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Synthesis of Functionalized Helical BN-benzo[*c*]phenanthrenes

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Electronic Supplementary Information

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GENERAL EXPERIMENTAL DETAILS

Starting materials sourced from commercial suppliers were used as received unless otherwise stated. Dry solvents, where necessary, were dried by a MBRAUN MB-SPS-800 apparatus. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60FS-254) using UV light for visualization. Column chromatography was performed using silica gel (60 F254, 70–200 mm) as the stationary phase. All melting points were determined in open capillary tubes on a Stuart Scientific SMP3 melting point apparatus. 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. Coupling constants (*J*) are in hertz (Hz) and signals are described as follows: s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet; b, broad; ap, apparent. High-resolution analysis (HRMS) were performed on an Agilent 6210 time of-flight LC/MS. Elemental analysis were performed in a LECO CHNSO-932 instrument.

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.

EXPERIMENTAL PROCEDURES AND DATA

SYNTHESIS OF PRECURSORS:

2-vinylaniline, 1-bromo-2-vinylbenzene, and 2-bromo-5-chlorobenzaldehyde are commercially available from Sigma-Aldrich, but can also be conveniently prepared according to the following procedures.

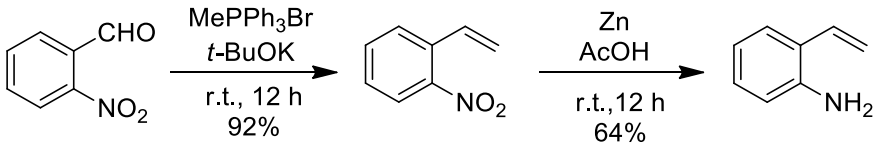
General procedure for the Wittig reaction

In a round bottom flask, $MePPh_3Br$ (1.3 equiv.) and *t*-BuOK (1.5 equiv.) were dissolved in dry THF (0.3 M), and the resulting yellow suspension was stirred at room temperature for 2 h. The reaction mixture was cooled to 0 ºC and the corresponding aldehyde was added (1 equiv.), and the reaction mixture was stirred overnight at room temperature. Then, silica gel was added, and the solvents were removed under reduced pressure. Purification by flash column chromatography on silica gel delivered the corresponding vinyl products.

General procedure for the reduction of nitrobenzenes with zinc

In a round bottom flask, the corresponding vinyl product (1 equiv.) was dissolved in AcOH (0.6 M). Then, zinc powder (5 equiv.) was added in portions and the resulting suspension was stirred at room temperature overnight. After, the reaction was quenched by addition of saturated aqueous solution of $NaHCO_3$. The mixture was extracted with Et_2O and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel to give the corresponding anilines.

Preparation of 2-vinylaniline



Synthesis of 1-nitro-2-vinylbenzene

Following the general procedure, $MePPh_3Br$ (11.8 g, 32.5 mmol), *t*-BuOK (4.43 g, 37.5 mmol) were dissolved in dry THF (75 mL). Then, 2-nitrobenzaldehyde (3.86 g, 25.0 mmol) was added to the reaction mixture. Purification by flash column chromatography on silica gel (5% EtOAc in Hexane) gave 1-nitro-2-vinylbenzene (3.45 g, 23.1 mmol) as yellow oil in **92%** yield. Spectroscopic data are in agreement with those reported in the literature.[1]

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.91 (dd, J = 8.1, 0.9 Hz, 1H, H-6), 7.61 (dd, J = 7.8, 1.9 Hz, 1H, H-3), 7.59-7.54 (m, 1H, H-4), 7.40 (ddd, J = 8.1, 7.0, 1.9 Hz, 1H, H-5), 7.16 (dd, J_{trans} = 17.1 Hz, J_{cis} = 10.9 Hz, 1H, H-7), 5.73 (dd, J_{trans} = 17.1 Hz, J_{gem} = 0.9 Hz, 1H, H-8), 5.47 (dd, J_{cis} = 10.9 Hz, J_{gem} = 0.9 Hz, 1H, H-8).

Synthesis of 2-vinylaniline

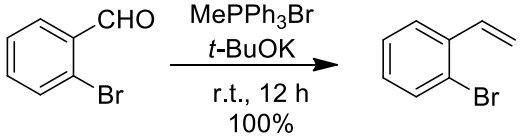
Following the general procedure, 1-nitro-2-vinylbenzene (2.98 g, 20.0 mmol) was dissolved in AcOH (33 mL). Then, zinc powder (6.54 g, 100 mmol) was added in portions. Purification by flash column chromatography (10% EtOAc in Hexane) gave 2-vinylaniline

[1] S. E. Denmark, C. R. Butler, *Org. Lett.,* 2006, **8**, 63.

(1.53 g, 12.8 mmol) as orange oil in **64%** yield. Spectroscopic data are in agreement with those reported in the literature.[2]

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.35 (d, *J* = 7.7 Hz, 1H, H-3), 7.13 (ap t, *J* = 7.3 Hz, 1H, H-5), 6.85-6.76 (m, 2H, H-4, H-7), 6.69 (d, *J* = 7.9 Hz, 1H, H-6), 5.68 (d, J_{trans} = 17.4 Hz, 1H, H-8), 5.36 (d, J_{cis} = 11.0 Hz, 1H, H-8), 3.74 (bs, 2H, NH_2),

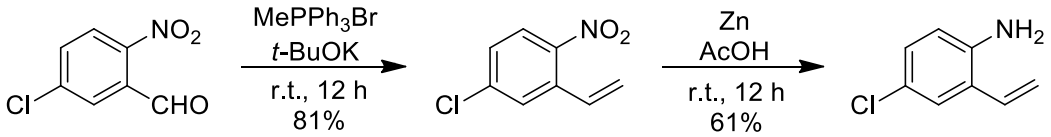
Preparation of 1-bromo-2-vinylbenzene



Following the general procedure, $MePPh_3Br$ (14.2 g, 39.0 mmol), *t*-BuOK (5.15 g, 45.0 mmol) were dissolved in dry THF (100 mL). Then, 2-bromobenzaldehyde (3.57 mL, 30.0 mmol) was added to the reaction mixture. Purification by flash column chromatography on silica gel (Hexane) gave 1-bromo-2-vinylbenzene (5.54 g, 30.0 mmol) as a pale yellow oil in **100%** yield. Spectroscopic data are in agreement with those reported in the literature.[3]

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.57-7.54 (m, 2H, H-3, H-6), 7.31-7.25 (m, 1H, H-4), 7.14-7.09 (m, 1H, H-5), 7.08 (dd, J_{trans} = 17.4 Hz, J_{cis} = 11.2 Hz, 1H, H-7), 5.71 (dd, J_{trans} = 17.4 Hz, J_{gem} = 1.3 Hz, 1H, H-8), 5.37 (dd, J_{cis} = 11.2 Hz, J_{gem} = 1.3 Hz, 1H, H-8).

Preparation of 4-chloro-2-vinylaniline



Synthesis of 4-chloro-1-nitro-2-vinylbenzene

Following the general procedure, $MePPh_3Br$ (10.4 g, 28.6 mmol), *t*-BuOK (3.90 g, 33.0 mmol) were dissolved in dry THF (75 mL). Then, 5-chloro-2-nitrobenzaldehyde (4.21 g, 22.0 mmol) was added to the reaction mixture. Purification by flash column chromatography on silica gel (2% EtOAc in Hexane) gave 4-chloro-1-nitro-2-vinylbenzene (3.27 g, 17.8 mmol) as yellow oil in **81%** yield.

IR (NaCl) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3071, 1601, 1562, 1521, 1344, 881, 745, 697.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.90 (d, *J* = 8.7 Hz, 1H, H-6), 7.57 (d, *J* = 2.3 Hz, 1H, H-3), 7.35 (dd, *J* = 8.7, 2.3 Hz, 1H, H-5), 7.14 (dd, J_{trans} = 17.3 Hz, J_{cis} = 11.0 Hz, 1H, H-7), 5.74 (d, J_{trans} = 17.3 Hz, 1H, H-8), 5.52 (d, J_{cis} = 11.0 Hz, 1H, H-8).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 139.6 (C-1), 135.3 (C-4), 133.8 (C-2), 131.7 (C-7), 128.5 (C-5), 128.3 (C-3), 126.0 (C-6), 120.2 (C-8).

HRMS (EI) calculated for $C_8H_6ClNO_2$ $[M]^+$: 183.0082. Found $[M]^+$: 183.0074.

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[2] G. D. Vo, J. F. Hartwig, *J. Am. Chem. Soc.,* 2009, **131**, 11049.

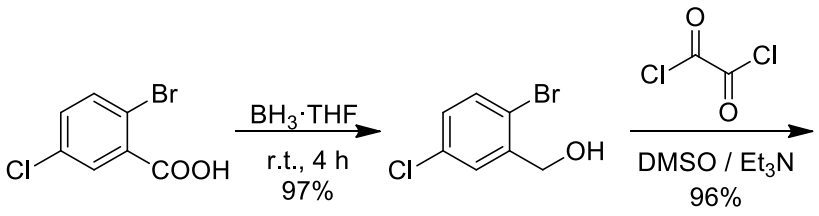
[3] N. Dieltiens, C. V. Stevens, *Synlett*, 2006, **17**, 2771.

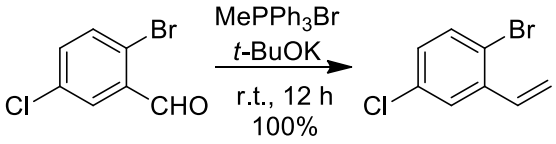
Synthesis of 4-chloro-2-vinylaniline

Following the general procedure, 4-chloro-1-nitro-2-vinylbenzene (2.39 g, 13.0 mmol) was dissolved in AcOH (25 mL). Then, zinc powder (4.25 g, 65.0 mmol) was added in portions. Purification by flash column chromatography (10% EtOAc in Hexane) gave 4-chloro-2-vinylaniline (1.22 g, 7.93 mmol) as yellow oil in **61%** yield. Spectroscopic data are in agreement with those reported in the literature.[4]

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.24 (d, J = 2.5 Hz, 1H, H-3), 7.02 (dd, J = 8.5, 2.5 Hz, 1H, H-5), 6.67 (dd, J_{trans} = 17.4 Hz, J_{cis} = 11.0 Hz, 1H, H-7), 6.58 (d, J = 8.5 Hz, 1H, H-6), 5.62 (dd, J_{trans} = 17.4 Hz, J_{gem} = 1.4 Hz, 1H, H-8), 5.34 (dd, J_{cis} = 11.0 Hz, J_{gem} = 1.4 Hz, 1H, H-8), 3.68 (bs, 2H, NH_2).

Preparation of 1-bromo-4-chloro-2-vinylbenzene





Synthesis of (2-bromo-5-chlorophenyl)methanol

To a solution of 2-bromo-5-chlorobenzoic acid (5.18 g, 21.1 mmol, 1.0 equiv.) in anhydrous THF (70 mL, 0.3 M) under nitrogen was added dropwise a BH_3-THF solution (1.0 M, 27 mL, 1.3 equiv.) at 0 ºC and the reaction mixture was stirred for 4 h at room temperature. Then the mixture was cooled on an ice bath and MeOH (20 mL) was added dropwise to decompose excess BH_3. The resulting mixture was stirred until no bubble was released and then 10% NaOH (10 mL) was added. The mixture was concentrated under reduced pressure and the residue was mixed with brine (100 mL) and extracted with EtOAc (3 x 100 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated to dryness. The residue was purified by flash column chromatography on silica gel (10% EtOAc in Hexane) to give (2-bromo-5-chlorophenyl)methanol[5] (4.53 g, 20.5 mmol) as white solid in **97%** yield.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.49 (d, J = 2.7 Hz, 1H, H-6), 7.43 (d, J = 8.5 Hz, 1H, H-3), 7.12 (dd, J = 8.5, 2.7 Hz, 1H, H-4), 4.70 (d, J = 5.8 Hz, 2H, H-7), 2.03 (t, J = 5.8 Hz, 1H, OH).

[4] B. S. Lee, J. H. Lee, D. Y. Chi, *J. Org. Chem.,* 2002, **67**, 7884.

[5] S. J. Baker, Y.-K. Zhang, T. Akama, A. Lau, H. Zhou, V. Hernandez, W. Mao, M. R. K. Alley, V. Sanders, J. J. Plattner, *J. Med. Chem.*, 2006, **49**, 4447.

Synthesis of 2-bromo-5-chlorobenzaldehyde

DMSO (724 μL, 10.2 mmol, 2 equiv.) was added, at -78°C, to a solution of oxalyl chloride (545 μL, 6.12 mmol, 1.2 equiv.) in CH_2Cl_2 (10 mL). The resulting solution was stirred for 5 min at -78°C, then a solution of (2-bromo-5-chlorophenyl)methanol (1.13 g, 5.10 mmol, 1.0 equiv.) in CH_2Cl_2 (10 mL) was added. The resulting mixture was stirred for 15 min at -78°C and Et_3N (2.84 mL, 20.4 mmol, 4 equiv.) was then added. The solution was allowed to warm to room temperature and stirred at this temperature overnight. Then, the reaction was quenched by the addition of saturated $NaHCO_3$ (50 mL) and then diluted with Et_2O (50 mL). The layers were separated and the organic layer was washed with 1 M $KHSO_4$ (20 mL), saturated $NaHCO_3$ (20 mL) and brine (20 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The crude product was purified by flash column chromatography on silica gel (10% EtOAc in Hexane) to give 2-bromo-5-chlorobenzaldehyde (1.07 g, 4.88 mmol) as white solid in **96%** yield. Spectroscopic data are in agreement with those reported in the literature.[6]

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 10.28 (s, 1H, C*H*O), 7.86 (d, *J* = 2.7 Hz, 1H, H-6), 7.58 (d, *J* = 8.5 Hz, 1H, H-3), 7.40 (dd, *J* = 8.5, 2.7 Hz, 1H, H-4).

Synthesis of 1-bromo-4-chloro-2-vinylbenzene

Following the general procedure, $MePPh_3Br$ (2.27 g, 6.22 mmol), *t*-BuOK (847 mg, 7.17 mmol) were dissolved in dry THF (15 mL). Then, 2-bromo-5-chlorobenzaldehyde (1.05 g, 4.78 mmol) was added to the reaction mixture. Purification by flash column chromatography on silica gel (Hexane) gave 1-bromo-4-chloro-2-vinylbenzene (1.04 g, 4.78 mmol) as a pale yellow oil in **100%** yield. Spectroscopic data are in agreement with those reported in the literature.[7]

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.49 (d, *J* = 2.6 Hz, 1H, H-3), 7.45 (d, *J* = 8.5 Hz, 1H, H-6), 7.07 (dd, *J* = 8.5, 2.6 Hz, 1H, H-5), 6.96 (dd, J_{trans} = 17.4 Hz, J_{cis} = 11.0 Hz, 1H, H-7), 5.69 (d, J_{trans} = 17.4 Hz, 1H, H-8), 5.40 (d, J_{cis} = 11.0 Hz, 1H, H-8).

SYNTHESIS OF BN-BENZO[*c*]PHENANTHRENES 3a-c:

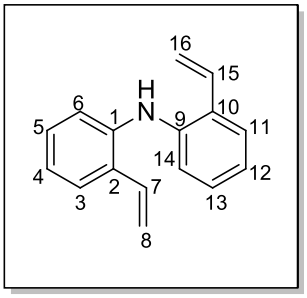
General procedure for the Buchwald-Hartwig reaction

To an oven-dried Biotage microwave vial equipped with a stir bar were added $[PdCl(allyl)]_2$ (0.5 mol%), JohnPhos (1.0 mol%), and *t*-BuONa (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 (0.6 M) was added, followed by the corresponding 2-bromostyrene (1.0 equiv.) and the corresponding 2-vinylaniline (1.2 equiv.). The resulting mixture was heated to the temperature indicated in each case and stirred until full consumption of the corresponding 2-bromostyrene was observed by TLC. The reaction mixture was cooled to room temperature, diluted with Et_2O, and filtered over Celite. The solvent was removed *in vacuo*, and the crude product was purified by flash column chromatography on silica gel.

[6] E. Dubost, C. Fossey, T. Cailly, S. Rault, F. Fabis, *J. Org. Chem.,* 2011, **76**, 6414.

[7] S. C. Schmid, R. Van Hoveln, J. W. Rigoli, J. M. Schomaker, *Organometallics*, 2015, **34**, 4164.

Synthesis of bis(2-vinylphenyl)amine (1a)



Following the general procedure, $[PdCl(allyl)]_2$ (7.0 mg, 0.020 mmol), JohnPhos (12.0 mg, 0.040 mmol), and *t*-BuONa (509 mg, 5.14 mmol) were dissolved in toluene (6 mL). Then, 2-bromostyrene (672 mg, 3.67 mmol) was added, followed by 2-vinylaniline (525 mg, 4.41 mmol). The resulting mixture was heated to 80 ºC for 24 h. Purification by flash column chromatography on silica gel (2% EtOAc in Hexane) gave amine **1a** (735 mg, 3.32 mmol) as orange oil in **90%** yield.

IR (NaCl) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3400, 3083, 1624, 1597, 1577, 1504, 1455, 1299, 995, 913, 747.

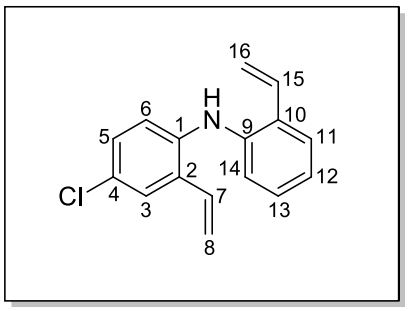
^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.46 (dd, J = 7.8, 1.6 Hz, 2H, H-3, H-11), 7.17 (ddd, J = 8.3, 7.2, 1.6 Hz, 2H, H-5, H-13), 7.01-6.95 (m, 4H, H-4, H-12, H-6, H-14), 6.87 (dd, J_{trans} = 17.4 Hz, J_{cis} = 10.9 Hz, 2H, H-7, H-15), 5.70 (dd, J_{trans} = 17.4 Hz, J_{gem} = 1.6 Hz, 2H, H-8, H-16), 5.49 (bs, 1H, N*H*), 5.32 (dd, J_{cis} = 10.9 Hz, J_{gem} = 1.6 Hz, 2H, H-8, H-16).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 140.9 (2C, C-1, C-9), 132.7 (2C, C-7, C-15), 129.0 (2C, C-2, C-10), 128.6 (2C, C-5, C-13), 127.1 (2C, C-3, C-11), 121.8 (2C, C-4, C-12), 119.2 (2C, C-6, C-14), 116.3 (2C, C-8, C-16).

MS (ESI) *m/z* (relative intensity) 222 ($M+H^+$, 100).

Elemental analysis calculated for $C_{16}H_{15}N$ (221.30 g/mol): C, 86.84; H, 6.83; N, 6.33. Found: C, 86.11; H, 6.61; N, 6.62.

Synthesis of 4-chloro-2-vinyl-*N*-(2-vinylphenyl)aniline (1b)



Following the general procedure, $[PdCl(allyl)]_2$ (6.5 mg, 0.017 mmol), JohnPhos (10.5 mg, 0.035 mmol), and *t*-BuONa (481 mg, 4.86 mmol) were dissolved in toluene (6 mL). Then, 2-bromostyrene (636 mg, 3.47 mmol) was added, followed by 4-chloro-2-vinylaniline (640 mg, 4.20 mmol). The resulting mixture was heated to 50 ºC for 48 h. Purification by flash column chromatography on silica gel (1% EtOAc in Hexane) gave amine **1b** (826 mg, 3.23 mmol) as yellow oil in **93%** yield.

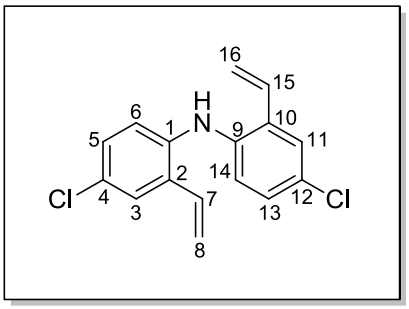
IR (NaCl) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3401, 3085, 1624, 1576, 1501, 1417, 1290, 1117, 993, 916, 759.

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 7.45 (dd, J = 7.7, 1.8 Hz, 1H, H-11), 7.39 (d, J = 2.5 Hz, 1H, H-3), 7.17 (ap td, J = 7.7, 1.8 Hz, 1H, H-13), 7.09 (dd, J = 8.6, 2.5 Hz, 1H, H-5), 7.01-6.96 (m, 1H, H-12), 6.95 (dd, J = 8.1, 1.4 Hz, 1H, H-14), 6.87 (d, J = 8.6 Hz, 1H, H-6), 6.82 (dd, J_{trans} = 17.5 Hz, J_{cis} = 11.0 Hz, 1H, H-15), 6.78 (dd, J_{trans} = 17.4 Hz, J_{cis} = 11.0 Hz, 1H, H-7), 5.70 (dd, J_{trans} = 17.4 Hz, J_{gem} = 1.4 Hz, 1H, H-8), 5.69 (dd, J_{trans} = 17.5 Hz, J_{gem} = 1.5 Hz, 1H, H-16), 5.41 (bs, 1H, N*H*), 5.36 (dd, J_{cis} = 11.0 Hz, J_{gem} = 1.4 Hz, 1H, H-8), 5.31 (dd, J_{cis} = 11.0 Hz, J_{gem} = 1.5 Hz, 1H, H-16).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 140.4 (C-9), 139.7 (C-1), 132.5 (C-15), 131.6 (C-7), 130.2 (C-2), 129.5 (C-10), 128.7 (C-13), 128.4 (C-5), 127.2 (C-11), 126.9 (C-3), 126.6 (C-4), 122.4 (C-12), 120.2 (C-6), 119.7 (C-14), 117.6 (C-8), 116.6 (C-16).

HRMS (ESI-TOF) calculated for $C_{16}H_{15}ClN$ $[M+H]^+$: 256.0888. Found $[M+H]^+$: 256.0886.

Synthesis of bis(4-chloro-2-vinylphenyl)amine (1c)



Following the general procedure, $[PdCl(allyl)]_2$ (9.0 mg, 0.024 mmol), JohnPhos (15.0 mg, 0.048 mmol), and *t*-BuONa (670 mg, 6.76 mmol) were dissolved in toluene (8 mL). Then, 1-bromo-4-chloro-2-vinylbenzene (1.05 g, 4.83 mmol) was added, followed by 4-chloro-2-vinylaniline (890 mg, 5.79 mmol). The resulting mixture was heated to 50 ºC for 48 h. Purification by flash column chromatography on silica gel (1% DCM in Hexane) gave amine **6**) (1.28 g, 4.43 mmol) as orange oil in **92%** yield.

IR (NaCl) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3403, 3088, 1625, 1481, 1417, 1312, 1289, 1114, 992, 919, 882, 811, 757.

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 7.41 (d, J = 2.5 Hz, 2H, H-3, H-11), 7.11 (dd, J = 8.6, 2.5 Hz, 2H, H-5, H-13), 6.84 (d, J = 8.6 Hz, 2H, H-6, H-14), 6.75 (dd, J_{trans} = 17.4 Hz, J_{cis} = 11.0 Hz, 2H, H-7, H-15), 5.70 (dd, J_{trans} = 17.4 Hz, J_{gem} = 1.4 Hz, 2H, H-8, H-16), 5.36 (dd, J_{cis} = 11.0 Hz, J_{gem} = 1.4 Hz, 2H, H-8, H-16), 5.34 (s, 1H, N*H*).

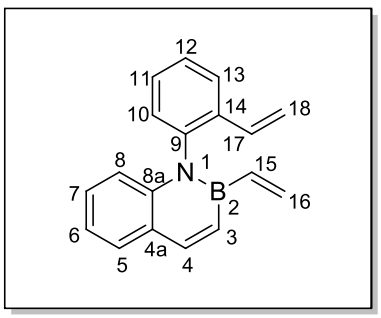
^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 139.2 (2C, C-1, C-9), 131.4 (2C, C-7, C-15), 130.6 (2C, C-2, C-10), 128.5 (2C, C-5, C-13), 127.3 (2C, C-3, C-11), 126.9 (2C, C-4, C-12), 120.6 (2C, C-6, C-14), 117.8 (2C, C-8, C-16).

HRMS (APCI-TOF) calculated for $C_{16}H_{14}Cl_2N$ $[M+H]^+$: 290.0498. Found $[M+H]^+$: 290.0503.

General procedure for the preparation of 2,1-borazaronaphthalenes

To an oven-dried Biotage microwave vial equipped with a stir bar was added potassium vinyltrifluoroborate (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 and toluene (1:1, 0.25 M) were added, followed by the corresponding 2-aminostyrene (1.2 equiv.), $SiCl_4$ (1.0 equiv.) and Et_3N (1.5 equiv.) under argon. The resulting mixture was heated to the temperature and time indicated in each case. Then the reaction mixture was cooled to room temperature, diluted with Et_2O, filtered over a plug of silica gel and flushed with Et_2O. The solvent was removed *in vacuo* and the resulting product was purified via flash column chromatography on silica gel (hexanes) to provide the desired 2,1-borazaronaphthalenes.

Synthesis of 2-vinyl-1-(2-vinylphenyl)-1-aza-2-boranaphthalene (2a)



Following the general procedure, potassium vinyltrifluoroborate (390 mg, 2.77 mmol) was dissolved in CMPE (5.5 mL) and toluene (5.5 mL). Then, amine **1a** (735 mg, 3.32 mmol), $SiCl_4$ (321 μL, 2.77 mmol) and Et_3N (579 μL, 4.16 mmol) were added under argon. The resulting mixture was heated to 80 ºC for 24 h to give diene **2a** (470 mg, 1.83 mmol) as yellow oil in **66%** yield.

IR (NaCl) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3057, 3028, 1605, 1547, 1488, 1415, 1298, 1252, 808, 762.

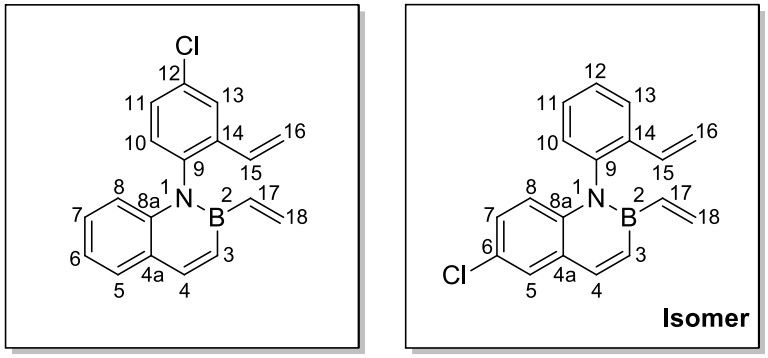
^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.10 (d, *J* = 11.6 Hz, 1H, H-4), 7.78 (dd, *J* = 7.5, 2.3 Hz, 1H, H-13), 7.67 (dd, *J* = 7.8, 1.8 Hz, 1H, H-5), 7.48-7.43 (m, 1H, H-12), 7.44-7.39 (m, 1H, H-11), 7.26 (ddd, *J* = 8.5, 7.0, 1.8 Hz, 1H, H-7), 7.19 (d, *J* = 11.6 Hz, 1H, H-3), 7.19-7.14 (m, 1H, H-6), 7.10 (dd, *J* = 6.9, 2.2 Hz, 1H, H-10), 6.70 (d, *J* = 8.5 Hz, 1H, H-8), 6.232 (dd, J_{trans} = 17.5 Hz, J_{cis} = 11.0 Hz, 1H, H-17), 6.231 (dd, J_{trans} = 16.9 Hz, J_{cis} = 6.5 Hz, 1H, H-15), 5.87 (d, J_{cis} = 6.5 Hz, 1H, H-16), 5.83 (d, J_{trans} = 16.9 Hz, 1H, H-16), 5.68 (d, J_{trans} = 17.5 Hz, 1H, H-18), 5.06 (d, J_{cis} = 11.0 Hz, 1H, H-18).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 144.9 (C-4), 142.1 (C-8a), 141.3 (C-9), 135.2 (C-14), 133.5 (C-15*), 133.2 (C-16), 131.6 (C-17), 129.6 (C-5), 129.4 (C-10), 129.0 (C-11), 128.3 (C-7), 127.7 (C-12), 127.2 (C-3*), 126.1 (C-4a), 125.9 (C-13), 121.0 (C-6), 117.4 (C-8), 116.1 (C-18). *Carbon not observed in ^{13}C-NMR, assigned by gHSQC.

^{11}B-NMR (160 MHz, $CDCl_3$) δ (ppm) 33.4.

HRMS (ESI-TOF) calculated for $C_{18}H_{16}BN$ $[M+H]^+$: 258.1454. Found $[M+H]^+$: 258.1452.

Synthesis of 1-(4-chloro-2-vinylphenyl)-2-vinyl-1-aza-2-boranaphthalene (2b)



Following the general procedure, potassium vinyltrifluoroborate (391 mg, 2.77 mmol) was dissolved in CMPE (5.5 mL) and toluene (5.5 mL). Then, amine **1b** (850 mg, 3.32 mmol), $SiCl_4$ (321 μL, 2.77 mmol) and Et_3N (579 μL, 4.16 mmol) were added under argon. The resulting mixture was heated to 100 ºC for 24 h to give a 5:1 mixture of **2b** and **2b-isomer** as a pale yellow oil in **89%** yield (720 mg, 2.47 mmol).

IR (NaCl) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3060, 3029, 1600, 1546, 1477, 1415, 1298, 1254, 1179, 808, 762.

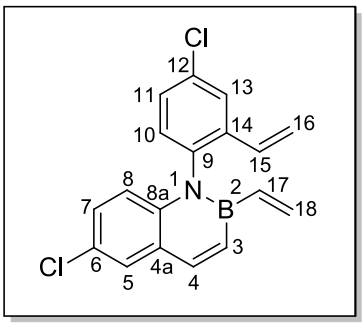
^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.08 (d, *J* = 11.6 Hz, 1H, H-4), 7.75 (d, *J* = 2.4 Hz, 1H, H-13), 7.66 (dd, *J* = 7.8, 1.7 Hz, 1H, H-5), 7.39 (dd, *J* = 8.3, 2.4 Hz, 1H, H-11), 7.27 (ddd, *J* = 8.5, 7.0, 1.7 Hz, 1H, H-7), 7.19-7.16 (m, 1H, H-6), 7.13 (d, *J* = 11.6 Hz, 1H, H-3), 7.05 (d, *J* = 8.3 Hz, 1H, H-10), 6.69 (d, *J* = 8.5 Hz, 1H, H-8), 6.23 (dd, J_{trans} = 18.9 Hz, J_{gem} = 4.3 Hz, 1H, H-18), 6.15 (dd, J_{trans} = 17.5 Hz, J_{cis} = 11.0 Hz, 1H, H-15), 5.88 (dd, J_{cis} = 13.5 Hz, J_{gem} = 4.3 Hz, 1H, H-18), 5.81 (dd, J_{trans} = 18.9 Hz, J_{cis} = 13.5 Hz, 1H, H-17), 5.69 (dd, J_{trans} = 17.5 Hz, J_{gem} = 1.1 Hz, 1H, H-16), 5.11 (dd, J_{cis} = 11.0 Hz, J_{gem} = 1.1 Hz, 1H, H-16).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 145.0 (C-4), 141.8 (C-8a), 139.8 (C-9), 137.0 (C-17*), 136.9 (C-14), 133.7 (C-18), 133.5 (C-12), 130.8 (C-10), 130.7 (C-15), 129.7 (C-5), 129.0 (C-11), 128.4 (C-7), 127.0 (C-3*), 126.1 (C-4a), 126.0 (C-13), 121.3 (C-6), 117.5 (C-16), 117.2 (C-8). *Carbon not observed in ^{13}C-NMR, assigned by gHSQC.

^{11}B-NMR (160 MHz, $CDCl_3$) δ (ppm) 33.3.

HRMS (EI) calculated for $C_{18}H_{15}BClN$ $[M]^+$: 291.0981. Found $[M]^+$: 291.0984.

Synthesis of 6-chloro-1-(4-chloro-2-vinylphenyl)-2-vinyl-1-aza-2-boranaphthalene (2c)



Following the general procedure, potassium vinyltrifluoroborate (520 mg, 3.69 mmol) was dissolved in CMPE (7.5 mL) and toluene (7.5 mL). Then, amine **1c** (1.28 g, 4.43 mmol), $SiCl_4$ (427 μL, 3.69 mmol) and Et_3N (771 μL, 5.54 mmol) were added under argon. The resulting mixture was heated to 80 ºC for 24 h to give diene **2c** (1.16 g, 3.56 mmol) as a pale yellow solid in **96%** yield.

M. p.: 80-82 ºC.

IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3063, 3029, 1604, 1539, 1477, 1379, 1298, 1249, 957, 922, 881.

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 7.97 (d, *J* = 11.6 Hz, 1H, H-4), 7.72 (d, *J* = 2.4 Hz, 1H, H-13), 7.62 (d, *J* = 2.5 Hz, 1H, H-5), 7.38 (dd, *J* = 8.3, 2.4 Hz, 1H, H-11), 7.19 (d, *J* = 11.6 Hz, 1H, H-3), 7.18 (dd, *J* = 9.0, 2.5 Hz, 1H, H-7), 7.02 (d, *J* = 8.3 Hz, 1H, H-10), 6.60 (d, *J* = 9.0 Hz, 1H, H-8), 6.21 (dd, J_{trans} = 19.3 Hz, J_{gem} = 3.9 Hz, 1H, H-18), 6.09 (dd, J_{trans} = 17.5 Hz, J_{cis} = 11.1 Hz, 1H, H-15), 5.89 (dd, J_{cis} = 13.5 Hz, J_{gem} = 3.9 Hz, 1H, H-18), 5.77 (dd, J_{trans} = 19.3 Hz, J_{cis} = 13.5 Hz, 1H, H-17), 5.67 (d, J_{trans} = 17.5 Hz, 1H, H-16), 5.12 (d, J_{cis} = 11.1 Hz, 1H, H-16).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 143.9 (C-4), 140.3 (C-8a), 139.4 (C-9), 137.0 (C-17*), 136.9 (C-14), 134.2 (C-18), 133.8 (C-12), 130.6 (C-10), 130.5 (C-15), 129.1 (C-11), 128.7 (C-5), 128.6 (C-3**), 128.4 (C-7), 127.2 (C-4a), 126.6 (C-6), 126.2 (C-13), 118.6 (C-8), 117.9 (C-16). *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) 33.6.

MS (DIP-EI) *m/z* (relative intensity, %): 325 (M^+, 100).

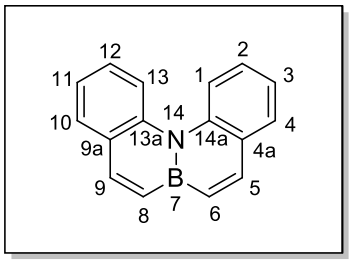
Elemental analysis calculated for $C_{18}H_{14}BCl_2N$ (326.03 g/mol): C, 66.31; H, 4.33; N, 4.30. Found: C, 66.55; H, 4.52; N, 4.39.

General procedure for the preparation of BN-benzo[c]phenanthrenes by ring closing metathesis

General Procedure A: the ruthenium catalyst Hoveyda-Grubbs Second Generation (**H-G**, 10 mol%) in anhydrous 1,2-dichloroethane (0.05 M) was added to a solution of the corresponding diene (1.0 equiv.) in anhydrous 1,2-dichloroethane (0.1 M) under an argon atmosphere. The reaction mixture was stirred at 80 ºC for 24 h. Then, the reaction mixture was cooled to room temperature, diluted with CH_2Cl_2, filtered over a plug of silica gel and flushed with CH_2Cl_2. The solvent was removed *in vacuo* and the resulting product was purified via flash column chromatography on silica gel (hexanes) to afford the corresponding BN-benzo[*c*]phenanthrenes.

General Procedure B: the ruthenium catalyst Grubbs Second Generation (**G-II**, 10 mol%) in anhydrous CH_2Cl_2 (0.05 M) was added to a solution of the corresponding diene (1.0 equiv.) in anhydrous CH_2Cl_2 (0.1 M) under an argon atmosphere. The reaction mixture was stirred at 40 ºC for 24 h. Then, the reaction mixture was cooled to room temperature, diluted with CH_2Cl_2, filtered over a plug of silica gel and flushed with CH_2Cl_2. The solvent was removed *in vacuo* and the resulting product was purified via flash column chromatography on silica gel (hexanes) to afford the corresponding BN-phenanthrenes.

Synthesis of 12b-aza-6a-borabenzo[*c*]phenanthrene (3a)



Following the general procedure **A**, **H-G** catalyst (87 mg, 0.14 mmol) in 1,2-DCE (3 mL) and diene **2a** (348 mg, 1.35 mmol) in 1,2-DCE (14 mL) gave BN-benzo[*c*]phenanthrene **3a** (288 mg, 1.26 mmol) as white solid in **93%** yield.

M. p.: 68-70 ºC.

IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 2923, 2852, 1598, 1468, 1442, 1415, 1285, 1166, 813, 765, 746.

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.51 (d, *J* = 8.6 Hz, 2H, H-1, H-13), 8.02 (d, *J* = 11.2 Hz, 2H, H-5, H-9), 7.78 (dd, *J* = 7.7, 1.7 Hz, 2H, H-4, H-10), 7.44 (ddd, *J* = 8.6, 7.1, 1.7 Hz, 2H, H-2, H-12), 7.34-7.33 (ddd, *J* = 7.7, 7.1, 1.1 Hz, 2H, H-3, H-11), 7.23 (d, *J* = 11.2 Hz, 2H, H-6, H-8).

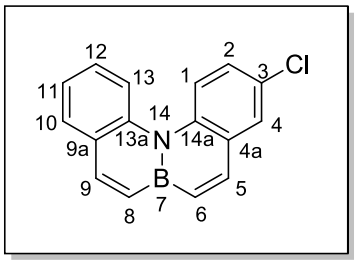
^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 143.0 (2C, C-5, C-9), 138.8 (2C, C-13a, C-14a), 130.5 (2C, C-6*, C-8*), 129.7 (2C, C-4, C-10), 129.5 (2C, C-4a, C-9a), 126.3 (2C, C-2, C-12), 122.8 (2C, C-3, C-11), 121.0 (2C, C-1, C-13). *Carbon not observed in ^{13}C-NMR, assigned by gHSQC.

^{11}B-NMR (160 MHz, $CDCl_3$) δ (ppm) 30.2.

MS (DIP-EI) *m/z* (relative intensity, %): 229 (M^+, 100).

Elemental analysis calculated for $C_{16}H_{12}BN$ (229.08 g/mol): C, 83.89; H, 5.28; N, 6.11. Found: C, 83.42; H, 5.91; N, 5.51.

Synthesis of 3-chloro-12b-aza-6a-borabenzo[*c*]phenanthrene (3b)



Following the general procedure **A**, **H-G** catalyst (127 mg, 0.20 mmol) in 1,2-DCE (4 mL) and diene **2b** (583 mg, 2.00 mmol) in 1,2-DCE (20 mL) gave BN-benzo[*c*]phenanthrene **3b** (522 mg, 1.98 mmol) as white solid in **99%** yield.

M. p.: 110-112 ºC.

IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3010, 1591, 1531, 1467, 1288, 1214, 878, 805, 792, 749.

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.40 (d, *J* = 9.1 Hz, 1H, H-1), 8.38 (d, *J* = 8.7 Hz, 1H, H-13), 8.00 (d, *J* = 11.2 Hz, 1H, H-9), 7.88 (d, *J* = 11.2 Hz, 1H, H-5), 7.76 (dd, *J* = 7.7, 1.8 Hz, 1H, H-10), 7.71 (d, *J* = 2.5 Hz, 1H, H-4), 7.42 (ddd, *J* = 8.7, 7.0, 1.8 Hz, 1H, H-12), 7.35 (dd, *J* = 9.1, 2.5 Hz, 1H, H-2), 7.33-7.31 (m, 1H, H-11), 7.25 (d, *J* = 11.2 Hz, 1H, H-6), 7.20 (d, *J* = 11.2 Hz, 1H, H-8).

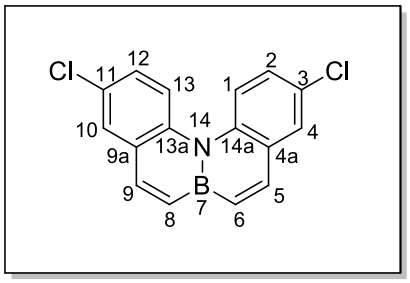
^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 143.2 (C-9), 141.8 (C-5), 138.5 (C-13a), 137.2 (C-14a), 132.0 (C-6*), 130.7 (C-4a), 130.2 (C-8*), 129.8 (C-10), 129.5 (C-9a), 128.6 (C-4), 127.8 (C-3), 126.5 (C-12), 126.2 (C-2), 123.1 (C-11), 122.4 (C-1), 120.8 (C-13). *Carbon not observed in ^{13}C-NMR, assigned by gHSQC.

^{11}B-NMR (160 MHz, $CDCl_3$) δ (ppm) 30.1.

MS (DIP-EI) *m/z* (relative intensity, %): 263 (M^+, 100).

Elemental analysis calculated for $C_{16}H_{11}BClN$ (263.53 g/mol): C, 72.92; H, 4.21; N, 5.32. Found: C, 73.31; H, 5.09; N, 5.02.

Synthesis of 3,10-dichloro-12b-aza-6a-borabenzo[*c*]phenanthrene (3c)



Following the general procedure **A**, **H-G** catalyst (65 mg, 0.10 mmol) in 1,2-DCE (2 mL) and diene **2c** (326 mg, 1.00 mmol) in 1,2-DCE (10 mL) gave BN-benzo[*c*]phenanthrene **3c** (271 mg, 0.91 mmol) as white solid in **91%** yield.

M. p.: 198-200 ºC.

IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3020, 2924, 1597, 1526, 1464, 1287, 1206, 878, 829, 798.

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.32 (d, *J* = 9.1 Hz, 2H, H-1, H-13), 7.91 (d, *J* = 11.2 Hz, 2H, H-5, H-9), 7.73 (d, *J* = 2.5 Hz, 2H, H-4, H-10), 7.38 (dd, *J* = 9.1, 2.5 Hz, 2H, H-2, H-12), 7.25 (d, *J* = 11.2 Hz, 2H, H-6, H-8).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 142.1 (2C, C-5, C-9), 137.0 (2C, C-13a, C-14a), 132.0 (2C, C-6*, C-8*), 130.8 (2C, C-4a, C-9a), 128.8 (2C, C-4, C-10), 128.2 (2C, C-3, C-11), 126.5 (2C, C-2, C-12), 122.2 (2C, C-1, C-13). *Carbon not observed in ^{13}C-NMR, assigned by gHSQC.

^{11}B-NMR (160 MHz, $CDCl_3$) δ (ppm) 30.2.

MS (DIP-EI) *m/z* (relative intensity, %): 297 (M^+, 100).

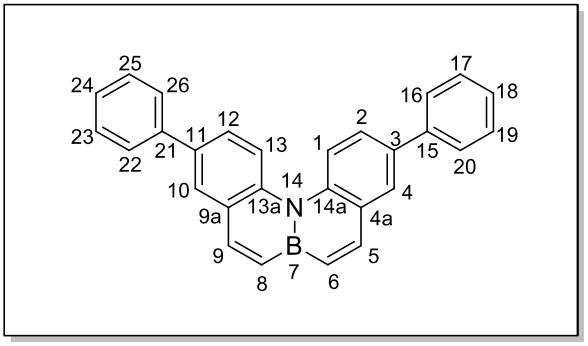
Elemental analysis calculated for $C_{16}H_{10}BCl_2N$ (297.97 g/mol): C, 64.49; H, 3.38; N, 4.70. Found: C, 64.87; H, 3.53; N, 4.82.

PALLADIUM-CATALYZED CROSS-COUPLING REACTIONS OF Cl-SUBSTITUTED BN-BENZO[*c*]PHENANTHRENES:

General procedure for the Suzuki reaction

To an oven-dried Biotage microwave vial equipped with a stir bar was added $Pd(OAc)_2$ (10 mol%), JohnPhos (20 mol%), *t*-BuONa (1.5 or 3.0 equiv.), phenylboronic acid (2.0 or 4.0 equiv.) and the corresponding BN-benzo[*c*]phenanthrene (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. Toluene (0.1 M) was added and the resulting mixture was heated to 110 ºC for 24 h. Then, the reaction mixture 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 to give the corresponding coupled products.

Synthesis of 3,10-diphenyl-12b-aza-6a-borabenzo[*c*]phenanthrene (3d)



Following the general procedure, $Pd(OAc)_2$ (3.8 mg, 0.017 mmol), JohnPhos (10.2 mg, 0.034 mmol), *t*-BuONa (51 mg, 0.51 mmol), phenylboronic acid (86 mg, 0.67 mmol) and BN-benzo[*c*]phenanthrene **3c** (50 mg, 0.17 mmol) were dissolved in toluene (2 mL). Purification by flash column chromatography on silica gel (10% CH_2Cl_2 in Hexane) gave BN-derivative **3d** (52 mg, 0.14 mmol) as white solid in **80%** yield.

M. p.: 252-254 ºC.

IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 2918, 2850, 1559, 1449, 1241, 1200, 893, 800, 762, 696.

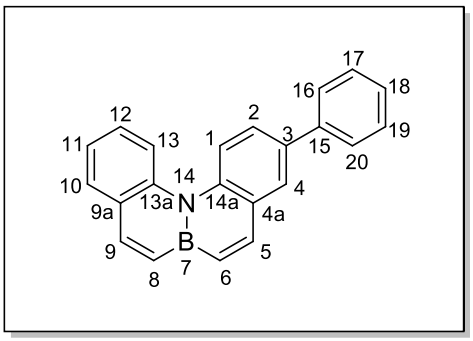
^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.61 (d, *J* = 8.8 Hz, 2H, H-1, H-13), 8.08 (d, *J* = 11.2 Hz, 2H, H-5, H-9), 8.00 (d, *J* = 2.3 Hz, 2H, H-4, H-10), 7.74-7.70 (m, 6H, H-2, H-12, H-16, H-20, H-22, H-26), 7.50-7.47 (m, 4H, H-17, H-19, H-23, H-25), 7.37 (tt, *J* = 7.4, 1.3 Hz, 2H, H-18, H-24), 7.27 (d, *J* = 11.2 Hz, 2H, H-6, H-8).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 143.3 (2C, C-5, C-9), 140.3 (2C, C-15, C-21), 138.1 (2C, C-13a, C-14a), 135.7 (2C, C-3, C-11), 130.8 (2C, C-6*, C-8*), 129.9 (2C, C-4a, C-9a), 128.9 (4C, C-17, C-19, C-23, C-25), 127.9 (2C, C-4, C-10), 127.3 (2C, C-18, C-24), 127.1 (4C, C-16, C-20, C-22, C-26), 125.3 (2C, C-2, C-12), 121.6 (2C, C-1, C-13). *Carbon not observed in ^{13}C-NMR, assigned by gHSQC.

^{11}B-NMR (160 MHz, $CDCl_3$) δ (ppm) 31.4.

HRMS (EI) calculated for $C_{28}H_{20}BN$ $[M]^+$: 381.1683. Found $[M]^+$: 381.1693.

Synthesis of 3-phenyl-12b-aza-6a-borabenzo[*c*]phenanthrene (3e)



Following the general procedure, $Pd(OAc)_2$ (4.3 mg, 0.019 mmol), JohnPhos (11.5 mg, 0.038 mmol), *t*-BuONa (28 mg, 0.29 mmol), phenylboronic acid (49 mg, 0.38 mmol) and BN-benzo[*c*]phenanthrene **3b** (50 mg, 0.19 mmol) were dissolved in toluene (2 mL). Purification by flash column chromatography on silica gel (hexanes) gave BN-derivative **3e** (39 mg, 0.13 mmol) as white solid in **67%** yield.

M. p.: 108-110 ºC.

IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3024, 2921, 1591, 1535, 1472, 1430, 1295, 1256, 890, 814, 756, 694.

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.57 (d, *J* = 8.8 Hz, 1H, H-1), 8.54 (d, *J* = 8.6 Hz, 1H, H-13), 8.07 (d, *J* = 11.2 Hz, 1H, H-5), 8.02 (d, *J* = 11.2 Hz, 1H, H-9), 7.99 (d, *J* = 2.3 Hz, 1H, H-4), 7.78 (dd, *J* = 7.7, 1.6 Hz, 1H, H-10), 7.73-7.71 (m, 2H, H-16, H-20), 7.68 (dd, *J* = 8.8, 2.3 Hz, 1H, H-2), 7.51-7.47 (m, 2H, H-17, H-19), 7.46 (ddd, *J* = 8.6, 7.1, 1.6 Hz, 1H, H-12), 7.37 (tt, *J* = 7.4, 1.4 Hz, 1H, H-18), 7.34 (ddd, *J* = 7.7, 7.1, 1.1 Hz, 1H, H-11), 7.26 (d, *J* = 11.2 Hz, 1H, H-6), 7.24 (d, *J* = 11.2 Hz, 1H, H-8).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 143.1 (C-5), 143.0 (C-9), 140.3 (C-15), 138.7 (C-13a), 138.1 (C-14a), 135.6 (C-3), 130.9 (C-6*), 130.6 (C-8*), 129.80 (C-10), 129.77 (C-4a**), 129.5 (C-9a), 128.9 (2C, C-17, C-19), 127.8 (C-4), 127.2 (C-18), 127.0 (2C, C-16, C-20), 126.4 (C-12), 125.1 (C-2), 122.9 (C-11), 121.5 (C-1), 121.1 (C-13). *Carbon not observed in ^{13}C-NMR, assigned by gHSQC. **Carbon not observed in ^{13}C-NMR, assigned by gHMBC.

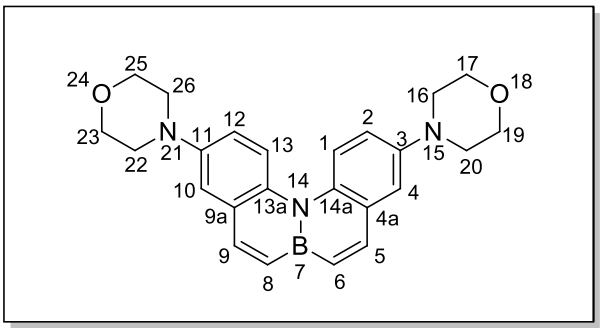
^{11}B-NMR (160 MHz, $CDCl_3$) δ (ppm) 30.4.

HRMS (EI) calculated for $C_{22}H_{16}BN$ $[M]^+$: 305.1370. Found $[M]^+$: 305.1372.

General procedure for the Buchwald-Hartwig reaction

To an oven-dried Biotage microwave vial equipped with a stir bar was added $Pd(OAc)_2$ (10 mol%), JohnPhos (20 mol%), *t*-BuONa (1.5 or 3.0 equiv.) and the corresponding BN-benzo[*c*]phenanthrene (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. Toluene (0.1 M) was added following of morpholine (2.0 or 4.0 equiv.), and the resulting mixture was heated to 110 ºC for 24 h. Then, the reaction mixture 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 to give the corresponding coupled products.

Synthesis of 3,10-dimorpholino-12b-aza-6a-borabenzo[*c*]phenanthrene (3f)



Following the general procedure, $Pd(OAc)_2$ (3.8 mg, 0.017 mmol), JohnPhos (10.2 mg, 0.034 mmol), *t*-BuONa (51 mg, 0.51 mmol) and BN-benzo[*c*]phenanthrene **3c** (50 mg, 0.17 mmol) were dissolved in toluene (2 mL). Then, morpholine (59 μL, 0.67 mmol) was added. Purification by flash column chromatography on silica gel (Hexane/EtOAc 1:1) gave BN-derivative **3f** (57 mg, 0.14 mmol) as white solid in **84%** yield.

M. p.: 224-226 ºC.

IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 2956, 2852, 2817, 1589, 1530, 1471, 1447, 1265, 1235, 1185, 1116, 970, 923, 872, 802.

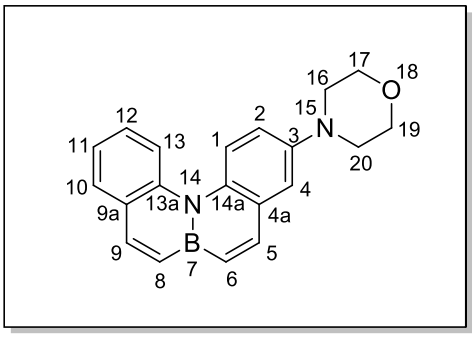
^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.38 (d, *J* = 9.3 Hz, 2H, H-1, H-13), 7.91 (d, *J* = 11.2 Hz, 2H, H-5, H-9), 7.19 (d, *J* = 11.2 Hz, 2H, H-6, H-8), 7.17 (d, *J* = 2.9 Hz, 2H, H-4, H-10), 7.07 (dd, *J* = 9.3, 2.9 Hz, 2H, H-2, H-12), 3.92-3.90 (m, 8H, H-17, H-19, H-23, H-25), 3.25-3.23 (m, 8H, H-16, H-20, H-22, H-26).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 146.4 (2C, C-3, C-11), 142.4 (2C, C-5, C-9), 133.0 (2C, C-13a, C-14a), 131.0 (2C, C-6*, C-8*), 130.2 (2C, C-4a, C-9a), 121.8 (2C, C-1, C-13), 115.8 (2C, C-2, C-12), 114.5 (2C, C-4, C-10), 67.0 (4C, C-17, C-19, C-23, C-25), 49.9 (4C, C-16, C-20, C-22, C-26). *Carbon not observed in ^{13}C-NMR, assigned by gHSQC.

^{11}B-NMR (160 MHz, $CDCl_3$) δ (ppm) 29.7.

HRMS (EI) calculated for $C_{24}H_{26}BN_3O_2$ $[M]^+$: 399.2113. Found $[M]^+$: 399.2118.

Synthesis of 3-morpholino-12b-aza-6a-borabenzo[*c*]phenanthrene (3g)



Following the general procedure, $Pd(OAc)_2$ (4.3 mg, 0.019 mmol), JohnPhos (11.5 mg, 0.038 mmol), *t*-BuONa (28 mg, 0.29 mmol) and BN-benzo[*c*]phenanthrene **3b** (50 mg, 0.19 mmol) were dissolved in toluene (2 mL). Then, morpholine (34 μL, 0.38 mmol) was added. Purification by flash column chromatography on silica gel (Hexane/EtOAc 8:2) gave BN-derivative **3g** (37 mg, 0.12 mmol) as white solid in **63%** yield.

M. p.: 119-121 ºC.

IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 2960, 2852, 2820, 1589, 1560, 1534, 1474, 1444, 1262, 1237, 1121, 810.

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.48 (d, *J* = 8.7 Hz, 1H, H-13), 8.41 (d, *J* = 9.3 Hz, 1H, H-1), 8.00 (d, *J* = 11.2 Hz, 1H, H-9), 7.93 (d, *J* = 11.2 Hz, 1H, H-5), 7.76 (dd, *J* = 7.7, 1.7 Hz, 1H, H-10), 7.42 (ddd, *J* = 8.7, 7.1, 1.7 Hz, 1H, H-12), 7.30 (ddd, *J* = 7.7, 7.1, 1.1 Hz, 1H, H-11), 7.22 (d, *J* = 11.2 Hz, 1H, H-8), 7.20 (d, *J* = 11.2 Hz, 1H, H-6), 7.17 (d, *J* = 3.0 Hz, 1H, H-4), 7.07 (dd, *J* = 9.3, 3.0 Hz, 1H, H-2), 3.93-3.90 (m, 4H, H-17, H-19), 3.26-3.23 (m, 4H, H-16, H-20).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 146.7 (C-3), 142.9 (C-5), 142.6 (C-9), 138.8 (C-13a), 132.8 (C-14a), 130.8 (C-6*), 130.7 (C-8*), 130.4 (C-4a), 129.8 (C-10), 129.4 (C-9a), 126.2 (C-12), 122.5 (C-11), 122.0 (C-1), 120.8 (C-13), 115.7 (C-2), 114.4 (C-4), 66.9 (2C, C-17, C-19), 49.8 (2C, C-16, C-20). *Carbon not observed in ^{13}C-NMR, assigned by gHSQC.

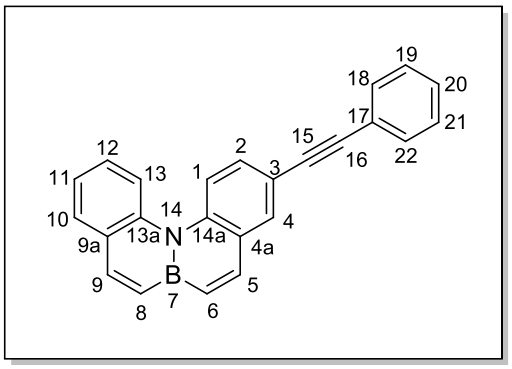
^{11}B-NMR (160 MHz, $CDCl_3$) δ (ppm) 29.6.

HRMS (EI) calculated for $C_{20}H_{19}BN_2O$ $[M]^+$: 314.1585. Found $[M]^+$: 314.1598.

General procedure for the Sonogashira reaction

To an oven-dried Biotage microwave vial equipped with a stir bar was added $PdCl_2(MeCN)_2$ (5 mol%), XPhos (15 mol%), Cs_2CO_3 (2.5 or 5.0 equiv.) and the corresponding BN-benzo[*c*]phenanthrene (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. Acetonitrile (0.1 M) was added, and the resulting suspension was stirred at room temperature for 30 min. Then, the corresponding alkyne (1.3 or 2.6 equiv.) was injected, and the mixture was heated to 100 ºC until full consumption of starting material was observed by TLC. 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 to give the corresponding coupled products.

Synthesis of 3-(phenylethynyl)-12b-aza-6a-borabenzo[*c*]phenanthrene (3h)



Following the general procedure, $PdCl_2(MeCN)_2$ (1.4 mg, 0.0055 mmol), XPhos (8.1 mg, 0.0165 mmol), Cs_2CO_3 (90 mg, 0.28 mmol) and BN-benzo[*c*]phenanthrene **3b** (30 mg, 0.11 mmol) were dissolved in acetonitrile (1 mL). Then, phenylacetylene (17 μL, 0.15 mmol) was injected, and the mixture was heated to 100 ºC for 4 h. Purification by flash column chromatography on silica gel (1% EtOAc in Hexane) gave BN-derivative **3h** (30 mg, 0.091 mmol) as white solid in **83%** yield.

M. p.: 103-105 ºC.

IR (KBr) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3014, 2923, 2851, 1595, 1558, 1532, 1470, 1435, 1287, 891, 810, 754, 690.

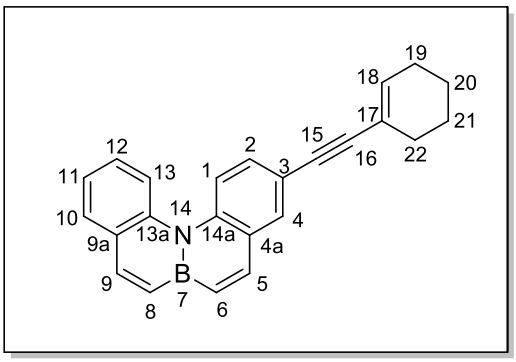
^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.46 (d, *J* = 8.8 Hz, 1H, H-1), 8.44 (d, *J* = 8.5 Hz, 1H, H-13), 8.01 (d, *J* = 11.2 Hz, 1H, H-9), 7.97 (d, *J* = 11.3 Hz, 1H, H-5), 7.96 (d, *J* = 2.1 Hz, 1H, H-4), 7.77 (dd, *J* = 7.7, 1.8 Hz, 1H, H-10), 7.58-7.55 (m, 3H, H-2, H-18, H-22), 7.45 (ddd, *J* = 8.5, 7.0, 1.8 Hz, 1H, H-12), 7.39-7.32 (m, 4H, H-11, H-19, H-20, H-21), 7.25 (d, *J* = 11.3 Hz, 1H, H-6), 7.21 (d, *J* = 11.2 Hz, 1H, H-8).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 143.3 (C-9), 142.5 (C-5), 138.6 (C-14a), 138.5 (C-13a), 133.0 (C-4), 131.61 (2C, C-18, C-22), 131.60 (C-6*), 130.7 (C-8*), 129.9 (C-10), 129.6 (C-9a), 129.4 (C-4a), 129.2 (C-2), 128.4 (2C, C-19, C-21), 128.2 (C-20), 126.5 (C-12), 123.3 (C-17), 123.2 (C-11), 121.13 (C-1), 121.07 (C-13), 117.6 (C-3), 89.2 (C-16), 89.1 (C-15). *Carbon not observed in ^{13}C-NMR, assigned by gHSQC.

^{11}B-NMR (160 MHz, $CDCl_3$) δ (ppm) 30.2.

HRMS (EI) calculated for $C_{24}H_{16}BN$ $[M]^+$: 329.1370. Found $[M]^+$: 329.1386.

Synthesis of 3-(cyclohex-1-en-1-ylethynyl)-12b-aza-6a-borabenzo[*c*]phenanthrene (3i)



Following the general procedure, $PdCl_2(MeCN)_2$ (1.4 mg, 0.0055 mmol), XPhos (8.1 mg, 0.0165 mmol), Cs_2CO_3 (90 mg, 0.28 mmol) and BN-benzo[*c*]phenanthrene **3b** (30 mg, 0.11 mmol) were dissolved in acetonitrile (1 mL). Then, 1-ethynylcyclohexene (18 μL, 0.15 mmol) was injected, and the mixture was heated to 100 ºC for 4 h. Purification by flash column chromatography on silica gel (1% EtOAc in Hexane) gave BN-derivative **3i** (23 mg, 0.069 mmol) as yellow oil in **63%** yield.

IR (NaCl) $\tilde{\upsilon}_{max}$ (cm^{-1}) 3477, 3379, 3027, 2926, 2856, 1614, 1531, 1493, 1262, 1031, 815, 749.

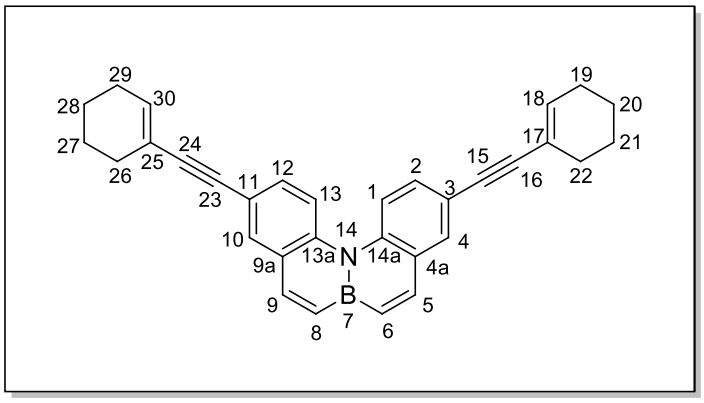
^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.42 (d, *J* = 8.6 Hz, 1H, H-13), 8.41 (d, *J* = 8.8 Hz, 1H, H-1), 7.99 (d, *J* = 11.2 Hz, 1H, H-9), 7.93 (d, *J* = 11.2 Hz, 1H, H-5), 7.83 (d, *J* = 2.1 Hz, 1H, H-4), 7.75 (dd, *J* = 7.7, 1.8 Hz, 1H, H-10), 7.45 (dd, *J* = 8.8, 2.1 Hz, 1H, H-2), 7.42 (ddd, *J* = 8.6, 7.0, 1.8 Hz, 1H, H-12), 7.32 (ddd, *J* = 7.7, 7.0, 1.1 Hz, 1H, H-11), 7.22 (d, *J* = 11.2 Hz, 1H, H-6), 7.19 (d, *J* = 11.2 Hz, 1H, H-8), 6.26-6.23 (m, 1H, H-18), 2.28-2.24 (m, 2H, H-22), 2.18-2.14 (m, 2H, H-19), 1.72-1.67 (m, 2H, H-21), 1.65-1.60 (m, 2H, H-20).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 143.2 (C-9), 142.5 (C-5), 138.5 (C-13a), 138.2 (C-14a), 135.2 (C-18), 132.7 (C-4), 131.0 (C-6*), 130.5 (C-8*), 129.8 (C-10), 129.6 (C-9a), 129.3 (C-4a), 129.2 (C-2), 126.5 (C-12), 123.1 (C-11), 121.1 (C-13), 121.0 (C-1), 120.8 (C-17), 118.1 (C-3), 91.1 (C-16), 86.4 (C-15), 29.3 (C-22), 25.8 (C-19), 22.4 (C-21), 21.5 (C-20). *Carbon not observed in ^{13}C-NMR, assigned by gHSQC.

^{11}B-NMR (160 MHz, $CDCl_3$) δ (ppm) 29.5.

HRMS (EI) calculated for $C_{24}H_{20}BN$ $[M]^+$: 333.1683. Found $[M]^+$: 333.1672.

Synthesis of 3,10-bis(cyclohex-1-en-1-ylethynyl)-12b-aza-6a-borabenzo[*c*]phenanthrene (3j)



Following the general procedure, $PdCl_2(MeCN)_2$ (1.7 mg, 0.0065 mmol), XPhos (9.6 mg, 0.0195 mmol), Cs_2CO_3 (213 mg, 0.65 mmol) and BN-benzo[*c*]phenanthrene **3c** (40 mg, 0.13 mmol) were dissolved in acetonitrile (2.5 mL). Then, 1-ethynylcyclohexene (41 μL, 0.35 mmol) was injected, and the mixture was heated to 100 ºC for 2 h. Purification by

flash column chromatography on silica gel (1% EtOAc in Hexane) gave BN-derivative **3j** (28 mg, 0.064 mmol) as yellow oil in **49%** yield.

IR (NaCl) $\tilde{\upsilon}_{max}$ (cm^{-1}) 2927, 2856, 1585, 1467, 1298, 1262, 1027, 891, 808.

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.33 (d, *J* = 8.8 Hz, 2H, H-1, H-13), 7.92 (d, *J* = 11.2 Hz, 2H, H-5, H-9), 7.82 (d, *J* = 2.0 Hz, 2H, H-4, H-10), 7.45 (dd, *J* = 8.8, 2.0 Hz, 2H, H-2, H-12), 7.20 (d, *J* = 11.2 Hz, 2H, H-6, H-8), 6.25-6.23 (m, 2H, H-18, H-30), 2.27-2.23 (m, 4H, H-22, H-26), 2.18-2.14 (m, 4H, H-19, H-29), 1.72-1.67 (m, 4H, H-21, H-27), 1.65-1.60 (m, 4H, H-20, H-28).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 142.7 (2C, C-5, C-9), 137.9 (2C, C-13a, C-14a), 135.3 (2C, C-18, C-30), 132.7 (2C, C-4, C-10), 130.8 (2C, C-6*, C-8*), 129.4 (2C, C-4a, C-9a), 129.3 (2C, C-2, C-12), 121.0 (2C, C-1, C-13), 120.7 (2C, C-17, C-25), 118.4 (2C, C-3, C-11), 91.3 (2C, C-16, C-24), 86.3 (2C, C-15, C-23), 29.3 (2C, C-22, C-26), 25.8 (2C, C-19, C-29), 22.4 (2C, C-21, C-27), 21.6 (2C, C-20, C-28). *Carbon not observed in ^{13}C-NMR, assigned by gHSQC.

^{11}B-NMR (160 MHz, $CDCl_3$) δ (ppm) 30.8.

HRMS (EI) calculated for $C_{23}H_{28}BN$ $[M]^+$: 437.2309. Found $[M]^+$: 437.2314.

X-RAY CRYSTALLOGRAPHIC DATA FOR 3a

Colourless crystals were grown by slow evaporation of a hexane solution with some drops of diethylether. The crystals were removed from the vial and covered with a layer of a viscous perfluoropolyether (FomblinY). A suitable crystal, selected with the aid of a microscope, was 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.

The structure was solved, using the WINGX package,[8] by direct methods (SHELXS-2013)[9] and refined by least-squares against F^2 (SHELXL-2014/7).[10]

All non-hydrogen atoms were anisotropically refined, whereas the hydrogen atoms were positioned geometrically and refined by using a riding model.

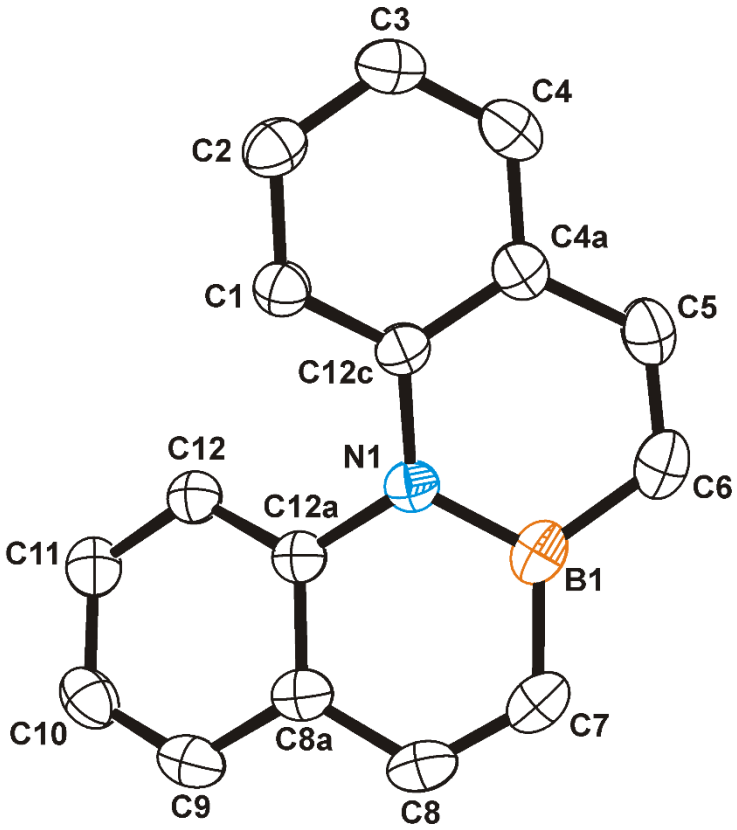


Figure S1. X-ray structure and numbering scheme for **3a**. Thermal ellipsoids are drawn at the 50% probability level.

[8] L. J. Farrugia *J. Appl. Crystallogr.* **2012**, *45*, 849-854.

[9] G. M. Sheldrick *Acta Crystallogr.* **2008**, *A64*, 112-122.

[10] G. M. Sheldrick *Acta Crystallogr.* **2015**, *C71*, 3-8.

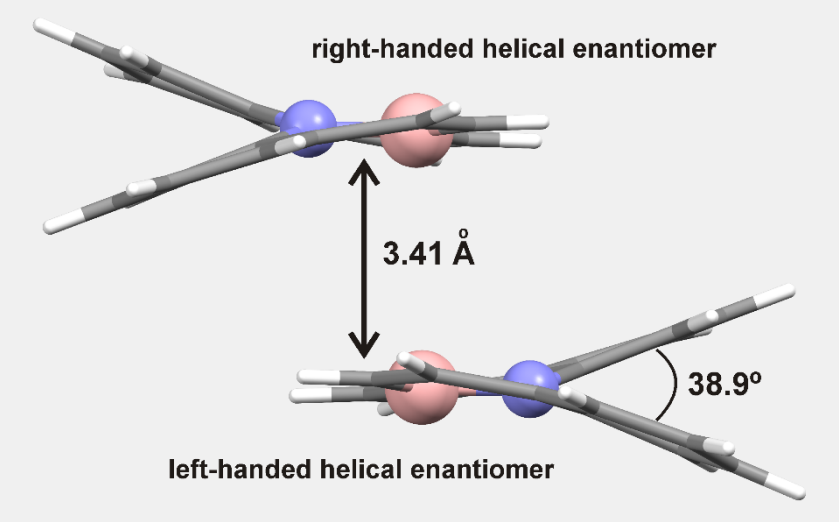


Figure S2. Association of the two enantiomers of **3a** in pairs. Nitrogen and boron atoms are represented by blue and pink spheres, respectively.

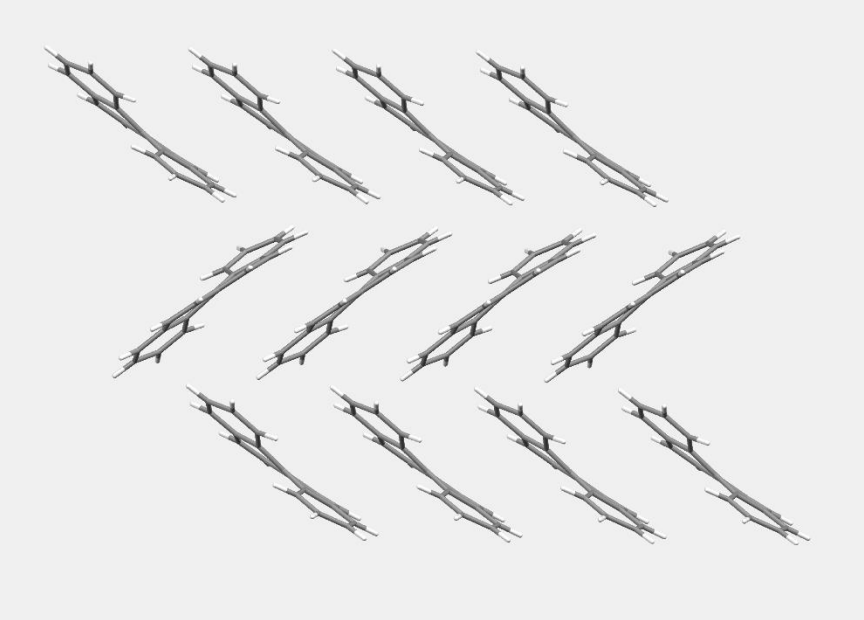
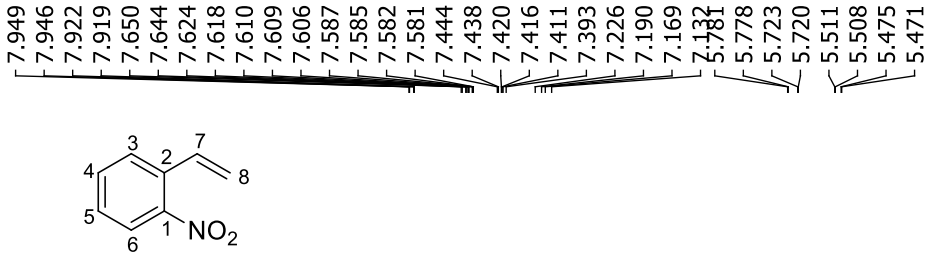


Figure S3. Crystal packing of benzo[*c*]phenanthrene in a herringbone motif.

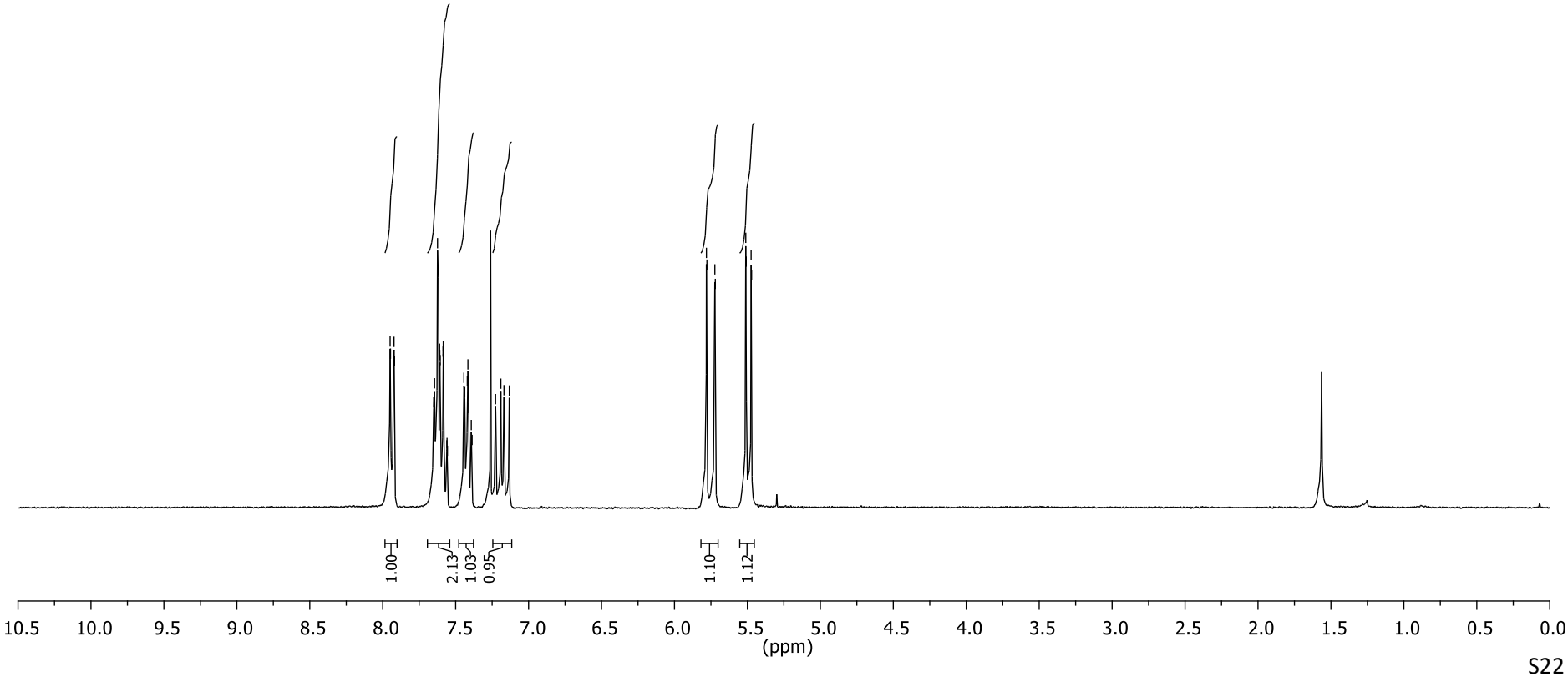
Table S1. Experimental data for the X-ray diffraction study on compound **3a**

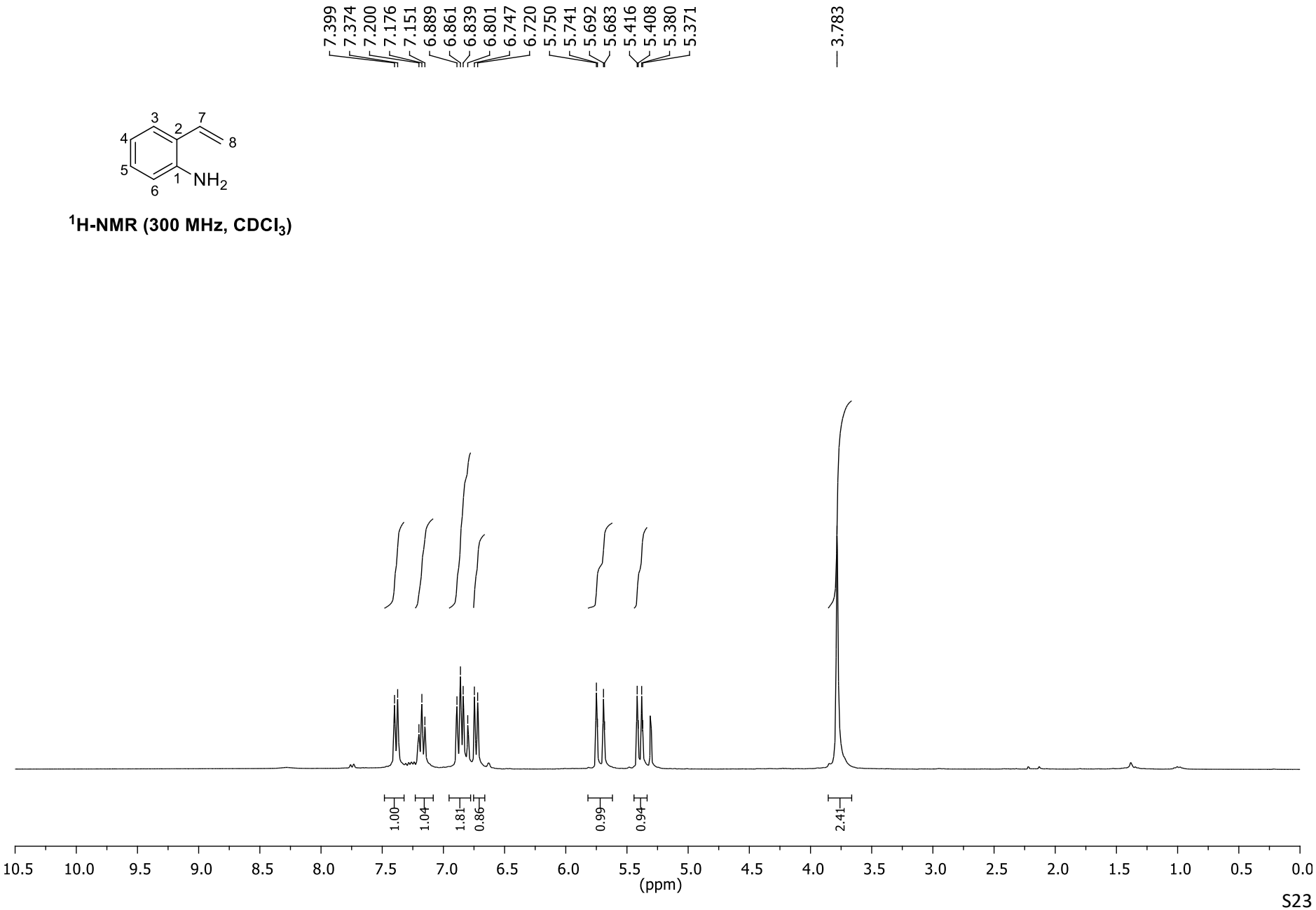
formula	$C_{16}H_{12}BN$
M_r	229.08
T [K]	200
λ [Å]	0.71073
crystal system	monoclinic
space group	$P2_1/c$
a [Å]	10.177(1)
b [Å]; β (º)	7.848(1); 108.89(1)
c [Å]	15.407(1)
V [Å^3]	1164.2(1)
Z	4
ρ_{calcd} [g cm^{-3}]	1.307
$\mu_{MoK\alpha}$ [mm^{-1}]	0.075
F(000)	480
crystal size [mm^3]	0.28 × 0.25 × 0.14
θ range (deg)	3.35 to 27.49
index ranges	−13 to 13 −10 to 10 −20 to 20
reflns collected	25671
unique data	2671 [R(int) = 0.080]
obsd data [$I > 2\sigma(I)$]	1784
GOF on F^2	1.058
final R[a] indices [$I > 2\sigma(I)$]	R1 = 0.056 wR2 = 0.124
R[a] indices (all data)	R1 = 0.099 wR2 = 0.152
largest diff. peak/hole [e Å^{-3}]	0.215 and −0.229

[a] $R1 = \sum||F_0|-|F_c||/[\sum|F_0|]$; $wR2 = \{[\sum w(F_0^2 - F_c^2)^2]/[\sum w(F_0^2)^2$

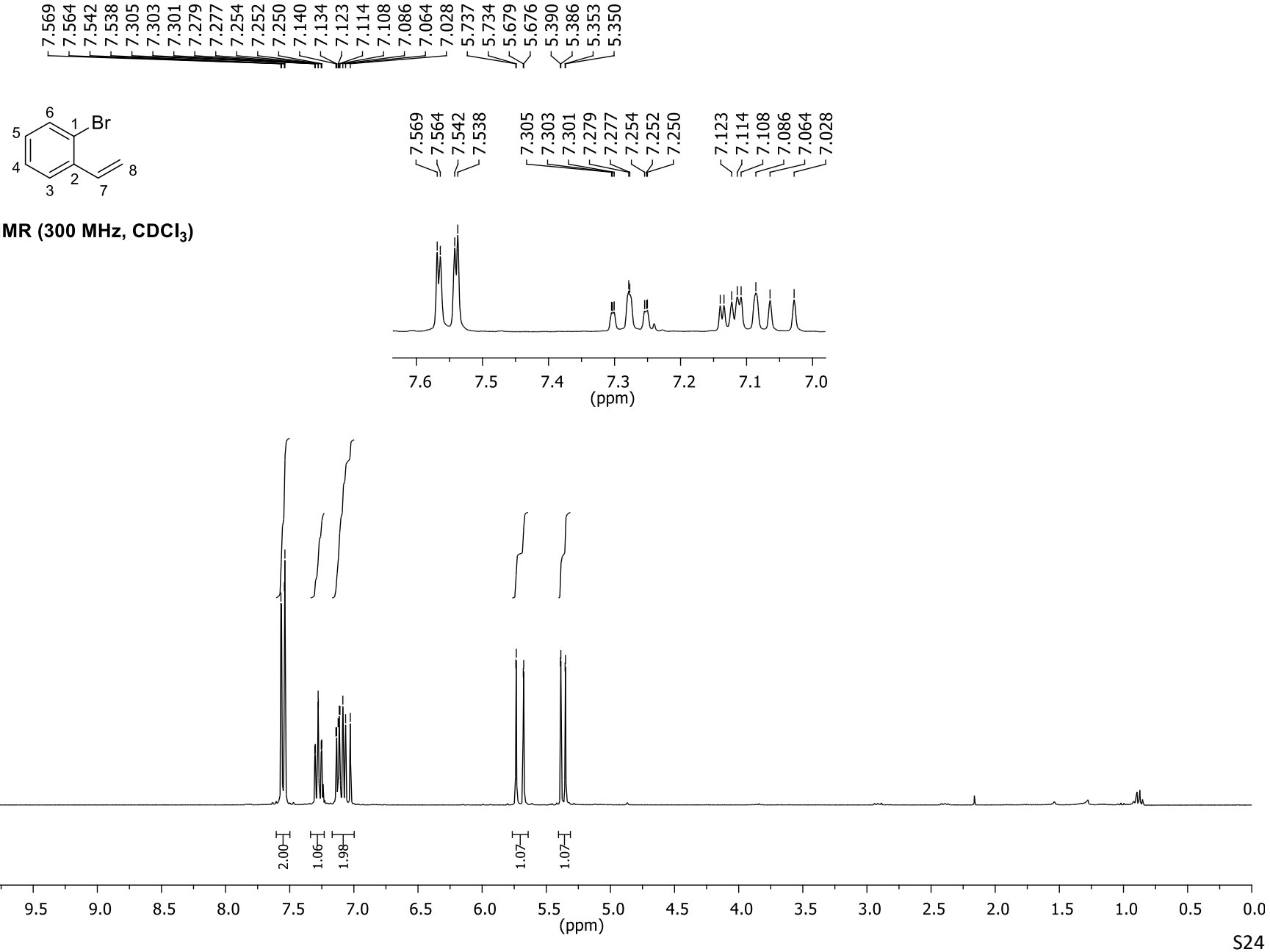


^{1}H-NMR (300 MHz, $CDCl_3$)

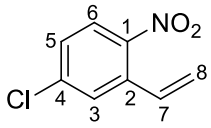




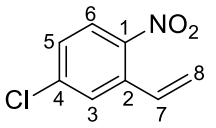
^{1}H-NMR (300 MHz, $CDCl_3$)



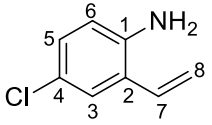
^{1}H-NMR (300 MHz, $CDCl_3$)



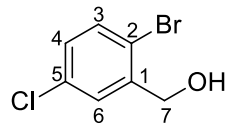
^{1}H-NMR (300 MHz, $CDCl_3$)



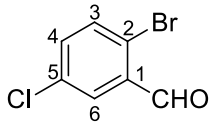
^{13}C-NMR (75 MHz, $CDCl_3$)



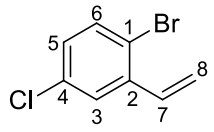
^{1}H-NMR (300 MHz, $CDCl_3$)



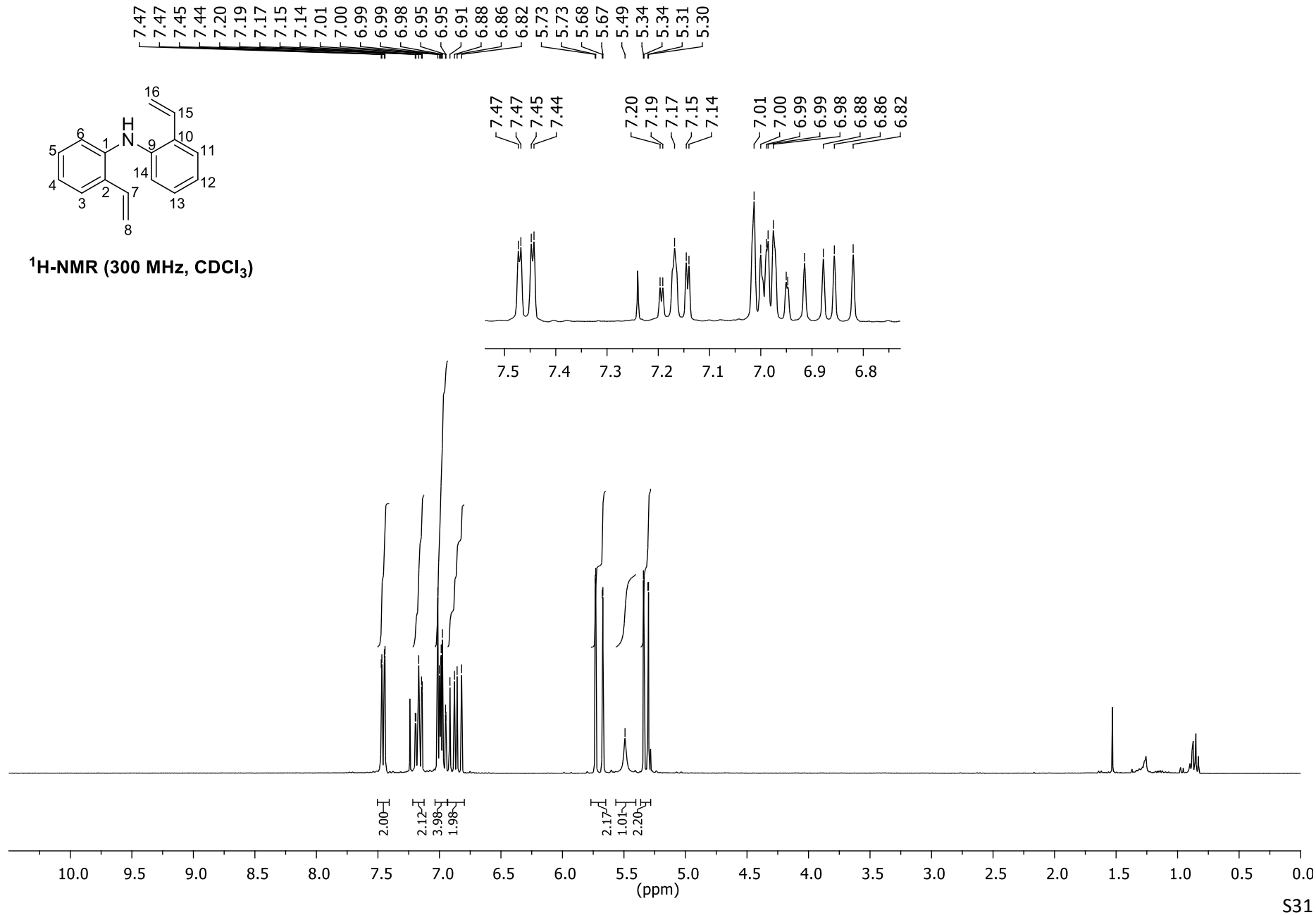
^{1}H-NMR (300 MHz, $CDCl_3$)



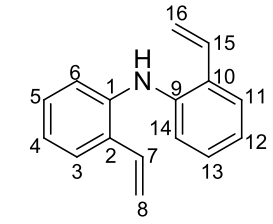
^{1}H-NMR (300 MHz, $CDCl_3$)



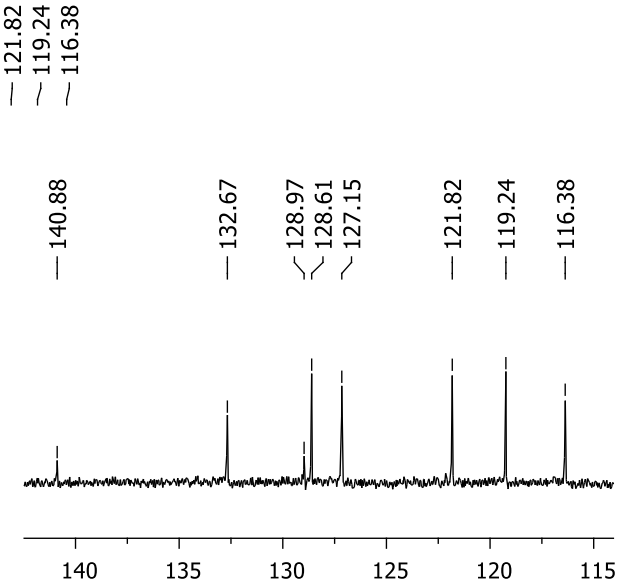
^{1}H-NMR (300 MHz, $CDCl_3$)

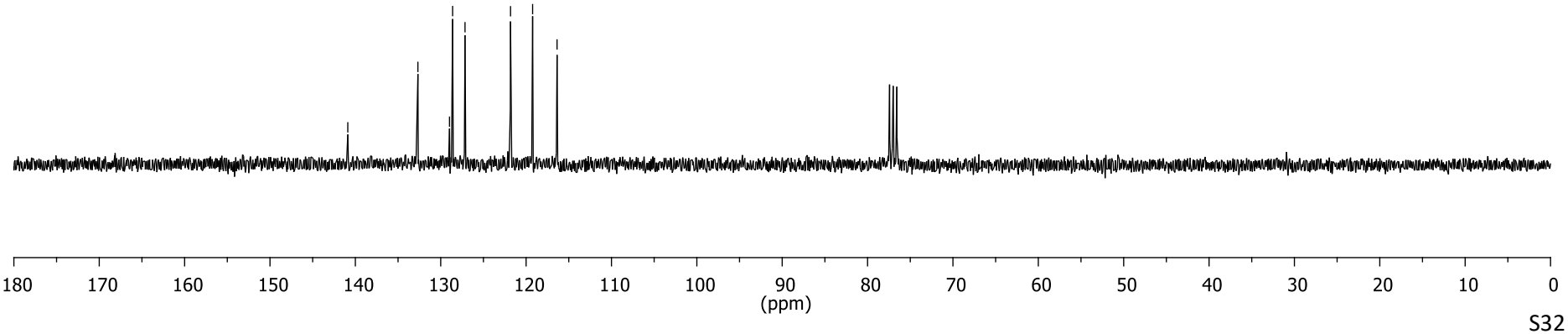


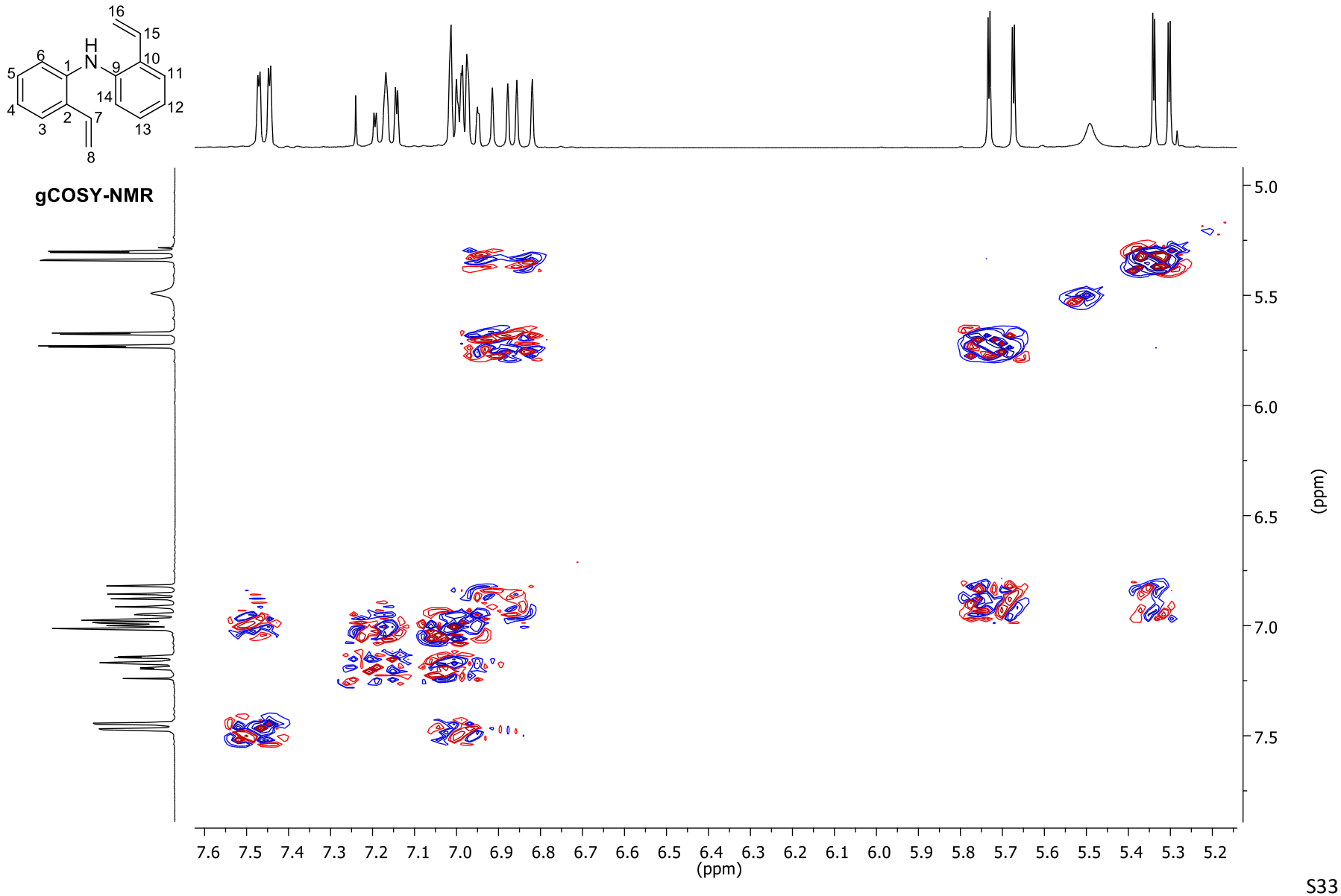
^{1}H-NMR (300 MHz, $CDCl_3$)

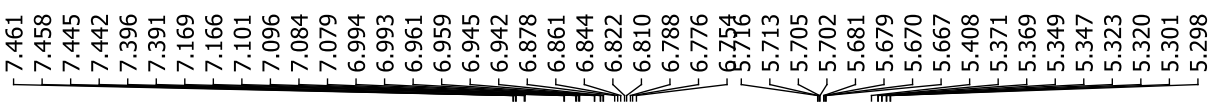


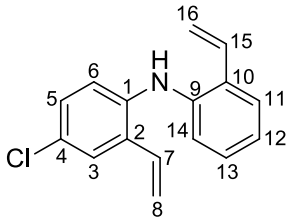
^{13}C-NMR (75 MHz, $CDCl_3$)



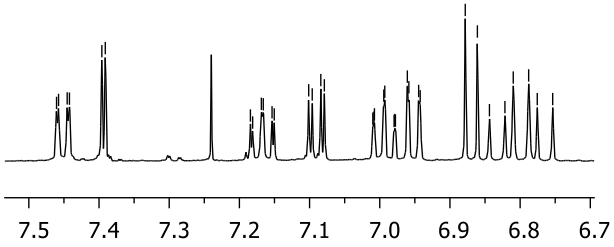


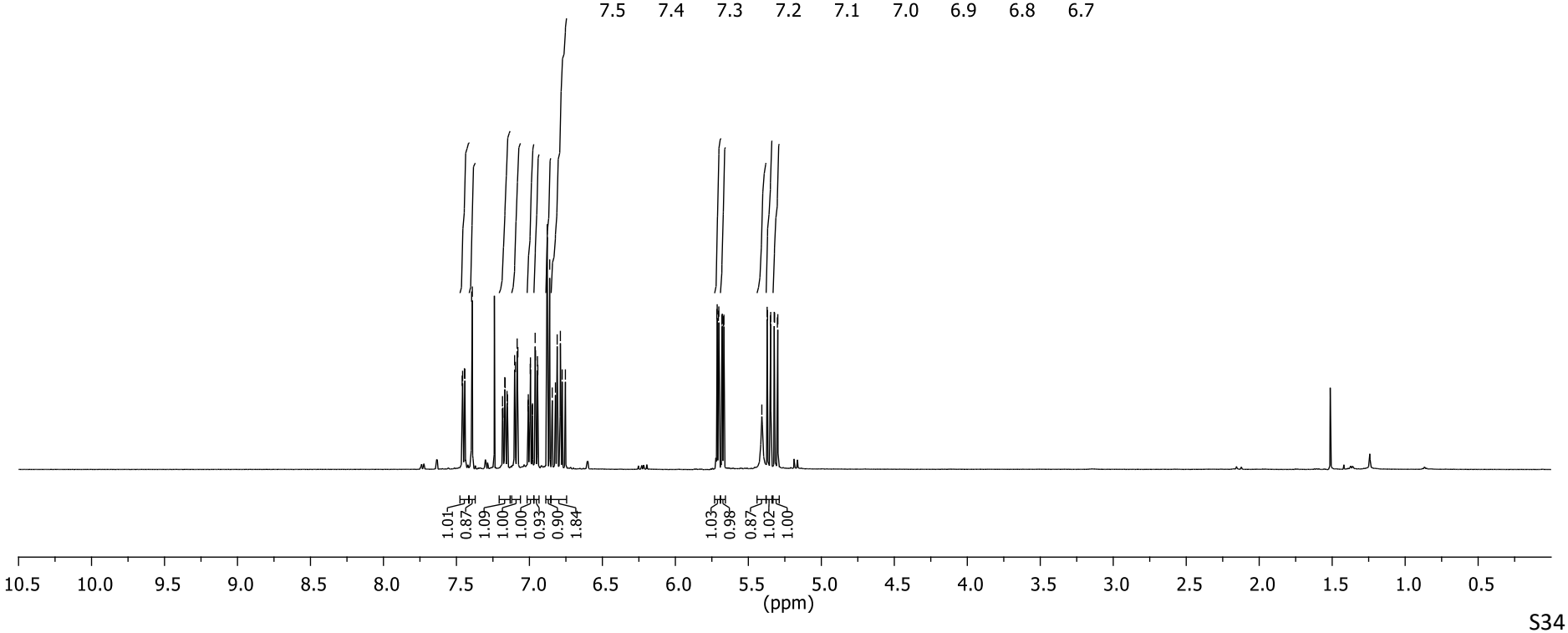

gCOSY-NMR
16
15
6
1
H
N
9
10
11
5
14
4
2
7
12
3
13
8
7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2
(ppm)
5.0
5.5
6.0
6.5
7.0
7.5
(ppm)

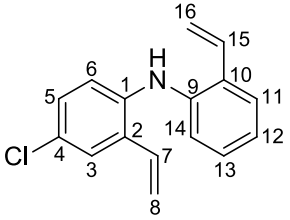




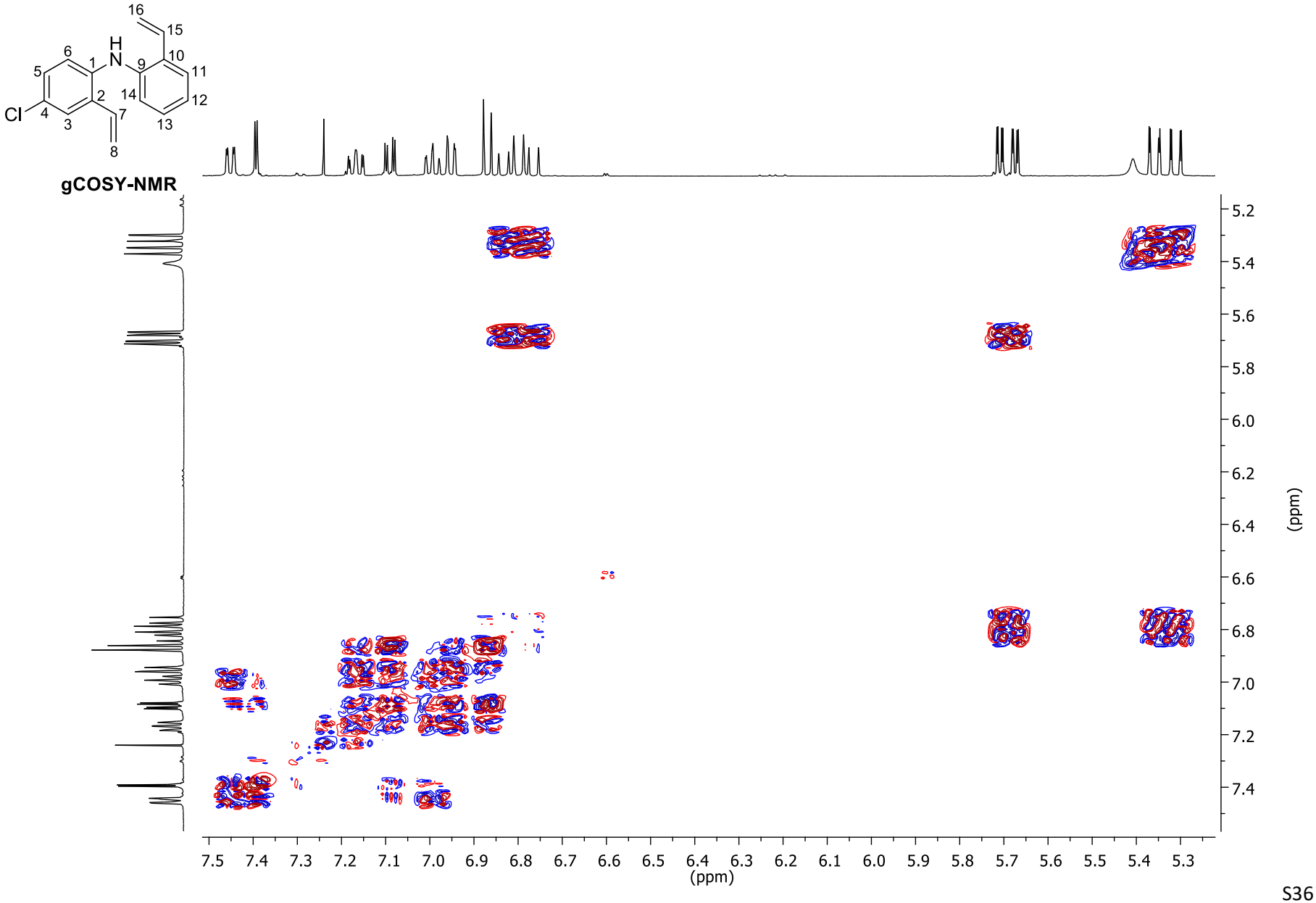
^{1}H-NMR (500 MHz, $CDCl_3$)

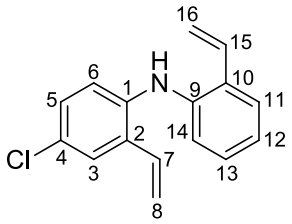




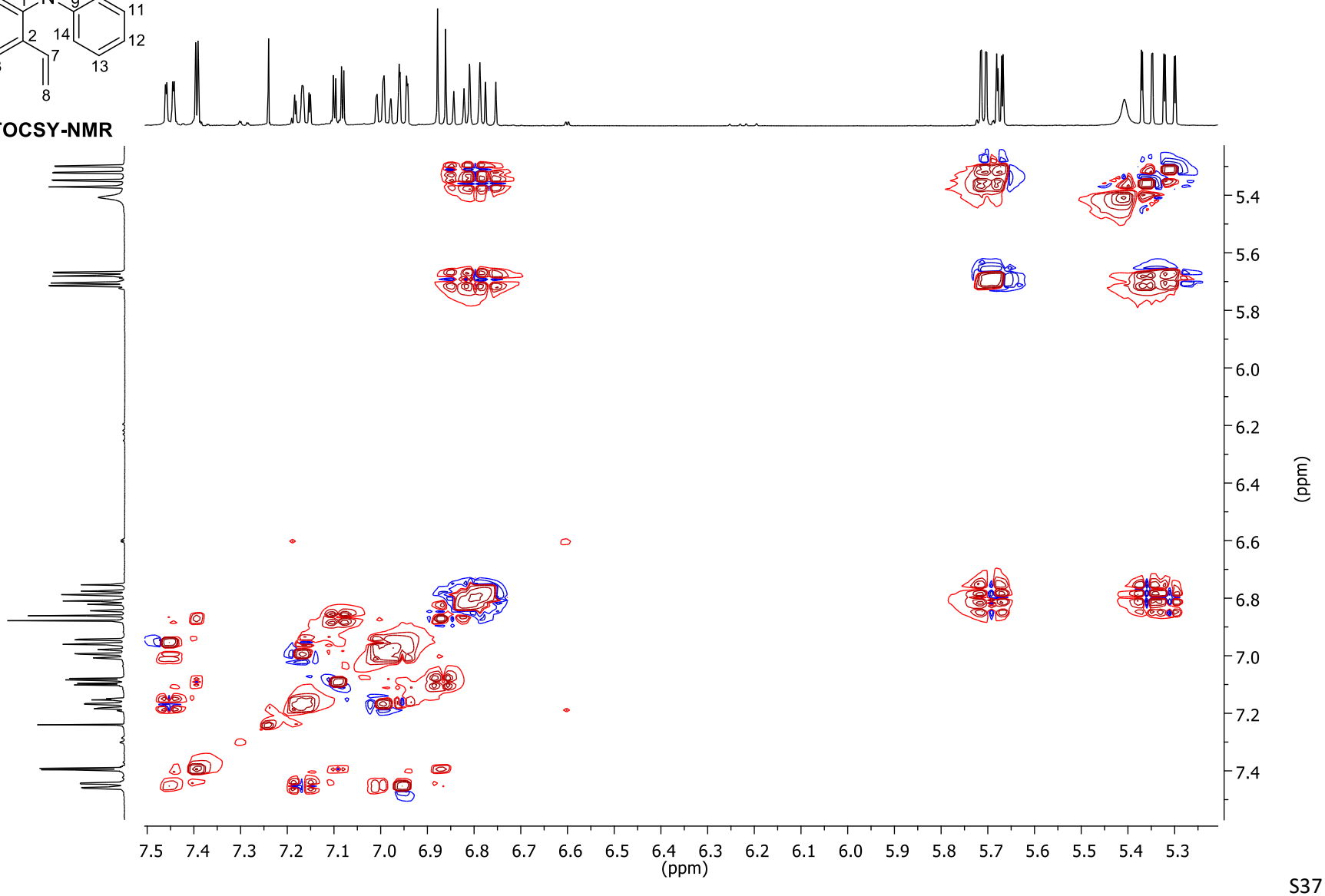


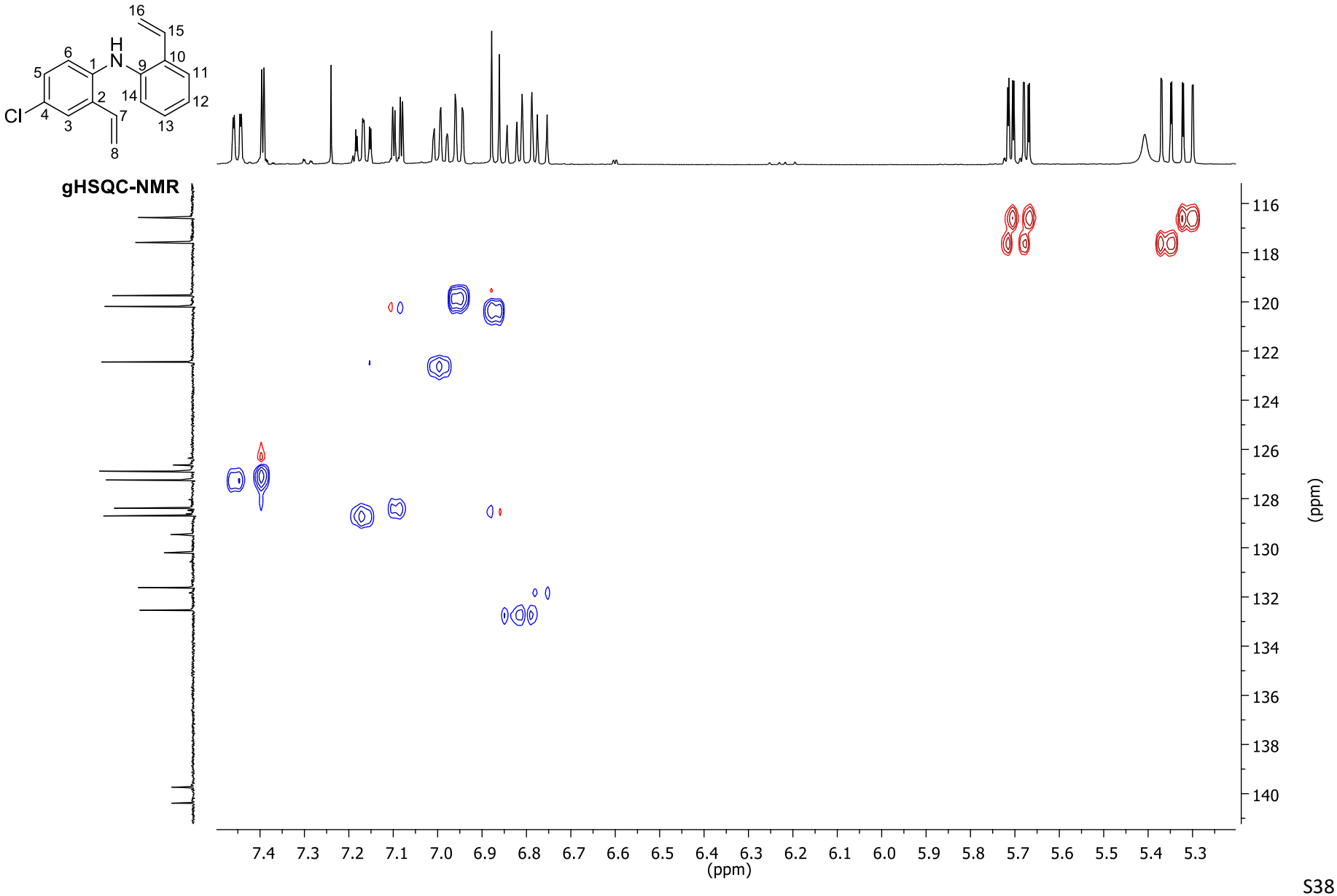
^{13}C-NMR (125 MHz, $CDCl_3$)

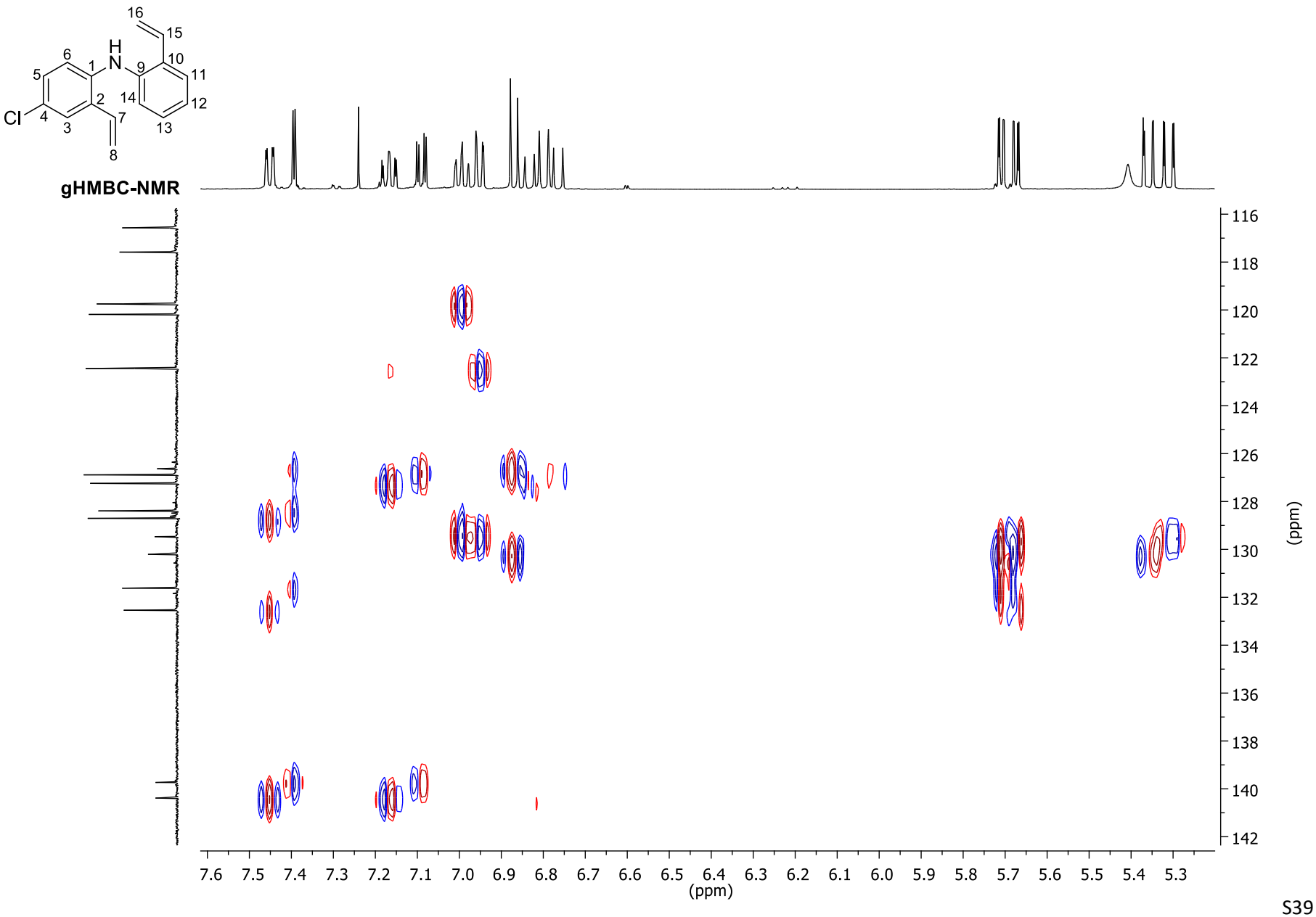

gCOSY-NMR
Cl
H
N
(ppm)
(ppm)

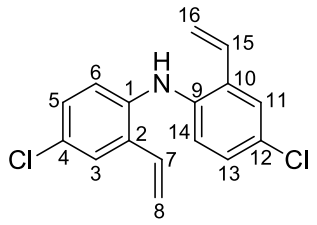

16
15
6
H
N
10
5
1
9
11
2
14
12
Cl
4
7
3
13
8

TOCSY-NMR

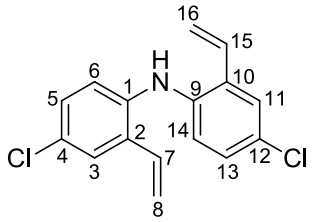

5.4
5.6
5.8
6.0
6.2
6.4
6.6
6.8
7.0
7.2
7.4
(ppm)
7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3
(ppm)


gHSQC-NMR
16
15
H
N
6
1
9
10
11
5
2
14
12
Cl
4
7
3
13
8
116
118
120
122
124
126
128
130
132
134
136
138
140
(ppm)
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2
6.1
6.0
5.9
5.8
5.7
5.6
5.5
5.4
5.3
(ppm)

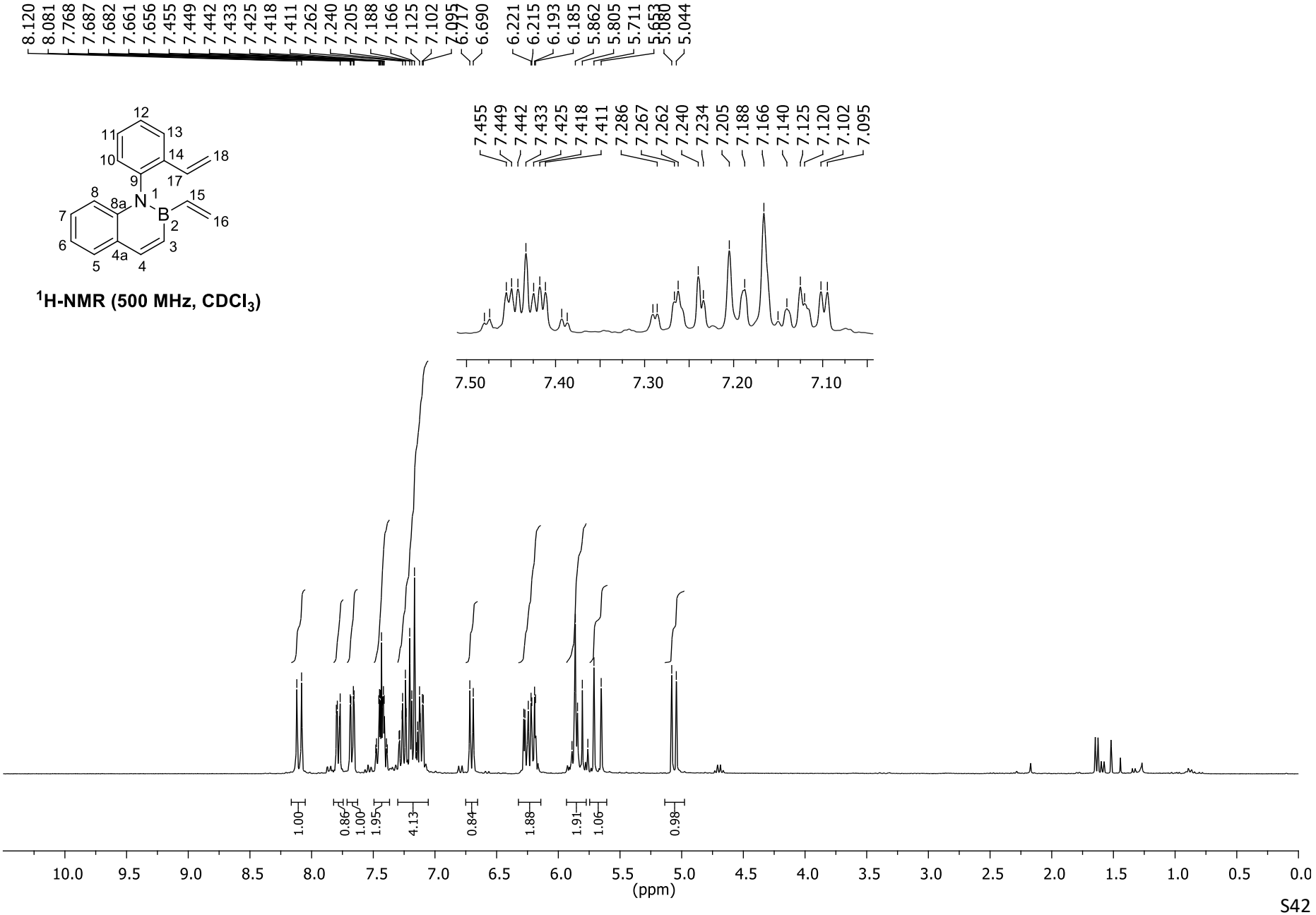

16
15
H
N
6
1
9
10
11
5
2
14
12
Cl
4
3
7
13
8
gHMBC-NMR
116
118
120
122
124
126
128
130
132
134
136
138
140
142
(ppm)
7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3
(ppm)



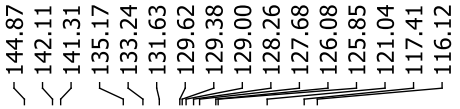
^{1}H-NMR (500 MHz, $CDCl_3$)

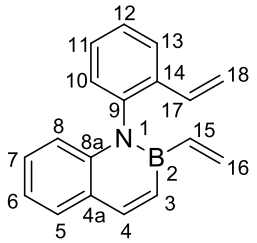


^{13}C-NMR (125 MHz, $CDCl_3$)

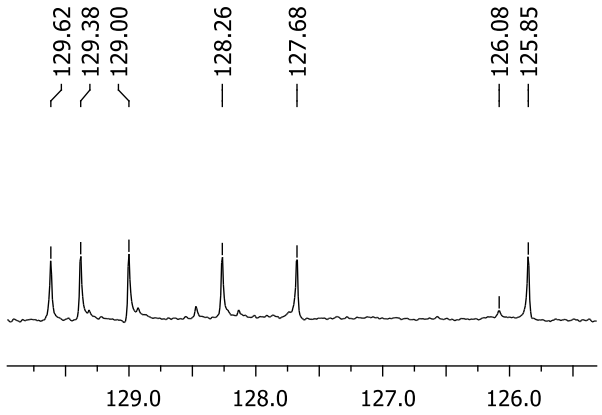


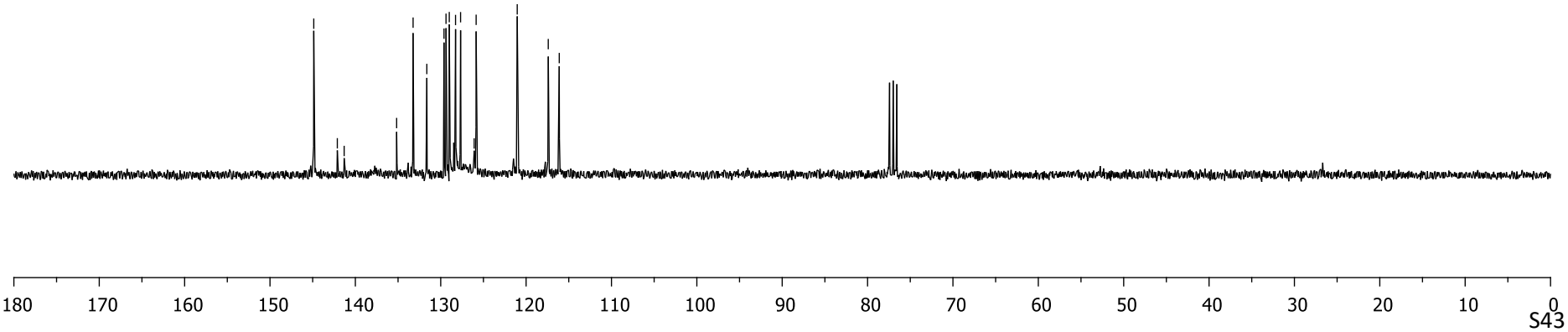
^{1}H-NMR (500 MHz, $CDCl_3$)

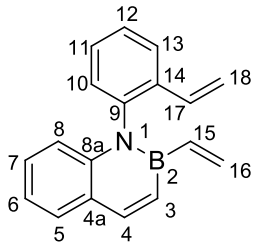




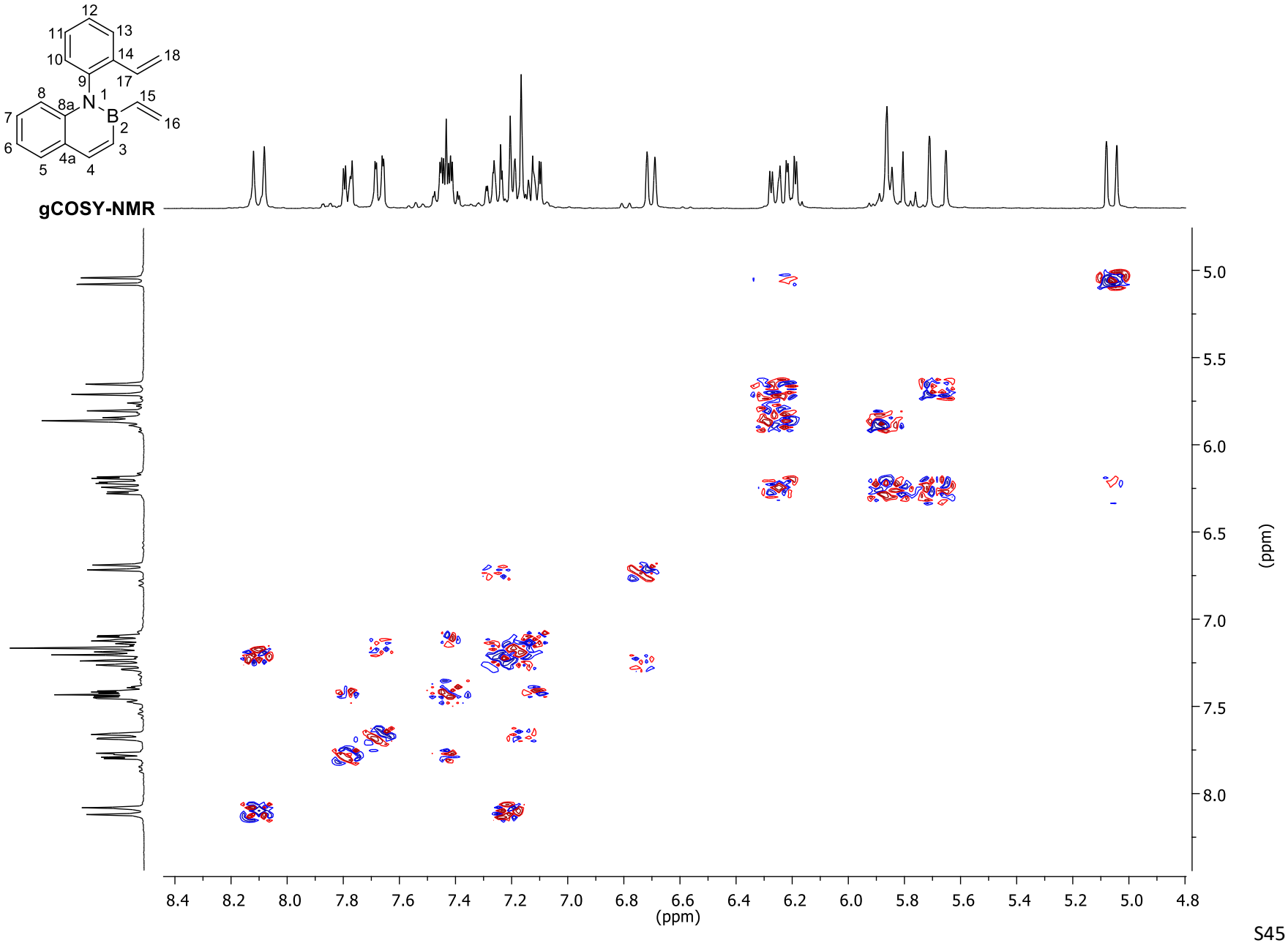
^{13}C-NMR (125 MHz, $CDCl_3$)







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


gCOSY-NMR
12
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17
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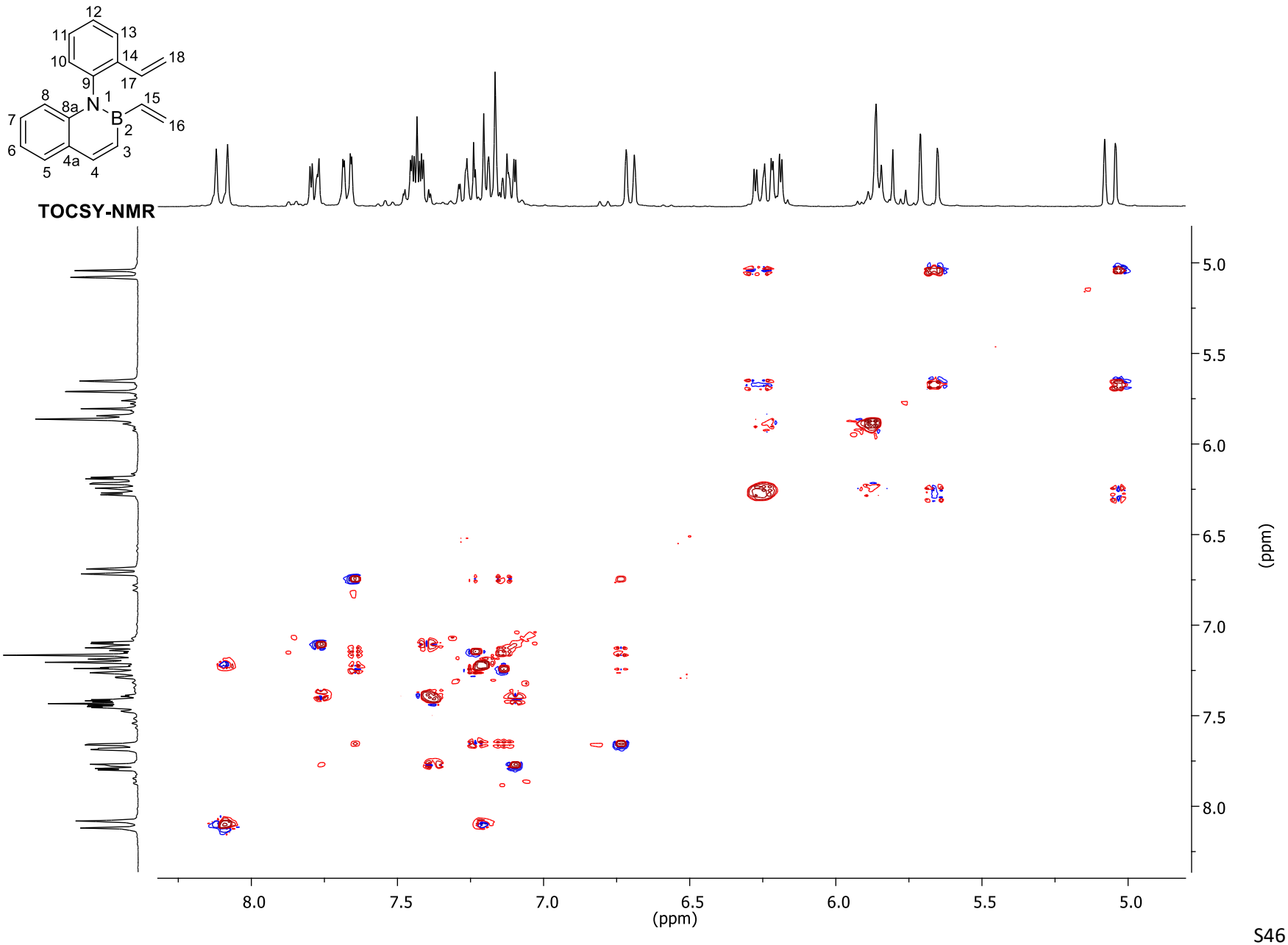
8a
N
1
15
7
B
2
16
6
3
4a
5
4
5.0
5.5
6.0
6.5
7.0
7.5
8.0
(ppm)
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
(ppm)


12
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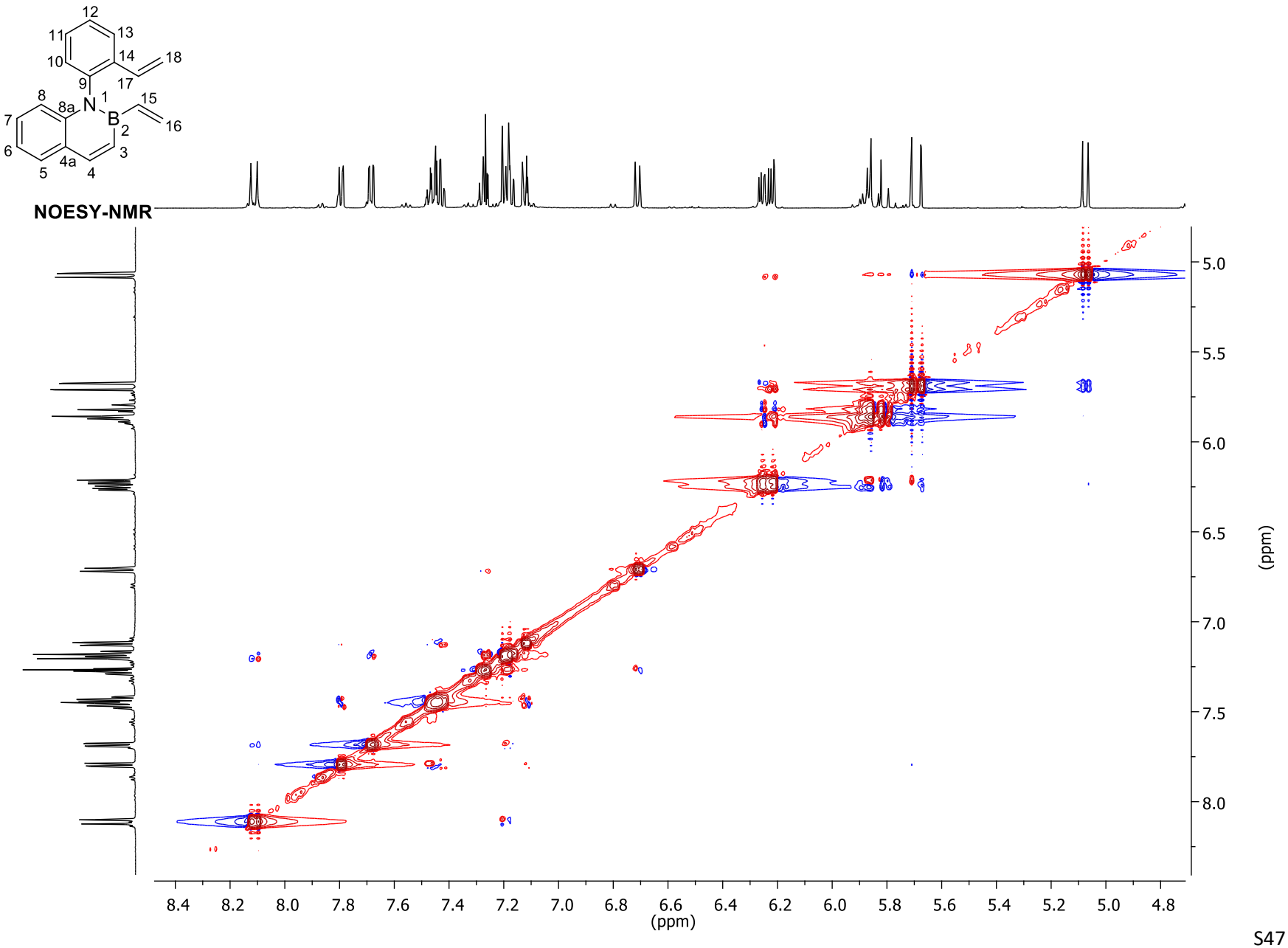
1
15
8a
N
B
7
2
16
6
3
4a
5
4
TOCSY-NMR
5.0
5.5
6.0
6.5
7.0
7.5
8.0
(ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
(ppm)


12
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8
N
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8a
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16
7
6
3
4a
5
4
NOESY-NMR
5.0
5.5
6.0
6.5
7.0
7.5
8.0
(ppm)
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
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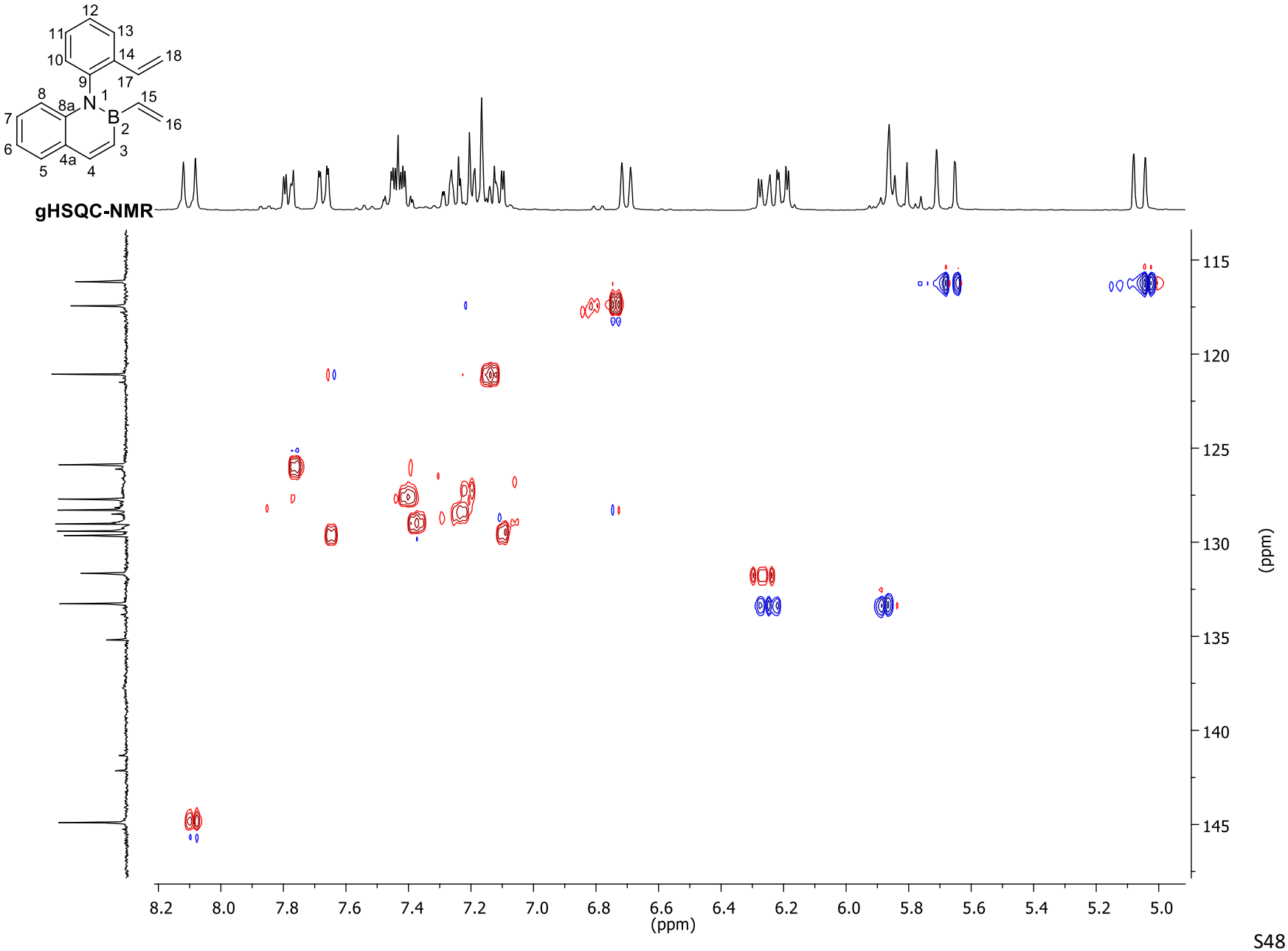
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
(ppm)


12
11
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N
1
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8a
B
2
16
7
3
6
4a
5
4
gHSQC-NMR
115
120
125
130
135
140
145
(ppm)
8.2
8.0
7.8
7.6
7.4
7.2
7.0
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6.2
6.0
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5.6
5.4
5.2
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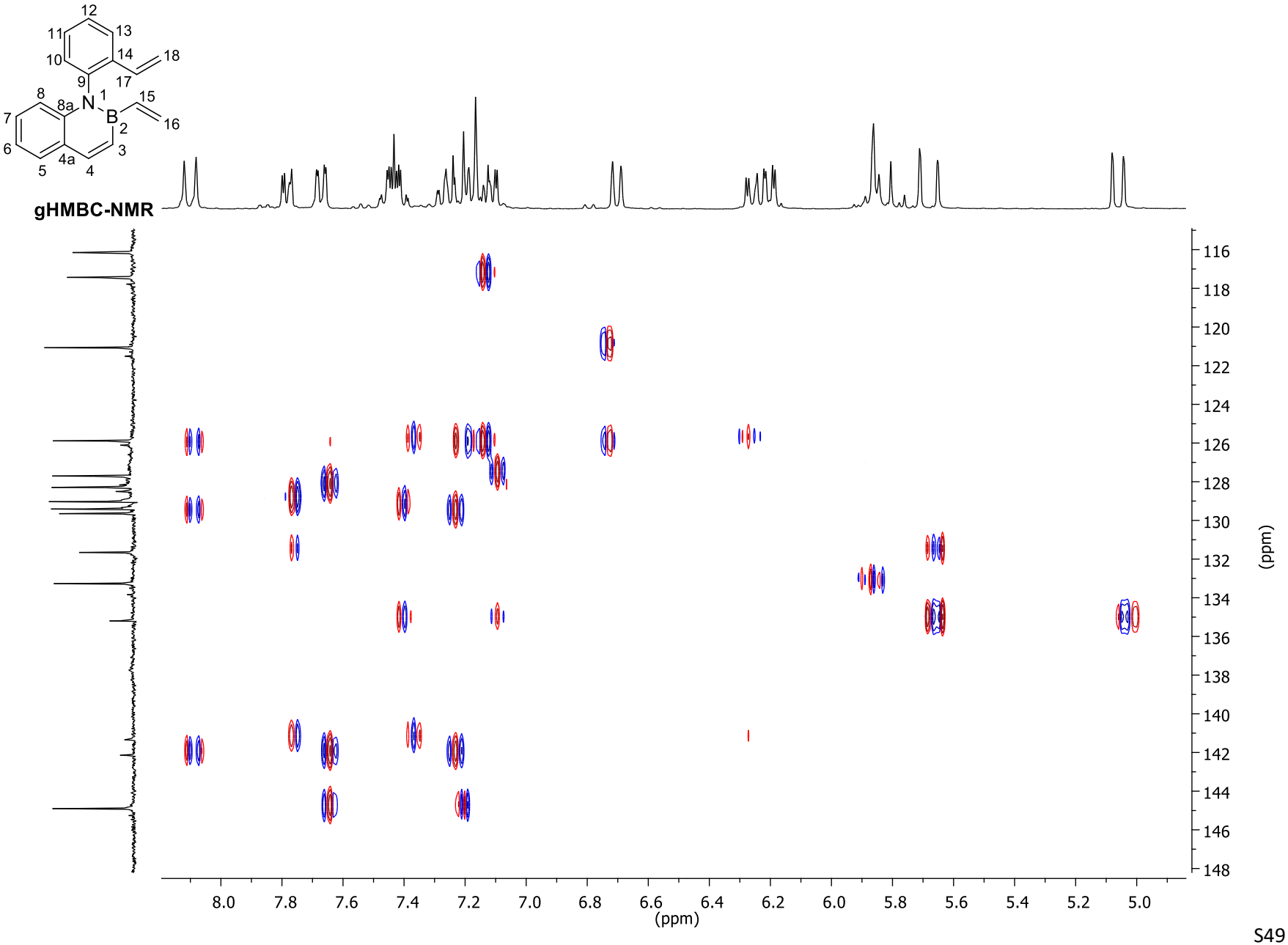
(ppm)


12
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8a
N
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16
6
3
4a
5
4
gHMBC-NMR
116
118
120
122
124
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128
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132
134
136
138
140
142
144
146
148
(ppm)
8.0
7.8
7.6
7.4
7.2
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6.6
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6.2
6.0
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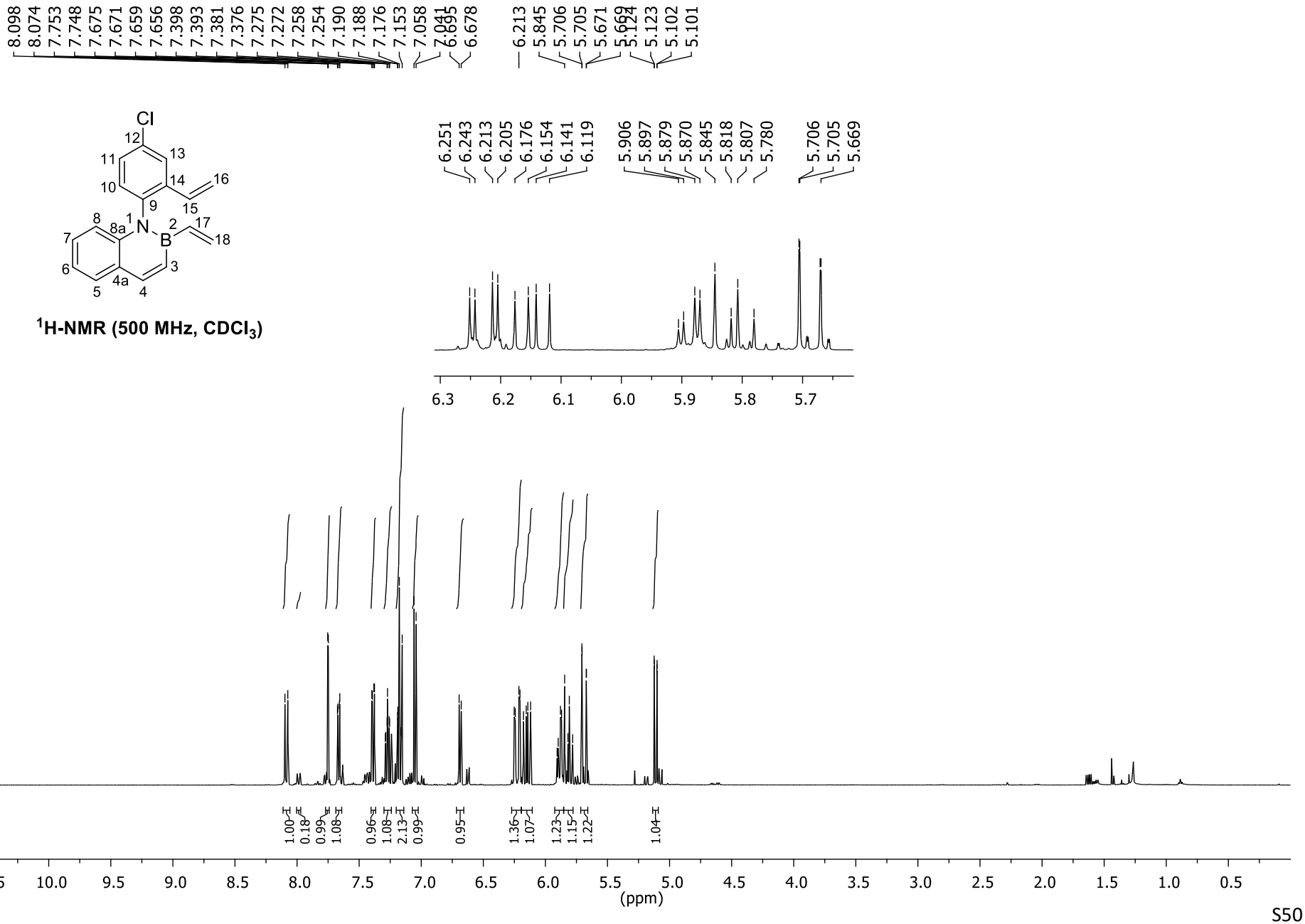
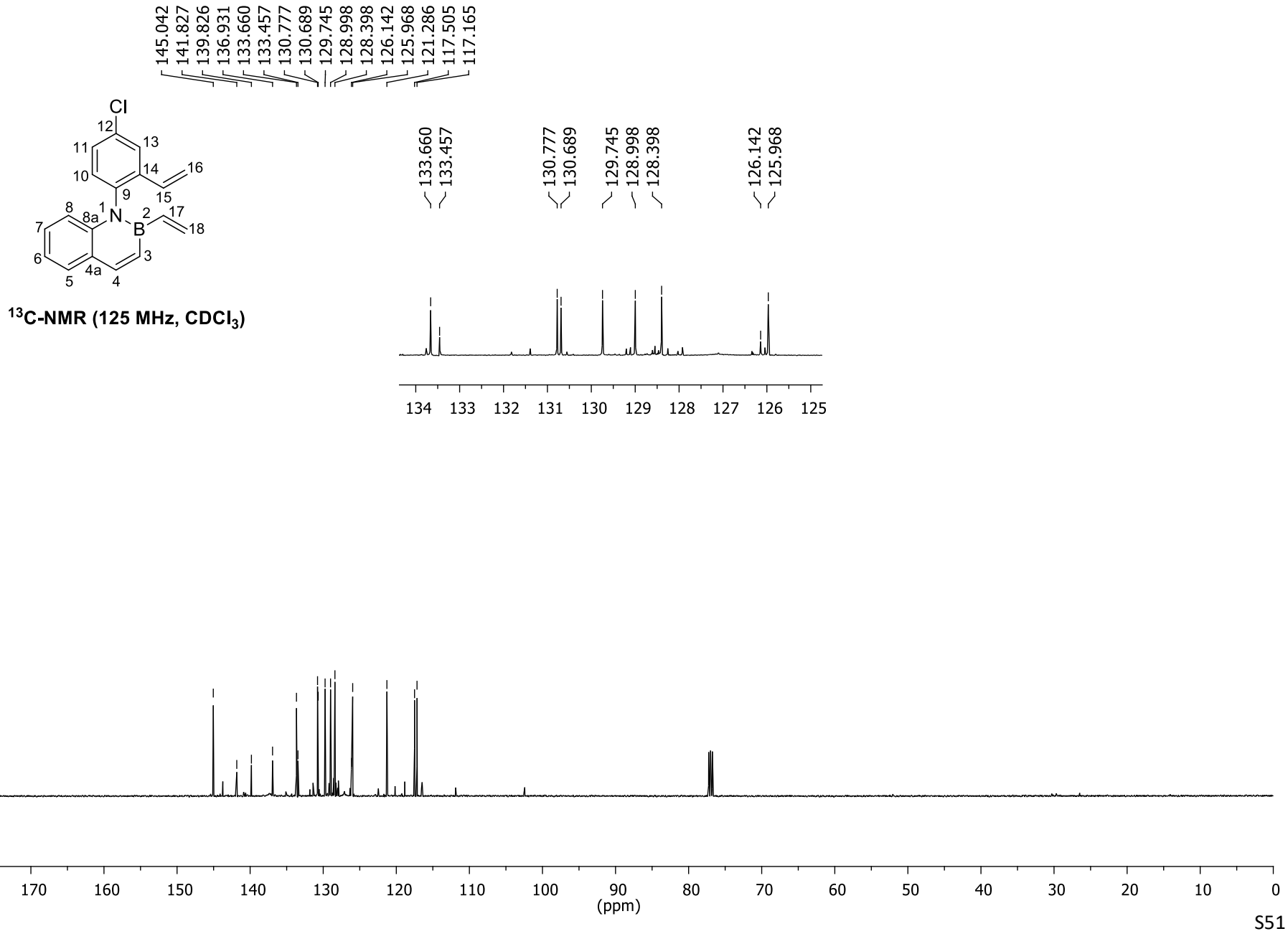
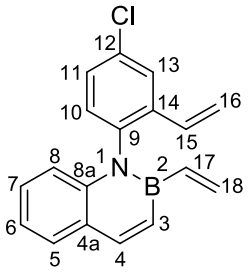
5.6
5.4
5.2
5.0
(ppm)



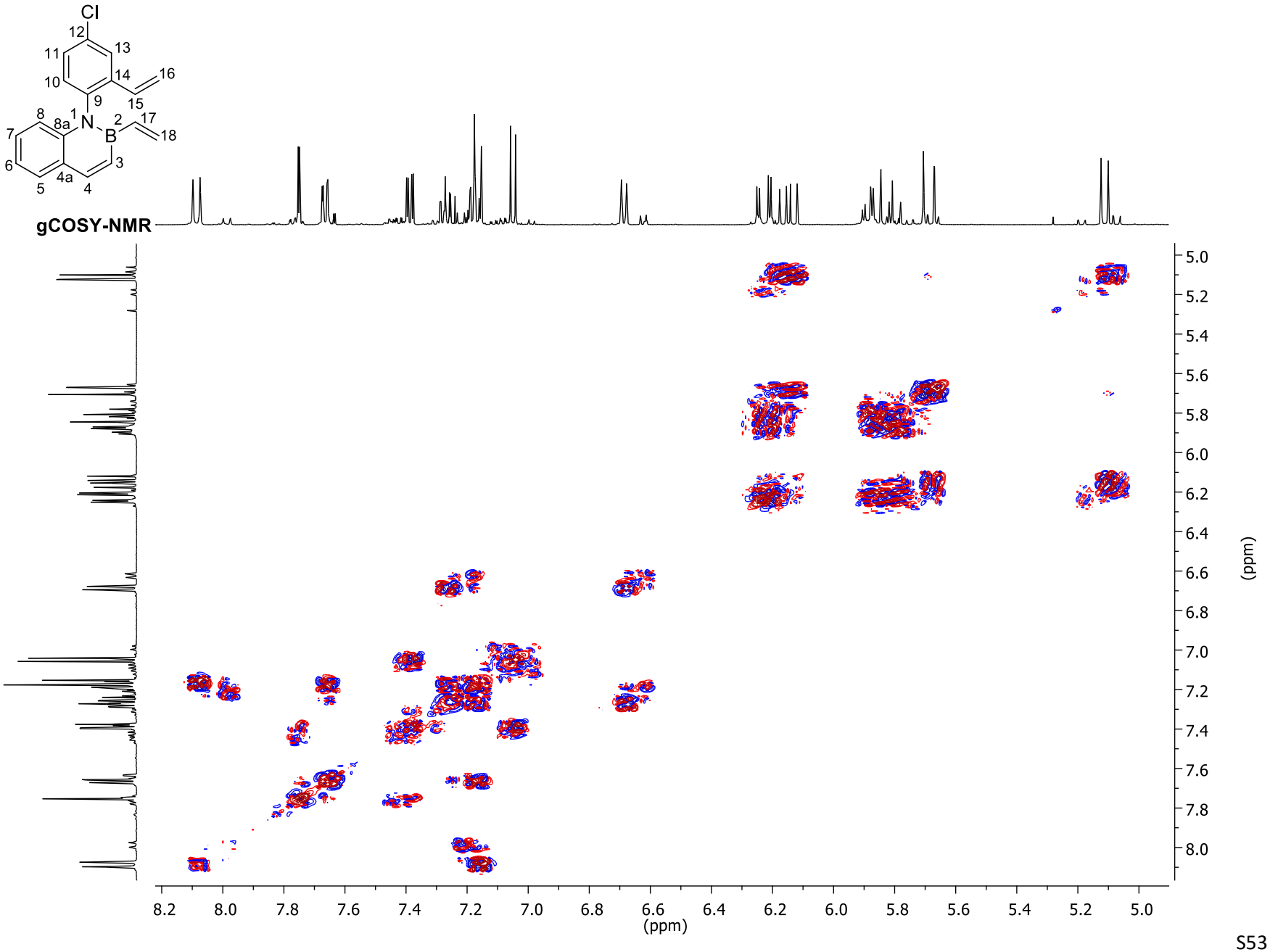
^{1}H-NMR (500 MHz, $CDCl_3$)



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



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


Cl
12
11
13
10
14
16
9
15
8
1
N
2
17
8a
B
18
7
3
6
4a
5
4
gCOSY-NMR
5.0
5.2
5.4
5.6
5.8
6.0
6.2
6.4
6.6
6.8
7.0
7.2
7.4
7.6
7.8
8.0
(ppm)
8.2
8.0
7.8
7.6
7.4
7.2
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6.2
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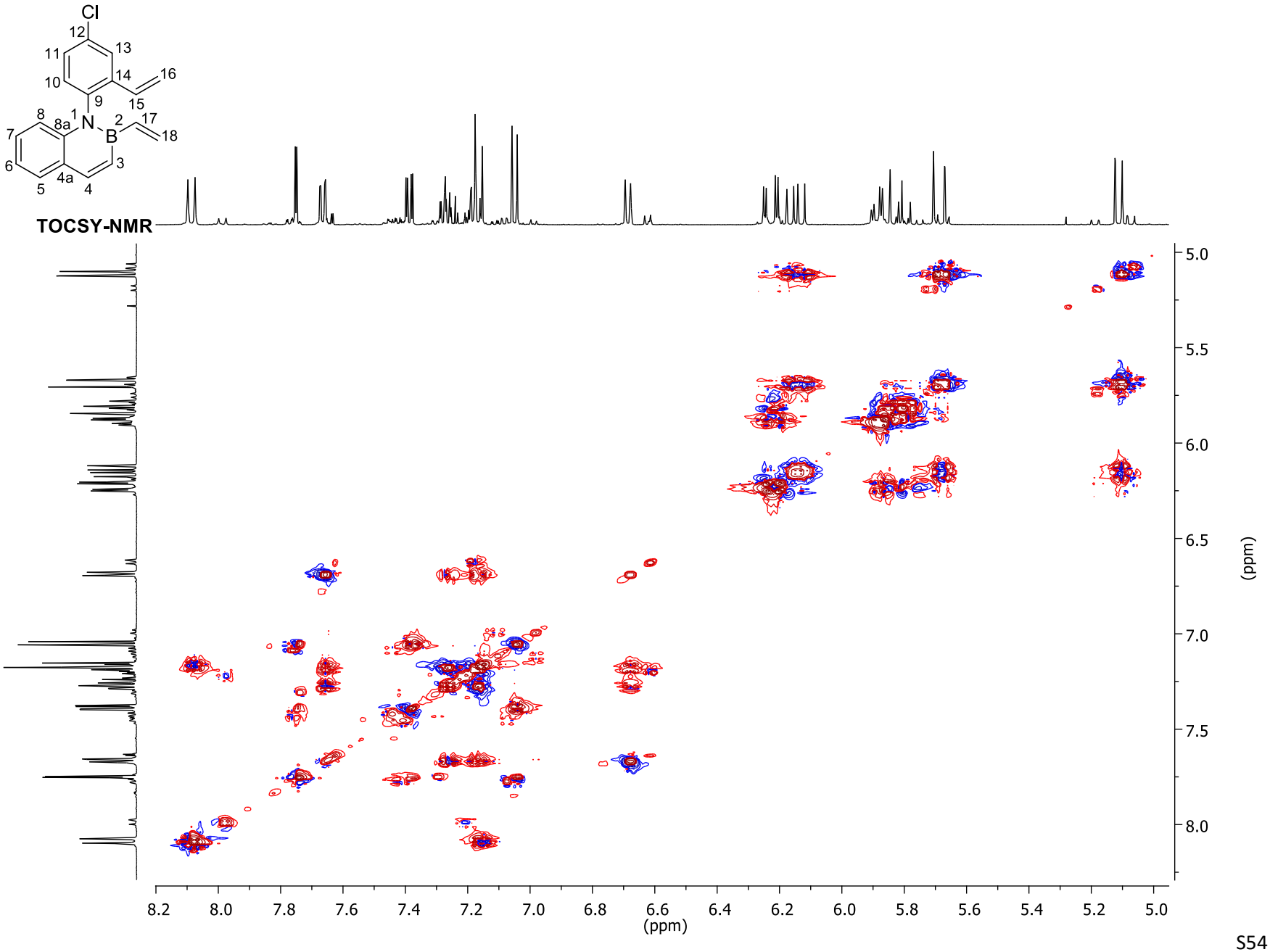
5.6
5.4
5.2
5.0
(ppm)


Cl
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13
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16
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17
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8a
N
B
18
6
3
4a
5
4
TOCSY-NMR
5.0
5.5
6.0
6.5
7.0
7.5
8.0
(ppm)
8.2
8.0
7.8
7.6
7.4
7.2
7.0
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6.2
6.0
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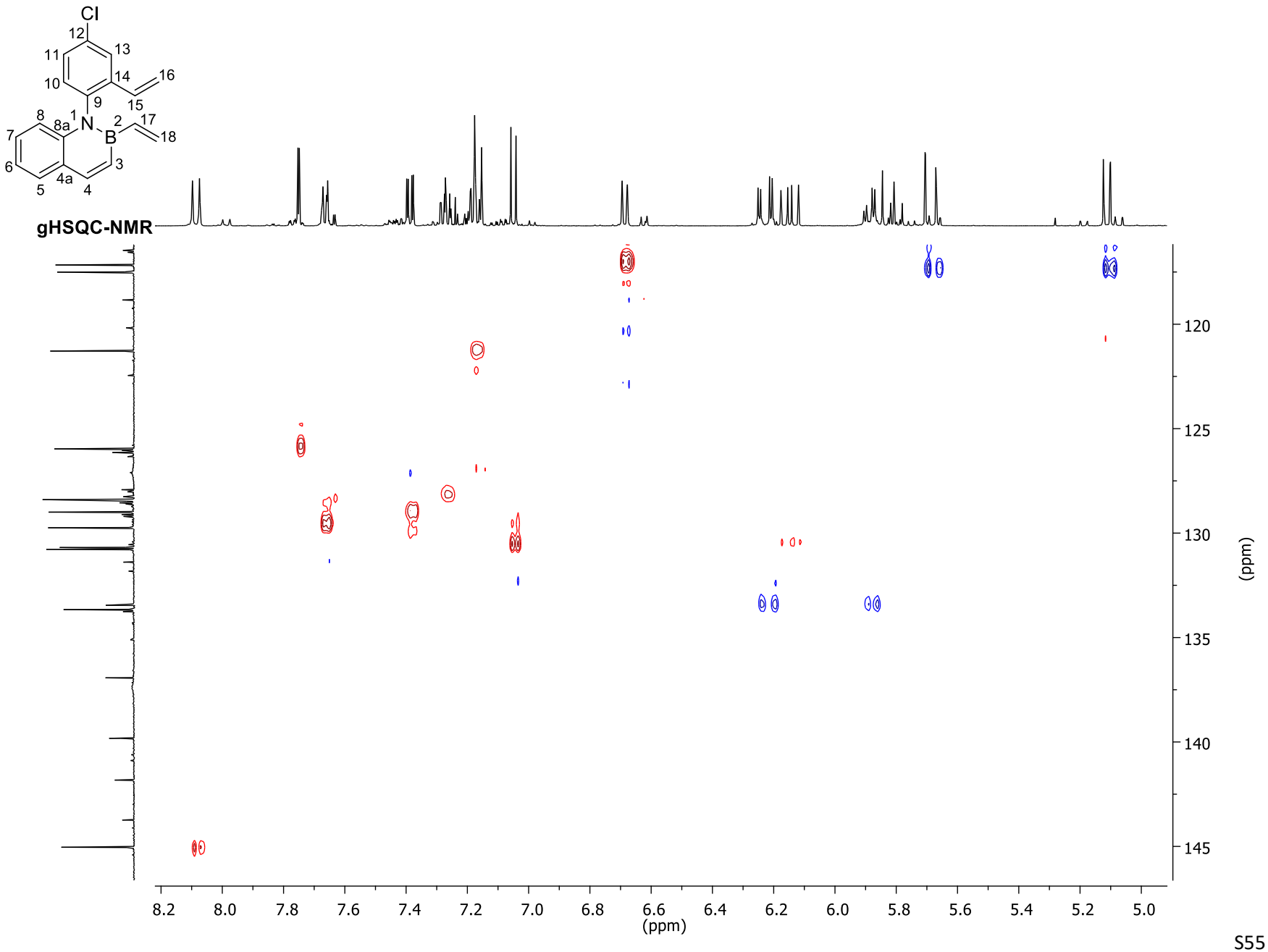
5.6
5.4
5.2
5.0
(ppm)


Cl
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14
16
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N
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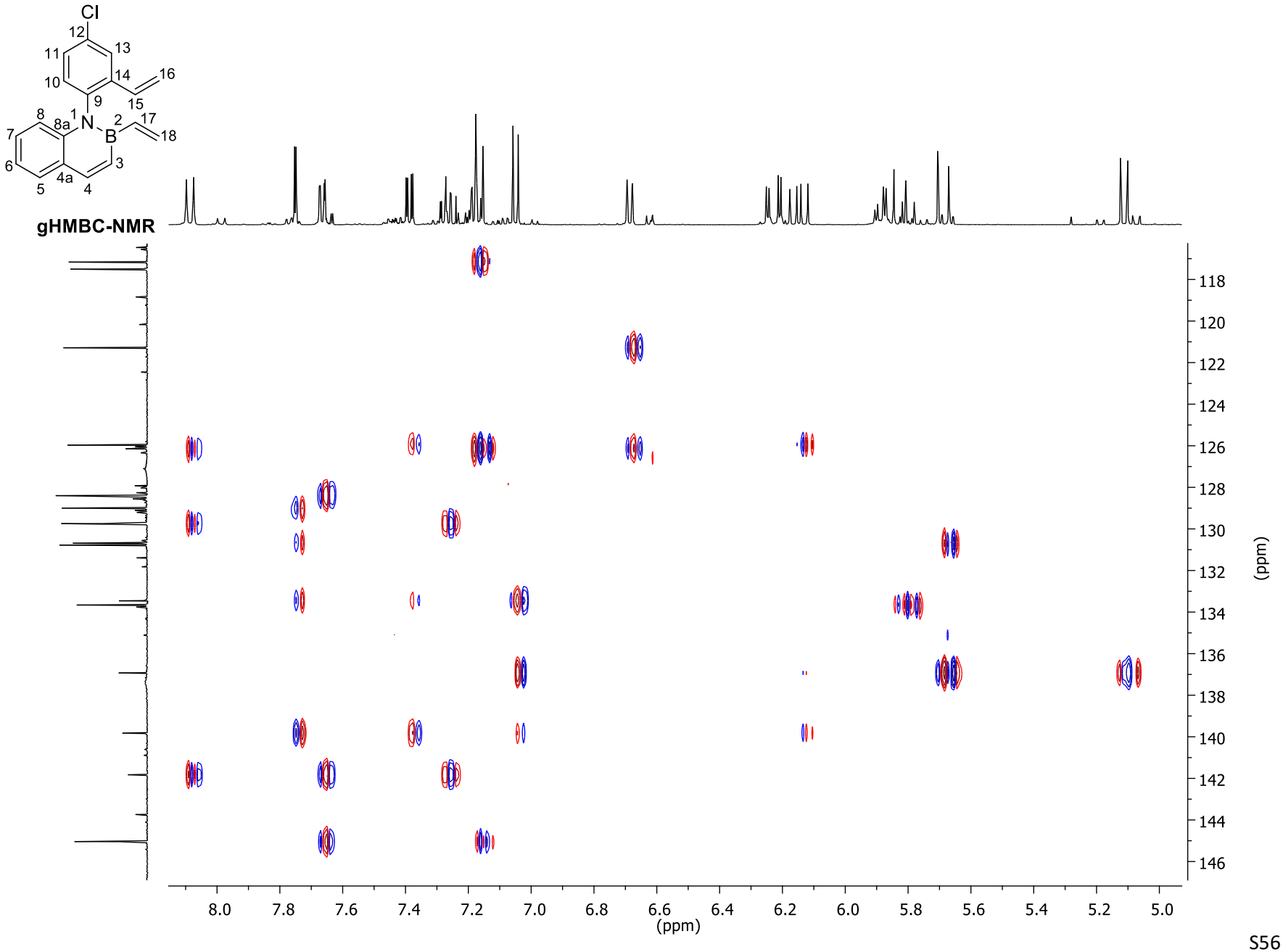
7
8a
B
18
6
3
4a
5
4
gHSQC-NMR
120
125
130
135
140
145
(ppm)
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
(ppm)


Cl
12
13
11
14
16
10
9
15
8
1
N
2
17
8a
B
18
7
3
6
4a
5
4
gHMBC-NMR
118
120
122
124
126
128
130
132
134
136
138
140
142
144
146
(ppm)
8.0
7.8
7.6
7.4
7.2
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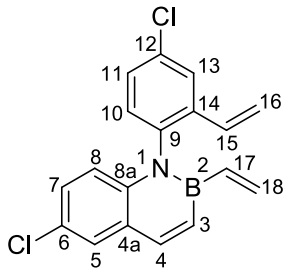
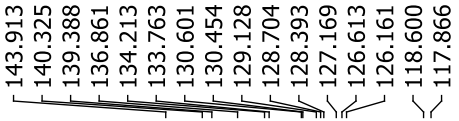
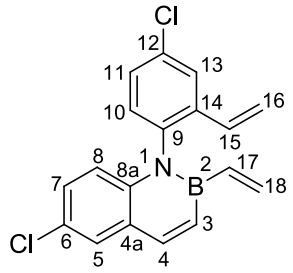
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
(ppm)

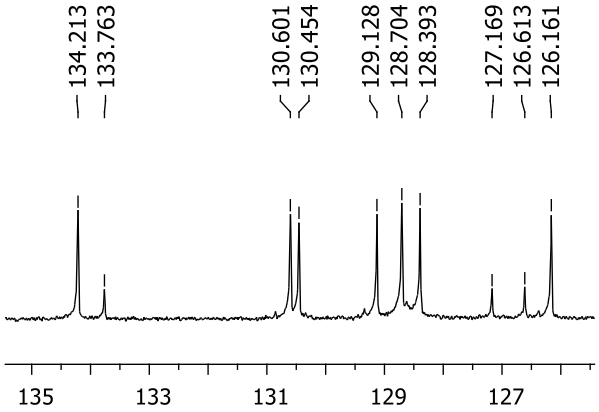


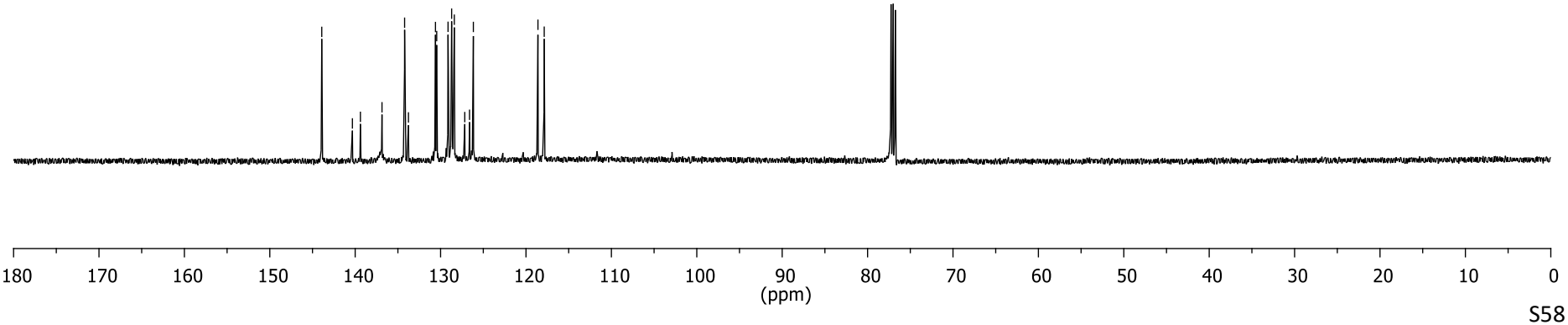
^{1}H-NMR (500 MHz, $CDCl_3$)

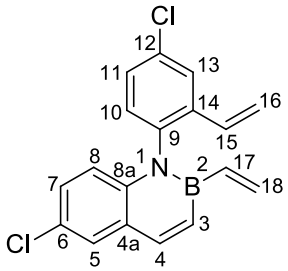




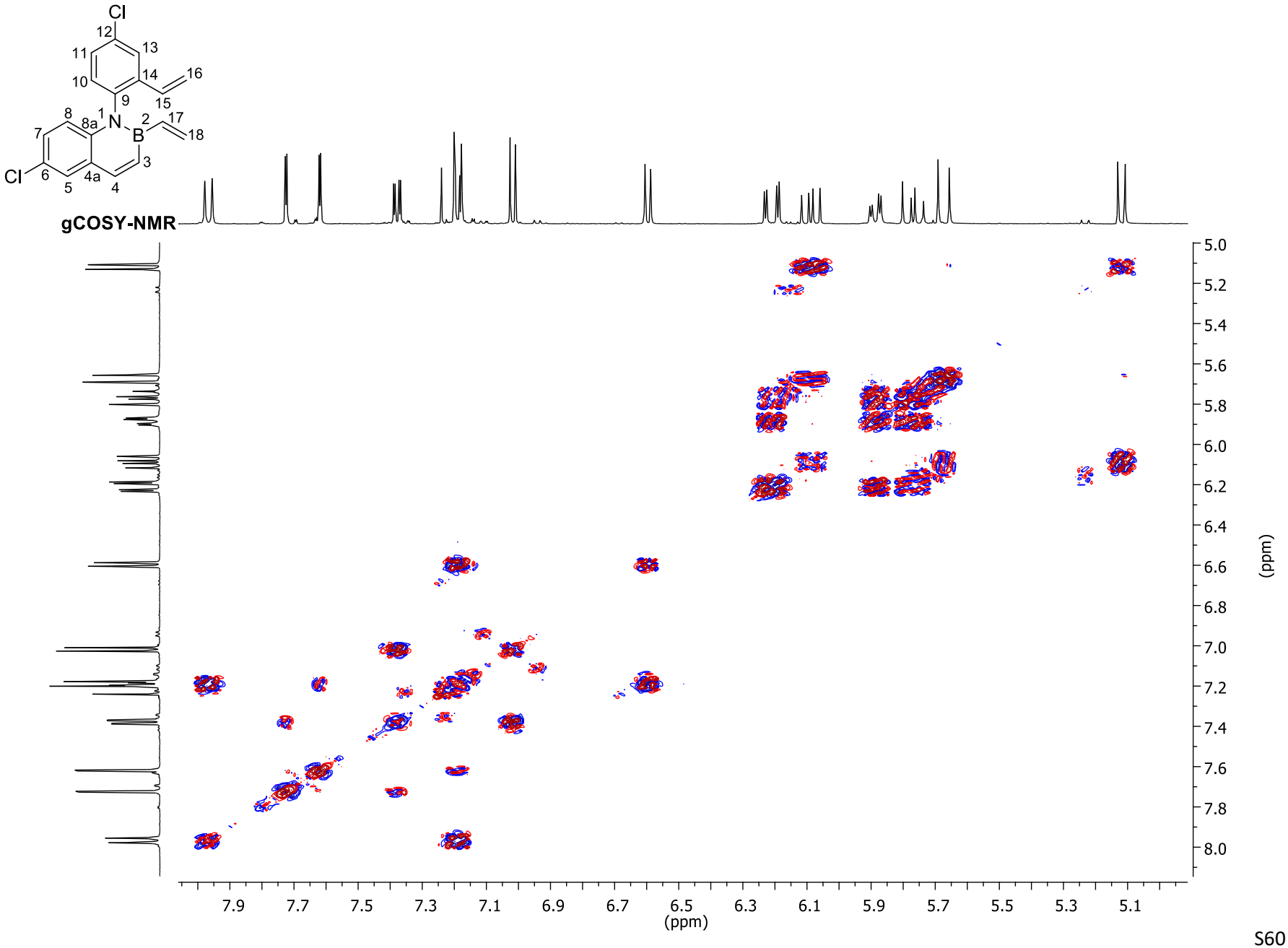
^{13}C-NMR (125 MHz, $CDCl_3$)

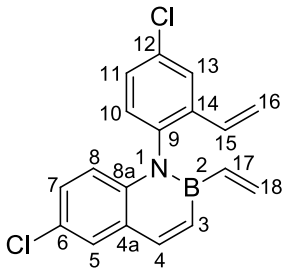






^{11}B-NMR (160 MHz, $CDCl_3$)


Cl
12
13
11
14
16
10
9
15
8
1
N
2
17
8a
B
18
7
3
Cl
6
4a
5
4
gCOSY-NMR
5.0
5.2
5.4
5.6
5.8
6.0
6.2
6.4
6.6
6.8
7.0
7.2
7.4
7.6
7.8
8.0
(ppm)
7.9
7.7
7.5
7.3
7.1
6.9
6.7
6.5
6.3
6.1
5.9
5.7
5.5
5.3
5.1
(ppm)


Cl
12
13
11
14
16
10
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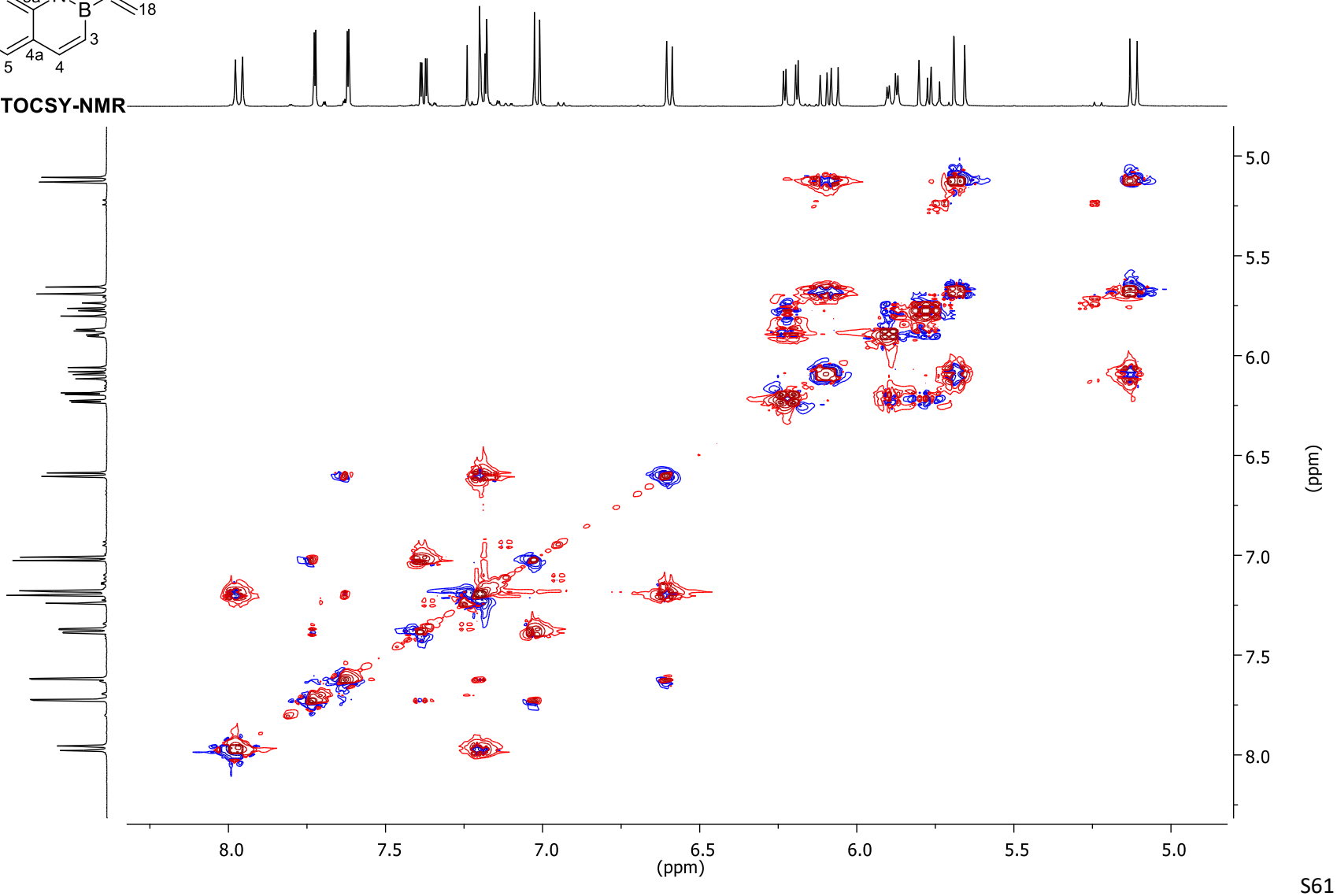
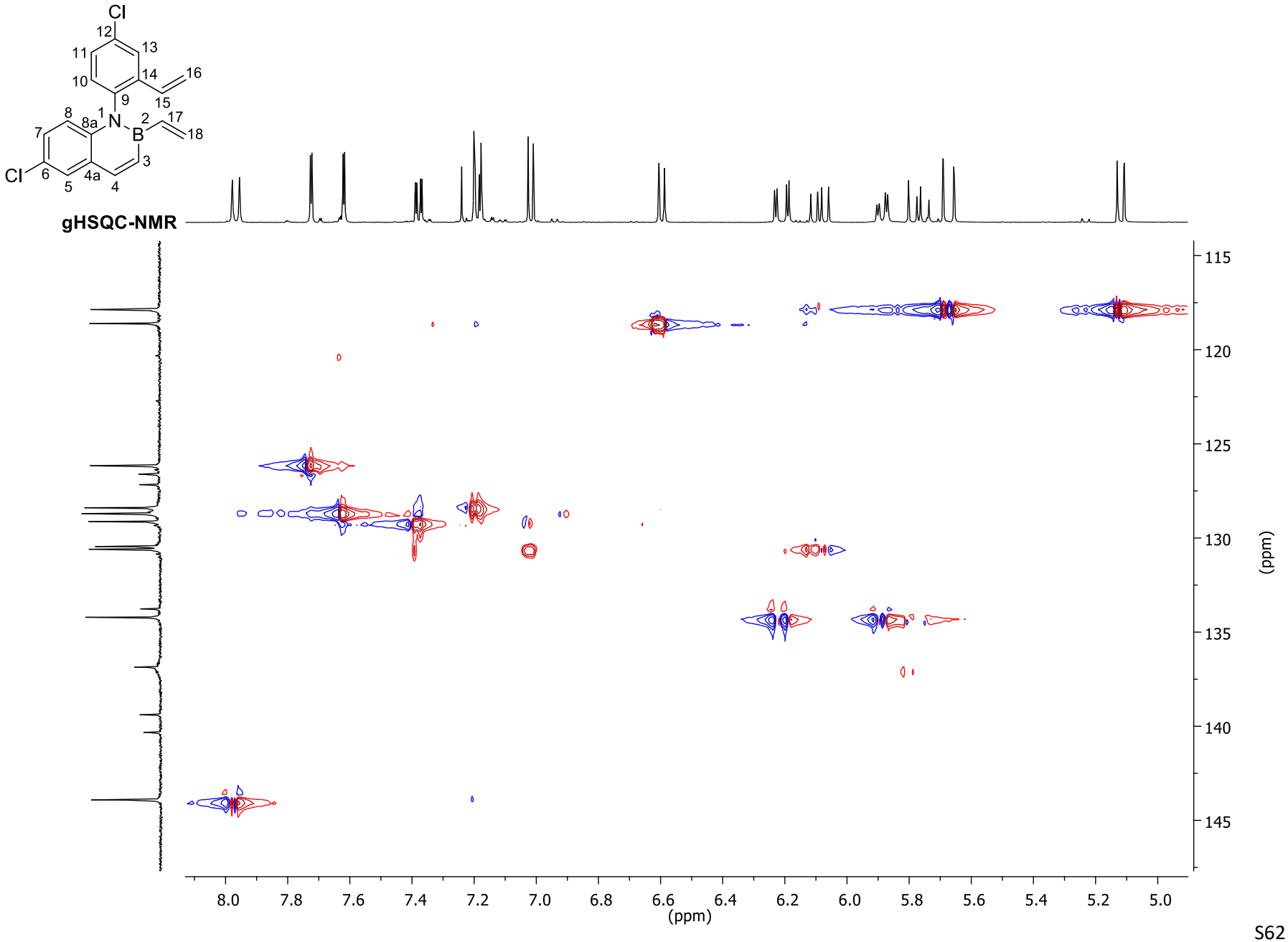
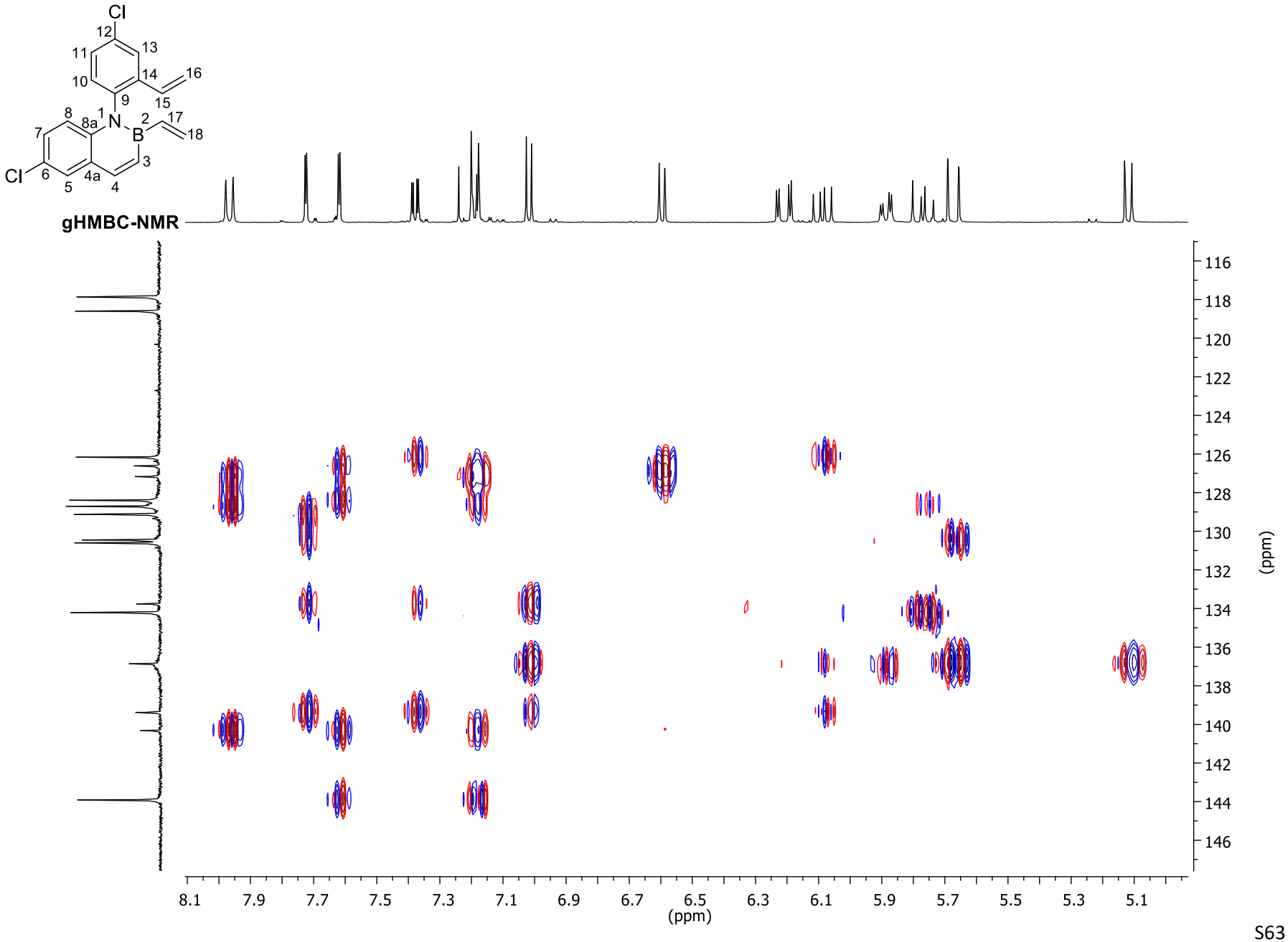
15
8
1
N
2
17
8a
B
18
7
3
Cl
6
4a
5
4

TOCSY-NMR


5.0
5.5
6.0
6.5
7.0
7.5
8.0
(ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
(ppm)


Cl
12
13
11
14
16
10
9
15
8
1
2
17
8a
N
B
18
7
3
Cl
6
4a
5
4
gHSQC-NMR
115
120
125
130
135
140
145
(ppm)
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
(ppm)


Cl
12
13
11
14
16
10
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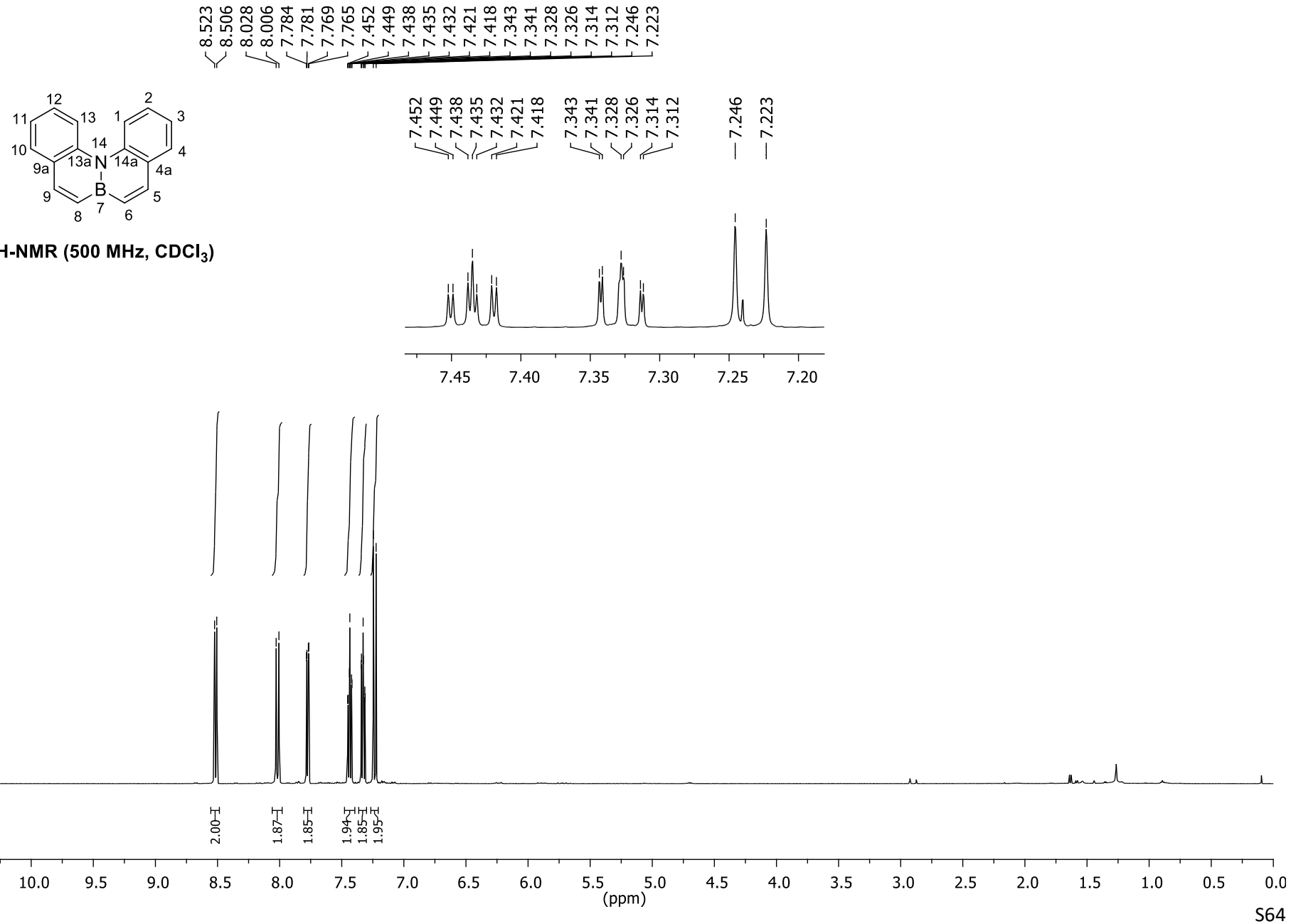
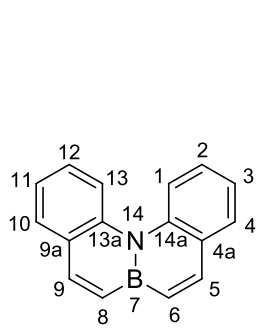
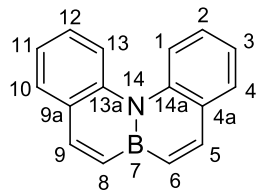
15
8
1
2
17
7
8a
N
B
18
3
Cl
6
4a
5
4
gHMBC-NMR
116
118
120
122
124
126
128
130
132
134
136
138
140
142
144
146
(ppm)
8.1
7.9
7.7
7.5
7.3
7.1
6.9
6.7
6.5
6.3
6.1
5.9
5.7
5.5
5.3
5.1
(ppm)



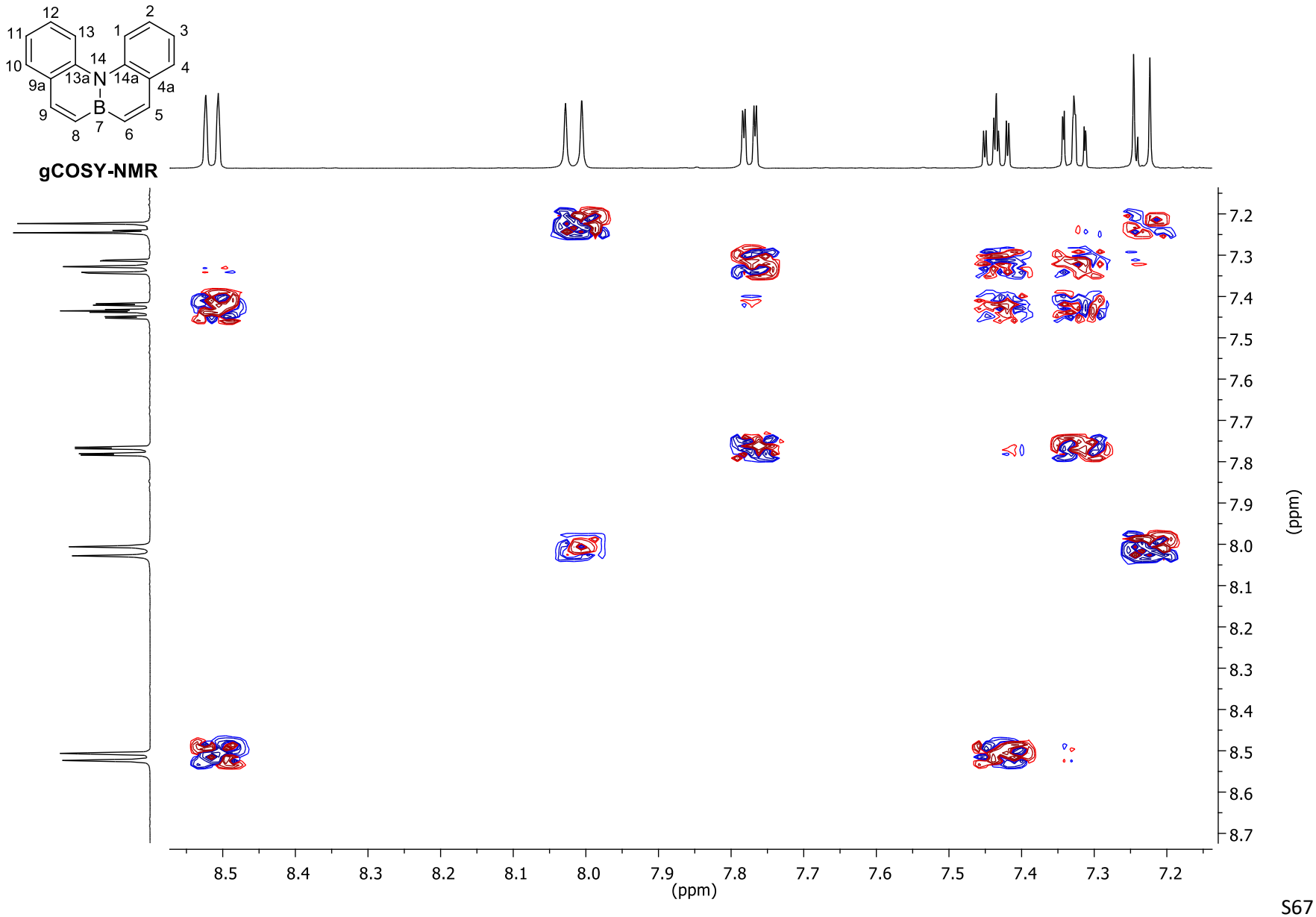
^{1}H-NMR (500 MHz, $CDCl_3$)

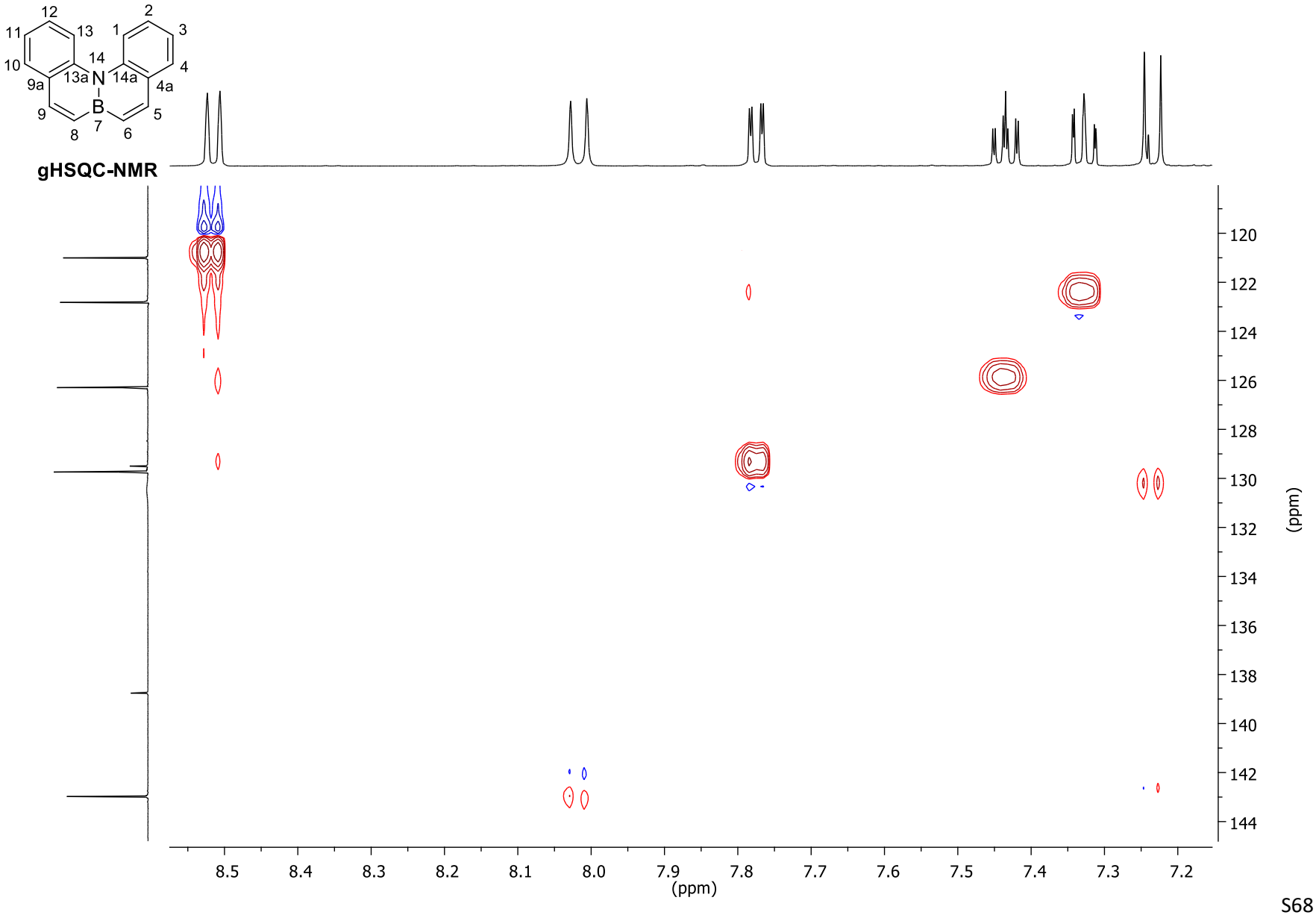


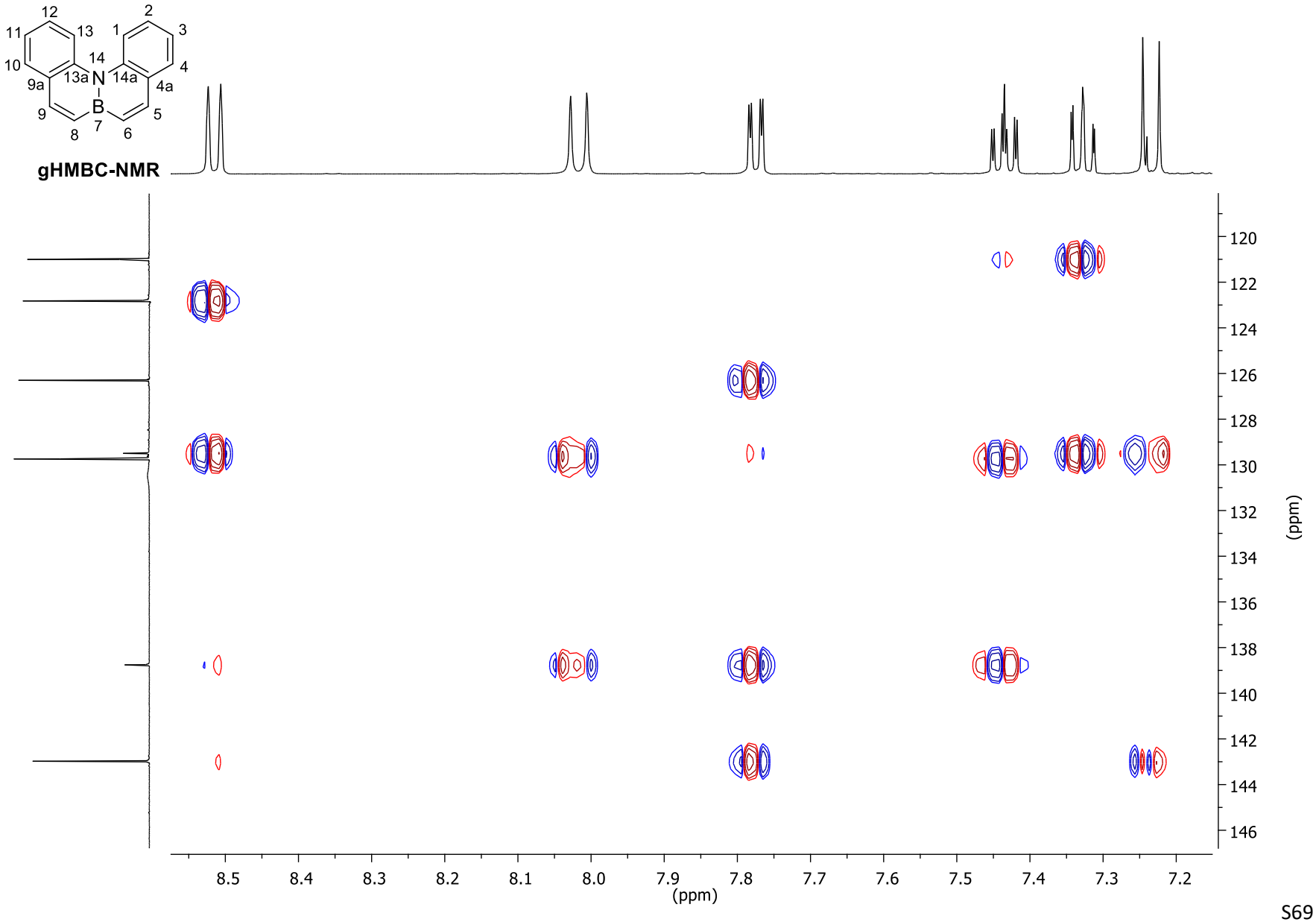
^{13}C-NMR (125 MHz, $CDCl_3$)



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


12
11
13
1
2
3
10
14
4
13a
N
14a
9a
4a
B
9
5
8
7
6
gCOSY-NMR
7.2
7.3
7.4
7.5
7.6
7.7
7.8
7.9
8.0
8.1
8.2
8.3
8.4
8.5
8.6
8.7
(ppm)
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
(ppm)


12
11
13
1
2
3
10
14
4
9a
13a
N
14a
4a
9
B
5
8
7
6
gHSQC-NMR
120
122
124
126
128
130
132
134
136
138
140
142
144
(ppm)
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
(ppm)


12
2
11
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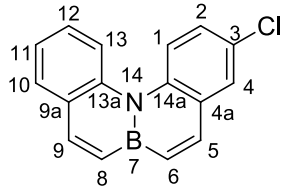
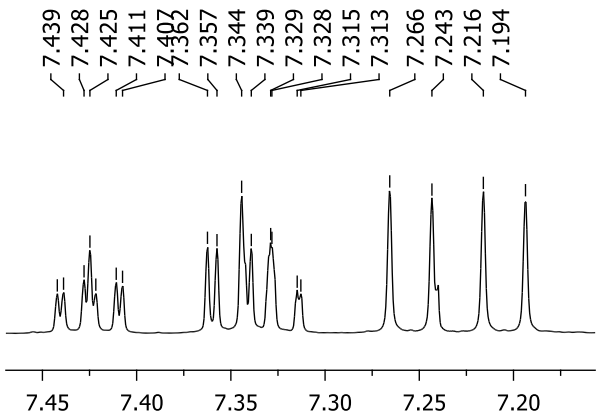
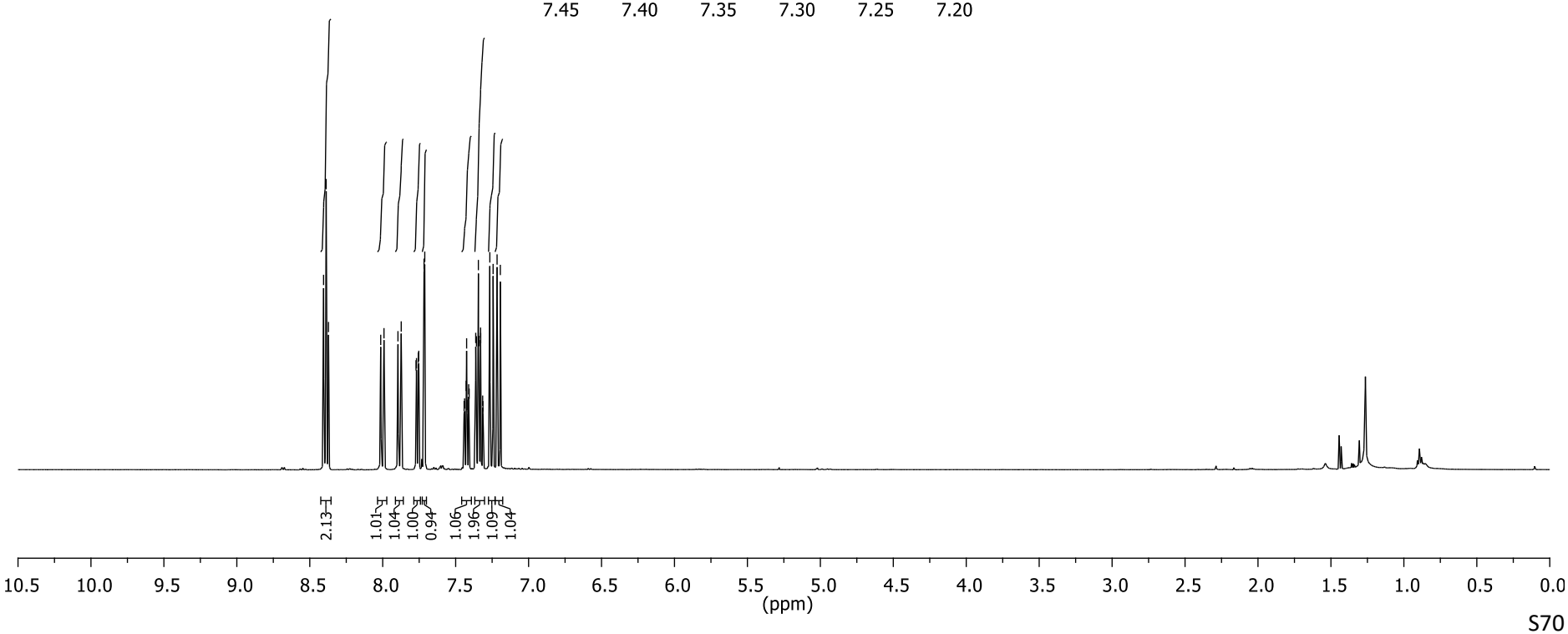
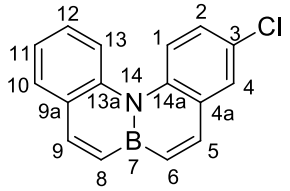
1
3
14
10
4
9a
13a
N
14a
4a
B
9
5
7
8
6
gHMBC-NMR
120
122
124
126
128
130
132
134
136
138
140
142
144
146
(ppm)
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
(ppm)



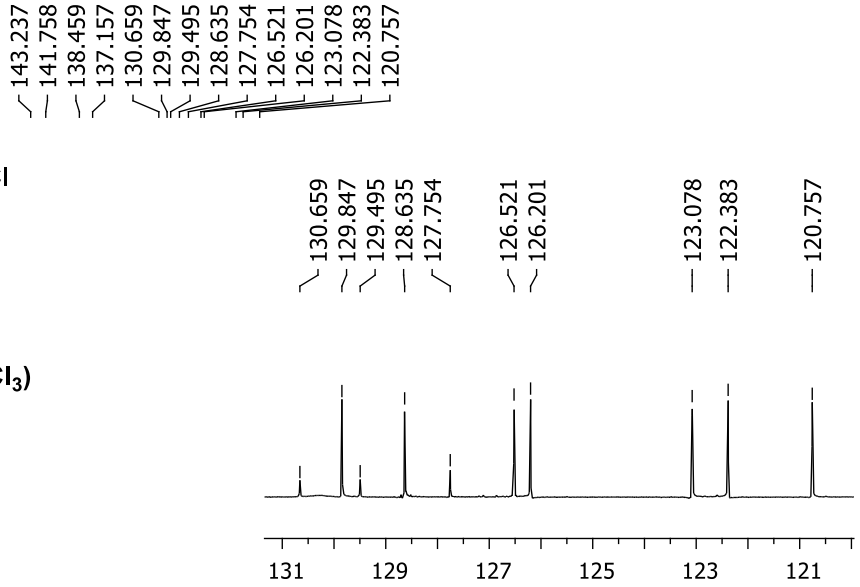
^{1}H-NMR (500 MHz, $CDCl_3$)

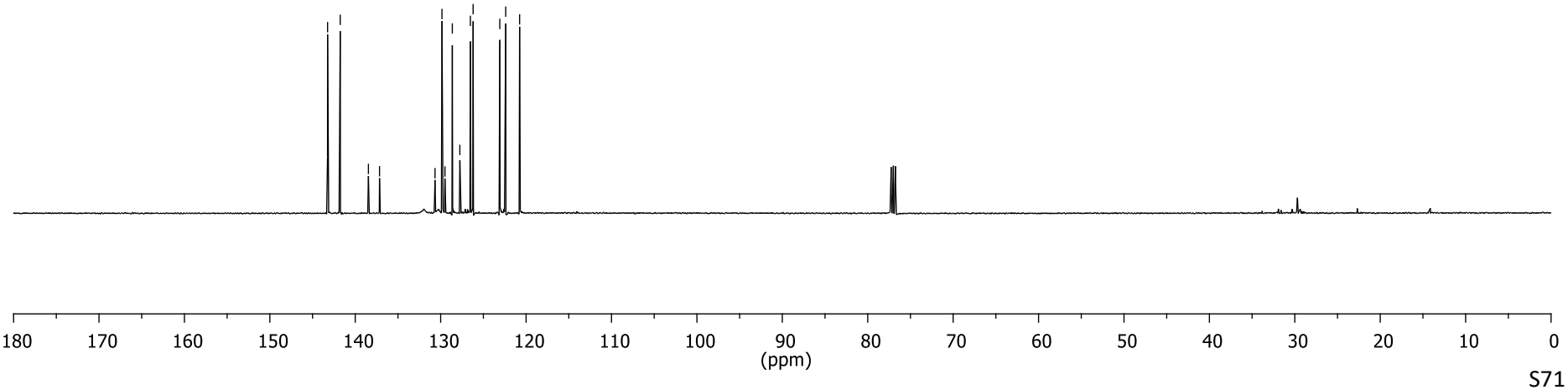


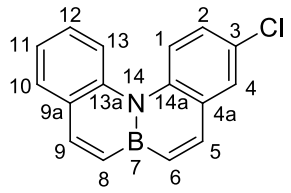




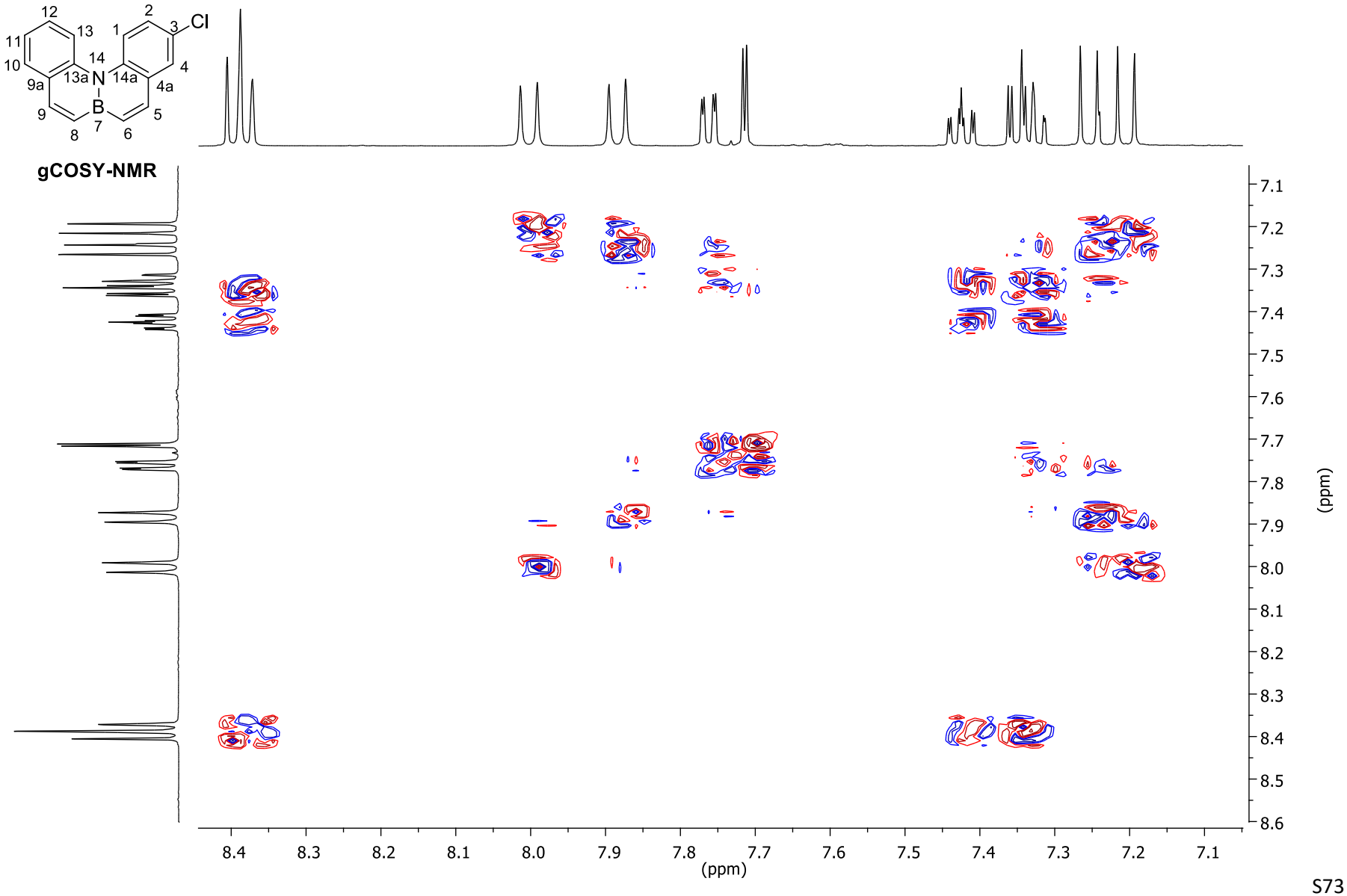
^{13}C-NMR (125 MHz, $CDCl_3$)

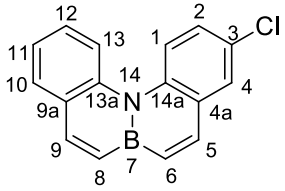






^{11}B-NMR (160 MHz, $CDCl_3$)


gCOSY-NMR
12
13
1
2
3
Cl
11
14
10
4
13a
N
14a
9a
4a
9
B
5
7
8
6
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
(ppm)
7.1
7.2
7.3
7.4
7.5
7.6
7.7
7.8
7.9
8.0
8.1
8.2
8.3
8.4
8.5
8.6
(ppm)


12
13
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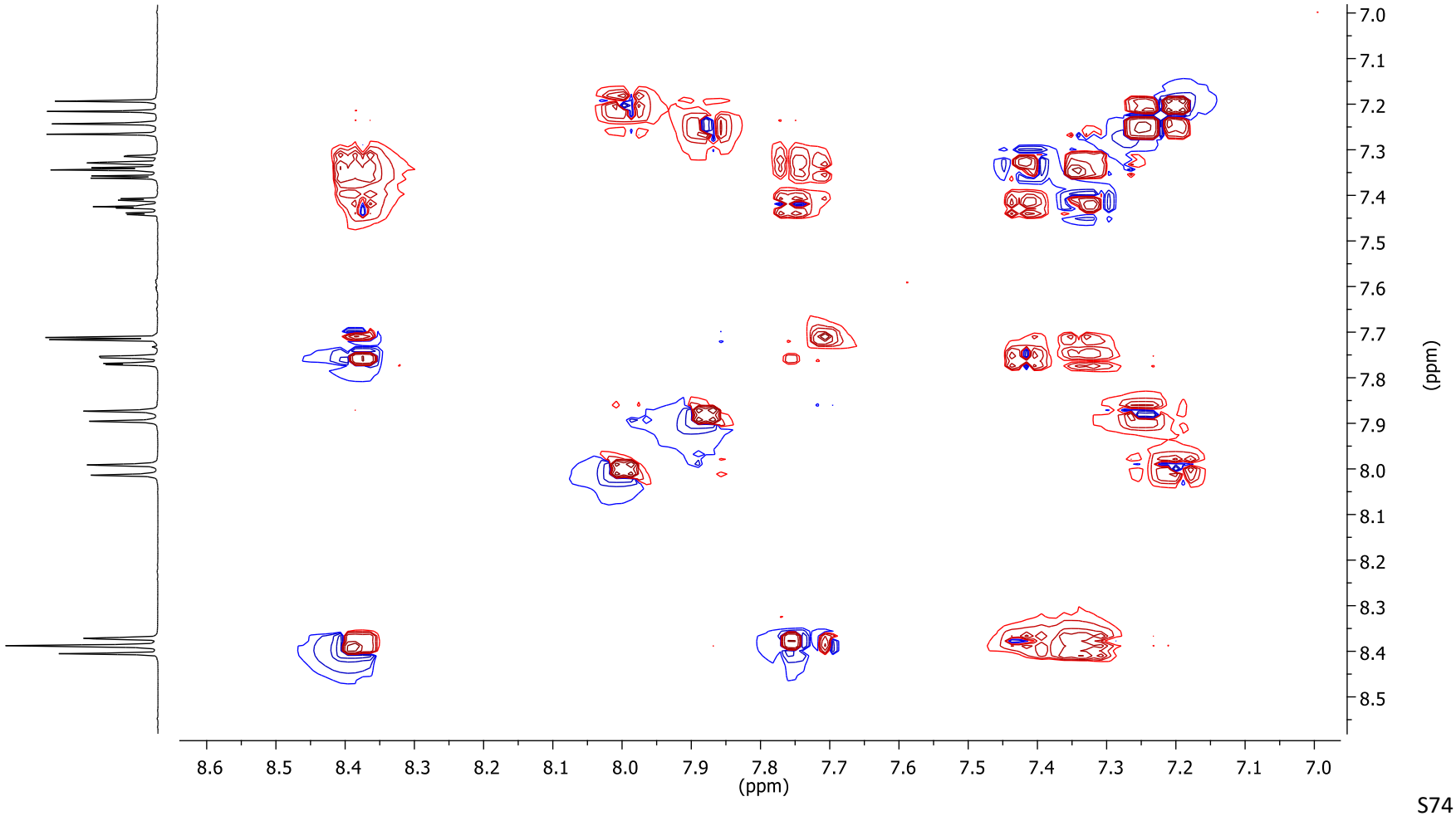
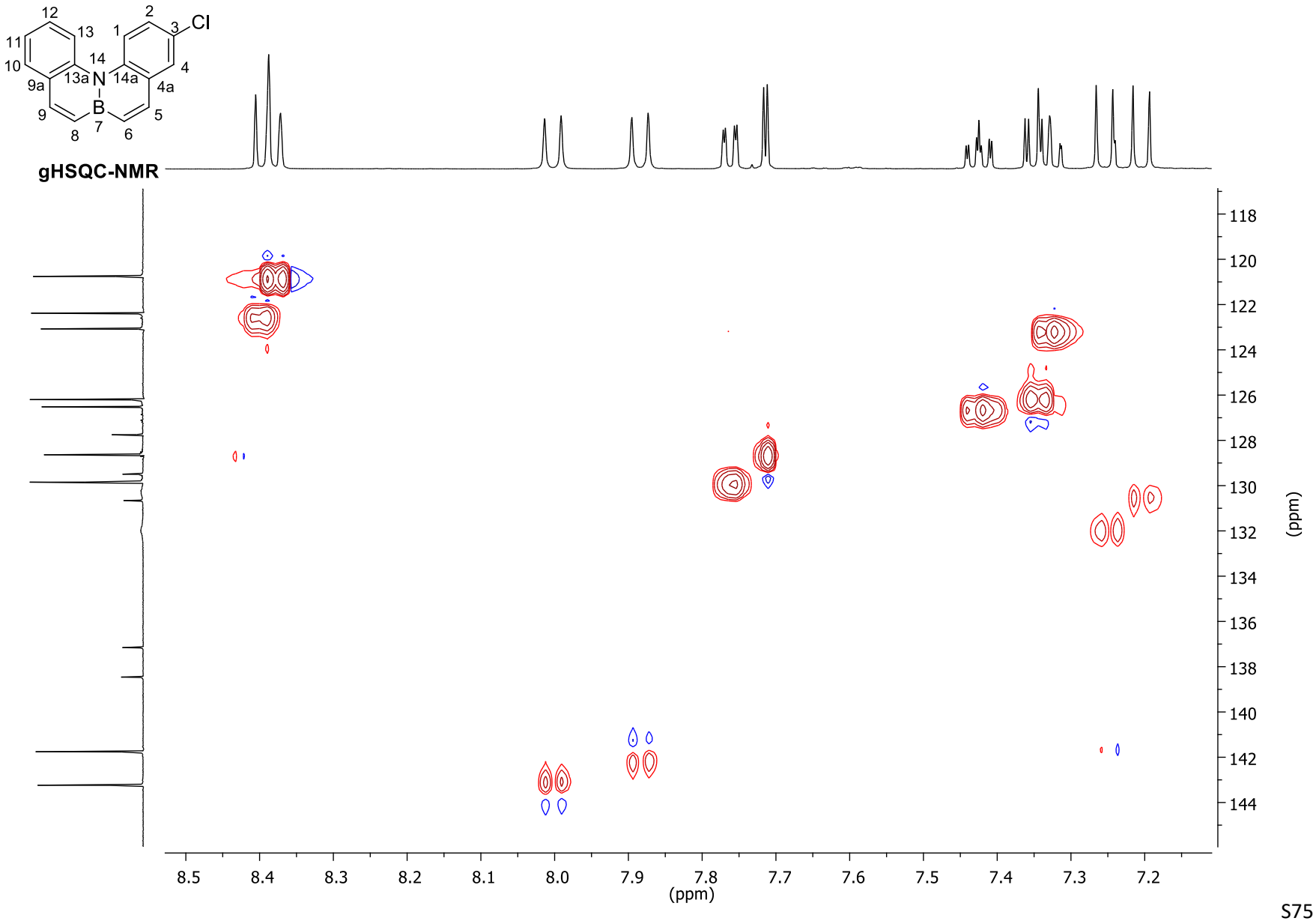
1
3
Cl
11
14
10
4
9a
13a
N
14a
4a
B
9
5
8
7
6

TOCSY-NMR


7.0
7.1
7.2
7.3
7.4
7.5
7.6
7.7
7.8
7.9
8.0
8.1
8.2
8.3
8.4
8.5
(ppm)
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
(ppm)


12
13
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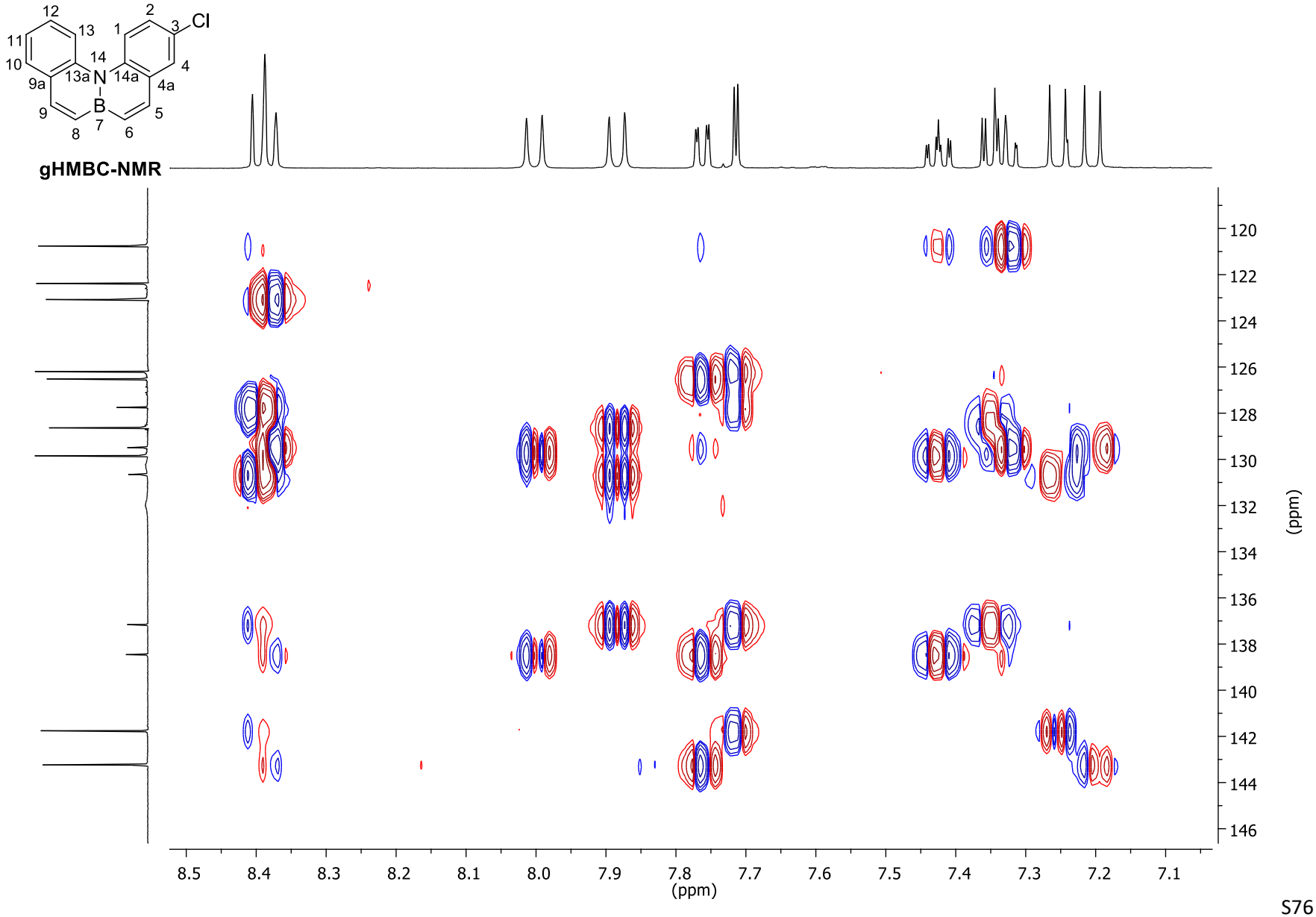
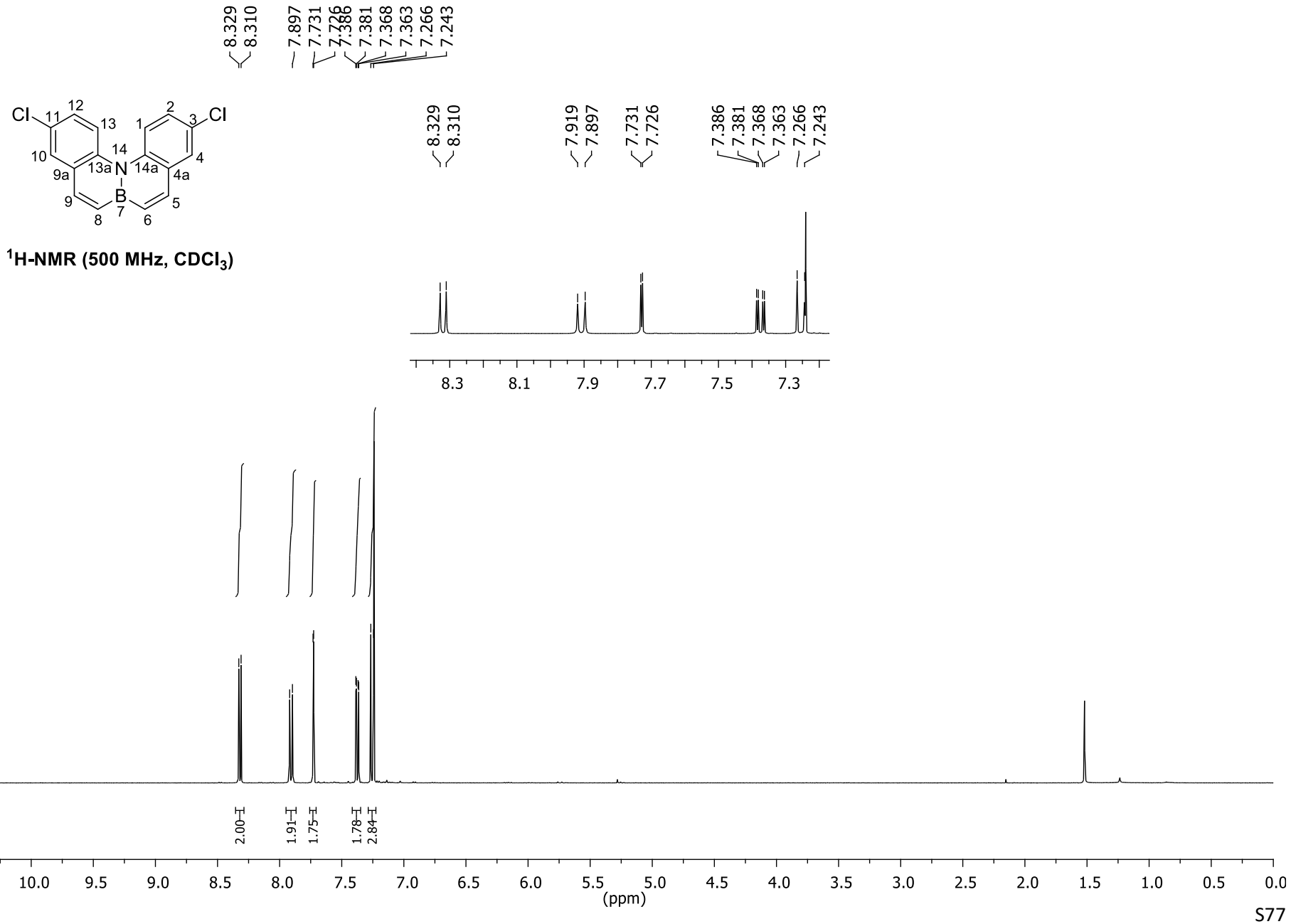
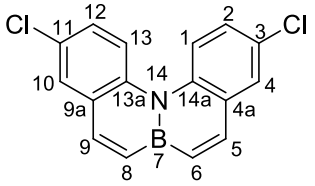
1
3
Cl
11
14
10
4
13a
N
14a
9a
4a
B
9
5
8
7
6
gHSQC-NMR
118
120
122
124
126
128
130
132
134
136
138
140
142
144
(ppm)
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
(ppm)

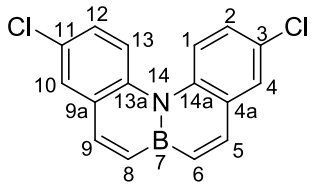

12
13
1
2
3
Cl
11
10
14
9a
13a
N
14a
4
4a
9
B
5
8
7
6
gHMBC-NMR
120
122
124
126
128
130
132
134
136
138
140
142
144
146
(ppm)
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
(ppm)



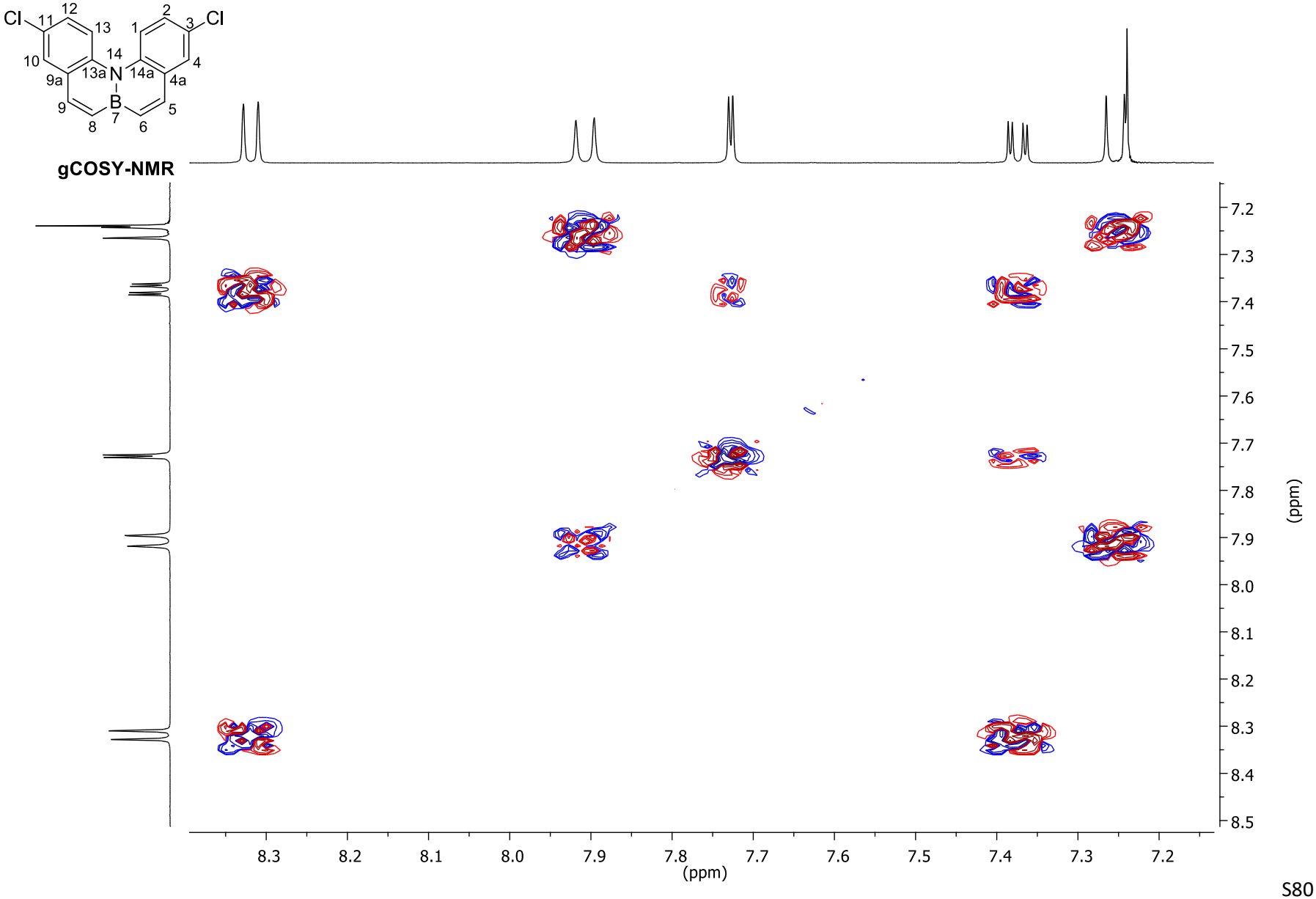
^{1}H-NMR (500 MHz, $CDCl_3$)

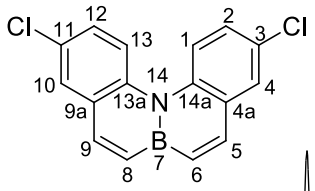


^{13}C-NMR (125 MHz, $CDCl_3$)



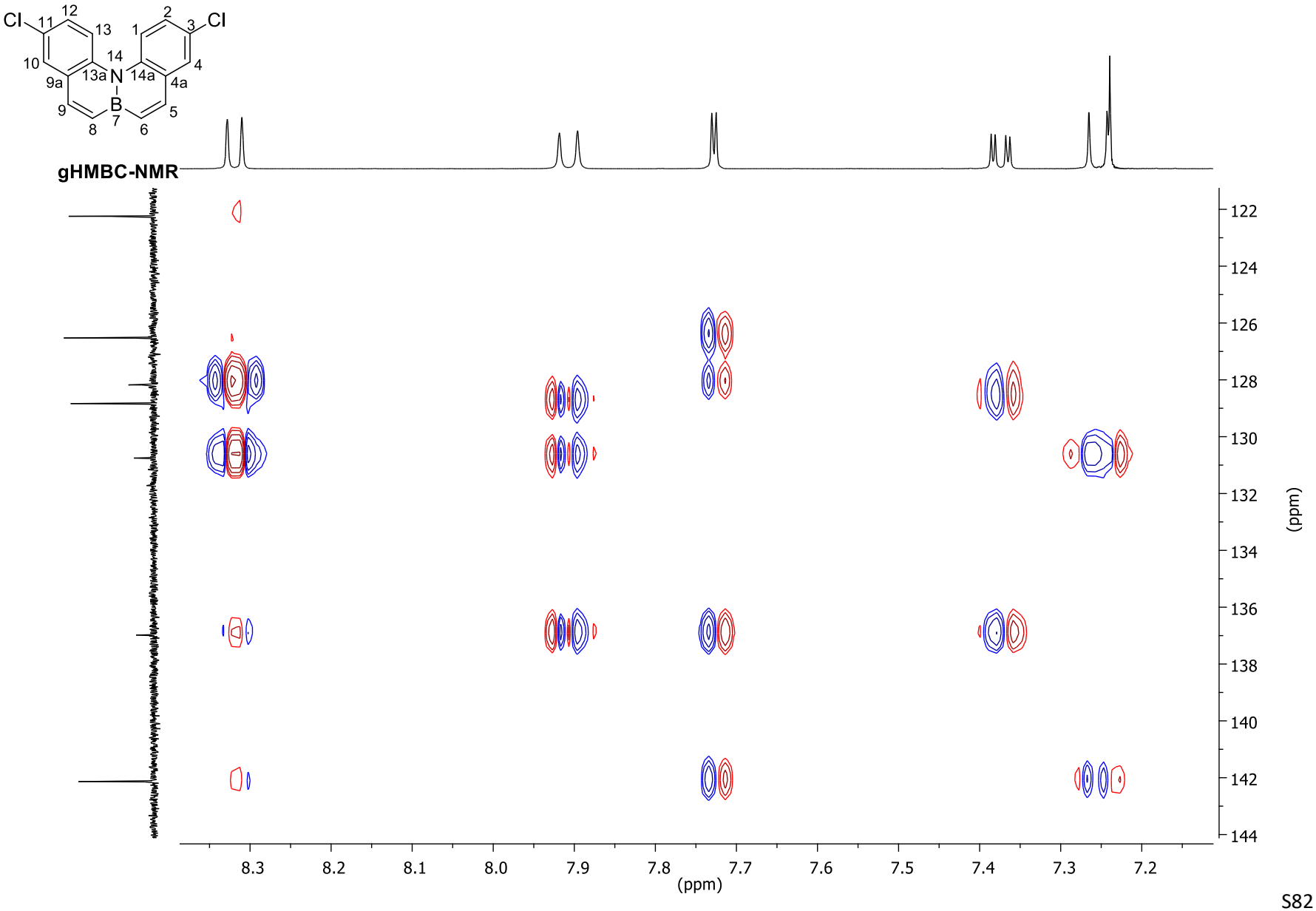
^{11}B-NMR (160 MHz, $CDCl_3$)

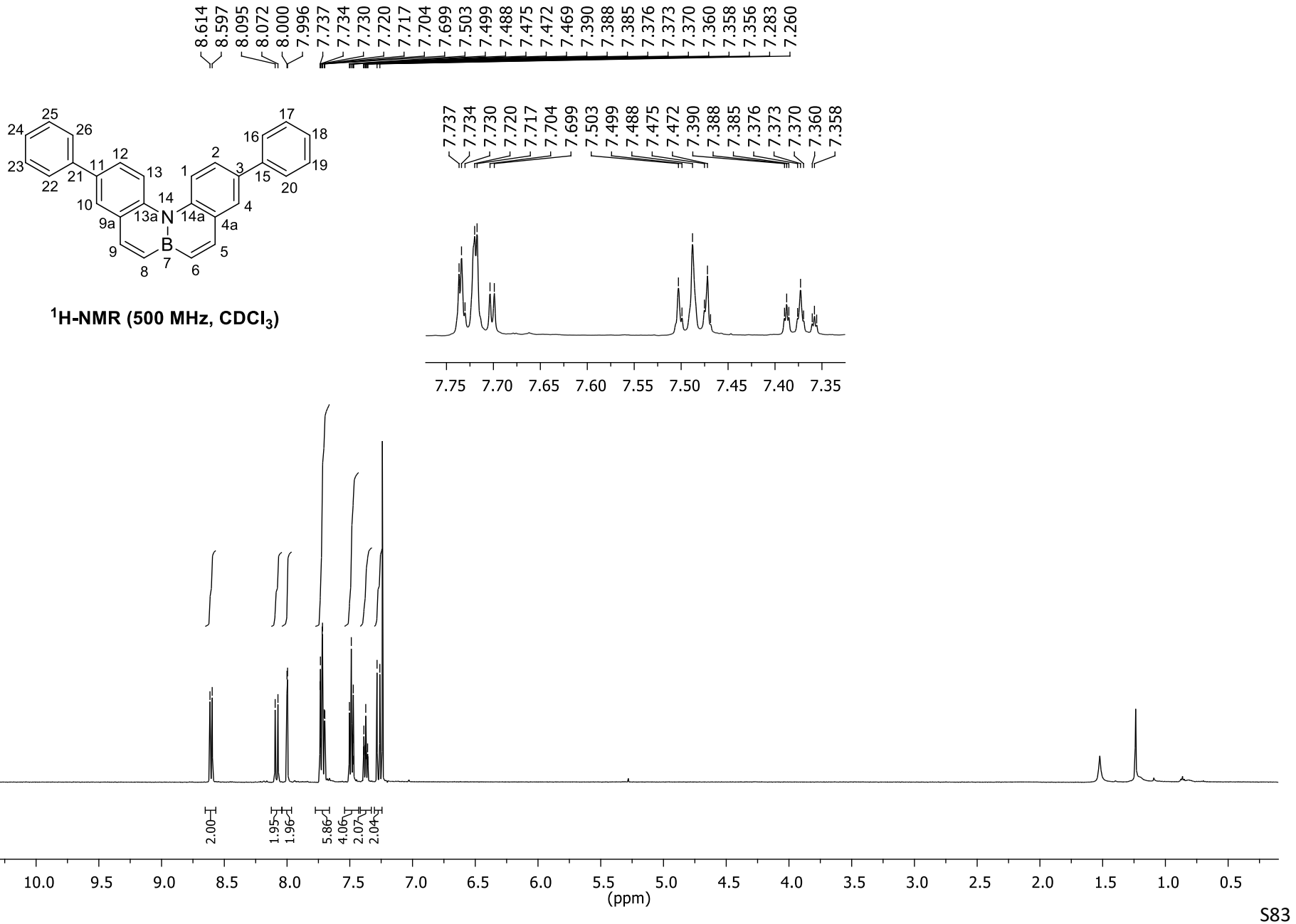

Cl
Cl
N
B
gCOSY-NMR
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
(ppm)
7.2
7.3
7.4
7.5
7.6
7.7
7.8
7.9
8.0
8.1
8.2
8.3
8.4
8.5
(ppm)


Cl
Cl
N
B

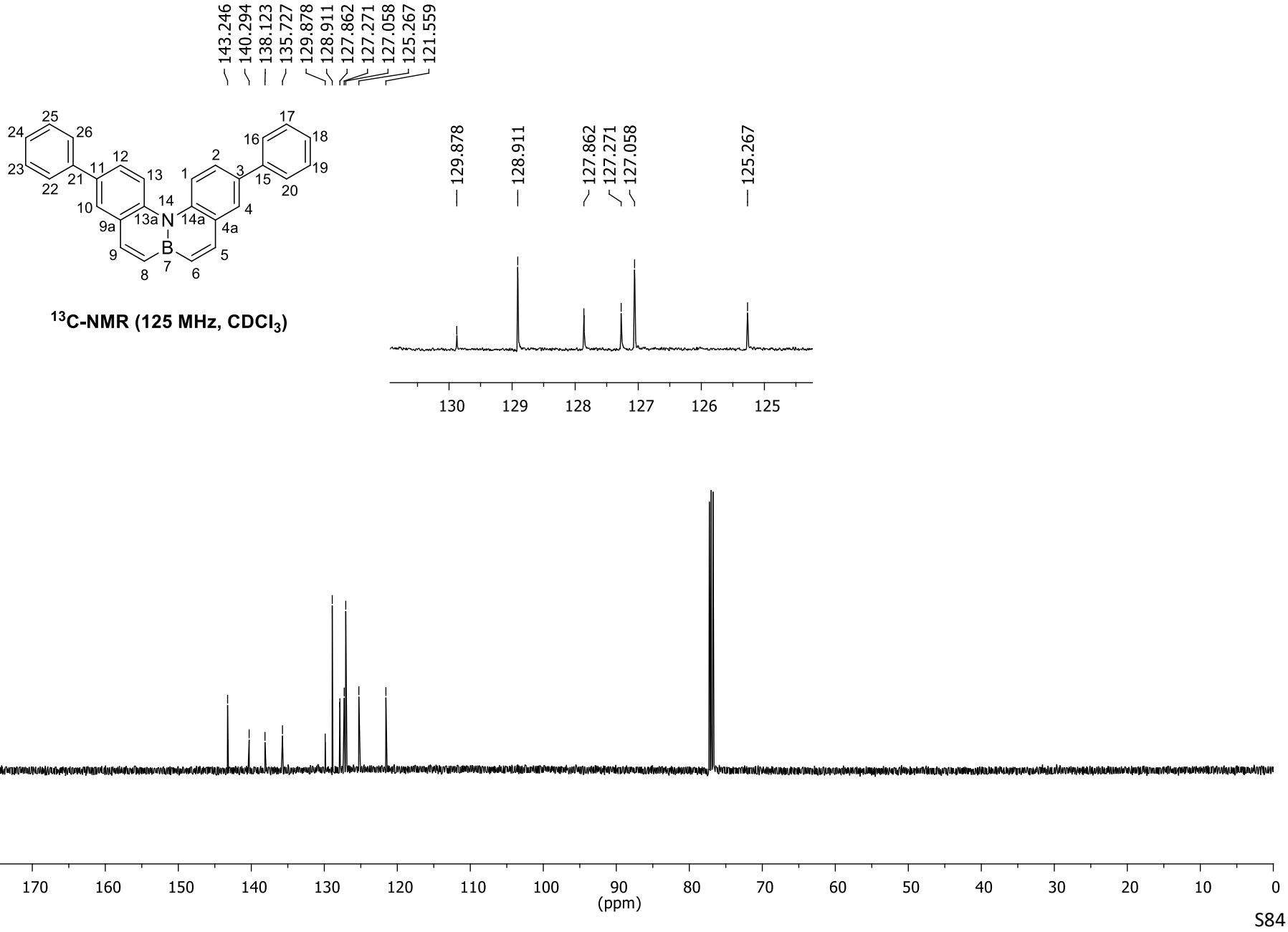
gHSQC-NMR

8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
(ppm)
120
122
124
126
128
130
132
134
136
138
140
142
144
(ppm)

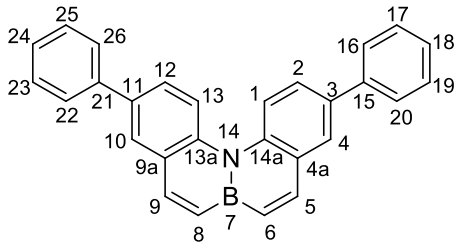

Cl
Cl
gHMBC-NMR
(ppm)
(ppm)



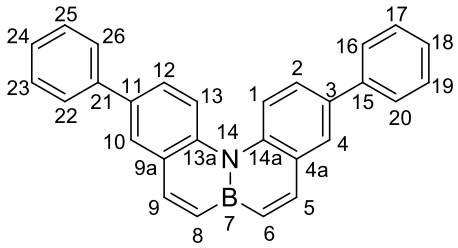
^{1}H-NMR (500 MHz, $CDCl_3$)



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



^{11}B-NMR (160 MHz, $CDCl_3$)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9a
13a
N
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14a
4a
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1
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16
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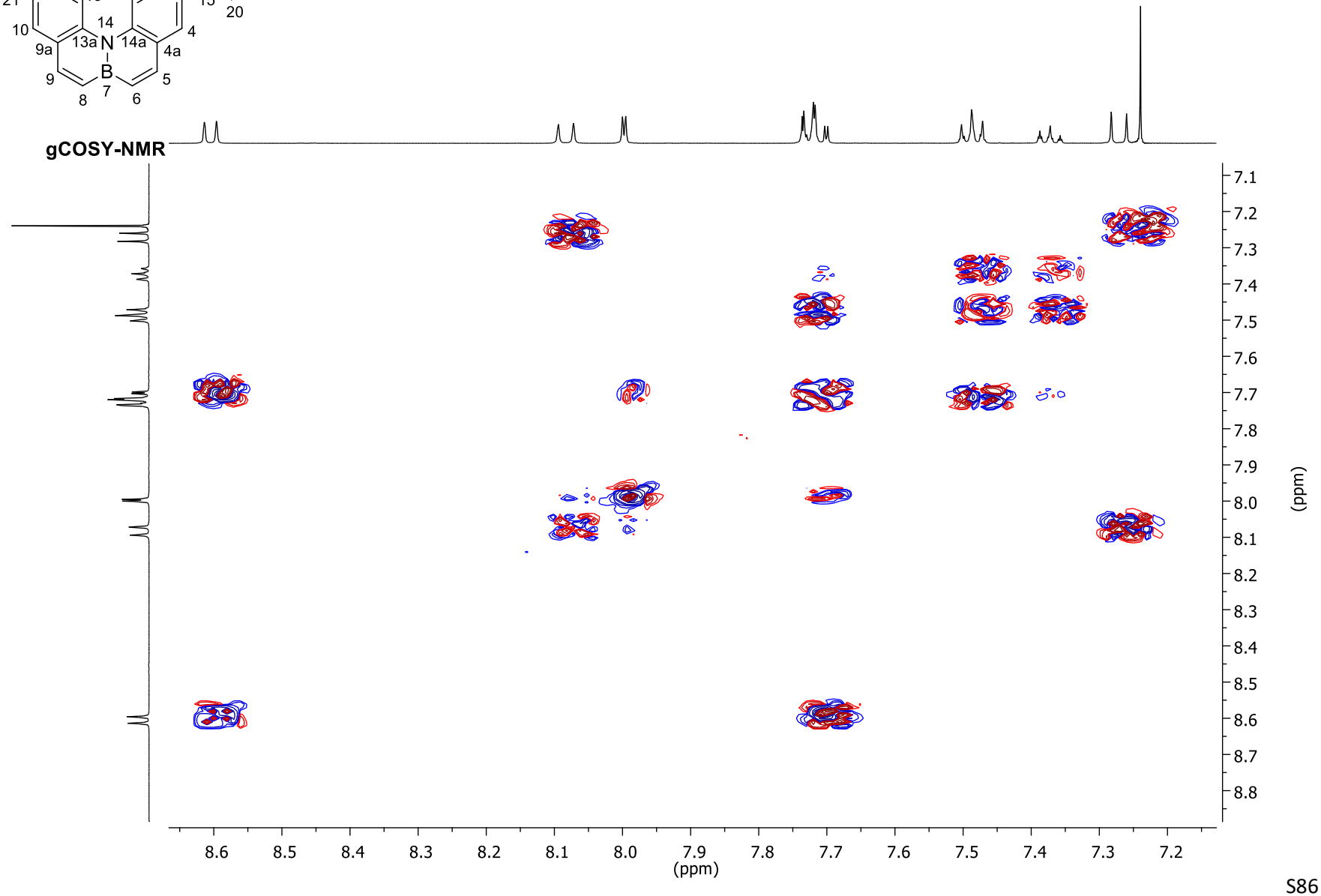
20

gCOSY-NMR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8.6
8.7
8.8
(ppm)
8.6
8.5
8.4
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8.2
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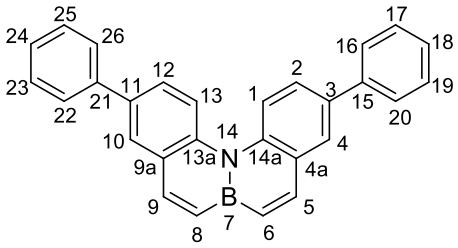
7.2
(ppm)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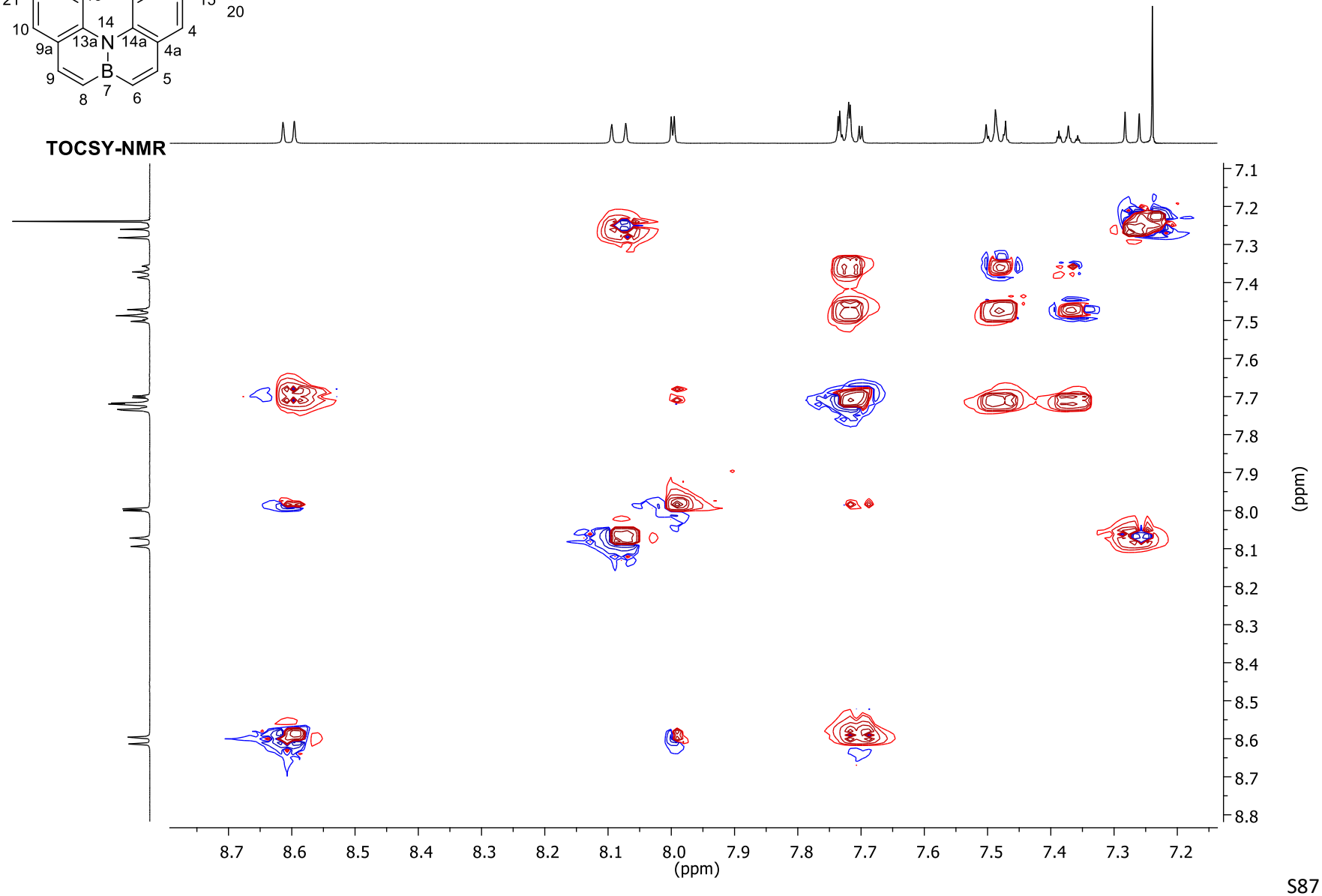
TOCSY-NMR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7.8
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8.4
8.5
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8.7
8.8
(ppm)
8.7
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8.5
8.4
8.3
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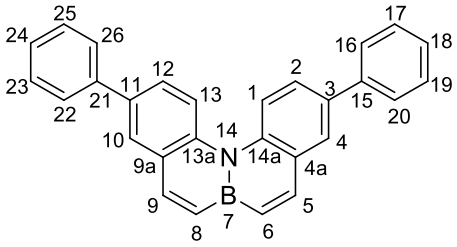
(ppm)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N
14a
4a
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9
B
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8
7
6

gHSQC-NMR

120
122
124
126
128
130
132
134
136
138
140
142
144
(ppm)
8.6
8.5
8.4
8.3
8.2
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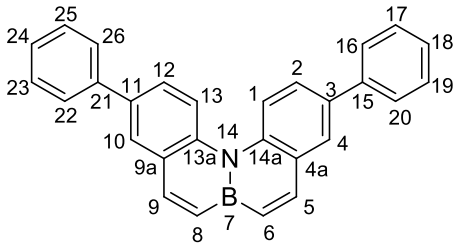
7.8
7.7
7.6
7.5
7.4
7.3
7.2
(ppm)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9a
13a
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1
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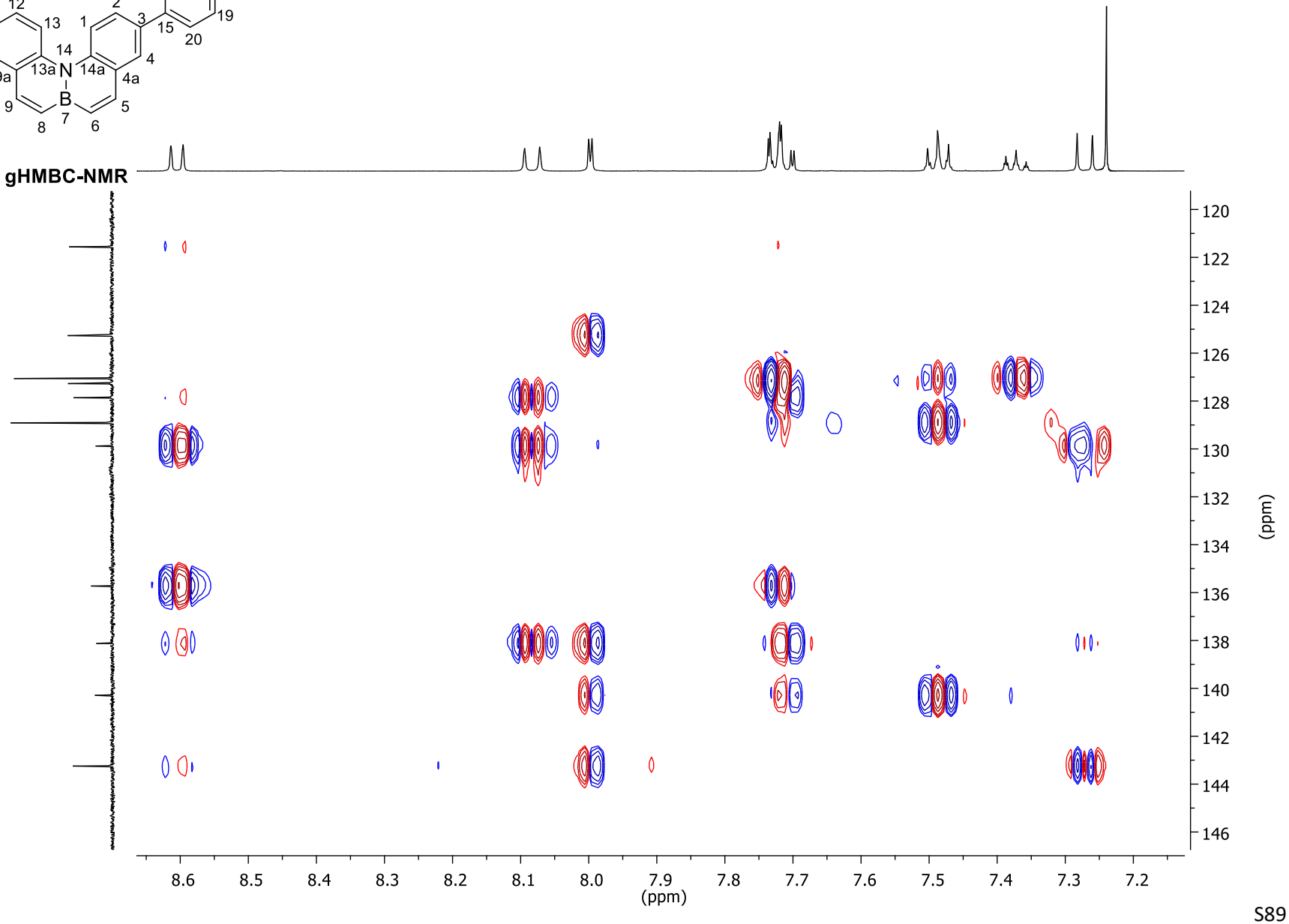
20

gHMBC-NMR


120
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140
142
144
146
(ppm)
8.6
8.5
8.4
8.3
8.2
8.1
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7.7
7.6
7.5
7.4
7.3
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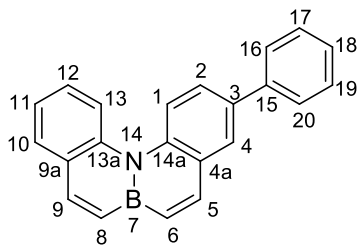
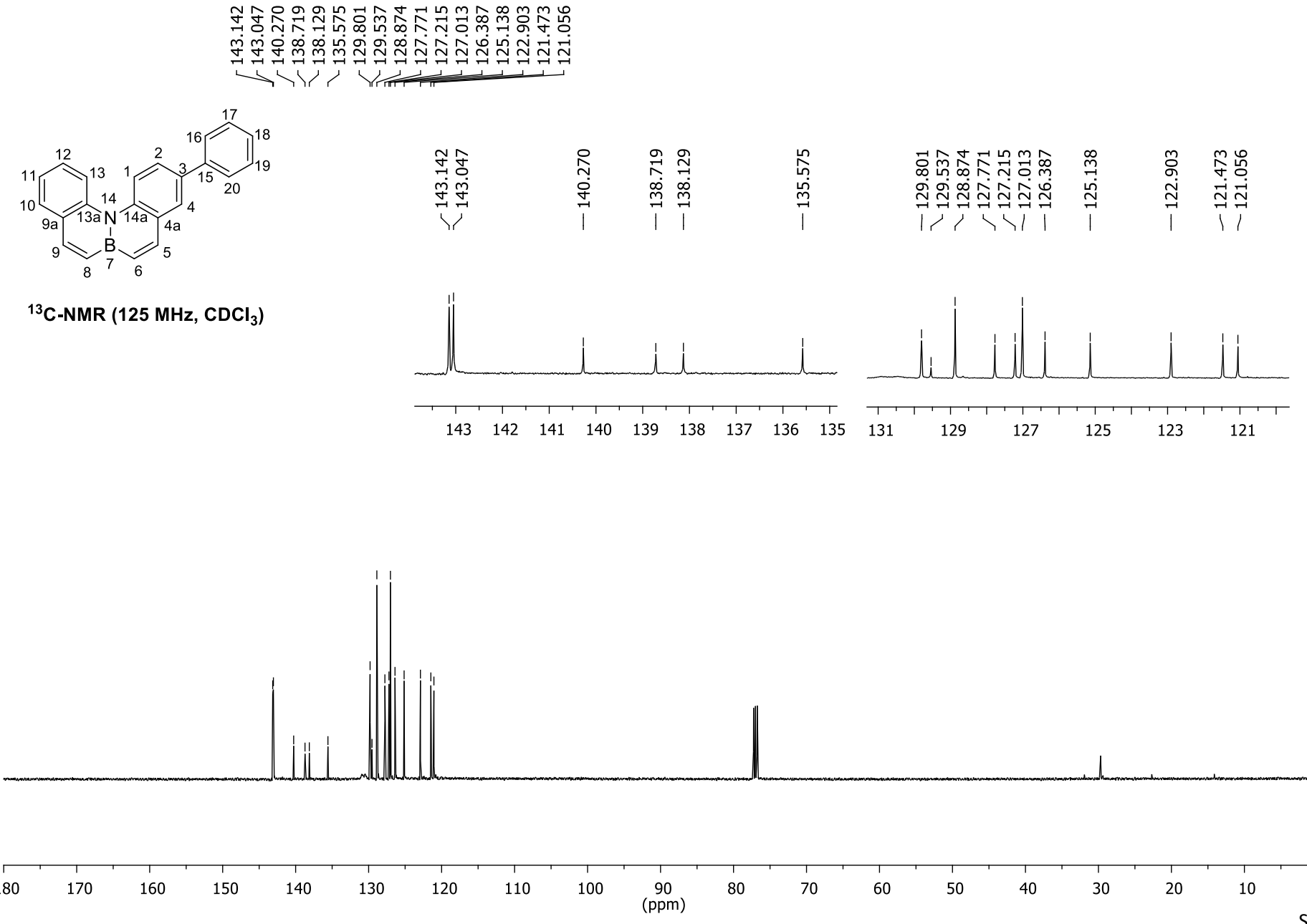
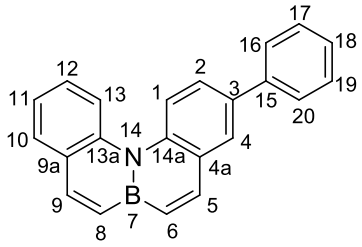
(ppm)



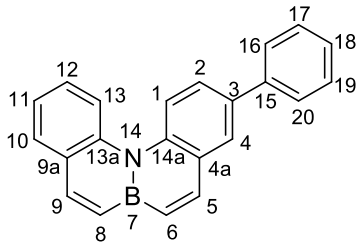
^{1}H-NMR (500 MHz, $CDCl_3$)



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



^{11}B-NMR (160 MHz, $CDCl_3$)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16
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13
1
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13a
N
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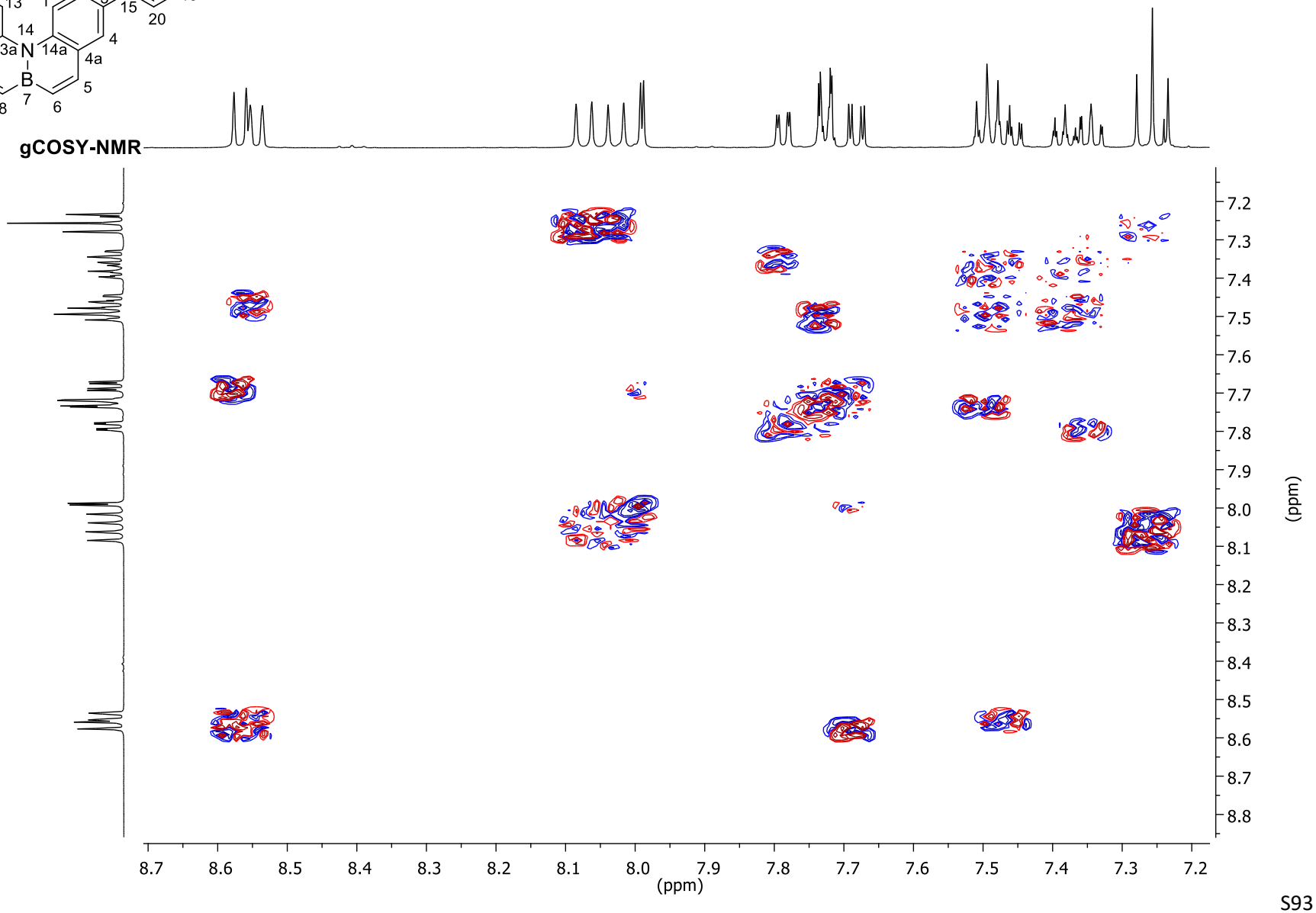
4a
9
B
5
7
8
6

gCOSY-NMR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7.7
7.8
7.9
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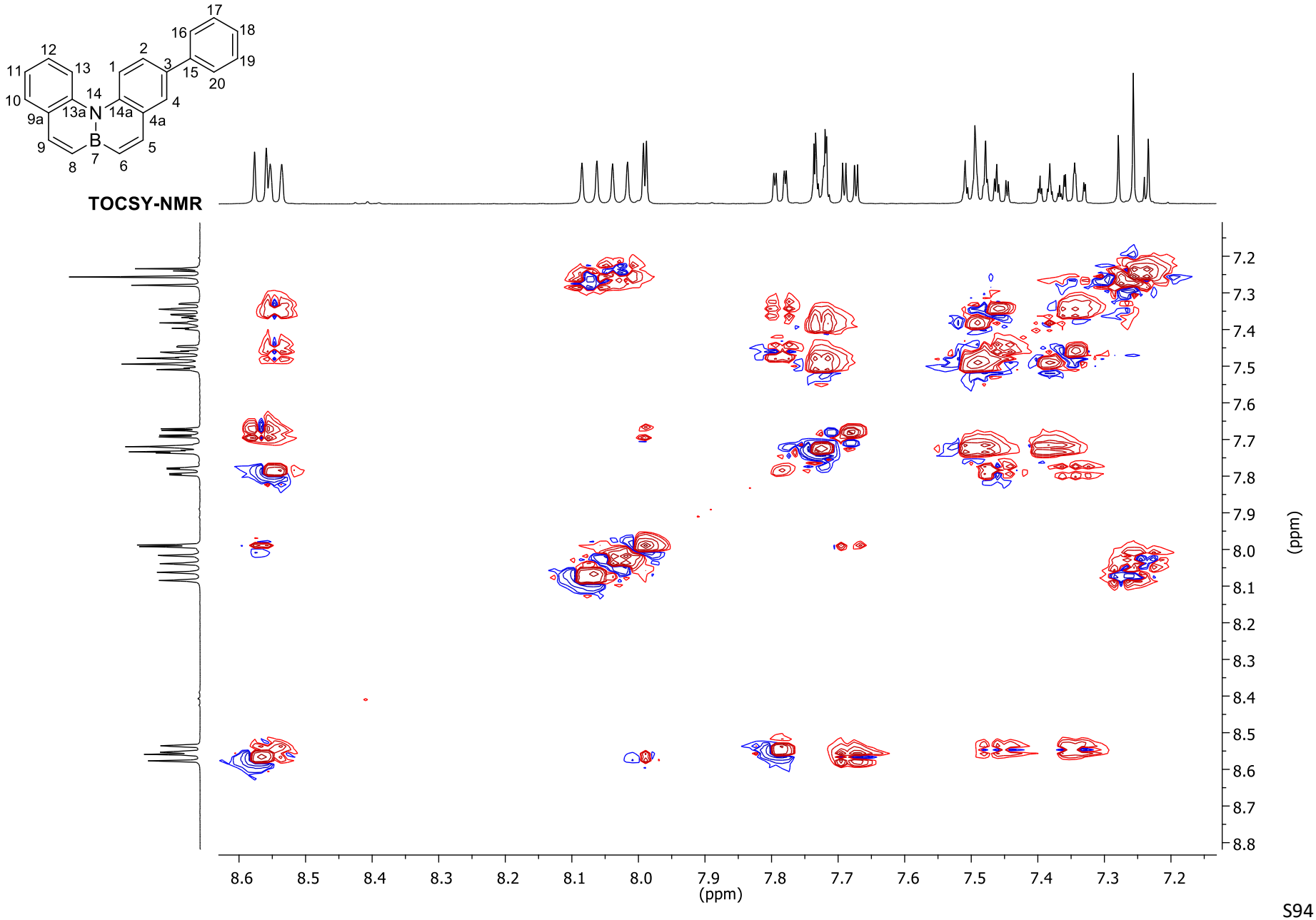
8.1
8.2
8.3
8.4
8.5
8.6
8.7
8.8
(ppm)
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
(ppm)


TOCSY-NMR
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
(ppm)
7.2
7.3
7.4
7.5
7.6
7.7
7.8
7.9
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8.1
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8.5
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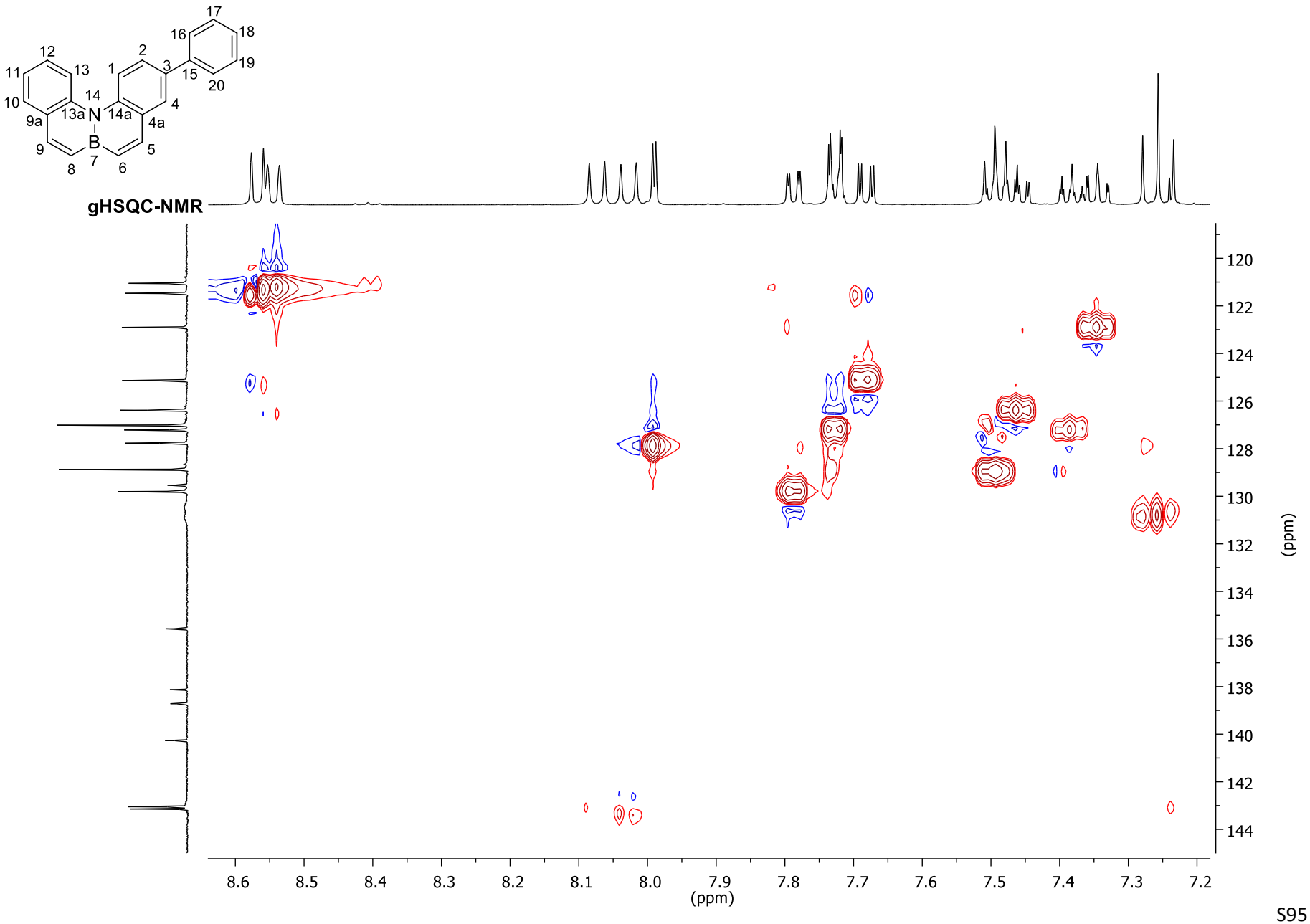
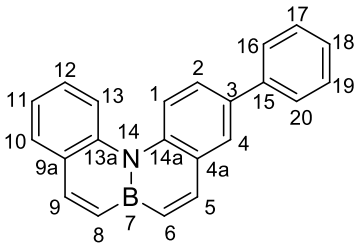
8.7
8.8
(ppm)


gHSQC-NMR
(ppm)
(ppm)


17
16
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12
2
19
11
13
1
3
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20
14
10
4
13a
N
14a
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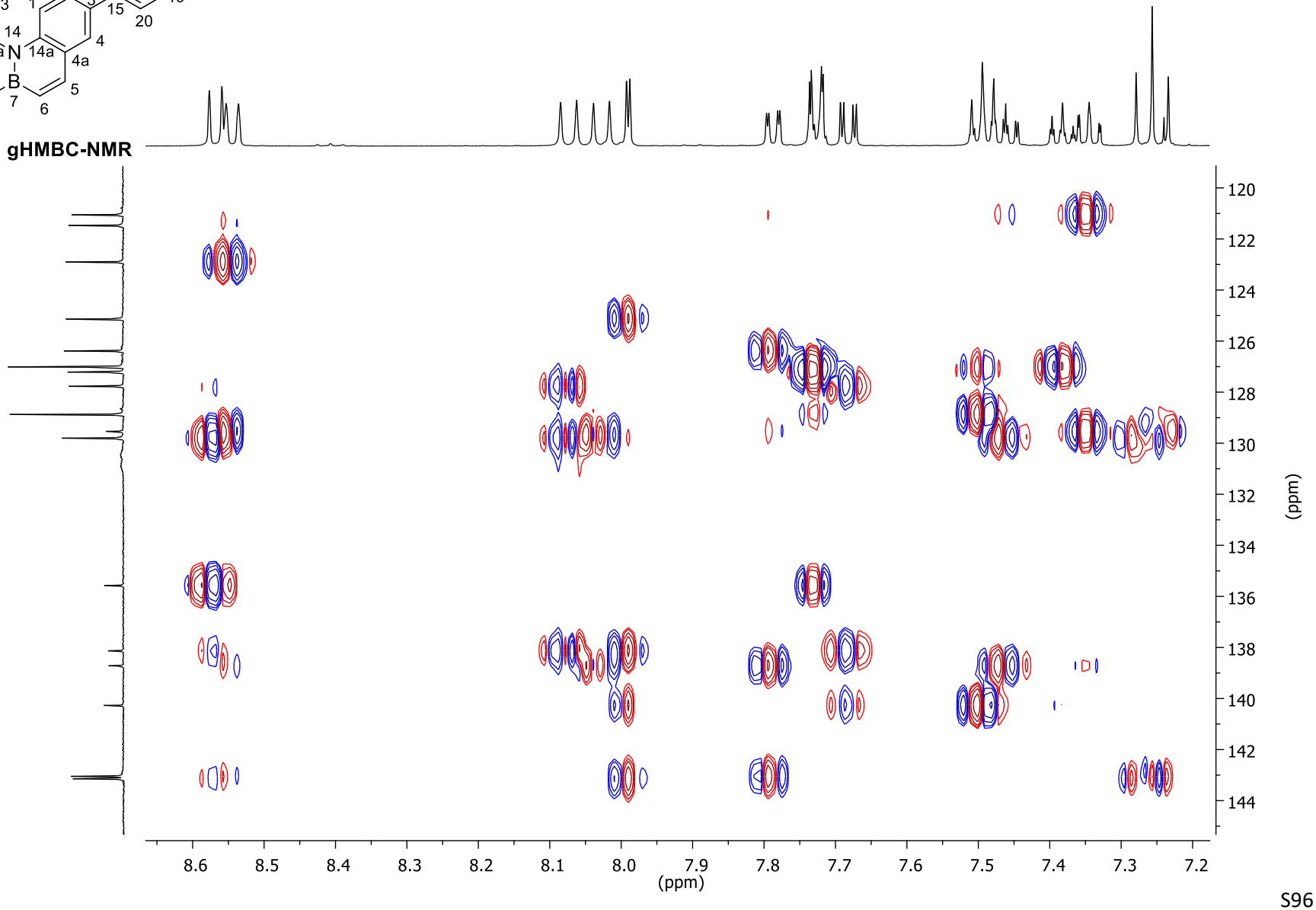
4a
B
9
5
7
8
6

gHMBC-NMR


120
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124
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128
130
132
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136
138
140
142
144
(ppm)
8.6
8.5
8.4
8.3
8.2
8.1
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7.9
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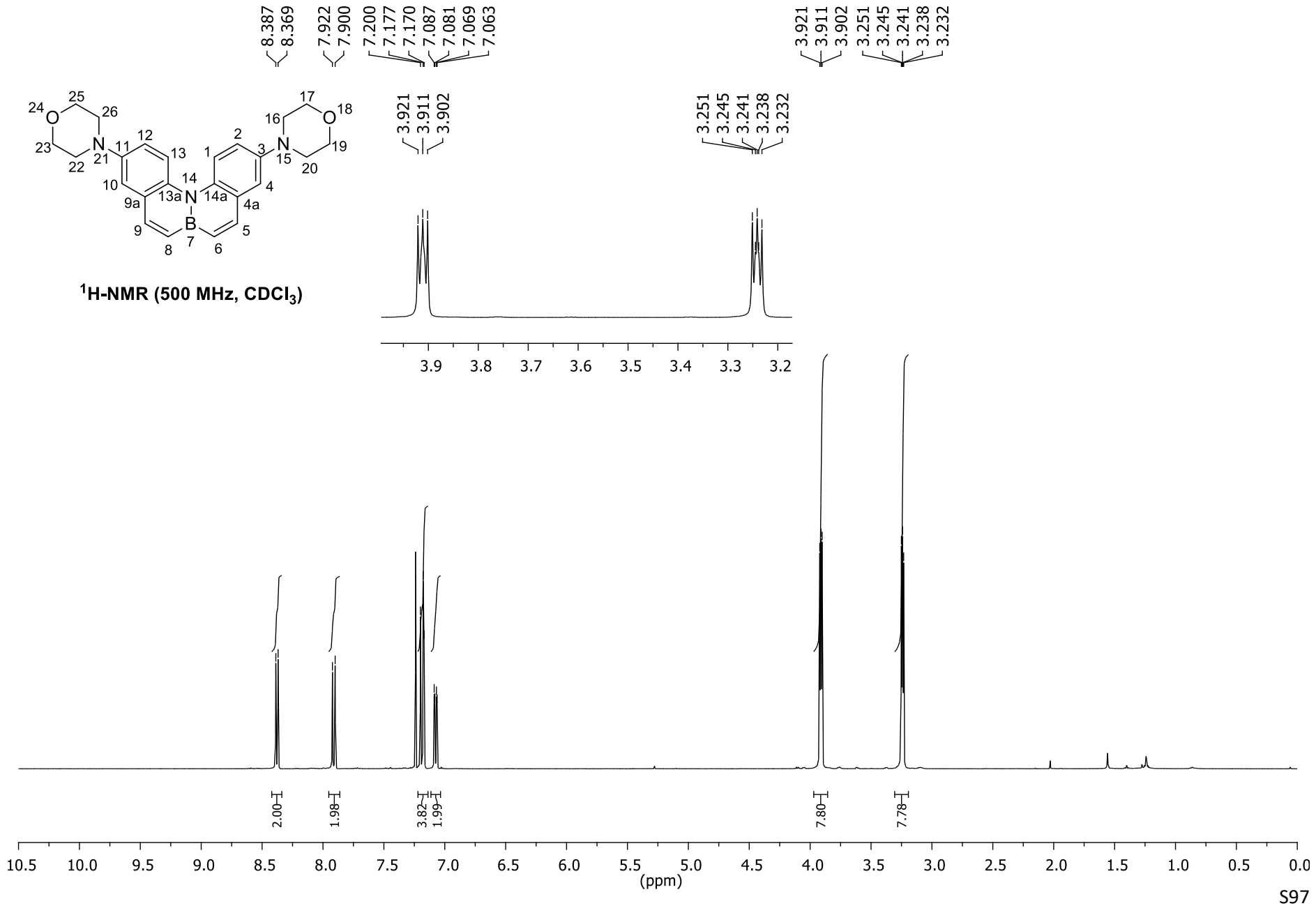
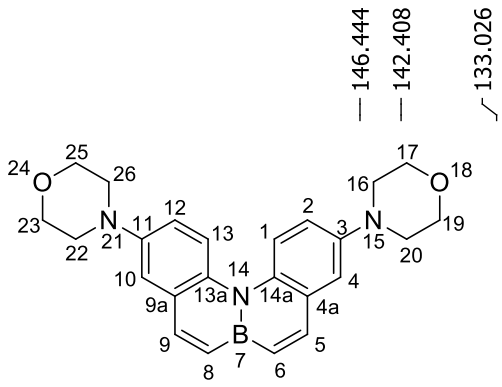
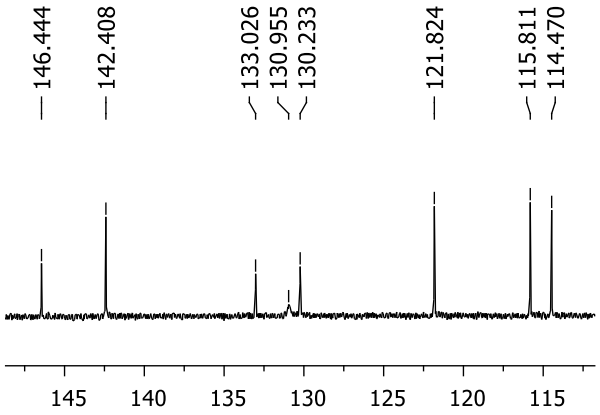
7.5
7.4
7.3
7.2
(ppm)

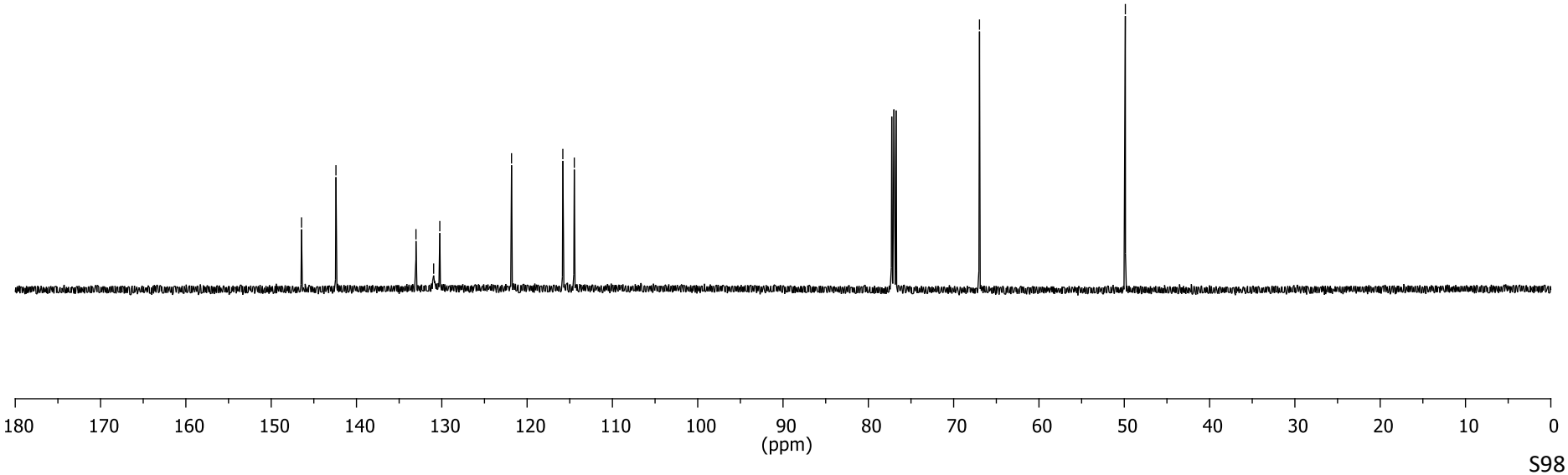


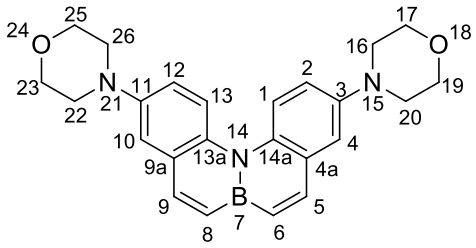
^{1}H-NMR (500 MHz, $CDCl_3$)



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

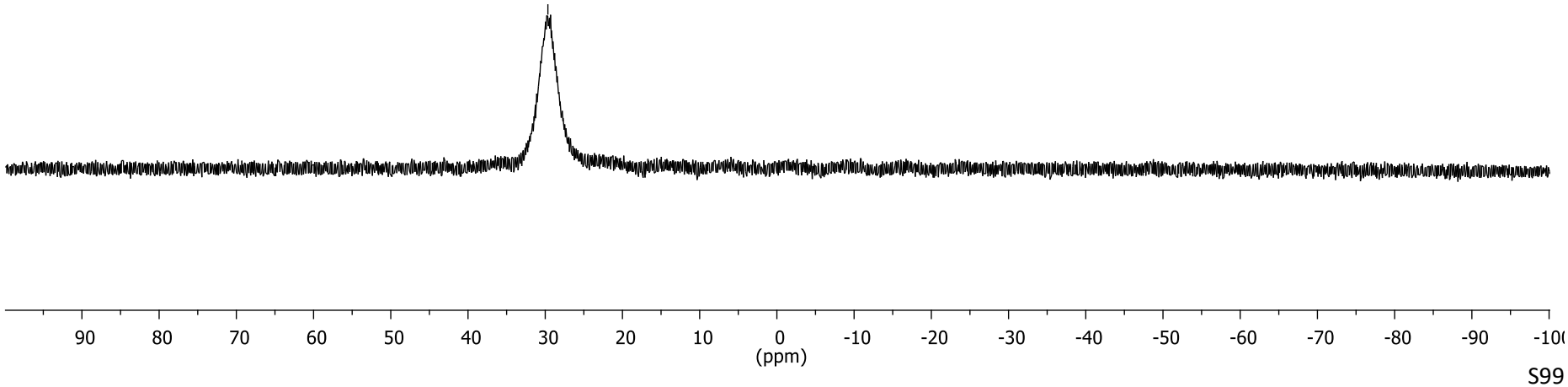


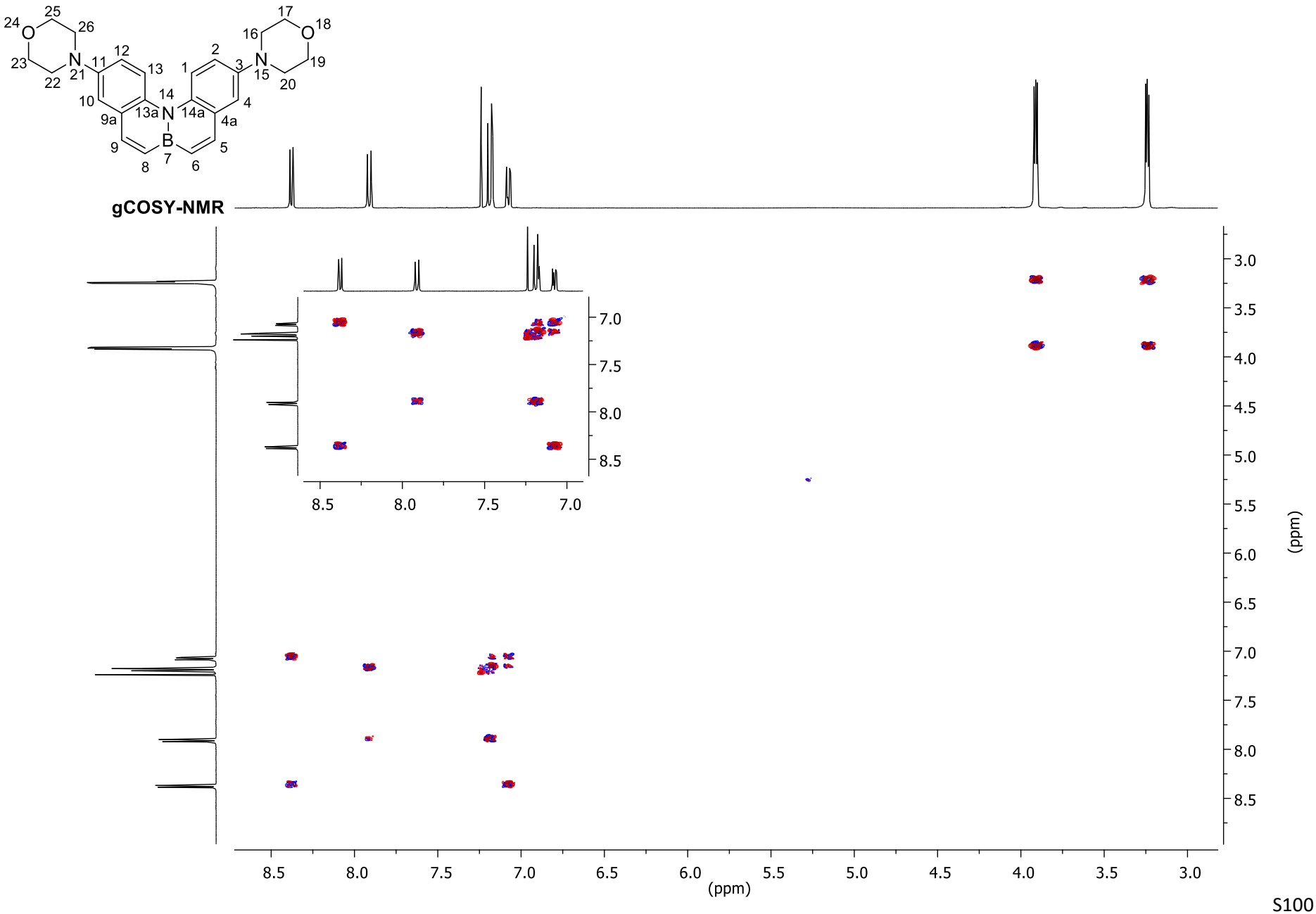


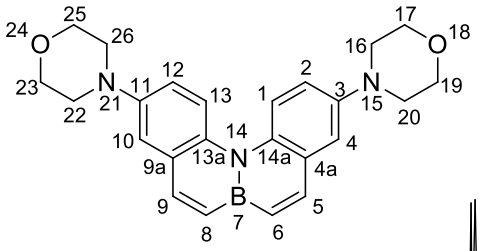


— 29.656

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




gCOSY-NMR
(ppm)
(ppm)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O
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13a
N
14a
4a
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B
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7
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16
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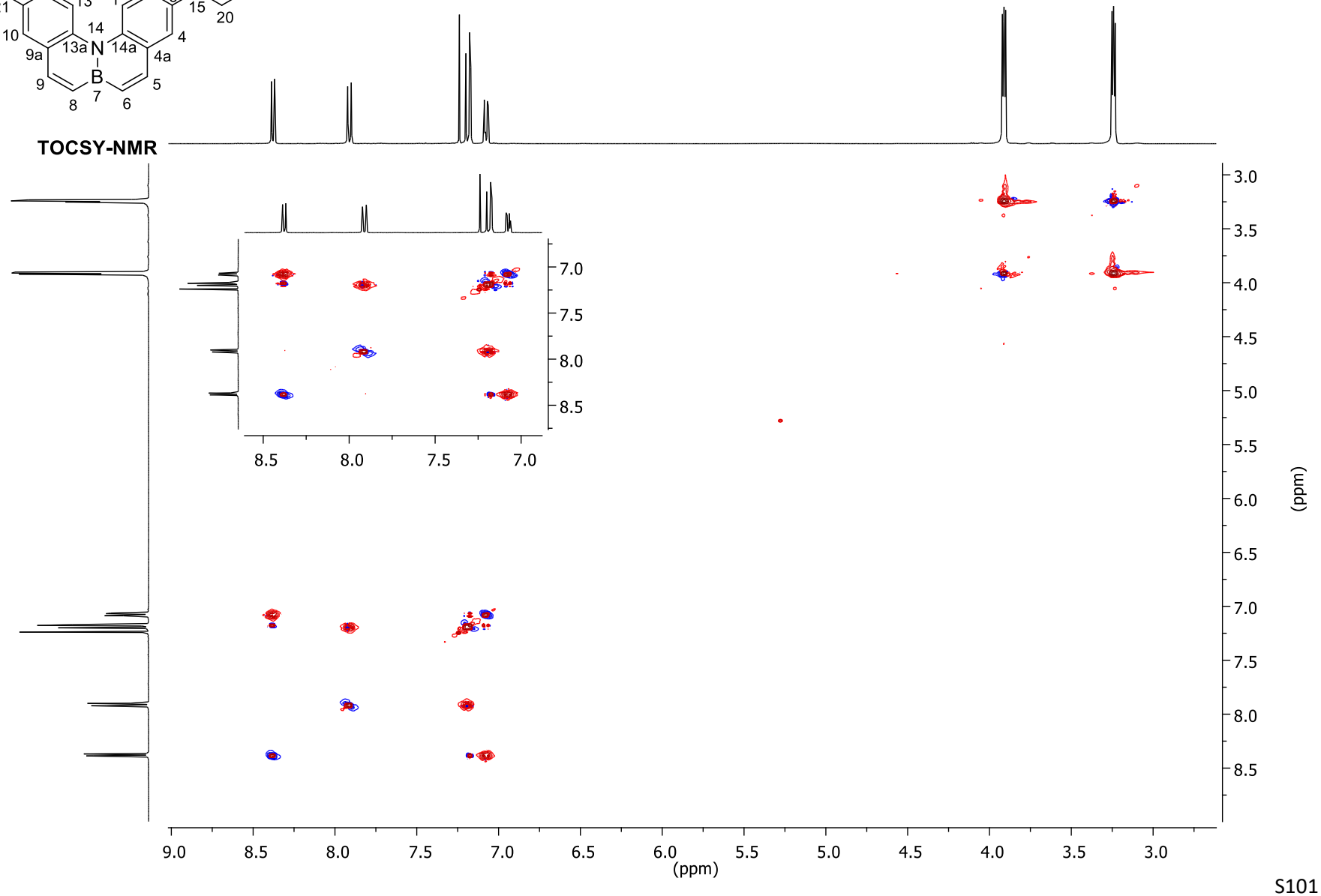
O
18
N
15
20
19

TOCSY-NMR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5.5
6.0
6.5
7.0
7.5
8.0
8.5
(ppm)
9.0
8.5
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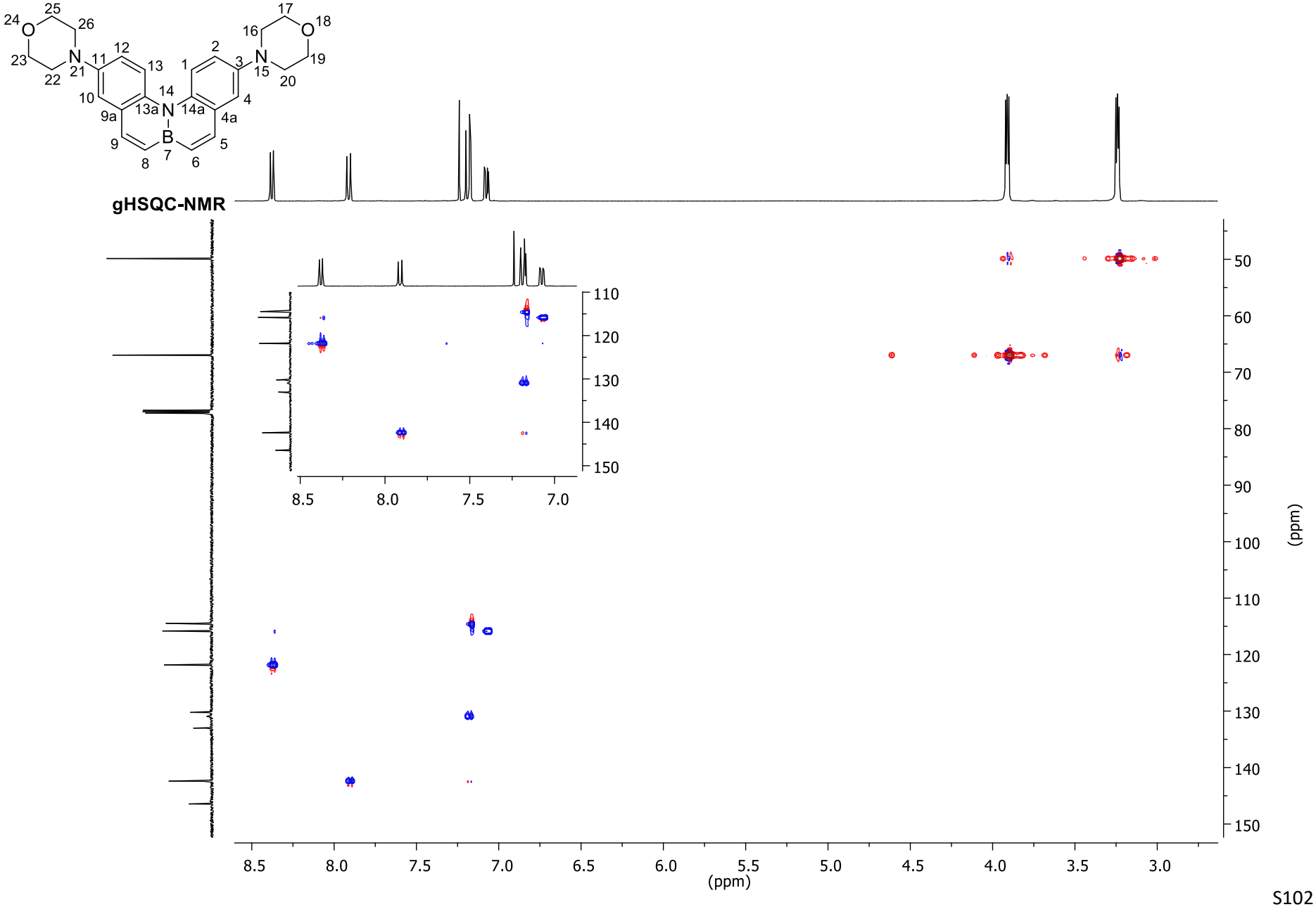
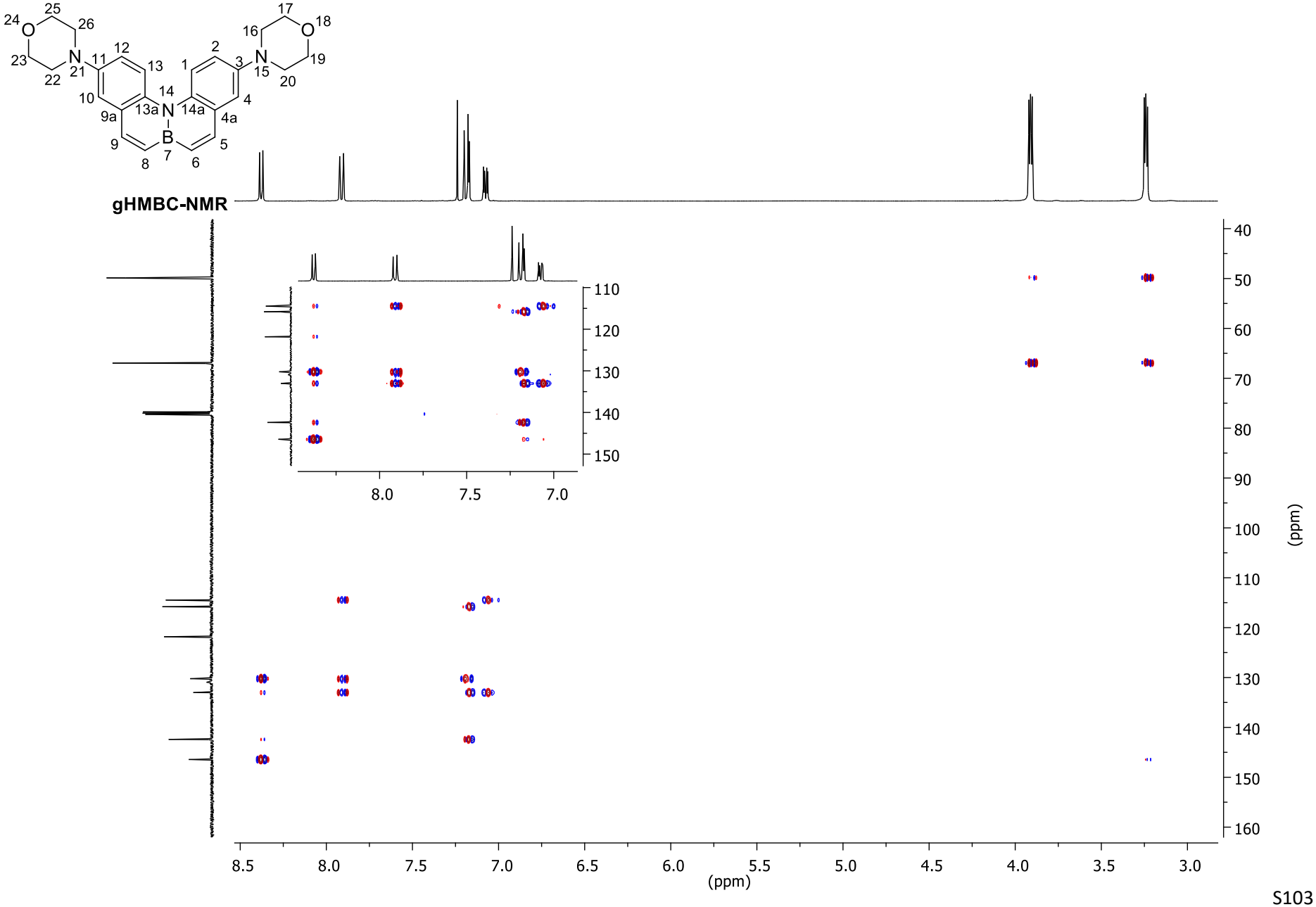
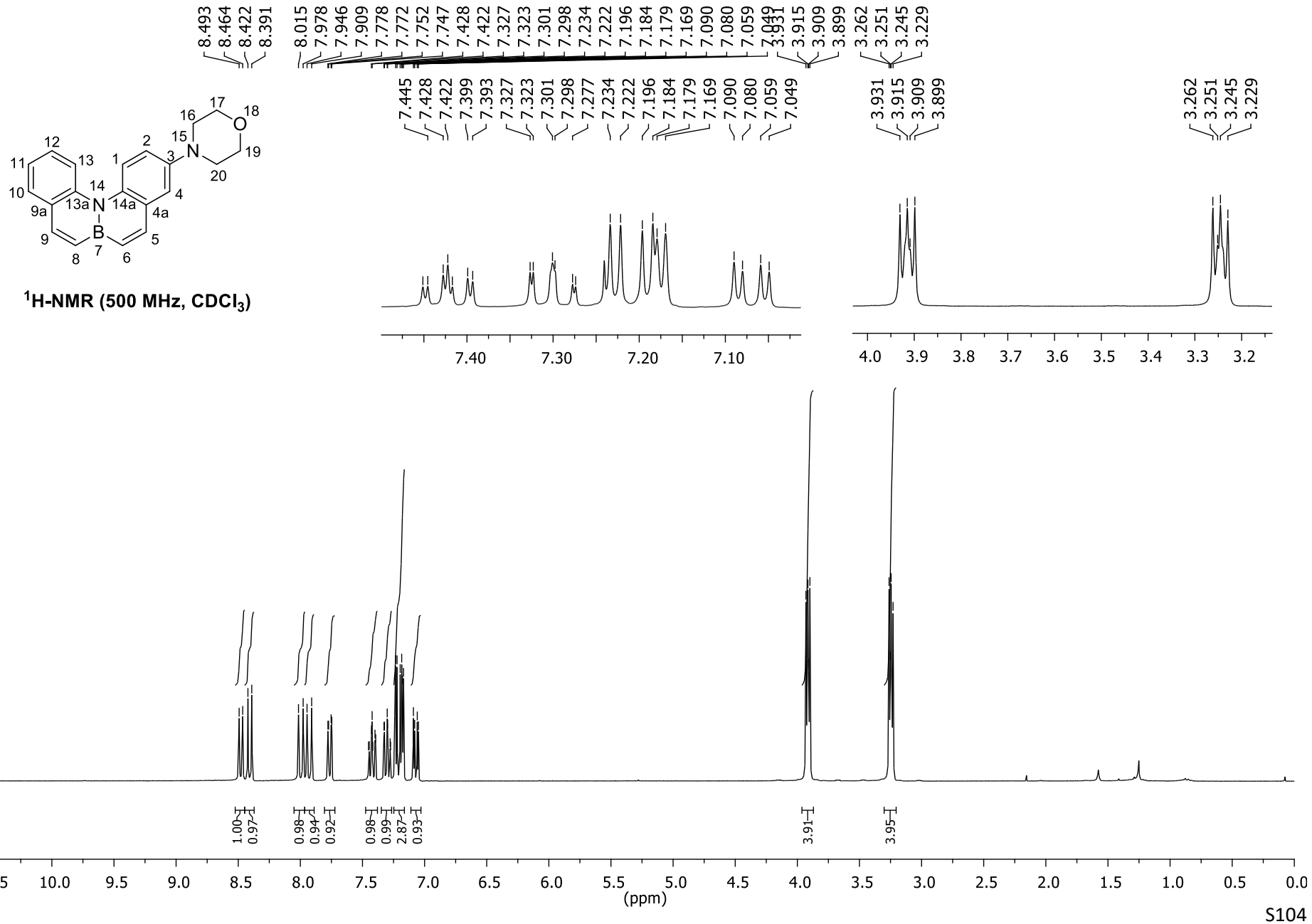
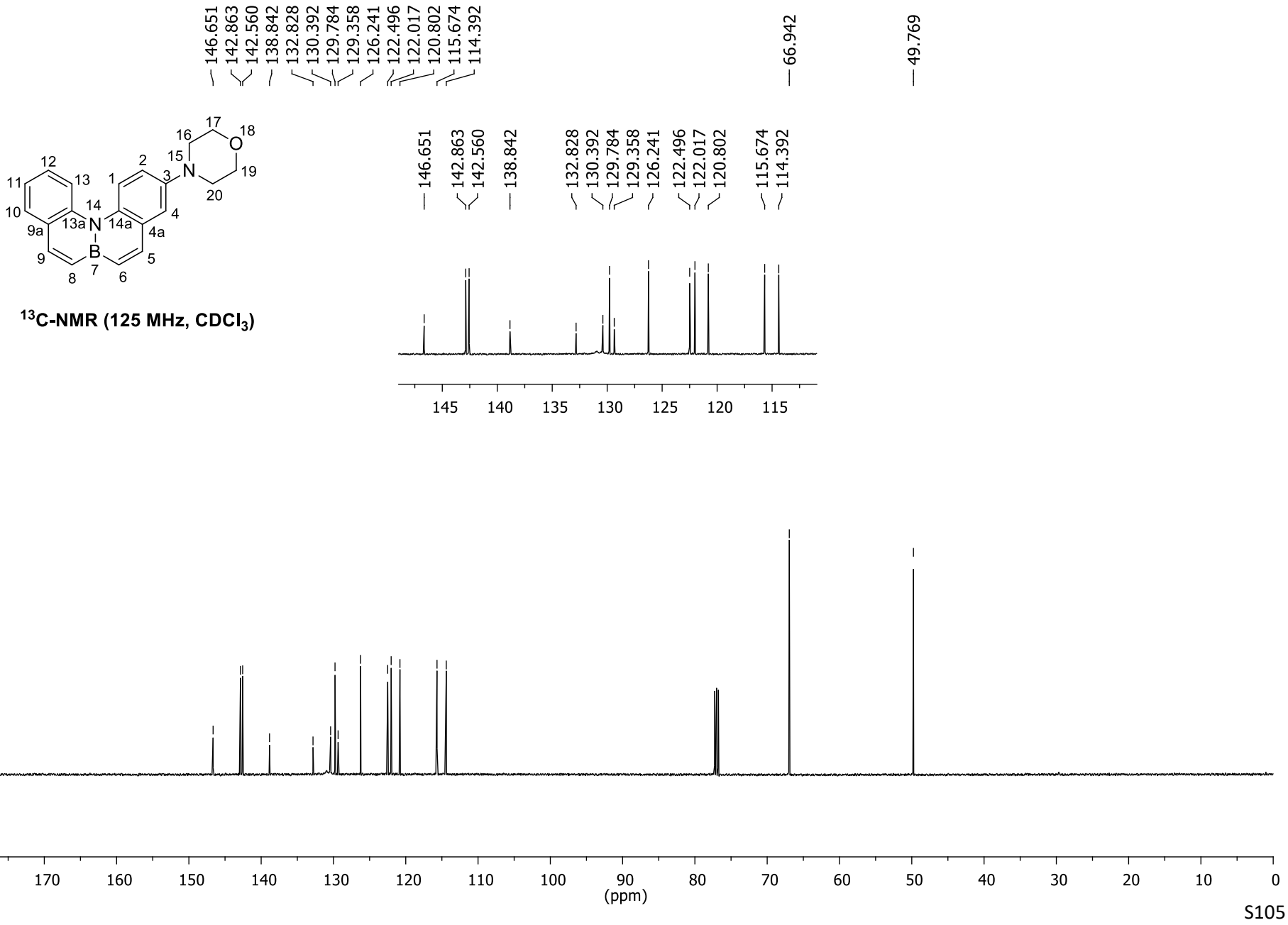
4.5
4.0
3.5
3.0
(ppm)


gHSQC-NMR
(ppm)
(ppm)

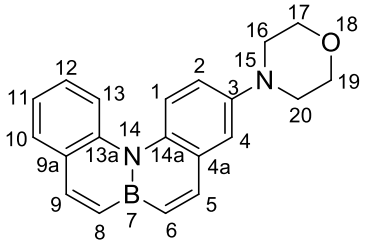

gHMBC-NMR
(ppm)
(ppm)



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

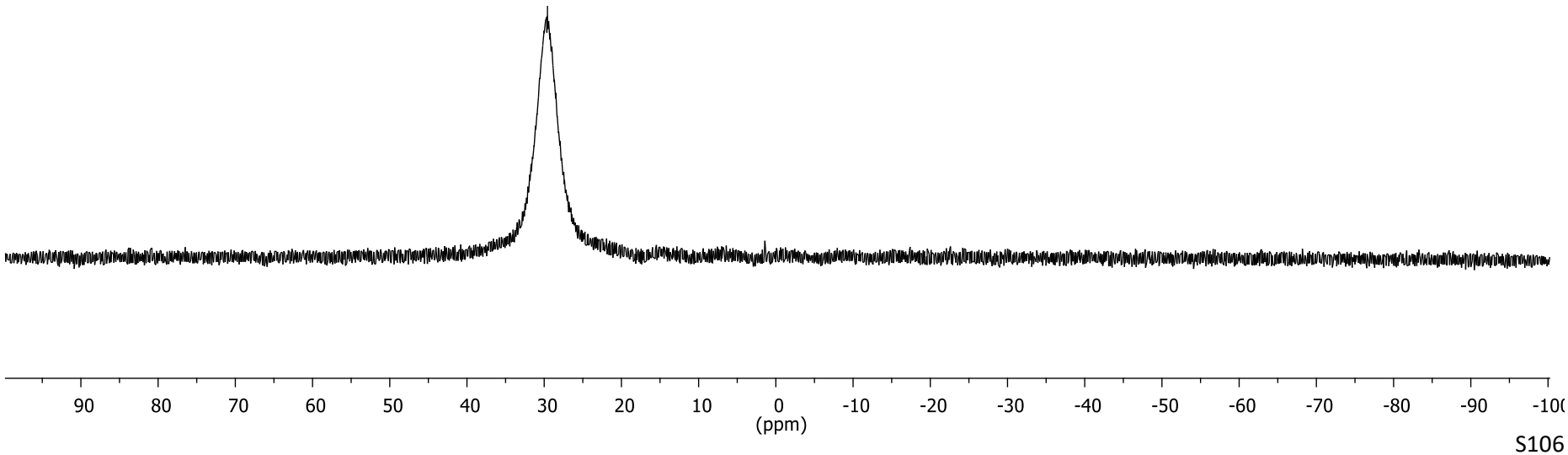


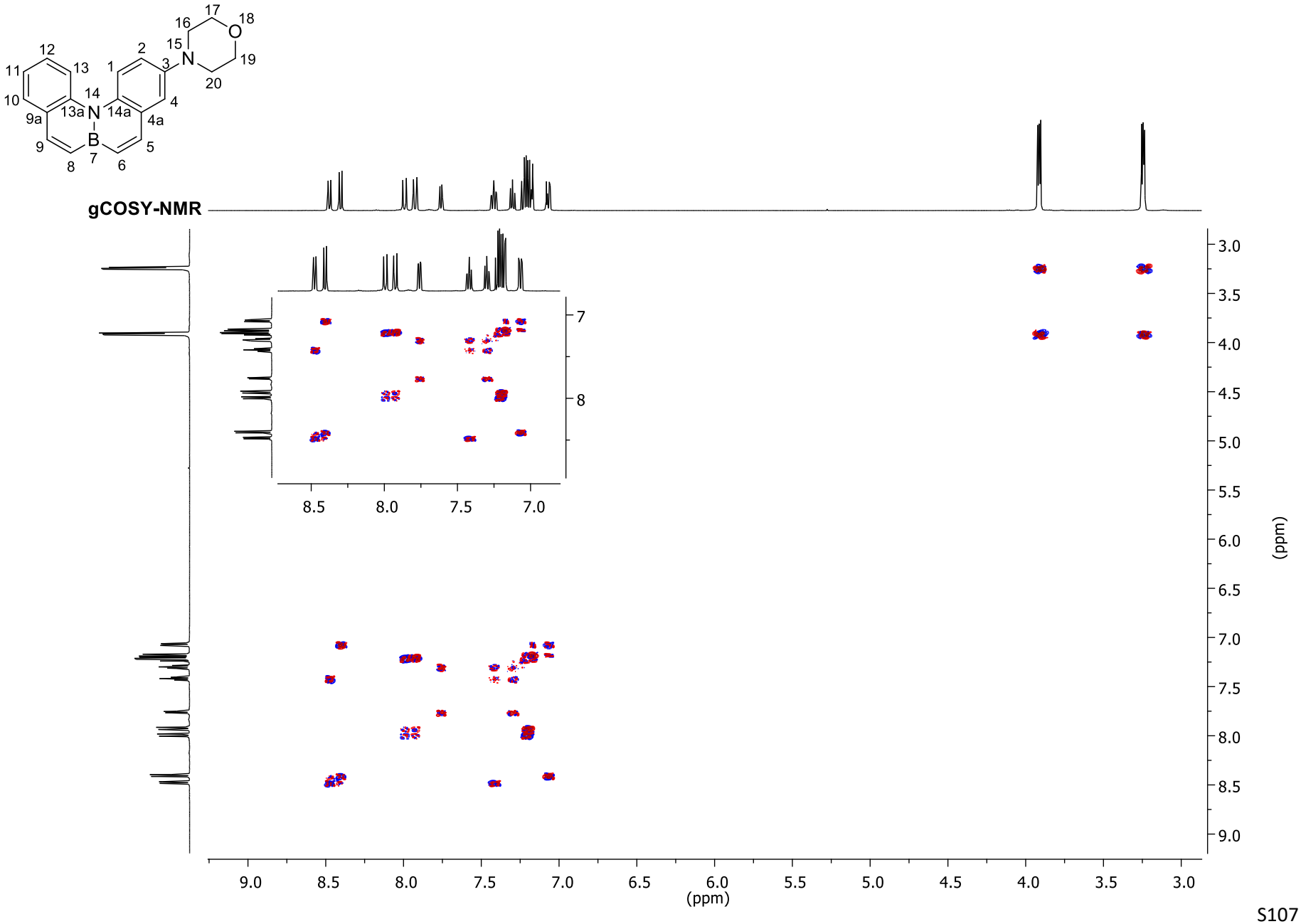
^{13}C-NMR (125 MHz, $CDCl_3$)

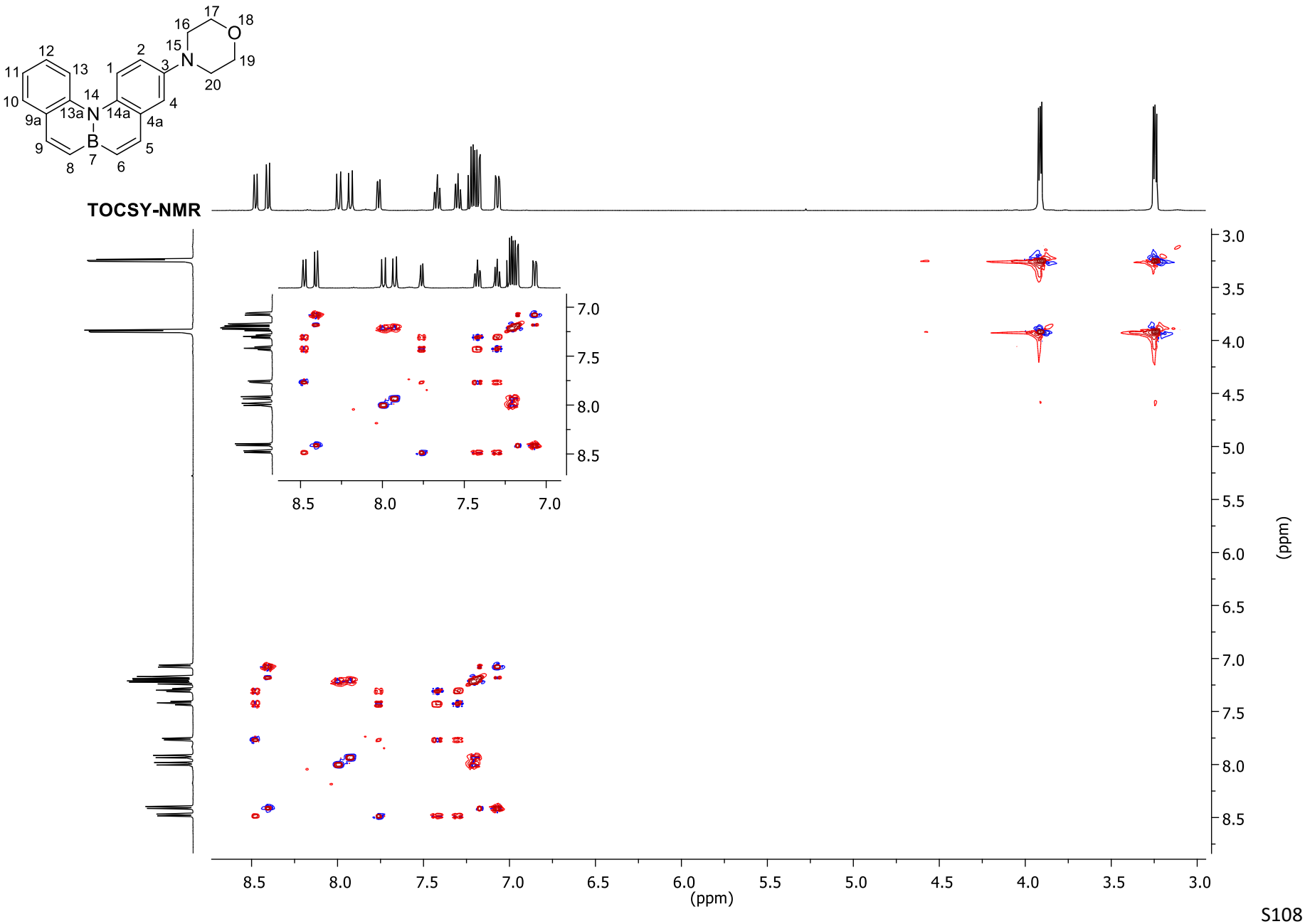


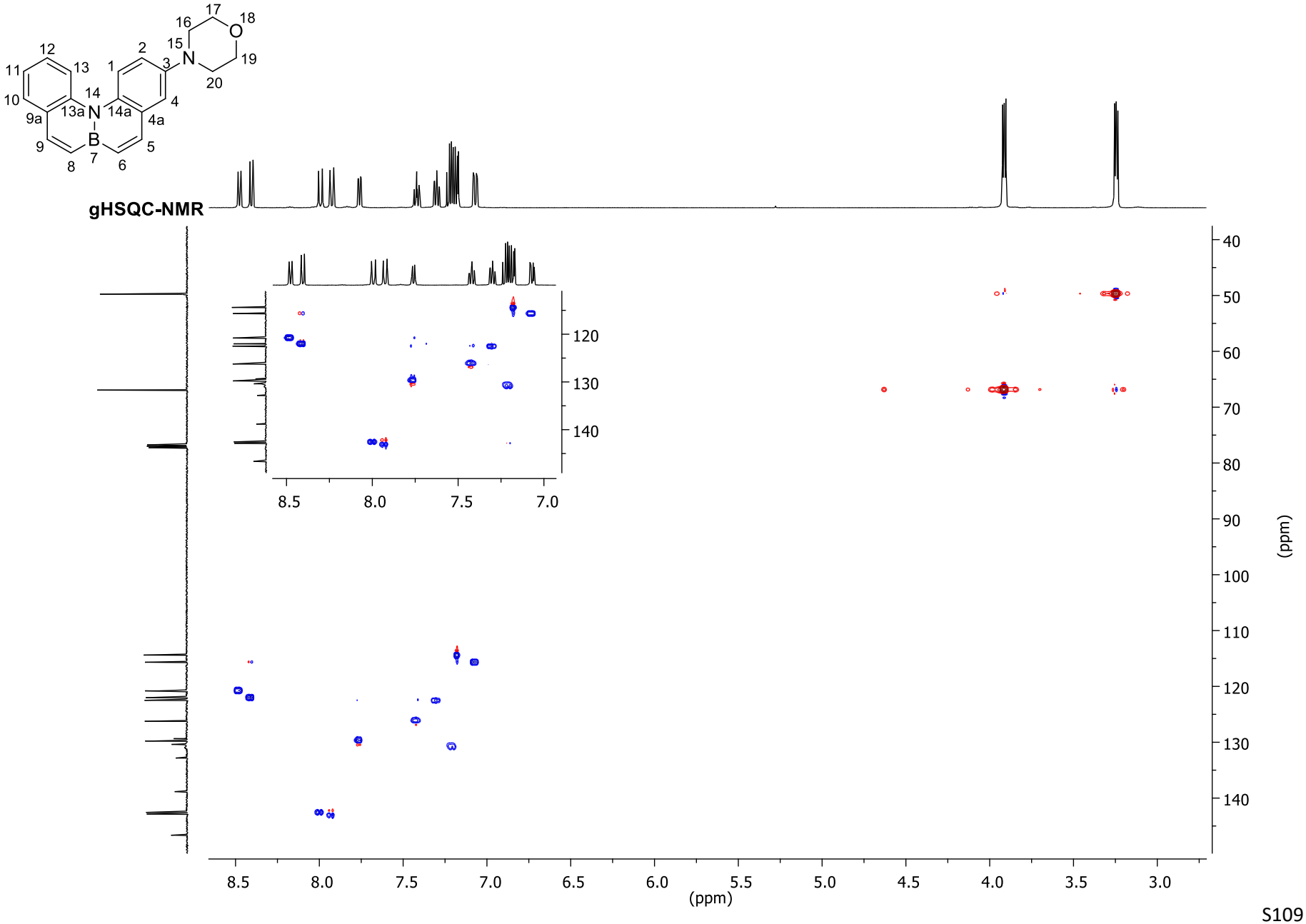
— 29.575

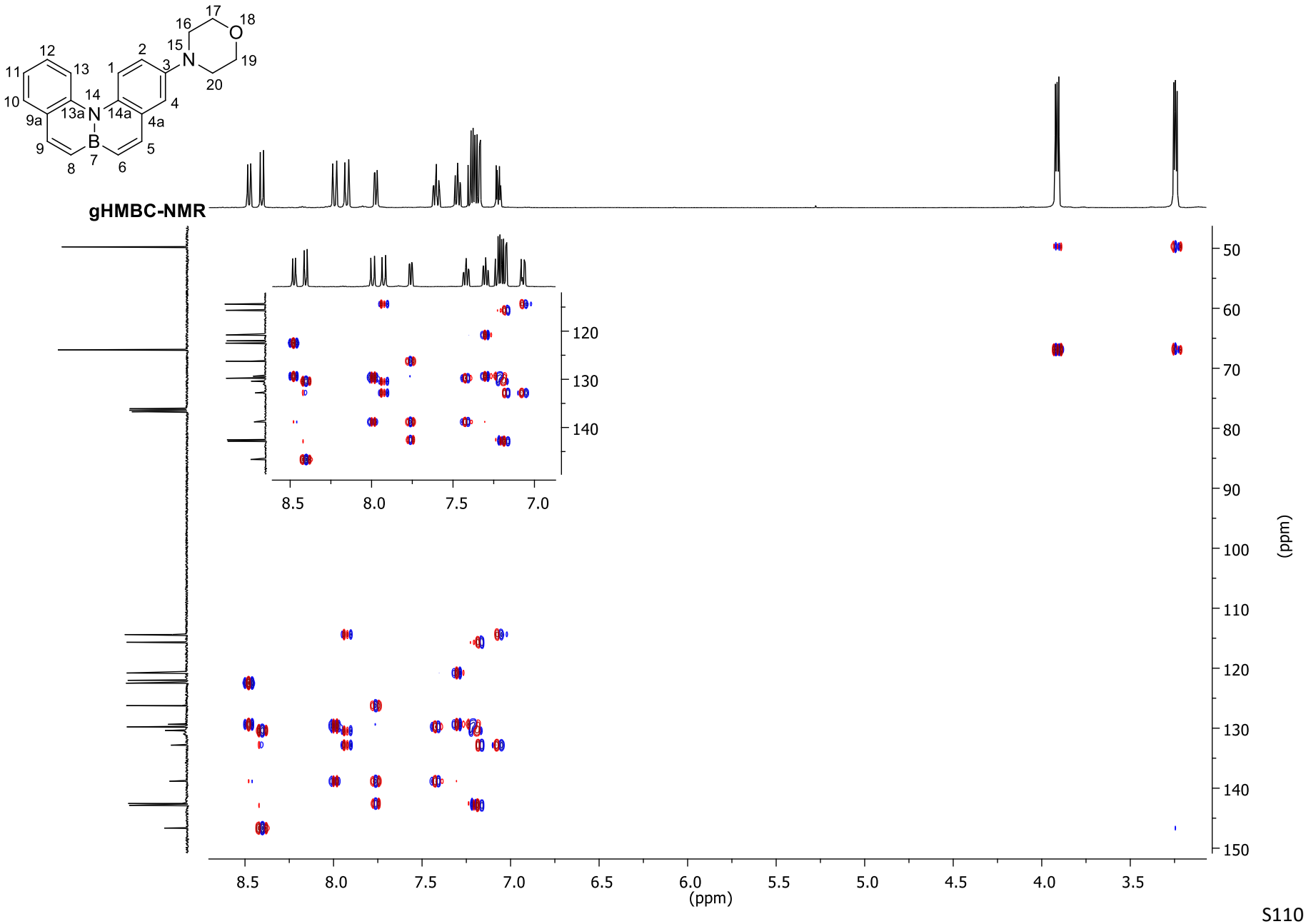
^{11}B-NMR (160 MHz, $CDCl_3$)

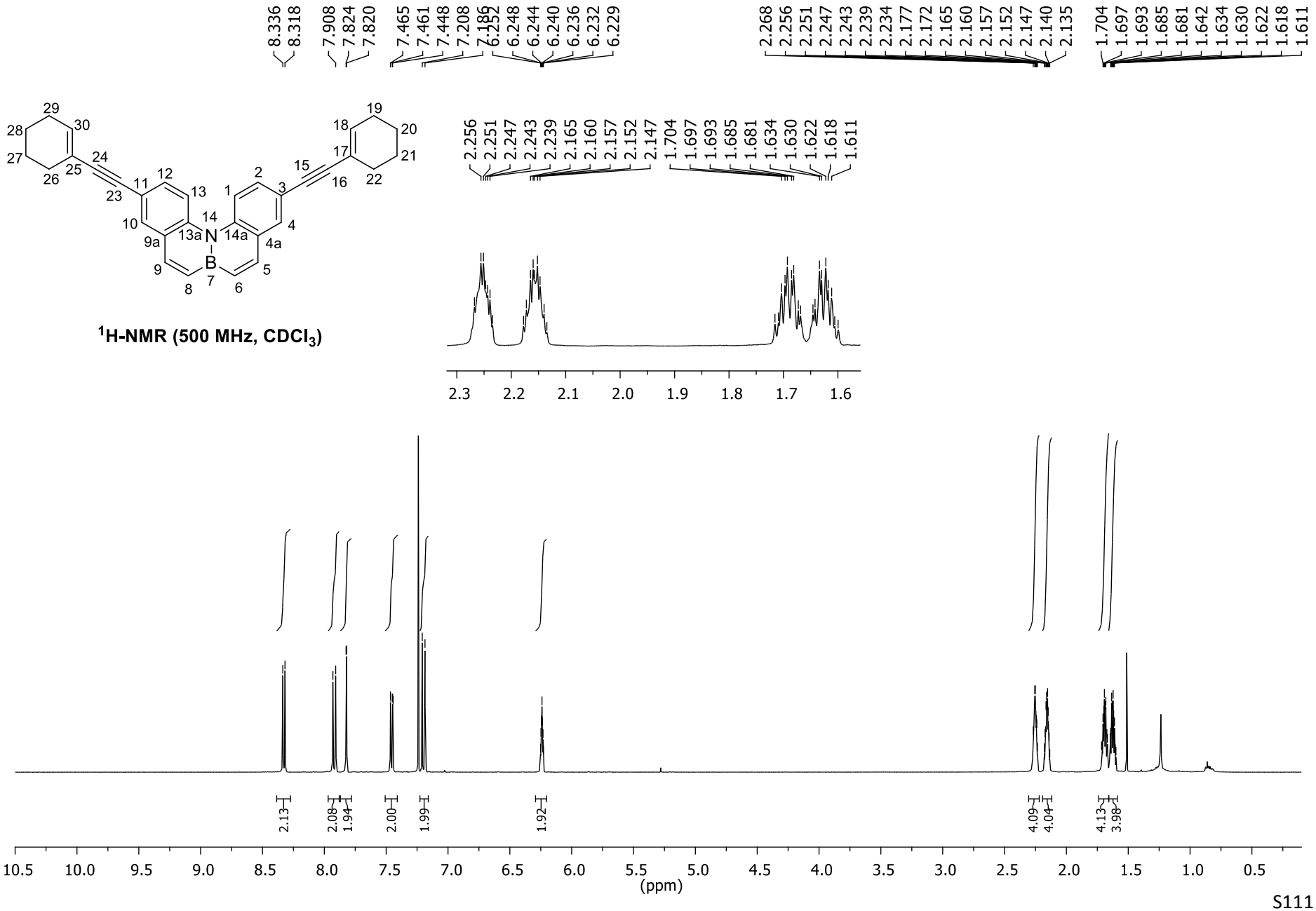



gCOSY-NMR
(ppm)
(ppm)

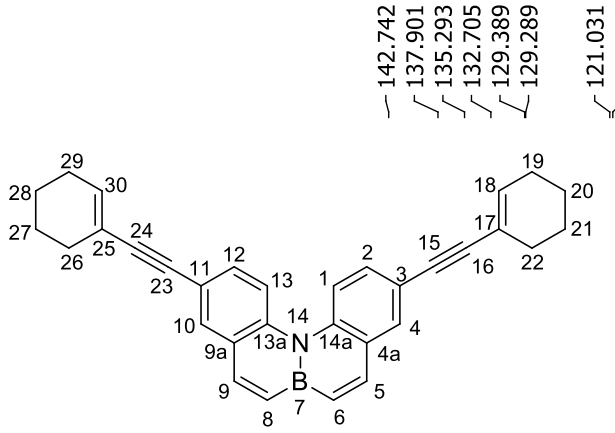

TOCSY-NMR
(ppm)
(ppm)


gHSQC-NMR
(ppm)
(ppm)


gHMBC-NMR
(ppm)
(ppm)

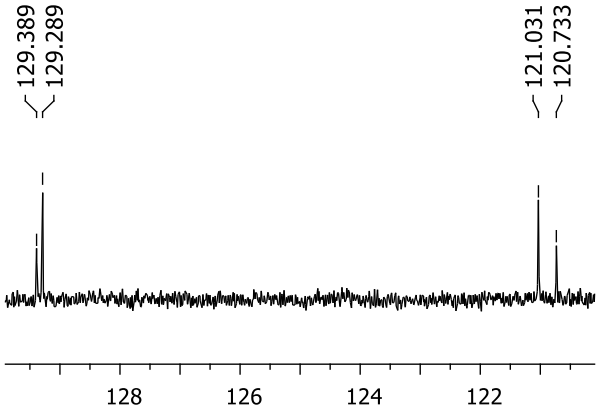


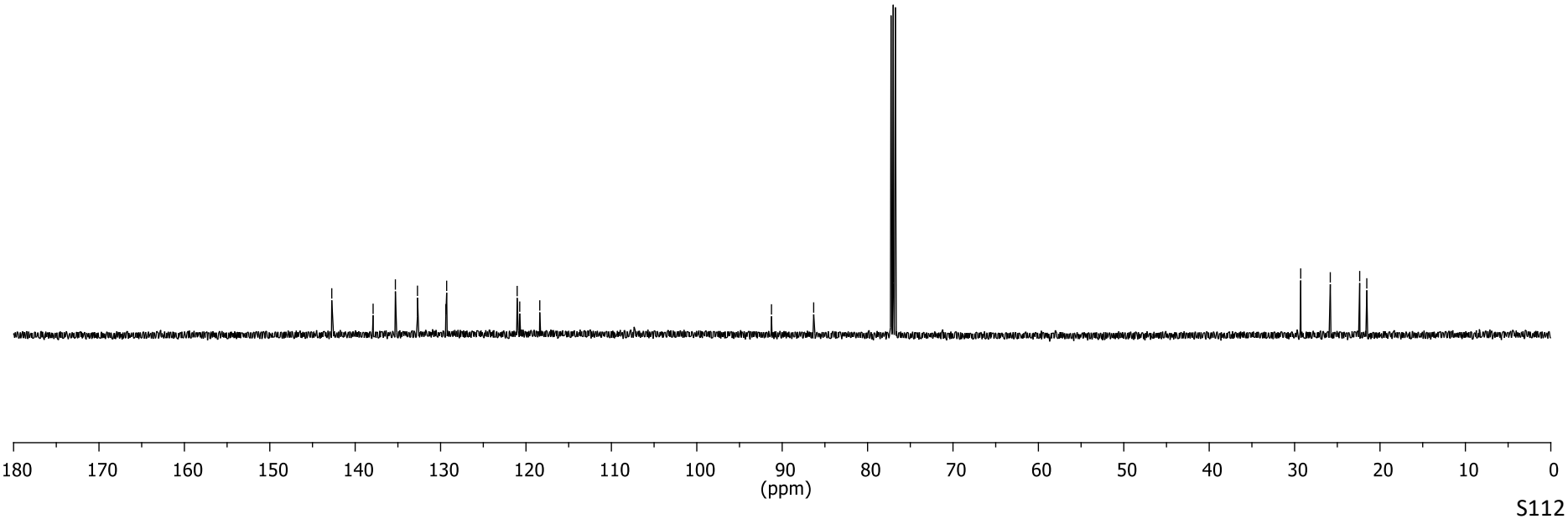
^{1}H-NMR (500 MHz, $CDCl_3$)

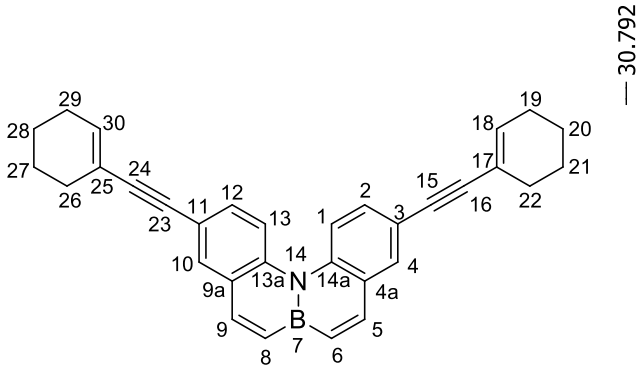


^{13}C-NMR (125 MHz, $CDCl_3$)

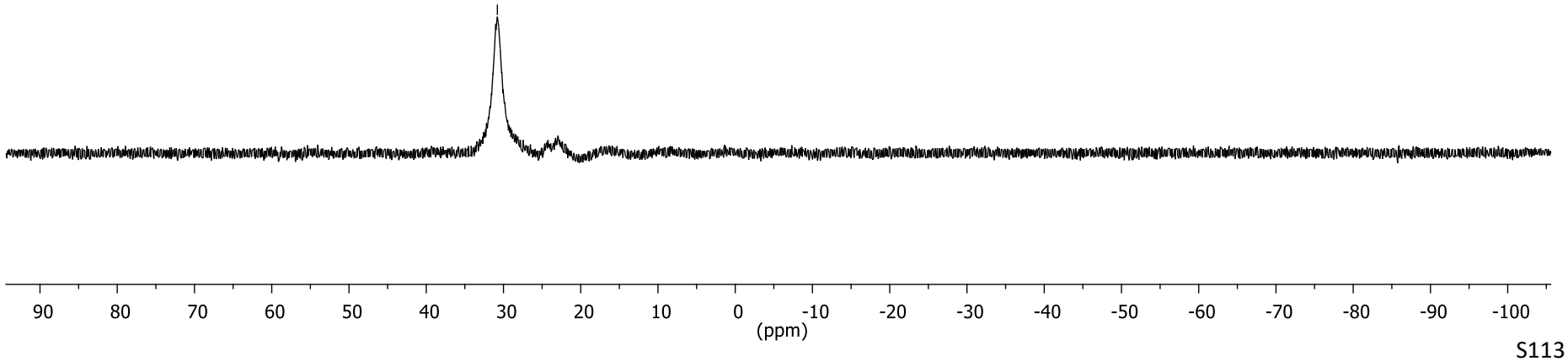
142.742
137.901
135.293
132.705
129.389
129.289
121.031
120.733
118.386
91.253
86.312
29.285
25.821
22.377
21.547

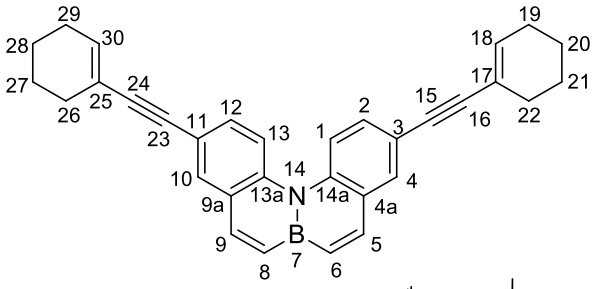




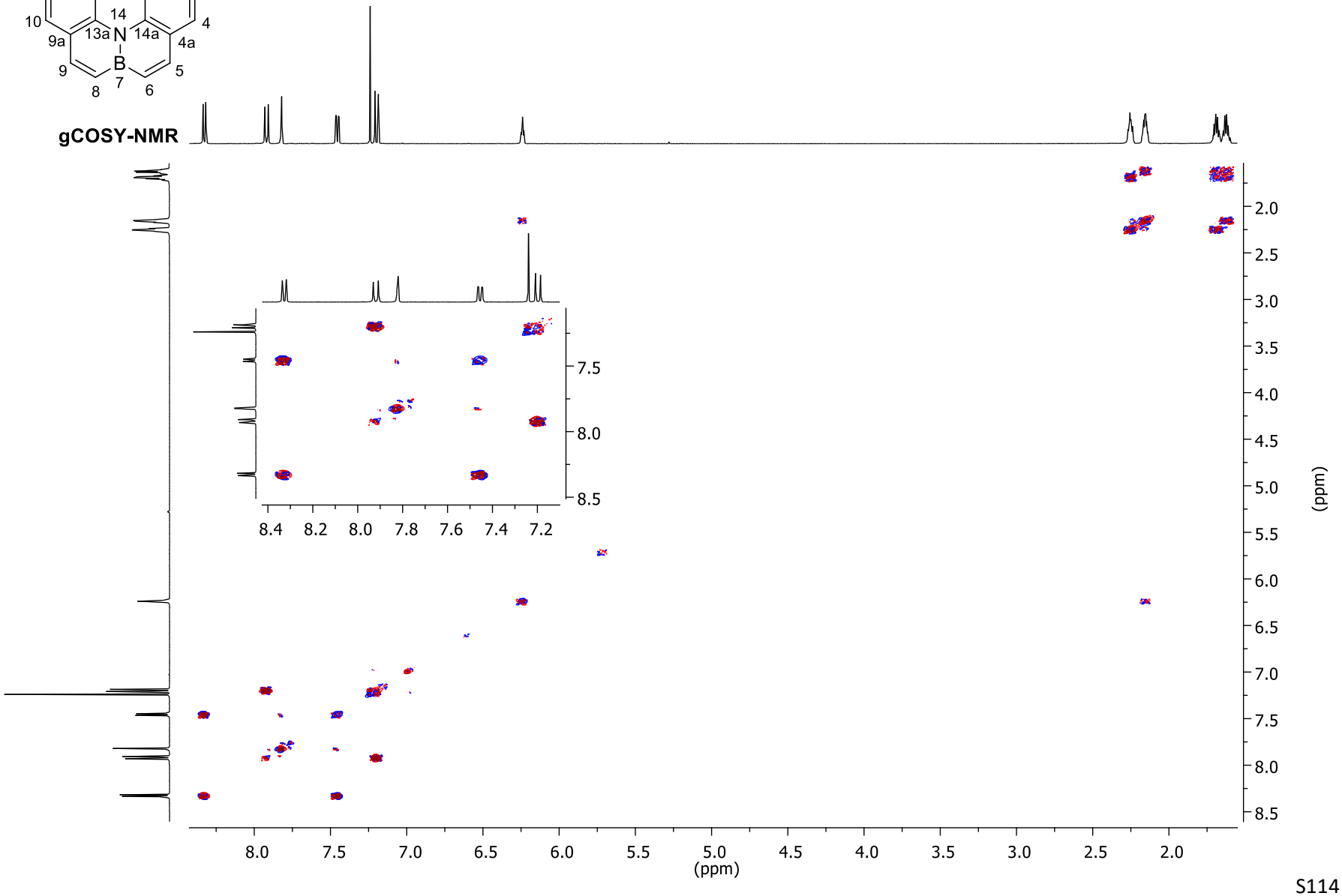


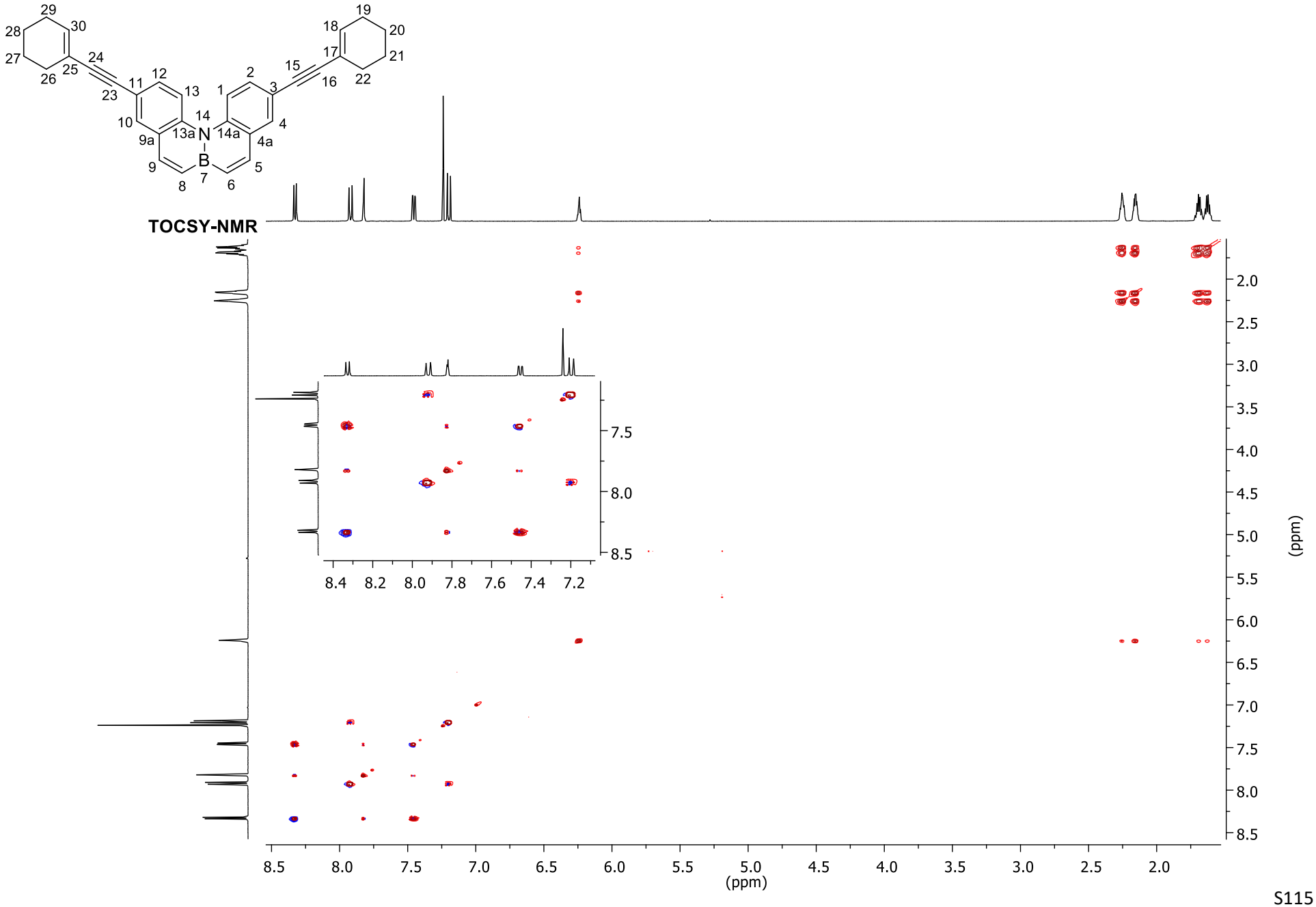
^{11}B-NMR (160 MHz, $CDCl_3$)

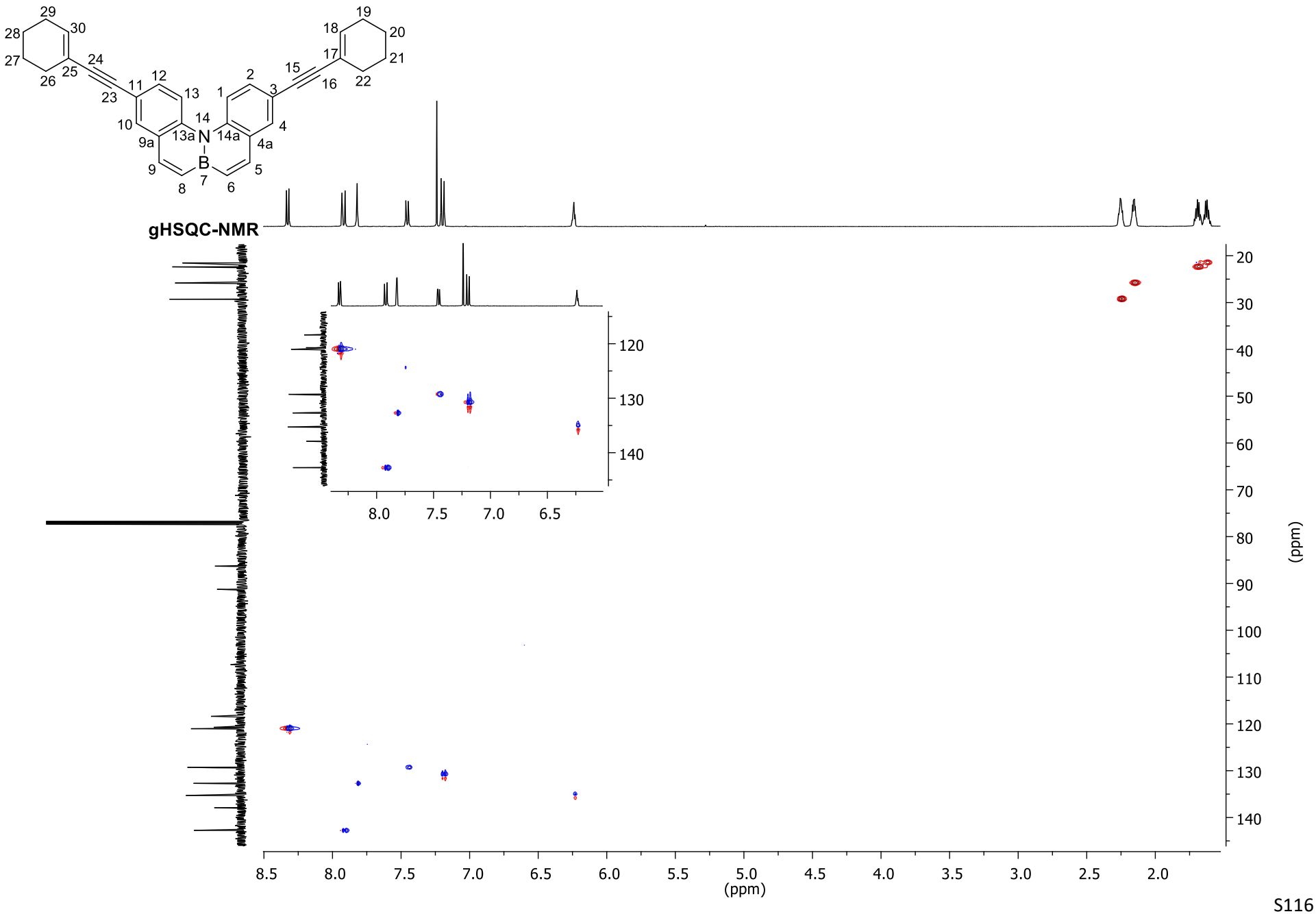


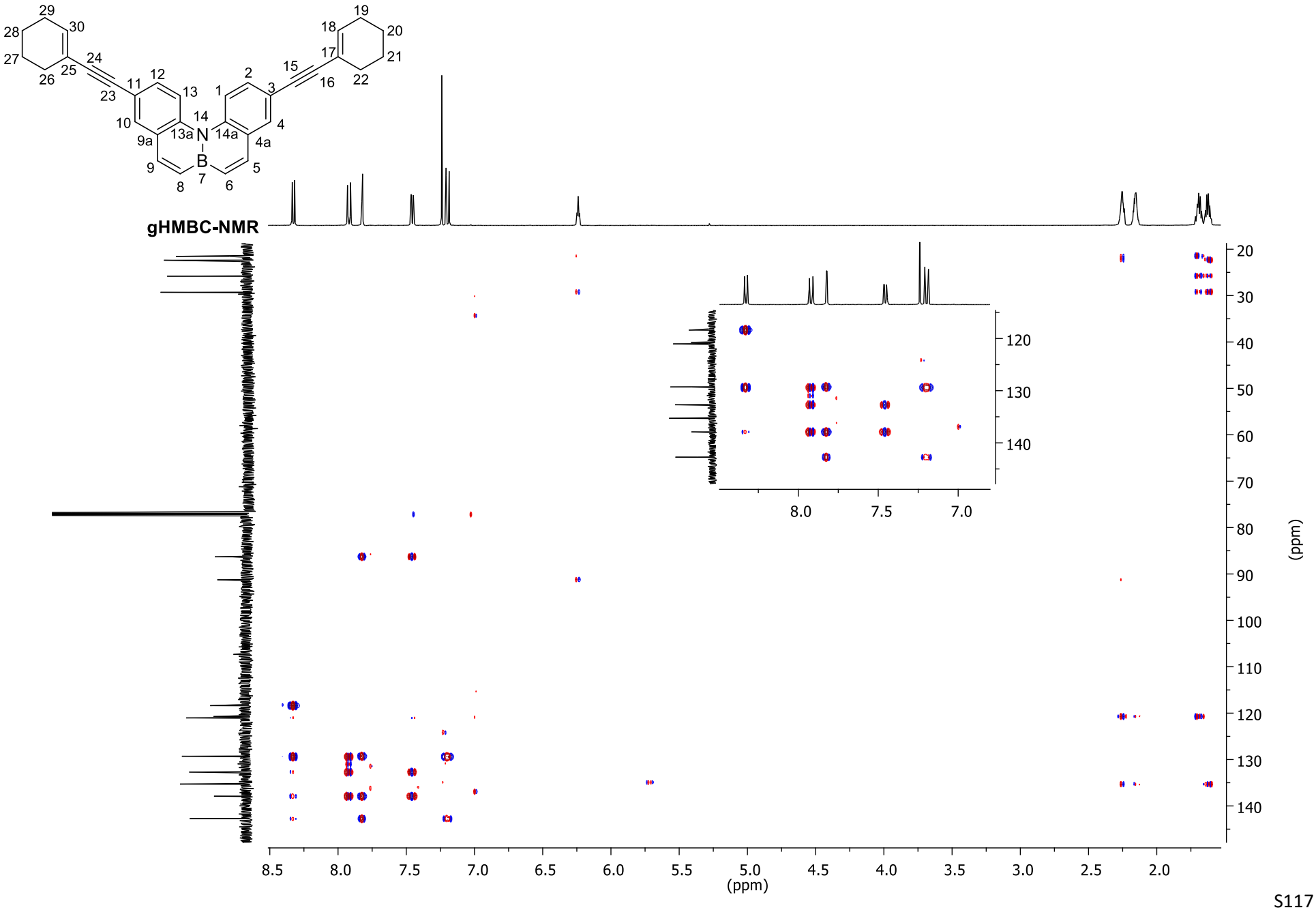

29
28
30
27
24
26
25
23
11
12
13
10
14
9a
13a
N
14a
4a
4
9
B
5
8
7
6
1
2
3
15
16
19
18
20
17
21
22

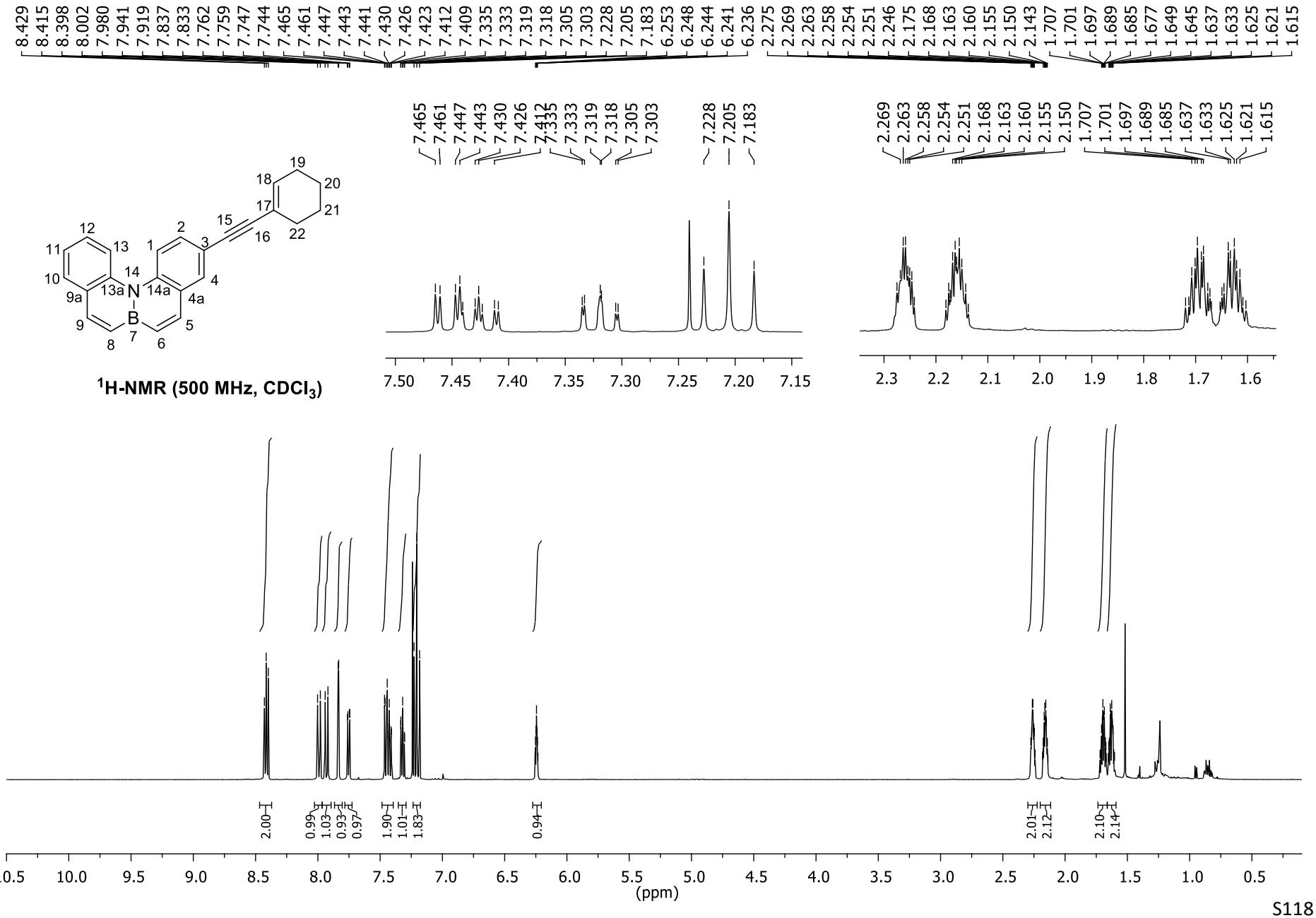
gCOSY-NMR


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)
8.4
8.2
8.0
7.8
7.6
7.4
7.2

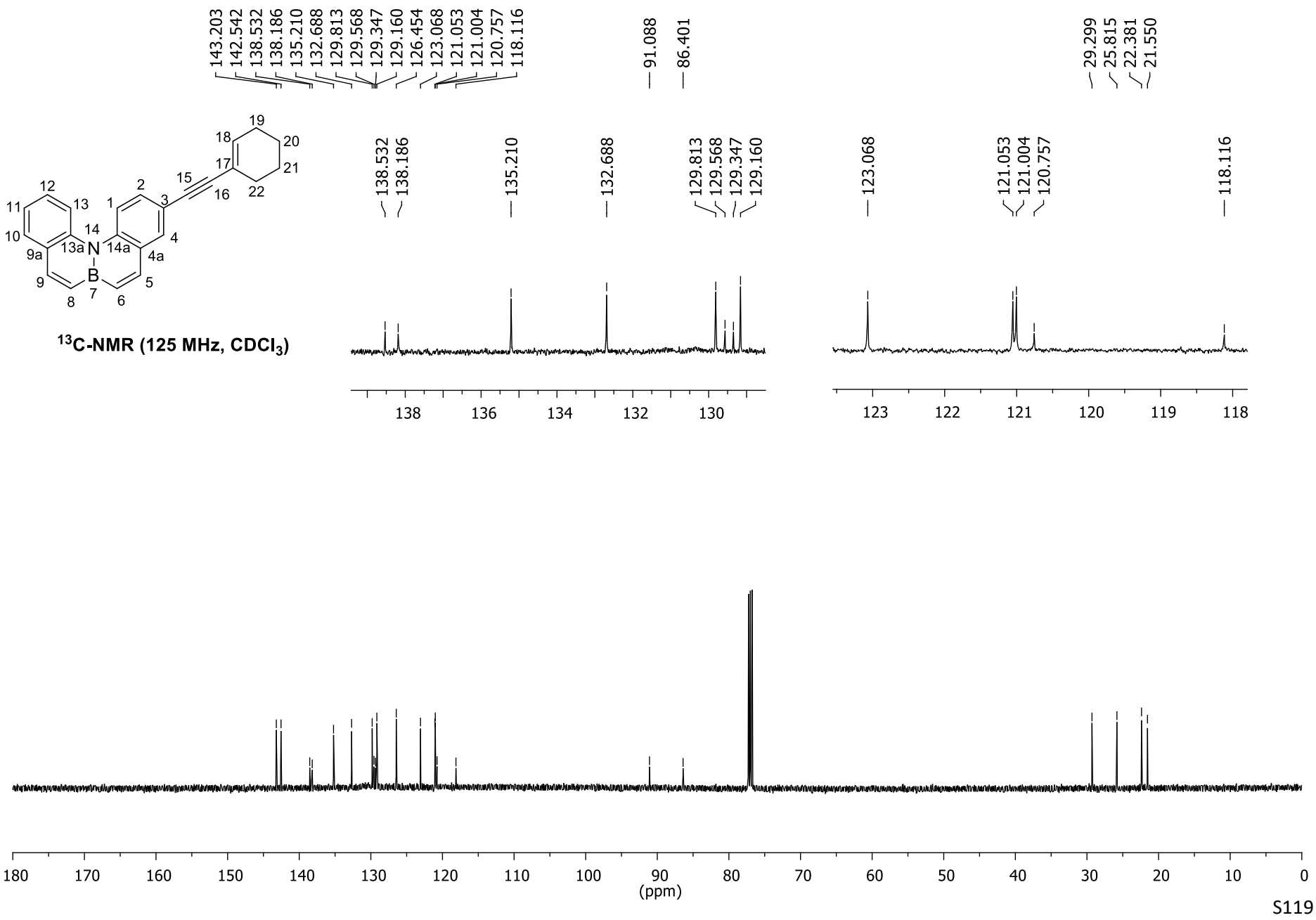

TOCSY-NMR
(ppm)
(ppm)


gHSQC-NMR
(ppm)
(ppm)

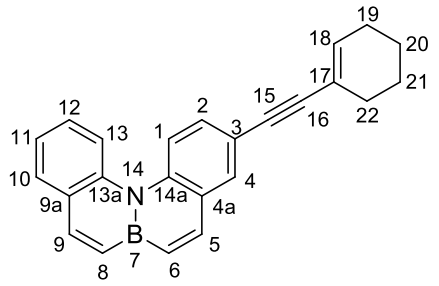

gHMBC-NMR
(ppm)
(ppm)



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

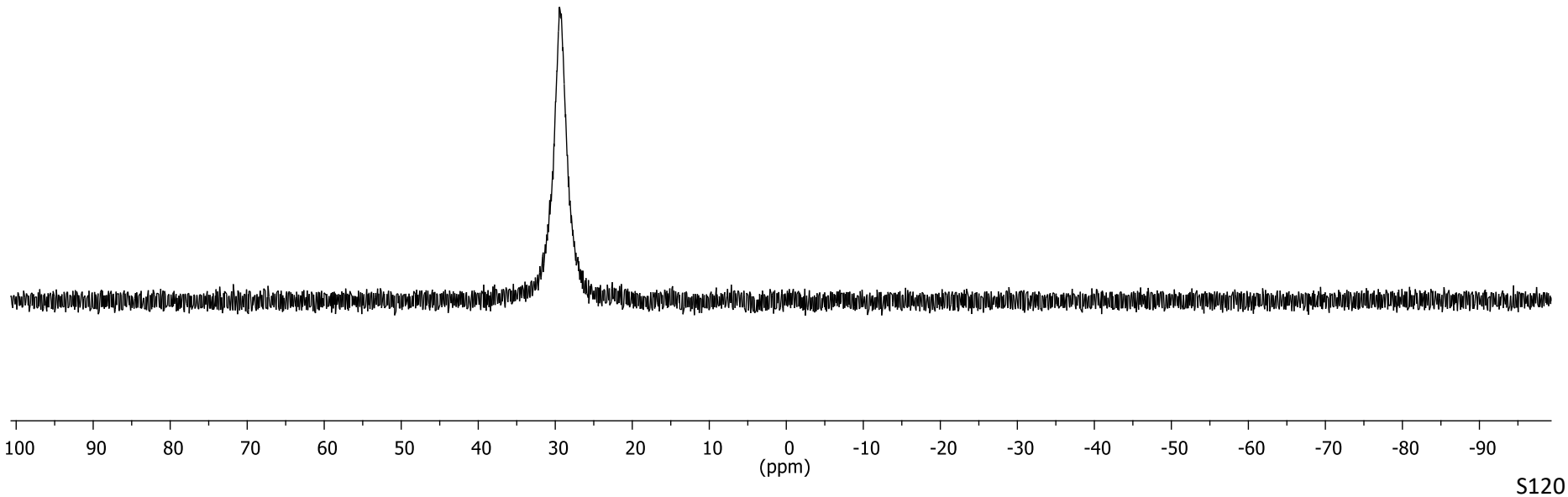


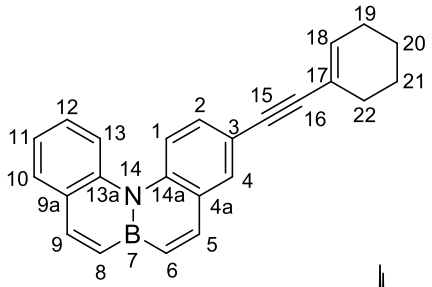
^{13}C-NMR (125 MHz, $CDCl_3$)



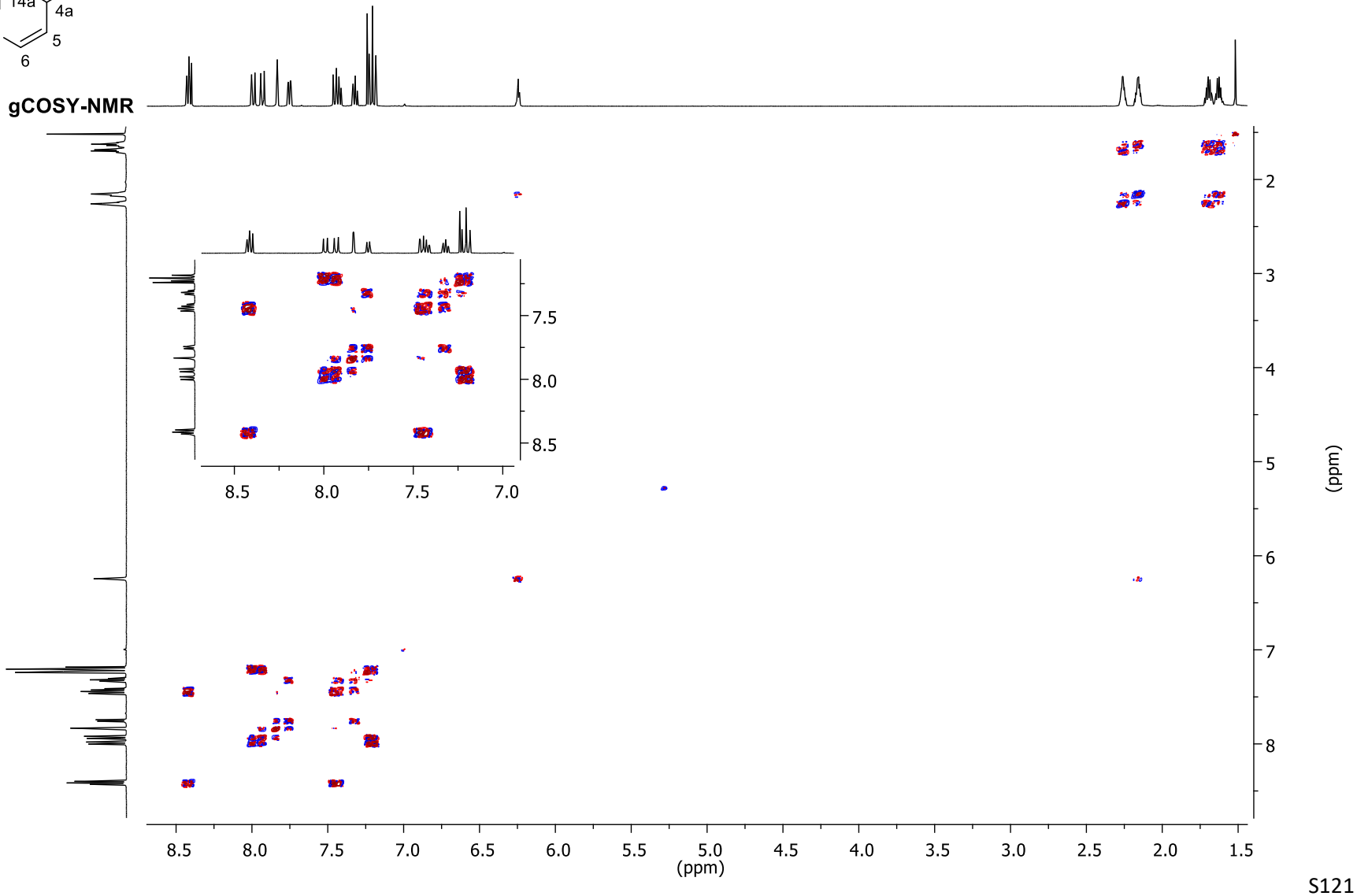
— 29.501

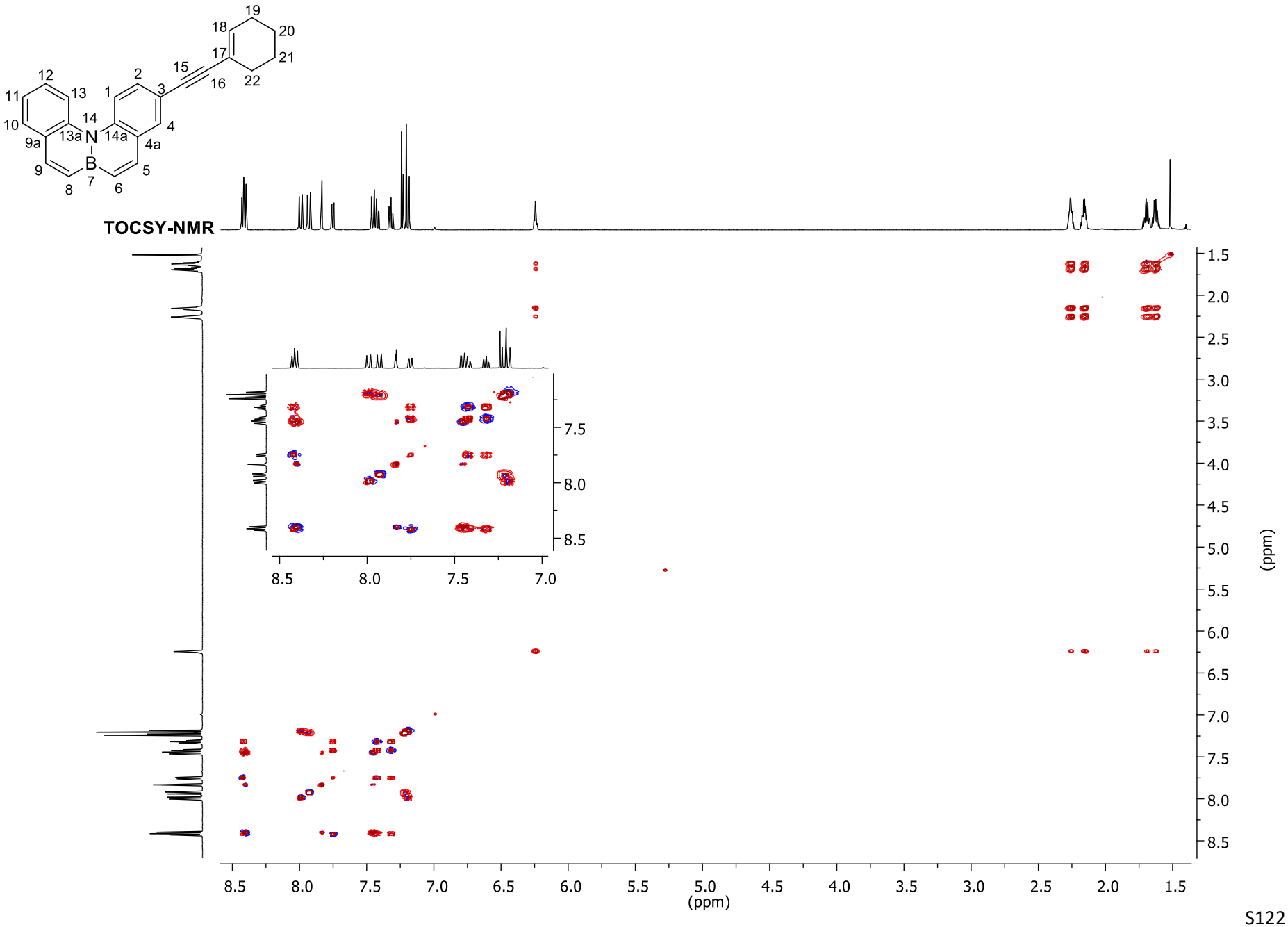
^{11}B-NMR (160 MHz, $CDCl_3$)

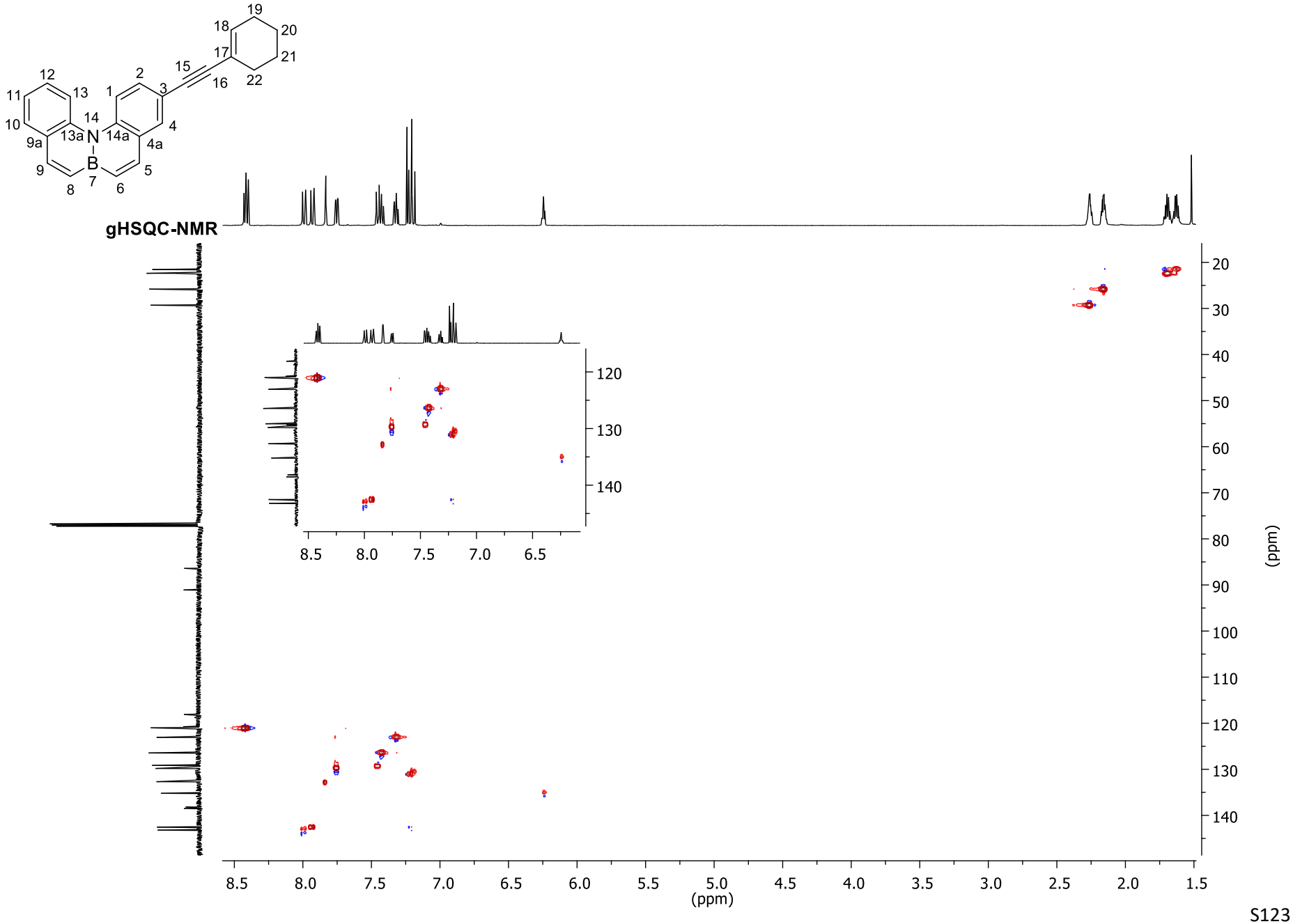


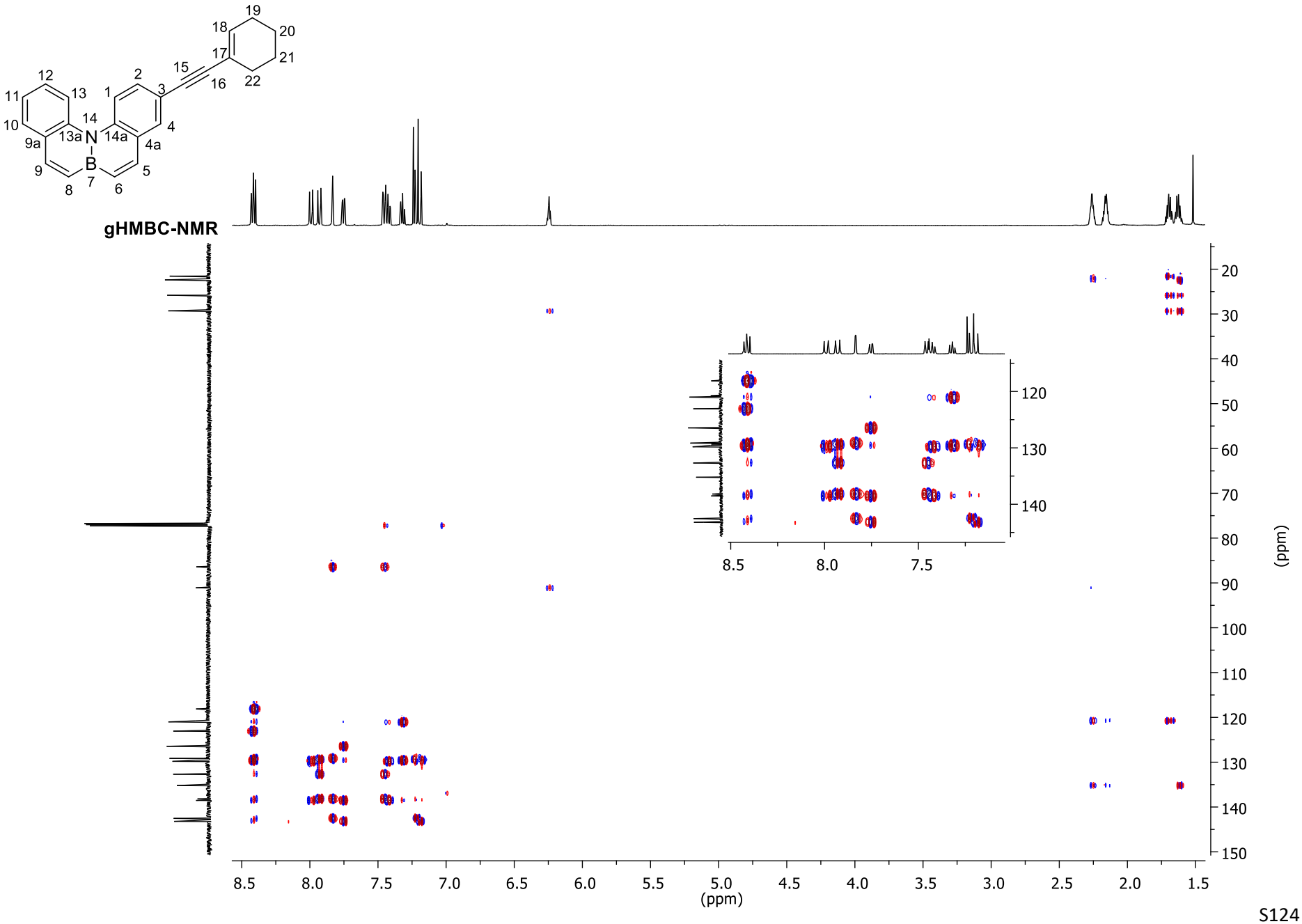

19
18
20
17
21
15
22
16
12
2
1
3
11
13
14
10
4
9a
13a
N
14a
4a
9
B
5
8
7
6

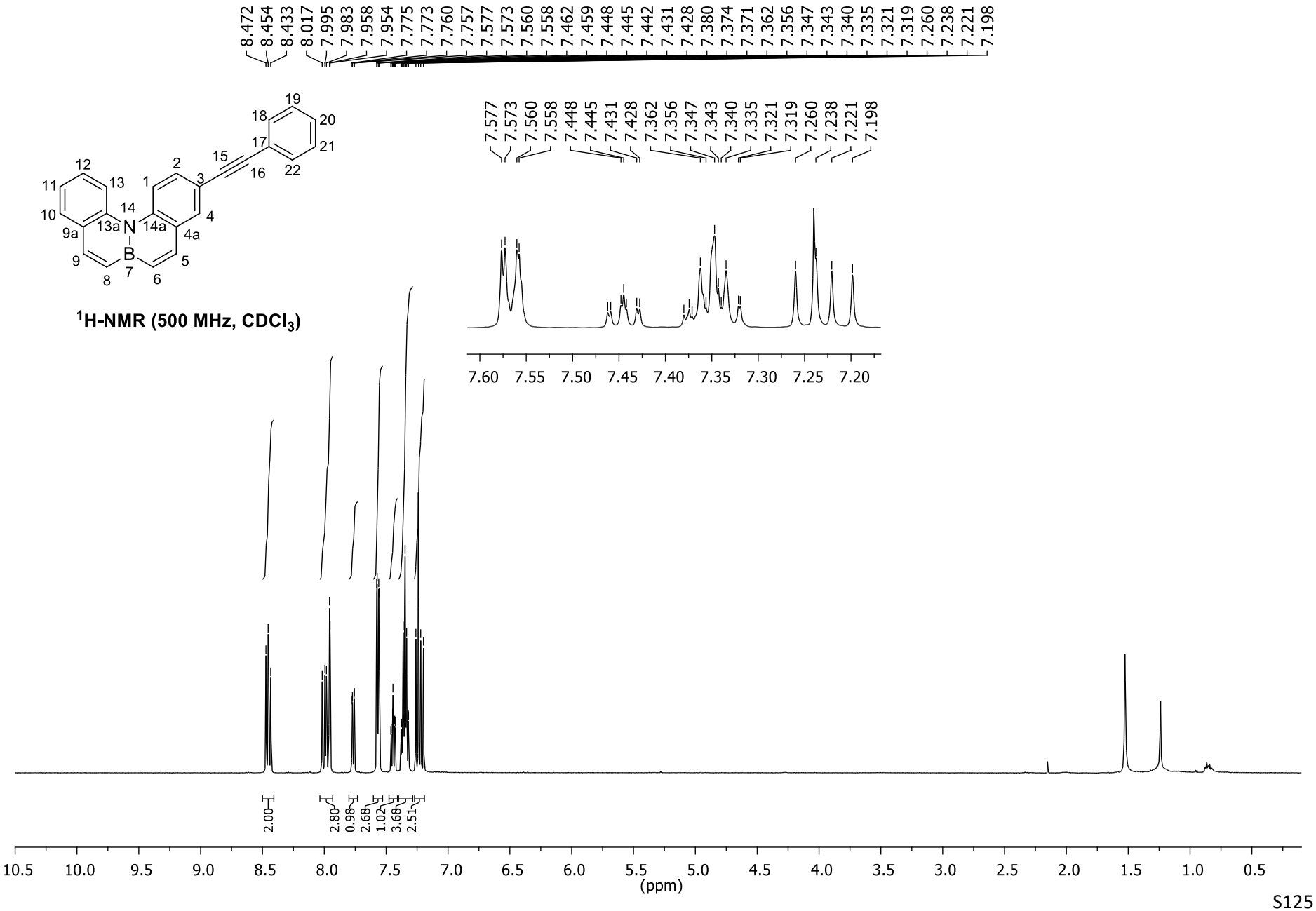
gCOSY-NMR

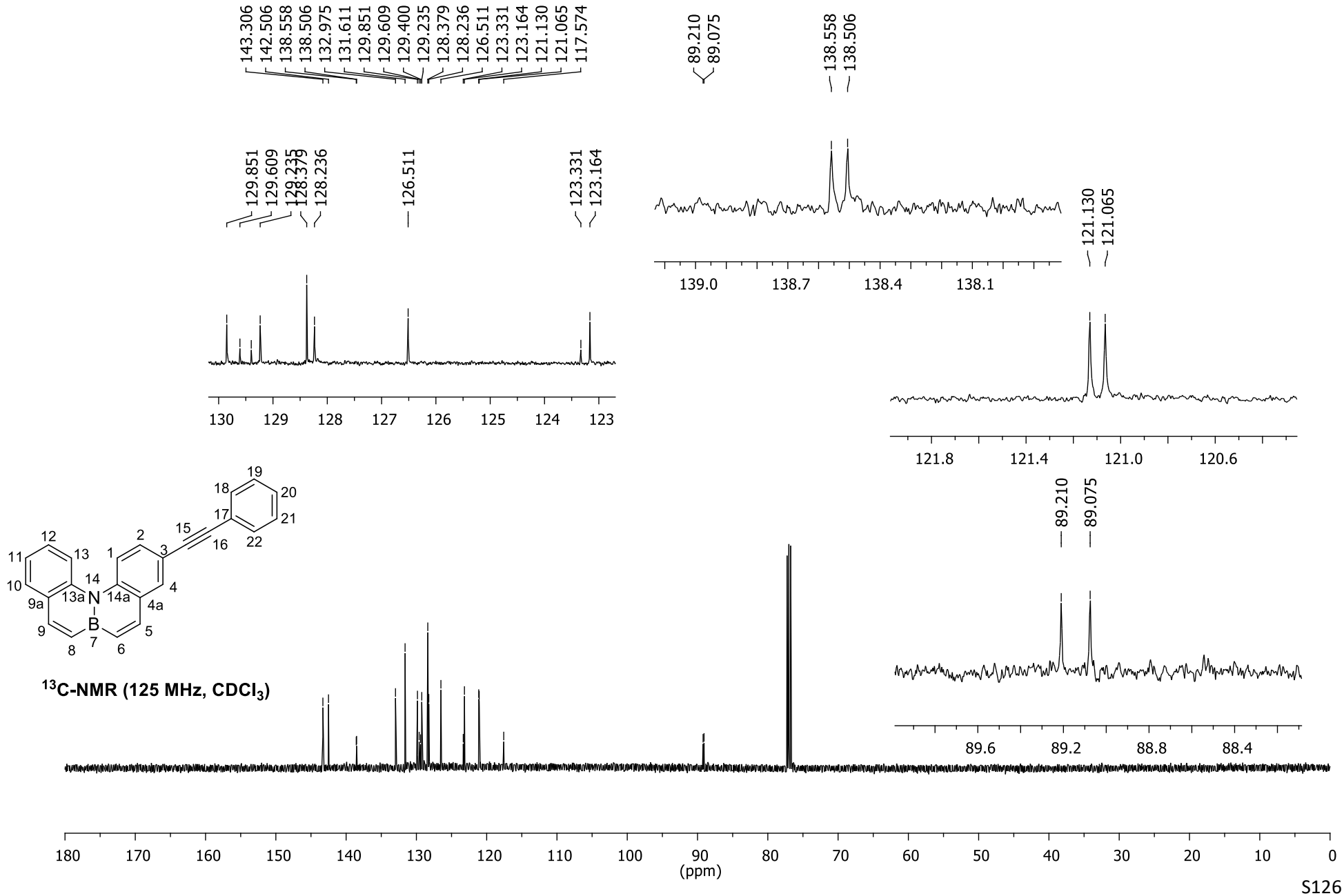

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
(ppm)
2
3
4
5
6
7
8
(ppm)


TOCSY-NMR
(ppm)
(ppm)

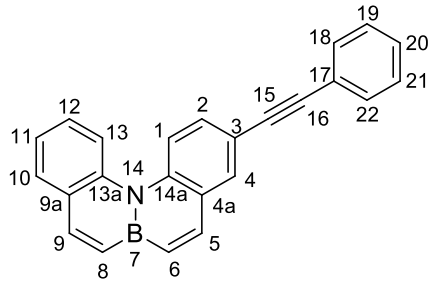

gHSQC-NMR
(ppm)
(ppm)


gHMBC-NMR
(ppm)
(ppm)


8.472
8.454
8.433
8.017
7.995
7.983
7.958
7.954
7.775
7.773
7.760
7.757
7.577
7.573
7.560
7.558
7.462
7.459
7.448
7.445
7.442
7.431
7.428
7.380
7.374
7.371
7.362
7.356
7.347
7.343
7.340
7.335
7.321
7.319
7.260
7.238
7.221
7.198
1H-NMR (500 MHz, CDCl3)
7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20
2.00
2.80
0.98
2.68
1.02
3.68
2.51
10.5 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)

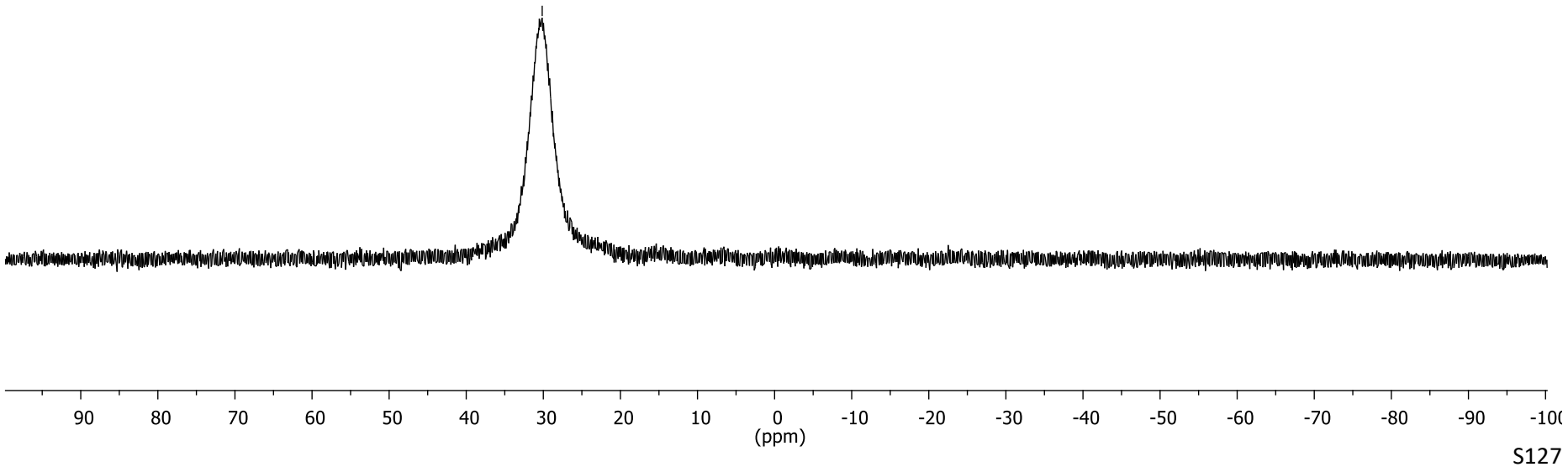


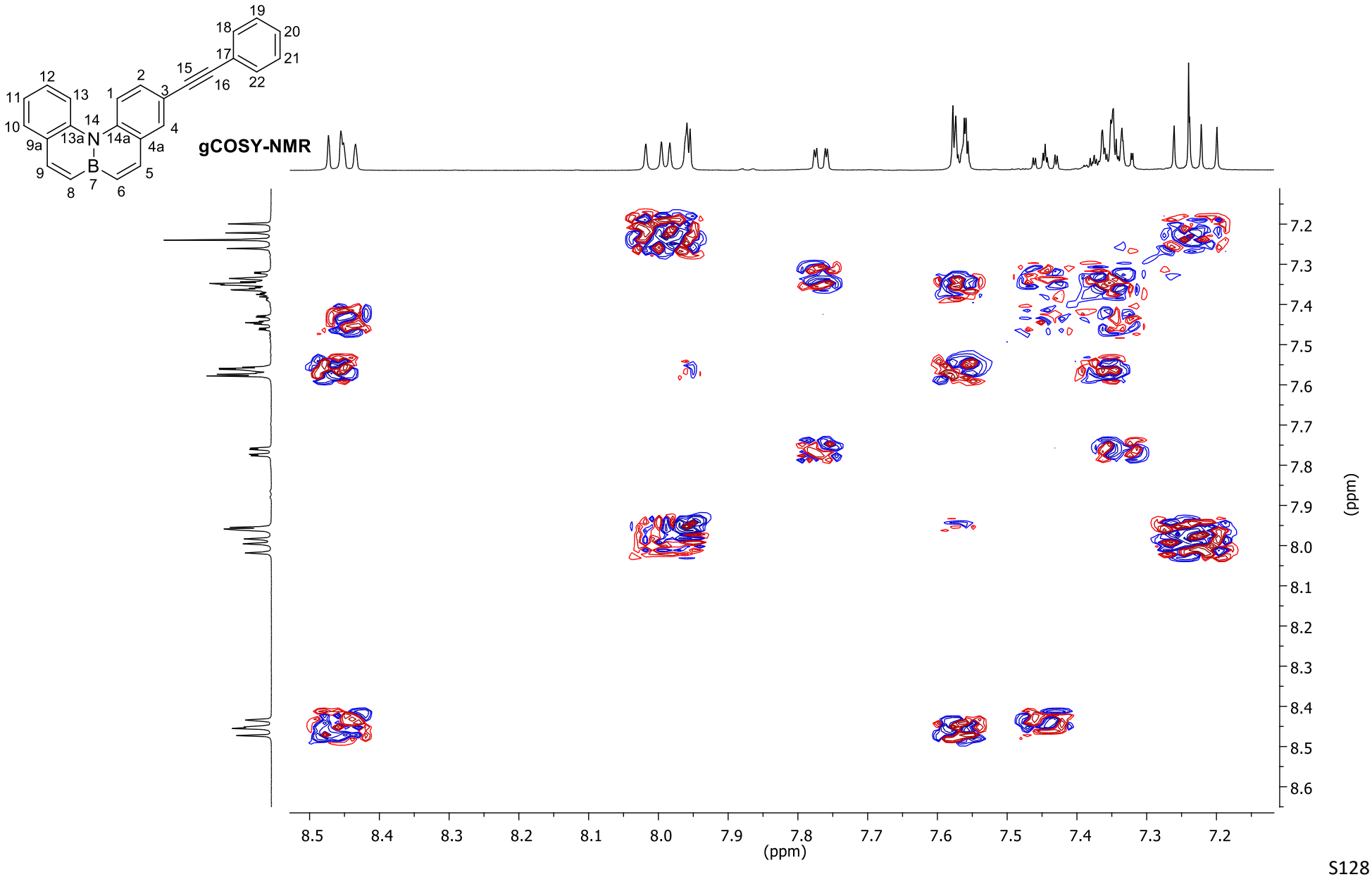
^{13}C-NMR (125 MHz, $CDCl_3$)

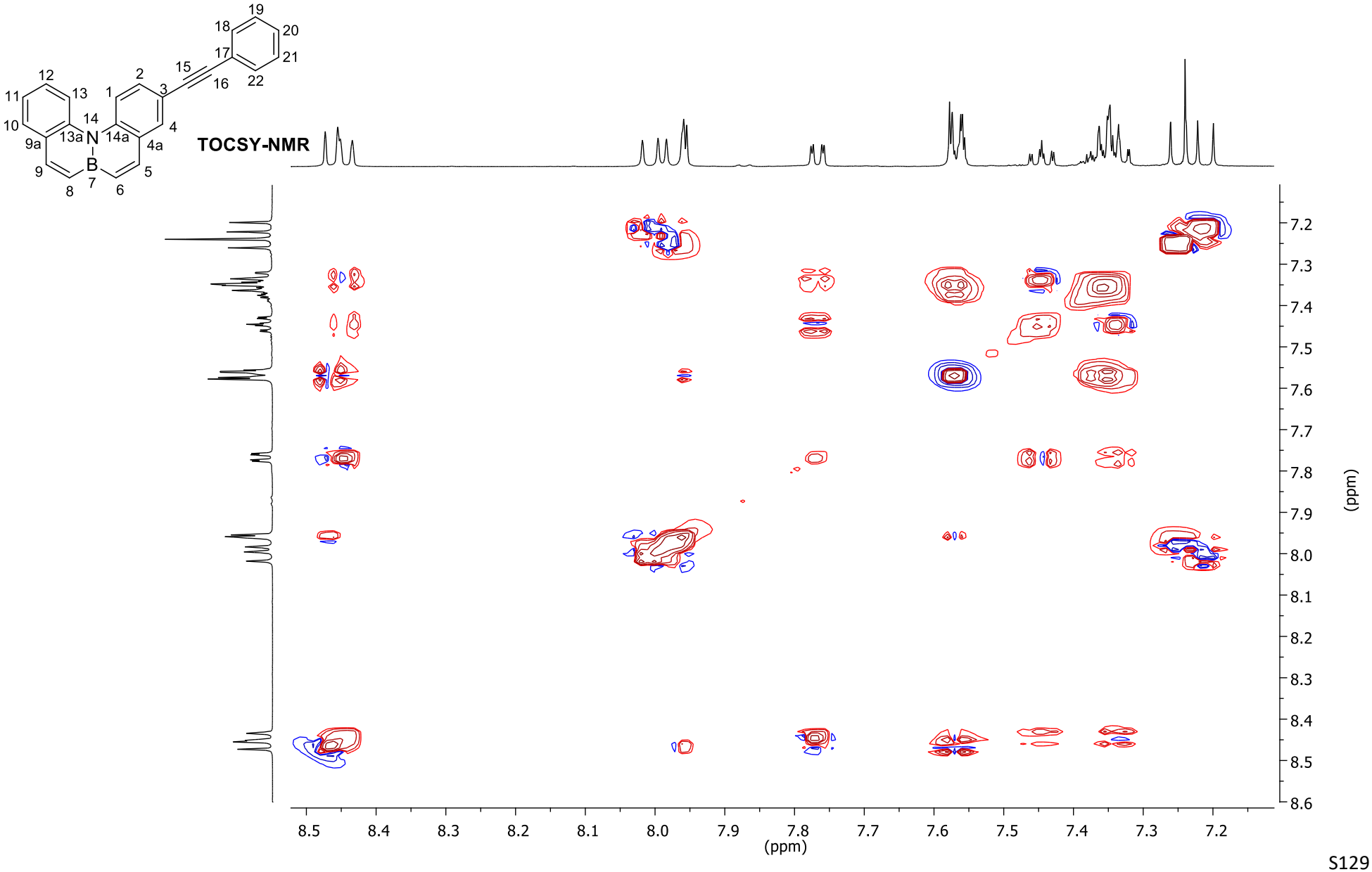


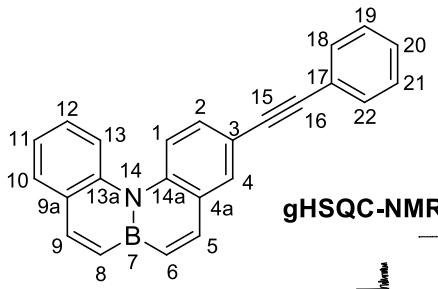
— 30.146

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




gCOSY-NMR
(ppm)
(ppm)


TOCSY-NMR
(ppm)
(ppm)


19
18
20
17
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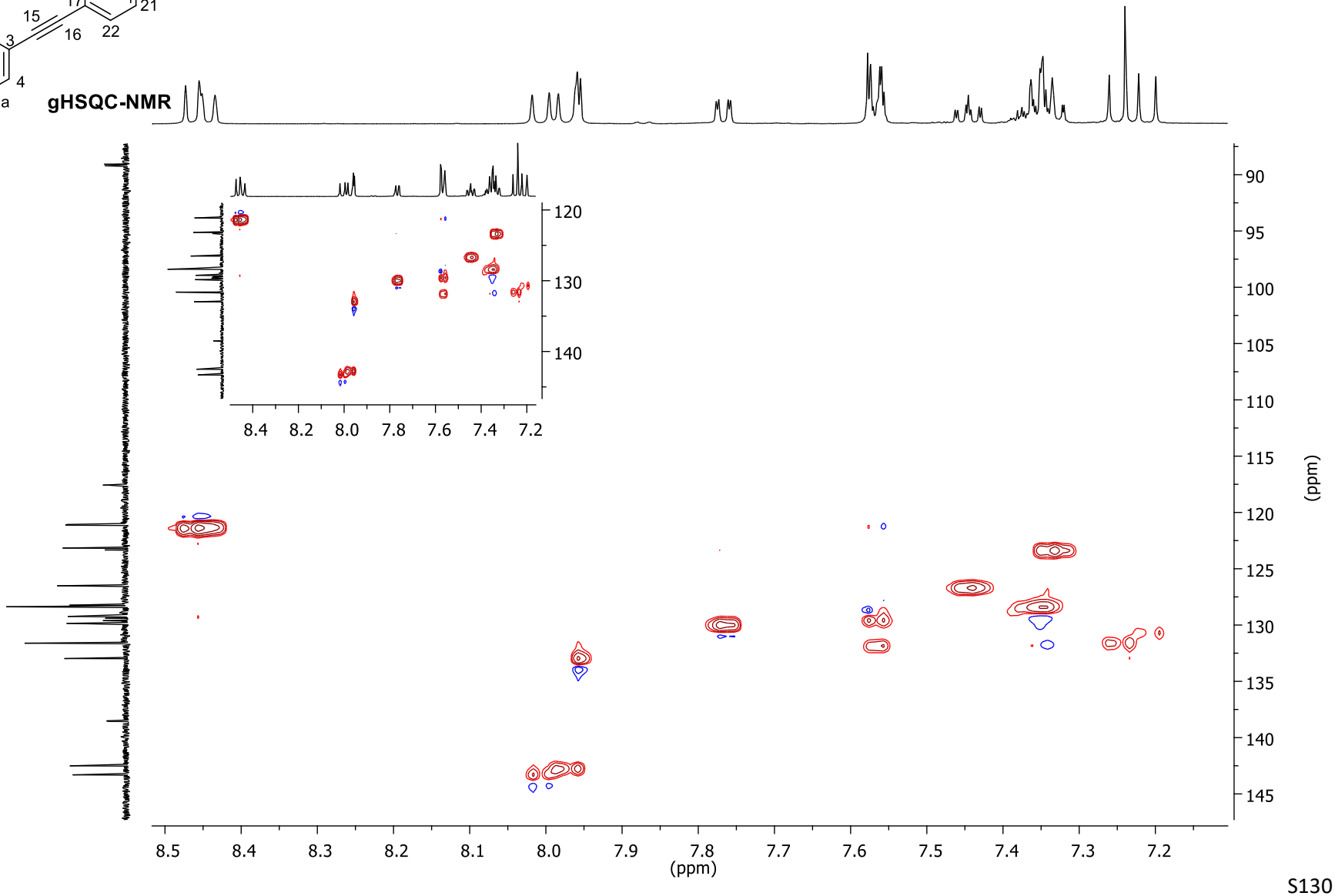
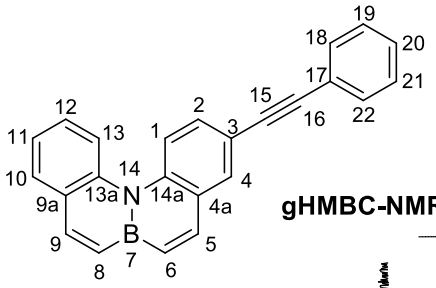
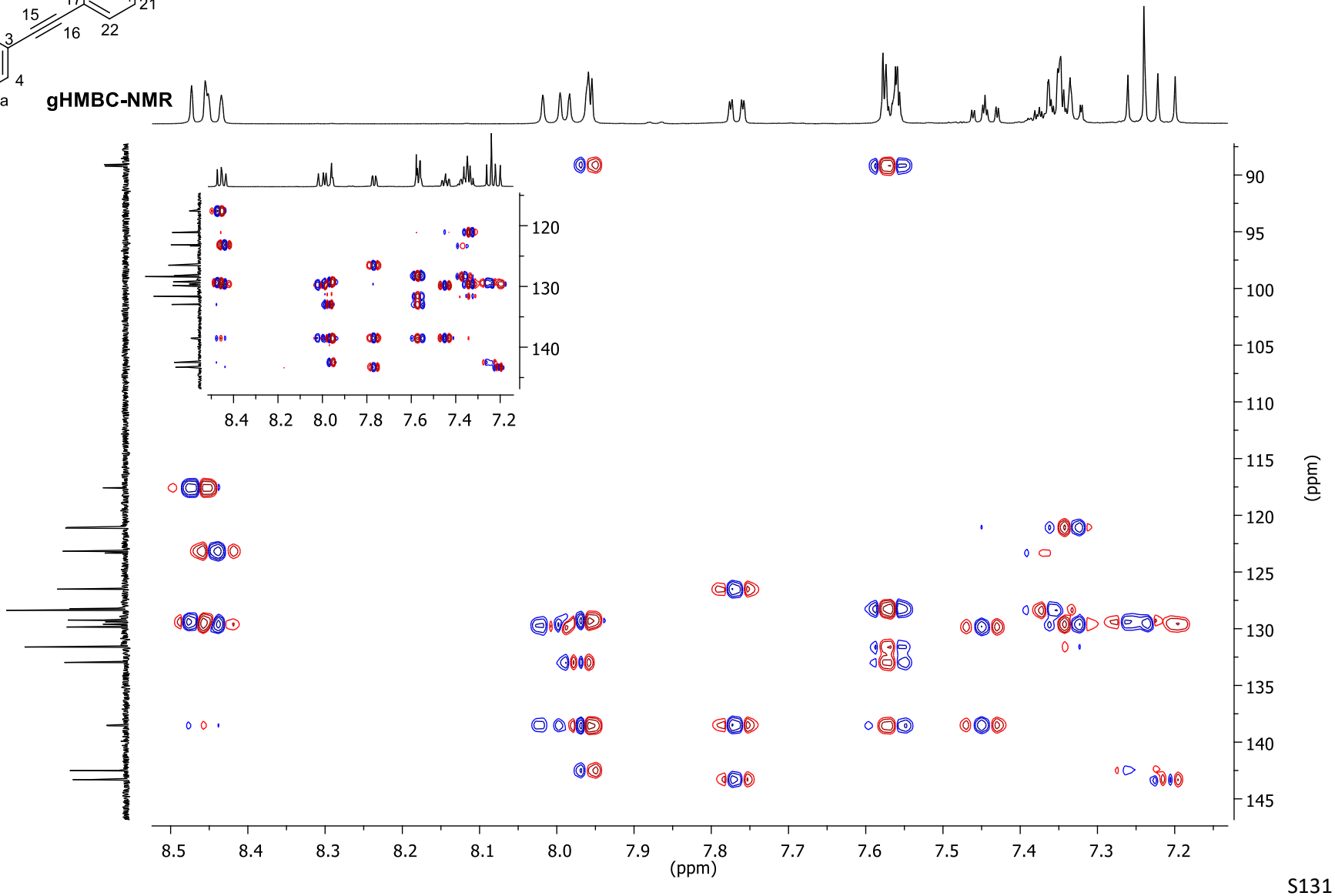
15
22
16
12
2
11
13
1
3
14
10
4
13a
N
14a
9a
4a
B
9
5
7
8
6

gHSQC-NMR


120
130
140
8.4
8.2
8.0
7.8
7.6
7.4
7.2
90
95
100
105
110
115
120
125
130
135
140
145
(ppm)
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
(ppm)


19
18
20
17
21
15
22
16
12
2
11
13
1
3
14
10
4
13a
14a
9a
4a
N
B
9
5
7
8
6

gHMBC-NMR


120
130
140
8.4
8.2
8.0
7.8
7.6
7.4
7.2
90
95
100
105
110
115
120
125
130
135
140
145
(ppm)
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
(ppm)