Supplementary Information

Rh-catalyzed mechanochemical transfer hydrogenation for synthesis of periphery-hydrogenated polycyclic aromatic compounds

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Table of Contents

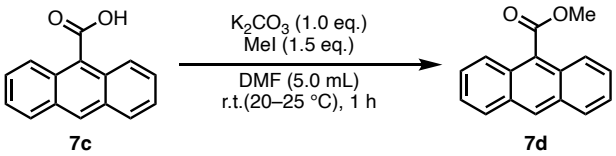
1. General

Unless otherwise noted, all materials including dry solvents were obtained from commercial suppliers and used without further purification. $[RhOH(cod)]_2$, $B_2(OH)_4$, NH_3BH_3, and $[Rh(Cl)cod]_2$ were purchased from Sigma-Aldrich. Tetrahydrofuran (THF), CH_2Cl_2, EtOH, *n*-BuOH, 2-PrOH, 2,2,2-trifluoroethanol were purchased from Kanto Chemical Co., Inc. Naphthalene, anthracene, tetracene, rubrene, perylene, and triphenylene were purchased from Tokyo Chemical Industry Co., Ltd.. Naphtho[8,1,2-*bcd*]perylene (**7j**) was synthesized by referring literatures.[S1] 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), C_6D_6 (δ 7.15 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 77.00 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. Synthesis of polycyclic aromatic compounds

2-1. Synthesis of 7d



7c **7d**

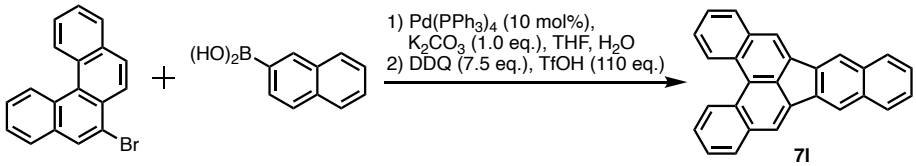
9-Phenanthrenecarboxylic acid (**7c**, 1.11 g, 5.0 mmol, 1.0 eq.) and K_2CO_3 (691.2 mg, 5.0 mmol, 1.0 eq.) were added to a round-bottom flask containing a magnetic stirring bar under open air, and then the flask was filled with N_2 gas. Then, dried DMF (5.0 mL) and methyl iodide (1.06 g, 7.5 mmol, 1.5 eq.) were added the flask successively, and the mixture was stirred at room temperature (20–25 °C) for 1 hour. The mixture was diluted with $CHCl_3$, and the organic phase was washed with H_2O (two times), 1N HCl solution and brine. The organic phase was dried over Na_2SO_4, filtered and concentrated by a rotary evaporator under reduced pressure. The residual solid was washed with hexane/ $CHCl_3$ = 10:1) to afford **7d** as a pale yellow solid (714.9 mg, 3.0 mmol, 61%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.03 (d, *J* = 8.9 Hz, 4H), 7.56–7.53 (m, 2H), 7.51–7.48 (m, 2H), 4.19 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 170.08, 130.94, 129.44, 128.60, 128.46, 127.67, 127.00, 125.47, 124.99, 52.63.

HRMS (DART, positive) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{13}O_2$ 237.09155; Found 237.09103.

2-2. Synthesis of 7l by cyclodehydrogenation



7l

6-Bromobenzo[*c*]phenanthrene (306.2 mg, 1.0 mmol, 1.0 eq.), nahthrene-2-ylboronic acid (206.4 mg, 1.2 mmol, 1.2 eq.), $Pd(PPh_3)_4$ (115.5 mg, 0.101 mmol, 10 mol%) and K_2CO_3 (138.4 mg, 1.0 mmol, 1.0 eq.) were added to a round-bottom flask containing a magnetic stirring bar under open air, and then the flask was filled with N_2 gas. THF (10 mL) and H_2O (1.0 mL) was added to the flask successively, and the mixture was stirred at 110 °C for 2 days. After the mixture was cooled to room temperature, the solvent was removed by a rotary evaporator. Then, the precipitate was filtered and washed with H_2O, and dried. The crude mixture was purified by washing (hexane) and use without purification next step. To a dried 500-mL three-neck round-bottom flask containing a magnetic stirring bar was added the crude product (1.00 mmol, 1.00 eq.) in CH_2Cl_2 (200 mL). After cooling to 0 °C, DDQ (1.70 g, 7.50 eq.) was added and stirred at 0 °C for 5 min. Then TfOH (10.0 mL, 113 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 layer was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4, and the solvent was removed by a rotary evaporator under reduced pressure. Finally, the residue was purified by

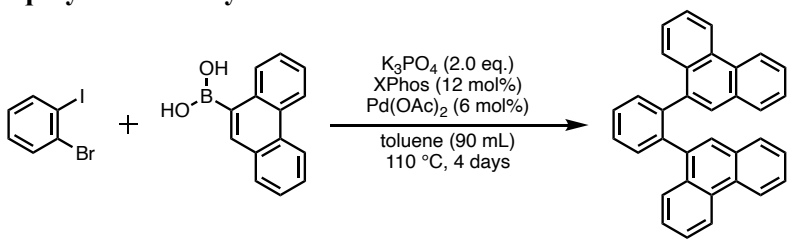
flash column chromatography on silica gel (eluent: hexane/$CHCl_3$) to afford **7l** as a brown solid (13.4 mg, 0.038 mmol, 4%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (d, *J* = 8.2 Hz, 2H), 8.45 (d, *J* = 2.7 Hz, 4H), 8.21 (d, *J* = 7.6 Hz, 2H), 7.99 (q, *J* = 3.0 Hz, 2H), 7.79–7.76 (m, 2H), 7.69 (t, *J* = 7.2 Hz, 2H), 7.53 (q, *J* = 3.2 Hz, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 137.69, 135.40, 134.75, 133.77, 130.97, 130.56, 128.72, 126.92, 126.81, 126.19, 126.02, 124.52, 120.71, 120.36.

HRMS (ESI, positive) *m/z*: $[M+H]^+$ Calcd for $C_{28}H_{17}$ 353.13303 ; Found 353.13191.

2-3. Synthesis of 7q' by Suzuki–Miyaura reaction



7q'

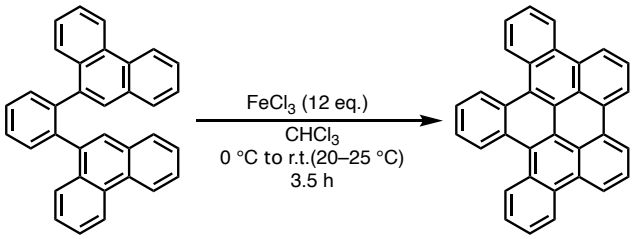
1-Iodo-2-bromobenzene (5.21 g, 18.4 mmol, 1.0 eq.), phenahthrene-9-ylboronic acid (8.59 g, 38.7 mmol, 2.1 eq.), $Pd(OAc)_2$ (124.1 mg, 0.553 mmol, 3 mol%), XPhos (527.0 mg, 1.11 mmol, 6 mol%), and 2.0 M K_3PO_4 aq. (18.4 mL, 36.9 mmol, 2.0 eq.) were added to a round-bottom flask containing a magnetic stirring bar under open air, and then the flask was filled with N_2 gas. Toluene (90 mL) was added to the flask successively, and the mixture was stirred at 110 °C for 3 days. Then, the additional phenahthrene-9-ylboronic acid (8.59 g, 38.7 mmol, 2.1 eq.), $Pd(OAc)_2$ (124.1 mg, 0.553 mmol, 3 mol%), XPhos (527.0 mg, 1.11 mmol, 6 mol%) were added to the flask for completion of the reaction, and the mixture was stirred at 110 °C for 1 day. After the mixture was cooled to room temperature, the solvent was removed by a rotary evaporator. Then, the precipitate was filtered and washed with H_2O, and dried. The residue was purified by washing (toluene/*n*-BuOH = 4:1) to afford **7q'** as a white solid (6.96 g, 16.2 mmol, 88%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58–8.56 (m, 1H), 8.49–8.44 (m, 3H), 7.93–7.87 (m, 2H), 7.67–7.30 (m, 16H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 140.47, 140.21, 137.48, 137.27, 132.09, 131.92, 131.56, 131.05, 131.02, 130.99, 130.16, 129.67, 129.63, 129.08, 128.39 (2C), 127.37, 127.33, 127.21, 127.08, 127.05, 126.39, 126.28, 126.22, 126.17, 126.09 (2C), 125.94, 125.82, 122.61, 122.47, 122.25, 122.17. One sp^2 carbon peak was overlapped. The ^{1}H and ^{13}C NMR spectra show existence of rotamers.

HRMS (ESI, positive) *m/z*: $[M+H]^+$ Calcd for $C_{34}H_{23}$ 431.1794; Found 431.1795.

2-4. Synthesis of 7q by cyclodehydrogenation



7q' **7q**

To a dried round-bottom flask containing a magnetic stirring bar was added a solution of **7q'** (6.90 g, 16.0 mmol, 1.0 eq.) in $CHCl_3$ (500 mL). After cooling to 0 °C, $FeCl_3$ (31.2 g, 192 mmol, 12 eq.) was added and stirred at room temperature (20–25 °C) for 3.5 hours. Then, MeOH was added to quench the reaction. The resulting green precipitate was obtained by filtration by washing with MeOH. The obtained solid was dissolved in PhCl (500 mL) with activated carbon, and the solution was further stirred at 140 °C for 30 min under air. Finally, the activated carbon was filtered off by suction filtration with Celite, and the filtrate was concentrated by a rotary evaporator to afford **7q** as a yellow solid (5.73 g, 13.4 mmol, 84%).

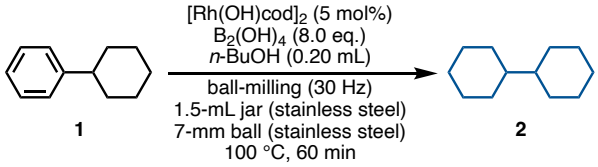
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18–9.12 (m, 2H), 9.02–8.97 (m, 2H), 8.89 (d, J = 7.7 Hz, 2H), 8.87 (d, J = 8.2 Hz, 2H), 8.85–8.81 (m, 2H), 8.01 (t, J = 7.9 Hz, 2H), 7.78–7.69 (m, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 131.26, 130.19, 129.96, 129.85, 129.56, 128.99, 128.41, 126.90 (3C), 126.49, 125.79, 125.28, 124.56, 123.82, 122.19, 121.84, 121.77.

HRMS (ESI, positive) *m/z*: $[M]^+$ Calcd for $C_{34}H_{18}$ 426.1403 ; Found 426.1404.

3. Experimental procedures

Synthesis of bicyclohexyl (2)



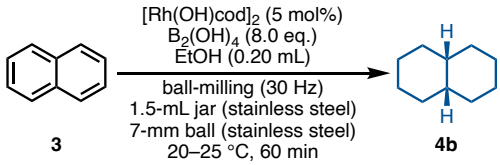
To a 1.5-mL stainless-steel jar containing a 7-mm-diameter stainless-steel ball were added cyclohexylbenzene (**1**) (32.8 mg, 0.204 mmol, 1.0 eq.), [RhOH(cod)]$_2$ (4.5 mg, 0.0099 mmol, 5.0 mol%), and $B_2(OH)_4$ (144.0 mg, 1.60 mmol, 8.0 eq.) under air. Then, *n*-BuOH (0.20 mL, 2.2 mmol, 11 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with a handmade 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 shaked at 30 Hz (1800 rpm) with heating by a heat-gun at 100 °C (heat-gun preset temperature) for 60 min. The catalyst was removed by filtration with a short pad of silica gel (eluent: $CHCl_3$). After concentrating filtrate, the crude mixture was purified by silica gel column chromatography (eluent: hexane) to afford **2** (31.5 mg, 0.189 mmol, 93%).

^{1}H NMR (600 MHz, C_6D_6) δ 1.74–1.71 (m, 4H), 1.67–1.63 (m, 6H), 1.24–1.07 (m, 6H), 1.04–0.99 (m, 2H), 0.99–0.90 (m, 4H).

^{13}C NMR (150 MHz, C_6D_6) δ 43.72, 30.44, 27.23 (2C).

HRMS (DART, positive) *m/z*: $[M–H]^+$ Calcd for $C_{12}H_{21}$ 165.16433; Found 165.16390.

Synthesis of *cis*-decalin (4b) at room temperature (20–25 °C)



The synthesis of *cis*-decline (**4b**) is described as a representative example of a general procedure for a 0.2-mmol scale reaction.

To a 1.5-mL stainless-steel jar containing a 7-mm-diameter stainless-steel ball were added naphthalene (**3**) (26.2 mg, 0.204 mmol, 1.0 eq.), [RhOH(cod)]$_2$ (4.4 mg, 0.0098 mmol, 5 mol%), and $B_2(OH)_4$ (142.1 mg, 1.59 mmol, 8.0 eq.) under air. Then, ethanol (0.20 mL, 3.4 mmol, 17 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with a handmade 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 shaked at 30 Hz (1800 rpm) at room temperature for 30 min. The catalyst was removed by filtration with a short pad of silica gel (eluent: $CHCl_3$). After concentrating filtrate, the crude mixture was purified by silica gel column chromatography (eluent: hexane) and then purified with GPC (eluent: $CHCl_3$) to afford **4b** (18.3 mg, 0.133 mmol, 65%). The spectra corresponded

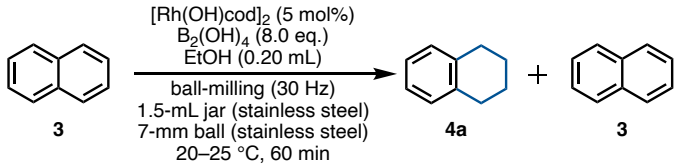
with the literature.[S2]

^{1}H NMR (600 MHz, C_6D_6) δ 1.64–1.44 (m, 10H), 1.29 (brs, 8H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 36.29.

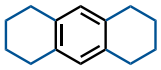
HRMS (ESI, positive) *m/z*: $[M–H]^+$ Calcd for $C_{10}H_{17}$ 137.1325; Found 137.1325.

Hydrogenation of naphthalene (3) with ball-milling for 10 min



To a 1.5-mL stainless-steel jar containing a 7-mm-diameter stainless-steel ball were added naphthalene (**3**) (26.3 mg, 0.204 mmol, 1.0 eq.), $[RhOH(cod)]_2$ (4.9 mg, 0.010 mmol, 5 mol%), and $B_2(OH)_4$ (142.3 mg, 1.59 mmol, 8.0 eq.) under air. Then, ethanol (0.20 mL, 3.4 mmol, 17 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with a handmade 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 shaked at 30 Hz (1800 rpm) at room temperature for 10 min. The catalyst was removed by filtration with a short pad of silica gel (eluent: $CHCl_3$) and the residue was washed with chloroform. After concentrating filtrate, the crude mixture was analyzed by ^{1}H NMR with dibromomethane as an internal standard to determine the formation of **4a** (46% NMR yield) and recovery of **3** (46% NMR yield).

Synthesis of 1,2,3,4,5,6,7,8-octahydroanthracene (8a)



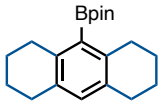
To a 1.5-mL stainless-steel jar containing a 7-mm-diameter stainless-steel ball were added anthracene (**7a**) (17.9 mg, 0.100 mmol, 1.0 eq.), $[RhOH(cod)]_2$ (9.1 mg, 0.020 mmol, 20 mol%), and $B_2(OH)_4$ (89.7 mg, 1.00 mmol, 10.0 eq.) under air. Then, *n*-BuOH (0.10 mL, 1.1 mmol, 11 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with a handmade 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 shaked at 30 Hz (1800 rpm) with heating by a heat-gun at 100 °C (heat-gun preset temperature) for 99 min. The catalyst was removed by filtration with a short pad of silica gel (eluent: $CHCl_3$). After concentrating filtrate, the crude mixture was purified by silica gel column chromatography (eluent: hexane) and then purified with GPC (eluent: $CHCl_3$) to afford **8a** (12.8 mg, 0.0687 mmol, 69%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.79 (s, 2H), 2.70 (s, 8H), 1.82–1.70 (m, 8H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 134.22, 129.47, 28.99, 23.45.

HRMS (DART, positive) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{19}$ 187.14833; Found 187.14868.

Synthesis of 4,4,5,5-tetramethyl-2-(1,2,3,4,5,6,7,8-octahydroanthracen-9-yl)-1,3,2-dioxaborolane (8b)



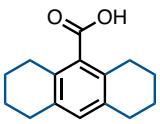
To a 1.5-mL stainless-steel jar containing a 7-mm-diameter stainless-steel ball were added 9-anthraceneboronicacid bis(pinacol) ester (**7b**) (61.0 mg, 0.200 mmol, 1.0 eq.), $[RhOH(cod)]_2$ (18.3 mg, 0.040 mmol, 20 mol%), and $B_2(OH)_4$ (144.9 mg, 1.61 mmol, 8.0 eq.) under air. Then, *n*-BuOH (0.10 mL, 1.1 mmol, 5.5 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with a handmade 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) with heating by a heat-gun at 100 °C (heat-gun preset temperature) for 99 min. The catalyst was removed by filtration with a short pad of silica gel (eluent: $CHCl_3$). After concentrating filtrate, the crude mixture was purified by GPC (eluent: $CHCl_3$) to afford **8b** (39.9 mg, 0.128 mmol, 64%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.74 (s, 1H), 2.76 (t, J = 6.0 Hz, 4H), 2.67 (t, J = 6.0 Hz, 4H), 1.82–1.68 (m, 8H), 1.37 (s, 12H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 137.30, 133.33, 130.91, 83.51, 29.54, 29.14, 25.04, 23.74, 23.15.

HRMS (DART, positive) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{30}BO_2$ 313.23388; Found 313.23309.

Synthesis of 1,2,3,4,5,6,7,8-octahydroanthracene-9-carboxylic acid (8c)



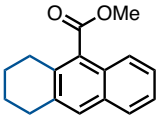
To a 1.5-mL stainless-steel jar containing a 7-mm-diameter stainless-steel ball were added 9-anthracenecarboxylic acid (**7c**) (44.4 mg, 0.200 mmol, 1.0 eq.), $[RhOH(cod)]_2$ (18.8 mg, 0.041 mmol, 21 mol%), and $B_2(OH)_4$ (144.2 mg, 1.60 mmol, 8.0 eq.) under air. Then, *n*-BuOH (0.10 mL, 11 mmol, 5.5 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with a handmade 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) with heating by a heat-gun at 100 °C (heat-gun preset temperature) for 99 min. The catalyst was removed by filtration with a short pad of silica gel (eluent: $CHCl_3$). After concentrating filtrate, the crude mixture was purified by GPC (eluent: $CHCl_3$) to afford **8c** (21.2 mg, 0.092 mmol, 46%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.88 (s, 1H), 2.79 (t, J = 5.8 Hz, 4H), 2.73 (t, J = 5.8 Hz, 4H), 1.82–1.76 (m, 8H). Broaden OH peak was observed between 10–12 ppm.

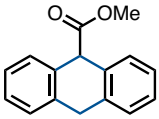
^{13}C NMR (150 MHz, $CDCl_3$) δ 174.96, 134.63, 132.73, 131.38, 130.73, 29.30, 26.54, 23.03, 22.80.

HRMS (DART, positive) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{19}O_2$ 231.13850; Found 231.13947.

Synthesis of methyl 1,2,3,4-tetrahydroanthracene-9-carboxylate (8d) and methyl 4a,9,9a,10-tetrahydroanthracene-9-carboxylate (8d')



8d



8d'

To a 1.5-mL stainless-steel jar containing a 7-mm-diameter stainless-steel ball were added methyl-9-anthracenecarboxylate (**7d**) (44.4 mg, 0.200 mmol, 1.0 eq.), $[RhOH(cod)]_2$ (18.3 mg, 0.040 mmol, 20 mol%), and $B_2(OH)_4$ (144.5 mg, 1.60 mmol, 8.0 eq.) under air. Then, *n*-BuOH (0.10 mL, 1.1 mmol, 5.5 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with a handmade 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) with heating by a heat-gun at 100 °C (heat-gun preset temperature) for 99 min. The catalyst was removed by filtration with a short pad of silica gel (eluent: $CHCl_3$). After concentrating filtrate, the crude mixture was purified by GPC (eluent: $CHCl_3$) to afford a mixture of **8d** and **8d'** (19.0 mg, 0.0791 mmol, 40% combined yield). The molar ratio of **8d** and **8d'** was determined to be 89:11 by ^{1}H NMR analysis.

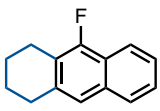
^{1}H NMR of 8d/8d' mixture (600 MHz, $CDCl_3$) δ 7.74–7.71 (m, 1H × 0.89), 7.68–7.65 (m, 1H× 0.89), 7.62 (s, 1H× 0.89), 7.44–7.38 (m, 2H× 0.89), 7.33 (d, J = 7.8 Hz, 2H × 0.11), 7.29–7.22 (m, 6H× 0.11), 5.01 (s, 1H× 0.11), 4.32 (d, J = 18.6 Hz, 1H × 0.11), 4.04 (s, 3H× 0.89), 3.90 (d, J = 18.6 Hz, 1H × 0.11), 3.58 (s, 1H× 0.11), 2.98 (t, J = 5.8 Hz, 2H× 0.89), 2.93 (t, J = 5.8 Hz, 2H× 0.89), 1.92–1.82 (m, 4H× 0.89). The spectra of **8d'** was identical to the literature.[S3]

^{13}C NMR of 8d/8d' mixture (150 MHz, $CDCl_3$) δ 170.50 (1C× 0.89), 135.66 (1C× 0.89), 133.46 (1C× 0.89), 131.63 (1C× 0.89), 130.09 (1C× 0.89), 128.73 (1C× 0.89), 128.44 (1C× 0.89), 128.23 (1C× 0.11), 128.01 (1C× 0.11), 127.47 (1C× 0.11), 127.34 (1C× 0.89), 126.35 (1C× 0.11), 125.99 (1C× 0.89), 125.41 (1C× 0.89), 124.09 (1C× 0.89), 52.18 (1C× 0.89), 30.02 (1C× 0.89), 27.36 (1C× 0.89), 22.90 (1C× 0.89), 22.74 (1C× 0.89). Other carbon peaks of **8d'** could not be observed because of its low intensities.

HRMS of **8d** (DART, positive) *m/z*: $[M]^+$ Calcd for $C_{16}H_{16}O_2$ 240.11503; Found 240.11463.

HRMS of **8d'** (DART, positive) *m/z*: $[M]^+$ Calcd for $C_{16}H_{14}O_2$ 238.09938; Found 238.10030.

Synthesis of 9-fluoro-1,2,3,4-tetrahydroanthracene (8e)



To a 1.5-mL stainless-steel jar containing a 7-mm-diameter stainless-steel ball were added 9-fluoroanthracene (**7e**) (39.3 mg, 0.200 mmol, 1.0 eq.), $[RhOH(cod)]_2$ (18.3 mg, 0.040 mmol, 20 mol%), and $B_2(OH)_4$ (144.3 mg, 1.60 mmol, 8.0 eq.) under air. Then, *n*-BuOH (0.10 mL, 1.1 mmol, 5.5 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with a handmade 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) with heating by a heat-gun at 100 °C (heat-gun preset temperature) for 99 min. The

catalyst was removed by filtration with a short pad of silica gel (eluent: $CHCl_3$). After concentrating filtrate, the crude mixture was purified by GPC (eluent: $CHCl_3$) to afford **8e** as a white solid (11.9 mg, 0.0594 mmol, 30%).

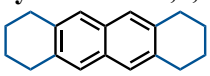
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01–7.99 (m, 1H), 7.72–7.71 (m, 1H), 7.43–7.40 (m, 2H), 7.36 (s, 1H), 2.99–2.94 (m, 4H), 1.90–1.83 (m, 4H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 155.60 (d, J_{C-F} = 248.53 Hz), 136.87 (d, J_{C-F} = 5.8 Hz), 132.54 (d, J_{C-F} = 4.3 Hz), 126.64, 125.74, 125.03, 121.82 (d, J_{C-F} = 2.9 Hz), 121.71, 119.99, 119.93 (d, J_{C-F} = 4.3 Hz), 29.84, 22.92, 22.44, 22.23.

^{19}F NMR (370 MHz, $CDCl_3$) δ –129.01.

HRMS (DART, positive) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{14}F$ 201.10795; Found 201.10715.

Synthesis of 1,2,3,4,7,8,9,10-octahydrotetracene (8f)



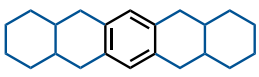
To a 1.5-mL stainless-steel jar containing a 7-mm-diameter stainless-steel ball were added tetracene (**7f**) (20.8 mg, 0.0911 mmol, 1.0 eq.), $[RhOH(cod)]_2$ (9.2 mg, 0.020 mmol, 20 mol%), and $B_2(OH)_4$ (71.2 mg, 0.794 mmol, 8.0 eq.) under air. Then, *n*-BuOH (0.10 mL, 1.1 mmol, 11 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with a handmade 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 shaked at 30 Hz (1800 rpm) with heating by a heat-gun at 100 °C (heat-gun preset temperature) for 99 min. The catalyst was removed by filtration with a short pad of silica gel (eluent: $CHCl_3$). After concentrating filtrate, the crude mixture was purified by silica gel column chromatography (eluent: hexane) and then purified with GPC (eluent: $CHCl_3$) to afford **8f** (13.9 mg, 0.0588 mmol, 65%).

^{1}H NMR (600 MHz, C_6D_6) δ 7.43 (s, 4H), 2.79 (s, 8H), 1.63 (quint, J = 3.3 Hz, 8H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 135.11, 130.86, 125.60, 29.74, 23.49.

HRMS (DART, positive) *m/z*: $[M]^+$ Calcd for $C_{18}H_{20}$ 236.15650; Found 236.15542.

Synthesis of 1,2,3,4,4a,5,7,7a,8,9,10,11,11a,12,14,14a-hexadecahydropentacene (8g)



To a 1.5-mL stainless-steel jar containing a 7-mm-diameter stainless-steel ball were added pentacene (**7g**) (56.6 mg, 0.203 mmol, 1.0 eq.), $[RhOH(cod)]_2$ (18.3 mg, 0.040 mmol, 20 mol%), and $B_2(OH)_4$ (147.8 mg, 1.61 mmol, 8.0 eq.) under air. Then, *n*-BuOH (0.20 mL, 2.2 mmol, 11 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with a handmade 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 shaked at 30 Hz (1800 rpm) with heating by a heat-gun at 100 °C (heat-gun preset temperature) for 99 min. The catalyst was removed by filtration with a short pad of silica gel (eluent: $CHCl_3$). After concentrating filtrate, the crude mixture

was purified by silica gel column chromatography (eluent: hexane) and then purified with GPC (eluent: $CHCl_3$) to afford **8g** as a single isomer (white solid, 10.9 mg, 0.0370 mmol, 18%).

^{1}H NMR (500 MHz, C_6D_6) δ 6.84 (s, 2H), 2.74–2.67 (m, 8H), 1.92–1.84 (m, 4H), 1.60–1.69 (2H), 1.60–1.30 (m, 18H).

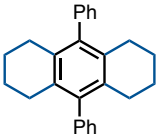
^{13}C NMR (125 MHz, C_6D_6) δ 132.57, 129.97, 34.22, 32.60, 29.23, 23.70.

HRMS (DART, positive) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{31}$ 295.24258; Found 295.24353.

Synthesis of 9,10-diphenyl-1,2,3,4,5,6,7,8-octahydroanthracene (8h) and 9,10-diphenyl-1,2,3,4-tetrahydroanthracene (8h')

To a 5.0-mL stainless-steel jar containing a 10-mm-diameter stainless-steel ball were added 9,10-diphenylanthracene (**7h**) (164.8 mg, 0.499 mmol, 1.0 eq.), $[RhOH(cod)]_2$ (45.5 mg, 0.0997 mmol, 20 mol%), and $B_2(OH)_4$ (358.9 mg, 4.00 mmol, 8.02 eq.) under air. Then, *n*-BuOH (0.35 mL, 4.0 mmol, 8.03 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with a handmade 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 shaked at 30 Hz (1800 rpm) with heating by a heat-gun at 100 °C (heat-gun preset temperature) for 99 min. The catalyst was removed by filtration with a short pad of silica gel (eluent: $CHCl_3$). After concentrating filtrate, the crude mixture was purified by silica gel column chromatography (eluent: hexane/$CHCl_3$ = 100:0 → 80:20) and then purified with GPC (eluent: $CHCl_3$) to afford **8h** as a white solid (69.8 mg, 0.206 mmol, 41%) and **8h'** as a white solid (81.2 mg, 0.243 mmol, 49%).

Compound data of 8h

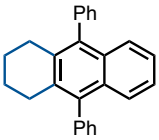


^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.44 (t, *J* = 7.6 Hz, 4H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.14 (dd, *J* = 8.2, 1.4 Hz, 4H), 2.31–2.26 (m, 8H), 1.61–1.56 (m, 8H).

^{13}C NMR (150 MHz, CD_2Cl_2) δ 141.89, 141.32, 132.55, 129.61, 128.89, 126.74, 29.25, 23.60.

HRMS (DART, positive) *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{27}$ 339.21128; Found 339.21111.

Compound data of 8h'

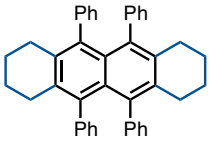


^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.53 (t, *J* = 7.6 Hz, 4H), 7.45 (t, *J* = 7.2 Hz, 2H), 7.32–7.26 (m, 6H), 7.23–7.19 (m, 2H), 2.63–2.58 (m, 4H), 1.74–1.68 (m, 4H).

^{13}C NMR (150 MHz, CD_2Cl_2) δ 140.55, 138.05, 134.11, 131.54, 130.53, 128.88, 127.31, 126.24, 124.89, 29.70, 23.37.

HRMS (DART, positive) *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{23}$ 335.17998; Found 335.18051.

Synthesis of 1,2,3,4,7,8,9,10-octahydrorubrene (8i)



To a 1.5-mL stainless-steel jar containing a 7-mm-diameter stainless-steel ball were added rubrene (**7i**) (53.1 mg, 0.100 mmol, 1.0 eq.), $[RhOH(cod)]_2$ (9.1 mg, 0.020 mmol, 20 mol%), and $B_2(OH)_4$ (71.9 mg, 0.802 mmol, 8.0 eq.) under air. Then, *n*-BuOH (0.20 mL, 2.2 mmol, 22 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with a handmade 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 shaked at 30 Hz (1800 rpm) with heating by a heat-gun at 100 °C (heat-gun preset temperature) for 99 min. The catalyst was removed by filtration with a short pad of silica gel (eluent: $CHCl_3$) and the residue was washed with chloroform. After concentrating filtrate, the crude mixture was purified by silica gel column chromatography (eluent: hexane/$CHCl_3$ = 100:0 → 80:20) and then purified with GPC (eluent: $CHCl_3$) to afford **8i** as a pale-yellow solid (27.8 mg, 0.0514 mmol, 51%).

–0.5-mmol scale reaction–

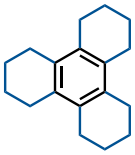
To a 10-mL stainless-steel jar containing two 10-mm-diameter stainless-steel balls were added rubrene (**7i**) (266.8 mg, 0.500 mmol, 1.0 eq.), $[RhOH(cod)]_2$ (76.1 mg, 0.167 mmol, 33 mol%), and $B_2(OH)_4$ (360.1 mg, 4.02 mmol, 8.0 eq.) and *n*-BuOH (0.70 mL, 7.7 mmol, 15 eq.) at 100 °C for 198 min (99 min *2) afforded **8i** as a pale-yellow solid (97.1 mg, 0.179 mmol, 36% yield) through purification by silica gel column chromatography (eluent: hexane/$CHCl_3$ = 100:0 → 60:40) and then purified with GPC (eluent: $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.99–6.91 (m, 12H), 6.64 (d, J = 7.6 Hz, 8H), 2.25 (s, 8H), 1.51 (s, 8H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 143.01, 137.38, 133.54, 130.71, 127.14, 124.75, 29.35, 23.06.

HRMS (DART, positive) *m/z*: $[M+H]^+$ Calcd for $C_{42}H_{37}$ 541.28953; Found 541.28946.

Synthesis of dodecahydrotriphenylene (8j)



To a 1.5-mL stainless-steel jar containing a 7-mm-diameter stainless-steel ball were added triphenylene (**7j**) (22.9 mg, 0.100 mmol, 1.0 eq.), $[RhOH(cod)]_2$ (9.2 mg, 0.020 mmol, 20 mol%), and $B_2(OH)_4$ (71.2 mg, 0.794 mmol, 8.0 eq.) under air. Then, *n*-BuOH (0.10 mL, 1.1 mmol, 11 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with a handmade 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 shaked at 30 Hz (1800 rpm) with heating by a heat-gun at 100 °C (heat-gun preset temperature) for 99 min. The catalyst was removed by filtration with a short pad of silica gel silica gel (eluent: $CHCl_3$). After concentrating filtrate, the crude mixture was purified with GPC (eluent: $CHCl_3$) to afford **8j** as a white solid (19.6 mg, 0.0815 mmol, 82%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.58 (brs, 12H), 1.79 (brs, 12H).

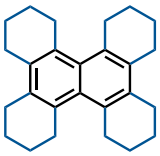
^{13}C NMR (150 MHz, $CDCl_3$) δ 132.61, 26.82, 23.06.

HRMS (DART, positive) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{25}$ 241.19563; Found 241.19471.

Synthesis of 1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16-hexadecahydrodibenzo[*g*,*p*]chrysene (8k)

To a 1.5-mL stainless-steel jar containing a 7-mm-diameter stainless-steel ball were added dibenzo[*g*,*p*]chrysene (**7k**) (65.8 mg, 0.200 mmol, 1.0 eq.), $[RhOH(cod)]_2$ (9.2 mg, 0.020 mmol, 20 mol%), and $B_2(OH)_4$ (151.0 mg, 1.60 mmol, 8.0 eq.) under air. Then, *n*-BuOH (0.10 mL, 1.1 mmol, 6 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with a handmade 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 shaked at 30 Hz (1800 rpm) with heating by a heat-gun at 90 °C (heat-gun preset temperature) for 60 min. The catalyst was removed by filtration with a short pad of silica gel silica gel (eluent: $CHCl_3$). After concentrating filtrate, the crude mixture was purified with GPC (eluent: $CHCl_3$) to afford **8k** as a white solid (6.7 mg, 0.0200 mmol, 9.7%), **8k'** as a white solid (8.0 mg, 0.0235 mmol, 12%), **8k''** as a white solid (11.3 mg, 0.0336 mmol, 17%), **8k'''** as a white solid (2.3 mg, 0.0069 mmol, 4%).

Compound data of 8k

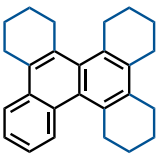


^{1}H NMR (600 MHz, $CDCl_3$) δ 3.06 (t, *J* = 5.5 Hz, 2H), 2.71 (t, *J* = 6.9 Hz, 2H), 1.93–1.87 (m, 2H), 1.63–1.56 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 134.28, 132.08, 131.03, 32.70, 27.27, 23.53, 23.46.

HRMS (DART, positive) *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{33}$ 345.25823; Found 345.25809.

Data of 1,2,3,4,5,6,7,8,9,10,11,12-dodecahydrodibenzo[*g*,*p*]chrysene (8k')



^{1}H NMR (600 MHz, $CDCl_3$) δ 8.44 (d, *J* = 8.2 Hz, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.49 (t, *J* = 6.9 Hz, 1H), 7.40 (t, *J* = 6.9 Hz, 1H), 3.41 (t, *J* = 5.8 Hz, 2H), 3.16 (t, *J* = 6.5 Hz, 2H), 3.14–3.06 (m, 4H), 2.82 (t, *J* = 7.2 Hz, 2H), 2.80 (t, *J* = 6.9 Hz, 2H), 2.06–1.90 (m, 6H), 1.72–1.58 (m, 6H).

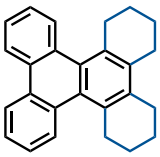
^{13}C NMR (150 MHz, $CDCl_3$) δ 134.52, 133.68, 132.96, 132.57, 131.80, 131.74, 131.24, 129.73, 129.50, 128.54, 128.13, 125.28, 123.27, 122.54, 33.94, 32.81, 32.57, 27.05, 26.76, 26.54, 23.86, 23.74, 23.53, 23.42, 23.31, 23.16.

HRMS (DART, positive) *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{29}$ 341.22693; Found 341.22586.

Data of 1,2,3,4,13,14,15,16-octahydrodibenzo[*g*,*p*]chrysene (8k'')

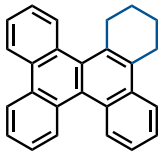
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.51 (d, *J* = 7.6 Hz, 2H), 8.37 (d, *J* = 8.2 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 2H), 3.41 (t, *J* = 5.8 Hz, 4H), 2.86 (t, *J* = 6.9 Hz, 4H), 2.03–1.97 (m, 4H), 1.68–1.62 (m, 4H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 134.56, 131.89, 130.76, 130.49, 130.34, 128.41, 125.96, 125.57, 123.30, 33.40, 26.36, 23.61, 23.31.



HRMS (DART, positive) *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{25}$ 337.19563; Found 337.19554.

Data of 1,2,3,4-tetrahydrodibenzo[*g*,*p*]chrysene (8k''')

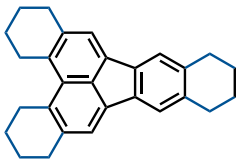


^{1}H NMR (600 MHz, $CDCl_3$) δ 8.71 (d, *J* = 8.2 Hz, 1H), 8.67–8.64 (m, 3H), 8.43 (d, *J* = 8.2 Hz, 1H), 8.15 (d, *J* = 8.2 Hz, 1H), 7.65–7.53 (m, 6H), 3.46 (t, *J* = 5.8 Hz, 2H), 3.34 (t, *J* = 6.9 Hz, 2H), 2.17–2.12 (m, 2H), 1.76–1.70 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 132.21, 132.09, 130.85, 130.50 (2C), 130.44, 130.06, 129.68, 129.41, 128.62, 128.40, 128.24, 128.08, 127.68, 126.42, 126.31, 126.11, 125.91, 125.65, 124.74, 123.42 (2C), 122.95, 33.67, 26.35, 26.03, 23.96, 23.60, 23.23.

HRMS (DART, positive) *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{21}$ 333.16433; Found 333.16478.

Synthesis of 1,2,3,4,5,6,7,8,11,12,13,14-dodecahydrobenzo[*a*]naphtho[2,3-*e*]acephenanthrylene (8l)



To a 1.5-mL stainless-steel jar containing a 7-mm-diameter stainless-steel ball were added tribenzo[*b,e,k*]fluoranthene (**7l**) (35.3 mg, 0.100 mmol, 1.0 eq.), $[RhOH(cod)]_2$ (9.2 mg, 0.020 mmol, 20 mol%), and $B_2(OH)_4$ (177.9 mg, 1.98 mmol, 19.8 eq.) added into the jar under air. Then, *n*-BuOH (0.10 mL, 1.1 mmol, 11 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with a handmade 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 shaked at 30 Hz (1800 rpm) with heating by a heat-gun at 100 °C (heat-gun preset temperature) for 99 min. The catalyst was removed by filtration with a short pad of silica gel (eluent: $CHCl_3$). After concentrating filtrate, the crude mixture was purified by silica gel column chromatography (eluent: hexane/$CHCl_3$ = 100:0 → 60:40) and then purified with GPC (eluent: $CHCl_3$) to afford **8l** as a white solid (19.2 mg, 0.0527 mmol, 53%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (s, 2H), 7.51 (s, 2H), 3.39 (s, 4H), 3.06 (s, 4H), 2.89 (s, 4H), 1.87 (s, 12H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 136.84, 136.60, 135.81, 134.80, 134.29, 131.32, 131.18, 121.24, 121.22, 32.18, 31.58, 30.05, 24.09, 23.4, 22.53.

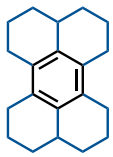
HRMS (DART, positive) *m/z*: $[M+H]^+$ Calcd for $C_{28}H_{29}$ 365.22693; Found 365.22605.

Synthesis of 1,2,3,3*a*,4,5,6,7,8,9,9*a*,10,11,12-tetradecahydroperylene (8m) and 1,2,3,10,11,12-hexahydroperylene (8m')

To a 1.5-mL stainless-steel jar containing a 7-mm-diameter stainless-steel ball were added perylene (**7i**) (25.3 mg, 0.100 mmol, 1.0 eq.), $[RhOH(cod)]_2$ (9.2 mg, 0.020 mmol, 20 mol%), and $B_2(OH)_4$ (90.0 mg, 1.00 mmol, 10 eq.) under air. Then, *n*-BuOH (0.10 mL, 1.1 mmol, 11 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with a handmade 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 shaked at 30 Hz (1800 rpm) at heating at 100 °C (heat-gun preset temperature) for 99 min. The catalyst was removed by filtration with silica gel (eluent: hexane). After concentrating filtrate, the crude mixture was purified by silica gel column chromatography (eluent: hexane) and then purified with GPC (eluent: $CHCl_3$) to afford **8m** as a mixture of *syn* and *anti* isomers (white solid,19.0 mg, 0.0713 mmol, 71%) and **8m'** as a white solid (3.2 mg, 0.012 mmol, 12%).

Compound data of 8m

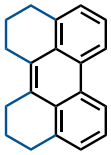


^{1}H NMR (400 MHz, $CDCl_3$) δ 2.81–2.71(m, 3H), 2.69–2.42 (m, 7H), 2.05–1.95 (m, 4H), 1.92–1.84 (m, 4H), 1.82–1.68 (m, 4H), 1.40–1.28 (m, 4H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 135.61(minor), 135.28(major), 131.57(major), 131.47(minor), 38.07(minor), 37.98(major), 30.75(major), 30.47(minor), 26.93(major), 26.87(minor), 23.21(major + minor). According to the integral ratio of carbon peaks, the ratio of isomers was roughly determined 3:1.

HRMS (DART, positive) *m/z*: $[M]^+$ Calcd for $C_{20}H_{26}$ 266.20345; Found 266.20290.

Compound data of 8m'

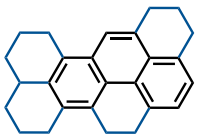


^{1}H NMR (600 MHz, $CDCl_3$) δ 8.53 (d, J = 8.5 Hz, 2H), 7.47 (t, J = 7.2 Hz, 2H), 7.34 (dd, J = 6.8, 1.0 Hz, 2H), 3.12 (t, J = 6.1 Hz, 4H), 3.08 (t, J = 6.1 Hz, 4H), 2.12–2.08 (m, 4H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 136.45, 129.56, 128.94, 128.74, 125.62, 124.82, 120.87, 31.58, 28.17, 23.03.

HRMS (DART, positive) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{19}$ 259.14868; Found 259.14740.

Synthesis of 3,4,5,7,8,9,9a,10,11,12,13,14-dodecahydronaphtho[8,1,2-*bcd*]perylene (8n)



To a 1.5-mL stainless-steel jar containing a 7-mm-diameter stainless-steel ball were added naphtho[8,1,2-*bcd*]perylene (**7n**) (34.3 mg, 0.104 mmol, 1.0 eq.), $[RhOH(cod)]_2$ (19.3 mg, 0.0404 mmol, 40 mol%), and $B_2(OH)_4$ (133.0 mg, 1.48 mmol, 14 eq.) under air. Then, *n*-BuOH (0.10 mL, 1.1 mmol, 11 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with a handmade 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 shaked at 30 Hz (1800 rpm) with heating by a heat-gun at 100 °C (heat-gun preset temperature) for 99 min. The catalyst was removed by filtration with a short pad of silica gel (eluent: $CHCl_3$). After concentrating filtrate, the crude mixture was purified by GPC (eluent: $CHCl_3$) to afford **8n** as a white solid (21.4 mg, 0.0632 mmol, 61%). The structure was determined by the number of proton peaks in aromatic and alkyl regions.

^{1}H NMR (600 MHz, C_6D_6) δ 7.70 (s, 1H), 7.25 (d, J = 6.9 Hz, 1H), 7.21 (d, J = 6.9 Hz, 1H), 3.20 (dd, J = 16.2, 5.8 Hz, 1H), 3.16–3.02 (m, 6H), 2.97 (t, J = 5.8 Hz, 2H), 2.95–2.89 (m, 1H), 2.85–2.77 (m,

1H), 2.72–2.65 (m, 1H), 2.62–2.56 (m, 1H), 2.00–1.70 (m, 8H), 1.36 (qd, J = 12.3, 3.6 Hz, 1H), 1.28 (qd, J = 12.3, 3.6 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 137.05, 133.96, 133.24, 132.90, 130.45, 130.11, 128.16, 128.00, 127.41, 127.36, 125.31, 124.64, 123.92, 119.06, 38.05, 32.19, 31.32, 30.97, 30.71, 29.69, 28.83, 27.24, 26.68, 24.61, 23.53, 23.05.

HRMS (DART, positive) *m/z*: $[M]^+$ Calcd for $C_{26}H_{26}$ 338.20345; Found 338.20272.

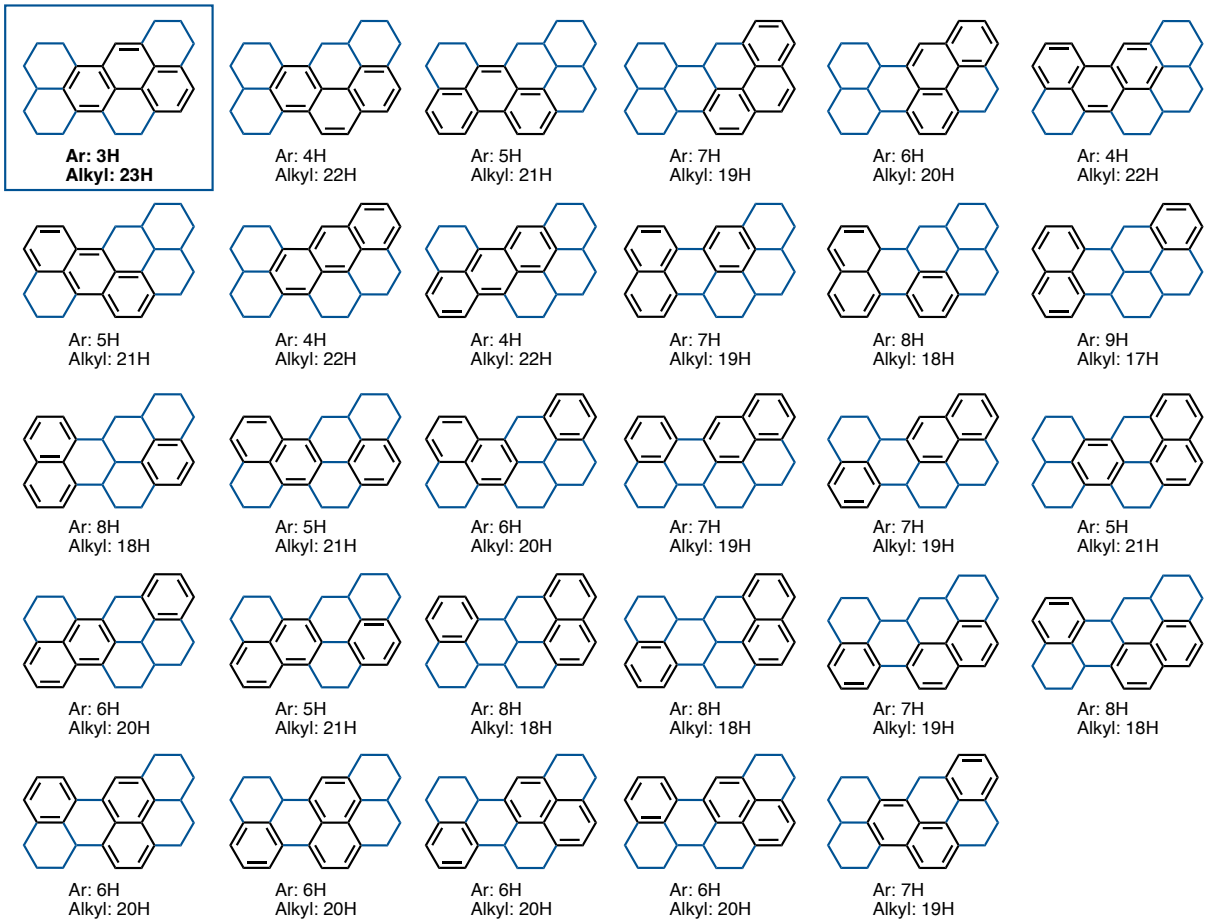
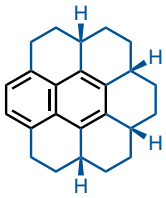


Figure S1. Possible isomers of $C_{26}H_{26}$.

Synthesis of (2aR,4aR,6aS,8aS)-1,2,2a,3,4,4a,5,6,6a,7,8,8a,9,10-tetradecahydrocoronene (8o)



To a 5.0-mL stainless-steel jar containing a 10-mm-diameter stainless-steel ball were added coronene (**7o**) (60.2 mg, 0.200 mmol, 1.0 eq.), $[RhOH(cod)]_2$ (18.4 mg, 0.0403 mmol, 20 mol%), and $B_2(OH)_4$ (144.9 mg, 1.62 mmol, 8.0 eq.) under air. Then, *n*-BuOH (0.35 mL, 3.8 mmol, 19 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with a handmade 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 shaked at 30 Hz (1800 rpm) with heating by a heat-gun at 100 °C (heat-gun preset temperature) for 99 min. The catalyst and remaining coronene were removed by filtration with a short pad of silica gel (eluent: hexane).

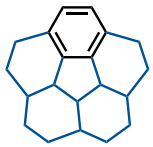
After concentrating filtrate, the crude mixture was purified by GPC (eluent: $CHCl_3$) to afford **8o** as a white solid (15.9 mg, 0.0566 mmol, 25%). A single crystal was obtained by recrystallization from hexane by slow evaporation, and the structure of **8o** was determined by X-ray diffraction analysis.

^{1}H NMR (600 MHz, C_6D_6) δ 7.13 (s, 2H), 3.07 (td, *J* = 13.9, 3.7 Hz, 2H), 2.94 (dt, *J* = 15.1, 3.1 Hz, 2H), 2.75–2.60 (m, 4H), 2.06–1.98 (m, 2H), 1.97–1.93 (m, 2H), 1.73–1.64 (m, 6H), 1.46 (qd, *J* = 12.7, 3.6 Hz, 2H), 1.32–1.20 (m, 4H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 135.02, 134.25, 131.68, 127.42, 122.61, 37.99, 31.19, 30.88, 30.67, 29.27, 28.42, 27.65.

HRMS (DART, positive) *m/z*: $[M+H]^+$ Calcd fo $C_{24}H_{27}$ 315.21128; Found 315.21176.

Synthesis of 1,2,2a,2a1,3,4,4a,4a1,5,6,6a,6a1,7,8-tetradecahydrodibenzo[*ghi*,*mno*]fluoranthene (8p)



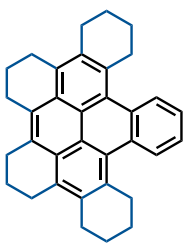
To a 5.0-mL stainless-steel jar containing a 10-mm-diameter stainless-steel ball were added corannulene (**7p**) (128.3 mg, 0.512 mmol, 1.0 eq.), $[RhOH(cod)]_2$ (48.4 mg, 0.105 mmol, 20 mol%), and $B_2(OH)_4$ (359.1 mg, 4.01 mmol, 7.8 eq.) under air. Then, *n*-BuOH (0.35 mL, 3.82 mmol, 7.5 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with a handmade 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 shaked at 30 Hz (1800 rpm) with heating by a heat-gun at 100 °C (heat-gun preset temperature) for 99 min. The catalyst was removed by filtration with a short pad of silica gel (eluent: $CHCl_3$). After concentrating filtrate, the crude mixture was purified by silica gel column chromatography (eluent: hexane) and then purified with GPC (eluent: $CHCl_3$) to afford **8p** as a single isomer (white solid, 11.8 mg, 0.0446 mmol, 9%).

^{1}H NMR (600 MHz, C_6D_6) δ 6.88 (s, 2H), 3.06 (t, *J* = 6.2 Hz, 2H), 2.66–2.57 (m, 5H), 2.04–2.00 (m, 2H), 1.85–1.78 (m, 2H), 1.75–1.70 (m, 2H), 1.51–1.48 (m, 1H), 1.30–1.24 (m, 2H), 1.14–1.02 (m, 4H), 0.91–0.83 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 143.75, 130.85, 125.60, 44.67, 43.35, 30.62, 29.21, 28.91, 28.60, 22.01, 21.96.

HRMS (DART, positive) *m/z*: $[M]^+$ Calcd for $C_{20}H_{24}$ 264.18780; Found 264.18586.

Synthesis of 1,2,3,4,5,6,7,8,9,10,11,12,13,14-tetradecahydrodibenzo[*fg*,*ij*]naphtho[1,2,3,4-*rst*]pentaphene (8q)



To a 1.5-mL stainless-steel jar containing a 7-mm-diameter stainless-steel ball were added dibenzo[*fg,ij*]naphtho[1,2,3,4-*rst*]pentaphene (**7q**) (43.1 mg, 0.101 mmol, 1.0 eq.), $[RhOH(cod)]_2$ (20.1 mg, 0.044 mmol, 0.43 eq.), and $B_2(OH)_4$ (90.8 mg, 1.01 mmol, 10 eq.) under air. Then, *n*-BuOH (0.20 mL, 2.2 mmol, 22 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with

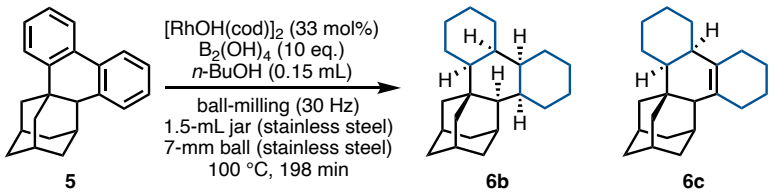
a handmade O-shaped packing made of 1-mm width polyethylene sheet, and the jar was sealed tightly with a wrench and a vise. The reaction jar and a same-weight blank jar (or a same-weight reaction jar) were fixed in a mixer mill (Retsch MM400) and shaked at 30 Hz (1800 rpm) with heating by a heat-gun at 100 °C (heat-gun preset temperature) for 99 min. The catalyst was removed by filtration with a short pad of silica gel (eluent: $CHCl_3$). After concentrating filtrate, the crude mixture was purified by silica gel column chromatography (eluent: hexane/$CHCl_3$ = 100:0 → 90:10) and then purified with GPC (eluent: $CHCl_3$) to afford **8q** as a yellow solid (4.9 mg, 0.011 mmol, 11%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50–8.42 (m, 2H), 7.48–7.42 (m, 2H), 3.65 (t, *J* = 5.5 Hz, 4H), 3.15–3.01 (m, 12H), 2.19–2.11 (m, 4H), 2.10–2.01 (m, 4H), 1.72–1.61 (m, 4H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 132.66, 132.35, 131.81, 131.70, 128.67, 127.24, 126.75, 125.14, 124.66, 123.14, 33.19, 27.59, 27.35, 26.22, 23.52, 23.08, 22.74.

HRMS (ESI, positive) *m/z*: $[M+H]^+$ Calcd for $C_{34}H_{33}$ 441.25823; Found 441.2581.

Synthesis of (4a*R*,4b*S*,8a*S*,8b*R*,10*R*,12*S*,14*R*,14a*R*,14b*R*)-Octadecahydro-1*H*-8b,12:10,14-dimethanocycloocta[*l*]phenanthrene (6b)



To a 1.5-mL stainless-steel jar containing a 7-mm-diameter stainless-steel ball were added 10,11,12,13,14,14a-hexahydro-*9H*-8b,12:10,14-dimethanocycloocta[*l*]phenanthrene (**5**) (27.6 mg, 0.0964 mmol, 1.0 eq.). $[RhOH(cod)]_2$ (14.0 mg, 0.0321 mmol, 33 mol%), and $B_2(OH)_4$ (89.7 mg, 1.00 mmol, 10 eq) under air. Then, *n*-BuOH (0.15 mL, 1.6 mmol, 17 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with a handmade 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 shaked at 30 Hz (1800 rpm) with heating by a heat-gun at 100 °C (heat-gun preset temperature) for 198 min (99 min × 2). The catalyst was removed by filtration with a short pad of silica gel (eluent: hexane). After concentrating filtrate, the crude mixture was purified by GPC (eluent: $CHCl_3$) to afford **6b** (4.9 mg, 0.0164 mmol, 17%) and **6c** (21.1 mg, 0.0712 mmol, 74%).

Compound data of 6b

^{1}H NMR (600 MHz, C_6D_6) δ 2.08–1.99 (m, 4H), 1.95–1.90 (m, 1H), 1.86–1.71 (m, 9H), 1.71–1.62 (m, 5H), 1.60–1.39 (m, 8H), 1.38–1.22 (m, 3H), 1.20–1.09 (m, 3H), 1.06 (dq, *J* = 11.9, 2.6 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 51.78, 47.78, 46.51, 44.93, 43.69, 41.25, 39.89, 39.23, 38.26, 37.00, 33.89, 33.53, 31.17, 30.17, 29.87, 28.98, 28.81, 28.04, 27.93, 25.72, 24.21, 23.9.

HRMS (DART) *m/z*: $[M]^+$ Calcd for $C_{22}H_{34}$ 298.26605; Found 298.26697.

The ^{1}H NMR and ^{13}C NMR spectra of **6b** was identical to those reported in the literature.[S4]

Compound data of 6c

^{1}H NMR (600 MHz, C_6D_6) δ 2.39–2.31 (m, 1H), 2.16–2.10 (m, 2H), 2.08-1.95 (m, 4H), 1.93–1.52 (m, 17H), 1.50–1.44 (m, 3H), 1.43–1.34 (m, 2H), 1.32–1.24 (m, 2H), 1.15–1.12 (m, 1H).

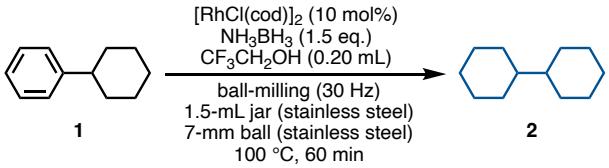
^{13}C NMR (150 MHz, $CDCl_3$) δ 131.67, 128.39, 52.55, 43.09, 42.58, 41.56, 38.63, 37.53, 36.90, 35.80, 32.40, 28.99, 28.86, 28.78, 28.04, 26.74, 26.25, 25.99, 24.63, 23.61, 23.55, 23.14.

HRMS (DART) *m/z*: $[M]^+$ Calcd for $C_{22}H_{32}$ 296.25040; Found 296.25097.

According to the ^{13}C NMR spectrum of **6c**, compound **6c** was found as a single isomer, but its relative configuration was not determined.

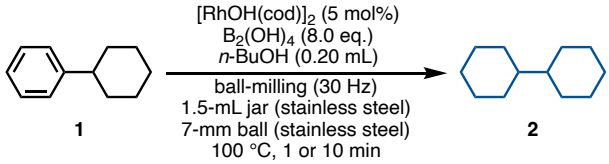
4. Control experiments

4-1. Conditions with [RhCl(cod)]$_2$, NH_3BH_3 and 2,2,2-trifluoroethanol. (Table 1, entry 2).



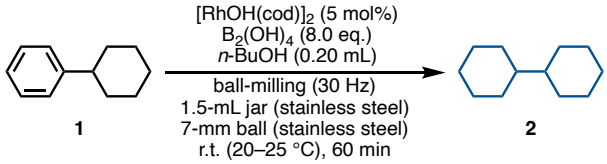
To a 1.5-mL stainless-steel jar containing a 7-mm-diameter stainless-steel ball were added cyclohexylbenzene (**1**) (32.5mg, 0.202 mmol, 1.0 eq), [RhCl(cod)]$_2$ (9.9 mg, 0.020 mmol, 10 mol%), and NH_3BH_3 (10.1 mg, 0.312 mmol, 1.5 eq.) under air. Then, 2,2,2-trifluoroethanol (0.20 mL, 2.78 mmol, 14 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with a handmade 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 shaked at 30 Hz (1800 rpm) with heating by a heat-gun at 100 °C for 60 min. The catalyst was removed by filtration with a short pad of silica gel (eluent: $CHCl_3$) and the residue was washed with chloroform. After concentrating the filtrate, the crude mixture was analyzed by ^{1}H NMR with dibromomethane as an internal standard to determine the formation of **2** (8% NMR yield) and recovery of **1** (89% NMR yield).

4-2. Control experiments with ball-milling for 1 or 10 min. (Table 1, entries 3 and 4.)



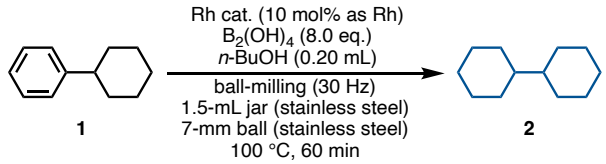
To a 1.5-mL stainless-steel jar containing a 7-mm-diameter stainless-steel ball were added cyclohexylbenzene (**1**) (32.1 mg, 0.200 mmol, 1.0 eq), [RhOH(cod)]$_2$ (4.9 mg, 0.010 mmol, 5.0 mol%), and $B_2(OH)_4$ (144.0 mg, 1.61 mmol, 8.0 eq.) under air. Then, *n*-BuOH (0.20 mL, 2.2 mmol, 11 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with a handmade 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 shaked at 30 Hz (1800 rpm) with heating by a heat-gun at 100 °C (heat-gun preset temperature) for 1 min. The catalyst was removed by filtration with a short pad of silica gel (eluent: $CHCl_3$). After concentrating the filtrate, the crude mixture was analyzed by ^{1}H NMR with dibromomethane as an internal standard to determine the formation of **2** (21% NMR yield). A similar experiment at 100 °C for 10 min resulted in the formation of **2** (99% NMR yield).

4-3. Control experiments at room temperature (20–25 °C). (Table 1, entry 5)



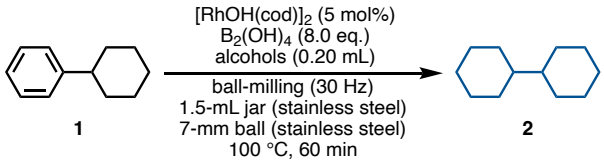
To a 1.5-mL stainless-steel jar containing a 7-mm-diameter stainless-steel ball were added cyclohexylbenzene (**1**) (32.1 mg, 0.200 mmol, 1.0 eq), $[RhOH(cod)]_2$ (4.6 mg, 0.010 mmol, 5.1 mol%), and $B_2(OH)_4$ (144.8 mg, 1.61 mmol, 8.0 eq.) under air. Then, *n*-BuOH (0.20 mL, 2.2 mmol, 11 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with a handmade 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 shaked at 30 Hz (1800 rpm) at room temperature (20–25 °C) for 60 min. The catalyst was removed by filtration with a short pad of silica gel (eluent: $CHCl_3$). After concentrating filtrate, the crude mixture was analyzed by ^1H NMR with dibromomethane as an internal standard to determine the formation of **2** (57% NMR yield) and recovery of **1** (41% NMR yield).

4-4. Control experiments with other Rh catalysts. (Table 1, entries 6–9.)



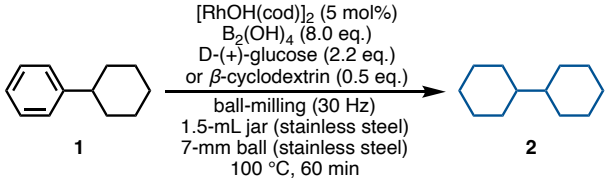
To a 1.5-mL stainless-steel jar containing a 7-mm-diameter stainless-steel ball were added cyclohexylbenzene (**1**) (32.0 mg, 0.200 mmol, 1.0 eq), RhCl(CAAC)(cod) (11.5 mg, 0.0201 mmol, 10 mol%), and $B_2(OH)_4$ (144.2 mg, 1.61 mmol, 8.0 eq.) under air. Then, *n*-BuOH (0.20 mL, 2.2 mmol, 11 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with a handmade 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 shaked at 30 Hz (1800 rpm) with heating by a heat-gun at 100 °C (heat-gun preset temperature) for 60 min. The catalyst was removed by filtration with a short pad of silica gel (eluent: $CHCl_3$). After concentrating filtrate, the crude mixture was analyzed by ^1H NMR with dibromomethane as an internal standard to determine the formation of **2** (9.5% NMR yield) and recovery of **1** (86% NMR yield). Similar experiments with $Rh(BF_4)(cod)_2$ (10 mol%) or $[RhCl(cod)]_2$ (5 mol%) resulted in the formation of **2** ($Rh(BF_4)(cod)_2$: 14%; $[RhCl(cod)]_2$: 57%) and recovery of **1** ($Rh(BF_4)(cod)_2$: 61%; $[RhCl(cod)]_2$: 41%).

4-5. Control experiments with other alcohols. (Table 1, entries 10–12.)



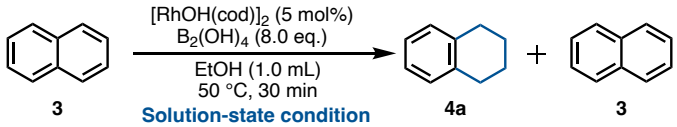
To a 1.5-mL stainless-steel jar containing a 7-mm-diameter stainless-steel ball were added cyclohexylbenzene (**1**) (32.9 mg, 0.205 mmol, 1.0 eq), $[RhOH(cod)]_2$ (4.4 mg, 0.0096 mmol, 4.7 mol%), and $B_2(OH)_4$ (144.9 mg, 1.61 mmol, 8.0 eq.) under air. Then, EtOH (0.20 mL) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with a handmade 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 shaked at 30 Hz (1800 rpm) with heating by a heat-gun at 100 °C (heat-gun preset temperature) for 60 min. The catalyst was removed by filtration with a short pad of silica gel (eluent: $CHCl_3$). After concentrating filtrate, the crude mixture was analyzed by ^1H NMR with dibromomethane as an internal standard to determine the formation of **2** (71% NMR yield). Similar experiments with 2-propanol or 2,2,2-trifluoroethanol resulted in the formation of **2** as indicated in table 1 of main manuscript.

4-6. Control experiments with solid state alcohols. (Table 1, entries 13, 14.)



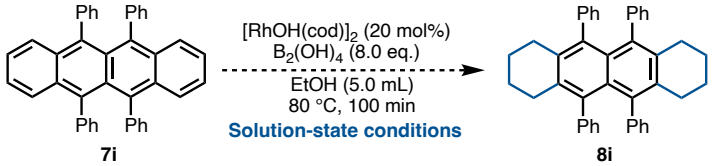
To a 1.5-mL stainless-steel jar containing a 7-mm-diameter stainless-steel ball were added cyclohexylbenzene (**1**) (32.2 mg, 0.200 mmol, 1.0 eq), $[RhOH(cod)]_2$ (4.6 mg, 0.010 mmol, 5.0 mol%), and $B_2(OH)_4$ (143.7 mg, 1.60 mmol, 8.0 eq.) under air. Then, D-(+)-glucose (79.3 mg, 0.440 mmol, 2.2 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with a handmade 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 shaked at 30 Hz (1800 rpm) with heating by a heat-gun at 100 °C (heat-gun preset temperature) for 60 min. The catalyst was removed by filtration with a short pad of silica gel (eluent: $CHCl_3$). After concentrating filtrate, the crude mixture was analyzed by ^1H NMR with dibromomethane as an internal standard to determine the formation of **2** (29% NMR yield). The starting material **1** was recovered 67% NMR yield. Similar experiment with *β*-cyclodextrin (113.4 mg, 0.10 mmol, 0.50 eq.) resulted in the formation of **2** (24% NMR yield) and recovery of **1** (70% NMR yield).

4-7. Solution state conditions with naphthalene.



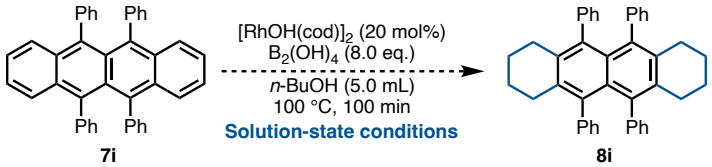
To a Schlenk flask were added naphthalene (**3**) (26.1 mg, 0.203 mmol, 1.0 eq.), $[RhOH(cod)]_2$ (4.8 mg, 0.011 mmol, 5.2 mol%), and $B_2(OH)_4$ (144.3 mg, 1.61 mmol, 8.0 eq) under Ar. Then, ethanol (1.0 mL, 17.1 mmol, 84 eq.) was added under Ar. The mixture was stirred at 50 °C for 30 min under Ar. After stirring, the reaction was diluted with $CHCl_3$, and the catalyst was removed by filtration with a short pad of silica gel (eluent: $CHCl_3$). After concentrating filtrate, the crude mixture was analyzed by ^1H NMR with dibromomethane as an internal standard to determine the formation of **4a** (45% NMR yield) and recovery of **3** (45% NMR yield).

4-8. Solution state conditions with rubrene in EtOH.



To a Schlenk flask were added rubrene (**7i**) (53.1 mg, 0.0997 mmol, 1.0 eq.), $[RhOH(cod)]_2$ (9.2 mg, 0.020 mmol, 20 mol%), and $B_2(OH)_4$ (71.8 mg, 0.801 mmol, 8.0 eq) under Ar. Then, ethanol (5.0 mL, 85.5 mmol, 860 eq.) was added under Ar. The mixture was stirred at 80 °C for 100 min under Ar. After stirring, the reaction was diluted with $CHCl_3$, and the catalyst was removed by filtration with a short pad of silica gel (eluent: $CHCl_3$). After concentrating filtrate, the crude mixture was analyzed by ^1H NMR with dibromomethane as an internal standard to determine only the recovery of **7i**. **8i** was not detected by APCI-MS.

4-9. Solution state conditions with rubrene in *n*-BuOH.



To a Schlenk flask were added rubrene (**7i**) (53.4 mg, 0.100 mmol, 1.0 eq.), $[RhOH(cod)]_2$ (9.4 mg, 0.021 mmol, 21 mol%), and $B_2(OH)_4$ (71.2 mg, 0.795 mmol, 8.0 eq) under Ar. Then, *n*-BuOH (1.0 mL, 11 mmol, 110 eq.) was added under Ar. The mixture was stirred at 100 °C for 100 min under Ar. After stirring, the reaction was diluted with $CHCl_3$, and the catalyst was removed by filtration with a short pad of silica gel (eluent: $CHCl_3$). After concentrating filtrate, the crude mixture was analyzed by ^1H NMR. The trace amount of **8i** was detected by ^1H NMR.

Unsuccessful substrates

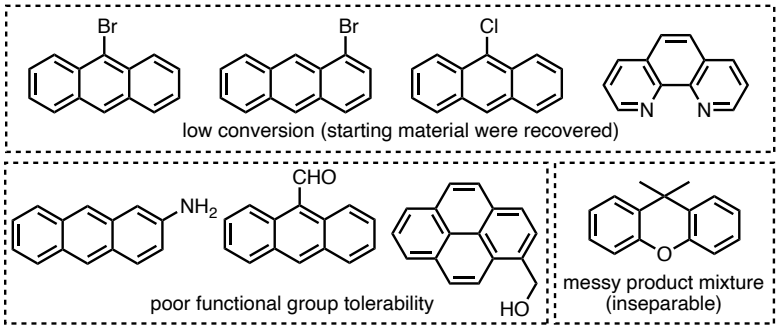


Figure S2. Unsuccessful Rh-catalyzed mechanochemical transfer hydrogenation using 9-bromoanthracene, 1-bromoanthracene, 9-chloroanthracene, 1,10-phenanthroline, 2-aminoanthracene, 9-anthracenecarboxaldehyde, 1-pyrenemethanol, and 9,9-dimethylxanthene.

Heating reaction at 100 °C

The reactions at higher temperature were conducted by direct heating to the stainless-steel jar with a heat-gun fixed 1 cm above it. According to the measurements of temperature using the stainless-steel jar containing crude mixture by a thermographic camera (FLIR, C2), the heat-gun preset temperature, outer surface temperature of reaction jar, and inner silica gel temperature during or after heating for 60 min were determined as shown in Table S1.

Table S1. Relationship of the reaction temperature and heat-gun preset temperature.

Inner volume of stainless-steel jar	**Weight of stainless-steel jar**	**Heat-gun preset temperature**	**Outer surface temperature of jar**	**Inner crude mixture temperature (reaction temperature)**
1.5 mL	458.0 g	100 °C	77.9 °C	70.3 °C
5.0 mL	437.9 g	100 °C	81.7 °C	74.4 °C

5. Measurements of photophysical properties of 8i

UV/Vis absorption spectra of **8i** (c = 1.53 × 10^{-5} M) in THF were recorded on a SHIMADZU UV-3600 spectrophotometer with a resolution of 0.5 nm. Emission spectrum of **8i** (c = 1.93 × 10^{-6} M) in CH_2Cl_2 was measured with a SHIMADZU RF-6000 spectrofluorophotometer with a resolution of 0.2 nm upon excitation at 340 nm. The dilute solution in degassed spectral grade THF in a 1.0 × 1.0 cm square quartz cell was used for measurements.

6. Measurements of AIE properties of 8i

Emission spectra of **8i** (c = 1.93 × 10^{-6} M) in THF/H_2O were measured with a SHIMADZU RF-6000 spectrofluorophotometer with a resolution of 0.2 nm upon excitation at 340 nm. The dilute solution in degassed spectral grade THF/H_2O in a 1.0 × 1.0 cm square quartz cell was used for measurements.

7. Solubility evaluation of 7i and 8i

Solubility measurements of rubrene (**7i**) and compound **8i** were conducted by according to the literature. The large amount of compound (rubrene and **8i**) and hexane were added vial and the mixture was stirred for eight hour at room temperature (20–25 °C). Then the saturated mixture was filtered using a syringe filter (pore size: 45 μm) and a fixed volume of hexane (1.5 mL) was measured from the filtrate with a syringe and concentrated into a flask or a vial under reduced pressure until the weight of concentrated solid (X mg) was not changed. The solubility was determined according to X/1.5 (mg/mL).

Rubrene: < 0.2 mg/mL

8i: 0.6 mg/mL (0.5712 mg/mL with precision balance)

8. X-ray crystallographic analysis

Details of the crystal data and a summary of the intensity data collection parameters for **6c**, **8i** and **8o** are listed in Table S2. 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)[S5] and refined by full-matrix least-squares techniques against F^2 (SHELXL-2018/3)[S6] by using Olex2 software package.[S7] The intensities were corrected for Lorentz and polarization effects. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions. CCDC 2389851 and 2389852 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S2. Crystallographic data and structure refinement details of **8i** and **8o**

	6c	**8i**	**8o**
CCDC number	2425787	2389852	2389851
formula	$C_{22}H_{32}$	$C_{42}H_{36}$	$C_{24}H_{26}$
FW	296.47	540.75	314.47
T (K)	123(2)	123(2)	123(2)
λ (Å)	0.71073	0.71073	0.71073
crystal system	*monoclinic*	*orthorhombic*	*triclinic*
space group	*C2/c*	*Ccce*	*P-1*
a (Å)	9.5878(7)	25.7173(12)	8.7615(3)
b (Å)	17.3304(17)	13.4757(4)	10.5013(3)
c (Å)	20.2331(15)	8.5134(4)	17.8315(3)
α (deg)	90	90	84.768(3)
β (deg)	102.886(8)	90	83.360(3)
γ (deg)	90	90	85.557(3)
V (Å^3)	3277.3(5)	2950.4(2)	1619.11(9)
Z	8	4	4
ρ_{calc} (g·cm^{-3})	1.202	1.217	1.290
μ (mm^{-1})	0.067	0.108	0.072
F (000)	1312.0	1152.0	680.0
cryst size (mm^3)	0.25 × 0.2 × 0.2	0.1 × 0.1 × 0.02	0.6 × 0.3 × 0.15
2θ range (deg)	4.7–58.934	5.878–59.114	3.904–59.614
reflections collected	10234	8767	22243
independent reflections/R_{int}	3835/0.0881	1797 / 0.0301	7678/ 0.0382
parameters	199	96	433
GOF on F^2	1.042	1.044	1.103
R_1, wR_2 [I>2σ(I)]	0.0720, 0.1933	0.0387,0.1035	0.0456, 0.1274
R_1, wR_2 (all data)	0.1014, 0.2108	0.0466, 0.1089	0.0561, 0.1334

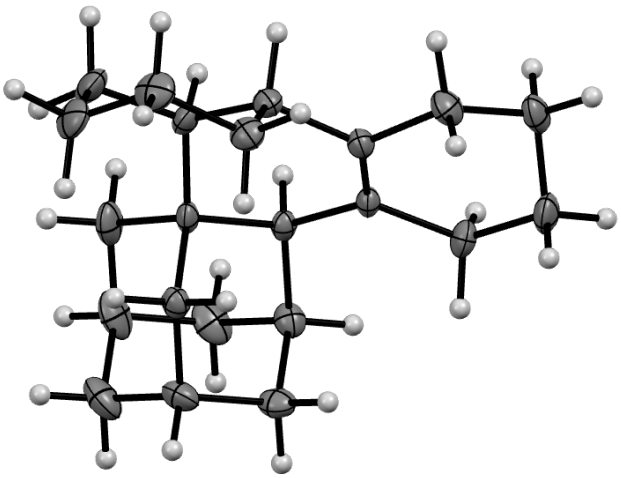


Figure S3. ORTEP drawing of **6c** with 50% probability.

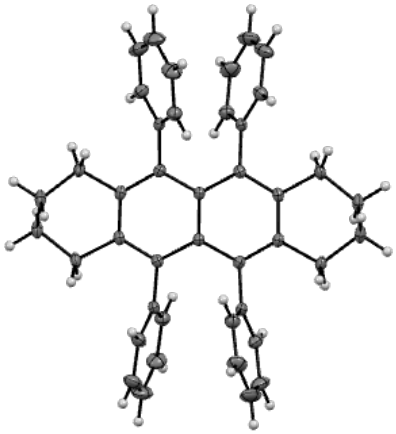


Figure S4. ORTEP drawing of **8**i with 50% probability.

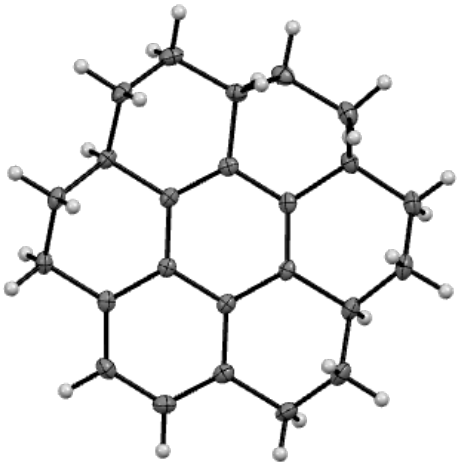


Figure S5. ORTEP drawing of **8o** with 50% probability.

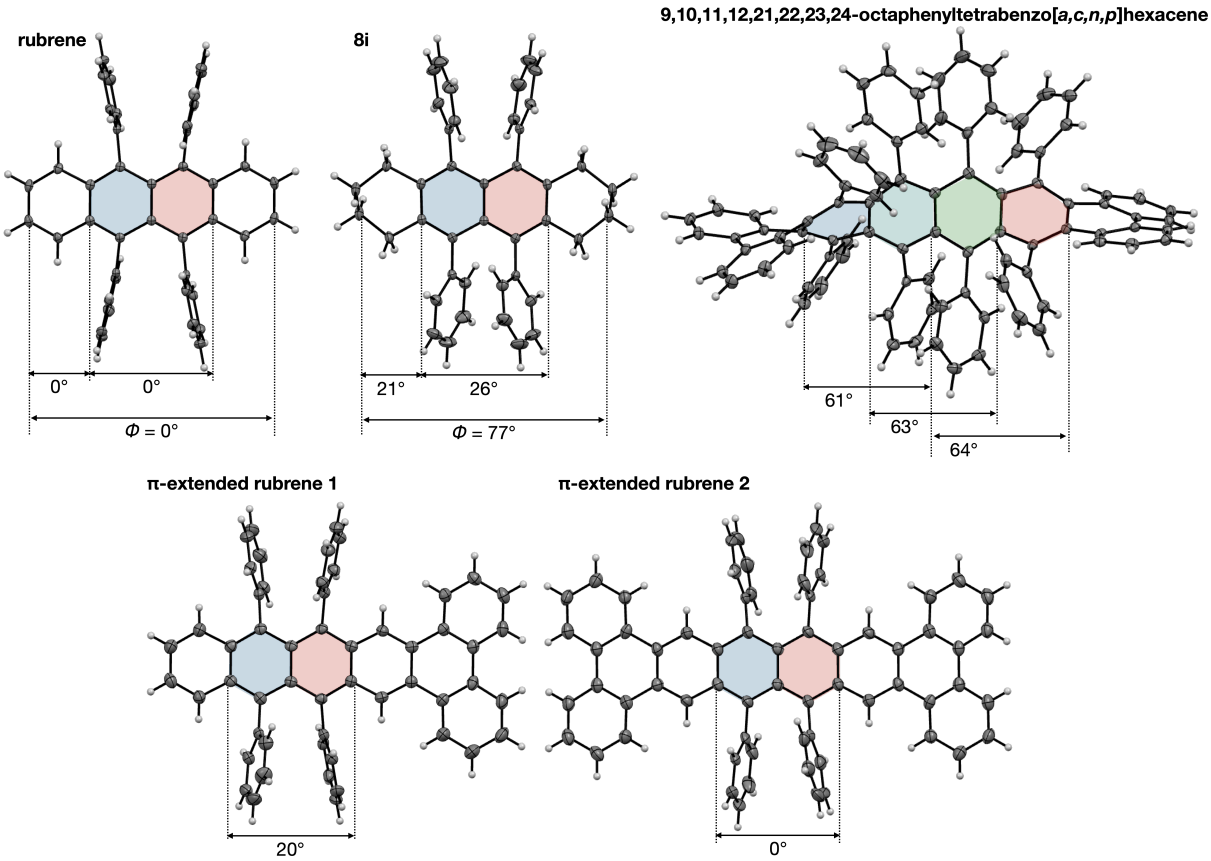


Figure S6. Oak Ridge Thermal-Ellipsoid Plot (ORTEP) program drawing of the top view of rubrene,[S8] **8i**, 9,10,11,12,21,22,23,24-octaphenyltetrabenzo[*a,c,n,p*]hexacene,[S9] and π-extended rubrenes.[S10] ϕ is an end-to-end dihedral angle of two terminal benzene cores.

9. Computational Study

The Gaussian 16 program[S11] running on a AMD EPYC 7763 (64 core, 2.45 GHz) system was used for optimization (B3LYP/6-31G+(d,p))[S12,S13]. Structures were optimized without any symmetry assumptions. Zero-point energy, enthalpy, and Gibbs free energy at 298.15 K and 1 atm were estimated in the gas-phase studies. Harmonic vibration frequency calculation at the same level was performed to verify all stationary points as local minima (with no imaginary frequency).

TD-DFT calculation of **8i**

C	-0.6940380	2.4551340	0.1703190	C	5.1623570	1.9009690	-0.4398520	H	-0.0708440	-4.9517580	1.5299030
C	0.6939580	2.4551400	-0.1704030	C	5.4205870	1.5306430	-1.7630760	H	1.0936080	-5.8986650	0.6060040
C	1.3960060	1.2517860	-0.2176920	C	4.3790160	1.0415180	-2.5550950	H	-1.0933490	-5.8987240	-0.6057770
C	0.7176270	0.0000160	0.0000920	C	3.0917750	0.9242810	-2.0248240	H	0.0711020	-4.9518860	-1.5297400
C	-0.7176280	-0.0000150	0.0000880	C	-2.8192120	1.2934670	0.6973350	H	-2.1498380	-3.9659840	0.3156090
C	-1.3960490	1.2517520	0.2177220	C	2.8192100	-1.2933800	0.6974480	H	-2.0001020	-3.6505110	-1.3921880
C	1.3960620	-1.2517340	0.2178060	C	3.0918420	-0.9244800	2.0249740	H	-3.6852810	-2.0712690	1.1154190
C	0.6940710	-2.4551200	0.1704270	C	4.3791060	-1.0417180	2.5551870	H	-5.9665530	-2.2752130	0.1878950
C	-0.6939250	-2.4551520	-0.1702930	C	5.4207090	-1.5305410	1.7630240	H	-6.4232350	-1.6226430	-2.1708750
C	-1.3959930	-1.2518010	-0.2176130	C	5.1624870	-1.9005680	0.4397140	H	-4.5658480	-0.7546150	-3.5862730
C	-1.4139260	3.7674990	0.4743280	C	3.8737180	-1.7876250	-0.0841150	H	-2.2824080	-0.5503330	-2.6458710
C	-0.4906460	4.9833920	0.5849750	C	-3.0918380	0.9250830	2.0250020	H	3.6852300	2.0721560	1.1149220
C	0.4904720	4.9833150	-0.5853760	C	-4.3791240	1.0424240	2.5551410	H	5.9664530	2.2759290	0.1872600
C	1.4138210	3.7674990	-0.4744750	C	-5.4207540	1.5308190	1.7627520	H	6.4231710	1.6222810	-2.1712070
C	1.4139840	-3.7674700	0.4744230	C	-5.1625410	1.9003110	0.4392910	H	4.5658540	0.7533780	-3.5861610
C	0.4906830	-4.9833280	0.5852560	C	-3.8737490	1.7872760	-0.0844630	H	2.2824550	0.5492900	-2.6456260
C	-0.4904340	-4.9833780	-0.5850960	H	-2.0002640	3.6505150	1.3921410	H	2.2824970	-0.5497230	2.6458860
C	-1.4137620	-3.7675270	-0.4743810	H	-2.1500070	3.9658820	-0.3156760	H	4.5659390	-0.7538110	3.5863190
C	-2.8191390	-1.2935530	-0.6972730	H	0.0708910	4.9519750	1.5296210	H	6.4233130	-1.6221740	2.1711080
C	-3.8736560	-1.7875990	0.0844020	H	-1.0935960	5.8987160	0.6056030	H	5.9666070	-2.2752890	-0.1875090
C	-5.1624230	-1.9006480	-0.4394090	H	1.0933620	5.8986740	-0.6061750	H	3.6853400	-2.0715300	-1.1150660
C	-5.4206320	-1.5309280	-1.7628070	H	-0.0710520	4.9516710	-1.5300220	H	-2.2824720	0.5506550	2.6460860
C	-4.3790210	-1.0422940	-2.5550760	H	2.1497770	3.9660280	0.3156140	H	-4.5659550	0.7549240	3.5863870
C	-3.0917590	-0.9249470	-2.0248810	H	2.0002880	3.6504370	-1.3921920	H	-6.4233760	1.6225260	2.1707750
C	2.8191380	1.2934690	-0.6973790	H	2.0004480	-3.6504390	1.3921450	H	-5.9666870	2.2746870	-0.1881070
C	3.8736140	1.7880150	0.0840370	H	2.1499460	-3.9659270	-0.3156790	H	-3.6853710	2.0707650	-1.1155290

Table S3. TD-DFT (B3LYP-D3/6-31G+(d,p)) vertical one-electron excitations (representative 9 states) calculated for the conformation of optimized **8i**.

Exited state	Energy / eV	Wavelength / nm	Oscillator strength (*f*)	Description
1	3.5142	352.81	0.2104	HOMO → LUMO
2	3.8311	323.63	0.0021	HOMO–1 → LUMO HOMO → LUMO+1
3	4.2329	292.91	0.0003	HOMO–2 → LUMO
4	4.2425	292.25	0.0000	HOMO → LUMO+2
5	4.2958	282.62	0.0100	HOMO–3 → LUMO
7	4.3784	283.17	0.0807	HOMO → LUMO+1 HOMO → LUMO+5
9	4.5195	274.33	0.2125	HOMO → LUMO+5 HOMO–1 → LUMO
16	4.8184	257.31	0.1956	HOMO → LUMO+10
19	4.9461	250.67	0.1058	HOMO–1 → LUMO+1

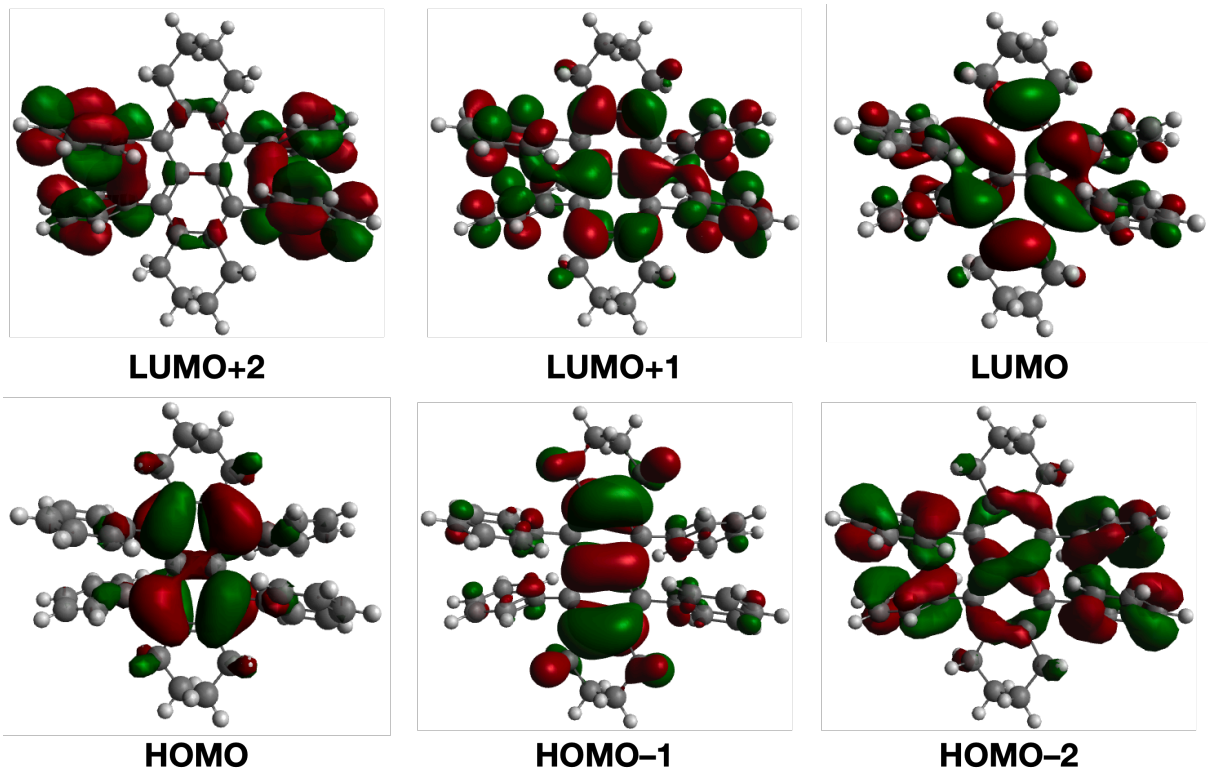


Figure S7. Frontier molecular orbitals of **8i**.

10. References

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11. ^{1}H and ^{13}C NMR spectra of compounds

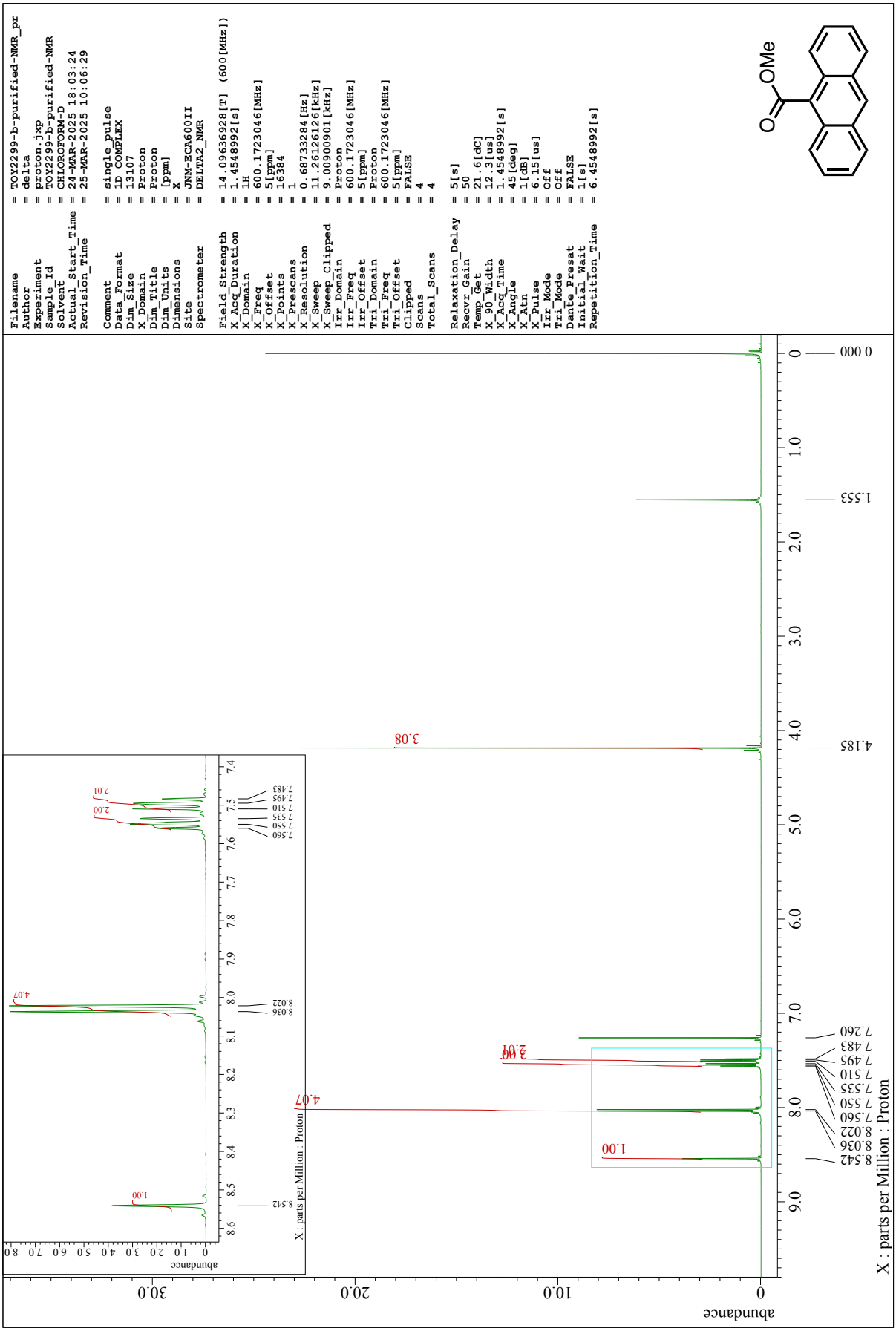

Figure S8. ^{1}H NMR spectrum of **7d** (600 MHz, $CDCl_3$).

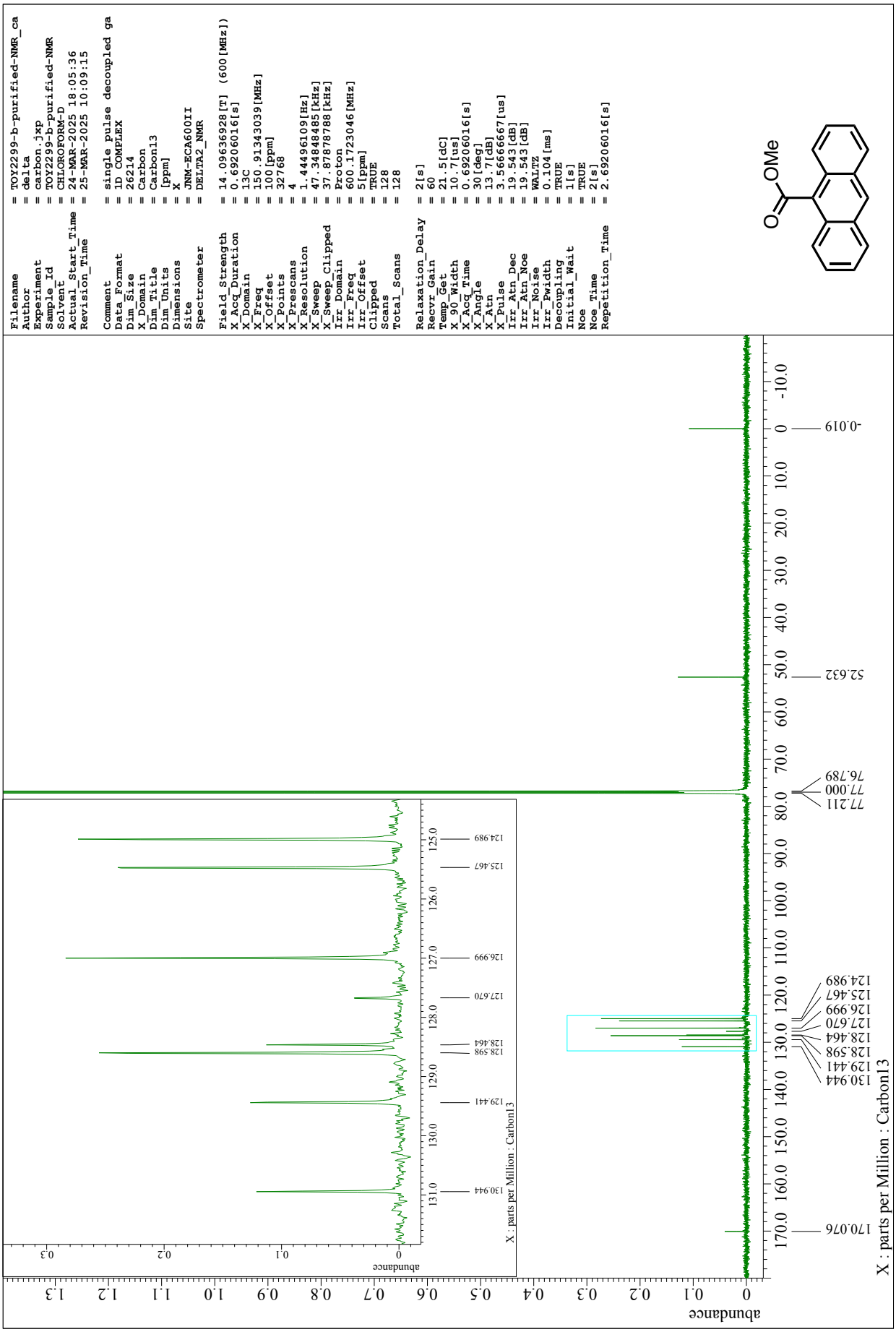

Figure S9. ^{13}C NMR spectrum of **7d** (150 MHz, $CDCl_3$).

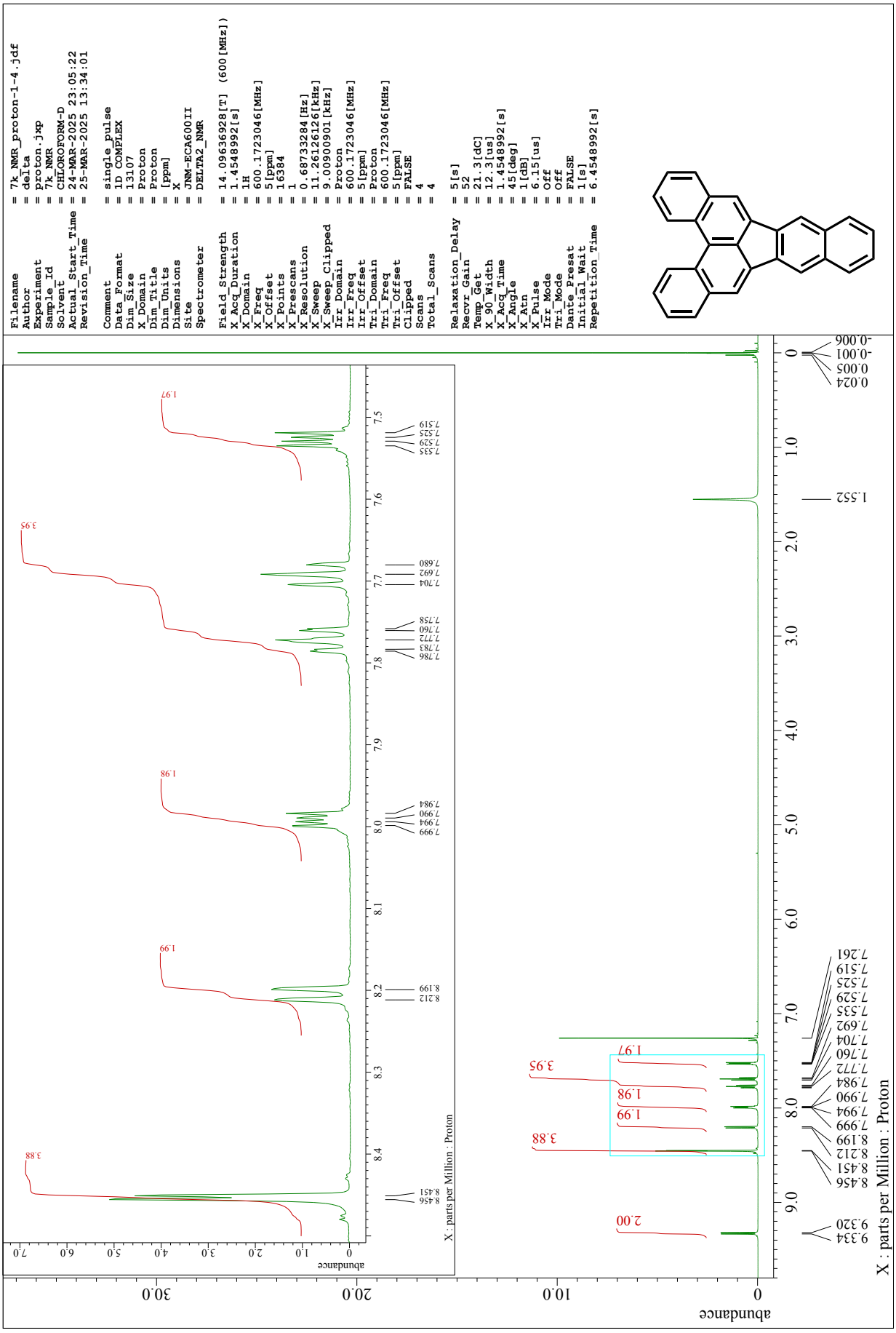

Figure S10. ^{1}H NMR spectrum of **7l** (600 MHz, $CDCl_3$).

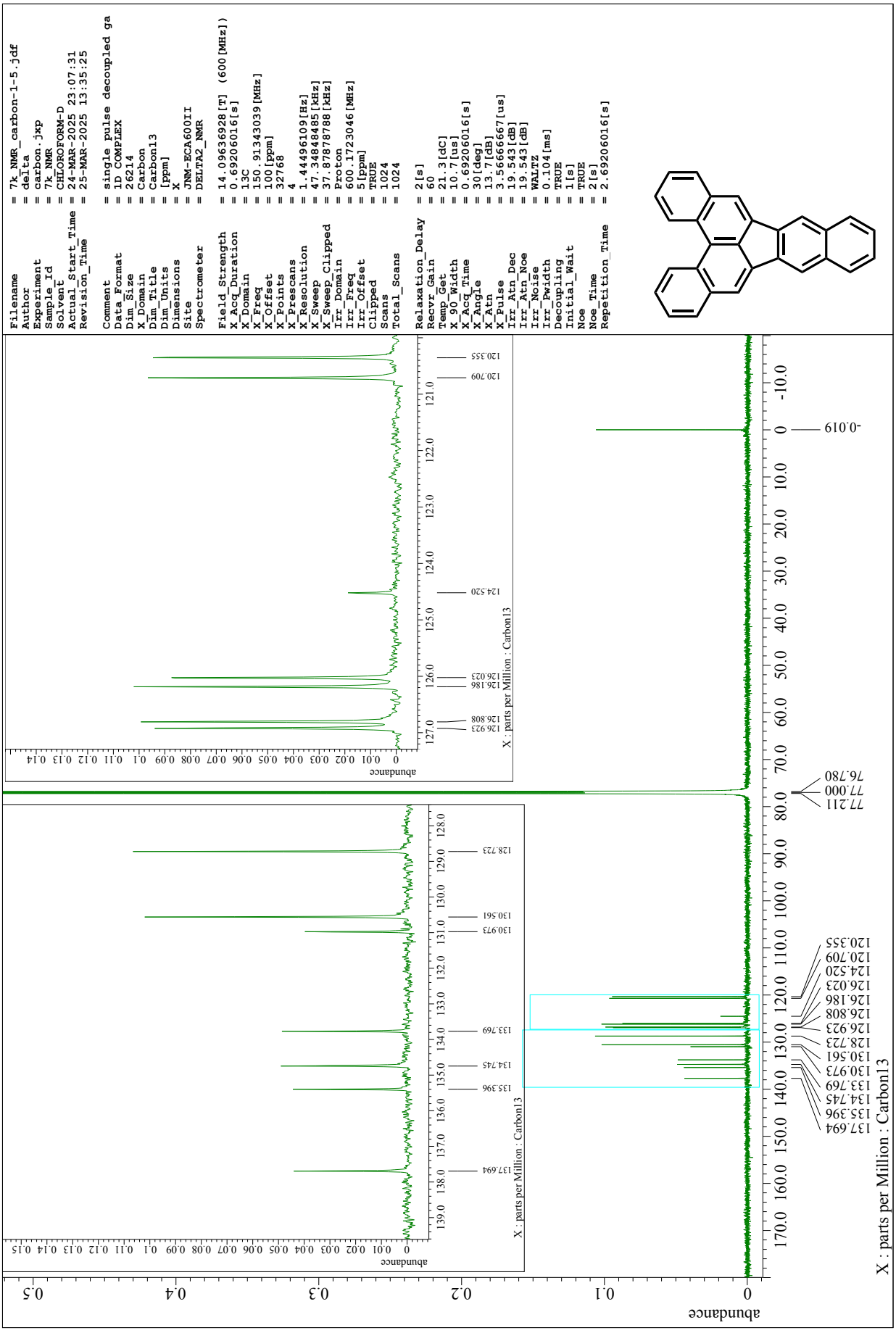

Figure S11. ^{13}C NMR spectrum of **7l** (150 MHz, $CDCl_3$).

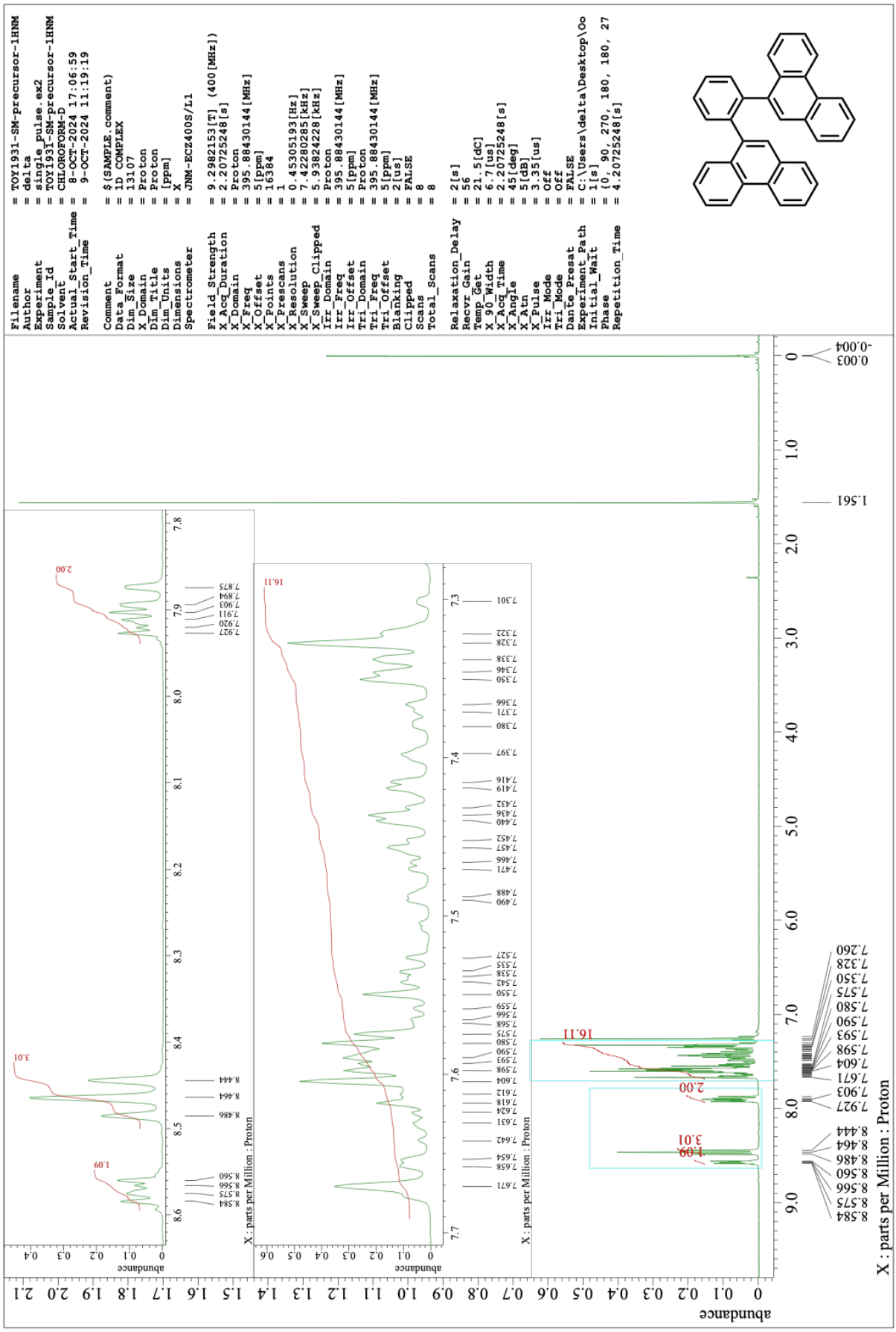

Figure S12. ^{1}H NMR spectrum of **7q'** (600 MHz, $CDCl_3$).

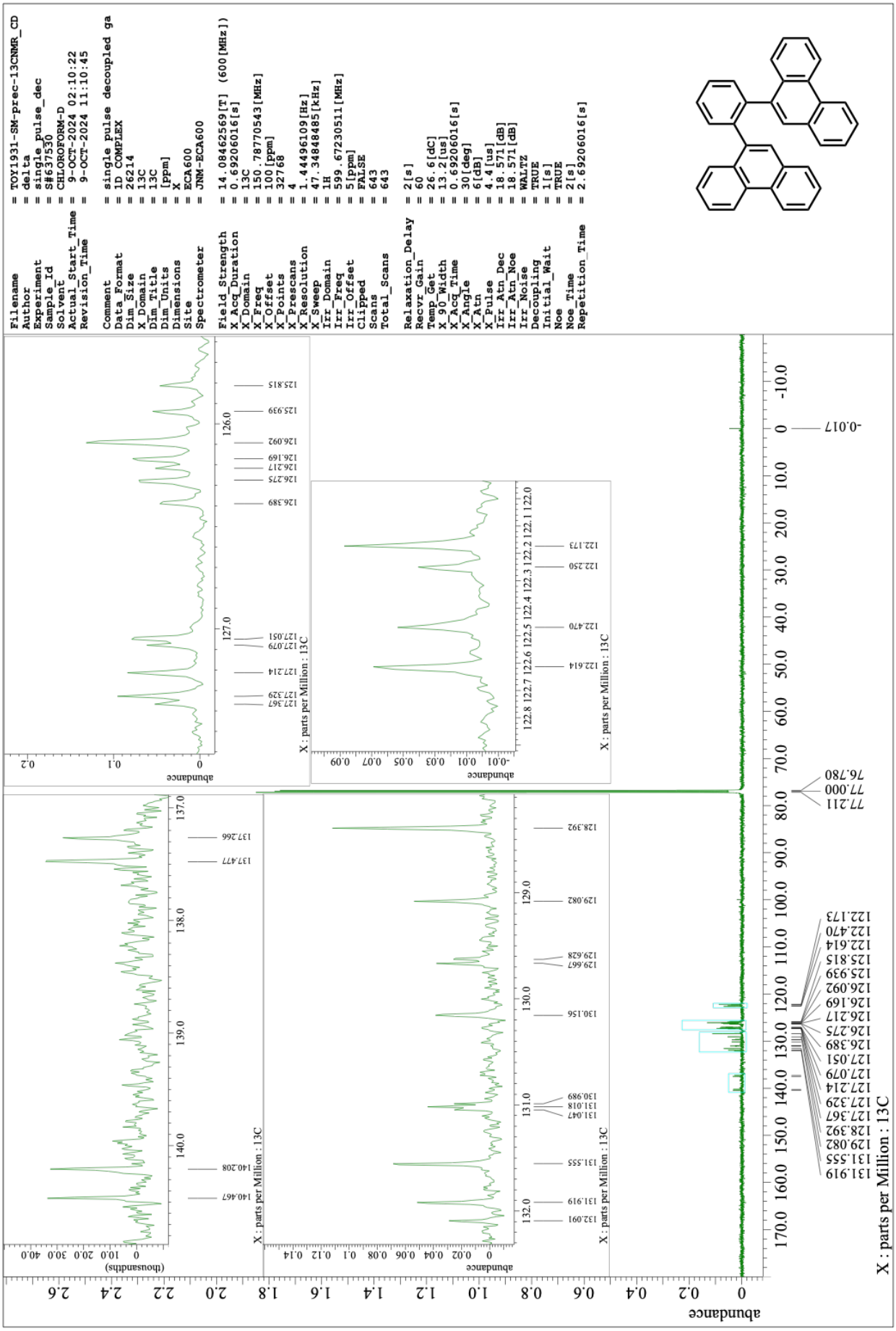

Figure S13. ^{13}C NMR spectrum of **7q'** (150 MHz, $CDCl_3$).

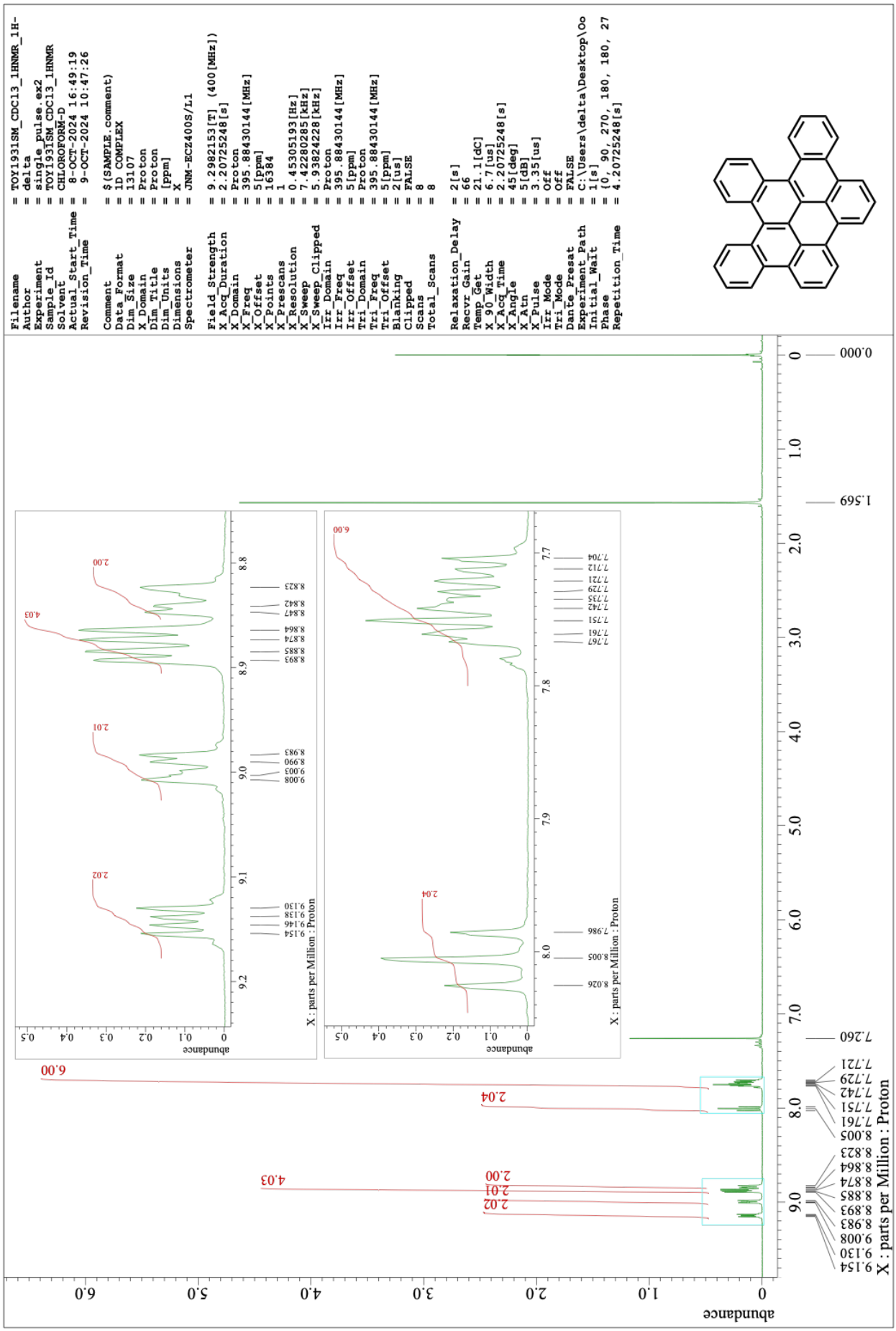

Figure S14. ^{1}H NMR spectrum of **7q** (600 MHz, $CDCl_3$).

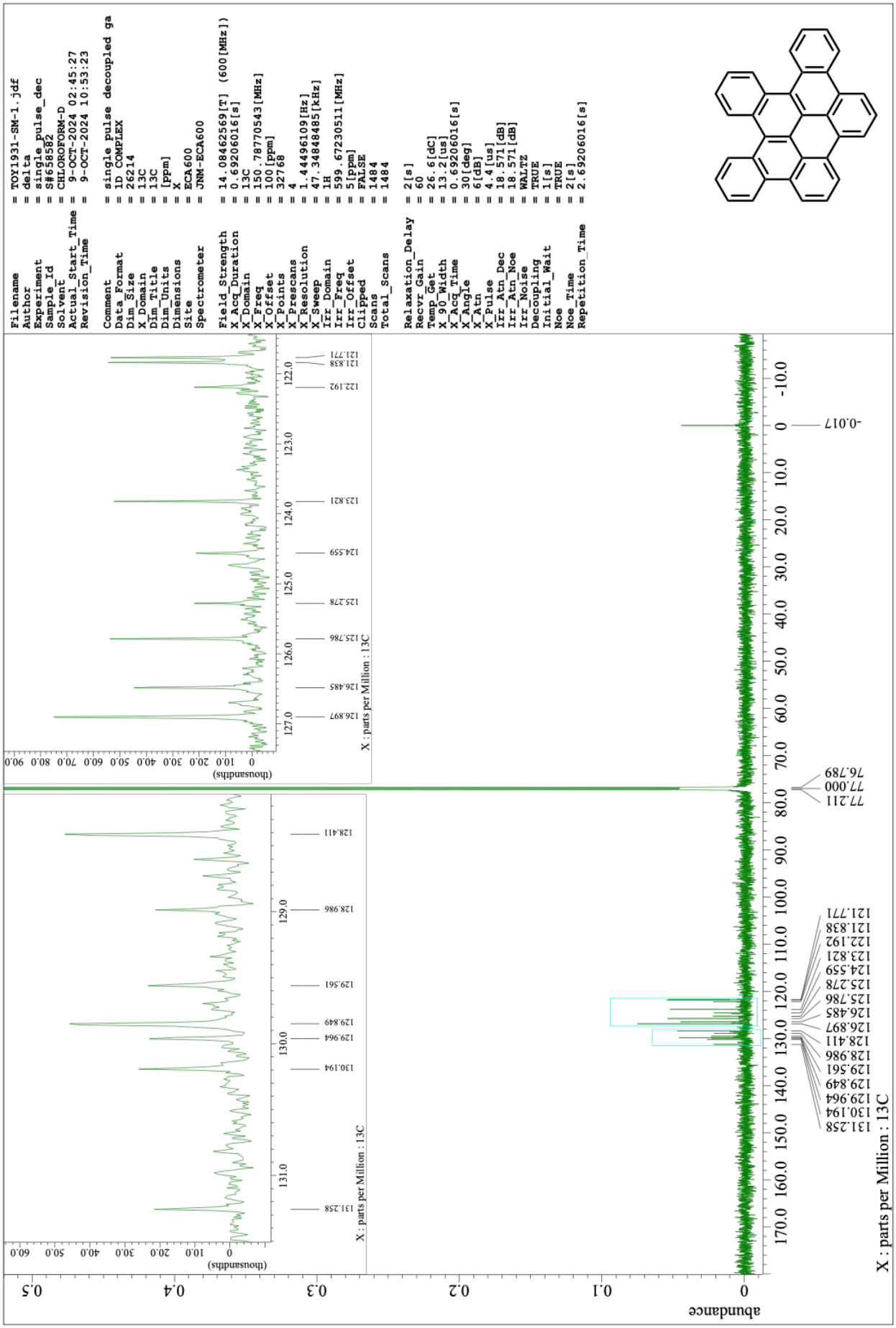

Figure S15. ^{13}C NMR spectrum of **7q** (150 MHz, $CDCl_3$).

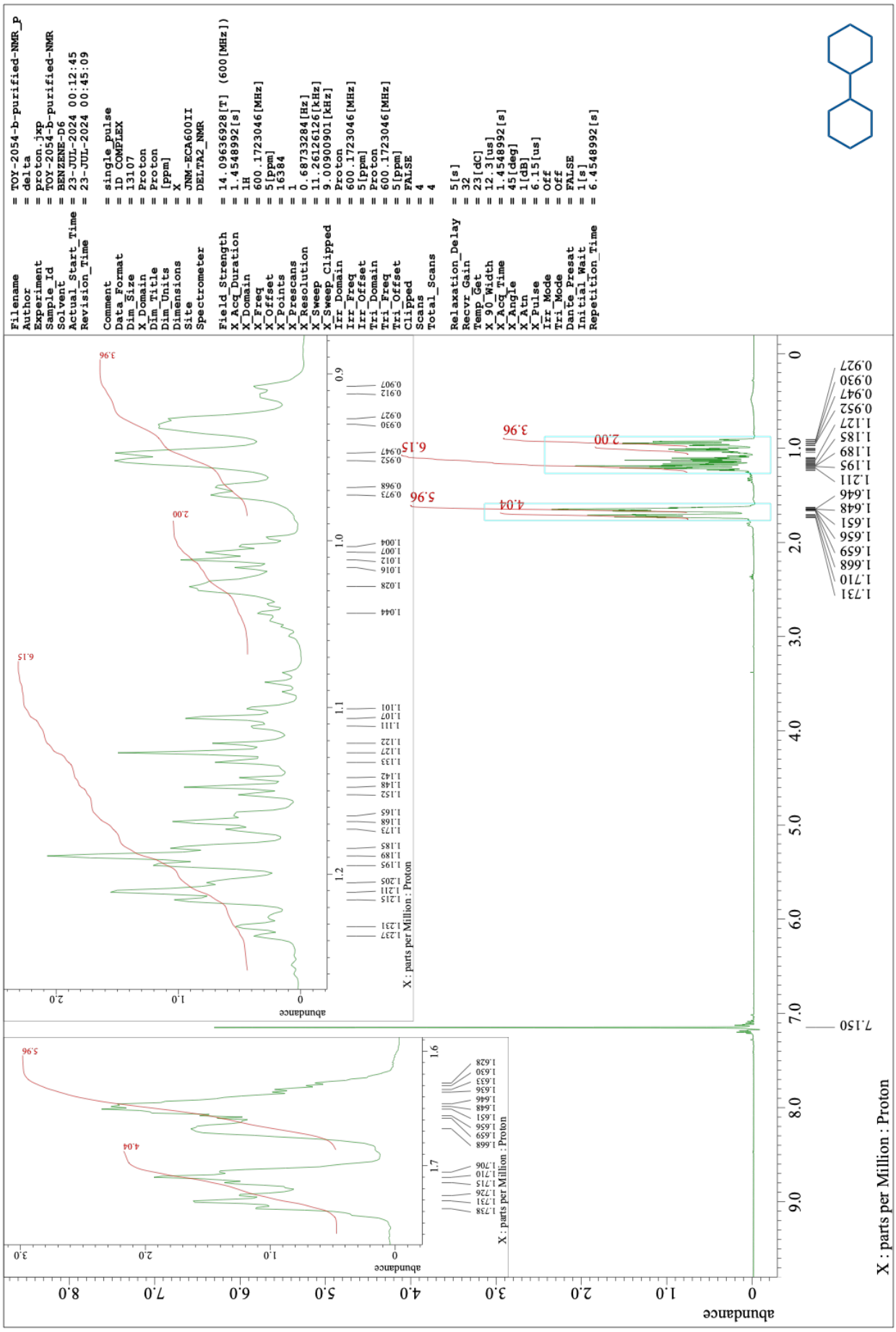

Figure S16. ^{1}H NMR spectrum of **2** (600 MHz, C_6D_6).

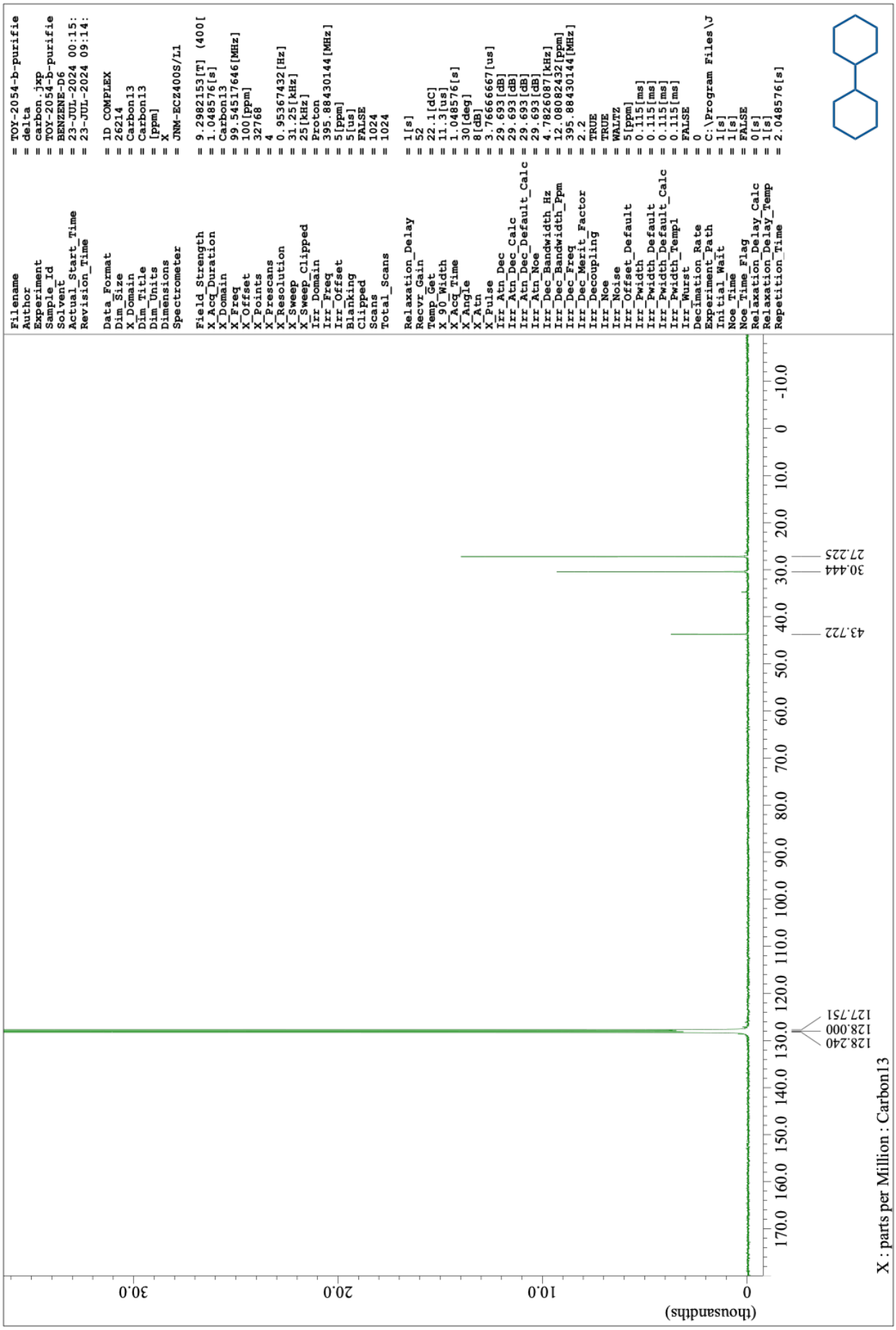

Figure S17. ^{13}C NMR spectrum of **2** (150 MHz, C_6D_6).

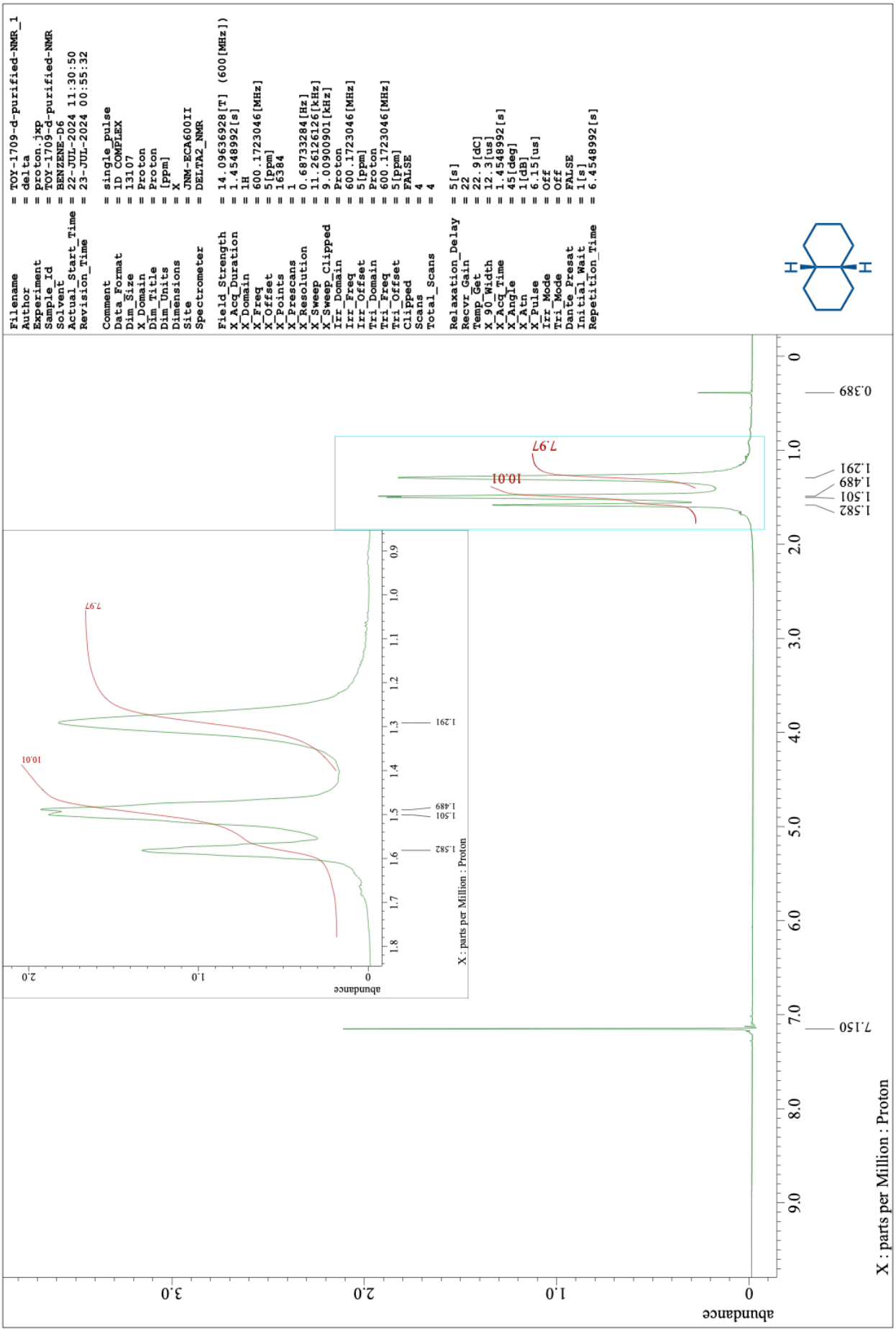

Figure S18. ^{1}H NMR spectrum of **4b** (600 MHz, C_6D_6).

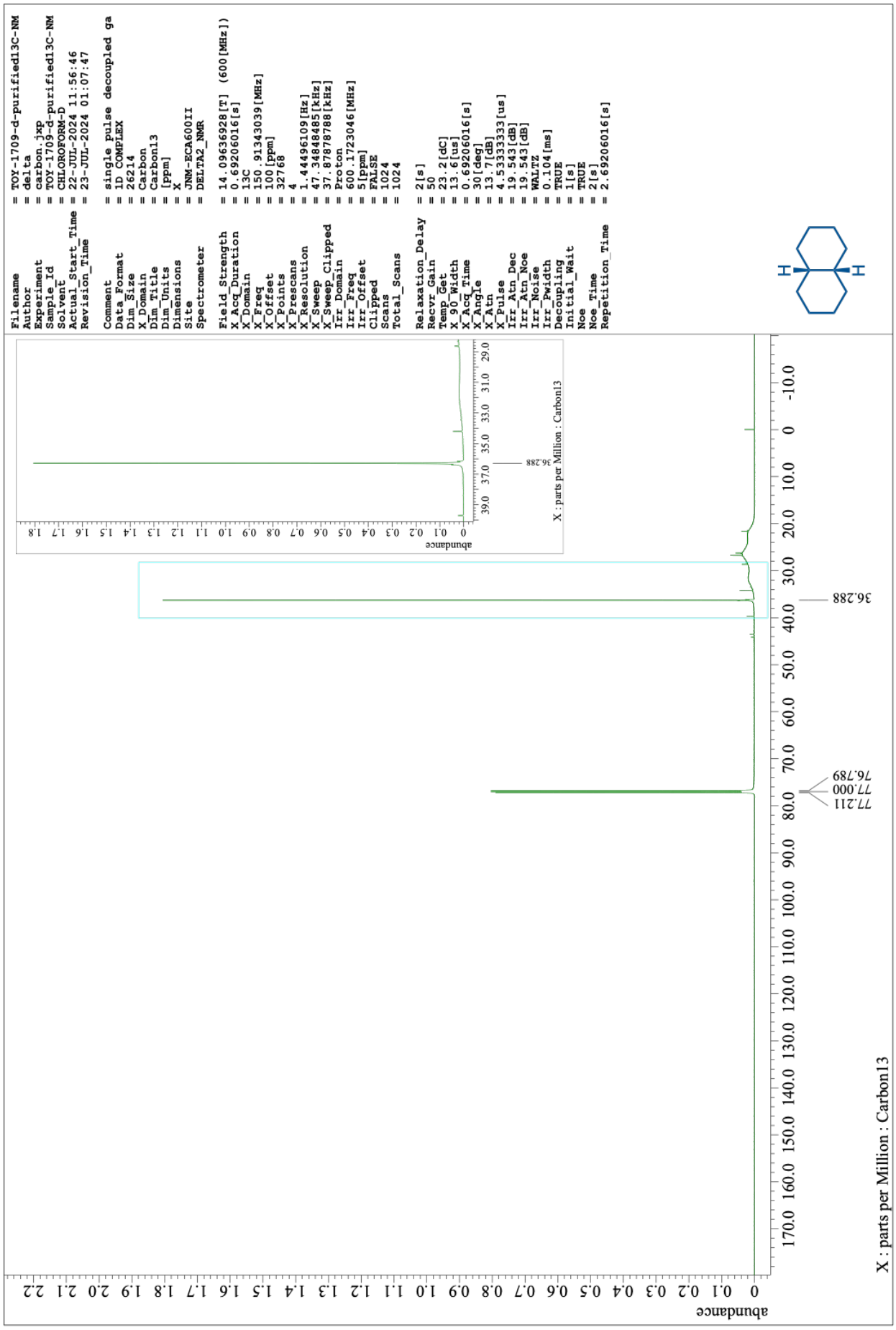

Figure S19. ^{13}C NMR spectrum of **4b** (150 MHz, C_6D_6).

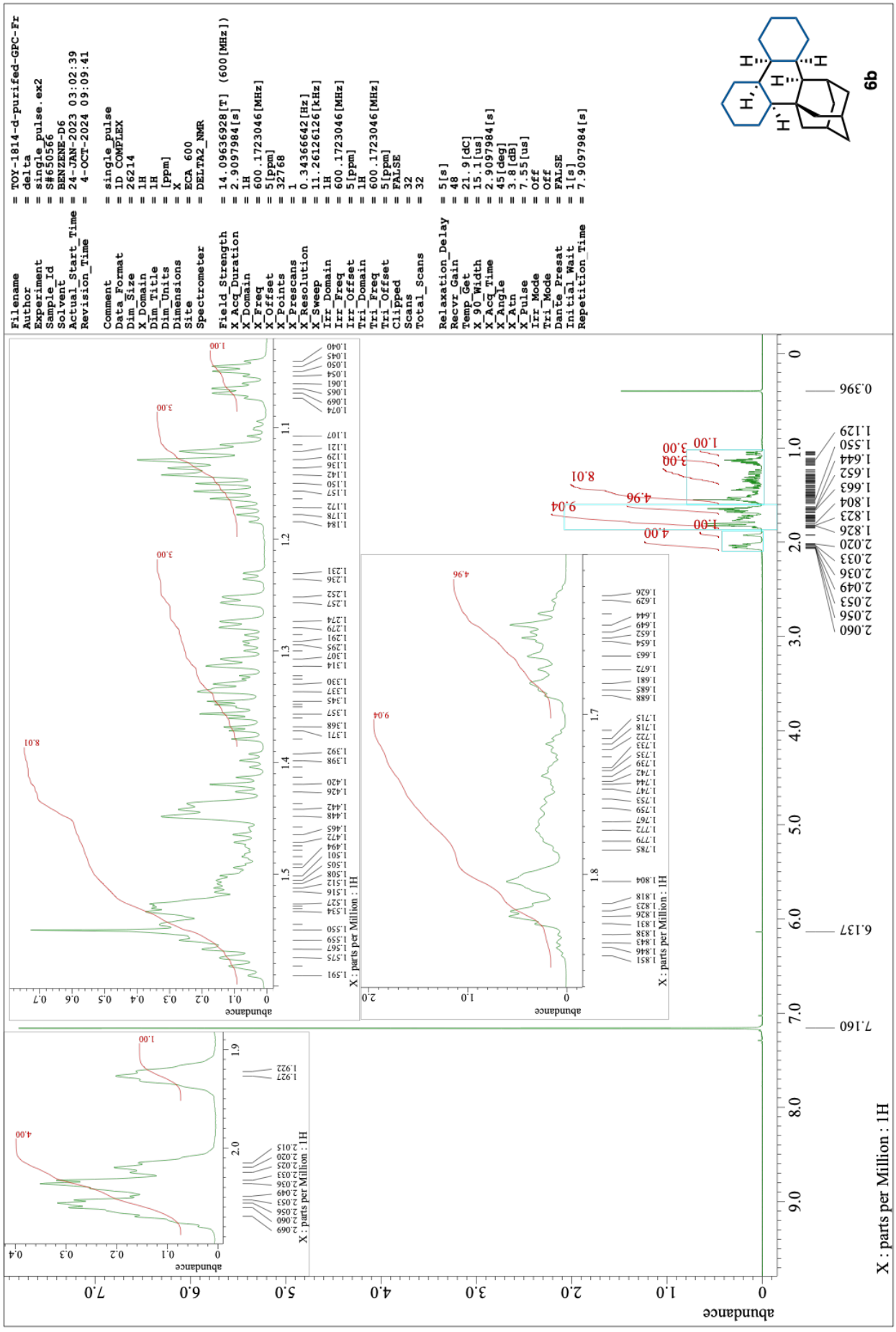

Figure S20. ^{1}H NMR spectrum of **6b** (600 MHz, C_6D_6).

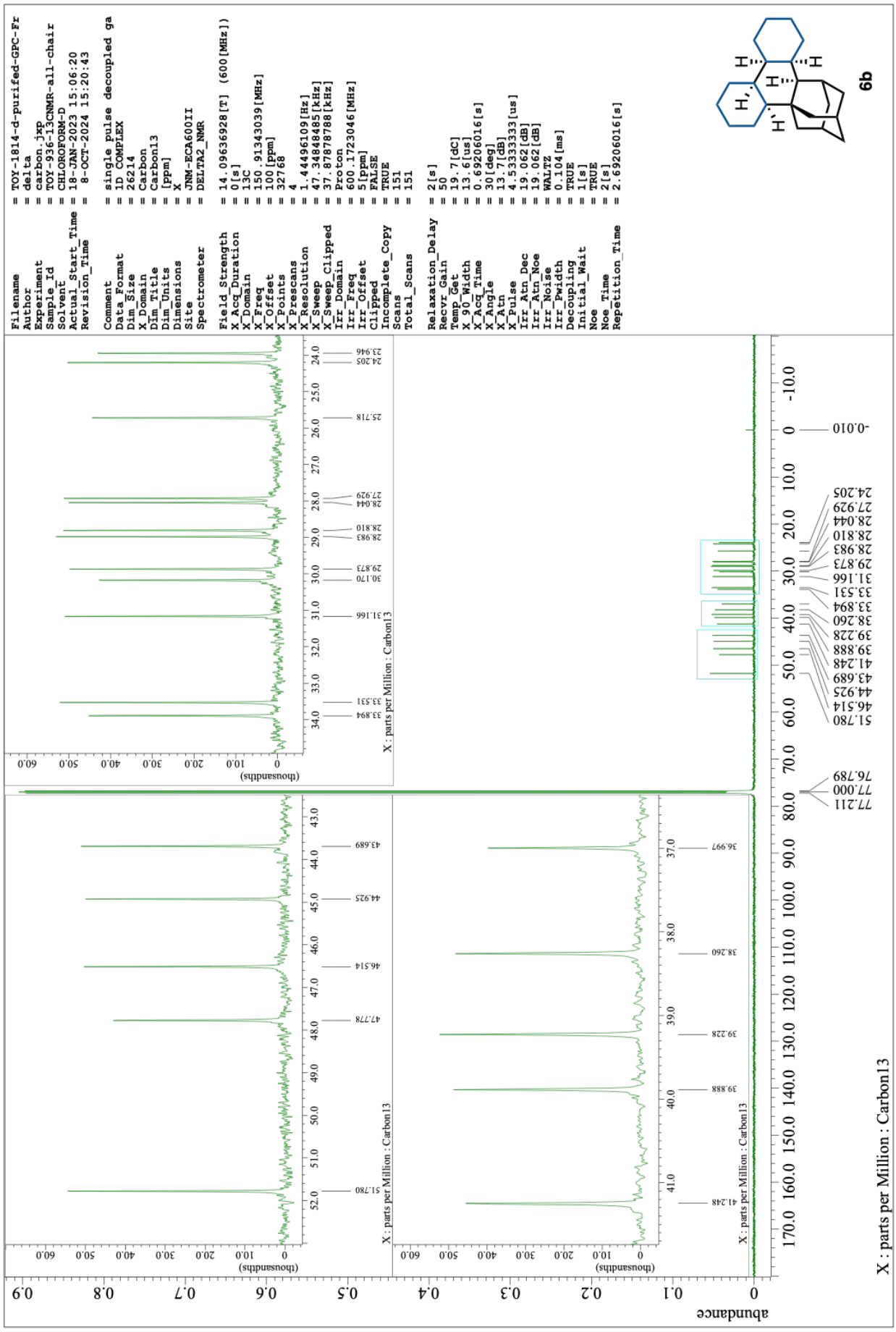

Figure S21. ^{13}C NMR spectrum of **6b** (150 MHz, $CDCl_3$).

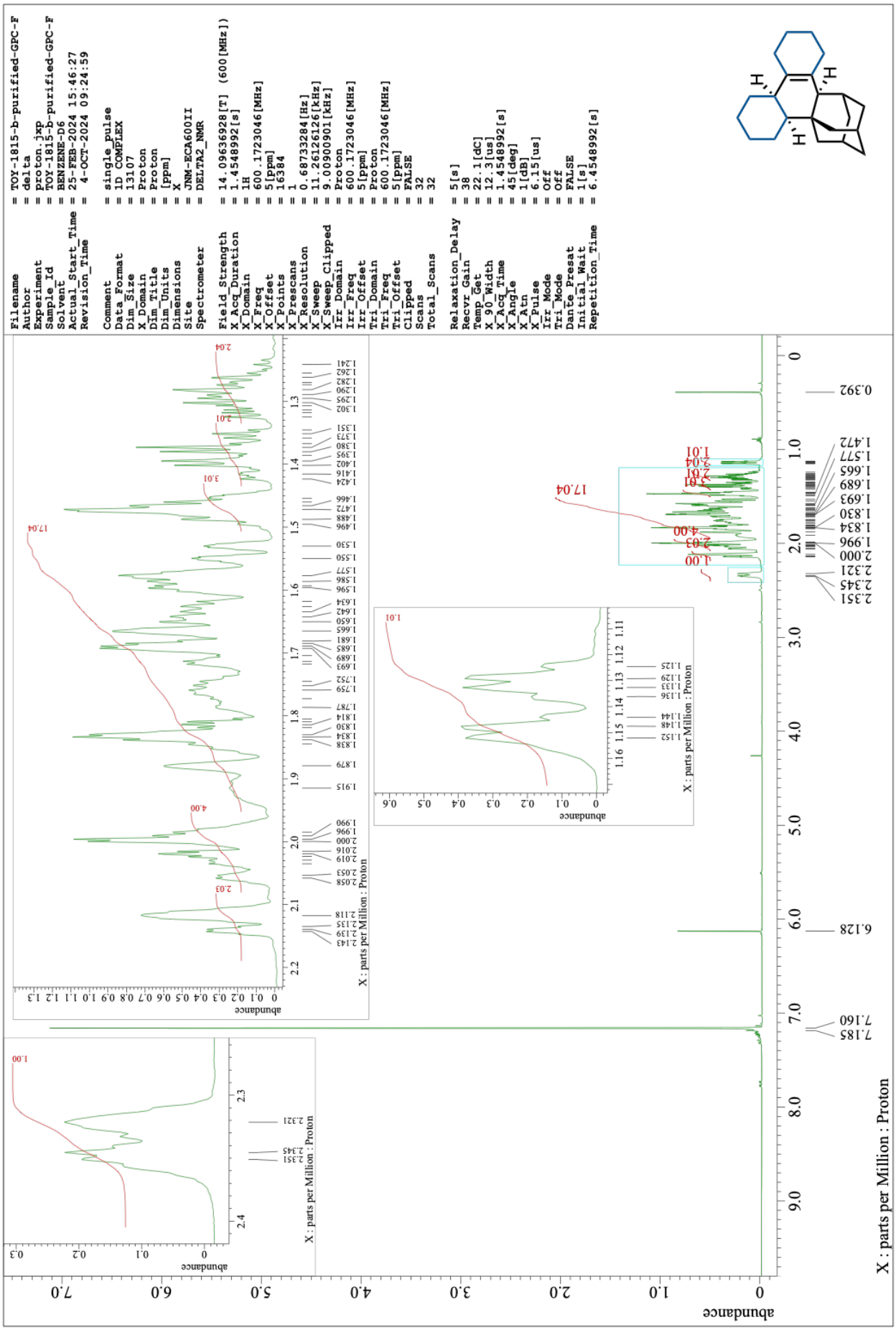

Figure S22. ^{1}H NMR spectrum of **6c** (600 MHz, C_6D_6).

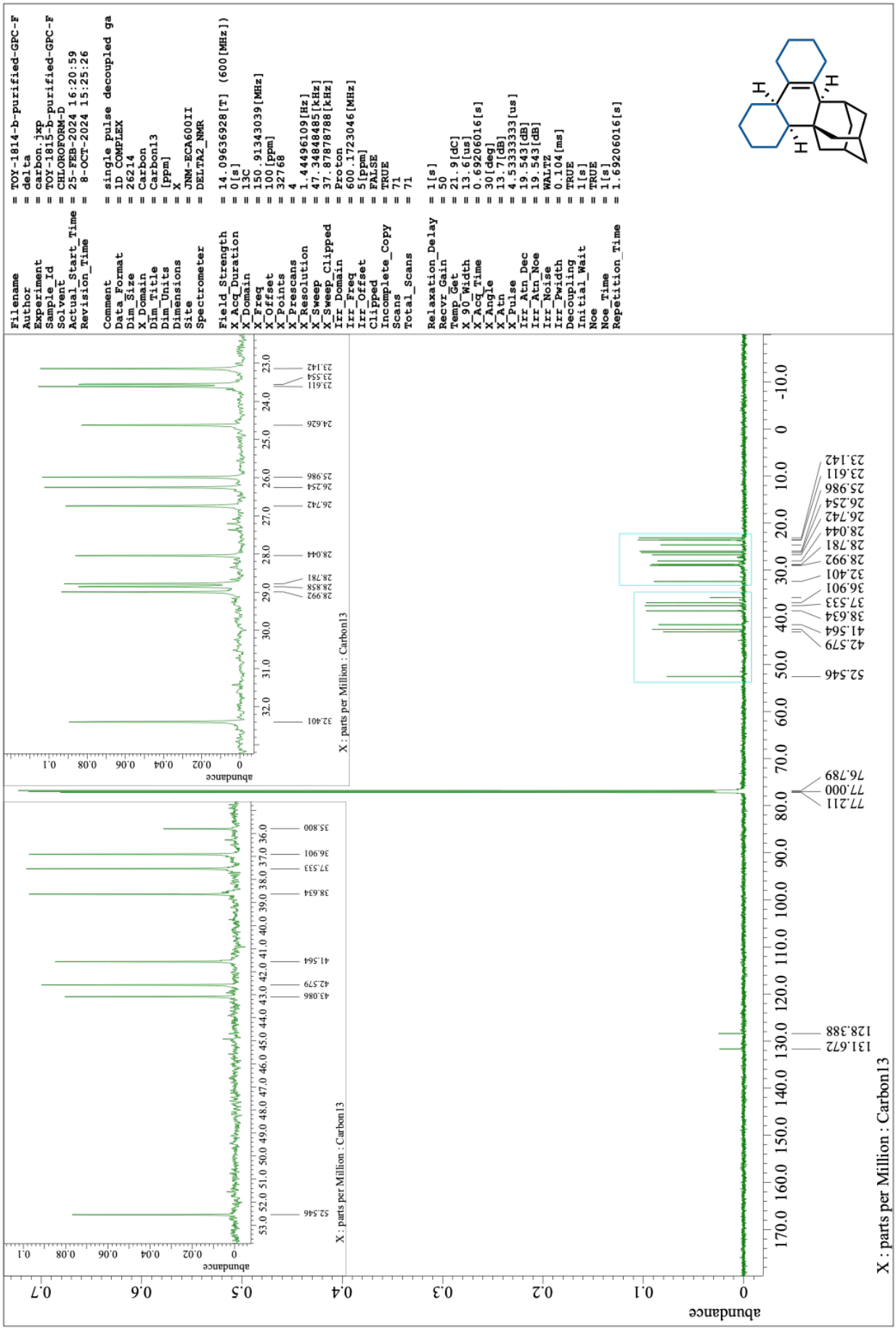

Figure S23. ^{13}C NMR spectrum of **6c** (150 MHz, $CDCl_3$).

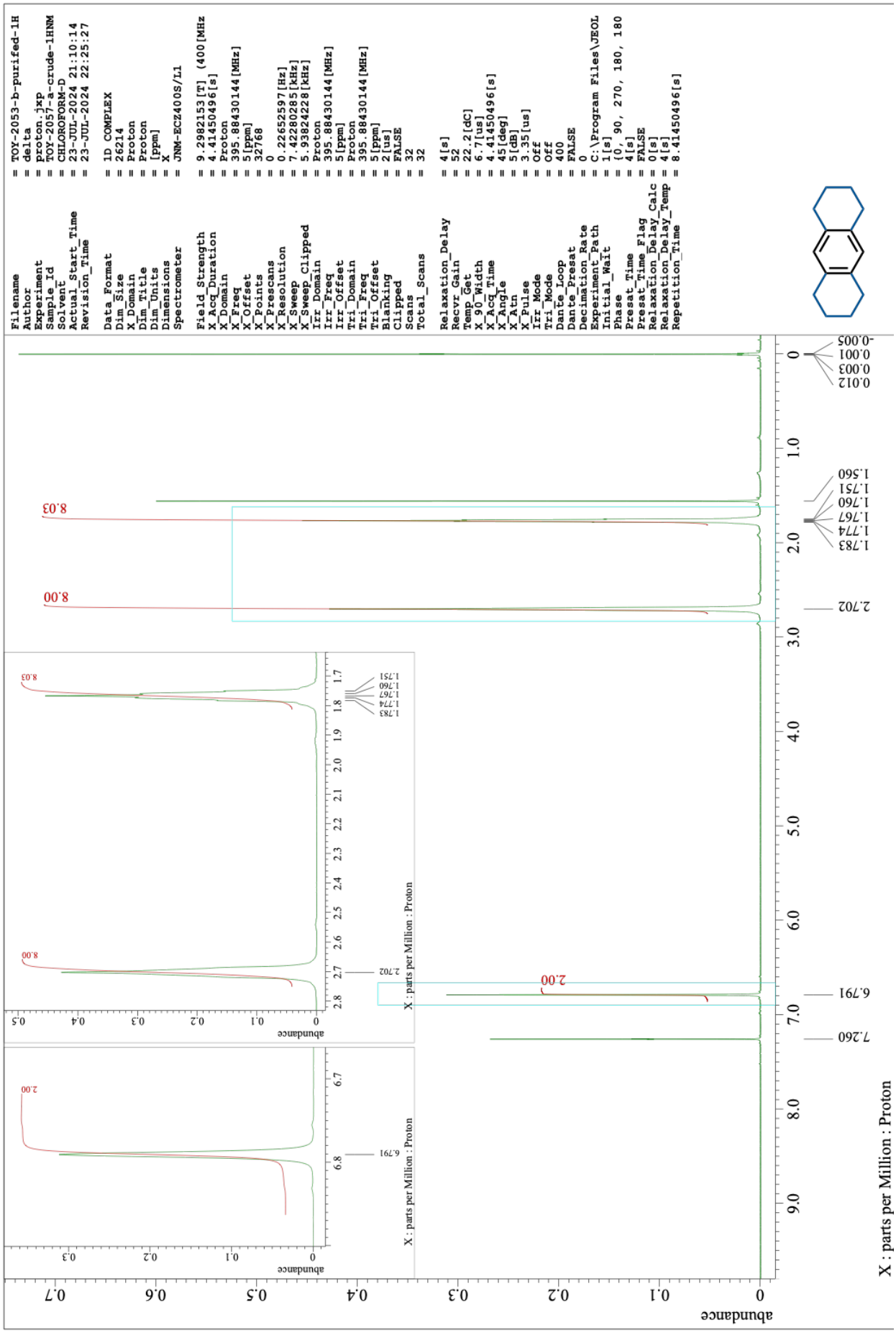

Figure S24. ^{1}H NMR spectrum of **8a** (600 MHz, $CDCl_3$).

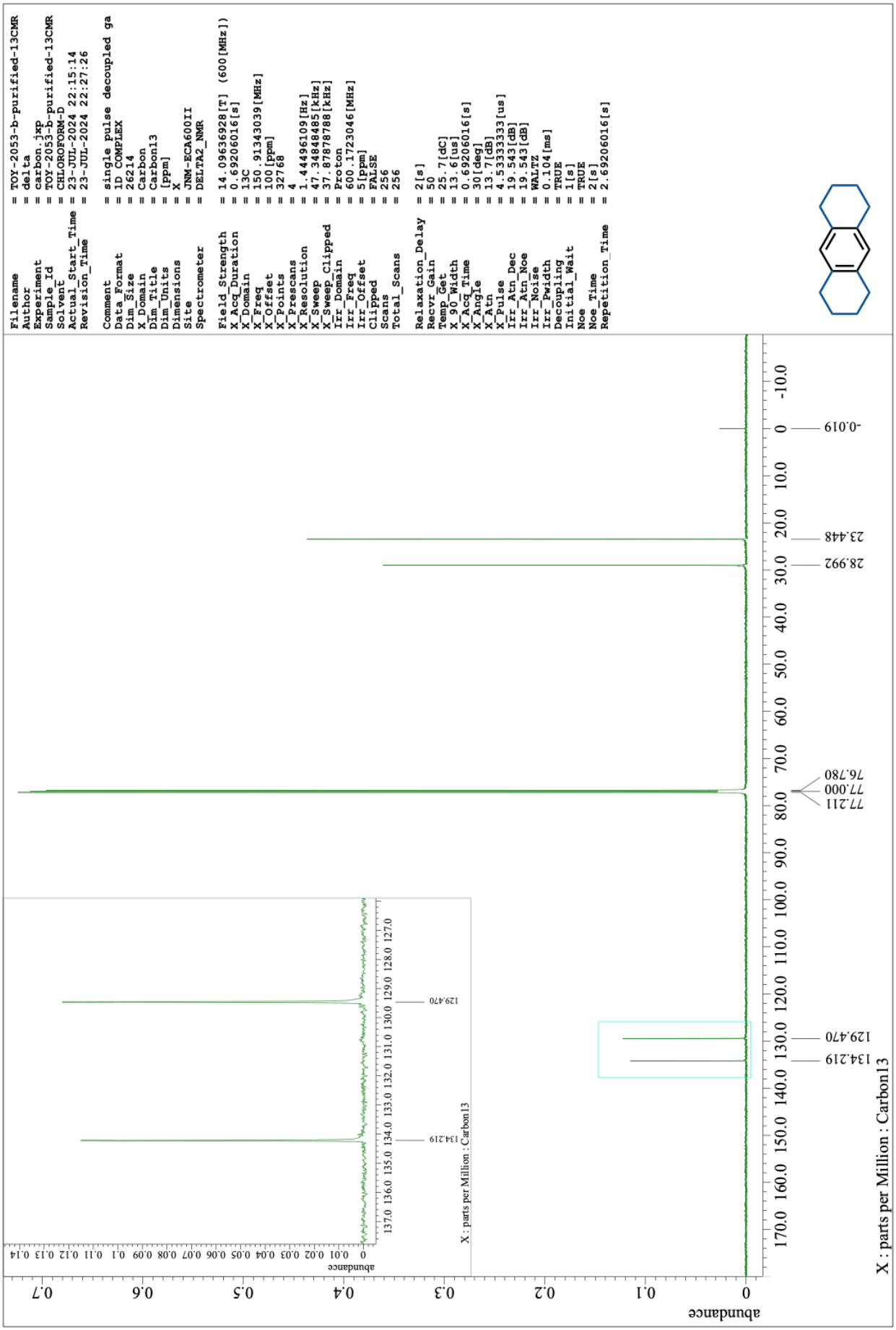

Figure S25. ^{13}C NMR spectrum of **8a** (150 MHz, $CDCl_3$).

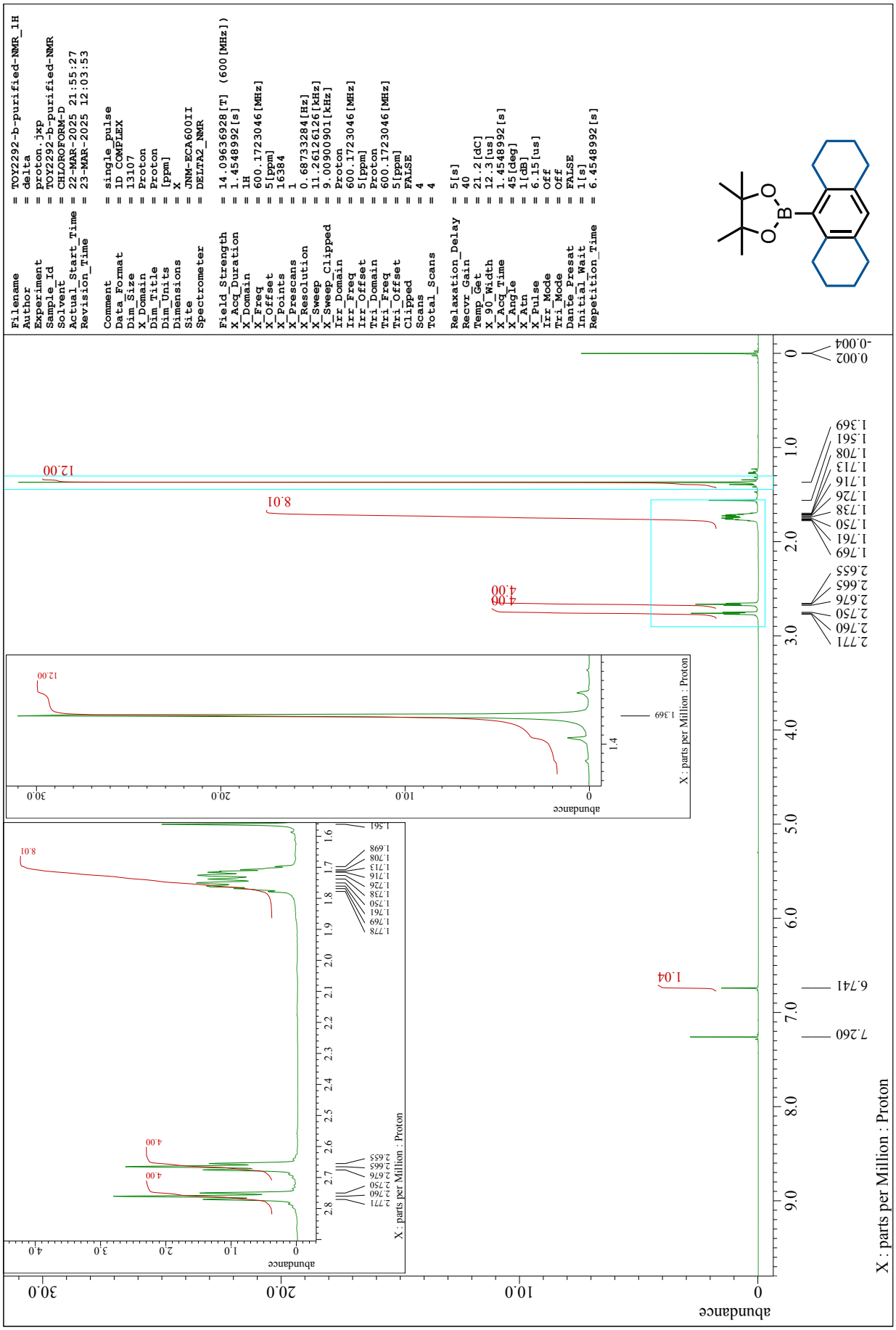

Figure S26. ^{13}H NMR spectrum of **8b** (600 MHz, $CDCl_3$).

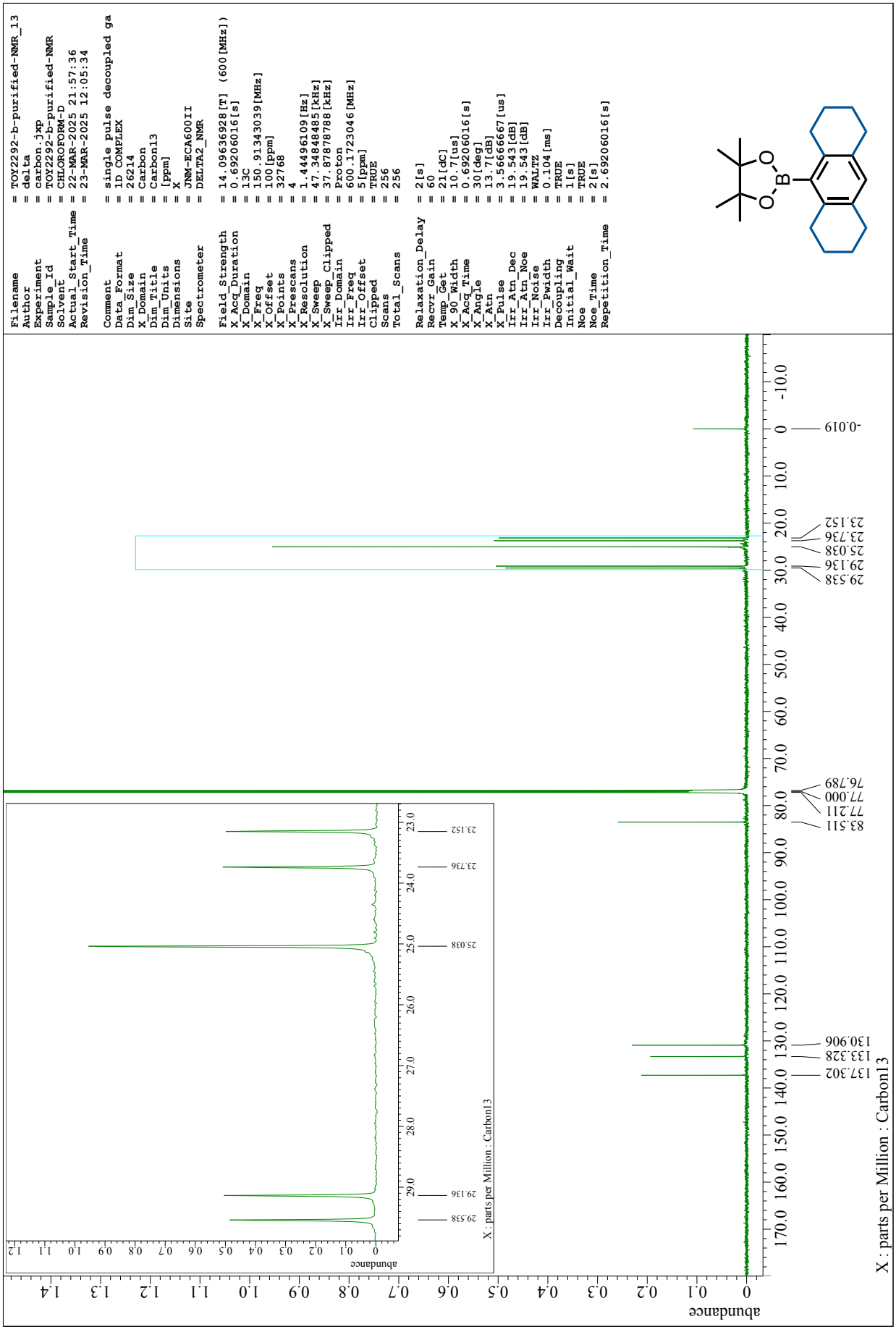

Figure S27. ^{13}C NMR spectrum of **8b** (150 MHz, $CDCl_3$).

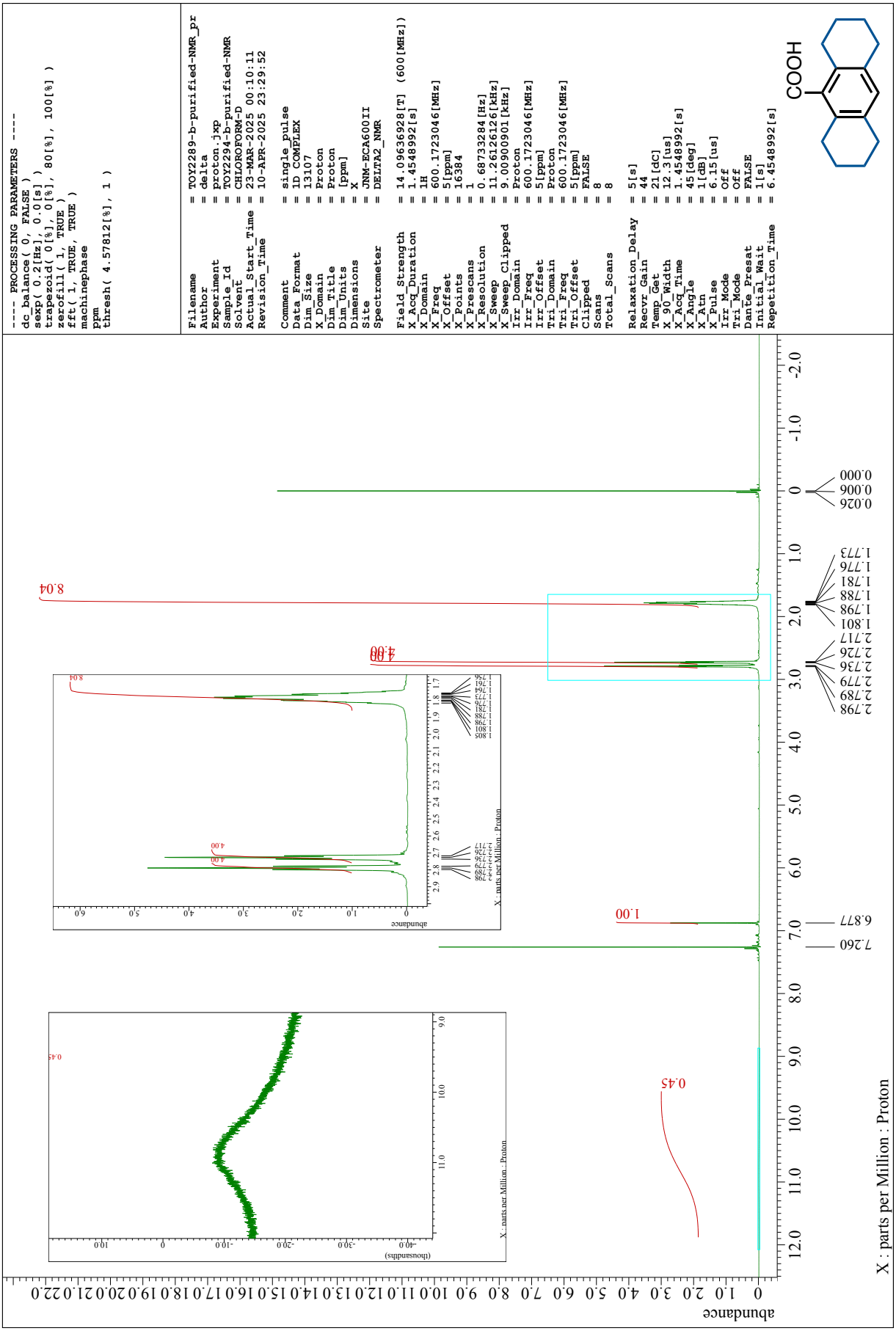

Figure S28. ^{13}H NMR spectrum of **8c** (600 MHz, $CDCl_3$).

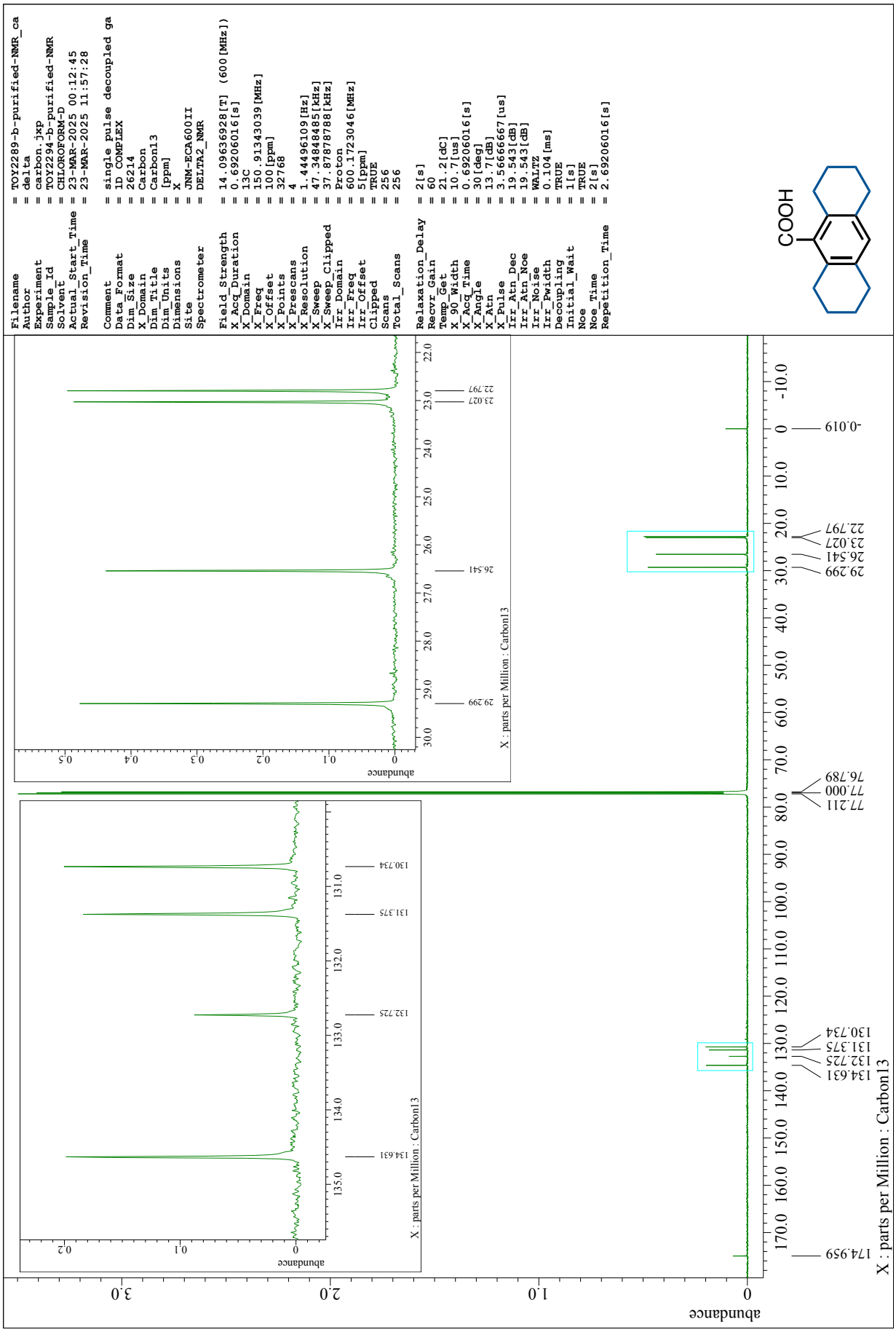

Figure S29. ^{13}C NMR spectrum of **8c** (150 MHz, $CDCl_3$).

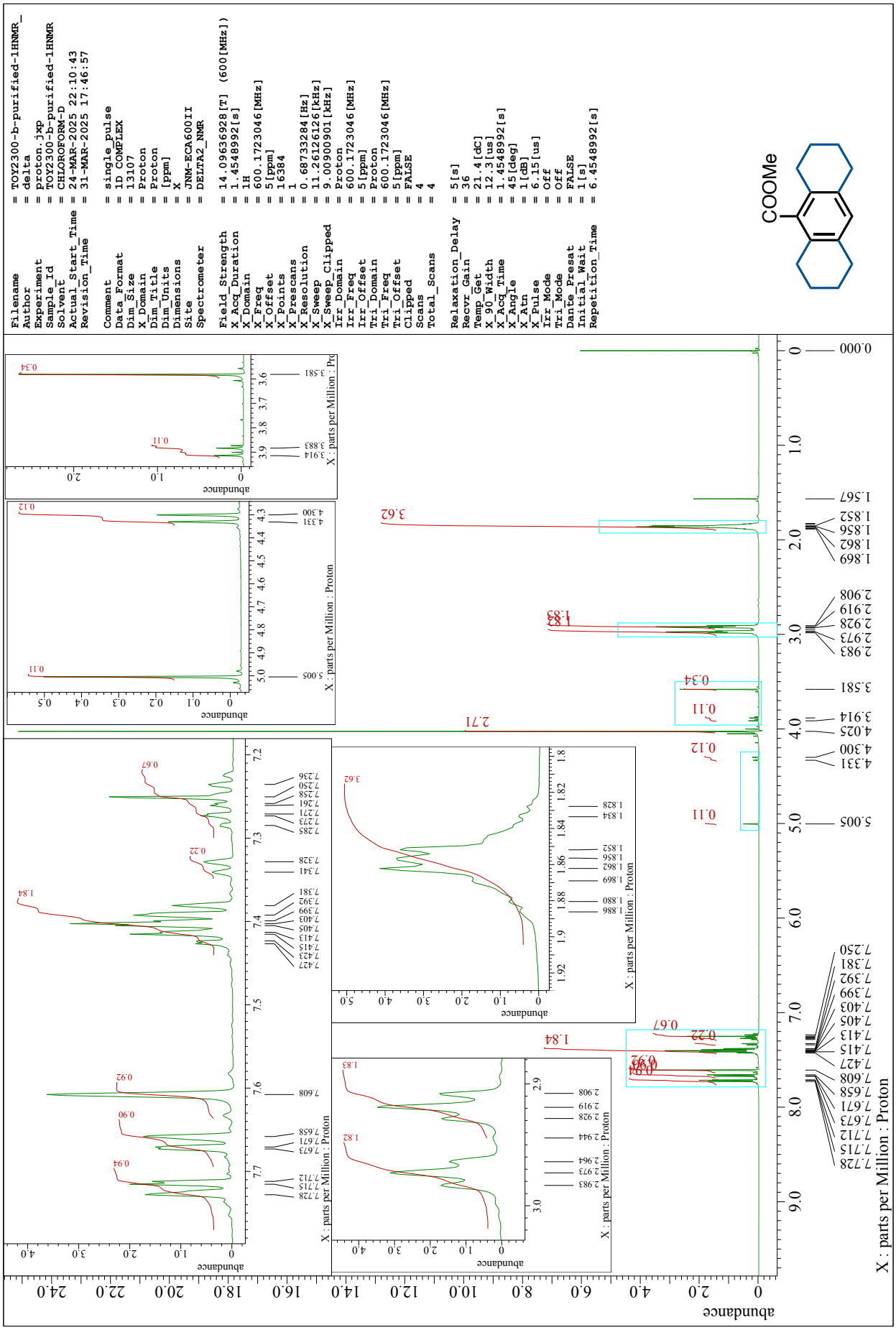

Figure S30. ^{13}H NMR spectrum of **8d** and **8d'** (600 MHz, $CDCl_3$).

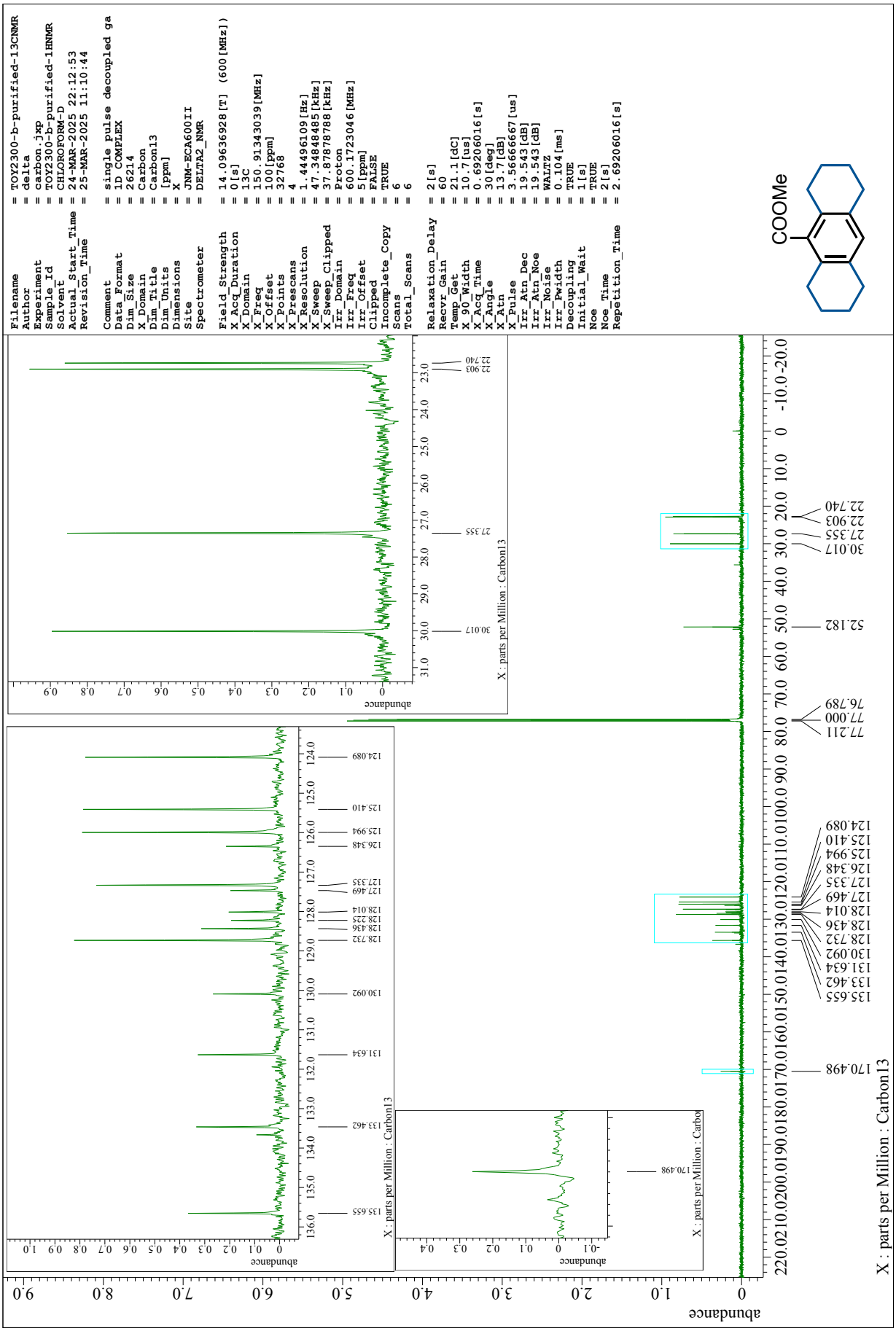

Figure S31. ^{13}C NMR spectrum of **8d** and **8d′** (150 MHz, $CDCl_3$).

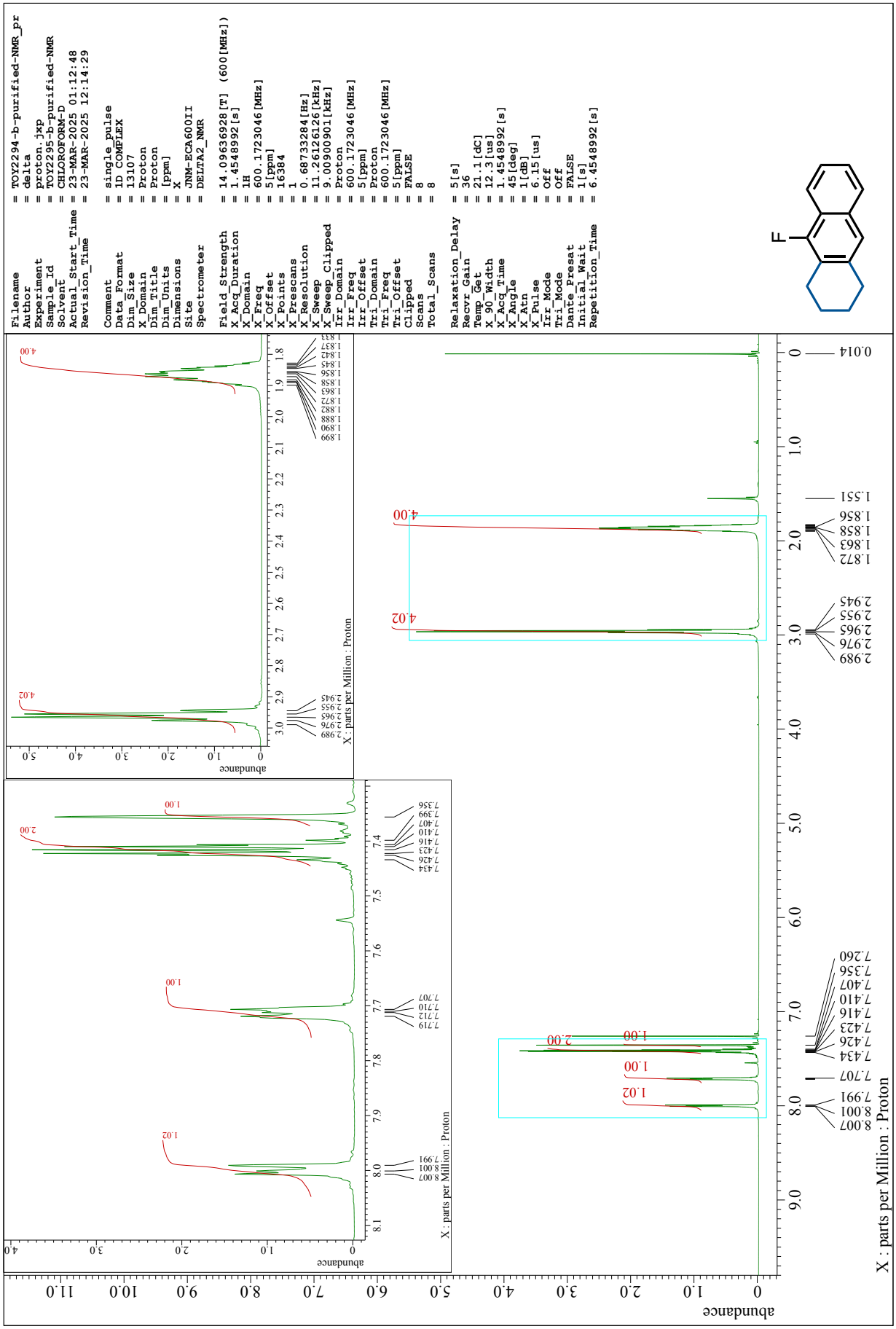

Figure S32. ^{13}H NMR spectrum of **8e** (600 MHz, $CDCl_3$).

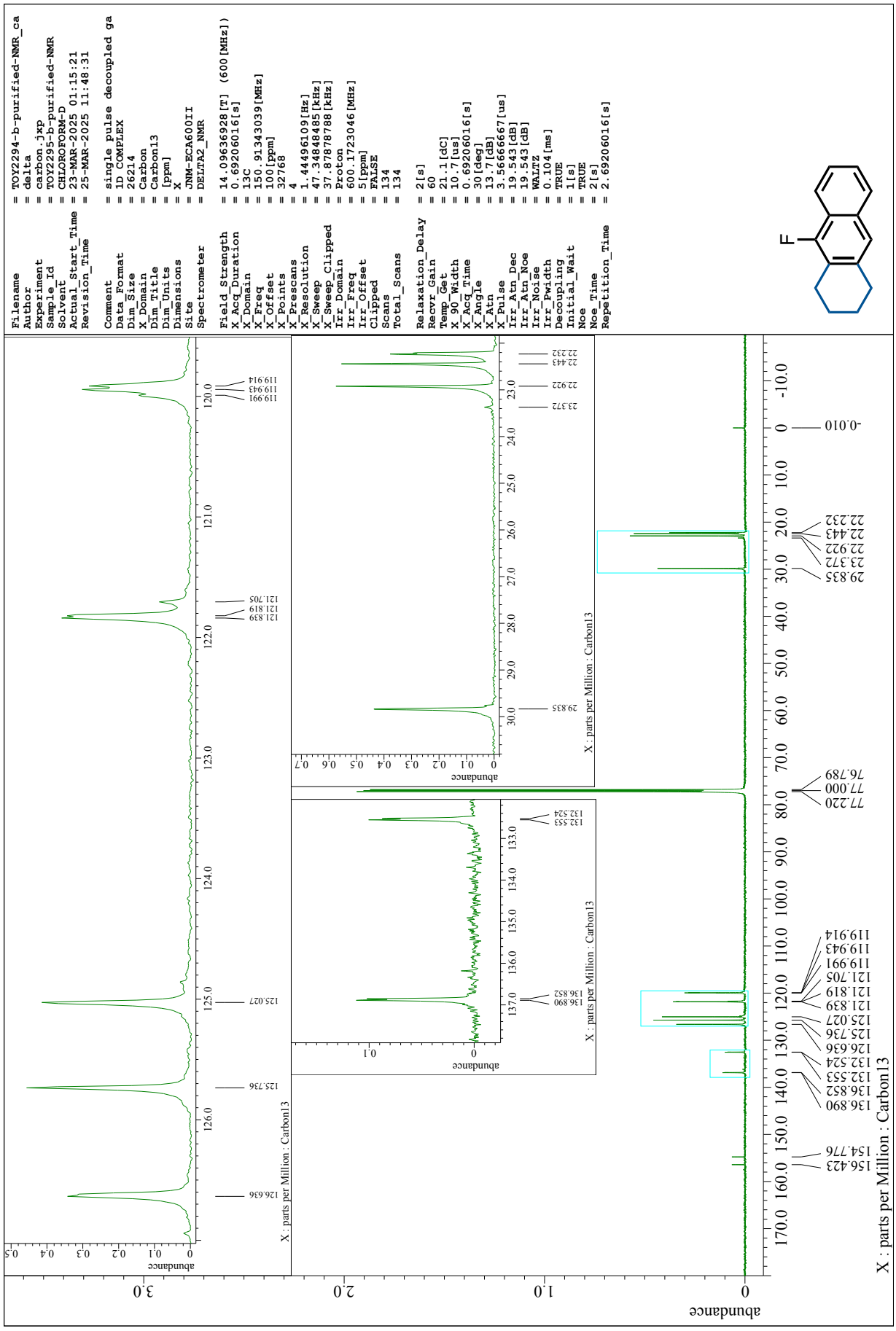

Figure S33. ^{13}C NMR spectrum of **8e** (150 MHz, $CDCl_3$).

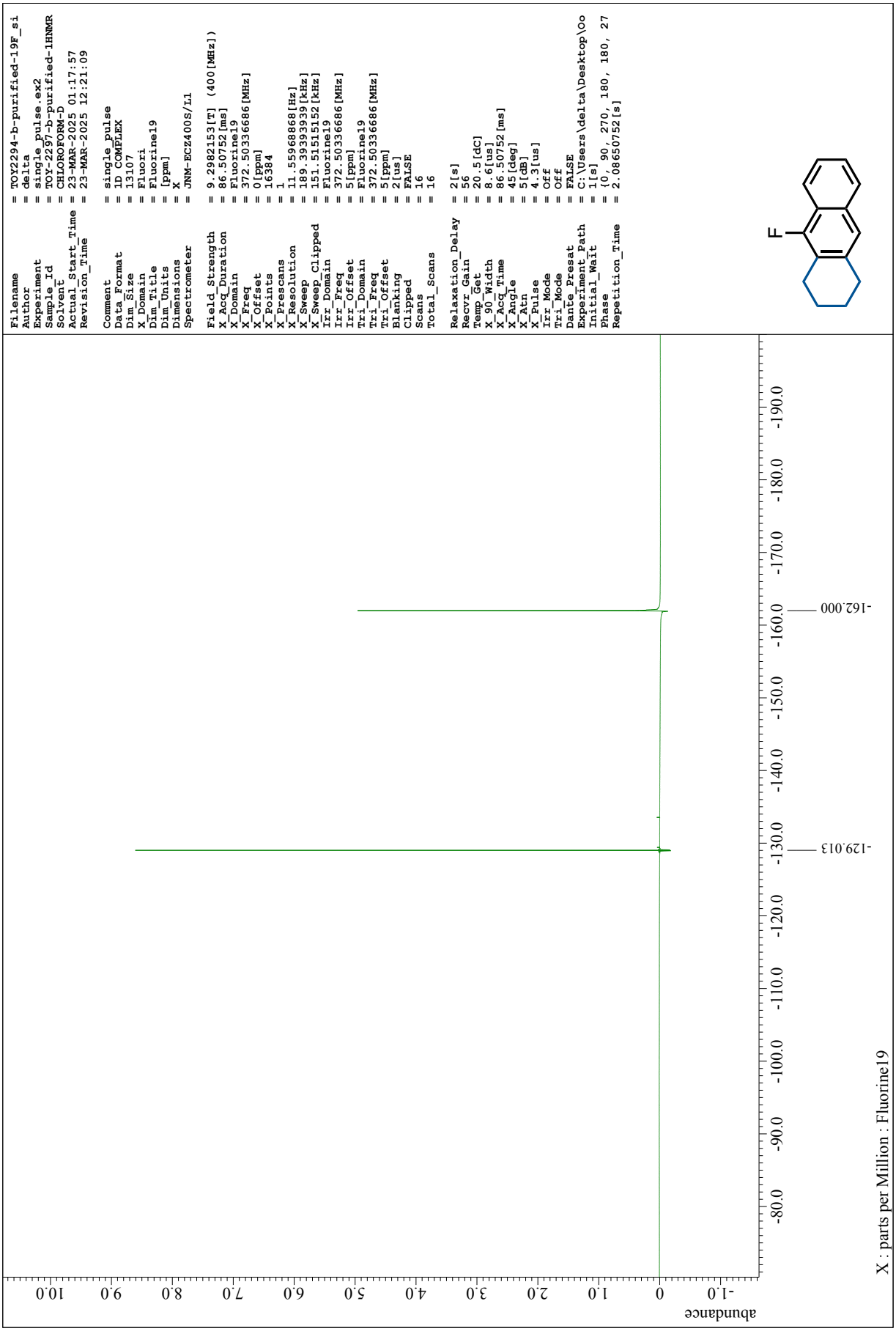

Figure S34. ^{19}F NMR spectrum of **8e** (370 MHz, $CDCl_3$).

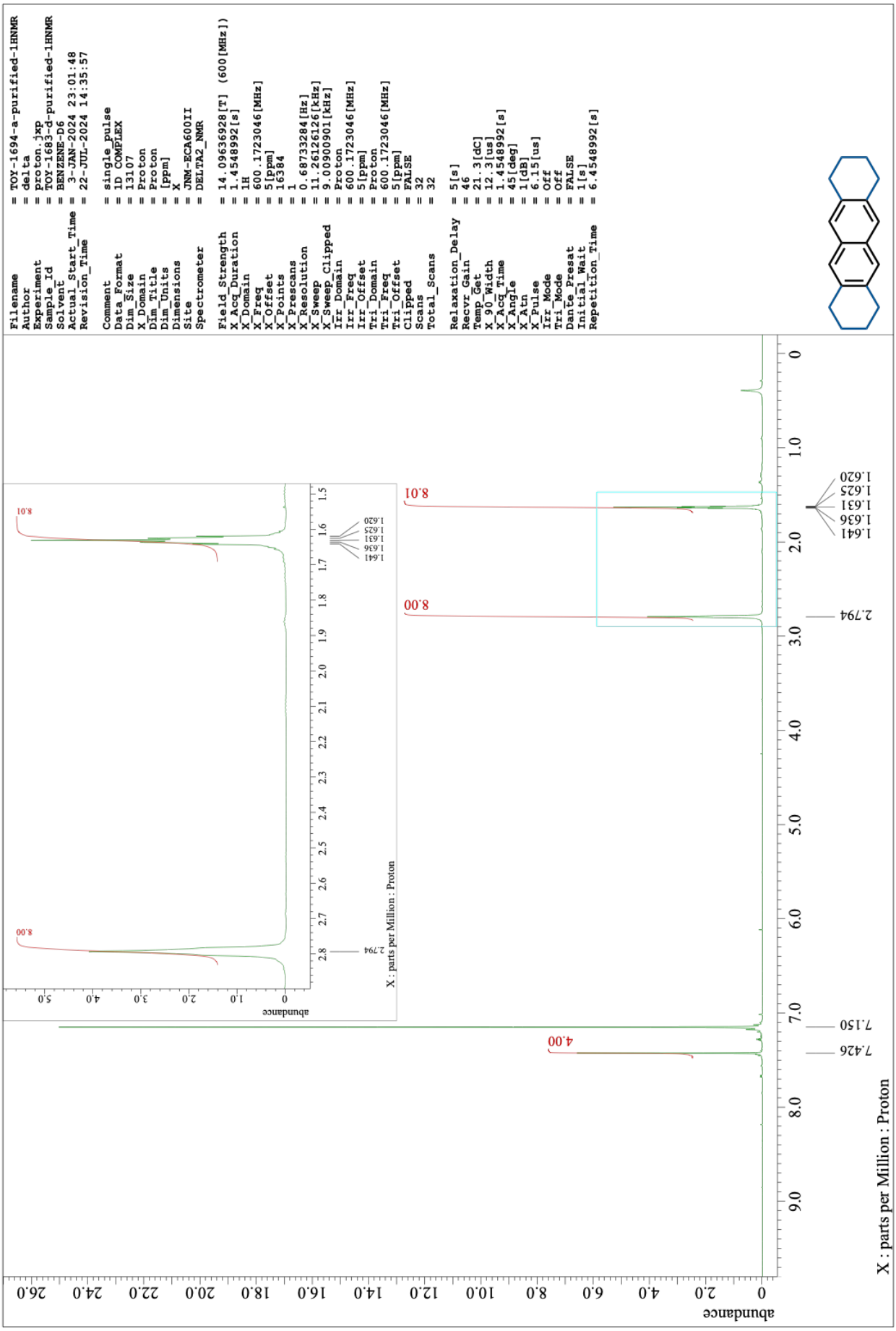

Figure S35. ^{1}H NMR spectrum of **8f** (600 MHz, C_6D_6).

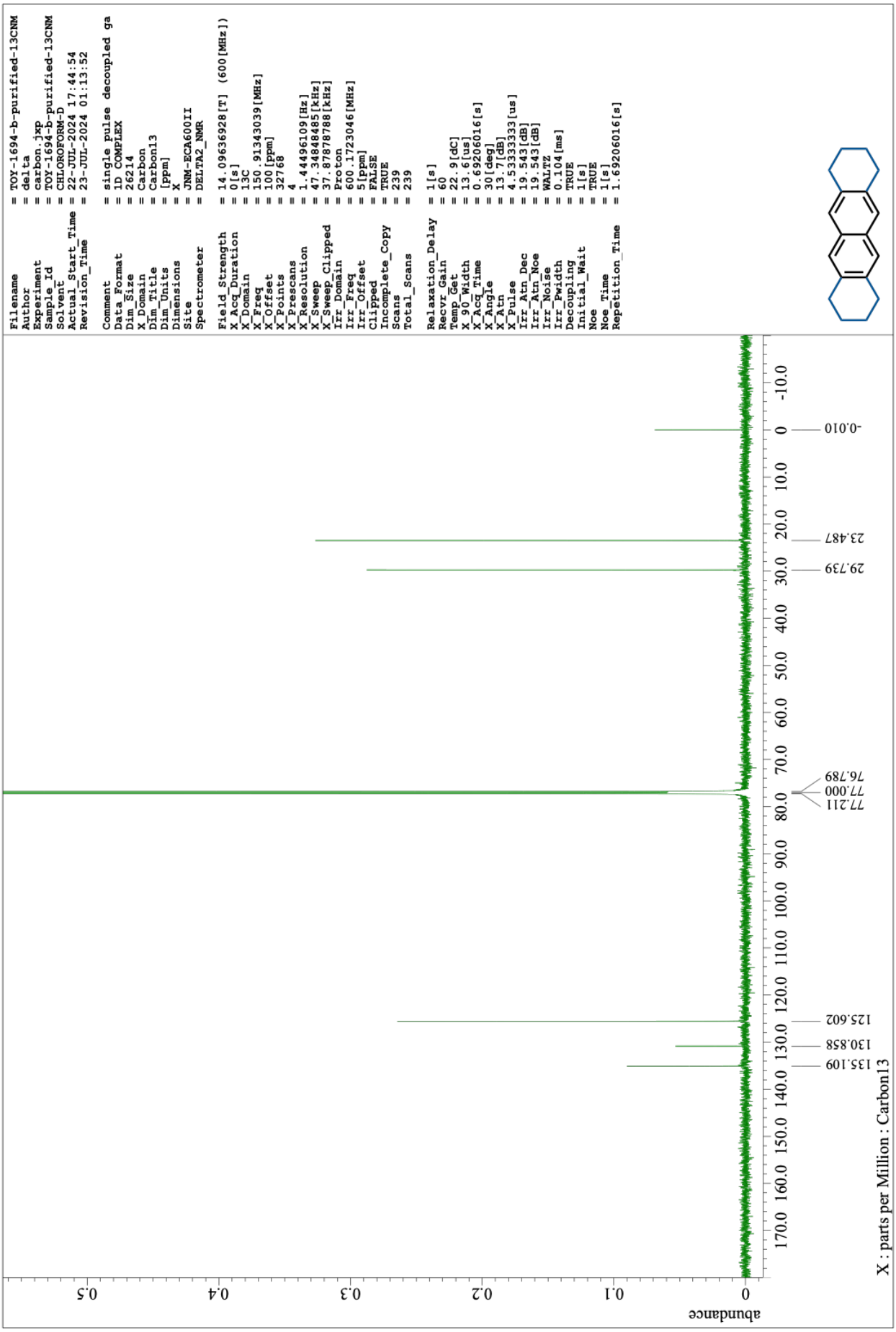

Figure S36. ^{13}C NMR spectrum of **8f** (150 MHz, $CDCl_3$).

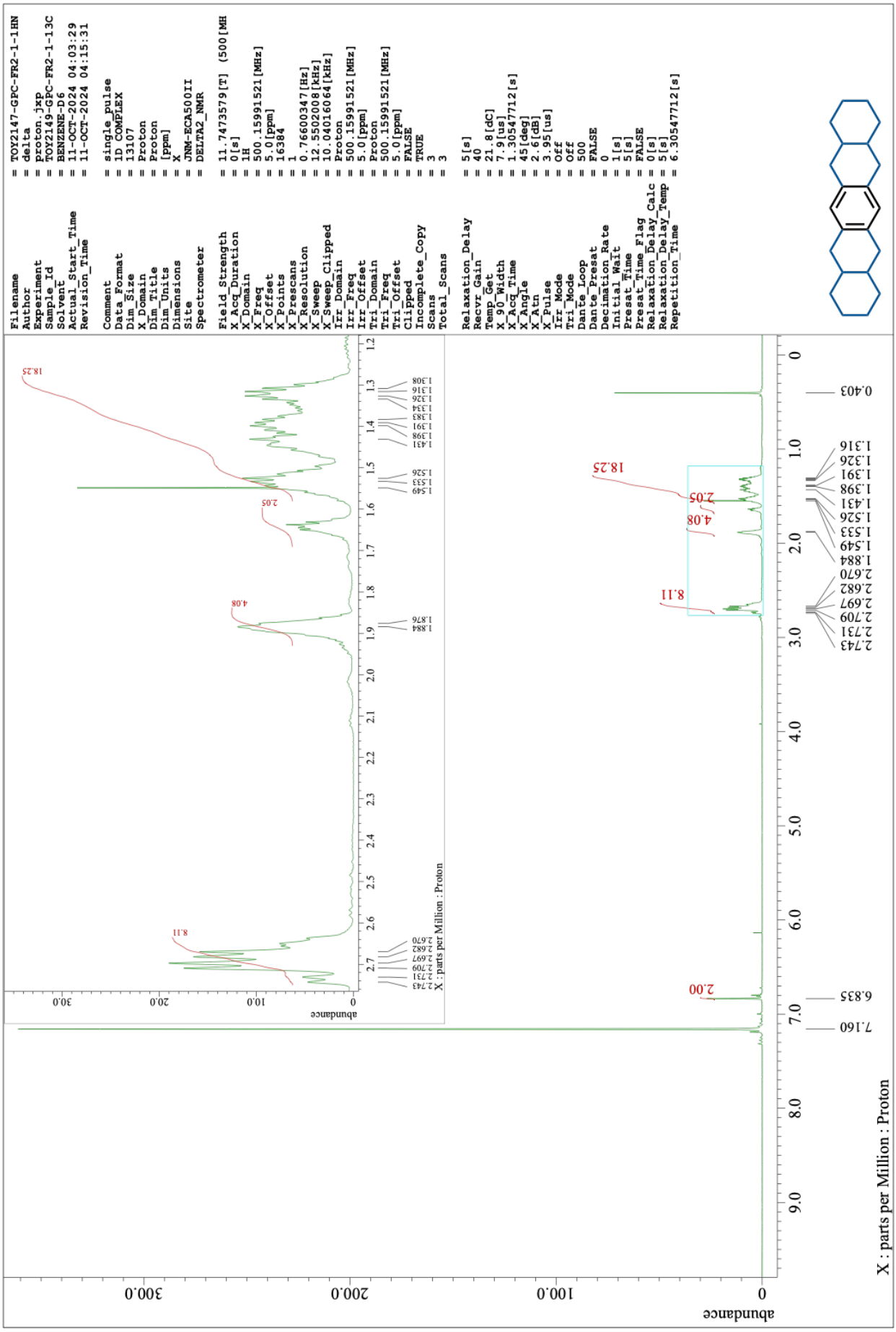

Figure S37. ^{1}H NMR spectrum of **8g** (600 MHz, C_6D_6).

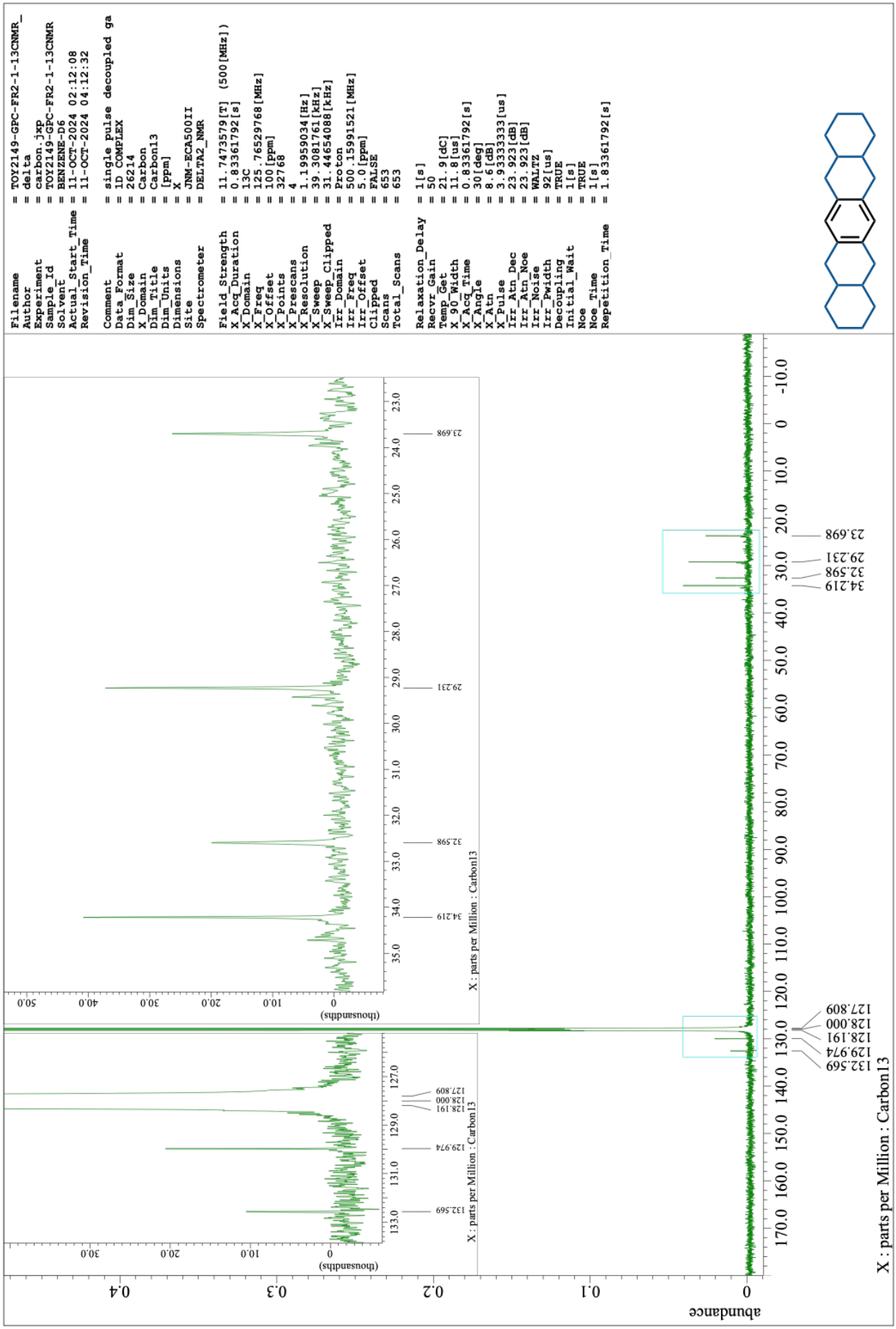

Figure S38. ^{13}C NMR spectrum of **8g** (150 MHz, C_6D_6).

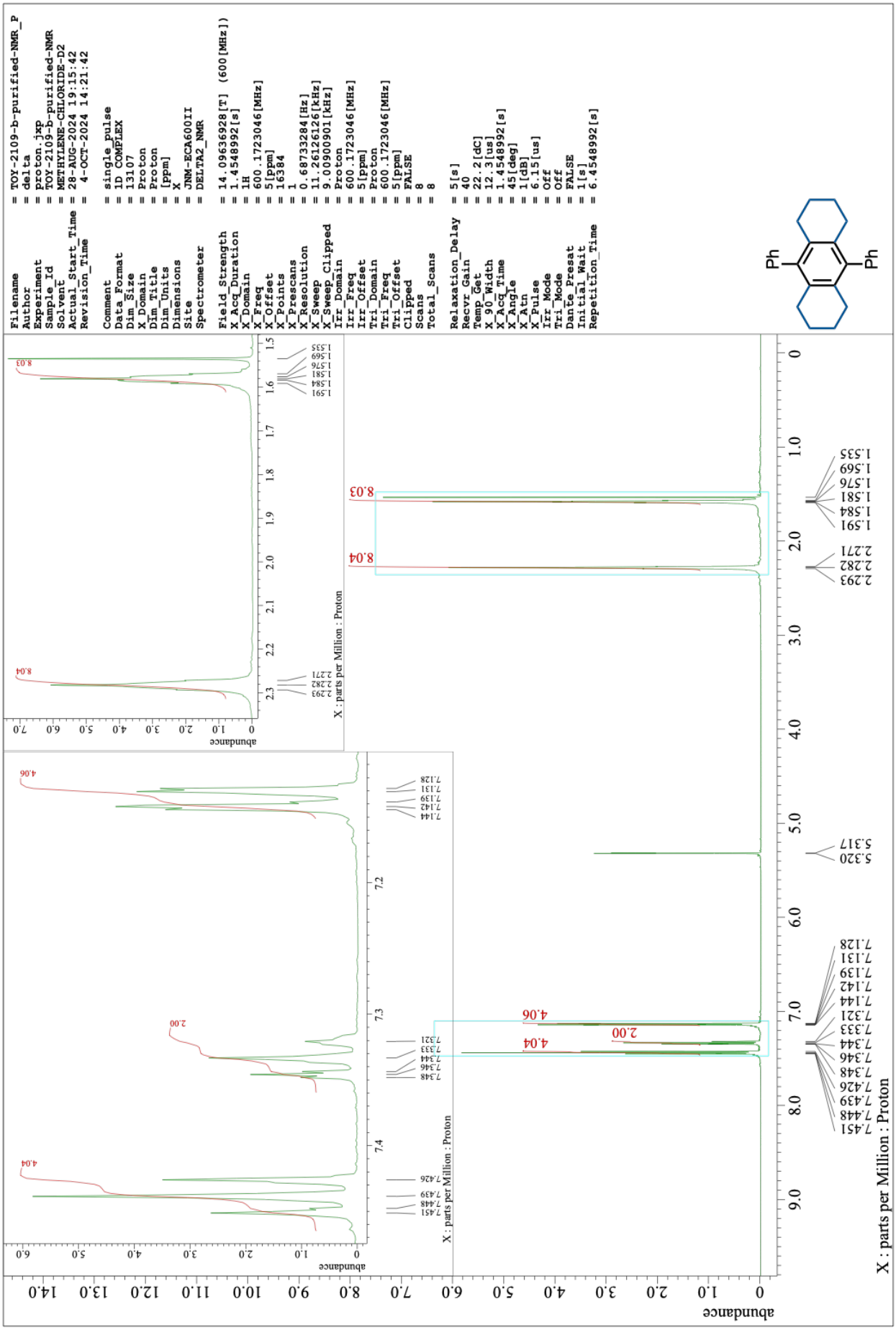

Figure S39. ^{1}H NMR spectrum of **8h** (600 MHz, CD_2Cl_2).

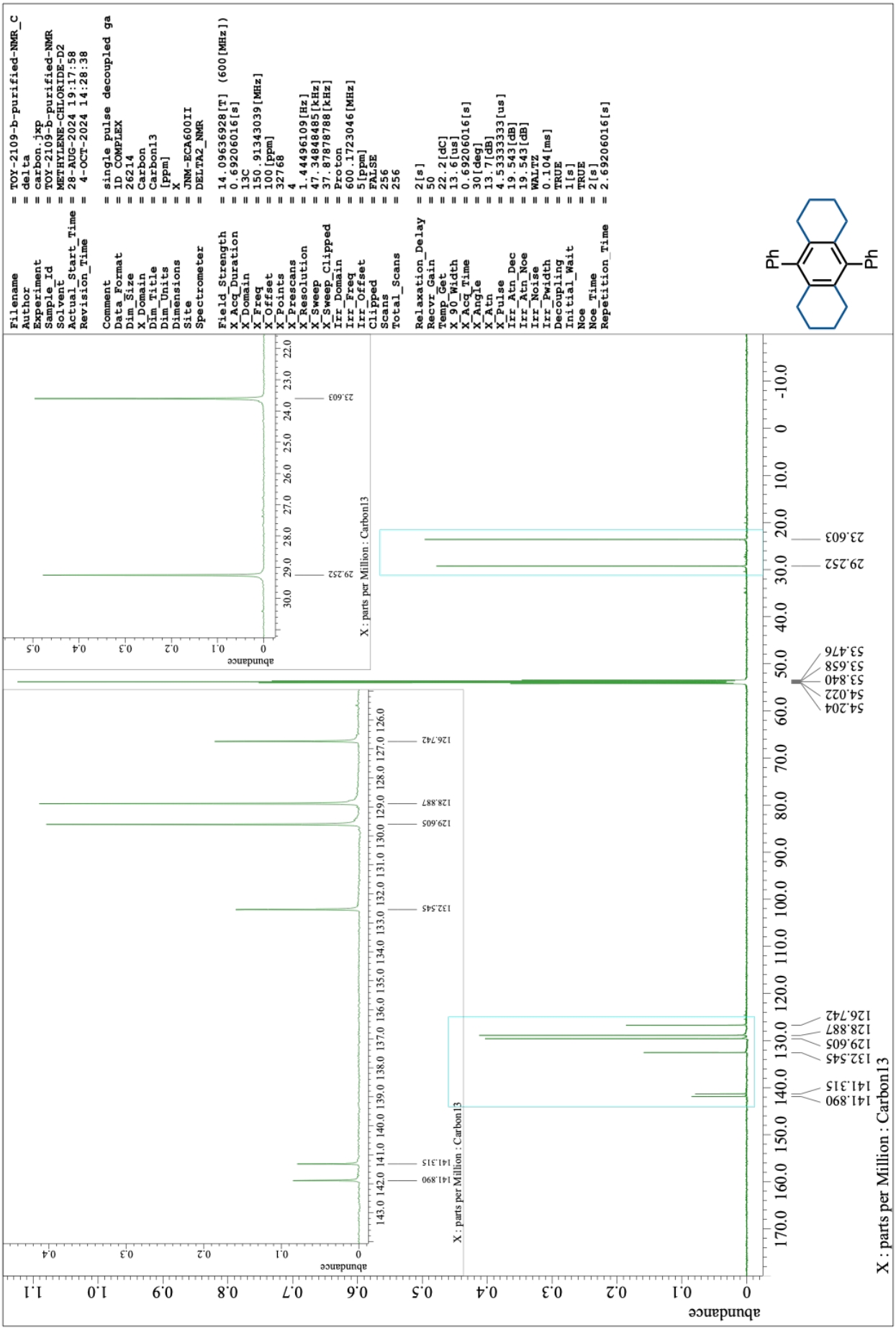

Figure S40. ^{13}C NMR spectrum of **8h** (150 MHz, CD_2Cl_2).

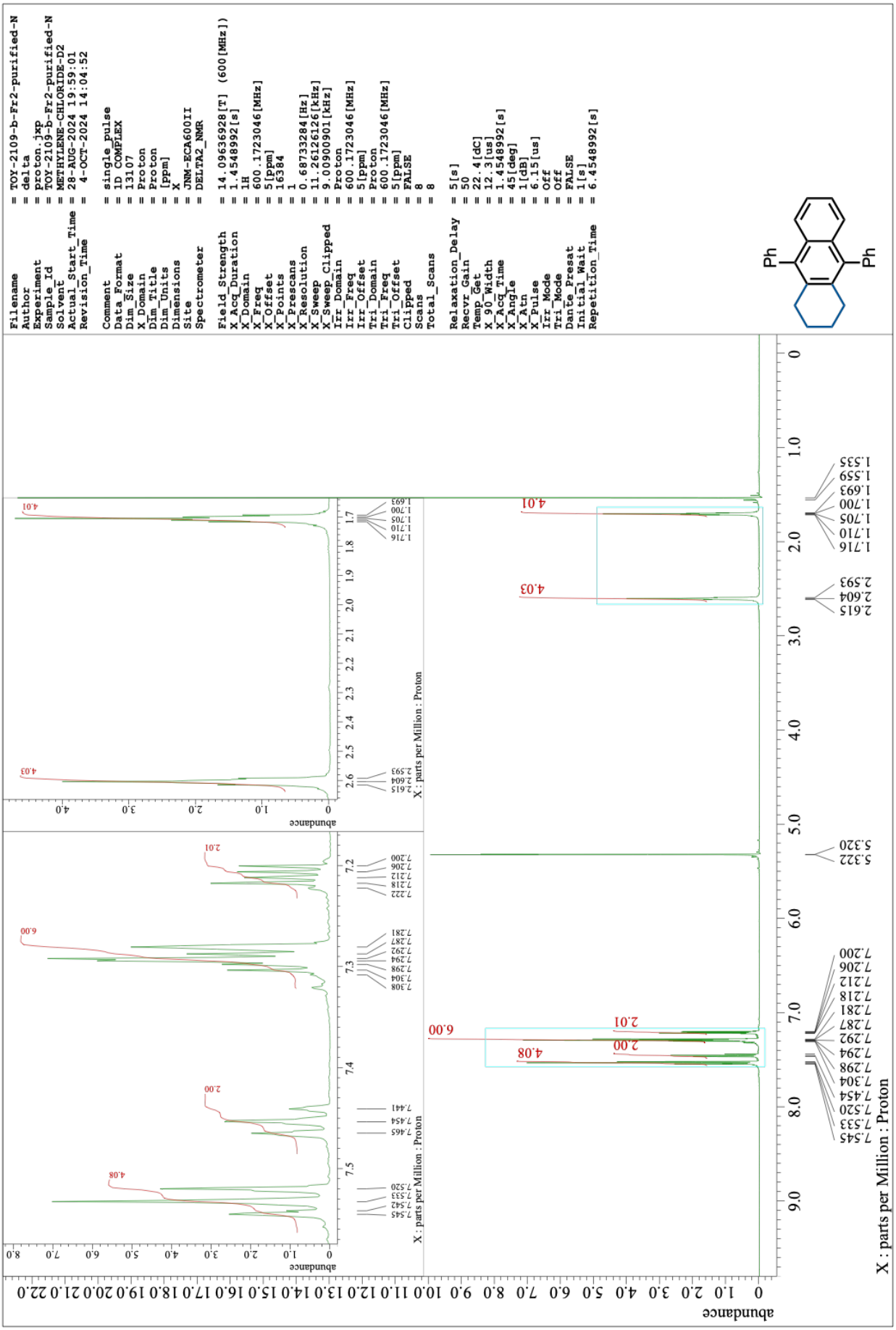

Figure S41. ^{1}H NMR spectrum of **8h'** (600 MHz, CD_2Cl_2).

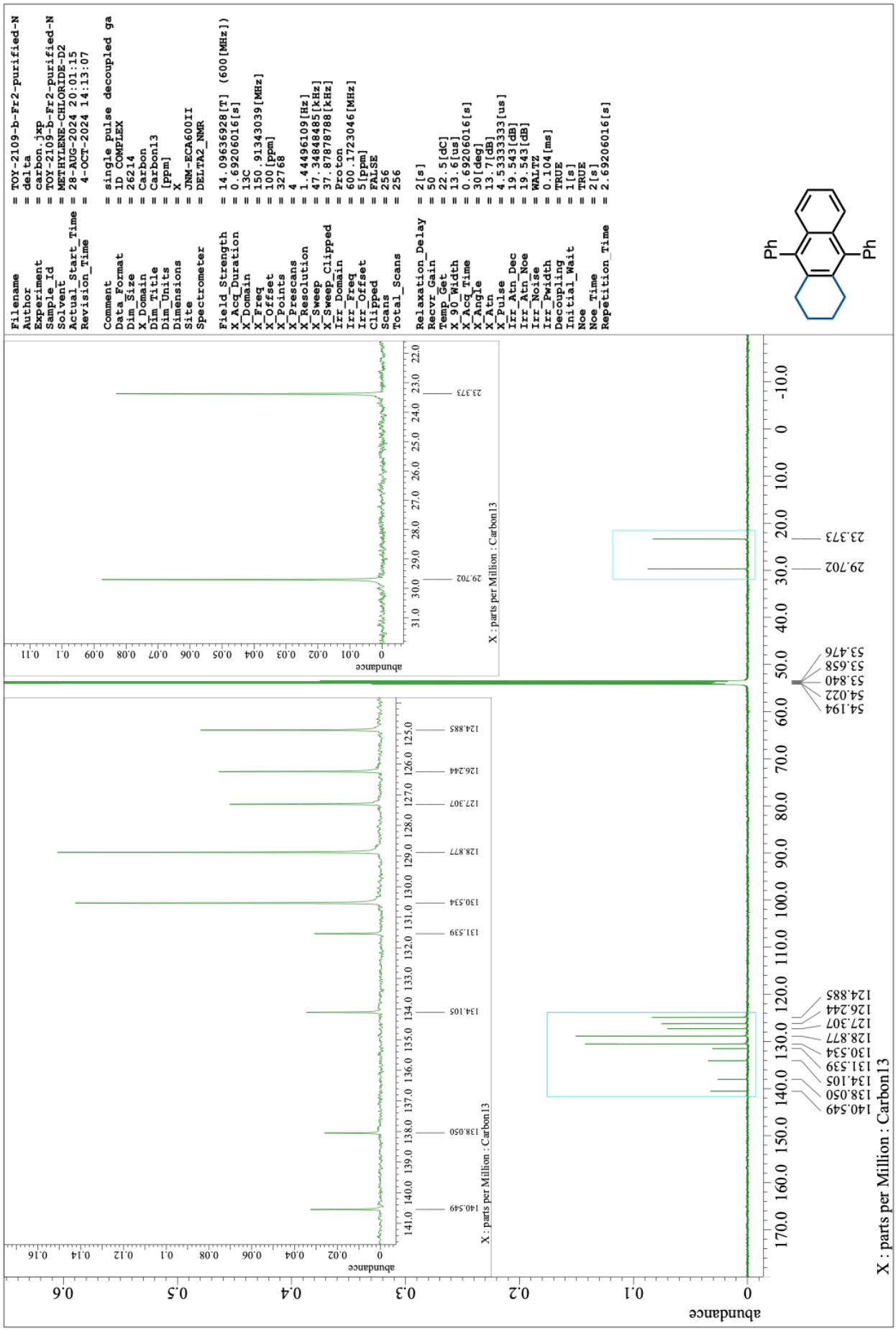

Figure S42. ^{13}C NMR spectrum of **8h'** (150 MHz, CD_2Cl_2).

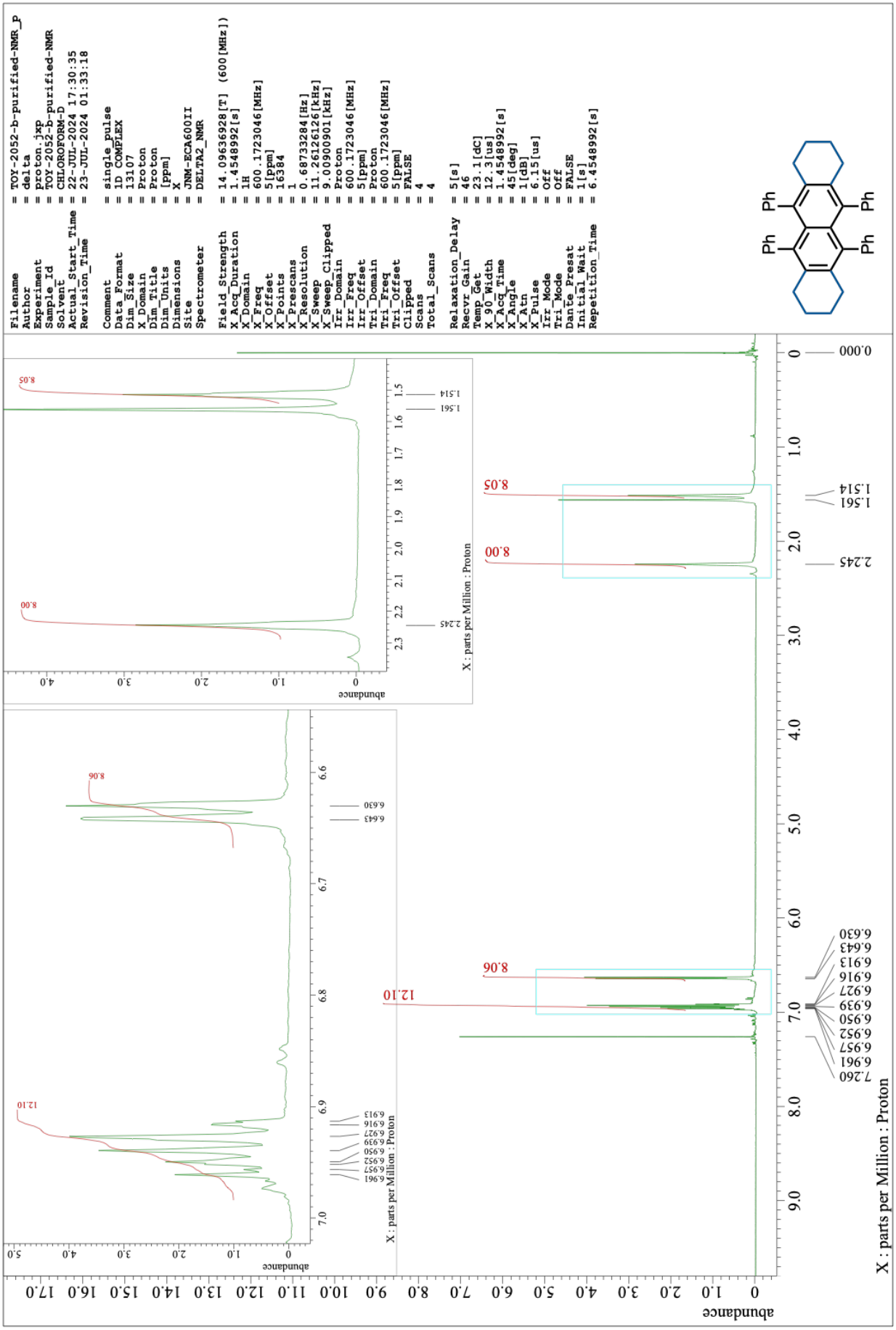

Figure S43. ^{1}H NMR spectrum of **8i** (600 MHz, $CDCl_3$).

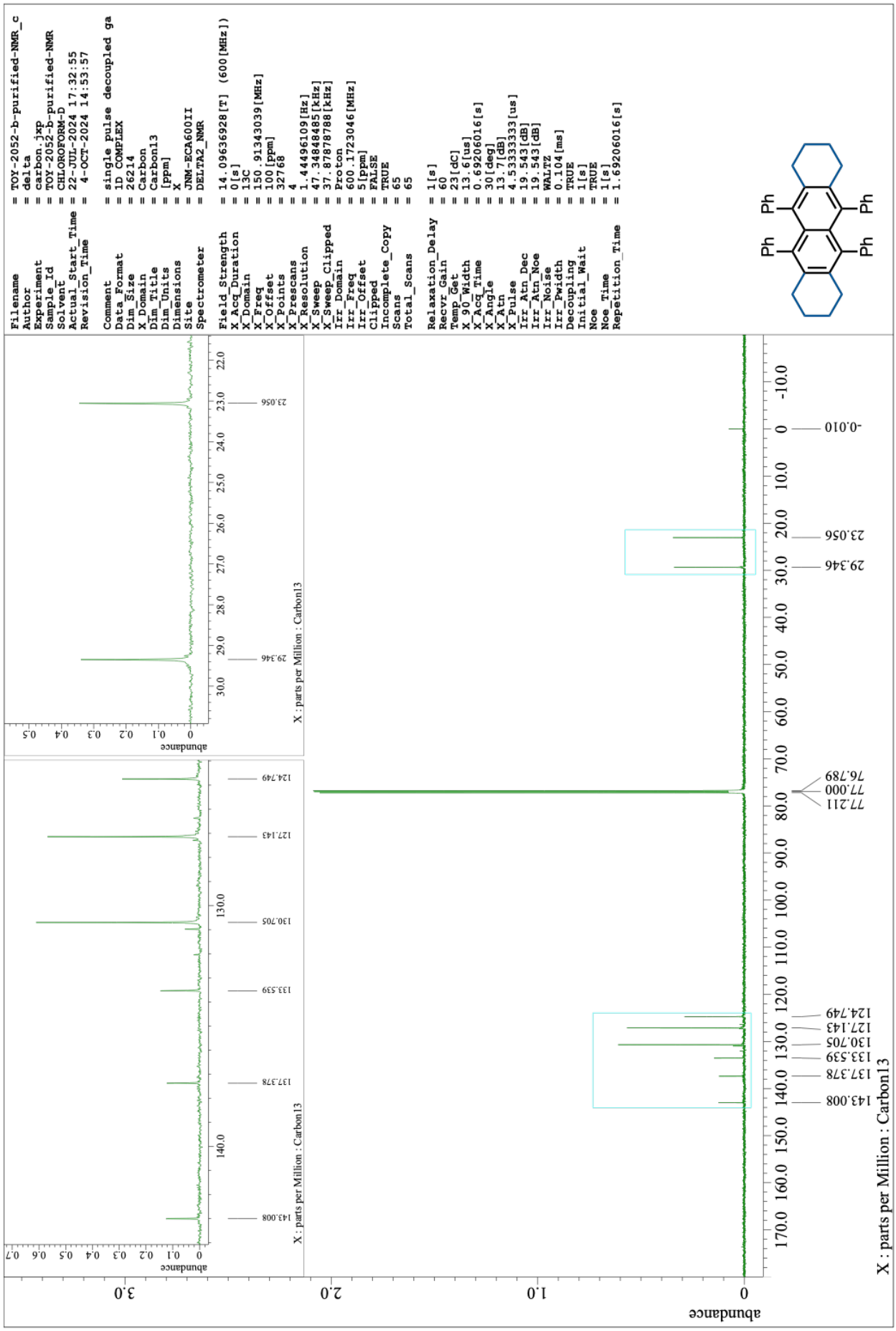

Figure S44. ^{13}C NMR spectrum of **8i** (150 MHz, $CDCl_3$).

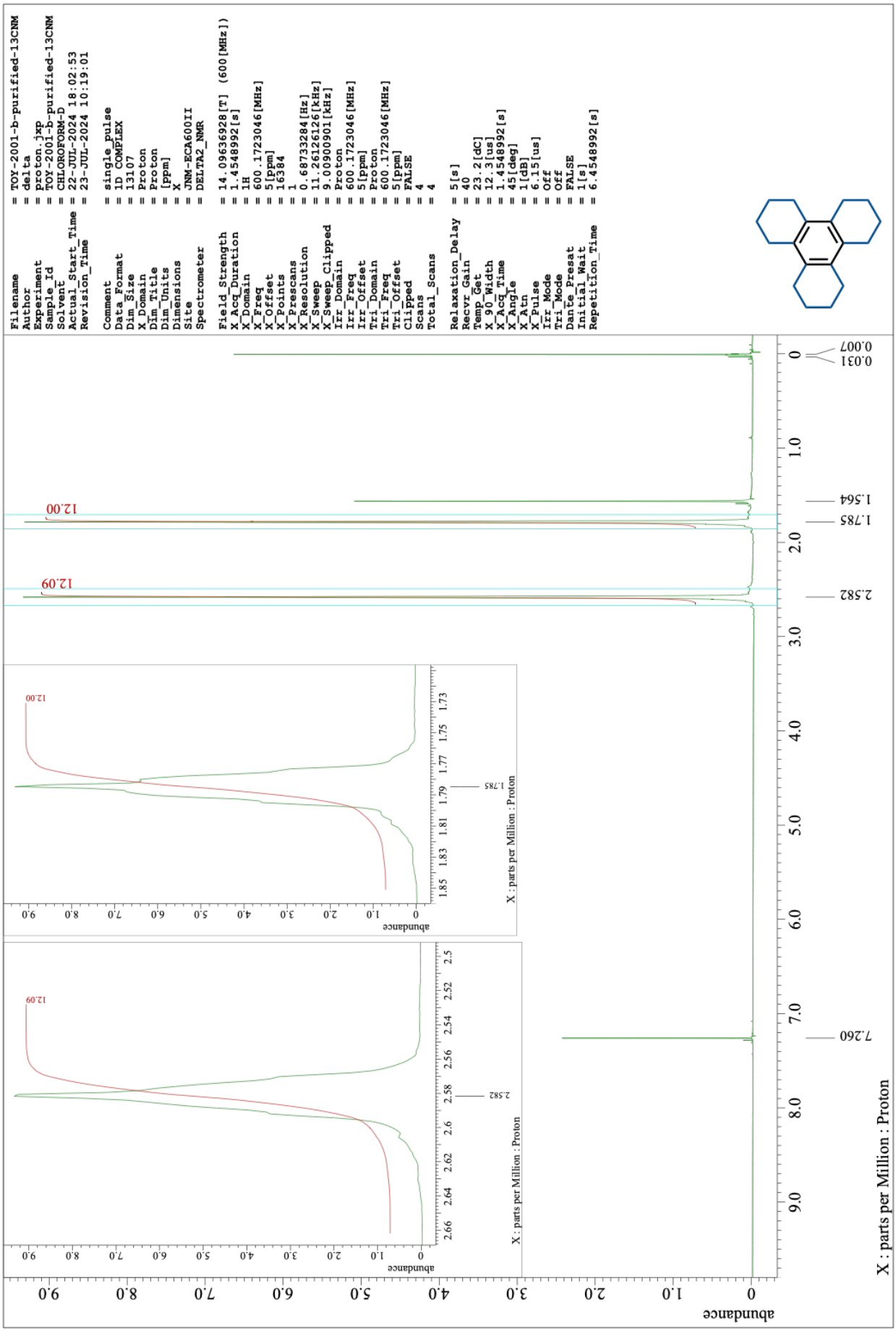

Figure S45. ^{1}H NMR spectrum of **8j** (600 MHz, $CDCl_3$).

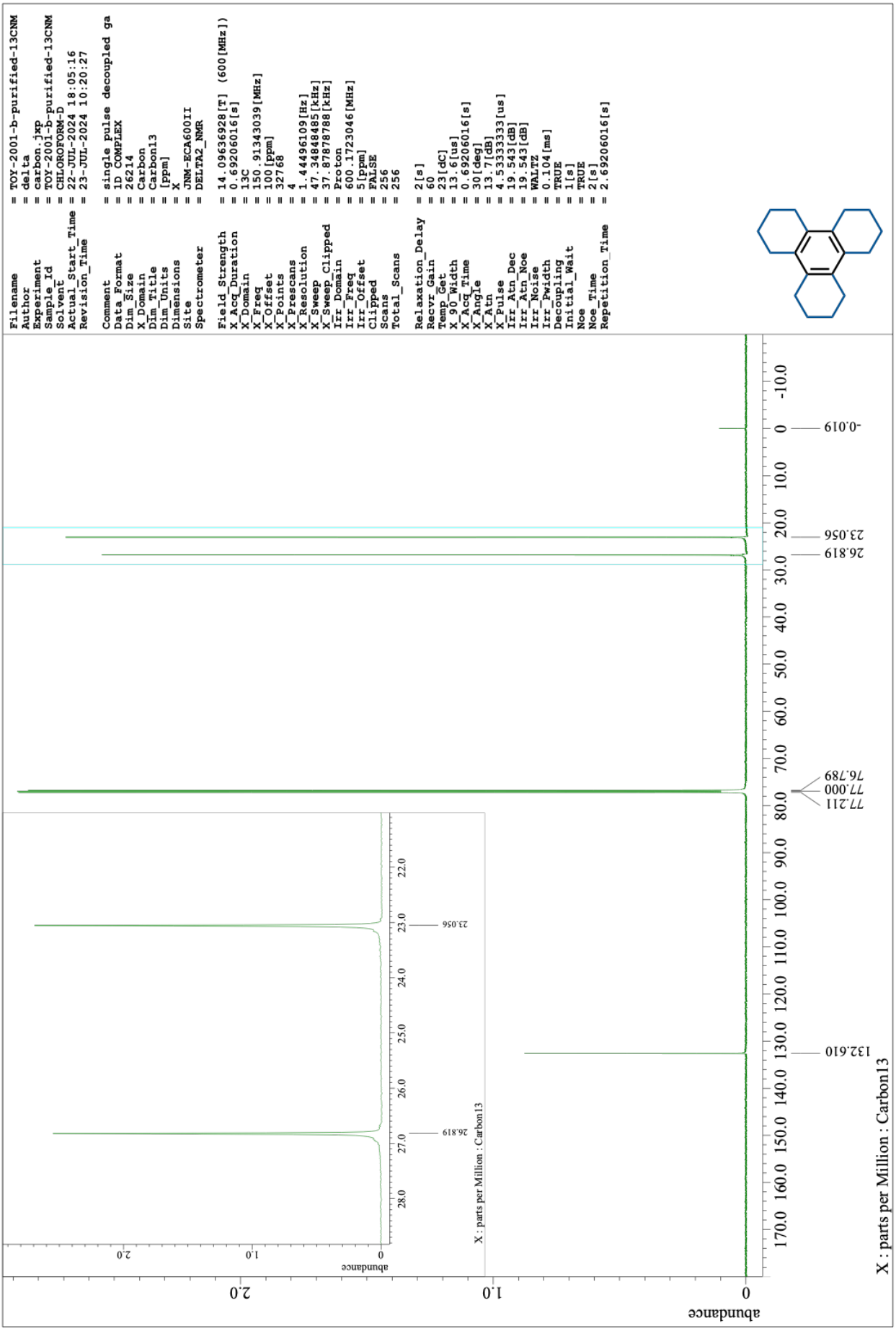

Figure S46. ^{13}C NMR spectrum of **8j** (150 MHz, $CDCl_3$).

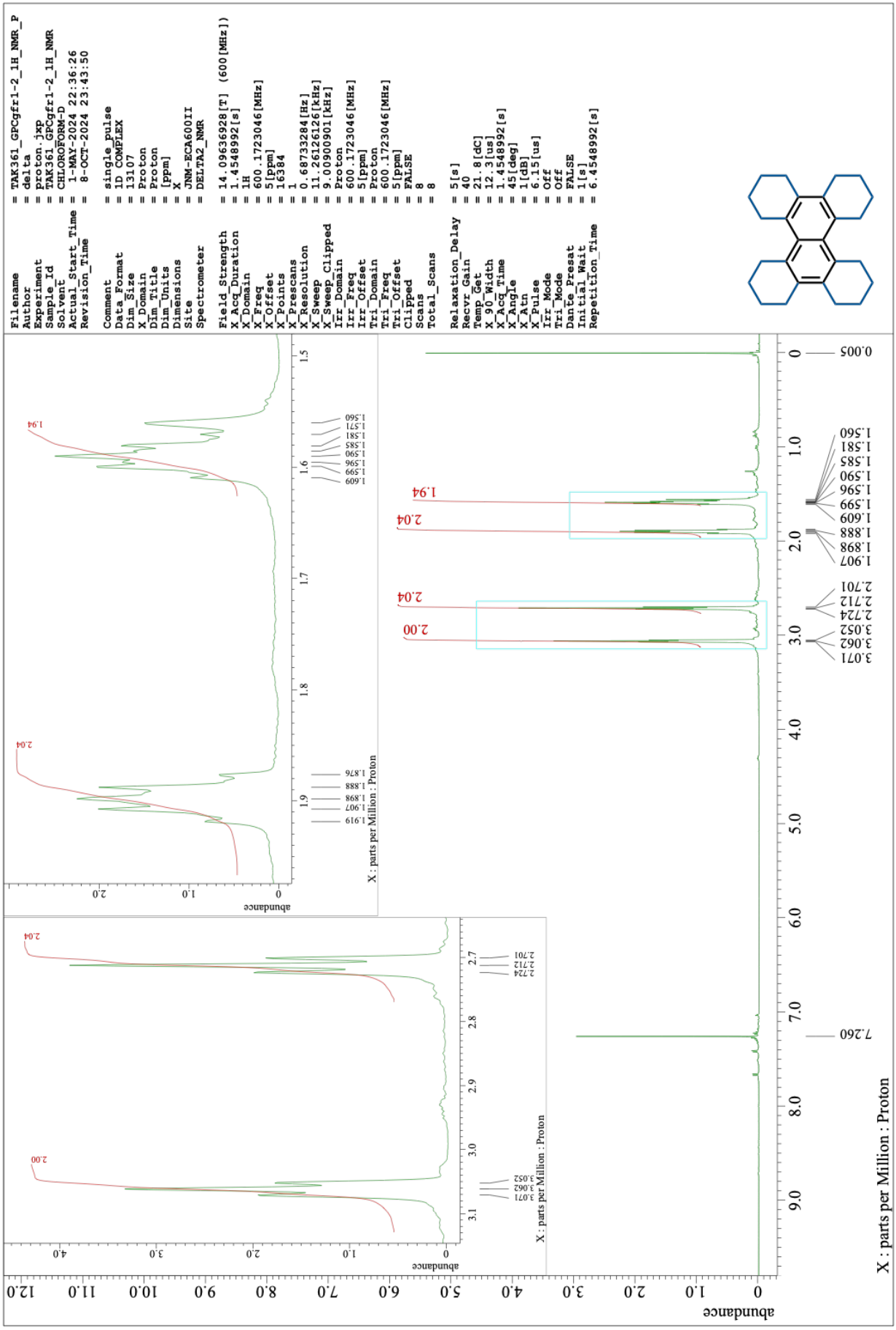

Figure S47. ^{1}H NMR spectrum of **8k** (600 MHz, $CDCl_3$).

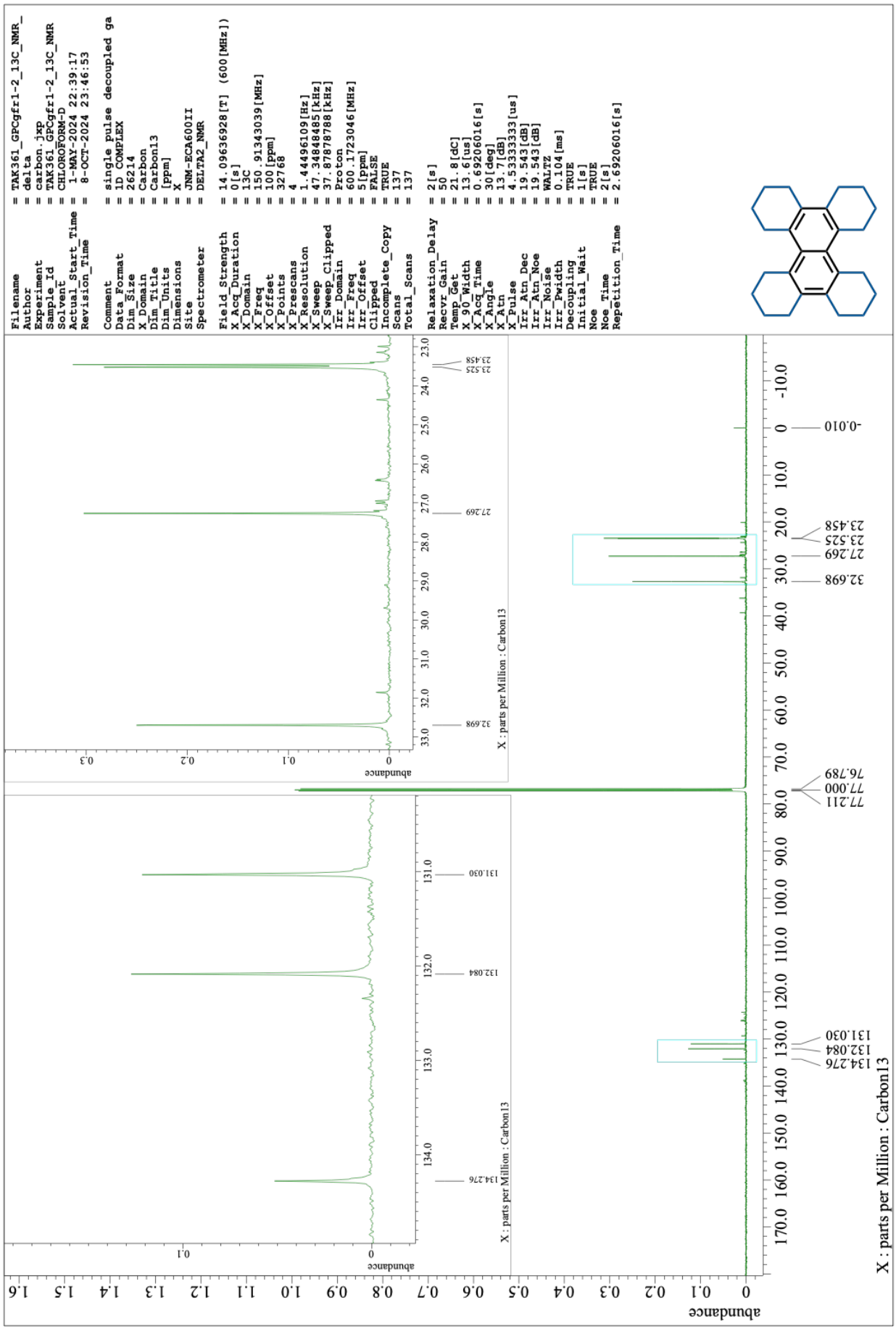

Figure S48. ^{13}C NMR spectrum of **8k** (150 MHz, $CDCl_3$).

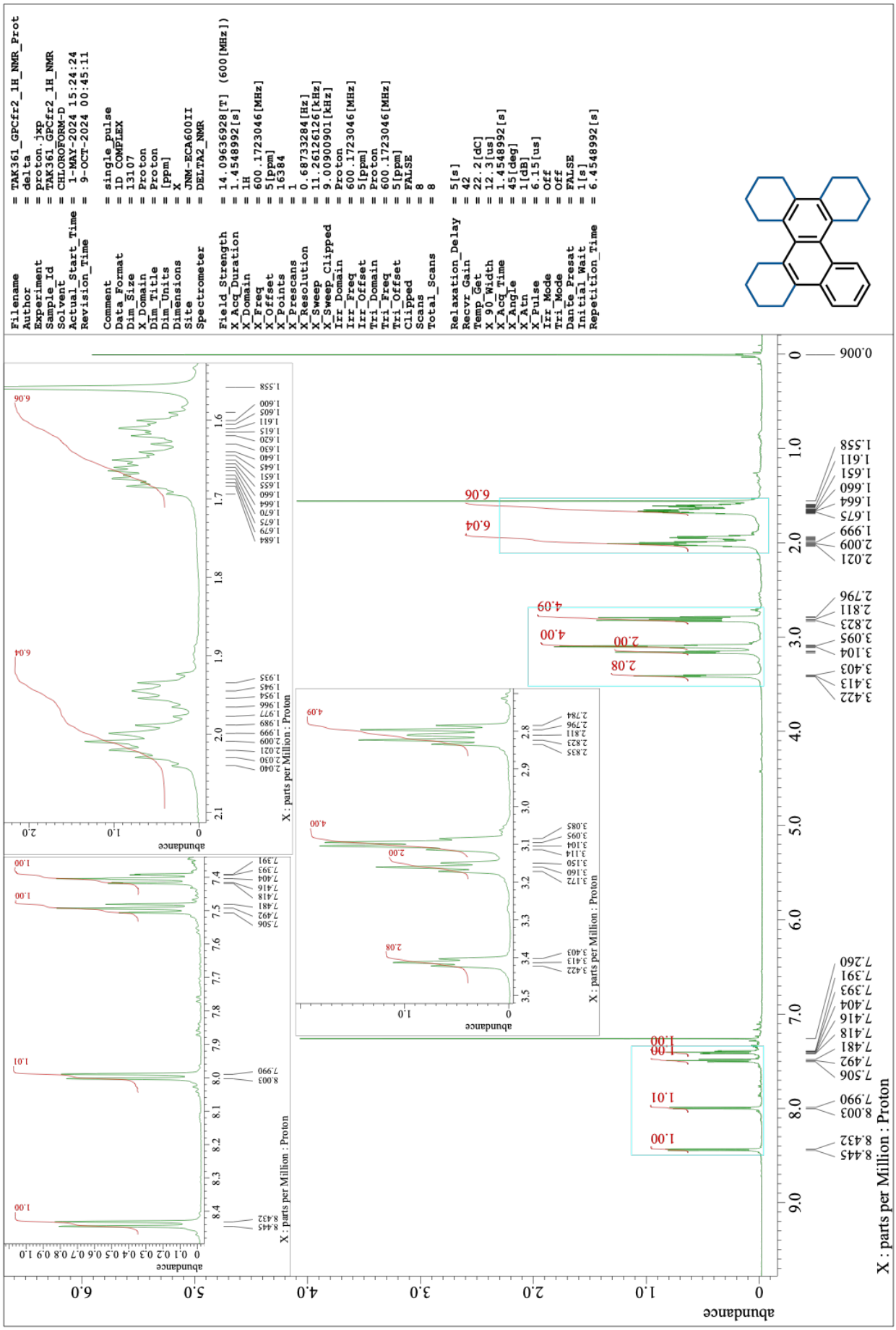

Figure S49. ^{1}H NMR spectrum of **8k'** (600 MHz, $CDCl_3$).

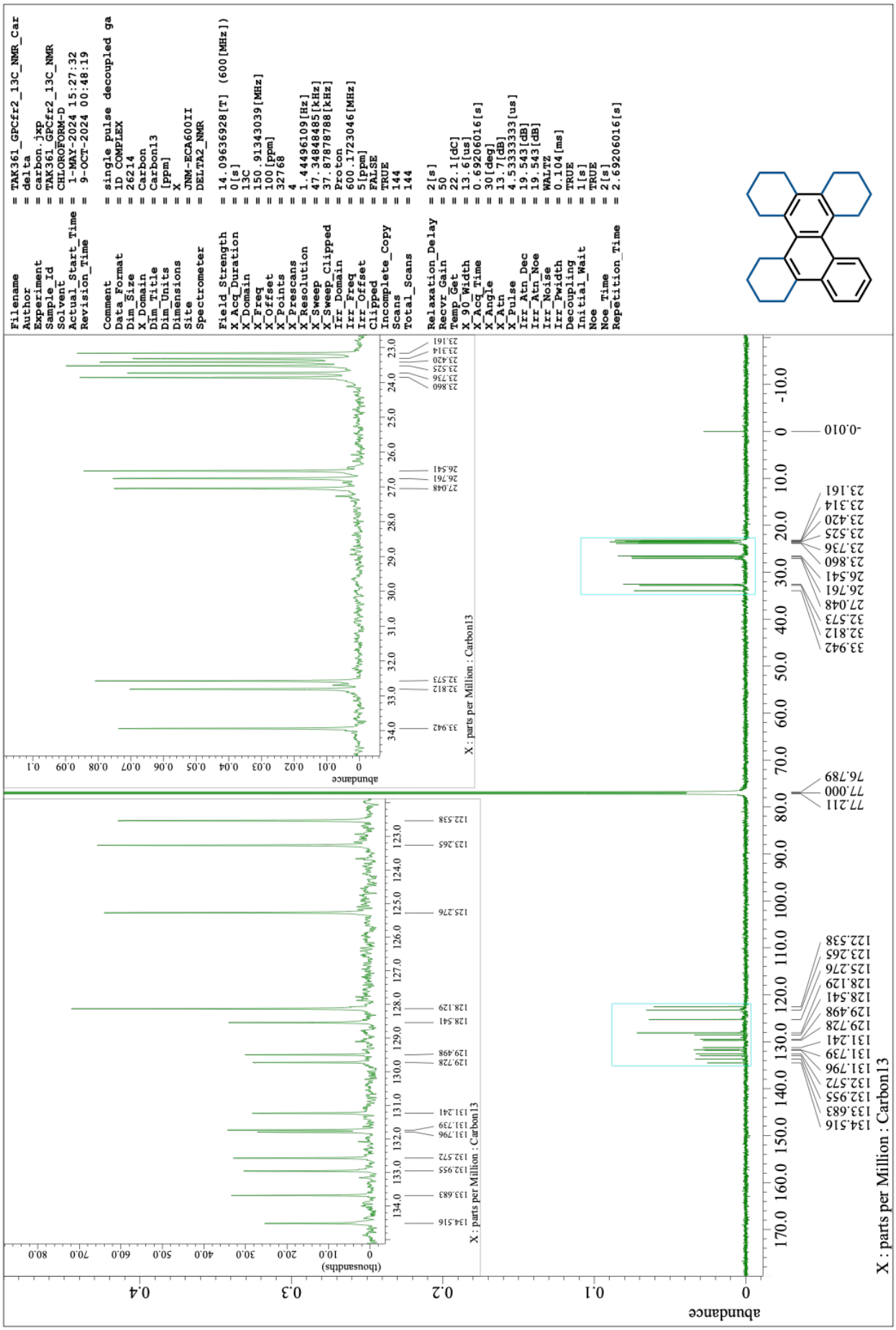

Figure S50. ^{13}C NMR spectrum of **8k'** (150 MHz, $CDCl_3$).

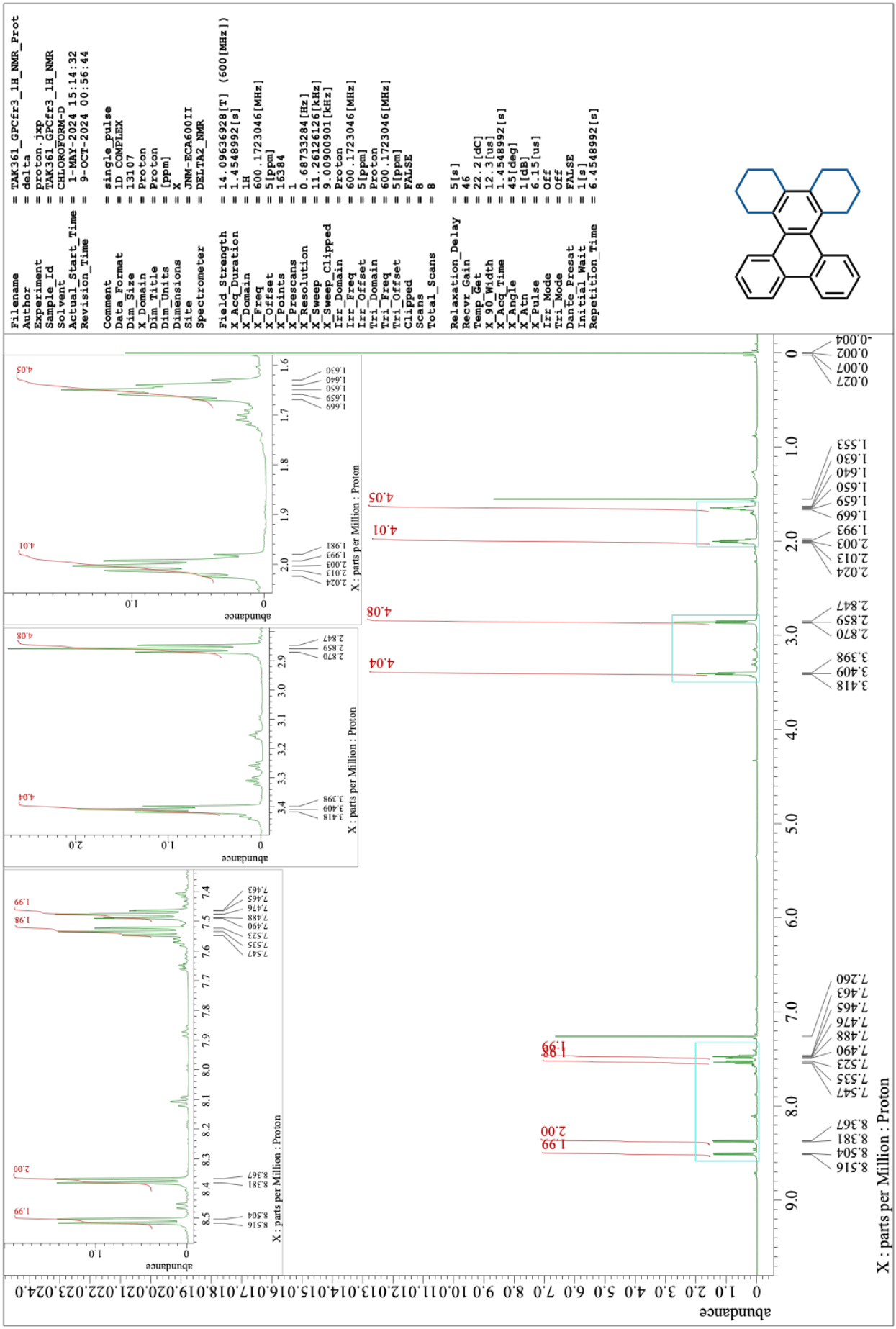

Figure S51. ^{1}H NMR spectrum of **8k''** (600 MHz, $CDCl_3$).

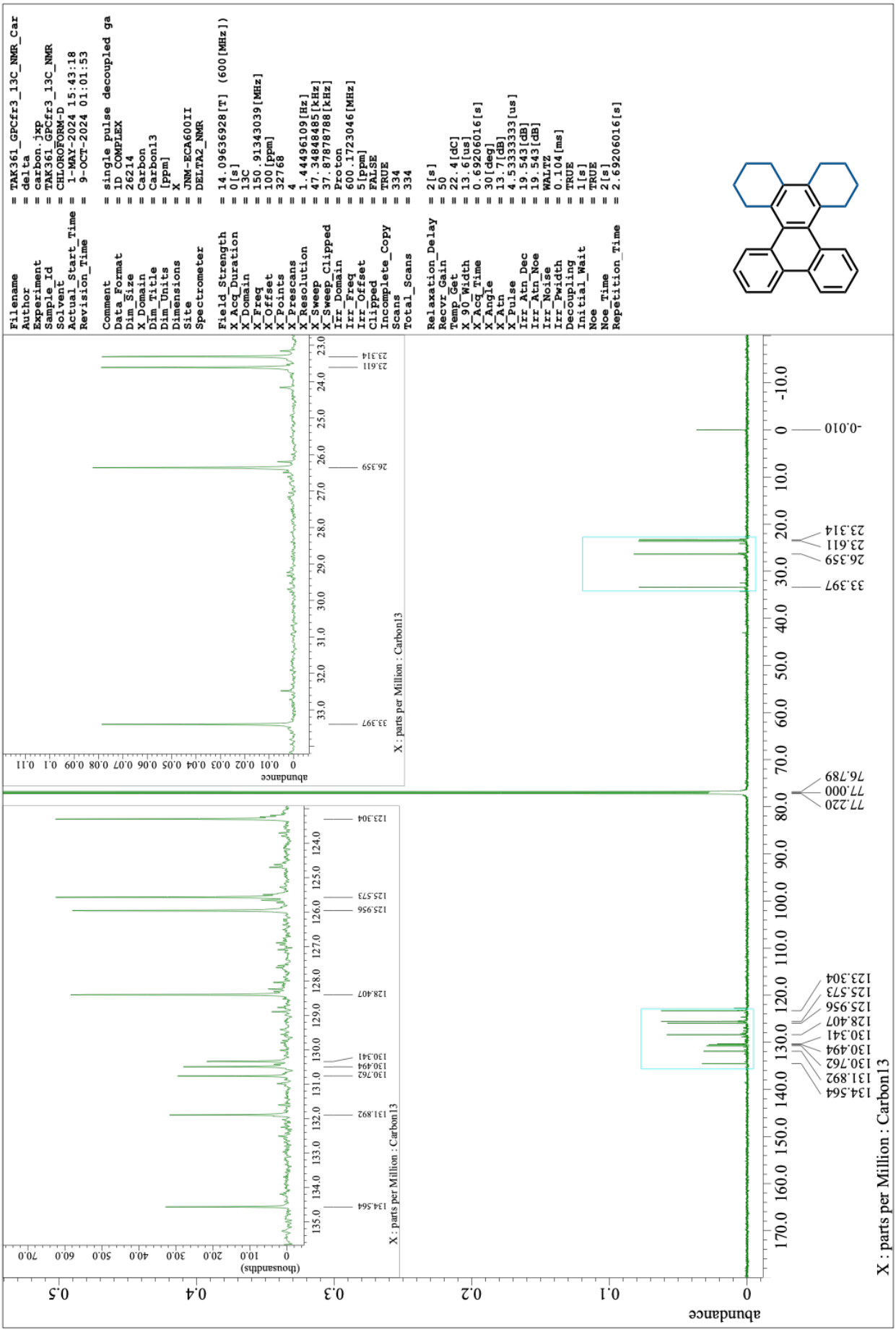

Figure S52. ^{13}C NMR spectrum of **8k''** (150 MHz, $CDCl_3$).

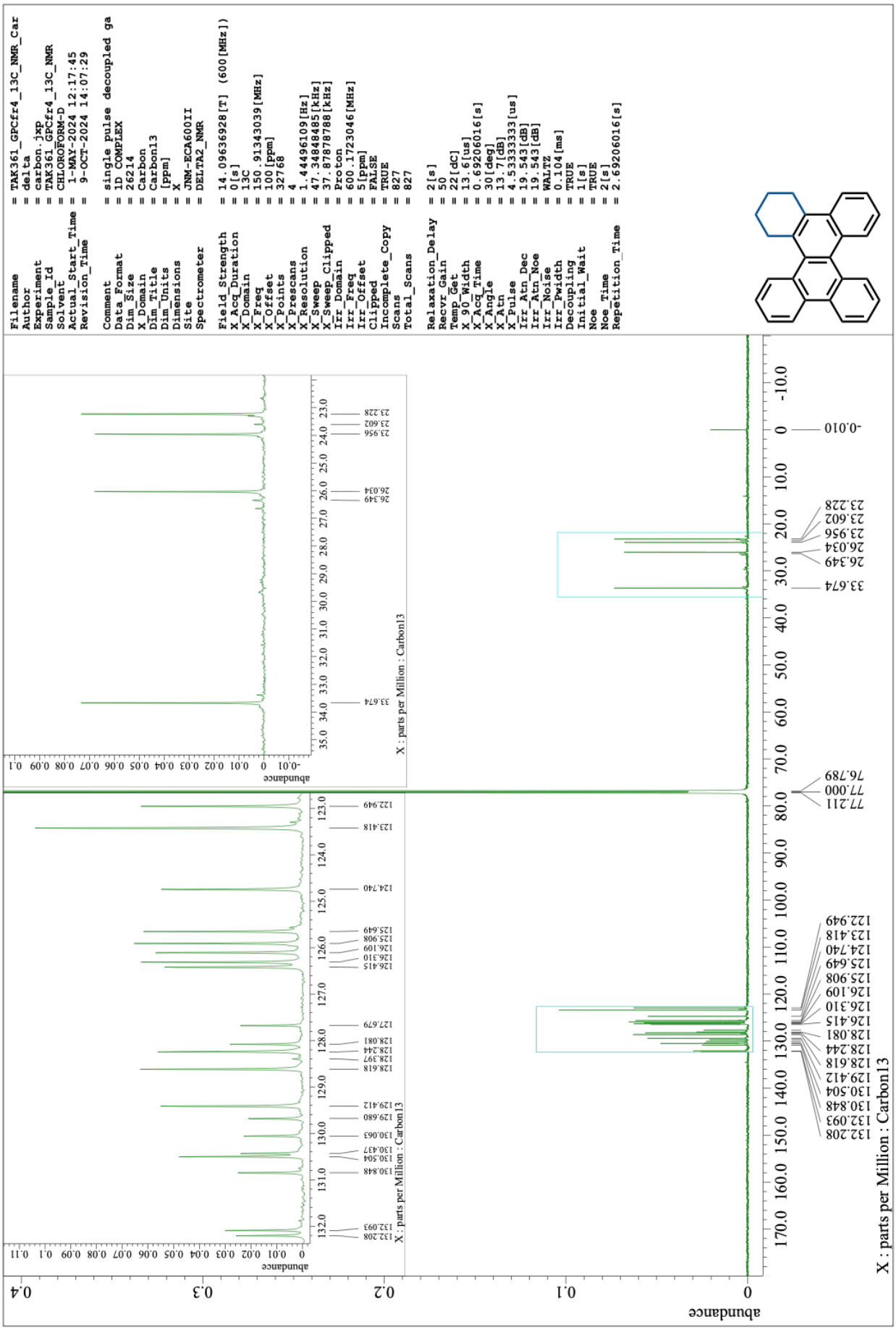

Figure S53. ^{1}H NMR spectrum of **8k'''** (600 MHz, $CDCl_3$).

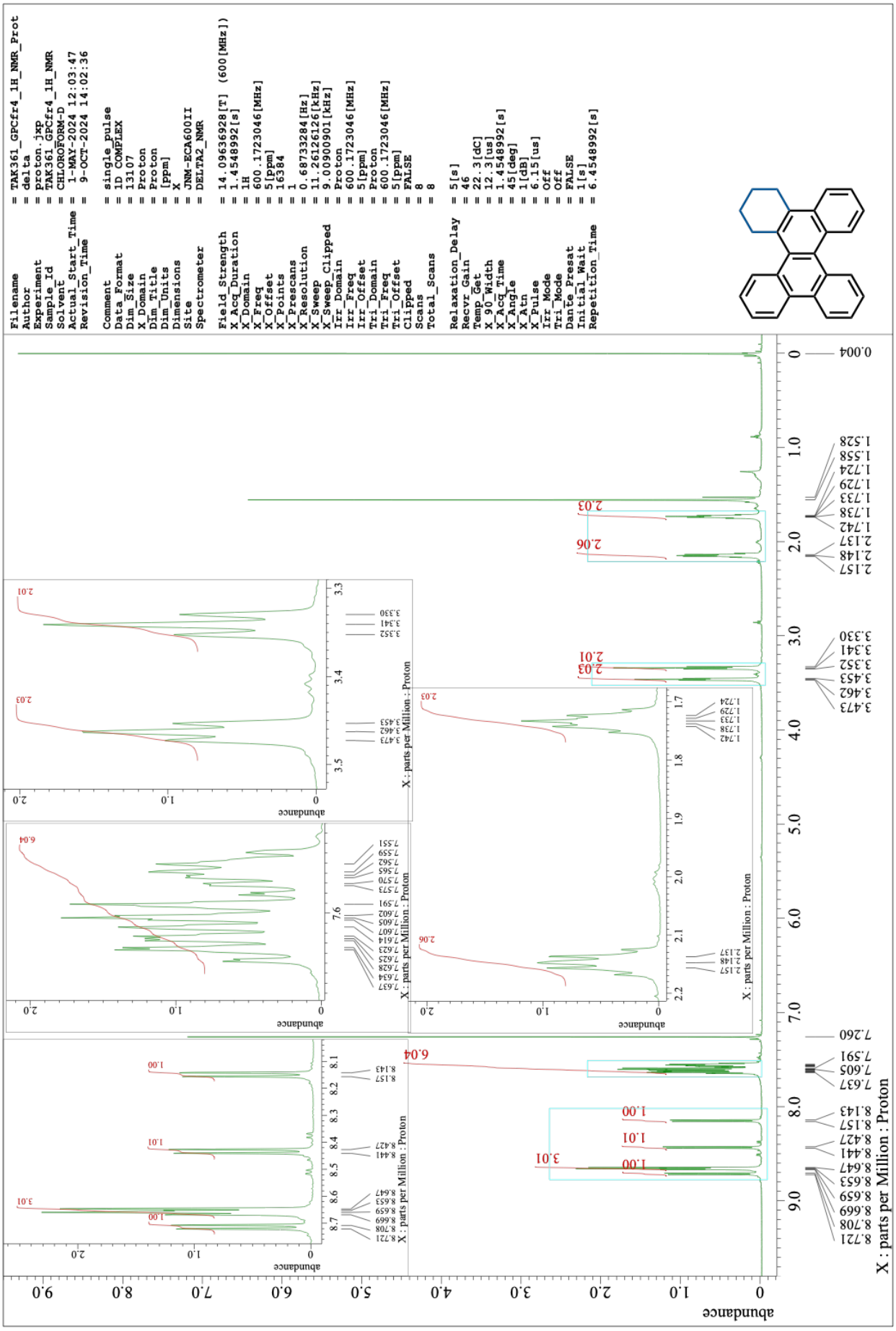

Figure S54. ^{13}C NMR spectrum of **8k'''** (150 MHz, $CDCl_3$).

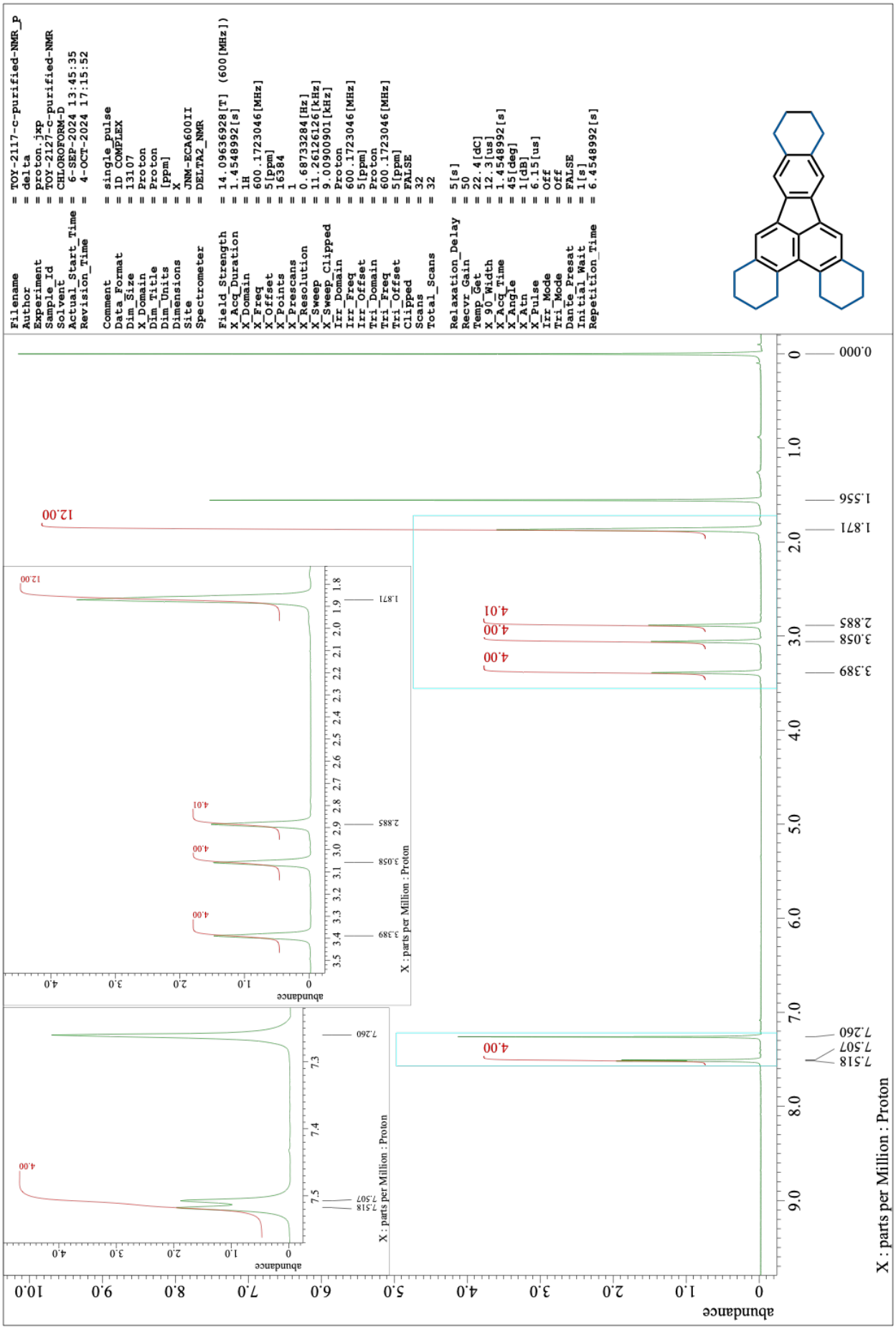

Figure S55. ^{1}H NMR spectrum of **8l** (600 MHz, $CDCl_3$).

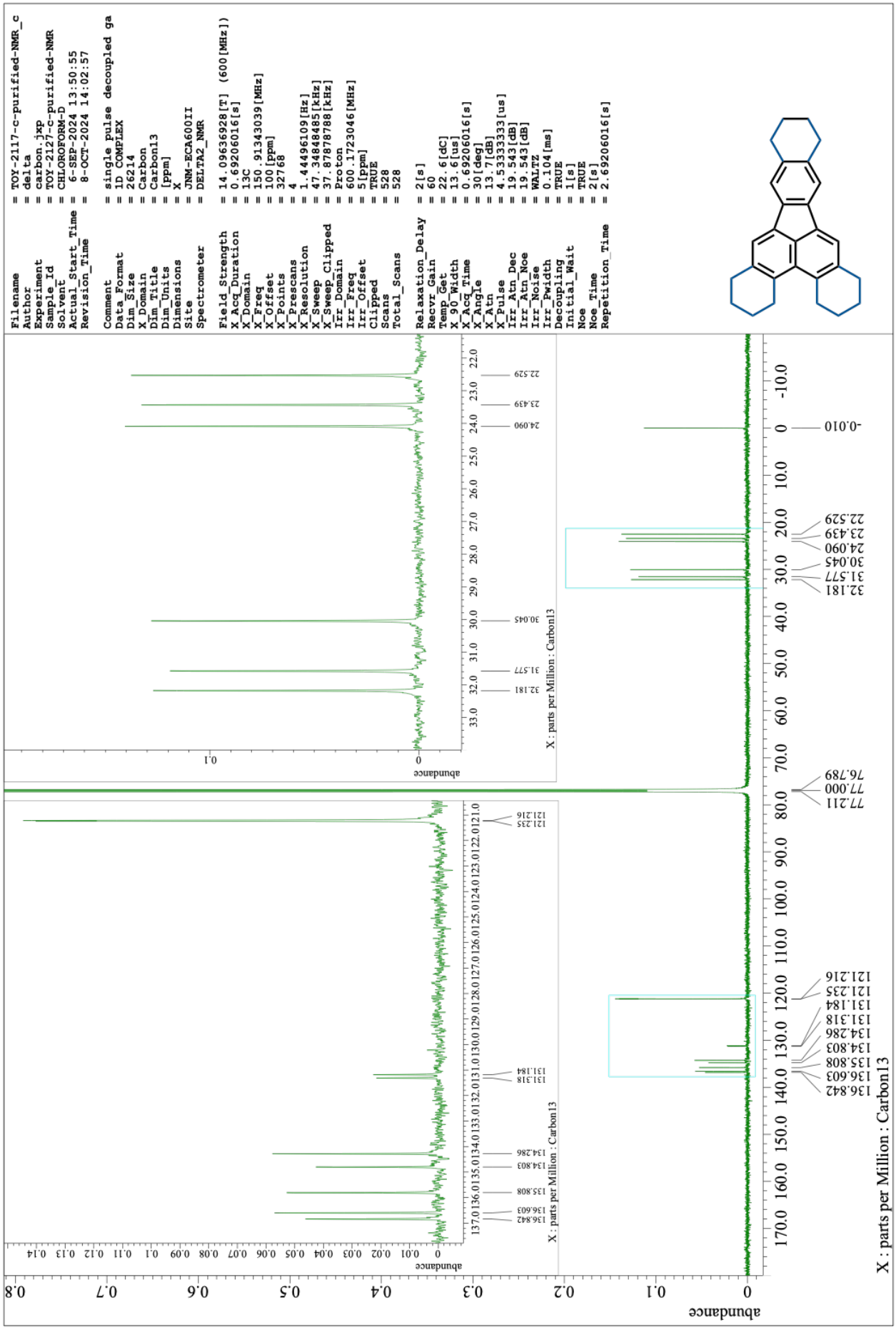

Figure S56. ^{13}C NMR spectrum of **8l** (150 MHz, $CDCl_3$).

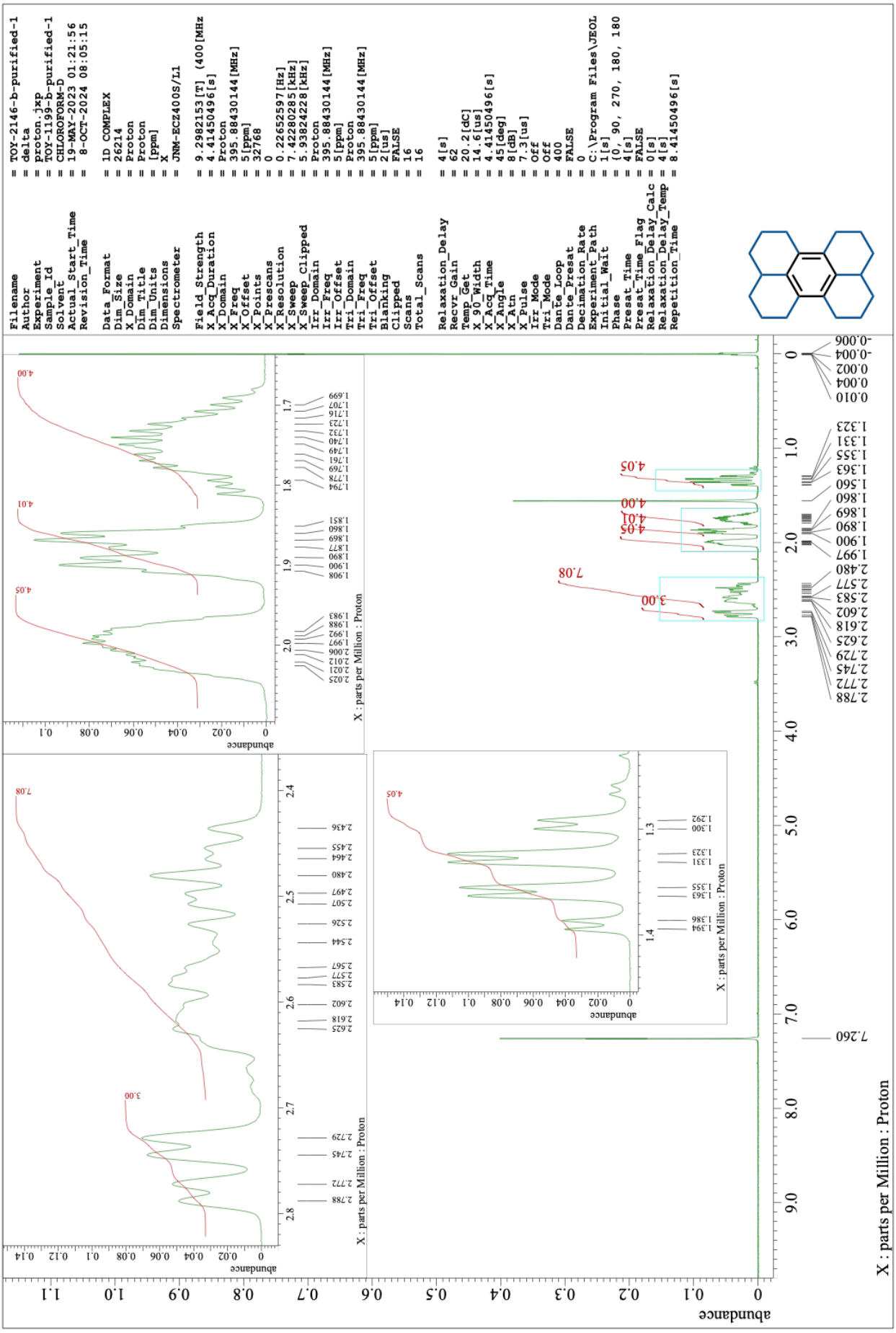

Figure S57. ^{1}H NMR spectrum of **8m** (400 MHz, $CDCl_3$).

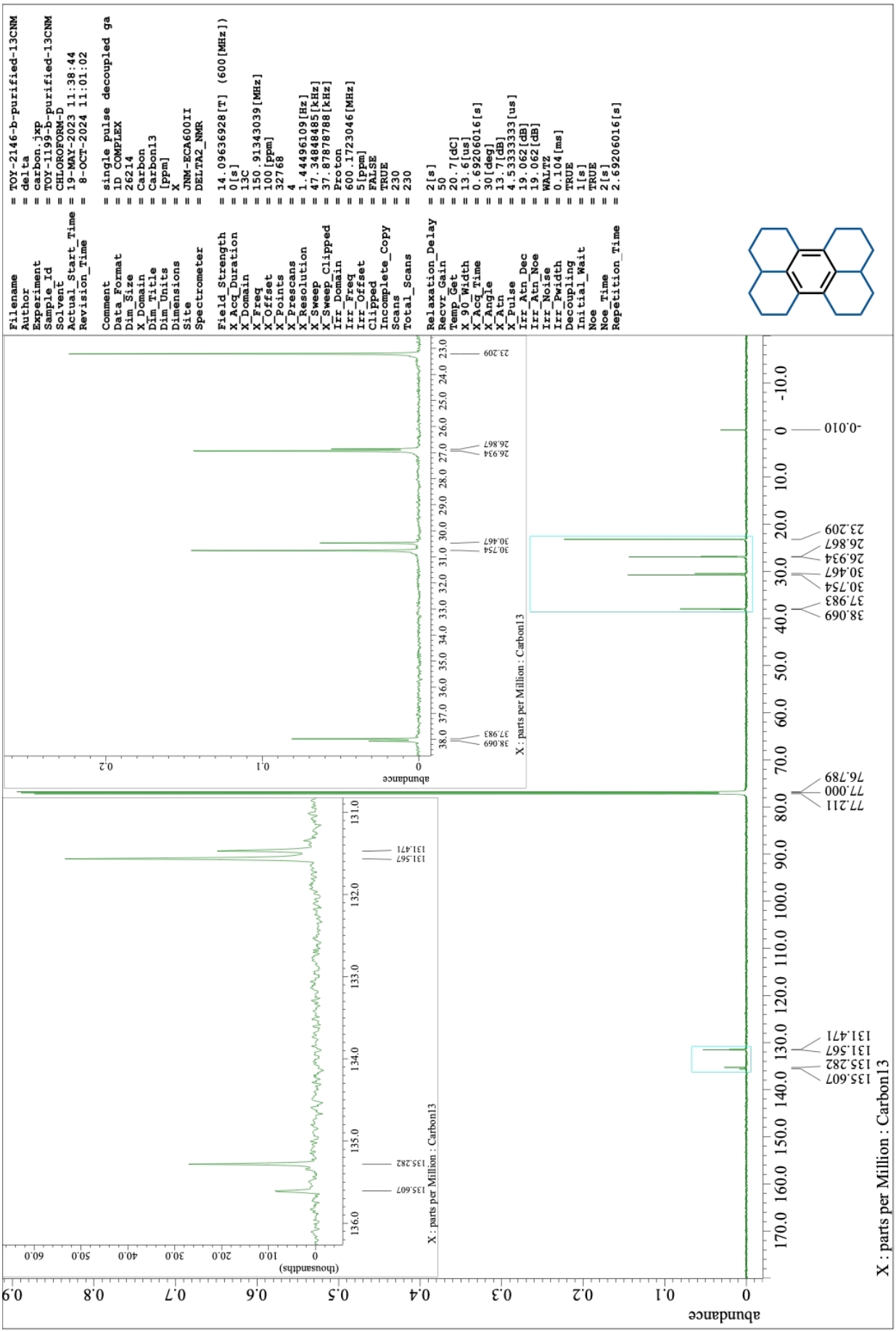

Figure S58. ^{13}C NMR spectrum of **8m** (150 MHz, $CDCl_3$).

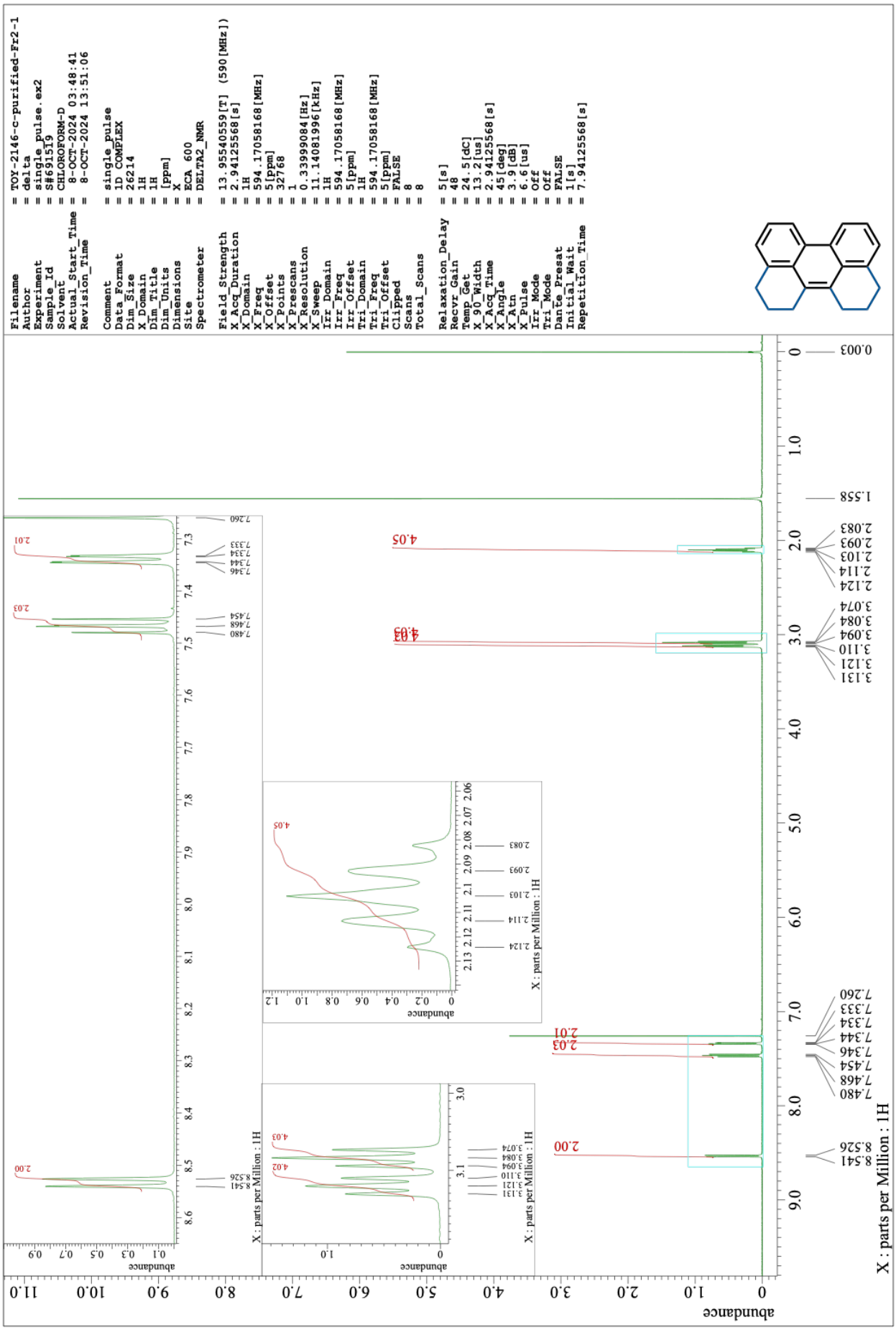

Figure S59. ^{1}H NMR spectrum of **8m'** (600 MHz, $CDCl_3$).

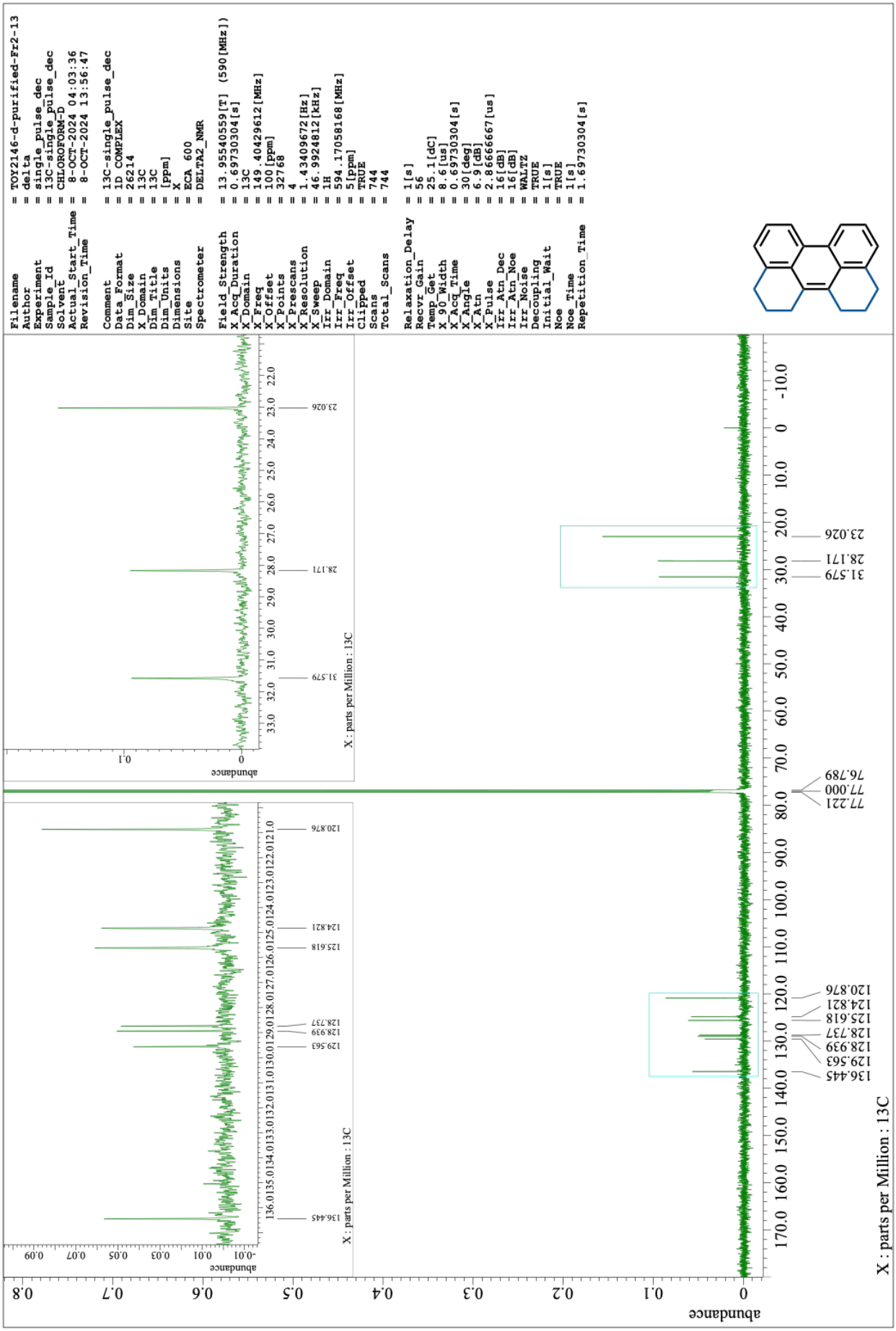

Figure S60. ^{13}C NMR spectrum of **8m'** (150 MHz, $CDCl_3$).

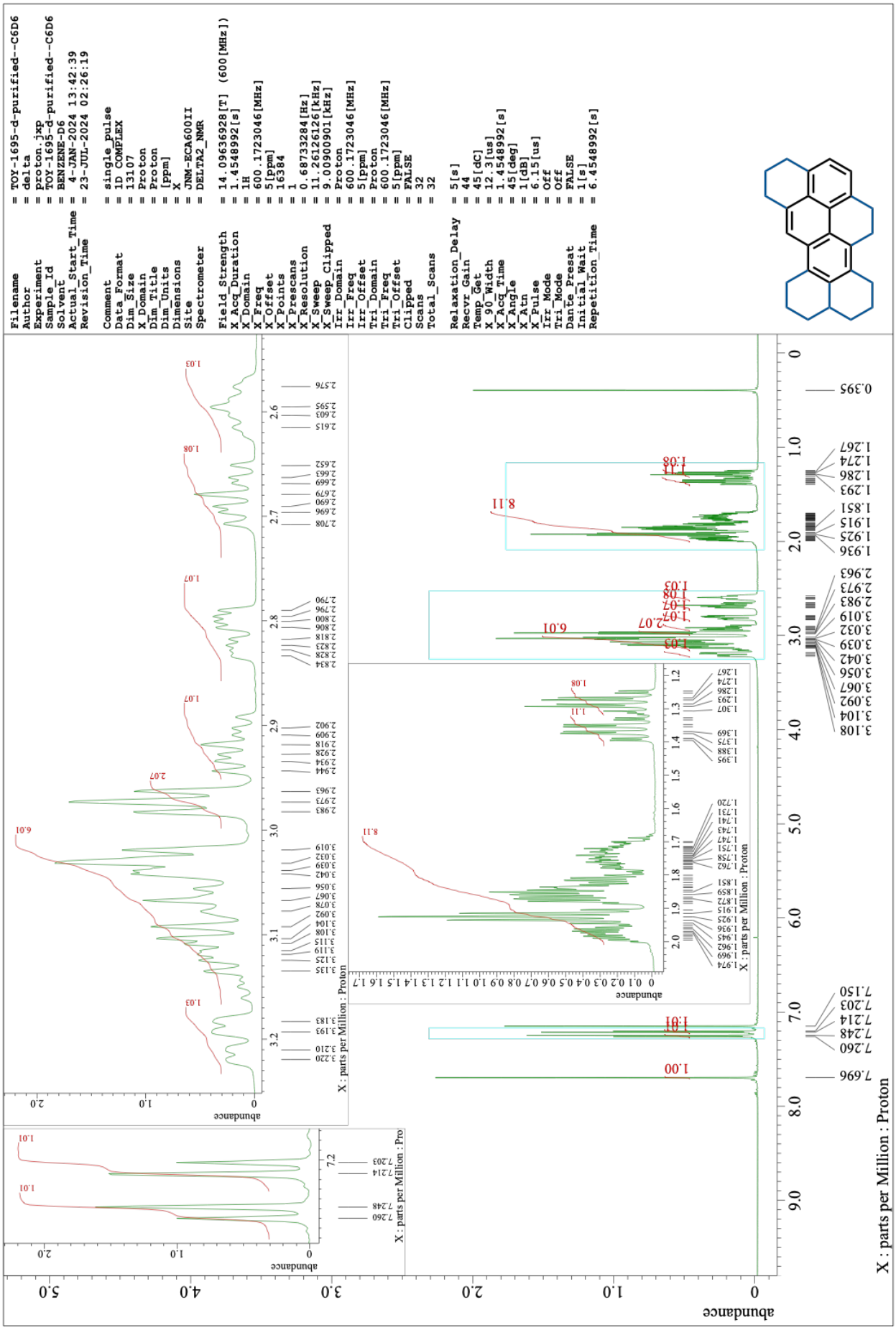

Figure S61. ^{1}H NMR spectrum of **8n** (600 MHz, C_6D_6).

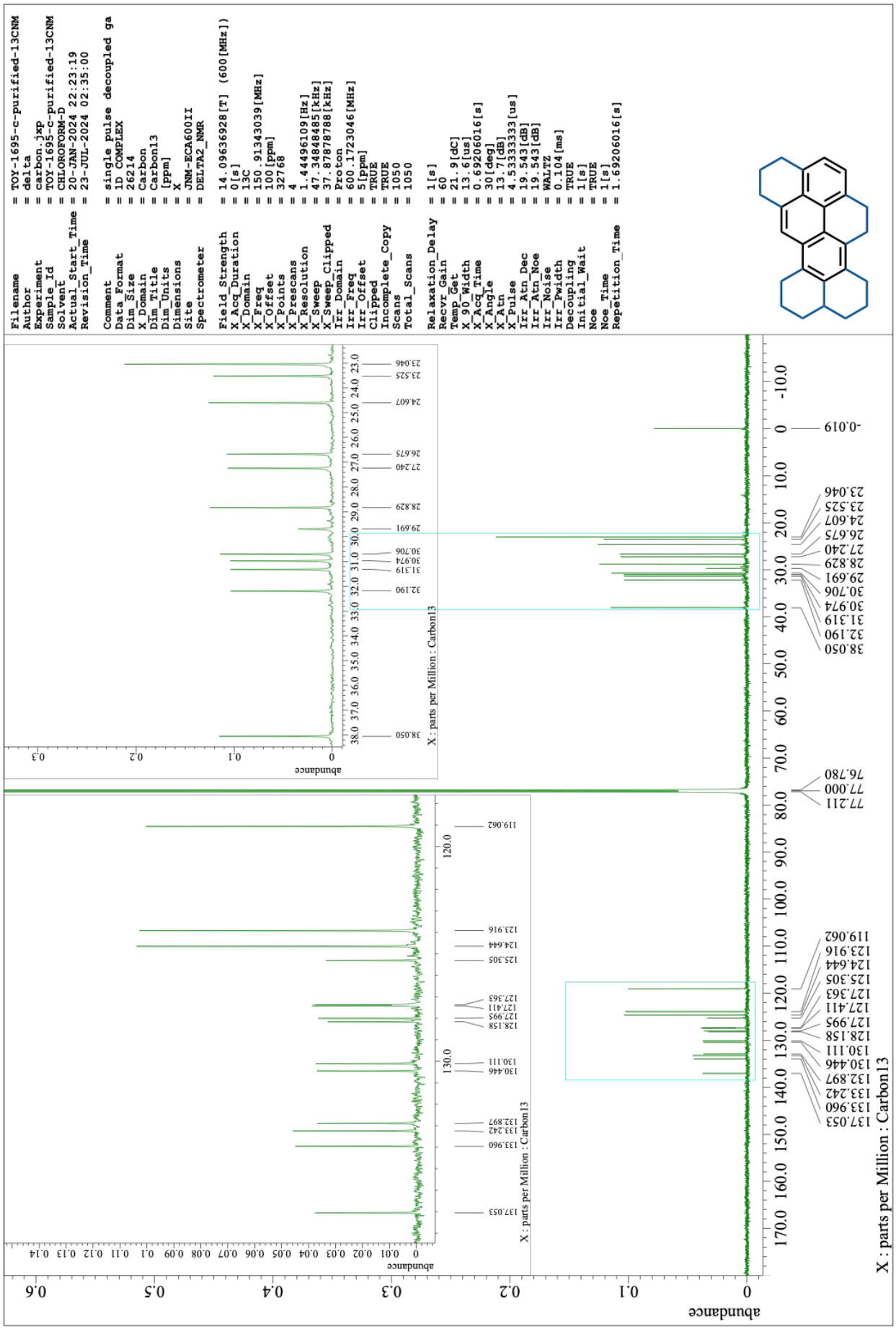

Figure S62. ^{13}C NMR spectrum of **8n** (150 MHz, $CDCl_3$).

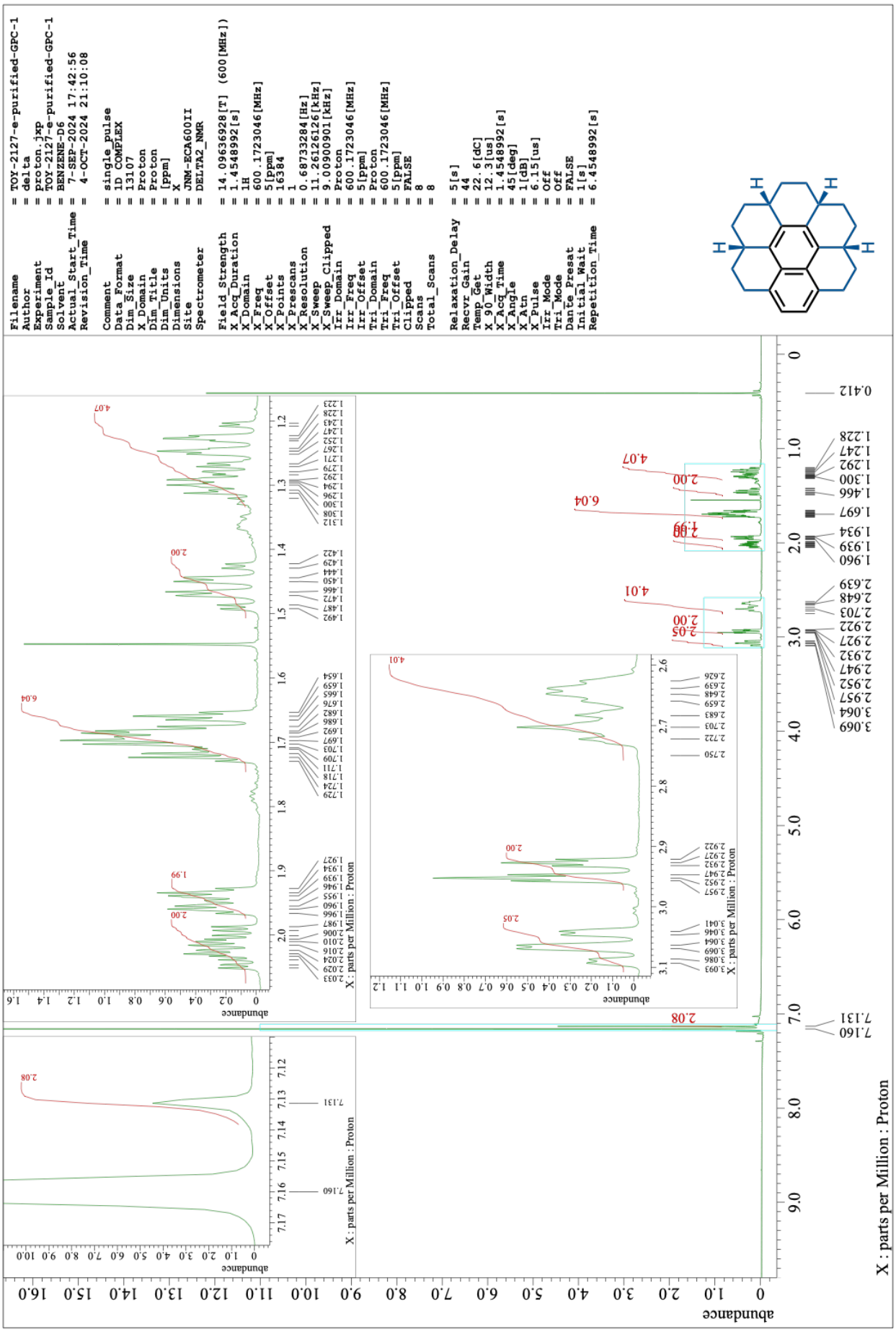

Figure S63. ^{1}H NMR spectrum of **8o** (600 MHz, C_6D_6).

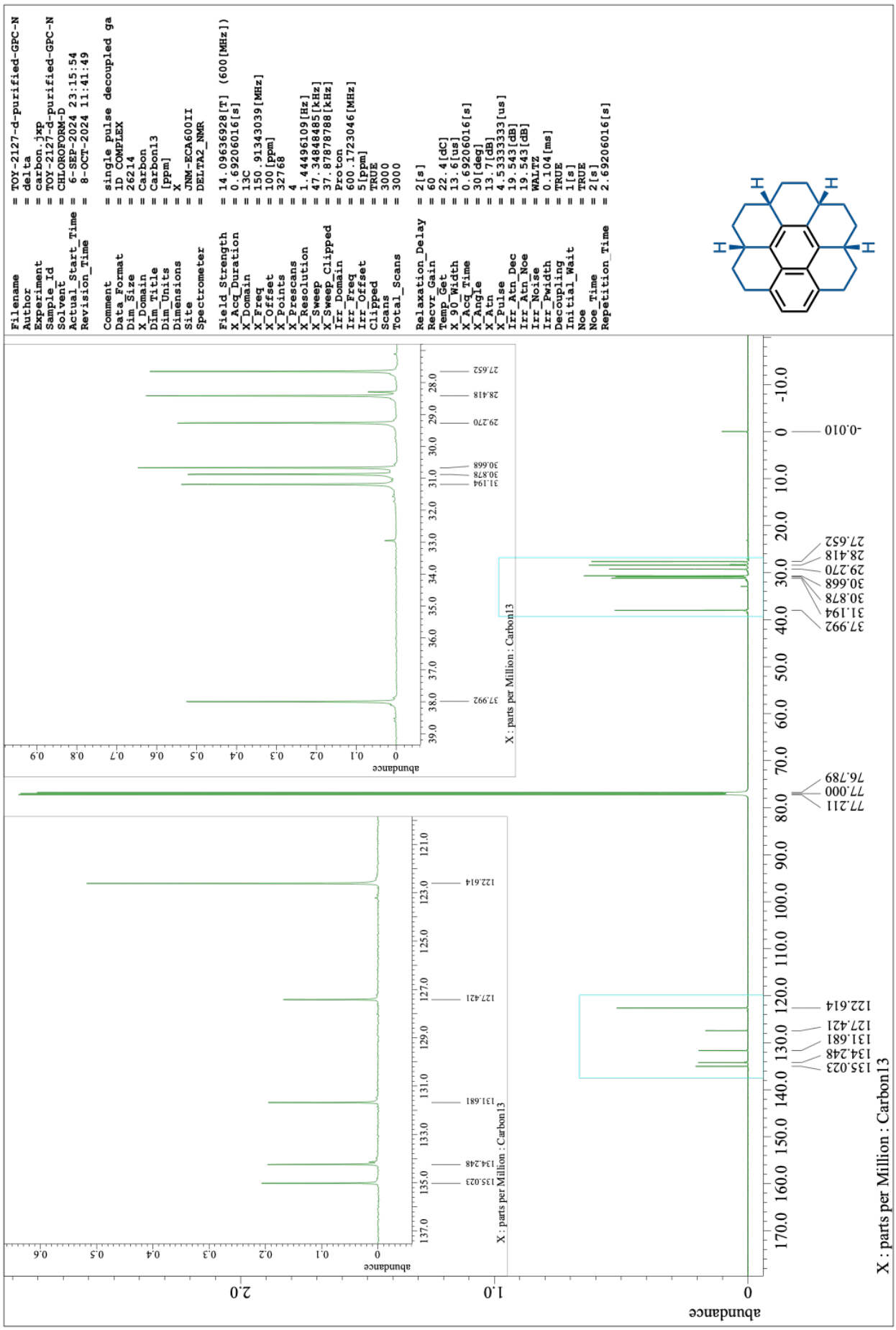

Figure S64. ^{13}C NMR spectrum of **8o** (150 MHz, $CDCl_3$).

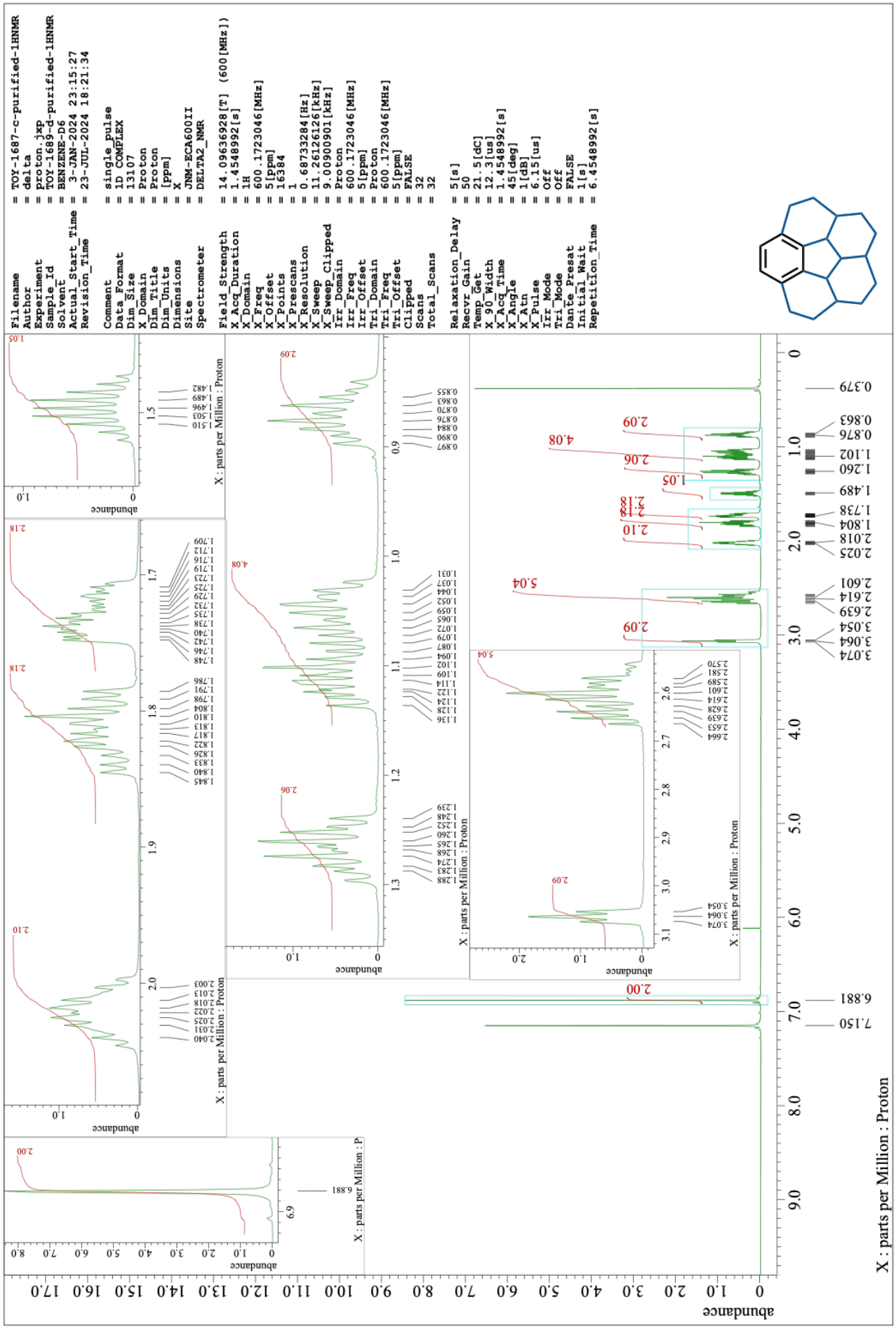

Figure S65. ^{1}H NMR spectrum of **8p** (600 MHz, C_6D_6).

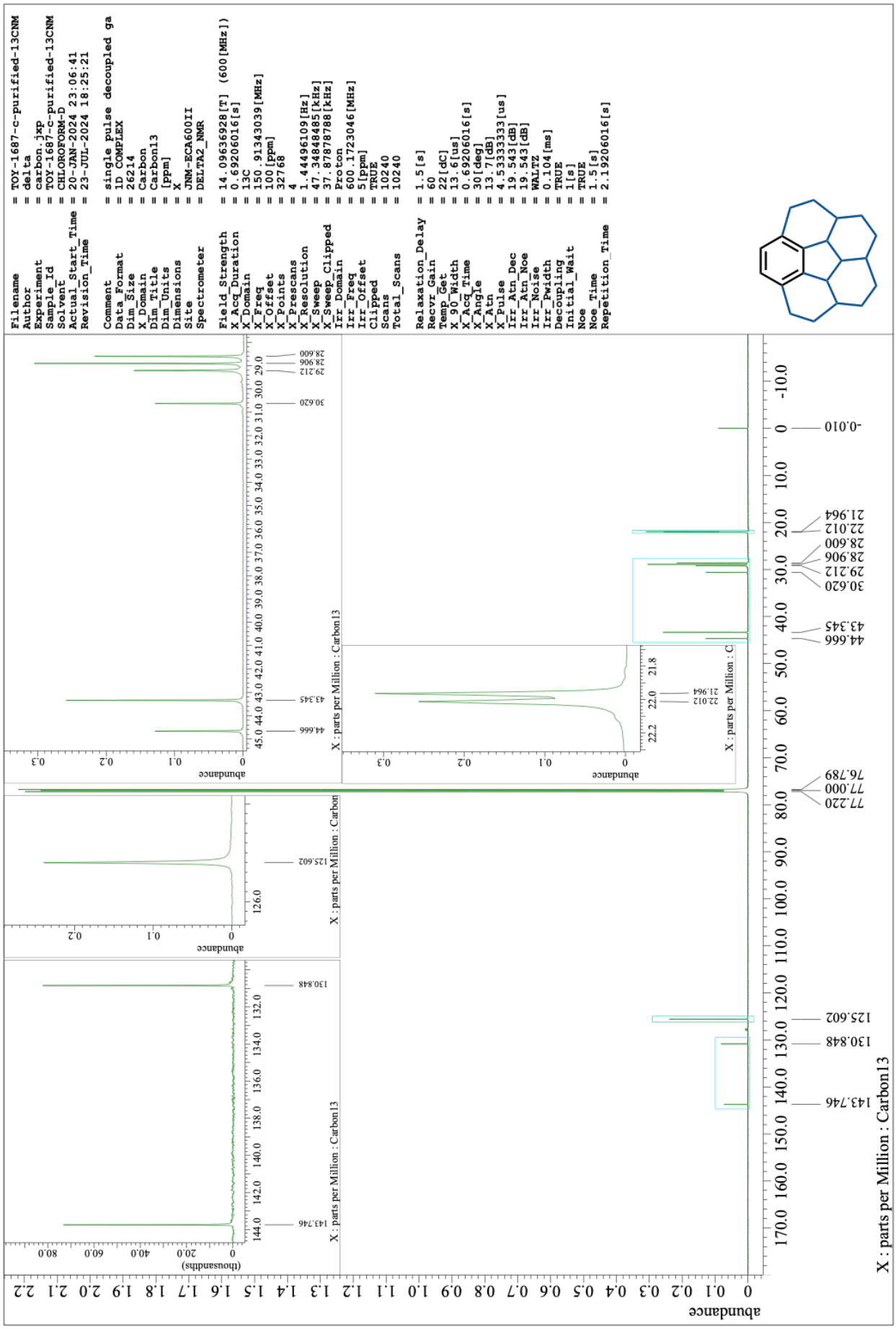

Figure S66. ^{13}C NMR spectrum of **8p** (150 MHz, $CDCl_3$).

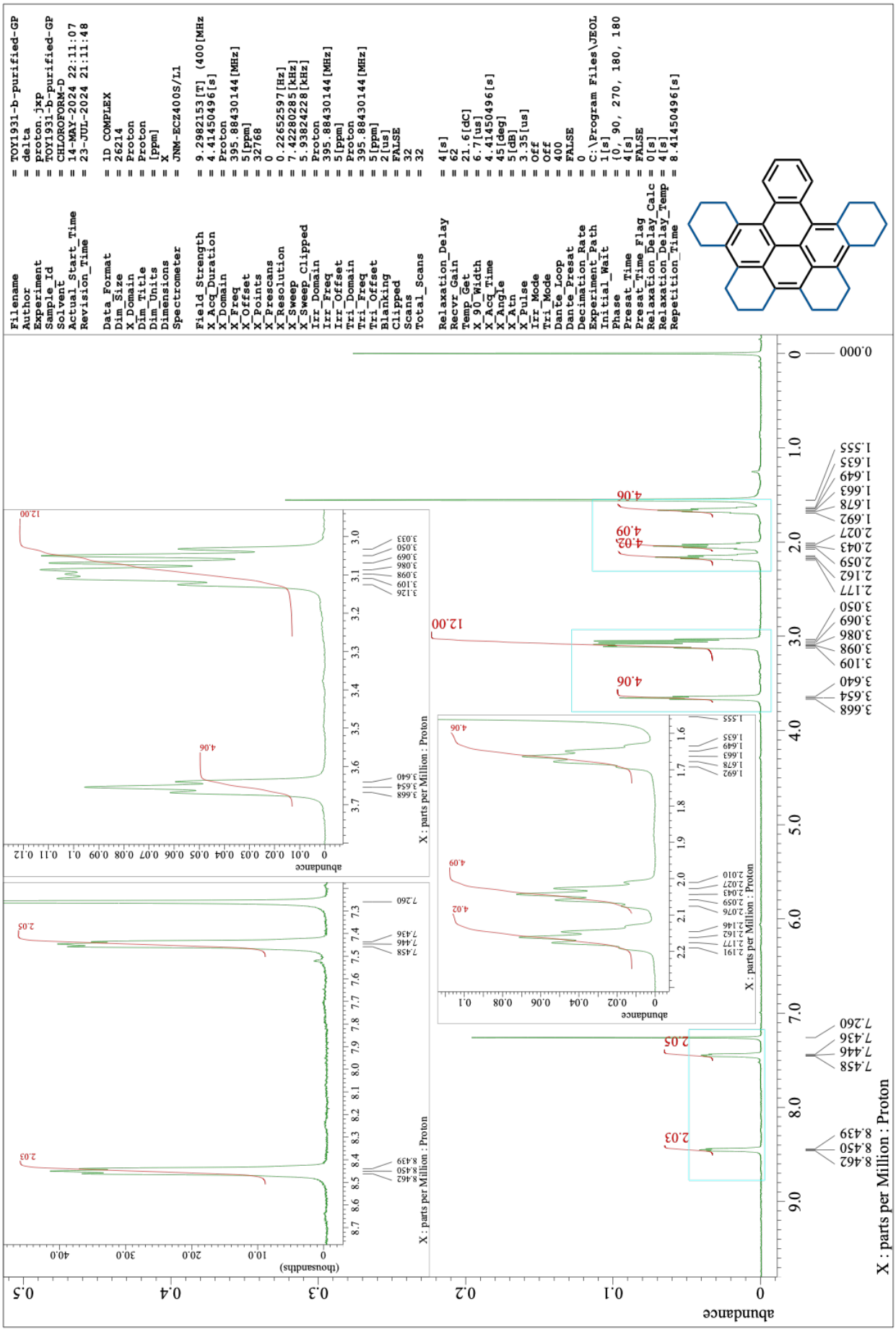

Figure S67. ^{1}H NMR spectrum of **8q** (600 MHz, $CDCl_3$).

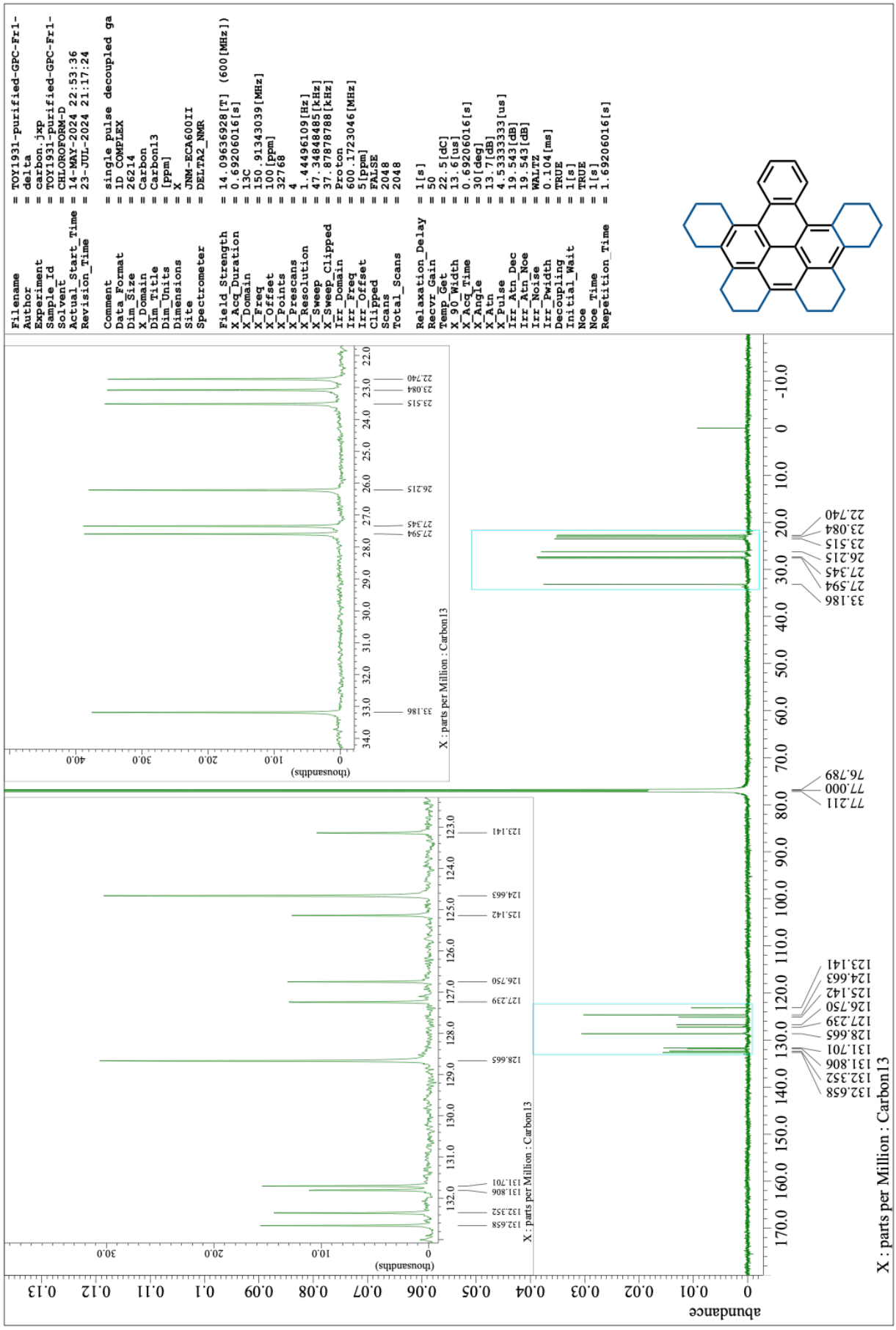

Figure S68. ^{13}C NMR spectrum of **8q** (150 MHz, $CDCl_3$).