Supplementary Information

Lithium-mediated Mechanochemical Annulative Dimerization of Diarylacetylenes for Synthesis of 1,4-Dihydrodinaphthopentalenes

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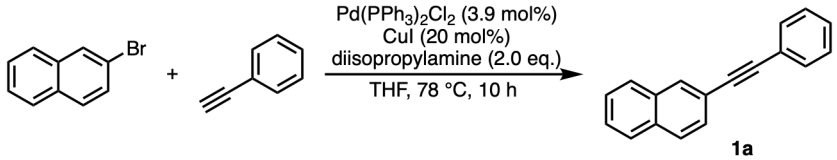
1. General

Unless otherwise noted, all materials including dry solvents were obtained from commercial suppliers and used without further purification. *N,N,N′,N′*-Tetramethylethylenediamine (TMEDA), triethylamine (Et_3N), diisopropylamine, and copper(I) iodide (CuI) was purchased from Kanto Chemical Co., Inc. 2-Bromonaphthalene, trimethylsilylacetylene, 1-*tert*-butyl-4-iodobenzene, 4-bromoanisole, 4-iodo-*N,N*-diphenylanilene, 4-Bromofluorobenzene, 3-bromo-benzonitrile, 2-bromotriphenylene, and dichlorobis(triphenylphosphine)palladium(II) ($PdCl_2(PPh_3)_2$) were purchased from Tokyo Chemical Industry Co., Ltd. Lithium wire (diam. 3.2 mm, 99.9% purity in mineral oil) was purchased from Sigma-Aldrich. 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-performance liquid chromatography (HPLC) was performed with LC-9210II NEXT instrument (SHIMADZU) equipped with a UV detector and a chiral column (DAICEL CHIRALPAK IF) using *n*-hexane and CH_2Cl_2 as an eluent at the flow rate of 0.5 mL/min. The absorption, fluorescence and CD spectra were obtained in a 1 cm quartz cell at 25 °C using a JASCO V-770 spectrophotometer, JASCO FP-6600, and JASCO J-1500 spectropolarimeter. High-resolution mass spectra (HRMS) were obtained from a JEOL JMS-T100TD (DART). GC-MS analysis was conducted on a Shimadzu GC-MS-QP2010 instrument equipped with a Restec-5HT column (30 m × 0.25 mm, Hewlett-Packard). Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL ECS-400 (^{1}H NMR: 400 MHz), JEOL ECS-600 (^{1}H NMR: 600 MHz, ^{13}C NMR: 150 MHz) spectrometers. Chemical shifts for ^{1}H NMR are expressed in parts per million (ppm) relative to $CDCl_3$ (δ 7.26 ppm), CD_2Cl_2 (δ 5.32 ppm), acetone-d_6 (δ 2.04 ppm), THF-d_8 (δ 1.72 ppm) or $Cl_2CDCDCl_2$ (δ 5.97 ppm). Chemical shifts for ^{13}C NMR are expressed in ppm relative to $CDCl_3$ (δ 77.16 ppm), CD_2Cl_2 (δ 53.84 ppm) or $Cl_2CDCDCl_2$ (δ 73.79 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, dt = doublet of triplets, ddd = doublet of doublet of doublets, t = triplet, td = triplet of doublets, tt = triplet of triplets, q = quartet, m = multiplet), coupling constant (Hz), and integration.

2. Synthesis of diarylacetylenes

2.1 Synthesis of 2-(phenylethynyl)naphthalene (1a)



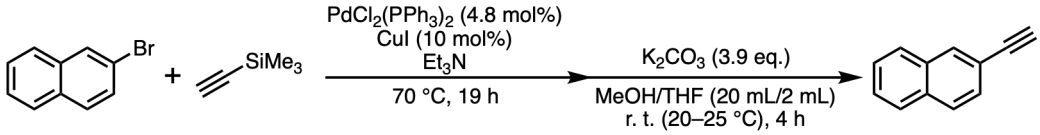
2-Bromonaphthalene (2.71 g, 10 mmol, 1.0 eq.), ethynylbenzene (1.23 g, 12 mmol, 1.2 eq.), $Pd(PPh_3)_2Cl_2$ (280 mg, 0.39 mmol, 3.9 mol%), and CuI (386 mg, 2.0 mmol, 20 mol%) were added to a 50-mL two-neck round-bottom flask containing a magnetic stirring bar under open air. The flask was filled with N_2 gas by a usual Schlenk technique. THF (15 mL) and diisopropylamine (2.8 mL, 20 mmol, 2.0 eq.) were added to the flask successively. The mixture was stirred at 78 °C for 10 h. After the mixture was cooled to room temperature (20–25 °C), sat. NH_4Cl aq. was added, and the mixture was extracted with $CHCl_3$ (three times). Then the combined organic layers were washed with brine, dried over Na_2SO_4, and then concentrated. The residue was purified by column chromatography on silica gel (eluent: hexane/EtOAc = 100:1) to afford **1a** (1.31 g, 5.7 mmol, 57%) as a white solid. ^1H and ^{13}C NMR spectrum was identical to that reported in the literature.[S1]

^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.87–7.80 (m, 3H), 7.61–7.56 (m, 3H), 7.52–7.48 (m, 2H), 7.42–7.34 (m, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 133.16, 132.94, 131.80, 131.58, 128.57, 128.54, 128.46, 128.15, 127.93, 126.81, 126.69, 123.43, 120.72, 89.93, 89.88.

HRMS (DART, positive) *m*/*z*: $[M+H]^+$ Calcd for $C_{18}H_{13}$ 229.10173; Found 229.10225.

2.2 Synthesis of 2-ethynylnaphthalene



2-Bromonaphthalene (2.12 g, 10 mmol, 1.0 eq.), $Pd(PPh_3)_2Cl_2$ (349 mg, 0.48 mmol, 4.8 mol%), and CuI (188 mg, 0.98 mmol, 9.8 mol%) were added to a 100-mL two-neck round-bottom flask containing a magnetic stirring bar under open air. The flask was filled with N_2 gas by a usual Schlenk technique. Et_3N (20 mL) and trimethylsilylacetylene (1.08 g, 11 mmol, 1.1 eq.) were added to the flask successively. The mixture was stirred at 70 °C for 25 h. After the mixture was cooled to room temperature (20–25 °C), sat. NH_4Cl aq. was added, and the mixture was extracted with EtOAc (three times). Then, the combined organic layers were washed with brine, dried over Na_2SO_4, and then concentrated. The residue was purified by column chromatography on silica gel with hexane to afford 2-[2-(trimethylsilyl)ethynyl]naphthalene as a yellow oil. The yellow oil was dissolved in MeOH/THF (20 mL/ 2 mL) in a 200-mL round-bottom flask containing a magnetic stirring bar under open air. Then, K_2CO_3 (5.93 g, 43 mmol, 4.3 eq.) was added to the mixture and stirred at room temperature (20–25 °C) for 4 h. The mixture was extracted with EtOAc (three times). Then, the combined organic layers were washed with brine, dried over Na_2SO_4, and then concentrated. The residue was purified by column chromatography on silica gel (eluent: hexane/EtOAc = 100:1) to afford 2-

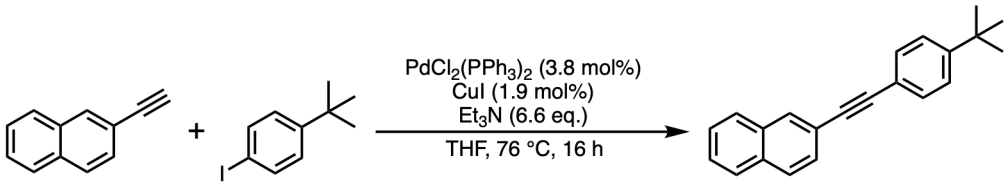
ethynylnaphthalene (1.12 g, 7.3 mmol, 73%) as a white solid. ^{1}H and ^{13}C NMR spectrum was identical to that reported in the literature.[S2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.82-7.78 (m, 3H), 7.54-7.49 (m, 3H), 3.15 (s, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 133.00, 132.78, 132.29, 128.52, 128.01, 127.76, 126.89, 126.60, 119.33, 83.98, 77.40.

HRMS (DART, positive) *m*/*z*: $[2M+H]^+$ Calcd for $C_{24}H_{17}$ 305.13303; Found 305.13284.

2.3 Synthesis of 2-[4-{(*tert*-butyl)phenyl}ethynyl]naphthalene (1d)



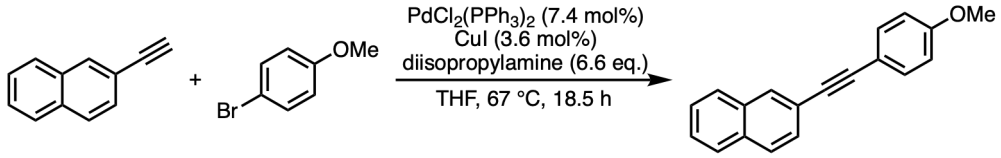
2-Ethynylnaphthalene (499 mg, 3.3 mmol, 1.1 eq.), $PdCl_2(PPh_3)_2$ (81.2 mg, 0.11 mmol, 3.8 mol%), and CuI (10.6 mg, 0.055 mmol, 1.9 mol%) were added to a 50-mL two-neck round-bottom flask containing a magnetic stirring bar under open air. The flask was filled with N_2 gas by a usual Schlenk technique. THF (15 mL), Et_3N (2.8 mL, 20 mmol, 6.6 eq.), and 1-(*tert*-butyl)-4-iodobenzene (790 mg, 3.0 mmol, 1.0 eq.) were added to the flask successively. The mixture was stirred at 76 °C for 16 h. After the mixture was cooled to room temperature (20–25 °C), sat. NH_4Cl aq. was added, and the mixture was extracted with $CHCl_3$ (three times). Then, the combined organic layers were washed with brine, dried over Na_2SO_4, and then concentrated. The residue was purified by column chromatography on silica gel (eluent: hexane/EtOAc = 100:1) to afford **1d** (488 mg, 1.7 mmol, 58%) as a yellow solid. ^{1}H and ^{13}C NMR spectrum was identical to that reported in the literature.[S1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.86–7.78 (m, 3H), 7.58 (d, J = 8.8 Hz, 1H), 7.54–7.45 (m, 4H), 7.39 (d, J = 8.0 Hz, 2H), 1.34 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 151.75, 133.19, 132.87, 131.53, 131.44, 128.63, 128.09, 127.91, 126.70, 126.65, 125.55, 120.96, 120.38, 90.06, 89.28, 34.97, 31.35. One tertiary carbon peak is overlapping.

HRMS (DART, positive) *m*/*z*: $[M]^+$ Calcd for $C_{22}H_{20}$ 284.15650; Found 284.15545.

2.4 Synthesis of 2-[(4-methoxypheny)lethynyl]naphthalene (1e)



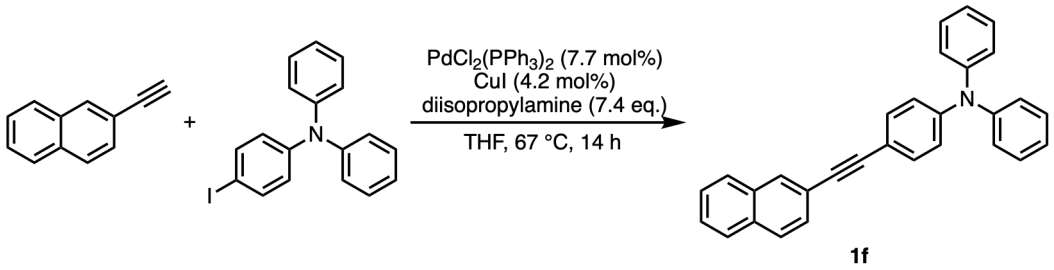
2-Ethynylnaphthalene (499 mg, 3.3 mmol, 1.1 eq.), $PdCl_2(PPh_3)_2$ (163 mg, 0.23 mmol, 7.4 mol%), and CuI (21.1 mg, 0.11 mmol, 3.6 mol%) were added to a 50-mL two-neck round-bottom flask containing a magnetic stirring bar under open air. The flask was filled with N_2 gas by a usual Schlenk technique. THF (15 mL), diisopropylamine (2.8 mL, 20 mmol 6.6 eq.), and 4-bromoanisole (580 mg, 3.0 mmol, 1.0 eq.) were added to the flask successively. The mixture was stirred at 67 °C for 18.5 h. After the mixture was cooled to room temperature (20–25 °C), sat. NH_4Cl aq. was added, and the mixture was extracted with $CHCl_3$ (three times). Then, the combined organic layers were washed with brine, dried over Na_2SO_4, and then concentrated. The residue was purified by column chromatography on silica gel (eluent: hexane/EtOAc = 20:1) to afford **1e** (63.7 mg, 0.25 mmol, 8.1%) as a white solid. ^{1}H NMR spectrum was identical to that reported in the literature.[S1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.84–7.77 (m, 3H), 7.60–7.45 (m, 5H), 6.90 (d, *J* = 8.2 Hz, 2H), 3.84 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 159.80, 133.26, 133.20, 132.79, 131.24, 128.57, 128.09, 127.90, 127.87, 126.63, 121.05, 115.52, 114.18, 89.89, 88.63, 55.47. One tertiary carbon peak is overlapping.

HRMS (DART, positive) *m*/*z*: $[M+H]^+$ Calcd for $C_{19}H_{15}O$ 259.11229; Found 259.11115.

2.5 Synthesis of 4-(naphthalen-2-ylethynyl)-*N*,*N*-diphenylaniline (1f)



1f

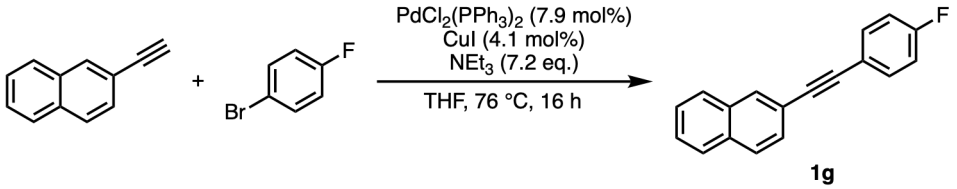
4-Iodo-*N*,*N*-diphenylanilene (1.04 g, 2.7 mmol, 1.0 eq.), 2-ethynylnaphthalene (499 mg, 3.3 mmol, 1.2 eq.), $PdCl_2(PPh_3)_2$ (153.1 mg, 0.21 mmol, 7.7 mol%), and CuI (22.2 mg, 0.12 mmol, 4.2 mol%) were added to a 100-mL two-neck round-bottom flask containing a magnetic stirring bar under open air. The flask was filled with N_2 gas by a usual Schlenk technique. THF (15 mL) and diisopropylamine (2.8 mL, 20 mmol, 7.4 eq.) were added to the flask successively. The mixture was stirred at 67 °C for 14 h. After the mixture was cooled to room temperature (20–25 °C), sat. NH_4Cl aq. was added, and the mixture was extracted with $CHCl_3$ (three times). Then, the combined organic layers were washed with brine, dried over Na_2SO_4, and then concentrated. The residue was purified by column chromatography on silica gel (eluent: hexane/EtOAc = 10:1) to afford **1f** (716 mg, 1.8 mmol, 66%) as a yellow solid.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.02 (s, 1H), 7.88–7.80 (m, 3H), 7.56 (d, *J* = 8.6 Hz, 1H), 7.55–7.47 (m, 2H), 7.42 (d, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 4H), 7.17–7.05 (m, 6H), 7.01 (d, *J* = 7.2 Hz, 2H).

^{13}C NMR (150 MHz, CD_2Cl_2) δ 148.47, 147.51, 133.46, 133.03, 132.85, 131.29, 129.77, 128.66, 128.34, 128.07, 128.01, 126.94, 125.49, 124.05, 122.37, 121.27, 116.13, 90.39, 89.16. One tertiary carbon peak is overlapping.

HRMS (DART, positive) *m/z*: $[M+H]^+$ Calcd for $C_{30}H_{22}N$ 396.17522; Found 396.17408.

2.6 Synthesis of 2-[(4-fluorophenyl)ethynyl]naphthalene (1g)



1g

1-Bromo-4-fluorobenzene (497 mg, 2.8 mmol, 1.0 eq.), 2-ethynylnaphthalene (498 mg, 3.3 mmol, 1.2 eq.), $PdCl_2(PPh_3)_2$ (159 mg, 0.22 mmol, 7.9 mol%), and CuI (20.9 mg, 0.12 mmol, 4.1 mol%) were added to a 50-mL two-neck round-bottom flask containing a magnetic stirring bar under open air. The flask was filled with N_2 gas by a usual Schlenk technique. THF (15 mL) and Et_3N (2.8 mL, 20 mmol, 7.2 eq.) were added to the flask successively. The mixture was stirred at 76 °C for 16 h. After the mixture was cooled to room temperature (20–25 °C), sat. NH_4Cl aq. was added, and the mixture was extracted with $CHCl_3$ (three times). Then, the combined organic layers were washed with brine, dried over Na_2SO_4, and then concentrated. The residue was purified by column chromatography on silica gel (eluent: hexane/EtOAc = 100:1) to afford **1g** (312 mg, 1.3 mmol, 46%) as a white solid. ^{1}H and ^{13}C NMR spectrum was identical to that reported in the literature.[S1]

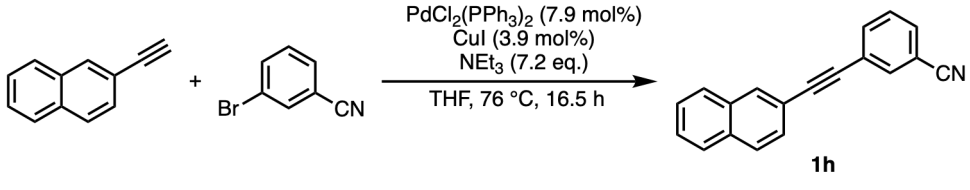
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.84–7.81 (m, 3H), 7.58–7.54 (m, 3H), 7.53–7.48 (m, 2H), 7.09–7.08 (d, J = 8.5 Hz, 1H), 7.06 (d. J = 8.5 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 162.68 (d, J^1_{C-F} = 249.5 Hz), 133.67 (d, J^{3C-F} = 8.6 Hz), 133.15, 132.97, 131.56, 128.46, 128.19, 127.92 (2C), 126.86, 126.74, 120.52, 119.53 (d, J^4_{C-F} = 2.9 Hz), 115.83 (d, J^2_{C-F} = 23.0 Hz), 115.76, 89.60, 88.78.

^{19}F NMR (564 MHz, $CDCl_3$) δ –111.14 (m).

HRMS (DART, positive) *m/z*: $[M]^+$ Calcd for $C_{18}H_{11}F$ 246.08448; Found 246.08443.

2.7 Synthesis of 3-(naphthalen-2-ylethynyl)benzonitrile (1h)



1h

3-Bromobenzonitrile (511 mg, 2.8 mmol, 1.0 eq.), 2-ethynylnaphthalene (501 mg, 3.3 mmol, 1.2 eq.), $PdCl_2(PPh_3)_2$ (158 mg, 0.22 mmol, 7.9 mol%), and CuI (20.9 mg, 0.11 mmol, 3.9 mol%) were added to a 50-mL two-neck round-bottom flask containing a magnetic stirring bar under open air. The flask was filled with N_2 gas by a usual Schlenk technique. THF (15 mL) and Et_3N (2.8 mL, 20 mmol, 7.2 eq.) were added to the flask successively. The mixture was stirred at 76 °C for 16.5 h. After the mixture was cooled to room

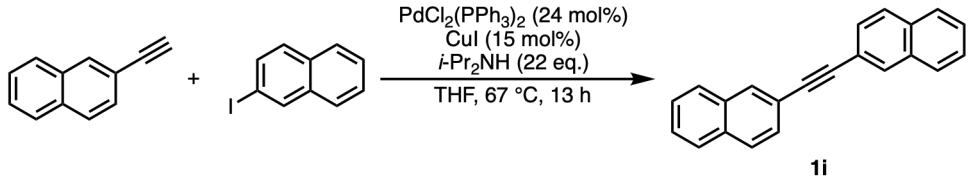
temperature (20–25 °C), sat. NH_4Cl aq. was added, and the mixture was extracted with $CHCl_3$ (three times). Then, the combined organic layers were washed with brine, dried over Na_2SO_4, and then concentrated. The residue was purified by column chromatography on silica gel (eluent: hexane/EtOAc = 39:1) to afforded **1h** (619 mg, 2.4 mmol, 89%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.88–7.82 (m, 4H), 7.78 (d, J = 7.9 Hz, 1H), 7.62 (d, J = 7.7 Hz, 1H), 7.57 (d, J = 8,4 Hz, 1H), 7.53–7.46 (m, 4H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 135.76, 135.03, 133.21, 133.03, 132.07, 131.50, 129.43, 128.34, 128.25, 128.01, 127.95, 127.22, 126.88, 125.08, 119.64, 118.23, 113.02, 92.36, 87.34.

HRMS (DART, positive) *m/z*: $[M]^+$ Calcd for $C_{19}H_{11}N$ 253.08915; Found 253.08926.

2.8 Synthesis of 1,2-di(naphthalen-2-yl)ethyne (1i)



1i

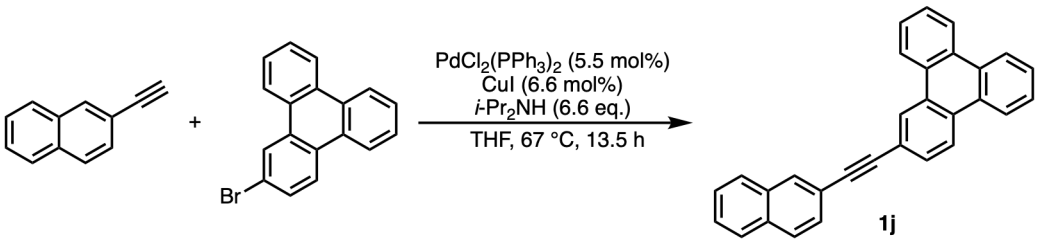
2-Iodonaphthalene (232 mg, 0.90 mmol, 1.0 eq.), 2-ethynylnaphthalene (510 mg, 3.3 mmol, 3.7 eq.), $Pd(PPh_3)_2Cl_2$ (157 mg, 0.22 mmol, 0.24 eq.), and CuI (25.7 mg, 0.13 mmol, 0.15 eq.) were added to a 30-mL two-neck round-bottom flask containing a magnetic stirring bar under open air. The flask was filled with N_2 gas by a usual Schlenk technique. THF (15 mL) and diisopropylamine (2.8 mL, 20 mmol, 22 eq.) were added to the flask successively. The mixture was stirred at 67 °C for 13 h. After the mixture was cooled to room temperature (20–25 °C), sat. NH_4Cl aq. was added, and the mixture was extracted with $CHCl_3$ (three times). Then, the combined organic layers were washed with brine, dried over Na_2SO_4, and then concentrated. The residue was purified by column chromatography on silica gel (eluent: hexane/EtOAc = 100:1) to afford **1i** (82.0 mg, 0.29 mmol, 28%) as a yellow solid. ^{1}H and ^{13}C NMR spectrum was identical to that reported in the literature.[S3]

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.11 (s, 2H), 7.87–7.80 (m, 6H), 7.63 (d, J = 8.6 Hz, 2H), 7.59–7.50 (m, 4H).

^{13}C NMR (150 MHz, CD_2Cl_2) δ 133.40, 133.20, 131.75, 128.67, 128.44, 128.09, 127.15, 127.01, 120.85, 90.34

HRMS (DART, positive) *m/z*: $[M]^+$ Calcd for $C_{22}H_{14}$ 278.10955; Found 278.10902.

2.9 Synthesis of 2-(naphthalen-2-ylethynyl)triphenylene (1j)



2-Bromotriphenylene (373 mg, 1.2 mmol, 1.0 eq.), 2-ethynylnaphthalene (208 mg, 1.4 mmol, 1.1 eq.), $PdCl_2(PPh_3)_2$ (65.2 mg, 0.090 mmol, 5.5 mol%), and CuI (15.1 mg, 0.079 mmol, 6.6 mol%) were added to a 100-mL two-neck round-bottom flask containing a magnetic stirring bar under open air. The flask was filled with N_2 gas by a usual Schlenk technique. THF (10 mL) and diisopropylamine (1.1 mL, 7.8 mmol, 6.6 eq.) were added to the flask successively. The mixture was stirred at 67 °C for 13.5 h. After the mixture was cooled to room temperature (20–25 °C), sat. NH_4Cl aq. was added, and the mixture was extracted with $CHCl_3$ (three times). Then, the combined organic layers were washed with brine, dried over Na_2SO_4, and then concentrated. The residue was purified by column chromatography on silica gel (eluent: hexane/EtOAc = 100:1) to afforded **1j** (173 mg, 0.46 mmol, 38%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (s, 1H), 8.74–8.62 (m, 5H), 8.16 (s, 1H), 7.90–7.80 (m, 4H), 7.74–7.66 (m, 5H), 7.58–7.50 (m, 2H).

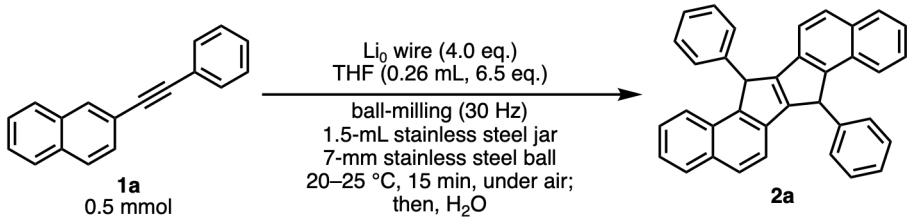
^{13}C NMR (150 MHz, $CDCl_3$) δ 133.24, 133.04, 131.75, 130.24, 130.16, 130.12, 129.93, 129.77, 129.50, 129.29, 128.60, 128.25, 128.00, 127.98, 127.79, 127.77, 127.57, 127.55, 127.07, 126.90, 126.77, 123.70, 123.66, 123.60, 123.54, 123.49, 122.11, 120.71, 90.81, 90.34.

HRMS (DART, positive) *m*/*z*: $[M+H]^+$ Calcd for $C_{30}H_{19}$ 379.14868; Found 379.14769.

3. Lithium-mediated mechanochemical annulative dimerization of alkynes

3.1. General procedure of mechanochemical annulative dimerization of diarylacetylenes

The synthesis of 7,14-diphenyl-7,14-dihydropentalene[2,1-*a*:5,4-*a'*]dinaphthalene (**2a**) is described as a representative example of the general procedure A for a 0.50-mmol scale reaction.



A 7-mm diameter stainless-steel ball and 2-(phenylethynyl)naphthalene (**1a**) (114 mg, 0.50 mmol, 1.0 eq.) were added to an oven-dried 1.5-mL stainless-steel jar. Pieces of Li (10.5 mg, 1.5 mmol, 3.0 eq.) cut from Li wire (3.2 mm in diameter, 99.9% purity) was washed with hexane for removing mineral oil, weighed on an electronic balance, and added into the jar under air. Then, THF (0.26 mL, 3.3 mmol, 6.5 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with an O-shaped packing made of 1-mm width polyethylene sheet, and the jar was sealed tightly with a wrench and a vise. The reaction jar and a same-weight blank jar (or a same-weight reaction jar) were fixed in a mixer mill (Retsch MM400 or MM500 Vario), and shaken at 30 Hz (1800 rpm) at room temperature (20–25 °C) for 15 min. After shaking, the reaction jar was opened and the reaction was quenched by adding sat. NH_4Cl aq. Then, the organic phase was extracted with chloroform (three times). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford a crude product. Then, the 23% of ^{1}H NMR yield using 1,1,2,2-tetrachloroethane and the 7.5:1.0 of *syn*/*anti* ratio were determined by integral ratio of benzylic proton signals (*syn*-**2a**: 5.28 ppm (in $CDCl_3$); *anti*-**2a**: 5.35 ppm (in $CDCl_3$)) using 1,1,2,2-tetrachloroethane as an internal standard in ^{1}H NMR spectrum of the crude product in $CDCl_3$. The crude product was purified by silica gel column chromatography (eluent: hexane/toluene = 3:1), affording a mixture of *syn*-**2a** and *anti*-**2a** in 54% combined yield (*syn*/*anti* = 18:1.0).as a yellow solid (7.0 mg, 0.030 mmol, 6.1% yield). Then, further purification by GPC (eluent: $CHCl_3$) to afford *syn*-**2a** as a yellow solid (18.2 mg, 0.040 mmol, 16%). In this purification, *anti*-**2a** could not be isolated due to its low quantity. A sigle crystal of *syn*-**2a** was obtained by recrystallization from $CHCl_3$ and pentane.

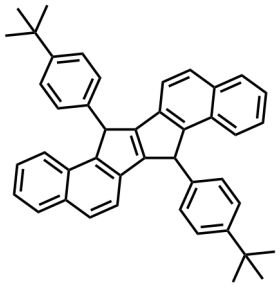
***syn*-7,14-Diphenyl-7,14-dihydropentalene[2,1-*a*:5,4-*a'*]dinaphthalene** (*syn*-**2a**)

^{1}H NMR (400 MHz, $Cl_2CDCDCl_2$) δ 7.80–7.75 (m, 2H), 7.72–7.64 (m, 4H), 7.37 (d, J = 8.6 Hz, 2H), 7.33–7.20 (m, 14H), 5.28 (s, 2H).

^{13}C NMR (150 MHz, $Cl_2CDCDCl_2$) δ 154.74, 147.54, 139.10, 138.14, 131.62, 130.04, 129.06, 128.88, 128.30, 128.00, 126.83, 126.30, 124.45, 123.11, 118.50, 50.85.

HRMS (DART, positive) *m*/*z*: $[M+H]^+$ Calcd for $C_{36}H_{25}$ 457.19563; Found 457.19334.

***syn*-7,14-Bis(4-(*tert*-butyl)phenyl)-7,14-dihydropentaleno[2,1-*a*:5,4-*a′*]dinaphthalene (*syn*-2d)**



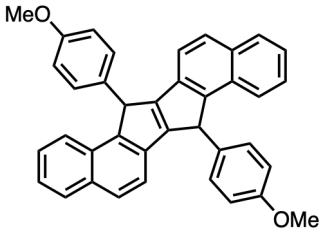
Using the general procedure, the reaction of 2-[{4-(*tert*-butyl)phenyl}ethynyl]naphthalene (71.4 mg, 0.25 mmol, 1.0 eq.) with Li (5.0 mg, 0.72 mmol, 2.9 eq.), THF (0.13 mL, 1.6 mmol, 6.4 eq.) at room temperature (20–25 °C) for 15 min. Purification by silica gel column chromatography (eluent: hexane/toluene = 3:1) was performed to afford a mixture of *syn*-**2d** and *anti*-**2d** in 79% combined isolated yield (*syn*/*anti* = 6.6:1.0). Taking into account the fact that the benzylic protons in *syn*-**2a** appear at the higher-magnetic field (5.28 ppm) than that in *anti*-**2a** (5.35 ppm), the signals at 5.26 and 5.32 ppm (in $CDCl_3$) were assigned for *syn*-**2e** and *anti*-**2e**, respectively. Then, further purification by GPC (eluent: $CHCl_3$) to afford *syn*-**2d** as a yellow solid (12.5 mg, 0.022 mmol, 18%). In this purification, *anti*-**2d** could not be isolated due to its low quantity.

^{1}H NMR (400 MHz, $Cl_2CDCDCl_2$) δ 7.78-7.71 (m, 4H), 7.69 (d, *J* = 8.8 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.31–7.25 (m, 8H), 7.20 (d, *J* = 8.4 Hz, 4H), 5.25 (s, 2H), 1.23 (s, 18H).

^{13}C NMR (150 MHz, $Cl_2CDCDCl_2$) δ 154.85, 149.51, 147.78, 138.25, 135.47, 131.53, 10.10, 128.82, 127.59, 126.16, 125.84, 124.32, 123.31, 118.82, 50.50, 34.26, 31.27.

HRMS (DART, positive) *m*/*z*: $[M+H]^+$ Calcd for $C_{44}H_{41}$ 569.32083; Found 569.31956.

***syn*- and *anti*-7,14-Bis(4-methoxyphenyl)-7,14-dihydropentaleno[2,1-*a*:5,4-*a′*]dinaphthalene** (*syn*-**2e** and *anti*-**2e**)



Using the general procedure, the reaction of 2-[(4-methoxyphenyl)ethynyl]naphthalene (61.1 mg, 0.24 mmol, 1.0 eq.) with Li (5.5 mg, 0.79 mmol, 3.3 eq.), THF (0.26 mL, 3.3 mmol, 14 eq.) at 70 °C (heat-gun preset temperature) for 99 min. Purification by silica gel column chromatography (eluent: hexane/toluene = 3:1→0:1) was performed to afford a mixture of *syn*-**2e** and *anti*-**2e** in 29% combined isolated yield (17.5 mg, *syn*/*anti* = 1.4:1.0). Taking into account the fact that the benzylic protons in *syn*-**2a** appear at the higher-magnetic field (5.28 ppm) than that in *anti*-**2a** (5.35 ppm), the signals at 5.24 and 5.30 ppm (in $CDCl_3$) were assigned for *syn*-**2e** and *anti*-**2e**, respectively. Then, further purification by GPC (eluent: $CHCl_3$) to afford *syn*-**2e** as a yellow solid (2.8 mg, 0.0054 mmol, 4.6%) and *anti*-**2e** as a yellow solid (0.90 mg, 0.0017 mmol, 1.5 %). Both compounds showed instability toward air and moisture, and we found significant loss of compounds by decomposition in the purification and NMR measurements.

Data of *syn*-2e

^{1}H NMR (400 MHz, $Cl_2CDCDCl_2$) δ 7.79–7.77 (m, 2H), 7.71–7.69 (m, 4H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.29–7.27 (m, 4H), 7.17 (d, *J* = 8.4 Hz, 4H), 6.82 (d, *J* = 8.8 Hz, 4H), 5.24 (s, 2H), 3.76 (s, 6H).

^{13}C NMR (150 MHz, $Cl_2CDCDCl_2$) δ 158.08 154.72, 147.70, 138.10, 131.62, 130.90, 130.07, 129.01, 128.89, 128.20, 126.23, 124.40, 123.17, 118.55, 114.44, 55.24, 50.09.

HRMS (DART, positive) *m*/*z*: $[M+H]^+$ Calcd for $C_{38}H_{29}O_2$ 517.21675; Found 517.21533.

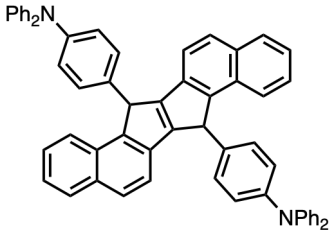
Data of *anti*-2e

^{1}H NMR (400 MHz, $Cl_2CDCDCl_2$) δ 7.81–7.76 (m, 2H), 7.70 (d, *J* = 8.2 Hz, 4H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.33–7.26 (m, 4H), 7.18 (d, *J* = 8.2 Hz, 4H), 6.81 (*d*, J = 8.2 Hz, 4H), 5.30 (s, 2H), 3.74 (s, 6H).

^{13}C NMR (150 MHz, $Cl_2CDCDCl_2$) δ 158.10, 154.45, 147.62, 138.14, 131.61, 130.66, 130.06, 129.08, 128.92, 128.24, 126.28, 124.41, 123.20, 118.51, 114.38, 55.25, 50.25.

HRMS (DART, positive) *m*/*z*: $[M+H]^+$ Calcd for $C_{38}H_{29}O_2$ 517.21675; Found 517.21563.

***syn*- and *anti*-4,4'-(7,14-Dihydropentaleno[2,1-*a*:5,4-*a'*]dinaphthalene-7,14-diyl)bis(*N*,*N*-diphenylaniline)** (*syn*-**2f** and *anti*-**2f**)



Using the general procedure, the reaction of 4-(naphthalen-2-ylethynyl)-*N*,*N*-diphenylaniline (198 mg, 0.50 mmol, 1.0 eq.) with Li (10.8 mg, 1.5 mmol, 3.0 eq.), THF (0.42 mL, 4.2 mmol, 8.4 eq.) at 70 °C (heat-gun preset temperature) for 99 min. Purification by silica gel column chromatography (eluent: hex/toluene = 3:1→1:1) was performed to afford a mixture of *syn*-**2f** and *anti*-**2f** in 33% combined isolated yield (*syn*/*anti* = 1.3:1.0). Taking into account the fact that the benzylic protons in *syn*-**2a** appear at the higher-magnetic field (5.28 ppm) than that in *anti*-**2a** (5.35 ppm), the signals at 5.24 and 5.31 ppm (in $CDCl_3$) were assigned for *syn*-**2f** and *anti*-**2f**, respectively. Then, further purification by GPC (eluent: $CHCl_3$) to afford *syn*-**2f** as a yellow solid (15.9 mg, 0.020 mmol, 8.0%) and *anti*-**2f** as a yellow solid (13.0 mg, 0.016 mmol, 6.6%).

Data of *syn*-2f

^{1}H NMR (400 MHz, $Cl_2CDCDCl_2$) δ 7.84–7.80 (m, 4H), 7.76 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.38−7.32 (m, 4H), 7.20–7.13 (m, 12H), 7.02–6.93 (m, 16H), 5.24 (s, 2H).

^{13}C NMR (150 MHz, $Cl_2CDCDCl_2$) δ 154.84, 147.64, 147.44, 146.24, 138.20, 132.77, 131.58, 130.14, 129.11, 128.88, 128.72, 128.23, 126.31, 124.50, 124.30, 123.99, 123.19, 122.51, 118.70, 50.30.

HRMS (MALDI, positive) *m*/*z*: $[M]^+$ Calcd for $C_{60}H_{42}N_2$ 790.33425; Found 790.33466.

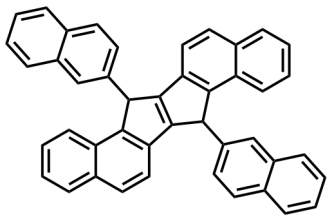
Data of *anti*-2f

^{1}H NMR (400 MHz, $Cl_2CDCDCl_2$) δ 7.84 (d, *J* = 9.1 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 4H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.35 (t, *J* = 3.4 Hz, 4H), 7.20 (t, *J* = 7.9 Hz, 8H), 7.14 (d, *J* = 8.2 Hz, 4H), 7.03–6.94 (m, 16H), 5.31 (s, 2H).

^{13}C NMR (150 MHz, $Cl_2CDCDCl_2$) δ 154.49, 147.49, 147.42, 146.18, 138.34, 132.63, 131.59, 130.11, 129.12, 128.92, 128.83, 128.35, 126.36, 124.50, 124.26, 123.97, 123.33, 122.54, 118.65, 50.47.

HRMS (MALDI, positive) *m*/*z*: $[M]^+$ Calcd for $C_{60}H_{42}N_2$ 790.33425; Found 790.33582.

***syn*-7,14-Di(naphthalen-2-yl)-7,14-dihydropentaleno[2,1-*a*:5,4-*a′*]dinaphthalene** (*syn*-**2i**)



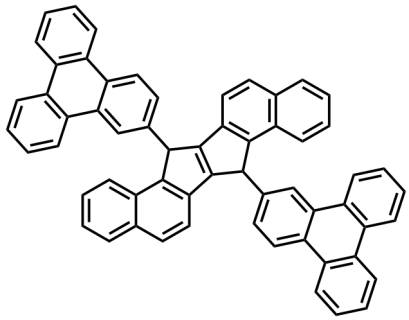
Using the general procedure, the reaction of 1,2-di(naphthalen-2-yl)ethyne (57.1 mg, 0.21 mmol, 1.0 eq.) with Li (6.0 mg, 0.86 mmol, 4.1 eq.), THF (0.10 mL, 1.2 mmol, 5.7 eq.) at room temperature (20–25 °C) for 1 h. Purification by silica gel column chromatography (eluent: hexane/EtOAc = 39 : 1) was performed to afford a mixture of *syn*-**2i** and *anti*-**2i** in 25% combined isolated yield (*syn*/*anti* = 17:1.0). Taking into account the fact that the benzylic protons in *syn*-**2a** appear at the higher-magnetic field (5.28 ppm) than that in *anti*-**2a** (5.35 ppm), the signals at 5.47 and 5.57 ppm (in $CDCl_3$) were assigned for *syn*-**2i** and *anti*-**2i**, respectively. Then, further purification by GPC (eluent: $CHCl_3$) to afford *syn*-**2i** as a yellow solid (2.6 mg, 0.0046 mmol, 4.6%). In this purification, *anti*-**2a** could not be isolated due to its low quantity.

^{1}H NMR (400 MHz, $Cl_2CDCDCl_2$) δ 8.12 (s, 2H), 7.91 (d, *J* = 8.2 Hz, 2H), 7.80–7.66 (m, 10H), 7.55–7.52 (m, 2H), 7.49–7.46 (m, 3H), 7.40 (dd, *J* = 8.2, 2.7 Hz, 2H), 7.27–7.19 (m, 4H), 7.02 (d, *J* = 8.2 Hz, 2H), 5.48 (s, 2H).

^{13}C NMR (150 MHz, $Cl_2CDCDCl_2$) δ 154.87, 147.36, 138.21, 137.16, 133.79, 132.43, 131.65, 130.17, 128.92, 128.89, 128.51, 127.70, 127.58, 127.33, 126.44, 126.11, 125.70, 125.48, 124.56, 122.96, 118.46, 50.98.

HRMS (DART, positive) *m*/*z*: $[M+H]^+$ Calcd for $C_{44}H_{29}$ 556.22693; Found 557.22437.

***syn*-7,14-Di(triphenylen-2-yl)-7,14-dihydropentaleno[2,1-*a*:5,4-*a′*]dinaphthalene** (*syn*-**2j**)



Using the general procedure, the reaction of 2-(naphthalen-2-ylethynyl)triphenylene (68.1 mg, 0.18 mmol, 1.0 eq.) with Li (3.6 mg, 0.52 mmol, 2.9 eq.), THF (0.19 mL, 2.4 mmol, 13 eq.) at 70 °C (heat-gun preset temperature) for 99 min. Purification by silica gel column chromatography (eluent: hexane/toluene = 3:1) was performed to afford a mixture of *syn*-**2j** and *anti*-**2j** in 14% combined isolated yield (*syn*/*anti* = 19:1.0). Taking into account the fact that the benzylic protons in *syn*-**2a** appear at the higher-magnetic field (5.28 ppm) than that in *anti*-**2a** (5.35 ppm), the signals at 5.69 and 5.77 ppm (in CD_2Cl_2) were assigned for *syn*-**2j** and *anti*-**2j**, respectively. Then, further purification by GPC (eluent: $CHCl_3$) to afford *syn*-**2j** as a yellow solid (3.2 mg, 0.0042 mmol, 4.7%). In this purification, *anti*-**2j** could not be isolated due to its low quantity.

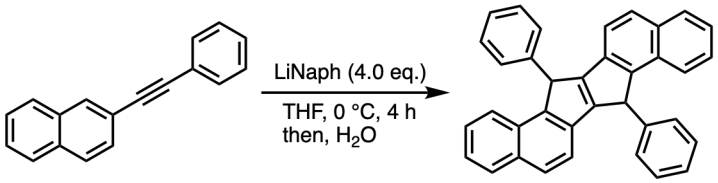
^{1}H NMR (400 MHz, $Cl_2CDCDCl_2$) δ 8.86 (s, 2H), 8.69 (d, *J* = 8.2 Hz, 6H), 8.58-8.52 (m, 4H), 7.78-7.66 (m, 14H), 7.47 (d, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 9.1 Hz, 2H), 7.27-7.19 (m, 4H), 5.61 (s, 2H).

^{13}C NMR (150 MHz, $Cl_2CDCDCl_2$) δ 155.12, 147.57, 138.63, 138.18, 131.75, 130.26, 130.10, 129.71, 129.33, 129.27, 128.93, 128.67, 128.58, 127.48, 127.32, 127.26, 126.63, 126.50, 124.59, 124.46, 123.42, 123.39, 123.32, 123.07, 122.99, 122.96, 118.47, 51.08.

HRMS (MALDI, positive) *m*/*z*: $[M]^+$ Calcd for $C_{60}H_{36}$ 756.28115; Found 756.28236.

3.2. Control experiments

3.2.1. Control experiment in the solution-state reaction (Table 1, entry 11)

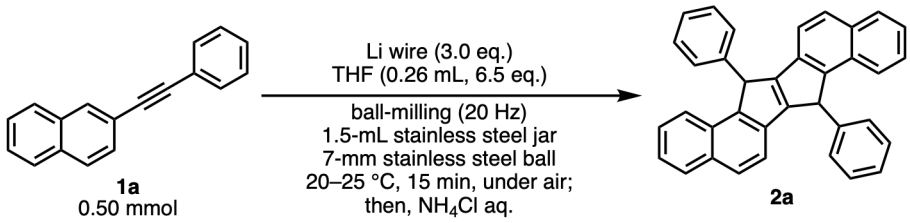


1a
0.50 mmol

2a

Pieces of Li (14.3 mg, 2.1 mmol, 4.1 eq.) cut from Li wire (3.2 mm in diameter, 99.9% purity) was washed with hexane for removing mineral oil, weighed on an electronic balance, and naphthalene (263 mg, 2.0 mmol, 4.0 eq.) were added to a 50-mL two-neck round-bottom flask containing a magnetic stirring bar under open air. The flask was filled with N_2 gas by a usual Schlenk technique. THF (10 mL) was added to the flask successively. The mixture was stirred at 67 °C for 16.5 h. After the mixture was cooled to room temperature (20–25 °C), 2-phenylethynylnaphthalene (**1a**) (114 mg, 0.50 mmol, 1.0 eq.) in 10 mL of THF was added dropwise to the flask at 0 °C and stirred at same temperature for 3 h. After the mixture was quenched with H_2O at 0 °C, the mixture was extracted with $CHCl_3$ (three times). Then, the organic layers were washed with brine, dried over Na_2SO_4, and then concentrated. Obtained crude mixture was analyzed by ^1H NMR to determine almost no reaction and recovery of **1a**.

3.2.2. Control experiment with ball-milling at 20 Hz (Table 1, entry 14)

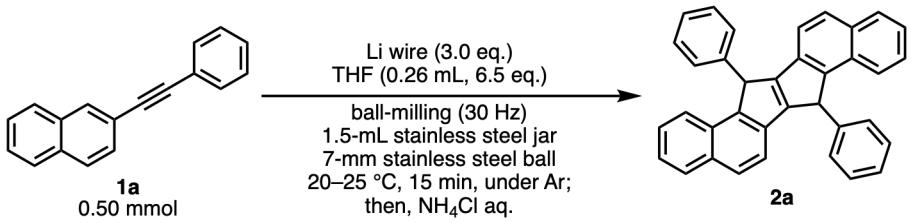


1a
0.50 mmol

2a

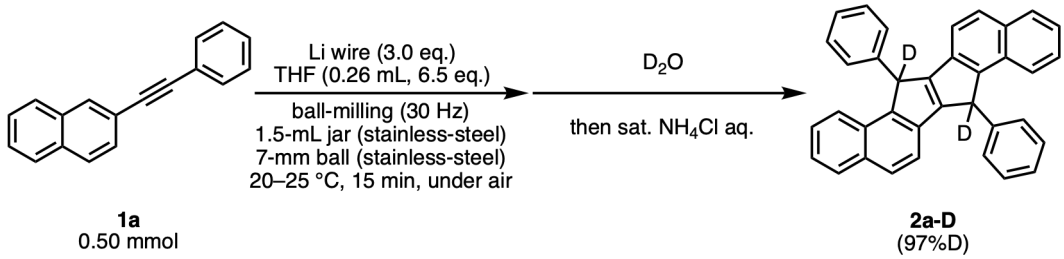
A 7-mm diameter stainless-steel ball and 2-(phenylethynyl)naphthalene (**1a**) (114 mg, 0.50 mmol, 1.0 eq.) were added to an oven-dried 1.5-mL stainless-steel jar. Pieces of Li (10.4 mg, 1.5 mmol, 3.0 eq.) cut from Li wire (3.2 mm in diameter, 99.9% purity) was washed with hexane for removing mineral oil, weighed on an electronic balance, and added into the jar under air. Then, THF (0.26 mL, 3.3 mmol, 6.5 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with an O-shaped packing made of 1-mm width polyethylene sheet, and the jar was sealed tightly with a wrench and a vise. The reaction jar and a same-weight blank jar (or a same-weight reaction jar) were fixed in a mixer mill (Retsch MM400), and shaken at 20 Hz (1200 rpm) at room temperature (20–25 °C) for 15 min. After shaking, the reaction jar was opened and the reaction was quenched by adding sat. NH_4Cl aq. Then, the organic phase was extracted with chloroform (three times). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford a crude product. Then, the 9.7% of ^1H NMR yield using 1,1,2,2-tetrachloroethane and the 5.4:1.0 of *syn*/*anti* ratio were determined by integral ratio of benzylic proton signals (*syn*-**2a**: 5.28 ppm (in $CDCl_3$); *anti*-**2a**: 5.35 ppm (in $CDCl_3$)) using 1,1,2,2-tetrachloroethane as an internal standard in ^1H NMR spectrum of the crude product in $CDCl_3$.

3.2.3. Control experiment in the glovebox under Ar (Table 1, entry 15)



A 7-mm diameter stainless-steel ball and 2-(phenylethynyl)naphthalene (**1a**) (114 mg, 0.50 mmol, 1.0 eq.) were added to an oven-dried 1.5-mL stainless-steel jar. Pieces of Li (10.4 mg, 1.5 mmol, 3.0 eq.) cut from Li wire (3.2 mm in diameter, 99.9% purity) was washed with hexane for removing mineral oil, weighed on an electronic balance, and added into the jar in a glovebox under Ar. Then, THF (0.26 mL, 3.3 mmol, 6.5 eq.) was added to the jar by a syringe in a glovebox. The jar was capped with a stainless-steel cap equipped with an O-shaped packing made of 1-mm width polyethylene sheet, and the jar was sealed tightly with a wrench and a vise. The reaction jar, which was brought outside the glove box, and a same-weight blank jar (or a same-weight reaction jar) were fixed in a mixer mill (Retsch MM400) under air, and shaken at 30 Hz (1800 rpm) at room temperature (20–25 °C) for 15 min. After shaking, the reaction jar was opened and the reaction was quenched by adding sat. NH_4Cl aq under Ar. Then, the organic phase was extracted with chloroform (three times). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford a crude product. Then, the 23% of ^1H NMR yield using 1,1,2,2-tetrachloroethane and the 4.9:1.0 of *syn*/*anti* ratio were determined by integral ratio of benzylic proton signals (*syn*-**2a**: 5.28 ppm (in $CDCl_3$); *anti*-**2a**: 5.35 ppm (in $CDCl_3$)) using 1,1,2,2-tetrachloroethane as an internal standard in ^1H NMR spectrum of the crude product in $CDCl_3$.

3.2.4. Trapping with D_2O for synthesis of 7,14-Diphenyl-7,14-dihydropentaleno[2,1-*a*:5,4-*a′*]dinaphthalene-7,14-d_2 (2a-D)



A 7-mm diameter stainless-steel ball and 2-(phenylethynyl)naphthalene (**1a**) (114 mg, 0.50 mmol, 1.0 eq.) were added to an oven-dried 1.5-mL stainless-steel jar. Pieces of Li (10.4 mg, 1.5 mmol, 3.0 eq.) cut from Li wire (3.2 mm in diameter, 99.9% purity) was washed with hexane for removing mineral oil, weighed on an electronic balance, and added into the jar under air. Then, THF (0.26 mL, 3.3 mmol, 6.5 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with an O-shaped packing made of 1-mm width polyethylene sheet, and the jar was sealed tightly with a wrench and a vise. The reaction jar and a same-weight blank jar (or a same-weight reaction jar) were fixed in a mixer mill (Retsch MM400), and shaken at 30 Hz (1800 rpm) at room temperature (20–25 °C) for 15 min. After shaking, the reaction jar was opened and the reaction was quenched by D_2O (0.10 mL, 5.5 mmol, 11 eq.). The jar was

then closed again and shaken at 30 Hz (1800 rpm) at r.t (20–25 °C) for 60 min. Then, the organic phase was extracted three times with chloroform. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to obtain a crude product, which was further purified by silica gel column chromatography (eluent: hexane/toluene = 3:1), then GPC (eluent: $CHCl_3$) to afford **2a-D** as a yellow solid (12.4 mg, 0.0272 mmol, %, 97% D/H exchange ratio). In the ^{1}H NMR spectrum of **2a-D**, a decreased singlet benzylic proton signal at δ 5.27 ppm with 0.0536 of the relative integral value to a signal at 7.78 ppm (d, 2H) and none of signal at δ 5.28 ppm (*trans*-isomer) were found, which can be assigned as *syn*-**2a** (2H) and/or its mono-deuterated one (1H). Taking into account that 0% deuteration and 100% deuteration correspond to 2.0 and 0.0 of integral ratios, the D/H exchange ratio was determined using the following equation (eq. 1).

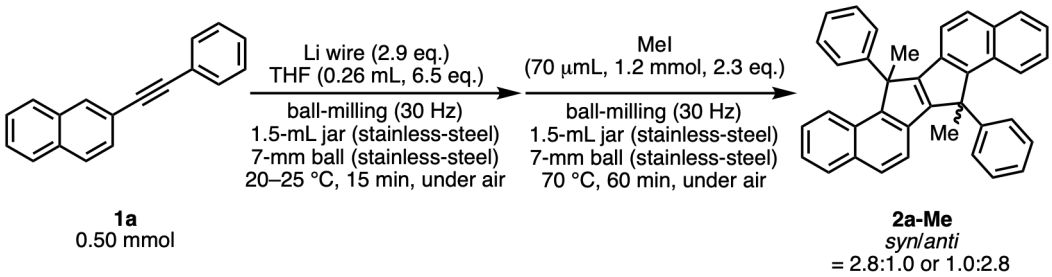
$$D/H\ exchange\ ratio = \frac{2.0-0.0536}{2} \times 100 = 97.3 \approx 97\% \qquad (eq.1)$$

^{1}H NMR (400 MHz, $Cl_2CDCDCl_2$) δ 7.78 (d, J = 7.7 Hz, 2H), 7.73–7.64 (m, 4H), 7.37 (d, J = 8.4 Hz, 2H), 7.33–7.20 (m, 14H).

^{13}C NMR (150 MHz, $Cl_2CDCDCl_2$) δ 154.80, 147.53, 139.09, 138.21, 131.64, 130.08, 129.06, 128.89, 128.32, 127.99, 126.84, 126.30, 124.44, 123.12, 118.51, 50.57 (br).

HRMS (DART, positive) *m*/*z*: $[M]^+$ Calcd for $C_{36}H_{22}D_2$ 458.20035; Found 458.19810.

3.2.5. Trapping with iodomethane for synthesis of mixture of *syn*- and *anti*-7,14-Dimethyl-7,14-diphenyl-7,14-dihydropentaleno[2,1-*a*:5,4-*a′*]dinaphthalene (**2a-Me**)



A 7-mm diameter stainless-steel ball and 2-(phenylethynyl)naphthalene (**1a**) (114 mg, 0.50 mmol, 1.0 eq.) were added to an oven-dried 1.5-mL stainless-steel jar. Pieces of Li (10.0 mg, 1.4 mmol, 2.9 eq.) cut from Li wire (3.2 mm in diameter, 99.9% purity) was washed with hexane for removing mineral oil, weighed on an electronic balance, and added into the jar under air. Then, THF (0.26 mL, 3.3 mmol, 6.5 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with an O-shaped packing made of 1-mm width polyethylene sheet, and the jar was sealed tightly with a wrench and a vise. The reaction jar and a same-weight blank jar (or a same-weight reaction jar) were fixed in a mixer mill (Retsch MM400), and shaken at 30 Hz (1800 rpm) at room temperature (20–25 °C) for 15 min. After shaking, the reaction jar was opened and the reaction was quenched by iodomethane (0.070 mL, 1.2 mmol, 2.3 eq.). The jar was then closed again and shaken at 30 Hz (1800 rpm) at 70 °C (a heat-gun preset temperature) for

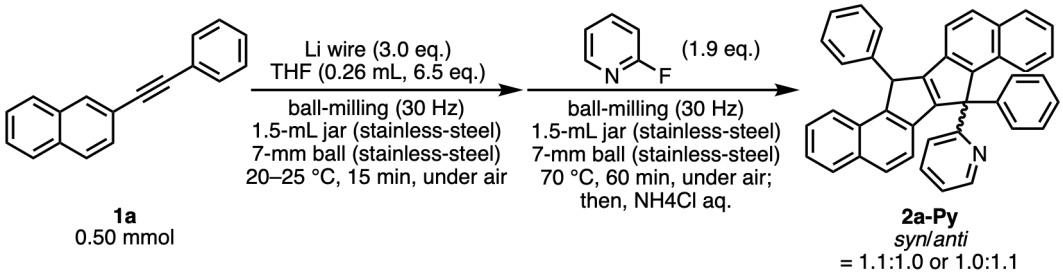
60 min. Then, the organic phase was extracted three times with chloroform. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to obtain a crude product, which was further purified by silica gel column chromatography (eluent: hexane/toluene = 3:1), then GPC (eluent: $CHCl_3$) to afford a mixture of *syn*-**2a-Me** and *anti*-**2a-Me** as a yellow solid (19.0 mg, 0.039 mmol, 16%). The *syn*/*anti* ratio was determined as 2.8:1 or 1:2.8 by ^{1}H NMR according to the proton signals of Me groups in 2.1–2.2 ppm.

^{1}H NMR of mixture of *syn*-**2a-Me** and *anti*-**2a-Me** (400 MHz, $Cl_2CDCDCl_2$, *syn*/*anti* or *anti*/*syn* = 74:16) δ 7.81 (d, *J* = 7.2 Hz 2H), 7.70 (d, *J* = 7.2 Hz 2H), 7.57–7.53 (m, 2H), 7.39–7.19 (m, 16H), 2.17 (s, 6H × 0.74), 2.13 (s, 6H×0.26).

^{13}C NMR of mixture of *syn*-**2a-Me** and *anti*-**2a-Me** (150 MHz, $Cl_2CDCDCl_2$, *syn*/*anti* or *anti*/*syn* = 74 (major):16 (minor)) δ 158.18 (major), 158.09 (minor), 153.29 (minor), 153.26 (major), 141.50 (minor), 141.27 (major), 135.88 (minor), 135.81 (major), 131.98 (major + minor), 129.09 (major + minor), 128.80 (major + minor), 128.71 (major + minor), 128.27 (major), 128.23 (minor), 126.49 (major + minor), 126.07 (major + minor), 126.01 (major + minor), 124.21 (major + minor), 122.89 (major + minor), 118.42 (major), 118.39 (minor), 52.87 (major + minor), 21.61 (major + minor).

HRMS (DART, positive) *m*/*z*: $[M+H]^+$ Calcd for $C_{38}H_{29}$ 458.22693; Found 458.22508.

3.2.6. Trapping with 2-fluoropyridine for synthesis of mixture of *syn*- and *anti*-2-(7,14-diphenyl-7,14-dihydropentaleno[2,1-*a*:5,4-*a′*]dinaphthalen-7-yl)pyridine (2a-Py)

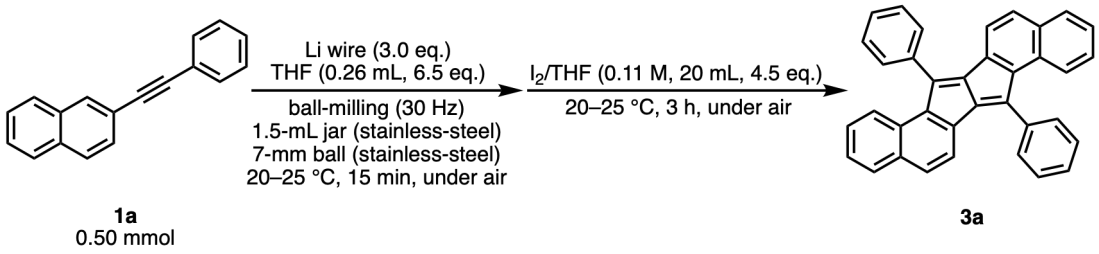


A 7-mm diameter stainless-steel ball and 2-(phenylethynyl)naphthalene (**1a**) (114 mg, 0.50 mmol, 1.0 eq.) were added to an oven-dried 1.5-mL stainless-steel jar. Pieces of Li (10.3 mg, 1.5 mmol, 3.0 eq.) cut from Li wire (3.2 mm in diameter, 99.9% purity) was washed with hexane for removing mineral oil, weighed on an electronic balance, and added into the jar under air. Then, THF (0.26 mL, 3.3 mmol, 6.5 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with an O-shaped packing made of 1-mm width polyethylene sheet, and the jar was sealed tightly with a wrench and a vise. The reaction jar and a same-weight blank jar (or a same-weight reaction jar) were fixed in a mixer mill (Retsch MM400), and shaken at 30 Hz (1800 rpm) at room temperature (20–25 °C) for 15 min. After shaking, the reaction jar was opened and the 2-fluoropyridine (0.080 mL, 0.93 mmol, 1.9 eq.) was added by a syringe. After the jar was then closed again and shaken at 30 Hz (1800 rpm) at 70 °C (heat-gun preset temperature) for 60 min, sat. NH_4Cl aq. was added to quench. Then, the organic phase was extracted three times with chloroform. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to obtain a crude product, which was further purified by silica gel column chromatography (eluent:

hexane/toluene = 3:1) to afford *syn*-**2a-Py** and *anti*-**2a-Py** mixture as a yellow solid (37.0 mg, 0.069 mmol, 28%). The *syn*/*anti* ratio was determined as 1.1:1.0 or 1.0:1.1 by ^{1}H NMR according to the benzylic proton signals in 5.3–5.4 ppm.

^{1}H NMR of mixture of *syn*-**2a-Py** and *anti*-**2a-Py** (400 MHz, $Cl_2CDCDCl_2$, *syn*/*anti* or *anti*/*syn* = 53:47) δ 8.80 (d, *J* = 4.5 Hz, 1H), 8.07 (d, *J* = 7.7 Hz, 1H×0.53), 8.00 (d, *J* = 7.7 Hz, 1H×0.47), 7.83–7.67 (m, 6H), 7.45–7.35 (m, 2H), 7.34–7.15 (m, 16H), 6.98 (d, *J* = 7.7 Hz, 1H×0.47), 6.93 (d, *J* = 7.7 Hz, 1H×0.53), 5.37 (s, 1H×0.47), 5.35 (s, 1H×0.53).
^{13}C NMR of mixture of *syn*-**2a-Py** and *anti*-**2a-Py** (150 MHz, $Cl_2CDCDCl_2$, *syn*/*anti* or *anti*/*syn* = 53:47) δ 159.24, 159.05, 158.80, 158.37, 153.84, 149.80, 149.12), 147.72, 147.70, 140.93, 140.67, 139.03, 138.94, 137.84, 137.63, 137.56, 137.47, 136.92, 132.23, 132.18, 131.56, 129.95, 129.87, 129.75, 129.30, 129.08, 128.81, 128.79, 128.72, 128.42, 128.14, 128.11, 128.03, 127.92, 126.92, 126.43, 126.25, 126.18, 126.01, 125.41, 125.21, 124.71, 124.65, 124.41, 123.15, 122.23, 122.10, 120.61, 120.24, 118.82, 66.22, 66.12, 50.92. All observed signals were shown, while peak overlapping could not be identified.
HRMS (DART, positive) *m*/*z*: $[M+H]^+$ Calcd for $C_{41}H_{28}N$ 534.22217; Found 534.22164.

3.2.7. Control experiments with quenching the reaction with iodine (Figure 2D)



A 7-mm diameter stainless-steel ball and 2-(phenylethynyl)naphthalene (**1a**) (114 mg, 0.50 mmol, 1.0 eq.) were added to an oven-dried 1.5-mL stainless-steel jar. Pieces of Li (10.3 mg, 1.5 mmol, 3.0 eq.) cut from Li wire (3.2 mm in diameter, 99.9% purity) was washed with hexane for removing mineral oil, weighed on an electronic balance, and added into the jar under air. Then, THF (0.26 mL, 3.3 mmol, 6.5 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with an O-shaped packing made of 1-mm width polyethylene sheet, and the jar was sealed tightly with a wrench and a vise. The reaction jar and a same-weight blank jar (or a same-weight reaction jar) were fixed in a mixer mill (Retsch MM400 or MM500 Vario), and shaken at 30 Hz (1800 rpm) at room temperature (20–25 °C) for 15 min. After shaking, the reaction jar was opened and the reaction was quenched by adding 0.11 M I_2 in THF (20 mL, 2.2 mmol, 4.5 eq.). The mixture was poured into a 100-mL round-bottom flask containing a magnetic stirring bar under open air and stirred for 3 hours at room temperature (20–25 °C). Then, sat. $Na_2S_2O_3$ aq. was added to quench and the mixture was further stirred for 30 min. The mixture was concentrated under reduced pressure to remove THF, and the organic phase of resulting mixture was extracted with chloroform (three times). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford a crude product, which was further purified by silica gel column chromatography (eluent:

hexane/toluene = 3:1) and GPC (eluent: $CHCl_3$) to afford dinaphtopentalene **3a** with inseparable impurities (19.2 mg, 17% crude yield). The ^1H and ^{13}C NMR spectra were identical to those reported literature,[S4] while these contain the signals derived from unidentified side products. **HRMS** (EI, positive) *m*/*z*: $[M]^+$ Calcd for $C_{36}H_{22}$ 454.17215; Found 454.17243.

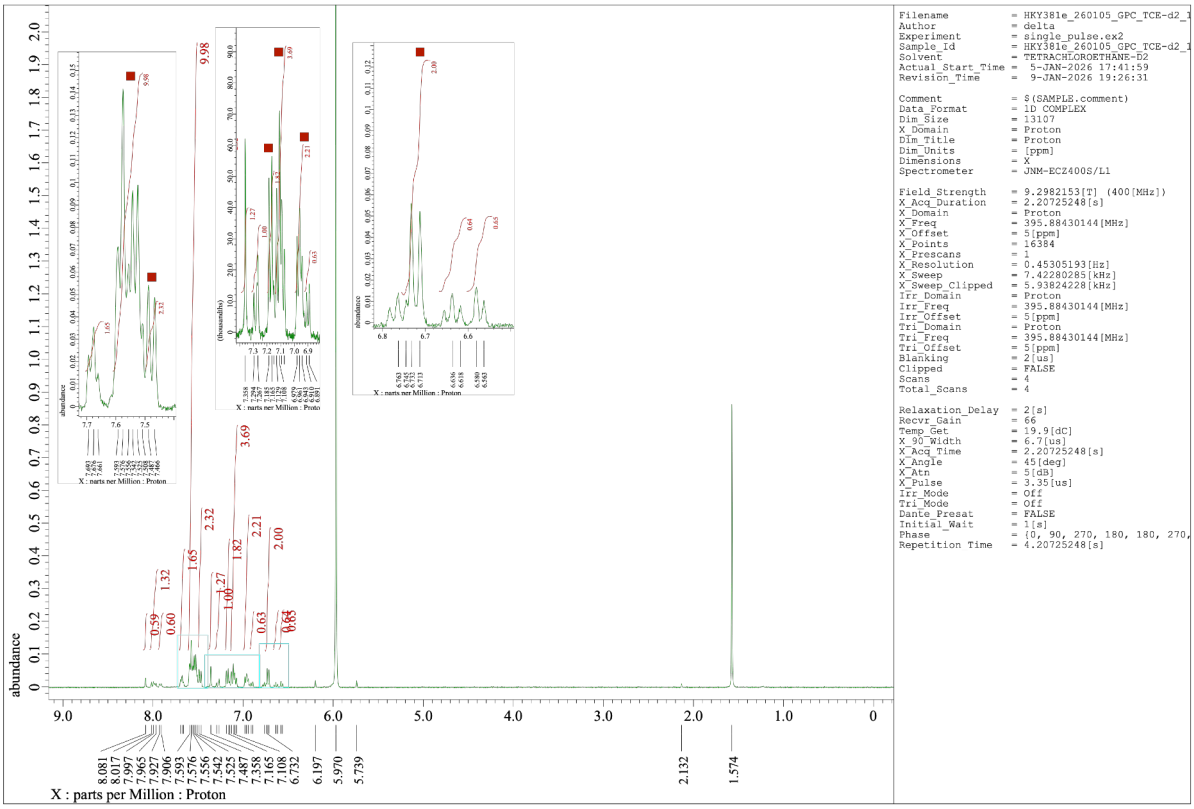


Figure S1. ^1H NMR spectrum of **3a** including impurities (400 MHz, $Cl_2CDCDCl_2$). Red-filled squares represent the identical proton peaks of **3a**.

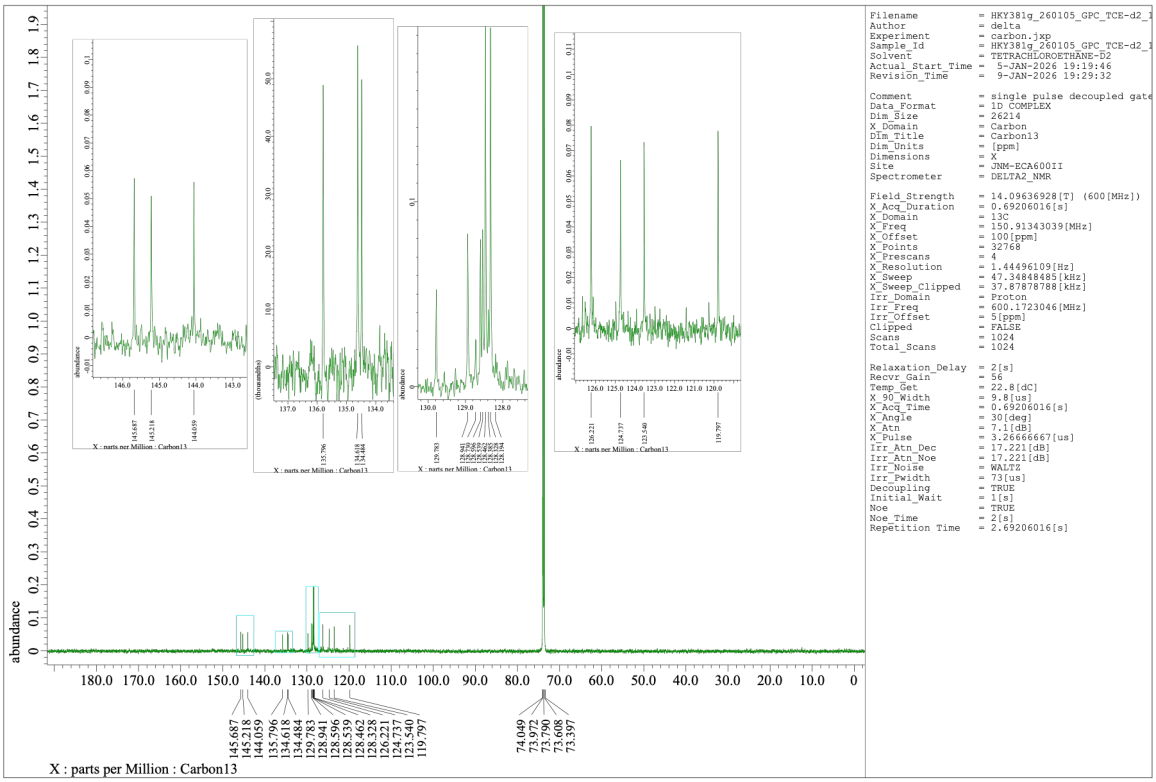
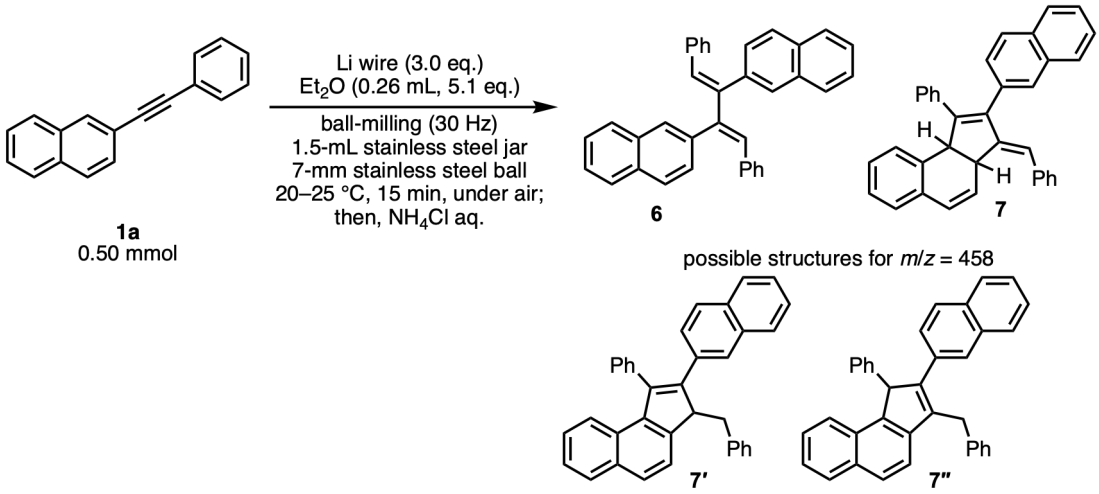


Figure S2. ^{13}C NMR spectrum of **3a** (150 MHz, $Cl_2CDCDCl_2$).

3.2.8. Control experiments with Et_2O instead of THF (Figure 2H)



A 7-mm diameter stainless-steel ball and 2-(phenylethynyl)naphthalene (**1a**) (114 mg, 0.50 mmol, 1.0 eq.) were added to an oven-dried 1.5-mL stainless-steel jar. Pieces of Li (10.3 mg, 1.5 mmol, 3.0 eq.) cut from Li wire (3.2 mm in diameter, 99.9% purity) was washed with hexane for removing mineral oil, weighed on an electronic balance, and added into the jar under air. Then, Et_2O (0.26 mL, 2.5 mmol, 5.1 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with an O-shaped packing made of 1-mm width polyethylene sheet, and the jar was sealed tightly with a wrench and a vise. The reaction jar and a same-weight blank jar (or a same-weight reaction jar) were fixed in a mixer mill (Retsch MM400), and shaken at 30 Hz (1800 rpm) at room temperature (20–25 °C) for 15 min. After shaking,

the reaction jar was opened and the reaction was quenched by adding sat. NH_4Cl aq. Then, the organic phase was extracted with chloroform (three times). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to obtain a crude product, which was further purified by silica gel column chromatography (eluent: hexane/DCM = 5:1) and GPC (eluent: $CHCl_3$) to afford the mixture of compounds showing a major mass peak at *m*/*z* = 458 (APCI-MS). Based on the presence of a singlet olefinic proton peak at 6.82 ppm in the ^{1}H NMR and benzylic and/or allylic proton/carbon peaks in 3.5–4.1 ppm in the ^{1}H NMR and 34–37 ppm in ^{13}C NMR (Figures S3 and S4), we expected that this mixture can contain butadiene **6** and mono-cyclized products **7**, **7′** and **7″**.

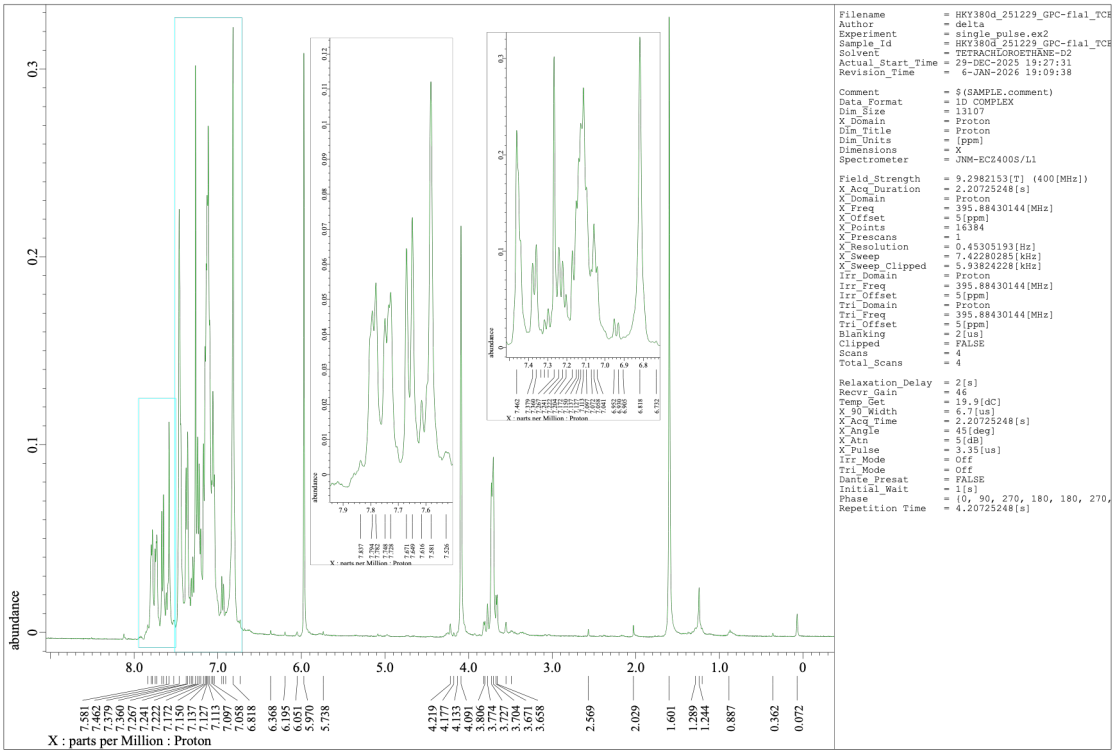


Figure S3. ^{1}H NMR spectrum of obtained mixture (400 MHz, $Cl_2CDCDCl_2$).

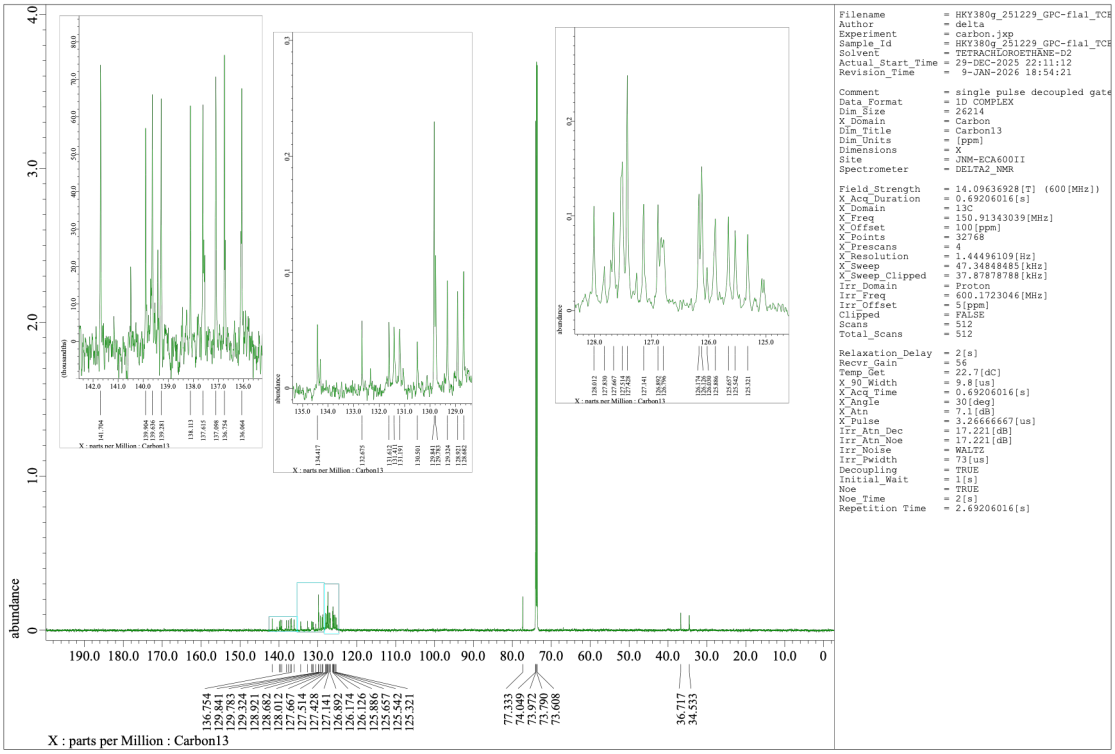
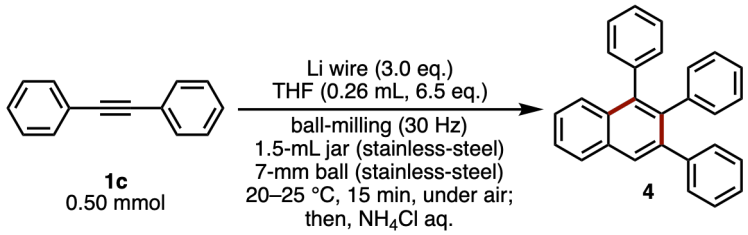


Figure S4. ^{13}C NMR spectrum of obtained mixture (150 MHz, $Cl_2CDCDCl_2$).

3.2.9. Synthesis of 1,2,3-triphenylnaphthalene (4)



A 7-mm diameter stainless-steel ball and diphenylacetylene (**1c**) (89.2 mg, 0.50 mmol, 1.0 eq.) were added to an oven-dried 1.5-mL stainless-steel jar. Pieces of Li (10.4 mg, 1.5 mmol, 3.0 eq.) cut from Li wire (3.2 mm in diameter, 99.9% purity) was washed with hexane for removing mineral oil, weighed on an electronic balance, and added into the jar under air. Then, THF (0.26 mL, 3.3 mmol, 6.5 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with an O-shaped packing made of 1-mm width polyethylene sheet, and the jar was sealed tightly with a wrench and a vise. The reaction jar and a same-weight blank jar (or a same-weight reaction jar) were fixed in a mixer mill (Retsch MM400), and shaken at 30 Hz (1800 rpm) at room temperature (20–25 °C) for 15 min. After shaking, the reaction jar was opened and the reaction was quenched by adding sat. NH_4Cl aq. Then, the organic phase was extracted with chloroform (three times). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford a crude product, which was further purified by silica gel column chromatography (eluent: hexane) and GPC (eluent: $CHCl_3$) to afford **4** as a white solid (27.6 mg, 0.0774

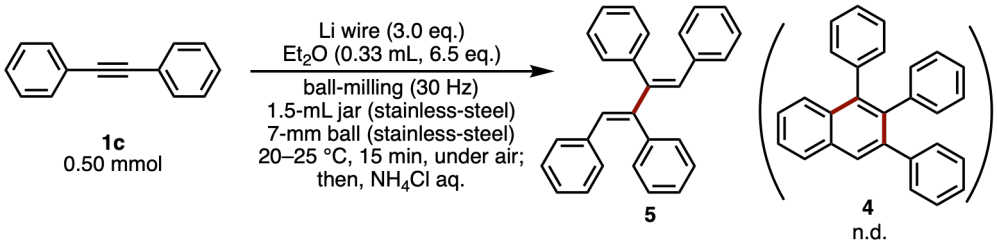
mmol, 31%). ^{1}H and ^{13}C NMR were identical to those reported in the literature.[S5]

^{1}H NMR (400 MHz, $Cl_2CDCDCl_2$) δ 7.94–7.92 (m, 2H), 7.57 (d, *J* = 8.6 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.27–7.11 (m, 10H), 6.94–6.88 (m, 3H), 6.84–6.79 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 142.11, 140.14, 140.00, 139.49, 139.29, 138.21, 132.80, 132.13, 131.65, 131.37, 130.16, 128.87, 128.05, 127.65 (2C), 127.04, 127.00, 126.58, 126.38, 126.29, 126.23, 125.77.

HRMS (DART, positive) *m/z*: $[M+H]^+$ Calcd for $C_{28}H_{21}$ 357.16433; Found 357.16354.

3.2.6 Synthesis of (1*E*,3*E*)-1,2,3,4-tetraphenyl-1,3-butadiene (5) (Figure 2G)



A 7-mm diameter stainless-steel ball and diphenylacetylene (**1c**) (88.9 mg, 0.50 mmol, 1.0 eq.) were added to an oven-dried 1.5-mL stainless-steel jar. Pieces of Li (13.8 mg, 2.0 mmol, 4.0 eq.) cut from Li wire (3.2 mm in diameter, 99.9% purity) was washed with hexane for removing mineral oil, weighed on an electronic balance, and added into the jar under air. Then, Et_2O (0.35 mL, 3.3 mmol, 6.5 eq.) was added to the jar by a syringe under air. The jar was capped with a stainless-steel cap equipped with an O-shaped packing made of 1-mm width polyethylene sheet, and the jar was sealed tightly with a wrench and a vise. The reaction jar and a same-weight blank jar (or a same-weight reaction jar) were fixed in a mixer mill (Retsch MM400), and shaken at 30 Hz (1800 rpm) at room temperature (20–25 °C) for 15 min. After shaking, the reaction jar was opened and the reaction was quenched by adding sat. NH_4Cl aq. Then, the organic phase was extracted with chloroform (three times). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford a crude product, which was further purified by silica gel column chromatography (eluent: hexane) and GPC (eluent: $CHCl_3$) to afford **5** as a white solid (29.2 mg, 0.0814 mmol, 33%). ^{1}H and ^{13}C NMR were identical to those reported in the literature.[S6]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43–7.39 (m, 4H), 7.37 (d, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 6.9 Hz, 4H), 7.06–7.01 (m, 6H), 6.76–6.73 (m, 4H), 6.30 (s, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 145.72, 139.87, 137.37, 131.78, 130.51, 129.61, 128.94, 127.92, 127.48, 126.73.

HRMS (ESI, positive) *m/z*: $[M+H]^+$ Calcd for $C_{28}H_{23}$; 359.1799 Found. 359.1795.

4. Enantiomer separation of *syn*-2a

(14*R*,7*R*)-*syn*-**2a** and (14*S*,7*S*)-*syn*-**2a** were successfully resolved from a racemic mixture of *syn*-**2a** by a chiral HPLC quipped with a single line of DAICEL CHIRALPAK IF column with *n*-hexane/CH_2Cl_2 = 80:20 as eluents at 0.5 mL/min of flow rate at room temperature (20–25 °C). The first fraction ((14*R*,7*R*)-*syn*-**2a**) and the second fraction ((14*S*,7*S*)-*syn*-**2a**) were eluted between 16.40–17.00 min and 17.90–18.60 min of retention time. The eluted fractions containing each enantiomer were evaporated by a vacuum pump, and the measurements of CD were performed (Figure S5).

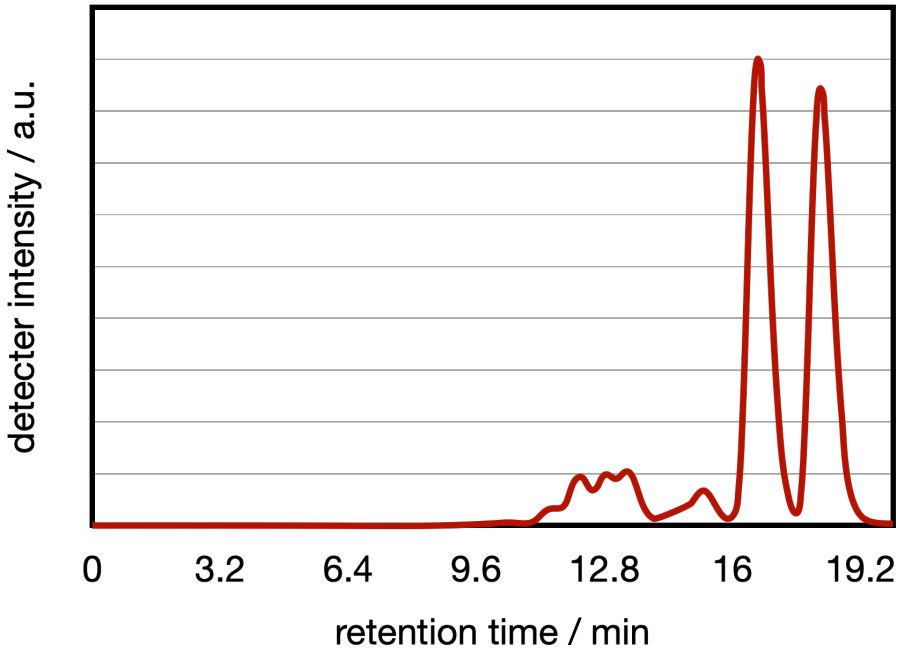
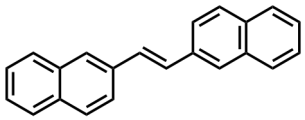


Figure S5. Chiral HPLC charts. HPLC conditions for chiral resolution: a single line of DAICEL CHIRALPAK IF column with *n*-hexane/CH_2Cl_2 = 80:20 as eluent at 0.5 mL/min of flow rate at room temperature (20–25 °C).

5. Measurements of photophysical properties of *syn*-2a and (*E*)-1,2-di(naphthalen-2-yl)ethene

(*E*)-1,2-Di(naphthalen-2-yl)ethene (**8**) was prepared for photophysical comparison according to the reported procedure.[S7]



(*E*)-1,2-di(naphthalen-2-yl)ethene

UV/Vis absorption spectra of *syn*-**2a** ($c = 2.02 \times 10^{-5}$ M) in CH_2Cl_2 and (*E*)-1,2-di(naphthalen-2-yl)ethene ($c = 9.81 \times 10^{-6}$ M) in CH_2Cl_2 were recorded on a JASCO V-770 spectrophotometer at room temperature (25 °C) with a resolution of 0.5 nm. The spectroscopic grade CH_2Cl_2 and a 1.0 × 1.0 cm square quartz cell were used for measurements.

Emission spectra of *syn*-**2a** ($c = 2.02 \times 10^{-6}$ M) in CH_2Cl_2 and **8** ($c = 9.81 \times 10^{-7}$ M) in degassed spectroscopic grade CH_2Cl_2 were measured with a JASCO FP-6600 spectrofluorophotometer at room temperature (25 °C) with a resolution of 0.4 nm upon excitation at 380 nm (for *syn*-**2a**) and 250 nm (for (*E*)-1,2-di(naphthalen-2-yl)ethene). The degassed solutions in spectroscopic grade CH_2Cl_2 and a 1.0 × 1.0 cm square quartz cell were used for measurements.

Circular dichroism (CD) spectra of (7*R*,14*R*)-*syn*-**2a** ($c = 2.0 \times 10^{-5}$ M) in CH_2Cl_2 and (7*S*,14*S*)-*syn*-**2a** ($c = 2.2 \times 10^{-5}$ M) in CH_2Cl_2 were recorded in CH_2Cl_2 with a JASCO J-1500 at 10 °C with a resolution of 0.2 nm. The spectroscopic grade CH_2Cl_2 and a 1.0 × 1.0 cm square quartz cell were used for measurements.

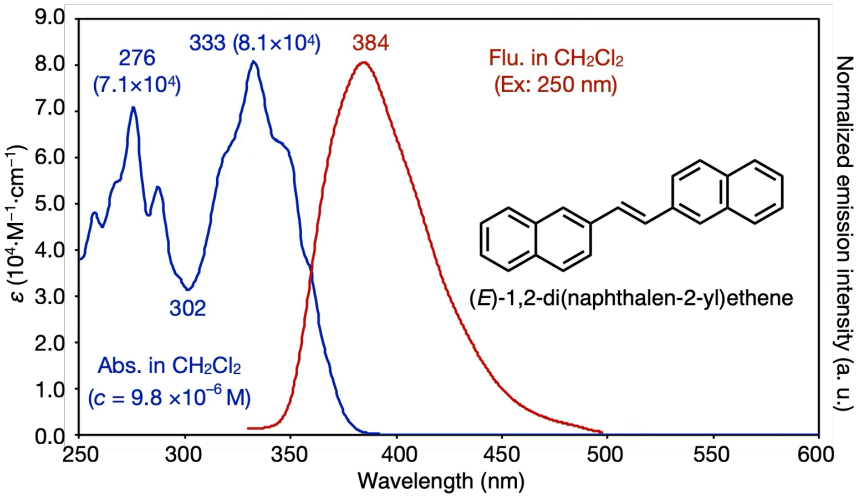


Figure S6. Absorption (blue line) and emission (red line) spectra of (*E*)-1,2-di(naphthalen-2-yl)ethene (**8**) in CH_2Cl_2. Excitation light: 250 nm.

6. X-ray crystallographic analysis

Details of the crystal data and a summary of the intensity data collection parameters for *syn*-**2a** is listed in Table S1. A suitable crystal was mounted with mineral oil on a MiTeGen MicroMounts and transferred to the goniometer of the kappa goniometer of a RIGAKU XtaLAB Synergy-S system with 1.2 kW MicroMax-007HF microfocus rotating anode (Graphite-monochromated Mo Kα radiation (λ = 0.71073 Å)) and PILATUS200K hybrid photon-counting detector. Cell parameters were determined and refined, and raw frame data were integrated using CrysAlis^{Pro} (Agilent Technologies, 2010). The structures were solved by direct methods with (SHELXT)[S8] and refined by full-matrix least-squares techniques against F^2 (SHELXL-2018/3)[S9] by using Olex2 software package.[S10] The intensities were corrected for Lorentz and polarization effects. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions. CCDC 2495836 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 S1. Crystallographic data and structure refinement details of *syn*-**2a**

	syn-**2a**
CCDC number	2495836
formula	$C_{36}H_{24}$
FW	456.55
T (K)	123(2)
λ (Å)	0.71073
crystal system	*monoclinic*
space group	*C2/c*
a (Å)	23.0283(10)
b (Å)	9.6069(4)
c (Å)	22.0625(9)
α (deg)	90
β (deg)	90.755(4)
γ (deg)	90
V (Å^3)	4880.5(4)
Z	8
ρ_{calc} (g·cm^{-3})	1.243
μ (mm^{-1})	0.070
F (000)	1920.0
cryst size (mm^3)	0.2 × 0.2 × 0.1
2θ range (deg)	3.538–59.61
reflections collected	21324
independent	5687/0.0513
parameters	325
GOF on F^2	1.041
R_1, wR_2 [I>2σ(I)]	0.0443, 0.1129
R_1, wR_2 (all data)	0.0563, 0.1204

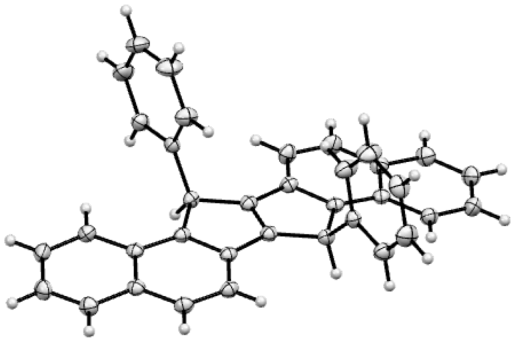


Figure S7. ORTEP drawing of *syn*-**2a**

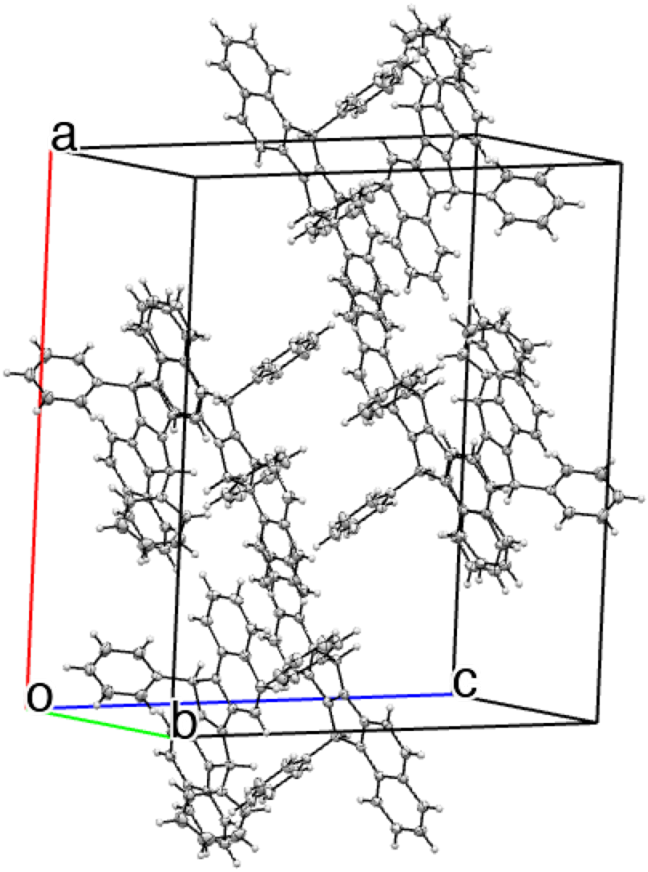


Figure S8. ORTEP drawing of the packing structure of *syn*-**2a**

7. 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))[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).

Table S2. Cartesian coordinates of (7*R*,14*R*)-*syn*-**2a** optimized at the B3LYP/6-31G(d) level of theory.

C	-5.9452360	0.0841280	-0.8266060	C	2.9919280	2.9601840	-0.7607060
C	-6.3307510	-1.2790070	-0.8377810	C	1.6501320	2.6544620	-0.7396530
C	-5.3714610	-2.2657380	-0.8132990	C	4.6152990	-0.4359730	-0.7906600
C	-3.9883450	-1.9447830	-0.7782330	C	5.9452360	-0.0841280	-0.8266070
C	-3.5961530	-0.5585210	-0.7649900	C	6.3307500	1.2790070	-0.8377810
C	-4.6152990	0.4359730	-0.7906600	C	5.3714610	2.2657380	-0.8132990
C	-2.9919280	-2.9601850	-0.7607060	H	-6.7084930	0.8576930	-0.8447450
C	-1.6501320	-2.6544620	-0.7396540	H	-7.3848180	-1.5414370	-0.8659950
C	-1.2580430	-1.2949810	-0.7294350	H	-5.6608840	-3.3142880	-0.8227180
C	-2.2114510	-0.2680000	-0.7329740	H	-4.3314900	1.4833570	-0.7722010
C	0.0587700	-0.6753490	-0.7294390	H	-3.3138860	-3.9989990	-0.7676490
C	-0.0587700	0.6753490	-0.7294390	H	-0.9010790	-3.4406470	-0.7238020
C	-1.5128600	1.0997450	-0.7362160	H	-1.7404370	1.6147690	-1.6816350
C	1.5128600	-1.0997450	-0.7362160	H	1.7404370	-1.6147690	-1.6816350
C	2.2114510	0.2680000	-0.7329740	H	-1.5916380	0.5650460	1.9490690
C	1.2580430	1.2949810	-0.7294350	H	-2.1272050	2.1104840	3.8066980
C	-1.8776460	2.0420070	0.4072680	H	-2.7249240	4.4788800	3.3312480
C	-1.8484710	1.5996010	1.7370490	H	-2.7804910	5.2835780	0.9767330
C	-2.1516150	2.4707980	2.7815180	H	-2.2439820	3.7331350	-0.8769420
C	-2.4875550	3.8012680	2.5155780	H	2.2439840	-3.7331350	-0.8769420
C	-2.5184880	4.2518420	1.1965580	H	2.7804930	-5.2835780	0.9767340
C	-2.2152090	3.3759830	0.1506780	H	2.7249240	-4.4788800	3.3312480
C	1.8776460	-2.0420080	0.4072680	H	2.1272040	-2.1104840	3.8066980
C	2.2152100	-3.3759830	0.1506780	H	1.5916360	-0.5650460	1.9490690
C	2.5184890	-4.2518420	1.1965580	H	3.3138860	3.9989990	-0.7676480
C	2.4875550	-3.8012680	2.5155790	H	0.9010790	3.4406460	-0.7238010
C	2.1516140	-2.4707980	2.7815190	H	4.3314900	-1.4833570	-0.7722020
C	1.8484700	-1.5996010	1.7370490	H	6.7084940	-0.8576930	-0.8447460
C	3.5961530	0.5585210	-0.7649910	H	7.3848180	1.5414370	-0.8659950
C	3.9883450	1.9447830	-0.7782330	H	5.6608830	3.3142880	-0.8227170

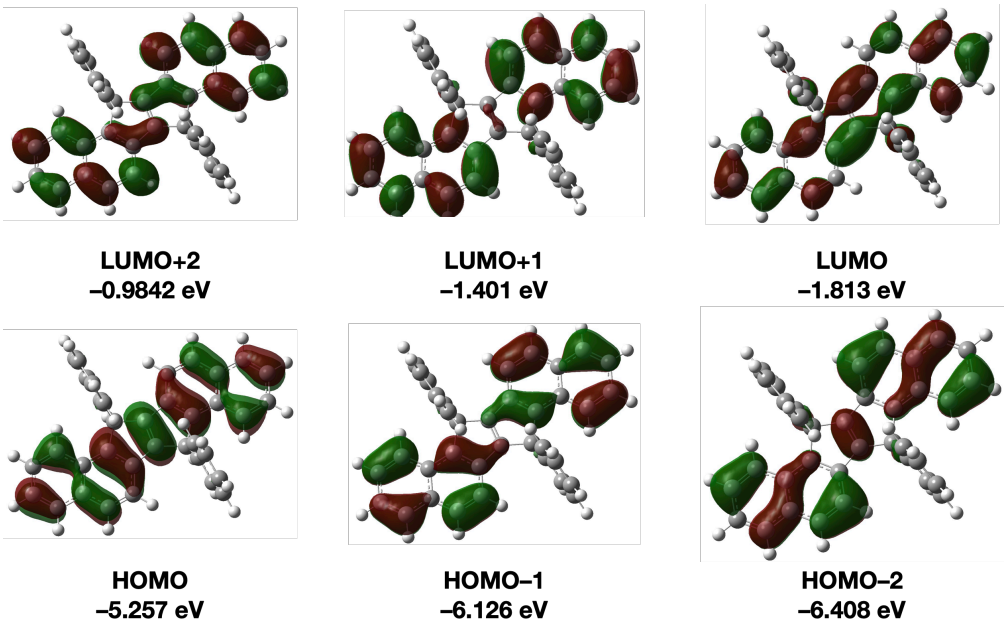


Figure S9. Frontier molecular orbitals of (7*R*,14*R*)-*syn*-**2a** calculated at the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level of theory.

Table S3. Uncorrected and thermal-corrected (298.15 K, 1 atm) energies of stationary points (Hartree) calculated by B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level of theory.

Structure	Basis set	*E*	*ZPE*	*H*	*corr-G*	*G*
syn-**2a**	B3LYP/6-31G(d)	-1386.3158	0.484686	-1385.8041	0.426821	-1385.889
syn-**2a**	B3LYP/6-311+G(d,p)	-1386.6407	–	–	–	–

Table S4. Representative vertical one-electron excitations of optimized (7*R*,14*R*)-*syn*-**2a** calculated by TD-DFT at the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level of theory. Excitation energy (eV), wavelength (nm) and oscillator strength (*f*), molecular orbital numbers, contribution of molecular orbitals are highlighted.

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 3.0313 eV 409.01 nm f = 0.3673 <S**2>=0.000
120 ->121 0.70251 (HOMO → LUMO)
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -1386.52929129
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.3057 eV 375.06 nm f = 0.0002 <S**2>=0.000
119 ->121 0.16671
120 ->122 0.67591 (HOMO → LUMO+1)

Excited State 3: Singlet-A 3.6431 eV 340.32 nm f = 0.1042 <S**2>=0.000
118 ->121 -0.31906
120 ->123 0.61542 (HOMO → LUMO+2)

Excited State 4: Singlet-A 3.8383 eV 323.02 nm f = 0.0001 <S**2>=0.000
119 ->121 0.66275 (HOMO−1→ LUMO)
120 ->122 -0.17621

Excited State 5: Singlet-A 4.0415 eV 306.77 nm f = 0.0216 <S**2>=0.000
120 ->124 0.65810 (HOMO→ LUMO+3)
120 ->126 0.23926

8. References

[S1] L. Liu, D. Zhou, M. Liu, Y. Zhou and T. Chen, *Org. Lett*., 2018, **20**, 2741.

[S2] S. Zhang, J. J. Ibrahim and Y. Yang, *Org. Lett*., 2018, **20**, 6265.

[S3] H. T. Kim, E. Kang, M. Kim and J. M. Joo, *Org. Lett*., 2021, **23**, 3657.

[S4] T. Kawase, T. Fujiwara, C. Kitamura, A. Konishi, Y. Hirao, K. Matsumoto, H. Kurata, T. Kubo, S. Shinamura, H. Mori, E. Miyazaki, K. Takimiya, *Angew. Chem. Int. Ed.*, 2010, **49**, 7728.

[S5] A. Sato and T. Kuwabara, *J. Org. Chem.,* 2025, **90**, 9258.

[S6] D. P. Ojha and K. R. Prabhu, *J. Org. Chem.* 2013, **78**, 12136.

[S7] M. T. Quick, M. Quick, I. N. Ioffe, C. Richter, R. Mahrwald, S. Druzhinin and S. A. Kovalenko, *J. Phys. Chem. B*, 2020, **124**, 1049.

[S8] G. M. Sheldrick, *Acta Crystallogr.,* 2015, **A71**, 3.

[S9] G. M. Sheldrick, *Acta Crystallogr*., 2015, **C71**, 3.

[S10] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.,* 2009, **42**, 339.

[S11] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji , X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams - Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. R anasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. B earpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian 16, Revision C .01, Gaussian, Inc., Wallingford CT, 2016.

[S12] A. D. Becke, *J. Chem. Phys.,* 1993, **98**, 5648.

[S13] C. Lee, W. Yang and R. G. Parr, *Phys. Rev., B* 1988, **37**, 785.

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

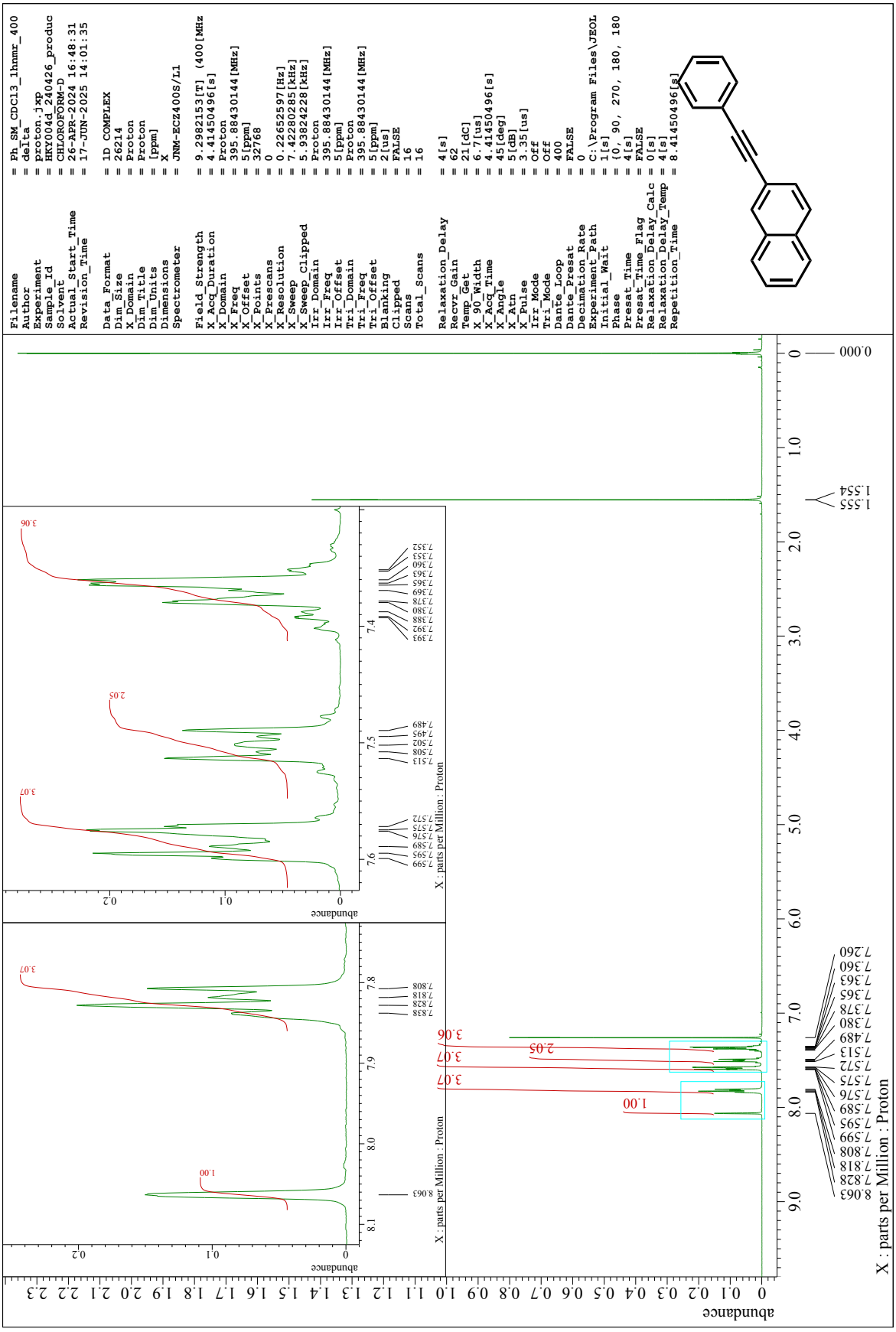


Figure S10. ^{1}H NMR spectrum of **1a** (400 MHz, $CDCl_3$).

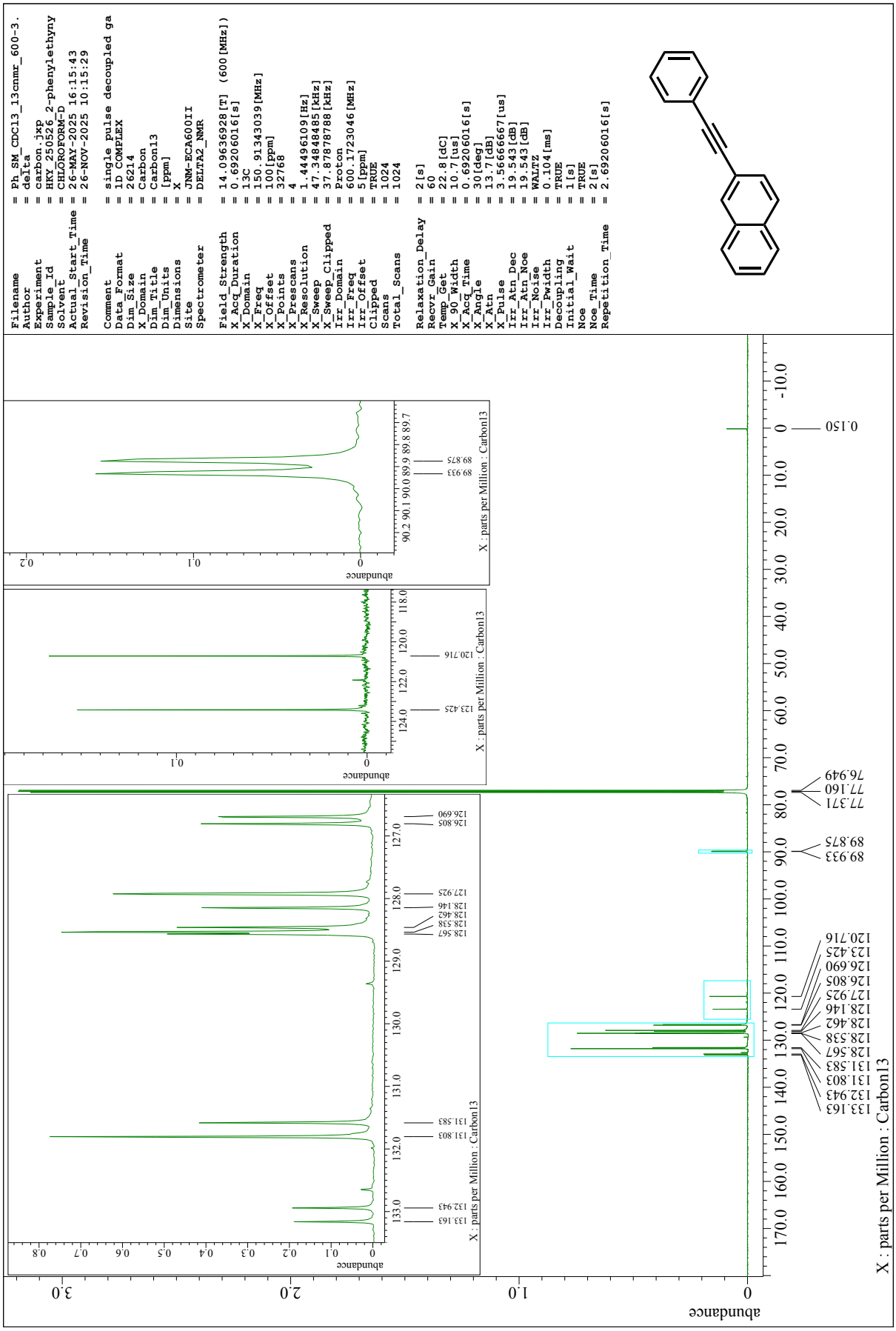


Figure S11. ^{13}C NMR spectrum of **1a** (150 MHz, $CDCl_3$).

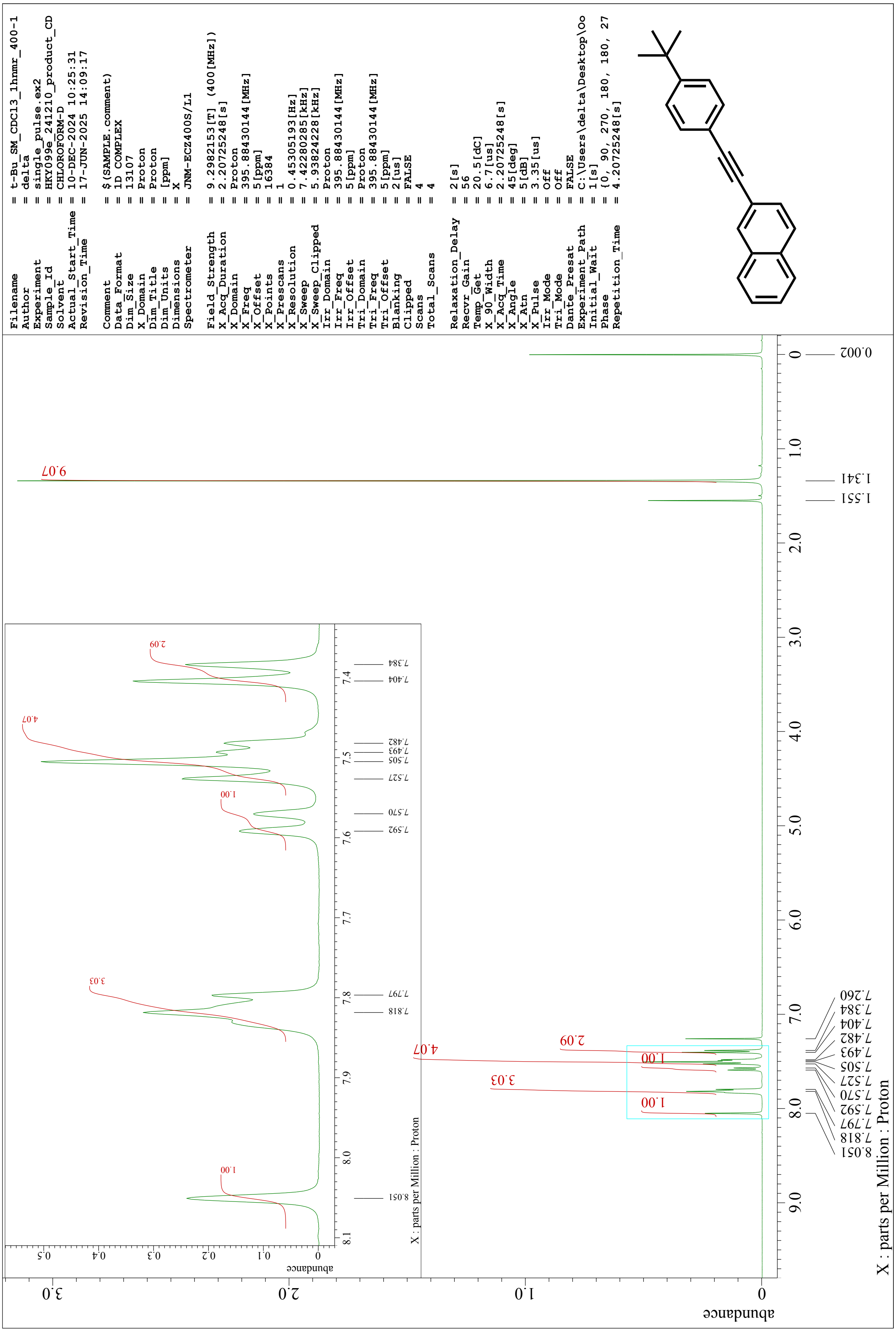


Figure S12. ^{1}H NMR spectrum of **1c** (400 MHz, $CDCl_3$).

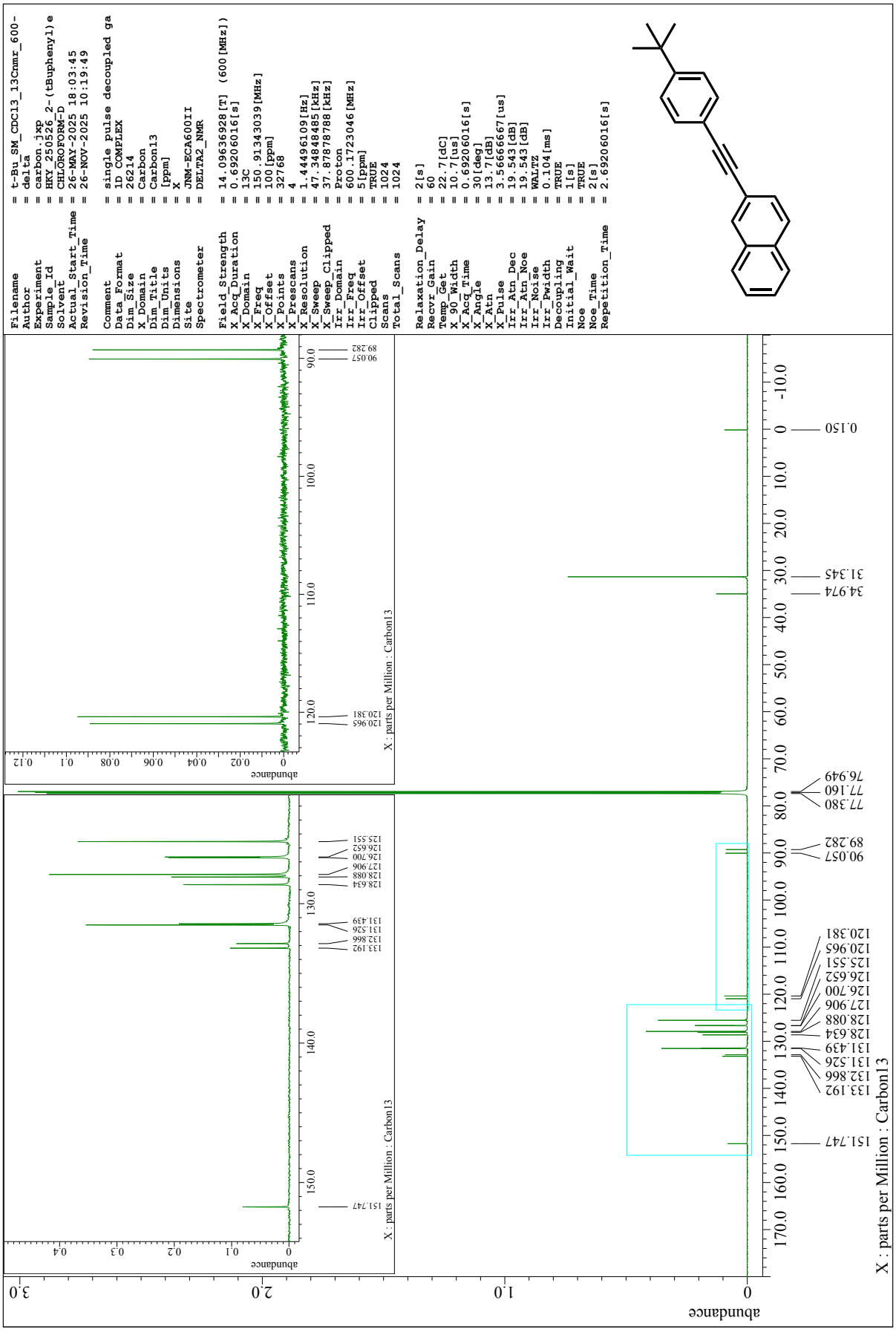


Figure S13. ^{13}C NMR spectrum of **1c** (150 MHz, $CDCl_3$).

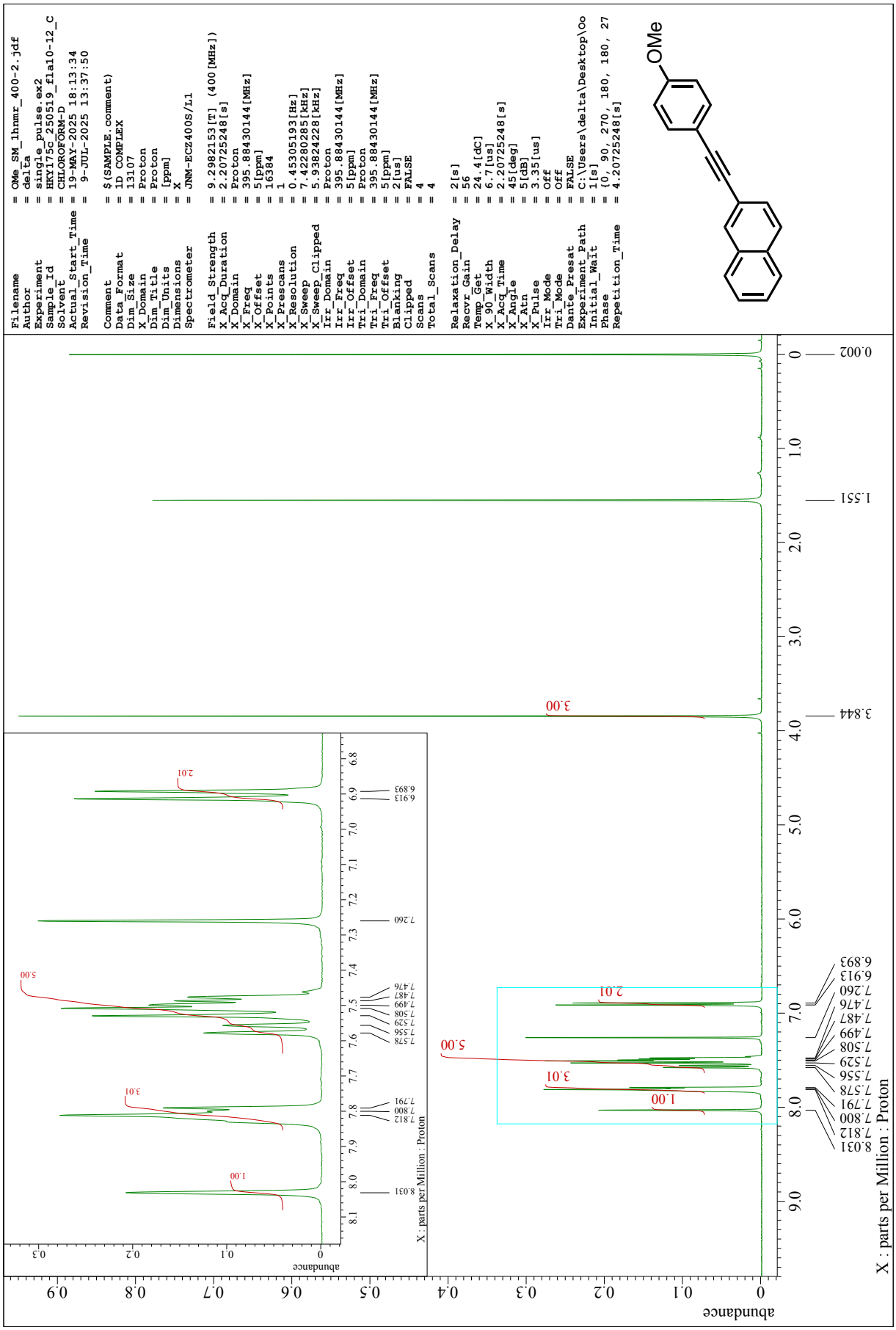


Figure S14. ^{1}H NMR spectrum of **1d** (400 MHz, $CDCl_3$).

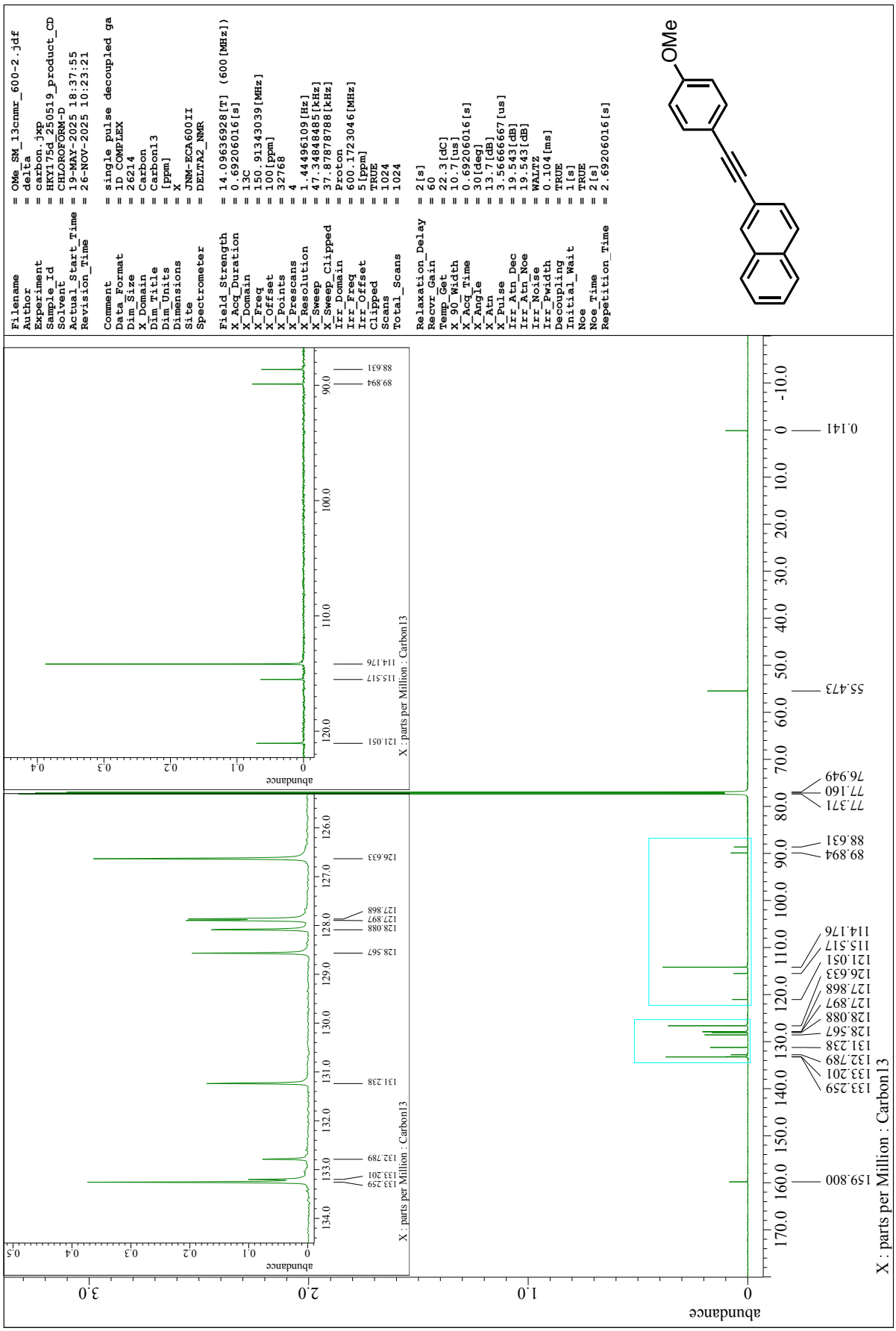


Figure S15. ^{13}C NMR spectrum of **1d** (150 MHz, $CDCl_3$).

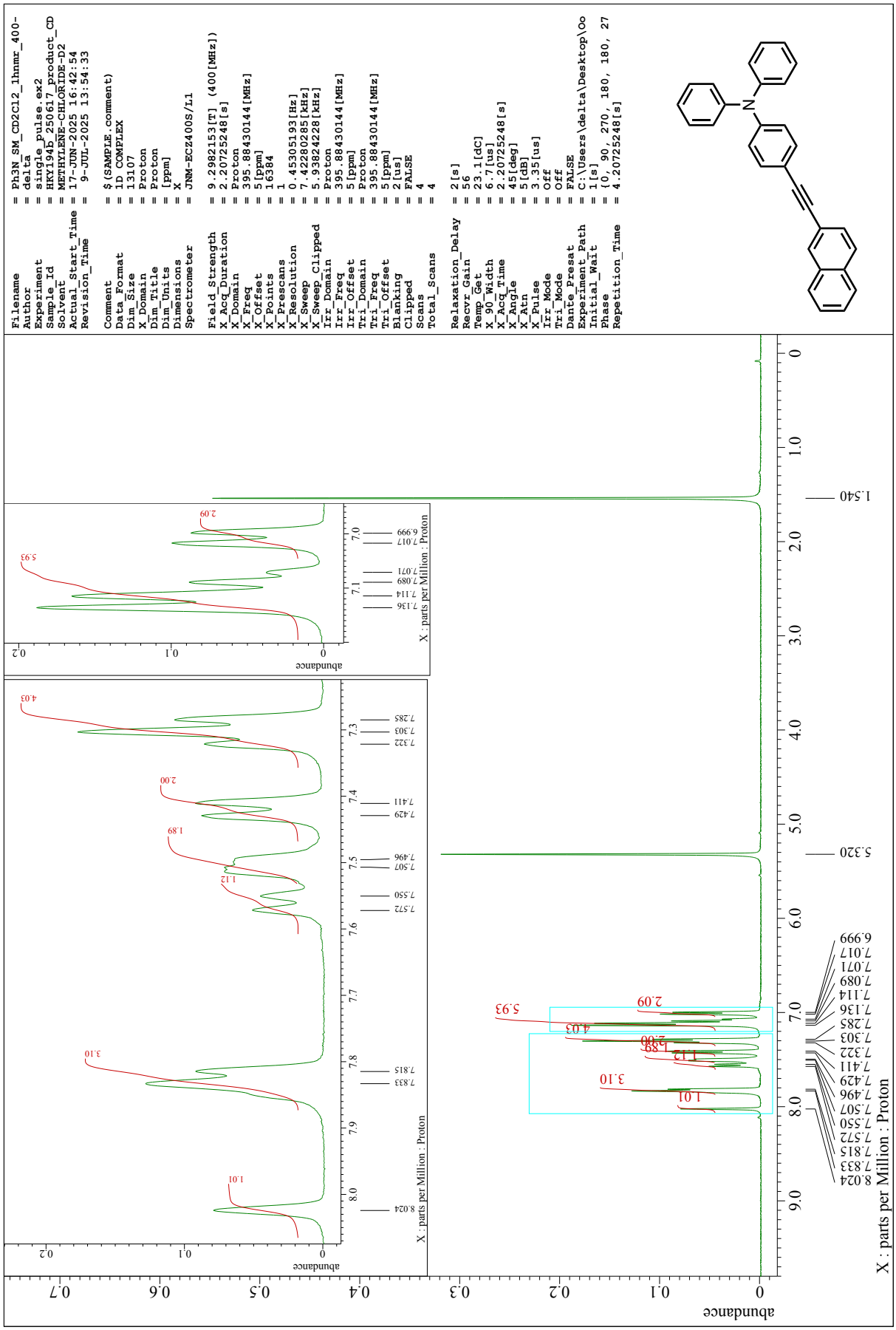


Figure S16. ^{1}H NMR spectrum of **1e** (400 MHz, CD_2Cl_2).

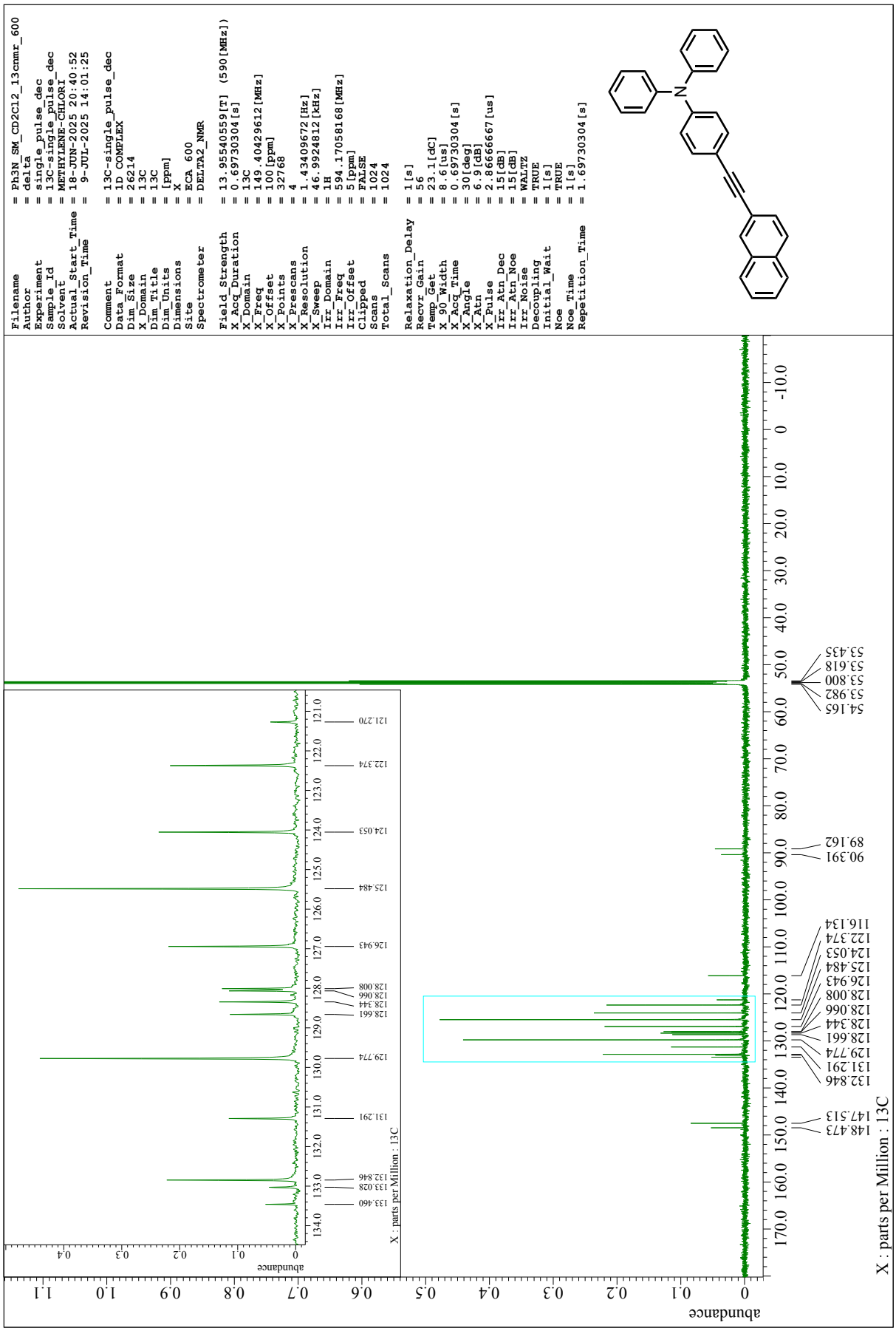


Figure S17. ^{13}C NMR spectrum of **1e** (150 MHz, CD_2Cl_2)

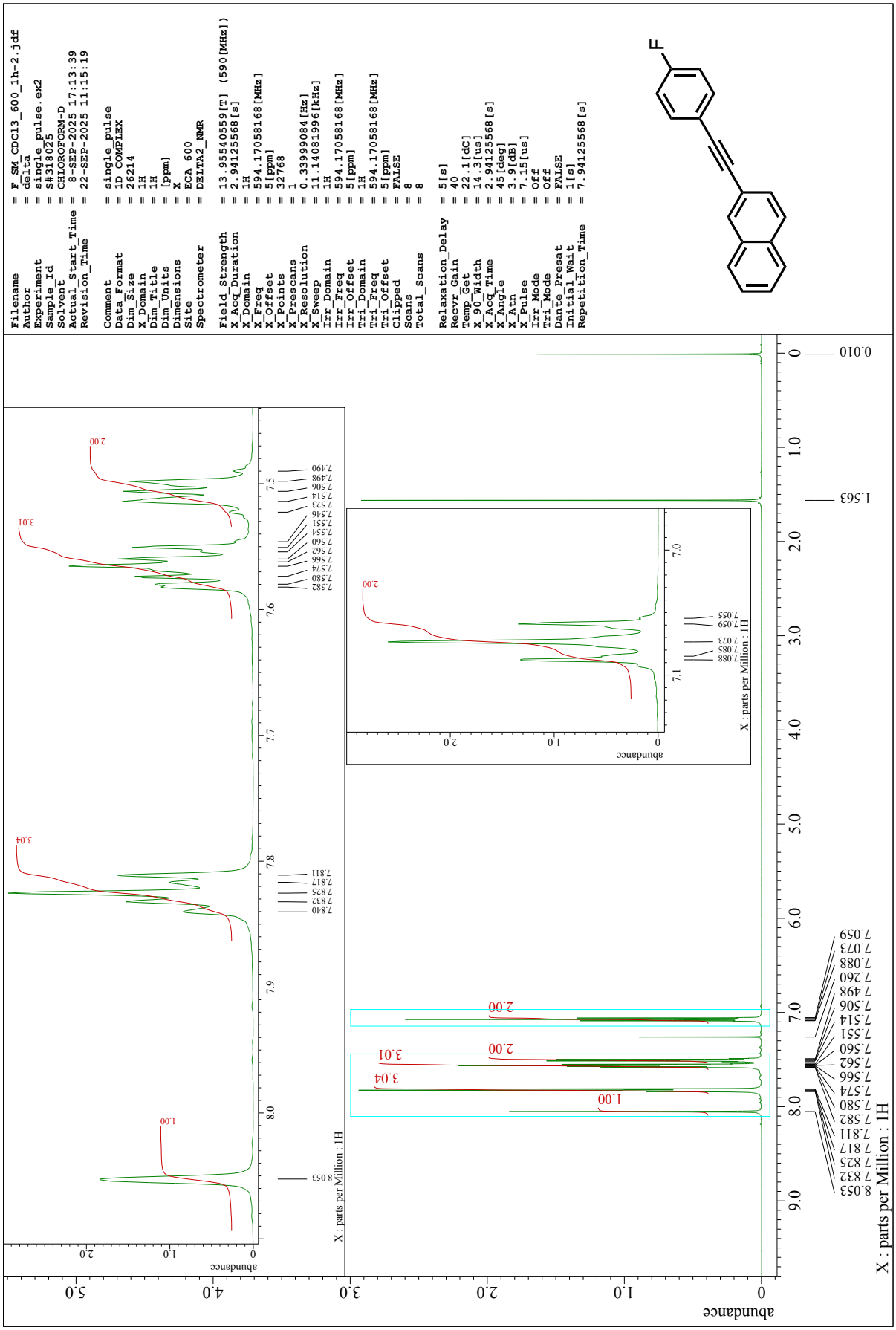


Figure S18. ^{1}H NMR spectrum of **1f** (400 MHz, $CDCl_3$).

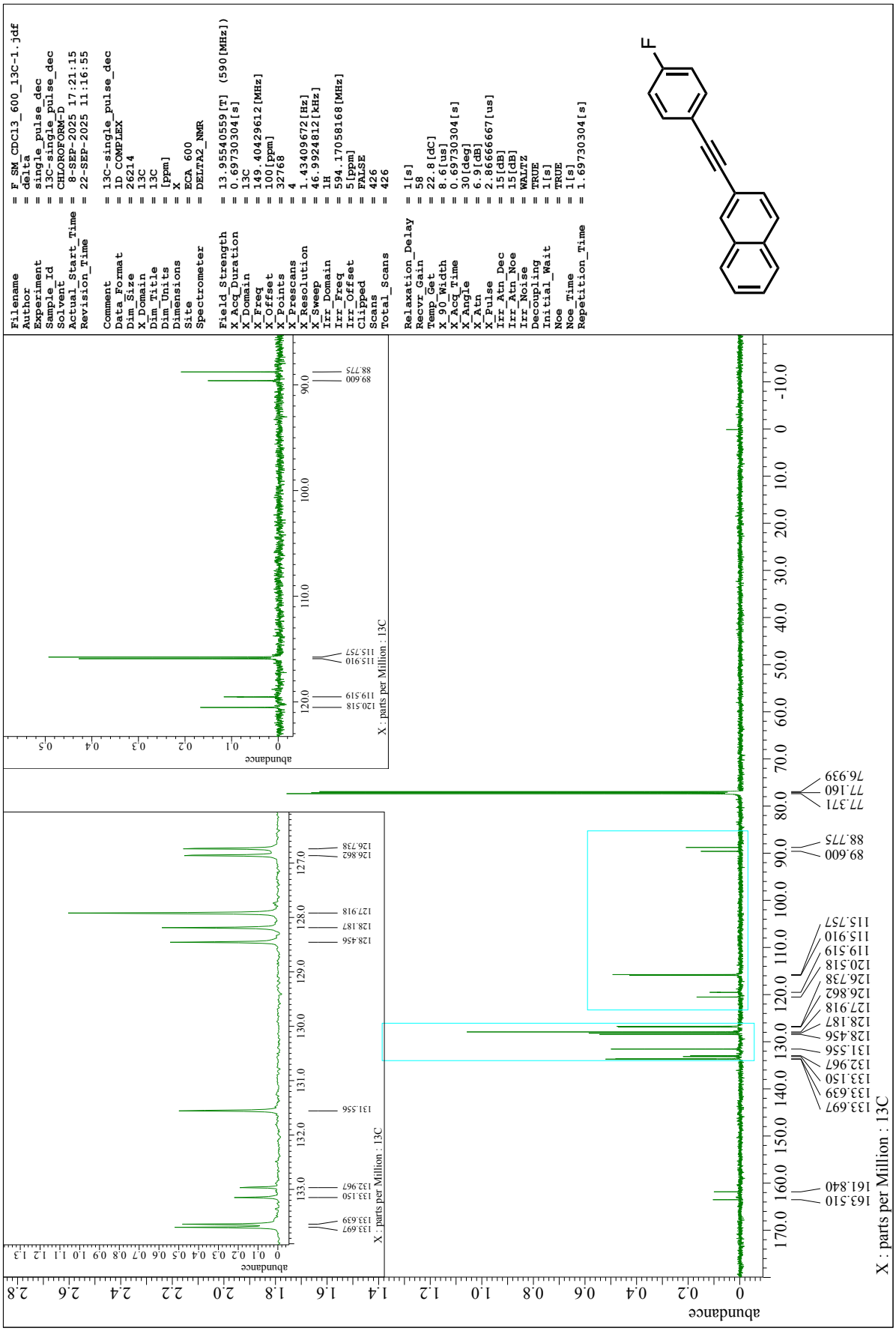


Figure S19. ^{13}C NMR spectrum of **1f** (150 MHz, $CDCl_3$)

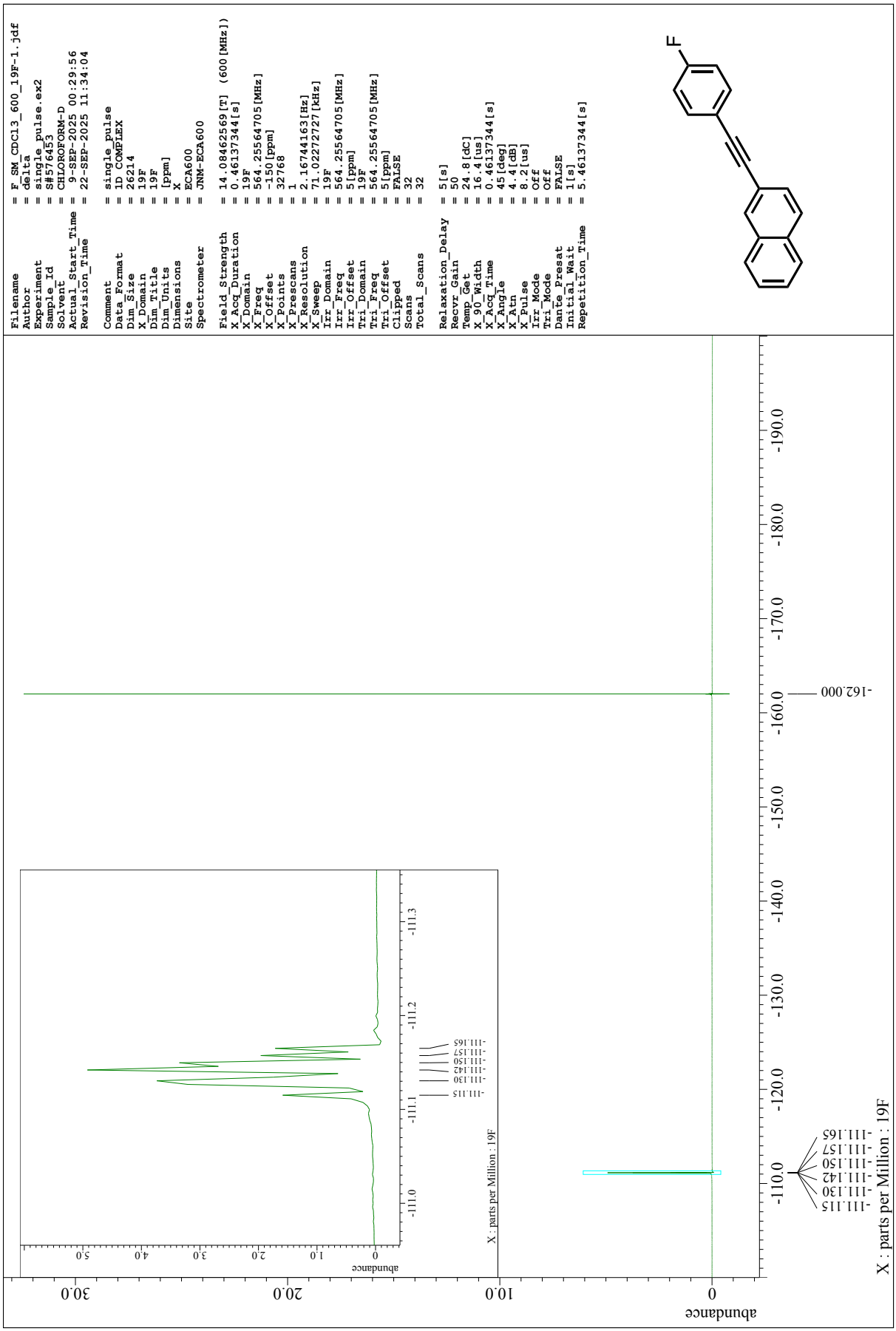


Figure S20. ^{19}F NMR spectrum of **1f** (564 MHz, $CDCl_3$)

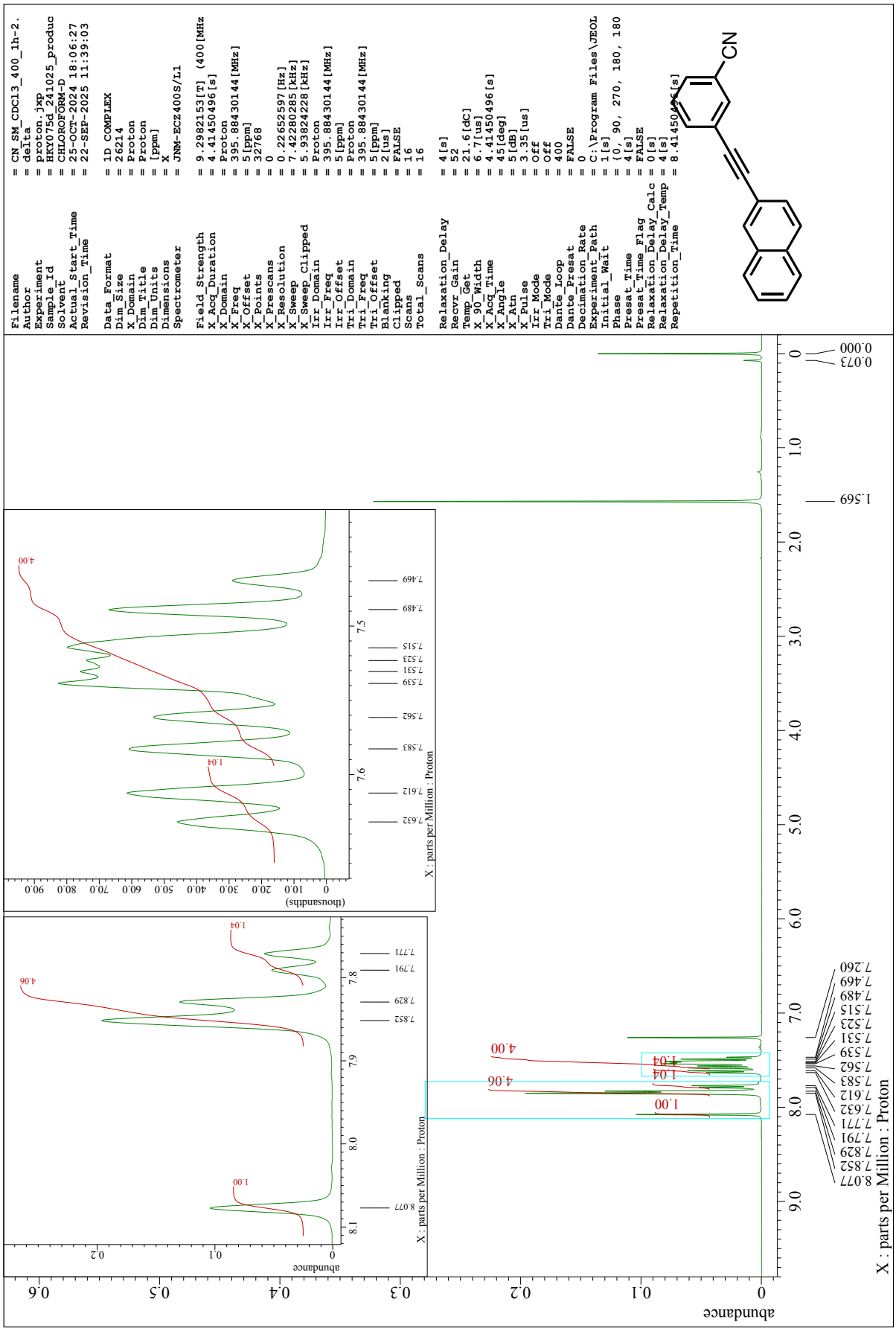


Figure S21. ^{1}H NMR spectrum of **1g** (400 MHz, $CDCl_3$).

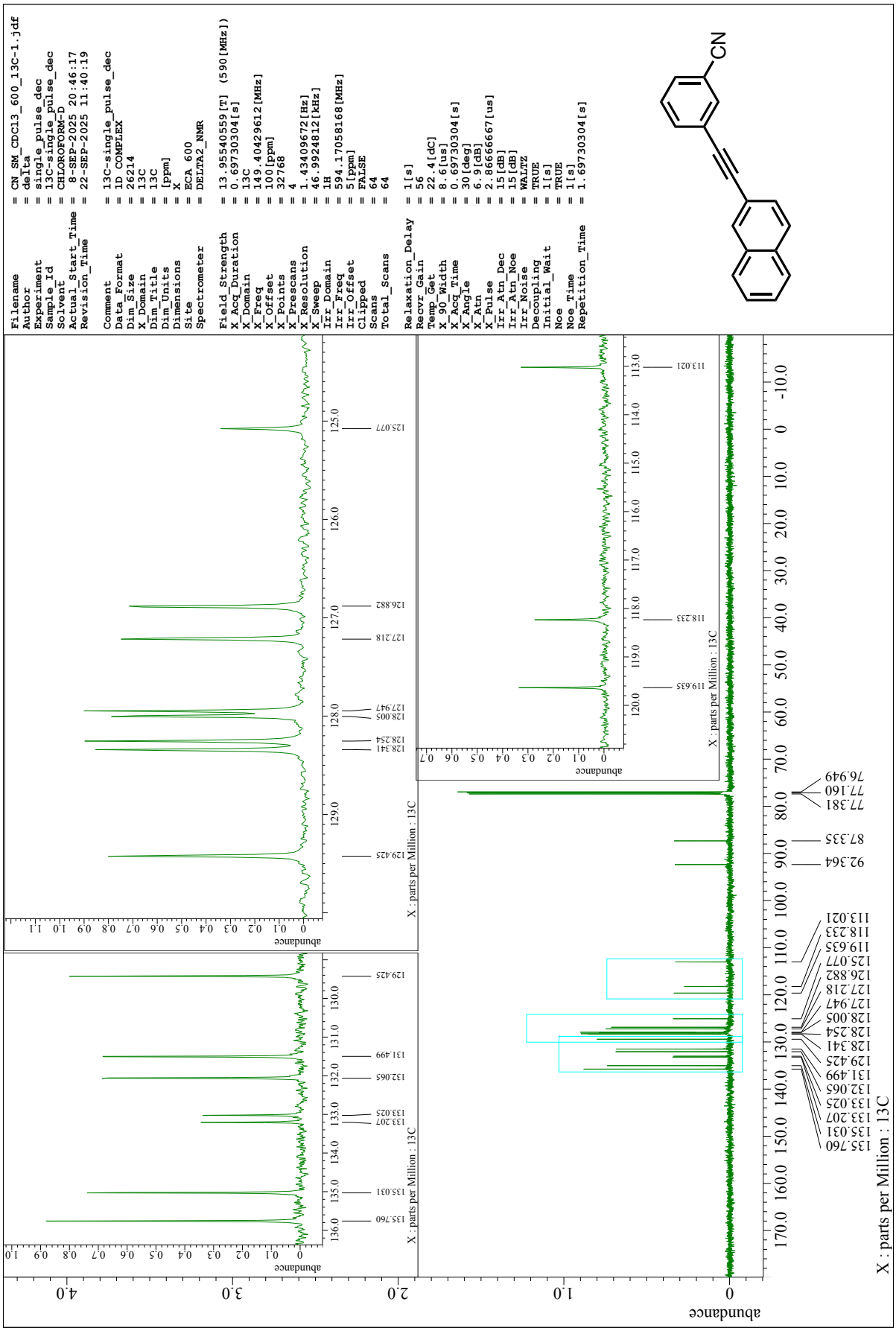


Figure S22. ^{13}C NMR spectrum of **1g** (150 MHz, $CDCl_3$)

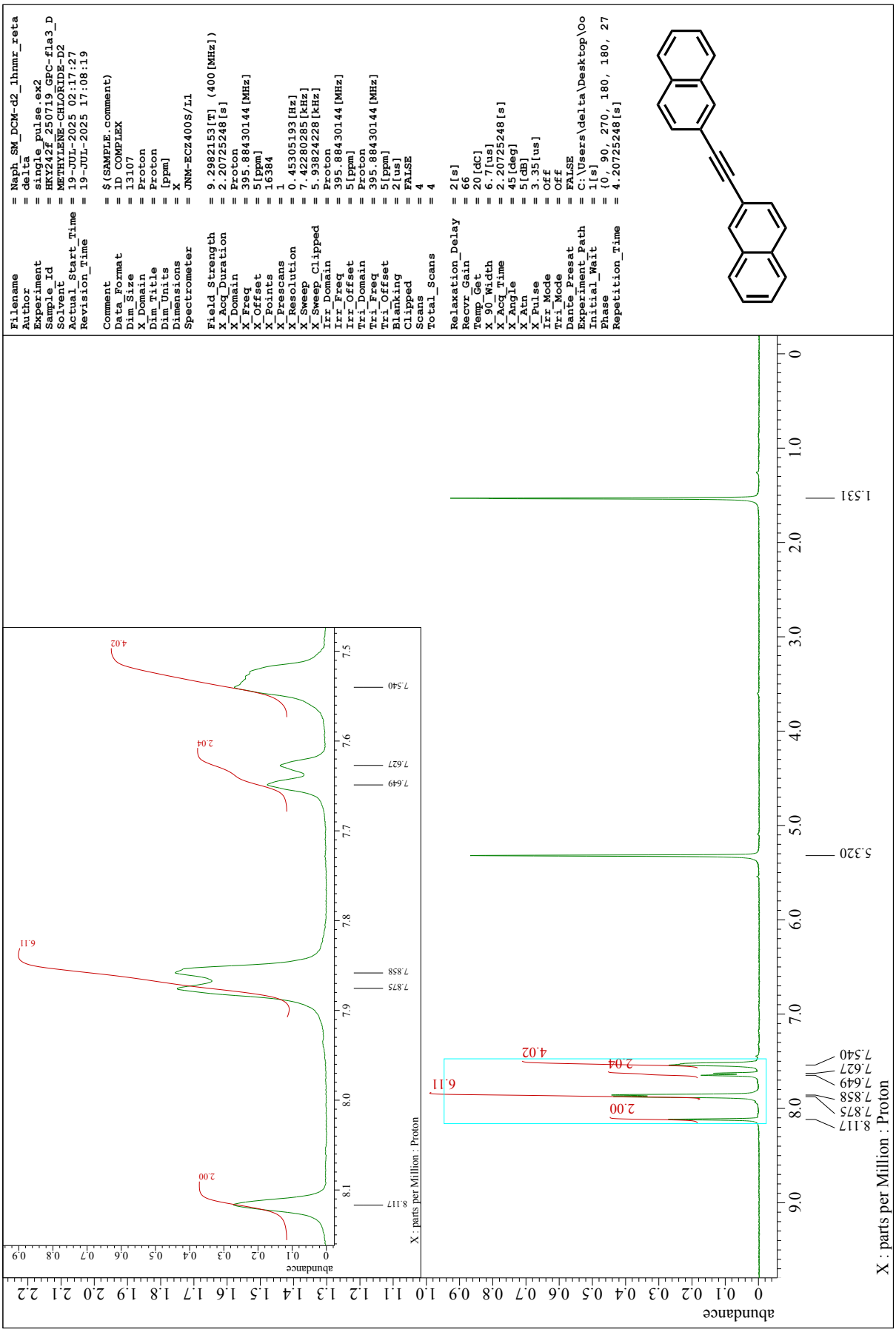


Figure S23. ^{1}H NMR spectrum of **1h** (400 MHz, CD_2Cl_2).

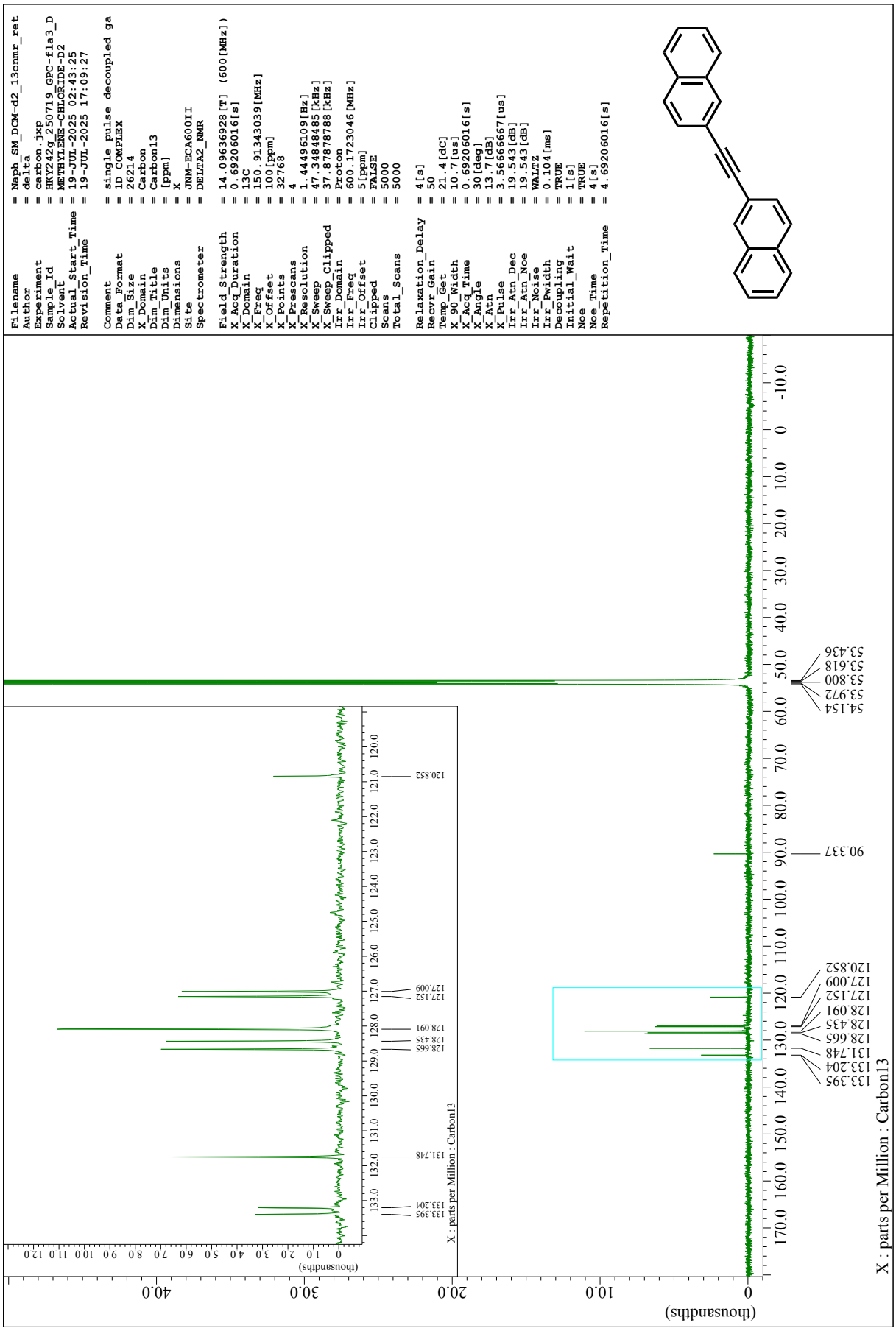


Figure S24. ^{13}C NMR spectrum of **1h** (150 MHz, CD_2Cl_2).

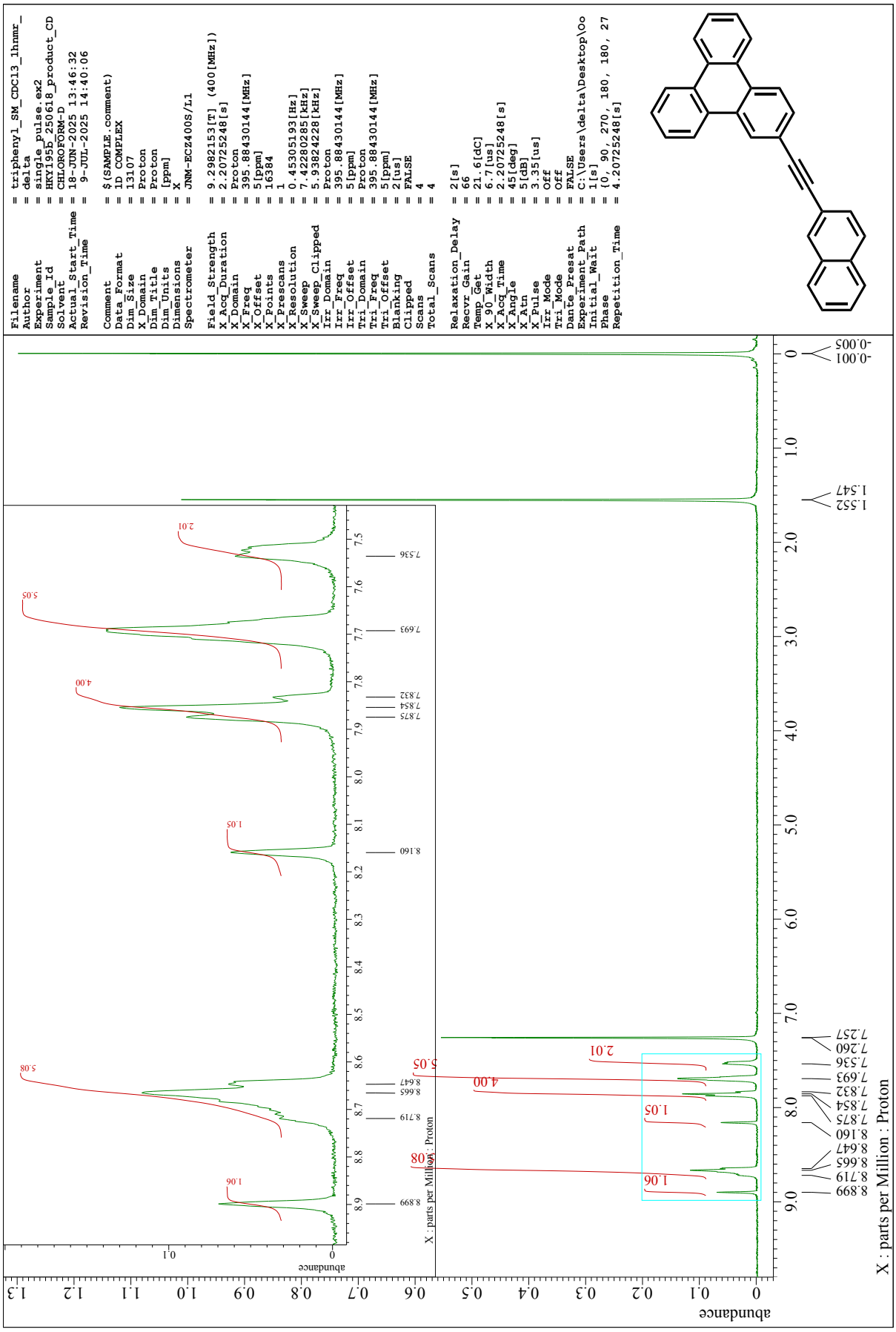


Figure S25. ^{1}H NMR spectrum of **1i** (400 MHz, $CDCl_3$).

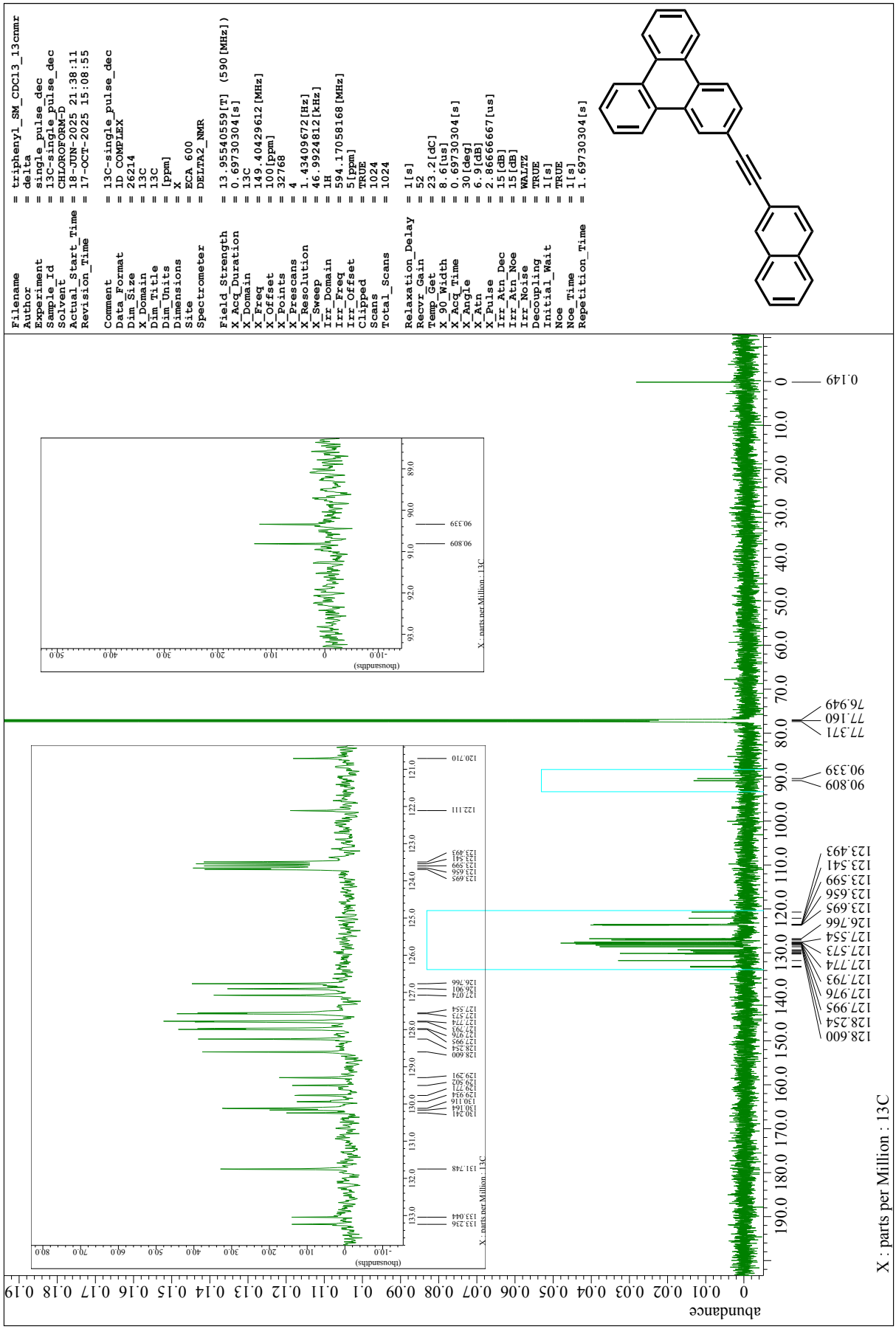


Figure S26. ^{13}C NMR spectrum of **1i** (150 MHz, $CDCl_3$).

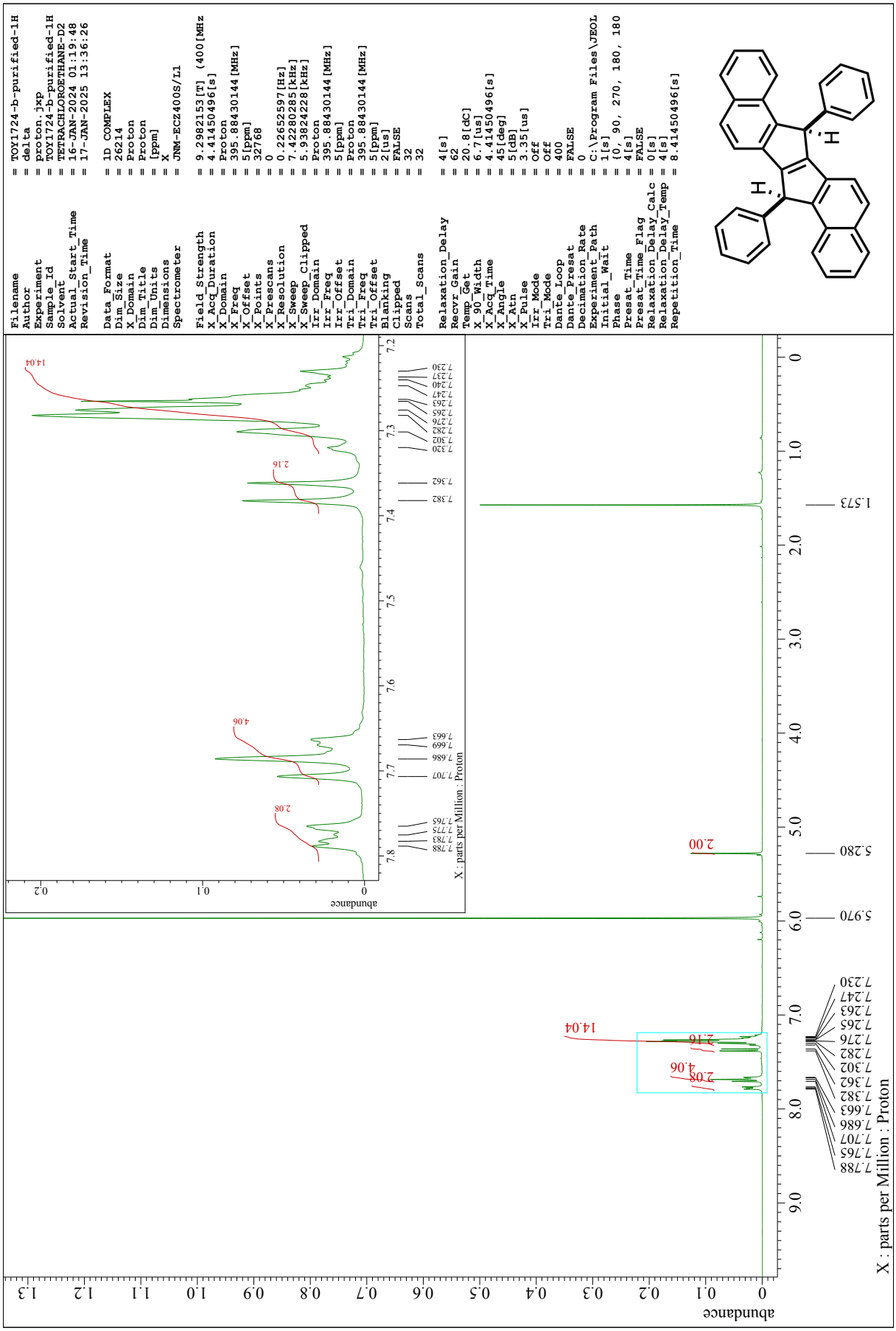


Figure S27. ^{1}H NMR spectrum of *syn*- **2a** (400 MHz, $Cl_2CDCDCl_2$).

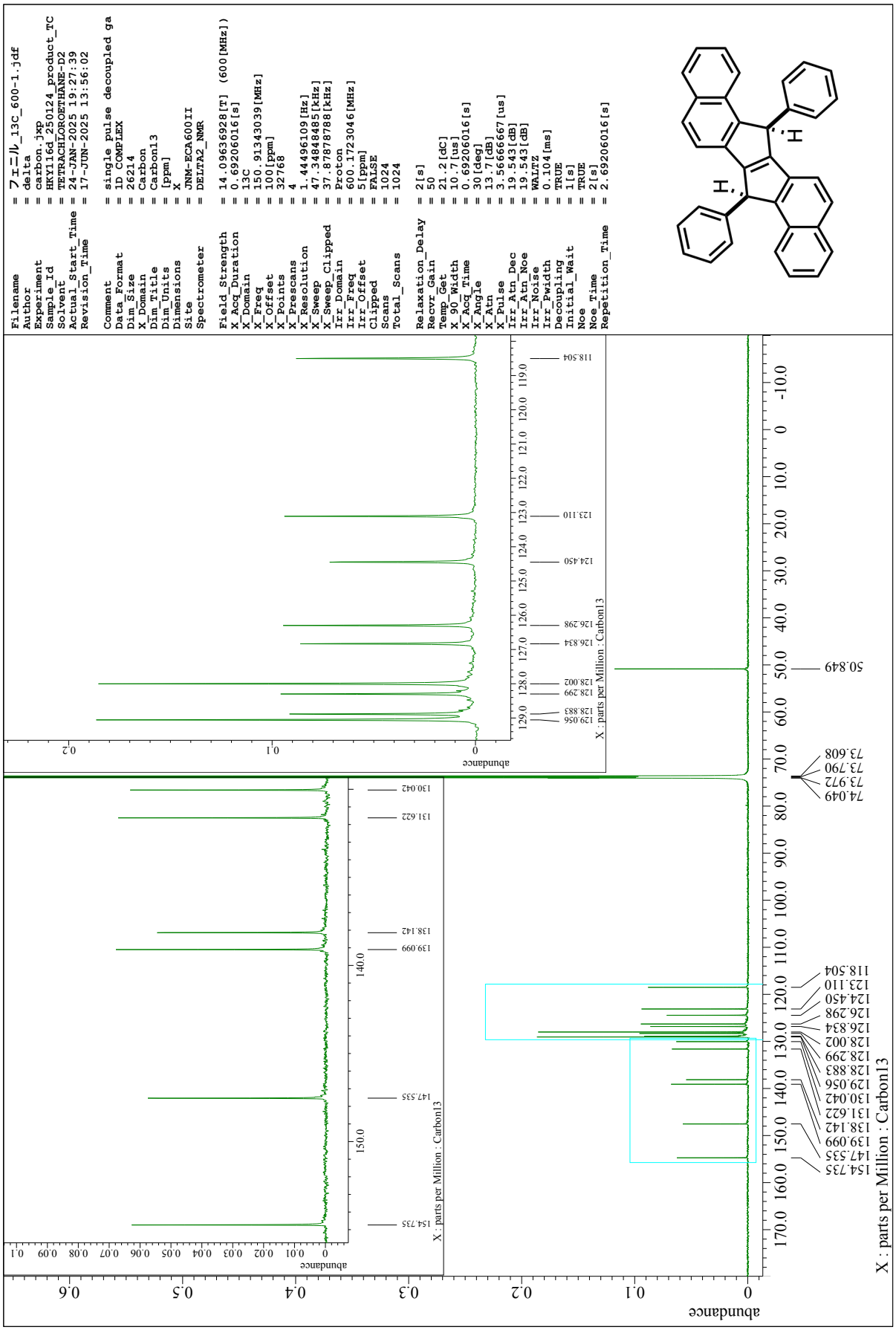


Figure S28. ^{13}C NMR spectrum of *syn*-**2a** (150 MHz, $Cl_2CDCDCl_2$).

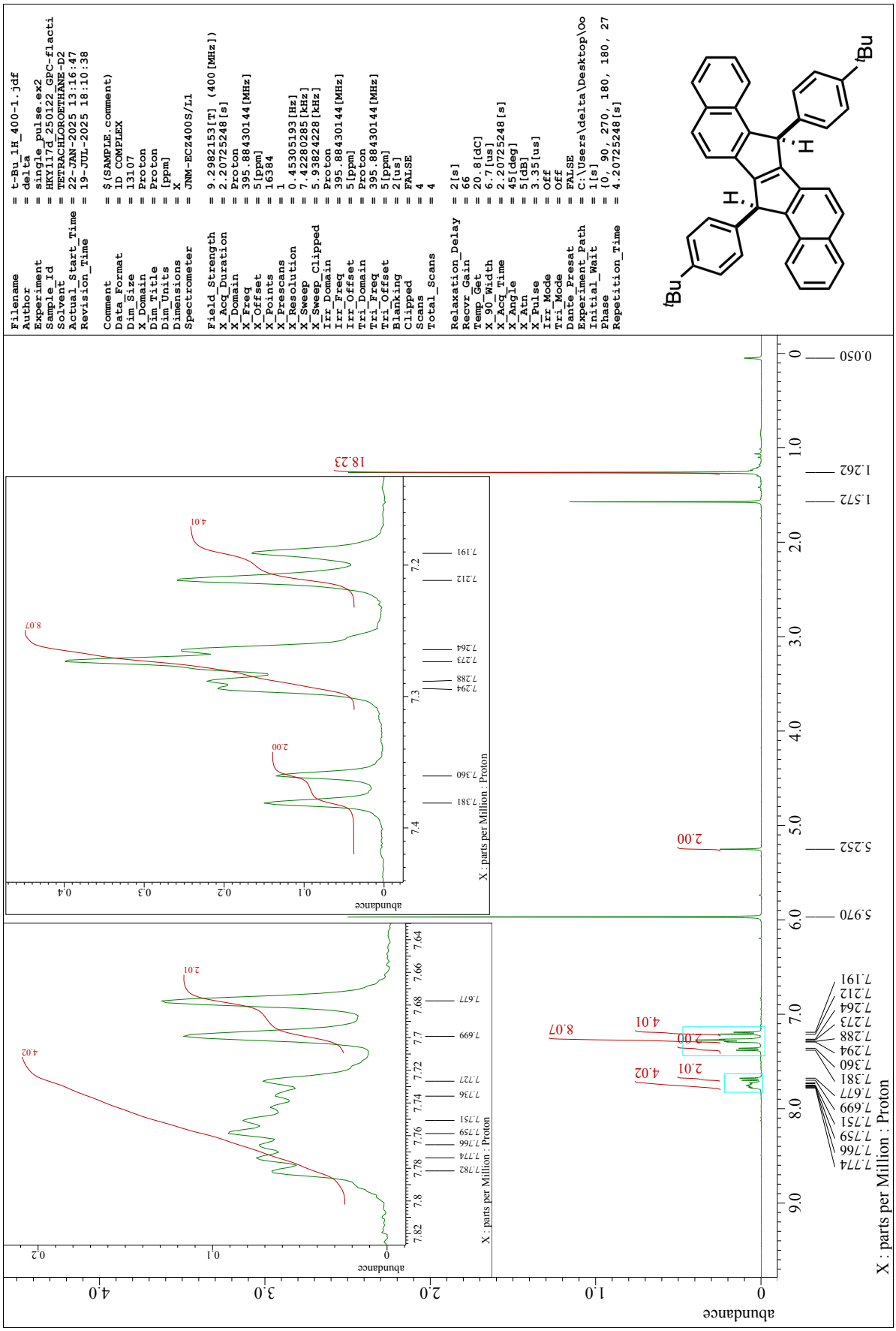


Figure S29. ^{1}H NMR spectrum of *syn*-**2d** (400 MHz, $Cl_2CDCDCl_2$).

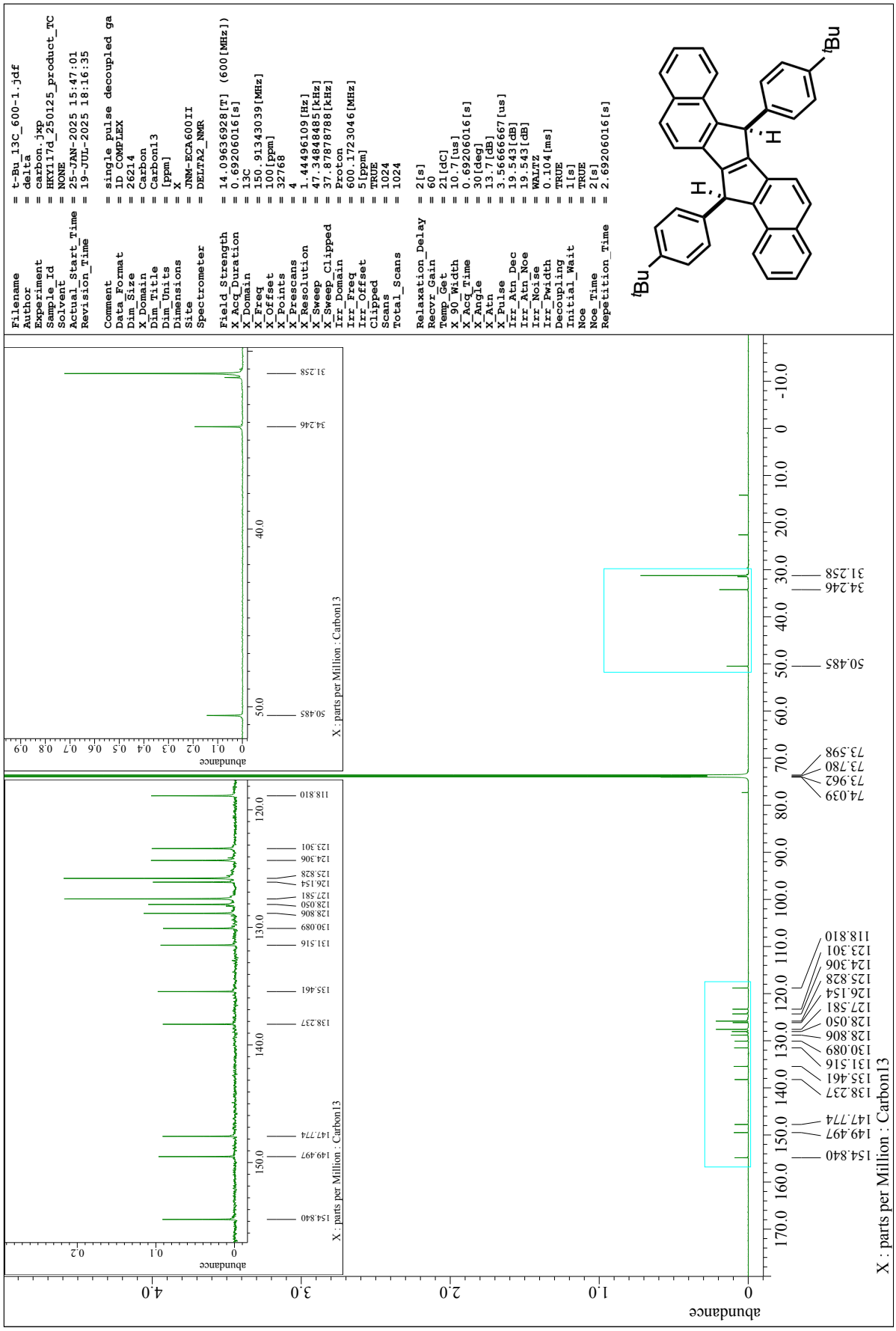


Figure S30. ^{13}C NMR spectrum of *syn*-**2d** (150 MHz, $Cl_2CDCDCl_2$).

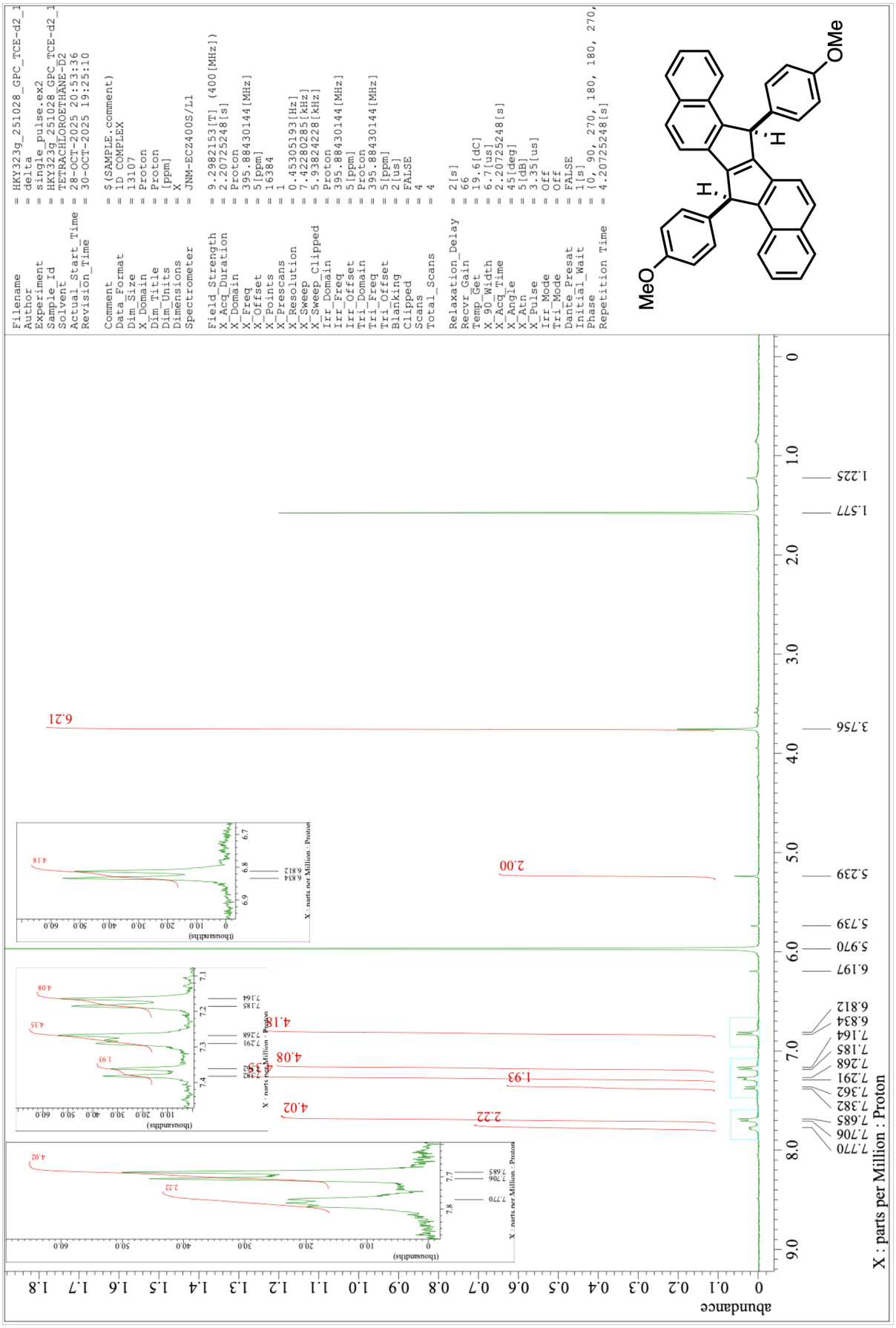


Figure S31. ^{1}H NMR spectrum of *syn*-**2e** (400 MHz, $Cl_2CDCDCl_2$).

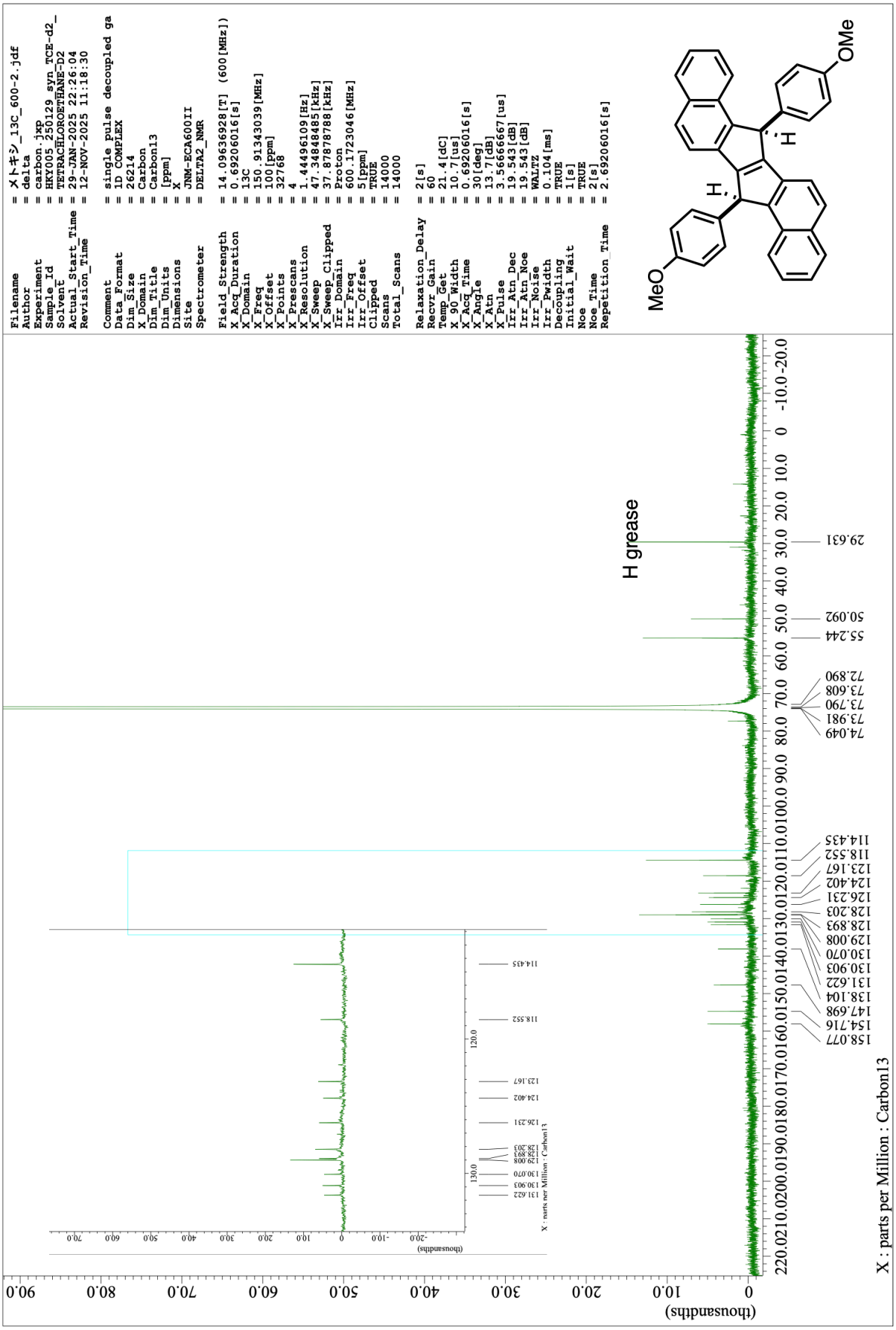


Figure S32. ^{13}C NMR spectrum of *syn*-**2e** (150 MHz, $Cl_2CDCDCl_2$).

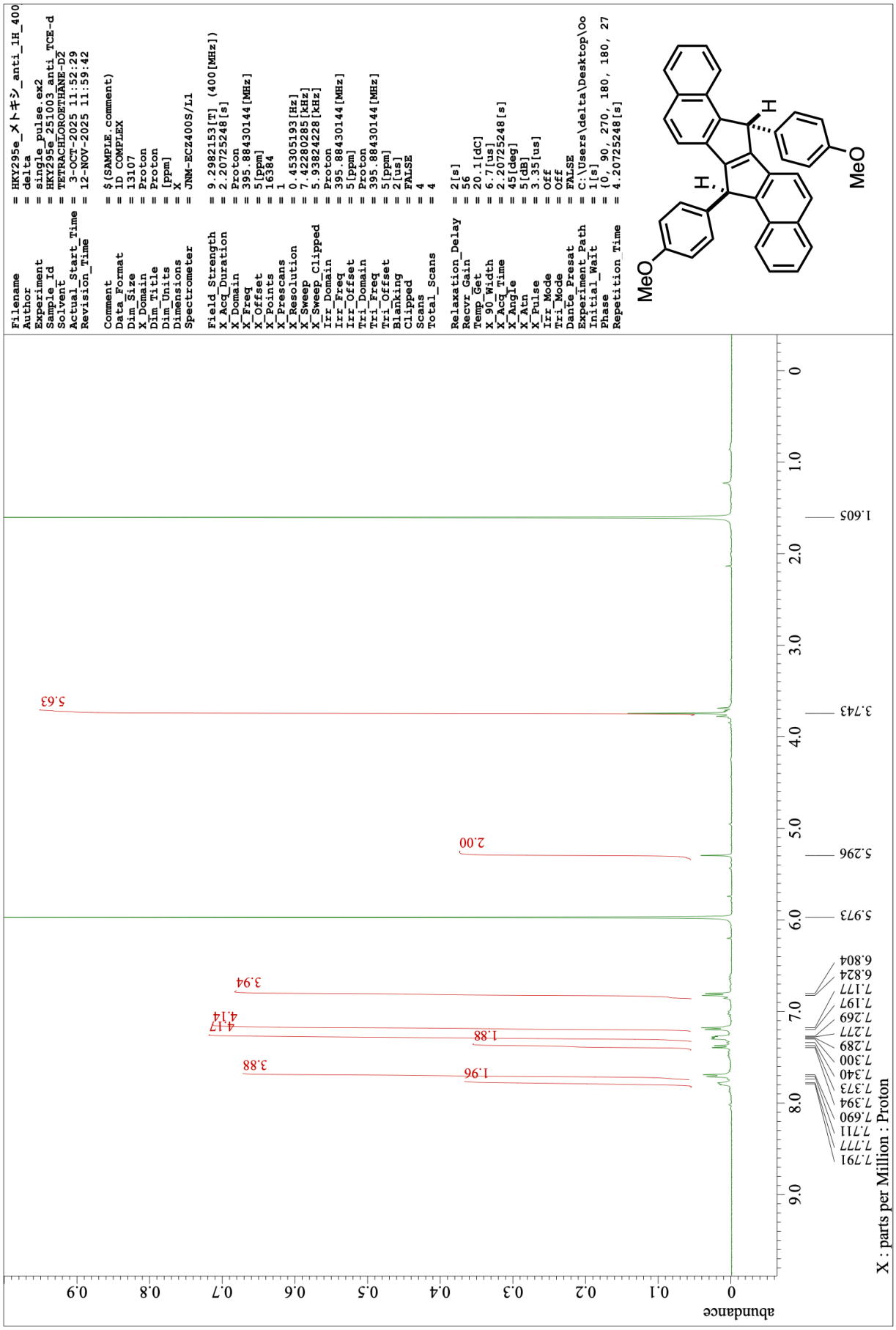


Figure S33. ^{1}H NMR spectrum of *anti*-**2e** (400 MHz, $Cl_2CDCDCl_2$).

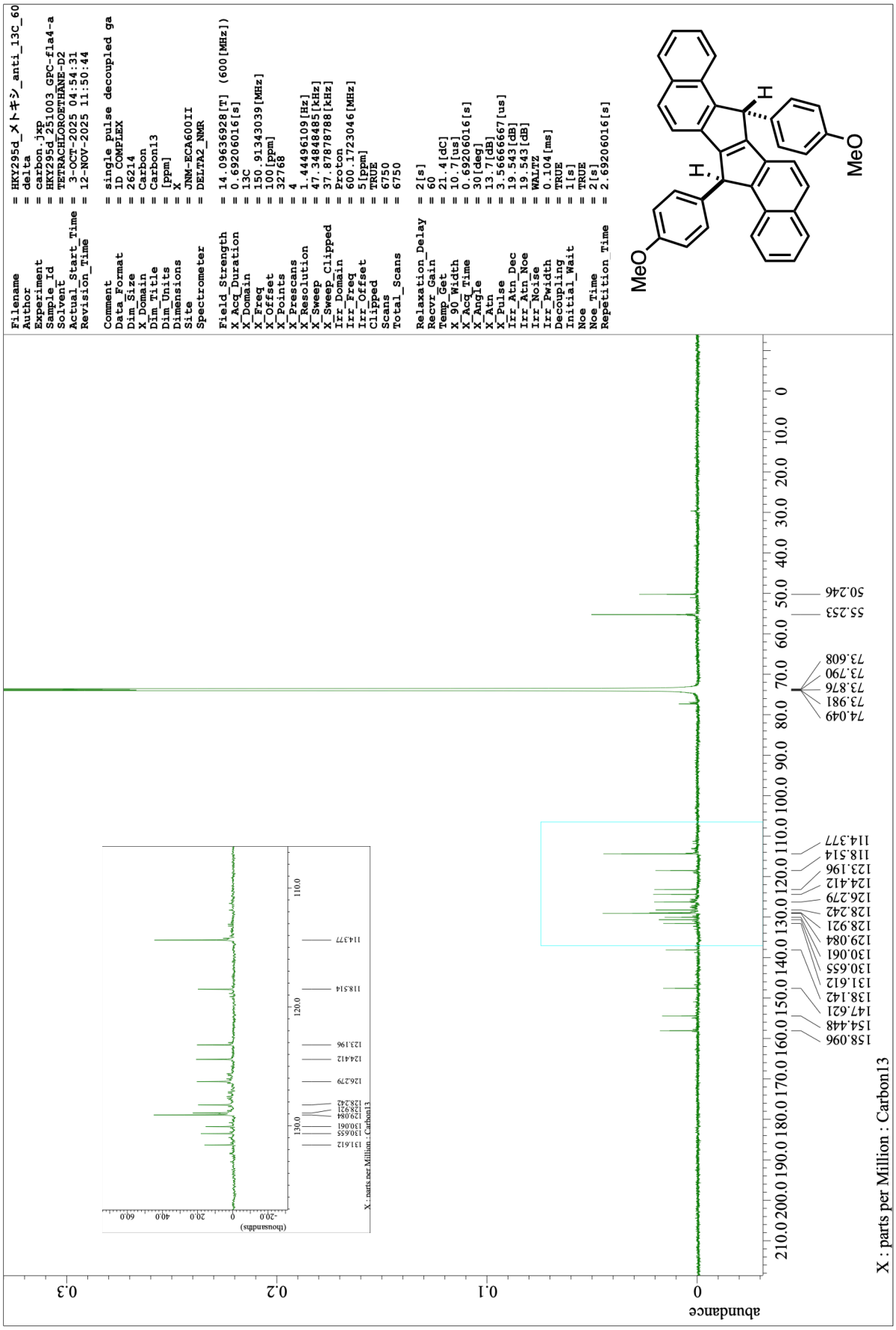


Figure S34. ^{13}C NMR spectrum of *anti*-**2e** (150 MHz, $Cl_2CDCDCl_2$).

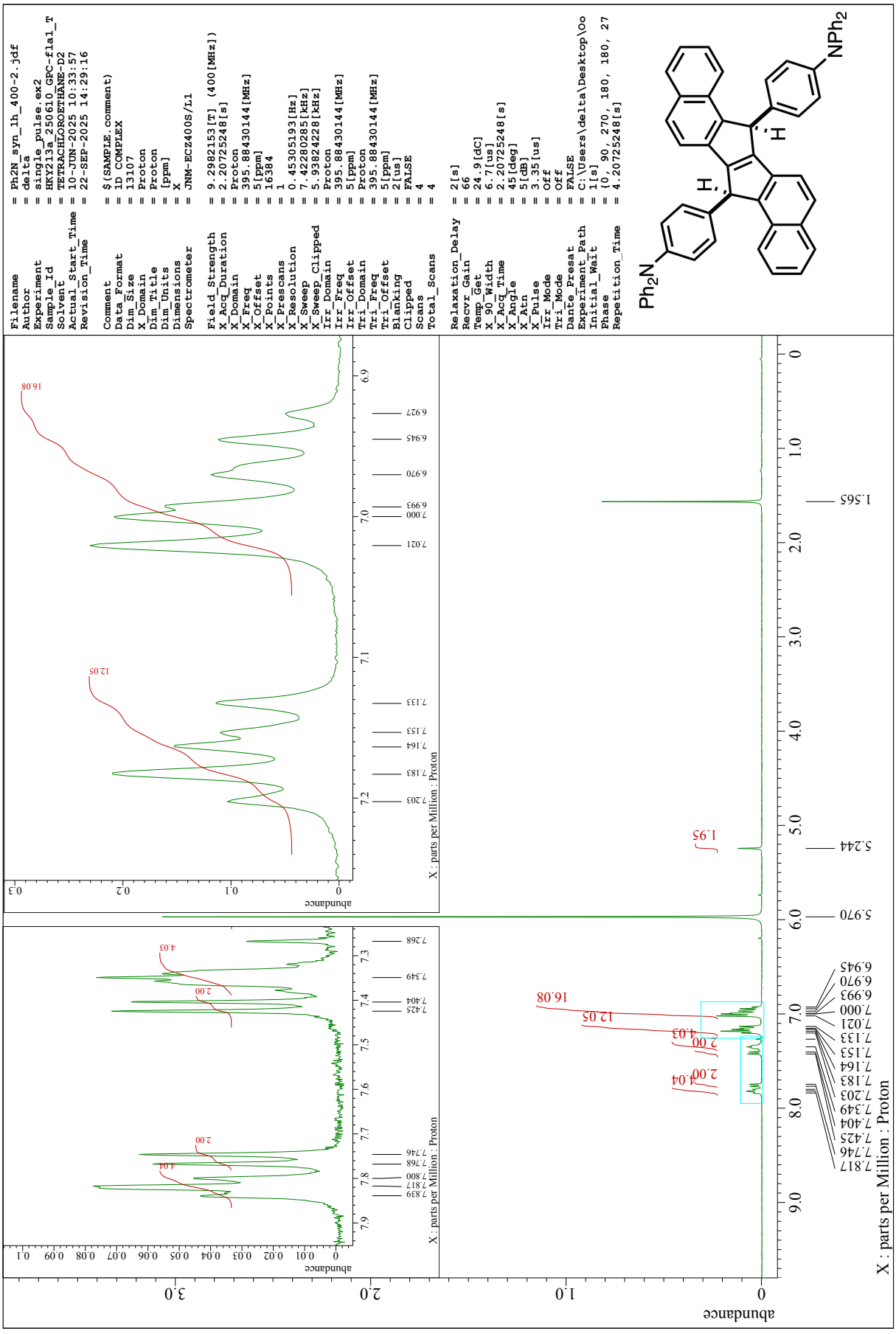


Figure S35. ^{1}H NMR spectrum of *syn*-**2f** (400 MHz, $Cl_2CDCDCl_2$).

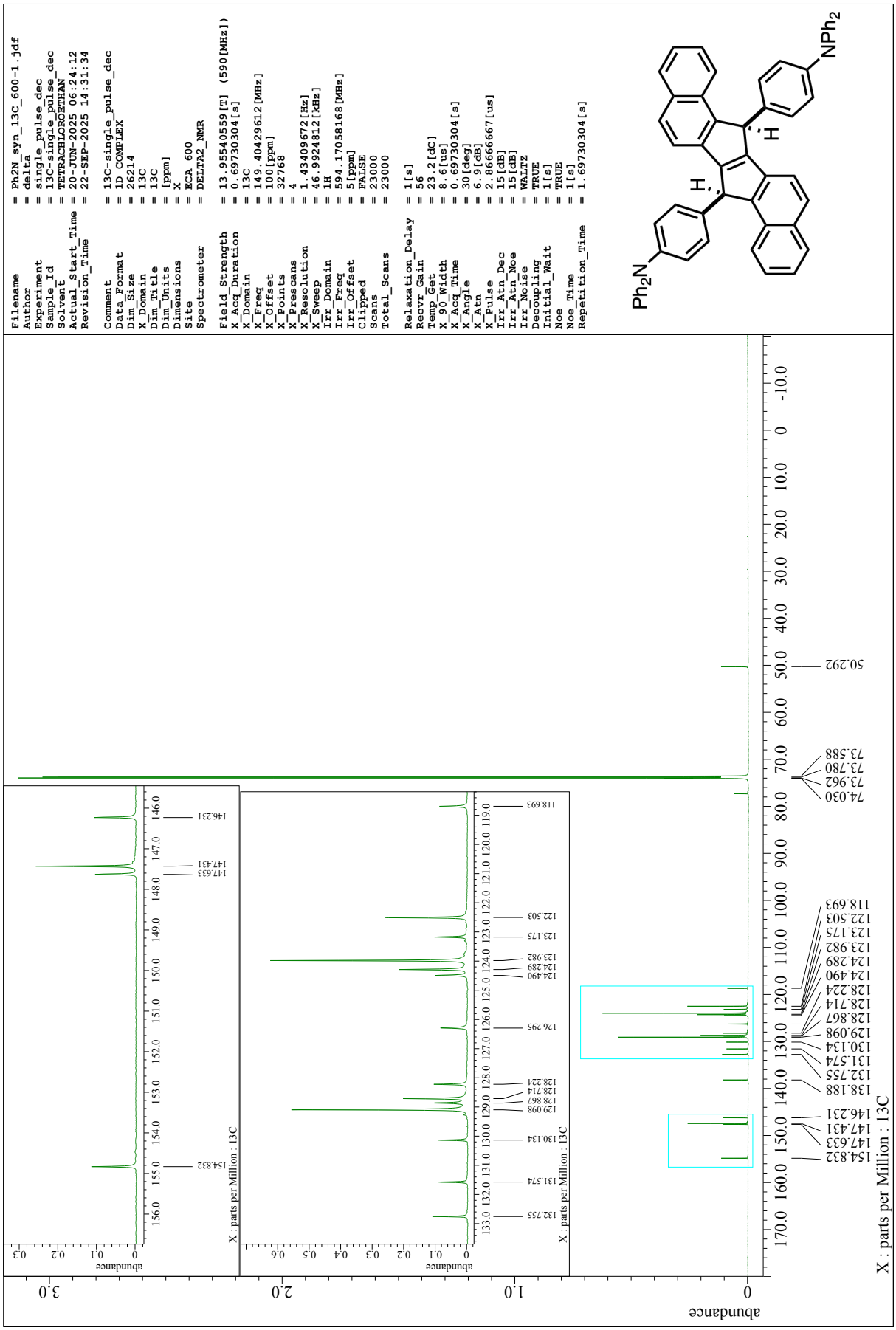


Figure S36. ^{13}C NMR spectrum of *syn*-**2f** (150 MHz, $Cl_2CDCDCl_2$).

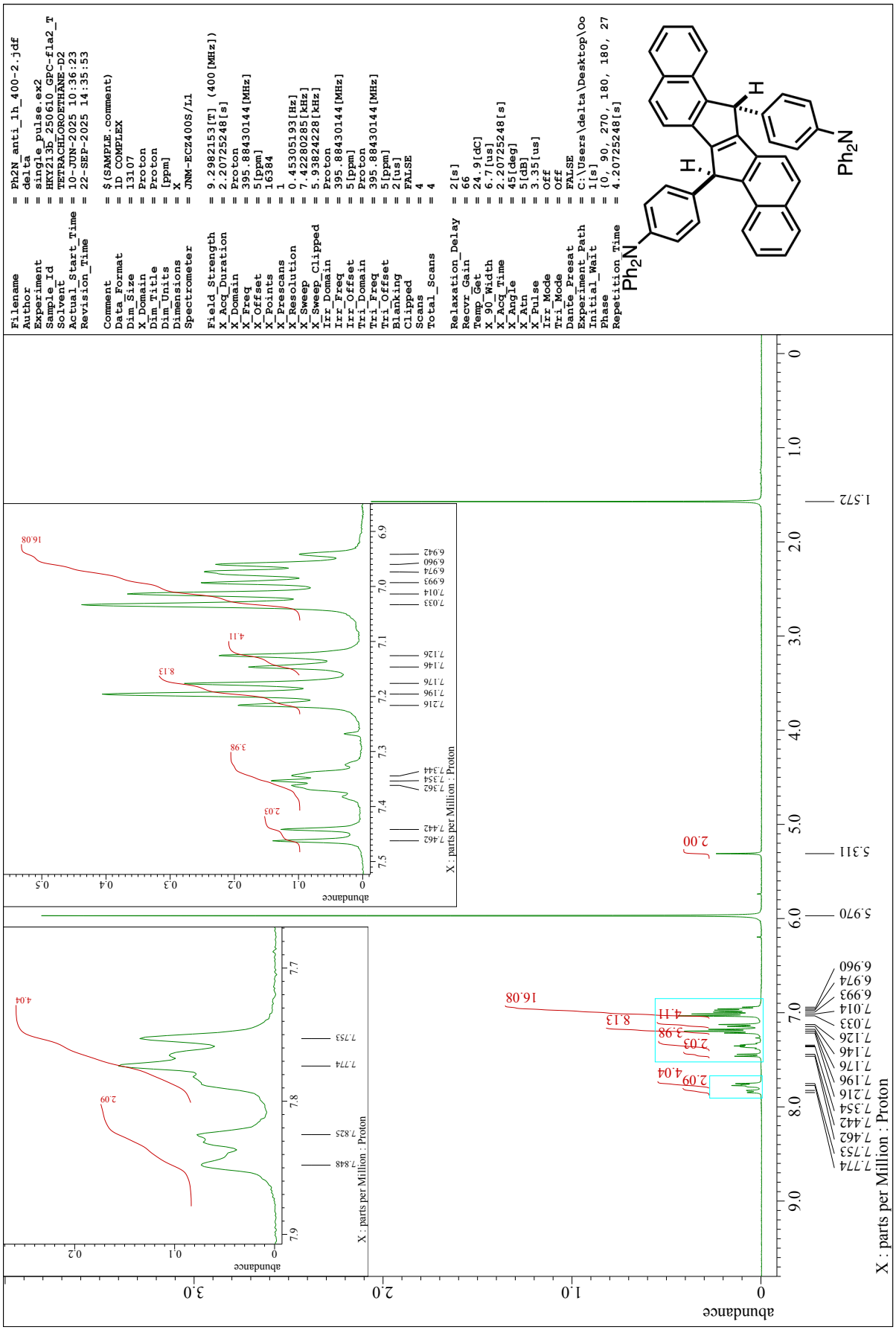


Figure S37. ^{1}H NMR spectrum of *anti*-**2f** (400 MHz, $Cl_2CDCDCl_2$).

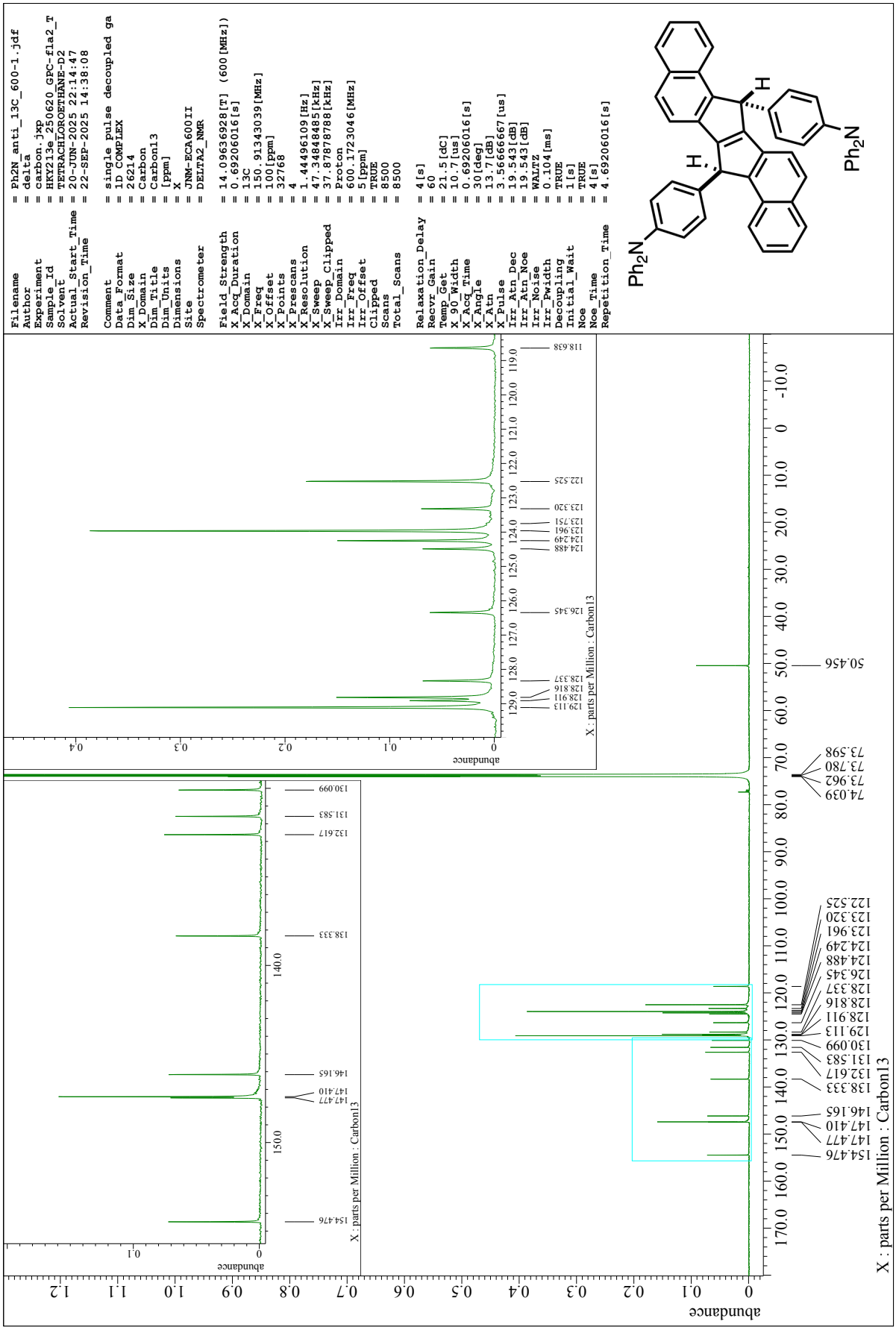


Figure S38. ^{13}C NMR spectrum of *anti*-**2f** (150 MHz, $Cl_2CDCDCl_2$).

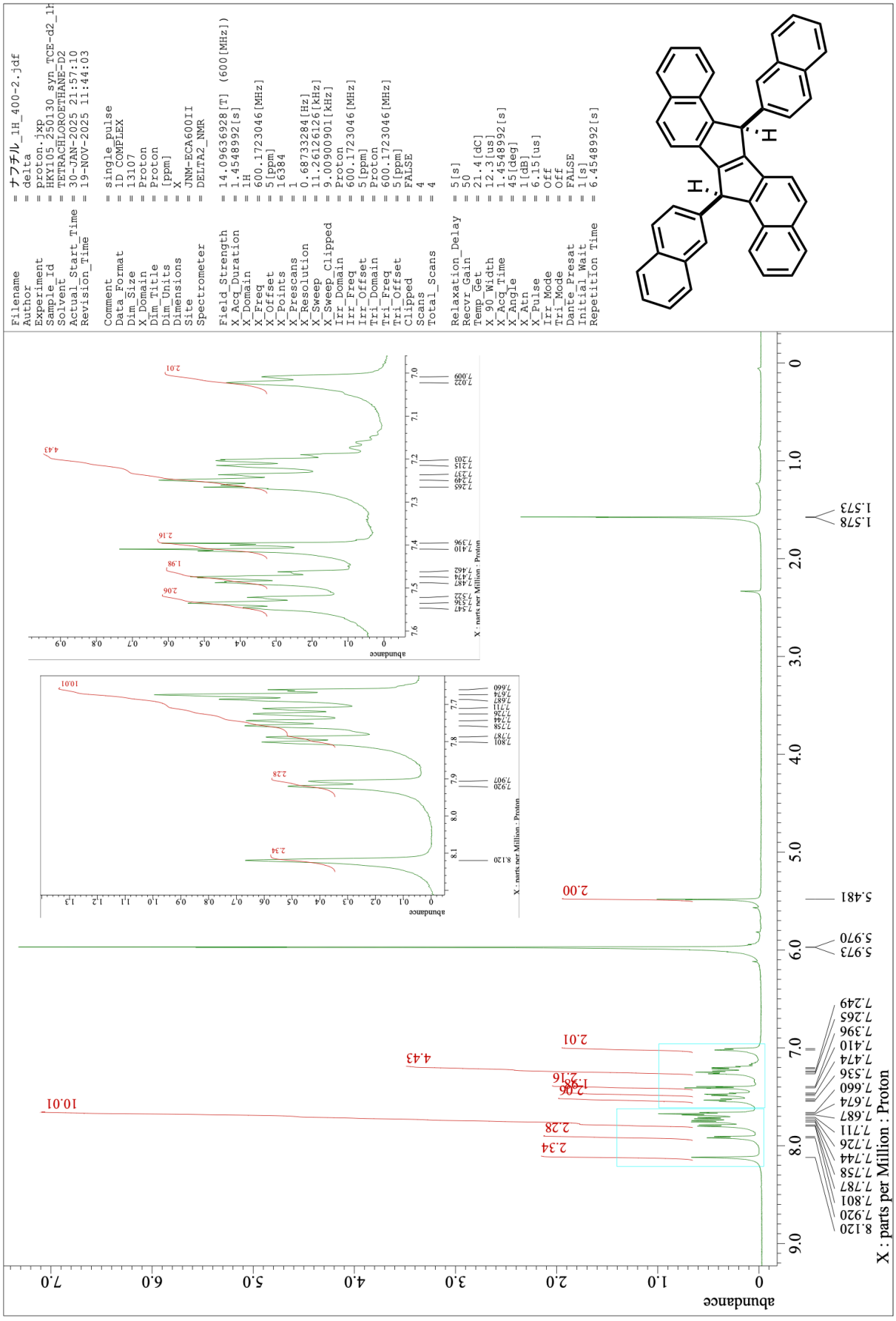


Figure S39. ^{1}H NMR spectrum of *syn*-**2i** (400 MHz, $Cl_2CDCDCl_2$).

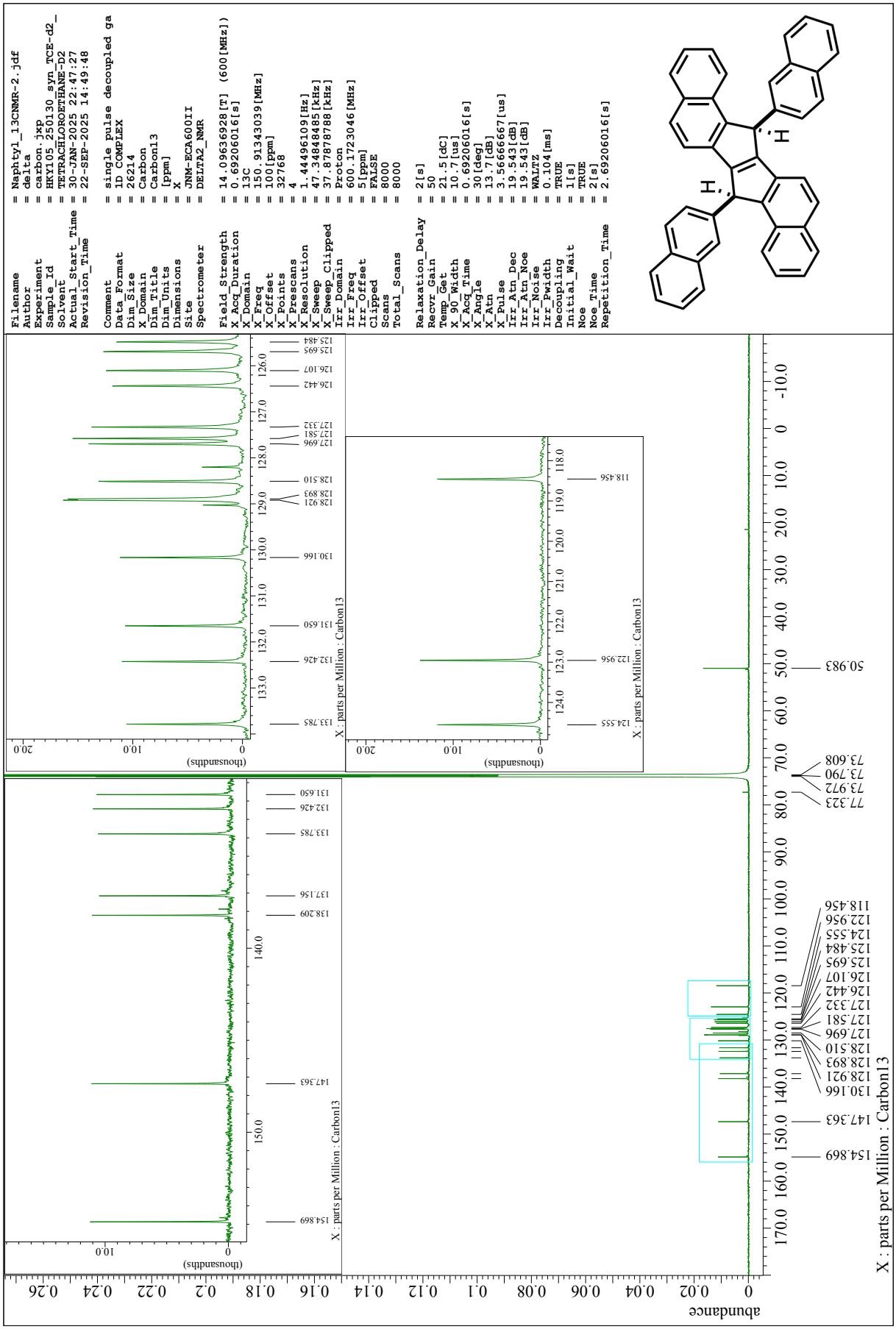


Figure S40. ^{13}C NMR spectrum of *syn*-**2i** (150 MHz, $Cl_2CDCDCl_2$).

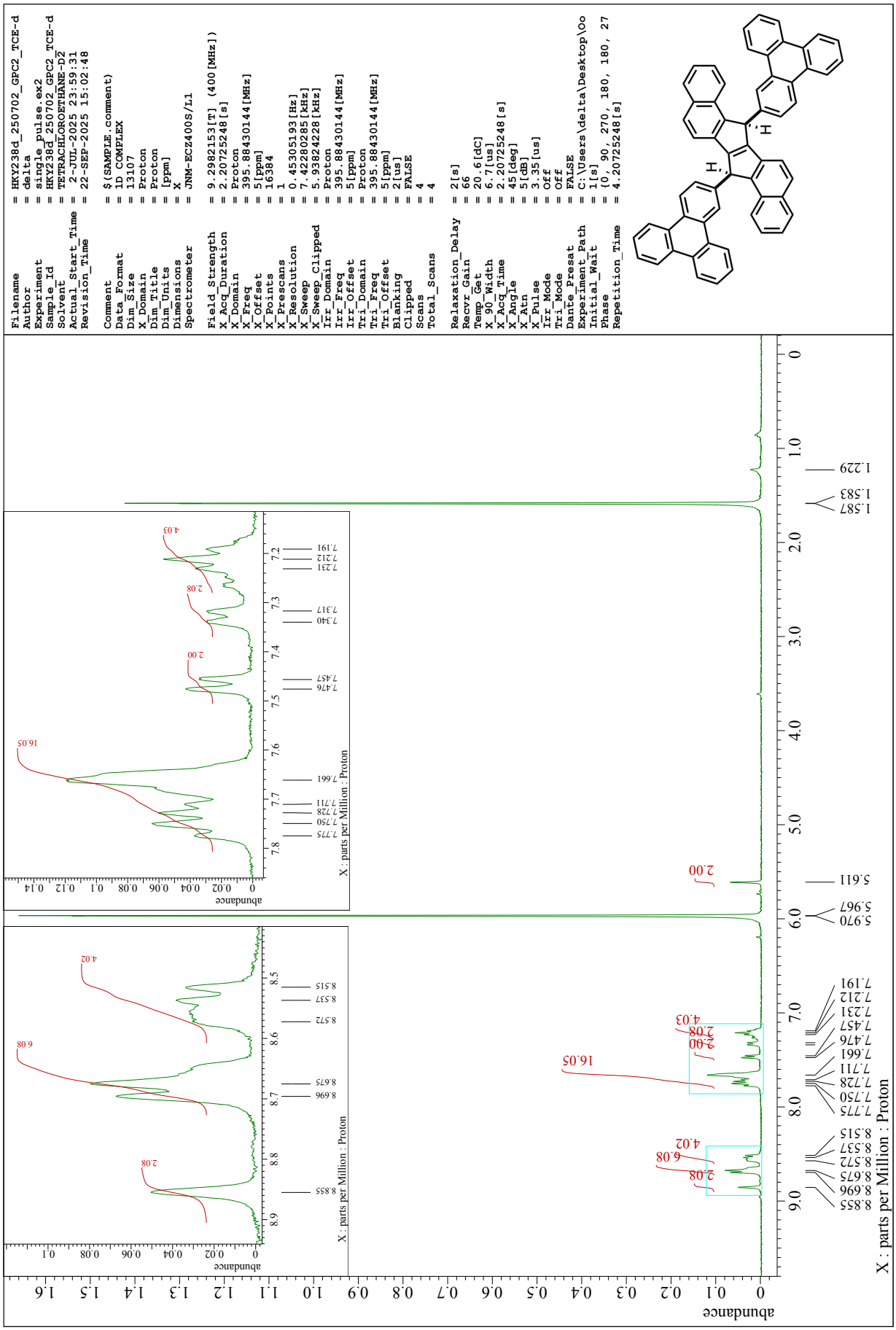


Figure S41. ^{1}H NMR spectrum of *syn*-**2j** (400 MHz, $Cl_2CDCDCl_2$).

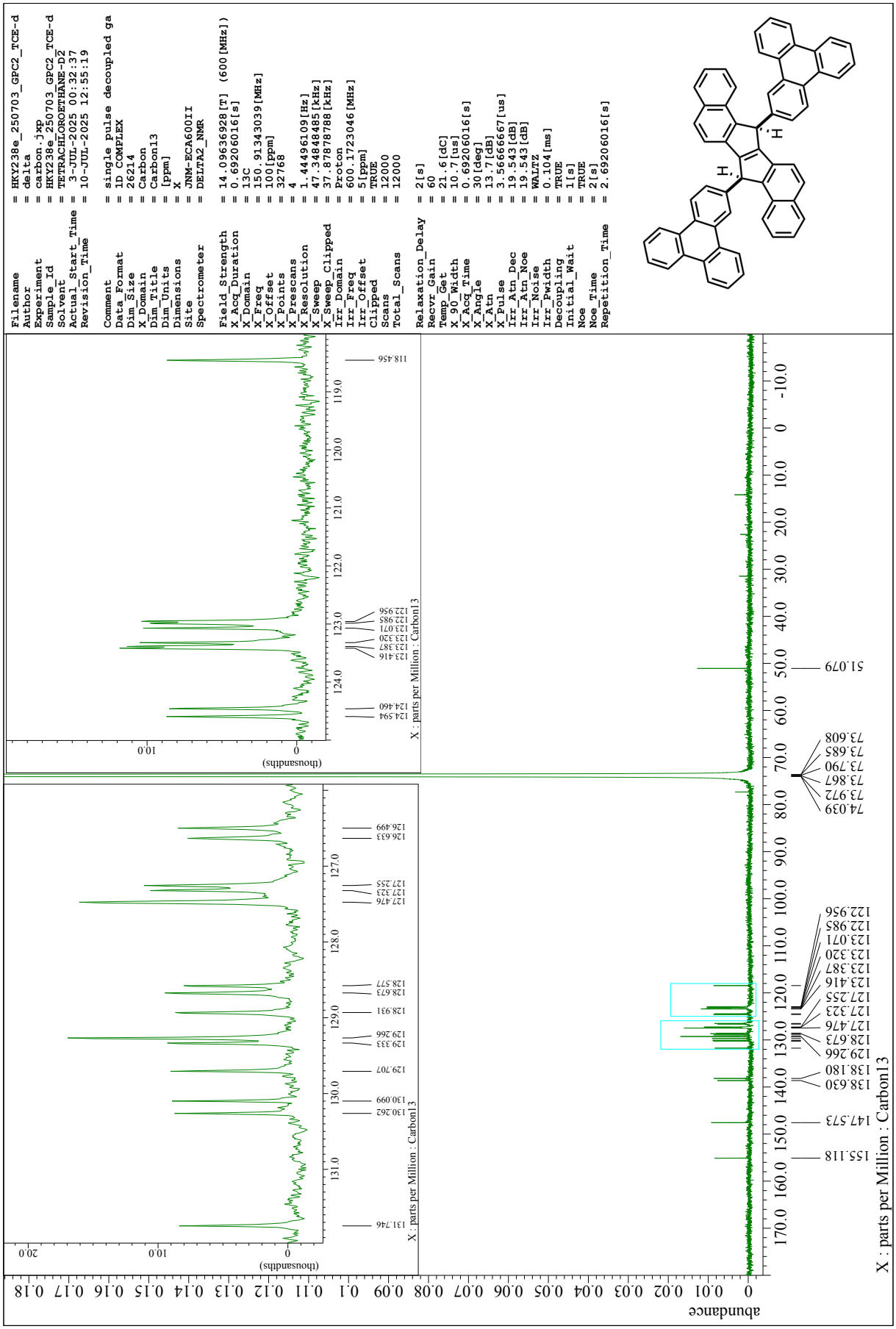


Figure S42. ^{13}C NMR spectrum of *syn*-**2j** (150 MHz, $Cl_2CDCDCl_2$).

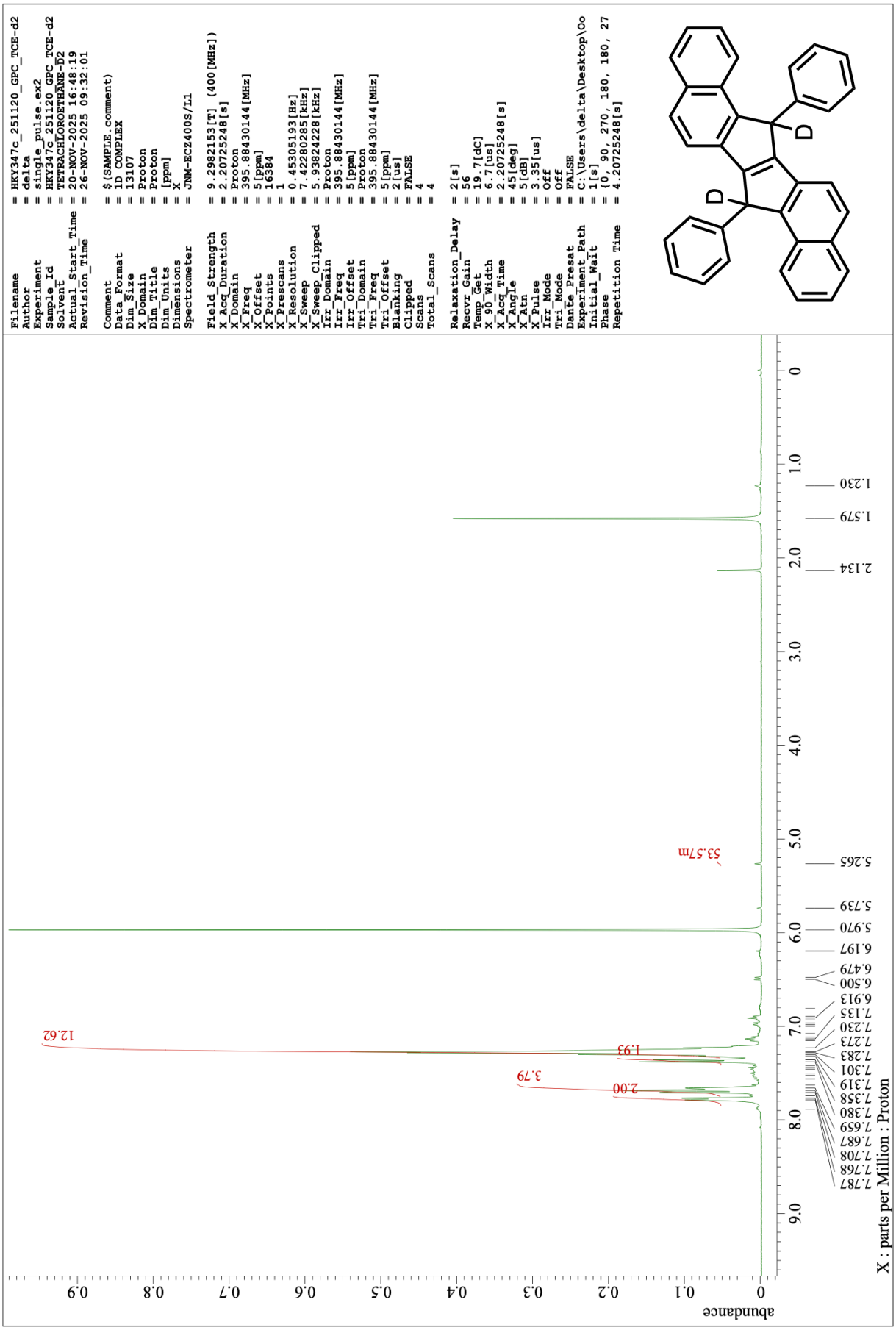


Figure S43. ^{1}H NMR spectrum of **2a-D** (400 MHz, $Cl_2CDCDCl_2$).

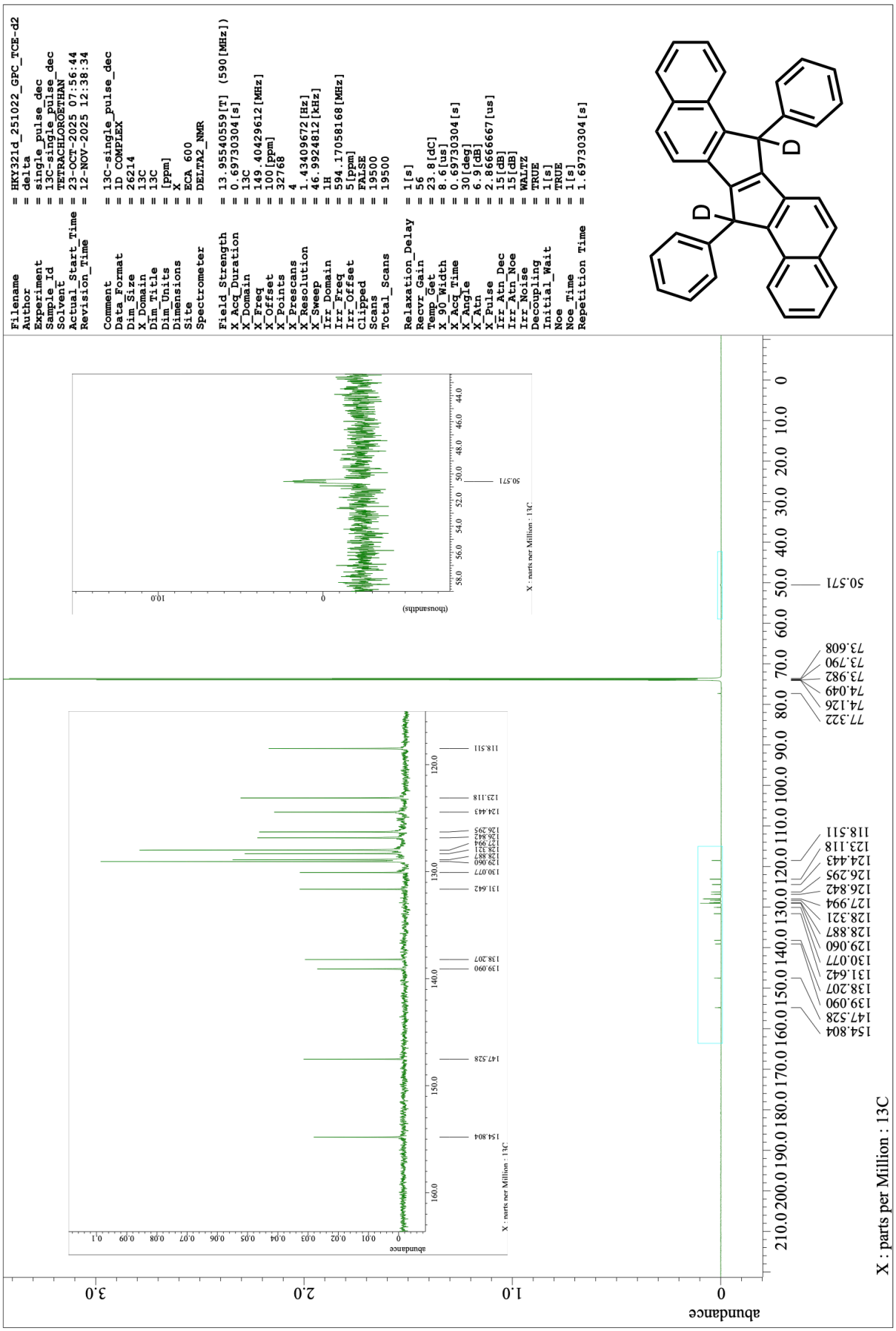


Figure S44. ^{13}C NMR spectrum of **2a-D** (150 MHz, $Cl_2CDCDCl_2$).

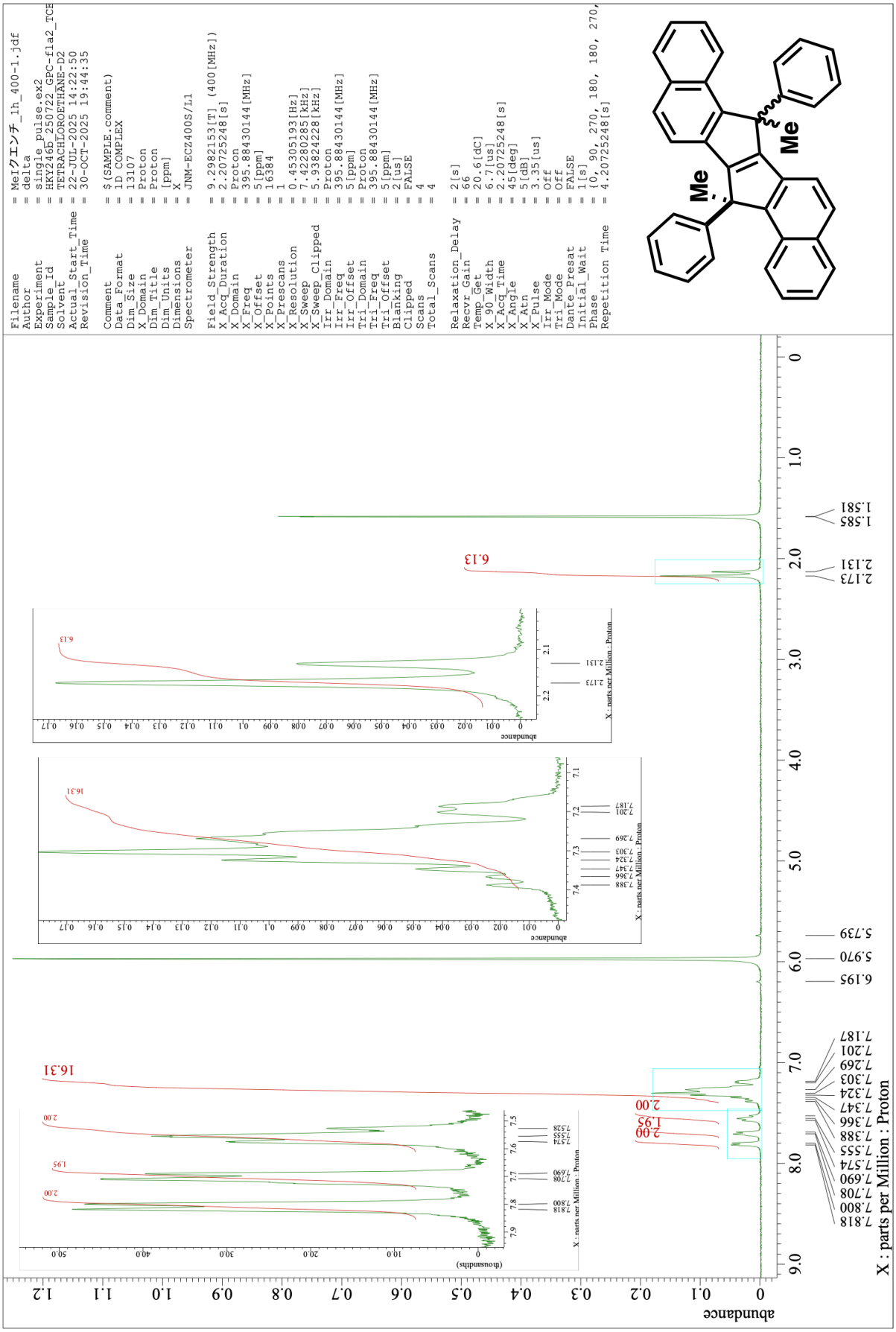


Figure S45. ^{1}H NMR spectrum of **2a-Me** (400 MHz, $Cl_2CDCDCl_2$).

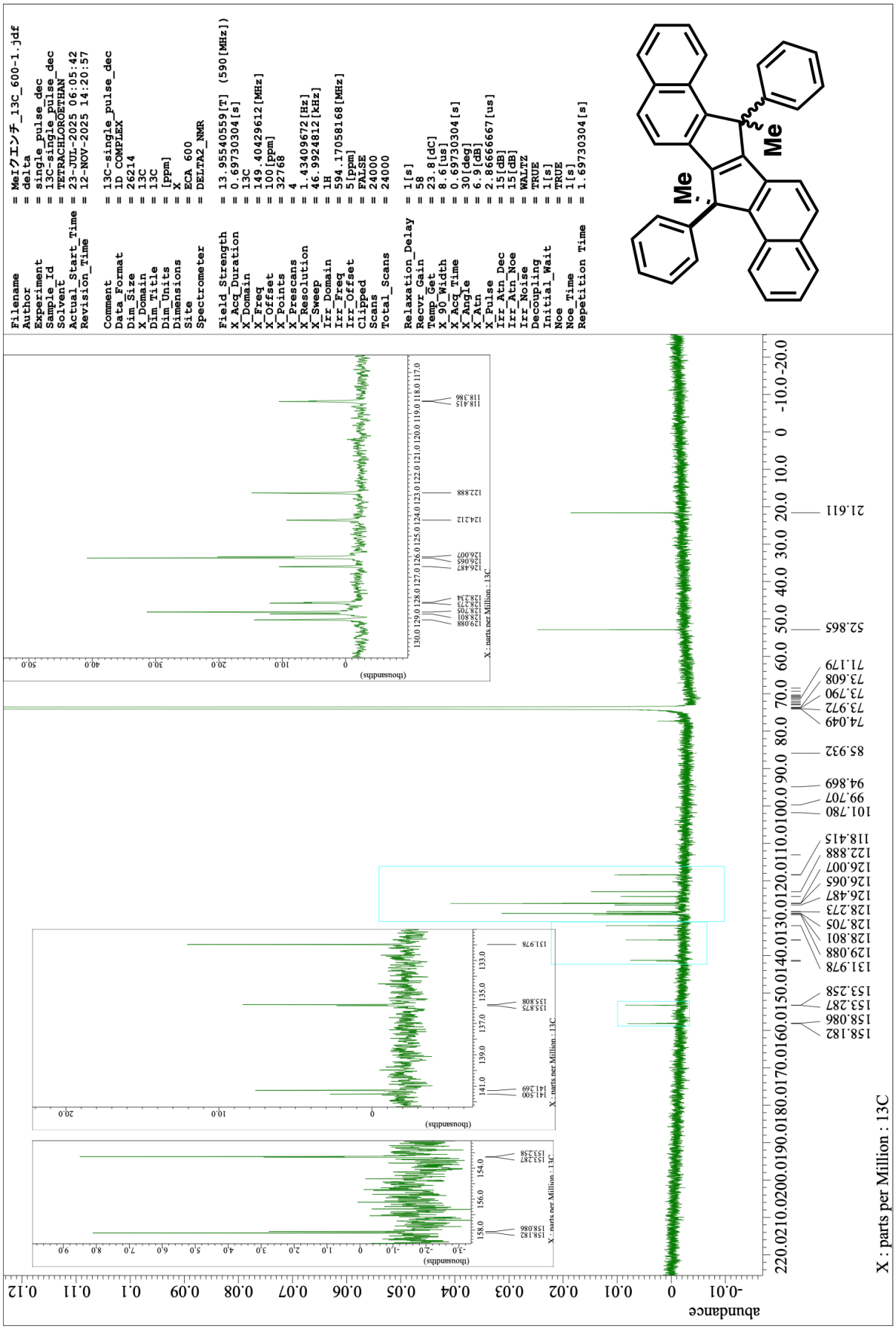


Figure S46. ^{13}C NMR spectrum of **2a-Me** (150 MHz, $Cl_2CDCDCl_2$).

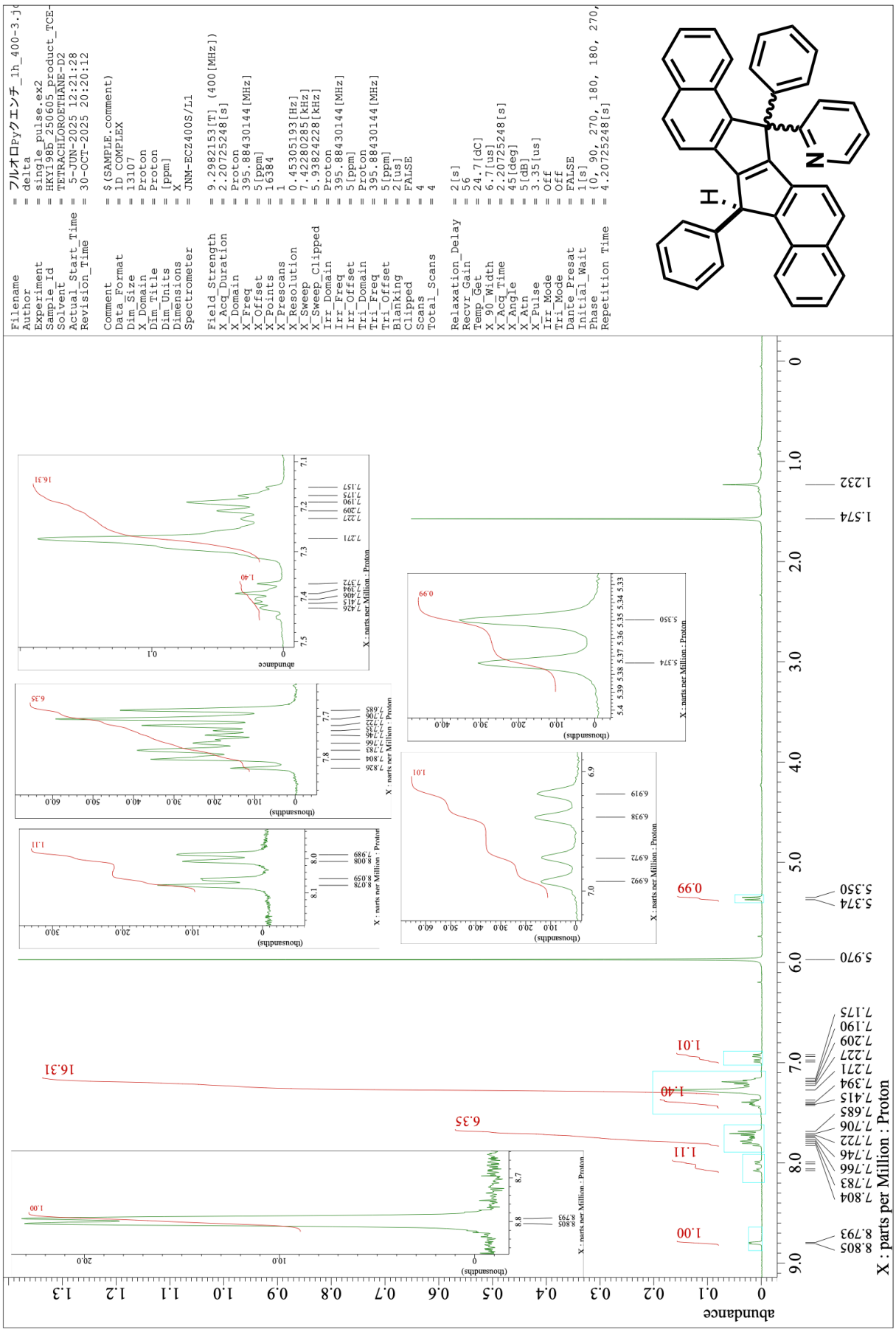


Figure S47. ^{1}H NMR spectrum of **2a-Py** (400 MHz, $Cl_2CDCDCl_2$).

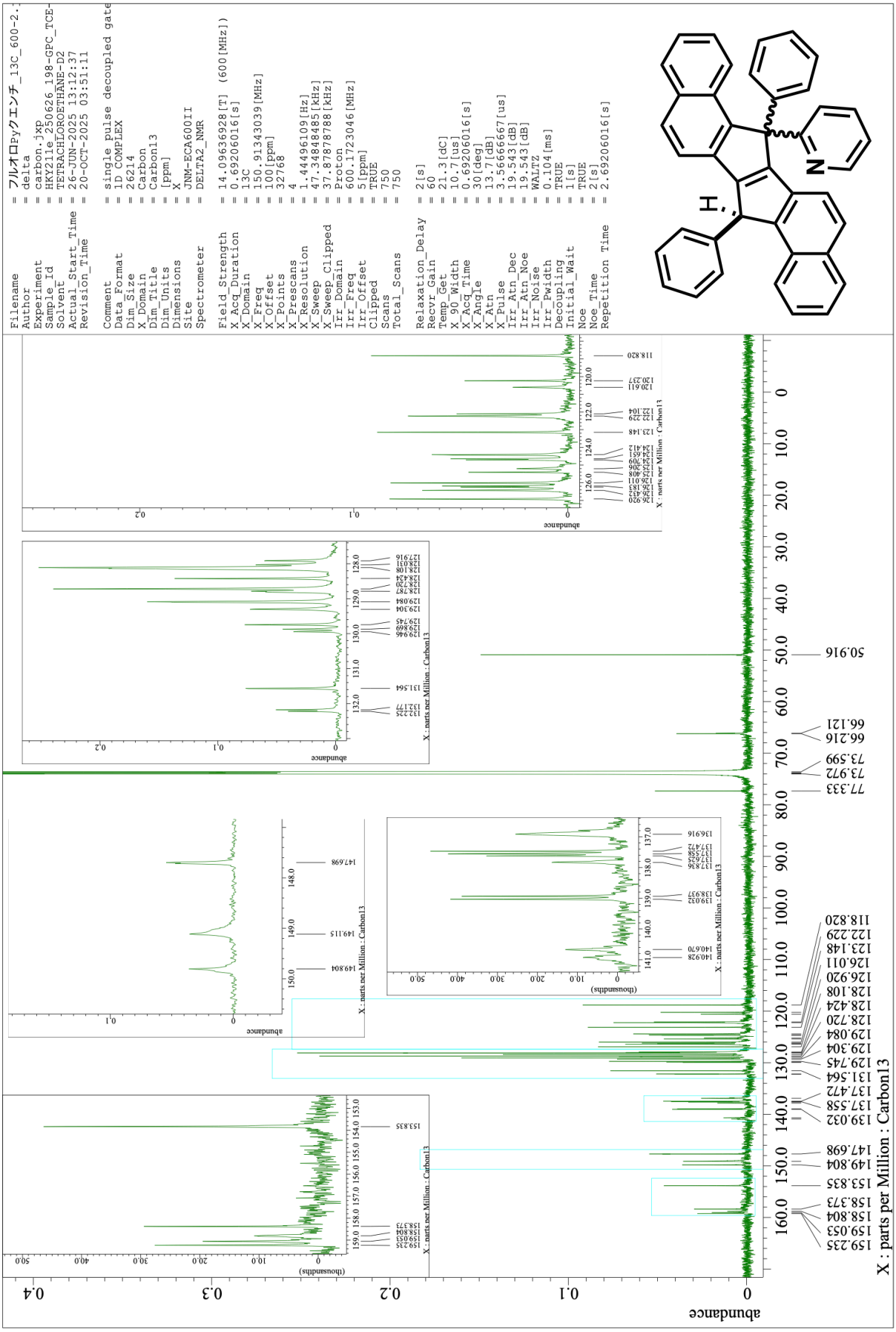


Figure S48. ^{13}C NMR spectrum of **2a-Py** (150 MHz, $Cl_2CDCDCl_2$).

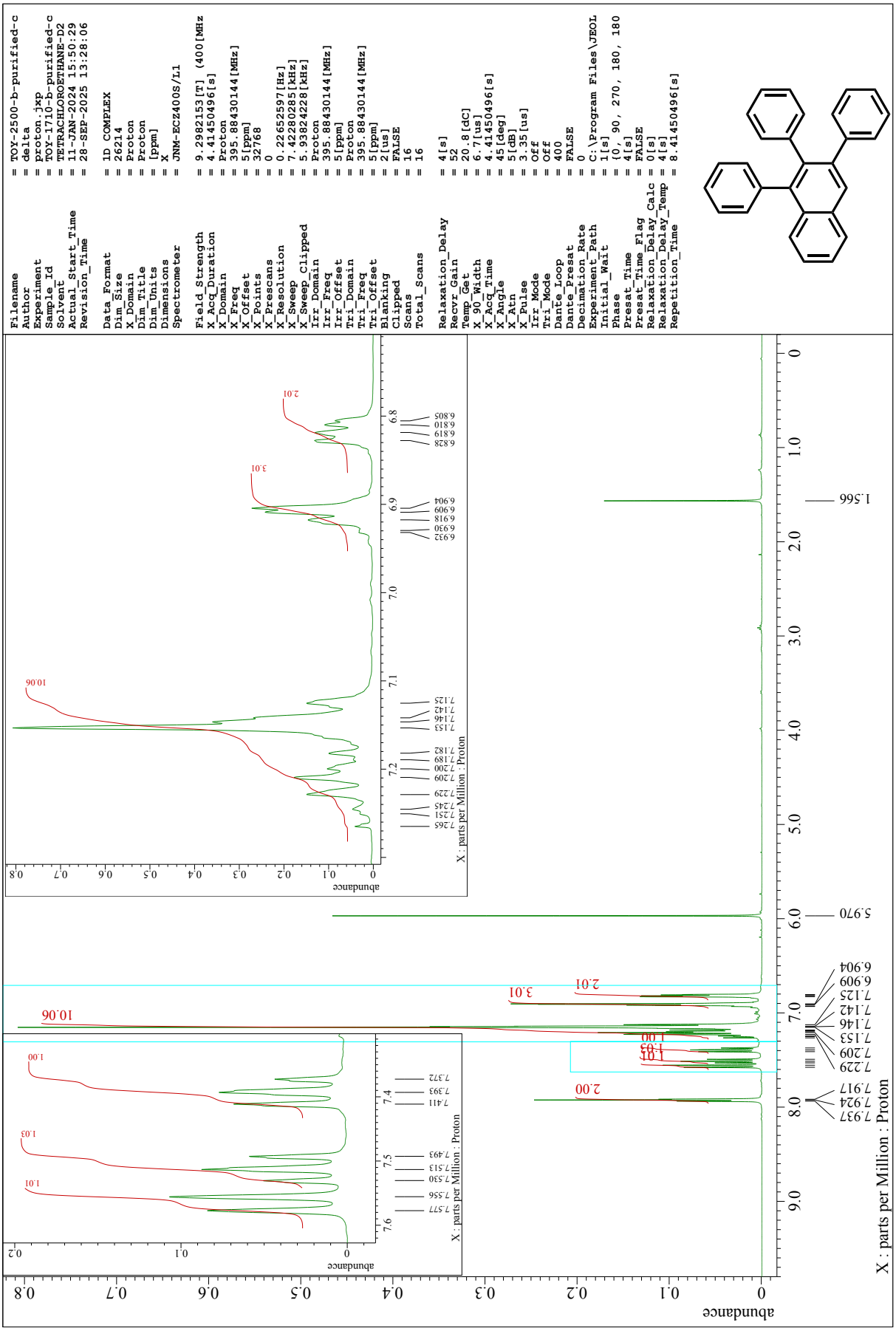


Figure S49. ^{1}H NMR spectrum of **3** (400 MHz, $Cl_2CDCDCl_2$).

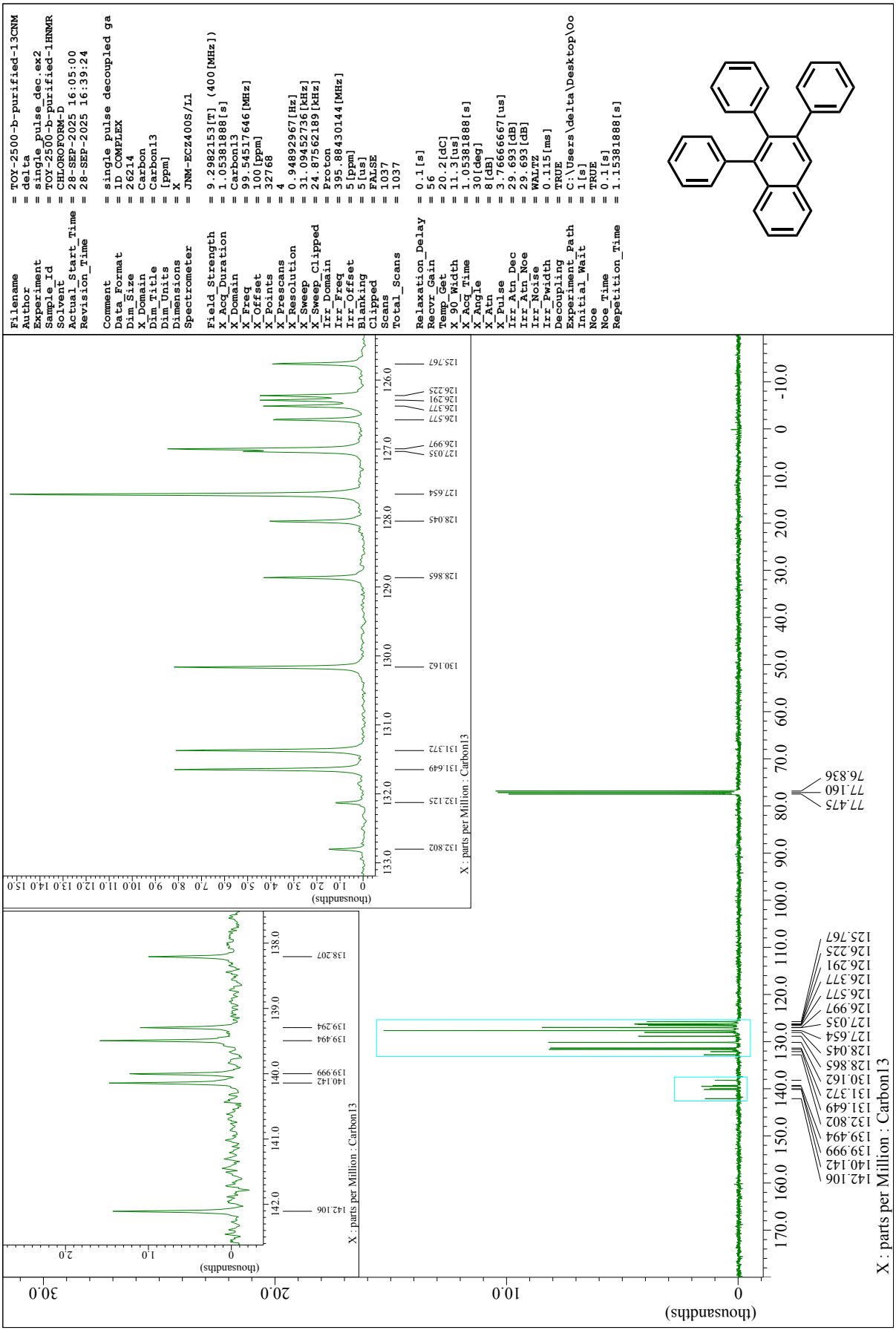


Figure S50. ^{13}C NMR spectrum of **3** (150 MHz, $CDCl_3$).

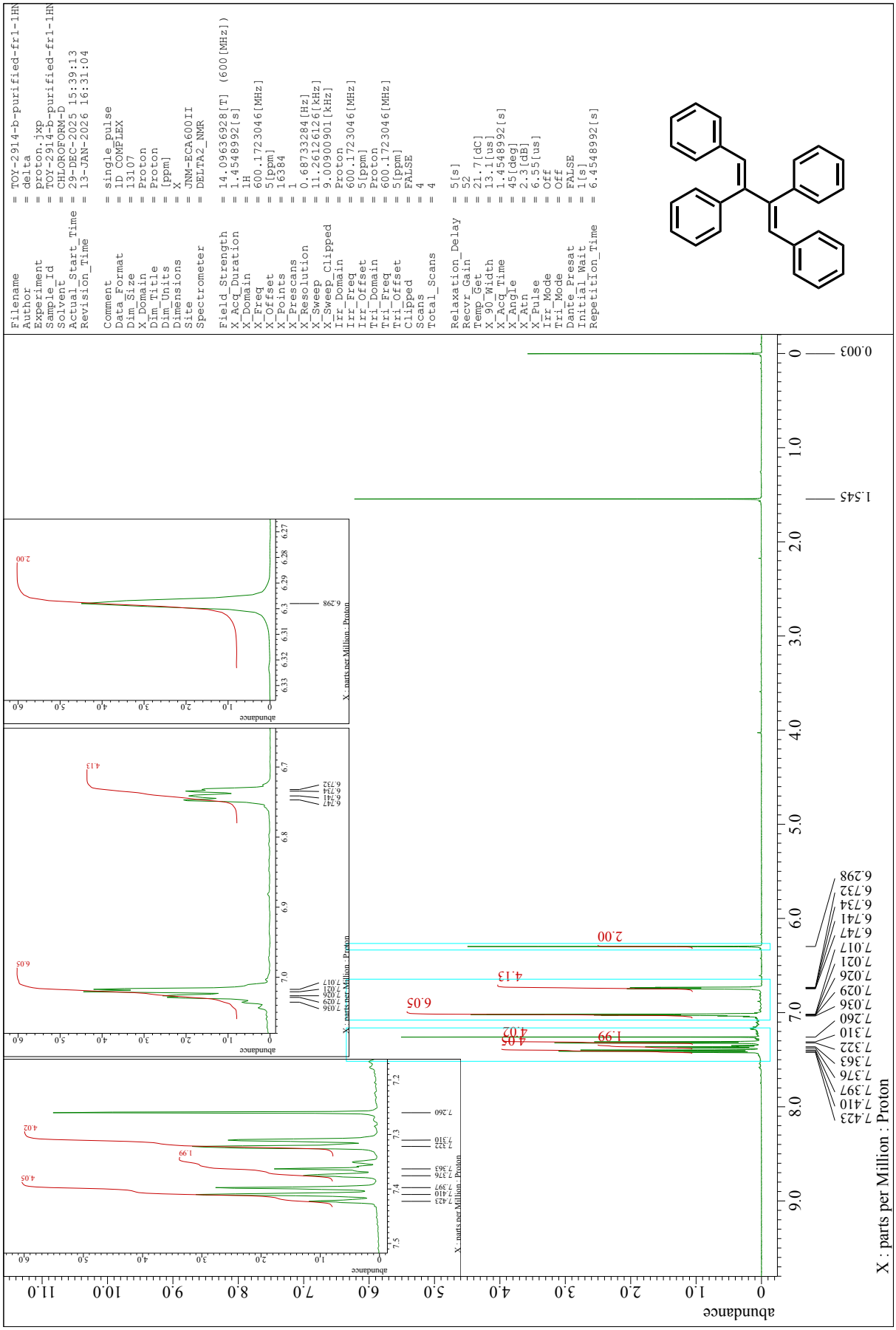


Figure S51. ^{1}H NMR spectrum of **4** (600 MHz, $CDCl_3$).

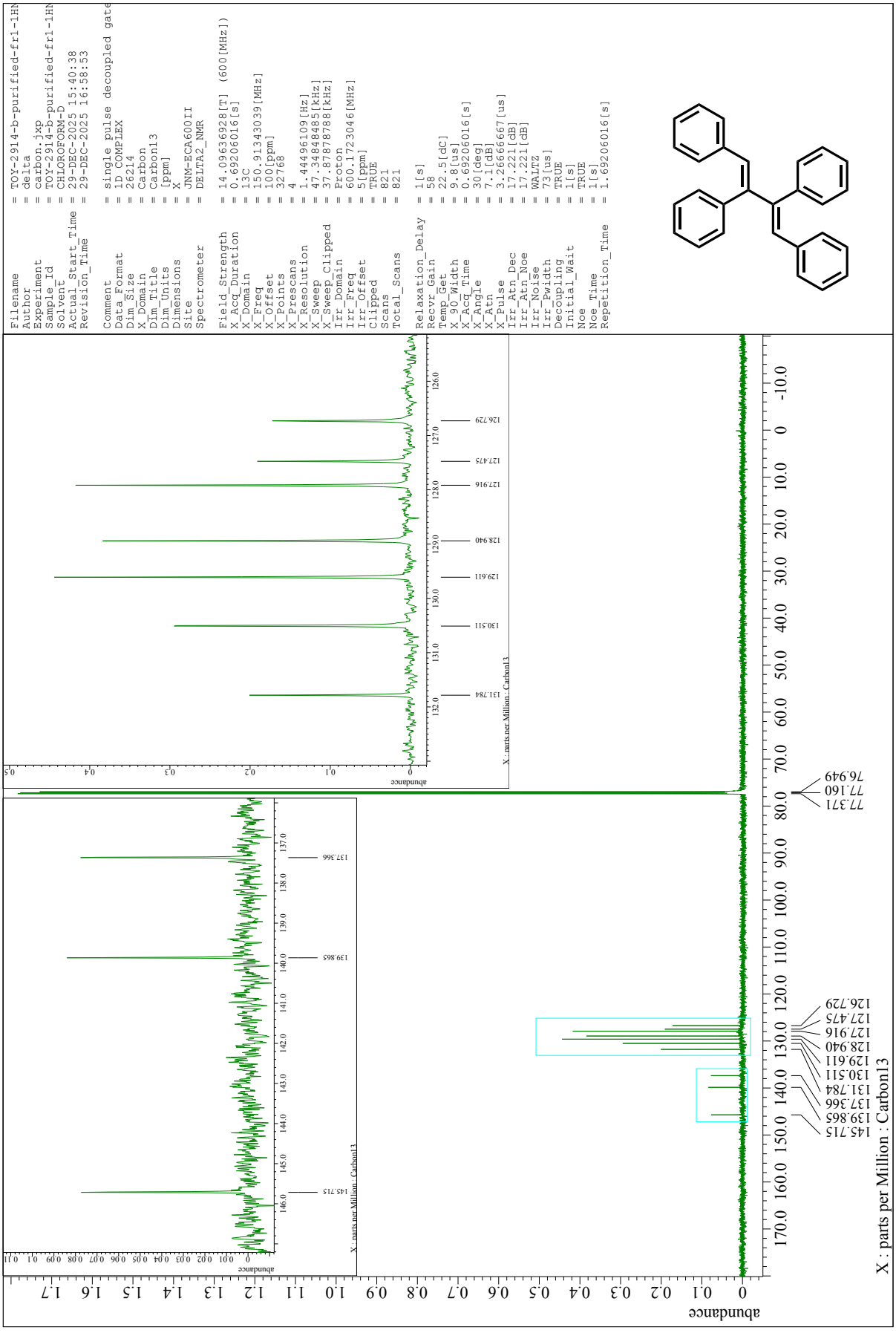


Figure S52. ^{13}C NMR spectrum of **4** (150 MHz, $CDCl_3$).