

Supporting information

A Photochemical Approach to Aromatic Extension of the Corannulene Nucleus

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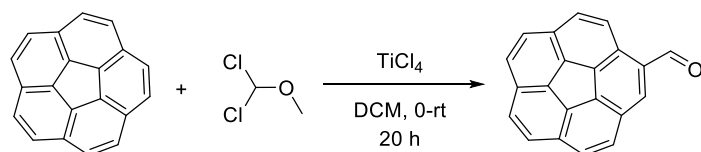
Experimental Section

General: All commercial reagents were used without further purification. Solvents were purified by standard procedures. All reactions relating to air- and moisture-sensitive reagents were performed in vacuum-dried reaction vessels under argon atmosphere. Column chromatography was carried out on silica gel 40–63 mesh as the stationary phase. Reactions were monitored by thin layer chromatography (TLC) with TLC silica gel coated aluminum plates (60 F254, Merck) and visualized by ultraviolet (UV) light ($\lambda = 254$ nm and $\lambda = 366$ nm). ^1H and ^{13}C NMR (nuclear magnetic resonance) spectra were recorded on a Bruker BBFO-400 instrument at room temperature (unless otherwise stated) by using CDCl_3 and $[d_6]\text{DMSO}$ as solvents. Chemical shifts were recorded in parts per million (ppm) relative to tetramethylsilane ($\delta = 0.00$ ppm), chloroform ($\delta = 7.26$ ppm), or DMSO ($\delta = 2.50$ ppm). ^1H NMR splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), m (multiplet), etc. ^{13}C NMR spectral values are reported relative to CDCl_3 ($\delta = 77.00$ ppm) and $[d_6]\text{DMSO}$ ($\delta = 39.52$ ppm). High-resolution mass spectras (HRMS) were recorded using JEOL Spiral TOF (JMS-S3000) (MALDI) for all starting materials and final compound. Photocyclization reactions were carried out in a 1.0 L water-cooled immersion well photochemical reactor equipped with a medium-pressure mercury lamp (125 W).

CCDC- 1476770 (**3b**), CCDC- 1476773 (**3e**), CCDC- 1476774 (**3f**), and CCDC- 1476771 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

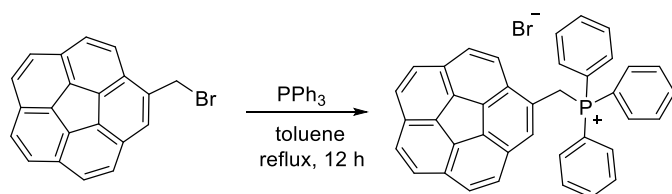
Synthetic Procedures

Multi-gram scale synthesis of corannulene carbaldehyde (**1**):¹



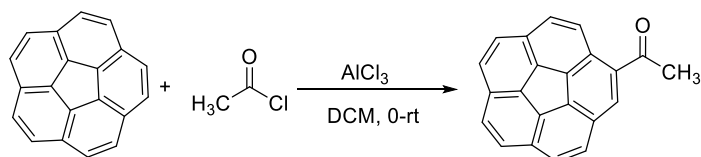
To a vacuum dried round bottom flask containing solution of corannulene (15.0 g, 59.9 mmol, 1 equiv.) and dichloromethyl methyl ether (10.3 g, 89.9 mmol, 1.5 equiv.) in dry CH_2Cl_2 (800 mL) was added a solution of TiCl_4 (239.7 mL, 4 equiv. 1 M solution in CH_2Cl_2) drop wise for 1h at 0 °C under N_2 atmosphere, and the reaction mixture was stirred for 20 h at room temperature. After completion of reaction, the reaction mixture was poured into ice-water and extracted. The resulting aqueous part was again extracted with CH_2Cl_2 (2×200 mL). The combined organic layer was washed with saturated aq. NaCl solution, dried over anhydrous Na_2SO_4 , and concentrated under vacuum. The resulting yellow solid was washed with hexane to afford 15.5 g pure corannulene carbaldehyde in 93% yield. ^1H NMR (400 MHz, CDCl_3): $\delta = 10.33$ (s, 1 H), 8.60 (d, $J = 8.9$ Hz, 1 H), 8.26 (s, 1 H), 8.00–7.67 (m, 7 H). ^{13}C NMR (101 MHz, CDCl_3): $\delta = 193.29, 139.16, 138.09, 136.51, 135.97, 135.19, 135.10, 134.90, 132.39, 131.16, 130.84, 128.88, 128.79, 128.70, 127.79, 127.68, 127.58, 127.35, 127.24, 127.09, 127.05, 127.04$.

Synthesis of corannulene methyl triphenylphosphonium bromide (4):



To a vacuum-dried round-bottomed flask containing a solution of corannulene methyl bromide (4.53 g, 13.2 mmol, 1 equiv.) in 200 mL of dry toluene was added triphenylphosphine (3.81 g, 14.52 mmol, 1.1 equiv.) and then this reaction mixture was refluxed for 12 h under N₂ atmosphere. The reaction mixture was cooled to room temperature and the resulting phosphonium salt precipitated out, which was collected by filtration and dried (8.44 g, yield 92%). ¹H NMR (400 MHz, CD₂Cl₂) δ 8.11 – 7.41 (m, 24H), 7.31 – 7.03 (m, 5H), 5.86 (d, *J* = 14.5 Hz, 2H), 2.34 (s, 3H). ¹³C NMR (101 MHz, DMSO) δ 137.25, 135.15, 135.12, 135.07, 134.67, 134.64, 134.43, 134.39, 134.33, 130.98, 130.78, 130.68, 130.37, 130.15, 130.09, 130.02, 129.74, 129.70, 128.82, 128.12, 128.00, 127.83, 127.73, 127.49, 127.36, 127.22, 126.88, 126.39, 126.29, 125.23, 125.14, 118.08, 117.23, 26.76, 26.29, 20.99. ³¹P NMR (162 MHz, DMSO) δ 23.69. HRMS (MALDI-TOF) *m/z* calcd for C₃₉H₂₆P [M-Br]⁺: 525.1767, found: 525.2070.

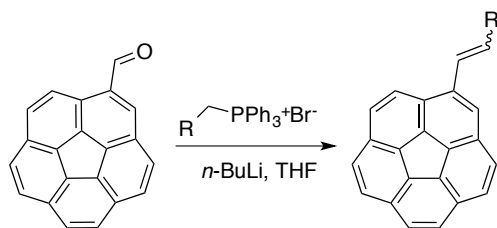
Synthesis of acetyl corannulene (5):



To a stirred solution of corannulene (1.0 g, 4.0 mmol) in dichloromethane (50 mL) was added aluminium(III) trichloride (AlCl₃) (799.0 mg, 5.99 mmol) and acetyl chloride (342.1 mL, 4.79 mmol) at 0 °C under nitrogen atmosphere. After the reaction mixture is warmed up to rt and stirred for 1-1.5 h, it was quenched with water and the organic layer was collected. The aqueous layer was extracted with additional dichloromethane (2X30 mL) and the combined organic layers dried over Na₂SO₄ and the solvent removed under reduced pressure. The residue was purified using flash column chromatography to yield the 1.05g of acetyl corannulene as a pale yellow solid (yield = 94%). ¹H NMR (400 MHz, CDCl₃) δ 8.58 (d, *J* = 9.0 Hz, 1H), 8.45 (s, 1H), 7.90 – 7.68 (m, 7H), 2.84 (s, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 199.62, 137.45, 136.43, 136.23, 135.74, 135.14, 134.87, 132.18, 131.98, 130.75, 128.68, 128.40, 128.31, 128.21, 128.10, 127.54, 127.40, 127.09, 127.03, 126.97, 28.48.

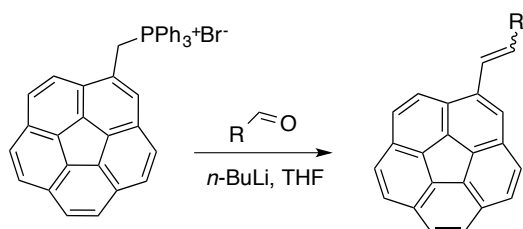
General procedure for synthesis of stilbene-like corannulene derivatives through Wittig reaction

Using corannulene carbaldehyde as a reactant:



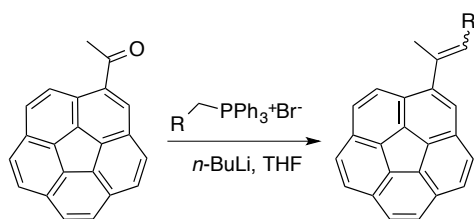
To a vacuum-dried round-bottom flask containing a suspension of benzyltriphenylphosphonium bromide (467.0 mg, 1.1 mmol, 1.5 equiv.) in 20 mL of dry THF was added *n*-BuLi (2.5 M solution in hexane) (0.431 mL, 1.5 equiv.) at 0 °C under N₂ atmosphere. The mixture was stirred for 30 min. Then corannulene carbaldehyde (200.0 mg, 0.718 mmol, 1 equiv.) in 5 mL of dry THF was added, and the solution was stirred at room temperature for 2-3 h. The progress of the reaction was monitored by TLC. After completion of reaction, the reaction mixture was quenched with water and then extracted with CH₂Cl₂ (3 × 100 mL). The combined organic extract was dried (Na₂SO₄) and concentrated. The residue was purified by column chromatography to give the alkenyl corannulenes as mixture of trans/cis isomers.

Using corannulene-based ylide as a reactant:



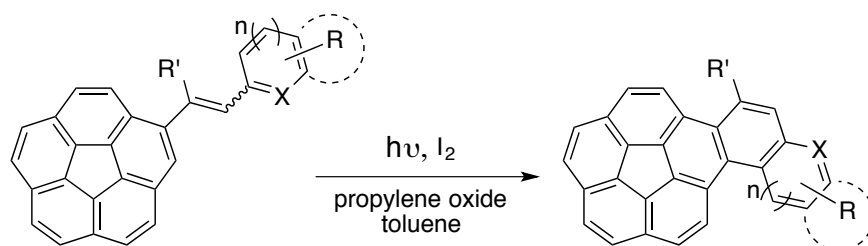
To a vacuum-dried round-bottom flask containing a suspension of corannulene-1-ylmethyltriphenylphosphonium bromide (350.0 mg, 0.578 mmol, 1 equiv.) in 20 mL of dry THF was added *n*-BuLi (2.5 M solution in hexane) (0.346 mL, 1.5 equiv.) at 0 °C under N₂ atmosphere. The resulting reaction mixture was stirred for 30 min. Then aromatic aldehyde of choice (1.1 equiv. in 5 mL of dry THF) was added, and the solution was stirred at room temperature for 2 h. The progress of the reaction was monitored by TLC. After the completion of reaction, the reaction mixture was quenched with water and then extracted with CH₂Cl₂ (3 × 100 mL). The combined organic extract was dried (Na₂SO₄) and concentrated. The residue was purified by column chromatography to give the alkenyl corannulenes as mixture of trans/cis isomers.

Using ketone as a reactant:



To a vacuum-dried round-bottomed flask containing a suspension of (4-methylbenzyl)triphenylphosphonium bromide (336.7 mg, 0.753 mmol, 1.1equiv.) in 20 mL of dry THF was added *n*-BuLi (2.5 M solution in hexane) (0.410 mL, 1.5 equiv) at 0 °C under N₂ atmosphere. The resulting reaction mixture was stirred for 30 min. Then acetyl corannulene (200 mg, 0.684 mmol 1 equiv.) in 5 mL of dry THF was added and the solution was stirred at 65 °C for 12 h. After completion of the reaction, it was quenched with water and then extracted with CH₂Cl₂ (3 × 100 mL). The combined organic extract was dried (Na₂SO₄) and concentrated. The residue was purified by column chromatography to give the stilbene-like corannulene derivative **2j** (150 mg) in 58% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, *J* = 8.8 Hz, 1H), 7.84 – 7.79 (m, 8H), 7.47 – 7.41 (m, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.01 (s, 1H), 2.58 (d, *J* = 1.4 Hz, 3H), 2.44 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 146.01, 136.73, 136.44, 136.41, 136.03, 135.78, 135.61, 135.37, 135.27, 132.63, 131.07, 130.94, 130.77, 129.75, 129.27, 129.19, 127.39, 127.35, 127.32, 127.20, 127.18, 127.00, 126.97, 123.87, 21.42, 20.31. (MALDI-TOF) *m/z* calcd for C₃₀H₂₀ [M]⁺: 380.1560, found: 380.1549.

General procedure for oxidative photocyclization of stilbene-like corannulene derivatives:



A solution of the alkenyl corannulenes (100 mg, 1 equiv.), iodine (1.1 equiv.), and propylene oxide (100 equiv.) in 350 mL of toluene was irradiated in a photo-reactor fitted with a water-cooled immersion flask and a medium-pressure Hg lamp (125 W) under N₂ atmosphere. The progress of the reaction was monitored by disappearance of the iodine color and thin layer chromatography (TLC). After the reaction completion, the reaction mixture was quenched with saturated Na₂S₂O₃ and extracted. The aqueous solution was extracted again with CH₂Cl₂ (2x20 mL). The combined organic extract was dried (Na₂SO₄) and concentrated. The residue was purified by column chromatography to give corannulene-based extended polyaromatics.

Photographs in Figure 1 illustrate the reaction set up. On the left, the reaction vessel contains a solution of alkenyl corannulene, iodine, and propylene oxide in toluene. It shows a red color. In the middle, the system is irradiated with light. On the right hand side, the system can be seen after the completion of the reaction. The color changes to a slight yellow one.

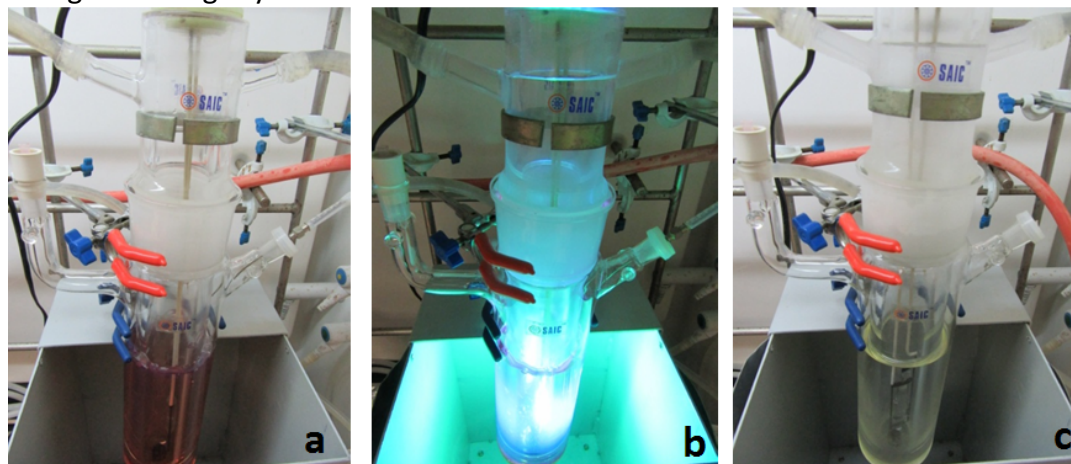
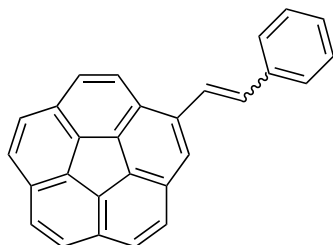


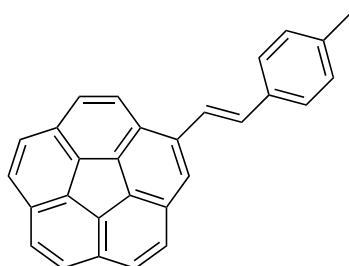
Figure 1. Digital photographs showing progress of the aromatic extension reaction. a) Reaction mixture before irradiation looks pink due to presence of iodine; b) irradiation with 125W medium pressure Hg lamp; and c) after completion of the reaction.

Structural characterization of stilbene-like precursors synthesized *via* corannulene carbaldehyde:

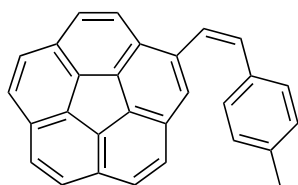
Note: In cases where separation of the cis/trans mixture was possible, separate characterization is given for the isomeric compounds.



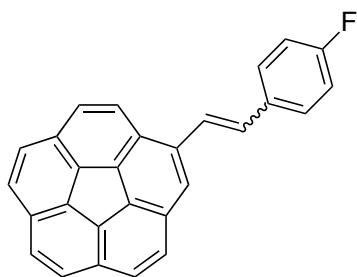
Yield: 239 mg, 95%; ^1H NMR (400 MHz, CDCl_3) δ 8.17 (d, $J = 8.8$ Hz, 1H), 7.94 (s, 1H), 7.90 – 7.73 (m, 8H), 7.68 (d, $J = 7.5$ Hz, 2H), 7.53 (d, $J = 16.2$ Hz, 1H), 7.45 (t, $J = 7.6$ Hz, 2H), 7.34 (t, $J = 7.3$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 137.71, 137.61, 136.41, 136.14, 135.85, 135.65, 135.46, 133.07, 131.09, 131.05, 130.87, 129.22, 128.96, 128.13, 127.63, 127.50, 127.42, 127.25, 127.16, 127.09, 127.01, 126.86, 126.66, 125.83, 124.53. HRMS (MALDI-TOF) m/z calcd for $\text{C}_{28}\text{H}_{16}$ $[\text{M}]^+$: 352.1247, found: 352.1247.



Yield: 152 mg, 63%; ^1H NMR (500 MHz, CDCl_3) δ 8.20 (d, $J = 8.5$ Hz, 1H), 7.96 (s, 1H), 7.92 – 7.80 (m, 7H), 7.76 (d, $J = 16.0$ Hz, 1H), 7.62 (d, $J = 7.7$ Hz, 2H), 7.55 (d, $J = 16.2$ Hz, 1H), 7.31 (d, $J = 7.8$ Hz, 2H), 2.47 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 138.10, 137.92, 136.37, 136.12, 135.83, 135.65, 135.35, 134.86, 133.02, 131.10, 131.06, 130.83, 130.79, 129.68, 129.25, 127.56, 127.46, 127.38, 127.23, 127.15, 127.01, 126.99, 126.79, 125.87, 125.65, 124.24, 21.49. HRMS (MALDI-TOF) m/z calcd for $\text{C}_{29}\text{H}_{18}$ $[\text{M}]^+$: 366.1403, found: 366.1399.

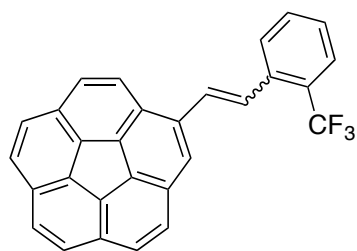


Yield: 53.5 mg, 22%; ^1H NMR (300 MHz, CDCl_3) δ 7.82 – 7.62 (m, 9H), 7.40 – 7.33 (m, 2H), 7.06 – 6.80 (m, 4H), 2.28 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 137.35, 137.11, 136.16, 135.82, 135.74, 135.37, 134.20, 132.70, 131.04, 130.88, 130.84, 130.61, 129.77, 129.57, 129.13, 127.21, 127.14, 127.09, 127.05, 127.03, 126.95, 126.80, 126.37, 21.41. HRMS (MALDI-TOF) m/z calcd for $\text{C}_{29}\text{H}_{18}$ $[\text{M}]^+$: 366.1403, found: 366.1424.

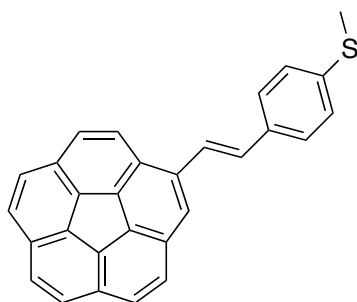


Yield: 212 mg, 80%; ^1H NMR (400 MHz, CDCl_3) δ 8.15 (d, J = 8.9 Hz, 1H), 7.92 (s, 1H), 7.89 – 7.77 (m, 7H), 7.70 – 7.59 (m, 3H), 7.47 (d, J = 16.2 Hz, 1H), 7.13 (t, J = 8.6 Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 137.56, 136.44, 136.17, 135.88, 135.68, 135.49, 133.85, 133.81, 131.85, 131.14, 131.05, 130.91, 129.16, 128.42, 128.34, 127.68, 127.56, 127.48, 127.29, 127.16, 127.14, 127.04, 126.47, 126.45, 125.75, 124.52, 116.04, 115.83. ^{19}F NMR (376 MHz, CDCl_3) δ -113.59, -113.87. HRMS (MALDI-TOF) m/z calcd for $\text{C}_{28}\text{H}_{15}\text{F}$ $[\text{M}]^+$: 370.1152, found: 370.1151.

Structural characterization of stilbene-like precursors synthesized via corannulene-based ylide compound:

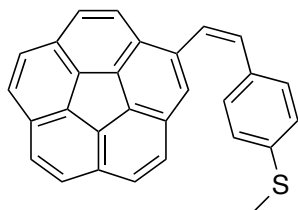


Yield: 162 mg, 54%; ^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, J = 8.8 Hz, 1H), 7.98 – 7.93 (m, 2H), 7.90 – 7.86 (m, 2H), 7.85 – 7.80 (m, 6H), 7.77 – 7.68 (m, 2H), 7.61 (t, J = 7.6 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 137.15, 136.60, 136.58, 136.47, 136.15, 135.86, 135.77, 135.62, 132.15, 131.13, 131.06, 130.92, 130.85, 130.79, 129.06, 128.56, 128.54, 127.90, 127.66, 127.59, 127.50, 127.30, 127.27, 127.20, 127.06, 126.23 (q, J = 5.6 Hz), 125.62. ^{19}F NMR (376 MHz, CDCl_3) δ -59.15. HRMS (MALDI-TOF) m/z calcd for $\text{C}_{29}\text{H}_{15}\text{F}_3$ $[\text{M}]^+$: 420.1120, found: 420.1123.

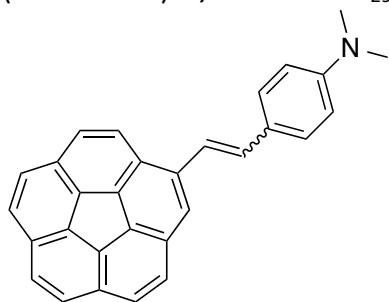


Yield: 178 mg, 68%; ^1H NMR (400 MHz, CDCl_3) δ 8.15 (d, J = 8.8 Hz, 1H), 7.91 (s, 1H), 7.88 – 7.64 (m, 8H), 7.59 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 16.2 Hz, 1H), 7.32 (d, J = 8.0

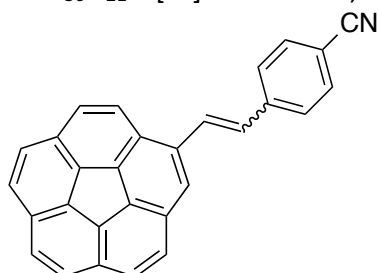
Hz, 2H), 2.55 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 138.55, 137.71, 136.39, 136.12, 135.83, 135.64, 135.40, 134.54, 132.38, 131.08, 131.05, 130.85, 130.83, 129.17, 127.61, 127.50, 127.42, 127.25, 127.23, 127.13, 127.06, 127.00, 126.88, 126.00, 125.80, 124.37, 15.95. HRMS (MALDI-TOF) m/z calcd for $\text{C}_{29}\text{H}_{18}\text{S}$ $[\text{M}]^+$: 398.1124, found: 398.1121.



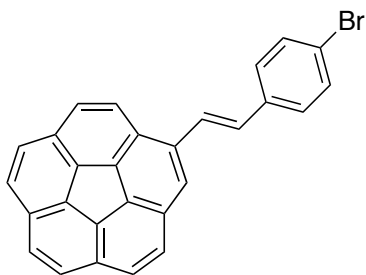
Yield: 63 mg, 24%; ^1H NMR (400 MHz, CDCl_3) δ 7.84 – 7.63 (m, 10H), 7.40 (d, J = 8.3 Hz, 2H), 7.12 – 7.03 (m, 2H), 6.97 (dd, J = 12.2, 1.1 Hz, 1H), 6.85 (d, J = 12.2 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 137.88, 136.94, 136.26, 135.90, 135.88, 135.81, 135.46, 133.81, 132.12, 131.07, 130.99, 130.97, 130.73, 130.03, 129.67, 127.32, 127.24, 127.17, 127.14, 127.11, 127.04, 126.30, 126.15, 15.61. HRMS (MALDI-TOF) m/z calcd for $\text{C}_{29}\text{H}_{18}\text{S}$ $[\text{M}]^+$: 398.1124, found: 398.1139.



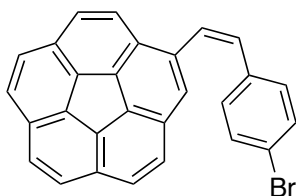
Yield: 178 mg, 68%; ^1H NMR (400 MHz, CDCl_3) δ 8.18 (d, J = 8.8 Hz, 1H), 7.93 – 7.74 (m, 8H), 7.69 – 7.40 (m, 4H), 6.87 – 6.71 (m, 2H), 3.03 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 150.54, 138.74, 136.36, 136.20, 135.87, 135.75, 135.04, 133.32, 131.36, 131.06, 130.82, 130.60, 129.43, 128.01, 127.39, 127.31, 127.20, 127.17, 126.97, 126.81, 126.10, 126.07, 123.22, 122.18, 112.61, 40.60. HRMS (MALDI-TOF) m/z calcd for $\text{C}_{30}\text{H}_{21}\text{N}$ $[\text{M}]^+$: 395.1669, found: 395.1657.



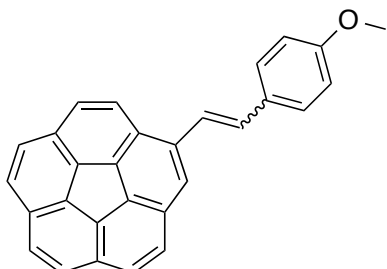
Yield: 174 mg, 70%; ^1H NMR (400 MHz, CDCl_3) δ 8.11 (d, J = 8.8 Hz, 1H), 7.95 (s, 1H), 7.88 – 7.78 (m, 8H), 7.67 (s, 4H), 7.52 – 7.43 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 141.95, 136.52, 136.43, 136.07, 135.81, 135.52, 132.69, 131.14, 131.11, 130.91, 130.81, 130.71, 130.39, 128.84, 127.92, 127.69, 127.60, 127.39, 127.34, 127.13, 127.11, 127.05, 125.69, 125.42, 119.14, 111.00. HRMS (MALDI-TOF) m/z calcd for $\text{C}_{29}\text{H}_{15}\text{N}$ $[\text{M}]^+$: 377.1199, found: 377.1192.



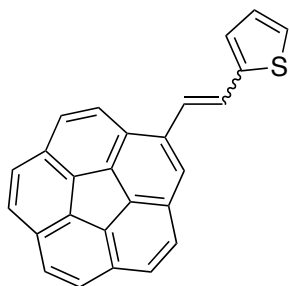
Yield: 241 mg, 85%; ^1H NMR (300 MHz, CDCl_3) δ 8.14 (d, $J = 8.8$ Hz, 1H), 7.97 – 7.66 (m, 10H), 7.64 – 7.51 (m, 4H), 7.46 (d, $J = 16.2$ Hz, 1H), 7.31 (d, $J = 16.5$ Hz, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 137.15, 136.44, 136.34, 136.04, 135.75, 135.54, 135.47, 131.97, 131.55, 130.99, 130.82, 130.76, 128.93, 128.18, 127.60, 127.45, 127.37, 127.33, 127.18, 127.07, 127.01, 126.92, 125.55, 124.72, 121.85. HRMS (MALDI-TOF) m/z calcd for $\text{C}_{28}\text{H}_{15}\text{Br}$ $[\text{M}]^+$: 430.0352, found: 430.0332.



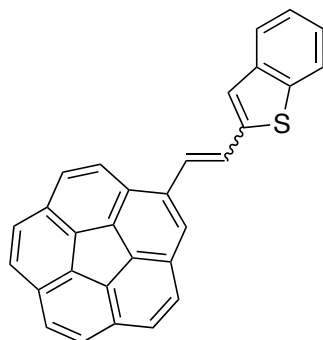
Yield: 27 mg, 10%; ^1H NMR (300 MHz, CDCl_3) δ 7.88 – 7.62 (m, 9H), 7.34 (s, 4H), 7.11 – 6.97 (m, 1H), 6.84 (d, $J = 12.2$ Hz, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 136.32, 136.26, 136.02, 135.87, 135.83, 135.79, 135.53, 131.58, 131.45, 131.17, 131.01, 130.94, 130.74, 129.42, 128.48, 127.39, 127.34, 127.31, 127.20, 127.05, 127.03, 126.07, 121.45. HRMS (MALDI-TOF) m/z calcd for $\text{C}_{28}\text{H}_{15}\text{Br}$ $[\text{M}]^+$: 430.0352, found: 430.0319.



Yield: 215 mg, 85%; ^1H NMR (400 MHz, CDCl_3) δ 7.81 – 7.65 (m, 11H), 7.48 – 7.32 (m, 2H), 6.94 – 6.81 (m, 2H), 6.79 – 6.69 (m, 2H), 3.89 (s, 0H), 3.75 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 159.03, 137.31, 136.25, 135.91, 135.84, 135.39, 132.30, 131.14, 130.97, 130.91, 130.72, 129.84, 129.69, 127.27, 127.19, 127.14, 127.13, 127.10, 127.07, 127.02, 126.46, 125.81, 113.84, 55.30. HRMS (MALDI-TOF) m/z calcd for $\text{C}_{29}\text{H}_{18}\text{O}$ $[\text{M}]^+$: 382.1352, found: 382.1353.

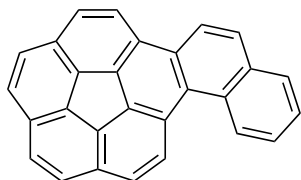


Yield: 198 mg, 95%; ^1H NMR (400 MHz, CDCl_3) δ 8.14 (d, $J = 8.8$ Hz, 1H), 7.92 – 7.72 (m, 16H), 7.70 – 7.53 (m, 2H), 7.28 (d, $J = 5.1$ Hz, 1H), 7.23 (d, $J = 3.4$ Hz, 1H), 7.20 – 7.14 (m, 1H), 7.12 – 7.04 (m, 3H), 6.93 – 6.83 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.15, 139.98, 137.25, 136.40, 136.38, 136.21, 136.11, 135.97, 135.83, 135.73, 135.63, 135.42, 131.09, 131.03, 131.00, 130.88, 130.85, 130.80, 130.05, 129.39, 129.03, 127.92, 127.65, 127.52, 127.51, 127.44, 127.30, 127.26, 127.24, 127.19, 127.12, 127.09, 127.01, 126.84, 126.51, 126.27, 126.16, 125.93, 125.88, 125.72, 125.58, 124.93, 124.31. HRMS (MALDI-TOF) m/z calcd for $\text{C}_{26}\text{H}_{14}\text{S}$ $[\text{M}]^+$: 358.0816, found: 358.0337.

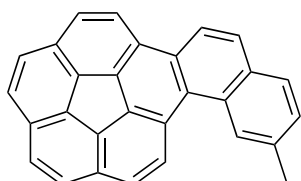


Yield: 225 mg, 95%; ^1H NMR (400 MHz, CDCl_3) δ 8.21 (d, $J = 8.8$ Hz, 1H), 8.00 – 7.75 (m, 30H), 7.73 – 7.67 (m, 3H), 7.58 (dd, $J = 8.1, 1.2$ Hz, 2H), 7.44 (s, 3H), 7.40 (d, $J = 4.1$ Hz, 1H), 7.34 – 7.17 (m, 7H), 7.10 (dd, $J = 11.9, 1.3$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.32, 140.17, 138.88, 136.79, 136.24, 135.96, 135.85, 135.59, 135.56, 131.07, 130.97, 130.92, 130.87, 130.85, 130.76, 130.03, 128.82, 127.97, 127.86, 127.72, 127.54, 127.44, 127.32, 127.32, 127.23, 127.17, 127.16, 127.07, 127.00, 126.47, 126.38, 126.28, 125.71, 125.59, 125.09, 124.88, 124.72, 124.34, 124.07, 123.68, 123.41, 122.37, 122.15. HRMS (MALDI-TOF) m/z calcd for $\text{C}_{30}\text{H}_{16}\text{S}$ $[\text{M}]^+$: 408.0967, found: 408.0970.

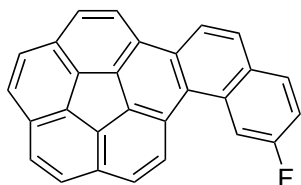
Structural characterization of the extended corannulenes:



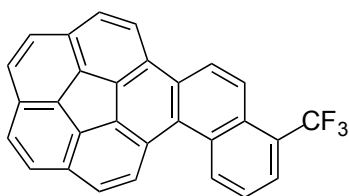
Yield: 95 mg, 95%; Mp: 256–257 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.50 (d, $J = 8.5$ Hz, 1H), 8.67 (dd, $J = 8.8, 2.0$ Hz, 2H), 8.35 (d, $J = 8.7$ Hz, 1H), 8.08 (dd, $J = 8.5, 3.8$ Hz, 2H), 7.96 (d, $J = 8.7$ Hz, 1H), 7.92 – 7.78 (m, 6H), 7.69 (t, $J = 7.5$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 137.89, 135.60, 135.35, 135.27, 134.89, 133.38, 131.91, 131.29, 131.21, 131.11, 130.79, 130.72, 129.13, 128.93, 128.85, 128.81, 128.58, 127.97, 127.94, 127.88, 127.41, 127.35, 127.10, 126.96, 126.88, 126.40, 124.61, 122.77. HRMS (MALDI-TOF) m/z calcd for $\text{C}_{28}\text{H}_{14}$ $[\text{M}]^+$: 350.1090, found: 350.1095.



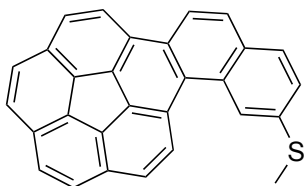
Yield: 71.8 mg, 72%; Mp: 229–230 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.31 (s, 1H), 8.69 (d, $J = 8.8$ Hz, 1H), 8.61 (d, $J = 8.6$ Hz, 1H), 8.36 (d, $J = 8.7$ Hz, 1H), 8.06 (d, $J = 8.7$ Hz, 1H), 8.02 – 7.78 (m, 7H), 7.54 (dd, $J = 8.2, 1.5$ Hz, 1H), 2.79 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 137.92, 136.71, 135.67, 135.31, 135.27, 134.92, 132.11, 131.56, 131.34, 131.12, 130.82, 130.80, 130.71, 129.30, 128.99, 128.96, 128.72, 128.45, 127.90, 127.88, 127.85, 127.74, 127.35, 127.06, 126.96, 124.66, 121.89, 22.53. HRMS (MALDI-TOF) m/z calcd for $\text{C}_{29}\text{H}_{16}$ $[\text{M}]^+$: 364.1247, found: 364.1254.



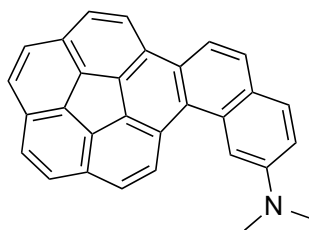
Yield: 93 mg, 94%; Mp: 250–251 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.14 (dd, $J = 11.7, 2.5$ Hz, 1H), 8.67 – 8.62 (m, 2H), 8.36 (d, $J = 8.8$ Hz, 1H), 8.11 – 7.82 (m, 8H), 7.47 (ddd, $J = 8.8, 7.9, 2.5$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 161.66 (d, $J = 246.70$ Hz), 137.84, 135.52, 135.19, 134.72, 132.76 (d, $J = 9.20$ Hz), 131.82, 131.06, 131.01, 130.92, 130.81, 130.78, 130.41 (d, $J = 7.0$ Hz), 130.11, 128.80, 128.53, 128.14, 128.04, 127.86, 127.52, 127.38, 127.27, 127.16, 126.90, 124.44, 122.15 (d, $J = 2.68$ Hz), 116.05 (d, $J = 24.87$ Hz), 112.47 (d, $J = 22.50$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -113.09; HRMS (MALDI-TOF) m/z calcd for $\text{C}_{28}\text{H}_{13}\text{F}$ $[\text{M}]^+$: 368.0996, found: 368.1005.



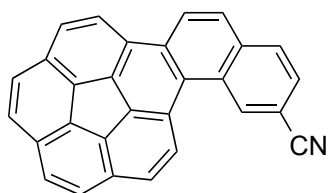
Yield: 75.7 mg, 76%; Mp: 215–216 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.57 (d, *J* = 8.6 Hz, 1H), 8.73 (d, *J* = 9.1 Hz, 1H), 8.43 (d, *J* = 8.8 Hz, 2H), 8.28 (d, *J* = 8.7 Hz, 1H), 8.04 (d, *J* = 7.3 Hz, 1H), 7.92 (d, *J* = 8.7 Hz, 1H), 7.87 – 7.66 (m, 7H). ¹³C NMR (101 MHz, CDCl₃) δ 137.90, 135.49, 134.75, 133.14, 132.51, 131.49, 131.13, 130.94, 130.82, 129.13, 128.72, 128.49, 128.23, 128.13, 127.68, 127.44, 127.31, 126.95, 125.03, 124.88 (q, *J* = 6.0 Hz), 124.55, 124.43, 123.37, 123.35. ¹⁹F NMR (376 MHz, CDCl₃) δ -58.94; HRMS (MALDI-TOF) *m/z* calcd for C₂₉H₁₃F₃ [M]⁺: 418.0964, found: 418.0946.



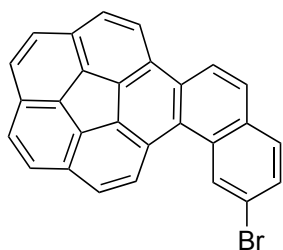
Yield: 71 mg, 71%; Mp: 250–251 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.31 (d, *J* = 1.8 Hz, 1H), 8.63 (dd, *J* = 18.9, 8.7 Hz, 2H), 8.35 (d, *J* = 8.7 Hz, 1H), 8.14 – 7.77 (m, 8H), 7.60 (dd, *J* = 8.5, 1.8 Hz, 1H), 2.81 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 137.54, 135.70, 135.42, 135.37, 134.91, 132.39, 131.81, 131.20, 131.17, 130.91, 130.83, 130.34, 129.16, 129.08, 128.81, 128.81, 128.40, 128.13, 127.98, 127.68, 127.47, 127.42, 127.20, 127.02, 125.89, 124.79, 124.64, 122.19, 16.40. HRMS (MALDI-TOF) *m/z* calcd for C₂₉H₁₆S [M]⁺: 396.0967, found: 396.0965.



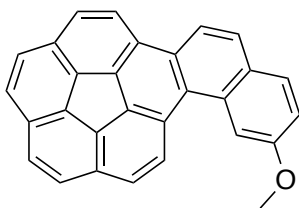
Yield: 72 mg, 72%; Mp: 235–236 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.84 (d, *J* = 8.8 Hz, 1H), 8.66 (d, *J* = 2.5 Hz, 1H), 8.44 (d, *J* = 8.6 Hz, 1H), 8.37 (d, *J* = 8.7 Hz, 1H), 8.02 – 7.80 (m, 8H), 7.35 (dd, *J* = 8.9, 2.5 Hz, 1H), 3.29 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 149.65, 137.92, 135.80, 135.33, 135.09, 134.96, 133.43, 131.89, 131.14, 130.93, 130.67, 129.92, 129.83, 129.69, 129.34, 128.02, 127.73, 127.70, 127.35, 127.13, 126.98, 126.93, 126.27, 124.80, 118.87, 115.88, 108.47, 41.23. HRMS (MALDI-TOF) *m/z* calcd for C₃₀H₁₉N [M]⁺: 393.1512, found: 393.1517.



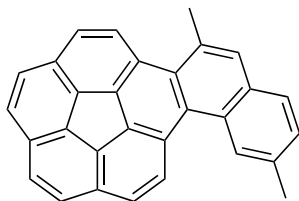
Yield: 70 mg, 70%; Mp: 249–250 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.76 (s, 1H), 8.71 (d, $J = 8.8$ Hz, 1H), 8.45 (d, $J = 8.7$ Hz, 1H), 8.25 (d, $J = 8.7$ Hz, 1H), 8.01 (t, $J = 8.1$ Hz, 2H), 7.92 (dd, $J = 8.7, 4.4$ Hz, 2H), 7.85 – 7.81 (m, 4H), 7.75 (dd, $J = 8.3, 1.5$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 137.85, 135.53, 135.47, 135.42, 134.70, 134.67, 134.25, 132.13, 131.18, 130.97, 130.95, 130.89, 129.89, 128.75, 128.21, 128.15, 127.92, 127.89, 127.84, 127.49, 127.45, 127.27, 127.09, 127.00, 126.01, 124.29, 119.81, 110.18. HRMS (MALDI-TOF) m/z calcd for $\text{C}_{29}\text{H}_{13}\text{N}$ $[\text{M}]^+$: 375.1048, found: 374.2094.



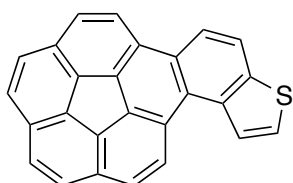
Yield: 86 mg, 86%; Mp: 269–270 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.67 – 9.60 (m, 1H), 8.67 (d, $J = 8.7$ Hz, 1H), 8.60 (d, $J = 8.7$ Hz, 1H), 8.33 (d, $J = 8.8$ Hz, 1H), 8.07 – 7.72 (m, 9H). ^1H NMR (400 MHz, CDCl_3) δ 9.67 – 9.60 (m, 1H), 8.67 (d, $J = 8.7$ Hz, 1H), 8.60 (d, $J = 8.7$ Hz, 1H), 8.33 (d, $J = 8.8$ Hz, 1H), 8.07 – 7.72 (m, 9H). ^{13}C NMR (101 MHz, $\text{CDCl}_3/\text{CS}_2$) δ 137.93, 135.55, 135.48, 135.40, 134.81, 132.96, 131.72, 131.61, 131.04, 130.79, 130.65, 130.25, 130.14, 129.56, 128.51, 128.30, 128.28, 127.93, 127.47, 127.44, 127.31, 127.20, 126.96, 124.37, 123.24, 121.44. HRMS (MALDI-TOF) m/z calcd for $\text{C}_{28}\text{H}_{13}\text{Br}$ $[\text{M}]^+$: 428.0195, found: 428.0192.



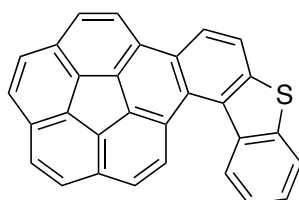
Yield: 86 mg, 86%; Mp: 218–219 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.89 (d, $J = 2.4$ Hz, 1H), 8.72 (d, $J = 8.8$ Hz, 1H), 8.54 (d, $J = 8.6$ Hz, 1H), 8.35 (d, $J = 8.7$ Hz, 1H), 8.08 – 7.77 (m, 8H), 7.38 (dd, $J = 8.8, 2.5$ Hz, 1H), 4.18 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 158.79, 137.95, 135.73, 135.37, 135.23, 134.89, 133.17, 131.79, 131.16, 130.93, 130.76, 130.35, 130.33, 129.38, 129.03, 128.63, 128.05, 127.96, 127.87, 127.71, 127.40, 127.34, 127.10, 126.96, 124.68, 120.57, 118.00, 108.50, 55.86. HRMS (MALDI-TOF) m/z calcd for $\text{C}_{29}\text{H}_{16}\text{O}$ $[\text{M}]^+$: 380.1196, found: 380.1208.



Yield: 53.3 mg, 54%; Mp: 208–209 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.26 (s, 1H), 8.63 (dd, $J = 8.8, 3.8$ Hz, 2H), 7.93 – 7.81 (m, 9H), 7.51 (dd, $J = 8.2, 1.5$ Hz, 1H), 3.32 (s, 3H), 2.76 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 138.14, 135.83, 135.64, 135.29, 134.72, 134.50, 133.68, 132.26, 132.12, 131.06, 131.04, 130.77, 130.70, 130.61, 130.58, 129.44, 129.34, 129.32, 128.65, 128.64, 128.39, 127.63, 127.55, 127.35, 127.13, 126.97, 126.89, 26.82, 22.50. HRMS (MALDI-TOF) m/z calcd for $\text{C}_{30}\text{H}_{18}$ $[\text{M}]^+$: 378.1403, found: 378.1397.

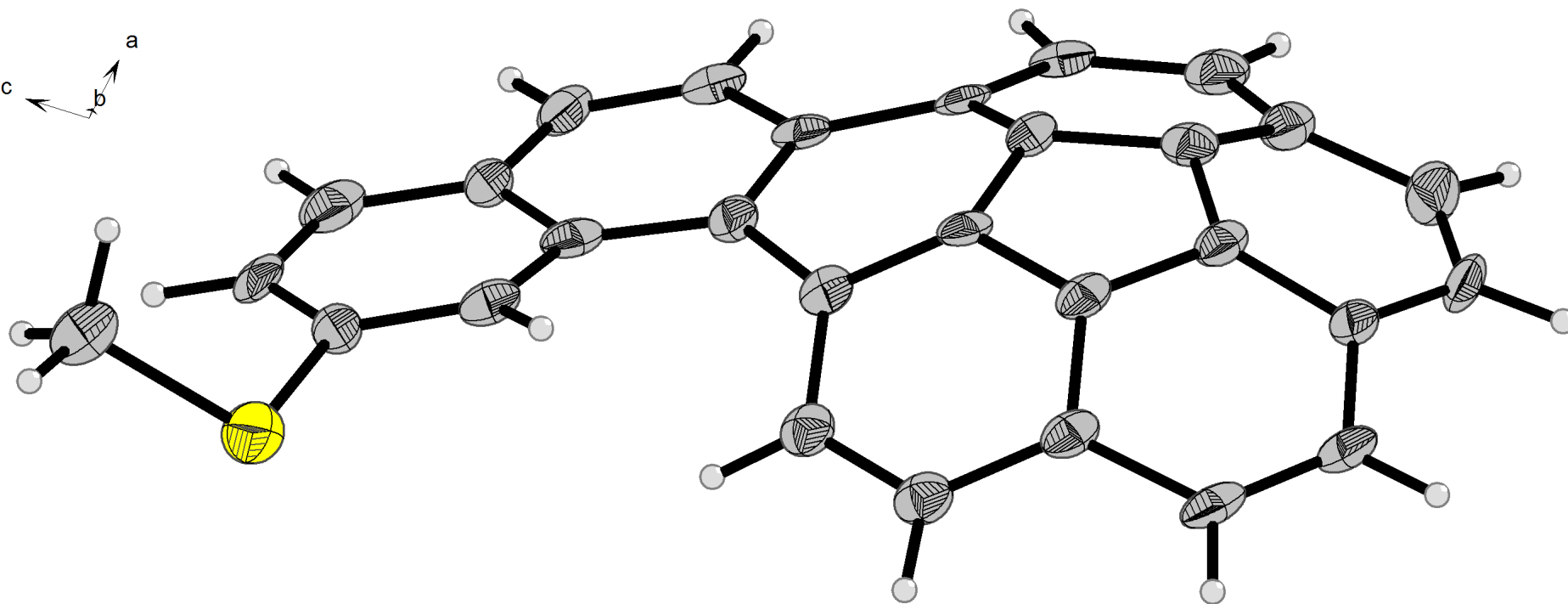
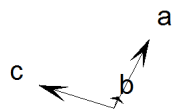
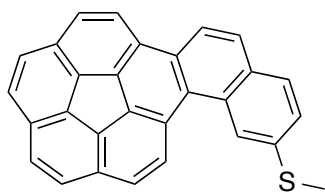


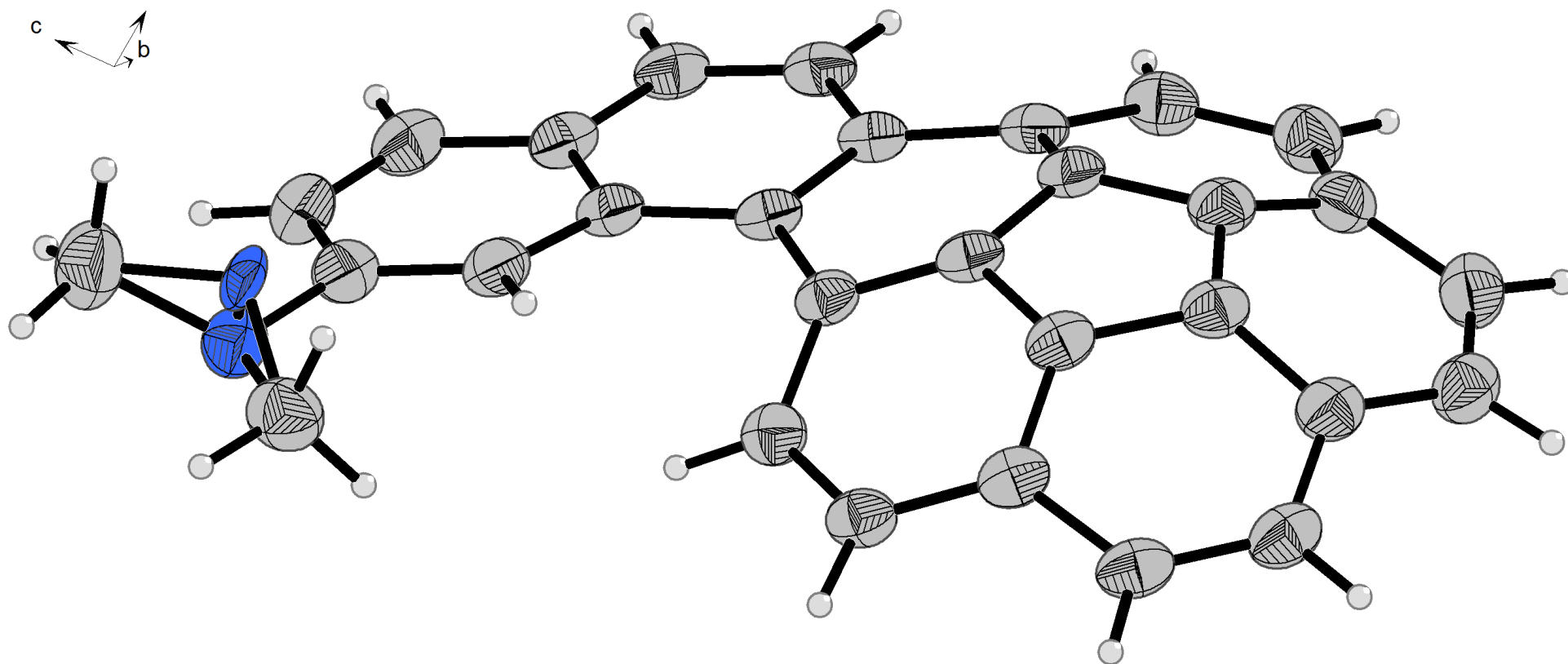
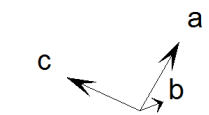
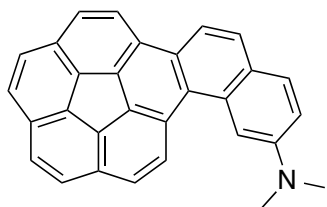
Yield: 93.2 mg, 93%; Mp: 215–216 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.69 (d, $J = 5.5$ Hz, 1H), 8.58 (dd, $J = 17.6, 8.7$ Hz, 2H), 8.27 (d, $J = 8.7$ Hz, 1H), 8.18 (dd, $J = 8.6, 0.9$ Hz, 1H), 7.92 (dd, $J = 8.7, 4.6$ Hz, 2H), 7.86 – 7.73 (m, 5H). ^{13}C NMR (101 MHz, $\text{CDCl}_3/\text{CS}_2$) δ 139.98, 137.72, 137.29, 135.26, 134.92, 134.88, 134.29, 130.79, 130.60, 130.24, 130.14, 129.05, 128.78, 128.60, 127.71, 127.69, 127.19, 127.17, 126.92, 126.85, 126.76, 124.94, 124.36, 121.55, 121.41. HRMS (MALDI-TOF) m/z calcd for $\text{C}_{26}\text{H}_{12}\text{S}$ $[\text{M}]^+$: 356.0654, found: 356.0651.



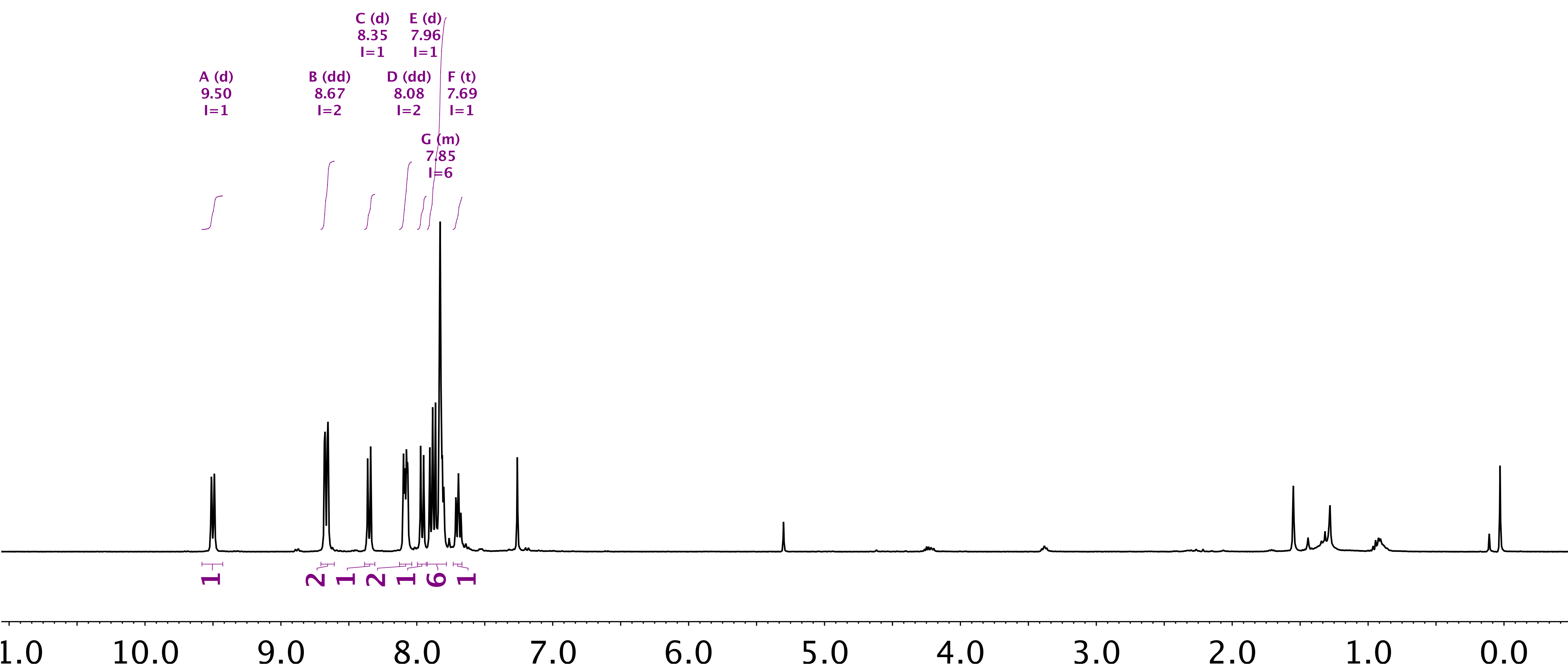
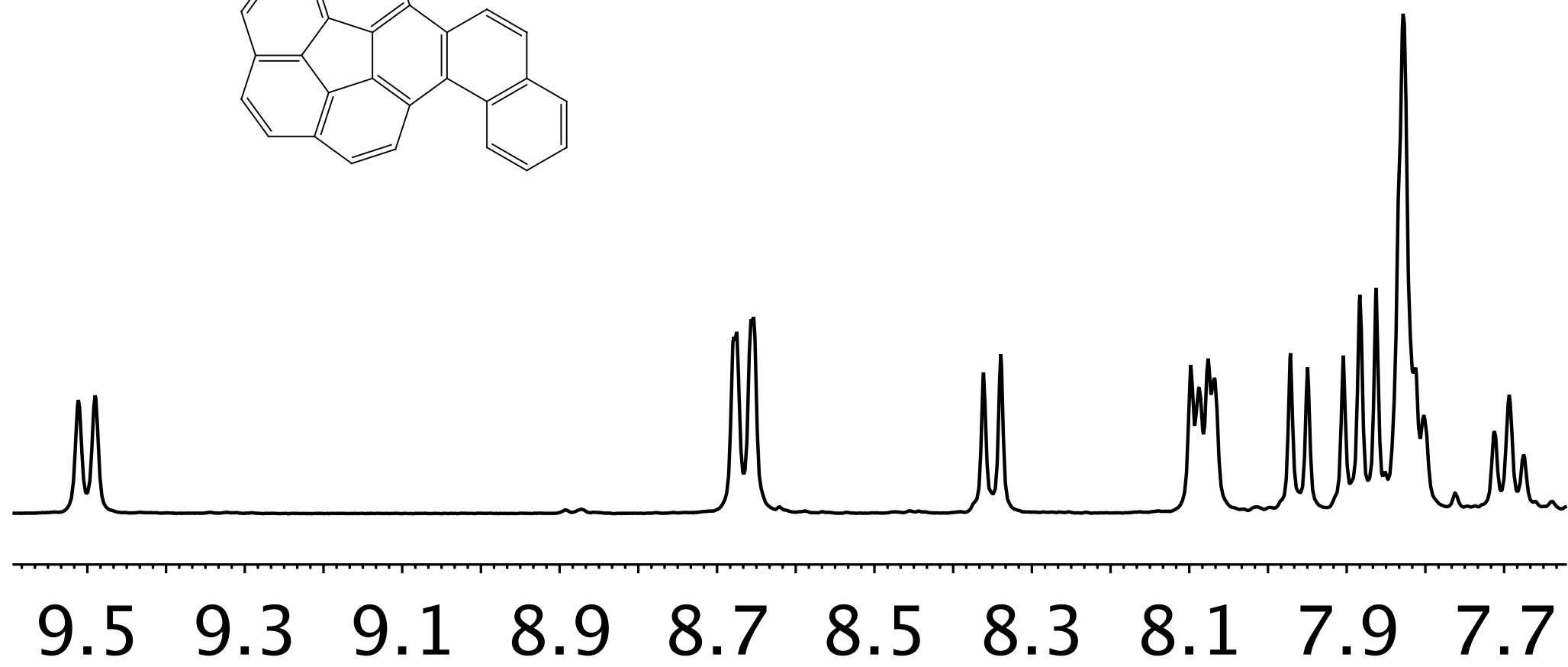
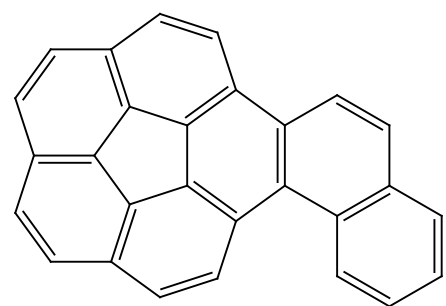
Yield: 67 mg, 67%; Mp: 289–290 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.59 – 9.44 (m, 1H), 8.67 (d, $J = 8.5$ Hz, 1H), 8.55 (d, $J = 8.7$ Hz, 1H), 8.34 (d, $J = 8.8$ Hz, 1H), 8.13 (d, $J = 8.5$ Hz, 1H), 8.04 – 7.95 (m, 2H), 7.87 (d, $J = 8.7$ Hz, 1H), 7.84 – 7.78 (m, 3H), 7.70 (d, $J = 8.7$ Hz, 1H), 7.61 – 7.54 (m, 2H). ^{13}C NMR (101 MHz, $\text{CDCl}_3/\text{CS}_2$) δ 140.39, 139.96, 138.36, 136.47, 136.07, 135.91, 135.36, 135.33, 133.03, 132.22, 131.09, 130.70, 130.59, 130.29, 128.52, 128.49, 128.15, 127.59, 127.42, 127.28, 127.02, 126.89, 126.81, 125.79, 125.32, 124.55, 123.86, 123.31, 123.05, 121.80. HRMS (MALDI-TOF) m/z calcd for $\text{C}_{30}\text{H}_{14}\text{S}$ $[\text{M}]^+$: 406.0811, found: 406.0816.

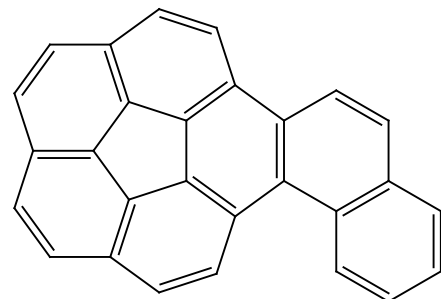
(1) Rajeshkumar, V.; Lee, Y. T.; Stuparu, M. C. *Eur. J. Org. Chem.* **2016**, No. 1, 36.





^1H NMR (400 MHz, CDCl_3) δ 9.50 (d, $J = 8.5$ Hz, 1H), 8.67 (dd, $J = 8.8, 2.0$ Hz, 2H), 8.35 (d, $J = 8.7$ Hz, 1H), 8.08 (dd, $J = 8.5, 3.8$ Hz, 2H), 7.96 (d, $J = 8.7$ Hz, 1H), 7.92 – 7.78 (m, 6H), 7.69 (t, $J = 7.5$ Hz, 1H).



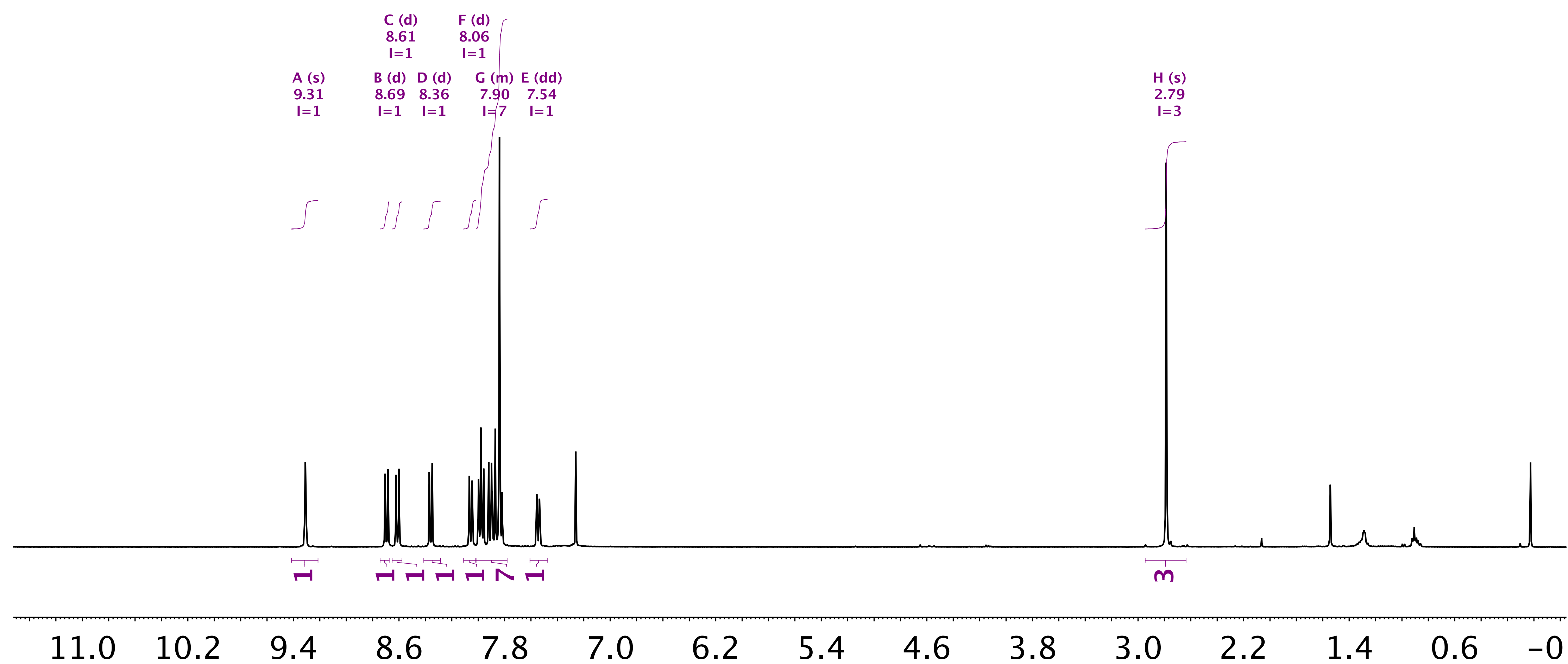
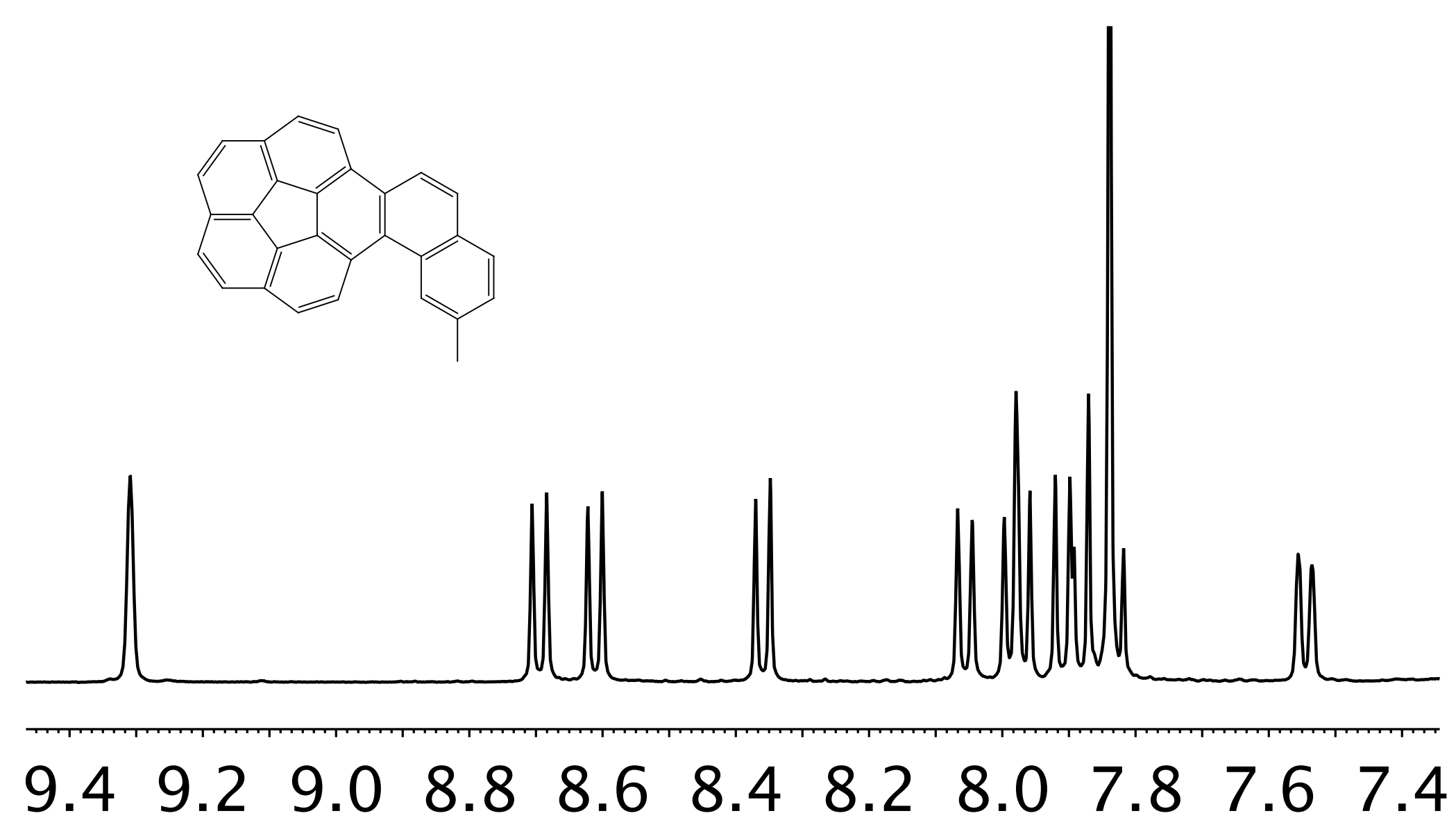
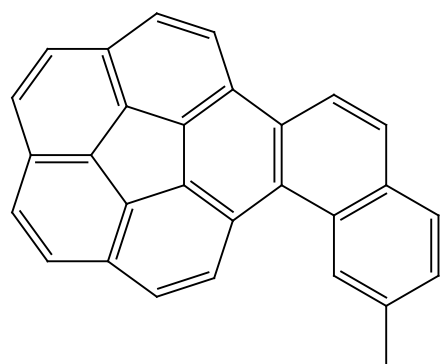


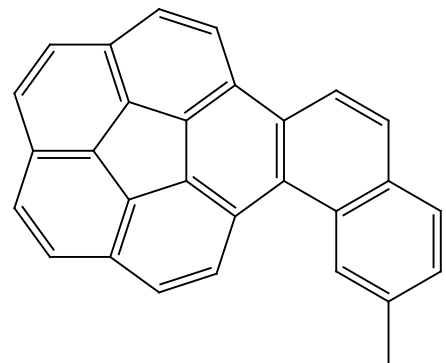
^{13}C NMR (101 MHz, CDCl_3) δ 137.89, 135.60, 135.35, 135.27, 134.89, 133.38, 131.91, 131.29, 131.21, 131.11, 130.79, 130.72, 129.13, 128.93, 128.85, 128.81, 128.58, 127.97, 127.94, 127.88, 127.41, 127.35, 127.10, 126.96, 126.88, 126.40, 124.61, 122.77.

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122.77

175 165 155 145 135 125 115 105 95 85 75 65 55 45 35 25 15 5

¹H NMR (400 MHz, CDCl₃) δ 9.31 (s, 1H), 8.69 (d, *J* = 8.8 Hz, 1H), 8.61 (d, *J* = 8.6 Hz, 1H), 8.36 (d, *J* = 8.7 Hz, 1H), 8.06 (d, *J* = 8.7 Hz, 1H), 8.02 – 7.78 (m, 7H), 7.54 (dd, *J* = 8.2, 1.5 Hz, 1H), 2.79 (s, 3H).



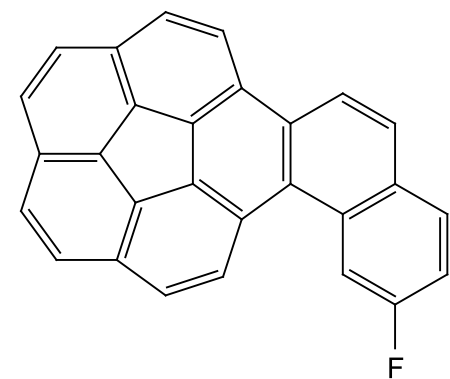


^{13}C NMR (101 MHz, CDCl_3) δ 137.92, 136.71, 135.67, 135.31, 135.27, 134.92, 132.11, 131.56, 131.34, 131.12, 130.82, 130.80, 130.71, 129.30, 128.99, 128.96, 128.72, 128.45, 127.90, 127.88, 127.85, 127.74, 127.35, 127.06, 126.96, 124.66, 121.89, 22.53.

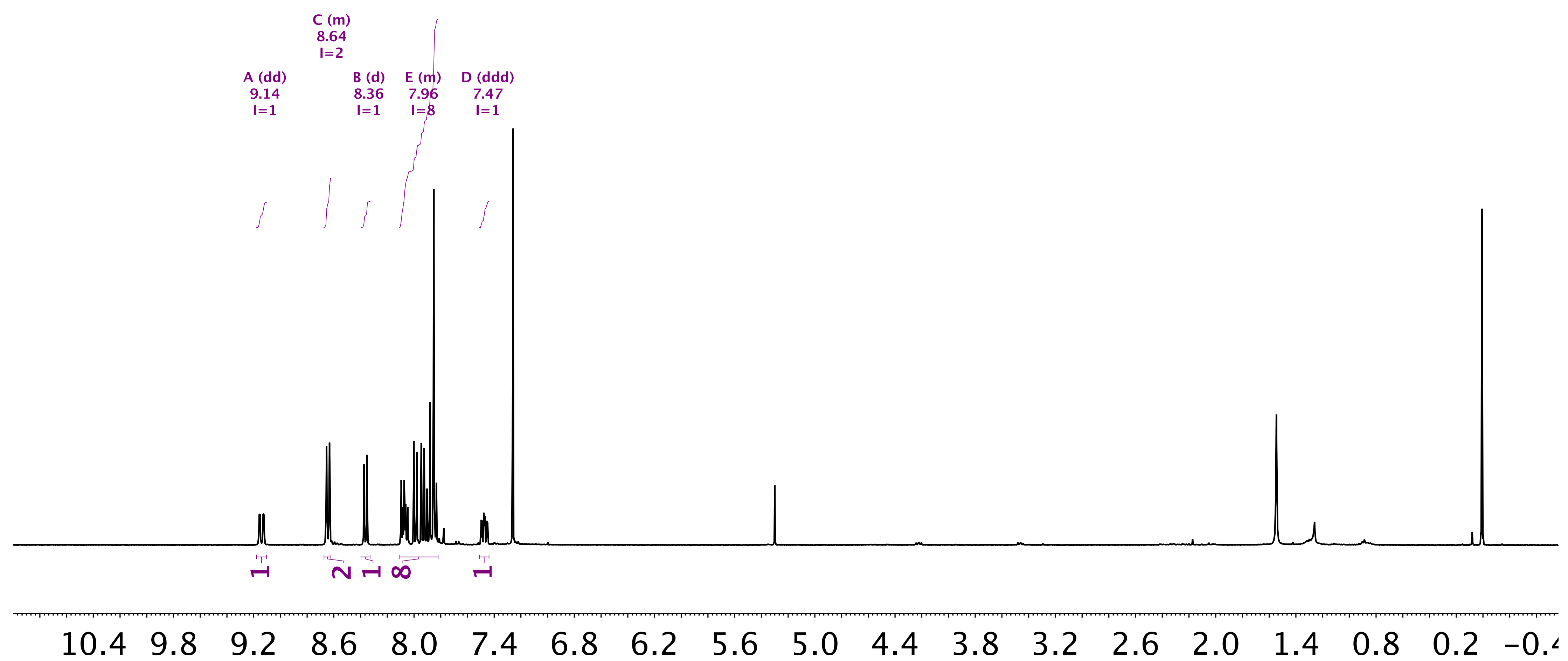
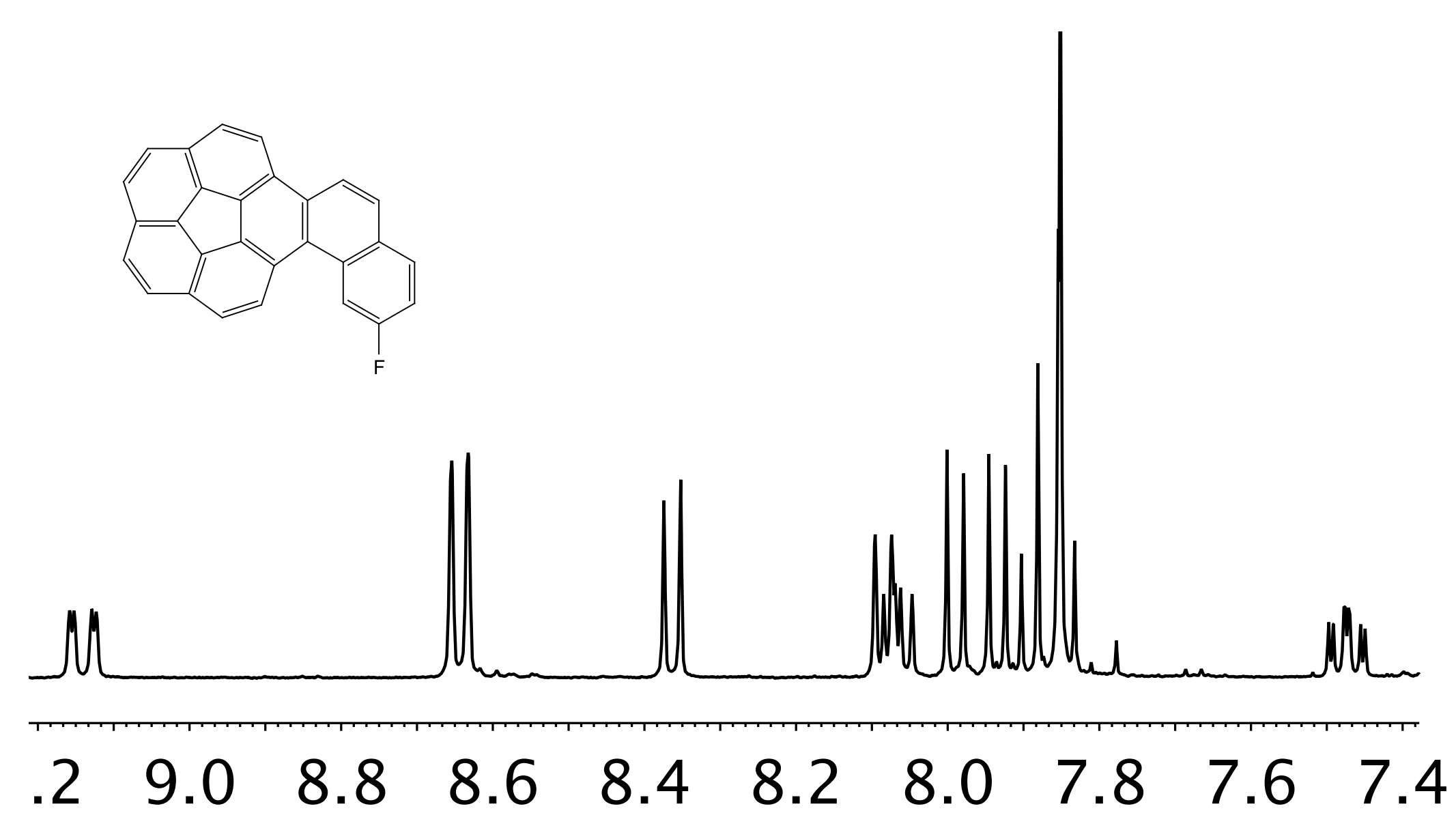
137.92
136.71
135.67
135.31
135.27
134.92
132.11
131.56
131.34
131.12
130.82
130.80
130.71
129.30
128.99
128.96
128.72
128.45
127.90
127.88
127.85
127.74
127.35
127.06
126.96
124.66
121.89

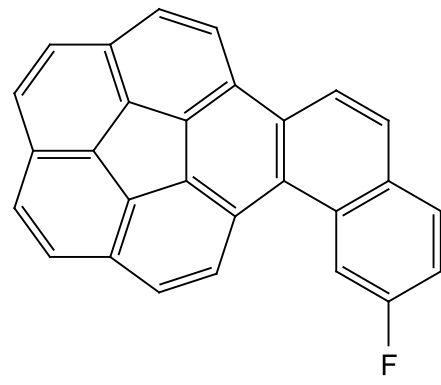
22.53

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.14 (dd, $J = 11.7, 2.5$ Hz, 1H), 8.67 – 8.62 (m, 2H), 8.36 (d, $J = 8.8$ Hz, 1H), 8.11 – 7.82 (m, 8H), 7.47 (ddd, $J = 8.8, 7.9, 2.5$ Hz, 1H).





^{13}C NMR (101 MHz, CDCl_3) δ 161.66 (d, $J = 246.70$ Hz), 137.84, 135.52, 135.19, 134.72, 132.76 (d, $J = 9.20$ Hz), 131.82, 131.06, 131.01, 130.92, 130.81, 130.78, 130.41 (d, $J = 7.0$ Hz), 130.11, 128.80, 128.53, 128.14, 128.04, 127.86, 127.52, 127.38, 127.27, 127.16, 126.90, 124.44, 122.15 (d, $J = 2.68$ Hz), 116.05 (d, $J = 24.87$ Hz), 112.47 (d, $J = 22.50$ Hz).

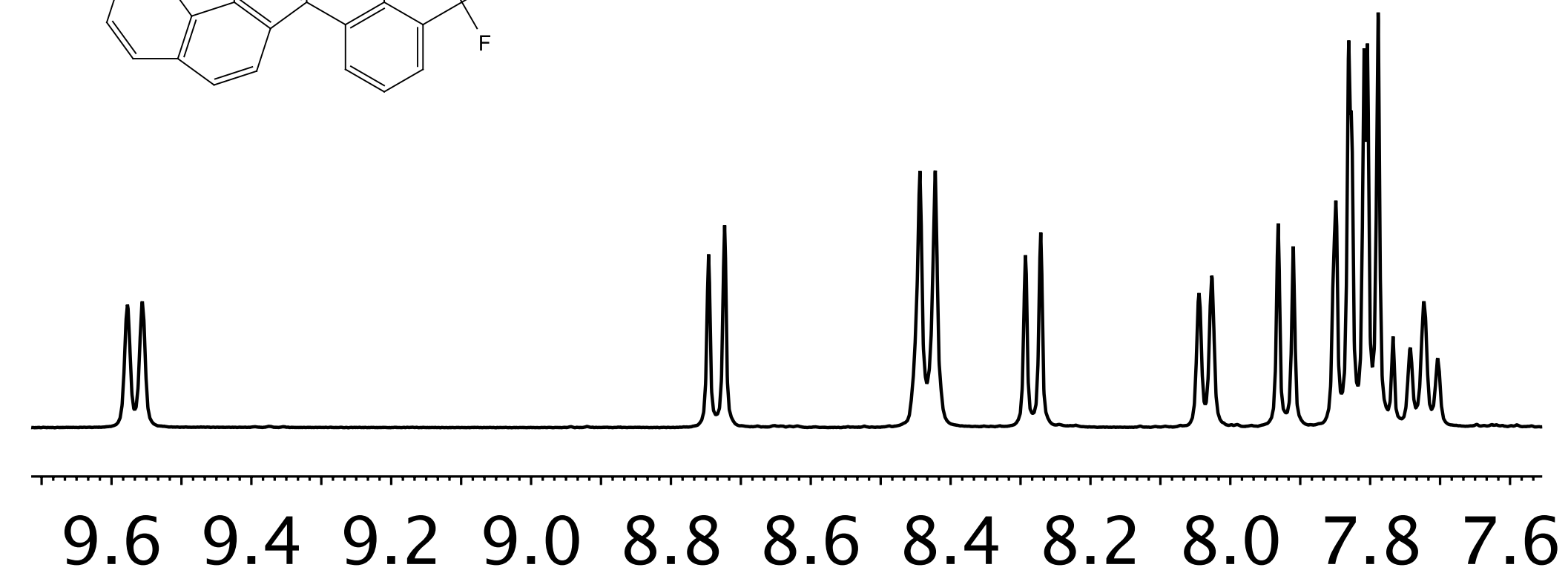
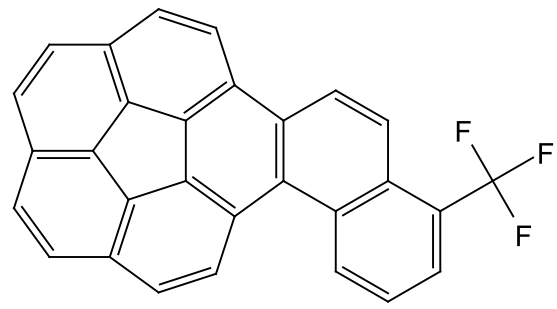
138.00
135.68
135.55
135.35
134.88
132.96
132.87
131.98
131.22
131.17
131.08
130.97
130.93
130.58
130.53
130.27
128.96
128.69
128.30
128.19
128.02
127.68
127.53
127.43
127.32
127.06
124.59
122.17
122.15

116.34
116.09
112.74
112.52

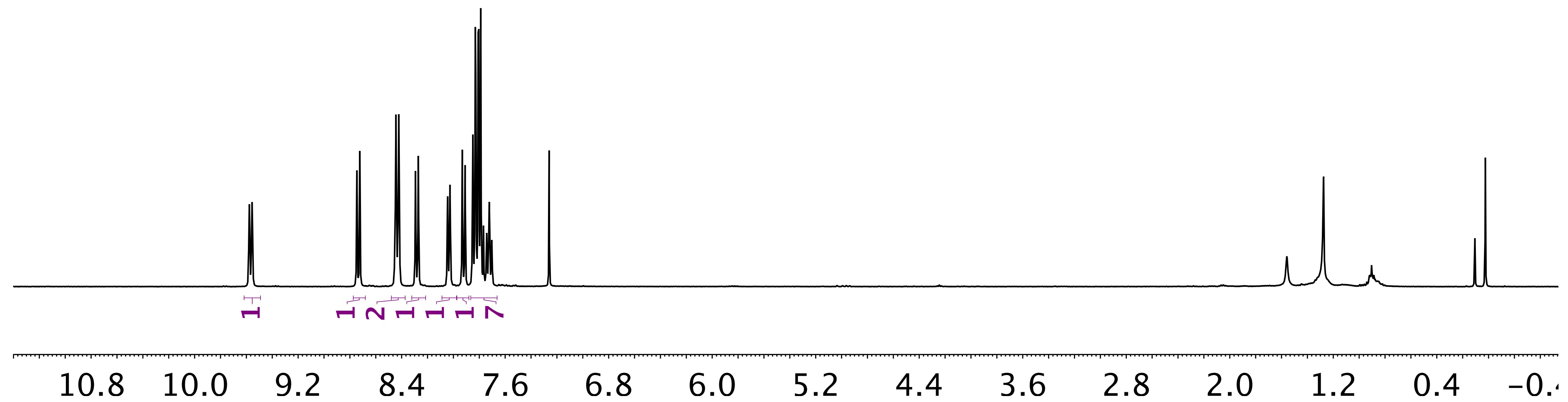
163.04
160.60

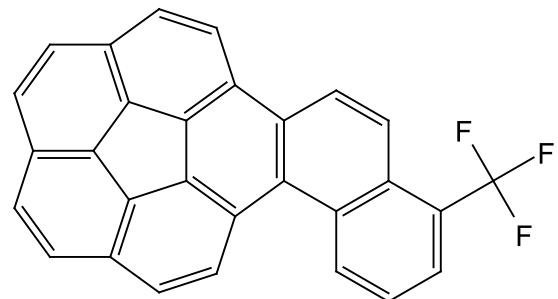
175 165 155 145 135 125 115 105 95 85 75 65 55 45 35 25 15 5

^1H NMR (400 MHz, CDCl_3) δ 9.57 (d, $J = 8.6$ Hz, 1H), 8.73 (d, $J = 9.1$ Hz, 1H), 8.43 (d, $J = 8.8$ Hz, 2H), 8.28 (d, $J = 8.7$ Hz, 1H), 8.04 (d, $J = 7.3$ Hz, 1H), 7.92 (d, $J = 8.7$ Hz, 1H), 7.87 – 7.66 (m, 7H).



	C (d)	E (d)	
	8.43	8.04	
	I=2	I=1	
A (d)	B (d)	D (d)	F (d)
9.57	8.73	8.28	7.92
I=1	I=1	I=1	I=1
		G (m)	
		7.81	
		I=7	





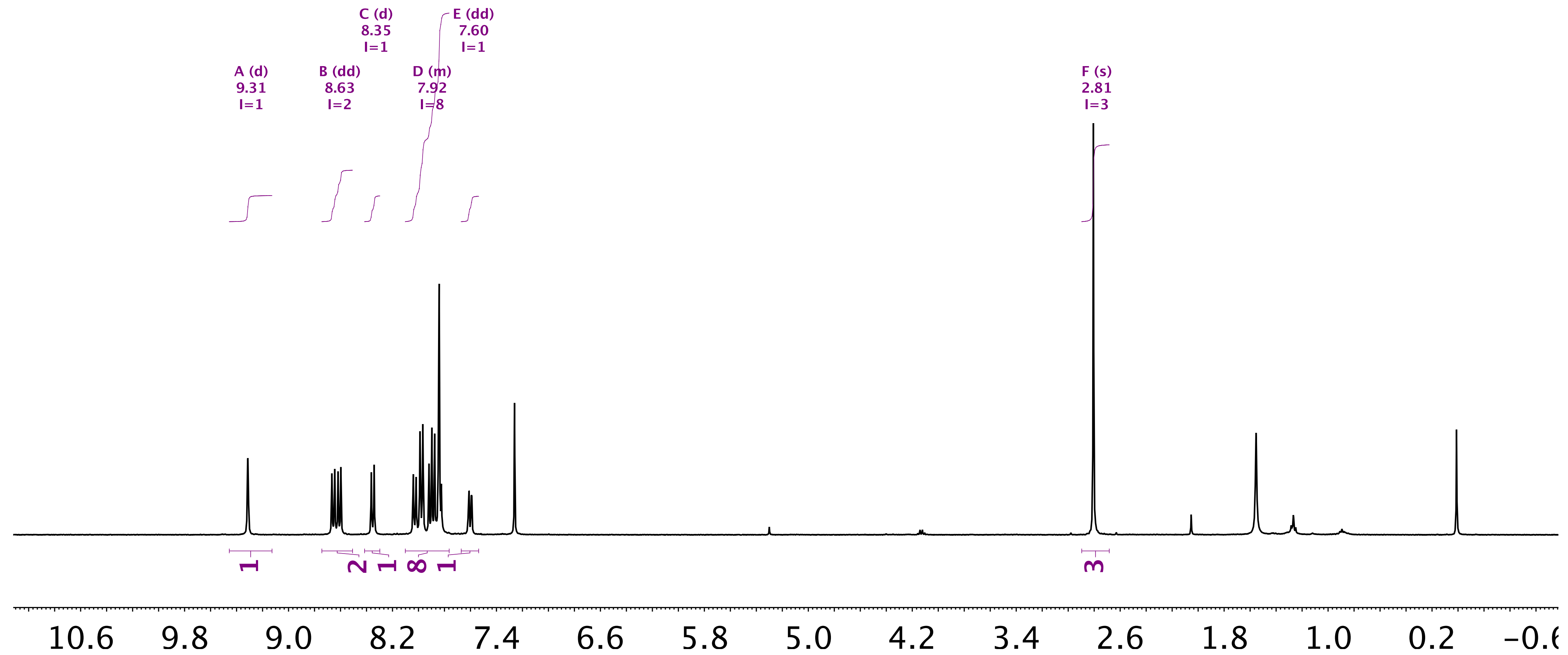
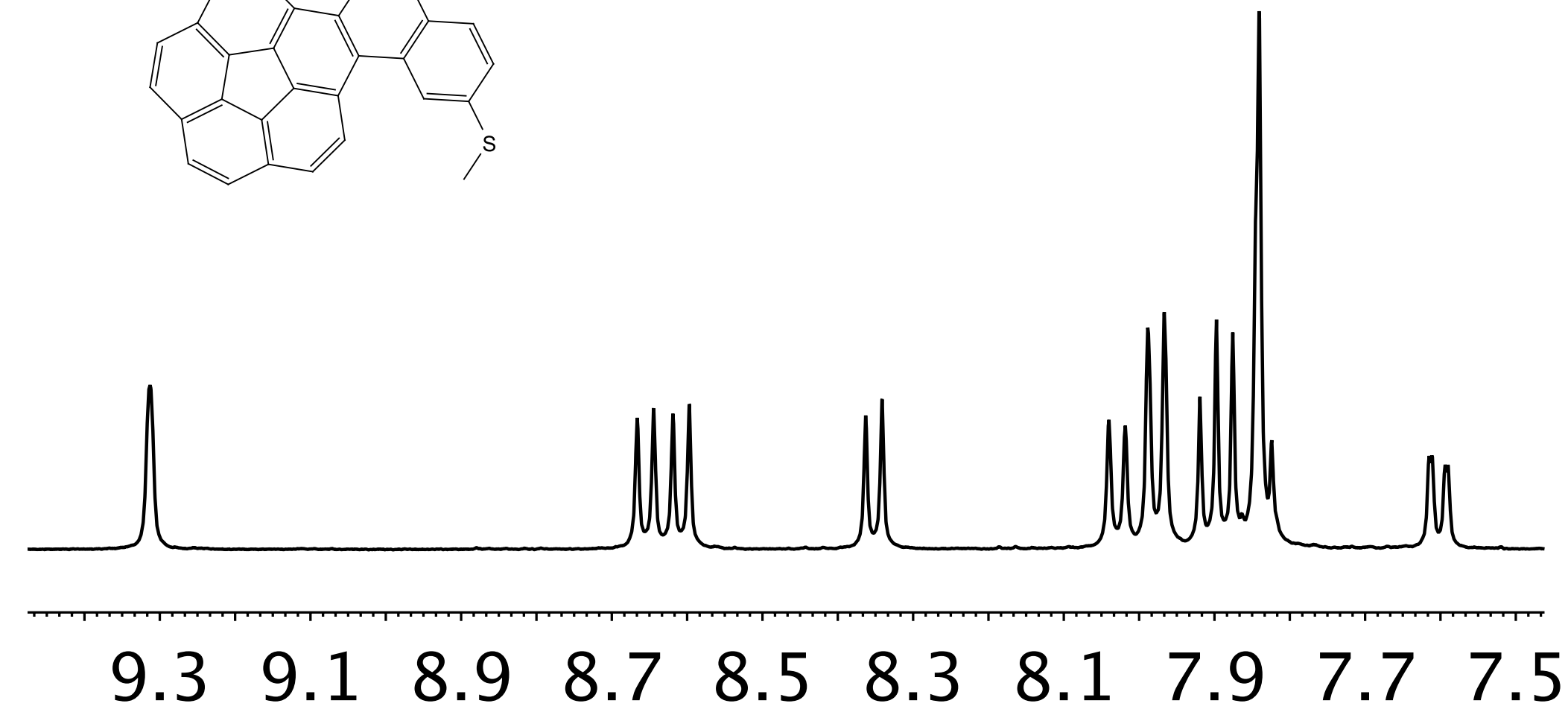
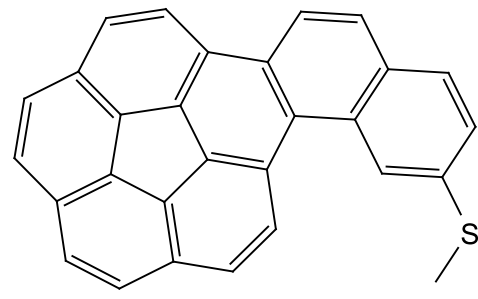
^{13}C NMR (101 MHz, CDCl_3) δ 137.90, 135.49, 134.75, 133.14, 132.51, 131.49, 131.13, 130.94, 130.82, 129.13, 128.72, 128.49, 128.23, 128.13, 127.68, 127.44, 127.31, 126.95, 125.03, 124.96, 124.90, 124.85, 124.79, 124.55, 124.43, 123.37, 123.35.

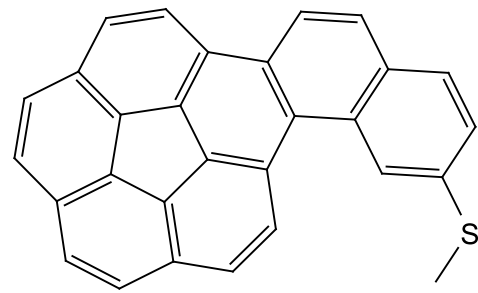
A (q)
124.88

137.90
135.49
134.75
133.14
132.51
131.49
131.13
130.94
130.82
129.13
128.72
128.49
128.23
128.13
127.68
127.44
127.31
126.95
125.03
124.96
124.90
124.85
124.79
124.55
124.43
123.37
123.35

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

^1H NMR (400 MHz, CDCl_3) δ 9.31 (d, $J = 1.8$ Hz, 1H), 8.63 (dd, $J = 18.9, 8.7$ Hz, 2H), 8.35 (d, $J = 8.7$ Hz, 1H), 8.10 – 7.76 (m, 8H), 7.60 (dd, $J = 8.5, 1.8$ Hz, 1H), 2.81 (s, 3H).





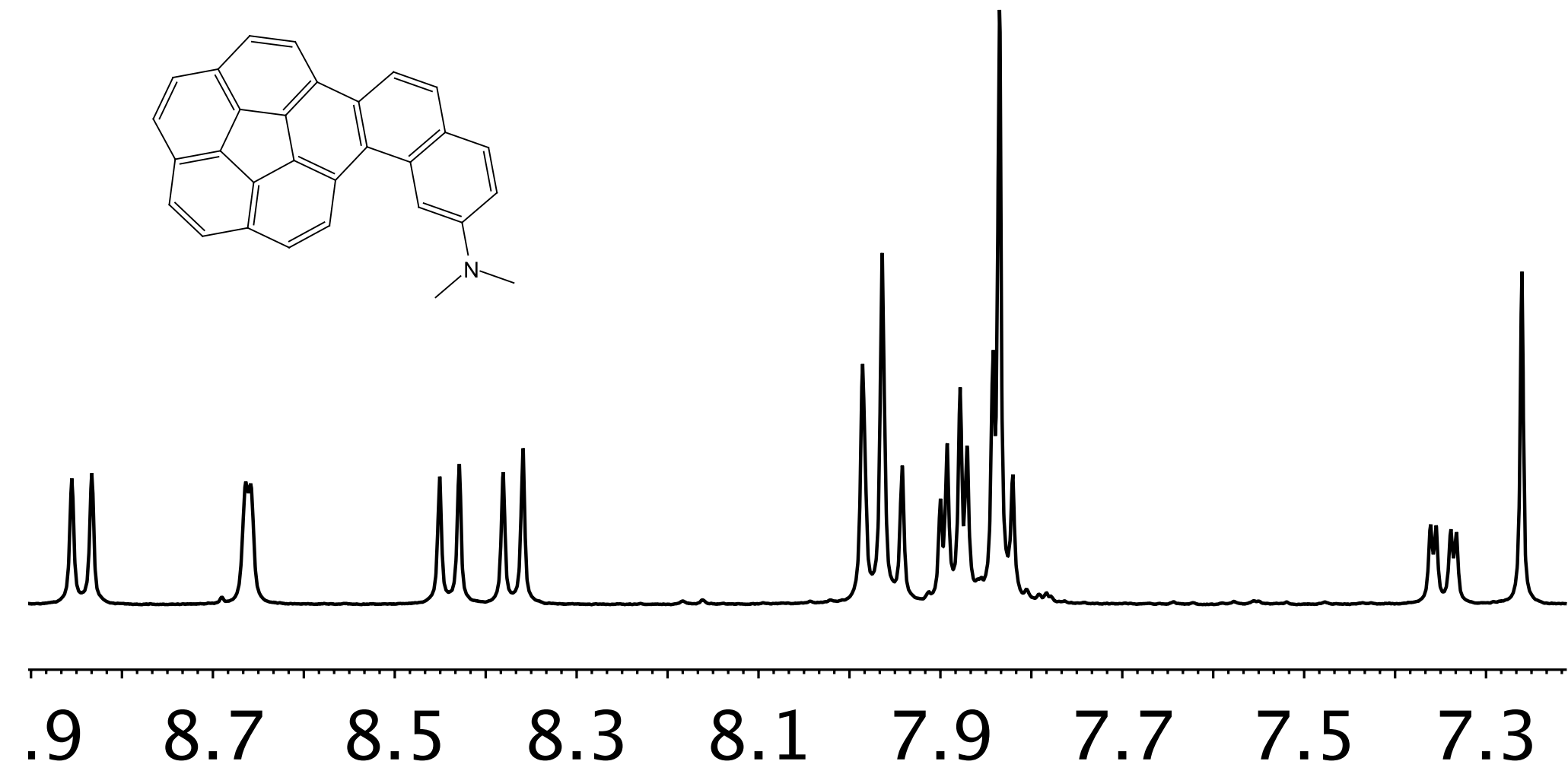
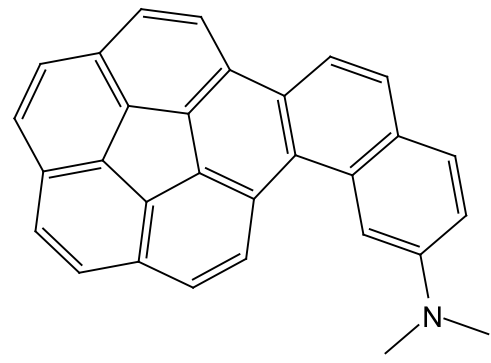
^{13}C NMR (101 MHz, CDCl_3) δ 137.54, 135.70, 135.42, 135.37, 134.91, 132.39, 131.81, 131.20, 131.17, 130.91, 130.83, 130.34, 129.16, 129.08, 128.81, 128.40, 128.13, 127.98, 127.68, 127.47, 127.42, 127.20, 127.02, 125.89, 124.79, 124.64, 122.19, 16.40.

137.54
135.70
135.42
135.37
134.91
132.39
131.81
131.20
131.17
130.91
130.83
130.34
129.16
129.08
128.81
128.40
128.13
127.98
127.68
127.47
127.42
127.20
127.02
125.89
124.79
124.64
122.19

16.40

90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

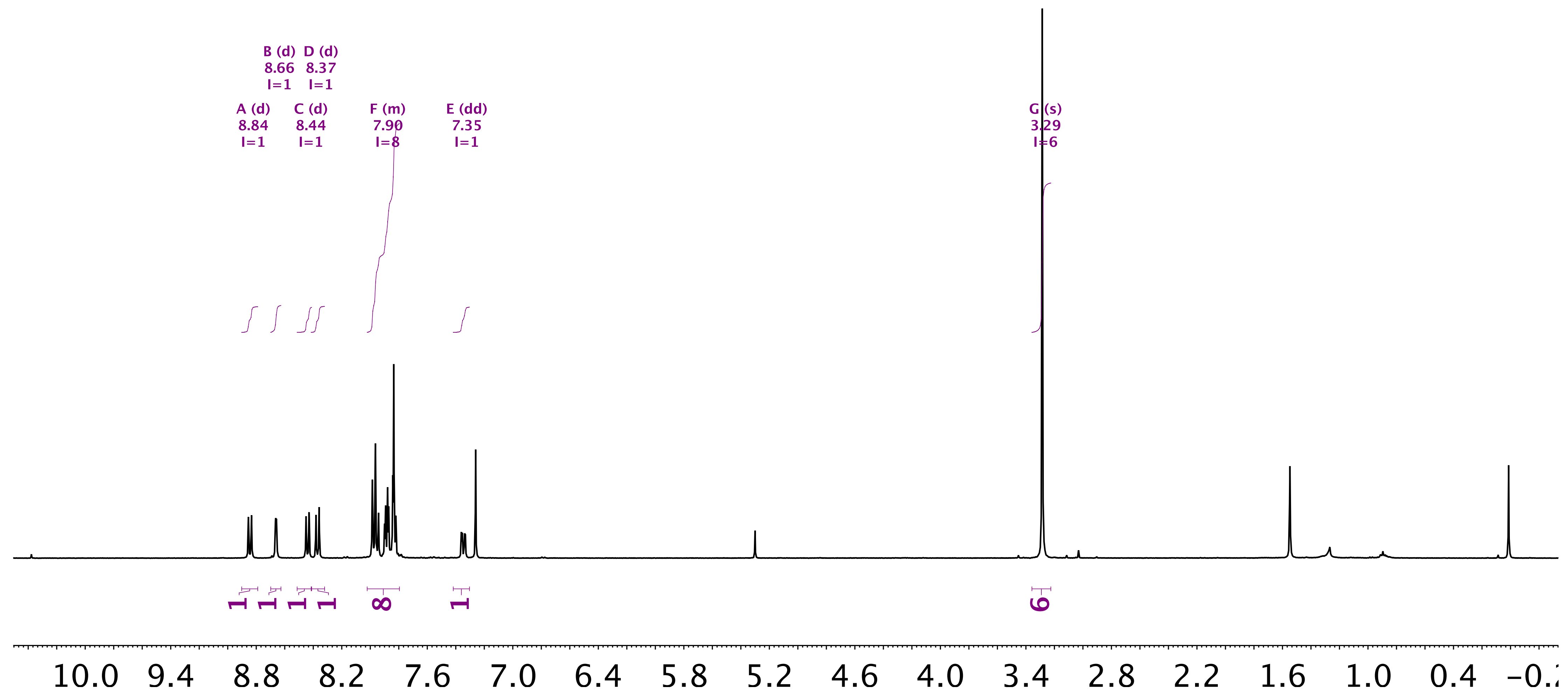
¹H NMR (400 MHz, CDCl₃) δ 8.84 (d, *J* = 8.8 Hz, 1H), 8.66 (d, *J* = 2.5 Hz, 1H), 8.44 (d, *J* = 8.6 Hz, 1H), 8.37 (d, *J* = 8.7 Hz, 1H), 8.02 – 7.80 (m, 8H), 7.35 (dd, *J* = 8.9, 2.5 Hz, 1H), 3.29 (s, 6H).

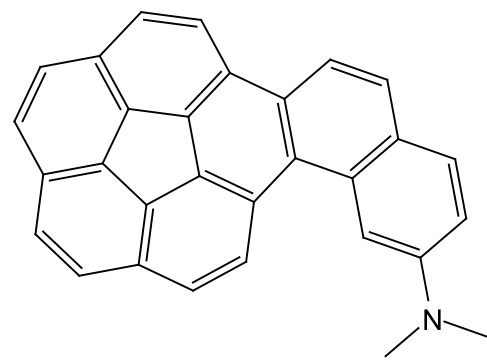


B (d) **D (d)**
8.66 8.37
I=1 I=1

A (d) **C (d)** **F (m)** **E (dd)**
8.84 8.44 7.90 7.35
I=1 I=1 I=8 I=1

G (s)
3.29
I=6





^{13}C NMR (101 MHz, CDCl_3) δ 149.65, 137.92, 135.80, 135.33, 135.09, 134.96, 133.43, 131.89, 131.14, 130.93, 130.67, 129.92, 129.83, 129.69, 129.34, 128.02, 127.73, 127.70, 127.35, 127.13, 126.98, 126.93, 126.27, 124.80, 118.87, 115.88, 108.47, 41.23.

137.92
135.80
135.33
135.09
134.96
133.43
131.89
131.14
130.93
130.67
129.92
129.83
129.69
129.34
128.02
127.73
127.70
127.35
127.13
126.98
126.93
126.27
124.80

149.65

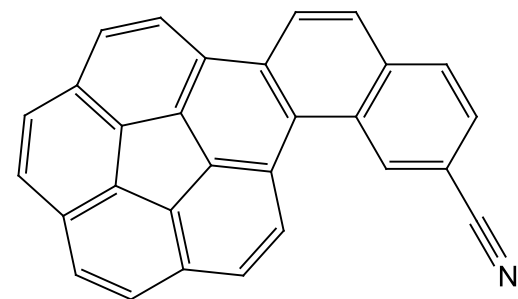
118.87

115.88

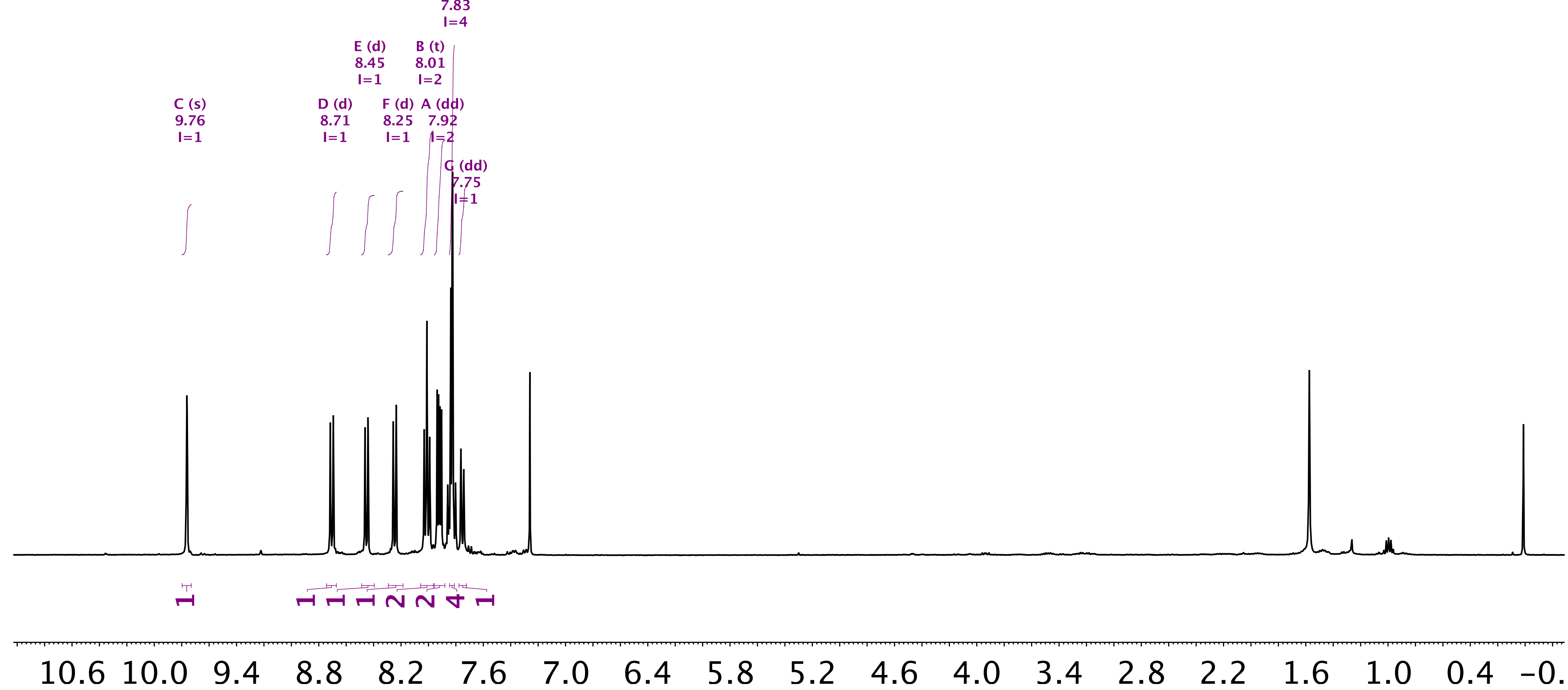
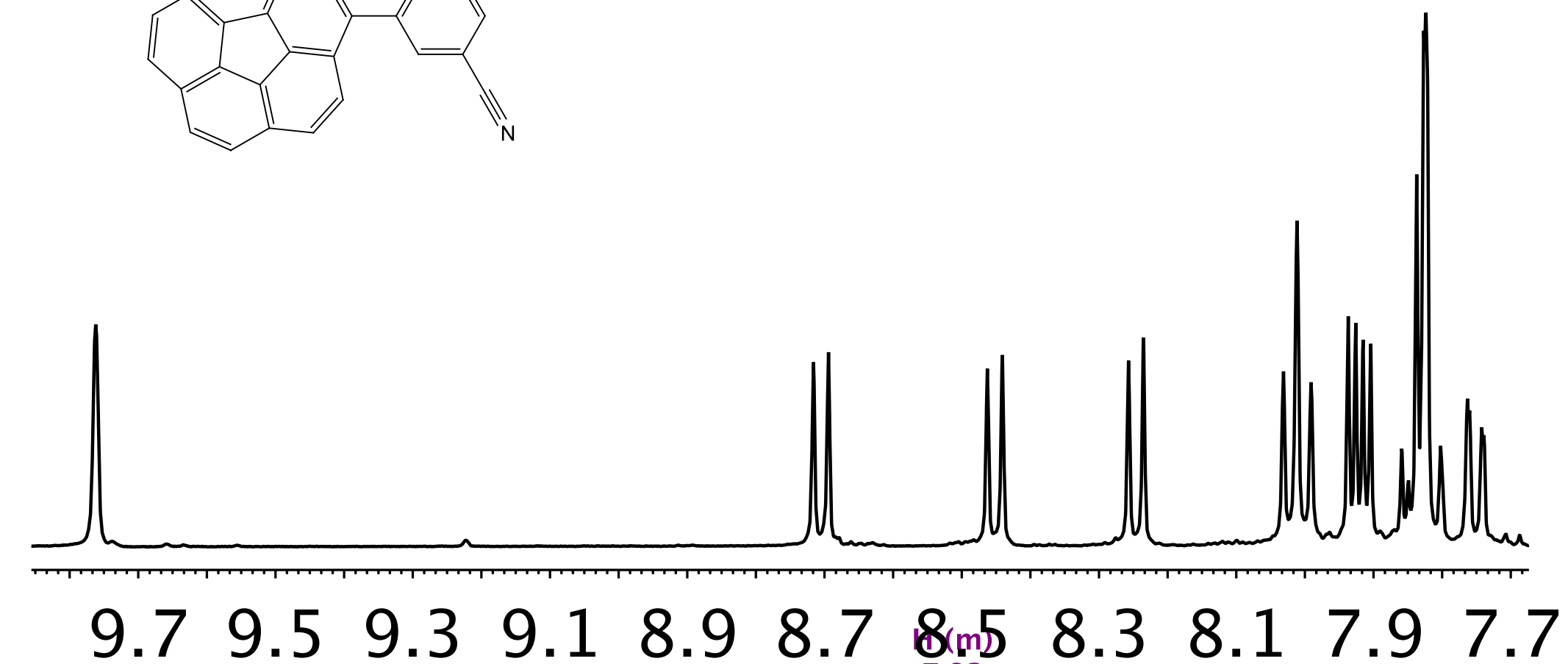
108.47

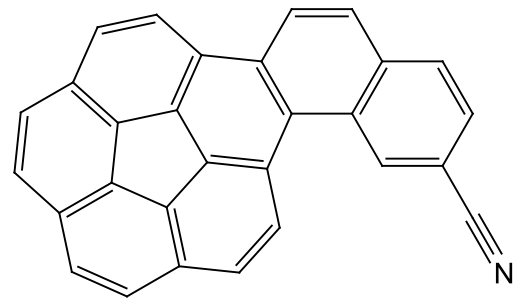
41.23

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 C



$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.76 (s, 1H), 8.71 (d, $J = 8.8$ Hz, 1H), 8.45 (d, $J = 8.7$ Hz, 1H), 8.25 (d, $J = 8.7$ Hz, 1H), 8.01 (t, $J = 8.1$ Hz, 2H), 7.92 (dd, $J = 8.7, 4.4$ Hz, 2H), 7.85 – 7.81 (m, 4H), 7.75 (dd, $J = 8.3, 1.5$ Hz, 1H).





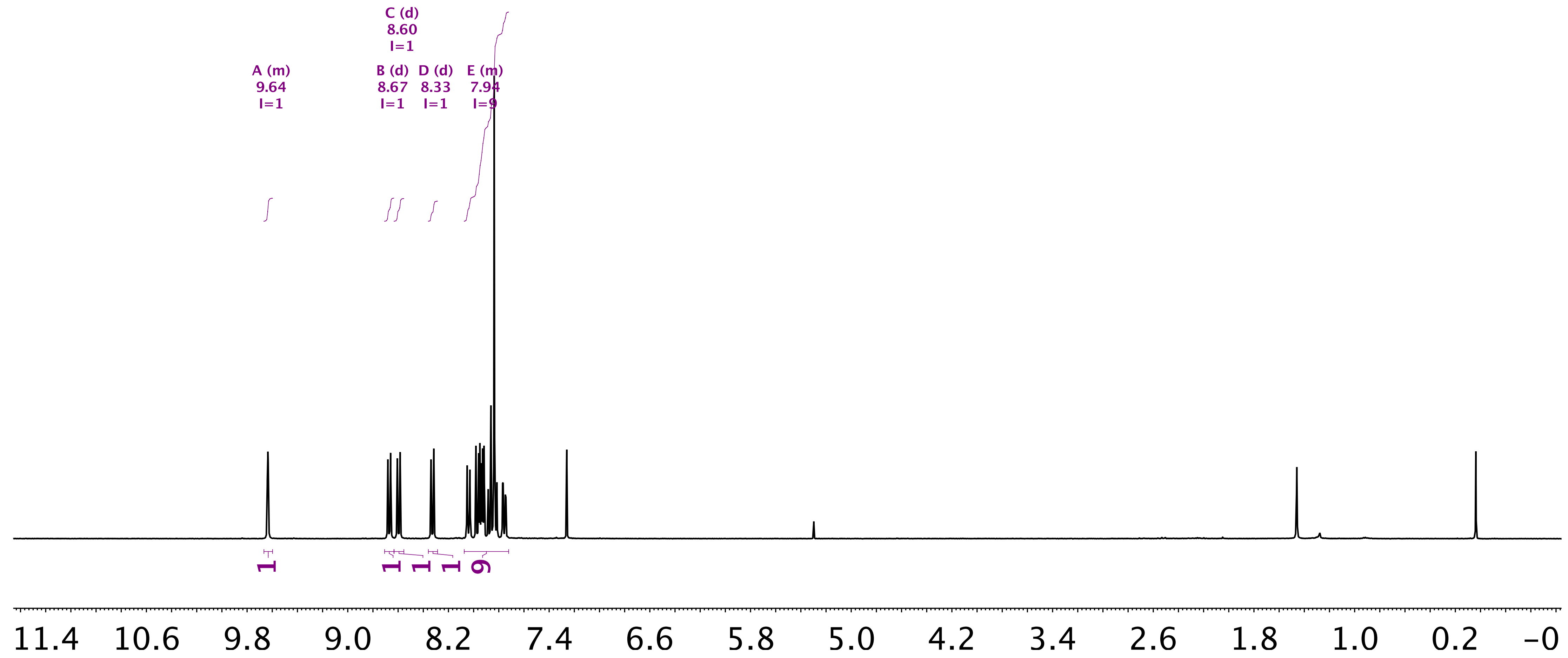
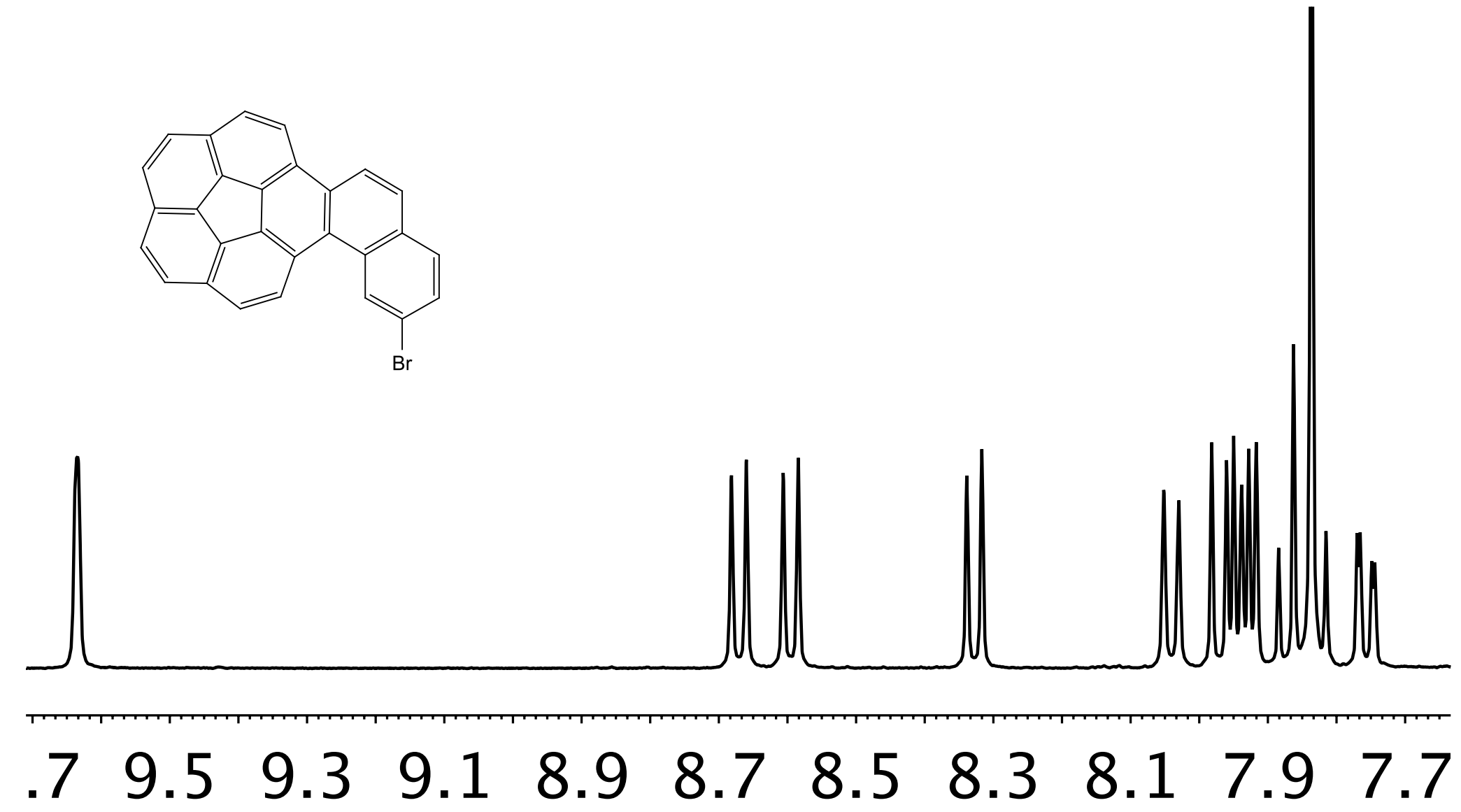
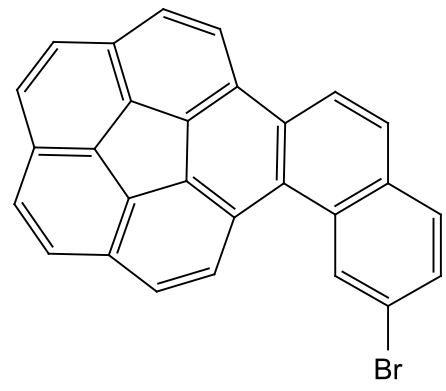
^{13}C NMR (101 MHz, CDCl_3) δ 137.85, 135.53, 135.47, 135.42, 134.70, 134.67, 134.25, 132.13, 131.18, 130.97, 130.95, 130.89, 129.89, 128.75, 128.21, 128.15, 127.92, 127.89, 127.84, 127.49, 127.45, 127.27, 127.09, 127.00, 126.01, 124.29, 119.81, 110.18.

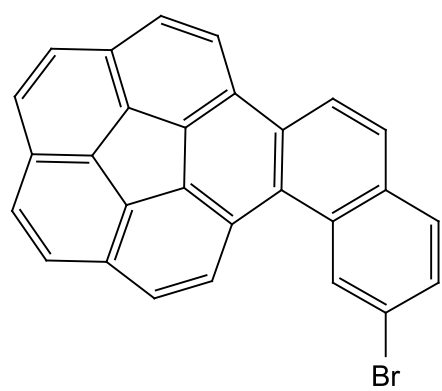
137.85
135.53
135.47
135.42
134.70
134.67
134.25
132.13
131.18
130.97
130.95
130.89
129.89
128.75
128.21
128.15
127.92
127.89
127.84
127.49
127.45
127.27
127.09
127.00
126.01
124.29
119.81

110.18

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

¹H NMR (400 MHz, CDCl₃) δ 9.67 – 9.60 (m, 1H), 8.67 (d, *J* = 8.7 Hz, 1H), 8.60 (d, *J* = 8.7 Hz, 1H), 8.33 (d, *J* = 8.8 Hz, 1H), 8.07 – 7.72 (m, 9H).

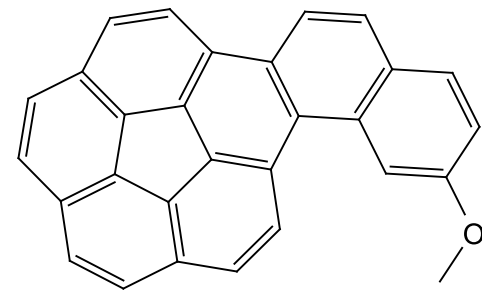




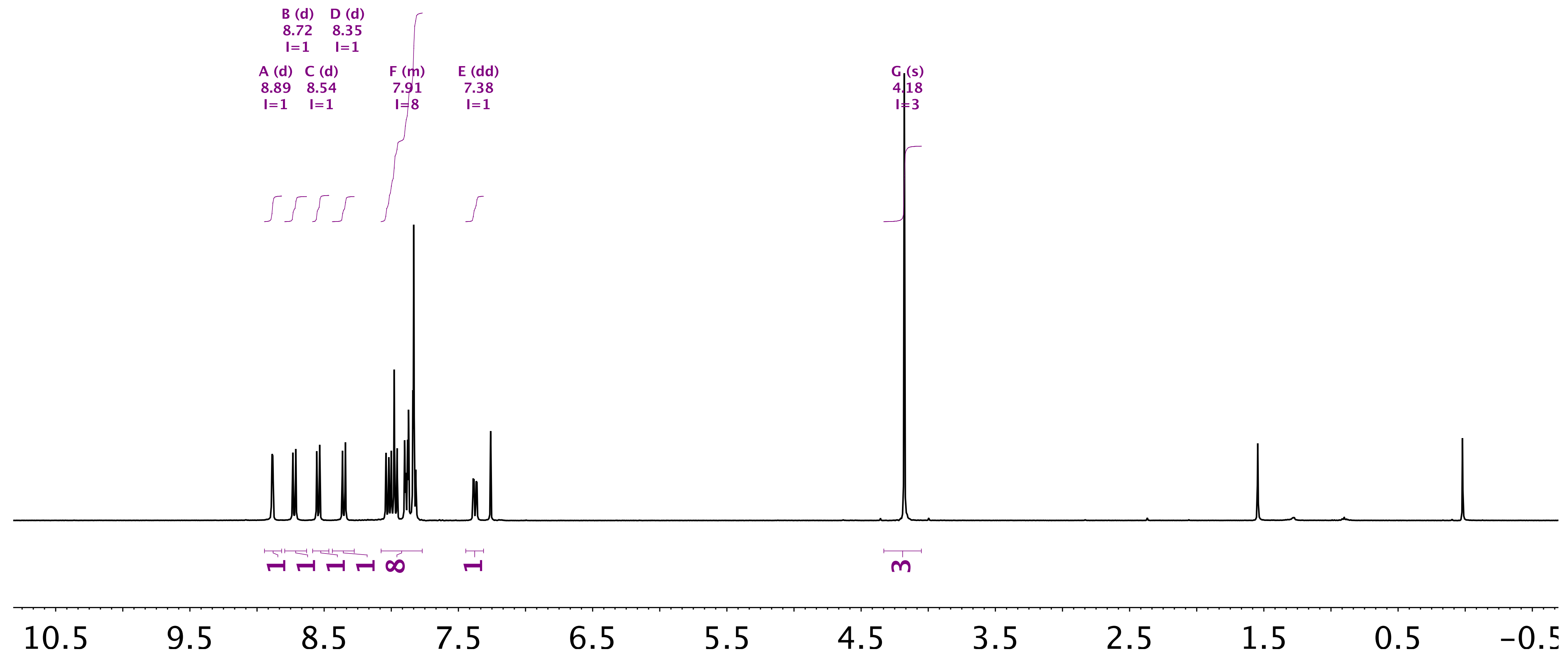
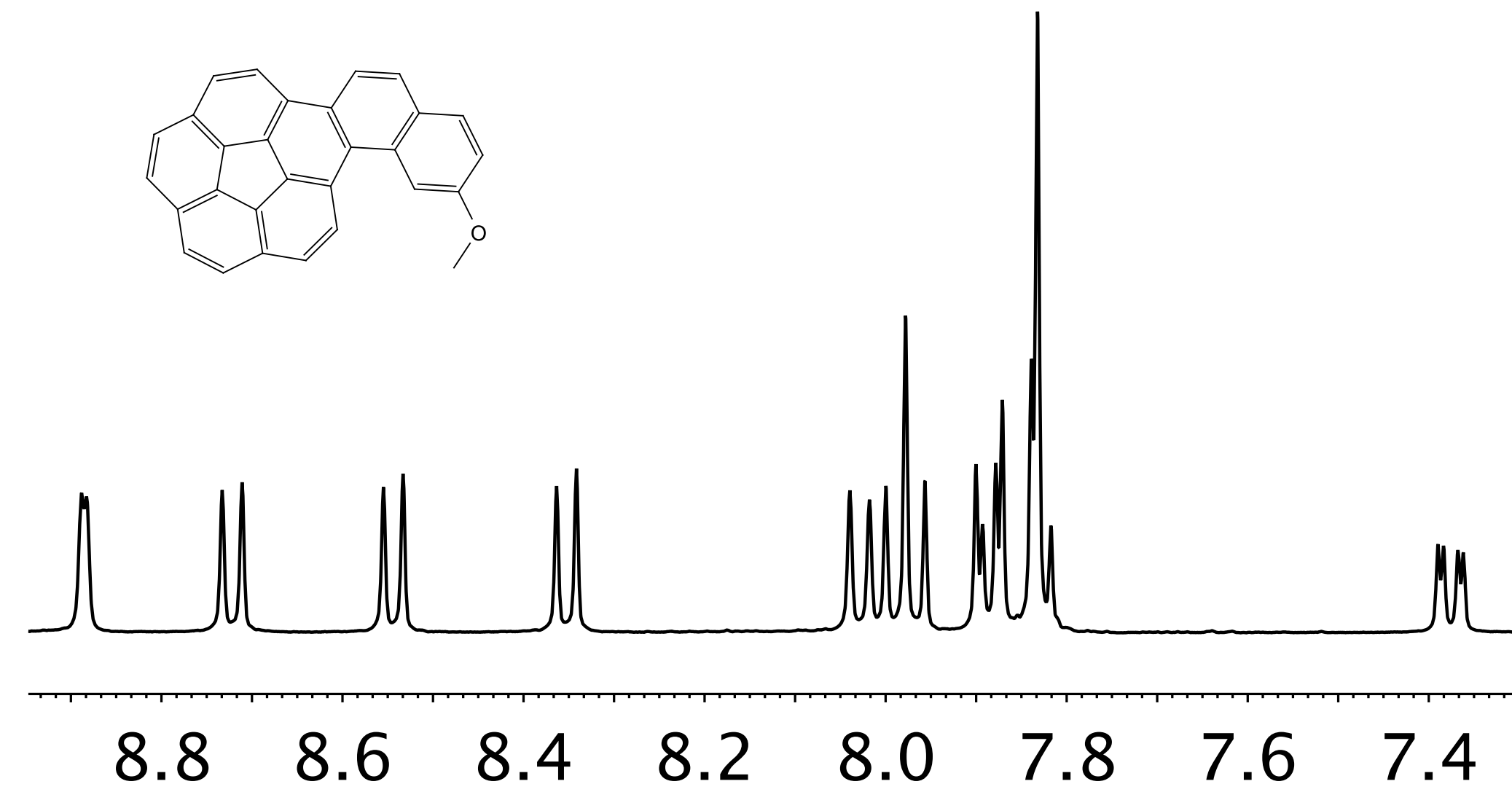
^{13}C NMR (101 MHz, $\text{CDCl}_3+\text{CS}_2$) δ 137.93, 135.55, 135.48, 135.40, 134.81, 132.96, 131.72, 131.61, 131.04, 130.79, 130.65, 130.25, 130.14, 129.56, 128.51, 128.30, 128.28, 127.93, 127.47, 127.44, 127.31, 127.20, 126.96, 124.37, 123.24, 121.44.

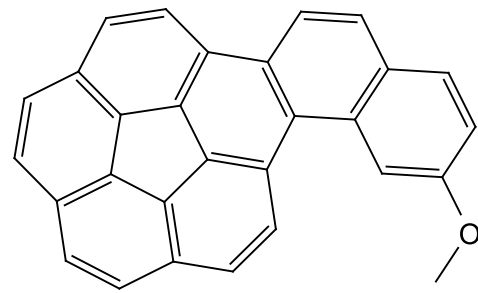
137.93
135.55
135.48
135.40
134.81
132.96
131.72
131.61
131.04
130.79
130.65
130.25
130.14
129.56
128.51
128.30
128.28
127.93
127.47
127.44
127.31
127.20
126.96
124.37
123.24
121.44

205 190 175 160 145 130 115 85 70 55 40 25 10 -



$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.89 (d, $J = 2.4$ Hz, 1H), 8.72 (d, $J = 8.8$ Hz, 1H), 8.54 (d, $J = 8.6$ Hz, 1H), 8.35 (d, $J = 8.7$ Hz, 1H), 8.08 – 7.77 (m, 8H), 7.38 (dd, $J = 8.8, 2.5$ Hz, 1H), 4.18 (s, 3H).





^{13}C NMR (101 MHz, CDCl_3) δ 158.79, 137.95, 135.73, 135.37, 135.23, 134.89, 133.17, 131.79, 131.16, 130.93, 130.76, 130.35, 130.33, 129.38, 129.03, 128.63, 128.05, 127.96, 127.87, 127.71, 127.40, 127.34, 127.10, 126.96, 124.68, 120.57, 118.00, 108.50, 55.86.

137.95
135.73
135.37
135.23
134.89
133.17
131.79
131.16
130.93
130.76
130.35
130.33
129.38
129.03
128.63
128.05
127.96
127.87
127.71
127.40
127.34
127.10
126.96
124.68
120.57
118.00

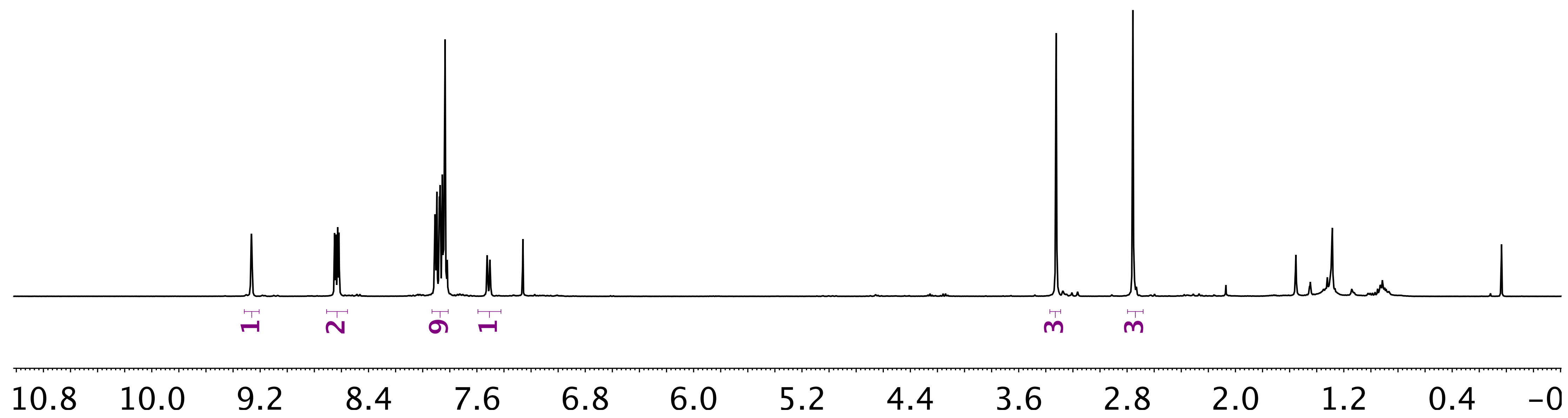
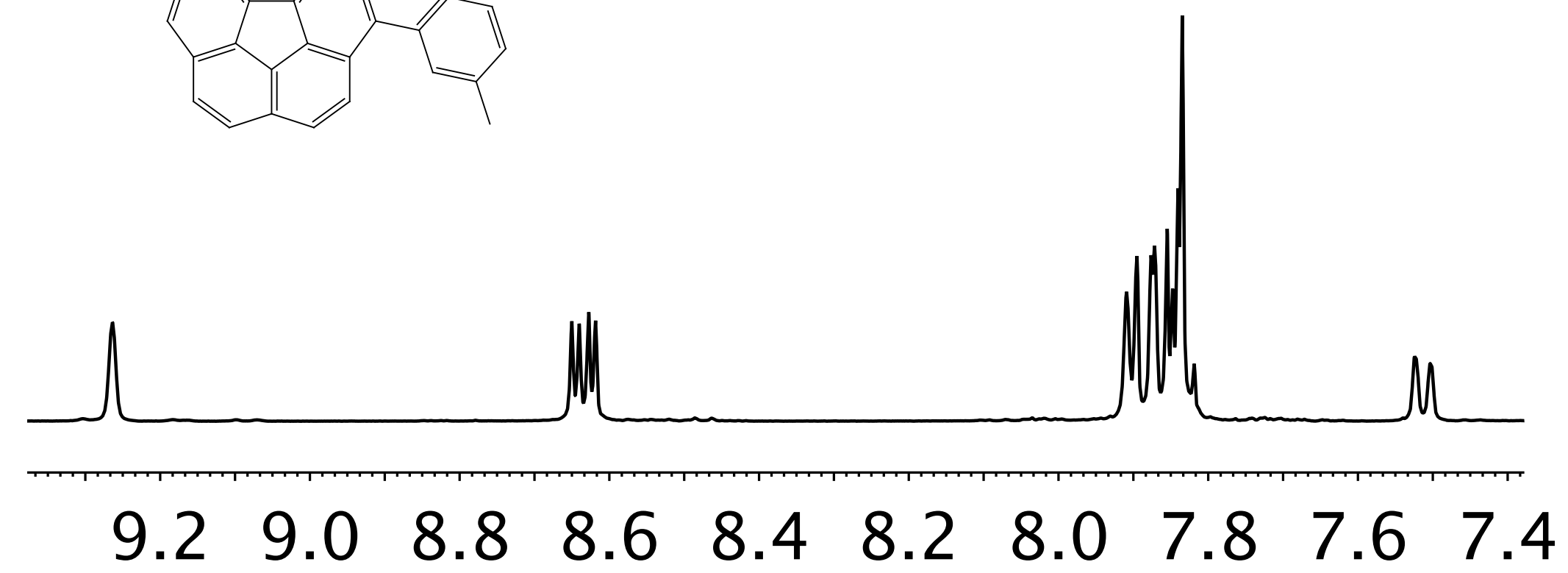
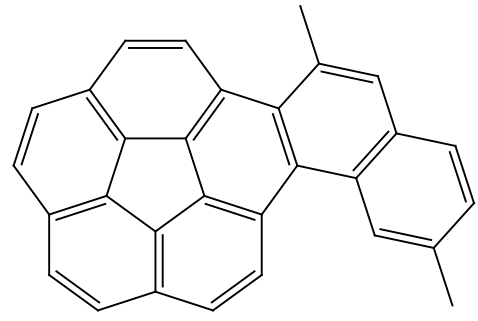
158.79

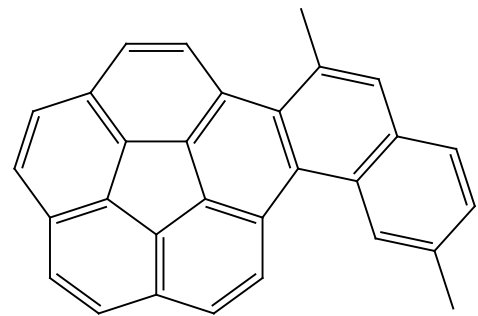
108.50

55.86

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 C

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.26 (s, 1H), 8.63 (dd, $J = 8.8, 3.8$ Hz, 2H), 7.93 – 7.81 (m, 9H), 7.51 (dd, $J = 8.2, 1.5$ Hz, 1H), 3.32 (s, 3H), 2.76 (s, 3H).





^{13}C NMR (101 MHz, CDCl_3) δ 138.14, 135.83, 135.64, 135.29, 134.72, 134.50, 133.68, 132.26, 132.12, 131.06, 131.04, 130.77, 130.70, 130.61, 130.58, 129.44, 129.34, 129.32, 128.65, 128.64, 128.39, 127.63, 127.55, 127.35, 127.13, 126.97, 126.89, 26.82, 22.50.

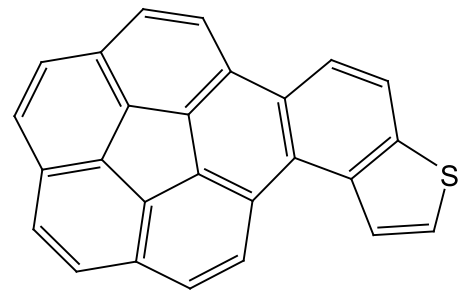
138.14
135.83
135.64
135.29
134.72
134.50
133.68
132.26
132.12
131.06
131.04
130.77
130.70
130.61
130.58
129.44
129.34
129.32
128.65
128.64
128.39
127.63
127.55
127.35
127.13
126.97
126.89

26.82

22.50

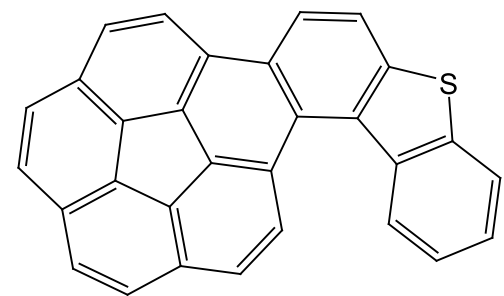
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

^{13}C NMR (101 MHz, $\text{CDCl}_3+\text{CS}_2$) δ 139.98, 137.72, 137.29, 135.26, 134.92, 134.88, 134.29, 130.79, 130.60, 130.24, 130.14, 129.05, 128.78, 128.60, 127.71, 127.69, 127.19, 127.17, 126.92, 126.85, 126.76, 124.94, 124.36, 121.55, 121.41.

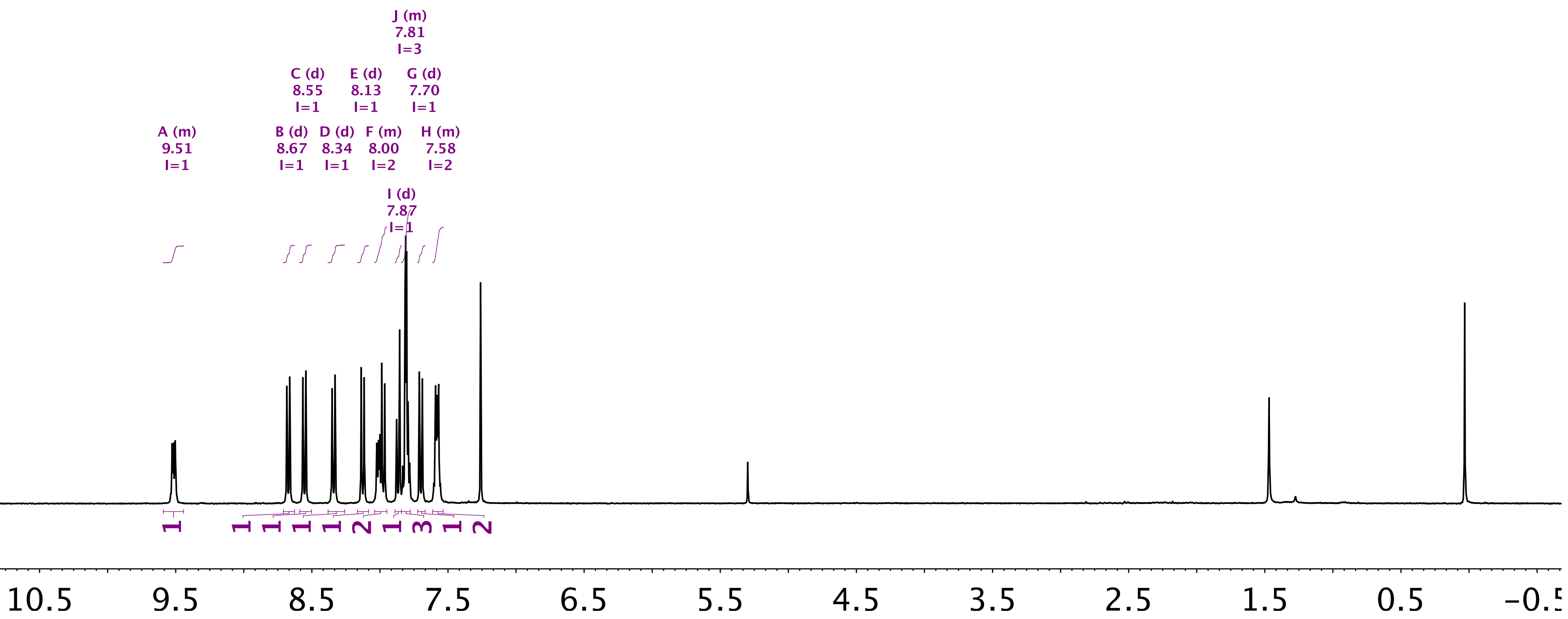
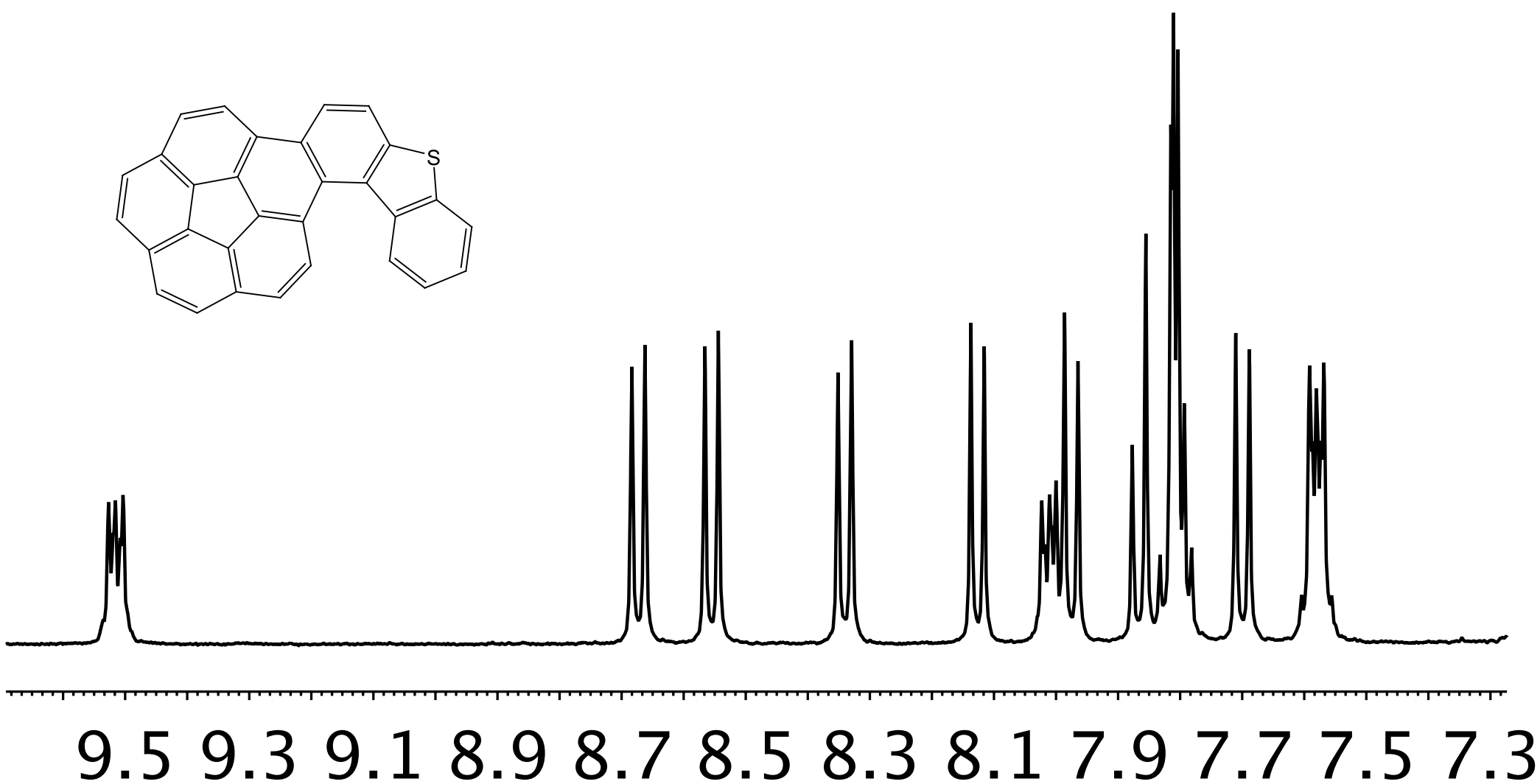


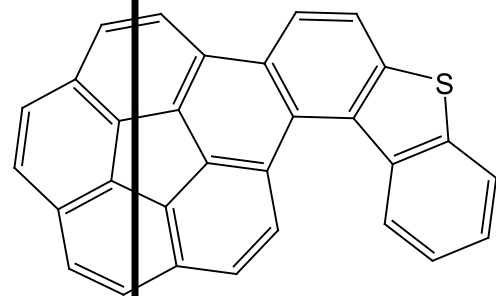
139.98
137.72
137.29
135.26
134.92
134.88
134.29
130.79
130.60
130.24
130.14
129.05
128.78
128.60
127.71
127.69
127.19
127.17
126.92
126.85
126.76
124.94
124.36
121.55
121.41

195 185 175 165 155 145 135 125 115 105 95 85 75 65 55 45 35 25 15 5



¹H NMR (400 MHz, CDCl₃) δ 9.59 – 9.44 (m, 1H), 8.67 (d, *J* = 8.5 Hz, 1H), 8.55 (d, *J* = 8.7 Hz, 1H), 8.34 (d, *J* = 8.8 Hz, 1H), 8.13 (d, *J* = 8.5 Hz, 1H), 8.04 – 7.95 (m, 2H), 7.87 (d, *J* = 8.7 Hz, 1H), 7.84 – 7.78 (m, 3H), 7.70 (d, *J* = 8.7 Hz, 1H), 7.61 – 7.54 (m, 2H).





^{13}C NMR (101 MHz, $\text{CDCl}_3+\text{CS}_2$) δ 140.39, 139.96, 138.36, 136.47, 136.07, 135.91, 135.36, 135.33, 133.03, 132.22, 131.09, 130.70, 130.59, 130.29, 128.52, 128.49, 128.15, 127.59, 127.42, 127.28, 127.02, 126.89, 126.81, 125.79, 125.32, 124.55, 123.86, 123.31, 123.05, 121.80.

140.39
139.96
138.36
136.47
136.07
135.91
135.36
135.33
133.03
132.22
131.09
130.70
130.59
130.29
128.52
128.49
128.15
127.59
127.42
127.28
127.02
126.89
126.81
125.79
125.32
124.55
123.86
123.31
123.05
121.80

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 C