ [M+H]$^+$: 317.04587, found: 317.04595.

M.p.: 209.1–210.4 °C

2,7-Di-*tert*-butyldibenzo[*a,c*]thianthrene (3da)



According to the general procedure of thia-APEX reaction, **3da** was obtained as a white solid (74.2 mg, 0.173 mmol, 87%) from **2a** (76.8 mg, 88_{wt}%, 0.201 mmol, 1.00 equiv), 2,7-di-*tert*-butylphenanthrene (**1d**) (58.1 mg, 0.200 mmol), TfOH (10 µL, 0.113 mmol, 0.57 equiv), and 1,2-dichloroethane (1.0 mL). Eluents of PTLC: hexane/AcOEt = 99:1.

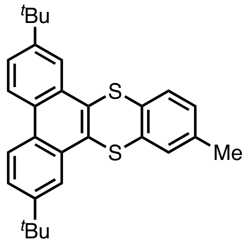
^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.61 (s, 2H), 8.60 (d, J = 6.7 Hz, 2H), 7.77 (dd, *J* = 8.7, 2.4 Hz, 2H), 7.72 (dd, J = 5.9, 3.2 Hz, 2H), 7.34 (dd, J = 5.7, 3.4 Hz, 2H), 1.50 (s, 18H)

^{13}C NMR (150 MHz, $CDCl_3$) δ 149.96, 137.11, 132.69, 130.18, 129.04, 127.88, 127.82, 125.49, 122.85, 121.15, 35.30, 31.58.

HRMS (DART$^+$) *m*/*z* calcd for $C_{28}H_{29}S_2$ [M+H]$^+$: 429.17107, found: 429.17127.

M.p.: 211.4–216.7 °C

2,7-Di-*tert*-butyl-11-methyl-dibenzo[*a*,*c*]thianthrene (3dc)



According to the general procedure of thia-APEX reaction, **3dc** was obtained as a white solid (63.0 mg, 0.142 mmol, 71%) from **2c** (70.1 mg, 0.200 mmol, 1.00 equiv), 2,7-di-*tert*-butylphenanthrene (**1d**) (58.1 mg, 0.200 mmol), TfOH (10 μL, 0.113 mmol, 0.57 equiv), and 1,2-dichloroethane (1.0 mL). Eluents of flash column chromatography on silica gel: hexane/AcOEt = 100:0 → 99:1.

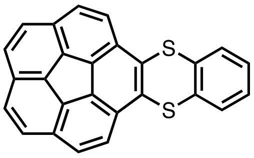
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.58–8.60 (m, 2H), 8.55 (d, *J* = 8.3 Hz, 2H), 7.71 (dd, *J* = 8.9, 1.2 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 1H), 7.52 (br s, 1H), 7.09 (br d, *J* = 8.3 Hz, 1H), 2.35 (s, 3H), 1.50 (s, 18H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 149.91 (2C), 138.05, 137.04, 133.59, 133.22, 132.75, 130.24, 130.20, 129.61, 128.79, 128.74, 127.78 (2C), 125.43, 125.40, 122.83 (2C), 121.18, 121.14, 35.29, 31.58, 21.07.

HRMS (DART$^+$) m/z calcd for $C_{29}H_{31}S_2$ [M+H]$^+$: 443.18672, found: 443.18627.

M.p.: 210.9–214.2 °C

Benzo[6,7]fluorantheno[1,10-*abc*]thianthrene (3ea)



According to the general procedure of thia-APEX reaction, **3ea** was obtained as a yellow solid (27.4 mg, 0.0705 mmol, 35%) from **2a** (76.8 mg, 88$_{wt}$%, 0.201 mmol, 1.00 equiv), corannulene (**1e**) (50.2 mg, 0.201 mmol), TfOH (10 μL, 0.113 mmol, 0.56 equiv), and 1,2-dichloroethane (1.0 mL). Purification was performed by PTLC (eluents: hexane/AcOEt = 99:1) followed by GPC using $CHCl_3$ as eluent.

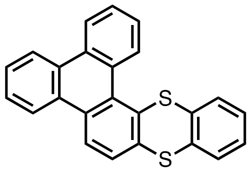
^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.20 (d, *J* = 8.7 Hz, 2H), 7.91 (d, *J* = 9.1 Hz, 2H), 7.82 (s, 4H), 7.57 (dd, *J* = 5.7, 3.4 Hz, 2H), 7.24 (dd, *J* = 5.7, 3.4 Hz, 2H). According to a DFT calculation in section 6, Figure S4, the singlet peaks were considered to be characterized to four protons of *rim*-regions opposite to the benzodithiine arm. The structure was determined by X-ray crystallographic analysis using a single crystal obtained by recrystallization from chloroform/pentane by vapor diffusion.

^{13}C NMR (150 MHz, CD_2Cl_2) δ 136.39, 135.94, 135.72, 135.70, 134.01, 131.43, 131.28, 131.16, 129.02, 128.55, 128.29, 127.92, 127.41, 125.82.

HRMS (DART$^+$) m/z calcd for $C_{26}H_{13}S_2$ [M+H]$^+$: 389.04587, found: 389.04672.

M.p.: 244.7–246.0 °C

Phenanthro[9,10-*a*]thianthrene (3fa)



According to the general procedure of thia-APEX reaction, **3fa** was obtained as an off-white solid (28.0 mg, 0.0764 mmol, 39%) from **2a** (72.1 mg, 93_{wt}%, 0.199 mmol, 1.01 equiv), triphenylene (**1f**) (44.9 mg, 0.197 mmol), TfOH (10 μL, 0.113 mmol, 0.58 equiv), and 1,2-dichloroethane (1.0 mL). Purification was performed by flash column chromatography on silica gel (eluents: hexane/AcOEt = 100:0 → 95:5) followed by GPC using $CHCl_3$ as eluent. The structure was determined by X-ray crystallographic analysis using a single crystal obtained by recrystallization from chloroform/pentane by vapor diffusion.

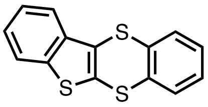
^{1}H NMR (400 MHz, $Cl_2CDCDCl_2$) δ 8.81 (dd, J = 7.9, 1.6 Hz, 1H), 8.65 (d, J = 7.9 Hz, 1H), 8.59-8.63 (m, 1H), 8.50-8.55 (m, 2H), 7.86 (d, J = 8.3 Hz, 1H), 7.72-7.80 (m, 2H), 7.64-7.71 (m, 2H), 7.60 (dd, J = 7.5, 1.2 Hz, 1H), 7.53 (dd, J = 7.9, 1.2 Hz, 1H), 7.32 (td, J = 7.5, 1.6 Hz, 1H), 7.24 (td, J = 7.7, 1.5 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 138.39, 136.62, 136.57, 133.79, 131.69, 131.24, 130.82, 130.22, 130.15, 129.46, 128.99, 128.80, 128.64, 128.30, 128.04, 127.92, 127.76, 127.63, 125.66, 123.67, 123.27, 123.20, 121.86.

HRMS (DART$^+$) m/z calcd for $C_{24}H_{15}S_2$ $[M+H]^+$: 367.06152, found: 367.06061.

M.p.: 190.7–198.2 °C

Benzo[*b*]benzo[4,5]thieno[2,3-*e*][1,4]dithiine (3ga)



According to the general procedure of thia-APEX reaction, **3ga** was obtained as a white solid (28.7 mg, 0.105 mmol, 53%) from **2a** (72.3 mg, 93_{wt}%, 0.200 mmol, 1.01 equiv), benzo[*b*]thiophene (**1g**) (26.5 mg, 0.197 mmol), TfOH (10 μL, 0.113 mmol, 0.57 equiv), and 1,2-dichloroethane (1.0 mL). Eluents of flash column chromatography on silica gel: hexane/AcOEt = 100:0 → 99:1.

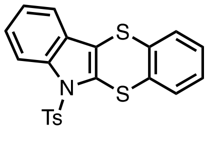
^{1}H NMR (400 MHz, $Cl_2CDCDCl_2$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.51-7.56 (m, 1H), 7.46-7.50 (m, 1H), 7.44 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.38 (td, *J* = 7.7, 1.3 Hz, 1H), 7.25-7.32 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 140.92, 136.97, 134.93 (2C), 131.32, 129.38, 129.02, 128.23, 127.82, 127.45, 124.99 (2C), 122.67, 121.18.

HRMS (DART$^+$) m/z calcd for $C_{14}H_9S_3$ $[M+H]^+$: 272.98664, found: 272.98590.

M.p.: 113.6–116.0 °C

6-Tosyl-6*H*-benzo[5,6][1,4]dithiino[2,3-*b*]indole (3ha)



According to the general procedure of thia-APEX reaction, **3ha** was obtained as a white solid (71.2 mg, 0.174 mmol, 86%) from **2a** (73.0 mg, 93_{wt}%, 0.202 mmol, 1.00 equiv), 1-tosyl-1H-indole (**1h**) (54.7 mg, 0.202 mmol), TfOH (10 µL, 0.113 mmol, 0.56 equiv), and 1,2-dichloroethane (1.0 mL). Eluents of flash column chromatography on silica gel: hexane/AcOEt = 97:3 → 90:10 → 50:50.

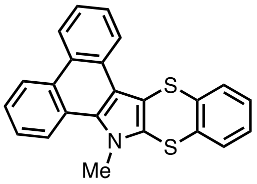
^{1}H NMR (400 MHz, $Cl_2CDCDCl_2$) δ 8.11 (d, J = 8.3 Hz, 1H), 7.90 (dt, J = 8.7, 1.9 Hz, 2H), 7.42-7.50 (m, 3H), 7.36 (ddd, J = 8.5, 7.2, 1.3 Hz, 1H), 7.30 (td, J = 7.5, 1.2 Hz, 1H), 7.21-7.27 (m, 4H), 2.33 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 145.48, 138.19, 134.97, 134.86, 134.04, 130.03, 129.97 (2C), 129.16, 129.04, 128.13, 128.05, 127.63, 127.30 (2C), 125.18, 124.12, 118.18, 115.77, 114.62, 21.74.

HRMS (ESI$^+$) m/z calcd for $C_{21}H_{15}NO_2S_3Na$ $[M+Na]^+$: 432.0157, found: 432.0161.

M.p.: 127.2–130.1 °C

9-Methyl-9*H*-dibenzo[*e*,*g*]benzo[5,6][1,4]dithiino[2,3-*b*]indole (3ia)



According to the general procedure of thia-APEX reaction, semi-pure **3ia** was obtained as a yellow solid (50.4 mg, 0.136 mmol, 69%) from **2a** (71.7 mg, 93$_{wt}$%, 0.198 mmol, 1.01 equiv), *N*-methyldibenzoindole **1i**[S2] (45.6 mg, 0.197 mmol), TfOH (10 µL, 0.113 mmol, 0.57 equiv), and 1,2-dichloroethane (1.0 mL). The purification by flash column chromatography on silica gel (eluents: hexane/AcOEt = 100:0 → 80:20) was performed to obtain **3ia** as the semi-pure product. Finally, recrystallization from chloroform/pentane by vapor diffusion afforded pure **3ia** as an off-white solid (30.6 mg, 0.0828 mmol, 42%).

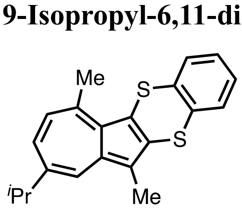
^{1}H NMR (400 MHz, $Cl_2CDCDCl_2$) δ 9.08 (dd, *J* = 8.2, 1.1 Hz, 1H), 8.77 (dd, *J* = 8.5, 1.0 Hz, 1H), 8.68 (d, *J* = 8.3 Hz, 1H), 8.50 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.53–7.70 (m, 5H), 7.24–7.31 (m, 2H), 4.36 (s, 3H)

^{13}C NMR (150 MHz, $CDCl_3$) δ 138.00, 135.01, 131.66, 129.67, 129.47, 129.30, 129.08, 128.04, 127.79, 127.46, 127.32, 126.99, 126.54, 124.65, 124.60, 124.35, 124.27, 124.20, 123.23, 121.01, 118.48, 109.46, 36.78.

HRMS (DART$^+$) m/z calcd for $C_{23}H_{16}NS_2$ $[M+H]^+$: 370.07242, found: 370.07061.

M.p.: 203.3–205.6 °C

9-Isopropyl-6,11-dimethylazuleno[1,2-*b*]benzo[*e*][1,4]dithiine (3ja)



According to the general procedure of thia-APEX reaction, **3ja** was obtained as a dark-green oil (51.8 mg, 0.154 mmol, 49%) from **2a** (73.0 mg, 93$_{wt}$%, 0.314 mmol, 1.00 equiv), guaiazulene (**1j**) (62.3 mg, 0.314 mmol), TfOH (16 µL, 0.181 mmol, 0.58 equiv), and 1,2-dichloroethane (1.6 mL). Eluents of flash column chromatography on silica gel: hexane/AcOEt = 100:0 → 98:2. This compound was fragile for silica-gel column chromatography and GPC. Therefore, there was a large variation of isolated yield in total four independent experiments, where the average yield was 25% (yield range: 12–49%)

^{1}H NMR (400 MHz, $Cl_2CDCDCl_2$) δ 7.94 (d, *J* = 2.0 Hz, 1H), 7.40-7.48 (m, 2H), 7.26 (dd, *J* = 10.9, 1.8 Hz, 1H), 7.18-7.23 (m, 2H), 6.90 (d, *J* = 10.3 Hz, 1H), 3.18 (s, 3H), 2.99 (sep, *J* = 6.9 Hz, 1H), 2.60 (s, 3H), 1.32 (d, *J* = 6.8 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 144.16, 142.56, 141.30, 138.75, 135.66, 134.93, 134.41, 132.46, 131.12, 129.05, 128.76, 128.21, 127.54, 127.47, 121.33, 114.99, 37.92, 28.01, 24.60 (2C), 11.31.

HRMS (DART$^+$) m/z calcd for $C_{21}H_{21}S_2$ $[M+H]^+$: 337.10847, found: 337.11000.

5. X-ray crystal structure analysis[S6,S7,S8]

Details of the crystal data and a summary of the intensity data collection parameters for **3ca**, **3ea** and **3fa** are listed in Table S1–S3. A single crystal of **3ca** was prepared by vapor diffusion recrystallization using $CHCl_3$ and pentane. A single crystal of **3ea** was prepared by vapor diffusion recrystallization from $CHCl_3$ and pentane. A single crystal of **3fa** was prepared by vapor diffusion recrystallization from $CHCl_3$ and pentane. A suitable crystal was mounted with mineral oil on a MiTeGen MicroMounts and transferred to the goniometer of the kappa goniometer of a RIGAKU XtaLAB Synergy-S system with 1.2 kW MicroMax-007HF microfocus rotating anode (Graphite-monochromated Mo K_α radiation (l = 0.71073 Å)) and PILATUS200K hybrid photon-counting detector. Cell parameters were determined and refined, and raw frame data were integrated using CrysAlis^{Pro} (Agilent Technologies, 2010). The structures were solved by direct methods with SHELXT[S6] and refined by full-matrix least-squares techniques against F^2 (SHELXL-2018/3)[S7] by using Olex2 software package.[S8] The intensities were corrected for Lorentz and polarization effects. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions. CCDC 2223786, 2223785, and 2241075 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Non-covalent interaction (NCI) plot for **3ea** was made using a NCIPLOT 4.0 program.[S9]

Table S1. Crystallographic data and structure refinement details for **3ca**.

CCDC deposition No.	2223786
formula	$C_{20}H_{12}S_2$
FW	316.42
T (K)	123(2) K
λ (Å)	0.71073 Å
cryst syst	Monoclinic
space group	$P2_1/n$
a (Å)	16.7176(12)
b (Å)	3.9059(2)
c (Å)	22.6639(19)
α (deg)	90
β (deg)	109.384(9)
γ (deg)	90
V (Å^3)	1396.00(18)
Z	4
D_{calc} (g / cm^3)	1.505
μ (mm^{-1})	0.373
F (000)	656.0
cryst size (mm)	0.2 × 0.1 × 0.03
θ range (deg)	5.166° to 59.656°
reflns collected	12465
indep reflns/R_{int}	3295/0.1229
params	199
GOF on F^2	1.050
R_1, wR_2 [$I>2\sigma(I)$]	0.0559, 0.1410
R_1, wR_2 (all data)	0.0768, 0.1518

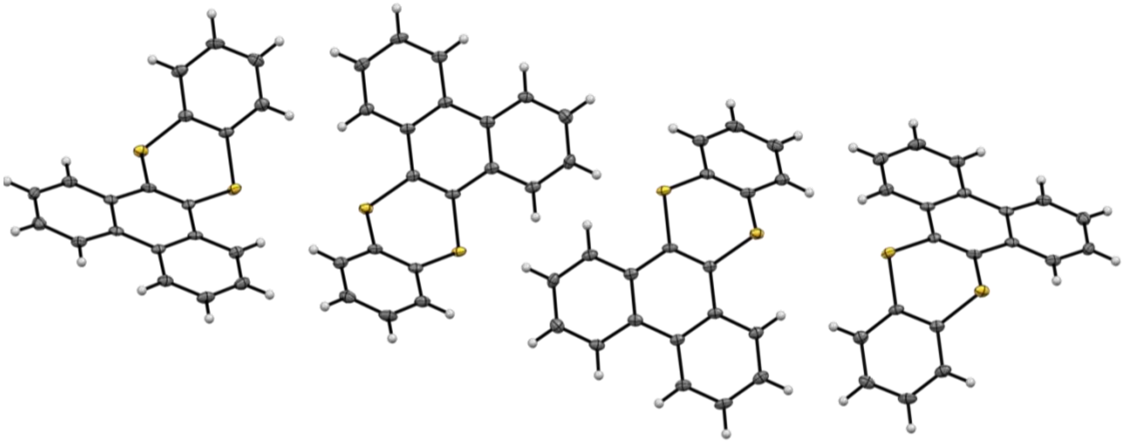


Figure S1. Crystallographic structure of **3ca** with the thermal ellipsoid at a 50% probability level.

Table S2. Crystallographic data and structure refinement details for **3ea**.

CCDC deposition No.	2223785
formula	$C_{26}H_{12}S_2$
FW	388.48
T (K)	123(2) K
λ (Å)	0.71073 Å
cryst syst	Monoclinic
space group	$P2_1/c$
a (Å)	9.7599(7)
b (Å)	24.6462(18)
c (Å)	7.4158(5)
α (deg)	90
β (deg)	103.413(7)
γ (deg)	90
V (Å^3)	1735.2(2)
Z	4
D_{calc} (g / cm^3)	1.487
μ (mm^{-1})	0.316
F (000)	800.0
cryst size (mm)	0.1 × 0.05 × 0.05
θ range (deg)	4.29° to 59.514°
reflns collected	18455
indep reflns/R_{int}	4146/ 0.0645
params	253
GOF on F^2	1.019
R_1, wR_2 [$I>2\sigma(I)$]	0.0415, 0.0969
R_1, wR_2 (all data)	0.0652, 0.1064

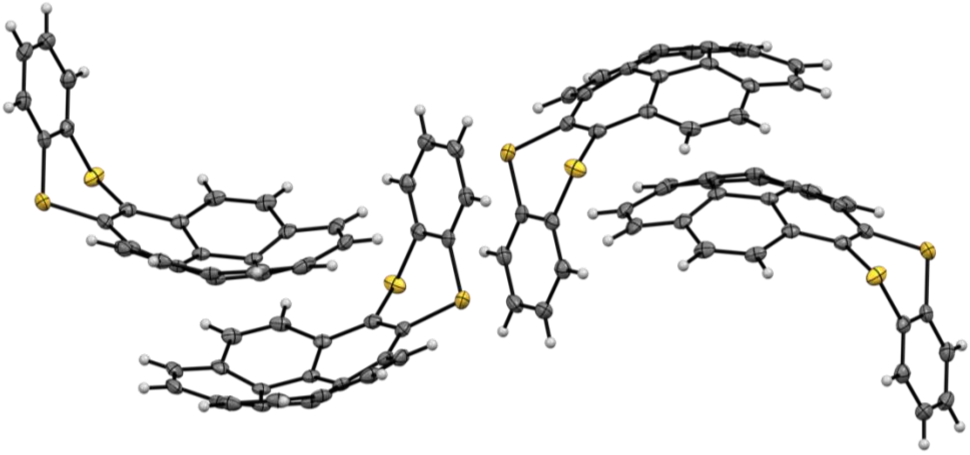


Figure S2. Crystallographic structure of **3ea** with the thermal ellipsoid at a 50% probability level.

Table S3. Crystallographic data and structure refinement details for **3fa**.

CCDC deposition No.	2241075
formula	$C_{24}H_{14}S_2$
FW	366.47
T (K)	123(2) K
λ (Å)	0.71073 Å
cryst syst	Monoclinic
space group	$P2_1/c$
a (Å)	14.0994(18)
b (Å)	8.9494(7)
c (Å)	14.8072(16)
α (deg)	90
β (deg)	118.315(16)
γ (deg)	90
V (Å^3)	1644.8(4)
Z	4
D_{calc} (g / cm^3)	1.480
μ (mm^{-1})	0.328
F (000)	760.0
cryst size (mm)	0.2 × 0.08 × 0.01
θ range (deg)	5.522° to 62.482°
reflns collected	11753
indep reflns/R_{int}	4260/ 0.0517
params	235
GOF on F^2	1.191
R_1, wR_2 [I>2σ(I)]	0.0972, 0.2284
R_1, wR_2 (all data)	0.1147, 0.2344

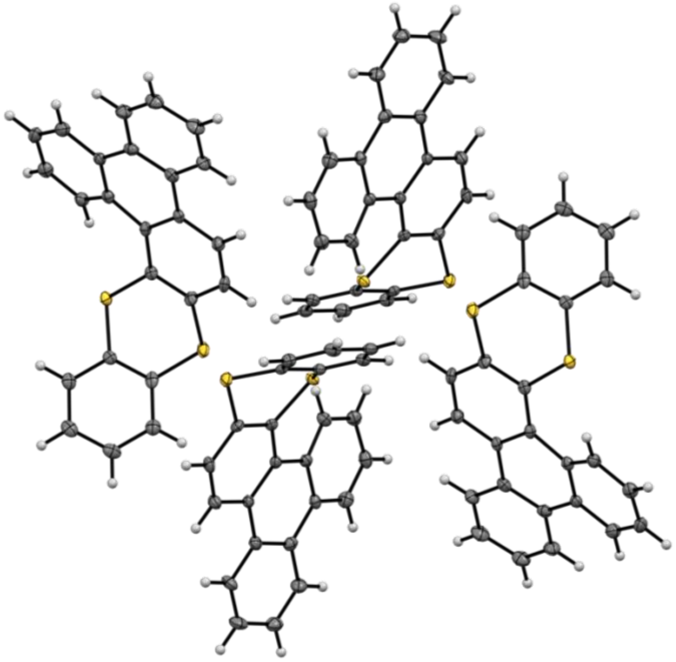


Figure S3. Crystallographic structure of **3fa** with the thermal ellipsoid at a 50% probability level.

6. DFT calculations

The Gaussian 16 program, revision C.01,[S10] was used for all computational investigations. Following the literature,[S11] geometry optimizations and harmonic vibration frequency calculations of the all local minima (with no imaginary frequency), and transition states (with one imaginary frequency) were conducted using the B3LYP/6-31+G(d,p) level of theories in the gas phase at 298.15 K without any symmetry assumptions,[S12] and those accurate energies were estimated by the single-point calculations of optimized geometries with the B3LYP/6-31+G(d,p) level of theory in CH_2Cl_2 (IEF-PCM[S13]) as needed.[S12] For investigations on photophysical properties, π-extended thianthrenes **3ca** and **3ea** were calculated by TD-DFT methods. Zero-point energy, enthalpy, and Gibbs free energy were estimated from the gas-phase unless otherwise noted. Harmonic vibration frequency calculations at the same level were performed to verify all stationary points as local minima with no imaginary frequency. ^{1}H NMR spectra of **3ea** was estimated using the GIAO-B3LYP/6-31+G(d,p) level of theory[S14] in CH_2Cl_2 (IEF-PCM). Visualization of the results was performed by use of GaussView 6.1 software.[S15]

Table S4. Uncorrected and thermal-corrected energies of optimized geometries (Hartree), with the B3LYP/6-31+G(d,p) level of theory.[a]

Structure	*E*	*ZPE*	*H*	*G*
3ca	-1565.802942	0.255801	-1565.530027	-1565.591065
3ea-ladle	-1794.424410	0.292961	-1794.112175	-1794.177032
3ea-spoon	-1794.422306	0.292826	-1794.110148	-1794.175168
TS1$_{\mathbf{3ca}}$	-1565.791948	0.255148	-1565.520177	-1565.579422
TS1$_{\mathbf{3ea}}$	-1794.412840	0.292349	-1794.101747	-1794.165130
TS2$_{\mathbf{3ea}}$	-1794.409079	0.292379	-1794.097993	-1794.161540
phenanthrene	-539.572509	0.194287	-539.367825	-539.413067
corannulene	-768.188342	0.231458	-767.944404	-767.993636
tetramethylsilane	-449.218326	0.147168	-449.060762	-449.103927

a) *E*: electronic energy; *ZPE*: zero-point energy; *H* (enthalpy) = *E* + *TCE*: sum of electronic energy (*E*) and thermal correction to enthalpy (*TCE*) ; *G* (free energy) = *E* + *TCF*: sum of electronic energy (*E*) and thermal corrections to free energies (*TCF*).

Table S5. Cartesian coordinates of optimized **3ca**.

H	0.3245260	-3.3888480	0.2995270
H	2.3738850	-4.6440170	-0.2223020
H	4.4967650	-3.4133300	-0.7061090
H	4.5326280	-0.9754860	-0.6795030
H	4.5326180	0.9755000	-0.6795290
H	4.4967460	3.4133440	-0.7061320
H	2.3738660	4.6440230	-0.2223020
H	0.3245150	3.3888460	0.2995390
H	-5.5756020	-1.2456690	-1.6006190
H	-3.7054030	-2.4848130	-0.5331880
H	-5.5756050	1.2456710	-1.6006080
H	-3.7054090	2.4848100	-0.5331670
C	2.3952720	-3.5585890	-0.1984190
C	3.5879030	-2.8664690	-0.4732700
C	3.6024240	-1.4832600	-0.4551660
C	2.4420660	-0.7285920	-0.1574140
C	1.2367490	-1.4356750	0.1360670
C	1.2444540	-2.8528730	0.0984990
C	2.4420630	0.7285980	-0.1574160
C	3.6024150	1.4832710	-0.4551800
C	3.5878880	2.8664790	-0.4732830
C	2.3952580	3.5585950	-0.1984210
C	1.2444440	2.8528750	0.0985050
C	1.2367440	1.4356760	0.1360710
C	0.0481400	-0.6863100	0.4911170
C	0.0481380	0.6863060	0.4911220
C	-2.6937710	-0.7008340	0.1259800
C	-2.6937730	0.7008280	0.1259870
C	-3.7240630	-1.3994690	-0.5159690
C	-4.7701890	-0.6991390	-1.1194280
C	-3.7240660	1.3994660	-0.5159560
C	-4.7701910	0.6991390	-1.1194220
S	-1.4162780	-1.5944530	0.9906300
S	-1.4162820	1.5944420	0.9906430

Table S6. Cartesian coordinates of optimized **3ea-ladle**.

H	-0.4601630	3.5013670	-0.2710690
H	1.7183930	4.2490490	0.4740510
H	1.7183930	-4.2490500	0.4740510
H	-0.4601630	-3.5013670	-0.2710690
H	-6.0169110	1.2459770	2.5071460
H	-4.4677450	2.4840290	1.0119570
H	-6.0169110	-1.2459770	2.5071460
H	-4.4677440	-2.4840290	1.0119580
H	5.6260300	1.4179090	1.7870870
H	4.2774070	3.3784540	1.3296900
H	5.6260300	-1.4179090	1.7870870
H	4.2774070	-3.3784540	1.3296900
C	1.6326520	3.2479200	0.0587430
C	2.7803630	2.3667920	0.0783280
C	2.5711410	1.1465830	-0.5441440
C	1.2965770	0.7090870	-0.9830860
C	0.1474590	1.4668040	-0.8277230
C	0.3794790	2.8207080	-0.3685200
C	1.2965770	-0.7090870	-0.9830860
C	2.5711420	-1.1465830	-0.5441440
C	2.7803630	-2.3667920	0.0783280
C	1.6326520	-3.2479200	0.0587430
C	0.3794790	-2.8207080	-0.3685200
C	0.1474590	-1.4668040	-0.8277230
C	-1.0859420	0.7008990	-0.9376880
C	-1.0859410	-0.7008990	-0.9376880
C	-3.6493300	0.7010920	0.1226720
C	-3.6493300	-0.7010920	0.1226720
C	-4.4895920	1.3986020	0.9996620
C	-5.3548480	0.6989900	1.8428180
C	-4.4895920	-1.3986020	0.9996620
C	-5.3548480	-0.6989900	1.8428180
C	3.3598530	0.0000000	-0.2758140
C	4.4076560	0.0000000	0.6308090
C	4.7729240	-1.3135090	1.1211600

C	3.9989320	-2.4390270	0.8585270
C	4.7729240	1.3135090	1.1211590
C	3.9989320	2.4390270	0.8585270
S	-2.6236520	1.6062080	-1.0267710
S	-2.6236520	-1.6062080	-1.0267710

Table S7. Cartesian coordinates of optimized **3ea-spoon**.

C	-1.8054470	3.2578380	0.1704210
C	-2.8904990	2.3703330	-0.1920410
C	-2.4768000	1.1464040	-0.6913860
C	-1.1299460	0.7080980	-0.6516170
C	-0.1068180	1.4686740	-0.1143400
C	-0.4812370	2.8314320	0.2051020
C	-1.1299470	-0.7080980	-0.6516170
C	-2.4767990	-1.1464040	-0.6913860
C	-2.8904990	-2.3703330	-0.1920410
C	-1.8054470	-3.2578380	0.1704200
C	-0.4812360	-2.8314320	0.2051020
C	-0.1068170	-1.4686740	-0.1143400
C	1.0686940	0.7012580	0.2713920
C	1.0686930	-0.7012570	0.2713920
H	0.2752060	3.5264330	0.5575990
H	-2.0270220	4.2680970	0.5055290
H	-2.0270210	-4.2680980	0.5055270
H	0.2752060	-3.5264330	0.5575980
S	2.4814770	1.6019690	0.9012930
S	2.4814770	-1.6019680	0.9012960
C	3.8282800	0.7011460	0.1525310
C	3.8282800	-0.7011460	0.1525310
C	4.9093660	1.3990990	-0.4002500
C	6.0033270	0.6990450	-0.9123500
C	4.9093660	-1.3990990	-0.4002490
C	6.0033260	-0.6990450	-0.9123500
H	6.8463420	1.2459000	-1.3235430
H	4.8915950	2.4843750	-0.4205590
H	6.8463420	-1.2459010	-1.3235430

H	4.8915950	-2.4843760	-0.4205570
C	-3.3089140	0.0000000	-0.7152640
C	-4.6086740	0.0000000	-0.2362120
C	-5.1218220	-1.3151760	0.0917120
C	-4.3054010	-2.4418810	0.1120480
C	-5.1218230	1.3151760	0.0917120
C	-4.3054010	2.4418800	0.1120490
H	-6.1540250	1.4211370	0.4164110
H	-4.7331470	3.3822190	0.4509470
H	-6.1540250	-1.4211380	0.4164120
H	-4.7331470	-3.3822190	0.4509460

Table S8. Cartesian coordinates of optimized **TS1**$_{\mathbf{3ca}}$.

C	0.0000000	3.5530050	-2.5388680
C	-0.0000010	2.8622870	-3.7618330
C	-0.0000010	1.4791950	-3.7663880
C	0.0000000	0.7274670	-2.5675330
C	0.0000010	1.4278220	-1.3262330
C	0.0000000	2.8471170	-1.3500920
C	0.0000000	-0.7274670	-2.5675330
C	0.0000010	-1.4791950	-3.7663880
C	0.0000010	-2.8622870	-3.7618330
C	0.0000000	-3.5530050	-2.5388680
C	0.0000000	-2.8471170	-1.3500920
C	-0.0000010	-1.4278220	-1.3262330
C	0.0000010	0.6855520	-0.0743560
C	-0.0000010	-0.6855520	-0.0743560
H	0.0000000	3.4044990	-0.4213510
H	0.0000000	4.6386790	-2.5214320
H	-0.0000010	3.4078090	-4.7006840
H	-0.0000020	0.9682250	-4.7212590
H	0.0000020	-0.9682250	-4.7212590
H	0.0000010	-3.4078090	-4.7006840
H	0.0000000	-4.6386790	-2.5214320
H	0.0000000	-3.4044990	-0.4213510
S	0.0000040	1.7426960	1.3716480

S	-0.0000040	-1.7426960	1.3716480
C	0.0000010	0.6983340	2.8098390
C	-0.0000010	-0.6983340	2.8098390
C	0.0000030	1.3870370	4.0331060
C	0.0000010	0.6984980	5.2443010
C	-0.0000030	-1.3870370	4.0331060
C	-0.0000010	-0.6984980	5.2443010
H	0.0000020	1.2516210	6.1782420
H	0.0000050	2.4737180	4.0284520
H	-0.0000020	-1.2516210	6.1782420
H	-0.0000050	-2.4737180	4.0284520

Table S9. Cartesian coordinates of optimized **TS1$_{3ea}$**.

C	-0.1442260	-1.8245890	3.2466250
C	0.0440860	-2.9570210	2.3674860
C	0.6138740	-2.6348530	1.1464630
C	0.8086240	-1.3020510	0.7082310
C	0.4438230	-0.2006630	1.4590110
C	0.0443140	-0.5141420	2.8167830
C	0.8086240	-1.3020510	-0.7082310
C	0.6138740	-2.6348530	-1.1464630
C	0.0440860	-2.9570210	-2.3674860
C	-0.1442260	-1.8245890	-3.2466250
C	0.0443140	-0.5141420	-2.8167830
C	0.4438230	-0.2006630	-1.4590110
C	0.3074910	1.0410990	0.6987670
C	0.3074910	1.0410990	-0.6987670
H	-0.2003540	0.2855410	3.5089210
H	-0.5288560	-1.9822670	4.2512370
H	-0.5288560	-1.9822670	-4.2512370
H	-0.2003540	0.2855410	-3.5089210
S	0.0581890	2.4615170	1.7492140
S	0.0581890	2.4615170	-1.7492140
C	-0.1062110	3.8919210	0.6995440
C	-0.1062110	3.8919210	-0.6995440
C	-0.2446710	5.1077140	1.3864750

C	-0.3880000	6.3110920	0.6981780
C	-0.2446710	5.1077140	-1.3864750
C	-0.3880000	6.3110920	-0.6981780
H	-0.4959400	7.2384900	1.2517370
H	-0.2396430	5.1041630	2.4731890
H	-0.4959400	7.2384900	-1.2517370
H	-0.2396430	5.1041630	-2.4731890
C	0.4973480	-3.4599650	0.0000000
C	-0.1970790	-4.6584010	0.0000000
C	-0.6099730	-5.1088390	-1.3143130
C	-0.4953410	-4.2999730	-2.4398830
C	-0.6099730	-5.1088390	1.3143130
C	-0.4953410	-4.2999730	2.4398830
H	-1.1047430	-6.0713690	1.4187560
H	-0.9050320	-4.6618960	3.3797130
H	-1.1047430	-6.0713690	-1.4187560
H	-0.9050320	-4.6618960	-3.3797130

Table S10. Cartesian coordinates of optimized **TS2$_{3ea}$**.

C	-1.7759660	-3.3496030	-0.0678040
C	-2.8964730	-2.4322500	0.1323620
C	-2.4773870	-1.1312760	0.0685560
C	-1.1695820	-0.6985640	-0.1678920
C	-0.0850520	-1.5056360	-0.3689820
C	-0.4585320	-2.9170270	-0.2998280
C	-1.1695820	0.6985640	-0.1678910
C	-2.4773860	1.1312760	0.0685570
C	-2.8964730	2.4322500	0.1323620
C	-1.7759650	3.3496030	-0.0678040
C	-0.4585310	2.9170260	-0.2998280
C	-0.0850520	1.5056360	-0.3689820
C	1.1224850	-0.7095550	-0.6162810
C	1.1224850	0.7095540	-0.6162820
H	0.3012080	-3.6820240	-0.4303930
H	-1.9423150	-4.4235240	-0.0384620
H	-1.9423130	4.4235240	-0.0384620

H	0.3012090	3.6820230	-0.4303930
S	2.6287660	-1.6003240	-0.9795180
S	2.6287660	1.6003230	-0.9795190
C	3.8267080	-0.7009900	-0.0065960
C	3.8267080	0.7009890	-0.0065970
C	4.7947350	-1.3991170	0.7259610
C	5.7827250	-0.6990040	1.4210140
C	4.7947360	1.3991170	0.7259600
C	5.7827260	0.6990040	1.4210130
H	6.5416140	-1.2458070	1.9723810
H	4.7743090	-2.4844850	0.7420430
H	6.5416140	1.2458080	1.9723800
H	4.7743090	2.4844860	0.7420410
C	-3.2860100	0.0000000	0.2126670
C	-4.6353070	0.0000000	0.4384830
C	-5.1500670	1.3669670	0.5209100
C	-4.3365780	2.5046560	0.3782900
C	-5.1500680	-1.3669670	0.5209100
C	-4.3365790	-2.5046560	0.3782900
H	-6.2091310	-1.5366000	0.6985710
H	-4.8240900	-3.4732260	0.4564540
H	-6.2091310	1.5366010	0.6985710
H	-4.8240890	3.4732270	0.4564530

Table S11. Cartesian coordinates of optimized phenanthrene.

H	-3.3513050	1.8390410	-0.0001800
H	1.2322580	3.0325450	0.0001050
H	4.6505970	-0.2728770	0.0000860
H	3.3513050	1.8390410	0.0002160
H	1.0079510	-2.5337680	-0.0003040
H	3.4480050	-2.4599410	-0.0002420
H	-1.2322570	3.0325450	-0.0001370
H	-4.6505960	-0.2728810	-0.0000330
H	-3.4480100	-2.4599390	0.0002350
H	-1.0079430	-2.5337650	0.0002710
C	3.5648860	-0.2970400	0.0000410

C	2.8399160	0.8797460	0.0001230
C	1.4238510	0.8667420	0.0000670
C	0.7294190	-0.3803870	-0.0000170
C	1.5007180	-1.5681010	-0.0001410
C	2.8848470	-1.5311900	-0.0001170
C	0.6806030	2.0960640	0.0000450
C	-0.7294200	-0.3803850	0.0000040
C	-1.4238500	0.8667420	-0.0000730
C	-0.6806040	2.0960640	-0.0000650
C	-2.8399180	0.879746 0	-0.0001000
C	-3.5648850	-0.2970390	-0.0000160
C	-2.8848450	-1.5311920	0.0001190
C	-1.5007190	-1.5681030	0.0001270

Table S12. Cartesian coordinates of optimized corannulene.

H	2.6792670	-3.3058070	-0.6136340
H	0.4395930	-4.2323820	-0.6137980
H	-2.3161550	-3.5696780	-0.6135420
H	-3.8895460	-1.7259990	-0.6134450
H	-4.1107180	1.0997010	-0.6134990
H	-2.8434610	3.1658070	-0.6134380
H	2.1321710	3.6825030	-0.6135850
H	-0.2243950	4.2492880	-0.6135940
H	4.1612340	-0.8898140	-0.6134030
H	3.9720070	1.5265240	-0.6135220
C	-0.2820430	-1.1726600	0.6192460
C	1.0281280	-0.6306030	0.6193200
C	0.9174540	0.7829270	0.6192580
C	-0.4611080	1.1144590	0.6192140
C	-1.2024440	-0.0941490	0.6192670
C	-0.5819950	-2.4197710	0.0947290
C	-1.9765100	-2.6010470	-0.2547300
C	-2.8795420	-1.5428870	-0.2546870
C	-2.4812330	-0.1942330	0.0948070
C	-0.9514640	2.2997060	0.0947010
C	-2.3571980	2.2618050	-0.2547190

C	-3.0845380	1.0759970	-0.2546990
C	1.8931740	1.6155520	0.0947760
C	1.4226900	2.9407090	-0.2548040
C	0.0701640	3.2659700	-0.2548940
C	2.1215460	-1.3012780	0.0948690
C	3.2364910	-0.4443100	-0.2546170
C	3.1278810	0.9425340	-0.2547050
C	1.8629930	-2.6834830	-0.2548080
C	0.5775550	-3.2152620	-0.2549450

Table S13. Cartesian coordinates of optimized tetramethylsilane.

H	1.4310380	-2.0164390	-0.4336960
H	1.4050180	-0.9536230	-1.8489790
H	0.0240980	-2.0069630	-1.5077620
H	2.0163140	0.4672590	1.4204990
H	0.9377160	1.8703500	1.3873510
H	1.9901060	1.5300950	0.0052690
H	-0.4446770	-1.4100800	2.0289530
H	-1.8515970	-1.4006040	0.9548570
H	-1.5231620	-0.0069610	1.9953690
H	-1.5698850	1.8868940	-0.5265180
H	-1.8980190	0.4931560	-1.5672220
H	-0.5171580	1.5466720	-1.9083520
C	0.7885130	-1.3720230	-1.0448920
C	1.3629780	1.0663060	0.7755160
C	-1.0528070	-0.7768050	1.3725830
C	-1.0986240	1.0825720	-1.1032590
Si	-0.0000110	-0.0000040	0.0000390

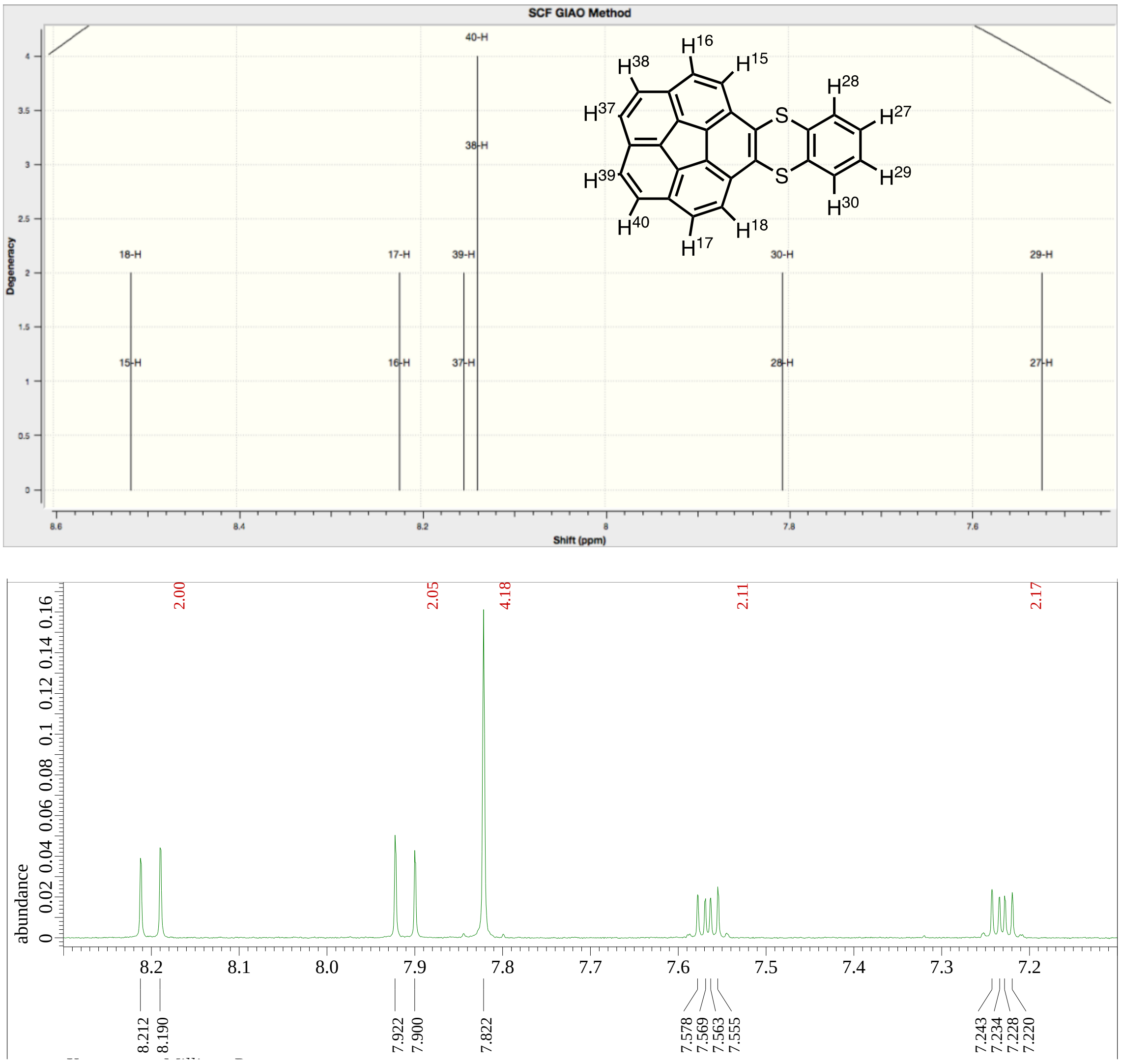


Figure S4. Comparison with calculated proton peaks in ^{1}H NMR (above, GIAO-B3LYP/6-31+G(d,p), in CH_2Cl_2 (IEF-PCM), reference: tetramethylsilane (magnetic shielding tensor = 31.6495 ppm, GIAO-B3LYP/6-31+G(d,p), in CH_2Cl_2 (IEF-PCM)) and experimental ^{1}H NMR spectra of **3ea** in CD_2Cl_2 with 400 MHz of resonant frequency (below).

7. Measurements of photophysical properties of 3ca, 3ea and 3ja

All photophysical measurements were conducted in the diluted solution of compounds in CH_2Cl_2 (super dehydrated grade, KANTO) in a 1 × 1 cm square quartz cell. UV/Vis absorption spectra of **3ca**, **3ea** and **3ja** in CH_2Cl_2 were recorded on a SHIMADZU UV-3600 spectrophotometer with a resolution of 0.5 nm. Emission spectra and fluorescence quantum yield of **3ca** in CH_2Cl_2 was measured with a SHIMADZU RF-6000 spectrofluorophotometer with a resolution of 1.0 nm upon excitation at 330 nm. Emission spectra and fluorescence quantum yield of **3ea** in CH_2Cl_2 was measured with a SHIMADZU RF-6000 spectrofluorophotometer with a resolution of 1.0 nm upon excitation at 350 nm. Fluorescence quantum yield of phenanthrene in CH_2Cl_2 was measured with a SHIMADZU RF-6000 spectrofluorophotometer with a resolution of 1.0 nm upon excitation at 295 nm. Fluorescence quantum yield of corannulene in CH_2Cl_2 was measured with a SHIMADZU RF-6000 spectrofluorophotometer with a resolution of 1.0 nm upon excitation at 324 nm. All quantum yield was measured using an integral sphere.

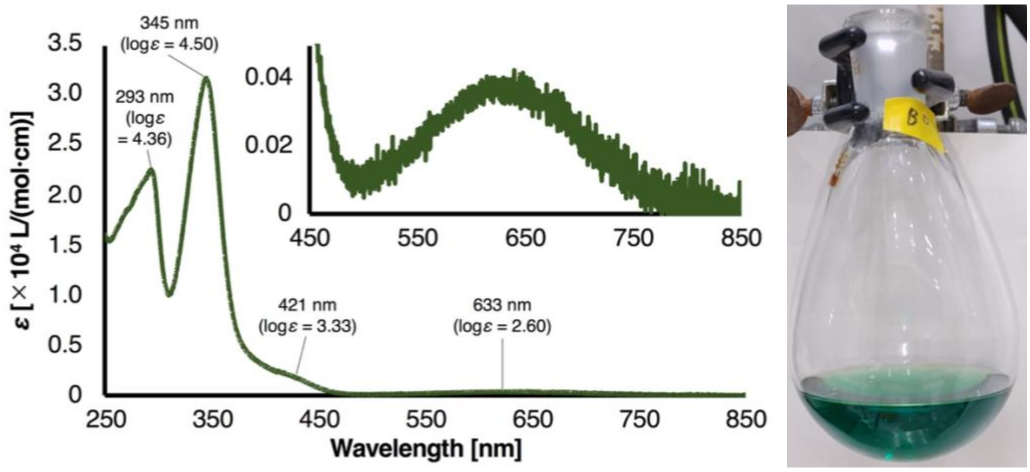


Figure S5. UV-vis absorption spectra of compound **3ja** in CH_2Cl_2 ($c = 1.8 \times 10^{-5}$ M). The picture describes a concentrated CH_2Cl_2 solution of compound **3ja** ($c = 1.9 \times 10^{-3}$ M).

8. References

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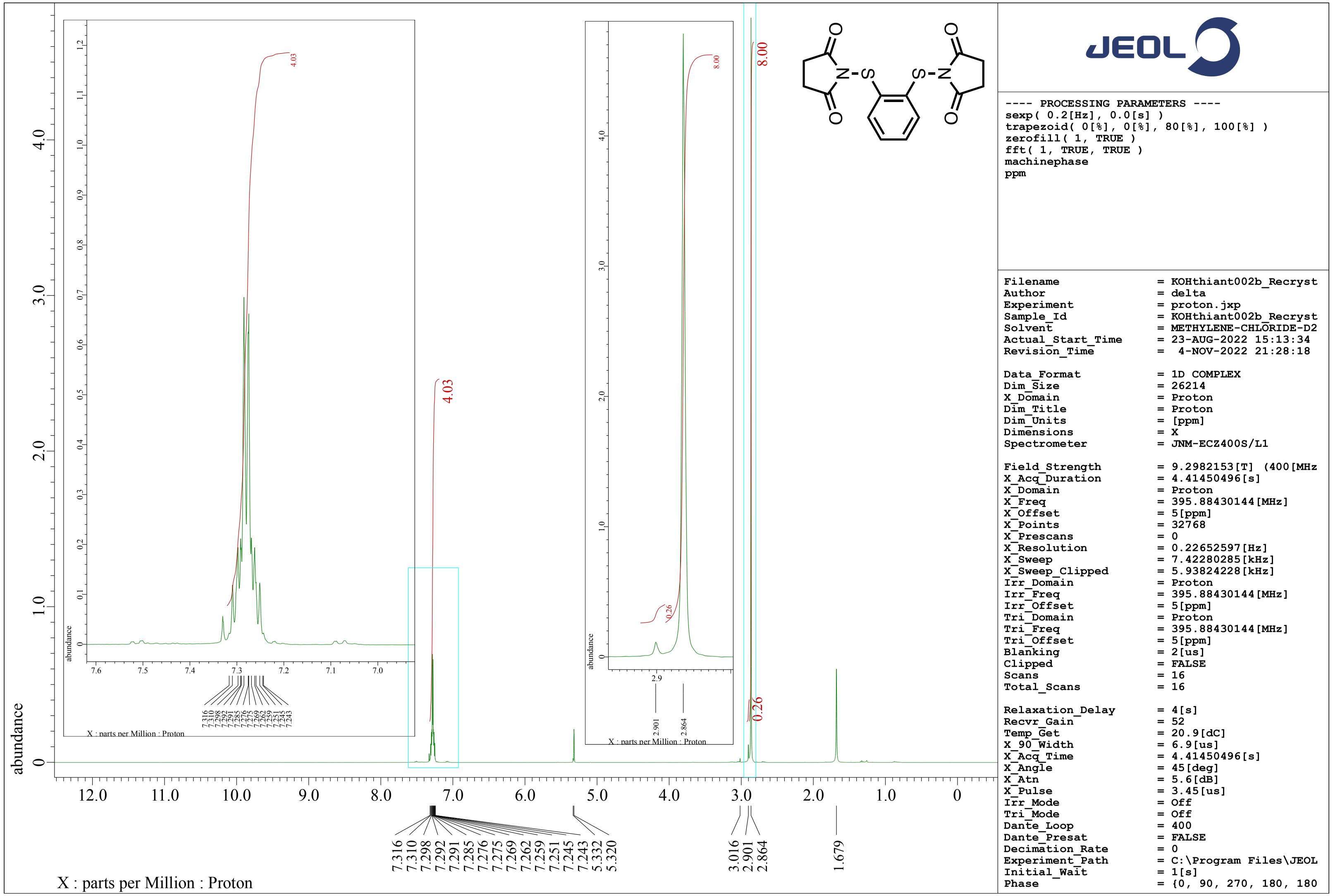
9. ^{1}H, ^{13}C, and ^{19}F NMR spectra of compounds



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fft( 1, TRUE, TRUE )
machinephase
ppm

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Author              = delta
Experiment          = proton.jxp
Sample_Id           = KOHthiant002b_Recryst
Solvent             = METHYLENE-CHLORIDE-D2
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Revision_Time       =  4-NOV-2022 21:28:18

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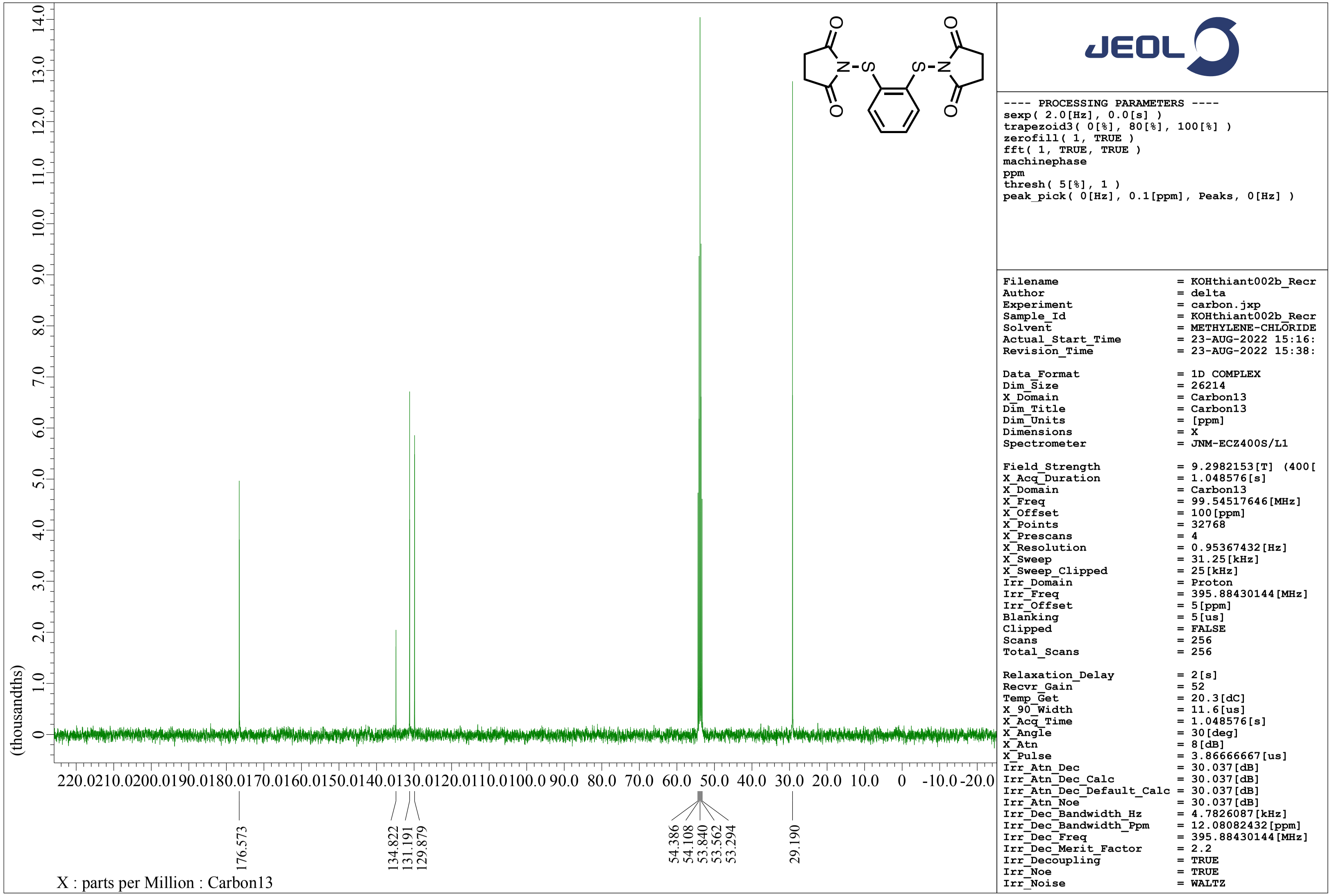
Dim_Title           = Proton
Dim_Units           = [ppm]
Dimensions          = X
Spectrometer        = JNM-ECZ400S/L1

Field_Strength      = 9.2982153[T] (400[MHz
X_Acq_Duration      = 4.41450496[s]
X_Domain            = Proton
X_Freq              = 395.88430144[MHz]
X_Offset            = 5[ppm]
X_Points            = 32768
X_Prescans          = 0
X_Resolution        = 0.22652597[Hz]
X_Sweep             = 7.42280285[kHz]
X_Sweep_Clipped     = 5.93824228[kHz]
Irr_Domain          = Proton
Irr_Freq            = 395.88430144[MHz]
Irr_Offset          = 5[ppm]
Tri_Domain          = Proton
Tri_Freq            = 395.88430144[MHz]
Tri_Offset          = 5[ppm]
Blanking            = 2[us]
Clipped             = FALSE
Scans               = 16
Total_Scans         = 16

Relaxation_Delay    = 4[s]
Recvr_Gain          = 52
Temp_Get            = 20.9[dC]
X_90_Width          = 6.9[us]
X_Acq_Time          = 4.41450496[s]
X_Angle             = 45[deg]
X_Atn               = 5.6[dB]
X_Pulse             = 3.45[us]
Irr_Mode            = Off
Tri_Mode            = Off
Dante_Loop          = 400
Dante_Presat        = FALSE
Decimation_Rate     = 0
Experiment_Path     = C:\Program Files\JEOL
Initial_Wait        = 1[s]
Phase               = {0, 90, 270, 180, 180
```

Figure S6. ^{1}H NMR spectra of **2a** (in CD_2Cl_2, 400 MHz)



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zerofill( 1, TRUE )
fft( 1, TRUE, TRUE )
machinephase
ppm
thresh( 5[%], 1 )
peak_pick( 0[Hz], 0.1[ppm], Peaks, 0[Hz] )
```

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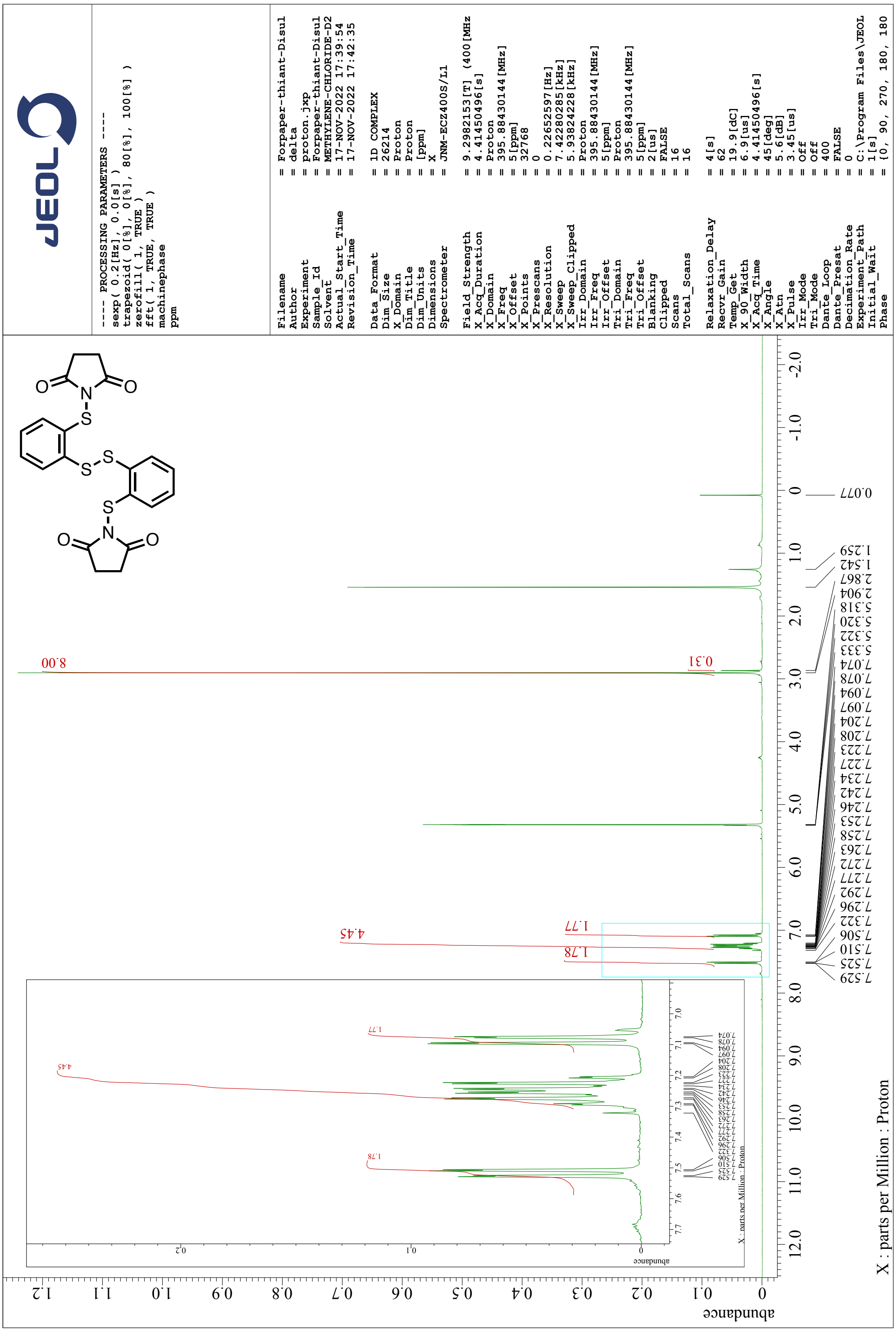
Author                   = delta
Experiment               = carbon.jxp
Sample_Id                = KOHthiant002b_Recr
Solvent                  = METHYLENE-CHLORIDE
Actual_Start_Time        = 23-AUG-2022 15:16:
Revision_Time            = 23-AUG-2022 15:38:

Data_Format              = 1D COMPLEX
Dim_Size                 = 26214
X_Domain                 = Carbon13
Dim_Title                = Carbon13
Dim_Units                = [ppm]
Dimensions               = X
Spectrometer             = JNM-ECZ400S/L1

Field_Strength           = 9.2982153[T] (400[
X_Acq_Duration           = 1.048576[s]
X_Domain                 = Carbon13
X_Freq                   = 99.54517646[MHz]
X_Offset                 = 100[ppm]
X_Points                 = 32768
X_Prescans               = 4
X_Resolution             = 0.95367432[Hz]
X_Sweep                  = 31.25[kHz]
X_Sweep_Clipped          = 25[kHz]
Irr_Domain               = Proton
Irr_Freq                 = 395.88430144[MHz]
Irr_Offset               = 5[ppm]
Blanking                 = 5[us]
Clipped                  = FALSE
Scans                    = 256
Total_Scans              = 256

Relaxation_Delay         = 2[s]
Recvr_Gain               = 52
Temp_Get                 = 20.3[dC]
X_90_Width               = 11.6[us]
X_Acq_Time               = 1.048576[s]
X_Angle                  = 30[deg]
X_Atn                    = 8[dB]
X_Pulse                  = 3.86666667[us]
Irr_Atn_Dec              = 30.037[dB]
Irr_Atn_Dec_Calc         = 30.037[dB]
Irr_Atn_Dec_Default_Calc = 30.037[dB]
Irr_Atn_Noe              = 30.037[dB]
Irr_Dec_Bandwidth_Hz     = 4.7826087[kHz]
Irr_Dec_Bandwidth_Ppm    = 12.08082432[ppm]
Irr_Dec_Freq             = 395.88430144[MHz]
Irr_Dec_Merit_Factor     = 2.2
Irr_Decoupling           = TRUE
Irr_Noe                  = TRUE
Irr_Noise                = WALTZ
```

Figure S7. ^{13}C NMR spectra of **2a** (in CD_2Cl_2, 100 MHz)



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fft( 1, TRUE, TRUE )
machinephase
ppm

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Author                = delta
Experiment            = proton.jxp
Sample_Id             = Forpaper-thiant-Disul
Solvent               = METHYLENE-CHLORIDE-D2
Actual_Start_Time     = 17-NOV-2022 17:39:54
Revision_Time         = 17-NOV-2022 17:42:35

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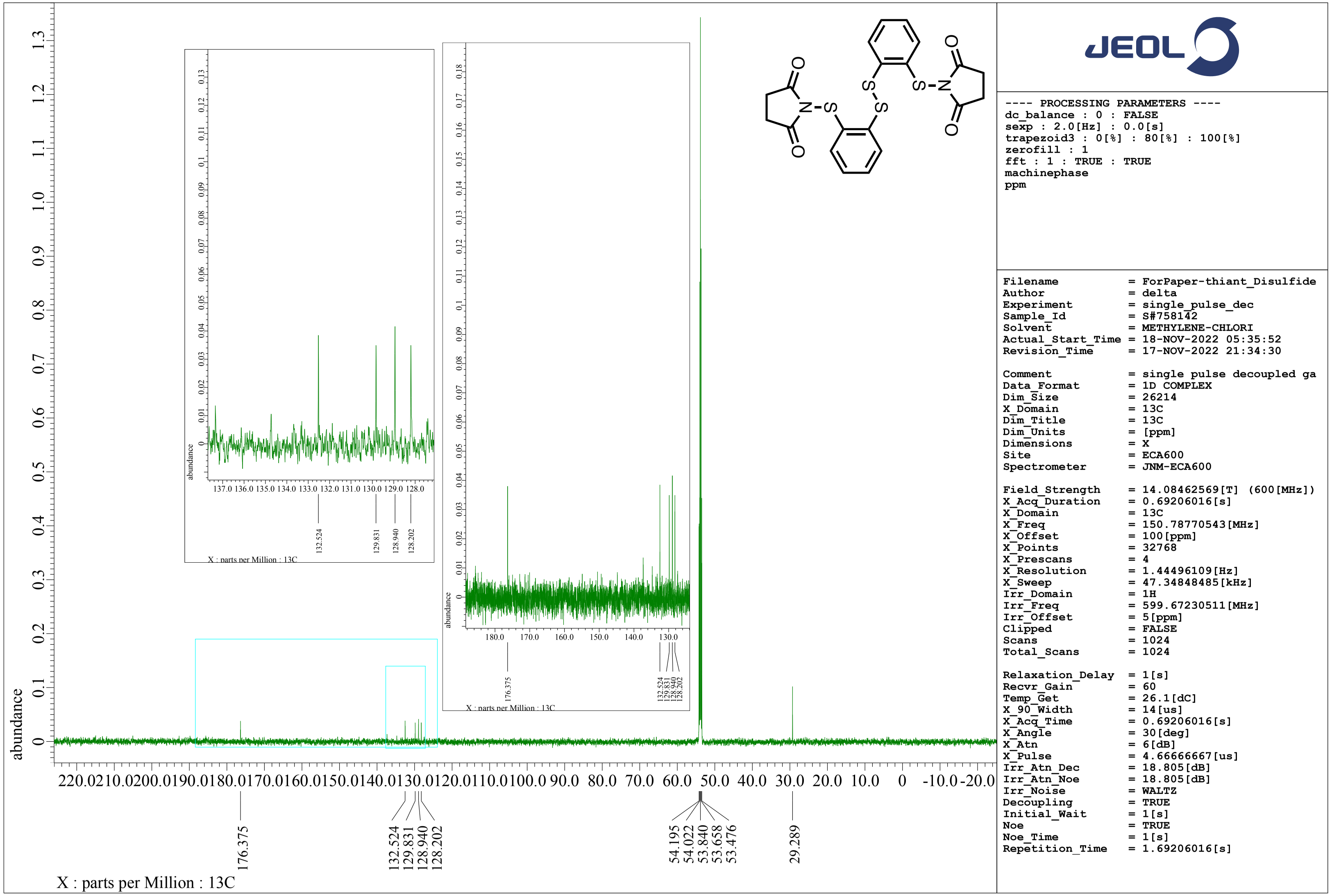
Dim_Title             = Proton
Dim_Units             = [ppm]
Dimensions            = X
Spectrometer          = JNM-ECZ400S/L1

Field_Strength        = 9.2982153[T] (400[MHz
X_Acq_Duration        = 4.41450496[s]
X_Domain              = Proton
X_Freq                = 395.88430144[MHz]
X_Offset              = 5[ppm]
X_Points              = 32768
X_Prescans            = 0
X_Resolution          = 0.22652597[Hz]
X_Sweep               = 7.42280285[kHz]
X_Sweep_Clipped       = 5.93824228[kHz]
Irr_Domain            = Proton
Irr_Freq              = 395.88430144[MHz]
Irr_Offset            = 5[ppm]
Tri_Domain            = Proton
Tri_Freq              = 395.88430144[MHz]
Tri_Offset            = 5[ppm]
Blanking              = 2[us]
Clipped               = FALSE
Scans                 = 16
Total_Scans           = 16

Relaxation_Delay      = 4[s]
Recvr_Gain            = 62
Temp_Get              = 19.9[dC]
X_90_Width            = 6.9[us]
X_Acq_Time            = 4.41450496[s]
X_Angle               = 45[deg]
X_Atn                 = 5.6[dB]
X_Pulse               = 3.45[us]
Irr_Mode              = Off
Tri_Mode              = Off
Dante_Loop            = 400
Dante_Presat          = FALSE
Decimation_Rate       = 0
Experiment_Path       = C:\Program Files\JEOL
Initial_Wait          = 1[s]
Phase                 = {0, 90, 270, 180, 180
```

Figure S8. ^{1}H NMR spectra of **2a′** (in CD_2Cl_2, 400 MHz)



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zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
```

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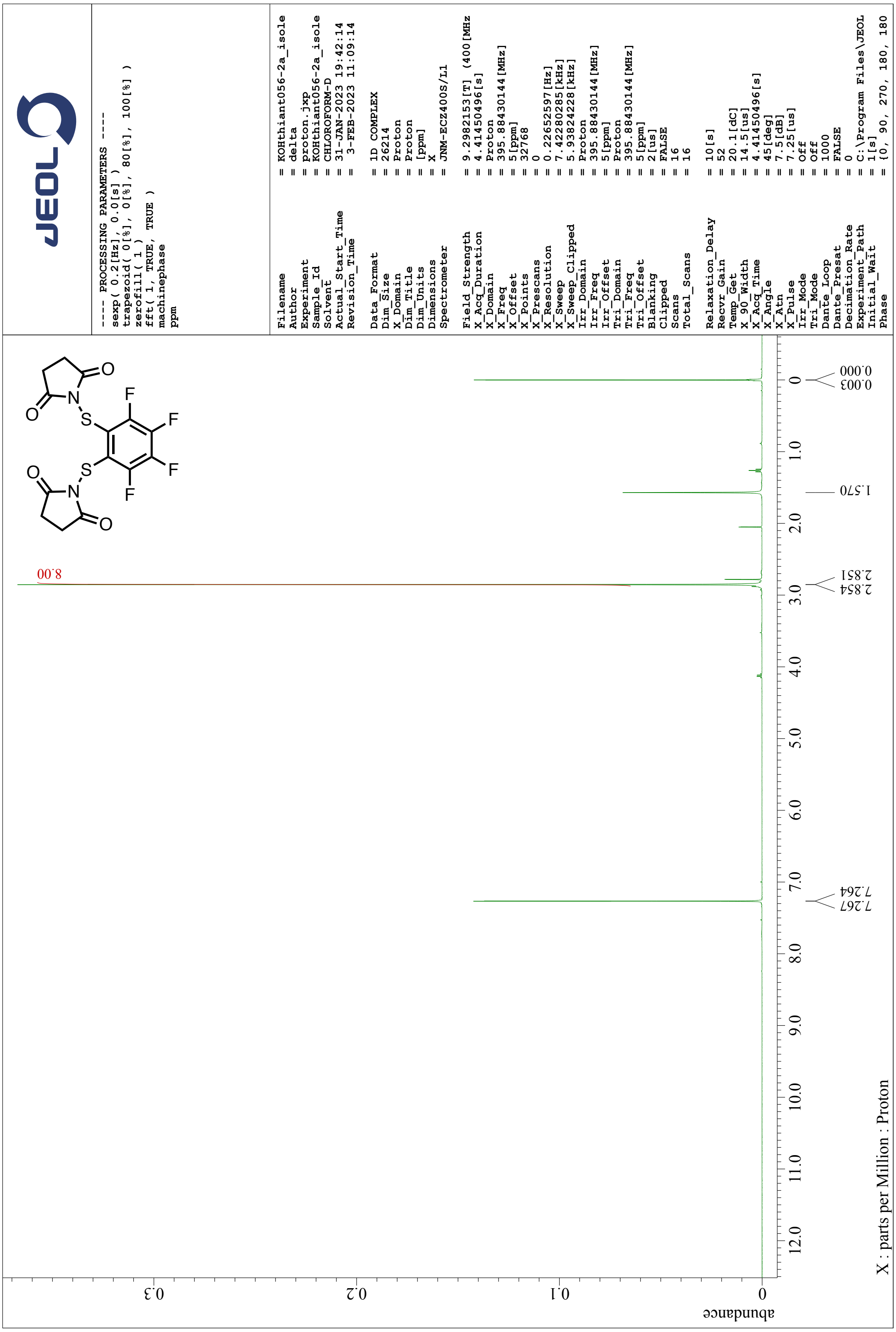
Filename           = ForPaper-thiant_Disulfide
Author             = delta
Experiment         = single_pulse_dec
Sample_Id          = S#758142
Solvent            = METHYLENE-CHLORI
Actual_Start_Time  = 18-NOV-2022 05:35:52
Revision_Time      = 17-NOV-2022 21:34:30

Comment            = single pulse decoupled ga
Data_Format        = 1D COMPLEX
Dim_Size           = 26214
X_Domain           = 13C
Dim_Title          = 13C
Dim_Units          = [ppm]
Dimensions         = X
Site               = ECA600
Spectrometer       = JNM-ECA600

Field_Strength     = 14.08462569[T] (600[MHz])
X_Acq_Duration     = 0.69206016[s]
X_Domain           = 13C
X_Freq             = 150.78770543[MHz]
X_Offset           = 100[ppm]
X_Points           = 32768
X_Prescans         = 4
X_Resolution       = 1.44496109[Hz]
X_Sweep            = 47.34848485[kHz]
Irr_Domain         = 1H
Irr_Freq           = 599.67230511[MHz]
Irr_Offset         = 5[ppm]
Clipped            = FALSE
Scans              = 1024
Total_Scans        = 1024

Relaxation_Delay   = 1[s]
Recvr_Gain         = 60
Temp_Get           = 26.1[dC]
X_90_Width         = 14[us]
X_Acq_Time         = 0.69206016[s]
X_Angle            = 30[deg]
X_Atn              = 6[dB]
X_Pulse            = 4.66666667[us]
Irr_Atn_Dec        = 18.805[dB]
Irr_Atn_Noe        = 18.805[dB]
Irr_Noise          = WALTZ
Decoupling         = TRUE
Initial_Wait       = 1[s]
Noe                = TRUE
Noe_Time           = 1[s]
Repetition_Time    = 1.69206016[s]
```

Figure S9. ^{13}C NMR spectra of **2a′** (in CD_2Cl_2, 150 MHz)



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zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

```
Filename             = KOHthiant056-2a_isole
Author               = delta
Experiment           = proton.jxp
Sample_Id            = KOHthiant056-2a_isole
Solvent              = CHLOROFORM-D
Actual_Start_Time    = 31-JAN-2023 19:42:14
Revision_Time        =  3-FEB-2023 11:09:14

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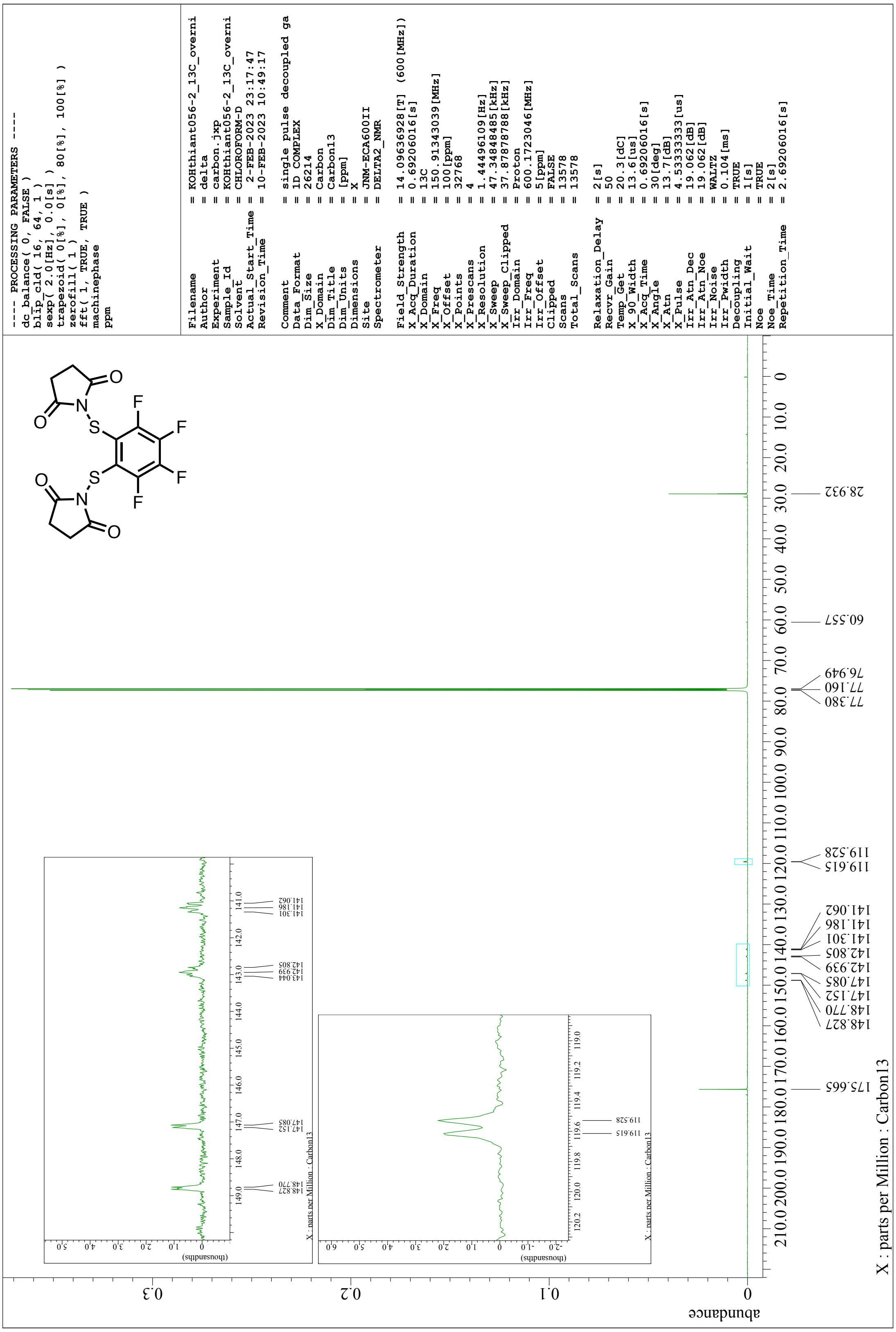
X_Domain             = Proton
Dim_Title            = Proton
Dim_Units            = [ppm]
Dimensions           = X
Spectrometer         = JNM-ECZ400S/L1

Field_Strength       = 9.2982153[T] (400[MHz
X_Acq_Duration       = 4.41450496[s]
X_Domain             = Proton
X_Freq               = 395.88430144[MHz]
X_Offset             = 5[ppm]
X_Points             = 32768
X_Prescans           = 0
X_Resolution         = 0.22652597[Hz]
X_Sweep              = 7.42280285[kHz]
X_Sweep_Clipped      = 5.93824228[kHz]
Irr_Domain           = Proton
Irr_Freq             = 395.88430144[MHz]
Irr_Offset           = 5[ppm]
Tri_Domain           = Proton
Tri_Freq             = 395.88430144[MHz]
Tri_Offset           = 5[ppm]
Blanking             = 2[us]
Clipped              = FALSE
Scans                = 16
Total_Scans          = 16

Relaxation_Delay     = 10[s]
Recvr_Gain           = 52
Temp_Get             = 20.1[dC]
X_90_Width           = 14.5[us]
X_Acq_Time           = 4.41450496[s]
X_Angle              = 45[deg]
X_Atn                = 7.5[dB]
X_Pulse              = 7.25[us]
Irr_Mode             = Off
Tri_Mode             = Off
Dante_Loop           = 1000
Dante_Presat         = FALSE
Decimation_Rate      = 0
Experiment_Path      = C:\Program Files\JEOL
Initial_Wait         = 1[s]
Phase                = {0, 90, 270, 180, 180
```

Figure S10. ^{1}H NMR spectra of **2b** (in $CDCl_3$, 400 MHz)



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zerofill( 1 )
fft( 1, TRUE, TRUE, TRUE )
machinephase
ppm
```

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Filename           = KOHthiant056-2_13C_overni
Author             = delta
Experiment         = carbon.jxp
Sample_Id          = KOHthiant056-2_13C_overni
Solvent            = CHLOROFORM-D
Actual_Start_Time  =  2-FEB-2023 23:17:47
Revision_Time      = 10-FEB-2023 10:49:17

Comment            = single pulse decoupled ga
Data_Format        = 1D COMPLEX
Dim_Size           = 26214
X_Domain           = Carbon
Dim_Title          = Carbon13
Dim_Units          = [ppm]
Dimensions         = X
Site               = JNM-ECA600II
Spectrometer       = DELTA2_NMR

Field_Strength     = 14.09636928[T] (600[MHz])
X_Acq_Duration     = 0.69206016[s]
X_Domain           = 13C
X_Freq             = 150.91343039[MHz]
X_Offset           = 100[ppm]
X_Points           = 32768
X_Prescans         = 4
X_Resolution       = 1.44496109[Hz]
X_Sweep            = 47.34848485[kHz]
X_Sweep_Clipped    = 37.87878788[kHz]
Irr_Domain         = Proton
Irr_Freq           = 600.1723046[MHz]
Irr_Offset         = 5[ppm]
Clipped            = FALSE
Scans              = 13578
Total_Scans        = 13578

Relaxation_Delay   = 2[s]
Recvr_Gain         = 50
Temp_Get           = 20.3[dC]
X_90_Width         = 13.6[us]
X_Acq_Time         = 0.69206016[s]
X_Angle            = 30[deg]
X_Atn              = 13.7[dB]
X_Pulse            = 4.53333333[us]
Irr_Atn_Dec        = 19.062[dB]
Irr_Atn_Noe        = 19.062[dB]
Irr_Noise          = WALTZ
Irr_Pwidth         = 0.104[ms]
Decoupling         = TRUE
Initial_Wait       = 1[s]
Noe                = TRUE
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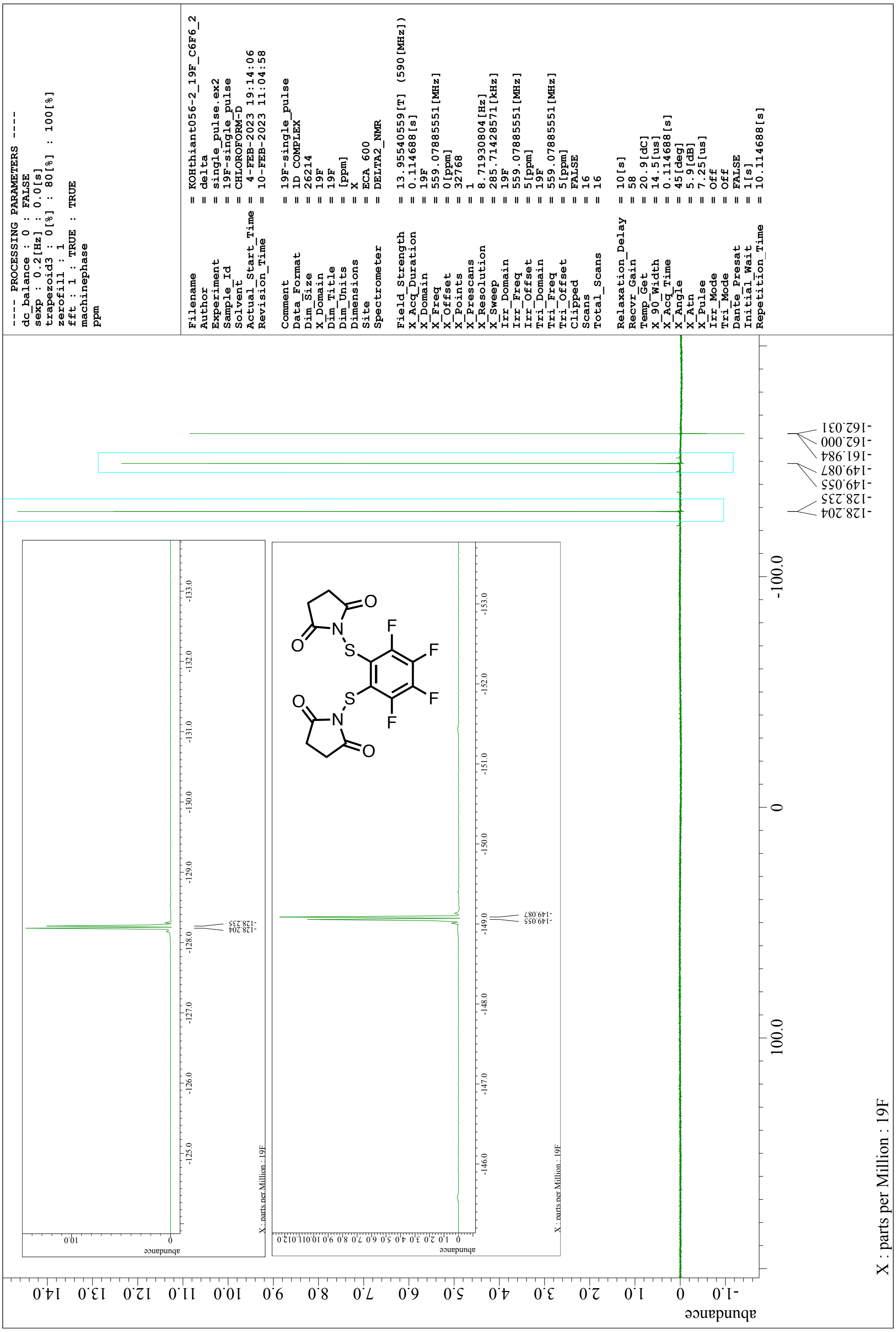
Figure S11. ^{13}C NMR spectra of **2b** (in CDCl$_3$, 150 MHz)



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zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

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Author              = delta
Experiment          = single_pulse.ex2
Sample_Id           = 19F-single_pulse
Solvent             = CHLOROFORM-D
Actual_Start_Time   =  4-FEB-2023 19:14:06
Revision_Time       = 10-FEB-2023 11:04:58

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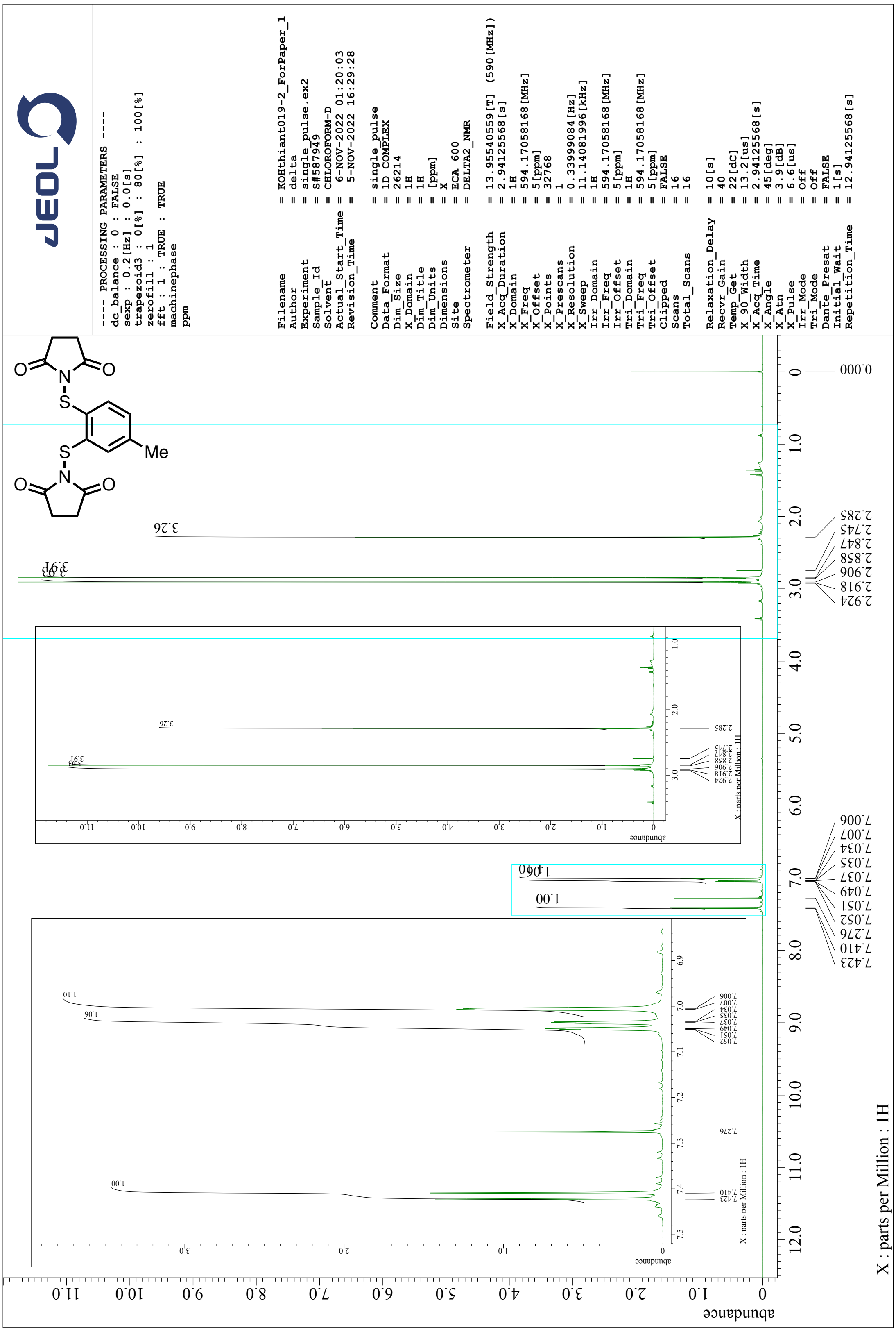
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = 19F
Dim_Title           = 19F
Dim_Units           = [ppm]
Dimensions          = X
Site                = ECA 600
Spectrometer        = DELTA2_NMR

Field_Strength      = 13.95540559[T] (590[MHz])
X_Acq_Duration      = 0.114688[s]
X_Domain            = 19F
X_Freq              = 559.07885551[MHz]
X_Offset            = 0[ppm]
X_Points            = 32768
X_Prescans          = 1
X_Resolution        = 8.71930804[Hz]
X_Sweep             = 285.71428571[kHz]
Irr_Domain          = 19F
Irr_Freq            = 559.07885551[MHz]
Irr_Offset          = 5[ppm]
Tri_Domain          = 19F
Tri_Freq            = 559.07885551[MHz]
Tri_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 16
Total_Scans         = 16

Relaxation_Delay    = 10[s]
Recvr_Gain          = 58
Temp_Get            = 20.9[dC]
X_90_Width          = 14.5[us]
X_Acq_Time          = 0.114688[s]
X_Angle             = 45[deg]
X_Atn               = 5.9[dB]
X_Pulse             = 7.25[us]
Irr_Mode            = Off
Tri_Mode            = Off
Dante_Presat        = FALSE
Initial_Wait        = 1[s]
Repetition_Time     = 10.114688[s]
```

Figure S12. ^{19}F NMR spectra of **2b** (in $CDCl_3$, 560 MHz)



```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

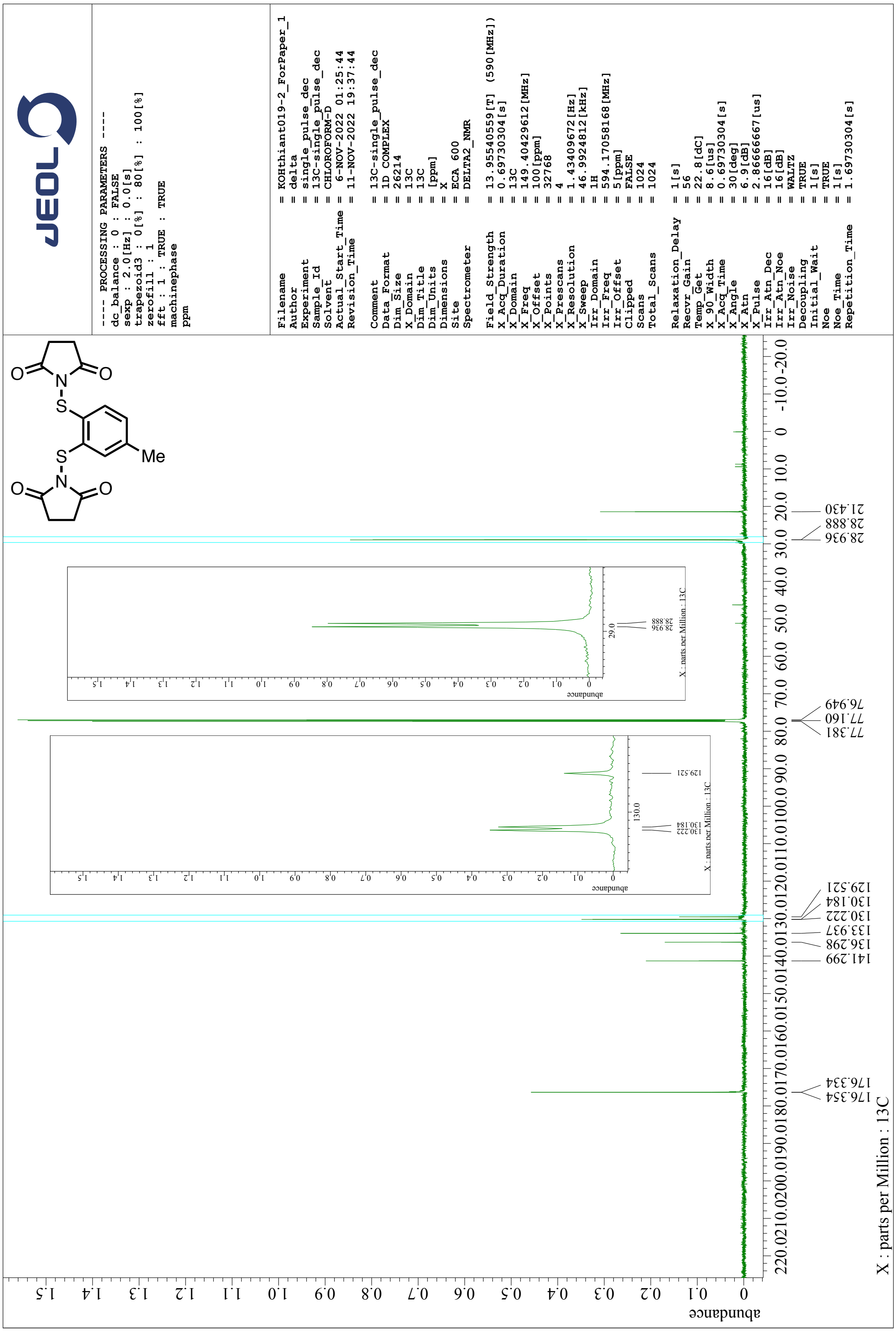
Filename            = KOHthiant019-2_ForPaper_1
Author              = delta
Experiment          = single_pulse.ex2
Sample_Id           = S#587949
Solvent             = CHLOROFORM-D
Actual_Start_Time   =  6-NOV-2022 01:20:03
Revision_Time       =  5-NOV-2022 16:29:28

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = 1H
Dim_Title           = 1H
Dim_Units           = [ppm]
Dimensions          = X
Site                = ECA 600
Spectrometer        = DELTA2_NMR

Field_Strength      = 13.95540559[T]  (590[MHz])
X_Acq_Duration      = 2.94125568[s]
X_Domain            = 1H
X_Freq              = 594.17058168[MHz]
X_Offset            = 5[ppm]
X_Points            = 32768
X_Prescans          = 1
X_Resolution        = 0.33999084[Hz]
X_Sweep             = 11.14081996[kHz]
Irr_Domain          = 1H
Irr_Freq            = 594.17058168[MHz]
Irr_Offset          = 5[ppm]
Tri_Domain          = 1H
Tri_Freq            = 594.17058168[MHz]
Tri_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 16
Total_Scans         = 16

Relaxation_Delay    = 10[s]
Recvr_Gain          = 40
Temp_Get            = 22[dC]
X_90_Width          = 13.2[us]
X_Acq_Time          = 2.94125568[s]
X_Angle             = 45[deg]
X_Atn               = 3.9[dB]
X_Pulse             = 6.6[us]
Irr_Mode            = Off
Tri_Mode            = Off
Dante_Presat        = FALSE
Initial_Wait        = 1[s]
Repetition_Time     = 12.94125568[s]
```

Figure S13. ^{1}H NMR spectra of **2c** (in $CDCl_3$, 600 MHz)



```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
```

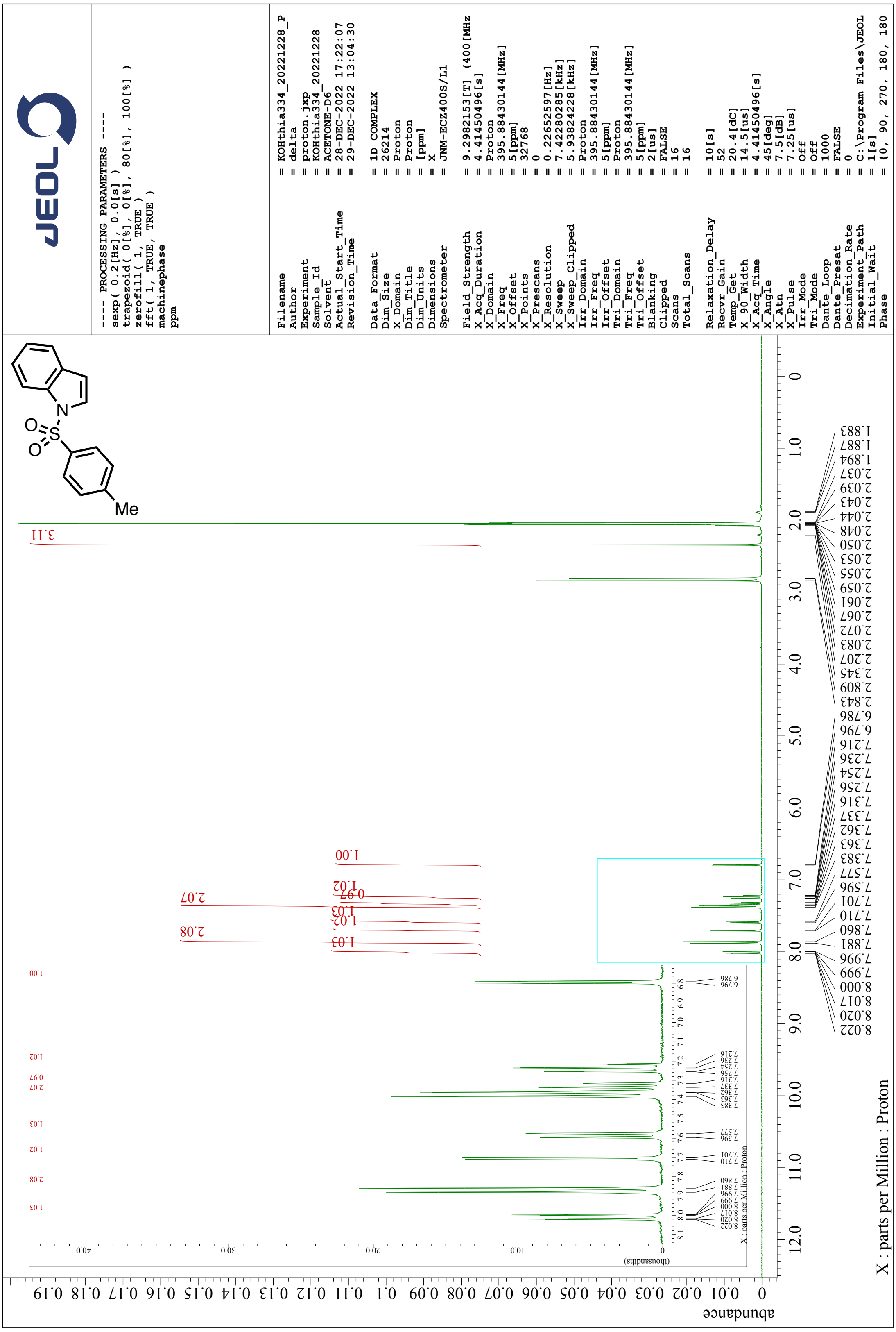
```
Filename              = KOHthiant019-2_ForPaper_1
Author                = delta
Experiment            = single_pulse_dec
Sample_Id             = 13C-single_pulse_dec
Solvent               = CHLOROFORM-D
Actual_Start_Time     =  6-NOV-2022 01:25:44
Revision_Time         = 11-NOV-2022 19:37:44

Comment               = 13C-single_pulse_dec
Data_Format           = 1D COMPLEX
Dim_Size              = 26214
X_Domain              = 13C
Dim_Title             = 13C
Dim_Units             = [ppm]
Dimensions            = X
Site                  = ECA 600
Spectrometer          = DELTA2_NMR

Field_Strength        = 13.95540559[T]  (590[MHz])
X_Acq_Duration        = 0.69730304[s]
X_Domain              = 13C
X_Freq                = 149.40429612[MHz]
X_Offset              = 100[ppm]
X_Points              = 32768
X_Prescans            = 4
X_Resolution          = 1.43409672[Hz]
X_Sweep               = 46.9924812[kHz]
Irr_Domain            = 1H
Irr_Freq              = 594.17058168[MHz]
Irr_Offset            = 5[ppm]
Clipped               = FALSE
Scans                 = 1024
Total_Scans           = 1024

Relaxation_Delay      = 1[s]
Recvr_Gain            = 56
Temp_Get              = 22.8[dC]
X_90_Width            = 8.6[us]
X_Acq_Time            = 0.69730304[s]
X_Angle               = 30[deg]
X_Atn                 = 6.9[dB]
X_Pulse               = 2.86666667[us]
Irr_Atn_Dec           = 16[dB]
Irr_Atn_Noe           = 16[dB]
Irr_Noise             = WALTZ
Decoupling            = TRUE
Initial_Wait          = 1[s]
Noe                   = TRUE
Noe_Time              = 1[s]
Repetition_Time       = 1.69730304[s]
```

Figure S14. ^{13}C NMR spectra of **2c** (in $CDCl_3$, 150 MHz)



```
---- PROCESSING PARAMETERS ----
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1, TRUE )
fft( 1, TRUE, TRUE )
machinephase
ppm

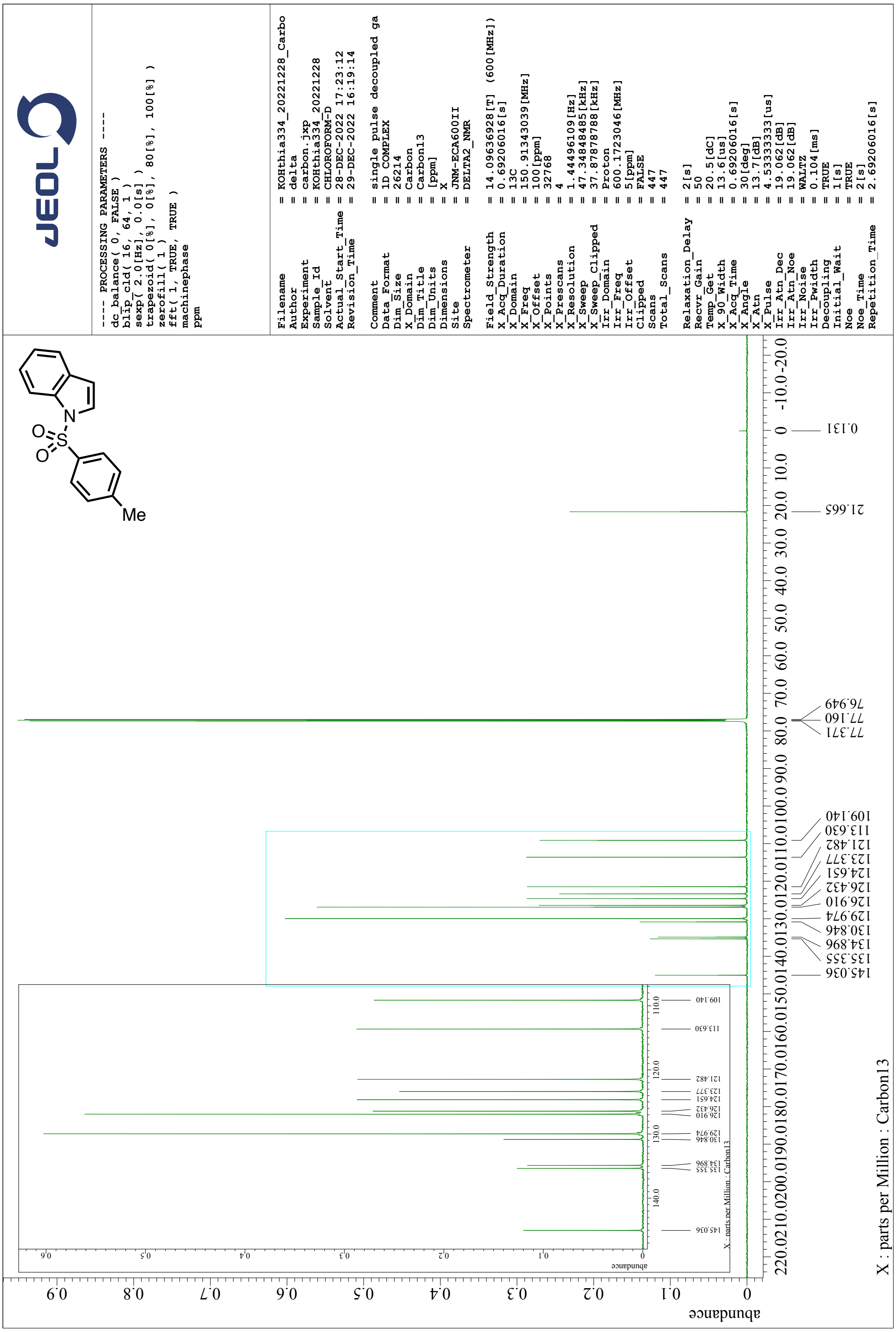
Filename              = KOHthia334_20221228_P
Author                = delta
Experiment            = proton.jxp
Sample_Id             = KOHthia334_20221228
Solvent               = ACETONE-D6
Actual_Start_Time     = 28-DEC-2022 17:22:07
Revision_Time         = 29-DEC-2022 13:04:30

Data_Format           = 1D COMPLEX
Dim_Size              = 26214
X_Domain              = Proton
Dim_Title             = Proton
Dim_Units             = [ppm]
Dimensions            = X
Spectrometer          = JNM-ECZ400S/L1

Field_Strength        = 9.2982153[T] (400[MHz
X_Acq_Duration        = 4.41450496[s]
X_Domain              = Proton
X_Freq                = 395.88430144[MHz]
X_Offset              = 5[ppm]
X_Points              = 32768
X_Prescans            = 0
X_Resolution          = 0.22652597[Hz]
X_Sweep               = 7.42280285[kHz]
X_Sweep_Clipped       = 5.93824228[kHz]
Irr_Domain            = Proton
Irr_Freq              = 395.88430144[MHz]
Irr_Offset            = 5[ppm]
Tri_Domain            = Proton
Tri_Freq              = 395.88430144[MHz]
Tri_Offset            = 5[ppm]
Blanking              = 2[us]
Clipped               = FALSE
Scans                 = 16
Total_Scans           = 16

Relaxation_Delay      = 10[s]
Recvr_Gain            = 52
Temp_Get              = 20.4[dC]
X_90_Width            = 14.5[us]
X_Acq_Time            = 4.41450496[s]
X_Angle               = 45[deg]
X_Atn                 = 7.5[dB]
X_Pulse               = 7.25[us]
Irr_Mode              = Off
Tri_Mode              = Off
Dante_Loop            = 1000
Dante_Presat          = FALSE
Decimation_Rate       = 0
Experiment_Path       = C:\Program Files\JEOL
Initial_Wait          = 1[s]
Phase                 = [0, 90, 270, 180, 180
```

Figure S15. ^{1}H NMR spectra of **1h** (in acetone-d^6, 400 MHz)



```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
blip_cld( 16, 64, 1 )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

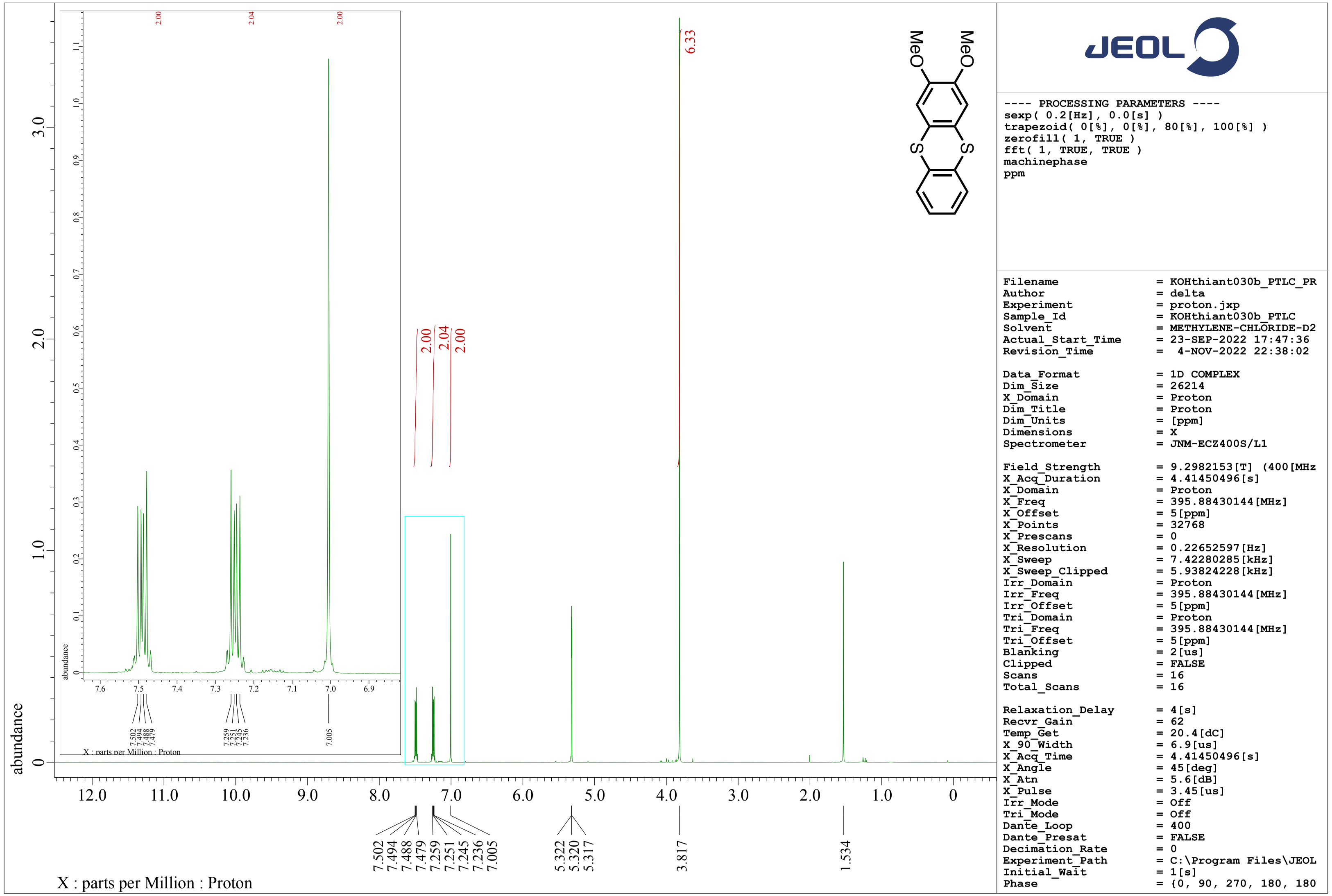
Filename          = KOHthia334_20221228_Carbo
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = KOHthia334_20221228
Solvent           = CHLOROFORM-D
Actual_Start_Time = 28-DEC-2022 17:23:12
Revision_Time     = 29-DEC-2022 16:19:14

Comment           = single pulse decoupled ga
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
X_Domain          = Carbon
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECA600II
Spectrometer      = DELTA2_NMR

Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 0.69206016[s]
X_Domain          = 13C
X_Freq            = 150.91343039[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.44496109[Hz]
X_Sweep           = 47.34848485[kHz]
X_Sweep_Clipped   = 37.87878788[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 447
Total_Scans       = 447

Relaxation_Delay  = 2[s]
Recvr_Gain        = 50
Temp_Get          = 20.5[dC]
X_90_Width        = 13.6[us]
X_Acq_Time        = 0.69206016[s]
X_Angle           = 30[deg]
X_Atn             = 13.7[dB]
X_Pulse           = 4.53333333[us]
Irr_Atn_Dec       = 19.062[dB]
Irr_Atn_Noe       = 19.062[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 0.104[ms]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.69206016[s]
```

Figure S16. ^{13}C NMR spectra of **1h** (in $CDCl_3$, 150 MHz)



```
---- PROCESSING PARAMETERS ----
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1, TRUE )
fft( 1, TRUE, TRUE )
machinephase
ppm

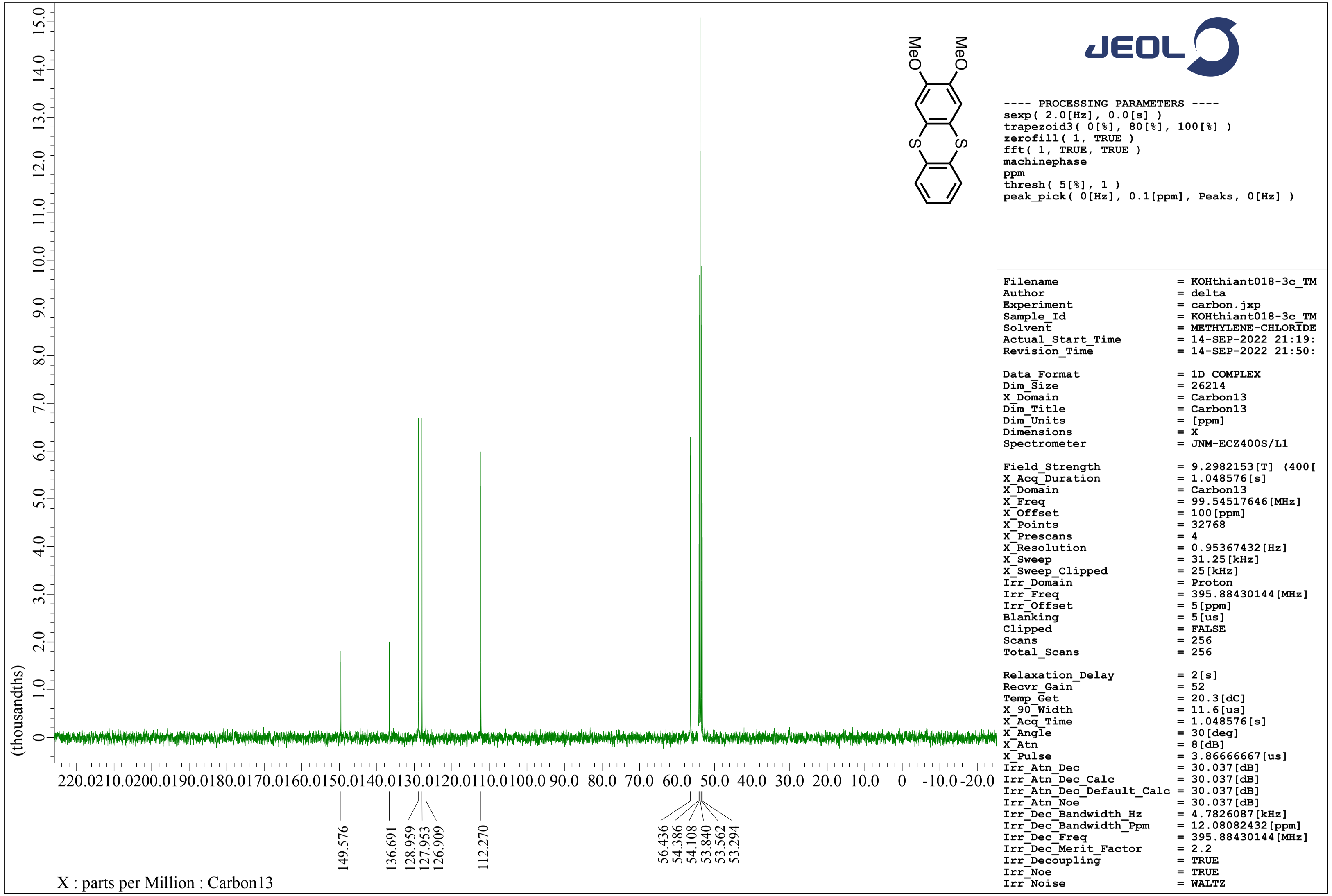
Filename                = KOHthiant030b_PTLC_PR
Author                  = delta
Experiment              = proton.jxp
Sample_Id               = KOHthiant030b_PTLC
Solvent                 = METHYLENE-CHLORIDE-D2
Actual_Start_Time       = 23-SEP-2022 17:47:36
Revision_Time           =  4-NOV-2022 22:38:02

Data_Format             = 1D COMPLEX
Dim_Size                = 26214
X_Domain                = Proton
Dim_Title               = Proton
Dim_Units               = [ppm]
Dimensions              = X
Spectrometer            = JNM-ECZ400S/L1

Field_Strength          = 9.2982153[T] (400[MHz
X_Acq_Duration          = 4.41450496[s]
X_Domain                = Proton
X_Freq                  = 395.88430144[MHz]
X_Offset                = 5[ppm]
X_Points                = 32768
X_Prescans              = 0
X_Resolution            = 0.22652597[Hz]
X_Sweep                 = 7.42280285[kHz]
X_Sweep_Clipped         = 5.93824228[kHz]
Irr_Domain              = Proton
Irr_Freq                = 395.88430144[MHz]
Irr_Offset              = 5[ppm]
Tri_Domain              = Proton
Tri_Freq                = 395.88430144[MHz]
Tri_Offset              = 5[ppm]
Blanking                = 2[us]
Clipped                 = FALSE
Scans                   = 16
Total_Scans             = 16

Relaxation_Delay        = 4[s]
Recvr_Gain              = 62
Temp_Get                = 20.4[dC]
X_90_Width              = 6.9[us]
X_Acq_Time              = 4.41450496[s]
X_Angle                 = 45[deg]
X_Atn                   = 5.6[dB]
X_Pulse                 = 3.45[us]
Irr_Mode                = Off
Tri_Mode                = Off
Dante_Loop              = 400
Dante_Presat            = FALSE
Decimation_Rate         = 0
Experiment_Path         = C:\Program Files\JEOL
Initial_Wait            = 1[s]
Phase                   = {0, 90, 270, 180, 180
```

Figure S17. ^{1}H NMR spectra of **3aa** (in CD_2Cl_2, 400 MHz)



```
---- PROCESSING PARAMETERS ----
sexp( 2.0[Hz], 0.0[s] )
trapezoid3( 0[%], 80[%], 100[%] )
zerofill( 1, TRUE )
fft( 1, TRUE, TRUE )
machinephase
ppm
thresh( 5[%], 1 )
peak_pick( 0[Hz], 0.1[ppm], Peaks, 0[Hz] )
```

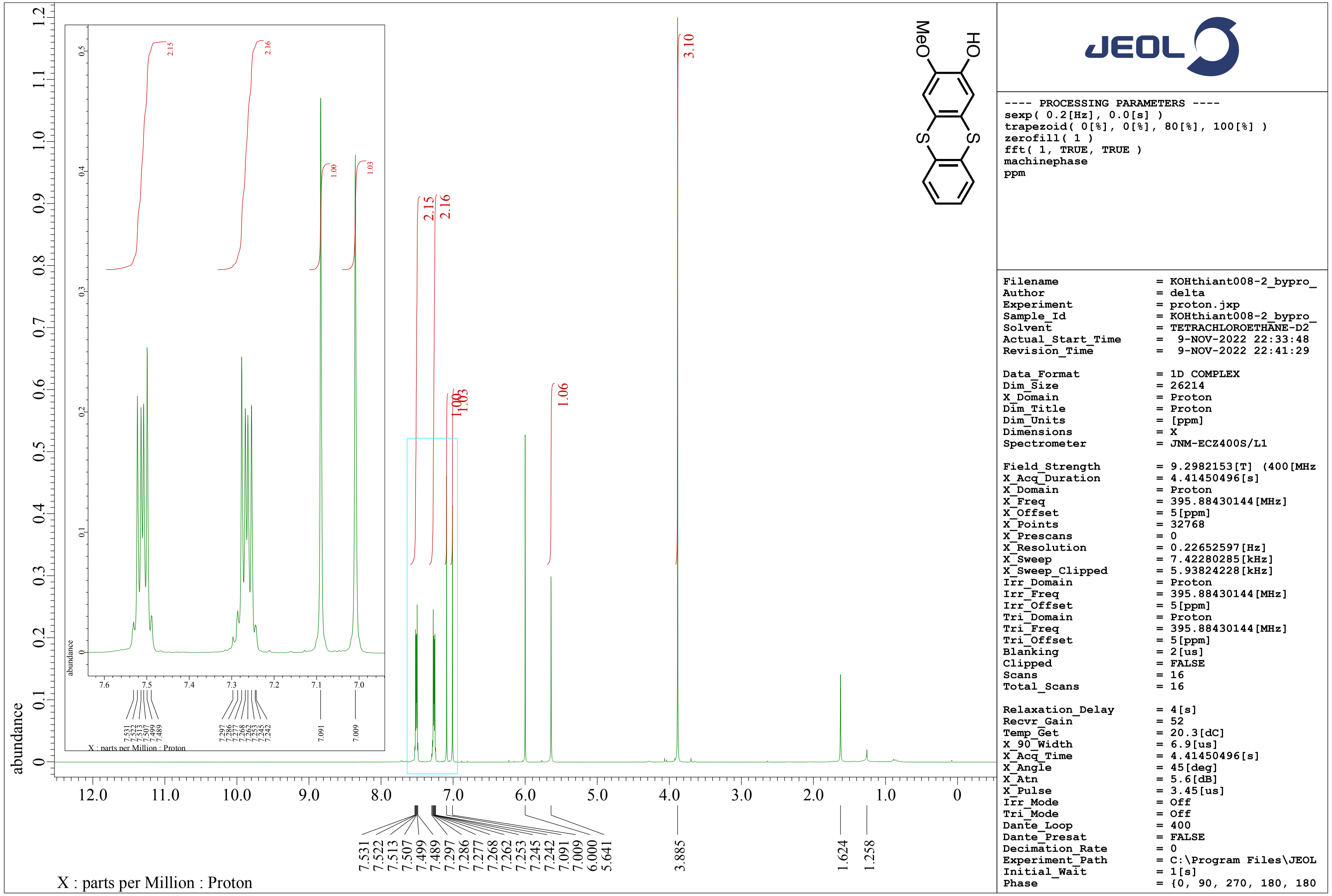
```
Filename                    = KOHthiant018-3c_TM
Author                      = delta
Experiment                  = carbon.jxp
Sample_Id                   = KOHthiant018-3c_TM
Solvent                     = METHYLENE-CHLORIDE
Actual_Start_Time           = 14-SEP-2022 21:19:
Revision_Time               = 14-SEP-2022 21:50:

Data_Format                 = 1D COMPLEX
Dim_Size                    = 26214
X_Domain                    = Carbon13
Dim_Title                   = Carbon13
Dim_Units                   = [ppm]
Dimensions                  = X
Spectrometer                = JNM-ECZ400S/L1

Field_Strength              = 9.2982153[T] (400[
X_Acq_Duration              = 1.048576[s]
X_Domain                    = Carbon13
X_Freq                      = 99.54517646[MHz]
X_Offset                    = 100[ppm]
X_Points                    = 32768
X_Prescans                  = 4
X_Resolution                = 0.95367432[Hz]
X_Sweep                     = 31.25[kHz]
X_Sweep_Clipped             = 25[kHz]
Irr_Domain                  = Proton
Irr_Freq                    = 395.88430144[MHz]
Irr_Offset                  = 5[ppm]
Blanking                    = 5[us]
Clipped                     = FALSE
Scans                       = 256
Total_Scans                 = 256

Relaxation_Delay            = 2[s]
Recvr_Gain                  = 52
Temp_Get                    = 20.3[dC]
X_90_Width                  = 11.6[us]
X_Acq_Time                  = 1.048576[s]
X_Angle                     = 30[deg]
X_Atn                       = 8[dB]
X_Pulse                     = 3.86666667[us]
Irr_Atn_Dec                 = 30.037[dB]
Irr_Atn_Dec_Calc            = 30.037[dB]
Irr_Atn_Dec_Default_Calc    = 30.037[dB]
Irr_Atn_Noe                 = 30.037[dB]
Irr_Dec_Bandwidth_Hz        = 4.7826087[kHz]
Irr_Dec_Bandwidth_Ppm       = 12.08082432[ppm]
Irr_Dec_Freq                = 395.88430144[MHz]
Irr_Dec_Merit_Factor        = 2.2
Irr_Decoupling              = TRUE
Irr_Noe                     = TRUE
Irr_Noise                   = WALTZ
```

Figure S18. ^{13}C NMR spectra of **3aa** (in $CDCl_3$, 100 MHz)



```
---- PROCESSING PARAMETERS ----
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

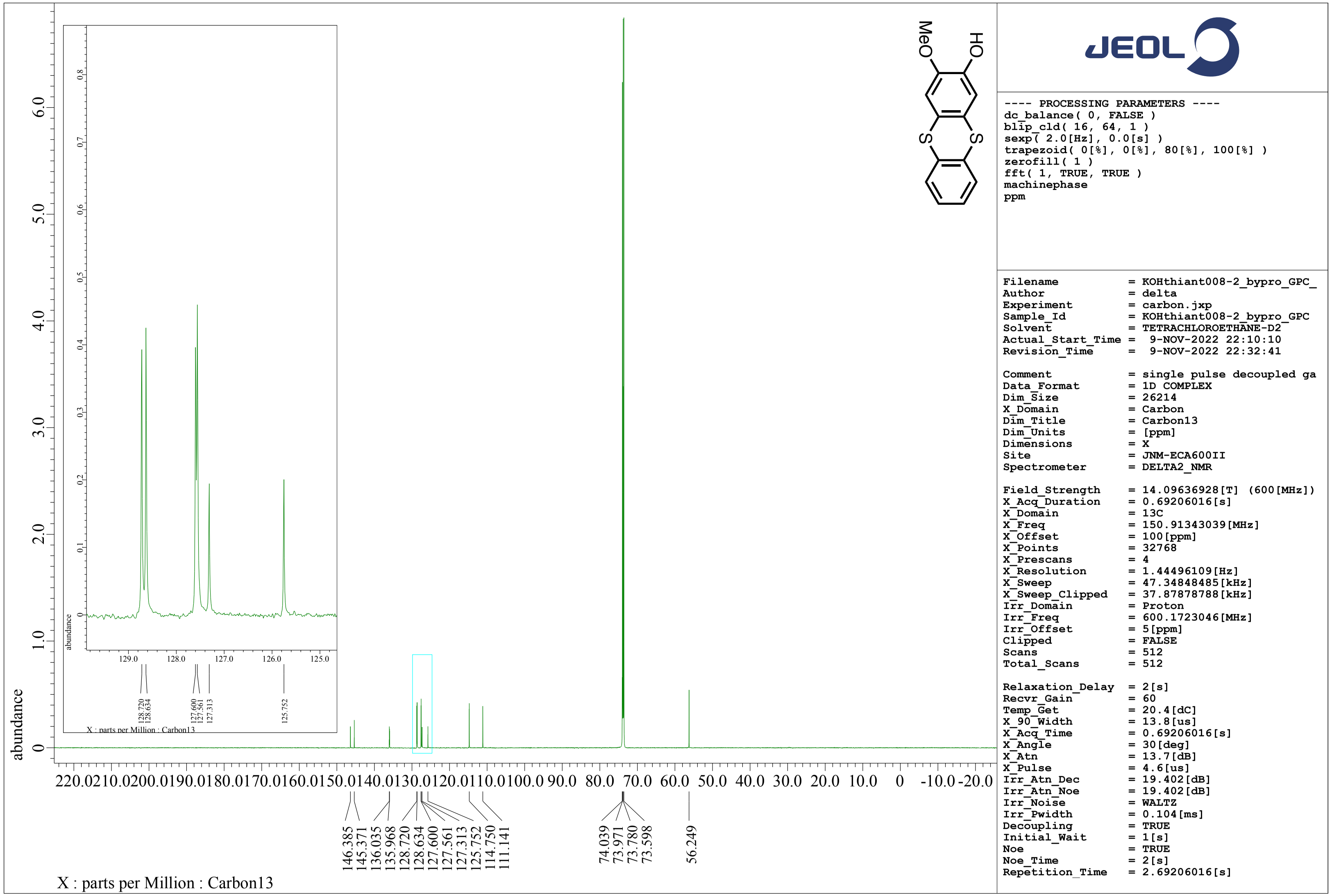
```
Filename               = KOHthiant008-2_bypro_
Author                 = delta
Experiment             = proton.jxp
Sample_Id              = KOHthiant008-2_bypro_
Solvent                = TETRACHLOROETHANE-D2
Actual_Start_Time      =  9-NOV-2022 22:33:48
Revision_Time          =  9-NOV-2022 22:41:29

Data_Format            = 1D COMPLEX
Dim_Size               = 26214
X_Domain               = Proton
Dim_Title              = Proton
Dim_Units              = [ppm]
Dimensions             = X
Spectrometer           = JNM-ECZ400S/L1

Field_Strength         = 9.2982153[T] (400[MHz
X_Acq_Duration         = 4.41450496[s]
X_Domain               = Proton
X_Freq                 = 395.88430144[MHz]
X_Offset               = 5[ppm]
X_Points               = 32768
X_Prescans             = 0
X_Resolution           = 0.22652597[Hz]
X_Sweep                = 7.42280285[kHz]
X_Sweep_Clipped        = 5.93824228[kHz]
Irr_Domain             = Proton
Irr_Freq               = 395.88430144[MHz]
Irr_Offset             = 5[ppm]
Tri_Domain             = Proton
Tri_Freq               = 395.88430144[MHz]
Tri_Offset             = 5[ppm]
Blanking               = 2[us]
Clipped                = FALSE
Scans                  = 16
Total_Scans            = 16

Relaxation_Delay       = 4[s]
Recvr_Gain             = 52
Temp_Get               = 20.3[dC]
X_90_Width             = 6.9[us]
X_Acq_Time             = 4.41450496[s]
X_Angle                = 45[deg]
X_Atn                  = 5.6[dB]
X_Pulse                = 3.45[us]
Irr_Mode               = Off
Tri_Mode               = Off
Dante_Loop             = 400
Dante_Presat           = FALSE
Decimation_Rate        = 0
Experiment_Path        = C:\Program Files\JEOL
Initial_Wait           = 1[s]
Phase                  = {0, 90, 270, 180, 180
```

Figure S19. ^{1}H NMR spectra of **4** (in $Cl_2CDCDCl_2$, 400 MHz)



```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
blip_cld( 16, 64, 1 )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

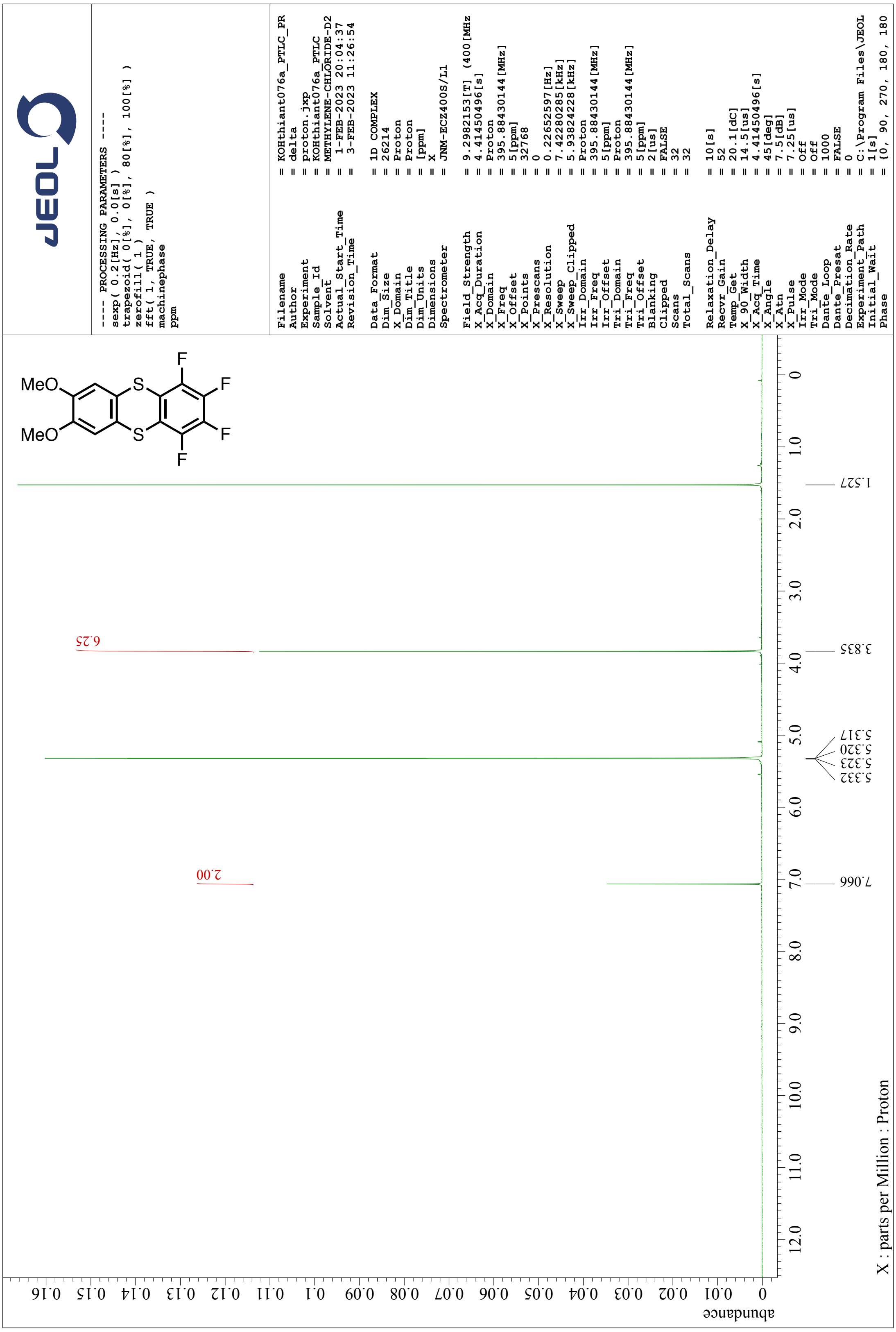
```
Filename            = KOHthiant008-2_bypro_GPC_
Author              = delta
Experiment          = carbon.jxp
Sample_Id           = KOHthiant008-2_bypro_GPC
Solvent             = TETRACHLOROETHANE-D2
Actual_Start_Time =   9-NOV-2022 22:10:10
Revision_Time     =   9-NOV-2022 22:32:41

Comment             = single pulse decoupled ga
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = Carbon
Dim_Title           = Carbon13
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECA600II
Spectrometer        = DELTA2_NMR

Field_Strength      = 14.09636928[T] (600[MHz])
X_Acq_Duration      = 0.69206016[s]
X_Domain            = 13C
X_Freq              = 150.91343039[MHz]
X_Offset            = 100[ppm]
X_Points            = 32768
X_Prescans          = 4
X_Resolution        = 1.44496109[Hz]
X_Sweep             = 47.34848485[kHz]
X_Sweep_Clipped     = 37.87878788[kHz]
Irr_Domain          = Proton
Irr_Freq            = 600.1723046[MHz]
Irr_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 512
Total_Scans         = 512

Relaxation_Delay    = 2[s]
Recvr_Gain          = 60
Temp_Get            = 20.4[dC]
X_90_Width          = 13.8[us]
X_Acq_Time          = 0.69206016[s]
X_Angle             = 30[deg]
X_Atn               = 13.7[dB]
X_Pulse             = 4.6[us]
Irr_Atn_Dec         = 19.402[dB]
Irr_Atn_Noe         = 19.402[dB]
Irr_Noise           = WALTZ
Irr_Pwidth          = 0.104[ms]
Decoupling          = TRUE
Initial_Wait        = 1[s]
Noe                 = TRUE
Noe_Time            = 2[s]
Repetition_Time     = 2.69206016[s]
```

Figure S20. ^{13}C NMR spectra of **4** (in $Cl_2CDCDCl_2$, 150 MHz)



```
---- PROCESSING PARAMETERS ----
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

```
Filename                = KOHthiant076a_PTLC_PR
Author                  = delta
Experiment              = proton.jxp
Sample_Id               = KOHthiant076a_PTLC
Solvent                 = METHYLENE-CHLORIDE-D2
Actual_Start_Time       =  1-FEB-2023 20:04:37
Revision_Time           =  3-FEB-2023 11:26:54

Data_Format             = 1D COMPLEX
Dim_Size                = 26214
X_Domain                = Proton
Dim_Title               = Proton
Dim_Units               = [ppm]
Dimensions              = X
Spectrometer            = JNM-ECZ400S/L1

Field_Strength          = 9.2982153[T] (400[MHz
X_Acq_Duration          = 4.41450496[s]
X_Domain                = Proton
X_Freq                  = 395.88430144[MHz]
X_Offset                = 5[ppm]
X_Points                = 32768
X_Prescans              = 0
X_Resolution            = 0.22652597[Hz]
X_Sweep                 = 7.42280285[kHz]
X_Sweep_Clipped         = 5.93824228[kHz]
Irr_Domain              = Proton
Irr_Freq                = 395.88430144[MHz]
Irr_Offset              = 5[ppm]
Tri_Domain              = Proton
Tri_Freq                = 395.88430144[MHz]
Tri_Offset              = 5[ppm]
Blanking                = 2[us]
Clipped                 = FALSE
Scans                   = 32
Total_Scans             = 32

Relaxation_Delay        = 10[s]
Recvr_Gain              = 52
Temp_Get                = 20.1[dC]
X_90_Width              = 14.5[us]
X_Acq_Time              = 4.41450496[s]
X_Angle                 = 45[deg]
X_Atn                   = 7.5[dB]
X_Pulse                 = 7.25[us]
Irr_Mode                = Off
Tri_Mode                = Off
Dante_Loop              = 1000
Dante_Presat            = FALSE
Decimation_Rate         = 0
Experiment_Path         = C:\Program Files\JEOL
Initial_Wait            = 1[s]
Phase                   = {0, 90, 270, 180, 180
```

Figure S21. ^{1}H NMR spectra of **3ab** (in CD_2Cl_2, 400 MHz)

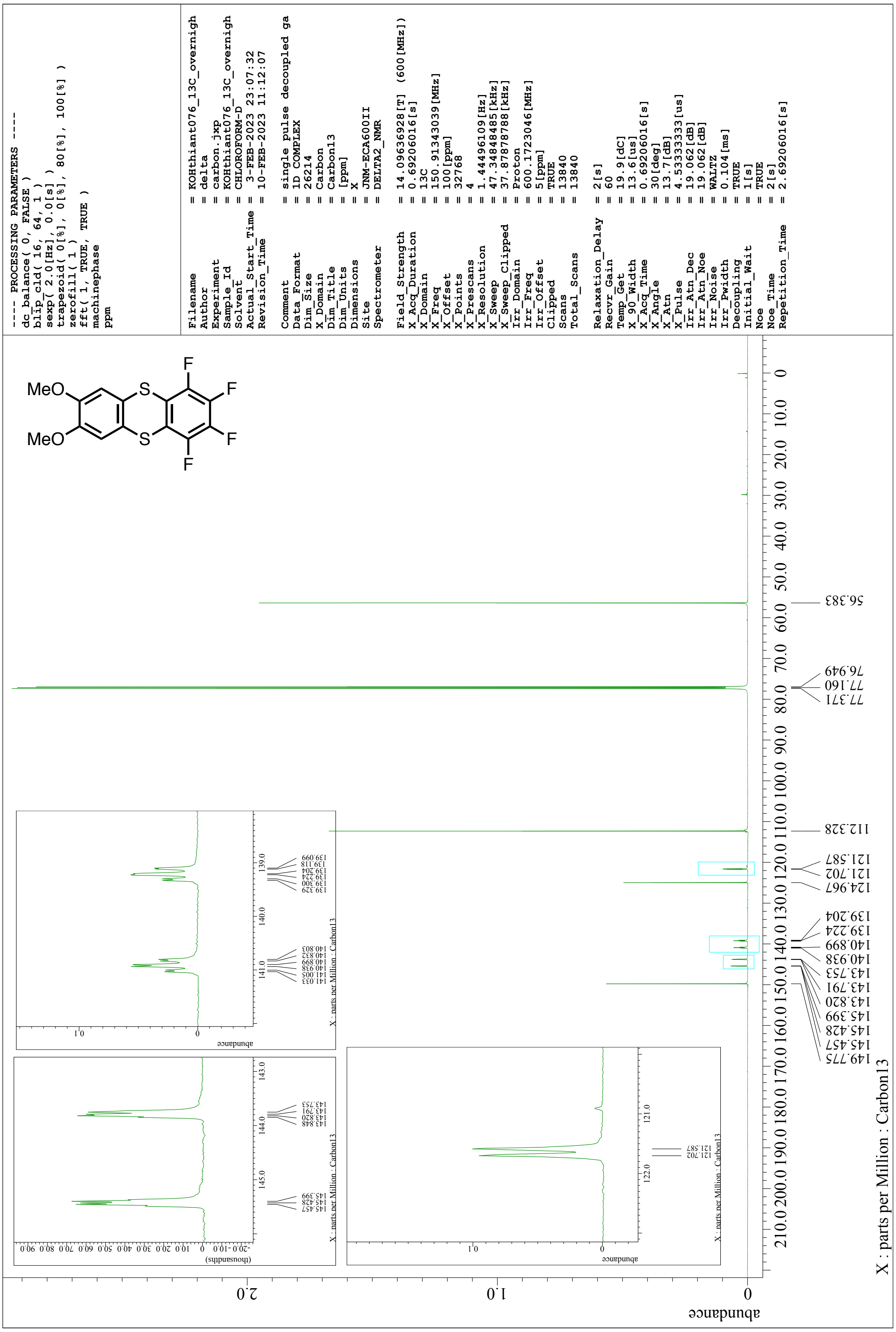
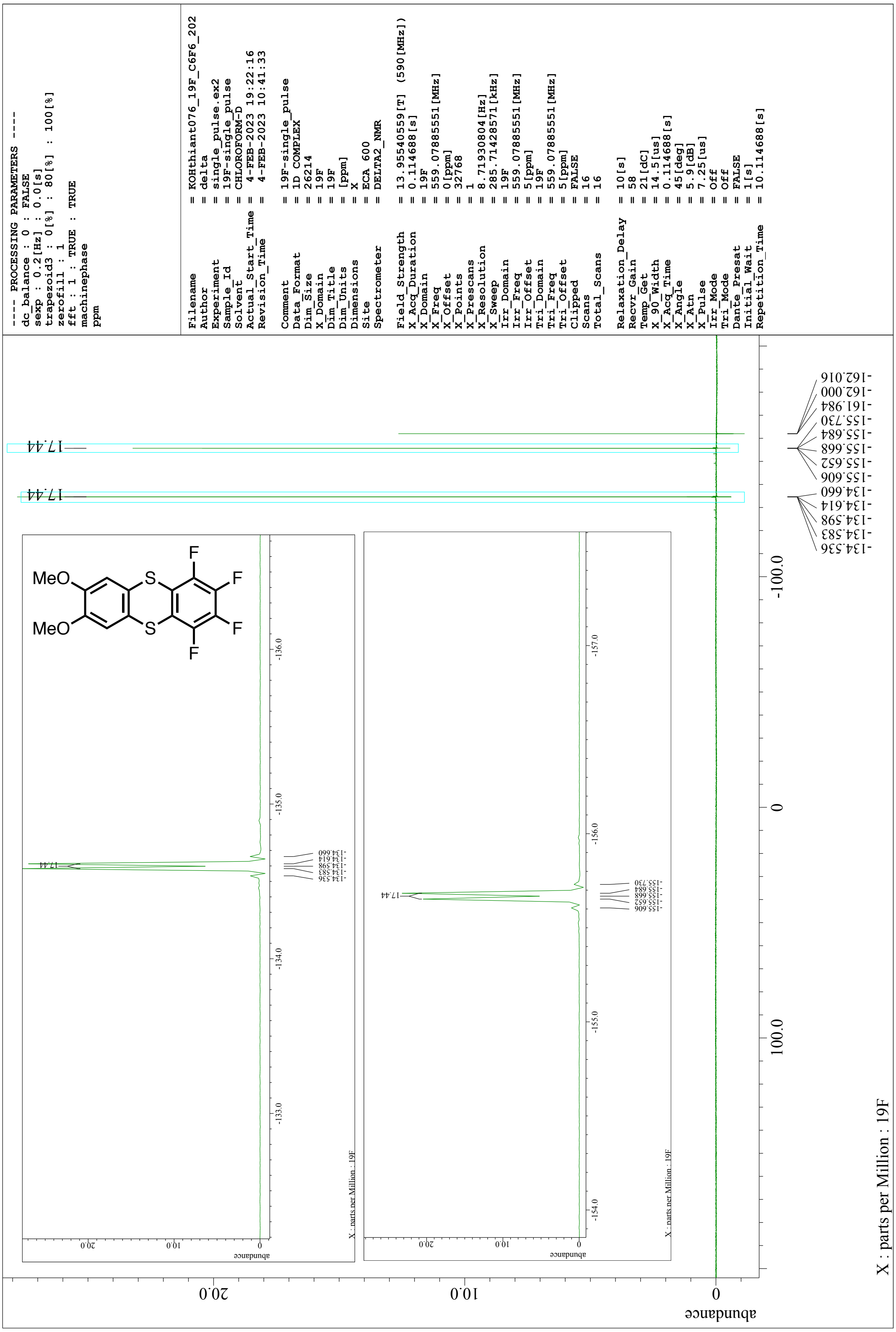


Figure S22. ^{13}C NMR spectra of **3ab** (in CDCl$_3$, 150 MHz)



```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

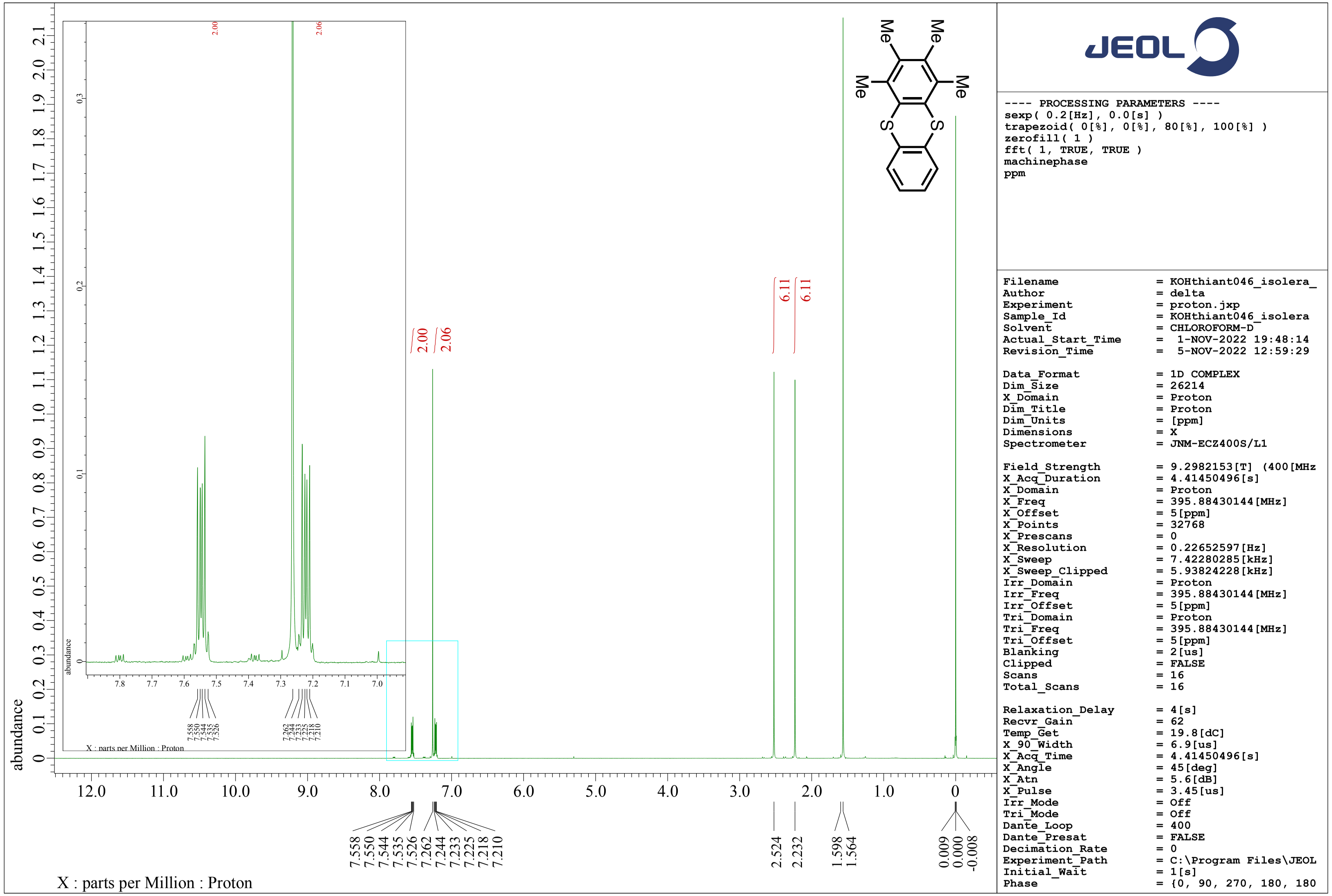
Filename            = KOHthiant076_19F_C6F6_202
Author              = delta
Experiment          = single_pulse.ex2
Sample_Id           = 19F-single_pulse
Solvent             = CHLOROFORM-D
Actual_Start_Time   =  4-FEB-2023 19:22:16
Revision_Time       =  4-FEB-2023 10:41:33

Comment             = 19F-single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = 19F
Dim_Title           = 19F
Dim_Units           = [ppm]
Dimensions          = X
Site                = ECA 600
Spectrometer        = DELTA2_NMR

Field_Strength      = 13.95540559[T] (590[MHz])
X_Acq_Duration      = 0.114688[s]
X_Domain            = 19F
X_Freq              = 559.07885551[MHz]
X_Offset            = 0[ppm]
X_Points            = 32768
X_Prescans          = 1
X_Resolution        = 8.71930804[Hz]
X_Sweep             = 285.71428571[kHz]
Irr_Domain          = 19F
Irr_Freq            = 559.07885551[MHz]
Irr_Offset          = 5[ppm]
Tri_Domain          = 19F
Tri_Freq            = 559.07885551[MHz]
Tri_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 16
Total_Scans         = 16

Relaxation_Delay    = 10[s]
Recvr_Gain          = 58
Temp_Get            = 21[dC]
X_90_Width          = 14.5[us]
X_Acq_Time          = 0.114688[s]
X_Angle             = 45[deg]
X_Atn               = 5.9[dB]
X_Pulse             = 7.25[us]
Irr_Mode            = Off
Tri_Mode            = Off
Dante_Presat        = FALSE
Initial_Wait        = 1[s]
Repetition_Time     = 10.114688[s]
```

Figure S23. ^{19}F NMR spectra of **3ab** (in CDCl$_3$, 560 MHz)



```
---- PROCESSING PARAMETERS ----
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

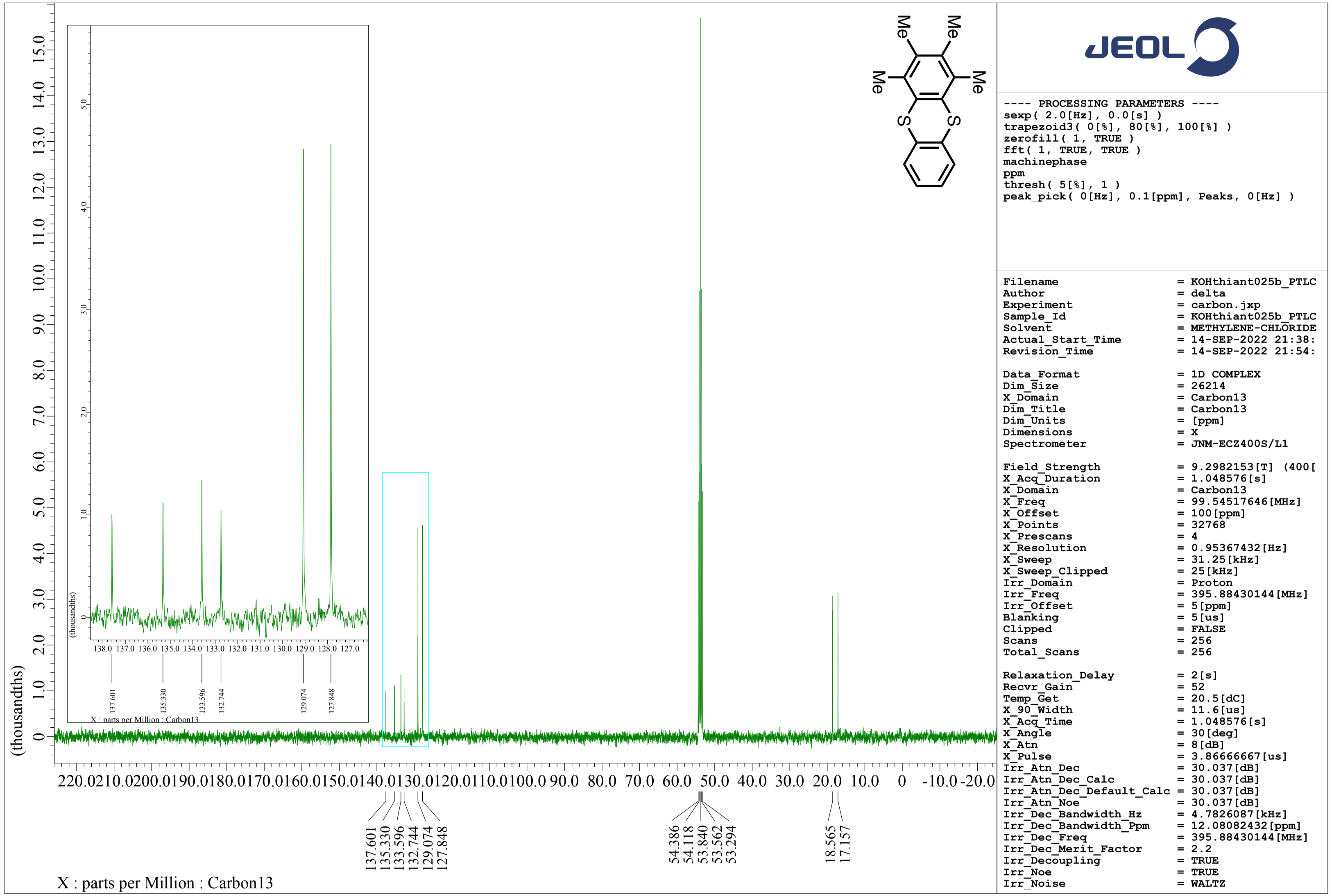
Filename               = KOHthiant046_isolera_
Author                 = delta
Experiment             = proton.jxp
Sample_Id              = KOHthiant046_isolera
Solvent                = CHLOROFORM-D
Actual_Start_Time      =  1-NOV-2022 19:48:14
Revision_Time          =  5-NOV-2022 12:59:29

Data_Format            = 1D COMPLEX
Dim_Size               = 26214
X_Domain               = Proton
Dim_Title              = Proton
Dim_Units              = [ppm]
Dimensions             = X
Spectrometer           = JNM-ECZ400S/L1

Field_Strength         = 9.2982153[T] (400[MHz
X_Acq_Duration         = 4.41450496[s]
X_Domain               = Proton
X_Freq                 = 395.88430144[MHz]
X_Offset               = 5[ppm]
X_Points               = 32768
X_Prescans             = 0
X_Resolution           = 0.22652597[Hz]
X_Sweep                = 7.42280285[kHz]
X_Sweep_Clipped        = 5.93824228[kHz]
Irr_Domain             = Proton
Irr_Freq               = 395.88430144[MHz]
Irr_Offset             = 5[ppm]
Tri_Domain             = Proton
Tri_Freq               = 395.88430144[MHz]
Tri_Offset             = 5[ppm]
Blanking               = 2[us]
Clipped                = FALSE
Scans                  = 16
Total_Scans            = 16

Relaxation_Delay       = 4[s]
Recvr_Gain             = 62
Temp_Get               = 19.8[dC]
X_90_Width             = 6.9[us]
X_Acq_Time             = 4.41450496[s]
X_Angle                = 45[deg]
X_Atn                  = 5.6[dB]
X_Pulse                = 3.45[us]
Irr_Mode               = Off
Tri_Mode               = Off
Dante_Loop             = 400
Dante_Presat           = FALSE
Decimation_Rate        = 0
Experiment_Path        = C:\Program Files\JEOL
Initial_Wait           = 1[s]
Phase                  = {0, 90, 270, 180, 180
```

Figure S24. ^{1}H NMR spectra of **3ba** (in $CDCl_3$, 400 MHz)



```
---- PROCESSING PARAMETERS ----
sexp( 2.0[Hz], 0.0[s] )
trapezoid3( 0[%], 80[%], 100[%] )
zerofill( 1, TRUE )
fft( 1, TRUE, TRUE )
machinephase
ppm
thresh( 5[%], 1 )
peak_pick( 0[Hz], 0.1[ppm], Peaks, 0[Hz] )
```

```
Filename                    = KOHthiant025b_PTLC
Author                      = delta
Experiment                  = carbon.jxp
Sample_Id                   = KOHthiant025b_PTLC
Solvent                     = METHYLENE-CHLORIDE
Actual_Start_Time           = 14-SEP-2022 21:38:
Revision_Time               = 14-SEP-2022 21:54:

Data_Format                 = 1D COMPLEX
Dim_Size                    = 26214
X_Domain                    = Carbon13
Dim_Title                   = Carbon13
Dim_Units                   = [ppm]
Dimensions                  = X
Spectrometer                = JNM-ECZ400S/L1

Field_Strength              = 9.2982153[T] (400[
X_Acq_Duration              = 1.048576[s]
X_Domain                    = Carbon13
X_Freq                      = 99.54517646[MHz]
X_Offset                    = 100[ppm]
X_Points                    = 32768
X_Prescans                  = 4
X_Resolution                = 0.95367432[Hz]
X_Sweep                     = 31.25[kHz]
X_Sweep_Clipped             = 25[kHz]
Irr_Domain                  = Proton
Irr_Freq                    = 395.88430144[MHz]
Irr_Offset                  = 5[ppm]
Blanking                    = 5[us]
Clipped                     = FALSE
Scans                       = 256
Total_Scans                 = 256

Relaxation_Delay            = 2[s]
Recvr_Gain                  = 52
Temp_Get                    = 20.5[dC]
X_90_Width                  = 11.6[us]
X_Acq_Time                  = 1.048576[s]
X_Angle                     = 30[deg]
X_Atn                       = 8[dB]
X_Pulse                     = 3.86666667[us]
Irr_Atn_Dec                 = 30.037[dB]
Irr_Atn_Dec_Calc            = 30.037[dB]
Irr_Atn_Dec_Default_Calc    = 30.037[dB]
Irr_Atn_Noe                 = 30.037[dB]
Irr_Dec_Bandwidth_Hz        = 4.7826087[kHz]
Irr_Dec_Bandwidth_Ppm       = 12.08082432[ppm]
Irr_Dec_Freq                = 395.88430144[MHz]
Irr_Dec_Merit_Factor        = 2.2
Irr_Decoupling              = TRUE
Irr_Noe                     = TRUE
Irr_Noise                   = WALTZ
```

Figure S25. ^{13}C NMR spectra of **3ba** (in CD_2Cl_2, 100 MHz)

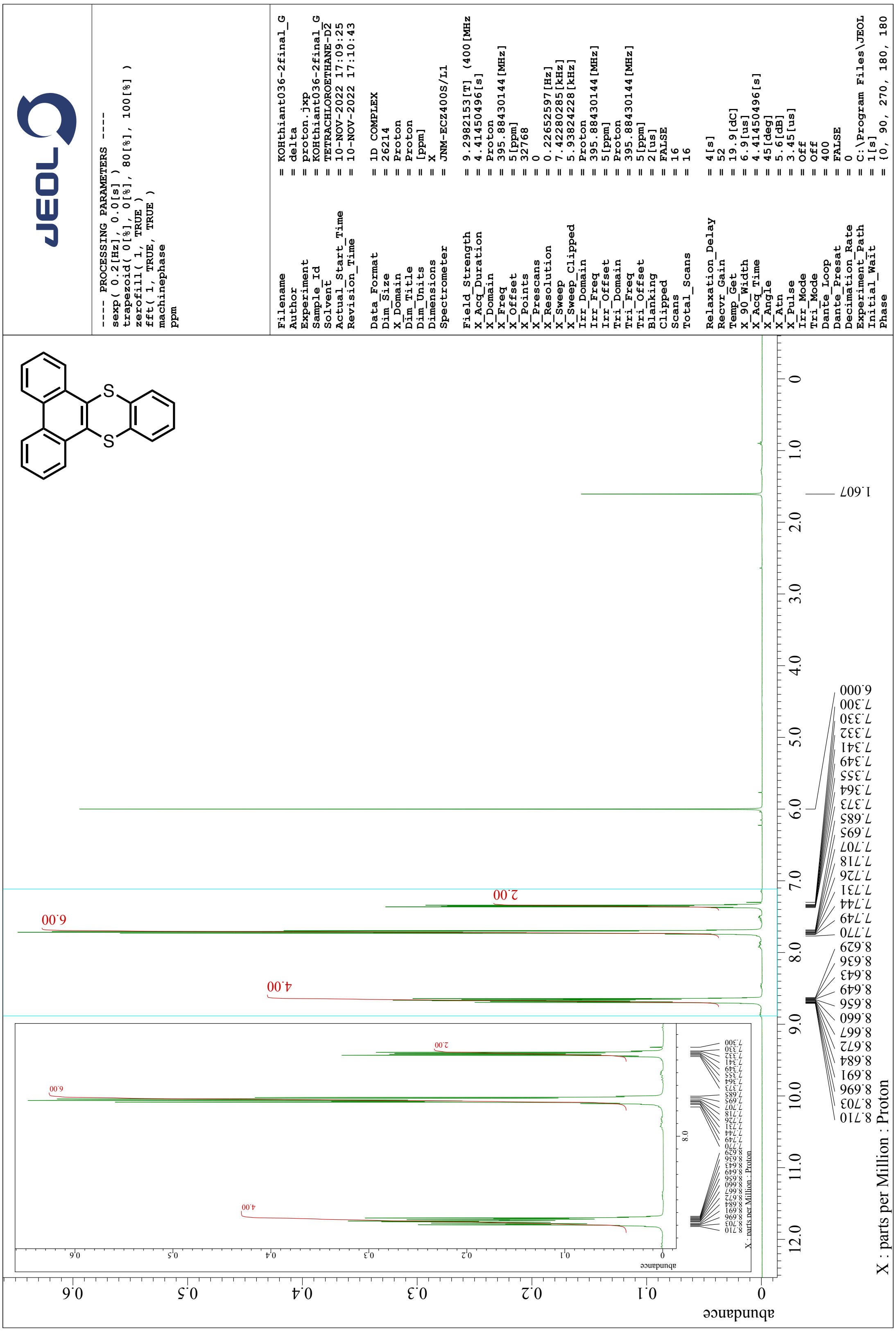
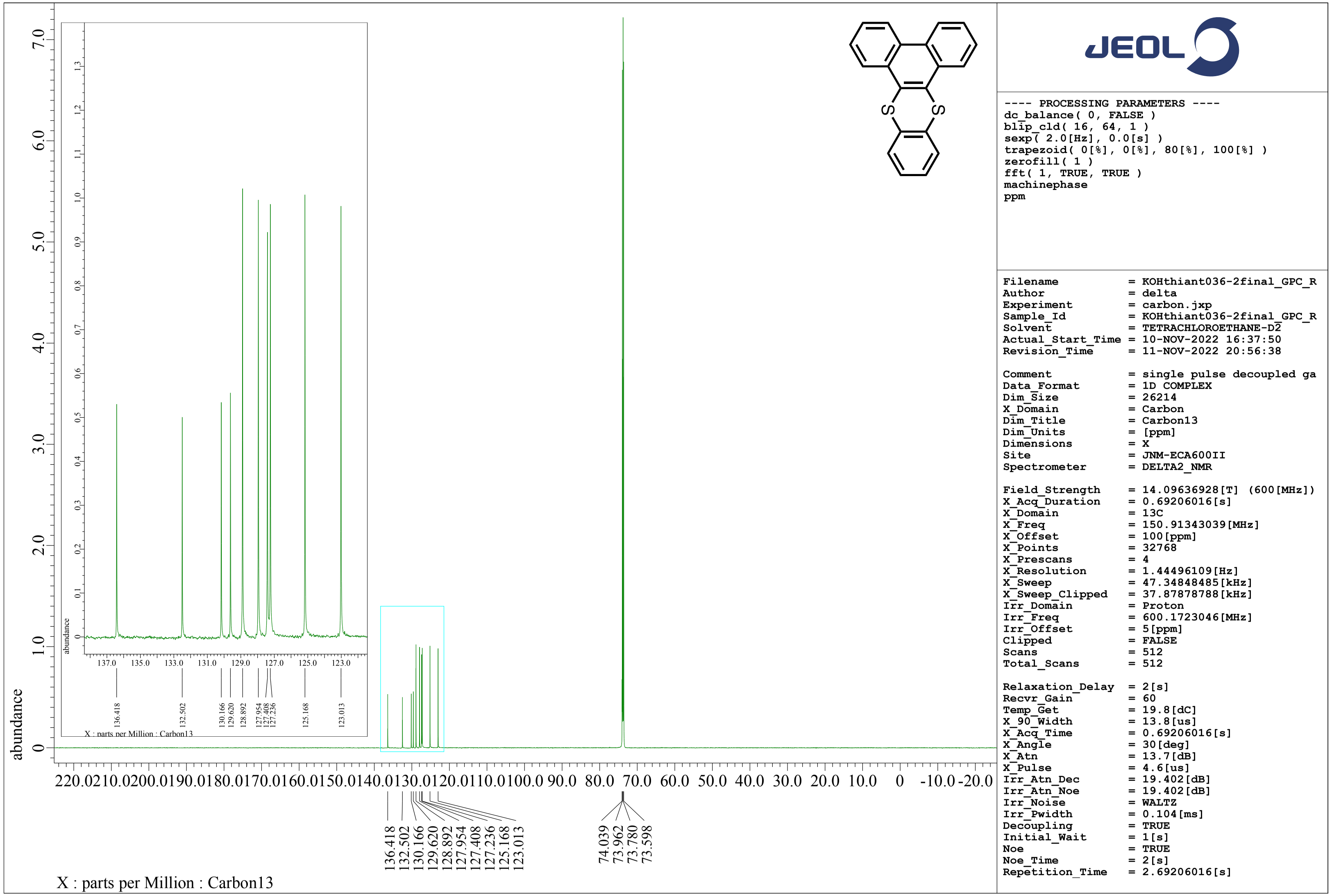


Figure S26. ^{1}H NMR spectra of **3ca** (in $Cl_2CDCDCl_2$, 400 MHz)



```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
blip_cld( 16, 64, 1 )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

```
Filename            = KOHthiant036-2final_GPC_R
Author              = delta
Experiment          = carbon.jxp
Sample_Id           = KOHthiant036-2final_GPC_R
Solvent             = TETRACHLOROETHANE-D2
Actual_Start_Time   = 10-NOV-2022 16:37:50
Revision_Time       = 11-NOV-2022 20:56:38

Comment             = single pulse decoupled ga
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = Carbon
Dim_Title           = Carbon13
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECA600II
Spectrometer        = DELTA2_NMR

Field_Strength      = 14.09636928[T] (600[MHz])
X_Acq_Duration      = 0.69206016[s]
X_Domain            = 13C
X_Freq              = 150.91343039[MHz]
X_Offset            = 100[ppm]
X_Points            = 32768
X_Prescans          = 4
X_Resolution        = 1.44496109[Hz]
X_Sweep             = 47.34848485[kHz]
X_Sweep_Clipped     = 37.87878788[kHz]
Irr_Domain          = Proton
Irr_Freq            = 600.1723046[MHz]
Irr_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 512
Total_Scans         = 512

Relaxation_Delay    = 2[s]
Recvr_Gain          = 60
Temp_Get            = 19.8[dC]
X_90_Width          = 13.8[us]
X_Acq_Time          = 0.69206016[s]
X_Angle             = 30[deg]
X_Atn               = 13.7[dB]
X_Pulse             = 4.6[us]
Irr_Atn_Dec         = 19.402[dB]
Irr_Atn_Noe         = 19.402[dB]
Irr_Noise           = WALTZ
Irr_Pwidth          = 0.104[ms]
Decoupling          = TRUE
Initial_Wait        = 1[s]
Noe                 = TRUE
Noe_Time            = 2[s]
Repetition_Time     = 2.69206016[s]
```

Figure S27. ^{13}C NMR spectra of **3ca** (in $Cl_2CDCDCl_2$, 150 MHz)

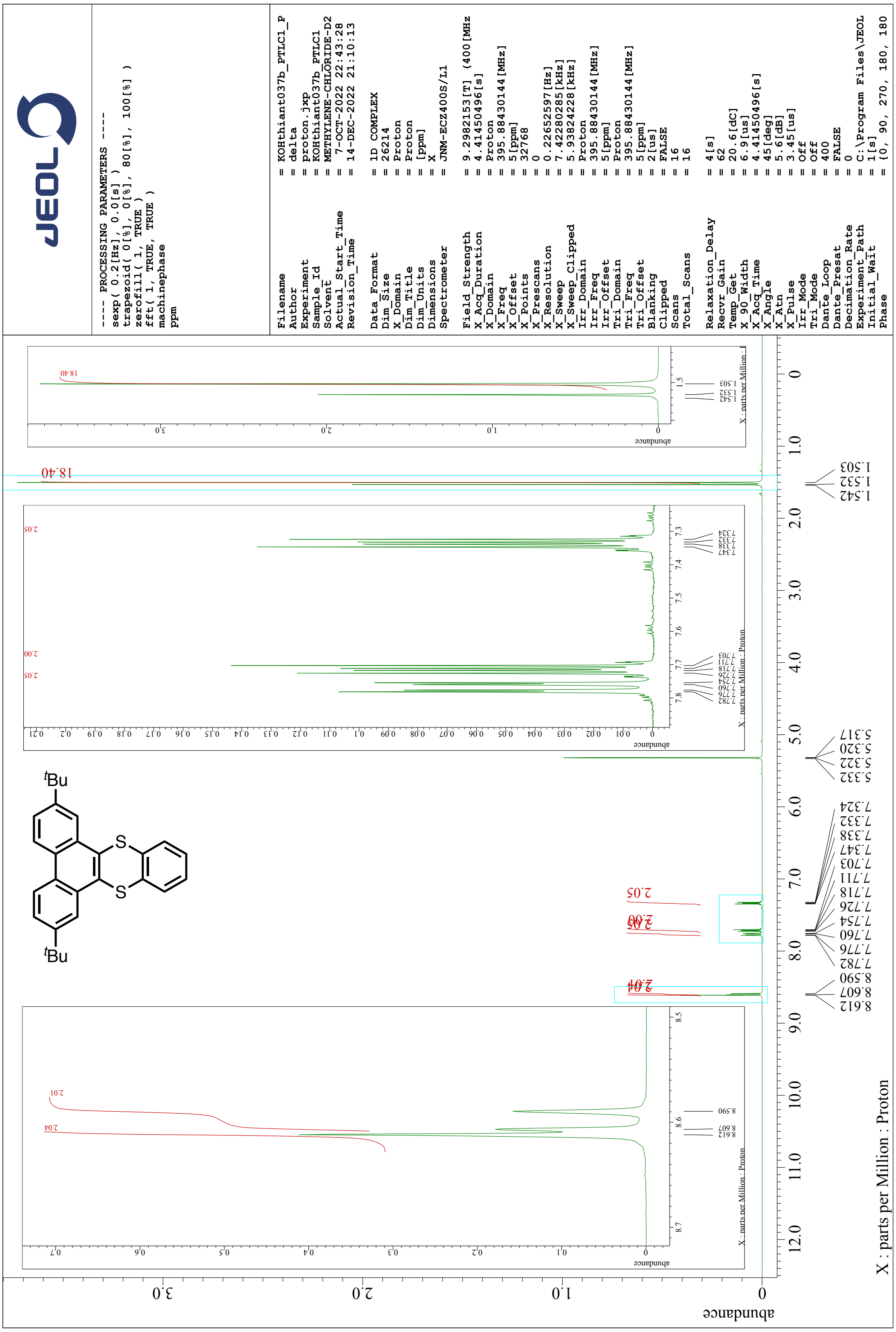
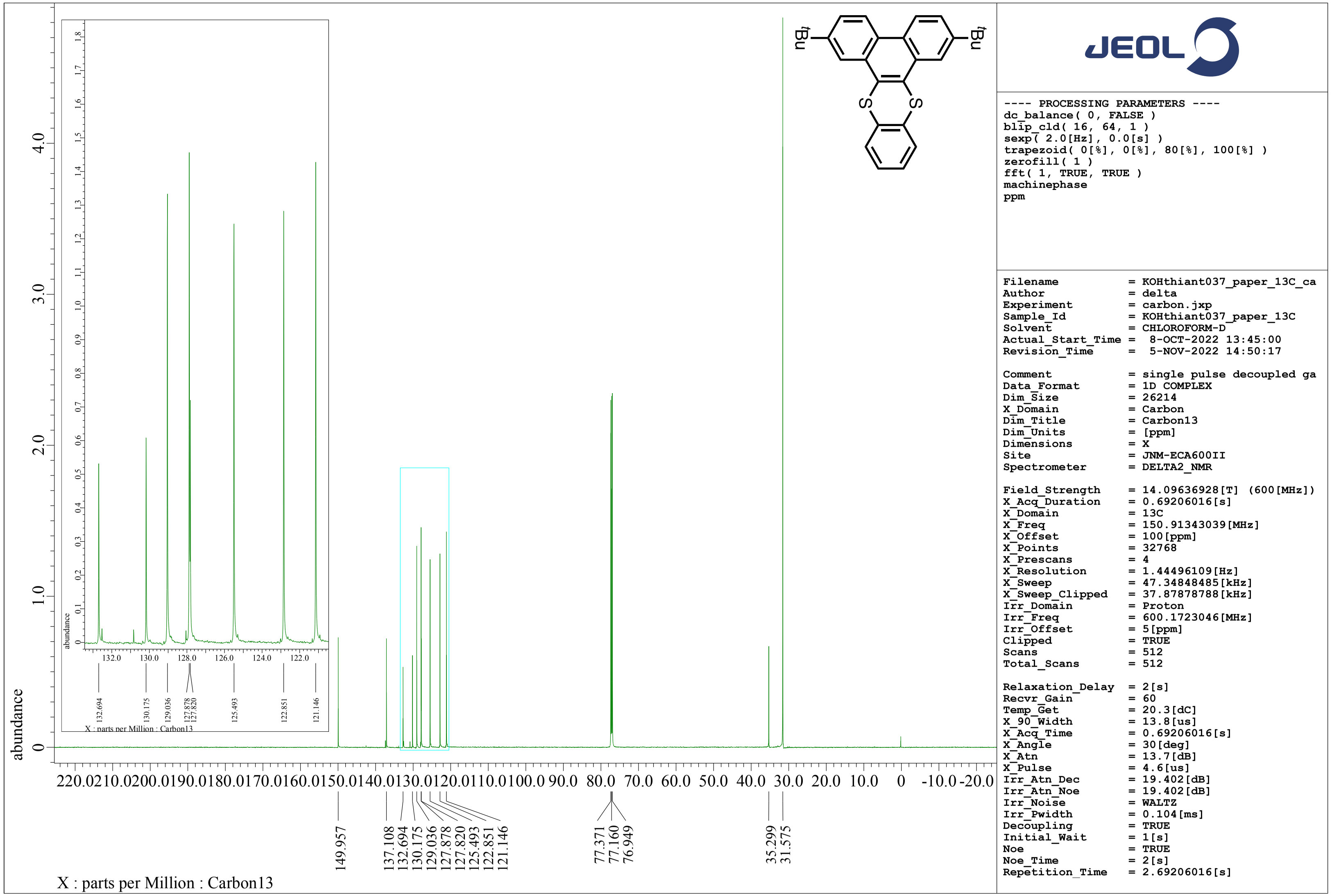


Figure S28. ^{1}H NMR spectra of **3da** (in CD_2Cl_2, 400 MHz)



```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
blip_cld( 16, 64, 1 )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

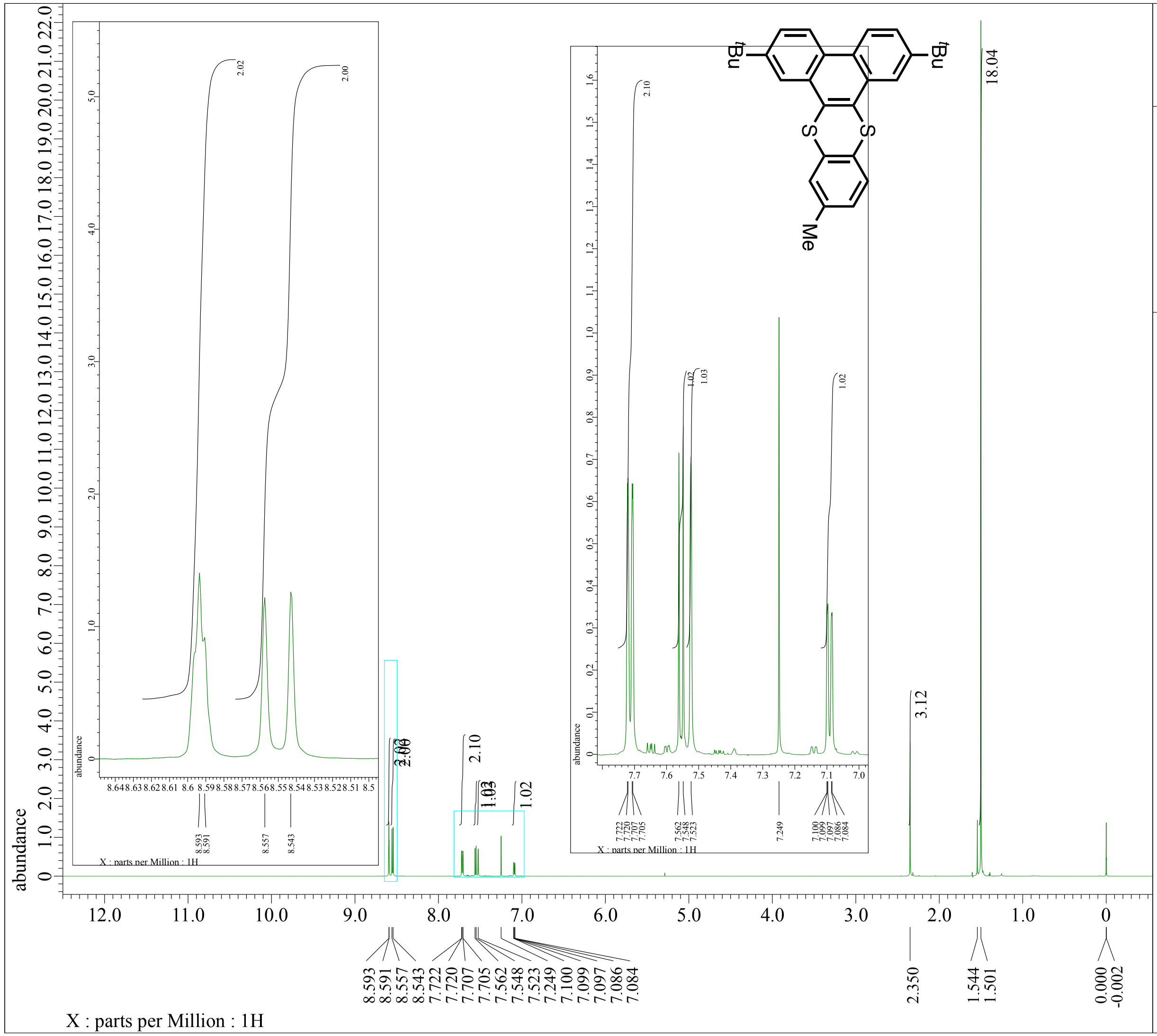
```
Filename            = KOHthiant037_paper_13C_ca
Author              = delta
Experiment          = carbon.jxp
Sample_Id           = KOHthiant037_paper_13C
Solvent             = CHLOROFORM-D
Actual_Start_Time =  8-OCT-2022 13:45:00
Revision_Time       =  5-NOV-2022 14:50:17

Comment             = single pulse decoupled ga
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = Carbon
Dim_Title           = Carbon13
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECA600II
Spectrometer        = DELTA2_NMR

Field_Strength      = 14.09636928[T] (600[MHz])
X_Acq_Duration      = 0.69206016[s]
X_Domain            = 13C
X_Freq              = 150.91343039[MHz]
X_Offset            = 100[ppm]
X_Points            = 32768
X_Prescans          = 4
X_Resolution        = 1.44496109[Hz]
X_Sweep             = 47.34848485[kHz]
X_Sweep_Clipped     = 37.87878788[kHz]
Irr_Domain          = Proton
Irr_Freq            = 600.1723046[MHz]
Irr_Offset          = 5[ppm]
Clipped             = TRUE
Scans               = 512
Total_Scans         = 512

Relaxation_Delay    = 2[s]
Recvr_Gain          = 60
Temp_Get            = 20.3[dC]
X_90_Width          = 13.8[us]
X_Acq_Time          = 0.69206016[s]
X_Angle             = 30[deg]
X_Atn               = 13.7[dB]
X_Pulse             = 4.6[us]
Irr_Atn_Dec         = 19.402[dB]
Irr_Atn_Noe         = 19.402[dB]
Irr_Noise           = WALTZ
Irr_Pwidth          = 0.104[ms]
Decoupling          = TRUE
Initial_Wait        = 1[s]
Noe                 = TRUE
Noe_Time            = 2[s]
Repetition_Time     = 2.69206016[s]
```

Figure S29. ^{13}C NMR spectra of **3da** (in $CDCl_3$, 150 MHz)



JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

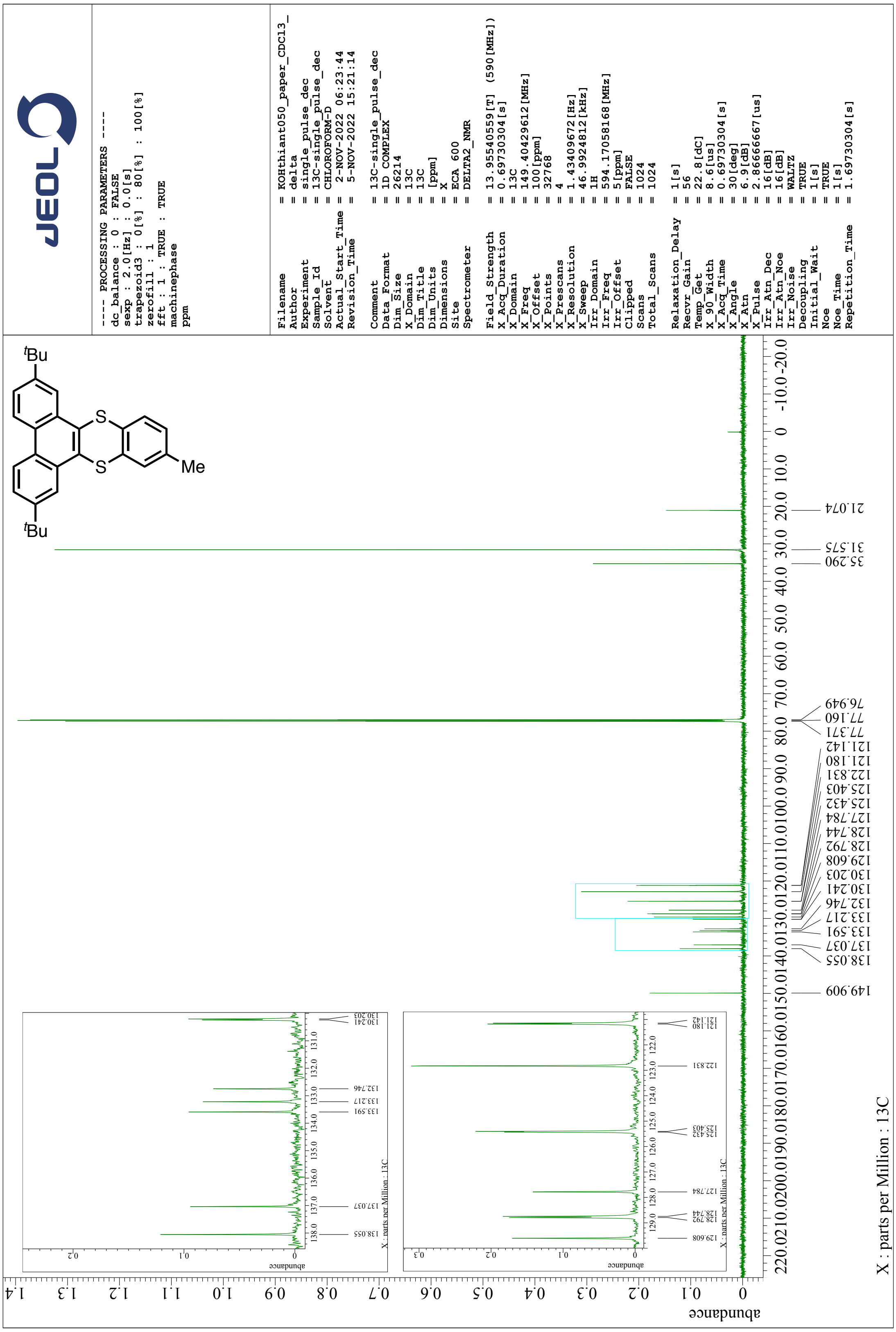
Filename            = KOHthiant050_paper_CDCl3_
Author              = delta
Experiment          = single_pulse.ex2
Sample_Id           = S#789601
Solvent             = CHLOROFORM-D
Actual_Start_Time =  2-NOV-2022 06:56:10
Revision_Time       =  5-NOV-2022 15:04:18

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = 1H
Dim_Title           = 1H
Dim_Units           = [ppm]
Dimensions          = X
Site                = ECA 600
Spectrometer        = DELTA2_NMR

Field_Strength      = 13.95540559[T] (590[MHz])
X_Acq_Duration      = 2.94125568[s]
X_Domain            = 1H
X_Freq              = 594.17058168[MHz]
X_Offset            = 5[ppm]
X_Points            = 32768
X_Prescans          = 1
X_Resolution        = 0.33999084[Hz]
X_Sweep             = 11.14081996[kHz]
Irr_Domain          = 1H
Irr_Freq            = 594.17058168[MHz]
Irr_Offset          = 5[ppm]
Tri_Domain          = 1H
Tri_Freq            = 594.17058168[MHz]
Tri_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 16
Total_Scans         = 16

Relaxation_Delay    = 10[s]
Recvr_Gain          = 38
Temp_Get            = 22.4[dC]
X_90_Width          = 13.2[us]
X_Acq_Time          = 2.94125568[s]
X_Angle             = 45[deg]
X_Atn               = 3.9[dB]
X_Pulse             = 6.6[us]
Irr_Mode            = Off
Tri_Mode            = Off
Dante_Presat        = FALSE
Initial_Wait        = 1[s]
Repetition_Time     = 12.94125568[s]
```

Figure S30. ^{1}H NMR spectra of **3db** (in $CDCl_3$, 600 MHz)



```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

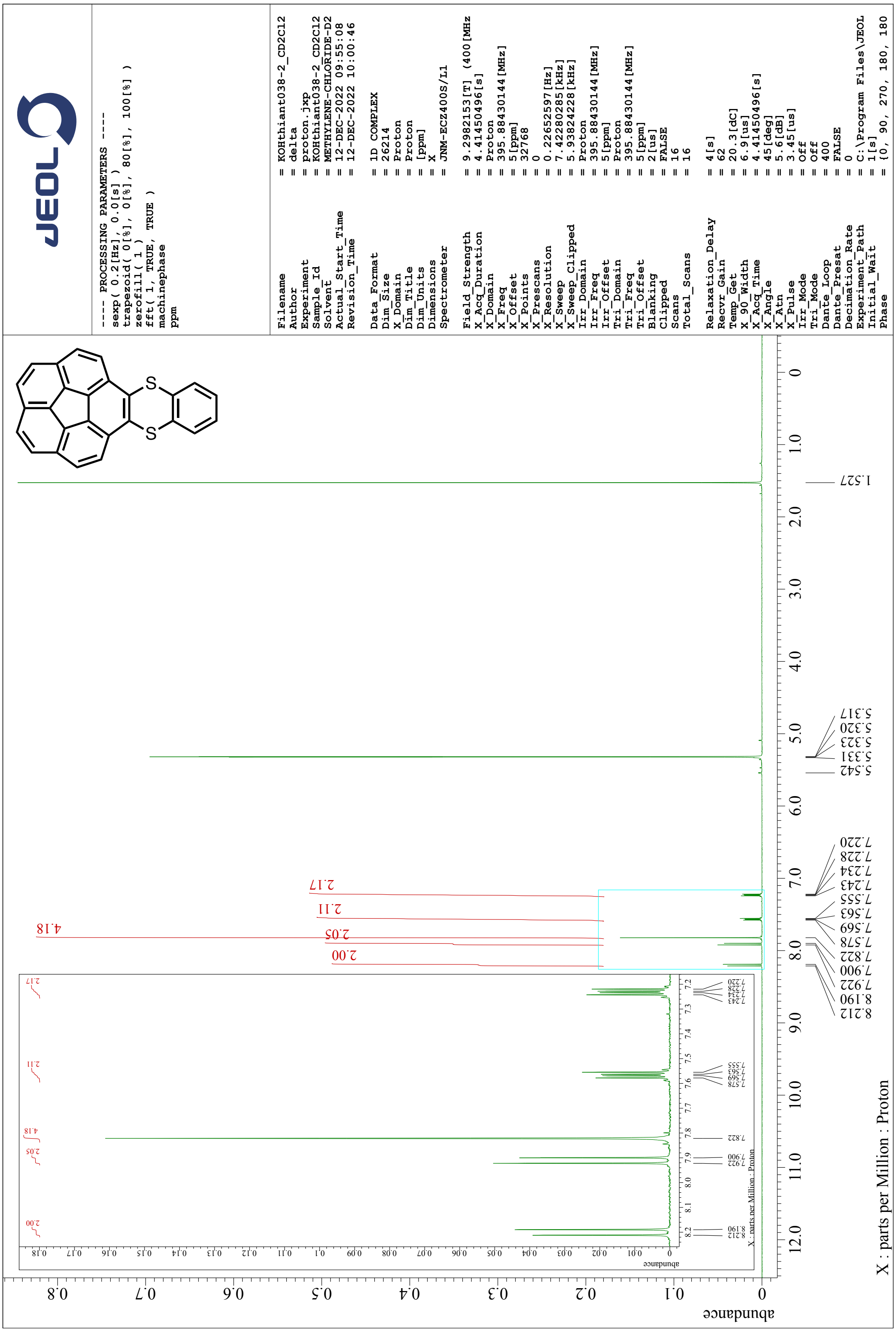
Filename            = KOHthiant050_paper_CDCl3_
Author              = delta
Experiment          = single_pulse_dec
Sample_Id           = 13C-single_pulse_dec
Solvent             = CHLOROFORM-D
Actual_Start_Time   =  2-NOV-2022 06:23:44
Revision_Time       =  5-NOV-2022 15:21:14

Comment             = 13C-single_pulse_dec
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = 13C
Dim_Title           = 13C
Dim_Units           = [ppm]
Dimensions          = X
Site                = ECA 600
Spectrometer        = DELTA2_NMR

Field_Strength      = 13.95540559[T] (590[MHz])
X_Acq_Duration      = 0.69730304[s]
X_Domain            = 13C
X_Freq              = 149.40429612[MHz]
X_Offset            = 100[ppm]
X_Points            = 32768
X_Prescans          = 4
X_Resolution        = 1.43409672[Hz]
X_Sweep             = 46.9924812[kHz]
Irr_Domain          = 1H
Irr_Freq            = 594.17058168[MHz]
Irr_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 1024
Total_Scans         = 1024

Relaxation_Delay    = 1[s]
Recvr_Gain          = 56
Temp_Get            = 22.8[dC]
X_90_Width          = 8.6[us]
X_Acq_Time          = 0.69730304[s]
X_Angle             = 30[deg]
X_Atn               = 6.9[dB]
X_Pulse             = 2.86666667[us]
Irr_Atn_Dec         = 16[dB]
Irr_Atn_Noe         = 16[dB]
Irr_Noise           = WALTZ
Decoupling          = TRUE
Initial_Wait        = 1[s]
Noe                 = TRUE
Noe_Time            = 1[s]
Repetition_Time     = 1.69730304[s]
```

Figure S31. ^{13}C NMR spectra of **3db** (in CDCl$_3$, 150 MHz)



```
---- PROCESSING PARAMETERS ----
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

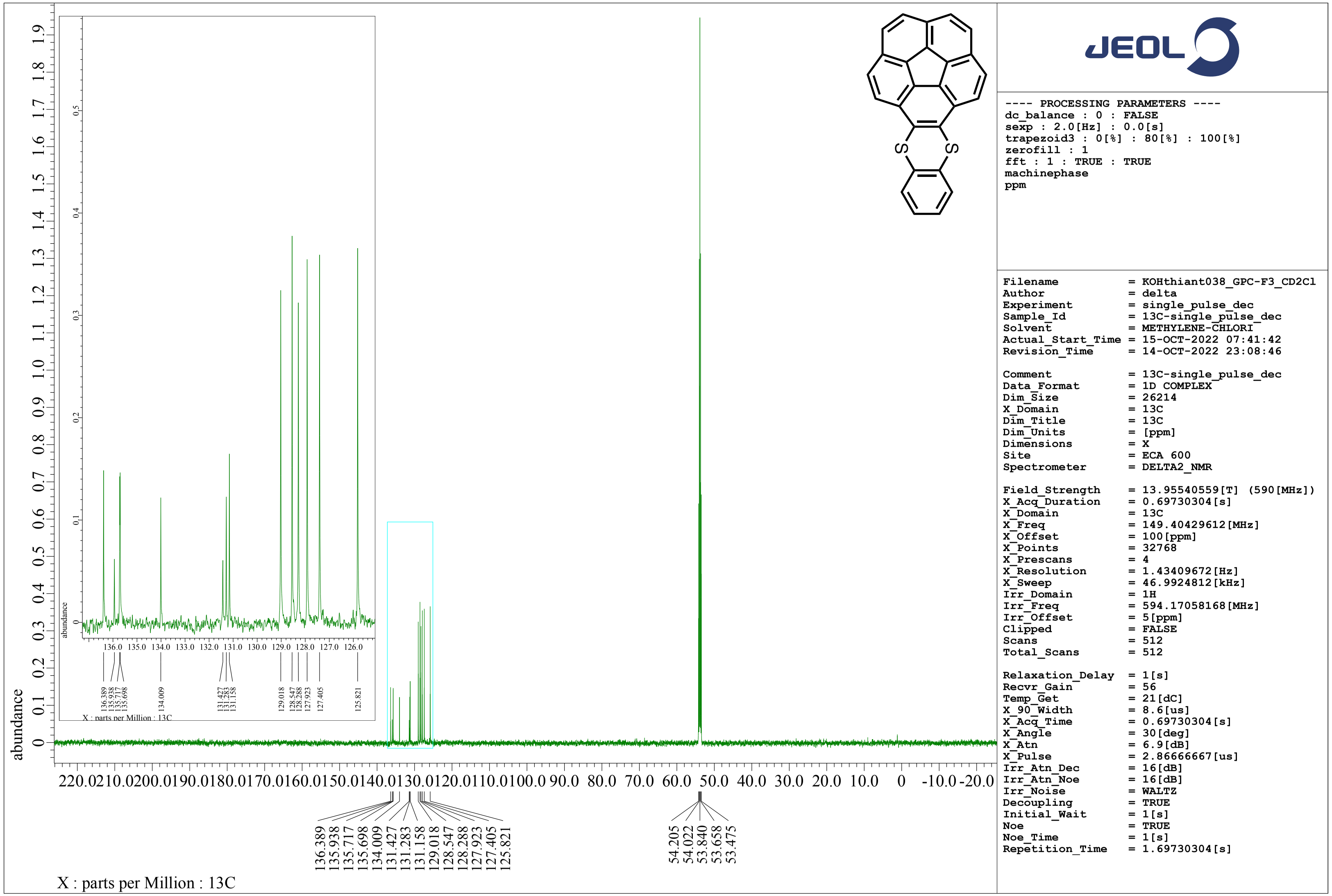
```
Filename              = KOHthiant038-2_CD2Cl2
Author                = delta
Experiment            = proton.jxp
Sample_Id             = KOHthiant038-2_CD2Cl2
Solvent               = METHYLENE-CHLORIDE-D2
Actual_Start_Time     = 12-DEC-2022 09:55:08
Revision_Time         = 12-DEC-2022 10:00:46

Data_Format           = 1D COMPLEX
Dim_Size              = 26214
X_Domain              = Proton
Dim_Title             = Proton
Dim_Units             = [ppm]
Dimensions            = X
Spectrometer          = JNM-ECZ400S/L1

Field_Strength        = 9.2982153[T] (400[MHz
X_Acq_Duration        = 4.41450496[s]
X_Domain              = Proton
X_Freq                = 395.88430144[MHz]
X_Offset              = 5[ppm]
X_Points              = 32768
X_Prescans            = 0
X_Resolution          = 0.22652597[Hz]
X_Sweep               = 7.42280285[kHz]
X_Sweep_Clipped       = 5.93824228[kHz]
Irr_Domain            = Proton
Irr_Freq              = 395.88430144[MHz]
Irr_Offset            = 5[ppm]
Tri_Domain            = Proton
Tri_Freq              = 395.88430144[MHz]
Tri_Offset            = 5[ppm]
Blanking              = 2[us]
Clipped               = FALSE
Scans                 = 16
Total_Scans           = 16

Relaxation_Delay      = 4[s]
Recvr_Gain            = 62
Temp_Get              = 20.3[dC]
X_90_Width            = 6.9[us]
X_Acq_Time            = 4.41450496[s]
X_Angle               = 45[deg]
X_Atn                 = 5.6[dB]
X_Pulse               = 3.45[us]
Irr_Mode              = Off
Tri_Mode              = Off
Dante_Loop            = 400
Dante_Presat          = FALSE
Decimation_Rate       = 0
Experiment_Path       = C:\Program Files\JEOL
Initial_Wait          = 1[s]
Phase                 = {0, 90, 270, 180, 180
```

Figure S32. ^{1}H NMR spectra of **3ea** (in CD_2Cl_2, 400 MHz)



```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
```

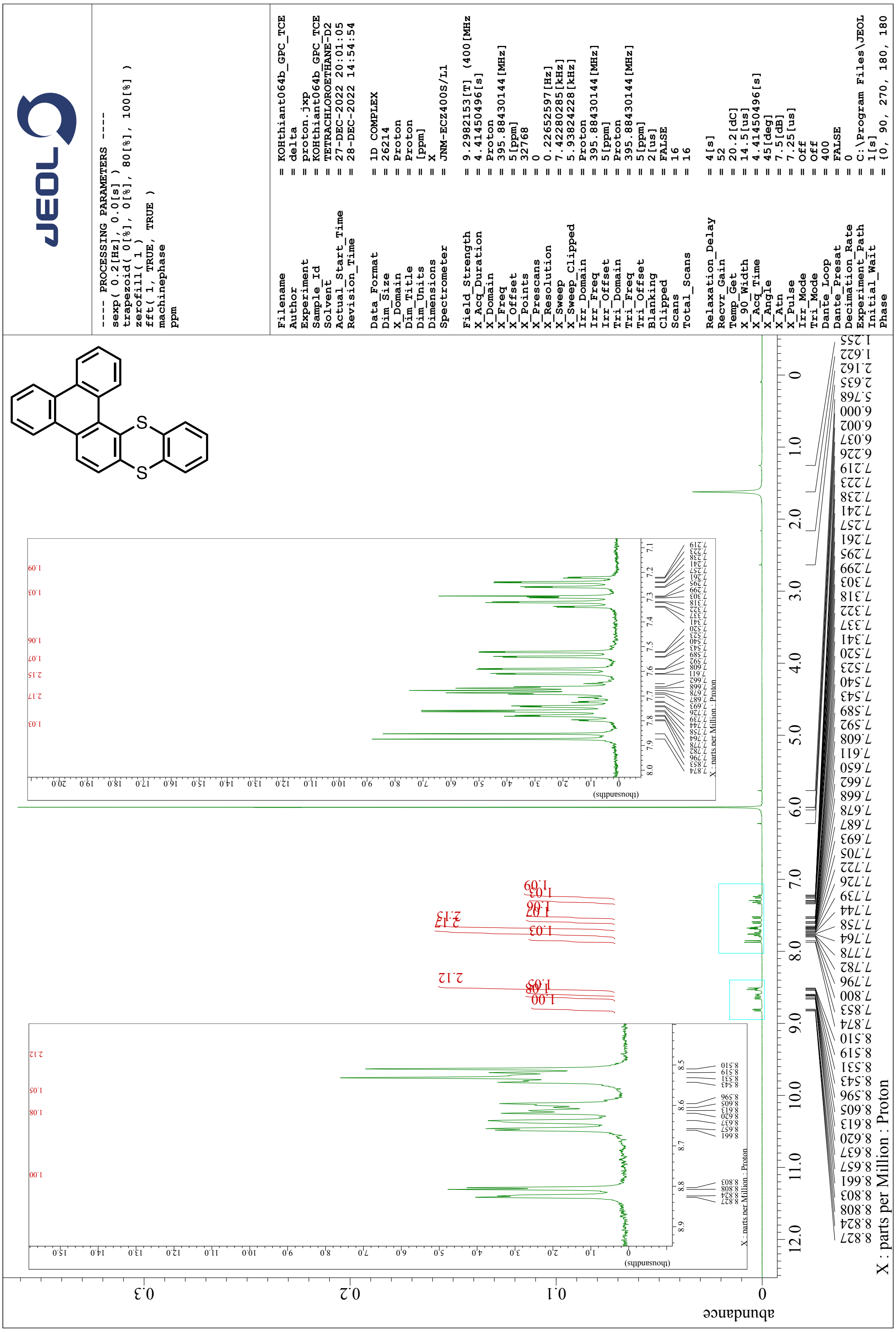
```
Filename          = KOHthiant038_GPC-F3_CD2Cl
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = 13C-single_pulse_dec
Solvent           = METHYLENE-CHLORI
Actual_Start_Time = 15-OCT-2022 07:41:42
Revision_Time     = 14-OCT-2022 23:08:46

Comment           = 13C-single_pulse_dec
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
X_Domain          = 13C
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 600
Spectrometer      = DELTA2_NMR

Field_Strength    = 13.95540559[T] (590[MHz])
X_Acq_Duration    = 0.69730304[s]
X_Domain          = 13C
X_Freq            = 149.40429612[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.43409672[Hz]
X_Sweep           = 46.9924812[kHz]
Irr_Domain        = 1H
Irr_Freq          = 594.17058168[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 512
Total_Scans       = 512

Relaxation_Delay  = 1[s]
Recvr_Gain        = 56
Temp_Get          = 21[dC]
X_90_Width        = 8.6[us]
X_Acq_Time        = 0.69730304[s]
X_Angle           = 30[deg]
X_Atn             = 6.9[dB]
X_Pulse           = 2.86666667[us]
Irr_Atn_Dec       = 16[dB]
Irr_Atn_Noe       = 16[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 1[s]
Repetition_Time   = 1.69730304[s]
```

Figure S33. ^{13}C NMR spectra of **3ea** (in CD_2Cl_2, 150 MHz)



```
---- PROCESSING PARAMETERS ----
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

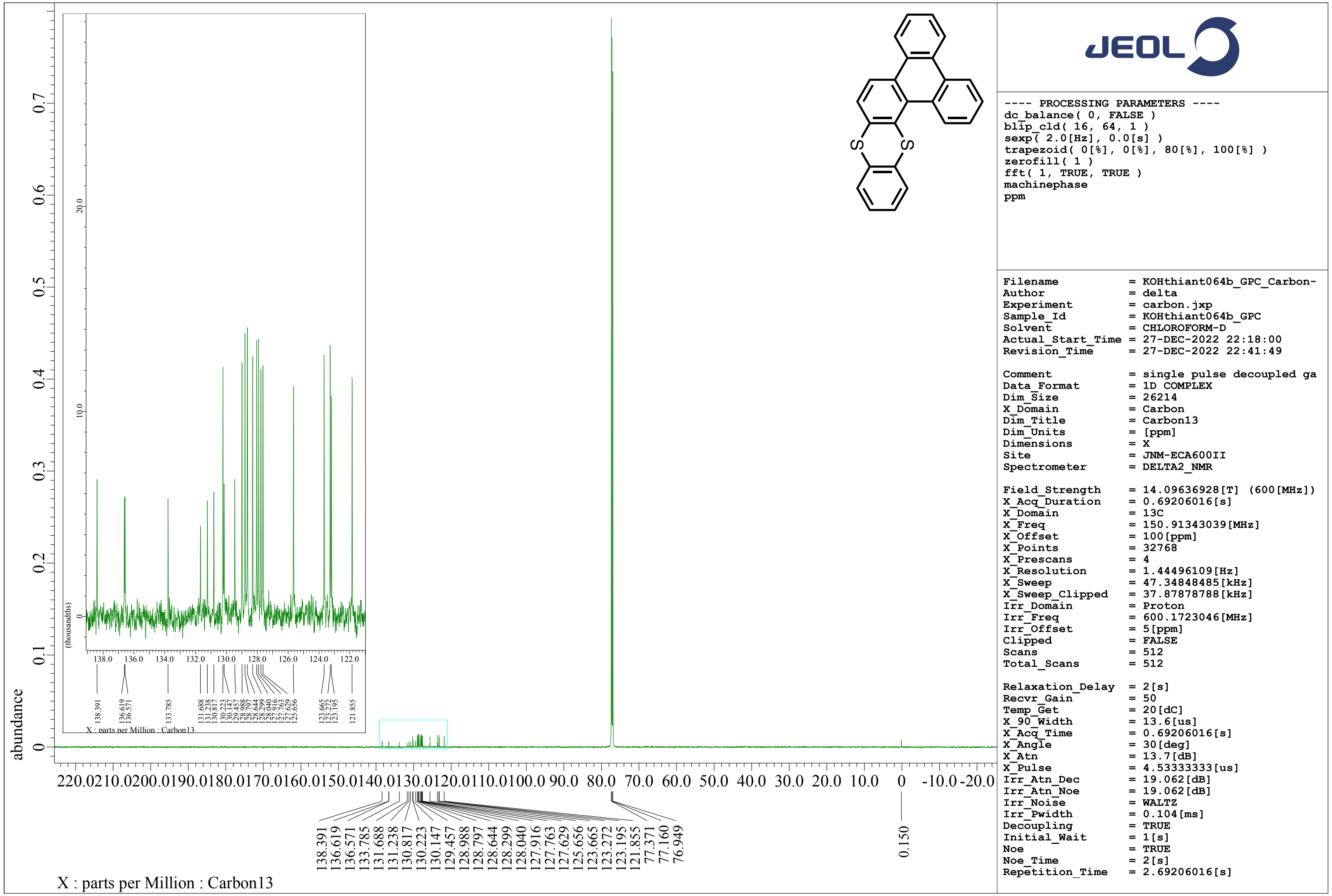
Filename            = KOHthiant064b_GPC_TCE
Author              = delta
Experiment          = proton.jxp
Sample_Id           = KOHthiant064b_GPC_TCE
Solvent             = TETRACHLOROETHANE-D2
Actual_Start_Time   = 27-DEC-2022 20:01:05
Revision_Time       = 28-DEC-2022 14:54:54

Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = Proton
Dim_Title           = Proton
Dim_Units           = [ppm]
Dimensions          = X
Spectrometer        = JNM-ECZ400S/L1

Field_Strength      = 9.2982153[T] (400[MHz
X_Acq_Duration      = 4.41450496[s]
X_Domain            = Proton
X_Freq              = 395.88430144[MHz]
X_Offset            = 5[ppm]
X_Points            = 32768
X_Prescans          = 0
X_Resolution        = 0.22652597[Hz]
X_Sweep             = 7.42280285[kHz]
X_Sweep_Clipped     = 5.93824228[kHz]
Irr_Domain          = Proton
Irr_Freq            = 395.88430144[MHz]
Irr_Offset          = 5[ppm]
Tri_Domain          = Proton
Tri_Freq            = 395.88430144[MHz]
Tri_Offset          = 5[ppm]
Blanking            = 2[us]
Clipped             = FALSE
Scans               = 16
Total_Scans         = 16

Relaxation_Delay    = 4[s]
Recvr_Gain          = 52
Temp_Get            = 20.2[dC]
X_90_Width          = 14.5[us]
X_Acq_Time          = 4.41450496[s]
X_Angle             = 45[deg]
X_Atn               = 7.5[dB]
X_Pulse             = 7.25[us]
Irr_Mode            = Off
Tri_Mode            = Off
Dante_Loop          = 400
Dante_Presat        = FALSE
Decimation_Rate     = 0
Experiment_Path     = C:\Program Files\JEOL
Initial_Wait        = 1[s]
Phase               = [0, 90, 270, 180]
```

Figure S34. ^{1}H NMR spectra of **3fa** (in $Cl_2CDCDCl_2$, 400 MHz)



```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
blip_cld( 16, 64, 1 )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

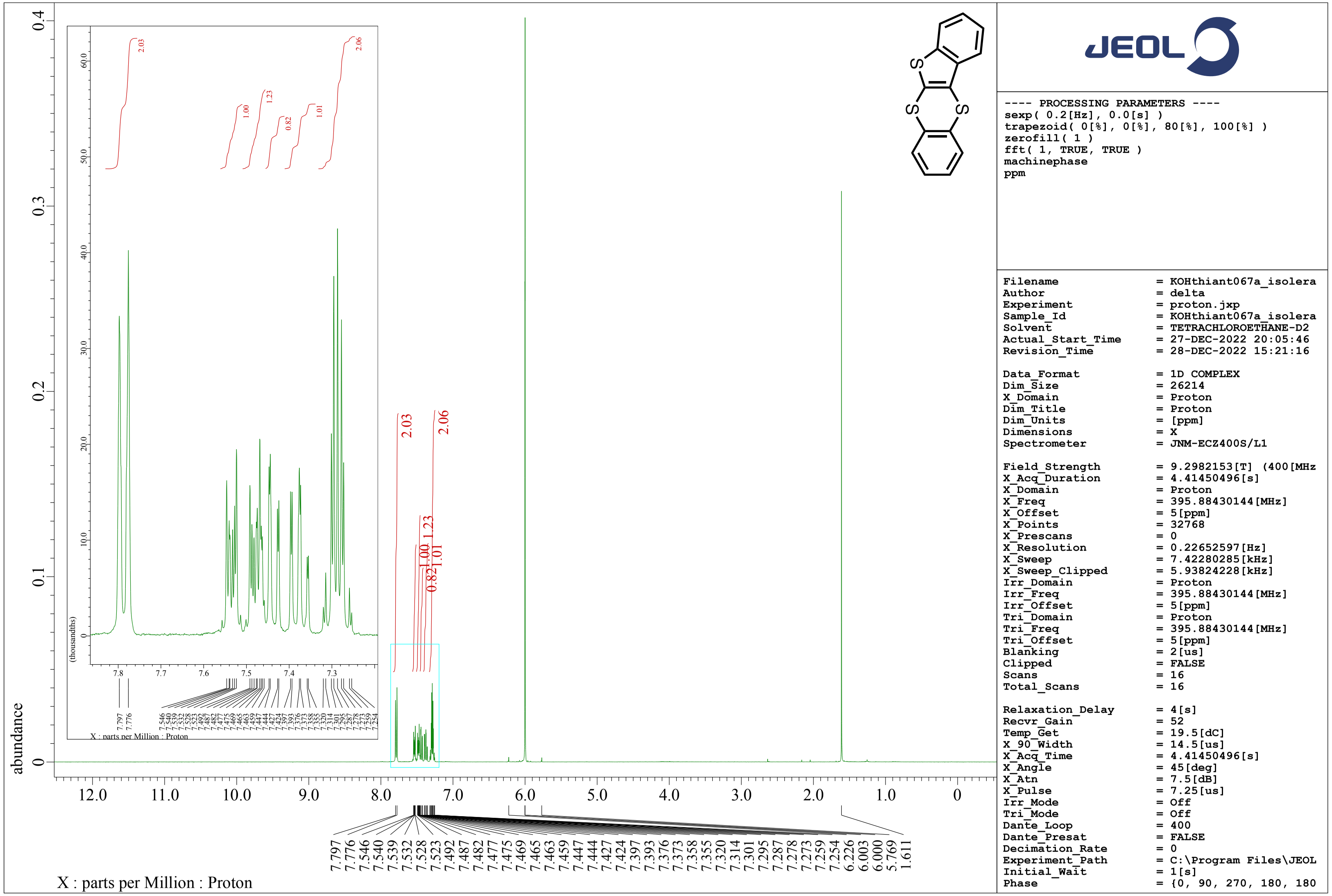
```
Filename            = KOHthiant064b_GPC_Carbon-
Author              = delta
Experiment          = carbon.jxp
Sample_Id           = KOHthiant064b_GPC
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 27-DEC-2022 22:18:00
Revision_Time       = 27-DEC-2022 22:41:49

Comment             = single pulse decoupled ga
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = Carbon
Dim_Title           = Carbon13
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECA600II
Spectrometer        = DELTA2_NMR

Field_Strength      = 14.09636928[T] (600[MHz])
X_Acq_Duration      = 0.69206016[s]
X_Domain            = 13C
X_Freq              = 150.91343039[MHz]
X_Offset            = 100[ppm]
X_Points            = 32768
X_Prescans          = 4
X_Resolution        = 1.44496109[Hz]
X_Sweep             = 47.34848485[kHz]
X_Sweep_Clipped     = 37.87878788[kHz]
Irr_Domain          = Proton
Irr_Freq            = 600.1723046[MHz]
Irr_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 512
Total_Scans         = 512

Relaxation_Delay    = 2[s]
Recvr_Gain          = 50
Temp_Get            = 20[dC]
X_90_Width          = 13.6[us]
X_Acq_Time          = 0.69206016[s]
X_Angle             = 30[deg]
X_Atn               = 13.7[dB]
X_Pulse             = 4.53333333[us]
Irr_Atn_Dec         = 19.062[dB]
Irr_Atn_Noe         = 19.062[dB]
Irr_Noise           = WALTZ
Irr_Pwidth          = 0.104[ms]
Decoupling          = TRUE
Initial_Wait        = 1[s]
Noe                 = TRUE
Noe_Time            = 2[s]
Repetition_Time     = 2.69206016[s]
```

Figure S35. ^{13}C NMR spectra of **3fa** (in $CDCl_3$, 150 MHz)



```
---- PROCESSING PARAMETERS ----
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

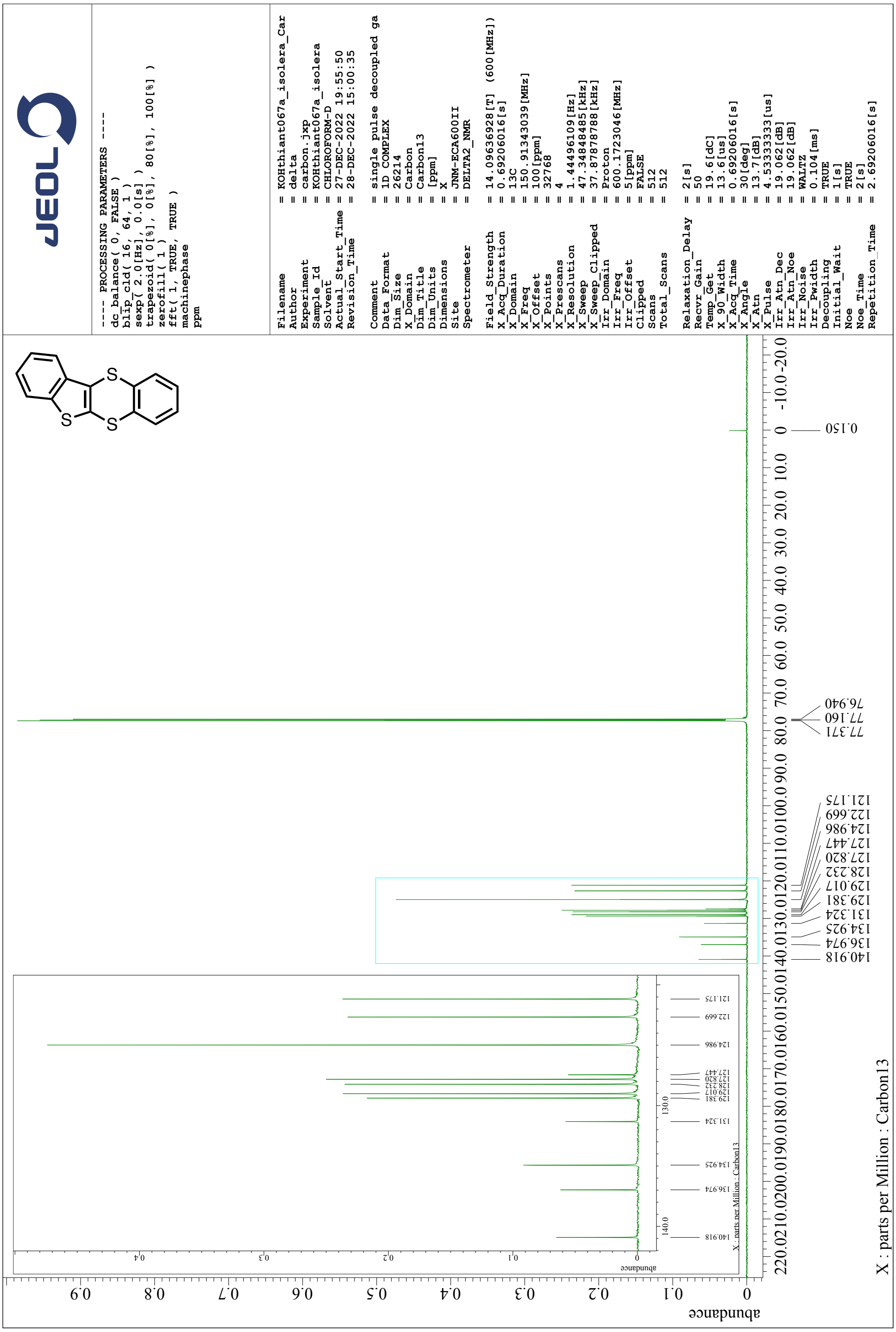
Filename               = KOHthiant067a_isolera
Author                 = delta
Experiment             = proton.jxp
Sample_Id              = KOHthiant067a_isolera
Solvent                = TETRACHLOROETHANE-D2
Actual_Start_Time      = 27-DEC-2022 20:05:46
Revision_Time          = 28-DEC-2022 15:21:16

Data_Format            = 1D COMPLEX
Dim_Size               = 26214
X_Domain               = Proton
Dim_Title              = Proton
Dim_Units              = [ppm]
Dimensions             = X
Spectrometer           = JNM-ECZ400S/L1

Field_Strength         = 9.2982153[T] (400[MHz
X_Acq_Duration         = 4.41450496[s]
X_Domain               = Proton
X_Freq                 = 395.88430144[MHz]
X_Offset               = 5[ppm]
X_Points               = 32768
X_Prescans             = 0
X_Resolution           = 0.22652597[Hz]
X_Sweep                = 7.42280285[kHz]
X_Sweep_Clipped        = 5.93824228[kHz]
Irr_Domain             = Proton
Irr_Freq               = 395.88430144[MHz]
Irr_Offset             = 5[ppm]
Tri_Domain             = Proton
Tri_Freq               = 395.88430144[MHz]
Tri_Offset             = 5[ppm]
Blanking               = 2[us]
Clipped                = FALSE
Scans                  = 16
Total_Scans            = 16

Relaxation_Delay       = 4[s]
Recvr_Gain             = 52
Temp_Get               = 19.5[dC]
X_90_Width             = 14.5[us]
X_Acq_Time             = 4.41450496[s]
X_Angle                = 45[deg]
X_Atn                  = 7.5[dB]
X_Pulse                = 7.25[us]
Irr_Mode               = Off
Tri_Mode               = Off
Dante_Loop             = 400
Dante_Presat           = FALSE
Decimation_Rate        = 0
Experiment_Path        = C:\Program Files\JEOL
Initial_Wait           = 1[s]
Phase                  = {0, 90, 270, 180, 180
```

Figure S36. ^{1}H NMR spectra of **3ga** (in $Cl_2CDCDCl_2$, 400 MHz)



```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
blip_cld( 16, 64, 1 )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

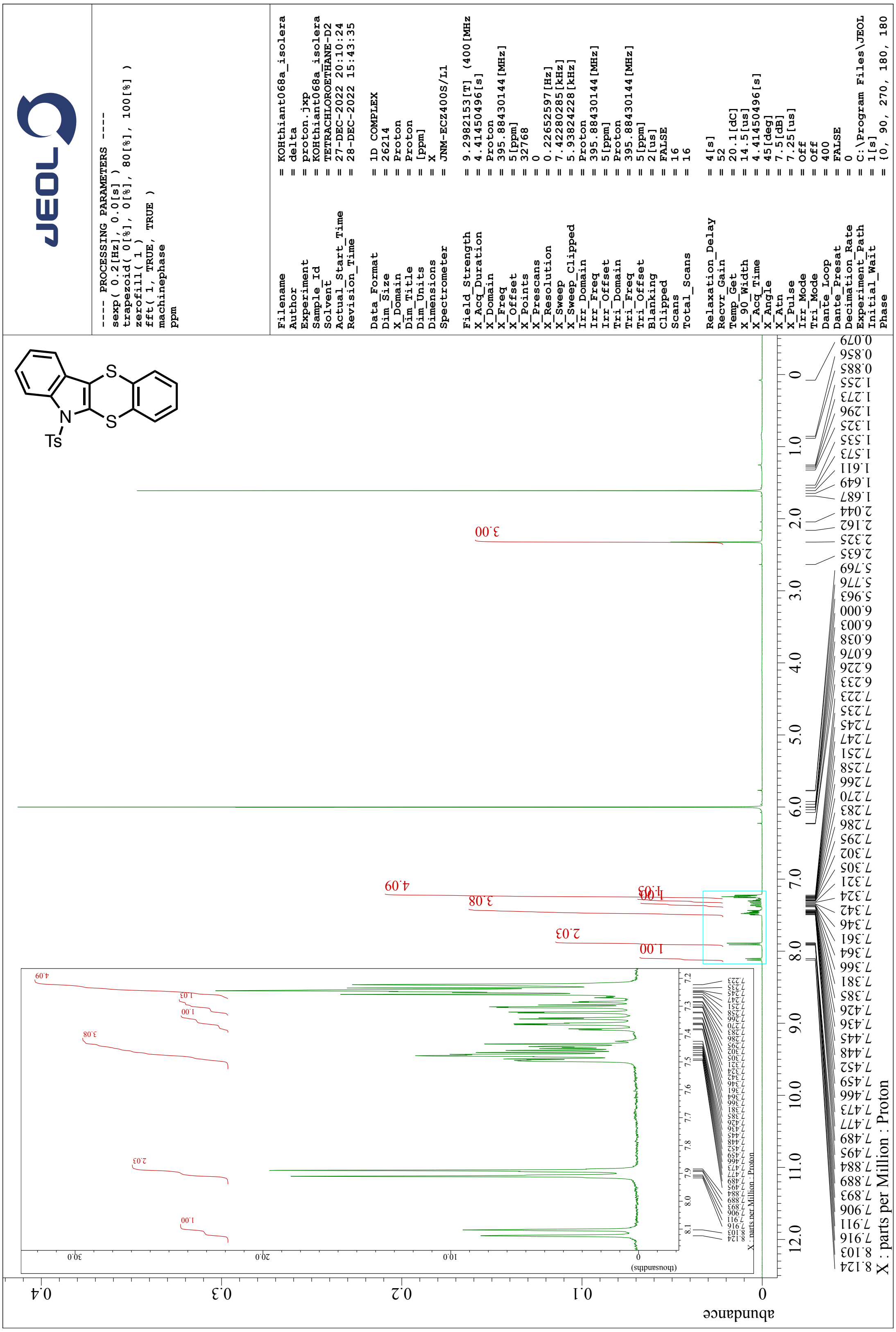
```
Filename               = KOHthiant067a_isolera_Car
Author                 = delta
Experiment             = carbon.jxp
Sample_Id              = KOHthiant067a_isolera
Solvent                = CHLOROFORM-D
Actual_Start_Time      = 27-DEC-2022 19:55:50
Revision_Time          = 28-DEC-2022 15:00:35

Comment                = single pulse decoupled ga
Data_Format            = 1D COMPLEX
Dim_Size               = 26214
X_Domain               = Carbon
Dim_Title              = Carbon13
Dim_Units              = [ppm]
Dimensions             = X
Site                   = JNM-ECA600II
Spectrometer           = DELTA2_NMR

Field_Strength         = 14.09636928[T] (600[MHz])
X_Acq_Duration         = 0.69206016[s]
X_Domain               = 13C
X_Freq                 = 150.91343039[MHz]
X_Offset               = 100[ppm]
X_Points               = 32768
X_Prescans             = 4
X_Resolution           = 1.44496109[Hz]
X_Sweep                = 47.34848485[kHz]
X_Sweep_Clipped        = 37.87878788[kHz]
Irr_Domain             = Proton
Irr_Freq               = 600.1723046[MHz]
Irr_Offset             = 5[ppm]
Clipped                = FALSE
Scans                  = 512
Total_Scans            = 512

Relaxation_Delay       = 2[s]
Recvr_Gain             = 50
Temp_Get               = 19.6[dC]
X_90_Width             = 13.6[us]
X_Acq_Time             = 0.69206016[s]
X_Angle                = 30[deg]
X_Atn                  = 13.7[dB]
X_Pulse                = 4.53333333[us]
Irr_Atn_Dec            = 19.062[dB]
Irr_Atn_Noe            = 19.062[dB]
Irr_Noise              = WALTZ
Irr_Pwidth             = 0.104[ms]
Decoupling             = TRUE
Initial_Wait           = 1[s]
Noe                    = TRUE
Noe_Time               = 2[s]
Repetition_Time        = 2.69206016[s]
```

Figure S37. ^{13}C NMR spectra of **3ga** (in CDCl$_3$, 150 MHz)



```
---- PROCESSING PARAMETERS ----
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

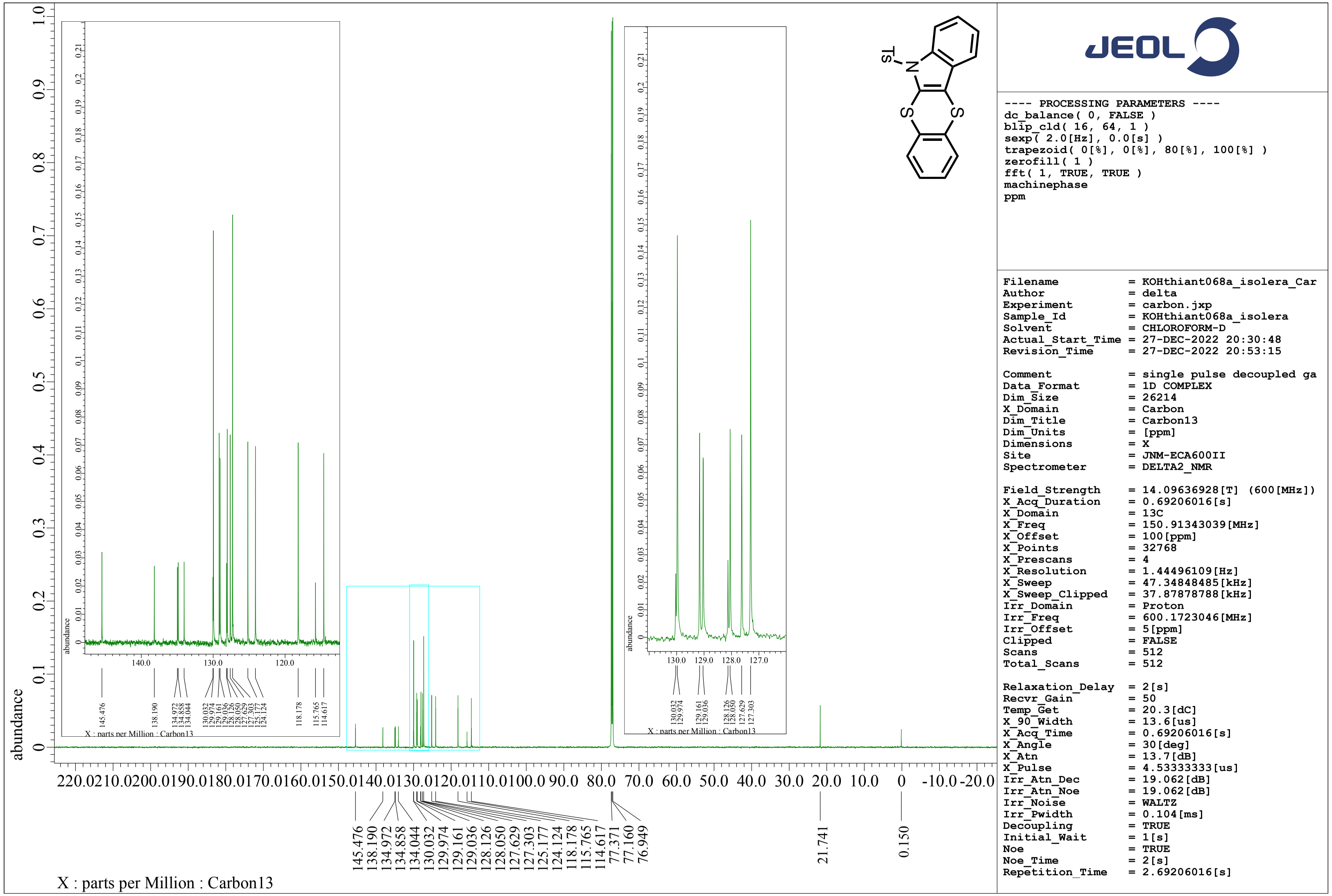
Filename                = KOHthiant068a_isolera
Author                  = delta
Experiment              = proton.jxp
Sample_Id               = KOHthiant068a_isolera
Solvent                 = TETRACHLOROETHANE-D2
Actual_Start_Time       = 27-DEC-2022 20:10:24
Revision_Time           = 28-DEC-2022 15:43:35

Data_Format             = 1D COMPLEX
Dim_Size                = 26214
X_Domain                = Proton
Dim_Title               = Proton
Dim_Units               = [ppm]
Dimensions              = X
Spectrometer            = JNM-ECZ400S/L1

Field_Strength          = 9.2982153[T] (400[MHz
X_Acq_Duration          = 4.41450496[s]
X_Domain                = Proton
X_Freq                  = 395.88430144[MHz]
X_Offset                = 5[ppm]
X_Points                = 32768
X_Prescans              = 0
X_Resolution            = 0.22652597[Hz]
X_Sweep                 = 7.42280285[kHz]
X_Sweep_Clipped         = 5.93824228[kHz]
Irr_Domain              = Proton
Irr_Freq                = 395.88430144[MHz]
Irr_Offset              = 5[ppm]
Tri_Domain              = Proton
Tri_Freq                = 395.88430144[MHz]
Tri_Offset              = 5[ppm]
Blanking                = 2[us]
Clipped                 = FALSE
Scans                   = 16
Total_Scans             = 16

Relaxation_Delay        = 4[s]
Recvr_Gain              = 52
Temp_Get                = 20.1[dC]
X_90_Width              = 14.5[us]
X_Acq_Time              = 4.41450496[s]
X_Angle                 = 45[deg]
X_Atn                   = 7.5[dB]
X_Pulse                 = 7.25[us]
Irr_Mode                = Off
Tri_Mode                = Off
Dante_Loop              = 400
Dante_Presat            = FALSE
Decimation_Rate         = 0
Experiment_Path         = C:\Program Files\JEOL
Initial_Wait            = 1[s]
Phase                   = {0, 90, 270, 180, 180
```

Figure S38. ^{1}H NMR spectra of **3ha** (in $Cl_2CDCDCl_2$, 400 MHz)



```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
blip_cld( 16, 64, 1 )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Filename          = KOHthiant068a_isolera_Car
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = KOHthiant068a_isolera
Solvent           = CHLOROFORM-D
Actual_Start_Time = 27-DEC-2022 20:30:48
Revision_Time     = 27-DEC-2022 20:53:15

Comment           = single pulse decoupled ga
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
X_Domain          = Carbon
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECA600II
Spectrometer      = DELTA2_NMR

Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 0.69206016[s]
X_Domain          = 13C
X_Freq            = 150.91343039[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.44496109[Hz]
X_Sweep           = 47.34848485[kHz]
X_Sweep_Clipped   = 37.87878788[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 512
Total_Scans       = 512

Relaxation_Delay  = 2[s]
Recvr_Gain        = 50
Temp_Get          = 20.3[dC]
X_90_Width        = 13.6[us]
X_Acq_Time        = 0.69206016[s]
X_Angle           = 30[deg]
X_Atn             = 13.7[dB]
X_Pulse           = 4.53333333[us]
Irr_Atn_Dec       = 19.062[dB]
Irr_Atn_Noe       = 19.062[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 0.104[ms]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.69206016[s]
```

Figure S39. ^{13}C NMR spectra of **3ha** (in CDCl$_3$, 150 MHz)

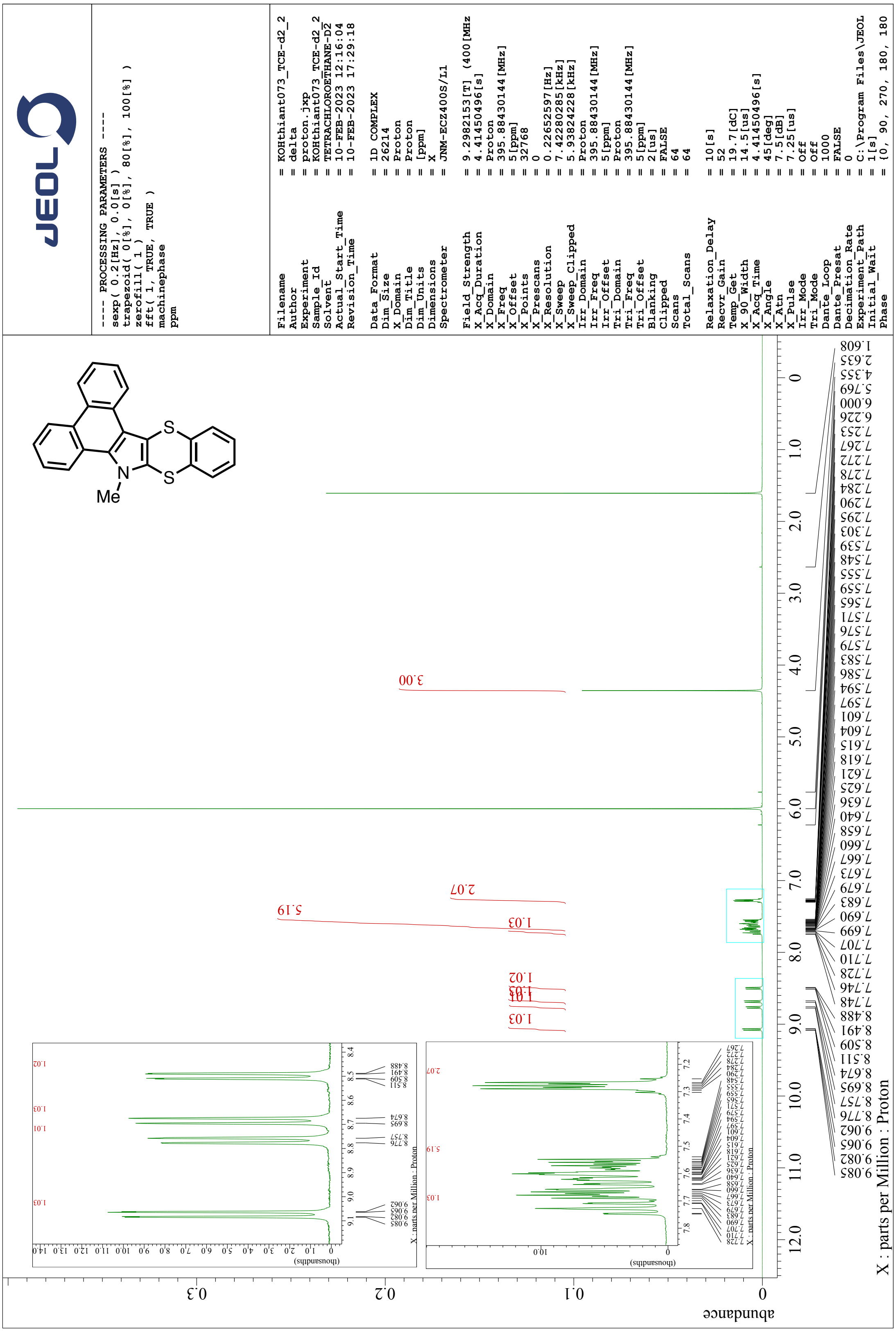
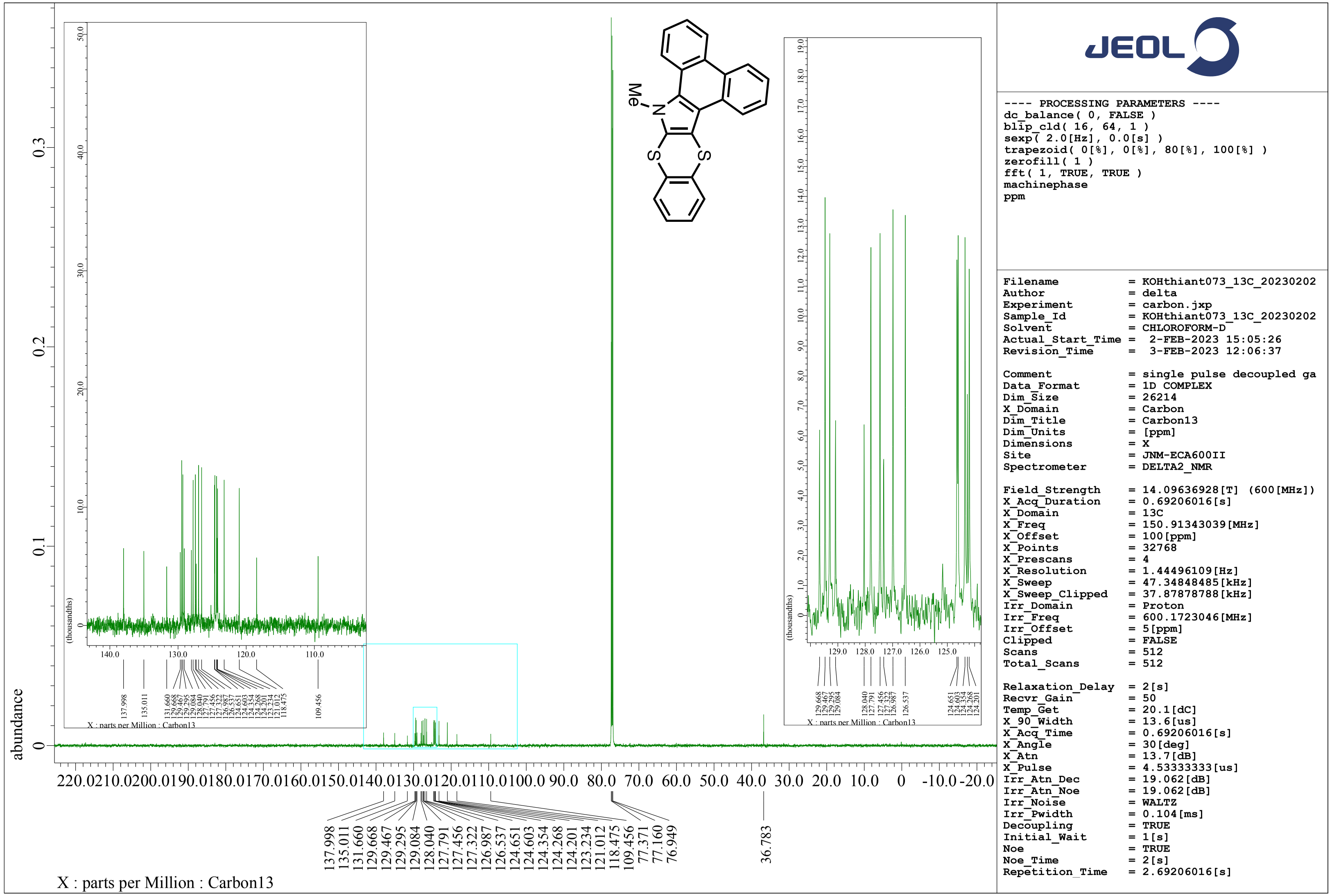


Figure S40. ^{1}H NMR spectra of **3ia** (in $Cl_2CDCDCl_2$, 400 MHz)



```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
blip_cld( 16, 64, 1 )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

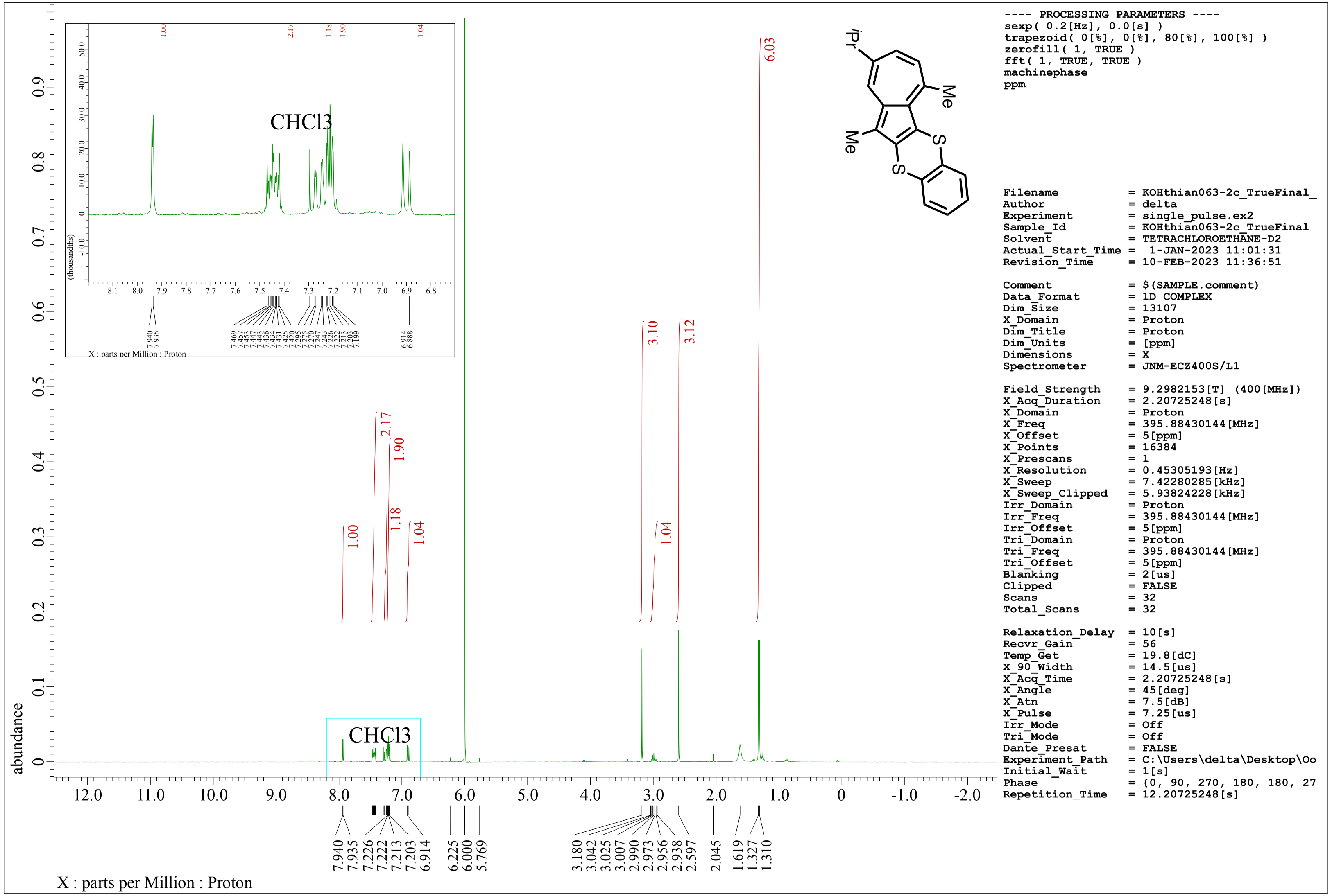
```
Filename            = KOHthiant073_13C_20230202
Author              = delta
Experiment          = carbon.jxp
Sample_Id           = KOHthiant073_13C_20230202
Solvent             = CHLOROFORM-D
Actual_Start_Time   =  2-FEB-2023 15:05:26
Revision_Time       =  3-FEB-2023 12:06:37

Comment             = single pulse decoupled ga
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = Carbon
Dim_Title           = Carbon13
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECA600II
Spectrometer        = DELTA2_NMR

Field_Strength      = 14.09636928[T] (600[MHz])
X_Acq_Duration      = 0.69206016[s]
X_Domain            = 13C
X_Freq              = 150.91343039[MHz]
X_Offset            = 100[ppm]
X_Points            = 32768
X_Prescans          = 4
X_Resolution        = 1.44496109[Hz]
X_Sweep             = 47.34848485[kHz]
X_Sweep_Clipped     = 37.87878788[kHz]
Irr_Domain          = Proton
Irr_Freq            = 600.1723046[MHz]
Irr_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 512
Total_Scans         = 512

Relaxation_Delay    = 2[s]
Recvr_Gain          = 50
Temp_Get            = 20.1[dC]
X_90_Width          = 13.6[us]
X_Acq_Time          = 0.69206016[s]
X_Angle             = 30[deg]
X_Atn               = 13.7[dB]
X_Pulse             = 4.53333333[us]
Irr_Atn_Dec         = 19.062[dB]
Irr_Atn_Noe         = 19.062[dB]
Irr_Noise           = WALTZ
Irr_Pwidth          = 0.104[ms]
Decoupling          = TRUE
Initial_Wait        = 1[s]
Noe                 = TRUE
Noe_Time            = 2[s]
Repetition_Time     = 2.69206016[s]
```

Figure S41. ^{13}C NMR spectra of **3ia** (in $CDCl_3$, 150 MHz)



```
---- PROCESSING PARAMETERS ----
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1, TRUE )
fft( 1, TRUE, TRUE )
machinephase
ppm

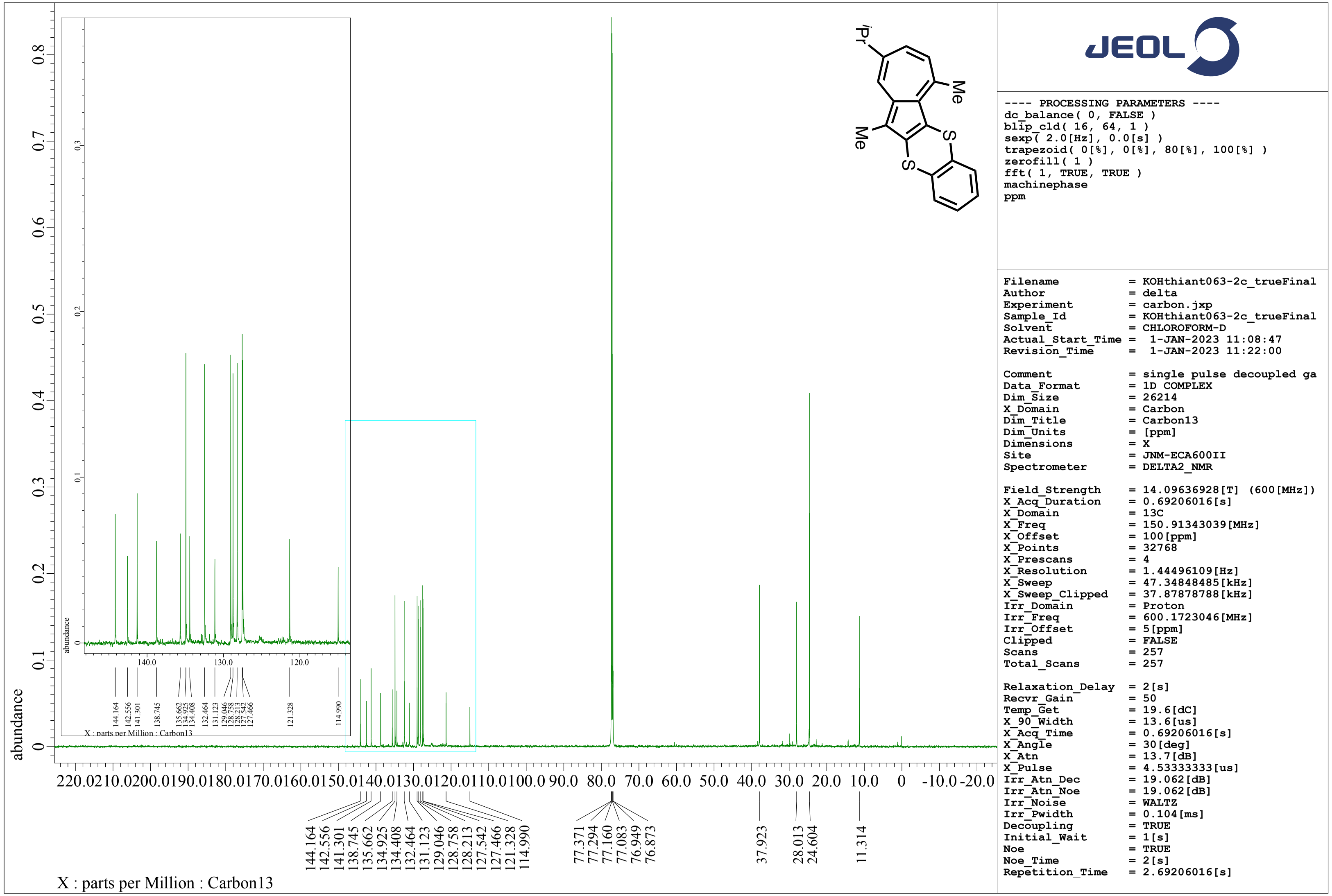
Filename            = KOHthian063-2c_TrueFinal_
Author              = delta
Experiment          = single_pulse.ex2
Sample_Id           = KOHthian063-2c_TrueFinal
Solvent             = TETRACHLOROETHANE-D2
Actual_Start_Time   =  1-JAN-2023 11:01:31
Revision_Time       = 10-FEB-2023 11:36:51

Comment             = $(SAMPLE.comment)
Data_Format         = 1D COMPLEX
Dim_Size            = 13107
X_Domain            = Proton
Dim_Title           = Proton
Dim_Units           = [ppm]
Dimensions          = X
Spectrometer        = JNM-ECZ400S/L1

Field_Strength      = 9.2982153[T] (400[MHz])
X_Acq_Duration      = 2.20725248[s]
X_Domain            = Proton
X_Freq              = 395.88430144[MHz]
X_Offset            = 5[ppm]
X_Points            = 16384
X_Prescans          = 1
X_Resolution        = 0.45305193[Hz]
X_Sweep             = 7.42280285[kHz]
X_Sweep_Clipped     = 5.93824228[kHz]
Irr_Domain          = Proton
Irr_Freq            = 395.88430144[MHz]
Irr_Offset          = 5[ppm]
Tri_Domain          = Proton
Tri_Freq            = 395.88430144[MHz]
Tri_Offset          = 5[ppm]
Blanking            = 2[us]
Clipped             = FALSE
Scans               = 32
Total_Scans         = 32

Relaxation_Delay    = 10[s]
Recvr_Gain          = 56
Temp_Get            = 19.8[dC]
X_90_Width          = 14.5[us]
X_Acq_Time          = 2.20725248[s]
X_Angle             = 45[deg]
X_Atn               = 7.5[dB]
X_Pulse             = 7.25[us]
Irr_Mode            = Off
Tri_Mode            = Off
Dante_Presat        = FALSE
Experiment_Path     = C:\Users\delta\Desktop\Oo
Initial_Wait        = 1[s]
Phase               = {0, 90, 270, 180, 180, 27
Repetition_Time     = 12.20725248[s]
```

Figure S42. ^{1}H NMR spectra of **3ja** (in $Cl_2CDCDCl_2$, 400 MHz)



```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
blip_cld( 16, 64, 1 )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Filename           = KOHthiant063-2c_trueFinal
Author             = delta
Experiment         = carbon.jxp
Sample_Id          = KOHthiant063-2c_trueFinal
Solvent            = CHLOROFORM-D
Actual_Start_Time  =  1-JAN-2023 11:08:47
Revision_Time      =  1-JAN-2023 11:22:00

Comment            = single pulse decoupled ga
Data_Format        = 1D COMPLEX
Dim_Size           = 26214
X_Domain           = Carbon
Dim_Title          = Carbon13
Dim_Units          = [ppm]
Dimensions         = X
Site               = JNM-ECA600II
Spectrometer       = DELTA2_NMR

Field_Strength     = 14.09636928[T] (600[MHz])
X_Acq_Duration     = 0.69206016[s]
X_Domain           = 13C
X_Freq             = 150.91343039[MHz]
X_Offset           = 100[ppm]
X_Points           = 32768
X_Prescans         = 4
X_Resolution       = 1.44496109[Hz]
X_Sweep            = 47.34848485[kHz]
X_Sweep_Clipped    = 37.87878788[kHz]
Irr_Domain         = Proton
Irr_Freq           = 600.1723046[MHz]
Irr_Offset         = 5[ppm]
Clipped            = FALSE
Scans              = 257
Total_Scans        = 257

Relaxation_Delay   = 2[s]
Recvr_Gain         = 50
Temp_Get           = 19.6[dC]
X_90_Width         = 13.6[us]
X_Acq_Time         = 0.69206016[s]
X_Angle            = 30[deg]
X_Atn              = 13.7[dB]
X_Pulse            = 4.53333333[us]
Irr_Atn_Dec        = 19.062[dB]
Irr_Atn_Noe        = 19.062[dB]
Irr_Noise          = WALTZ
Irr_Pwidth         = 0.104[ms]
Decoupling         = TRUE
Initial_Wait       = 1[s]
Noe                = TRUE
Noe_Time           = 2[s]
Repetition_Time    = 2.69206016[s]
```

Figure S43. ^{13}C NMR spectra of **3ja** (in $CDCl_3$, 150 MHz)