Synthesis, Functionalization and Optical Properties of 1,2-Dihydro-1-aza-2-boraphenanthrene and Several Highly Fluorescent Derivatives

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GENERAL EXPERIMENTAL DETAILS

Reagents were acquired from commercial sources and were used without further purification. Dry solvents, where necessary, were dried by a MBRAUN MB-SPS-800 apparatus. In general, reactions were carried out under an argon atmosphere using oven-dried glassware with magnetic stirring and dry solvents. Reactions were monitored by using analytical TLC plates (Merck; silica gel 60 F254, 0.25 mm), and compounds were visualized with UV radiation. Silica gel grade 60 (70-230 mesh, Merck) was used for column chromatography. All melting points were determined in open capillary tubes on a Stuart Scientific SMP3 melting point apparatus (uncorrected). IR spectra were obtained on a Perkin–Elmer FTIR spectrum 2000 spectrophotometer. ^{1}H, ^{13}C and ^{11}B-NMR spectra were recorded on either a Varian Mercury VX-300, Varian Unity 300 or Varian Unity 500 MHz spectrometer at room temperature. Chemical shifts are given in ppm (δ) downfield from TMS, with calibration on the residual protio-solvent used (δ_H = 7.24 ppm and δ_C = 77.0 ppm for $CDCl_3$). ^{11}B-NMR spectra were externally referenced to $BF_3{\cdot}OEt_2$ (δ_B = 0 ppm). Coupling constants (*J*) are in Hertz (Hz) and signals are described as follows: s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet; br, broad; ap, apparent. High-resolution analysis (HRMS) were performed on an Agilent 6210 time of-flight LC/MS.

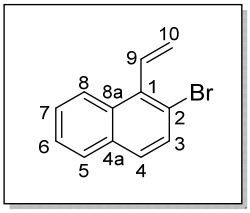
Absorption spectra were recorded in a UV-Vis Uvikon 941 (Kontron Instruments) spectrophotometer. Steady-state fluorescence measurements were carried out by using a PTI Quanta Master spectrofluorimeter equipped with a Xenon flash lamp as a light source, single concave grating monochromators and Glan-Thompson polarizers in the excitation and emission paths. Detection was allowed by a photomultiplier cooled by a Peltier system. Slit widths were selected at 6 nm for both excitation and emission paths and polarizers were fixed at the “magic angle” condition. Right angle geometry and rectangular 10 mm path cells were used for the fluorescence measurements.

Starting material 2-bromo-1-vinylnaphthalene (**7**) was prepared following reported procedures.[1]

[1] Grudzién, K.; Żukowska, K.; Malińska, M.; Woźniak, K.; Barbasiewicz, M. *Chem. Eur. J.* **2014**, *20*, 2819–2828.

EXPERIMENTAL PROCEDURES AND DATA

Synthesis of 2-bromo-1-vinylnaphthalene (7)

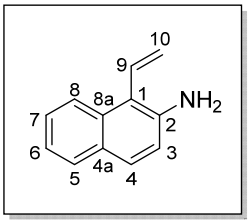


$MePPh_3Br$ (6.25 g, 17.1 mmol, 1.3 equiv.) and *t*-BuOK (2.27 g, 19.8 mmol, 1.5 equiv.) were dissolved in THF (60 mL), and the resulting yellow suspension was stirred at room temperature for 2 h. The reaction mixture was cooled to 0 °C and a solution of 2-bromo-1-naphthaldehyde (3.10 g, 13.2 mmol, 1.0 equiv.) in THF (6 mL) was added dropwise. Cooling bath was removed, and the mixture was stirred at room temperature for 3 h. Then, silica gel was added, and the solvents were removed under reduced pressure. Purification by flash column chromatography (Hexane) gave **7** (2.71 g, 11.6 mmol, 88%) as a colorless oil. Spectroscopy data agree with those reported in the literature.[1]

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.24–8.21 (m, 1H, H-8), 7.82–7.79 (m, 1H, H-5), 7.64 (d, *J* = 8.8 Hz, 1H, H-3), 7.60 (d, *J* = 8.8 Hz, 1H, H-4), 7.52–7.47 (m, 2H, H-6, H-7), 6.98 (dd, J_{trans} = 17.9 Hz, J_{cis} = 11.5 Hz, 1H, H-9), 5.84 (dd, J_{cis} = 11.5 Hz, J_{gem} = 1.7 Hz, 1H, H-10), 5.57 (dd, J_{trans} = 17.9 Hz, J_{gem} = 1.7 Hz, 1H, H-10).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 136.0 (C-1), 134.5 (C-9), 132.6 (C-4a), 132.5 (C-8a), 129.8 (C-3), 128.5 (C-4), 128.2 (C-5), 126.8 (C-7), 125.9 (C-6), 125.8 (C-8), 122.3 (C-10), 120.8 (C-2).

Synthesis of 1-vinylnaphthalen-2-amine (8a)



$Pd[P(o\text{-tol})_3]_2$ (24.0 mg, 0.0323 mmol, 2.5 mol%) and CyPF-P-*t*-Bu (18.0 mg, 0.0323 mmol, 2.5 mol%) were dissolved in dioxane (3 mL) in a Schlenk flask and mixed for 5 min. An oven-dried Biotage microwave vial equipped with a stir bar was charged with aryl halide **7** (300 mg, 1.29 mmol, 1.0 equiv.), ammonium sulfate (258 mg, 1.93 mmol, 1.5 equiv.) and sodium *tert*-butoxide (575 mg, 5.81 mmol, 4.5 equiv.). The vial was sealed with a cap lined with a disposable Teflon septum, evacuated under vacuum and purged with argon three times. Dioxane (10 mL) was added, followed by the solution of the catalyst. The reaction was stirred at 100 °C for 12 h. The reaction mixture was diluted with EtOAc (20 mL) and filtered through a pad of Celite. The filtrate was concentrated under reduced pressure and the remaining residue was purified by flash column chromatography (10% EtOAc/Hexane) to give **8a** (194 mg, 1.15 mmol, 89%) as an orange solid.

M.p.: 35–37 °C.

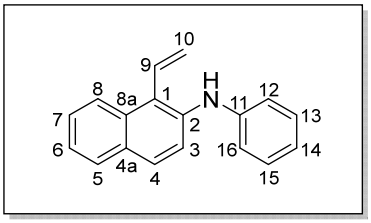
IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3468, 3381 (NH_2), 3054, 1623, 1512, 1471, 1349, 1147, 1000, 929, 814, 748.

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 7.96–7.94 (m, 1H, H-8), 7.78–7.76 (m, 1H, H-5), 7.65 (d, *J* = 8.7 Hz, 1H, H-4), 7.49 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H, H-7), 7.33 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H, H-6), 7.03 (dd, J_{trans} = 18.0 Hz, J_{cis} = 11.4 Hz, 1H, H-9), 6.98 (d, *J* = 8.7 Hz, 1H, H-3), 5.86 (dd, J_{cis} = 11.4 Hz, J_{gem} = 2.1 Hz, 1H, H-10), 5.69 (dd, J_{trans} = 18.0 Hz, J_{gem} = 2.1 Hz, 1H, H-10), 4.10 (br s, 2H, NH_2).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 140.9 (C-2), 132.7 (C-8a), 132.3 (C-9), 128.4 (C-4), 128.1 (C-5), 127.8 (C-4a), 126.3 (C-7), 123.2 (C-8), 122.1 (C-6), 120.9 (C-10), 118.2 (C-3), 115.7 (C-1).

HRMS (APCI) *m/z* calculated for $C_{12}H_{12}N$ $[M+H]^+$: 170.0964. Found $[M+H]^+$: 170.0974.

Synthesis of N-phenyl-1-vinylnaphthalen-2-amine (8b)



An oven-dried Biotage microwave vial equipped with a stir bar was charged with $[PdCl(allyl)]_2$ (7.2 mg, 0.0193 mmol, 0.5 mol%), JohnPhos (11.9 mg, 0.0386 mmol, 1.0 mol%) and sodium *tert*-butoxide (535 mg, 5.40 mmol, 1.4 equiv.). The vial was sealed with a cap lined with a disposable Teflon septum, evacuated under vacuum, and purged with argon three times. Toluene (6.4 mL) was added, followed by aryl halide **7** (900 mg, 3.86 mmol, 1.0 equiv.) and aniline (441 μL, 4.63 mmol, 1.2 equiv.). The reaction was stirred at 80 °C for 24 h. The reaction mixture was diluted with Et_2O (15 mL) and filtered through a pad of Celite. The filtrate was removed under reduced pressure and the remaining residue was purified by flash column chromatography (1% EtOAc/Hexane) to give **8b** (890 mg, 3.63 mmol, 94%) as a yellow solid.

M.p.: 68–70 °C.

IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3414 (NH), 3081, 3043, 1592, 1500, 1417, 1343, 1311, 1273, 995, 930, 812, 739, 692.

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 7.98 (d, *J* = 8.5 Hz, 1H, H-8), 7.74 (dd, *J* = 8.1, 0.5 Hz, 1H, H-5), 7.67 (d, *J* = 8.9 Hz, 1H, H-4), 7.52 (dd, *J* = 8.9, 0.7 Hz, 1H, H-3), 7.45–7.41 (m, 1H, H-7), 7.34–7.30 (m, 1H, H-6), 7.29–7.25 (m, 2H, H-13, H-15), 7.08–7.06 (m, 2H, H-12, H-16), 6.98–6.92 (m, 2H, H-9, H-14), 6.07 (br s, 1H, N*H*), 5.83 (ddd, J_{cis} = 11.4 Hz, J_{gem} = 2.0 Hz, *J* = 0.6 Hz, 1H, H-10), 5.63 (ddd, J_{trans} = 18.1 Hz, J_{gem} = 2.0 Hz, *J* = 0.8 Hz, 1H, H-10).

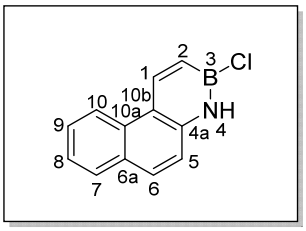
^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 143.4 (C-11), 137.5 (C-2), 132.6 (C-8a), 132.1 (C-9), 129.44 (C-4a**), 129.37 (2C, C-13, C-15), 128.2 (C-5), 128.1 (C-4), 126.4 (C-7), 124.2 (C-8), 123.4 (C-6), 122.3 (C-10), 122.1 (C-1), 121.3 (C-14), 119.0 (C-3), 118.2 (2C, C-12, C-16). **Carbon not observed in ^{13}C-NMR, assigned by gHMBC.

HRMS (APCI) *m/z* calculated for $C_{18}H_{16}N$ $[M+H]^+$: 246.1277. Found $[M+H]^+$: 246.1273.

General procedure for borylative cyclization with boron trichloride

The corresponding amine (1.0 equiv.) was dissolved in anhydrous toluene (0.05 M) in a Schlenk flask, and the resulting solution was cooled to –30 °C. Cold boron trichloride solution (1.0 M in hexanes, 2.0 equiv.) was added dropwise via syringe to the vigorously stirring cold solution of amine in toluene. At the conclusion of the addition, the reaction mixture was allowed to warm to room temperature over one hour, and then it was heated at reflux for 18 hours. At the end of the reaction, the mixture was concentrated under reduced pressure to afford the corresponding B–Cl intermediate as an air- and moisture-sensitive solid, which could be used as is in the next step without further purification.

Synthesis of 2-chloro-1,2-dihydro-1-aza-2-boraphenanthrene



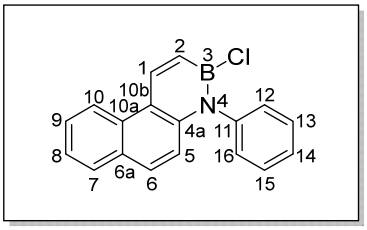
Following the general procedure, amine **8a** (440 mg, 2.60 mmol) was dissolved in toluene (52 mL) followed by addition of boron trichloride solution (5.2 mL, 5.20 mmol) to give 2-chloro-1,2-dihydro-1-aza-2-boraphenanthrene (552 mg, 2.59 mmol, 99%) as a red solid.

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.94 (d, *J* = 11.9 Hz, 1H, H-1), 8.45 (d, *J* = 8.5 Hz, 1H, H-10), 8.04 (br s, 1H, N*H*), 7.86 (d, *J* = 8.0 Hz, 1H, H-7), 7.83 (d, *J* = 8.8 Hz, 1H, H-6), 7.63 (ddd, *J* = 8.5, 6.9, 1.2 Hz, 1H, H-9), 7.49 (ddd, *J* = 8.0, 6.9, 1.0 Hz, 1H, H-8), 7.26 (d, *J* = 8.8 Hz, 1H, H-5), 6.94 (dd, *J* = 11.9, 2.2 Hz, 1H, H-2).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 141.7 (C-1), 138.2 (C-4a), 130.9 (C-10a), 130.3 (C-6), 129.5 (C-6a), 128.8 (C-7), 127.4 (C-9), 127.0 (C-2*), 124.7 (C-8), 121.7 (C-10), 119.0 (C-5), 118.2 (C-10b). *Carbon not observed in ^{13}C-NMR, assigned by gHSQC.

^{11}B-NMR (160 MHz, $CDCl_3$) δ (ppm) 32.70.

Synthesis of 2-chloro-1-phenyl-1,2-dihydro-1-aza-2-boraphenanthrene



Following the general procedure, amine **8b** (245 mg, 1.00 mmol) was dissolved in toluene (20 mL) followed by addition of boron trichloride solution (2.0 mL, 2.00 mmol) to give 2-chloro-1-phenyl-1,2-dihydro-1-aza-2-boraphenanthrene (288 mg, 0.99 mmol, 99%) as a brown solid.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 9.06 (d, *J* = 11.9 Hz, 1H, H-1), 8.56 (d, *J* = 8.5 Hz, 1H, H-10), 7.83 (dd, *J* = 8.0, 1.4 Hz, 1H, H-7), 7.70 (d, *J* = 9.4 Hz, 1H, H-6), 7.66 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H, H-9), 7.61–7.54 (m, 2H, H-13, H-15), 7.53–7.47 (m, 2H, H-8, H-14), 7.25–7.21 (m, 2H, H-12, H-16), 7.08 (d, *J* = 11.9 Hz, 1H, H-2), 6.99 (d, *J* = 9.4 Hz, 1H, H-5).

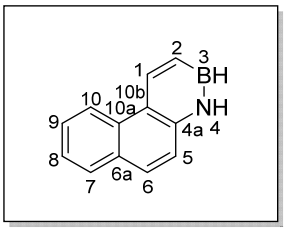
^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 142.6 (C-11), 141.2 (C-4a), 141.0 (C-1), 130.9 (C-10a), 129.8 (2C, C-13, C-15), 129.7 (C-6), 129.1 (C-6a), 128.7 (2C, C-12, C-16), 128.6 (C-7), 127.9 (C-14), 127.4 (C-9), 127.0 (C-2*), 124.9 (C-8), 122.0 (C-10), 118.9 (C-10b**), 118.1 (C-5). *Carbon not observed in ^{13}C-NMR, assigned by gHSQC. **Carbon not observed in ^{13}C-NMR, assigned by gHMBC.

^{11}B-NMR (160 MHz, $CDCl_3$) δ (ppm) 34.12.

General procedure for B–H bond formation with $LiAlH_4$

The corresponding B–Cl intermediate (1.0 equiv.) was dissolved in anhydrous Et_2O (0.05 M) in a Schlenk flask, and the resulting solution was cooled to –30 °C. Cold lithium aluminum hydride solution (1.0 M in Et_2O, 2.0 equiv.) was added dropwise via syringe, and the reaction mixture was allowed to warm to room temperature and stirred for 18 hours. Then, a hydrogen chloride solution (2.0 M in Et_2O, 2.2 equiv.) was added, and the resulting mixture was filtered through a silica gel plug. The filtrate was concentrated under reduced pressure to afford the corresponding B–H products without further purification.

Synthesis of 1,2-dihydro-1-aza-2-boraphenanthrene (6a)



Following the general procedure, 2-chloro-1,2-dihydro-1-aza-2-boraphenanthrene (552 mg, 2.59 mmol) was dissolved in Et_2O (52 mL) followed by addition of lithium aluminum hydride solution (5.2 mL, 5.18 mmol). At the end of the reaction, a hydrogen chloride solution (2.8 mL, 5.70 mmol) was added, to give **6a** (461 mg, 2.57 mmol, 99%) as a white solid.

M.p.: 64–66 °C.

IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3382 (NH), 2964, 2503 (BH), 1623, 1563, 1448, 1263, 1024, 886, 829, 806, 750, 716.

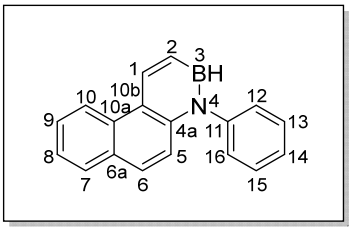
^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 9.04 (d, *J* = 11.7 Hz, 1H, H-1), 8.55 (d, *J* = 8.5 Hz, 1H, H-10), 8.45 (br s, 1H, N*H*), 7.87 (dd, *J* = 8.0, 1.4 Hz, 1H, H-7), 7.83 (d, *J* = 8.8 Hz, 1H, H-6), 7.63 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H, H-9), 7.49 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H, H-8), 7.37 (d, *J* = 8.8 Hz, 1H, H-5), 7.21 (ap dt, *J* = 11.7, 2.2 Hz, 1H, H-2), 5.57–4.72 (br s, 1H, B*H*).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 139.3 (C-1), 138.3 (C-4a), 131.2 (C-10a), 130.2 (C-2*), 129.4 (C-6a), 129.3 (C-6), 128.7 (C-7), 127.0 (C-9), 124.5 (C-8), 121.7 (C-10), 119.8 (C-5), 119.3 (C-10b). *Carbon not observed in ^{13}C-NMR, assigned by gHSQC.

^{11}B-NMR (160 MHz, $CDCl_3$) δ (ppm) 31.60.

HRMS (APCI) *m/z* calculated for $C_{12}H_{11}BN$ $[M+H]^+$: 180.0979. Found $[M+H]^+$: 180.0978.

Synthesis of 1-phenyl-1,2-dihydro-1-aza-2-boraphenanthrene (6b)



Following the general procedure, 2-chloro-1-phenyl-1,2-dihydro-1-aza-2-boraphenanthrene (288 mg, 0.99 mmol) was dissolved in Et_2O (20 mL) followed by addition of lithium aluminum hydride solution (2.0 mL, 1.98 mmol). At the end of the reaction, a hydrogen chloride solution (1.1 mL, 2.18 mmol) was added, to give **6b** (252 mg, 0.98 mmol, 99%) as a yellow solid.

M.p.: 116–118 °C.

IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3034, 2516 (BH), 1595, 1541, 1493, 1427, 1317, 1258, 1201, 875, 819, 747, 698.

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 9.14 (d, *J* = 11.7 Hz, 1H, H-1), 8.63 (d, *J* = 8.5 Hz, 1H, H-10), 7.84 (dd, *J* = 8.0, 1.4 Hz, 1H, H-7), 7.70 (d, *J* = 9.2 Hz, 1H, H-6), 7.64 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H, H-9), 7.54–7.40 (m, 4H, H-8, H-13, H-14, H-15), 7.32–7.28 (m, 2H, H-12, H-16), 7.23 (dd, *J* = 11.7, 2.6 Hz, 1H, H-2), 7.20 (d, *J* = 9.2 Hz, 1H, H-5), 5.84–4.58 (br s, 1H, B*H*).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 146.9 (C-11), 140.4 (C-4a), 139.4 (C-1), 131.2 (C-10a), 129.5 (C-2*), 129.4 (2C, C-13, C-15), 129.1 (C-6a), 128.9 (C-6), 128.5 (C-7), 127.9 (2C, C-12, C-16), 127.1 (2C, C-9, C-14), 124.7 (C-8), 122.1 (C-10), 120.0 (C-10b), 118.1 (C-5). *Carbon not observed in ^{13}C-NMR, assigned by gHSQC.

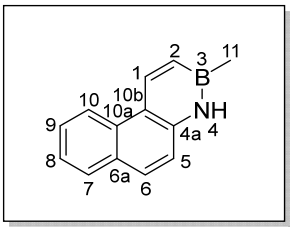
^{11}B-NMR (160 MHz, $CDCl_3$) δ (ppm) 33.78.

HRMS (EI) *m/z* calculated for $C_{18}H_{14}BN$ $[M]^+$: 255.1214. Found $[M]^+$: 255.1220.

General procedure for borylative cyclization with potassium organotrifluoroborates

An oven-dried Biotage microwave vial equipped with a stir bar was charged with the corresponding potassium organotrifluoroborate (1.0 equiv.). The vial was sealed with a cap lined with a disposable Teflon septum, evacuated under vacuum, and purged with argon three times. CMPE (0.5 M) and toluene (0.5 M) were added, followed by the corresponding amine (1.2 equiv.), $SiCl_4$ (1.0 equiv.) and Et_3N (1.5 equiv.) under argon. The reaction was stirred at 80 °C for 24 h. At the end of the reaction, the mixture was cooled to room temperature, diluted with Et_2O and filtered through a silica gel plug. The filtrate was concentrated under reduced pressure and the remaining residue was purified by flash column chromatography (using the eluent indicated in each case) to afford the corresponding 1,2-dihydro-1-aza-2-boraphenanthrenes.

Synthesis of 2-methyl-1,2-dihydro-1-aza-2-boraphenanthrene (6c)



Following the general procedure, potassium methyltrifluoroborate (255 mg, 2.09 mmol) was dissolved in CPME (4.2 mL) and toluene (4.2 mL), followed by addition of amine **8a** (425 mg, 2.51 mmol), $SiCl_4$ (242 μL, 2.09 mmol) and Et_3N (437 μL, 3.14 mmol). Purification by flash column chromatography (5% EtOAc/Hexane) gave **6c** (344 mg, 1.78 mmol, 85%) as a white solid.

M.p.: 70–72 °C.

IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3375 (NH), 2923, 1624, 1566, 1452, 1389, 1325, 1197, 1150, 828, 807, 720.

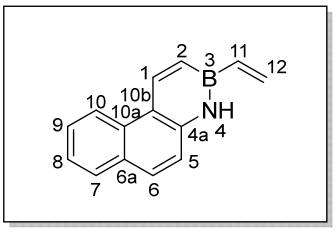
^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.87 (d, *J* = 11.7 Hz, 1H, H-1), 8.50 (d, *J* = 8.4 Hz, 1H, H-10), 7.90 (br s, 1H, N*H*), 7.85–7.83 (m, 1H, H-7), 7.79 (d, *J* = 8.8 Hz, 1H, H-6), 7.60 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H, H-9), 7.44 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H, H-8), 7.31 (d, *J* = 8.8 Hz, 1H, H-5), 6.99 (dd, *J* = 11.7, 2.1 Hz, 1H, H-2), 0.80 (s, 3H, H-11).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 138.5 (C-4a), 138.4 (C-1), 131.3 (C-10a), 130.6 (C-2*), 129.2 (C-6a), 129.0 (C-6), 128.6 (C-7), 126.9 (C-9), 124.0 (C-8), 121.6 (C-10), 119.7 (C-5), 118.1 (C-10b), 2.18 (C-11*). *Carbon not observed in ^{13}C-NMR, assigned by gHSQC.

^{11}B-NMR (160 MHz, $CDCl_3$) δ (ppm) 37.16.

HRMS (APCI) *m/z* calculated for $C_{13}H_{13}BN$ $[M+H]^+$: 194.1136. Found $[M+H]^+$: 194.1130.

Synthesis of 2-vinyl-1,2-dihydro-1-aza-2-boraphenanthrene (6d)



Following the general procedure, potassium vinyltrifluoroborate (56 mg, 0.40 mmol) was dissolved in CPME (0.8 mL) and toluene (0.8 mL), followed by addition of amine **8a** (81 mg, 0.48 mmol), $SiCl_4$ (46 μL, 0.40 mmol) and Et_3N (84 μL, 0.60 mmol). Purification by flash column chromatography (5% EtOAc/Hexane) gave **6d** (56 mg, 0.27 mmol, 69%) as a white solid.

M.p.: 103–105 °C.

IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3371 (NH), 2948, 2917, 1623, 1564, 1452, 1199, 947, 771, 731.

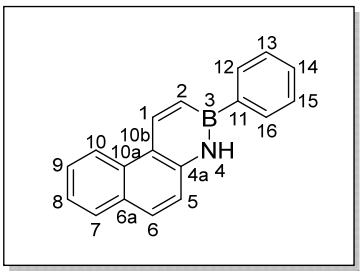
^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.98 (d, *J* = 11.8 Hz, 1H, H-1), 8.52 (d, *J* = 8.5 Hz, 1H, H-10), 8.02 (br s, 1H, N*H*), 7.87–7.85 (m, 1H, H-7), 7.81 (d, *J* = 8.8 Hz, 1H, H-6), 7.62 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H, H-9), 7.46 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H, H-8), 7.34 (d, *J* = 8.8 Hz, 1H, H-5), 7.24 (dd, *J* = 11.8, 2.1 Hz, 1H, H-2), 6.55 (dd, J_{trans} = 19.6 Hz, J_{cis} = 13.3 Hz, 1H, H-11), 6.26 (dd, J_{trans} = 19.6 Hz, J_{gem} = 3.5 Hz, 1H, H-12), 6.05 (dd, J_{cis} = 13.3 Hz, J_{gem} = 3.5 Hz, 1H, H-12).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 139.4 (C-1), 138.3 (C-4a), 131.8 (C-12), 131.5 (C-11*), 131.2 (C-10a), 129.33 (C-6), 129.31 (C-6a), 128.7 (C-7), 127.6 (C-2*), 127.0 (C-9), 124.2 (C-8), 121.7 (C-10), 119.8 (C-5), 119.0 (C-10b). *Carbon not observed in ^{13}C-NMR, assigned by gHSQC.

^{11}B-NMR (160 MHz, $CDCl_3$) δ (ppm) 32.31.

HRMS (APCI) *m/z* calculated for $C_{14}H_{13}BN$ $[M+H]^+$: 206.1136. Found $[M+H]^+$: 206.1128.

Synthesis of 2-phenyl-1,2-dihydro-1-aza-2-boraphenanthrene (6e)



Following the general procedure, potassium phenyltrifluoroborate (569 mg, 2.94 mmol) was dissolved in CPME (5.9 mL) and toluene (5.9 mL), followed by addition of amine **8a** (596 mg, 3.52 mmol), $SiCl_4$ (340 μL, 2.94 mmol) and Et_3N (615 μL, 4.41 mmol). Purification by flash column chromatography (10% EtOAc/Hexane) gave **6e** (660 mg, 2.59 mmol, 88%) as a white solid.

M.p.: 210–212 °C.

IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3379 (NH), 2921, 1432, 1250, 1197, 809, 744, 661.

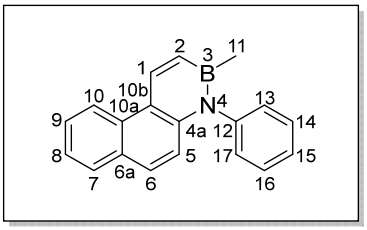
^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 9.08 (d, *J* = 11.8 Hz, 1H, H-1), 8.56 (d, *J* = 8.4 Hz, 1H, H-10), 8.39 (br s, 1H, N*H*), 7.97–7.95 (m, 2H, H-12, H-16), 7.89–7.87 (m, 1H, H-7), 7.86 (d, *J* = 8.7 Hz, 1H, H-6), 7.64 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H, H-9), 7.51–7.44 (m, 6H, H-2, H-5, H-8, H-13, H-14, H-15).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 140.0 (C-1), 138.5 (C-4a), 138.1 (C-11**), 132.6 (2C, C-12, C-16), 131.2 (C-10a), 129.6 (C-14), 129.5 (C-6), 129.4 (C-6a), 128.7 (C-7), 128.5 (C-2**), 128.3 (2C, C-13, C-15), 127.1 (C-9), 124.3 (C-8), 121.8 (C-10), 120.0 (C-5), 119.0 (C-10b). **Carbon not observed in ^{13}C-NMR, assigned by gHMBC.

^{11}B-NMR (160 MHz, $CDCl_3$) δ (ppm) 33.71.

HRMS (APCI) *m/z* calculated for $C_{18}H_{15}BN$ $[M+H]^+$: 256.1292. Found $[M+H]^+$: 256.1285.

Synthesis of 2-methyl-1-phenyl-1,2-dihydro-1-aza-2-boraphenanthrene (6f)



Following the general procedure, potassium methyltrifluoroborate (95 mg, 0.78 mmol) was dissolved in CPME (1.6 mL) and toluene (1.6 mL), followed by addition of amine **8b** (230 mg, 0.94 mmol), $SiCl_4$ (90 μL, 0.78 mmol) and Et_3N (163 μL, 1.17 mmol). Purification by flash column chromatography (Hexane) gave **6f** (143 mg, 0.53 mmol, 68%) as a white solid.

M.p.: 80–82 °C.

IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3053, 2922, 1594, 1543, 1492, 1432, 1395, 1304, 1229, 1205, 806, 754, 698.

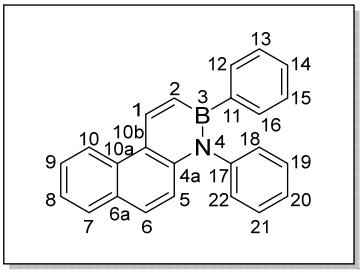
^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.97 (d, *J* = 11.7 Hz, 1H, H-1), 8.59 (d, *J* = 8.5 Hz, 1H, H-10), 7.81-7.79 (m, 1H, H-7), 7.64 (d, *J* = 9.1 Hz, 1H, H-6), 7.61 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H, H-9), 7.55–7.51 (m, 2H, H-14, H-16), 7.46–7.42 (m, 2H, H-8, H-15), 7.18–7.16 (m, 2H, H-13, H-17), 7.07 (d, *J* = 11.7 Hz, 1H, H-2), 6.98 (dd, *J* = 9.1, 0.5 Hz, 1H, H-5), 0.49 (s, 3H, H-11).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 144.8 (C-12), 141.0 (C-4a), 138.0 (C-1), 131.2 (C-10a), 130.8 (C-2*), 129.7 (2C, C-14, C-16), 128.7 (C-6a), 128.5 (3C, C-6*, C-13, C-17), 128.4 (C-7), 127.1 (C-15), 126.9 (C-9), 124.2 (C-8), 121.9 (C-10), 118.7 (C-10b), 118.3 (C-5), 3.8 (C-11*). *Carbon not observed in ^{13}C-NMR, assigned by gHSQC.

^{11}B-NMR (160 MHz, $CDCl_3$) δ (ppm) 38.20.

HRMS (APCI) *m/z* calculated for $C_{19}H_{17}BN$ $[M+H]^+$: 270.1449. Found $[M+H]^+$: 270.1442.

Synthesis of 1,2-diphenyl-1,2-dihydro-1-aza-2-boraphenanthrene (6g)



Following the general procedure, potassium phenyltrifluoroborate (194 mg, 1.00 mmol) was dissolved in CPME (2.0 mL) and toluene (2.0 mL), followed by addition of amine **8b** (294 mg, 1.20 mmol), $SiCl_4$ (116 μL, 1.00 mmol) and Et_3N (209 μL, 1.50 mmol). Purification by flash column chromatography (2% EtOAc/Hexane) gave **6g** (323 mg, 0.98 mmol, 98%) as a yellow solid.

M.p.: 139–141 °C.

IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3048, 2918, 1596, 1542, 1435, 1289, 1205, 1018, 809, 744, 698.

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 9.17 (d, *J* = 11.8 Hz, 1H, H-1), 8.65 (d, *J* = 8.4 Hz, 1H, H-10), 7.86–7.84 (m, 1H, H-7), 7.71 (d, *J* = 9.3 Hz, 1H, H-6), 7.66 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H, H-9), 7.49 (ddd, *J* = 7.9, 6.9, 1.0 Hz, 1H, H-8), 7.44–7.41 (m, 2H, H-19, H-21), 7.38 (tt, *J* = 7.3, 1.4 Hz, 1H, H-20), 7.35 (d, *J* = 11.8 Hz, 1H, H-2), 7.25–7.23 (m, 2H, H-12, H-16), 7.21–7.19 (m, 2H, H-18, H-22), 7.18–7.14 (m, 4H, H-5, H-13, H-14, H-15).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 144.1 (C-17), 140.74 (C-4a), 140.73 (C-11**), 139.4 (C-1), 133.8 (2C, C-12, C-16), 131.1 (C-10a), 131.0 (C-2*), 129.5 (2C, C-18, C-22), 129.4 (2C, C-19, C-21), 129.0 (C-6a), 128.9 (C-6), 128.5 (C-7), 127.5 (C-14), 127.3 (C-20), 127.09 (2C, C-13, C-15), 127.06

(C-9), 124.6 (C-8), 122.1 (C-10), 119.6 (C-10b), 118.4 (C-5). *Carbon not observed in ^{13}C-NMR, assigned by gHSQC. **Carbon not observed in ^{13}C-NMR, assigned by gHMBC.

^{11}B-NMR (160 MHz, $CDCl_3$) δ (ppm) 35.52.

HRMS (EI) *m/z* calculated for $C_{24}H_{18}BN$ $[M]^+$: 331.1527. Found $[M]^+$: 331.1532.

REACTIVITY WITH ORGANOLITHIUM COMPOUNDS

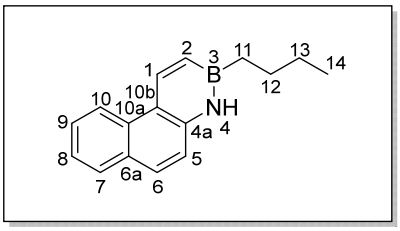
General procedure for the reaction with organolithium compounds

1,2-Dihydro-1-aza-2-boraphenanthrene **6a** (18 mg, 0.10 mmol, 1.0 equiv.) was loaded in a Schlenk flask under argon. Anhydrous THF (1.0 mL) was added, and the resulting solution was cooled to –78 °C. At this temperature the solution was treated with the corresponding organolithium compound (0.20 mmol, 2.0 equiv.). The reaction was stirred at low temperature for 2 h and then, it was allowed to warm to room temperature and stirred for 12 hours. At the end of the reaction, the mixture was quenched with saturated NH_4Cl solution (5 mL) and the aqueous layer was extracted with Et_2O (3 x 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The remaining residue was purified by flash column chromatography (5% EtOAc/Hexane) to afford the corresponding B-substituted products.

Synthesis of 2-methyl-1,2-dihydro-1-aza-2-boraphenanthrene (6c)

Following the general procedure, compound **6a** (18 mg, 0.10 mmol) was treated with methyllithium solution (1.6 M in Et_2O, 125 μL, 0.20 mmol) to give **6c** (18 mg, 0.093 mmol, 93%) as a white solid (spectroscopic data on page S8).

Synthesis of 2-butyl-1,2-dihydro-1-aza-2-boraphenanthrene (6h)



Following the general procedure, compound **6a** (18 mg, 0.10 mmol) was treated with *n*-butyllithium solution (1.6 M in hexanes, 125 μL, 0.20 mmol) to give **6h** (23 mg, 0.098 mmol, 98%) as a white solid.

M.p.: 55–57 °C.

IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3371 (NH), 2956, 2919, 2856, 1624, 1566, 1453, 1197, 1148, 742, 729.

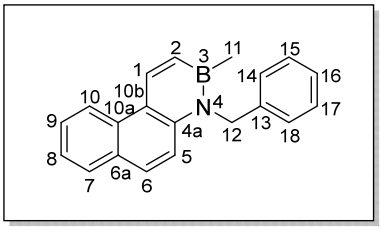
^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.89 (d, *J* = 11.8 Hz, 1H, H-1), 8.50 (d, *J* = 8.5 Hz, 1H, H-10), 7.89 (br s, 1H, N*H*), 7.84 (dd, *J* = 7.9, 1.3 Hz, 1H, H-7), 7.79 (d, *J* = 8.8 Hz, 1H, H-6), 7.59 (ddd, *J* = 8.5, 6.9, 1.3 Hz, 1H, H-9), 7.44 (ddd, *J* = 7.9, 6.9, 0.8 Hz, 1H, H-8), 7.33 (d, *J* = 8.8 Hz, 1H, H-5), 7.01 (dd, *J* = 11.8, 2.0 Hz, 1H, H-2), 1.65–1.59 (m, 2H, H-12), 1.46–1.39 (m, 2H, H-13), 1.32 (t, *J* = 8.0 Hz, 2H, H-11), 0.96 (t, *J* = 7.3 Hz, 3H, H-14).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 138.5 (C-1), 138.4 (C-4a), 131.3 (C-10a), 129.9 (C-2*), 129.2 (C-6a), 129.0 (C-6), 128.6 (C-7), 126.9 (C-9), 124.0 (C-8), 121.6 (C-10), 119.8 (C-5), 118.3 (C-10b), 28.3 (C-12), 25.7 (C-13), 18.4 (C-11*), 14.1 (C-14). *Carbon not observed in ^{13}C-NMR, assigned by gHSQC.

^{11}B-NMR (160 MHz, $CDCl_3$) δ (ppm) 37.80.

HRMS (APCI) *m/z* calculated for $C_{16}H_{19}BN$ $[M+H]^+$: 236.1605. Found $[M+H]^+$: 236.1599.

Synthesis of 1-benzyl-2-methyl-1,2-dihydro-1-aza-2-boraphenanthrene (6i)



2-Methyl-1,2-dihydro-1-aza-2-boraphenanthrene **6c** (29 mg, 0.15 mmol, 1.0 equiv.) was loaded in a Schlenk flask under argon. Anhydrous THF (1.5 mL) was added, and the resulting solution was cooled to –78 °C. At this temperature the solution was treated with *n*-butyllithium solution (1.6 M in hexanes, 94 μL, 0.15 mmol, 1.0 equiv.) and the reaction was stirred at low temperature for 2 h before addition of benzyl bromide (91 μL, 0.75 mmol, 5.0 equiv.). The mixture was stirred at –78 °C for further 2 h and then, it was allowed to warm to room temperature and stirred for 12 hours. At the end of the reaction, the mixture was quenched with saturated NH_4Cl solution (5 mL) and the aqueous layer was extracted with Et_2O (3 x 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The remaining residue was purified by flash column chromatography (2% EtOAc/Hexane) to afford **6i** (21 mg, 0.074 mmol, 49%) as a white solid.

M.p.: 76–78 °C.

IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3027, 2920, 1601, 1547, 1495, 1453, 1029, 882, 801, 749, 697.

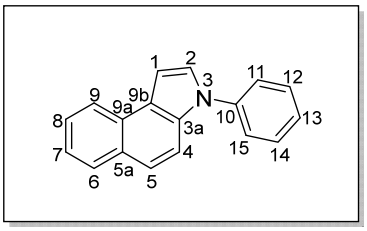
^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.96 (d, *J* = 11.7 Hz, 1H, H-1), 8.57 (d, *J* = 8.5 Hz, 1H, H-10), 7.79–7.77 (m, 1H, H-7), 7.71 (d, *J* = 9.3 Hz, 1H, H-6), 7.59 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H, H-9), 7.53 (d, *J* = 9.3 Hz, 1H, H-5), 7.42 (ddd, *J* = 8.0, 6.9, 1.0 Hz, 1H, H-8), 7.28–7.25 (m, 2H, H-15, H-17), 7.22–7.19 (m, 1H, H-16), 7.11–7.09 (m, 2H, H-14, H-18), 7.07 (d, *J* = 11.7 Hz, 1H, H-2), 5.44 (s, 2H, H-12), 0.88 (s, 3H, H-11).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 140.2 (C-4a), 138.6 (C-13), 138.1 (C-1), 131.7 (C-2*), 131.5 (C-10a), 129.0 (C-6), 128.8 (2C, C-15, C-17), 128.6 (C-6a), 128.3 (C-7), 126.9 (C-16), 126.8 (C-9), 125.8 (2C, C-14, C-18), 124.2 (C-8), 121.9 (C-10), 120.2 (C-10b), 116.9 (C-5), 51.5 (C-12), 3.6 (C-11*). *Carbon not observed in ^{13}C-NMR, assigned by gHSQC.

^{11}B-NMR (160 MHz, $CDCl_3$) δ (ppm) 39.02.

HRMS (APCI) *m/z* calculated for $C_{20}H_{19}BN$ $[M+H]^+$: 284.1605. Found $[M+H]^+$: 284.1601.

General procedure for the synthesis of 3-phenyl-3H-benzo[e]indole (9)



1,2-dihydro-1-aza-2-boraphenanthrene derivative **6f** (27 mg, 0.10 mmol, 1.0 equiv.) or **6g** (33 mg, 0.10 mmol, 1.0 equiv.) were loaded in a Schlenk flask under argon. Anhydrous THF (1.0 mL) was added, and the resulting solution was cooled to –78 °C. At this temperature the solution was treated with *n*-butyllithium solution (1.6 M in hexanes, 125 μL, 0.20 mmol, 2.0 equiv.) and the reaction was stirred at low temperature for 1 h before addition of propanal (149 μL, 2.0 mmol, 20 equiv.). The mixture was stirred at –78 °C for further 1 h and then, it was allowed to warm to room temperature and stirred for 12 hours. At the end of the reaction, the

mixture was quenched with saturated NH_4Cl solution (5 mL) and the aqueous layer was extracted with Et_2O (3 x 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The remaining residue was purified by flash column chromatography (2% EtOAc/Hexane) to afford **9** (14 mg, 0.058 mmol, 58% for **6f**; 12 mg, 0.049 mmol, 49% for **6g**) as a yellow solid.

M.p.: 68–70 °C.

IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3053, 2919, 1598, 1502, 1390, 1188, 924, 800, 745, 701.

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.27 (dd, *J* = 8.1, 1.2 Hz, 1H, H-9), 7.90 (dd, *J* = 8.1, 1.2 Hz, 1H, H-6), 7.65 (d, *J* = 9.0 Hz, 1H, H-4), 7.60 (d, *J* = 9.0 Hz, 1H, H-5), 7.57 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H, H-8), 7.56–7.52 (m, 4H, H-11, H-12, H-14, H-15), 7.43 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H, H-7), 7.42–7.38 (m, 2H, H-2, H-13), 7.21 (d, *J* = 3.1 Hz, 1H, H-1).

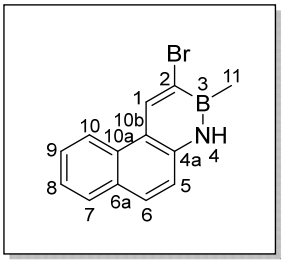
^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 139.7 (C-10), 132.4 (C-3a), 129.6 (2C, C-12, C-14), 129.3 (C-5a), 128.5 (C-6), 128.3 (C-9a), 126.9 (C-13), 126.2 (C-2), 125.9 (C-8), 124.8 (2C, C-11, C-15), 124.3 (C-9b), 123.6 (C-7), 123.2 (C-5), 123.0 (C-9), 112.1 (C-4), 102.5 (C-1).

HRMS (APCI) *m/z* calculated for $C_{18}H_{14}N$ $[M+H]^+$: 244.1121. Found $[M+H]^+$: 244.1113.

General procedure for the bromination of 1,2-dihydro-1-aza-2-boraphenanthrenes

The corresponding 1,2-dihydro-1-aza-2-boraphenanthrene (1.0 equiv.) was loaded in a Schlenk flask under argon. Anhydrous CH_2Cl_2 (0.1 M) was added, and the resulting solution was cooled to 0 °C. A recently prepared bromine solution (0.2 M in CH_2Cl_2, 1.1 equiv.) was added under argon at a rate of 1.1 mmol/h. After the addition, the reaction mixture was slowly warmed to room temperature. The reaction was monitored by TLC, and when it was complete (usually after stirring at r.t. for 1 hour), the mixture was concentrated under reduced pressure. The remaining residue was purified by flash column chromatography (using the eluent indicated in each case) to provide the desired 3-bromo-1,2-dihydro-1-aza-2-boraphenanthrene.

Synthesis of 3-bromo-1,2-dihydro-1-aza-2-boraphenanthrene (10a)



Following the general procedure, compound **6c** (19 mg, 0.10 mmol) was dissolved in CH_2Cl_2 (1.0 mL), followed by addition of bromine solution (550 μL, 0.11 mmol). Purification by flash column chromatography (5% EtOAc/Hexane) gave **10a** (27 mg, 0.099 mmol, 99%) as a white solid.

M.p.: 174–176 °C.

IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3342 (NH), 1564, 1454, 1408, 1283, 1219, 904, 815, 746.

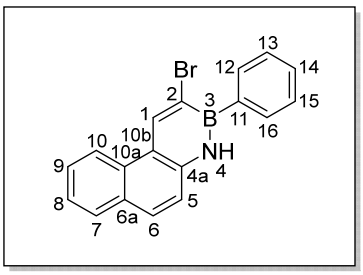
^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 9.11 (s, 1H, H-1), 8.39 (d, *J* = 8.4 Hz, 1H, H-10), 7.96 (br s, 1H, N*H*), 7.85–7.83 (m, 1H, H-7), 7.81 (d, *J* = 8.8 Hz, 1H, H-6), 7.61 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H, H-9), 7.46 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H, H-8), 7.28 (d, *J* = 8.8 Hz, 1H, H-5), 0.89 (s, 3H, H-11).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 139.6 (C-1), 137.6 (C-4a), 130.8 (C-2**), 130.2 (C10a), 129.6 (C-6), 129.2 (C-6a), 128.7 (C-7), 127.3 (C-9), 124.6 (C-8), 121.5 (C-10), 119.2 (C-5), 118.3 (C-10b), 2.4 (C-11*). *Carbon not observed in ^{13}C-NMR, assigned by gHSQC. **Carbon not observed in ^{13}C-NMR, assigned by gHMBC.

^{11}B-NMR (160 MHz, $CDCl_3$) δ (ppm) 36.83.

HRMS (APCI) *m/z* calculated for $C_{13}H_{12}BBrN$ $[M+H]^+$: 272.0241. Found $[M+H]^+$: 272.0238.

Synthesis of 3-bromo-2-phenyl-1,2-dihydro-1-aza-2-boraphenanthrene (10b)



Following the general procedure, compound **6e** (281 mg, 1.10 mmol) was dissolved in CH_2Cl_2 (11 mL), followed by addition of bromine solution (6.1 mL, 1.21 mmol). Purification by flash column chromatography (10% EtOAc/Hexane) gave **10b** (356 mg, 1.07 mmol, 97%) as a white solid.

M.p.: 158–160 °C.

IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3365 (NH), 3049, 1557, 1407, 1018, 904, 816, 725.

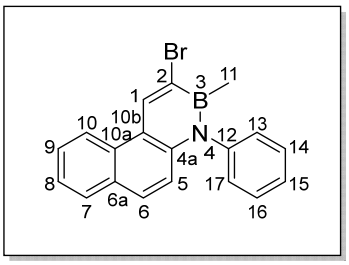
^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 9.33 (s, 1H, H-1), 8.45 (d, *J* = 8.4 Hz, 1H, H-10), 8.25 (br s, 1H, N*H*), 7.95–7.94 (m, 2H, H-12, H-16), 7.88–7.86 (m, 2H, H-6, H-7), 7.65 (ap t, *J* = 7.7 Hz, 1H, H-9), 7.52–7.45 (m, 4H, H-8, H-13, H-14, H-15), 7.35 (d, *J* = 8.8 Hz, 1H, H-5).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 142.1 (C-1), 138.1 (C-11**), 137.8 (C-4a), 133.3 (2C, C-12, C-16), 130.15 (C-6), 130.06 (C-10a), 129.5 (C-6a), 129.4 (C-14), 128.8 (C-7), 127.9 (2C, C-13, C-15), 127.48 (C-9), 127.45 (C-2**), 124.9 (C-8), 121.7 (C-10), 119.2 (C-5), 118.7 (C-10b). **Carbon not observed in ^{13}C-NMR, assigned by gHMBC.

^{11}B-NMR (160 MHz, $CDCl_3$) δ (ppm) 33.29.

HRMS (EI) *m/z* calculated for $C_{18}H_{13}BBrN$ $[M]^+$: 333.0319. Found $[M]^+$: 333.0321.

Synthesis of 3-bromo-2-methyl-1-phenyl-1,2-dihydro-1-aza-2-boraphenanthrene (10c)



Following the general procedure, compound **6f** (27 mg, 0.10 mmol) was dissolved in CH_2Cl_2 (1.0 mL), followed by addition of bromine solution (550 μL, 0.11 mmol). Purification by flash column chromatography (Hexane) gave **10c** (34 mg, 0.098 mmol, 98%) as a white solid.

M.p.: 124–126 °C.

IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3062, 2917, 1595, 1537, 1492, 1334, 1301, 813, 745, 702, 607.

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 9.27 (s, 1H, H-1), 8.50 (d, *J* = 8.6 Hz, 1H, H-10), 7.82–7.80 (m, 1H, H-7), 7.66 (d, *J* = 9.3 Hz, 1H, H-6), 7.64 (ddd, *J* = 8.6, 6.9, 1.4 Hz, 1H, H-9), 7.57–7.53 (m, 2H,

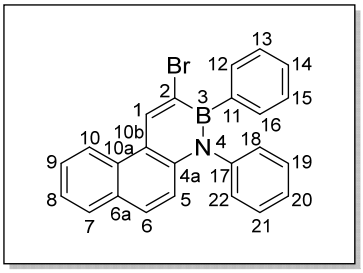
H-14, H-16), 7.49–7.45 (m, 2H, H-8, H-15), 7.17–7.14 (m, 2H, H-13, H-17), 6.91 (d, *J* = 9.3 Hz, 1H, H-5), 0.63 (s, 3H, H-11).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 144.5 (C-12), 140.3 (C-4a), 139.4 (C-1), 130.8 (C-2**), 130.2 (C-10a), 129.9 (2C, C-14, C-16), 129.0 (C-6), 128.9 (C-6a), 128.5 (C-7), 128.2 (2C, C-13, C-17), 127.5 (C-15), 127.3 (C-9), 124.8 (C-8), 121.8 (C-10), 118.6 (C-10b), 118.2 (C-5), 3.8 (C-11*). *Carbon not observed in ^{13}C-NMR, assigned by gHSQC. **Carbon not observed in ^{13}C-NMR, assigned by gHMBC.

^{11}B-NMR (160 MHz, $CDCl_3$) δ (ppm) 37.76.

HRMS (APCI) *m/z* calculated for $C_{19}H_{16}BBrN$ $[M+H]^+$: 348.0554. Found $[M+H]^+$: 348.0552.

Synthesis of 3-bromo-1,2-diphenyl-1,2-dihydro-1-aza-2-boraphenanthrene (10d)



Following the general procedure, compound **6g** (33 mg, 0.10 mmol) was dissolved in CH_2Cl_2 (1.0 mL), followed by addition of bromine solution (550 μL, 0.11 mmol). Purification by flash column chromatography (3% EtOAc/Hexane) gave **10d** (34 mg, 0.083 mmol, 83%) as a white solid.

M.p.: 68–70 °C.

IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 2919, 1593, 1535, 1491, 1334, 1297, 1025, 814, 747.

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 9.49 (s, 1H, H-1), 8.56 (d, *J* = 8.4 Hz, 1H, H-10), 7.86–7.84 (m, 1H, H-7), 7.72 (d, *J* = 9.3 Hz, 1H, H-6), 7.68 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H, H-9), 7.53 (ddd, *J* = 8.0, 6.9, 1.0 Hz, 1H, H-8), 7.35–7.31 (m, 2H, H-19, H-21), 7.28 (tt, *J* = 7.4, 1.3 Hz, 1H, H-20), 7.26–7.22 (m, 2H, H-12, H-16), 7.17–7.14 (m, 3H, H-13, H-14, H-15), 7.10–7.08 (m, 2H, H-18, H-22), 7.03 (d, *J* = 9.3 Hz, 1H, H-5).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 143.7 (C-17), 141.3 (C-1), 140.1 (C-4a), 139.0 (C-11**), 132.8 (2C, C-12, C-16), 130.1 (C-10a), 129.43 (C-6), 129.38 (C-2**), 129.2 (C-6a), 129.1 (2C, C-19, C-21), 129.0 (2C, C-18, C-22), 128.6 (C-7), 127.5 (C-9), 127.4 (C-20), 127.2 (C-14), 126.8 (2C, C-13, C-15), 125.2 (C-8), 122.0 (C-10), 119.4 (C-10b), 118.3 (C-5). **Carbon not observed in ^{13}C-NMR, assigned by gHMBC.

^{11}B-NMR (160 MHz, $CDCl_3$) δ (ppm) 34.78.

HRMS (EI) *m/z* calculated for $C_{24}H_{17}BBrN$ $[M]^+$: 409.0632. Found $[M]^+$: 409.0623.

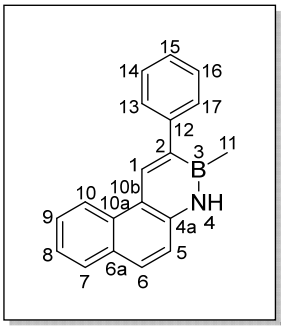
PALLADIUM-CATALYZED CROSS-COUPLING REACTIONS

General procedure for the Suzuki reaction

In an oven-dried Biotage microwave vial equipped with a stir bar the corresponding aryl bromide (0.15 mmol, 1.0 equiv.) and phenylboronic acid (27 mg, 0.21 mmol, 1.4 equiv.) were dissolved in toluene (0.6 mL) and methanol (0.2 mL). The resulting solution was treated with a suspension of sodium carbonate (375 mg) in distilled water (1.5 mL) before addition of $Pd(PPh_3)_4$ (8.8 mg, 0.0075 mmol, 5.0 mol%). The vial was sealed with a cap lined with a disposable Teflon septum

and the reaction was stirred at 70 °C for 12 hours. At the end of the reaction, the mixture was quenched with saturated NaCl solution (5 mL) and the aqueous layer was extracted with EtOAc (3 x 5 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure. The remaining residue was purified by flash column chromatography (5% EtOAc/Hexane) to afford the corresponding coupled products.

Synthesis of 2-methyl-3-phenyl-1,2-dihydro-1-aza-2-boraphenanthrene (11a)



Following the general procedure, aryl bromide **10a** (41 mg, 0.15 mmol) gave **11a** (30 mg, 0.11 mmol, 74%) as a white solid.

M.p.: 120–122 °C.

IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3370 (NH), 3053, 2925, 1625, 1564, 1455, 1407, 1271, 814, 766, 701.

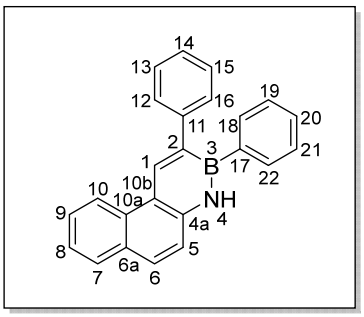
^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.79 (s, 1H, H-1), 8.55 (d, *J* = 8.4 Hz, 1H, H-10), 8.05 (br s, 1H, N*H*), 7.87–7.85 (m, 1H, H-7), 7.81 (d, *J* = 8.8 Hz, 1H, H-6), 7.60 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H, H-9), 7.52–7.49 (m, 2H, H-13, H-17), 7.47–7.42 (m, 3H, H-8, H-14, H-16), 7.36 (d, *J* = 8.8 Hz, 1H, H-5), 7.33–7.30 (m, 1H, H-15), 0.89 (s, 3H, H-11).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 145.5 (C-12), 144.3 (C-2**), 137.9 (C-4a), 136.4 (C-1), 131.3 (C-10a), 129.3 (C-6a), 129.2 (C-6), 128.7 (C-7), 128.4 (2C, C-13, C-17), 128.3 (2C, C-14, C-16), 127.0 (C-9), 126.0 (C-15), 124.2 (C-8), 121.7 (C-10), 119.2 (C-5), 118.2 (C-10b), 2.6 (C-11*). *Carbon not observed in ^{13}C-NMR, assigned by gHSQC. **Carbon not observed in ^{13}C-NMR, assigned by gHMBC.

^{11}B-NMR (160 MHz, $CDCl_3$) δ (ppm) 37.28.

HRMS (APCI) *m/z* calculated for $C_{19}H_{17}BN$ $[M+H]^+$: 270.1449. Found $[M+H]^+$: 270.1444.

Synthesis of 2,3-diphenyl-1,2-dihydro-1-aza-2-boraphenanthrene (11b)



Following the general procedure, aryl bromide **10b** (50 mg, 0.15 mmol) gave **11b** (42 mg, 0.13 mmol, 85%) as a light yellow solid.

M.p.: 104–106 °C.

IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3373 (NH), 3051, 3024, 1562, 1450, 1410, 1266, 1200, 1015, 816, 701.

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.96 (s, 1H, H-1), 8.60 (d, *J* = 8.5 Hz, 1H, H-10), 8.32 (br s, 1H, N*H*), 7.89 (d, *J* = 8.0 Hz, 1H, H-7), 7.87 (d, *J* = 8.8 Hz, 1H, H-6), 7.64 (ddd, *J* = 8.5, 7.0, 1.1 Hz, 1H, H-9), 7.52–7.48 (m, 3H, H-8, H-18, H-22), 7.44 (d, *J* = 8.8 Hz, 1H, H-5), 7.41–7.39 (m, 2H, H-12, H-16), 7.36–7.30 (m, 5H, H-13, H-15, H-19, H-20, H-21), 7.29–7.26 (m, 1H, H-14).

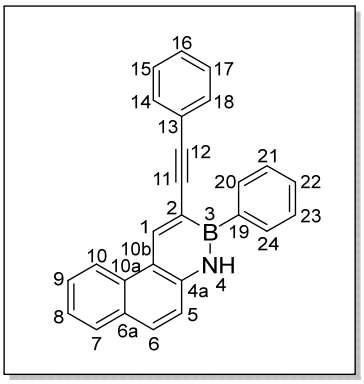
^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 144.8 (C-11), 143.3 (C-2**), 139.8 (C-17**), 138.5 (C-1), 138.0 (C-4a), 133.3 (2C, C-18, C-22), 131.2 (C-10a), 129.7 (C-6), 129.6 (C-6a), 128.9 (2C, C-12, C-16), 128.8 (C-20), 128.5 (C-7), 128.1 (2C, C-13, C-15), 127.8 (2C, C-19, C-21), 127.1 (C-9), 126.1

(C-14), 124.5 (C-8), 121.8 (C-10), 119.4 (C-5), 118.7 (C-10b). **Carbon not observed in ^{13}C-NMR, assigned by gHMBC.

^{11}B-NMR (160 MHz, $CDCl_3$) δ (ppm) 34.49.

HRMS (EI) *m/z* calculated for $C_{24}H_{18}BN$ $[M]^+$: 331.1527. Found $[M]^+$: 331.1530.

Synthesis of 2-phenyl-3-(phenylethynyl)-1,2-dihydro-1-aza-2-boraphenanthrene (12)



An oven-dried Biotage microwave vial equipped with a stir bar was charged with $PdCl_2(PPh_3)_2$ (5.3 mg, 0.0075 mmol, 5 mol%), CuI (1.4 mg, 0.0075 mmol, 5 mol%) and aryl bromide **10b** (50 mg, 0.15 mmol, 1.0 equiv.). The vial was sealed with a cap lined with a disposable Teflon septum, evacuated under vacuum, and purged with argon three times. Anhydrous DMF (1.5 mL) was added, followed by phenylacetylene (50 μL, 0.45 mmol, 3.0 equiv.) and Et_3N (63 μL, 0.45 mmol, 3.0 equiv.) under argon. The reaction was stirred at 80 °C for 24 h. At the end of the reaction, the mixture was quenched with saturated NaCl solution (10 mL) and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure. The remaining residue was purified by flash column chromatography (30% CH_2Cl_2/Hexane) to afford **12** (31 mg, 0.087 mmol, 58%) as a yellow solid.

M.p.: 148–150 °C.

IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3375 (NH), 3050, 2197 (C≡C), 1557, 1489, 1448, 1409, 1258, 1009, 815, 755, 691.

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 9.28 (s, 1H, H-1), 8.59 (d, *J* = 8.4 Hz, 1H, H-10), 8.41 (br s, 1H, N*H*), 8.19–8.18 (m, 2H, H-20, H-24), 7.89–7.87 (m, 2H, H-6, H-7), 7.67 (ddd, *J* = 8.4, 7.0, 1.1 Hz, 1H, H-9), 7.54–7.48 (m, 6H, H-8, H-14, H-18, H-21, H-22, H-23), 7.43 (d, *J* = 8.8 Hz, 1H, H-5), 7.36–7.33 (m, 2H, H-15, H-17), 7.32–7.29 (m, 1H, H-16).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 143.7 (C-1), 138.4 (C-4a), 138.0 (C-19**), 133.4 (2C, C-20, C-24), 131.4 (2C, C-14, C-18), 130.6 (2C, C-6, C-10a**), 129.6 (C-6a), 129.5 (C-22), 128.8 (C-7), 128.3 (2C, C-15, C-17), 128.0 (2C, C-21, C-23), 127.7 (C-16), 127.5 (C-9), 124.8 (C-8), 124.5 (C-13), 122.4 (C-2**), 121.9 (C-10), 119.4 (C-5), 118.5 (C-10b), 94.3 (C-12), 93.9 (C-11). **Carbon not observed in ^{13}C-NMR, assigned by gHMBC.

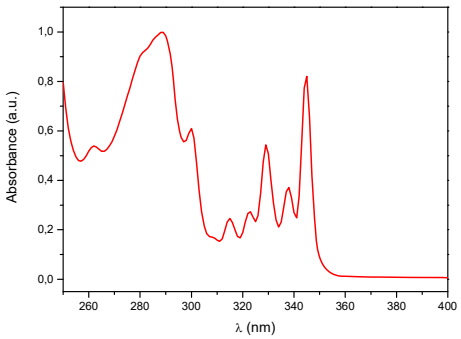
^{11}B-NMR (160 MHz, $CDCl_3$) δ (ppm) 33.97.

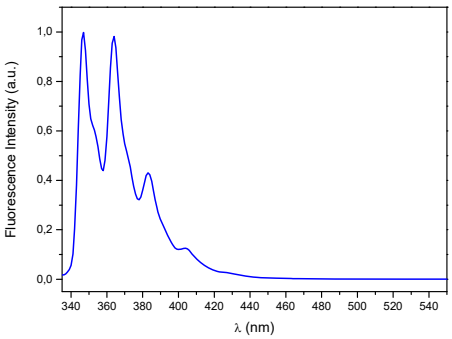
HRMS (EI) *m/z* calculated for $C_{26}H_{18}BN$ $[M]^+$: 355.1527. Found $[M]^+$: 355.1519.

PHOTOPHYSICAL DATA

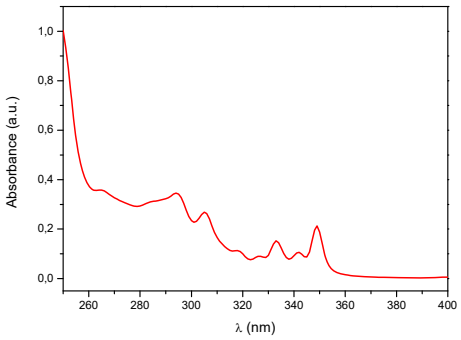
UV/Vis (Red) and Fluorescence (Blue) spectra of 1,2-dihydro-1-aza-2-boraphenanthrene derivatives.

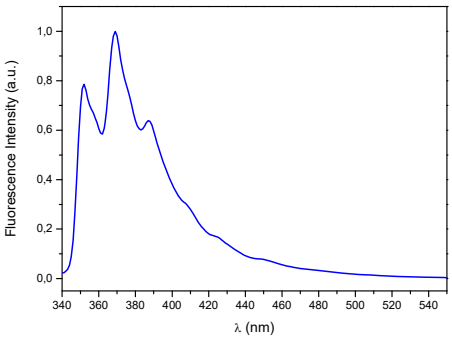
Compound 6a



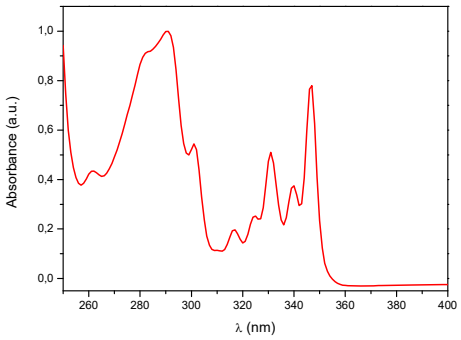


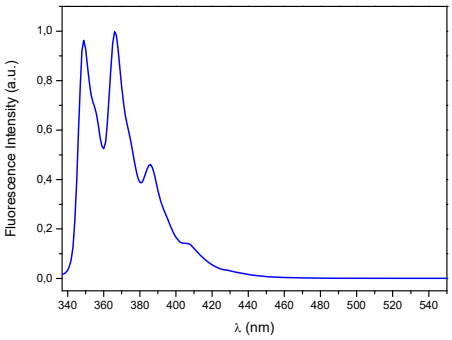
Compound 6b



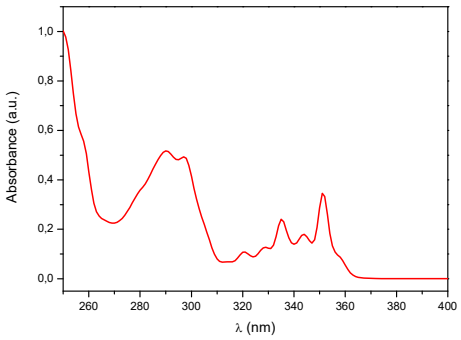


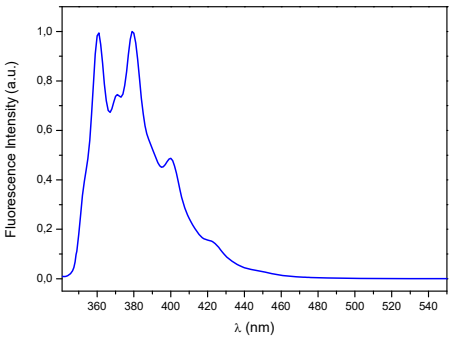
Compound 6c



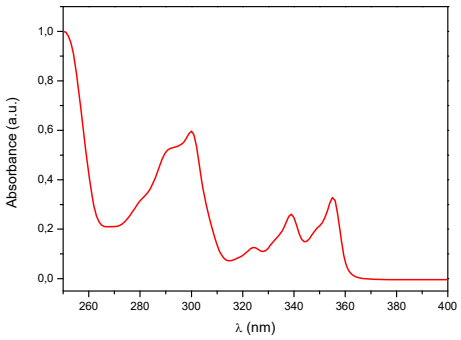


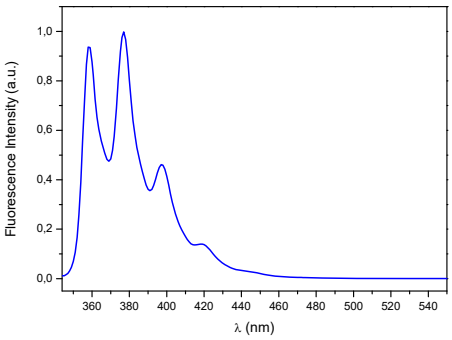
Compound 6d



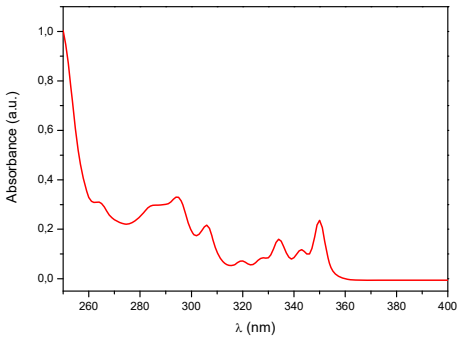


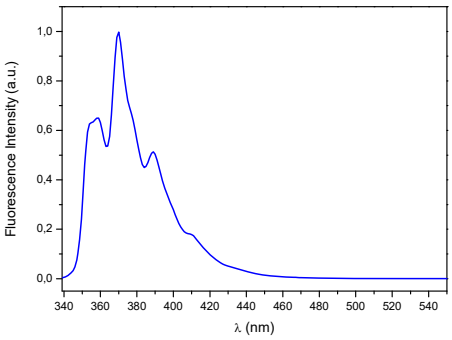
Compound 6e



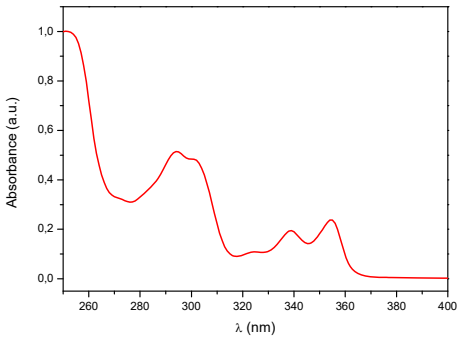


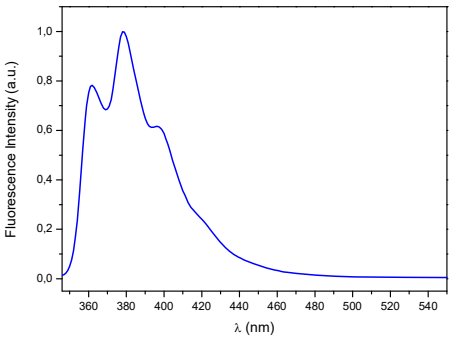
Compound 6f



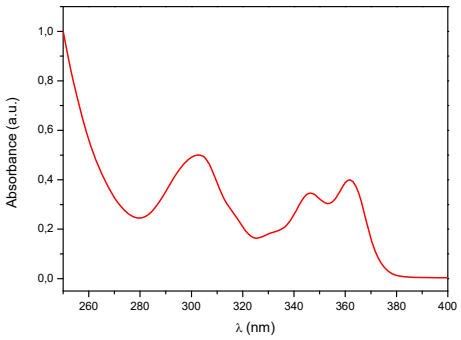


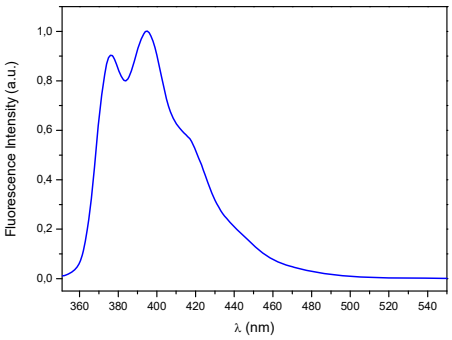
Compound 6g



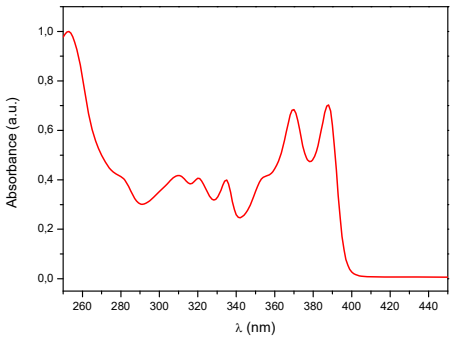


Compound 11b





Compound 12



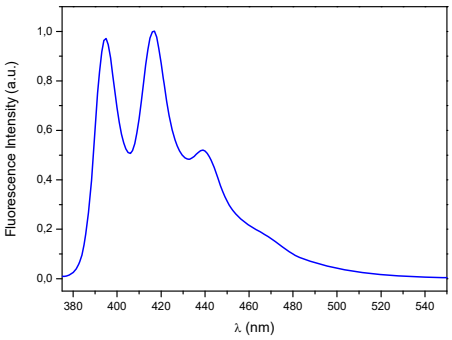
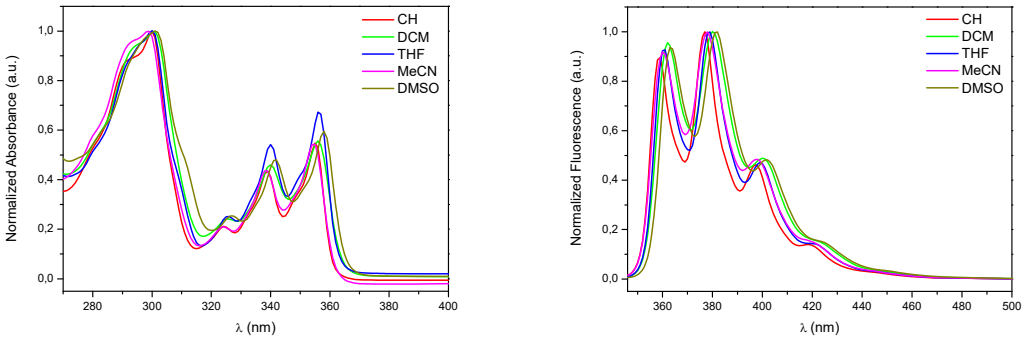


Table S1. Study of the emission of 6e in different solvents

Disolvente	UV/Vis $\lambda_{máx}$ (nm)	Fluorescence $\lambda_{máx}$ (nm)	Φ_F[a] (%)
Cyclohexane (CH)	355	377	93
Dichloromethane (DCM)	356	380	64
Tetrahydrofuran (THF)	356	379	68
Acetonitrile (MeCN)	355	378	68
Dimethyl sulfoxide (DMSO)	358	382	90

[a] Quantum yields reported relative to 9,10-diphenylanthracene (ϕ_F = 0.93).



UV/Vis (left) and Fluorescence (right) spectra

COMPUTATIONAL DATA

Computational details

The ground state minima of **1**-**6** were computed at the DFT level of theory and the vertical transitions at the TD-DFT level of theory. The solvent (cyclohexane) effect was taken into account using the polarizable continuum model (PCM).[2] The B3LYP[3] functional was used the 6-31+G** basis set. All calculations were performed using the Gaussian 16 software.[4]

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[2] Tomasi, J.; Mennucci, B.; Cammi, R. Quantum mechanical continuum solvation models. *Chem. Rev.* **2005**, *105*, 2999–3094.

[3] Becke, A. D. A new mixing of Hartree–Fock and local density-functional theories. *J. Chem. Phys.* **1993**, *98*, 1372–1377.

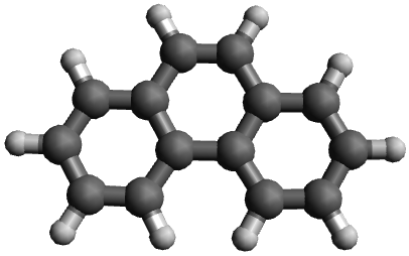
[4] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.;Robb, M. A.; Cheeseman; J. R.; Scalmani; G.; Barone; V.; Mennucci;B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H.P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M. N.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 16, revision A.03*; Gaussian, Inc.: Wallingford, CT, 2009.

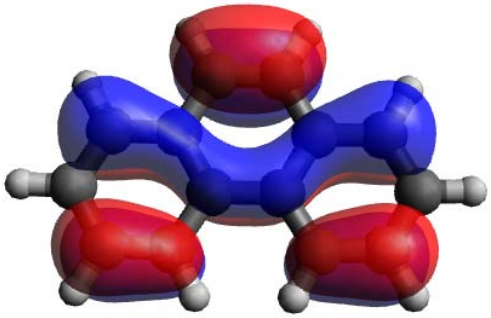
Computed absorption bands and orbitals involved for 1-6

- **1**

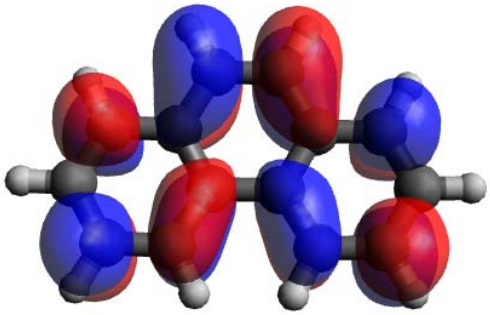
Absorption: 298 nm

f =0.14





HOMO

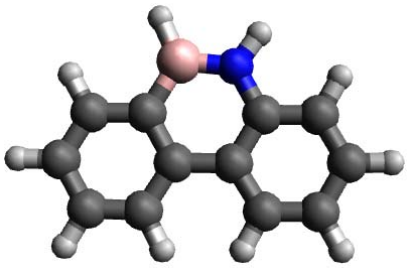


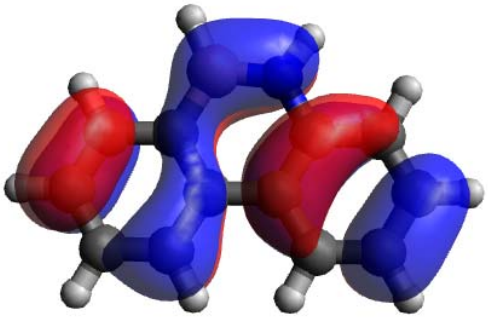
LUMO

- **2**

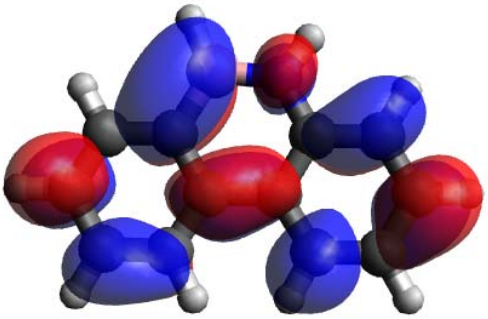
Absorption: 301 nm

f =0.22





HOMO

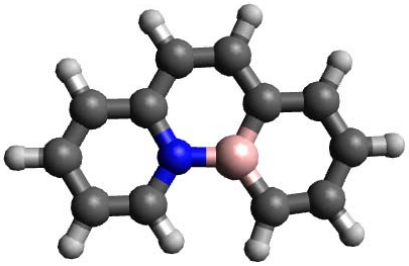


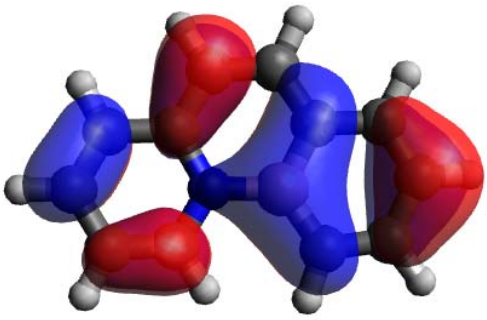
LUMO

- **3**

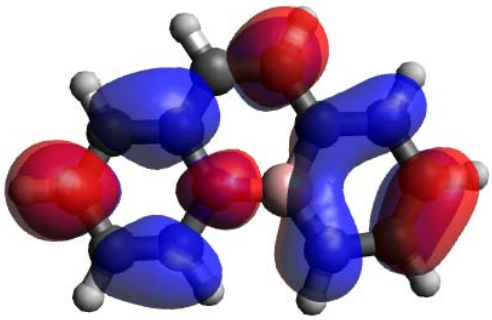
Absorption: 402 nm

f =0.32





HOMO

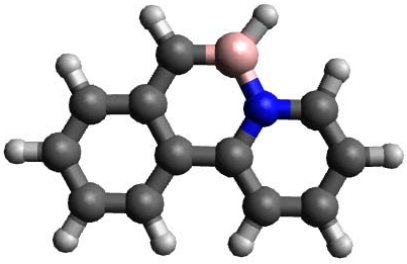


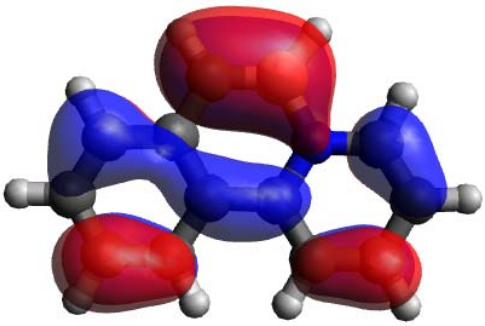
LUMO

- **4**

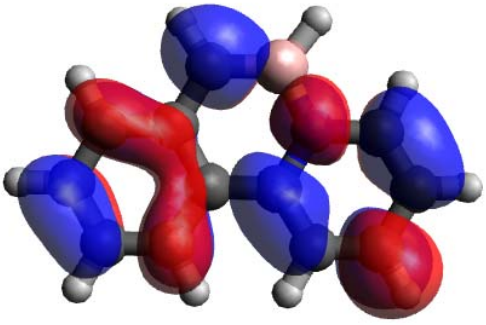
Absorption: 413 nm

f =0.30





HOMO

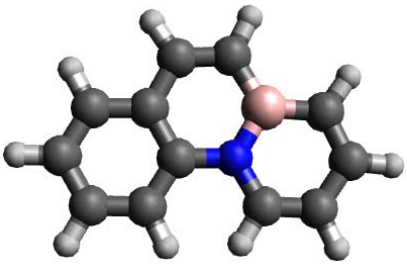


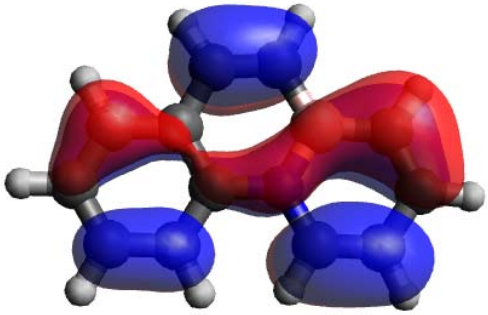
LUMO

- **5**

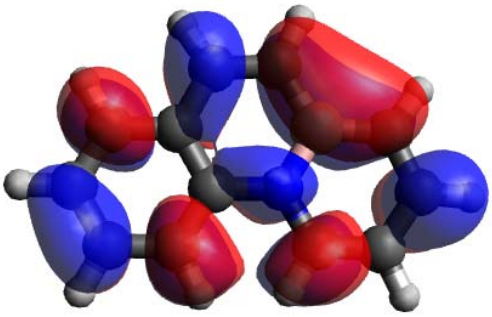
Absorption: 314 nm

f =0.06





HOMO

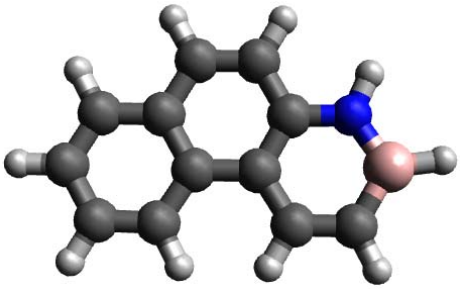


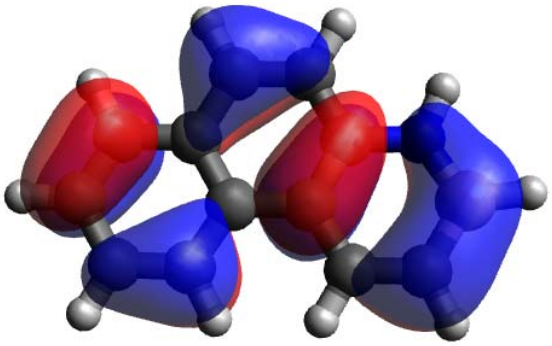
LUMO

- **6**

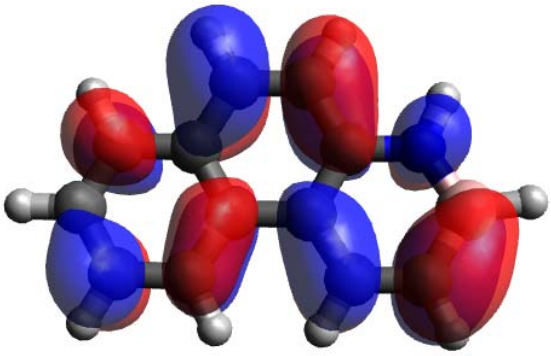
Absorption: 325 nm

f =0.24





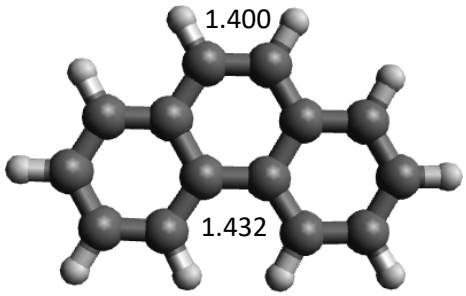
HOMO



LUMO

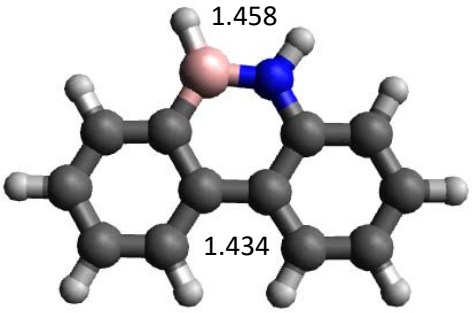
Computed emission and geometry for the excited state minimum for 1-6

- **1**



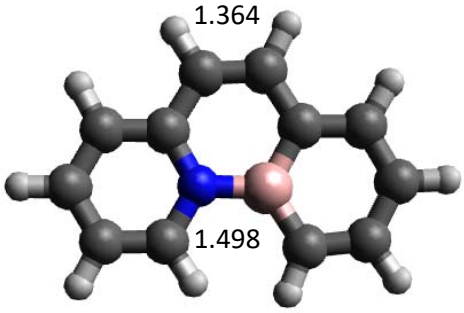
Emission: 336 nm

- **2**



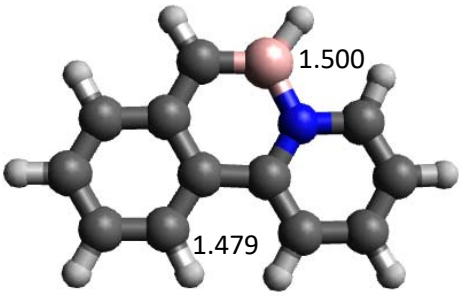
Emission: 325 nm

- **3**



Emission: 458 nm

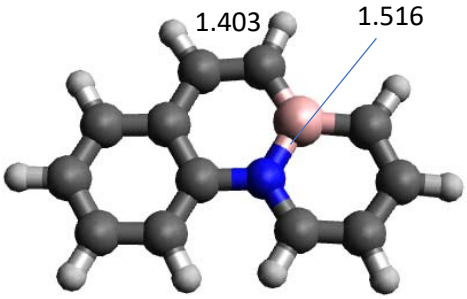
- **4**



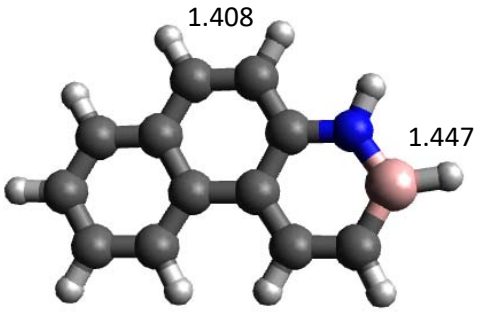
Emission: 503 nm

- **5**

Emission: 354 nm



- **6**



Emission: 356 nm

Cartesian Coordinates

- **1 Min S_0**

  Total Energy: -539.574280 Imaginary frequencies: 0

6	-0.298623	-1.626018	-2.093035
6	-0.988952	-2.799690	-2.094954
6	-2.425456	-2.817043	-2.095935
6	-3.148738	-1.585769	-2.094901
6	-2.408961	-0.328154	-2.092862
6	-0.981375	-0.361957	-2.091931
6	-4.563810	-1.648297	-2.095913
6	-5.233718	-2.860515	-2.097857
6	-4.514508	-4.072546	-2.098877
6	-3.132279	-4.044498	-2.097923
6	-3.041823	0.939186	-2.091741
6	-2.307792	2.113715	-2.089788
6	-0.899068	2.074004	-2.088862
6	-0.252018	0.852189	-2.089927
1	0.834058	0.807118	-2.089231
1	-0.460761	-3.749529	-2.095769
1	-5.043897	-5.020719	-2.100393
1	-2.565014	-4.971772	-2.098688
1	-5.146919	-0.734392	-2.095174
1	-6.319704	-2.874916	-2.098590
1	0.788198	-1.626209	-2.092309
1	-0.327383	2.997290	-2.087331
1	-2.823020	3.069781	-2.088974
1	-4.124020	1.004731	-2.092407

- **1 Min S_1**

  Total Energy: -539.569669 Imaginary frequencies: 0

6	-0.293905	-1.606655	-2.093013
6	-1.003582	-2.813108	-2.094977
6	-2.417013	-2.841578	-2.095957
6	-3.144365	-1.572341	-2.094880
6	-2.418529	-0.338413	-2.092883
6	-0.955778	-0.357449	-2.091911
6	-4.568810	-1.644486	-2.095906
6	-5.240571	-2.872682	-2.097874
6	-4.532938	-4.088842	-2.098911
6	-3.128311	-4.061203	-2.097941
6	-3.047606	0.941620	-2.091750
6	-2.300528	2.125505	-2.089769
6	-0.893739	2.097939	-2.088823

6	-0.235396	0.856843	-2.089906
1	0.850589	0.816486	-2.089202
1	-0.459543	-3.753647	-2.095768
1	-5.063524	-5.034979	-2.100426
1	-2.565368	-4.990752	-2.098714
1	-5.158003	-0.735289	-2.095172
1	-6.326672	-2.880679	-2.098598
1	0.792483	-1.625163	-2.092316
1	-0.324657	3.021433	-2.087290
1	-2.821281	3.078657	-2.088965
1	-4.128535	1.014772	-2.092416

- **2 Min S_0**

  Total Energy: -543.019370 Imaginary frequencies: 0

6	-0.250276	0.848644	-2.089917
6	-0.976517	-0.357258	-2.091925
6	-2.397623	-0.344002	-2.092880
6	-3.027611	0.920680	-2.091777
6	-2.306992	2.107442	-2.089810
6	-0.904431	2.071699	-2.088860
7	-0.290026	-1.571130	-2.092967
5	-0.910339	-2.839901	-2.094953
6	-2.445946	-2.847889	-2.095984
6	-3.152104	-1.610189	-2.094928
6	-4.565327	-1.640824	-2.095887
6	-5.255747	-2.846375	-2.097842
6	-4.564104	-4.068537	-2.098908
6	-3.175724	-4.056636	-2.097968
1	0.836509	0.808011	-2.089184
1	-0.227374	-3.819635	-2.095712
1	-5.111152	-5.006812	-2.100432
1	-2.627083	-4.995321	-2.098759
1	-5.138635	-0.720713	-2.095113
1	-6.342331	-2.838846	-2.098544
1	0.718575	-1.485226	-2.092209
1	-0.330528	2.993488	-2.087313
1	-2.830818	3.058164	-2.089020
1	-4.109979	0.977160	-2.092478

- **2 Min S_1**

  Total Energy: -543.013755 Imaginary frequencies: 0

6	-0.228497	0.855506	-2.089860
6	-0.954404	-0.357885	-2.091900
6	-2.422288	-0.363648	-2.092921

6	-3.048135	0.921203	-2.091843
6	-2.306352	2.104365	-2.089849
6	-0.895423	2.084093	-2.088820
7	-0.286229	-1.549579	-2.092943
5	-0.912700	-2.866035	-2.094992
6	-2.423583	-2.876515	-2.095990
6	-3.141835	-1.604404	-2.094886
6	-4.572396	-1.640924	-2.095838
6	-5.272727	-2.842326	-2.097820
6	-4.577051	-4.072598	-2.098946
6	-3.174075	-4.065505	-2.098001
1	0.857365	0.813684	-2.089108
1	-0.198766	-3.821045	-2.095709
1	-5.121518	-5.011717	-2.100486
1	-2.641363	-5.013872	-2.098839
1	-5.141467	-0.718003	-2.095013
1	-6.358529	-2.829334	-2.098488
1	0.724082	-1.467886	-2.092187
1	-0.333366	3.012044	-2.087268
1	-2.828137	3.056771	-2.089084
1	-4.128192	0.989601	-2.092576

- **3 Min S_0**

  Total Energy: -542.983123 Imaginary frequencies: 0

6	-0.225957	0.860359	-2.089865
6	-0.942136	-0.371372	-2.091940
5	-2.460278	-0.330291	-2.092947
6	-3.138067	1.026532	-2.091761
6	-2.320921	2.142599	-2.089781
6	-0.893385	2.068259	-2.088818
6	-0.294582	-1.625071	-2.093050
6	-1.016443	-2.806035	-2.095016
6	-2.430553	-2.838921	-2.096001
7	-3.160638	-1.650341	-2.095021
6	-4.538952	-1.715318	-2.095967
6	-5.229018	-2.893583	-2.097852
6	-4.508156	-4.117026	-2.098904
6	-3.137967	-4.075586	-2.097980
1	0.864323	0.849373	-2.089093
1	-0.506644	-3.763736	-2.095840
1	-5.034240	-5.066082	-2.100400
1	-2.550467	-4.987634	-2.098730
1	-5.042180	-0.758731	-2.095093
1	-6.312713	-2.876356	-2.098507

1	0.794501	-1.681167	-2.092359
1	-0.325506	2.995158	-2.087244
1	-2.764060	3.138303	-2.088878
1	-4.211546	1.212658	-2.092327

- **3 Min S_1**

  Total Energy: -542.975355 Imaginary frequencies: 0

6	-0.225140	0.847551	-2.089901
6	-0.911936	-0.366787	-2.091881
5	-2.448448	-0.343988	-2.092898
6	-3.144626	1.025383	-2.091741
6	-2.335395	2.151753	-2.089810
6	-0.917921	2.075535	-2.088890
6	-0.260115	-1.645311	-2.093009
6	-0.984802	-2.800864	-2.094927
6	-2.440978	-2.857018	-2.095983
7	-3.145930	-1.670166	-2.094938
6	-4.548485	-1.689776	-2.095865
6	-5.239862	-2.898181	-2.097882
6	-4.547210	-4.102873	-2.098994
6	-3.118241	-4.074728	-2.098001
1	0.864420	0.863627	-2.089108
1	-0.480767	-3.762093	-2.095767
1	-5.075853	-5.049910	-2.100562
1	-2.541856	-4.991966	-2.098793
1	-5.037938	-0.729150	-2.094903
1	-6.325013	-2.875710	-2.098550
1	0.827713	-1.702483	-2.092348
1	-0.345183	2.998965	-2.087363
1	-2.782428	3.144308	-2.088938
1	-4.219589	1.189874	-2.092319

- **4 Min S_0**

  Total Energy: -542.976298 Imaginary frequencies: 0

6	-0.312932	0.849083	-2.089939
7	-1.002640	-0.348258	-2.091855
6	-2.397786	-0.341760	-2.092825
6	-3.048129	0.924097	-2.091806
6	-2.346899	2.104715	-2.089914
6	-0.931253	2.065455	-2.088941
5	-0.213236	-1.606291	-2.092853
6	-0.976978	-2.860689	-2.095015
6	-2.389942	-2.840468	-2.095958
6	-3.110102	-1.590264	-2.094822

6	-4.536338	-1.626896	-2.095739
6	-5.230596	-2.815749	-2.097735
6	-4.526032	-4.047579	-2.098931
6	-3.152725	-4.053110	-2.098054
1	0.764047	0.743972	-2.089304
1	-0.502888	-3.840189	-2.095951
1	-5.076378	-4.984453	-2.100514
1	-2.607474	-4.993173	-2.098929
1	-5.106124	-0.705349	-2.094844
1	-6.316188	-2.809220	-2.098380
1	0.972223	-1.467227	-2.091831
1	-0.335776	2.970943	-2.087454
1	-2.872867	3.053709	-2.089195
1	-4.128570	0.954692	-2.092582

- **4 Min S_1**

  Total Energy: -542.966090 Imaginary frequencies: 0

6	-0.287484	0.857159	-2.090054
7	-1.035763	-0.326313	-2.092005
6	-2.396031	-0.309999	-2.092870
6	-3.073454	0.932764	-2.091748
6	-2.313625	2.150846	-2.089642
6	-0.940798	2.108544	-2.088819
5	-0.240601	-1.598312	-2.093025
6	-0.991385	-2.894868	-2.095027
6	-2.396043	-2.867776	-2.095939
6	-3.103667	-1.608964	-2.094941
6	-4.503359	-1.639454	-2.095981
6	-5.219171	-2.843128	-2.097904
6	-4.540149	-4.072434	-2.098843
6	-3.157398	-4.078761	-2.097879
1	0.783279	0.732374	-2.089517
1	-0.500313	-3.864446	-2.095844
1	-5.094638	-5.005678	-2.100315
1	-2.612636	-5.018722	-2.098598
1	-5.068500	-0.716860	-2.095323
1	-6.304258	-2.817859	-2.098661
1	0.940715	-1.474757	-2.092131
1	-0.343316	3.013889	-2.087235
1	-2.836856	3.102240	-2.088704
1	-4.150130	0.976508	-2.092365

- **5 Min S_0**

  Total Energy: -542.993946 Imaginary frequencies: 0

6	-0.196099	0.974502	-2.089706
5	-0.897936	-0.375814	-2.091863
7	-2.372737	-0.360920	-2.092876
6	-3.025409	0.859305	-2.091884
6	-2.364182	2.055232	-2.089945
6	-0.938577	2.126812	-2.088820
6	-0.213837	-1.743351	-2.093090
6	-0.972451	-2.869150	-2.095041
6	-2.416776	-2.812787	-2.095944
6	-3.117066	-1.571892	-2.094847
6	-4.527903	-1.598299	-2.095756
6	-5.225704	-2.799325	-2.097731
6	-4.541787	-4.024154	-2.098860
6	-3.157583	-4.016521	-2.097950
1	0.889719	1.053094	-2.088834
1	-0.527424	-3.863667	-2.095992
1	-5.089194	-4.961448	-2.100402
1	-2.606223	-4.953016	-2.098767
1	-5.106551	-0.684770	-2.094931
1	-6.311386	-2.779709	-2.098386
1	0.870019	-1.843189	-2.092468
1	-0.472589	3.110749	-2.087279
1	-2.959267	2.962094	-2.089290
1	-4.104640	0.852213	-2.092709

- **5 Min S_1**

  Total Energy: -542.985314 Imaginary frequencies: 0

6	-0.178564	1.002110	-2.089025
5	-0.855716	-0.384838	-2.091433
7	-2.371598	-0.372925	-2.092783
6	-2.997833	0.824429	-2.092608
6	-2.333882	2.064636	-2.090596
6	-0.929943	2.171197	-2.088659
6	-0.185110	-1.708860	-2.092847
6	-0.993474	-2.856106	-2.095313
6	-2.415154	-2.823691	-2.096199
6	-3.144773	-1.587832	-2.094653
6	-4.537295	-1.597383	-2.094928
6	-5.260073	-2.827347	-2.097191
6	-4.567861	-4.032034	-2.099016
6	-3.169812	-4.038808	-2.098510
1	0.906299	1.084740	-2.087658
1	-0.539101	-3.846477	-2.096485
1	-5.109920	-4.973829	-2.100776

1	-2.626511	-4.979079	-2.099820
1	-5.116453	-0.683362	-2.093345
1	-6.344687	-2.804763	-2.097465
1	0.894147	-1.835327	-2.092156
1	-0.471662	3.156251	-2.087034
1	-2.958134	2.951729	-2.090629
1	-4.078472	0.833563	-2.094241

- **6 Min S_0**

  Total Energy: -543.012080 Imaginary frequencies: 0

6	-0.300458	-1.613968	-2.093073
6	-0.990201	-2.794281	-2.095003
6	-2.418602	-2.815822	-2.095937
6	-3.139619	-1.579133	-2.094898
6	-2.406343	-0.326567	-2.092878
6	-0.996097	-0.369760	-2.091936
6	-4.558189	-1.646251	-2.095894
6	-5.223296	-2.858827	-2.097808
6	-4.505234	-4.074433	-2.098826
6	-3.125404	-4.045948	-2.097897
6	-3.054010	0.958333	-2.091800
6	-2.366023	2.145155	-2.089844
5	-0.845455	2.117302	-2.088717
7	-0.275999	0.809017	-2.089909
1	0.729822	0.687260	-2.089223
1	-0.453716	-3.739204	-2.095862
1	-5.036135	-5.021595	-2.100317
1	-2.556316	-4.972160	-2.098653
1	-5.145378	-0.735419	-2.095151
1	-6.309398	-2.873525	-2.098521
1	0.786910	-1.608998	-2.092457
1	-0.108310	3.056676	-2.086981
1	-2.947446	3.064223	-2.089176
1	-4.140686	0.973915	-2.092607

- **6 Min S_1**

  Total Energy: -543.005774 Imaginary frequencies: 0

6	-0.273839	-1.596818	-2.092995
6	-0.988391	-2.810496	-2.094990
6	-2.401828	-2.825243	-2.095939
6	-3.142053	-1.584537	-2.094900
6	-2.418164	-0.319410	-2.092869
6	-0.951489	-0.374649	-2.091907
6	-4.548970	-1.650831	-2.095893

6	-5.253659	-2.877526	-2.097872
6	-4.535796	-4.069686	-2.098875
6	-3.129488	-4.041424	-2.097917
6	-3.060517	0.944626	-2.091791
6	-2.370154	2.155490	-2.089782
5	-0.852264	2.132593	-2.088755
7	-0.256080	0.813696	-2.089925
1	0.751110	0.708066	-2.089284
1	-0.449651	-3.753242	-2.095796
1	-5.051265	-5.025378	-2.100383
1	-2.577114	-4.977442	-2.098701
1	-5.131039	-0.736714	-2.095126
1	-6.338183	-2.877080	-2.098574
1	0.812447	-1.601715	-2.092343
1	-0.116639	3.072034	-2.087094
1	-2.956224	3.071023	-2.089090
1	-4.146333	0.960655	-2.092568

X-RAY CRYSTALLOGRAPHIC DATA FOR 10b

Colourless crystals were grown by slow evaporation at room temperature from a solution in a mixture of hexane and dichloromethane. The crystals were removed from the vial and covered with a layer of a viscous perfluoropolyether (FomblinY). Suitable crystals, selected with the aid of a microscope, were mounted on a cryoloop and placed in the low temperature nitrogen stream of the diffractometer. The intensity data sets were collected at 200 K on a Bruker-Nonius KappaCCD diffractometer equipped with an Oxford Cryostream 700 unit. Crystallographic data for compounds **10b** are presented in Table S1.

Table S2. Experimental data for the X-ray diffraction study on compounds **10b**.

	10b
formula	$C_{18}H_{13}BBrN$
CCDC[a] code	1905045
M_r	334.01
T [K]	200(2)
λ [Å]	0.71073
crystal system	orthorhombic
space group	*Pcab*
a [Å]	7.393(1)
b [Å]; β (º)	14.149(1)
c [Å]	27.740(2)
V [Å^3]	2901.6(5)
Z	8
ρ_{calcd} [g cm^{-3}]	1.529
$\mu_{MoK\alpha}$ [mm^{-1}]	2.824
F(000)	1344
crystal size [mm^3]	0.40 × 0.20 × 0.13
θ range (deg)	3.20 to 27.50
index ranges	−9 to 9 −18 to 17 −36 to 35
reflns collected	33900
unique data	3324 [R(int) = 0.053]
obsd data [$I > 2\sigma(I)$]	2413
GOF on F^2	1.122
final R[b] indices [$I > 2\sigma(I)$]	R1 = 0.042 wR2 = 0.076
R[b] indices (all data)	R1 = 0.074 wR2 = 0.088
largest diff. peak/hole [e Å^{-3}]	0.484 and −0.290

[a] Cambridge Crystallographic Data Centre. [b] R1 = $\sum||F_0|-|F_c|| / [\sum|F_0|]$; wR2 = $\{[\sum w(F_0^2 - F_c^2)^2] / [\sum w(F_0^2)^2$

The structure was solved, using the WINGX package,[5] by direct methods (SHELXS-2013),[6] and refined by least-squares against F^2 (SHELXL-2014/7).[6] All non-hydrogen atoms were anisotropically refined, whereas all the hydrogen atoms were positioned geometrically and refined by using a riding model, except the hydrogen H(1) bound to nitrogen, which was located in the difference Fourier map and refined isotropically.

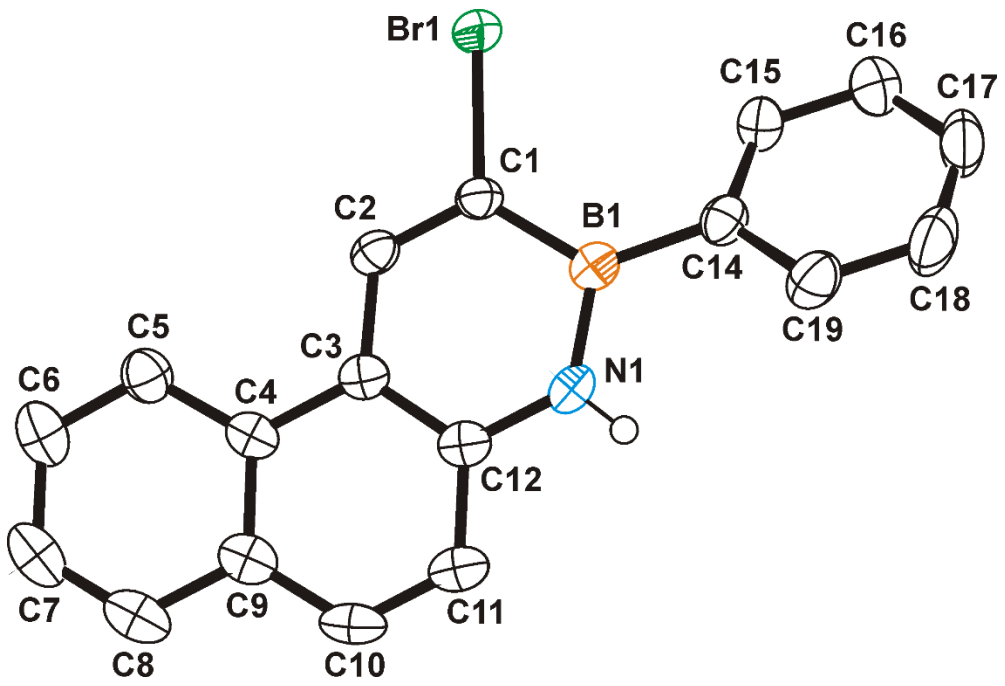


Figure S1. X-ray structure and numbering scheme for **10b**. Thermal ellipsoids are drawn at the 50% probability level.

[5] L. J. Farrugia, *J. Appl. Crystallogr.* **2012**, *45*, 849-854.
[6] G. M. Sheldrick, *Acta Crystallogr.* **2015**, *C71*, 3-8.

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for shelx. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	2947(4)	5973(2)	4120(1)	29(1)
C(2)	2919(4)	5961(2)	4607(1)	30(1)
C(3)	4489(4)	6167(2)	4889(1)	29(1)
C(4)	4454(4)	6188(2)	5412(1)	30(1)
C(5)	2887(4)	6001(2)	5687(1)	38(1)
C(6)	2887(5)	6091(2)	6180(1)	45(1)
C(7)	4447(5)	6370(2)	6426(1)	47(1)
C(8)	5992(5)	6540(2)	6173(1)	45(1)
C(9)	6052(4)	6448(2)	5662(1)	36(1)
C(10)	7665(4)	6630(2)	5401(1)	39(1)
C(11)	7701(4)	6600(2)	4912(1)	37(1)
C(12)	6102(4)	6382(2)	4650(1)	30(1)
C(14)	4999(4)	6238(2)	3278(1)	32(1)
C(15)	4101(4)	5648(2)	2953(1)	38(1)
C(16)	4438(4)	5669(2)	2461(1)	44(1)
C(17)	5687(4)	6295(2)	2280(1)	49(1)
C(18)	6605(5)	6893(3)	2586(1)	53(1)
C(19)	6272(4)	6863(2)	3077(1)	43(1)
B(1)	4680(4)	6199(2)	3834(1)	30(1)
Br(1)	702(1)	5703(1)	3802(1)	43(1)
N(1)	6130(3)	6397(2)	4154(1)	33(1)

Table S4. Bond lengths [Å] and angles [°] for shelx.

C(1)-C(2)	1.353(4)	C(5)-C(6)	1.373(4)	C(14)-C(15)	1.397(4)
C(1)-B(1)	1.541(4)	C(6)-C(7)	1.398(5)	C(14)-C(19)	1.406(4)
C(1)-Br(1)	1.918(3)	C(7)-C(8)	1.362(5)	C(14)-B(1)	1.560(4)
C(2)-C(3)	1.428(4)	C(8)-C(9)	1.422(4)	C(15)-C(16)	1.388(4)
C(3)-C(12)	1.398(4)	C(9)-C(10)	1.419(4)	C(16)-C(17)	1.375(4)
C(3)-C(4)	1.453(4)	C(10)-C(11)	1.358(4)	C(17)-C(18)	1.377(5)
C(4)-C(5)	1.411(4)	C(11)-C(12)	1.422(4)	C(18)-C(19)	1.386(4)
C(4)-C(9)	1.419(4)	C(12)-N(1)	1.377(4)	B(1)-N(1)	1.420(4)
C(2)-C(1)-B(1)	122.0(2)	C(8)-C(7)-C(6)	119.4(3)	C(19)-C(14)-B(1)	121.0(3)
C(2)-C(1)-Br(1)	116.3(2)	C(7)-C(8)-C(9)	121.5(3)	C(16)-C(15)-C(14)	122.5(3)
B(1)-C(1)-Br(1)	121.6(2)	C(4)-C(9)-C(10)	119.8(3)	C(17)-C(16)-C(15)	119.5(3)
C(1)-C(2)-C(3)	122.1(3)	C(4)-C(9)-C(8)	119.0(3)	C(16)-C(17)-C(18)	120.2(3)
C(12)-C(3)-C(2)	118.6(3)	C(10)-C(9)-C(8)	121.1(3)	C(17)-C(18)-C(19)	120.0(3)
C(12)-C(3)-C(4)	119.0(2)	C(11)-C(10)-C(9)	121.4(3)	C(18)-C(19)-C(14)	121.8(3)
C(2)-C(3)-C(4)	122.4(2)	C(10)-C(11)-C(12)	120.1(3)	N(1)-B(1)-C(1)	110.3(3)
C(5)-C(4)-C(9)	117.9(3)	N(1)-C(12)-C(3)	119.3(2)	N(1)-B(1)-C(14)	119.8(3)
C(5)-C(4)-C(3)	123.4(3)	N(1)-C(12)-C(11)	119.7(3)	C(1)-B(1)-C(14)	129.9(3)
C(9)-C(4)-C(3)	118.7(3)	C(3)-C(12)-C(11)	120.9(3)	C(12)-N(1)-B(1)	127.7(3)
C(6)-C(5)-C(4)	121.4(3)	C(15)-C(14)-C(19)	116.0(3)		
C(5)-C(6)-C(7)	120.8(3)	C(15)-C(14)-B(1)	123.0(3)		

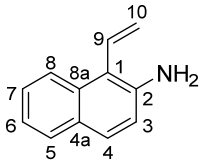
Symmetry transformations used to generate equivalent atoms:

Table S5. Anisotropic displacement parameters ($Å^2 x 10^3$) for shelx. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	25(1)	32(2)	31(1)	-4(1)	-3(1)	-2(1)
C(2)	26(1)	29(2)	36(2)	-2(1)	1(1)	-3(1)
C(3)	29(1)	22(1)	35(1)	-2(1)	-2(1)	0(1)
C(4)	37(2)	21(1)	32(1)	-1(1)	-7(1)	2(1)
C(5)	43(2)	36(2)	36(2)	-2(1)	1(1)	-1(1)
C(6)	64(2)	38(2)	32(2)	1(1)	2(2)	-2(2)
C(7)	72(2)	37(2)	31(2)	-2(1)	-7(2)	3(2)
C(8)	57(2)	36(2)	42(2)	-3(1)	-19(2)	2(2)
C(9)	43(2)	24(2)	40(2)	0(1)	-9(1)	4(1)
C(10)	33(2)	32(2)	51(2)	-4(1)	-18(1)	2(1)
C(11)	29(2)	33(2)	49(2)	-2(1)	-6(1)	-2(1)
C(12)	29(1)	23(1)	38(2)	-2(1)	-3(1)	2(1)
C(14)	28(1)	33(2)	36(2)	1(1)	4(1)	3(1)
C(15)	38(2)	43(2)	32(2)	3(1)	6(1)	-2(1)
C(16)	47(2)	51(2)	36(2)	-3(2)	3(2)	0(2)
C(17)	51(2)	64(2)	33(2)	6(2)	15(2)	6(2)
C(18)	46(2)	62(2)	50(2)	13(2)	19(2)	-8(2)
C(19)	37(2)	43(2)	47(2)	1(2)	7(1)	-8(2)
B(1)	29(2)	25(2)	36(2)	-1(1)	1(1)	2(1)
Br(1)	26(1)	69(1)	34(1)	-10(1)	-1(1)	-7(1)
N(1)	24(1)	37(1)	37(1)	1(1)	6(1)	-2(1)

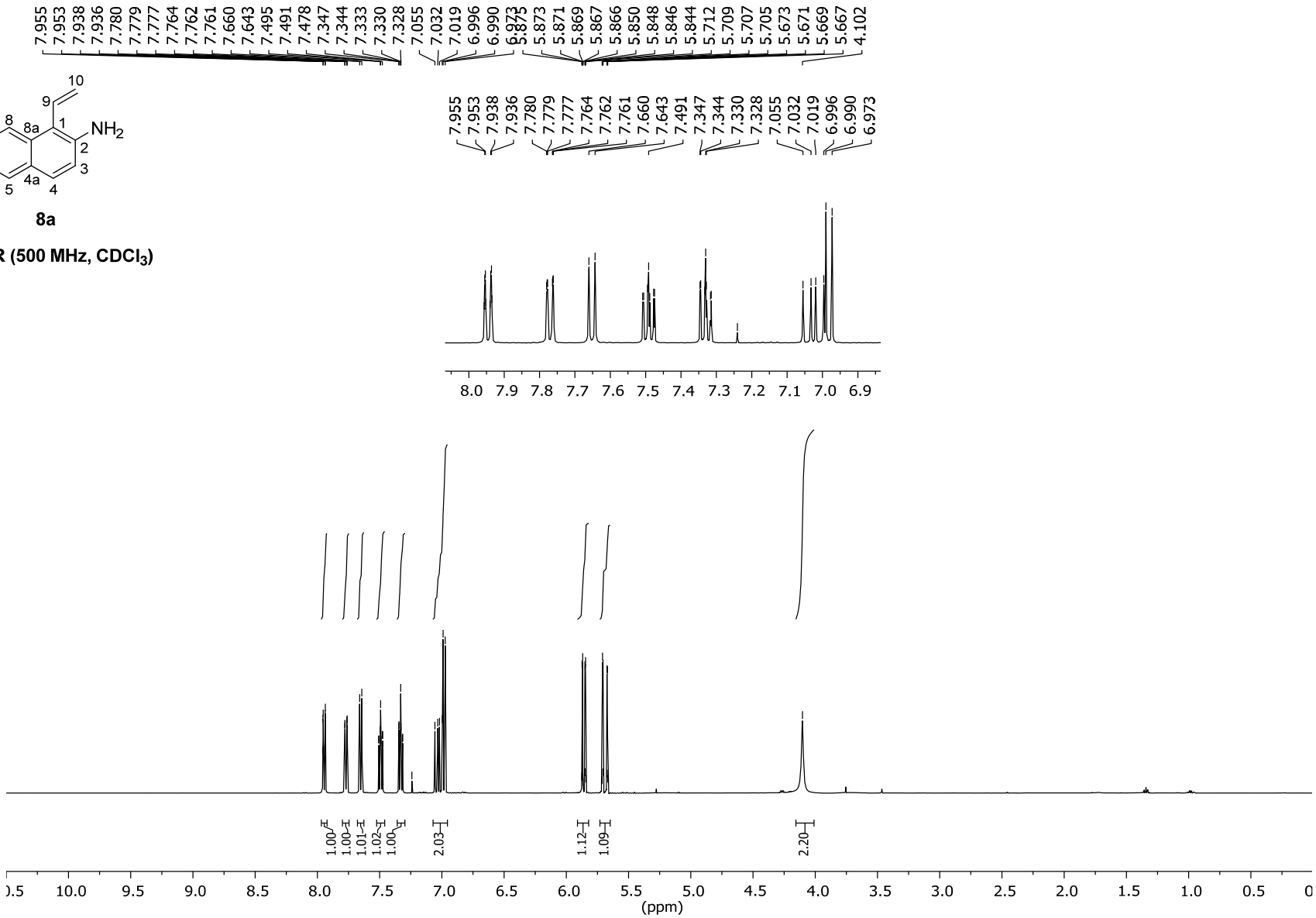
Table S6. Hydrogen coordinates ($x 10^4$) and isotropic displacement parameters ($Å^2 x 10^3$) for shelx.

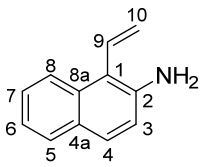
	x	y	z	U(eq)
H(2)	1821	5811	4768	36
H(5)	1810	5810	5527	46
H(6)	1813	5961	6355	54
H(7)	4430	6441	6766	56
H(8)	7054	6725	6341	54
H(10)	8742	6776	5572	47
H(11)	8796	6725	4745	44
H(15)	3227	5217	3073	45
H(16)	3810	5253	2250	53
H(17)	5918	6316	1943	59
H(18)	7465	7327	2460	64
H(19)	6923	7275	3284	51
H(1)	7050(40)	6500(20)	4045(11)	37(9)



8a

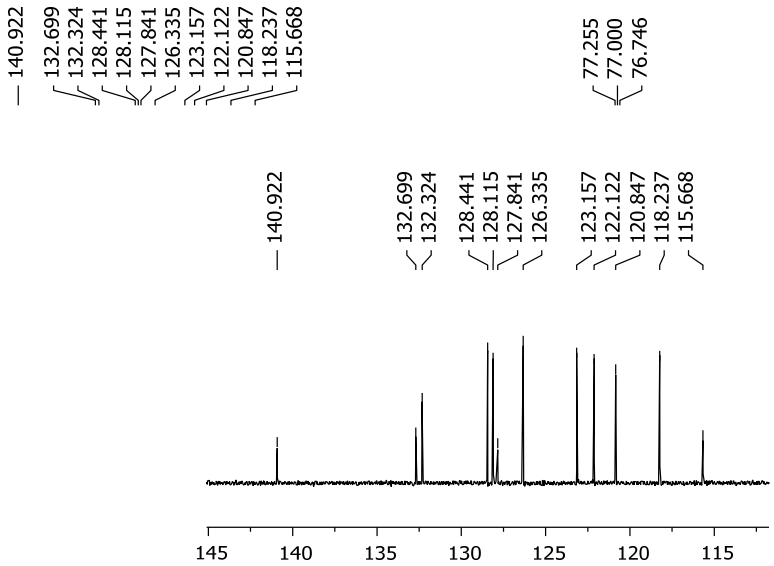
^{1}H-NMR (500 MHz, $CDCl_3$)

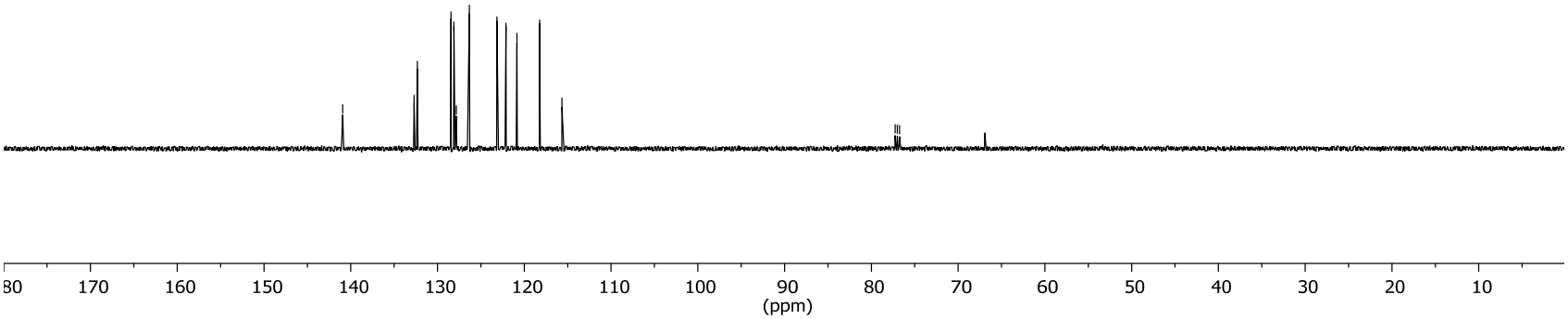


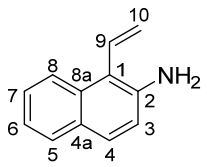


8a

^{13}C-NMR (125 MHz, $CDCl_3$)

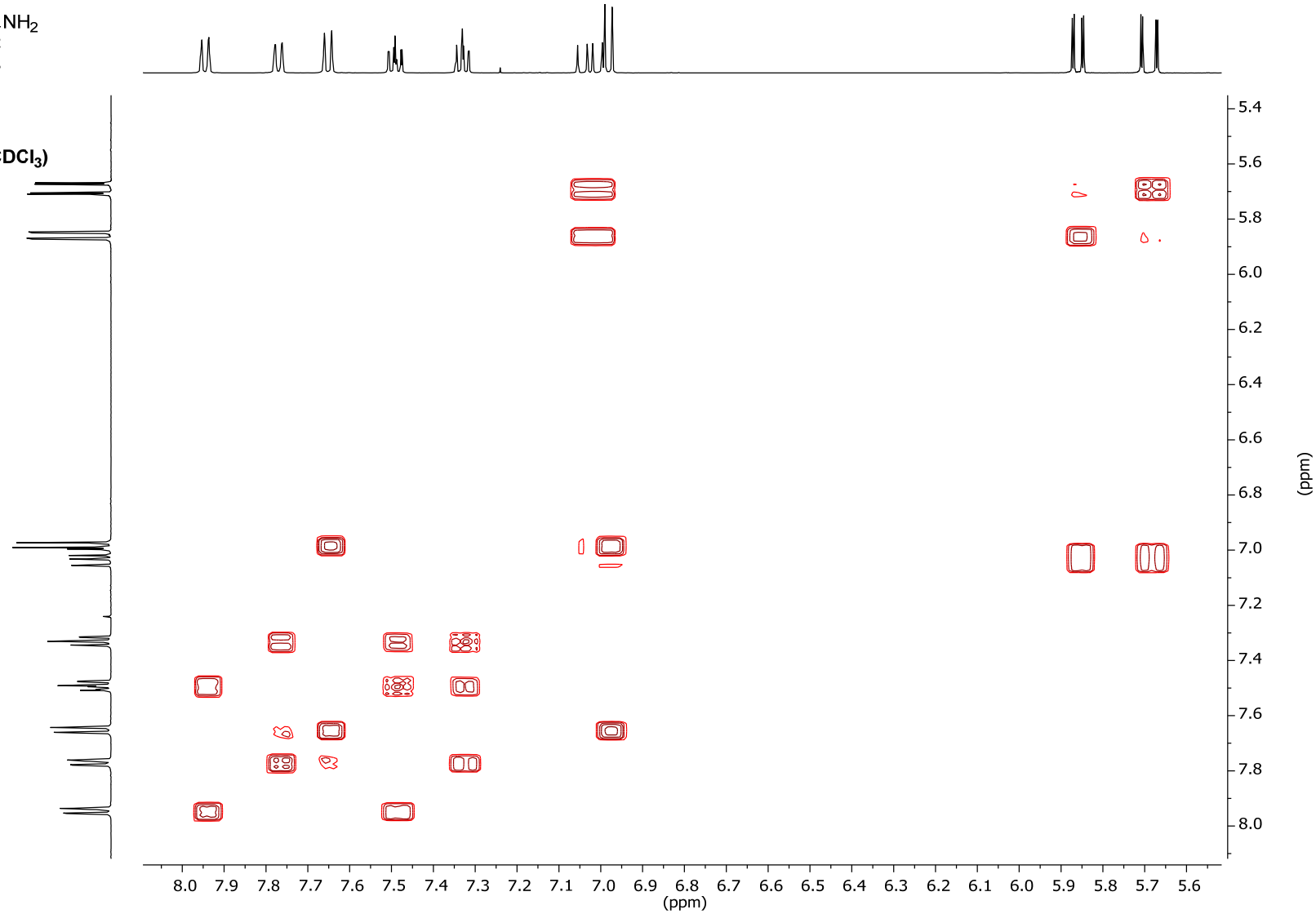


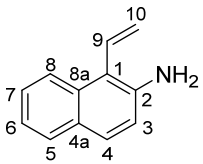




8a

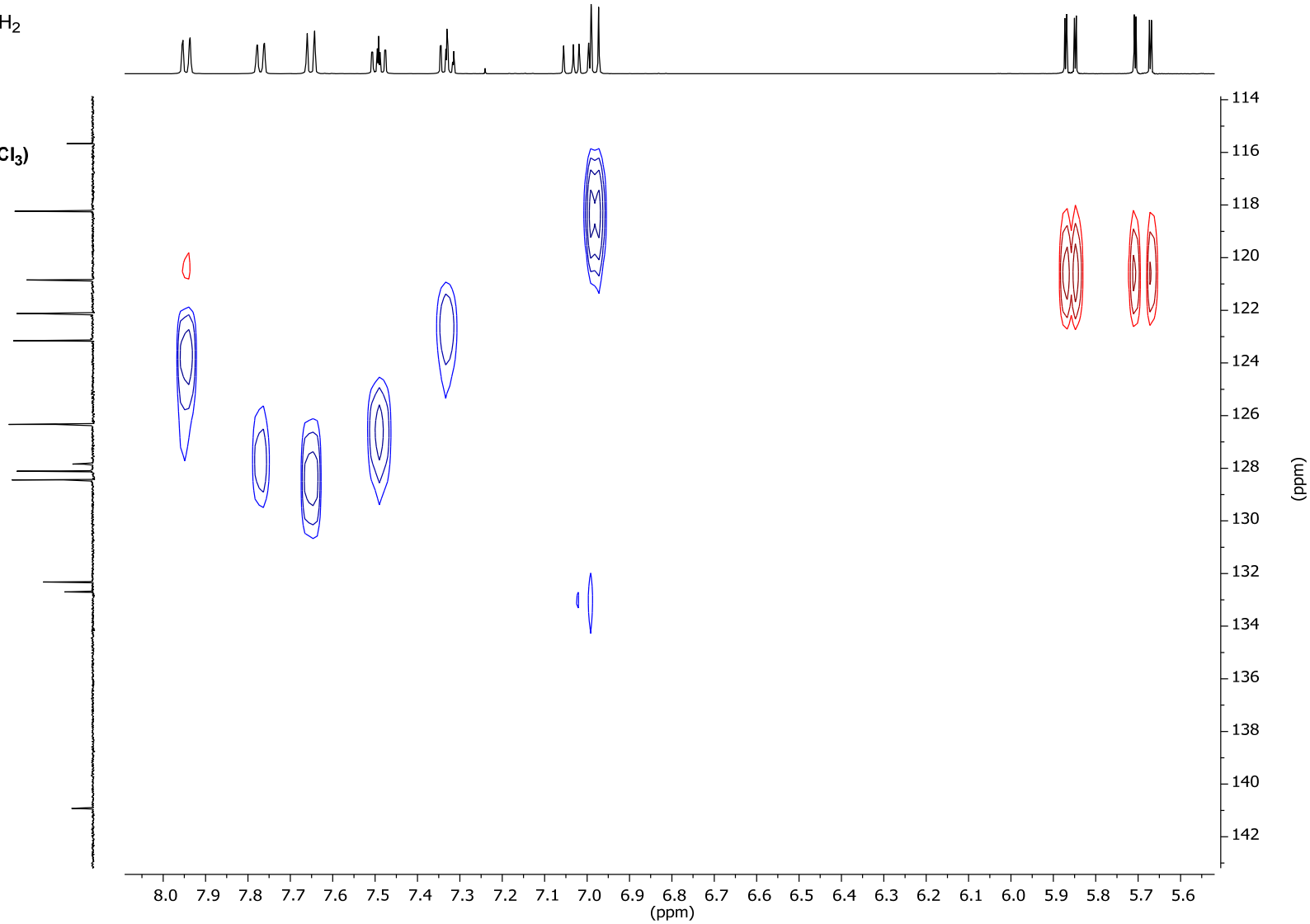
gCOSY-NMR ($CDCl_3$)

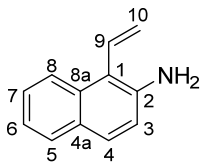




8a

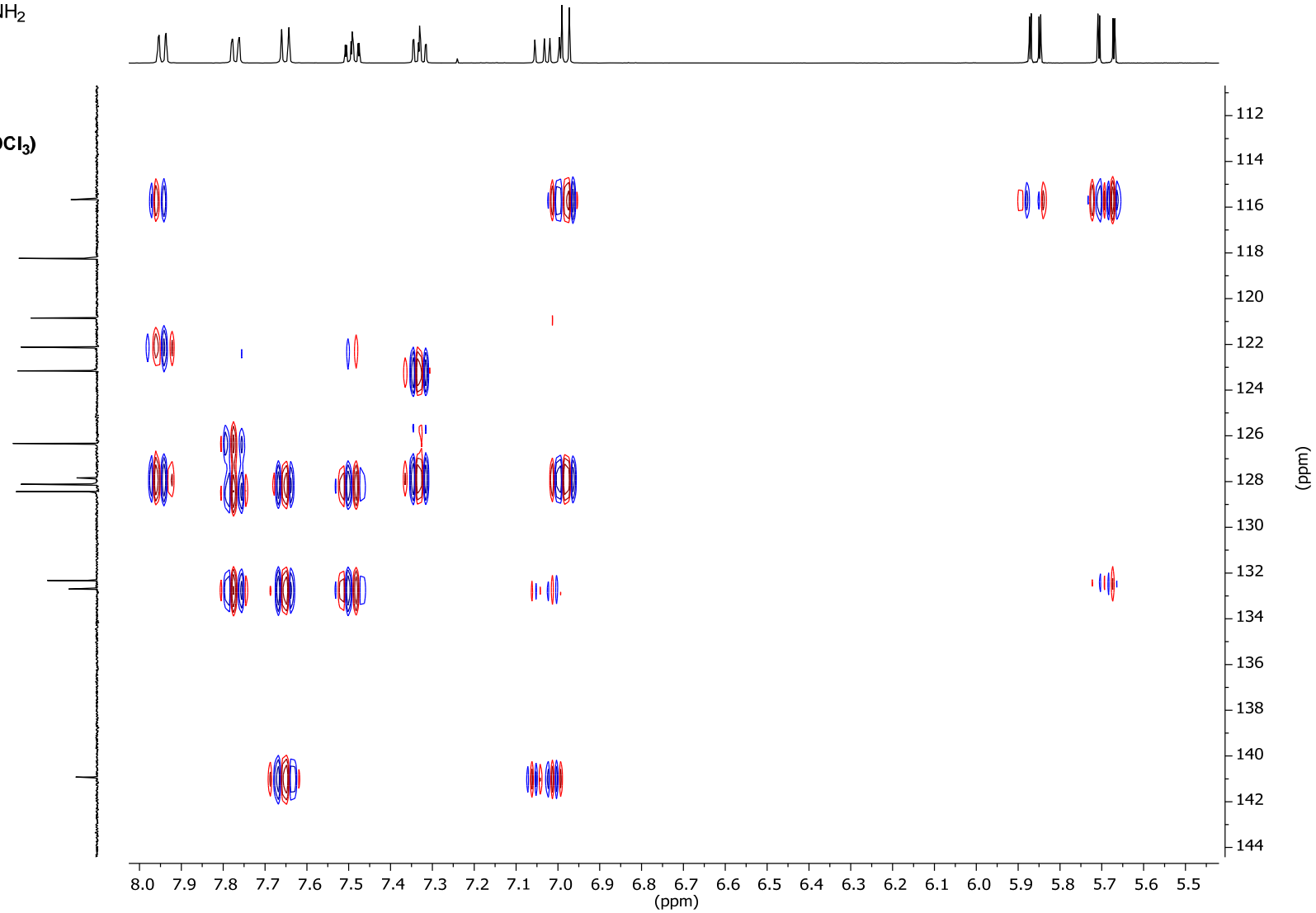
gHSQC-NMR ($CDCl_3$)

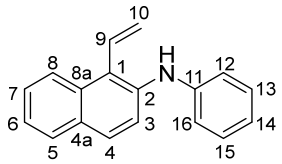




8a

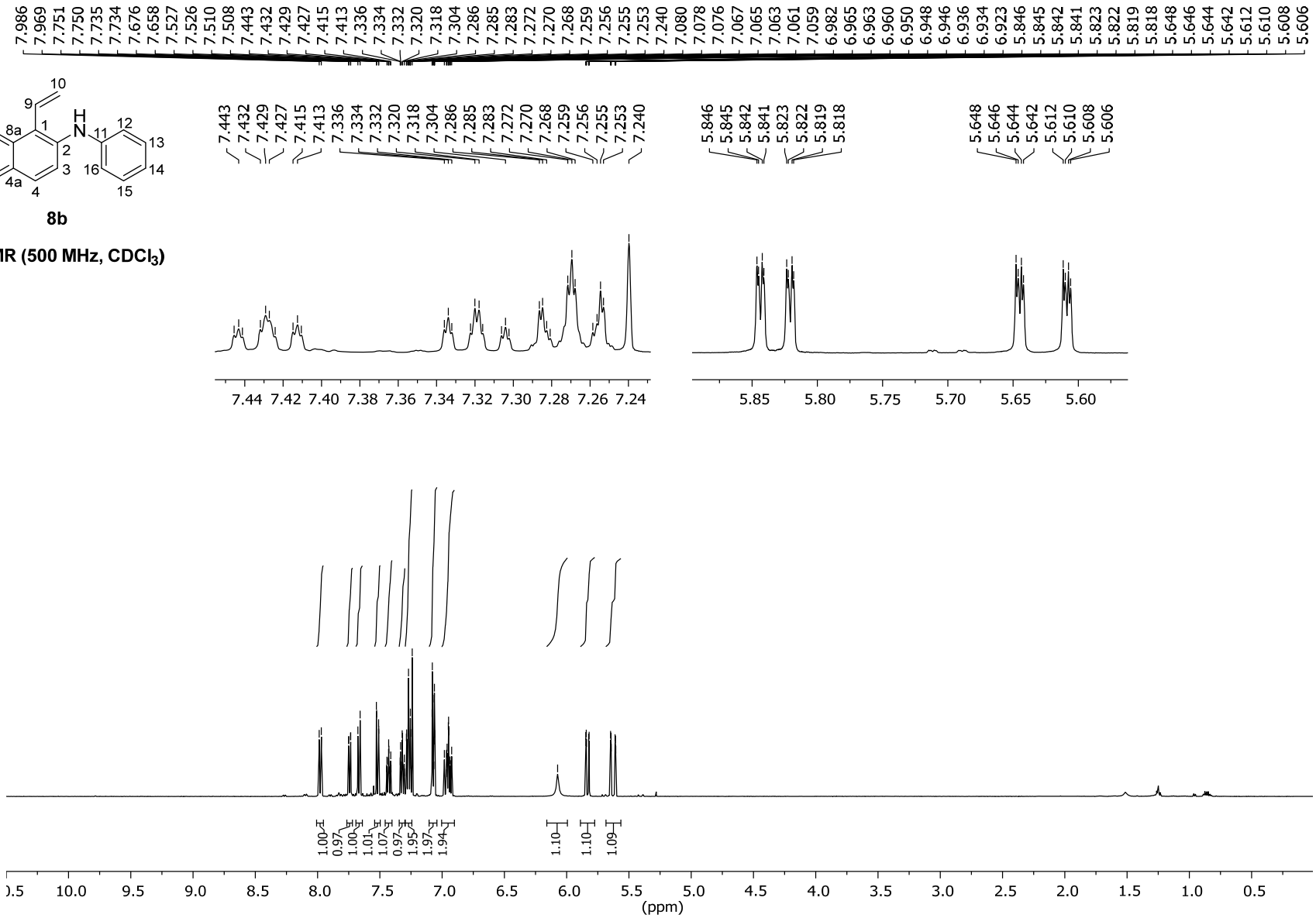
gHMBC-NMR ($CDCl_3$)

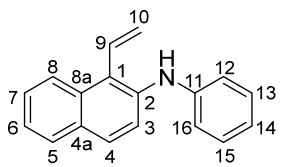




8b

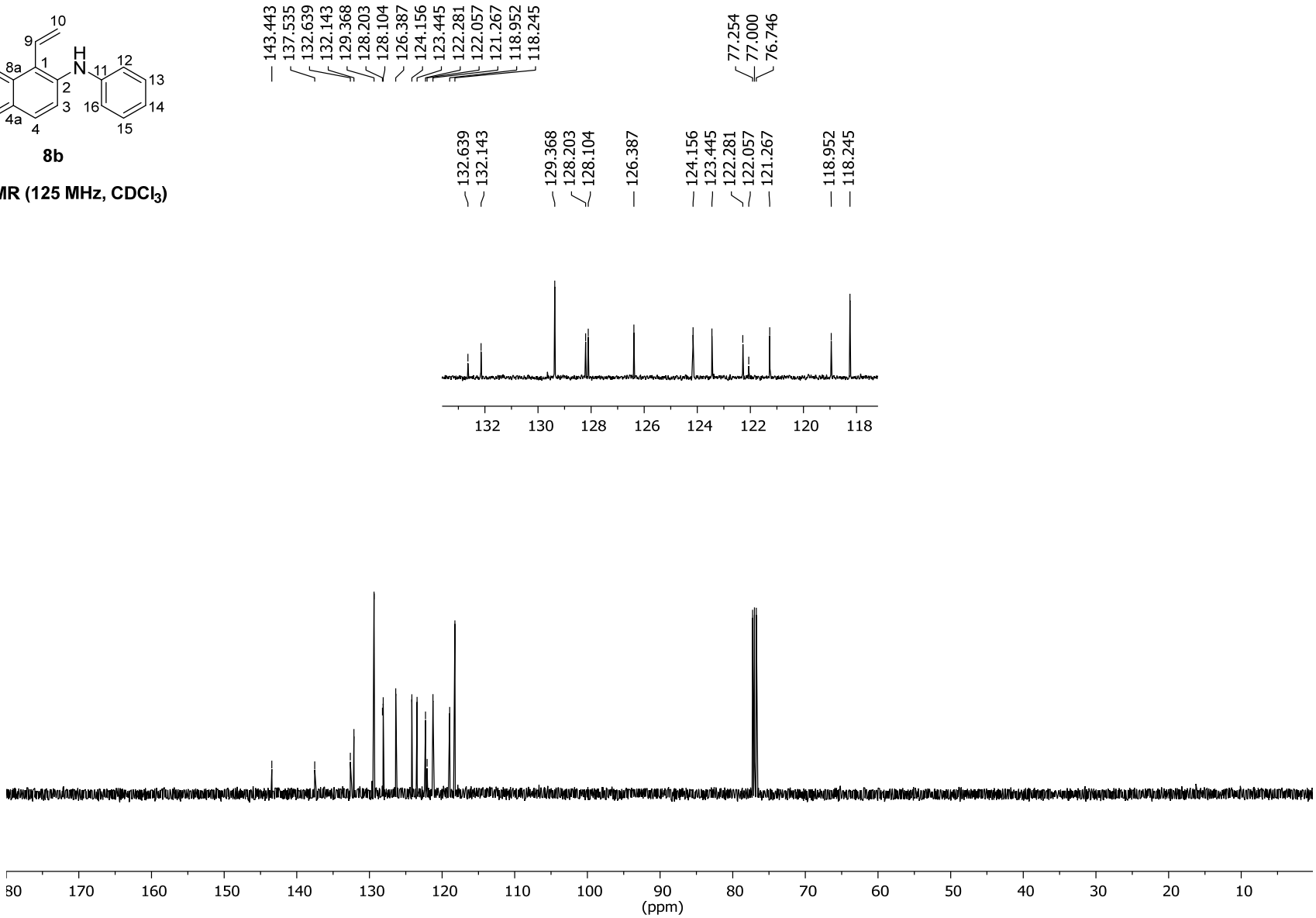
^{1}H-NMR (500 MHz, $CDCl_3$)

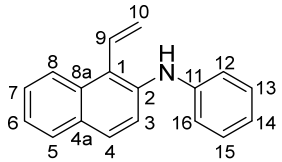




8b

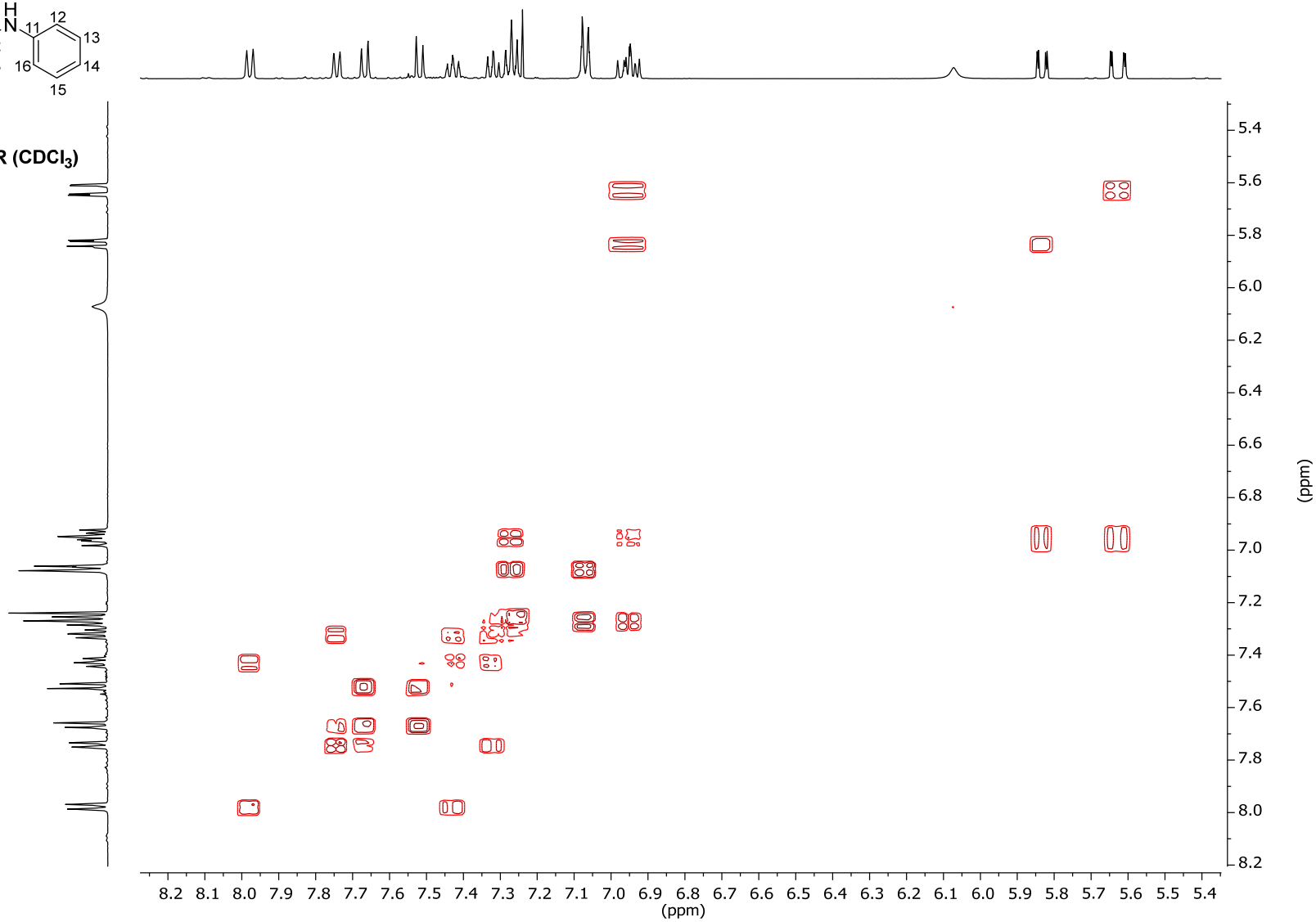
^{13}C-NMR (125 MHz, $CDCl_3$)

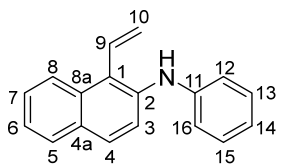




8b

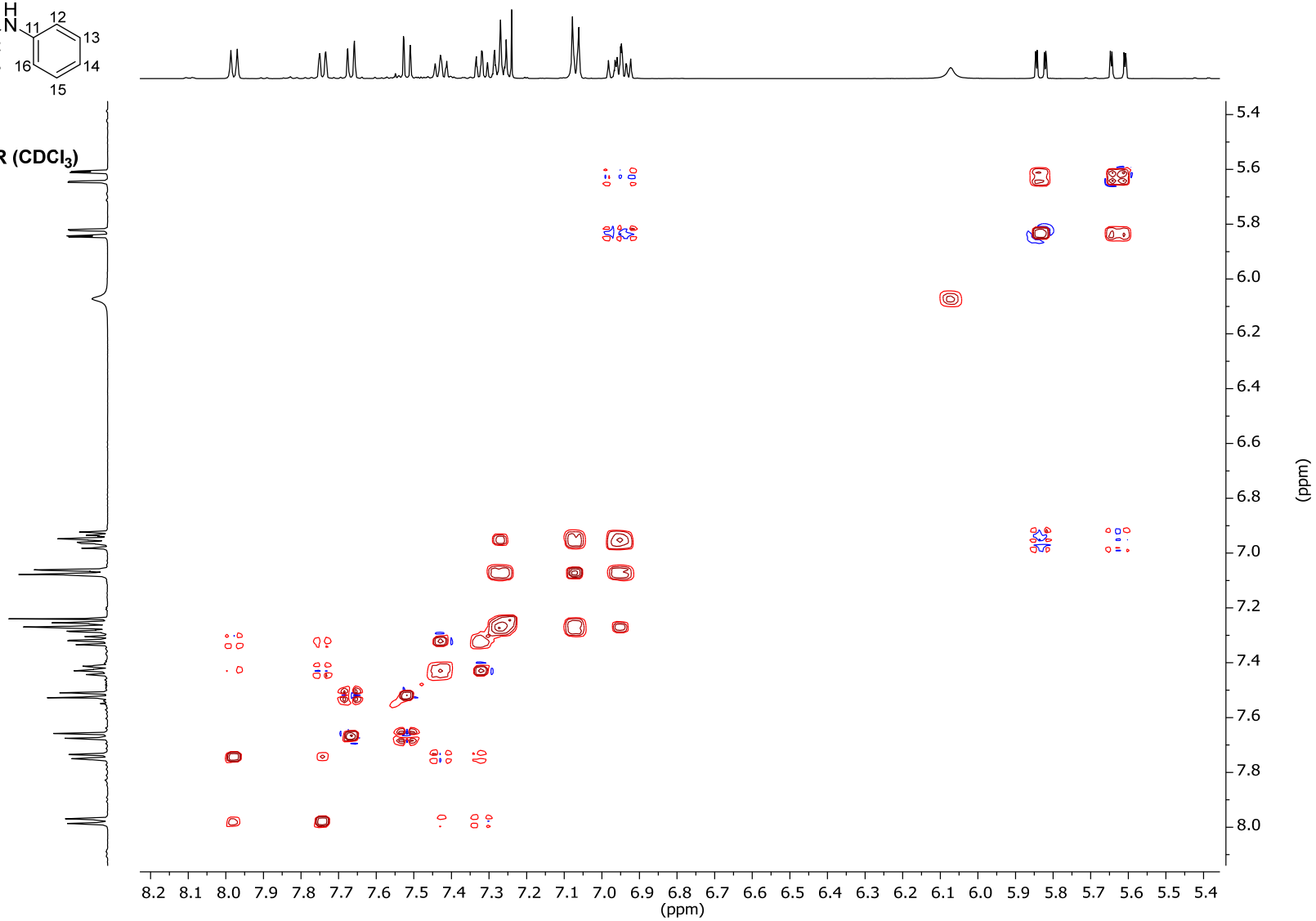
gCOSY-NMR ($CDCl_3$)

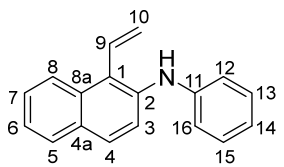




8b

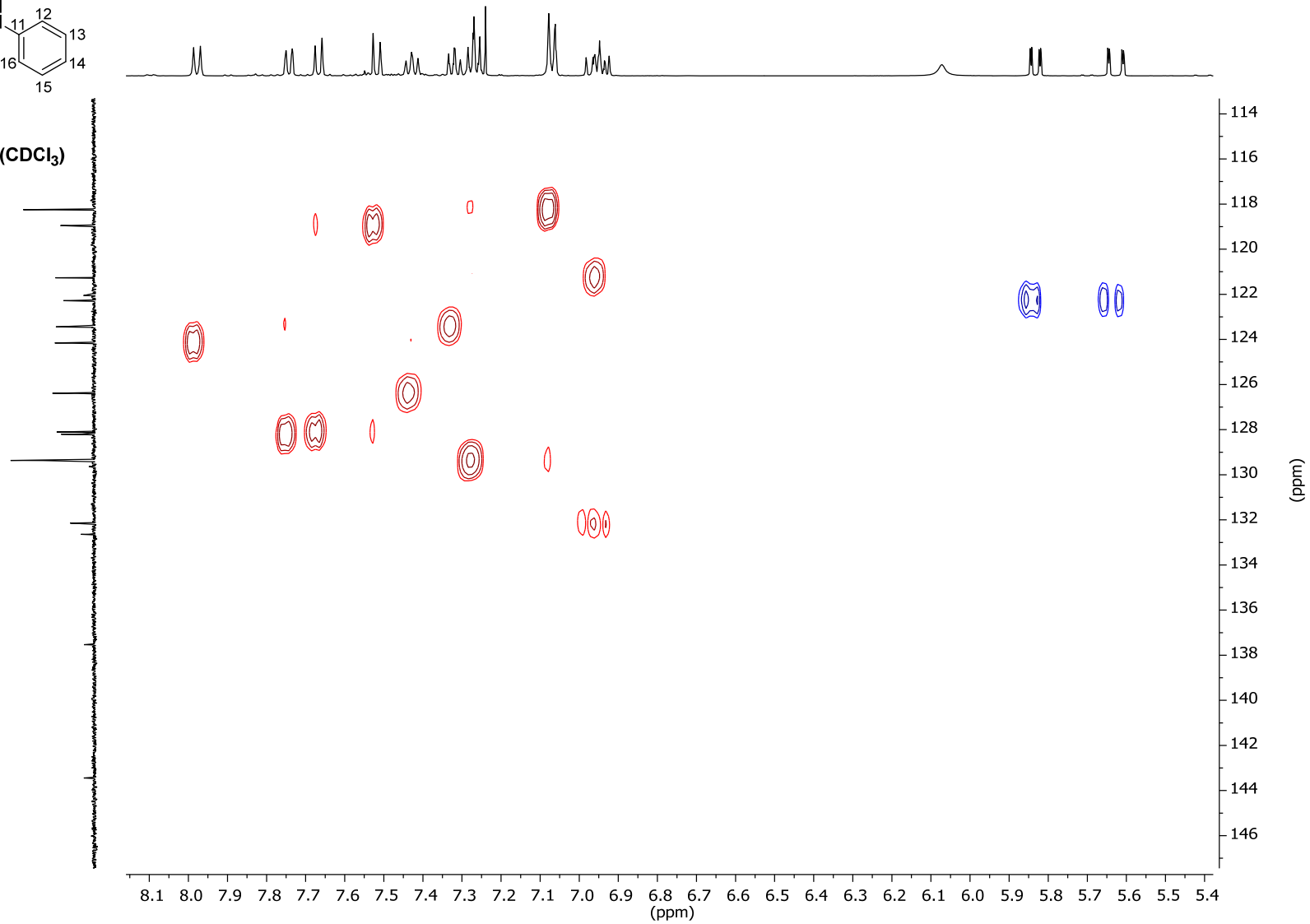
TOCSY-NMR ($CDCl_3$)

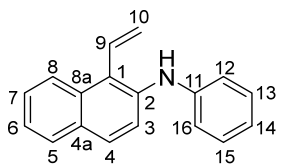




8b

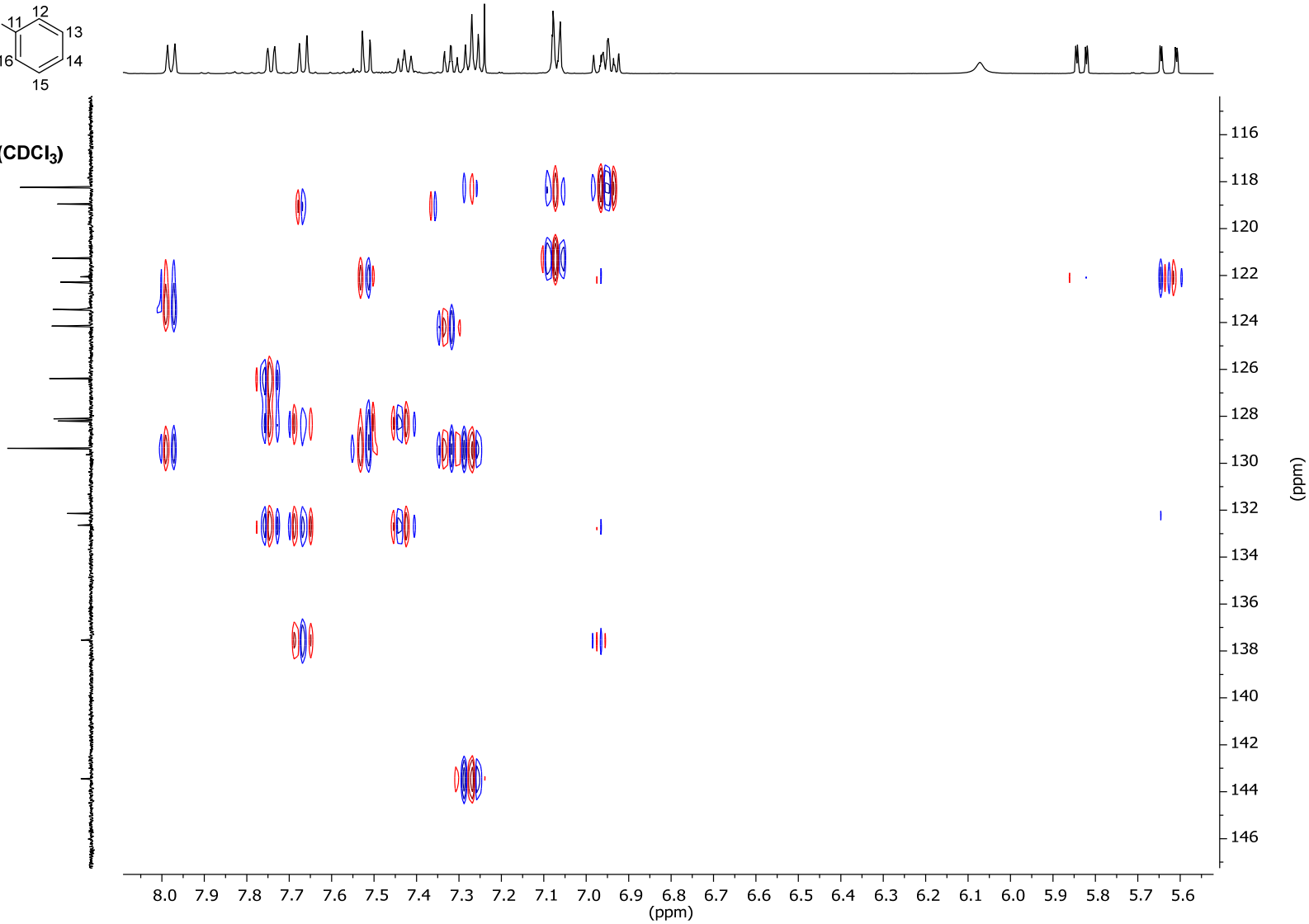
gHSQC-NMR ($CDCl_3$)

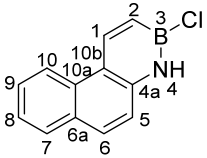




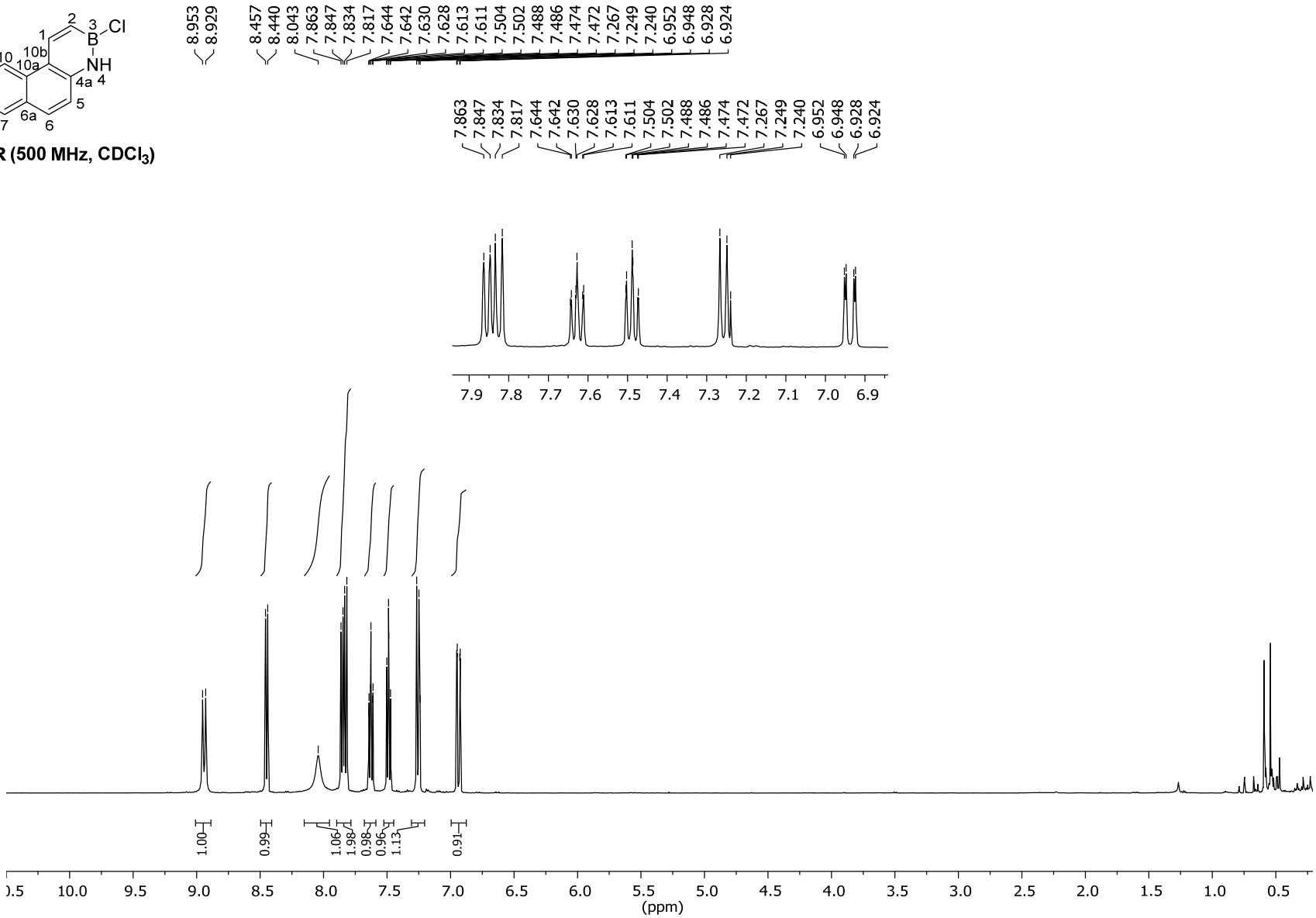
8b

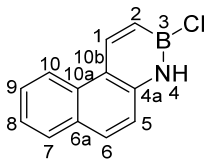
gHMBC-NMR ($CDCl_3$)



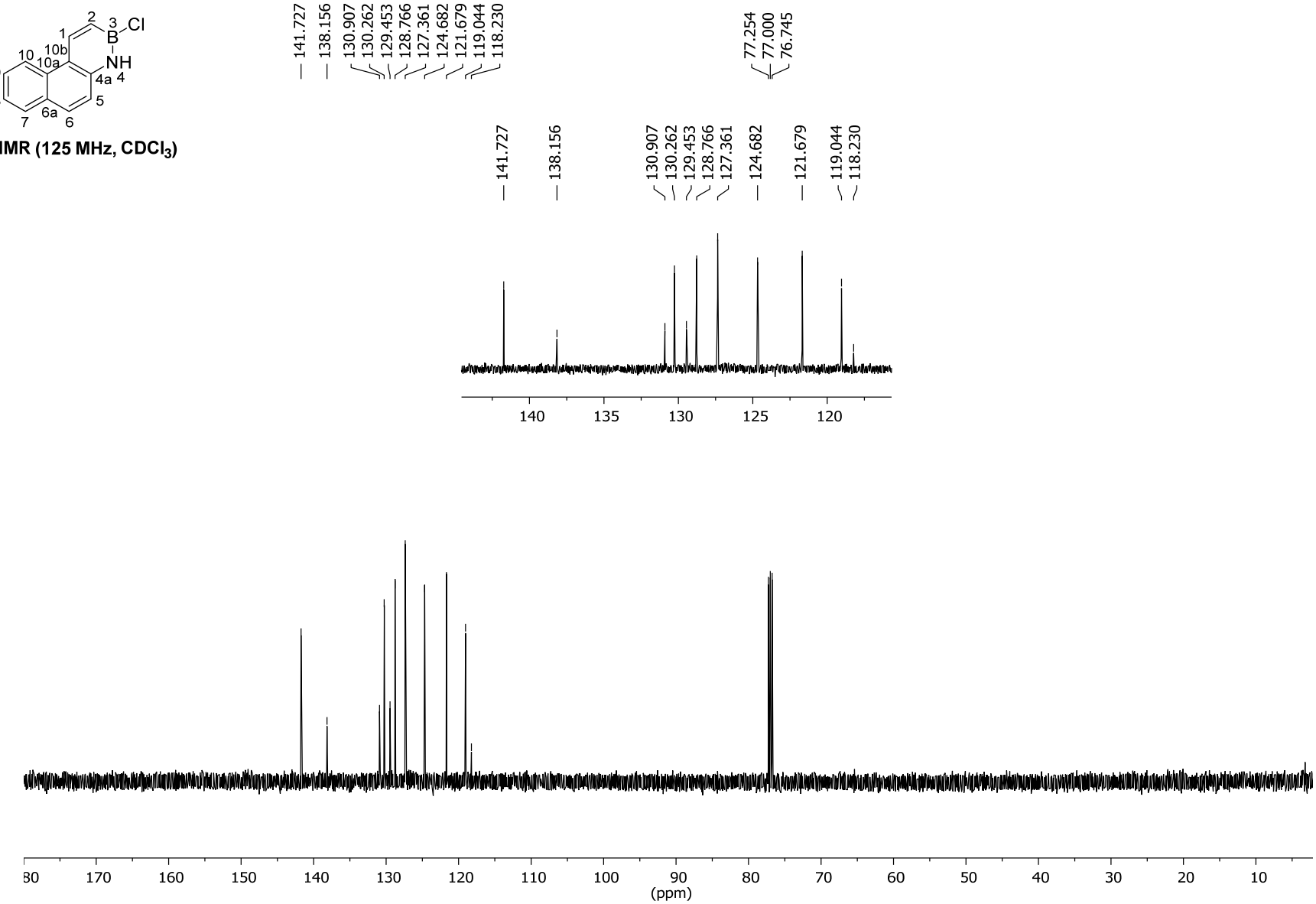


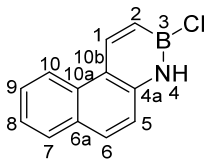
^{1}H-NMR (500 MHz, $CDCl_3$)



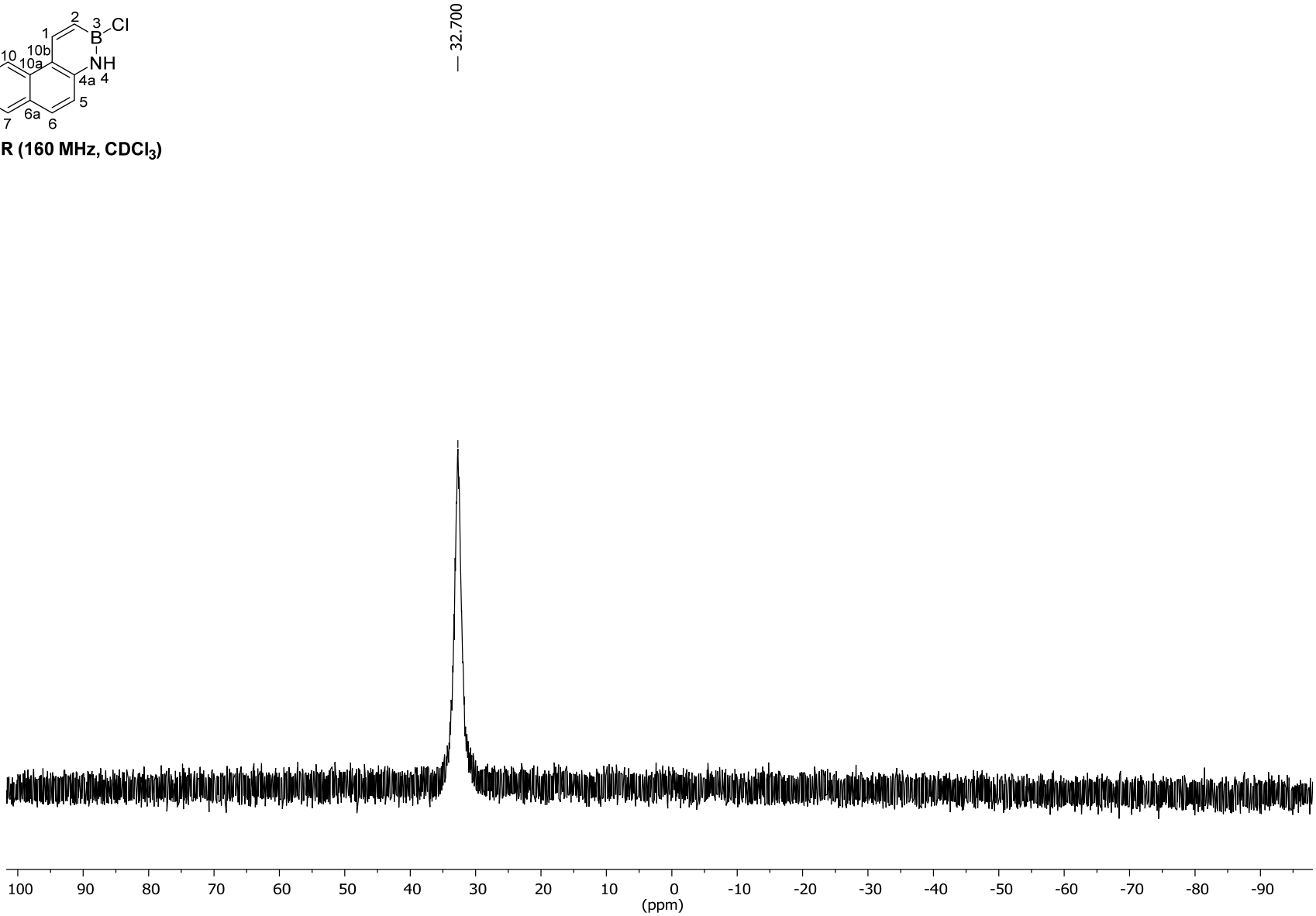


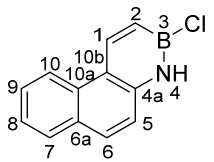
^{13}C-NMR (125 MHz, $CDCl_3$)



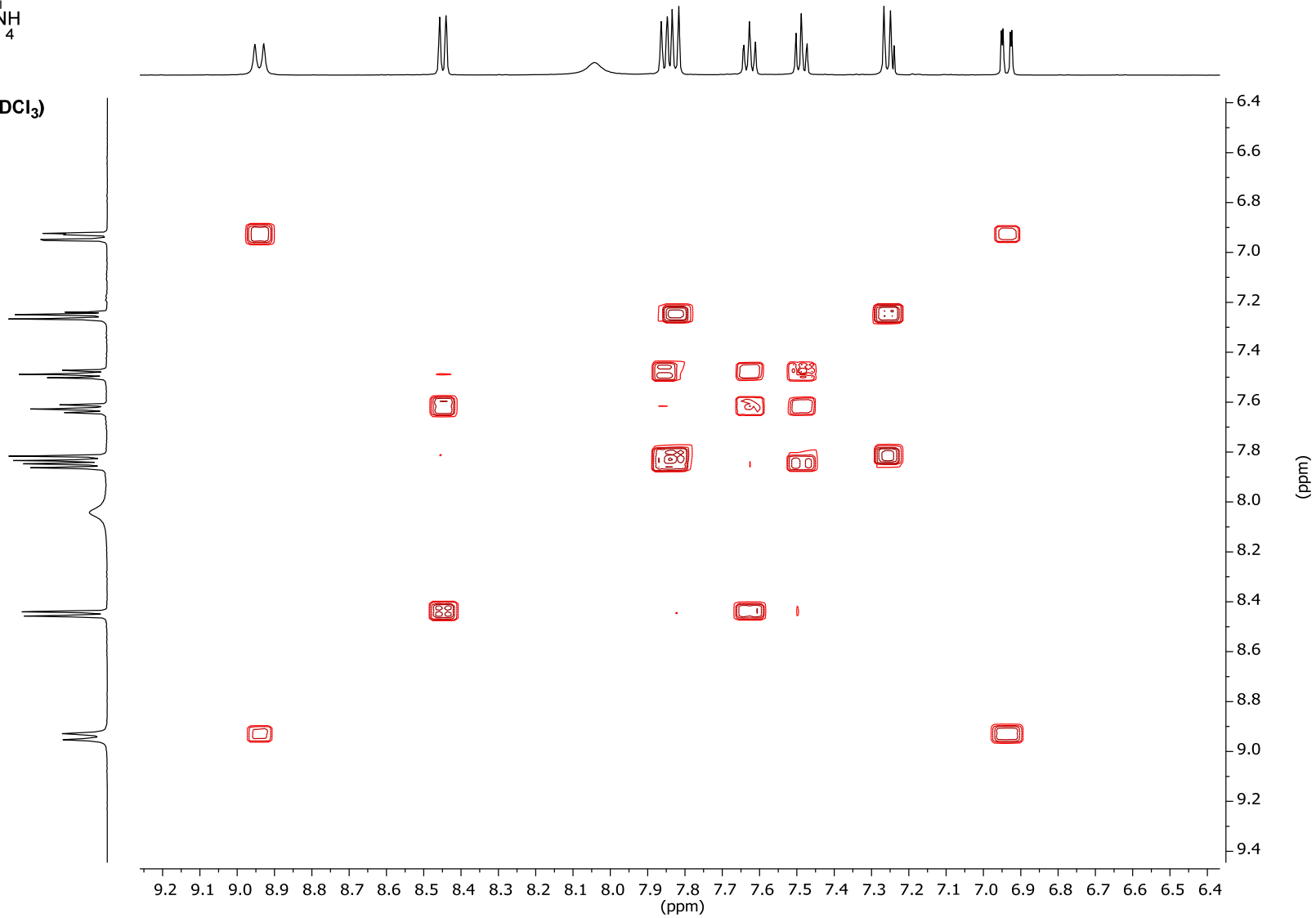


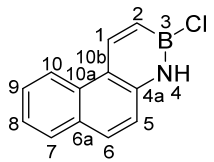
^{11}B-NMR (160 MHz, $CDCl_3$)



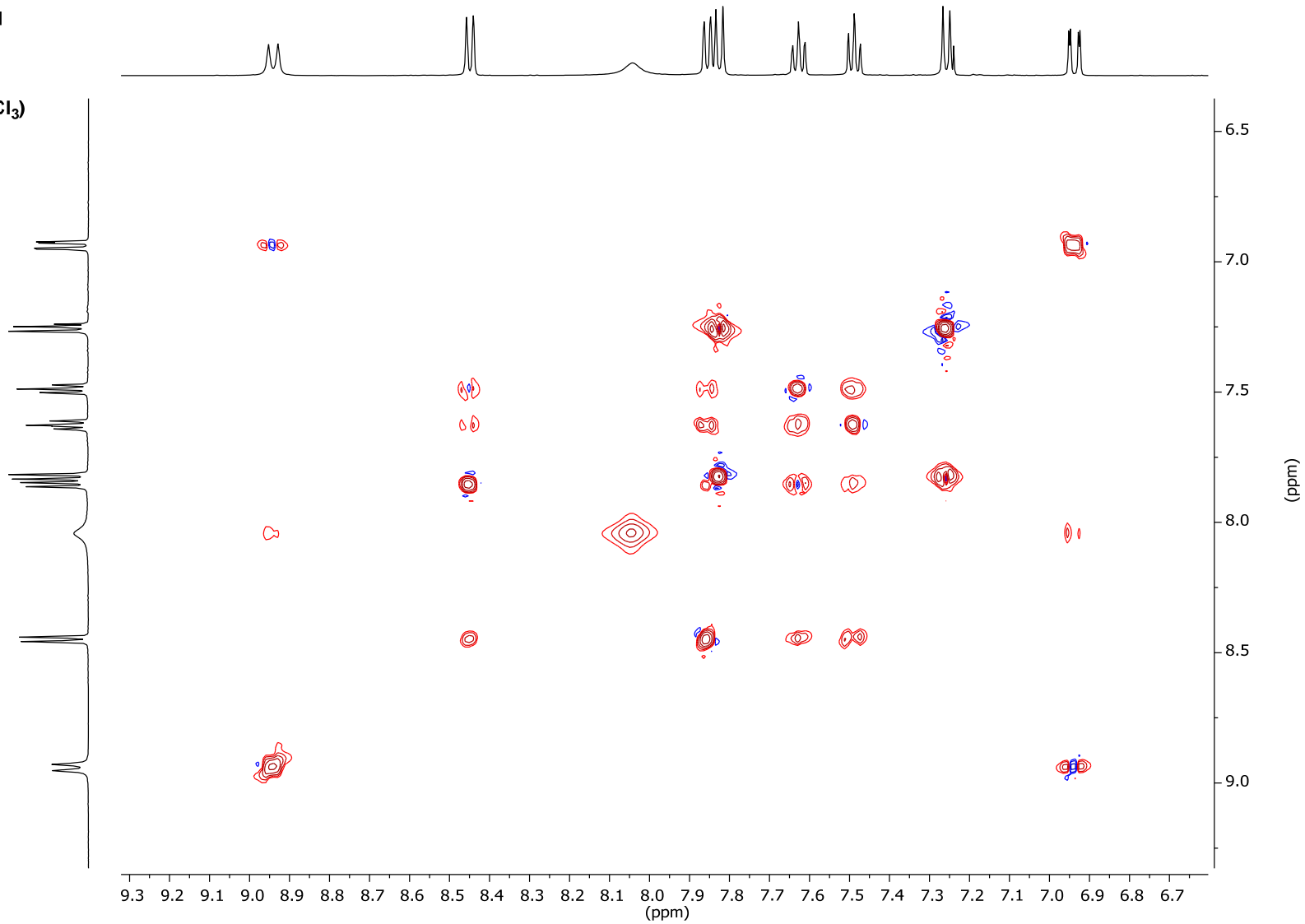


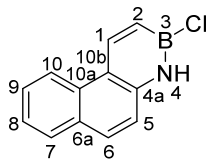
gCOSY-NMR ($CDCl_3$)



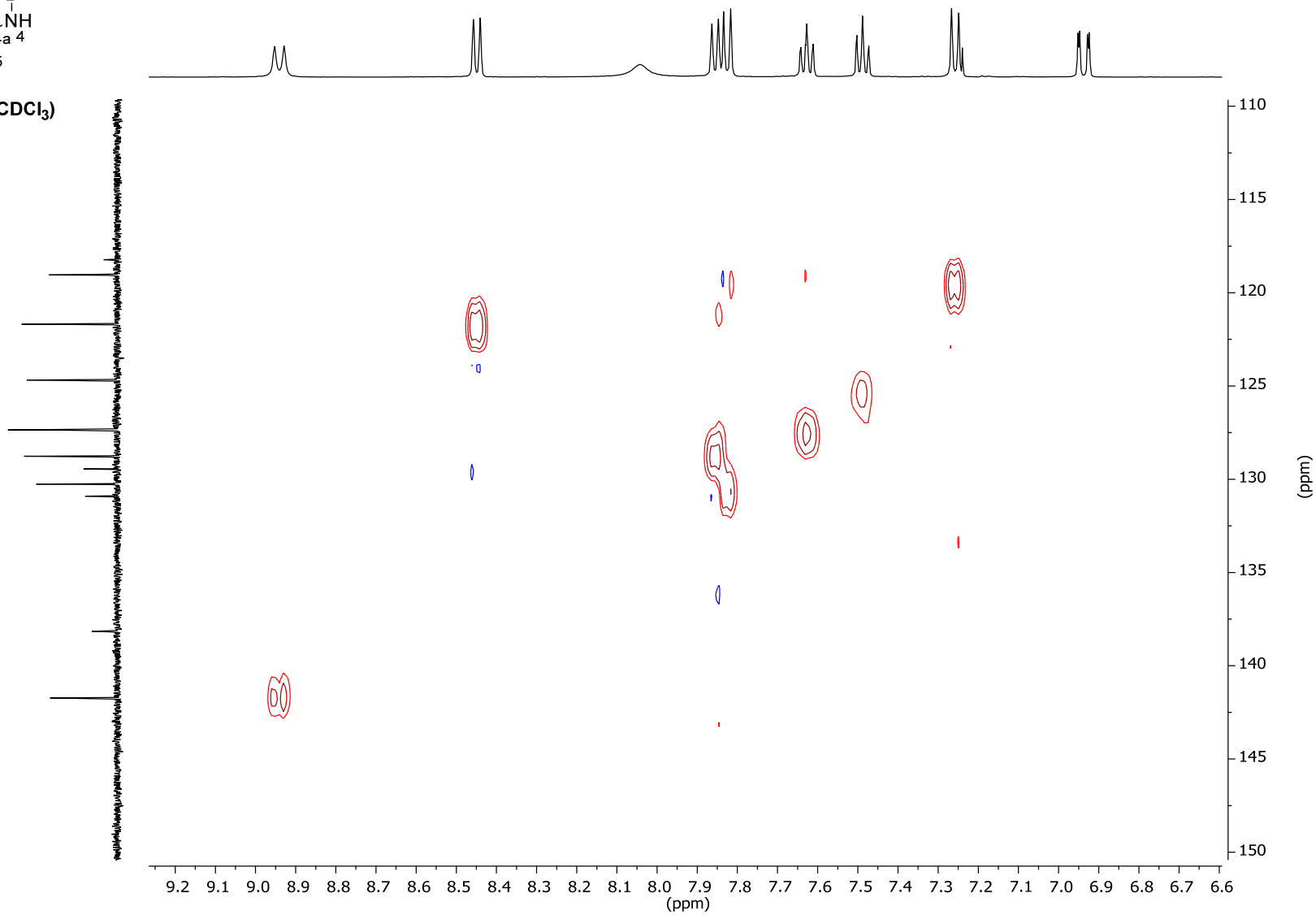


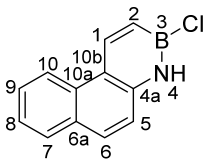
TOCSY-NMR ($CDCl_3$)



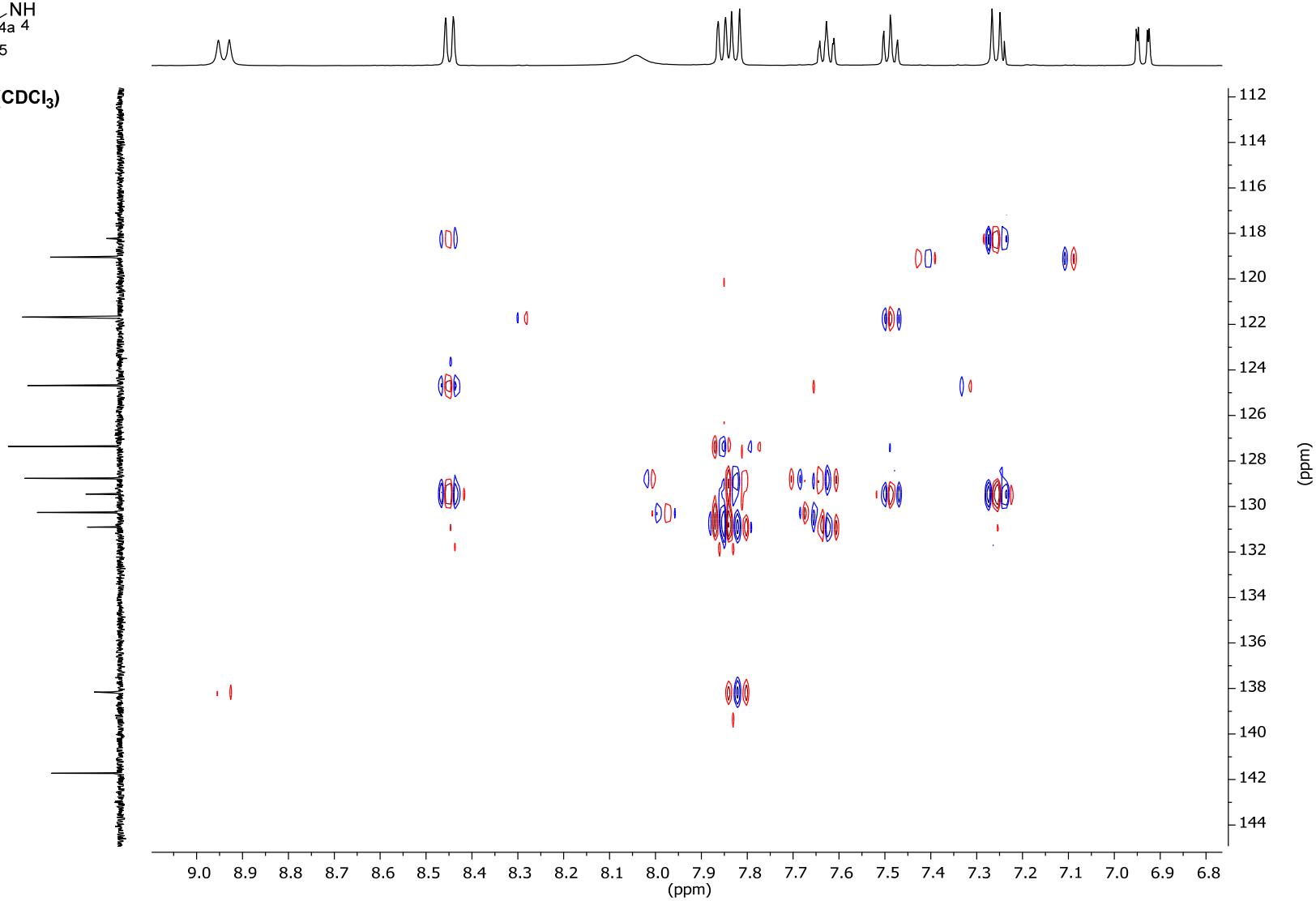


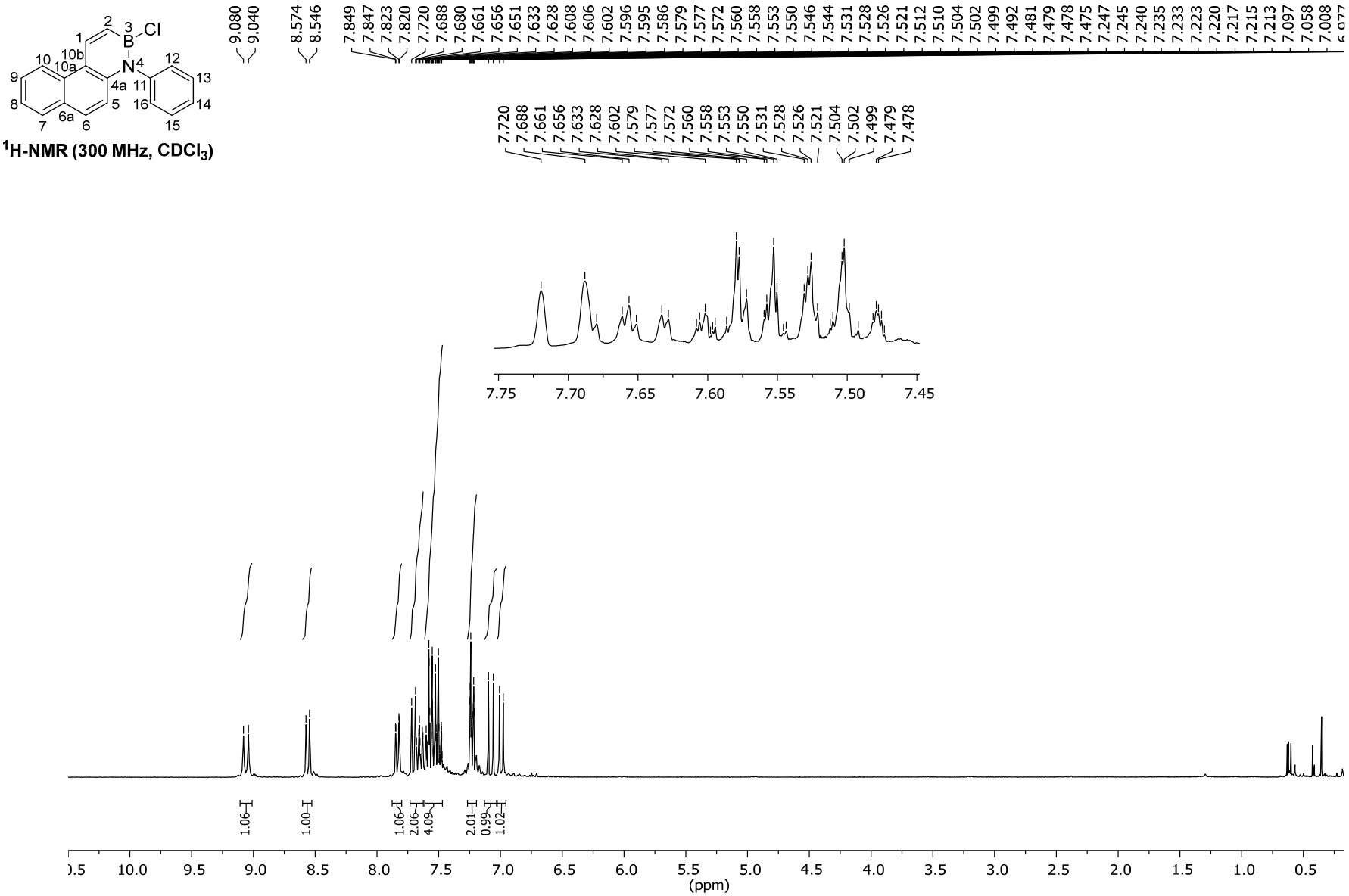
gHSQC-NMR ($CDCl_3$)

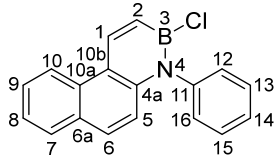




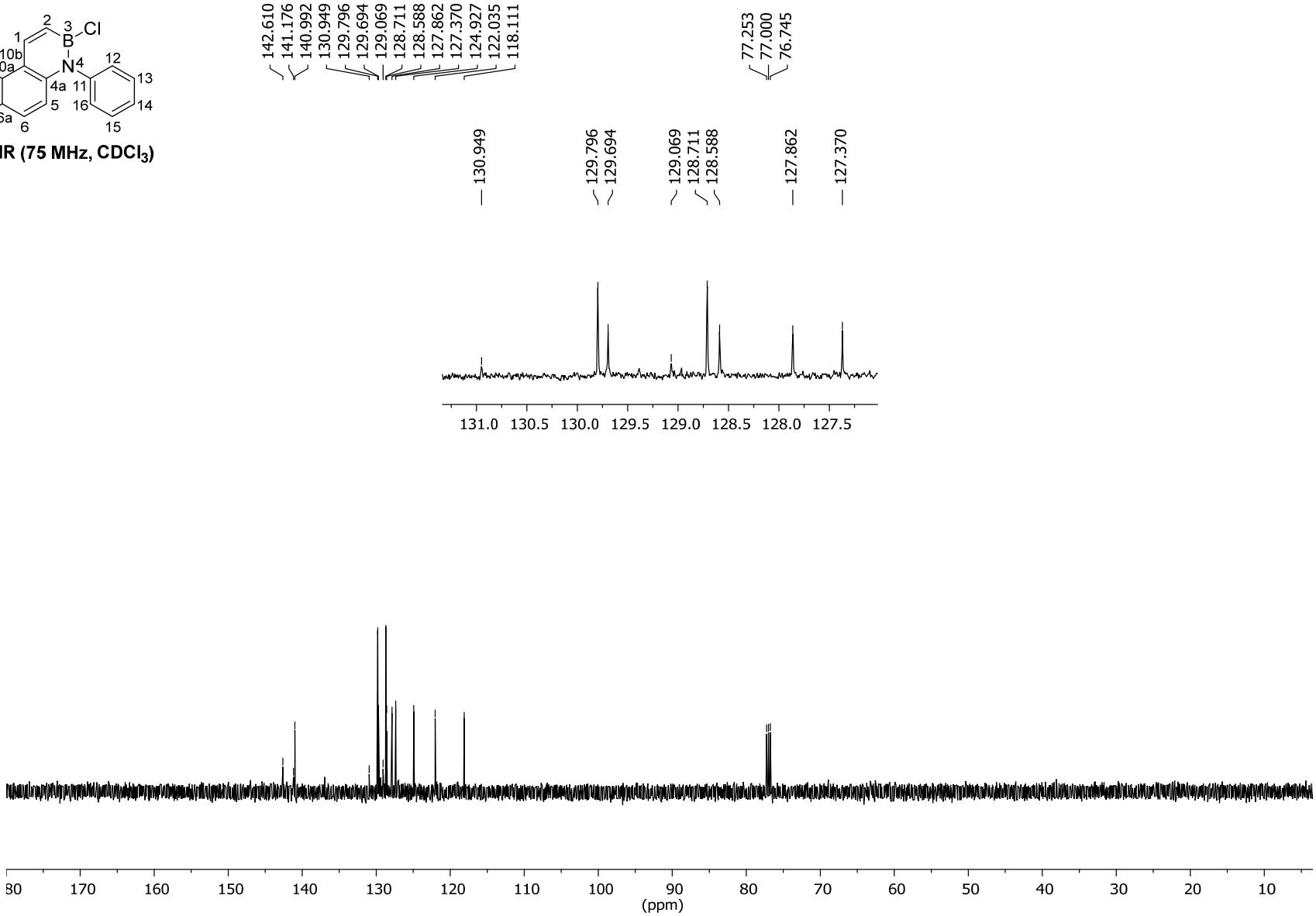
gHMBC-NMR ($CDCl_3$)

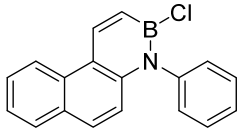



1H-NMR (300 MHz, CDCl3)
9.080
9.040
8.574
8.546
7.849
7.847
7.823
7.820
7.720
7.688
7.680
7.661
7.656
7.651
7.633
7.628
7.608
7.606
7.602
7.596
7.595
7.586
7.579
7.577
7.572
7.560
7.558
7.553
7.550
7.546
7.544
7.531
7.528
7.526
7.521
7.512
7.510
7.504
7.502
7.499
7.492
7.481
7.479
7.478
7.475
7.247
7.245
7.240
7.235
7.233
7.223
7.220
7.217
7.215
7.213
7.097
7.058
7.008
7.720
7.688
7.661
7.656
7.633
7.628
7.602
7.579
7.577
7.572
7.560
7.558
7.553
7.550
7.531
7.528
7.526
7.521
7.504
7.502
7.499
7.479
7.478
7.75
7.70
7.65
7.60
7.55
7.50
7.45
1.06
1.00
1.06
2.06
4.09
2.01
0.99
1.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

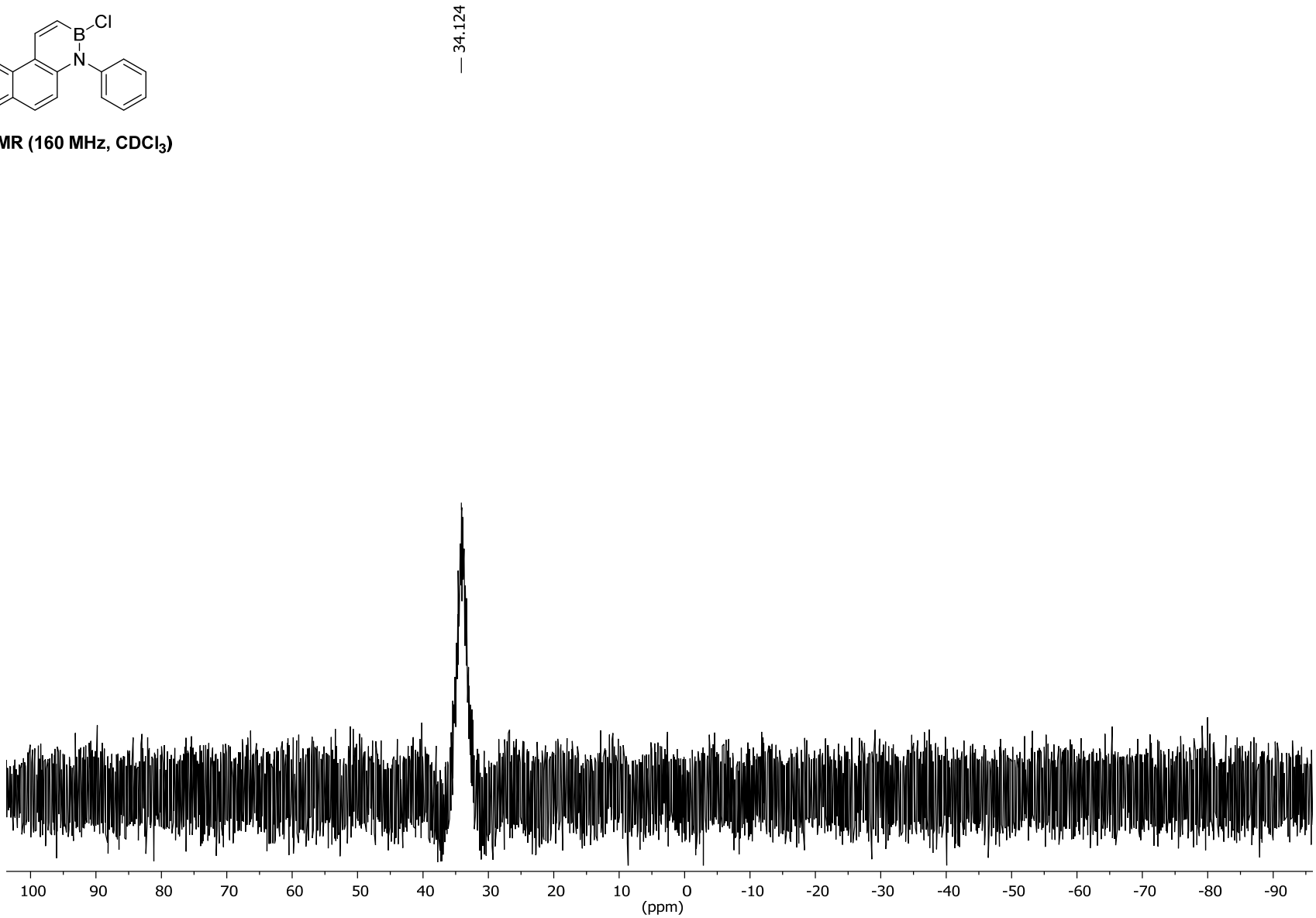


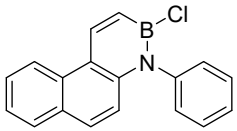
^{13}C-NMR (75 MHz, $CDCl_3$)



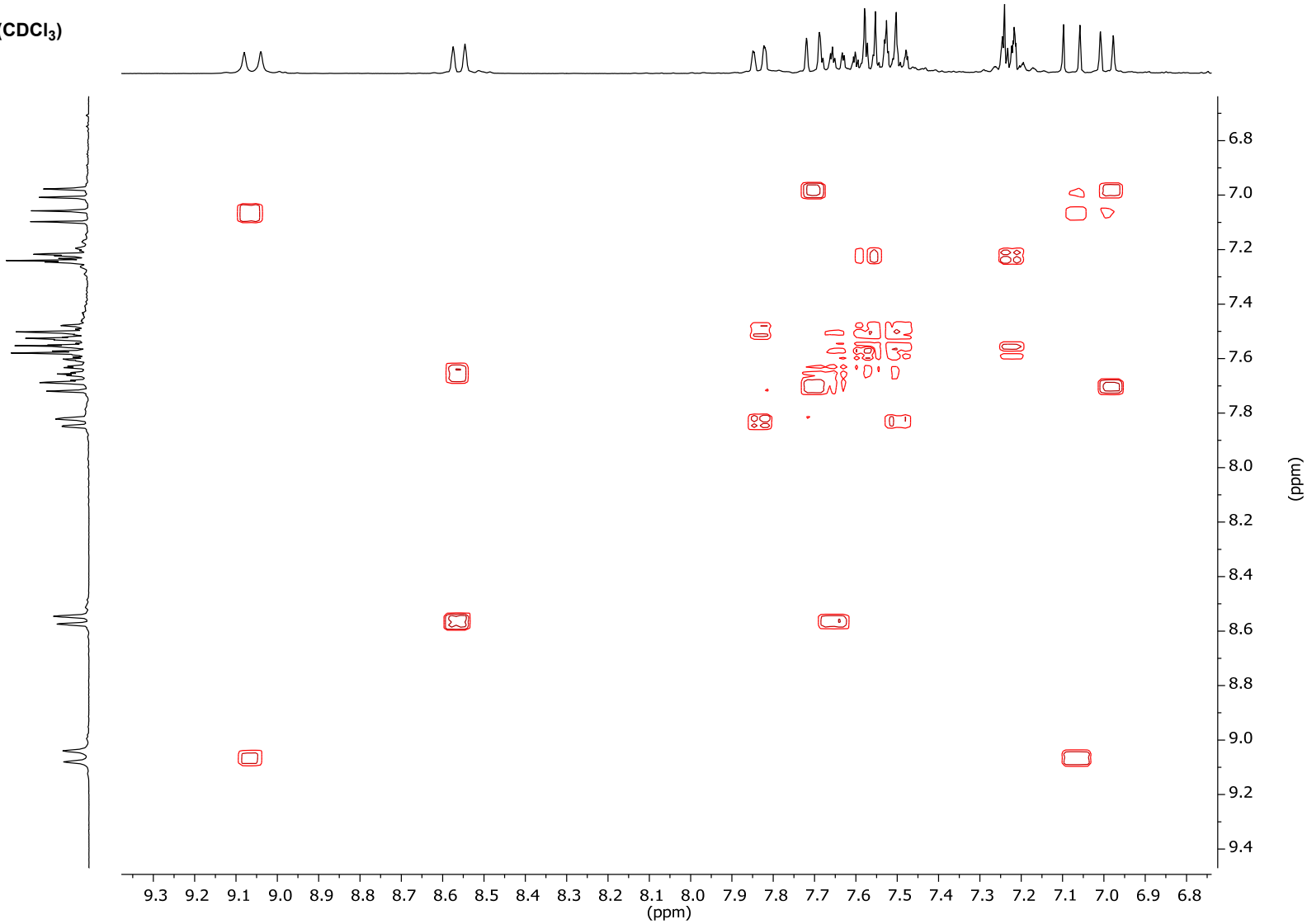


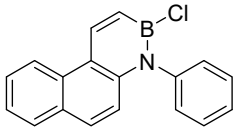
^{11}B-NMR (160 MHz, $CDCl_3$)



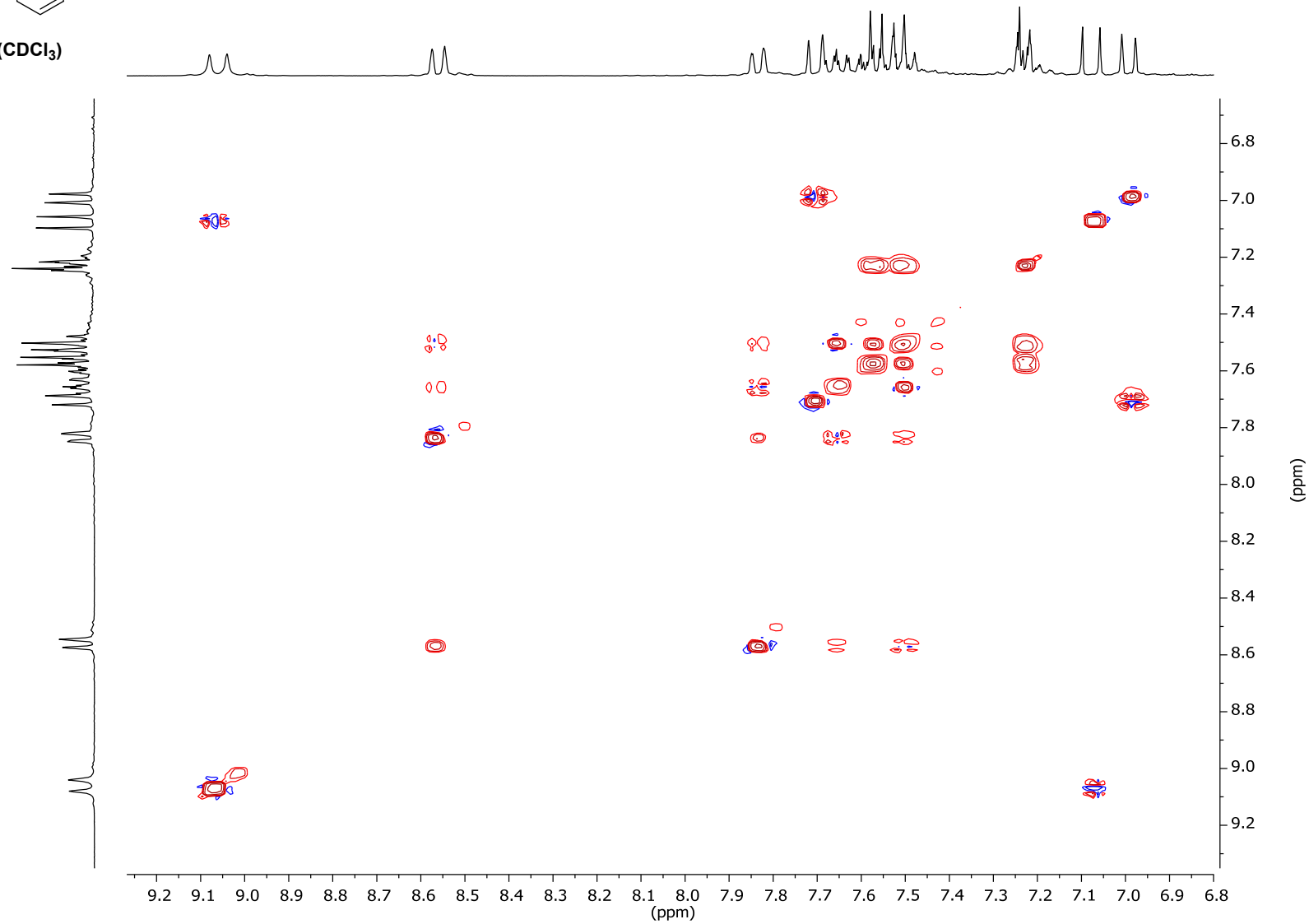


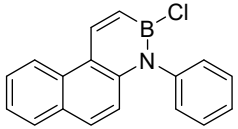
gCOSY-NMR ($CDCl_3$)



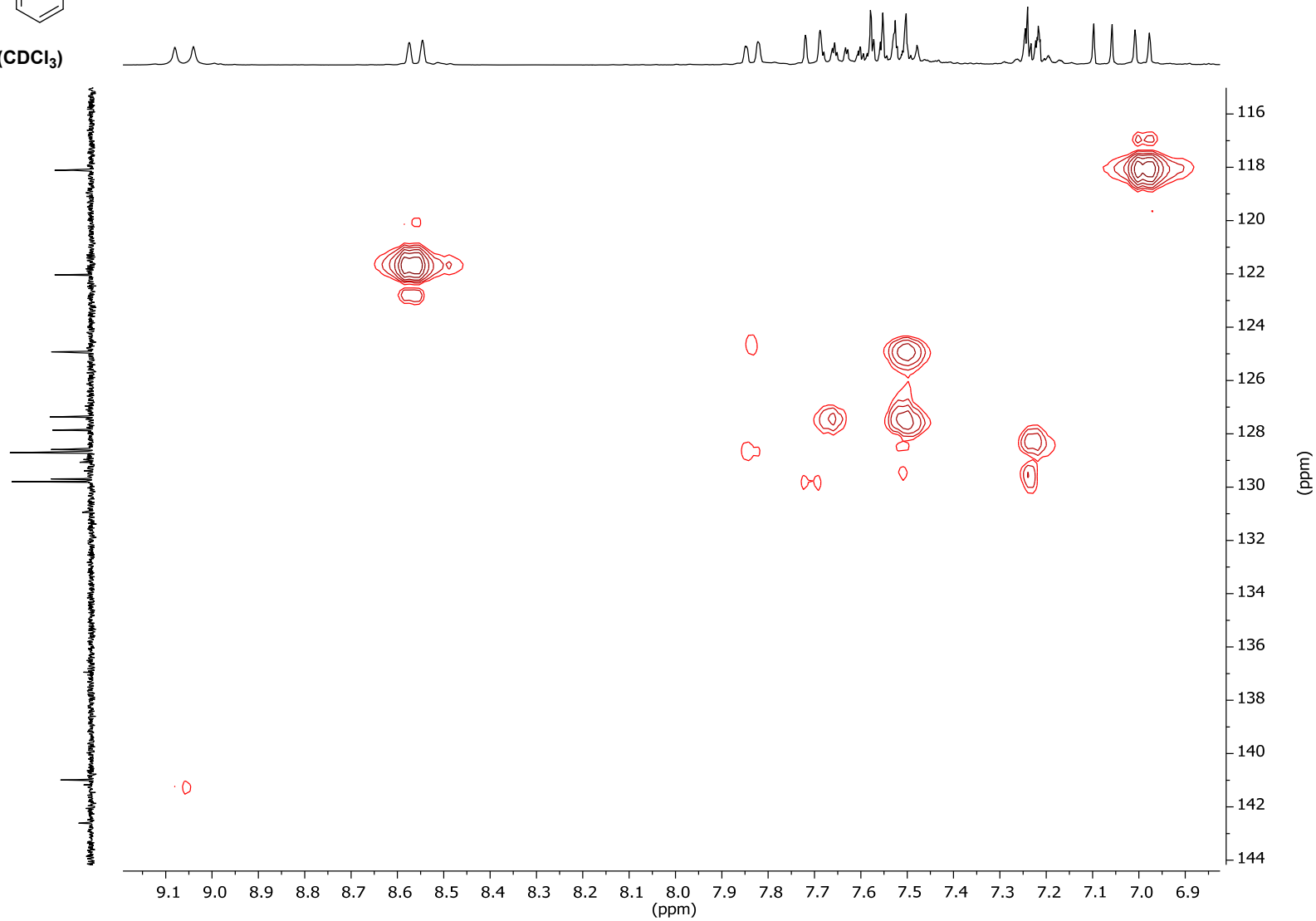


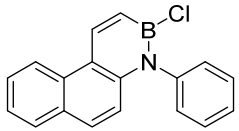
TOCSY-NMR ($CDCl_3$)



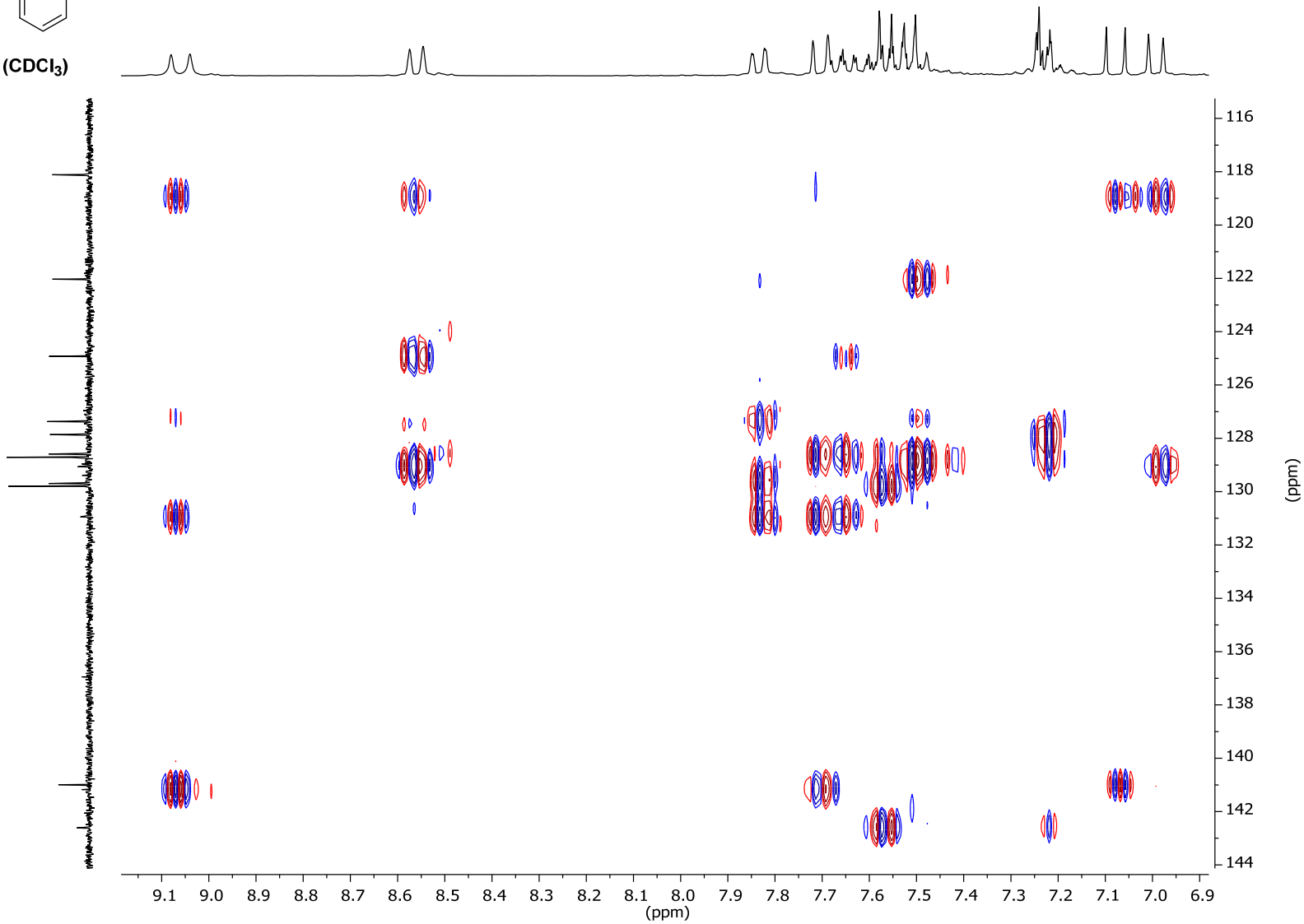


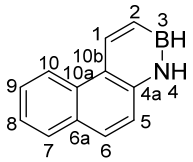
gHSQC-NMR ($CDCl_3$)





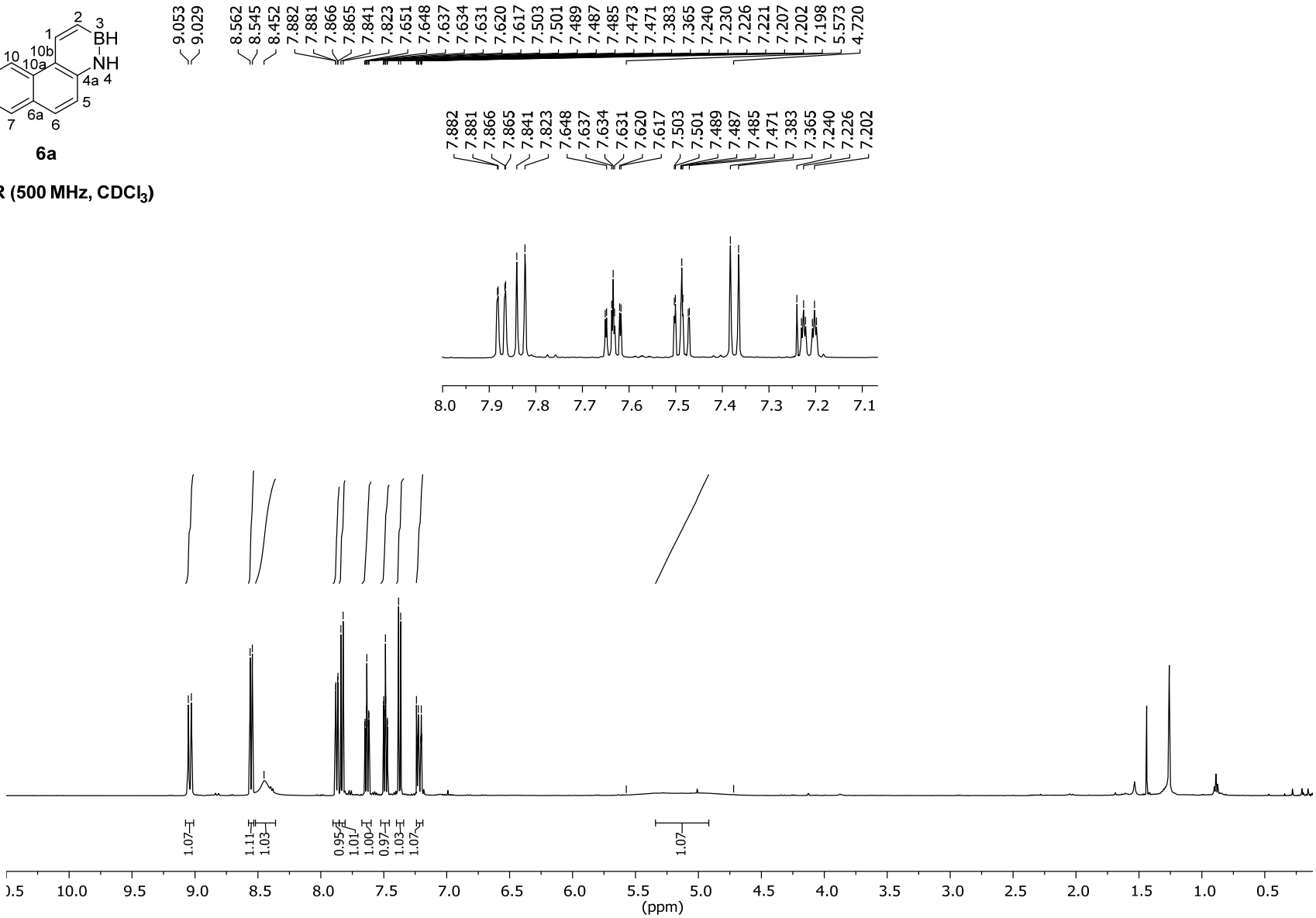
gHMBC-NMR ($CDCl_3$)

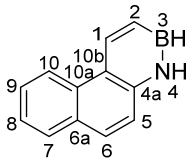




6a

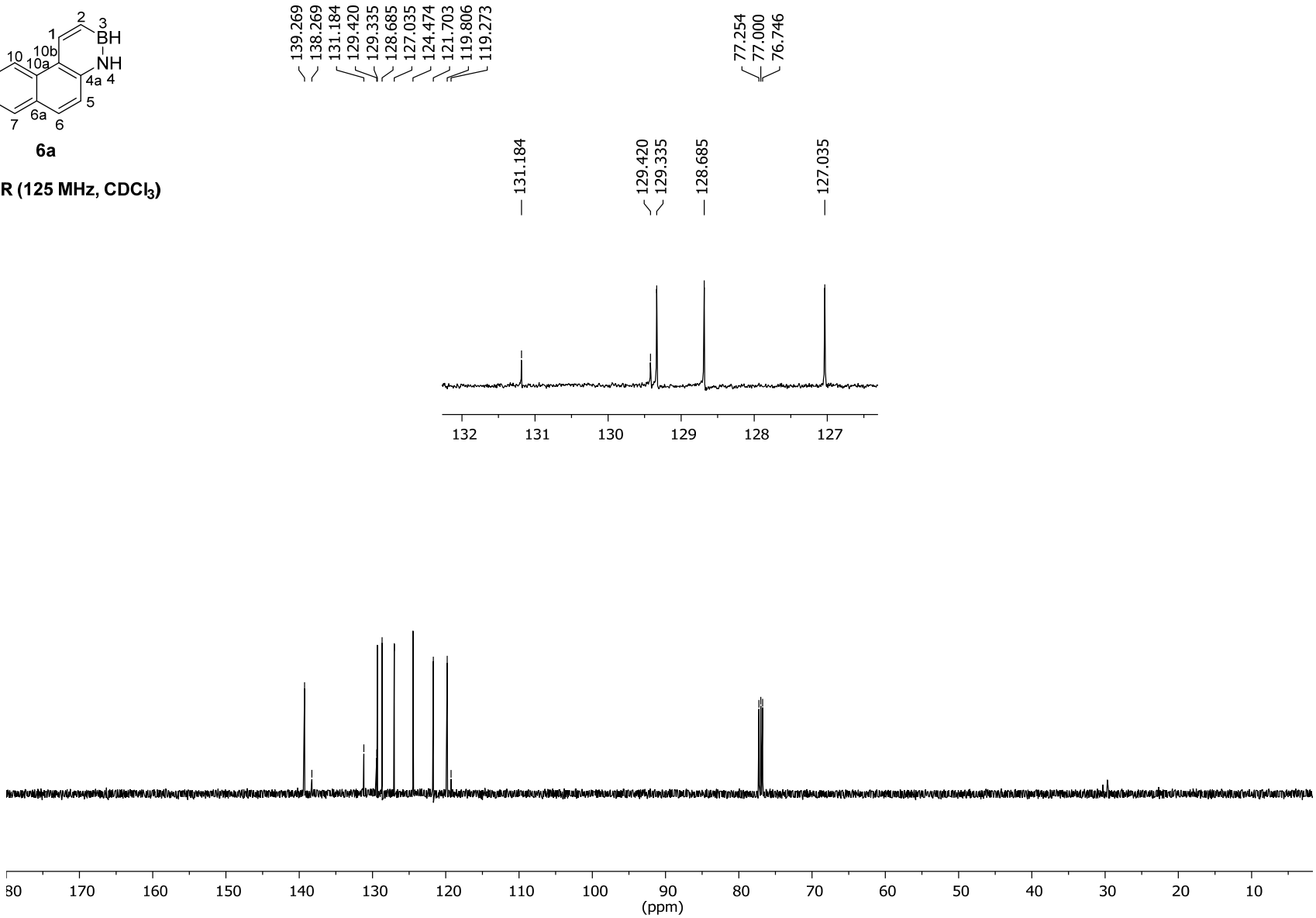
^{1}H-NMR (500 MHz, $CDCl_3$)

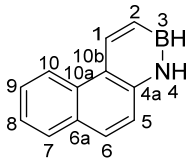




6a

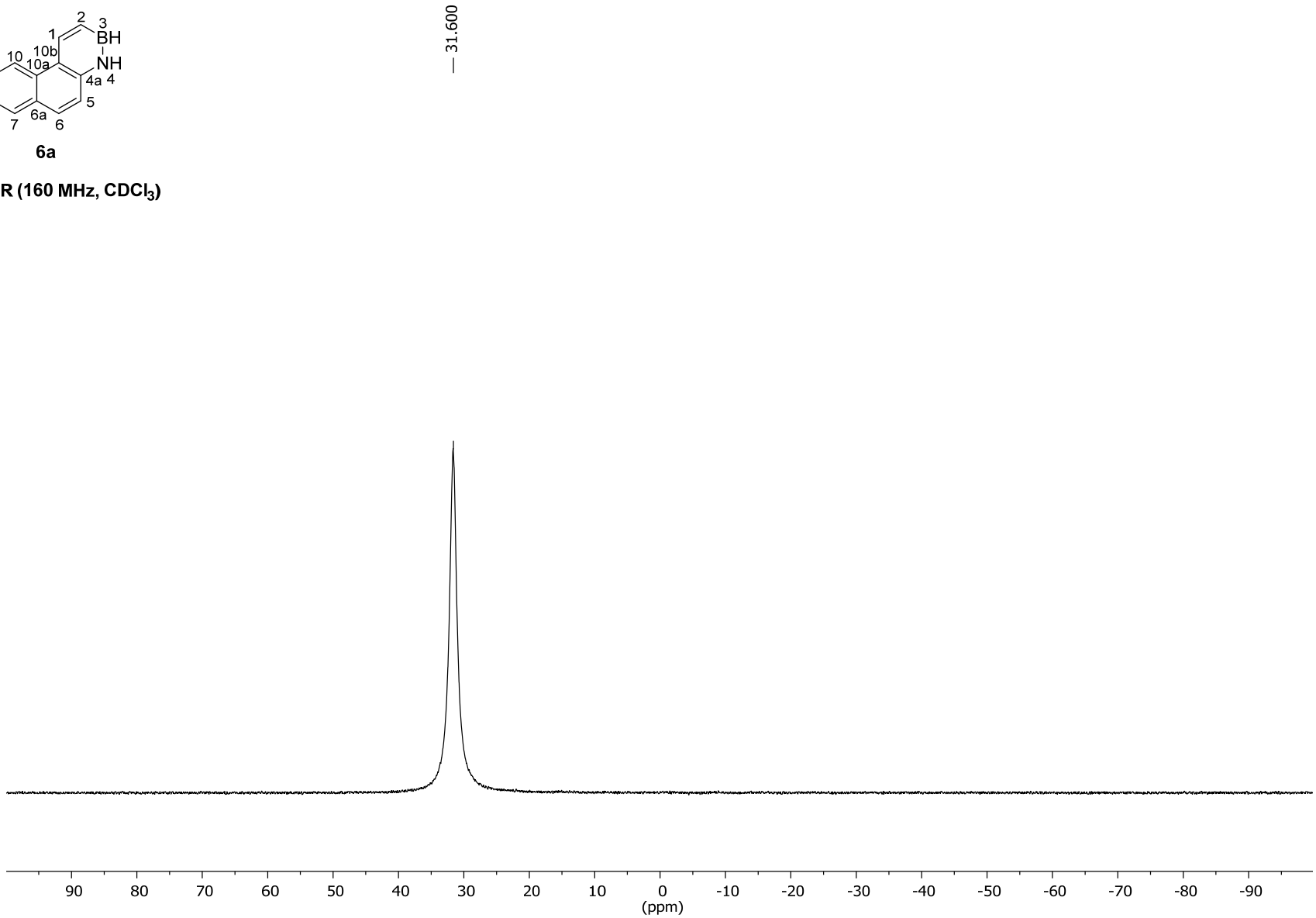
^{13}C-NMR (125 MHz, $CDCl_3$)

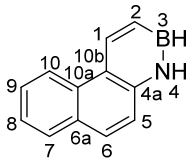




6a

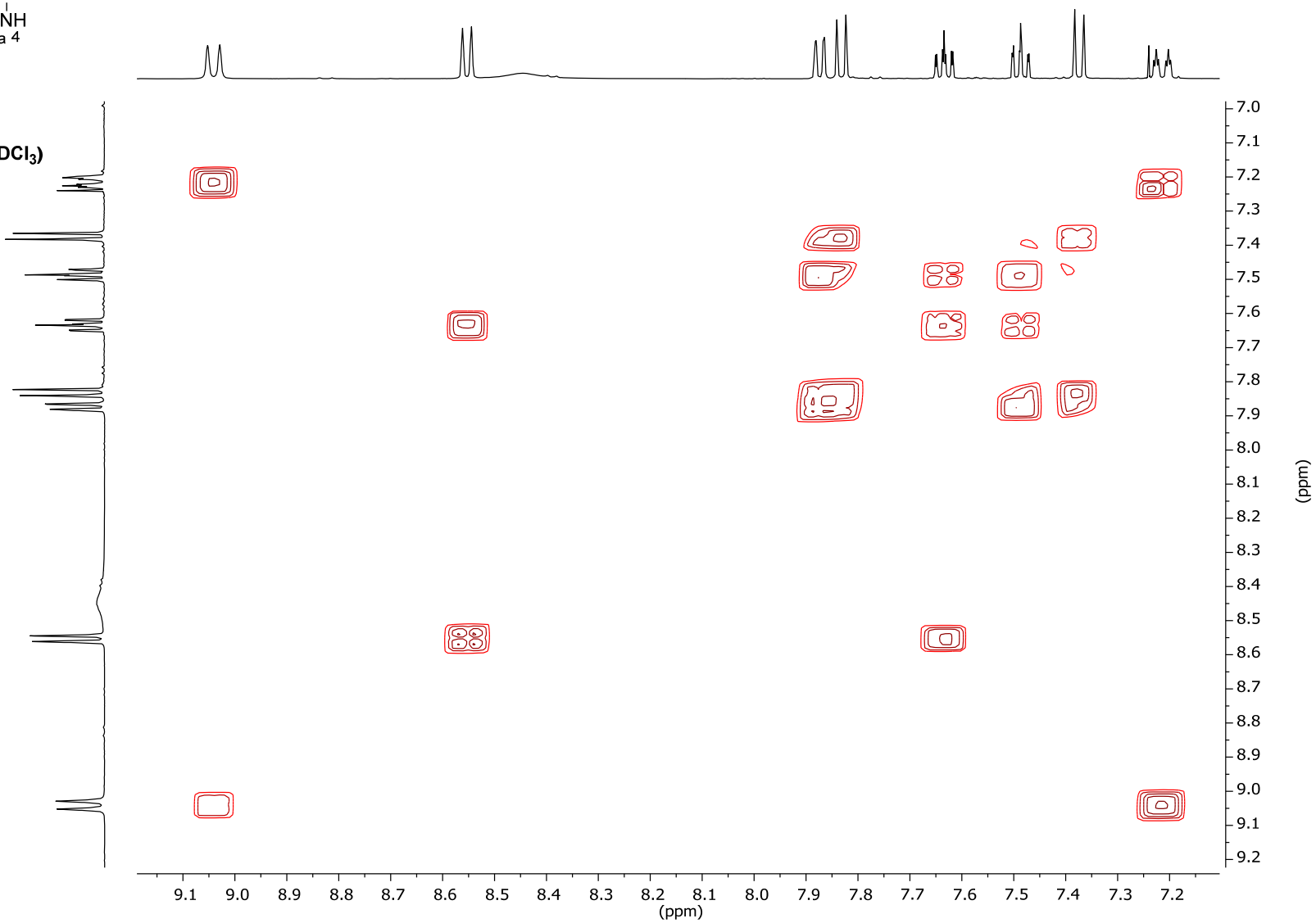
^{11}B-NMR (160 MHz, $CDCl_3$)

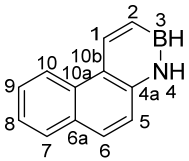




6a

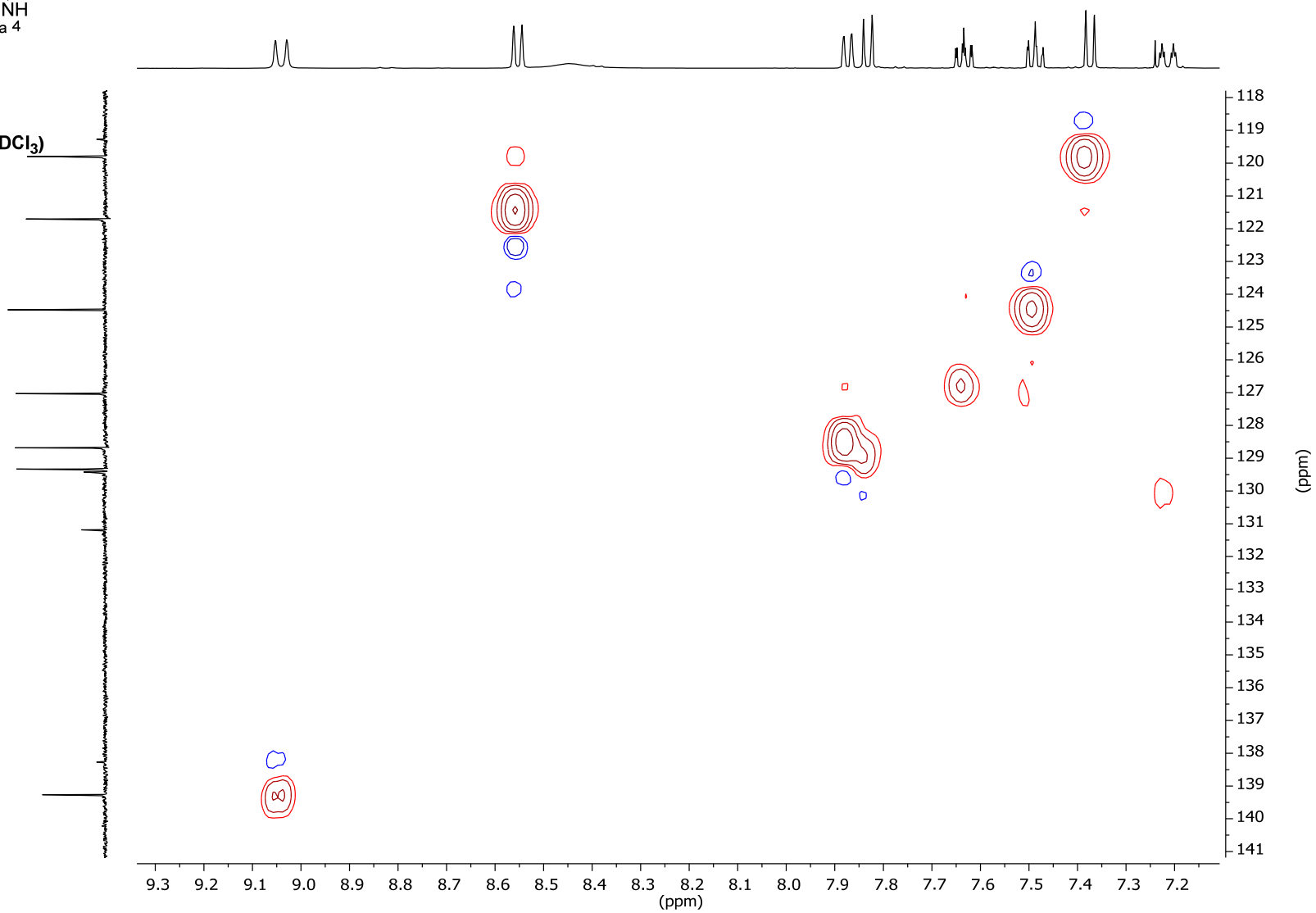
gCOSY-NMR ($CDCl_3$)

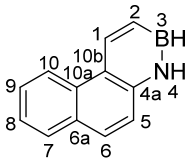




6a

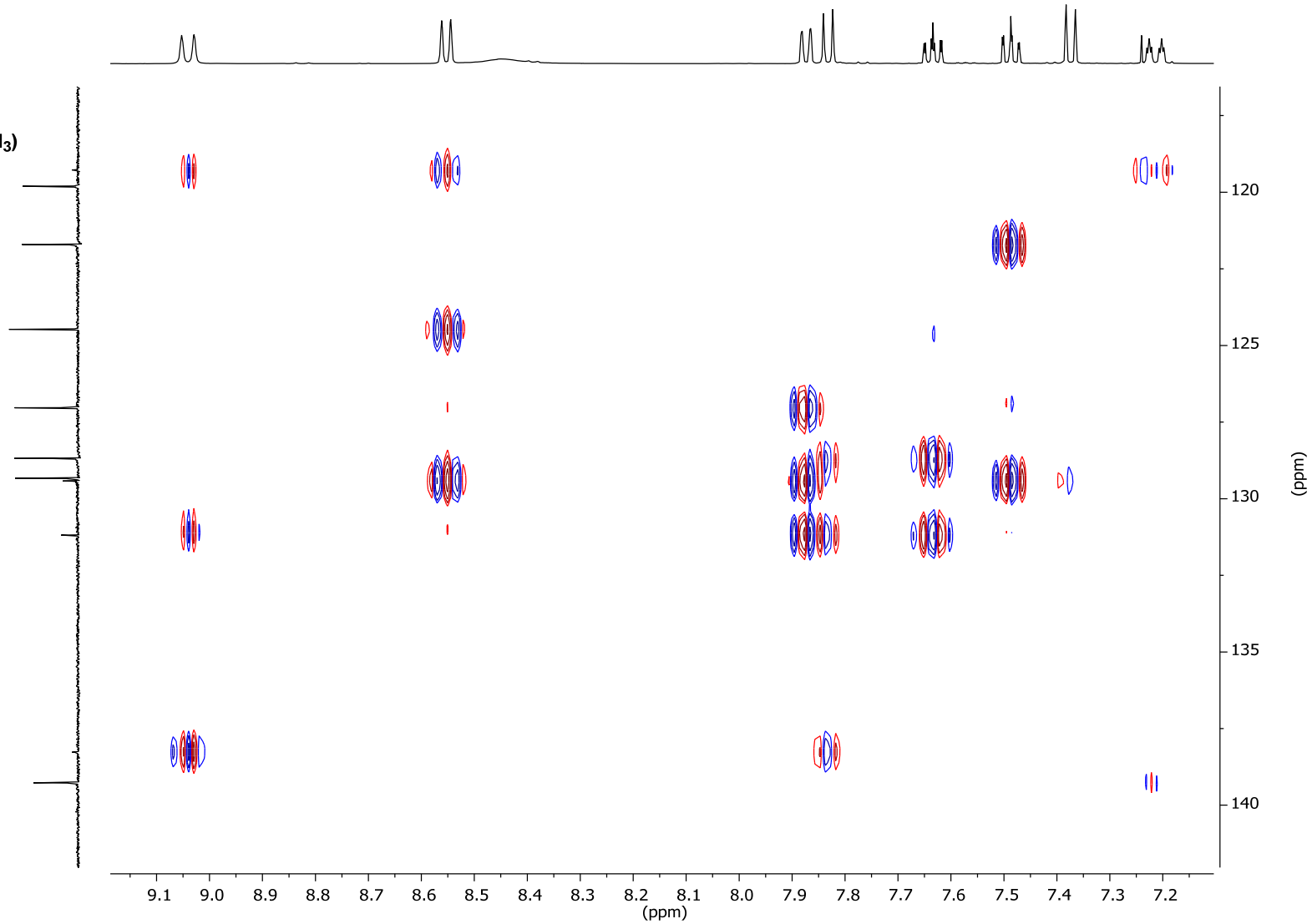
gHSQC-NMR ($CDCl_3$)

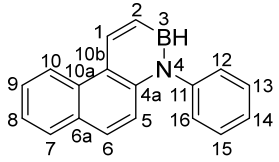




6a

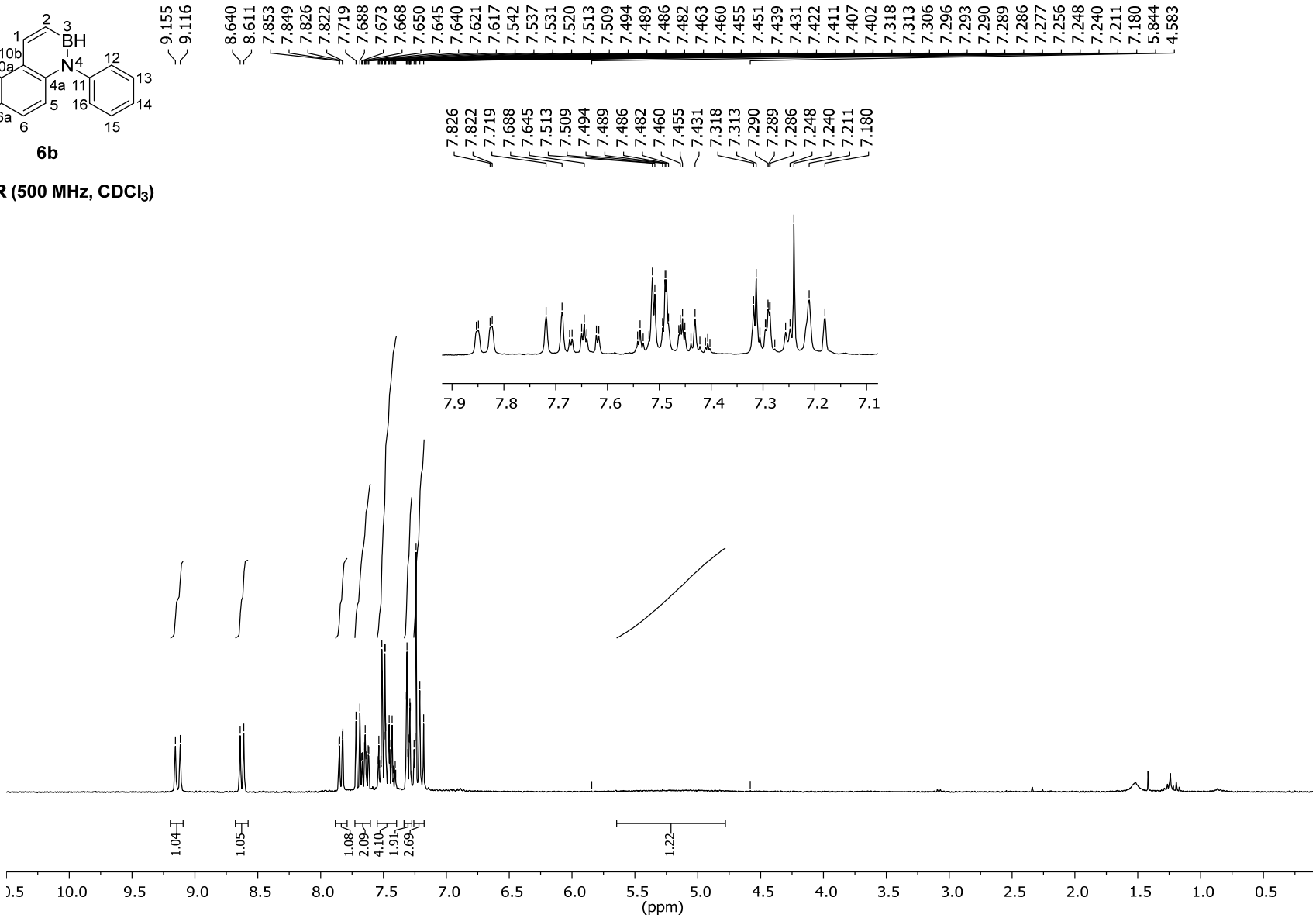
gHMBC-NMR ($CDCl_3$)

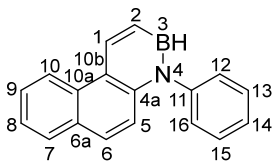




6b

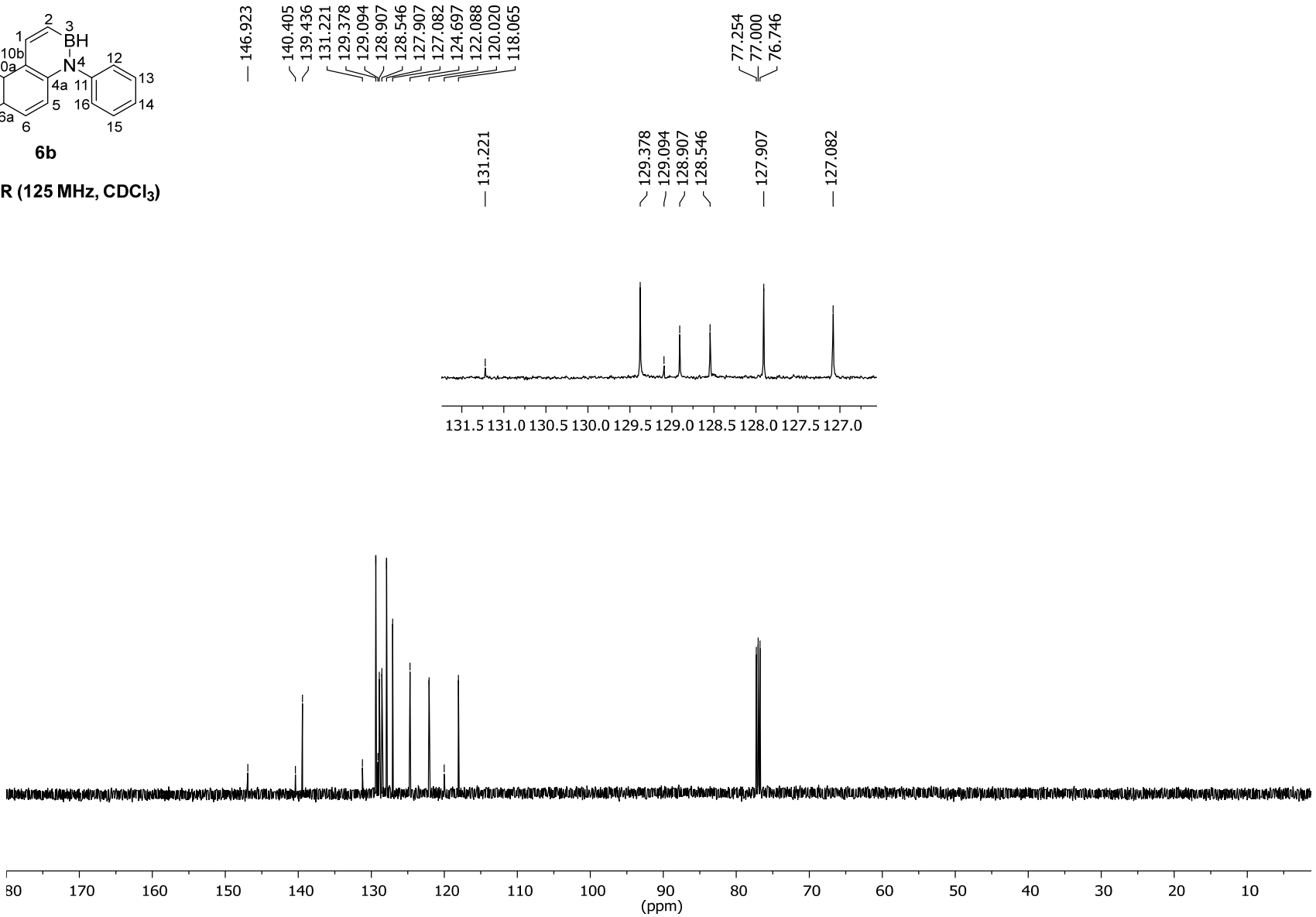
^{1}H-NMR (500 MHz, $CDCl_3$)

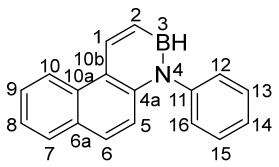




6b

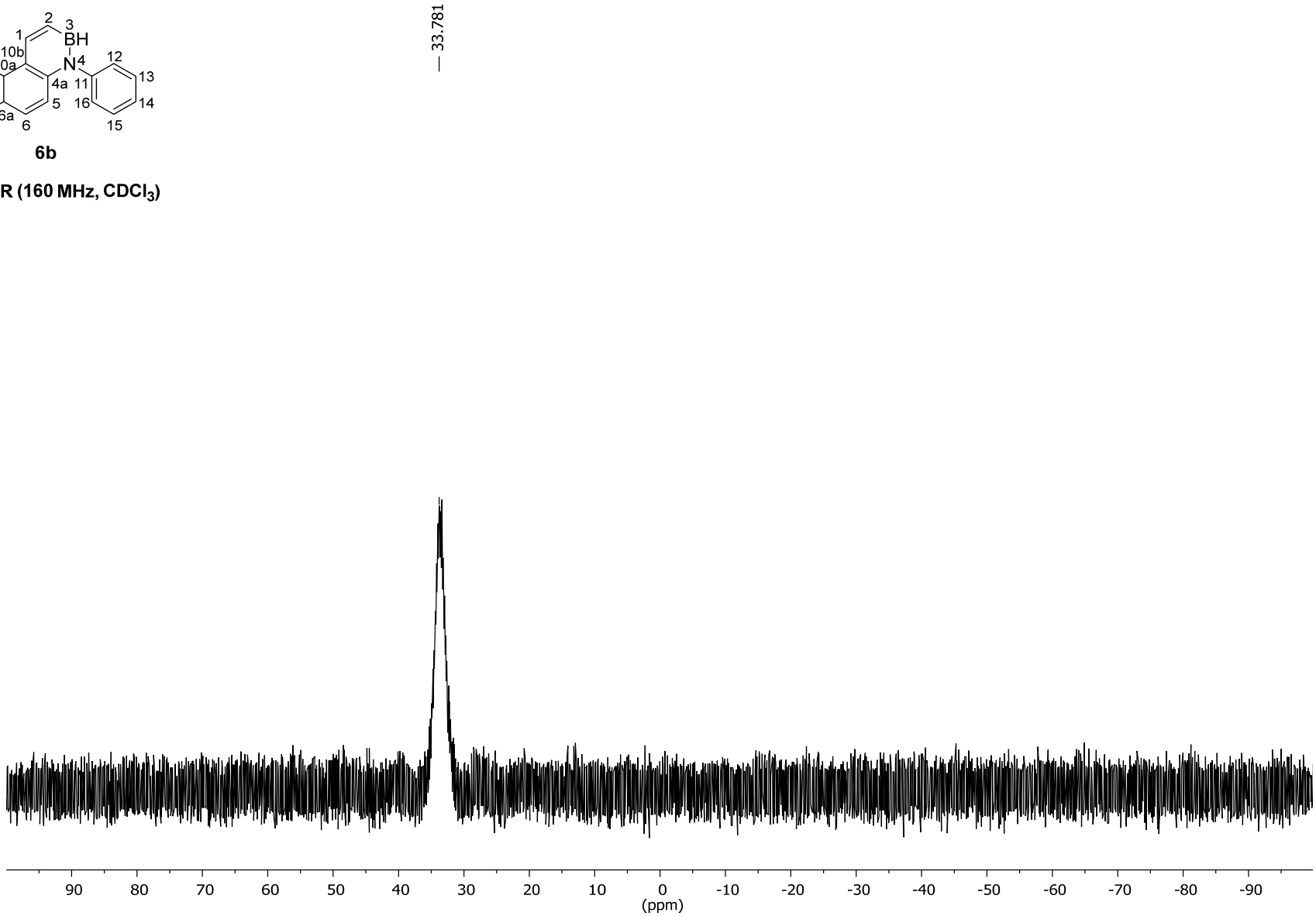
^{13}C-NMR (125 MHz, $CDCl_3$)

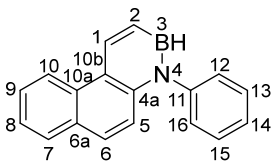




6b

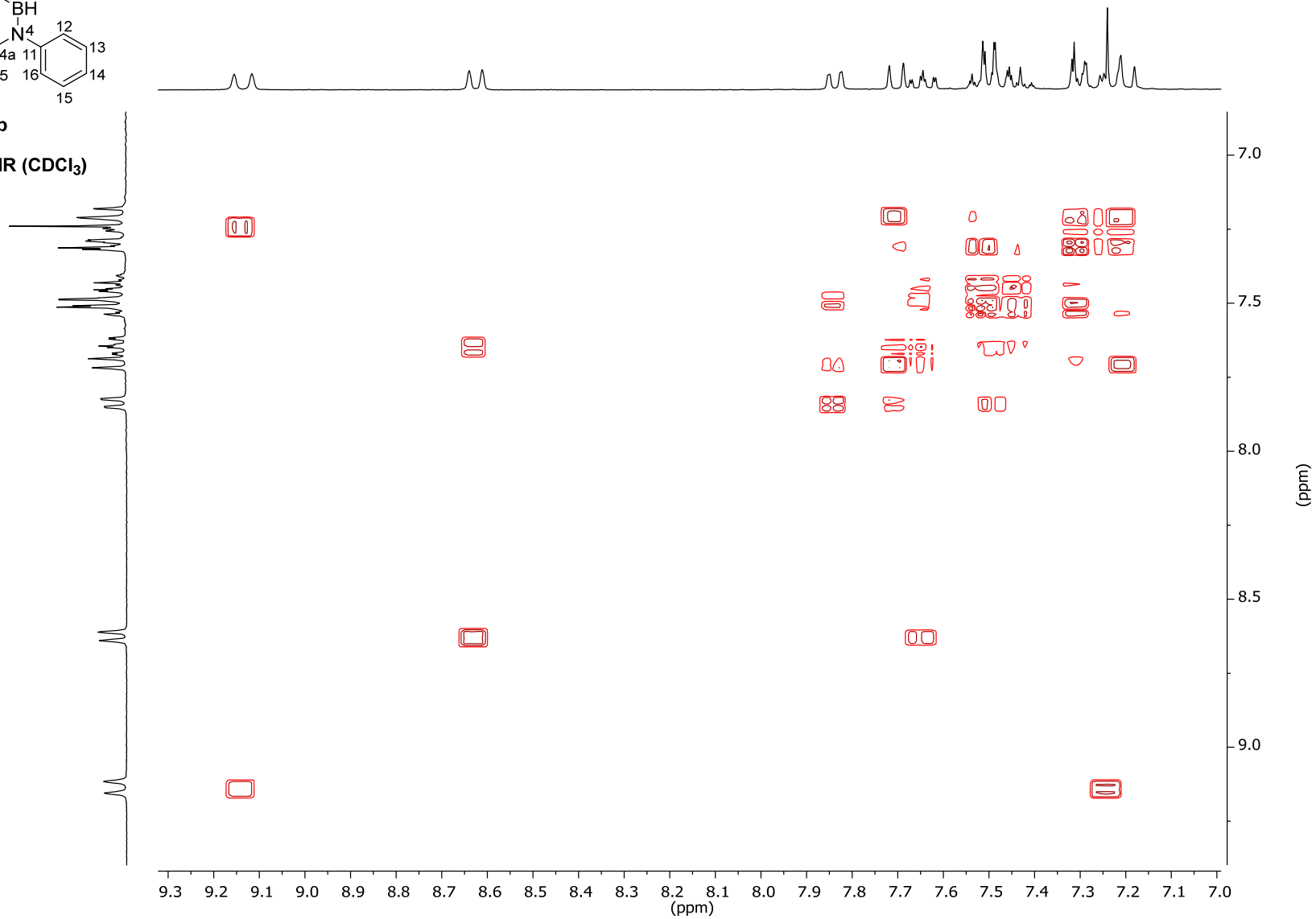
^{11}B-NMR (160 MHz, $CDCl_3$)

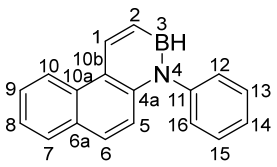




6b

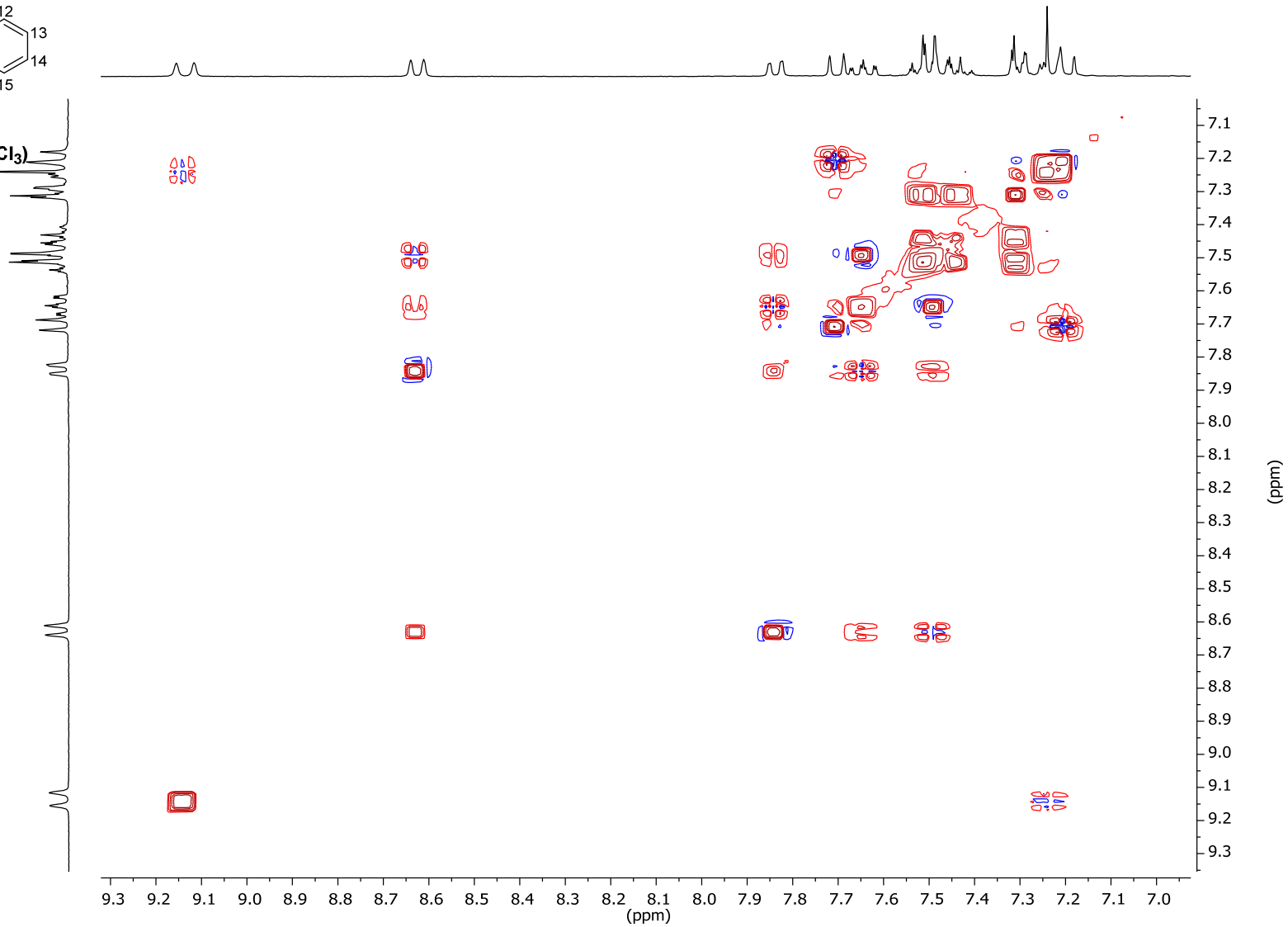
gCOSY-NMR ($CDCl_3$)

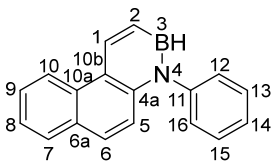




6b

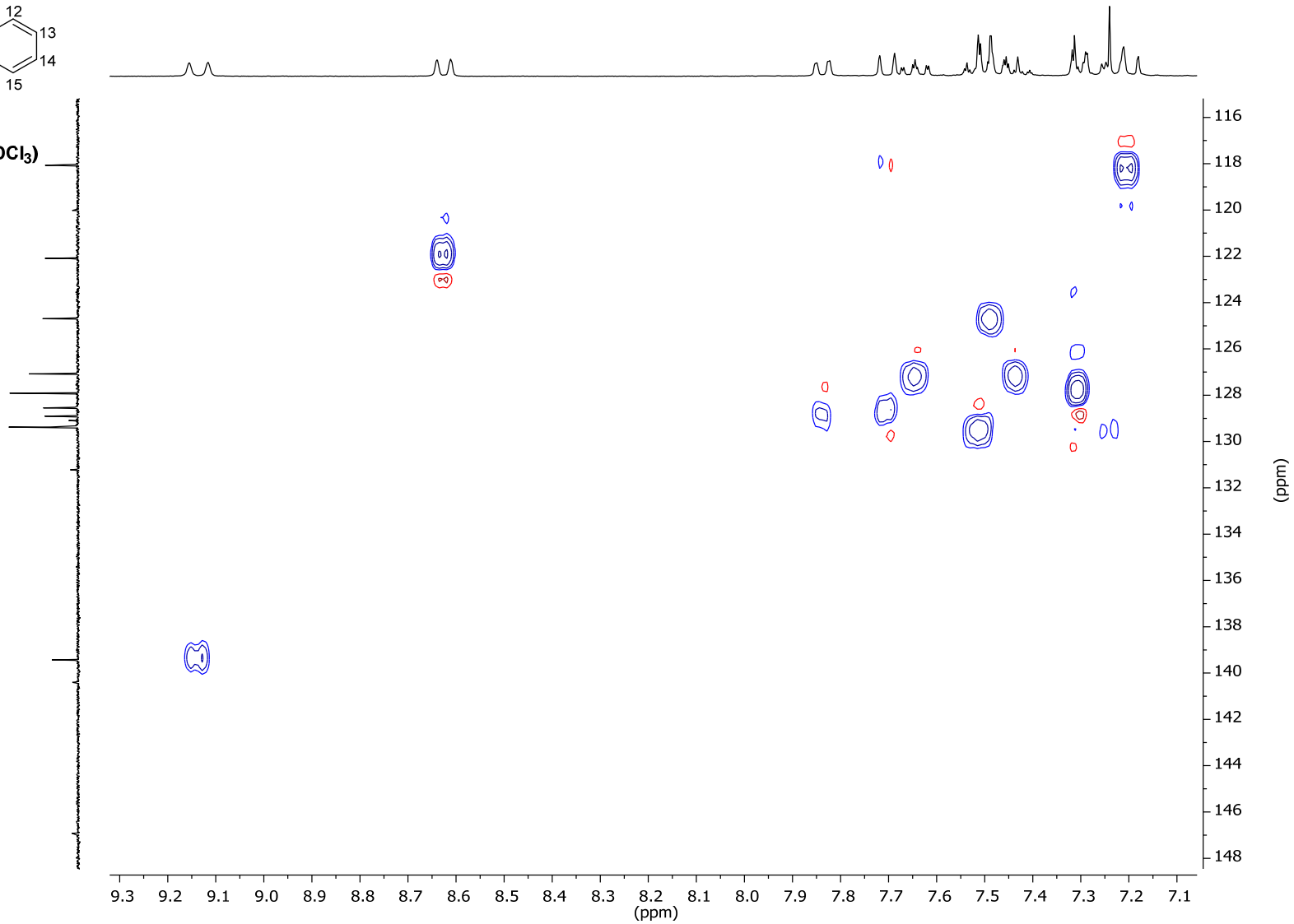
TOCSY-NMR ($CDCl_3$)

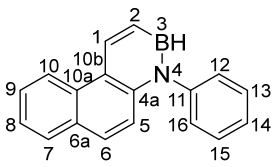




6b

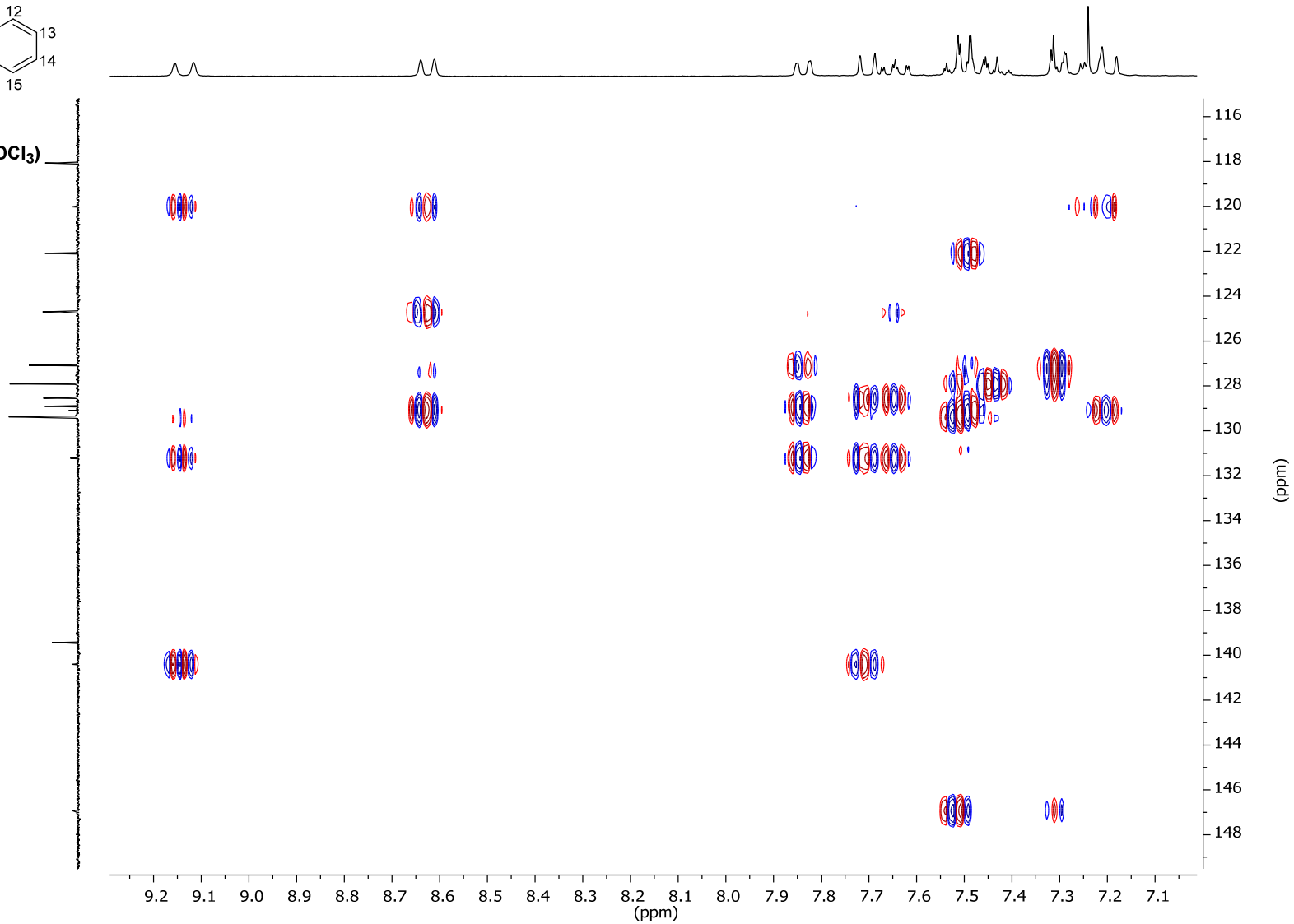
gHSQC-NMR ($CDCl_3$)

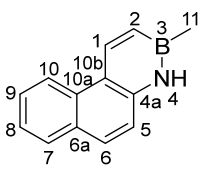




6b

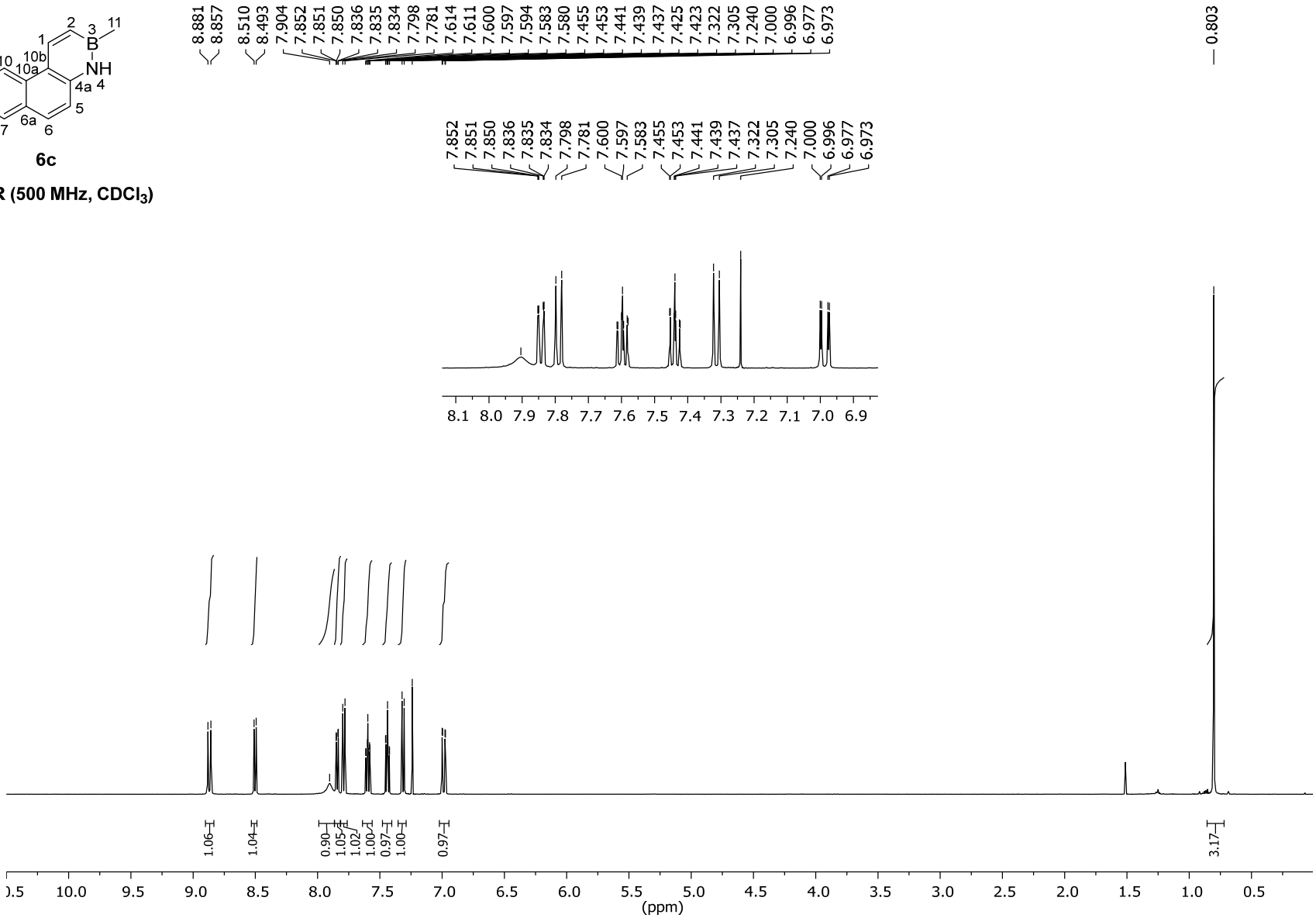
gHMBC-NMR ($CDCl_3$)

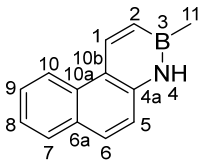




6c

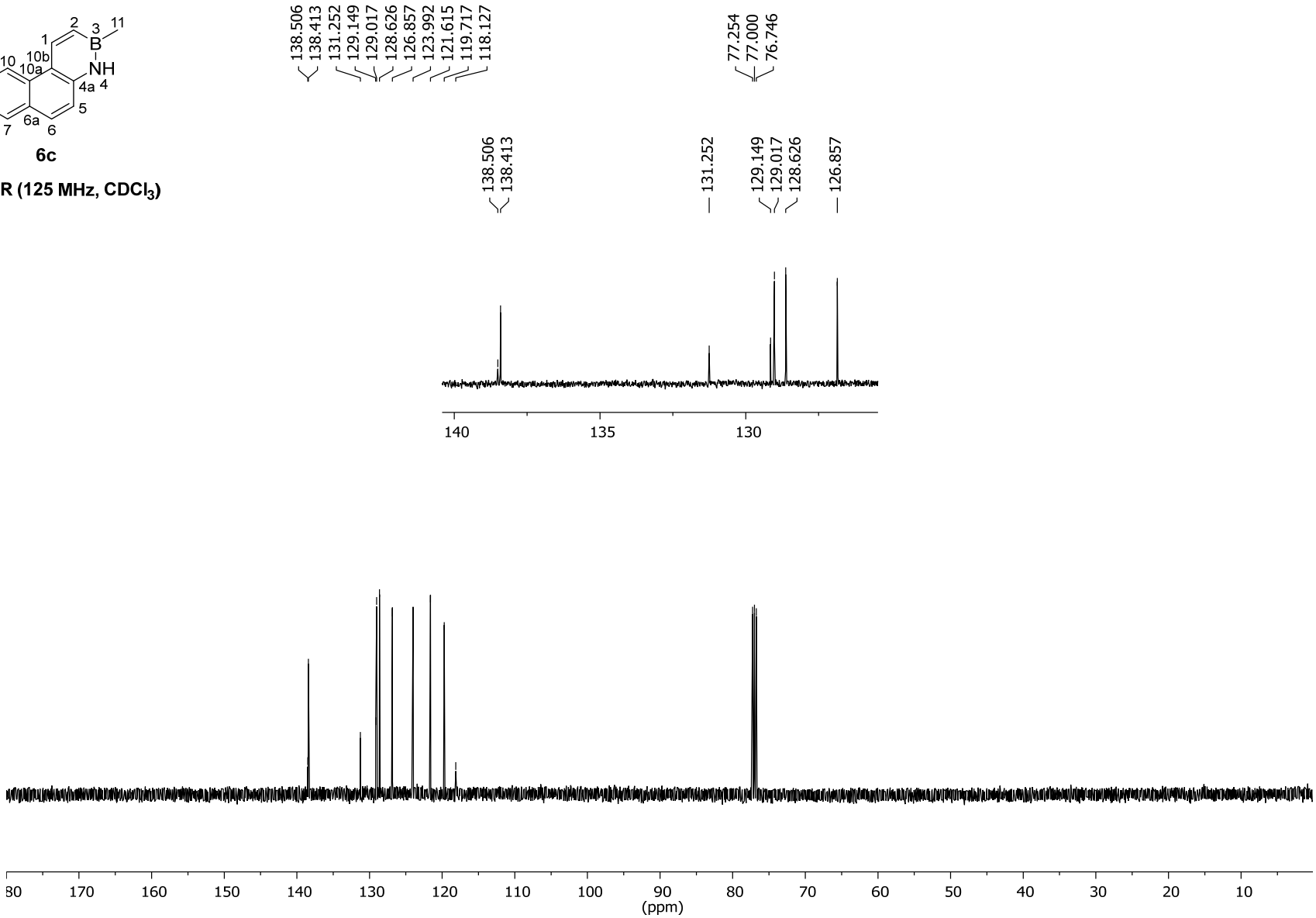
^{1}H-NMR (500 MHz, $CDCl_3$)

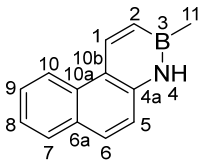




6c

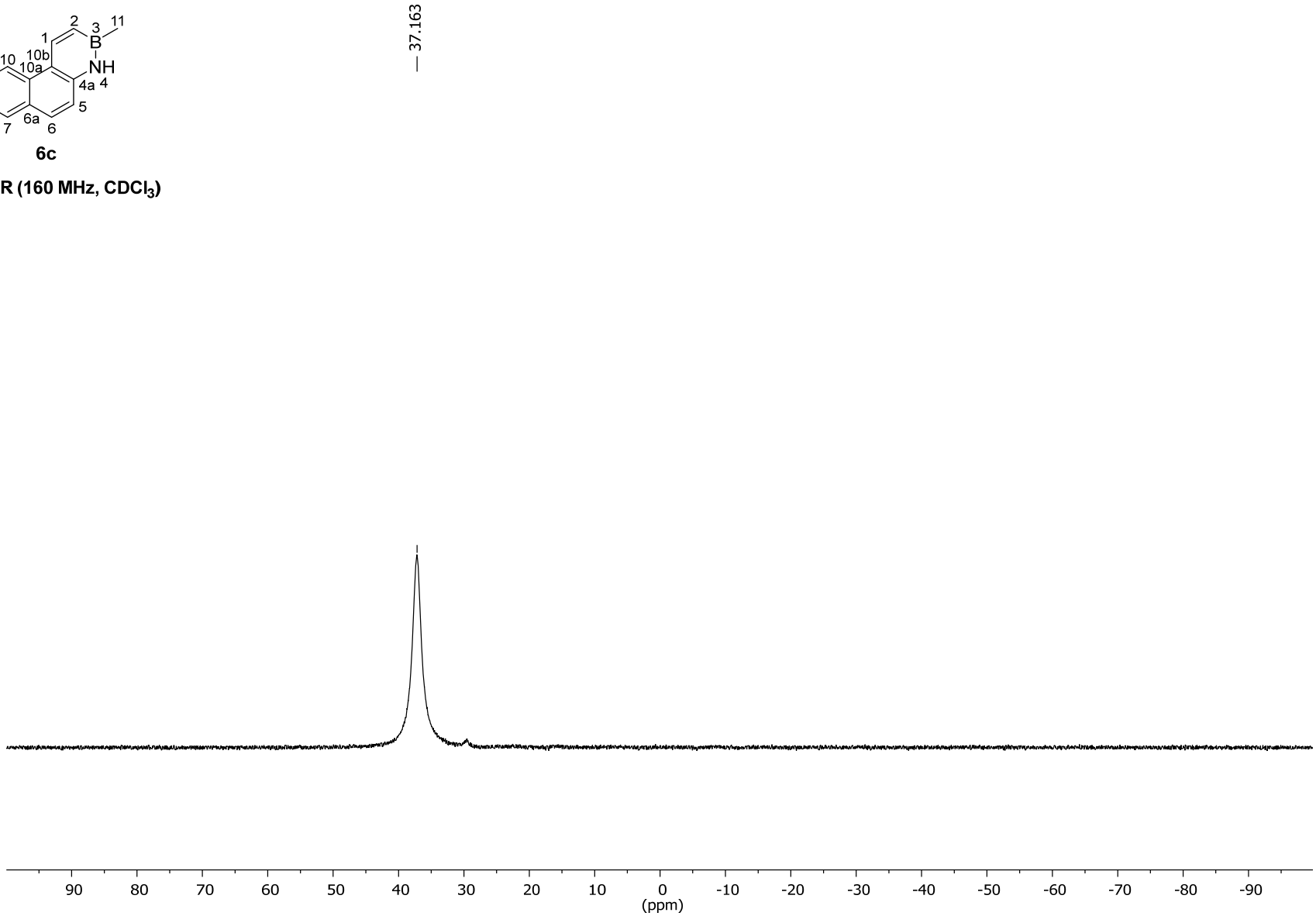
^{13}C-NMR (125 MHz, $CDCl_3$)

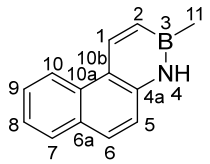




6c

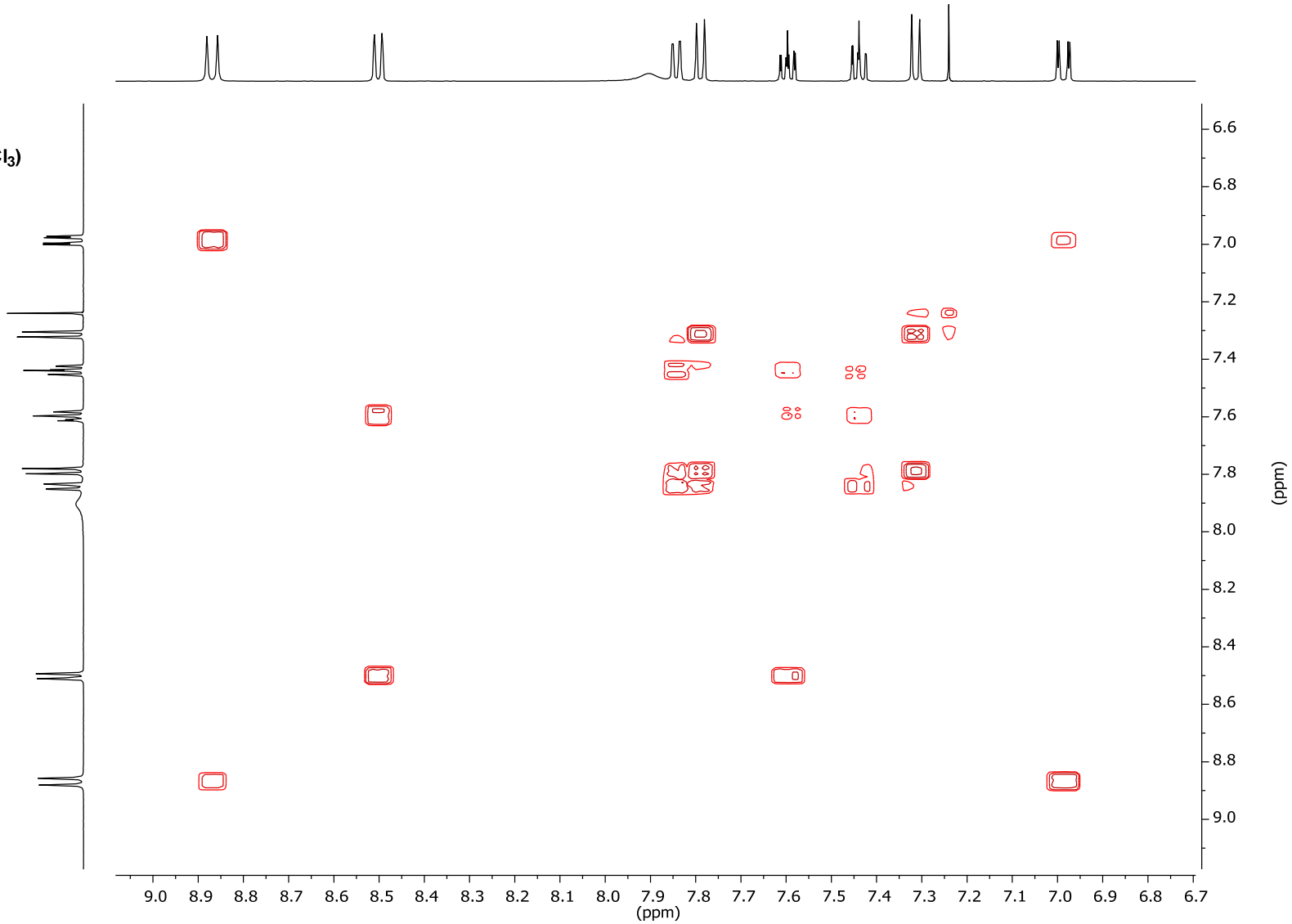
^{11}B-NMR (160 MHz, $CDCl_3$)

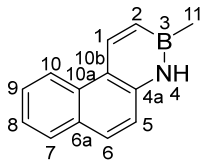




6c

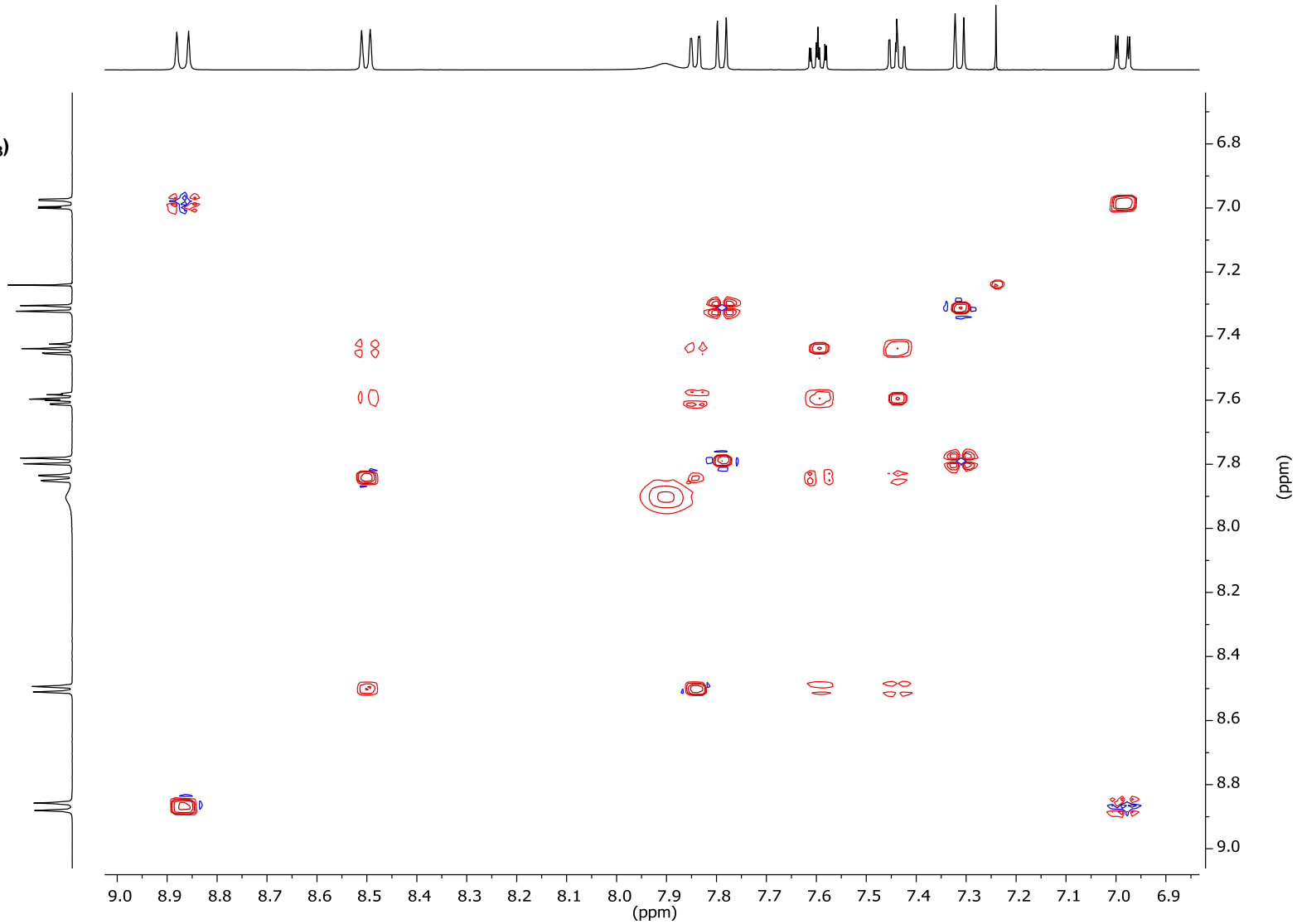
gCOSY-NMR ($CDCl_3$)

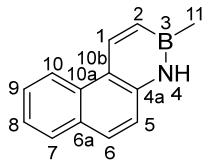




6c

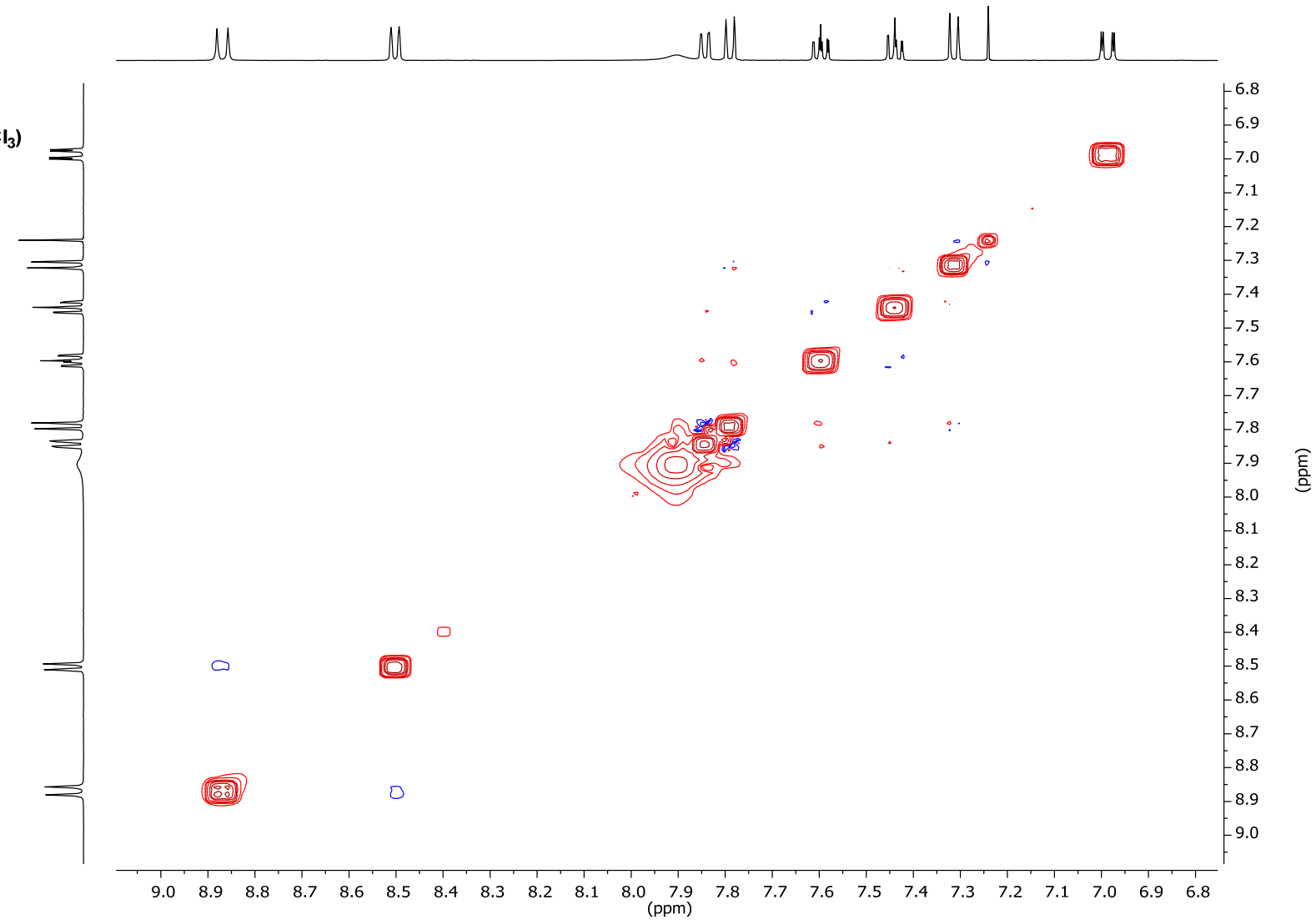
TOCSY-NMR ($CDCl_3$)

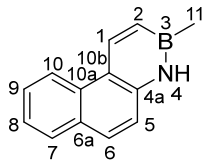




6c

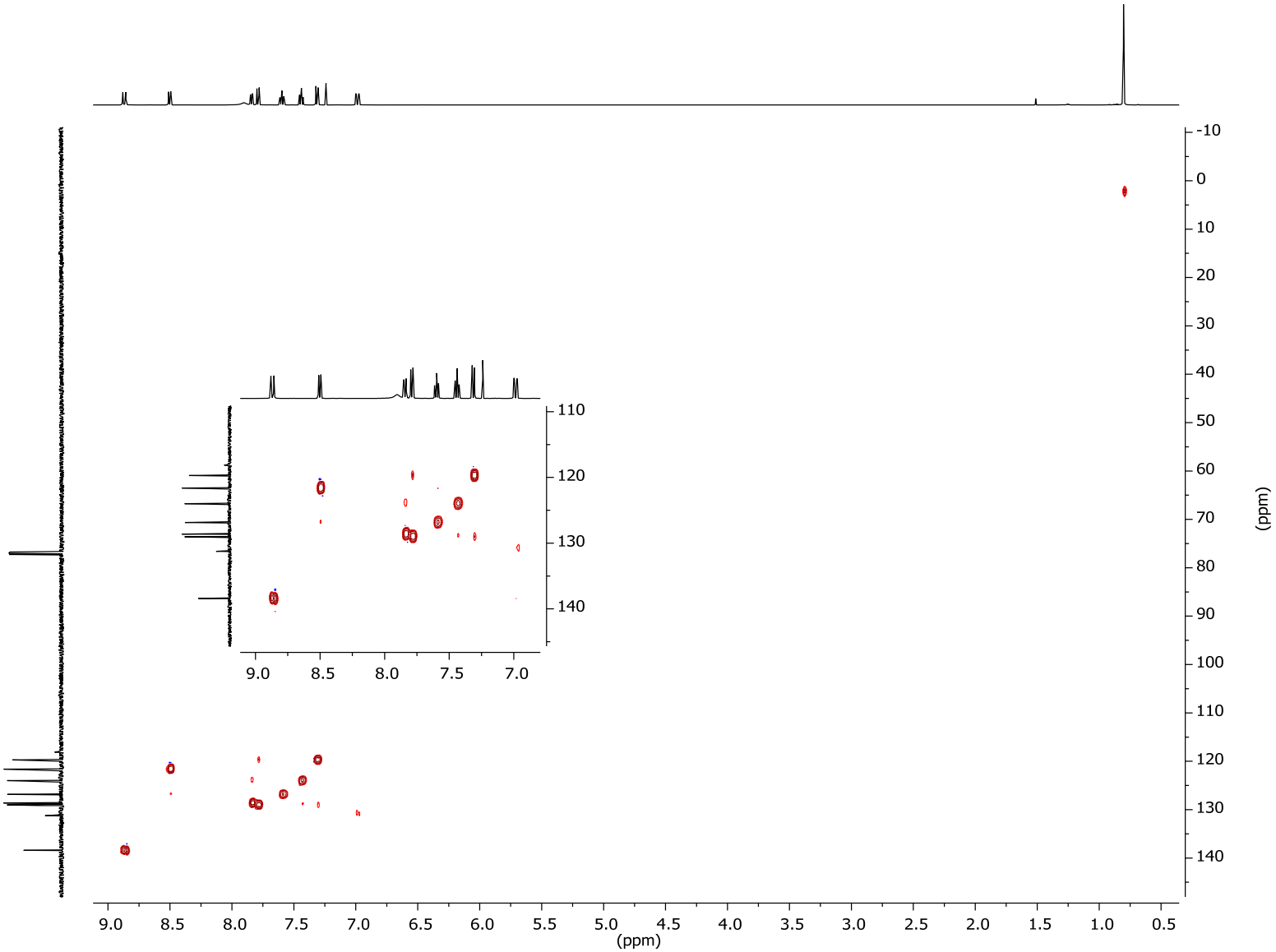
NOESY-NMR ($CDCl_3$)

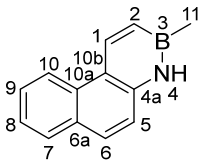




6c

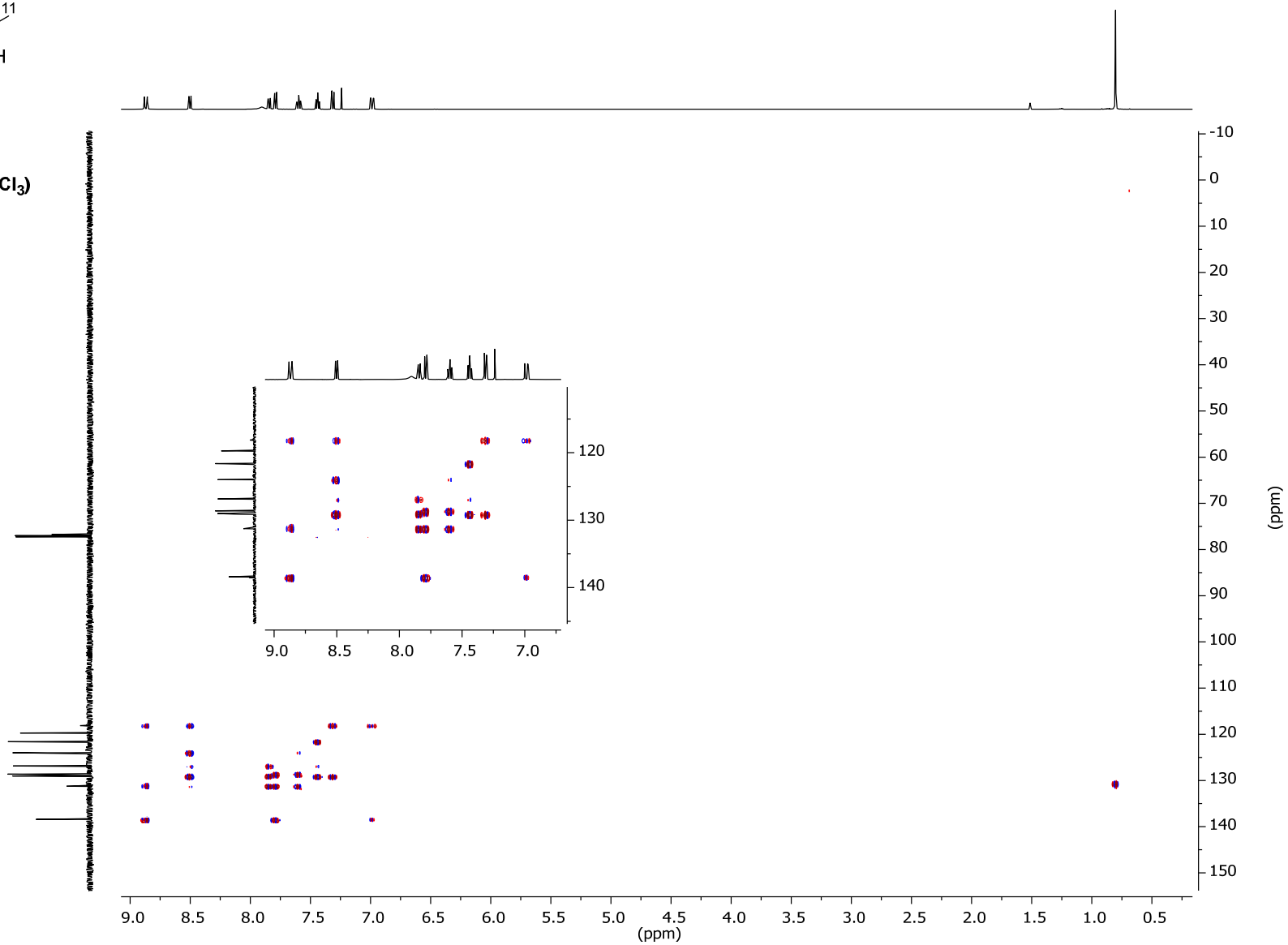
gHSQC-NMR ($CDCl_3$)

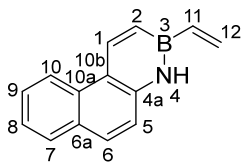




6c

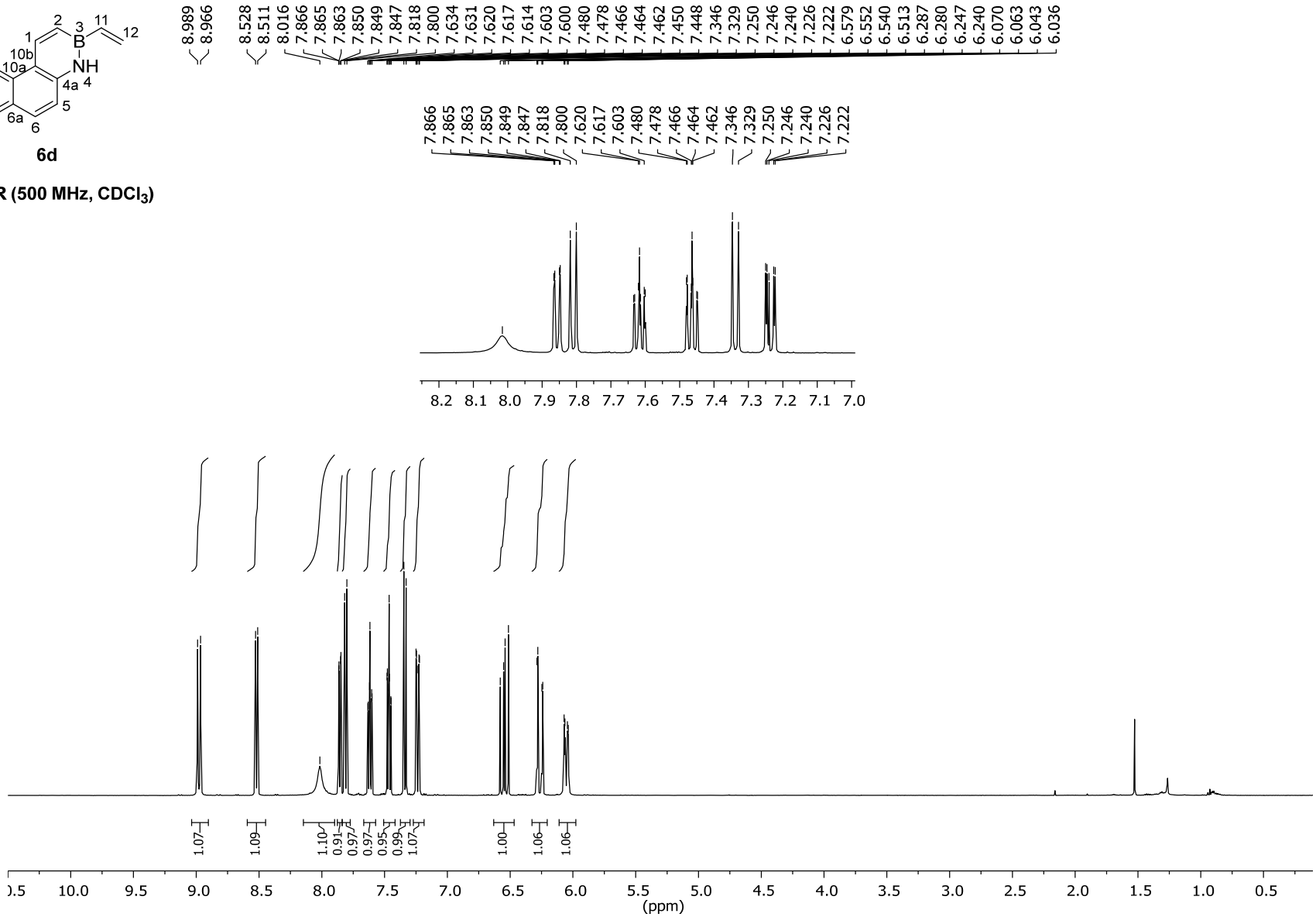
gHMBC-NMR ($CDCl_3$)

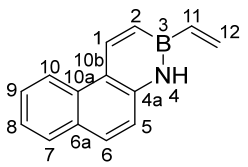




6d

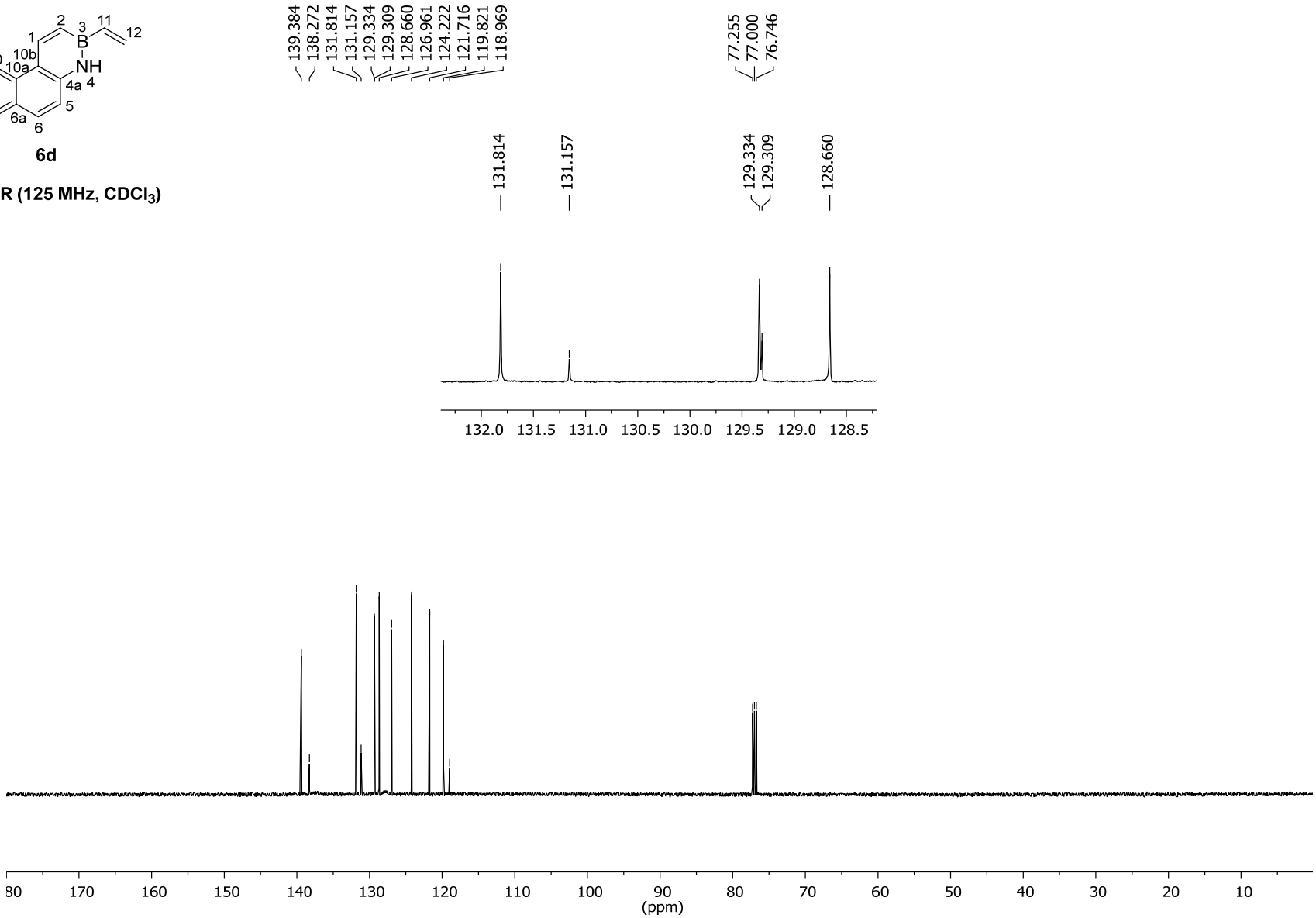
^{1}H-NMR (500 MHz, $CDCl_3$)

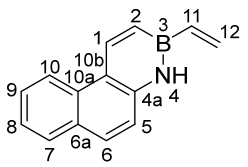




6d

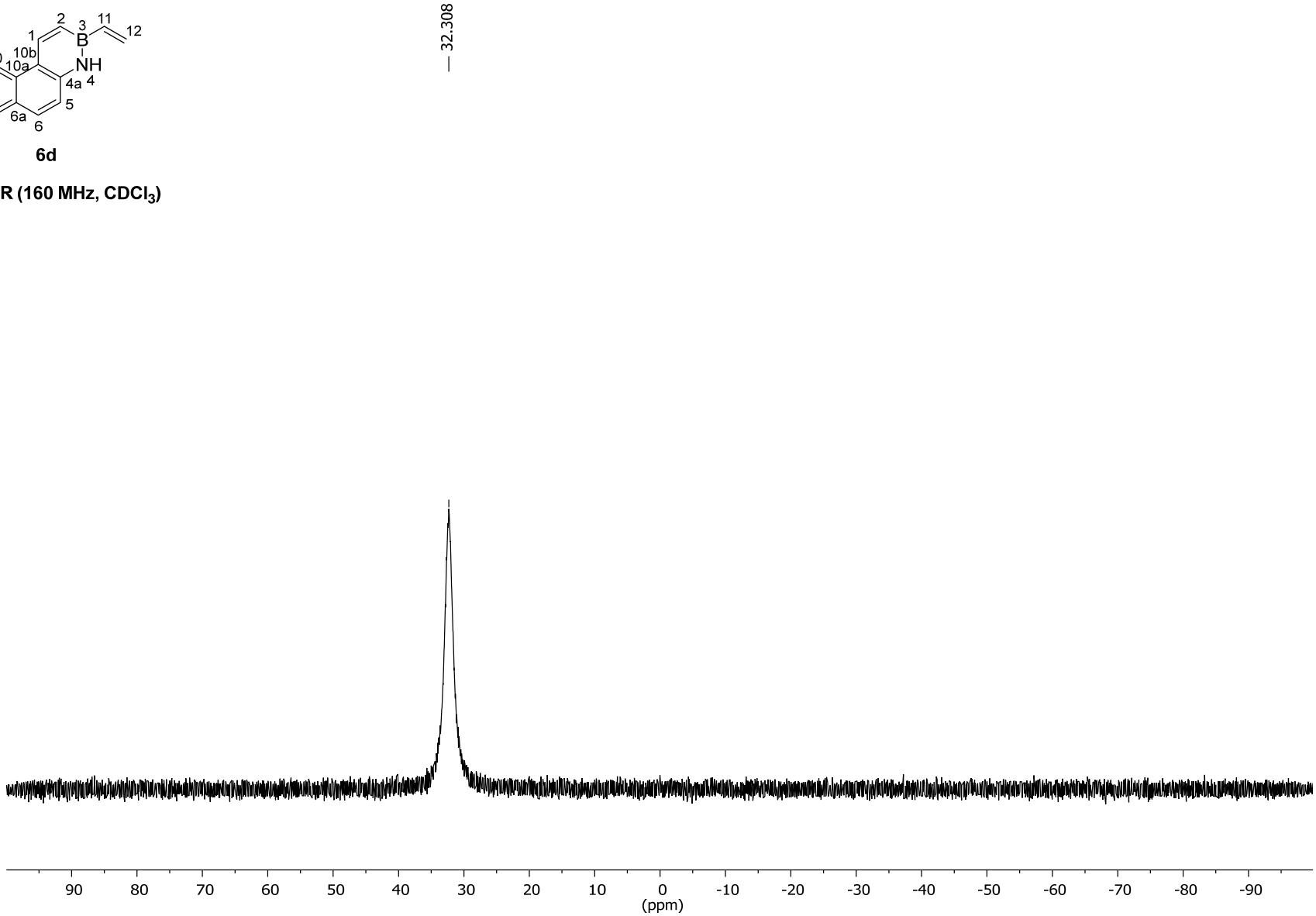
^{13}C-NMR (125 MHz, $CDCl_3$)

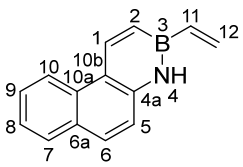




6d

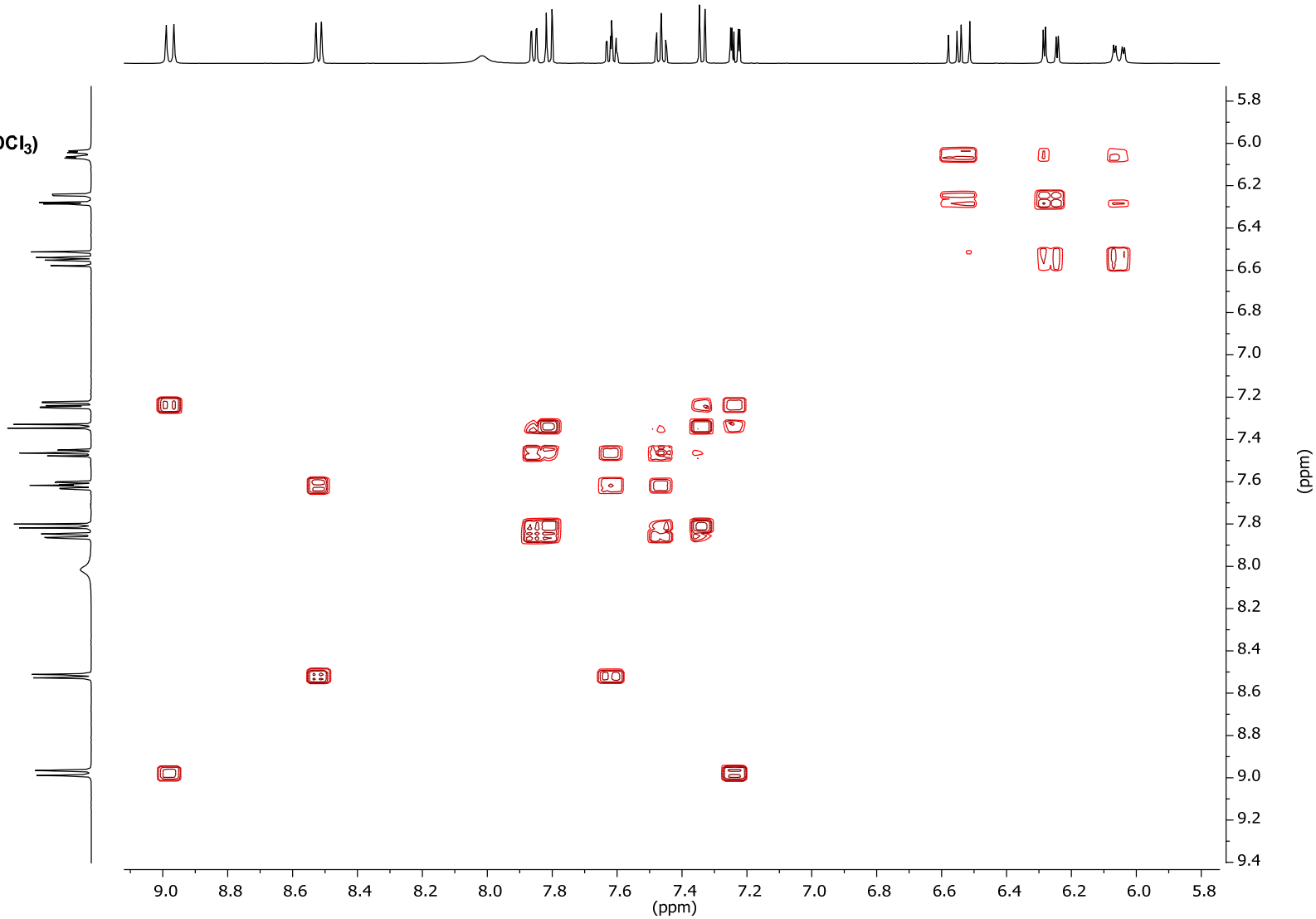
^{11}B-NMR (160 MHz, $CDCl_3$)

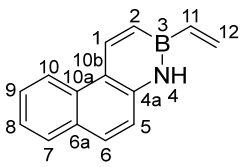




6d

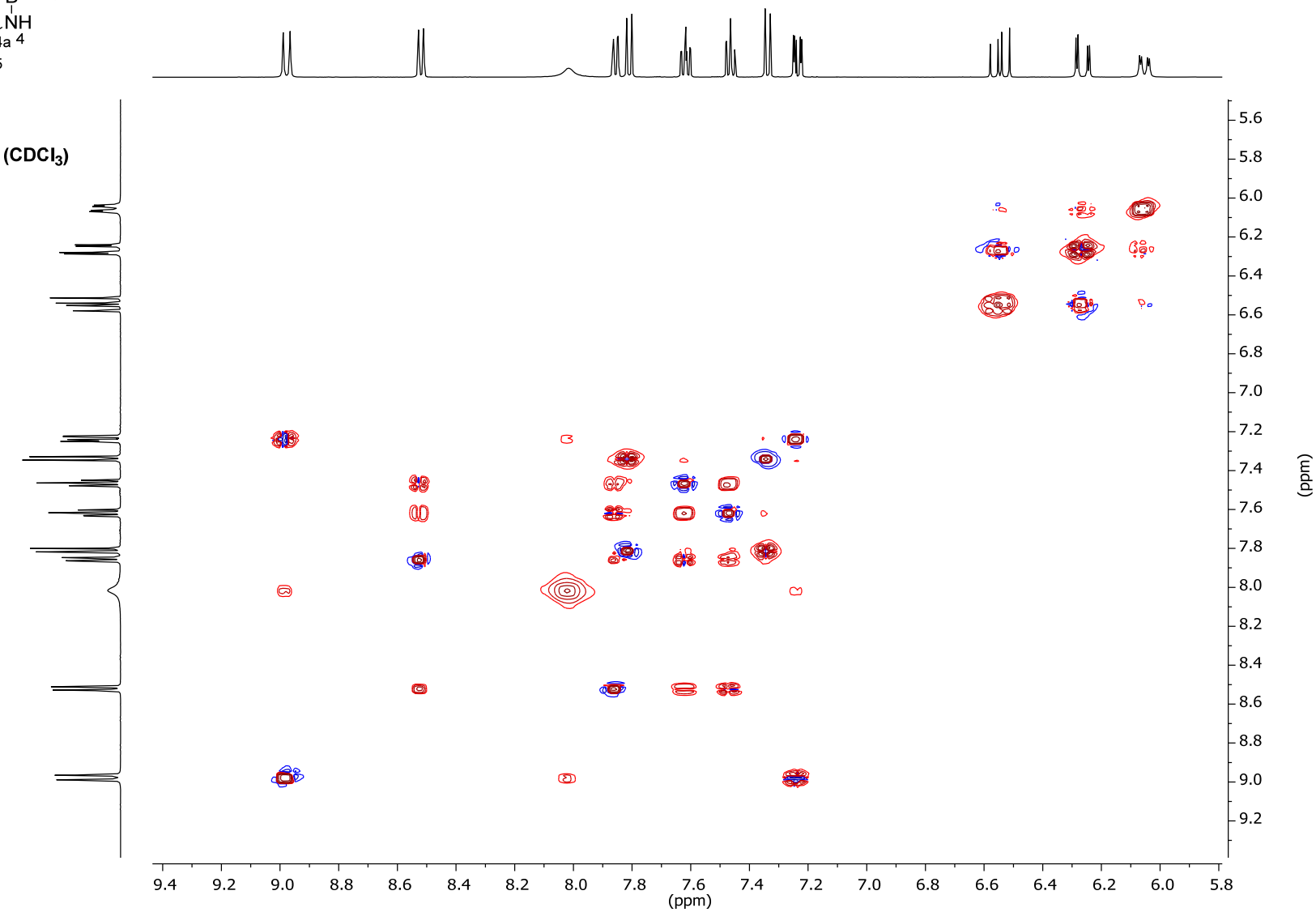
gCOSY-NMR ($CDCl_3$)

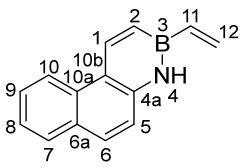




6d

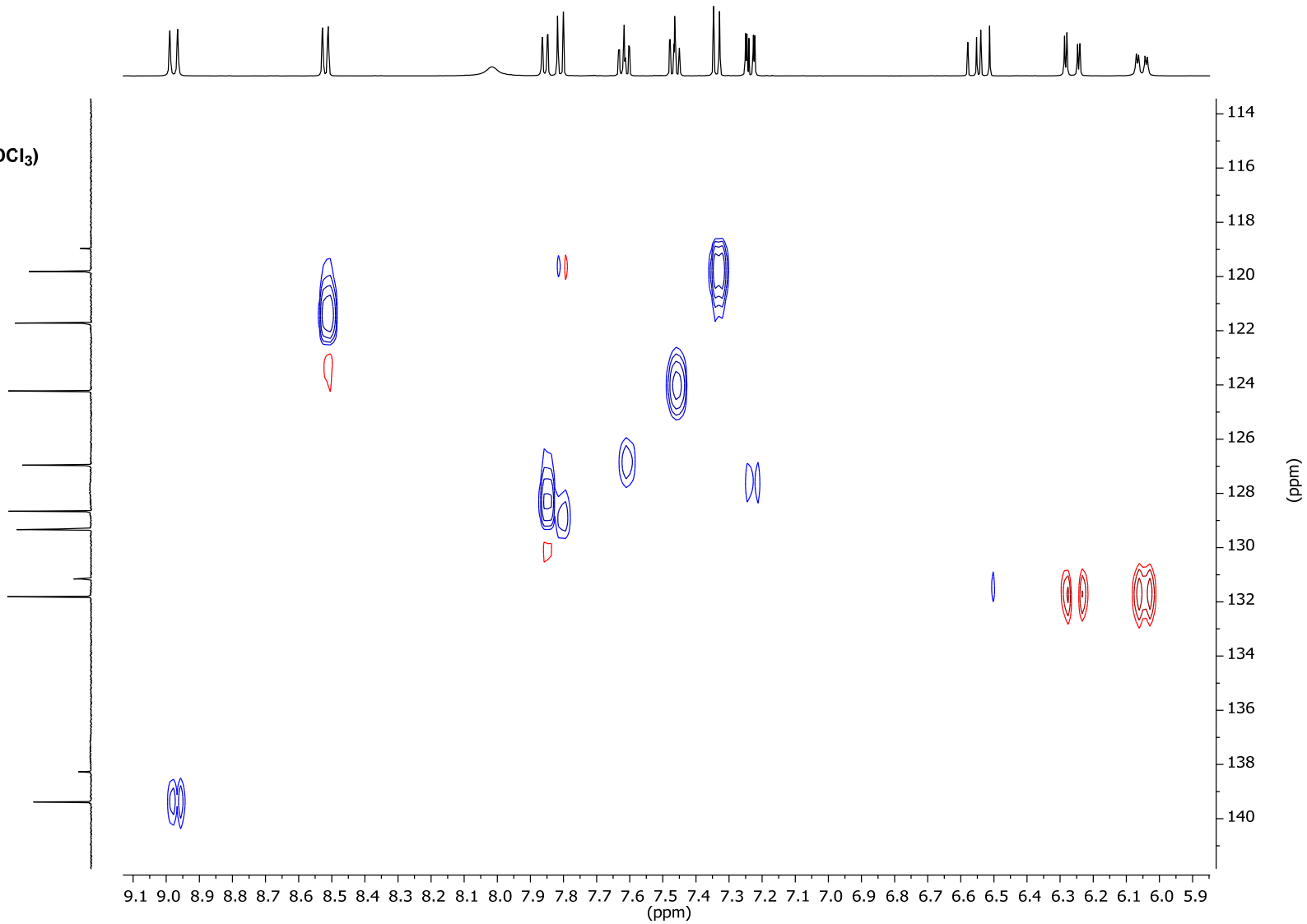
TOCSY-NMR ($CDCl_3$)

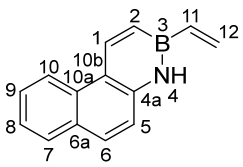




6d

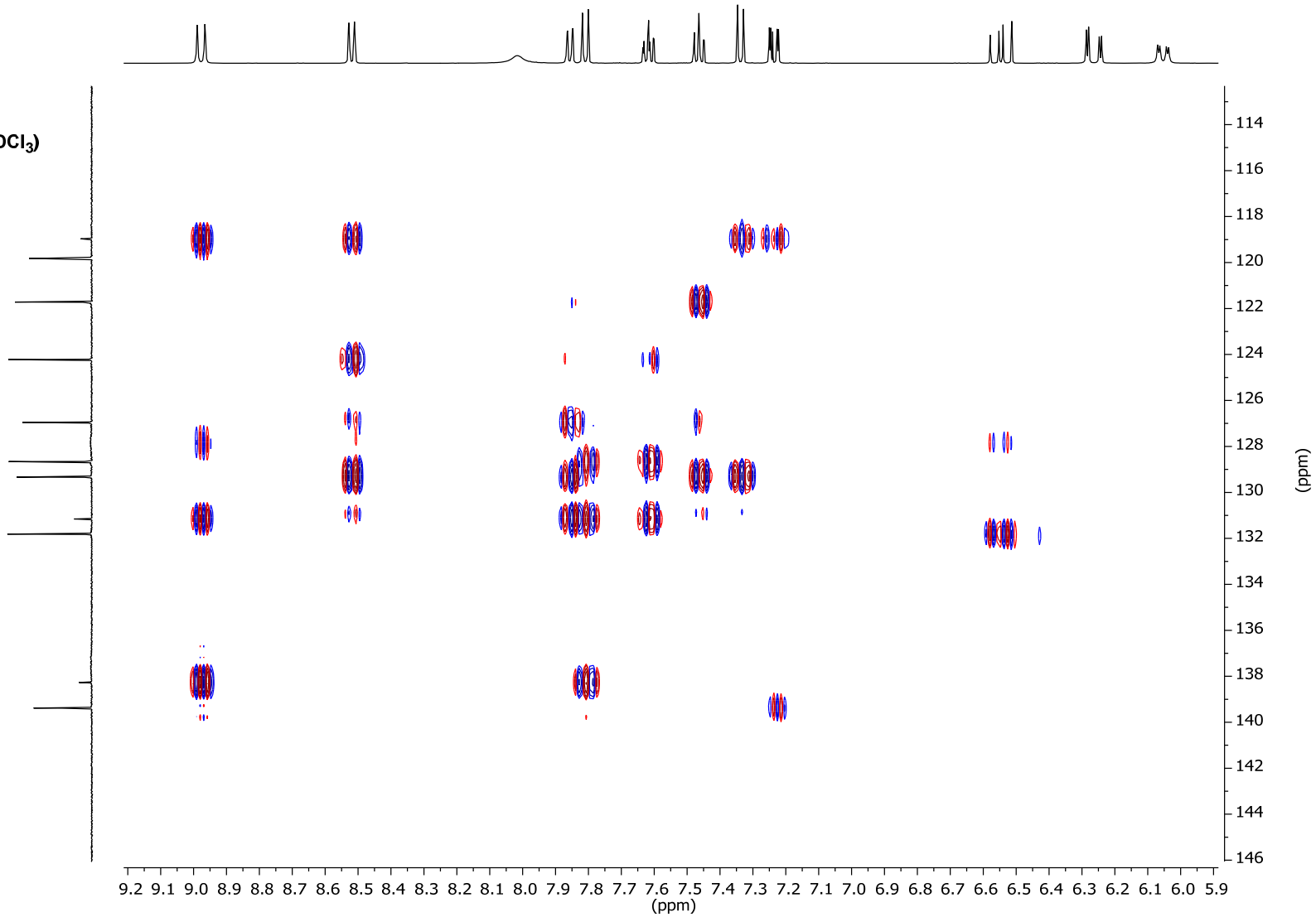
gHSQC-NMR ($CDCl_3$)

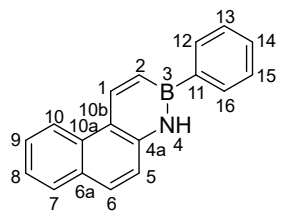




6d

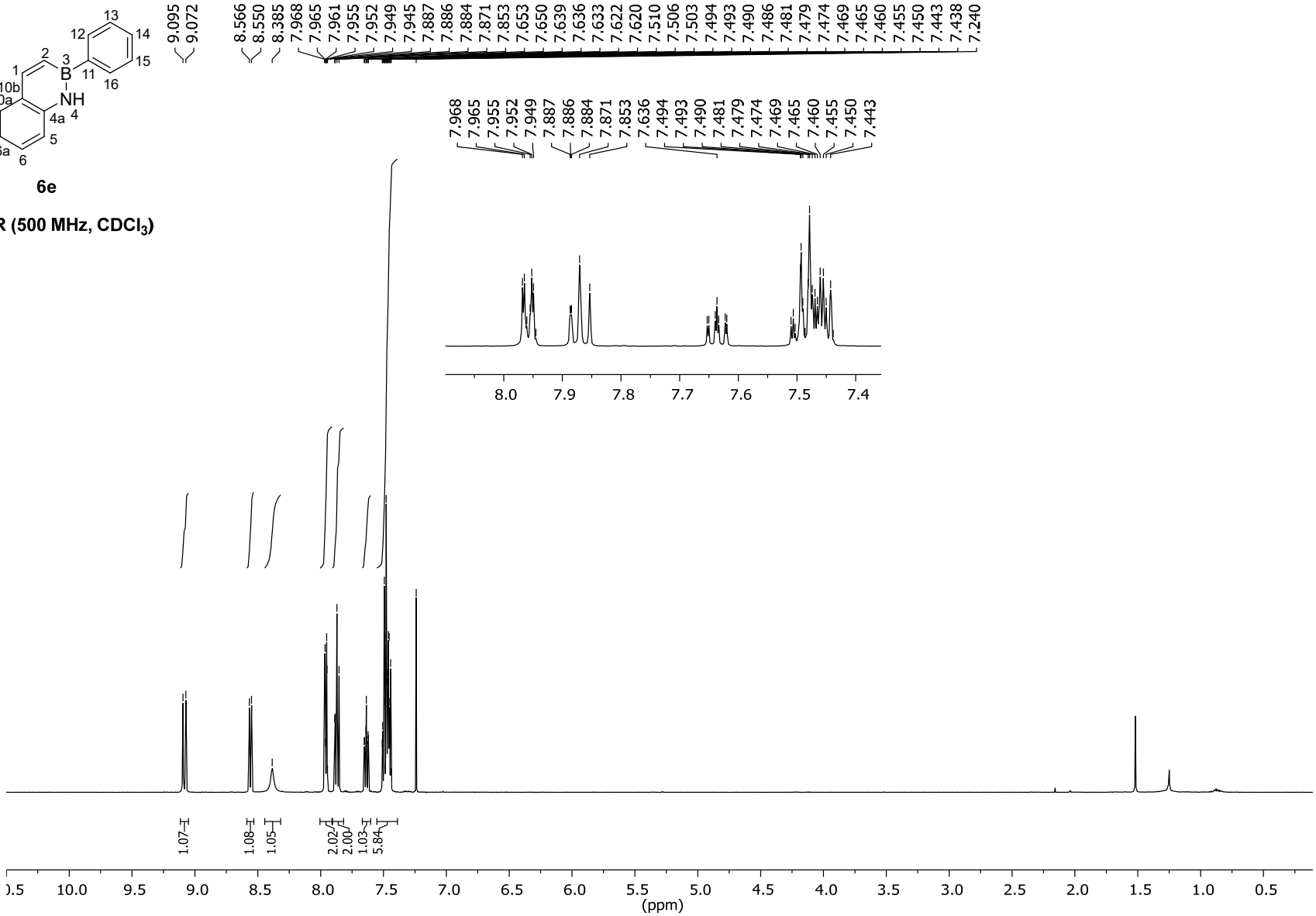
gHMBC-NMR ($CDCl_3$)

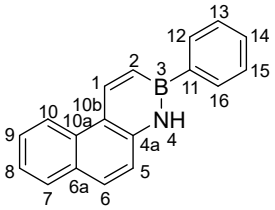




6e

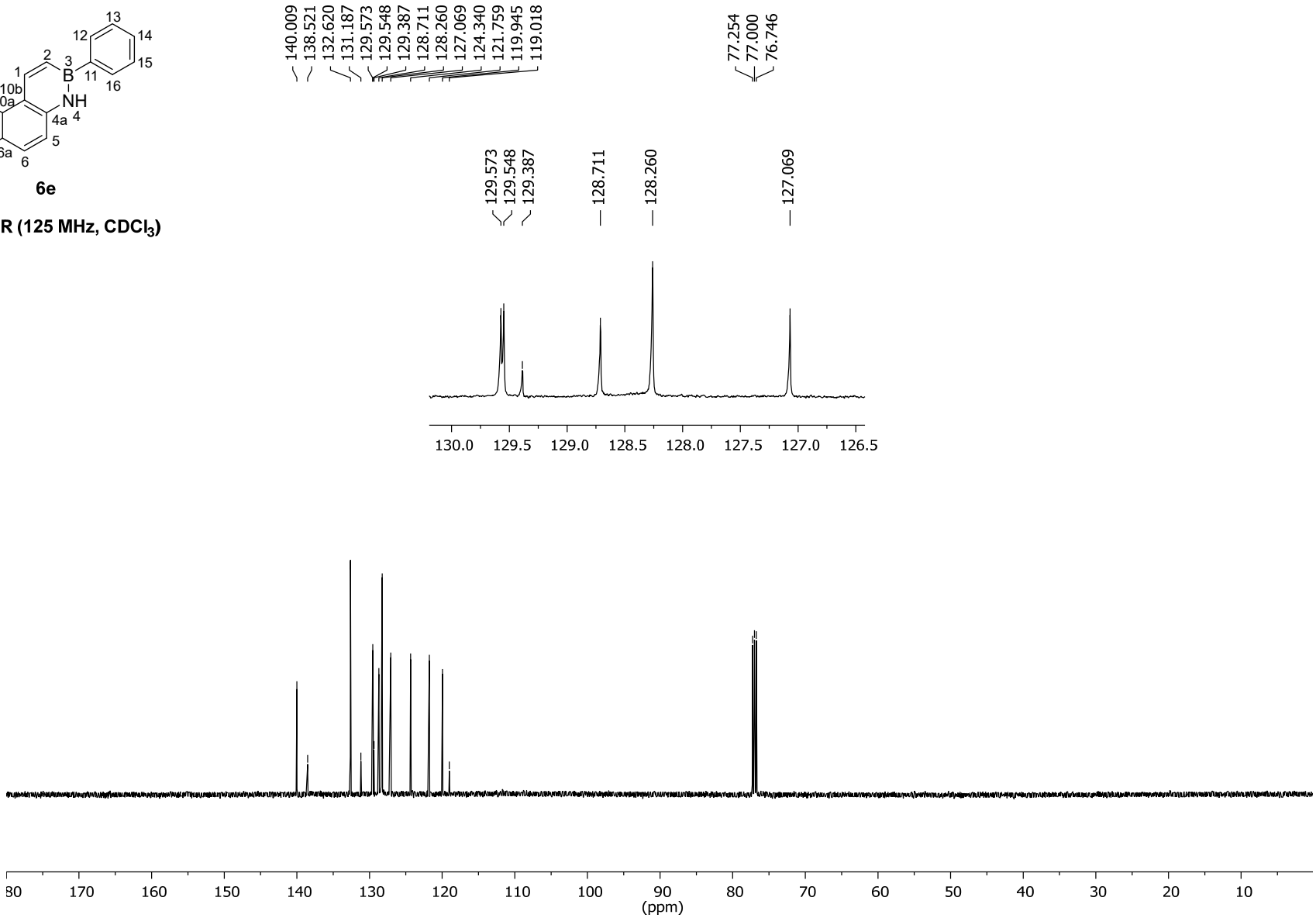
^{1}H-NMR (500 MHz, $CDCl_3$)

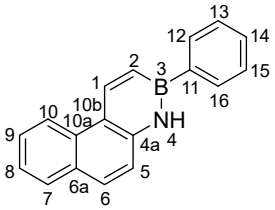




6e

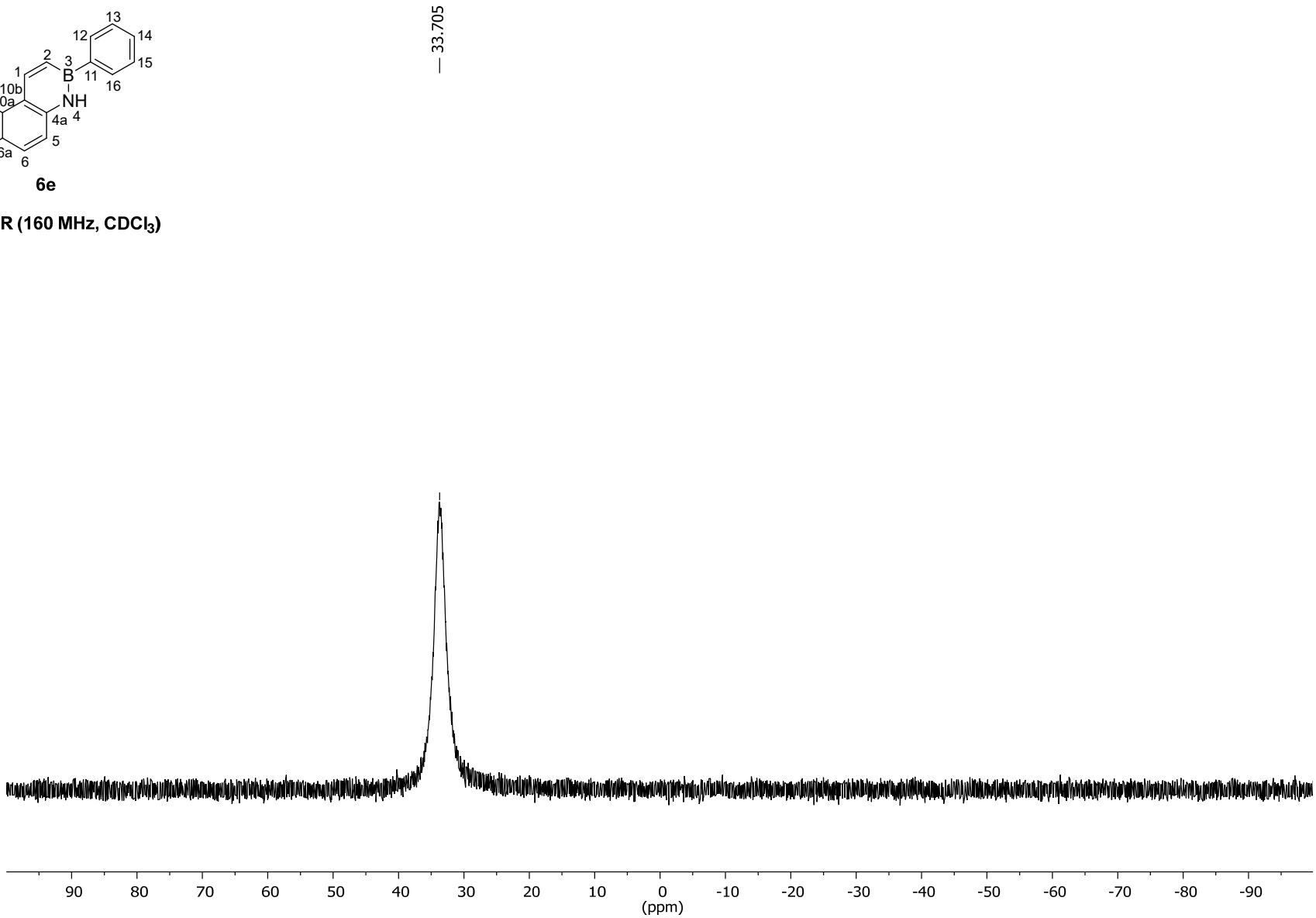
^{13}C-NMR (125 MHz, $CDCl_3$)

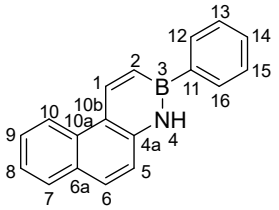




6e

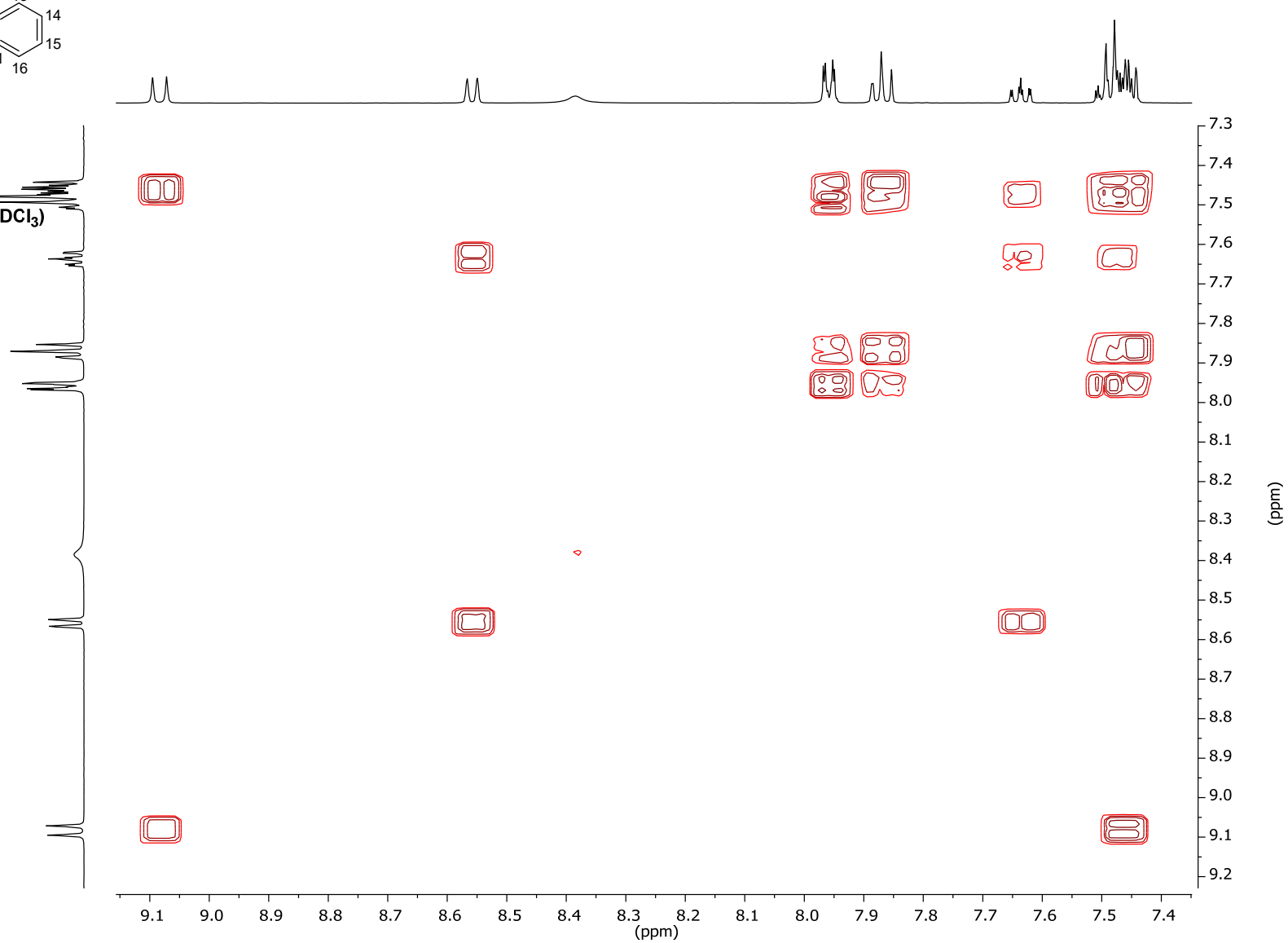
^{11}B-NMR (160 MHz, $CDCl_3$)

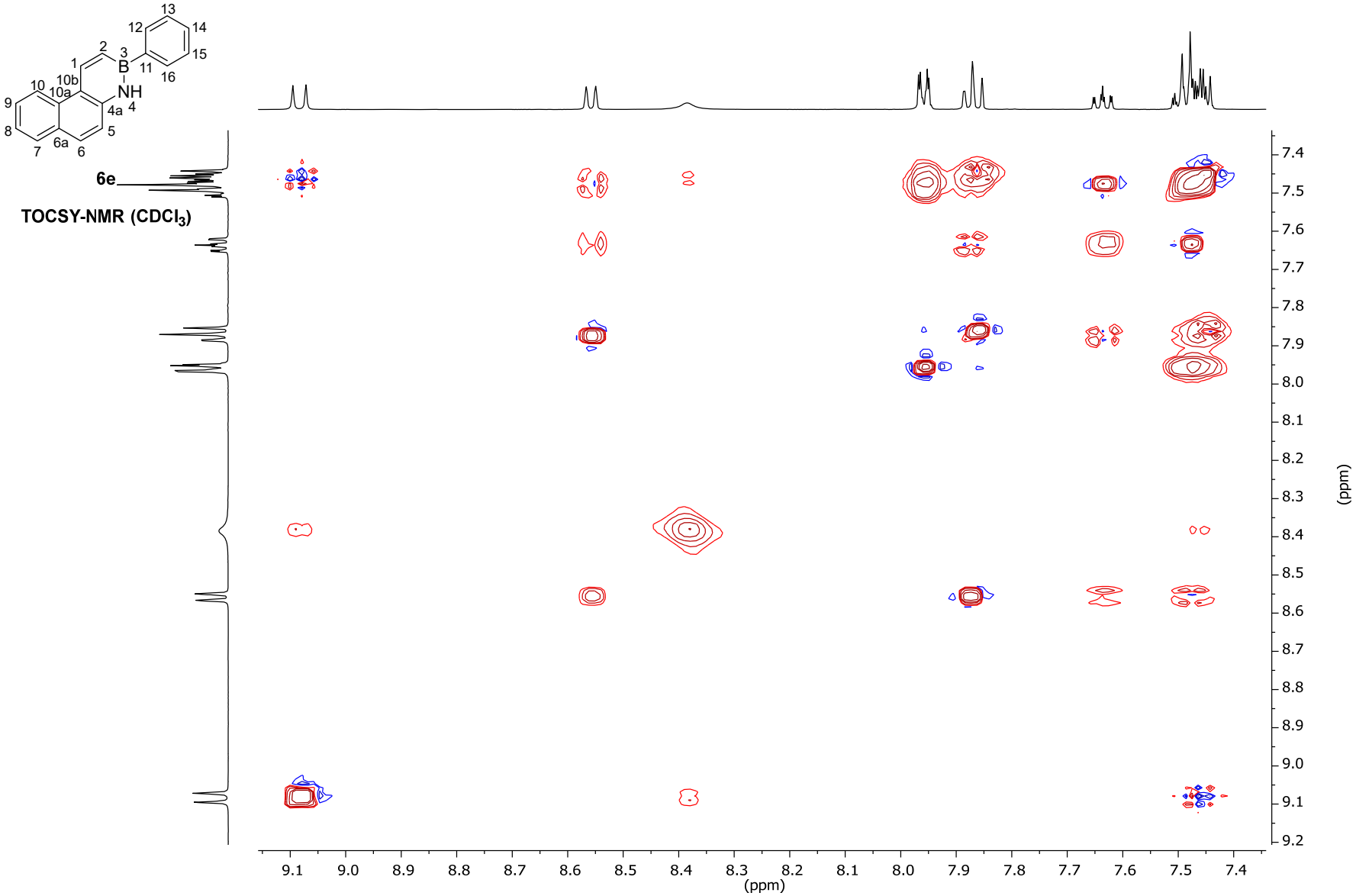


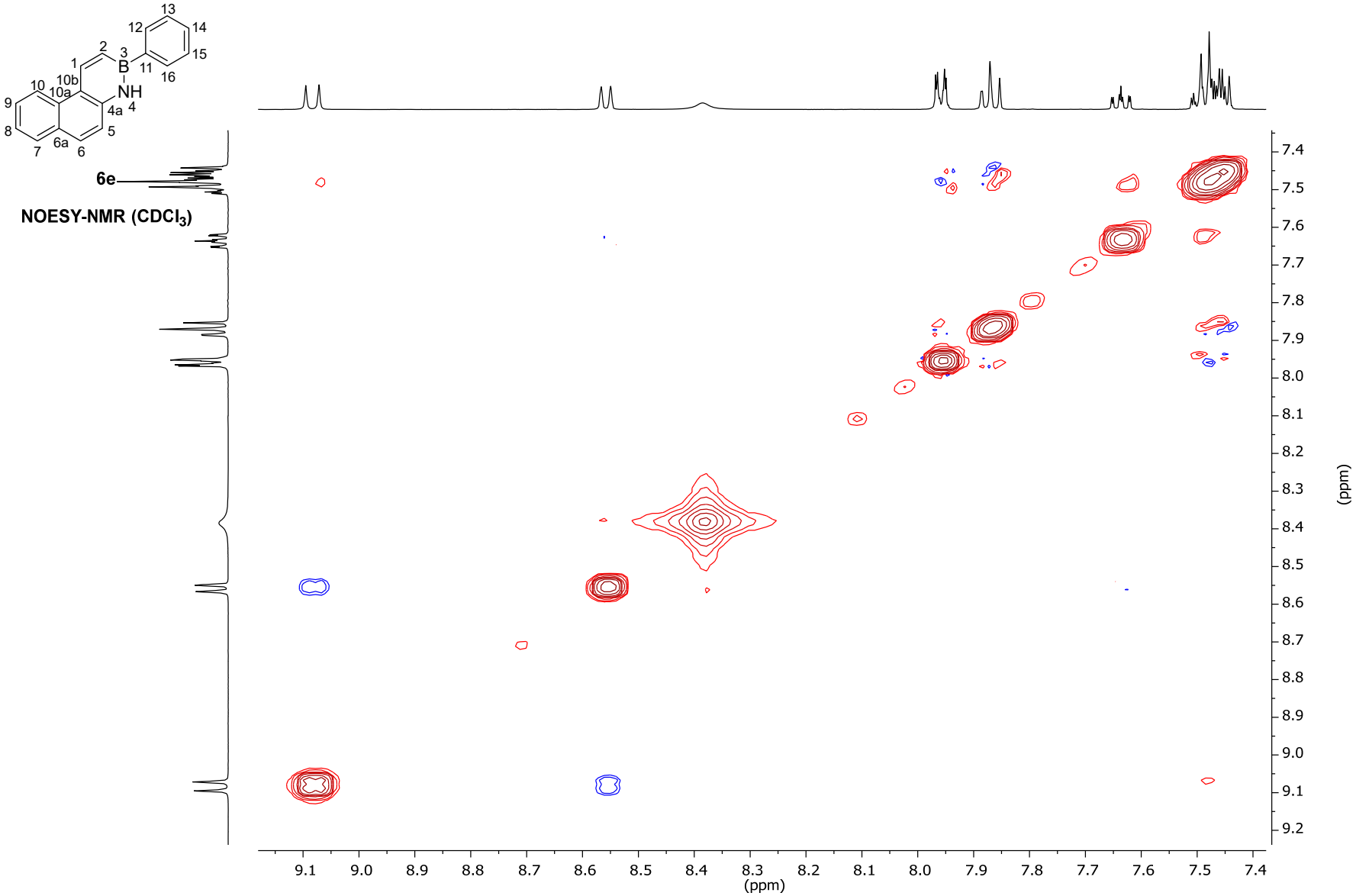


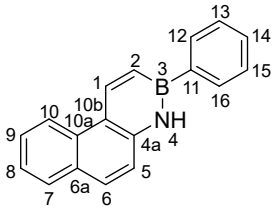
6e

gCOSY-NMR ($CDCl_3$)



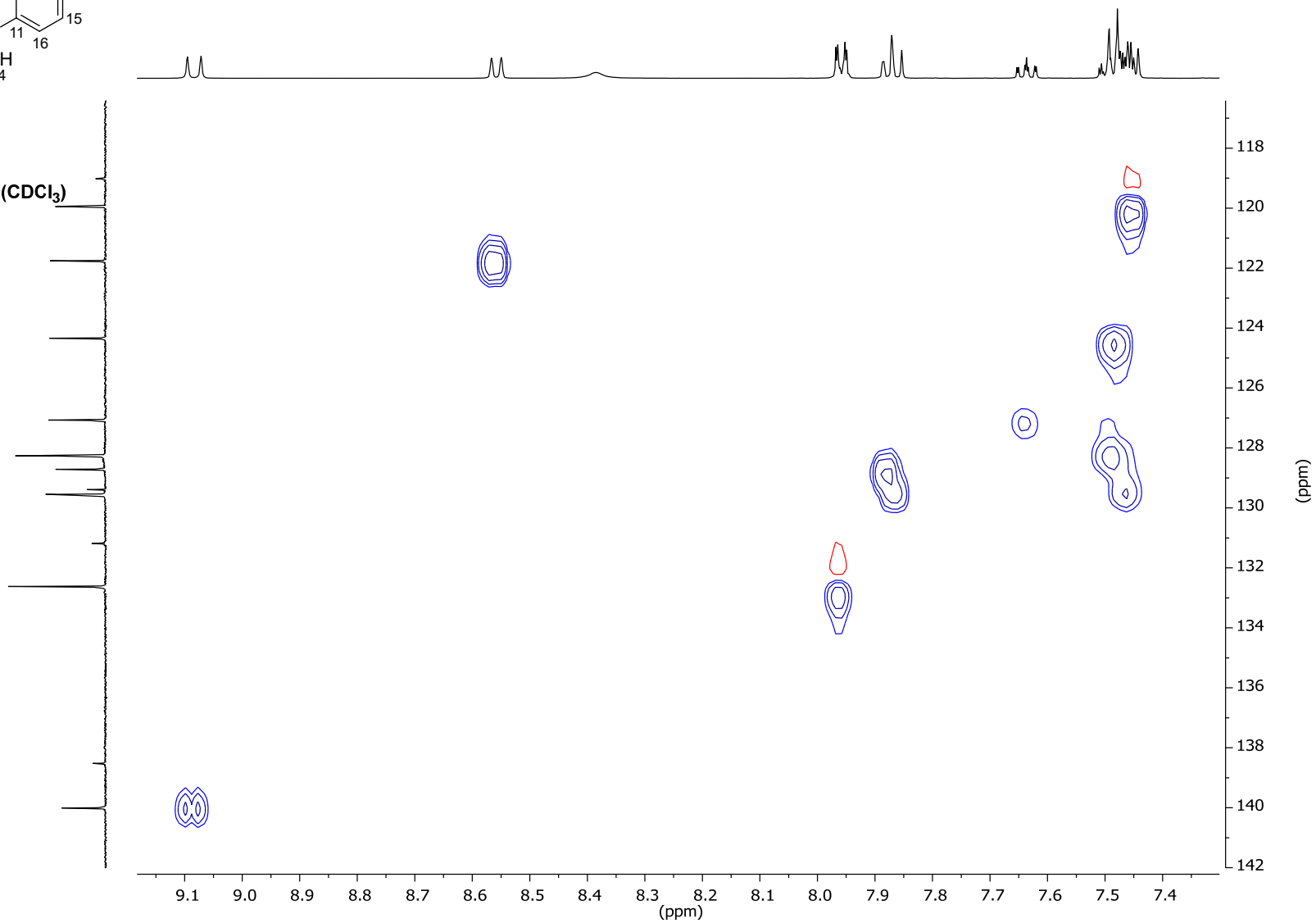

6e
TOCSY-NMR (CDCl3)
(ppm)
(ppm)

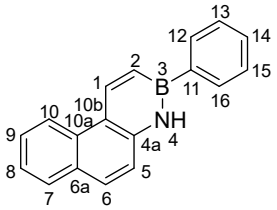

6e
NOESY-NMR (CDCl3)
(ppm)
(ppm)



6e

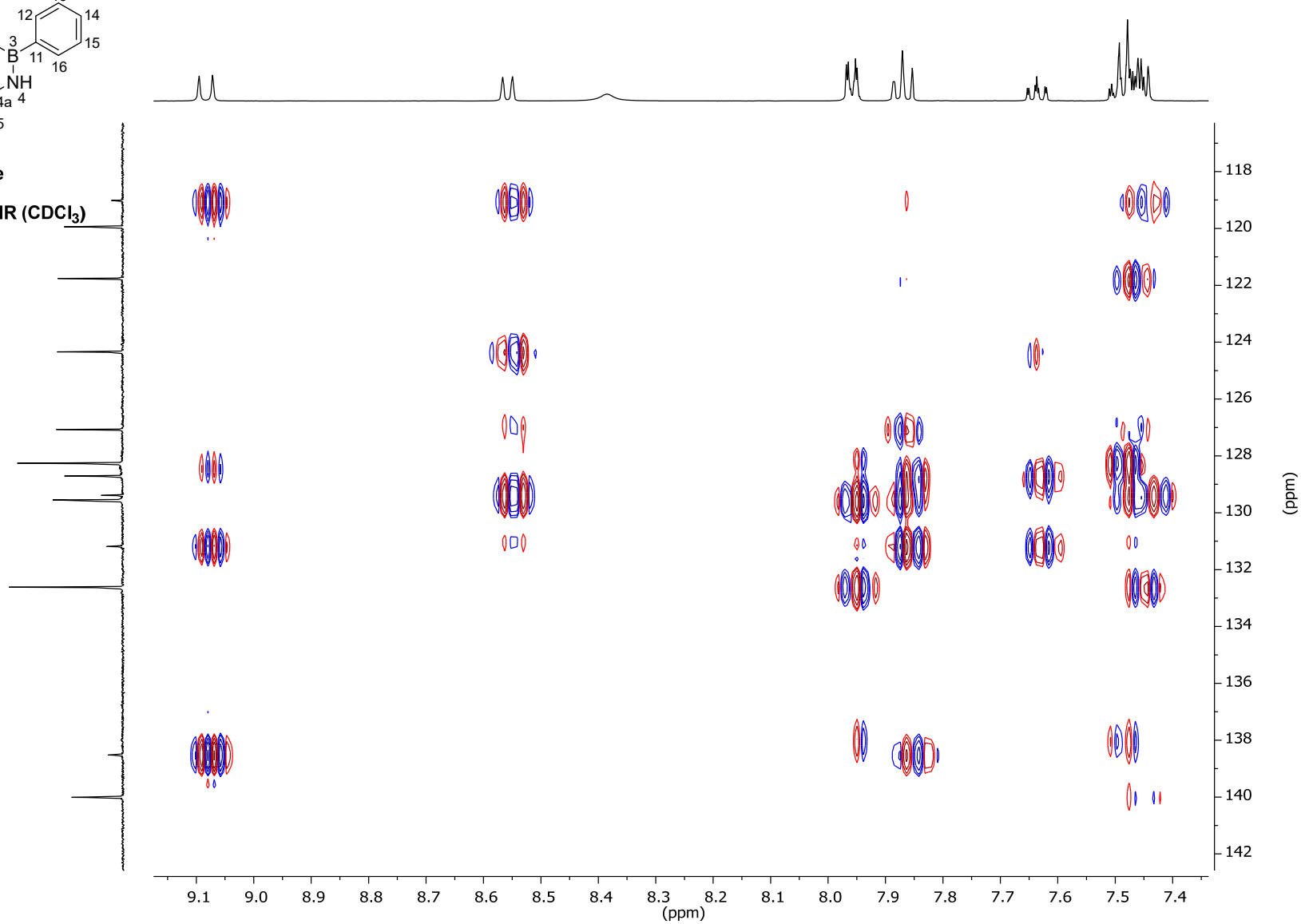
gHSQC-NMR ($CDCl_3$)

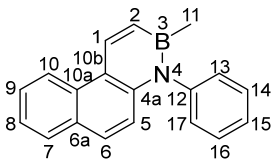




6e

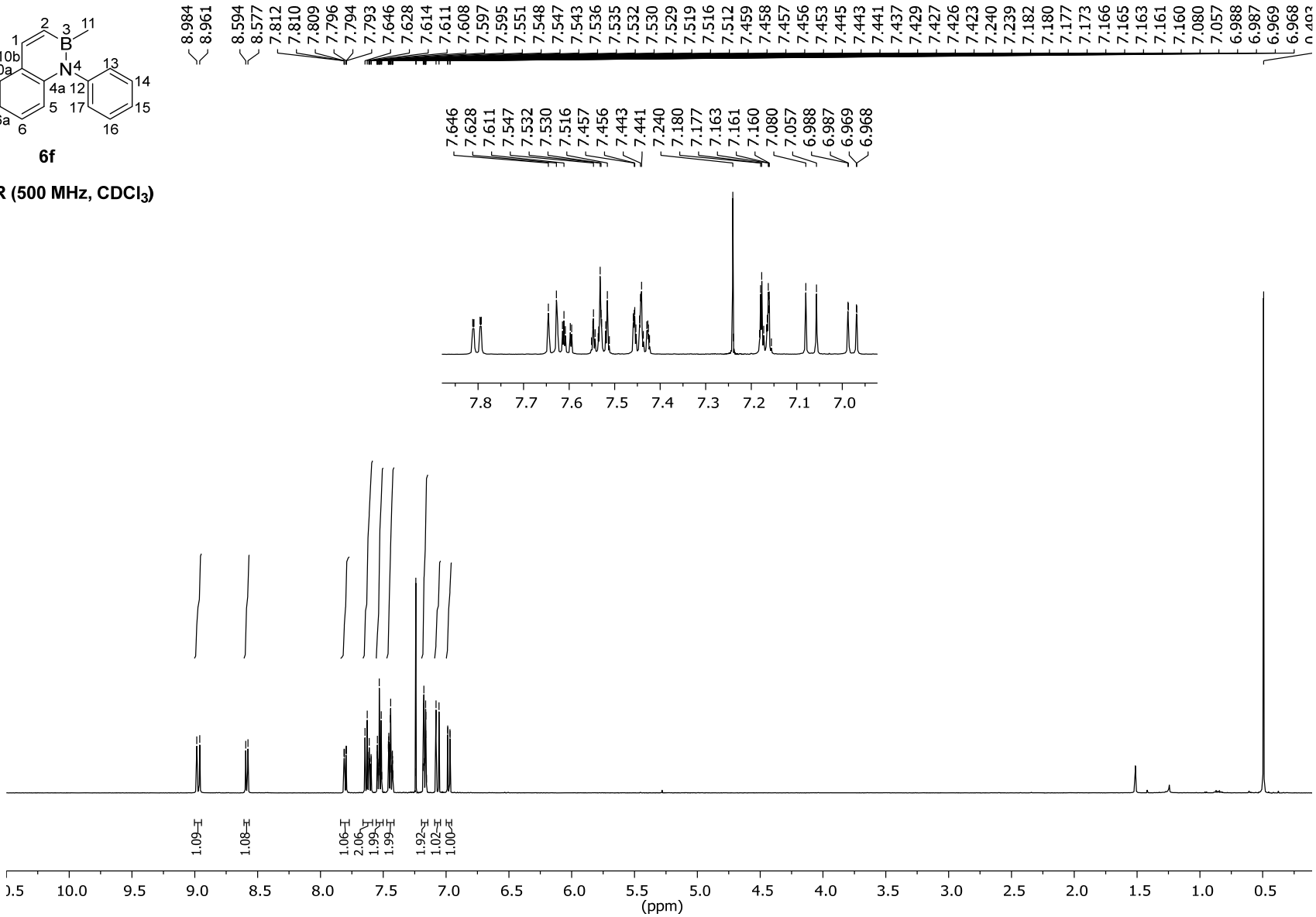
gHMBC-NMR ($CDCl_3$)

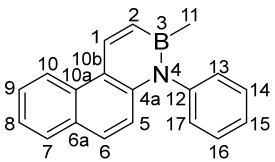




6f

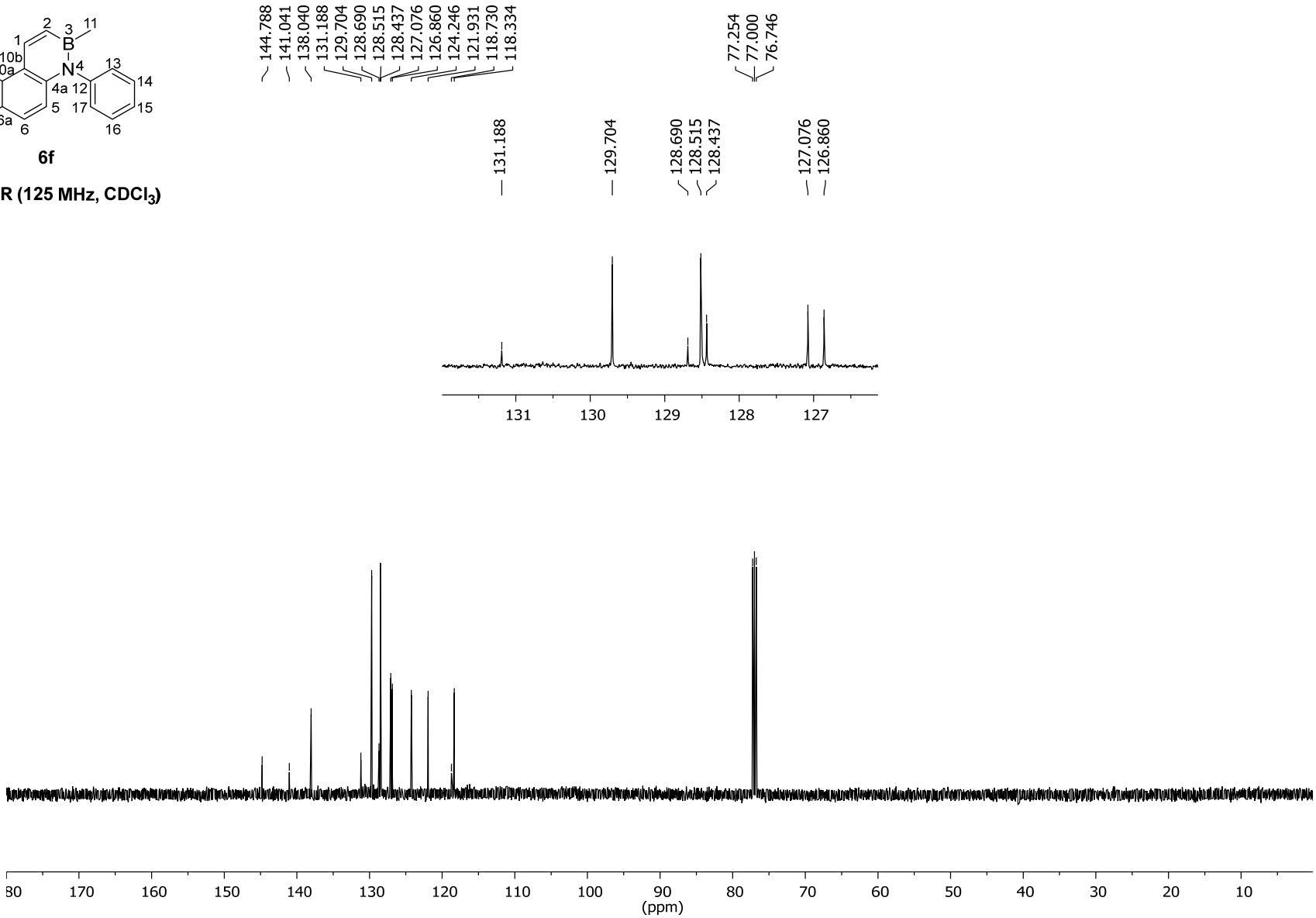
^{1}H-NMR (500 MHz, $CDCl_3$)

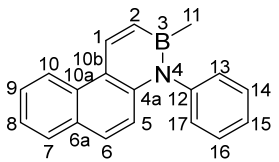




6f

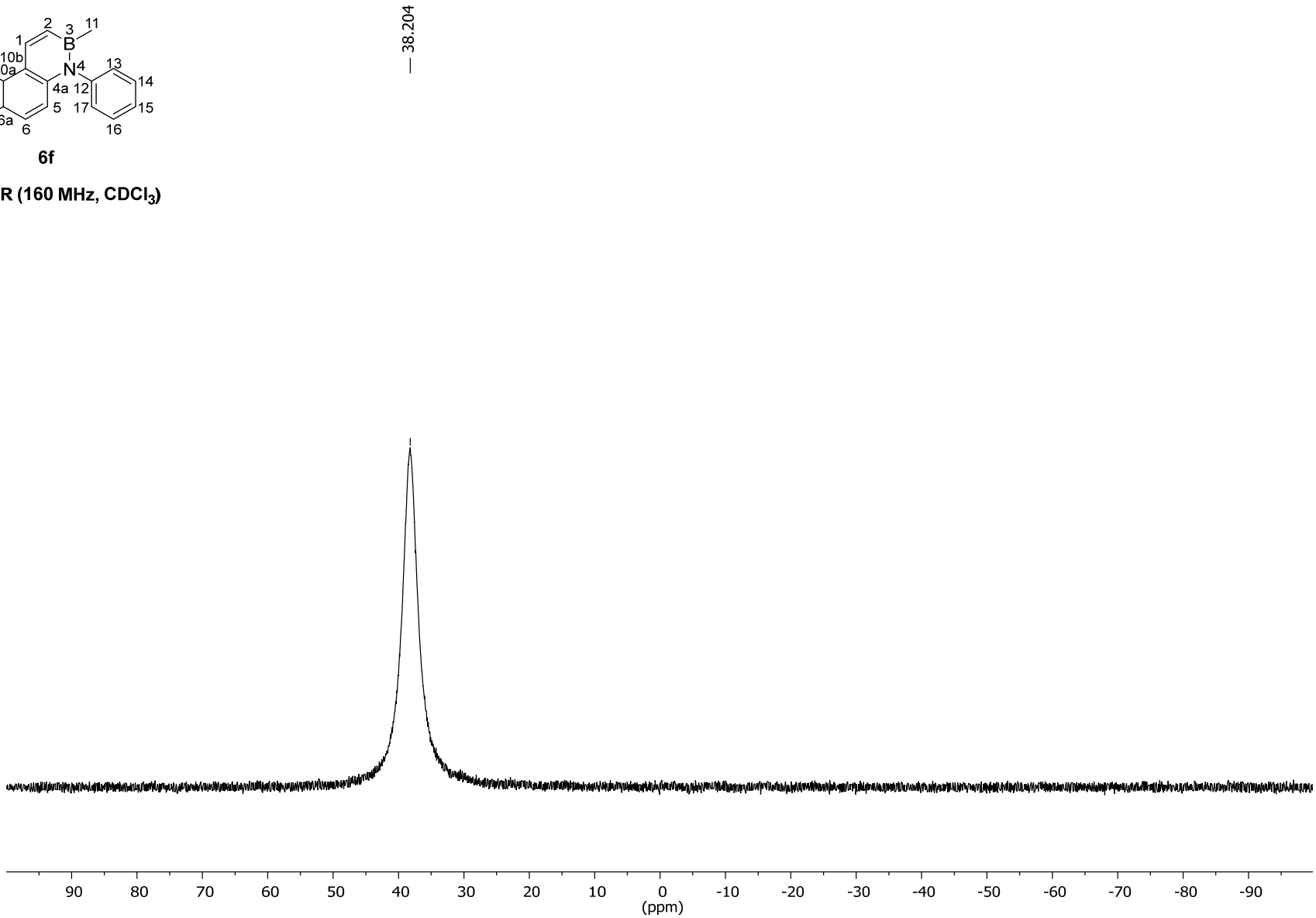
^{13}C-NMR (125 MHz, $CDCl_3$)

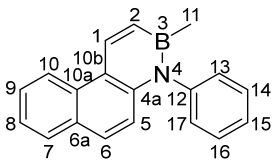




6f

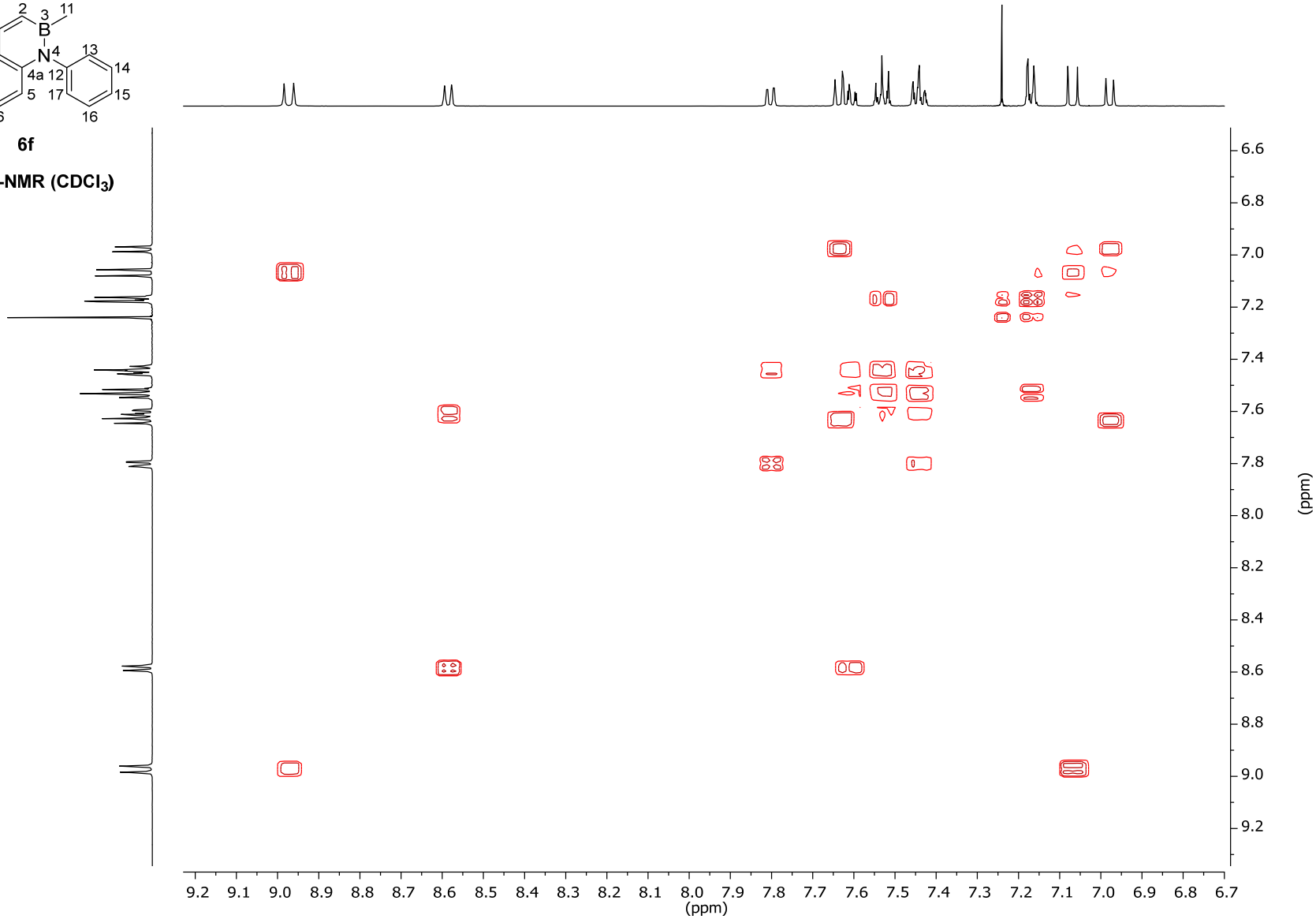
^{11}B-NMR (160 MHz, $CDCl_3$)

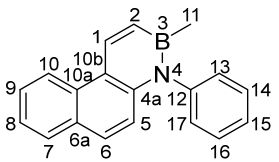




6f

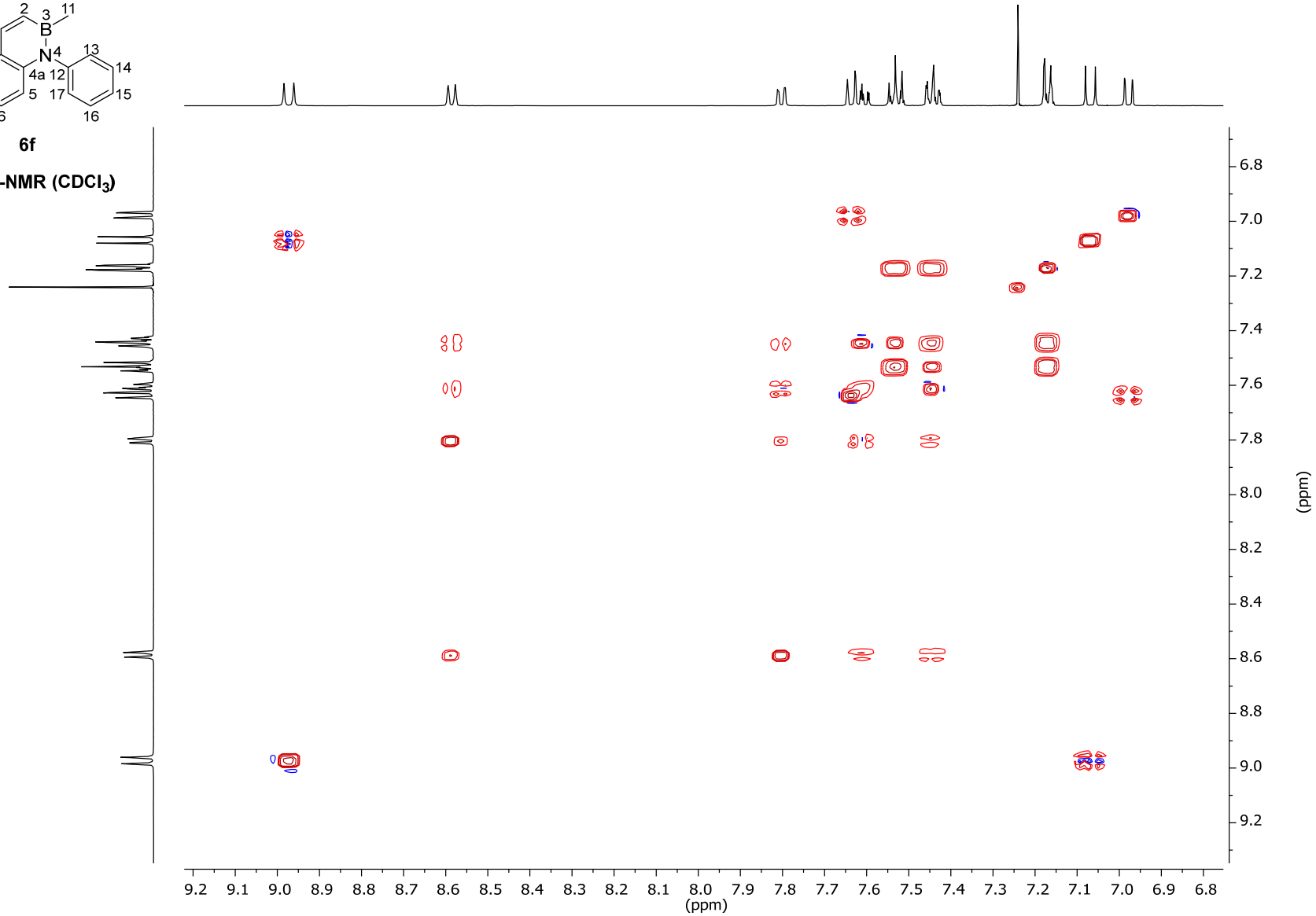
gCOSY-NMR ($CDCl_3$)

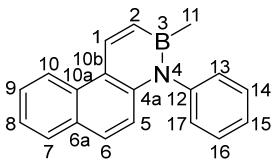




6f

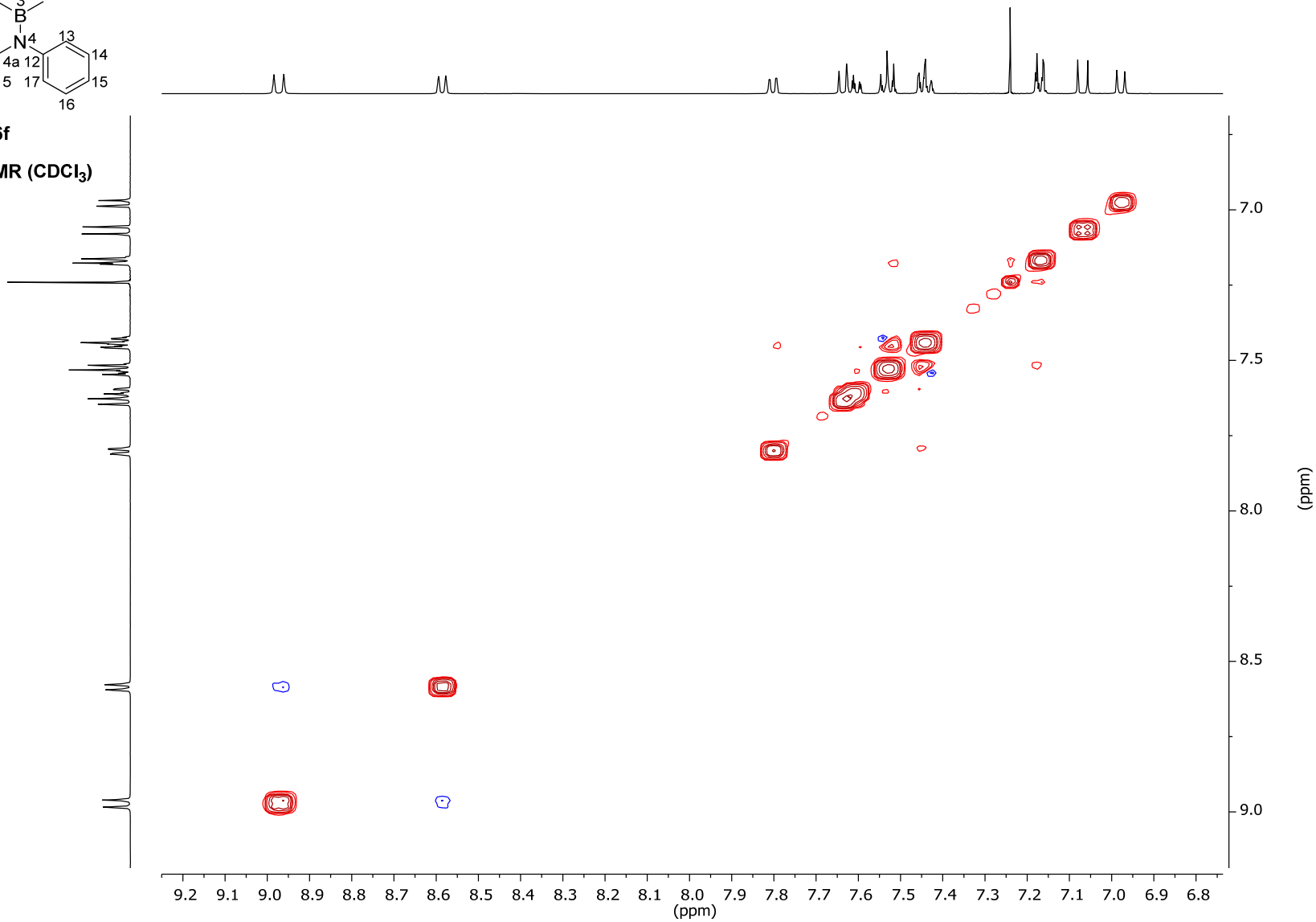
TOCSY-NMR ($CDCl_3$)

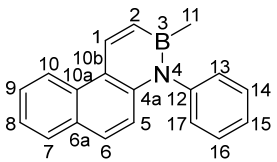




6f

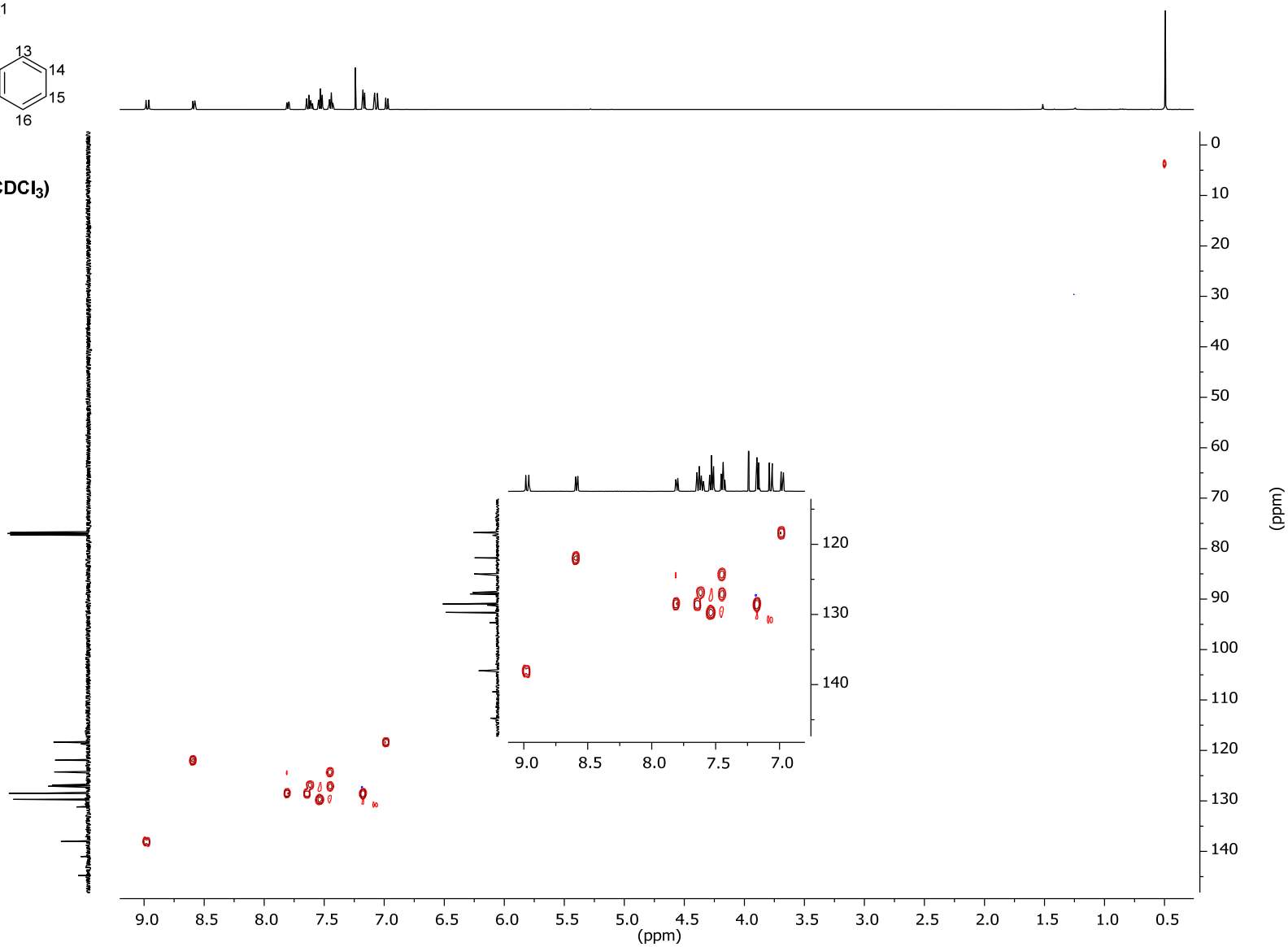
NOESY-NMR ($CDCl_3$)

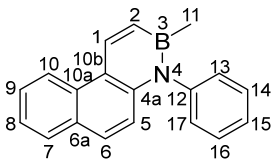




6f

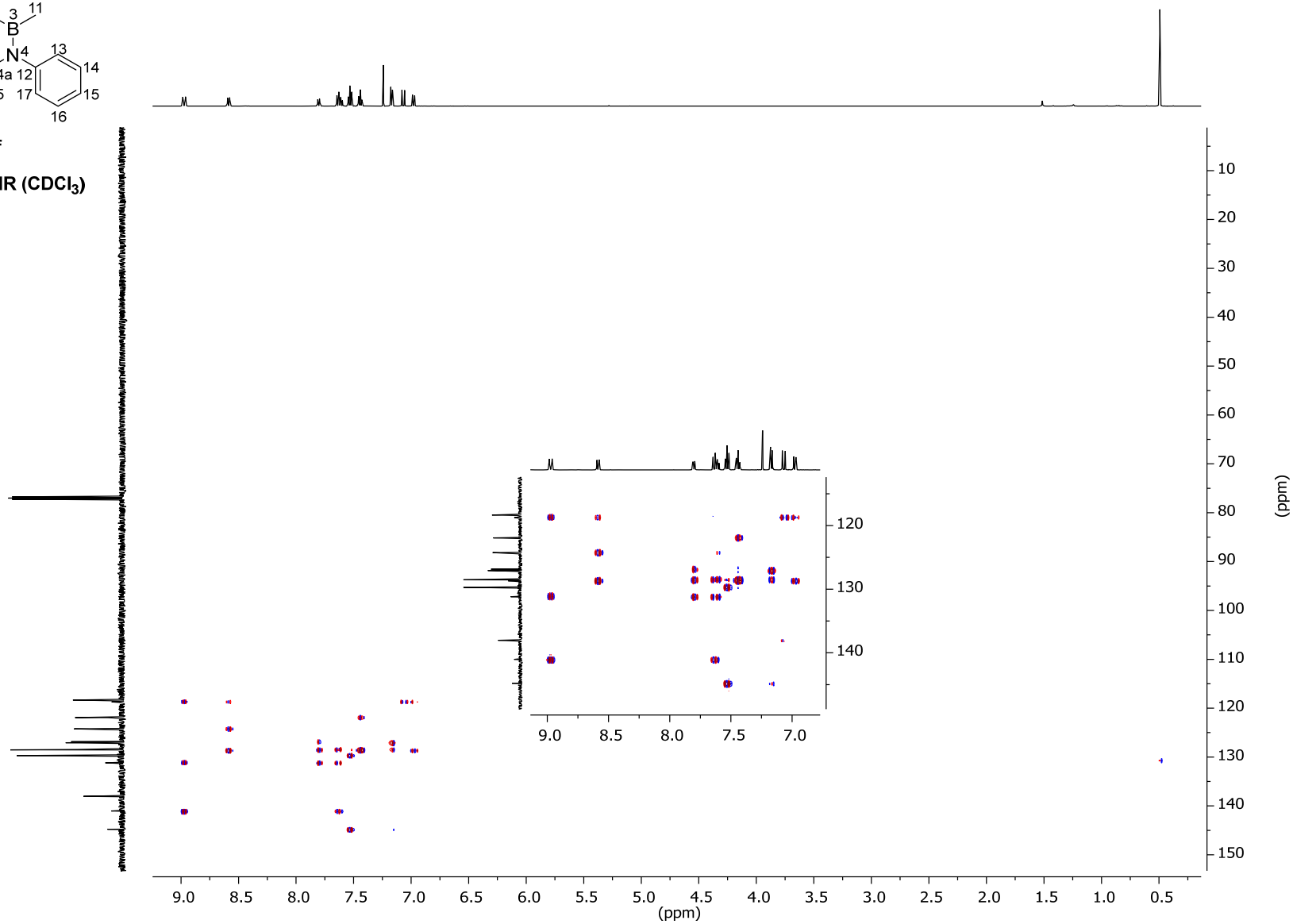
gHSQC-NMR ($CDCl_3$)

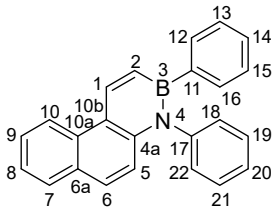




6f

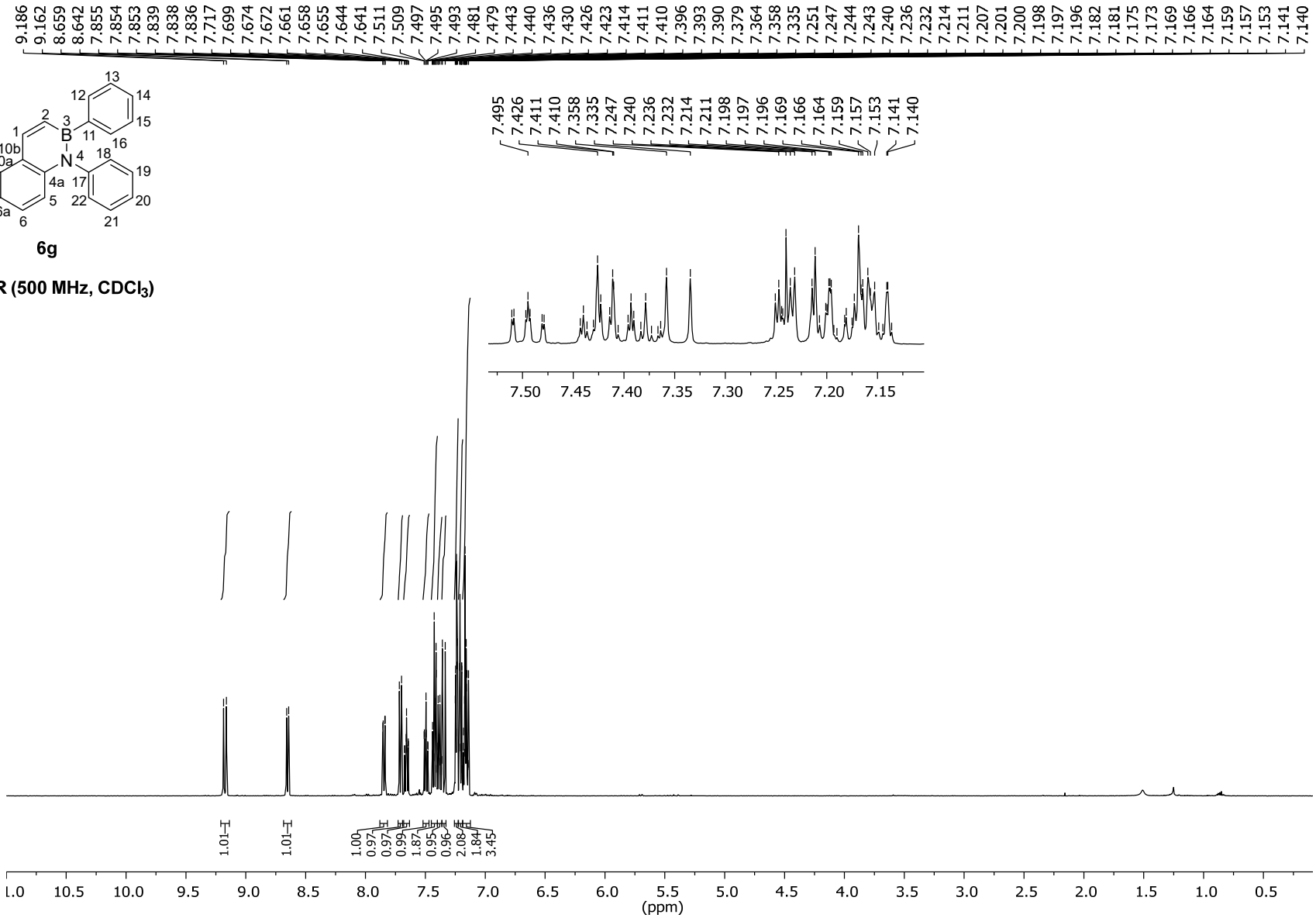
gHMBC-NMR ($CDCl_3$)

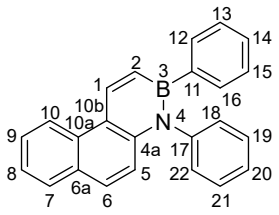




6g

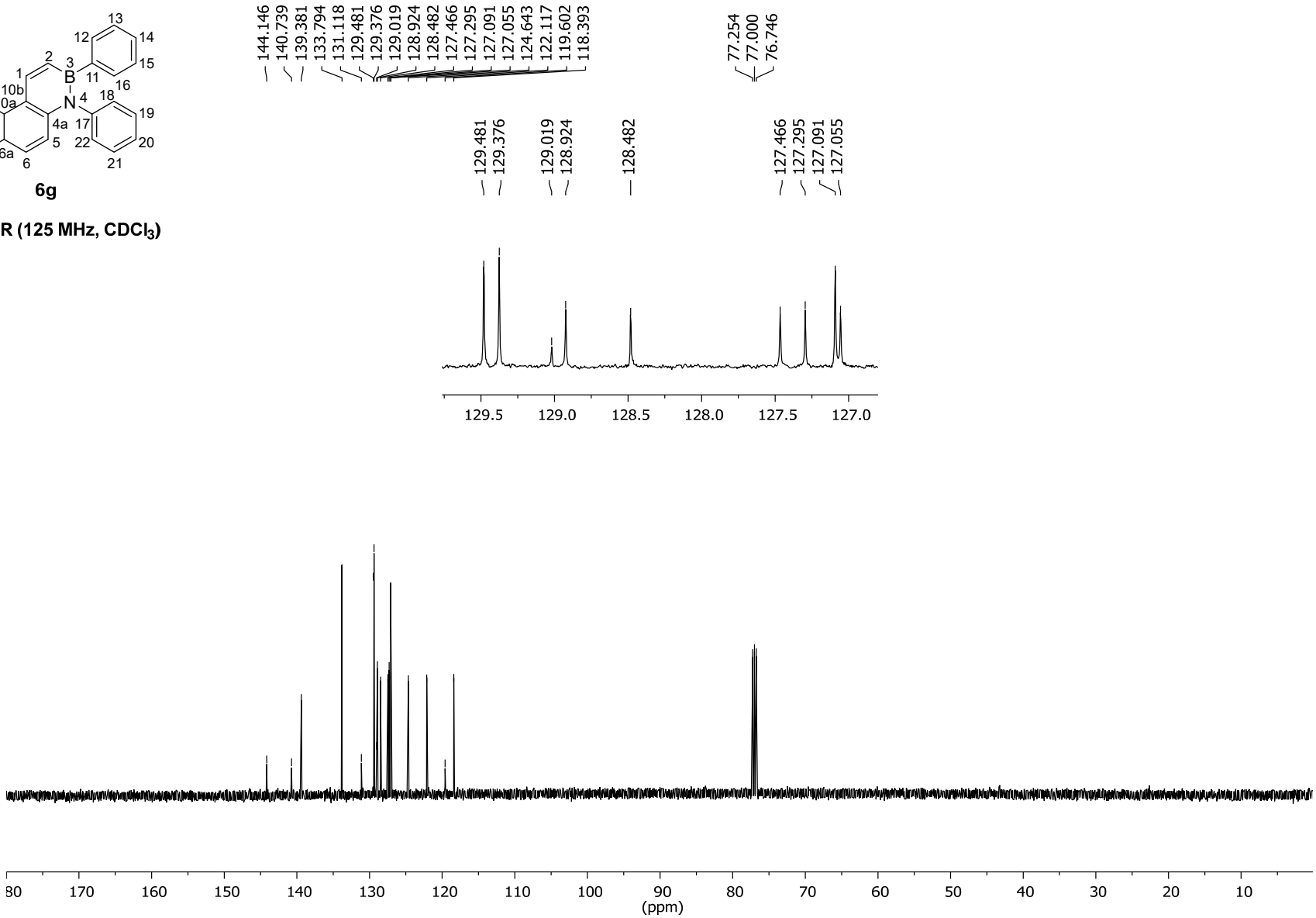
^{1}H-NMR (500 MHz, $CDCl_3$)

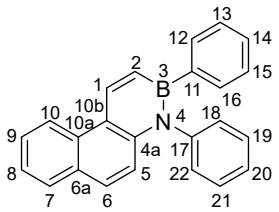




6g

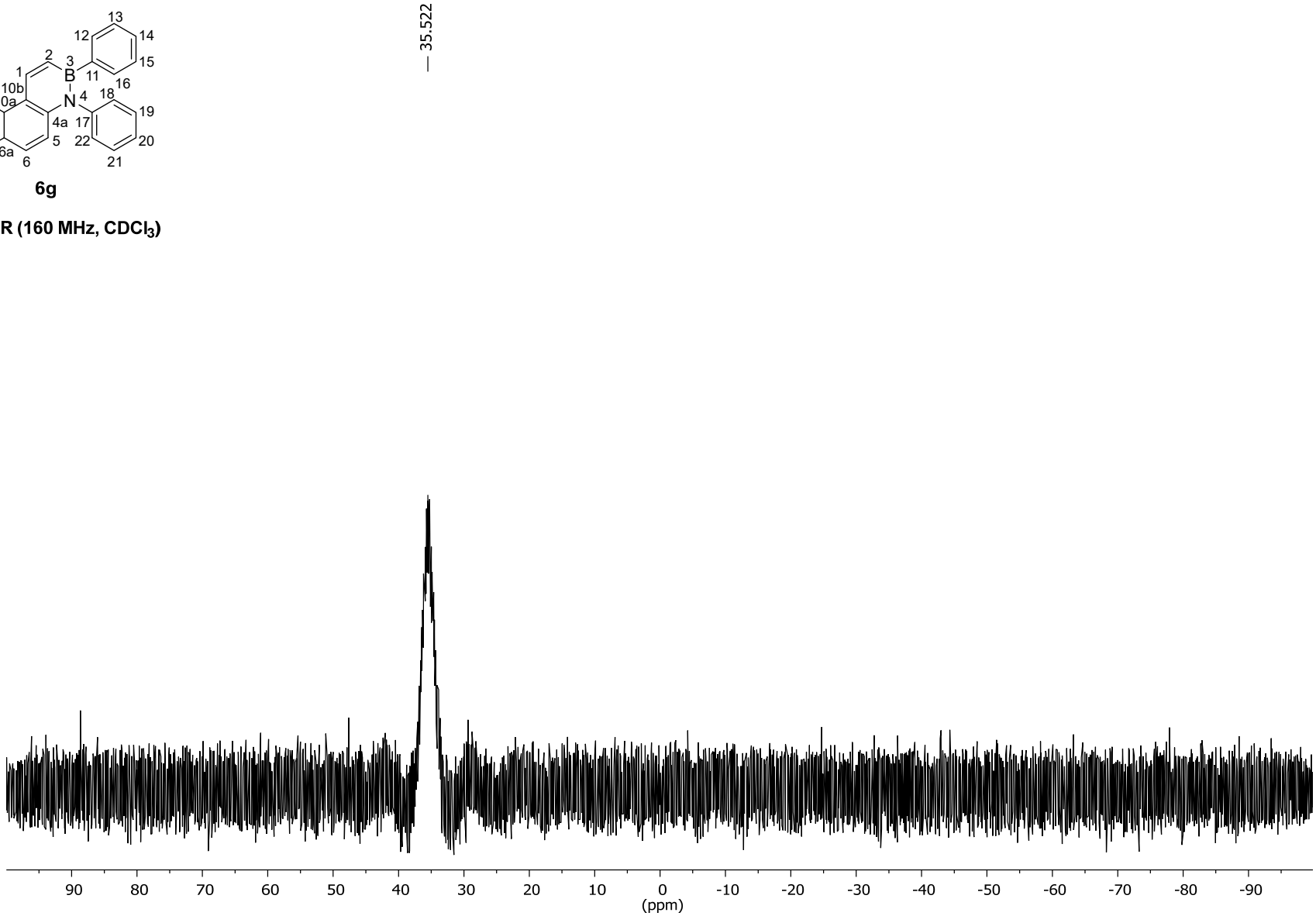
^{13}C-NMR (125 MHz, $CDCl_3$)

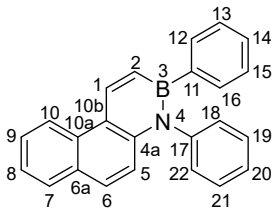




6g

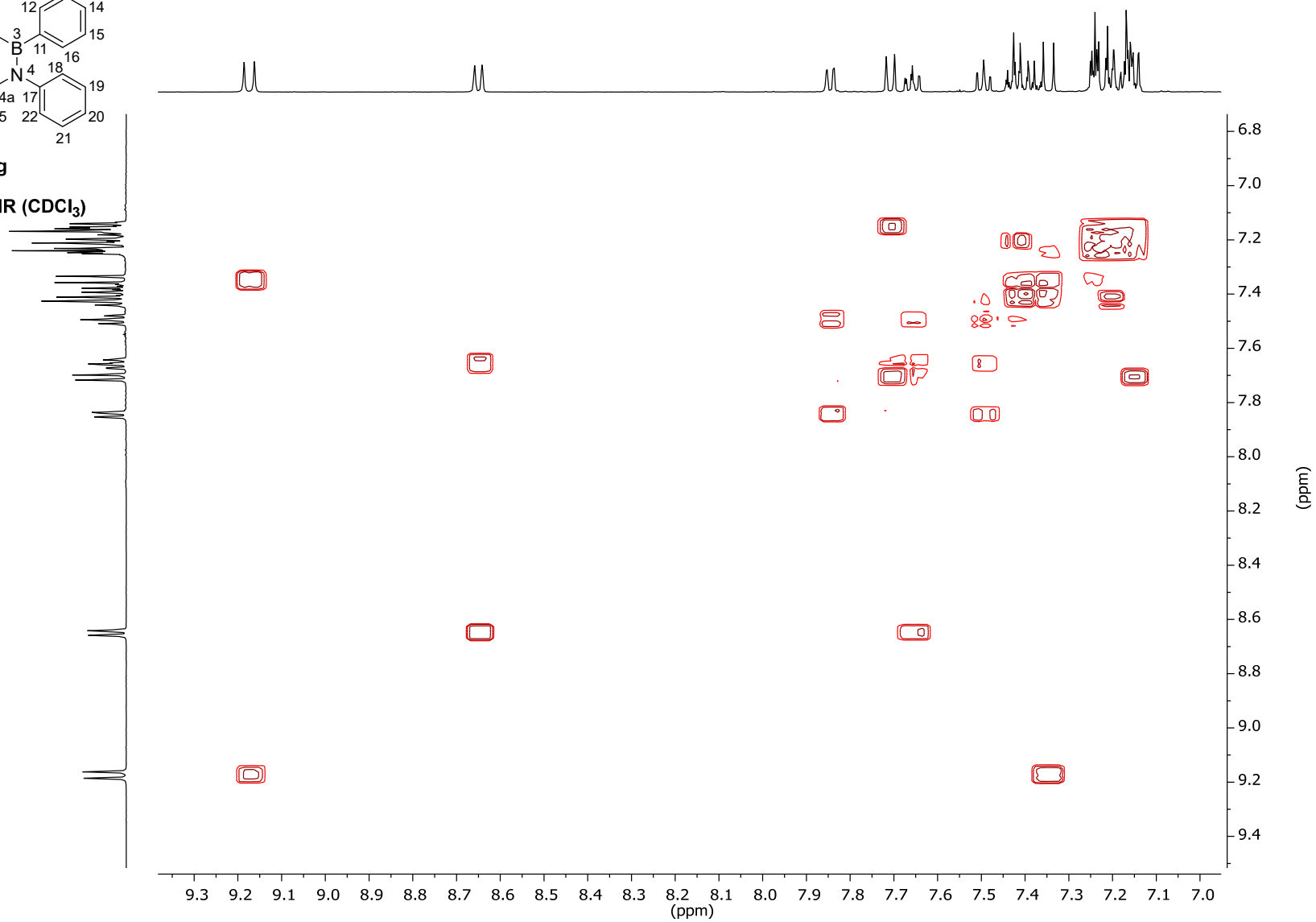
^{11}B-NMR (160 MHz, $CDCl_3$)

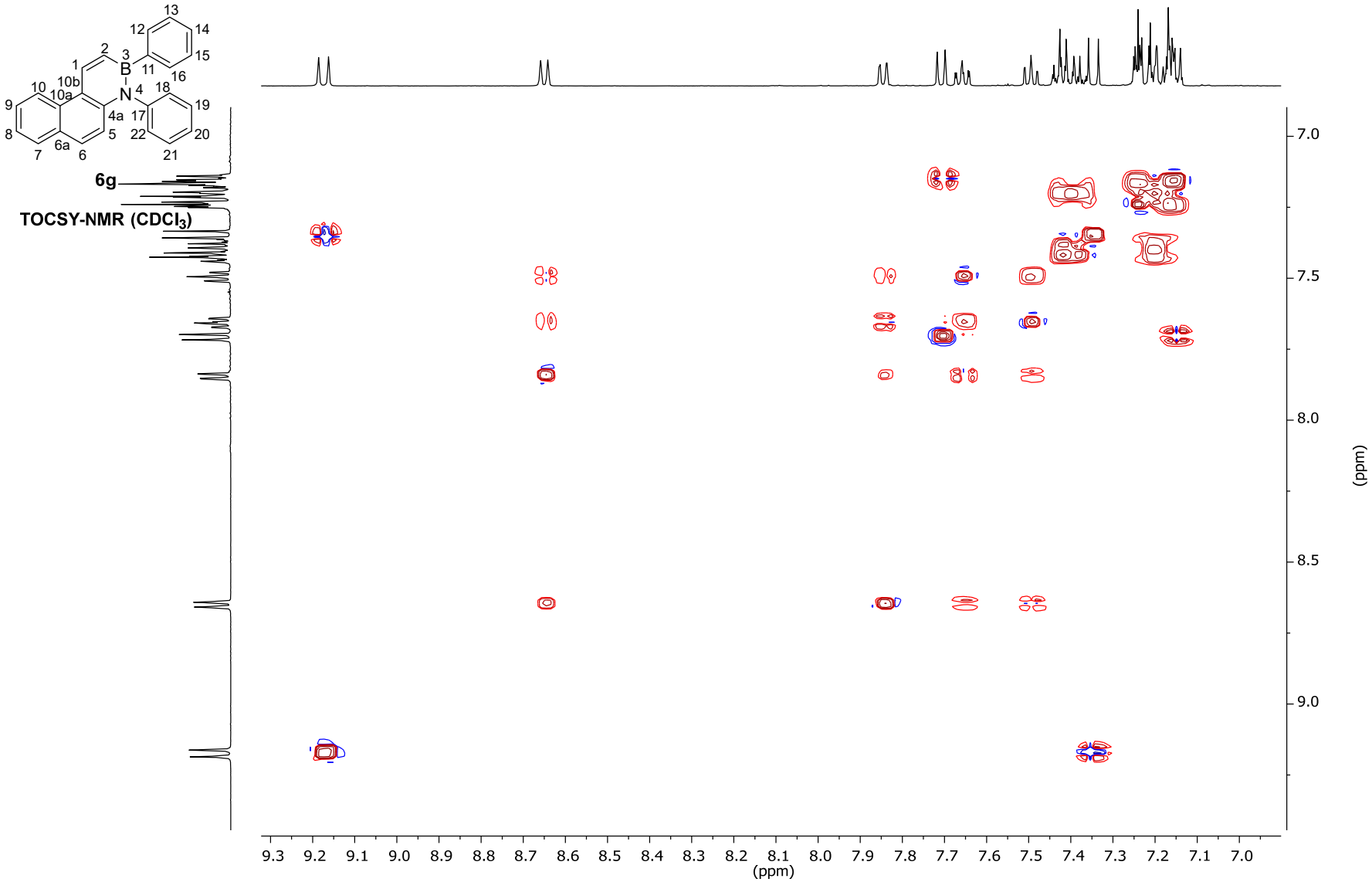


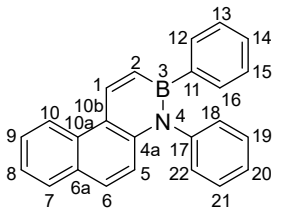


6g

gCOSY-NMR ($CDCl_3$)

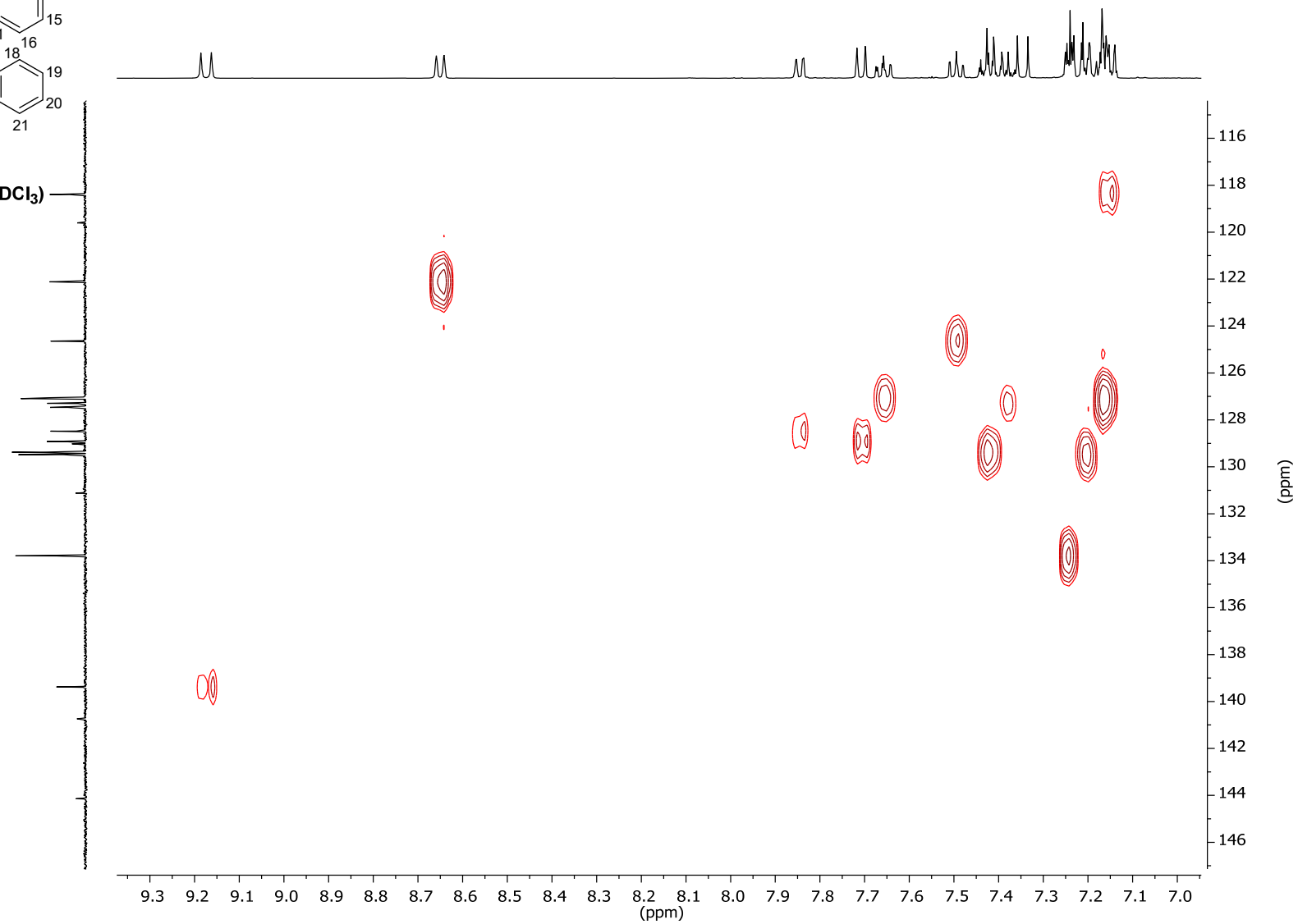


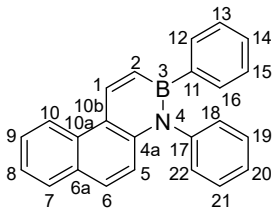

6g
TOCSY-NMR (CDCl3)
(ppm)
(ppm)



6g

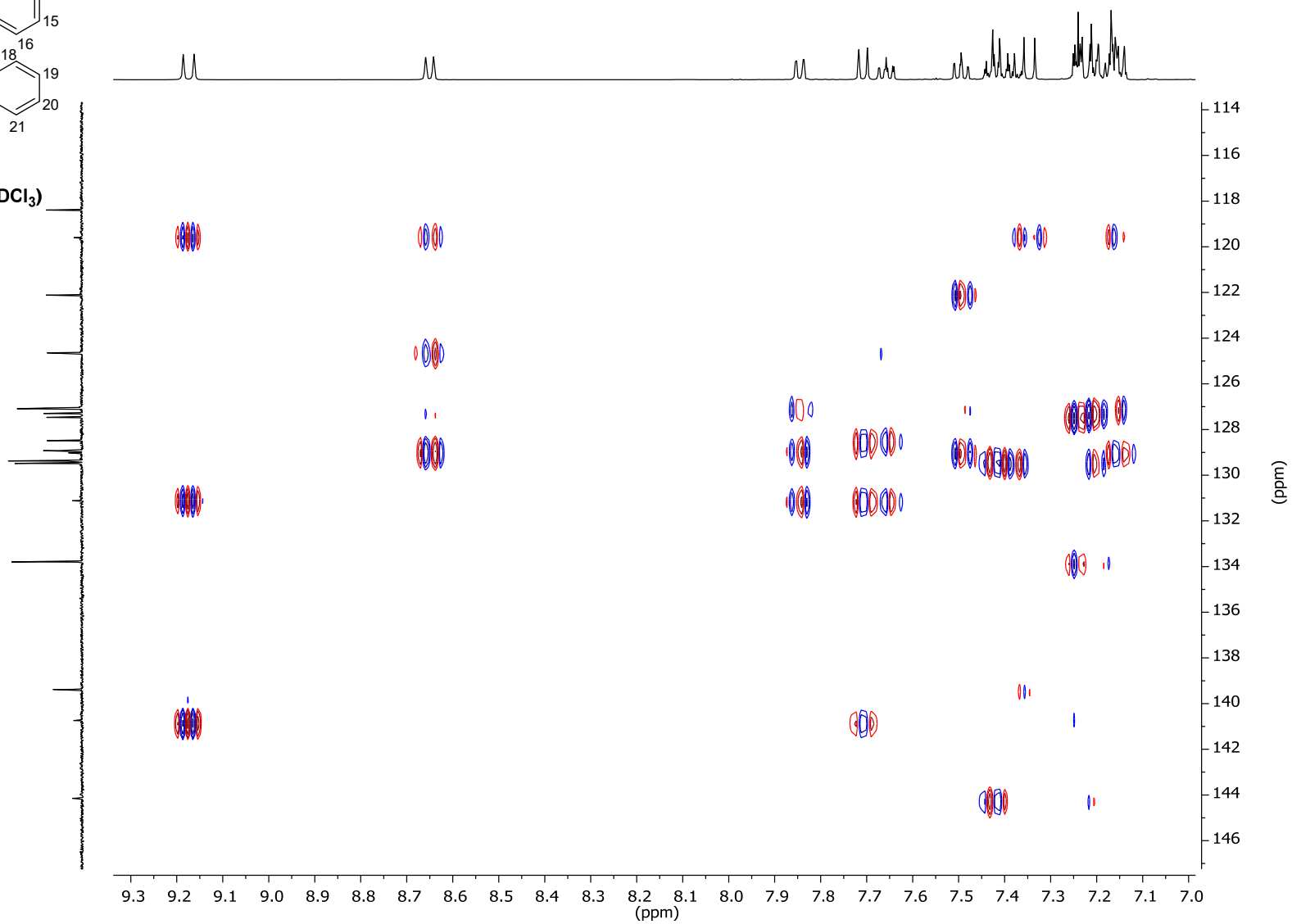
gHSQC-NMR ($CDCl_3$)

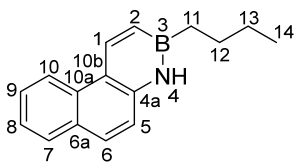




6g

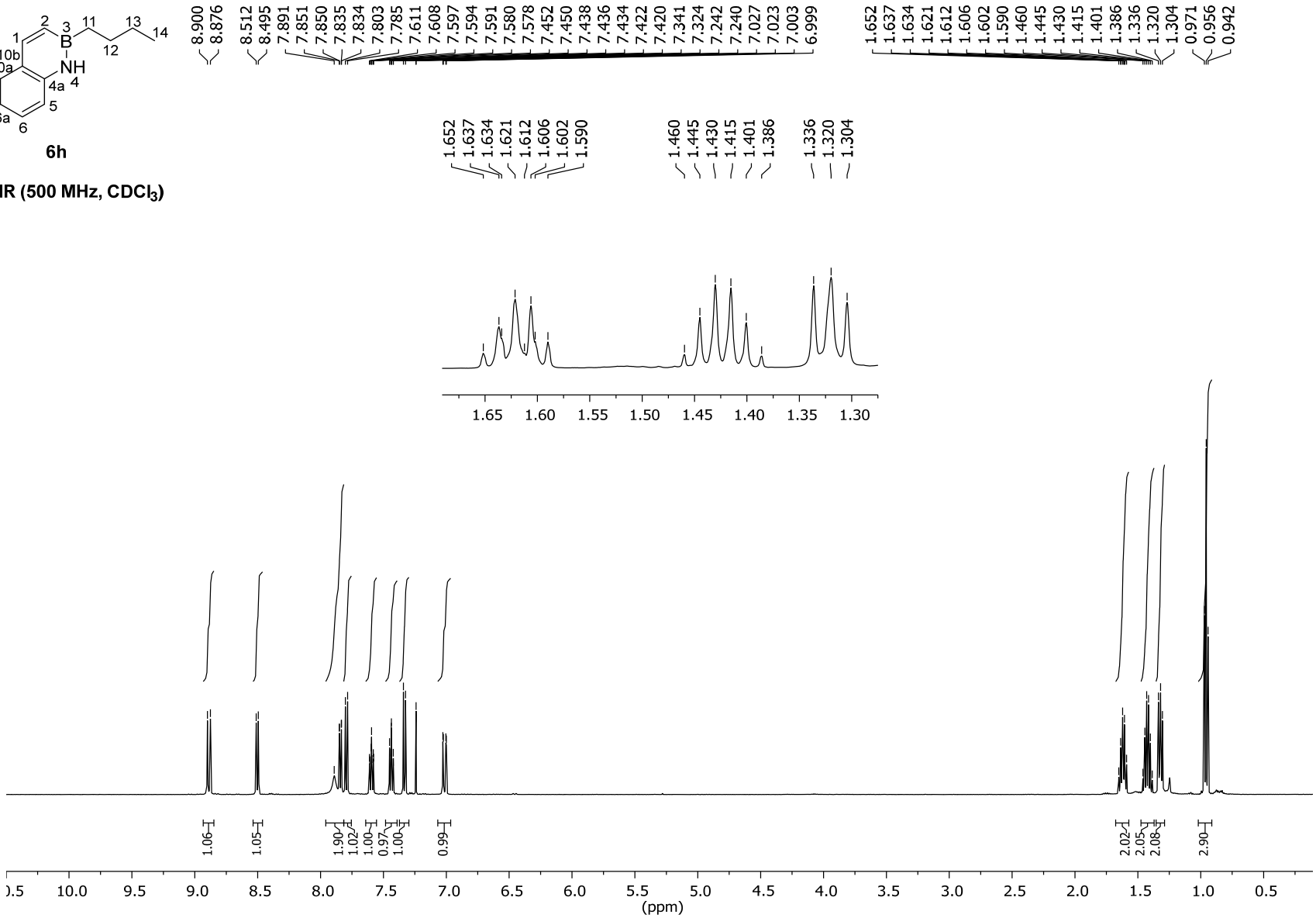
gHMBC-NMR ($CDCl_3$)

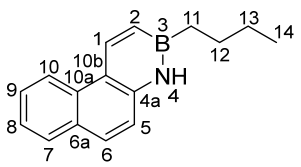




6h

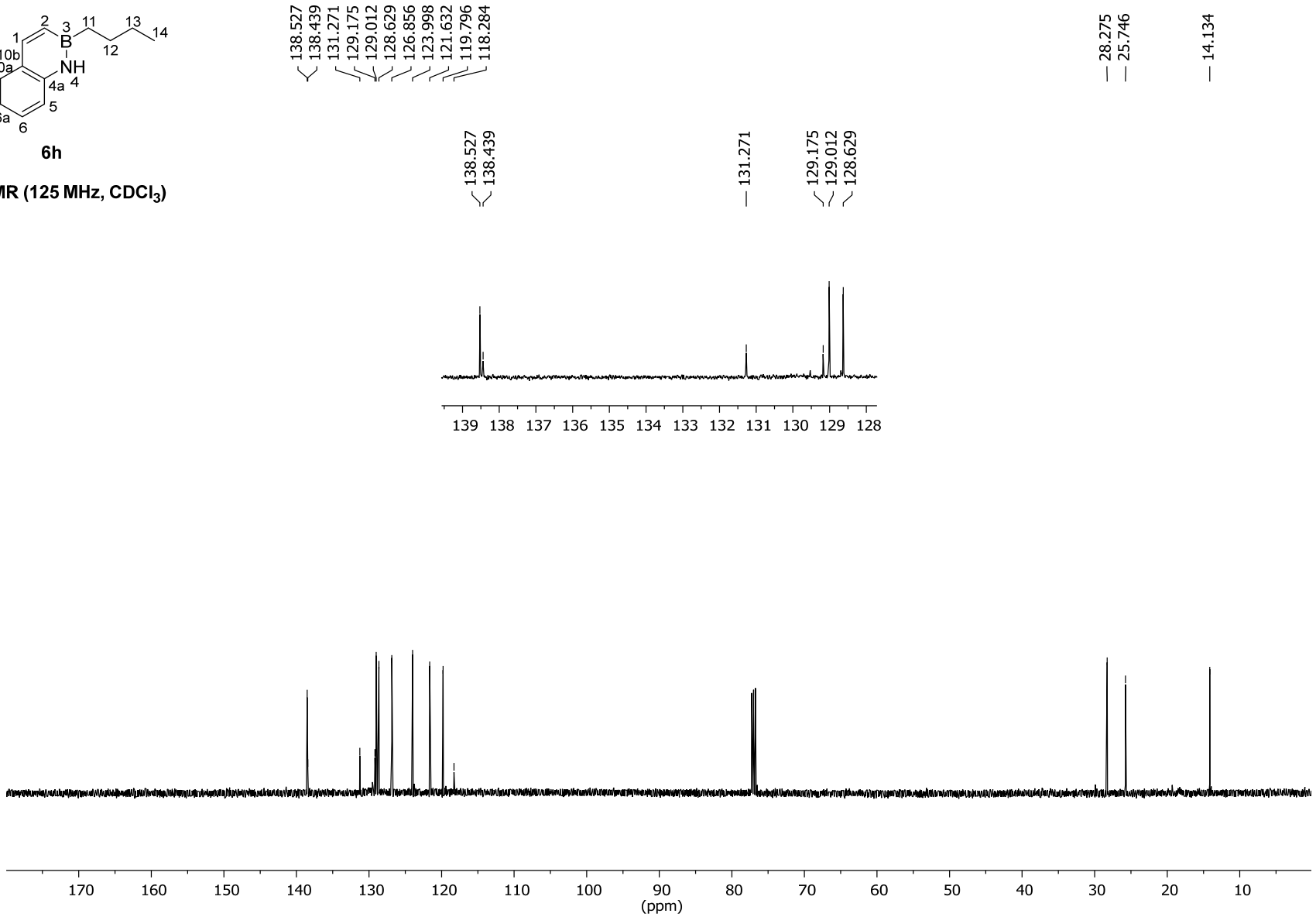
^{1}H-NMR (500 MHz, $CDCl_3$)

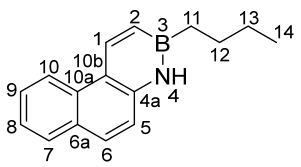




6h

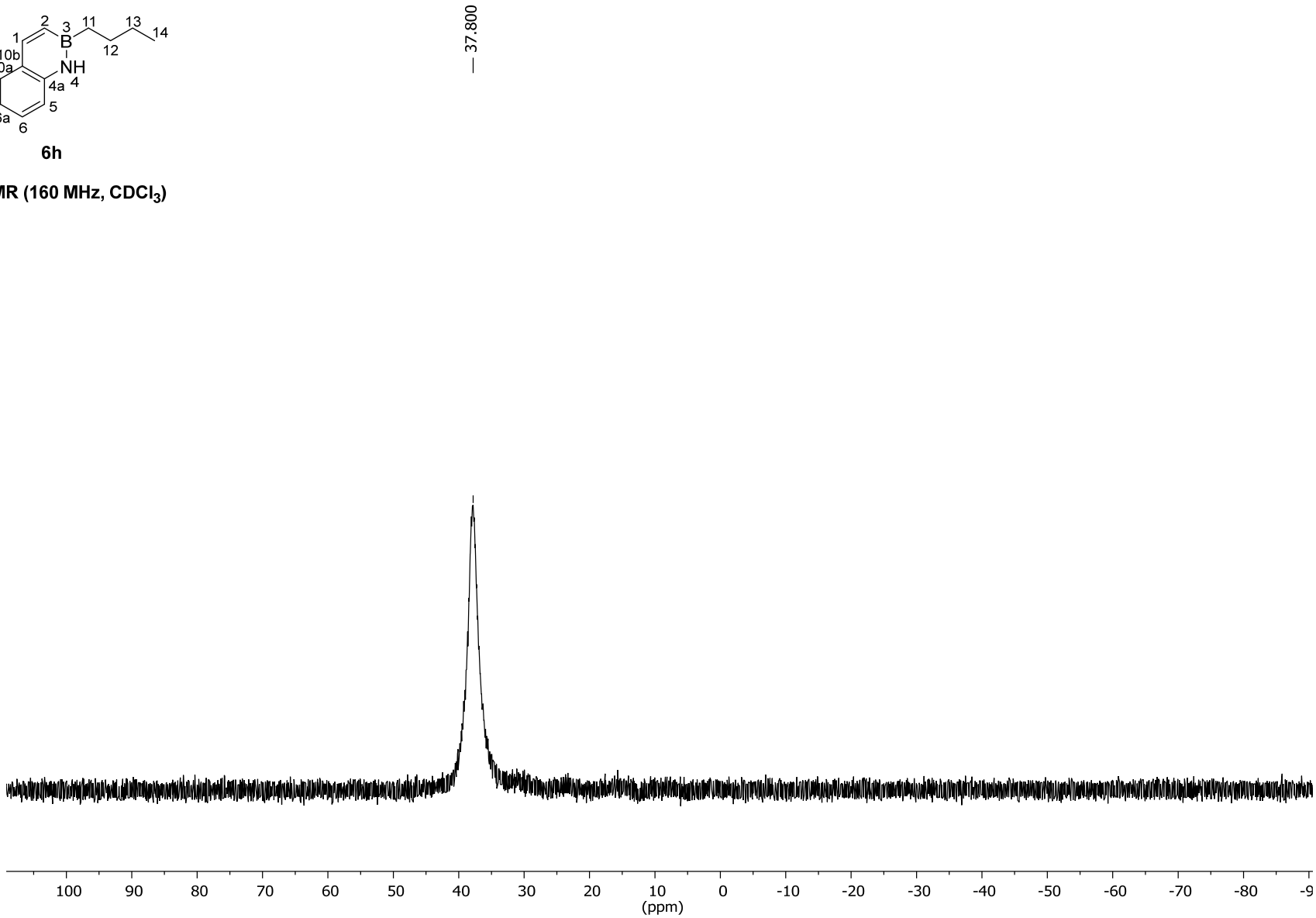
^{13}C-NMR (125 MHz, $CDCl_3$)

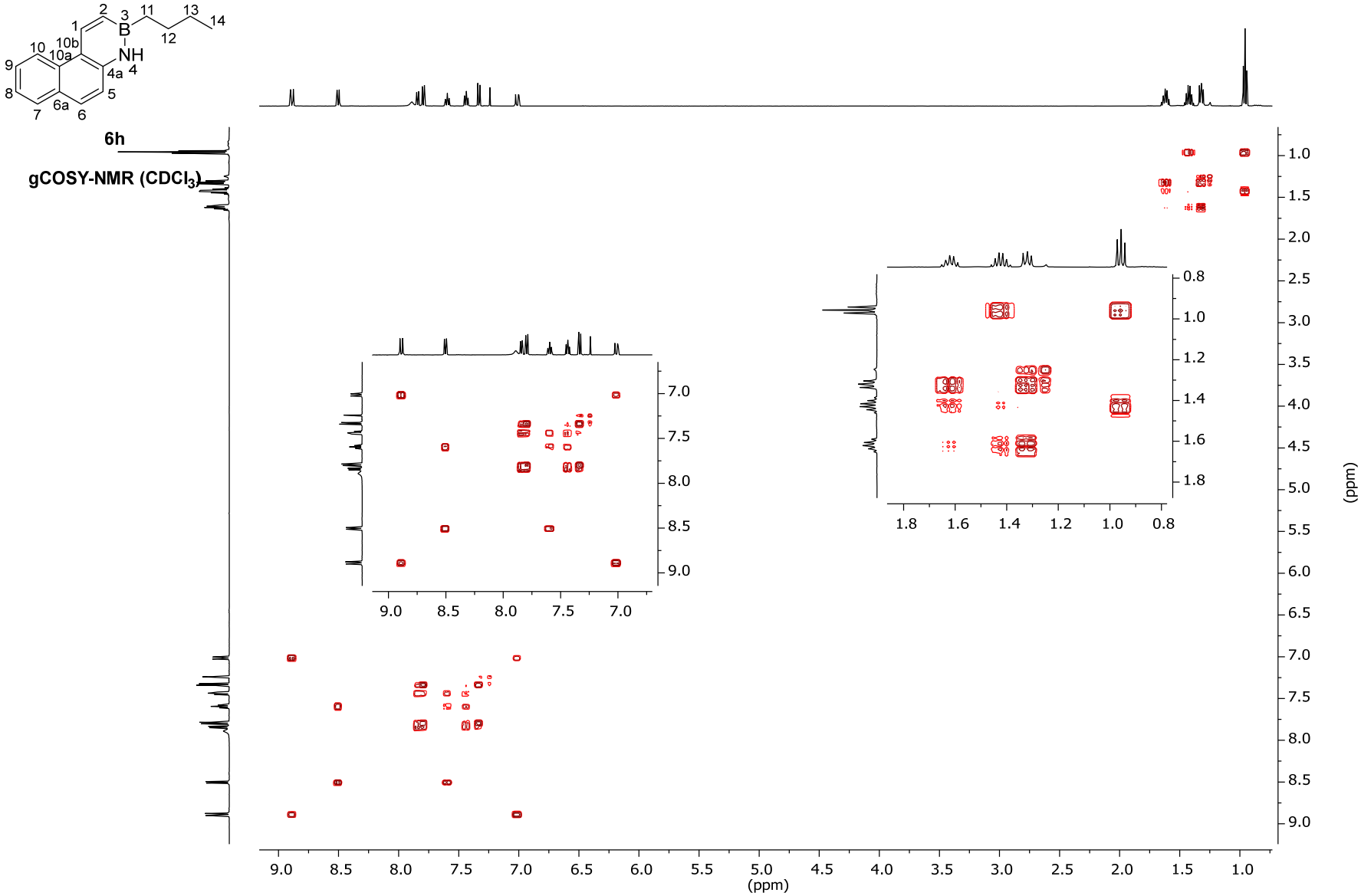


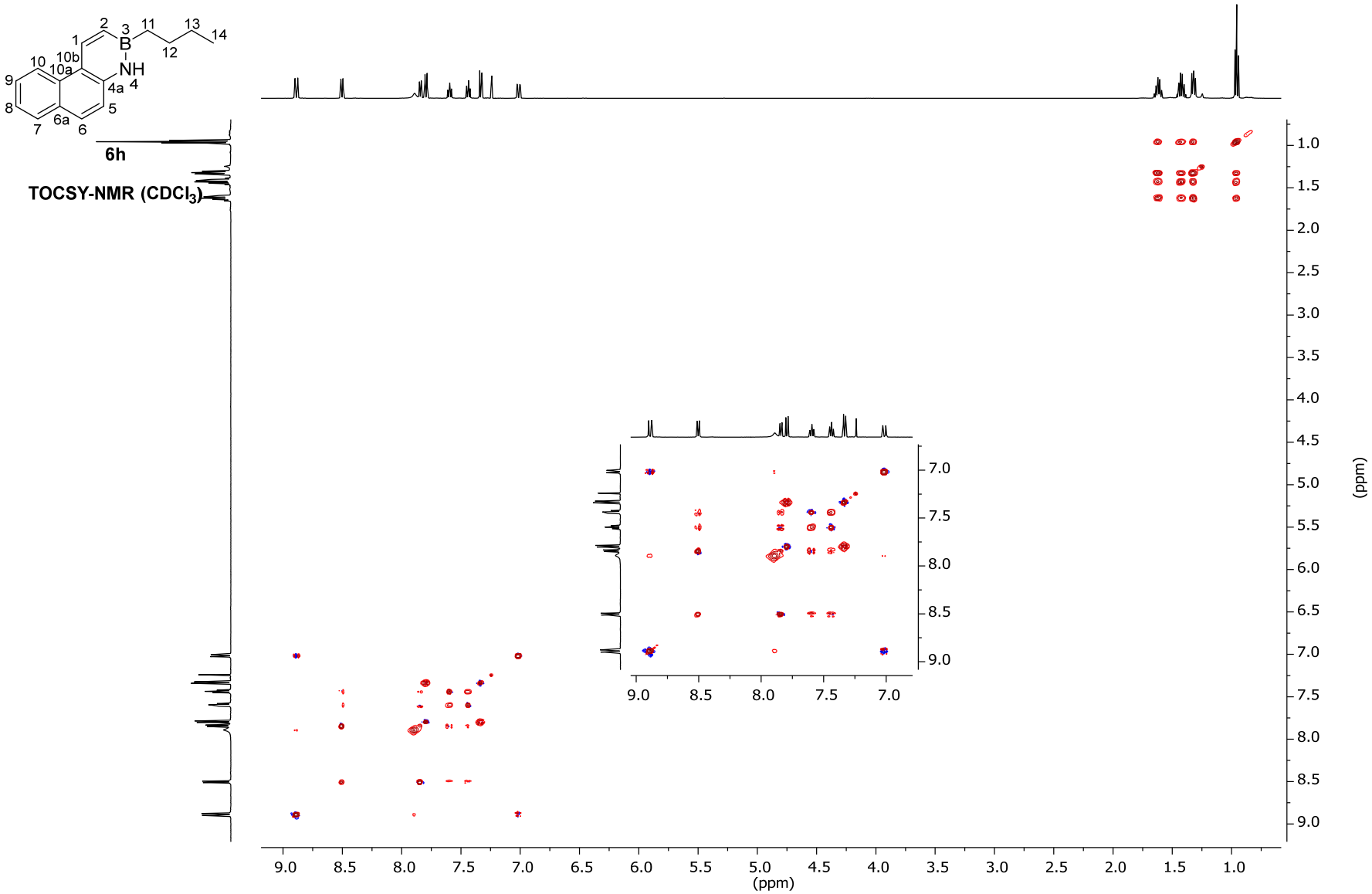


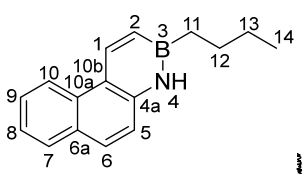
6h

^{11}B-NMR (160 MHz, $CDCl_3$)



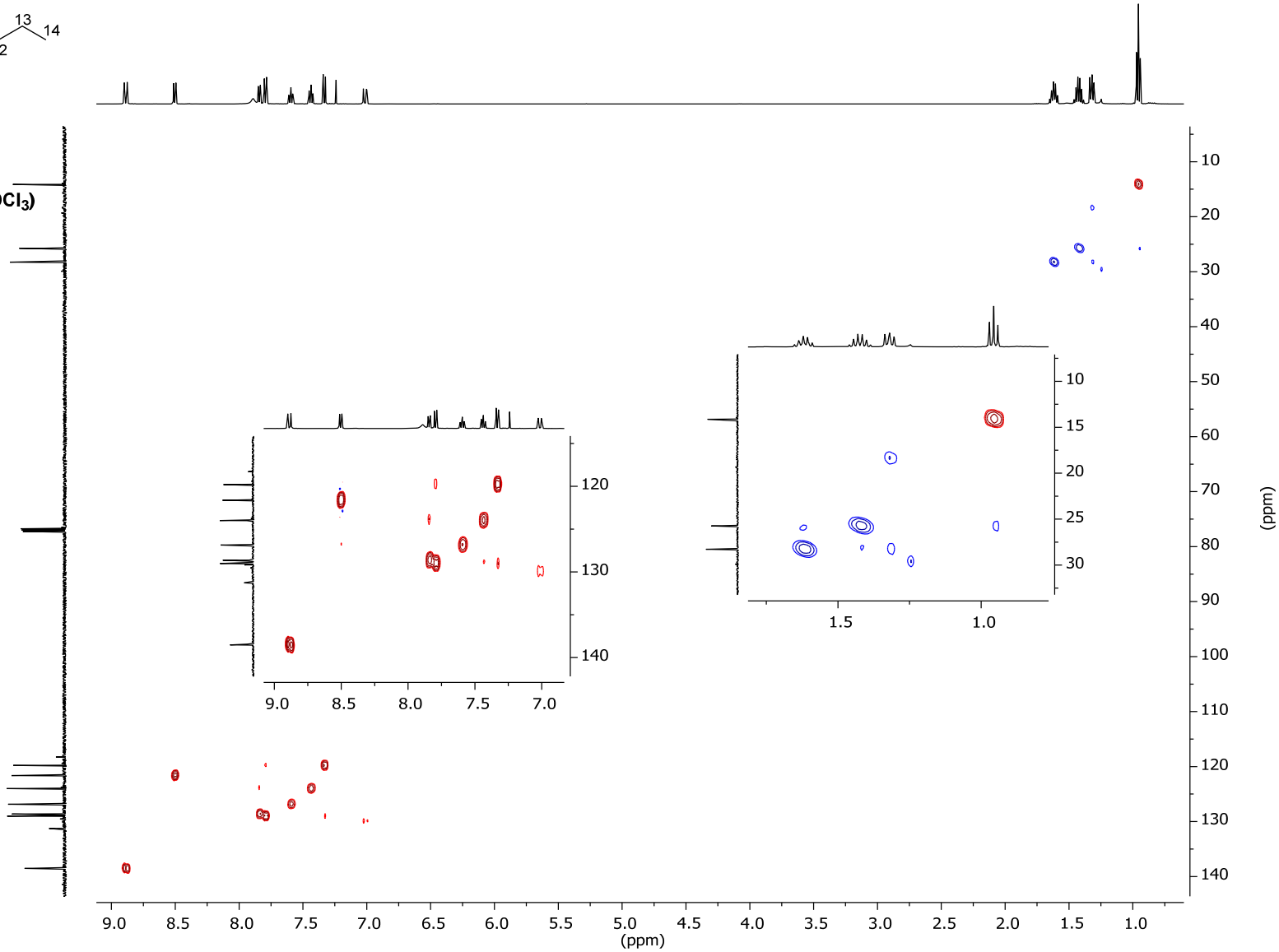

6h
gCOSY-NMR (CDCl3)
(ppm)

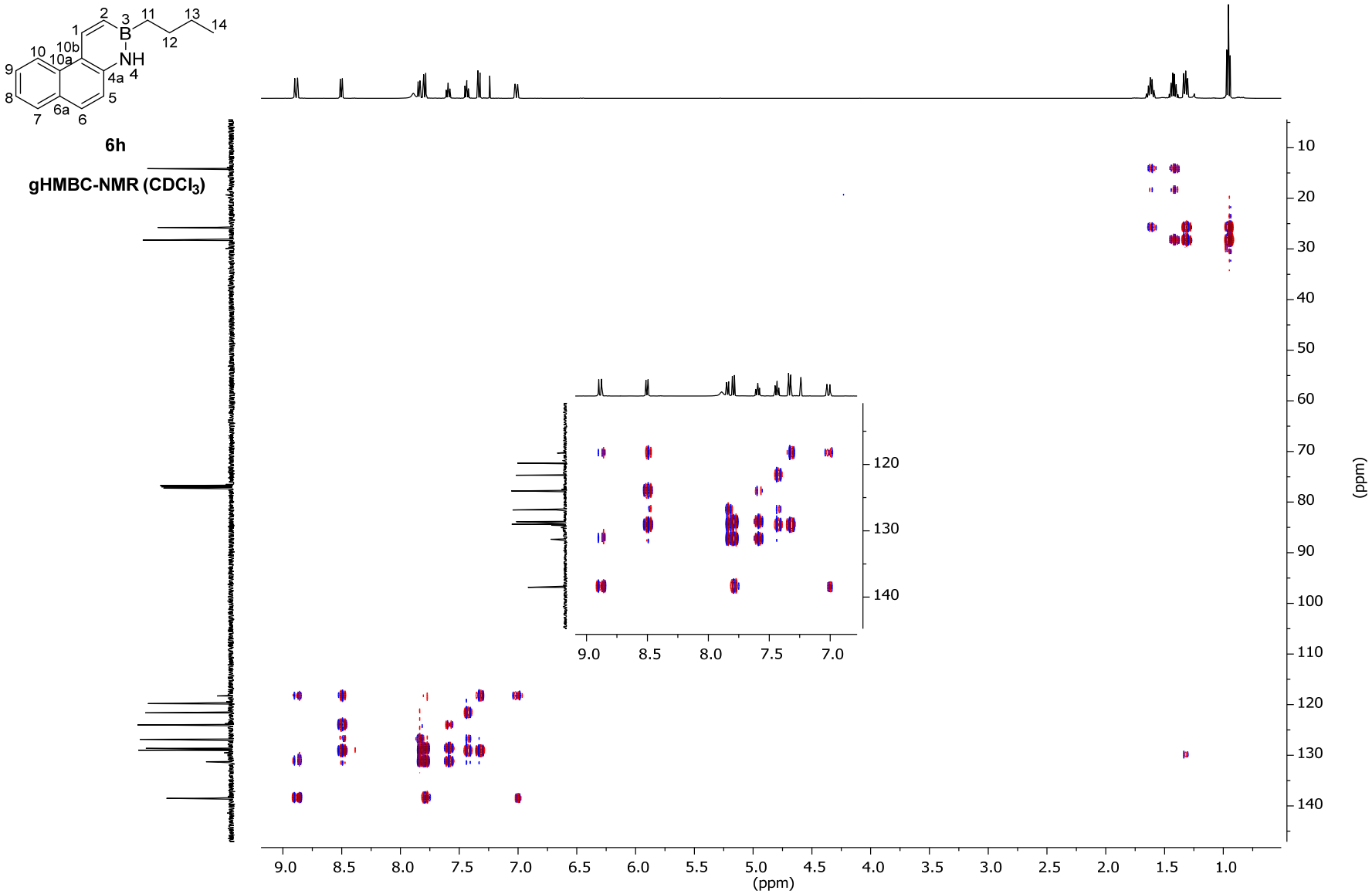

6h
TOCSY-NMR (CDCl3)
(ppm)

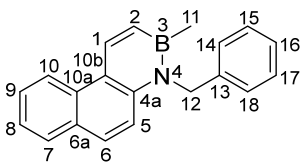


6h

gHSQC-NMR ($CDCl_3$)

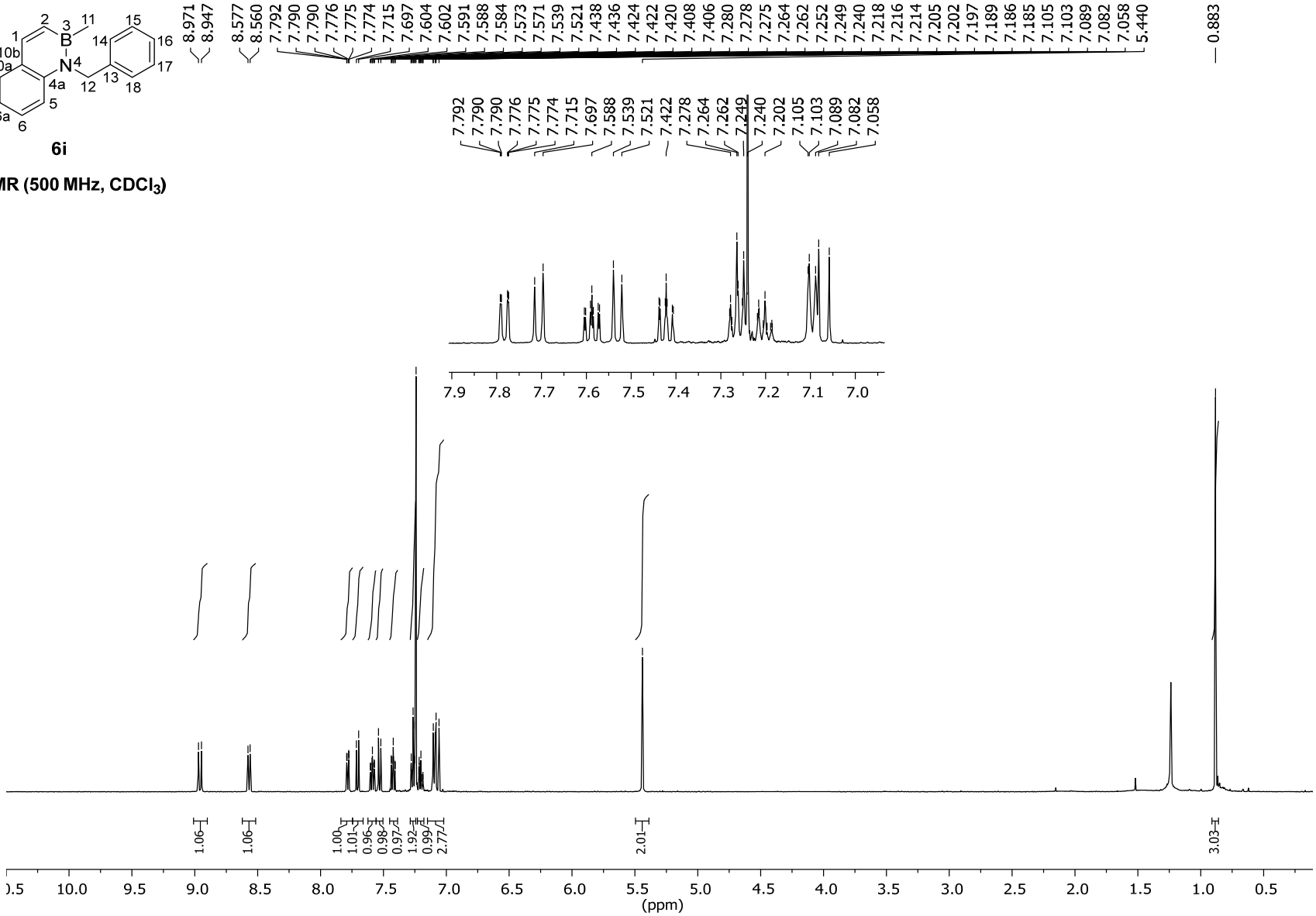


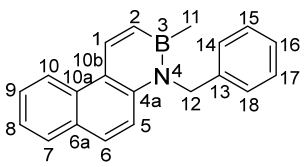

6h
gHMBC-NMR (CDCl3)
(ppm)
(ppm)



6i

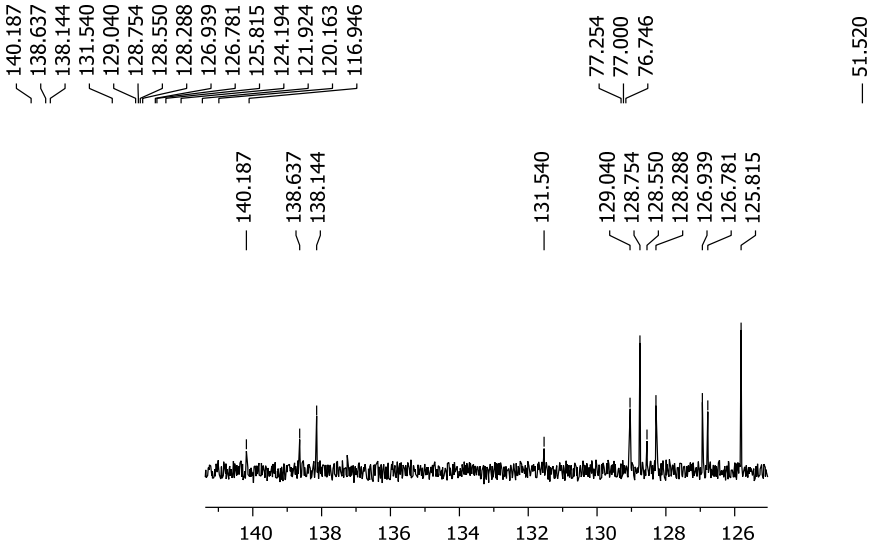
^{1}H-NMR (500 MHz, $CDCl_3$)

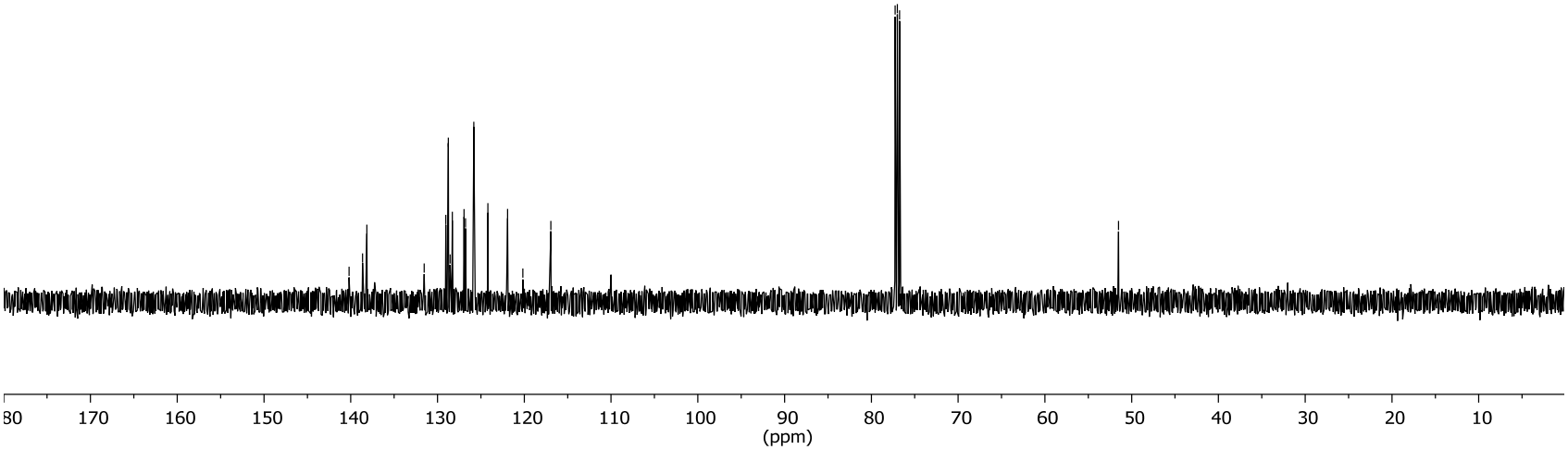


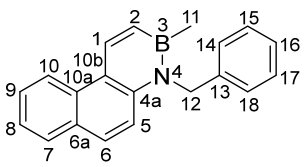


6i

^{13}C-NMR (125 MHz, $CDCl_3$)

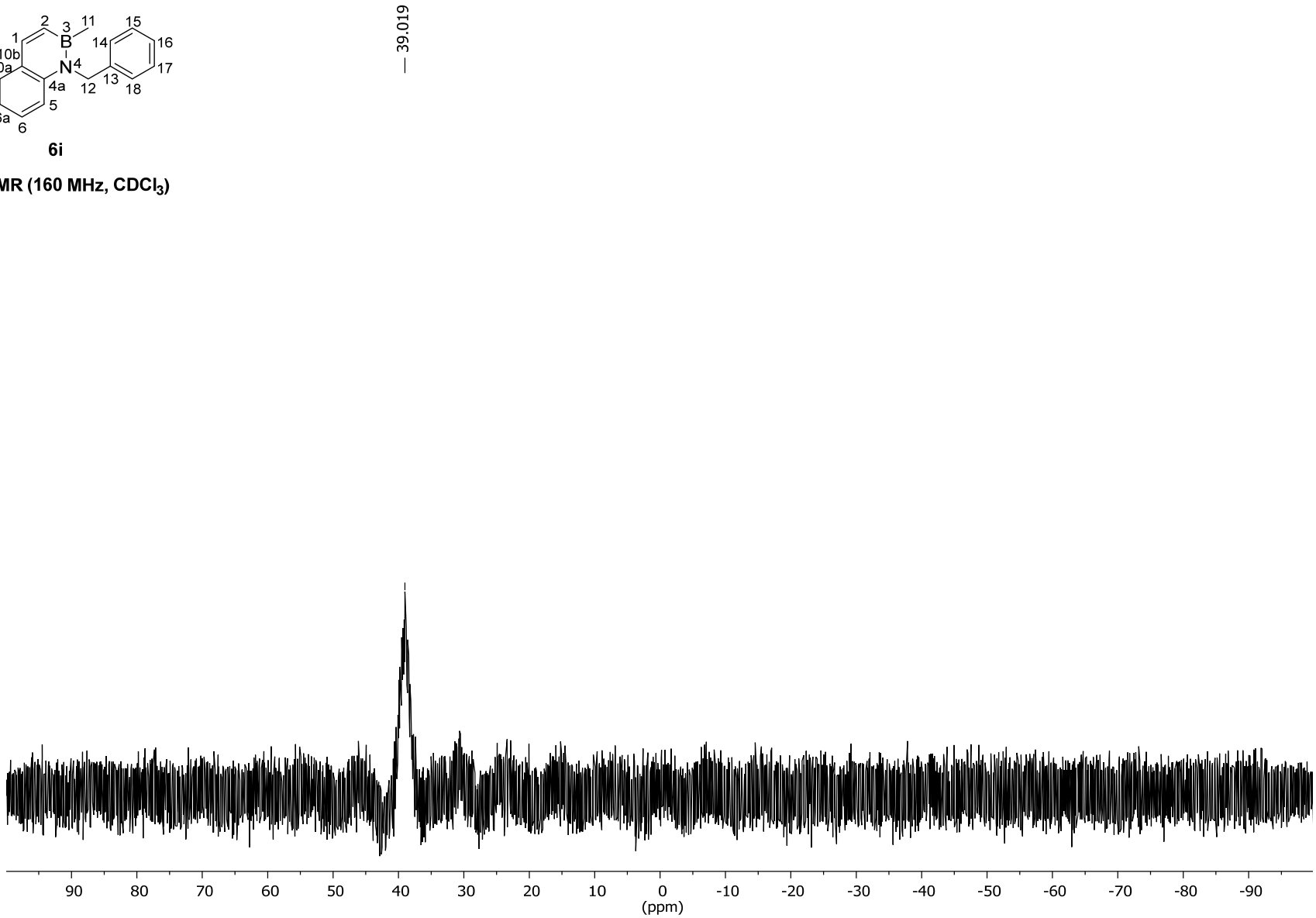


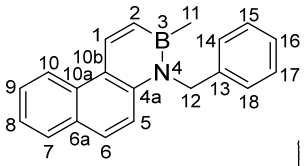




6i

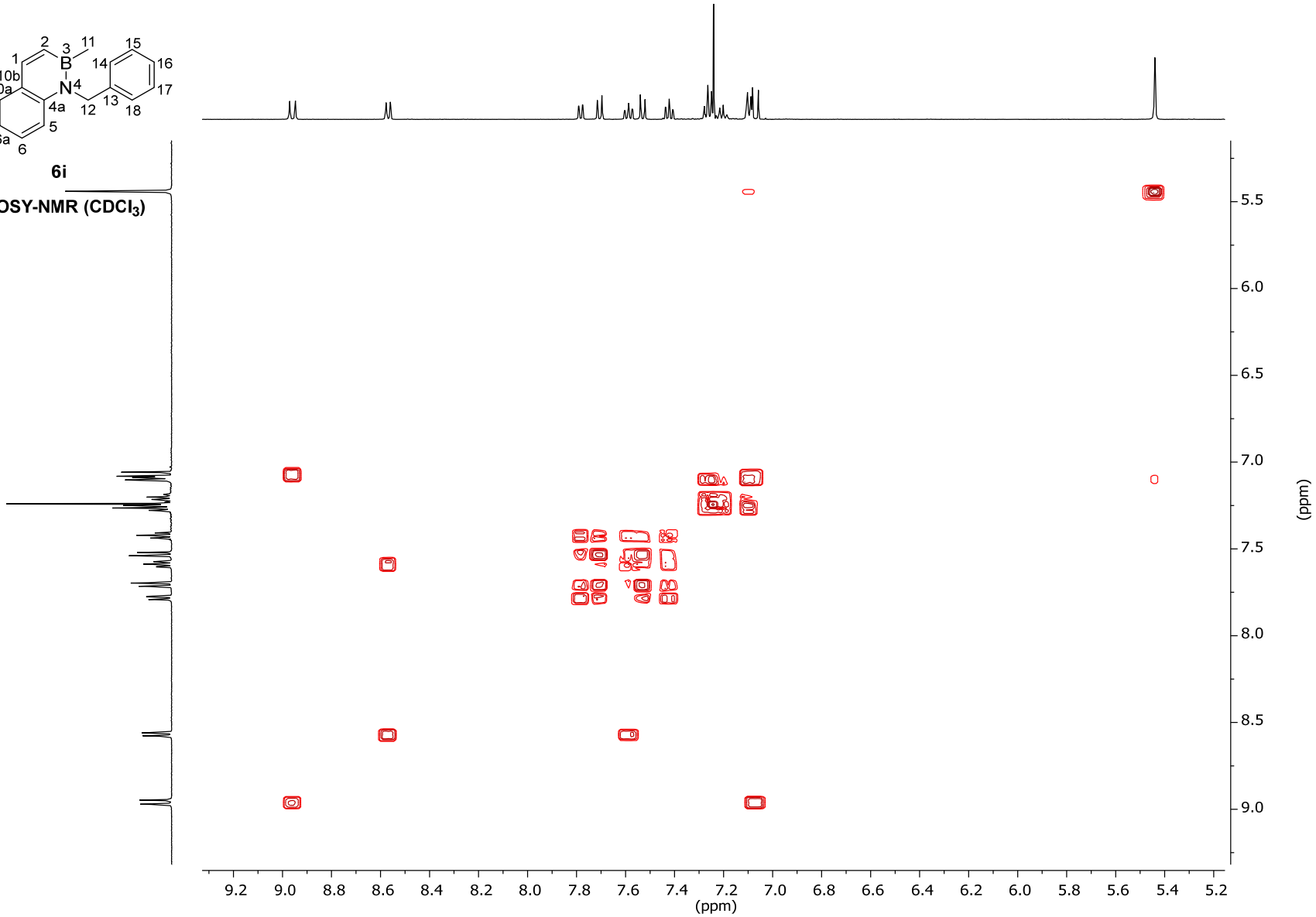
^{11}B-NMR (160 MHz, $CDCl_3$)

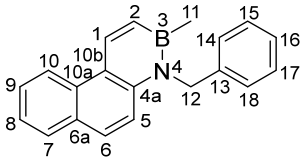




6i

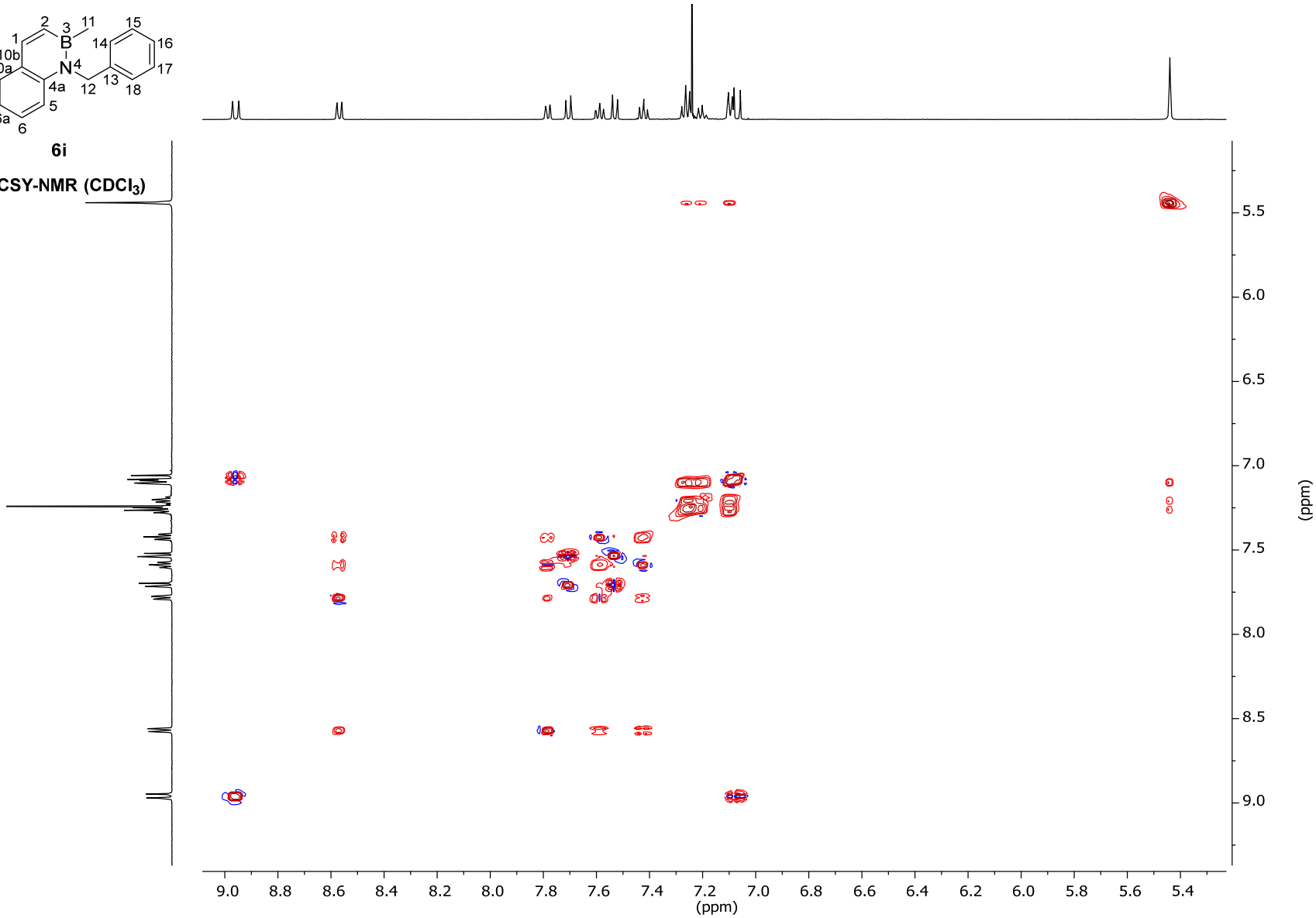
gCOSY-NMR ($CDCl_3$)

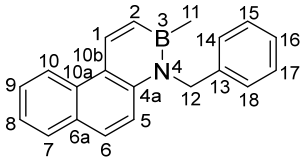




6i

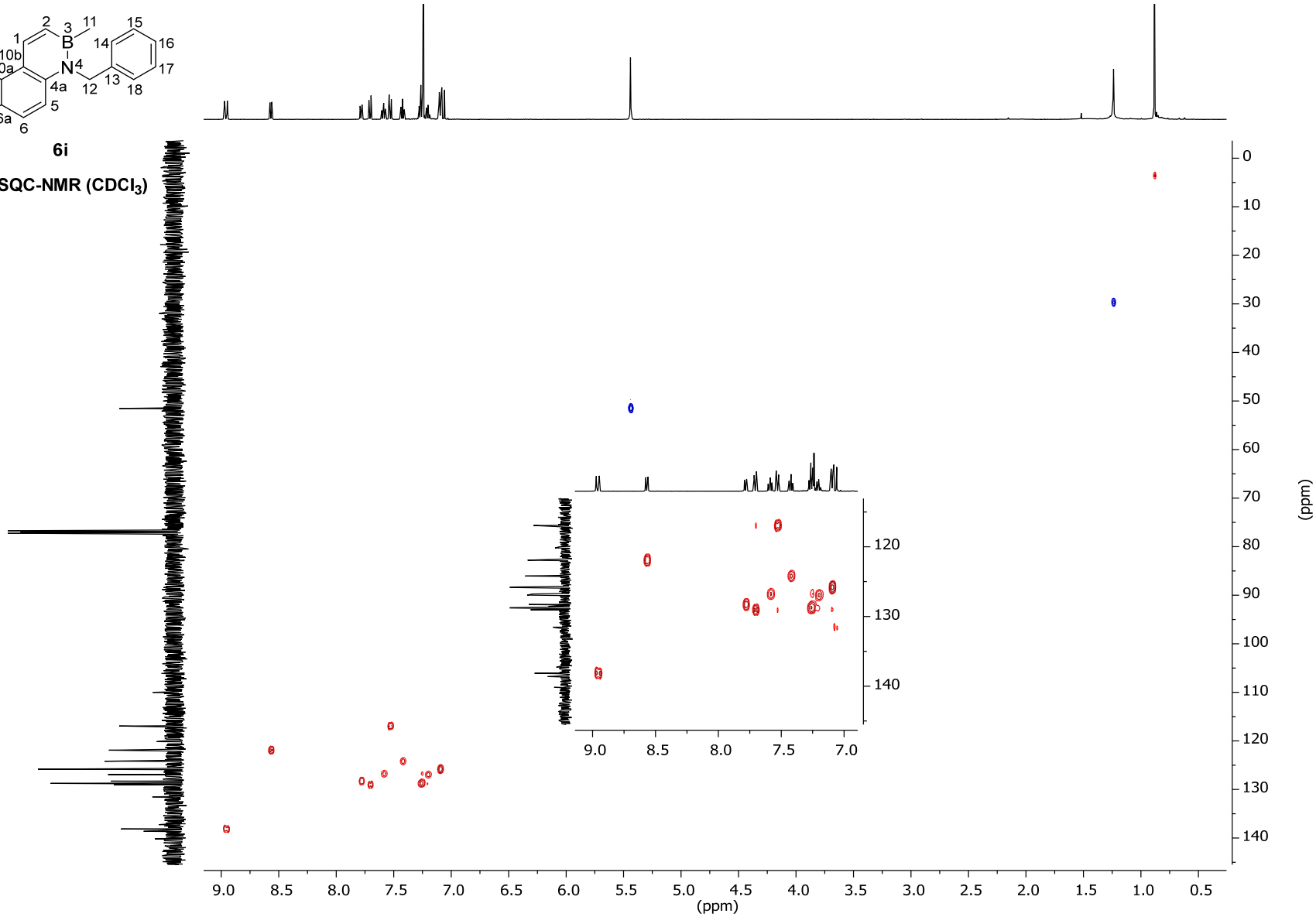
TOCSY-NMR ($CDCl_3$)

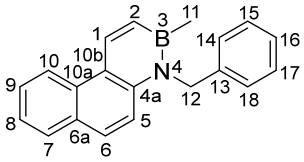




6i

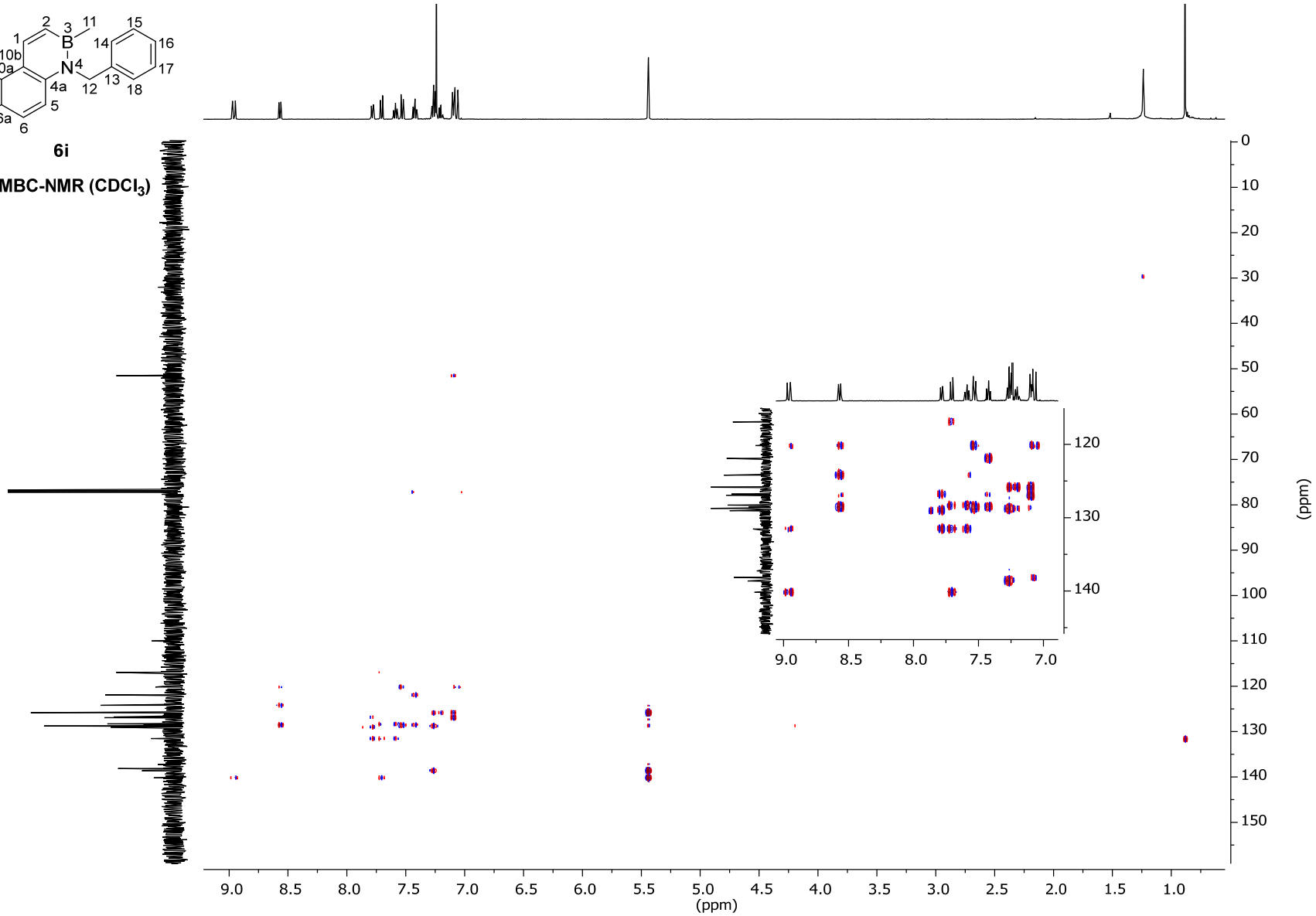
gHSQC-NMR ($CDCl_3$)

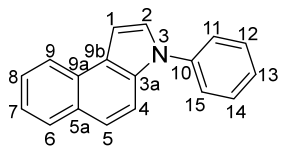




6i

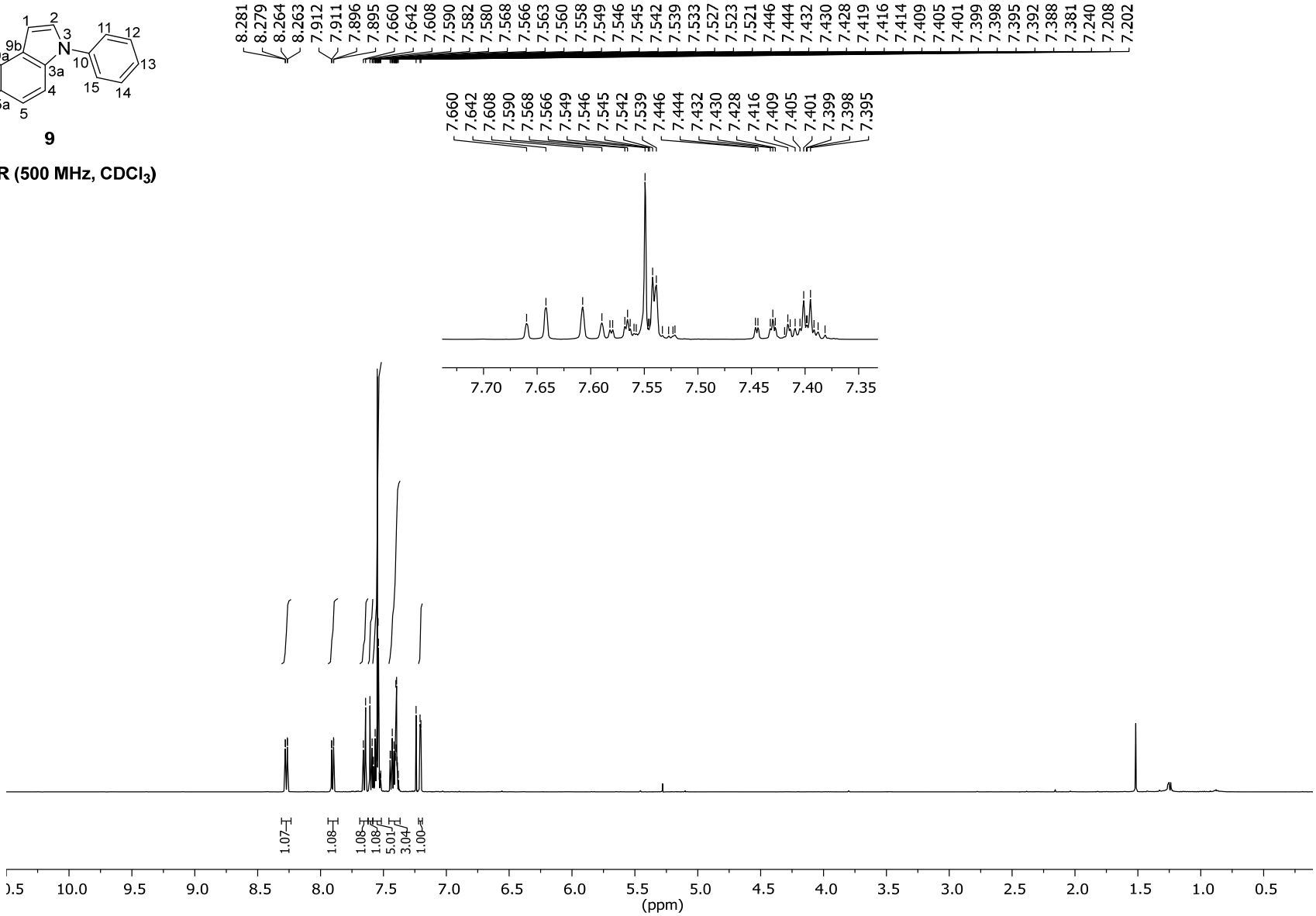
gHMBC-NMR ($CDCl_3$)

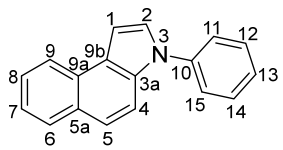




9

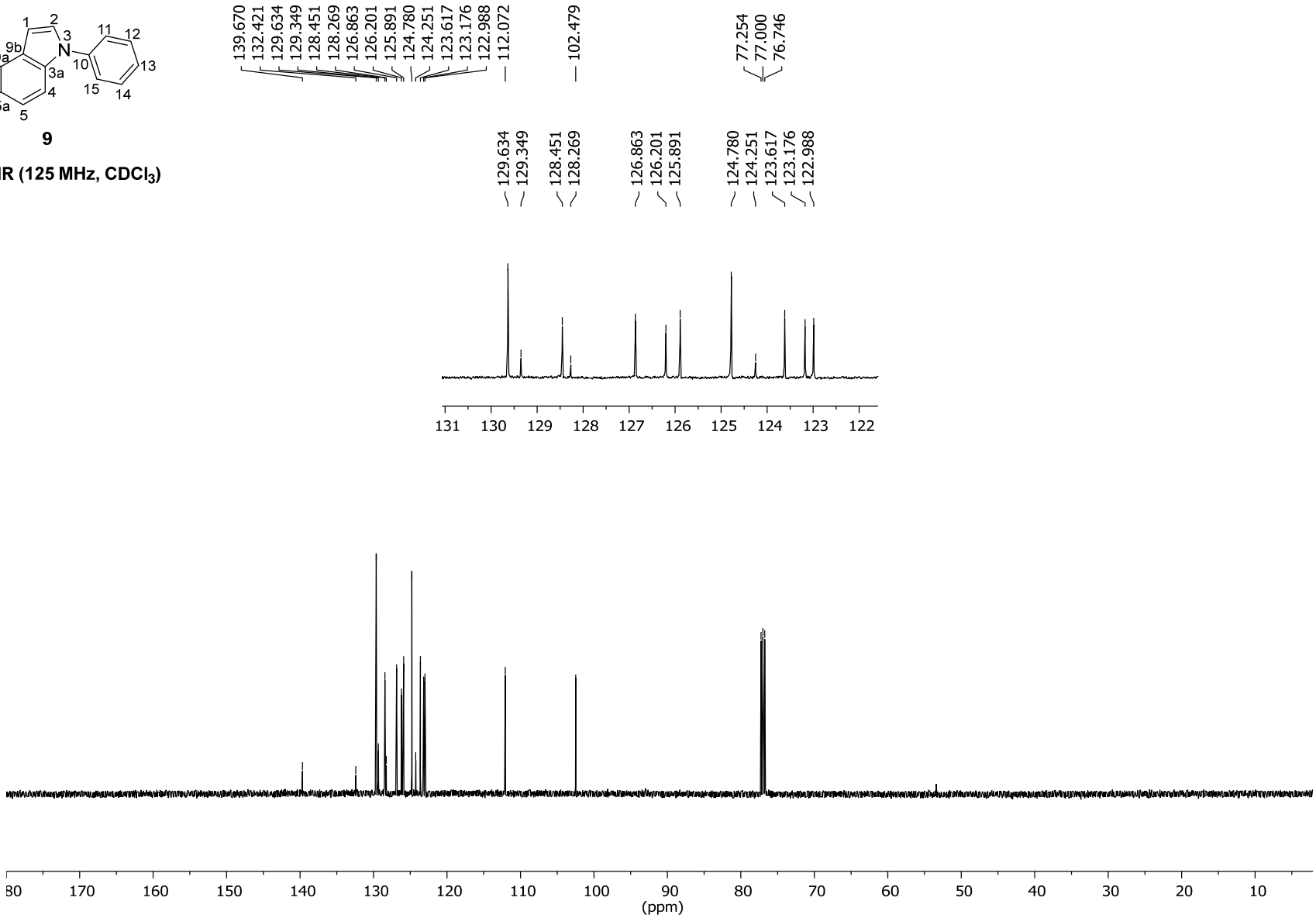
^{1}H-NMR (500 MHz, $CDCl_3$)

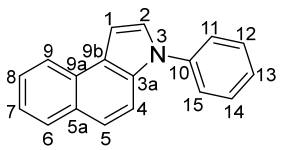




9

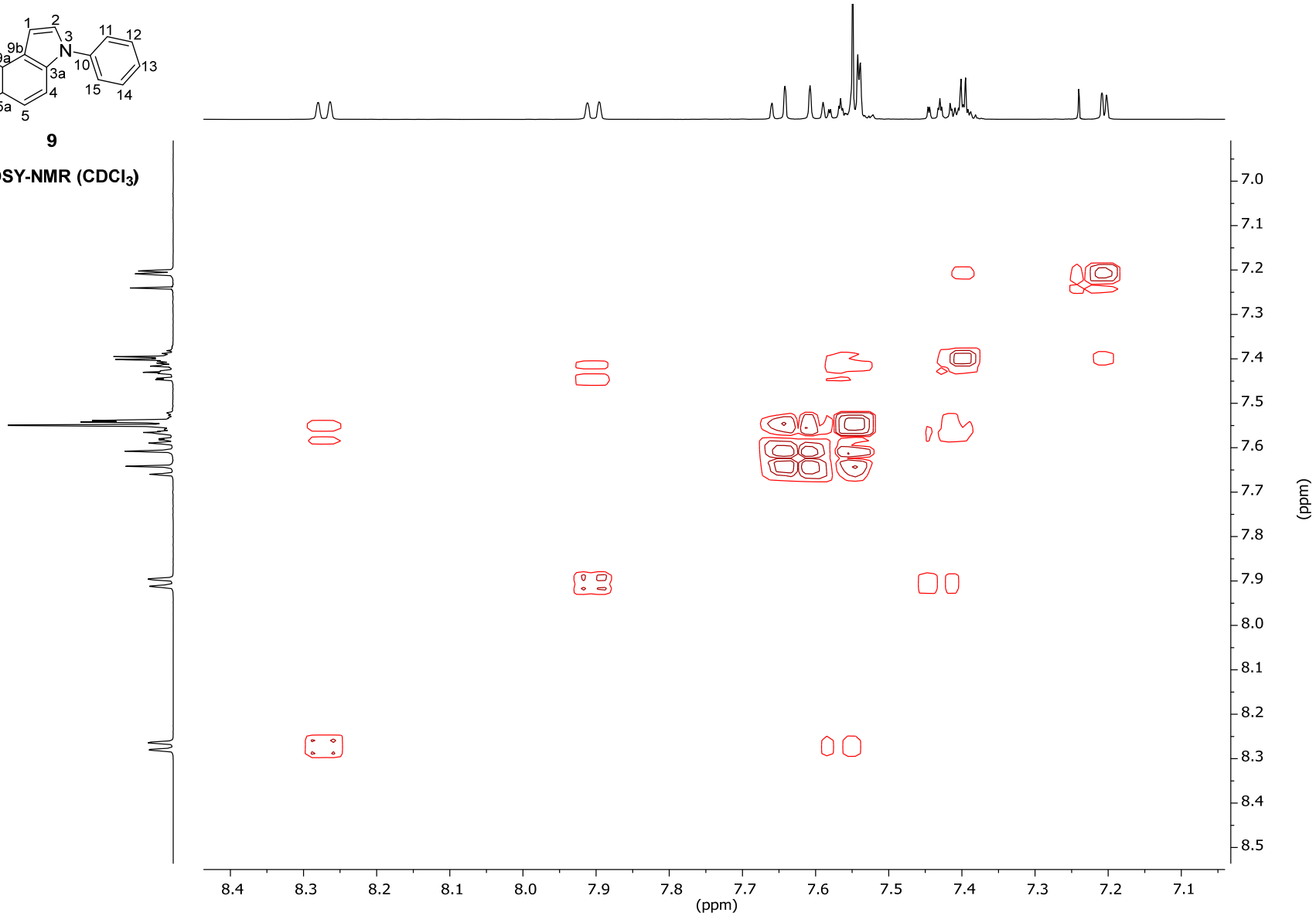
^{13}C-NMR (125 MHz, $CDCl_3$)

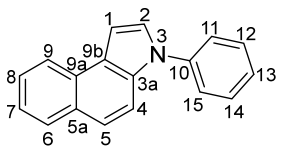




9

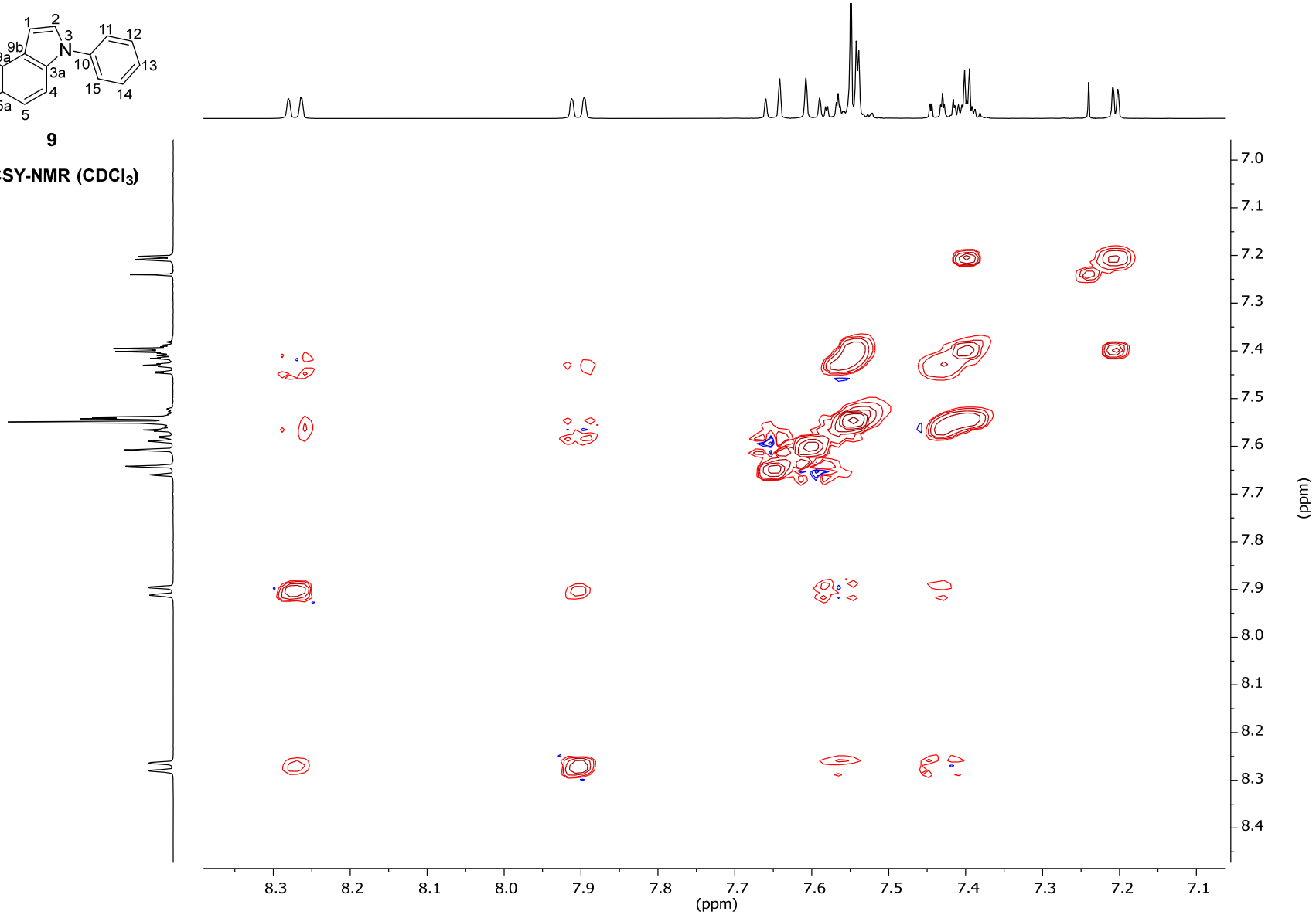
gCOSY-NMR ($CDCl_3$)

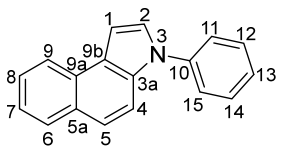




9

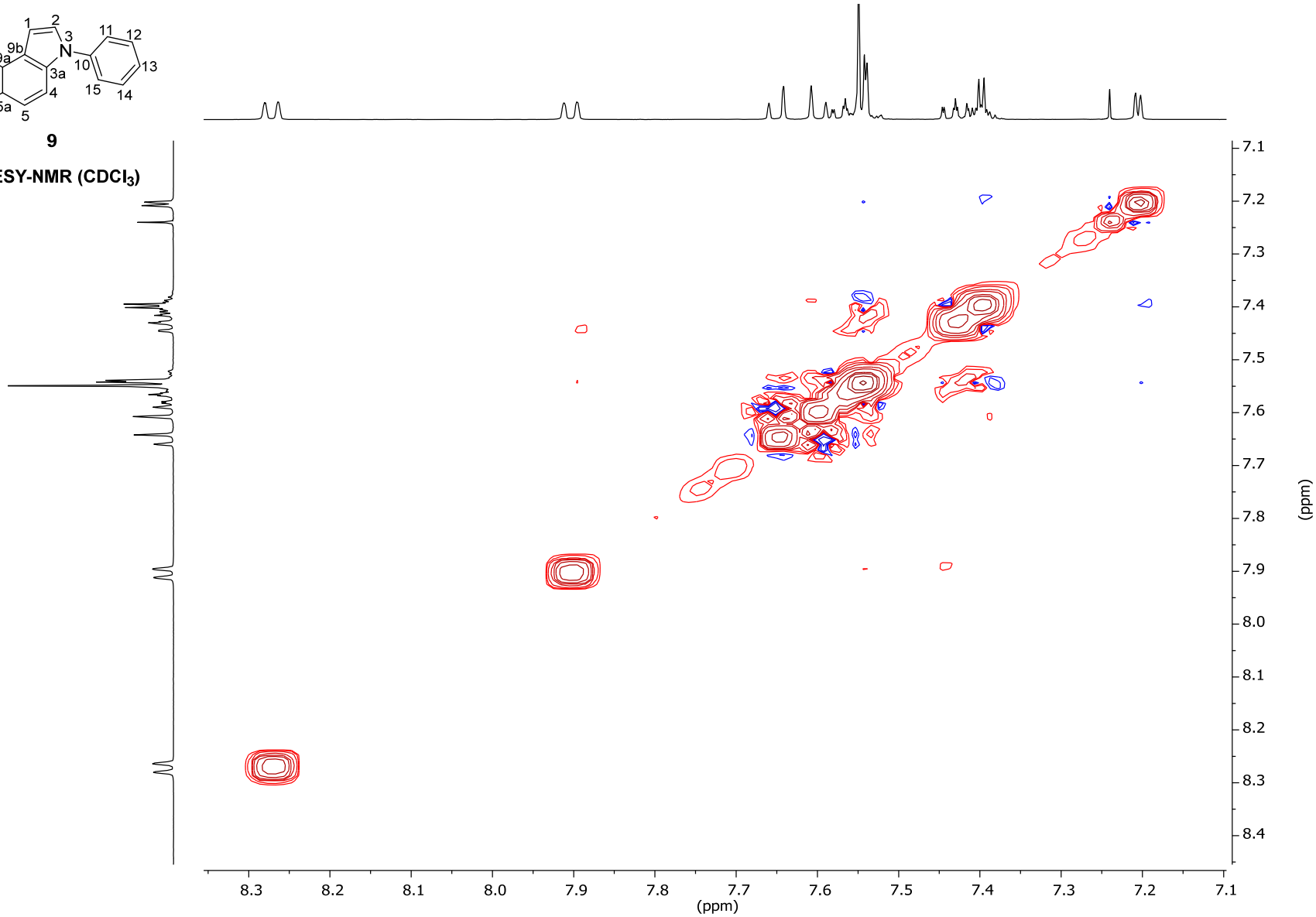
TOCSY-NMR ($CDCl_3$)

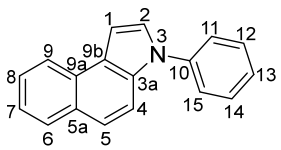




9

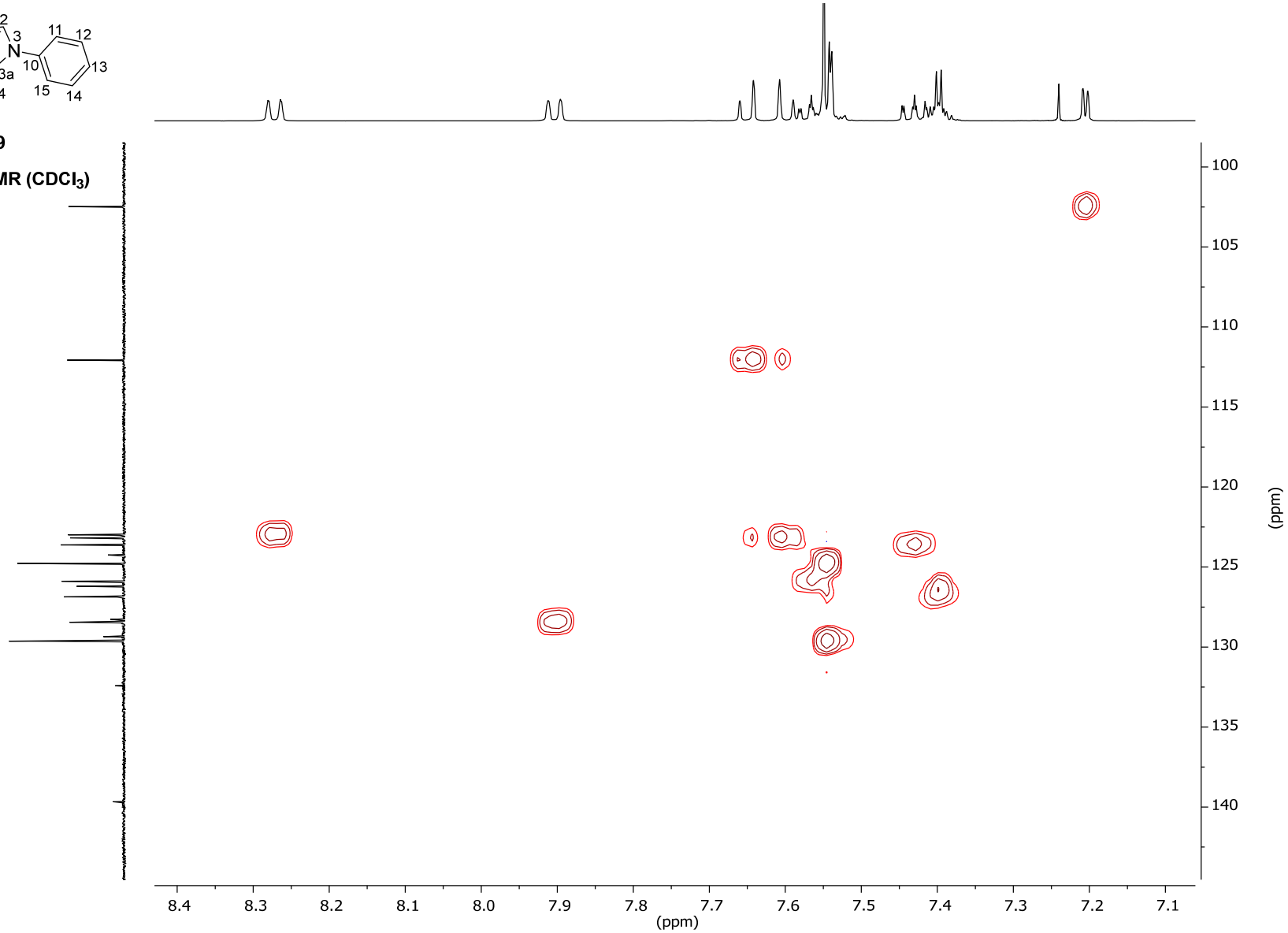
NOESY-NMR ($CDCl_3$)

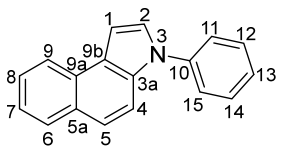




9

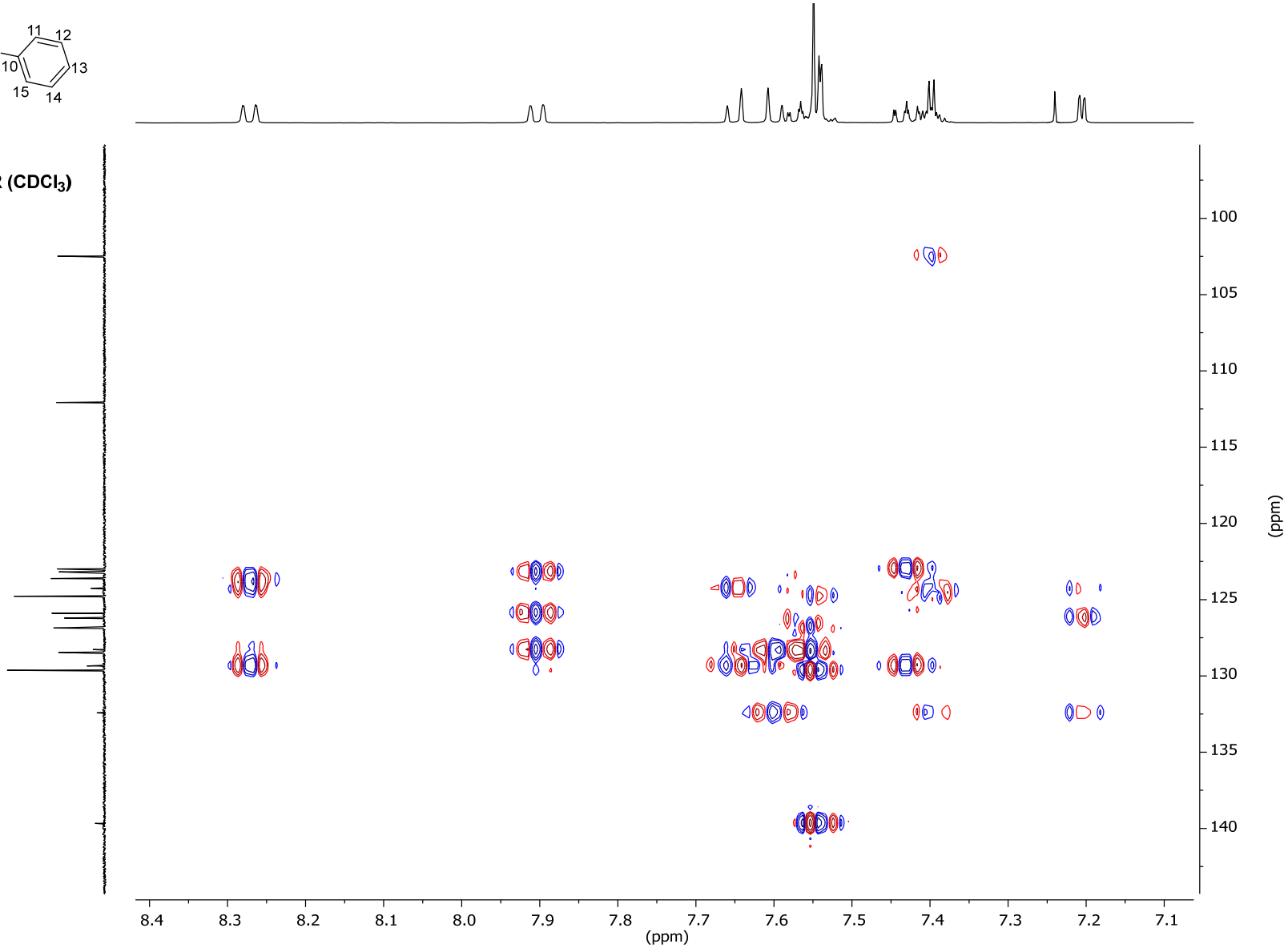
gHSQC-NMR ($CDCl_3$)

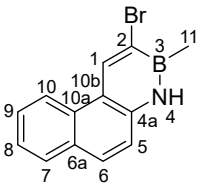




9

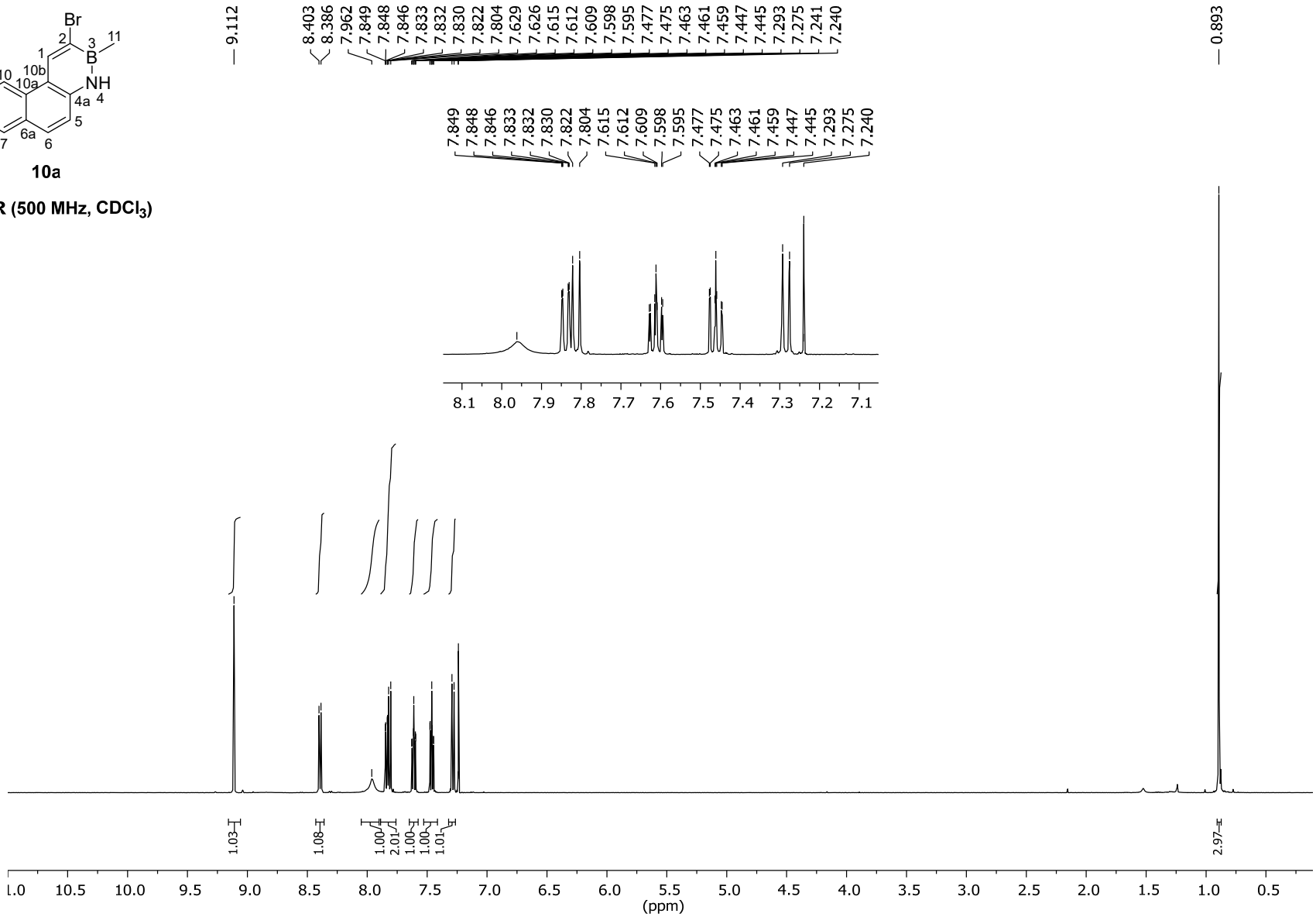
gHMBC-NMR ($CDCl_3$)

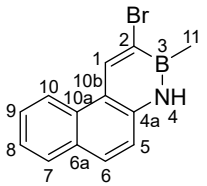




10a

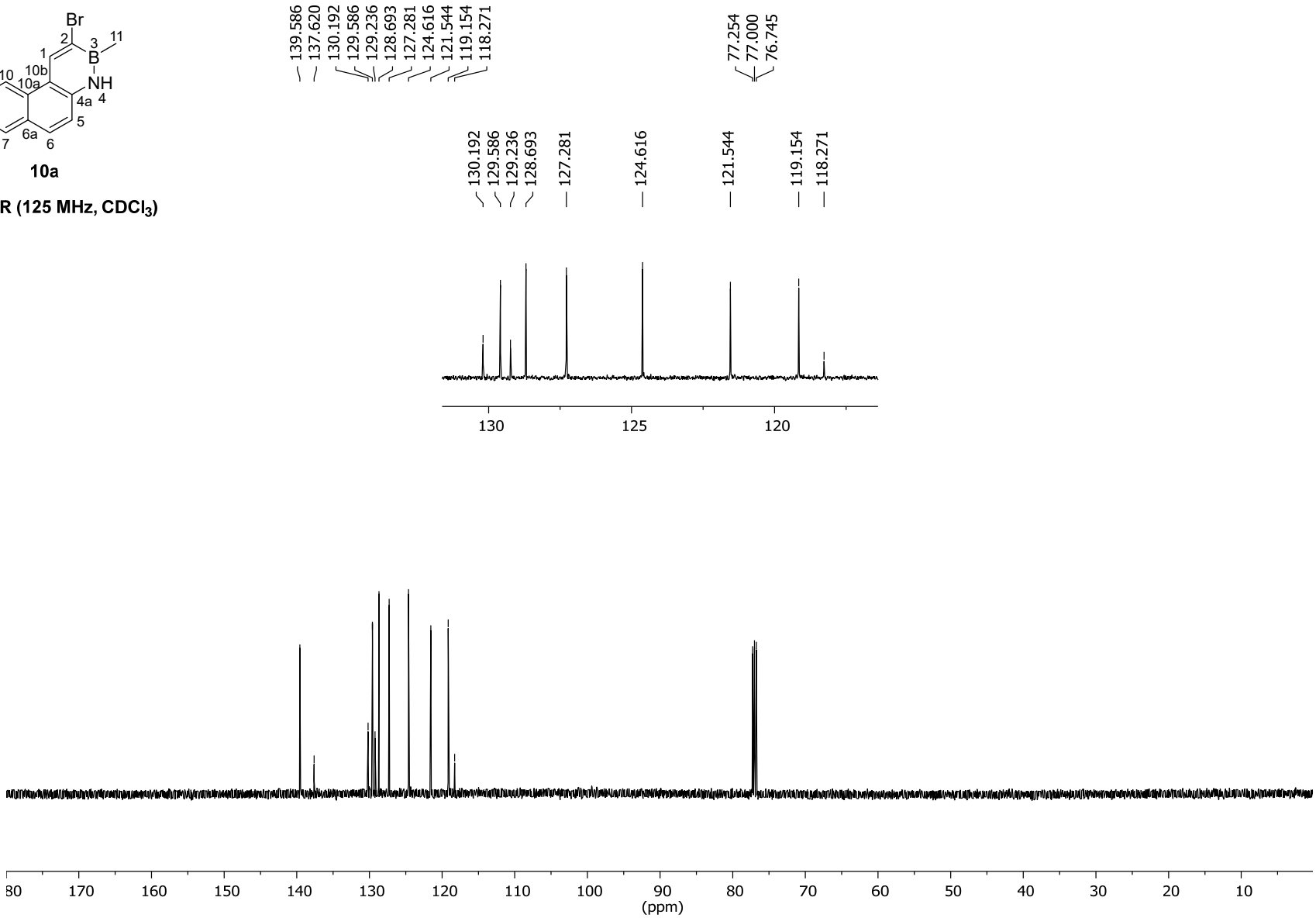
^{1}H-NMR (500 MHz, $CDCl_3$)

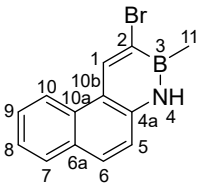




10a

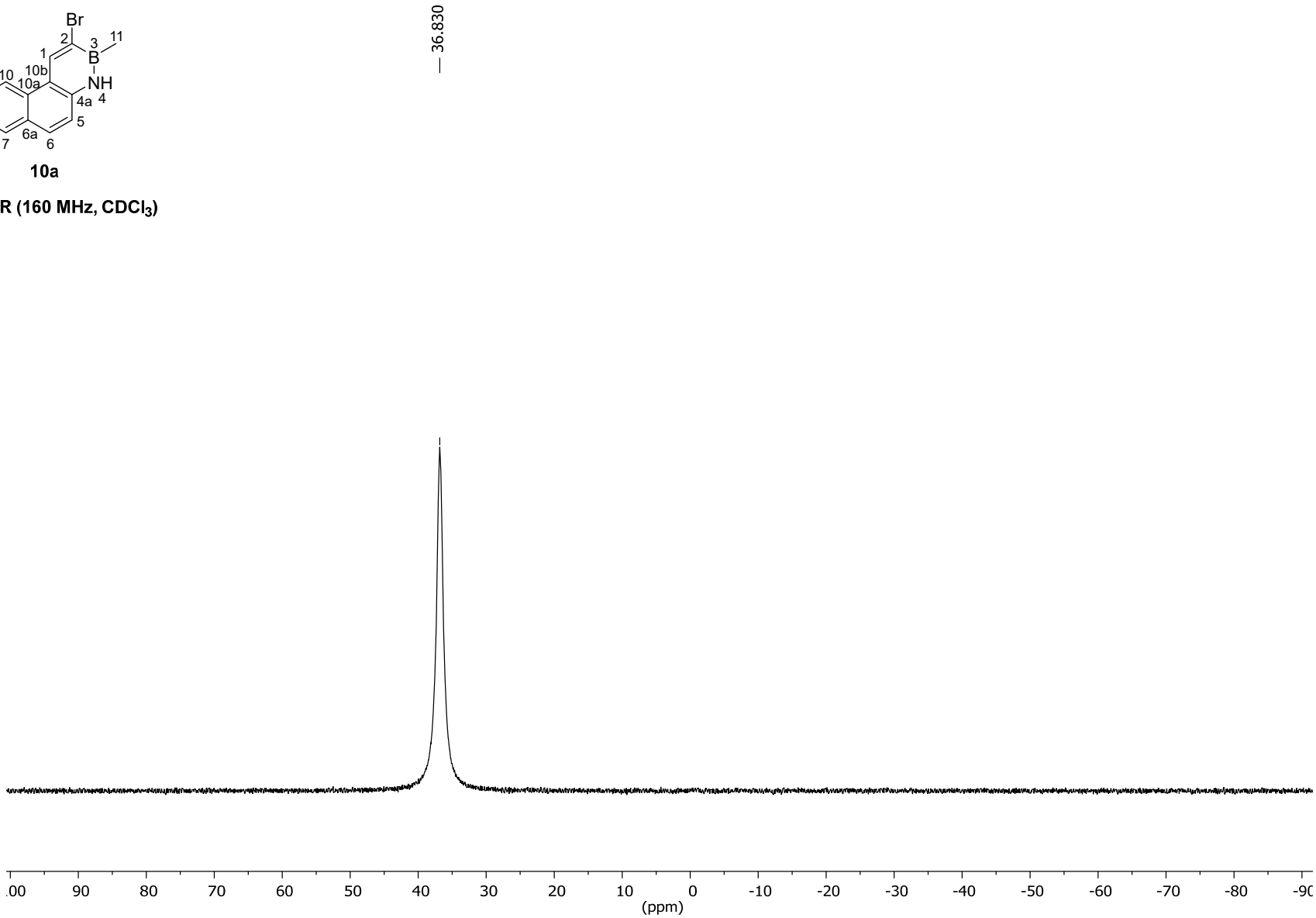
^{13}C-NMR (125 MHz, $CDCl_3$)

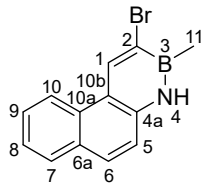




10a

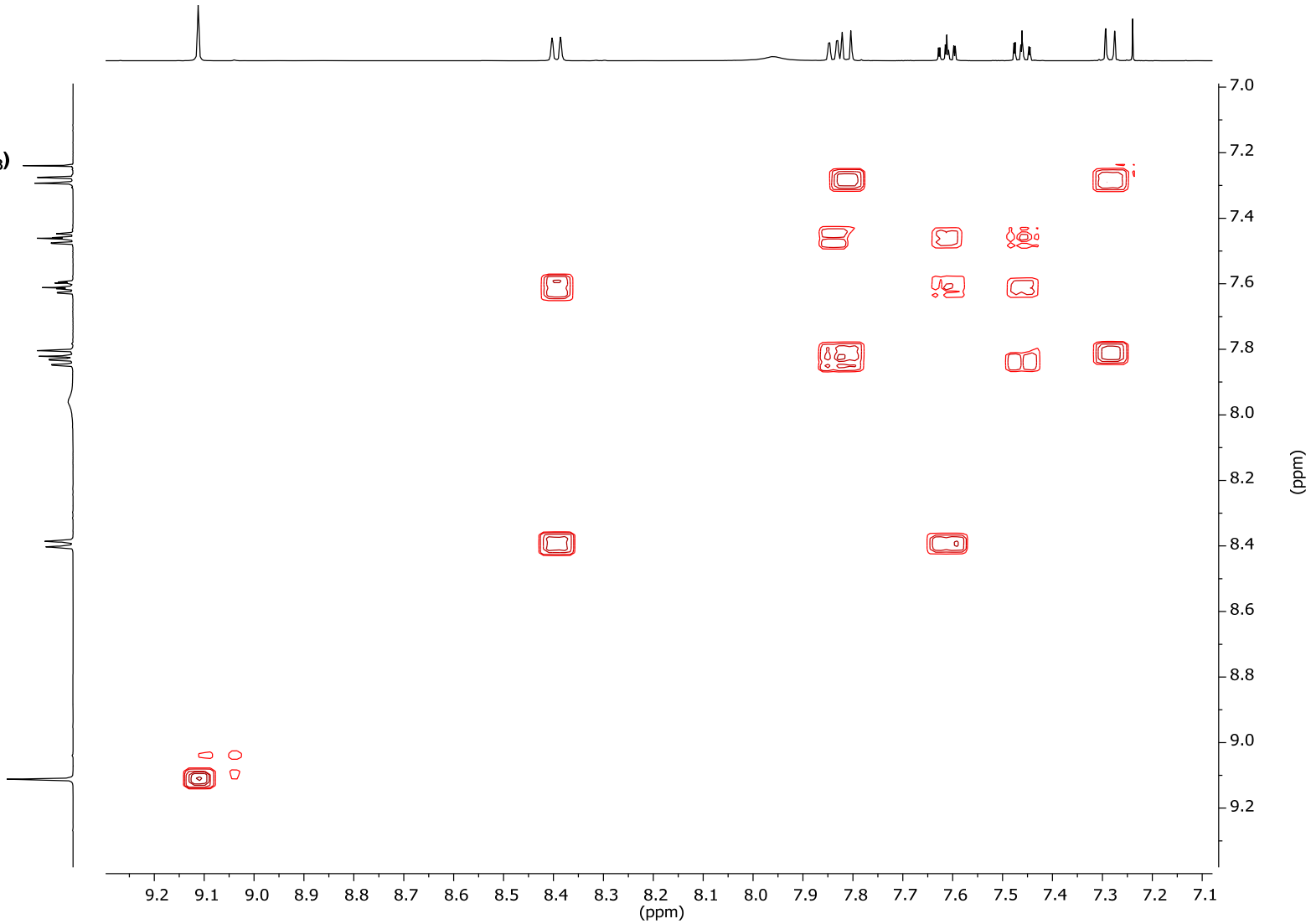
^{11}B-NMR (160 MHz, $CDCl_3$)

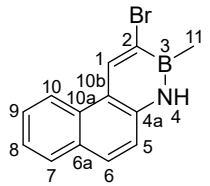




10a

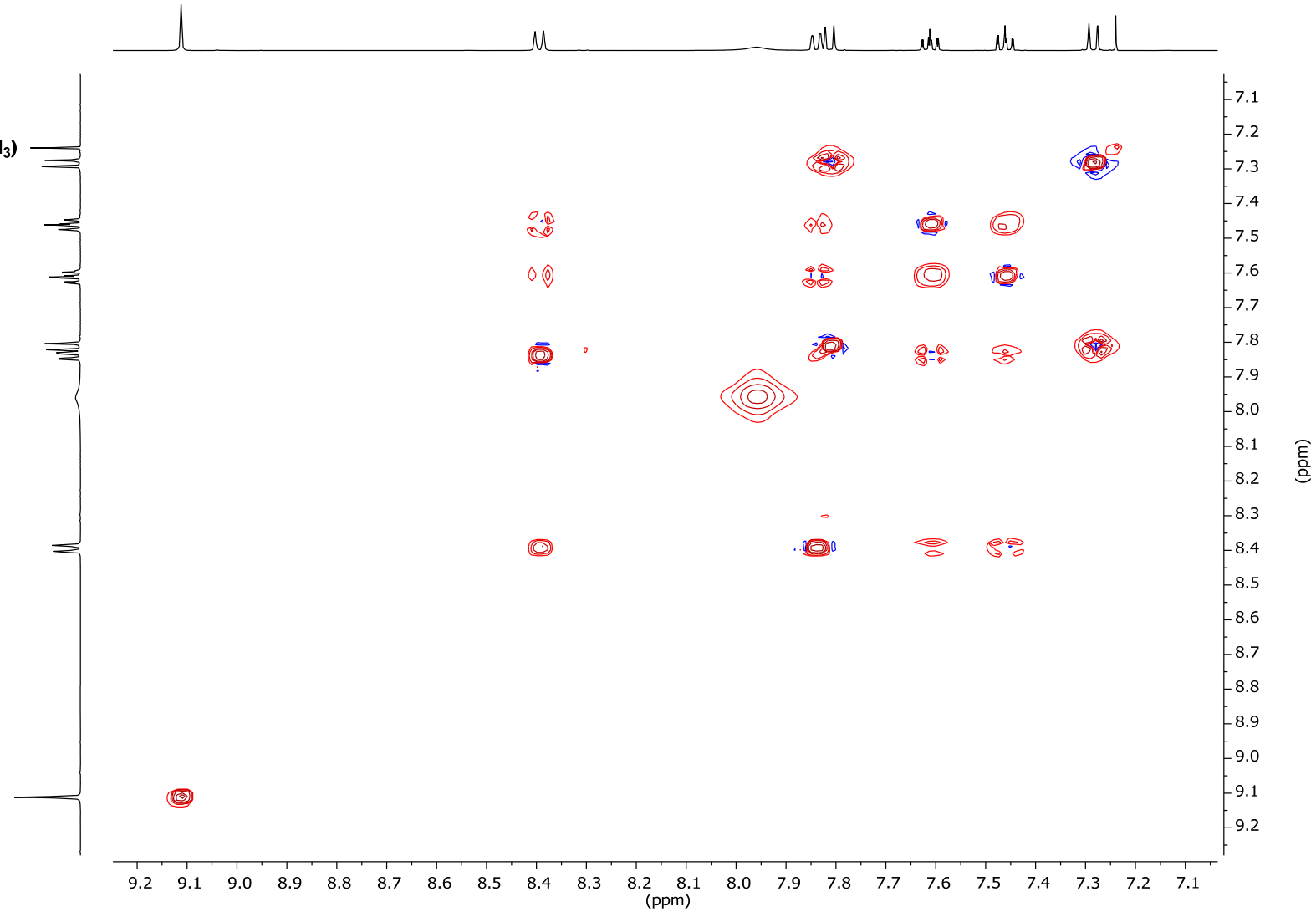
gCOSY-NMR ($CDCl_3$)

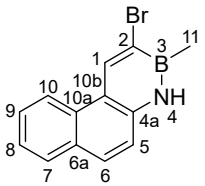




10a

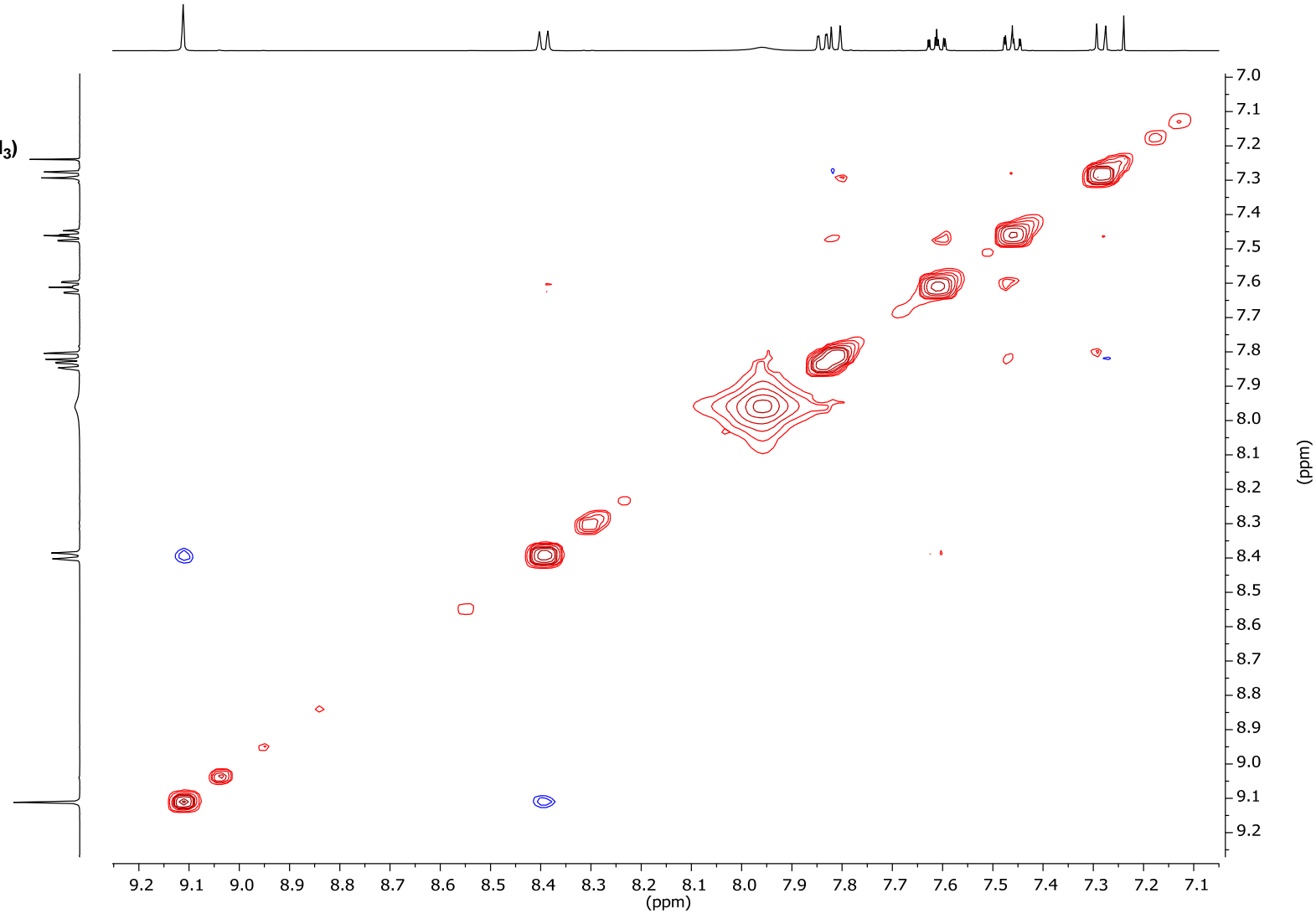
TOCSY-NMR ($CDCl_3$)

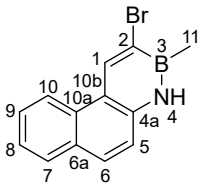




10a

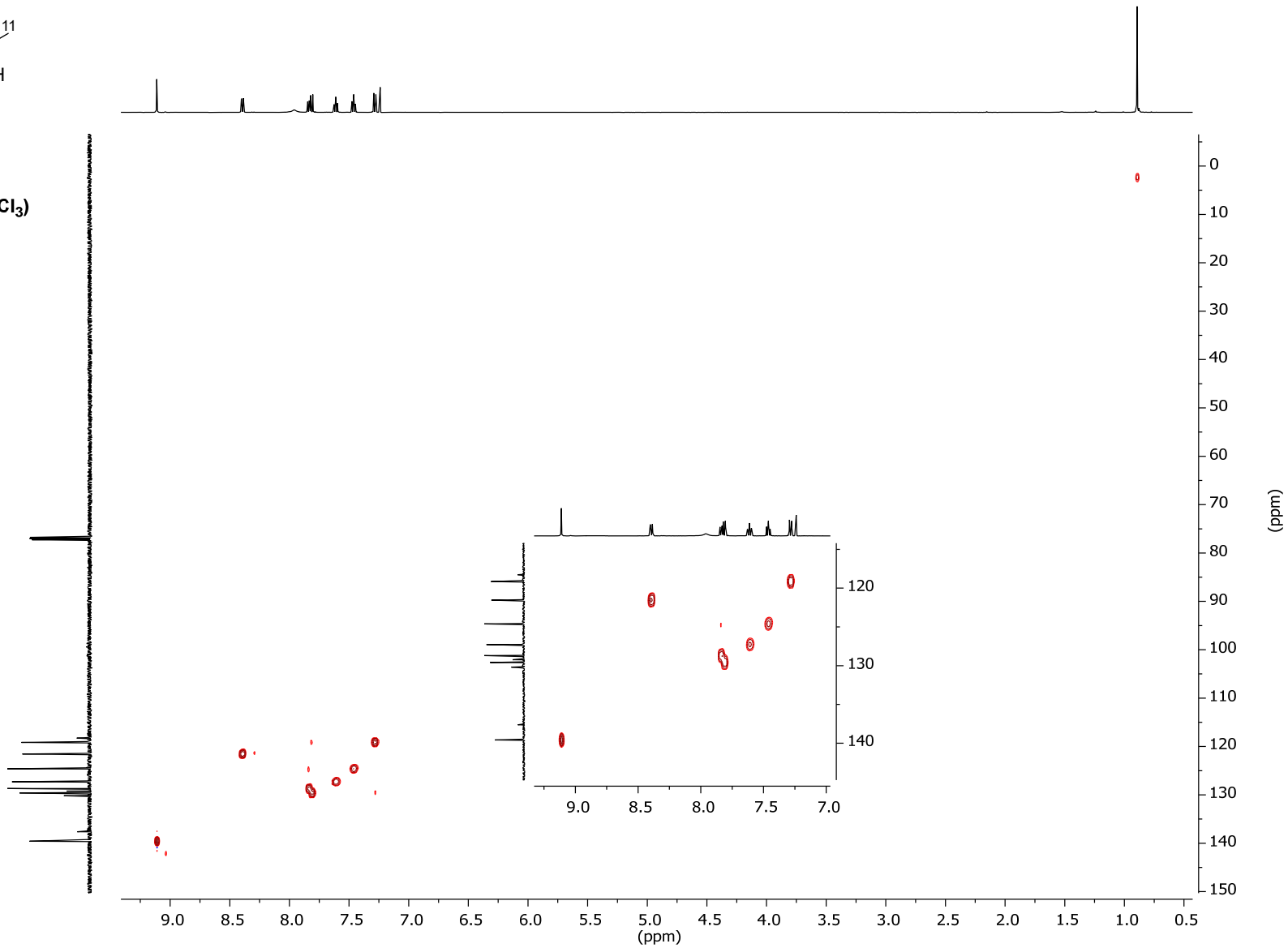
NOESY-NMR ($CDCl_3$)

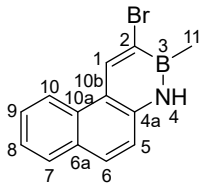




10a

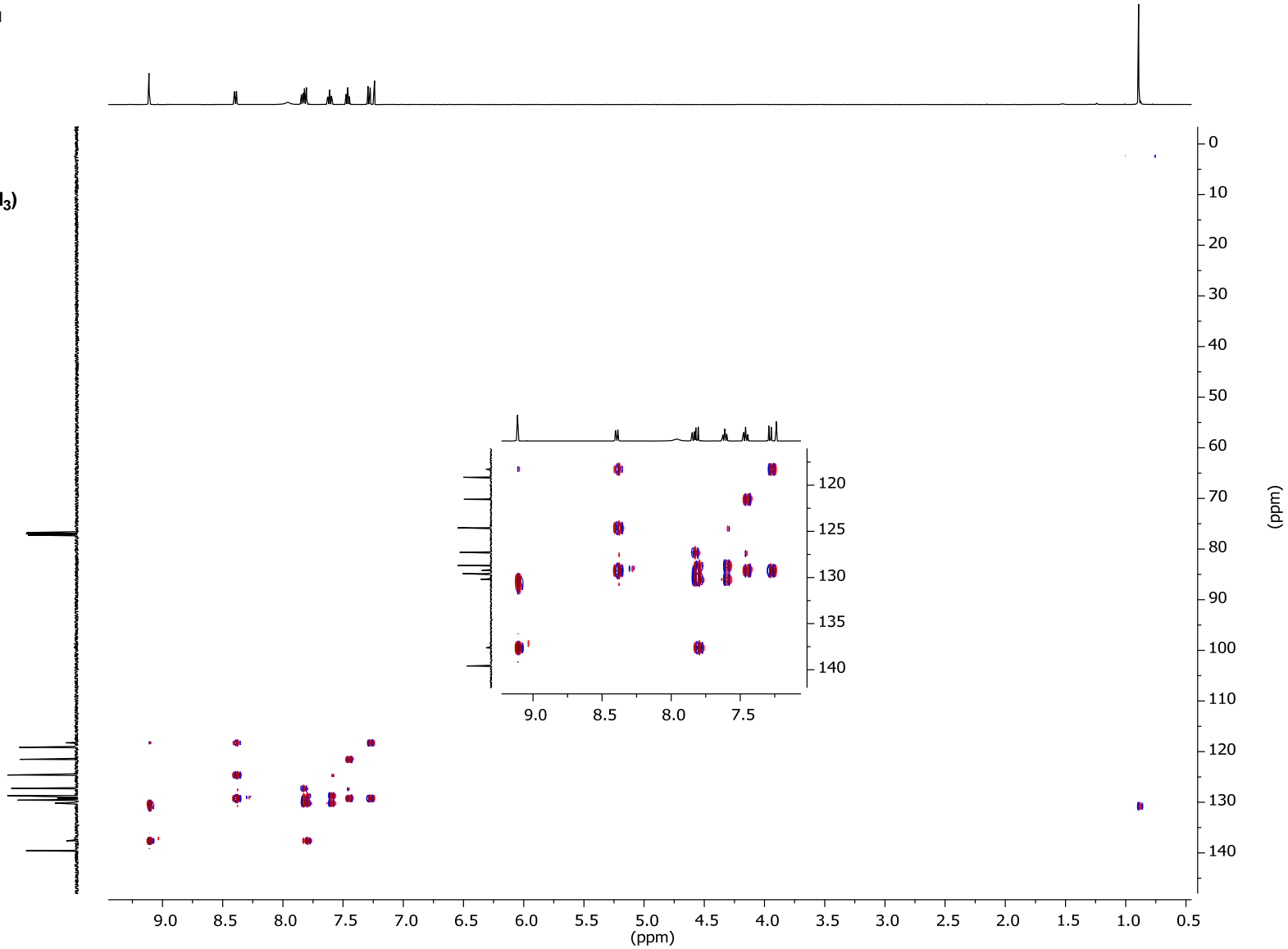
gHSQC-NMR ($CDCl_3$)

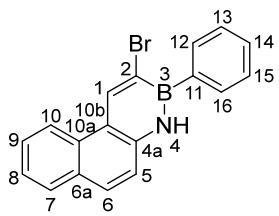




10a

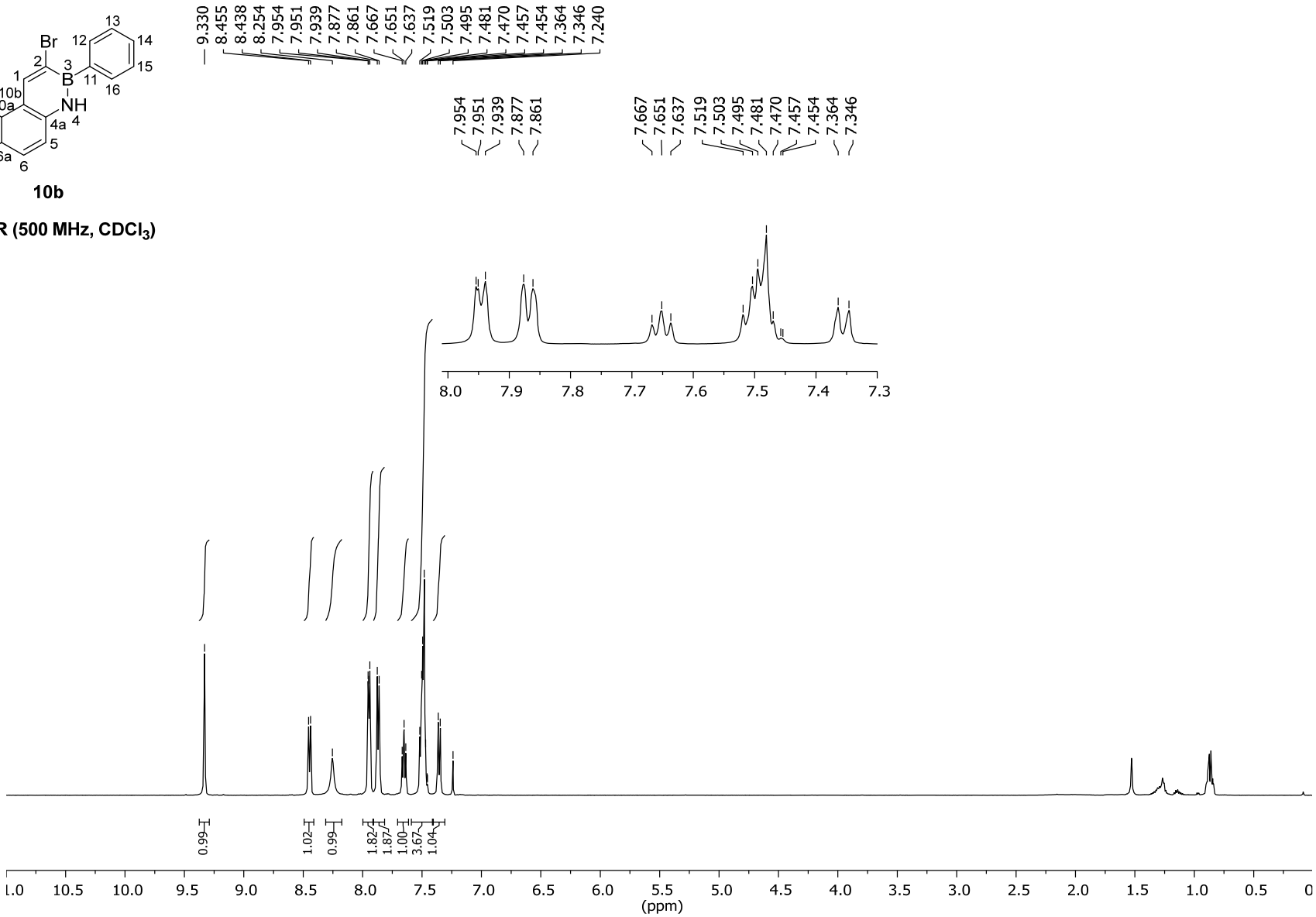
gHMBC-NMR ($CDCl_3$)

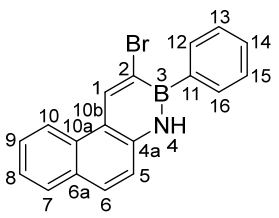




10b

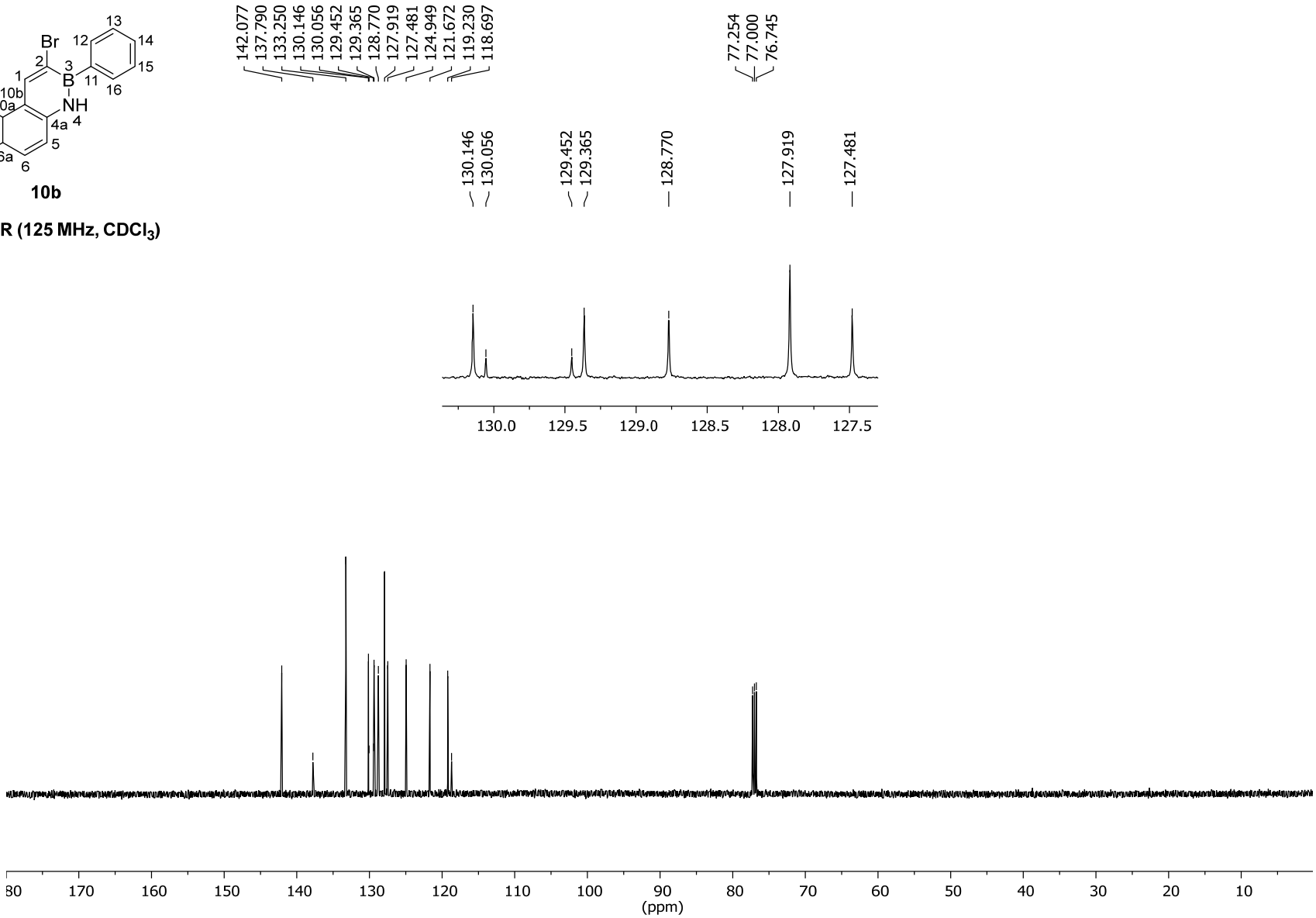
^{1}H-NMR (500 MHz, $CDCl_3$)

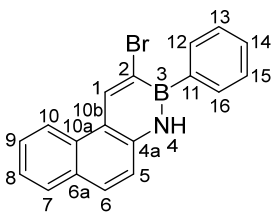




10b

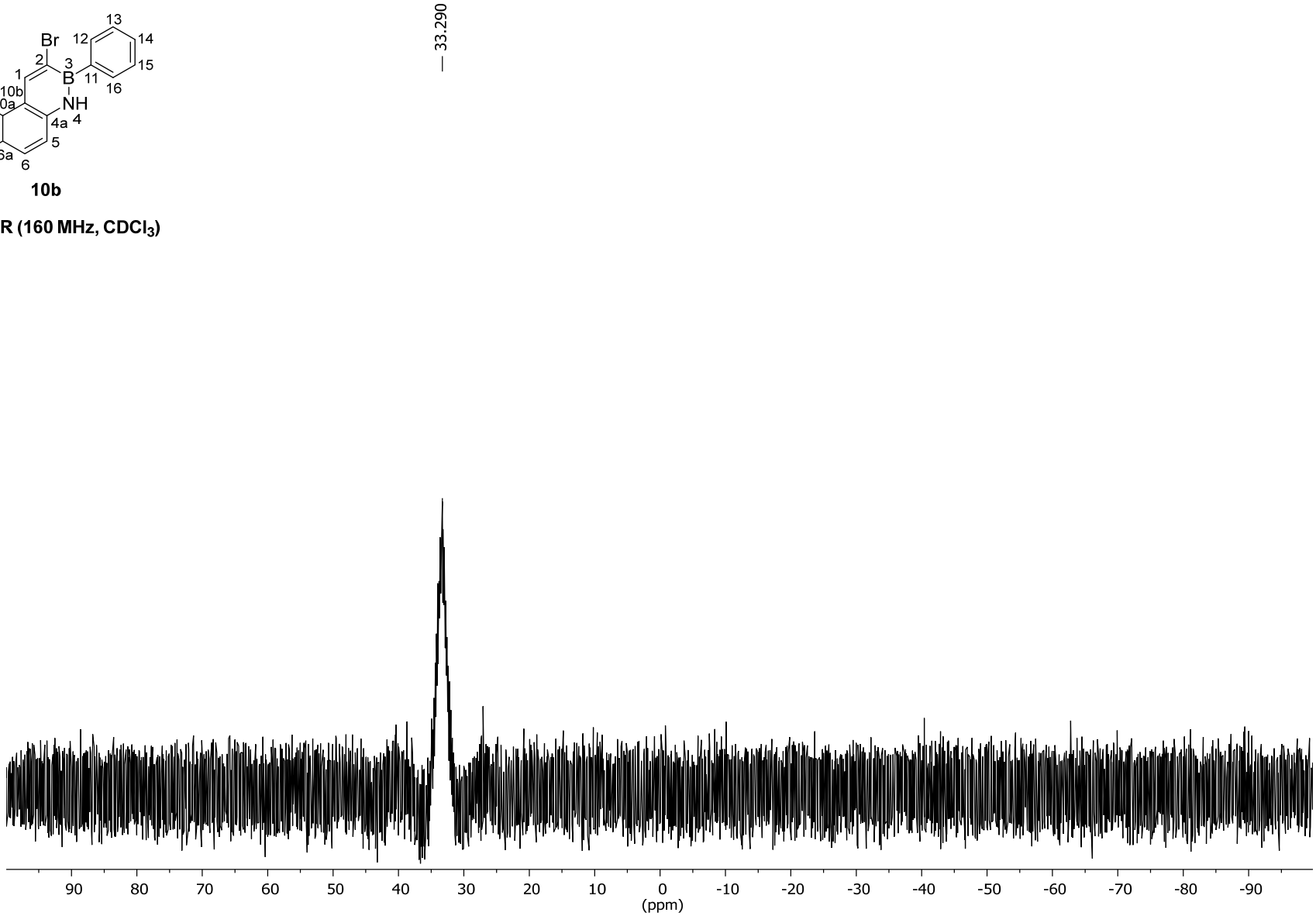
^{13}C-NMR (125 MHz, $CDCl_3$)

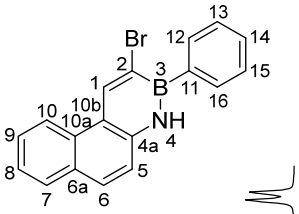




10b

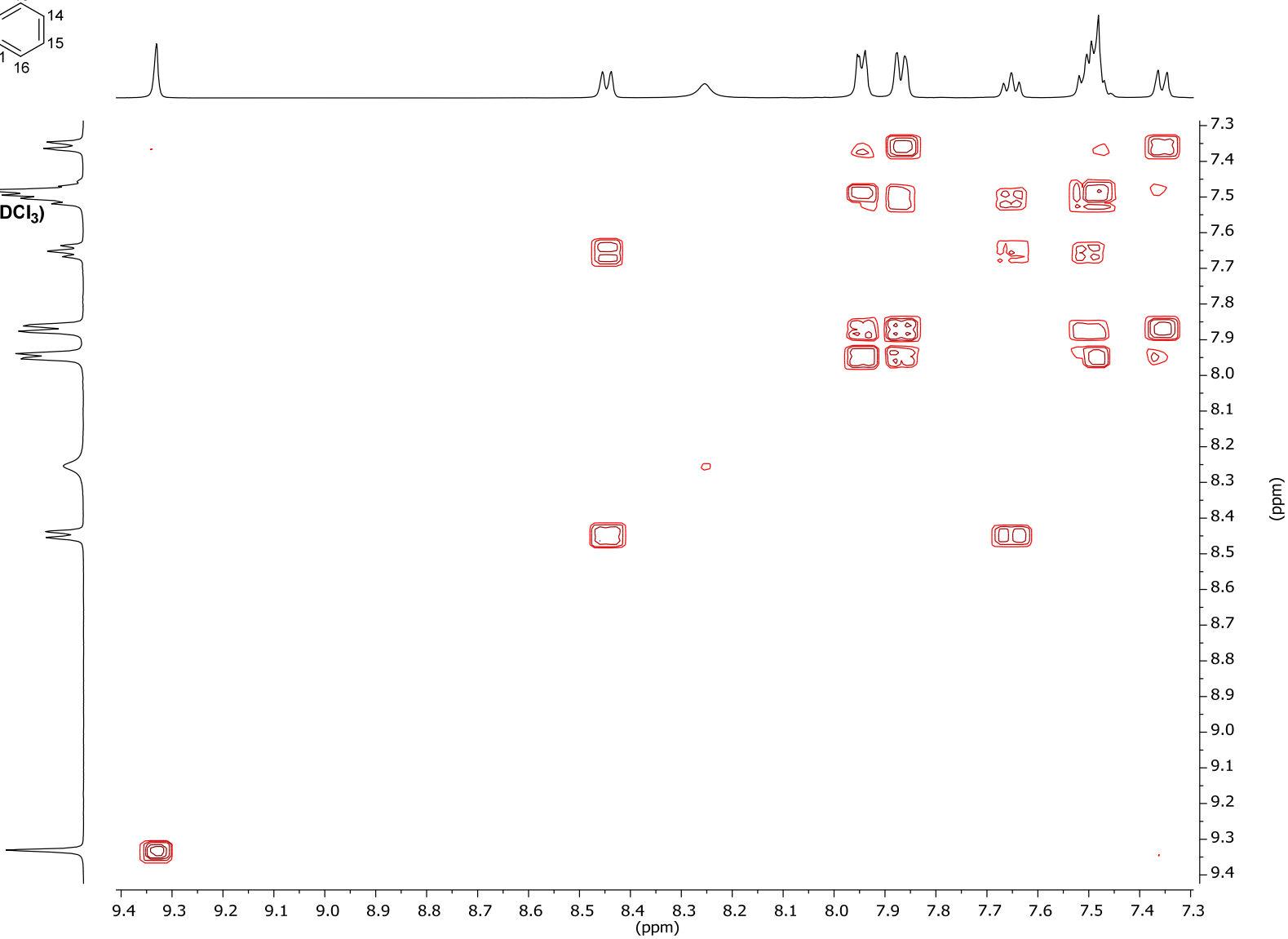
^{11}B-NMR (160 MHz, $CDCl_3$)

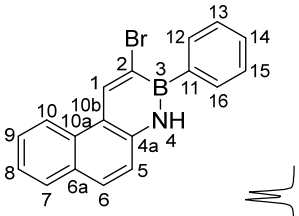




10b

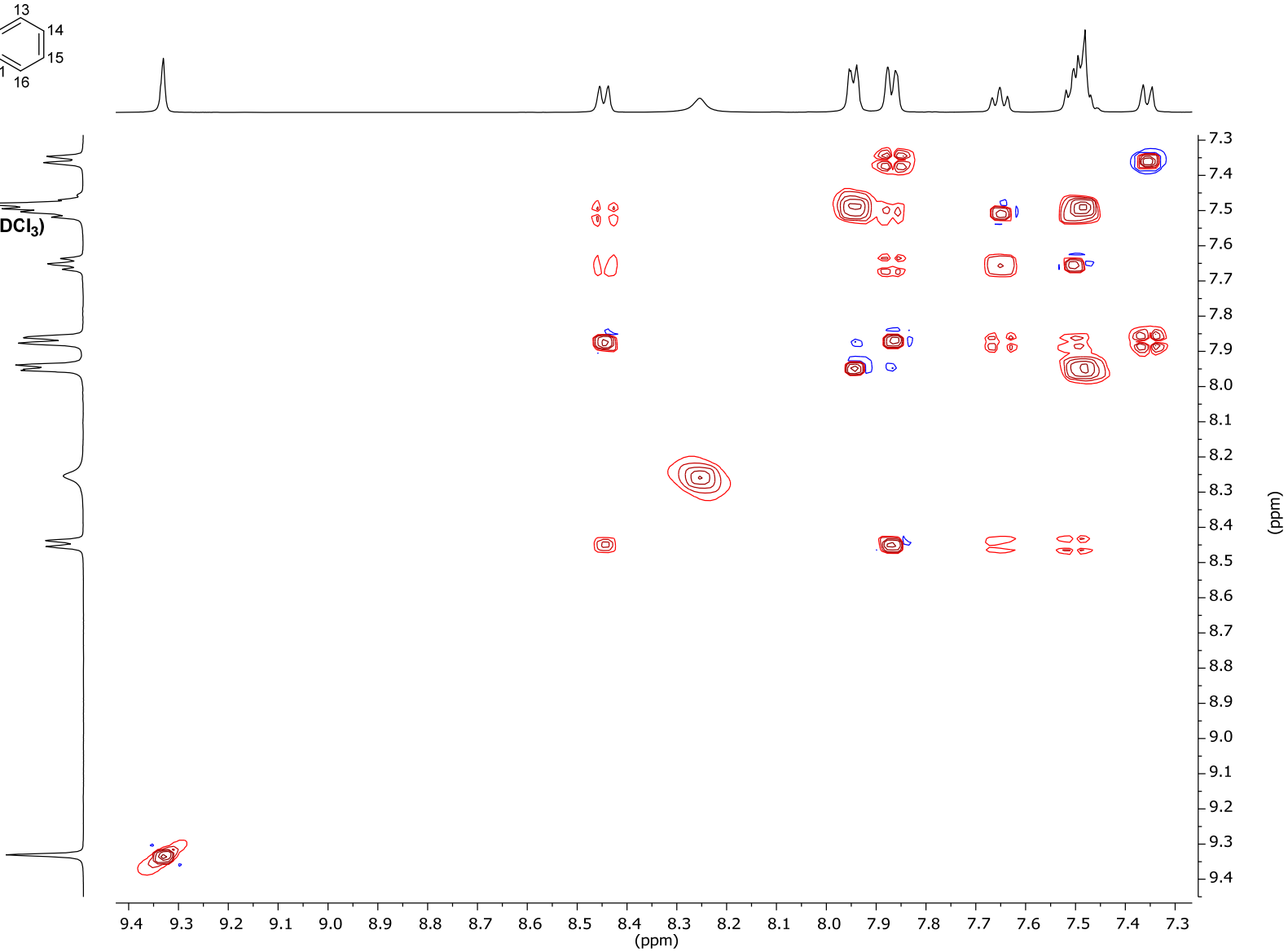
gCOSY-NMR ($CDCl_3$)

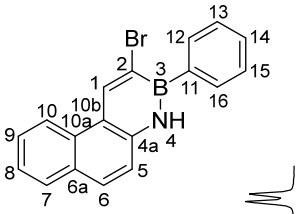




10b

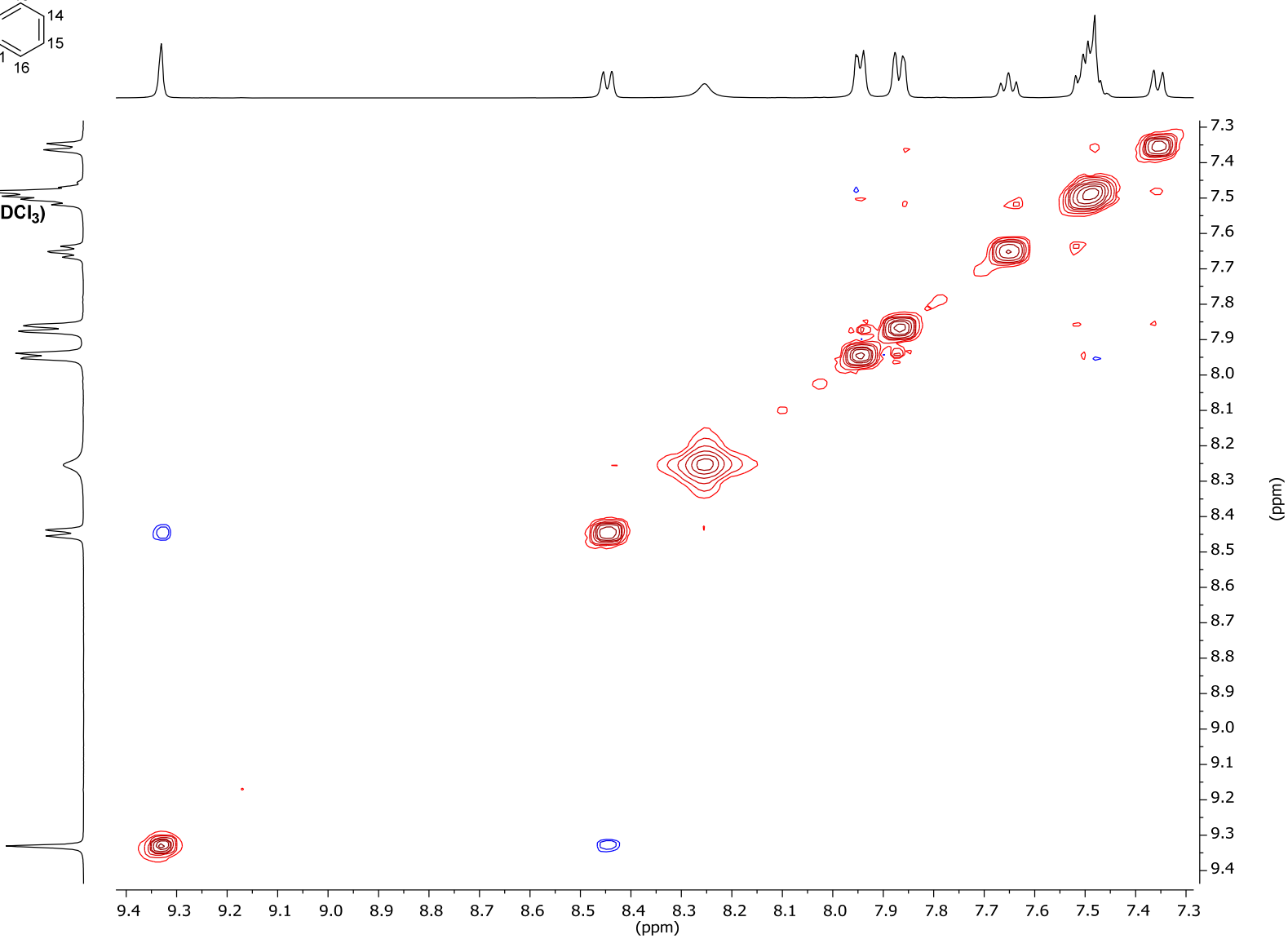
TOCSY-NMR ($CDCl_3$)

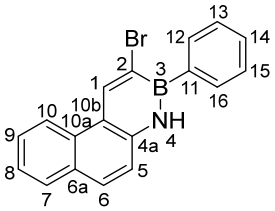




10b

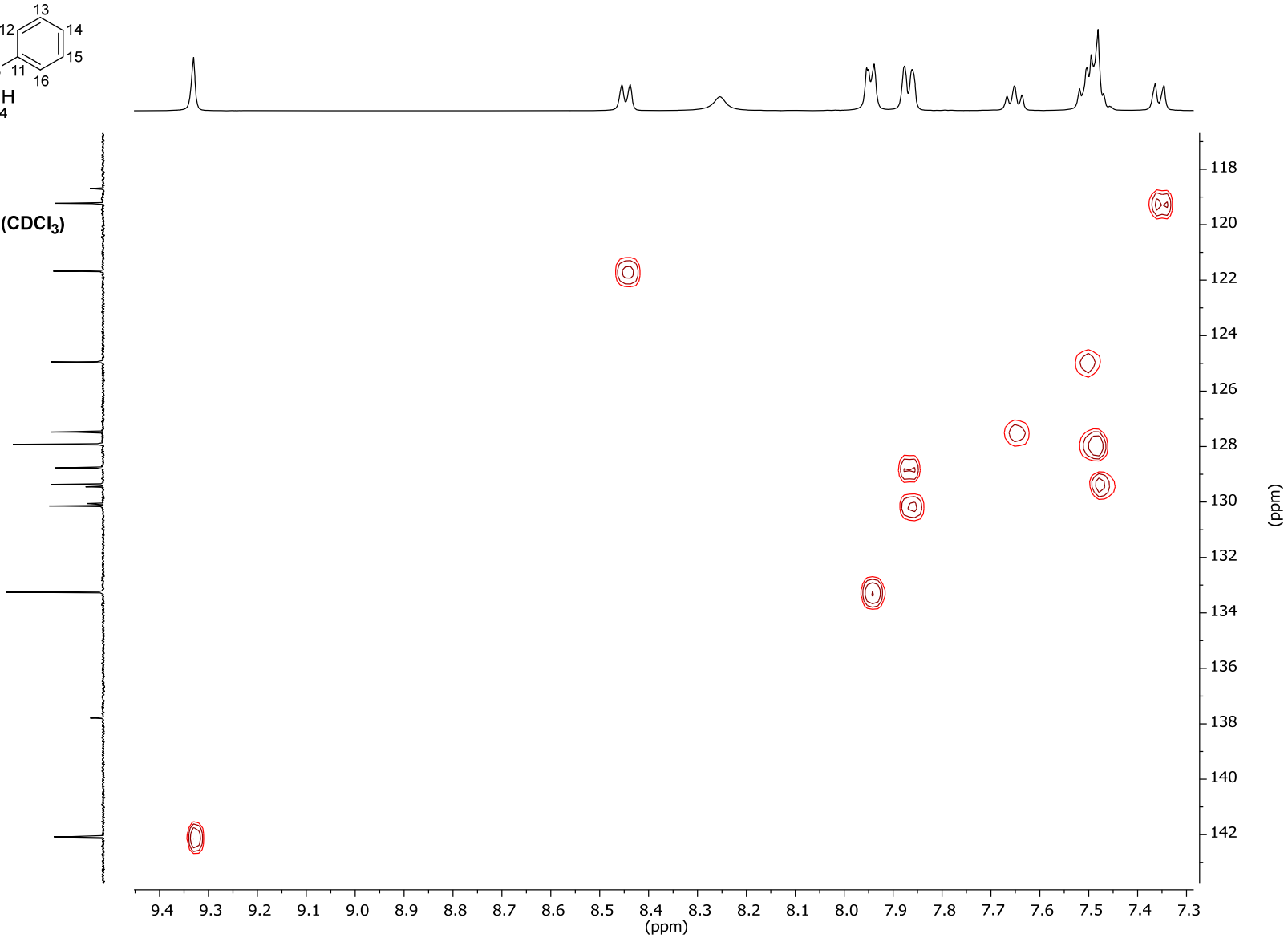
NOESY-NMR ($CDCl_3$)

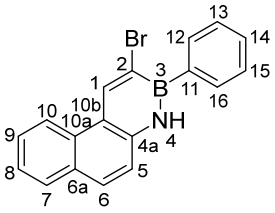




10b

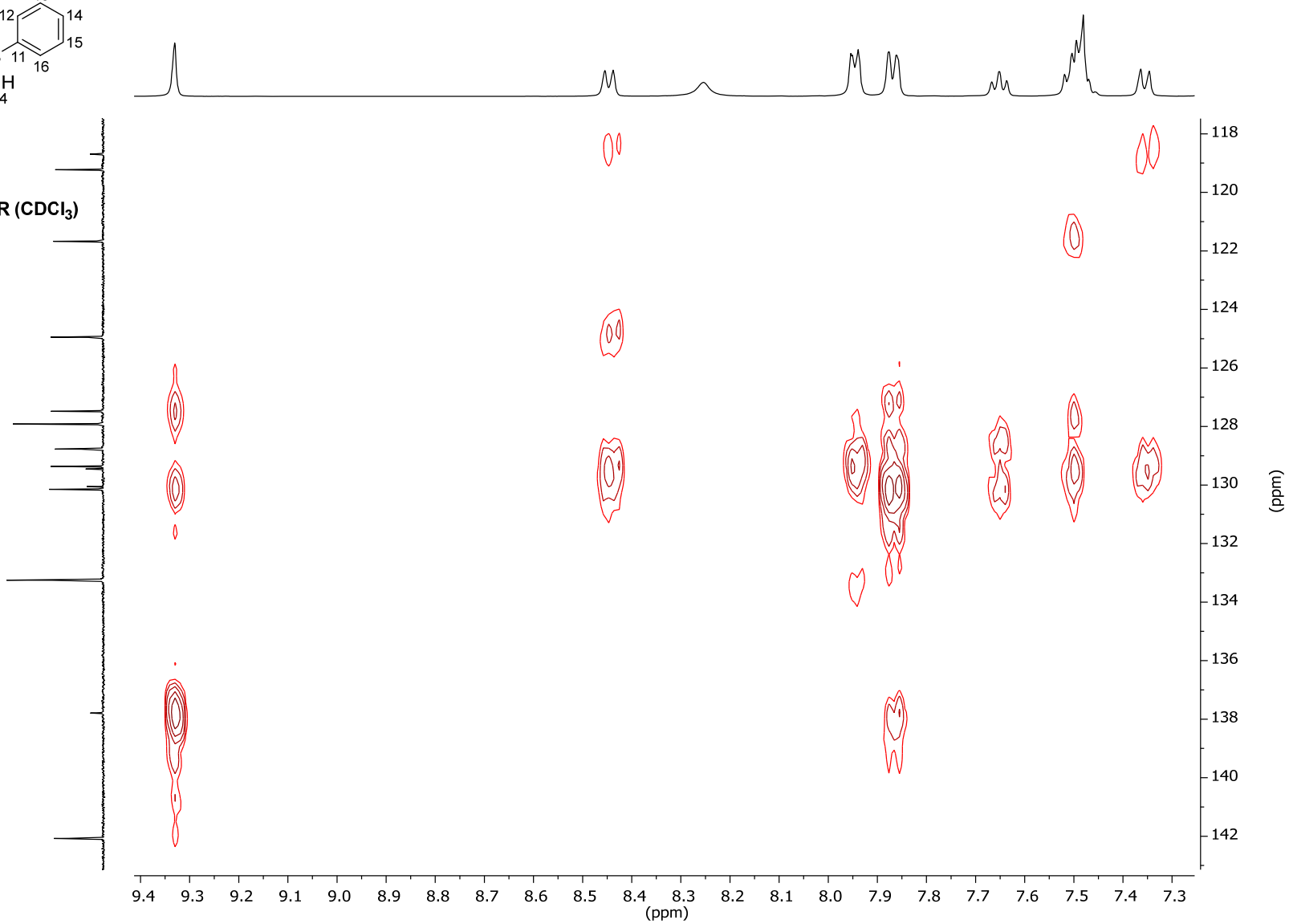
gHSQC-NMR ($CDCl_3$)

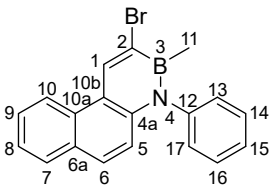




10b

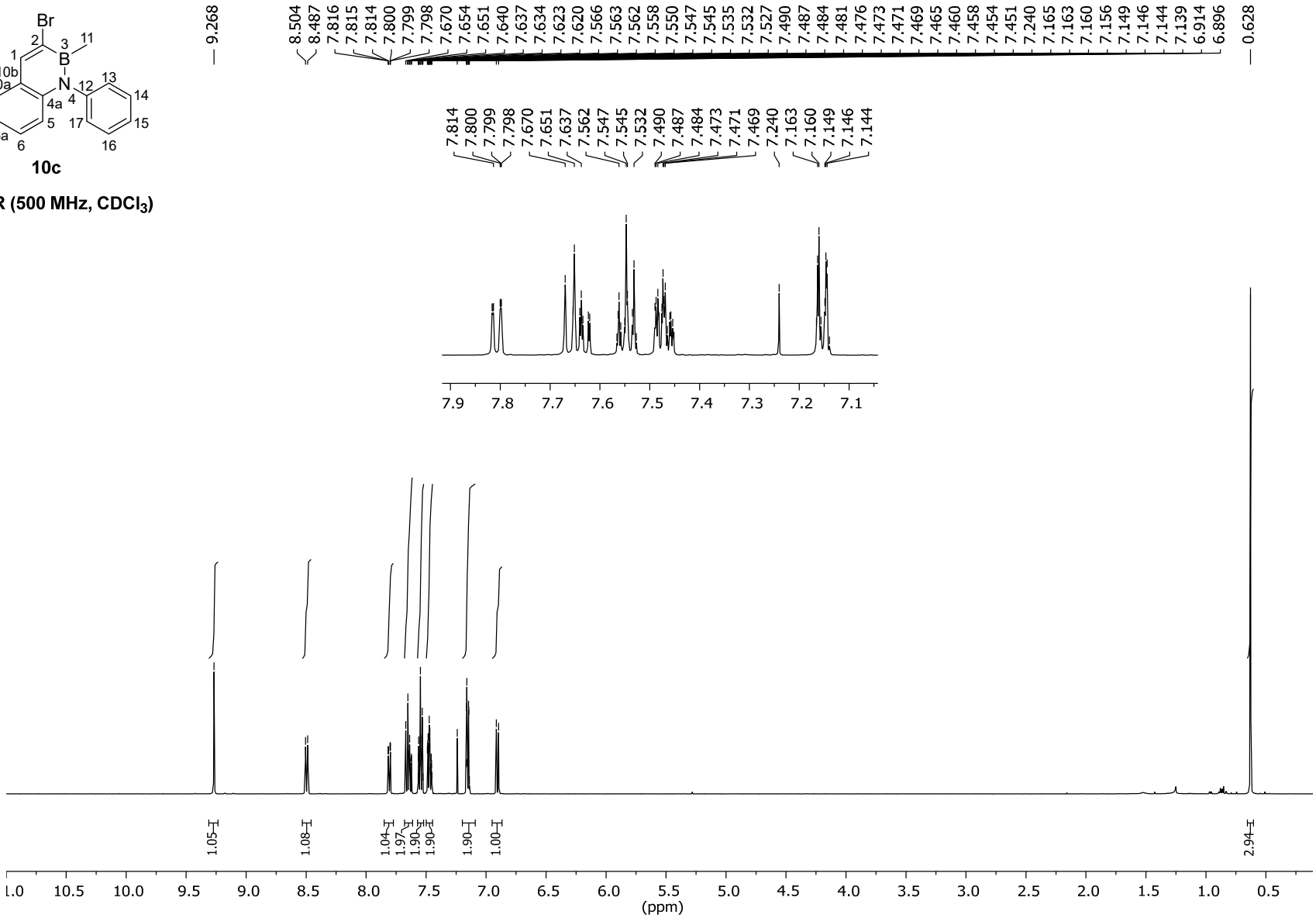
gHMBCAD-NMR ($CDCl_3$)

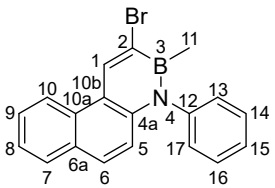




10c

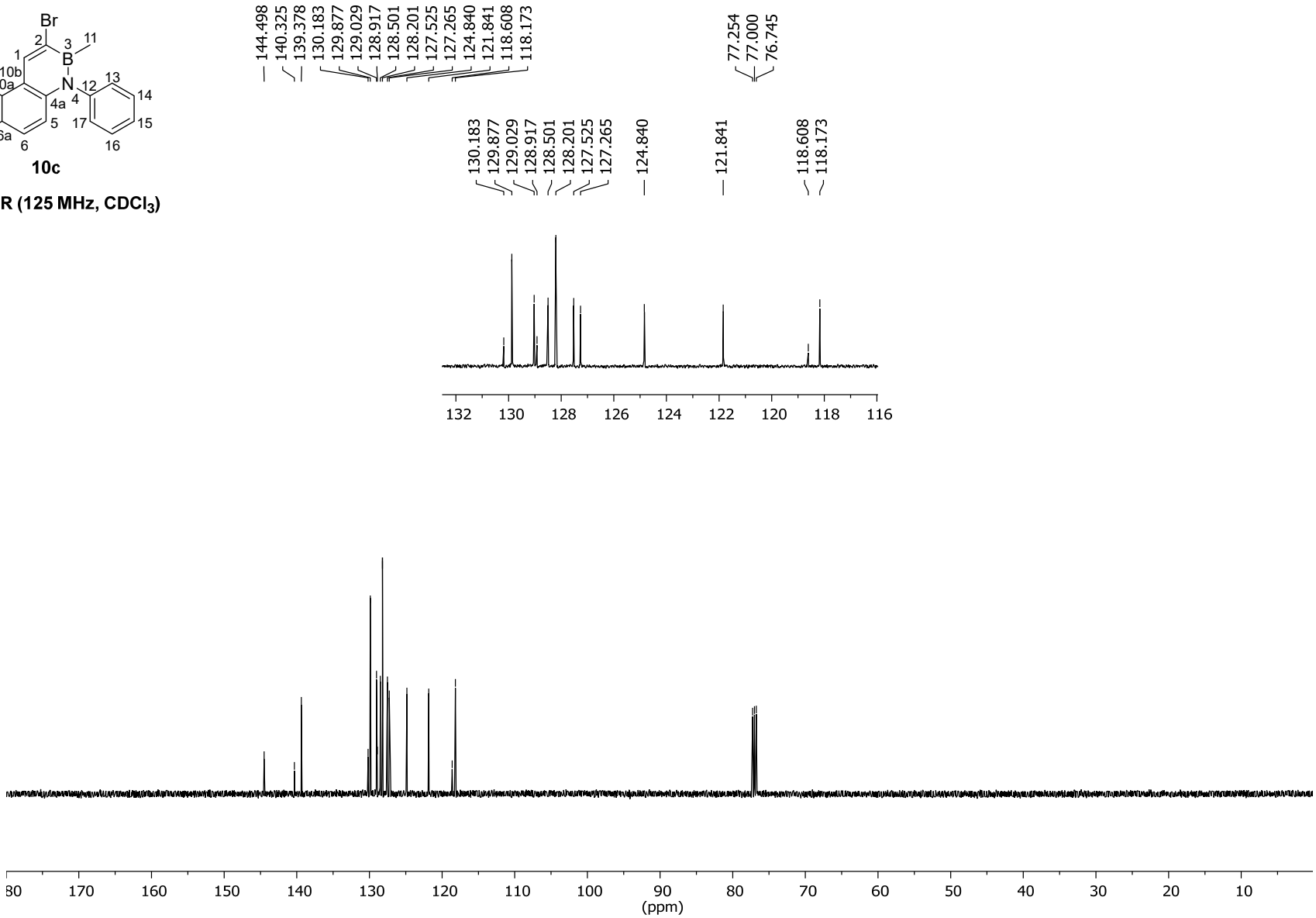
^{1}H-NMR (500 MHz, $CDCl_3$)

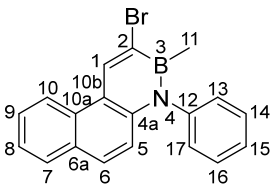




10c

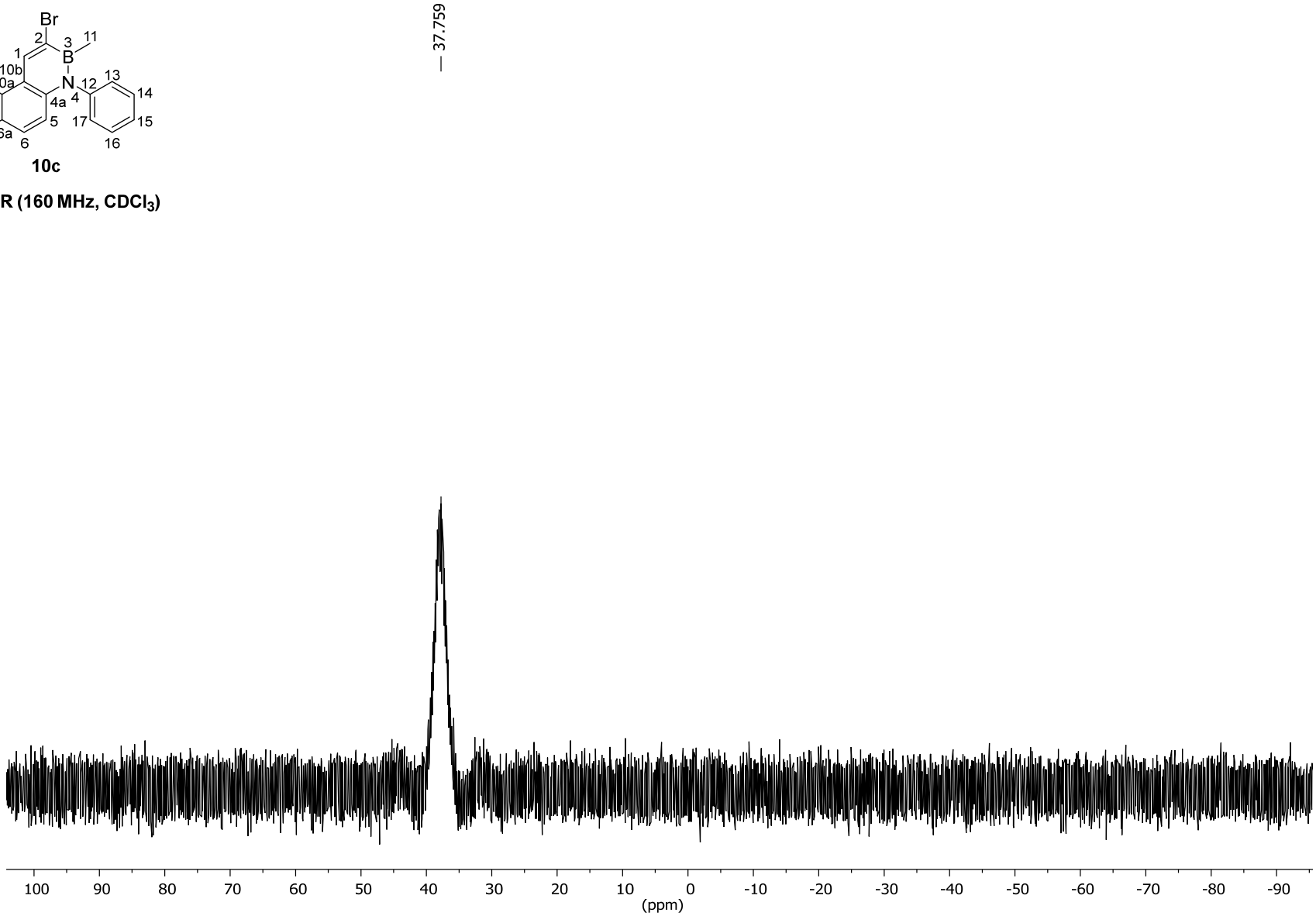
^{13}C-NMR (125 MHz, $CDCl_3$)

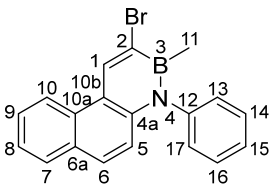




10c

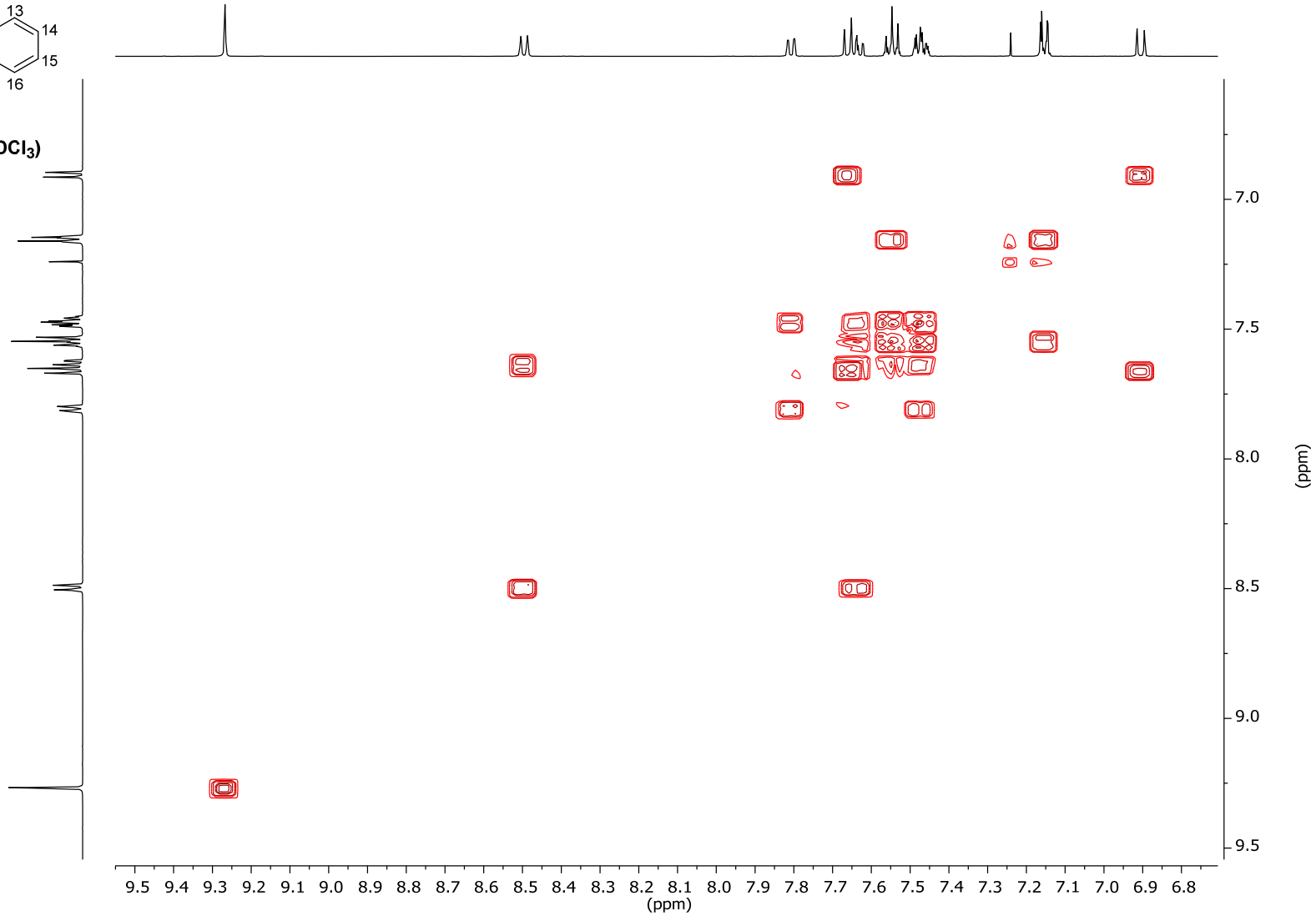
^{11}B-NMR (160 MHz, $CDCl_3$)

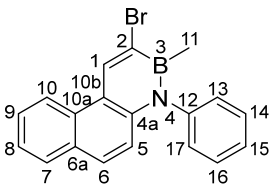




10c

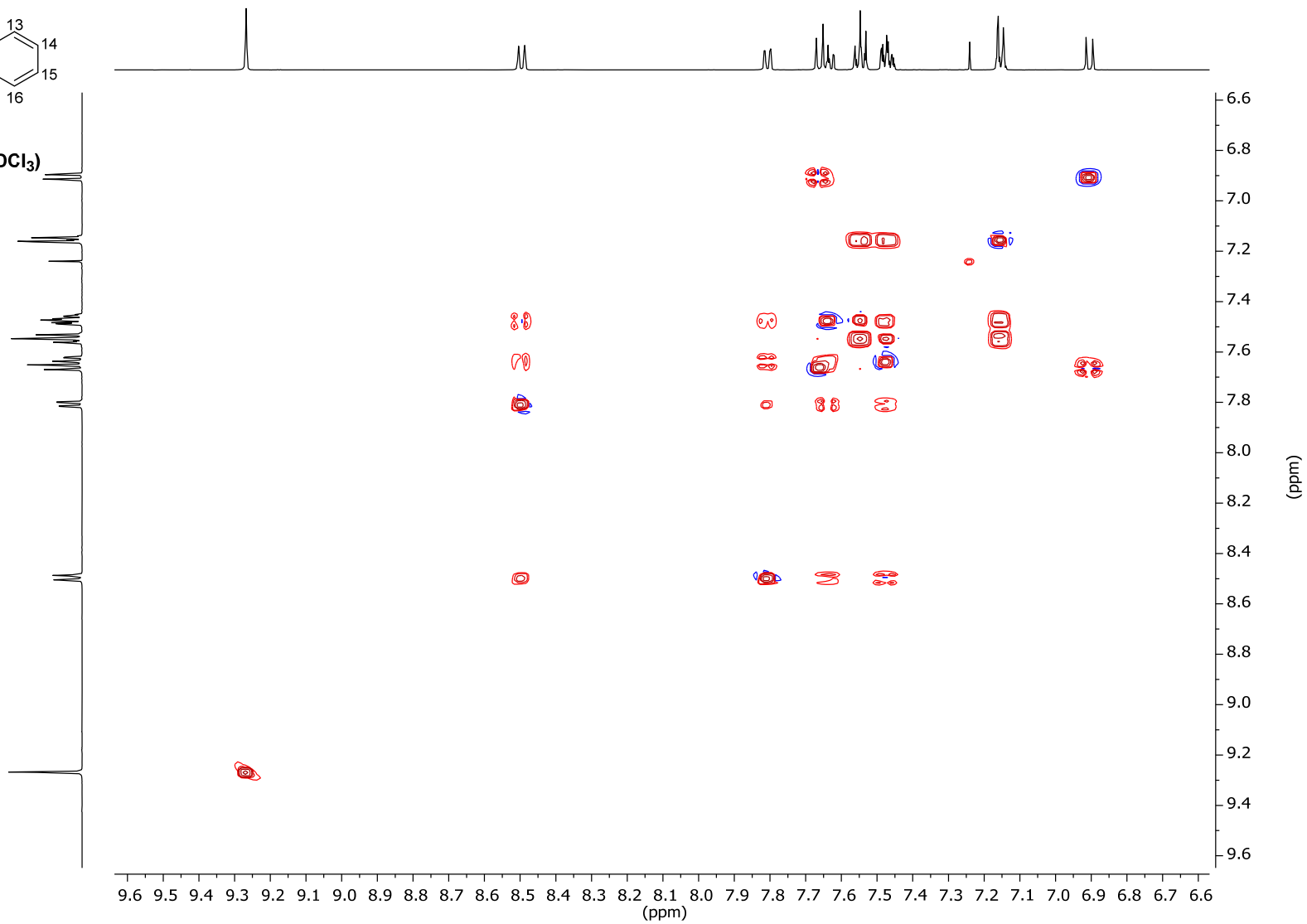
gCOSY-NMR ($CDCl_3$)

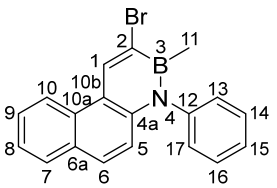




10c

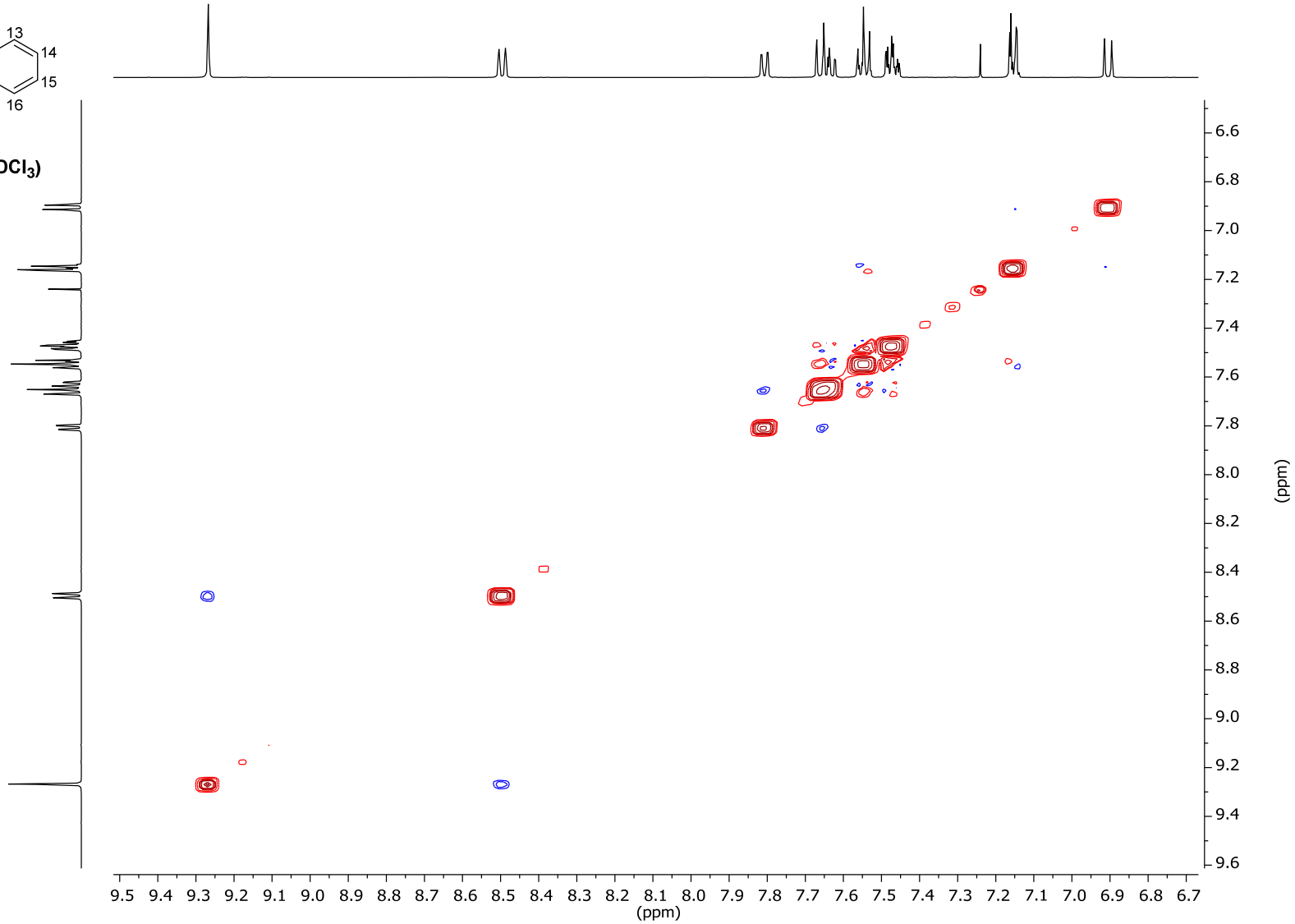
TOCSY-NMR ($CDCl_3$)

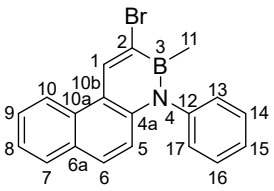




10c

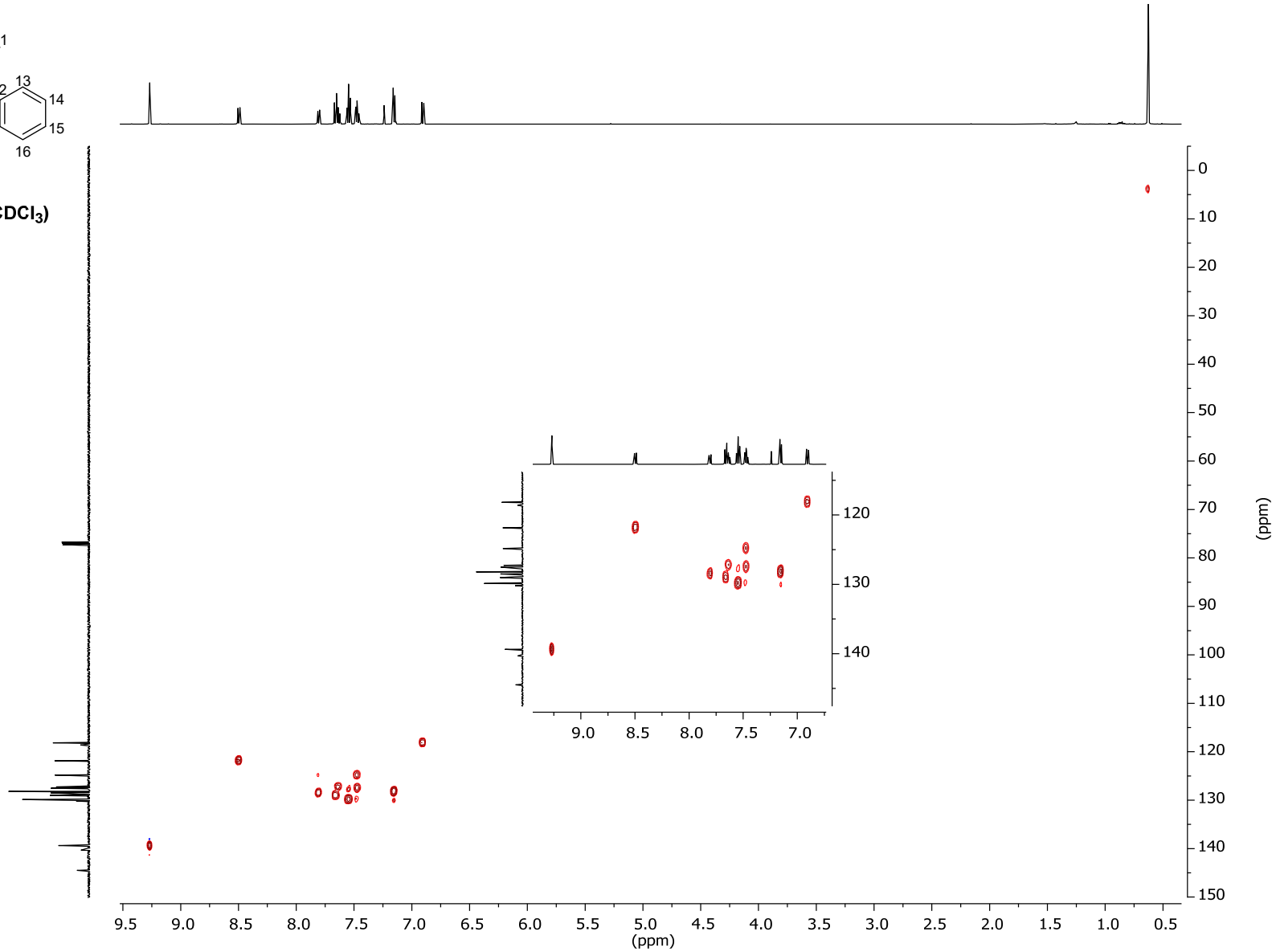
NOESY-NMR ($CDCl_3$)

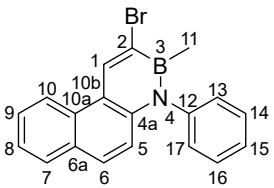




10c

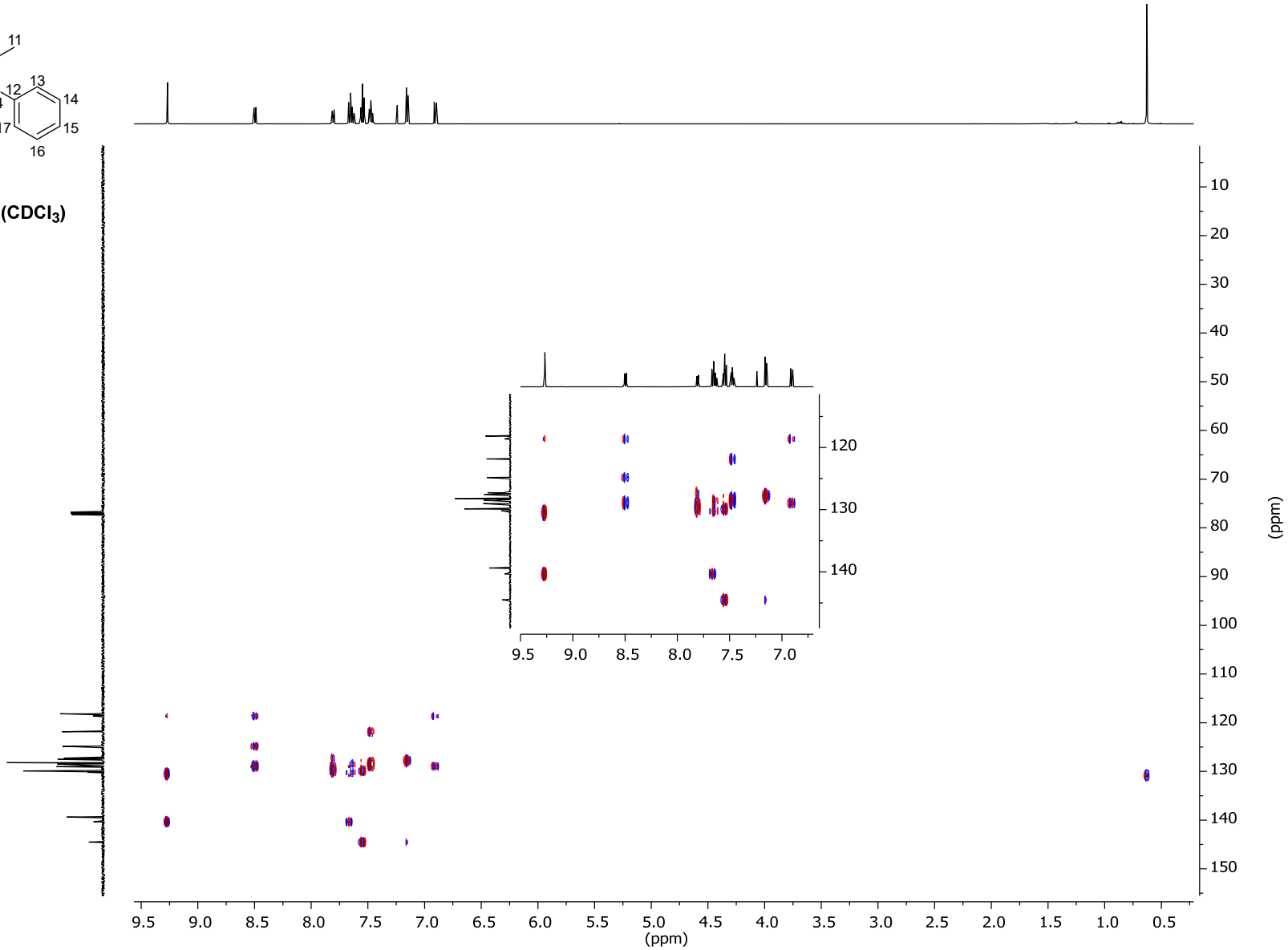
gHSQC-NMR ($CDCl_3$)

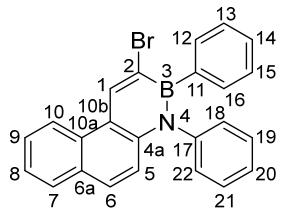




10c

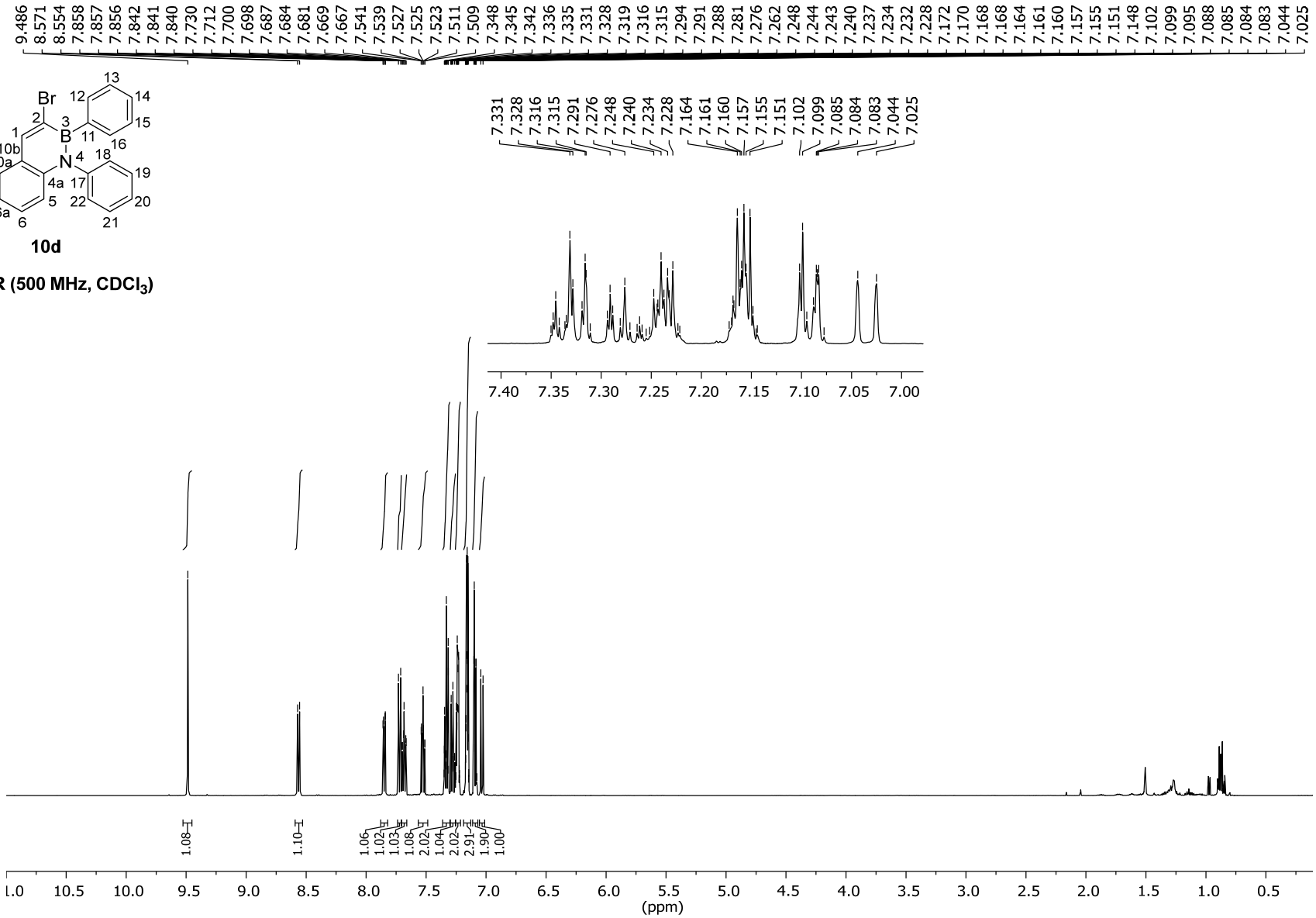
gHMBC-NMR ($CDCl_3$)

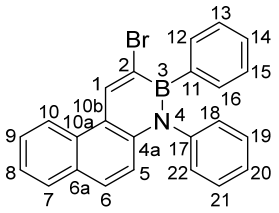




10d

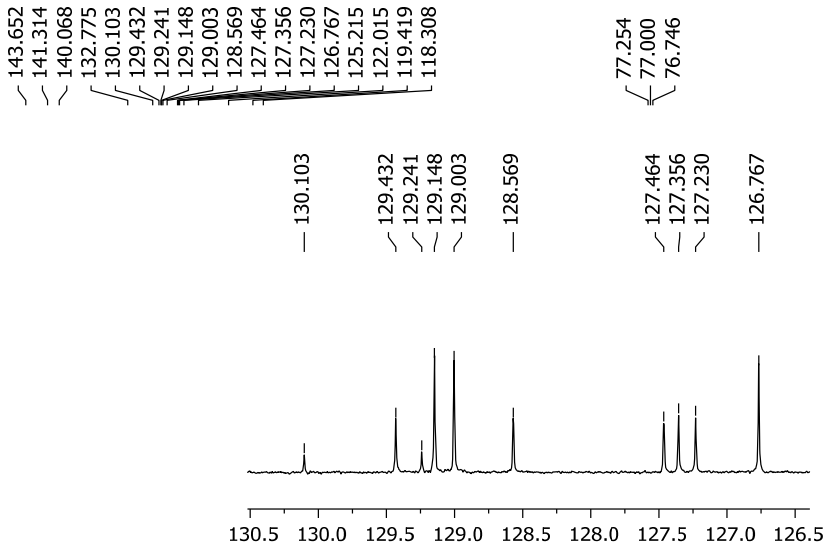
^{1}H-NMR (500 MHz, $CDCl_3$)

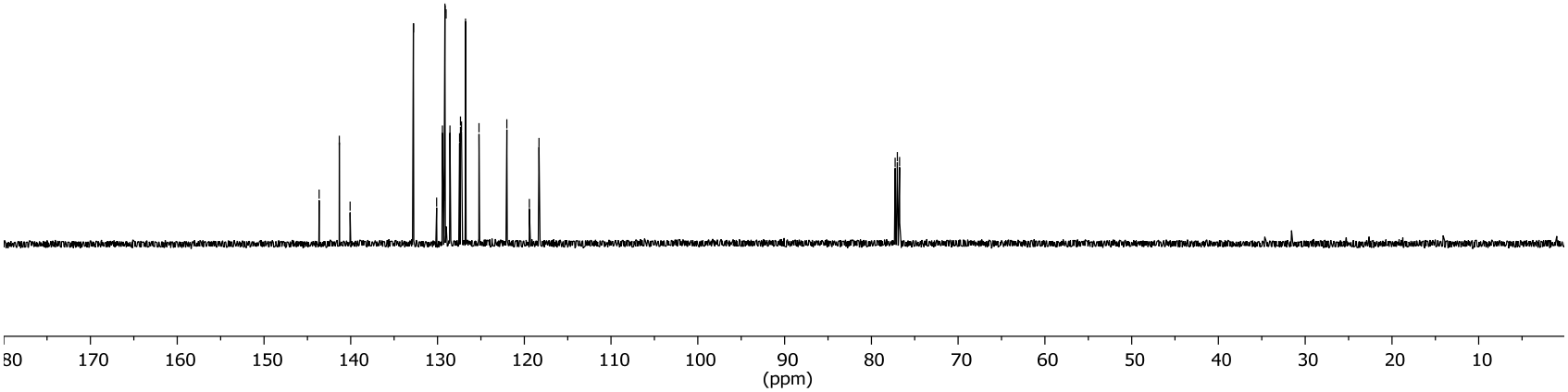


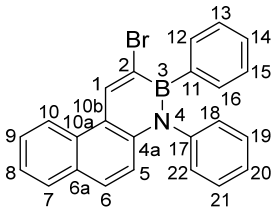


10d

^{13}C-NMR (125 MHz, $CDCl_3$)

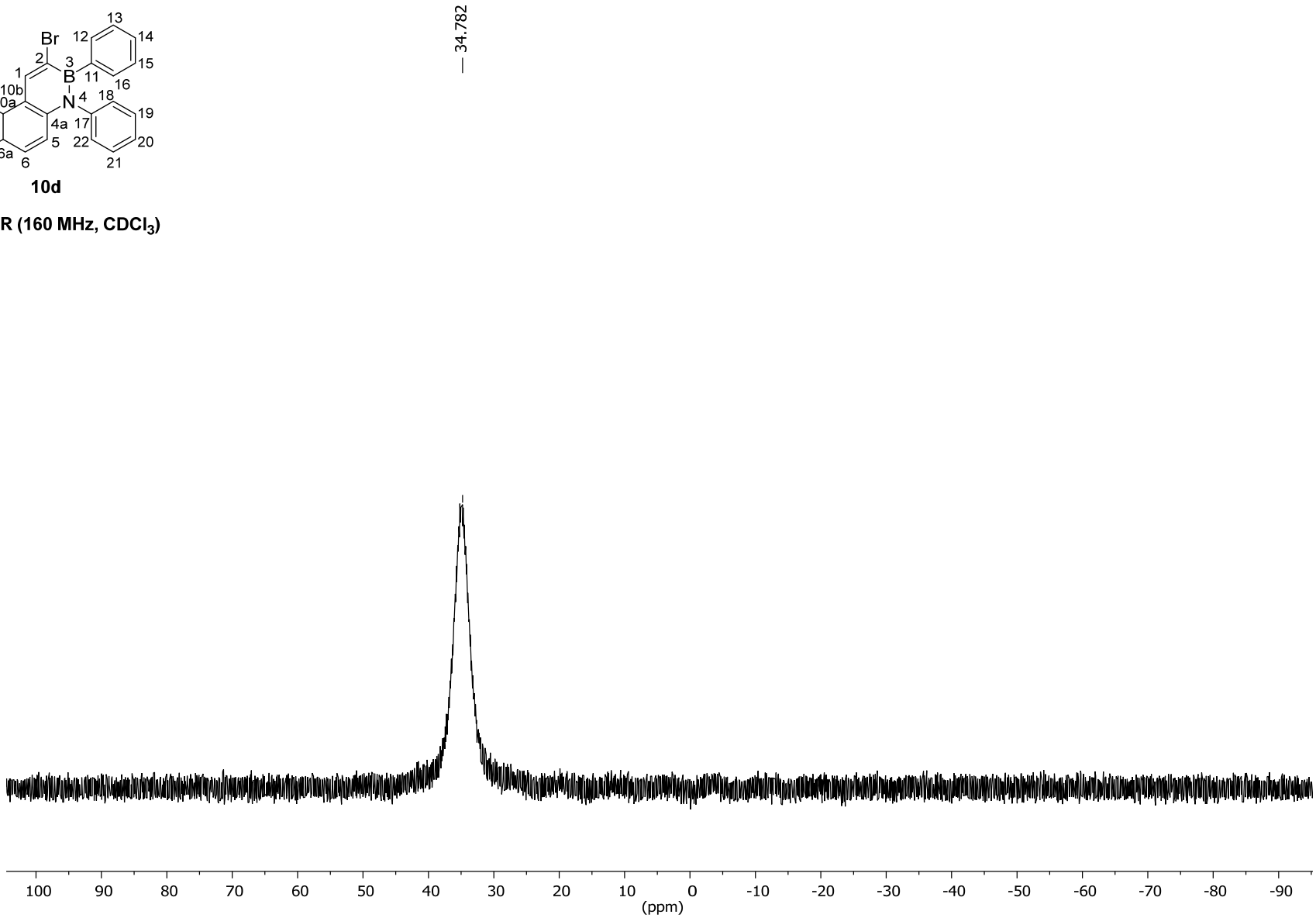


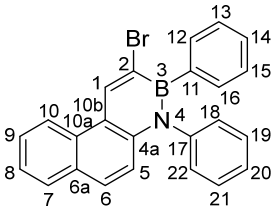




10d

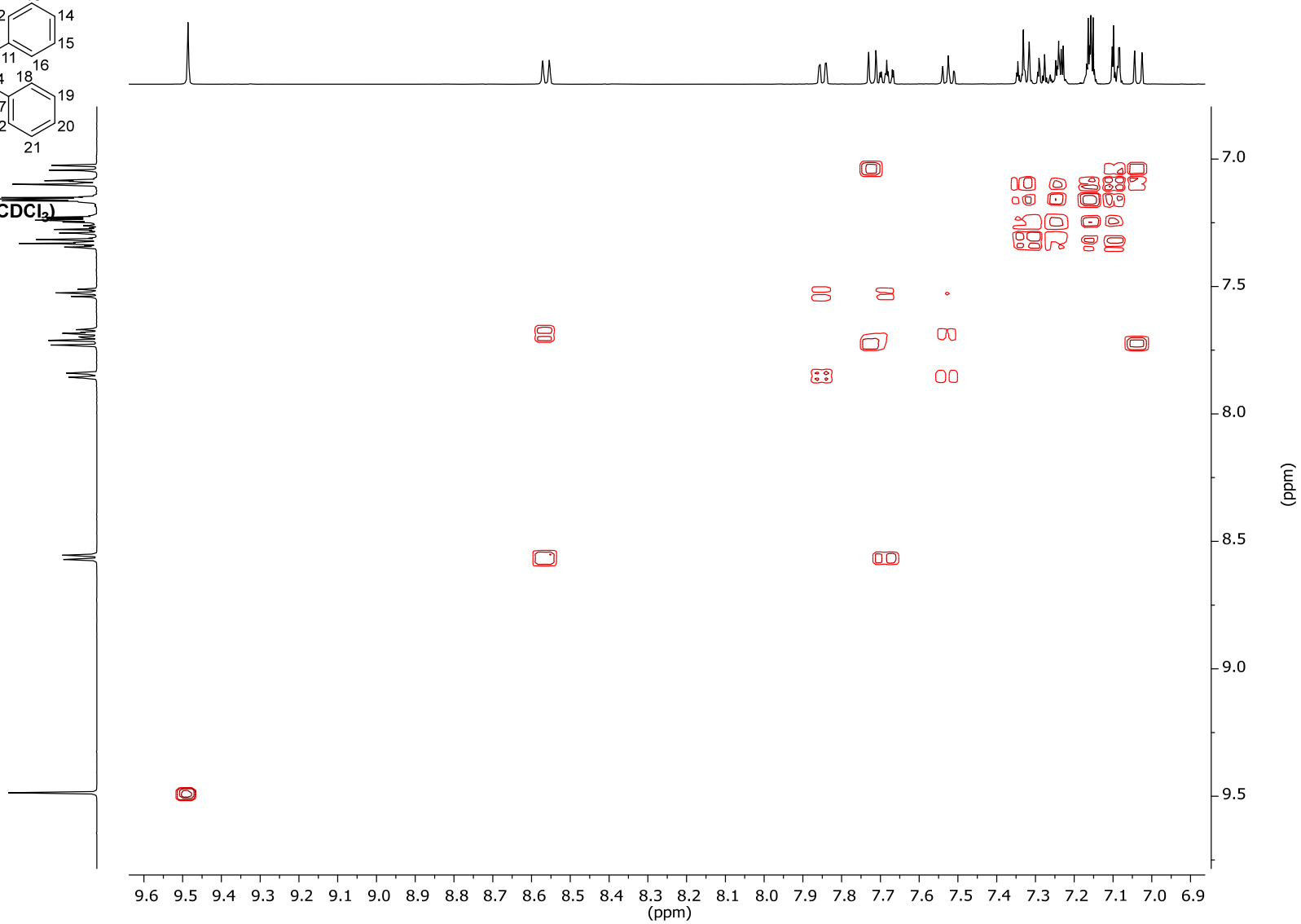
^{11}B-NMR (160 MHz, $CDCl_3$)

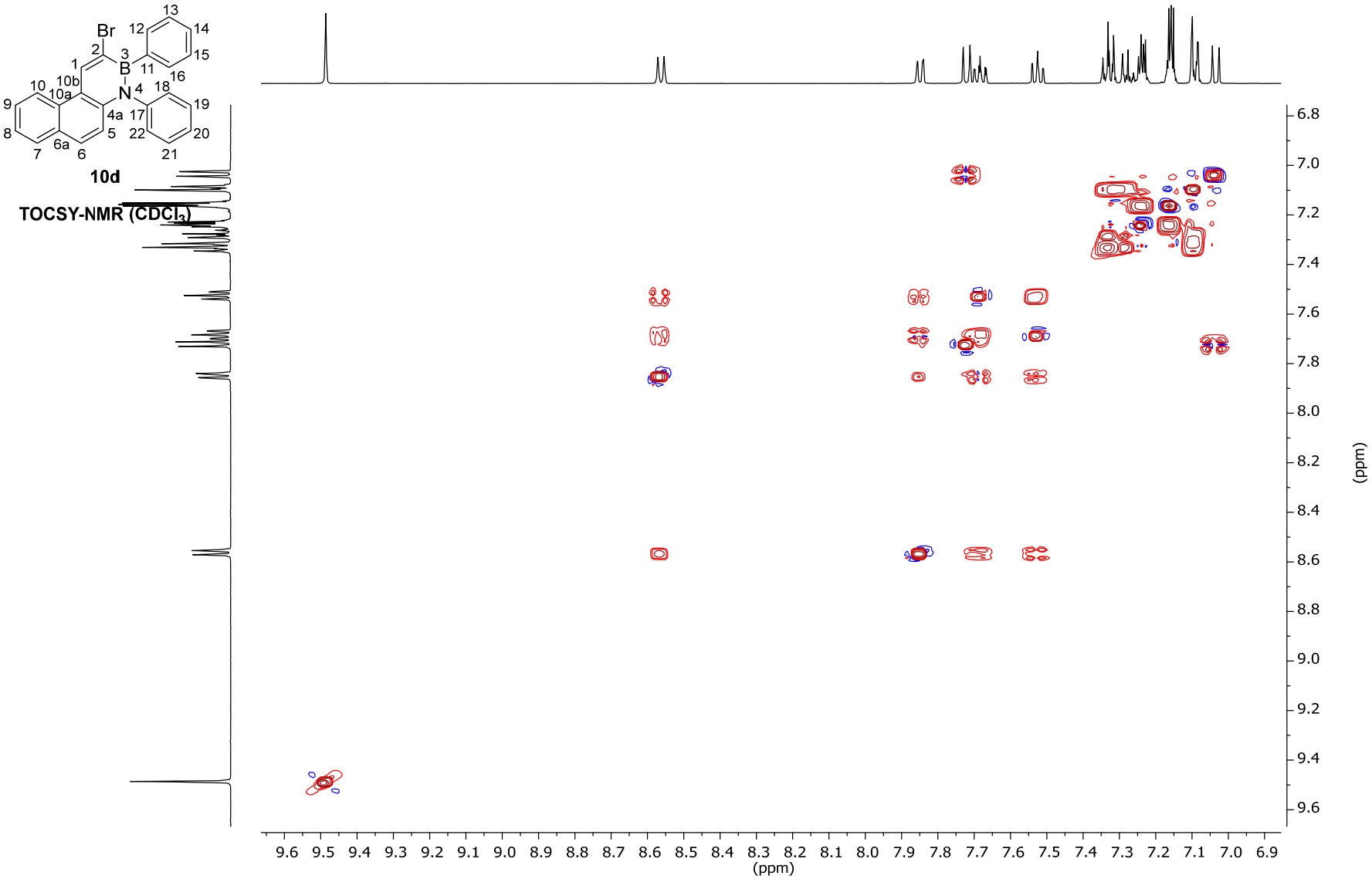


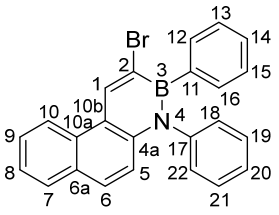


10d

gCOSY-NMR ($CDCl_3$)

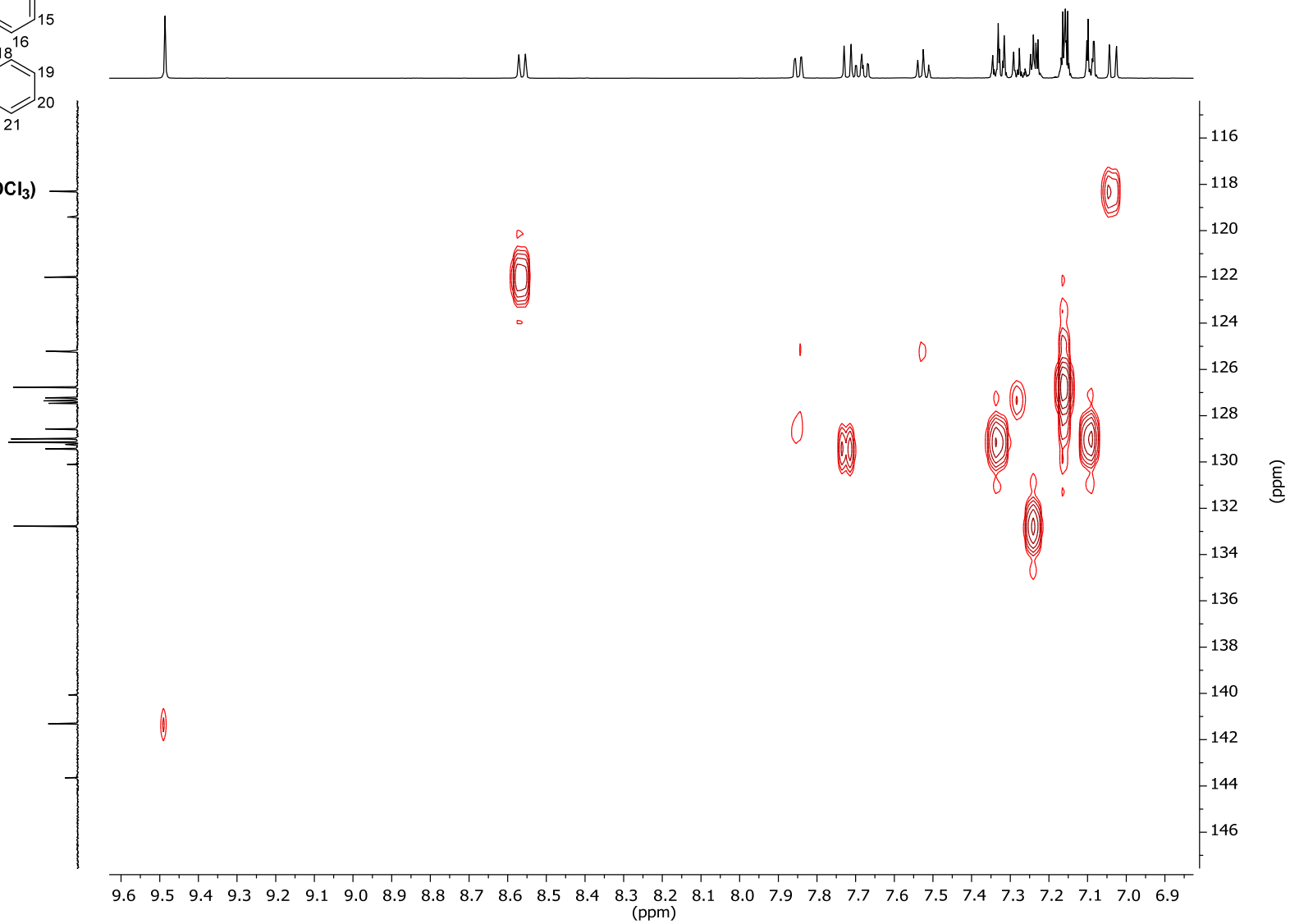


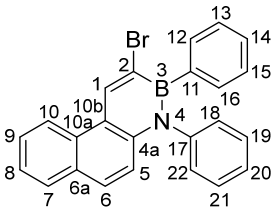

10d
TOCSY-NMR (CDCl3)
(ppm)
(ppm)



10d

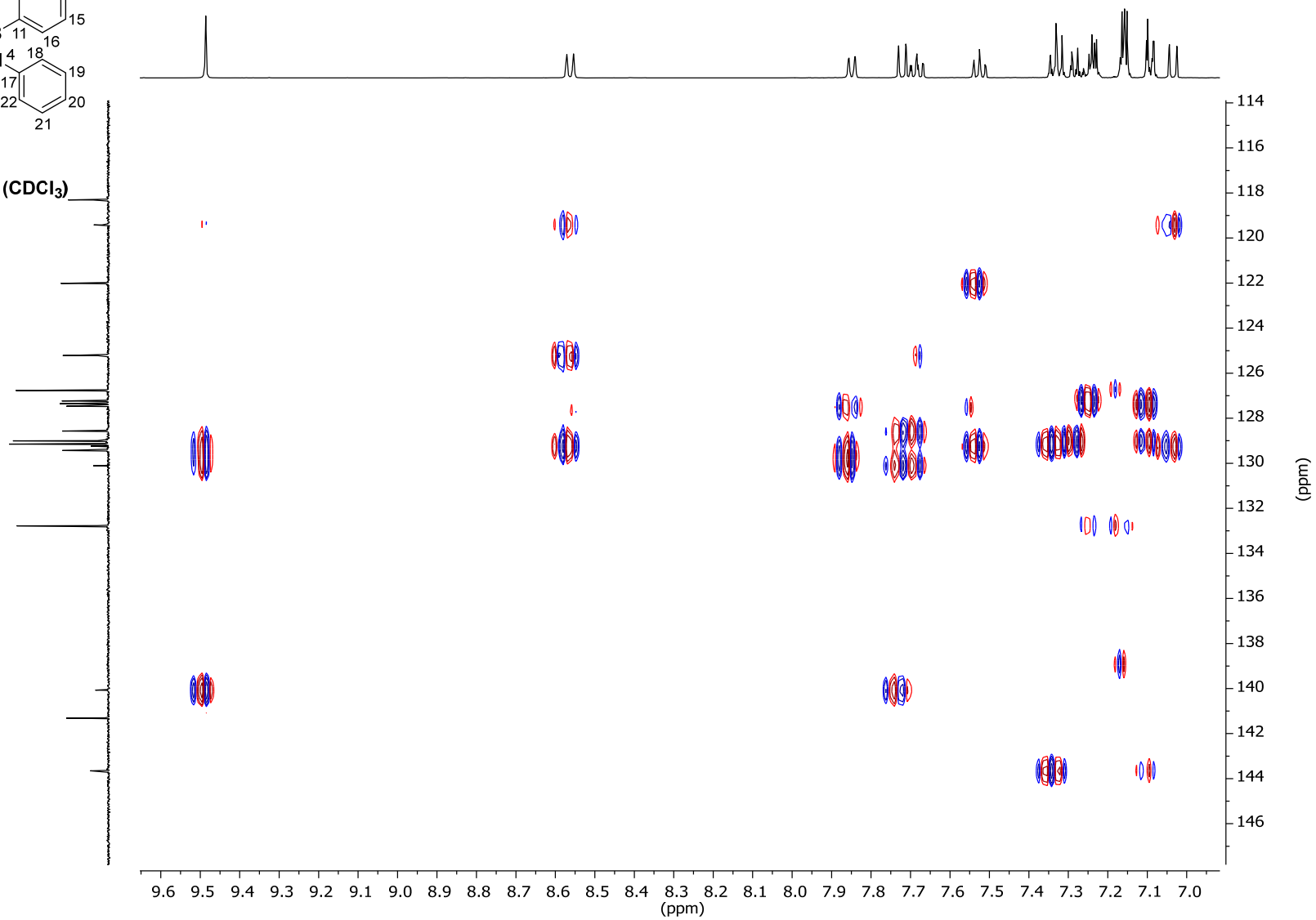
gHSQC-NMR ($CDCl_3$)

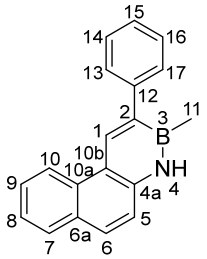




10d

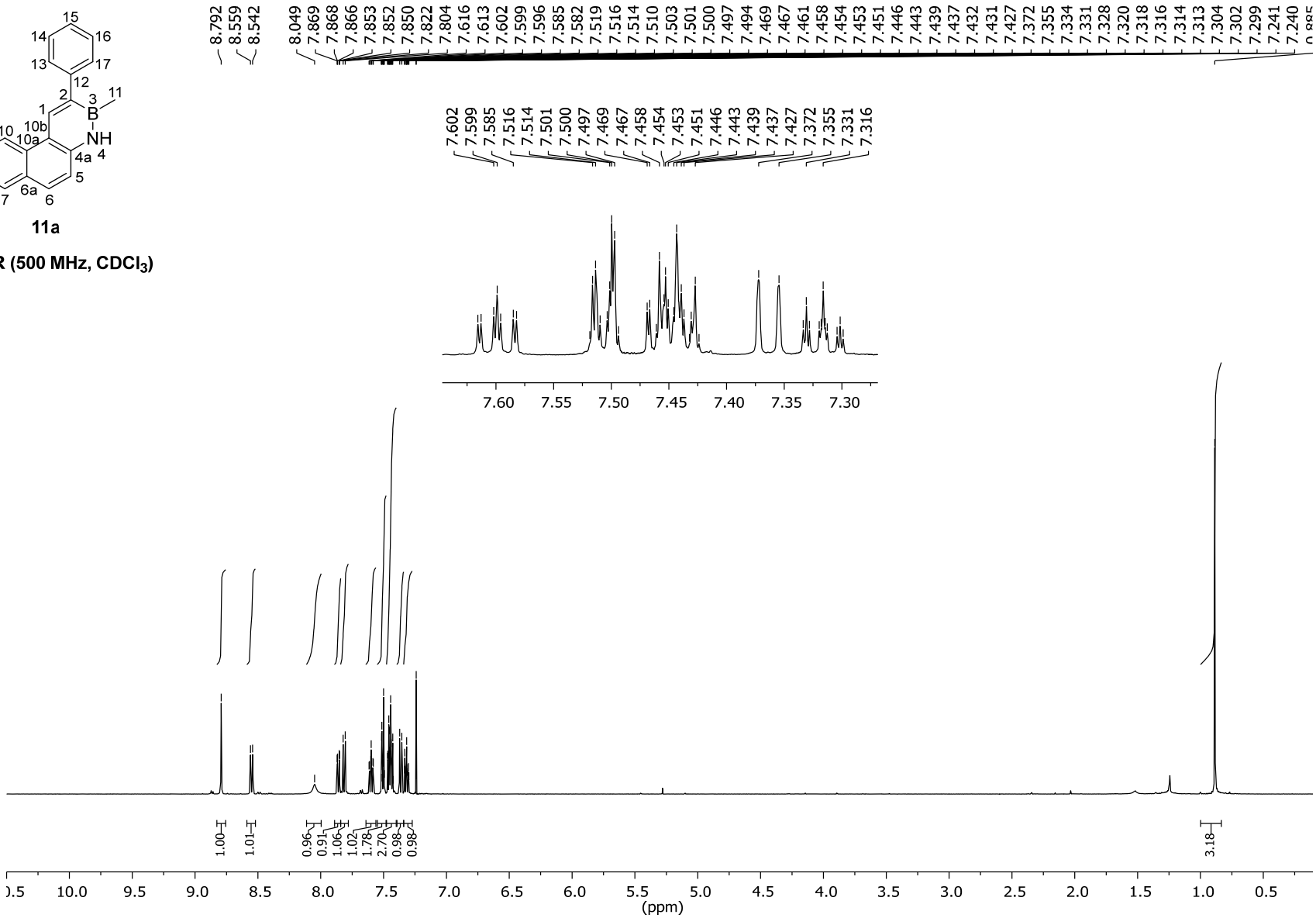
gHMBC-NMR ($CDCl_3$)

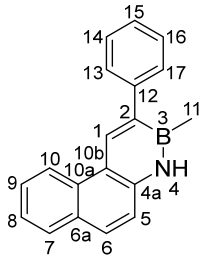




11a

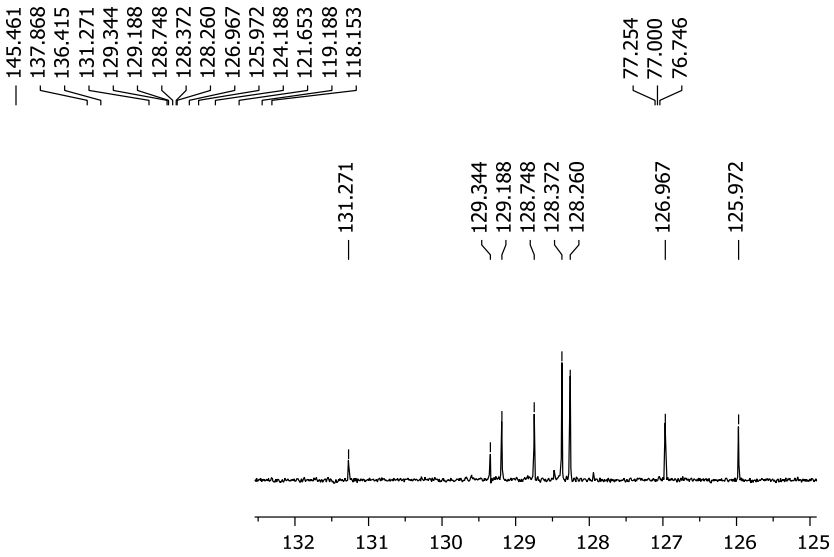
^{1}H-NMR (500 MHz, $CDCl_3$)

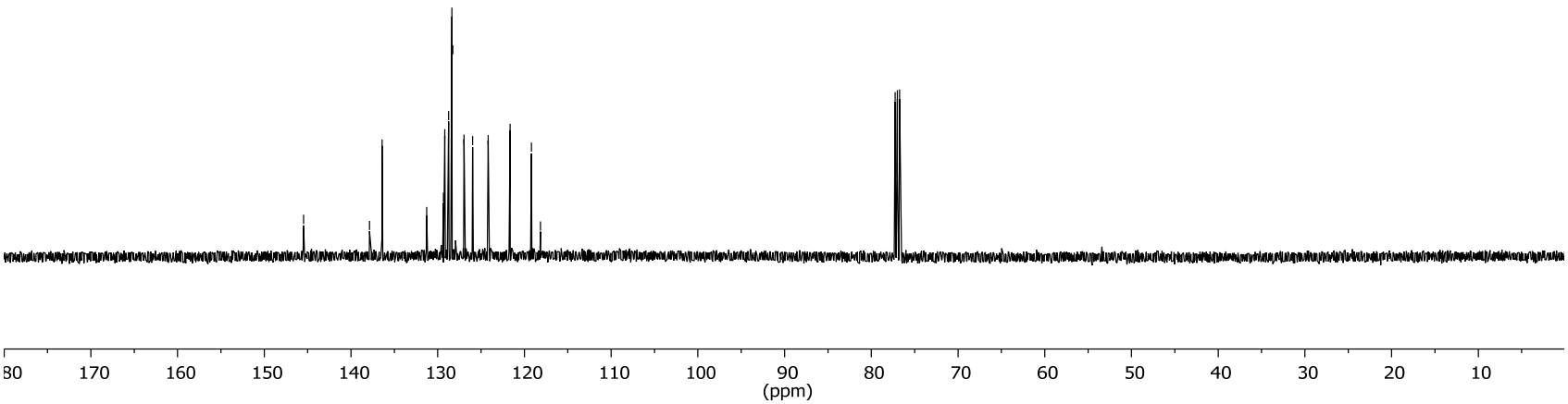


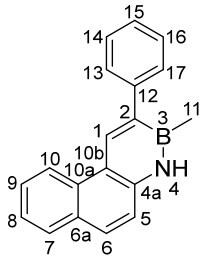


11a

^{13}C-NMR (125 MHz, $CDCl_3$)

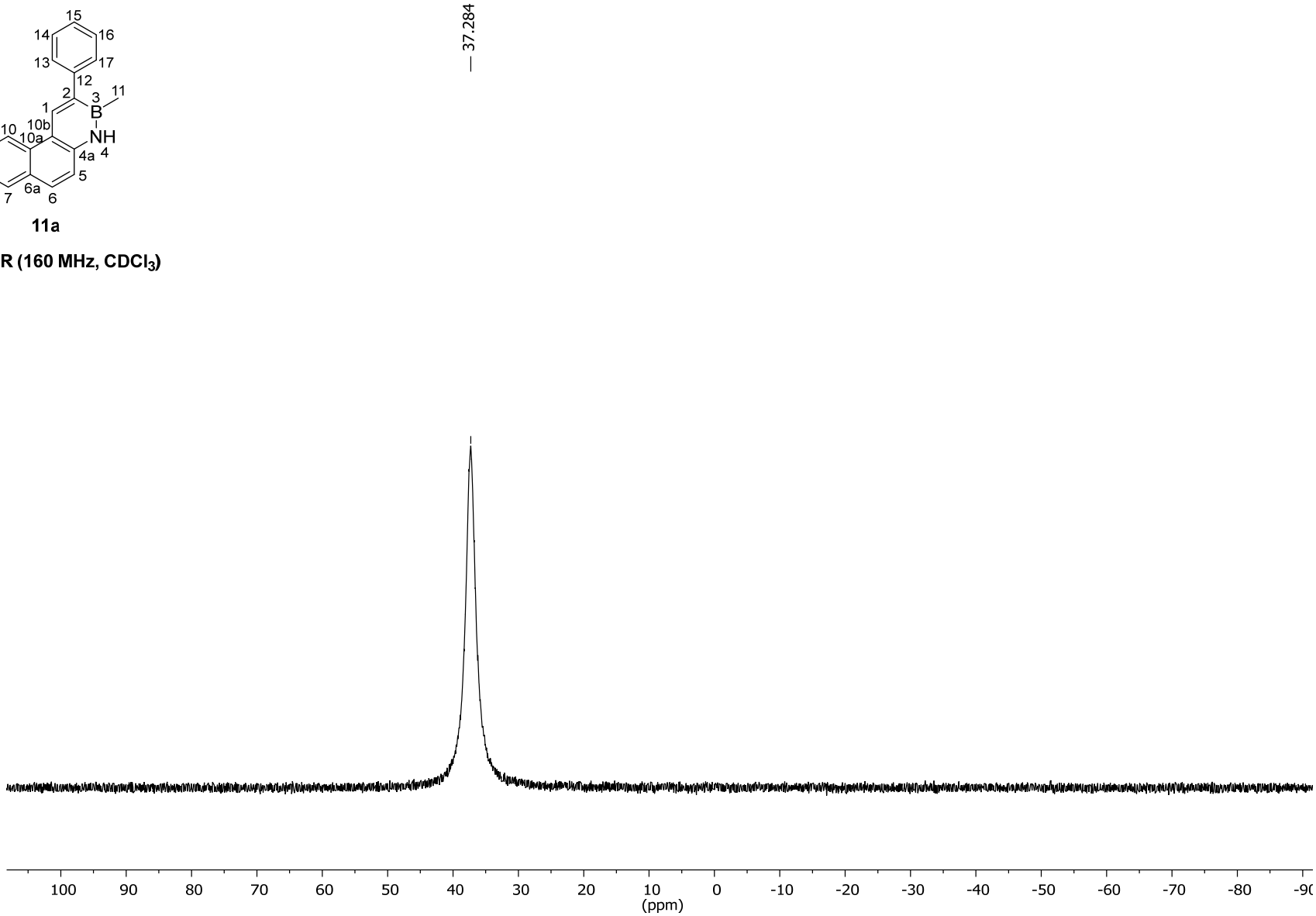


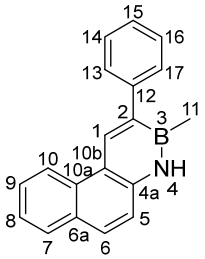




11a

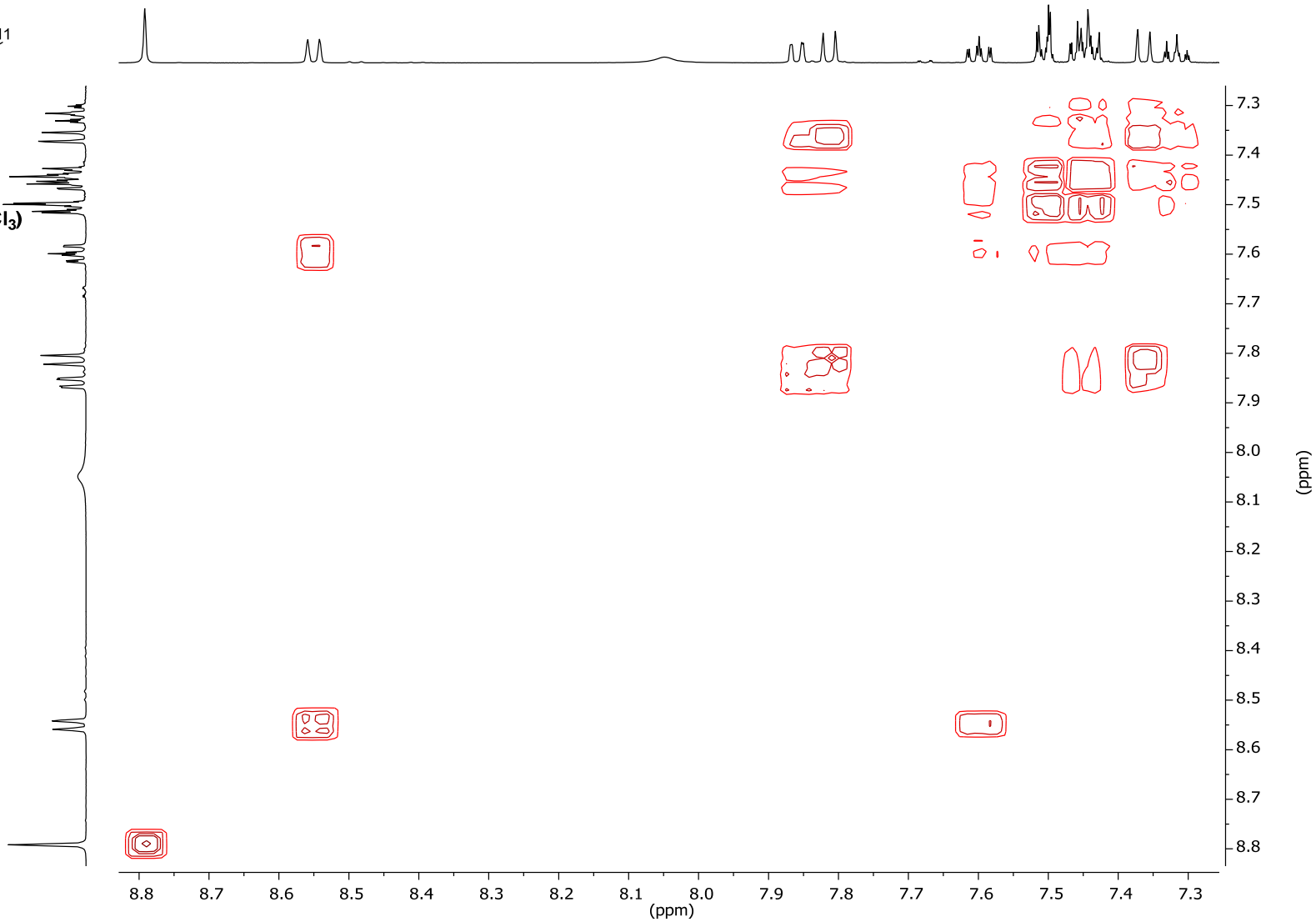
^{11}B-NMR (160 MHz, $CDCl_3$)

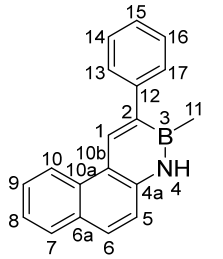




11a

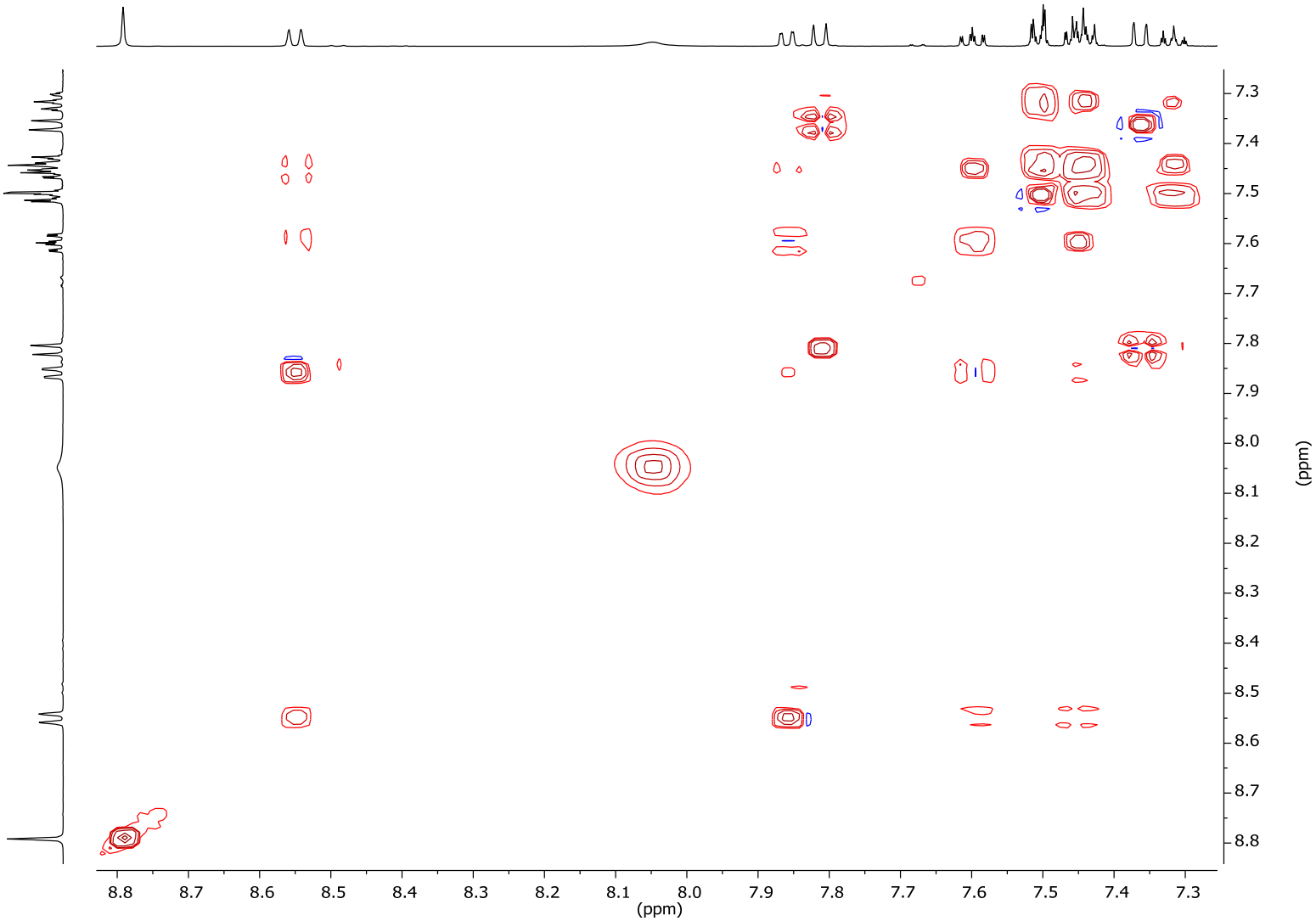
gCOSY-NMR ($CDCl_3$)

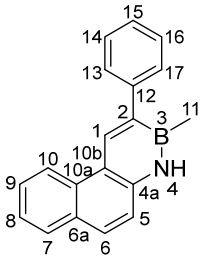




11a

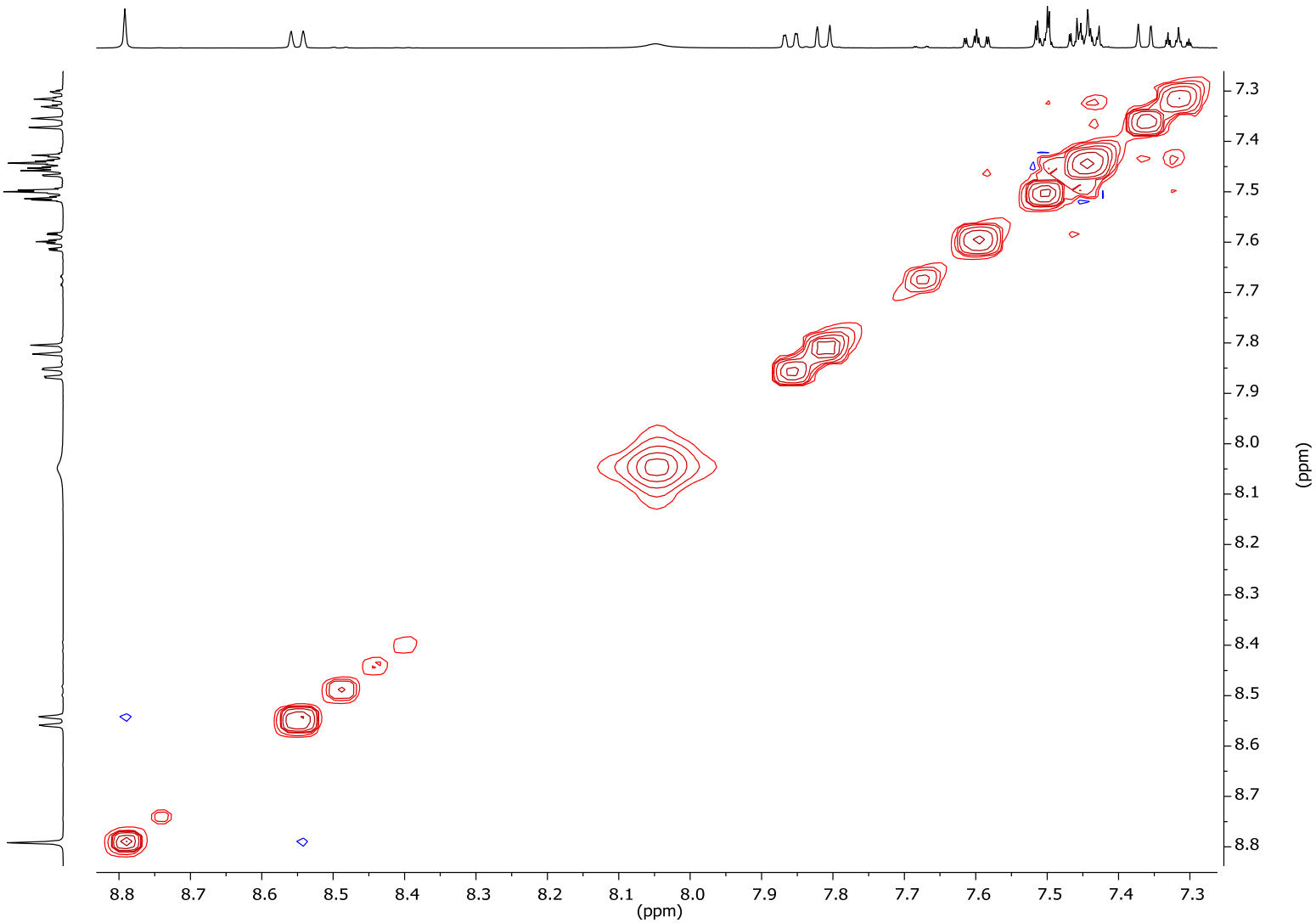
TOCSY-NMR ($CDCl_3$)

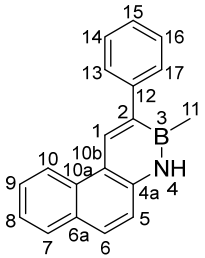




11a

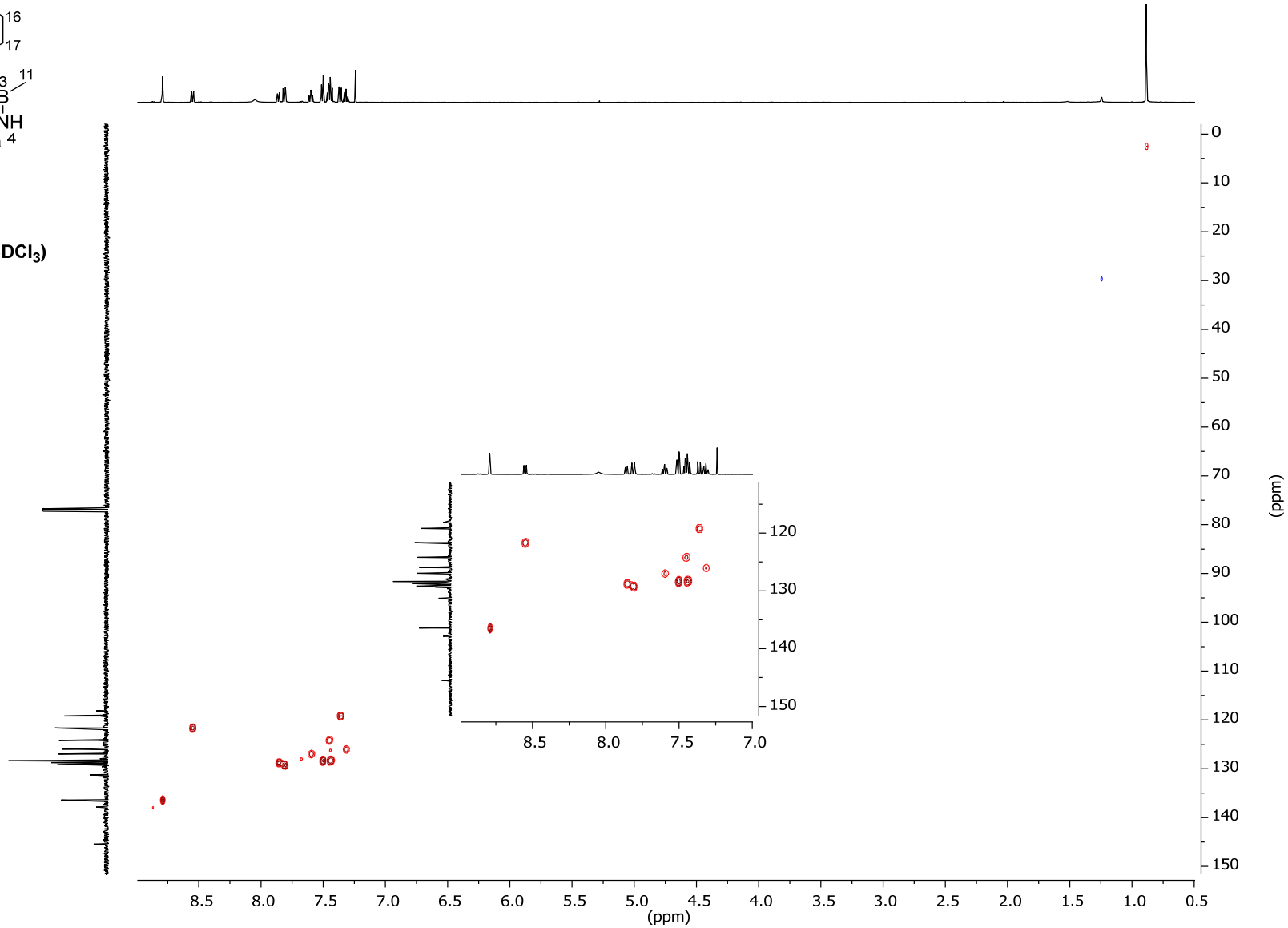
NOESY-NMR ($CDCl_3$)

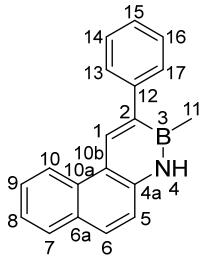




11a

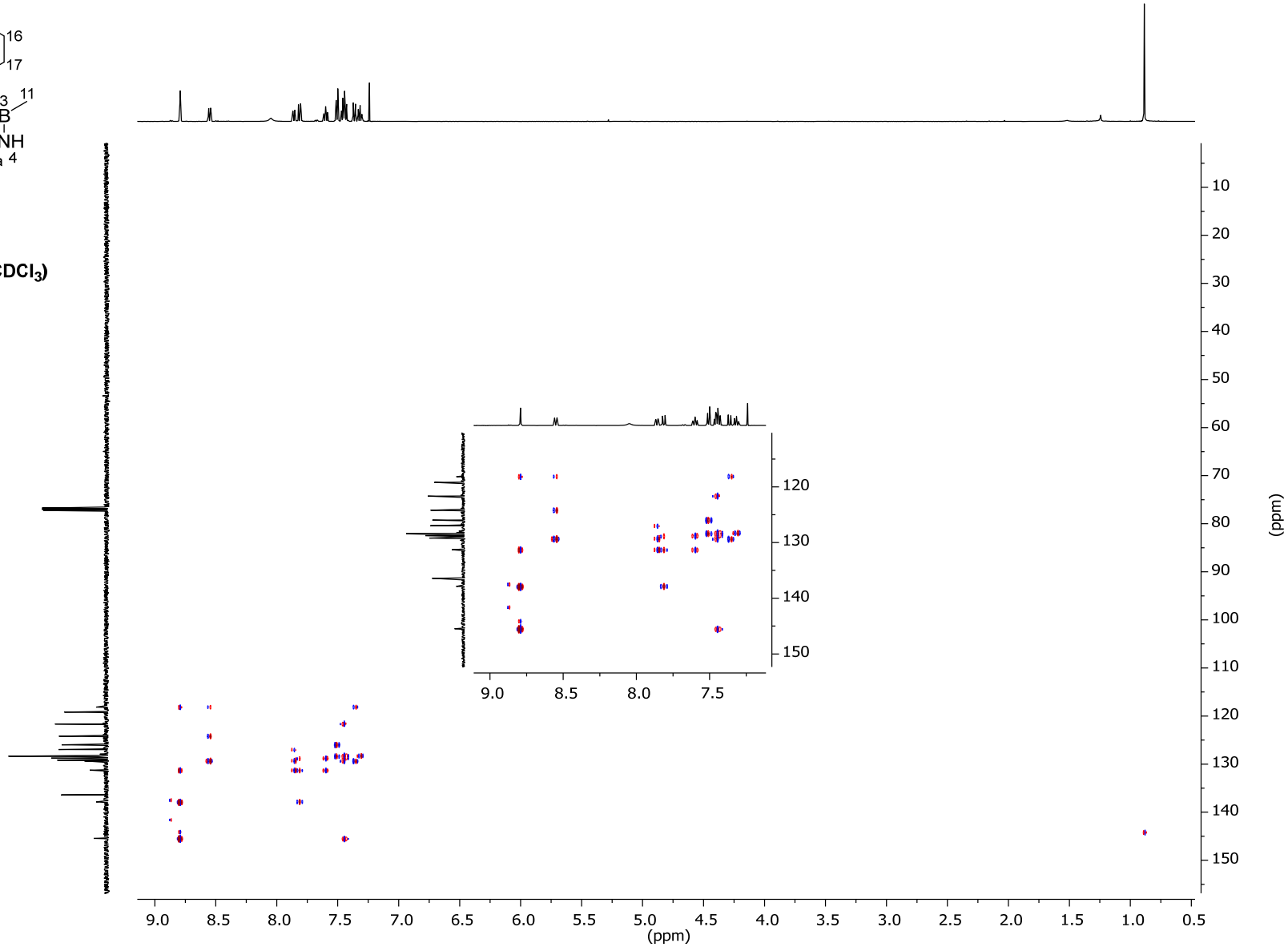
gHSQC-NMR ($CDCl_3$)

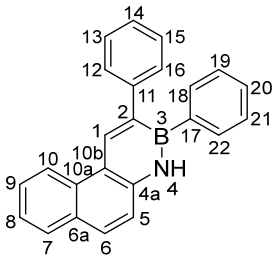




11a

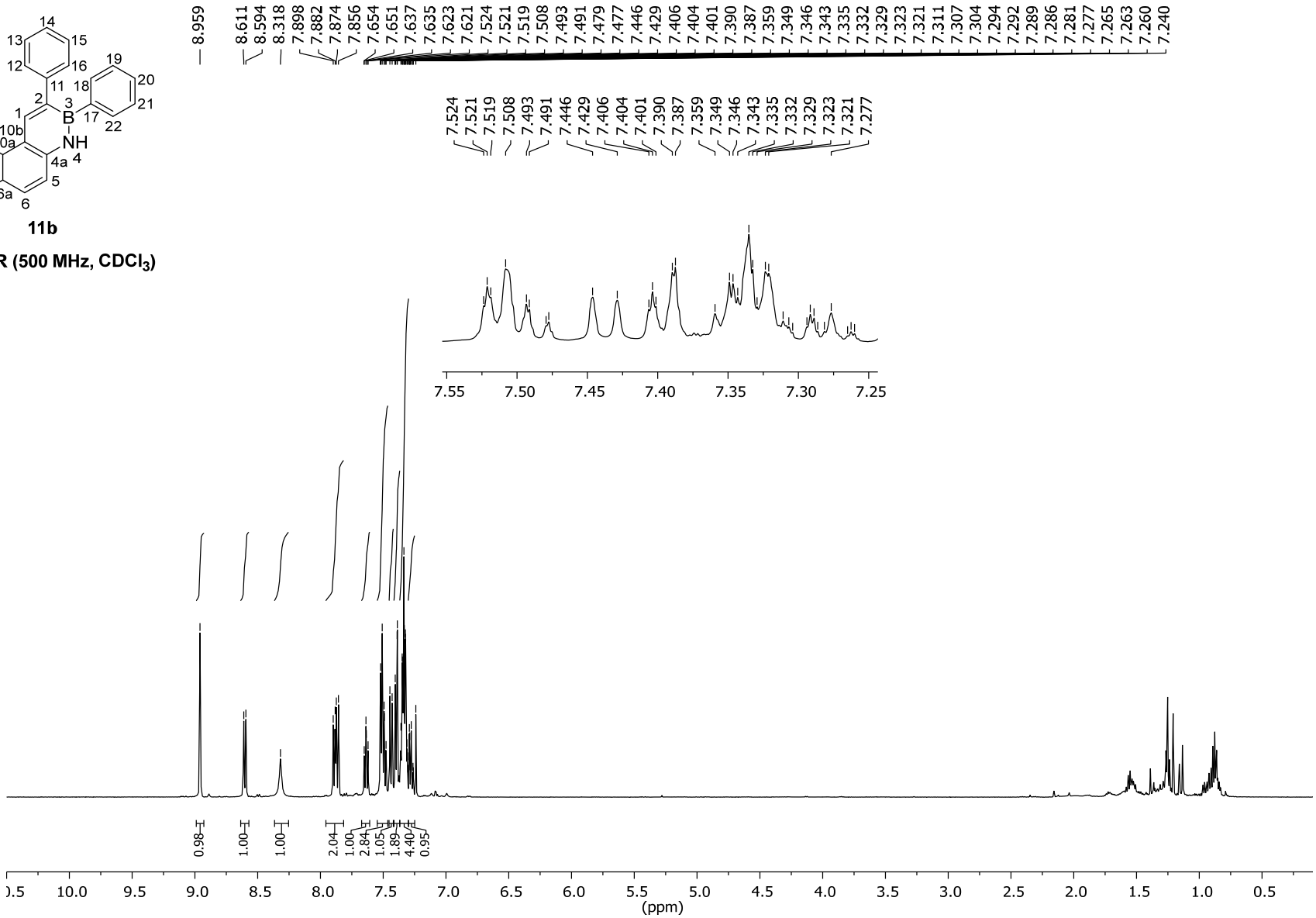
gHMBC-NMR ($CDCl_3$)

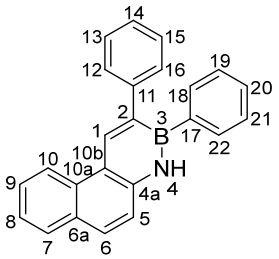




11b

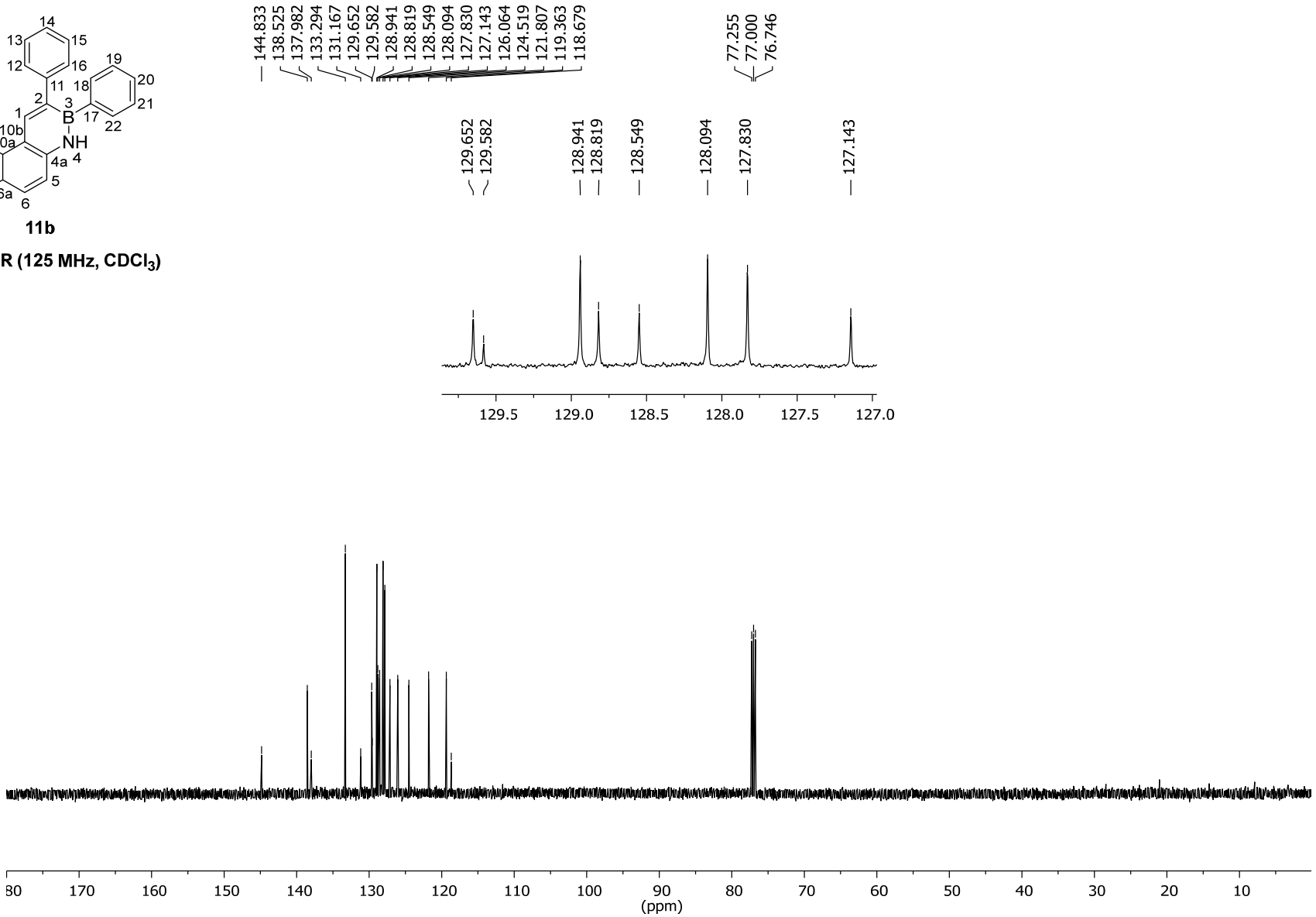
^{1}H-NMR (500 MHz, $CDCl_3$)

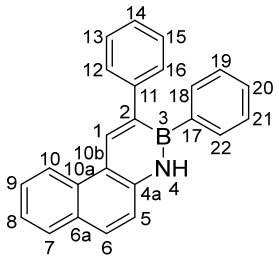




11b

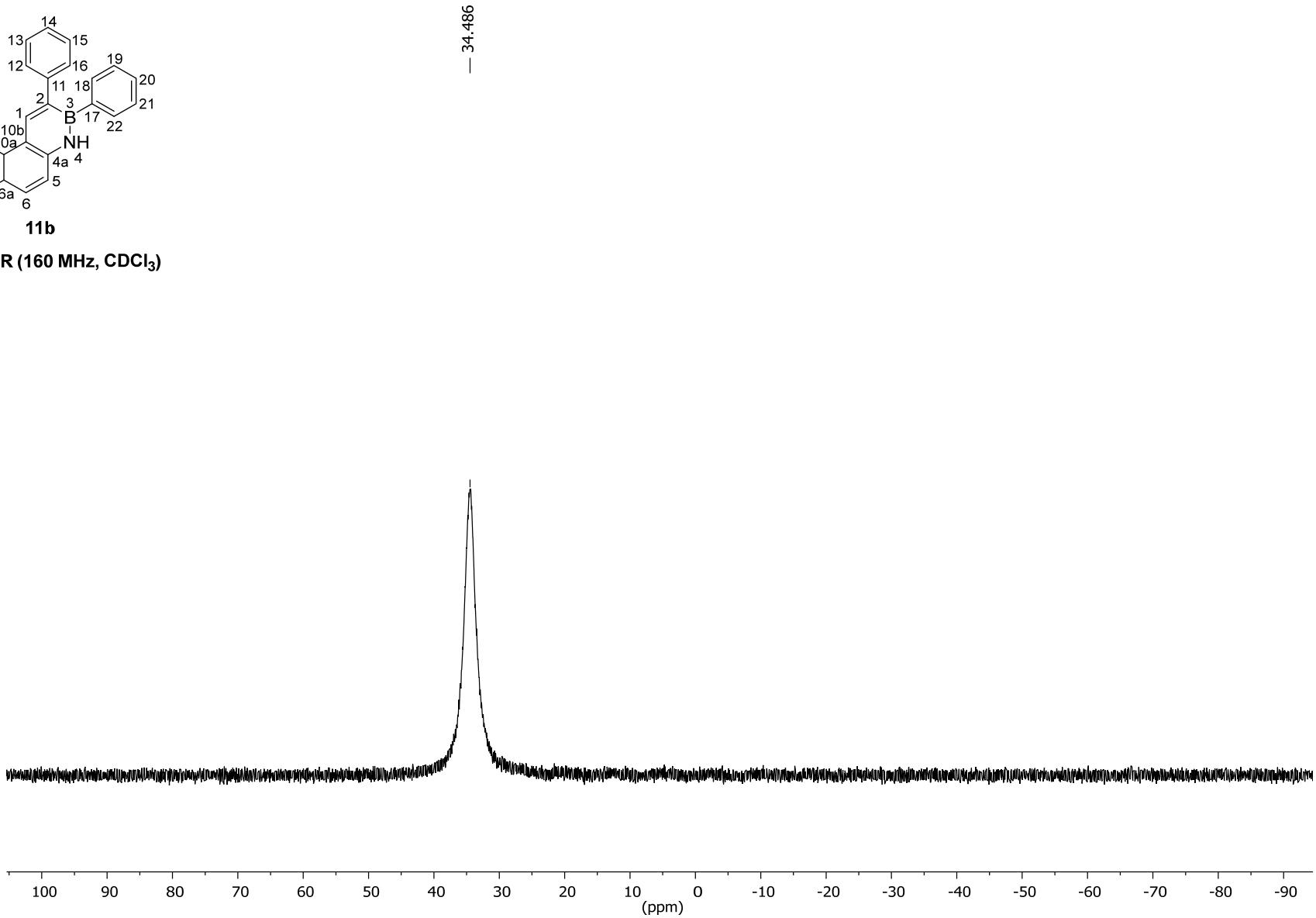
^{13}C-NMR (125 MHz, $CDCl_3$)

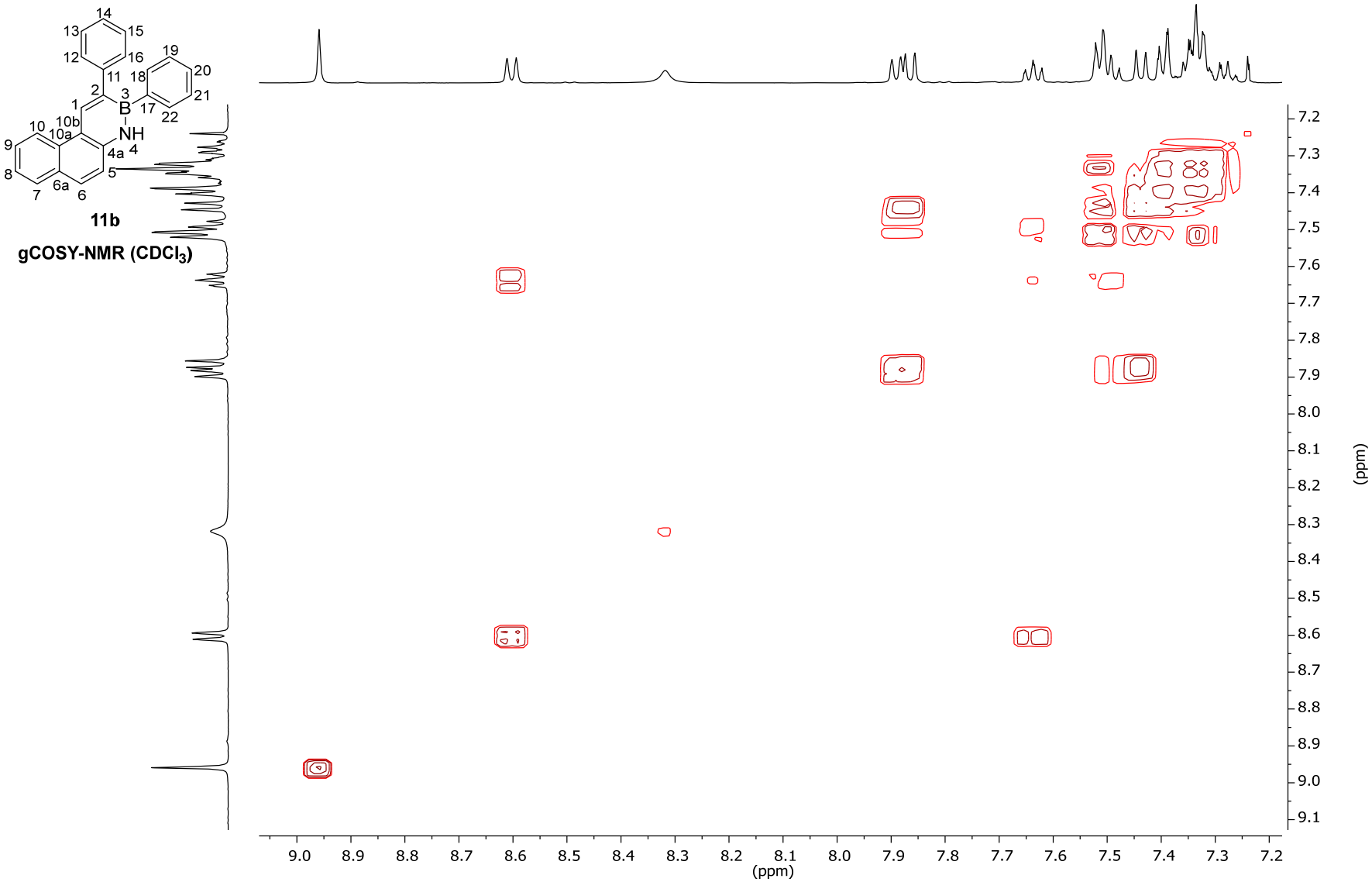


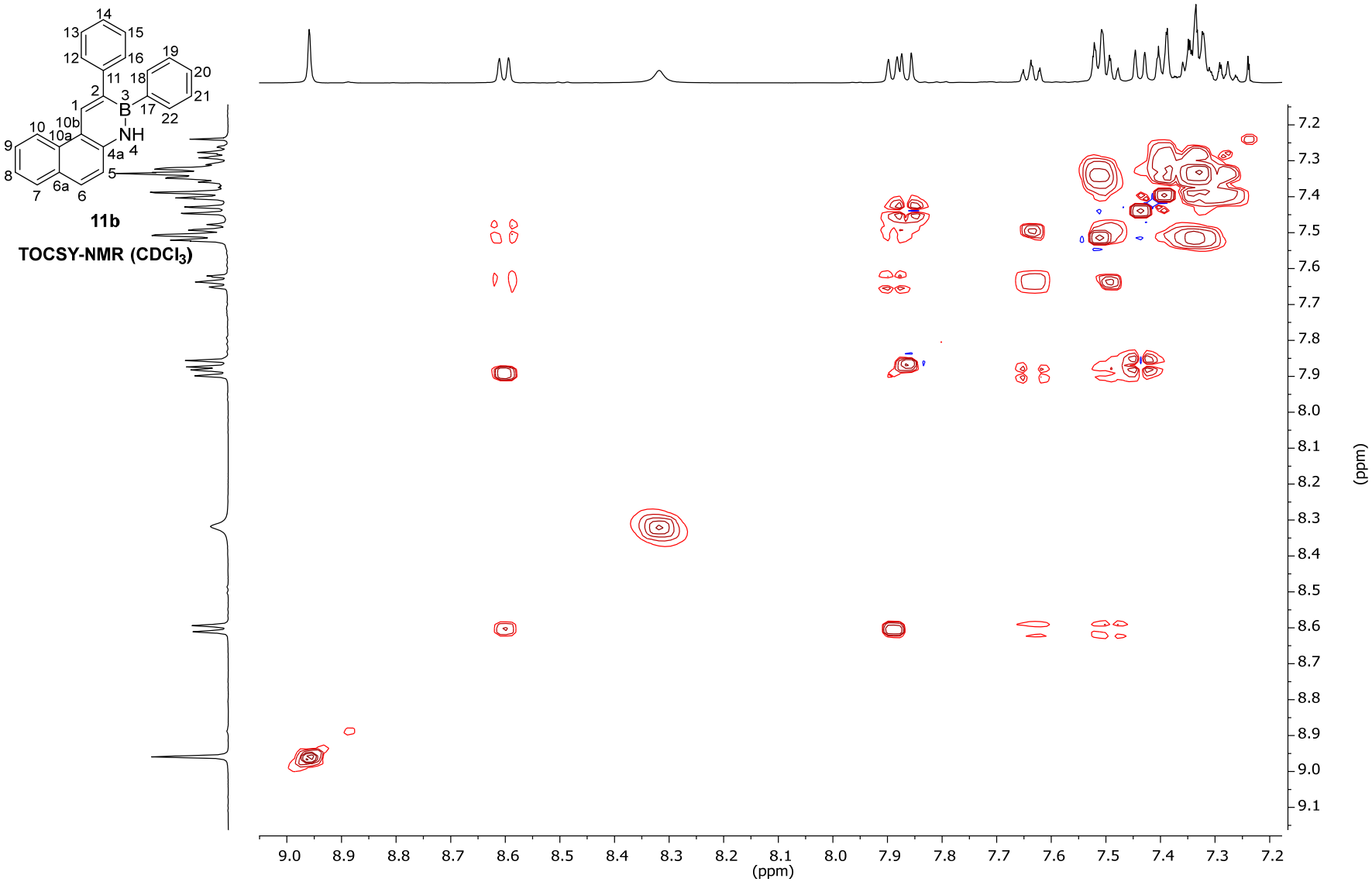


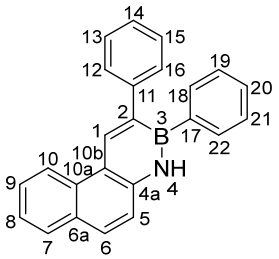
11b

^{11}B-NMR (160 MHz, $CDCl_3$)



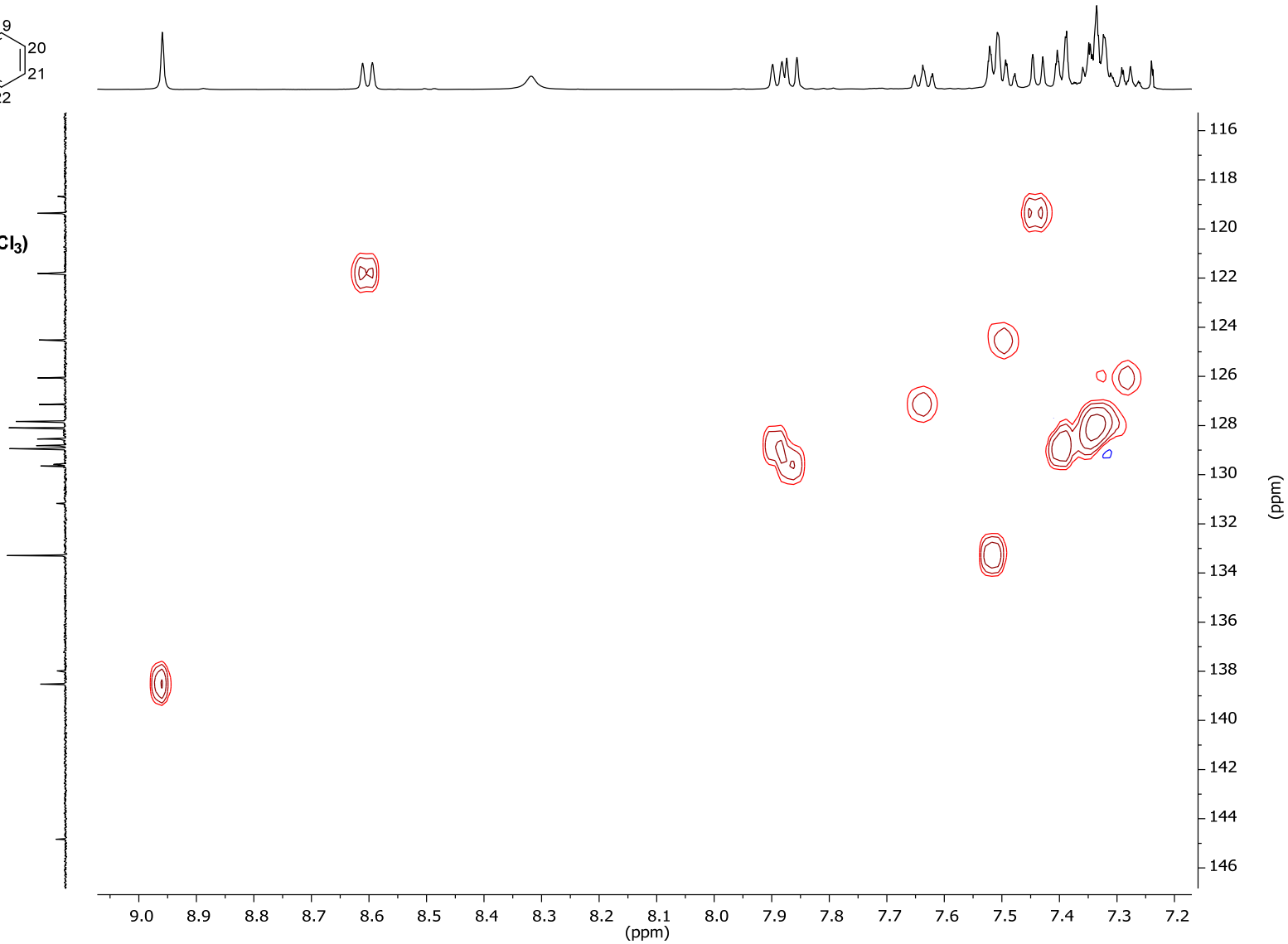

11b
gCOSY-NMR (CDCl3)
(ppm)
(ppm)

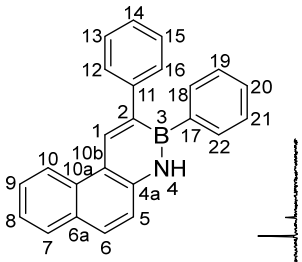

11b
TOCSY-NMR (CDCl3)
(ppm)
(ppm)



11b

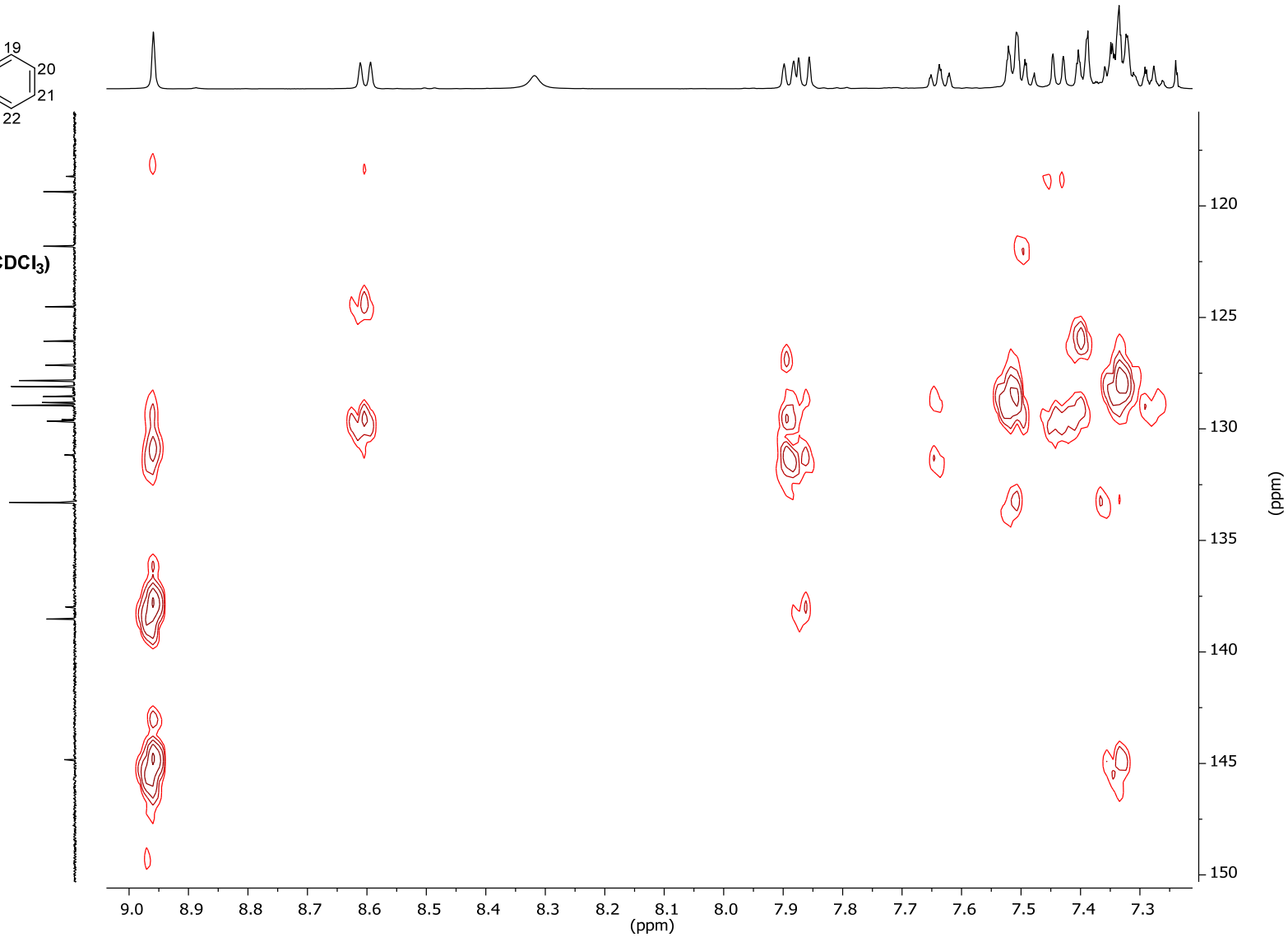
gHSQC-NMR ($CDCl_3$)

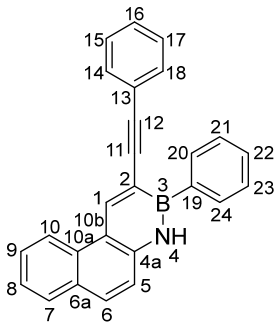




11b

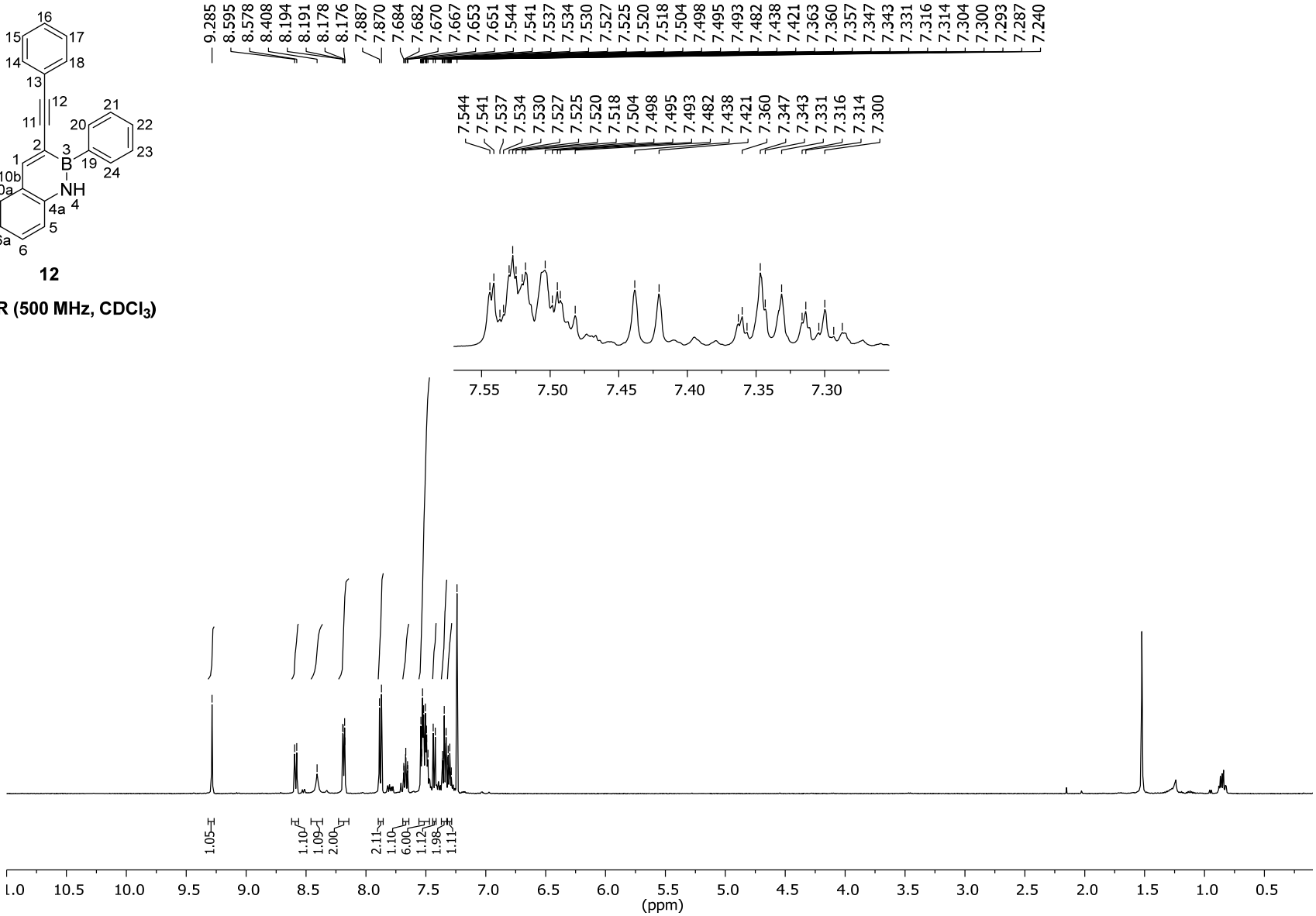
gHMBCAD-NMR ($CDCl_3$)

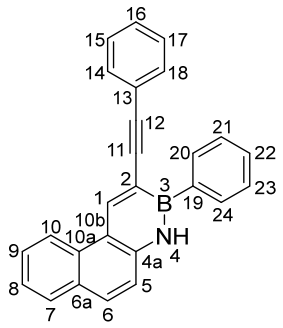




12

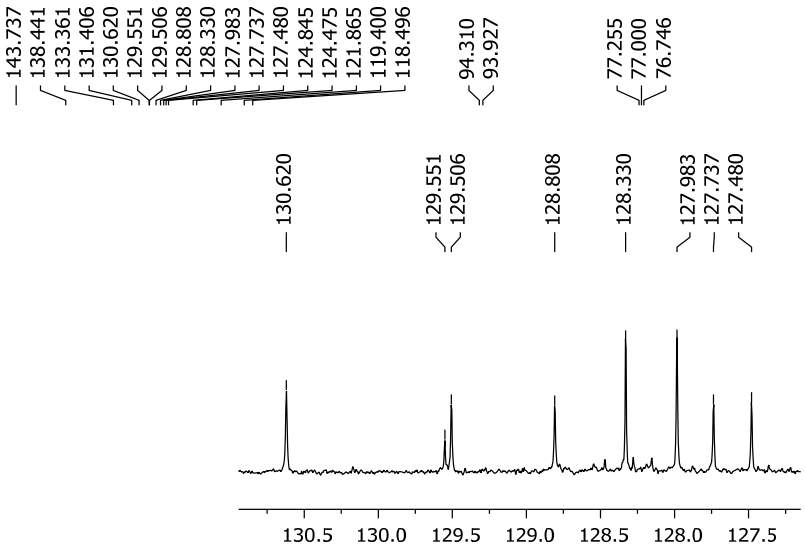
^{1}H-NMR (500 MHz, $CDCl_3$)

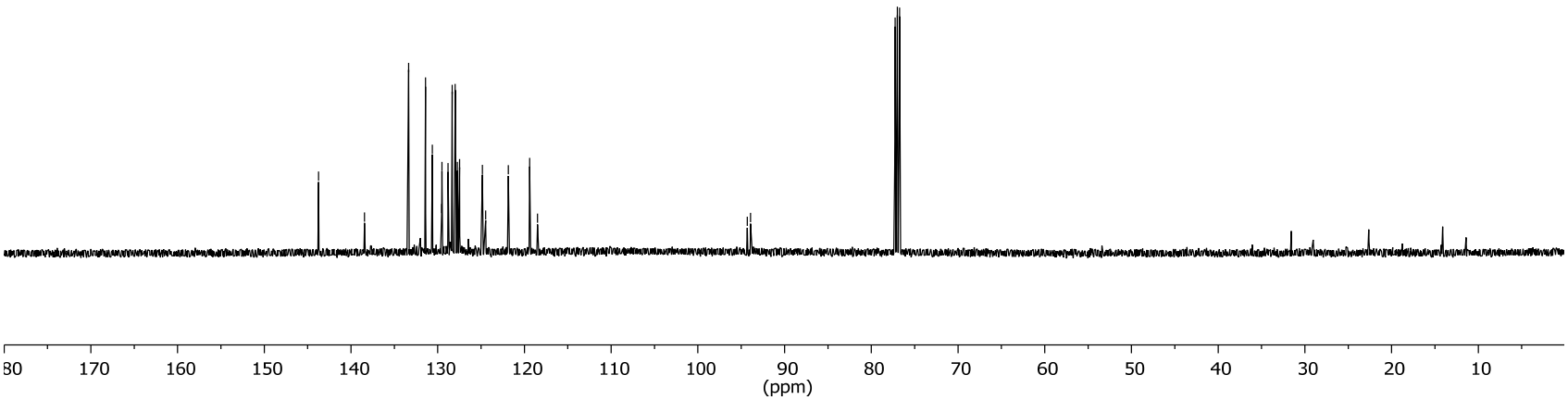


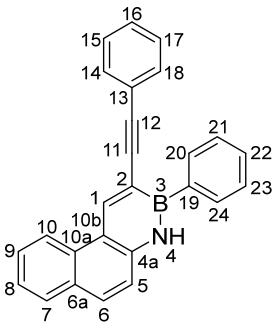


12

^{13}C-NMR (125 MHz, $CDCl_3$)

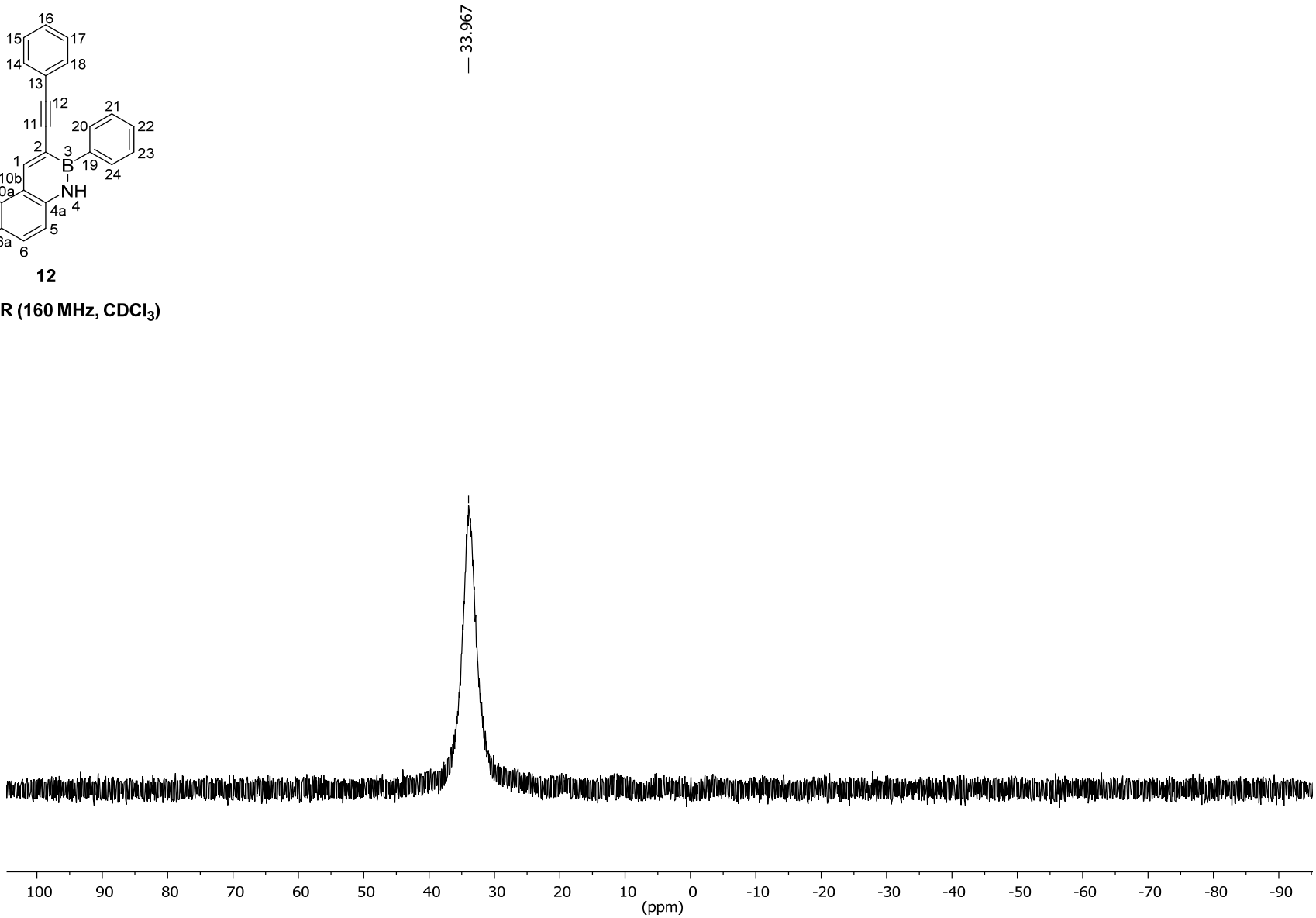


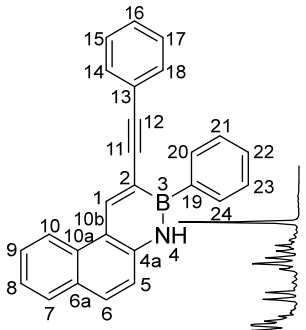




12

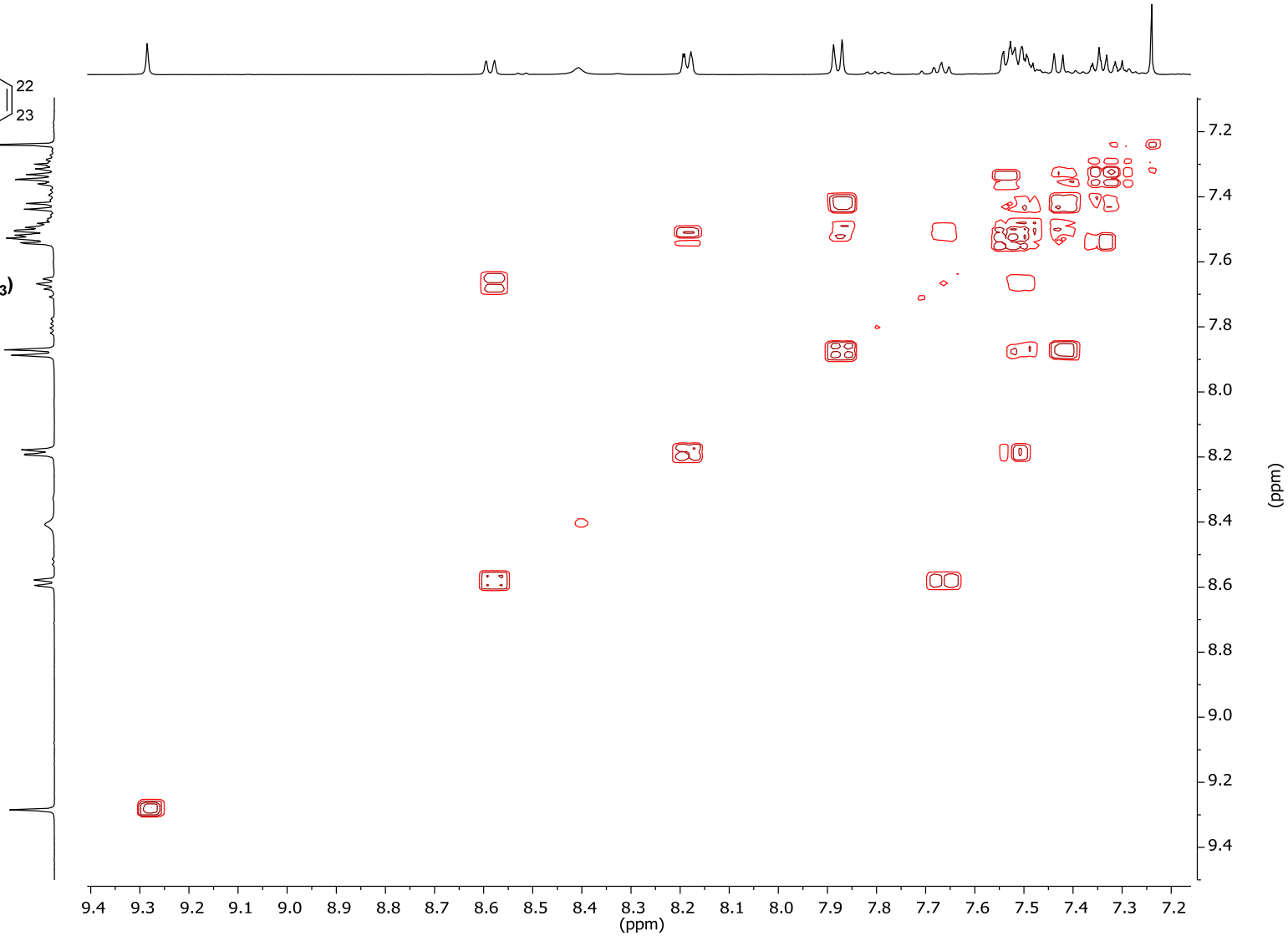
^{11}B-NMR (160 MHz, $CDCl_3$)

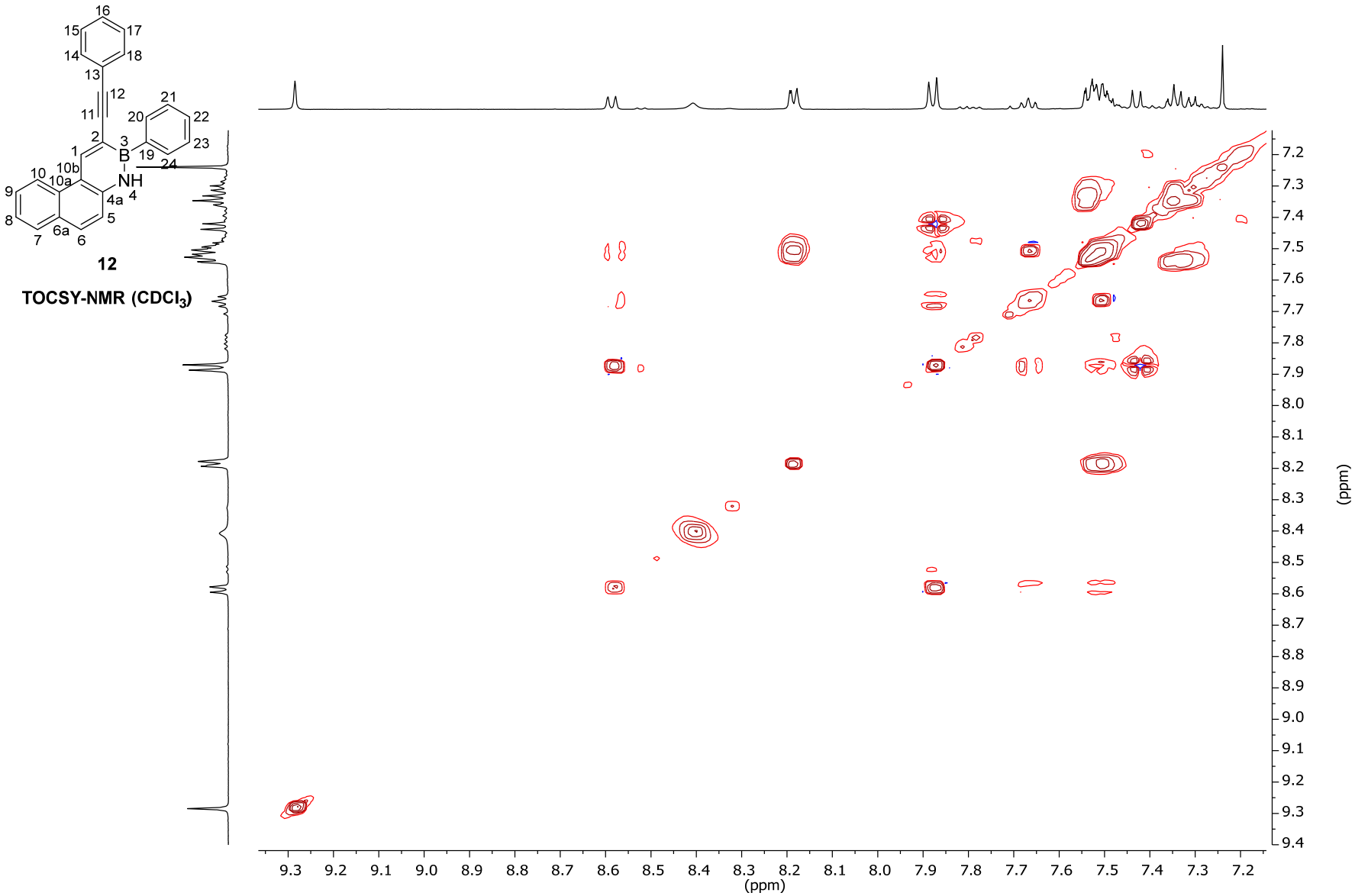


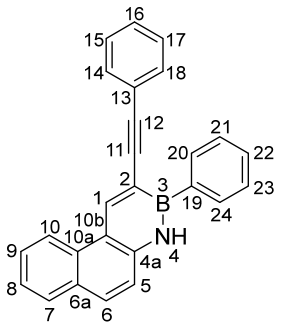


12

gCOSY-NMR ($CDCl_3$)

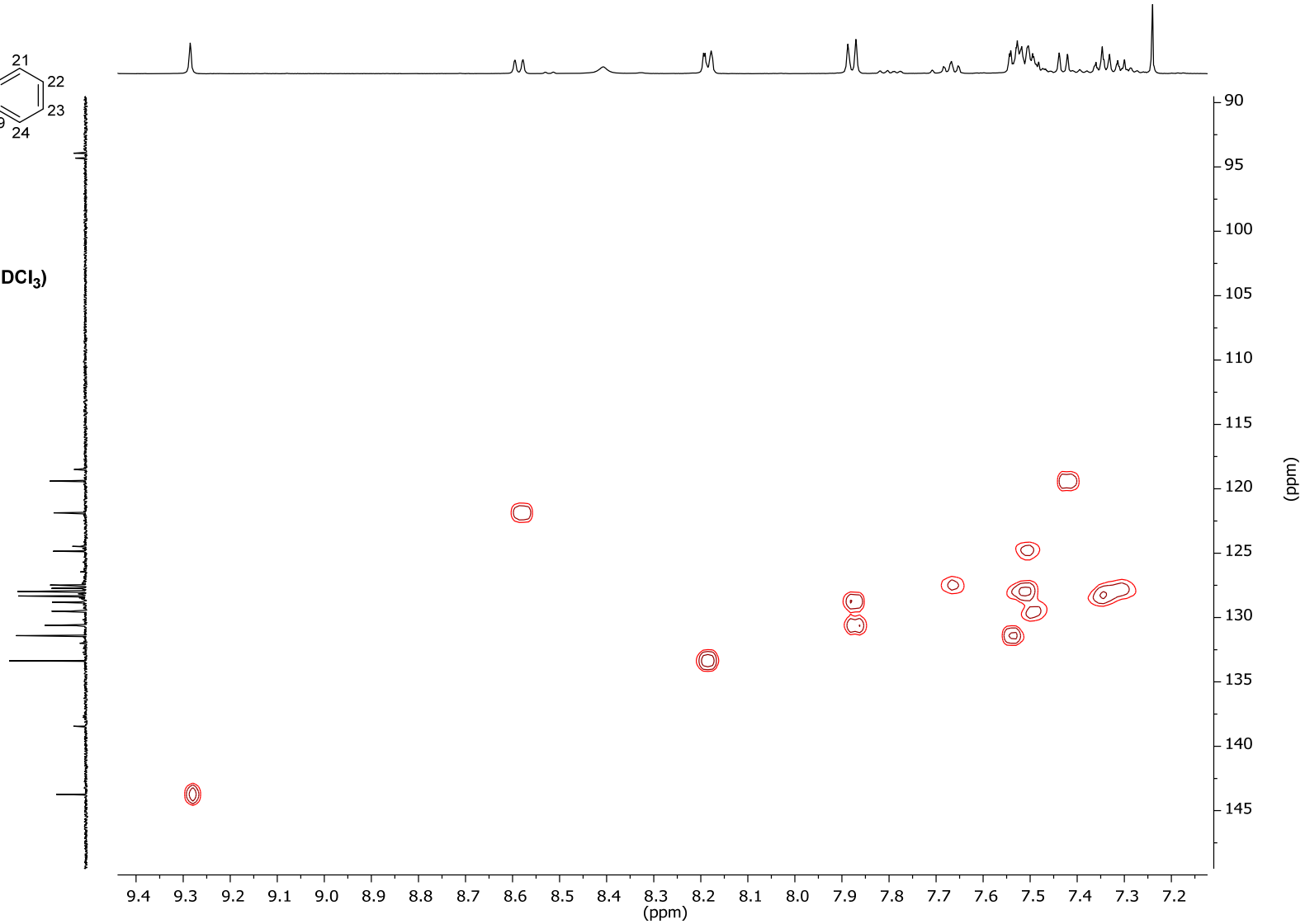


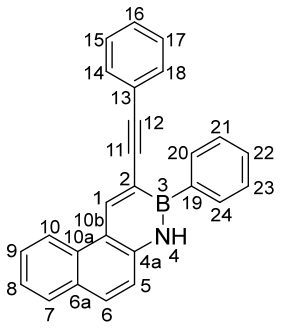

12
TOCSY-NMR (CDCl3)
(ppm)
(ppm)



12

gHSQC-NMR ($CDCl_3$)





12

gHMBCAD-NMR ($CDCl_3$)