Electronic Supporting Information for Publication

Studies on the preparation of aminobipyridines and bipyridine sultams via an intramolecular free radical pathway

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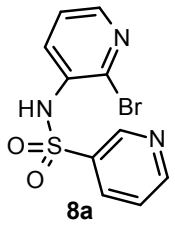
Table of contents

General Information

Reagents of the highest commercial quality were purchased and used without further purification, unless stated otherwise. 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 and ^{13}C NMR spectra were recorded with either a Varian Mercury VX-300, Varian Unity 300, or Varian Unity 500 MHz spectrometer. 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; br, broad. Samples were analyzed by high pressure liquid chromatography (HP 1260 series) coupled to a mass spectrometer Quadrupole (6120 series) from Agilent Tecnhologies. The chromatographic separation was carried out with a Luna C18 column (100 mm x 4,6 mm x 3 µm) (supplied by Phenomenex). LC conditions were: flow rate, 1 mL/min; mobile phases, water containing 0,1 % formic acid (A) and methanol containing 0.1 % formic acid (solvent B); elution gradient: 10−100 % B in 20 minutes, 100−10% for 1 min, and 10% for 5 min in order to re-equilibrate the column at the initial conditions; injected volumen, 5 µL; temperature 50 ºC. High-resolution analyses (HRMS) were performed on an Agilent 6210 time-of-flight LC/MS. Compounds **6a**[12], **6b**[11], **10a,b**[14] and **4cb**[17] have been previously described.

Preparation of compounds 8a–8c, 3ba, **3d and 3e**

***N*-(2-Bromo-3-pyridyl)pyridine-3-sulfonamide 8a**



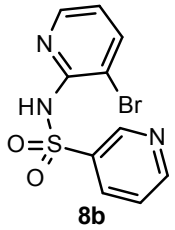
8a

Method C: To a stirred solution of 2-bromopyridin-3-amine **7a** (173 mg, 1 mmol) in pyridine (2 mL), pyridine-3-sulfonyl chloride **6a** (354 mg, 2 mmol) was portionwise added during 15 min, at room temperature. The reaction mixture was heated at reflux for an additional period of 5 h. Then, at room temperature, the reaction mixture was treated with water (10 mL) and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (1:1 EtOAc/ hexanes) to supply **8a** as a white solid (204 mg, 0.65 mmol, 65%). Mp: 164−165 ºC. IR (KBr) υ_{max} (cm^{-1}) 3062, 1581, 1339, 1169, 586. ^{1}H NMR (300 MHz, CD_3OD) δ (ppm) 8.85 (d, J = 2.3 Hz, 1H), 8.78

[12] Birch, M.; Sibley, G. E. M.; Law, D.; Oliver, J. D. *PCT. Int. Appl.,* WO 2009144473 A1, 2009.
[11] Dupont-Passelaigue, E.; Le Roy, I.; Pignier, C. *PCT. Int. Appl*., WO 2012069503 A1, 2012.
[14] (a) S. Blanchard, I. Rodriguez, C. Kuehm-Caubere, P. Renard, B. Pfeiffer, G. Guillaumet and P. Caubere, *Tetrahedron*, 2002, **58**, 3513; (b) G. Abbiati, E.M. Beccalli, G. Broggini, G. Paladino and E. Rossi, *Synthesis*, 2005, 2881.
[17] L. Kaczmarek, *B. Pol. Acad. Sci.-Chem.*, 1985, **33**, 401.

(dd, J = 4.9, 1.6 Hz, 1H), 8.20 (dd, J = 4.7, 1.8 Hz, 1H), 8.11 (ddd, J = 8.1, 2.4, 1.6 Hz, 1H), 7.97 (dd, J = 8.0, 1.8 Hz, 1H), 7.57 (ddd, J = 8.1, 4.9, 0.8 Hz, 1H), 7.45 (dd, J = 8.0, 4.7 Hz, 1H). ^{13}C NMR (75 MHz, CD_3OD) δ (ppm) 154.4, 148.9, 148.6, 140.0, 138.5, 138.0, 136.7, 134.2, 125.6, 125.0. HRMS (ESI-TOF) m/z calcd for $C_{10}H_9{}^{79}BrN_3O_2S$ $[M + H]^+$ 313.9593, found: 313.9591.

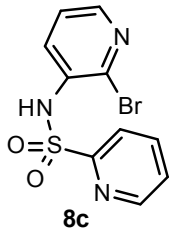
***N*-(3-Bromo-2-pyridyl)pyridine-3-sulfonamide 8b**



8b

Method C: To a stirred solution of 3-bromopyridin-2-amine **7b** (173 mg, 1 mmol) in pyridine (2 mL), pyridine-3-sulfonyl chloride **6a** (354 mg, 2 mmol) was portionwise added during 15 min, at room temperature. The reaction mixture was heated at reflux for an additional period of 5 h. Then, at room temperature, the reaction mixture was treated with water (10 mL) and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (1:1 EtOAc/ hexanes) to supply **8b** as a white solid (132 mg, 0.42 mmol, 42%). Mp: 162−164 ºC. IR (KBr) υ_{max} (cm^{-1}) 3064, 1580, 1445, 1167, 917, 698. ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm) 10.84 (brs, 1H), 9.12 (brs, 1H), 8.79 (brs, 1H), 8.34 (brs, 1H), 8.11 (brs, 2H), 7.62 (brs, 1H), 6.98 (brs, 1H. HPLC-Ms (ES-API) 314.0, 316.0 $[M + H]^+$, t_R 7.829 min (100%). HRMS (ESI-TOF) m/z calcd for $C_{10}H_9{}^{79}BrN_3O_2S$ $[M + H]^+$ 313.9593, found: 313.9588.

***N*-2-Bromo-3-pyridyl)pyridine-2- sulfonamide 8c**

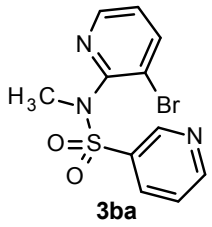


8c

Method C: To a stirred solution of 2-bromopyridin-3-amine **7a** (173 mg, 1 mmol) in pyridine (2 mL), pyridine-2-sulfonyl chloride **6b** (354 mg, 2 mmol) was portionwise added during 15 min, at room temperature. The reaction mixture was heated at reflux for an additional period of 5 h. Then, at room temperature, the reaction mixture was treated with water (10 mL) and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (3:7 EtOAc/ hexanes) to supply **8c** as a white solid (194 mg, 0.62 mmol, 62%). Mp: 129−131 ºC. IR (KBr) υ_{max} (cm^{-1}) 3060, 1447, 1181, 593. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.68 (d, J = 4.7 Hz, 1H), 8.16 – 8.05 (m, 2H), 7.98 – 7.86 (m, 2H), 7.51 (ddd, J = 7.5, 4.7, 1.3 Hz, 1H), 7.29 (brs, 1H), 7.23 (dd, J = 8.0, 4.6 Hz,

1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 156.3, 150.6, 145.4, 142.1, 138.3, 131.1, 130.2, 127.6, 123.4, 122.5. HRMS (ESI-TOF) m/z calcd for $C_{10}H_9{}^{79}BrN_3O_2S$ $[M + H]^+$ 313.9593, found: 313.9587.

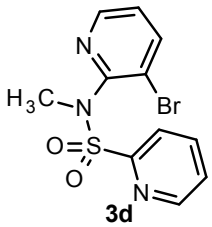
***N*-(3-Bromo-2-pyridyl)-*N*-methyl-pyridine-3-sulfonamide 3ba**



3ba

Method C: To a stirred solution of 3-bromo-*N*-methyl-pyridin-2-amine **10a** (187 mg, 1 mmol) in pyridine (2 mL), pyridine-3-sulfonyl chloride **6a** (355 mg, 2 mmol) was portionwise added during 15 min, at room temperature. The reaction mixture was heated at reflux for an additional period of 5 h. Then, at room temperature, the reaction mixture was treated with a saturated $NaHCO_3$ solution (10 mL) and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (7:3 EtOAc/ hexanes) to supply **3ba** as a white solid (192 mg, 0.58 mmol, 58%). Mp: 106−111 ºC. IR (KBr) υ_{max} (cm^{-1}) 3060, 1575, 1409, 1163, 752, 603. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.09 (d, *J* = 1.7 Hz, 1H), 8.84 (dd, *J* = 4.8, 1.7 Hz, 1H), 8.34 (dd, *J* = 4.6, 1.7 Hz, 1H), 8.20 (ddd, *J* = 8.0, 2.2, 1.7 Hz, 1H), 8.05 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.50 (dd, *J* = 8.1, 4.9 Hz, 1H), 7.19 (dd, *J* = 8.0, 4.6 Hz, 1H), 3.15 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 153.1, 152.4, 149.4, 147.8, 143.1, 136.7, 135.1, 125.1, 123.7, 121.7, 37.1. HRMS (ESI-TOF) m/z calcd for $C_{11}H_{11}{}^{79}BrN_3O_2S$ $[M + H]^+$ 327.9750, found: 327.9751.

***N*-(3-Bromo-2-pyridyl)-*N*-methyl-pyridine-2-sulfonamide 3d**

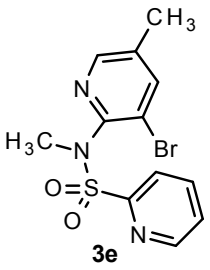


3d

Method C: To a stirred solution of 3-bromo-*N*-methyl-pyridin-2-amine **10a** (187 mg, 1 mmol) in pyridine (2 mL), pyridine-2-sulfonyl chloride **6b** (354 mg, 2 mmol) was portionwise added during 15 min, at room temperature. The reaction mixture was heated at reflux for an additional period of 5 h. Then, at room temperature, the reaction mixture was treated with a saturated $NaHCO_3$ solution (10 mL) and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (7:3 EtOAc/ hexanes) to supply **3d** as a white solid (203 mg, 0.62 mmol, 62%). Mp: 121−123 ºC. IR (KBr) υ_{max} (cm^{-1}) 3035, 1567, 1354, 1172, 607, 569. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.77 (d, *J* = 4.5 Hz, 1H), 8.21 (dd, *J* = 4.6, 1.7 Hz, 1H), 7.99 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.93 – 7.84 (m, 2H), 7.52 (ddd,

J = 6.7, 4.7, 2.2 Hz, 1H), 7.12 (dd, *J* = 8.0, 4.6 Hz, 1H), 3.43 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 157.3, 152.5, 149.9, 147.6, 142.9, 137.8, 126.8, 124.8, 123.3, 121.1, 38.3. HRMS (ESI-TOF) m/z calcd for $C_{11}H_{11}{}^{79}BrN_3O_2S$ $[M + H]^+$ 327.9749, found: 327.9746.

***N*-(3-Bromo-5-methyl-2-pyridyl)-*N*-methyl-pyridine-2-sulfonamide 3e**

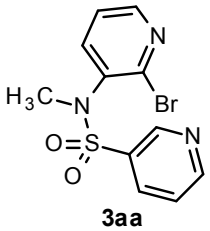


3e

Method C: To a stirred solution of 3-bromo-N,5-dimethyl-pyridin-2-amine **10b** (201 mg, 1 mmol) in pyridine (2 mL), pyridine-2-sulfonyl chloride **6b** (354 mg, 2 mmol) was portionwise added during 15 min, at room temperature. The reaction mixture was heated at reflux for an additional period of 5 h. Then, at room temperature, the reaction mixture was treated with a saturated $NaHCO_3$ solution (10 mL) and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (6:4 EtOAc/ hexanes) to supply **3e** as a white solid (318 mg, 0.93 mmol, 93%). Mp: 114−116 ºC. IR (KBr) υ_{max} (cm^{-1}) 3060, 1576, 1557, 1353, 1169, 743, 584. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.76 (dd, *J* = 4.7, 1.6 Hz, 1H), 8.02 (dd, *J* = 2.1, 0.7 Hz, 1H), 7.91−7.83 (m, 2H), 7.81 (dd, *J* = 2.1, 0.7 Hz, 1H), 7.50 (ddd, *J* = 6.7, 4.7, 2.1 Hz, 1H), 3.39 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 157.5, 150.1, 149.9, 148.1, 143.1, 137.7, 135.3, 126.7, 123.3, 120.7, 38.3, 17.7. HRMS (ESI-TOF) m/z calcd for $C_{12}H_{13}{}^{79}BrN_3O_2S$ $[M + H]^+$ 341.9905, found: 341.9894.

Preparation of compounds 3aa, 3ab, 3bb, 3ca and 3cb

***N*-(2-Bromo-3-pyridyl)-*N*-methyl- pyridine-3-sulfonamide 3aa**

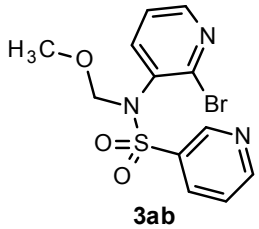


3aa

To a stirred solution of *N*-(2-bromo-3-pyridyl)pyridine-3-sulfonamide **8a** (314 mg, 1 mmol) in dry DMF (3 mL) and at 0 ºC, NaH 60% (48 mg, 1.2 mmol) was added. The reaction mixture was stirred for 20 min at the same temperature and methyl iodide (156 mg, 1.1 mmol, 68 µL) was added. The reaction mixture was stirred at the same temperature for 30 additional min and then at room temperature for 5h. The reaction mixture was treated with a saturated $NaHCO_3$ solution (10 mL) and extracted with EtOAc. The combined

organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (6:4 EtOAc/ hexanes) to supply **3aa** as a white solid (213 mg, 0.65 mmol, 65%). Mp: 82−84 ºC. IR (KBr) υ_{max} (cm^{-1}) 3063, 1561, 1350, 1163, 1040, 757, 568. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.02 (d, *J* = 2.3 Hz, 1H), 8.85 (dd, *J* = 4.9, 1.6 Hz, 1H), 8.37 (dd, *J* = 4.7, 1.8 Hz, 1H), 8.04 (ddd, *J* = 8.1, 2.4, 1.7 Hz, 1H), 7.76 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.48 (ddd, *J* = 8.0, 4.9, 0.8 Hz, 1H), 7.35 (dd, *J* = 7.8, 4.6 Hz, 1H), 3.31 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 153.7, 149.8, 148.4, 143.1, 140.5, 137.0, 135.7, 135.2, 123.8, 123.4, 38.0. HRMS (ESI-TOF) m/z calcd for $C_{11}H_{11}{}^{79}BrN_3O_2S$ $[M + H]^+$ 327.9749, found: 327.9749.

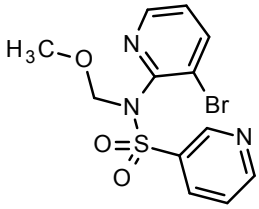
***N*-(2-Bromo-3-pyridyl)-*N*-(methoxymethyl)pyridine-3-sulfonamide 3ab**



3ab

To a stirred solution of *N*-(2-bromo-3-pyridyl)pyridine-3-sulfonamide **8a** (314 mg, 1 mmol) in dry DMF (3 mL) and at 0 ºC, NaH 60% (48 mg, 1.2 mmol) was added. The reaction mixture was stirred for 20 min at the same temperature and methoxymethyl chloride (89 mg, 1.1 mmol, 84 µL) was added. The reaction mixture was stirred at the same temperature for 30 additional min and then at room temperature for 5h. The reaction mixture was treated with a saturated $NaHCO_3$ solution (10 mL) and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (4:6 EtOAc/ CH_2Cl_2) to supply **3ab** as a yellow solid (295 mg, 0.82 mmol, 82%). Mp: 82−84 ºC. IR (KBr) υ_{max} (cm^{-1}) 3052, 1573, 1402, 1175, 1052, 743. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.92 (d, *J* = 2.2 Hz, 1H), 8.81 (dd, *J* = 4.8, 1.4 Hz, 1H), 8.37 (dd, *J* = 4.7, 1.8 Hz, 1H), 7.95 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.73 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.42 (dd, *J* = 8.0, 4.9 Hz, 1H), 7.34 (dd, *J* = 7.8, 4.7 Hz, 1H), 5.32 (brs, 1H), 4.83 (brs, 1H), 3.47 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 153.7, 150.2, 148.6, 143.8, 142.4, 136.2, 135.3, 133.7, 123.6, 123.3, 81.9, 56.5. HRMS (ESI-TOF) m/z calcd for $C_{12}H_{13}{}^{79}BrN_3O_3S$ $[M + H]^+$ 357.9856, found: 357.9851.

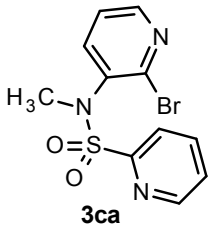
***N*-(3-Bromo-2-pyridyl)-*N*-(methoxymethyl)pyridine-3-sulfonamide 3bb**



3bb

To a stirred solution of *N*-(3-bromo-2-pyridyl)pyridine-3-sulfonamide **8b** (314 mg, 1 mmol) in dry DMF (3 mL) and at 0 ºC, NaH 60% (48 mg, 1.2 mmol) was added. The reaction mixture was stirred for 20 min at the same temperature and methoxymethyl chloride (89 mg, 1.1 mmol, 84 µL) was added. The reaction mixture was stirred at the same temperature for 30 additional min and then at room temperature for 5h. The reaction mixture was treated with a saturated $NaHCO_3$ solution (10 mL) and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (7:3 EtOAc/ hexanes) to supply **3bb** as a white solid (291 mg, 0.81 mmol, 81%). Mp: 102−103 ºC. IR (KBr) υ_{max} (cm^{-1}) 3066, 1428, 1354, 1175, 1014, 621. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 9.10 (d, *J* = 2.2 Hz, 1H), 8.81 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.38 (dd, *J* = 4.6, 1.6 Hz, 1H), 8.22 (ddd, *J* = 8.1, 2.3, 1.7 Hz, 1H), 8.05 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.46 (ddd, *J* = 8.1, 4.9, 0.7 Hz, 1H), 7.21 (dd, *J* = 7.9, 4.6 Hz, 1H), 5.05 (s, 2H), 3.32 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 153.4, 151.1, 149.3, 147.9, 143.2, 137.4, 136.0, 125.3, 123.5, 122.5, 82.7, 57.0. HRMS (ESI-TOF) m/z calcd for $C_{12}H_{13}{}^{79}BrN_3O_3S$ $[M + H]^+$ 357.9856, found: 357.9849.

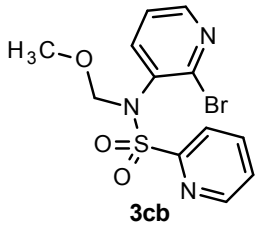
***N*-(2-Bromo-3-pyridyl)-*N*-methyl-pyridine-2-sulfonamide 3ca**



3ca

To a stirred solution of *N*-2-bromo-3-pyridyl)pyridine-2-sulfonamide **8c** (314 mg, 1 mmol) in dry DMF (3 mL) and at 0 ºC, NaH 60% (48 mg, 1.2 mmol) was added. The reaction mixture was stirred for 20 min at the same temperature and methyl iodide (156 mg, 1.1 mmol, 68 µL) was added. The reaction mixture was stirred at the same temperature for 30 additional min and then at room temperature for 5h. The reaction mixture was treated with a saturated $NaHCO_3$ solution (10 mL) and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (4:6 EtOAc/ hexanes) to supply **3ca** as a white solid (298 mg, 0.90 mmol, 90%). Mp: 80−84 ºC. IR (KBr) υ_{max} (cm^{-1}) 3037, 1558, 1399, 1355, 1111, 742, 571. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.76 (d, *J* = 4.7 Hz, 1H), 8.32 (dd, *J* = 4.7, 1.8 Hz, 1H), 7.93−7.89 (m, 2H), 7.87 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.54 (ddd, *J* = 6.2, 4.7, 2.6 Hz, 1H), 7.30 (dd, *J* = 7.9, 4.7 Hz, 1H), 3.38 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 157.2, 150.3, 149.5, 144.0, 140.3, 138.3, 137.9, 127.2, 123.5, 123.0, 39.0. HRMS (ESI-TOF) m/z calcd for $C_{11}H_{11}{}^{79}BrN_3O_2S$ $[M + H]^+$ 327.9749, found: 327.9746.

***N*-(2-Bromo-3-pyridyl)-*N*-(methoxymethyl)pyridine-2-sulfonamide 3cb**

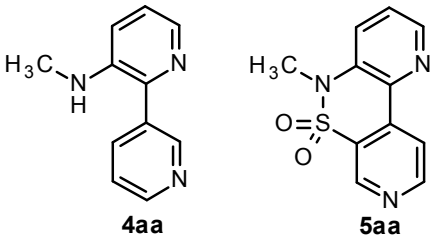


3cb

To a stirred solution of *N*-(2-bromo-3-pyridyl)pyridine-2-sulfonamide **8c** (314 mg, 1 mmol) in dry DMF (3 mL) and at 0 ºC, NaH 60% (48 mg, 1.2 mmol) was added. The reaction mixture was stirred for 20 min at the same temperature and methoxymethyl chloride (89 mg, 1.1 mmol, 84 µL) was added. The reaction mixture was stirred at the same temperature for 30 additional min and then at room temperature for 5h. The reaction was treated with a saturated $NaHCO_3$ solution (10 mL) and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (4:6 EtOAc/ hexanes) to supply **3cb** as a white solid (340 mg, 0.95 mmol, 95%). Mp: 134−136 ºC. IR (KBr) υ_{max} (cm^{-1}) 3083, 2937, 1401, 1357, 1177, 1012, 742, 599. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.71 (d, *J* = 4.7 Hz, 1H), 8.33 (dd, *J* = 4.7, 1.8 Hz, 1H), 7.89 – 7.76 (m, 3H), 7.50 (dd, *J* = 7.3, 4.6 Hz, 1H), 7.28 (dd, *J* = 7.8, 4.7 Hz, 1H), 5.18 (brs, 2H), 3.47 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 157.4, 151.0, 150.3, 149.6, 142.8, 138.2, 132.4, 127.2, 123.2, 122.5, 82.8, 56.6. HRMS (ESI-TOF) m/z calcd for $C_{12}H_{13}{}^{79}BrN_3O_3S$ $[M + H]^+$ 357.9856, found: 357.9862.

Preparation of compounds 4aa, 5aa–bb, 4ca-cb, 4d and 4e

***N*- Methyl-2-(3-pyridyl)pyridin-3-amine 4aa and 5-methyldipyrido[3,2-c:3',2'-f]thiazine 6,6-dioxide 5aa**

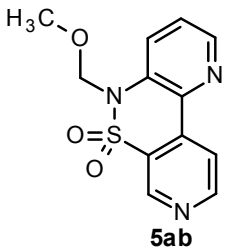


4aa **5aa**

A solution of TTMSS (223 mg, 0.9 mmol) and AIBN (147 mg, 0.9 mmol) in dry *m*-xylene (10 mL) and dry acetonitrile (0.2 mL) was added dropwise, by using a syringe pump during 36 h, to a stirred solution of **3aa** (98 mg, 0.3 mmol) in dry *m*-xylene (1 mL) at 80 °C (bath temperature), under an atmosphere of dry argon. When the addition was finished, the reaction mixture was stirred for an additional 12 h period, at the same temperature, until full consumption of **3aa** (TLC analysis). The resulting solution was concentrated, treated with a saturated $NaHCO_3$ solution and the mixture extracted with EtAcO. The combined organic layer was dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Separation and purification by TLC (silica gel, hexane/EtOAc (1:9)) provided **4aa** as white semisolid (9 mg, 0.049 mmol, 16%, R_f = 0.15) and **5aa** (28 mg, 0.133 mmol, 38%, R_f = 0.40). **4aa**: IR (KBr) υ_{max} (cm^{-1}) 3423, 2925,

1581, 1498, 1161, 714. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.90 (d, *J* = 2.3 Hz, 1H), 8.64 (dd, *J* = 4.8, 1.7 Hz, 1H), 8.08 (dd, *J* = 4.7, 1.4 Hz, 1H), 7.96 (ddd, *J* = 7.8, 2.3, 1.7 Hz, 1H), 7.41 (ddd, *J* = 7.8, 4.9, 0.9 Hz, 1H), 7.20 (dd, *J* = 8.3, 4.7 Hz, 1H), 7.00 (dd, *J* = 8.3, 1.4 Hz, 1H), 4.05 (brs, 1H), 2.82 (d, *J* = 4.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.7, 149.4, 143.10, 142.3, 138.3, 136.6, 134.5, 123.9, 123.8, 117.1, 30.6. HRMS (ESI-TOF) m/z calcd for $C_{11}H_{12}N_3$ $[M + H]^+$ 186.1026, found: 186.1025. **5aa**: Mp: 158−162 ºC. IR (KBr) υ_{max} (cm^{-1}) 3288, 1584, 1322, 1163, 728, 619. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.23 (d, *J* = 0.8 Hz, 1H), 9.00 (d, *J* = 5.3 Hz, 1H), 8.64 (dd, *J* = 4.5, 1.5 Hz, 1H), 8.44 (dd, *J* = 5.3, 0.8 Hz, 1H), 7.63 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.54 (dd, *J* = 8.4, 4.4 Hz, 1H), 3.53 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 153.3, 145.5, 143.5, 139.6, 138.9, 137.9, 130.3, 126.3, 126.0, 119.5, 31.6. HRMS (ESI-TOF) m/z calcd for $C_{11}H_{10}N_3O_2S$ $[M + H]^+$ 248.0488, found: 248.0490.

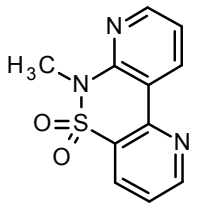
5-(Methoxymethyl)dipyrido[3,2-c:3',2'-f]thiazine 6,6-dioxide 5ab



5ab

A solution of TTMSS (223 mg, 0.9 mmol) and AIBN (147 mg, 0.9 mmol) in dry *m*-xylene (10 mL) and dry acetonitrile (0.2 mL) was added dropwise, by using a syringe pump during 36 h, to a stirred solution of **3ab** (107 mg, 0.3 mmol) in dry *m*-xylene (1 mL) at 80 °C (bath temperature), under an atmosphere of dry argon. When the addition was finished, the reaction mixture was stirred for an additional 12 h period, at the same temperature, until full consumption of **3ab** (TLC analysis). The resulting solution was concentrated, treated with a saturated $NaHCO_3$ solution and the mixture extracted with EtAcO. The combined organic layer was dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by TLC (silica gel, hexane/EtOAc (5:95)) provided **5ab** as white solid (36.0 mg, 0.194 mmol, 64%). Mp: 158−162 ºC. IR (KBr) υ_{max} (cm^{-1}) 3055, 2944, 1655, 1584, 1345, 1183, 1080, 754. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.20 (d, *J* = 0.6 Hz, 1H), 8.99 (d, *J* = 5.3 Hz, 1H), 8.67 (dd, *J* = 4.5, 1.4 Hz, 1H), 8.42 (dd, *J* = 5.3, 0.7 Hz, 1H), 8.03 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.51 (dd, *J* = 8.4, 4.5 Hz, 1H), 5.26 (s, 2H), 3.52 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 153.4, 146.8, 143.2, 139.7, 139.6, 136.9, 131.4, 128.5, 126.5, 119.8, 80.3, 56.7. HRMS (ESI-TOF) m/z calcd for $C_{12}H_{12}N_3O_3S$ $[M + H]^+$ 278.0594, found: 278.0591.

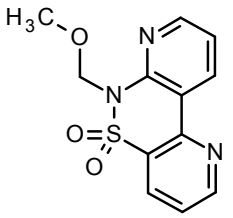
6-Methyldipyrido[2,3-b:2',3'-d]thiazine 5,5-dioxide 5ba



5ba

A solution of TTMSS (223 mg, 0.9 mmol) and AIBN (147 mg, 0.9 mmol) in dry *m*-xylene (10 mL) and dry acetonitrile (0.2 mL) was added dropwise, by using a syringe pump during 36 h, to a stirred solution of **3ba** (98 mg, 0.3 mmol) in dry *m*-xylene (1 mL) at 80 °C (bath temperature), under an atmosphere of dry argon. When the addition was finished, the reaction mixture was stirred for an additional 12 h period, at the same temperature, until full consumption of **3ba** (TLC analysis). The resulting solution was concentrated, treated with a saturated $NaHCO_3$ solution and the mixture extracted with EtAcO. The combined organic layer was dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by TLC (silica gel, hexane/EtOAc (1:1)) provided **5ba** as white solid (41 mg, 0.166 mmol, 55%). Mp: 158−160 ºC. IR (KBr) υ_{max} (cm^{-1}) 3071, 1582, 1429, 1322, 1165, 887. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.95 (dd, *J* = 4.7, 1.7 Hz, 1H), 8.92 (dd, *J* = 7.8, 1.9 Hz, 1H), 8.58 (dd, *J* = 4.8, 1.9 Hz, 1H), 8.32 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.53 (dd, *J* = 8.0, 4.8 Hz, 1H), 7.30 (dd, *J* = 7.8, 4.8 Hz, 1H), 3.68 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 153.2, 150.8, 150.0, 147.1, 135.3, 130.5, 129.8, 123.1, 119.4, 118.4, 28.6. HRMS (ESI-TOF) m/z calcd for $C_{11}H_{10}N_3O_2S$ $[M + H]^+$ 248.0488, found: 308.0491.

6-(Methoxymethyl)dipyrido[2,3-b:2',3'-d]thiazine 5,5-dioxide 5bb

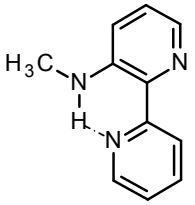


5bb

A solution of TTMSS (223 mg, 0.9 mmol) and AIBN (147 mg, 0.9 mmol) in dry *m*-xylene (10 mL) and dry acetonitrile (0.2 mL) was added dropwise, by using a syringe pump during 36 h, to a stirred solution of **3bb** (107 mg, 0.3 mmol) in dry *m*-xylene (1 mL) at 80 °C (bath temperature), under an atmosphere of dry argon. When the addition was finished, the reaction mixture was stirred for an additional 12 h period, at the same temperature, until full consumption of **3bb** (TLC analysis). The resulting solution was concentrated, treated with a saturated $NaHCO_3$ solution and the mixture extracted with EtAcO. The combined organic layer was dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by TLC (silica gel, hexane/EtOAc (3:7)) provided **5bb** as white solid (44 mg, 0.158 mmol, 53%). Mp: 129−132 ºC. IR (KBr) υ_{max} (cm^{-1}) 2960, 1583, 1425, 1328, 1261, 1060, 841. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm)

9.06 – 8.87 (m, 2H), 8.64 (dd, J = 4.7, 1.9 Hz, 1H), 8.33 (dd, J = 8.0, 1.6 Hz, 1H), 7.55 (dd, J = 8.0, 4.7 Hz, 1H), 7.37 (dd, J = 7.8, 4.8 Hz, 1H), 5.72 (s, 2H), 3.44 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 153.4, 151.3, 149.5, 147.5, 135.9, 130.9, 130.5, 123.3, 120.7, 119.4, 75.7, 57.4. HRMS (ESI-TOF) m/z calcd for $C_{12}H_{12}N_3O_3S$ $[M + H]^+$ 278.0594, found: 278.0596.

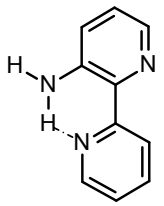
_N_-Methyl-2-(2-pyridyl)pyridin-3-amine 4ca



4ca

A solution of TTMSS (223 mg, 0.9 mmol) and AIBN (147 mg, 0.9 mmol) in dry *m*-xylene (10 mL) and dry acetonitrile (0.2 mL) was added dropwise, by using a syringe pump during 36 h, to a stirred solution of **3ca** (98 mg, 0.3 mmol) in dry *m*-xylene (1 mL) at 80 °C (bath temperature), under an atmosphere of dry argon. When the addition was finished, the reaction mixture was stirred for an additional 12 h period, at the same temperature, until full consumption of **3ca** (TLC analysis). The resulting solution was concentrated, treated with a saturated $NaHCO_3$ solution and the mixture extracted with EtAcO. The combined organic layer was dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by TLC (silica gel, hexane/EtOAc (7:3)) provided **4ca** as white solid (41 mg, 0.221 mmol, 74%). Mp: 66−68 ºC. IR (KBr) υ_{max} (cm^{-1}) 3062, 2982, 1582, 1339, 1170, 1113, 700, 587. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.19 (brs, 1H), 8.61 – 8.50 (m, 2H), 8.00 (dd, J = 4.4, 1.5 Hz, 1H), 7.79 (ddd, J = 8.2, 7.4, 1.9 Hz, 1H), 7.23 – 7.15 (m, 2H), 7.03 (dd, J = 8.4, 1.4 Hz, 1H), 2.95 (d, J = 5.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 159.7, 146.5, 146.2, 136.6, 136.5, 135.7, 124.9, 122.5, 121.8, 117.7, 29.4. HRMS (ESI-TOF) m/z calcd for $C_{11}H_{12}N_3$ $[M + H]^+$ 186.1026, found: 186.1026.

2-(2-Pyridyl)pyridin-3-amine 4cb[17]



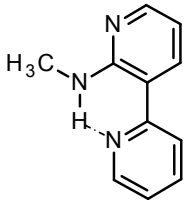
4cb

A solution of TTMSS (223 mg, 0.9 mmol) and AIBN (147 mg, 0.9 mmol) in dry *m*-xylene (10 mL) and dry acetonitrile (0.2 mL) was added dropwise, by using a syringe pump during 36 h, to a stirred solution of **3cb** (107 mg, 0.3 mmol) in dry *m*-xylene (1 mL) at 80 °C (bath temperature), under an atmosphere of dry

[17] L. Kaczmarek, *B. Pol. Acad. Sci.-Chem.*, 1985, **33**, 401.

argon. When the addition was finished, the reaction mixture was stirred for an additional 12 h period, at the same temperature, until full consumption of **3cb** (TLC analysis). The resulting solution was concentrated, treated with a saturated $NaHCO_3$ solution and the mixture extracted with EtAcO. The combined organic layer was dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by TLC (silica gel, hexane/EtOAc (7:3)) provided **4cb** as white solid (33 mg, 0.193 mmol, 64%). Mp: 102−106 ºC. IR (KBr) υ_{max} (cm^{-1}) 3389, 3264, 3044, 1601, 1446, 1147, 751, 631. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.57 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 8.50 (dt, *J* = 8.2, 1.0 Hz, 1H), 8.07 (dd, *J* = 4.2, 1.7 Hz, 1H), 7.81 (ddd, *J* = 8.2, 7.5, 1.9 Hz, 1H), 7.22 (ddd, *J* = 7.4, 4.9, 1.2 Hz, 1H), 7.09 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.04 (dd, *J* = 8.2, 1.7 Hz, 1H), 6.36 (brs, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 159.5, 147.0, 144.0, 138.2, 137.2, 136.7, 124.6, 124.5, 122.4, 122.0. HRMS (ESI-TOF) m/z calcd for $C_{10}H_{10}N_3$ $[M + H]^+$ 172.0870, found: 172.0873.

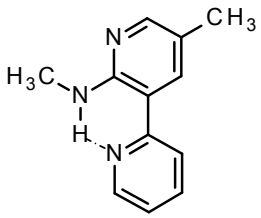
***N*-Methyl-3-(2-pyridyl)pyridin-2-amine 4d**



4d

A solution of TTMSS (223 mg, 0.9 mmol) and AIBN (147 mg, 0.9 mmol) in dry *m*-xylene (10 mL) and dry acetonitrile (0.2 mL) was added dropwise, by using a syringe pump during 36 h, to a stirred solution of **3d** (98 mg, 0.3 mmol) in dry *m*-xylene (1 mL) at 80 °C (bath temperature), under an atmosphere of dry argon. When the addition was finished, the reaction mixture was stirred for an additional 12 h period, at the same temperature, until full consumption of **3d** (TLC analysis). The resulting solution was concentrated, treated with a saturated $NaHCO_3$ solution and the mixture extracted with EtAcO. The combined organic layer was dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by TLC (silica gel, hexane/EtOAc (7:3)) provided **4d** as yellow oil (47 mg, 0.254 mmol, 85%). IR (NaCl) υ_{max} (cm^{-1}) 3418, 1595, 1519, 1386, 1241, 1100, 769, 569. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.93 (brs, 1H), 8.58 (d, *J* = 4.8 Hz, 1H), 8.21 (dd, *J* = 4.9, 1.8 Hz, 1H), 7.78 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.72 (dd, *J* = 7.1, 1.8 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.18 (ddd, *J* = 6.5, 4.9, 1.4 Hz, 1H), 6.59 (dd, *J* = 7.6, 4.9 Hz, 1H), 3.09 (d, *J* = 4.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 157.6, 149.1 (2C), 147.6, 137.0, 135.9, 121.7, 121.3, 116.1, 111.2, 28.2. HRMS (ESI-TOF) m/z calcd for $C_{11}H_{12}N_3$ $[M + H]^+$ 186.1026, found: 186.1030.

***N*,5-Dimethyl-3-(2-pyridyl)pyridin-2-amine 4e**



4e

A solution of TTMSS (223 mg, 0.9 mmol) and AIBN (147 mg, 0.9 mmol) in dry *m*-xylene (10 mL) and dry acetonitrile (0.2 mL) was added dropwise, by using a syringe pump during 36 h, to a stirred solution of **3e** (103 mg, 0.3 mmol) in dry *m*-xylene (1 mL) at 80 °C (bath temperature), under an atmosphere of dry argon. When the addition was finished, the reaction mixture was stirred for an additional 12 h period, at the same temperature, until full consumption of **3e** (TLC analysis). The resulting solution was concentrated, treated with a saturated $NaHCO_3$ solution and the mixture extracted with EtAcO. The combined organic layer was dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by TLC (silica gel, hexane/EtOAc (7:3)) provided **4e** as yellow oil (53 mg, 0.266 mmol, 89%). IR (KBr) υ_{max} (cm^{-1}) 3423, 1666, 1618, 1221, 1019, 795, 568. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.60 (brs, 1H), 8.58 (dd, J = 4.9, 1.7 Hz, 1H), 8.04 (d, J = 2.2 Hz, 1H), 7.77–7.65 (m, 2H), 7.62 (d, J = 1.8 Hz, 1H), 7.18 (ddd, J = 7.1, 4.9, 1.4 Hz, 1H), 3.08 (d, J = 4.8 Hz, 3H), 2.25 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 157.6, 155.9, 148.6, 147.6, 137.0, 136.9, 121.7, 121.2, 119.7, 115.9, 28.5, 17.7. HRMS (ESI-TOF) m/z calcd for $C_{12}H_{14}N_3$ $[M + H]^+$ 200.1182, found: 200.1179.

X-ray crystallographic data for 5ba

Colourless crystals of **5ba** were obtained from a recrystallization process in toluene. The crystals were covered with a layer of a viscous perfluoropolyether (FomblinY). A suitable crystal was selected with the aid of a microscope, mounted on a cryoloop, and placed in the low temperature nitrogen stream of the diffractometer. The intensity data sets were collected at 200 K on a Bruker-Nonius KappaCCD diffractometer equipped with an Oxford Cryostream 700 unit. Crystallographic data are presented in Table S1. The structure was solved, using the WINGX package,[18] by intrinsic phasing methods (SHELXT),[19] and refined by least-squares against F^2 (SHELXL-2014/7).[20] All non-hydrogen atoms were anisotropically refined, whereas hydrogen atoms were included, positioned geometrically and refined by using a riding model.

Table S1. Experimental data for the X-ray diffraction study on **5ba**.

	5ba
CCDC[a] code	1967009
Formula	$C_{11}H_9N_3O_2S$
M_r	247.27
T [K]	200(2)
λ [Å]	0.71073
crystal system	Triclinic
space group	$P\bar{1}$
a [Å]; α [º]	6.974(1); 99.96(1)
b [Å]; β [º]	7.876(1); 95.92(1)
c [Å]; γ [º]	9.808(1); 97.05(1)
V [Å^3]	522.3(1)
Z	2
ρ_{calcd} [g cm^{-3}]	1.572
$\mu_{MoK\alpha}$ [mm^{-1}]	0.302
F(000)	256
crystal size [mm^3]	0.39×0.36×0.22
θ range (deg)	2.65 to 27.50
index ranges	−9 to 9, −10 to 10, −12 to 12
Reflections collected	13956
Unique data	2389 [R_{int} = 0.034]
obsd data [I>2σ(I)]	2086
Goodness-of-fit on F^2	1.159
final R^a indices [I>2σ(I)]	$R1$ = 0.042, w$R2$ = 0.104
R^b indices (all data)	$R1$ = 0.050, w$R2$ = 0.112
largest diff. peak/hole [e Å^{-3}]	0.424/−0.747

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

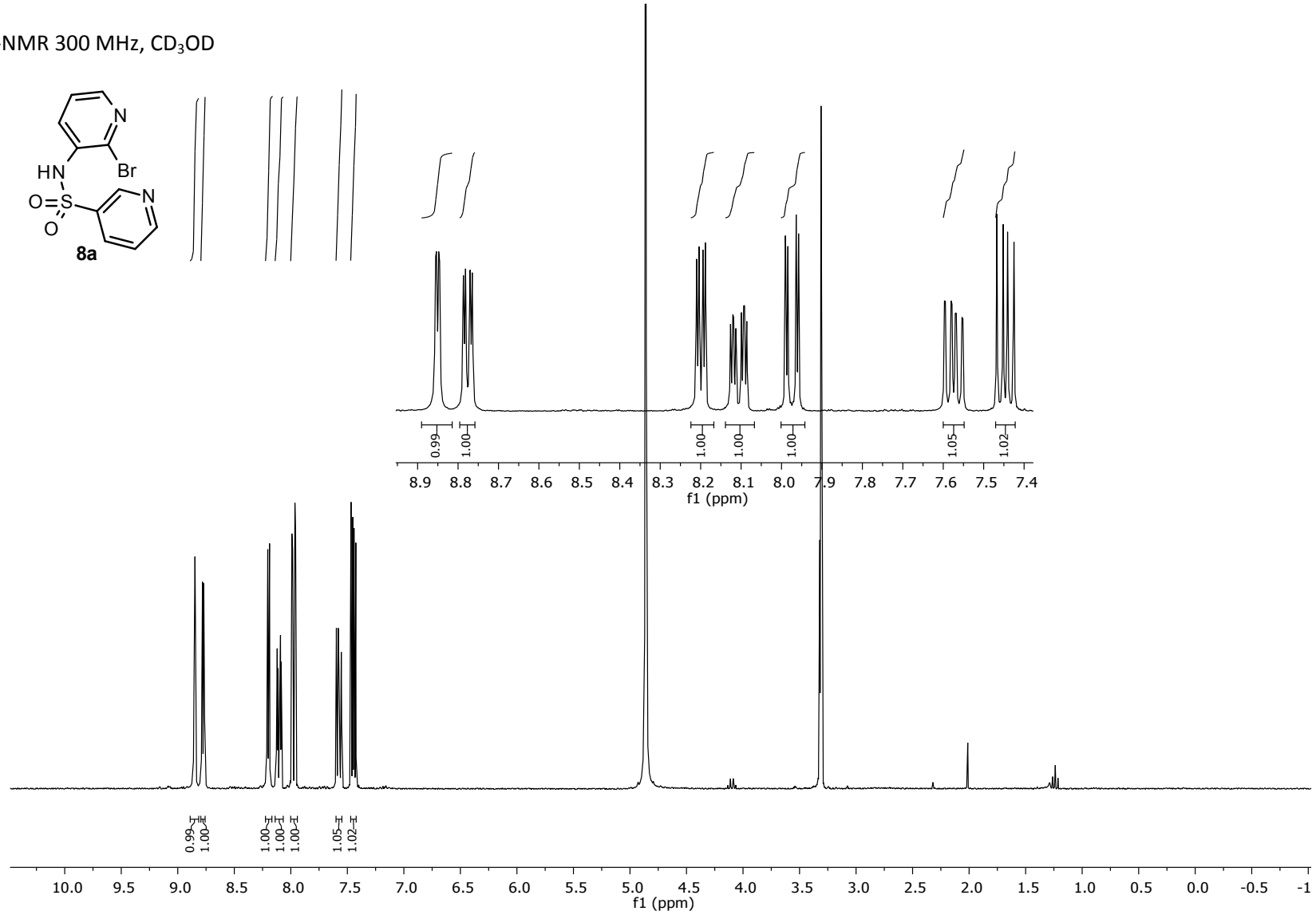
Copies of ^{1}H and ^{13}C-NMR spectra for compounds **8a–c, 3ba, 3d,e, 4aa, 5aa–bb, 4ca–4cb, 4d, 4f**

[18] L. J. Farrugia, *J. Appl. Crystallogr.* 2012, **45**, 849.

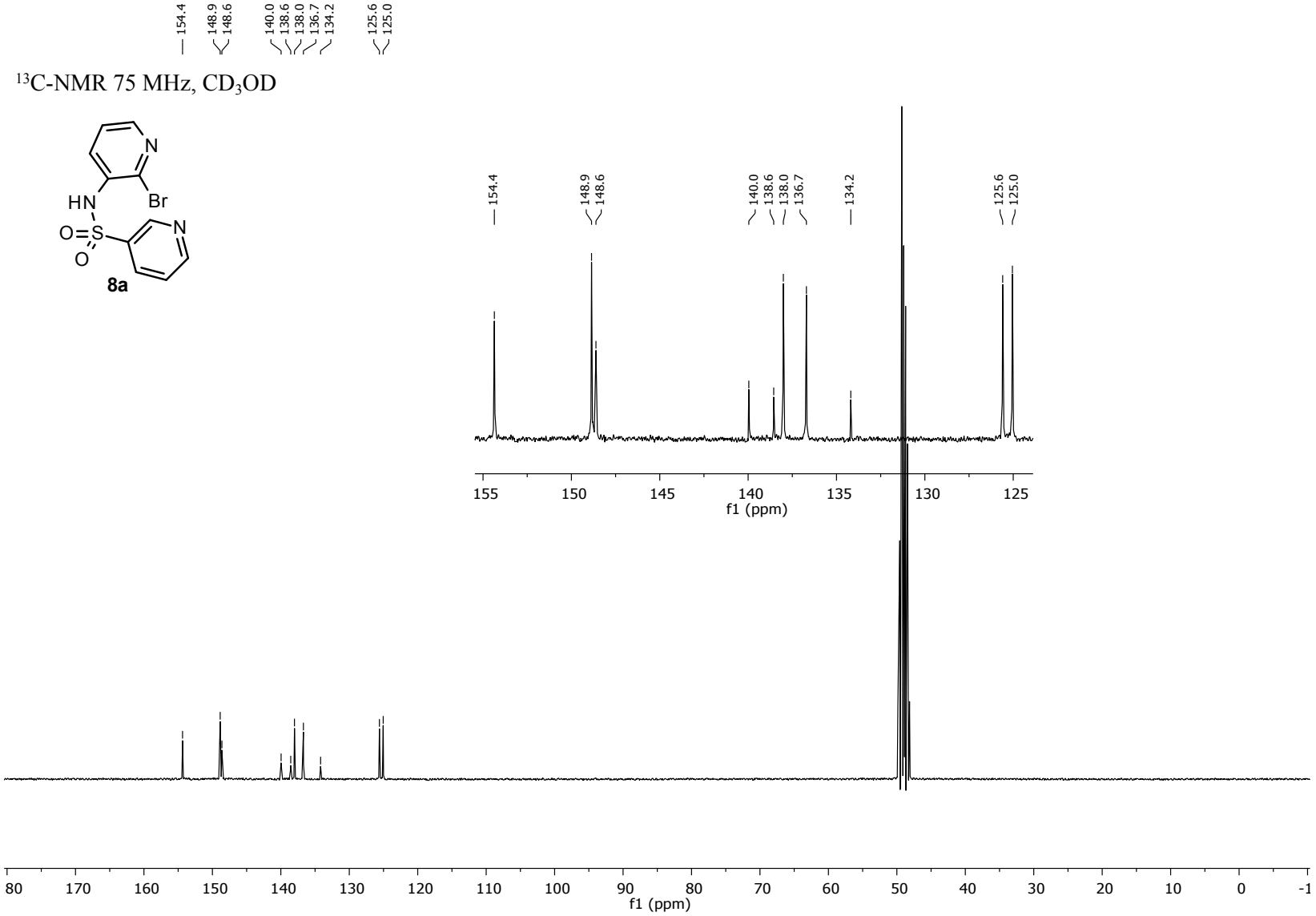
[19] G. M. Sheldrick, *Acta Crystallogr., Sect. A* 2015, **71**, 3.

[20] G. M. Sheldrick, *Acta Crystallogr., Sect. C* 2015, ***71***, 3.

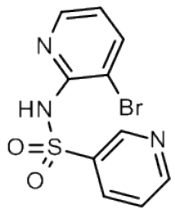
^{1}H-NMR 300 MHz, CD_3OD



^{13}C-NMR 75 MHz, CD_3OD

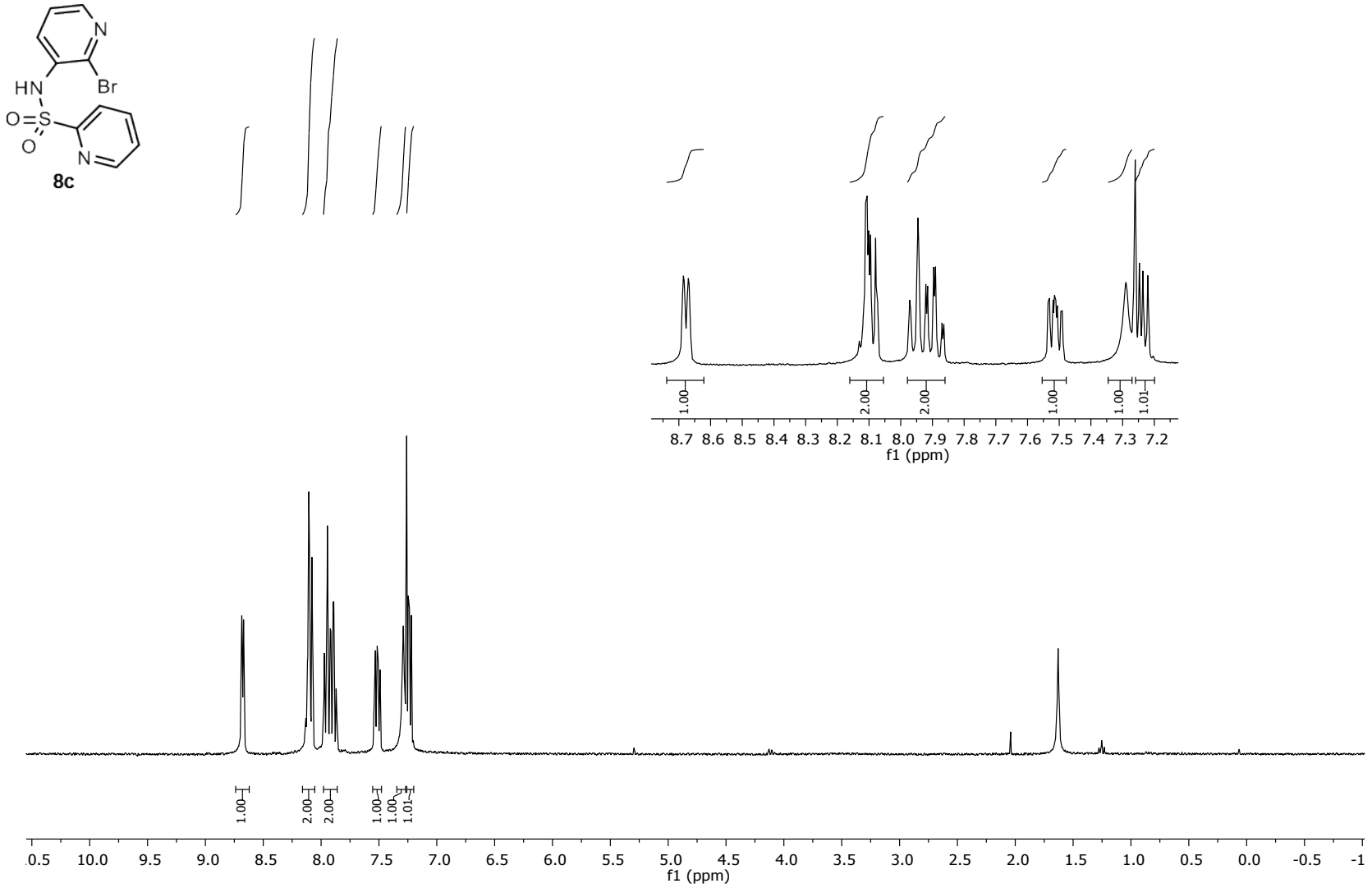


^{1}H-NMR 500 MHz, DMSO-d_6 (40 °C)

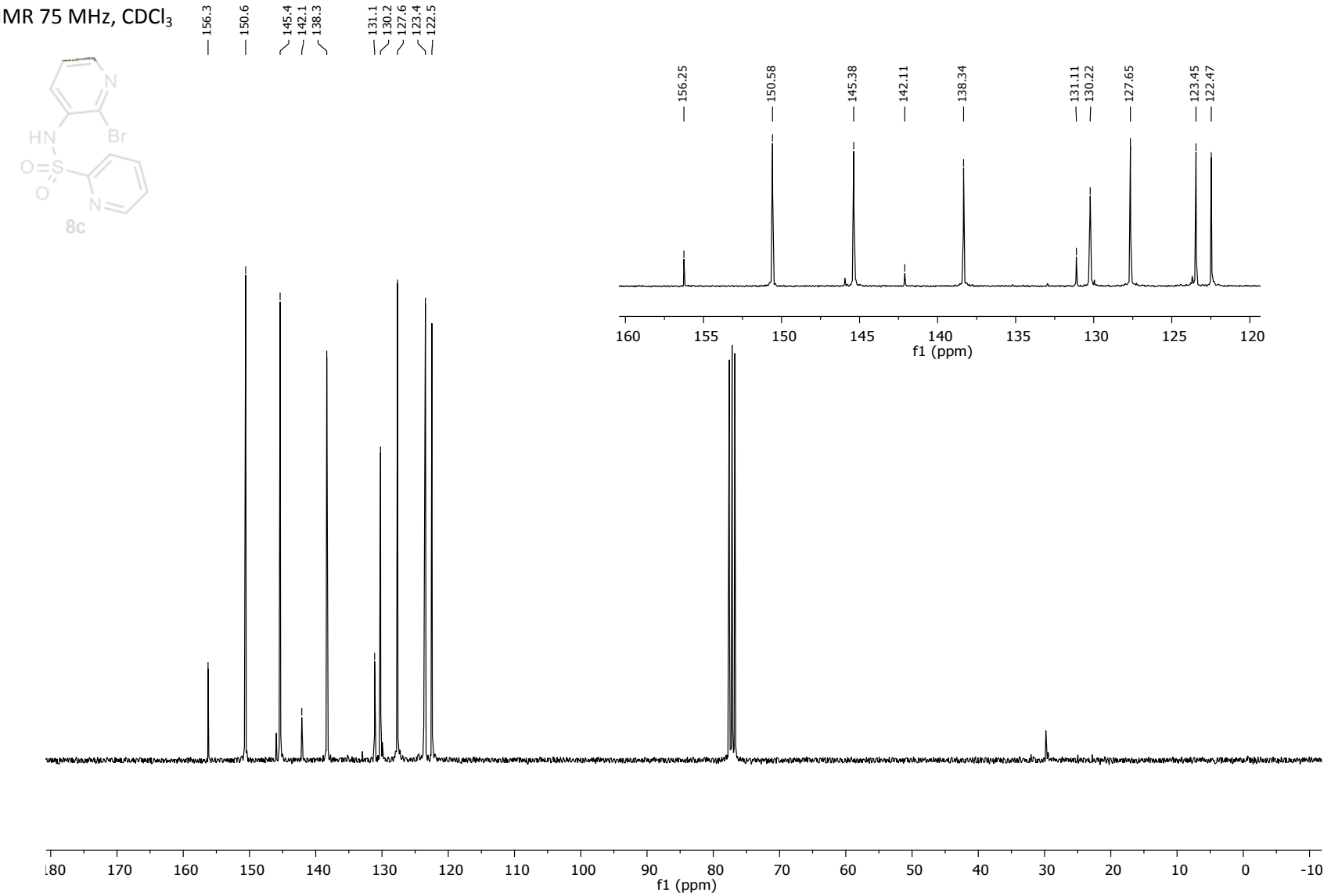


8b

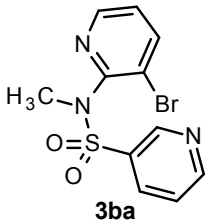
^{1}H-NMR 300 MHz, $CDCl_3$



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

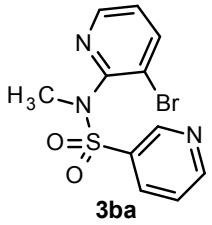


^{1}H-NMR 300 MHz, $CDCl_3$



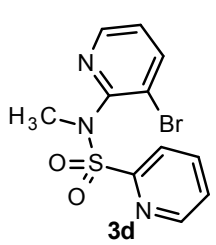
3ba

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

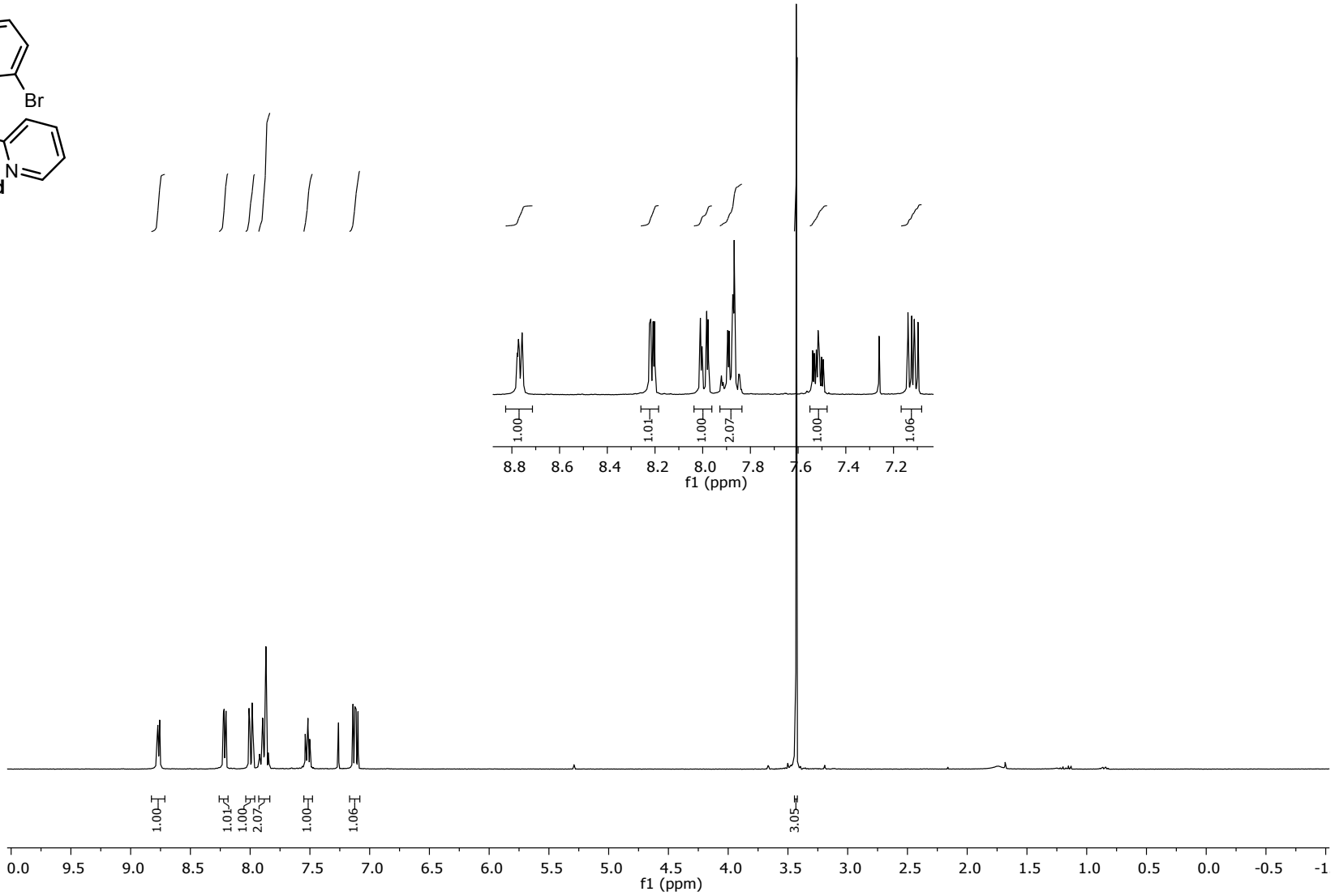


3ba

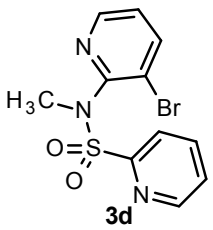
H-NMR 300 MHz, $CDCl_3$



3d

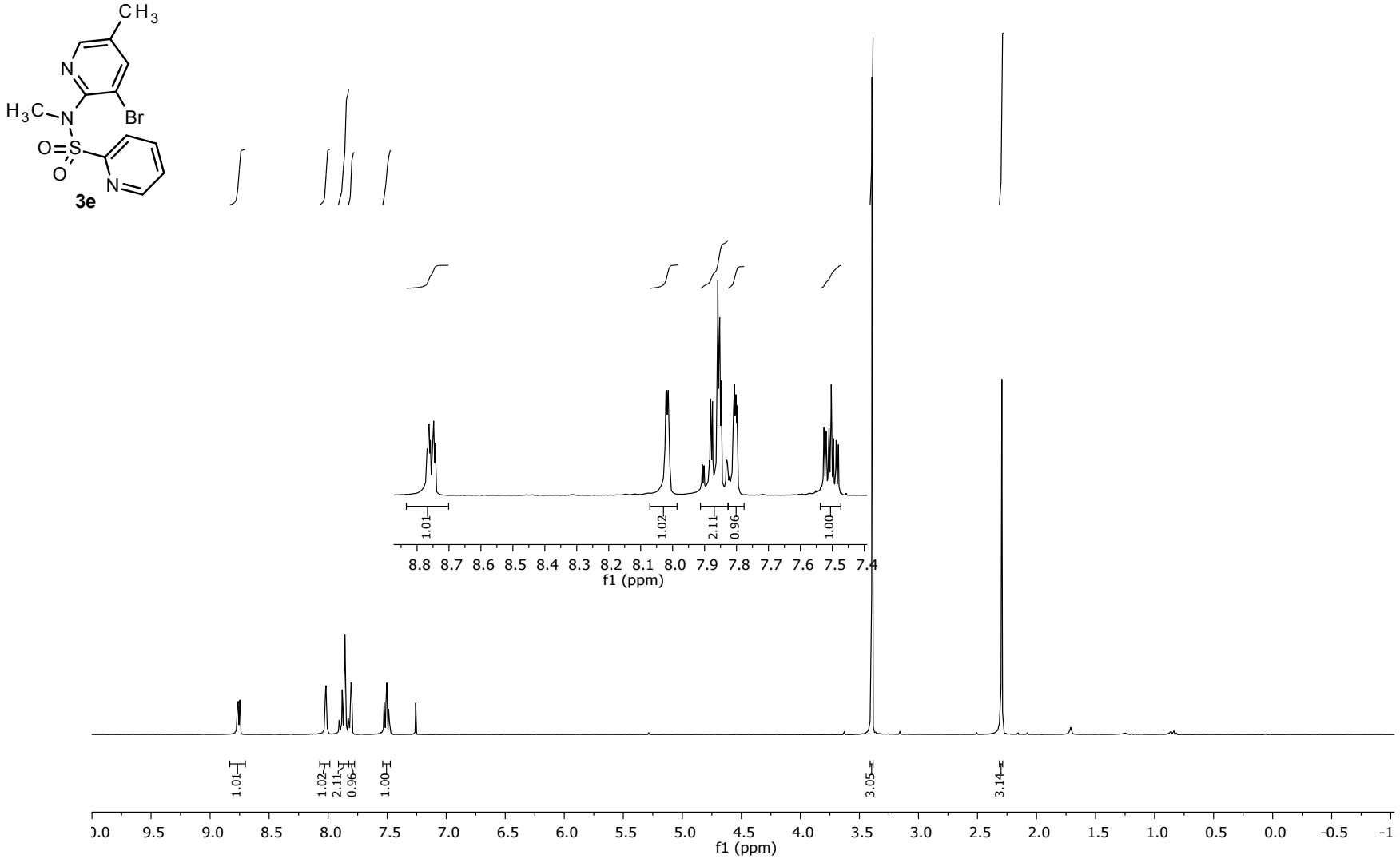


^{13}C-NMR 75 MHz, $CDCl_3$

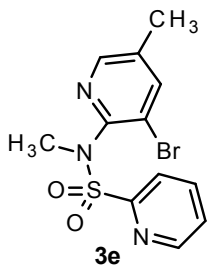


3d

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

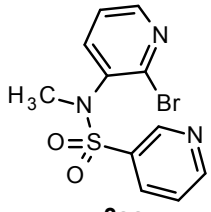


^{13}C-NMR 75 MHz, $CDCl_3$

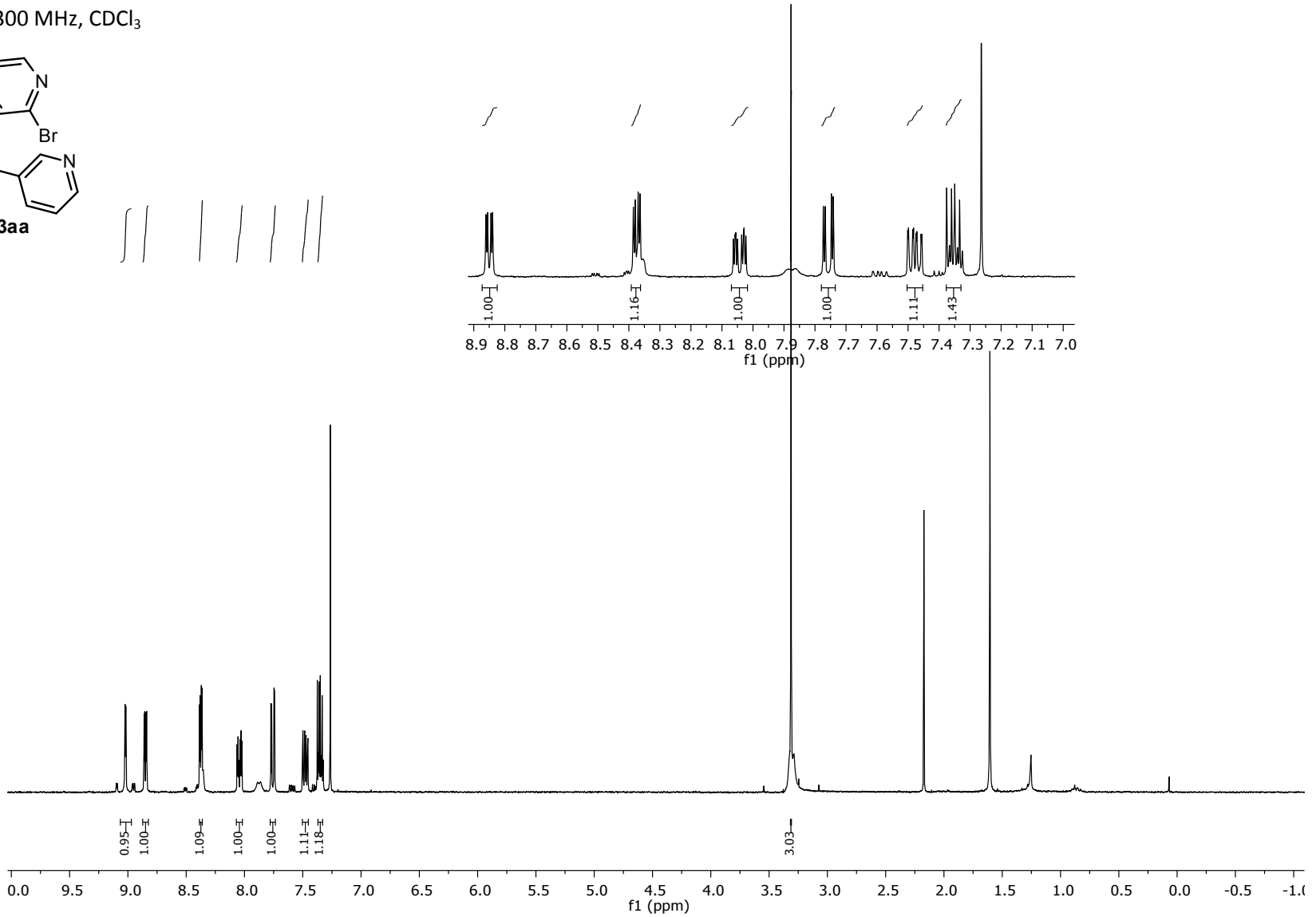


3e

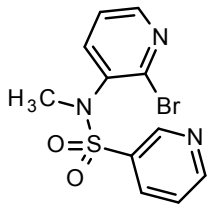
^{1}H-NMR 300 MHz, $CDCl_3$



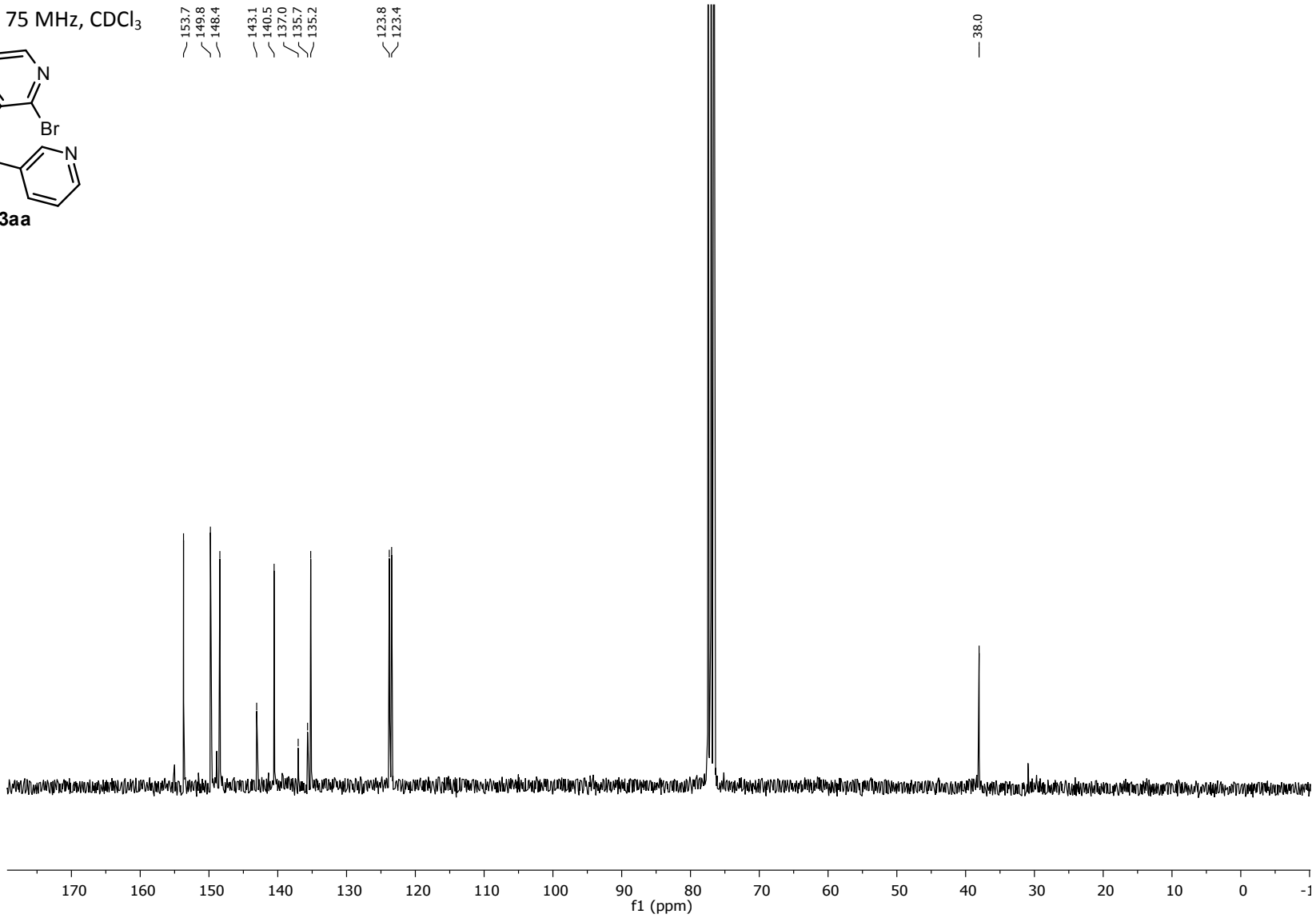
3aa



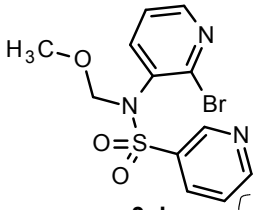
^{13}C-NMR 75 MHz, $CDCl_3$



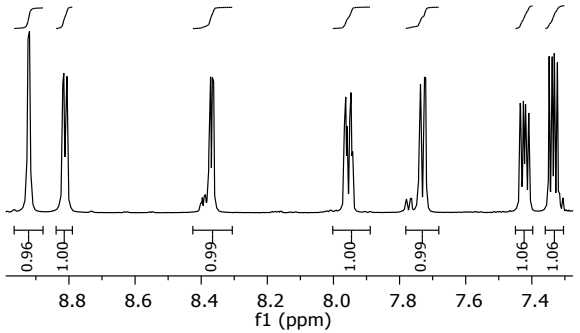
3aa

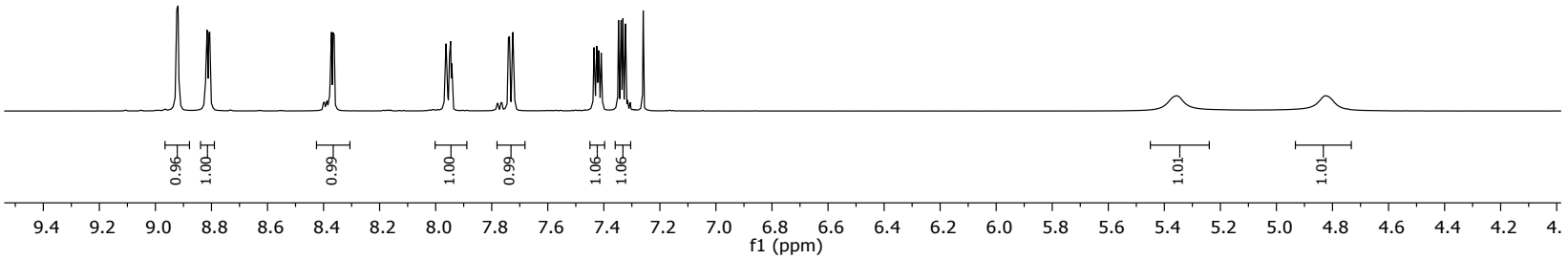


^{1}H-NMR 500 MHz, $CDCl_3$

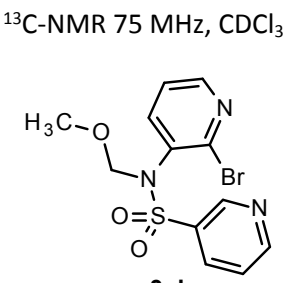


3ab



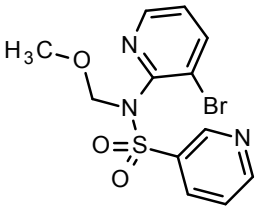


^{13}C-NMR 75 MHz, $CDCl_3$

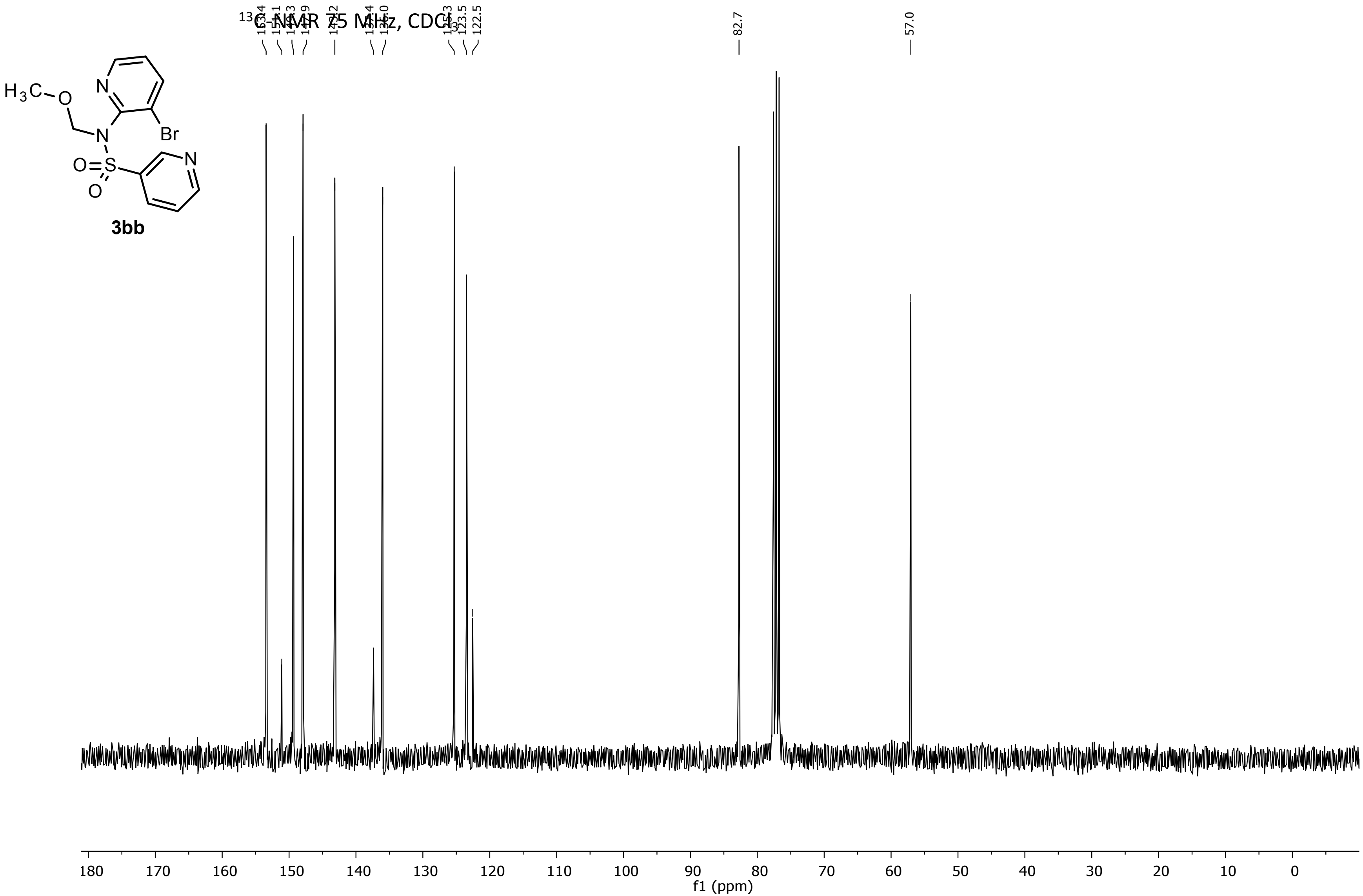


3ab

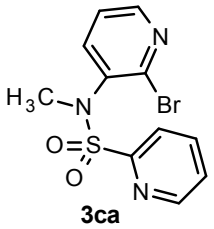
^{1}H-NMR 500 MHz, $CDCl_3$



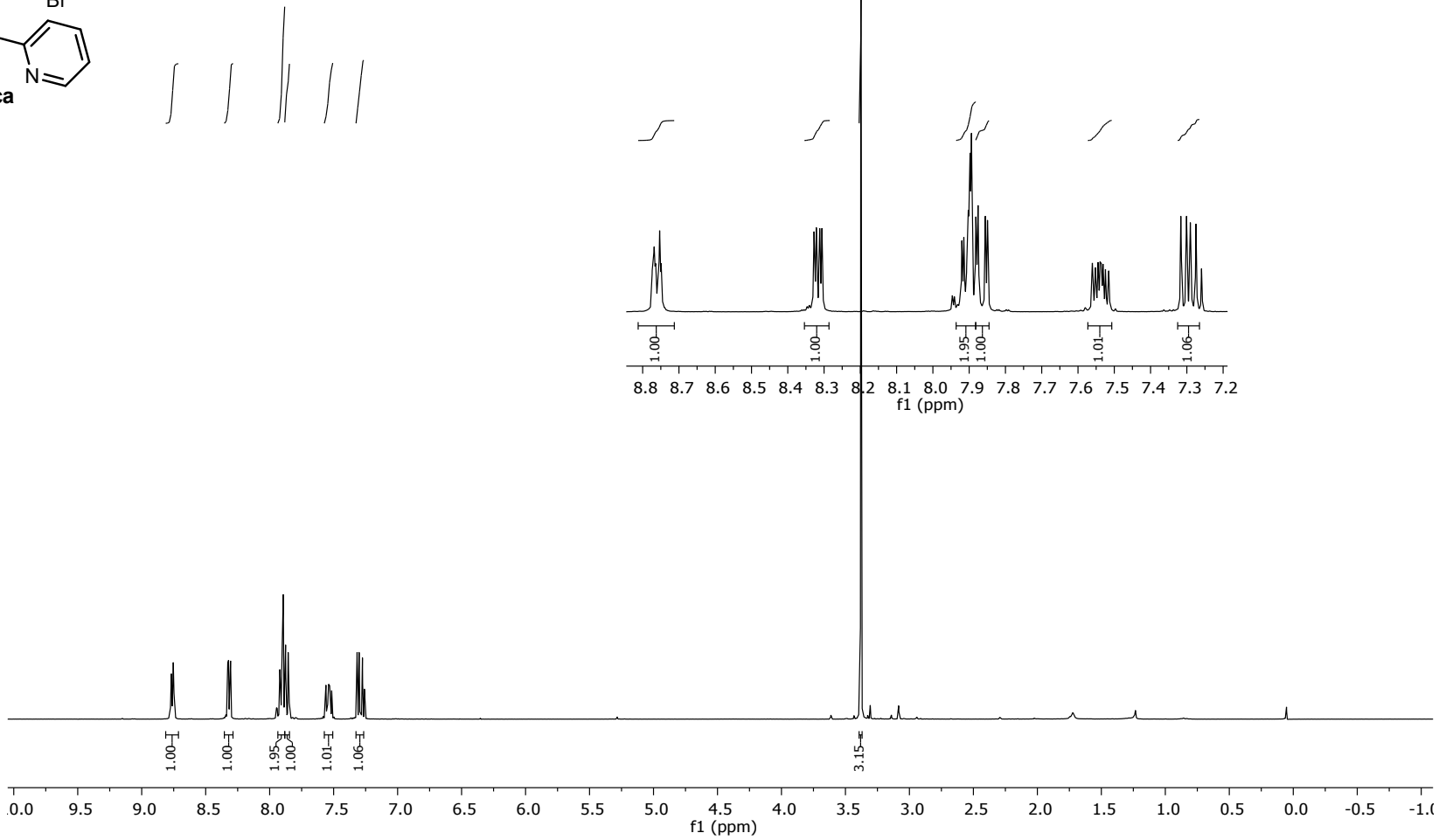
3bb


H3C
O
N
N
Br
O
S
O
N
3bb
13C-NMR 75 MHz, CDCl3
153.4
151.1
149.3
147.9
143.2
137.4
136.0
125.3
123.5
122.5
82.7
57.0
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

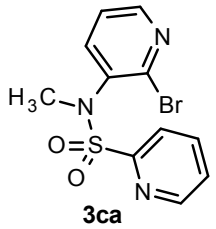
^{1}H-NMR 300 MHz, $CDCl_3$



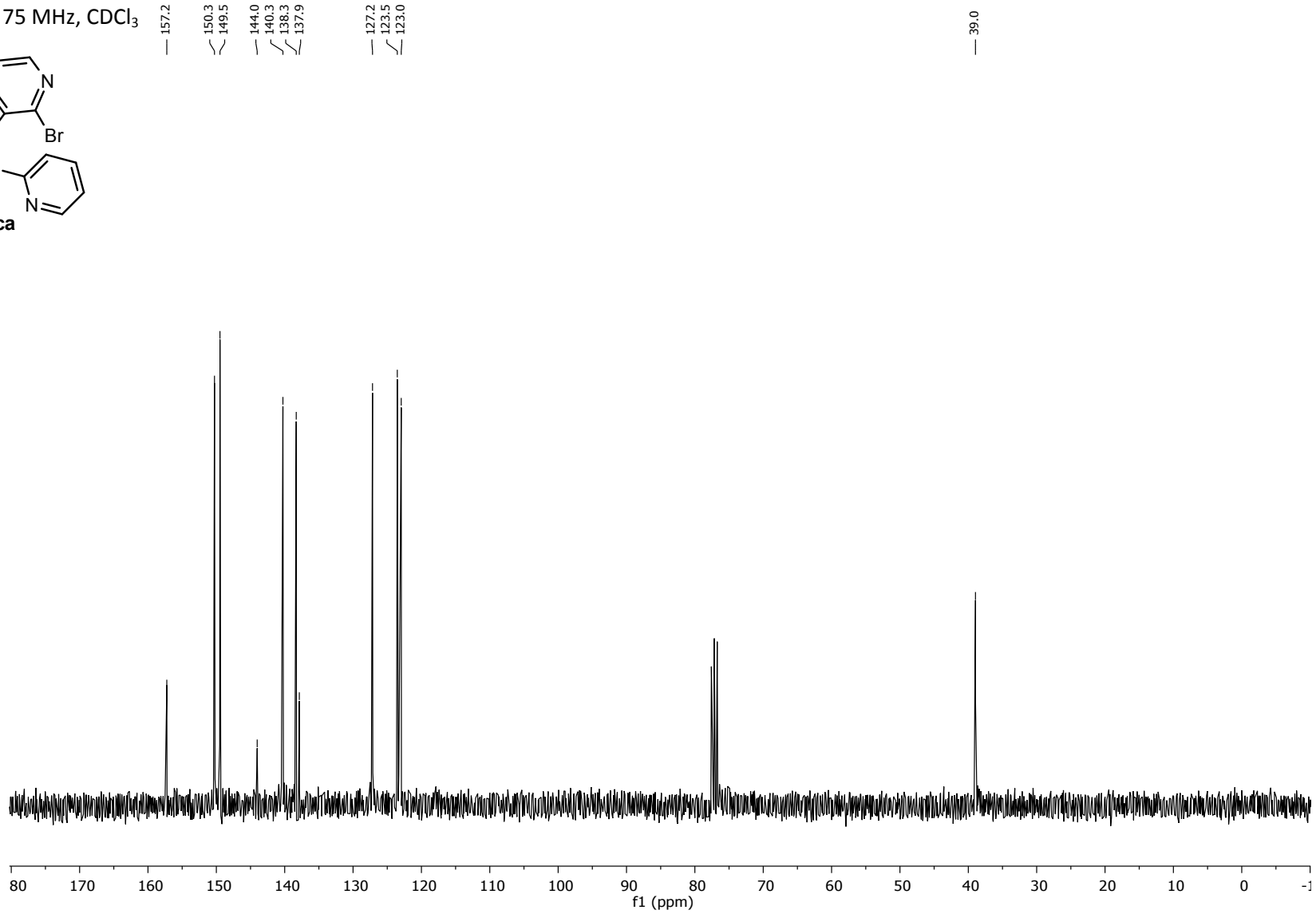
3ca



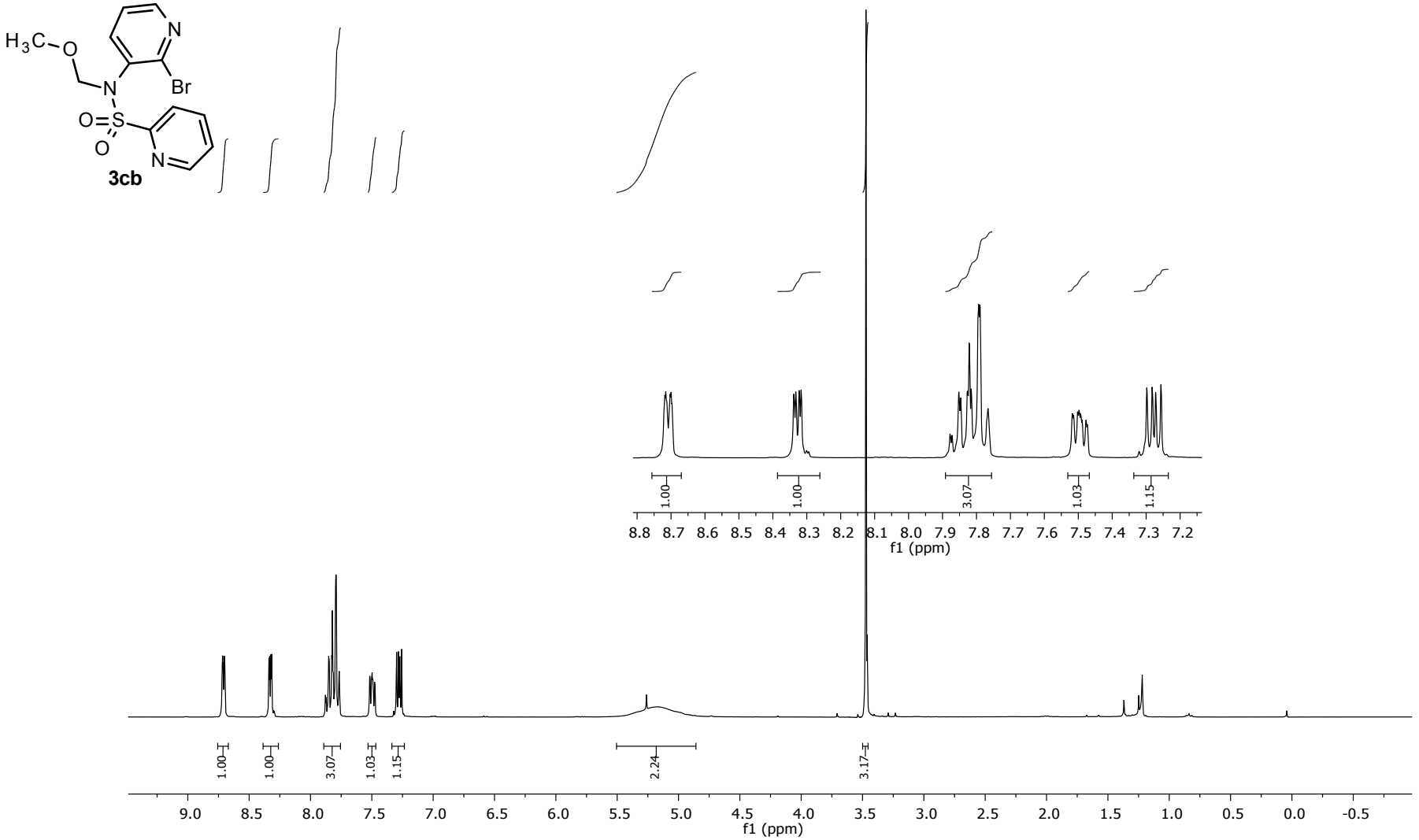
^{13}C-NMR 75 MHz, $CDCl_3$



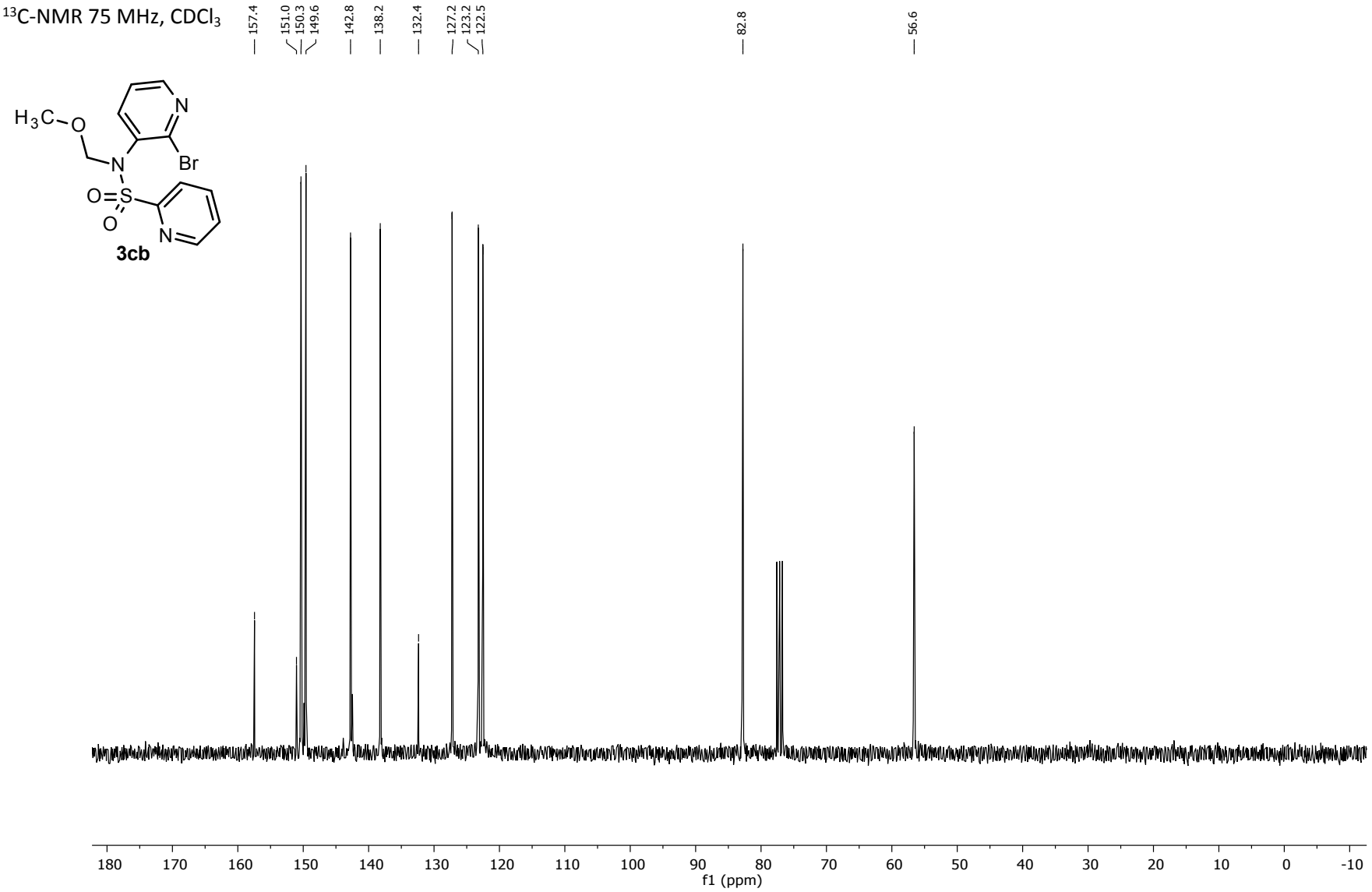
3ca



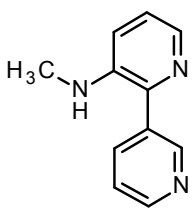
^{1}H-NMR 300 MHz, $CDCl_3$



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

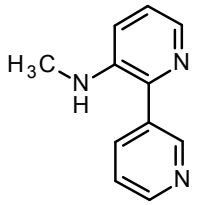


^{1}H-NMR 300 MHz, $CDCl_3$



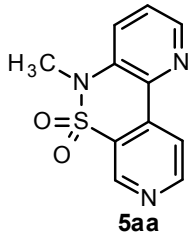
4aa

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

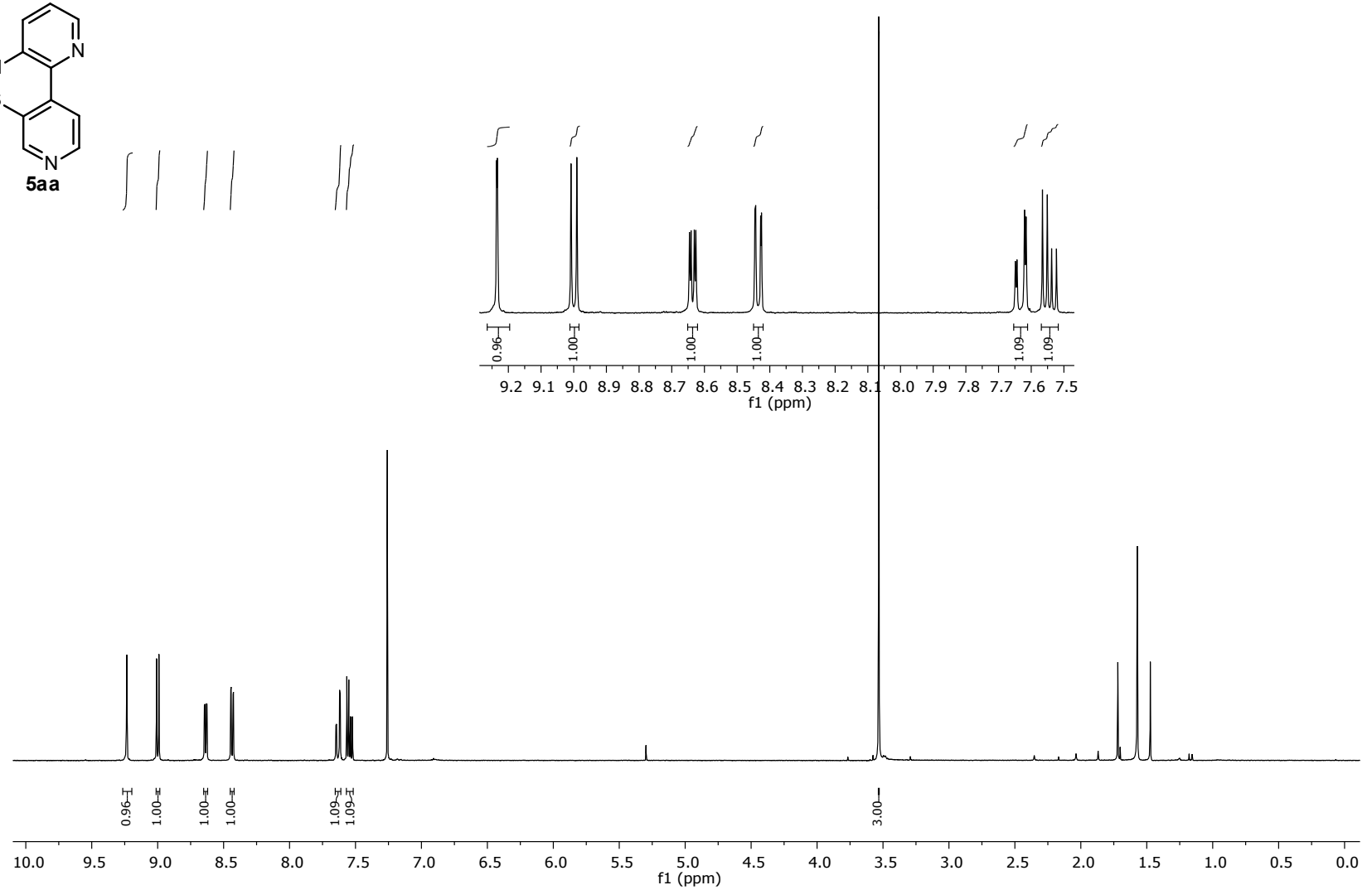


4aa

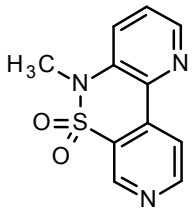
^{1}H-NMR 300 MHz, $CDCl_3$



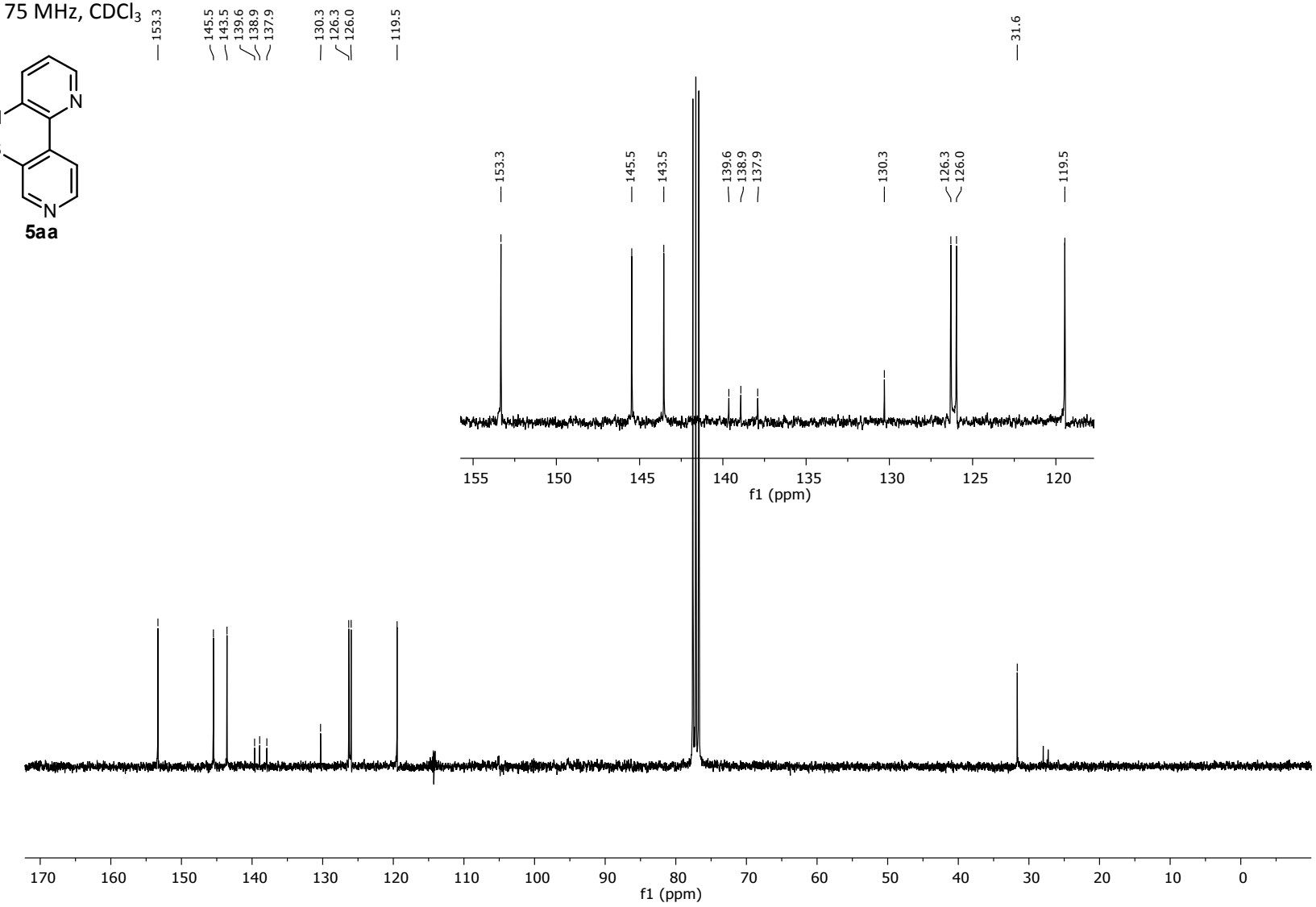
5aa



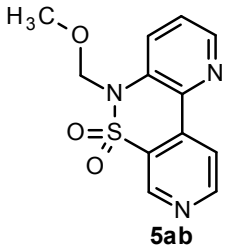
^{13}C-NMR 75 MHz, $CDCl_3$



5aa

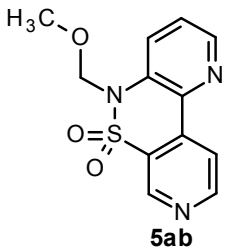


^{1}H-NMR 300 MHz, $CDCl_3$



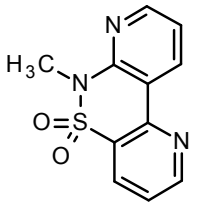
5ab

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

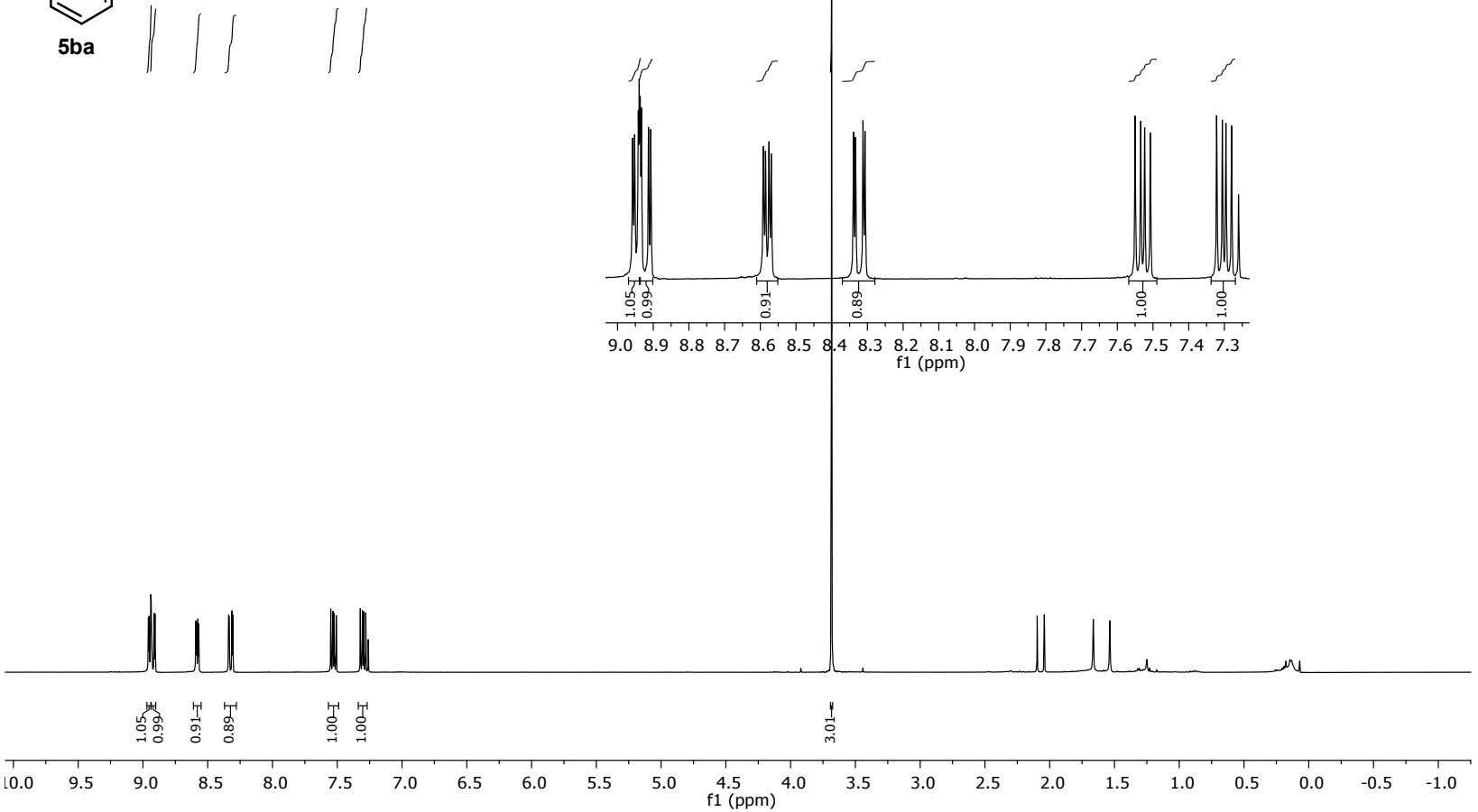


5ab

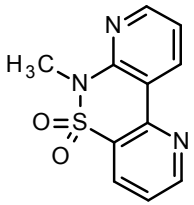
^{1}H-NMR 300 MHz, $CDCl_3$



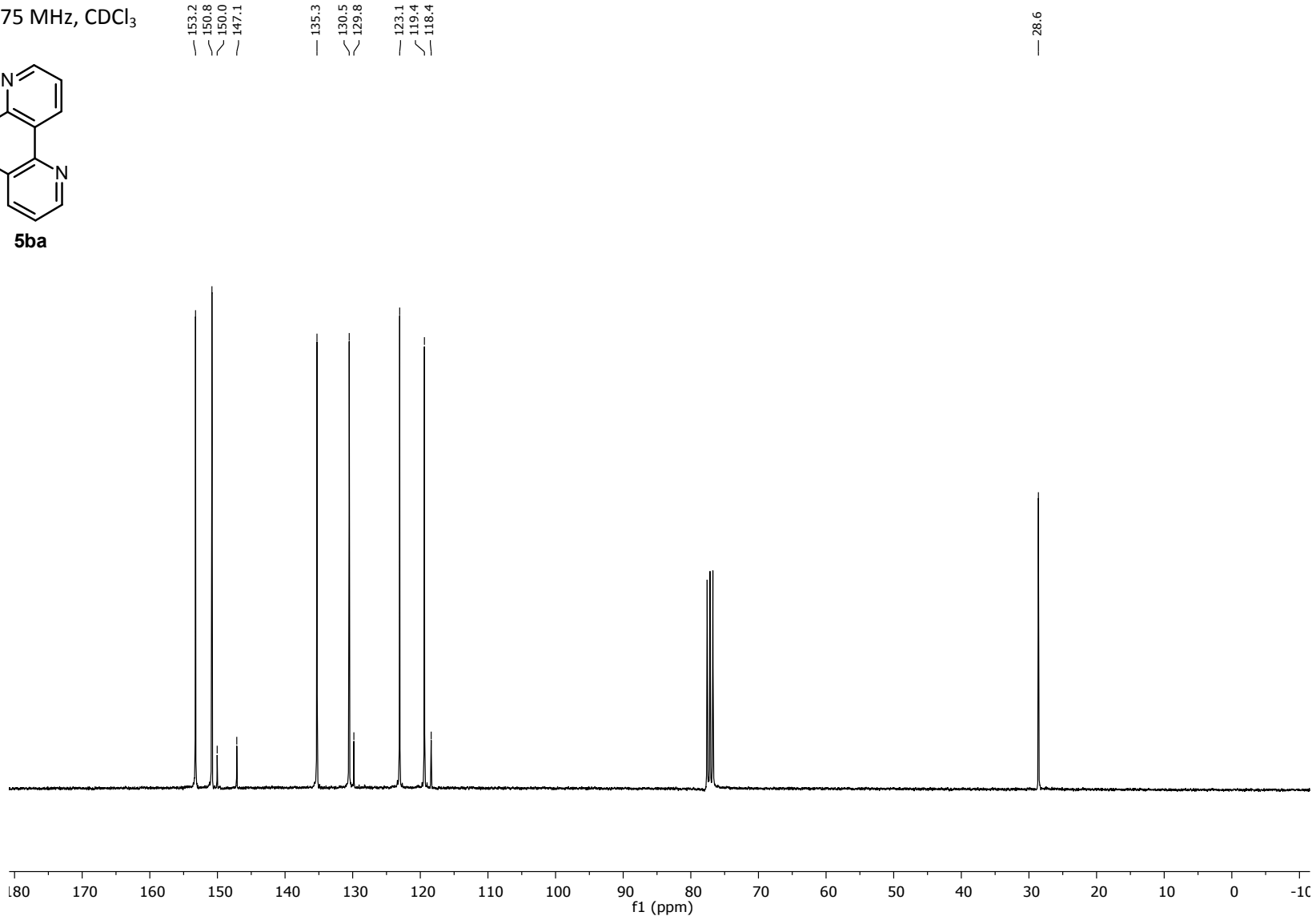
5ba



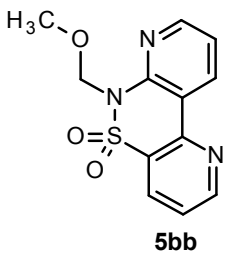
^{13}C-NMR 75 MHz, $CDCl_3$



5ba

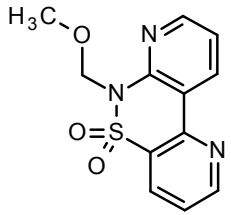


^{1}H-NMR 500 MHz, $CDCl_3$



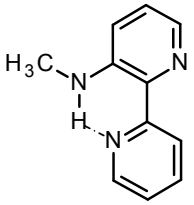
5bb

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

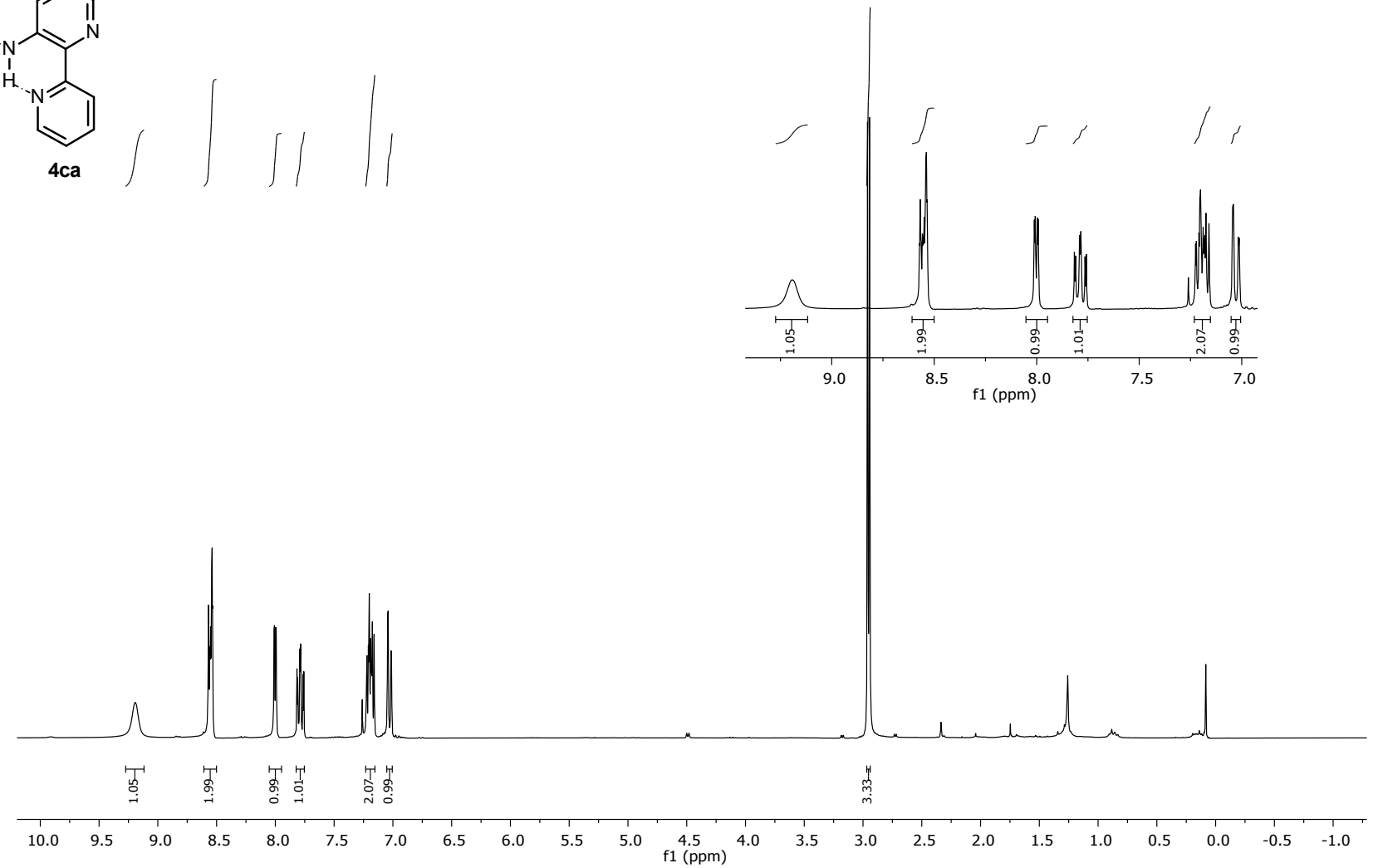


5bb

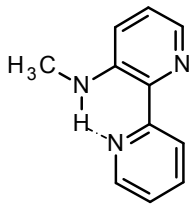
^{1}H-NMR 300 MHz, $CDCl_3$



4ca

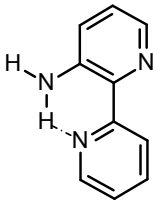


^{13}C-NMR 75 MHz, $CDCl_3$

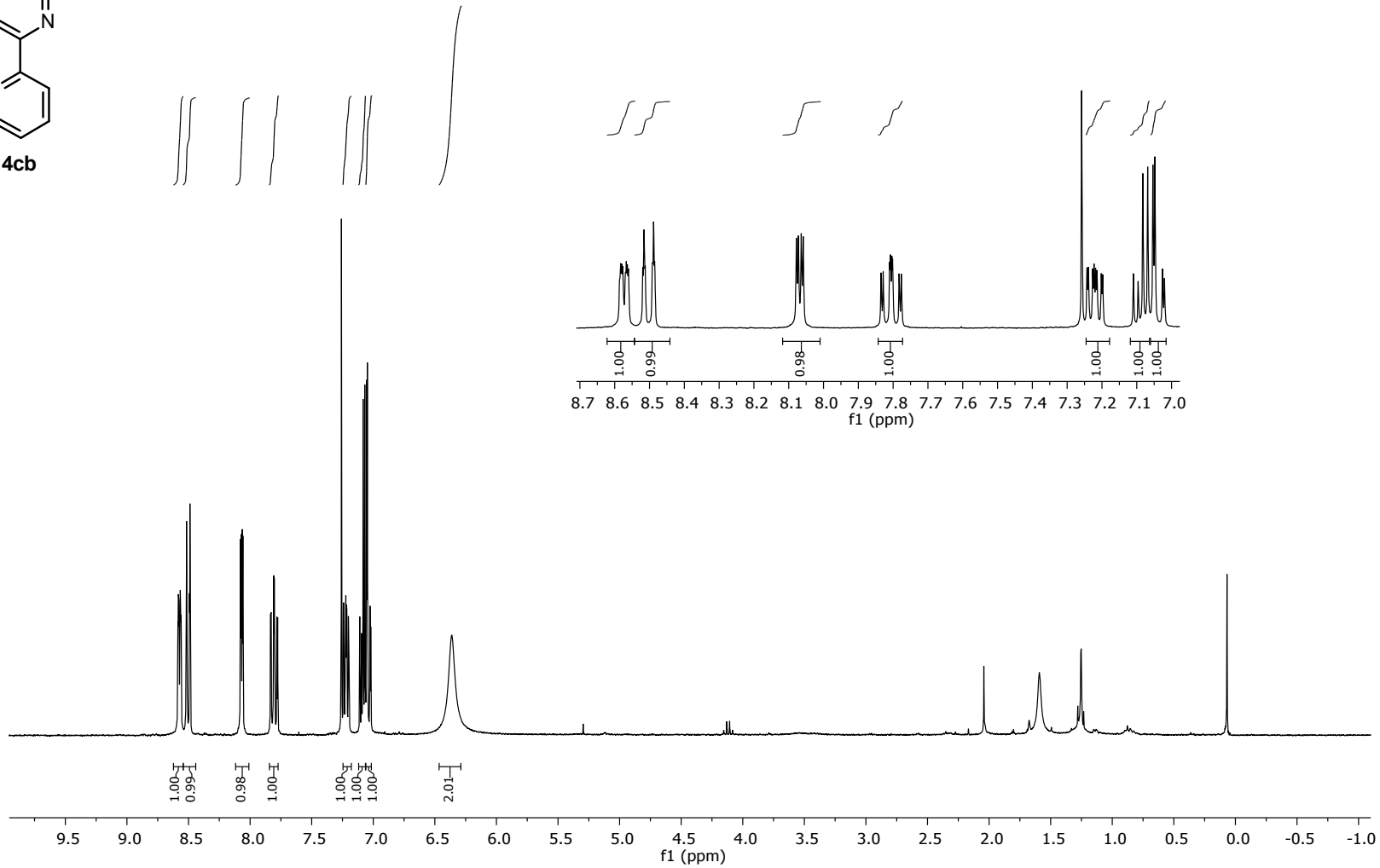


4ca

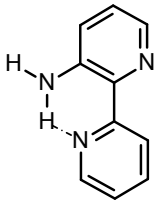
^{1}H-NMR 300 MHz, $CDCl_3$



4cb

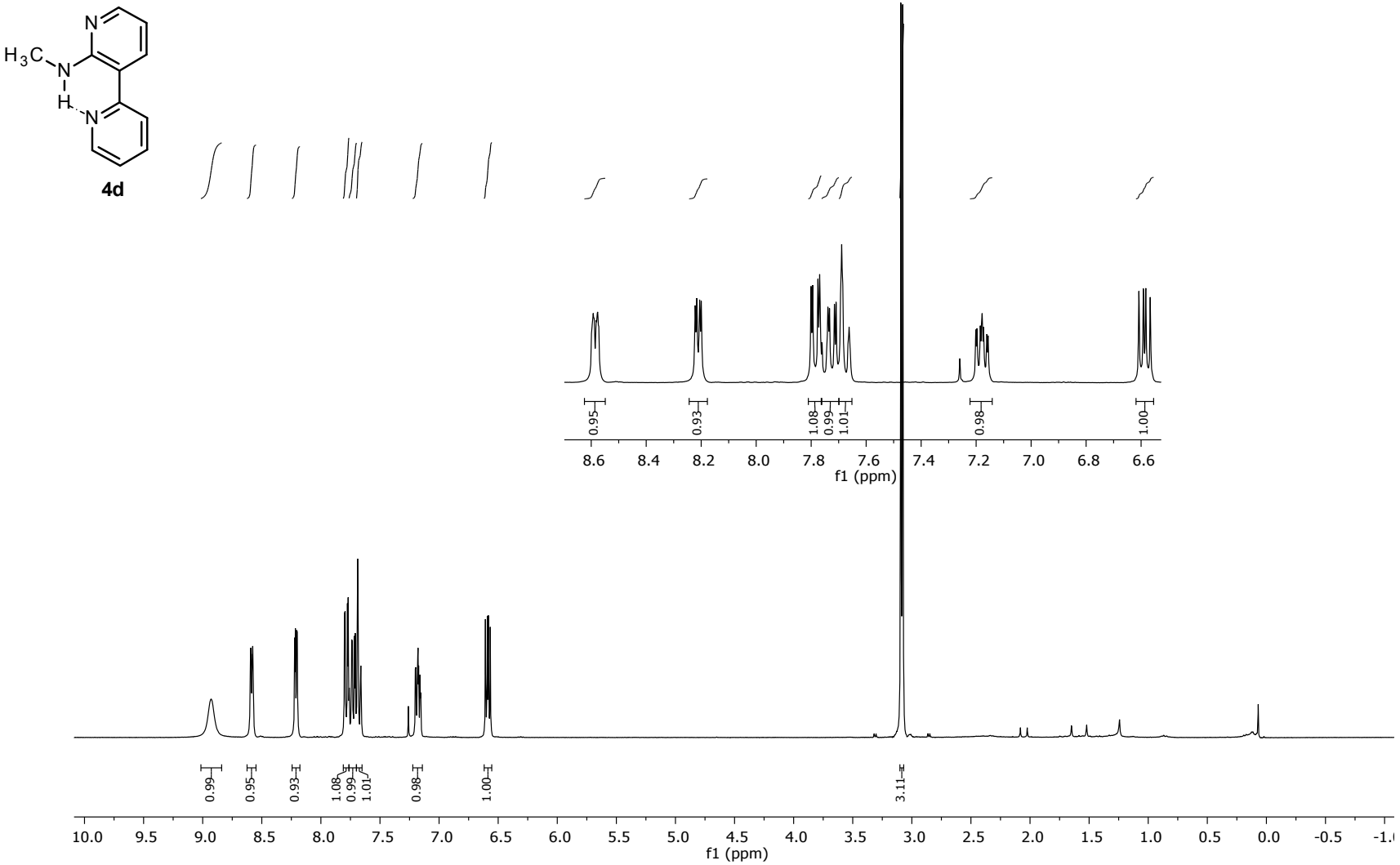


^{13}C-NMR 126 MHz, $CDCl_3$

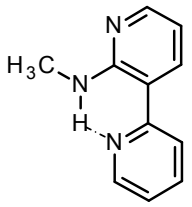


4cb

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

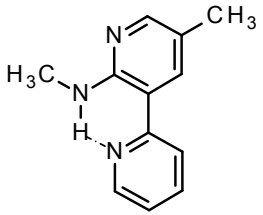


^{13}C-NMR 75 MHz, $CDCl_3$

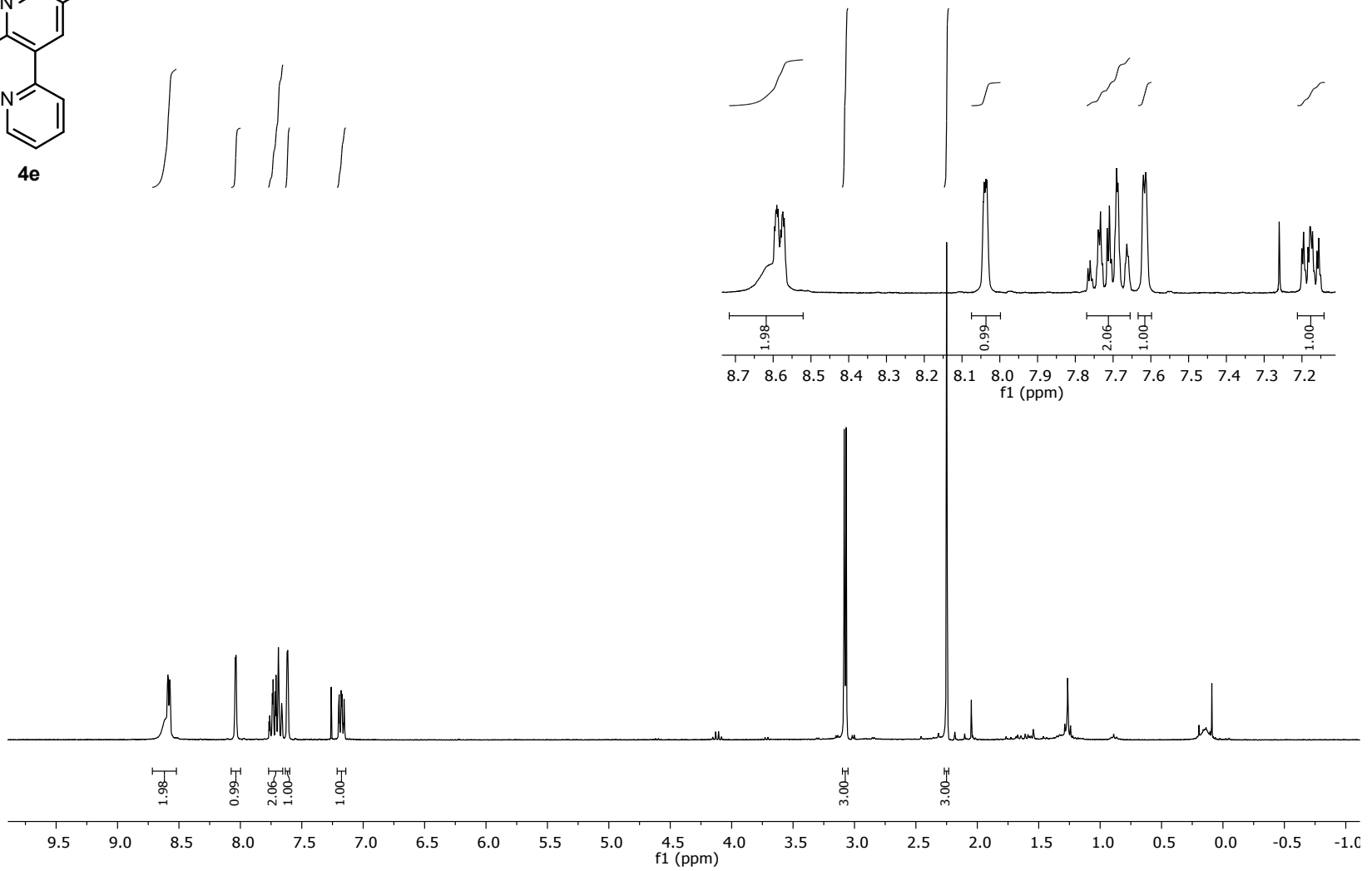


4d

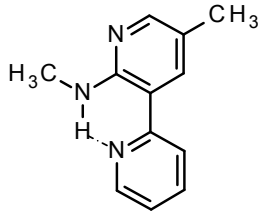
^{1}H-NMR 300 MHz, $CDCl_3$



4e



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



4e