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Expanding the BN-Embedded PAH Family: 4a-aza-12a-borachrysene

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Electronic Supplementary Information

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EXPERIMENTAL PROCEDURES AND DATA

General Methods. Reagents were acquired from commercial sources and used without further purification. When required, solvents were dried using an 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 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 using a Stuart Scientific SMP3 melting point apparatus (uncorrected). IR spectra were obtained using a Perkin-Elmer FTIR spectrum 2000 spectrophotometer. ^{1}H, ^{13}C{^{1}H} and ^{11}B{^{1}H} NMR spectra were recorded using 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 with respect to the residual protonated solvent used (δ_H = 7.24 ppm and δ_C = 77.0 ppm for $CDCl_3$). ^{11}B{^{1}H} NMR spectra were referenced externally 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) was performed using an Agilent 6210 time of-flight LC/MS. Absorption spectra were recorded using a Uvikon 941 (Kontron Instruments) UV-Vis spectrophotometer. Steady-state fluorescence measurements were carried out 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 (**2**) was prepared following reported procedures.[1]

***N*-(But-3-en-1-yl)-1-vinylnaphthalen-2-amine (3).** To an oven-dried Biotage microwave vial equipped with a stir bar were added Pd(μ-Cl) dimer (6.7 mg, 0.018 mmol, 0.5 mol%), JohnPhos (11.0 mg, 0.036 mmol, 1.0 mol%), and *t*-BuONa (497 mg, 5.01 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 mL) was added, followed by 2-bromo-1-vinylnaphthalene **2** (835 mg, 3.58 mmol, 1.0 equiv.) and 3-butenylamine (406 μL, 4.30 mmol, 1.2 equiv.). The reaction mixture was heated to 80 ºC for 24 h. The crude mixture was cooled to room temperature, diluted with Et_2O (10 mL) and filtered through a pad of Celite®. The solvent was removed under reduced pressure and the remaining oil was purified by flash column chromatography (2% EtOAc/Hexane) to give **3** (602 mg, 2.70 mmol, 76%) as a yellow oil. IR (NaCl) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3413 (NH), 3077, 3057, 2977, 2914, 2849, 1620, 1598, 1514, 1494, 1429, 1339, 1293, 996, 917, 808, 745. ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 7.91 (dd, *J* = 8.5, 1.1 Hz, 1H, H-8), 7.75 (dd, *J* = 8.1, 1.4 Hz, 1H, H-5), 7.74 (d, *J* = 9.0 Hz, 1H, H-4), 7.44 (ddd, *J* = 8.5, 6.8, 1.4 Hz, 1H, H-7), 7.27 (ddd, *J* = 8.1, 6.8, 1.1 Hz, 1H, H-6), 7.14 (d, *J* = 9.0 Hz, 1H, H-3), 6.94 (dd, J_{trans} = 18.1 Hz, J_{cis} = 11.4 Hz, 1H, H-9), 5.89 (ddt, J_{trans} = 17.1 Hz, J_{cis} = 10.2 Hz, *J* = 6.9 Hz, 1H, H-13), 5.85 (dd, J_{cis} = 11.4 Hz, J_{gem} = 2.3 Hz, 1H, H-10), 5.63 (dd, J_{trans} = 18.1 Hz, J_{gem} = 2.3 Hz, 1H, H-10), 5.20 (ap dq, J_{trans} = 17.1 Hz, *J* = 1.6 Hz, 1H, H-14), 5.20-5.17 (m, 1H, H-14), 4.57 (bs, 1H, N*H*), 3.37 (t, *J* = 6.7 Hz, 2H, H-11), 2.45 (ap qt, *J* = 6.8, 1.2 Hz, 2H, H-12). ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$) δ (ppm) 142.6 (C-

[1] K. Grudzien, K. Zukowska, M. Malinska, K. Wozniak and M. Barbasiewicz, *Chem. Eur. J.*, 2014, **20**, 2819–2828.

2), 135.7 (C-13), 132.6 (C-8a), 132.4 (C-9), 128.7 (C-4), 128.1 (C-5), 127.0 (C-4a), 126.2 (C-7), 123.2 (C-8), 121.7 (C-6), 121.5 (C-10), 117.1 (C-14), 115.9 (C-1), 113.8 (C-3), 43.3 (C-11), 34.0 (C-12). HRMS (APCI) calculated for $C_{16}H_{18}N$ $[M+H]^+$: 224.1434. Found $[M+H]^+$: 224.1427.

1-(But-3-en-1-yl)-2-vinyl-1-aza-2-boraphenanthrene (4). To an oven-dried Biotage microwave vial equipped with a stir bar was added potassium vinyltrifluoroborate (263 mg, 1.87 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. CMPE (3.8 mL) and toluene (3.8 mL) were added, followed by amine **3** (500 mg, 2.24 mmol, 1.2 equiv.), $SiCl_4$ (216 μL, 1.87 mmol, 1.0 equiv.) and Et_3N (391 μL, 2.81 mmol, 1.5 equiv.) under argon. The reaction mixture was heated to 80 ºC for 24 h. The crude mixture was cooled to room temperature, diluted with Et_2O (10 mL) and filtered through a pad of silica gel. The solvent was removed under reduced pressure and the remaining residue was purified by flash column chromatography (Hexane) to give **4** (485 mg, 1.87 mmol, 99%) as a white solid. M. p.: 69-71 ºC. IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 2946, 2930, 1641, 1547, 1434, 1414, 1212, 950, 903, 805, 748. ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.98 (d, *J* = 11.8 Hz, 1H, H-1), 8.56 (d, *J* = 8.5 Hz, 1H, H-10), 7.91 (d, *J* = 9.4 Hz, 1H, H-6), 7.87-7.85 (m, 1H, H-7), 7.76 (d, *J* = 9.4 Hz, 1H, H-5), 7.60 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H, H-9), 7.46 (ddd, *J* = 7.9, 6.9, 1.0 Hz, 1H, H-8), 7.23 (d, *J* = 11.8 Hz, 1H, H-2), 6.76 (dd, J_{trans} = 19.4 Hz, J_{cis} = 13.6 Hz, 1H, H-11), 6.26 (dd, J_{trans} = 19.4 Hz, J_{gem} = 3.7 Hz, 1H, H-12), 6.09 (dd, J_{cis} = 13.6 Hz, J_{gem} = 3.7 Hz, 1H, H-12), 5.93 (ddt, J_{trans} = 17.0 Hz, J_{cis} = 10.2 Hz, *J* = 6.8 Hz, 1H, H-15), 5.16 (ap dq, J_{trans} = 17.0 Hz, *J* = 1.6 Hz, 1H, H-16), 5.12-5.10 (m, 1H, H-16), 4.36-4.32 (m, 2H, H-13), 2.61-2.55 (m, 2H, H-14). ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$) δ (ppm) 139.3 (C-4a), 138.4 (C-1), 138.2 (C-11*), 134.7 (C-15), 132.8 (C-12), 131.6 (C-10a), 129.3 (C-6), 128.64 (C-2*), 128.58 (C-6a), 128.3 (C-7), 126.8 (C-9), 124.3 (C-8), 122.0 (C-10), 120.5 (C-10b), 116.9 (C-16), 115.7 (C-5), 46.8 (C-13), 34.9 (C-14). *Carbon not observed in ^{13}C{^{1}H}-NMR, assigned by gHSQC. ^{11}B{^{1}H}-NMR (160 MHz, $CDCl_3$) δ (ppm) 33.99. HRMS (APCI) calculated for $C_{18}H_{19}BN$ $[M+H]^+$: 260.1605. Found $[M+H]^+$: 260.1599.

3,4-Dihydro-4a-aza-12a-borachrysene (5). The ruthenium catalyst Grubbs Second Generation (42 mg, 0.05 mmol, 10 mol%) in CH_2Cl_2 (1 mL) was added to a solution of the diene **4** (130 mg, 0.50 mmol, 1.0 equiv.) in CH_2Cl_2 (4 mL) under argon. The reaction mixture was heated to reflux for 24 h. The crude mixture was cooled to room temperature, diluted with CH_2Cl_2 (10 mL) and filtered through a pad of silica gel. The solvent was removed under reduced pressure and the remaining residue was purified by flash column chromatography (2% EtOAc/Hexane) to give **5** (89 mg, 0.39 mmol, 77%) as a white solid. M. p.: 176-178 ºC. IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3005, 2925, 2879, 1611, 1544, 1472, 1297, 1207, 777, 745. ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.99 (d, *J* = 11.7 Hz, 1H, H-1), 8.55 (d, *J* = 8.6 Hz, 1H, H-14), 7.90 (d, *J* = 9.4 Hz, 1H, H-10), 7.86 (dd, *J* = 7.9, 1.3 Hz, 1H, H-11), 7.82 (d, *J* = 9.4 Hz, 1H, H-9), 7.60 (ddd, *J* = 8.6, 6.9, 1.3 Hz, 1H, H-13), 7.45 (ddd, *J* = 7.9, 6.9, 1.0 Hz, 1H, H-12), 7.02 (d, *J* = 11.7 Hz, 1H, H-2), 6.77 (dt, *J* = 11.7, 4.1 Hz, 1H, H-5), 6.41 (dt, *J* = 11.7, 1.5 Hz, 1H, H-4), 4.18 (t, *J* = 7.3 Hz, 2H, H-7), 2.60 (tdd, *J* = 7.3, 4.1, 1.5 Hz, 2H, H-6). ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$) δ (ppm) 141.7 (C-5), 140.2 (C-8a), 139.1 (C-1), 131.7 (C-14a), 130.4 (C-4*), 129.3 (C-10), 128.6 (C-2*), 128.40 (C-10a), 128.38 (C-11), 126.9 (C-13), 124.1 (C-12), 122.0 (C-14), 120.1 (C-14b), 114.8 (C-9), 43.1 (C-7), 28.4 (C-6). *Carbon not observed in ^{13}C{^{1}H}-NMR, assigned by gHSQC. ^{11}B{^{1}H}-NMR (160 MHz, $CDCl_3$) δ (ppm) 30.87. HRMS (APCI) calculated for $C_{16}H_{15}BN$ $[M+H]^+$: 232.1292. Found $[M+H]^+$: 232.1286.

4a-Aza-12a-borachrysene (1). To a solution of BN-chrysene derivative **5** (60 mg, 0.26 mmol, 1.0 equiv.) in decane (1.7 mL) and *m*-xylene (1.7 mL) was added Pd/C 30% (24 mg, 40% w/w). The reaction mixture was heated to 140 ºC for 12 h. The crude mixture was cooled to room temperature, diluted with dichloromethane (5 mL) and filtered through a pad of Celite®. The solvent was removed under reduced pressure and the remaining residue was purified by flash column chromatography (2% CH_2Cl_2/Hexane) to give **1** (41 mg, 0.18 mmol, 69%) as a white solid.

M. p.: 190-192 ºC. IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3027, 2923, 1612, 1549, 1508, 1453, 1394, 1290, 1208, 746. ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 9.05 (d, *J* = 11.8 Hz, 1H, H-1), 8.81 (d, *J* = 7.5 Hz, 1H, H-7), 8.71 (d, *J* = 8.5 Hz, 1H, H-14), 8.39 (d, *J* = 9.4 Hz, 1H, H-9), 8.03 (d, *J* = 9.4 Hz, 1H, H-10), 7.95 (dd, *J* = 7.9, 1.4 Hz, 1H, H-11), 7.80 (dd, *J* = 10.9, 6.2 Hz, 1H, H-5), 7.68 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H, H-13), 7.60 (d, *J* = 11.8 Hz, 1H, H-2), 7.56 (ddd, *J* = 7.9, 6.9, 1.0 Hz, 1H, H-12), 7.50 (dd, *J* = 10.9, 1.7 Hz, 1H, H-4), 6.87 (ddd, *J* = 7.5, 6.2, 1.7 Hz, 1H, H-6). ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$) δ (ppm) 139.5 (C-5), 135.6 (C-8a), 134.7 (C-1), 132.3 (C-4*), 131.7 (C-2*), 131.6 (C-14a), 130.2 (C-10a), 129.0 (C-10), 128.4 (2C, C-7, C-11), 127.1 (C-13), 125.4 (C-12), 123.1 (C-14), 122.4 (C-14b), 114.8 (C-9), 114.4 (C-6). *Carbon not observed in ^{13}C{^{1}H}-NMR, assigned by gHSQC. ^{11}B{^{1}H}-NMR (160 MHz, $CDCl_3$) δ (ppm) 28.78. HRMS (APCI) calculated for $C_{16}H_{13}BN$ $[M+H]^+$: 230.1136. Found $[M+H]^+$: 230.1130.

1-Bromo-4a-aza-12a-borachrysene (6): BN-chrysene **1** (137 mg, 0.60 mmol, 1.0 equiv.) was loaded into a Schlenk flask under argon. Anhydrous CH_2Cl_2 (6 mL, 0.1 M) was then added, and the resulting solution was cooled to 0 °C. A previously prepared bromine solution (0.2 M in CH_2Cl_2, 1.02 mmol, 1.7 equiv.) was added under argon at a rate of 1.1 mmol/h. After addition, the reaction mixture was slowly warmed to 25 ºC. The reaction was monitored by TLC, and when complete (usually after stirring for 1 h), the mixture was concentrated under reduced pressure. The remaining residue was purified by flash column chromatography (2% CH_2Cl_2/Hexane) to provide **6** as a white solid (141 mg, 0.46 mmol, 76%). M. p.: 221-223 ºC. ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 9.12 (d, *J* = 11.9 Hz, 1H, H-1), 8.77 (d, *J* = 7.2 Hz, 1H, H-7), 8.71 (d, *J* = 8.4 Hz, 1H, H-14), 8.33 (d, *J* = 9.4 Hz, 1H, H-9), 8.05 (d, *J* = 9.4 Hz, 1H, H-10), 8.00 (d, *J* = 7.2 Hz, 1H, H-5), 7.96 (dd, *J* = 7.9, 1.4 Hz, 1H, H-11), 7.80 (d, *J* = 11.9 Hz, 1H, H-2), 7.71 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H, H-13), 7.59 (ddd, *J* = 7.9, 6.9, 1.0 Hz, 1H, H-12), 6.70 (ap t, *J* = 7.2 Hz, 1H, H-6). ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$) δ (ppm) 140.2 (C-7), 136.3 (C-1), 135.1 (C-8a**), 131.6 (C-4*), 131.4 (C-14a**), 130.4 (C-10a**), 130.3 (C-2**), 129.6 (C-10), 128.5 (C-11), 128.0 (C-5), 127.4 (C-13), 125.8 (C-12), 123.1 (C-14), 122.6 (C-14b), 114.7 (C-9), 113.5 (C-6). *Carbon not observed in ^{13}C{^{1}H}-NMR, assigned by gHSQC. **Carbon not observed in ^{13}C{^{1}H}-NMR, assigned by gHMBC. ^{11}B{^{1}H}-NMR (160 MHz, $CDCl_3$) δ (ppm) 27.97. HRMS (APCI) calculated for $C_{16}H_{12}BBrN$ $[M+H]^+$: 308.0241. Found $[M+H]^+$: 308.0237.

1-Phenyl-4a-aza-12a-borachrysene (7). In a round bottom flask equipped with a stir bar the brominated BN-chrysene **6** (40.0 mg, 0.13 mmol, 1.0 equiv.) and phenylboronic acid (44.0 mg, 0.36 mmol, 2.8 equiv.) were dissolved in 0.52 mL toluene and 0.13 mL methanol and treated with a suspension of Na_2CO_3 (330.0 mg) in 1.3 mL of water. Then $Pd(PPh_3)_4$ (7.5 mg, 0.006 mmol, 5 mol%) was added and the mixture was heated to 70 ºC and stirred overnight. After addition of water (10 mL) and extraction with CH_2Cl_2 (3x10 mL), the combined organic layers were dried over Na_2SO_4, filtered and concentrated under vacuum. The crude organic product was purified by flash column chromatography on silica gel (2% CH_2Cl_2/Hexane) to give **7** as a white solid (36.0 mg, 0.12 mmol, 90%). M. p.: 210-212 ºC. ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 9.05 (d, *J* = 12.0 Hz, 1H, H-1), 8.84 (d, *J* = 7.4 Hz, 1H, H-7), 8.71 (d, *J* = 8.6 Hz, 1H, H-14), 8.43 (d, *J* = 9.4 Hz, 1H, H-9), 8.06 (d, *J* = 9.4 Hz, 1H, H-10), 7.97 (d, *J* = 7.8 Hz, 1H, H-11), 7.73 (d, *J* = 6.4 Hz, 1H, H-5), 7.70-7.66 (m, 2H, H-2, H-13), 7.61-7.54 (m, 3H, H-12, H-15, H-19), 7.48-7.36 (m, 2H, H-16, H-18), 7.38-7.32 (m, 1H, H-17), 6.97-6.92 (m, 1H, H-6). ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$) δ (ppm) 146.6 (C-4**), 144.6 (C-20), 137.1 (C-5), 134.9 (C-1), 131.5 (C-14a), 131.0 (C-2*), 130.2 (C-10a), 129.2 (C-15, C-19), 129.2 (C-10), 128.4 (C-11), 128.3 (C-16, C-18) 127.9 (C-7), 127.2 (C-13), 126.0 (C-17), 125.6 (C-12), 123.1 (C-14), 122.2 (C-14b), 115.1 (C-9), 113.8 (C-6). *Carbon not observed in ^{13}C-NMR, assigned by gHSQC. **Carbon not observed in ^{13}C{^{1}H}-NMR, assigned by gHMBC. ^{11}B{^{1}H}-NMR

(160 MHz, $CDCl_3$) δ (ppm) 28.33. HRMS (APCI) calculated for $C_{22}H_{17}BN$ $[M+H]^+$: 306.1449. Found $[M+H]^+$: 306.1446.

1-(Phenylethynyl)-4a-aza-12a-borachrysene (8). To an oven-dried Biotage microwave vial equipped with a stir bar was added $PdCl_2(MeCN)_2$ (0.8 mg, 0.003 mmol, 5 mol%), XPhos (4.3 mg, 0.009 mmol, 15 mol%), Cs_2CO_3 (49 mg, 0.15 mmol, 2.5 equiv.) and the brominated BN-chrysene **6** (20 mg, 0.06 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. MeCN (0.6 mL, 0.1 M) was added, and the resulting suspension was stirred at room temperature for 30 min. Then, the corresponding alkyne (9 µL, 0.08 mmol, 1.3 equiv.) was injected, and the mixture was heated to 100 ºC until full consumption of starting material was observed by TLC (3 hours). Afterwards, the reaction was cooled to room temperature, diluted with CH_2Cl_2 and water. The layers were separated and the aqueous layer was extracted twice with CH_2Cl_2. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (5% CH_2Cl_2/Hexane) to give **8** as a yellow solid (19 mg, 0.06 mmol, 94%). M. p.: 169-171 ºC. ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 9.11 (d, *J* = 11.8 Hz, 1H, H-1), 8.78 (d, *J* = 7.2 Hz, 1H, H-7), 8.72 (d, *J* = 7.6 Hz, 1H, H-14), 8.34 (d, *J* = 9.4 Hz, 1H, H-9), 8.03 (d, *J* = 9.4 Hz, 1H, H-10), 7.98-7.90 (m, 3H, H-2, H-5, H-11), 7.70 (ap t, *J* = 7.6 Hz, 1H, H-13), 7.63 (d, *J* = 7.4 Hz, 2H, H-18, H-22), 7.58 (ap t, *J* = 7.6 Hz, 1H, H-12), 7.38 (t, *J* = 7.4 Hz, 2H, H-19, H-21), 7.32 (t, *J* = 7.4 Hz, 1H, H-20), 6.86 (t, *J* = 7.2 Hz, 1H, H-6). ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$) δ (ppm) 142.0 (C-5), 135.5 (C-1), 135.2 (C-8a), 131.6 (C-18, C-22), 131.5 (C-14a), 130.3 (C-10a), 130.0 (C-2*), 129.3 (C-10), 128.7 (C-7), 128.5 (C-11), 128.3 (C-19, C-21) 127.7 (C-20), 127.3 (C-13), 125.7 (C-12), 125.4 (C-4**), 124.5 (C-17), 123.1 (C-14), 122.7 (C-14b), 114.6 (C-9), 113.9 (C-6), 95.0 (C-16), 92.1 (C-15). *Carbon not observed in ^{13}C{^{1}H}-NMR, assigned by gHSQC. **Carbon not observed in ^{13}C{^{1}H}-NMR, assigned by gHMBC. ^{11}B{^{1}H}-NMR (160 MHz, $CDCl_3$) δ (ppm) 29.07. HRMS (APCI) calculated for $C_{24}H_{17}BN$ $[M+H]^+$: 330.1449. Found $[M+H]^+$: 330.1445.

1-(*N*-morpholinyl)-4a-aza-12a-borachrysene (9). To an oven-dried Biotage microwave vial equipped with a stir bar were added $[PdCl(allyl)]_2$ (1.2 mg, 0.003 mmol, 2.5 mol%), JohnPhos (1.9 mg, 0.006 mmol, 5.0 mol%), and *t*-BuONa (18 mg, 0.18 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 (0.32 mL) was added, followed by brominated BN-chrysene **6** (40.0 mg, 0.13 mmol, 1.0 equiv.) and morpholine (14 µL, 0.16 mmol, 1.2 eq.). The resulting mixture was heated to 80 ºC and stirred until full consumption of **6** was observed by TLC (24 h). The reaction mixture was cooled to room temperature, diluted with Et_2O (5 mL), and filtered over Celite. The solvent was removed in vacuo, and the resulting product was purified by flash column chromatography on silica gel (hexanes/EtOAc 9:1). Compound **9** was obtained as green solid (38 mg, 0.12 mmol, 93%). M. p.: 168-170 ºC. ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 9.01 (d, *J* = 12.0 Hz, 1H, H-1), 8.68 (d, *J* = 8.5 Hz, 1H, H-14), 8.37 (d, *J* = 7.3 Hz, 1H, H-7), 8.32 (d, *J* = 9.4 Hz, 1H, H-9), 8.01 (d, *J* = 9.4 Hz, 1H, H-10), 7.95-7.92 (m, 1H, H-11), 7.68 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H, H-13), 7.62 (d, *J* = 12.0 Hz, 1H, H-2) 7.55 (ddd, *J* = 9.6, 6.9, 1.8 Hz, 1H, H-12), 6.86 (d, *J* = 7.3 Hz, 1H, H-5), 6.69 (ap t, *J* = 7.3 Hz, 1H, H-6), 4.03-3.94 (m, 4H, H-17, H-19), 3.26-3.21 (m, 4H, H-16, H-20). ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$) δ (ppm) 158.7 (C-4**), 136.2 (C-8a), 134.5 (C-1), 131.5 (C-14a), 130.0 (C-10a), 139.1 (C-10), 129.0 (C-2*), 128.4 (C-11), 127.2 (C-13), 125.4 (C-12) 122.9 (C-14), 122.3 (C-7), 121.7 (C-14b), 118.1 (C-5), 115.5 (C-9), 113.4 (C-6), 67.3 (C-17, C-19), 53.3 (C-16, C-20). *Carbon not observed in ^{13}C{^{1}H}-NMR, assigned by gHSQC. **Carbon not observed in ^{13}C{^{1}H}-NMR, assigned by gHMBC. ^{11}B{^{1}H}-NMR (160 MHz, $CDCl_3$) δ (ppm) 28.24. HRMS (APCI) calculated for $C_{20}H_{20}BN_2O$ $[M+H]^+$: 315.1663. Found $[M+H]^+$: 315.1661.

General procedure for the reaction of 4a-aza-12a-borachrysene (1) with organolithium compounds and carbonyl derivatives: BN-chrysene **1** (40 mg, 0.18 mmol, 1.0 equiv.) was loaded in a Schlenk flask under argon. THF (2.0 mL) was added to the above flask and the resulting solution was then cooled to -50 ºC. At this temperature, the solution was treated with the corresponding organolithium compound (0.36 mmol, 2.0 equiv.) and the mixture was stirred for 1 h before addition of the corresponding carbonyl compound (20.0 equiv.). The reaction mixture was stirred at low temperature for further 1 h, and then it was allowed to warm to room temperature, quenched with aqueous NH_4Cl (5 mL), and 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 crude product was purified by flash column chromatography (2% CH_2Cl_2/Hexane).

3-(2,2-Dimethylpentan-3-yl)-4a-aza-12a-borachrysene (10). Prepared following the general procedure outlined above using BN-chrysene **1** (40 mg, 0.18 mmol), *t*-BuLi (206 µL, 0.35 mmol, 1.7 M in pentane) and propanal (260 µL, 3.6 mmol). Purification by flash column chromatography provided compound **10** (42 mg, 0.13 mmol, 71%) as a white solid. M. p.: 128-130 ºC. ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 9.04 (d, *J* = 11.8 Hz, 1H, H-1), 8.72 (d, *J* = 8.5 Hz, 1H, H-14), 8.54 (s, 1H, H-7), 8.41 (d, *J* = 9.4 Hz, 1H, H-9), 8.03 (d, *J* = 9.4 Hz, 1H, H-10), 7.95 (dd, *J* = 8.0, 1.1 Hz, 1H, H-11), 7.73 (d, *J* = 11.2 Hz, 1H, H-5), 7.68 (ddd, *J* = 8.5, 6.9, 1.1 Hz, 1H, H-13), 7.59 (d, *J* = 11.8 Hz, 1H, H-2), 7.55 (ddd, *J* = 8.0, 6.9, 1.0 Hz, 1H, H-12), 7.42 (m, 1H, H-4), 2.30 (dd, *J* = 12.0, 3.2 Hz, 1H, H-15), 1.98-1.72 (m, 2H, H-16), 0.96 (s, 9H, H-19, H-20, H-21), 0.76 (t, *J* = 7.3 Hz, 3H, H-17). ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$) δ (ppm) 135.6 (C-8a), 134.3 (C-1), 131.5 (C-14a), 131.1 (C-2*), 130.9 (C-4*), 130.0 (C-10a), 128.8 (C-10), 128.4 (C-11), 128.4 (C-7), 128.0 (C-6), 127.1 (C-13), 125.3 (C-12), 123.1 (C-14), 122.3 (C-14b), 115.0 (C-9), 57.7 (C-15), 34.3 (C-18), 28.6 (3 CH_3, C-19, C-20, C-21), 21.8 (C-16), 13.4 (C-17). *Carbon not observed in ^{13}C{^{1}H}-NMR, assigned by gHSQC. C-5 not observed due to steric hindrance. ^{11}B{^{1}H}-NMR (160 MHz, $CDCl_3$) δ (ppm) 27.69. HRMS (APCI) calculated for $C_{23}H_{27}BN$ $[M+H]^+$: 328.2231. Found $[M+H]^+$: 328.2227.

3-(Heptan-3-yl)-4a-aza-12a-borachrysene (11). Prepared following the general procedure outlined above using BN-chrysene **1** (40 mg, 0.18 mmol), *n*-BuLi (219 µL, 0.35 mmol, 1.6 M in hexanes) and propanal (260 µL, 3.6 mmol). Purification by flash column chromatography provided compound **11** (36 mg, 0.11 mmol, 61%) as a yellow solid. M. p.: 61-63 ºC. ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 9.04 (d, *J* = 11.8 Hz, 1H, H-1), 8.72 (d, *J* = 8.5 Hz, 1H, H-14), 8.53 (s, 1H, H-7), 8.43 (d, *J* = 9.4 Hz, 1H, H-9), 8.03 (d, *J* = 9.4 Hz, 1H, H-10), 7.95 (dd, *J* = 8.0, 1.1 Hz, 1H, H-11), 7.73-7.65 (m, 2H, H-5, H-13), 7.58 (d, *J* = 11.8 Hz, 1H, H-2), 7.56-7.53 (m, 1H, H-12), 7.46 (d, *J* = 8.5 Hz, 1H, H-4), 2.51-2.43 (m, 1H, H-15), 1.82-1.56 (m, 4H, $2CH_2$), 1.35-1.09 (m, 4H, $2CH_2$), 0.86-0.78 (m, 6H, $2CH_3$). ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$) δ (ppm) 139.8 (C-5), 135.6 (C-8a), 134.3 (C-1), 132.1 (C-4*), 131.7 (C-14a), 131.3 (C-2*), 130.6 (C-6), 130.0 (C-10a), 128.8 (C-10), 128.4 (C-11), 127.1 (C-13), 126.7 (C-7), 125.3 (C-12), 123.1 (C-14), 122.3 (C-14b), 115.0 (C-9), 46.8 (C-15), 35.9 (CH_2), 30.0 (CH_2), 29.3 (CH_2), 22.8 (CH_2), 14.1 (CH_3), 12.4 (CH_3). *Carbon not observed in ^{13}C{^{1}H}-NMR, assigned by gHSQC. ^{11}B{^{1}H}-NMR (160 MHz, $CDCl_3$) δ (ppm) 27.76. HRMS (APCI) calculated for $C_{23}H_{26}BN$ $[M]^+$: 327.2158. Found $[M]^+$: 327.2172.

3-(*sec*-Butyl)- 4a-aza-12a-borachrysene (12). Prepared following the general procedure outlined above using BN-chrysene **1** (40 mg, 0.18 mmol), MeLi (219 µL, 0.35 mmol, 1.6 M in hexanes) and propanal (260 µL, 3.6 mmol). Purification by flash column chromatography provided compound **12** (26 mg, 0.09 mmol, 52%) as a light-yellow solid. M. p.: 121-123 ºC. ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 9.04 (d, *J* = 11.8 Hz, 1H, H-1), 8.72 (d, *J* = 8.6 Hz, 1H, H-14), 8.60 (s, 1H, H-7), 8.43 (d, *J* = 9.4 Hz, 1H, H-9), 8.02 (d, *J* = 9.4 Hz, 1H, H-10), 7.95 (d, *J* = 7.9 Hz, 1H, H-

11), 7.75 (d, *J* = 11.2 Hz, 1H, H-5), 7.70-7.64 (m, 1H, H-13), 7.59-7,54 (m, 2H, H-2, H-12), 7.48 (d, *J* = 11.2 Hz, 1H, H-4), 2.76-2.65 (m, 1H, H-15), 1.77-1.65 (m, 2H, H-16), 1.36 (d, *J* = 6.5 Hz, 3H, H-18), 0.89 (t, *J* = 7.4 Hz, 3H, H-17). $^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$) δ (ppm) 140.0 (C-5), 135.7 (C-8a), 134.3 (C-1), 132.3 (C-6), 132.1 (C-4*), 131.7 (C-14a), 131.2 (C-2*), 130.0 (C-10a), 128.8 (C-10), 128.4 (C-11), 127.0 (C-13), 125.8 (C-7), 125.3 (C-12), 123.1 (C-14), 122.3 (C-14b), 115.0 (C-9), 40.7 (C-15), 30.7 (C-16), 21.9 (C-18), 12.4 (C-17). *Carbon not observed in $^{13}C\{^1H\}$-NMR, assigned by gHSQC. $^{11}B\{^1H\}$-NMR (160 MHz, $CDCl_3$) δ (ppm) 27.85. HRMS (APCI) calculated for $C_{20}H_{20}BN$ $[M+H]^+$: 286.1762. Found $[M+H]^+$: 286.1756.

3-(1-Phenylpentyl)-4a-aza-12a-borachrysene (13). Prepared following the general procedure outlined above using BN-chrysene **1** (40 mg, 0.18 mmol), *n*-BuLi (219 µL, 0.35 mmol, 1.6 M in hexanes) and benzaldehyde (366 µL, 3.6 mmol). Purification by flash column chromatography provided compound **13** (36 mg, 0.09 mmol, 53%) as a white solid. M. p.: 77-79 ºC. ^1H-NMR (500 MHz, $CDCl_3$) δ (ppm) 9.04 (d, *J* = 11.8 Hz, 1H, H-1), 8.74-8.66 (m, 2H, H-7, H-14), 8.38 (d, *J* = 9.4 Hz, 1H, H-9), 8.03 (d, *J* = 9.4 Hz, 1H, H-10), 7.97-7.94 (m, 1H, H-11), 7.74 (dd, *J* = 11.2, 1.3 Hz, 1H, H-5), 7.69-7.66 (m, 1H, H-13), 7.59-7.54 (m, 2H, H-2, H-12), 7.45 (d, *J* = 11.2 Hz, 1H, H-4), 7.35 (m, 4H, H-21, H-22, H-24, H-25), 7.24-7.22 (m, 1H, H-23), 4.01 (t, *J* = 7.7 Hz, 1H, H-15), 2.17 (ap q, *J* = 7.7 Hz, 2H, H-16), 1.49-1.30 (m, 4H, H-17, H-18), 0.91 (t, *J* = 7.2 Hz, 3H, H-19). $^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$) δ (ppm) 144.9 (C-20), 141.0 (C-5), 135.7 (C-8a), 134.6 (C-1), 132.2 (C-4*), 131.7 (C-14a), 131.2 (C-2*), 130.6 (C-6), 130.0 (C-10a), 128.9 (C-10), 128.5 (C-22, C-24) 128.4 (C-11), 128.0 (C-21, C-25), 127.1 (C-13), 126.5 (C-7), 126.2 (C-23), 125.3 (C-12), 123.0 (C-14), 122.4 (C-14b), 114.9 (C-9), 50.1 (C-15), 35.0 (C-16), 30.3 (C-17), 22.75 (C-18), 14.05 (C-19). *Carbon not observed in $^{13}C\{^1H\}$-NMR, assigned by gHSQC. $^{11}B\{^1H\}$-NMR (160 MHz, $CDCl_3$) δ (ppm) 27.91. HRMS (APCI) calculated for $C_{27}H_{27}BN$ $[M+H]^+$: 376.2231. Found $[M+H]^+$: 376.2228.

3-[2,2-Dimethyl-1-(thiophen-2-yl)propyl]-4a-aza-12a-borachrysene (14). Prepared following the general procedure outlined above using BN-chrysene **1** (40 mg, 0.18 mmol), *t*-BuLi (206 µL, 0.35 mmol, 1.7 M in pentane) and 2-thiophenecarboxaldehyde (82 µL, 0.87 mmol). Purification by flash column chromatography provided compound **14** (28 mg, 0.07 mmol, 47%) as a yellow oil. ^1H-NMR (500 MHz, $CDCl_3$) δ (ppm) 9.02 (d, *J* = 11.8 Hz, 1H, H-1), 8.82 (s, 1H, H-7), 8.70 (d, *J* = 8.5 Hz, 1H, H-14), 8.40 (d, *J* = 9.4 Hz, 1H, H-9), 8.04 (d, *J* = 9.4 Hz, 1H, H-10), 8.01 (dd, *J* = 11.2, 1.4 Hz, 1H, H-5), 7.95 (dd, *J* = 8.0, 1.1 Hz, 1H, H-11), 7.67 (ddd, *J* = 8.5, 6.9, 1.1 Hz, 1H, H-13), 7.57-7.54 (m, 2H, H-2, H-12), 7.42 (d, *J* = 11.2 Hz, 1H, H-4), 7.18-7.17 (m, 1H, H-18), 7.06 (dd, *J* = 3.5, 1.1 Hz, 1H, H-20), 6.95 (dd, *J* = 5.1, 3.5 Hz, 1H, H-19), 4.18 (s, 1H, H-15), 1.11 (s, 9H, H-22. H-23, H-24). $^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$) δ (ppm) 145.5 (C-16), 142.5 (C-5), 135.6 (C-8a), 134.6 (C-1), 131.7 (C-14b), 131.2 (C-2*), 131.1 (C4*), 130.1 (C-10a), 129.0 (C-10), 128.6 (C-7), 128.4 (C-11), 127.7 (C-6), 127.1 (C-13), 126.3 (C-18), 126.2 (C-17), 125.4 (C-12), 123.5 (C-19), 123.1 (C-14), 122.4 (C-14b), 114,9 (C-9), 58.1 (C-15), 35.7 (C-21), 28.9 (3 CH_3, C-22, C-23, C-24). *Carbon not observed in $^{13}C\{^1H\}$-NMR, assigned by gHSQC. $^{11}B\{^1H\}$-NMR (160 MHz, $CDCl_3$) δ (ppm) 27.65. HRMS (APCI) calculated for $C_{25}H_{25}BNS$ $[M+H]^+$: 382.1790. Found $[M+H]^+$: 382.1795.

X-RAY CRYSTALLOGRAPHIC DATA FOR 1

Colourless crystals of **1** were obtained from a chloroform/dichloromethane solution. The crystals were covered with a layer of a viscous perfluoropolyether (FomblinY). A suitable crystal was selected with the aid of a microscope, 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 are presented in Table S1. The structure was solved, using the WINGX package,[2] by intrinsic phasing methods (SHELXT),[3] and refined by least-squares against F^2 (SHELXL-2014/7).[3] All non-hydrogen atoms were anisotropically refined, whereas hydrogen atoms were included, positioned geometrically and refined by using a riding model.

Table S1. Experimental data for the X-ray diffraction study on **1**.

	1
CCDC[a] code	1969346
Formula	$C_{16}H_{12}BN$
M_r	229.08
T [K]	200(2)
λ [Å]	0.71073
crystal system	Monoclinic
space group	$P2_1/c$
a [Å]; α [º]	9.493(4)
b [Å]; β [º]	8.936(1); 96.47(5)
c [Å]; γ [º]	13.533(10)
V [Å^3]	1141(1)
Z	4
ρ_{calcd} [g cm^{-3}]	1.334
$\mu_{MoK\alpha}$ [mm^{-1}]	0.076
F(000)	480
crystal size [mm^3]	0.44×0.25×0.08
θ range (deg)	3.03 to 27.50
index ranges	-12 to 12, -11 to 10, -17 to 17
Reflections collected	22885
Unique data	2618 [R_{int} = 0.088]
obsd data [I>2σ(I)]	1467
Goodness-of-fit on F^2	1.027
final R^a indices [I>2σ(I)]	$R1$ = 0.065, w$R2$ = 0.153
R^b indices (all data)	$R1$ = 0.131, w$R2$ = 0.192
largest diff. peak/hole[e.Å^{-3}]	0.281/-0.198

[a]Cambridge Crystallographic Data Centre. [b]$R1 = \Sigma||F_0|-|F_c|| / [\Sigma|F_0|]$, w$R2 = \{[\Sigma w(F_0^2-F_c^2)^2] / [\Sigma w(F_0^2)^2]\}^{1/2}$

[2] L. J. Farrugia, *J. Appl. Crystallogr.*, 2012, **45**, 849–854.
[3] G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2015, **71**, 3–8.

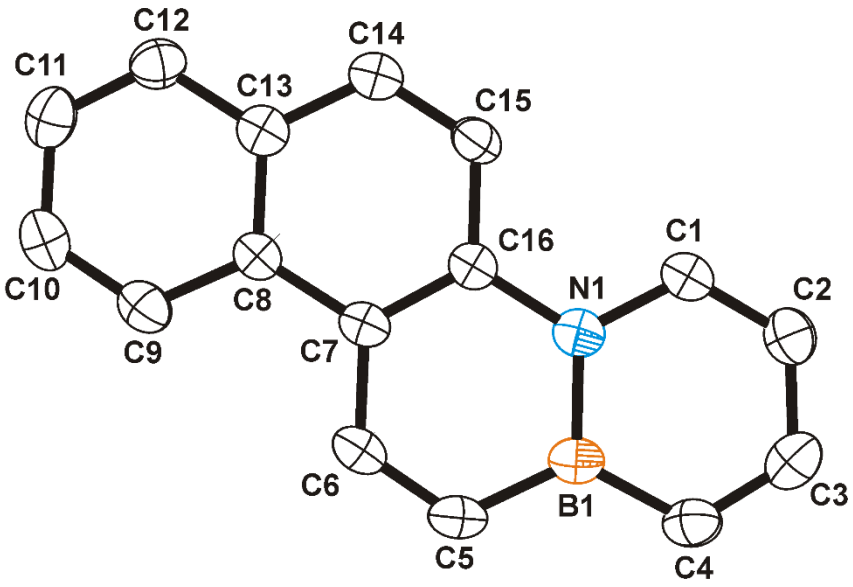

Figure S1. X-ray structure and numbering scheme for **1**. Thermal ellipsoids are drawn at the 50% probability level.

PHOTOPHYSICAL DATA

Spectroscopic Measurements

Absorption spectra were recorded in a UV-Vis UVIKON 941 Spectrophotometer in the 230-650 nm range. Steady-state fluorescence measurements were performed by using a PTI spectrofluorimeter equipped with single monochromators in the excitation and emission paths. Polarizers were fixed at the magic angle conditions. Fluorescence decay measurements were carried out on a PTI time-correlated single-photon-counting (TCSPC) spectrometer upgraded to use Horiba Nanoleds. A Nanoled emitting at 335 nm was employed as the excitation source. Photons were detected by a sensitive cooled photomultiplier. The data acquisition was carried out by a multichannel analyzer (1024 channels), with a time window width of 125 ns. A total of 10,000 counts, in the maximum peak channel, was taken for each measurement. Instrumental response functions were regularly obtained by measuring the scattering of a Ludox solution. Intensity fluorescence profiles were fitted to the usual multi-exponential decay functions,

$$I(t) = \sum_{i=1}^{n} A_i e^{-t/\tau_i}$$

by using the iterative deconvolution method, under the assumption that each component behaves independently.[4] The average lifetime of a multiple-exponential decay function can be defined as,

$$\langle \tau \rangle = \frac{\sum_{i=1}^{n} A_i \tau_i^2}{\sum_{i=1}^{n} A_i \tau_i}$$

where A_i is the pre-exponential factor of the component with a lifetime τ_i of the multi-exponential function intensity decay.[5] Right angle geometry and rectangular 1.0 cm path cells were used for all the measurements.

Fluorescence Quenching[6]

Collisional or dynamic quenching of the fluorescence of a single chromophore is described by the Stern-Volmer equation:

$$\frac{F_0}{F} = \frac{\tau_0}{\tau} = 1 + K_D[Q] = 1 + k_q \tau_0 [Q]$$

where F_0 and F (τ_o *and* τ) are the chromophore fluorescence intensities (fluorescence lifetimes) in the absence and presence of a quencher; k_q is the bimolecular quenching constant; τ_0 is the lifetime of the chromophore in the absence of Q. The Stern-Volmer quenching constant is given by $K_D = k_q \tau_0$.

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[4] D. V. O'Connor, W. R. Ware and J. C. Andre, *J. Phys. Chem.*, 1979, **83**, 1333–1343.

[5] J. R. Lakowicz, *Principles of Fluorescence Spectroscopy, 3rd edition* Springer-Verlag , Boston MA, pp 97–155, 2006.

[6] J. R. Lakowicz, *Principles of Fluorescence Spectroscopy, 3rd edition* Springer-Verlag , Boston MA, pp 277–330, 2006.

Fluorescence quenching can also occur as a result of the formation of a non-fluorescent ground-state complex between the chromophore and quencher (static quenching). In this case, the intensity (F) decreasing can also be fitted to a Stern-Volmer equation,

$$\frac{F_0}{F} = 1 + K_S[Q]$$

which is identical to that observed for dynamic quenching, although K_s is now the binding constant for the complex formation. However, static quenching does not open any new excited stated deactivation ways, therefore $\tau_0/\tau = 1$.

It is necessary to point out, that the binding constants obtained from Stern-Volmer plots are only valid when: (i) the complexed chromophores are non-fluorescent and when (ii) during the quenching experiment the initial quencher concentration [Q] >> [chromophore] and the complexed Q concentration ([Q-F]) can be neglected.

These two points are not fulfilled in our experiment as the complex of **1** and F^- is also fluorescent and [TBAF] is of the same order as [**1**] during part of the titration.

It is a better option to get binding constants as described in the next section.

Thermodynamics of the 1 to ligand binding

For the 1:1 stoichiometry **1**:*L* complex formation, according to the following equilibrium:

$$\mathbf{1} + L \underset{\longleftarrow}{\overset{K}{\longrightarrow}} \mathbf{1}:L$$

the association constant of the 1:*L* complex (C) is defined as,

$$K = \frac{[C]}{[\mathbf{1}][L]} \qquad \text{(S1)}$$

Taking into account the corresponding mass balances:

$$[\mathbf{1}]_0 = [\mathbf{1}] + [C] \qquad \text{(S2)}$$

$$[L]_0 = [L] + [C] \qquad \text{(S3)}$$

where [*C*], [**1**] and [*L*] are the complex, free fluorescent compound and ligand (fluoride) concentrations respectively at the equilibrium and $[\mathbf{1}]_0$ and $[L]_0$ are the initial **1** derivative and ligand concentrations.

For higher order stoichiometries 1:*n* for the complex the total L concentration in solution is:

$$[L]_0 = [L] + n[C] \qquad \text{(S4)}$$

and the fraction complexed species can be related to the equilibrium constant by:

$$\frac{n[C]}{[\mathbf{1}]_0} = \frac{nK[L]}{1 + K[L]} \qquad \text{(S5)}$$

By the substitution of [*L*] from previous equations, the [*C*] concentration is:

$$[C] = \frac{\left\{1 + K[L]_0 + nK[\mathbf{1}]_0\right\} \pm \sqrt{\left\{1 + K[L]_0 + nK[\mathbf{1}]_0\right\}^2 - 4nK^2[L]_0[\mathbf{1}]_0}}{2nK} \qquad \text{(S6)}$$

The free [**1**] can be determined as:

$$[\mathbf{1}] = \frac{\left\{nK[\mathbf{1}]_0 - K[L]_0 - 1\right\} \pm \sqrt{\left\{1 + K[L]_0 + nK[\mathbf{1}]_0\right\}^2 - 4nK^2[L]_0[\mathbf{1}]_0}}{2nK} \qquad \text{(S7)}$$

The total fluorescence intensity (*I*) due to the fluorescents **1** and complex is

$$I = x_1 I_1 + x_C I_C = \frac{[\mathbf{1}]}{[\mathbf{1}]_0} I_1 + \frac{[C]}{[\mathbf{1}]_0} I_C \quad \text{or} \quad I = \frac{[\mathbf{1}]}{[\mathbf{1}]_0} I_0 + \frac{[\mathbf{1}]}{[\mathbf{1}]_0} I_\infty \qquad \text{(S8)}$$

Substracting I_0 gives,

$$\Delta I = I - I_0 = I_\infty - I_0 \left(1 - \frac{[\mathbf{1}]}{[\mathbf{1}]_0} \right) \qquad \text{(S9)}$$

or,

$$\Delta I = \left(I_\infty - I_0 \right) \frac{[C]}{[\mathbf{1}]_0} \qquad \text{(S10)}$$

where I_0 is the fluorescence intensity for the uncomplexed **1**, I_∞ is the fluorescence intensity of the *C* complex, $[\mathbf{1}]_0$ the total concentration of fluorescent **1** and *K* the association constant of the host-guest system.

The substitution of [*C*] from S6 into S10 results in,

$$\Delta I = (I_\infty - I_0) \frac{\left\{ 1/[\mathbf{1}]_0 + K[L]_0/[\mathbf{1}]_0 + nK \right\} \pm \sqrt{\left\{ 1 + K[L]_0/[\mathbf{1}]_0 + nK \right\}^2 - 4nK^2 [L]_0/[\mathbf{1}]_0}}{2nK} \qquad \text{(S11)}$$

(S11) can be modified as:

$$\frac{\Delta \mathrm{I}}{\mathrm{I}_0} = \left(\frac{\mathrm{I}_\infty - \mathrm{I}_0}{\mathrm{I}_0} \right) \frac{\left\{ 1/[\mathbf{1}]_0 + KR + nK \right\} \pm \sqrt{\left\{ 1 + KR + nK \right\}^2 - 4nK^2 R}}{2nK} \qquad \text{(S12)}$$

where *R* is the $[\mathbf{L}]_0/[\mathbf{1}]_0$ molar ratio or equivalents of L added during titration.

Equations S11 and S12 are valid for titrations of fluorescent derivatives and both, fluorescent complexes or non-fluorescent ones, *i.e.*, the fluorescence decreases or increases upon titration. In addition, these equations are valid for any L (or quencher) concentration.

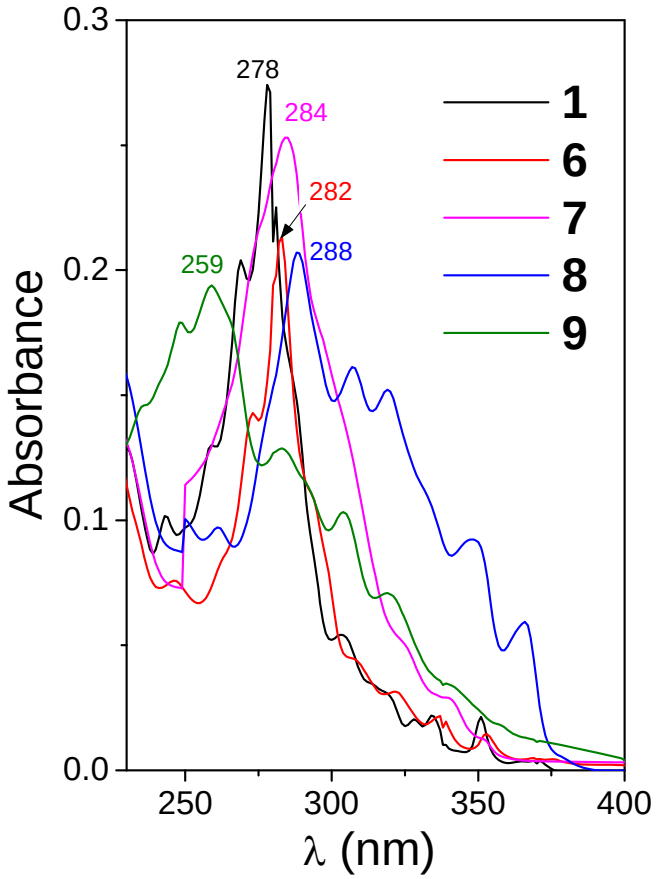


Figure S2. UV/Vis absorption spectra for selected BN-chrysenes **1**, **6**, **7**, **8** and **9** in cyclohexane. Chrysene which shows similar spectra to **1** exhibits the maximum absorption at 269 nm.

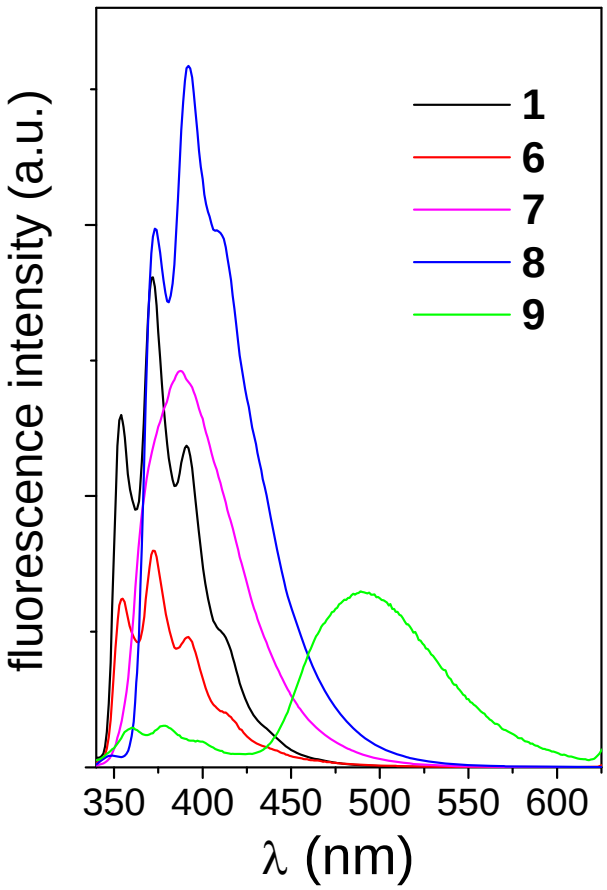
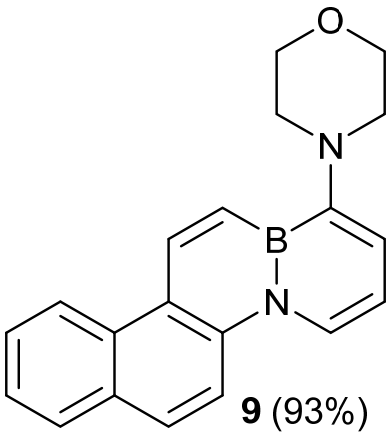


Figure S3. Fluorescence spectra for selected BN-chrysene derivatives **1**, **6**, **7**, **8** and **9** in cyclohexane at 25ºC upon excitation of 334, 321, 323, 348 and 319nm respectively.

***π-π stacking* ground state aggregates of derivative 9 in solution.**



9 (93%)

9 derivative emission spectrum exhibits bands at 378 nm and 489 nm in cyclohexane. The second one (489nm) was attributed to the presence of quite stable ground state π-π stacking aggregates in solution. Several facts confirm this hypothesis:

1. The ratio of intensities of emission spectra measured at 489 nm (attributed to n-mers π-π stacking aggregates) and 378 nm (emission of the monomeric species) significantly increases with the solution concentration of **9** in cyclohexane. This agrees with the proposed aggregation in solution. The band at 489 nm is responsible for the emission of such aggregate species (Figure S4).

2. Excitation spectra for **9** in cyclohexane solutions at 25ºC upon selecting the emission at 378 nm and 489 nm excludes the possibility that the band at 489 nm would correspond to the emission of an intermolecular BN-chrysene excimer. Instead, the band would correspond to a complex that is stable in the ground state. The excitation of the monomer is not necessary for the emission at 489 nm (Figure S5).

3. From the emission spectra for BN-chrysene derivative **9** in cyclohexane at 25ºC, by using several excitation wavelengths, it can be inferred that the presence of the second band at 489 nm does not require the excitation of the monomer. This reinforces the idea that the band centered at 489 nm does not correspond to an intermolecular excimer. Therefore, It can be attributed to a species that is stable in the ground state (Figure S6).

4. Emission spectra for **9** in cyclohexane (CYC), DMSO and n-methylformamide (NMF) solutions at 25ºC show that the intensity and location of the band responsible for the emission of π-π stacking aggregates is sensitive to the nature of the solvent (Figure S7). In NMF the presence of aggregates considerably decreases.

5. More complex fluorescence intensity decays at 278 and 489 nm (upon 335nm excitation) than the single mono-exponential one would be expected from the hypothetical presence of a monomer–excimer equilibrium in the excited state. This also discharges the presence of an excimer and reinforces the idea of a ground state complex which emits at 489 nm.

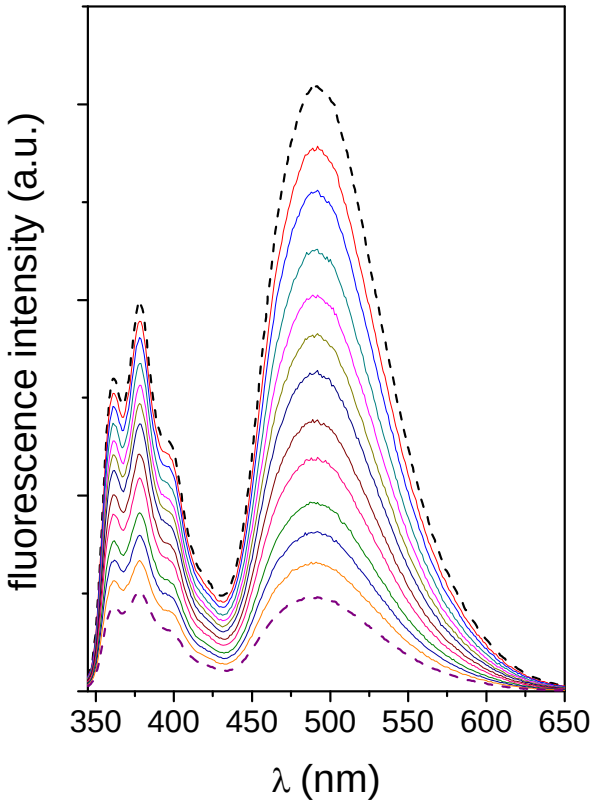


Figure S4. Emission spectra for solutions of **9** in cyclohexane upon increasing concentration. Notice that the ratio of intensities measured at 489 nm and 378 nm significantly increases with concentration which means that the amount of species stable in the ground state emitting at 489 nm increases with concentration agreeing with aggregation. Concentrations range from 5.80×10^{-6}M to 4.68×10^{-5} M.

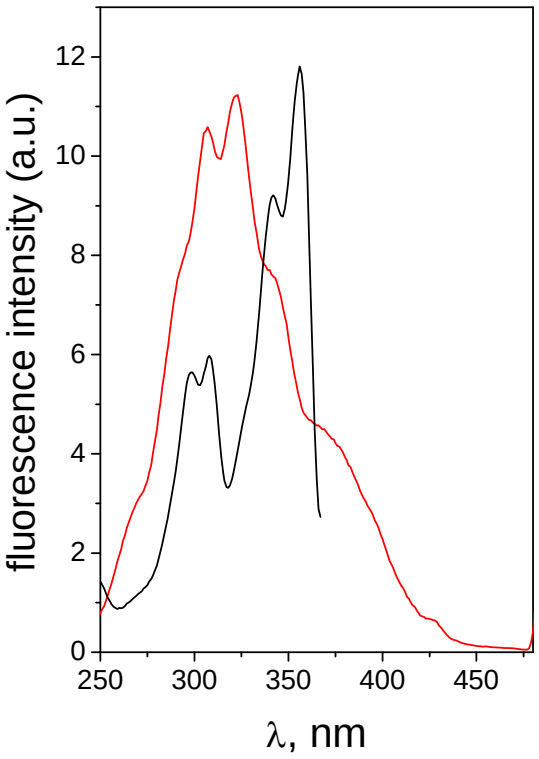


Figure S5. Excitation spectra for **9** in cyclohexane solutions at 25ºC. λ_{em} =378 nm (black) and 489 (red). Notice that the differences in the excitation spectra exclude the possibility that the band at 489 nm would correspond to the emission of an intermolecular BN-chrysene excimer. Instead a complex stable in the ground state is formed.

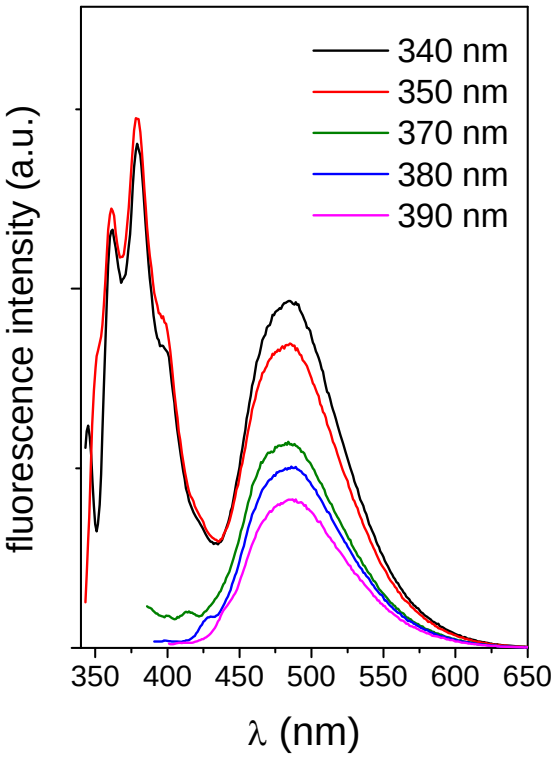


Figure S6. Emission spectra for derivative **9** in cyclohexane at 25ºC upon excitation at different wavelengths (showed in the graph). Notice that the band at 489 changes in intensity with the excitation wavelength but even at the wavelengths were the monomer band (centered at 378 nm) disappears the band at 489 nm still appears. The presence of the second band at 489 nm does not require the excitation of a monomer, concluding that the band centered at 489 nm corresponds to a species that is stable in the ground state.

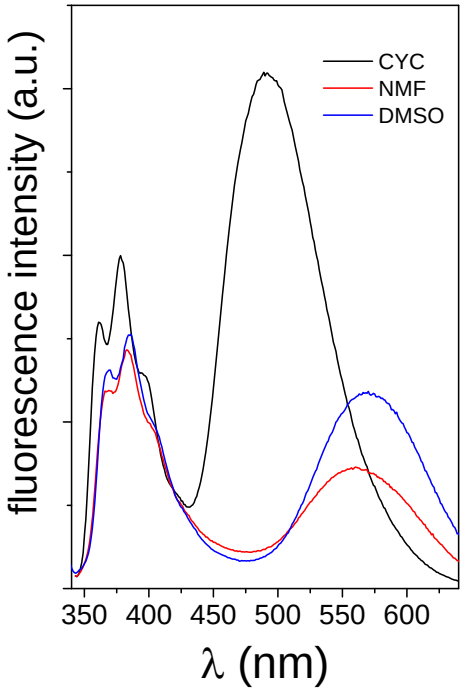


Figure S7. Emission spectra for **9** in cyclohexane (CYC), DMSO and *n*-methylformamide (NMF) solutions at 25ºC at the same absorbance (0.3) upon excitation of λ_{ex} =319 nm. Intensity and location of the band responsible for the emission of π-π stacking aggregates is sensitive to the nature of the solvent.

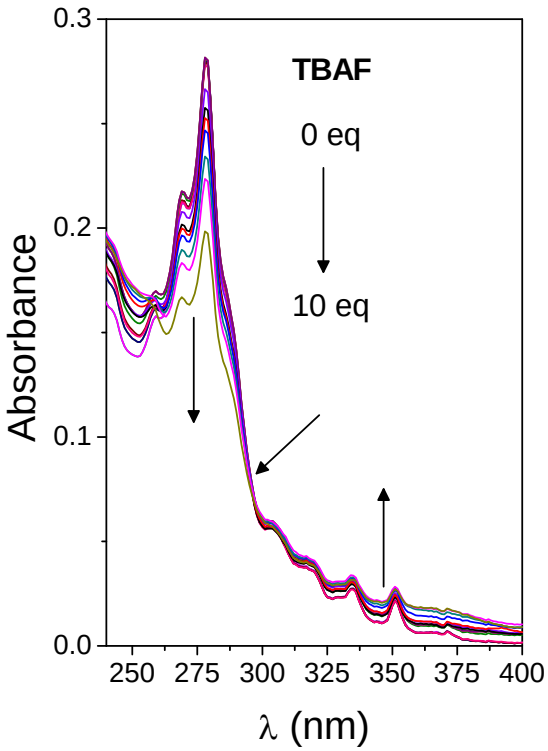


Figure S8. Absorbances for **1** in cyclohexane solutions at 25ºC for different equivalents of TBAF added during titration. [**1**] =4.7410^{-6} M.

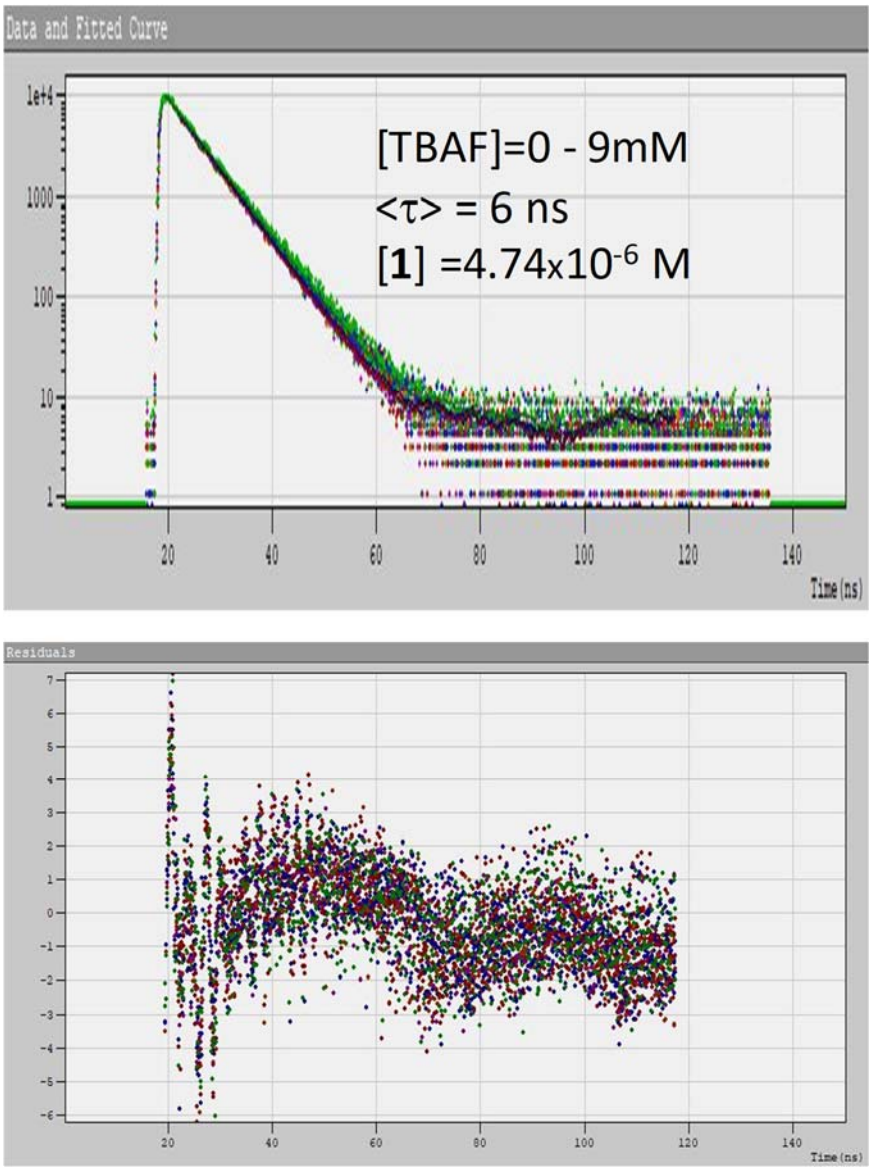


Figure S9. Fluorescence intensity decay profiles during titration of **1** ([**1**] =4.7410^{-6} M) in cyclohexane upon the addition of 0, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 1.75, 2.0, 4, 6 and 9 equivalents of TBAF at 25ºC (λ_{ex} = 334 nm, λ_{em}= 378 nm).

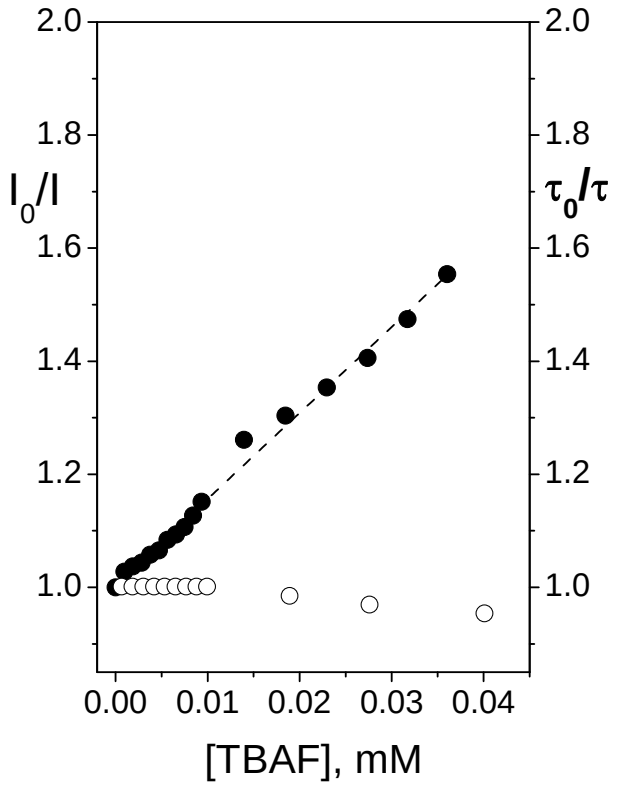


Figure S10. Stern-Volmer plots of fluorescence intensities measured as the area under emission spectra (filled symbols, λ_{ex} =334 nm) and lifetimes (open symbols, λ_{ex} =335 nm and λ_{em} =371 nm) for quenching of **1** cyclohexane solutions upon the addition of TBAF at 25ºC ([**1**] =4.7410^{-6} M). Results denote the absence of dynamic quenching. A slope of the intensity plot would provide binding constants for the complex of 15200 $\pm$ 300 M^{-1}.

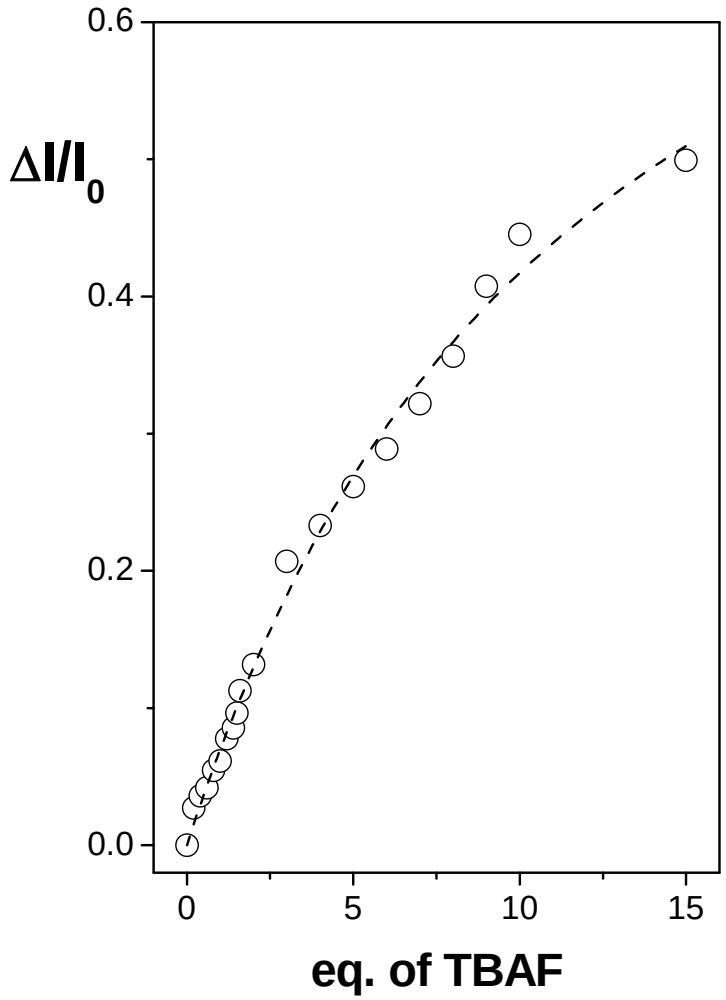
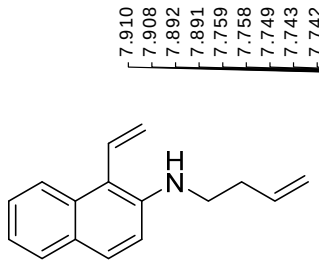
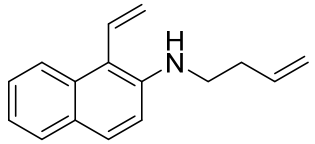


Figure S11. Normalized variation of the fluorescence intensities for **1** cyclohexane solutions at 25ºC (measured as the area under emission spectra) versus equivalents of TBAF added during titration (λ_{ex} =334 nm, [**1**] =4.7410^{-6} M). The curve was the result of the adjustment of the experimental data to equation S12.



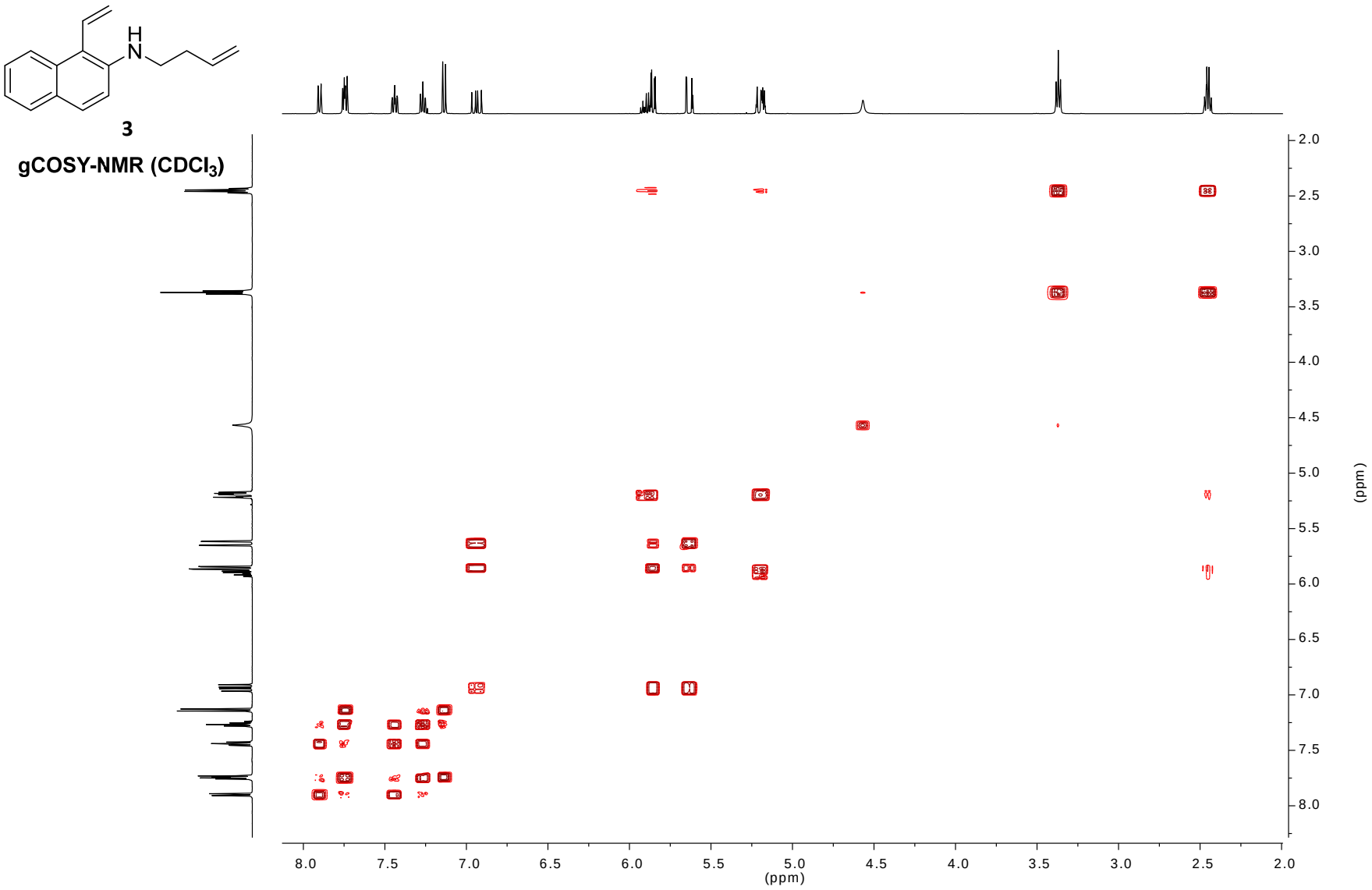
3

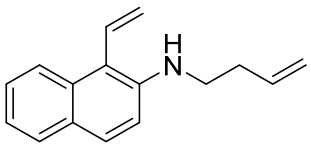
^{1}H-NMR (500 MHz, $CDCl_3$)



3

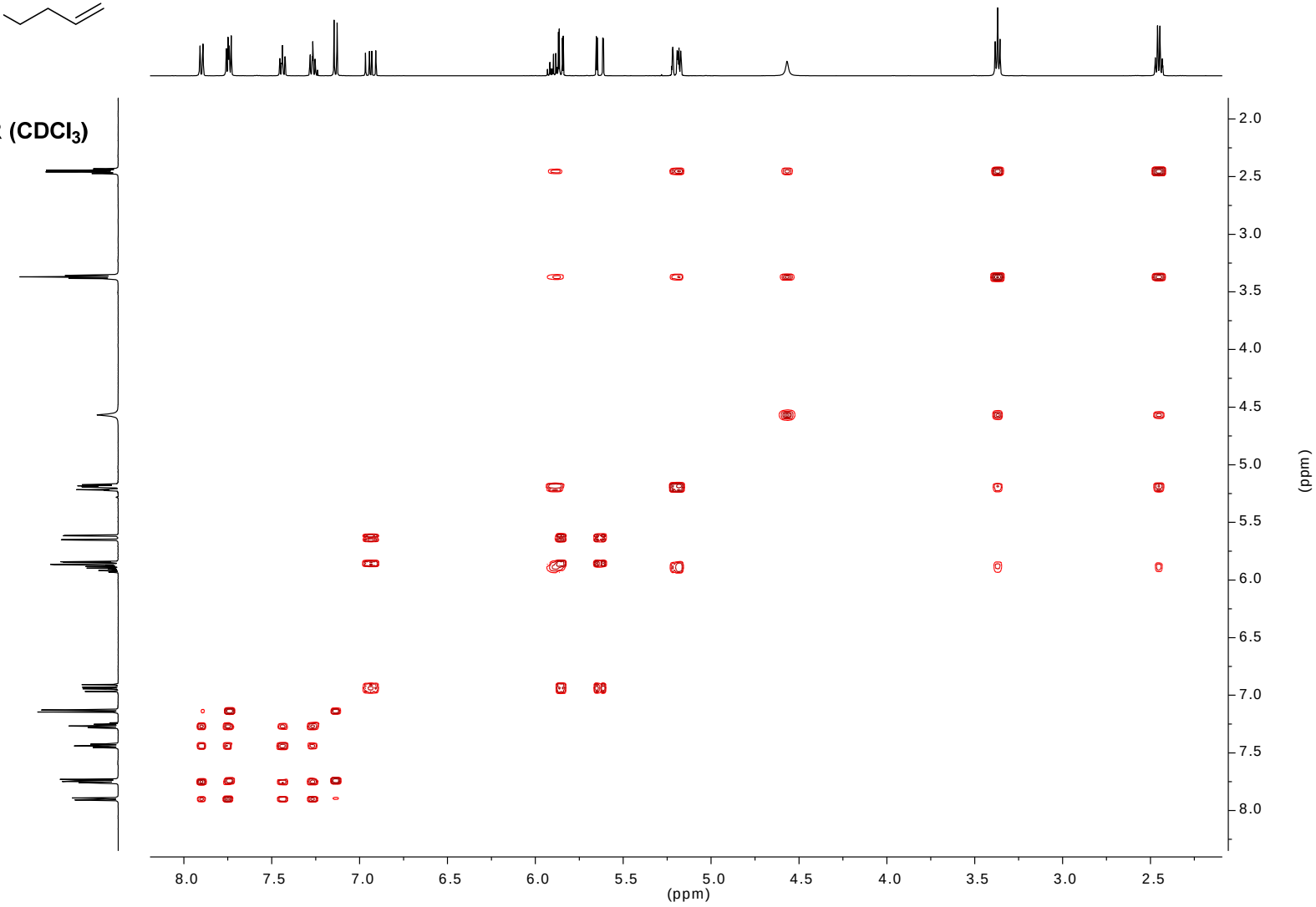
^{13}C-NMR (125 MHz, $CDCl_3$)

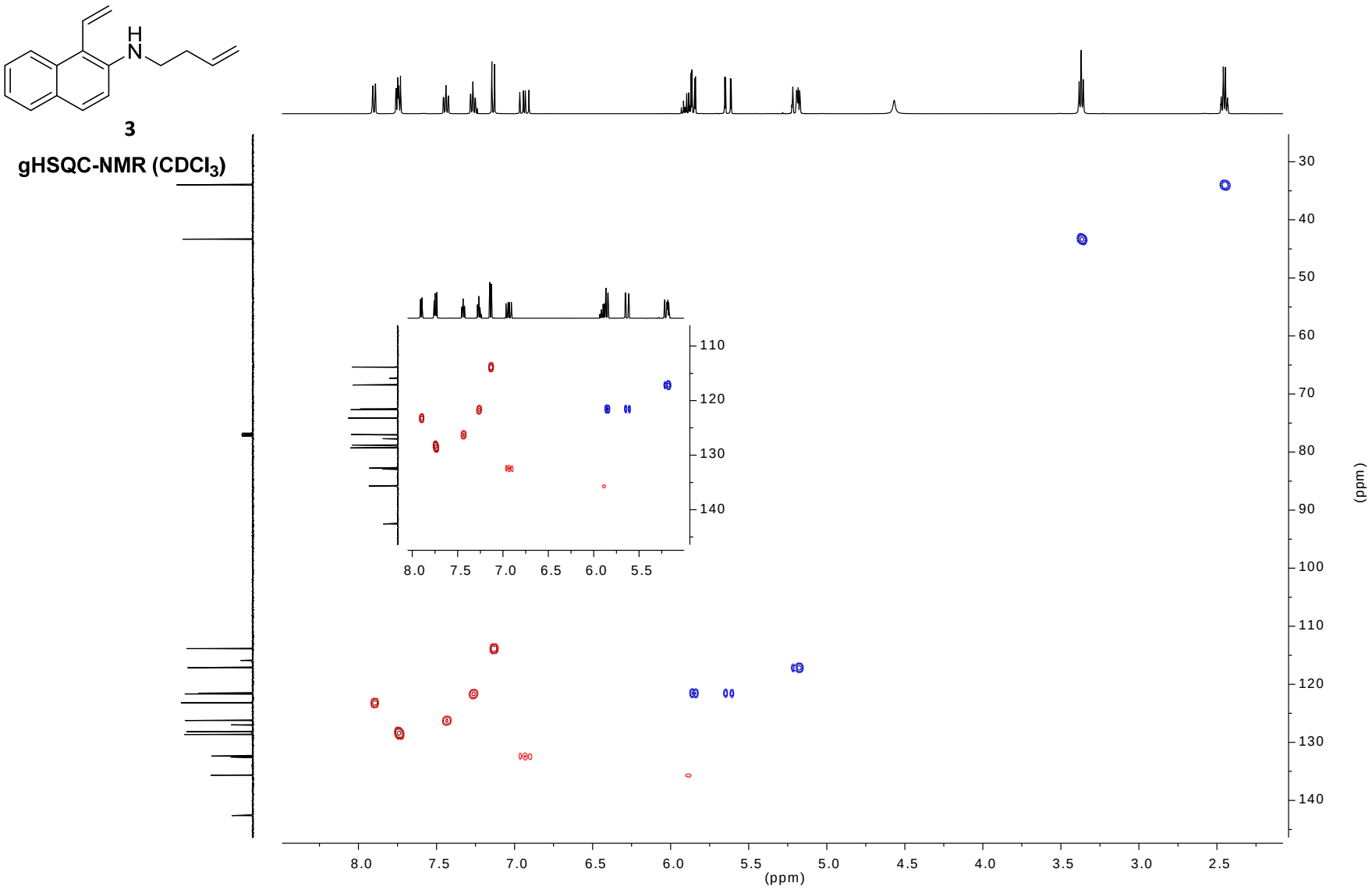

3
gCOSY-NMR ($CDCl_3$)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
(ppm)
(ppm)



3

TOCSY-NMR ($CDCl_3$)

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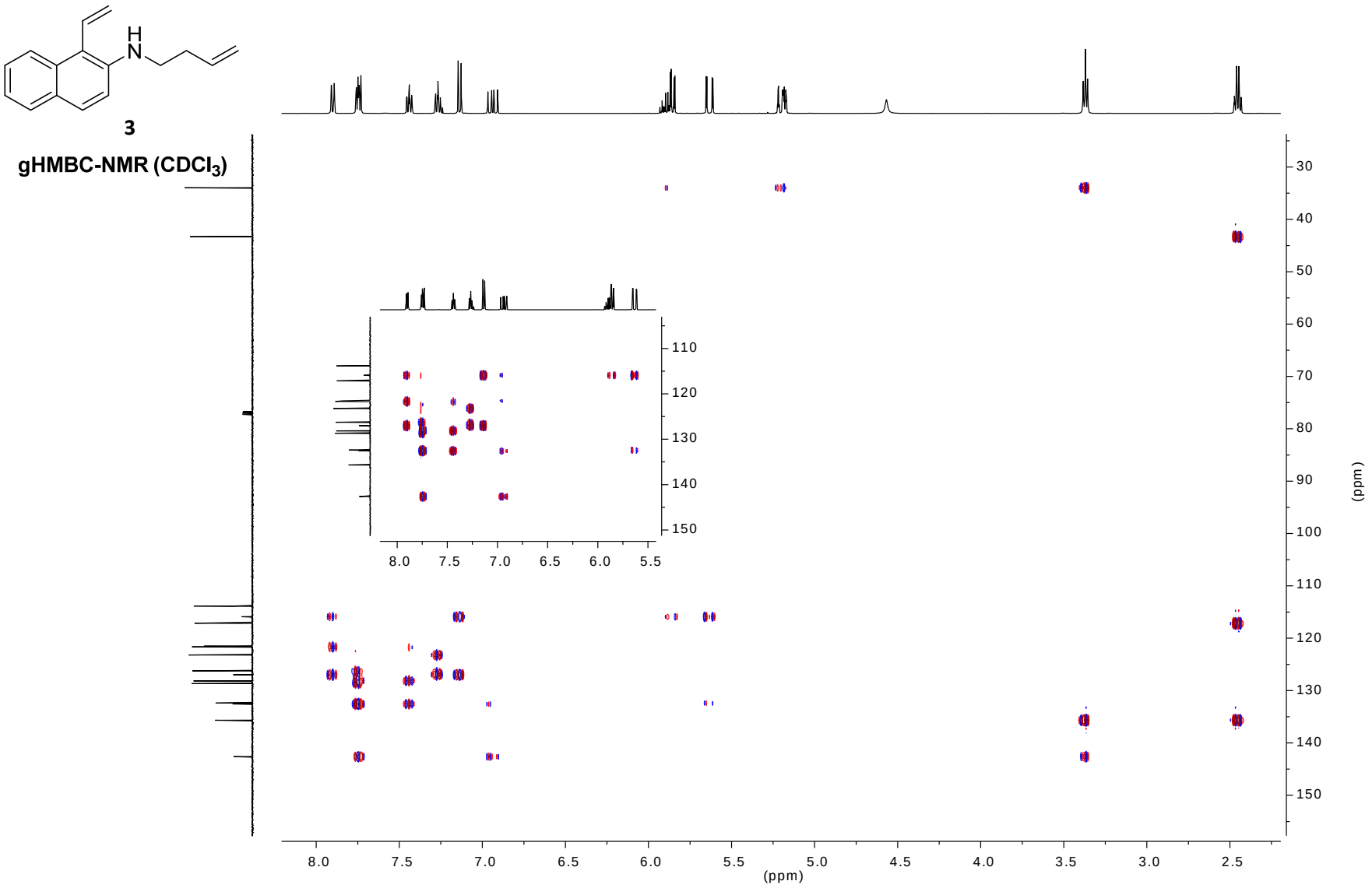
(ppm)
(ppm)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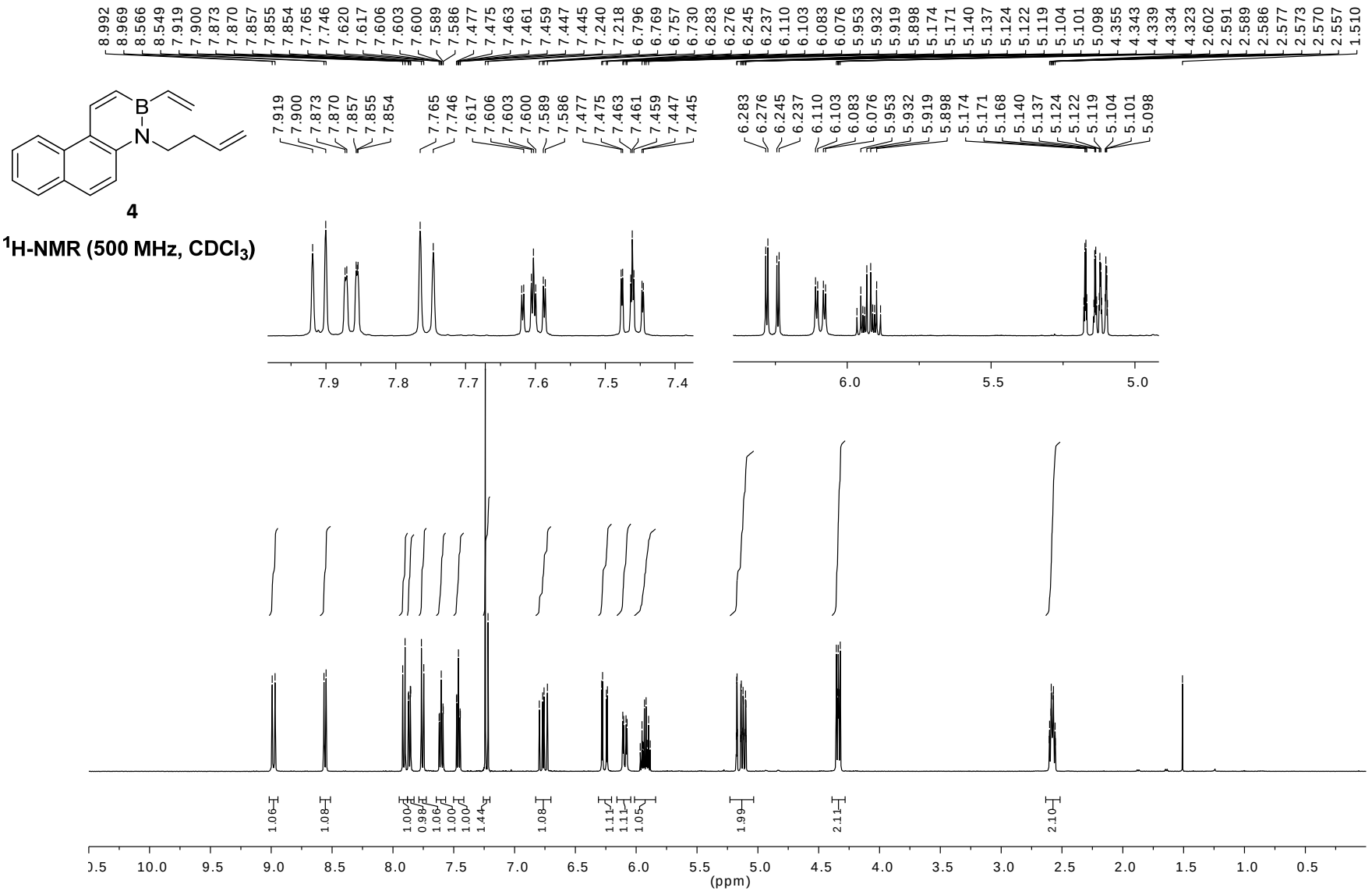
gHMBC-NMR (CDCl3)
(ppm)
(ppm)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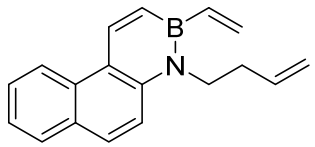
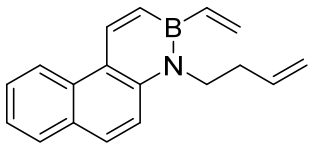
(ppm)



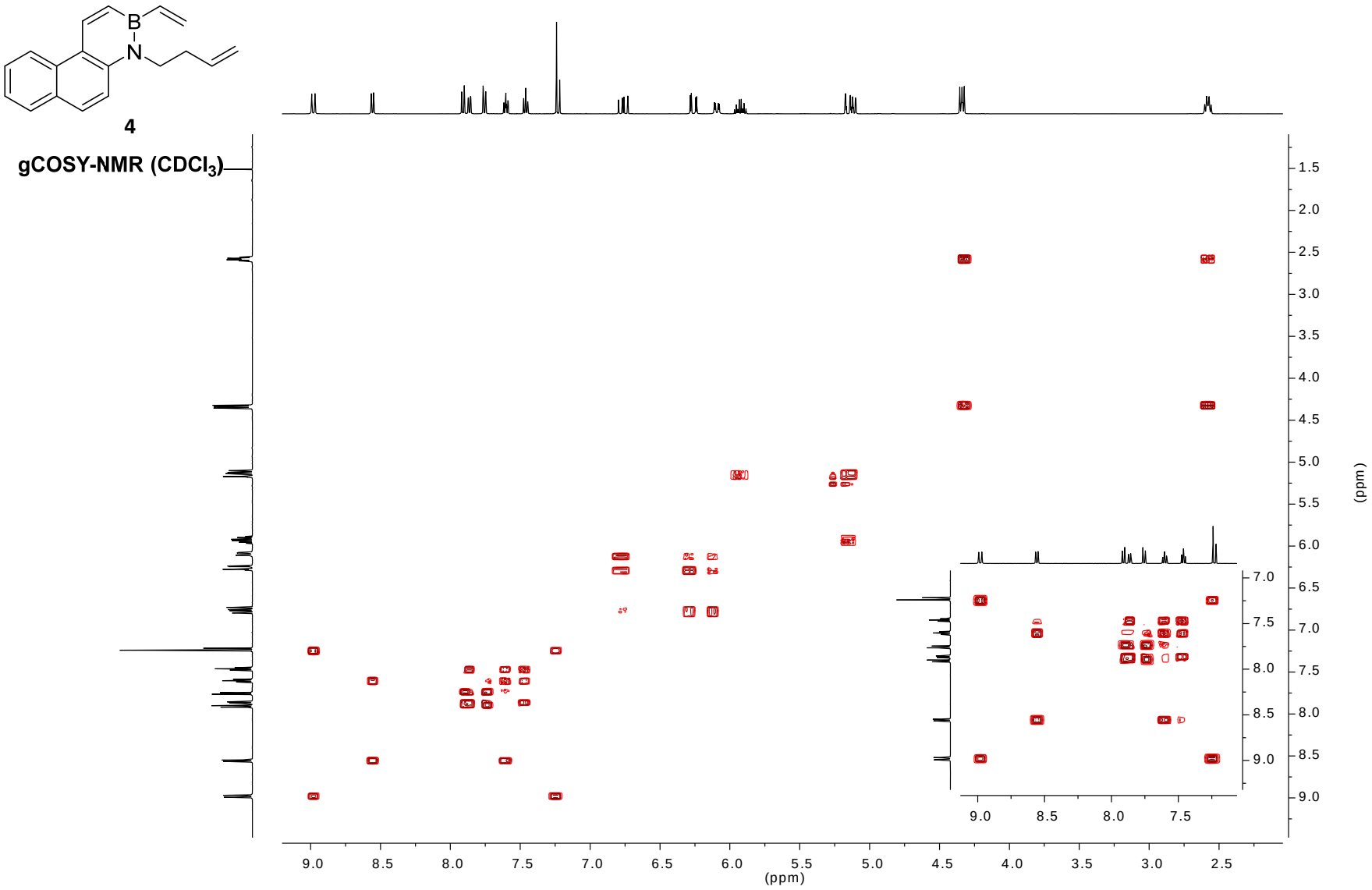
4

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



4

^{11}B-NMR (160 MHz, $CDCl_3$)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7.5
7.0
6.5
6.0
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5.0
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4.0
3.5
3.0
2.5
(ppm)
1.5
2.0
2.5
3.0
3.5
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7.5
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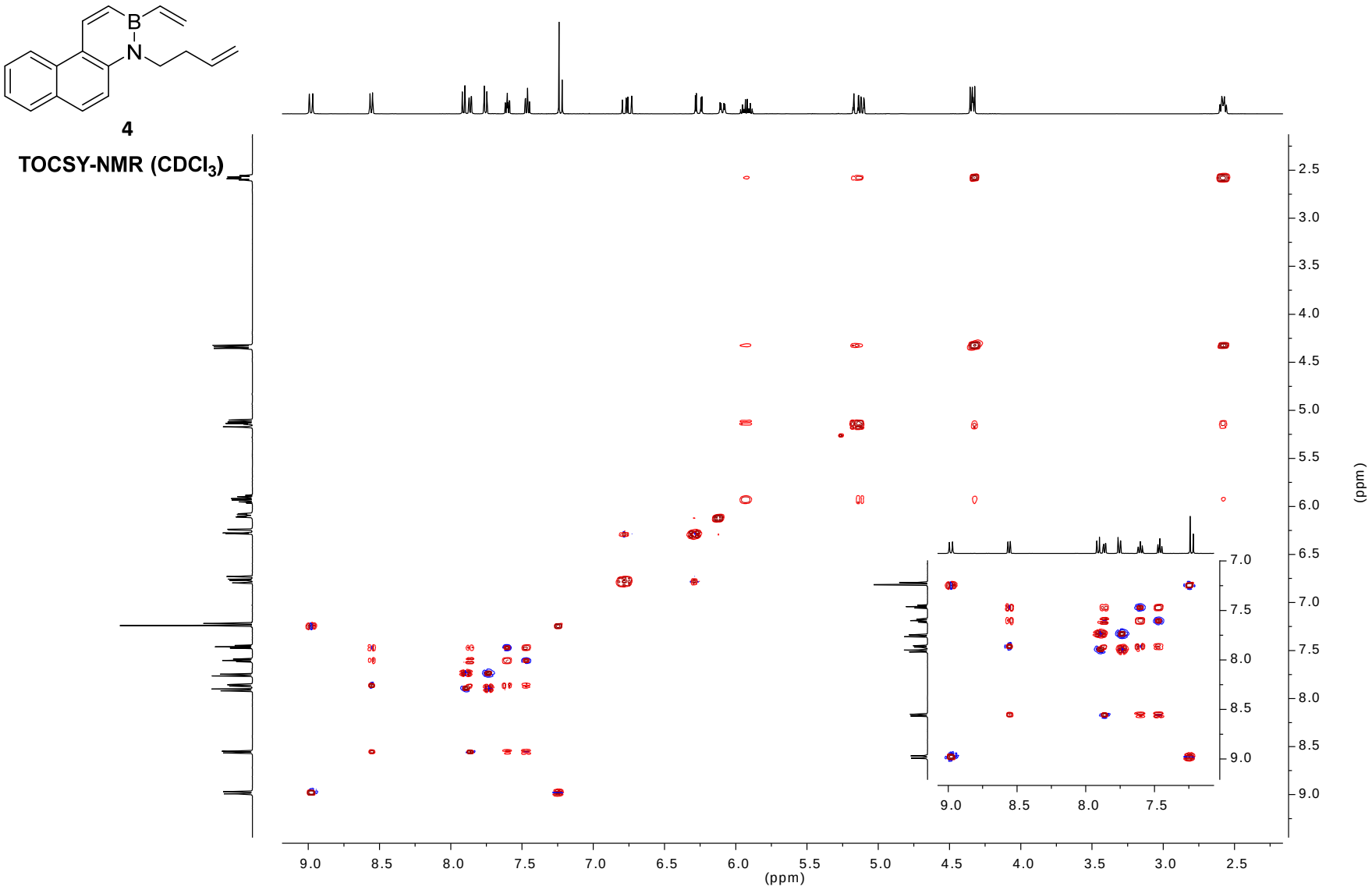
(ppm)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4.5
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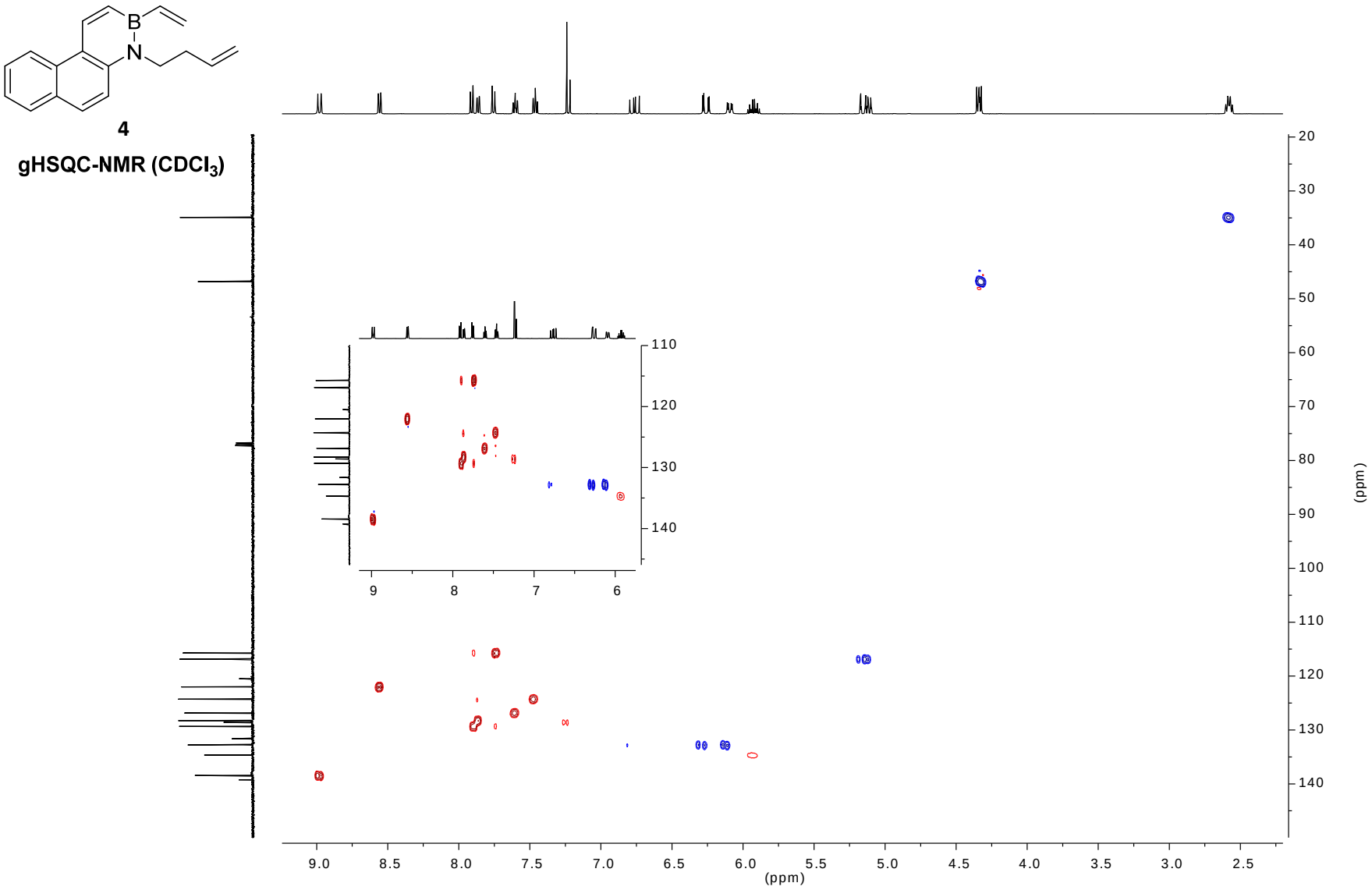
(ppm)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(ppm)
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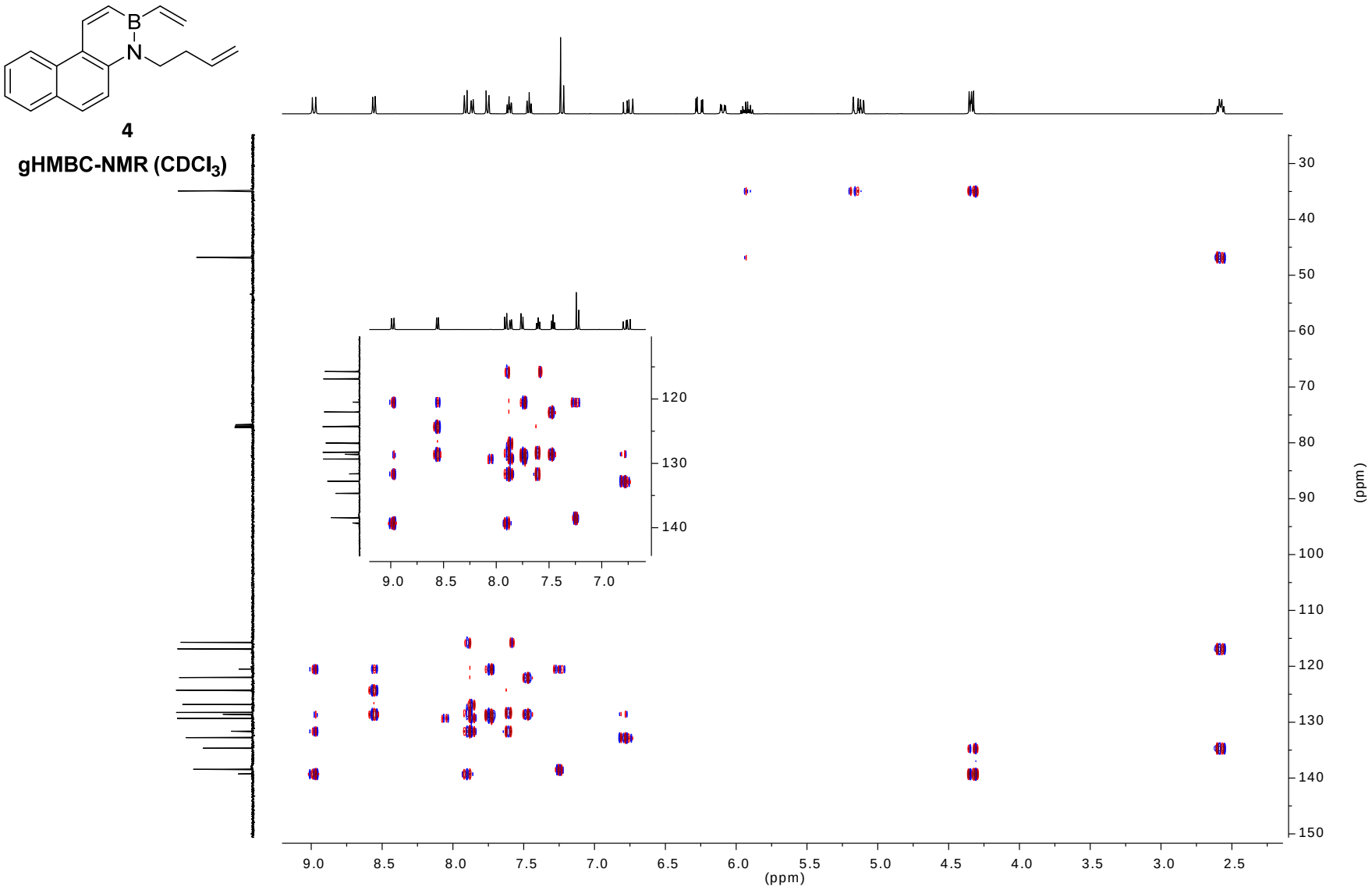
7
6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(ppm)
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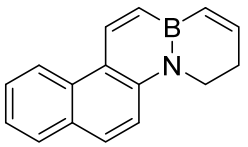
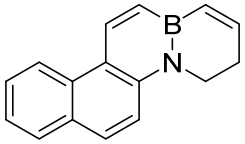
130
140



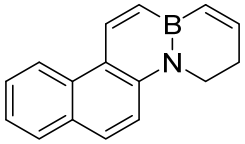
5

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



5

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



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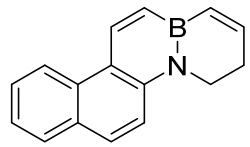
^{11}B-NMR (160 MHz, $CDCl_3$)



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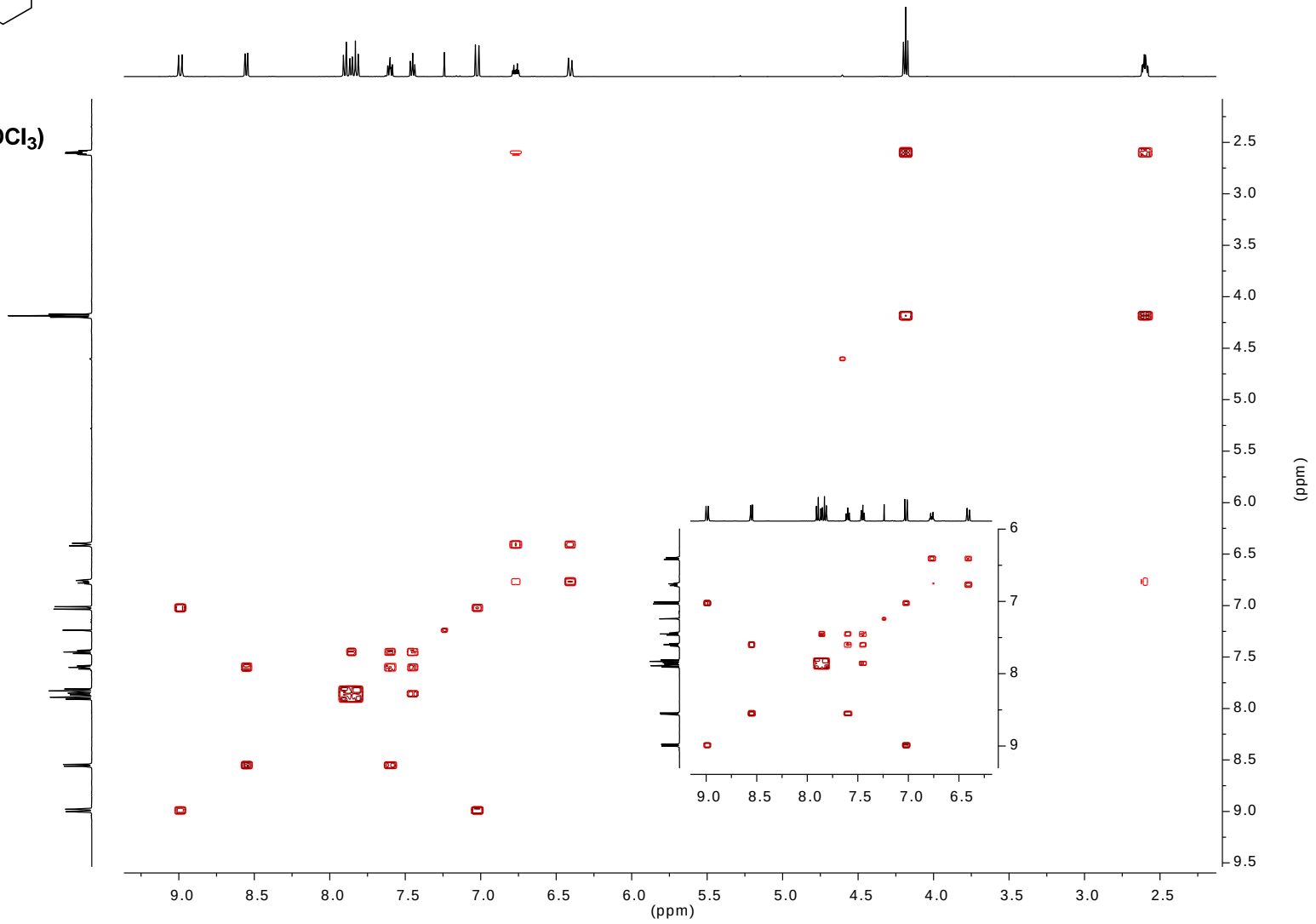
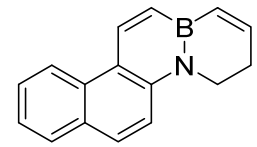
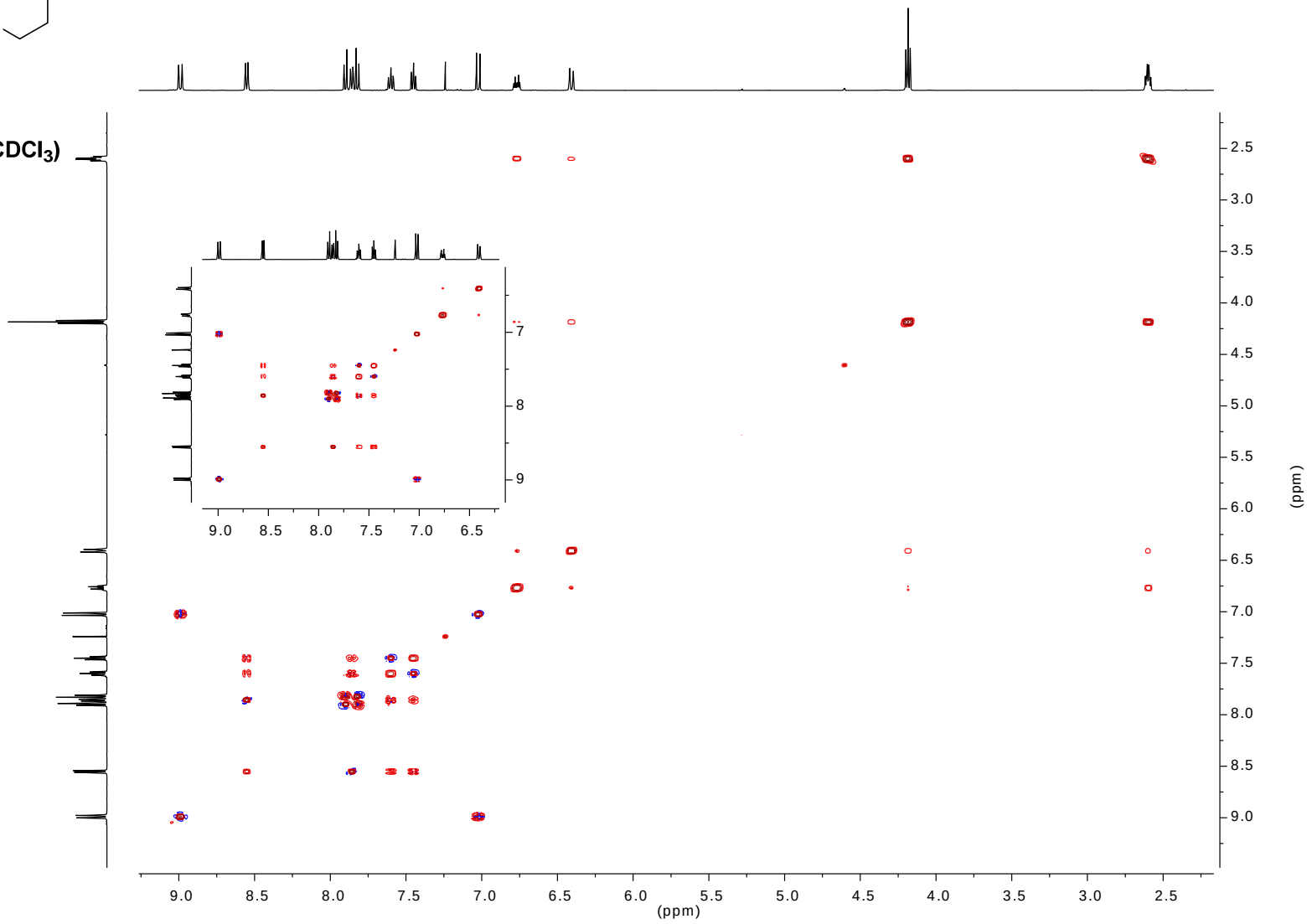
gCOSY-NMR ($CDCl_3$)

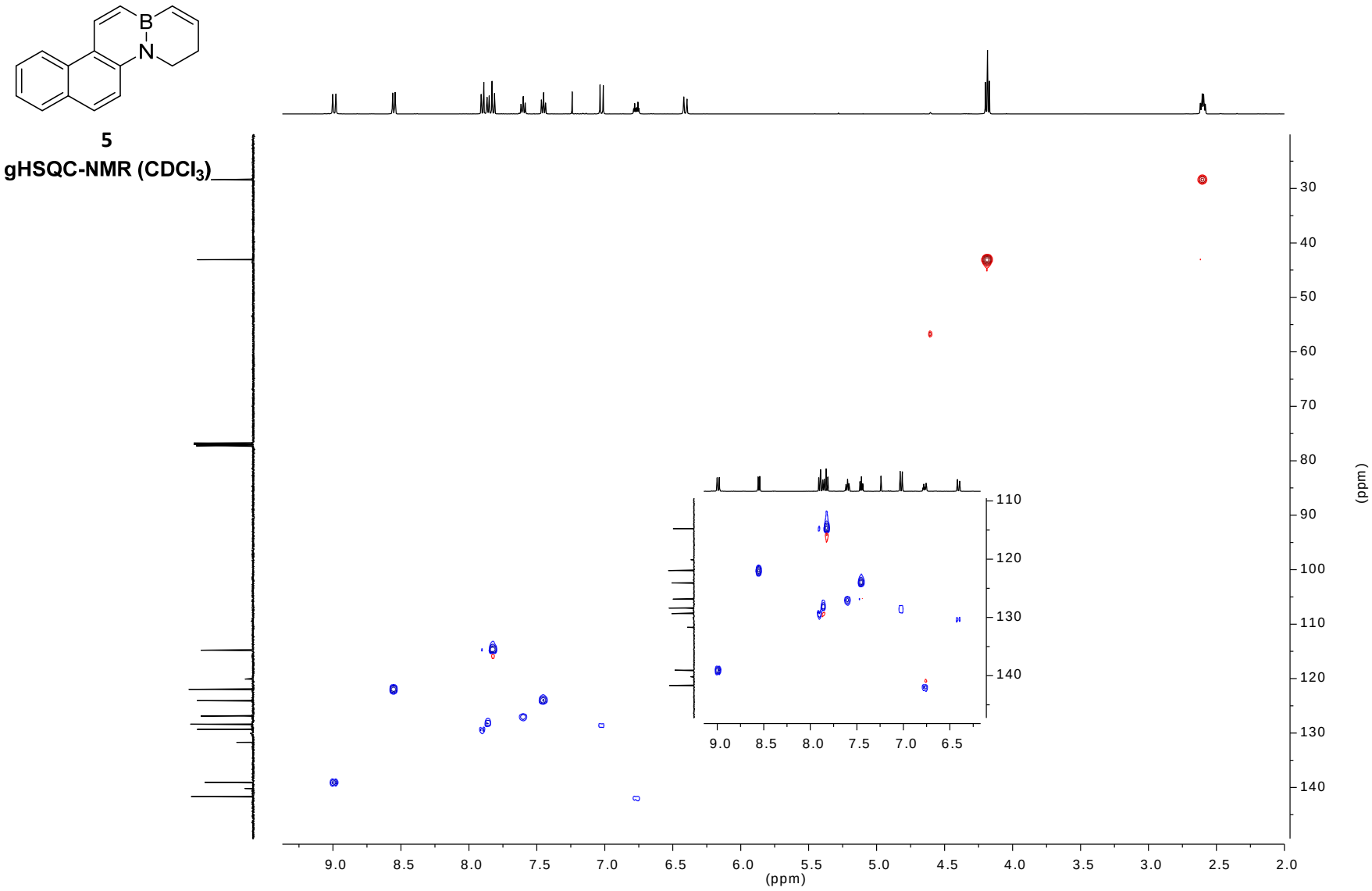




5

TOCSY-NMR ($CDCl_3$)

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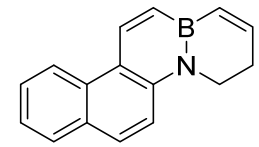

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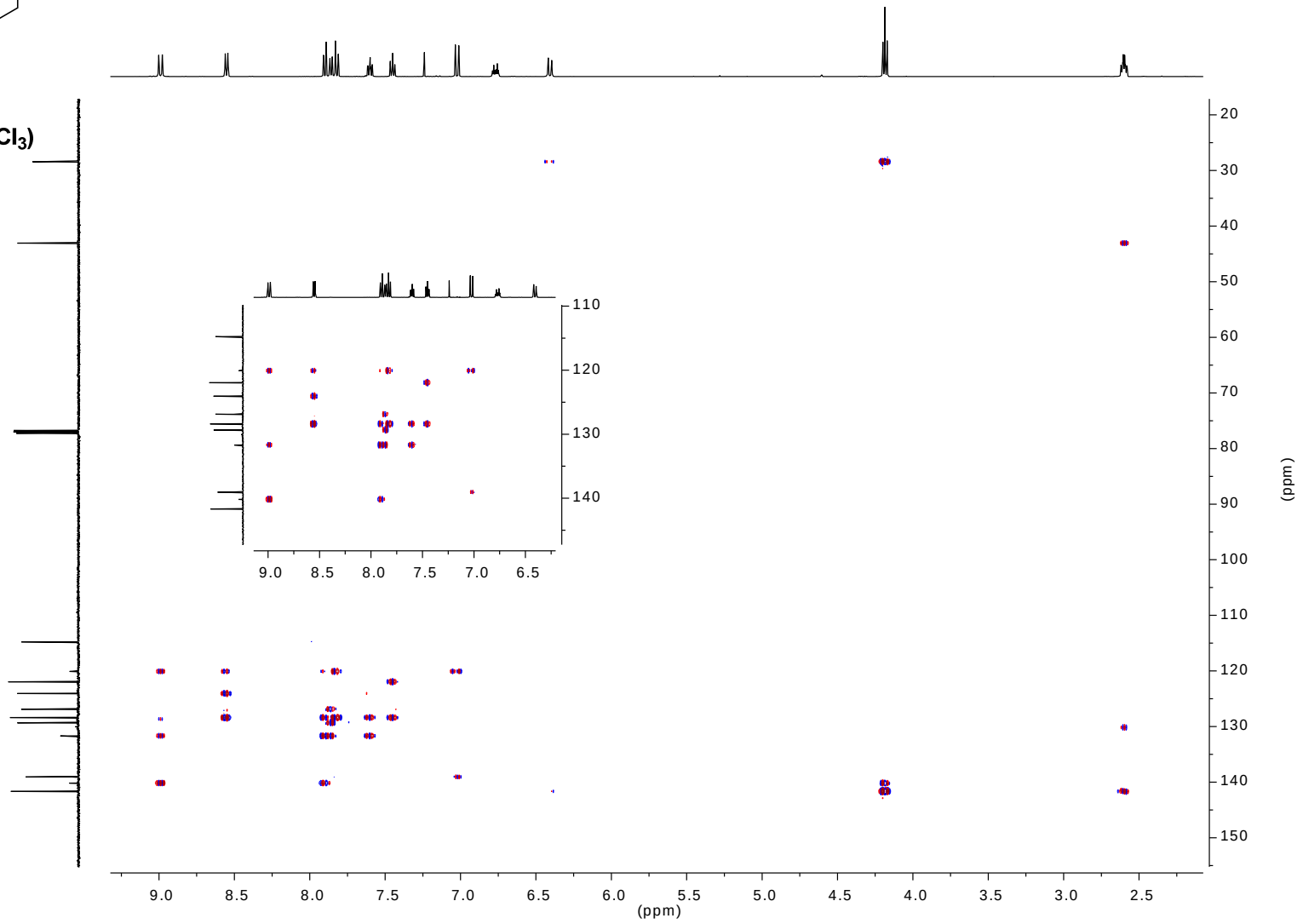
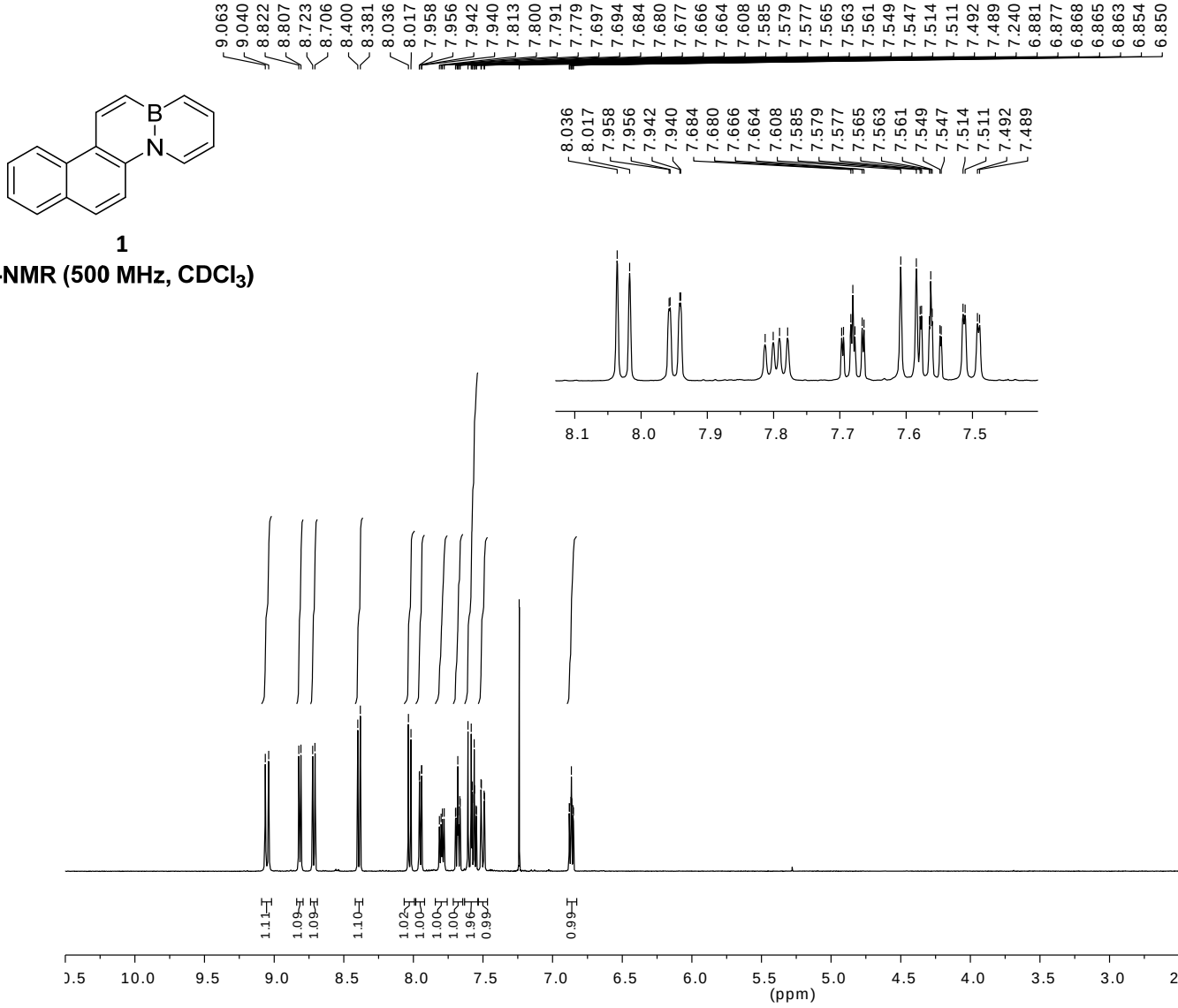
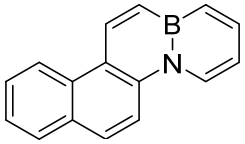
gHMBC-NMR ($CDCl_3$)





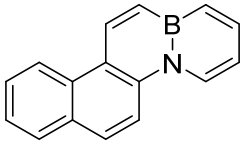
1

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



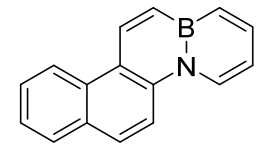
1

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



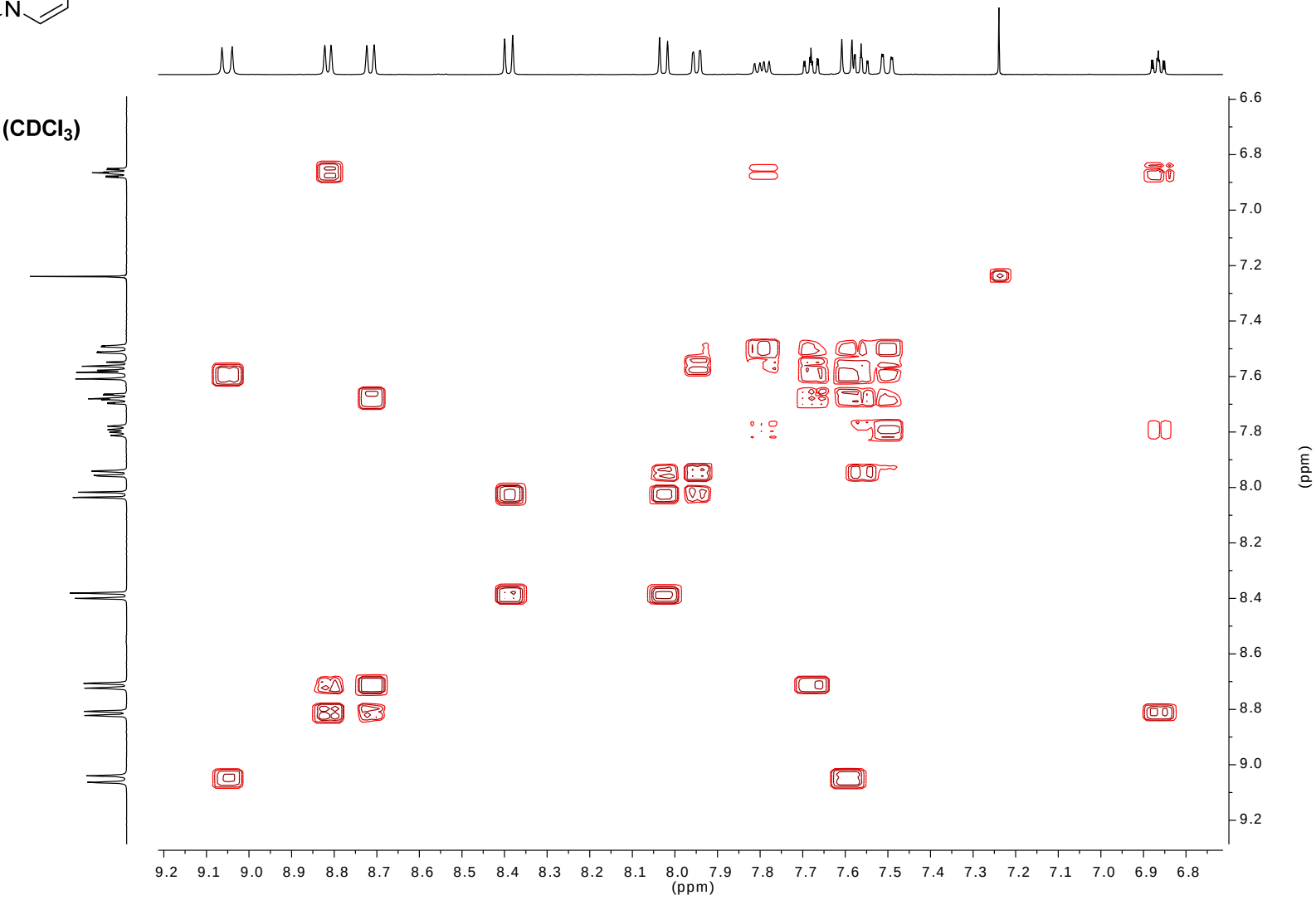
1

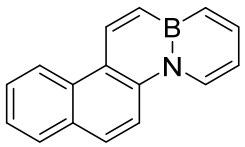
^{11}B-NMR (160 MHz, $CDCl_3$)



1

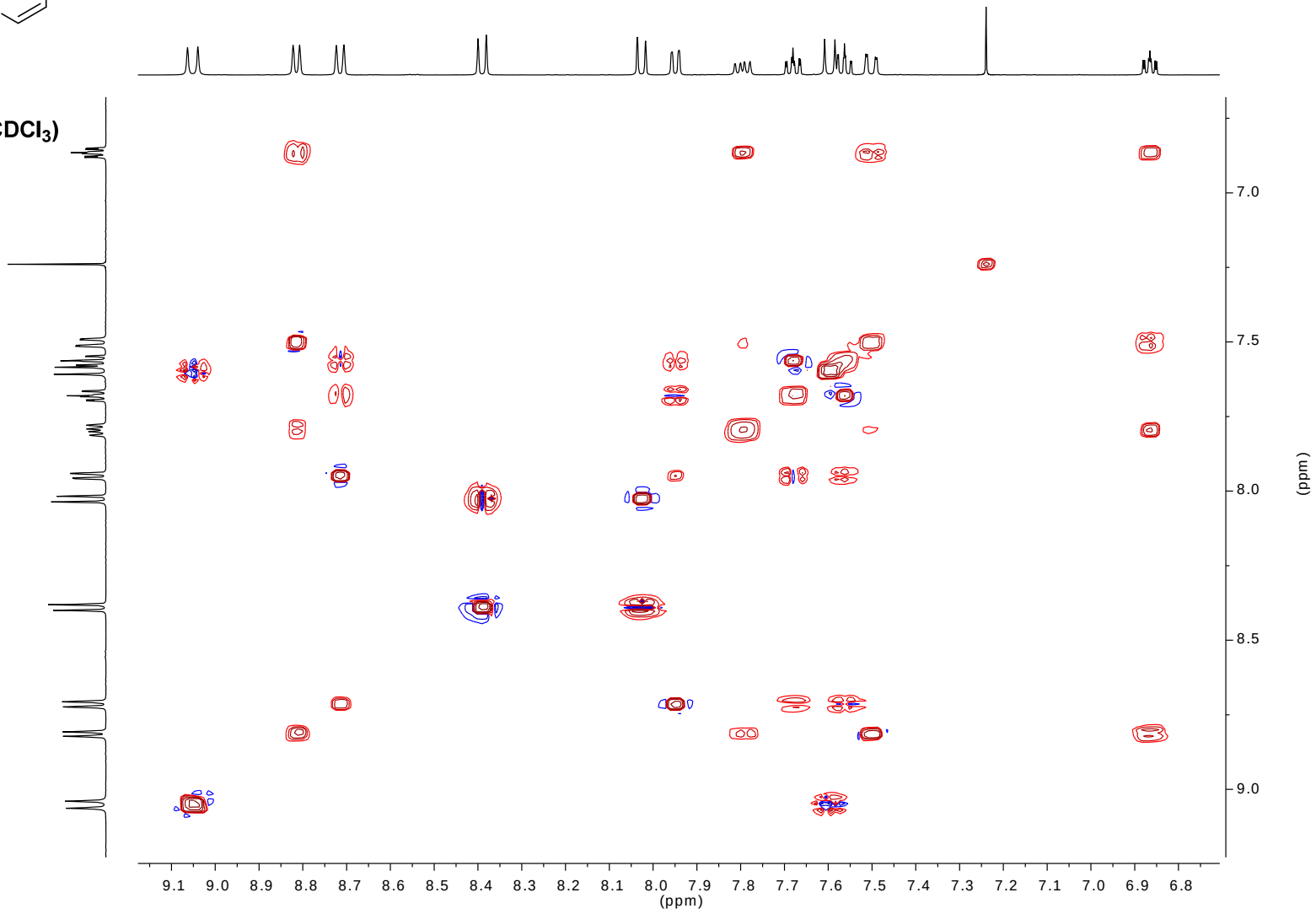
gCOSY-NMR ($CDCl_3$)

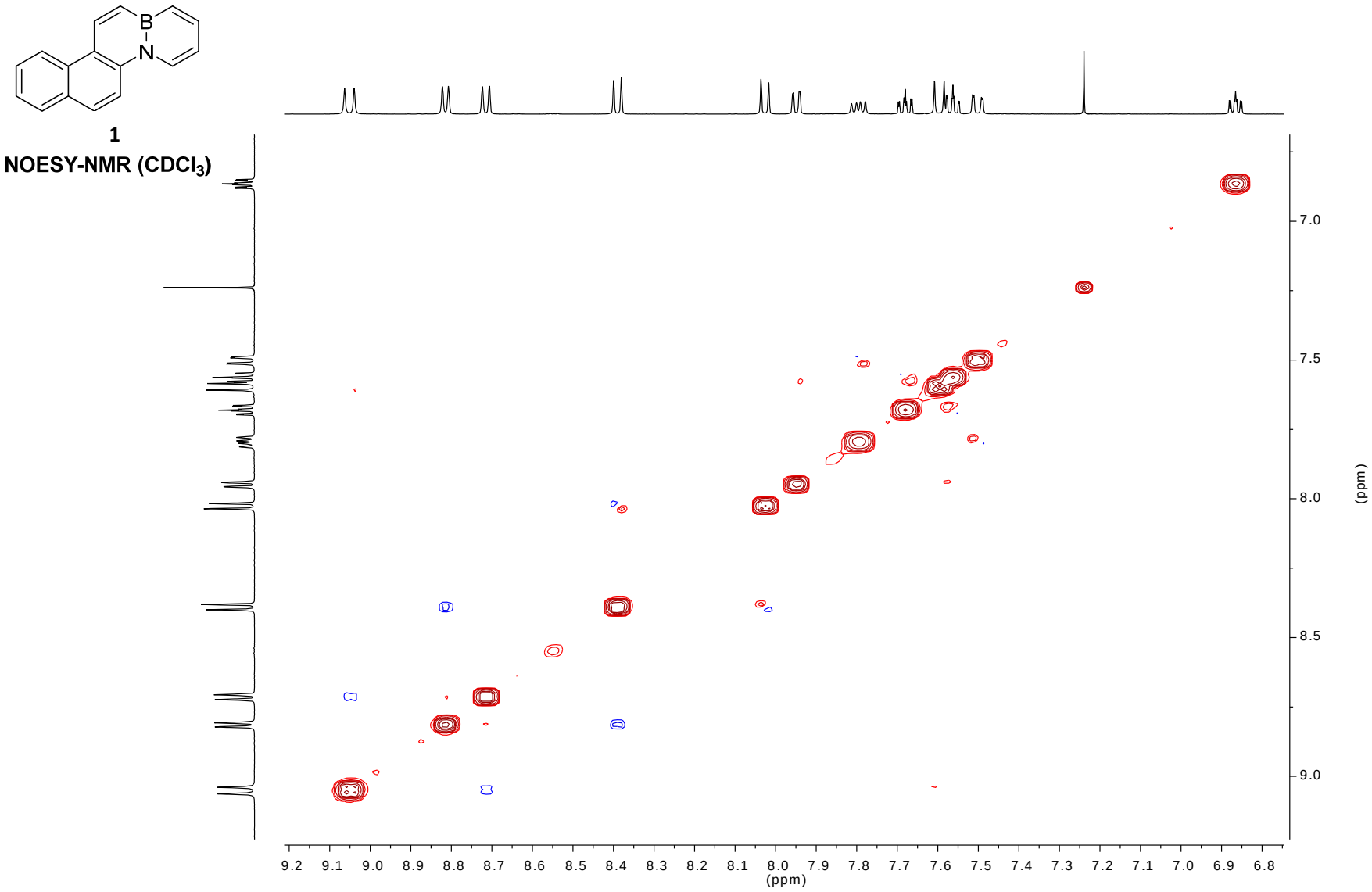


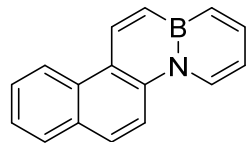


1

TOCSY-NMR ($CDCl_3$)

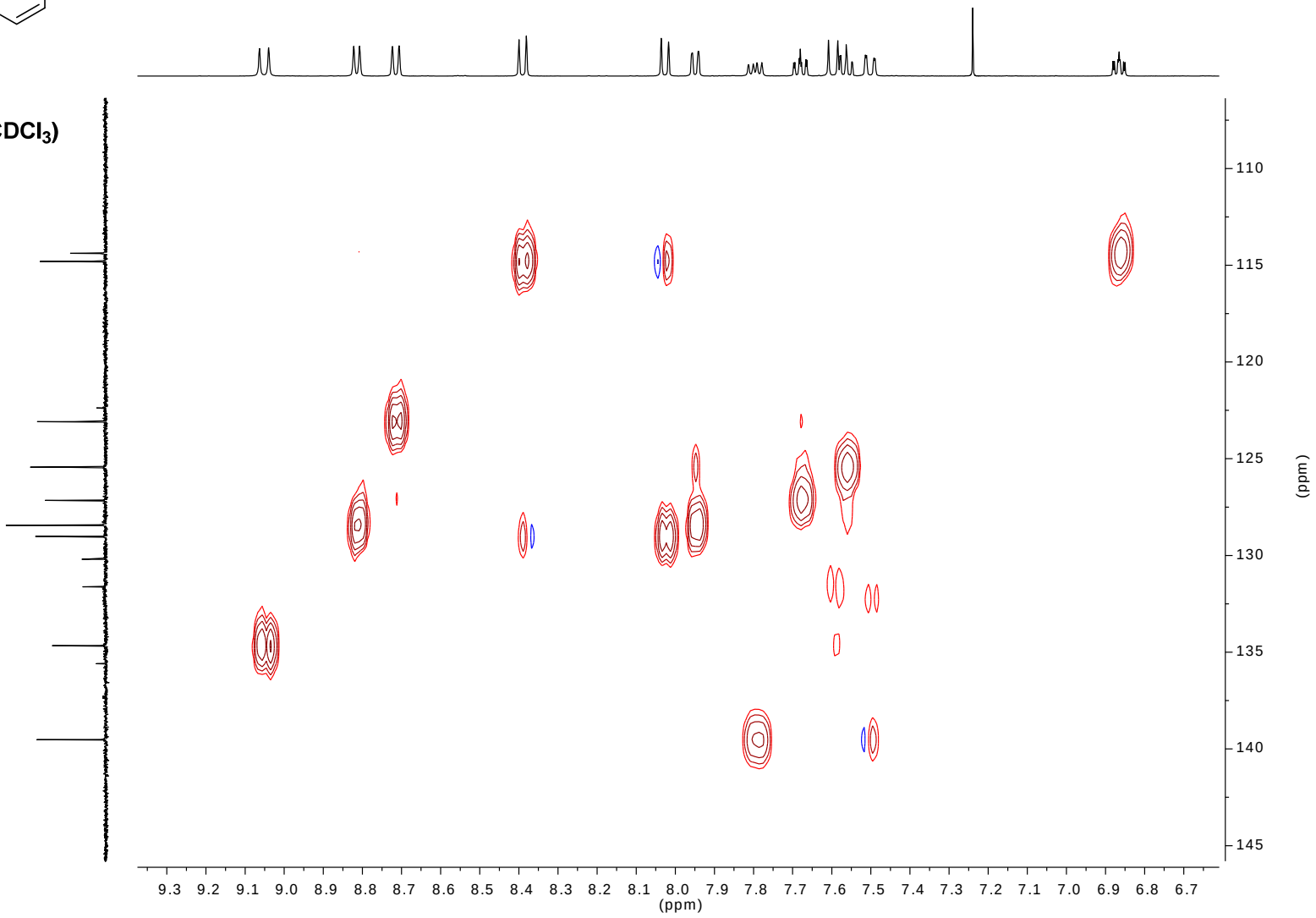


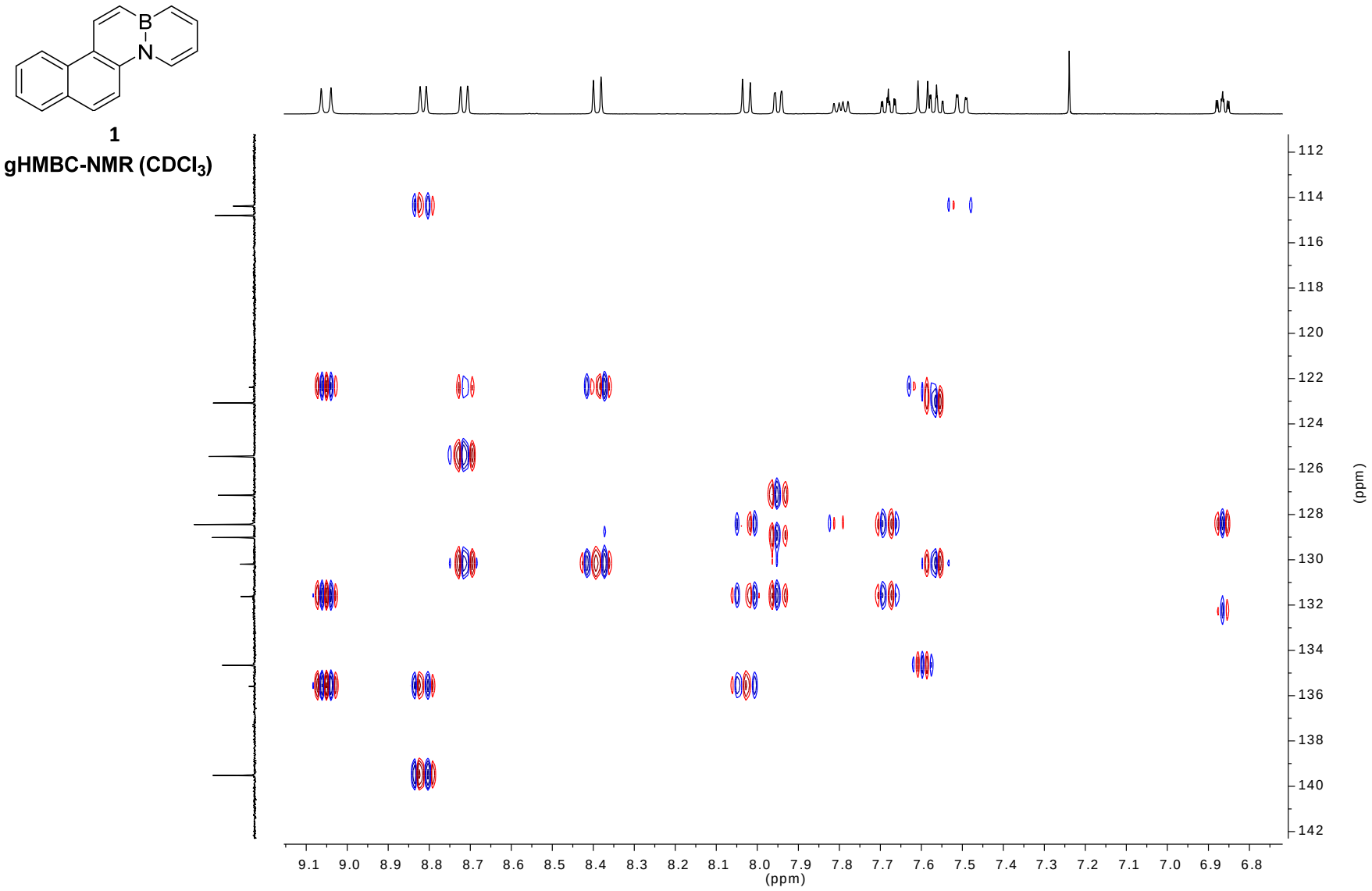

B
N
1
NOESY-NMR (CDCl3)
9.2 9.1 9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
(ppm)
7.0
7.5
8.0
8.5
9.0
(ppm)

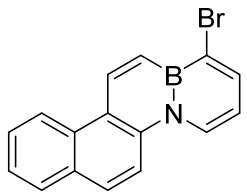


1

gHSQC-NMR ($CDCl_3$)

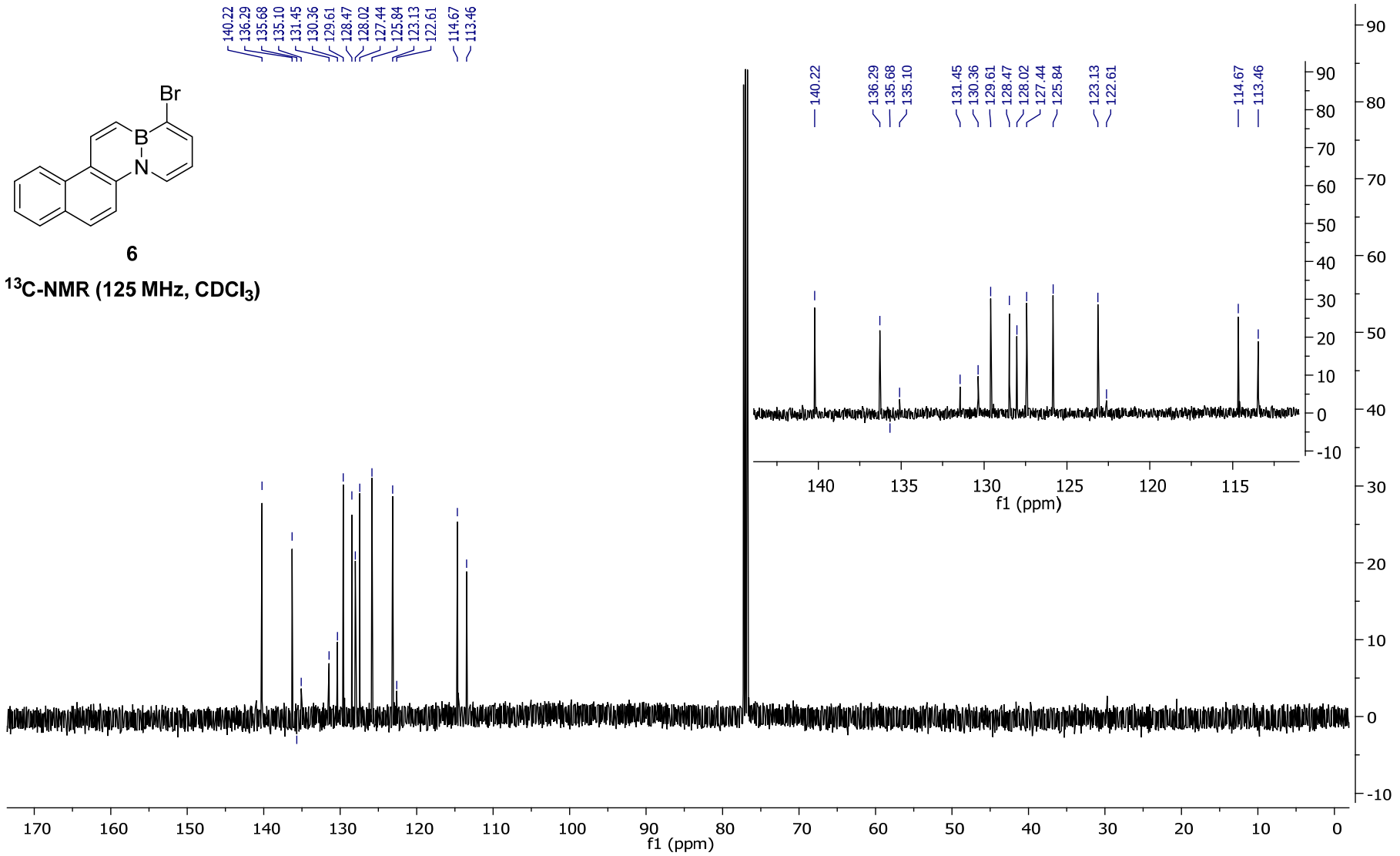


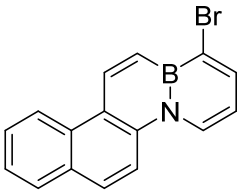

B
N
1
gHMBC-NMR (CDCl3)
9.1 9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
(ppm)
112 114 116 118 120 122 124 126 128 130 132 134 136 138 140 142
(ppm)



6

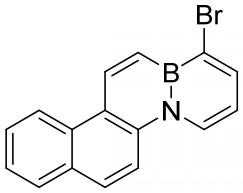
^{1}H-NMR (500 MHz, $CDCl_3$)


140.22
136.29
135.68
135.10
131.45
130.36
129.61
128.47
128.02
127.44
125.84
123.13
122.61
114.67
113.46
Br
B
N
6
^{13}C-NMR (125 MHz, CDCl$_3$)
f1 (ppm)



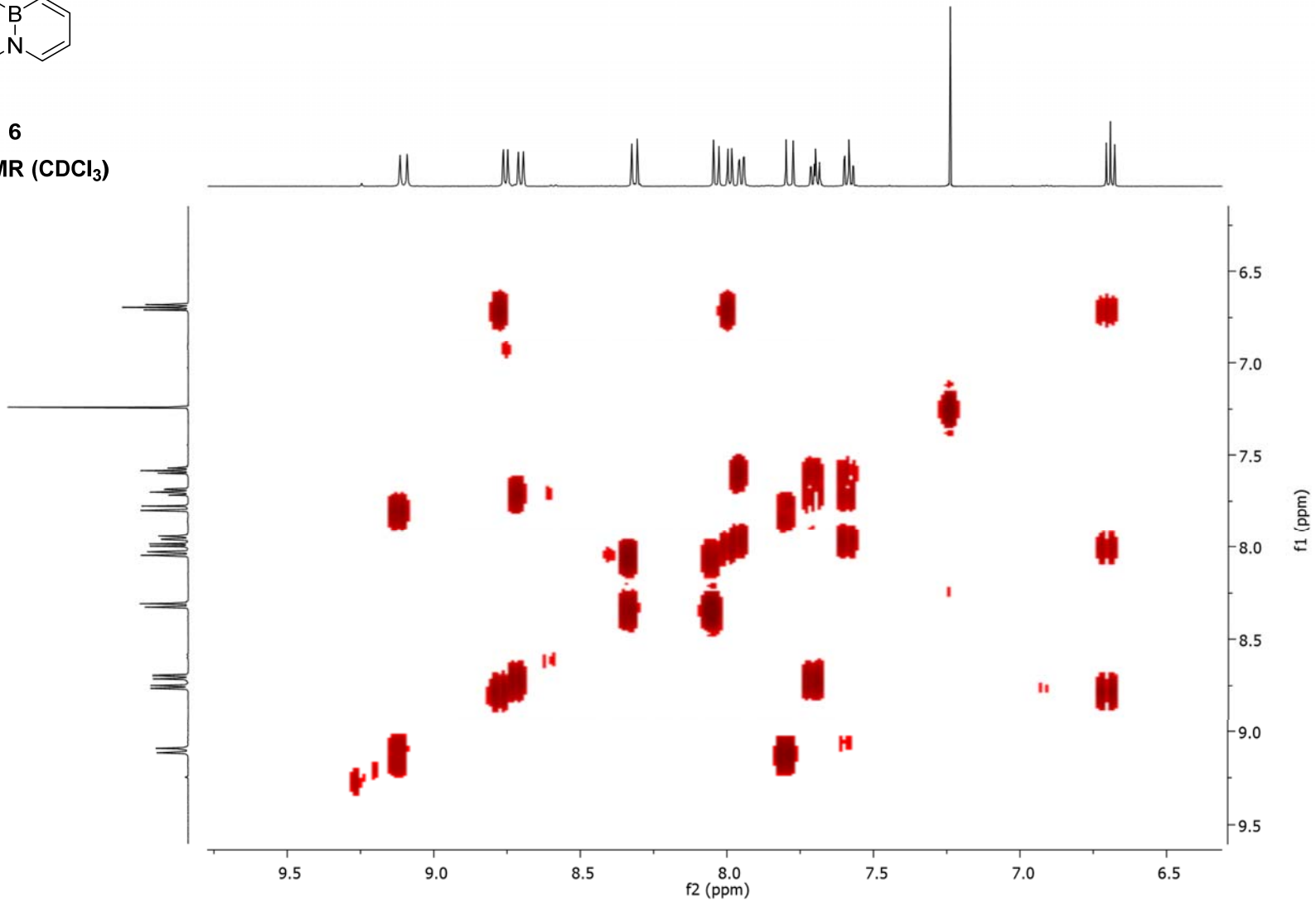
6

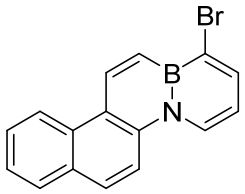
^{11}B-NMR (160 MHz, $CDCl_3$)



6

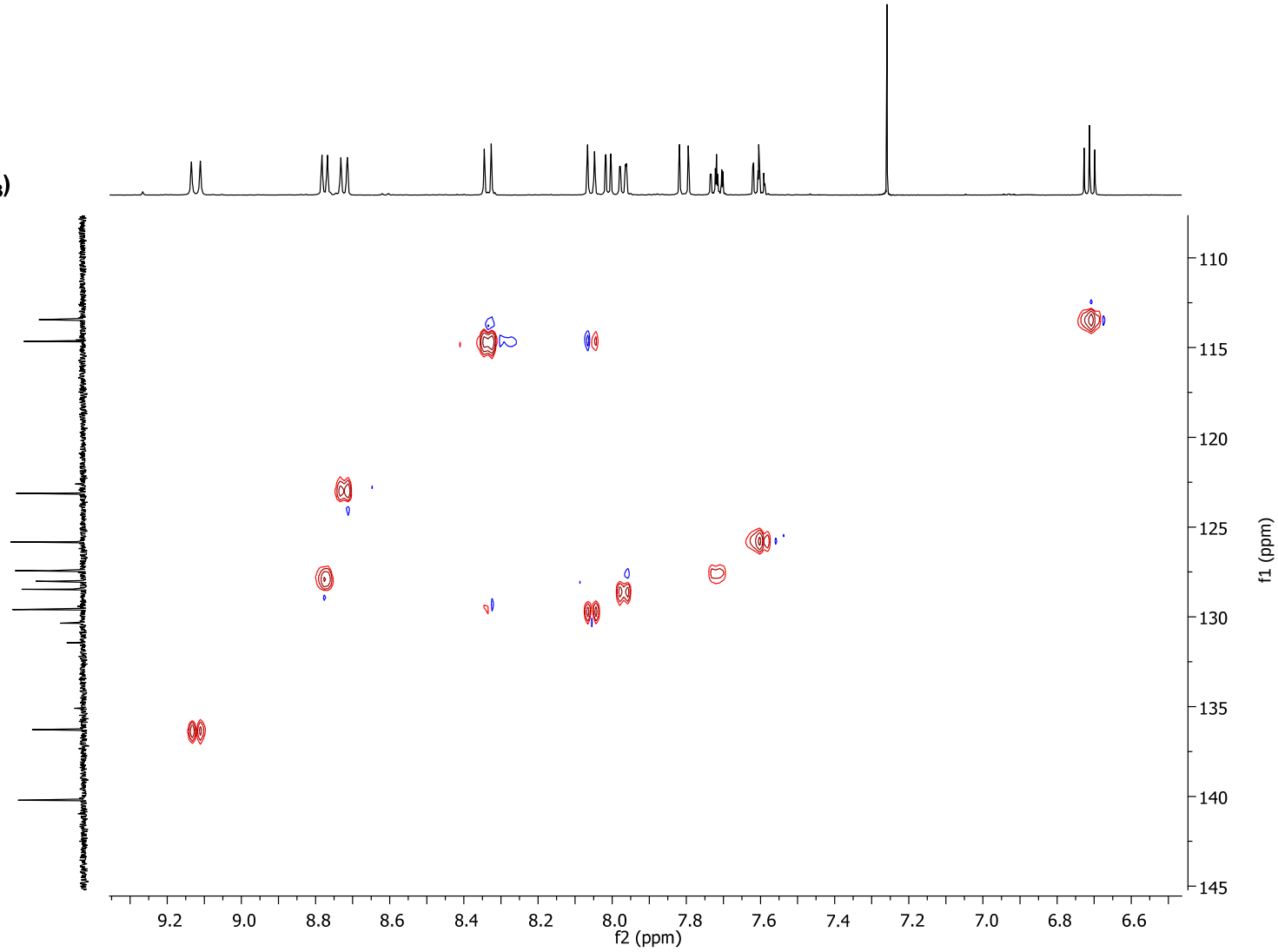
gCOSY-NMR ($CDCl_3$)

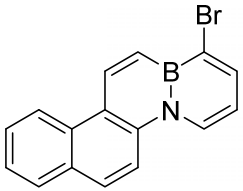




6

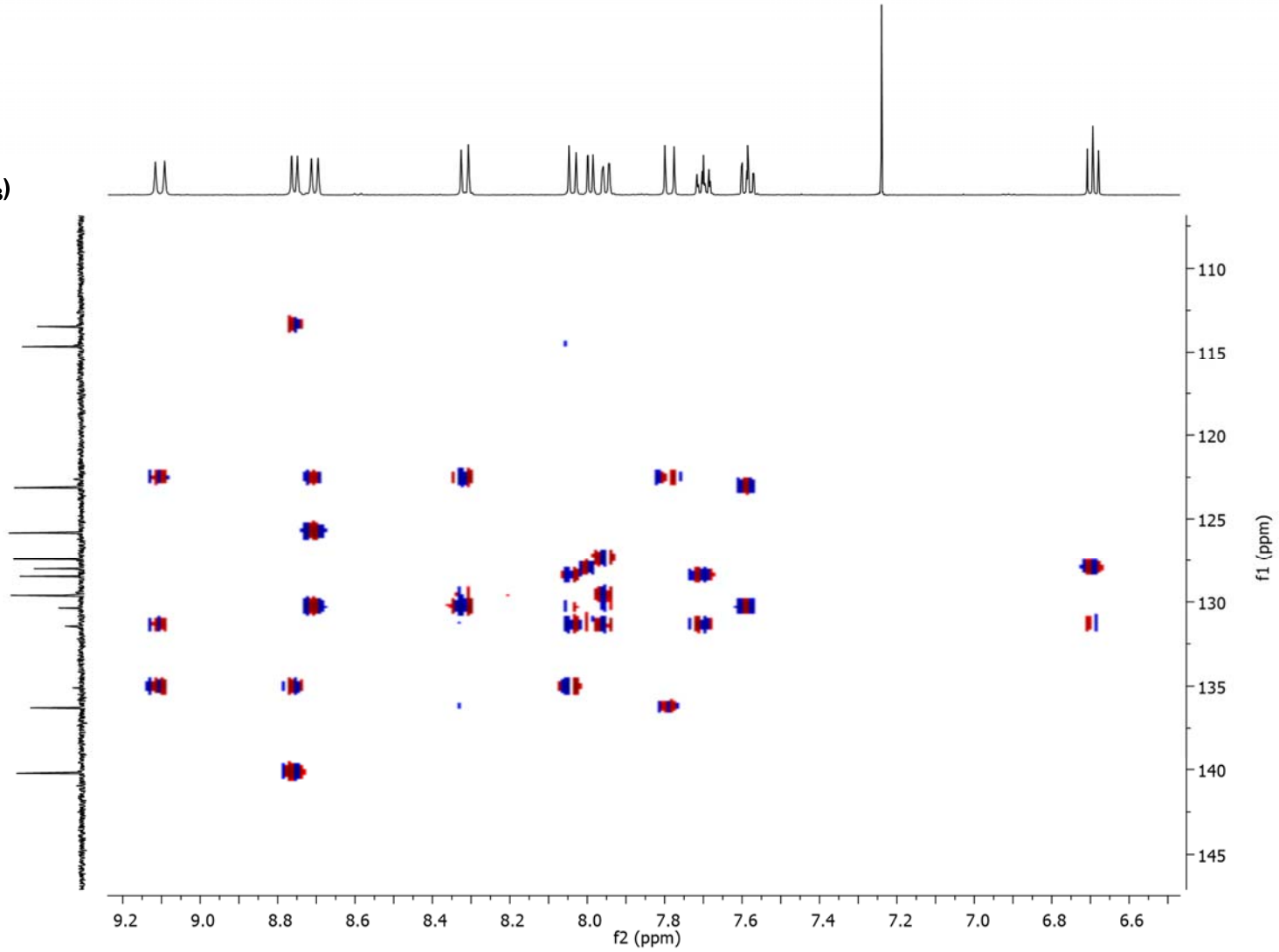
gHSQC-NMR ($CDCl_3$)

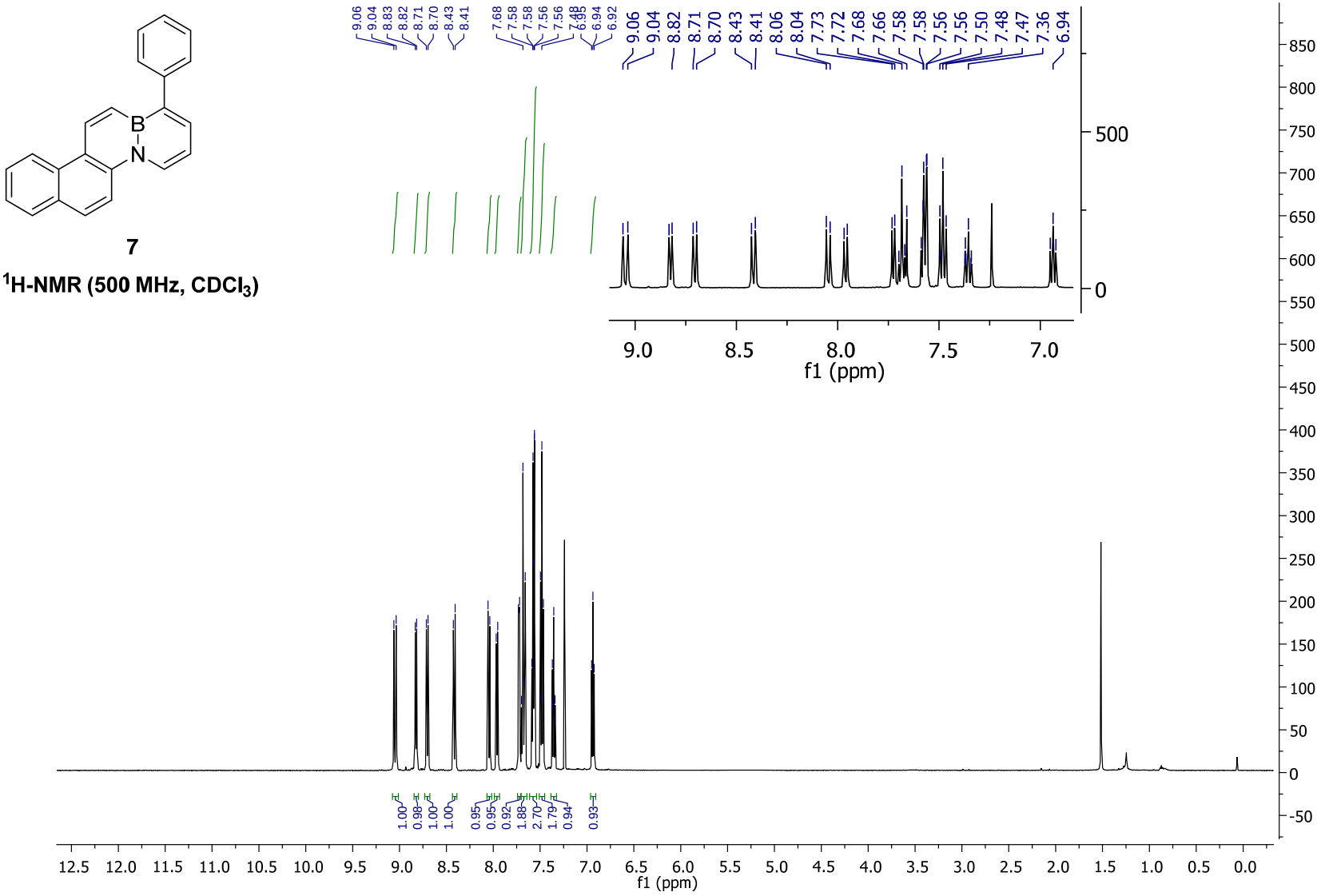




6

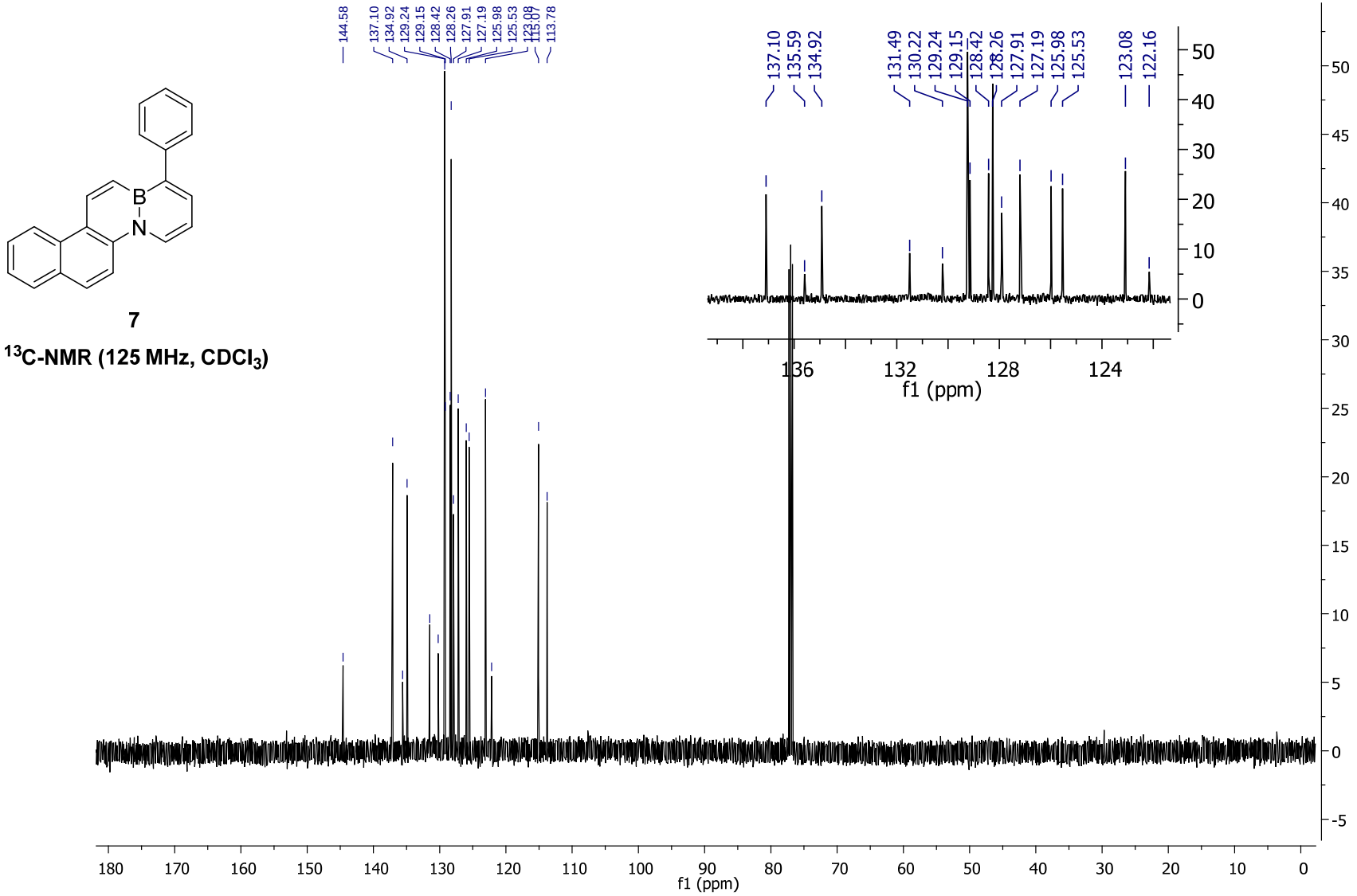
gHMBC-NMR ($CDCl_3$)

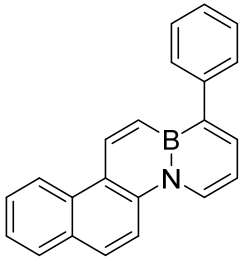




7

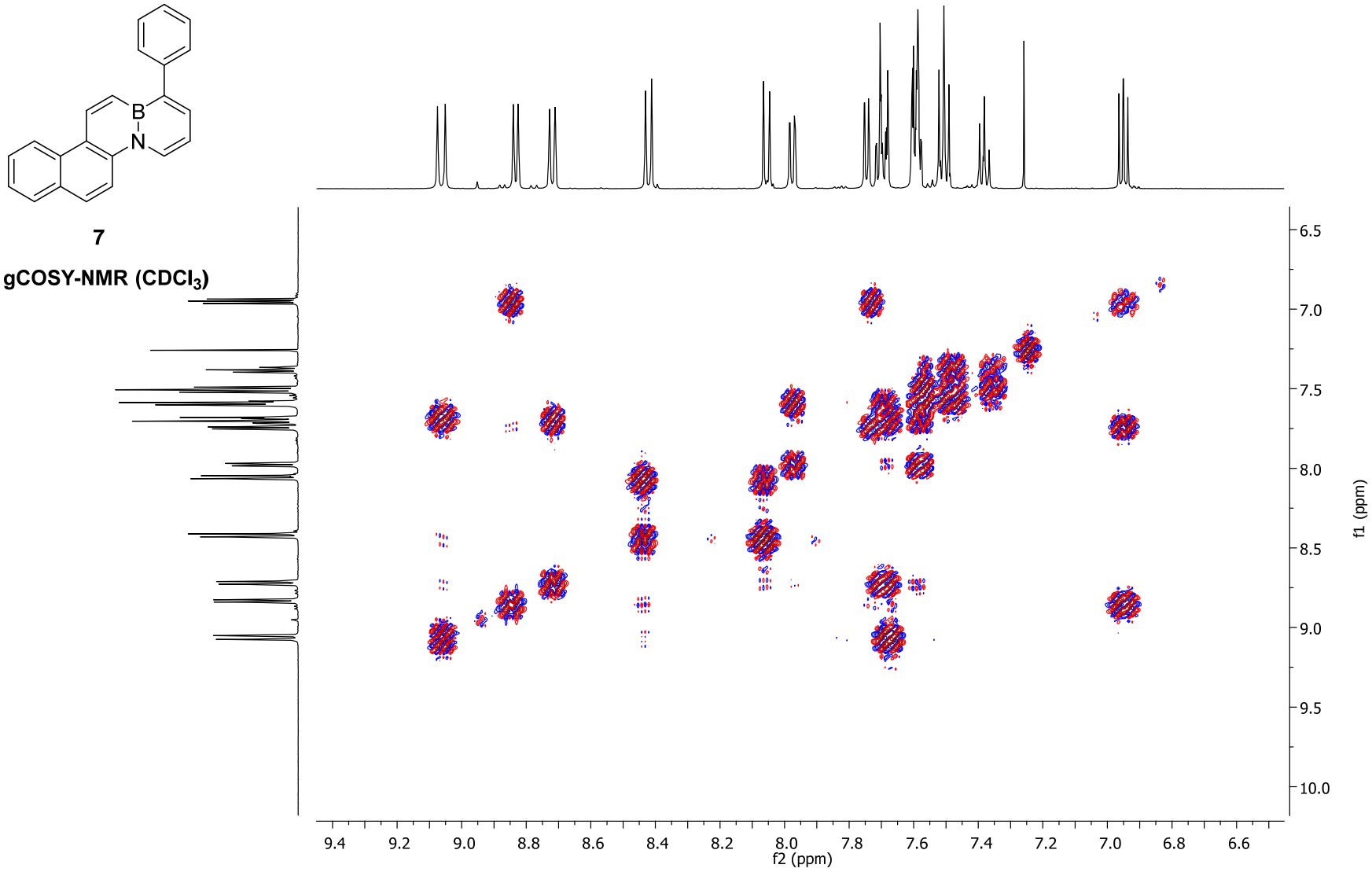
^{1}H-NMR (500 MHz, $CDCl_3$)

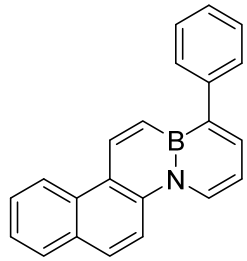

144.58
137.10
134.92
129.24
129.15
128.42
128.26
127.91
127.19
125.98
125.53
123.08
122.16
113.78
B
N
7
13C-NMR (125 MHz, CDCl3)
f1 (ppm)



7

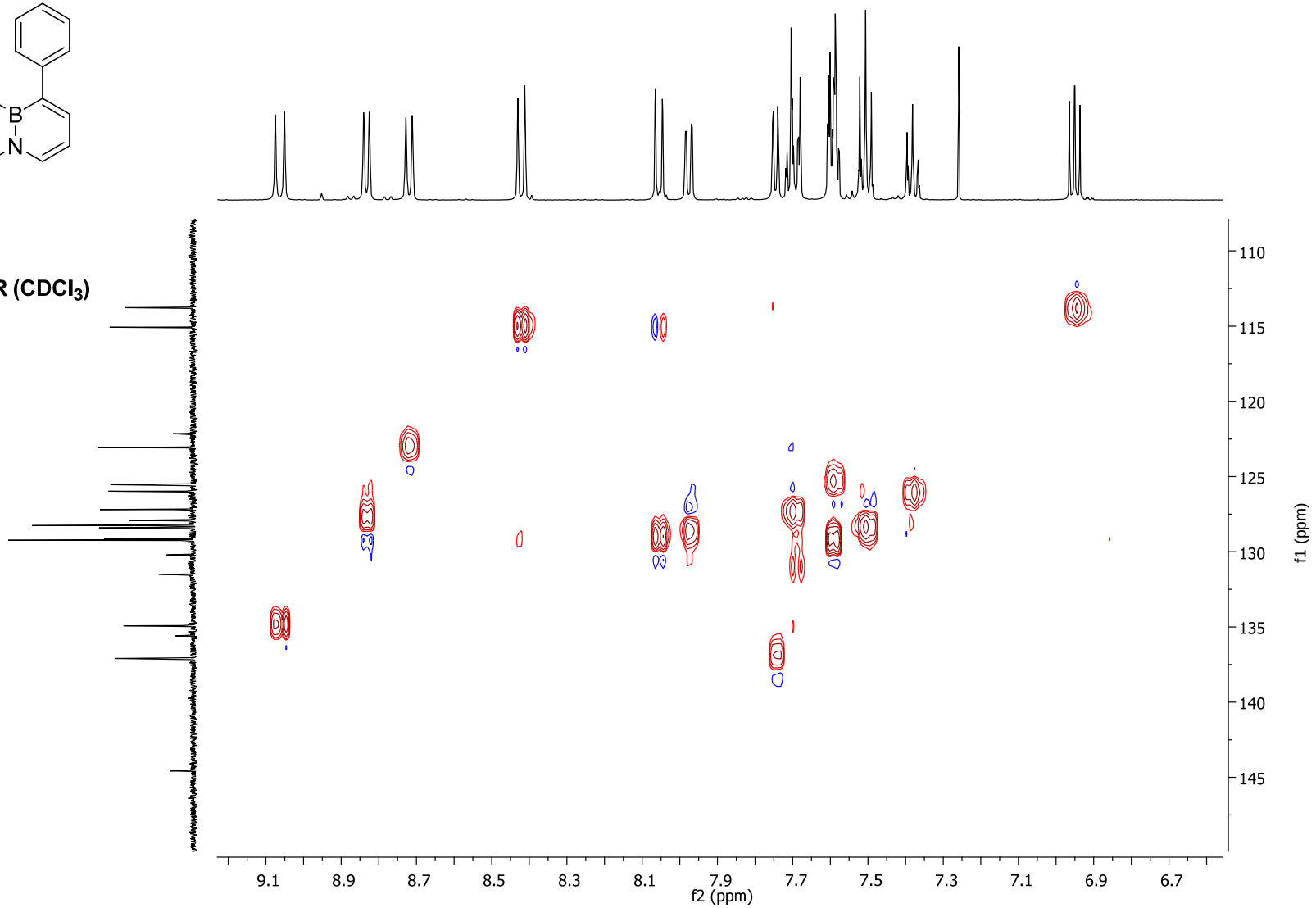
^{11}B-NMR (160 MHz, $CDCl_3$)

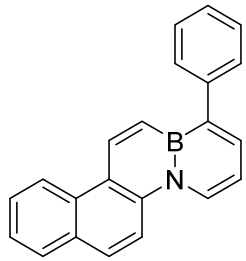

B
N
7
gCOSY-NMR (CDCl3)
9.4
9.2
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
f2 (ppm)
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
f1 (ppm)



7

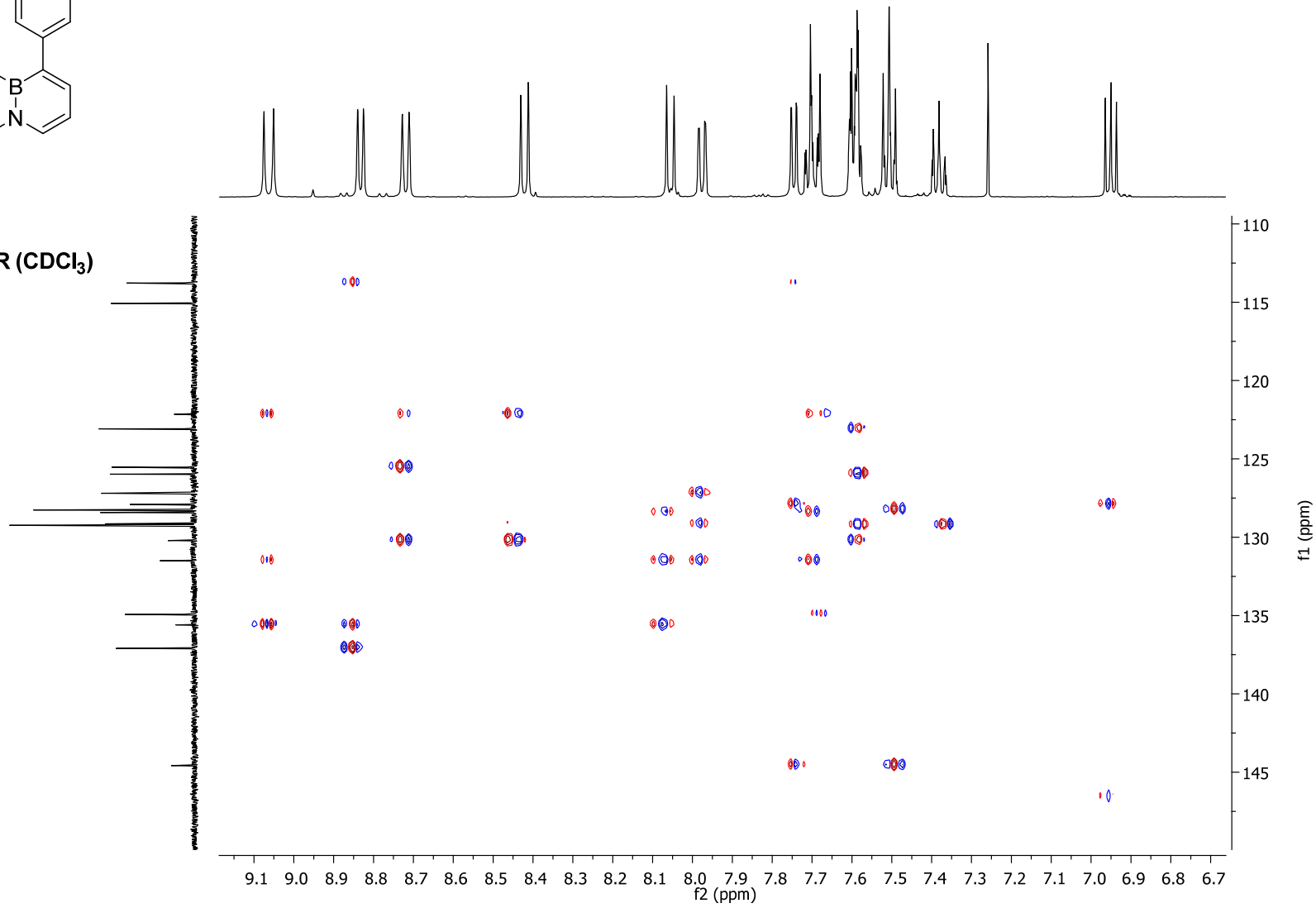
gHSQC-NMR ($CDCl_3$)





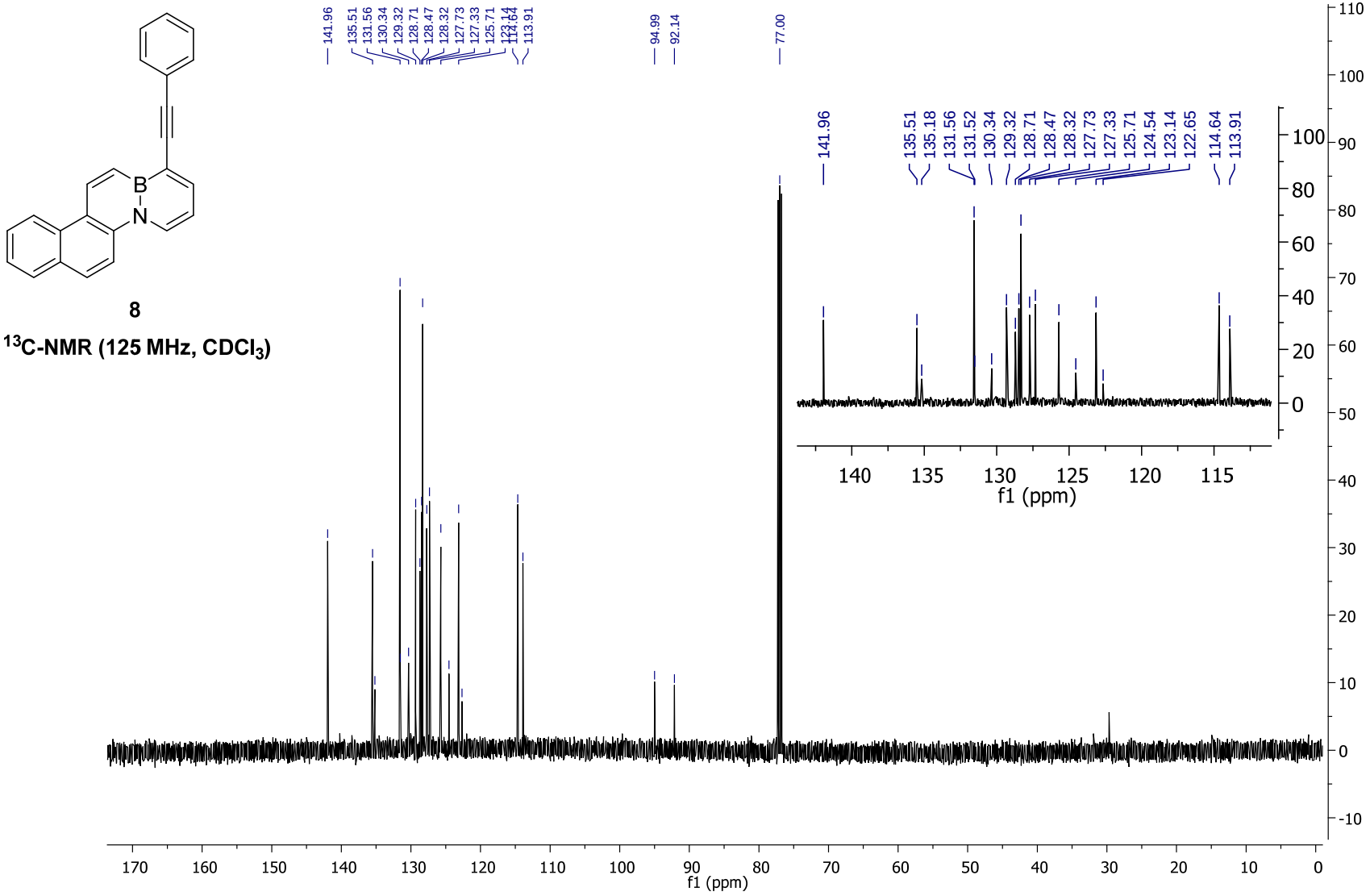
7

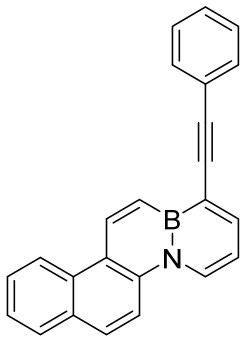
gHMBC-NMR ($CDCl_3$)



8

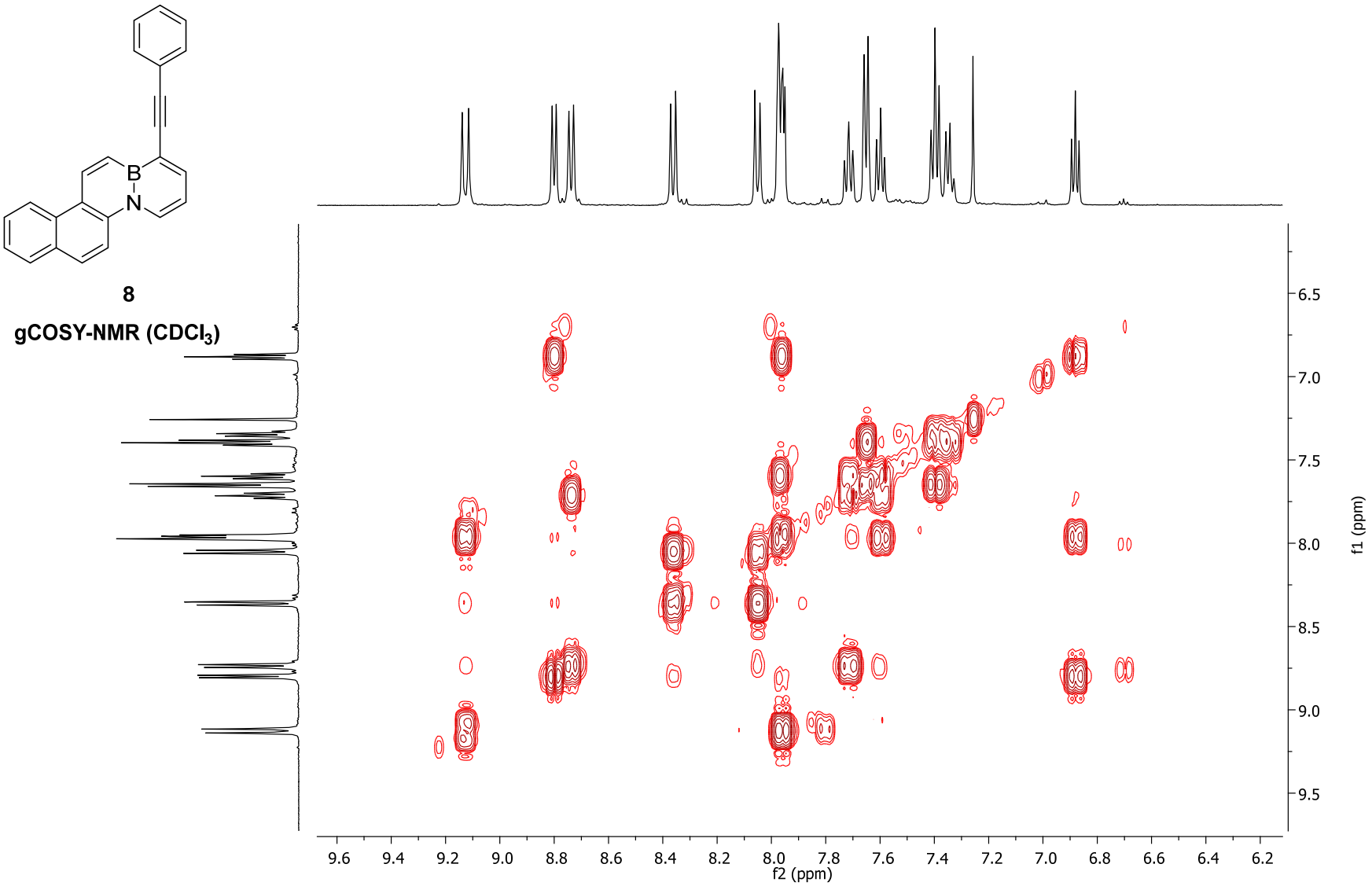
^{1}H-NMR (500 MHz, $CDCl_3$)

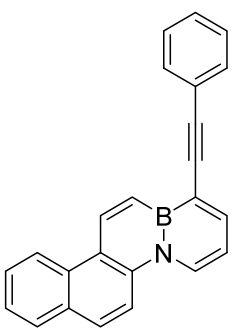

141.96
135.51
131.56
130.34
129.32
128.71
128.47
128.32
127.73
127.33
125.71
123.14
114.64
113.91
94.99
92.14
77.00
B
N
8
13C-NMR (125 MHz, CDCl3)
f1 (ppm)



8

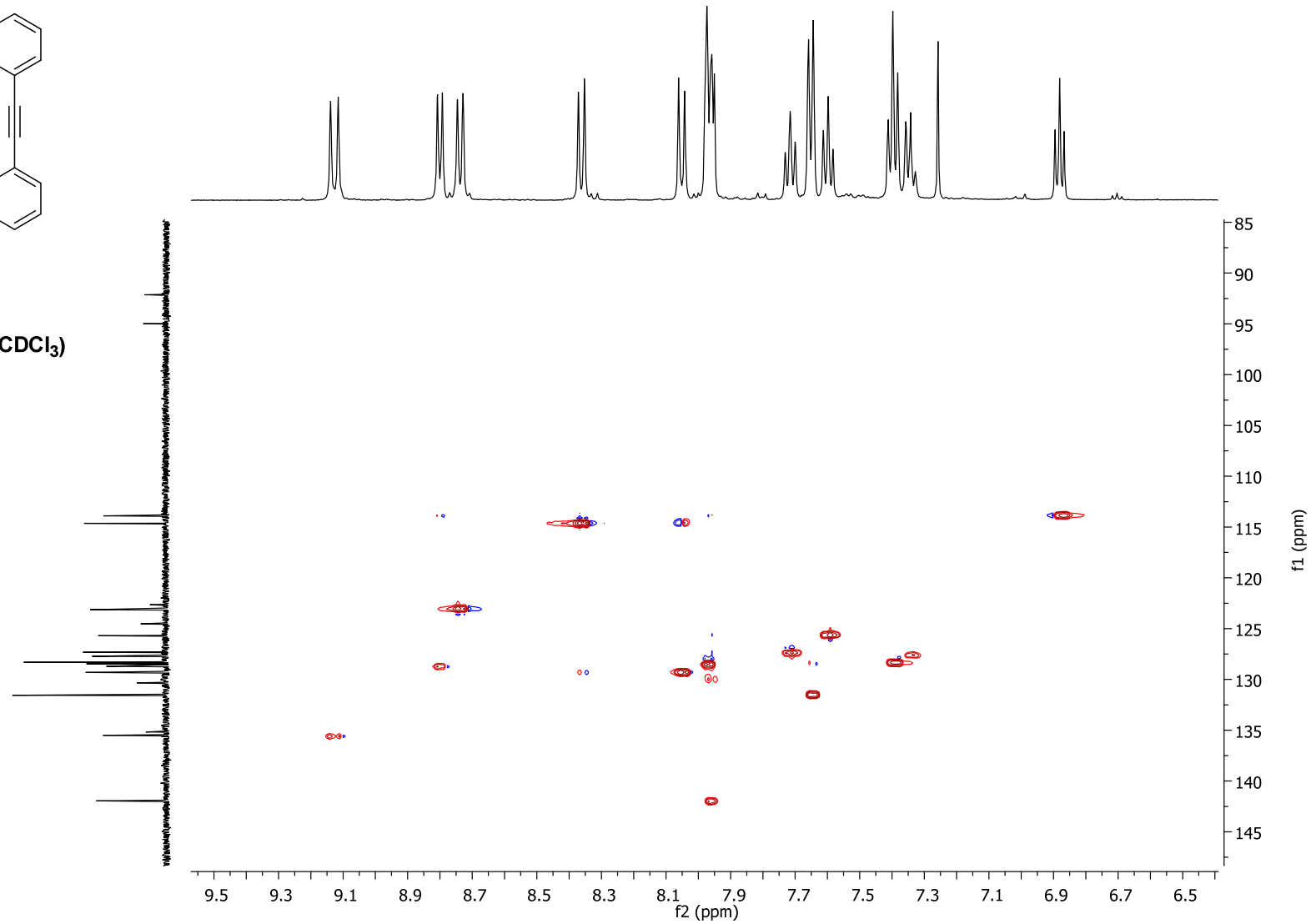
^{11}B-NMR (160 MHz, $CDCl_3$)

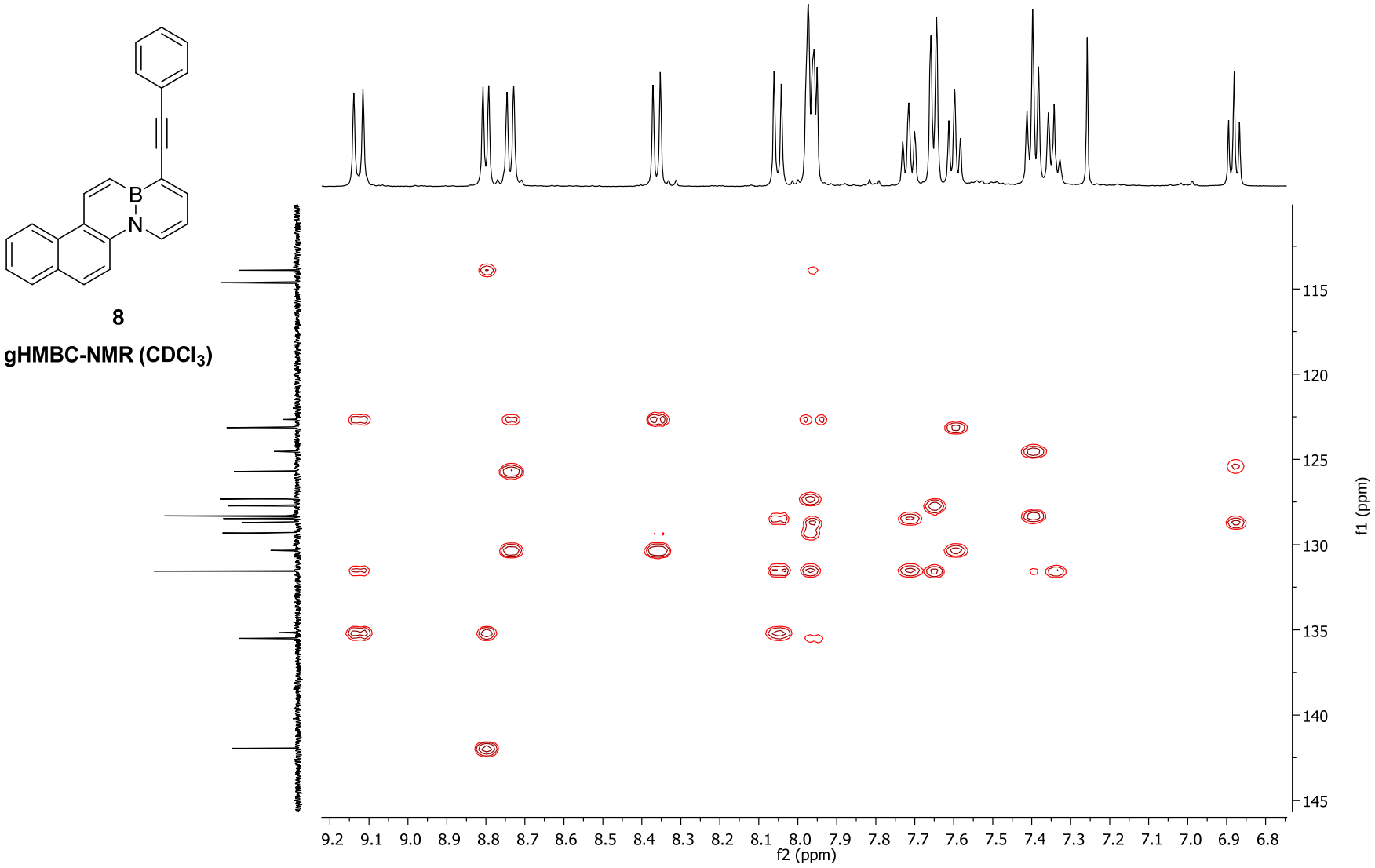

B
N
8
gCOSY-NMR (CDCl3)
9.6
9.4
9.2
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
f2 (ppm)
6.5
7.0
7.5
8.0
8.5
9.0
9.5
f1 (ppm)

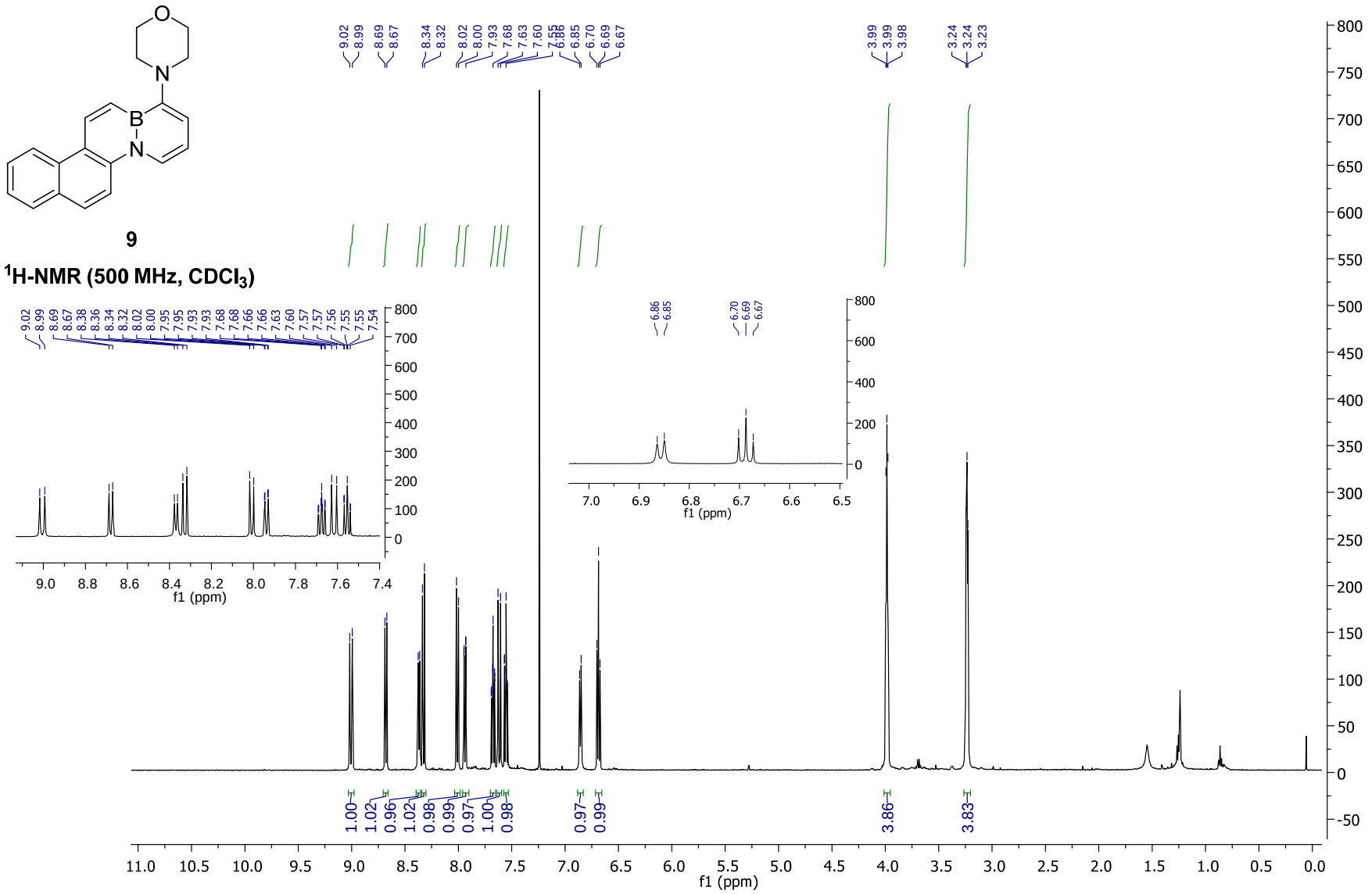


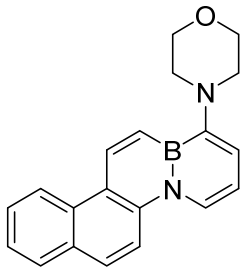
8

gHSQC-NMR ($CDCl_3$)



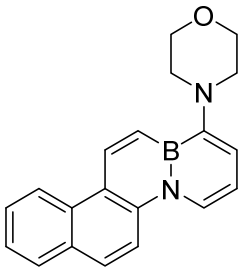

B
N
8
gHMBC-NMR (CDCl3)
9.2 9.1 9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
f2 (ppm)
115 120 125 130 135 140 145
f1 (ppm)


9
1H-NMR (500 MHz, CDCl3)
f1 (ppm)



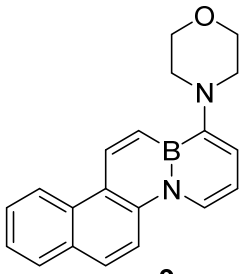
9

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



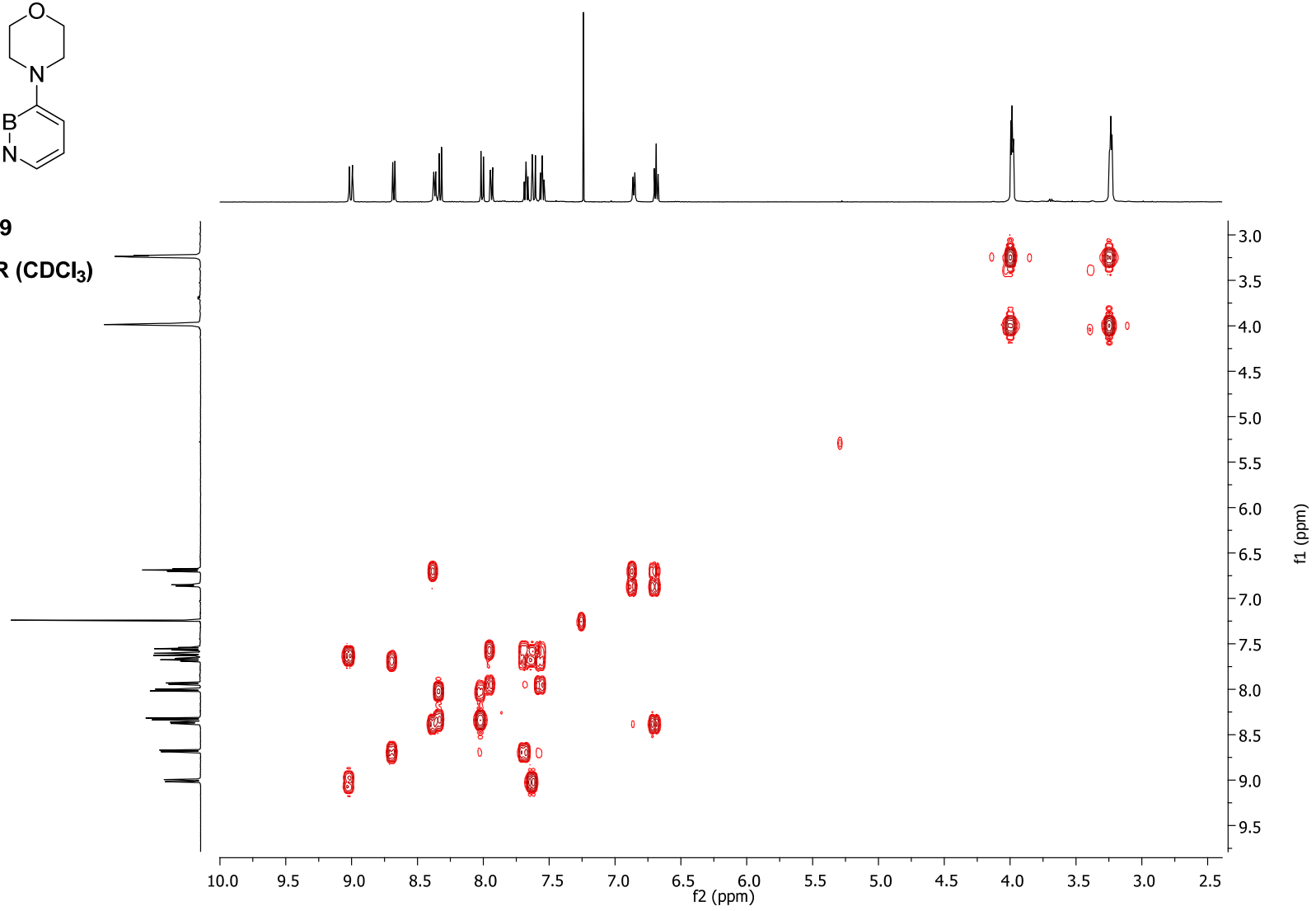
9

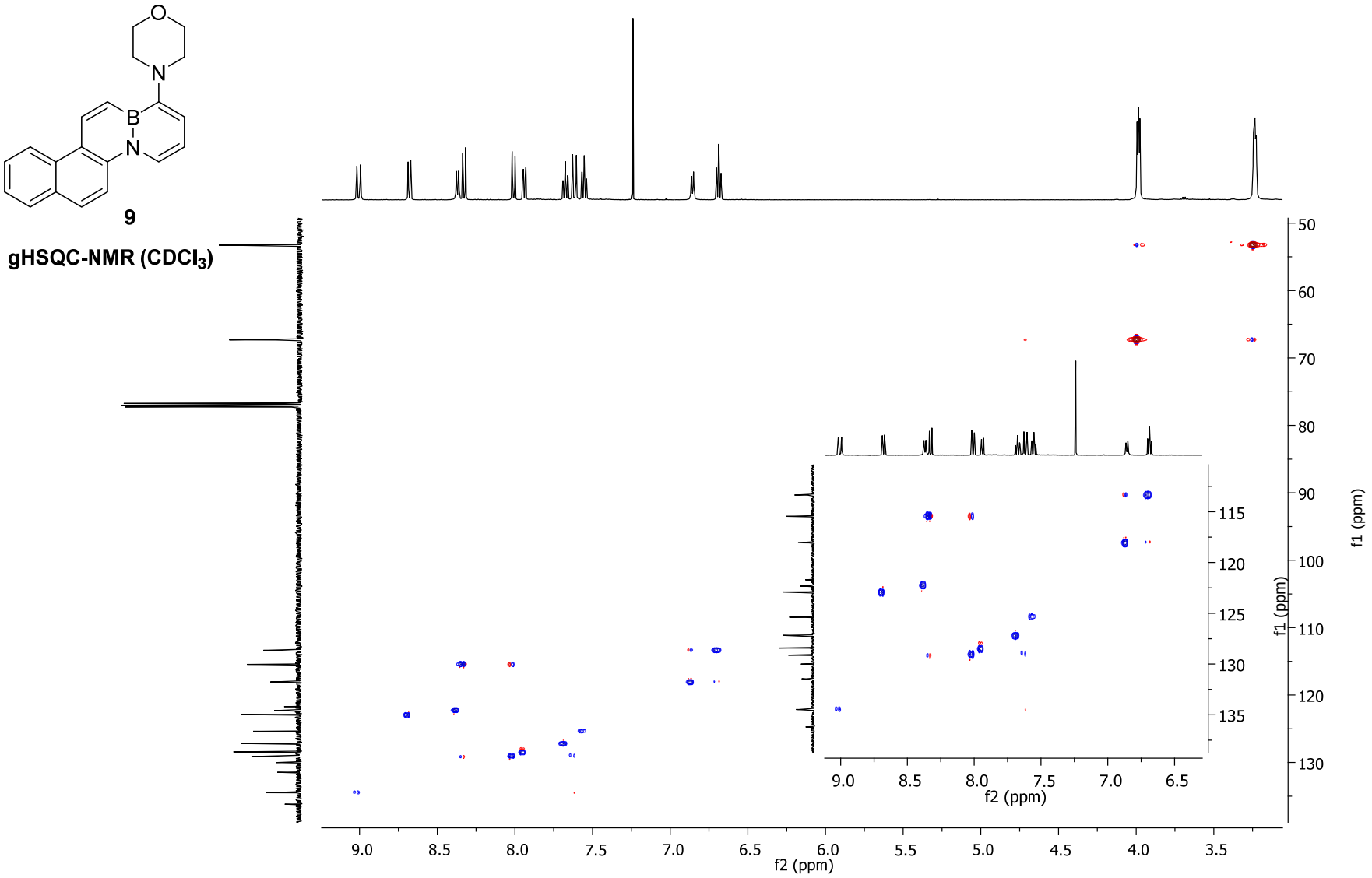
^{11}B-NMR (160 MHz, $CDCl_3$)

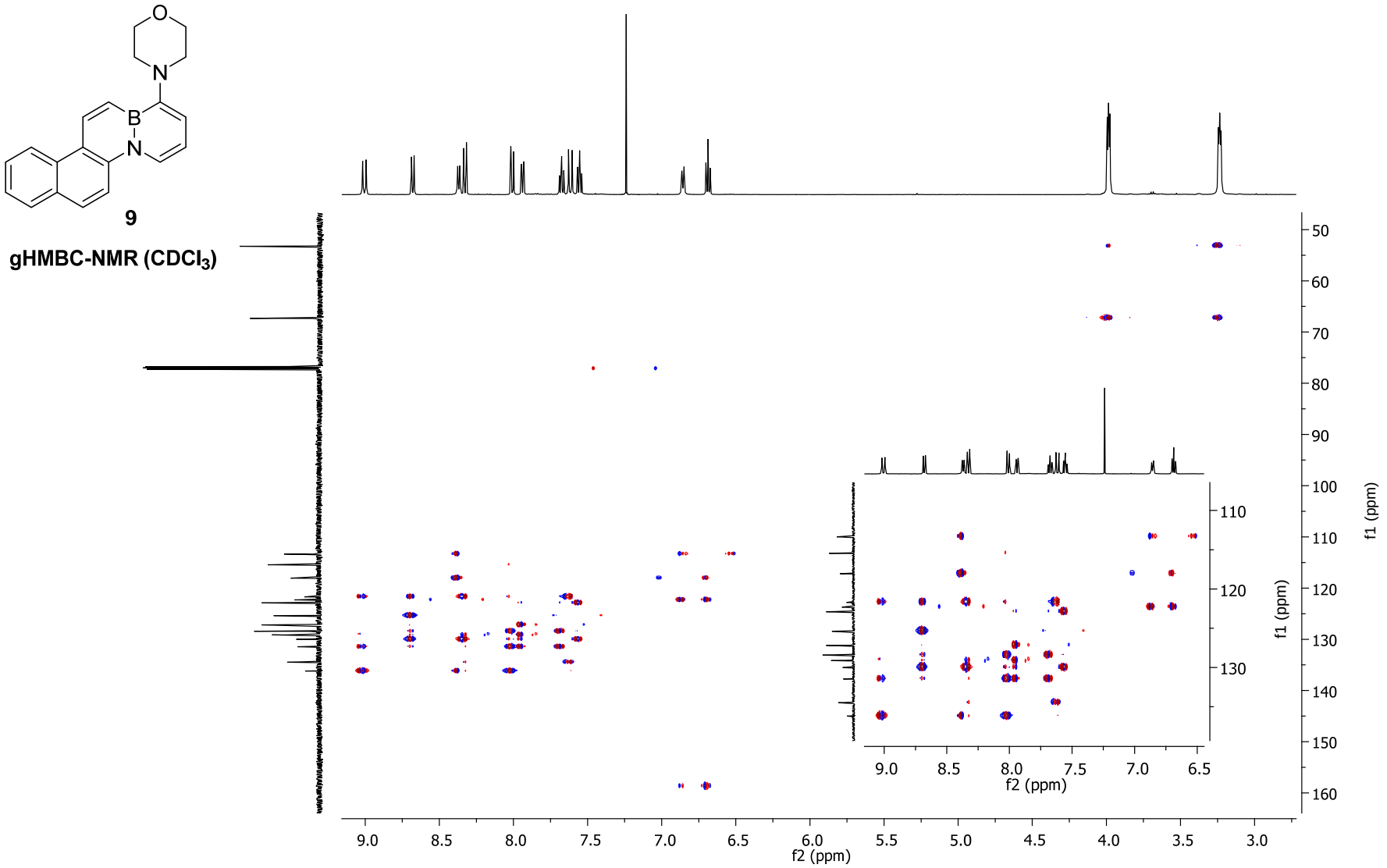


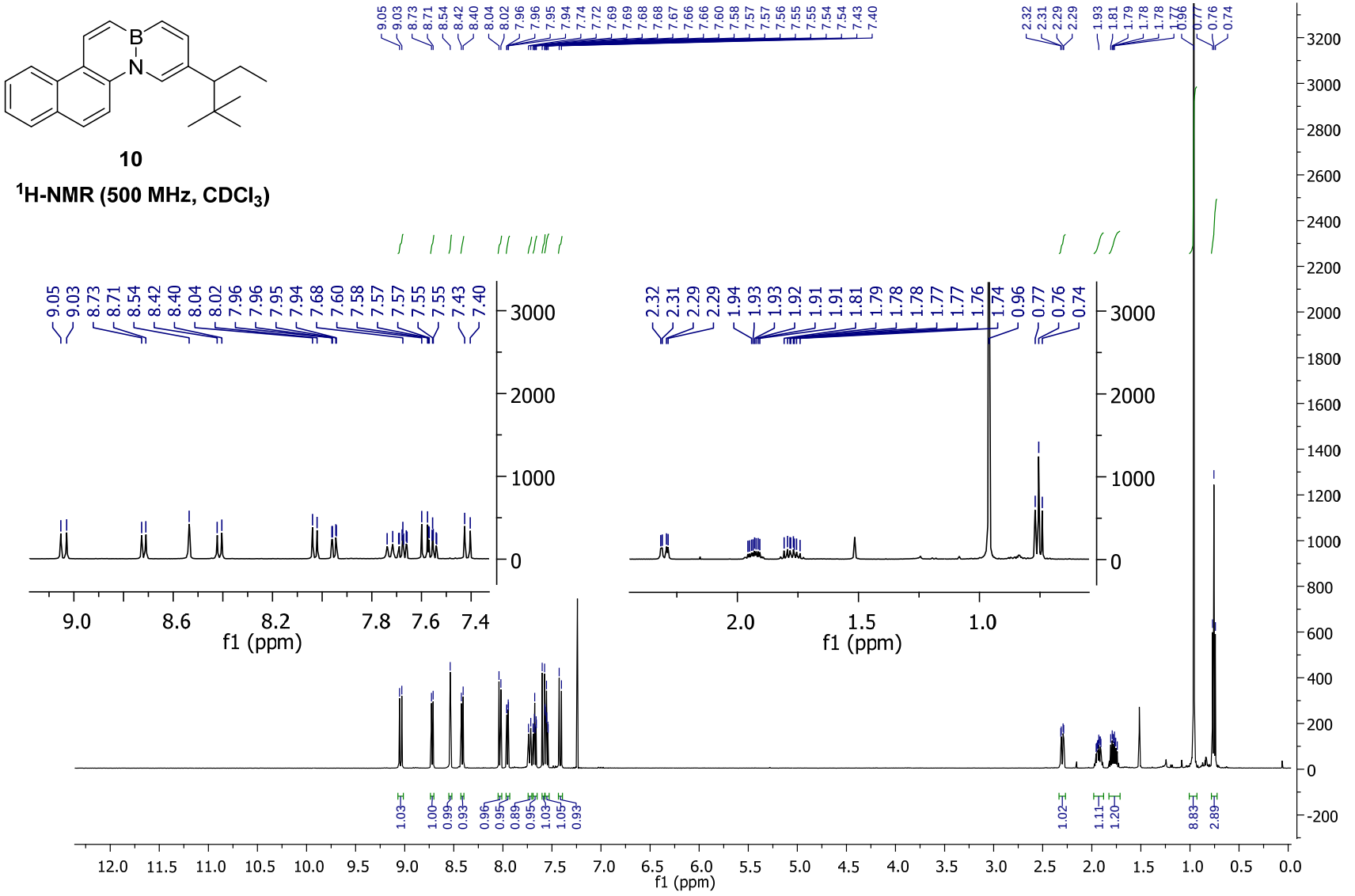
9

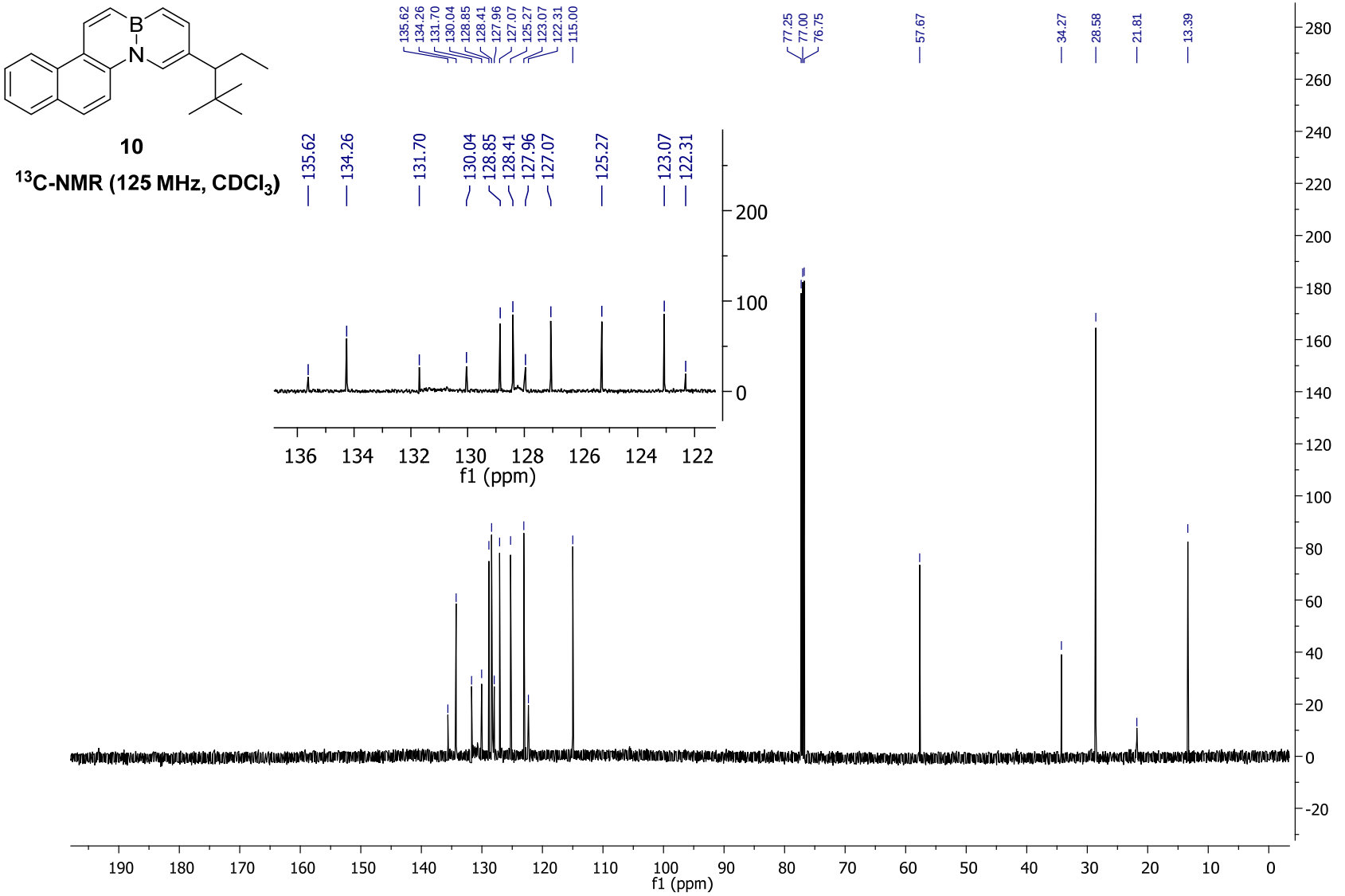
gCOSY-NMR ($CDCl_3$)

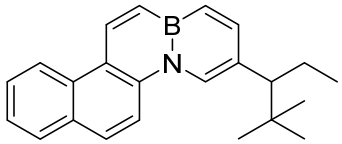



O
N
B
N
9
gHSQC-NMR (CDCl3)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
f2 (ppm)
50
60
70
80
90
100
110
120
130
f1 (ppm)
115
120
125
130
135
120
130
9.0
8.5
8.0
7.5
7.0
6.5
f2 (ppm)
f1 (ppm)


O
N
B
N
9
gHMBC-NMR (CDCl3)
f2 (ppm)
f1 (ppm)

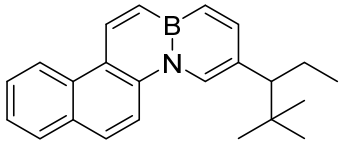

B
N
10
1H-NMR (500 MHz, CDCl3)
f1 (ppm)


10
13C-NMR (125 MHz, CDCl3)
135.62
134.26
131.70
130.04
128.85
128.41
127.96
127.07
125.27
123.07
122.31
115.00
77.25
77.00
76.75
57.67
34.27
28.58
21.81
13.39
f1 (ppm)



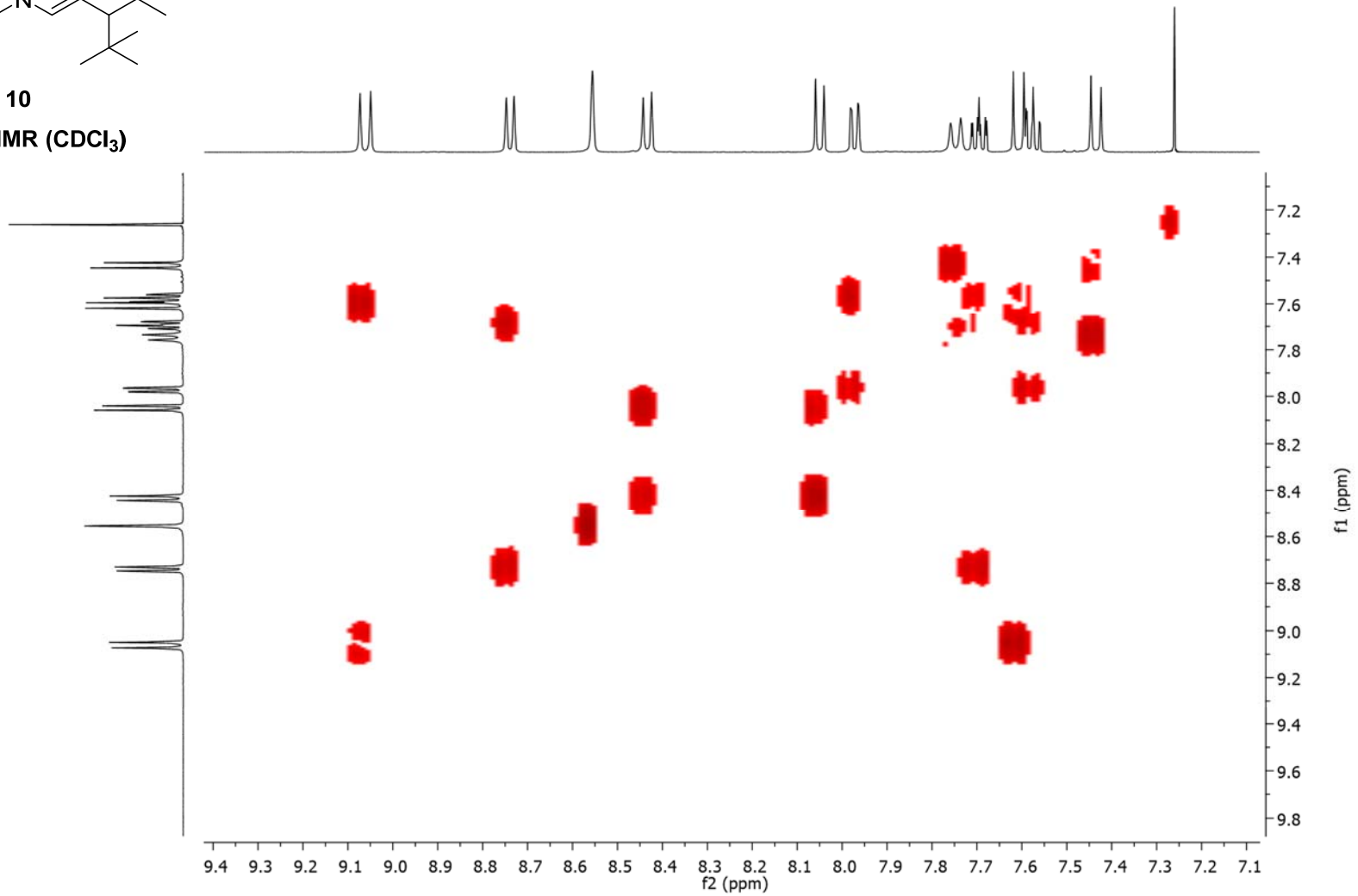
10

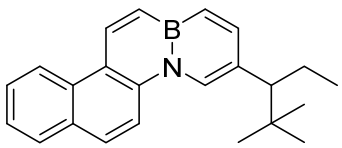
^{11}B-NMR (160 MHz, $CDCl_3$)



10

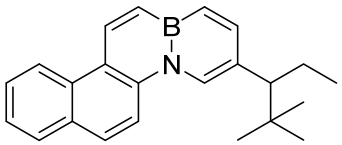
gCOSY-NMR ($CDCl_3$)





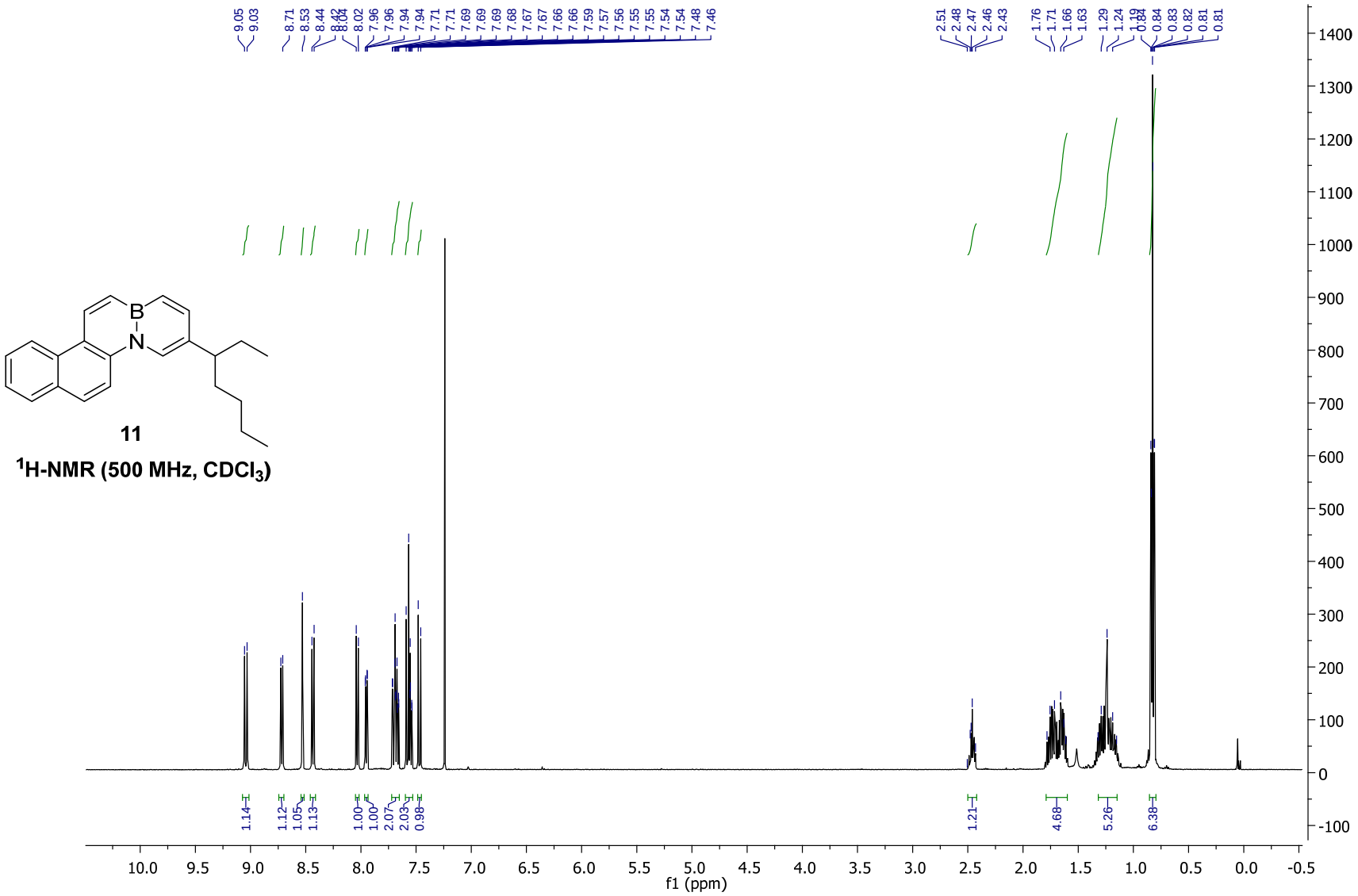
10

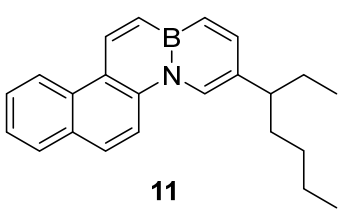
gHSQC-NMR ($CDCl_3$)



10

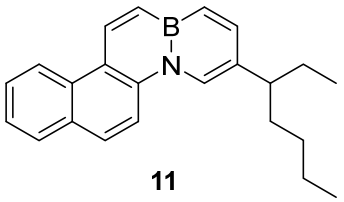
gHMBC-NMR ($CDCl_3$)


9.05
9.03
8.71
8.53
8.44
8.42
8.04
8.02
7.96
7.96
7.94
7.94
7.71
7.71
7.69
7.69
7.69
7.68
7.67
7.67
7.66
7.66
7.59
7.57
7.56
7.55
7.55
7.54
7.54
7.48
7.46
2.51
2.48
2.47
2.46
2.43
1.76
1.71
1.66
1.63
1.29
1.24
1.19
0.84
0.84
0.83
0.82
0.81
0.81
B
N
11
1H-NMR (500 MHz, CDCl3)
1.14
1.12
1.05
1.13
1.00
1.00
2.07
2.03
0.98
1.21
4.68
5.26
6.38
f1 (ppm)



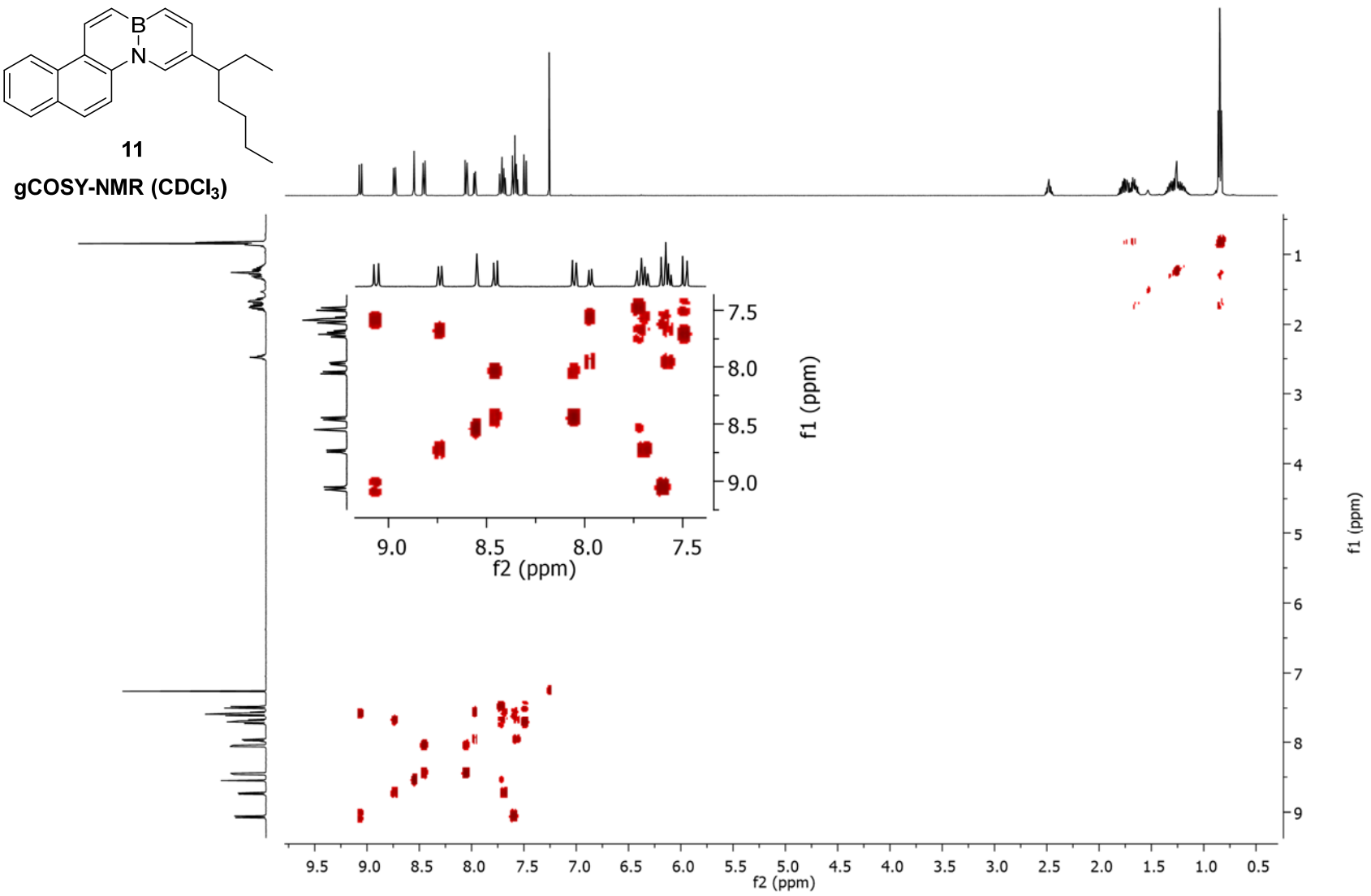
11

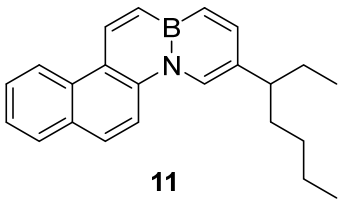
^{13}C-NMR (125 MHz, $CDCl_3$)



11

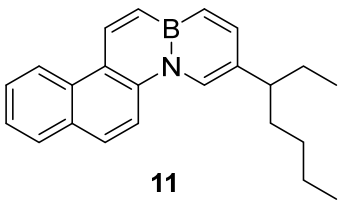
^{11}B-NMR (160 MHz, $CDCl_3$)


B
N
11
gCOSY-NMR (CDCl3)
f2 (ppm)
f1 (ppm)



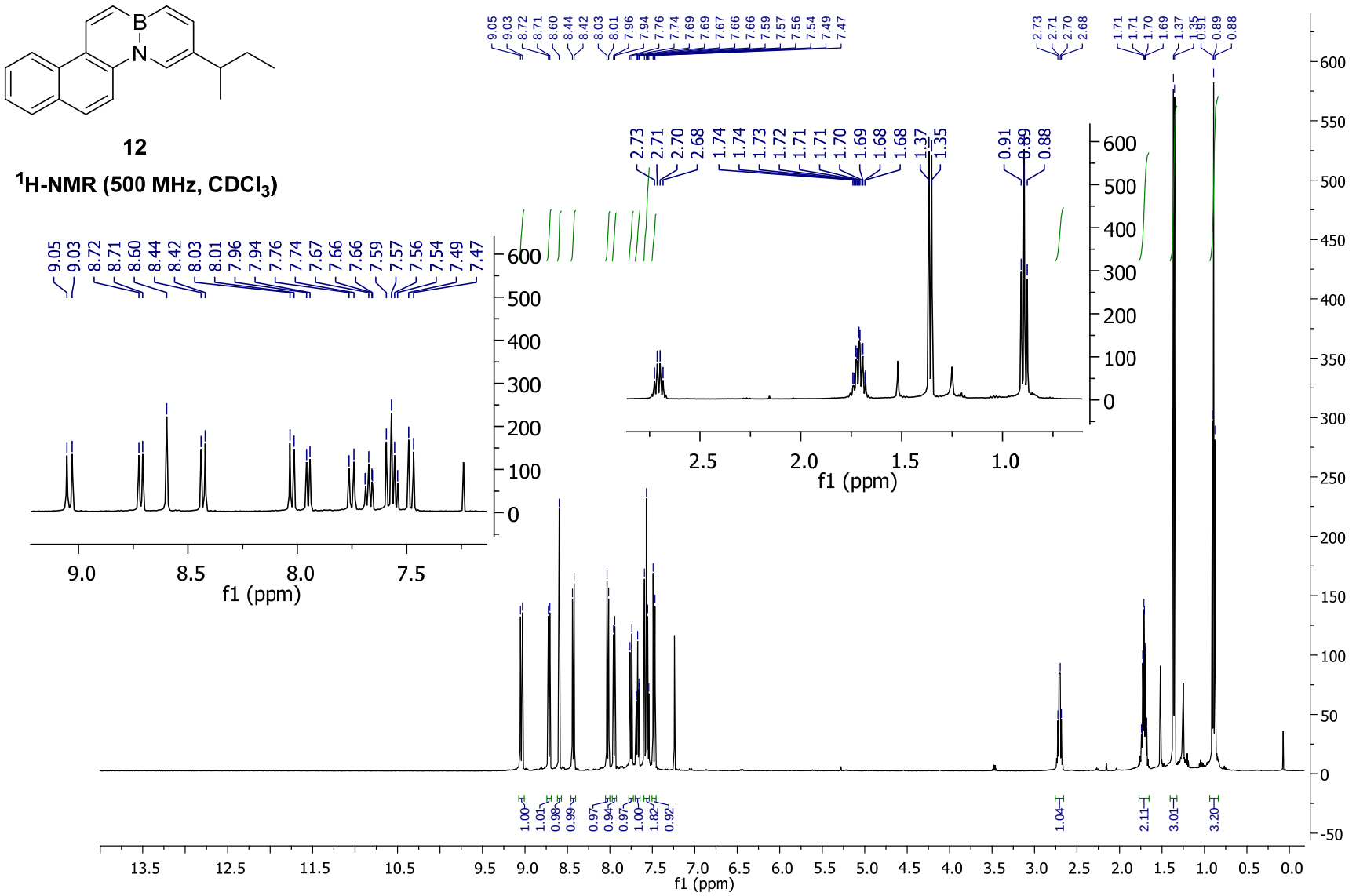
11

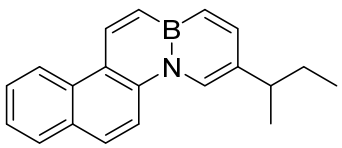
gHSQC-NMR ($CDCl_3$)



11

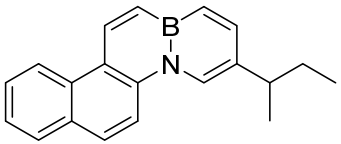
gHMBC-NMR ($CDCl_3$)


12
1H-NMR (500 MHz, CDCl3)
f1 (ppm)



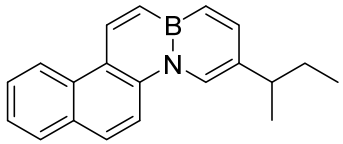
12

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



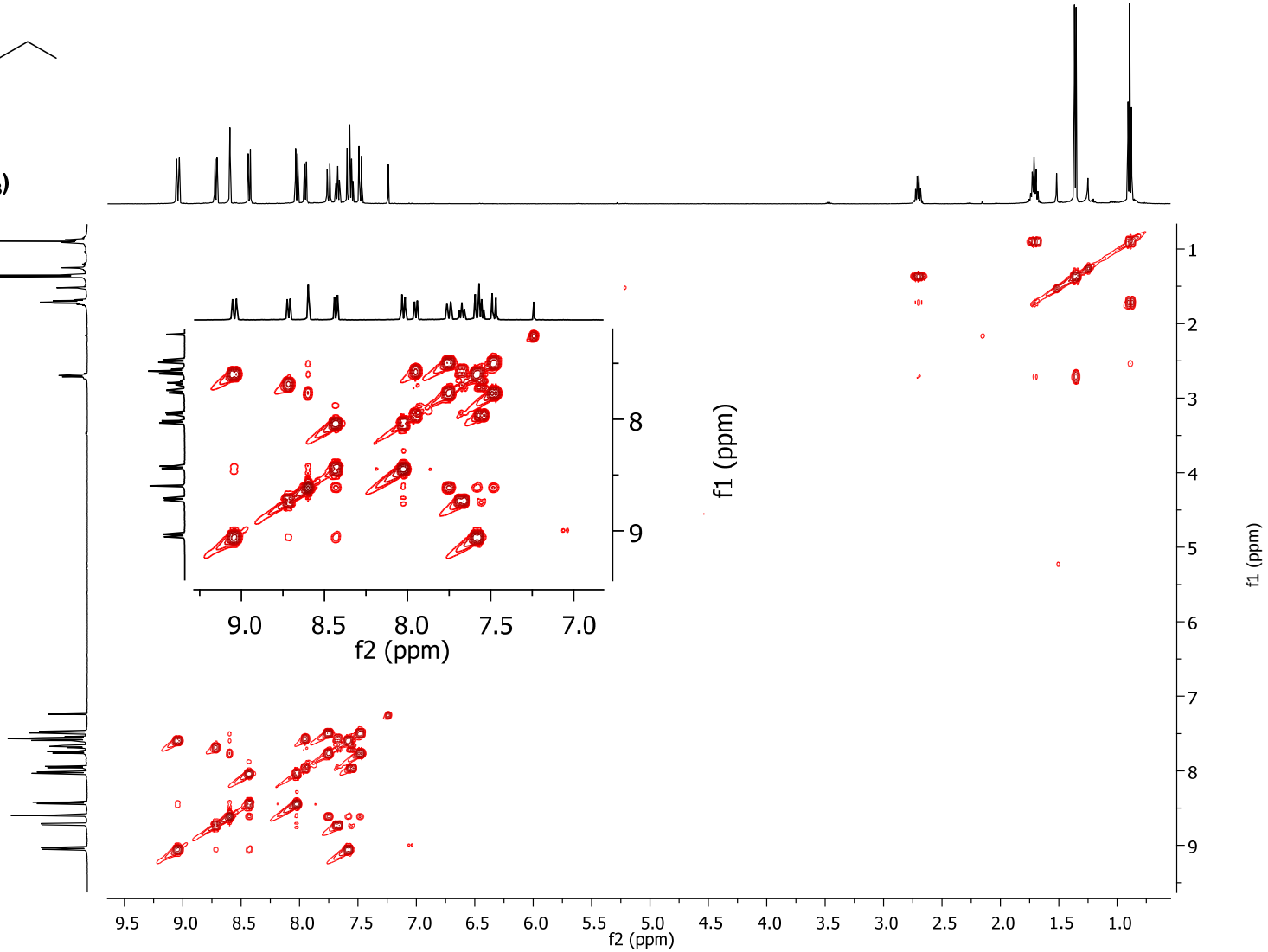
12

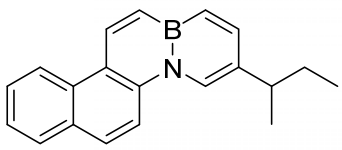
^{11}B-NMR (160 MHz, $CDCl_3$)



12

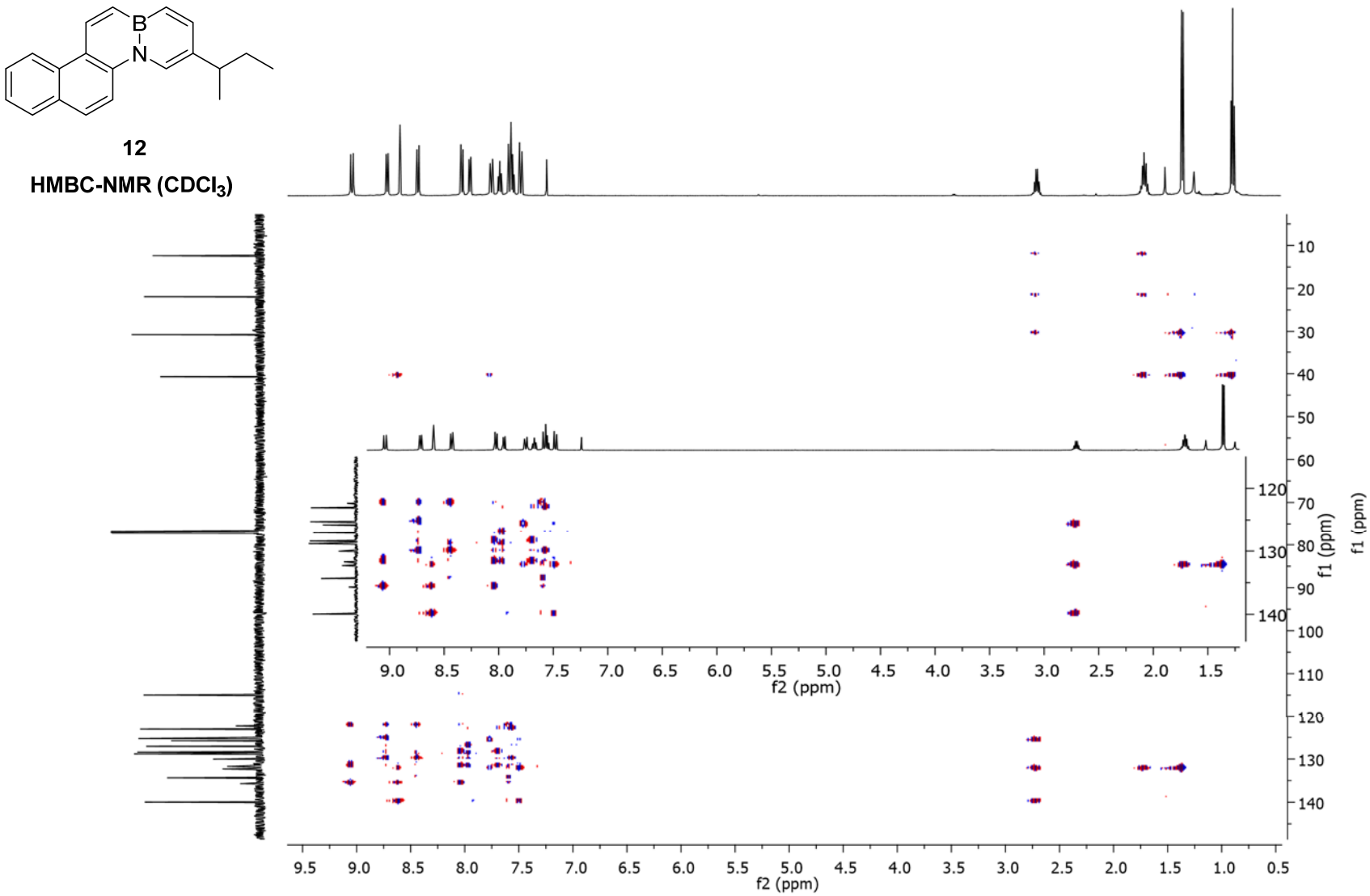
COSY-NMR ($CDCl_3$)

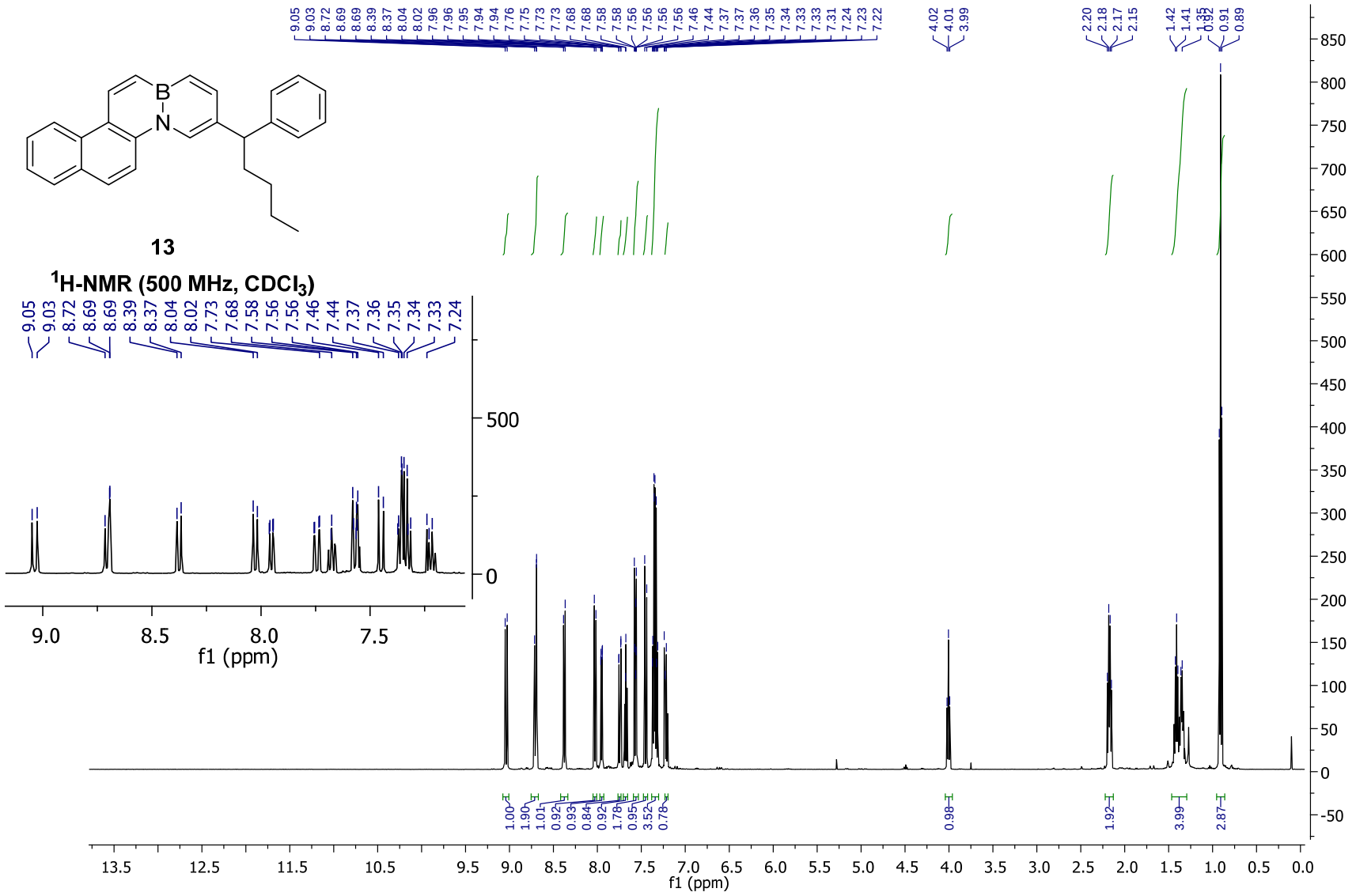


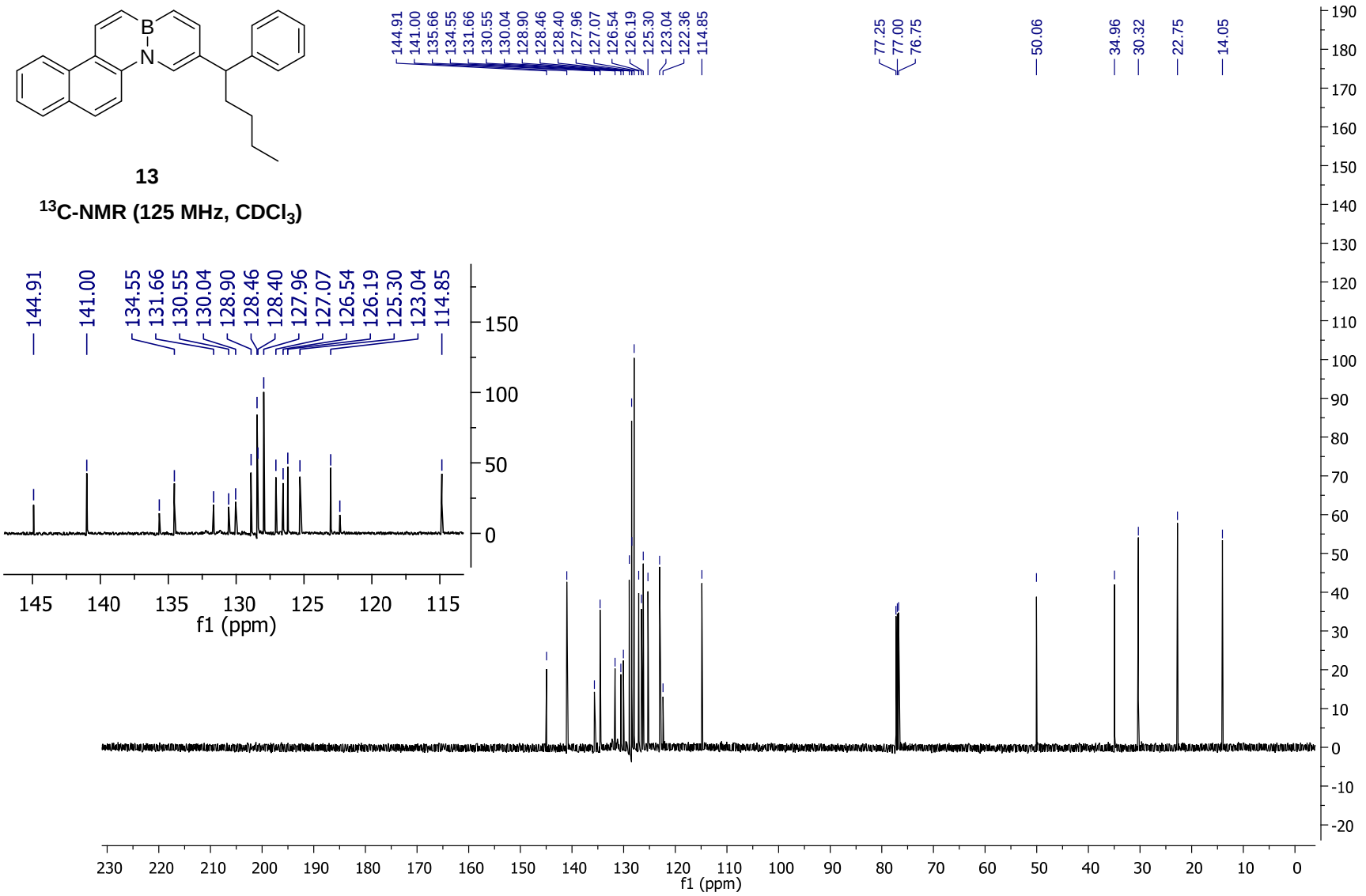


12

HSQC-NMR ($CDCl_3$)

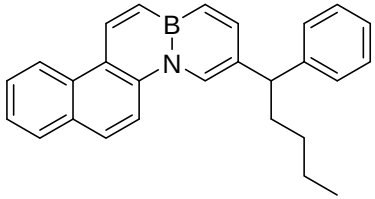

B
N
12
HMBC-NMR (CDCl3)
f2 (ppm)
f1 (ppm)


13
1H-NMR (500 MHz, CDCl3)
f1 (ppm)



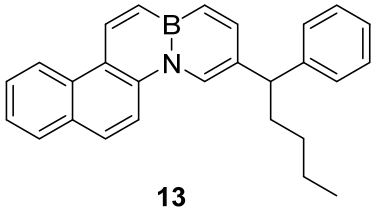
13

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



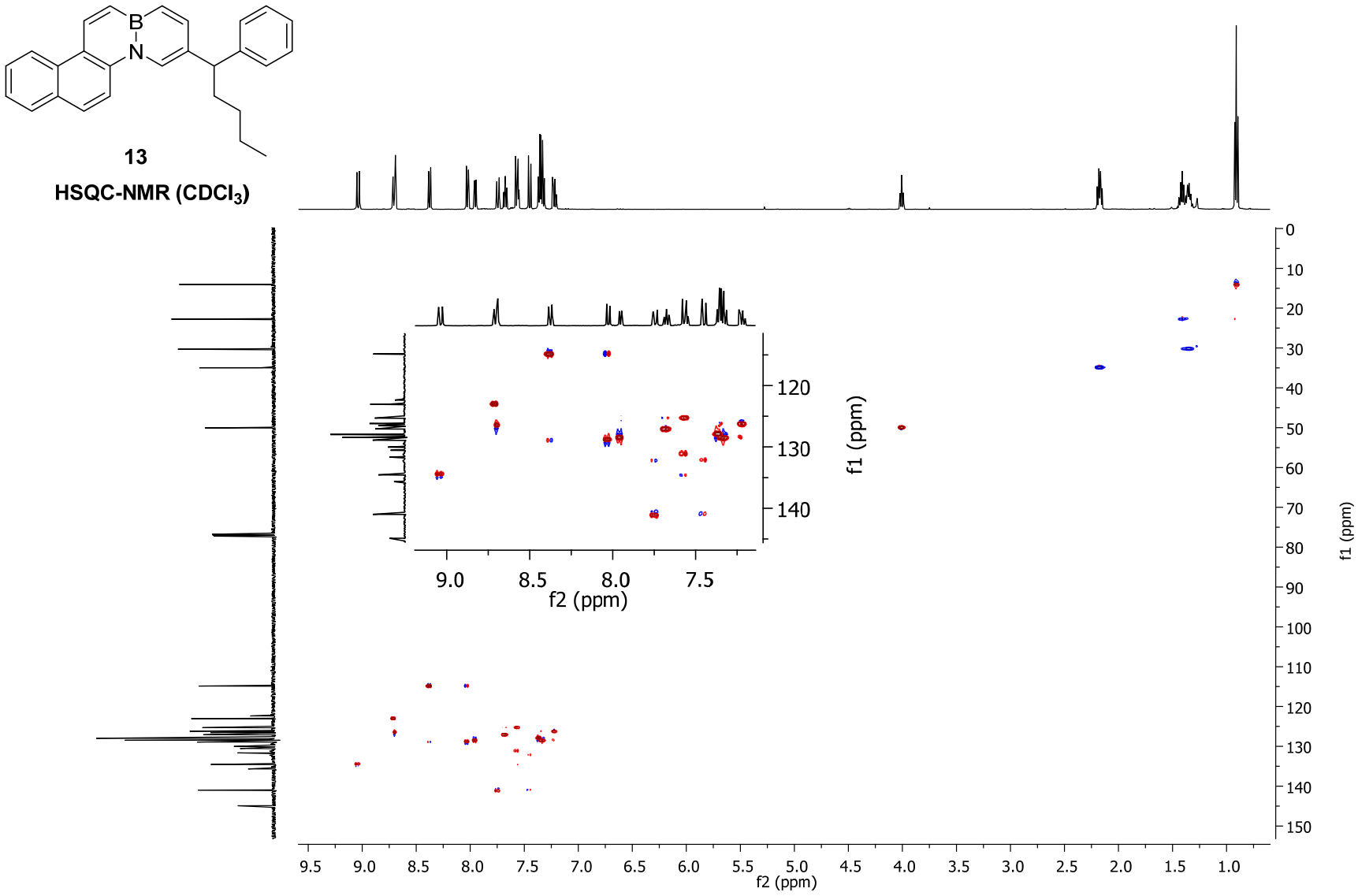
13

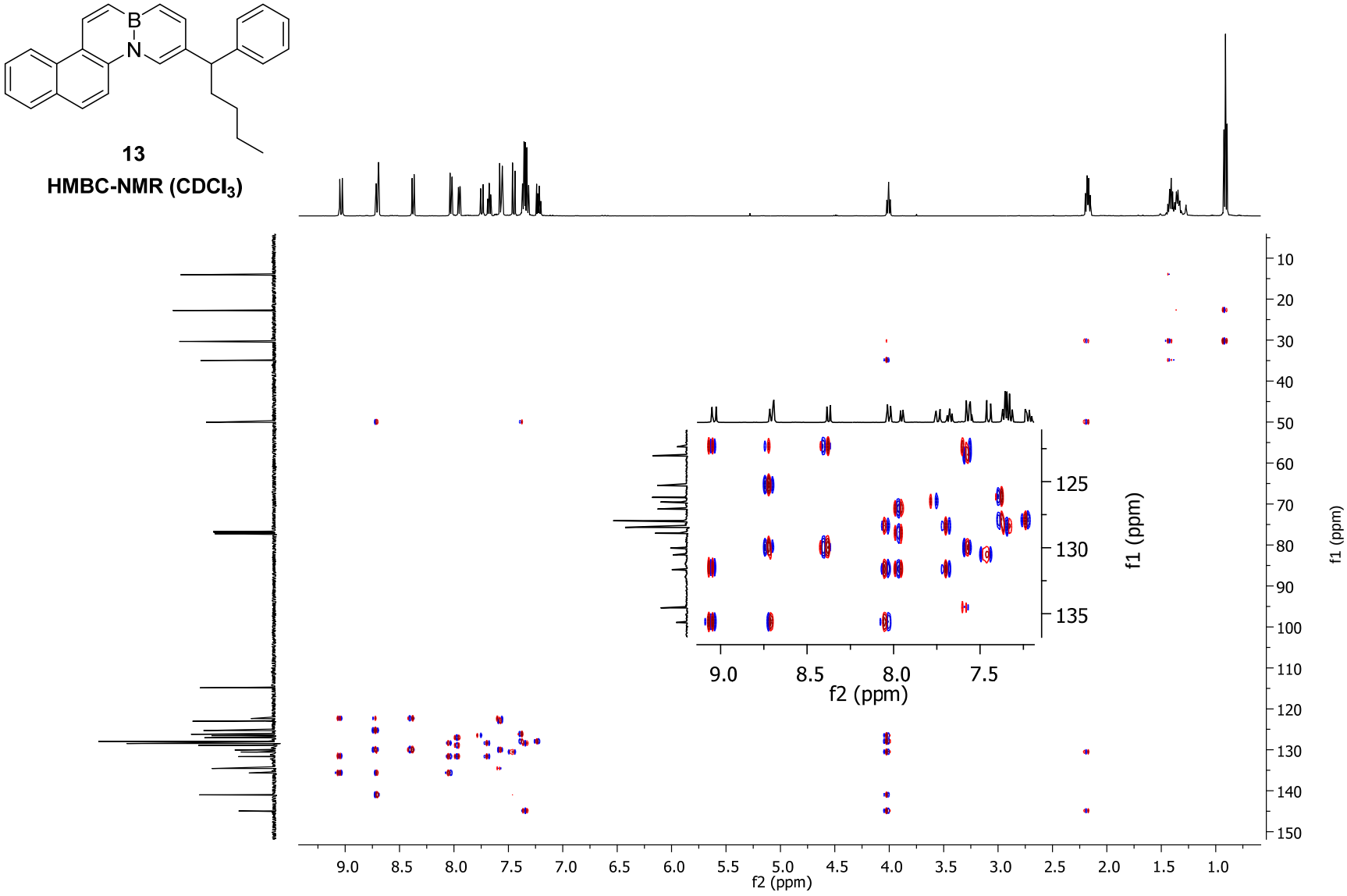
^{11}B-NMR (160 MHz, $CDCl_3$)

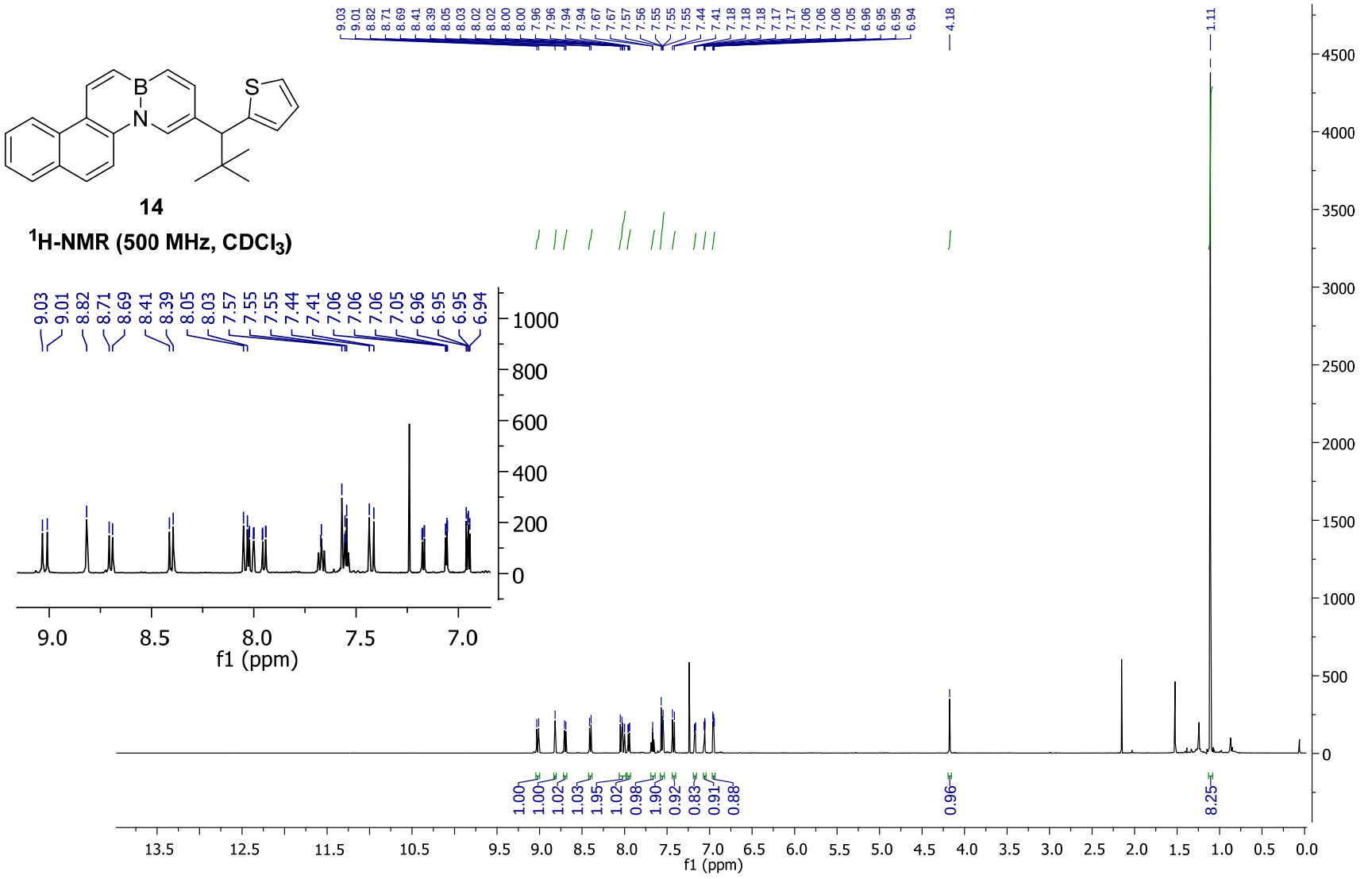


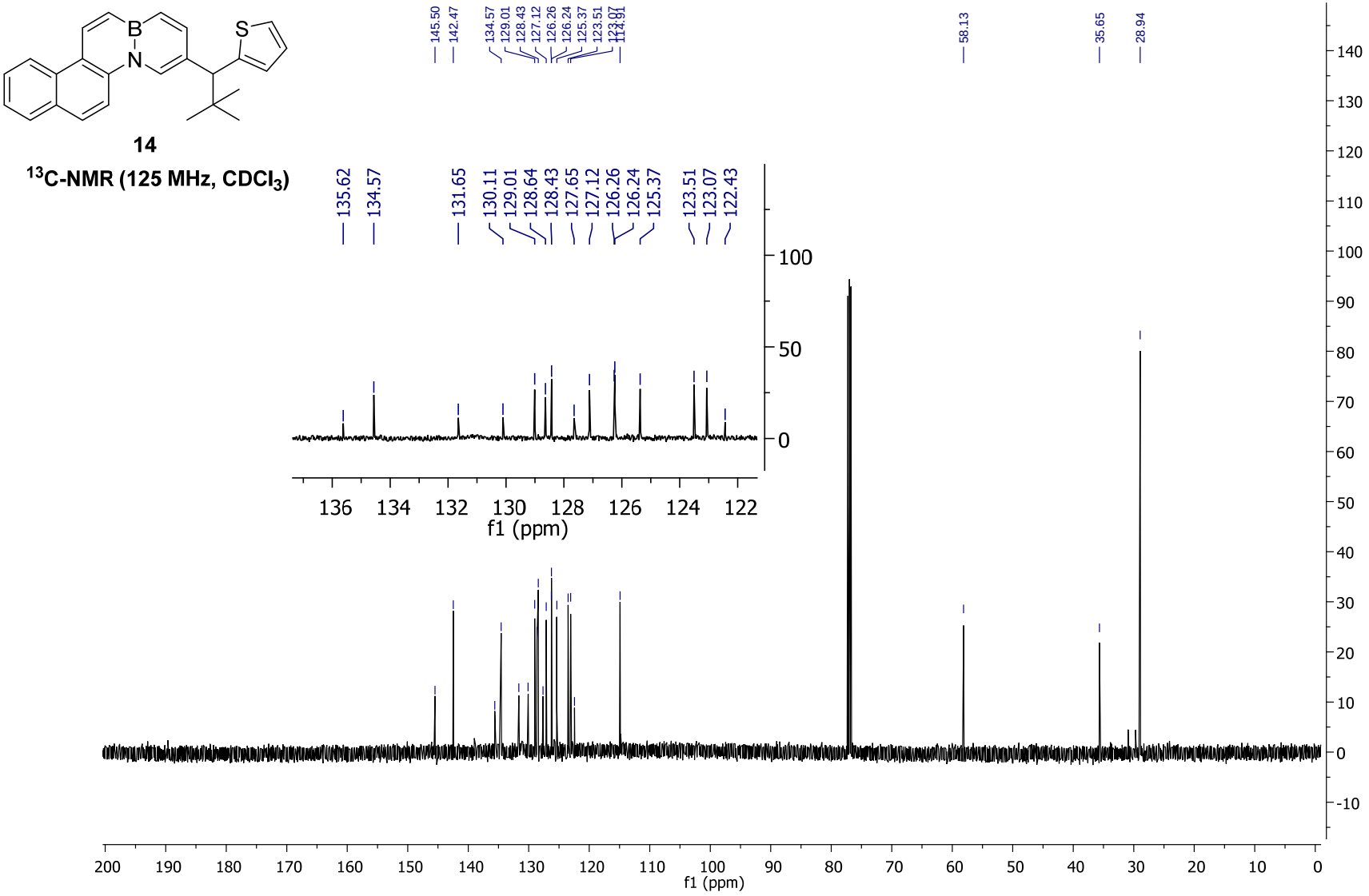
13

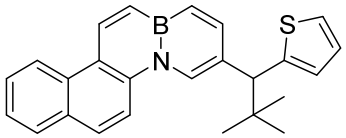
COSY-NMR ($CDCl_3$)


B
N
13
HSQC-NMR (CDCl3)
f1 (ppm)
f2 (ppm)
9.0
8.5
8.0
7.5
120
130
140
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
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150


B
N
13
HMBC-NMR (CDCl3)
f2 (ppm)
f1 (ppm)
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
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
125
130
135

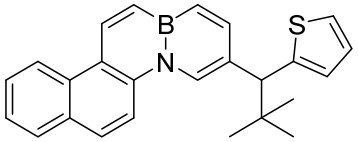

B
N
S
14
1H-NMR (500 MHz, CDCl3)
9.03
9.01
8.82
8.71
8.69
8.41
8.39
8.05
8.03
8.02
8.02
8.00
8.00
7.96
7.96
7.94
7.94
7.67
7.57
7.56
7.55
7.55
7.55
7.44
7.41
7.18
7.18
7.17
7.17
7.06
7.06
7.06
7.05
6.96
6.95
6.95
6.94
4.18
1.11
f1 (ppm)
1.00
1.00
1.02
1.03
1.95
1.02
0.98
1.90
0.92
0.83
0.91
0.88
0.96
8.25


B
N
S
14
13C-NMR (125 MHz, CDCl3)
145.50
142.47
134.57
129.01
128.43
127.12
126.26
126.24
125.37
123.51
58.13
35.65
28.94
135.62
134.57
131.65
130.11
129.01
128.64
128.43
127.65
127.12
126.26
126.24
125.37
123.51
123.07
122.43
f1 (ppm)
f1 (ppm)



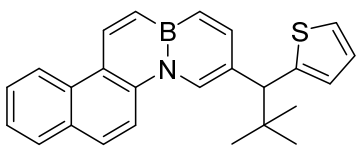
14

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



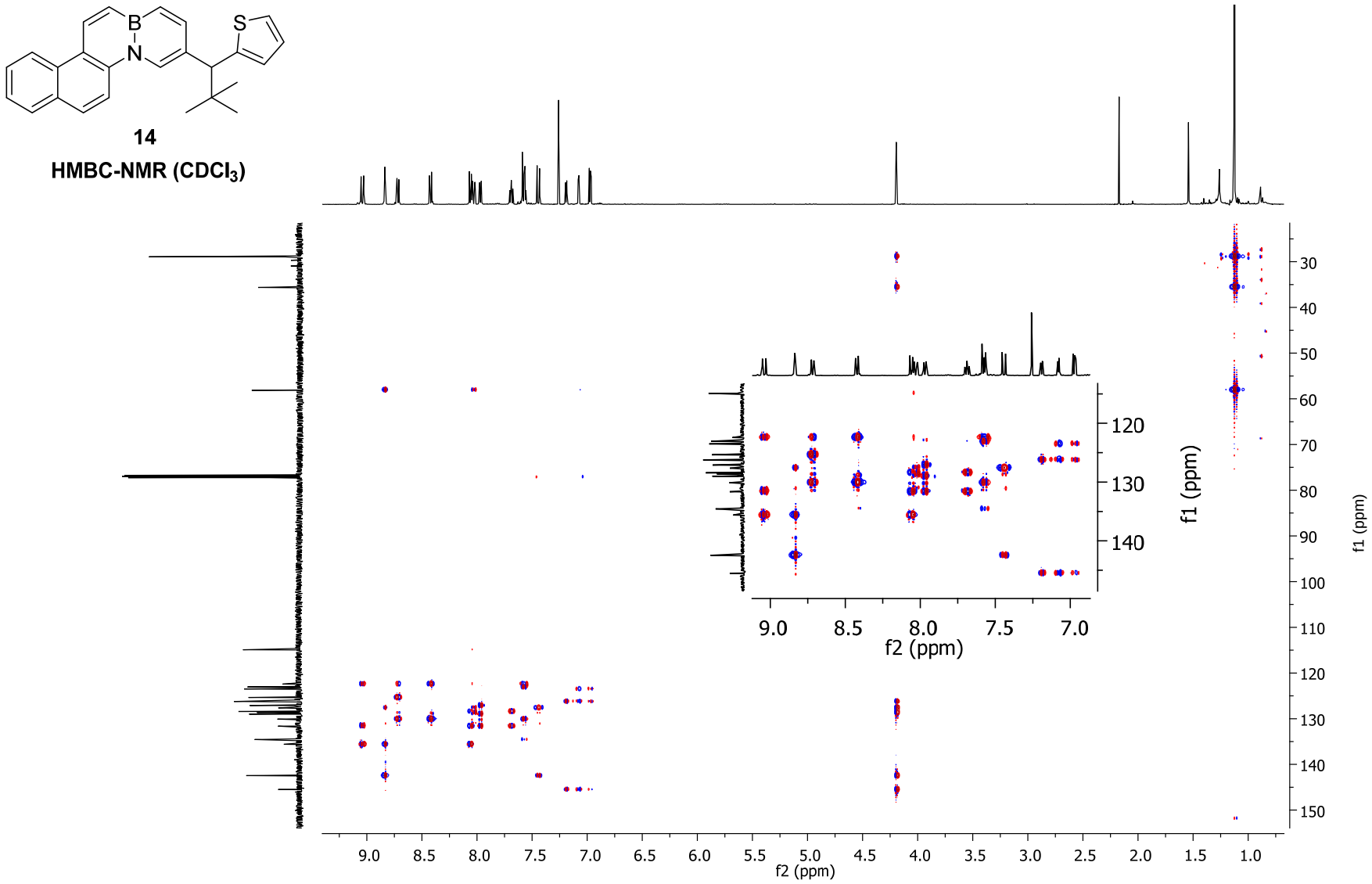
14

COSY-NMR ($CDCl_3$)



14

HSQC-NMR ($CDCl_3$)


B
N
S
14
HMBC-NMR (CDCl3)
f2 (ppm)
f1 (ppm)