Supporting Information

Annulative π-Extension (APEX) of Heteroarenes with Dibenzosiloles and Dibenzogermoles by Palladium/*o*-chloranil Catalysis

Kyohei Ozaki[†], Wataru Matsuoka[†], Hideto Ito[*,†] and Kenichiro Itami[*,†,‡,#]

[†] *Graduate School of Science, Nagoya University, Chikusa, Nagoya 464-8602, Japan.*
[‡] *JST-ERATO, Itami Molecular Nanocarbon Project, Nagoya University, Chikusa, Nagoya 464-8602, Japan.*
[#] *Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University, Chikusa, Nagoya 464-8602, Japan.*

[*]E-mail: itami@chem.nagoya-u.ac.jp

[*]E-mail: ito.hideto@g.mbox.nagoya-u.ac.jp

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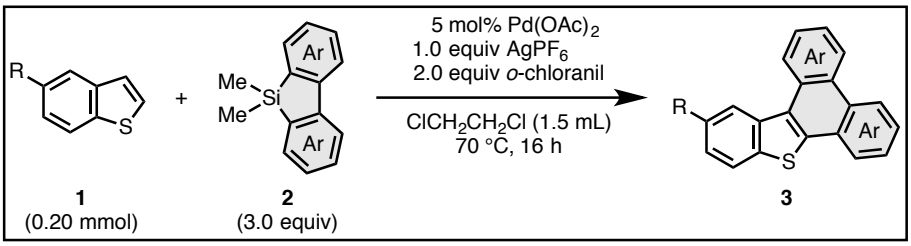
1. General

Unless otherwise noted, all materials including dry solvents were obtained from commercial suppliers and used without further purification. $Pd(OAc)_2$ was purchased from Wako. AgOTf was purchased from Wako and stored in glovebox filled by argon prior to use. $AgPF_6$ and $AgSbF_6$ were purchased from Aldrich and stored in glovebox filled by argon prior to use. *o*-Chloranil was purchased from TCI and recrystallized from benzene before use. Benzo[*b*]thiophene (**1a**) was purchased from Wako. 5-Bromobenzo[*b*]thiophene (**1d**) was purchased from TCI. 2,3-Benzofuran (**5**) was purchased from TCI and distilled before use. Benzo[*b*]thiophene derivatives (**1b**, **1c**, **1e**, **1f**)[1], 2,3-diphenylthiophene (**1g**)[2], 3-methoxy-2-(4-nitrophenyl)thiophene (**1h**)[3], *N*-tosylindole (**5**)[4], dibenzosiloles (**2a**[5a], **2b**[5a], **2c**[5b]), and dibenzogermole **2d**[6] were synthesized according to procedures reported in the literature. Unless otherwise noted, all reactions were performed with dry solvents under an atmosphere of nitrogen or argon 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 F_{254} precoated plates (0.25 mm). The developed chromatogram was analyzed by UV lamp (254 nm). Flash column chromatography was performed with 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. Preparative gel permeation chromatography (GPC) was performed with a JAI LC-9204 instrument equipped with JAIGEL-1H/JAIGEL-2H columns using chloroform as an eluent. Gas chromatography (GC) analysis was conducted on a Shimadzu GC-2010 instrument equipped with a HP-5 column (30 m × 0.25 mm, Hewlett-Packard). The developed chromatogram was analyzed by UV lamp (254 nm and 365 nm). High-resolution mass spectra (HRMS) were obtained from a JMS-T100TD instrument (DART). Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL ECS-600 (^{1}H 600 MHz, ^{13}C 150 MHz, ^{19}F 565 MHz) spectrometer and a 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). Chemical shifts for ^{13}C NMR are expressed in ppm relative to $CDCl_3$ (δ 77.0 ppm) or CD_2Cl_2 (δ 53.84 ppm). Chemical shifts for ^{19}F NMR are expressed in parts per million (ppm) relative to hexafluorobenzene (δ −162.00 ppm) as an external standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), and integration.

2. Annulative π-Extension of Heteroarenes

2-1. General procedure

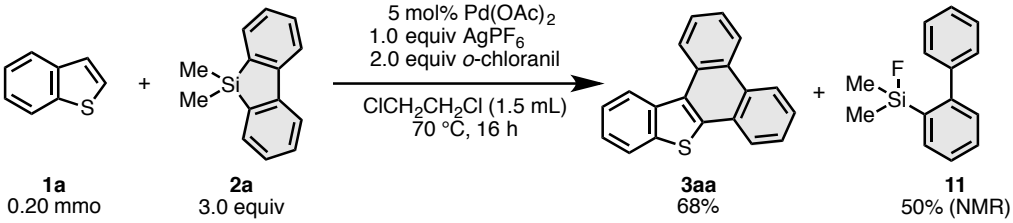


In the glovebox, to a screw cap glass tube containing a magnetic stirrer bar was added $AgPF_6$ (51 mg, 0.20 mmol, 1.0 equiv). The vessel was taken out of the glovebox, then to this were added benzo[*b*]thiophene (**1a**) (0.20 mmol, 1.0 equiv), dibenzosilole **2** (0.60 mmol, 3.0 equiv), $Pd(OAc)_2$ (2.2 mg, 10 μmol, 5 mol%), *o*-chloranil (98 mg, 0.40 mmol, 2.0 equiv), and 1,2-dichloroethane (1.5 mL) under a stream of nitrogen. After stirring for 16 h at 70 °C, the reaction mixture was cooled to room temperature, and then passed through a short pad of silica gel (eluent: hexane/CH_2Cl_2 = 1:1). After the organic solvent was removed under reduced pressure, the residue was purified by PTLC to yield π-extended benzo[*b*]thiophenes.

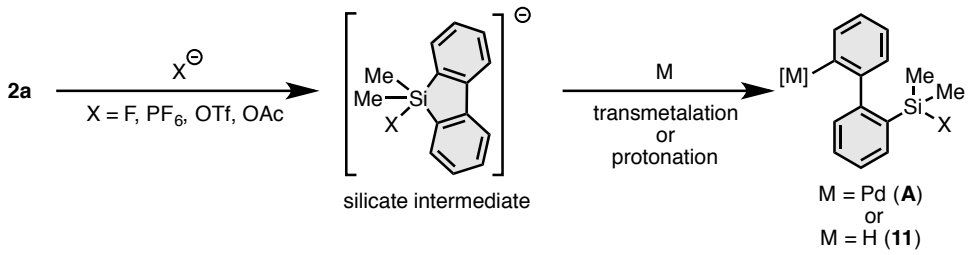
2-2. Further mechanistic considerations

Transmetalation of palladium catalyst with dibenzosilole.

Prior to carbopalladation of biphenyl palladium intermediate **A**, transmetalation of dibenzosiloles with palladium(II) must occur.[7] It is worth to note that the formation of significant amount of hydrofluorinated by-product **11** derived from dibenzosilole **2a** was observed in ^{1}H and ^{19}F NMR spectra, and the mass spectrum analysis after the APEX of **1a** under the conditions shown in entry 13 of Table 1 (Scheme S1). As well known in the transmetalation step in Hiyama coupling of aryl halides and arylsilanes[8], the transmetalation of dibenzosilole could also occurred *via* (i) addition of anion such as F^- (PF_6^-, OTf^-, and AcO^- also have potential) to a silicon atom to provide a silicate intermediate, followed by (ii) electrophilic palladation (Scheme S2). Furthermore, by-product **11** is expected to be formed by the protonation of a silicate intermediate.

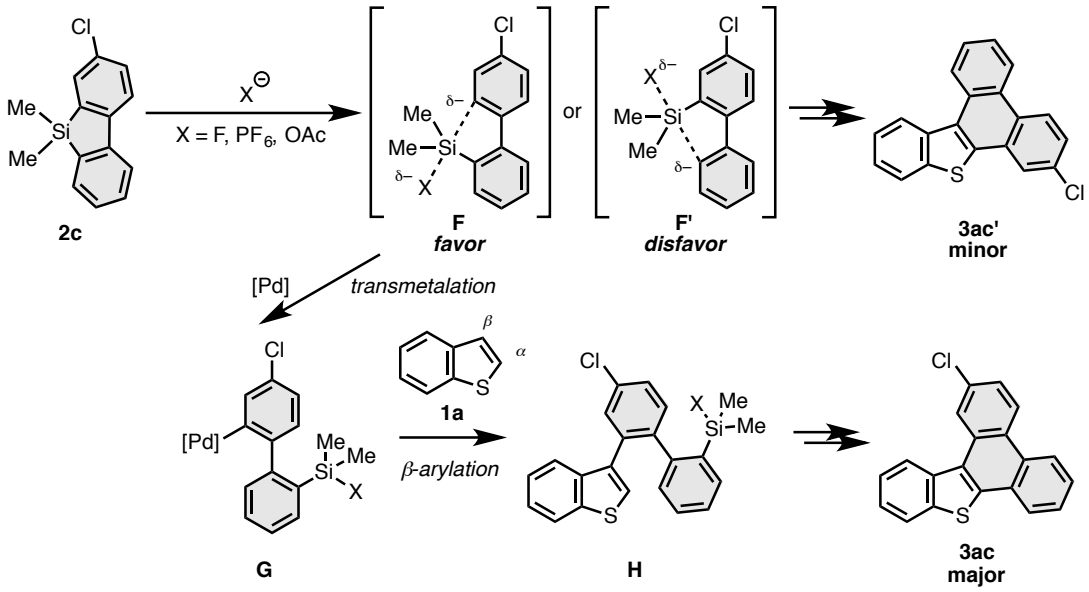


Scheme S1. APEX of benzo[*b*]thiophene (**1a**) accompanied with fluoride adduct **11**.



Scheme S2. Possible mechanism in the transmetalation and hydrofluorination steps of dibenzosiloles **2a**.

The result of APEX reaction of **1a** with monochloro-substituted dibenzosilole **2c** described in Table 2 in the main manuscript well supports the above mechanism. The selectivity in the formation of regioisomers **3ac** and **3ac'** would be determined in the transmetalation of palladium with a silicate intermediate. Preference of cleaving C(sp^2)–Si bond can be explained as follows; a sp^2-carbon on the chloro-substituted benzene ring more easily charges negatively due to an electron-withdrawing chloro substituent (**F**) than a sp^2-carbon on the other benzene ring (**F'**). Thus the transmetalation (palladation) could occur on the chloro-substituted benzene ring, which can lead to the selective formation of **3ac** through the subsequent β-arylation of benzothiophene **1a** by biphenyl palladium **G** and the intramolecular α-arylation events in intermediate **H** (Scheme S3).

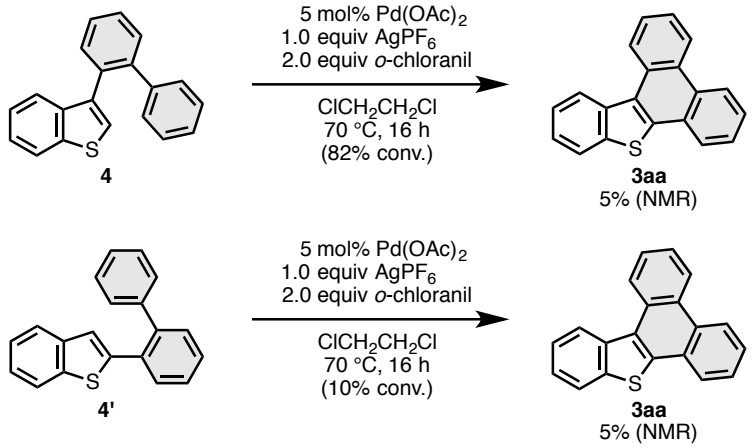


Scheme S3. Possible catalytic cycle for Pd-catalyzed APEX reaction of **1a** with dibenzosilole **2c**.

Consideration of alternative possible reaction pathways to APEX product

Encouraged by the result that β-biphenylbenzo[*b*]thiophene (**4**) was obtained in the APEX reaction of **1a** with dibenzosilole **2a** in the presence of DTBQ (Table 1 in the main manuscript, entry 10), experiments on another possible reaction pathways were also examined (Scheme S4). The both

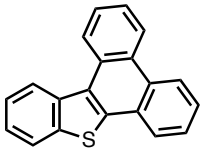
reactions of β- and α-biphenylbenzo[*b*]thiophene (**4**) and (**4'**), which are potent by-products in the current APEX, gave the cyclodehydrogenation product **3aa** only in 5% yields along with considerable decomposition of the starting material in the case of the reaction of **4**. Hence these cyclodehydrogenations are scarcely incorporated as an alternative pathway.



Scheme S4. Cyclodehydrogenative coupling of biphenylbenzotiophenes **4** and **4'** under the standard reaction conditions.

2-3. Compound data

Benzo[*b*]phenanthro[9,10-*d*]thiophene (3aa)



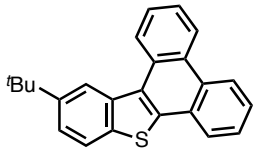
PTLC: hexane/CH_2Cl_2 = 15:1, Yield: 39.0 mg, 68%, white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.02 (d, *J* = 8.2 Hz, 1H), 8.81 (d, *J* = 8.9 Hz, 1H), 8.80 (d, *J* = 9.6 Hz, 1H), 8.71 (dd, *J* = 8.2, 0.8 Hz, 1H), 8.18 (dd, *J* = 7.6, 1.4 Hz, 1H), 8.02 (d, *J* = 7.9 Hz, 1H), 7.76 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.70–7.64 (m, 3H), 7.58 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.49 (ddd, *J* = 7.8, 6.6, 1.2 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 139.2, 138.3, 137.6, 129.9, 129.6, 129.4, 128.0 (2C), 127.32, 127.29 (2C), 125.6, 125.2, 125.1, 125.0, 124.7, 123.9, 123.8, 123.4, 123.2.

HRMS (DART, ESI$^+$) *m/z* calcd for $C_{20}H_{13}S$ $[M+H]^+$: 285.0738, found: 285.0734.

12-(*tert*-Butyl)benzo[*b*]phenanthro[9,10-*d*]thiophene (3ba)



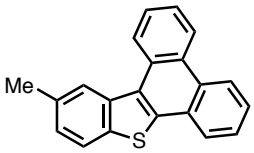
PTLC: hexane/CH_2Cl_2 = 15:1, Yield: 34.6 mg, 51%, white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.01 (d, *J* = 8.4 Hz, 1H), 8.82 (d, *J* = 1.8 Hz, 1H), 8.78 (d, *J* = 7.8 Hz, 1H), 8.69 (d, *J* = 8.4 Hz, 1H), 8.15 (dd, *J* = 7.2, 1.8 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.78 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.69–7.61 (m, 3H), 7.57 (dd, *J* = 8.4, 1.8 Hz, 1H), 1.53 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 148.0, 138.7, 137.7, 136.3, 130.0, 129.7, 129.3, 128.15, 128.12, 127.3, 127.2, 127.1, 125.4, 125.1, 123.85, 123.79, 123.4, 123.3, 122.6, 121.0, 35.1, 31.8.

HRMS (DART, ESI$^+$) *m/z* calcd for $C_{24}H_{21}S$ $[M+H]^+$: 341.1364, found: 341.1353.

12-Methylbenzo[*b*]phenanthro[9,10-*d*]thiophene (3ca)



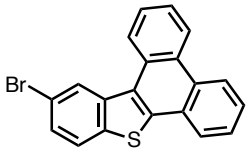
PTLC: hexane/CH_2Cl_2 = 15:1, Yield: 25.1 mg, 42%, white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.04 (d, *J* = 8.3 Hz, 1H), 8.81 (d, *J* = 8.3 Hz, 1H), 8.73 (d, *J* = 7.6 Hz, 1H), 8.63 (s, 1H), 8.18 (dd, *J* = 7.2, 1.0 Hz, 1H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.79 (ddd, *J* = 8.4, 7.2, 1.8 Hz, 1H), 7.71–7.64 (m, 3H), 7.33 (dd, *J* = 7.8, 0.7 Hz, 1H), 2.64 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 138.7, 137.9, 136.3, 134.6, 130.0, 129.6, 129.4, 128.1, 127.8, 127.3, 127.23, 127.18, 126.7, 125.5, 125.1, 124.9, 124.0, 123.8, 123.4, 122.8, 22.1.

HRMS (DART, ESI$^+$) *m/z* calcd for $C_{21}H_{15}S$ $[M+H]^+$: 299.0895, found: 299.0884.

12-Bromobenzo[*b*]phenanthro[9,10-*d*]thiophene (3da)



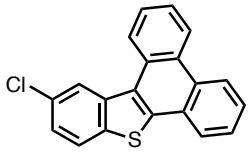
PTLC: hexane/CH_2Cl_2 = 15:1, Yield: 18.3 mg, 25%, white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.95 (d, *J* = 1.7 Hz, 1H), 8.91 (d, *J* = 7.6 Hz, 1H), 8.82 (d, *J* = 8.3 Hz, 1H), 8.74 (d, *J* = 8.3 Hz, 1H), 8.18 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.81 (ddd, *J* = 8.4, 6.6, 1.2 Hz, 1H), 7.75–7.67 (m, 3H), 7.60 (dd, *J* = 8.4, 1.8 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 139.6, 139.3, 137.8, 129.7 (2C), 129.6, 128.1, 127.8, 127.7, 127.6, 127.5, 127.4, 127.1, 126.0, 125.2, 124.4, 123.9, 123.7, 123.5, 119.1.

HRMS (DART, ESI$^+$) *m/z* calcd for $C_{20}H_{12}BrS$ $[M+H]^+$: 362.9843, found: 362.9830.

12-Chlorobenzo[*b*]phenanthro[9,10-*d*]thiophene (3ea)



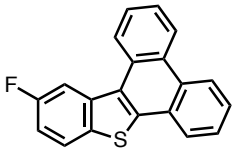
PTLC: hexane/CH_2Cl_2 = 15:1, Yield: 23.1 mg, 36%, white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.90 (d, *J* = 7.8 Hz, 1H), 8.81 (d, *J* = 8.4 Hz, 1H), 8.78 (s, 1H), 8.73 (d, *J* = 8.4 Hz, 1H), 8.17 (d, *J* = 7.8 Hz, 1H), 7.93 (d, *J* = 9.0 Hz, 1H), 7.79 (t, *J* = 8.4 Hz, 1H), 7.74–7.66 (m, 3H), 7.47 (dd, *J* = 8.4, 1.8 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 139.7, 138.8, 137.3, 131.2, 129.64 (2C), 129.56, 127.7 (2C), 127.6, 127.5, 127.2, 125.9, 125.4, 125.2, 124.5, 124.0, 123.9, 123.7, 123.5.

HRMS (DART, ESI$^+$) *m/z* calcd for $C_{20}H_{12}ClS$ $[M+H]^+$: 319.0348, found: 319.0341.

12-Fluorobenzo[*b*]phenanthro[9,10-*d*]thiophene (3fa)



PTLC: hexane/CH_2Cl_2 = 15:1, Yield: 13.5 mg, 22%, white solid.

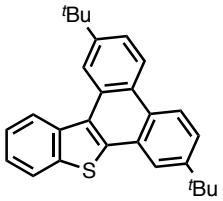
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.87 (d, *J* = 7.8 Hz, 1H), 8.81 (d, *J* = 8.2 Hz, 1H), 8.73 (d, *J* = 8.2 Hz, 1H), 8.48 (dd, $^3J_{H–F}$ = 11.4 Hz, *J* = 2.4 Hz, 1H), 8.17 (dd, *J* = 7.8, 0.6 Hz, 1H), 7.94 (dd, *J* = 8.9 Hz, $^4J_{H–F}$ = 5.3 Hz, 1H), 7.78 (ddd, *J* = 7.8, 6.6, 0.6 Hz, 1H), 7.73–7.66 (m, 3H), 7.28–7.24 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 161.2 (d, $^1J_{C–F}$ = 240.0 Hz), 140.3, 138.6 (d, $^3J_{C–F}$ = 8.7 Hz), 134.4, 129.64, 129.58 (2C), 127.9, 127.7, 127.6, 127.5, 127.4, 125.8, 125.2, 124.0 (d, $^3J_{C–F}$ = 10.0 Hz), 123.9, 123.5, 123.4, 113.5 (d, $^2J_{C–F}$ = 24.5 Hz), 111.0 (d, $^2J_{C–F}$ = 24.5 Hz).

^{19}F NMR (564 MHz, $CDCl_3$) δ −117.3.

HRMS (DART, ESI$^+$) *m/z* calcd for $C_{20}H_{12}FS$ $[M+H]^+$: 303.0644, found: 303.0640.

2,7-Di-*tert*-butylbenzo[*b*]phenanthro[9,10-*d*]thiophene (3ab)



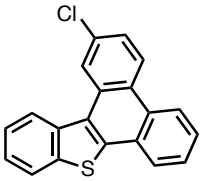
PTLC: hexane/CH_2Cl_2 = 15:1, Yield: 22.4 mg, 28%, white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.02 (d, *J* = 1.7 Hz, 1H), 8.82 (d, *J* = 8.2 Hz, 1H), 8.71 (d, *J* = 8.9 Hz, 1H), 8.63 (d, *J* = 8.6 Hz, 1H), 8.12 (d, *J* = 2.0 Hz, 1H), 8.04 (d, *J* = 7.9 Hz, 1H), 7.75 (dd, *J* = 8.9, 2.0 Hz, 2H), 7.61 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 1.57 (s, 9H), 1.51 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 150.0, 149.7, 139.3, 138.6, 137.9, 129.6, 128.3, 127.5, 127.4, 127.2, 125.6, 125.0, 124.9, 124.5, 123.7, 123.4, 123.3, 123.1, 120.8, 120.0, 35.2, 35.0, 31.6, 31.4.

HRMS (DART, ESI$^+$) *m/z* calcd for $C_{28}H_{28}S$ $[M]^+$: 396.1912, found: 396.1913.

2-Chlorobenzo[*b*]phenanthro[9,10-*d*]thiophene (3ac)



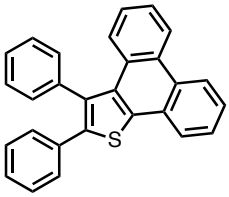
PTLC: hexane/CH_2Cl_2 = 15:1, Yield: 24.0 mg, 38% as a mixture of **3ac** and **3ac'** (78:22), white solid. **3ac** was isolated by recrystallization ($CHCl_3$/hexane), and identified by ^{1}H and ^{13}C NMR comparing with NMR spectra of the mixture of **3ac** and **3ac'**.

^{1}H NMR of **3ac** (600 MHz, $CDCl_3$) δ 8.98 (d, *J* = 2.4 Hz, 1H), 8.75 (d, *J* = 8.4 Hz, 1H), 8.73 (d, *J* = 8.4 Hz, 1H), 8.68–8.65 (m, 1H), 8.21–8.18 (m, 1H), 8.04 (dd, *J* = 7.8, 0.6 Hz, 1H), 7.73–7.67 (m, 2H), 7.67–7.61 (m, 2H), 7.53 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 139.5, 139.1, 137.1, 133.4, 130.8, 128.8, 128.0, 127.9, 127.6 (2C), 126.9, 125.9, 125.4, 125.3, 125.2 (2C), 124.3, 123.4, 123.29, 123.28.

HRMS (DART, ESI$^+$) *m/z* calcd for $C_{20}H_{12}ClS$ $[M+H]^+$: 319.0348, found: 319.0345.

2,3-Diphenylphenanthro[9,10-*b*]thiophene (3ga)



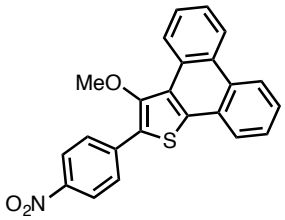
PTLC: hexane/CH_2Cl_2 = 10:1, Yield: 38.6 mg, 50%, white solid.

^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.74–8.69 (m, 2H), 8.25–8.22 (m, 1H), 7.68–7.65 (m, 2H), 7.56 (dd, *J* = 8.4, 0.7 Hz, 1H), 7.53 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.49–7.46 (m, 3H), 7.43–7.41 (m, 2H), 7.34–7.31 (m, 2H), 7.26–7.23 (m, 3H), 7.22 (ddd, *J* = 9.0, 7.2, 1.8 Hz, 1H).

^{13}C NMR (150 MHz, CD_2Cl_2) δ 139.8, 138.8, 137.3, 136.8, 134.8, 133.9, 131.2, 130.3, 130.2, 129.9, 129.4, 128.8, 128.6, 128.32, 128.26, 127.9, 127.8, 127.0, 126.6, 126.0, 125.0, 124.4, 123.91, 123.87.

HRMS (DART, ESI$^+$) *m/z* calcd for $C_{28}H_{19}S$ $[M+H]^+$: 387.1208, found: 387.1207.

3-Methoxy-2-(4-nitrophenyl)phenanthro[9,10-*b*]thiophene (3ha)



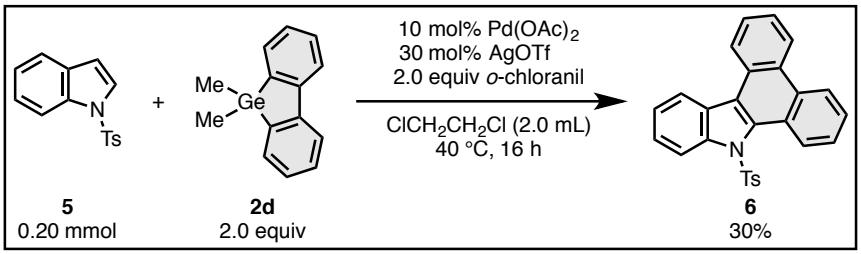
PTLC: hexane/CH_2Cl_2 = 1:1, Yield: 27.7 mg, 36%, yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.04 (d, *J* = 7.2 Hz, 1H), 8.74 (d, *J* = 8.4 Hz, 1H), 8.70 (d, *J* = 7.2 Hz, 1H), 8.34 (d, *J* = 9.6 Hz, 2H), 8.18–8.11 (m, 3H), 7.75–7.63 (m, 4H), 3.89 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 154.0, 146.4, 139.6, 135.2, 129.4, 129.1, 128.4, 127.8, 127.53, 127.48, 127.41, 127.3, 126.5, 124.6, 124.3, 123.8, 123.7, 123.4, 123.1, 60.8. One carbon peak is overlapped.

HRMS (APCI$^+$) *m/z* calcd for $C_{23}H_{15}NO_3S$ $[M+Na]^+$: 408.0665, found: 408.0660.

9-Tosyl-9*H*-dibenzo[*a*,*c*]carbazole (6)



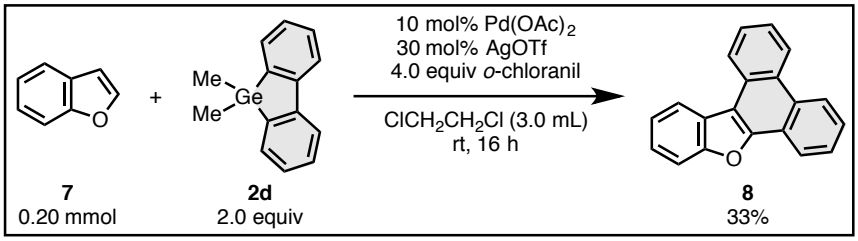
In the glovebox, to a screw cap glass tube containing a magnetic stirrer bar was added AgOTf (15 mg, 60 μmol, 30 mol%). The vessel was taken out of the glovebox, then to this were added *N*-tosylindole (**5**) (54.3 mg, 0.20 mmol, 1.0 equiv), dimethyldibenzogermole (**2d**) (102 mg, 0.40 mmol, 2.0 equiv), $Pd(OAc)_2$ (4.5 mg, 20 μmol, 10 mol%), *o*-chloranil (98 mg, 0.40 mmol, 2.0 equiv), and 1,2-dichloroethane (2.0 mL) under a stream of nitrogen. After stirring for 16 h at 40 °C, the reaction mixture was cooled to room temperature, and then passed through a short pad of silica gel (eluent: hexane/Et_2O = 1:1). After the organic solvent was removed under reduced pressure, the residue was purified by PTLC (hexane/Et_2O = 4:1) to afford 9-tosyl-9*H*-dibenzo[*a*,*c*]carbazole (**6**) (25.1 mg, 30%) as a white solid.

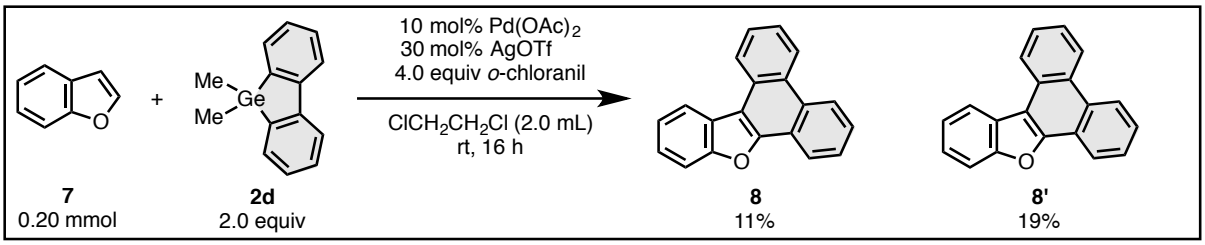
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.98–8.95 (m, 1H), 8.82–8.78 (m, 1H), 8.74–8.72 (m, 1H), 8.55–8.53 (m, 1H), 8.41 (d, *J* = 8.2 Hz, 1H), 8.16 (d, *J* = 7.9 Hz, 1H), 7.76–7.66 (m, 4H), 7.46 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.41 (td, *J* = 7.1, 1.0 Hz, 1H), 6.83 (d, *J* = 8.2 Hz, 2H), 6.67 (d, *J* = 7.9 Hz, 2H), 2.07 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 144.2, 142.0, 136.9, 131.0, 130.7, 130.6, 130.1, 128.7, 128.4, 127.6, 127.2, 127.0, 126.9, 126.3, 126.1, 125.91, 125.85, 125.6, 124.2, 124.0, 123.7, 122.8, 121.8, 119.9, 21.3.

HRMS (DART, ESI$^+$) *m/z* calcd for $C_{27}H_{19}NO_2S$ $[M]^+$: 421.1137, found: 421.1152.

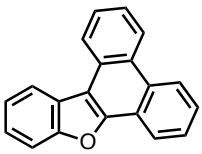
Phenanthro[9,10-*b*]benzofuran (8)





In the glovebox, to a screw cap glass tube containing a magnetic stirrer bar was added AgOTf (15 mg, 60 μmol, 30 mol%). The vessel was taken out of the glovebox, then to this were added benzofuran (**7**) (24 mg, 0.20 mmol, 1.0 equiv), dimethyldibenzogermole (**2d**) (102 mg, 0.40 mmol, 2.0 equiv), $Pd(OAc)_2$ (4.5 mg, 20 μmol, 10 mol%), and 1,2-dichloroethane (1.0 mL) under a stream of nitrogen. Then, a 0.40 M solution of *o*-chloranil in 1,2-dichloroethane (2.0 mL, 0.80 mmol, 4.0 equiv) was slowly added by using syringe pump (rate: 0.50 mL/h) with stirring at room temperature. After 16 h, the reaction mixture was passed through a short pad of silica gel (eluent: hexane/CH_2Cl_2 = 1:1). After the organic solvent was removed under reduced pressure, the residue was purified by PTLC (hexane /CH_2Cl_2 = 15:1) to afford phenanthro[9,10-*b*]benzofuran (**8**) (17.8 mg, 33%) as a white solid. The reaction using a 0.40 M *o*-cholranil solution in 1,2-dichloroehane (1.0 mL, 0.40 mmol, 2.0 equiv) under the same reaction conditions and the purification by flash column chromatography on silica gel (eluent: hexane/CH2Cl2 = 100:0 to 5:1) gave phenanthro[9,10-*b*]benzofuran (**8**) (10.0 mg, 19%) and *cis*-8*b*,13*b*-dihydrophenanthro[9,10-*b*]benzofuran (**8'**) (12.3 mg, 23%). The colorless needle crystalline of **8'** was obtained by the recrystallization from $CHCl_3$/pentane. The structure of **8'** was confirmed by the X-ray crystallographic analysis (Figure S2 and Table S1).

Phenanthro[9,10-*b*]benzofuran (8)

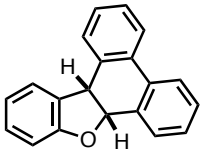


^{1}H NMR (600 MHz, $CDCl_3$) δ 8.79 (d, *J* = 7.8 Hz, 1H), 8.77–8.74 (m, 1H), 8.65 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.53–8.50 (m, 1H), 8.40–8.38 (m, 1H), 7.80–7.70 (m, 4H), 7.68 (ddd, *J* = 7.8, 6.6, 1.2 Hz, 1H), 7.52–7.46 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 155.8, 151.2, 130.5, 128.5, 128.2, 127.4, 127.15, 127.08, 125.6, 125.4, 125.1, 124.1, 123.8, 123.41, 123.35, 122.2, 121.74, 121.68, 114.3, 112.0.

HRMS (DART, ESI$^+$) *m/z* calcd for $C_{20}H_{13}O$ $[M+H]^+$: 269.0966, found: 269.0959.

***cis*-8*b*,13*b*-Dihydrophenanthro[9,10-*b*]benzofuran (8')**



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91–7.88 (m, 1H), 7.85 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.68 (dd, *J* = 7.3, 0.7 Hz, 1H), 7.49–7.47 (m, 1H), 7.39 (td, *J* = 7.1, 1.2 Hz, 1H), 7.36–7.32 (m, 3H), 7.25 (d, *J* = 6.2 Hz, 1H), 7.11 (t, *J* = 7.9 Hz, 1H), 6.86 (td, *J* = 7.6, 1.0 Hz, 1H), 6.82 (d, *J* = 7.9 Hz, 1H), 5.99 (d, *J* = 8.6 Hz, 1H), 4.74 (d, *J* = 8.9 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 158.7, 132.6, 132.4, 131.8, 131.3, 130.5, 129.6 (2C), 129.3, 128.4, 128.23, 128.19, 127.7, 124.7, 123.6, 123.0, 120.9, 110.0, 81.9, 44.4.

HRMS (DART, ESI$^+$) *m/z* calcd for $C_{20}H_{15}O$ $[M+H]^+$: 271.1123, found: 271.1115.

3. X-ray crystallographic analysis of 3da and 8'

Recrystallization of **3da** and **8'** from $CHCl_3$/*n*-pentane yielded colorless crystals of **3da** and **8'** suitable for X-ray crystal structure analysis. Details of the crystal data and a summary of the intensity data collection parameters for **3da** and **8'** are listed in Table S1. A suitable crystal was mounted with mineral oil on a glass fiber and transferred to the goniometer of a Rigaku PILATUS diffractometer. Graphite-monochromated Mo Kα radiation (λ = 0.71075 Å) was used. The structures were solved by direct methods with (SIR-97)[9] and refined by full-matrix least-squares techniques against F^2 (SHELXL-2014/3)[10] by using Yadokari-XG software package.[11] The intensities were corrected for Lorentz and polarization effects. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions. CCDC 1534024, 1534025 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.

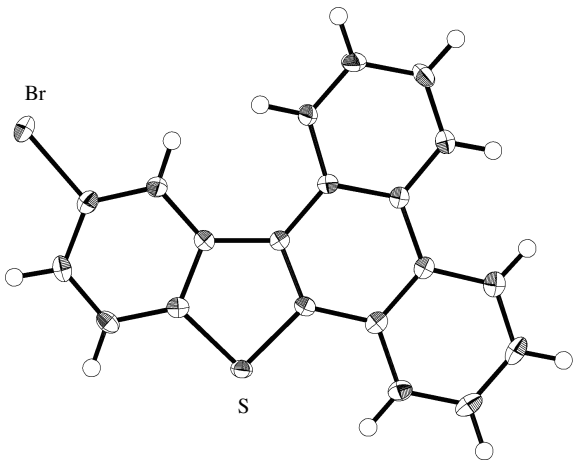


Figure S1. ORTEP drawing of 12-bromobenzo[*b*]phenanthro[9,10-*d*]thiophene (**3da**) with 50% thermal ellipsoid.

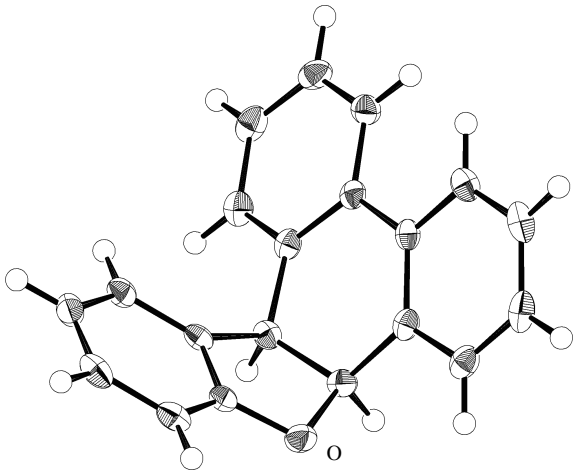


Figure S2. ORTEP drawing of intermediate **8'** with 50% thermal ellipsoid.

Table S1. Crystallographic data and structure refinement details for **3da** and **8'**.

	3da	**8'**
CCDC deposition number	1534025	1534024
formula	$C_{20}H_{11}BrS$	$C_{20}H_{14}O$
fw	363.26	270.31
T (K)	123(2)	123(2)
λ (Å)	0.71075	0.71075
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a (Å)	5.1414(5)	4.6243(8)
b (Å)	15.2261(18)	15.592(3)
c (Å)	18.358(2)	18.442(4)
α (deg)	90	90
β (deg)	97.590(3)	95.480(4)
γ (deg)	90	90
V (Å^3)	1424.5(3)	1323.6(4)
Z	4	4
D_{calc} (g / cm^3)	1.694	1.356
μ (mm^{-1})	3.024	0.082
F(000)	728	568
cryst size (mm)	0.25 × 0.10 × 0.05	0.20 × 0.05 × 0.03
2θ range, (deg)	3.489 – 25.000°	3.429 – 24.998°
reflns collected	10270	9428
indep reflns/R_{int}	2479/0.0213	2337/0.0193
params	199	190
GOF on F^2	1.037	1.034
R_1, wR_2 [$I>2\sigma(I)$]	0.0212, 0.0544	0.0321, 0.0757
R_1, wR_2 (all data)	0.0271, 0.0569	0.0439, 0.0819

4. References

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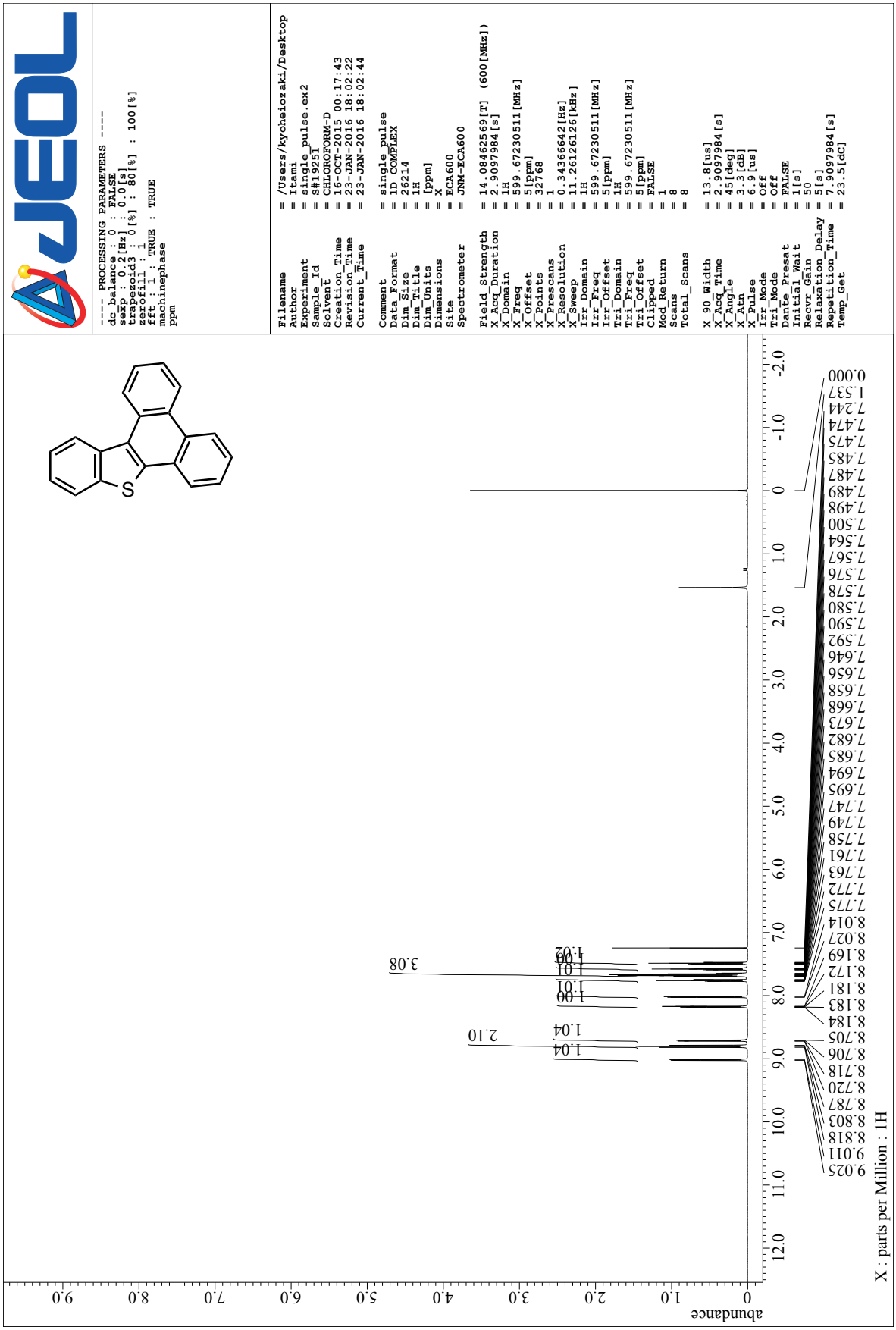
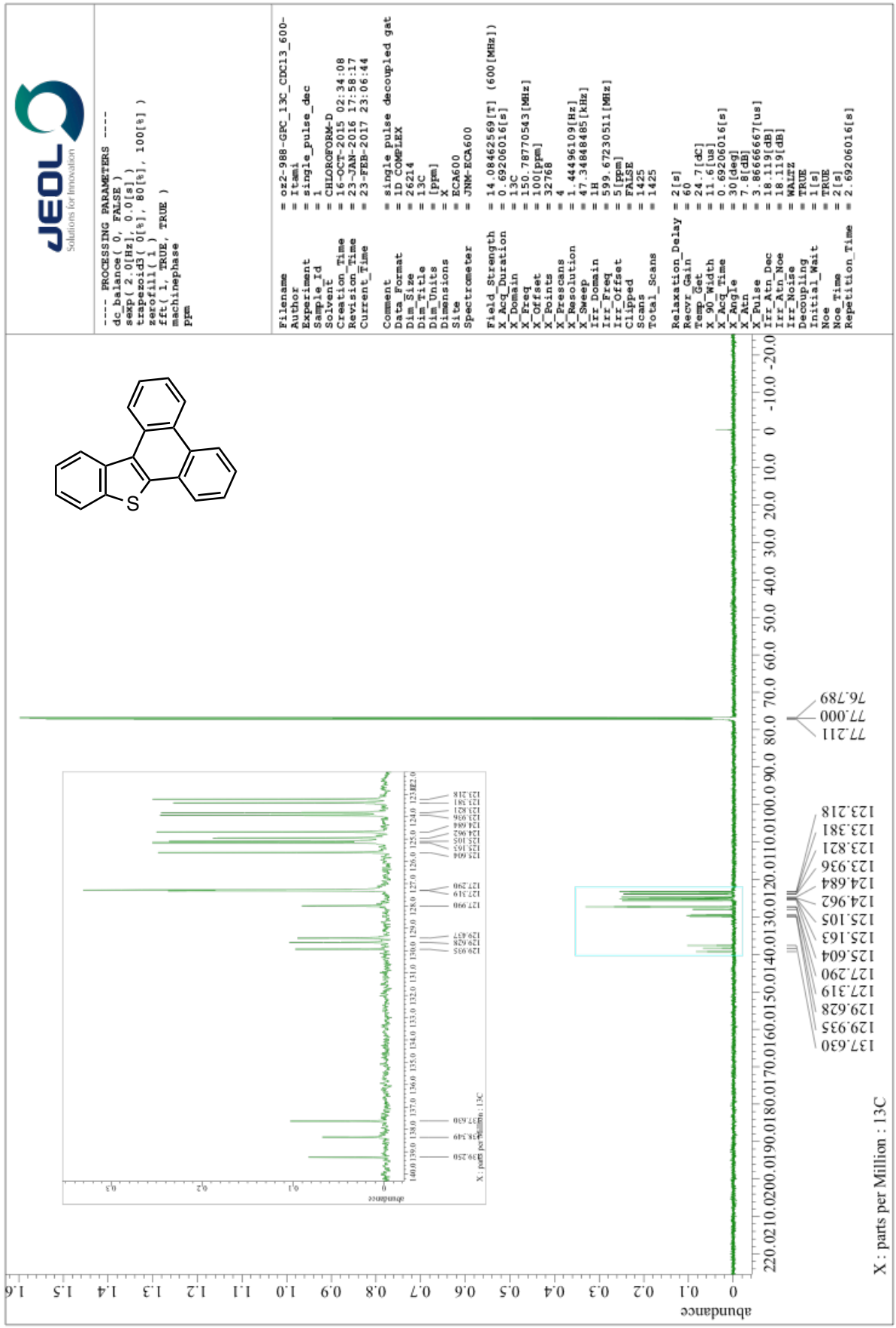
5. ^{1}H and ^{13}C NMR Spectra of Products

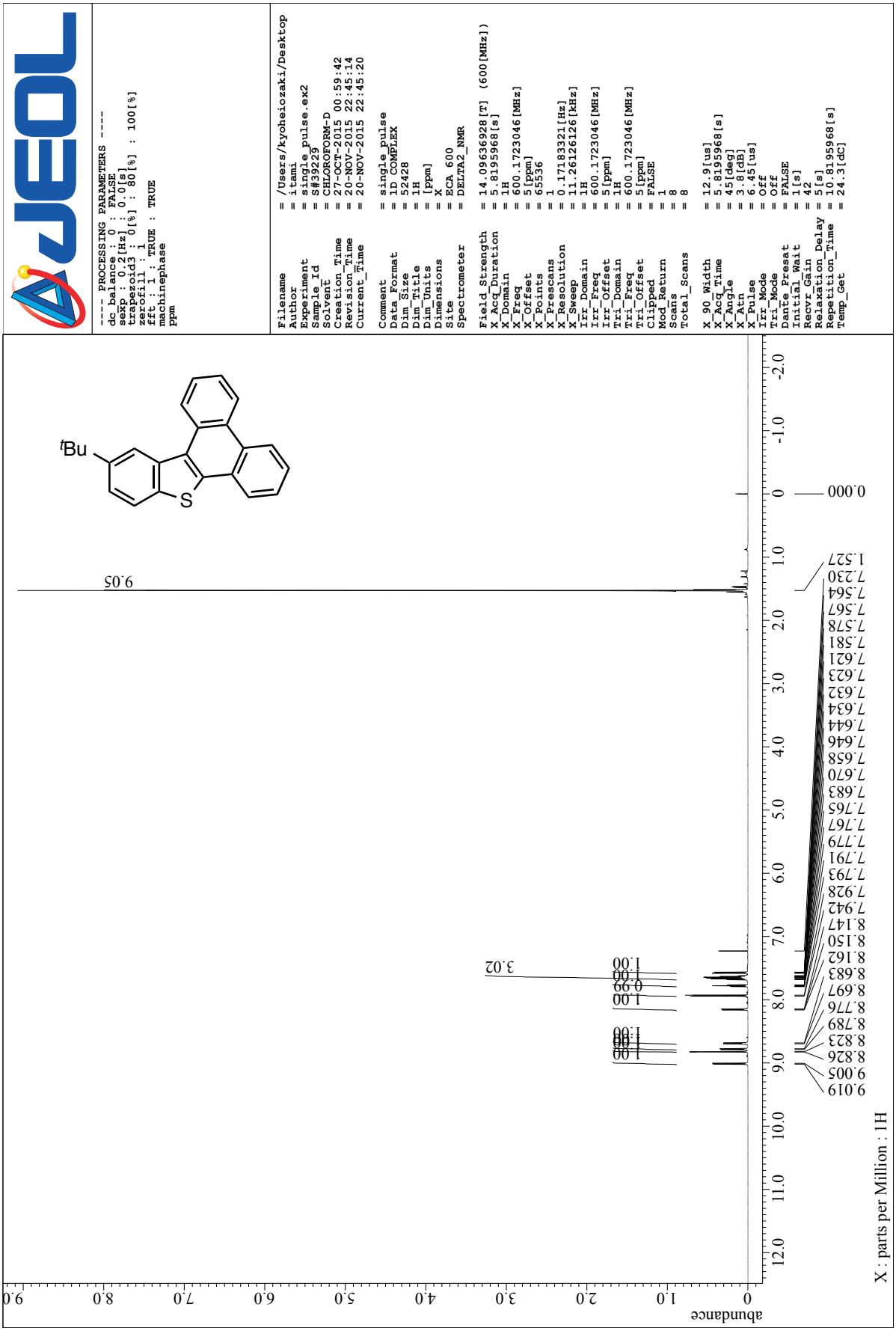
^{1}H NMR (600 MHz, $CDCl_3$) of 3aa



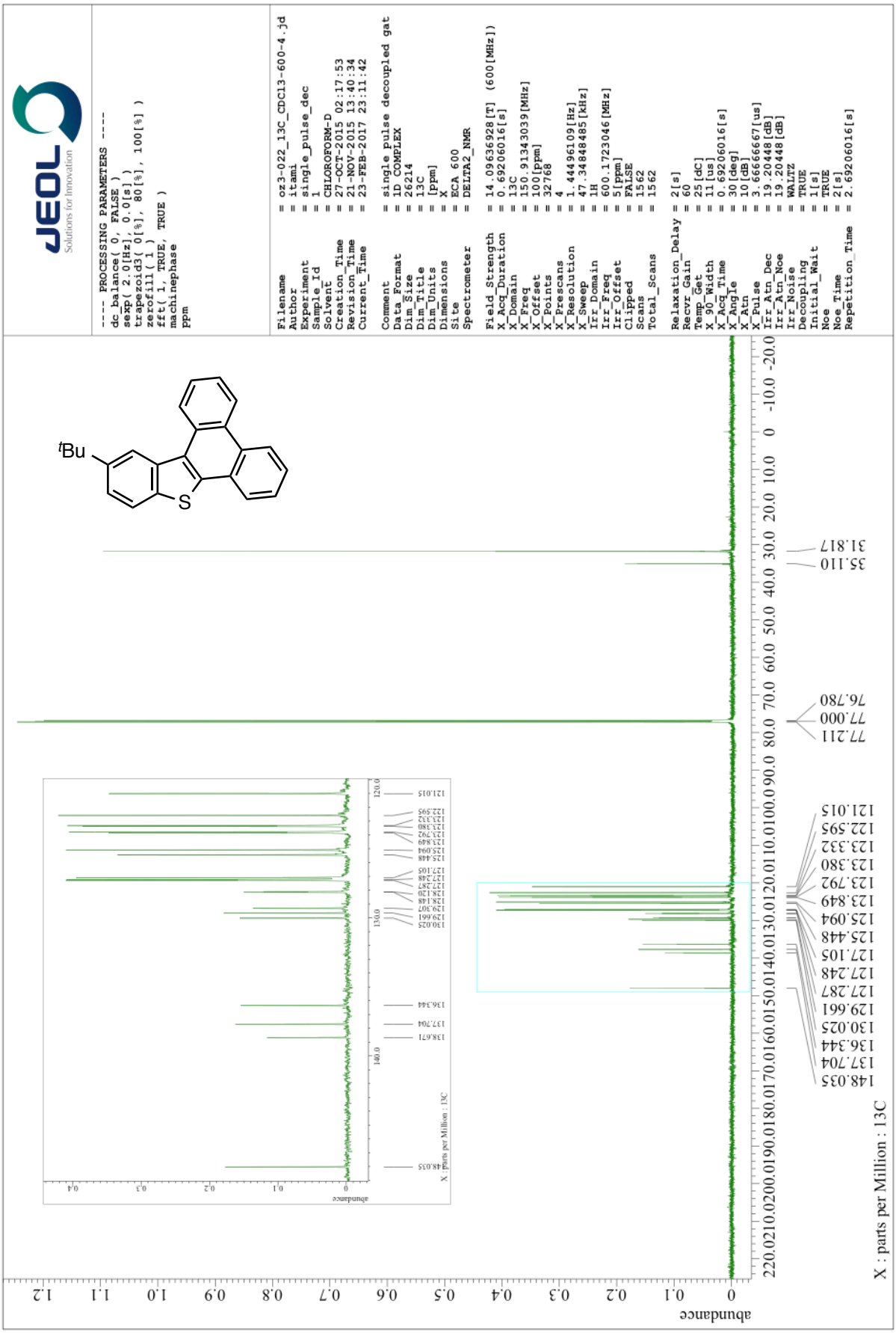
^{13}C NMR (150 MHz, $CDCl_3$) of 3aa



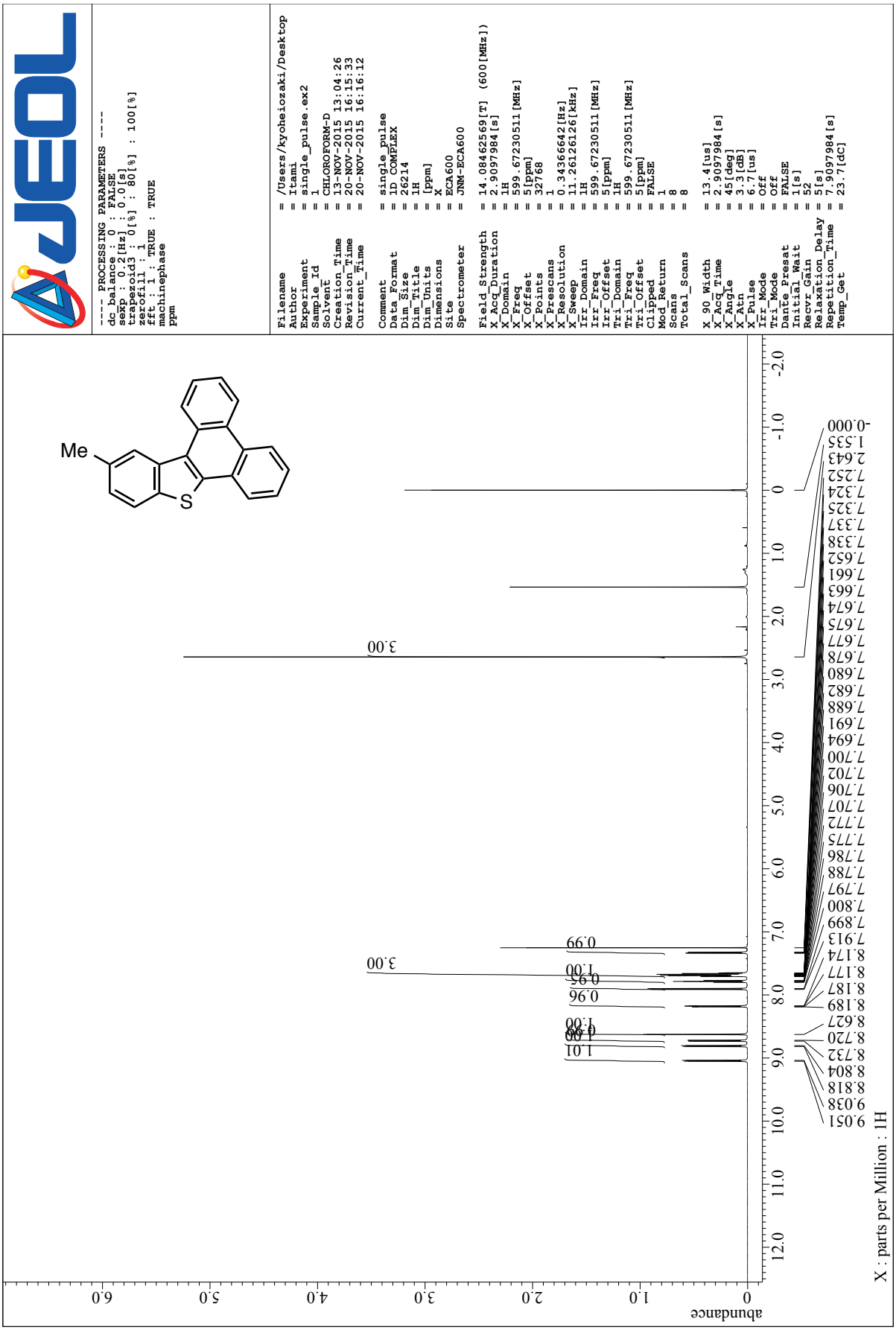
^{1}H NMR (600 MHz, $CDCl_3$) of 3ba



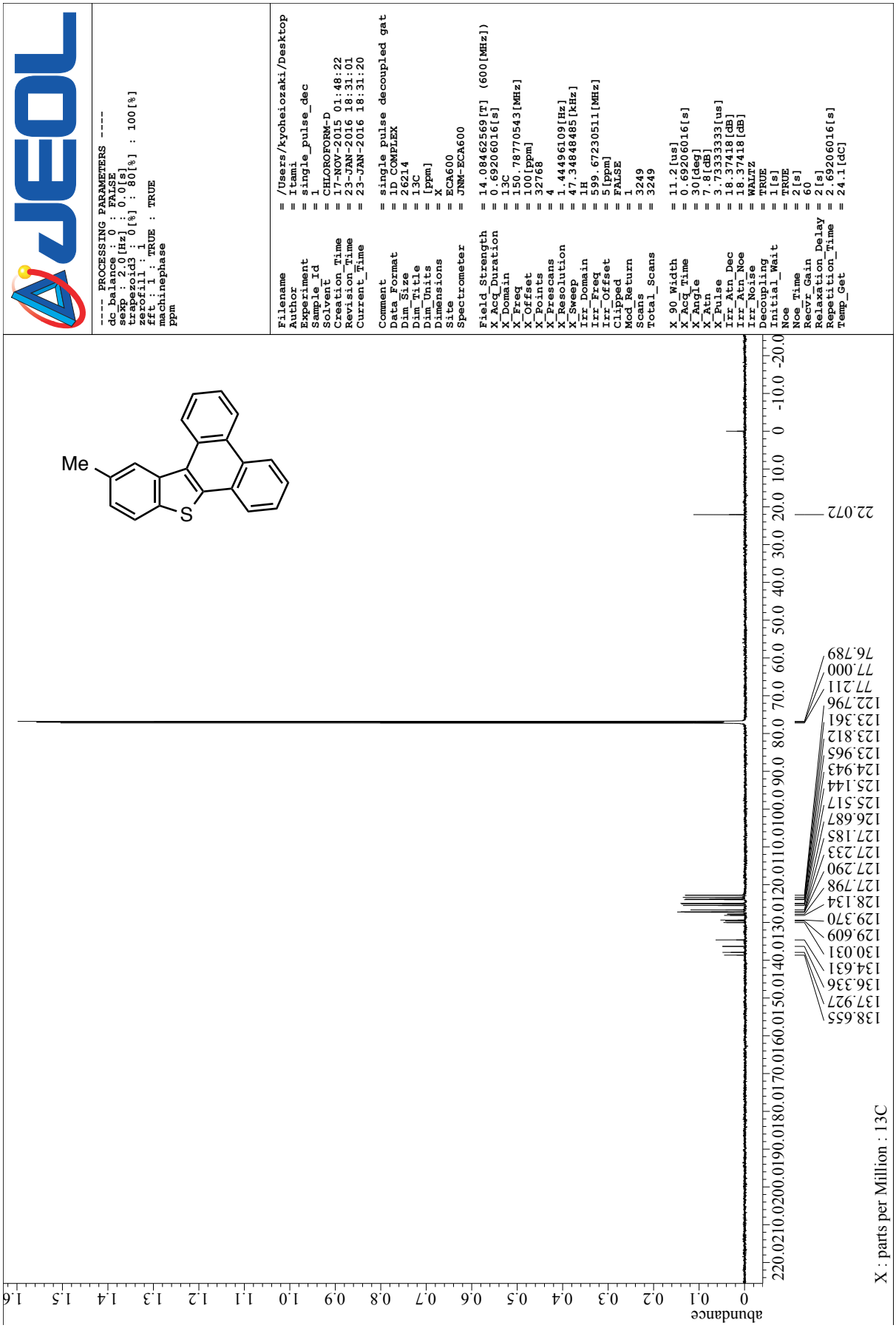
^{13}C NMR (150 MHz, $CDCl_3$) of 3ba



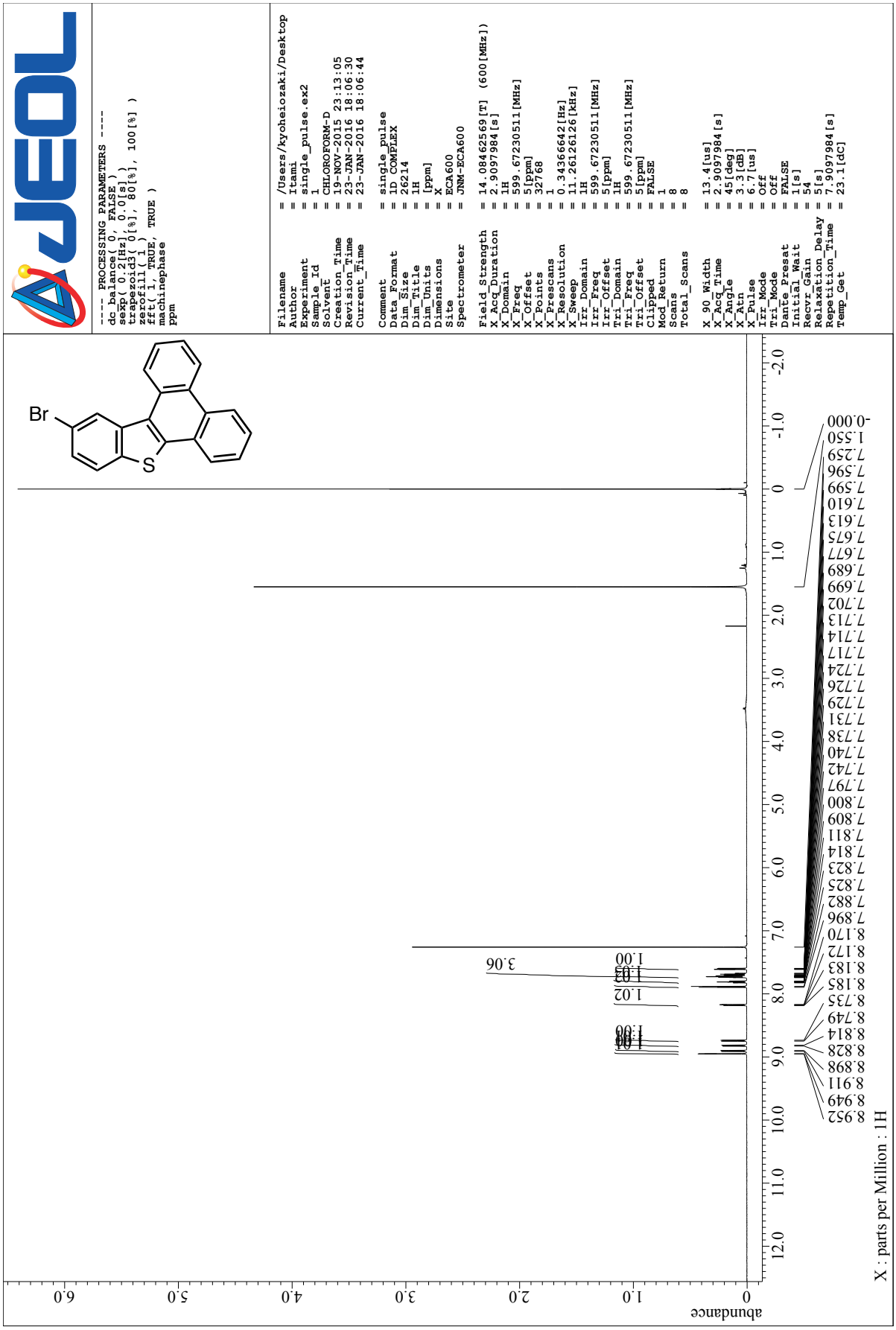
^{1}H NMR (600 MHz, $CDCl_3$) of 3ca



^{13}C NMR (150 MHz, $CDCl_3$) of 3ca



^{1}H NMR (600 MHz, $CDCl_3$) of 3da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1.00
1.02
1.00
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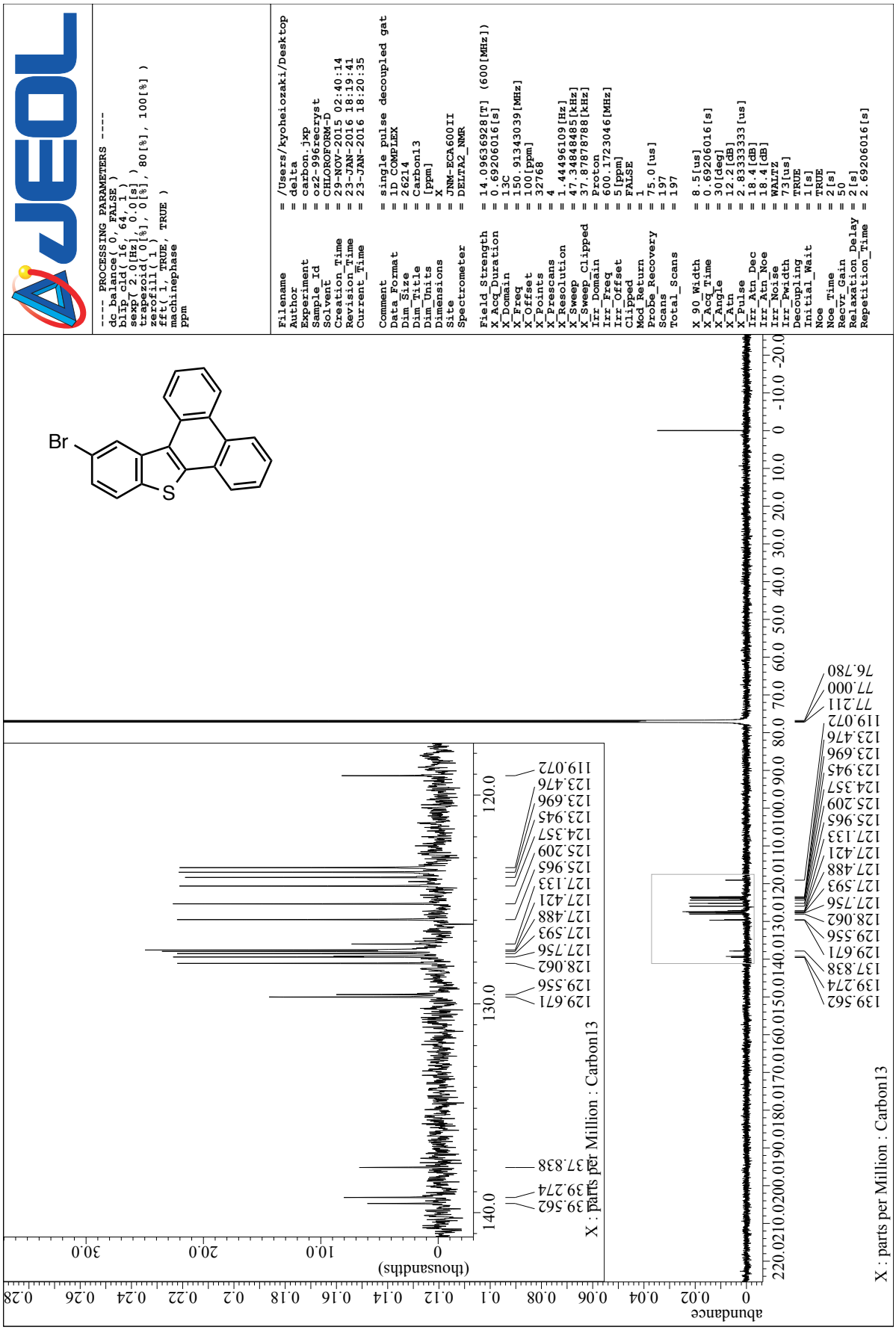
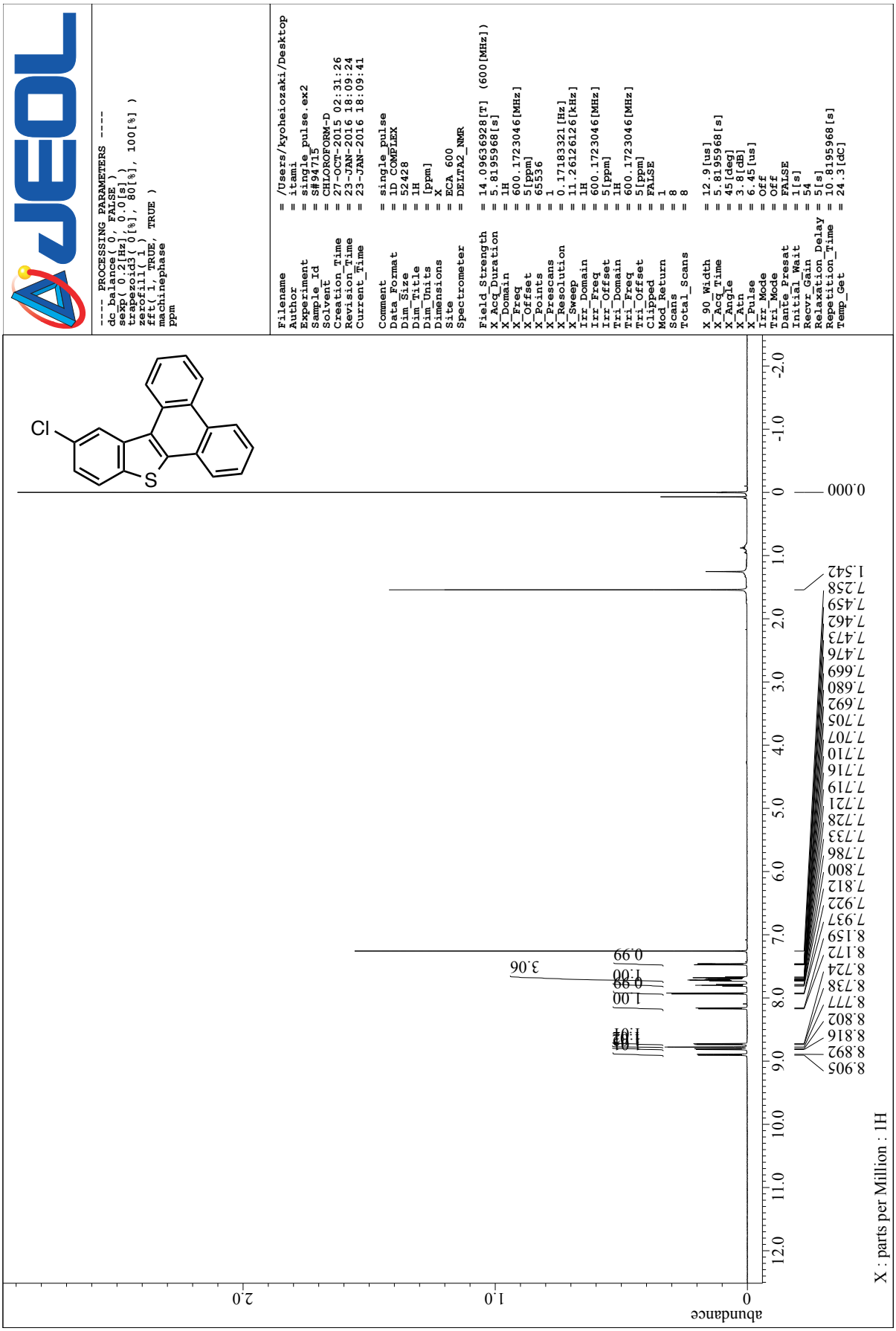
1.00

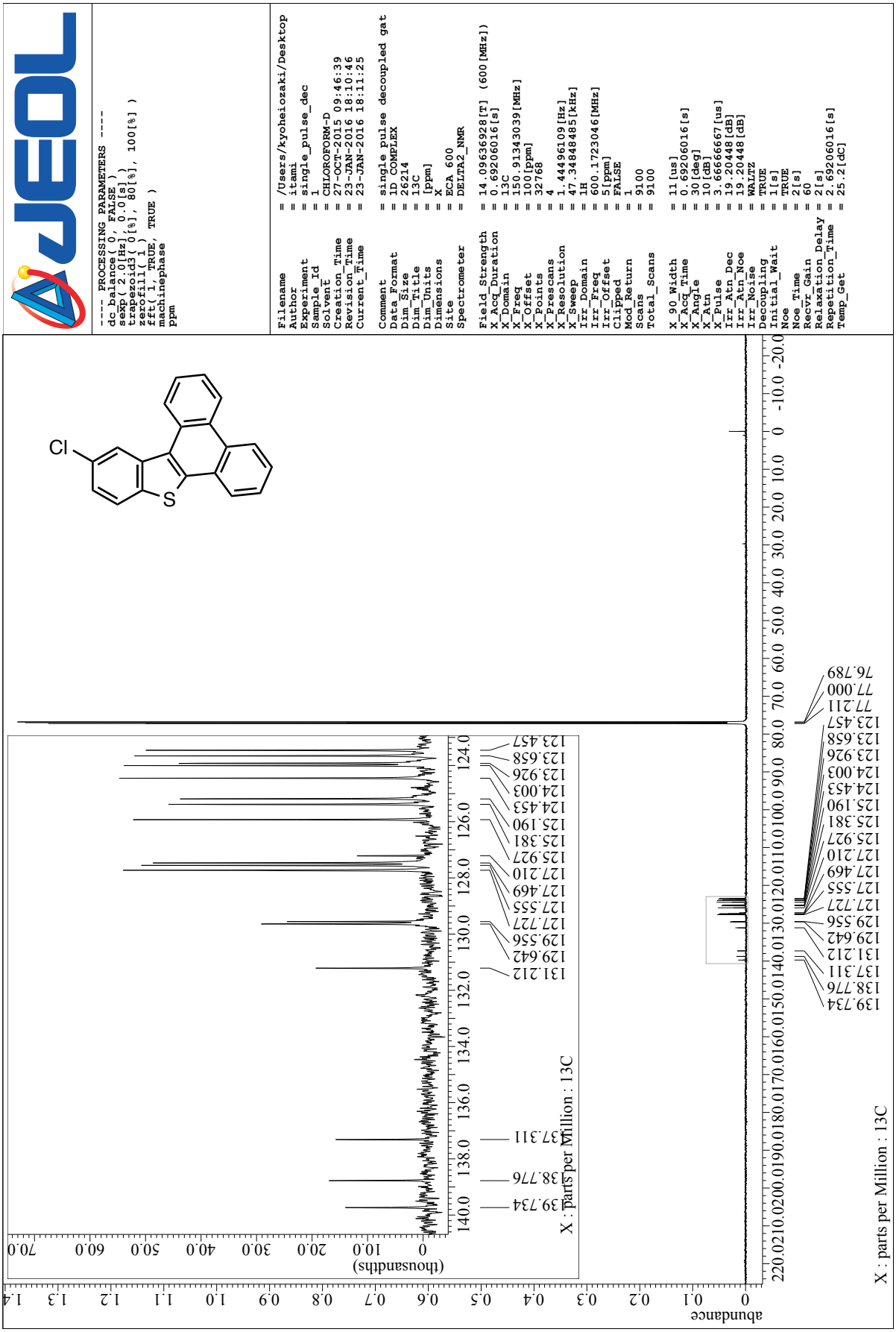
^{13}C NMR (150 MHz, $CDCl_3$) of 3da



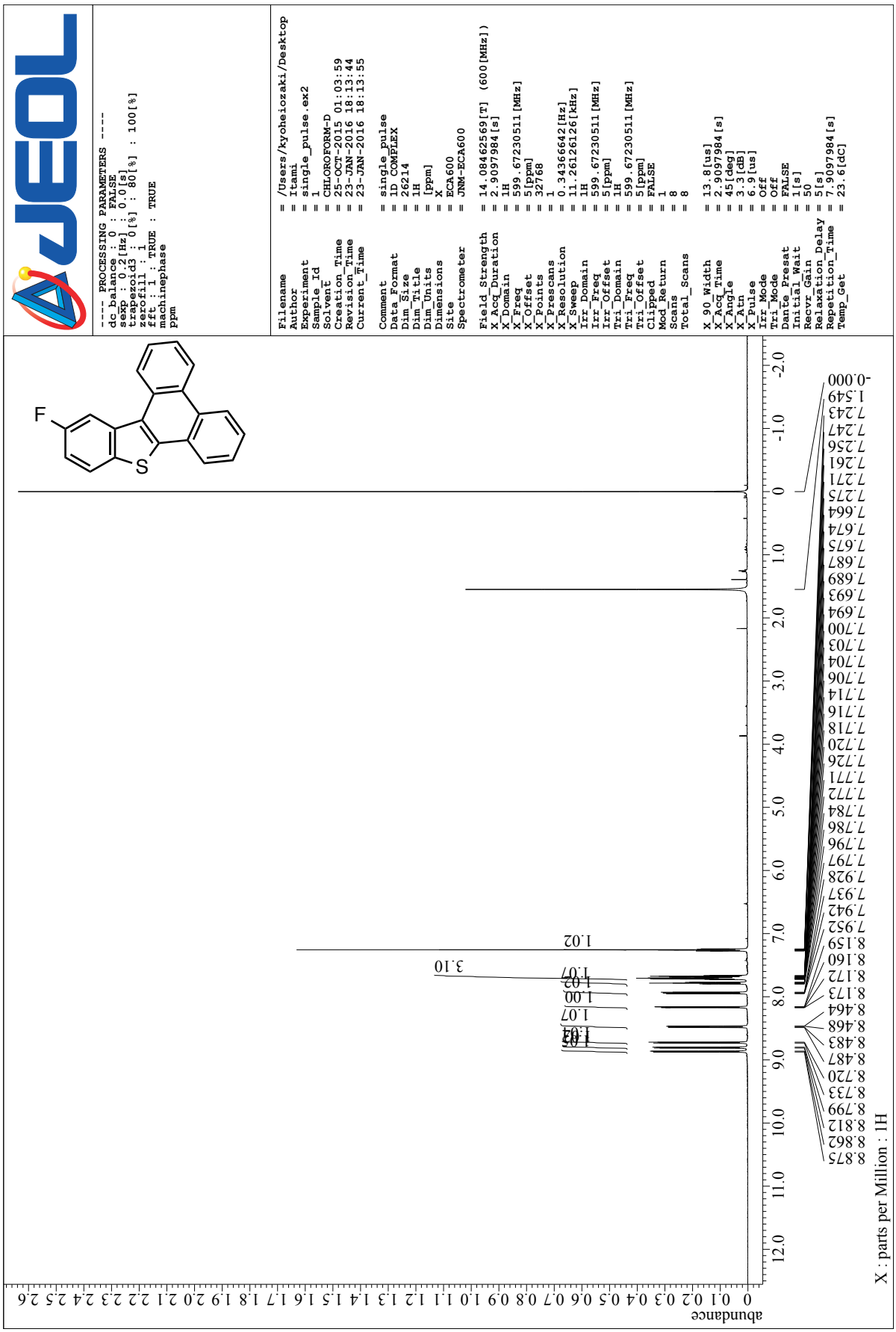
^{1}H NMR (600 MHz, $CDCl_3$) of 3ea



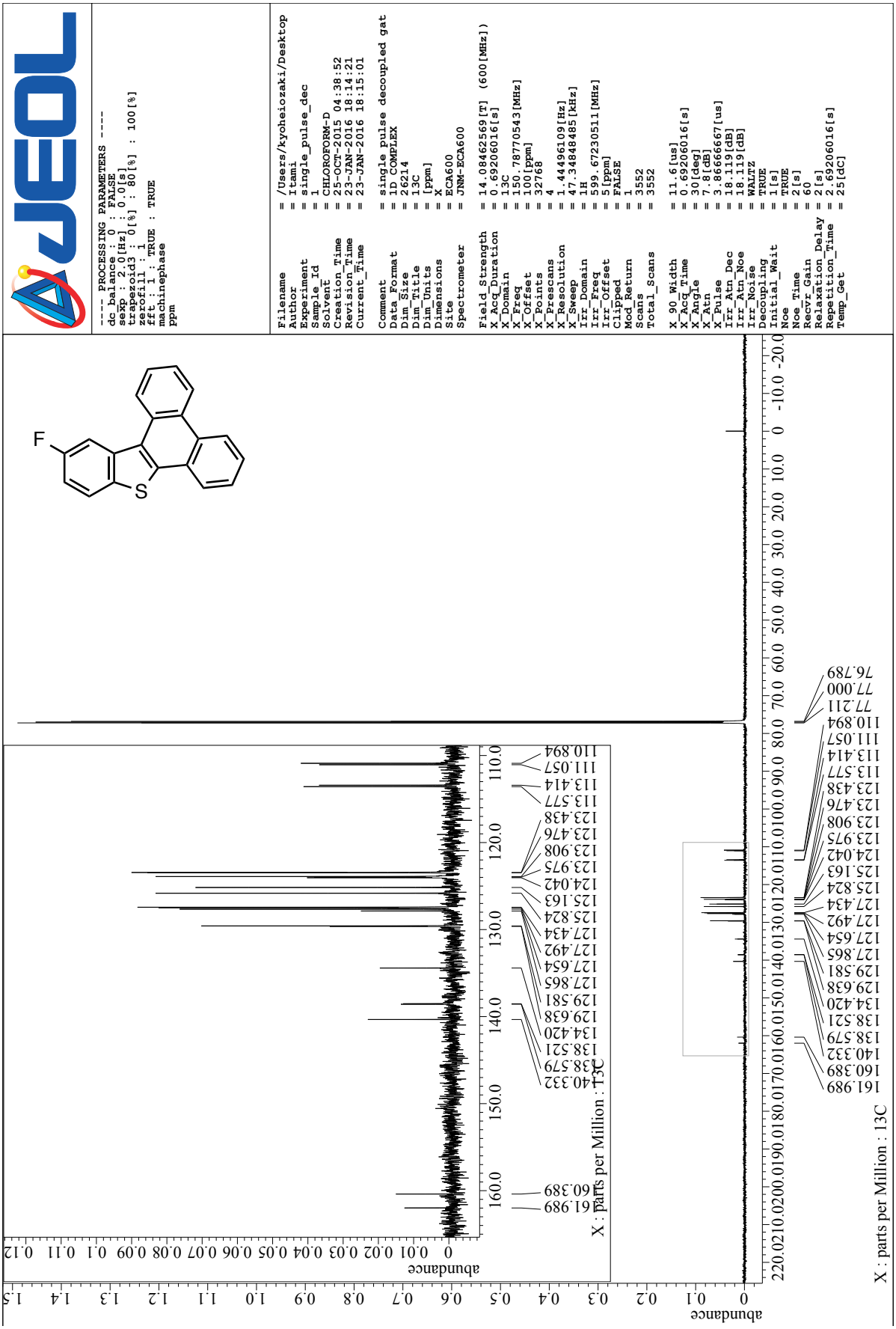
^{13}C NMR (150 MHz, $CDCl_3$) of 3ea



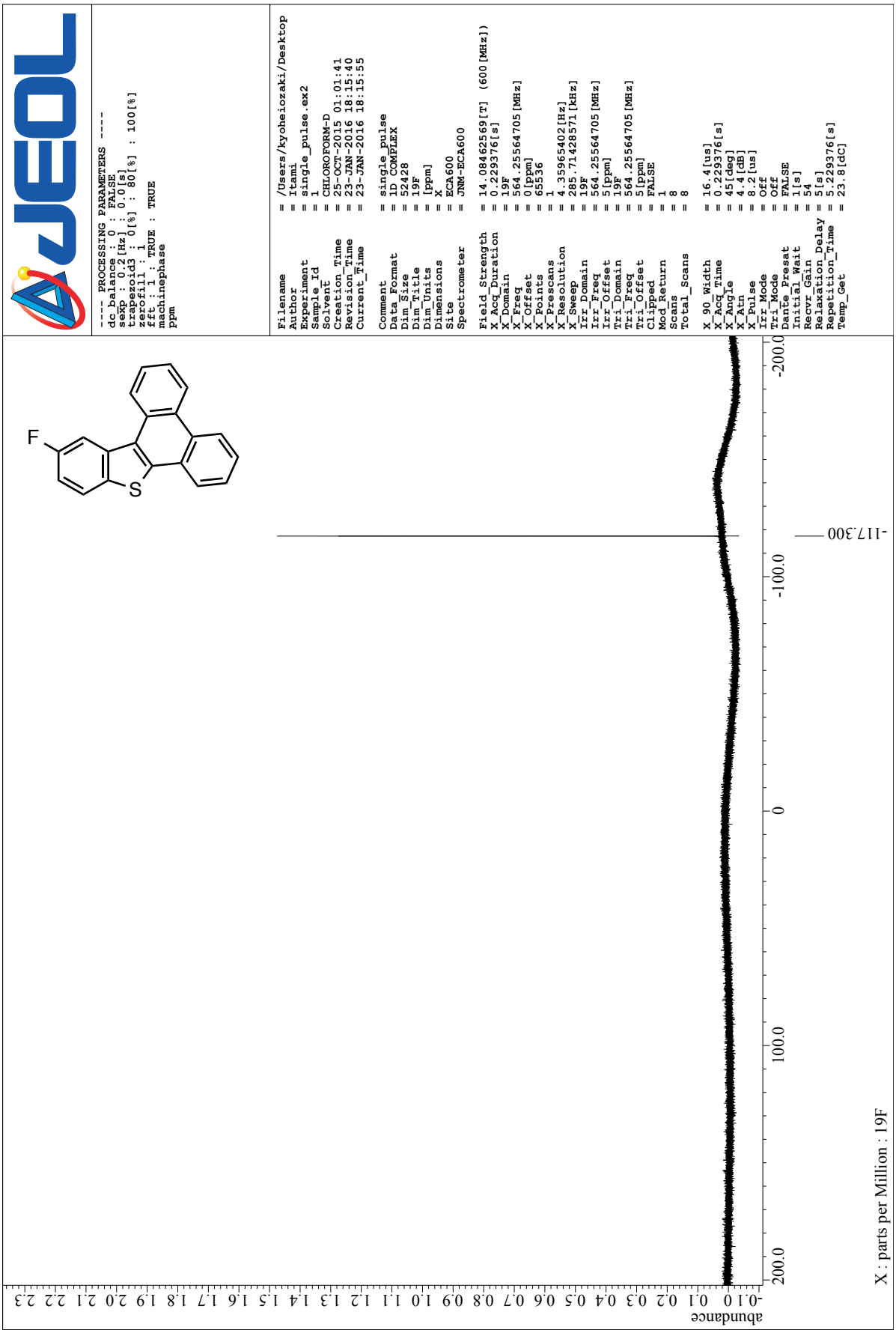
^{1}H NMR (600 MHz, $CDCl_3$) of 3fa



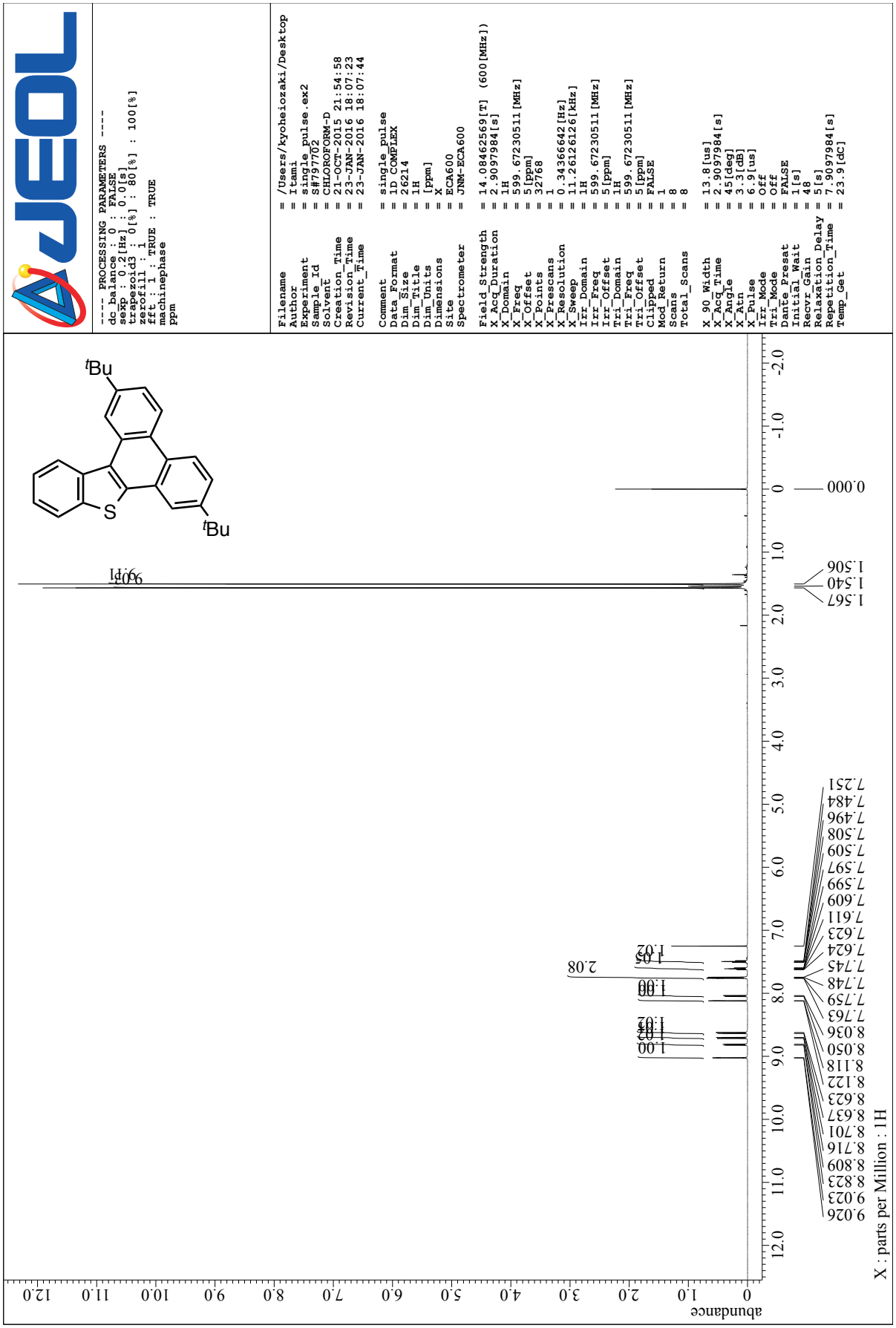
^{13}C NMR (150 MHz, $CDCl_3$) of 3fa



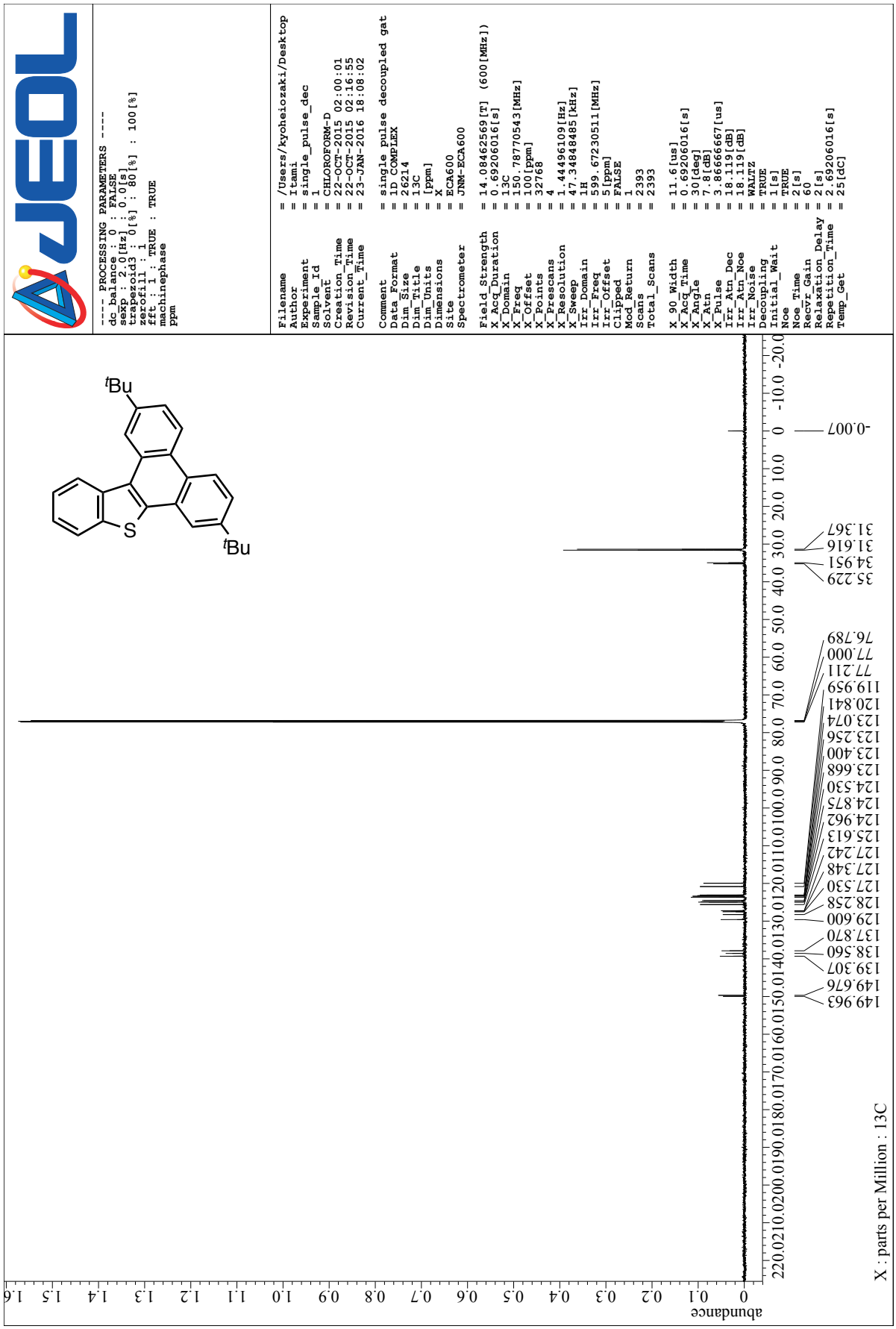
^{19}F NMR (564 MHz, $CDCl_3$) of 3fa



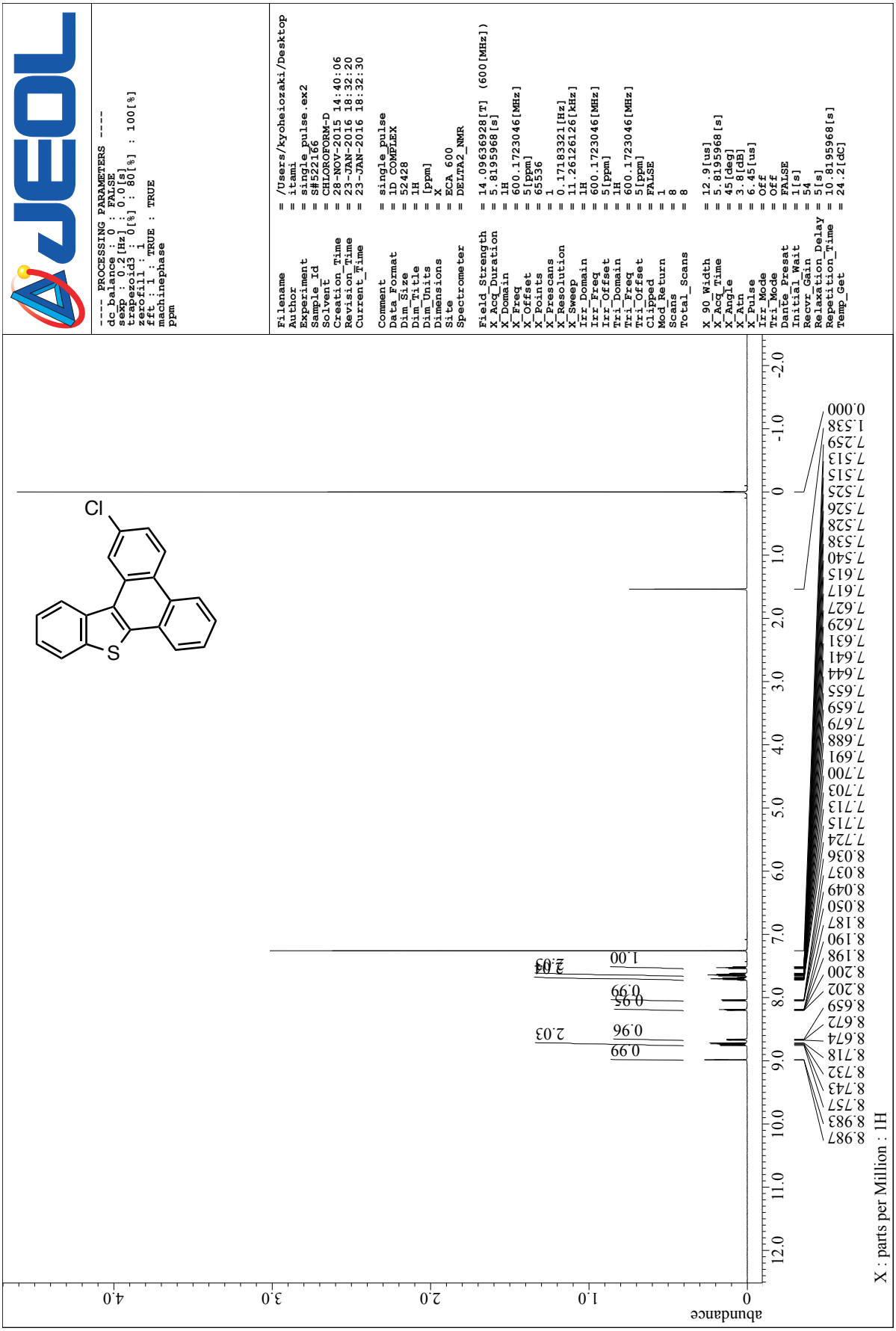
^{1}H NMR (600 MHz, $CDCl_3$) of 3ab



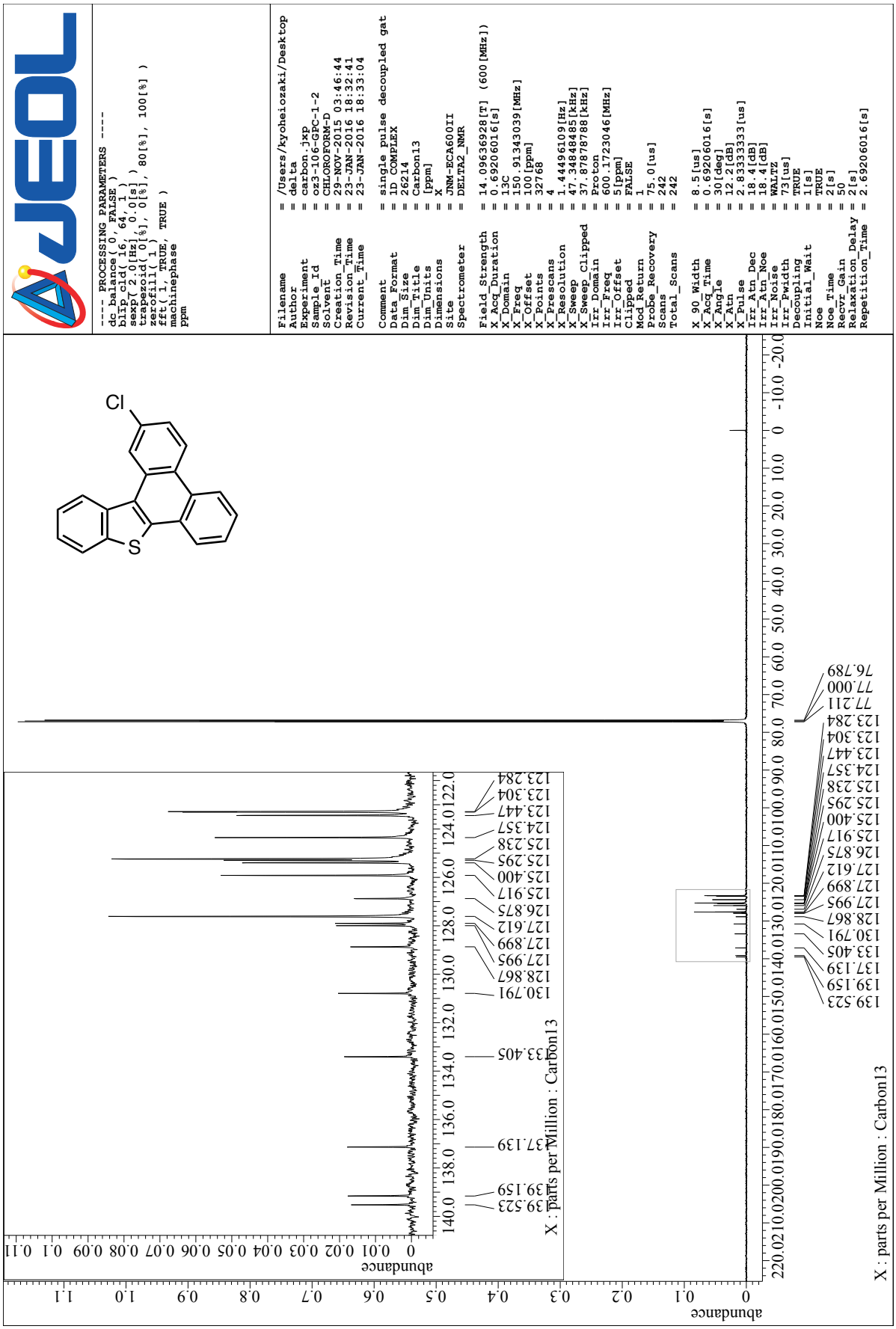
^{13}C NMR (150 MHz, $CDCl_3$) of 3ab



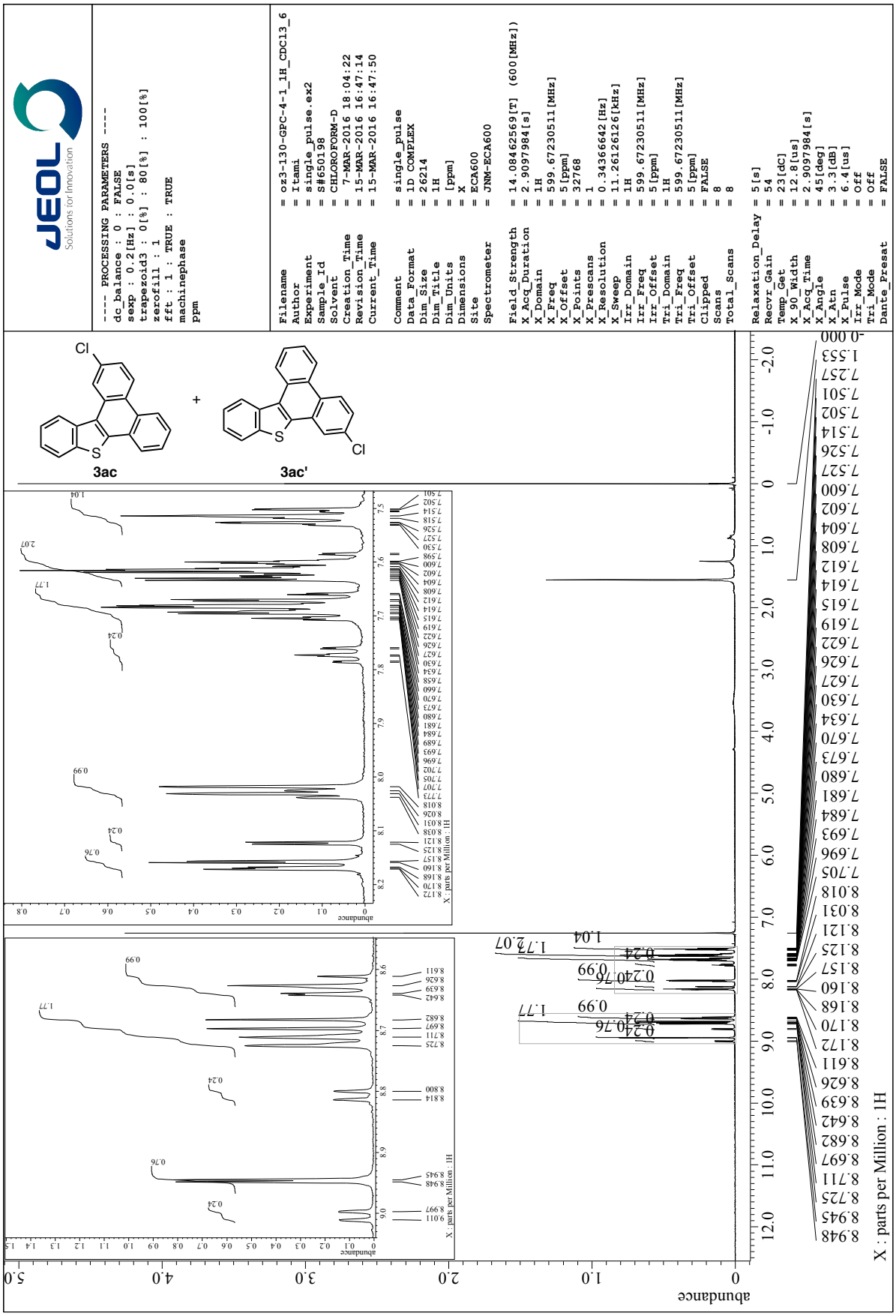
^{1}H NMR (600 MHz, $CDCl_3$) of 3ac



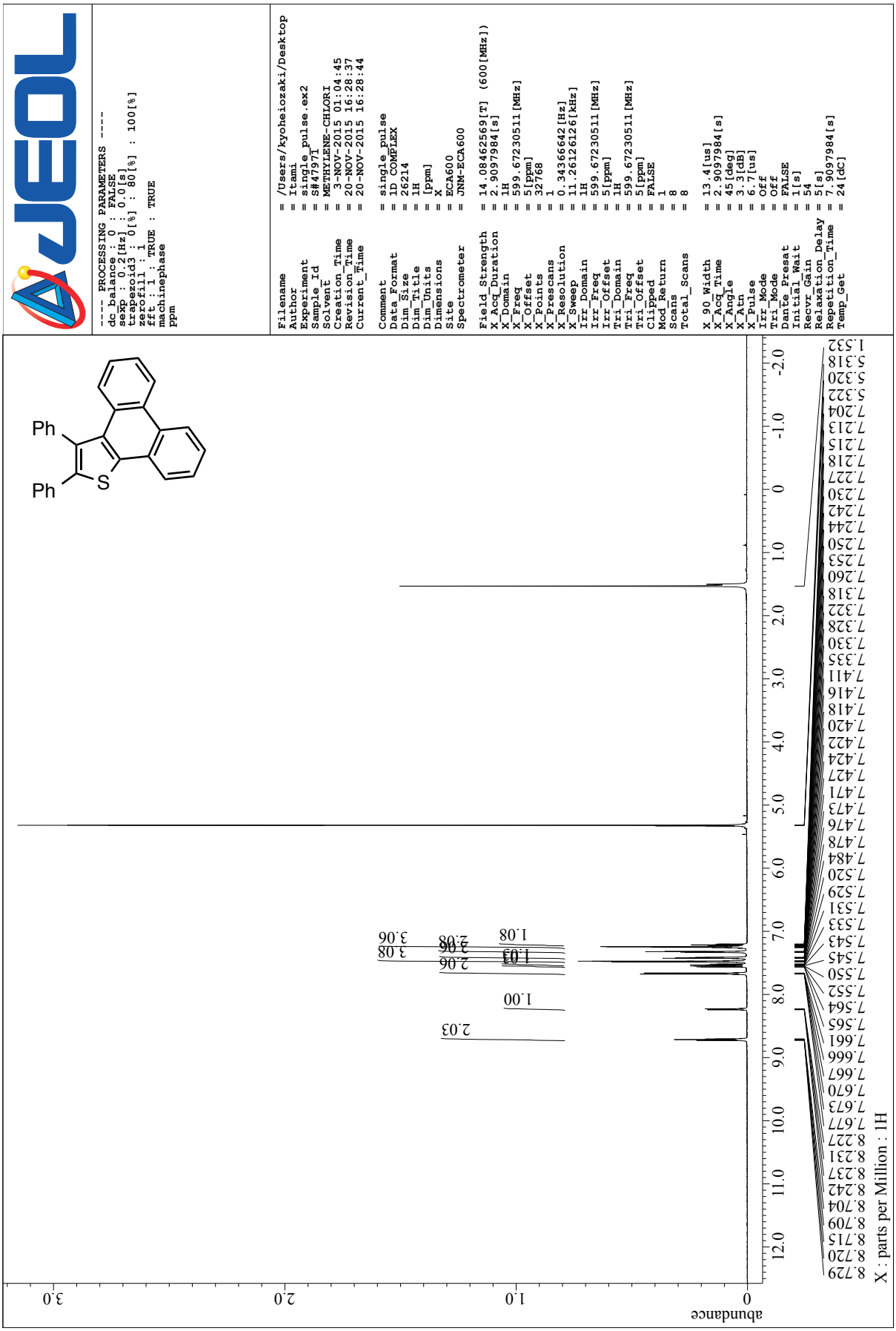
^{13}C NMR (150 MHz, $CDCl_3$) of 3ac



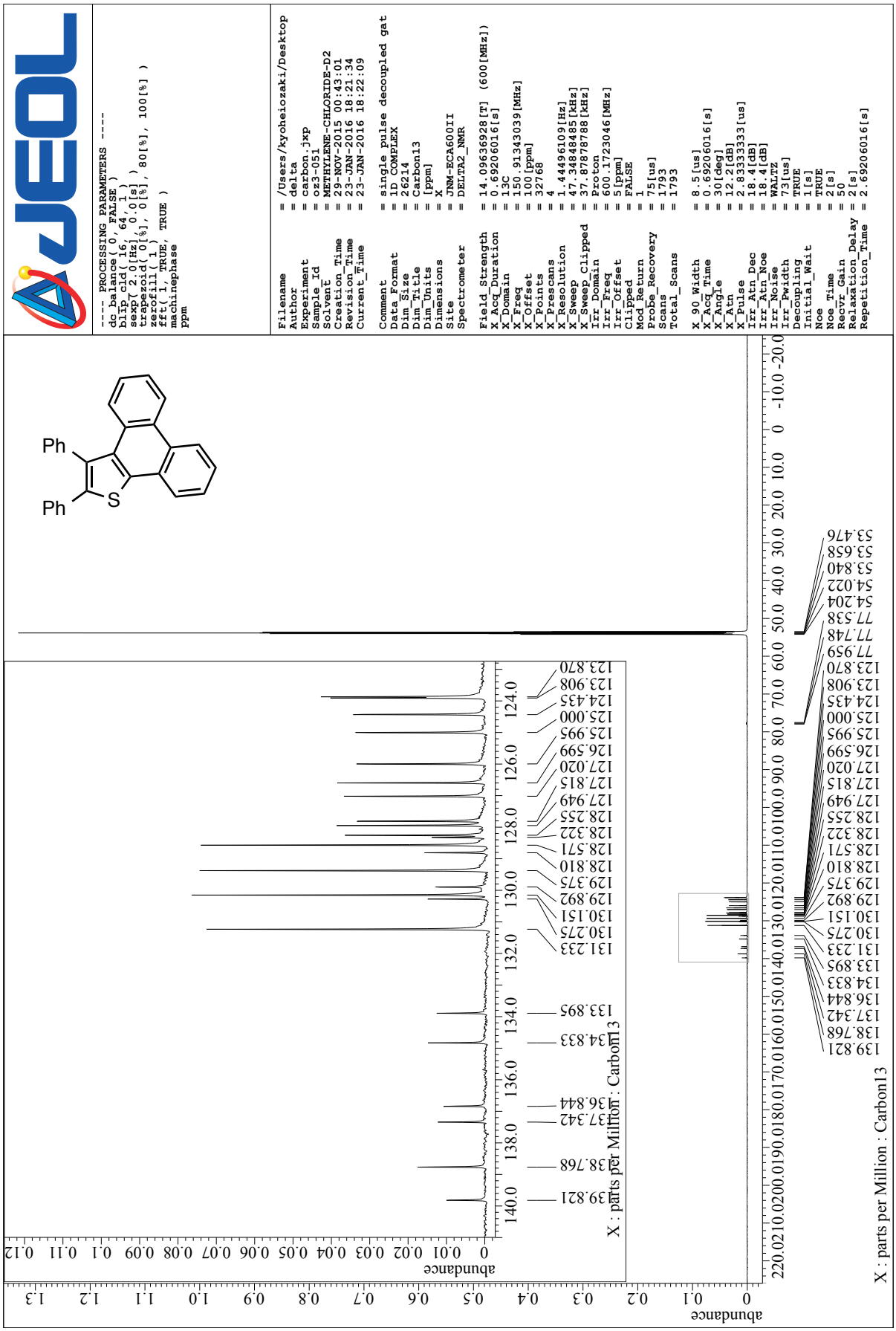
^{1}H NMR (600 MHz, $CDCl_3$) of 3ac + 3ac'



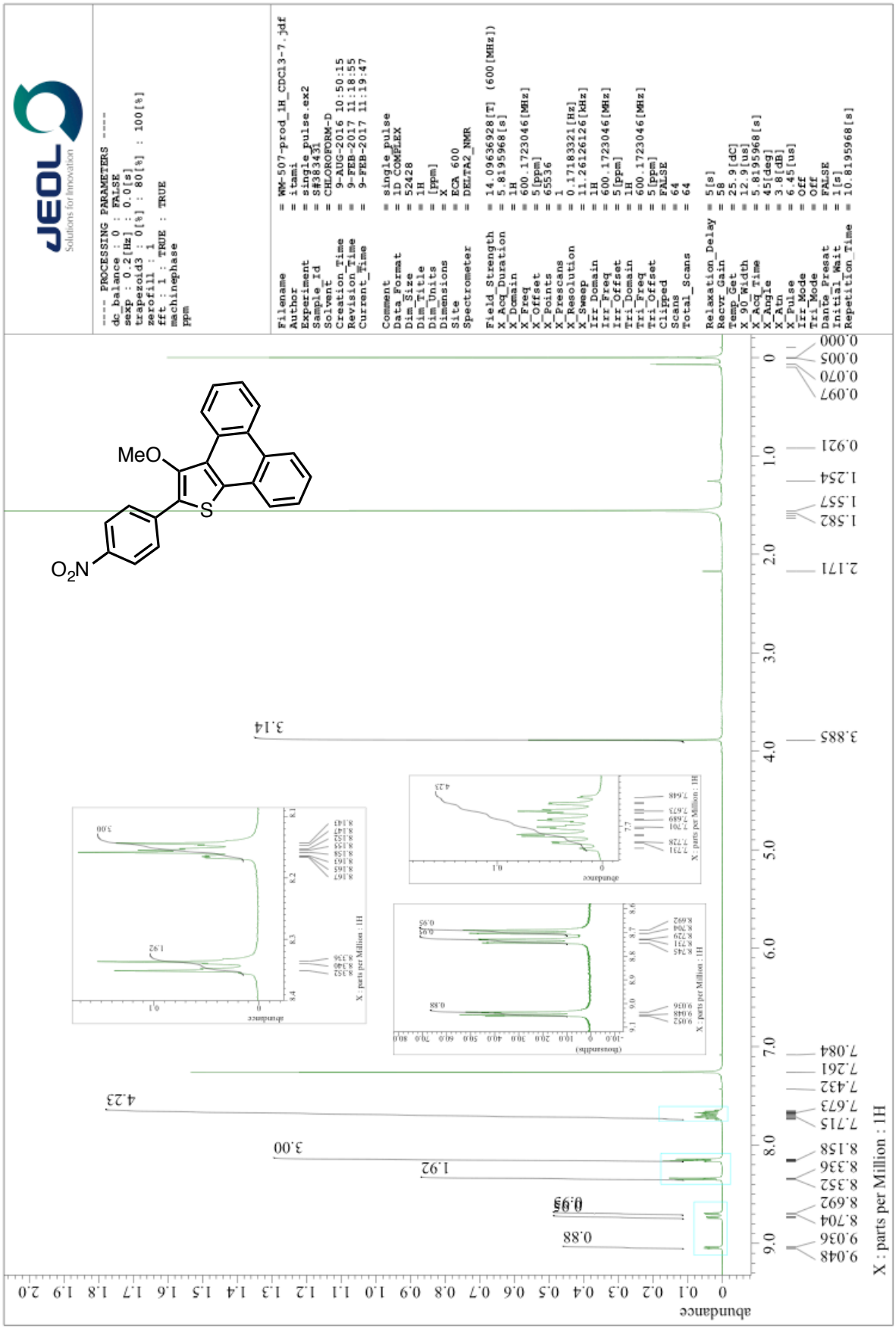
^{1}H NMR (600 MHz, CD_2Cl_2) of 3ga



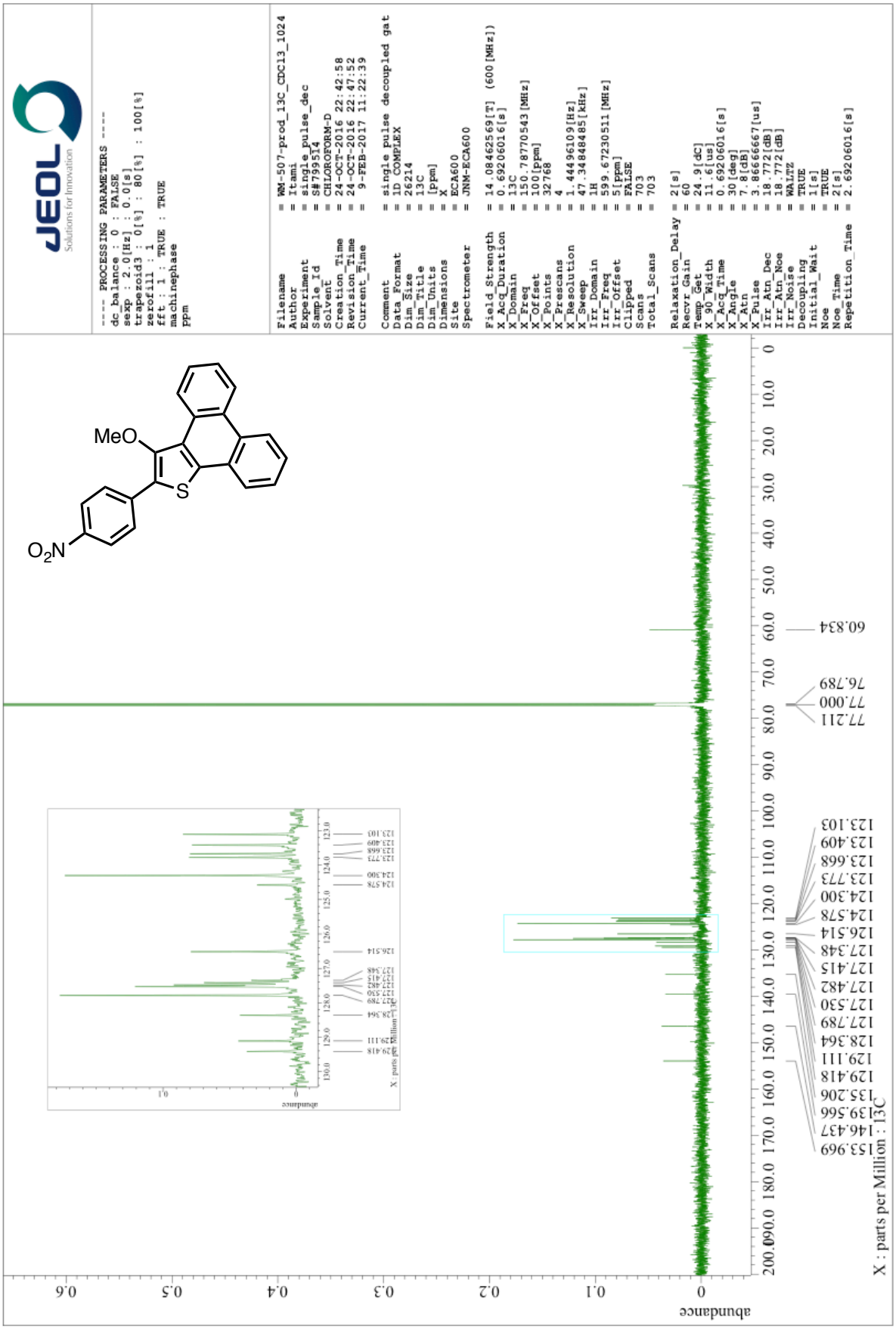
^{13}C NMR (150 MHz, CD_2Cl_2) of 3ga



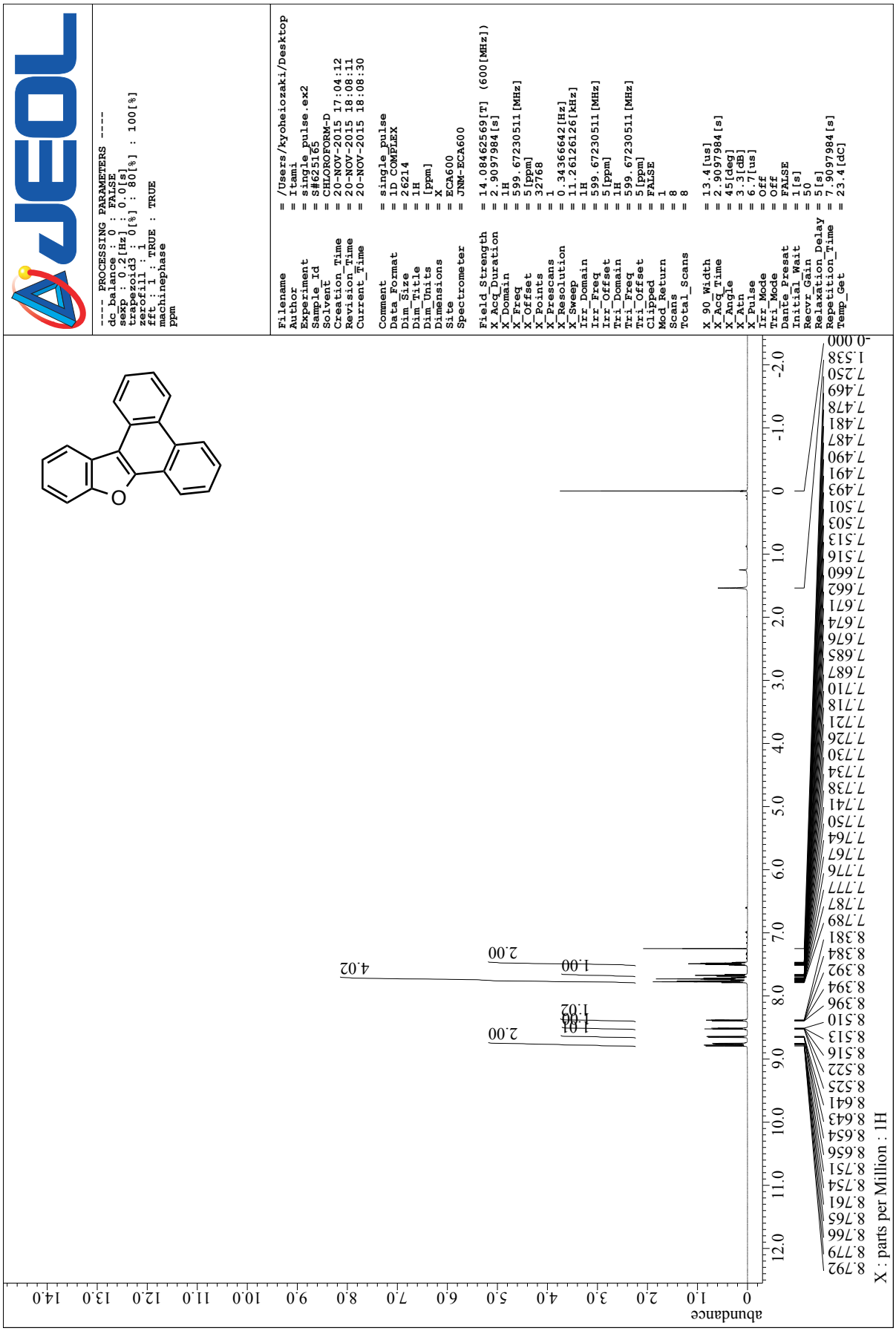
^{1}H NMR (600 MHz, CD_2Cl_2) of 3ha



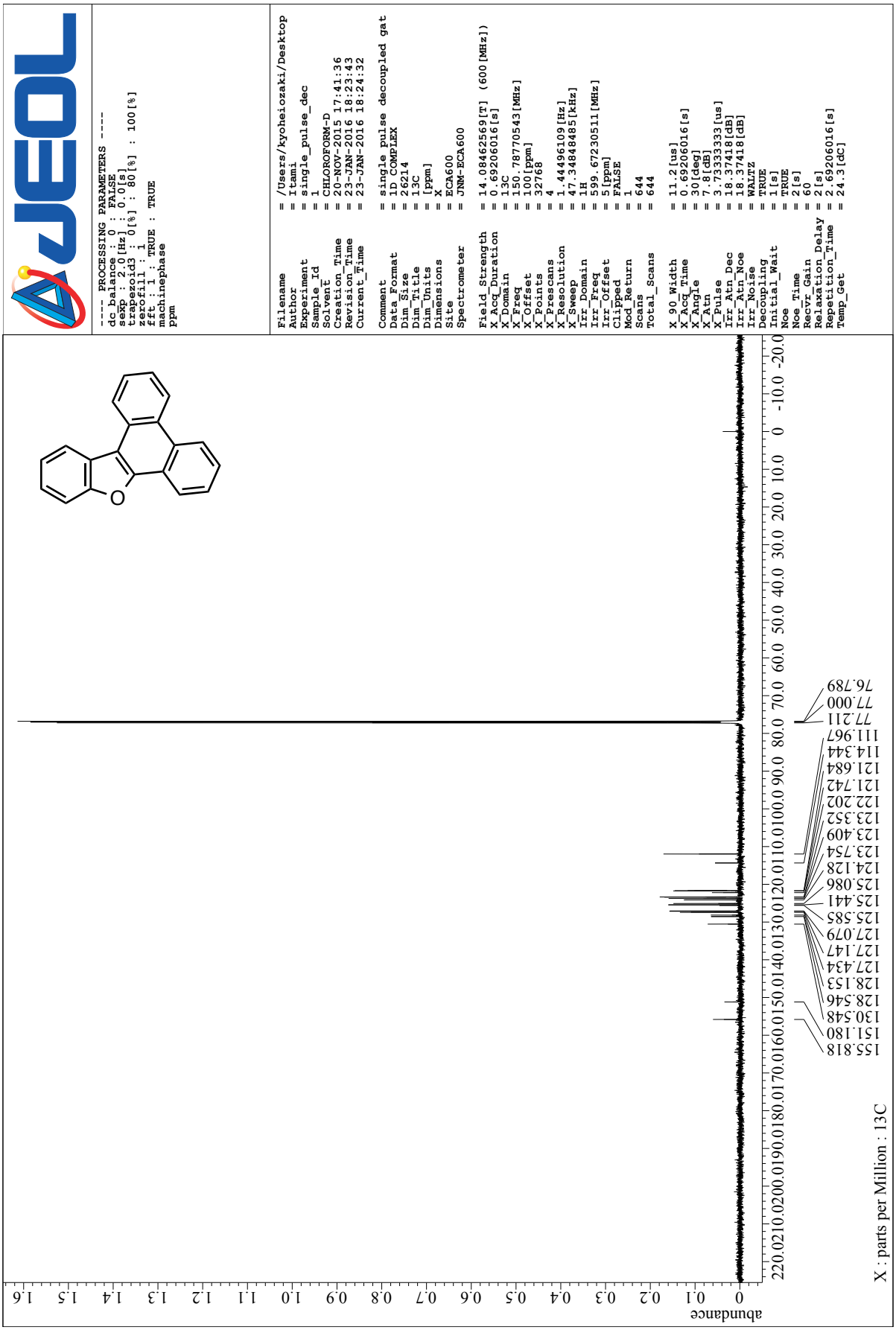
^{13}C NMR (150 MHz, CD_2Cl_2) of 3ha



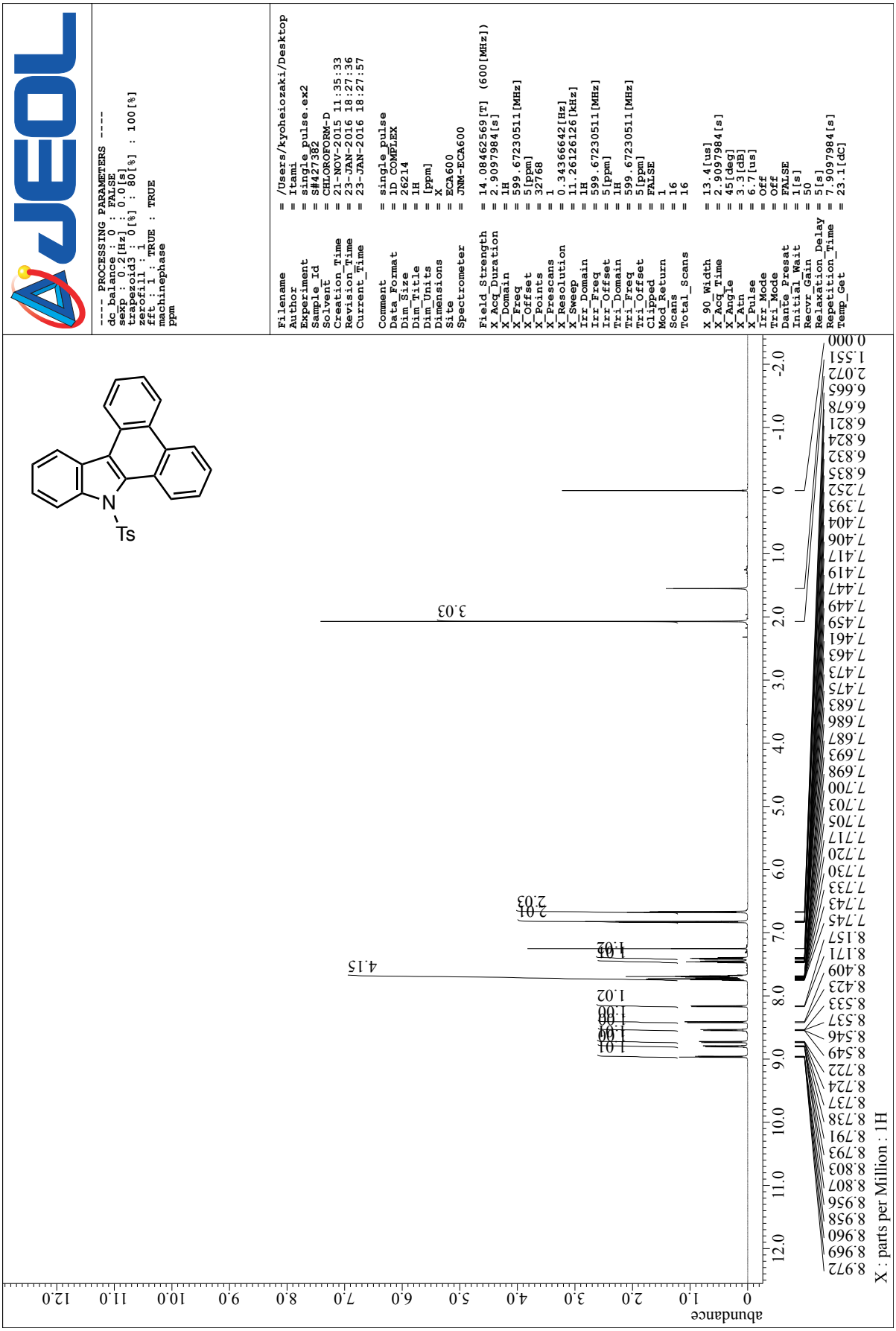
^{1}H NMR (600 MHz, $CDCl_3$) of 8



^{13}C NMR (150 MHz, $CDCl_3$) of 8



^{1}H NMR (600 MHz, $CDCl_3$) of 6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machinephase
ppm
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Author = Itami
Experiment = single_pulse.ex2
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Solvent = CHLOROFORM-D
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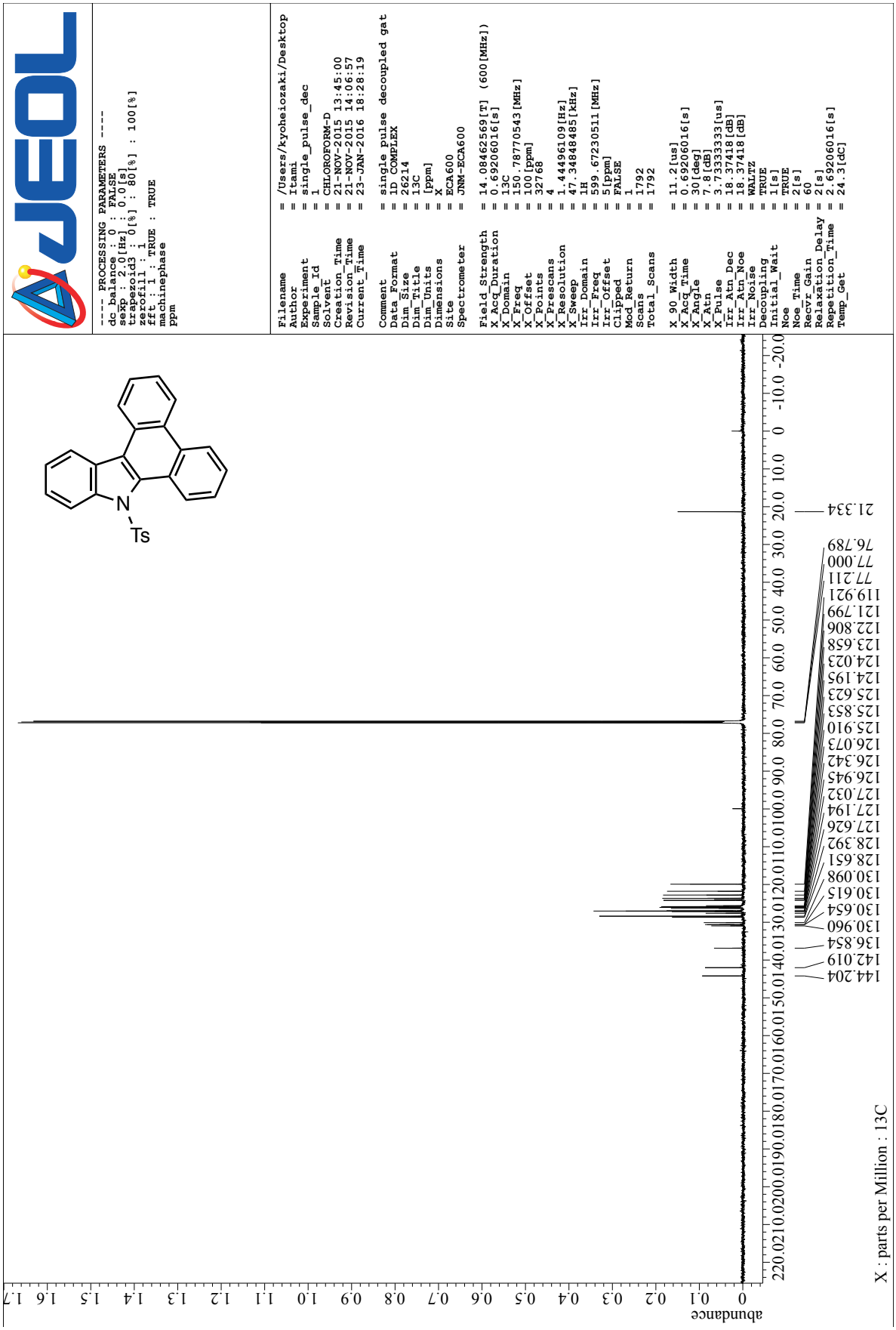
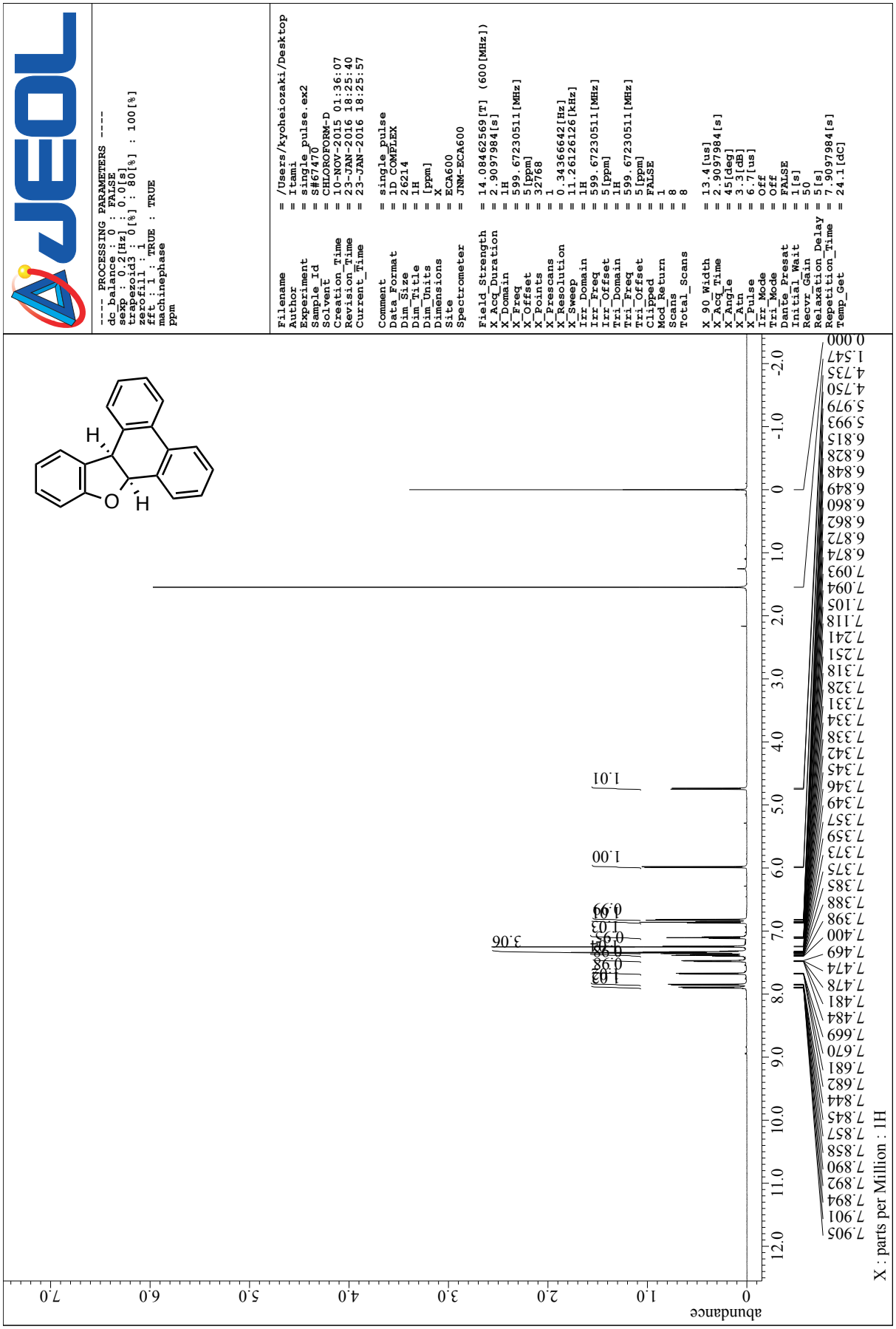
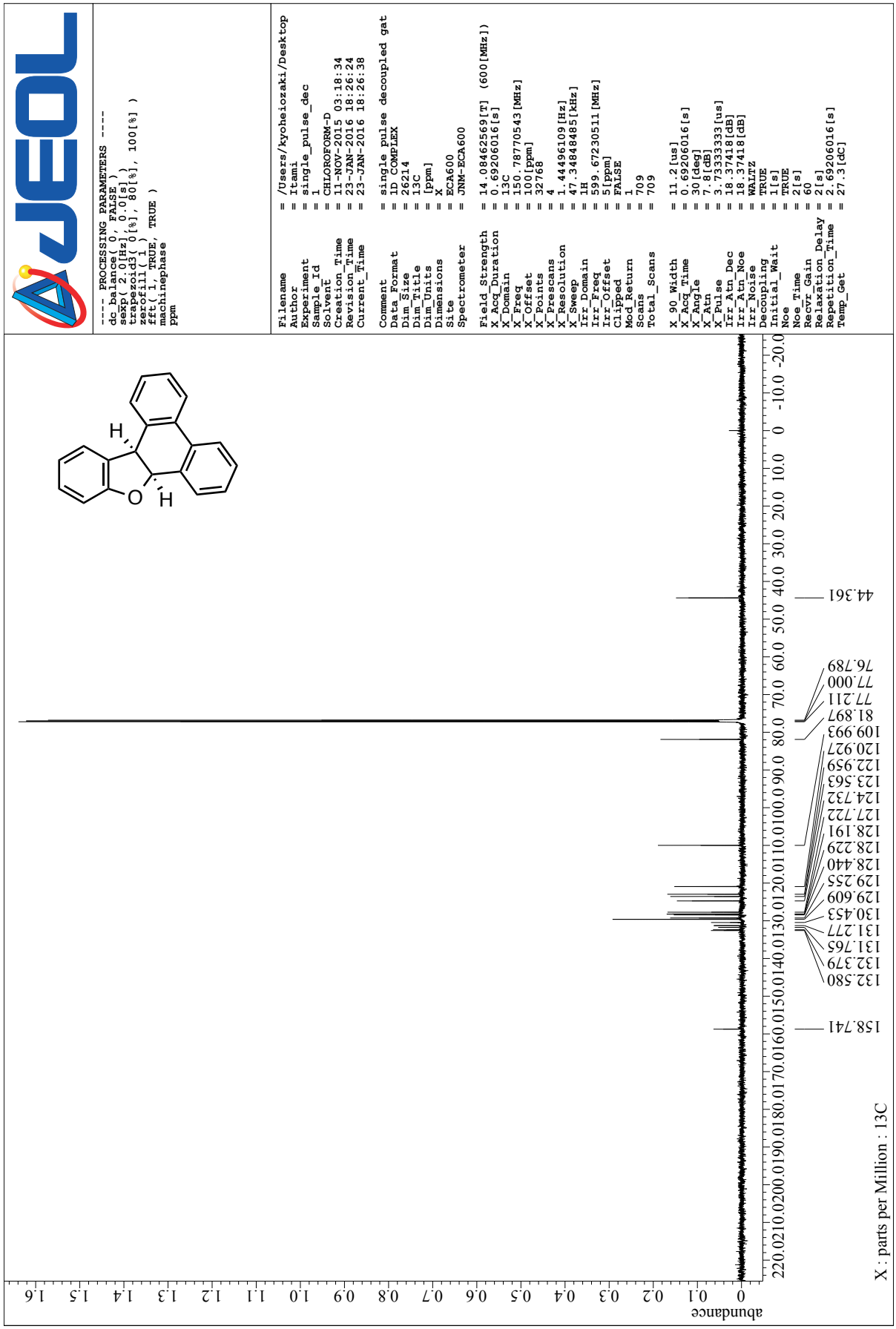
1.00
1.00

^{13}C NMR (150 MHz, $CDCl_3$) of 6



^{1}H NMR (600 MHz, $CDCl_3$) of 8'



^{13}C NMR (150 MHz, $CDCl_3$) of 8'