Supporting Information
for

Azine-fused [6]carbohelicenes: synthesis, crystal structure, stereoisomerism and optical properties

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Experimental details, copies of NMR spectra, UV-vis spectra, X-ray crystallographic details

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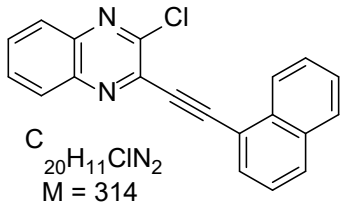
Experimental section

***General information*:**
Reactions were monitored by thin layer chromatography (silica gel 60 F_{254}) and visualized using UV. Flash column chromatography was performed using silica gel (230–400 mesh, grade 60). ^{1}H, ^{13}C NMR spectra were recorded on 250 MHz spectrometer. Chemical shifts were reported in ppm relative to Me_4Si. Electronic absorption spectra were recorded on an Agilent 8454 spectrophotometer. Fluorescence emission and excitation spectra were recorded on a Varian Cary Eclipse spectrofluorimeter. The quantum yield of fluorescence was determined using quinine sulfate in 0.1 M H_2SO_4 water (Φ = 0.53 ± 0.023) as reference with optically matched samples having absorbances of 0.1 at λ_{ex} =365 nm; the experimental error in Φ_{FL} is ±20% [Adams M.J., Highfield J.G., Kirkbright G.F. *Anal. Chem.*, **1977**, *49*, 1850–1852]. Mass spectra were performed in electrospray ionization (ESI) modes (HR-ESI MS). Melting points were determined in glass capillaries and are uncorrected. Commercial *p*-tolylacetylene, naphthalen-2-ylboronic acid, Pd-catalysts, ICl, 2,3-dihaloazines, alkylamines, PPh_3, TFA, anhydrous DMSO, THF were used as received. 3-Bromo-2-(naphthalen-2-yl)pyridine **6** [1], 1-ethynylnaphthalene [2], 1-ethynylpyrene [3], 3-ethynyl-9-methyl-9*H*-carbazole [4], 2-ethynyl- and 4-ethynyl-*N*^{1},*N*^{1},*N*^{8},*N*^{8}-tetramethylnaphthalene-1,8-diamines [5] were synthesized as it was described earlier

***Crystal Structure Determination*:** X-Ray measurements were conducted with diffractometer SyperNova, Dual, Cu at home/near, AtlasS2'. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC) and allocated the deposition numbers CCDC 2544975 (**8b**), CCDC 2544977 (**9a**), CCDC 2544980 (**9b**), CCDC 2544981 (**9c**) and CCDC 2544984 (**9d**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2-Chloro-3-(naphthalen-1-ylethynyl)quinoxaline (2a)

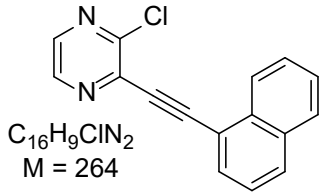


A mixture of 2,3-dichloroquinoxaline (199 mg, 1 mmol), $Pd(PPh_3)_2Cl_2$ (10 mg, 0.014 mmol), CuI (2 mg, 0.011 mmol), *i*-Pr_2NH (1 mL) and DMSO (3 mL) was stirred under argon for 20 min at room temperature. Then a solution of 1-ethynylnaphthalene (161 mg, 1.1 mmol) in *i*-Pr_2NH (1 mL) was added by portions for 1 h. The reaction mixture was stirred for 5 h at room temperature then evaporated without heating to remove *i*-Pr_2NH, treated with H_2O (150 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The extract was dried over Na_2SO_4 and evaporated to dryness. The residue was purified by flash column chromatography on silica gel (3.5 × 32 cm) with $CHCl_3$ – hexane (2:1, v/v) as the eluent. The colorless fraction with R_f 0.6 and violet fluorescence under UV (356 nm) gave **2a** (224 mg, 71%). For crystallization the crude product **2a** was heated with EtOH (3 mL).

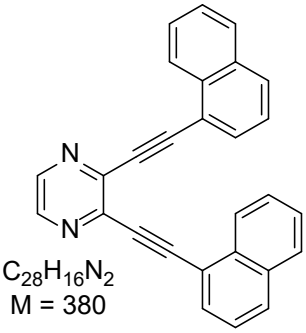
With a 2-fold increase in loadings, the yield of compound **2a** increased to 84%.

Compound **2a** was obtained as a yellow solid with m.p. 157–158 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.46–7.59 (m, 2 H), 7.66 (ddd, *J* = 8.3, 7.0, 1.3 Hz, 1 H), 7.74–7.81 (m, 2 H), 7.86–8.02 (m, 4 H), 8.08–8.15 (m, 1 H), 8.61 (d, *J* = 8.3 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 90.3, 95.7, 118.9, 125.3, 126.2, 126.9, 127.6, 128.3, 128.5, 128.9, 130.7, 130.8, 131.4, 132.5, 133.1, 133.6, 138.7, 140.3, 140.9, 148.0 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{20}H_{12}ClN_2^+$ [M+H$^+$]: 315.0684 (^{35}Cl), 317.0654 (^{37}Cl), found 315.0699 (^{35}Cl), 317.0676 (^{37}Cl).

2-Chloro-3-(naphthalen-1-ylethynyl)pyrazine (2b) and 2,3-bis(naphthalen-1-ylethynyl)-pyrazine (3)



$C_{16}H_9ClN_2$
M = 264



$C_{28}H_{16}N_2$
M = 380

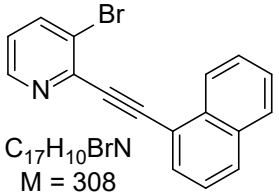
A mixture of 2,3-dichloropyrazine (179 mg, 1.2 mmol), $Pd(PPh_3)_2Cl_2$ (12 mg, 0.017 mmol), CuI (3 mg, 0.016 mmol), *i*-Pr_2NH (1 mL) and DMSO (3 mL) was stirred under argon for 20 min at room temperature. Then a solution of 1-ethynylnaphthalene (194 mg, 1.3 mmol) in *i*-Pr_2NH (1 mL) was added by portions for 1 h. The reaction mixture was stirred for 5 h at room temperature then evaporated without heating to remove *i*-Pr_2NH, treated with H_2O (150 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The extract was dried over Na_2SO_4 and evaporated to dryness. The residue was purified by flash column chromatography on silica gel (3.5 × 36 cm) with CH_2Cl_2 as the eluent. The colorless fraction with R_f 0.5 and violet fluorescence under UV (356 nm) gave 2-chloro-3-(naphthalen-1-ylethynyl)pyrazine **2b** (202 mg, 63%). The violet fraction with R_f 0.3 gave 2,3-di(naphthalen-1-ylethynyl)pyrazine **3** (42 mg, 9%).

With a 4-fold increase in loadings, the yield of compound **2b** was not change, while the yield of dialkynyl derivative **3** increased (25%). In this case, a chromatographic column (3.5 × 39 cm) has been used.

After recrystallization from *i*-PrOH compound **2b** was obtained as colorless fibrous crystals with m.p. 87–88 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.49 (dd, J = 8.2, 7.3 Hz, 1 H), 7.55 (ddd, J = 8.1, 7.1, 1.3 Hz, 1 H), 7.64 (ddd, J = 8.3, 6.9, 1.4 Hz, 1 H), 7.85–7.92 (m, 3 H), 8.25 (d, J = 2.4 Hz, 1 H), 8.48 (d, J = 2.4 Hz, 1 H), 8.54 (d, J = 8.2 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 89.4, 96.0, 118.9, 125.3, 126.1, 126.9, 127.6, 128.5, 130.7, 132.2, 133.1, 133.4, 139.7, 141.7, 142.4, 150.6 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{16}H_{10}ClN_2^+$ [M+H$^+$]: 265.0527 (^{35}Cl), 267.0527 (^{37}Cl), found 265.0532 (^{35}Cl), 267.0510 (^{37}Cl).

After recrystallization from *i*-PrOH compound **3** was obtained as grey crystals with m.p. 126–127 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.12 (ddd, J = 8.2, 6.9, 1.2 Hz, 2 H), 7.41–7.50 (m, 4 H), 7.85–7.96 (m, 6 H), 8.53 (d, J = 8.4 Hz, 2 H), 8.61 (s, 2 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 90.9, 94.7, 119.2, 125.2, 126.3, 126.7, 127.3, 128.3, 130.3, 132.1, 133.1, 133.4, 141.8, 142.6 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{28}H_{17}N_2^+$ [M+H$^+$]: 381.1386, found 381.1388.

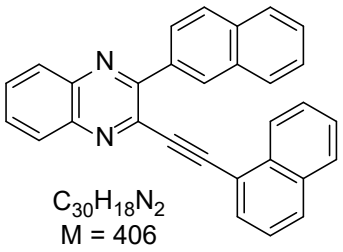
3-Bromo-2-(naphthalen-1-ylethynyl)pyridine (2c)



$C_{17}H_{10}BrN$
M = 308

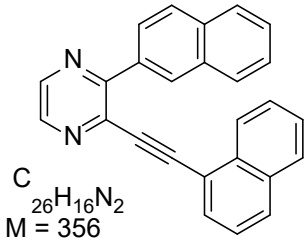
A mixture of 2,3-dibromopyridine (356 mg, 1.5 mmol), $Pd(PPh_3)_2Cl_2$ (21 mg, 0.03 mmol), CuI (3 mg, 0.016 mmol), *i*-Pr_2NH (1 mL) and DMSO (3 mL) was stirred under argon for 20 min at room temperature. Then a solution of 1-ethynylnaphthalene (251 mg, 1.65 mmol) in *i*-Pr_2NH (2 mL) was added by portions for 1 h. The reaction mixture was stirred for 5 h at room temperature then evaporated without heating to remove *i*-Pr_2NH, treated with H_2O (150 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The extract was dried over Na_2SO_4 and evaporated to dryness. The residue was purified by flash column chromatography on silica gel (3.5 × 22 cm) with CH_2Cl_2 as the eluent. The colorless fraction with R_f 0.6 and violet fluorescence under UV (356 nm) gave 3-bromo-2-(naphthalen-1-ylethynyl)pyridine **2c** (446 mg, 97%). For crystallization compound **2c** was heated with *i*-PrOH. Colorless solid with m.p. 81–82 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.00–7.20 (m, 1 H), 7.45–7.58 (m, 2 H), 7.63 (ddd, J = 8.3, 6.9, 1.3 Hz, 1 H), 7.36–7.97 (m, 4 H), 8.64 (d, J = 8.2 Hz, 2 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 92.4, 119.7, 123.6, 125.3, 126.5, 126.7, 127.2, 128.4, 130.0, 131.8, 133.2, 133.5, 139.9, 143.9, 148.4 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{17}H_{11}BrN^+$ [M+H$^+$]: 308.0069 (^{79}Br), found 308.0071 (^{79}Br); *m*/*z* calcd. for $C_{17}H_{10}BrNNa^+$ [M+Na$^+$]: 329.9889 (^{79}Br), found 329.9891 (^{79}Br).

2-(Naphthalen-1-ylethynyl)-3-(naphthalen-2-yl)quinoxaline (4a)



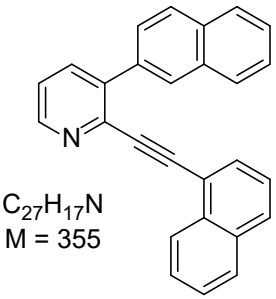
2-Chloro-3-(naphthalen-1-ylethynyl)quinoxaline **2a** (315 mg, 1 mmol), naphthalen-2-ylboronic acid (193 mg, 1.2 mmol), 5% Pd/C (52 mg, 0.049 mmol Pd), PPh_3 (26 mg, 0.1 mmol), toluene (2.5 mL) and a solution of K_2CO_3 (462 mg, 3.35 mmol) in water (2 mL) were stirred at 100 °C for 24 h under argon. The reaction mixture was then diluted with water (50 mL) and extracted with CH_2Cl_2 (3 × 25 mL). The extract was dried over Na_2SO_4 and purified by flash column chromatography on silica gel (3.5 × 30 cm) with CH_2Cl_2 as the eluent. The yellow fraction with R_f 0.7 gave 361 mg (89%) of **4a**. For crystallization the crude product **4a** was heated with EtOH (3 mL). Compound **4a** was obtained as a yellow solid with m.p. 178–179 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.83 (ddd, J = 8.3, 6.9, 1.2 Hz, 1 H), 7.34 – 7.44 (m, 2 H), 7.53 – 7.66 (m, 3 H), 7.75 – 7.86 (m, 5 H), 7.96 – 8.05 (m, 3 H), 8.16 – 8.25 (m, 3 H), 8.66 (d, J = 1.3 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 93.1, 93.9, 119.3, 125.2, 126.1, 126.56, 126.59, 126.8, 126.9, 127.2, 127.9, 128.1, 128.4, 128.91, 128.93, 129.4, 129.6 (2C), 130.2, 130.4, 130.8, 132.1, 133.0, 133.1, 133.3, 135.5, 138.7, 140.8, 141.3, 155.4 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{30}H_{18}N_2Na^+$ [M+Na^+]: 429.1362, found 429. 1362.

2-(Naphthalen-1-ylethynyl)-3-(naphthalen-2-yl)pyrazine (4b)



2-Chloro-3-(naphthalen-1-ylethynyl)pyrazine **2b** (397 mg, 1.5 mmol), naphthalen-2-ylboronic acid (290 mg, 1.7 mmol), 5% Pd/C (78 mg, 0.037 mmol Pd), PPh_3 (39 mg, 0.15 mmol), toluene (3.7 mL) and a solution of K_2CO_3 (693 mg, 5 mmol) in water (3 mL) were stirred at 100 °C for 24 h under argon. The reaction mixture was then diluted with water (50 mL) and extracted with CH_2Cl_2 (3 × 25 mL). The extract was dried over Na_2SO_4 and purified by flash column chromatography on silica gel (3.5 × 18.5 cm) with CH_2Cl_2 as the eluent. The yellowish fraction with R_f 0.3 gave 486 mg (91%) of **4b**. For crystallization the crude product **4b** was heated with EtOH (3 mL). Compound **4b** was obtained as yellow needles with m.p. 144–146 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.03 (ddd, J = 8.2, 6.9, 1.2 Hz, 1 H), 7.38 – 7.44 (m, 2 H), 7.57 (pd, J = 6.9, 1.3 Hz, 2 H), 7.76 – 7.98 (m, 6 H), 8.01 (d, J = 8.6 Hz, 1 H), 8.17 (dd, J = 8.6, 1.8 Hz, 1 H), 8.63 (q, J = 2.4 Hz, 2 H), 8.67 (d, J = 1.5 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 92.3, 93.4, 119.5, 125.2, 126.1, 126.6 (3 C), 127.1, 127.2, 127.8, 128.2, 128.3, 128.9, 129.4, 130.1, 131.8, 133.0 (2 C), 133.3, 133.9, 134.8, 138.0, 142.4, 142.6, 155.8 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{26}H_{16}N_2Na^+$ [M+Na^+]: 379.1206, found 379.1201.

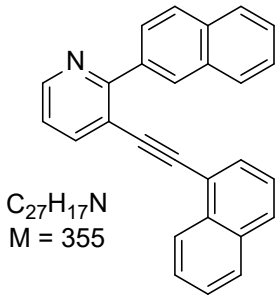
2-(Naphthalen-1-ylethynyl)-3-(naphthalen-2-yl)pyridine (4c)



3-bromo-2-(naphthalen-1-ylethynyl)pyridine **2c** (123 mg, 0.4 mmol), naphthalen-2-ylboronic acid (83 mg, 0.48 mmol), 5% Pd/C (85 mg, 0.04 mmol Pd), PPh_3 (42 mg, 0.16 mmol), toluene (4 mL) and a solution of K_2CO_3 (221 mg, 1.6 mmol) in water (2 mL) were stirred at 100 °C for 24 h under argon. The reaction mixture was then diluted with water (50 mL) and extracted with CH_2Cl_2 (3 × 25 mL). The extract was dried over Na_2SO_4 and purified by flash column chromatography on silica gel (2.5 × 20 cm) with CH_2Cl_2 as the eluent. The colorless fraction with R_f 0.5 gave 118 mg (83%) of **4c**. For crystallization the crude product **4c** was heated with EtOH (3 mL). Compound **4c** was obtained as colorless solid with m.p. 139–140 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.72 (ddd, J = 8.2, 6.9, 1.1 Hz, 1 H), 7.29–7.41 (m, 3 H), 7.49 (d, J = 8.4 Hz, 1 H), 7.53–7.63 (m, 2 H), 7.68–7.98 (m, 8 H), 8.16 (br s, 1 H), 8.72 (dd, J = 4.7, 1.5 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 90.7, 93.4, 120.0, 122.8, 125.2, 126.2, 126.3, 126.59 (2C), 126.61, 127.3, 127.8, 128.0, 128.3, 128.4, 128.5, 129.4, 131.4, 132.9, 133.1, 133.2, 133.3, 136.2,

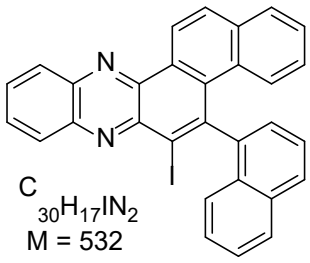
137.2, 140.3, 142.0, 149.0 ppm. HRMS (ESI): *m/z* calcd. for $C_{27}H_{18}N^+$ [M+H$^+$]: 356.1434, found 356.1440.

3-(Naphthalen-1-ylethynyl)-2-(naphthalen-2-yl)pyridine (4d)



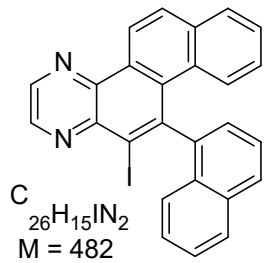
A mixture of 3-bromo-2-(naphthalen-2-yl)pyridine **6** (169 mg, 0.6 mmol), $Pd(PPh_3)_2Cl_2$ (42 mg, 0.06 mmol), CuI (6 mg, 0.03 mmol), *i*-Pr_2NH (1.5 mL) and DMSO (6 mL) was stirred at 100 °C for 20 min under argon. Then a solution of 1-ethynylnaphthalene (137 mg, 0.9 mmol) in *i*-Pr_2NH (2.5 mL) was added by portions for 1 h. The reaction mixture was refluxed for 4 h, evaporated without heating to remove *i*-Pr_2NH, treated with H_2O (50 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The extract was dried over Na_2SO_4 and evaporated to dryness. The residue was purified by flash column chromatography on silica gel (2.5 × 20 cm) with CH_2Cl_2 as the eluent. The fraction with R_f 0.25 and blue fluorescence under UV (365 nm) gave 187 mg (88%) of **4d**. The crude product was crystallized by heating with EtOH. Compound **4d** was obtained as an off-white solid with m.p. 104–106 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.07 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1 H), 7.29–7.46 (m, 3 H), 7.49–7.62 (m, 2 H), 7.66 (dd, *J* = 7.2, 1.1 Hz, 1 H), 7.77–7.84 (m, 2 H), 7.86–8.03 (m, 4 H), 8.10 (dd, *J* = 7.8, 1.7 Hz, 1 H), 8.17 (dd, *J* = 8.5, 1.7 Hz, 1 H), 8.63 (d, *J* = 1.3 Hz, 1 H), 8.74 (dd, *J* = 4.8, 1.7 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 92.2, 93.4, 118.6, 120.5, 121.6, 125.2, 126.2, 126.3, 126.5, 126.7, 126.8, 127.0, 127.8, 127.9, 128.2, 128.9, 129.1, 129.2, 130.7, 133.1, 133.2, 133.6, 137.2, 141.1, 148.7, 159.8 ppm. HRMS (ESI): *m/z* calcd. for $C_{27}H_{18}N^+$ [M+H$^+$]: 356.1434, found 356.1435.

6-Iodo-5-(naphthalen-1-yl)naphtho[2,1-*a*]phenazine (7a)



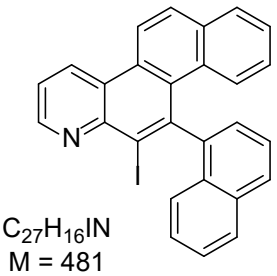
To a suspension of 2-(naphthalen-1-ylethynyl)-3-(naphthalen-2-yl)-quinoxaline **4a** (296 mg, 0.73 mmol) in dry CH_3CN (28 mL), a solution of ICl (236 mg, 1.46 mmol) in dry CH_3CN (2 mL) was added. The reaction mixture was kept at room temperature for 24 h in the dark and evaporated to dryness. The residue was shaken with $CHCl_3$ (20 mL) and solution of $Na_2S_2O_3$ (158 mg, 1 mmol) in water (10 mL). After separation water layer was additionally extracted with $CHCl_3$ (3 × 20 mL). The extract was dried over Na_2SO_4 and purified by flash column chromatography on silica gel (2 × 40 cm) with $CHCl_3$ as the eluent. The bright yellow fraction with R_f 0.9 gave 357 mg (92%) of **7a**. For crystallization the crude product **7a** was heated with EtOH (3-5 mL). Compound **7a** was obtained as bright yellow needles with m.p. 257–258 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.90 (ddd, *J* = 8.8, 6.8, 1.6 Hz, 1 H), 7.29–7.46 (m, 4 H), 7.54 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1 H), 7.62 (dd, *J* = 8.4, 0.9 Hz, 1 H), 7.68 (dd, *J* = 8.2, 7.1 Hz, 1 H), 7.90–8.00 (m, 3 H), 8.05 (d, *J* = 8.2 Hz, 1 H), 8.13 (d, *J* = 8.3 Hz, 1 H), 8.22 (d, *J* = 8.8 Hz, 1 H), 8.43–8.54 (m, 2 H), 9.78 (d, *J* = 8.9 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 114.2, 122.8, 122.9, 125.9, 126.0, 126.3, 126.5, 126.8, 126.9, 127.4, 127.9, 128.6, 128.8, 129.0, 129.4, 129.7, 129.8, 130.3, 130.7, 130.9, 131.4, 131.9, 133.9, 135.3, 140.8, 141.4, 143.1, 144.0, 146.2, 148.3 ppm. HRMS (ESI): *m/z* calcd. for $C_{30}H_{17}IN_2Na^+$ [M+Na$^+$]: 555.0329, found 555.0331.

12-Iodo-11-(naphthalen-1-yl)naphtho[2,1-*f*]quinoxaline (7b)



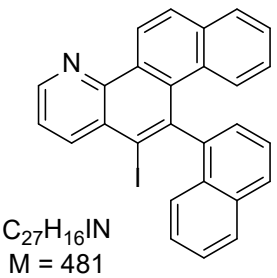
To a suspension of 2-(naphthalen-1-ylethynyl)-3-(naphthalen-2-yl)-pyrazine **4b** (71 mg, 0.2 mmol) in dry CH_3CN (10 mL), a solution of ICl (65 mg, 0.4 mmol) in dry CH_3CN (5 mL) was added. The reaction mixture was kept at room temperature for 24 h in the dark and evaporated to dryness. The residue was shaken with $CHCl_3$ (10 mL) and solution of $Na_2S_2O_3$ (32 mg, 0.2 mmol) in water (5 mL). After separation water layer was additionally extracted with $CHCl_3$ (3 × 10 mL). The extract was dried over Na_2SO_4 and purified by flash column chromatography on silica gel (2 × 45 cm) with $CHCl_3$ as the eluent. The bright yellow fraction with R_f 0.7 gave 84 mg (88%) of **7b**. For crystallization the crude product **7b** was heated with EtOH (3 mL). Compound **7b** was obtained as bright yellow needles with m.p. 241–243 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.91 (ddd, *J* = 8.6, 6.9, 1.5 Hz, 1 H), 7.26–7.44 (m, 4 H), 7.49–7.57 (m, 2 H), 7.67 (dd, *J* = 8.2, 7.2 Hz, 1 H), 7.92 (dd, *J* = 8.0, 1.1 Hz, 1 H), 8.05 (d, *J* = 8.2 Hz, 1 H), 8.15–8.18 (m, 2 H), 9.02 (d, *J* = 1.8 Hz, 1 H), 9.07 (d, *J* = 1.8 Hz, 1 H), 9.52 (d, *J* = 9.0 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 113.3, 122.2, 125.7, 126.1, 126.4, 126.6, 126.91, 126.94, 127.4, 128.0, 128.6, 128.9, 129.0, 129.6, 130.2, 131.4, 131.5, 131.9, 134.0, 134.9, 140.5, 141.2, 144.5, 145.8, 145.9, 147.2 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{26}H_{16}N_2^+$ [M+H$^+$]: 483.0353, found 483.0349.

12-Iodo-11-(naphthalen-1-yl)naphtho[2,1-*f*]quinoline (7c)



To a solution of 3-(naphthalen-1-ylethynyl)-2-(naphthalen-2-yl)pyridine **4c** (178 mg, 0.5 mmol) in dry CH_3CN (10 mL), a solution of ICl (162 mg, 1 mmol) in dry CH_3CN (5 mL) was added. The bright yellow residue was gradually formed. The reaction mixture was kept at room temperature for 24 h in the dark and evaporated to dryness. The residue was shaken with CH_2Cl_2 (10 mL) and solution of $Na_2S_2O_3$ (79 mg, 0.5 mmol) in water (5 mL). After separation water layer was additionally extracted with CH_2Cl_2 (3 × 10 mL). The extract was dried over Na_2SO_4 and purified by flash column chromatography on silica gel (2 × 45 cm) with CH_2Cl_2 as the eluent. The fraction with R_f 0.8 gave 180 mg (75%) of **7c**. For crystallization the crude product **7c** was heated with EtOH (3 mL). Compound **7c** was obtained as a biege solid with m.p. 218–219 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.88 (ddd, *J* = 8.7, 6.9, 1.5 Hz, 1 H), 7.27–7.40 (m, 4 H), 7.49–7.61 (m, 2 H), 7.64 (dd, *J* = 8.2, 7.1 Hz, 1 H), 7.72 (dd, *J* = 8.4, 4.4 Hz, 1 H), 7.88 (dd, *J* = 7.9, 1.1 Hz, 1 H), 8.02–8.12 (m, 3 H), 8.76 (d, *J* = 9.1 Hz, 1 H), 9.12–9.17 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 116.2, 120.6, 122.5, 125.4, 125.9, 126.0, 126.3, 126.4 (2C), 126.8, 127.5, 128.2, 128.6 (2C), 129.7, 129.9, 130.1, 132.0, 132.1, 133.8, 134.0, 146.2, 146.3, 146.7, 151.1 ppm. HRMS (ESI): *m/z* calcd. for $C_{27}H_{17}NI^+$ [M+H$^+$]: 482.0400, found 482.0405.

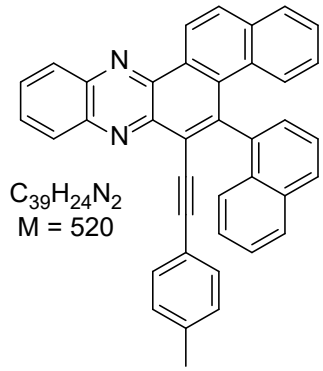
12-Iodo-11-(naphthalen-1-yl)naphtho[1,2-*h*]quinoline (7d)



To a solution of 3-(naphthalen-1-ylethynyl)-2-(naphthalen-2-yl)pyridine **4d** (124 mg, 0.35 mmol) in dry CH_3CN (5 mL), a solution of ICl (114 mg, 0.7 mmol) in dry CH_3CN (5 mL) was added. The bright yellow residue was gradually formed. The reaction mixture was kept at room temperature for 24 h in the dark and evaporated to dryness. The residue was shaken with CH_2Cl_2 (10 mL) and solution of $Na_2S_2O_3$ (79 mg, 0.5 mmol) in water (5 mL). After separation water layer was additionally extracted with CH_2Cl_2 (3 × 10 mL). The extract was dried over Na_2SO_4 and purified by flash column chromatography on silica gel (2 × 45 cm) with CH_2Cl_2 as the eluent. The yellowish fraction with R_f 0.8 gave 156 mg (93%) of **7d**. For crystallization the crude product **7d** was heated with EtOH (3 mL). Compound **7d** was obtained as a biege solid with m.p. 198–200 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.88 (ddd, *J* = 8.7, 6.9, 1.5 Hz, 1 H), 7.25–7.41 (m,

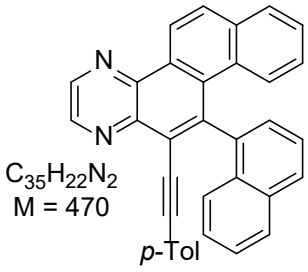
4 H), 7.49–7.57 (m, 2 H), 7.61–7.69 (m, 2 H), 7.90 (dd, *J* = 8.0, 1.3 Hz, 1 H), 8.04 (dd, *J* = 8.9, 1.2 Hz, 1 H), 8.08–8.17 (m, 2 H), 8.78 (dd, *J* = 8.4, 1.6 Hz, 1 H), 9.08 (dd, *J* = 4.2, 1.6 Hz, 1 H), 9.67 (d, *J* = 9.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 110.5, 122.8, 123.5, 125.7, 125.8, 126.4, 126.5, 126.9, 127.8, 127.9, 128.6, 128.7, 128.9, 129.7, 129.8, 131.3, 131.8, 132.3, 134.0, 134.7, 142.4, 143.1, 145.7, 147.0, 150.1 ppm. HRMS (ESI): *m/z* calcd. for $C_{27}H_{17}NI^+$ [M+H$^+$]: 482.0400, found 482.0391.

5-(Naphthalen-1-yl)-6-(*p*-tolylethynyl)naphtho[2,1-*a*]phenazine (8a)



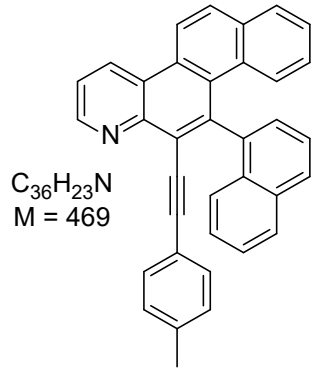
6-Iodo-5-(naphthalen-1-yl)naphtho[2,1-*a*]phenazine **7a** (133 mg, 0.25 mmol), $Pd(PPh_3)_4$ (29 mg, 0.025 mmol) and piperidine (5 mL) were stirred for 20 min at 105 ºC under argon. Then a solution of *p*-tolylacetylene (83 mg, 0.8 mmol) in piperidine (3 mL) was added by portions for 1 h. The reaction mixture was stirred for total 24 h at 100–105 ºC. Then it was evaporated to dryness, treated with H_2O (50 mL) and extracted with CH_2Cl_2 (3 × 15 mL). The extract was dried over Na_2SO_4 and evaporated. The residue was purified by flash column chromatography on silica gel (3.5 × 30 cm) with $CHCl_3$ as the eluent. The yellow fraction with R_f 0.7 gave 111 mg (85%) of **8a**. After recrystallization from EtOH compound **8a** was obtained as yellow brown crystals, decomp. >210 ºC. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.28 (s, 3 H), 6.71–6.75 (m, 2 H), 6.90–6.98 (m, 3 H), 7.32 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1 H), 7.42 (ddd, *J* = 8.0, 7.0, 0.9 Hz, 1 H), 7.49–7.56 (m, 3 H), 7.65 (dd, *J* = 8.1, 7.2 Hz, 1 H), 7.82 (d, *J* = 8.4 Hz, 1 H), 7.89–7.99 (m, 3 H), 8.08 (t, *J* = 8.7 Hz, 2 H), 8.22 (d, *J* = 8.8 Hz, 1 H), 8.46–8.50 (m, 2 H), 9.78 (d, *J* = 8.9 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.5, 86.8, 102.1, 120.3, 122.7, 124.0, 125.9, 126.2, 126.3, 126.5, 126.7, 126.8, 127.3, 127.8, 128.4 (2C), 128.7, 128.9, 129.8, 130.1, 130.2, 130.3, 130.4, 130.5, 130.7, 130.9, 131.6, 132.2, 134.0, 135.2, 138.3, 141.1, 141.2, 141.7, 142.8, 143.5, 145.8 ppm. HRMS (ESI): *m/z* calcd. for $C_{39}H_{24}N_2Na^+$ [M+Na$^+$]: 543.1832, found 543.1846.

11-(Naphthalen-1-yl)-12-(*p*-tolylethynyl)naphtho[2,1-*f*]quinoxaline (8b)



12-Iodo-11-(naphthalen-1-yl)naphtho[2,1-*f*]quinoxaline **7b** (241 mg, 0.5 mmol), $Pd(PPh_3)_4$ (58 mg, 0.05 mmol) and piperidine (11 mL) were stirred for 20 min at 105 ºC under argon. Then a solution of *p*-tolylacetylene (156 mg, 1.5 mmol) in piperidine (5 mL) was added by portions for 3 h. The reaction mixture was stirred for total 24 h at 100–105 ºC. Then it was evaporated to dryness, treated with H_2O (50 mL) and extracted with CH_2Cl_2 (3 × 15 mL). The extract was dried over Na_2SO_4 and evaporated. The residue was purified by flash column chromatography on silica gel (3.5 × 35 cm) with CH_2Cl_2 as the eluent. The yellow fraction with R_f 0.8 gave 206 mg (87%) of **8b**. After recrystallization from EtOH compound **8b** was obtained as yellow crystals with m.p. 209–211 ºC. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.26 (s, 3 H), 6.68–6.71 (m, 2 H), 6.91–6.98 (m, 3 H), 7.31 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1 H), 7.39–7.45 (m, 1 H), 7.48–7.57 (m, 3 H), 7.62–7.72 (m, 2 H), 7.93 (dd, *J* = 8.0, 1.1 Hz, 1 H), 8.03–8.11 (m, 2 H), 8.14 (d, *J* = 9.0 Hz, 1 H), 9.08 (d, *J* = 1.9 Hz, 1 H), 9.12 (d, *J* = 1.9 Hz, 1 H), 9.51 (d, *J* = 9.0 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.5, 86.4, 101.8, 120.0, 122.0, 122.1, 123.8, 126.0, 126.2, 126.3, 126.7, 126.8, 127.3, 127.9, 128.4, 128.7, 128.9, 130.0, 130.1, 130.6, 130.8, 131.6, 132.2, 134.0, 134.8, 138.3, 140.4, 141.0, 141.2, 144.1, 145.0, 145.4 ppm. HRMS (ESI): *m/z* calcd. for $C_{35}H_{23}N_2^+$ [M+H$^+$]: 471.1856, found 471.1862.

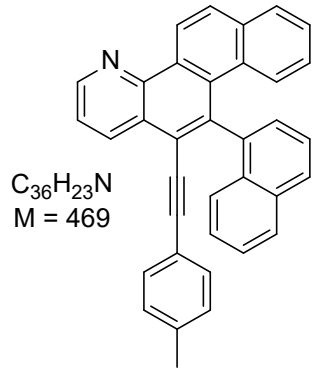
11-(Naphthalen-1-yl)-12-(*p*-tolylethynyl)naphtho[2,1-*f*]quinoline (8c)



$C_{36}H_{23}N$
M = 469

A mixture of 12-iodo-11-(naphthalen-1-yl)naphtho[2,1-*f*]quinoline **7c** (96 mg, 0.2 mmol), $Pd(PPh_3)_4$ (23 mg, 0.02 mmol), piperidine (4 mL) was stirred for 20 min at 105 ºC under argon. A solution of *p*-tolylacetylene (70 mg, 0.6 mmol) in piperidine (2 mL) was then added by portions for 1 h. The reaction mixture was stirred at 105 ºC for 24 h and evaporated without heating to dryness. The residue was treated with H_2O (50 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The extract was dried over Na_2SO_4, concentrated and purified by flash column chromatography on silica gel (2.5 × 15 cm) using CH_2Cl_2 as the eluent. The yellowish fraction with R_f 0.4 gave compound **8c** (73 mg, 78%). For crystallization the crude product **8c** was heated with EtOH (3 mL). Compound **8c** was obtained as sand-colored solid with m.p. 211-212 ºC. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.26 (s, 3 H), 6.66 (dm, *J* = 8.1 Hz, 2 H), 6.88–6.95 (m, 3 H), 7.30 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1 H), 7.39 (ddd, *J* = 7.9, 7.0, 1.0 Hz, 1 H), 7.44 (dd, *J* = 7.1, 1.2 Hz, 1 H), 7.48–7.56 (m, 2 H), 7.62 (dd, *J* = 8.2, 7.1 Hz, 1 H), 7.70–7.77 (m, 2 H), 7.89 (dd, *J* = 7.9, 1.3 Hz, 1 H), 8.02–8.10 (m, 3 H), 8.75 (d, *J* = 9.1 Hz, 1 H), 9.12–9.24 (m, 2 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.5, 87.5, 101.6, 120.4, 120.6, 122.0, 124.9, 125.1, 126.1, 126.2, 126.3, 126.5, 126.6, 127.4, 128.1 (2C), 128.3, 128.5, 128.6, 128.7, 129.2, 129.7, 130.4, 131.5, 131.8, 132.4, 133.7, 134.0, 138.0, 141.6, 144.0, 146.7, 150.9 ppm. HRMS (ESI): *m/z* calcd. for $C_{36}H_{24}N^+$ [M+H$^+$]: 470.1903, found 470.1896.

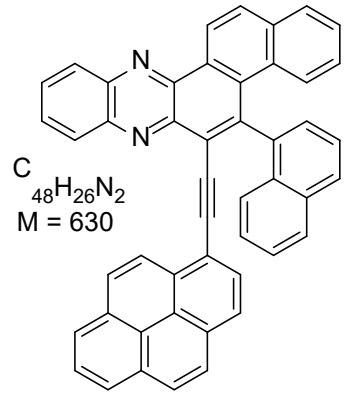
11-(Naphthalen-1-yl)-12-(*p*-tolylethynyl)naphtho[1,2-*h*]quinoline (8d)



$C_{36}H_{23}N$
M = 469

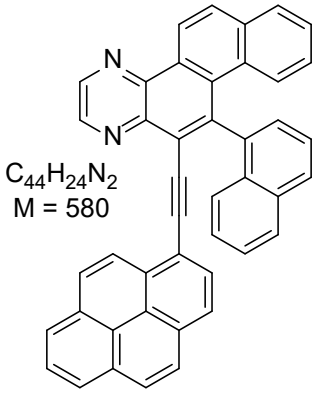
A mixture of 12-iodo-11-(naphthalen-1-yl)naphtho[1,2-*h*]quinoline **7c** (202 mg, 0.42 mmol), $Pd(PPh_3)_4$ (49 mg, 0.042 mmol), piperidine (9 mL) was stirred for 20 min at 105 ºC under argon. A solution of *p*-tolylacetylene (146 mg, 1.26 mmol) in piperidine (4 mL) was then added by portions for 2 h. The reaction mixture was stirred at 105 ºC for 24 h and evaporated without heating to dryness. The residue was treated with H_2O (50 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The extract was dried over Na_2SO_4, concentrated and purified by flash column chromatography on silica gel (2.5 × 30 cm) using CH_2Cl_2 as the eluent. The yellowish fraction with R_f 0.6 gave compound **8c** (178 mg, 90%). After recrystallization from C_6H_6-EtOH (1:1) compound **8c** was obtained as yellowish solid with m.p. 253-255 ºC. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.29 (s, 3 H), 6.69 (d, *J* = 8.0 Hz, 2 H), 6.90–7.00 (m, 3 H), 7.27–7.34 (m, 1 H), 7.40 (t, *J* = 7.0 Hz, 1 H), 7.49–7.74 (m, 6 H), 7.93 (d, *J* = 7.7 Hz, 1 H), 8.07 (t, *J* = 8.7 Hz, 2H), 8.14 (d, *J* = 9.0 Hz, 1 H), 8.93 (dd, *J* = 8.3, 1.6 Hz, 1 H), 9.19 (dd, *J* = 4.2, 1.7 Hz, 1 H), 9.65 (d, *J* = 9.0 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.5, 86.5, 100.4, 119.9, 121.9, 122.4, 122.5, 122.6, 125.6, 125.7, 126.2, 126.3, 126.5, 127.6, 127.8, 128.1, 128.3, 128.8, 128.9, 129.6, 130.2, 130.4, 131.2, 131.3, 132.5, 134.0, 134.6, 134.9, 135.0, 135.1, 138.5, 140.9, 141.7, 145.4, 149.7 ppm. HRMS (ESI): *m/z* calcd. for $C_{36}H_{24}N^+$ [M+H$^+$]: 470.1903, found 470.1901.

5-(Naphthalen-1-yl)-6-(pyren-1-ylethynyl)naphtho[2,1-*a*]phenazine (8e)



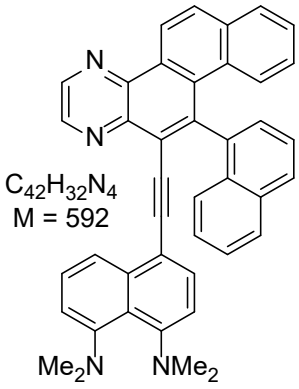
6-Iodo-5-(naphthalen-1-yl)naphtho[2,1-*a*]phenazine **7a** (250 mg, 0.47 mmol), $Pd(PPh_3)_4$ (58 mg, 0.05 mmol) and piperidine (15 mL) were stirred for 20 min at 80 ºC under argon. Then a solution of 1-ethynylpyrene (160 mg, 0.7 mmol) in piperidine (5 mL) was added by portions for 1 h. The reaction mixture was stirred for total 24 h at 80-85 ºC. Then it was evaporated to dryness, treated with H_2O (50 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The extract was dried over Na_2SO_4 and evaporated. The residue was purified by flash column chromatography on silica gel (3.5 × 40 cm) with CH_2Cl_2-hexane (1:1, v/v) as the eluent. The red fraction with R_f 0.7 was collected and underwent additional column chromatography on silica gel (2 × 70 cm) with $CHCl_3$-hexane (2:1, v/v) as the eluent. The red fraction with R_f 0.7 gave 217 mg (73%) of **8e**. After recrystallization from EtOH compound **8e** was obtained as red crystals with m.p. 277-279 ºC. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.79 (ddd, J = 8.7, 6.9, 1.5 Hz, 1 H), 7.35 (ddd, J = 8.2, 6.9, 1.2 Hz, 1 H), 7.45 (ddd, J = 7.9, 7.0, 0.9 Hz, 1 H), 7.51–7.60 (m, 3 H), 7.67 (dd, J = 7.1, 1.3 Hz, 1 H), 7.73–7.79 (m, 1 H), 7.90 (d, J = 8.6 Hz, 1 H), 7.96–8.10 (m, 8 H), 8.15–8.19 (m, 2 H), 8.23–8.28 (m, 4 H), 8.52 – 8.58 (m, 1 H), 8.61 – 8.68 (m, 1 H), 9.84 (d, J = 8.8 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 93.1, 101.2, 118.2, 122.8, 124.3, 124.4, 125.4, 125.5, 126.0, 126.1, 126.3, 126.4, 126.5, 126.8, 126.9, 127.2, 127.5, 127.8, 127.9, 128.1, 128.5, 128.6, 128.9, 129.8, 130.0, 130.2, 130.3, 130.6, 130.7, 131.1, 131.17, 131.24, 131.28, 132.21, 132.32, 134.2, 135.3, 141.2, 141.3, 142.1, 143.0, 143.7, 145.3 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{48}H_{27}N_2^+$ [M+H$^+$]: 631.2169, found 631.2176.

11-(Naphthalen-1-yl)-12-(pyren-1-ylethynyl)naphtho[2,1-*f*]quinoxaline (8f)



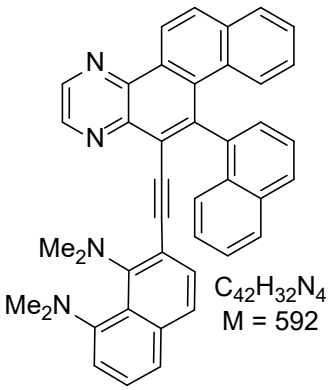
A mixture of 12-iodo-11-(naphthalen-1-yl)naphtho[2,1-*f*]quinoxaline **7b** (241 mg, 0.5 mmol), $Pd(PPh_3)_4$ (58 mg, 0.05 mmol) and piperidine (11 mL) were stirred under argon for 20 min at 80-85 ºC. Then a solution of 1-ethynylpyrene (170 mg, 0.75 mmol) in piperidine (5 mL) was added by portions for 3 h. The reaction mixture was stirred for total 24 h at 80–85 ºC. Then it was evaporated to dryness, treated with H_2O (50 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The extract was dried over Na_2SO_4 and evaporated. The residue was purified by flash column chromatography on silica gel (3.5 × 35 cm) with CH_2Cl_2 as the eluent. The yellow fraction with R_f 0.8 gave 249 mg (86%) of **8f**. After recrystallization from EtOH compound **8f** was obtained as light yellow crystals with m.p. 273–275 ºC. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.96 (ddd, J = 8.7, 6.9, 1.5 Hz, 1 H), 7.33 (ddd, J = 8.2, 6.8, 1.2 Hz, 1 H), 7.44 (ddd, J = 7.9, 6.9, 1.0 Hz, 1 H), 7.50–7.59 (m, 2 H), 7.62–7.66 (m, 3 H), 7.71–7.80 (m, 2 H), 7.90–8.10 (m, 6 H), 8.13–8.24 (m, 5 H), 9.17 (d, J = 1.9 Hz, 1 H), 9.26 (d, J = 1.9 Hz, 1 H), 9.56 (d, J = 8.9 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 92.5, 100.7, 117.9, 121.1, 124.0, 124.1, 124.18, 124.22, 124.24, 125.3, 125.5, 126.0, 126.08, 126.09, 126.2, 126.5, 126.8, 126.9, 127.2, 127.5, 127.8, 127.9, 128.1, 128.5, 128.6, 128.9, 129.9, 130.1, 130.3, 130.6, 131.0, 131.1, 131.2, 131.3, 131.9, 132.3, 134.2, 134.9, 140.5, 141.1, 141.7, 144.3, 144.5, 145.7 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{44}H_{24}N_2Na^+$ [M+Na$^+$]: 603.1832, found 603.1837.

N^1,N^1,N^8,N^8-Tetramethyl-4-((11-(naphthalen-1-yl)naphtho[2,1-*f*]quinoxalin-12-yl)ethynyl)-naphthalene-1,8-diamine (8g)



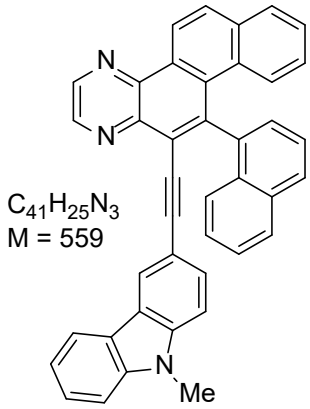
A mixture of 12-iodo-11-(naphthalen-1-yl)naphtho[2,1-*f*]quinoxaline **7b** (241 mg, 0.5 mmol), $Pd(PPh_3)_4$ (58 mg, 0.05 mmol) and piperidine (11 mL) was stirred for 20 min at 80-85 °C under argon. Then a solution of 4-ethynyl-N^1,N^1,N^8,N^8-tetramethylnaphthalene-1,8-diamine (244 mg, 1.02 mmol) in piperidine (5 mL) was added by portions for 3 h. The reaction mixture was stirred for total 24 h at 80–85 °C. Then it was evaporated to dryness, treated with H_2O (50 mL) and extracted with CH_2Cl_2 (3 × 25 mL). The extract was dried over Na_2SO_4 and evaporated. The residue was purified by flash column chromatography on Al_2O_3 (2.5 × 35 cm) with EtOAc - hexane (5:1, v/v) as the eluent. The dark brown fraction with R_f 0.7 gave **8g**. For crystallization the crude product was heated with hexane. Yield 249 mg (84%). Compound **8g** was obtained as brown crystals with m.p. 248–250 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.70 (s, 6 H), 2.76 (s, 6 H), 6.69 (d, J = 8.1 Hz, 1 H), 6.84–6.87 (m, 1 H), 6.92 (ddd, J = 8.7, 7.0, 1.4 Hz, 1 H), 7.00–7.06 (m, 2 H), 7.13–7.16 (m, 1 H), 7.26–7.32 (m, 1 H), 7.38–7.59 (m, 3 H), 7.64–7.72 (m, 3 H), 7.91–7.94 (m, 1 H), 8.08–8.18 (m, 3 H), 9.11 (d, J = 1.9 Hz, 1 H), 9.19 (d, J = 1.9 Hz, 1 H), 9.52 (d, J = 8.9 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 43.9, 44.0, 90.4, 101.9, 111.4, 112.7, 112.8, 119.0, 120.0, 122.1, 125.9, 126.1, 126.3, 126.4, 126.5, 126.6, 126.7, 127.4, 127.8, 128.3, 128.4, 128.6, 128.8, 129.7, 130.1, 130.4, 131.3, 132.0, 132.1, 132.2, 132.3, 134.2, 134.8, 137.6, 140.5, 141.3, 141.8, 143.0, 144.0, 145.5, 150.7, 151.6 ppm. HRMS (ESI): m/z calcd. for $C_{42}H_{33}N_4^+$ [M+H$^+$]: 593.2700, found 593.2714.

N^1,N^1,N^8,N^8-Tetramethyl-2-((11-(naphthalen-1-yl)naphtho[2,1-*f*]quinoxalin-12-yl)ethynyl)-naphthalene-1,8-diamine (8h)



A mixture of 12-iodo-11-(naphthalen-1-yl)naphtho[2,1-*f*]quinoxaline **7b** (165 mg, 0.34 mmol), $Pd(PPh_3)_4$ (39 mg, 0.034 mmol) and piperidine (7 mL) was stirred for 20 min at 80-85 °C under argon. Then a solution of 2-ethynyl-N^1,N^1,N^8,N^8-tetramethylnaphthalene-1,8-diamine (164 mg, 0.069 mmol) in piperidine (4 mL) was added by portions for 1 h. The reaction mixture was stirred for total 24 h at 80–85 °C. Then it was evaporated to dryness, treated with H_2O (30 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The extract was dried over Na_2SO_4 and evaporated. The residue was purified by flash column chromatography on Al_2O_3 (2.5 × 14 cm) with CH_2Cl_2 - EtOAc (10:1, v/v) as the eluent. The orange fraction with R_f 0.15 gave **8h**. For crystallization the crude product was heated with hexane. Yield 179 mg (89%). Compound **8h** was obtained as brown crystals with m.p. 198–201 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.70 (s, 6 H), 2.92 (s, 6 H), 6.23 (d, J = 8.4 Hz, 1 H), 6.84–6.94 (m, 2 H), 7.02 (d, J = 8.4 Hz, 1 H), 7.16–7.55 (m, 7 H), 7.64–7.98 (m, 2 H), 7.92 (d, J = 7.6 Hz, 1 H), 8.04–8.15 (m, 3 H), 9.10 (pseudodoublet, J = 1.8 Hz, 2 H), 9.50 (d, J = 8.9 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 44.4, 44.5, 92.4, 103.6, 113.1, 113.2, 121.2, 121.3, 121.7, 122.1, 124.8, 125.8, 126.29, 126.30, 126.33, 126.67, 126.70, 127.5, 127.9, 128.4, 128.8, 129.7, 130.0, 130.5, 131.1, 132.3, 134.2, 134.8, 138.0, 140.4, 141.2, 142.0, 143.2, 144.0, 145.2, 151.6, 151.7 ppm. HRMS (ESI): m/z calcd. for $C_{42}H_{33}N_4^+$ [M+H$^+$]: 593.2700, found 593.2732.

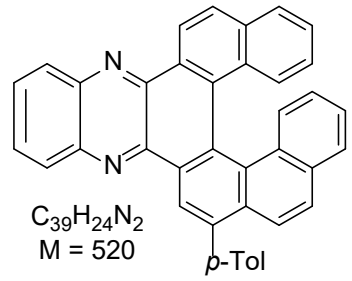
12-((9-Methyl-9*H*-carbazol-3-yl)ethynyl)-11-(naphthalen-1-yl)naphtho[2,1-*f*]quinoxaline (8i)



$C_{41}H_{25}N_3$
M = 559

12-Iodo-11-(naphthalen-1-yl)naphtho[2,1-*f*]quinoxaline **7b** (241 mg, 0.5 mmol), $Pd(PPh_3)_4$ (58 mg, 0.05 mmol) and piperidine (11 mL) were stirred for 20 min at 105 ºC under argon. Then a solution of 3-ethynyl-9-methyl-9*H*-carbazole (307 mg, 1.5 mmol) in piperidine (5 mL) was added by portions for 3 h. The reaction mixture was stirred for total 24 h at 100–105 ºC. Then it was evaporated to dryness, treated with H_2O (50 mL) and extracted with CH_2Cl_2 (3 × 15 mL). The extract was dried over Na_2SO_4 and evaporated. The residue was purified by flash column chromatography on silica gel (4 × 18 cm) with CH_2Cl_2 as the eluent. The yellow fraction with R_f 0.7 gave 251 mg (90%) of **8i**. After crystallization from EtOH compound **8i** was obtained as yellow crystals with m.p. 242–243 ºC (decomp.). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.78 (s, 3 H), 6.94–6.99 (m, 2 H), 7.15 (d, *J* = 8.5 Hz, 1 H), 7.29–7.61 (m, 9 H), 7.69 (t, *J* = 8.0 Hz, 1 H), 7.82 (d, *J* = 8.4 Hz, 1 H), 7.95 (d, *J* = 7.6 Hz, 1 H), 8.03 (d, *J* = 7.6 Hz, 1 H), 8.14–8.17 (m, 3 H), 9.12 (d, *J* = 1.8 Hz, 1 H), 9.18 (d, *J* = 1.8 Hz, 1 H), 9.53 (d, *J* = 8.9 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 29.1, 85.7, 103.5, 108.0, 108.6, 113.1, 119.4, 120.4, 122.1, 122.5, 124.3, 124.5, 125.9, 126.0, 126.4, 126.6, 126.7, 126.8, 127.4, 128.0, 128.3, 128.4, 128.8, 129.3, 129.9, 130.0, 130.6, 130.8, 132.4, 134.2, 134.9, 140.5, 140.6, 141.3, 141.4, 144.1, 144.4, 145.4 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{41}H_{26}N_3^+$ [M+H$^+$]: 560.2121, found 560.2122.

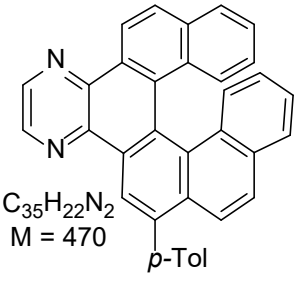
20-(*p*-Tolyl)naphtho[2,1-*a*]phenanthro[4,3-*c*]phenazine (9a)



$C_{39}H_{24}N_2$
M = 520

A stirred solution of 5-(naphthalen-1-yl)-6-(*p*-tolylethynyl)-naphtho[2,1-*a*]phenazine **8a** (100 mg, 0.19 mmol) in CF_3COOH (4 mL) was heated at 60 ºC for 6 h. The reaction mixture was evaporated to dryness, treated with saturated Na_2CO_3 (10 mL) and extracted with CH_2Cl_2 (3 × 15 mL). The organic layer was dried over Na_2SO_4 and purified by flash column chromatography on silica gel (2.5 × 37 cm) with $CHCl_3$ as the eluent. The bright yellow fraction with R_f 0.8 gave cyclization product **9a** (74 mg, 74%). Compound **9a** was obtained as a bright yellow solid with mp 243–244 ºC (decomp., EtOH). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.56 (s, 3 H), 6.66–6.78 (m, 2 H), 7.19–7.30 (m, 2 H), 7.42–7.47 (m, 3 H), 7.51 (d, *J* = 8.5 Hz, 1 H), 7.68 (d, *J* = 7.8 Hz, 2 H), 7.78 (d, *J* = 8.0 Hz, 1 H), 7.82–7.91 (m, 4 H), 8.06–8.16 (m, 2 H), 8.32–8.36 (m, 1 H), 8.40–8.44 (m, 1 H), 9.47 (d, *J* = 8.7 Hz, 1 H), 9.53 (s, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.4, 122.3, 123.8, 124.2, 124.6, 125.1, 126.0, 126.2, 126.5, 127.4, 127.8, 128.0, 128.3, 128.4, 128.5, 128.9, 129.2, 129.5, 129.6, 129.7, 129.8, 129.9, 130.3, 130.4, 130.5, 131.0, 131.5, 131.6, 133.9, 137.4, 137.7, 140.5, 142.3, 142.4, 142.5, 142.8 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{39}H_{25}N_2^+$ [M+H$^+$]: 521.2012, found 521.2014.

6-(*p*-Tolyl)naphtho[2,1-*f*]phenanthro[4,3-*h*]quinoxaline (9b)

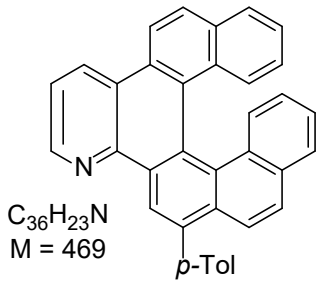


$C_{35}H_{22}N_2$
M = 470

A solution of 11-(naphthalen-1-yl)-12-(*p*-tolylethynyl)naphtho[2,1-*f*]-quinoxaline **8b** (81 mg, 0.17 mmol) in CF_3COOH (7 mL) was stirred for 6 h at 60 ºC. Then the dark red reaction mixture was evaporated to dryness, shaken with saturated solution of Na_2CO_3 (10 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The orange organic phase was dried over Na_2SO_4 and purified by flash column chromatography on silica gel (2 × 19 cm) with CH_2Cl_2 as the eluent. The yellow fraction with R_f 0.8 gave 58 mg (71%) of **9b**. Compound **9b** was obtained as a beige solid with m.p. 236–238 ºC (EtOH). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.54 (s, 3 H), 6.65–6.77 (m, 2 H), 7.19–7.30 (m, 2 H), 7.42 (d, *J* = 7.9 Hz, 2 H), 7.51 (d, *J* = 8.6 Hz, 2 H), 7.66 (d, *J* = 7.9 Hz, 2 H), 7.79 (d, *J* = 7.9 Hz, 1 H), 7.86 (d, *J* = 8.7 Hz, 2 H), 8.11 (dd, *J* = 8.8, 6.7 Hz,

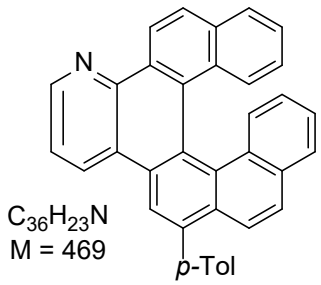
2 H), 8.97 (d, *J* = 6.0 Hz, 2 H), 9.30 (d, *J* = 8.8 Hz, 1 H), 9.35 (s, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.4, 121.4, 123.0, 124.2, 124.7, 124.8, 125.1, 126.1, 126.4, 127.4, 127.8, 127.9, 128.0, 128.2, 128.4, 128.9, 129.2, 129.3, 129.6, 129.8, 129.9, 130.2, 130.4, 131.0, 131.6, 133.4, 137.3, 137.6, 140.5, 141.4, 141.5, 143.5, 143.6 ppm. HRMS (ESI): *m/z* calcd. for $C_{35}H_{22}N_2Na^+$ [M+Na$^+$]: 493.1675, found 493.1678.

17-(*p*-Tolyl)naphtho[2,1-*f*]phenanthro[4,3-*h*]quinoline (9c)



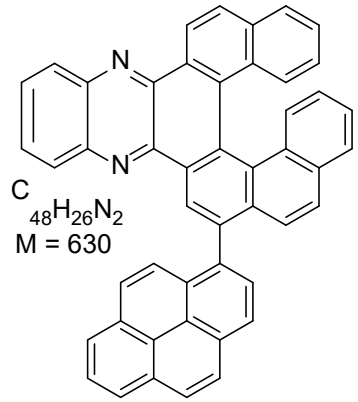
The stirred solution of 11-(naphthalen-1-yl)-12-(*p*-tolylethynyl)-naphtho[1,2-*h*]quinoline **8c** (47 mg, 0.1 mmol) in CF_3COOH (3 mL) was heated at 60 ºC for 16 h. The reaction mixture was evaporated to dryness, treated with saturated Na_2CO_3 (50 mL) and extracted with $CHCl_3$ (3 × 15 mL). The organic phase was dried over Na_2SO_4 and purified by flash column chromatography on silica gel (2 × 15 cm) with $CHCl_3$ as the eluent. The yellowish fraction with R_f 0.8 gave cyclization product **9c** (42 mg, 89%). Compound **9c** was obtained as an off-white solid with m.p. 220–222 ºC (MeCN). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.53 (s, 3 H), 6.65 (ddd, *J* = 8.4, 7.0, 1.3 Hz, 1 H), 6.72 (ddd, *J* = 8.5, 6.9, 1.3 Hz, 1 H), 7.16–7.26 (m, 2 H), 7.39–7.53 (m, 4 H), 7.63–7.68 (m, 3 H), 7.76–7.85 (m, 3 H), 8.06–8.11 (m, 2 H), 8.66 (d, *J* = 8.9 Hz, 1 H), 9.01–9.06 (m, 2 H), 9.46 (s, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.4, 120.3, 122.0, 123.3, 124.3, 124.5, 125.1, 125.2, 125.82, 125.83, 126.4, 127.3, 127.5, 127.7, 127.9, 128.1, 128.2, 128.5, 129.1 (2C), 129.2, 130.1, 130.3, 130.4, 130.5 (2C), 131.0, 131.1, 131.6, 132.3, 137.1, 137.9, 140.2, 146.5, 149.1 ppm. HRMS (ESI): *m/z* calcd. for $C_{36}H_{24}N^+$ [M+H$^+$]: 470.1903, found 470.1910.

6-(*p*-Tolyl)naphtho[1,2-*h*]phenanthro[3,4-*f*]quinoline (9d)



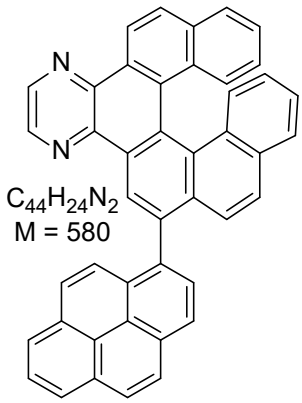
The stirred solution of 11-(naphthalen-1-yl)-12-(*p*-tolylethynyl)-naphtho[1,2-*h*]quinoline **8d** (113 mg, 0.24 mmol) in CF_3COOH (5 mL) was heated at 60 ºC for 16 h. The reaction mixture was evaporated to dryness, treated with saturated Na_2CO_3 (50 mL) and extracted with $CHCl_3$ (3 × 15 mL). The organic phase was dried over Na_2SO_4 and purified by flash column chromatography on silica gel (2 × 15 cm) with $CHCl_3$ as the eluent. The yellowish fraction with R_f 0.7 gave cyclization product **9d** (96 mg, 85%). Compound **9d** was obtained as an off-white solid with m.p. 262–263 ºC (C_6H_6-EtOH, 1:1). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.56 (s, 3 H), 6.66–6.76 (m, 2 H), 7.19–7.27 (m, 2 H), 7.39–7.65 (m, 7 H), 7.78 (d, *J* = 7.8 Hz, 1 H), 7.82–7.89 (m, 2 H), 8.03 (d, *J* = 8.9 Hz, 1H), 8.14 (d, *J* = 8.8 Hz, 1 H), 8.64 (s, 1 H), 8.97 (dd, *J* = 8.3, 1.2 Hz, 1 H), 9.09 (dd, *J* = 4.3, 1.4 Hz, 1 H), 9.46 (d, *J* = 8.8 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.4, 121.4, 121.5, 121.9, 122.0, 122.1, 123.1, 123.9, 124.7, 124.8, 124.9, 126.0, 126.1, 127.3, 127.7, 127.9, 128.3, 128.6, 129.3, 129.4, 129.67, 129.68, 129.69, 130.3, 130.4, 131.2, 131.6, 133.1, 137.5, 137.8, 139.9, 146.7, 149.1 ppm. HRMS (ESI): *m/z* calcd. for $C_{36}H_{24}N^+$ [M+H$^+$]: 470.1903, found 470.1908.

20-(Pyren-1-yl)naphtho[2,1-*a*]phenanthro[4,3-*c*]phenazine (9e)



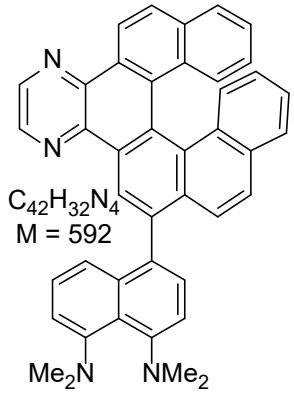
A stirred solution of 5-(naphthalen-1-yl)-6-(pyren-1-ylethynyl)-naphtho[2,1-*a*]phenazine **8e** (100 mg, 0.16 mmol) in CF_3COOH (5 mL) was heated at 60 °C for 10 h. The reaction mixture was evaporated to dryness, treated with saturated Na_2CO_3 (10 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The organic layer was dried over Na_2SO_4 and purified by flash column chromatography on silica gel (2.5 × 70 cm) with CH_2Cl_2-hexane (2:1, v/v) as the eluent. The bright yellow fraction with R_f 0.6 gave cyclization product **9e** (88 mg, 88%). Yellow solid with m.p. >329 °C (decomp., EtOH). ^{1}H NMR (250 MHz, $CDCl_3$) for a mixture of stereoisomers: δ = 6.71–6.89 (m, 4 H), 7.21–7.37 (m, 5 H), 7.51–8.48 (m, 43 H), 9.55 (d, *J* = 8.8 Hz, 1 H), 9.56 (d, *J* = 8.6 Hz, 1 H), 9.73 (s, 1 H), 9.77 (s, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$) for a mixture of stereoisomers: δ = 122.3, 122.4, 124.5, 124.6, 124.70, 124.71, 124.8, 125.2, 125.3, 125.4, 125.86, 125.92, 126.17, 126.19, 126.30, 126.32, 126.6, 127.52, 127.54, 127.55, 127.57, 127.75, 127.77, 127.9, 128.0, 138.5, 128.6, 128.9, 129.1, 129.55, 129.58, 129.6, 129.9, 130.3, 131.8, 132.8, 132.9, 134.0, 134.01, 135.6, 135.7, 139.0, 139.4, 142.43, 142.45, 142.5, 142.6, 142.8 ppm. HRMS (ESI): *m/z* calcd. for $C_{48}H_{27}N_2^+$ [M+H$^+$]: 631.2169, found 631.2164.

6-(Pyren-1-yl)naphtho[2,1-*f*]phenanthro[4,3-*h*]quinoxaline (9f)



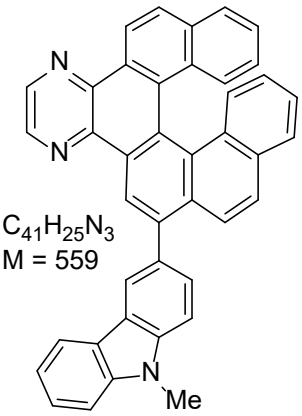
Compound **9f** was prepared similarly to the compound **9b** from 11-(naphthalen-1-yl)-12-(pyren-1-ylethynyl)naphtho[2,1-*f*]quinoxaline **8f** (58 mg, 0.1 mmol) and CF_3COOH (4 mL). $CHCl_3$ was used for extraction (3 × 30 mL). The orange organic phase was dried over Na_2SO_4 and purified by flash column chromatography on silica gel (2 × 26 cm) with $CHCl_3$ as the eluent. The yellow fraction with R_f 0.8 gave **9f**. The crude product was crystallized by heating with EtOH. Yield 54 mg (92%)**.** The compound **9e** was obtained as a pale yellow solid with m.p. 289–295 °C. ^{1}H NMR (250 MHz, $CDCl_3$) for a mixture of stereoisomers: *δ* = 6.70–6.81 (m, 3 H), 6.82–6.89 (m, 1 H), 7.21–7.37 (m, 4 H), 7.54–7.66 (m, 5 H), 7.69–7.79 (m, 6 H), 7.84–8.09 (m, 7 H), 8.12–8.32 (m, 12 H), 8.37–8.42 (m, 2 H), 8.91 (d, *J* = 2.1 Hz, 1 H), 8.94 (d, *J* = 2.1 Hz, 1 H), 9.00–9.02 (m, 2 H), 9.36 (d, *J* = 2.8 Hz, 1 H), 9.39 (d, *J* = 2.8 Hz, 1 H), 9.57 (s, 1 H), 9.60 (s, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$) for a mixture of stereoisomers: *δ* = 121.5, 121.6, 124.51, 124.54, 124.58, 124.7, 124.8, 124.9, 125.1, 125.2, 125.3, 125.4, 125.8, 125.9, 126.14, 126.16, 126.2, 126.3, 126.4, 126.5, 127.5, 127.6, 127.7, 127.8, 127.9, 128.0, 128.1, 128.26, 128.28, 129.1, 129.7, 130.2, 131.0, 131.2, 131.5, 131.7, 132.3, 132.4, 133.4, 133.5, 135.5, 135.7, 138.9, 139.4, 141.3, 141.4, 141.6, 143.59, 143.62, 143.64, 143.7 ppm. HRMS (ESI): *m/z* calcd. for $C_{44}H_{25}N_2^+$ [M+H$^+$]: 581.2012, found 581.2012.

N^1,N^1,N^8,N^8-Tetramethyl-4-(naphtho[2,1-*f*]phenanthro[4,3-*h*]quinoxalin-6-yl)naphthalene-1,8-diamine (9g)



A solution of N^1,N^1,N^8,N^8-tetramethyl-4-((11-(naphthalen-1-yl)-naphtho[2,1-*f*]quinoxalin-12-yl)ethynyl)naphthalene-1,8-diamine **8g** (59 mg, 0.1 mmol) in CF_3COOH (4 mL) was stirred at 60 ºC for 10 h. Then the dark red reaction mixture was evaporated to dryness, shaken with saturated solution of Na_2CO_3 (10 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The orange organic phase was dried over Na_2SO_4 and purified by flash column chromatography on Al_2O_3 (2 × 70 cm) with EtOAc - hexane (5:1, v/v) as the eluent. The dark brown fraction with R_f 0.6 gave **9g**. The crude product was crystallized from hexane. Yield 46 mg (78%). Compound **9g** was obtained as yellow brown crystals with m.p. 260–264 ºC. ^{1}H NMR (250 MHz, $CDCl_3$) for a mixture of stereoisomers: δ = 2.93 (s, 6 H), 2.97 (s, 6 H), 6.65–6.84 (m, 2 H), 6.82–7.09 (m, 2 H), 7.12–7.33 (m, 4 H), 7.48–7.58 (m, 3 H), 7.63–7.77 (m, 4 H), 7.86–7.92 (m, 1 H), 8.14–8.18 (m, 1 H), 8.91 (d, J = 2.1 Hz, 0.5 H), 8.93 (d, J = 2.1 Hz, 0.5 H), 8.98–9.00 (m, 1 H), 9.32 (d, J = 2.5 Hz, 0.5 H), 9.35 (d, J = 2.5 Hz, 0.5 H), 9.37 (s, 0.5 H), 9.42 (s, 0.5 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$) for a mixture of stereoisomers: δ = 29.7, 120.1, 120.2, 121.4, 121.5, 124.3, 124.4, 124.6, 124.7, 125.0, 125.1, 126.0, 126.3, 126.4, 127.4, 127.8, 127.9, 128.1, 128.2, 128.4, 128.6, 128.8, 129.7, 129.9, 130.0, 130.1, 130.3, 131.7, 131.9, 132.0, 132.1, 132.2, 133.3, 133.4, 141.4, 141.5, 141.6, 143.5, 143.57, 143.60 ppm. HRMS (ESI): m/z calcd. for $C_{42}H_{33}N_4^+$ [M+H$^+$]: 593.2700, found 593.2710.

6-(9-Methyl-9*H*-carbazol-3-yl)naphtho[2,1-*f*]phenanthro[4,3-*h*]quinoxaline (9i)



A solution of 12-((9-methyl-9*H*-carbazol-3-yl)ethynyl)-11-(naphthalen-1-yl)naphtho[2,1-*f*]quinoxaline **8i** (112 mg, 0.2 mmol) in CF_3COOH (5 mL) was stirred for 24 h at 60 ºC. Then the dark red reaction mixture was evaporated to dryness, shaken with saturated solution of Na_2CO_3 (10 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The orange organic phase was dried over Na_2SO_4 and purified by flash column chromatography on silica gel (2 × 15 cm) with CH_2Cl_2 as the eluent. The yellow fraction with R_f 0.6 gave **9i**. The product was crystallized by heating with ethanol. Yield 68 mg (60%). Compound **9i** was obtained as a yellow solid with m.p. 211–214 ºC (EtOH). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.99 (s, 3 H), 6.73 (dddd, J = 16.7, 8.5, 6.9, 1.4 Hz, 2 H), 7.20–7.32 (m, 3 H), 7.48–7.63 (m, 5 H), 7.80 (dd, J = 8.1, 1.1 Hz, 1 H), 7.87–7.90 (m, 3 H), 8.13–8.19 (m, 3 H), 8.48 (d, J = 1.6 Hz, 1 H), 8.98 (d, J = 2.1 Hz, 1 H), 9.01 (d, J = 2.1 Hz, 1 H), 9.33 (d, J = 8.7 Hz, 1 H), 9.47 (s, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 29.3, 108.3, 108.7, 119.2, 120.6, 121.4, 122.3, 122.9, 123.0, 123.3, 124.5, 124.6, 124.7, 125.0, 126.0, 126.1, 126.4, 127.4, 127.8, 127.9, 128.0, 128.3 (2C), 128.4, 128.8, 129.4, 129.7, 129.9, 130.3, 131.2, 131.5, 131.6, 133.4, 140.6, 141.4, 141.5, 141.6, 141.7, 143.5, 143.6 ppm. HRMS (ESI): m/z calcd. for $C_{41}H_{26}N_3^+$ [M+H$^+$]: 560.2121, found 560.2122.

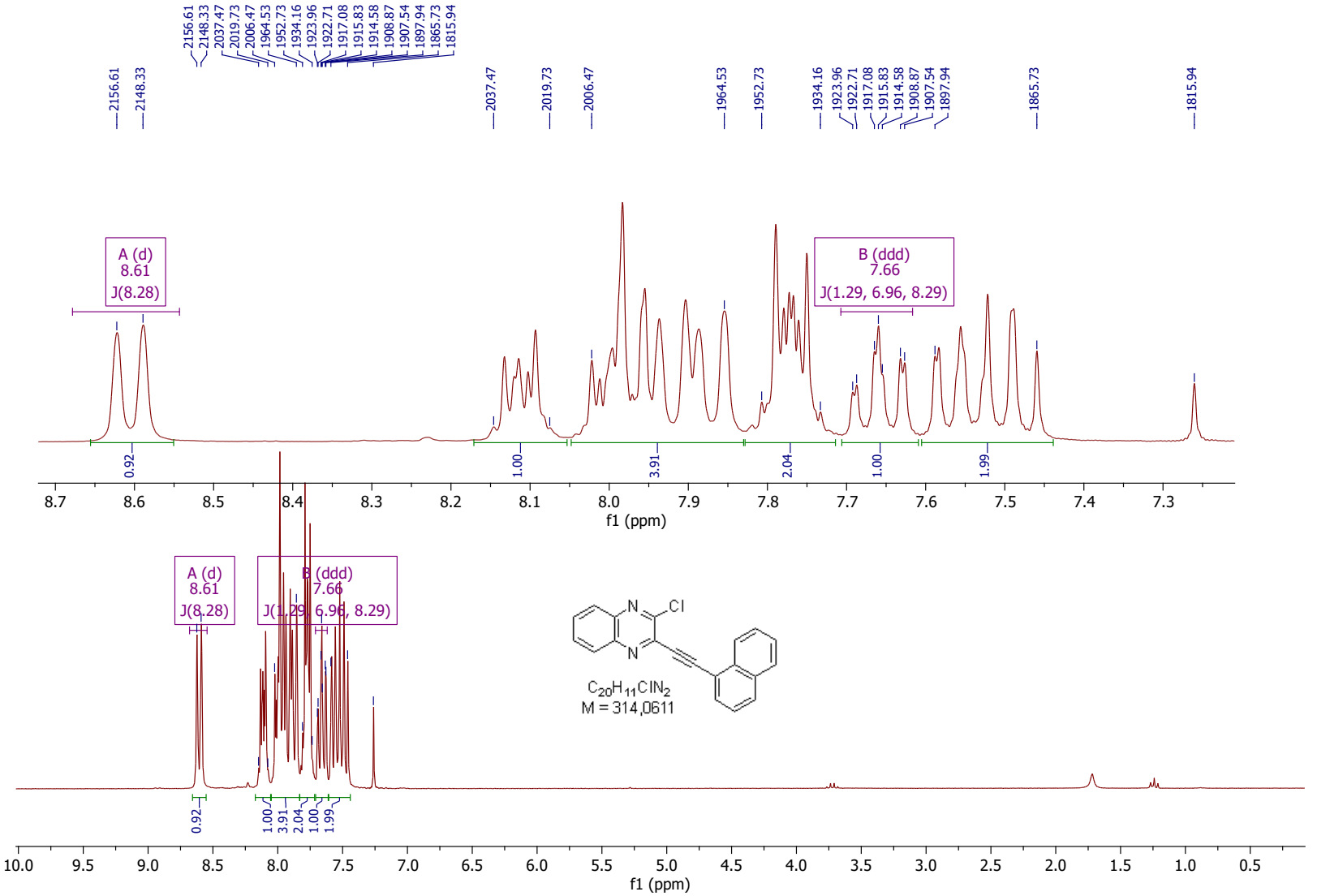


Fig. S1. ^{1}H NMR spectrum of compound **2a** (250 MHz, $CDCl_3$).

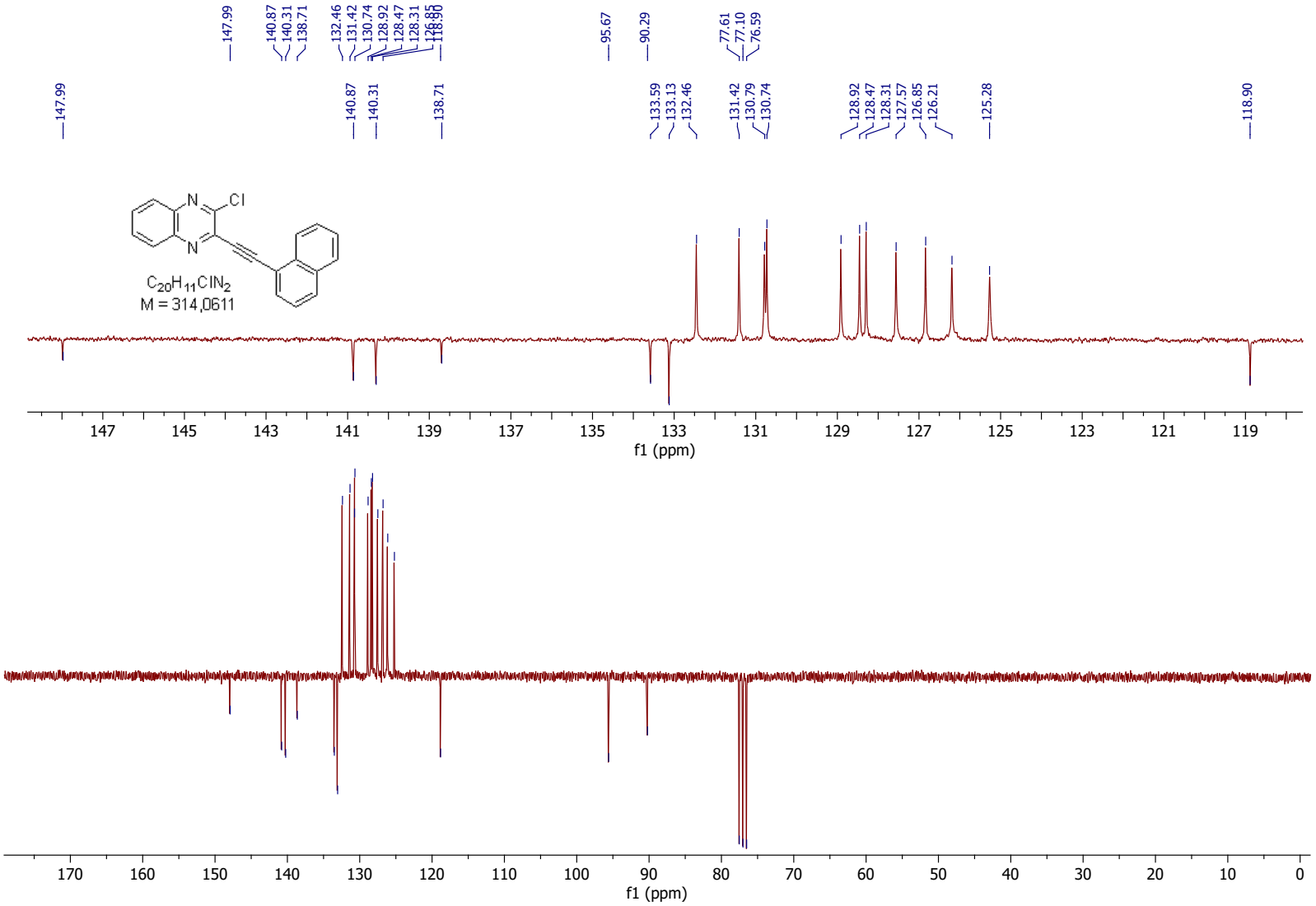


Fig. S2. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **2a** (62.9 MHz, $CDCl_3$).

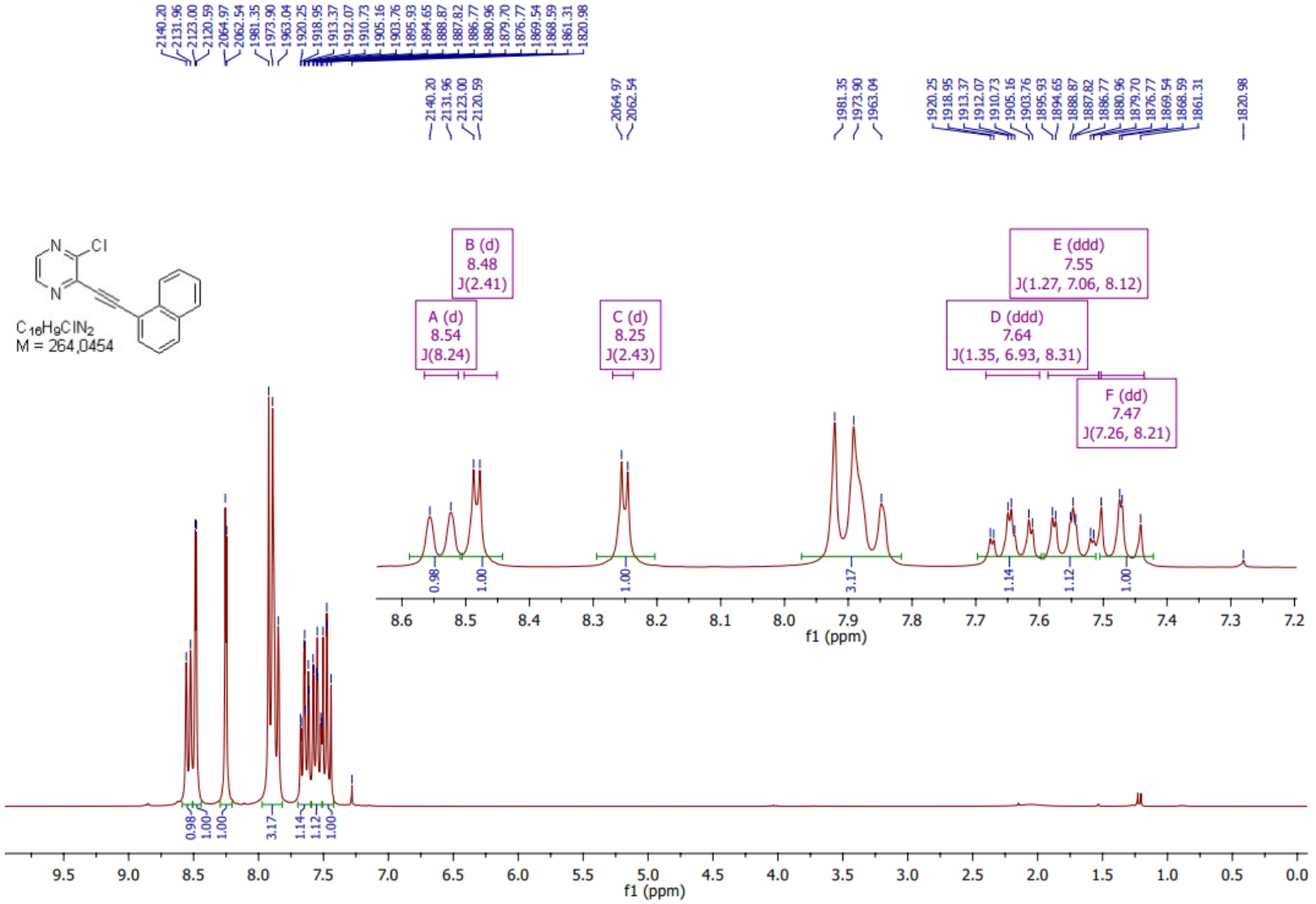


Fig. S3. ^{1}H NMR spectrum of compound **2b** (250 MHz, $CDCl_3$).

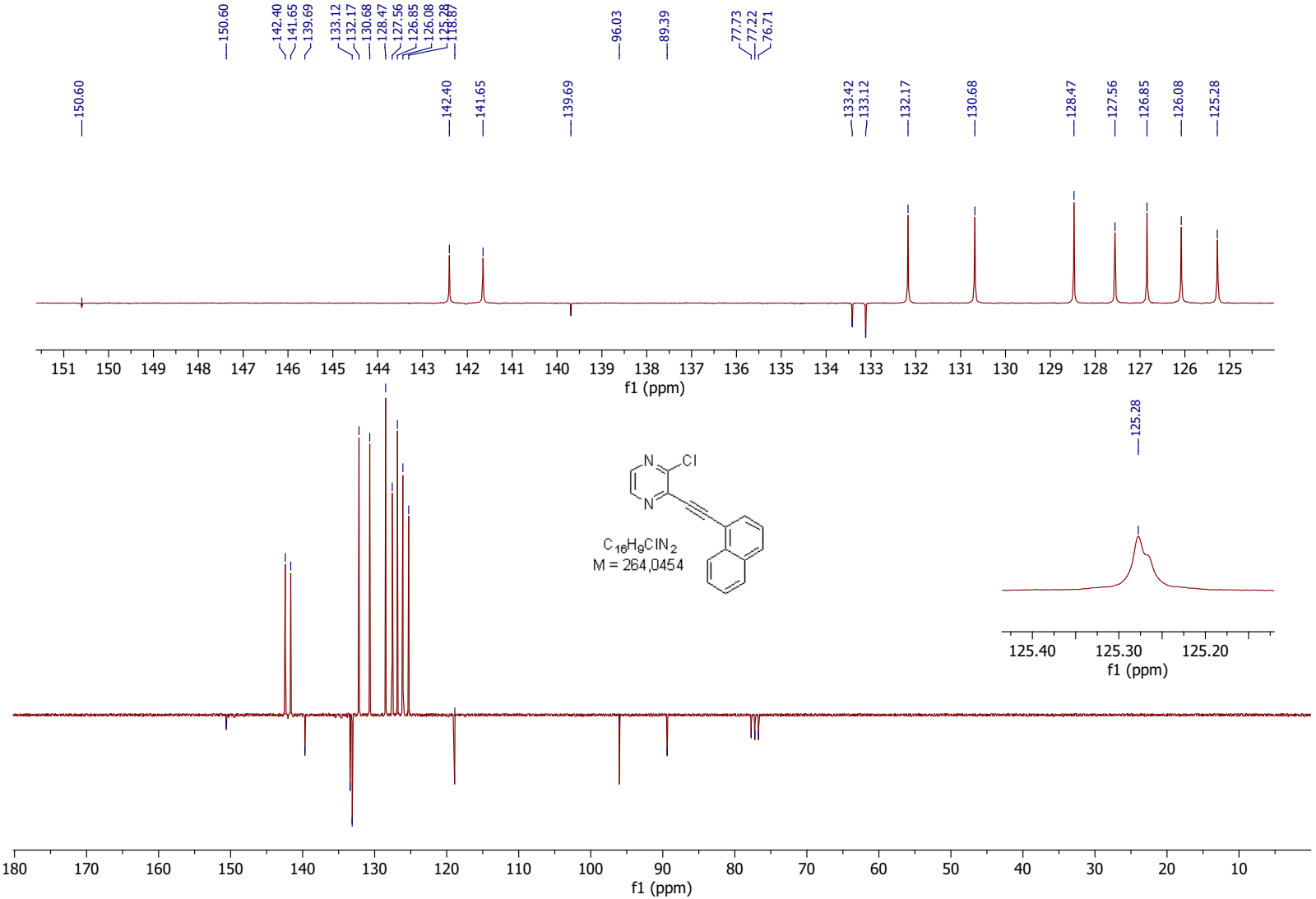


Fig. S4. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **2b** (62.9 MHz, $CDCl_3$).

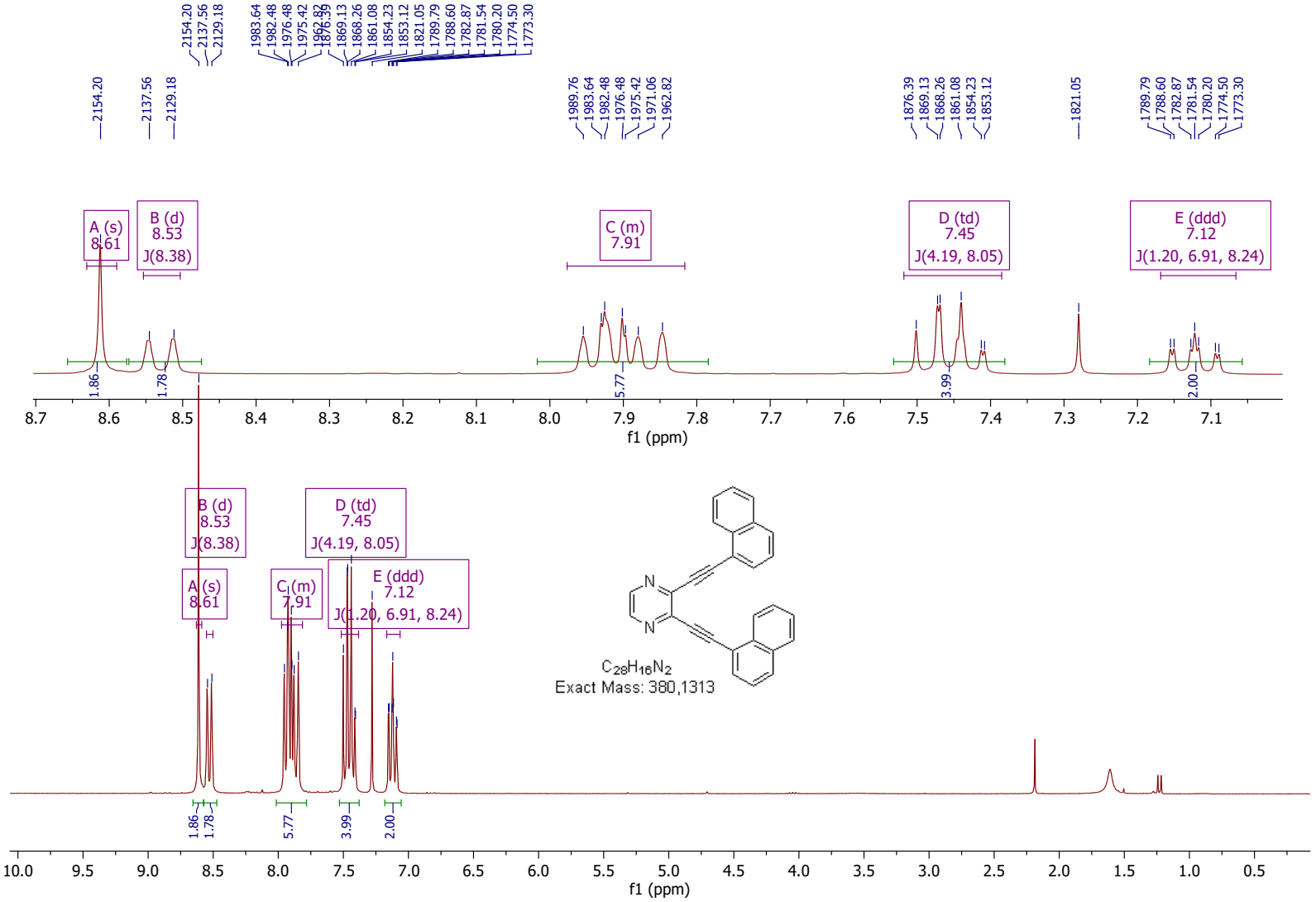


Fig. S5. ^{1}H NMR spectrum of compound **3** (250 MHz, $CDCl_3$).

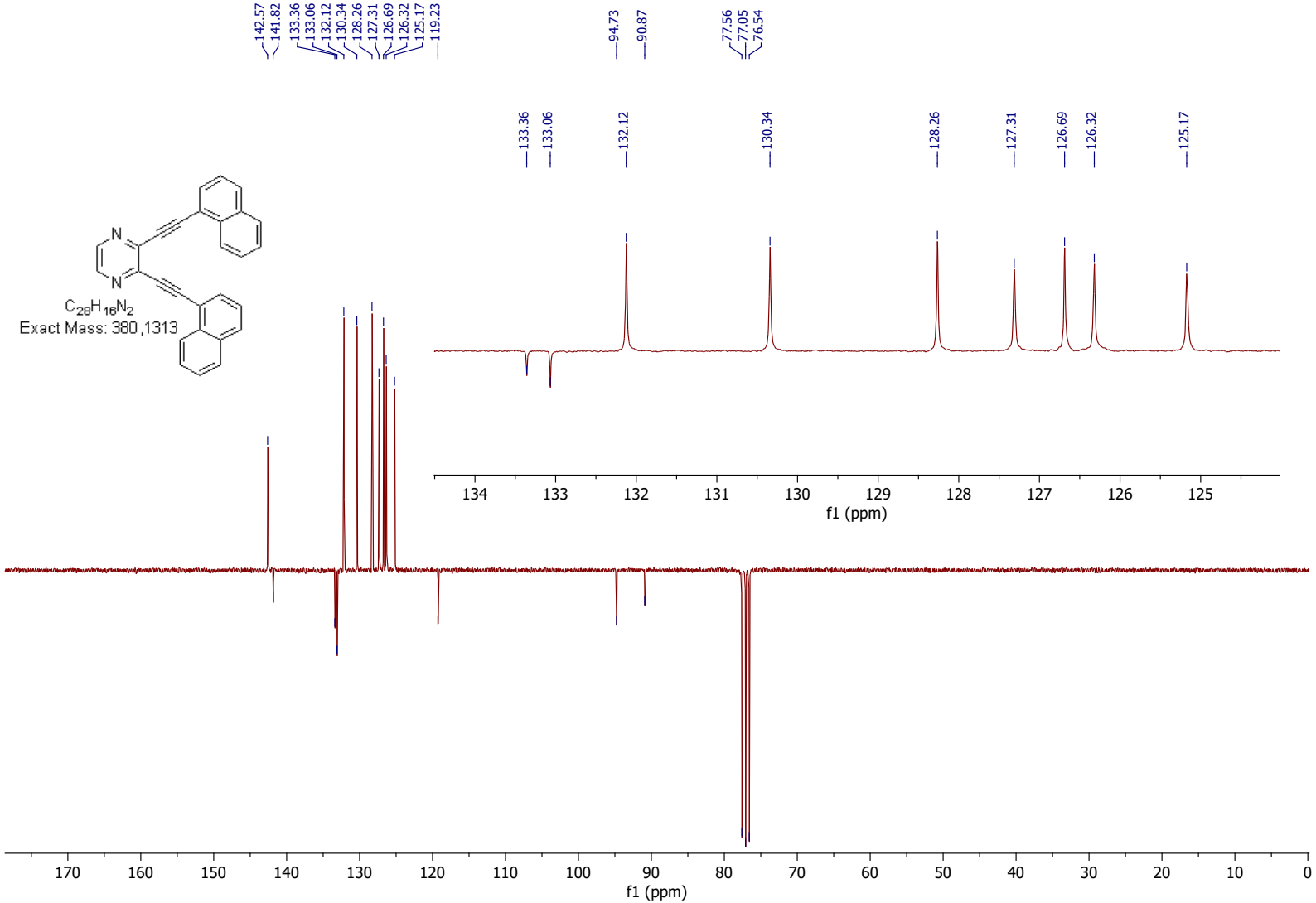


Fig. S6. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **3** (62.9 MHz, $CDCl_3$).

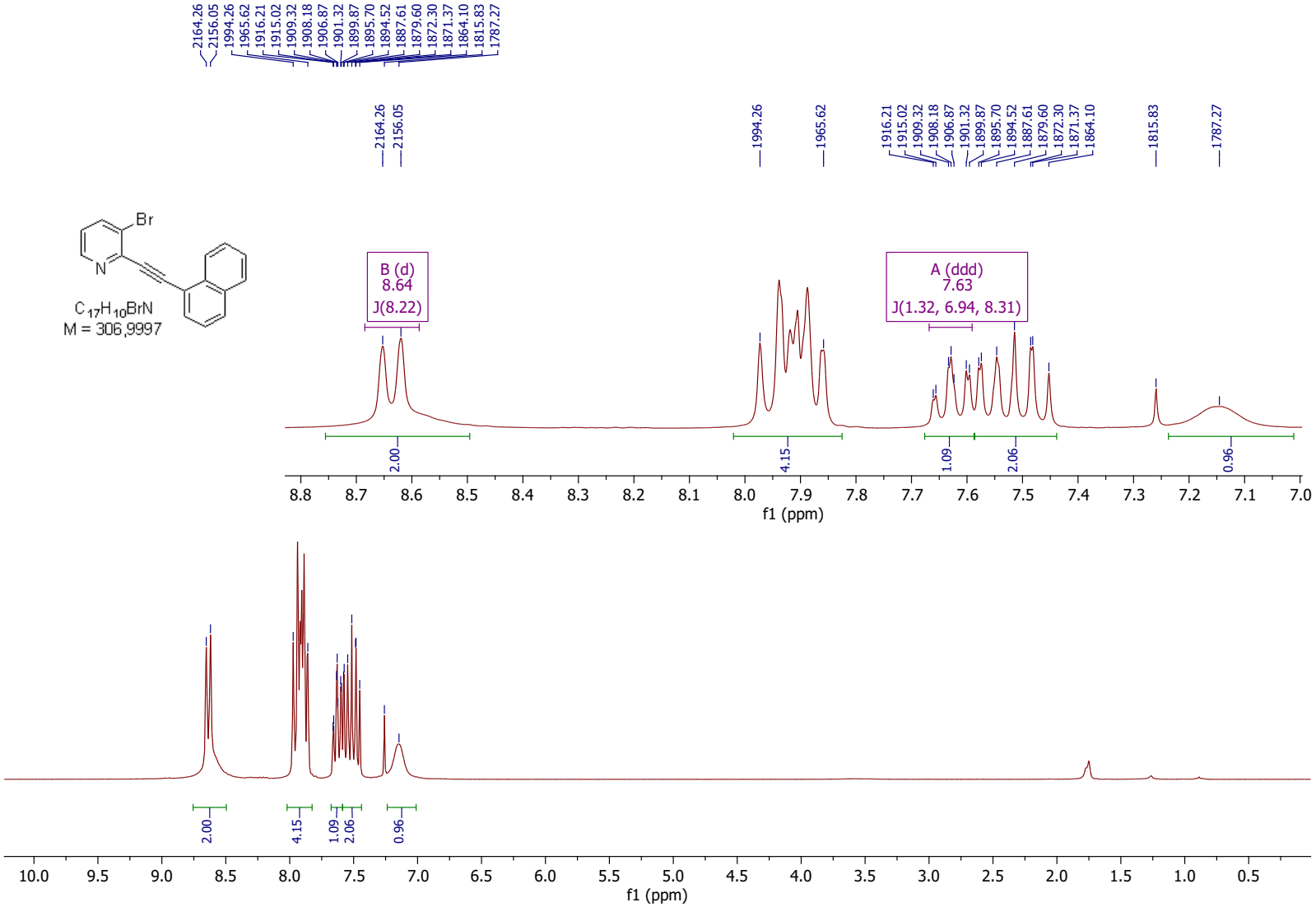


Fig. S7. ^{1}H NMR spectrum of compound **2c** (250 MHz, $CDCl_3$).

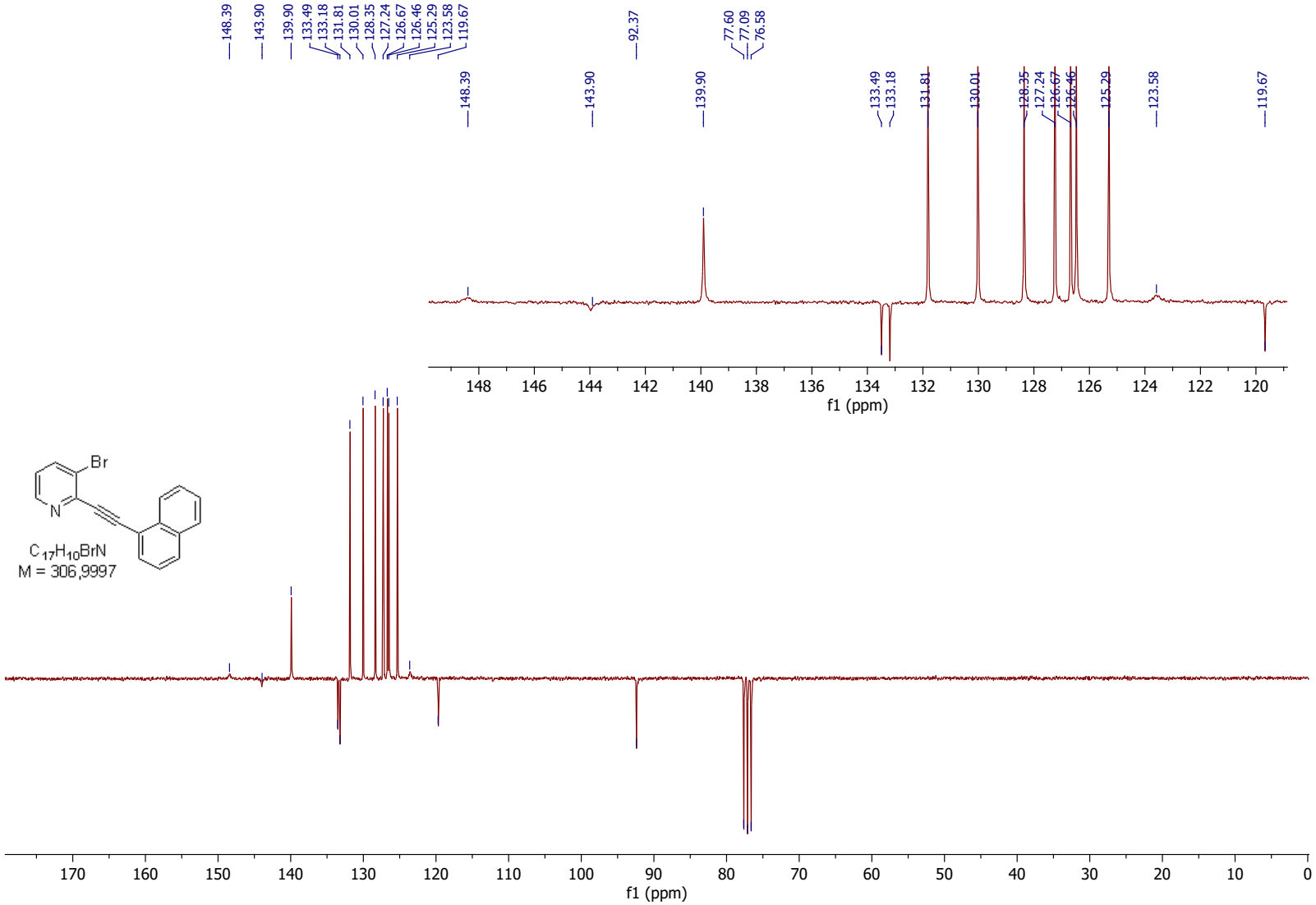


Fig. S8. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **2c** (62.9 MHz, $CDCl_3$).

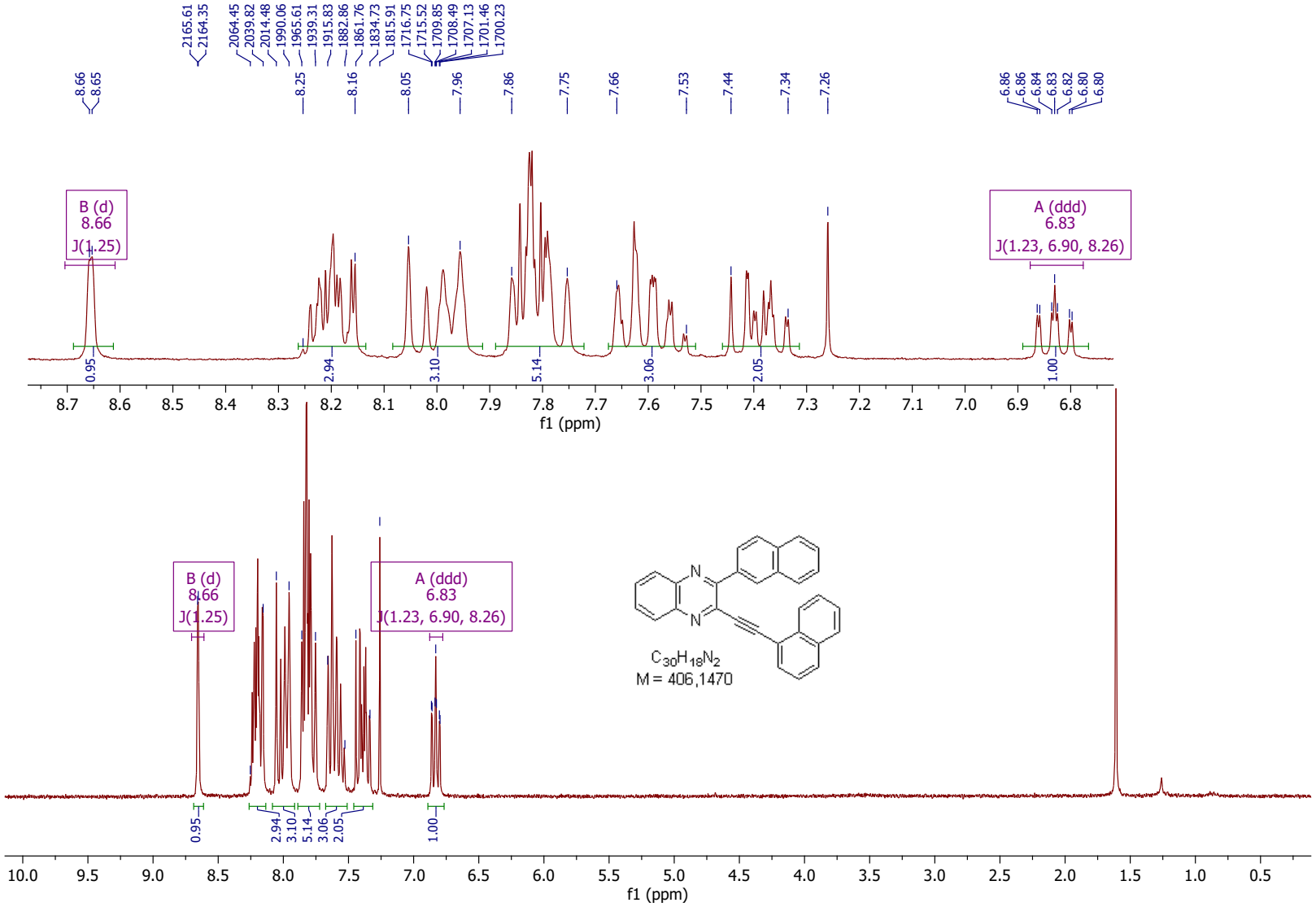


Fig. S9. ^{1}H NMR spectrum of compound **4a** (250 MHz, $CDCl_3$).

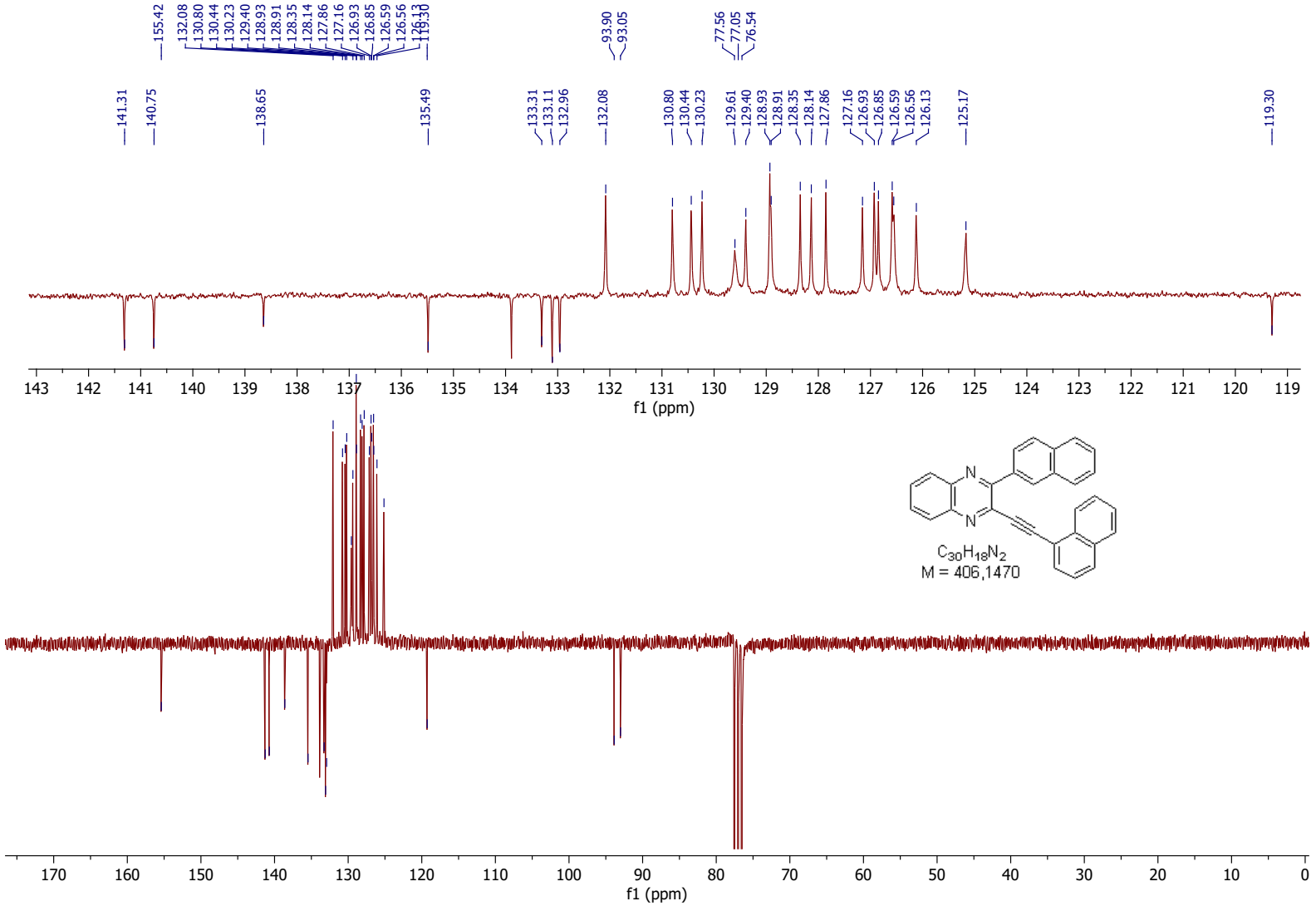


Fig. S10. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **4a** (62.9 MHz, $CDCl_3$).

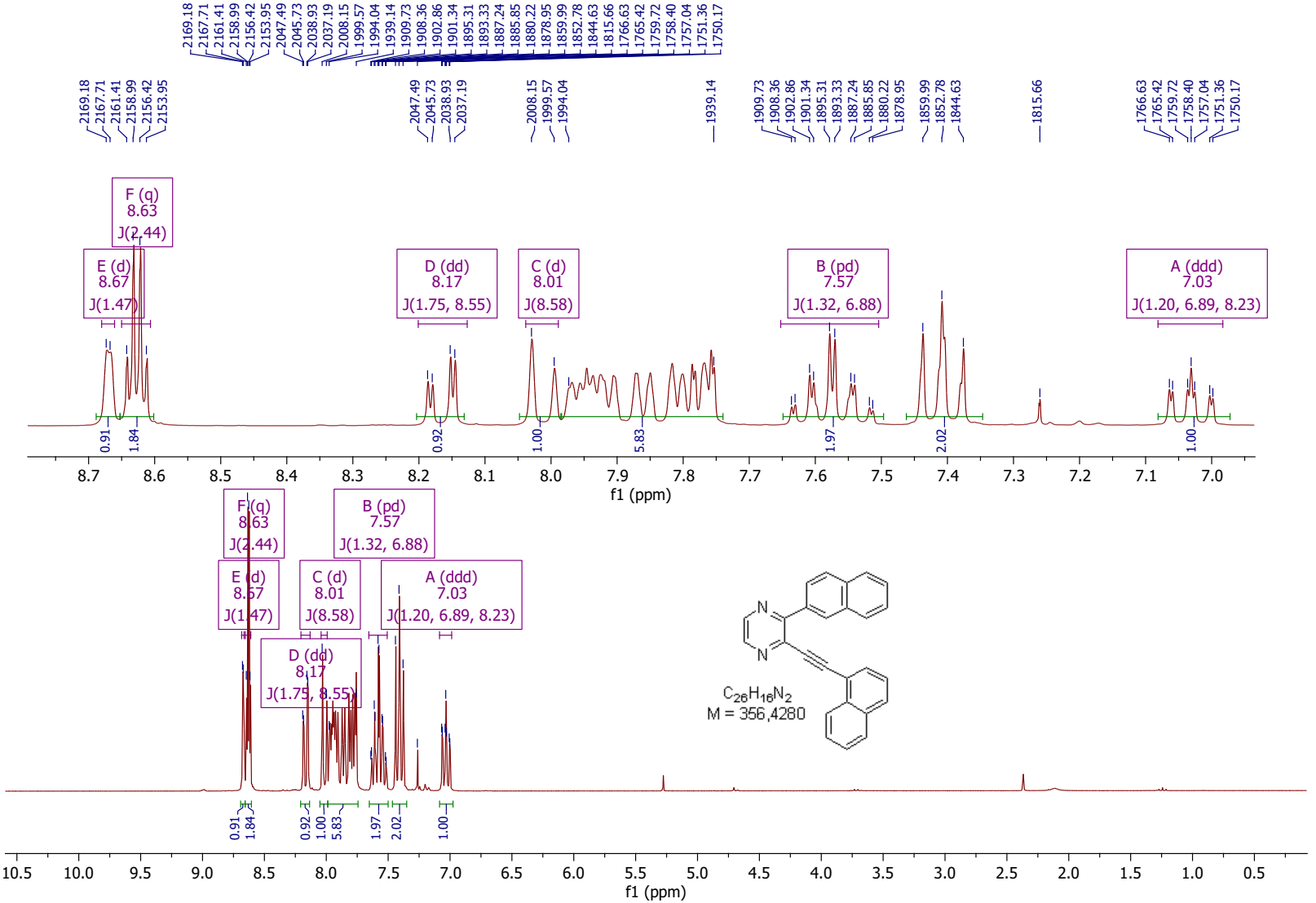


Fig. S11. ^{1}H NMR spectrum of compound **4b** (250 MHz, $CDCl_3$).

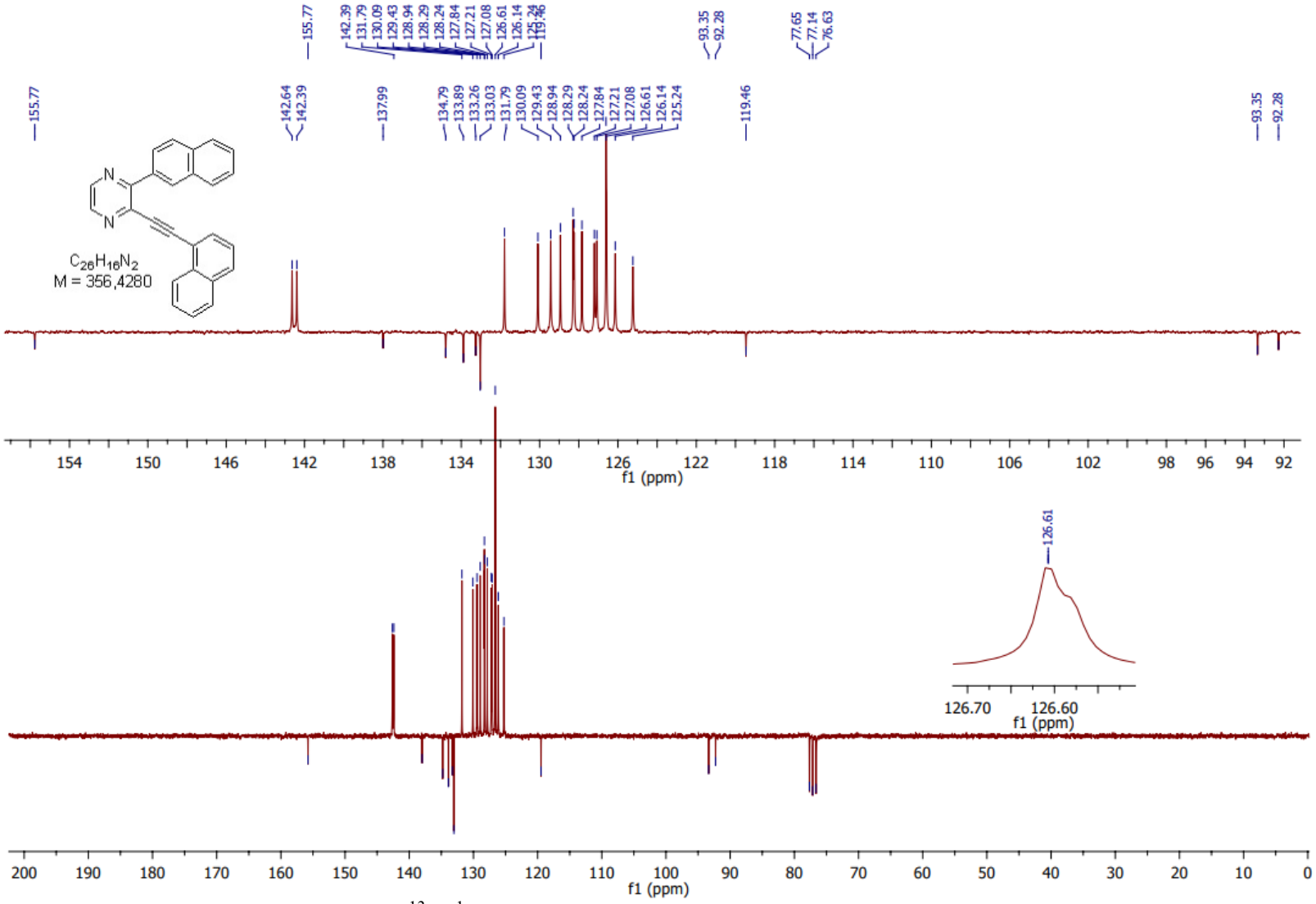


Fig. S12. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **4b** (62.9 MHz, $CDCl_3$).

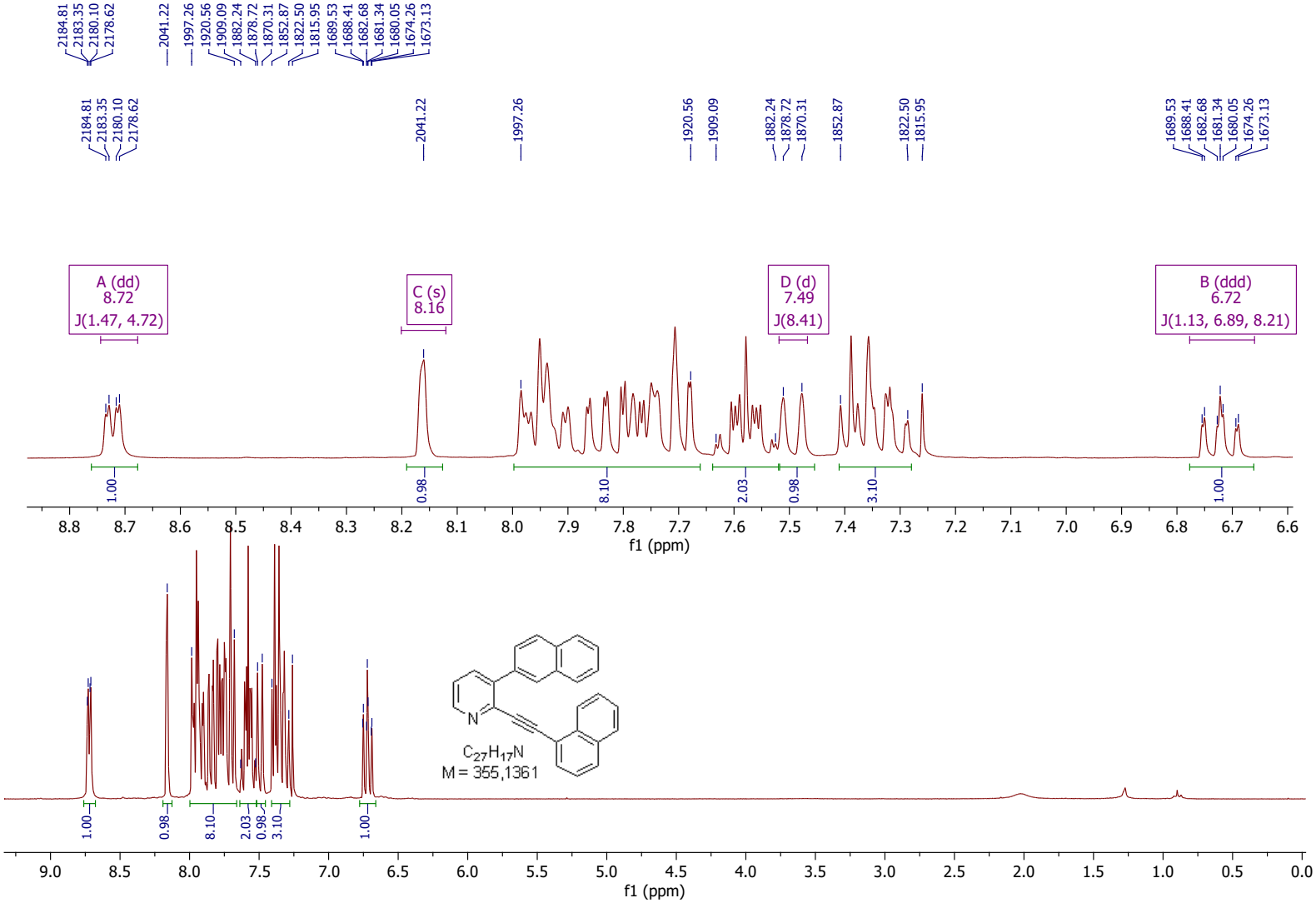


Fig. S13. ^{1}H NMR spectrum of compound **4c** (250 MHz, $CDCl_3$).

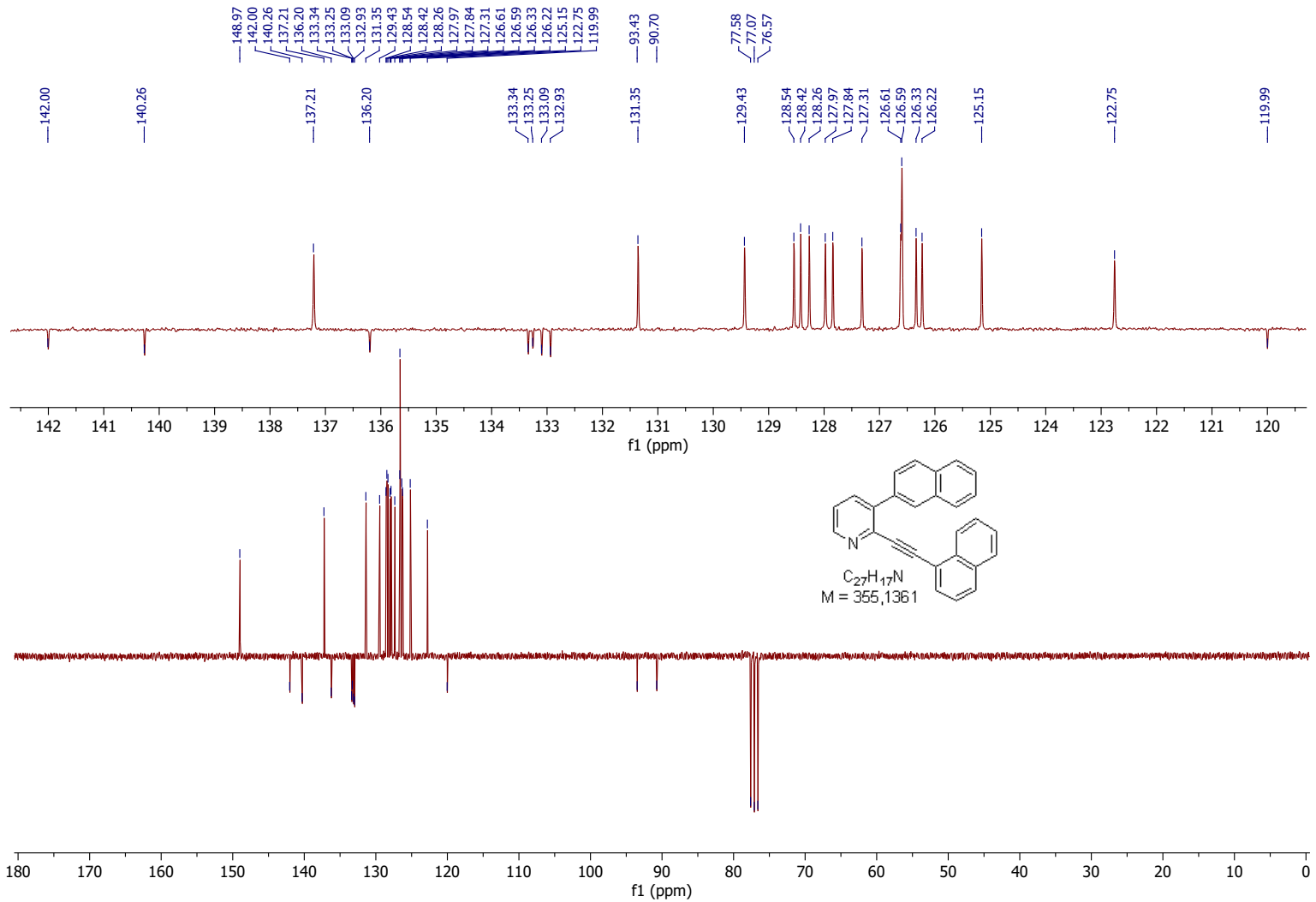


Fig. S14. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **4c** (62.9 MHz, $CDCl_3$).

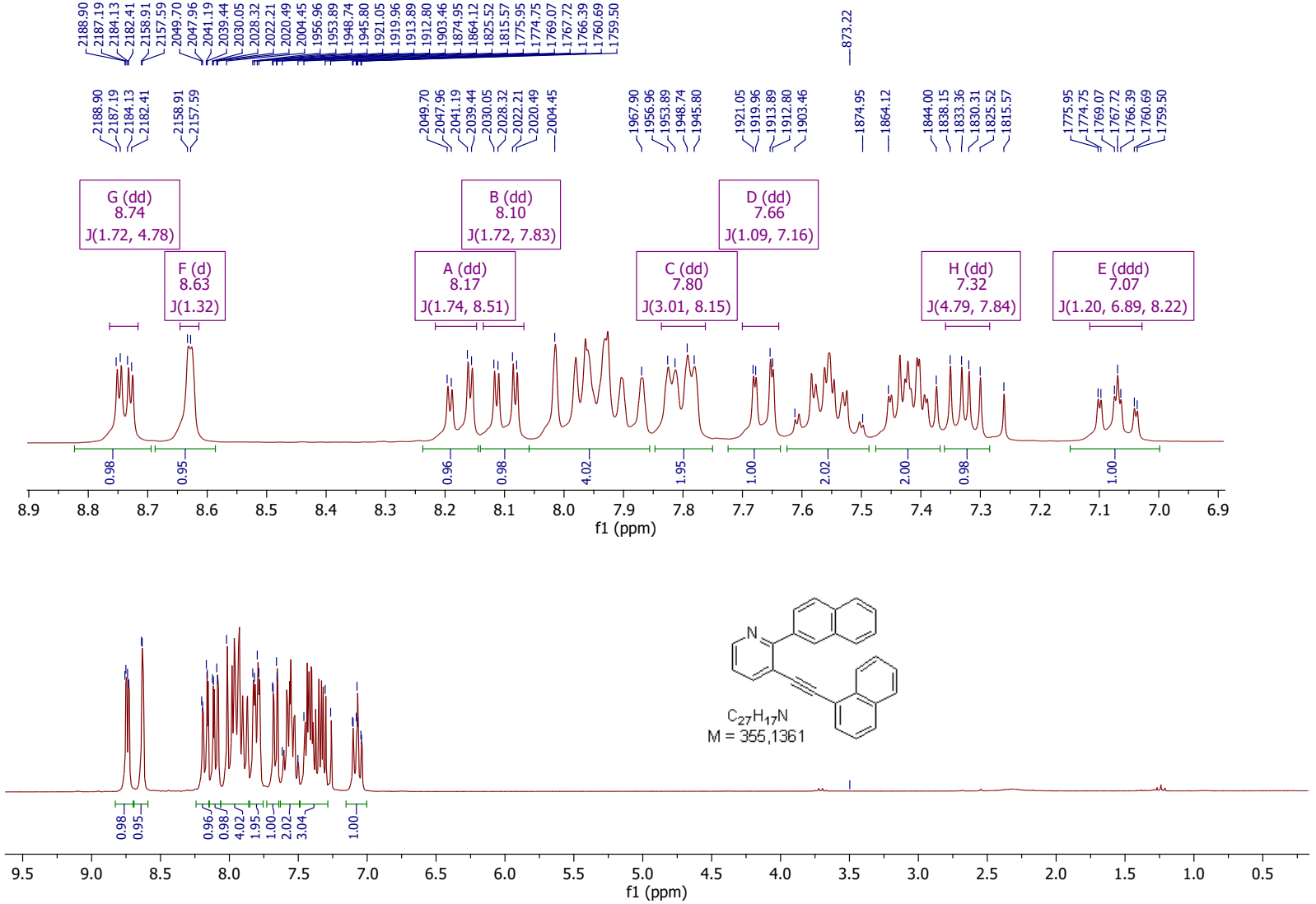


Fig. S15. ^{1}H NMR spectrum of compound **4d** (250 MHz, $CDCl_3$).

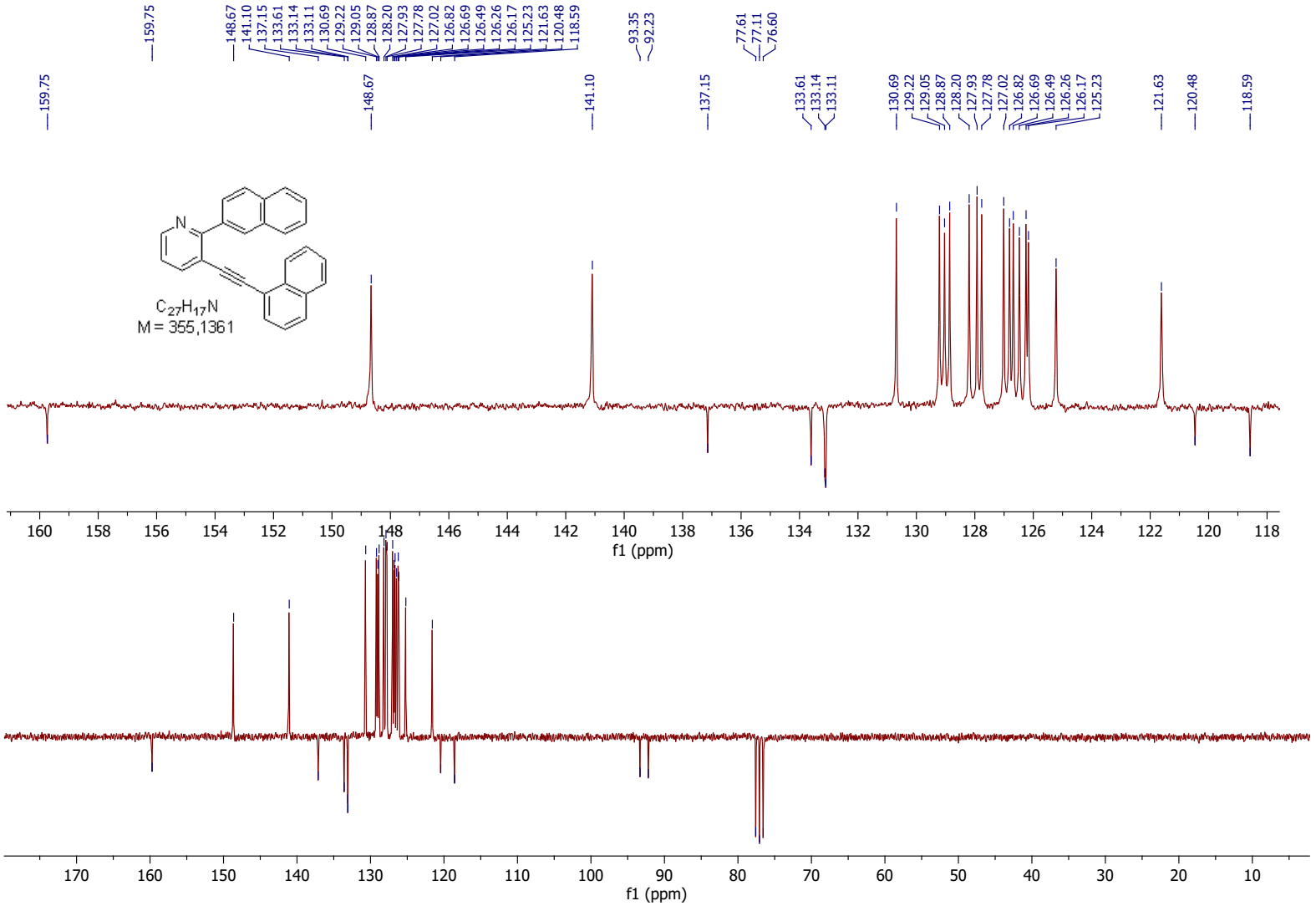


Fig. S16. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **4d** (62.9 MHz, $CDCl_3$).

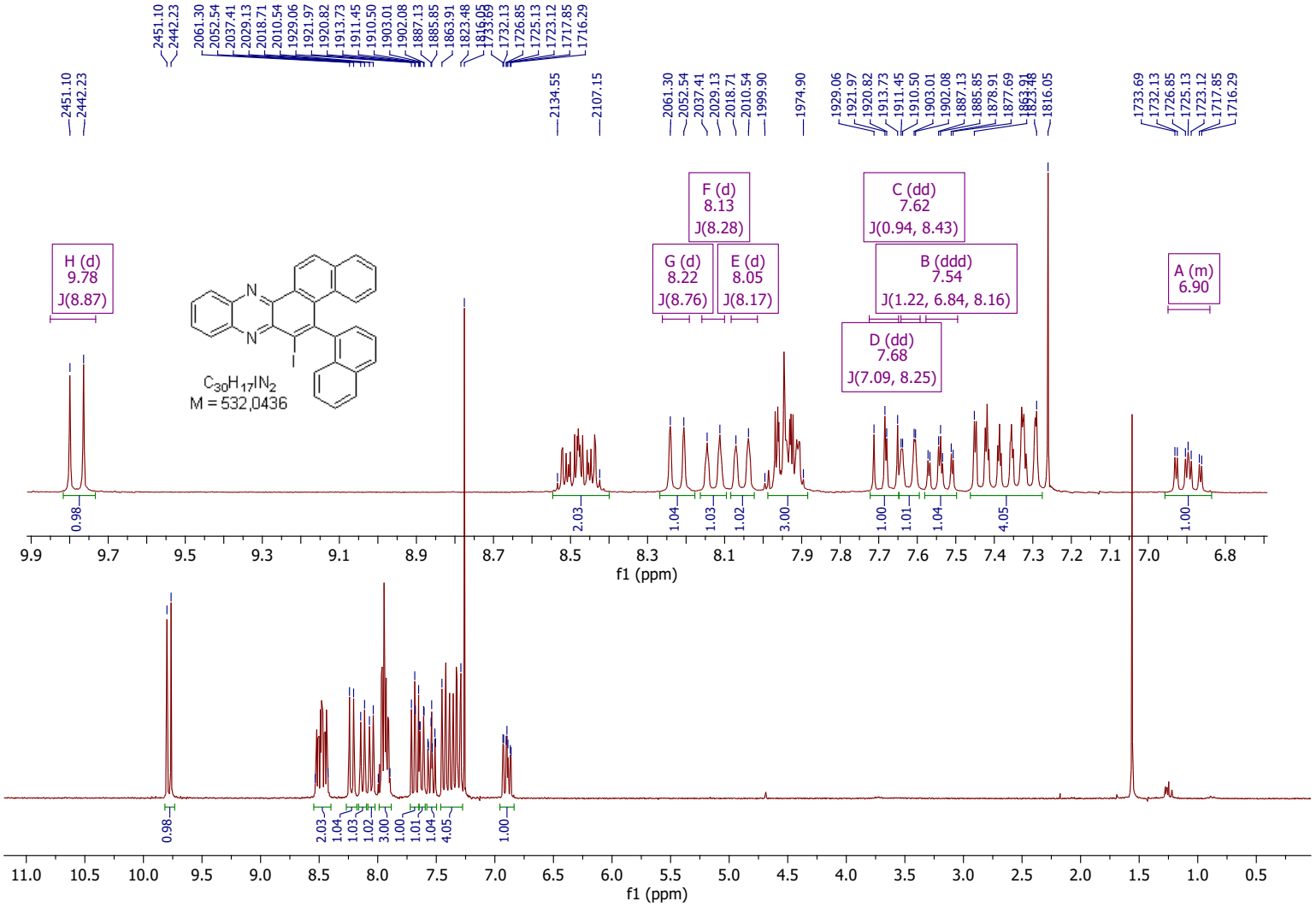


Fig. S17. ^{1}H NMR spectrum of compound **7a** (250 MHz, $CDCl_3$).

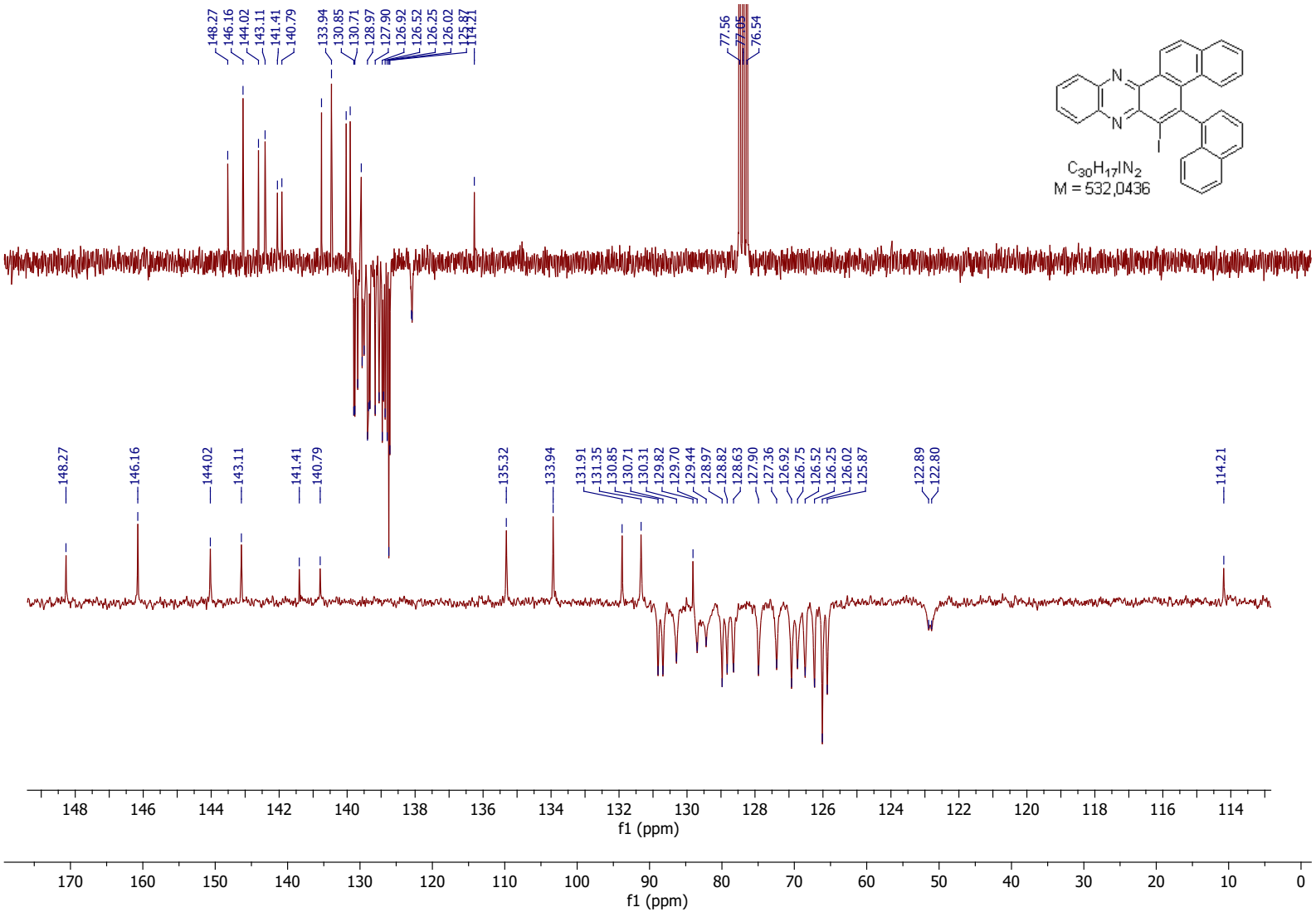


Fig. S18. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **7a** (62.9 MHz, $CDCl_3$).

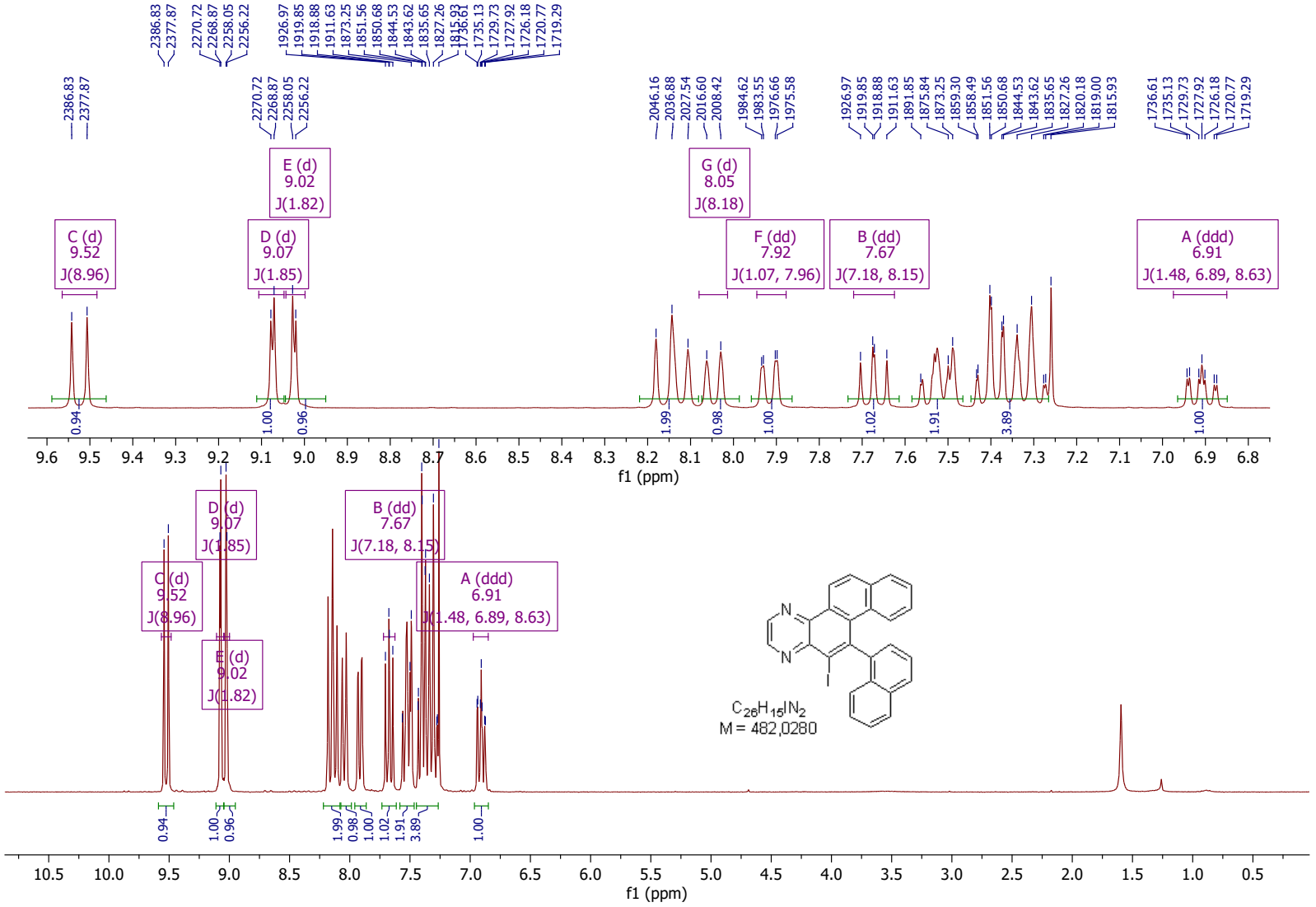


Fig. S19. ^{1}H NMR spectrum of compound **7b** (250 MHz, $CDCl_3$).

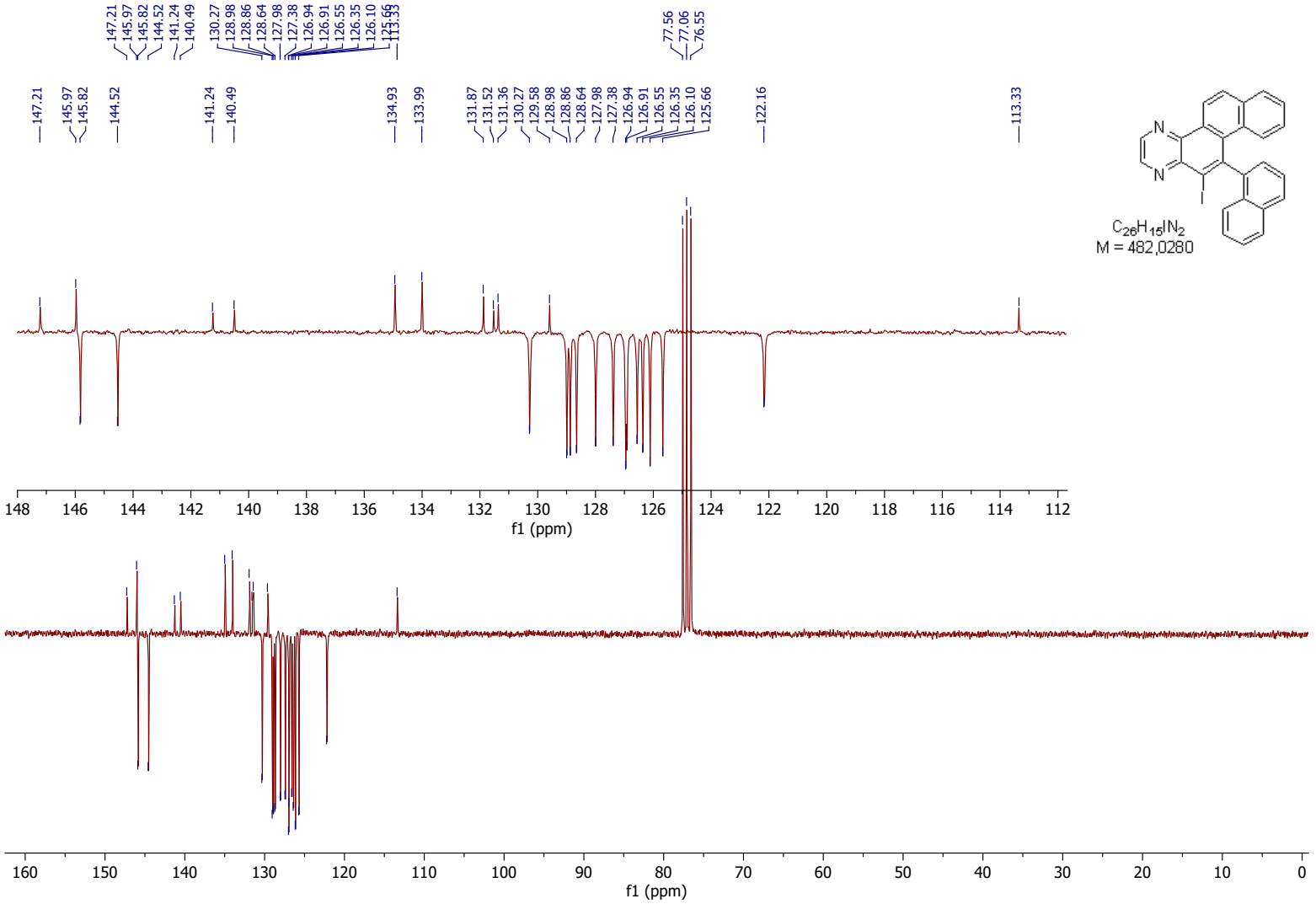


Fig. S20. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **7b** (62.9 MHz, $CDCl_3$).

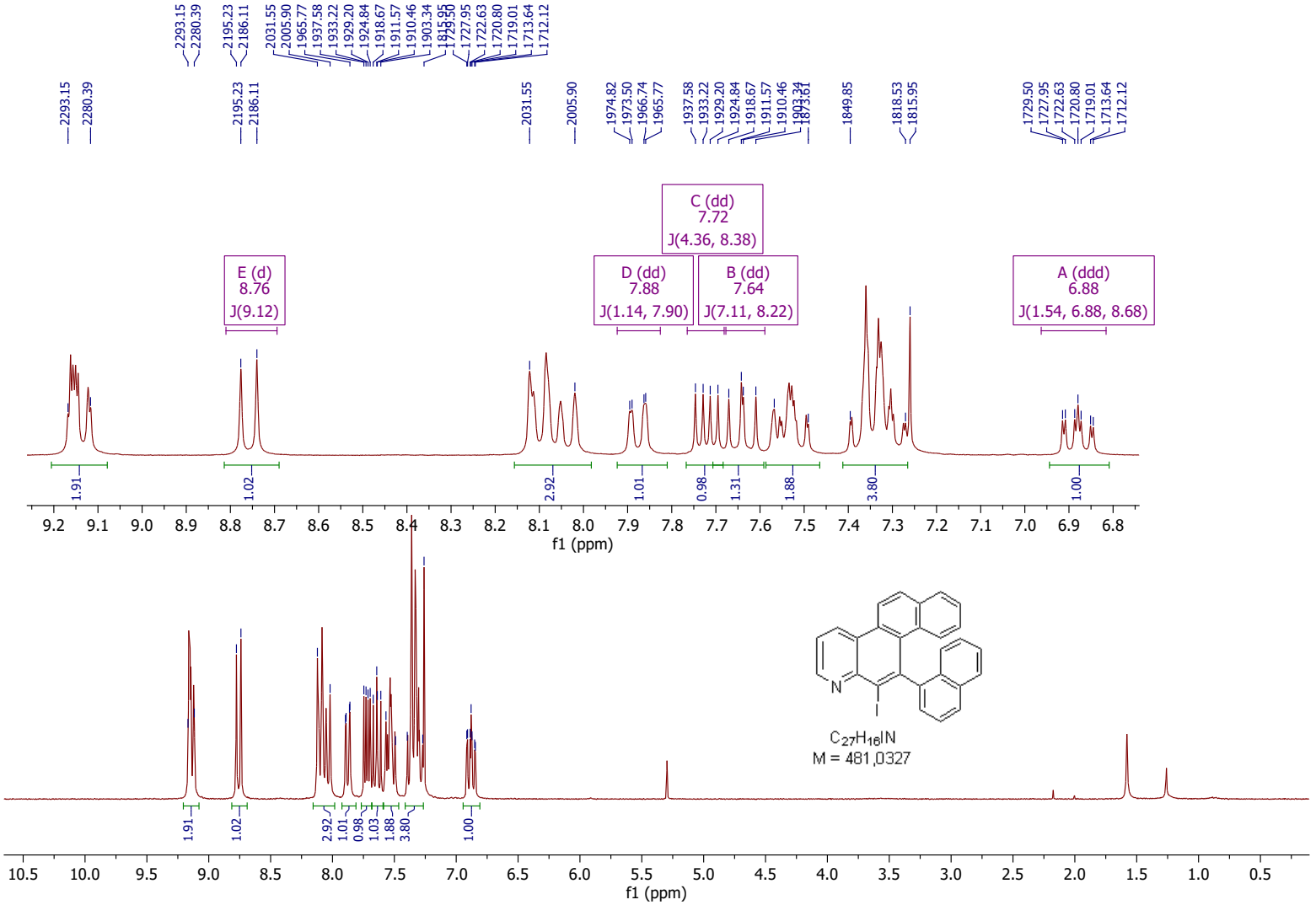


Fig. S21. ^{1}H NMR spectrum of compound **7c** (250 MHz, $CDCl_3$).

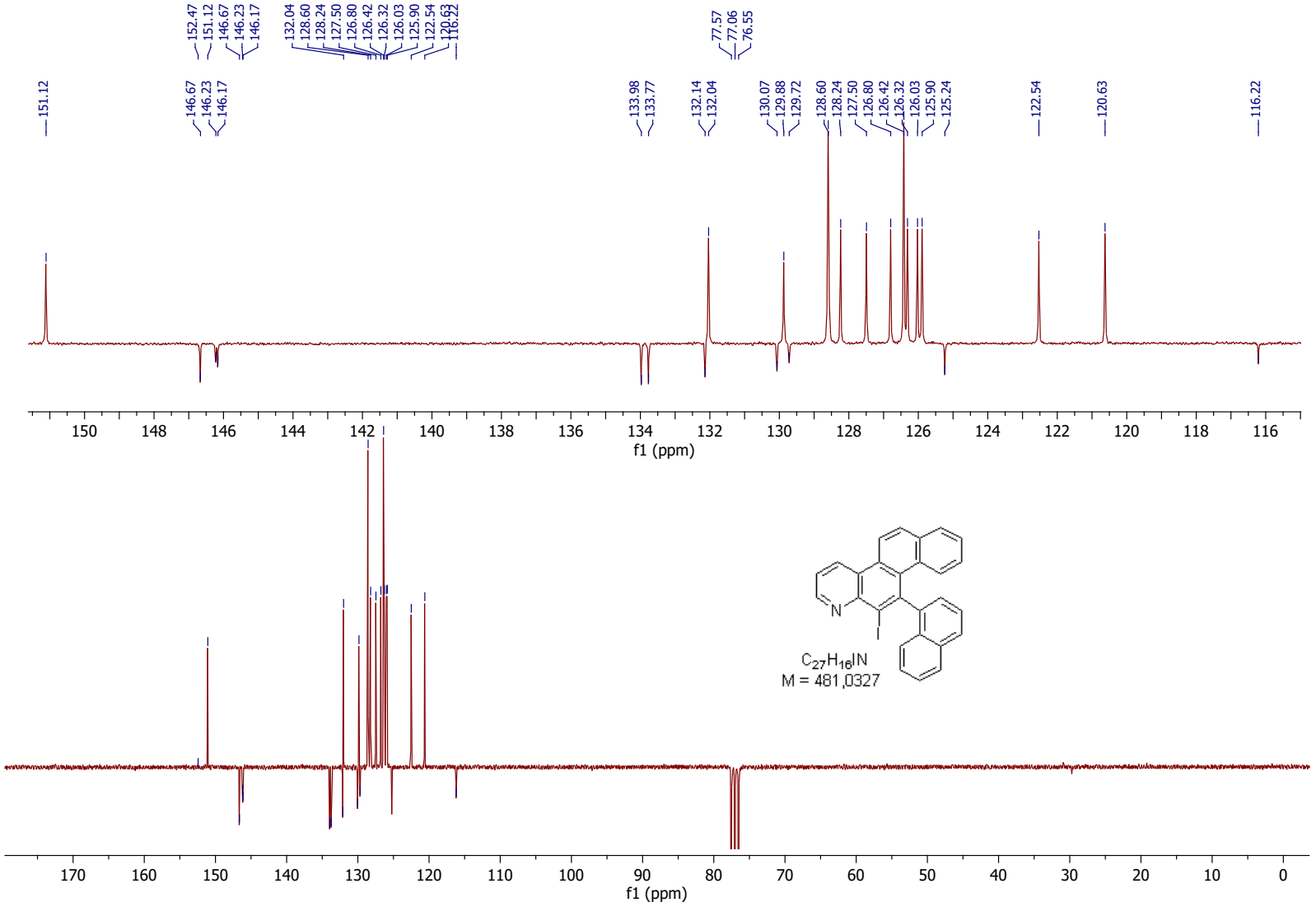


Fig. S22. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **7c** (62.9 MHz, $CDCl_3$).

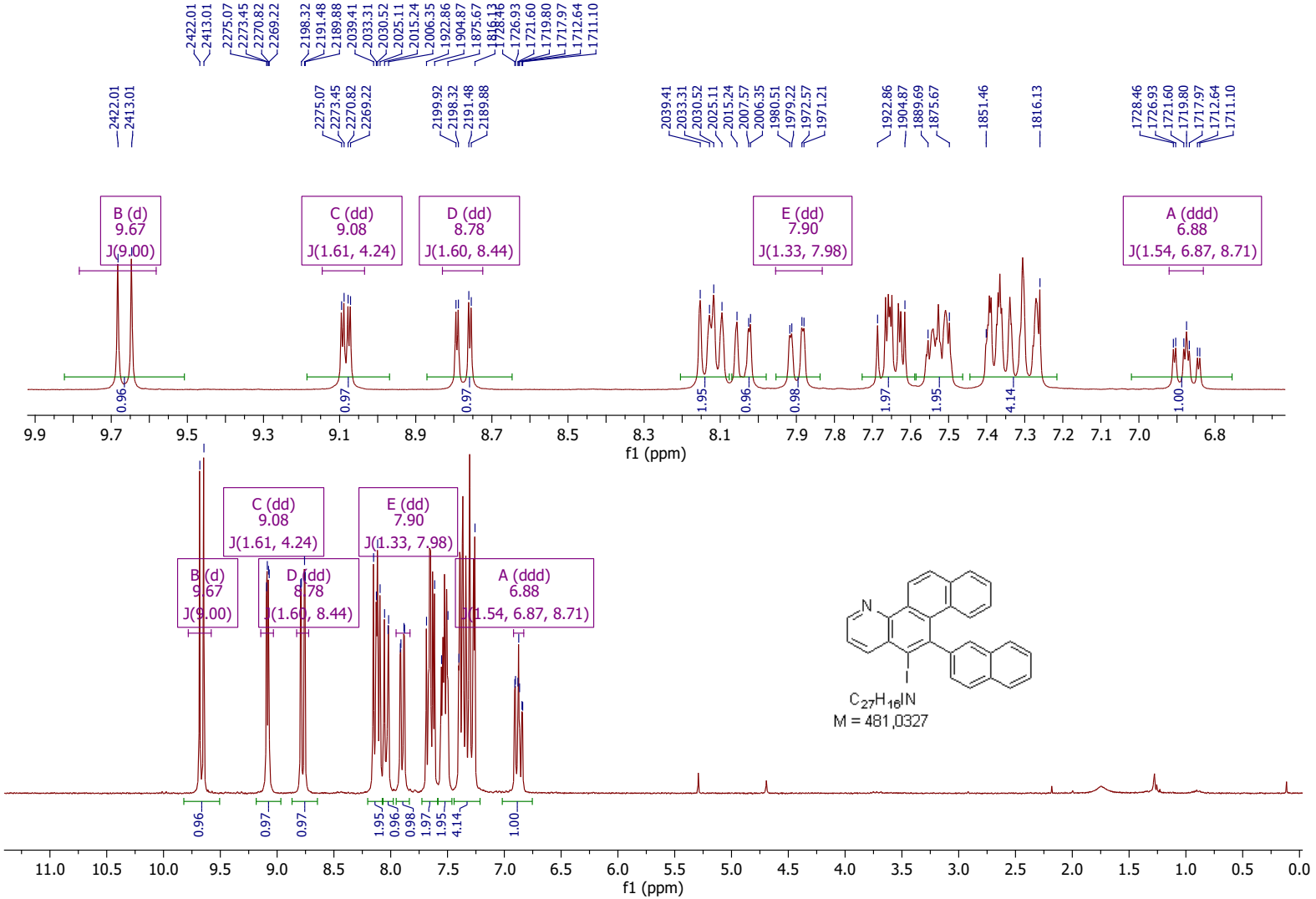


Fig. S23. ^{1}H NMR spectrum of compound **7d** (250 MHz, $CDCl_3$).

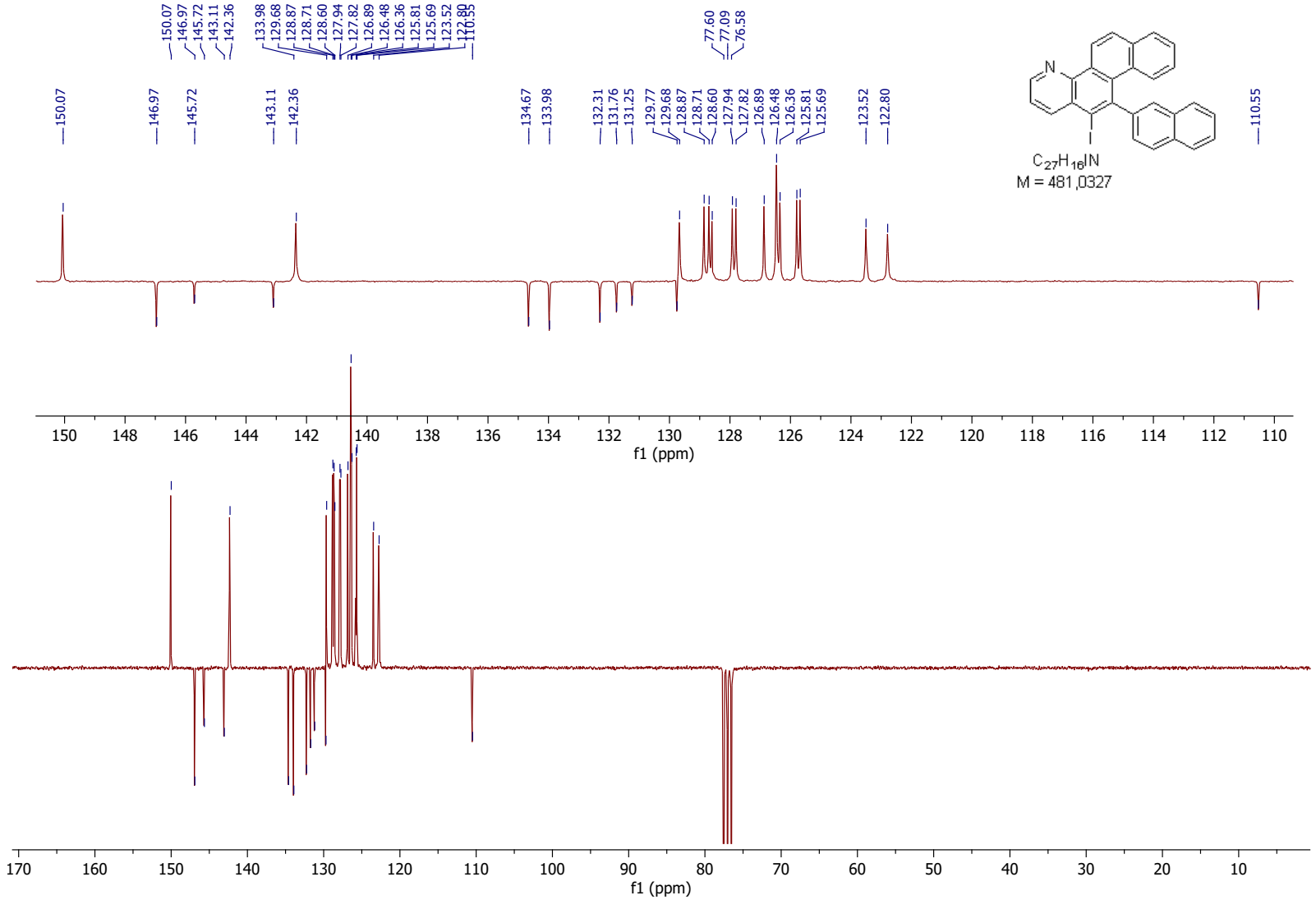


Fig. S24. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **7d** (62.9 MHz, $CDCl_3$).

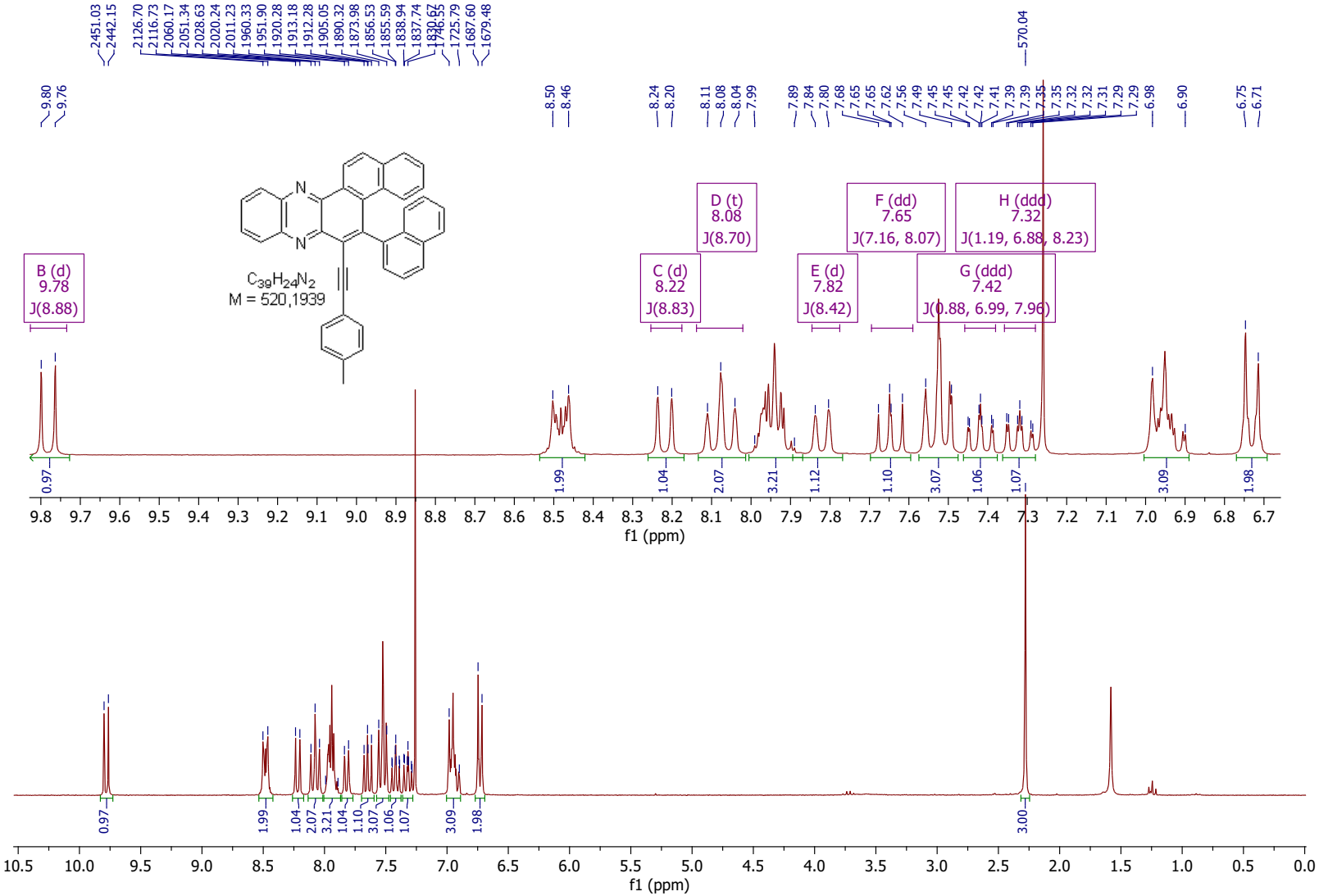


Fig. S25. ^{1}H NMR spectrum of compound **8a** (250 MHz, $CDCl_3$).

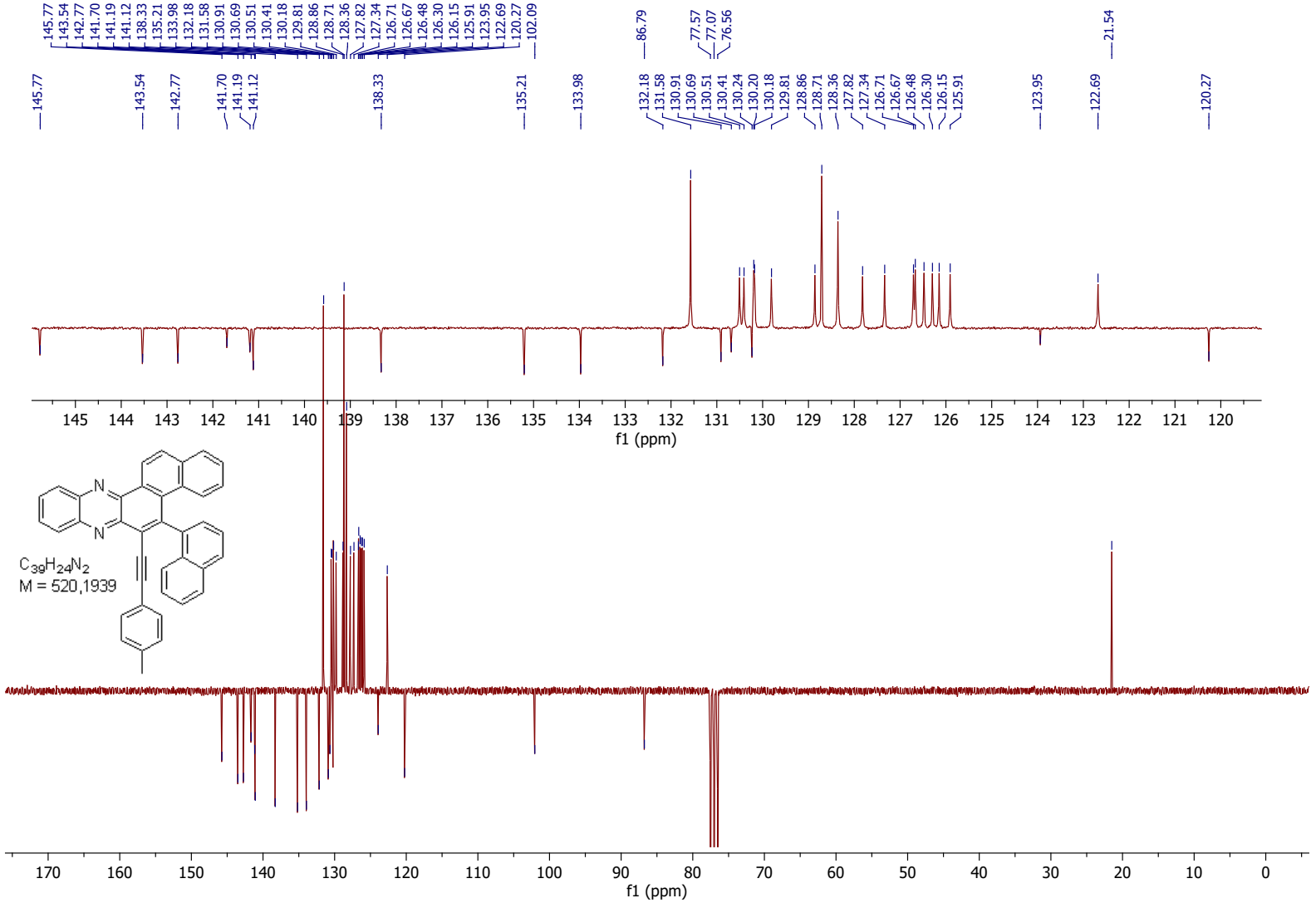


Fig. S26. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **8a** (62.9 MHz, $CDCl_3$).

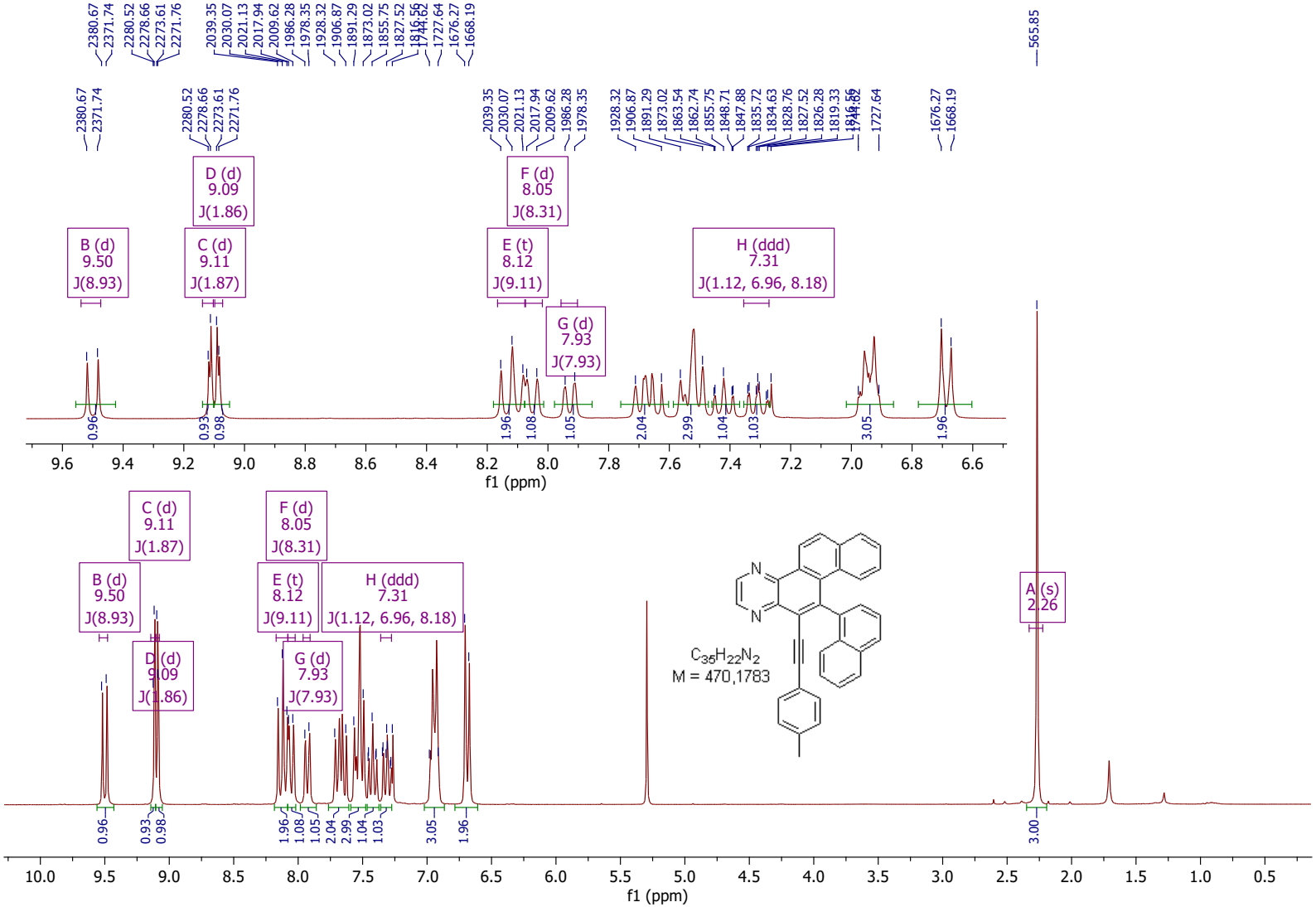


Fig. S27. ^{1}H NMR spectrum of compound **8b** (250 MHz, $CDCl_3$).

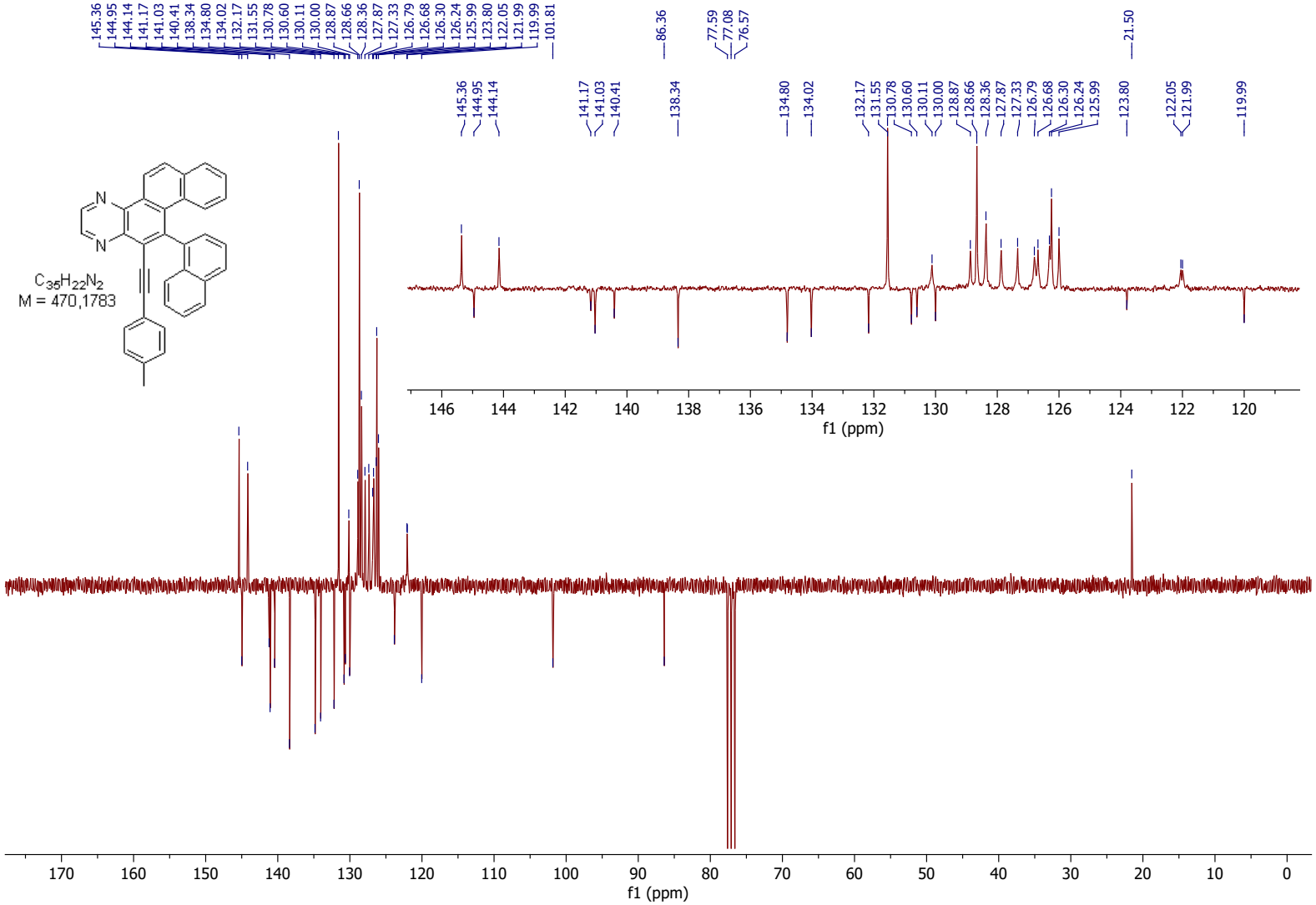


Fig. S28. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **8b** (62.9 MHz, $CDCl_3$).

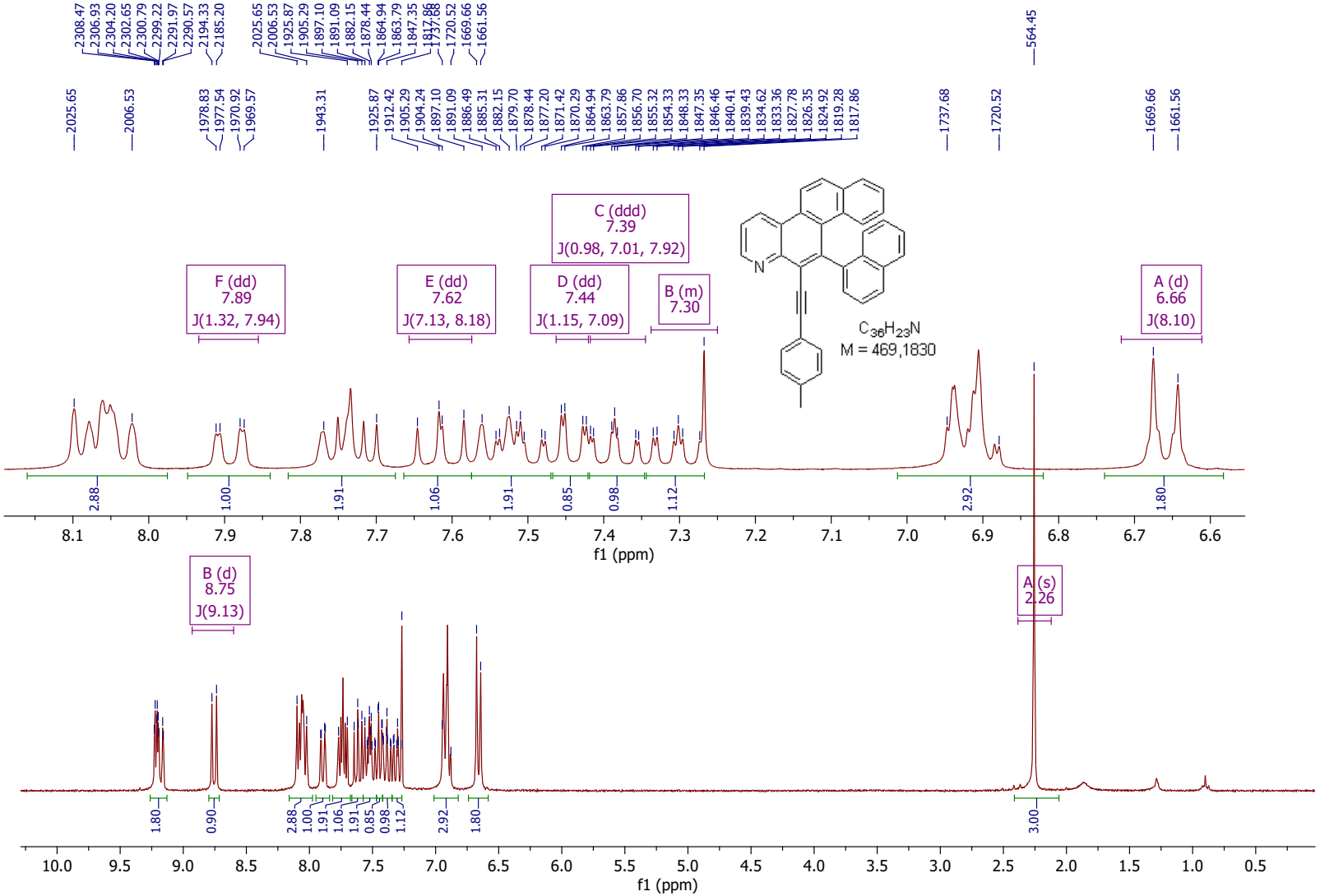


Fig. S29. ^{1}H NMR spectrum of compound **8c** (250 MHz, $CDCl_3$).

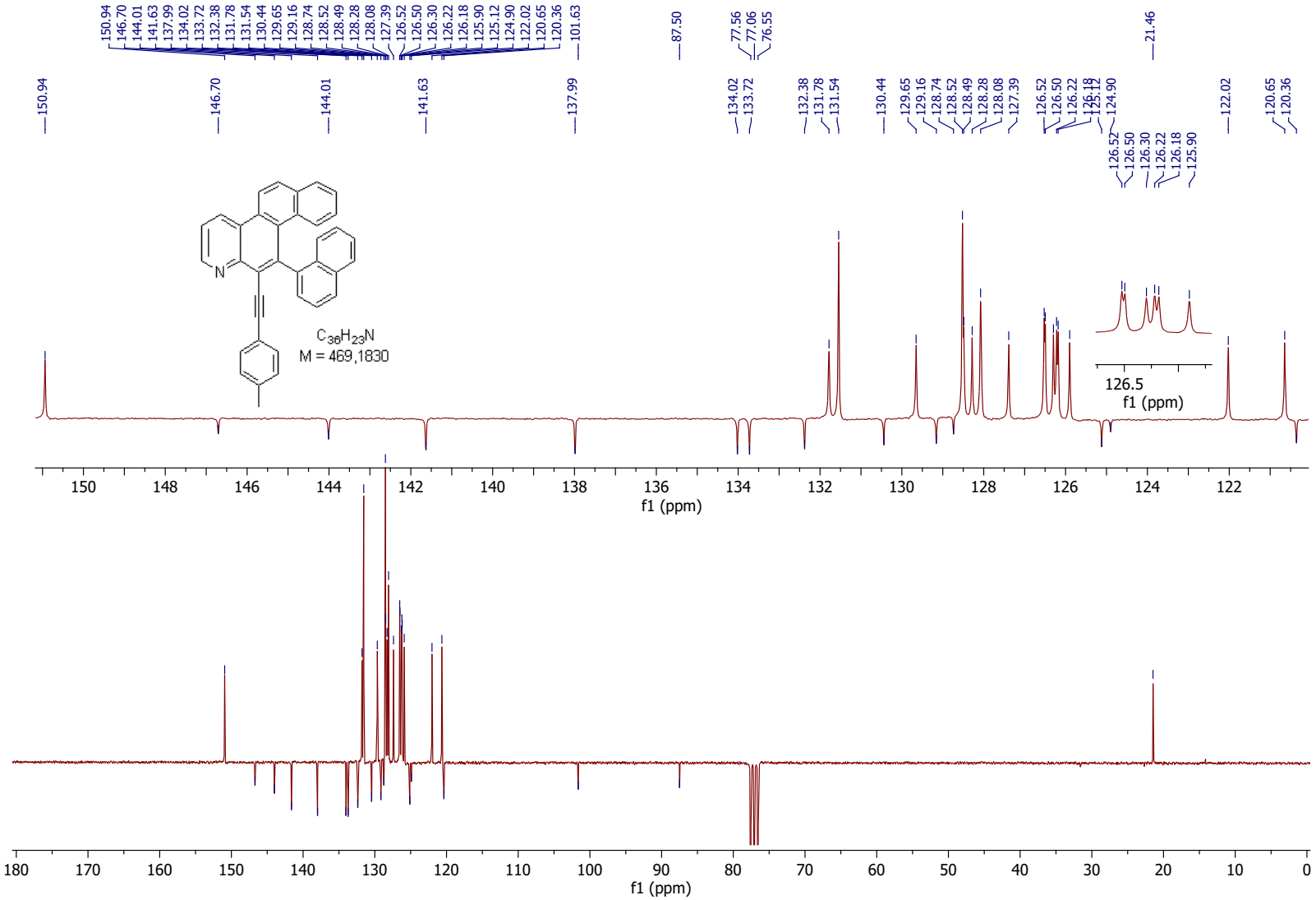


Fig. S30. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **8c** (62.9 MHz, $CDCl_3$).

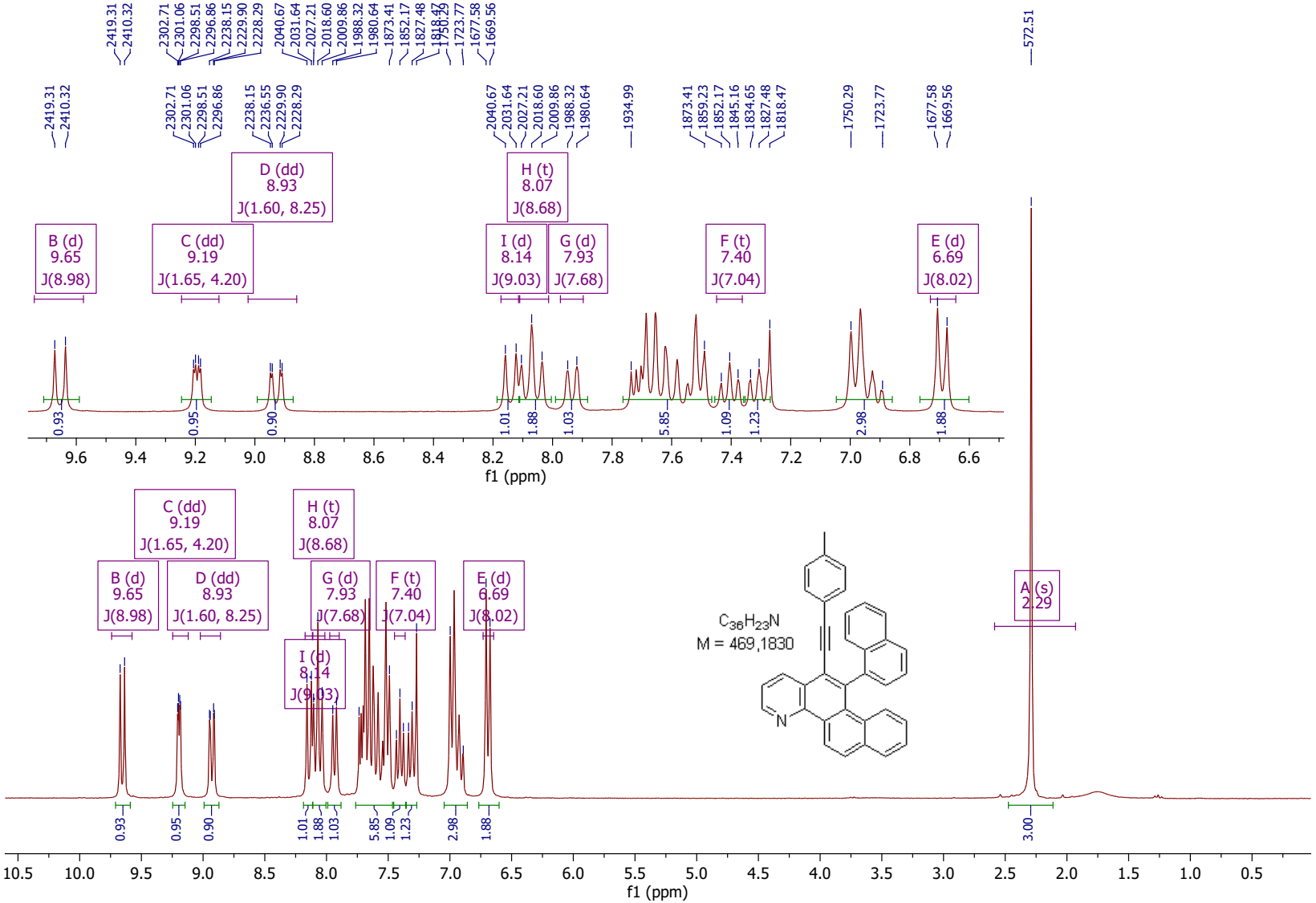


Fig. S31. ^{1}H NMR spectrum of compound **8d** (250 MHz, $CDCl_3$).

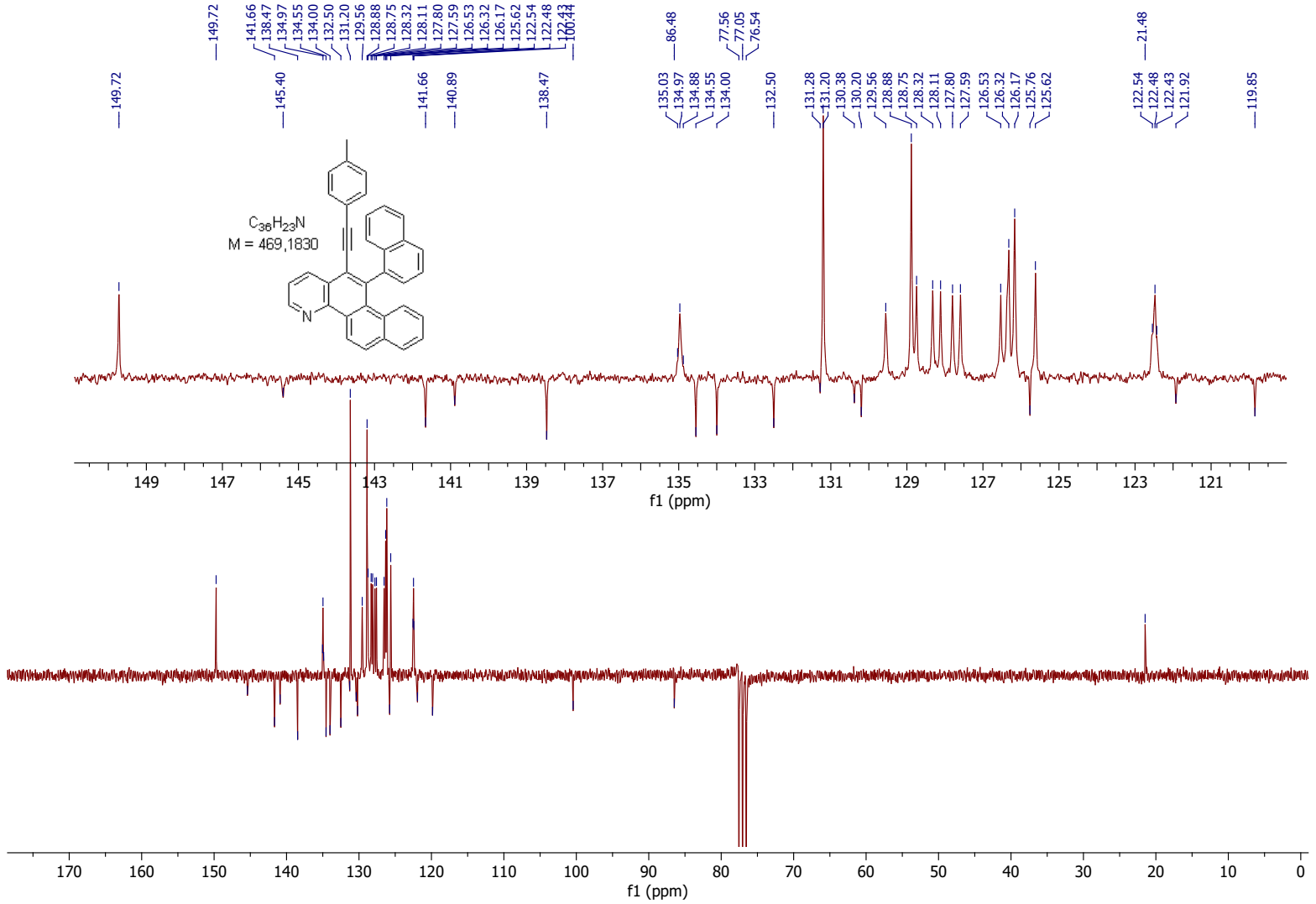


Fig. S32. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **8d** (62.9 MHz, $CDCl_3$).

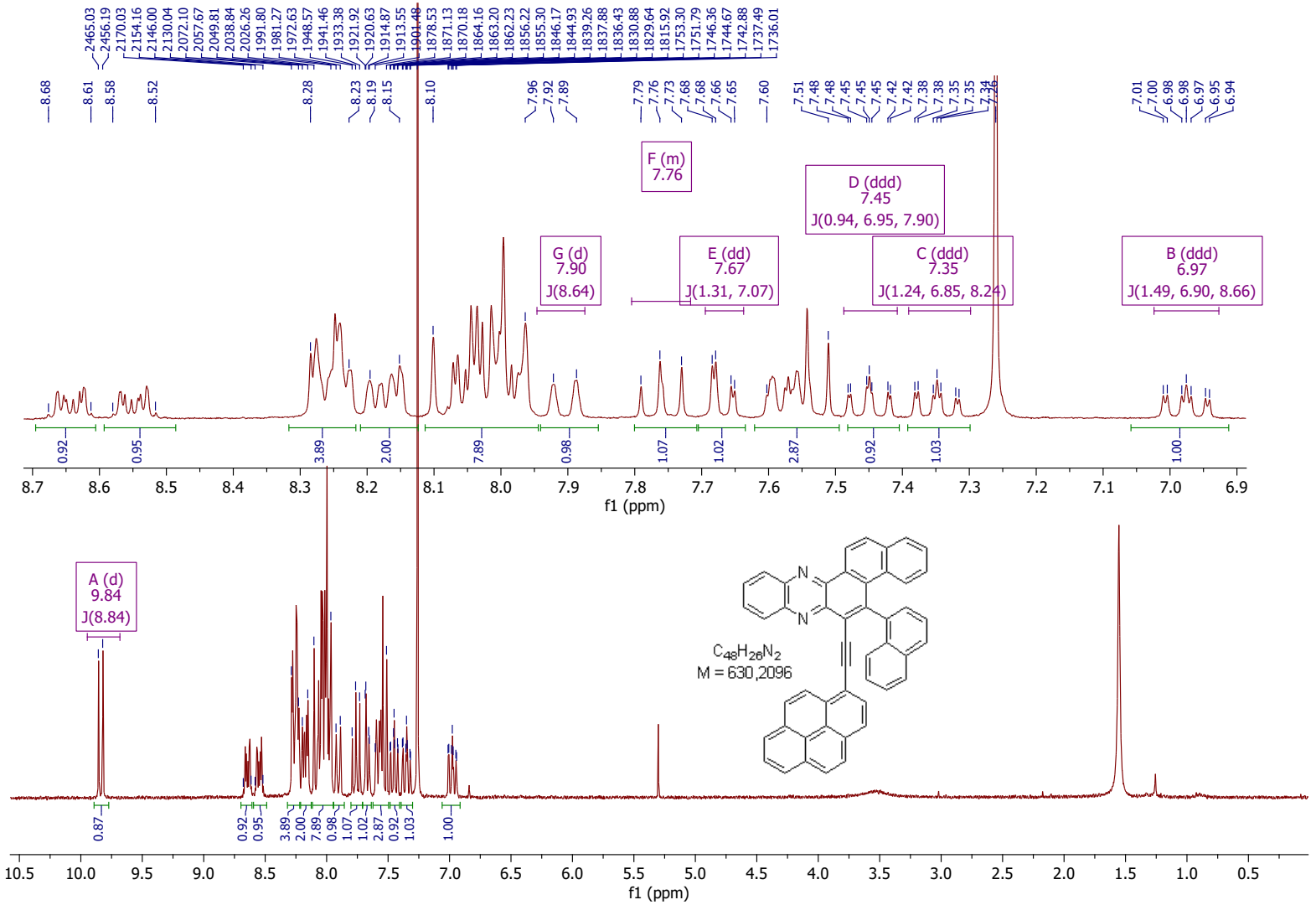


Fig. S33. ^{1}H NMR spectrum of compound **8e** (250 MHz, $CDCl_3$).

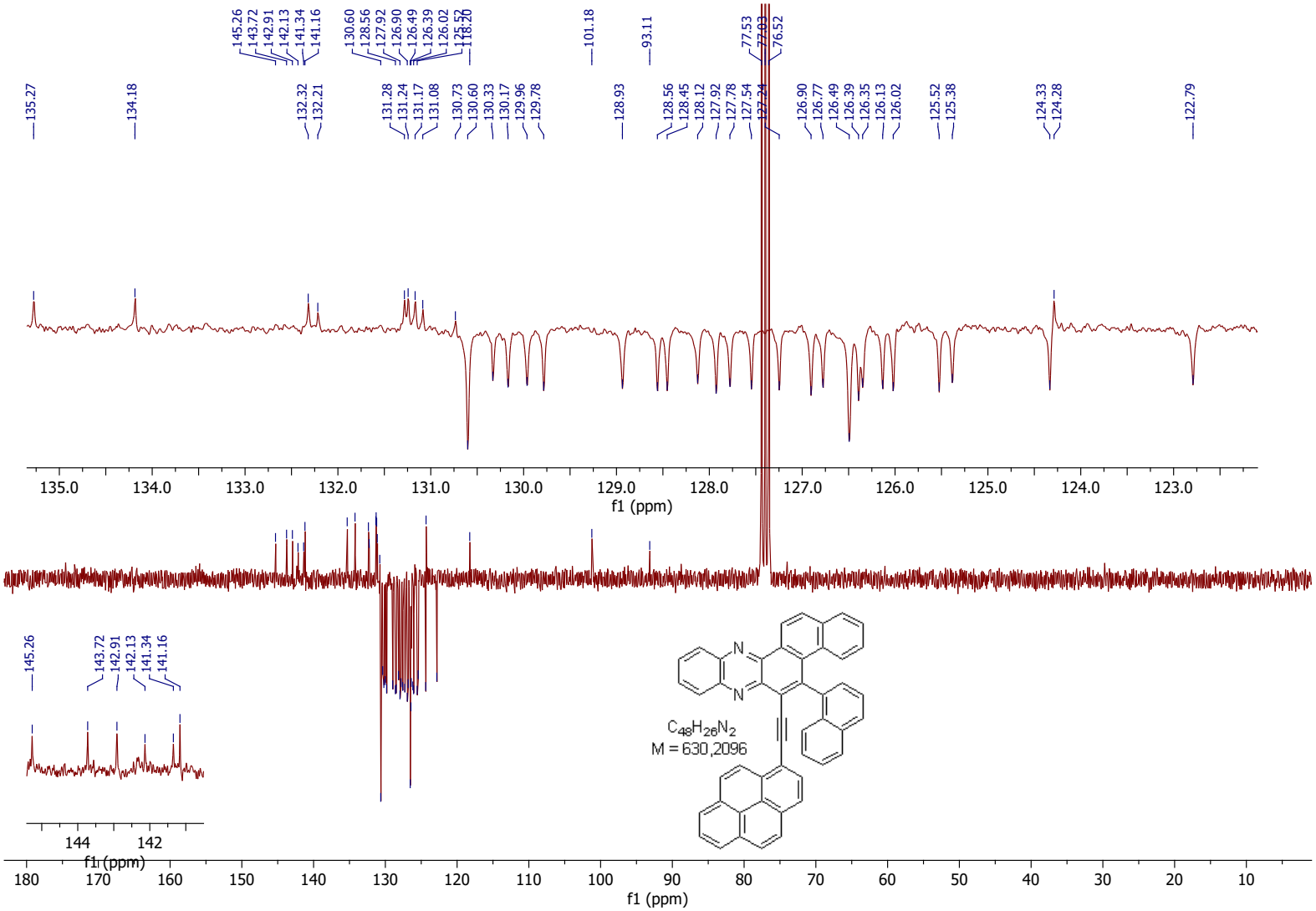


Fig. S34. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **8e** (62.9 MHz, $CDCl_3$).

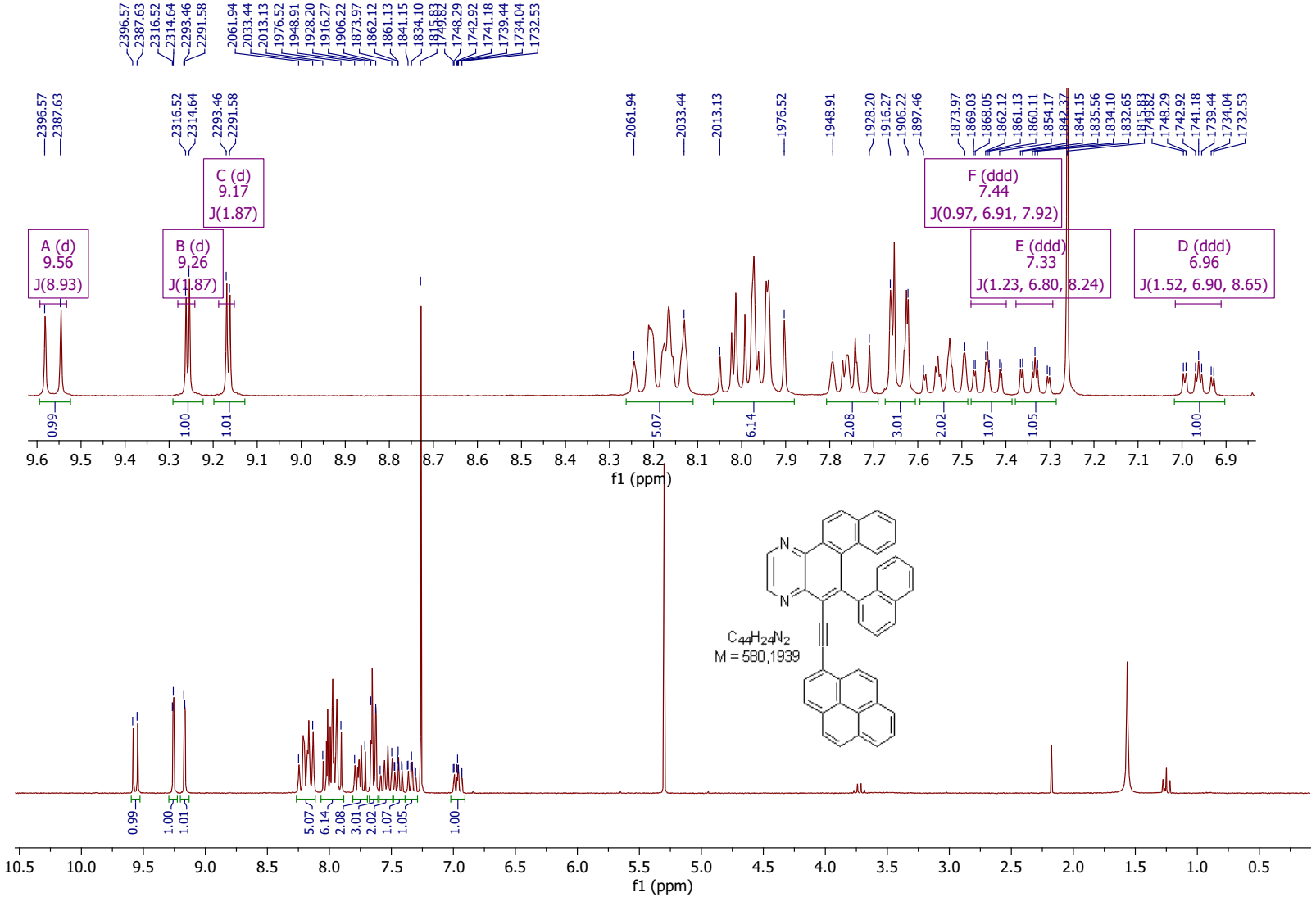


Fig. S35. ^{1}H NMR spectrum of compound **8f** (250 MHz, $CDCl_3$).

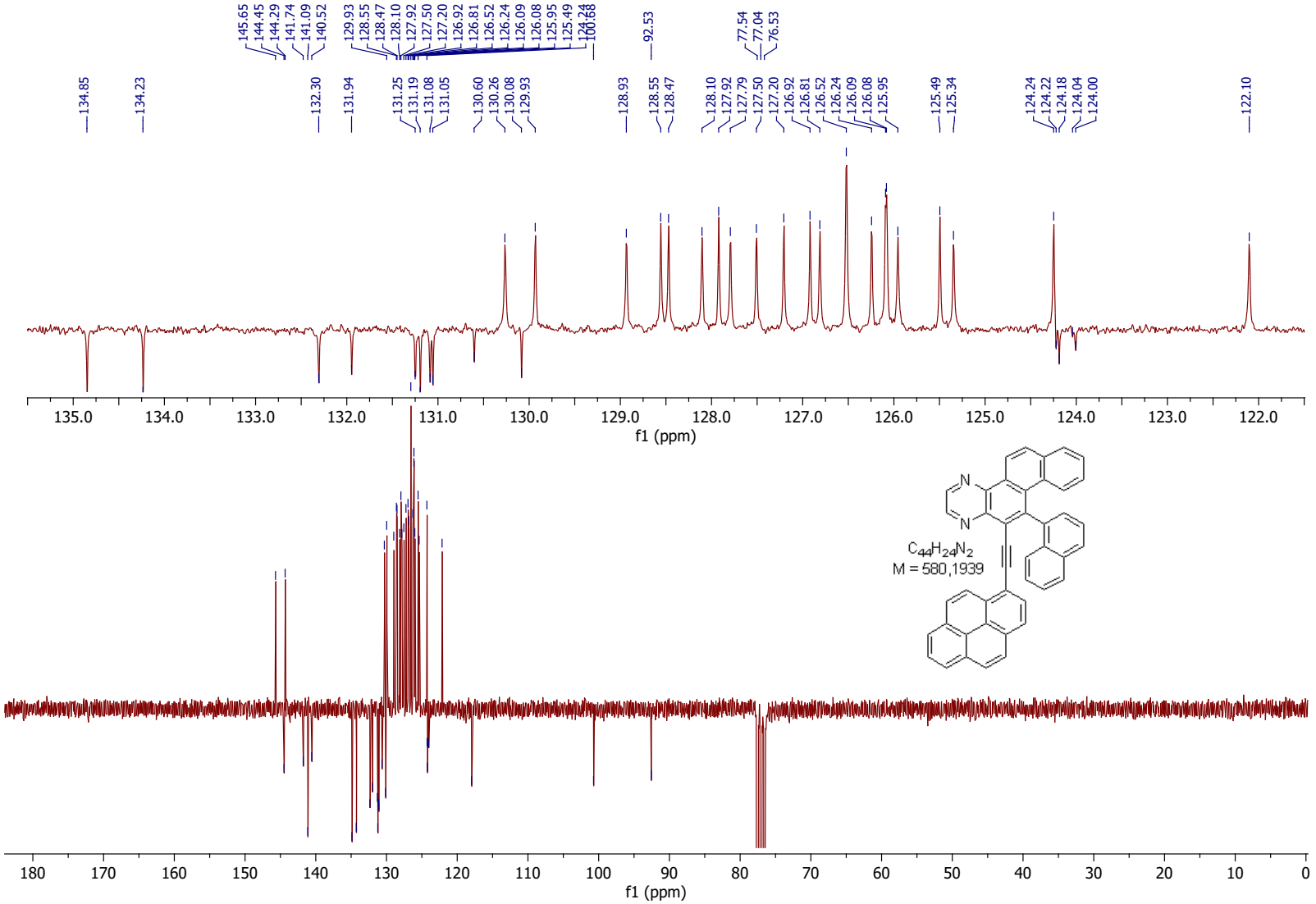


Fig. S36. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **8f** (62.9 MHz, $CDCl_3$).

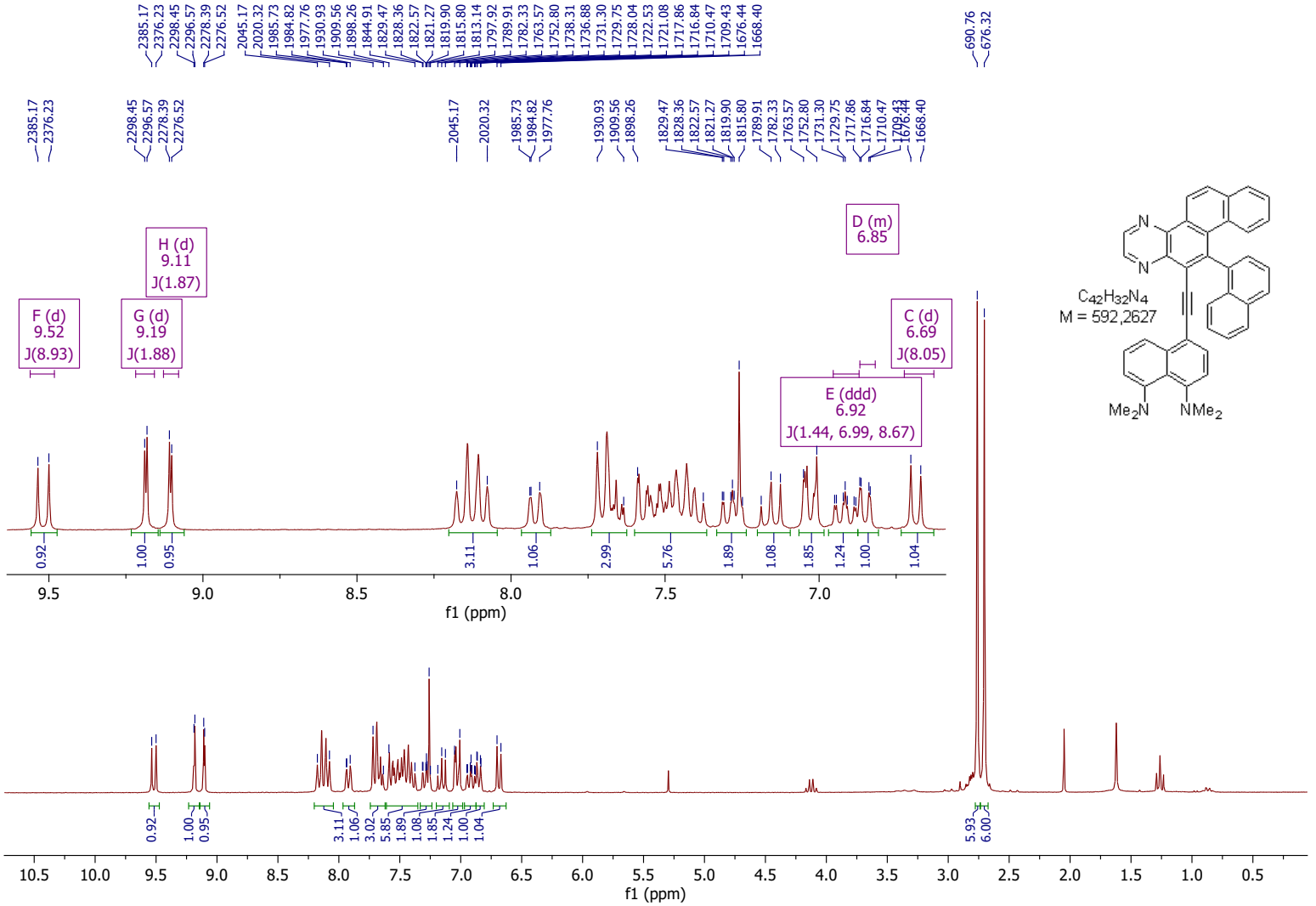


Fig. S37. ^{1}H NMR spectrum of compound **8g** (250 MHz, $CDCl_3$).

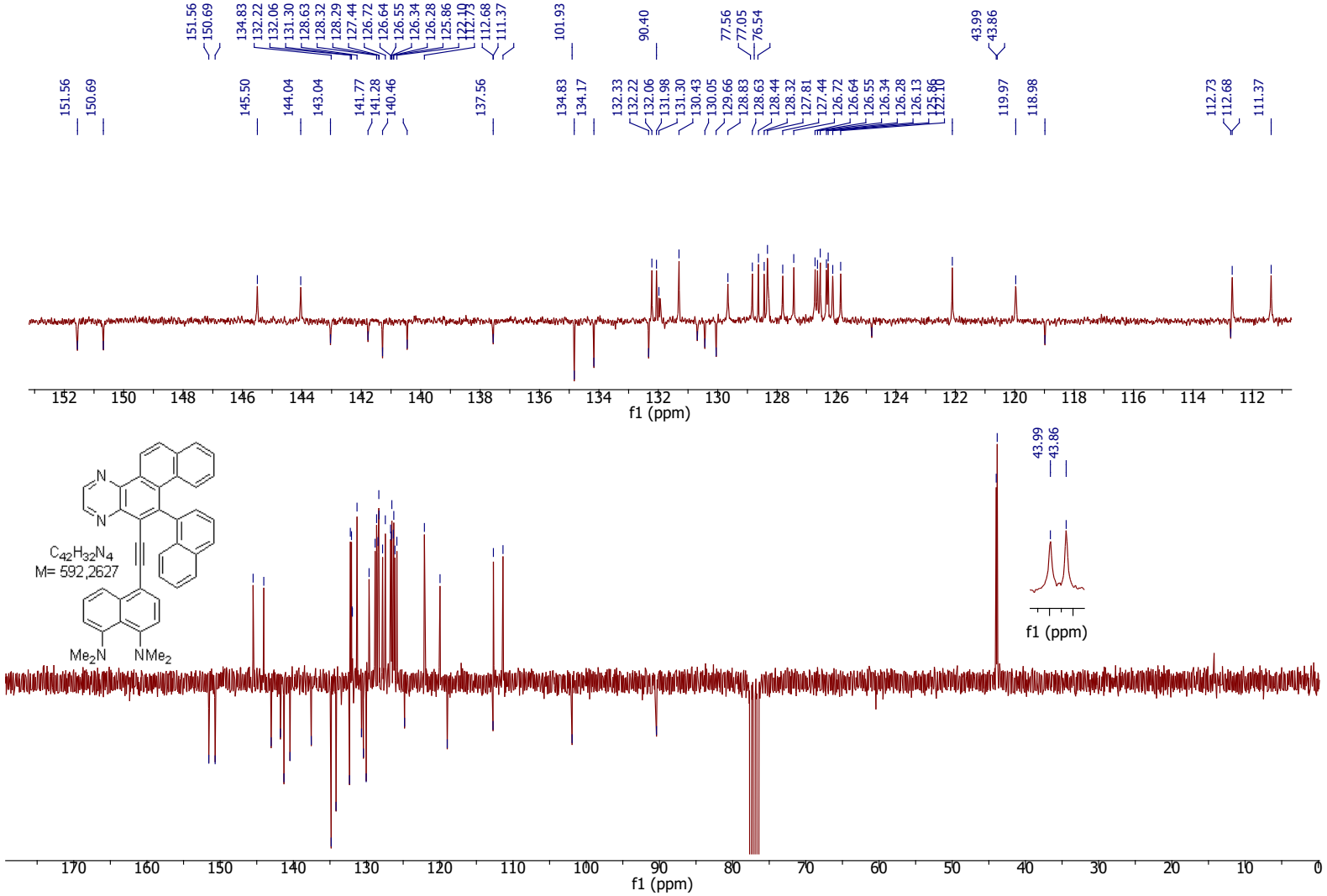


Fig. S38. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **8g** (62.9 MHz, $CDCl_3$).

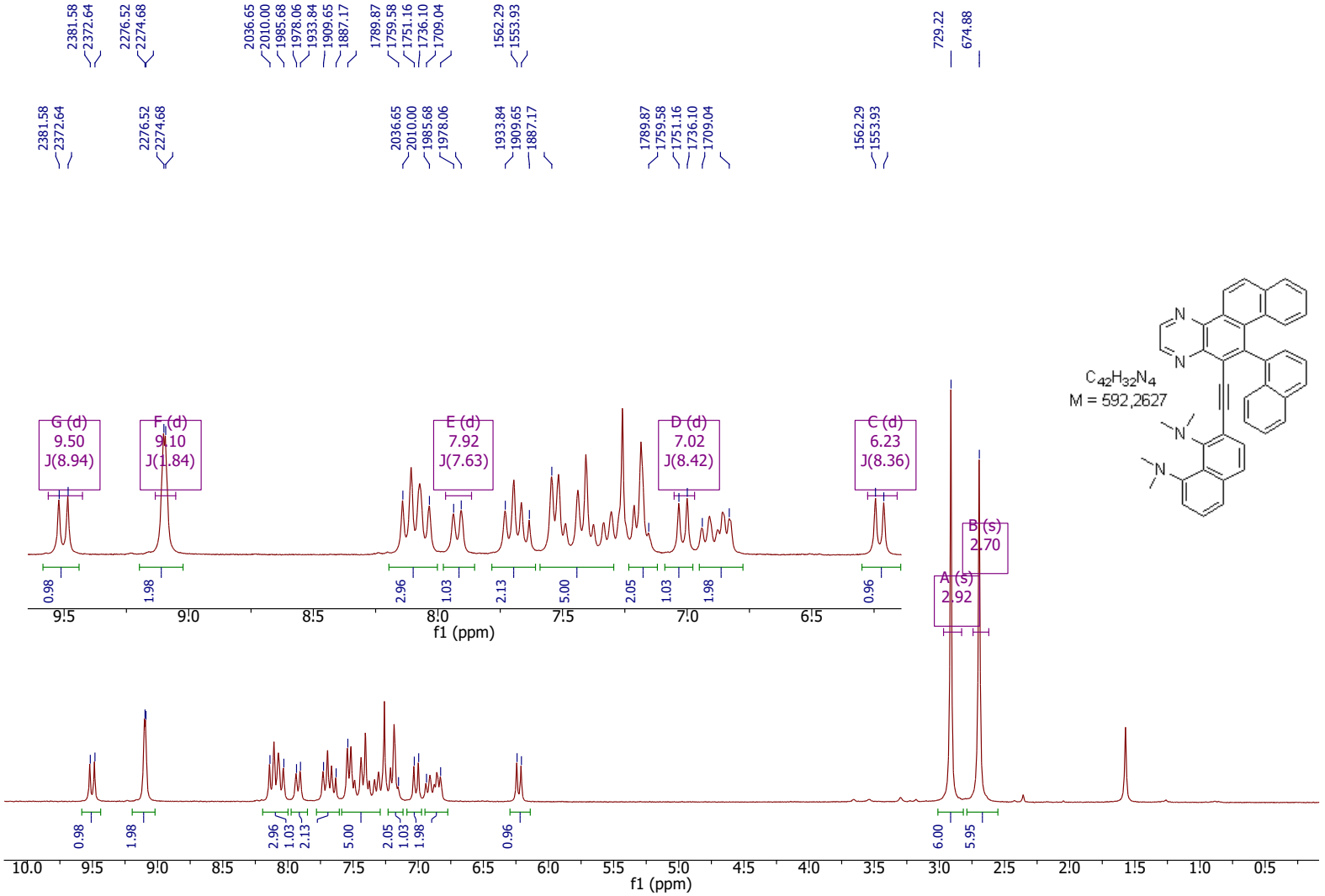


Fig. S39. ^{1}H NMR spectrum of compound **8h** (250 MHz, $CDCl_3$).

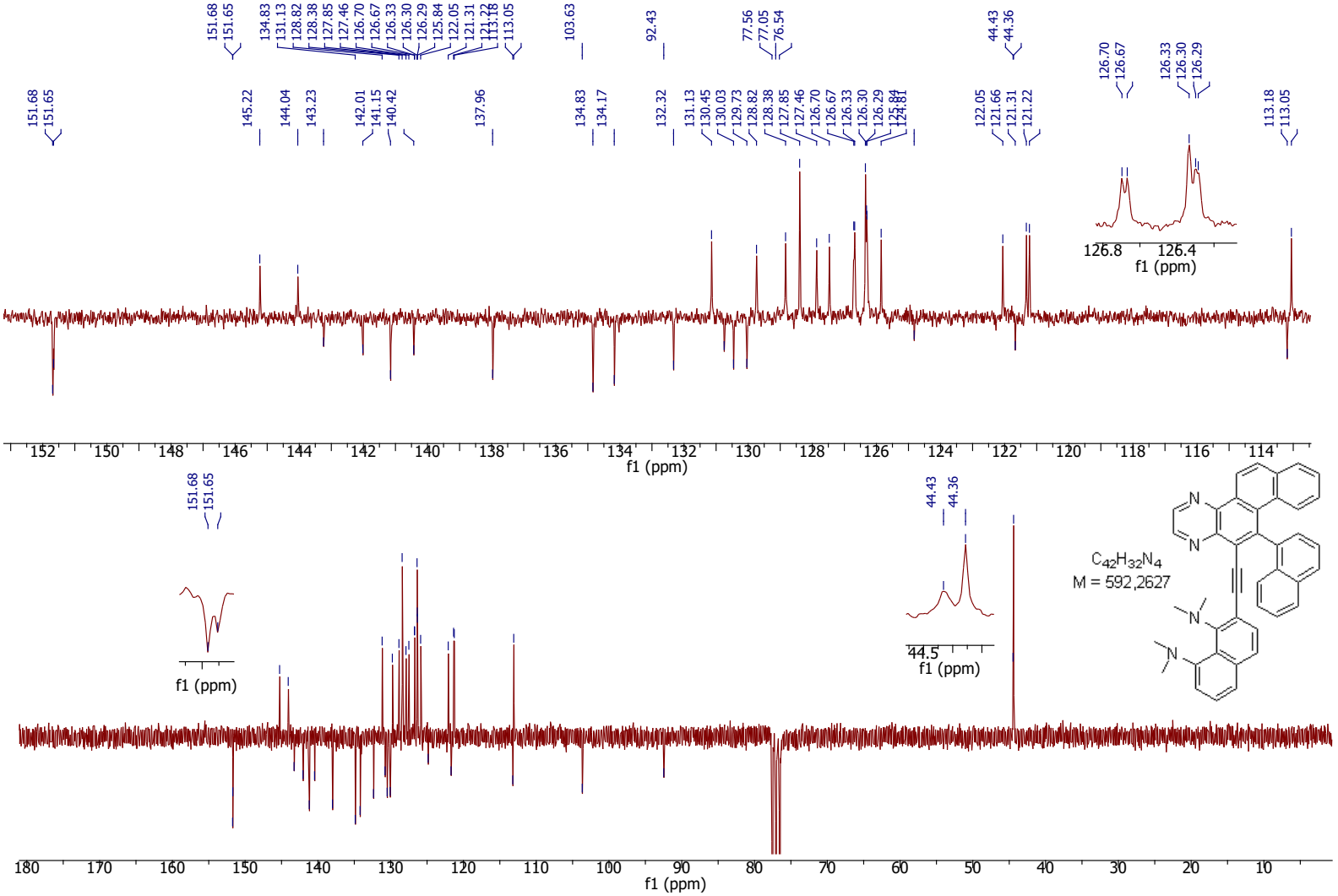


Fig. S40. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **8h** (62.9 MHz, $CDCl_3$).

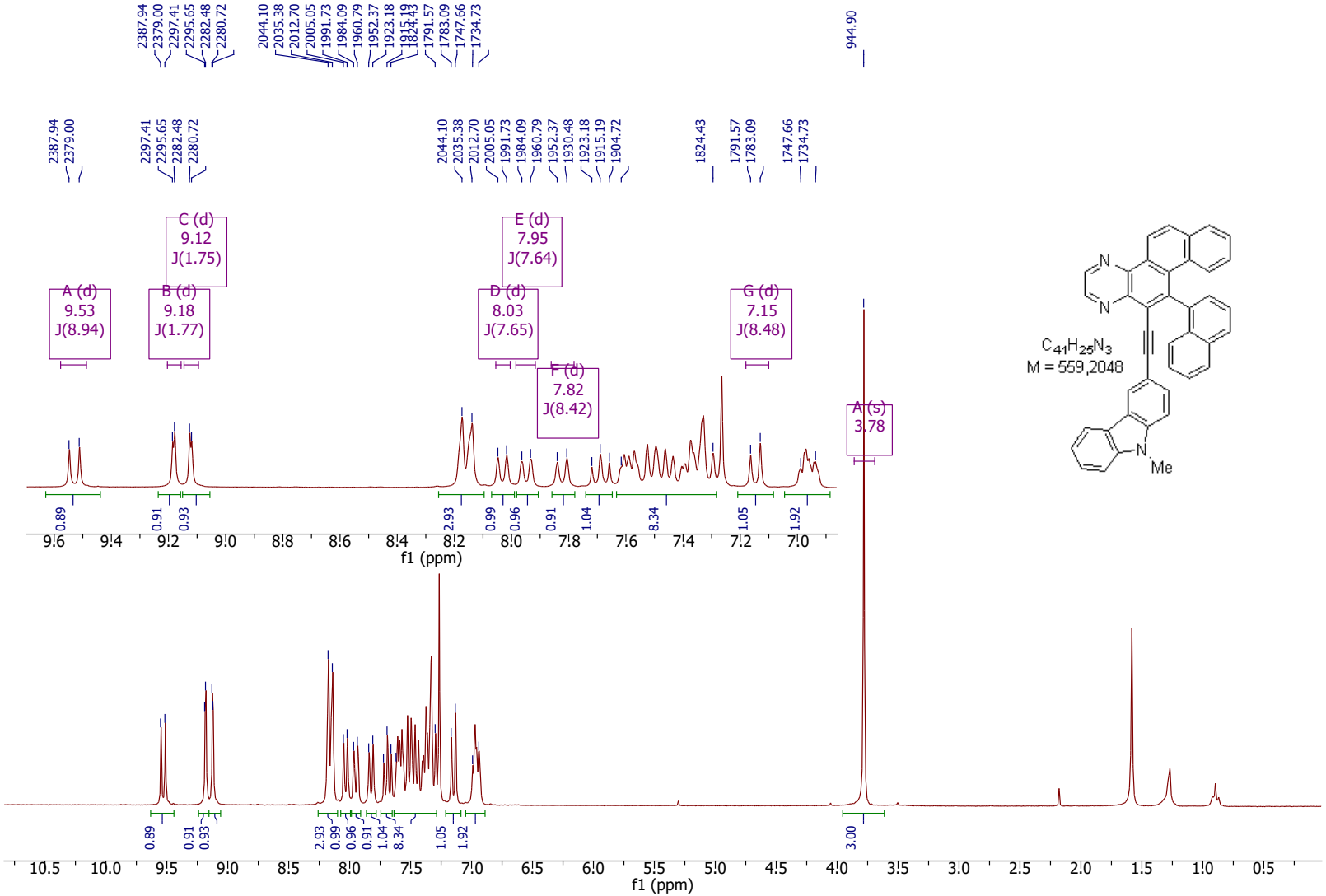


Fig. S41. ^{1}H NMR spectrum of compound **8i** (250 MHz, $CDCl_3$).

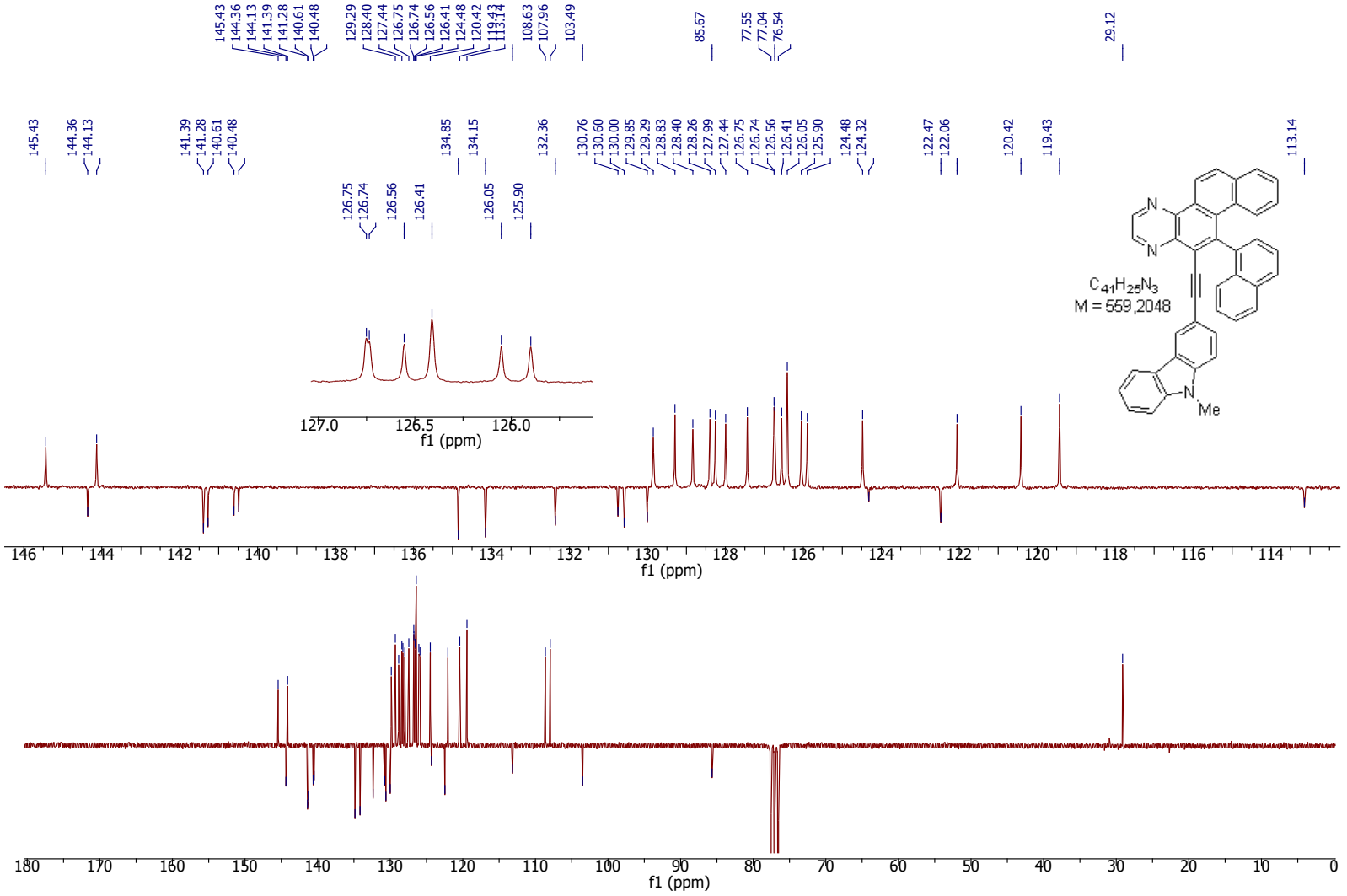


Fig. S42. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **8i** (62.9 MHz, $CDCl_3$).

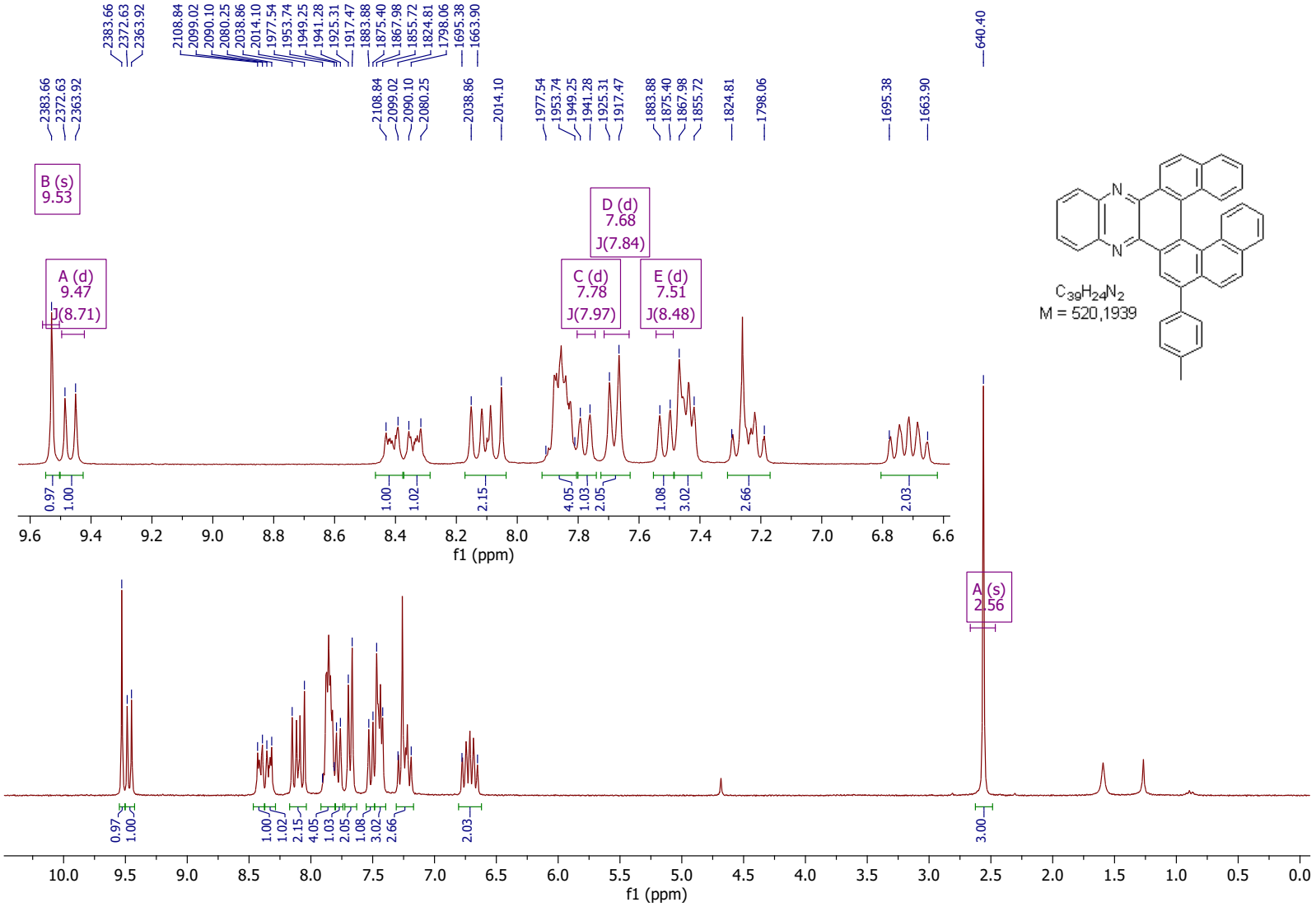


Fig. S43. ^{1}H NMR spectrum of compound **9a** (250 MHz, $CDCl_3$).

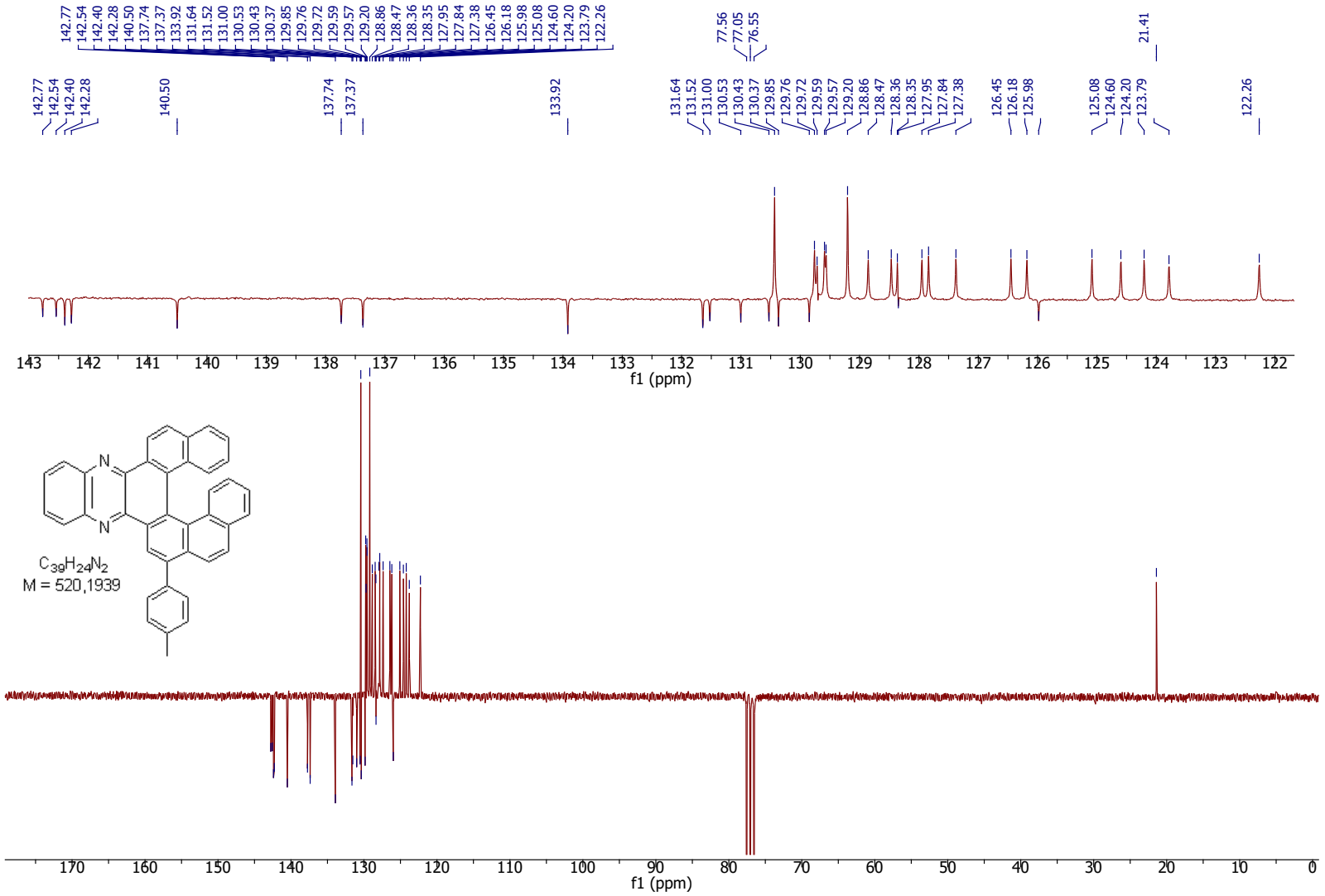


Fig. S44. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **9a** (62.9 MHz, $CDCl_3$).

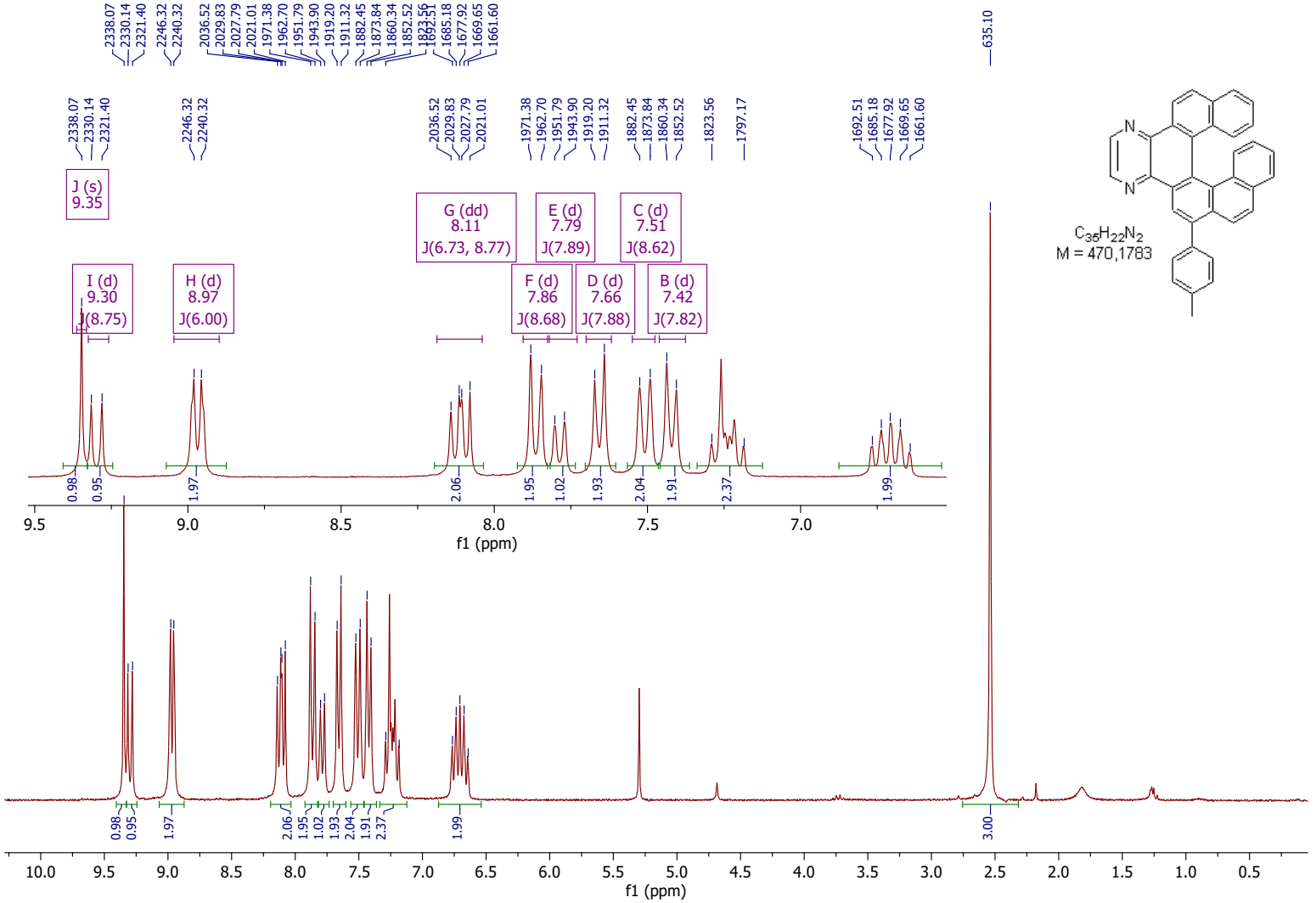


Fig. S45. ^{1}H NMR spectrum of compound **9b** (250 MHz, $CDCl_3$).

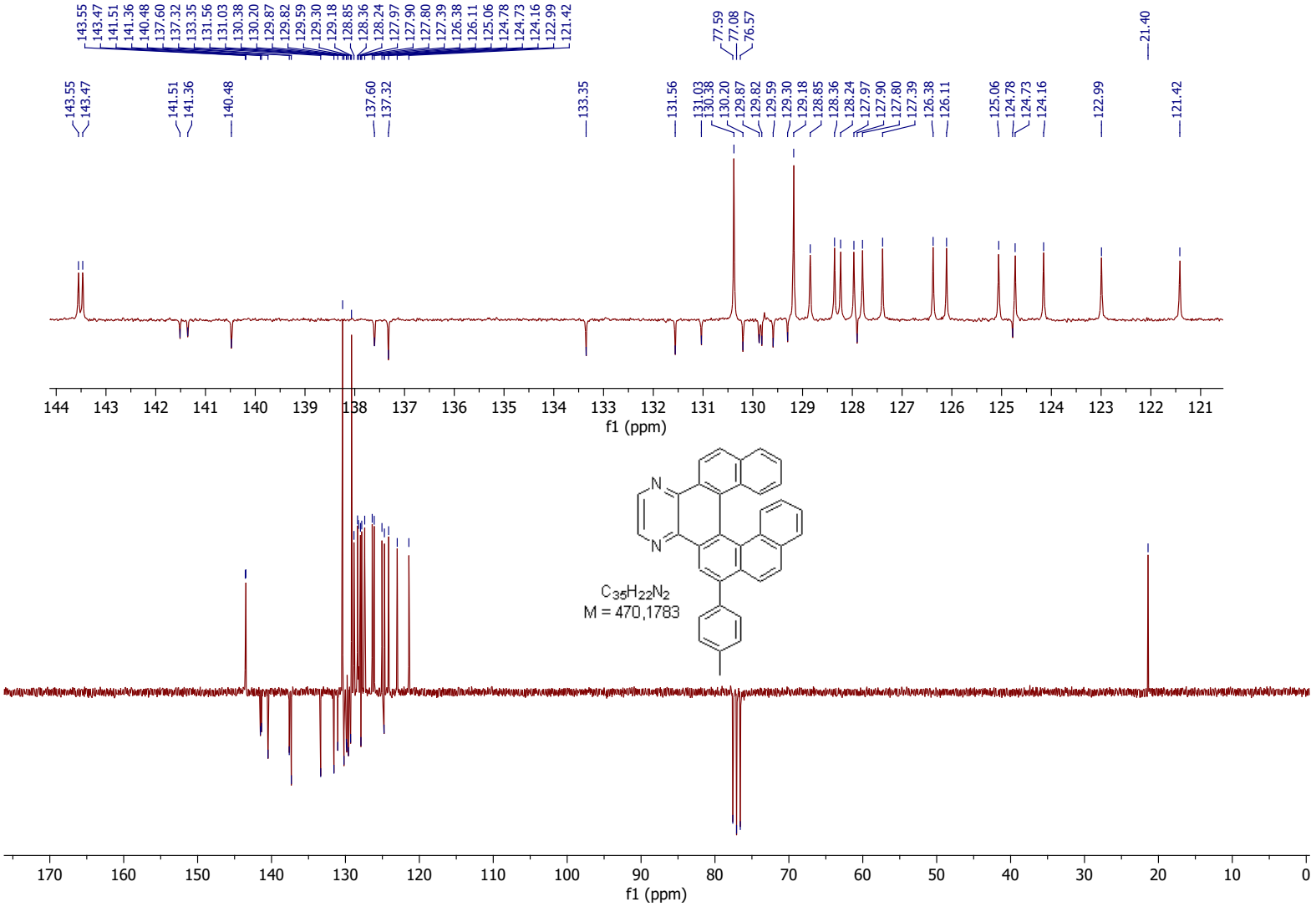


Fig. S46. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **9b** (62.9 MHz, $CDCl_3$).

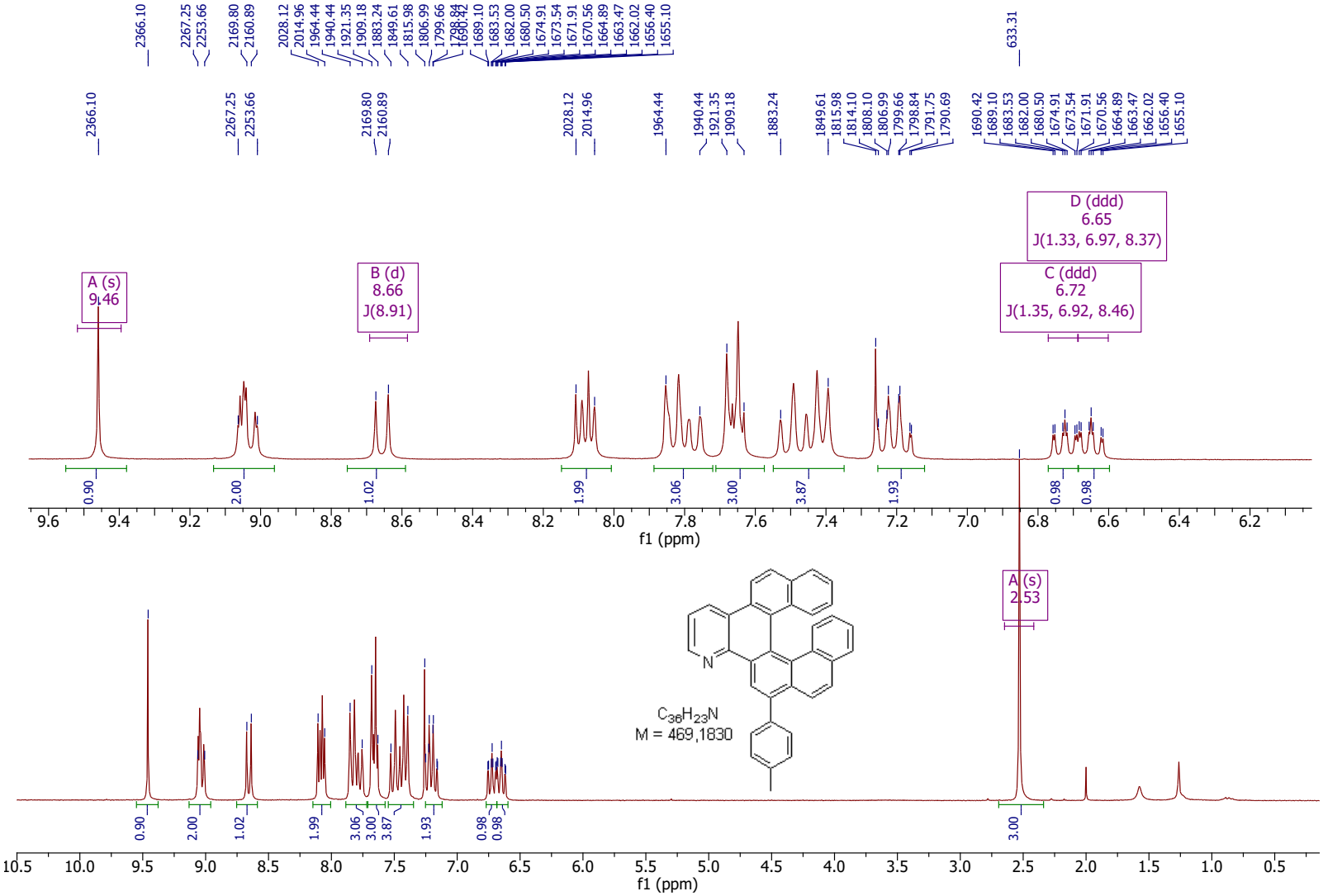


Fig. S47. ^{1}H NMR spectrum of compound **9c** (250 MHz, $CDCl_3$).

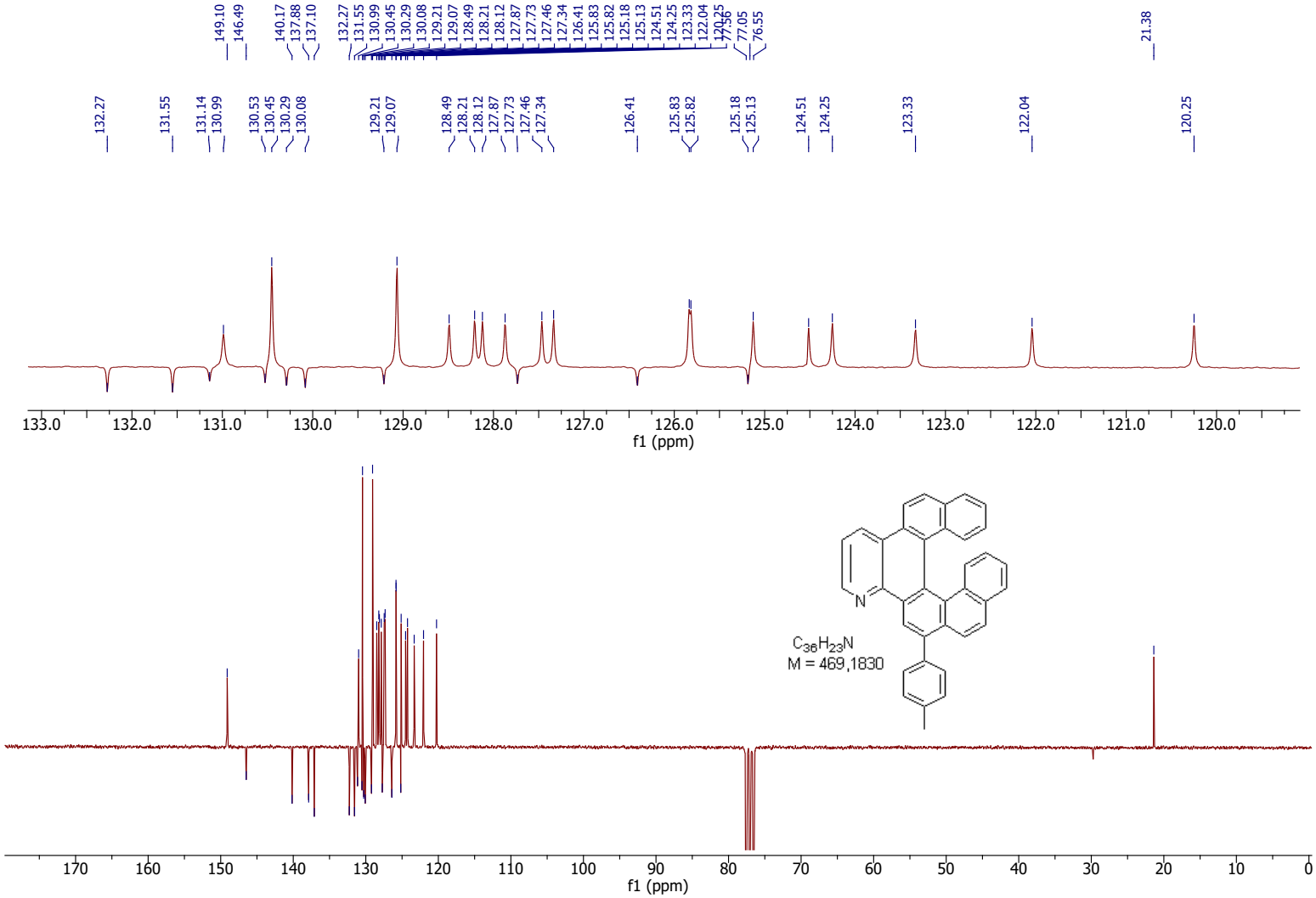


Fig. S48. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **9c** (62.9 MHz, $CDCl_3$).

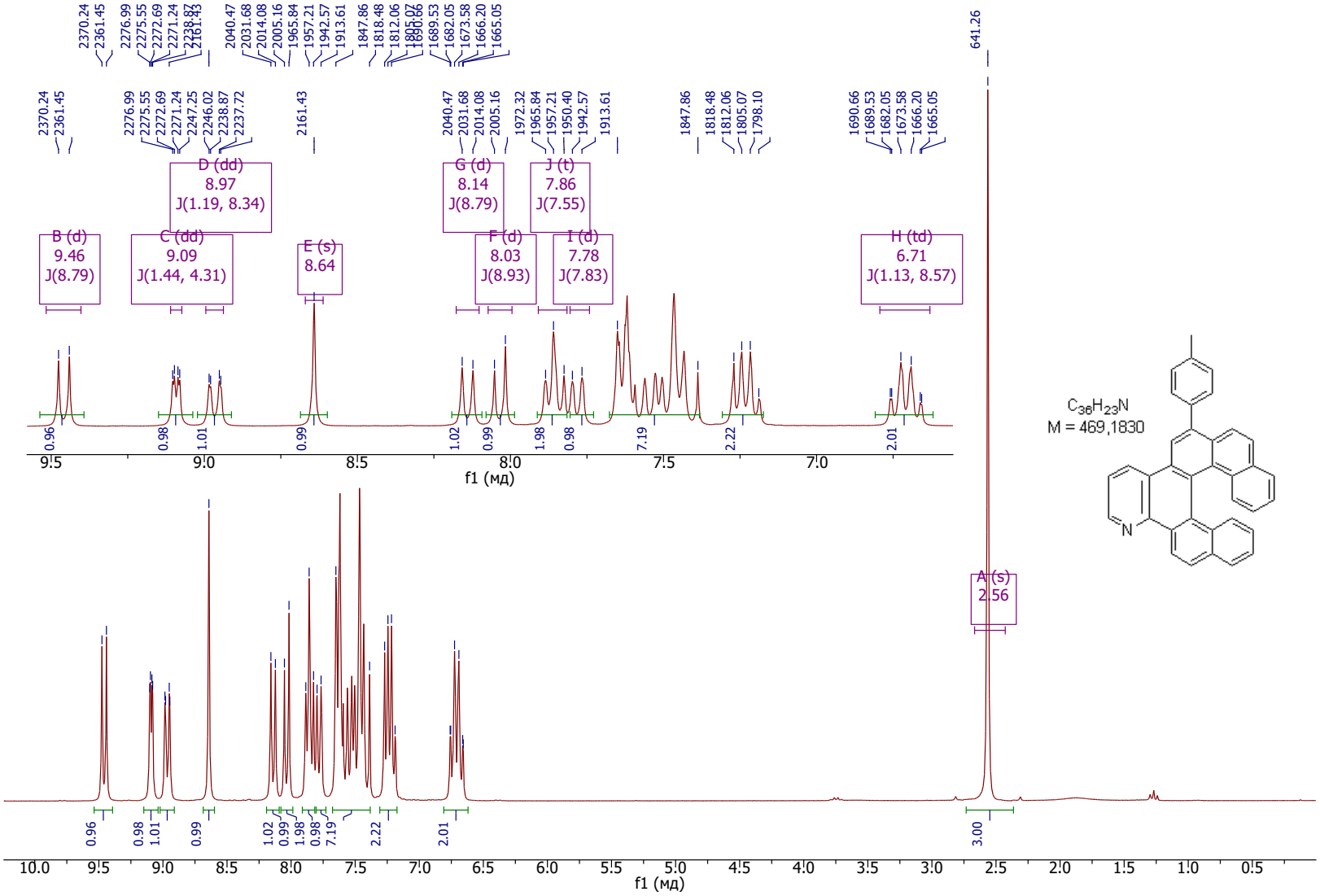


Fig. S49. ^{1}H NMR spectrum of compound **9d** (250 MHz, $CDCl_3$).

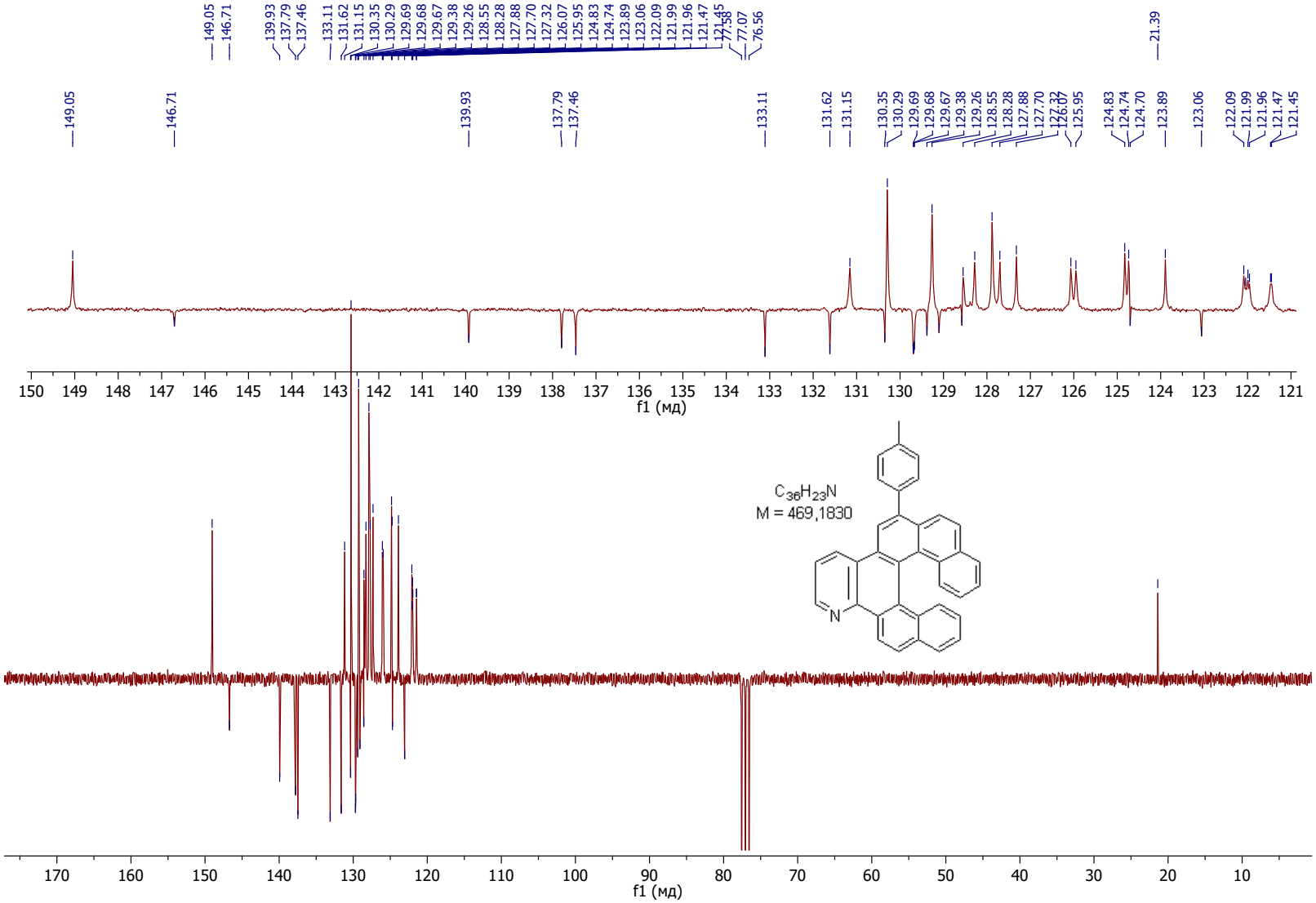


Fig. S50. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **9d** (62.9 MHz, $CDCl_3$).

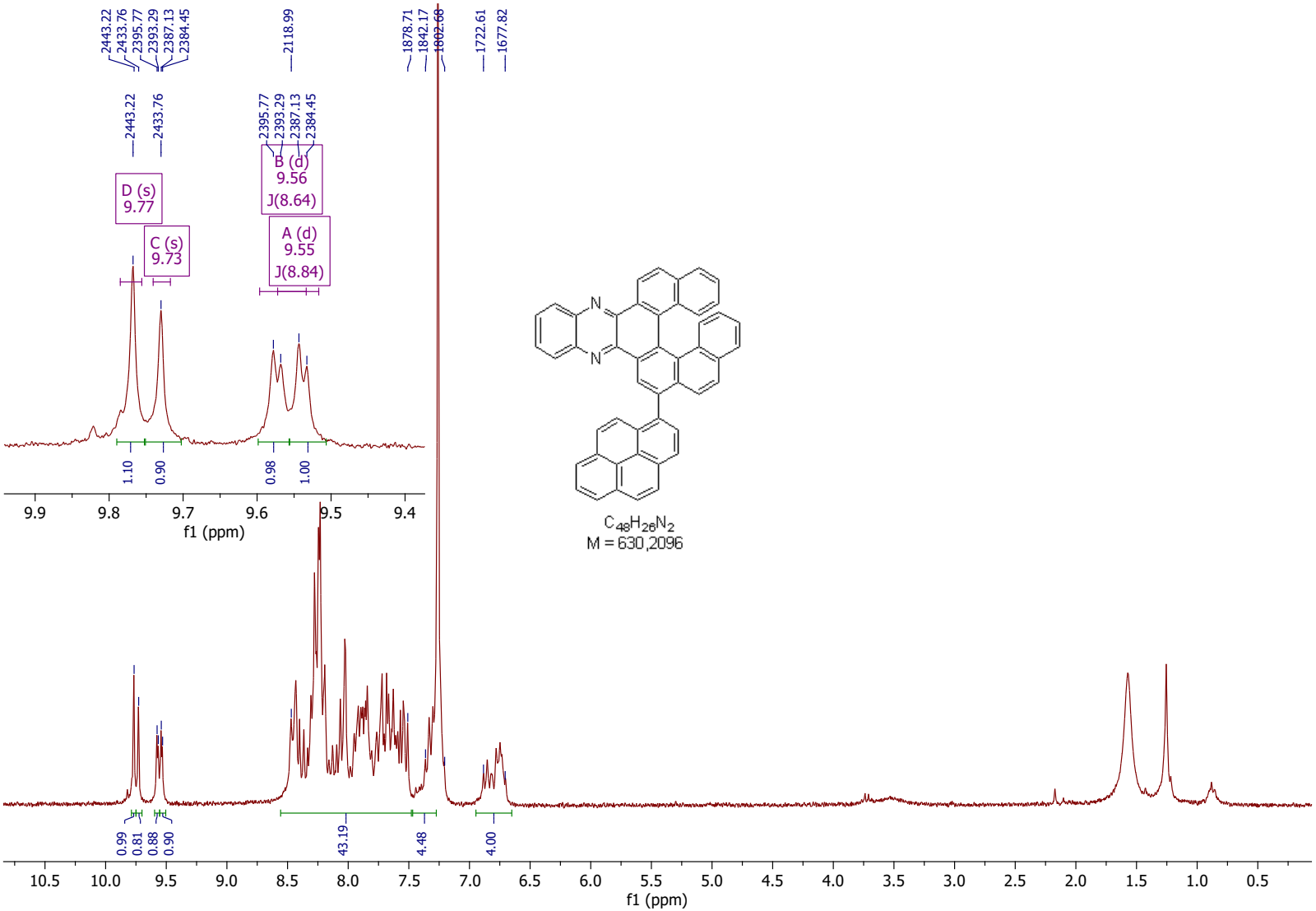


Fig. S51. ^{1}H NMR spectrum of compound **9e** (mixture of stereoisomers) (250 MHz, $CDCl_3$).

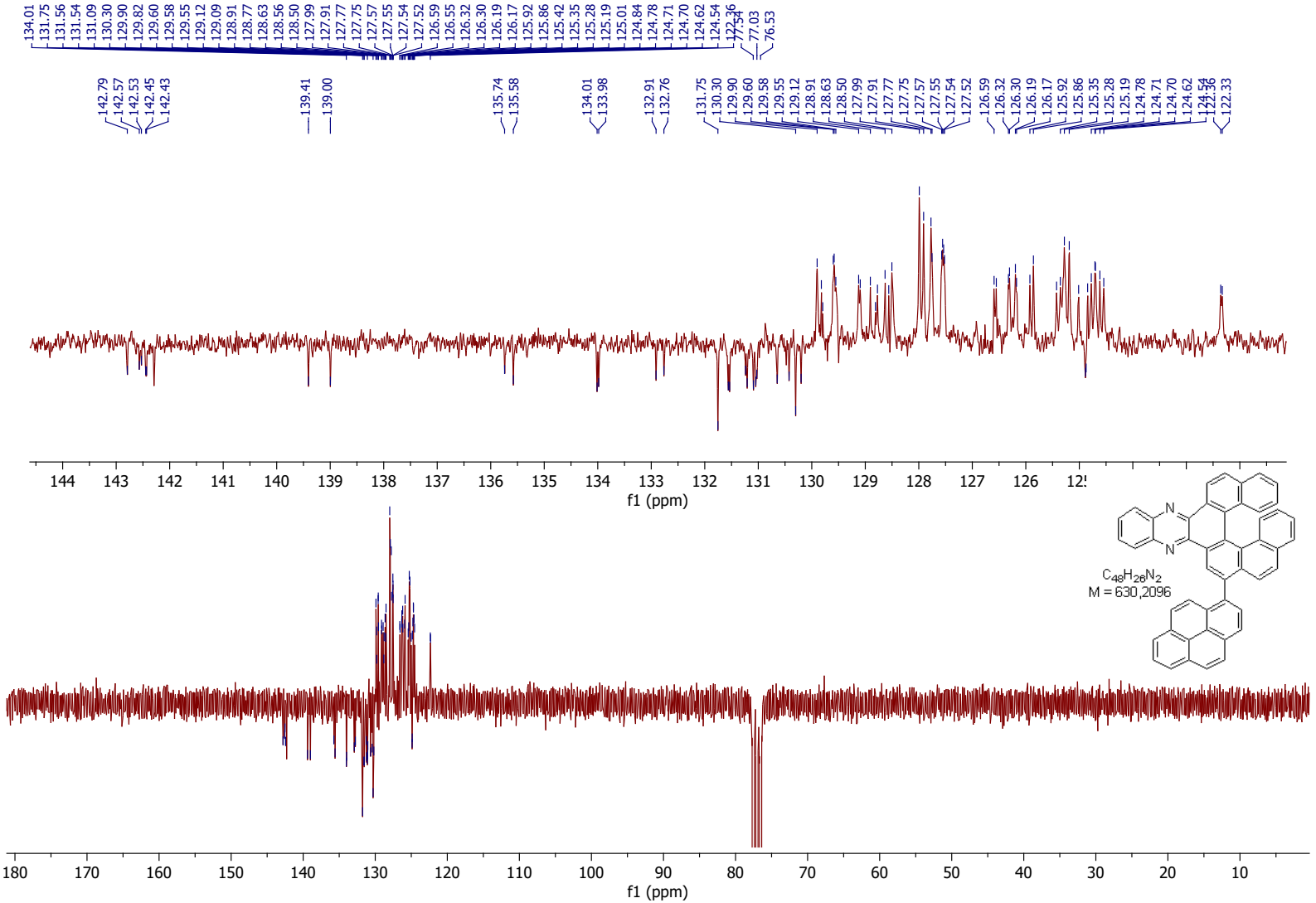


Fig. S52. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **9e** (mixture of stereoisomers) (62.9 MHz, $CDCl_3$).

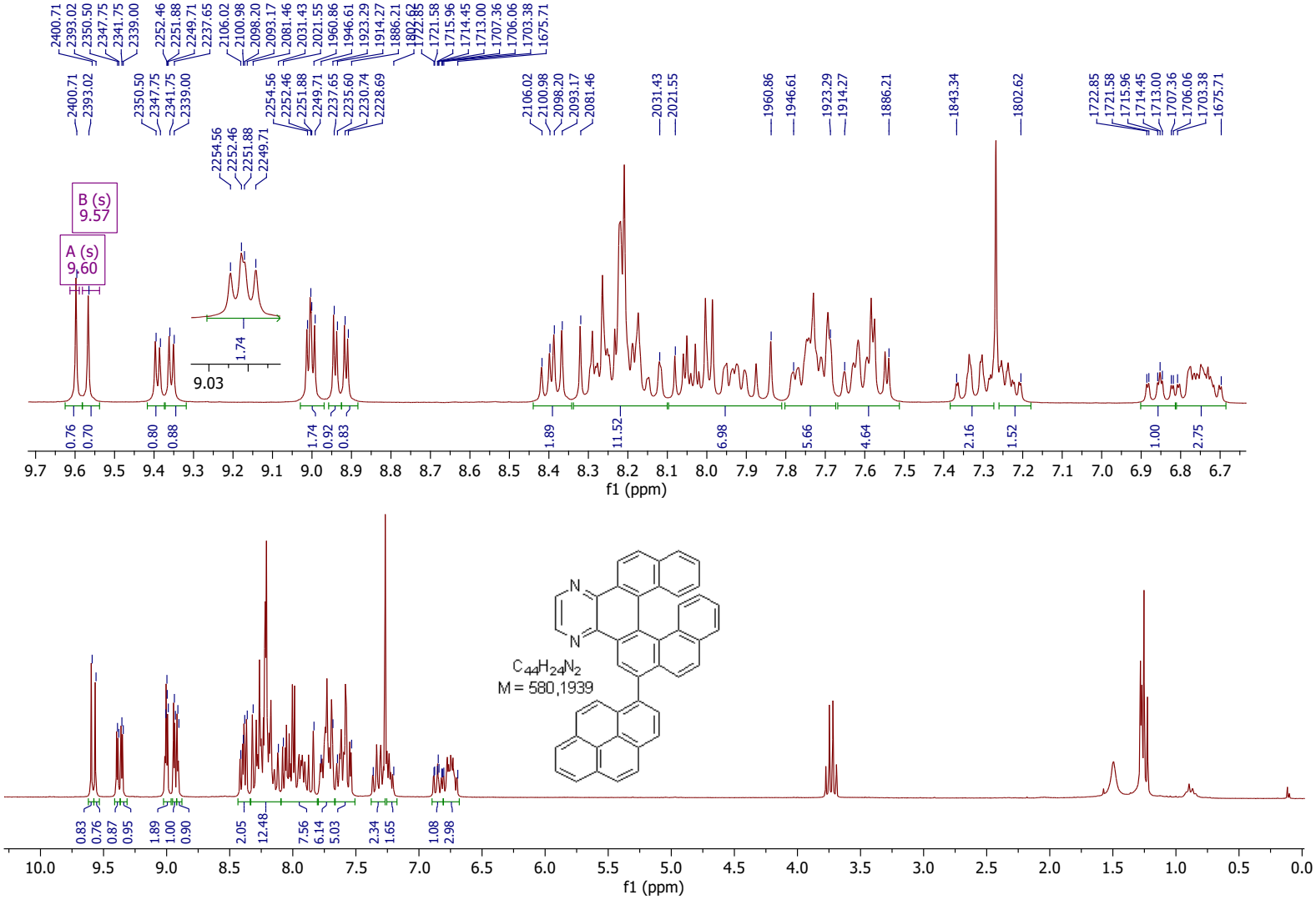


Fig. S53. ^{1}H NMR spectrum of compound **9f** (mixture of stereoisomers) (250 MHz, $CDCl_3$).

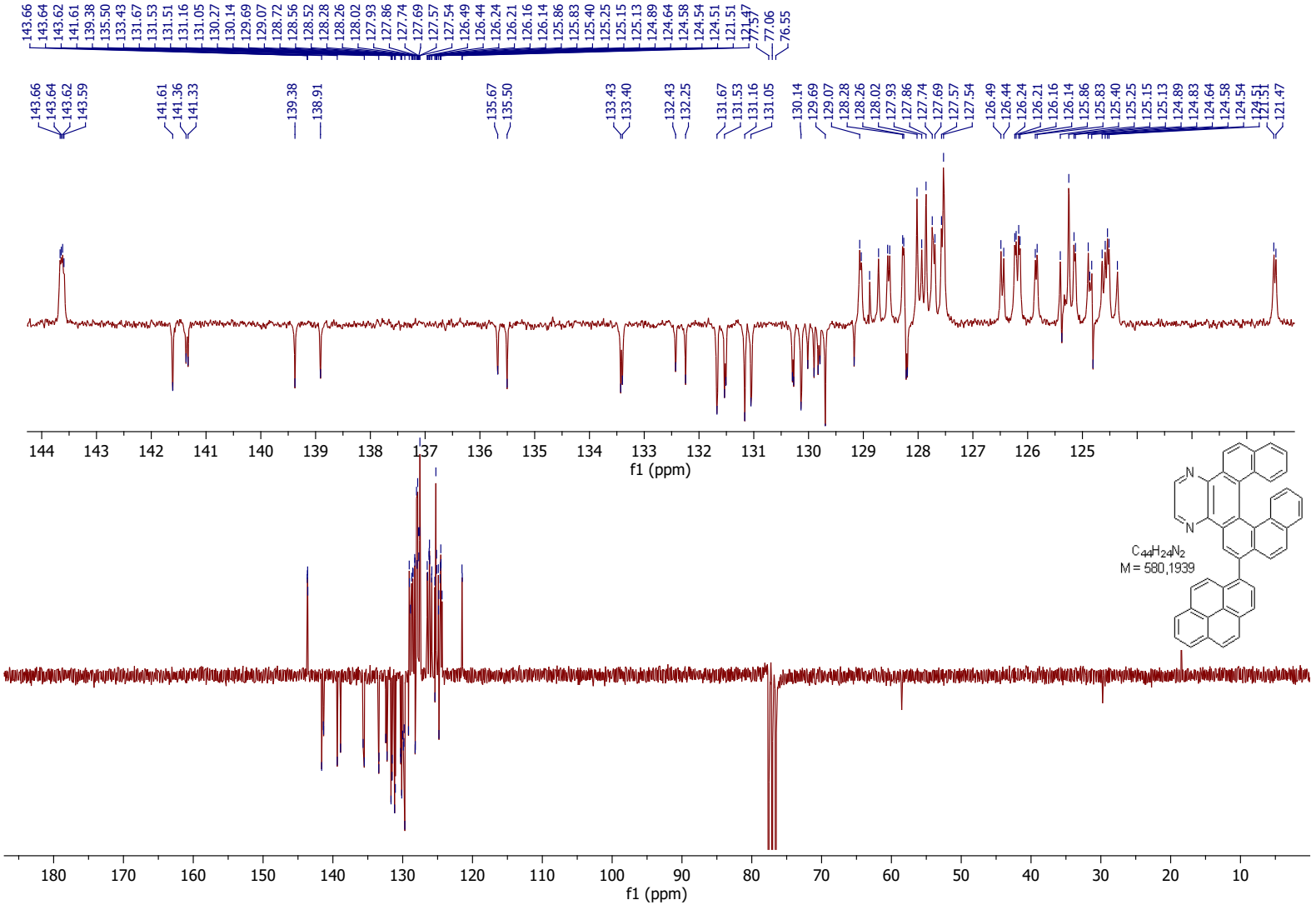


Fig. S54. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **9f** (mixture of stereoisomers) (62.9 MHz, $CDCl_3$).

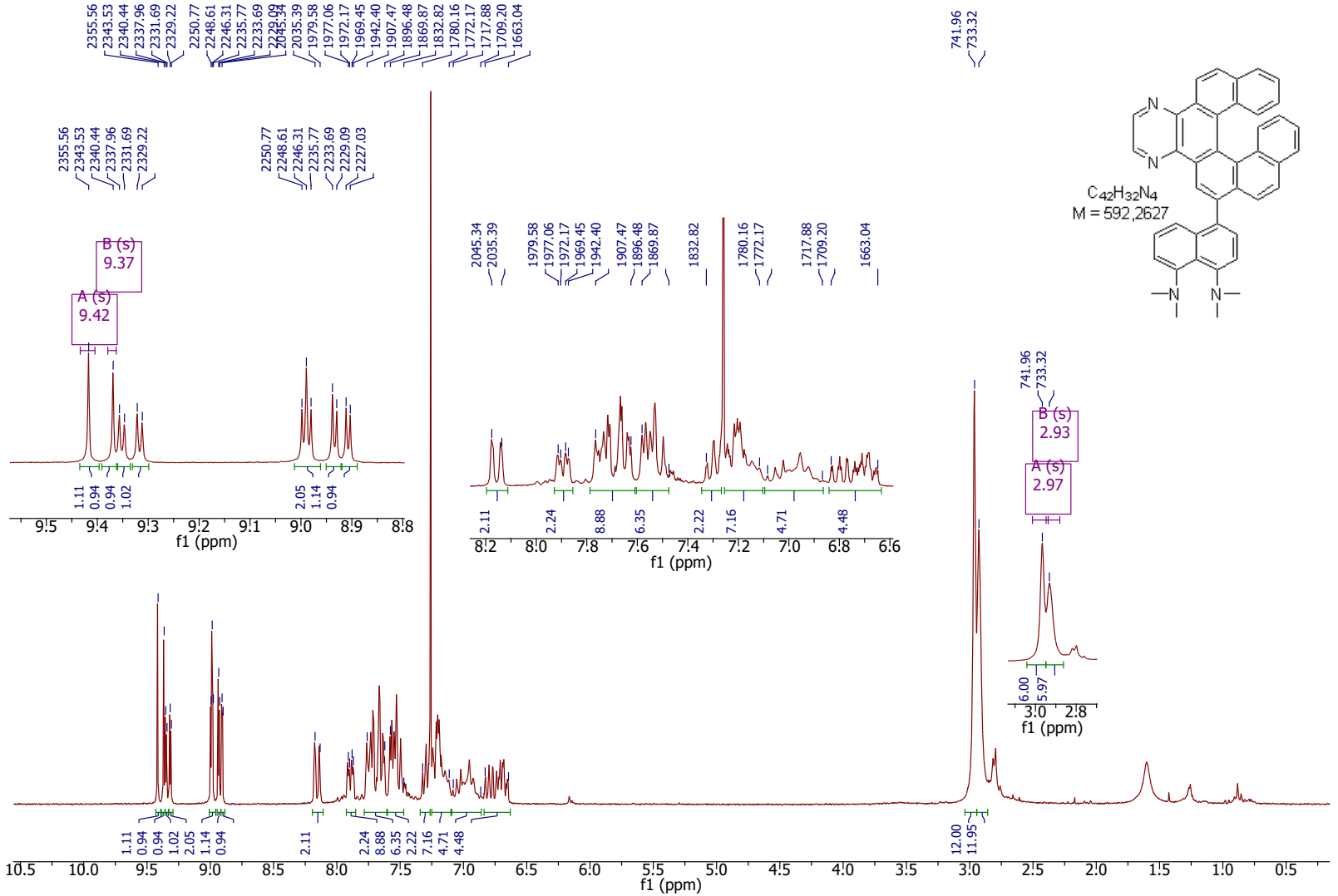


Fig. S55. ^{1}H NMR spectrum of compound **9g** (mixture of stereoisomers) (250 MHz, $CDCl_3$).

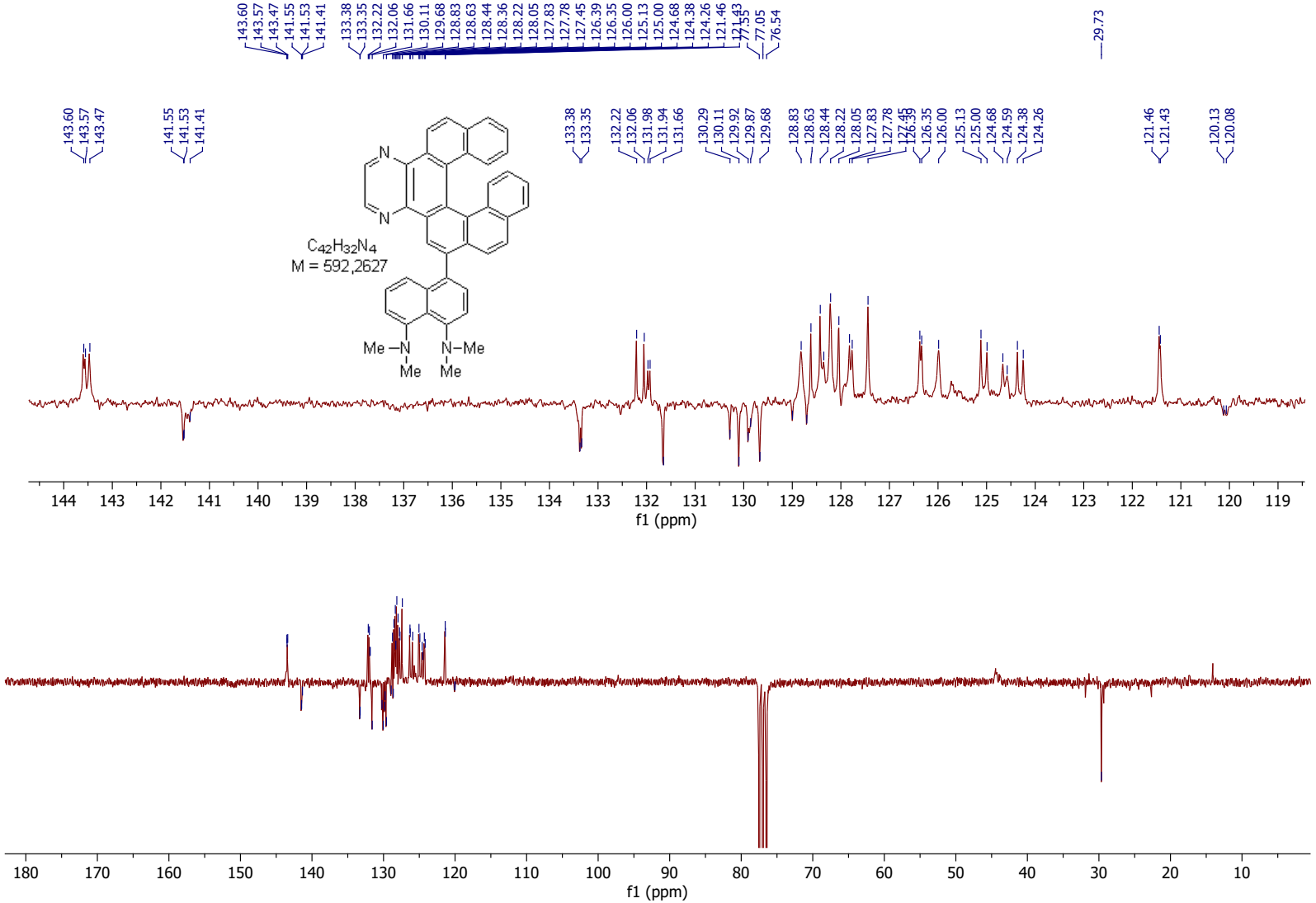


Fig. S56. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **9g** (mixture of stereoisomers) (62.9 MHz, $CDCl_3$).

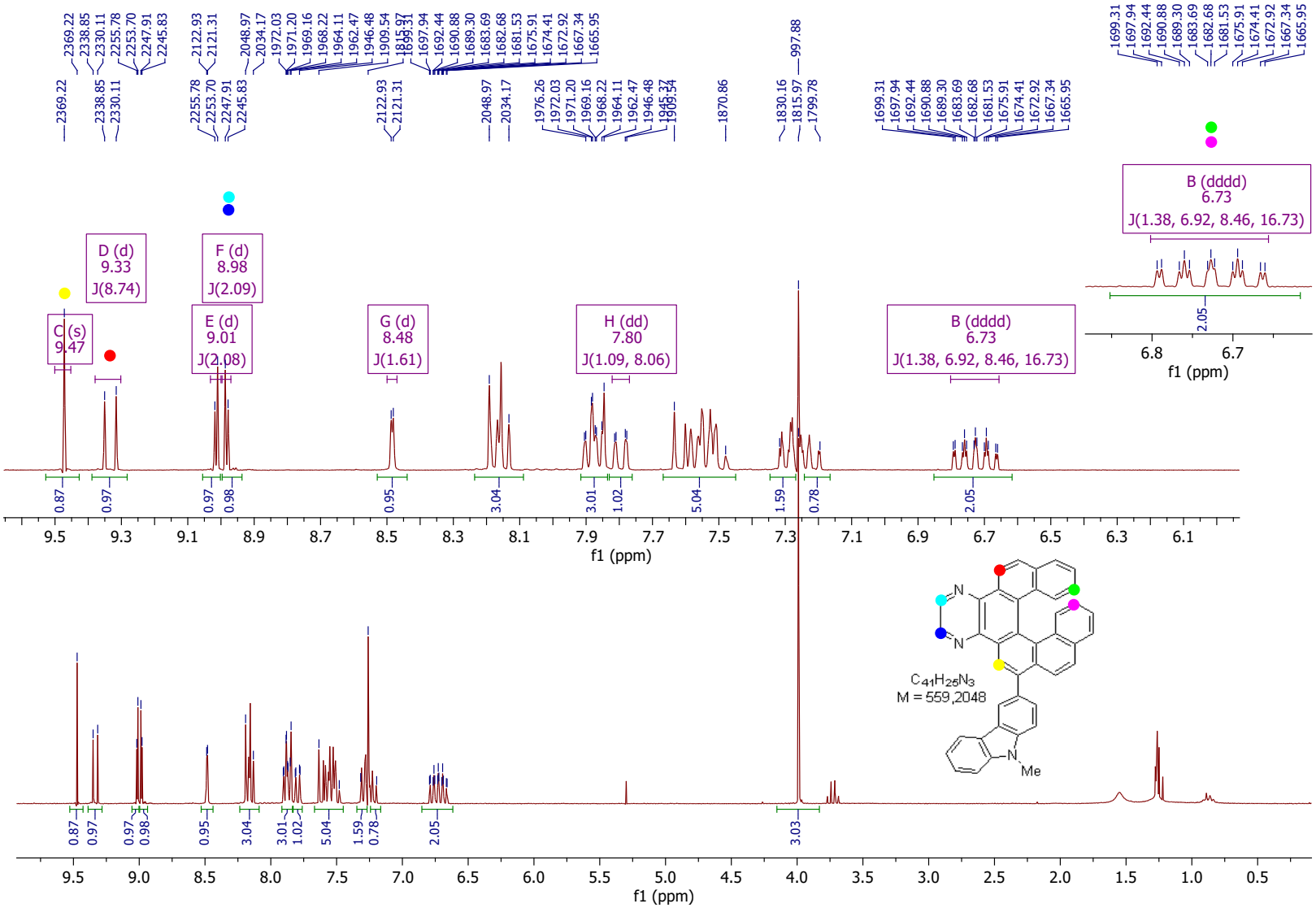


Fig. S57. ^{1}H NMR spectrum of compound **9i** (250 MHz, $CDCl_3$).

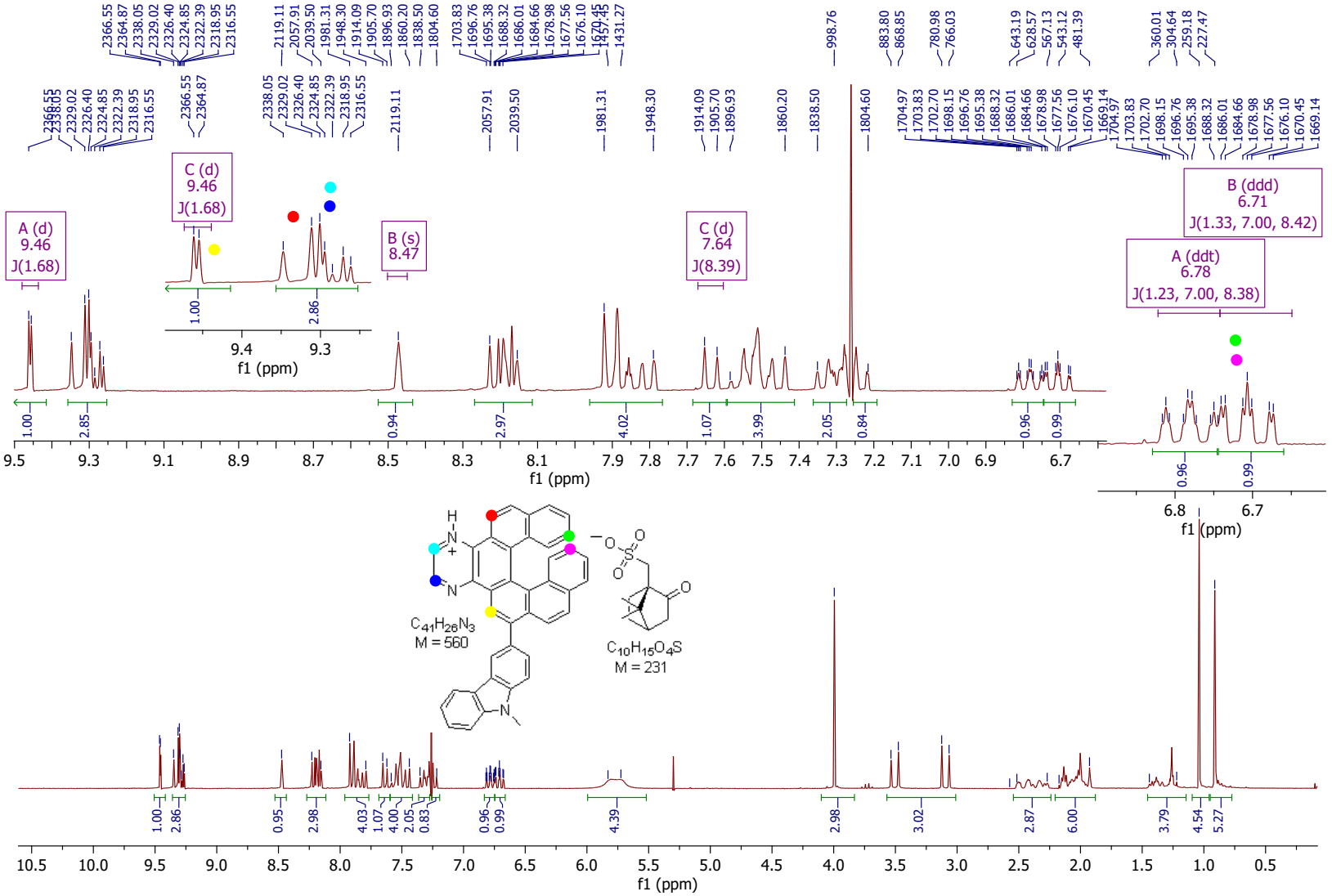


Fig. S58. ^{1}H NMR spectrum of a mixture of compound **9i** and (1*R*)-camphor-10-sulfonic acid (1:1) (250 MHz, $CDCl_3$).

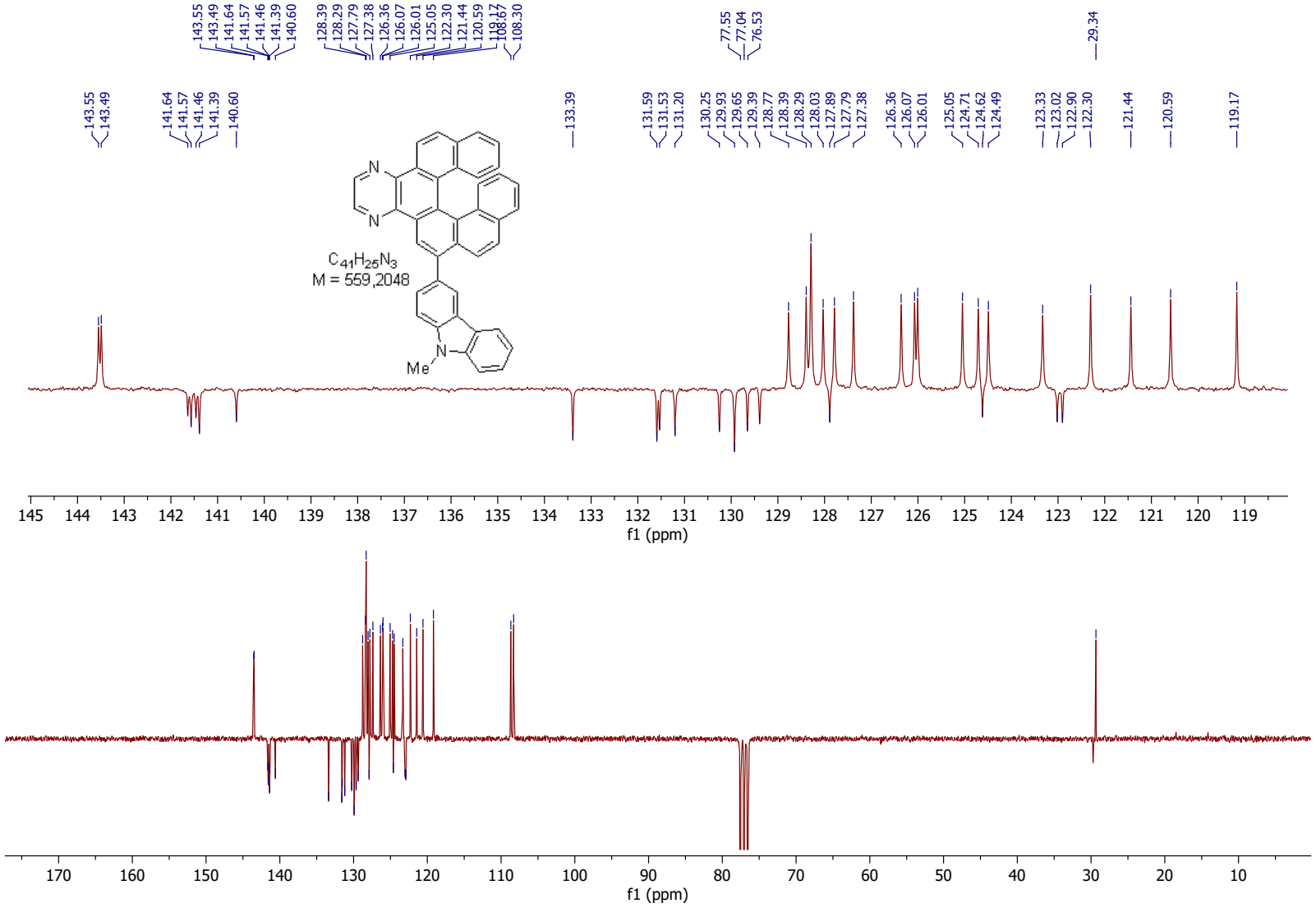


Fig. S59. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **9i** (62.9 MHz, $CDCl_3$).

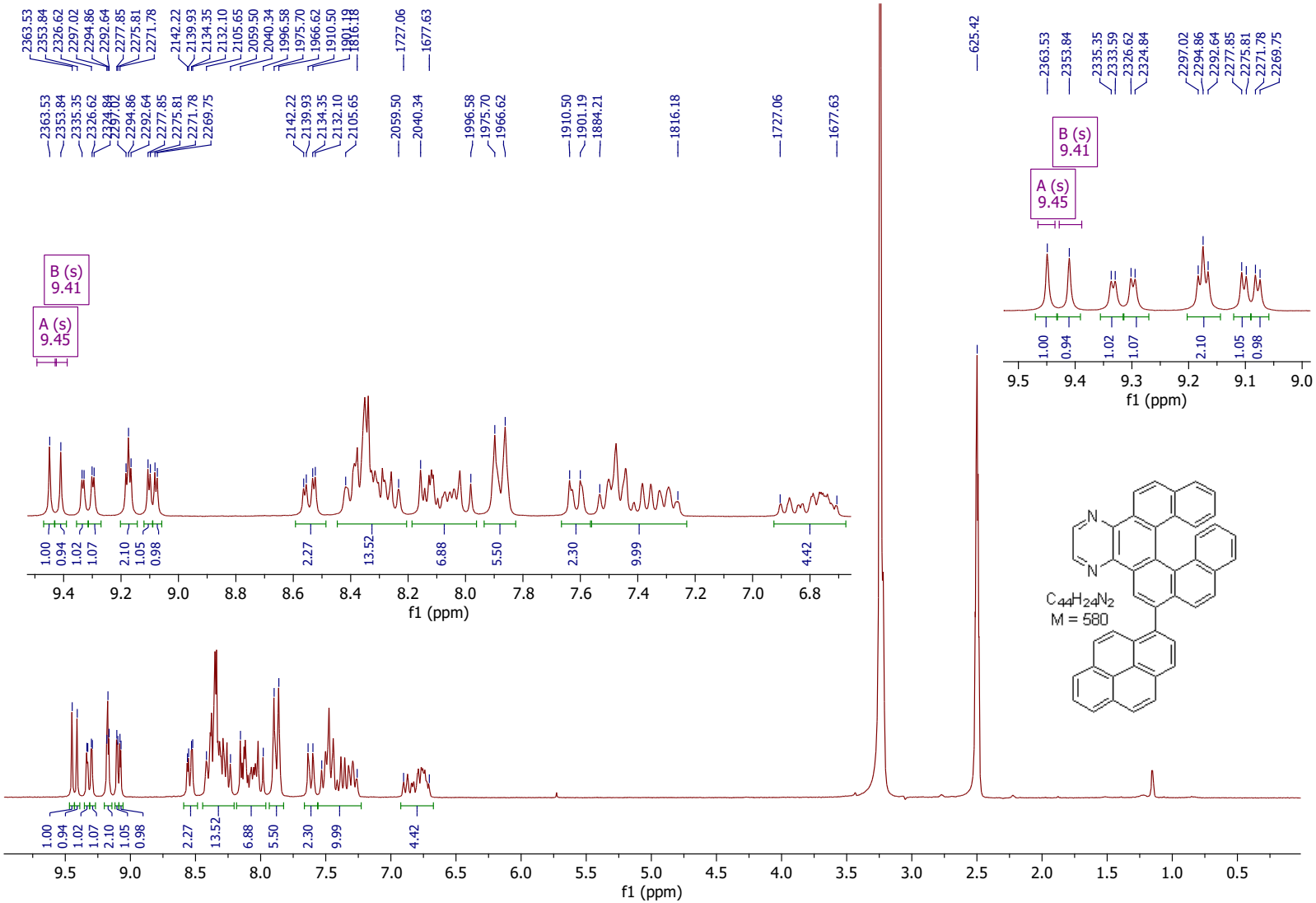


Fig. S60. ^{1}H NMR spectrum of compound **9f** (mixture of stereoisomers) *before heating* to 150 °C (250 MHz, DMSO-d_6).

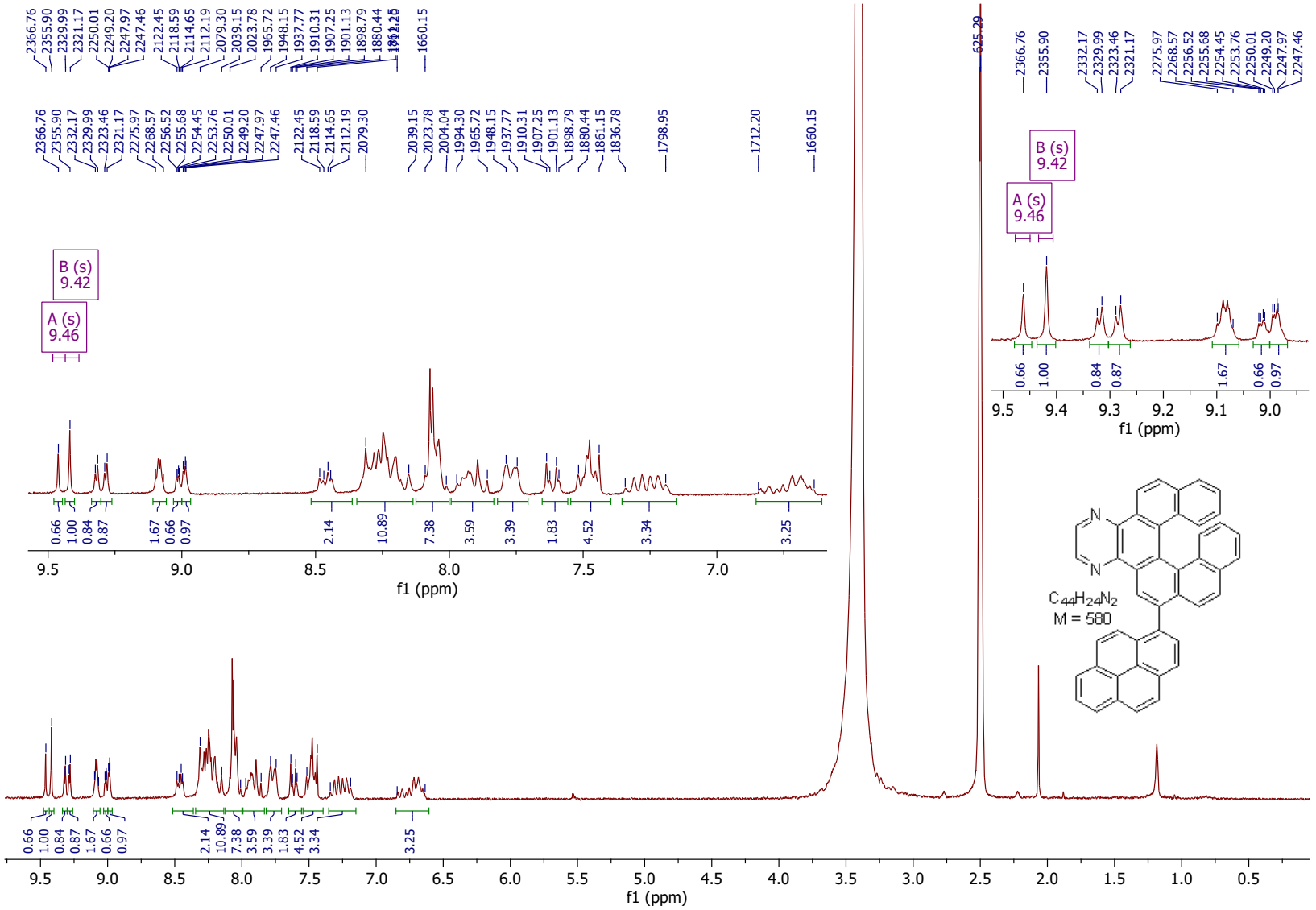


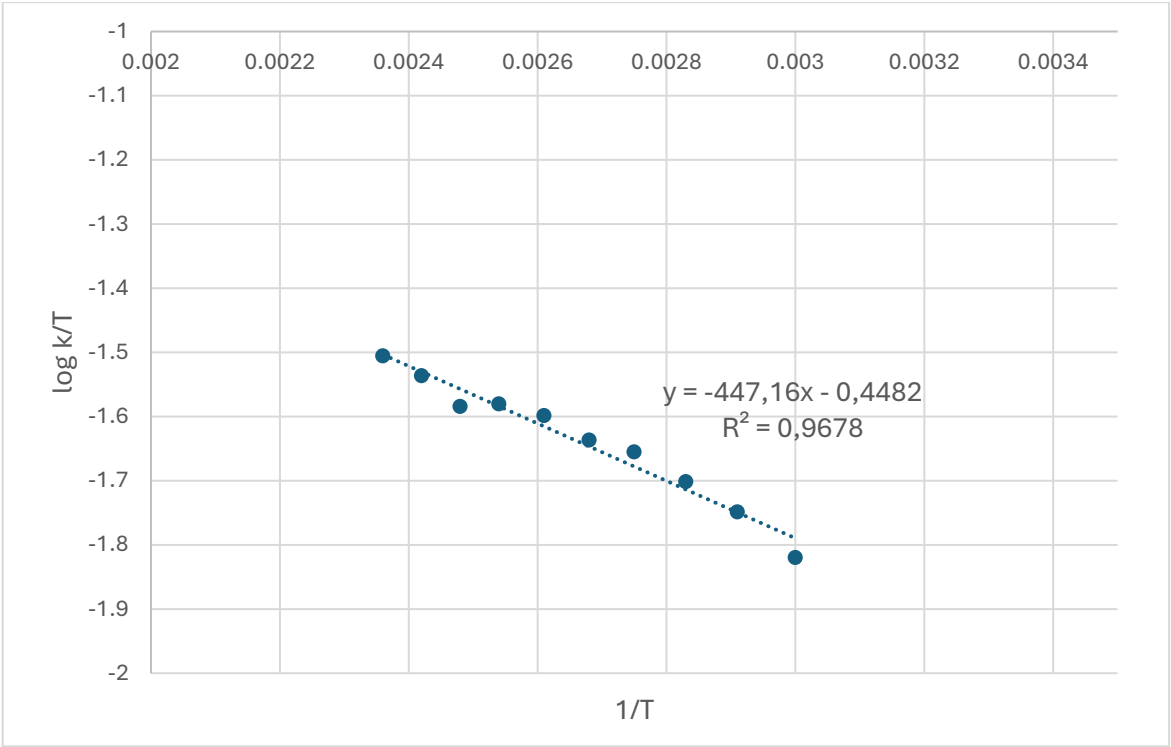
Fig. S61. ^{1}H NMR spectrum of compound **9f** (mixture of stereoisomers*) after heating* to 150 °C (250 MHz, DMSO-d_6).

Calculations of the experimental atropisomerization barrier of compound 9f

The atropisomerization barrier of compound **9e** was estimated by the dynamic NMR, coalescence method (H. Günther, *NMR Spectroscopy: An Introduction*, John Wiley and Sons, Chichester – New York – Brisbane – Toronto, 1980, 436 p.).

Table S1. Calculation of the atropisomerization barrier of compound **9f** using the Eyring plot (signals of the H(5) protons at +40….+150 ºC were used for calculations, $\Delta\nu_{AB}$ - difference in chemical shifts of signals of the H(5) protons of rotamers under conditions of rapid exchange, $\Delta\nu_{AB}^{*}$ - difference in chemical shifts of signals of the H(5) protons of rotamers under conditions of slow exchange (+40 ºC))

T, ºC	T, K	1/T	$\Delta\nu_{AB}$, Hz	$\Delta\nu_{AB}^2$	$\sqrt{(\Delta\nu_{AB}^{*2} - \Delta\nu_{AB}^2)}$	$k = \pi \sqrt{(\Delta\nu_{AB}^{*2} - \Delta\nu_{AB}^2)}/\sqrt{2}$	log k/T
40	313	0,00319	9.69	93,8961	0		
50	323	0,00310	9.57	91,5849	1,52026	3,33057	-1,98668
60	333	0,00300	9.42	88,7364	2,27150	5,04273	-1,81978
70	343	0,00291	9.29	86,3041	2,75536	6,11690	-1,74876
80	353	0,00283	9.16	83,9056	3,16077	7,01691	-1,70163
90	363	0,00275	8.99	80,8201	3,61607	8,02767	-1,65532
100	373	0,00268	8.88	78,8544	3,87836	8,60996	-1,63671
110	383	0,00261	8.66	74,9956	4,34747	9,65138	-1,59861
120	393	0,00254	8.50	72,25	4,65254	10,32864	-1,58035
130	403	0,00248	8.46	71,5716	4,72488	10,48923	-1,58456
140	413	0,00242	8.04	64,6416	5,40874	12,00740	-1,53650
150	423	0,00236	7.65	58,5225	5,94757	13,20360	-1,50565



$-447.16 = -\Delta H^{\neq} / 19.14 \qquad \Delta H^{\neq} = 8558{,}64 \text{ J mol}^{-1}$

$-0.4482 = 10.32 + \Delta S^{\neq}/19.14 \qquad \Delta S^{\neq} = -206.1 \text{ J mol}^{-1} \text{ K}^{-1}$

$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$?

if T = 423K then $\Delta G^{\neq} = 95738 \text{ J mol}^{-1} = 22.9 \text{ kcal mol}^{-1}$

Quantum-chemical calculations of the *R/S*-atropisomerization and *P/M*-enantiomerization barriers of compound 9f

All quantum chemical calculations were performed using the Orca 5.0.4[6] software package. The exchange-correlation DFT functional PBE0[7] was used in conjunction with a triple-ζ valence polarized def2-TZVP(-f) basis set[8] and auxiliary basis set def2/J[9]. Dispersion correction was accounted for by means of Grimme's model (D4).[10] The PBE0 functional has demonstrated robust performance across various applications in computational chemistry, as evidenced by studies.[11-13] Consequently, it was selected for use in this investigation. Solvent effects (DMSO) were considered through the CPCM model.[14] Free energies were estimated using modified GoodVibes-2 [https://github.com/TheorChemGroup/GoodVibes2] with Truhlar's quasi-harmonic correction[15] and a cut-off value of 175 cm^{-1}, which was found[16] to be optimal and were computed at 373 K and concentrations of 1 mol/L. All energies are given in kcal/mol.

Conformational sampling of all stationary points, including all intermediates and transition states (TSs), was performed using the CREST program [17,18] with the GFN2-xTB[19] method, accounting for solvent effects (DMSO) via the ALPB solvation model[20]. The lowest-energy conformer obtained from this search was selected for subsequent quantum chemical calculations.

First, we located the transition states for *P/M*-isomerization of helicene **9f** for both its *S*-form (TS-*(P/M,Sa)*-**9f**) and *R*-form (TS-*(P/M,Ra)*-**9f**). The energy barrier for the *P/M*-isomerization was determined by locating the corresponding transition state (Figure S62, S63, Figure 4). To this end, we employed a constrained pre-optimization protocol[21]. The initial structural guess for the transition state was constructed based on the geometry reported by Jorge Barroso et al.[22] Each optimized transition state exhibited a single imaginary vibrational mode, whose correspondence to the targeted isomerization pathway was confirmed by intrinsic reaction coordinate (IRC) calculations.

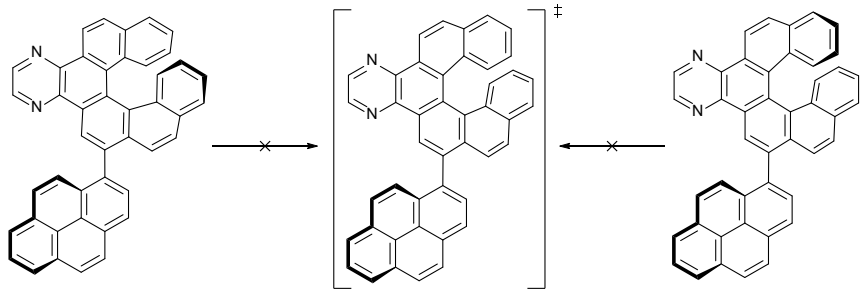


Figure S62. Energies of *P/M*-isomerization of (*Sa*)-**9f**.

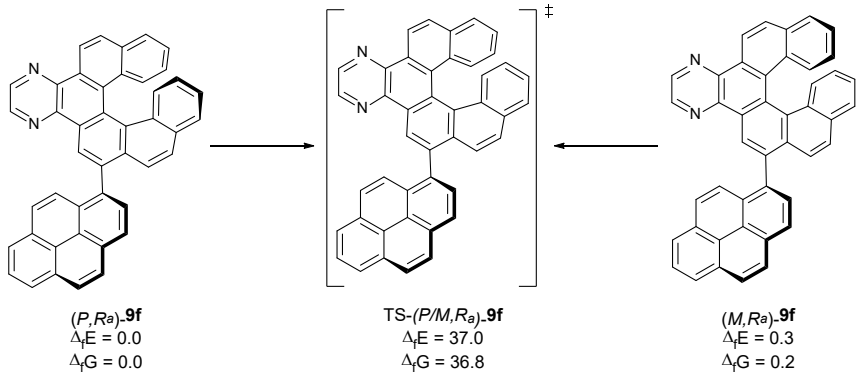


Figure S63. Energies of *P/M*-isomerization of (*Ra*)-**9f**.

We also found that the *(P,Ra)*-**9f** and enantiomeric *(M,Sa)*-**9f** isomers are 0.2–0.3 kcal/mol more stable than their diastereomeric counterparts (*P,Sa)*-**9f** and *(M,Ra)*-**9f**, indicating that all of these structures are nearly equivalent in stability (Figure S64).

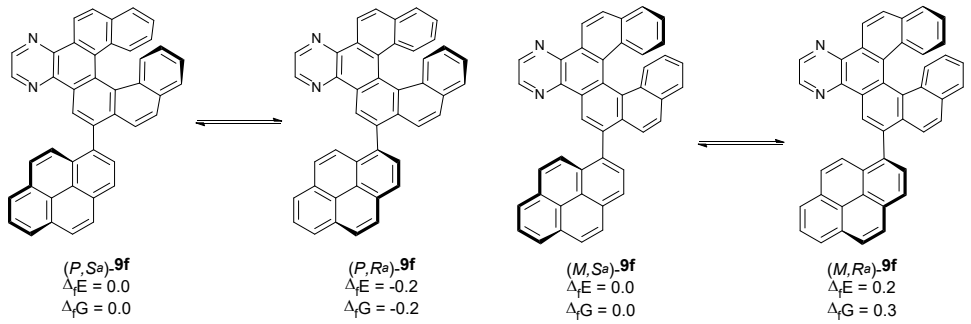


Figure S64. Energies of *R/S*-atropisomerization of (*P*)-**9f** (left) and (*M*)-**9f** (right).

We next examined the atropisomerization of helicene **9f**. Since attempts to locate a saddle point for the transitions between the diastereomeric pairs (*P,Sa*)-**9f** ↔ (*P,Ra*)-**9f** and (*M,Sa*)-**9f** ↔ (*M,Ra*)-**9f** were unsuccessful, the corresponding atropisomerizations were investigated by means of relaxed potential energy surface scans. In these scans, the relevant dihedral angle was constrained, while all remaining geometrical parameters were fully optimized. Initially, scans were performed with a step of 10°, and the energies of the maxima were subsequently refined using a 4° step. The combined energy profiles are shown in Figures S65 and S66.

To avoid convergence issues of the geometry optimizer, relaxed scans of the corresponding dihedral angle were carried out in both directions and then merged; for each dihedral value, the lower energy from the two scans was selected. This procedure yielded smooth and continuous energy profiles for the studied transformations.

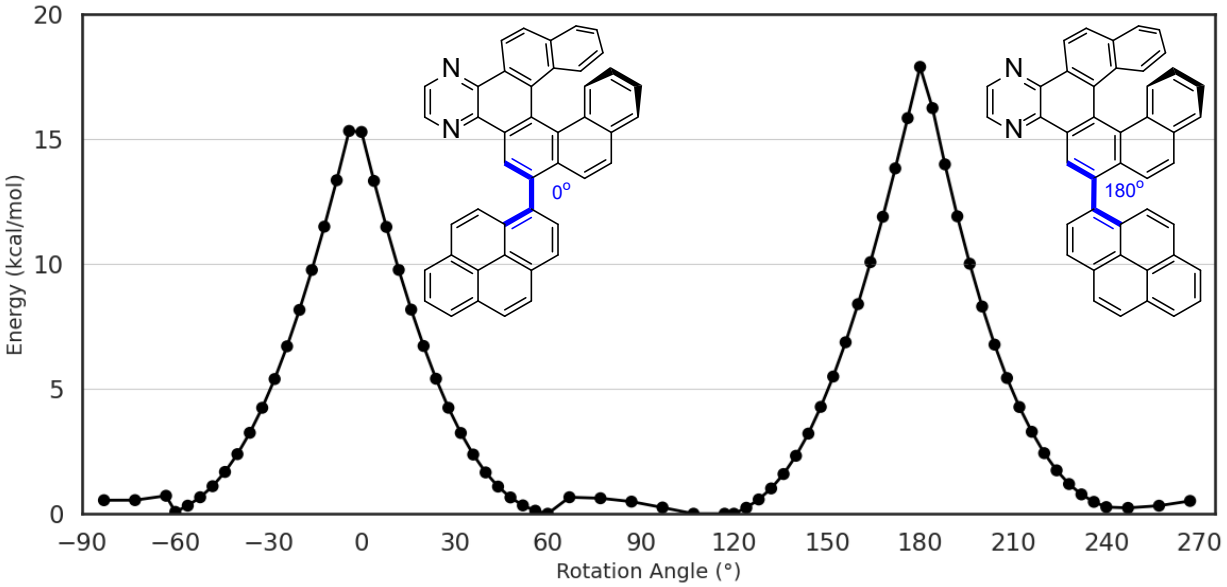


Figure S65. Dependence of the electronic energy (kcal/mol) on dihedral angle for *(P)*-helicene **9f**.

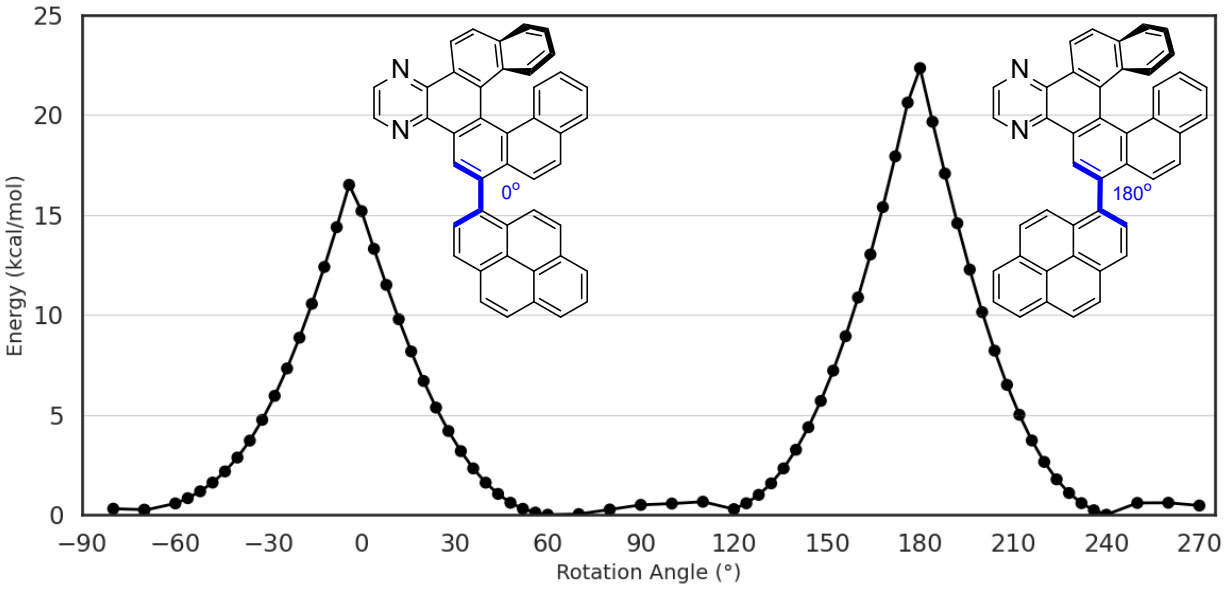


Figure S66. Dependence of the electronic energy (kcal/mol) on dihedral angle for *(M)*-helicene **9f**.

Notably, even combining forward and reverse relaxed dihedral scans does not provide a quantitatively reliable estimate of the barrier. In a relaxed scan, the optimized geometry necessarily retains "memory" of the preceding structure and tends to follow a pathway-dependent branch of the potential-energy surface (hysteresis), which complicates identification of the true saddle point where the structure is maximally distinct from either neighboring minimum. Consequently, these relaxed scans can only be used to bracket the atropisomerization barrier, which is estimated to lie in the range of *ca.* 16–30 kcal/mol based on the profiles in Figures S67–S68.

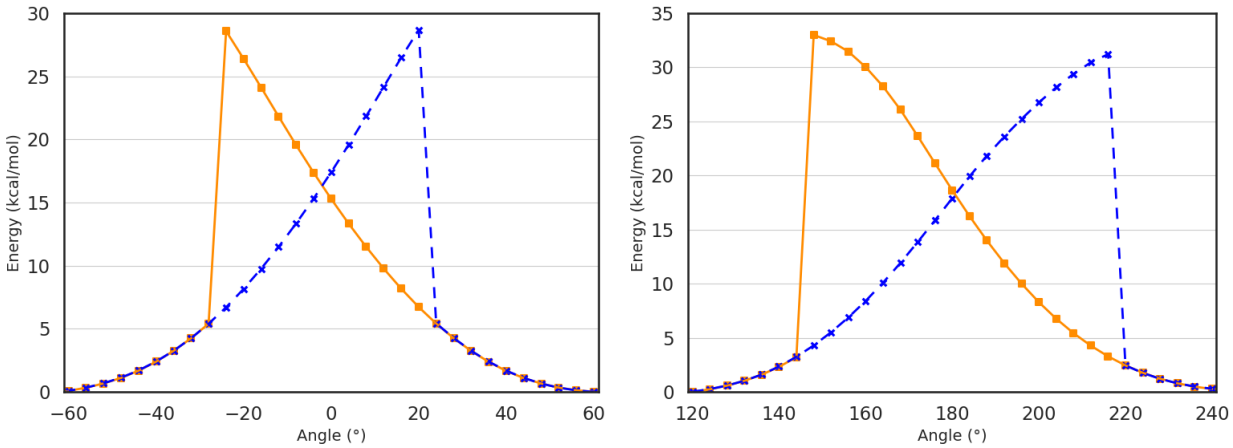


Figure S67. Relaxed scans of the dihedral angle for *(P)*-helicene **9f** in the forward (blue) and reverse (orange) directions.

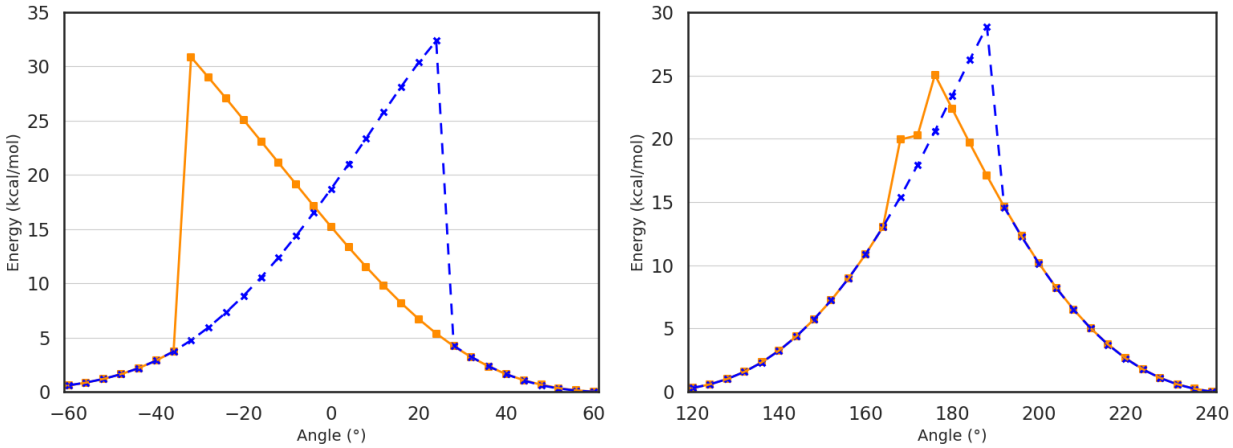


Figure S68. Relaxed scans of the dihedral angle for *(M)*-helicene **9f** in the forward (blue) and reverse (orange) directions.

X-Ray study

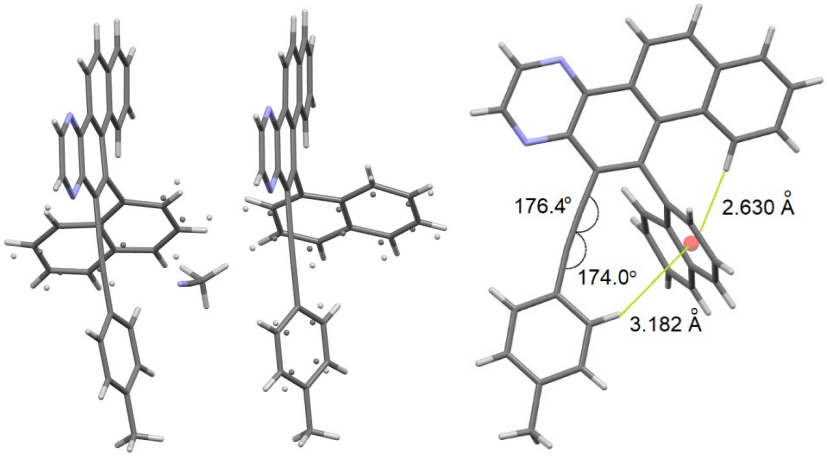


Figure S69. X-Ray structure of compound **8b** (two independent molecules in a crystal unit cell).

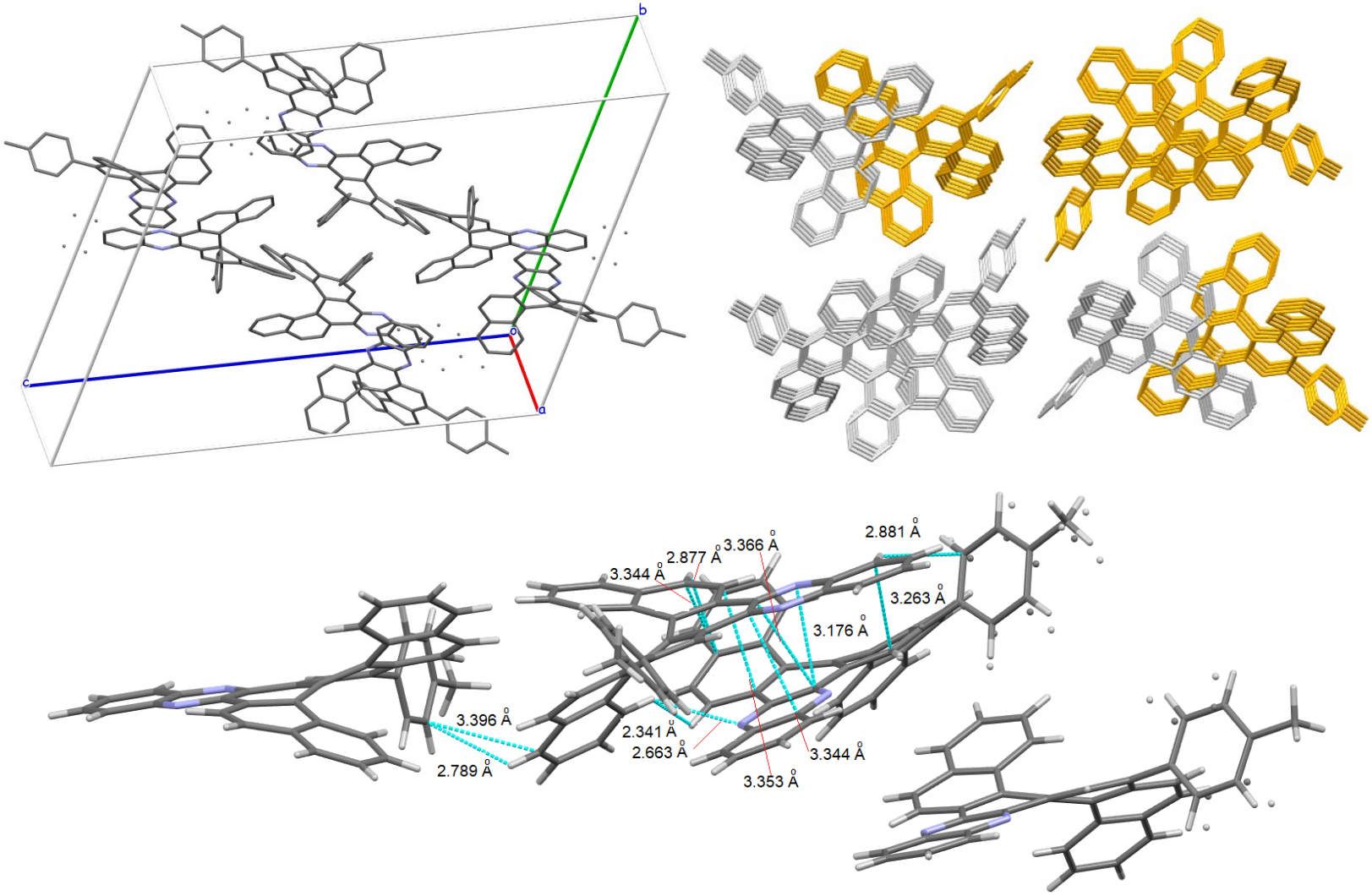


Figure S70. Crystal unit cell (four independent molecules in it), packing (view along *a* axis, molecules are colored by symmetry operation) and short contacts of **9a**.

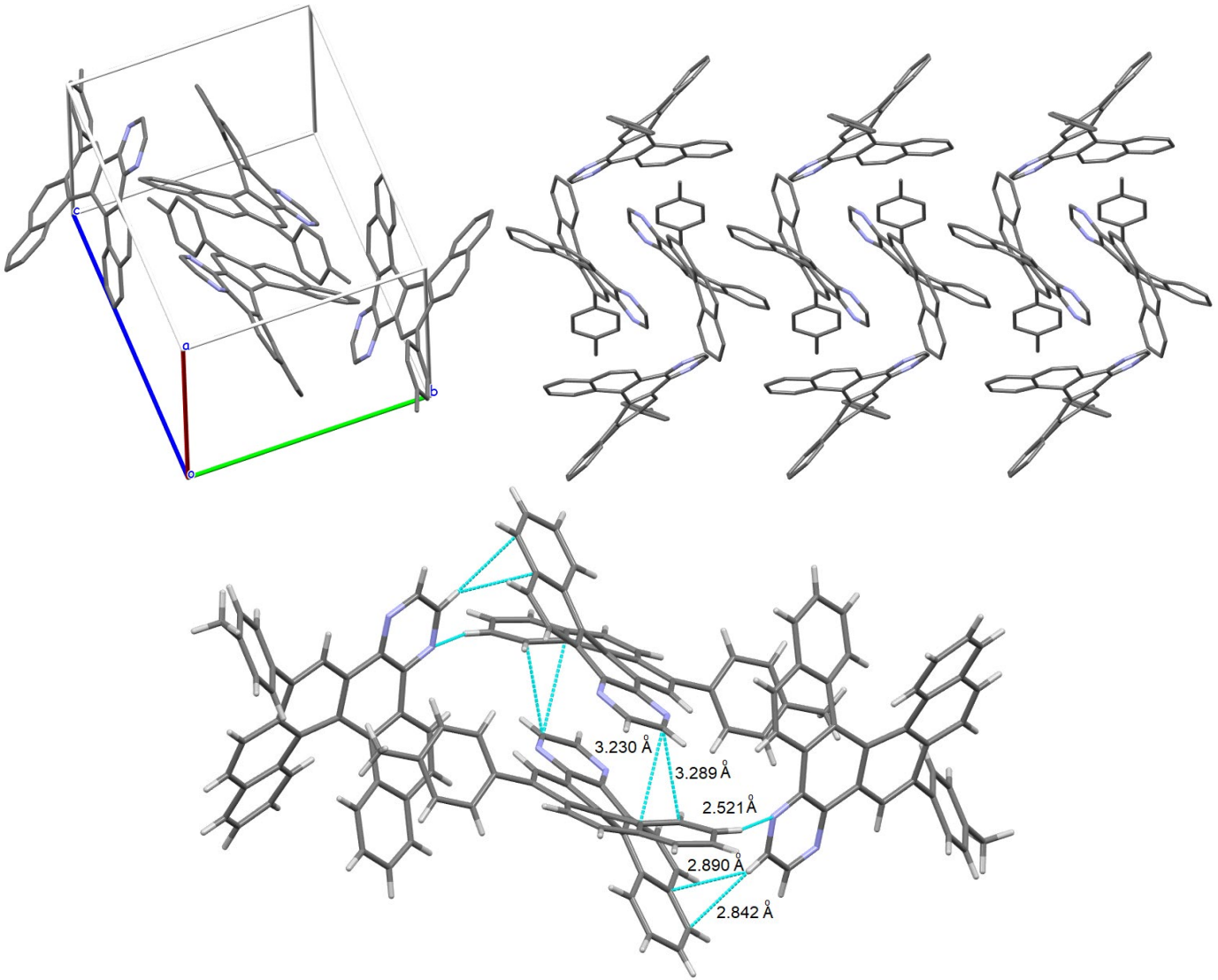


Fig. S71. Crystal unit cell (one independent molecule in it), packing (view along *b* axis) and short contacts of **9b**

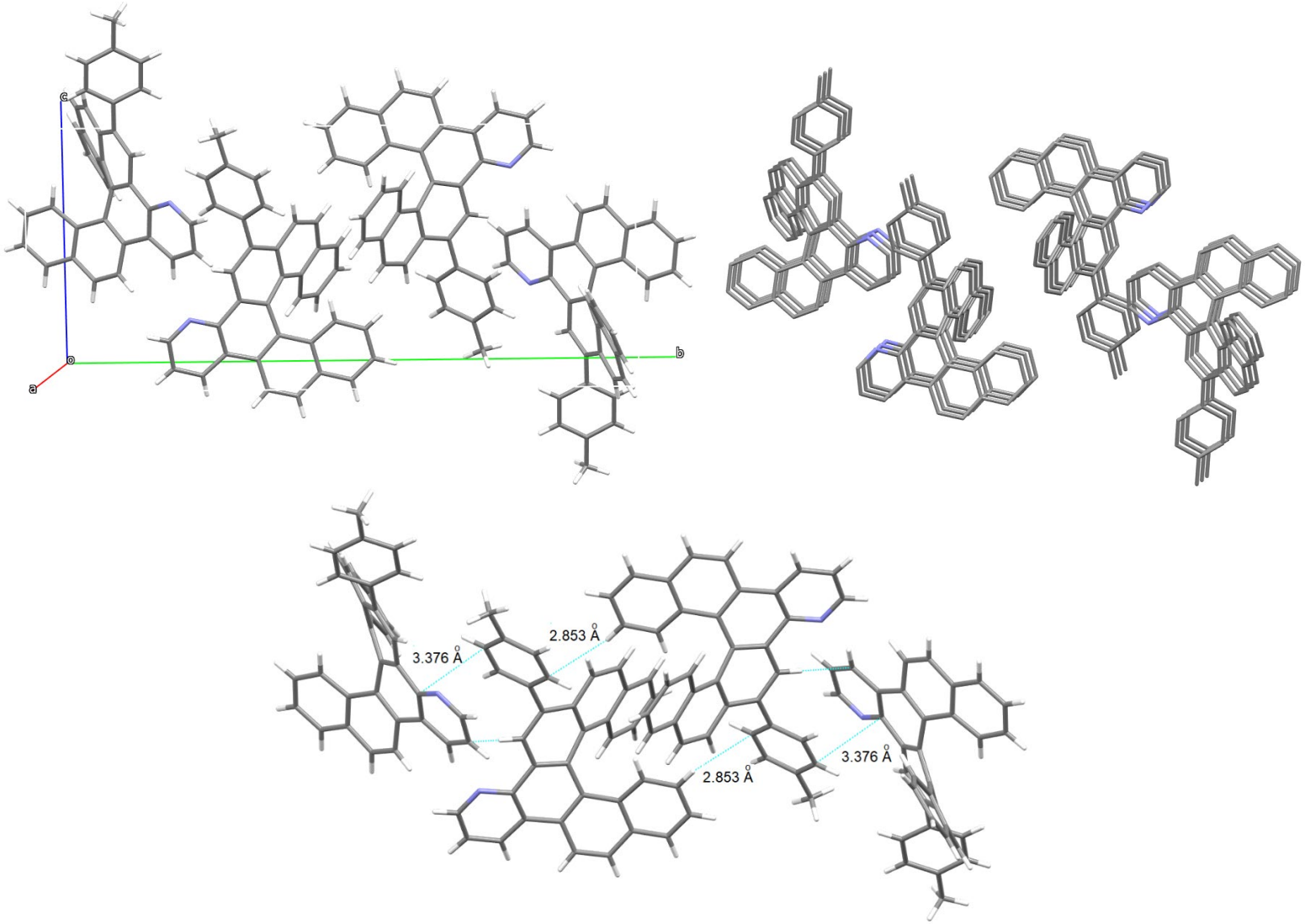


Fig. S72. Crystal unit cell (one independent molecule in it), packing (view along *b* axis, molecules are colored by symmetry operation) and short contacts of **9c**.

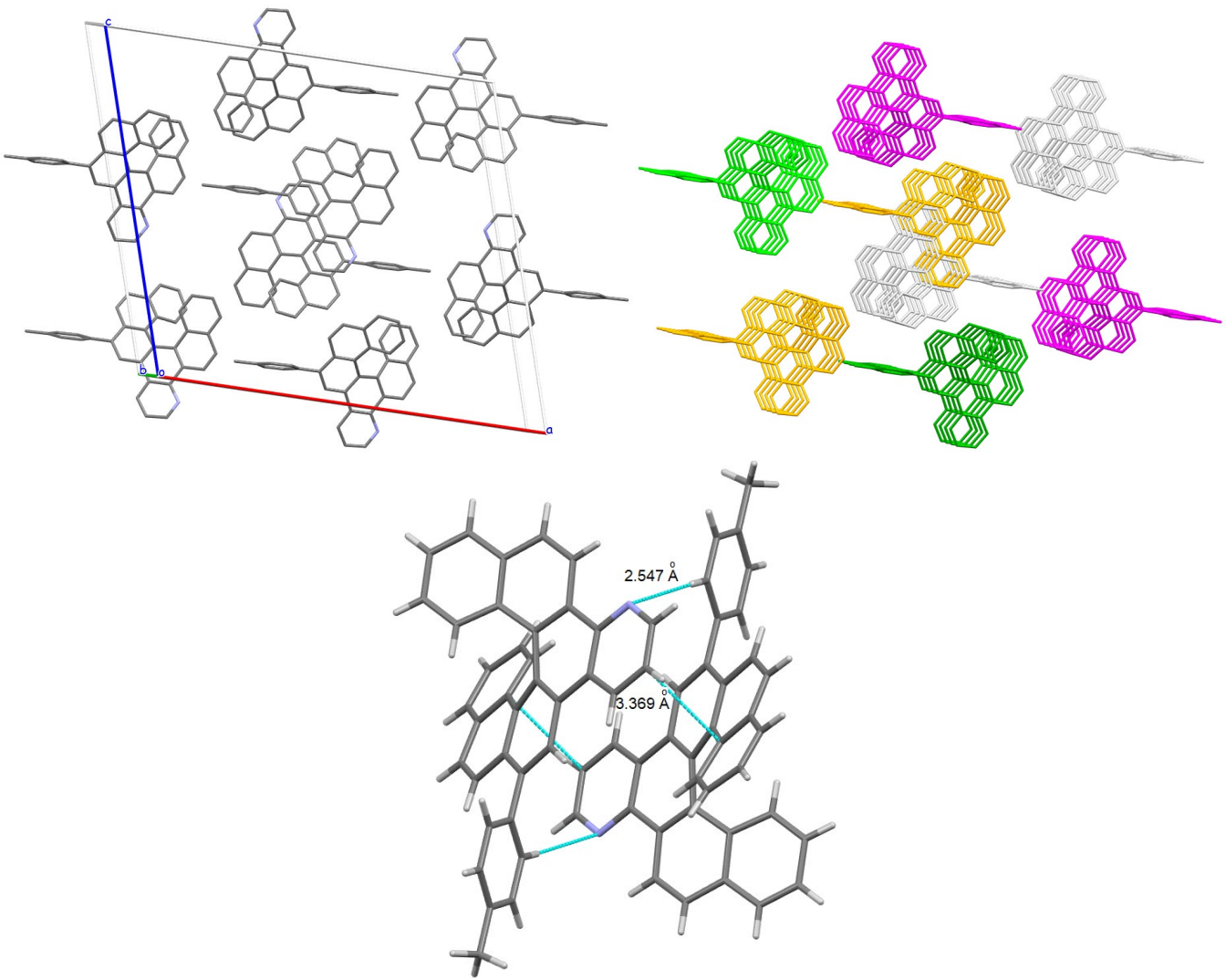


Fig. S73. Crystal unit cell (one independent molecule in it), packing (view along *b* axis, molecules are colored by symmetry operation) and short contacts of **9d**.

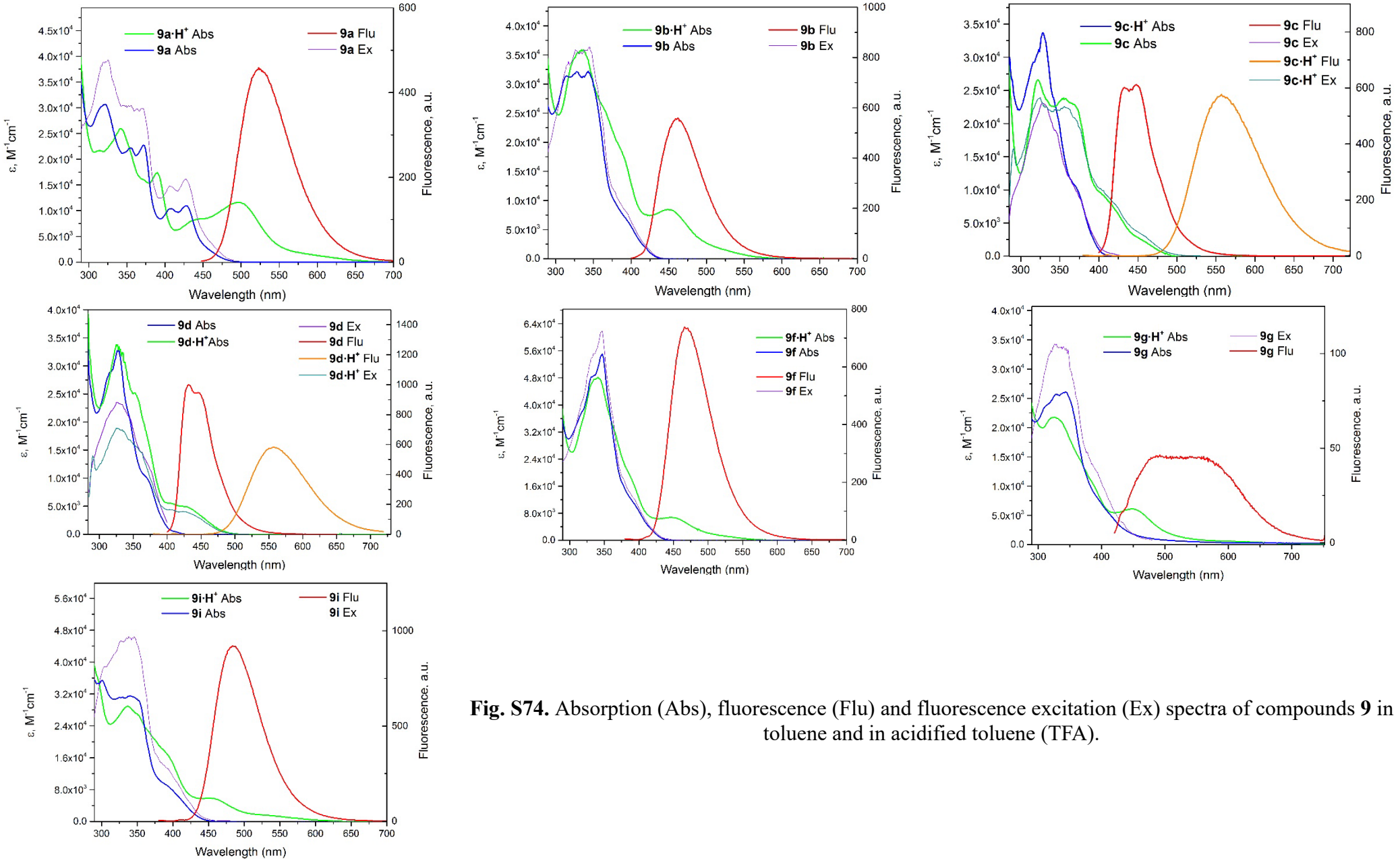
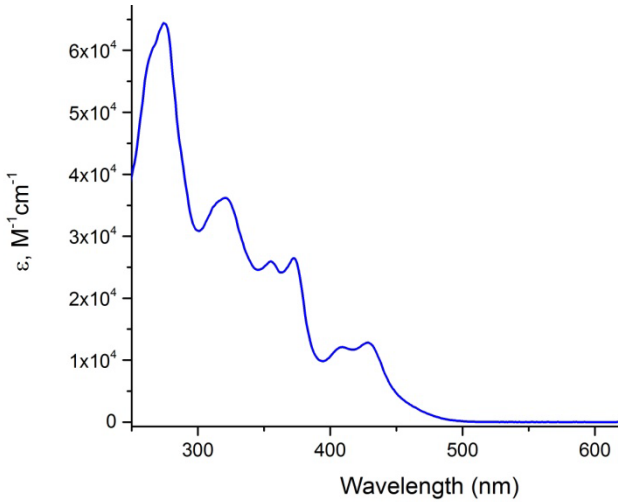
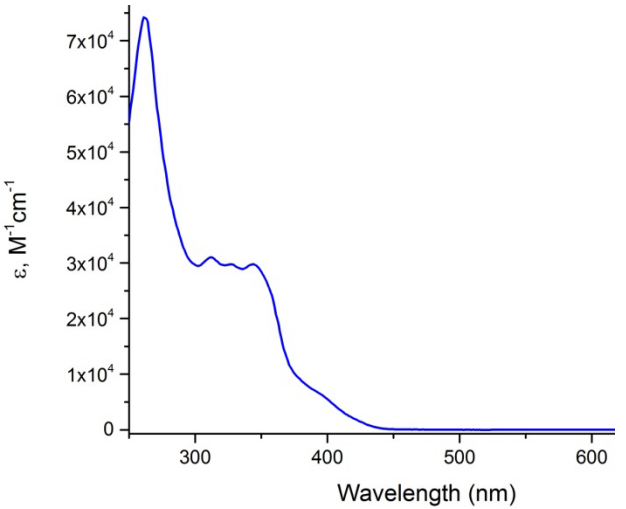


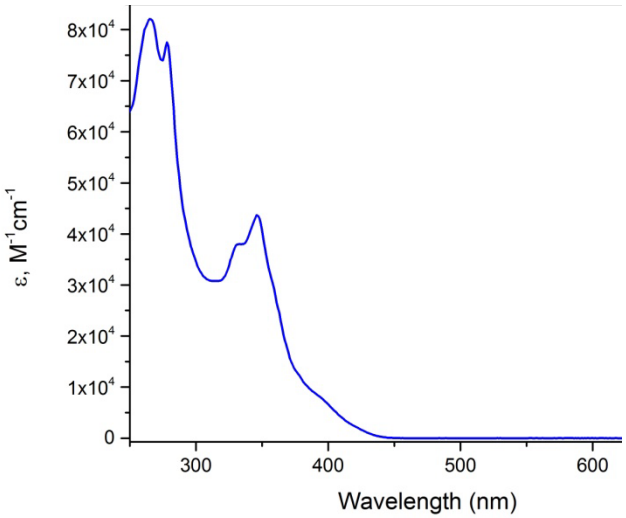
Fig. S74. Absorption (Abs), fluorescence (Flu) and fluorescence excitation (Ex) spectra of compounds **9** in toluene and in acidified toluene (TFA).



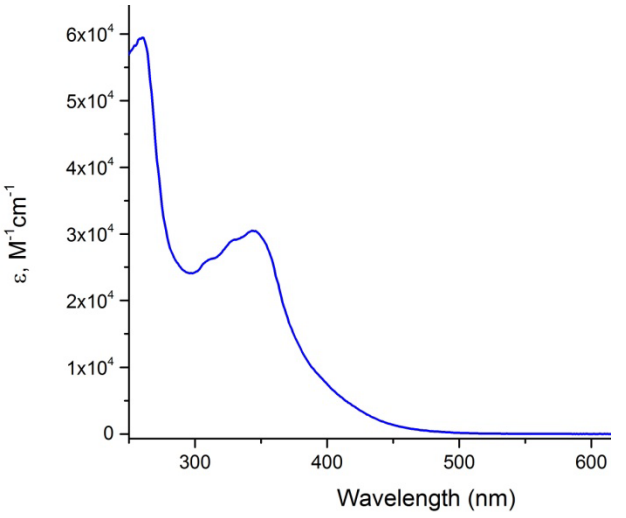
UV-vis spectrum of **9a** in chloroform, λ_{max} nm (ε, M^{-1} cm^{-1}): 274 (63970), 321 (35820), 355 (25550), 372 (26100), 409 (11800), 428 (12534).



UV-vis spectrum of **9b** in chloroform, λ_{max} nm (ε, M^{-1} cm^{-1}): 261 (74220), 312 (30840), 344 (29620), sh 384 (7910).



UV-vis spectrum of **9f** in chloroform, λ_{max} nm (ε, M^{-1} cm^{-1}): 265 (82055), 278 (77497), sh 332 (37634), 346 (43445), sh 360 (27453), sh 380 (10902).



UV-vis spectrum of **9g** in chloroform, λ_{max} nm (ε, M^{-1} cm^{-1}): 260 (59438), 343 (30389), sh 395 (8393).

Fig. S75. UV-vis spectra of compounds **9** in chloroform.

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