Supplementary Information (SI) for Organic Chemistry Frontiers.

Supplementary Information

Alkali/alkaline earth metal-mediated mechanochemical Wurtz reactions

Yoshifumi Toyama[a] and Hideto Ito*[a]

[a] *Graduate School of Science, Nagoya University, Chikusa, Nagoya 464-8602, Japan.*

Table of Contents

1. General

Unless otherwise noted, all materials including dry solvents were obtained from commercial suppliers and used without further purification. Lithium wire (diam. 3.2 mm, 99.9% purity in mineral oil), 1-bromomethylnaphthalene, and was purchased from Sigma-Aldrich. Sodium lump (99% purity) was purchased from Nakarai Chemical Co., Ltd. 2-bromomethylnaphthalene, tetrahydrofuran (THF), calcium shot (99% purity), CH_2Cl_2 were purchased from Kanto Chemical Co., Inc. α-Bromodiphenylmethane, 2,2′-bis(bromomethyl)-1,1′-biphenyl, α,α′-dibromo-*o*-xylene, 2-bromo-4′-methylacetophenone, 2-bromo-4′-fluoroacetophenone, 9-(bromomethyl)anthracene, 2-bromo-4′-bromoacetophenone and 1-bromododecane were purchased from Tokyo Chemical Industry Co., Ltd. 2,3-Bis(bromomethyl)naphthalene was synthesized following the previous report.[S1] 8,9-bis(bromomethyl)fluoranthene was synthesized following the previous report.[S2] Unless otherwise noted, all in-flask 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. All mechanochemical reactions were carried out using a Retsch MM400 or Retsch MM500 Vario mixer mil (Verder Scientific). The stainless-steel reaction jars (SUS400B, 1.5-mL, 5.0-mL, 10-mL, 50-mL volumes) and stainless-steel balls (SUS420J2, 7- and 10-mm diameters) were used for reactions. The heat-gun (Takagi HG-1450B) with a temperature control function was used for high-temperature ball-milling reactions.

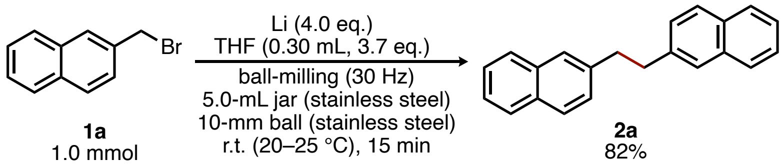
Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25-mm thickness). The developed chromatogram was analyzed by UV lamp (254 nm). Flash column chromatography was performed with KANTO Silica Gel 60N (spherical, neutral, 40–50 µm) or Biotage Isolera® equipped with Biotage SNAP Cartridge KP-Sil columns. Preparative thin-layer chromatography (PTLC) was performed using Wako-gel® B5-F silica coated plates (0.75-mm thickness) prepared in our laboratory. Gel permeation chromatography (GPC) was performed with a JAI LaboACE LC-5060 II NEXT instrument equipped with JAIGEL-1HR/JAIGEL-2HR columns using chloroform as an eluent. The developed chromatogram was analyzed by UV lamp (254 nm and 365 nm). High-resolution mass spectra (HRMS) were obtained from a JEOL JMS-T100TD (DART). GC-MS analysis was conducted on a Shimadzu GC-MS-QP2010 instrument equipped with a Restec-5HT column (30 m × 0.25 mm, Hewlett-Packard). Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL ECS-400 (^{1}H NMR: 400 MHz), JEOL ECS-600 (^{1}H NMR: 600 MHz, ^{13}C NMR: 150 MHz) spectrometers. Chemical shifts for ^{1}H NMR are expressed in parts per million (ppm) relative to $CDCl_3$ (δ 7.26 ppm), CD_2Cl_2 (δ 5.32 ppm) or $Cl_2CDCDCl_2$ (δ 5.97 ppm). Chemical shifts for ^{13}C NMR are expressed in ppm relative to $CDCl_3$ (δ 77.16 ppm), 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, quint = quintet, m = multiplet), coupling constant (Hz), and integration.

2. General procedures and compound characterization

2-1. General Procedure A for lithium(0)-mediated mechanochemical Wurtz reaction

Synthesis of 1,2-di(naphthalen-2-yl)ethane (2a)

The synthesis of 1,2-di(naphthalen-2-yl)ethane (**2a**) is described as a representative example of the general procedure A.



A 10-mm diameter stainless-steel ball and 2-(bromomethyl)naphthalene (**1a**) (221.3 mg, 1.0 mmol, 1.0 eq.) were added to an oven-dried 5.0-mL stainless-steel jar. Pieces of Li (27.7 mg, 4.0 mmol, 4.0 eq.) cut from Lithium wire (3.2 mm in diameter, 99.9% purity) was washed with hexane for removing mineral oil, weighed on an electronic balance, and added into the jar under air. Then, THF (0.30 mL, 3.7 mmol, 3.7 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with an O-shaped packing made of 1-mm width polyethylene sheet, and the jar was sealed tightly with a wrench and a vise. The reaction jar and a same-weight blank jar (or a same-weight reaction jar) were fixed in a mixer mill (Retsch MM400), and shaken at 30 Hz (1800 rpm) at room temperature (20–25 °C) for 15 min. After shaking, the reaction jar was opened and the reaction was quenched by adding sat. NH_4Cl aq. Then, the organic phase was extracted with chloroform (three times). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford a crude product. The crude product was purified by silica gel column chromatography (eluent: hexane/$CHCl_3$ = 10:0→10:1), affording a 1,2-di(naphthalen-2-yl)ethane (**2a**) as a white solid (115.6 mg, 0.41 mmol, 82% yield).

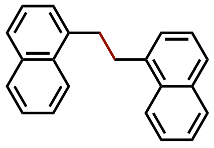
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.80–7.75 (m, 4H), 7.66 (s, 2H), 7.47–7.41 (m, 4H), 7.37 (dd, *J* = 8.6, 1.7 Hz, 2H), 3.19 (s, 4H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 139.41, 133.76, 132.19, 128.04, 127.76, 127.61, 127.50, 126.64, 126.05, 125.34, 38.17.

HRMS (DART, positive) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{19}$ 283.14868; Found 283.14828.

The ^{1}H and ^{13}C NMR spectra were identical to those reported literature.[S3]

Synthesis of 1,2-di(naphthalen-1-yl)ethane (2d)



–1.0-mmol scale reaction–

Using the general procedure A, the reaction of 1-(bromomethyl)naphthalene (**1d**) (221.4 mg, 1.0 mmol, 1.0 eq.) with Li (27.8 mg, 4.0 mmol, 4.0 eq.), THF (0.30 mL, 3.7 mmol, 3.7 eq.) was conducted at room temperature (20–25 °C) for 15 min. Purification by washing (eluent: hexane) and afforded **2d** as a white solid (131.2 mg, 0.47 mmol, 93% yield).

–5.0-mmol scale reaction–

Using the general procedure A, the reaction of 1-(bromomethyl)naphthalene (**1d**) (1.11 g, 5.0 mmol, 1.0 eq), Li (137.9 mg, 19.9 mmol, 4.0 eq.), THF (0.60 mL, 7.4 mmol, 1.5 eq.), two 10-mm-diameter stainless-steel balls in a 10-mL stainless-steel jar were conducted at room temperature (20–25 °C) for 60 min. Purification by washing (eluent: hexane) and afforded **2d** as a white solid (510.9 mg, 1.81 mmol, 72% yield).

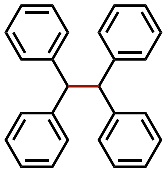
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.2 Hz, 2H), 7.90 (d, J = 7.7 Hz, 2H), 7.76 (d, J = 8.2 Hz, 2H), 7.57–7.49 (m, 4H), 7.42 (t, J = 7.5 Hz, 2H), 7.36 (d, J = 6.8 Hz, 2H), 3.53 (s, 4H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 138.21, 134.06, 131.99, 129.02, 126.96, 126.08 (2C), 125.75, 125.67, 123.08, 34.25.

HRMS (DART, positive) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{19}$ 283.14868; Found 283.14823.

The ^{1}H and ^{13}C NMR spectra were identical to those reported literature.[S3]

Synthesis of 1,1,2,2-tetraphenylethane (2e)



Using the general procedure A, the reaction of α-bromodiphenylmethane (**1d**) (248.2 mg, 1.0 mmol, 1.0 eq.) with Li (27.6 mg, 4.0 mmol, 4.0 eq.), THF (0.30 mL, 3.7 mmol, 3.7 eq.) was conducted at room temperature (20–25 °C) for 15 min. Purification by recrystallization from $CHCl_3$ and afforded **2e** as a white solid (71.3 mg, 0.21 mmol, 43% yield).

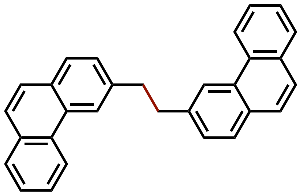
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, J = 7.2 Hz, 8H), 7.11 (t, J = 7.5 Hz, 8H), 7.02 (t, J = 7.0 Hz, 4H), 4.78 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.58, 128.64, 128.27, 125.98, 56.45.

HRMS (DART, positive) *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{21}$ 333.16433; Found 333.16496.

The ^{1}H and ^{13}C NMR spectra were identical to those reported literature.[S4]

Synthesis of 1,2-di(phenanthren-3-yl)ethane (2f)



This experiment was conducted in two batches. Using the general procedure A, to a 1.5-mL stainless-steel jar containing a 7-mm-diameter stainless-steel ball was added 3-(bromomethyl)phenanthrene (**1f**) (batch 1: 54.1 mg, 0.20 mmol, 1.0 eq.; batch 2: 53.9 mg, 0.20 mmol, 1.0 eq.) with sodium (batch 1: 10.3 mg, 0.44 mmol, 2.2 eq.; batch 2: 10.9 mg, 0.44 mmol, 2.2 eq.), THF (batch 1: 0.10 mL, 1.2 mmol, 6.2 eq.; batch 2: 0.10 mL, 1.2 mmol, 6.2 eq.). The reaction jars were fixed in a mixer mill (Retsch MM400) and shaking at 30 Hz (1800 rpm) at room temperature (20–25 °C) for 180 min. After shaking, the reaction jars were opened and the reactions were quenched by adding sat. NH_4Cl aq. Then, the contents in the two jars were combined and poured into a separation funnel, and the organic phase was extracted with chloroform (three times). Purification by silica gel column chromatography (eluent: hexane/$CHCl_3$ = 4:1) followed by GPC (eluent: $CHCl_3$) afforded **2f** (27.3 mg, 0.0713 mmol, 18%).

Note: The larger scale reaction of **1f** than 0.20 mmol in one batch resulted in the lower yield of **2f**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71–8.64 (m, 2H), 8.56 (s, 2H), 7.92–7.80 (m, 4H), 7.77–7.65 (m, 4H), 7.64–7.55 (m, 4H), 7.53–7.45 (m, 4H), 3.36 (s, 4H).

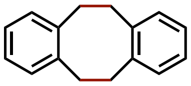
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.24, 132.34, 130.60, 130.54, 130.26, 128.75, 128.70, 127.83, 126.86, 126.63, 126.52, 126.40, 122.79, 122.26, 39.00.

HRMS (DART, positive) *m/z*: $[M+H]^+$ Calcd for $C_{30}H_{23}$ 383.17998; Found 383.17851.

Synthesis of 2g, 2g′ and 2g″

Using the general procedure A, to a 10-mL stainless-steel jar containing two 10-mm-diameter stainless-steel balls was added α,α'-dibromo-*o*-xylene (**1g**) (batch 1: 791.8 mg, 3.0 mmol, 1.0 eq.; batch 2: 791.9 mg, 3.0 mmol, 1.0 eq.), with Li (batch 1: 84.1 mg, 12.1 mmol, 4.0 eq.; batch 2: 83.7 mg, 12.1 mmol, 4.0 eq.), THF (batch 1: 0.60 mL, 7.4 mmol, 2.5 eq.; batch2: 0.60 mL, 7.4 mmol, 2.5 eq.). The reaction jars were fixed in a mixer mill (Retsch MM400) and shaking at 30 Hz (1800 rpm) at room temperature (20–25 °C) for 120 min. After shaking, the reaction jar was opened and the reaction was quenched by adding sat. NH_4Cl aq. Then, the organic phase was extracted with chloroform (three times). Purification by silica gel column chromatography (eluent: hexane/$CHCl_3$ = 20:1→10:1) followed by GPC (eluent: $CHCl_3$) afforded **2g** (100.8 mg, 0.484 mmol, 16%), **2g′** (89.1 mg, 0.285 mmol, 14%) and **2g″** (41.1 mg, 0.0661 mmol, 7%) as white solids respectively.

Compound data of 5,6,11,12-tetrahydrodibenzo[a,e][8]annulene (2g)



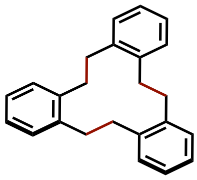
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.10–6.90 (m, 8H), 3.07 (br s, 8H)

^{13}C NMR (150 MHz, $CDCl_3$) δ 140.74, 129.82, 126.24, 35.30.

HRMS (ESI, positive) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{17}$ 209.1325; Found 209.1324.

The ^{1}H and ^{13}C NMR spectra were identical to those reported literature.[S5]

Compound data of 5,6,11,12,17,18-hexahydrotribenzo[*a*,*e*,*i*][12]annulene (2g′)



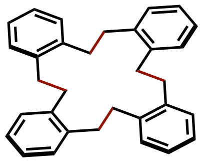
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 5.5, 3.4 Hz, 6H), 7.25 (dd, *J* = 5.5, 3.4 Hz, 6H), 3.05 (s, 12H).

^{13}C NMR (150 MHz, $CDCl_3$) δ140.22, 130.62, 126.87, 37.43.

HRMS (ESI, positive) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{25}$ 313.1956; Found 313.1950.

The ^{1}H and ^{13}C NMR spectra were identical to those reported literature.[S5]

Compound data of 5,6,11,12,17,18,23,24-octahydrotetrabenzo[*a*,*e*,*i*,*m*][16]annulene (2g″)



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24–7.19 (m, 8H), 7.19–7.16 (m, 8H), 2.89 (s, 16H).

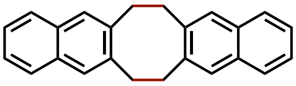
^{13}C NMR (150 MHz, $CDCl_3$) δ 139.66, 128.80, 126.46, 33.41.

HRMS (DART, positive) *m/z*: $[M+H]^+$ Calcd for $C_{32}H_{33}$ 417.25823; Found 417.25824.

Synthesis of 2h, 2h′ and 2h″

Using the general procedure A, the reaction of 2,3-bis(bromomethyl)naphthalene (**1h**) (315.0 mg, 1.0 mmol, 1.0 eq.) with Li (27.8 mg, 4.0 mmol, 4.0 eq.), THF (0.30 mL, 3.7 mmol, 3.7 eq.) was conducted at room temperature (20–25 °C) for 15 min. Purification by silica gel column chromatography (eluent: hexane/$CHCl_3$ =10:0→3:2) afforded **2h** (51.2 mg, 0.17 mmol, 33%), **2h′** (18.3 mg, 0.040 mmol, 12%), and **2h″**(11.2 mg, 0.024 mmol, 7%) as white solids respectively.

Compound data of 6,7,14,15-tetrahydrocycloocta[1,2-*b*:5,6-*b′*]dinaphthalene (2h)

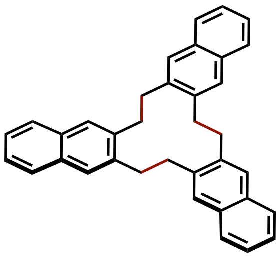


^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (br s, 4H), 7.49 (br s, 4H), 7.31 (br s, 4H), 3.31 (br s, 8H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 132.50, 127.95, 127.09, 125.19, 35.60 (br).

HRMS (DART, positive) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{21}$ 309.16433; Found 309.16379.

Compound data of 6,7,14,15,22,23-hexahydrocyclododeca[1,2-*b*:5,6-*b′*:9,10-*b″*]trinaphthalene (2h′)

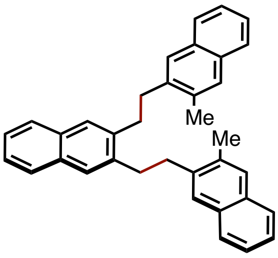


^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (s, 6H), 7.88–7.84 (m, 6H), 7.49–7.45 (m, 6H), 3.33 (s, 12H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 138.76, 132.82, 129.11, 127.28, 125.75, 38.15.

HRMS (DART, positive) *m/z*: $[M+H]^+$ Calcd for $C_{36}H_{31}$ 463.24258; Found 463.24179.

Compound data of 2,3-bis(2-(3-methylnaphthalen-2-yl)ethyl)naphthalene (2h″)

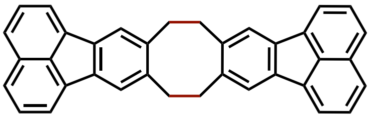


^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (dd, J = 5.5, 3.4 Hz, 2H), 7.75 (s, 2H), 7.75 (d, J = 7.6 Hz, 2H), 7.70 (d, J = 7.6 Hz, 2H), 7.64 (s, 2H), 7.63 (s, 2H), 7.47–7.34 (m, 6H), 3.21–3.14 (m, 8H), 2.50 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 139.06, 138.72, 134.86, 132.59, 132.53, 128.29, 127.53, 127.26 (2C), 127.00, 126.84, 125.55, 125.44, 125.27, 35.32, 33.92, 20.06.

HRMS (DART, positive) *m/z*: $[M+H]^+$ Calcd for $C_{36}H_{33}$ 465.25823; Found 465.25599.

Synthesis of 8,9,18,19-tetrahydrocycloocta[1,2-*k*:5,6-*k′*]bis(fluoranthene) (2i)



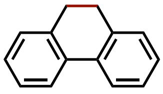
Using the general procedure A, the reaction of 8,9-bis(bromomethyl)fluoranthene (**1i**) (194.2 mg, 0.50 mmol, 1.0 eq), Li (27.7 mg, 4.0 mmol, 8.0 eq.), and THF (0.30 mL, 3.7 mmol, 7.4 eq.) was conducted at room temperature (20–25 °C) for 8 h. Purification by silica gel column chromatography (eluent: hexane/$CHCl_3$ = 6:1→4:1) followed by GPC (eluent: $CHCl_3$) afforded **2i** as a white solid (19.1 mg, 0.418 mmol, 16%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 6.9 Hz, 4H), 7.70 (d, *J* = 8.2 Hz, 4H), 7.55 (s, 4H), 7.53–7.52 (t, *J* = 7.6 Hz, 4H), 3.30 (s, 8H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 140.07 (br), 137.83, 137.28, 132.74, 130.00, 127.88, 126.19, 123.18, 119.60, 35.74.

HRMS (DART, positive) *m/z*: $[M+H]^+$ Calcd for $C_{36}H_{25}$ 457.19563; Found 457.19451.

Synthesis of 9,10-dihydrophenanthrene (2j)



Using the general procedure A, the reaction of 2,2′-bis(bromomethyl)-1,1′-biphenyl (**1j**) (341.1 mg, 1.0 mmol, 1.0 eq.) with Li (27.9 mg, 4.0 mmol, 4.0 eq.), THF (0.30 mL, 3.7 mmol, 3.7 eq.) was conducted at room temperature (20–25 °C) for 15 min. Purification by a short pass column (eluent: hexane) afforded **2j** as a white solid (141.2 mg, 0.78 mmol, 78% yield).

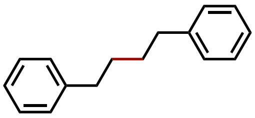
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.7 Hz, 2H), 7.33–7.29 (m, 2H), 7.26–7.21 (m, 4H), 2.88 (s, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.53, 134.61, 128.27, 127.51, 127.08, 123.84, 29.17.

LRMS (EI, positive) *m/z*: $[M]^+$ Calcd for $C_{14}H_{12}$ 180.09390; Found 180.09405.

The ^{1}H and ^{13}C NMR spectra were identical to those reported literature[S4].

Synthesis of 1,4-diphenylbutane (2k)



Using the general procedure A, the reaction of phenethyl bromide (**1k**) (185.3 mg, 1.0 mmol, 1.0 eq.) with Li (27.7 mg, 4.0 mmol, 4.0 eq.), THF (0.30 mL, 3.7 mmol, 3.7 eq.) was conducted at room temperature (20–25 °C) for 60 min. Purification by a short pass column (eluent: hexane) afforded **2k** as a white solid (77.2 mg, 0.37 mmol, 73% yield).

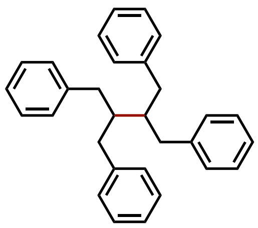
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.25 (m, 4H), 7.20–7.14 (m, 6H), 2.63 (br s, 4H), 1.67 (br s, 4H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 142.72, 128.55, 128.40, 125.78, 35.95, 31.23.

HRMS (ESI, positive) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{19}$ 211.1481; Found 211.1480.

The ^{1}H and ^{13}C NMR spectra were identical to those reported literature.[S6]

Synthesis of (2-(1,3-diphenylpropan-2-yl)propane-1,3-diyl)dibenzene (2l)



Using the general procedure A, the reaction of 1,1′-(2-bromo-1,3-propanediyl)bis[benzene] (**1l**) (138.2 mg, 0.50 mmol, 1.0 eq.) with Li (13.9 mg, 2.0 mmol, 4.0 eq.), THF (0.20 mL, 2.5 mmol, 2.5 eq.) was conducted at room temperature (20–25 °C) for 8 h. Purification by silica gel column chromatography (eluent: hexane/$CHCl_3$ = 10:0 → 10:1) followed by GPC (eluent: $CHCl_3$) afforded **2l** as a pale-yellow solid (41.1 mg, 0.11 mmol, 42%). The single crystal of **2l** was obtained from hexane.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26–7.19 (m, 8H), 7.19–7.13 (m, 4H), 6.96 (d, J = 7.2 Hz, 8H), 2.76 (dd, J = 13.6, 7.7 Hz, 4H), 2.48 (dd, J = 13.6, 7.7 Hz, 4H), 2.02 (quint, J = 7.3 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.24, 129.13, 128.35, 125.90, 41.47, 36.25.

HRMS (ESI, positive) *m/z*: $[M]^+$ Calcd for $C_{30}H_{30}$ 390.2342; Found 390.2342.

Synthesis of *n*-tetraicosane (2m)

Using the general procedure A with slight modification using Na instead of Li, the reaction of 1-bromododecane (**1m**) (250.9 mg, 1.0 mmol, 1.0 eq.) with Na lump (91.9 mg, 4.0 mmol, 4.0 eq.), THF (0.30 mL, 3.7 mmol, 3.7 eq.) was conducted at room temperature (20–25 °C) for 1 h. Purification by silica gel column chromatography (eluent: hexane) followed by GPC (eluent: $CHCl_3$) afforded **2m** as a white solid (59.9 mg, 0.177 mmol, 35%).

^{1}H NMR (600 MHz, C_6D_6) δ 1.39–1.25 (m, 44H), 0.92 (t, J = 6.9 Hz, 6H).

^{13}C NMR (150 MHz, C_6D_6) δ 32.31, 30.18 (7C), 30.10, 29.80, 23.09, 14.34.

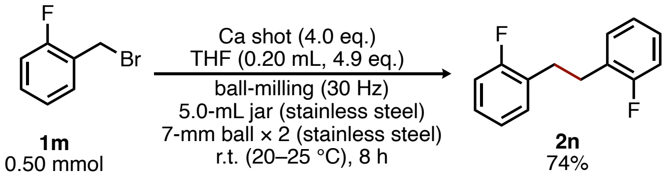
HRMS (DART, positive) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{50}$ 338.39125 ; Found 338.39028.

The ^{1}H and ^{13}C NMR spectra were identical to those reported literature.[S7]

2-2. General Procedure B for calcium(0)-mediated mechanochemical Wurtz reaction

Synthesis of 1,2-bis(2-fluorophenyl)ethane (2n)

The synthesis of 1,2-bis(2-fluorophenyl)ethane (**2n**) is described as a representative example of the general procedure B.



Two 7.0-mm diameter stainless-steel balls and 2-fluorobenzyl bromide (**1n**) (94.4 mg, 0.50 mmol, 1.0 eq.) were added to an oven-dried 5.0-mL stainless-steel jar. Calcium shot (80.9 mg, 2.0 mmol, 4.0 eq., 99.5% purity) was weighed on an electronic balance, and added to the jar under air. Then, THF (0.20 mL, 2.5 mmol, 4.9 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with an O-shaped packing made of 1-mm width polyethylene sheet, and the jar was sealed tightly with a wrench and a vise. The reaction jar and a same-weight blank jar (or a same-weight reaction jar) were fixed in a mixer mill (Retsch MM400 or MM500 Vario), and shaken at 30 Hz (1800 rpm) at room temperature (20–25 °C) for 8 h. After shaking, the reaction jar was opened and the reaction was quenched by adding sat. NH_4Cl aq. Then, the organic phase was extracted with chloroform (three times). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford a crude product. The crude product was purified by silica gel column chromatography (eluent: pentane), affording a 1,2-bis(2-fluorophenyl)ethane (**2n**) as a colorless oil (40.2 mg, 0.18 mmol, 74% yield). The ^{1}H, ^{13}C and ^{19}F NMR spectra were identical to those reported literature.[S8]

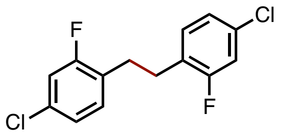
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21–7.15 (m, 2H), 7.13 (td, *J* = 1.7, 7.7 Hz, 2H), 7.05–7.00 (m, 4H), 2.96 (s, 4H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 161.33 (d, $J_{C–F}$ = 244.2 Hz), 130.86 (d, $J_{C–F}$ = 4.3 Hz), 128.38 (d, $J_{C–F}$ = 15.9 Hz), 127.91 (d, $J_{C–F}$ = 7.2 Hz), 124.02 (d, $J_{C–F}$ = 4.3 Hz), 115.33 (d, $J_{C–F}$ = 23.1 Hz), 29.86.

^{19}F NMR (372 MHz, $CDCl_3$) δ –119.33.

HRMS (DART, positive) *m/z*: $[M]^+$ Calcd for $C_{14}H_{12}F_2$ 218.09071; Found 218.09087.

Synthesis of 1,2-bis(4-chloro-2-fluorophenyl)ethane (2o)



Using the general procedure B, the reaction of 4-chloro-3-fluorobenzyl bromide (**1o**) (223.5 mg, 1.0 mmol, 1.0 eq.) with calcium shot (160.8 mg, 4.0 mmol, 4.0 eq.), THF (0.20 mL, 2.5 mmol, 2.5 eq.) was conducted at room temperature (20–25 °C) for 2 h. Purification by silica gel column chromatography (eluent: hexane) afforded **2o** as a white solid (84.7 mg, 0.29 mmol, 60%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.6 Hz, 2H), 7.06 (t, *J* = 7.4 Hz, 2H), 6.87 (t, *J* = 8.2 Hz, 2H), 2.97 (s, 4H).

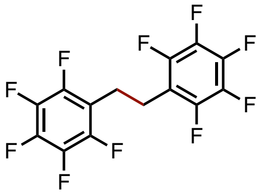
^{13}C NMR (100 MHz, $CDCl_3$) δ 161.23 (d, $J_{C–F}$ = 247.7 Hz), 134.58 (d, $J_{C–F}$ = 2.9 Hz), 134.48, 131.53

(d, $J_{C\text{–}F}$ = 8.5 Hz), 116.87 (d, $J_{C\text{–}F}$ = 24.7 Hz), 114.05 (d, $J_{C\text{–}F}$ = 20.9 Hz), 33.22.

^{19}F NMR (372 MHz, CDCl$_3$) δ –114.99.

HRMS (DART, positive) *m/z*: [M]$^+$ Calcd for $C_{14}H_{10}Cl_2F_2$ 286.01276; Found 286.01400.

Synthesis of 1,2-bis(perfluorophenyl)ethane (2p)



Using the general procedure B, the reaction of 4-chloro-3-fluorobenzyl bromide (**1p**) (130.4 mg, 0.50 mmol, 1.0 eq.) with calcium shot (80.8 mg, 2.0 mmol, 4.0 eq.), THF (0.20 mL, 2.5 mmol, 4.9 eq.) was conducted at room temperature (20–25 °C) for 8 h. Purification by silica gel column chromatography (eluent: hexane) afforded **2p** as a white solid (30.2 mg, 0.083 mmol, 33%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 3.01 (s, 4H).

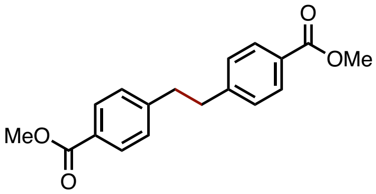
^{13}C NMR (100 MHz, CDCl$_3$) δ 146.05(m), 144.23 (m), 141.08 (m), 139.46 (m), 138.38 (m), 136.75 (m), 112.89 (td, *J* = 13.5, 4.3 Hz), 21.95.

^{19}F NMR (372 MHz, CDCl$_3$) δ –142.47, –152.30 (m), –161.41 (t, *J* = 19.2 Hz).

HRMS (EI, positive) *m/z*: [M]$^+$ Calcd for $C_{14}H_4F_{10}$ 362.01533; Found 362.01703.

The ^{1}H, ^{13}C and ^{19}F NMR spectra were identical to those reported literature.[S9]

Synthesis of dimethyl 4,4'-(ethane-1,2-diyl)dibenzoate (2r)



Using the general procedure B, the reaction of methyl-4-(bromomethyl)benzoate (**1r**) (229.9 mg, 1.00 mmol, 1.0 eq.) with calcium shot (160.9 mg, 4.0 mmol, 4.0 eq.), THF (0.20 mL, 2.5 mmol, 2.5 eq.) was conducted at room temperature (20–25 °C) for 6 h. Purification by silica gel column chromatography (eluent: hexane/CHCl$_3$ = 10:0 → 5:1) afforded **2r** as a white solid (71.2 mg, 0.24 mmol, 48%).

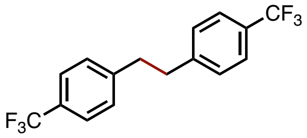
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.01 (d, *J* = 6.5 Hz, 4H), 7.46 (d, *J* = 8.2 Hz, 4H), 4.50 (s, 4H), 3.92 (s, 6H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 166.68, 142.75, 130.22, 129.17, 52.38, 32.38.

HRMS (DART, positive) *m/z*: [M+H]$^+$ Calcd for $C_{18}H_{19}O_4$ 299.12833; Found 299.12757.

The ^{1}H, ^{13}C and ^{19}F NMR spectra were identical to those reported literature.[S10]

Synthesis of 1,2-bis(4-trifluoromethylphenyl)ethane (2s)



Using the general procedure B, the reaction of methyl-4-(bromomethyl)benzoate (**1s**) (120.1 mg, 0.50 mmol, 1.0 eq.) with calcium shot (80.2 mg, 2.0 mmol, 4.0 eq.), THF (0.20 mL, 2.5 mmol, 4.9 eq.) was conducted at room temperature (20–25 °C) for 8 h. Purification by silica gel column chromatography (eluent: pentane) afforded **2s** as a white solid (61.8 mg, 0.19 mmol, 78%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.53 (d, *J* = 7.9 Hz, 4H), 7.25 (d, *J* = 7.3 Hz, 4H), 2.99 (s, 4H).

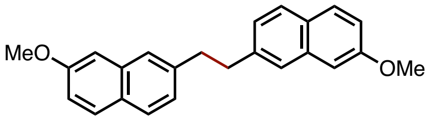
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.16, 128.92 (2C), 125.52 (q, *J* = 3.6 Hz), 124.42 (q, *J* = 271.7 Hz), 37.38.

^{19}F NMR (372 MHz, $CDCl_3$) δ –62.63.

HRMS (EI, positive) *m/z*: $[M]^+$ Calcd for $C_{16}H_{12}F_6$ 318.08432; Found 318.08424.

The ^{1}H, ^{13}C and ^{19}F NMR spectra were identical to those reported literature.[S11]

Synthesis of 1,2-bis(7-methoxynaphthalen-2-yl)ethane (2t)



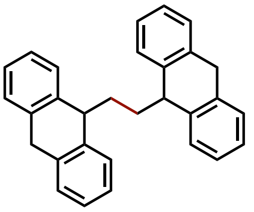
Using the general procedure B, the reaction of 2-(bromomethyl)-7-methoxynaphthalene (**1t**) (251.9 mg, 1.00 mmol, 1.0 eq.) with calcium shot (162.0 mg, 4.0 mmol, 4.0 eq.), THF (0.20 mL, 2.5 mmol, 2.5 eq.) was conducted at room temperature (20–25 °C) for 8 h. Purification by silica gel column chromatography (eluent: hexane/$CHCl_3$ = 10:0 → 4:1) afforded **2t** as a pale-brown solid (106.2 mg, 0.31 mmol, 62%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 4H), 7.56 (s, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.09 (d, *J* = 10.9 Hz, 2H), 7.08 (s, 2H), 3.91 (s, 6H), 3.14 (s, 4H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 157.86, 140.09, 134.93, 129.26, 127.80, 127.67, 125.65, 125.23, 118.11, 105.63, 55.43, 38.22.

HRMS (DART, positive) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{23}O_2$ 343.16980; Found 343.16827.

Synthesis of 1,2-bis(9,10-dihydroanthracen-9-yl)ethane (2u)



Using the general procedure B, the reaction of 9-(bromomethyl)anthracene (**1u**) (81.9 mg, 0.30 mmol, 1.0 eq.) with calcium shot (49.1 mg, 1.2 mmol, 4.0 eq.), THF (0.20 mL, 2.5 mmol, 8.2 eq.) was conducted at room temperature (20–25 °C) for 8 h. Purification by silica gel column chromatography (eluent: hexane/$CHCl_3$ = 4:1) followed by GPC (eluent: $CHCl_3$) afforded **2u** as a white solid (27.1 mg, 0.070 mmol, 46%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.24 (m, 4H), 7.17–7.11 (m, 12H), 4.01 (d, *J* = 18.1 Hz, 2H), 3.81–3.76 (m, 4H), 1.65–1.60 (m, 4H).

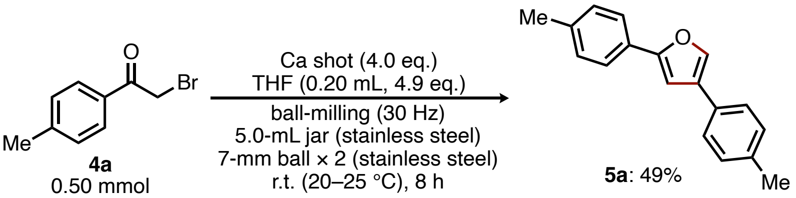
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.68, 136.32, 128.13, 127.86, 126.18, 126.09, 47.59, 35.48, 35.00.

HRMS (ESI, positive) *m/z*: $[M–H]^+$ Calcd for $C_{30}H_{25}$ 385.1951; Found 385.1951.

2-3. General procedure C for calcium(0)-mediated mechanochemical synthesis of furans

Synthesis of 2,4-di-*p*-tolylfuran (5a)

The synthesis of 2,4-di-*p*-tolylfuran (**5a**) is described as a representative example of the general procedure C.



Two 7.0-mm diameter stainless-steel balls and 2-bromo-4'-methylacetophenone (**4a**) (107.2 mg, 0.50 mmol, 1.0 eq.) were added to an oven-dried 5.0-mL stainless-steel jar. Calcium shot (80.9 mg, 2.0 mmol, 4.0 eq., 99.5% purity) were weighed on an electronic balance, and added to the jar under air. Then, THF (0.20 mL, 2.5 mmol, 4.9 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with an O-shaped packing made of 1-mm width polyethylene sheet, and the jar was sealed tightly with a wrench and a vise. The reaction jar and a same-weight blank jar (or a same-weight reaction jar) were fixed in a mixer mill (Retsch MM400 or MM500 Vario), and shaken at 30 Hz (1800 rpm) at room temperature (20–25 °C) for 8 h. After shaking, the reaction jar was opened and the reaction was quenched by adding sat. NH_4Cl aq. Then, the organic phase was extracted with chloroform (three times). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford a crude product. The crude product was purified by silica gel column chromatography (eluent: hexane/$CHCl_3$ = 10:0 → 10:1), affording a 2,4-di-*p*-tolylfuran (**5a**) as a pale-yellow solid (29.1 mg, 0.12 mmol, 49% yield).

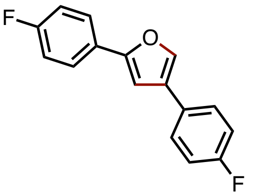
The ^{1}H and ^{13}C NMR spectra were identical to those reported literature.[S12]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 7.6 Hz, 2H), 6.89 (s, 1H), 2.37 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.08, 137.53, 137.35, 136.93, 129.68, 129.62, 129.52, 128.33, 128.19, 125.82, 123.94, 103.46, 21.44, 21.34.

HRMS (DART, positive) *m/z*: [M]$^+$ Calcd for $C_{18}H_{16}O$ 248.12011; Found 248.12043.

Synthesis of 2,4-bis(4-fluorophenyl)furan (5b)



Using the general procedure C, the reaction of 2-bromo-4'-fluoroacetophenone (**4b**) (108.2 mg, 0.50 mmol, 1.0 eq.) with calcium shot (80.8mg, 2.0 mmol, 4.0 eq.), THF (0.20 mL, 2.5 mmol, 4.9 eq.) was conducted at room temperature (20–25 °C) for 8 h. Purification by silica gel column chromatography (eluent: hexane/$CHCl_3$ = 1:0 → 9:1) afforded **2q** as a pale-yellow solid (21.1 mg, 0.082 mmol, 33%).

The ^{1}H, ^{13}C and ^{19}F NMR spectra were identical to those reported literature.[S12]

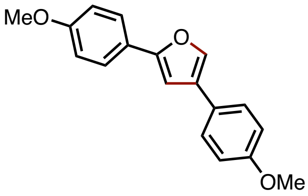
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70–7.65 (m, 3H), 7.50–7.46 (m, 2H), 7.11 (d, J = 8.3 Hz, 2H), 7.08 (d, J = 8.9 Hz, 2H), 6.84 (s, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 162.46 (d, $J_{C–F}$ = 247.1 Hz), 162.2 (d, $J_{C–F}$ = 247.1 Hz), 154.28, 137.69, 128.54 (d, $J_{C–F}$ = 2.9 Hz), 127.70, 127.52 (d, $J_{C–F}$ = 7.2 Hz), 127.05 (d, $J_{C–F}$ = 2.9 Hz), 125.80 (d, $J_{C–F}$ = 8.7 Hz), 115.94 (d, $J_{C–F}$ = 21.7 Hz), 115.92 (d, $J_{C–F}$ = 21.7 Hz), 103.80.

^{19}F NMR (373 MHz, $CDCl_3$) δ –103.44.

HRMS (DART, positive) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{11}F_2O$ 257.07780; Found 257.07859.

Synthesis of 2,4-bis(4-methoxyphenyl)furan (5c)



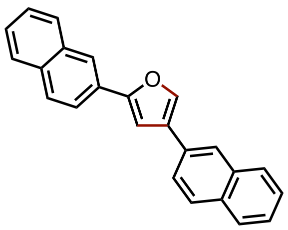
Using the general procedure C, the reaction of 2-bromo-4'-methoxyacetophenone (**4c**) (115.1 mg, 0.50 mmol, 1.0 eq.) with calcium shot (81.1 mg, 2.0 mmol, 4.0 eq.), THF (0.20 mL, 2.5 mmol, 4.9 eq.) was conducted at room temperature (20–25 °C) for 8 h. Purification by silica gel column chromatography (eluent: hexane/$CHCl_3$ = 10:0 → 5:1) afforded **5c** as a pale-yellow solid (44.3 mg, 0.16 mmol, 63%).

^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.68–7.63 (m, 3H), 7.47 (d, J = 8.2 Hz, 2H), 6.95 (d, J = 8.3 Hz, 2H), 6.93 (d, J = 7.6 Hz, 2H), 6.83 (s, 1H), 3.83 (s, 3H), 3.82 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 159.30, 158.91, 154.90, 136.60, 128.05, 127.08, 125.43, 125.29, 123.99, 114.37, 114.29, 102.67, 55.48 (2C).

HRMS (ESI, positive) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{17}O_3$ 281.1177; Found 281.1172.

Synthesis of 2,4-di(naphthalen-2-yl)furan (5d)



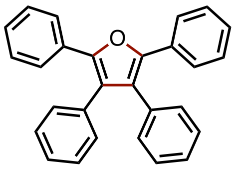
Using the general procedure C, the reaction of 2-bromoacetylnaphthalene (**4d**) (124.8 mg, 0.50 mmol, 1.0 eq.) with calcium shot (100.3 mg, 2.5 mmol, 5.0 eq.), THF (0.20 mL, 2.5 mmol, 4.9 eq.) was conducted at room temperature (20–25 °C) for 8 h. Purification by silica gel column chromatography (eluent: hexane/$CHCl_3$ = 10:1 → 4:1) afforded **5d** as a white solid (60.8 mg, 0.19 mmol, 76%). The single crystal of **2g** was obtained from $CHCl_3$. The single crystal of **5d** was obtained from $CHCl_3$/MeOH.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 8.02 (s, 1H), 7.94 (s, 1H), 7.91–7.84 (m, 7H), 7.70 (d, J = 8.4 Hz, 1H), 7.55–7.45 (m, 4H), 7.24 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.27, 138.71, 133.87, 133.66, 132.96, 132.78, 129.83, 128.67, 128.64, 128.38, 128.01, 127.94, 127.89, 126.72, 126.59, 126.23, 125.92, 124.50, 124.19, 122.54, 122.44, 104.76. Two quaternary carbon peaks are missing due to overlapping.

HRMS (ESI, positive) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{17}O$ 321.1279; Found 321.1274.

Synthesis of 2,3,4,5-tetraphenylfuran (5f)



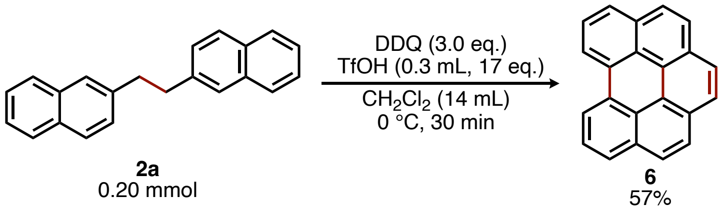
Using the general procedure C, the reaction of 2-bromo-1,2-diphenylethanone (**4f**) (275.8 mg, 1.0 mmol, 1.0 eq.) with calcium shot (161.2 mg, 4.0 mmol, 4.0 eq.), THF (0.30 mL, 3.7 mmol, 3.7 eq.) was conducted at room temperature (20–25 °C) for 8 h. Purification by silica gel column chromatography (eluent: hexane/$CHCl_3$ = 10:1) afforded **5f** as a white solid (58.2 mg, 0.16 mmol, 31%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54–7.50 (m, 4H), 7.28–7.20 (m, 12H), 7.19–7.14 (m, 4H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 147.83, 133.30, 131.03, 130.54, 128.52, 128.50, 127.45, 127.30, 125.99, 125.24. The ^{1}H, ^{13}C and ^{19}F NMR spectra were identical to those reported literature.[S13]

HRMS (ESI, positive) *m/z*: $[M+H]^+$ Calcd for $C_{28}H_{21}O$ 373.1592; Found 373.1587.

3. Synthesis of benzo[*ghi*]perylene (6) from 2a



To a dried 50-mL two-neck round-bottom flask containing a magnetic stirring bar were added 1,2-di(naphthalen-2-yl)ethane (**2a**) (56.3 mg, 0.20 mmol, 1.00 eq.) and DDQ (136.1 g, 0.60 mmol, 3.0 eq.) in CH_2Cl_2 (14 mL). After cooling to 0 °C, TfOH (0.30 mL, 3.4 mmol, 17 eq.) was added, and the mixture was stirred at 0 °C for 30 min. Then, saturated aqueous $NaHCO_3$ solution was added to quench the reaction, and the organic phase was extracted with $CHCl_3$ three times. The combined organic layers were dried over Na_2SO_4, and the solvent was removed by a rotary evaporator under reduced pressure. Finally, the residue was purified by flash column chromatography on silica gel (eluent: hexane/$CHCl_3$ = 10:0 → 10:1) to afford benzo[*ghi*]perylene (**6**) as a light green solid (31.1 mg, 0.11 mmol, 57%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.04 (d, J = 7.6 Hz, 2H), 8.38 (s, 2H), 8.22 (d, J = 7.6 Hz, 2H), 8.16 (d, J = 8.9 Hz, 2H), 8.11 (d, J = 8.2 Hz, 2H), 8.04 (t, J = 7.6 Hz, 2H).

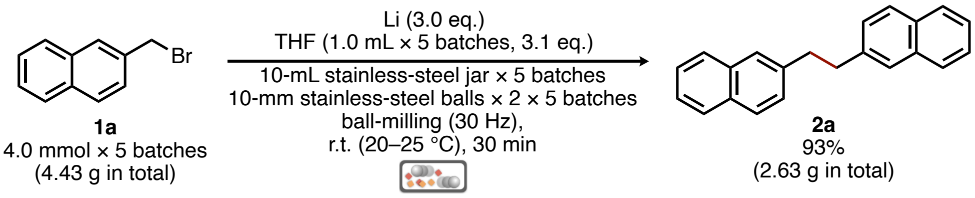
^{13}C NMR (150 MHz, $CDCl_3$) δ 132.39, 130.60, 129.36, 127.56 (2C), 126.69, 126.39, 125.91, 125.81, 124.13, 120.87.

The ^{1}H and ^{13}C NMR spectra were identical to those reported literature.[S4]

HRMS (DART, positive) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{13}$ 277.10173; Found 277.10188.

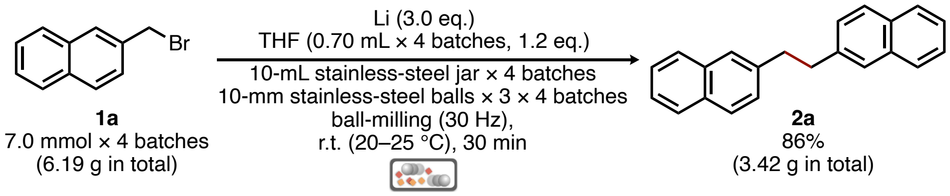
4. Large scale synthesis of 2a

4-1. A 20-mmol scale Wurtz reaction of 1a in the parallel five batches



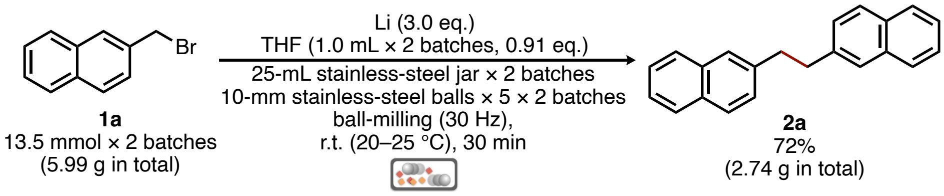
Two 10-mm diameter stainless-steel balls and 2-(bromomethyl)naphthalene (**1a**) (884.3 mg, 4.00 mmol, 1.0 eq.) were added to an oven-dried 10-mL stainless-steel jar. Pieces of Li (84.1 mg, 12.1 mmol, 3.0 eq.) cut from lithium wire (3.2 mm in diameter, 99.9% purity) was washed with hexane for removing mineral oil, weighed on an electronic balance, and added into the jar under air. Then, THF (1.0 mL, 12.3 mmol, 3.1 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with an O-shaped packing made of 1-mm width polyethylene sheet, and the jar was sealed tightly with a wrench and a vise. Other four-batch reaction jars were also prepared in a same manner, and totally five reactions jars containing 2-(bromomethyl)naphthalene (**1a**) (4.43 g, 20 mmol, 1.0 eq.), pieces of Li (0.42 g, 60 mmol, 3.0 eq.) and THF (5.0 mL, 62 mmol, 3.1 eq.) and one blank reaction jar with a same-weight were fixed in a mixer mill (MM500 Vario), and shaken at 30 Hz (1800 rpm) at room temperature (20–25 °C) for 30 min. After shaking, the reaction jars were opened and the reactions were quenched by adding sat. NH_4Cl aq. Then, the contents were combined and poured into a separation funnel. The organic phase was extracted with chloroform (three times). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford a crude product. The crude product was purified by short pass silica gel column chromatography (eluent: $CHCl_3$), affording a 1,2-di(naphthalen-2-yl)ethane (**2a**) as a white solid (2.63 g, 9.32 mmol, 93% yield).

4-2. A 28-mmol scale Wurtz reaction of 1a in the parallel four batches



Three 10-mm diameter stainless-steel balls and 2-(bromomethyl)naphthalene (**1a**) (1.545 g, 7.0 mmol, 1.0 eq) were added to an oven-dried 10-mL stainless-steel jar. Pieces of Li (145.8 mg, 21.0 mmol, 3.0 eq.) cut from lithium wire (3.2 mm in diameter, 99.9% purity) was washed with hexane for removing mineral oil, weighed on an electronic balance, and added into the jar under air. Then, THF (0.70 mL, 8.6 mmol, 1.2 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with an O-shaped packing made of 1-mm width polyethylene sheet, and the jar was sealed tightly with a wrench and a vise. Other three-batch reaction jars were also prepared in a same manner, and totally four reactions jars containing 2-(bromomethyl)naphthalene (**1a**) (6.19 g, 28 mmol, 1.0 eq.), pieces of Li (0.58 g, 84 mmol, 3.0 eq.) and THF (2.8 mL, 34 mmol, 1.2 eq.) and two blank reaction jars with a same-weight were fixed in a mixer mill (MM500 Vario), and shaken at 30 Hz (1800 rpm) at room temperature (20–25 °C) for 30 min. After shaking, the reaction jars were opened and the reactions were quenched by adding sat. NH_4Cl aq. Then, the contents were combined and poured into a separation funnel. The organic phase was extracted with chloroform (three times). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford a crude product. The crude product was purified by short pass silica gel column chromatography (eluent: $CHCl_3$), affording a 1,2-di(naphthalen-2-yl)ethane (**2a**) as a white solid (3.42 g, 12.1 mmol, 86% yield).

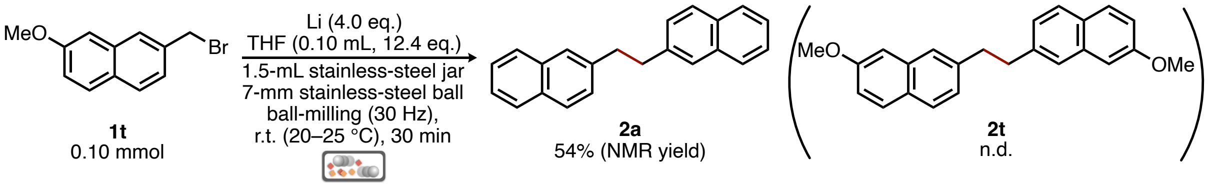
4-3. A 27-mmol scale Wurtz reaction of 1a in the parallel two batches



Five 10-mm diameter stainless-steel balls and 2-(bromomethyl)naphthalene (**1a**) (2.99 g, 13.5 mmol, 1.0 eq.) were added to an oven-dried 10-mL stainless-steel jar. Pieces of Li (274.2 mg, 39.5 mmol, 3.0 eq.) cut from lithium wire (3.2 mm in diameter, 99.9% purity) was washed with hexane for removing mineral oil, weighed on an electronic balance, and added into the jar under air. Then, THF (1.0 mL, 12 mmol, 0.91 eq) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with an O-shaped packing made of 1-mm width polyethylene sheet, and the jar was sealed tightly with a wrench and a vise. Other one-batch reaction jar was also prepared in a same manner, and totally four reactions jars containing 2-(bromomethyl)naphthalene (**1a**) (5.99 g, 27 mmol, 1.0 eq.), pieces of Li (0.55 g, 80 mmol, 3.0 eq.) and THF (2.0 mL, 25 mmol, 0.91 eq.) and four blank reaction jars with a same-weight were fixed in a mixer mill (MM500 Vario), and shaken at 30 Hz (1800 rpm) at room temperature (20–25 °C) for 30 min. After shaking, the reaction jars were opened and the reactions were quenched by adding sat. NH_4Cl aq. Then, the contents were combined and poured into a separation funnel. The organic phase was extracted with chloroform (three times). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford a crude product. The crude product was purified by short pass silica gel column chromatography (eluent: $CHCl_3$), affording a 1,2-di(naphthalen-2-yl)ethane (**2a**) as a white solid (2.74 g, 9.7 mmol, 72% yield).

5. Control experiments

5-1. Control experiment using 1t and lithium(0) wire



1t
0.10 mmol

2a
54% (NMR yield)

2t
n.d.

Using the general procedure A, to a 1.5-mL stainless-steel jar containing a 7-mm-diameter stainless-steel ball was added with 2-(bromomethyl)-7-methoxynaphthalene (**1t**) (25.1 mg, 0.10 mmol, 1.0 eq.), Li (2.4 mg, 4.0 mmol, 4.0 eq.), and THF (0.30 mL, 3.7 mmol, 3.7 eq.). The reaction jar was fixed in a mixer mill (Retsch MM400) and shaking at 30 Hz (1800 rpm) at room temperature (20–25 °C) for 30 min. After shaking, the reaction jar was opened and the reaction was quenched by adding sat. NH_4Cl aq. Then, the organic phase was extracted with chloroform (three times). The combined organic phase was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford a crude product. The crude mixture was dissolved in EtOAc and analyzed by GC-MS. The spectra of 2-methylnephthalene (retention time: ca. 4.5 min) and **2a** (retention time: ca. 9.8 min) were detected, and **2t** was not detected. ^{1}H NMR with dibromomethane as an internal standard to determine the formation of **2a** (54% NMR yield).

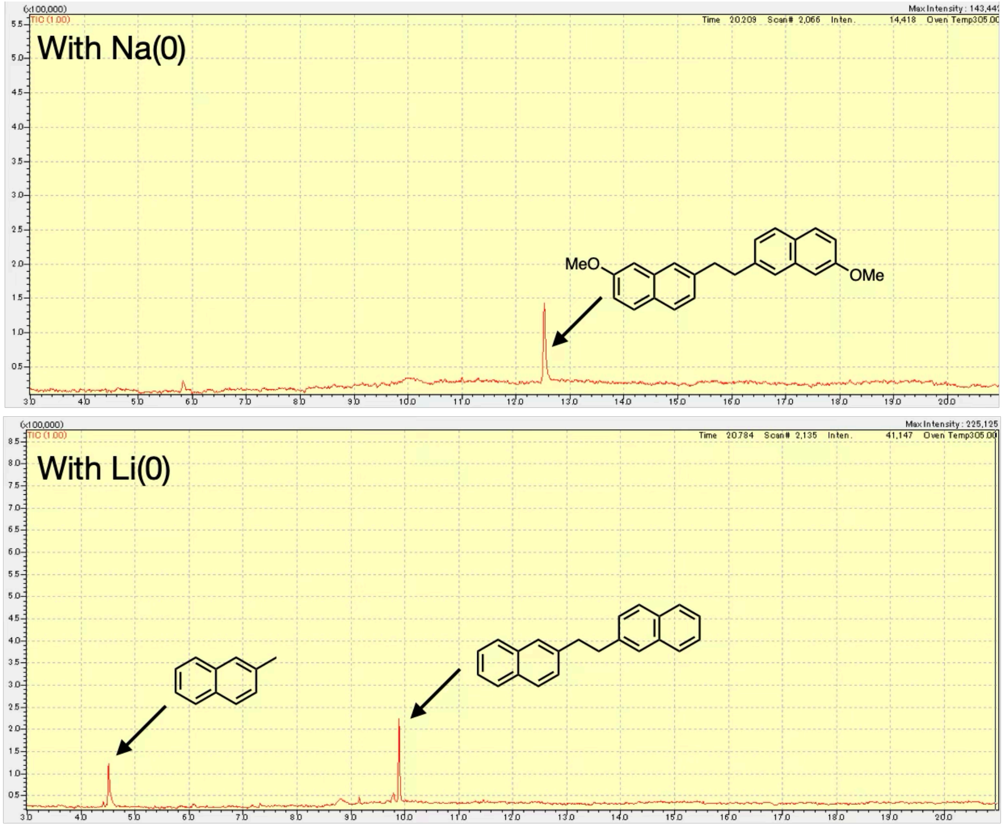
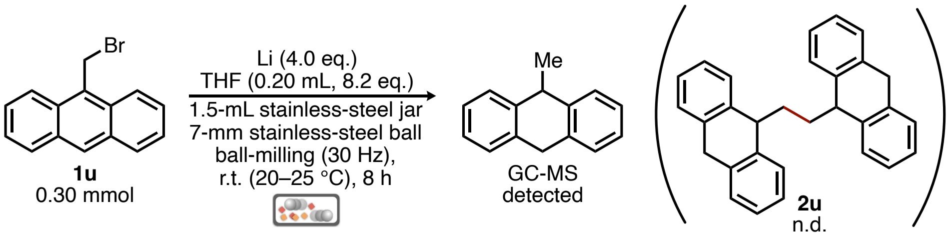


Figure S1. GC-MS spectra of crude mixture. Top: Using Na(0) Bottom: Using Li(0).

5-2. Control experiment using 1u and lithium(0) wire



Using the general procedure A, to a 1.5-mL stainless-steel jar containing a 7-mm-diameter stainless-steel ball was added with 9-(bromomethyl)anthracene (**1u**) (82.0 mg, 0.30 mmol, 1.0 eq), Li (8.3 mg, 1.2 mmol, 4.0 eq.), and THF (0.20 mL, 2.5 mmol, 8.2 eq.). The reaction jar was fixed in a mixer mill (Retsch MM400) and shaking at 30 Hz (1800 rpm) at room temperature (20–25 °C) for 8 h. After shaking, the reaction jar was opened and the reaction was quenched by adding sat. NH_4Cl aq. Then, the organic phase was extracted with chloroform (three times). The combined organic phase was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford a crude product. The crude mixture was dissolved in EtOAc and analyzed by GC-MS. The spectra of 9-methyl-9,10-dihydroanthracene (retention time: ca. 6.3 min) and **1u** (retention time: ca. 8.4 min) were detected, and **2u** was not detected. The crude mixture was analyzed by APCI-MS, and **2u** was not detected.

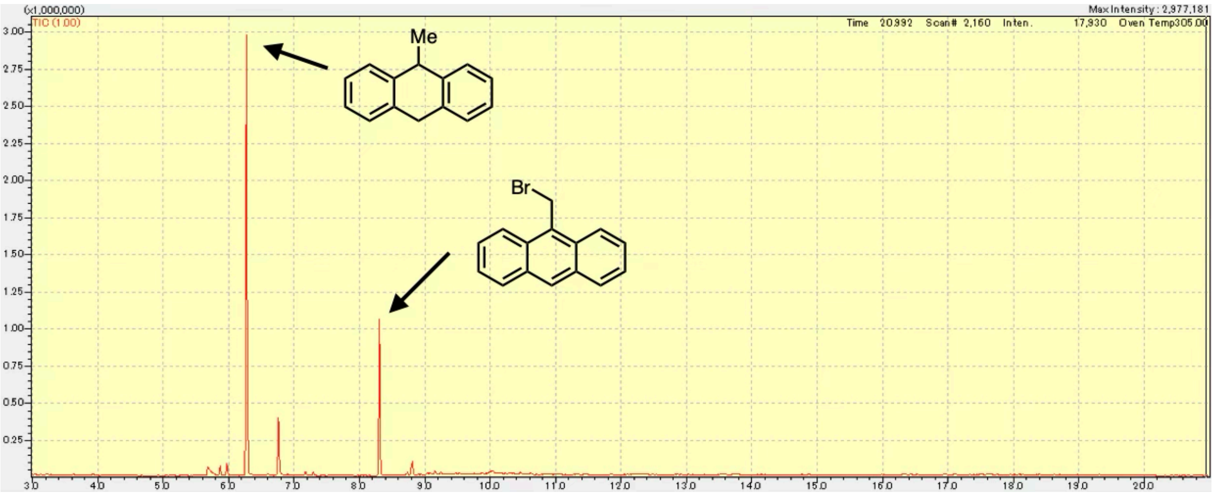


Figure S2. GC-MS spectra of crude mixture.

5-3. Ball-milling for 5 or 60 min (Table 1, entries 2 and 3)

A 1.5-mm diameter stainless-steel ball and anthracene (**1a**) (221.3 mg, 1.0 mmol, 1.0 eq.) were added to an oven-dried 5.0-mL stainless-steel jar. Pieces of Li (27.7 mg, 4.0 mmol, 4.0 eq.) cut from Lithium wire (3.2 mm in diameter, 99.9% purity) was washed with hexane for removing mineral oil, weighed on an electronic balance, and added into the jar under air. Then, THF (0.15 mL, 3. mmol, 3.7 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with an O-shaped packing made of 1-mm width polyethylene sheet, and the jar was sealed tightly with a wrench and a vise. The reaction jar and a same-weight blank jar (or a same-weight reaction jar) were fixed in a mixer mill (Retsch MM400), and shaken at 30 Hz (1800 rpm) at room temperature (20–25 °C) for 5 min or 60 min. After shaking, the reaction jar was opened and the reaction was quenched by adding sat. NH_4Cl aq. Then, the organic phase was extracted with chloroform (three times). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford a crude product. The crude mixture was analyzed by GC using *n*-decane as an internal standard.

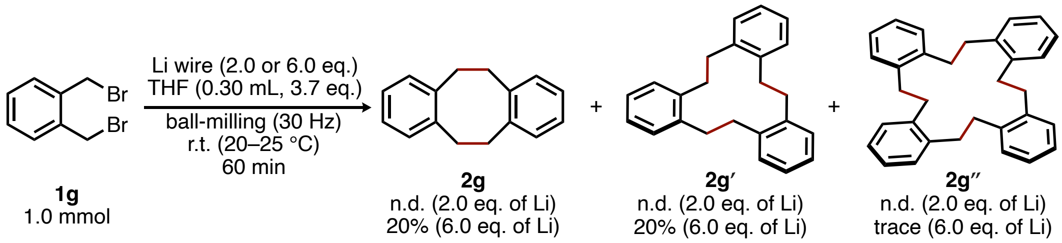
5-4. The reaction with other LAG additives (Table 1, entries 4–7)

A 5.0-mm diameter stainless-steel ball and 2-(bromomethyl)naphthalene (**1a**) (221.2 mg, 1.0 mmol, 1.0 eq.) were added to an oven-dried 5.0-mL stainless-steel jar. Pieces of Li (27.4 mg, 4.0 mmol, 4.0 eq.) cut from lithium wire (3.2 mm in diameter, 99.9% purity) was washed with hexane for removing mineral oil, weighed on an electronic balance, and added into the jar under air. Then, ethylenediamine (0.30 mL, 4.5 mmol, 4.5 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with an O-shaped packing made of 1-mm width polyethylene sheet, and the jar was sealed tightly with a wrench and a vise. The reaction jar and a same-weight blank jar (or a same-weight reaction jar) were fixed in a mixer mill (Retsch MM400), and shaken at 30 Hz (1800 rpm) at room temperature (20–25 °C) for 60 min. After shaking, the reaction jar was opened and the reaction was quenched by adding sat. NH_4Cl aq. Then, the organic phase was extracted with chloroform (three times). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford a crude product. The crude mixture was purified by silica gel column chromatography (eluent: hexane) and afforded **2a** in 31% yield (43.8 mg, 0.16 mmol). A similar experiment using TMEDA (0.30 mL, 2.0 eq.) instead of THF afforded **2a** in 0% yield. A similar experiment using 1,4-dioxane (0.30 mL, 3.5 eq.) instead of THF afforded **2a** in 18% yield (25.4 mg, 0.090 mmol) after purification by silica gel column chromatography (eluent: hexane). A similar experiment using 2-methyltetrahydrofuran (0.37 mL, 3.7 eq.) instead of THF afforded **2a** in 34% yield (45.4 mg, 0.17 mmol) after purification by silica gel column chromatography (eluent: hexane).

5-5. Equivalent of lithium(0) in the reaction of 1a

A 5.0-mm diameter stainless-steel ball and 2-(bromomethyl)naphthalene (**1a**) (221.9 mg, 1.0 mmol, 1.0 eq.) were added to an oven-dried 5.0-mL stainless-steel jar. Pieces of Li (14.2 mg, 2.1 mmol, 2.1 eq.) cut from lithium wire (3.2 mm in diameter, 99.9% purity) was washed with hexane for removing mineral oil, weighed on an electronic balance, and added into the jar under air. Then, THF (0.30 mL, 3.7 mmol, 3.7 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with an O-shaped packing made of 1-mm width polyethylene sheet, and the jar was sealed tightly with a wrench and a vise. The reaction jar and a same-weight blank jar (or a same-weight reaction jar) were fixed in a mixer mill (Retsch MM400), and shaken at 30 Hz (1800 rpm) at room temperature (20–25 °C) for 60 min. After shaking, the reaction jar was opened and the reaction was quenched by adding sat. NH_4Cl aq. Then, the organic phase was extracted with chloroform (three times). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford a crude product. The crude mixture was purified by silica gel column chromatography (eluent: hexane) and afforded **2a** in 16% yield (22.4 mg, 0.16 mmol).

5-6. Equivalent of lithium (0) in the reaction of 1g



Using general procedure A, the reaction of α,α'-dibromo-*o*-xylene (**1g**) (266.0 mg, 1.0 mmol, 1.0 eq.) with Li (43.0 mg, 6.0 mmol, 6.0 eq.) and THF (0.30 mL, 3.7 mmol, 3.7 eq.) was conducted at room temperature (20–25 °C) for 60 min. Purification by silica gel column chromatography (eluent: hexane), followed by GPC (eluent: $CHCl_3$), afforded **2g** (20.9 mg, 0.10 mmol, 20%) and **2g′** (22.1 mg, 0.072 mmol, 21%) as white solids, along with a trace amount of **2g″**. In a similar experiment using Li (14.4 mg, 2.0 mmol, 2.0 eq.), **1g** remained unreacted and was recovered (158.8 mg, 59% recovery).

6. X-ray crystallographic analysis

Details of the crystal data and a summary of the intensity data collection parameters for **2l** and **5d** are listed in Table S1. 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 Kα radiation (λ = 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)[S14] and refined by full-matrix least-squares techniques against F^2 (SHELXL-2018/3)[S15] by using Olex2 software package.[S16] The intensities were corrected for Lorentz and polarization effects. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions. CCDC2513489 contains the supplementary crystallographic data for **2l** (Figure S3). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. The structure of **5d** was also elucidated to 2,4-di(naphthalen-2-yl)furan by X-ray diffraction analysis and ^{1}H and ^{13}C NMR spectra as shown in Figure S4 albeit Alert B (Alert B, C and G with R_1, = 0.0469, wR_2 = 0.1314 and GOF = 1.087) for CCDC deposition. The refinement as an inversion twin was examined; however, the refined BASF parameter converged to an insignificant value and no improvement in the refinement statistics was observed. Re-measurement of diffraction data led to essentially identical results, indicating that crystal twinning is unlikely. Several disorder models were also tested. Splitting of selected oxygen atoms resulted in a slight improvement in R values; however, the Hooft parameter remained unimproved. Moreover, the split models required additional constraints (e.g., AFIX restraints for the five-membered ring) to retain chemically reasonable geometries, suggesting that such disorder treatments are not appropriate for the present structure. Application of ADP restraints (RIGU and DELU) to oxygen atoms did not eliminate Alert level B, which is attributed to the limited precision in determining the oxygen atomic positions rather than to deficiencies in the structural model. Based on these considerations, the final refinement was carried out without twinning or disorder modeling. The absolute structure could not be reliably determined owing to weak anomalous scattering. We also tried to assign the same crystallographic data as other possible isomer 2,5-di(naphthalen-2-yl)furan, resulting in lower quality of data (Alert B, C and G with R_1, = 0.0689, wR_2 = 0.2053 and GOF = 1.089, see the right column of Table S1). As a result, we concluded that the structure of **5d** as 2,4-di(naphthalen-2-yl)furan seems be to certain rather than 2,5-di(naphthalen-2-yl)furan.

Table S1. Crystallographic data and structure refinement details of **2l** and **5d**

	2l	**5d** assigned as 2,4-di(naphthalen-2-yl)furan	**5d** assigned as 2,5-di(naphthalen-2-yl)furan
CCDC number	2513489	2519748	N.A
CCDC alert	C, G	B, C, G	B, C, G
formula	$C_{30}H_{30}$	$C_{24}H_{16}O$	$C_{24}H_{16}O$
FW	390.54	320.37	320.37
T (K)	123(2)	123(2)	123(2)
λ (Å)	0.71073	0.71073	0.71073
crystal system	*monoclinic*	*orthorhombic*	*orthorhombic*
space group	*C2/c*	$Pna2_1$	$Pna2_1$
a (Å)	13.5363(4)	7.8386(5)	7.8386(5)
b (Å)	18.5669(6)	5.8767(4)	5.8767(4)
c (Å)	18.7109(7)	34.430(3)	34.430(3)
α (deg)	90	90	90
β (deg)	104.586(4)	90	90
γ (deg)	90	90	90
V (Å^3)	4551.0(3)	1586.02(19)	1586.02(19)
Z	8	4	4
ρ_{calc} (g·cm^{-3})	1.140	1.342	1.342
μ (mm^{-1})	0.064	0.080	0.080
F (000)	1680.0	672.0	672.0
cryst size (mm^3)	0.7 × 0.55 × 0.45	0.2 × 0.15 × 0.05	0.2 × 0.15 × 0.05
2θ range (deg)	3.806–59.61	4.732–59.522	4.732–59.522
reflections collected	19876	8615	8615
independent reflections/R_{int}	5343/ 0.0434	3011/0.0350	3011/0.0350
parameters	271	226	226
GOF on F^2	1.063	1.087	1.089
R_1, wR_2 [I>2σ(I)]	0.0465,0.1148	0.0469, 0.1314	0.0689, 0.2053
R_1, wR_2 (all data)	0.0506, 0.1181	0.0498, 0.1337	0.0781, 0.2216

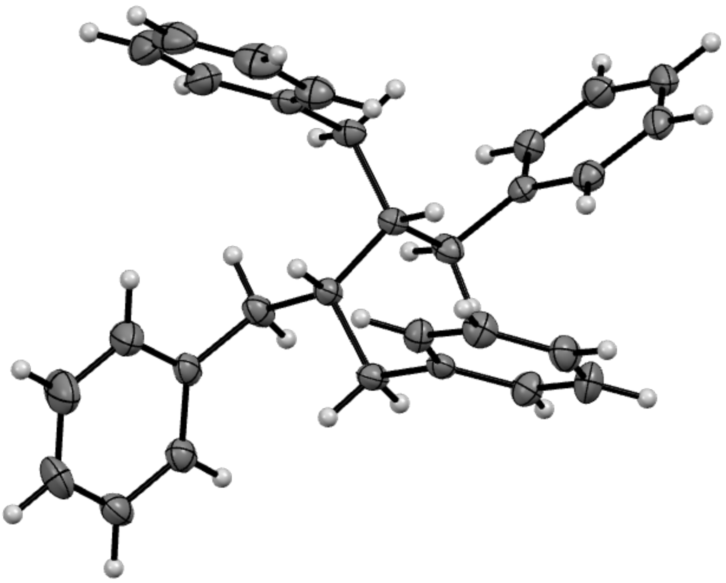


Figure S3. ORTEP drawing of **2l** with 50% probability.

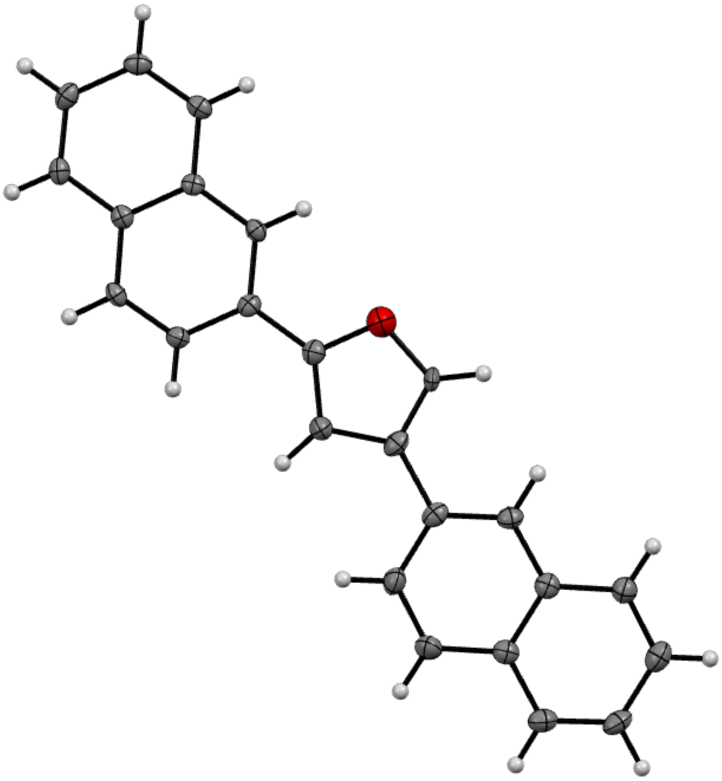


Figure S4. ORTEP drawing of **5d** assigned as 2,4-di(naphthalen-2-yl)furan with 50% probability.

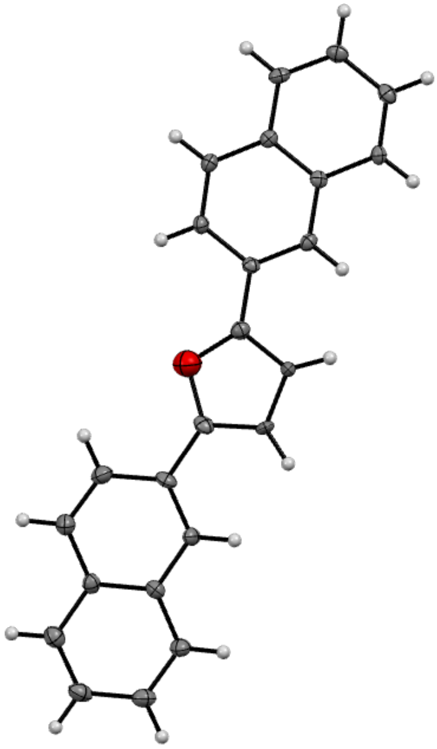


Figure S5. ORTEP drawing of **5d** assigned as 2,5-di(naphthalen-2-yl)furan with 50% probability.

7. References

[S1] M. Nibbelink and W. Bill, *Eur. J. Org. Chem.*, 2004, **2004**, 506–512.

[S2] S. Kotha and M. Meshram, *Synthesis*, 2014, **46**, 1525–1531.

[S3] M. K. Sahu, S. Pattanaik, G. Joshi, E. D. Jemmis and C. Gunanathan, *Angew. Chem. Int. Ed.*, 2025, **64**, e202520176.

[S4] SDBSWeb : https://sdbs.db.aist.go.jp/Disclaimer.aspx (National Institute of Advanced Industrial Science and Technology)

[S5] G. Franck, M. Brill and G. Helmchen, *Org. Synth*., 2012, **89**, 55.

[S6] G. S. Vanier, *Synlett.,* 2007, **1**, 131.

[S7] K. Komeyama, R. Tsunemitsu, T. Michiyuki, H. Yoshida and I. Osaka, *Molecules*, 2019, **24**, 1458.

[S8] Z. Hao, Z. Wang, D. Huang, X. Huangfu, X. Yang, J. Wei, W. Liu and W.-X. Zhang, *Green Synth. Catal.*, 2025, **6**, 324.

[S9] K. Ping, M. Alam, S. R. Kahnert, R. Bhadoria, A. Mere, V. Mikli, M. Käärik, J. Aruväli, P. Paiste, A. Kikas, V. Kisand, I. Järving, J. Leis, N. Kongi and P. Starkov, *Mater. Adv.*, 2021, **2**, 4009.

[S10] A. Taladriz, A. Healy, E. J. Flores Pérez, V. Herrero García, C. Ríos Martínez, A. A. M. Alkhaldi, A. A. Eze, M. Kaiser, H. P. de Koning, A. Chana, and C. Dardonville, *J. Med. Chem.* 2012, **55**, 2606.

[S11] Y. Li, P. Ren, D. Zhang, W. Qiao, D. Wang, X. Yang, X. Wen, M. H. Rummeli, H. Niemantsverdriet, J. P. Lewis, F. Besenbacher, H. Xiang, Y. Li, and R. Su, *ACS Catal.* 2021, **11**, 4338.

[S12] R. Fernandes, K. Mhaske, and R. Narayan, *Tetrahedron*, 2022, **103**, 132553.

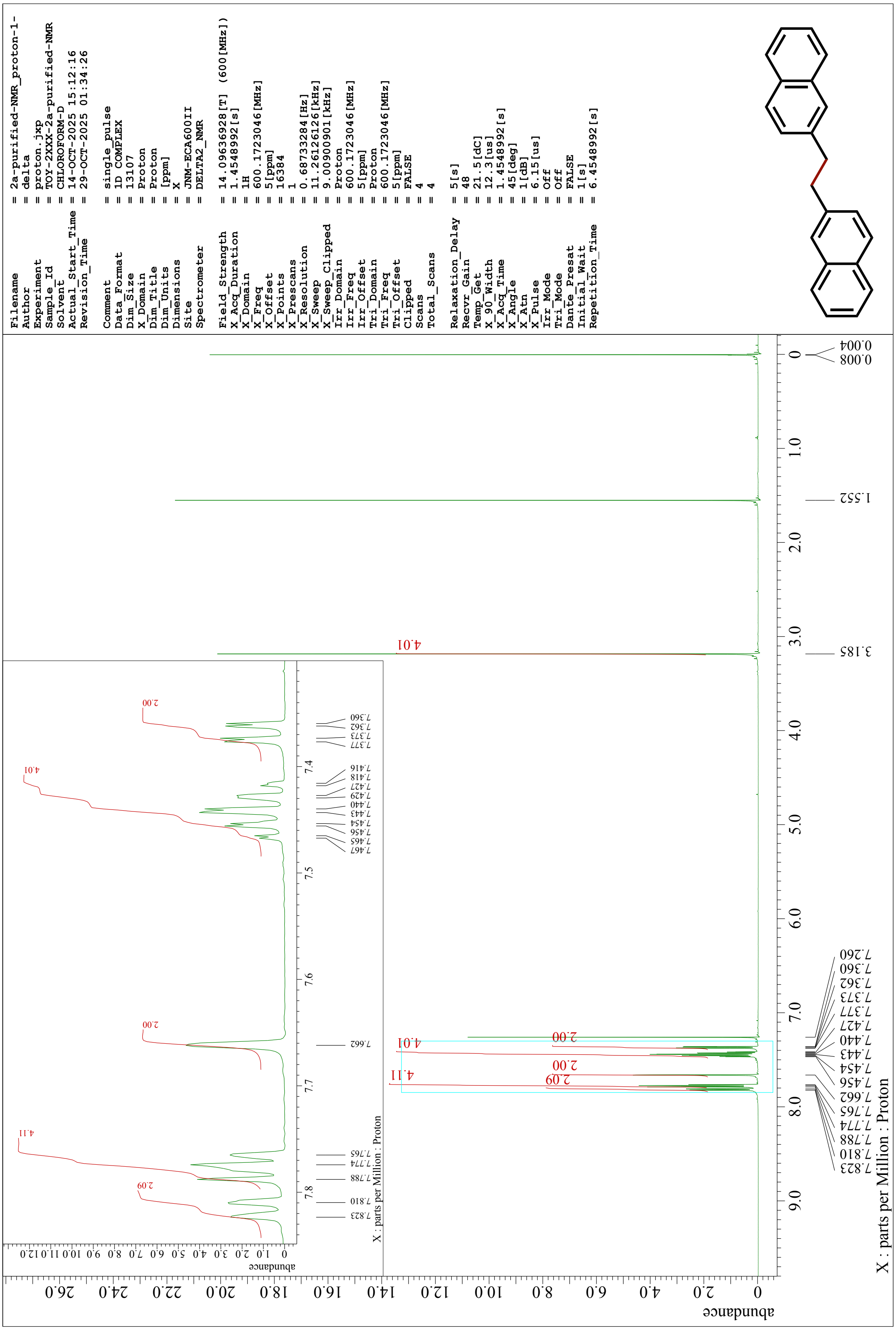
[S13] I. Y. Ajibola, L. Ai and B. Li, *ChemistrySelect* 2022, **7**, e202103038.

[S14] G. M. Sheldrick, *Acta Crystallogr.* 2015, **A71**, 3.

[S15] G. M. Sheldrick, *Acta Crystallogr*. 2015, **C71**, 3.

[S16] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Crystallogr.* 2009, **42**, 339.

8. ^{1}H, ^{13}C and ^{19}F NMR spectra of compounds



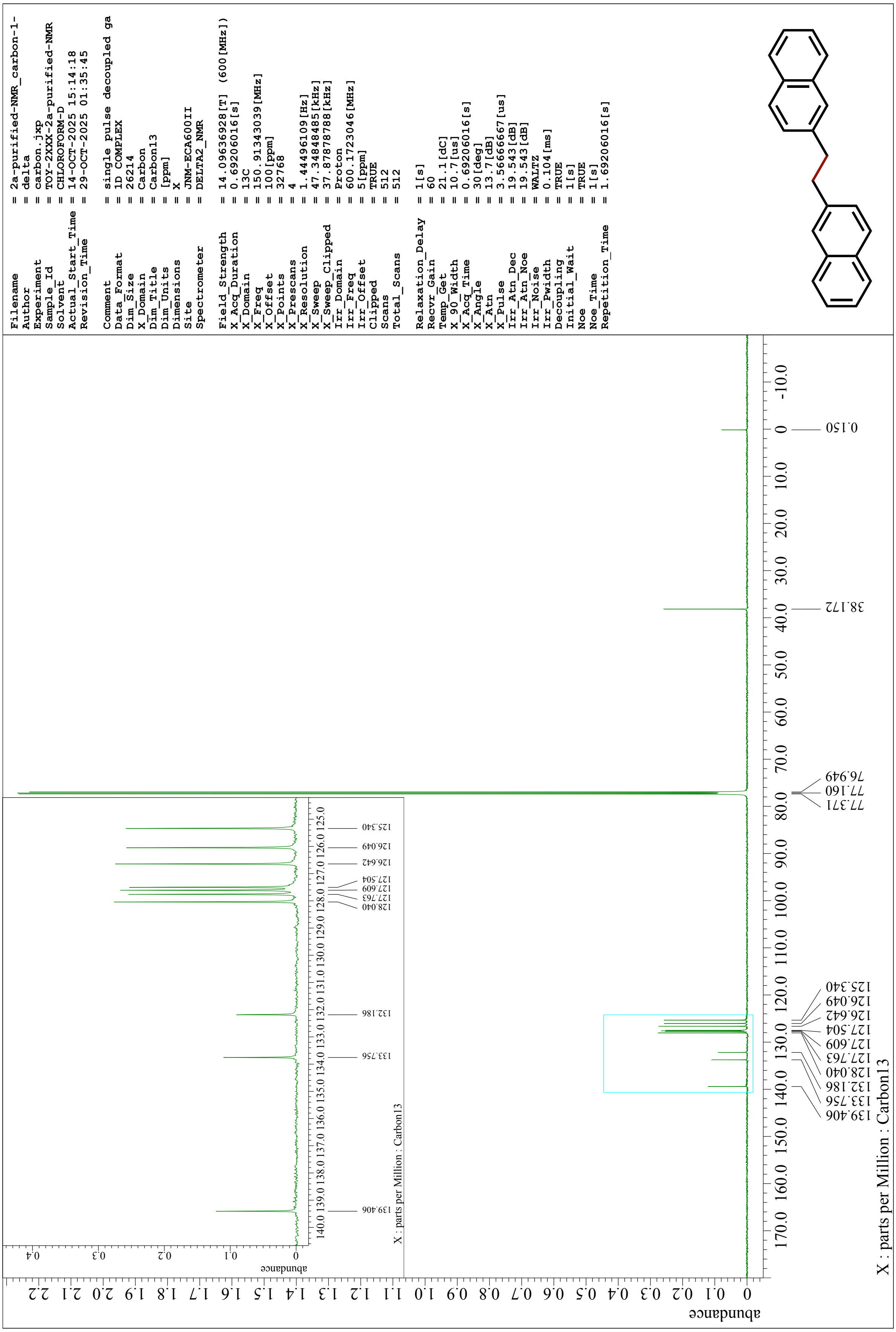
```
Filename              = 2a-purified-NMR_proton-1-
Author                = delta
Experiment            = proton.jxp
Sample_Id             = TOY-2XXX-2a-purified-NMR
Solvent               = CHLOROFORM-D
Actual_Start_Time     = 14-OCT-2025 15:12:16
Revision_Time         = 29-OCT-2025 01:34:26

Comment               = single_pulse
Data_Format           = 1D COMPLEX
Dim_Size              = 13107
X_Domain              = Proton
Dim_Title             = Proton
Dim_Units             = [ppm]
Dimensions            = X
Site                  = JNM-ECA600II
Spectrometer          = DELTA2_NMR

Field_Strength        = 14.09636928[T] (600[MHz])
X_Acq_Duration        = 1.4548992[s]
X_Domain              = 1H
X_Freq                = 600.1723046[MHz]
X_Offset              = 5[ppm]
X_Points              = 16384
X_Prescans            = 1
X_Resolution          = 0.68733284[Hz]
X_Sweep               = 11.2612612 6[kHz]
X_Sweep_Clipped       = 9.00900901[kHz]
Irr_Domain            = Proton
Irr_Freq              = 600.1723046[MHz]
Irr_Offset            = 5[ppm]
Tri_Domain            = Proton
Tri_Freq              = 600.1723046[MHz]
Tri_Offset            = 5[ppm]
Clipped               = FALSE
Scans                 = 4
Total_Scans           = 4

Relaxation_Delay      = 5[s]
Recvr_Gain            = 48
Temp_Get              = 21.5[dC]
X_90_Width            = 12.3[us]
X_Acq_Time            = 1.4548992[s]
X_Angle               = 45[deg]
X_Atn                 = 1[dB]
X_Pulse               = 6.15[us]
Irr_Mode              = Off
Tri_Mode              = Off
Dante_Presat          = FALSE
Initial_Wait          = 1[s]
Repetition_Time       = 6.4548992[s]
```

Figure S6. ^{1}H NMR spectrum of **2a** (600 MHz, CDCl$_3$).



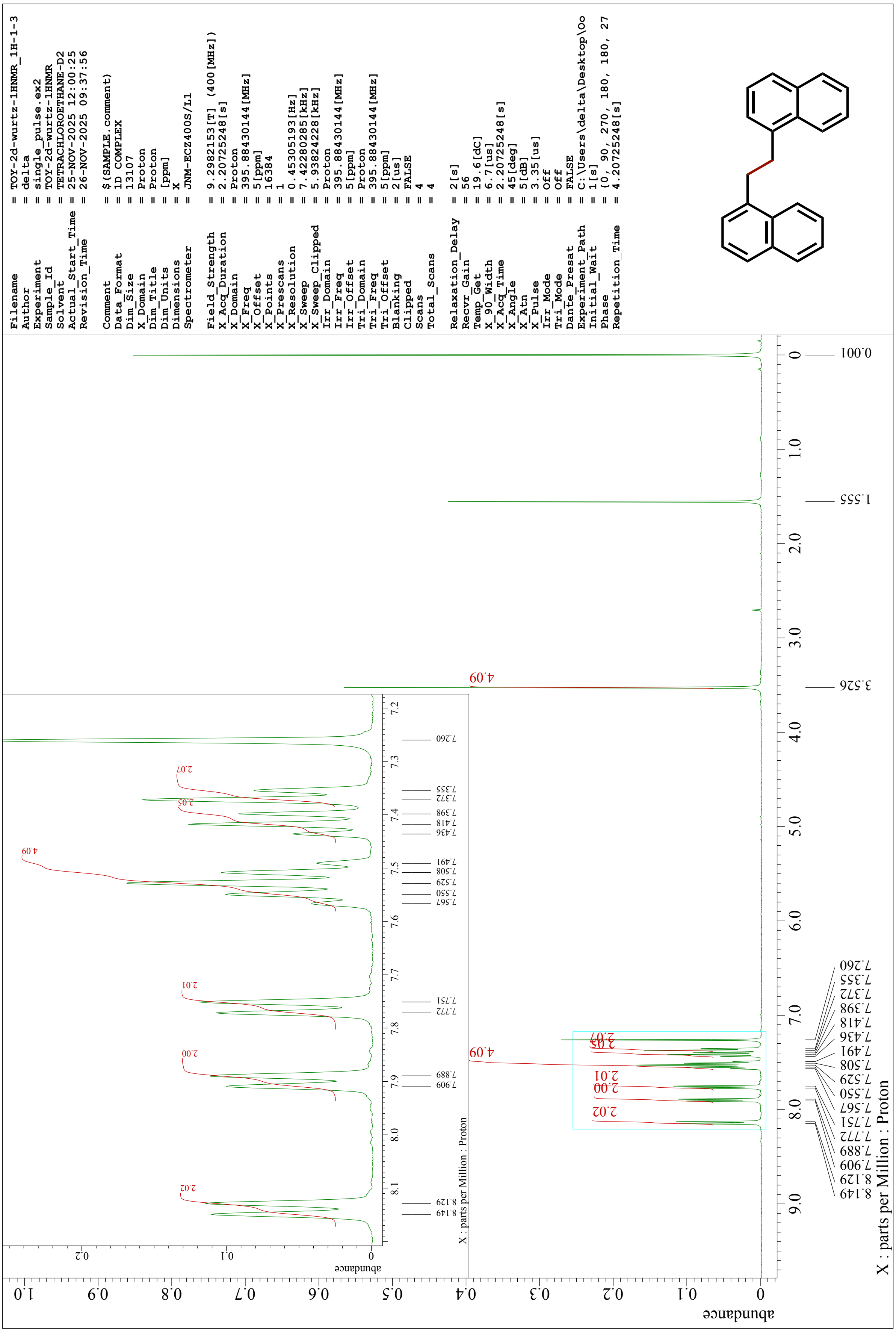
```
Filename             = 2a-purified-NMR_carbon-1-
Author               = delta
Experiment           = carbon.jxp
Sample_Id            = TOY-2XXX-2a-purified-NMR
Solvent              = CHLOROFORM-D
Actual_Start_Time    = 14-OCT-2025 15:14:18
Revision_Time        = 29-OCT-2025 01:35:45

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     = 1[s]
Recvr_Gain           = 60
Temp_Get             = 21.1[dC]
X_90_Width           = 10.7[us]
X_Acq_Time           = 0.69206016[s]
X_Angle              = 30[deg]
X_Atn                = 13.7[dB]
X_Pulse              = 3.56666667[us]
Irr_Atn_Dec          = 19.543[dB]
Irr_Atn_Noe          = 19.543[dB]
Irr_Noise            = WALTZ
Irr_Pwidth           = 0.104[ms]
Decoupling           = TRUE
Initial_Wait         = 1[s]
Noe                  = TRUE
Noe_Time             = 1[s]
Repetition_Time      = 1.69206016[s]
```

Figure S7. ^{13}C NMR spectrum of **2a** (150 MHz, $CDCl_3$).



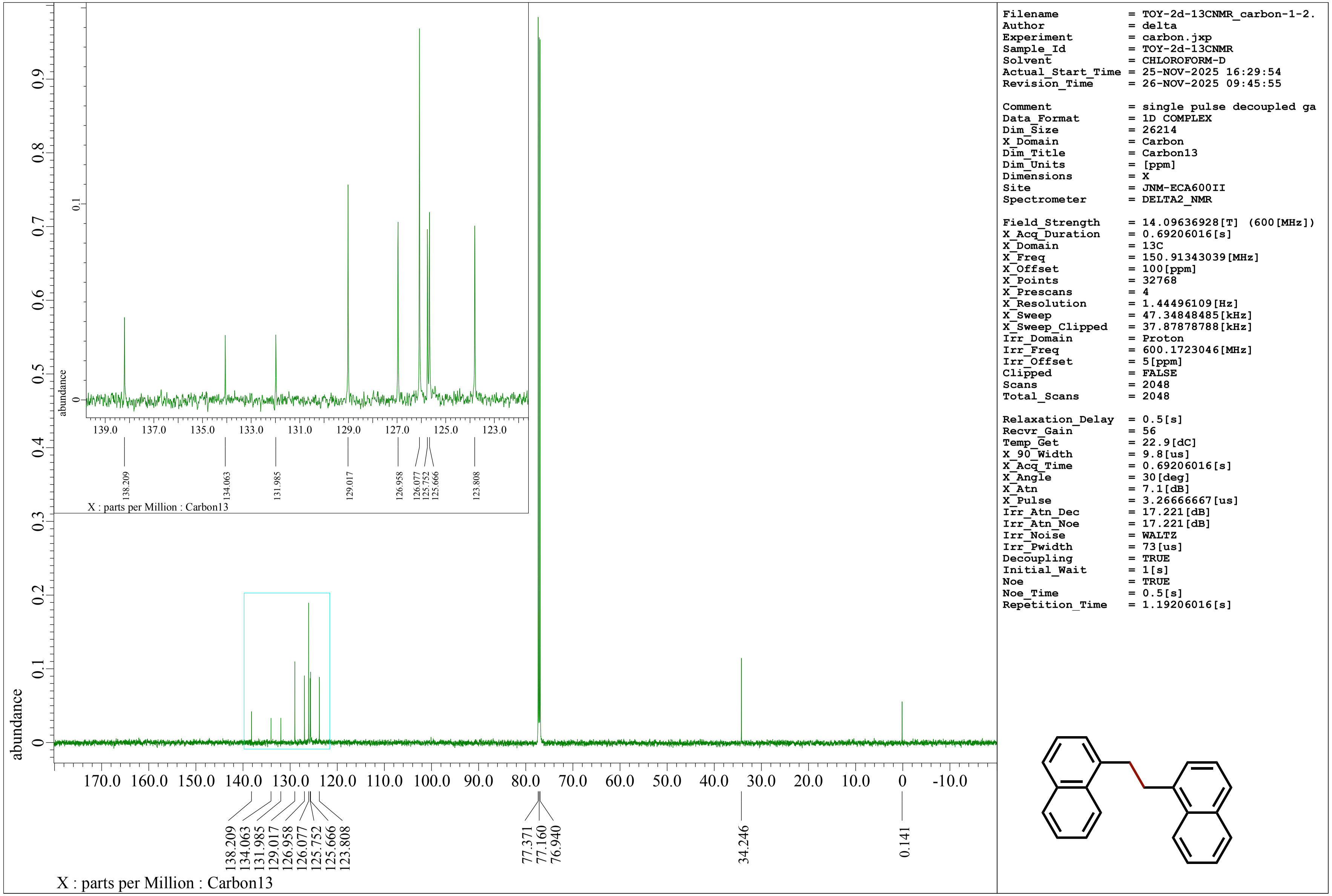
```
Filename              = TOY-2d-wurtz-1HNMR_1H-1-3
Author                = delta
Experiment            = single_pulse.ex2
Sample_Id             = TOY-2d-wurtz-1HNMR
Solvent               = TETRACHLOROETHANE-D2
Actual_Start_Time     = 25-NOV-2025 12:00:25
Revision_Time         = 26-NOV-2025 09:37:56

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                 = 4
Total_Scans           = 4

Relaxation_Delay      = 2[s]
Recvr_Gain            = 56
Temp_Get              = 19.6[dC]
X_90_Width            = 6.7[us]
X_Acq_Time            = 2.20725248[s]
X_Angle               = 45[deg]
X_Atn                 = 5[dB]
X_Pulse               = 3.35[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       = 4.20725248[s]
```

Figure S8. ^{1}H NMR spectrum of **2d** (400 MHz, $CDCl_3$).



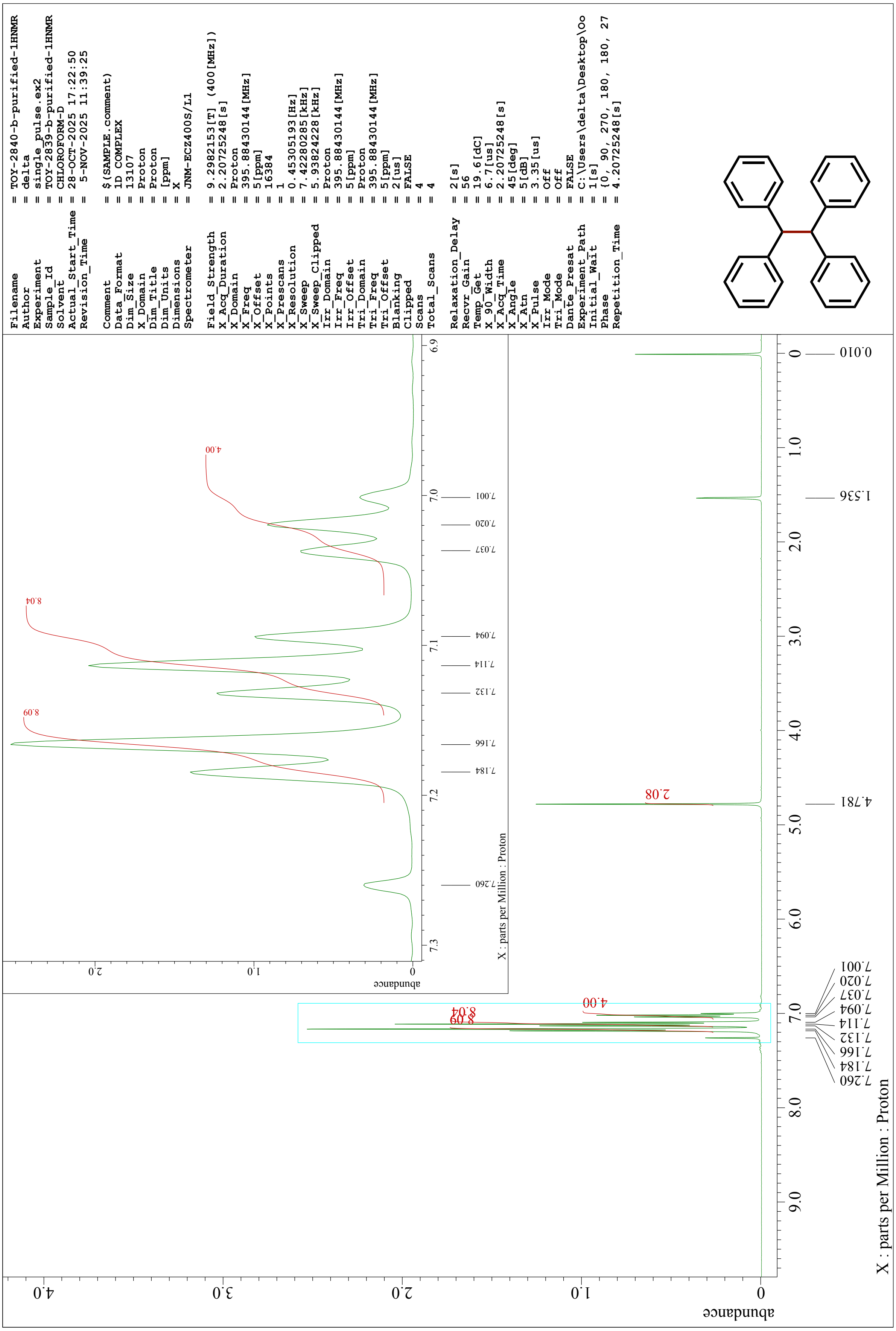
```
Filename           = TOY-2d-13CNMR_carbon-1-2.
Author             = delta
Experiment         = carbon.jxp
Sample_Id          = TOY-2d-13CNMR
Solvent            = CHLOROFORM-D
Actual_Start_Time = 25-NOV-2025 16:29:54
Revision_Time      = 26-NOV-2025 09:45:55

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              = 2048
Total_Scans        = 2048

Relaxation_Delay   = 0.5[s]
Recvr_Gain         = 56
Temp_Get           = 22.9[dC]
X_90_Width         = 9.8[us]
X_Acq_Time         = 0.69206016[s]
X_Angle            = 30[deg]
X_Atn              = 7.1[dB]
X_Pulse            = 3.26666667[us]
Irr_Atn_Dec        = 17.221[dB]
Irr_Atn_Noe        = 17.221[dB]
Irr_Noise          = WALTZ
Irr_Pwidth         = 73[us]
Decoupling         = TRUE
Initial_Wait       = 1[s]
Noe                = TRUE
Noe_Time           = 0.5[s]
Repetition_Time    = 1.19206016[s]
```

Figure S9. ^{13}C NMR spectrum of **2d** (100 MHz, CDCl$_3$).



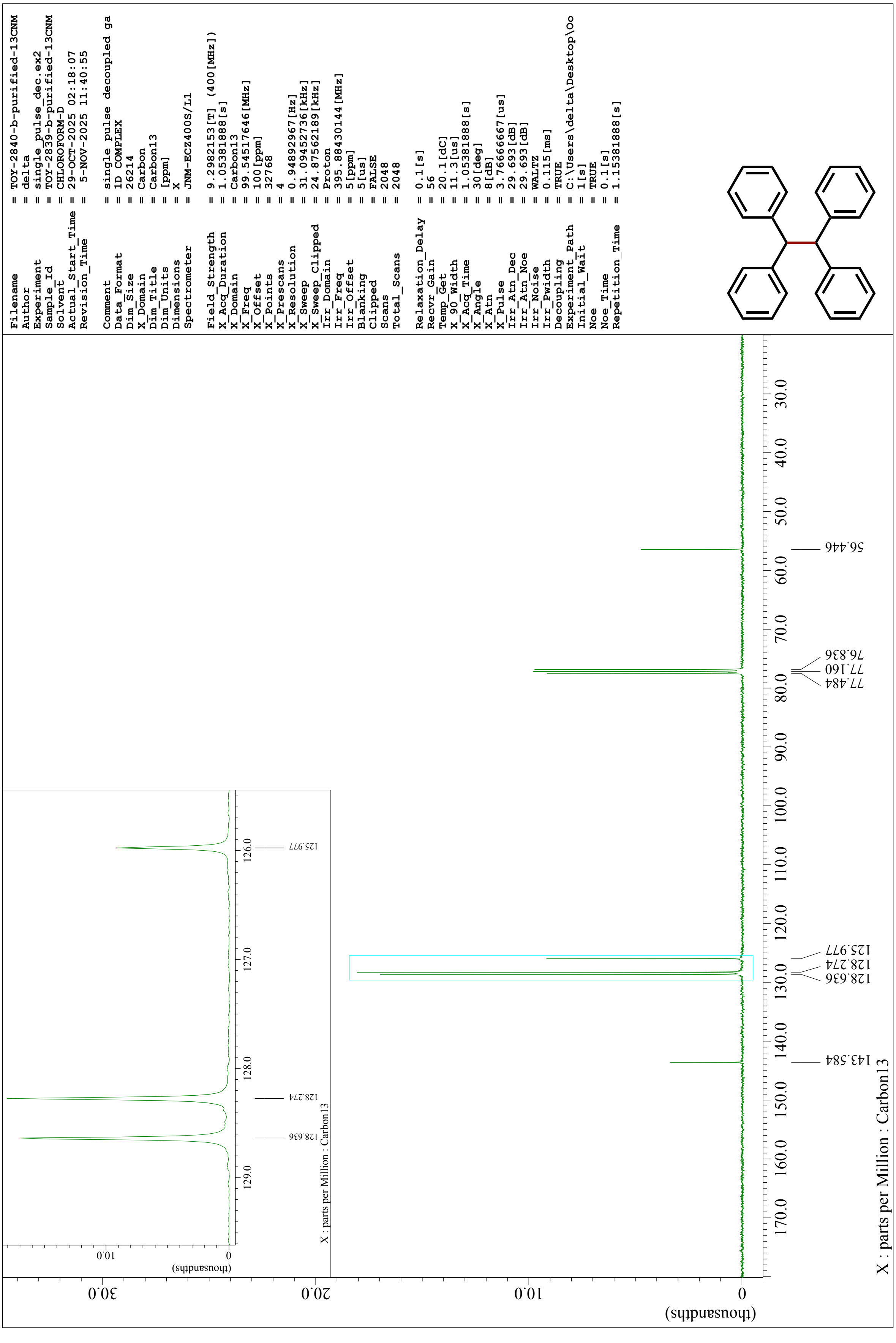
```
Filename            = TOY-2840-b-purified-1HNMR
Author              = delta
Experiment          = single_pulse.ex2
Sample_Id           = TOY-2839-b-purified-1HNMR
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 28-OCT-2025 17:22:50
Revision_Time       =  5-NOV-2025 11:39:25

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               = 4
Total_Scans         = 4

Relaxation_Delay    = 2[s]
Recvr_Gain          = 56
Temp_Get            = 19.6[dC]
X_90_Width          = 6.7[us]
X_Acq_Time          = 2.20725248[s]
X_Angle             = 45[deg]
X_Atn               = 5[dB]
X_Pulse             = 3.35[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     = 4.20725248[s]
```

Figure S10. ^{1}H NMR spectrum of **2e** (400 MHz, $CDCl_3$).



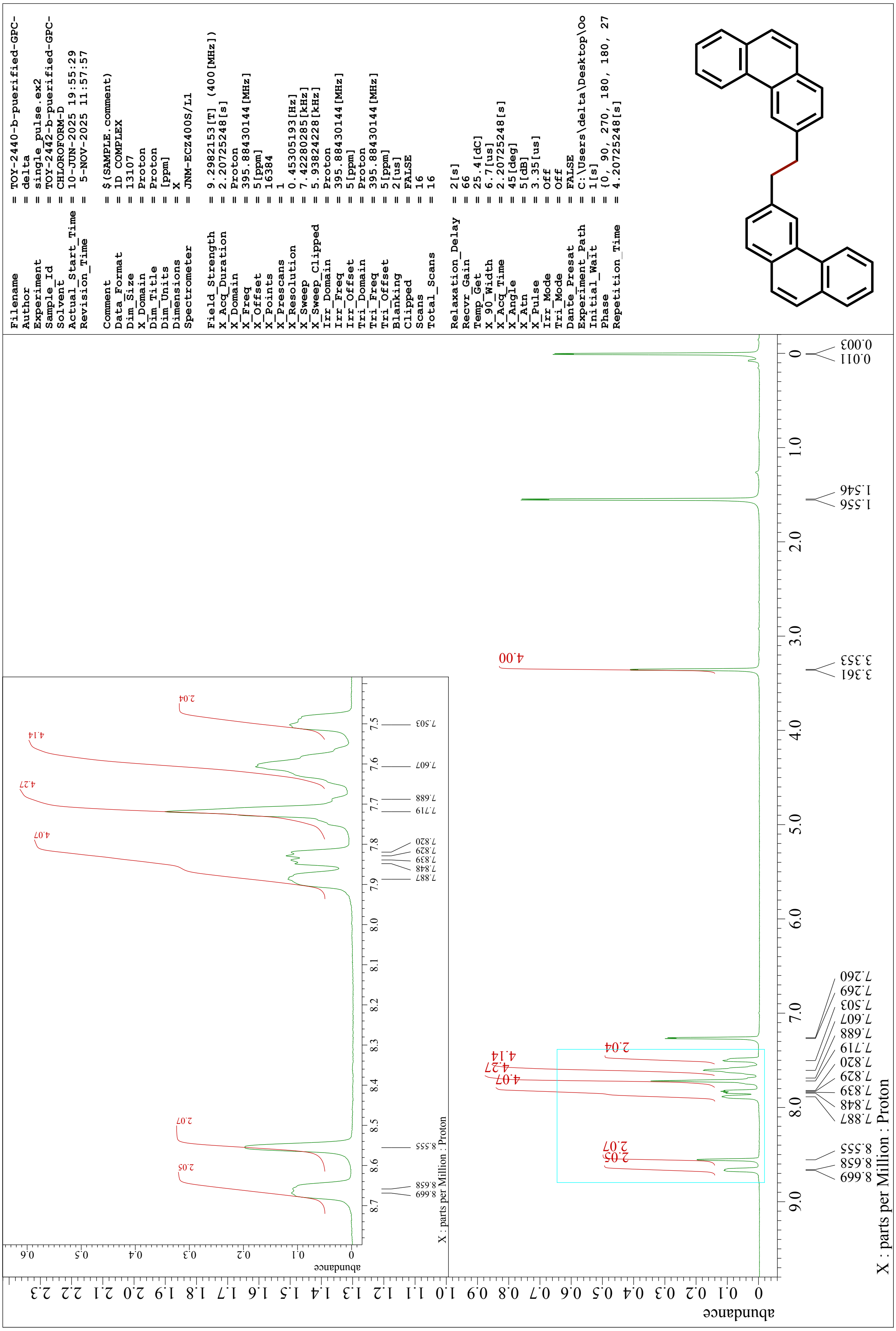
```
Filename              = TOY-2840-b-purified-13CNM
Author                = delta
Experiment            = single_pulse_dec.ex2
Sample_Id             = TOY-2839-b-purified-13CNM
Solvent               = CHLOROFORM-D
Actual_Start_Time     = 29-OCT-2025 02:18:07
Revision_Time         =  5-NOV-2025 11:40:55

Comment               = single pulse decoupled ga
Data_Format           = 1D COMPLEX
Dim_Size              = 26214
X_Domain              = Carbon
Dim_Title             = Carbon13
Dim_Units             = [ppm]
Dimensions            = X
Spectrometer          = JNM-ECZ400S/L1

Field_Strength        = 9.2982153[T] (400[MHz])
X_Acq_Duration        = 1.05381888[s]
X_Domain              = Carbon13
X_Freq                = 99.54517646[MHz]
X_Offset              = 100[ppm]
X_Points              = 32768
X_Prescans            = 4
X_Resolution          = 0.94892967[Hz]
X_Sweep               = 31.09452736[kHz]
X_Sweep_Clipped       = 24.87562189[kHz]
Irr_Domain            = Proton
Irr_Freq              = 395.88430144[MHz]
Irr_Offset            = 5[ppm]
Blanking              = 5[us]
Clipped               = FALSE
Scans                 = 2048
Total_Scans           = 2048

Relaxation_Delay      = 0.1[s]
Recvr_Gain            = 56
Temp_Get              = 20.1[dC]
X_90_Width            = 11.3[us]
X_Acq_Time            = 1.05381888[s]
X_Angle               = 30[deg]
X_Atn                 = 8[dB]
X_Pulse               = 3.76666667[us]
Irr_Atn_Dec           = 29.693[dB]
Irr_Atn_Noe           = 29.693[dB]
Irr_Noise             = WALTZ
Irr_Pwidth            = 0.115[ms]
Decoupling            = TRUE
Experiment_Path       = C:\Users\delta\Desktop\Oo
Initial_Wait          = 1[s]
Noe                   = TRUE
Noe_Time              = 0.1[s]
Repetition_Time       = 1.15381888[s]
```

Figure S11. ^{13}C NMR spectrum of **2e** (100 MHz, CDCl$_3$).



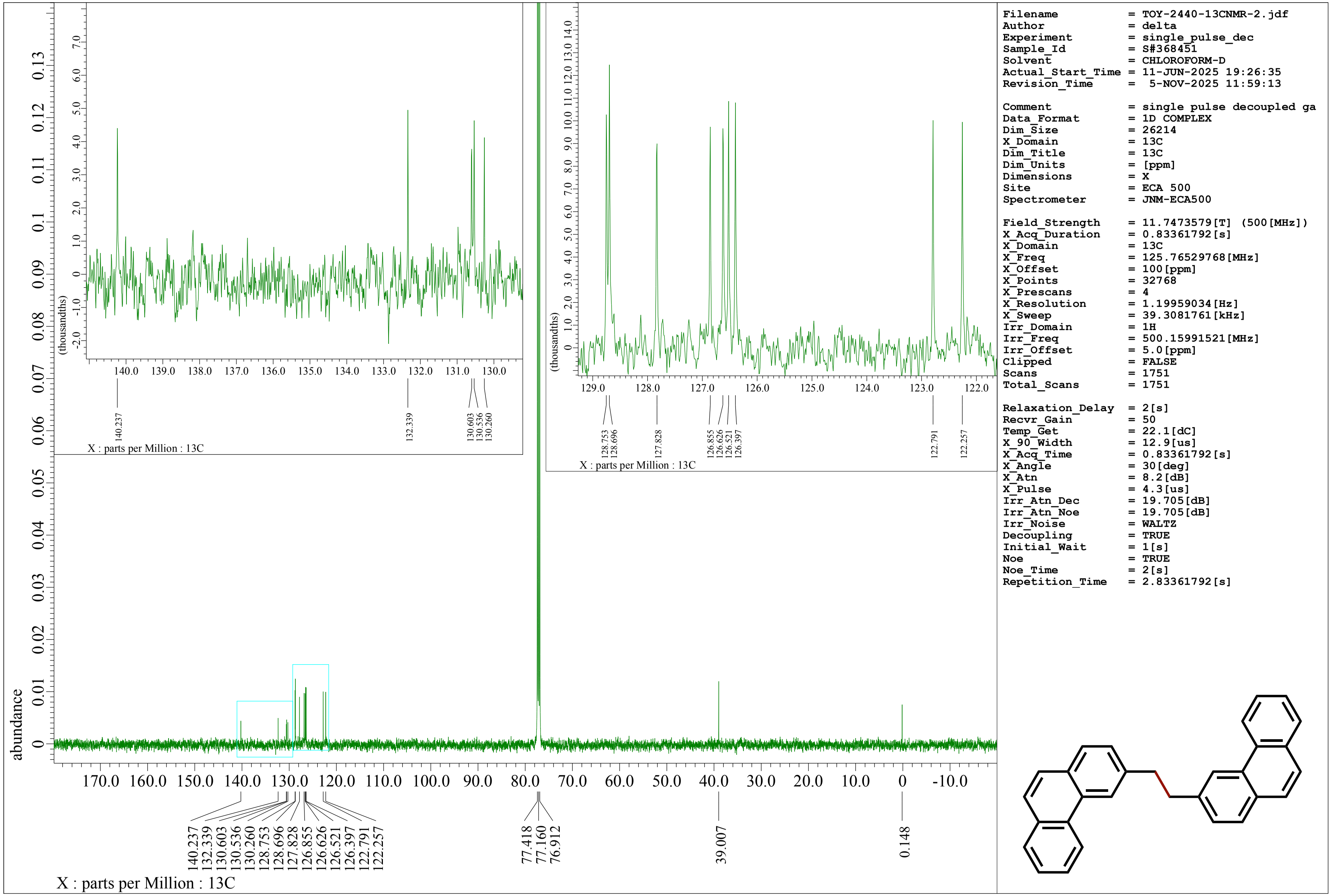
```
Filename             = TOY-2440-b-puerified-GPC-
Author               = delta
Experiment           = single_pulse.ex2
Sample_Id            = TOY-2442-b-puerified-GPC-
Solvent              = CHLOROFORM-D
Actual_Start_Time    = 10-JUN-2025 19:55:29
Revision_Time        =  5-NOV-2025 11:57:57

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                = 16
Total_Scans          = 16

Relaxation_Delay     = 2[s]
Recvr_Gain           = 66
Temp_Get             = 25.4[dC]
X_90_Width           = 6.7[us]
X_Acq_Time           = 2.20725248[s]
X_Angle              = 45[deg]
X_Atn                = 5[dB]
X_Pulse              = 3.35[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      = 4.20725248[s]
```

Figure S12. ^{1}H NMR spectrum of **2f** (400 MHz, CDCl$_3$).



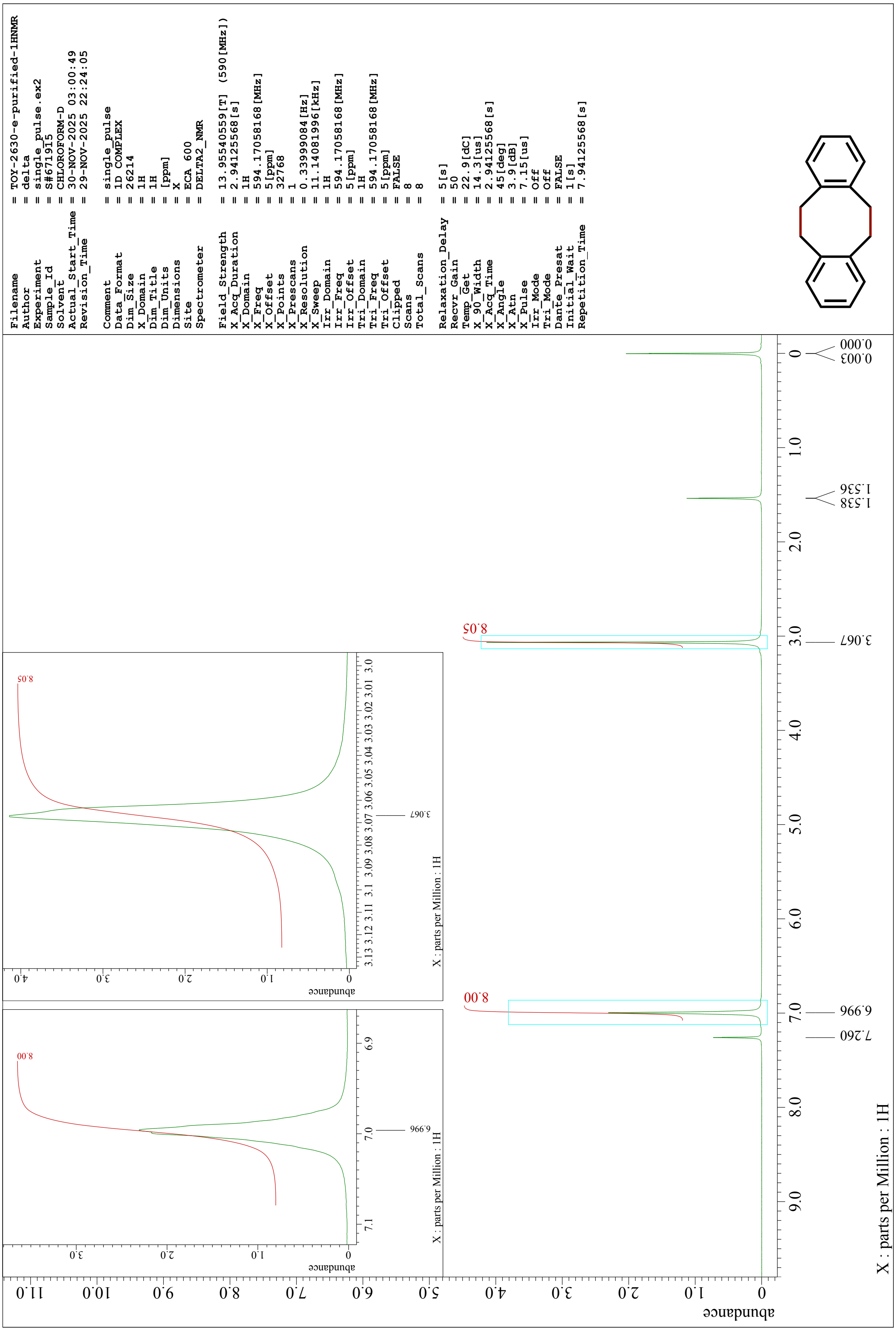
```
Filename             = TOY-2440-13CNMR-2.jdf
Author               = delta
Experiment           = single_pulse_dec
Sample_Id            = S#368451
Solvent              = CHLOROFORM-D
Actual_Start_Time    = 11-JUN-2025 19:26:35
Revision_Time        =  5-NOV-2025 11:59:13

Comment              = single pulse decoupled ga
Data_Format          = 1D COMPLEX
Dim_Size             = 26214
X_Domain             = 13C
Dim_Title            = 13C
Dim_Units            = [ppm]
Dimensions           = X
Site                 = ECA 500
Spectrometer         = JNM-ECA500

Field_Strength       = 11.7473579[T] (500[MHz])
X_Acq_Duration       = 0.83361792[s]
X_Domain             = 13C
X_Freq               = 125.76529768[MHz]
X_Offset             = 100[ppm]
X_Points             = 32768
X_Prescans           = 4
X_Resolution         = 1.19959034[Hz]
X_Sweep              = 39.3081761[kHz]
Irr_Domain           = 1H
Irr_Freq             = 500.15991521[MHz]
Irr_Offset           = 5.0[ppm]
Clipped              = FALSE
Scans                = 1751
Total_Scans          = 1751

Relaxation_Delay     = 2[s]
Recvr_Gain           = 50
Temp_Get             = 22.1[dC]
X_90_Width           = 12.9[us]
X_Acq_Time           = 0.83361792[s]
X_Angle              = 30[deg]
X_Atn                = 8.2[dB]
X_Pulse              = 4.3[us]
Irr_Atn_Dec          = 19.705[dB]
Irr_Atn_Noe          = 19.705[dB]
Irr_Noise            = WALTZ
Decoupling           = TRUE
Initial_Wait         = 1[s]
Noe                  = TRUE
Noe_Time             = 2[s]
Repetition_Time      = 2.83361792[s]
```

Figure S13. ^{13}C NMR spectrum of **2f** (125 MHz, $CDCl_3$).



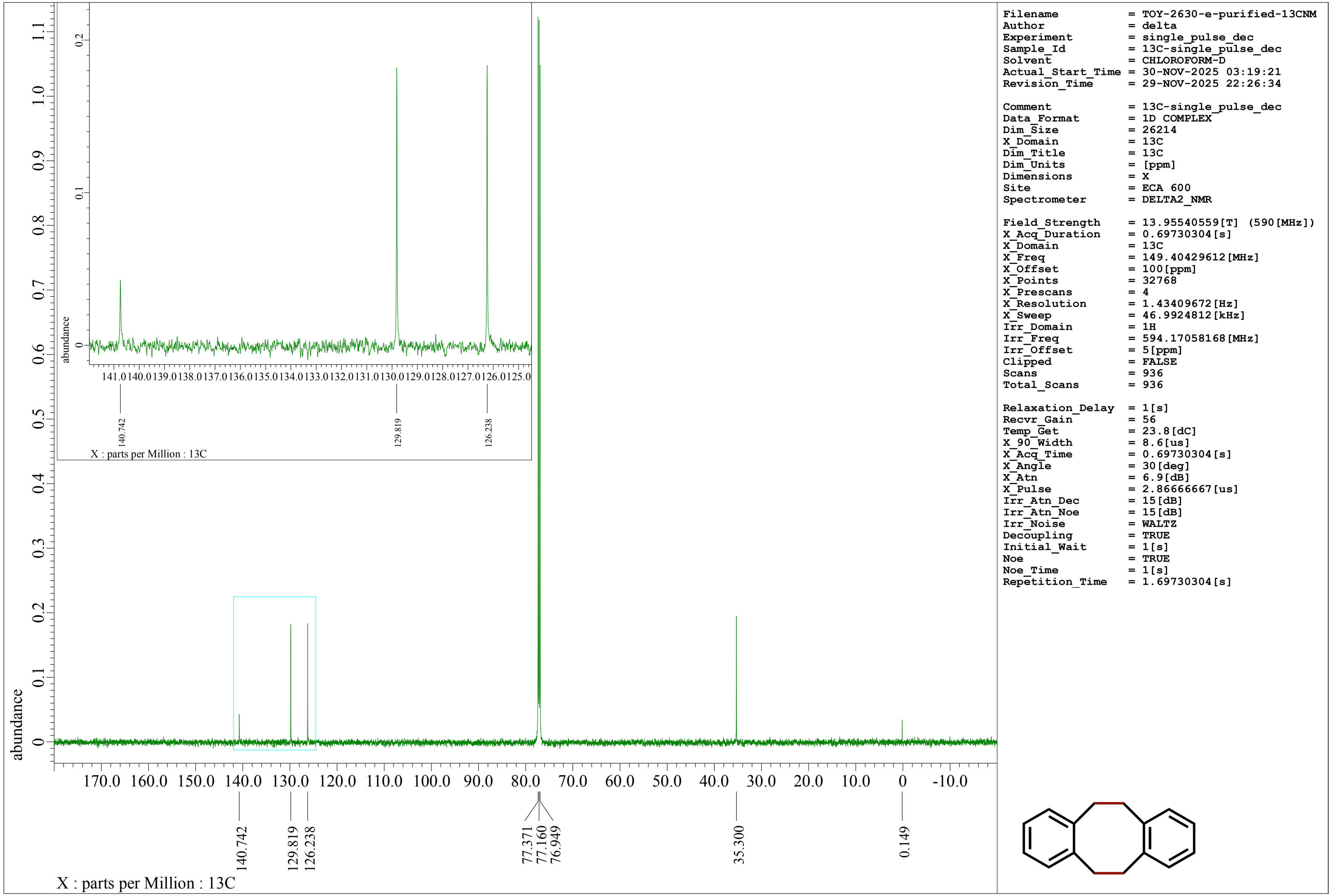
```
Filename            = TOY-2630-e-purified-1HNMR
Author              = delta
Experiment          = single_pulse.ex2
Sample_Id           = S#671915
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 30-NOV-2025 03:00:49
Revision_Time       = 29-NOV-2025 22:24:05

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               = 8
Total_Scans         = 8

Relaxation_Delay    = 5[s]
Recvr_Gain          = 50
Temp_Get            = 22.9[dC]
X_90_Width          = 14.3[us]
X_Acq_Time          = 2.94125568[s]
X_Angle             = 45[deg]
X_Atn               = 3.9[dB]
X_Pulse             = 7.15[us]
Irr_Mode            = Off
Tri_Mode            = Off
Dante_Presat        = FALSE
Initial_Wait        = 1[s]
Repetition_Time     = 7.94125568[s]
```

Figure S14. ^{1}H NMR spectrum of **2g** (600 MHz, $CDCl_3$).



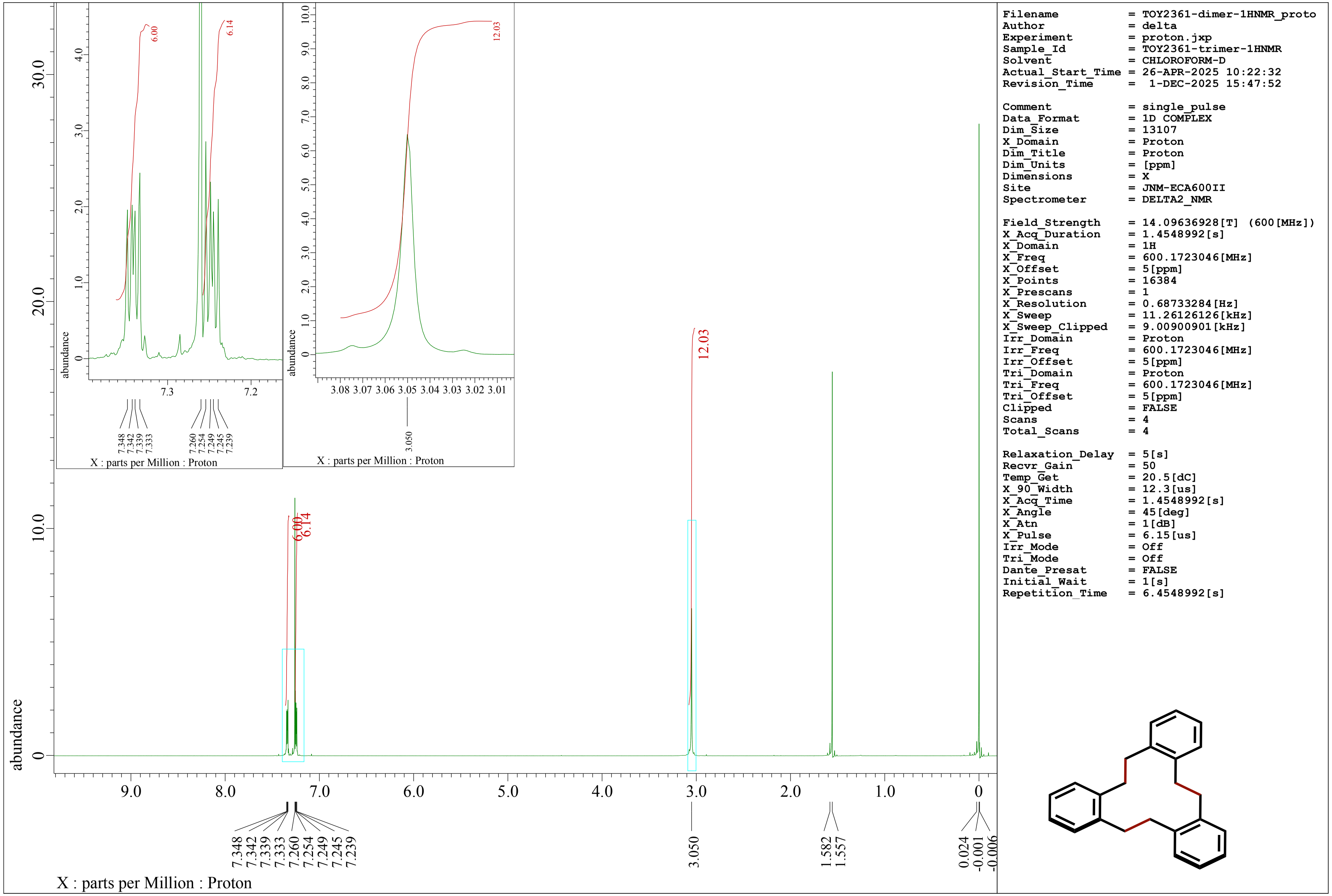
```
Filename           = TOY-2630-e-purified-13CNM
Author             = delta
Experiment         = single_pulse_dec
Sample_Id          = 13C-single_pulse_dec
Solvent            = CHLOROFORM-D
Actual_Start_Time  = 30-NOV-2025 03:19:21
Revision_Time      = 29-NOV-2025 22:26:34

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              = 936
Total_Scans        = 936

Relaxation_Delay   = 1[s]
Recvr_Gain         = 56
Temp_Get           = 23.8[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        = 15[dB]
Irr_Atn_Noe        = 15[dB]
Irr_Noise          = WALTZ
Decoupling         = TRUE
Initial_Wait       = 1[s]
Noe                = TRUE
Noe_Time           = 1[s]
Repetition_Time    = 1.69730304[s]
```

Figure S15. ^{13}C NMR spectrum of **2g** (150 MHz, $CDCl_3$).



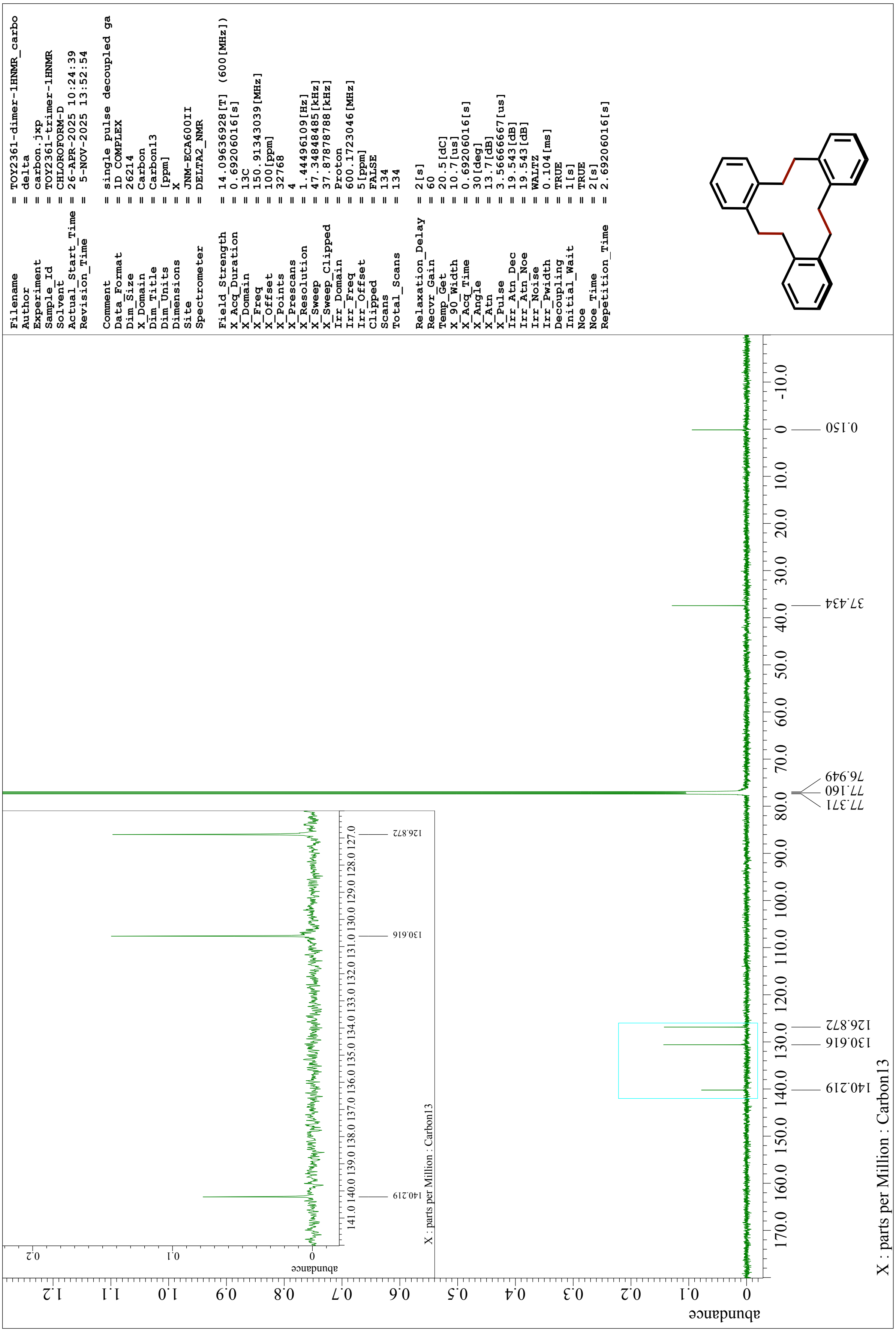
```
Filename            = TOY2361-dimer-1HNMR_proto
Author              = delta
Experiment          = proton.jxp
Sample_Id           = TOY2361-trimer-1HNMR
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 26-APR-2025 10:22:32
Revision_Time       =  1-DEC-2025 15:47:52

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 13107
X_Domain            = Proton
Dim_Title           = Proton
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECA600II
Spectrometer        = DELTA2_NMR

Field_Strength      = 14.09636928[T] (600[MHz])
X_Acq_Duration      = 1.4548992[s]
X_Domain            = 1H
X_Freq              = 600.1723046[MHz]
X_Offset            = 5[ppm]
X_Points            = 16384
X_Prescans          = 1
X_Resolution        = 0.68733284[Hz]
X_Sweep             = 11.26126126[kHz]
X_Sweep_Clipped     = 9.00900901[kHz]
Irr_Domain          = Proton
Irr_Freq            = 600.1723046[MHz]
Irr_Offset          = 5[ppm]
Tri_Domain          = Proton
Tri_Freq            = 600.1723046[MHz]
Tri_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 4
Total_Scans         = 4

Relaxation_Delay    = 5[s]
Recvr_Gain          = 50
Temp_Get            = 20.5[dC]
X_90_Width          = 12.3[us]
X_Acq_Time          = 1.4548992[s]
X_Angle             = 45[deg]
X_Atn               = 1[dB]
X_Pulse             = 6.15[us]
Irr_Mode            = Off
Tri_Mode            = Off
Dante_Presat        = FALSE
Initial_Wait        = 1[s]
Repetition_Time     = 6.4548992[s]
```

Figure S16. ^{1}H NMR spectrum of **2g′** (600 MHz, $CDCl_3$).



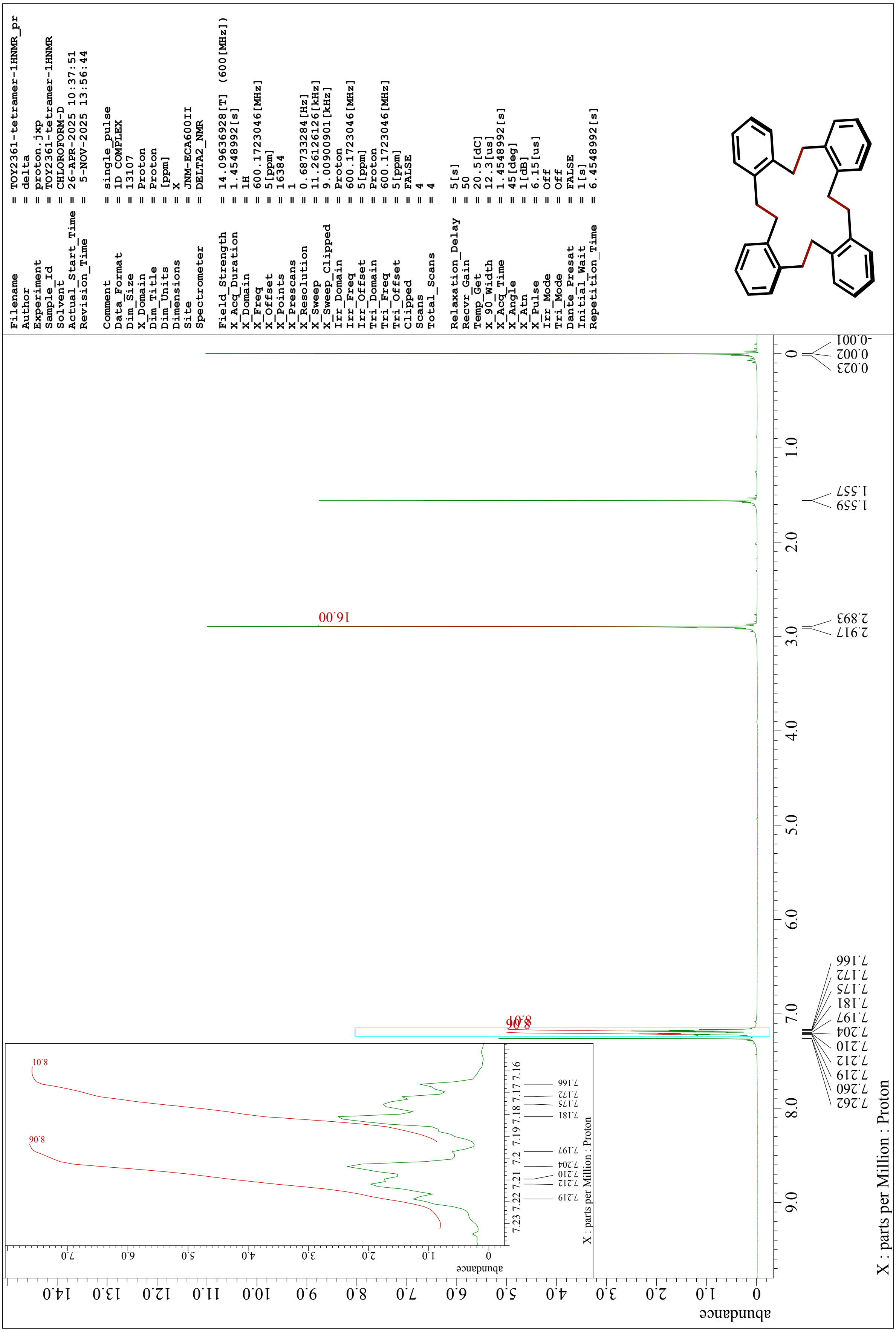
```
Filename             = TOY2361-dimer-1HNMR_carbo
Author               = delta
Experiment           = carbon.jxp
Sample_Id            = TOY2361-trimer-1HNMR
Solvent              = CHLOROFORM-D
Actual_Start_Time    = 26-APR-2025 10:24:39
Revision_Time        =  5-NOV-2025 13:52:54

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                = 134
Total_Scans          = 134

Relaxation_Delay     = 2[s]
Recvr_Gain           = 60
Temp_Get             = 20.5[dC]
X_90_Width           = 10.7[us]
X_Acq_Time           = 0.69206016[s]
X_Angle              = 30[deg]
X_Atn                = 13.7[dB]
X_Pulse              = 3.56666667[us]
Irr_Atn_Dec          = 19.543[dB]
Irr_Atn_Noe          = 19.543[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 S17. ^{13}C NMR spectrum of **2g′** (150 MHz, CDCl$_3$).



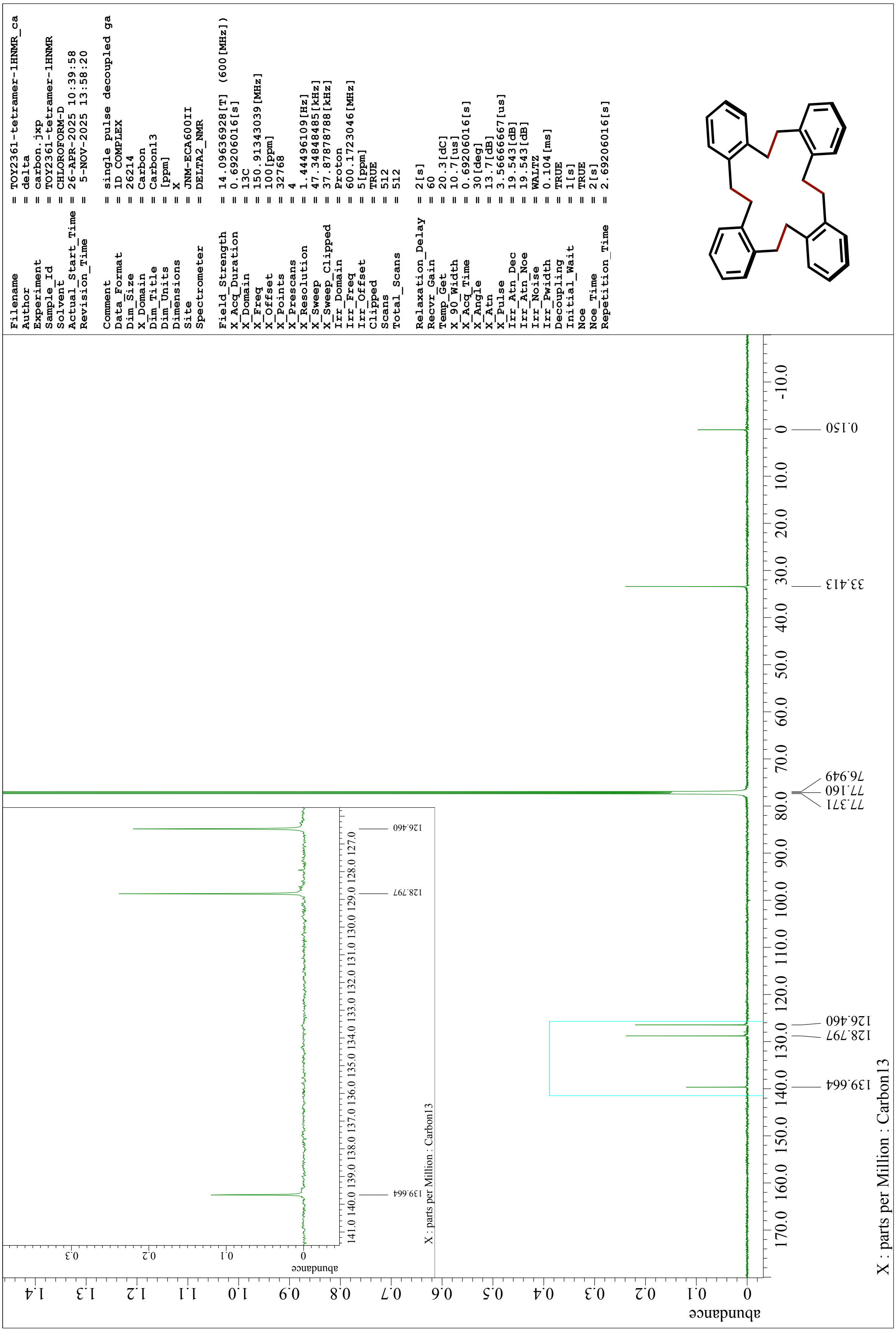
```
Filename          = TOY2361-tetramer-1HNMR_pr
Author            = delta
Experiment        = proton.jxp
Sample_Id         = TOY2361-tetramer-1HNMR
Solvent           = CHLOROFORM-D
Actual_Start_Time = 26-APR-2025 10:37:51
Revision_Time     =  5-NOV-2025 13:56:44

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
X_Domain          = Proton
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECA600II
Spectrometer      = DELTA2_NMR

Field_Strength    = 14.09636928[T] (600[MHz])
X_Acq_Duration    = 1.4548992[s]
X_Domain          = 1H
X_Freq            = 600.1723046[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.68733284[Hz]
X_Sweep           = 11.26126126[kHz]
X_Sweep_Clipped   = 9.00900901[kHz]
Irr_Domain        = Proton
Irr_Freq          = 600.1723046[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = Proton
Tri_Freq          = 600.1723046[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 4
Total_Scans       = 4

Relaxation_Delay  = 5[s]
Recvr_Gain        = 50
Temp_Get          = 20.5[dC]
X_90_Width        = 12.3[us]
X_Acq_Time        = 1.4548992[s]
X_Angle           = 45[deg]
X_Atn             = 1[dB]
X_Pulse           = 6.15[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 6.4548992[s]
```

Figure S18. ^{1}H NMR spectrum of **2g''** (600 MHz, $CDCl_3$).



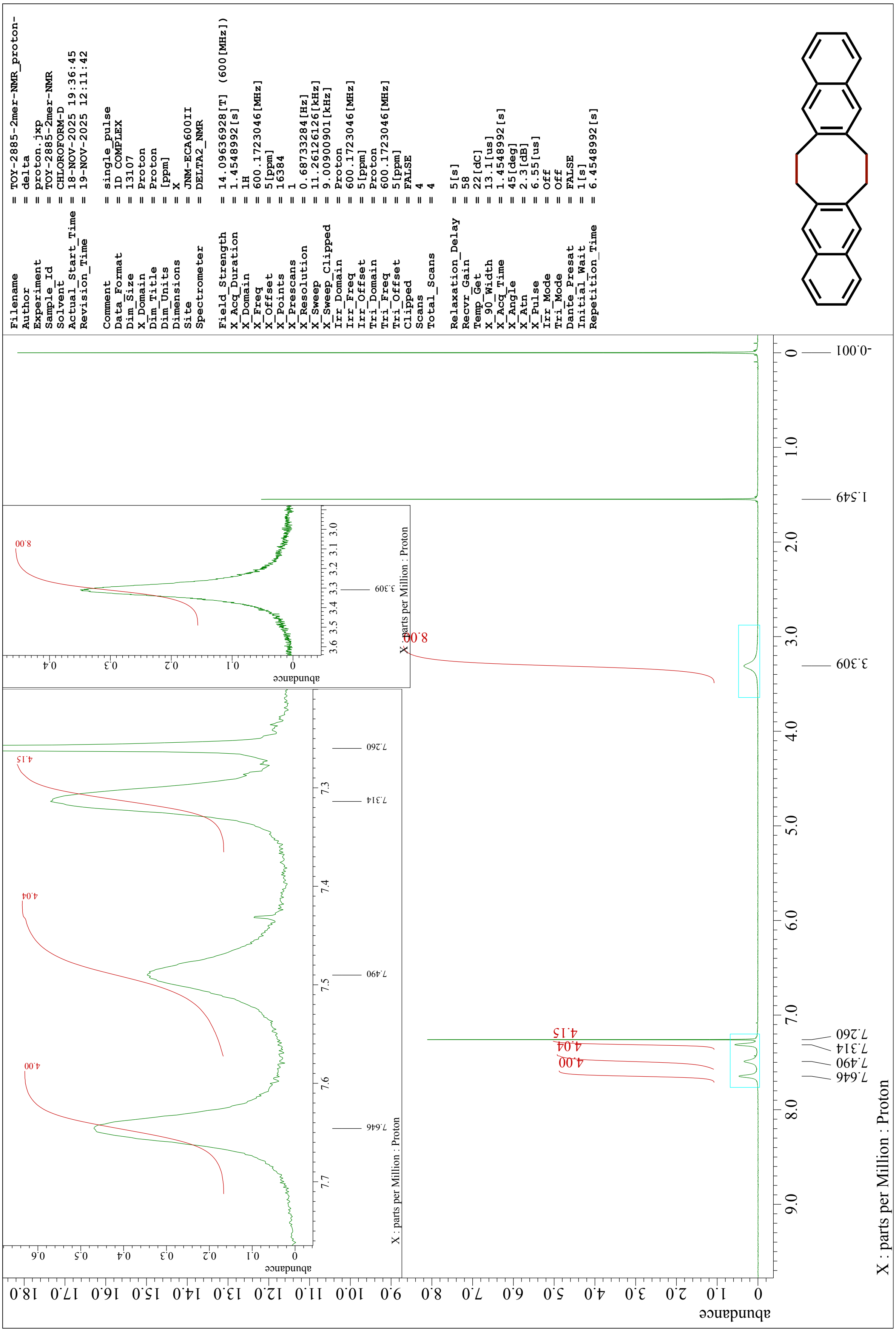
```
Filename             = TOY2361-tetramer-1HNMR_ca
Author               = delta
Experiment           = carbon.jxp
Sample_Id            = TOY2361-tetramer-1HNMR
Solvent              = CHLOROFORM-D
Actual_Start_Time    = 26-APR-2025 10:39:58
Revision_Time        =  5-NOV-2025 13:58:20

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              = 47.3484485[kHz]
X_Sweep_Clipped      = 37.8787878[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           = 10.7[us]
X_Acq_Time           = 0.69206016[s]
X_Angle              = 30[deg]
X_Atn                = 13.7[dB]
X_Pulse              = 3.56666667[us]
Irr_Atn_Dec          = 19.543[dB]
Irr_Atn_Noe          = 19.543[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 S19. ^{13}C NMR spectrum of **2g''** (150 MHz, CDCl$_3$).



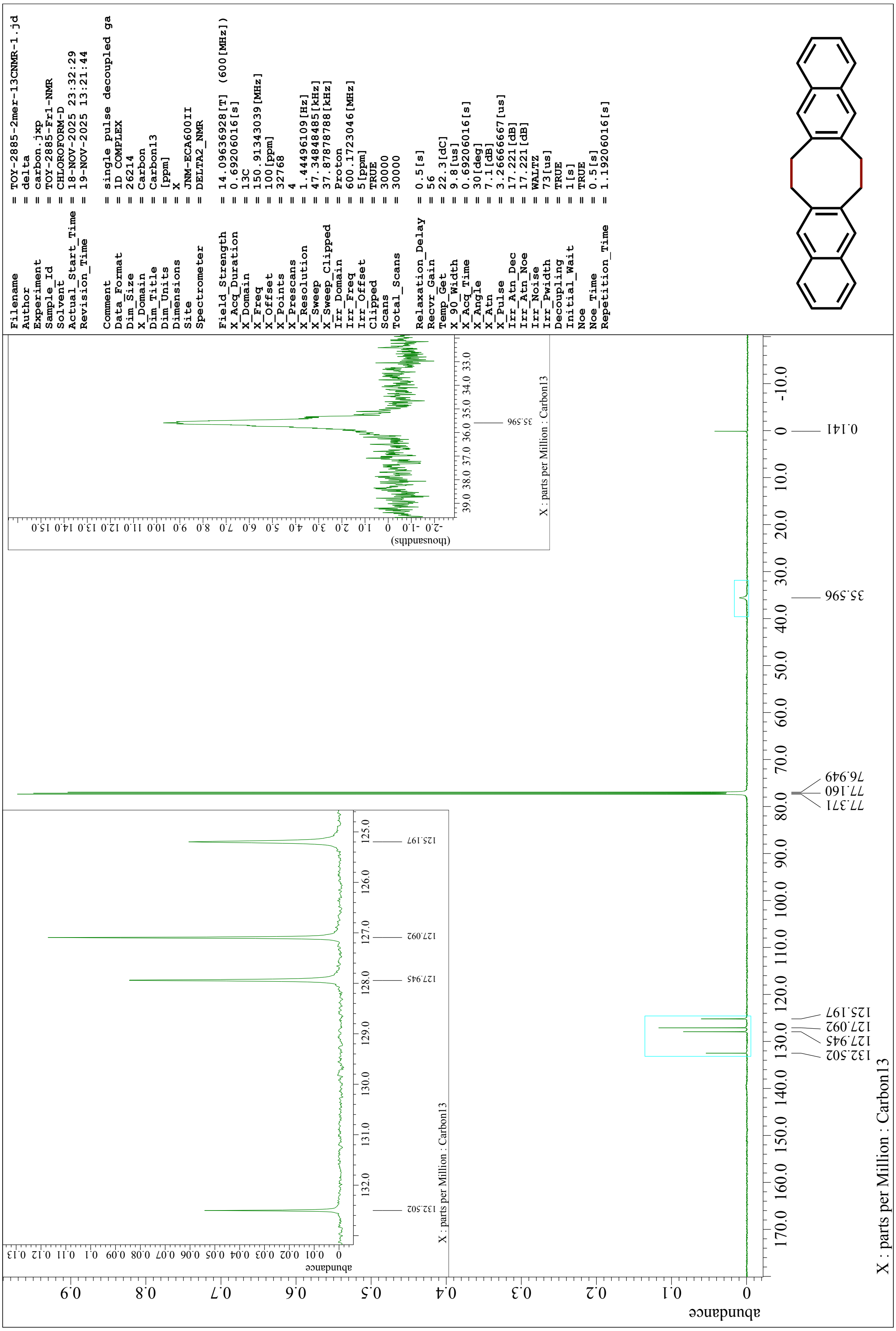
```
Filename            = TOY-2885-2mer-NMR_proton-
Author              = delta
Experiment          = proton.jxp
Sample_Id           = TOY-2885-2mer-NMR
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 18-NOV-2025 19:36:45
Revision_Time       = 19-NOV-2025 12:11:42

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 13107
X_Domain            = Proton
Dim_Title           = Proton
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECA600II
Spectrometer        = DELTA2_NMR

Field_Strength      = 14.09636928[T] (600[MHz])
X_Acq_Duration      = 1.4548992[s]
X_Domain            = 1H
X_Freq              = 600.1723046[MHz]
X_Offset            = 5[ppm]
X_Points            = 16384
X_Prescans          = 1
X_Resolution        = 0.68733284[Hz]
X_Sweep             = 11.26126126[kHz]
X_Sweep_Clipped     = 9.00900901[kHz]
Irr_Domain          = Proton
Irr_Freq            = 600.1723046[MHz]
Irr_Offset          = 5[ppm]
Tri_Domain          = Proton
Tri_Freq            = 600.1723046[MHz]
Tri_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 4
Total_Scans         = 4

Relaxation_Delay    = 5[s]
Recvr_Gain          = 58
Temp_Get            = 22[dC]
X_90_Width          = 13.1[us]
X_Acq_Time          = 1.4548992[s]
X_Angle             = 45[deg]
X_Atn               = 2.3[dB]
X_Pulse             = 6.55[us]
Irr_Mode            = Off
Tri_Mode            = Off
Dante_Presat        = FALSE
Initial_Wait        = 1[s]
Repetition_Time     = 6.4548992[s]
```

Figure S20. ^{1}H NMR spectrum of **2h** (600 MHz, $CDCl_3$).



```
Filename            = TOY-2885-2mer-13CNMR-1.jd
Author              = delta
Experiment          = carbon.jxp
Sample_Id           = TOY-2885-Fr1-NMR
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 18-NOV-2025 23:32:29
Revision_Time       = 19-NOV-2025 13:21:44

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               = 30000
Total_Scans         = 30000

Relaxation_Delay    = 0.5[s]
Recvr_Gain          = 56
Temp_Get            = 22.3[dC]
X_90_Width          = 9.8[us]
X_Acq_Time          = 0.69206016[s]
X_Angle             = 30[deg]
X_Atn               = 7.1[dB]
X_Pulse             = 3.26666667[us]
Irr_Atn_Dec         = 17.221[dB]
Irr_Atn_Noe         = 17.221[dB]
Irr_Noise           = WALTZ
Irr_Pwidth          = 73[us]
Decoupling          = TRUE
Initial_Wait        = 1[s]
Noe                 = TRUE
Noe_Time            = 0.5[s]
Repetition_Time     = 1.19206016[s]
```

Figure S21. ^{13}C NMR spectrum of **2h** (150 MHz, CDCl$_3$).

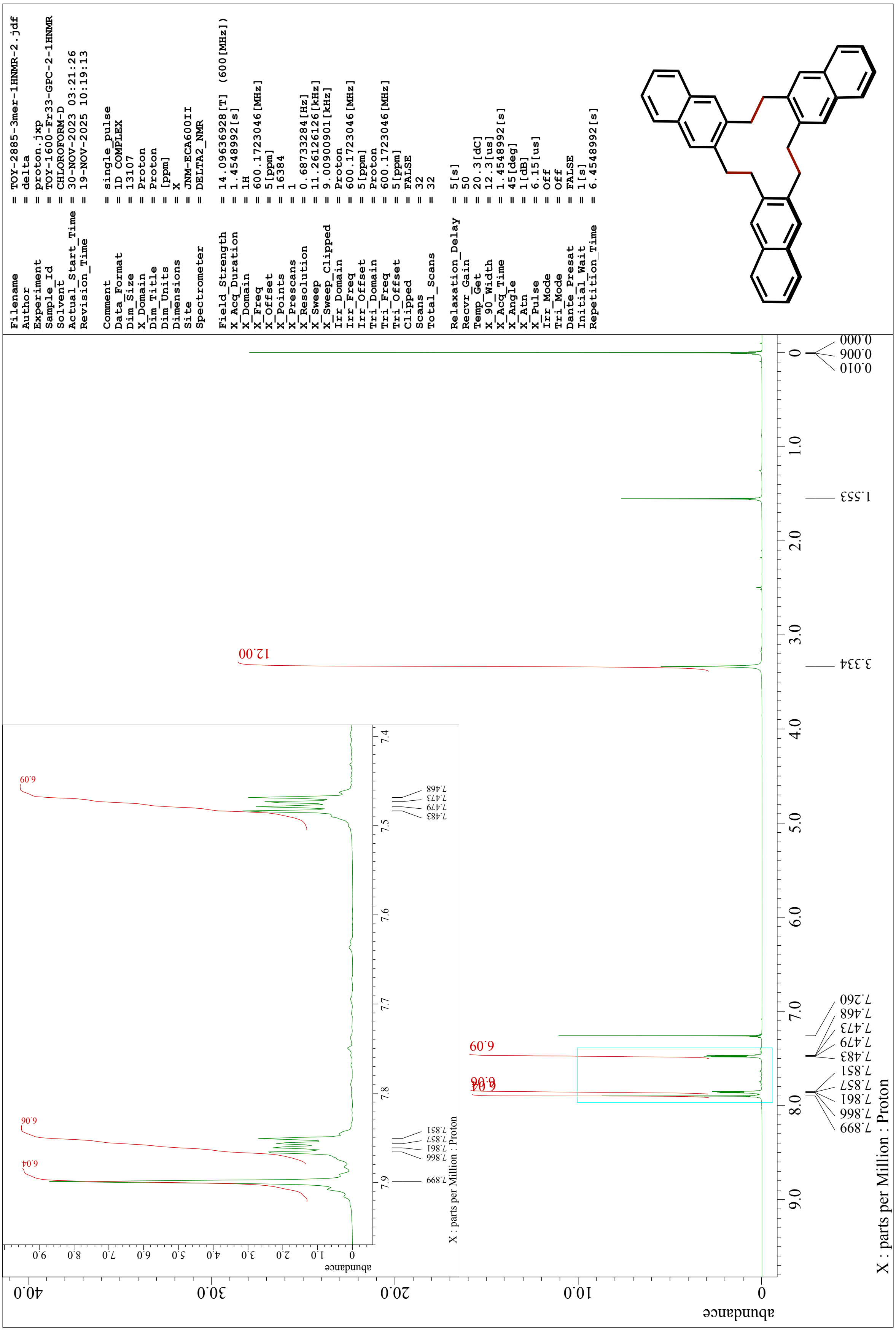
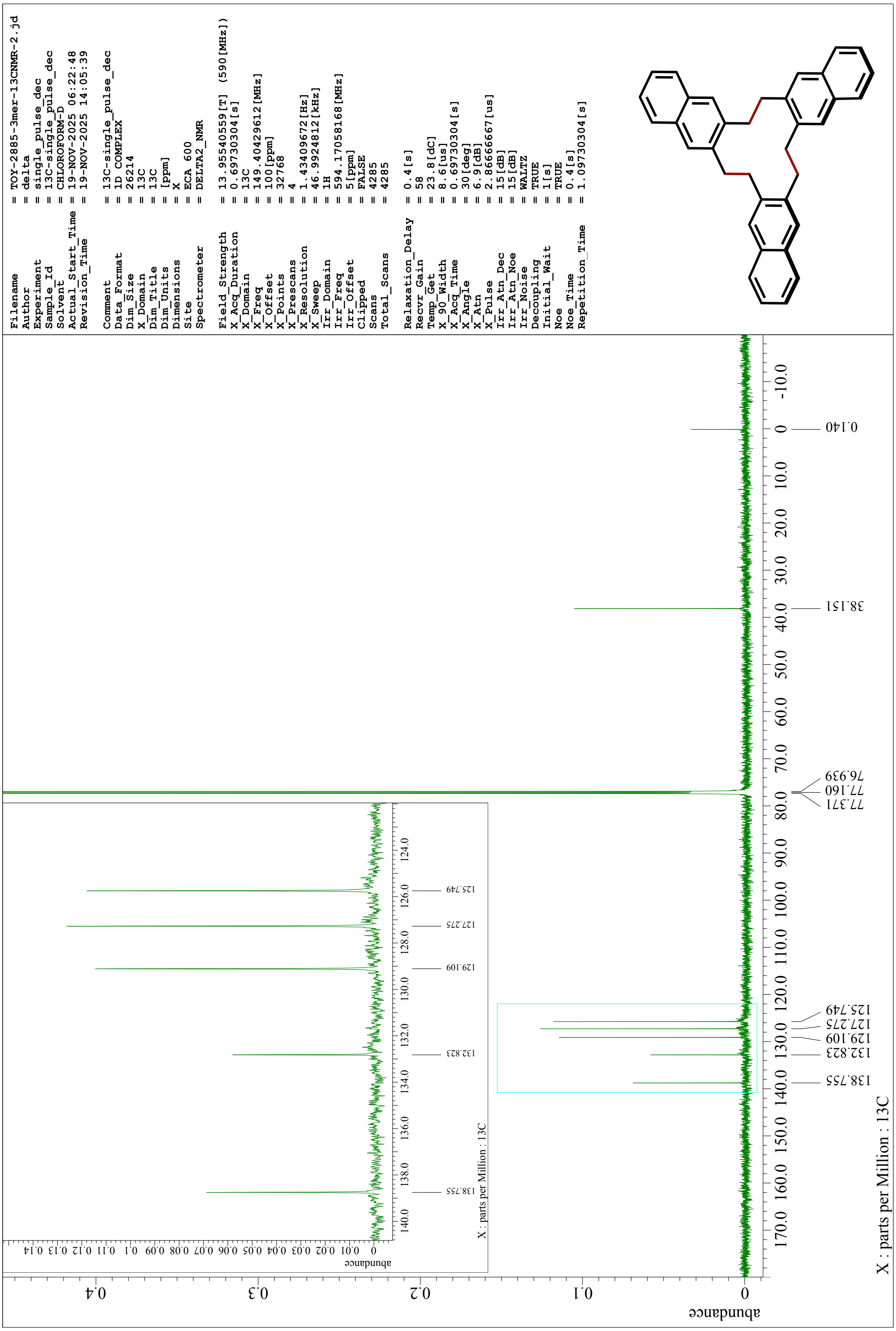


Figure S22. ^{1}H NMR spectrum of **2h′** (600 MHz, $CDCl_3$).



```
Filename              = TOY-2885-3mer-13CNMR-2.jd
Author                = delta
Experiment            = single_pulse_dec
Sample_Id             = 13C-single_pulse_dec
Solvent               = CHLOROFORM-D
Actual_Start_Time     = 19-NOV-2025 06:22:48
Revision_Time         = 19-NOV-2025 14:05:39

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                 = 4285
Total_Scans           = 4285

Relaxation_Delay      = 0.4[s]
Recvr_Gain            = 58
Temp_Get              = 23.8[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           = 15[dB]
Irr_Atn_Noe           = 15[dB]
Irr_Noise             = WALTZ
Decoupling            = TRUE
Initial_Wait          = 1[s]
Noe                   = TRUE
Noe_Time              = 0.4[s]
Repetition_Time       = 1.09730304[s]
```

Figure S23. ^{13}C NMR spectrum of **2h′** (150 MHz, CDCl$_3$).

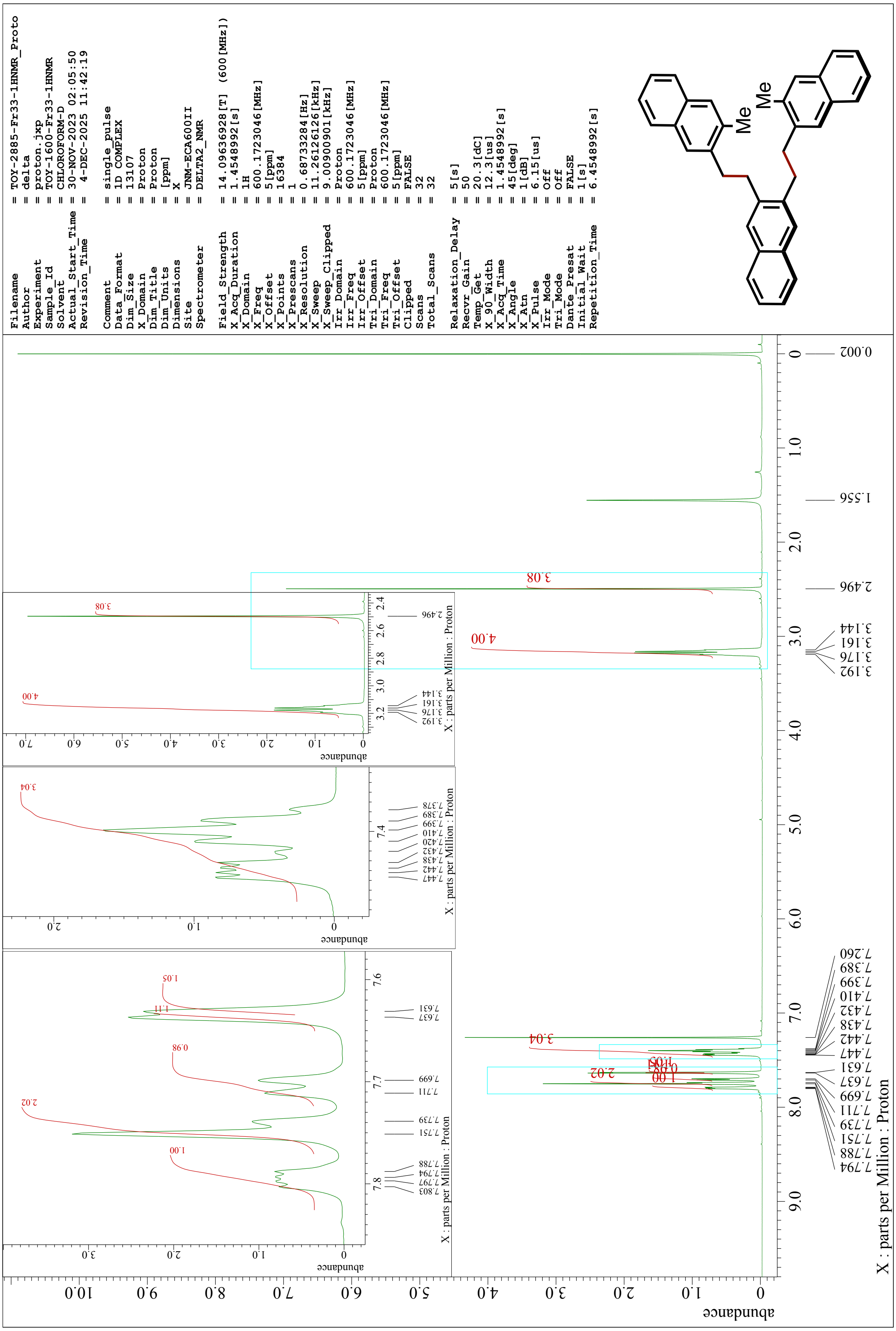
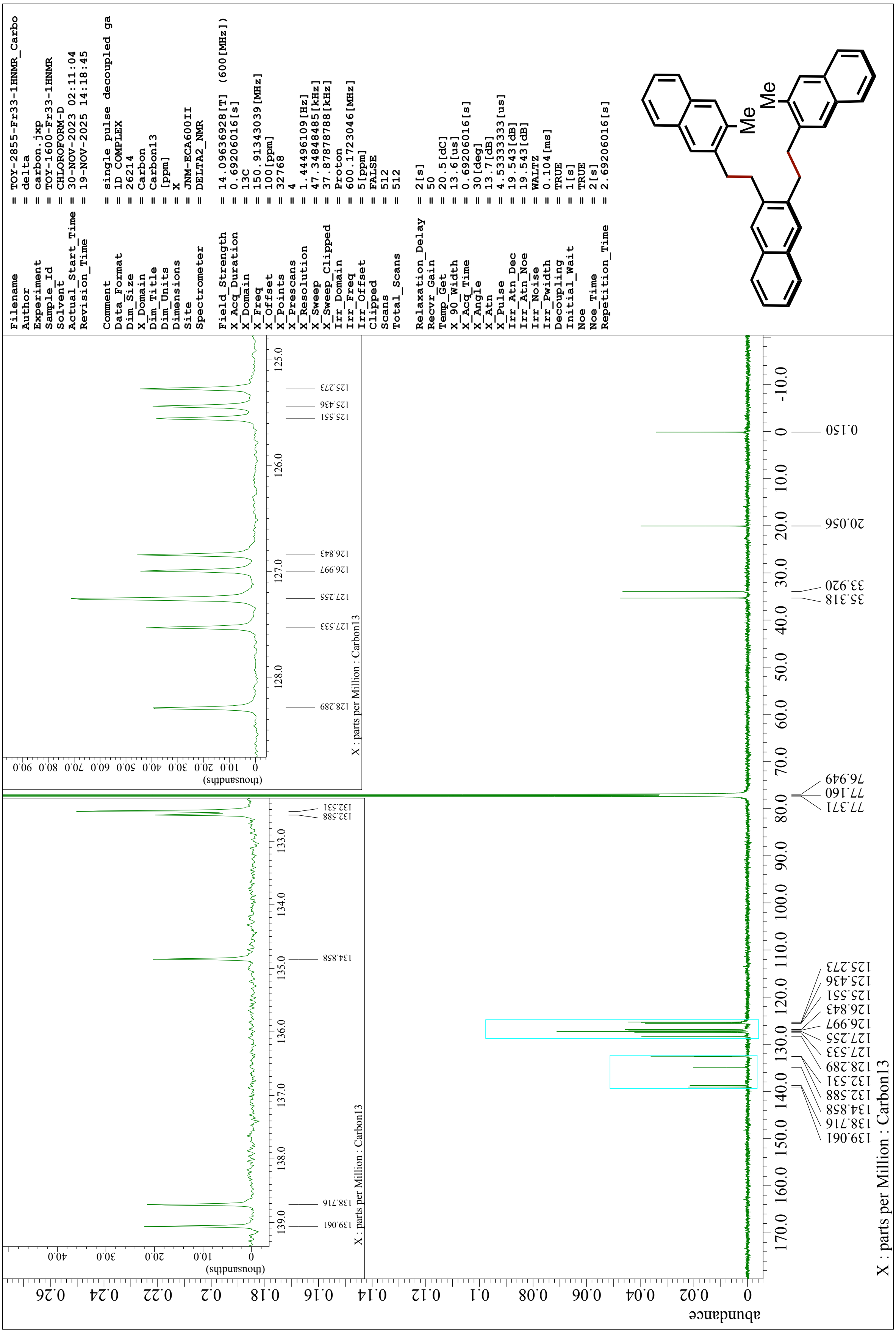


Figure S24. ^{1}H NMR spectrum of **2h′′** (600 MHz, $CDCl_3$).



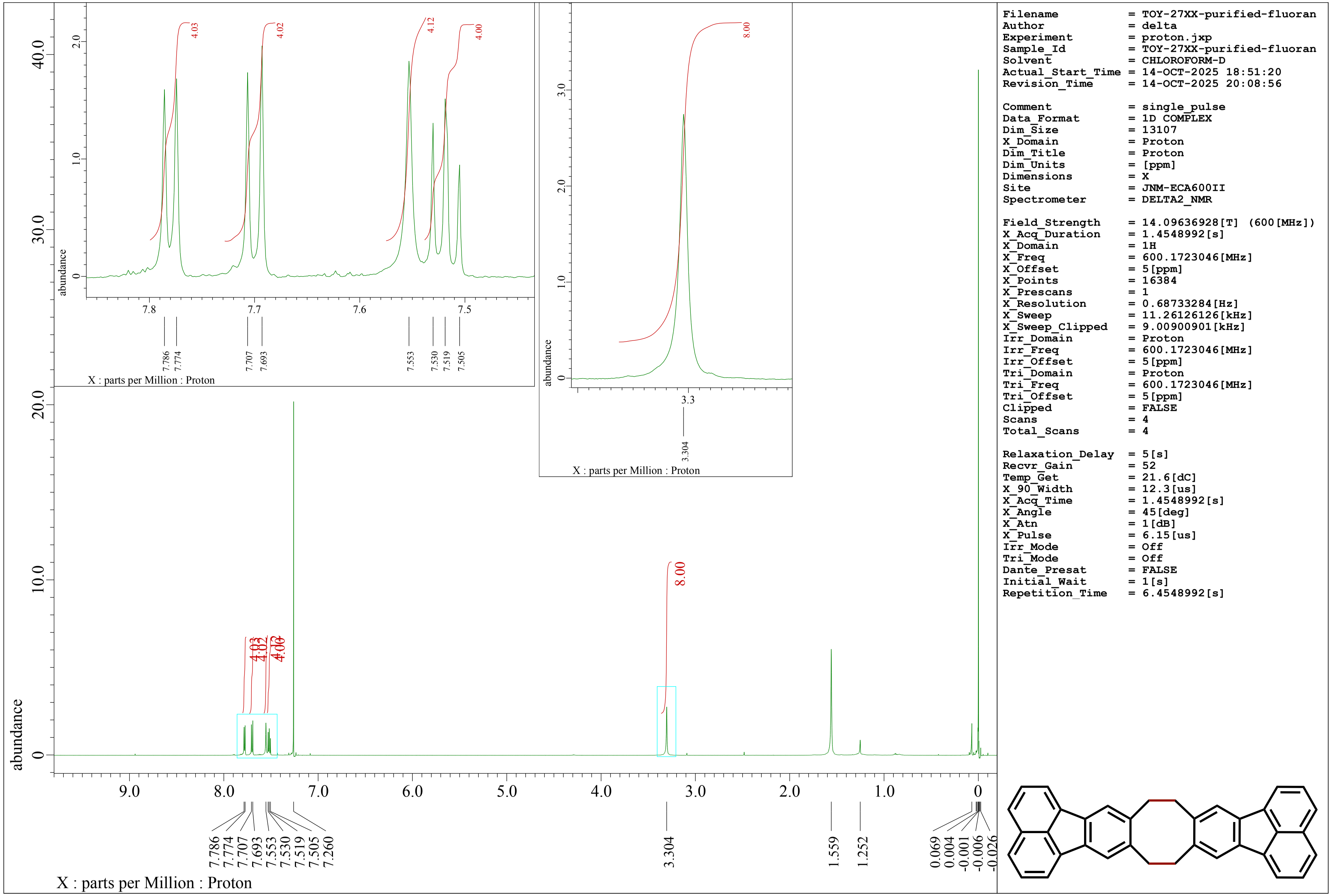
```
Filename            = TOY-2855-Fr33-1HNMR_Carbo
Author              = delta
Experiment          = carbon.jxp
Sample_Id           = TOY-1600-Fr33-1HNMR
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 30-NOV-2023 02:11:04
Revision_Time       = 19-NOV-2025 14:18:45

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             = 47.3484485[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            = 20.5[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         = 19.543[dB]
Irr_Atn_Noe         = 19.543[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 S25. ^{13}C NMR spectrum of **2h″** (150 MHz, CDCl$_3$).



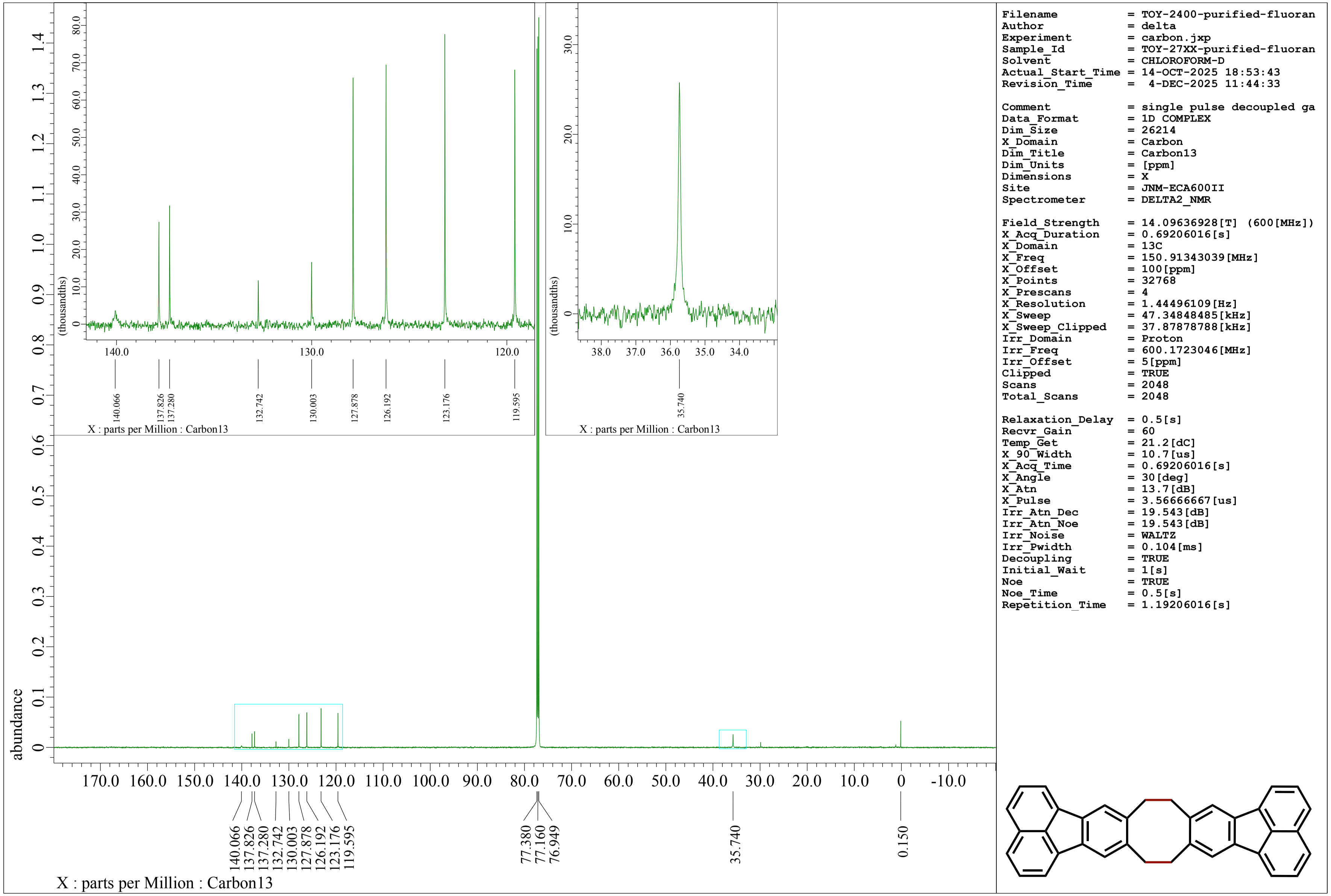
```
Filename             = TOY-27XX-purified-fluoran
Author               = delta
Experiment           = proton.jxp
Sample_Id            = TOY-27XX-purified-fluoran
Solvent              = CHLOROFORM-D
Actual_Start_Time    = 14-OCT-2025 18:51:20
Revision_Time        = 14-OCT-2025 20:08:56

Comment              = single_pulse
Data_Format          = 1D COMPLEX
Dim_Size             = 13107
X_Domain             = Proton
Dim_Title            = Proton
Dim_Units            = [ppm]
Dimensions           = X
Site                 = JNM-ECA600II
Spectrometer         = DELTA2_NMR

Field_Strength       = 14.09636928[T]  (600[MHz])
X_Acq_Duration       = 1.4548992[s]
X_Domain             = 1H
X_Freq               = 600.1723046[MHz]
X_Offset             = 5[ppm]
X_Points             = 16384
X_Prescans           = 1
X_Resolution         = 0.68733284[Hz]
X_Sweep              = 11.26126126[kHz]
X_Sweep_Clipped      = 9.00900901[kHz]
Irr_Domain           = Proton
Irr_Freq             = 600.1723046[MHz]
Irr_Offset           = 5[ppm]
Tri_Domain           = Proton
Tri_Freq             = 600.1723046[MHz]
Tri_Offset           = 5[ppm]
Clipped              = FALSE
Scans                = 4
Total_Scans          = 4

Relaxation_Delay     = 5[s]
Recvr_Gain           = 52
Temp_Get             = 21.6[dC]
X_90_Width           = 12.3[us]
X_Acq_Time           = 1.4548992[s]
X_Angle              = 45[deg]
X_Atn                = 1[dB]
X_Pulse              = 6.15[us]
Irr_Mode             = Off
Tri_Mode             = Off
Dante_Presat         = FALSE
Initial_Wait         = 1[s]
Repetition_Time      = 6.4548992[s]
```

Figure S26. ^{1}H NMR spectrum of **2i** (600 MHz, $CDCl_3$).



```
Filename            = TOY-2400-purified-fluoran
Author              = delta
Experiment          = carbon.jxp
Sample_Id           = TOY-27XX-purified-fluoran
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 14-OCT-2025 18:53:43
Revision_Time       =  4-DEC-2025 11:44:33

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               = 2048
Total_Scans         = 2048

Relaxation_Delay    = 0.5[s]
Recvr_Gain          = 60
Temp_Get            = 21.2[dC]
X_90_Width          = 10.7[us]
X_Acq_Time          = 0.69206016[s]
X_Angle             = 30[deg]
X_Atn               = 13.7[dB]
X_Pulse             = 3.56666667[us]
Irr_Atn_Dec         = 19.543[dB]
Irr_Atn_Noe         = 19.543[dB]
Irr_Noise           = WALTZ
Irr_Pwidth          = 0.104[ms]
Decoupling          = TRUE
Initial_Wait        = 1[s]
Noe                 = TRUE
Noe_Time            = 0.5[s]
Repetition_Time     = 1.19206016[s]
```

Figure S27. ^{13}C NMR spectrum of **2i** (150 MHz, $CDCl_3$).

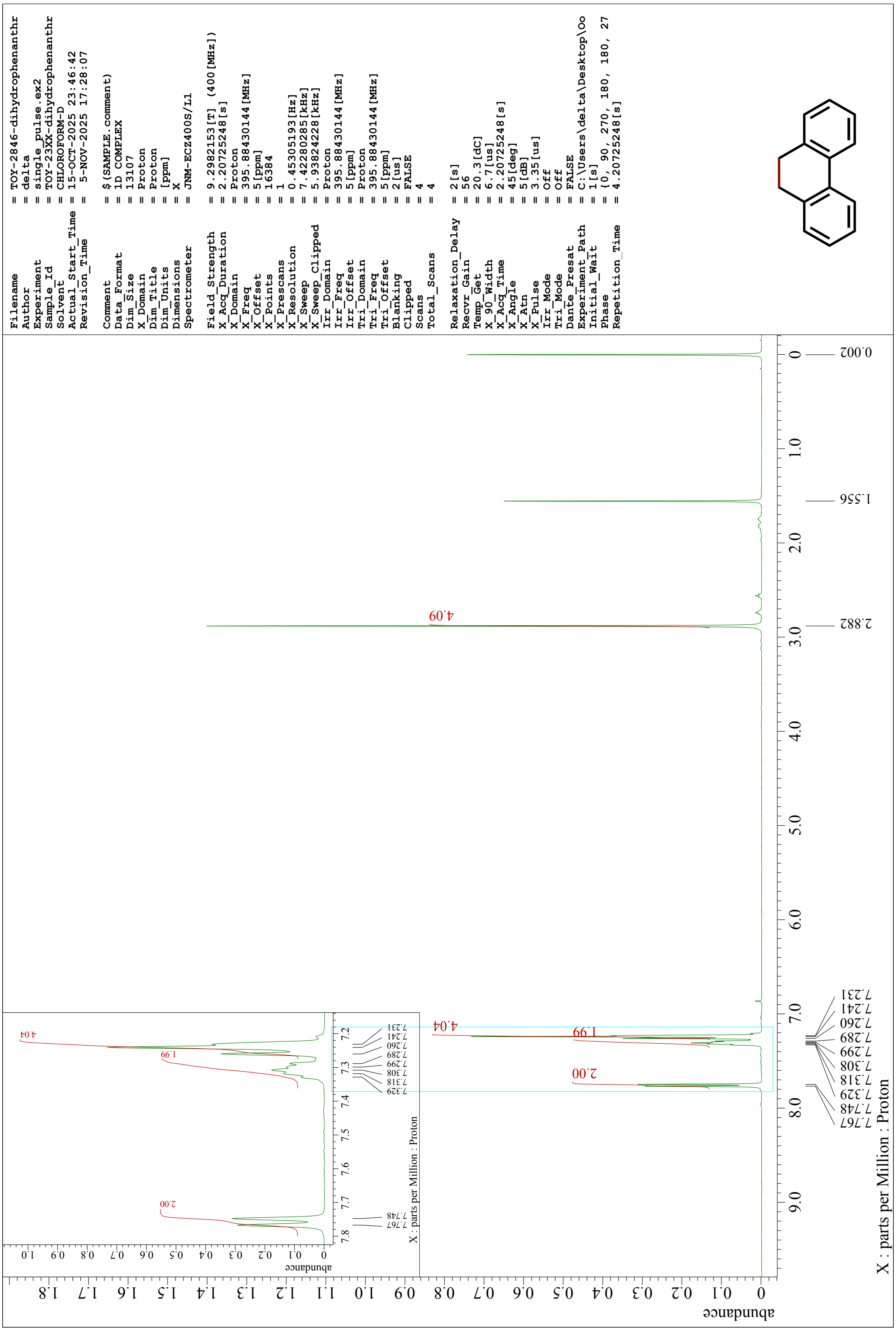
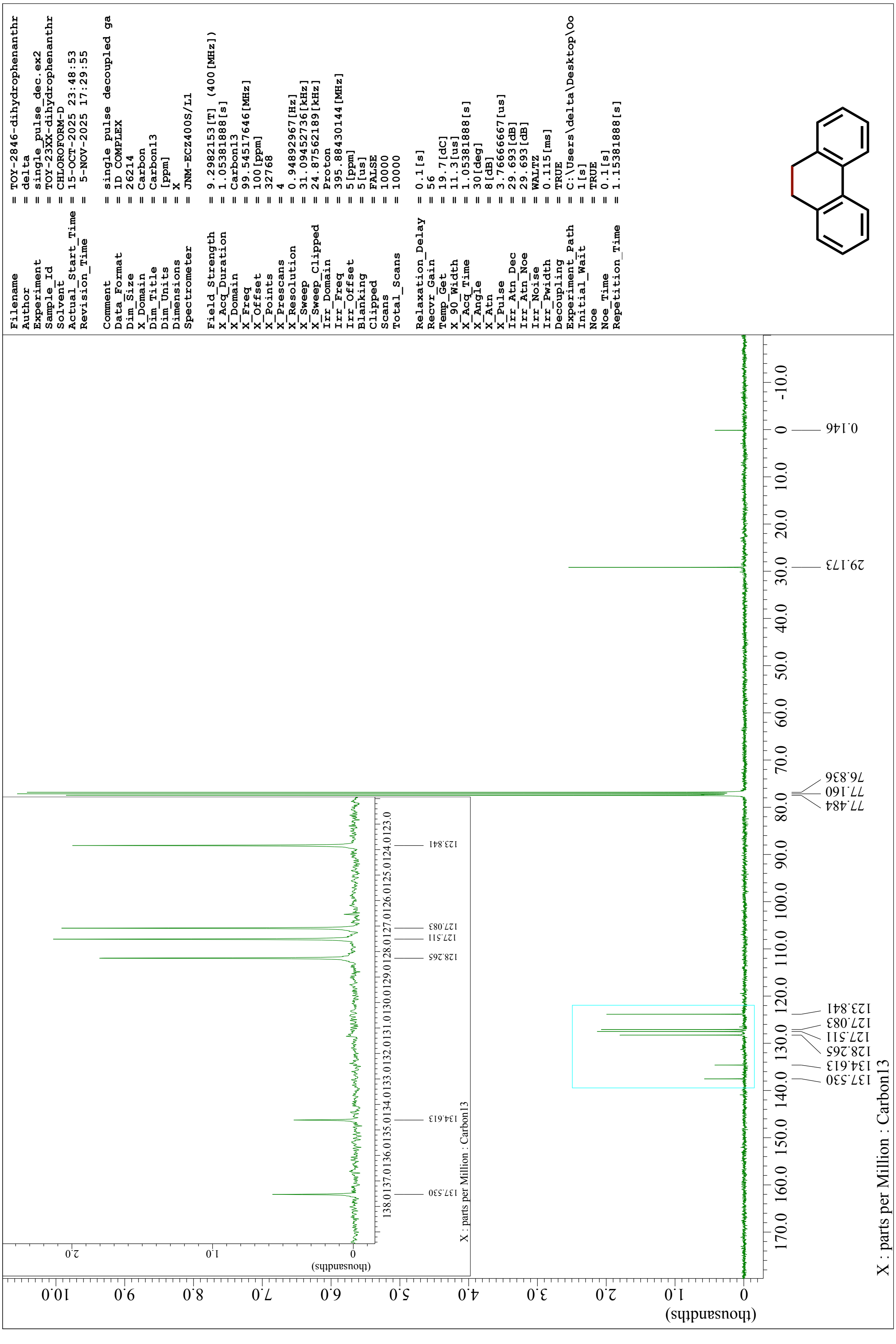


Figure S28. ^{1}H NMR spectrum of **2j** (600 MHz, CDCl$_3$).



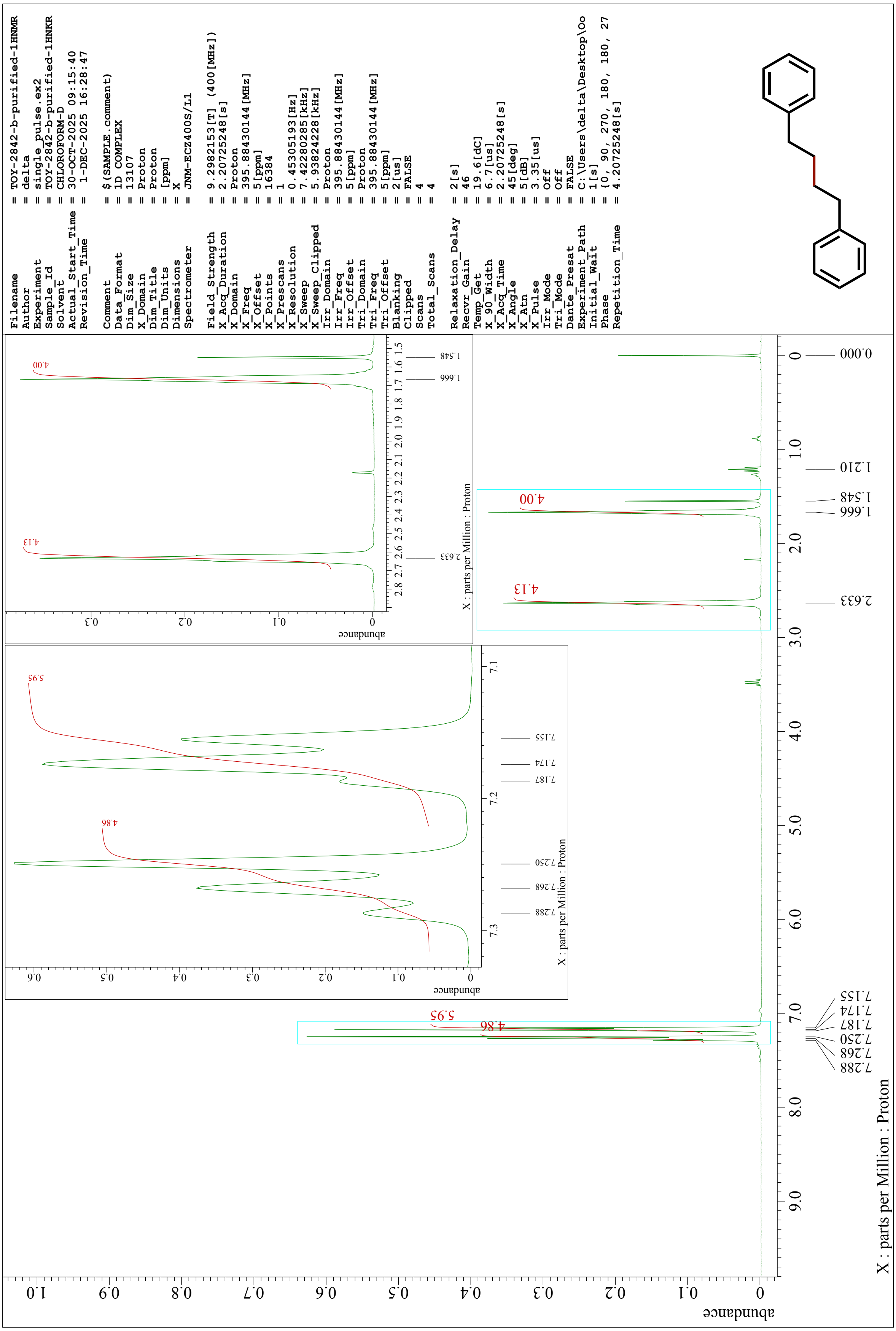
```
Filename            = TOY-2846-dihydrophenanthr
Author              = delta
Experiment          = single_pulse_dec.ex2
Sample_Id           = TOY-23XX-dihydrophenanthr
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 15-OCT-2025 23:48:53
Revision_Time       =  5-NOV-2025 17:29:55

Comment             = single pulse decoupled ga
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = Carbon
Dim_Title           = Carbon13
Dim_Units           = [ppm]
Dimensions          = X
Spectrometer        = JNM-ECZ400S/L1

Field_Strength      = 9.2982153[T] (400[MHz])
X_Acq_Duration      = 1.05381888[s]
X_Domain            = Carbon13
X_Freq              = 99.54517646[MHz]
X_Offset            = 100[ppm]
X_Points            = 32768
X_Prescans          = 4
X_Resolution        = 0.94892967[Hz]
X_Sweep             = 31.09452736[kHz]
X_Sweep_Clipped     = 24.87562189[kHz]
Irr_Domain          = Proton
Irr_Freq            = 395.88430144[MHz]
Irr_Offset          = 5[ppm]
Blanking            = 5[us]
Clipped             = FALSE
Scans               = 10000
Total_Scans         = 10000

Relaxation_Delay    = 0.1[s]
Recvr_Gain          = 56
Temp_Get            = 19.7[dC]
X_90_Width          = 11.3[us]
X_Acq_Time          = 1.05381888[s]
X_Angle             = 30[deg]
X_Atn               = 8[dB]
X_Pulse             = 3.76666667[us]
Irr_Atn_Dec         = 29.693[dB]
Irr_Atn_Noe         = 29.693[dB]
Irr_Noise           = WALTZ
Irr_Pwidth          = 0.115[ms]
Decoupling          = TRUE
Experiment_Path     = C:\Users\delta\Desktop\Oo
Initial_Wait        = 1[s]
Noe                 = TRUE
Noe_Time            = 0.1[s]
Repetition_Time     = 1.15381888[s]
```

Figure S29. ^{13}C NMR spectrum of **2j** (100 MHz, $CDCl_3$).



```
Filename            = TOY-2842-b-purified-1HNMR
Author              = delta
Experiment          = single_pulse.ex2
Sample_Id           = TOY-2842-b-purified-1HNKR
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 30-OCT-2025 09:15:40
Revision_Time       =  1-DEC-2025 16:28:47

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               = 4
Total_Scans         = 4

Relaxation_Delay    = 2[s]
Recvr_Gain          = 46
Temp_Get            = 19.6[dC]
X_90_Width          = 6.7[us]
X_Acq_Time          = 2.20725248[s]
X_Angle             = 45[deg]
X_Atn               = 5[dB]
X_Pulse             = 3.35[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     = 4.20725248[s]
```

Figure S30. ^{1}H NMR spectrum of **2k** (400 MHz, $CDCl_3$).

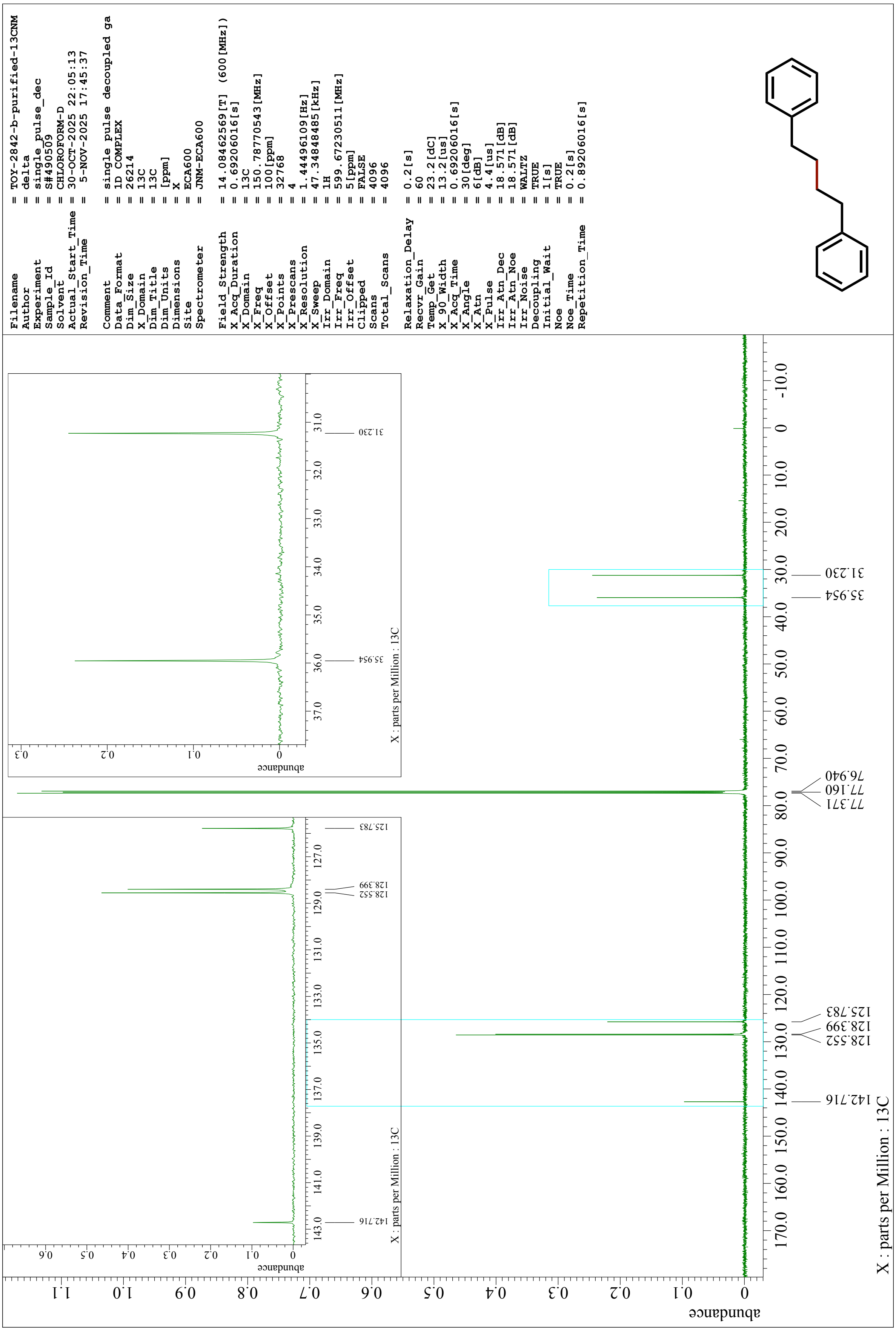
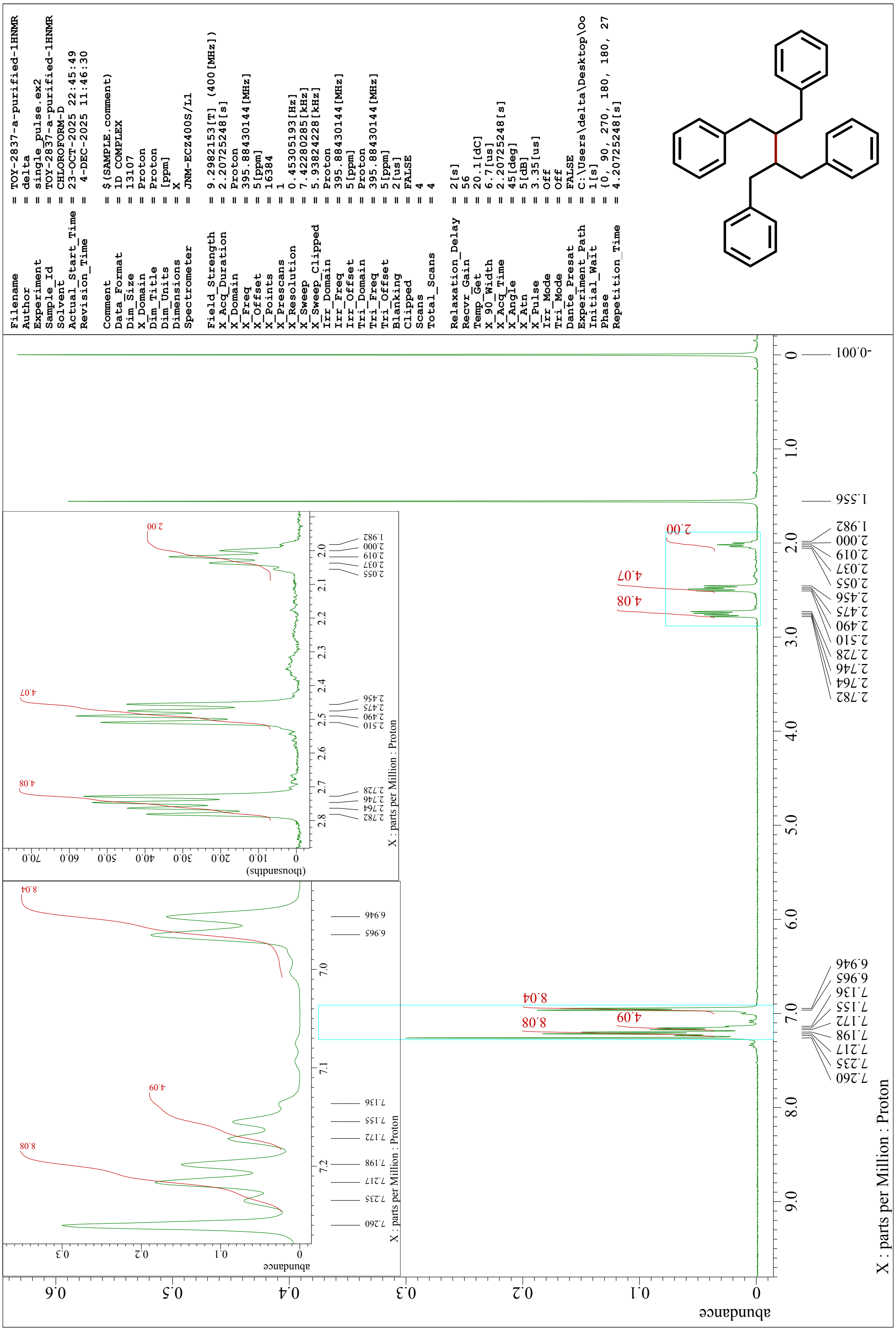


Figure S31. ^{13}C NMR spectrum of **2k** (150 MHz, CDCl$_3$).



```
Filename              = TOY-2837-a-purified-1HNMR
Author                = delta
Experiment            = single_pulse.ex2
Sample_Id             = TOY-2837-a-purified-1HNMR
Solvent               = CHLOROFORM-D
Actual_Start_Time     = 23-OCT-2025 22:45:49
Revision_Time         = 4-DEC-2025 11:46:30

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                 = 4
Total_Scans           = 4

Relaxation_Delay      = 2[s]
Recvr_Gain            = 56
Temp_Get              = 20.1[dC]
X_90_Width            = 6.7[us]
X_Acq_Time            = 2.20725248[s]
X_Angle               = 45[deg]
X_Atn                 = 5[dB]
X_Pulse               = 3.35[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       = 4.20725248[s]
```

Figure S32. ^{1}H NMR spectrum of **2l** (400 MHz, $CDCl_3$).

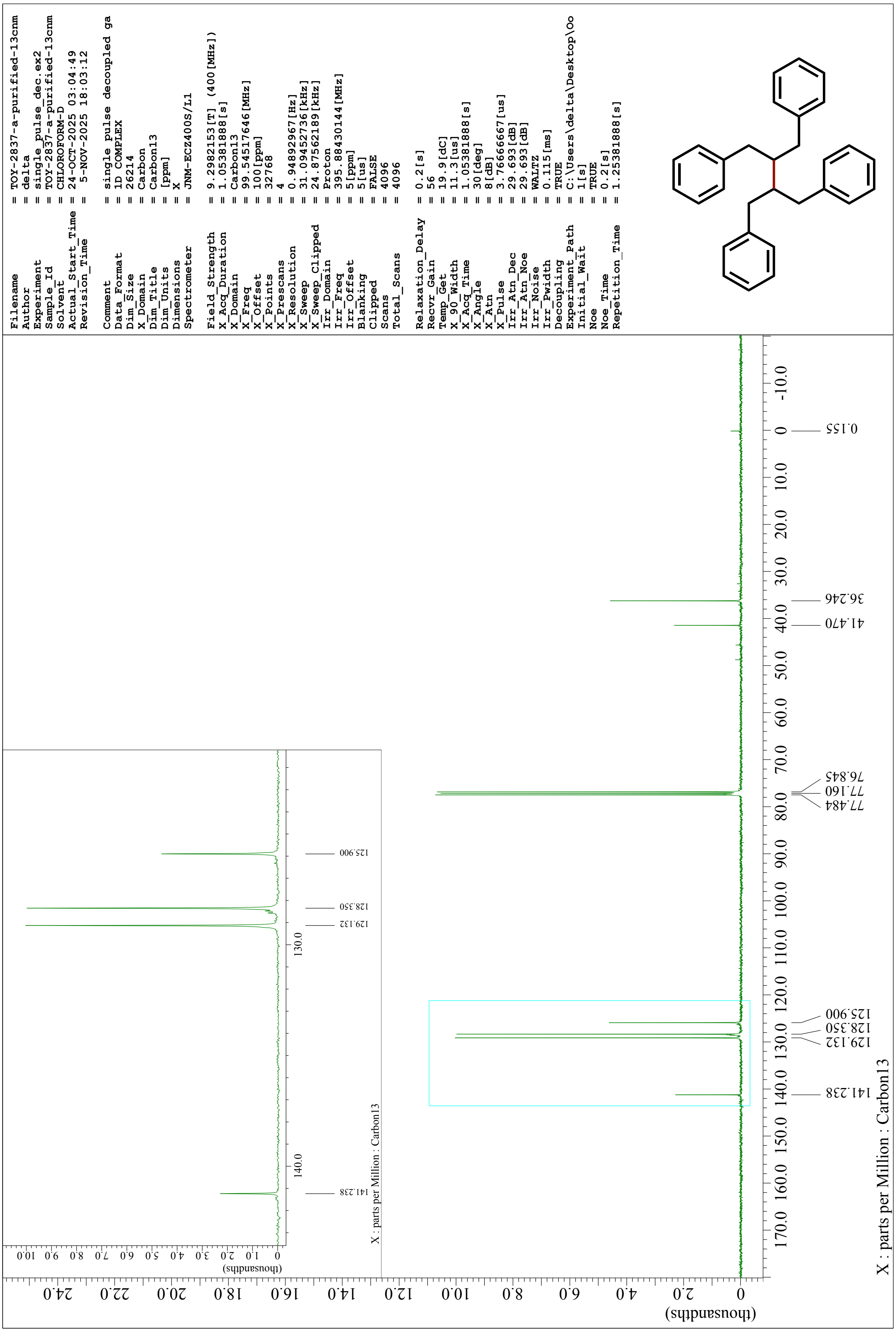
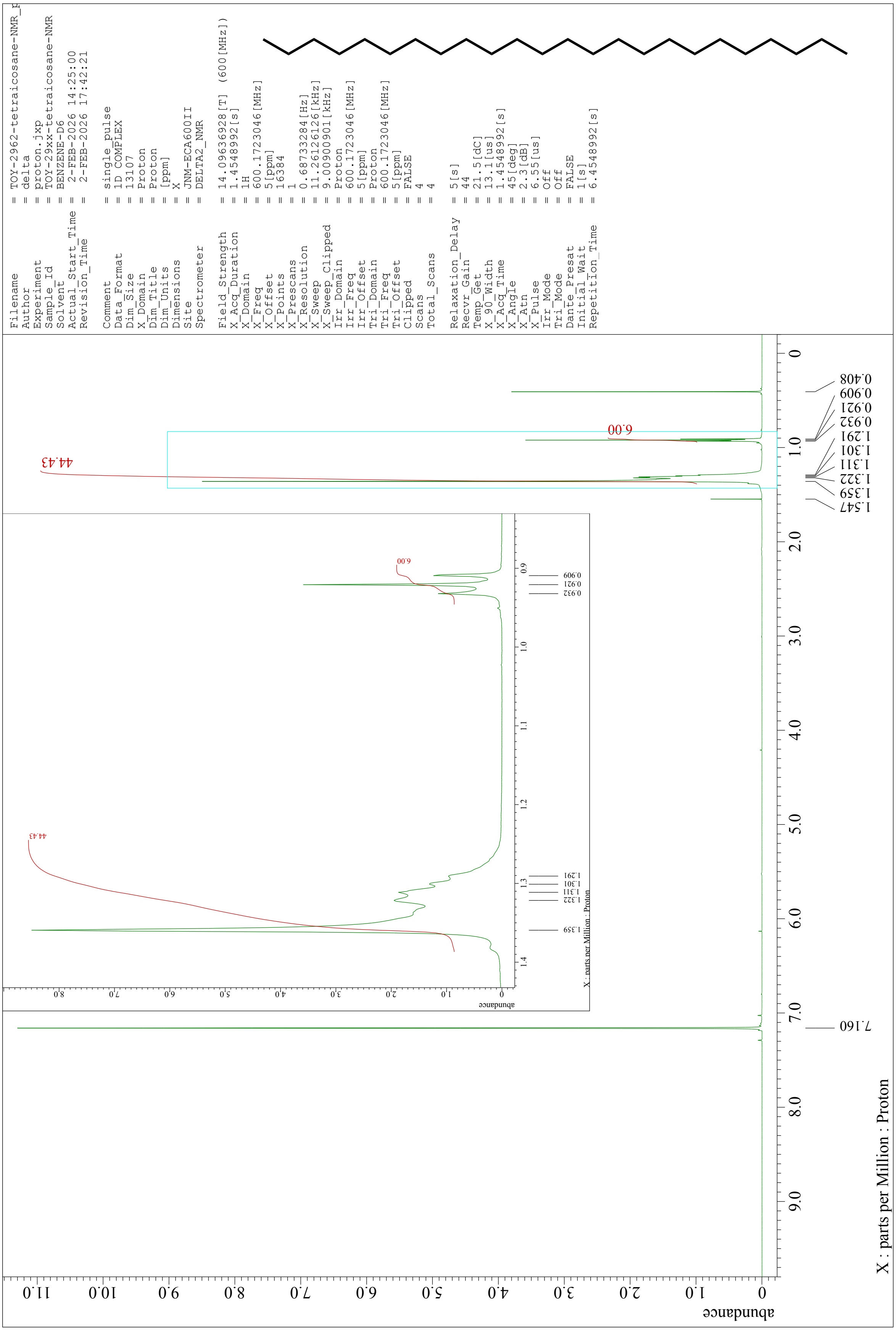


Figure S33. ^{13}C NMR spectrum of **2l** (100 MHz, CDCl$_3$).



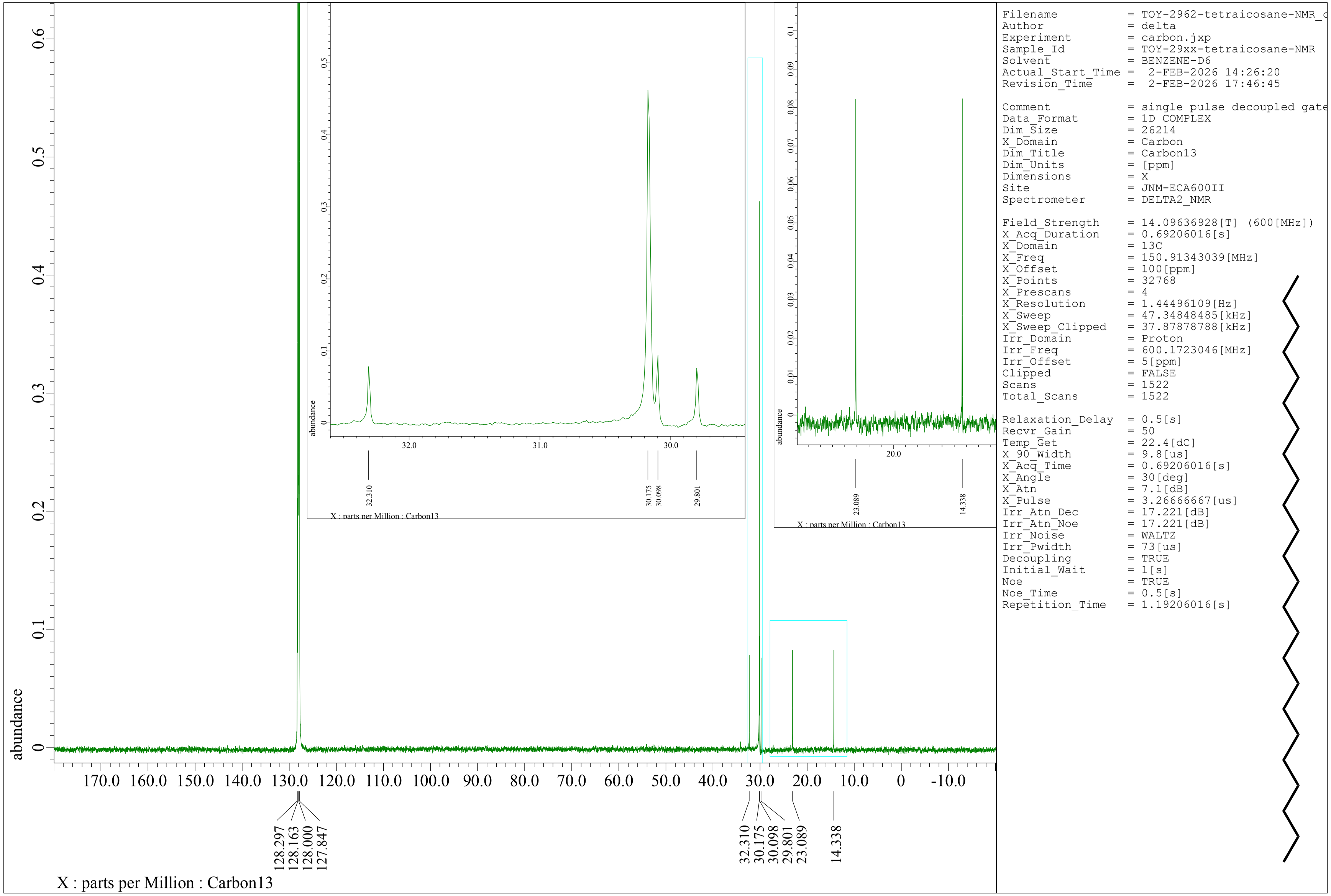
```
Filename            = TOY-2962-tetraicosane-NMR_p
Author              = delta
Experiment          = proton.jxp
Sample_Id           = TOY-29xx-tetraicosane-NMR
Solvent             = BENZENE-D6
Actual_Start_Time   =   2-FEB-2026 14:25:00
Revision_Time       =   2-FEB-2026 17:42:21

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 13107
X_Domain            = Proton
Dim_Title           = Proton
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECA600II
Spectrometer        = DELTA2_NMR

Field_Strength      = 14.09636928[T] (600[MHz])
X_Acq_Duration      = 1.4548992[s]
X_Domain            = 1H
X_Freq              = 600.1723046[MHz]
X_Offset            = 5[ppm]
X_Points            = 16384
X_Prescans          = 1
X_Resolution        = 0.68733284[Hz]
X_Sweep             = 11.26126126[kHz]
X_Sweep_Clipped     = 9.00900901[kHz]
Irr_Domain          = Proton
Irr_Freq            = 600.1723046[MHz]
Irr_Offset          = 5[ppm]
Tri_Domain          = Proton
Tri_Freq            = 600.1723046[MHz]
Tri_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 4
Total_Scans         = 4

Relaxation_Delay    = 5[s]
Recvr_Gain          = 44
Temp_Get            = 21.5[dC]
X_90_Width          = 13.1[us]
X_Acq_Time          = 1.4548992[s]
X_Angle             = 45[deg]
X_Atn               = 2.3[dB]
X_Pulse             = 6.55[us]
Irr_Mode            = Off
Tri_Mode            = Off
Dante_Presat        = FALSE
Initial_Wait        = 1[s]
Repetition_Time     = 6.4548992[s]
```

Figure S34. ^{1}H NMR spectrum of **2m** (600 MHz, C_6D_6).



```
Filename             = TOY-2962-tetraicosane-NMR_c
Author               = delta
Experiment           = carbon.jxp
Sample_Id            = TOY-29xx-tetraicosane-NMR
Solvent              = BENZENE-D6
Actual_Start_Time    =  2-FEB-2026 14:26:20
Revision_Time        =  2-FEB-2026 17:46:45

Comment              = single pulse decoupled gate
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                = 1522
Total_Scans          = 1522

Relaxation_Delay     = 0.5[s]
Recvr_Gain           = 50
Temp_Get             = 22.4[dC]
X_90_Width           = 9.8[us]
X_Acq_Time           = 0.69206016[s]
X_Angle              = 30[deg]
X_Atn                = 7.1[dB]
X_Pulse              = 3.26666667[us]
Irr_Atn_Dec          = 17.221[dB]
Irr_Atn_Noe          = 17.221[dB]
Irr_Noise            = WALTZ
Irr_Pwidth           = 73[us]
Decoupling           = TRUE
Initial_Wait         = 1[s]
Noe                  = TRUE
Noe_Time             = 0.5[s]
Repetition Time      = 1.19206016[s]
```

Figure S35. ^{13}C NMR spectrum of **2m** (150 MHz, C_6D_6).

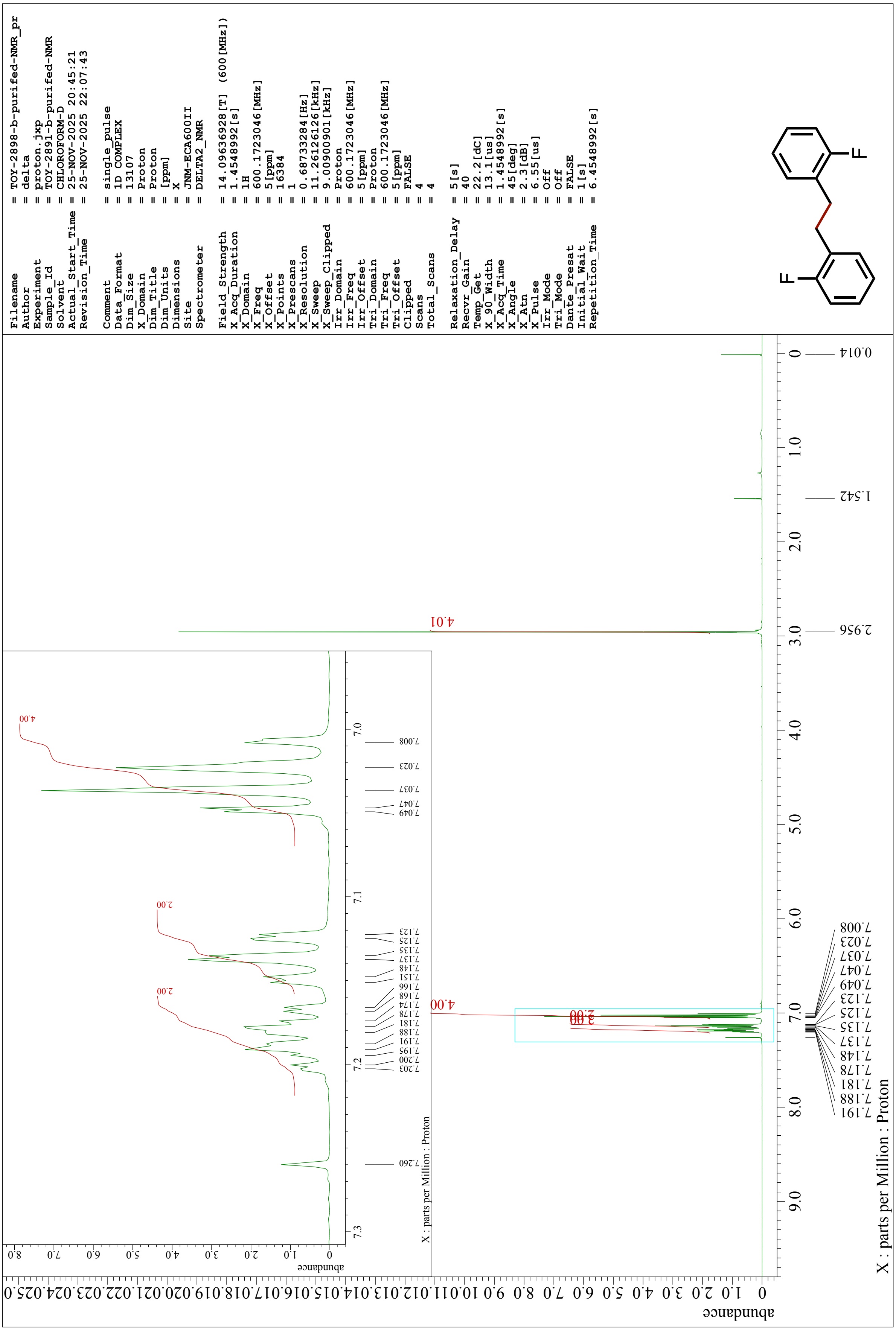
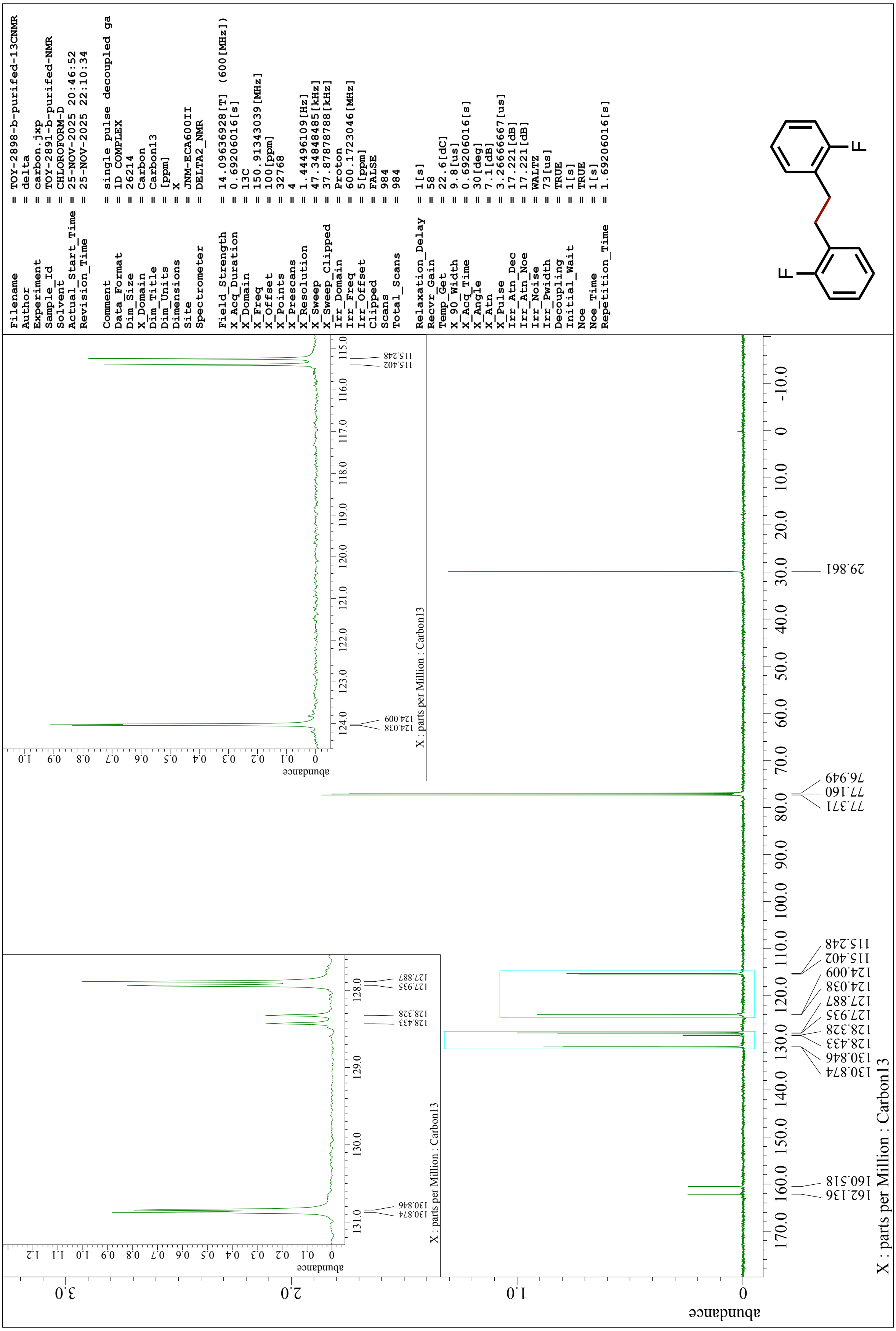


Figure S36. ^{1}H NMR spectrum of **2n** (600 MHz, $CDCl_3$).



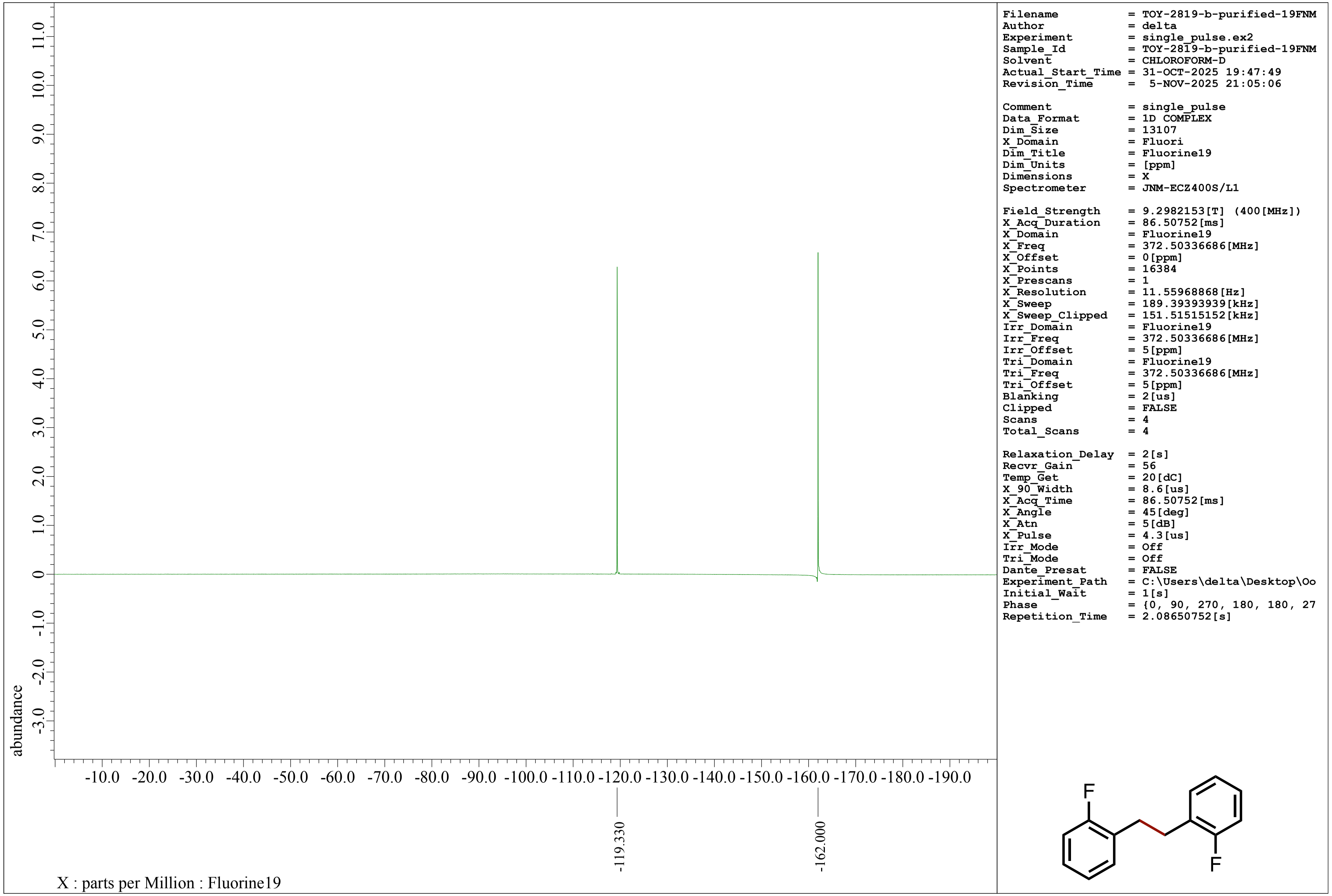
```
Filename            = TOY-2898-b-purifed-13CNMR
Author              = delta
Experiment          = carbon.jxp
Sample_Id           = TOY-2891-b-purifed-NMR
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 25-NOV-2025 20:46:52
Revision_Time       = 25-NOV-2025 22:10:34

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             = 47.3484485[kHz]
X_Sweep_Clipped     = 37.8787888[kHz]
Irr_Domain          = Proton
Irr_Freq            = 600.1723046[MHz]
Irr_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 984
Total_Scans         = 984

Relaxation_Delay    = 1[s]
Recvr_Gain          = 58
Temp_Get            = 22.6[dC]
X_90_Width          = 9.8[us]
X_Acq_Time          = 0.69206016[s]
X_Angle             = 30[deg]
X_Atn               = 7.1[dB]
X_Pulse             = 3.26666667[us]
Irr_Atn_Dec         = 17.221[dB]
Irr_Atn_Noe         = 17.221[dB]
Irr_Noise           = WALTZ
Irr_Pwidth          = 73[us]
Decoupling          = TRUE
Initial_Wait        = 1[s]
Noe                 = TRUE
Noe_Time            = 1[s]
Repetition_Time     = 1.69206016[s]
```

Figure S37. ^{13}C NMR spectrum of **2n** (100 MHz, $CDCl_3$).



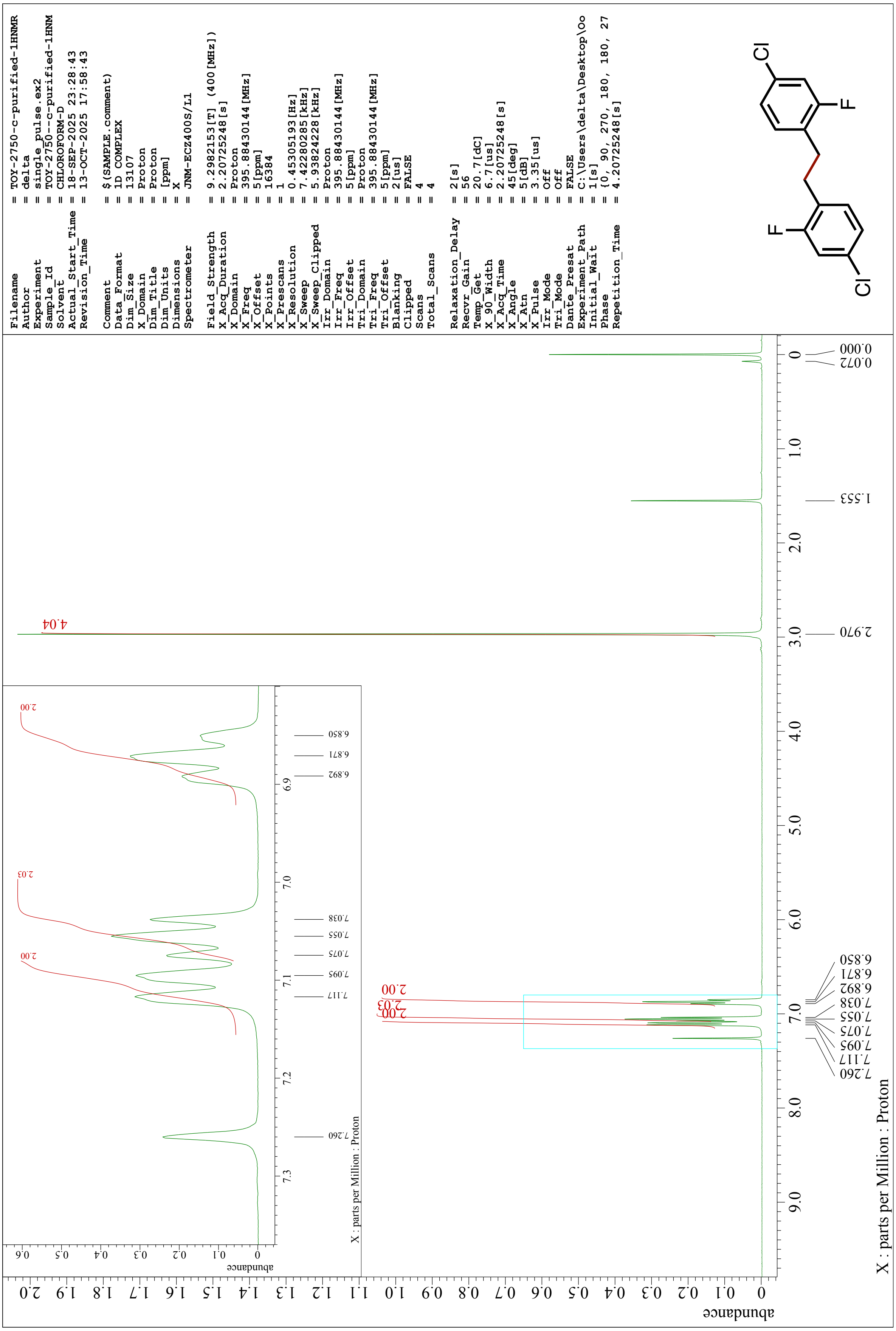
```
Filename           = TOY-2819-b-purified-19FNM
Author             = delta
Experiment         = single_pulse.ex2
Sample_Id          = TOY-2819-b-purified-19FNM
Solvent            = CHLOROFORM-D
Actual_Start_Time  = 31-OCT-2025 19:47:49
Revision_Time      =  5-NOV-2025 21:05:06

Comment            = single_pulse
Data_Format        = 1D COMPLEX
Dim_Size           = 13107
X_Domain           = Fluori
Dim_Title          = Fluorine19
Dim_Units          = [ppm]
Dimensions         = X
Spectrometer       = JNM-ECZ400S/L1

Field_Strength     = 9.2982153[T] (400[MHz])
X_Acq_Duration     = 86.50752[ms]
X_Domain           = Fluorine19
X_Freq             = 372.50336686[MHz]
X_Offset           = 0[ppm]
X_Points           = 16384
X_Prescans         = 1
X_Resolution       = 11.55968868[Hz]
X_Sweep            = 189.39393939[kHz]
X_Sweep_Clipped    = 151.51515152[kHz]
Irr_Domain         = Fluorine19
Irr_Freq           = 372.50336686[MHz]
Irr_Offset         = 5[ppm]
Tri_Domain         = Fluorine19
Tri_Freq           = 372.50336686[MHz]
Tri_Offset         = 5[ppm]
Blanking           = 2[us]
Clipped            = FALSE
Scans              = 4
Total_Scans        = 4

Relaxation_Delay   = 2[s]
Recvr_Gain         = 56
Temp_Get           = 20[dC]
X_90_Width         = 8.6[us]
X_Acq_Time         = 86.50752[ms]
X_Angle            = 45[deg]
X_Atn              = 5[dB]
X_Pulse            = 4.3[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    = 2.08650752[s]
```

Figure S38. ^{19}F NMR spectrum of **2n** (372 MHz, CDCl$_3$).



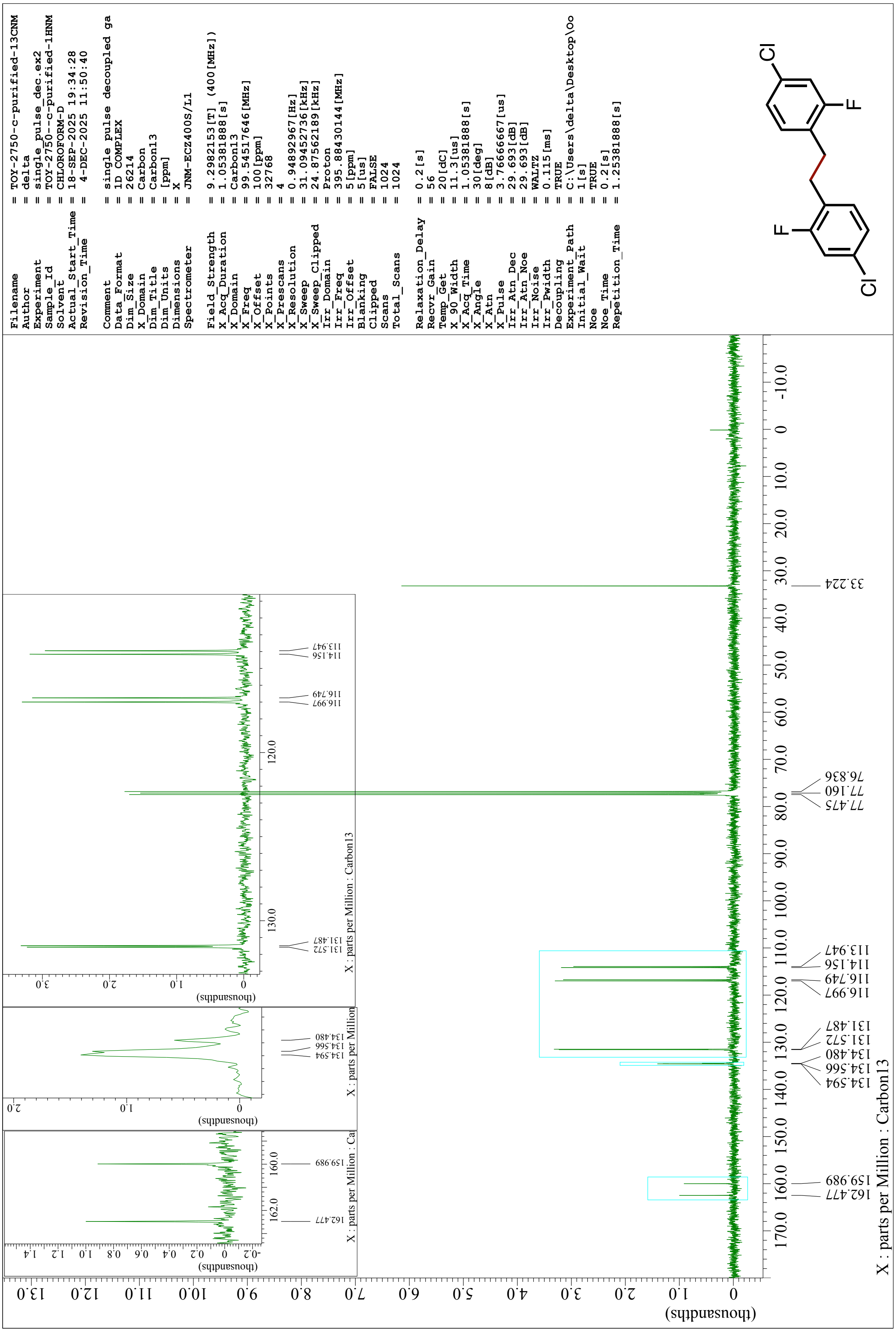
```
Filename             = TOY-2750-c-purified-1HNMR
Author               = delta
Experiment           = single_pulse.ex2
Sample_Id            = TOY-2750--c-purified-1HNM
Solvent              = CHLOROFORM-D
Actual_Start_Time    = 18-SEP-2025 23:28:43
Revision_Time        = 13-OCT-2025 17:58:43

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                = 4
Total_Scans          = 4

Relaxation_Delay     = 2[s]
Recvr_Gain           = 56
Temp_Get             = 20.7[dC]
X_90_Width           = 6.7[us]
X_Acq_Time           = 2.20725248[s]
X_Angle              = 45[deg]
X_Atn                = 5[dB]
X_Pulse              = 3.35[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      = 4.20725248[s]
```

Figure S39. ^{1}H NMR spectrum of **2o** (400 MHz, $CDCl_3$).



```
Filename             = TOY-2750-c-purified-13CNM
Author               = delta
Experiment           = single_pulse_dec.ex2
Sample_Id            = TOY-2750--c-purified-1HNM
Solvent              = CHLOROFORM-D
Actual_Start_Time    = 18-SEP-2025 19:34:28
Revision_Time        =   4-DEC-2025 11:50:40

Comment              = single pulse decoupled ga
Data_Format          = 1D COMPLEX
Dim_Size             = 26214
X_Domain             = Carbon
Dim_Title            = Carbon13
Dim_Units            = [ppm]
Dimensions           = X
Spectrometer         = JNM-ECZ400S/L1

Field_Strength       = 9.2982153[T] (400[MHz])
X_Acq_Duration       = 1.05381888[s]
X_Domain             = Carbon13
X_Freq               = 99.54517646[MHz]
X_Offset             = 100[ppm]
X_Points             = 32768
X_Prescans           = 4
X_Resolution         = 0.94892967[Hz]
X_Sweep              = 31.09452736[kHz]
X_Sweep_Clipped      = 24.87562189[kHz]
Irr_Domain           = Proton
Irr_Freq             = 395.88430144[MHz]
Irr_Offset           = 5[ppm]
Blanking             = 5[us]
Clipped              = FALSE
Scans                = 1024
Total_Scans          = 1024

Relaxation_Delay     = 0.2[s]
Recvr_Gain           = 56
Temp_Get             = 20[dC]
X_90_Width           = 11.3[us]
X_Acq_Time           = 1.05381888[s]
X_Angle              = 30[deg]
X_Atn                = 8[dB]
X_Pulse              = 3.76666667[us]
Irr_Atn_Dec          = 29.693[dB]
Irr_Atn_Noe          = 29.693[dB]
Irr_Noise            = WALTZ
Irr_Pwidth           = 0.115[ms]
Decoupling           = TRUE
Experiment_Path      = C:\Users\delta\Desktop\Oo
Initial_Wait         = 1[s]
Noe                  = TRUE
Noe_Time             = 0.2[s]
Repetition_Time      = 1.25381888[s]
```

Figure S40. ^{13}C NMR spectrum of **2o** (100 MHz, $CDCl_3$).

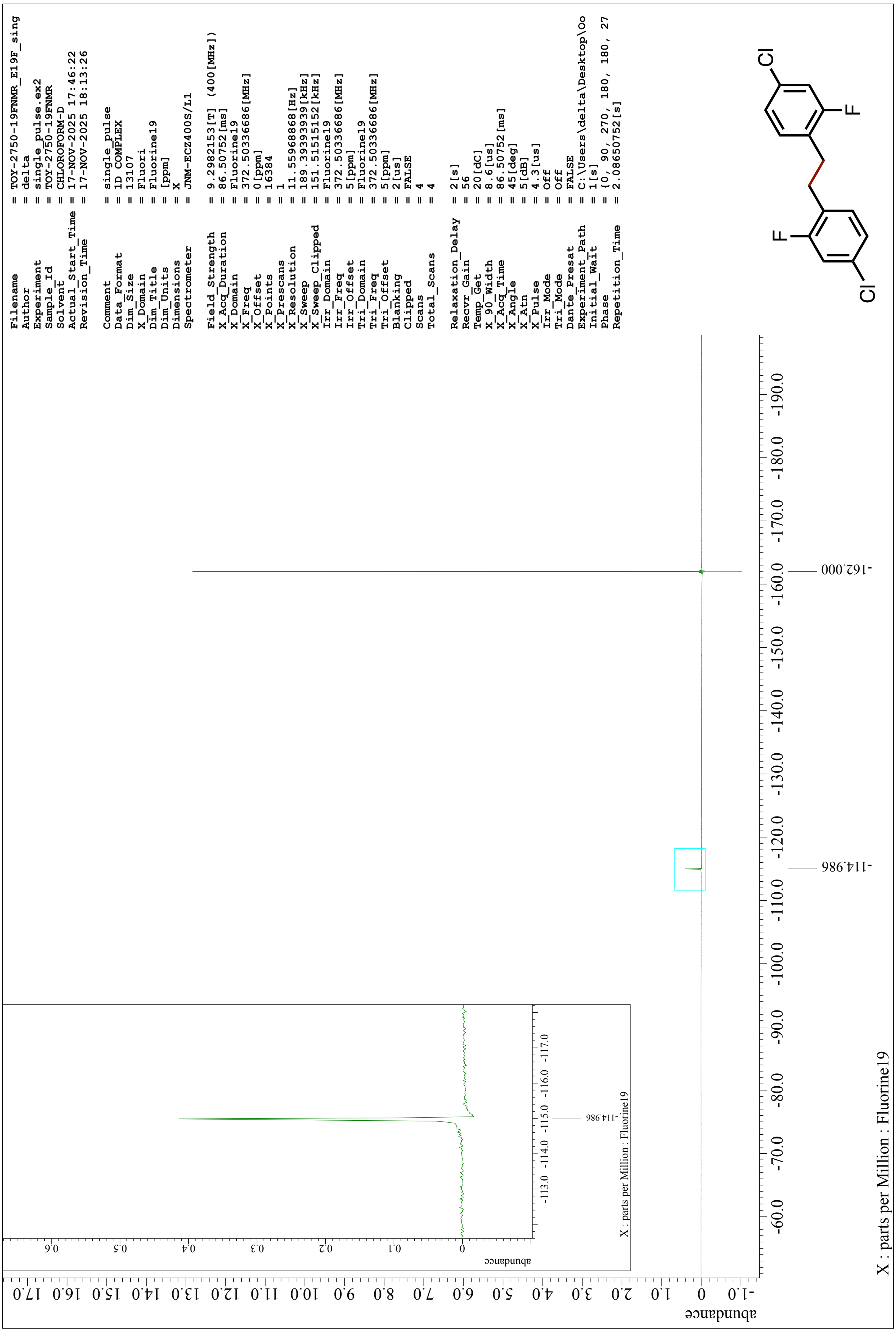
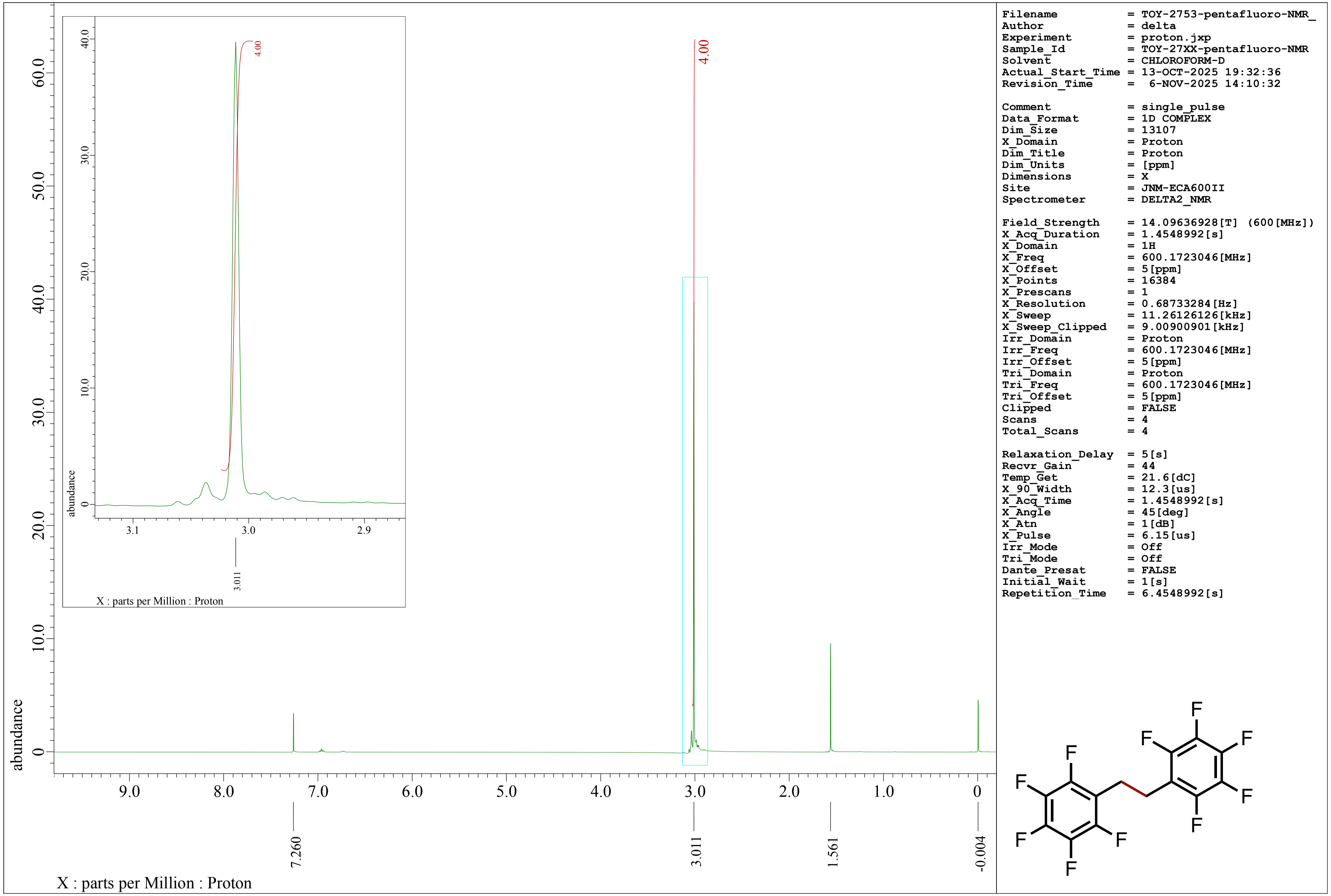


Figure S41. ^{19}F NMR spectrum of **2o** (372 MHz, CDCl$_3$).



```
Filename           = TOY-2753-pentafluoro-NMR_
Author             = delta
Experiment         = proton.jxp
Sample_Id          = TOY-27XX-pentafluoro-NMR
Solvent            = CHLOROFORM-D
Actual_Start_Time  = 13-OCT-2025 19:32:36
Revision_Time      =  6-NOV-2025 14:10:32

Comment            = single_pulse
Data_Format        = 1D COMPLEX
Dim_Size           = 13107
X_Domain           = Proton
Dim_Title          = Proton
Dim_Units          = [ppm]
Dimensions         = X
Site               = JNM-ECA600II
Spectrometer       = DELTA2_NMR

Field_Strength     = 14.09636928[T] (600[MHz])
X_Acq_Duration     = 1.4548992[s]
X_Domain           = 1H
X_Freq             = 600.1723046[MHz]
X_Offset           = 5[ppm]
X_Points           = 16384
X_Prescans         = 1
X_Resolution       = 0.68733284[Hz]
X_Sweep            = 11.26126126[kHz]
X_Sweep_Clipped    = 9.00900901[kHz]
Irr_Domain         = Proton
Irr_Freq           = 600.1723046[MHz]
Irr_Offset         = 5[ppm]
Tri_Domain         = Proton
Tri_Freq           = 600.1723046[MHz]
Tri_Offset         = 5[ppm]
Clipped            = FALSE
Scans              = 4
Total_Scans        = 4

Relaxation_Delay   = 5[s]
Recvr_Gain         = 44
Temp_Get           = 21.6[dC]
X_90_Width         = 12.3[us]
X_Acq_Time         = 1.4548992[s]
X_Angle            = 45[deg]
X_Atn              = 1[dB]
X_Pulse            = 6.15[us]
Irr_Mode           = Off
Tri_Mode           = Off
Dante_Presat       = FALSE
Initial_Wait       = 1[s]
Repetition_Time    = 6.4548992[s]
```

Figure S42. ^{1}H NMR spectrum of **2p** (600 MHz, $CDCl_3$).

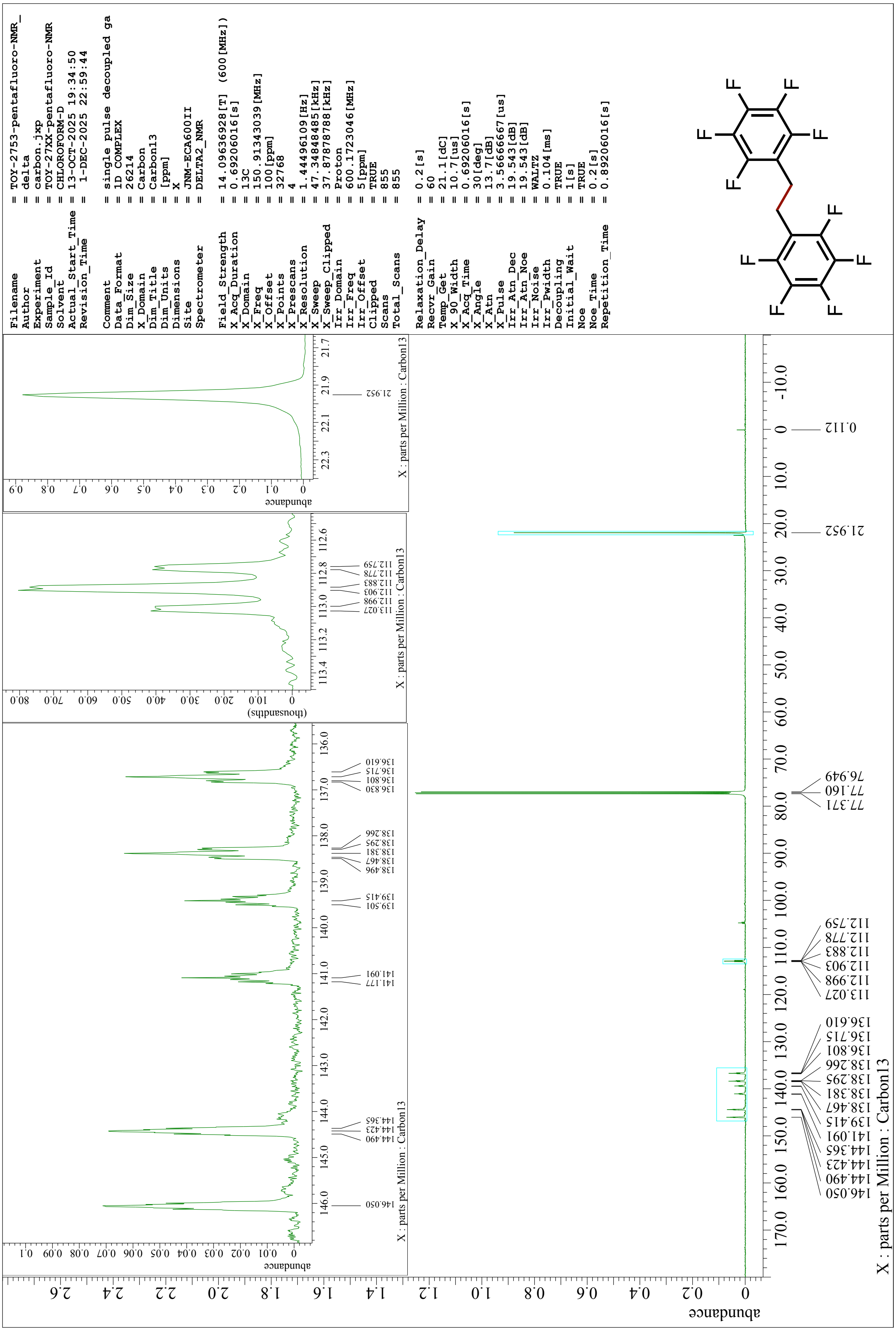
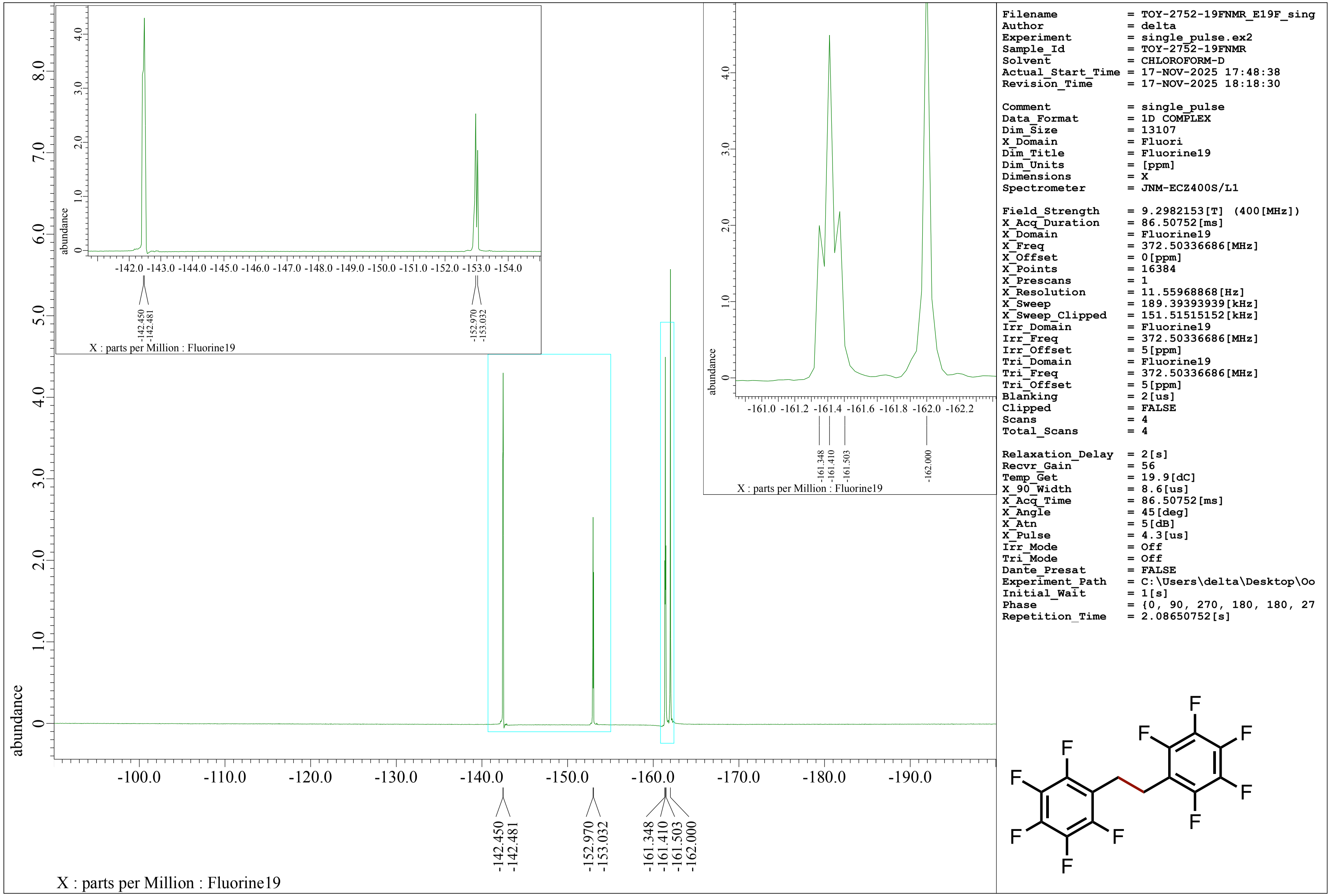


Figure S43. ^{13}C NMR spectrum of **2p** (100 MHz, CDCl$_3$).



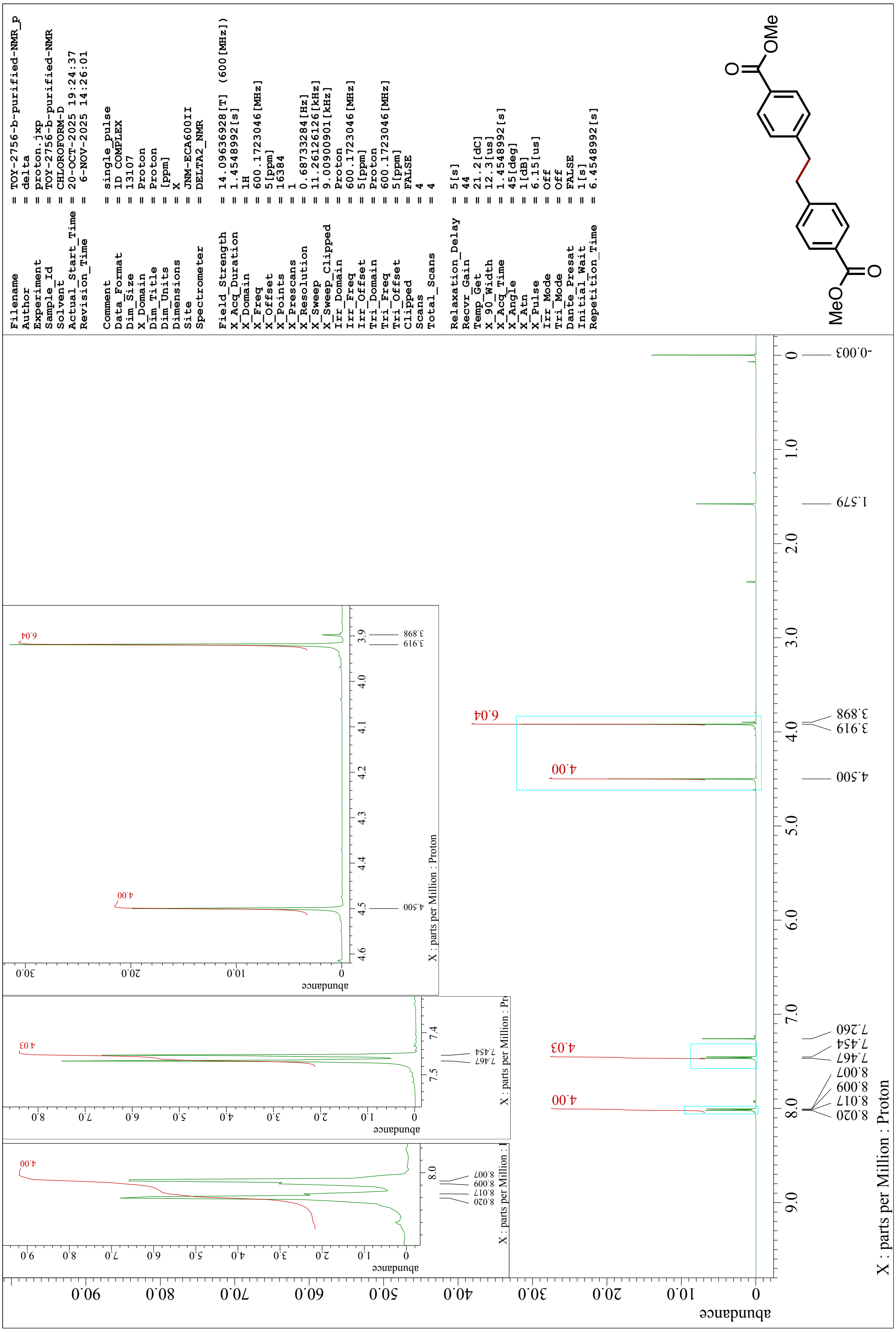
```
Filename             = TOY-2752-19FNMR_E19F_sing
Author               = delta
Experiment           = single_pulse.ex2
Sample_Id            = TOY-2752-19FNMR
Solvent              = CHLOROFORM-D
Actual_Start_Time    = 17-NOV-2025 17:48:38
Revision_Time        = 17-NOV-2025 18:18:30

Comment              = single_pulse
Data_Format          = 1D COMPLEX
Dim_Size             = 13107
X_Domain             = Fluori
Dim_Title            = Fluorine19
Dim_Units            = [ppm]
Dimensions           = X
Spectrometer         = JNM-ECZ400S/L1

Field_Strength       = 9.2982153[T] (400[MHz])
X_Acq_Duration       = 86.50752[ms]
X_Domain             = Fluorine19
X_Freq               = 372.50336686[MHz]
X_Offset             = 0[ppm]
X_Points             = 16384
X_Prescans           = 1
X_Resolution         = 11.55968868[Hz]
X_Sweep              = 189.39393939[kHz]
X_Sweep_Clipped      = 151.51515152[kHz]
Irr_Domain           = Fluorine19
Irr_Freq             = 372.50336686[MHz]
Irr_Offset           = 5[ppm]
Tri_Domain           = Fluorine19
Tri_Freq             = 372.50336686[MHz]
Tri_Offset           = 5[ppm]
Blanking             = 2[us]
Clipped              = FALSE
Scans                = 4
Total_Scans          = 4

Relaxation_Delay     = 2[s]
Recvr_Gain           = 56
Temp_Get             = 19.9[dC]
X_90_Width           = 8.6[us]
X_Acq_Time           = 86.50752[ms]
X_Angle              = 45[deg]
X_Atn                = 5[dB]
X_Pulse              = 4.3[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      = 2.08650752[s]
```

Figure S44. ^{19}F NMR spectrum of **2p** (372 MHz, $CDCl_3$).



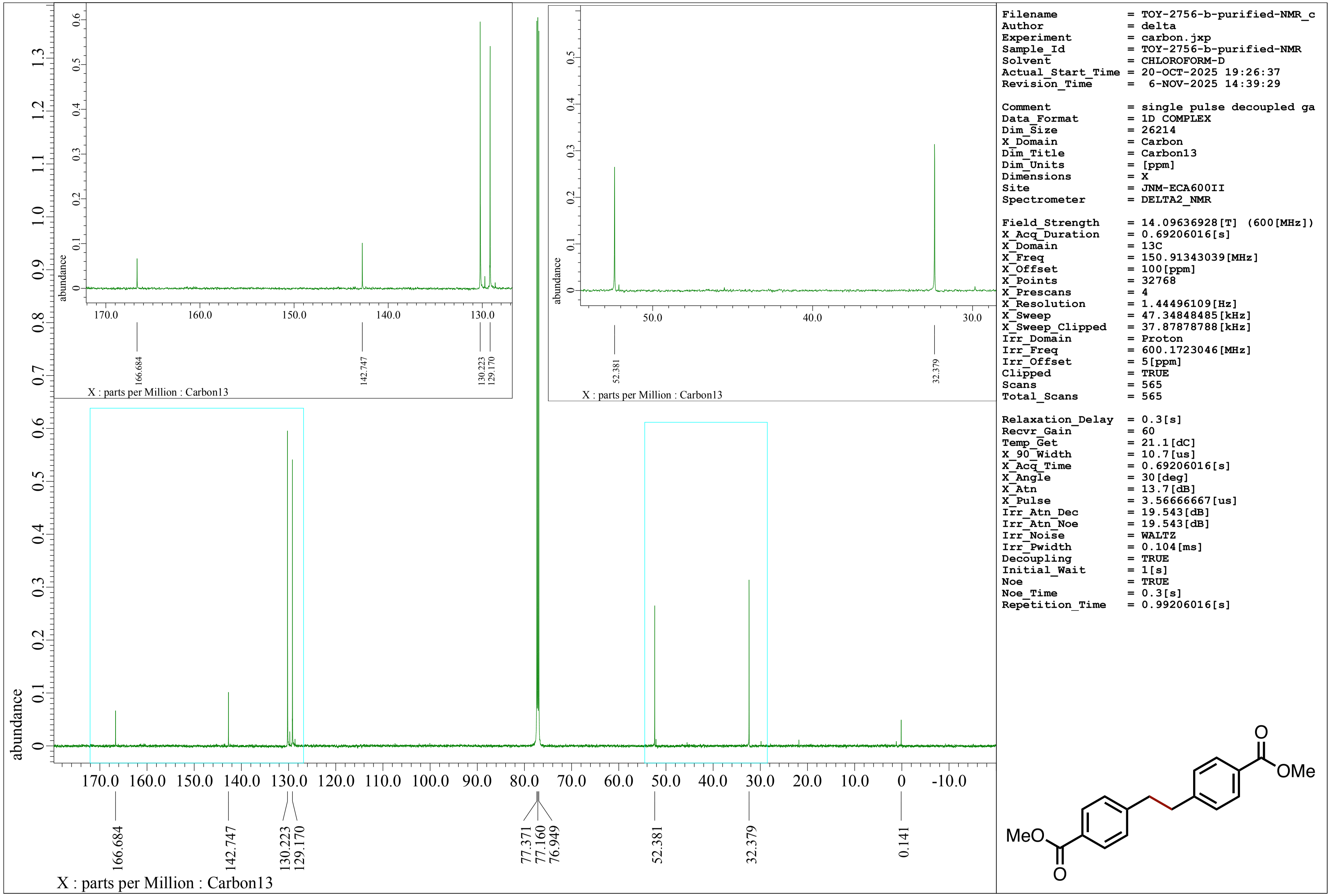
```
Filename            = TOY-2756-b-purified-NMR_p
Author              = delta
Experiment          = proton.jxp
Sample_Id           = TOY-2756-b-purified-NMR
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 20-OCT-2025 19:24:37
Revision_Time       = 6-NOV-2025 14:26:01

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 13107
X_Domain            = Proton
Dim_Title           = Proton
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECA600II
Spectrometer        = DELTA2_NMR

Field_Strength      = 14.09636928[T] (600[MHz])
X_Acq_Duration      = 1.4548992[s]
X_Domain            = 1H
X_Freq              = 600.1723046[MHz]
X_Offset            = 5[ppm]
X_Points            = 16384
X_Prescans          = 1
X_Resolution        = 0.68733284[Hz]
X_Sweep             = 11.26126126[kHz]
X_Sweep_Clipped     = 9.00900901[kHz]
Irr_Domain          = Proton
Irr_Freq            = 600.1723046[MHz]
Irr_Offset          = 5[ppm]
Tri_Domain          = Proton
Tri_Freq            = 600.1723046[MHz]
Tri_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 4
Total_Scans         = 4

Relaxation_Delay    = 5[s]
Recvr_Gain          = 44
Temp_Get            = 21.2[dC]
X_90_Width          = 12.3[us]
X_Acq_Time          = 1.4548992[s]
X_Angle             = 45[deg]
X_Atn               = 1[dB]
X_Pulse             = 6.15[us]
Irr_Mode            = Off
Tri_Mode            = Off
Dante_Presat        = FALSE
Initial_Wait        = 1[s]
Repetition_Time     = 6.4548992[s]
```

Figure S45. ^{1}H NMR spectrum of **2r** (600 MHz, CDCl$_3$).



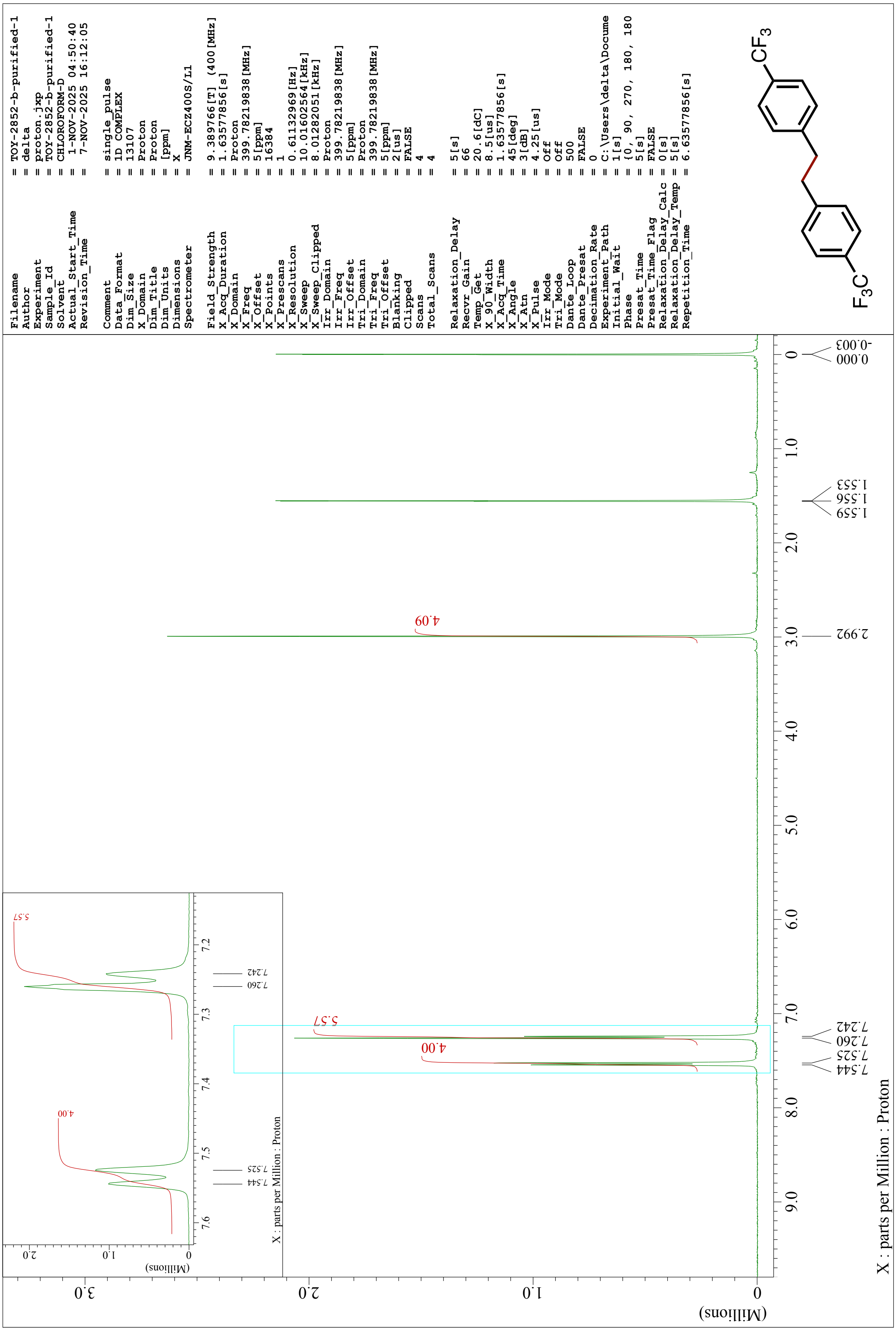
```
Filename           = TOY-2756-b-purified-NMR_c
Author             = delta
Experiment         = carbon.jxp
Sample_Id          = TOY-2756-b-purified-NMR
Solvent            = CHLOROFORM-D
Actual_Start_Time  = 20-OCT-2025 19:26:37
Revision_Time      =  6-NOV-2025 14:39:29

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              = 565
Total_Scans        = 565

Relaxation_Delay   = 0.3[s]
Recvr_Gain         = 60
Temp_Get           = 21.1[dC]
X_90_Width         = 10.7[us]
X_Acq_Time         = 0.69206016[s]
X_Angle            = 30[deg]
X_Atn              = 13.7[dB]
X_Pulse            = 3.56666667[us]
Irr_Atn_Dec        = 19.543[dB]
Irr_Atn_Noe        = 19.543[dB]
Irr_Noise          = WALTZ
Irr_Pwidth         = 0.104[ms]
Decoupling         = TRUE
Initial_Wait       = 1[s]
Noe                = TRUE
Noe_Time           = 0.3[s]
Repetition_Time    = 0.99206016[s]
```

Figure S46. ^{13}C NMR spectrum of **2r** (150 MHz, $CDCl_3$).



```
Filename               = TOY-2852-b-purified-1
Author                 = delta
Experiment             = proton.jxp
Sample_Id              = TOY-2852-b-purified-1
Solvent                = CHLOROFORM-D
Actual_Start_Time      =  1-NOV-2025 04:50:40
Revision_Time          =  7-NOV-2025 16:12:05

Comment                = single_pulse
Data_Format            = 1D COMPLEX
Dim_Size               = 13107
X_Domain               = Proton
Dim_Title              = Proton
Dim_Units              = [ppm]
Dimensions             = X
Spectrometer           = JNM-ECZ400S/L1

Field_Strength         = 9.389766[T] (400[MHz]
X_Acq_Duration         = 1.63577856[s]
X_Domain               = Proton
X_Freq                 = 399.78219838[MHz]
X_Offset               = 5[ppm]
X_Points               = 16384
X_Prescans             = 1
X_Resolution           = 0.61132969[Hz]
X_Sweep                = 10.01602564[kHz]
X_Sweep_Clipped        = 8.01282051[kHz]
Irr_Domain             = Proton
Irr_Freq               = 399.78219838[MHz]
Irr_Offset             = 5[ppm]
Tri_Domain             = Proton
Tri_Freq               = 399.78219838[MHz]
Tri_Offset             = 5[ppm]
Blanking               = 2[us]
Clipped                = FALSE
Scans                  = 4
Total_Scans            = 4

Relaxation_Delay       = 5[s]
Recvr_Gain             = 66
Temp_Get               = 20.6[dC]
X_90_Width             = 8.5[us]
X_Acq_Time             = 1.63577856[s]
X_Angle                = 45[deg]
X_Atn                  = 3[dB]
X_Pulse                = 4.25[us]
Irr_Mode               = Off
Tri_Mode               = Off
Dante_Loop             = 500
Dante_Presat           = FALSE
Decimation_Rate        = 0
Experiment_Path        = C:\Users\delta\Docume
Initial_Wait           = 1[s]
Phase                  = {0, 90, 270, 180, 180
Presat_Time            = 5[s]
Presat_Time_Flag       = FALSE
Relaxation_Delay_Calc  = 0[s]
Relaxation_Delay_Temp  = 5[s]
Repetition_Time        = 6.63577856[s]
```

Figure S47. ^{1}H NMR spectrum of **2s** (600 MHz, $CDCl_3$).

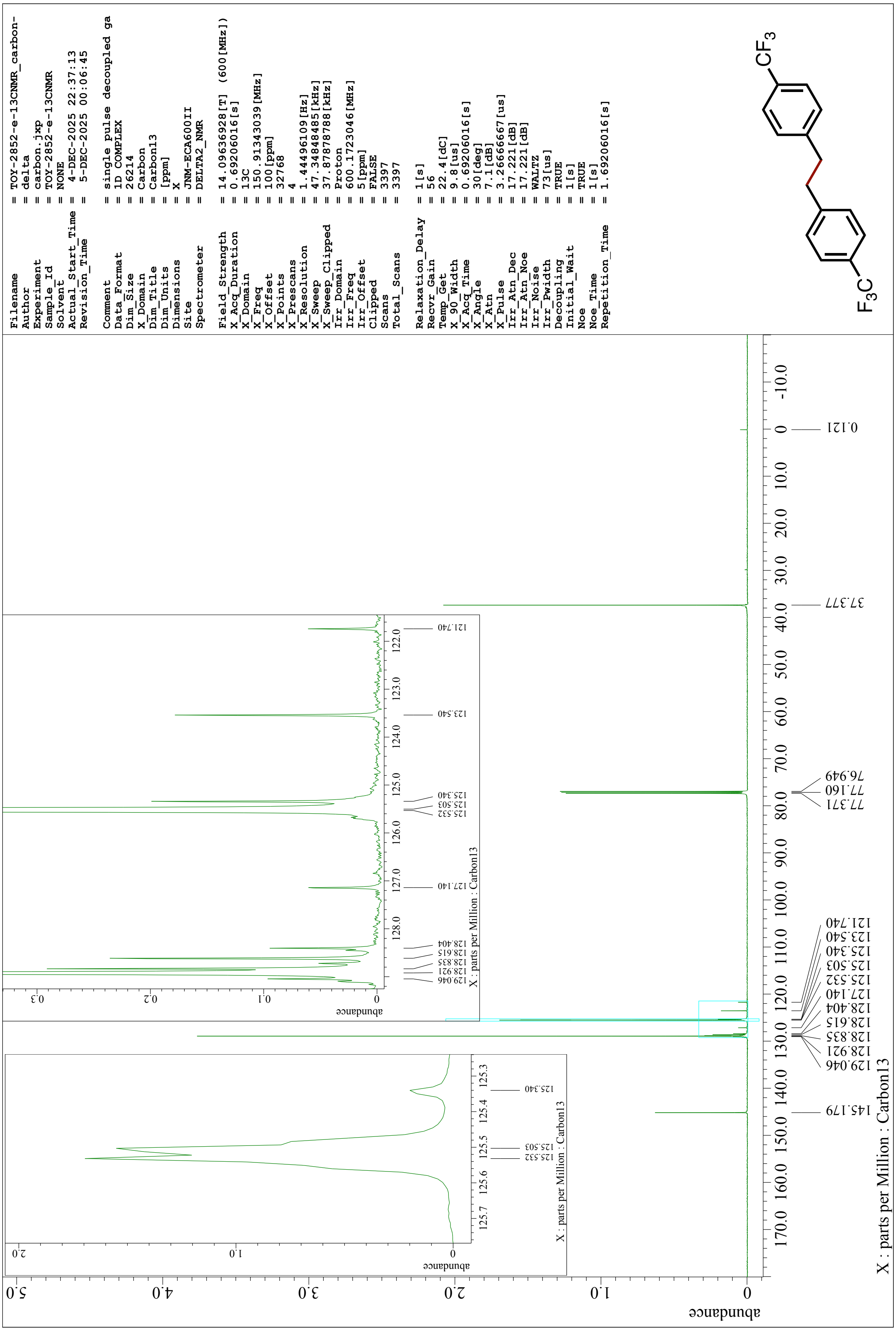
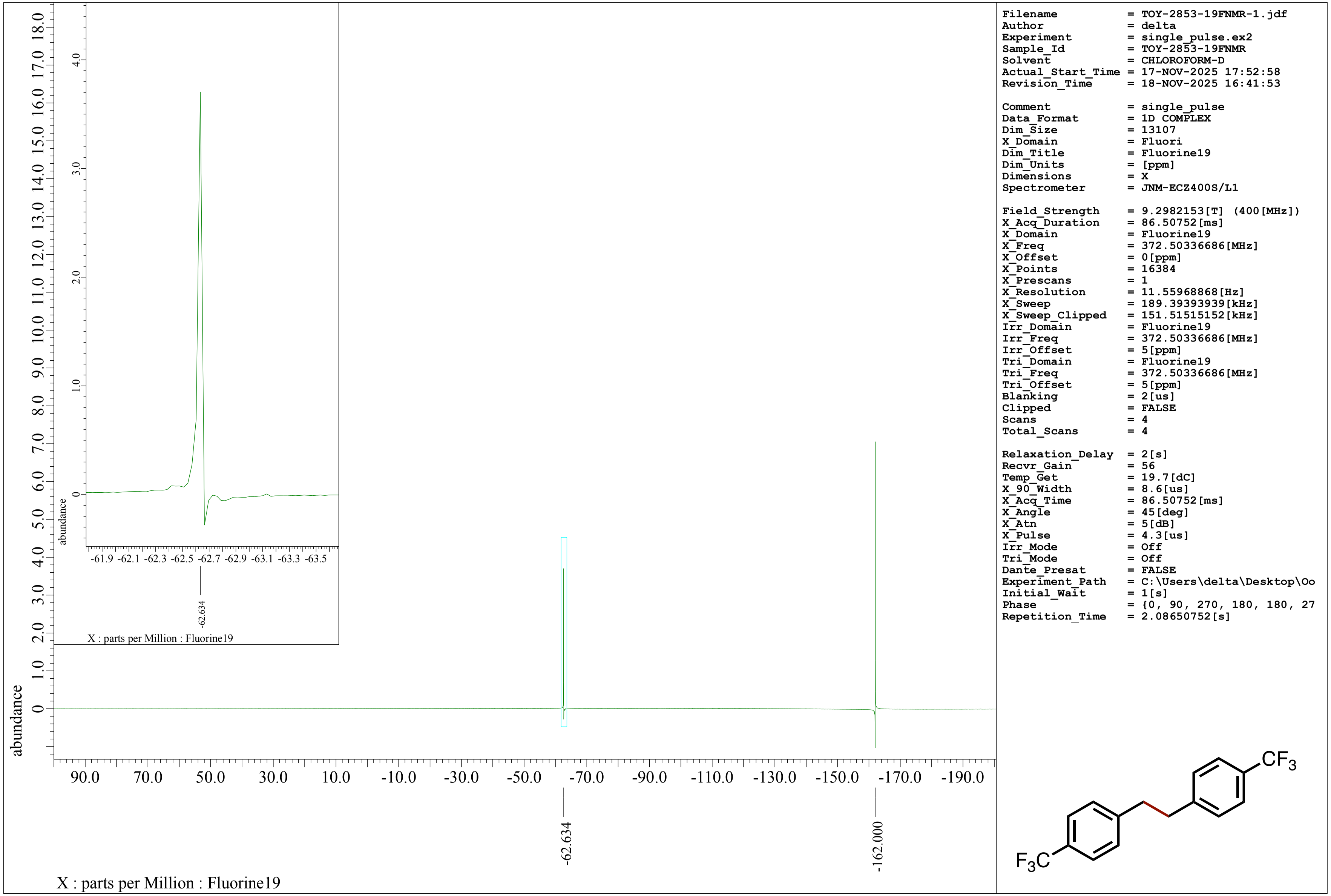


Figure S48. ^{13}C NMR spectrum of **2s** (150 MHz, $CDCl_3$).



```
Filename           = TOY-2853-19FNMR-1.jdf
Author             = delta
Experiment         = single_pulse.ex2
Sample_Id          = TOY-2853-19FNMR
Solvent            = CHLOROFORM-D
Actual_Start_Time  = 17-NOV-2025 17:52:58
Revision_Time      = 18-NOV-2025 16:41:53

Comment            = single_pulse
Data_Format        = 1D COMPLEX
Dim_Size           = 13107
X_Domain           = Fluori
Dim_Title          = Fluorine19
Dim_Units          = [ppm]
Dimensions         = X
Spectrometer       = JNM-ECZ400S/L1

Field_Strength     = 9.2982153[T] (400[MHz])
X_Acq_Duration     = 86.50752[ms]
X_Domain           = Fluorine19
X_Freq             = 372.50336686[MHz]
X_Offset           = 0[ppm]
X_Points           = 16384
X_Prescans         = 1
X_Resolution       = 11.55968868[Hz]
X_Sweep            = 189.39393939[kHz]
X_Sweep_Clipped    = 151.51515152[kHz]
Irr_Domain         = Fluorine19
Irr_Freq           = 372.50336686[MHz]
Irr_Offset         = 5[ppm]
Tri_Domain         = Fluorine19
Tri_Freq           = 372.50336686[MHz]
Tri_Offset         = 5[ppm]
Blanking           = 2[us]
Clipped            = FALSE
Scans              = 4
Total_Scans        = 4

Relaxation_Delay   = 2[s]
Recvr_Gain         = 56
Temp_Get           = 19.7[dC]
X_90_Width         = 8.6[us]
X_Acq_Time         = 86.50752[ms]
X_Angle            = 45[deg]
X_Atn              = 5[dB]
X_Pulse            = 4.3[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    = 2.08650752[s]
```

Figure S49. ^{19}F NMR spectrum of **2s** (372 MHz, $CDCl_3$).

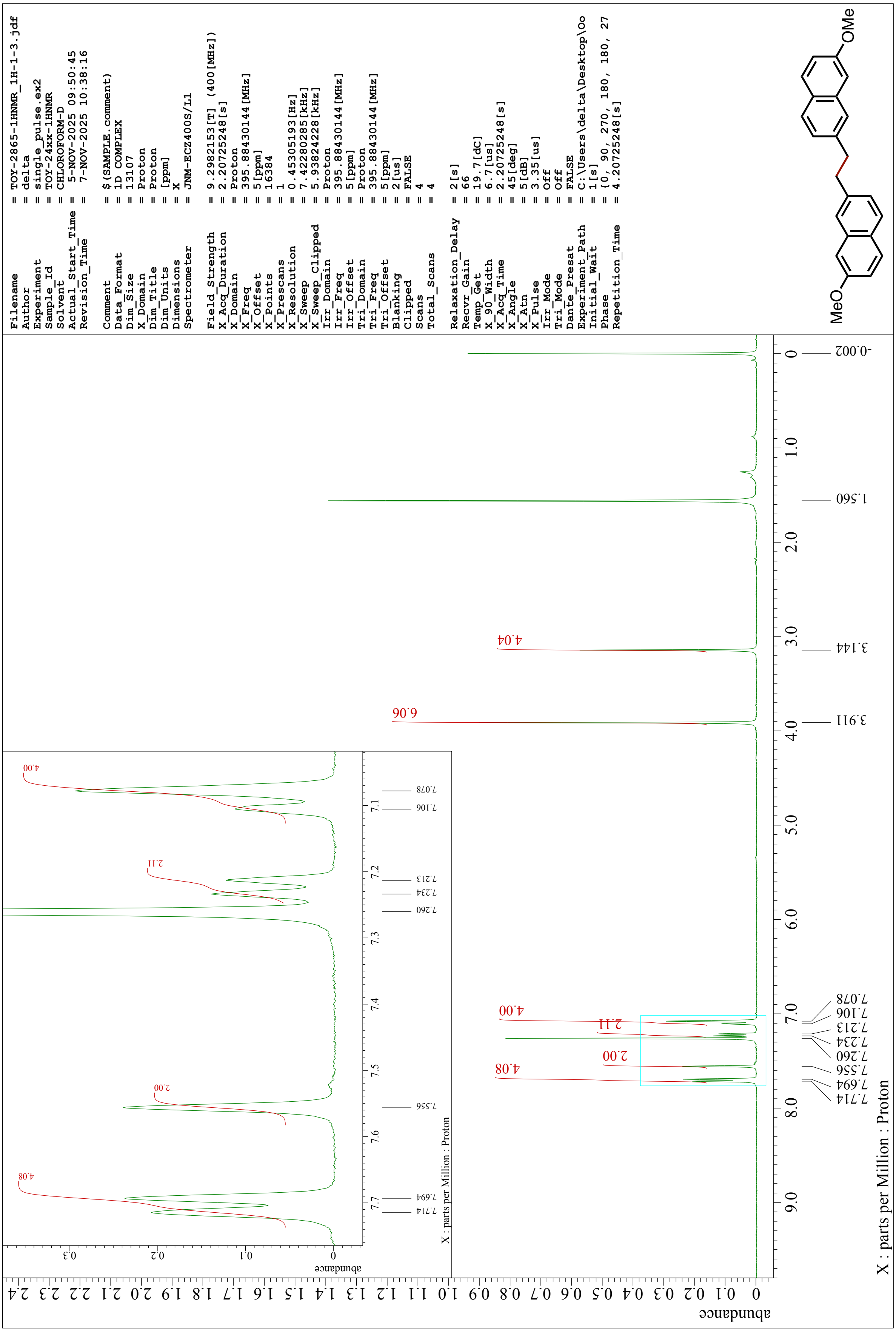


Figure S50. ^{1}H NMR spectrum of **2t** (400 MHz, $CDCl_3$).

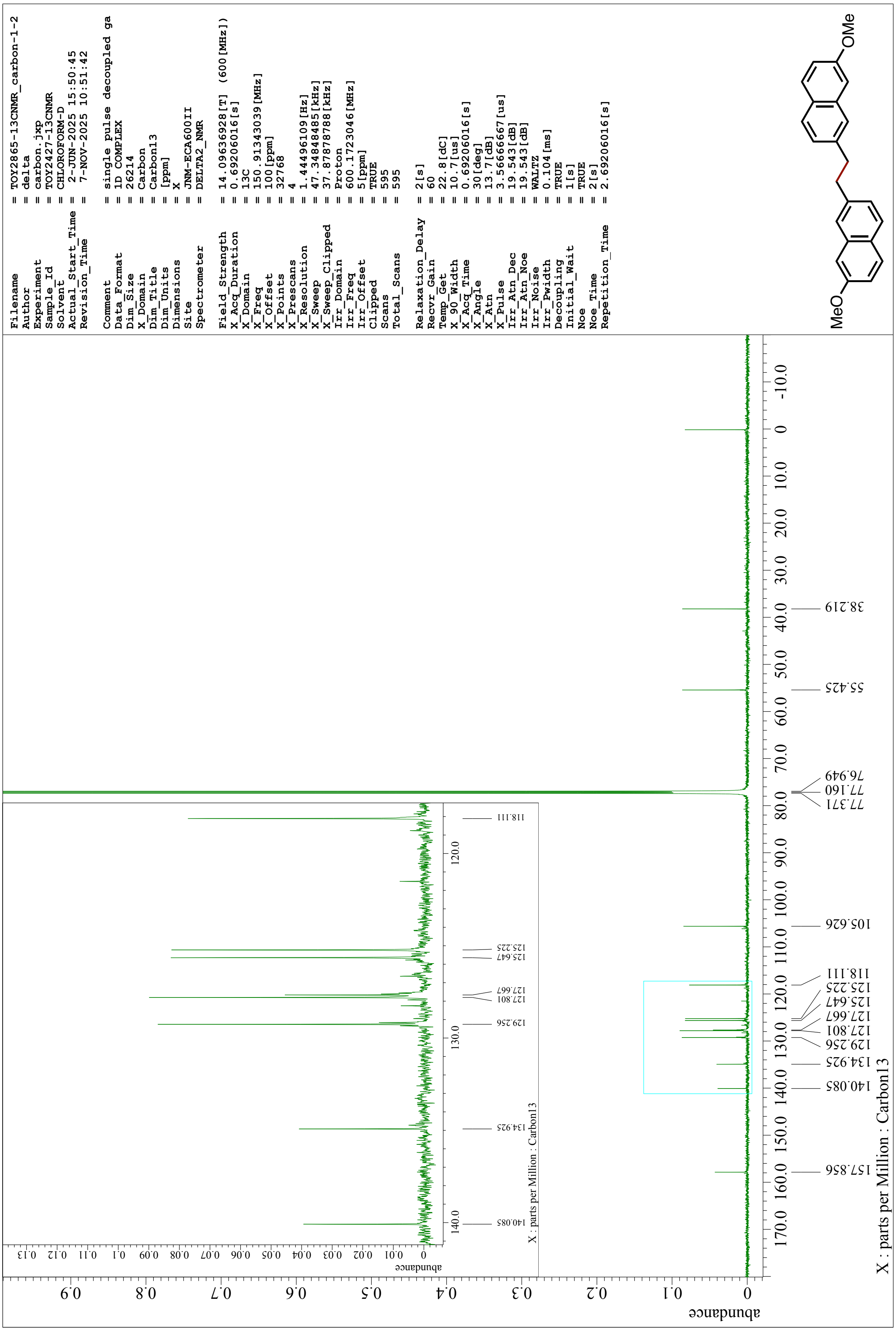
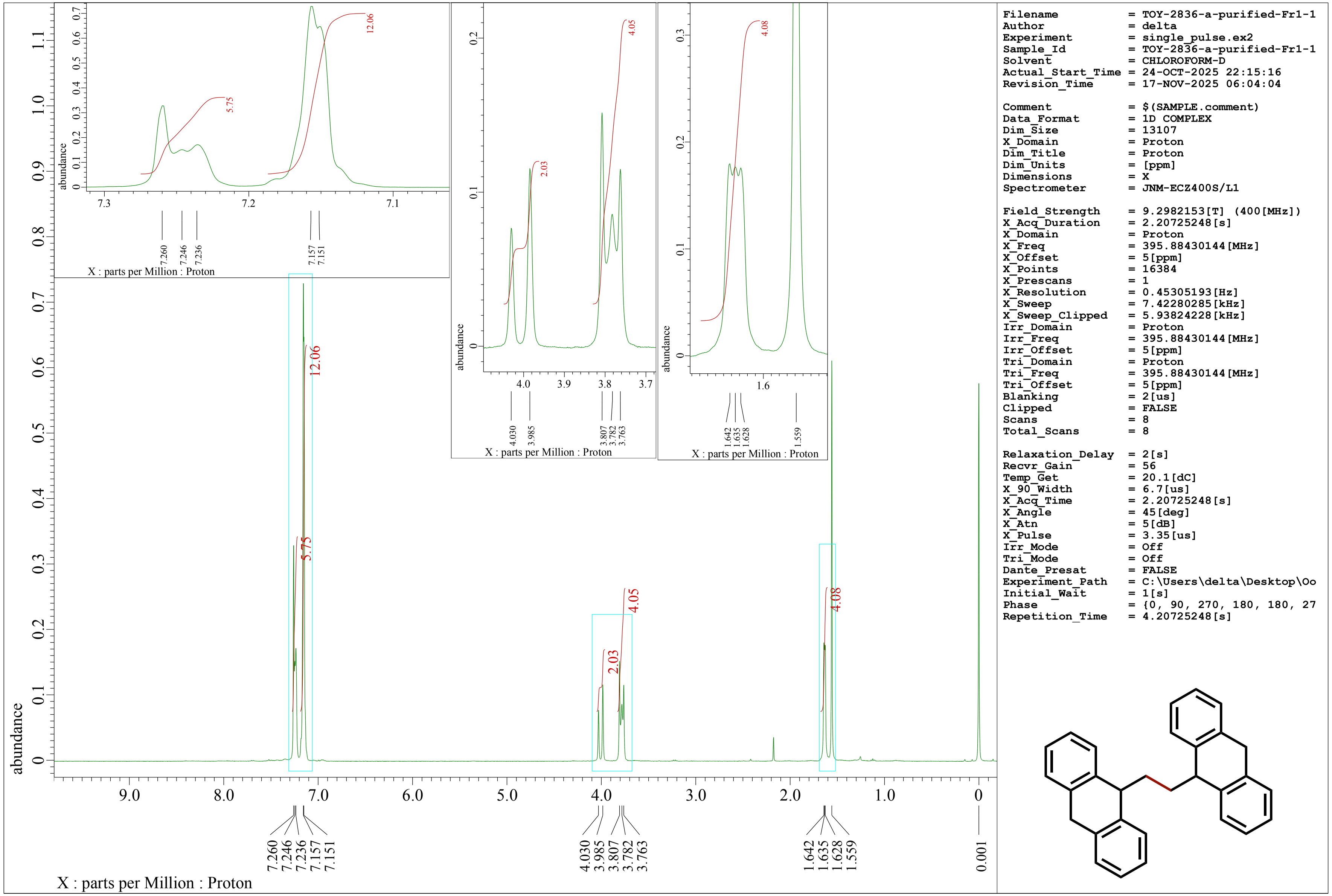


Figure S51. ^{13}C NMR spectrum of **2t** (150 MHz, $CDCl_3$).



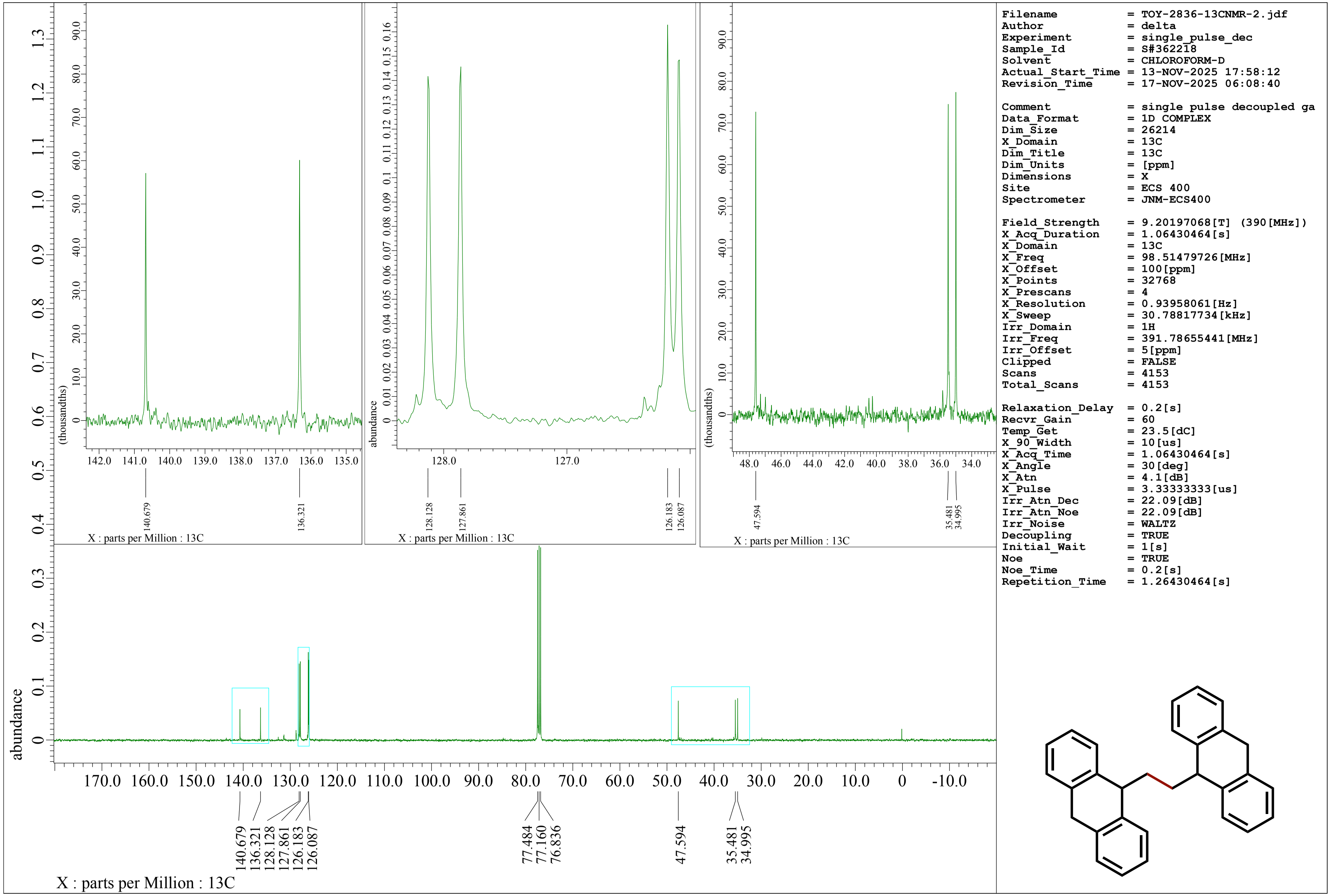
```
Filename           = TOY-2836-a-purified-Fr1-1
Author             = delta
Experiment         = single_pulse.ex2
Sample_Id          = TOY-2836-a-purified-Fr1-1
Solvent            = CHLOROFORM-D
Actual_Start_Time  = 24-OCT-2025 22:15:16
Revision_Time      = 17-NOV-2025 06:04:04

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              = 8
Total_Scans        = 8

Relaxation_Delay   = 2[s]
Recvr_Gain         = 56
Temp_Get           = 20.1[dC]
X_90_Width         = 6.7[us]
X_Acq_Time         = 2.20725248[s]
X_Angle            = 45[deg]
X_Atn              = 5[dB]
X_Pulse            = 3.35[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    = 4.20725248[s]
```

Figure S52. ^{1}H NMR spectrum of **2u** (400 MHz, $CDCl_3$).



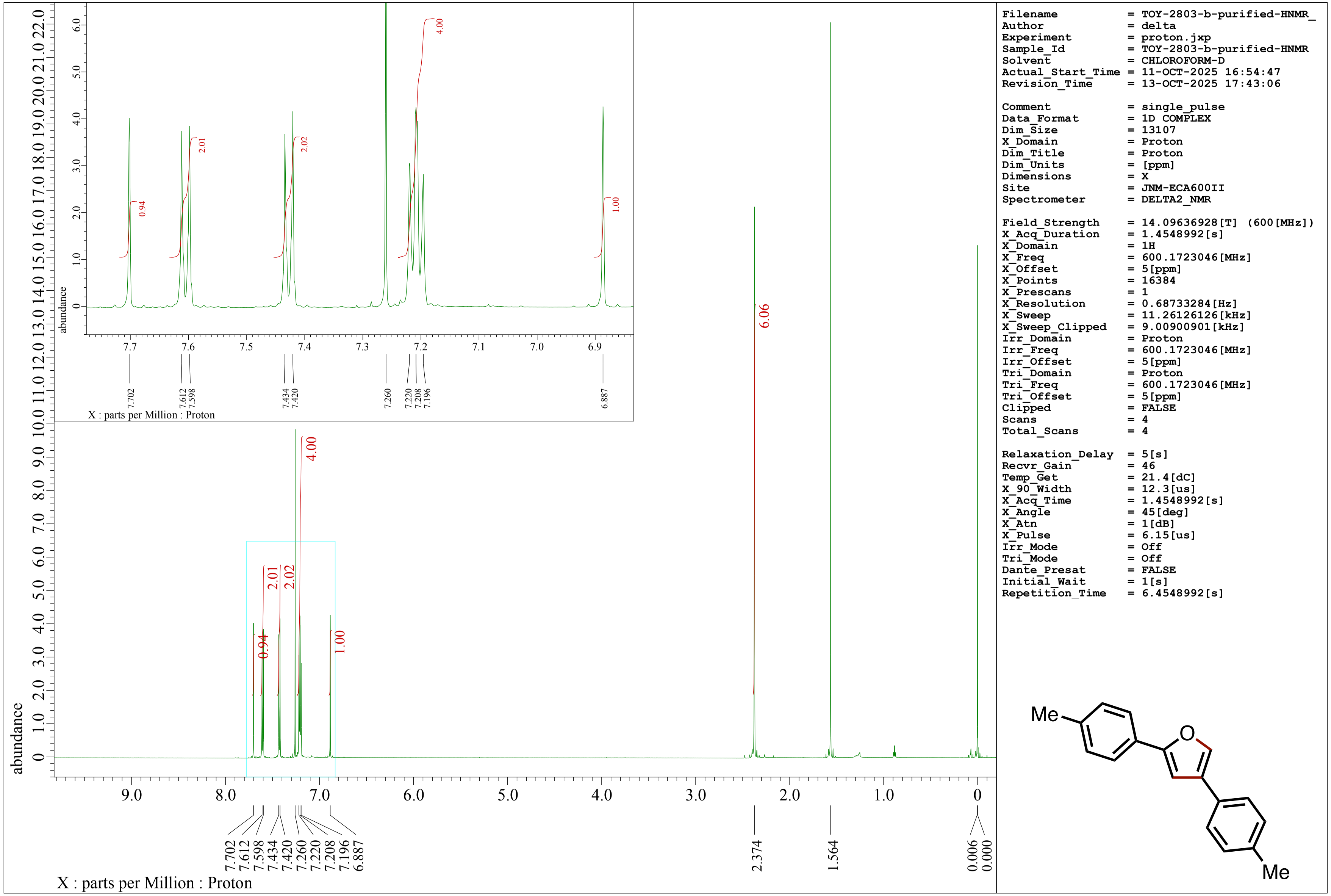
```
Filename             = TOY-2836-13CNMR-2.jdf
Author               = delta
Experiment           = single_pulse_dec
Sample_Id            = S#362218
Solvent              = CHLOROFORM-D
Actual_Start_Time    = 13-NOV-2025 17:58:12
Revision_Time        = 17-NOV-2025 06:08:40

Comment              = single pulse decoupled ga
Data_Format          = 1D COMPLEX
Dim_Size             = 26214
X_Domain             = 13C
Dim_Title            = 13C
Dim_Units            = [ppm]
Dimensions           = X
Site                 = ECS 400
Spectrometer         = JNM-ECS400

Field_Strength       = 9.20197068[T] (390[MHz])
X_Acq_Duration       = 1.06430464[s]
X_Domain             = 13C
X_Freq               = 98.51479726[MHz]
X_Offset             = 100[ppm]
X_Points             = 32768
X_Prescans           = 4
X_Resolution         = 0.93958061[Hz]
X_Sweep              = 30.78817734[kHz]
Irr_Domain           = 1H
Irr_Freq             = 391.78655441[MHz]
Irr_Offset           = 5[ppm]
Clipped              = FALSE
Scans                = 4153
Total_Scans          = 4153

Relaxation_Delay     = 0.2[s]
Recvr_Gain           = 60
Temp_Get             = 23.5[dC]
X_90_Width           = 10[us]
X_Acq_Time           = 1.06430464[s]
X_Angle              = 30[deg]
X_Atn                = 4.1[dB]
X_Pulse              = 3.33333333[us]
Irr_Atn_Dec          = 22.09[dB]
Irr_Atn_Noe          = 22.09[dB]
Irr_Noise            = WALTZ
Decoupling           = TRUE
Initial_Wait         = 1[s]
Noe                  = TRUE
Noe_Time             = 0.2[s]
Repetition_Time      = 1.26430464[s]
```

Figure S53. ^{13}C NMR spectrum of **2u** (150 MHz, CDCl$_3$).



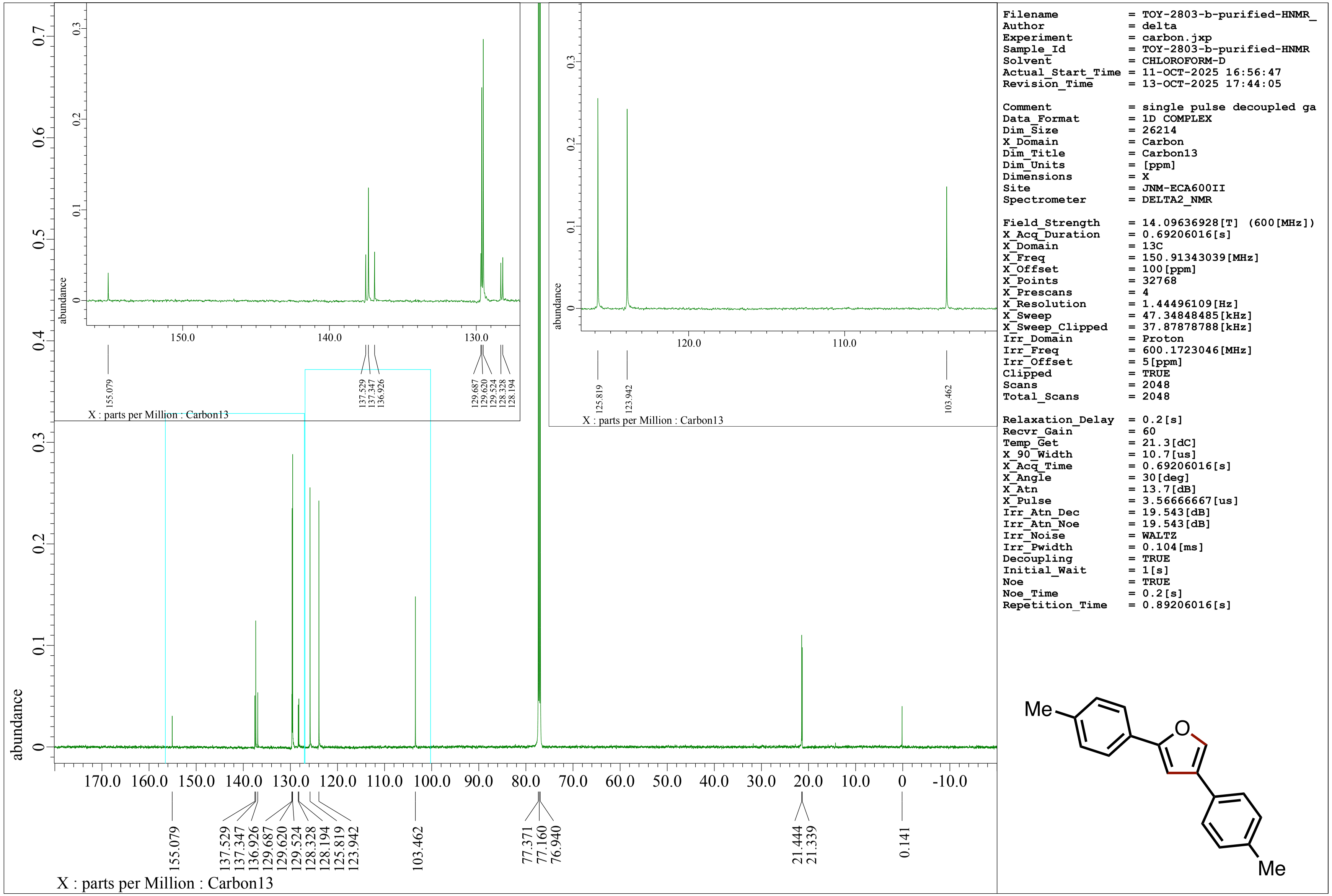
```
Filename            = TOY-2803-b-purified-HNMR_
Author              = delta
Experiment          = proton.jxp
Sample_Id           = TOY-2803-b-purified-HNMR
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 11-OCT-2025 16:54:47
Revision_Time       = 13-OCT-2025 17:43:06

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 13107
X_Domain            = Proton
Dim_Title           = Proton
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECA600II
Spectrometer        = DELTA2_NMR

Field_Strength      = 14.09636928[T] (600[MHz])
X_Acq_Duration      = 1.4548992[s]
X_Domain            = 1H
X_Freq              = 600.1723046[MHz]
X_Offset            = 5[ppm]
X_Points            = 16384
X_Prescans          = 1
X_Resolution        = 0.68733284[Hz]
X_Sweep             = 11.26126126[kHz]
X_Sweep_Clipped     = 9.00900901[kHz]
Irr_Domain          = Proton
Irr_Freq            = 600.1723046[MHz]
Irr_Offset          = 5[ppm]
Tri_Domain          = Proton
Tri_Freq            = 600.1723046[MHz]
Tri_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 4
Total_Scans         = 4

Relaxation_Delay    = 5[s]
Recvr_Gain          = 46
Temp_Get            = 21.4[dC]
X_90_Width          = 12.3[us]
X_Acq_Time          = 1.4548992[s]
X_Angle             = 45[deg]
X_Atn               = 1[dB]
X_Pulse             = 6.15[us]
Irr_Mode            = Off
Tri_Mode            = Off
Dante_Presat        = FALSE
Initial_Wait        = 1[s]
Repetition_Time     = 6.4548992[s]
```

Figure S54. ^{1}H NMR spectrum of **5a** (600 MHz, $CDCl_3$).



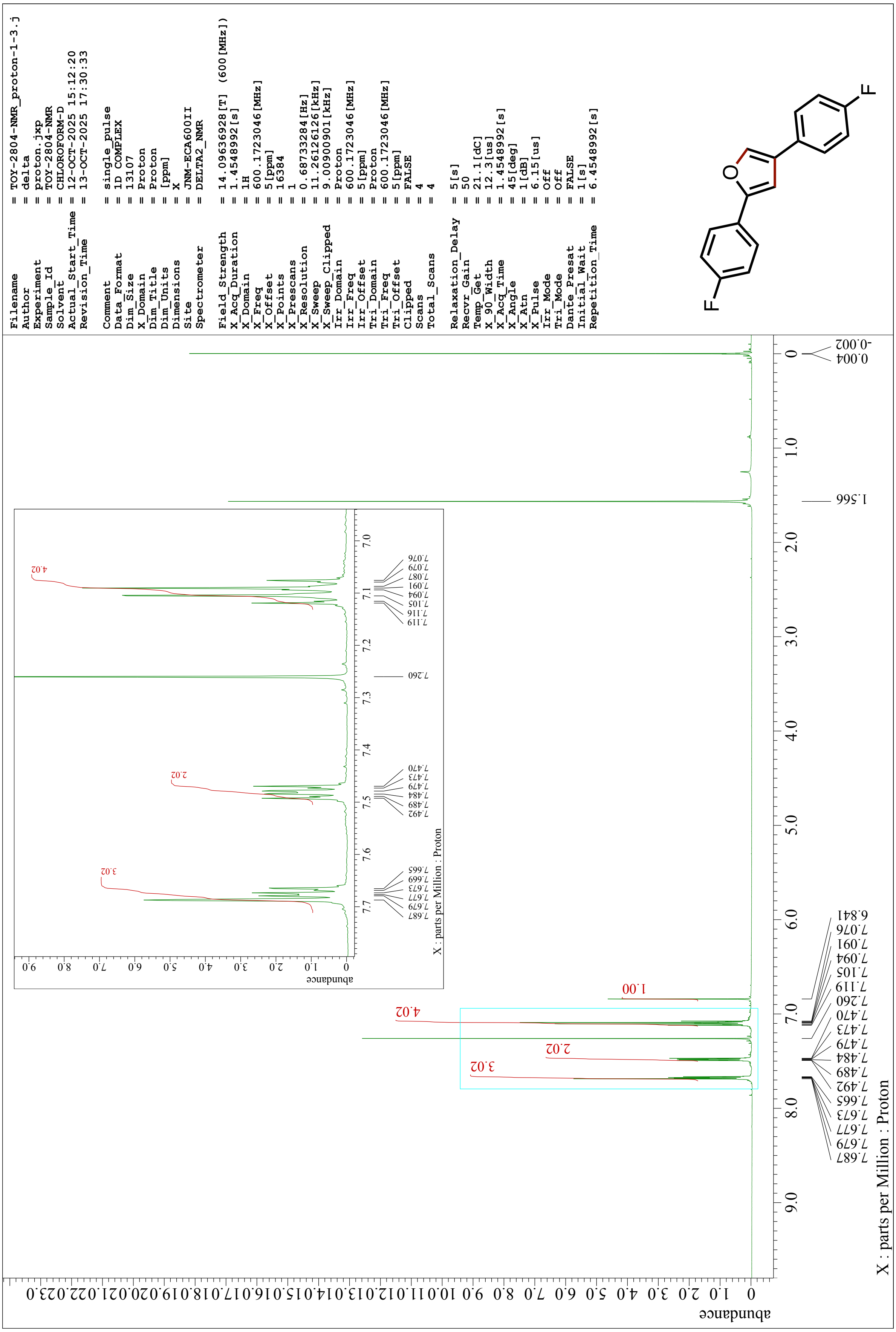
```
Filename            = TOY-2803-b-purified-HNMR_
Author              = delta
Experiment          = carbon.jxp
Sample_Id           = TOY-2803-b-purified-HNMR
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 11-OCT-2025 16:56:47
Revision_Time       = 13-OCT-2025 17:44:05

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               = 2048
Total_Scans         = 2048

Relaxation_Delay    = 0.2[s]
Recvr_Gain          = 60
Temp_Get            = 21.3[dC]
X_90_Width          = 10.7[us]
X_Acq_Time          = 0.69206016[s]
X_Angle             = 30[deg]
X_Atn               = 13.7[dB]
X_Pulse             = 3.56666667[us]
Irr_Atn_Dec         = 19.543[dB]
Irr_Atn_Noe         = 19.543[dB]
Irr_Noise           = WALTZ
Irr_Pwidth          = 0.104[ms]
Decoupling          = TRUE
Initial_Wait        = 1[s]
Noe                 = TRUE
Noe_Time            = 0.2[s]
Repetition_Time     = 0.89206016[s]
```

Figure S55. ^{13}C NMR spectrum of **5a** (150 MHz, CDCl$_3$).



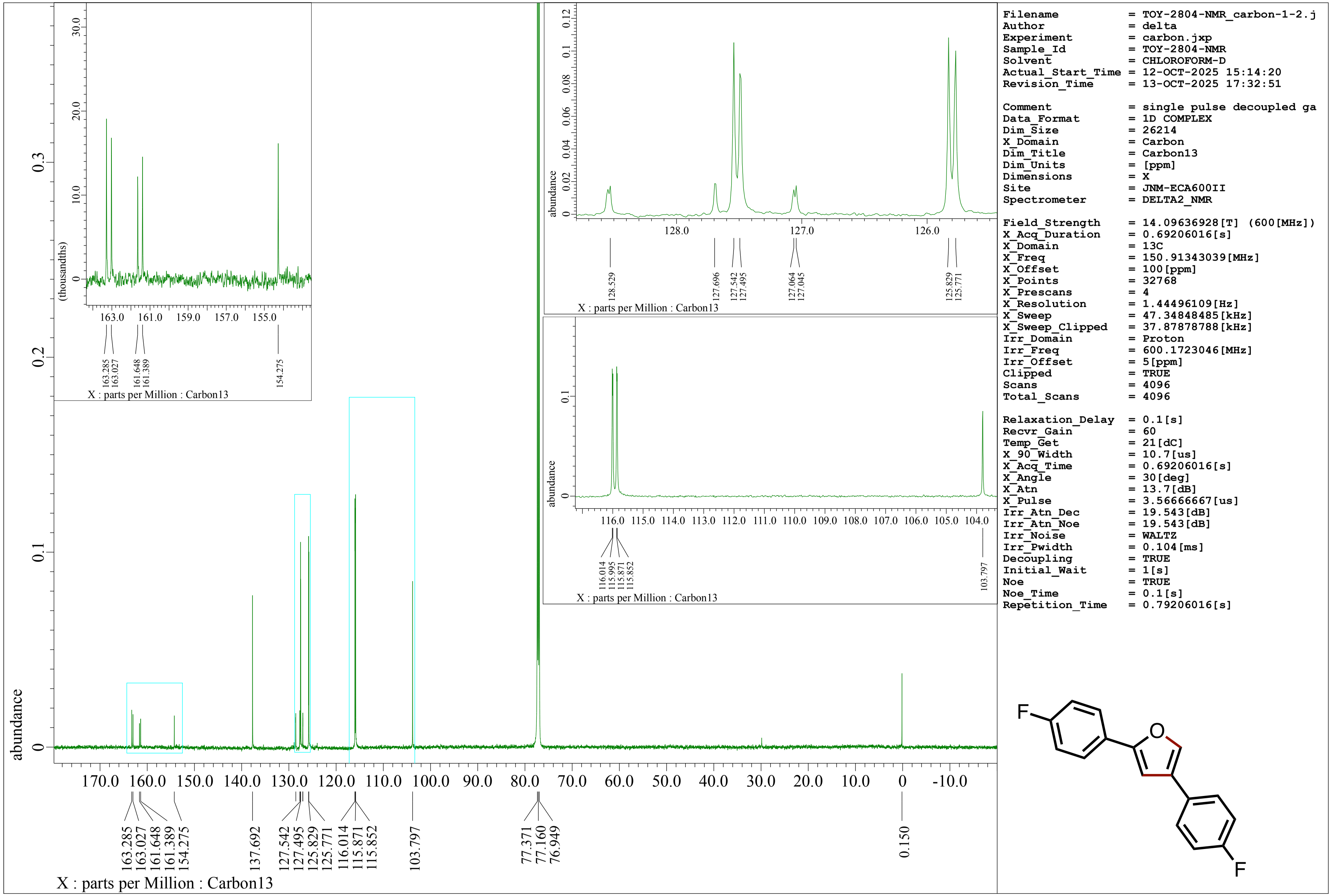
```
Filename            = TOY-2804-NMR_proton-1-3.j
Author              = delta
Experiment          = proton.jxp
Sample_Id           = TOY-2804-NMR
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 12-OCT-2025 15:12:20
Revision_Time       = 13-OCT-2025 17:30:33

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 13107
X_Domain            = Proton
Dim_Title           = Proton
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECA600II
Spectrometer        = DELTA2_NMR

Field_Strength      = 14.09636928[T] (600[MHz])
X_Acq_Duration      = 1.4548992[s]
X_Domain            = 1H
X_Freq              = 600.1723046[MHz]
X_Offset            = 5[ppm]
X_Points            = 16384
X_Prescans          = 1
X_Resolution        = 0.68733284[Hz]
X_Sweep             = 11.26126126[kHz]
X_Sweep_Clipped     = 9.00900901[kHz]
Irr_Domain          = Proton
Irr_Freq            = 600.1723046[MHz]
Irr_Offset          = 5[ppm]
Tri_Domain          = Proton
Tri_Freq            = 600.1723046[MHz]
Tri_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 4
Total_Scans         = 4

Relaxation_Delay    = 5[s]
Recvr_Gain          = 50
Temp_Get            = 21.1[dC]
X_90_Width          = 12.3[us]
X_Acq_Time          = 1.4548992[s]
X_Angle             = 45[deg]
X_Atn               = 1[dB]
X_Pulse             = 6.15[us]
Irr_Mode            = Off
Tri_Mode            = Off
Dante_Presat        = FALSE
Initial_Wait        = 1[s]
Repetition_Time     = 6.4548992[s]
```

Figure S56. ^{1}H NMR spectrum of **5b** (600 MHz, CDCl$_3$).



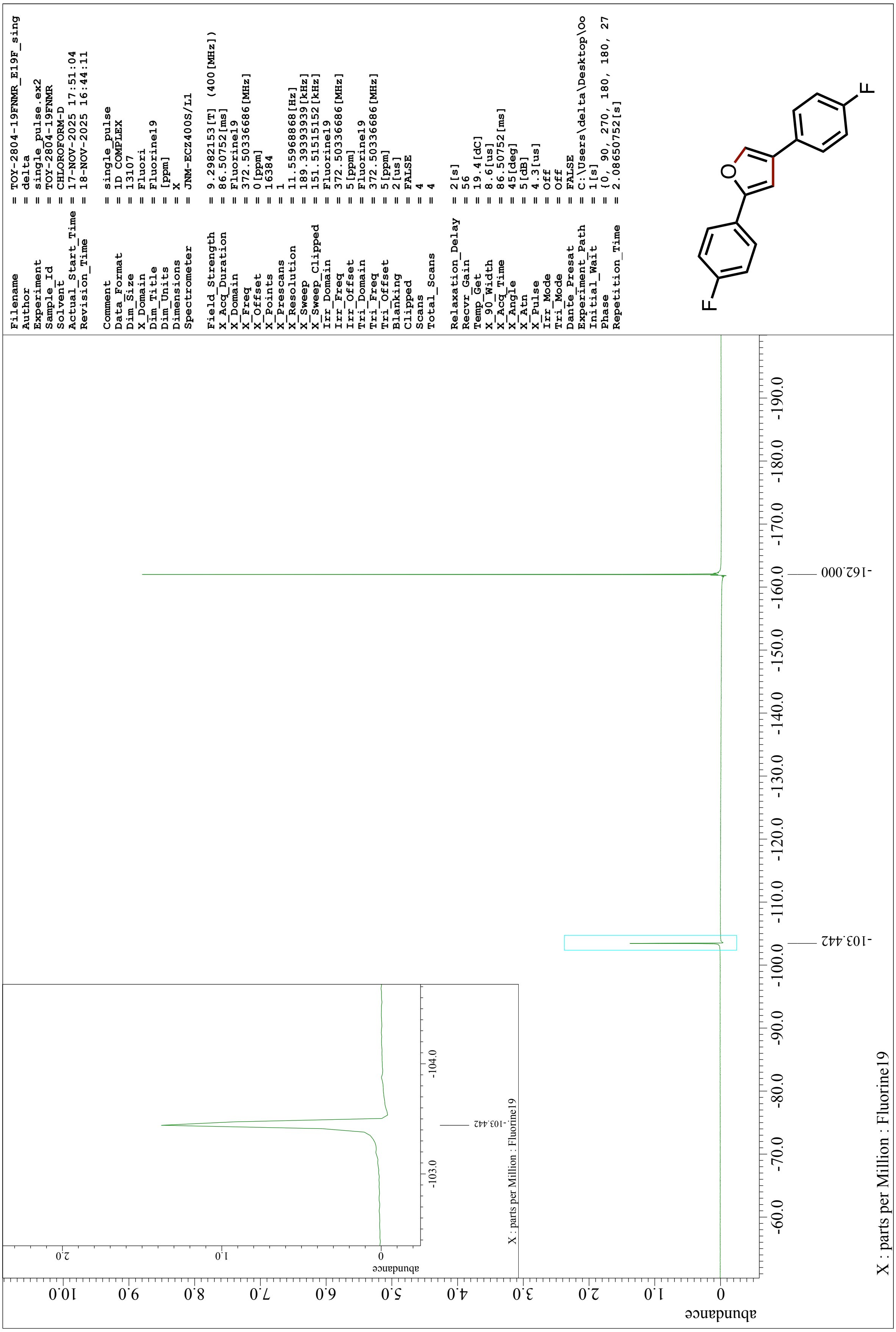
```
Filename             = TOY-2804-NMR_carbon-1-2.j
Author               = delta
Experiment           = carbon.jxp
Sample_Id            = TOY-2804-NMR
Solvent              = CHLOROFORM-D
Actual_Start_Time    = 12-OCT-2025 15:14:20
Revision_Time        = 13-OCT-2025 17:32:51

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                = 4096
Total_Scans          = 4096

Relaxation_Delay     = 0.1[s]
Recvr_Gain           = 60
Temp_Get             = 21[dC]
X_90_Width           = 10.7[us]
X_Acq_Time           = 0.69206016[s]
X_Angle              = 30[deg]
X_Atn                = 13.7[dB]
X_Pulse              = 3.56666667[us]
Irr_Atn_Dec          = 19.543[dB]
Irr_Atn_Noe          = 19.543[dB]
Irr_Noise            = WALTZ
Irr_Pwidth           = 0.104[ms]
Decoupling           = TRUE
Initial_Wait         = 1[s]
Noe                  = TRUE
Noe_Time             = 0.1[s]
Repetition_Time      = 0.79206016[s]
```

Figure S57. ^{13}C NMR spectrum of **5b** (150 MHz, $CDCl_3$).



```
Filename              = TOY-2804-19FNMR_E19F_sing
Author                = delta
Experiment            = single_pulse.ex2
Sample_Id             = TOY-2804-19FNMR
Solvent               = CHLOROFORM-D
Actual_Start_Time     = 17-NOV-2025 17:51:04
Revision_Time         = 18-NOV-2025 16:44:11

Comment               = single_pulse
Data_Format           = 1D COMPLEX
Dim_Size              = 13107
X_Domain              = Fluori
Dim_Title             = Fluorine19
Dim_Units             = [ppm]
Dimensions            = X
Spectrometer          = JNM-ECZ400S/L1

Field_Strength        = 9.2982153[T] (400[MHz])
X_Acq_Duration        = 86.50752[ms]
X_Domain              = Fluorine19
X_Freq                = 372.50336686[MHz]
X_Offset              = 0[ppm]
X_Points              = 16384
X_Prescans            = 1
X_Resolution          = 11.55968868[Hz]
X_Sweep               = 189.39393939[kHz]
X_Sweep_Clipped       = 151.51515152[kHz]
Irr_Domain            = Fluorine19
Irr_Freq              = 372.50336686[MHz]
Irr_Offset            = 5[ppm]
Tri_Domain            = Fluorine19
Tri_Freq              = 372.50336686[MHz]
Tri_Offset            = 5[ppm]
Blanking              = 2[us]
Clipped               = FALSE
Scans                 = 4
Total_Scans           = 4

Relaxation_Delay      = 2[s]
Recvr_Gain            = 56
Temp_Get              = 19.4[dC]
X_90_Width            = 8.6[us]
X_Acq_Time            = 86.50752[ms]
X_Angle               = 45[deg]
X_Atn                 = 5[dB]
X_Pulse               = 4.3[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       = 2.08650752[s]
```

Figure S58. ^{19}F NMR spectrum of **5b** (372 MHz, $CDCl_3$).

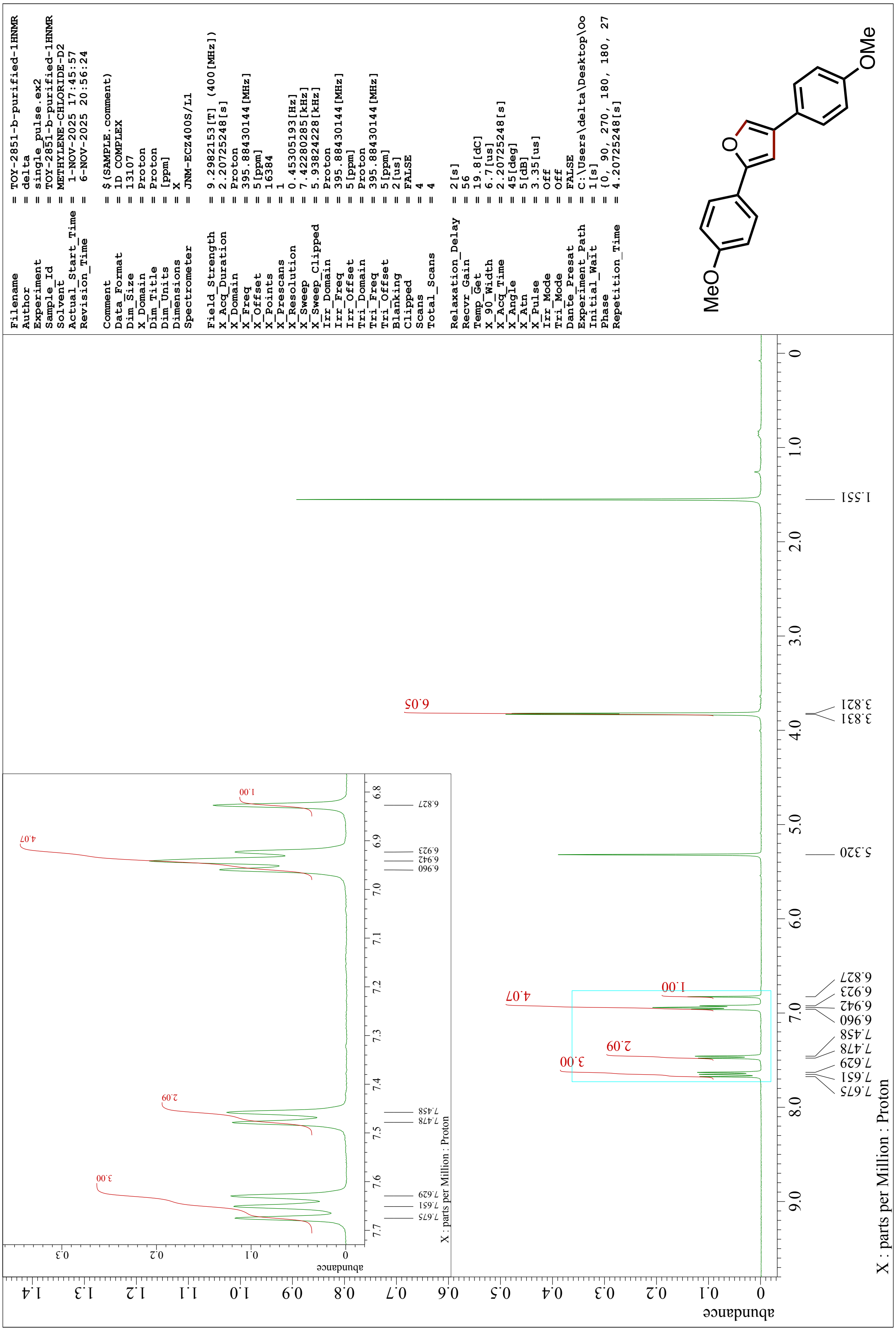
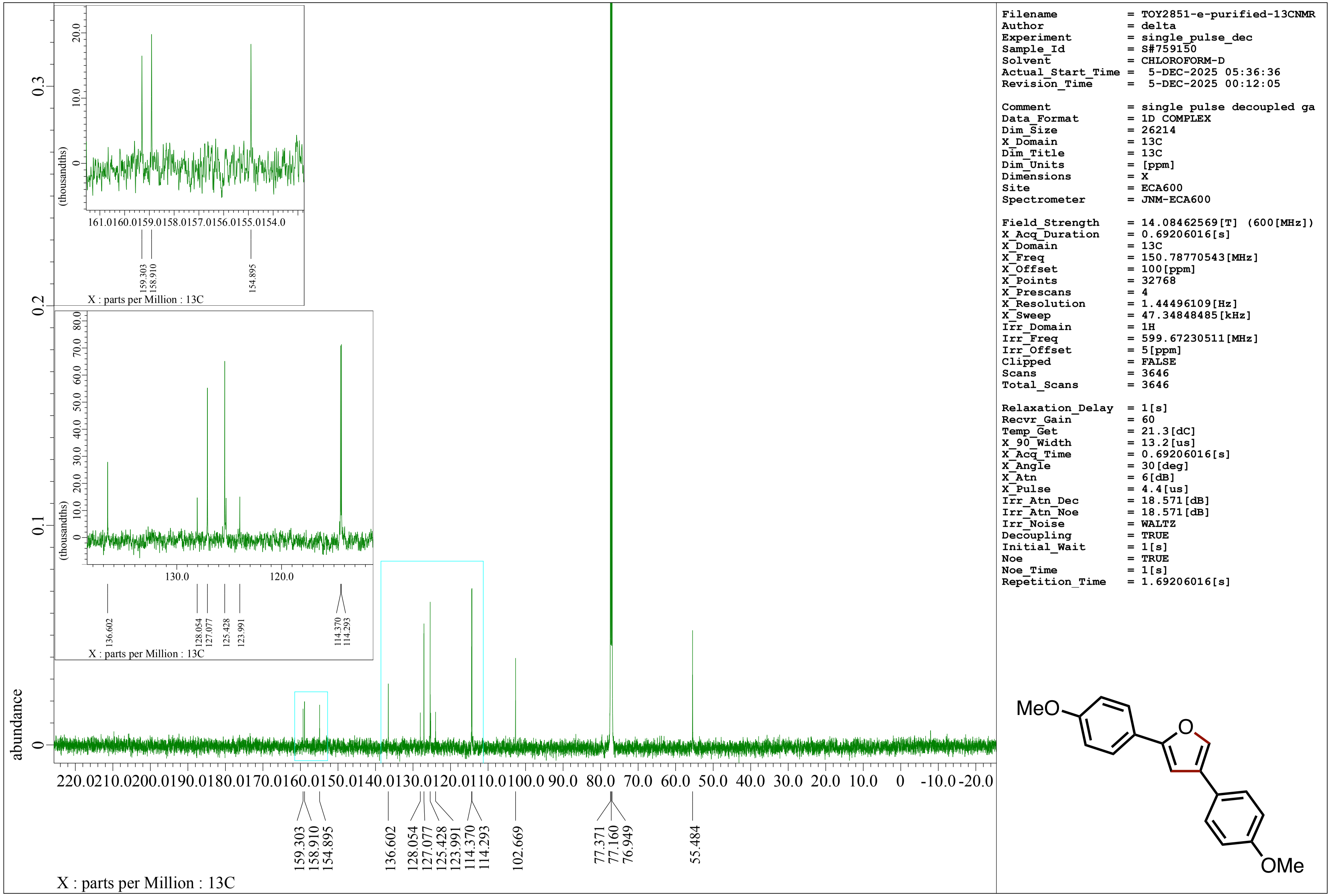


Figure S59. ^{1}H NMR spectrum of **5c** (600 MHz, CD_2Cl_2).



```
Filename             = TOY2851-e-purified-13CNMR
Author               = delta
Experiment           = single_pulse_dec
Sample_Id            = S#759150
Solvent              = CHLOROFORM-D
Actual_Start_Time    =  5-DEC-2025 05:36:36
Revision_Time        =  5-DEC-2025 00:12:05

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                = 3646
Total_Scans          = 3646

Relaxation_Delay     = 1[s]
Recvr_Gain           = 60
Temp_Get             = 21.3[dC]
X_90_Width           = 13.2[us]
X_Acq_Time           = 0.69206016[s]
X_Angle              = 30[deg]
X_Atn                = 6[dB]
X_Pulse              = 4.4[us]
Irr_Atn_Dec          = 18.571[dB]
Irr_Atn_Noe          = 18.571[dB]
Irr_Noise            = WALTZ
Decoupling           = TRUE
Initial_Wait         = 1[s]
Noe                  = TRUE
Noe_Time             = 1[s]
Repetition_Time      = 1.69206016[s]
```

Figure S60. ^{13}C NMR spectrum of **5c** (150 MHz, $CDCl_3$).

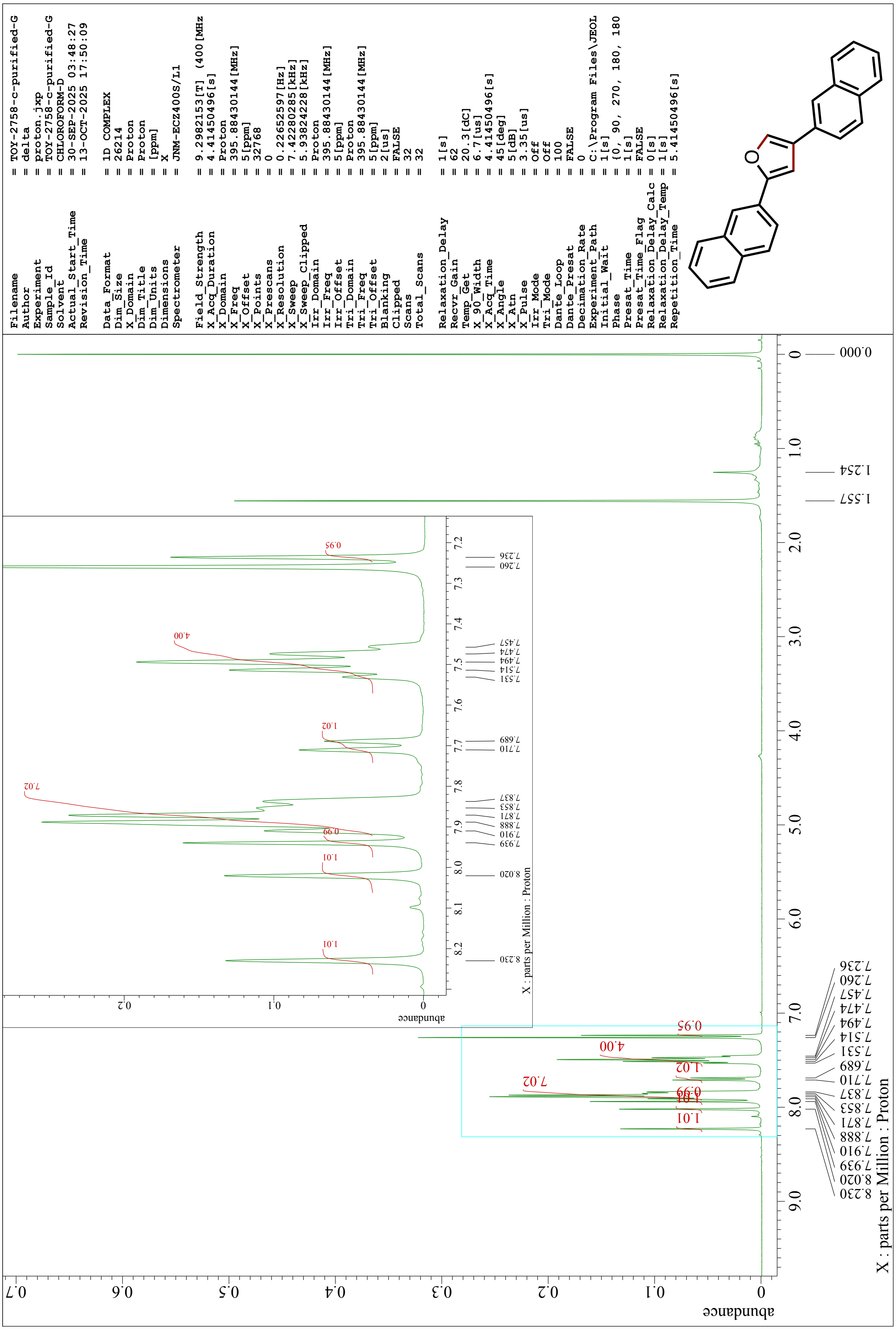


Figure S61. ^{1}H NMR spectrum of **5d** (600 MHz, CDCl$_3$).

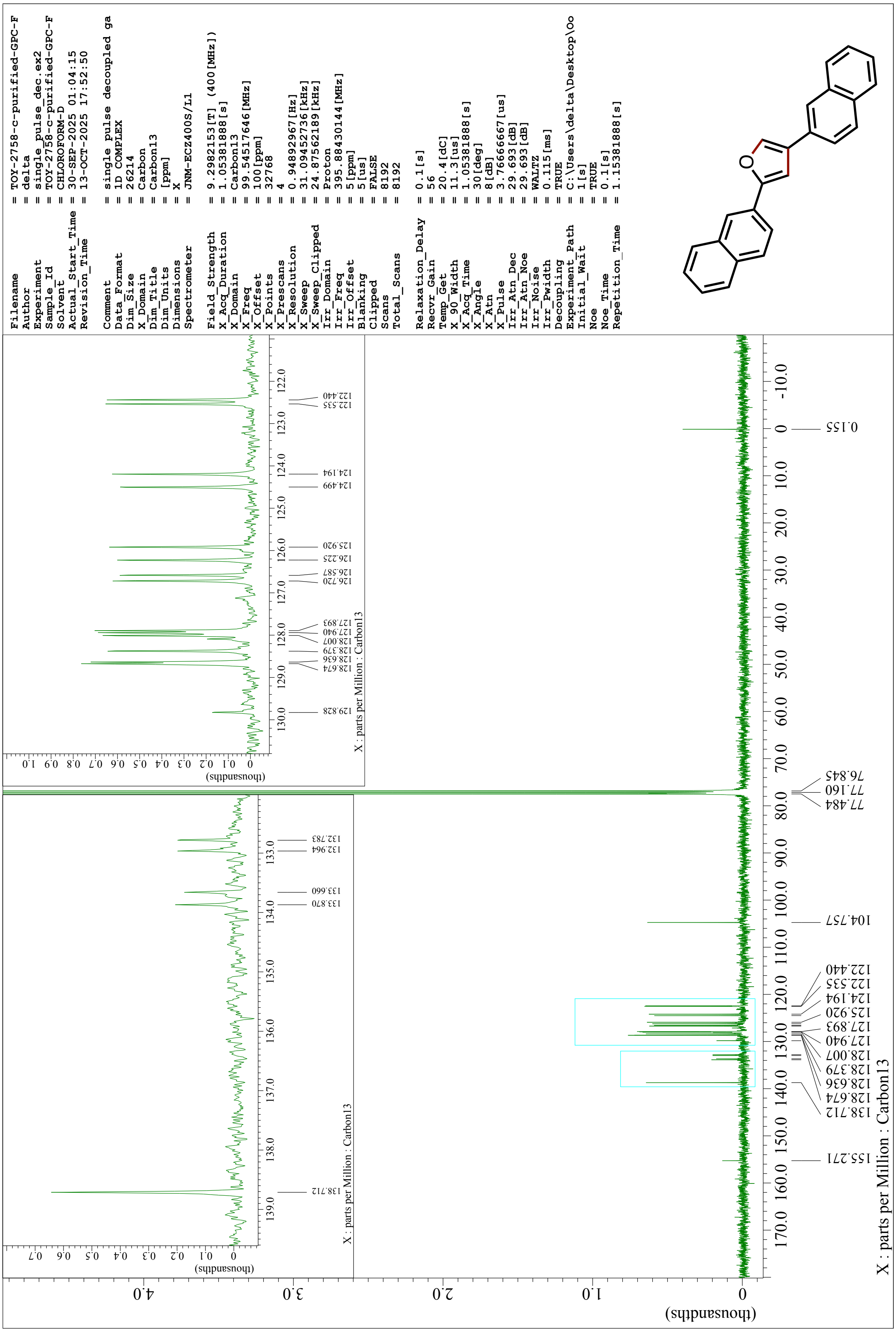
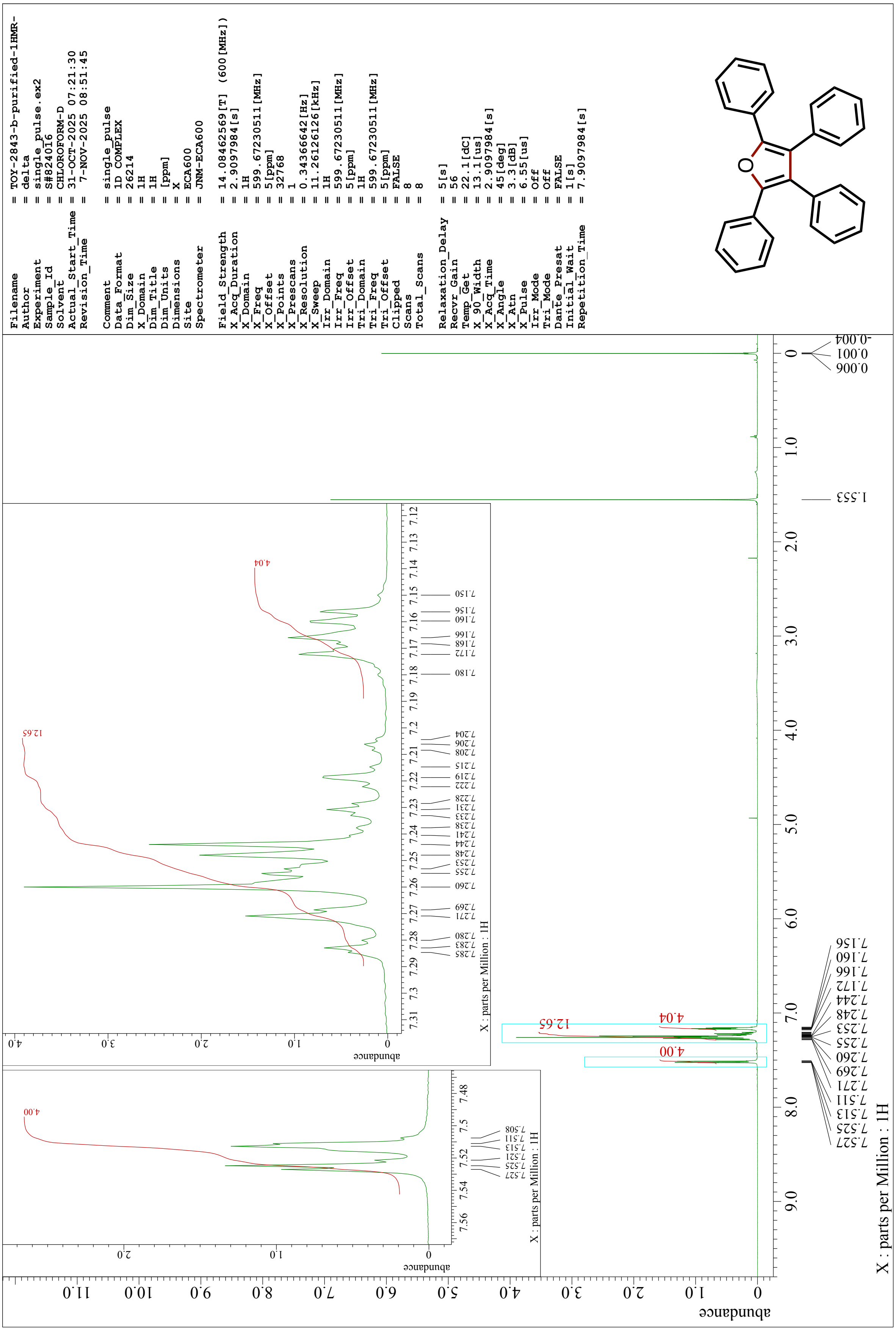


Figure S62. ^{13}C NMR spectrum of **5d** (150 MHz, CDCl$_3$).



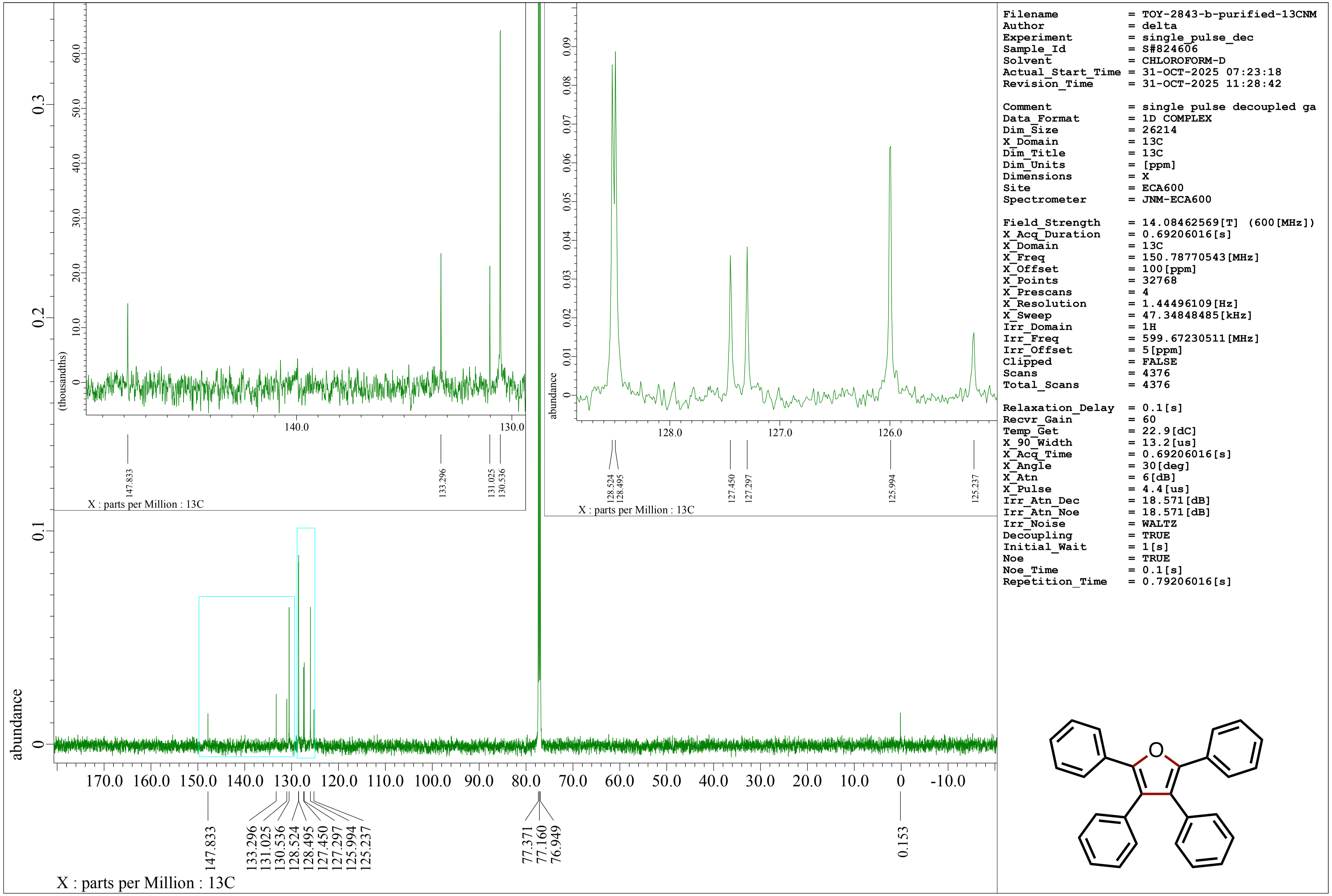
```
Filename            = TOY-2843-b-purified-1HMR-
Author              = delta
Experiment          = single_pulse.ex2
Sample_Id           = S#824016
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 31-OCT-2025 07:21:30
Revision_Time       =  7-NOV-2025 08:51:45

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = 1H
Dim_Title           = 1H
Dim_Units           = [ppm]
Dimensions          = X
Site                = ECA600
Spectrometer        = JNM-ECA600

Field_Strength      = 14.08462569[T] (600[MHz])
X_Acq_Duration      = 2.9097984[s]
X_Domain            = 1H
X_Freq              = 599.67230511[MHz]
X_Offset            = 5[ppm]
X_Points            = 32768
X_Prescans          = 1
X_Resolution        = 0.34366642[Hz]
X_Sweep             = 11.26126126[kHz]
Irr_Domain          = 1H
Irr_Freq            = 599.67230511[MHz]
Irr_Offset          = 5[ppm]
Tri_Domain          = 1H
Tri_Freq            = 599.67230511[MHz]
Tri_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 8
Total_Scans         = 8

Relaxation_Delay    = 5[s]
Recvr_Gain          = 56
Temp_Get            = 22.1[dC]
X_90_Width          = 13.1[us]
X_Acq_Time          = 2.9097984[s]
X_Angle             = 45[deg]
X_Atn               = 3.3[dB]
X_Pulse             = 6.55[us]
Irr_Mode            = Off
Tri_Mode            = Off
Dante_Presat        = FALSE
Initial_Wait        = 1[s]
Repetition_Time     = 7.9097984[s]
```

Figure S63. ^{1}H NMR spectrum of **5f** (600 MHz, $CDCl_3$).



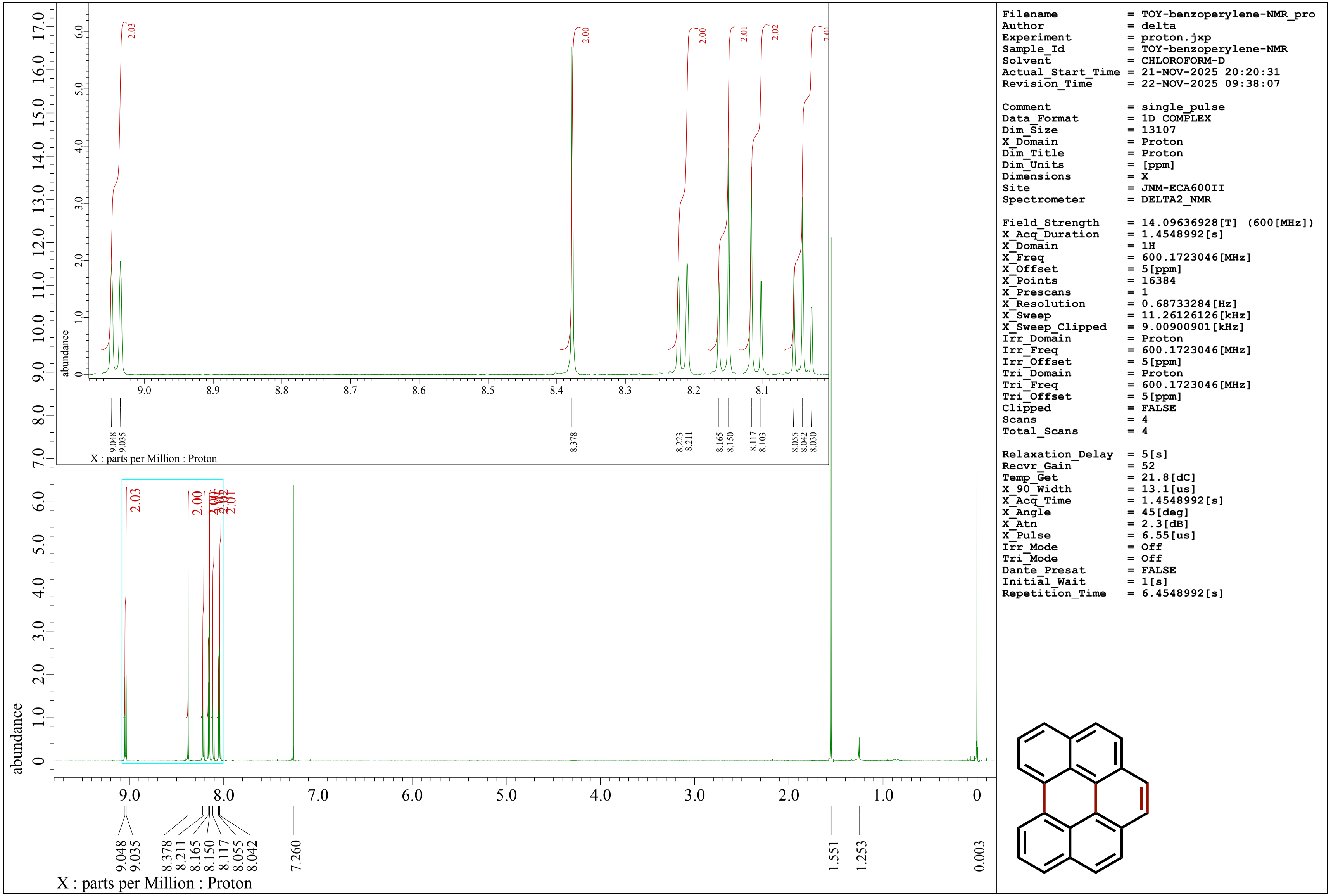
```
Filename            = TOY-2843-b-purified-13CNM
Author              = delta
Experiment          = single_pulse_dec
Sample_Id           = S#824606
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 31-OCT-2025 07:23:18
Revision_Time       = 31-OCT-2025 11:28:42

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               = 4376
Total_Scans         = 4376

Relaxation_Delay    = 0.1[s]
Recvr_Gain          = 60
Temp_Get            = 22.9[dC]
X_90_Width          = 13.2[us]
X_Acq_Time          = 0.69206016[s]
X_Angle             = 30[deg]
X_Atn               = 6[dB]
X_Pulse             = 4.4[us]
Irr_Atn_Dec         = 18.571[dB]
Irr_Atn_Noe         = 18.571[dB]
Irr_Noise           = WALTZ
Decoupling          = TRUE
Initial_Wait        = 1[s]
Noe                 = TRUE
Noe_Time            = 0.1[s]
Repetition_Time     = 0.79206016[s]
```

Figure S64. ^{13}C NMR spectrum of **5f** (150 MHz, CDCl$_3$).



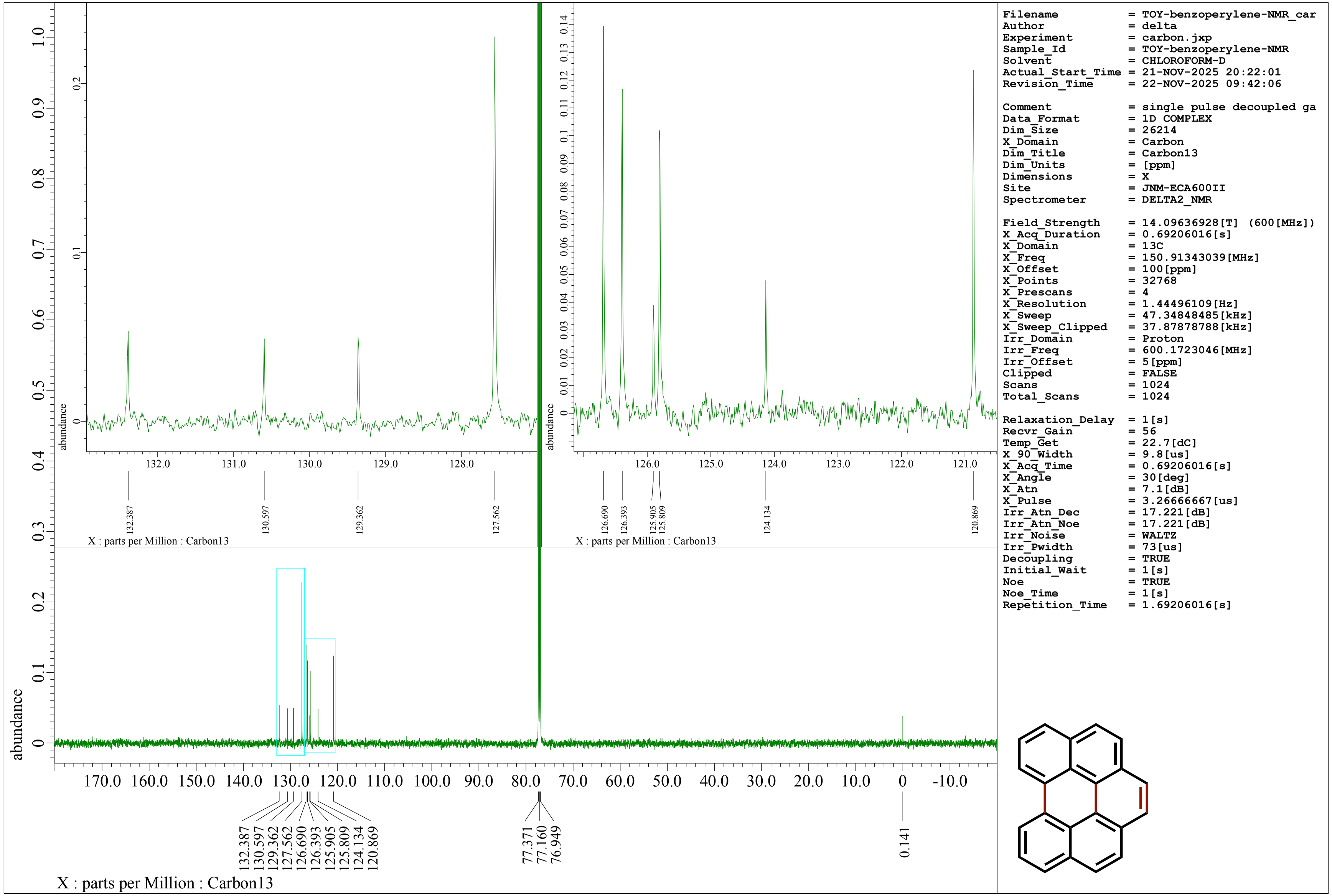
```
Filename            = TOY-benzoperylene-NMR_pro
Author              = delta
Experiment          = proton.jxp
Sample_Id           = TOY-benzoperylene-NMR
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 21-NOV-2025 20:20:31
Revision_Time       = 22-NOV-2025 09:38:07

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 13107
X_Domain            = Proton
Dim_Title           = Proton
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECA600II
Spectrometer        = DELTA2_NMR

Field_Strength      = 14.09636928[T] (600[MHz])
X_Acq_Duration      = 1.4548992[s]
X_Domain            = 1H
X_Freq              = 600.1723046[MHz]
X_Offset            = 5[ppm]
X_Points            = 16384
X_Prescans          = 1
X_Resolution        = 0.68733284[Hz]
X_Sweep             = 11.26126126[kHz]
X_Sweep_Clipped     = 9.00900901[kHz]
Irr_Domain          = Proton
Irr_Freq            = 600.1723046[MHz]
Irr_Offset          = 5[ppm]
Tri_Domain          = Proton
Tri_Freq            = 600.1723046[MHz]
Tri_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 4
Total_Scans         = 4

Relaxation_Delay    = 5[s]
Recvr_Gain          = 52
Temp_Get            = 21.8[dC]
X_90_Width          = 13.1[us]
X_Acq_Time          = 1.4548992[s]
X_Angle             = 45[deg]
X_Atn               = 2.3[dB]
X_Pulse             = 6.55[us]
Irr_Mode            = Off
Tri_Mode            = Off
Dante_Presat        = FALSE
Initial_Wait        = 1[s]
Repetition_Time     = 6.4548992[s]
```

Figure S65. ^{1}H NMR spectrum of **6** (600 MHz, $CDCl_3$).



```
Filename            = TOY-benzoperylene-NMR_car
Author              = delta
Experiment          = carbon.jxp
Sample_Id           = TOY-benzoperylene-NMR
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 21-NOV-2025 20:22:01
Revision_Time       = 22-NOV-2025 09:42:06

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               = 1024
Total_Scans         = 1024

Relaxation_Delay    = 1[s]
Recvr_Gain          = 56
Temp_Get            = 22.7[dC]
X_90_Width          = 9.8[us]
X_Acq_Time          = 0.69206016[s]
X_Angle             = 30[deg]
X_Atn               = 7.1[dB]
X_Pulse             = 3.26666667[us]
Irr_Atn_Dec         = 17.221[dB]
Irr_Atn_Noe         = 17.221[dB]
Irr_Noise           = WALTZ
Irr_Pwidth          = 73[us]
Decoupling          = TRUE
Initial_Wait        = 1[s]
Noe                 = TRUE
Noe_Time            = 1[s]
Repetition_Time     = 1.69206016[s]
```

Figure S66. ^{13}C NMR spectrum of **6** (150 MHz, CDCl$_3$).