Electronic Supplementary Information (ESI)

Synthesis of carbazoles via aryl C–H activation triggered by surfactant-associated palladium nanoparticles under microwave-assisted heating

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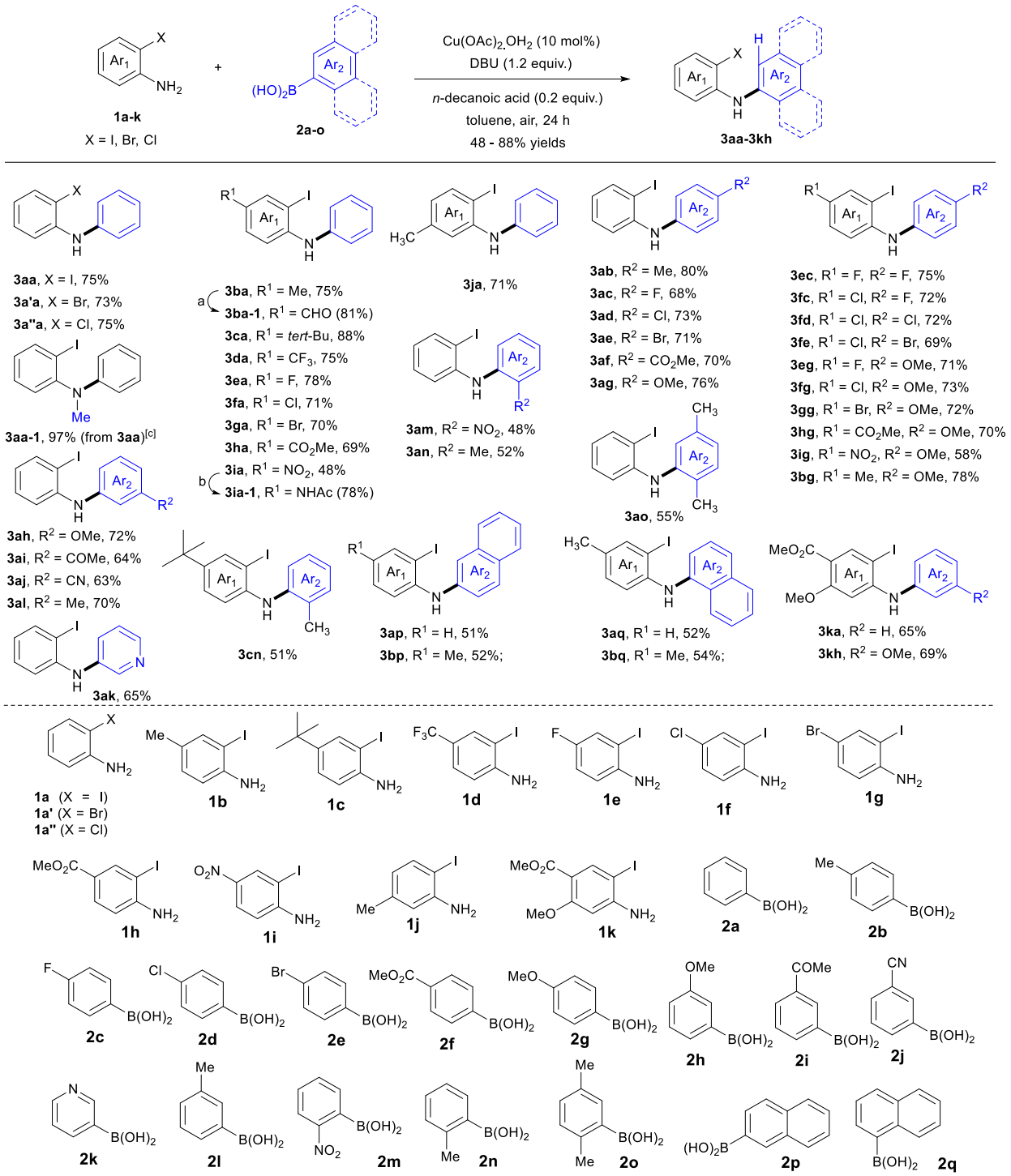
1. Materials and Instruments

All reactions were performed using oven-dried glassware and anhydrous solvents, unless mentioned otherwise. All reagents and spectroscopic grade solvents were purchased from commercial sources. Palladium catalysts and surfactants were purchased from Sigma-Aldrich. Organic base, inorganic bases, and other reagents were purchased from Spectrochem Pvt. Ltd.. All anhydrous solvents were prepared by standard drying methods and distilled before use. CEM Discover and Anton Paar microwave reactor were utilized for reactions under microwave irradiation. Progress of all reactions was monitored by thin layer chromatography (TLC) on commercial aluminum coated TLC plates from Merck (60 F254) using an ultraviolet light (256 nm) chamber and iodine chamber for visualization. Silica gel 100-200 mesh (Merck) was used for column chromatography. Melting points were measured in open capillaries and are uncorrected. IR spectra were recorded with a Shimadzu FTIR spectrometer IR Affinity-1S using the ATR (Attenuated Total Reflectance) method. Ultraviolet (UV-Vis) absorption spectra were recorded with a Shimadzu UV/Vis spectrophotometer at 25±0.1 ºC in a quartz cuvette of 1.00 cm path length. The Powdered X-ray diffraction (PXRD) study was done by Bruker D8 Advance X-ray diffractometer using Cu-Kα (λ = 1.5418 Å) radiation. The Field emission scanning electron microscopy (FE-SEM) images were taken from QUANTA FEG 250 instrument. The High resolution transmission electron microscopy (HR-TEM) images were collected from JEOL, JEM-2100F instrument, operating at an accelerating voltage of 200 kV. The EDS mapping related to this was recorded using the same instrument. NMR spectra were recorded on Bruker 250, 400 and 500 spectrometers (250 MHz, 400 MHz, 500 MHz for ^{1}H NMR, and 62.5 MHz, 100 MHz, 125 MHz for ^{13}C NMR respectively). Chemical shifts (δ) are reported in parts per million (ppm) with Me_4Si or solvent ($CDCl_3$, CD_3OD, CD_3CN, DMSO-d_6, acetone-d_6 and D_2O) signal as internal standard, and coupling constants (J) are given in Hz. Standard abbreviations are used to denote the multiplicities of the signals, such as - s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); dt (doublet of triplets); td (triplet of doublets), tt (triplet of triplets), ddd (doublet of doublet of doublets); m (multiplet); and brs (broad singlet signal). High resolution mass spectra were recorded with FTMS-ESI and mass analyzer with an Agilent system from ThermoFisher. Mass spectra were recorded on a Q-TOF micromass instrument. LCMS analysis was performed using Column: YMC TRIART C18 (50×4.6 mm, 5µ, 100 Å), mobile phase: from 95% (0.05% formic acid in water) and 5% acetonitrile to 10% (0.05% formic acid in water) and 90% acetonitrile in 5 min, Flow: 1.5 ml/min on Agilent 1200 series instrument.

2. Synthesis and characterization data of 2-halo-*N*-arylanilines 3.

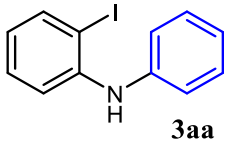
2.1 General procedure for the preparation of 2-iodo-*N*-pheylaniline 3aa: To a mixture of *o*-iodoaniline **1a** (219 mg, 1 mmol), phenylboronic acid **2a** (183 mg, 1.5 mmol) and $Cu(OAc)_2.H_2O$ (20 mg, 0.1 mmol), *n*-decanoic acid (34 mg, 0.2 mmol) was added in a 25 ml round bottom flask fitted with $CaCl_2$ guard tube. Then DBU (183 mg, 1.2 mmol) and dry toluene (3 ml) were added successively to the reaction mixture and stirred at room temperature for 24 h. The reaction mixture was diluted with water (15 ml) and extracted with ethyl acetate (15 ml × 2). Then combined organic layer was washed with water (15 ml) followed by brine solution (15 ml), and dried over anhydrous Na_2SO_4. After removal of the volatiles under reduced pressure, the residue was purified by column

chromatography on silica gel using hexane/ethyl acetate mixtures (99:1) as the eluent to yield 2-iodo-*N*-phenylaniline (**3aa**, 221 mg, 75%) as an orange gel (Scheme S1). Similarly, compounds **3a'a**, **3a"a**, **3ab-3an, 3ba-3ka, 3bn, 3bo** and **3kh** were prepared from the suitable *o*-haloanilines (**1a', 1a"** and **1b-1k**) and arylboronic acids (**2a-2q**).



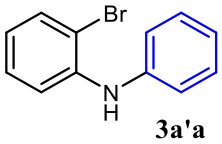
Scheme S1. Copper-catalyzed synthesis of 2-halo-*N*-arylanilines **3**. **Reaction conditions: 1** (1.0 mmol), **2** (1.5 mmol), $Cu(OAc)_2.H_2O$ (0.1 mmol), DBU (1.2 mmol), *n*-decanoic acid (0.2 mmol), dry toluene (3 ml), air, rt, 24 h. [a] DDQ (3 equiv), MeOH/THF/H_2O (16:6:1), rt, 1 h. [b] Fe dust (5 equiv.), acetic acid, reflux, 3 h. [c] **3aa** (1 mmol), MeI (2 equiv.), NaH (2 equiv.), DMF, 0 °C - rt, 8 h.

2.2 Synthesis and characterization data of 2-halo-*N*-arylanilines 3aa, 3a'a, 3a''a, 3ab-3an, 3ba-3ka, 3bn, 3bo, 3kh, 3ba-1, 3ia-1 and 3aa-1.



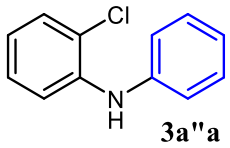
3aa

2-Iodo-*N*-phenylaniline (3aa)[1]**:** Compound **3aa** was prepared according to the general procedure from *o*-iodoaniline **1a** (219 mg, 1 mmol) and phenylboronic acid **2a** (183 mg, 1.5 mmol); and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (99:1). Orange gel (221 mg, 75% yield). ^{1}H NMR (400 MHz, DMSO-D_6): δ = 7.84 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.32-7.27 (m, 2H Ar–H), 7.22 (brs, 1H, N–H), 7.19 (d, *J* = 8.0 Hz, 2H, Ar–H), 6.94 (d, *J* = 8.0 Hz, 2H, Ar–H), 6.82 (t, *J* = 7.3 Hz, 1H, Ar–H), 6.75 (t, *J* = 7.4 Hz, 1H, Ar–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.96 (C), 142.03 (C), 139.54 (CH), 129.47 (2CH), 129.04 (CH), 122.57 (CH), 121.93 (CH), 120.02 (2 CH), 115.88 (CH), 88.77 (C) ppm; IR (ATR): $\tilde{\nu}$ = 3381 (N–H), 3010, 1575, 1495, 1444, 1307, 1007, 745, 693 cm^{-1}; LCMS: *m/z* calcd. for $[C_{12}H_{10}IN+H]^+$: 295.99; found: 295.90.



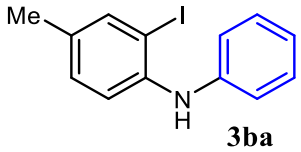
3a'a

2-Bromo-*N*-phenylaniline (3a'a)[1]**:** Compound **3a'a** was prepared according to the general procedure from *o*-bromoaniline **1a'** (172 mg, 1 mmol) and phenylboronic acid **2a** (183 mg, 1.5 mmol); and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (99:1). Colorless gel (181 mg, 73%). ^{1}H NMR (500 MHz, $CDCl_3$): δ= 7.51 (dd, *J* = 8.0, 1.5 Hz, 1H, Ar–H), 7.33-7.29 (m, 2H, Ar–H), 7.25-7.23 (m, 1H, Ar–H), 7.17-7.13 (m, 3H, Ar–H), 7.03 (tt, *J* = 8.5, 1.0 Hz, 1H, Ar–H), 6.73 (td, *J* = 7.0, 1.5 Hz, 1H, Ar–H), 6.07 (brs, 1H, N–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.63 (C), 141.46 (C), 132.98 (CH), 129.46 (2CH), 128.09 (CH), 122.71 (CH), 120.90 (CH), 120.30 (2CH), 115.82 (CH), 112.20 (C) ppm; IR (ATR): $\tilde{\nu}$ = 3405 (N–H), 3015, 1586, 1507, 1449, 1311, 1021, 748, 693 cm^{-1}; LCMS: *m/z* calcd. for $[C_{12}H_{10}BrN+H]^+$: 248.00; found: 248.00.



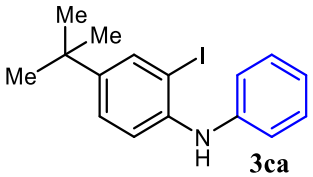
3a"a

2-Chloro-*N*-phenylaniline (3a"a)[1]**:** Compound **3a"a** was prepared according to the general procedure from *o*-chloroaniline **1a"** (127 mg, 1 mmol) and phenylboronic acid **2a** (183 mg, 1.5 mmol); and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (99:1). Colorless gel (153 mg, 75%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.35 (dd, *J* = 8.0, 1.5 Hz, 1H, Ar–H), 7.31 (tt, *J* = 7.5, 2.0 Hz, 2H, Ar–H), 7.26 (dd, *J* = 8.0, 1.5 Hz, 1H, Ar–H), 7.16-7.14 (m, 2H, Ar–H), 7.11 (td, *J* = 8.5, 1.5 Hz, 1H, Ar–H), 7.03 (tt, *J* = 7.5, 1.0 Hz, 1H, Ar–H), 6.79 (td, *J* = 7.5, 1.5 Hz, 1H, Ar–H), 6.09 (brs, 1H, N–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.49 (C), 140.28 (C), 129.72 (CH), 129.42 (2CH), 127.39 (CH), 122.63 (CH), 121.48 (C), 120.34 (CH), 120.17 (2 CH), 115.54 (CH) ppm; IR (ATR): $\tilde{\nu}$ = 3400 (N–H), 3017, 1575, 1509, 1465, 1301, 1041, 760 cm^{-1}; LCMS: *m/z* calcd for $[C_{12}H_{10}ClN+H]^+$: 204.05; found: 204.00.



3ba

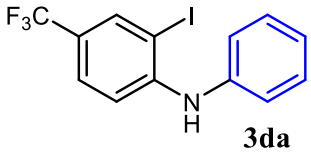
2-Iodo-4-methyl-*N*-phenylaniline (3ba)[1]**:** Compound **3ba** was prepared according to the general procedure from 4-methyl-2-iodoaniline **1b** (233 mg, 1 mmol) and phenylboronic acid **2a** (183 mg, 1.5 mmol); and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (99:1). Orange gel (232 mg, 75%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 1.5 Hz, 1H, Ar–H), 7.27-7.25 (m, 2H, Ar–H), 7.11 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.05-6.99 (m, 3H, Ar–H), 6.95 (tt, *J* = 8.5, 1.0 Hz, 1H, Ar–H), 5.73 (brs, 1H, N–H), 2.24 (s, 3H, CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.04 (C), 141.51 (C), 139.92 (C), 132.45 (CH), 129.96 (CH), 129.61 (2CH), 121.95 (CH), 119.01 (2CH), 117.25 (CH), 90.11 (C), 20.27 (CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3382 (N–H), 2950, 1602, 1507, 1246, 1033, 828 cm^{-1}; LCMS: *m/z* calcd. for $[C_{13}H_{12}IN+H]^+$: 310.00; found: 310.00.



3ca

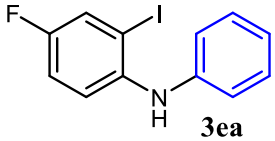
4-(*tert*-Butyl)-2-iodo-*N*-phenylaniline (3ca)[1]**:** Compound **3ca** was prepared according to the general procedure from 4-(*tert*-butyl)-2-iodoaniline **1c** (275 mg, 1 mmol) and phenylboronic acid **2a** (183 mg, 1.5 mmol); and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (99:1). Brown gel (309 mg, 88%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 2.0 Hz, 1H, Ar–H), 7.33 (td, *J* = 7.5, 1.0 Hz ,1H, Ar–H), 7.30-7.24 (m, 1H, Ar–H), 7.23 (dd, *J* = 8.5, 2.0 Hz, 1H, Ar–H), 7.16 (d, *J* = 8.5 Hz, 1H, Ar–H), 7.11-7.07 (m, 2H, Ar–H), 7.02-6.96 (m, 1H,

Ar–H), 5.79 (brs, 1H, N–H), 1.28 (s, 9H, $C(CH_3)_3$ ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.20 (C), 145.57 (C), 142.56 (C), 141.19 (C), 136.30 (CH), 129.39 (2CH), 126.15 (CH), 121.83 (CH), 119.00 (2CH), 116.32 (CH), 89.72 (C), 31.34 ($3CH_3$) ppm; IR (ATR): $\tilde{\nu}$ = 3388 (N–H), 3049, 2961, 1595, 1496, 1468, 1388, 1366, 1304, 1265, 1201, 1177, 1119, 1074, 1026, 883, 816, 747, 688, 664, 624, 592 cm^{-1}; LCMS**:** *m/z* calcd. for $[C_{16}H_{18}IN+H]^+$: 352.05.00; found: 352.20.



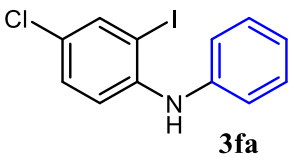
3da

2-Iodo-*N*-phenyl-4-(trifluoromethyl)aniline (3da): Compound **3da** was prepared according to the general procedure from 2-iodo-4-(trifluoromethyl)aniline **1d** (287 mg, 1 mmol) and phenylboronic acid **2a** (183 mg, 1.5 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (97:3). Red gel (272 mg, 75%); ^1H NMR (500 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 2.0 Hz, 1H, Ar–H), 7.33-7.35 (m, 1H, Ar–H), 7.33 (td, *J* = 7.5, 2.0 Hz, 1H, Ar–H), 7.19 (dd, *J* = 7.5, 2.5 Hz, 2H, Ar–H), 7.15 (t, *J* = 7.5 Hz, 1H, Ar–H), 7.11-7.08 (m, 1H, Ar–H), 7.01 (dd, *J* = 6.5, 1.0 Hz, 1H, Ar–H), 6.20 (brs, 1H, N–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.21 (C), 147.24 (C), 140.24 (C), 136.50 (C), 129.71 (2CH), 124.45 (CH), 122.22 (3CH), 118.87 (CH), 112.90 (CH), 85.62 (C) ppm; IR (ATR): $\tilde{\nu}$ = 3386 (N–H), 3018, 2914, 2852, 1732, 1597, 1503, 1493, 1471, 1389, 1306, 1274, 1224, 1169, 1151, 1078, 1025, 995, 881, 872, 808, 736, 694, 663, 539, 528 cm^{-1}; LCMS: *m/z* calcd. for $[C_{13}H_9F_3IN+H]^+$: 363.98; found: 364.00.



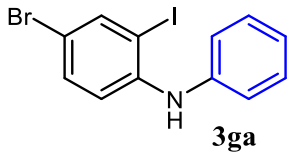
3ea

4-Fluoro-2-iodo-*N*-phenylaniline (3ea)[1]**:** Compound **3ea** was prepared according to the general procedure from 4-fluoro-2-iodoaniline **1e** (237 mg, 1 mmol) and phenylboronic acid **2a** (183 mg, 1.5 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (98:2). Light yellow gel (244 mg, 78%). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.50 (dd, *J* = 8.0, 3.0 Hz, 1H, Ar–H), 7.28 (t, *J* = 7.5 Hz, 2H, Ar–H), 7.15 (dd, *J* = 9.0, 5.0 Hz, 1H, Ar–H), 7.02-6.94 (m, 4H, Ar–H), 5.67 (brs, 1H, N–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.78 (d, J_{CF} = 244.4 Hz, C), 142.76 (C), 140.47 (C), 129.52 (2CH), 125.84 (d, J_{CF} = 24.5 Hz, CH), 122.05 (CH), 118.79 (2CH), 117.98 (d, J_{CF} = 7.7 Hz, CH), 115.98 (d, J_{CF} = 21.8 Hz, CH), 89.06 (d, J_{CF} = 8.1 Hz, C) ppm; IR (ATR): $\tilde{\nu}$ = 3384 (N–H), 2920, 1508, 1458, 1238, 1180, 1034, 833 cm^{-1}; LCMS: *m/z* calcd. for $[C_{12}H_9FIN+H]^+$: 313.98; found: 314.00.



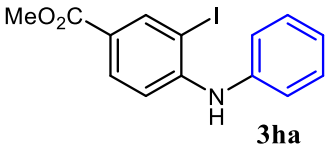
3fa

4-Chloro-2-iodo-*N*-phenylaniline (3fa)[1]**:** Compound **3fa** was prepared according to the general procedure from 4-chloro-2-iodoaniline **1f** (253 mg, 1 mmol) and phenylboronic acid **2a** (183 mg, 1.5 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (99:1). Light yellow gel (234 mg, 71%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.72 (d, J = 2.5 Hz, 1H, Ar–H), 7.31 (t, J = 8.0 Hz, 2H, Ar–H), 7.15 (dd, J = 9.0, 2.5 Hz, 1H, Ar–H), 7.10-7.03 (m, 4H, Ar–H), 5.85 (brs, 1H, N–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.95 (C), 141.64 (C), 138.39 (CH), 129.58 (2CH), 129.02 (CH), 125.17 (C), 123.03 (CH), 120.29 (2CH), 115.96 (CH), 88.06 (C) ppm; IR (ATR): $\tilde{\nu}$ = 3383 (N–H), 1591, 1507, 1462, 1313, 759 cm^{-1}; LCMS: *m/z* calcd. for $[C_{12}H_9ClIN+H]^+$: 329.95; found: 329.90.



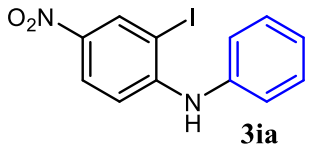
3ga

4-Bromo-2-iodo-*N*-phenylaniline (3ga)[1]**:** Compound **3ga** was prepared according to the general procedure from 4-bromo-2-iodoaniline **1g** (298 mg, 1 mmol) and phenylboronic acid **2a** (183 mg, 1.5 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (99:1). Colourless gel (262 mg, 70%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.85 (d, J = 2.3 Hz, 1H, Ar–H), 7.30 (td, J = 7.4, 2.0 Hz, 2H, Ar–H), 7.26 (dd, J = 8.4, 2.4 Hz, 1H, Ar–H), 7.10-7.07 (m, 2H, Ar–H), 7.04 (tt, J = 7.2, 1.3 Hz, 1H, Ar–H), 7.00 (d, J = 8.8 Hz, 1H, Ar–H), 5.86 (brs, 1H, N–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.63 (C), 141.68 (C), 141.20 (CH), 132.10 (CH), 129.81 (2CH), 123.40 (CH), 120.71 (2CH), 116.51 (CH), 112.23 (C), 88.63 (C) ppm; IR (ATR): $\tilde{\nu}$ = 3386 (N–H), 2928, 1584, 1510, 1452, 1316, 1073, 1010, 812, 748 cm^{-1}; LCMS: *m/z* calcd. for $[C_{12}H_9BrIN+H]^+$: 373.90; found: 373.90.



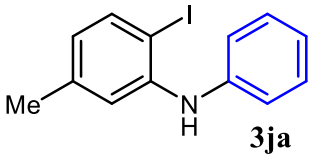
3ha

Methyl 3-iodo-4-(phenylamino)benzoate (3ha)[1]**:** Compound **3ha** was prepared from methyl 4-amino-3-iodobenzoate **1h** (277 mg, 1 mmol) and phenylboronic acid **2a** (183 mg, 1.5 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (98:2). Colorless gel (244 mg, 69% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.43 (d, J = 2.0 Hz, 1H, Ar–H), 7.82 (dd, J = 8.5, 2.0 Hz, 1H, Ar–H), 7.37 (t, J = 7.5 Hz, 2H, Ar–H), 7.20 (d, J = 7.5 Hz, 2H, Ar–H), 7.16 (t, J = 7.5 Hz, 1H, Ar–H), 7.04 (d, J = 8.5 Hz, 1H, Ar–H), 6.32 (brs, 1H, N–H), 3.88 (s, 3H, CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.65 (C=O), 148.19 (C), 141.27 (CH), 140.11 (C), 130.95 (CH), 129.69 (2CH), 124.59 (CH), 122.52 (2CH), 122.20 (C), 112.22 (CH), 85.45 (C), 51.92 (CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3369 (N–H), 2947, 1708 (C=O), 1585, 1513, 1497, 1436, 1265, 1115, 762 cm^{-1}; LCMS: *m/z* calcd. for $[C_{14}H_{12}INO_2+H]^+$: 353.99; found: 354.00.



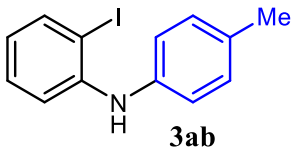
3ia

2-Iodo-4-nitro-*N*-phenylaniline (3ia)[1]**:** Compound **3ia** was prepared according to the general procedure from 2-iodo-4-nitroaniline **1i** (264 mg, 1 mmol) and phenylboronic acid **2a** (183 mg, 1.5 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (97:3). Yellow gel (163 mg, 48% yield).^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.66 (d, J = 2.5 Hz, 1H, Ar–H), 8.07 (dd, J = 9.3, 2.2 Hz, 1H, Ar–H), 7.43 (td, J = 8.2, 0.6 Hz, 2H, Ar–H), 7.25-7.23 (m, 3H, Ar–H), 6.95 (d, J = 9.5 Hz, 1H, Ar–H), 6.59 (brs, 1H, N–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 150.15 (C), 139.77 (C), 139.01 (C), 135.64 (CH), 129.97 (2CH), 125.97 (CH), 125.55 (CH), 123.72 (2CH), 110.96 (CH), 83.60 (C) ppm; IR (ATR): $\tilde{\nu}$ = 3360 (N–H), 2917, 1572, 1490 (N–O), 1308, 1281, 1113, 893, 743 cm^{-1}; LCMS: *m/z* calcd. for $[C_{12}H_9IN_2O_2+H]^+$: 340.97; found: 341.10.



3ja

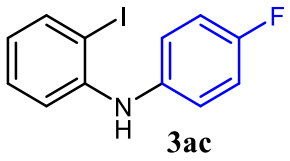
2-Iodo-5-methyl-*N*-phenylaniline (3ja)[1]**:** Compound **3ja** was prepared according to the general procedure from 2-iodo-5-methylaniline **1j** (233 mg, 1 mmol) and phenylboronic acid **2a** (183 mg, 1.5 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (99:1). Orange gel (219 mg, 71%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.61 (d, J = 8.0 Hz, 1H, Ar–H), 7.31 (td, J = 7.5, 2.0 Hz, 2H, Ar–H), 7.11 (dt, J = 7.4, 1.2 Hz, 2H, Ar–H), 7.02 (tt, J = 7.5, 1.2 Hz, 2H, Ar–H), 6.46 (dd, J = 8.0, 2.5 Hz, 1H, Ar–H), 5.91 (brs, 1H, N–H), 2.22 (s, 3H, CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.67 (C), 142.05 (C), 139.26 (C), 139.12 (CH), 129.44 (2CH), 123.17 (CH), 122.39 (CH), 119.96 (2CH), 116.66 (CH), 84.89 (C), 21.24 (CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3379 (N–H), 2920, 1587, 1515, 1309, 1008, 744 cm^{-1}; LCMS: *m/z* calcd. for $[C_{13}H_{12}IN-H]^+$: 310.00; found: 310.20.



3ab

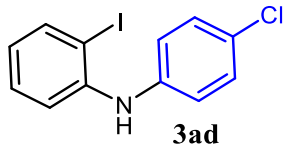
2-Iodo-*N*-(*p*-tolyl)aniline (3ab)[1]**:** Compound **3ab** was prepared from 2-iodoaniline **1a** (219 mg, 1 mmol) and *p*-tolylboronic acid **2b** (205 mg, 1.5 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (99:1). Light yellow gel (247 mg, 80% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.74 (dd, J = 7.8, 1.5 Hz, 1H, Ar–H), 7.17-7.12 (m, 3H, Ar–H), 7.08-7.03 (m, 3H, Ar–H), 6.56 (td, J = 7.4, 1.6 Hz, 1H, Ar–H), 5.83 (brs, 1 H, N–H), 2.32 (s, 3H, CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 144.88 (C), 139.64 (CH), 139.41 (C),

132.07 (C), 130.10 (2CH), 129.23 (CH), 121.40 (3CH), 115.14 (CH), 88.04 (C), 21.02 (CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3378 (N–H), 2920, 1587, 1514, 1448, 1308, 1007, 806, 743 cm^{-1}; LCMS: *m/z* calcd.for $[C_{13}H_{12}IN+H]^+$: 310.00; found: 310.00.



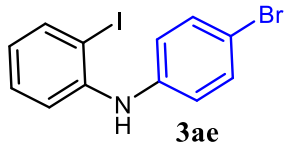
3ac

***N*-(4-fluorophenyl)-2-iodoaniline (3ac)[1]:** Compound **3ac** was prepared according to the general procedure from 2-iodoaniline **1a** (219 mg, 1 mmol) and 4-fluorophenylboronic acid **2c** (210 mg, 1.5 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (98:2). Red gel (213 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (dd, *J* = 7.9, 1.2 Hz, 1H, Ar–H), 7.15 (td, *J* = 8.2, 1.2 Hz, 1H, Ar–H), 7.11-7.07 (m, 2H, Ar–H), 7.03-6.96 (m, 3H, Ar–H), 6.58 (td, *J* = 8.4, 1.2 Hz, 1H, Ar–H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.61 (d, J_{CF} = 234.6 Hz, C), 144.70 (C), 140.12 (C), 139.57 (2CH), 129.07 (2CH), 123.33 (d, J_{CF} = 4.4 Hz, CH), 119.41 (d, J_{CF} = 7.5 Hz, CH), 119.34 (d, J_{CF} = 7.5 Hz, CH), 115.53 (d, J_{CF} = 22.1 Hz, CH), 91.87 (C) ppm; IR (ATR): $\tilde{\nu}$ = 3350 (N–H), 2900, 1495, 1455, 1242, 1177, 1031, 828 cm^{-1}; LCMS: *m/z* calcd. for$[C_{12}H_9FIN+H]^+$: 313.98; found: 314.00.



3ad

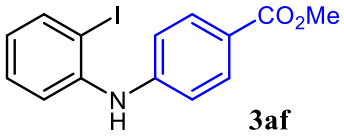
***N*-(4-chlorophenyl)-2-iodoaniline (3ad):** Compound **3ad** was prepared according to the general procedure from 2-iodoaniline **1a** (219 mg, 1 mmol) and 4-chlorophenylboronic acid **2d** (234 mg, 1.5 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (98:2). Brown gel (241 mg, 73%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.77 (dd, *J* = 8.0, 1.5 Hz, 1H, Ar–H), 7.26-7.13 (m, 4H, Ar–H), 7.05-7.02 (m, 2H, Ar–H), 6.65 (td, *J* = 7.0, 1.5 Hz, 1H, Ar–H), 5.85 (brs, 1H, N–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.48 (C), 140.72 (C), 139.61 (CH), 129.44 (2CH), 129.12 (CH), 127.19 (C), 122.45 (CH), 120.93 (2CH), 116.18 (CH), 89.13 (C) ppm; IR (ATR): $\tilde{\nu}$ = 3381 (N–H), 2929, 1585, 1505, 1450, 1311, 1012, 750 cm^{-1}; LCMS: *m/z* calcd. for$[C_{12}H_9ClIN+H]^+$: 329.95; found: 330.00.



3ae

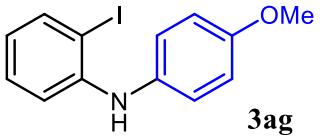
***N*-(4-bromophenyl)-2-iodoaniline (3ae)[1]:** Compound **3ae** was prepared according to the general procedure from 2-iodoaniline **1a** (233 mg, 1 mmol) and (4-bromophenyl)boronic acid **2e** (301 mg, 1.5 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (99:1). Off white solid (266 mg, 71%); m.p.: 46-48 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.39 (dd, *J* = 8.4, 2.0 Hz, 2H, Ar–H), 7.23-7.15

(m, 2H, Ar–H), 6.98 (dd, J = 8.4, 1.6 Hz, 2H, Ar–H), 6.66 (td, J = 7.6, 1.6 Hz, 1H, Ar–H), 5.84 (brs, 1H, N–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.35 (C), 141.35 (C), 139.67 (CH), 132.40 (2CH), 129.17 (CH), 122.68 (CH), 121.10 (2CH), 116.53 (CH), 114.48 (C), 89.46 (C) ppm; IR (ATR): $\tilde{\nu}$ = 3385 (N–H), 2927, 1584, 1509, 1452, 1315, 1009, 748 cm^{-1}; LCMS: *m/z* calcd. for$[C_{12}H_9BrIN+H]^+$: 373.90; found: 373.90.



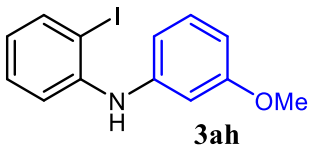
3af

Methyl 4-((2-iodophenyl)amino)benzoate (3af)[1]**:** Compound **3af** was prepared according to the general procedure from 2-iodoaniline **1a** (219 mg, 1 mmol) and 4-carbomethoxyphenylboronic acid **2f** (270 mg, 1.5 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (90:10). Colorless gel (247 mg, 70%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.95 (dd, J = 7.0, 2.0 Hz, 2H, Ar–H), 7.83 (dd, J = 8.0, 1.5 Hz, 1H, Ar–H), 7.37 (dd, J = 8.0, 1.5 Hz, 1H, Ar–H), 7.29 (td, J = 8.5, 1.5 Hz, 1H, Ar–H), 7.03 (dd, J = 7.0, 2.0 Hz, 2H, Ar–H), 6.76 (td, J = 7.5, 1.5 Hz, 1H, Ar–H), 6.07 (brs, 1H, N–H), 3.88 (s, 3H, CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.81 (C=O), 147.02 (C), 141.86 (C), 139.81 (CH), 131.49 (2CH), 129.18 (CH), 124.35 (CH), 122.44 (C), 119.48 (CH), 115.97 (2CH), 91.77 (C), 51.82 (CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3379, 3338 (N–H), 2946, 1702 (C=O), 1605, 1585, 1518, 1434, 1279, 1175, 1110, 1012, 767 cm^{-1}; LCMS: *m/z* calcd. for $[C_{14}H_{12}INO_2+H]^+$: 353.99; found: 354.00.



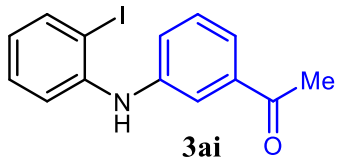
3ag

2-Iodo-*N*-(4-methoxylphenyl)aniline (3ag)[1]**:** Compound **3ag** was prepared from 2-iodoaniline **1a** (219 mg, 1 mmol) and 4-methoxyphenylboronic acid **2g** (228 mg, 1.5 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (98:2). Light yellow gel (247 mg, 76% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.71 (dd, J = 8.0, 1.5 Hz, 1H, Ar–H), 7.12-7.09 (m, 3H Ar–H), 6.89-6.86 (m, 3H, Ar–H), 6.52 (td, J = 8.0, 1.5 Hz, 1H, Ar–H), 5.77 (brs, 1H, N–H), 3.81 (s, 3H, CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.41 (C), 145.74 (C), 139.35 (CH), 134.56 (C), 129.09 (CH), 124.60 (2CH), 120.53 (CH), 114.80 (2CH), 113.81 (CH), 86.61 (C), 55.58 (CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3392 (N–H), 3186, 2361, 1624, 1582, 1473, 1438, 1300, 1005, 893, 743 cm^{-1}; LCMS: *m/z* calcd. for $[C_{13}H_{12}INO+H]^+$: 326.00; found: 326.00.



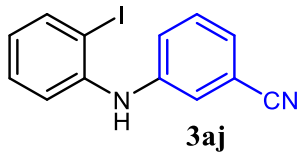
3ah

2-Iodo-*N*-(3-methoxylphenyl)aniline (3ah)[1]**:** Compound **3ah** was prepared according to the general procedure from 2-iodoaniline **1a** (219 mg, 1 mmol) and 3-methoxyphenylboronic acid **2h** (228 mg, 1.5 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (98:2). Light yellow gel (234 mg, 72%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.77 (dd, *J* = 8.0, 1.5 Hz, 1H, Ar–H), 7.23-7.18 (m, 3H, Ar–H), 6.67 (dd, *J* = 8.0, 2.0 Hz, 1 H, Ar–H), 6.42 (t, *J* = 2.0 Hz, 1H, Ar–H), 6.62 (td, *J* = 8.0, 2.0 Hz, 1H, Ar–H), 6.57 (ddd, *J* = 8.0, 2.0, 0.5 Hz, 1H, Ar–H), 5.89 (brs, 1H, N–H), 3.79 (s, 3H, CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.96 (C), 143.87 (C), 143.64 (C), 139.73 (CH), 130.39 (CH), 129.25 (CH), 122.41 (CH), 116.85 (CH), 112.31 (CH), 108.00 (CH), 105.61 (CH), 89.40 (C), 55.49 (CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3384 (N–H), 2982, 2358, 1601, 1492, 1158, 1044, 1009, 745 cm^{-1}. LCMS: *m/z* calcd. for $[C_{13}H_{12}INO+H]^+$: 326.00; found: 326.00.



3ai

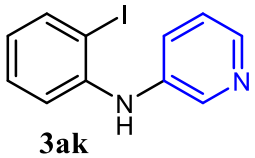
2-Iodo-*N*-(3-acetylphenyl)aniline (3ai)[1]**:** Compound **3ai** was prepared from 2-iodoaniline **1a** (219 mg, 1 mmol) and 3-acetylphenylboronic acid **2i** (184 mg, 1.5 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (95:5). Off-white solid (216 mg, 64% yield); m.p.: 86-88 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.80 (dd, *J* = 8.0, 1.0 Hz, 1H, Ar–H), 7.67 (t, *J* = 2.0 Hz, 1 H, Ar–H), 7.57 (dd, *J* = 8.0, 1.5 Hz, 1–H, Ar–H), 7.38 (t, *J* = 8.0 Hz, 1H, Ar–H), 7.30 (dd, *J* = 8.0, 2.5 Hz, 1H, Ar–H), 7.22 (td, *J* = 7.0, 1.5 Hz, 2H, Ar–H), 6.68 (td, *J* = 8.5, 2.5 Hz, 1H, Ar–H), 5.97 (brs, 1H, N–H), 2.56 (s, 3H, CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.89 (C=O), 143.17 (C), 142.81 (C), 139.73 (CH), 138.55 (C), 129.67 (CH), 129.22 (CH), 123.50 (CH), 122.94 (CH), 122.17 (CH), 118.44 (CH), 116.77 (CH), 89.76 (C), 26.75 (CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3328 (N–H), 2921, 1670 (C=O), 1596, 1575, 1518, 1480, 1439, 1353, 1308, 1006, 905, 784, 750 cm^{-1}; LCMS: *m/z* calcd. for $[C_{14}H_{12}INO+H]^+$: 338.00; found: 338.20.



3aj

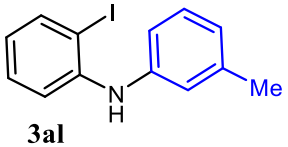
2-**Iodo-*N*-(3-cyanophenyl)aniline (3aj)**[1]**:** Compound **3aj** was prepared from 2-iodoaniline **1a** (219 mg, 1 mmol) and 3-cyanophenylboronic acid **2j** (220 mg, 1.5 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (98:2). Off-white solid (202 mg, 63% yield); m.p.: 92-94 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.83 (dd, *J* = 8.0, 1.5 Hz, 1H, Ar–H), 7.35 (t, *J* = 8.0 Hz, 1H, Ar–H), 7.31-7.21 (m, 5H, Ar–H), 6.76 (td, *J* = 8.0, 1.5 Hz, 1H, Ar–H), 5.93 (brs, 1H, N–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.64 (C), 142.09 (C), 139.92 (CH), 130.35 (CH), 129.35 (CH), 124.87 (CH), 124.28 (CH), 122.23 (CH), 120.46 (CH), 118.75 (C), 118.54 (CH), 113.44

(CN), 91.27 (C) ppm; IR (ATR): $\tilde{\nu}$ = 3342 (N–H), 2917, 2227 (C–N), 1601, 1573, 1520, 1460, 1344, 1300, 1014, 848, 785, 757 cm^{-1}; LCMS: *m/z* calcd. for $[C_{13}H_9IN_2+H]^+$: 320.98; found: 321.00.



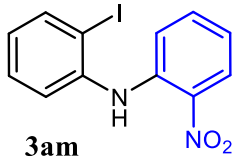
3ak

***N*-(2-iodophenyl)pyridin-3-amine (3ak)[1]:** Compound **3ak** was prepared according to the general procedure from 2-iodoaniline **1a** (109 mg, 0.5 mmol) and 3-pyridylboronic acid **2k** (92 mg, 0.75 mmol); and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (85:15). Red gel (96 mg, 65%); ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.38 (d, *J*=2.8 Hz, 1H; Ar–H), 8.20 (dd, *J*=4.8, 1.2 Hz, 1H; Ar–H), 7.73 (dd, *J*= 8.0, 1.6 Hz, 1H; Ar–H), 7.38-7.35 (m, 1H; Ar–H), 7.17-7.14 (m, 2H; Ar–H), 7.11-7.09 (m, 1H; Ar–H), 6.63 (ddd, *J*= 8.2, 7.6, 1.6 Hz, 1H; Ar–H), 5.80 (brs, 1H; N–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ= 143.47 (CH), 142.94 (CH), 141.90 (CH), 139.79 (CH), 138.82 (C), 129.27 (CH), 125.83 (CH), 123.88 (C), 123.15 (CH), 116.44 (CH), 89.68 (C) ppm; IR (ATR): $\tilde{\nu}$ = 3385 (N–H), 3024, 2361, 1570, 1485, 1325, 1050, 755 cm^{-1}. LCMS: *m/z* calcd. for $[C_{11}H_9IN_2+H]^+$: 296.98; found: 297.00.



3al

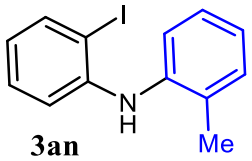
2-Iodo-*N*-(*m*-tolyl)aniline (3al): Compound **3al** was prepared according to the general procedure from 2-iodoaniline **1a** (219 mg, 1 mmol) and m-tolylboronic acid **2l** (205 mg, 1.5 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (98:2). Light Brown solid (216 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.26-7.24 (m, 3H, Ar–H), 7.01-6.90 (m, 3H, Ar–H) 6.69-6.65 (m, 1H, Ar–H), 5.93 (brs, 1H, N–H) 2.31 (s, 3H, -CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 144.48 (C), 142.38 (C), 139.95 (CH), 139.86 (C), 129.73 (CH), 129.48 (CH), 123.88 (CH), 122.23 (CH), 121.17 (CH), 117.49 (CH), 116.36 (CH), 89.18 (C), 21.94 (CH_3) ppm; LCMS: *m/z* calcd. for $[C_{13}H_{12}IN+H]^+$: 310.00; found: 310.20.



3am

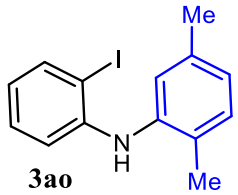
2-Iodo-*N*-(2-nitrophenyl)aniline (3am)[1]: Compound **3am** was prepared according to the general procedure from 2-iodoaniline **1a** (219 mg, 1 mmol) and 2-nitrophenylboronic acid **2m** (250 mg, 1.5 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (95:5). Red solid (163 mg, 48%); m.p.: 62-64 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.33 (brs, 1 H, N–H), 8.16 (dd, *J* = 8.4, 1.2 Hz, 1H, Ar–H), 7.88 (dd, *J* = 8.2, 1.2 Hz, 1H, Ar–H), 7.34-7.29 (m, 3H, Ar–H), 6.96 (dd, *J* = 8.8, 1.2 Hz, 1H, Ar–H), 6.89 (ddd, *J* = 8.4, 8.4, 2.8 Hz, 1H, Ar–H), 6.77 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H, Ar–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.99 (C), 140.71 (C), 140.34

(CH), 135.67 (CH), 133.84 (C), 129.28 (CH), 127.27 (CH), 126.72 (CH), 125.12 (CH), 118.42 (CH), 116.20 (CH), 96.41 (C) ppm; IR (ATR): $\tilde{\nu}$ = 3325 (N–H), 2920, 2359, 1610, 1570, 1510 (N-O), 1346, 1252, 1145, 738 cm^{-1}; LCMS: *m/z* calcd. for $[C_{12}H_9IN_2O_2+H]^+$: 340.97; found: 341.00.



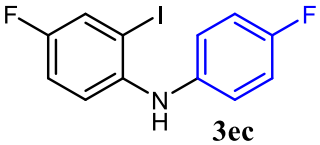
3an

2-Iodo-*N*-(*o*-tolyl)aniline (3an): Compound **3an** was prepared according to the general procedure from 2-iodoaniline **1a** (219 mg, 1 mmol) and 2-methylphenylboronic acid **2n** (205 mg, 1.5 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (98:2). Brown gel (161 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 7.7 Hz, 1H, Ar–H), 7.23-7.12 (m, 4H, Ar–H), 7.04-7.01 (m, 1H, Ar–H), 6.83 (d, *J* = 8.0 Hz, 1H, Ar–H), 6.56 (t, *J* = 7.8 Hz, 1H, Ar–H), 2.25 (s, 3H, -CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.18 (C), 144.51 (C), 140.02 (C), 139.30 (CH), 131.10 (CH), 129.05 (CH), 126.84 (CH), 123.74 (CH), 121.69 (CH), 121.06 (CH), 114.94 (CH), 87.78 (C), 18.00 (CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3390 (N–H), 2911, 1580, 1512, 1480, 1452, 1373, 1301, 1247, 1155, 1041, 1002, 890, 807, 744, 683, 645 cm^{-1}; LCMS: *m/z* calcd. for $[C_{13}H_{12}IN+H]^+$: 310.00; found: 310.10.



3ao

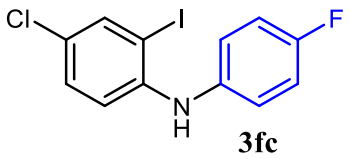
***N*-(2-iodophenyl)-2,5-dimethylaniline (3ao):** Compound **3ao** was prepared according to the general procedure from 2-iodoaniline **1a** (219 mg, 1 mmol) and 2,5-dimethylphenylboronic acid **2o** (225 mg, 1.5 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (98:2). Colourless gel (178 mg, 55%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.74 (dd, *J* = 8.0, 2.0, Hz, 1H, Ar–H), 7.16 (d, *J* = 2.0, 1H, Ar–H), 7.13 (t, *J* = 7.5, Hz, 1H, Ar–H), 7.03 (s, 1H, Ar–H), 6.85 (dd, *J* = 7.5 ,1.0 Hz, 1H, Ar–H), 6.82 (dd, *J* = 8.0, 1.5 Hz, 1H, Ar–H), 6.56 (td, *J* = 7.5, 1.5 Hz, 1H, Ar–H), 5.69 (brs, 1H, N–H), 2.29 (s, CH_3), 2.21 (s, CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 144.70 (C), 139.79 (C), 139.26 (CH), 136.58 (C), 130.89 (CH), 129.04 (CH), 127.83 (C), 124.61 (CH), 122.56 (CH), 120.88 (CH), 114.91 (CH), 87.64 (C), 21.05 (CH_3), 17.53 (CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3391 (N–H), 2916, 2850, 1580, 1515, 1484, 1448, 1375, 1304, 1253, 1156, 1121, 1043, 1002, 878, 807, 744, 683, 564 cm^{-1}; LCMS: *m/z* calcd. for $[C_{14}H_{14}IN+H]^+$: 324.02; found: 324.20.



3ec

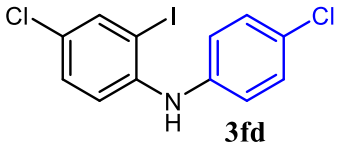
4-Fluoro-N-(4-fluorophenyl)-2-iodoaniline (3ec): Compound **3ec** was prepared according to the general procedure from 4-fluoro-2-iodoaniline **1e** (237 mg, 1 mmol) and 4-fluorophenylboronic acid **2c** (210 mg, 1.5 mmol),

and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (98:2). Colourless gel (248 mg, 75%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.50 (dd, J = 8.0, 2.5 Hz, 1H, Ar–H), 7.02-6.92 (m, 6H, Ar–H), 5.60 (brs, 1H, N–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.67 (d, J_{CF} = 240.0 Hz, C), 156.46 (d, J_{CF} = 242.2, Hz, C), 141.20 (d, J_{CF} = 2.4 Hz, C), 138.52 (d, J_{CF} = 2.5 Hz, C), 125.84 (d, J_{CF} = 24.7 Hz, CH), 121.87 (d, J_{CF} = 8.1 Hz, CH), 116.30 (2CH), 116.18 (d, J_{CF} = 14.7 Hz, CH), 115.98 (d, J_{CF} = 22.2 Hz, CH), 87.73 (d, J_{CF} = 8.6 Hz, C) ppm; IR (ATR): $\tilde{\nu}$ = 3360 (N–H), 2925, 2850, 1881, 1575, 1506, 1460, 1380, 1306, 1230, 1210, 1160, 1080, 1020, 850, 780, 725, 650 cm^{-1}; LCMS: *m/z* calcd. for $[C_{12}H_8F_2IN+H]^+$: 331.97; found: 332.00.



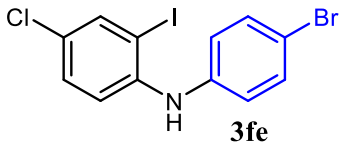
3fc

4-Chloro-*N*-(4-fluorophenyl)-2-iodoaniline (3fc): Compound **3fc** was prepared according to the general procedure from 4- chloro-2-iodoaniline **1f** (253 mg, 1 mmol) and 4-fluorophenylboronic acid **2c** (210 mg, 1.5 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (98:2). Colourless gel (250 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, J = 4.0, Hz, 1H, Ar–H), 7.17-7.04 (m, 5H, Ar–H), 6.92-6.89 (m, 1H, Ar–H), 5.82 (brs, 1 H, N–H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.24 (d, J_{CF} = 242.0 Hz, C), 143.69 (C), 138.39 (CH), 137.46 (d, J_{CF} = 3.0 Hz, C), 129.14 (CH), 124.80 (C), 123.44 (d, J_{CF} = 4.0 Hz, 2CH), 116.37 (d, J_{CF} = 22.0 Hz, 2CH), 114.93 (CH), 87.14 (C) ppm; IR (ATR): $\tilde{\nu}$ = 3383 (N–H), 2921, 2854, 1878, 1582, 1508, 1453, 1376, 1225, 1153, 1089, 866, 779 cm^{-1}; LCMS: *m/z* calcd. for $[C_{12}H_8ClFIN+H]^+$: 347.94; found: 348.00.



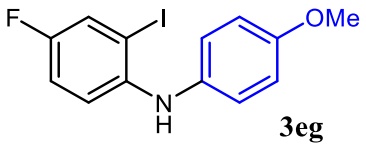
3fd

4-Chloro-*N*-(4-chlorophenyl)-2-iodoaniline (3fd): Compound **3fd** was prepared according to the general procedure from 4- chloro-2-iodoaniline **1f** (253 mg, 1 mmol) and 4-chlorophenylboronic acid **2d** (234 mg, 1.5 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (98:2). Off White solid (262 mg, 72%); mp: 60-62 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.74 (d, J = 8.0 Hz, 1H, Ar–H), 7.28-7.26 (m, 2H, Ar–H), 7.18-7.16 (m, 1H, Ar–H), 7.03-7.01 (m, 3H, Ar–H), 5.80 (brs, 1H, N–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.49 (C), 140.33 (C), 138.50 (CH), 129.57 (2CH), 129.12 (CH), 127.74 (C), 125.77 (C), 121.23 (2CH), 116.28 (CH), 88.48 (C) ppm; IR (ATR): $\tilde{\nu}$ = 3382 (N–H), 2950, 2855, 1712, 1604, 1575, 1505, 1471, 1360, 1215, 1153, 1098, 1040, 919, 871, 835, 767, 676, 567 cm^{-1}; LCMS: *m/z* calcd. for $[C_{12}H_8Cl_2IN+H]^+$: 363.91; found: 364.00.



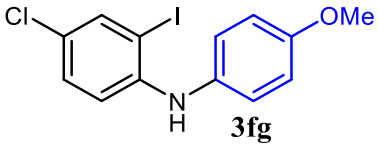
3fe

4-Chloro-2-iodo-*N*-(4-bromophenyl)aniline (3fe)[1]**:** Compound **3fe** was prepared according to the general procedure from 4-chloro-2-iodoaniline **1f** (253 mg, 1.0 mmol) and 4-bromophenylboronic acid **2e** (301 mg, 1.5 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (99:1). Off-white solid (282 mg, 69%); mp: 60-62 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.74 (d, J = 2.0 Hz, 1H, Ar–H), 7.40 (dt, J = 8.7, 3.0 Hz, 2H, Ar–H), 7.18 (dd, J = 8.5, 2.0 Hz, 1H, Ar–H), 7.05 (d, J = 9.0 Hz, 1H, Ar–H), 6.95 (dt, J = 8.8, 3.0 Hz, 2H, Ar–H), 5.79 (brs, 1H, N–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.33 (C), 140.94 (C), 138.54 (CH), 132.51 (2CH), 129.14 (CH), 126.01 (C), 121.36 (2CH), 116.58 (CH), 115.03 (C), 88.77 (C) ppm; IR (ATR): $\tilde{\nu}$ = 3368 (N–H), 2924, 1576, 1482, 1377, 1305, 1265, 1067, 1007, 867, 802, 694 cm^{-1}; LCMS: *m/z* calcd. for $[C_{12}H_8BrClIN+H]^+$: 407.86; found: 407.90.



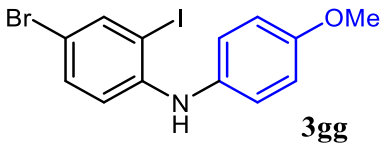
3eg

4-Fluoro-2-iodo-*N*-(4-methoxyphenyl)aniline (3eg) [1]**:** Compound **3eg** was prepared from 4-fluoro-2-iodoaniline **1e** (237 mg, 1 mmol) and 4-methoxyphenylboronic acid **2g** (228 mg, 1.5 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (95:5). Colorless gel (243 mg, 71% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.46 (dd, J = 8.0, 3.0 Hz, 1H, Ar–H), 7.05-7.03 (m, 2H, Ar–H), 6.89-6.84 (m, 3H, Ar–H), 6.83 (dd, J = 9.0, 5.0 Hz, 1H, Ar–H), 5.58 (brs, 1H, N–H), 3.80 (s, 3H, CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.18 (C), 155.85 (d, J_{CF} = 240.9 Hz, C), 142.43 (d, J_{CF} = 2.4 Hz, C), 135.24 (C), 125.61 (d, J_{CF} = 24.5 Hz, CH), 123.71 (2CH), 115.86 (d, J_{CF} = 22.1 Hz, CH), 114.88 (2CH), 114.75 (d, J_{CF} = 7.4 Hz, CH), 85.95 (d, J_{CF} = 8.8 Hz, C), 55.59 (CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3383 (N–H), 2917, 1507, 1237, 1034, 831 cm^{-1}; LCMS: *m/z* calcd. for $[C_{13}H_{11}IFNO+H]^+$: 343.99; found: 344.00.



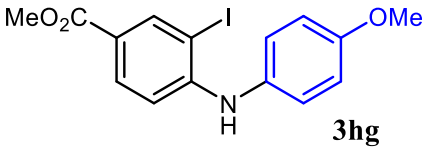
3fg

4-Chloro-2-iodo-*N*-(4-methoxylphenyl)aniline (3fg)[1]**:** Compound **3fg** was prepared according to the general procedure from 4-chloro-2-iodoaniline **1f** (253 mg, 1 mmol) and 4-methoxyphenylboronic acid **2g** (228 mg, 1.5 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (95:5). Colorless gel (131 mg, 73%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.67 (d, J = 2.5 Hz, 1H, Ar–H), 7.08-7.06 (m, 3H, Ar–H), 6.89-6.87 (m, 2H, Ar–H), 6.75 (d, J = 9.0 Hz, 1H, Ar–H), 5.73 (brs, 1H, N–H), 3.80 (s, 3H, CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.67 (C), 144.72 (C), 138.12 (CH), 134.12 (C), 129.00 (CH), 124.79 (2CH), 123.68 (C), 114.88 (2CH), 113.98 (CH), 85.80 (C), 55.55 (CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3369 (N–H), 2930, 1583, 1510, 1313, 1266, 1028, 863, 841 cm^{-1}; LCMS: *m/z* calcd. for $[C_{13}H_{11}ClINO+H]^+$: 359.96; found: 360.00.



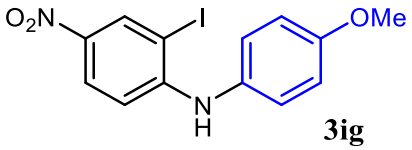
3gg

4-Bromo-2-iodo-*N*-(4-methoxylphenyl)aniline (3gg)[1]**:** Compound **3gg** was prepared according to the general procedure from 4-bromo-2-iodoaniline **1g** (298 mg, 1 mmol) and 4-methoxyphenylboronic acid **2g** (228 mg, 1.5 mmol); and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (95:5). White solid (290 mg, 72%); m.p.: 84-86 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.79 (d, J = 2.4 Hz, 1H, Ar–H), 7.18 (dd, J = 8.7, 2.2 Hz, 1H, Ar–H), 7.07 (dt, J = 6.6, 2.2 Hz, 2H, Ar–H), 6.88 (dt, J = 6.6, 2.3 Hz, 2H, Ar–H), 6.68 (d, J = 8.8 Hz, 1 H, Ar–H), 5.74 (brs, 1H, N–H), 3.79 (s, 3H, CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.98 (C), 145.37 (C), 140.91 (CH), 134.17 (C), 132.06 (CH), 125.30 (2CH), 115.11 (2CH), 114.67 (CH), 110.67 (C), 86.47 (C), 55.77 (CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3364 (N–H), 2929, 2834, 1576, 1506, 1379, 1238, 1165, 1104, 1028, 862, 813 cm^{-1}; LCMS: *m/z* calcd. for $[C_{13}H_{11}BrINO+H]^+$: 403.91; found: 404.00.



3hg

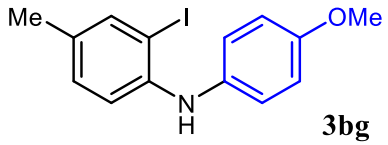
Methyl 3-iodo-4-((4-methoxyphenyl)amino)benzoate (3hg) [1]**:** Compound **3hg** was prepared from methyl 4-amino-3-iodobenzoate **1h** (277 mg, 1.0 mmol) and 4-methoxyphenylboronic acid **2g** (228 mg, 1.5 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (95:5). Orange gel (268 mg, 70% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.40 (d, J = 2.0 Hz, 1H, Ar–H), 7.77 (dd, J = 9.0, 2.5 Hz, 1H, Ar–H), 7.15 (dt, J = 6.5, 2.5 Hz, 2H Ar–H), 6.93 (dt, J = 6.5, 2.5 Hz, 2H, Ar–H), 6.74 (d, J = 9.0 Hz, 1H, Ar–H), 6.20 (brs, 1H, N–H), 3.85 (s, 3H, CH_3), 3.83 (s, 3H, CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.81 (C=O), 157.49 (C), 149.63 (C), 141.18 (CH), 132.68 (C), 131.03 (CH), 126.16 (2CH), 121.28 (C), 114.96 (2CH), 111.29 (CH), 84.09 (C), 55.56 (CH_3), 51.84 (CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3374 (N–H), 2923, 2853, 1707 (C=O), 1592, 1509, 1434, 1267, 1251, 1112, 1035, 829, 763 cm^{-1}; LCMS: *m/z* calcd. for $[C_{15}H_{14}INO_3+H]^+$: 384.00; found: 384.10.



3ig

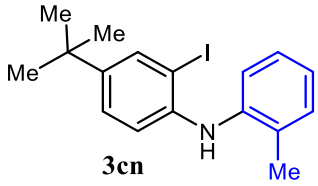
4-Nitro-2-iodo-*N*-(4-methoxylphenyl)aniline (3ig)[1]**:** Compound **3ig** was prepared according to the general procedure from 2-iodo-4-nitroaniline **1i** (264 mg, 1 mmol) and 4-methoxyphenylboronic acid **2g** (228 mg, 0.75 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (95:5). Yellow solid (215 mg, 58%); mp: 100-102 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.61 (dd, J = 2.5, 0.5 Hz, 1H, Ar–H), 7.99 (dd, J = 6.5, 2.5 Hz, 1H, Ar–H), 7.15 (dt, J = 7.0, 2.0 Hz, 2H, Ar–H), 6.94 (dt, J = 7.0, 2.5 Hz, 2H, Ar–H), 6.66 (d, J = 9.0 Hz, 1H, Ar–H), 6.44 (brs, 1H, N–H), 3.82 (s, 3H, CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.23 (C), 151.35 (C), 139.26 (C), 135.61 (CH), 131.51 (C), 126.82 (2CH), 125.64 (CH), 115.19 (2CH), 110.34 (CH), 82.46 (C), 55.58 (CH_3) ppm;

IR (ATR): $\tilde{\nu}$ = 3332 (N–H), 2927, 1588, 1573, 1507, 1490 (N–O), 1314, 1284, 1256, 1167, 1020, 834 cm^{-1}; LCMS: *m/z* calcd. for $[C_{13}H_{11}IN_2O_3+H]^+$: 370.98; found: 371.00.



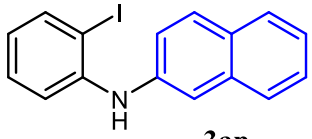
3bg

2-Iodo-*N*-(4-methoxyphenyl)-4-methylaniline (3bg): Compound **3bg** was prepared according to the general procedure from 4-methyl-2-iodoaniline **1b** (233 mg, 1 mmol) and 4-methoxyphenylboronic acid **2g** (228 mg, 1.5 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (98:2). Colourless gel (264 mg, 78%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.56 (d, *J* = 1.8 Hz, 1H, Ar–H), 7.08-7.05 (m, 2H, Ar–H), 6.95 (dd, *J* = 8.2, 2.0 Hz, 1H, Ar–H), 6.88 (t, *J* = 5.6 Hz, 1H, Ar–H), 6.86 (t, *J* = 5.8 Hz, 1H, Ar–H), 6.82 (d, *J* = 8.3 Hz, 1H, Ar–H), 5.63 (brs, 1H, N–H), 3.80 (s, 3H, OCH_3), 2.22 (s, 3H, CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.84 (C), 143.13 (C), 139.48 (CH), 135.26 (C), 130.46 (C), 129.74 (CH), 123.52 (2CH), 114.69 (2CH), 114.35 (CH), 87.28 (C), 55.56 (OCH_3), 19.94 (CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3362 (N–H), 2945, 1735, 1600, 1573, 1510, 1460, 1340, 1296, 1217, 1143, 1092, 1030, 996, 881, 820, 767 cm^{-1}; LCMS: *m/z* calcd. for $[C_{14}H_{14}INO+H]^+$: 340.01; found: 340.10.



3cn

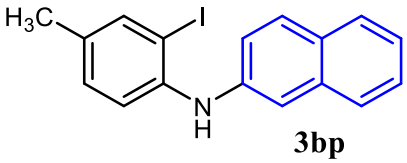
4-(*tert*-Butyl)-2-iodo-*N*-(*o*-tolyl)aniline (3cn): Compound **3cn** was prepared according to the general procedure from 4-(*tert*-butyl)-2-iodoaniline **1c** (275 mg, 1 mmol) and *o*-tolylboronic acid **2n** (205 mg, 1.5 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (98:2). Brown gel (186 mg, 51%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 2.5 Hz, 1H, Ar–H), 7.25-7.17 (m, 4H, Ar–H), 7.10-6.96 (m, 1H, Ar–H), 6.89 (d, *J* = 8.5 Hz, 1H, Ar–H), 5.60 (brs, 1H, N–H), 2.27 (s, 3H, Ar–CH_3), 1.28 (s, 9H, $C(CH_3)_3$) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 144.75 (C), 141.77 (C), 140.64 (C), 136.13 (CH), 131.07 (CH), 129.54 (C), 126.76 (CH), 126.15 (CH), 122.82 (CH), 120.11 (CH), 115.49 (CH), 88.84 (C), 34.01 (C of $C(CH_3)_3$), 31.36 ($C(CH_3)_3$), 17.92 (Ar–CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3362 (N–H), 2945, 1730, 1600, 1575, 1515, 1471, 1345, 1287, 1215, 1140, 1050, 880, 775 cm^{-1}; LCMS: *m/z* calcd. for $[C_{17}H_{20}IN+H]^+$: 366.06; found: 366.10.



3ap

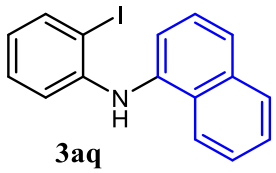
***N*-(2-iodophenyl)naphthalen-2-amine (3ap):** Compound **3ap** was prepared according to the general procedure from 2-iodoaniline **1a** (219 mg, 1 mmol) and naphthalen-2-ylboronic acid **2p** (258 mg, 1.5 mmol); and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (98:2). Brown gel (176 mg, 51%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.82-7.75 (m, 3H, Ar–H), 7.68 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.48 (brs, 1H, N–H), 7.45-7.32 (m, 3H,

Ar–H), 7.29-7.26 (m, 2H, Ar–H), 7.22-7.20 (m, 1H, Ar–H), 6.65 (t, J = 8.0 Hz, 1H, Ar–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ =143.76 (C), 139.66 (C), 139.57 (CH), 134.42 (C), 129.87 (C), 129.30 (CH), 129.09 (CH), 127.68 (CH), 126.71 (CH), 126.52 (CH), 124.16 (CH), 122.30 (CH), 121.10 (CH), 116.36 (CH), 114.61 (CH), 89.17 (C) ppm; IR (ATR): $\tilde{\nu}$ = 3360 (N–H), 2950, 1732, 1573, 1515, 1468, 1298, 1210, 1095, 980, 730 cm^{-1}; LCMS: *m/z* calculated for $C_{16}H_{12}IN$-H]$^+$: 346.00, found: 346.00.



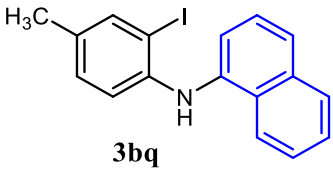
3bp

***N*-(2-iodo-4-methylphenyl)naphthalen-2-amine (3bp):** Compound **3bp** was prepared according to the general procedure from 4- methyl-2-iodoaniline **1b** (233 mg, 1 mmol) and naphthalen-2-ylboronic acid **2p** (258 mg, 1.5 mmol); and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (98:2). Brown gel (187 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87-7.63 (m, 4H, Ar–H), 7.45-7.21 (m, 5H, Ar–H), 7.04 (d, J = 8.1 Hz, 1H, Ar–H), 5.90 (brs, 1H, N–H), 2.27 (s, 3H, Ar–CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ =141.08 (C), 140.52 (C), 139.76 (CH), 134.51 (C), 132.71 (C), 129.82 (CH), 129.48 (C), 129.24 (CH), 127.65 (CH), 126.55 (CH), 126.47 (CH), 123.78 (CH), 120.44 (CH), 117.62 (CH), 112.87 (CH), 90.37 (C), 20.14 (CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3362 (N–H), 2945, 1735, 1600, 1573, 1510, 1460, 1340, 1296, 1209, 1143, 1092, 902, 739 cm^{-1}; LCMS: *m/z* calculated for $C_{17}H_{14}IN$-+H]$^+$: 360.02, found: 360.10.



3aq

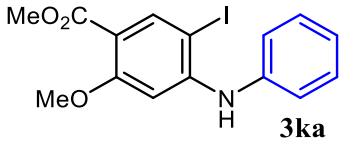
***N*-(2-iodophenyl)naphthalen-1-amine (3aq):** Compound **3aq** was prepared according to the general procedure from 2-iodoaniline **1a** (219 mg, 1 mmol) and naphthalen-1-ylboronic acid **2q** (258 mg, 1.5 mmol); and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (98:2). Brown gel (179 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, J = 7.2 Hz, 1H, Ar–H), 7.90-7.87 (m, 1H, Ar–H), 7.78 (d, J = 7.6 Hz, 1H, Ar–H), 7.68-7.61 (m, 1H, Ar–H), 7.56-7.32 (m, 4H, Ar–H), 7.09 (t, J = 8.0 Hz, 1H, Ar–H), 6.78 (d, J = 8.0 Hz, 1H, Ar–H), 6.55 (t, J = 7.2 Hz, 1H, Ar–H), 6.21 (brs, 1H, N–H) ppm; IR (ATR): $\tilde{\nu}$ =3362 (N–H), 2945, 1735, 1600, 1573, 1510, 1460, 1340, 1296, 1217, 1143, 1030, 996, 881, 767 cm^{-1}; LCMS: *m/z* calculated for [$C_{16}H_{12}IN$-H]$^+$: 346.00, found: 346.10.



3bq

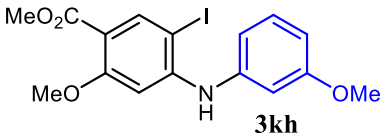
***N*-(2-iodo-4-methylphenyl)naphthalen-1-amine (3bq):** Compound **3bq** was prepared according to the general procedure from 4- methyl-2-iodoaniline **1b** (233 mg, 1 mmol) and naphthalen-1-ylboronic acid **2q** (258 mg, 1.5 mmol); and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (98:2). Brown gel

(194 mg, 54%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30 (d, J = 8.0 Hz, 1H, Ar–H), 7.98 (d, J = 7.4 Hz, 1H, Ar–H), 7.93-7.91 (m, 1H, Ar–H), 7.85-7.80 (m, 1H, Ar–H), 7.56-7.38 (m, 4H, Ar–H), 7.30-7.27 (m, 1H, Ar–H), 6.98-6.92 (m, 1H, Ar–H), 6.76 (d, J = 8.0 Hz, 1H, Ar–H), 6.20 (brs, 1H, N–H) ppm, 2.24 (s, 3H, -CH_3) ppm; IR (ATR): $\tilde{\nu}$ =3362, 2945, 1735, 1600, 1573, 1510, 1460, 1340, 1296, 1210, 1140, 1040, 880, 740 cm^{-1}; LCMS: *m/z* calculated for $[C_{17}H_{14}IN+H]^+$: 360.02, found: 360.10.



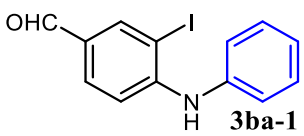
3ka

Methyl 5-iodo-2-methoxy-4-(phenylamino)benzoate (3ka)[1]**:** Compound **3ka** was prepared according to the general procedure from methyl 4-amino-5-iodo-2-methoxybenzoate **1k** (307 mg, 1 mmol) and phenylboronic acid **2a** (183 mg, 1.5 mmol); and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (90:10). Off-white solid (249 mg, 65%); m.p.: 138-140 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.25 (s, 1H, Ar–H), 7.35 (tt, J = 8.0, 2.0 Hz, 2H; Ar–H), 7.21 (d, J = 8.5 Hz, 2H, Ar–H), 7.12 (tt, J = 7.5, 1.5 Hz, 1H, Ar–H), 6.63 (s, 1H, Ar–H), 6.23 (brs, 1H, N–H), 3.82 (s, 3H, CH_3), 3.68 (s, 3H, CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 164.77 (C=O), 161.56 (C), 148.93 (C), 142.91 (CH), 140.12 (C), 137.16 (C), 129.76 (2CH), 124.65 (CH), 122.46 (2CH), 112.18 (CH), 96.85 (C), 55.98 (CH_3), 51.71 (CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3335 (N–H), 2954, 1694 (C=O), 1579, 1553, 1495, 1459, 1426, 1391, 1325, 1172, 1076, 826, 772 cm^{-1}; LCMS: *m/z* calcd. for $[C_{15}H_{14}INO_3+H]^+$: 384.00; found: 384.10.



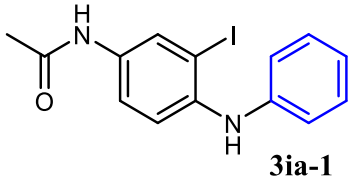
3kh

Methyl 5-iodo-2-methoxy-4-((3-methoxyphenyl)amino)benzoate (3kh)[1]**:** Compound **3kh** was prepared according to the general procedure from methyl 4-amino-5-iodo-2-methoxybenzoate **1k** (307 mg, 1 mmol) and 3-methoxyphenylboronic acid **2h** (228 mg, 1.5 mmol); and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (90:10). Red gel (285 mg, 69%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.25 (s, 1H, Ar–H), 7.25 (t, J = 8.2 Hz, 1H, Ar–H), 6.78 (dd, J = 8.0, 1.5 Hz, 1H, Ar–H), 6.75 (t, J = 2.2 Hz, 1H, Ar–H), 6.70 (s, 1H, Ar–H), 6.69 (ddd, J = 7.5, 2.0, 0.7 Hz, 1H, Ar–H), 6.22 (brs, 1H, N–H), 3.82 (s, 3H, CH_3), 3.78 (s, 3H, CH_3), 3.73 (s, 3 H, CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.06 (C=O), 161.72 (C), 161.06 (C), 157.12 (C), 148.91 (C), 143.09 (C), 130.66 (CH), 114.58 (CH), 110.35 (CH), 108.02 (CH), 106.54 (CH), 101.76 (CH), 97.51 (C), 55.21 (CH_3), 55.58 (CH_3), 51.97 (CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3365 (N–H), 2947, 1714, 1696 (C=O), 1582, 1491, 1433, 1392, 1236, 1218, 1156, 1093, 1042, 956, 779 cm^{-1}; LCMS: *m/z* calcd. for $[C_{16}H_{16}INO_4+H]^+$: 414.01; found: 414.20.



3ba-1

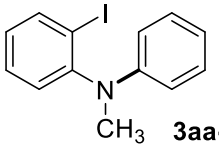
4-((2-Iodophenyl)amino)benzaldehyde (3ba-1): 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 1021 mg, 3 equiv.) was added to the solution of compound **3ba** (464 mg, 1.5 mmol) in a mixture of MeOH/THF/H_2O (16:6:1 by volume), and the reaction mixture was stirred for 1 h at room temperature. Then volatiles were evaporated and the residue was dissolved in ethyl acetate (5 ml). The reaction mixture was diluted with water (15 ml) and extracted with ethyl acetate (15 ml × 2). Then combined organic layer was washed with water (15 ml) followed by brine solution (15 ml), and dried over anhydrous Na_2SO_4. After removal of the volatiles under reduced pressure, the residue was purified by column chromatography on silica gel using hexane/ethyl acetate mixtures (95:5) as the eluent to yield 4-((2-iodophenyl)amino)benzaldehyde (**3ba-1**, 271 mg, 81%) as an off-white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.83 (s, 1H, CHO), 7.86 (dd, *J* = 8.0, 1.5 Hz, 1H, Ar–H), 7.79 (d, *J* = 9.0, 2H, Ar–H), 7.42 (dd, *J* = 8.0, 1.0 Hz, 1H, Ar–H), 7.33 (td, *J* = 8.0, 1.0 Hz, 1H, Ar–H), 7.07 (d, *J* = 8.5 Hz, 2H, Ar–H), 6.83 (td, *J* = 8.0, 1.5 Hz, 1H, Ar–H), 6.16 (brs, 1H, N–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 190.42 (C=O), 148.70 (C), 141.10 (C), 139.88 (CH), 132.05 (2CH), 129.46 (C), 129.25 (CH), 125.27 (CH), 120.82 (CH), 115.56 (2CH), 92.82 (C) ppm; IR (ATR): $\tilde{\nu}$ = 3318 (N–H), 2742, 1663 (C=O), 1599, 1571, 1521, 1460, 1416, 1320, 1292, 1221, 1158, 1010, 815, 748, 712 cm^{-1}; LCMS: *m/z* calculated for $[C_{13}H_{10}INO+H]^+$: 323.98, found: 324.20.



3ia-1

***N*-(3-iodo-4-(phenylamino)phenyl)acetamide (3ia-1):** To a solution of compound **3ai** (510 mg, 1.5 mmol) in glacial acetic acid (5 ml), Fe dust (419 mg, 5 equiv.) was added at room temperature. Then the reaction mixture was refluxed for 3 h. After cooling to room temperature the reaction mixture was neutralized with saturated $NaHCO_3$ (aq.) under cold condition. Then product was extracted with ethyl acetate (25 ml × 2). The combined organic layer was washed with water (50 ml × 2) followed by brine solution (50 ml), and dried over anhydrous Na_2SO_4. After removal of the volatiles under reduced pressure, the residue of the crude product was purified by column chromatography on silica gel using hexane/ethyl acetate mixtures (90:10) as the eluent to yield *N*-(3-iodo-4-(phenylamino)phenyl)acetamide (**3ai-1**, 412 mg, 78%) as a grey solid. ^{1}H NMR (400 MHz, DMSO-D_6): δ = 9.94 (brs, 1H, Ar-N–H($COCH_3$), 8.20 (brs, 1H, N–H), 7.45-7.44 (m, 1H, Ar–H), 7.33 (s, 1H, Ar–H), 7.16-7.12 (m, 3H, Ar–H), 6.78-6.73 (m, 3H, Ar–H), 2.02 (s, 3H, $COCH_3$) ppm; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.96 (brs, 1H, Ar-N–H($COCH_3$), 7.32-7.26 (m, 4H, Ar–H), 7.22 (brs, 1H, N–H), 7.15 (d, *J* = 9.0 Hz, 1H, Ar–H), 7.05 (d, *J* = 7.5 Hz, 2H, Ar–H), 6.99 (t, *J* = 7.5 Hz, 1H, Ar–H), 2.15 (s, 3H, $COCH_3$) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.23 (C), 142.37 (C), 140.66 (C), 131.72 (C), 131.28 (CH), 129.46 (2CH), 122.08 (CH), 121.59 (CH), 119.06 (2CH), 116.50 (CH), 89.06 (C), 24.34 (CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3407 (N–H), 3287, 3244, 3176, 3112, 1651 (C=O), 1596, 1536, 1504, 1468, 1380, 1293, 1265, 1173, 1074, 1030, 862, 807, 751, 696, 599, 548 cm^{-1}; LCMS: *m/z* calculated for $[C_{14}H_{13}OIN_2+H]^+$: 353.01, found: 353.20.

Preparation of 2-iodo-*N*-methyl-*N*-phenylaniline (3aa-1): To an ice-cold solution of 2-iodo-*N*-phenylaniline **3aa** (295 mg, 1 mmol) in dry DMF (5 ml) in a 25 ml round bottom flask, NaH (80 mg, 2 mmol, 60% dispersion in mineral oil) was added in two portions, and allowed to stir at 0 °C for 5 min. To this mixture, methyl iodide (MeI, 284 mg, 2 mmol) was added at 0 °C, and allowed to stir at room temperature for 8 h. Then cold water (20 ml) was added to the reaction mixture and the organic part was extracted with ethyl acetate (20 ml × 2). The combined ethyl acetate part was washed with brine solution (20 ml), dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was purified through a silica gel (100-200 mesh) column using hexane/ethyl acetate mixtures (99:1) as the eluent to afford the 2-iodo-*N*-methyl-*N*-phenylaniline (**3aa-1**, brown gel, 300 mg, 97%).



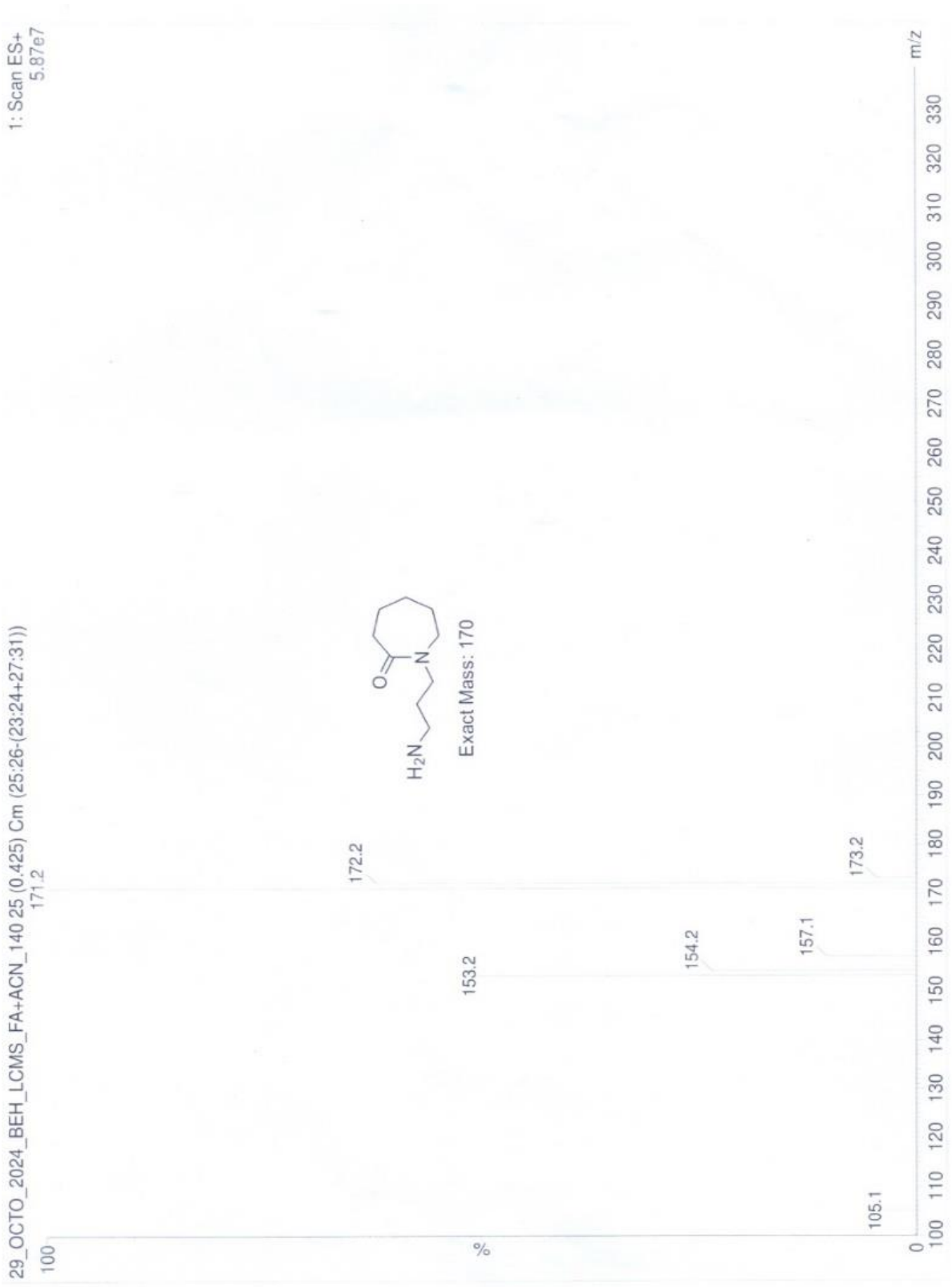
3aa-1

2-Iodo-*N*-methyl-*N*-phenylaniline (3aa-1)[1]**:** Compound **3aa-1**, brown gel (300 mg, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (dd, *J* = 8.0, 1.2 Hz, 1H, Ar–H), 7.31 (td, *J* = 8.0, 1.6 Hz, 1H, Ar–H), 7.18-7.09 (m, 3H, Ar–H), 6.92 (td, *J* = 8.0, 1.6 Hz, 1H, Ar–H), 6.68 (t, *J* = 7.2 Hz, 1H, Ar–H), 6.47 (dd, *J* = 8.4, 0.8 Hz, 2H, Ar–H), 3.13 (s, 3H, CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 150.78 (C), 148.79 (C), 140.56 (CH), 130.23 (CH), 129.91 (CH), 129.15 (2 CH), 128.33 (CH), 117.91 (CH), 113.69 (CH), 101.36 (C), 39.36 (CH_3) ppm; LCMS: *m/z* calcd. for $[C_{13}H_{12}IN+H]^+$: 310.00; found: 310.10.

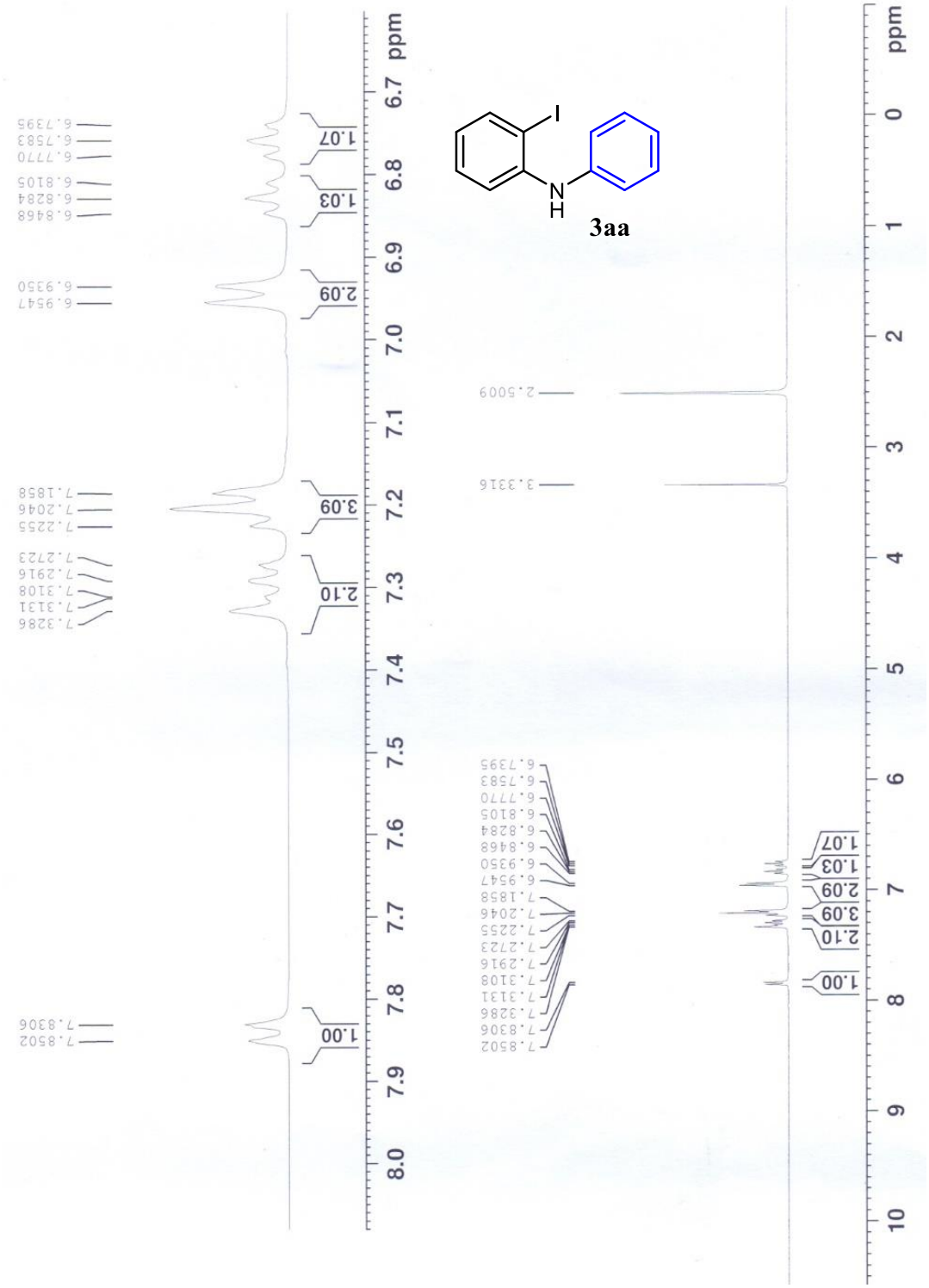
3. Optimization of Pd-catalyzed intramolecular aryl C–H activation of 2-iodo-*N*-phenylaniline 3aa in water to give carbazole 4-1.

During optimization study, reaction of 2-iodo-*N*-phenylaniline **3aa**, without addition of a cationic surfactant (e.g. CTAB: cetyltrimethylammonium bromide) in water, showed formation of some carbazole **4-1** with a reasonable amount of diphenylamine **5**, probably due to the high concentration of water that enhances both the C–Pd bond protolysis of the in situ generated aryl-palladium species (from **3aa**), and the hydrolysis of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene). Mass spectrum of the aqueous part of the reaction mixture showed the presence of a possible hydrolyzed compound of DBU, that is *N*-(3-aminopropyl)caprolactam, LCMS: *m/z* calculated for $[C_9H_{18}N_2O+H]^+$: 171.14, found: 171.20 (Figure S1a). Thus for further optimization, reactions were attempted with adding a variable amount of CTAB in water. Besides TLC monitoring, ^{1}H NMR spectra of 2-iodo-*N*-phenylaniline **3aa**, carbazole **4-1**, diphenylamine **5**, and the reaction mixture of **3aa** were collected to monitor the reactions. Few of the ^{1}H NMR spectra are given here (Figure S1b-e).

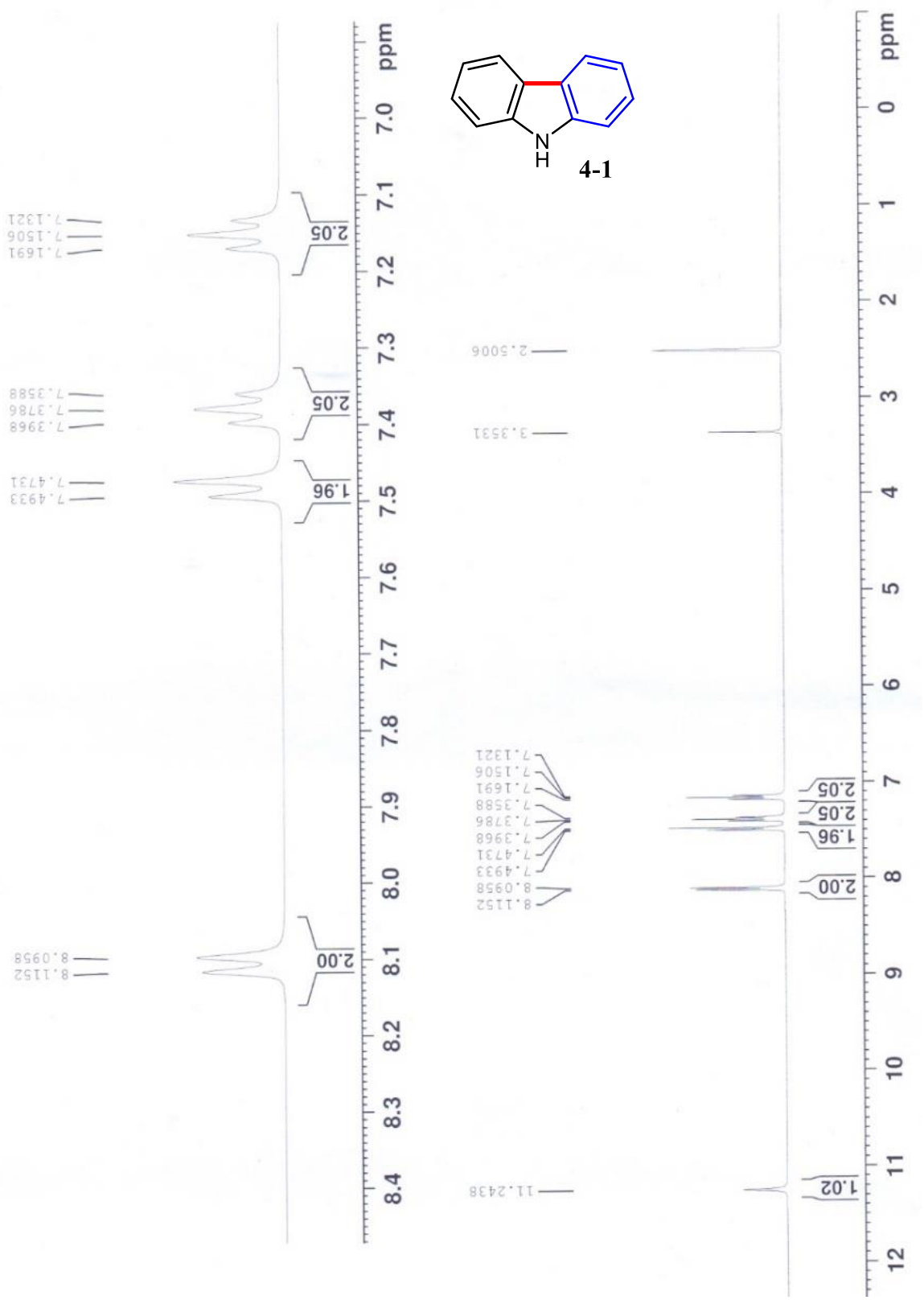
(a) Mass (LCMS) spectrum of DBU hydrolyzed compound.



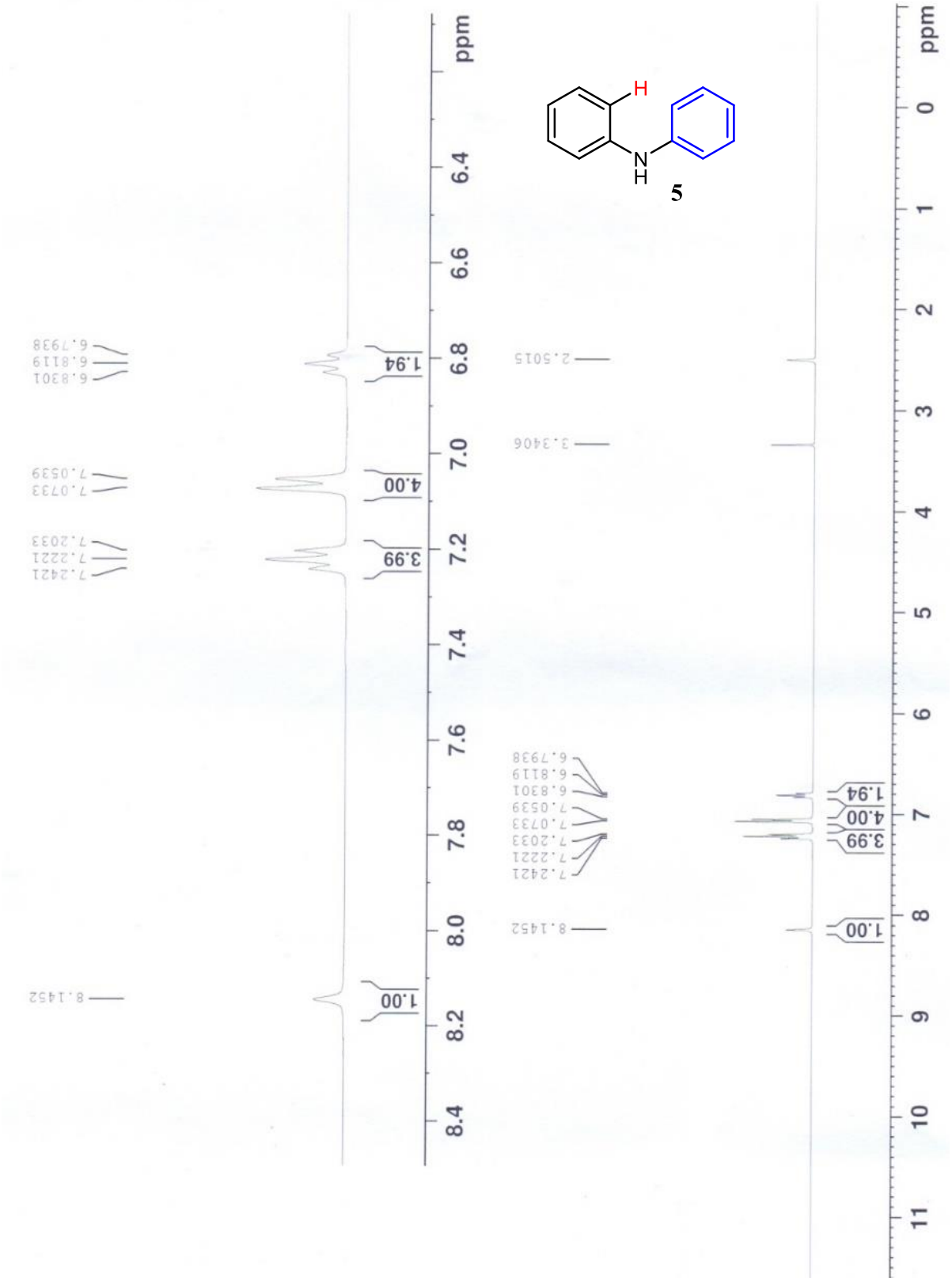
(b) ^{1}H NMR spectrum of 2-iodo-*N*-pheylaniline **3aa** in DMSO-D_6.



(c) ^{1}H NMR spectrum of carbazole **4-1** in DMSO-D_6.



(d) ^{1}H NMR spectrum of diphenylamine **5** in DMSO-D_6.



(e) ^{1}H NMR spectrum of reaction mixture of **3aa** using 0.02 equiv. CTAB in DMSO-D_6.

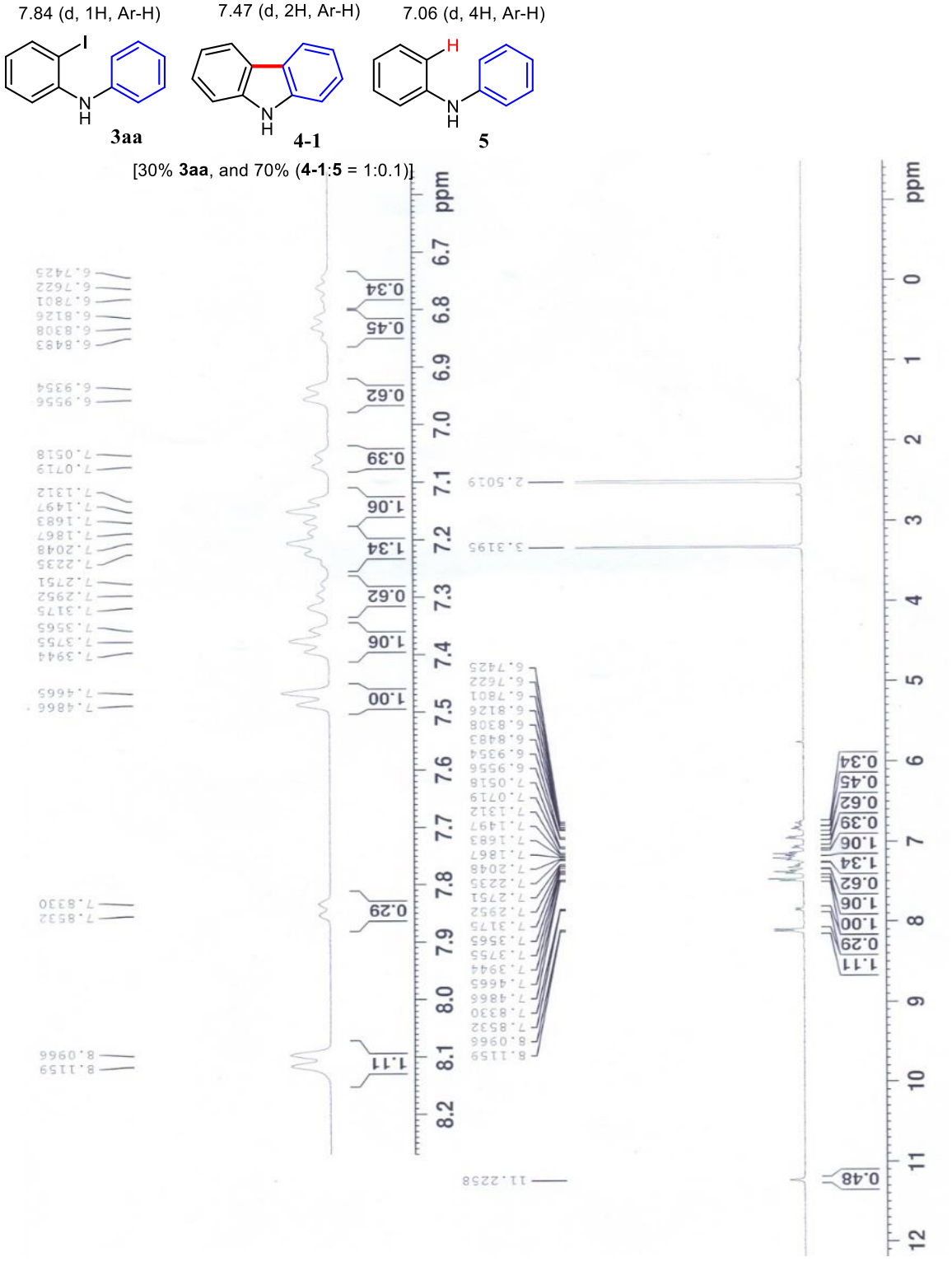
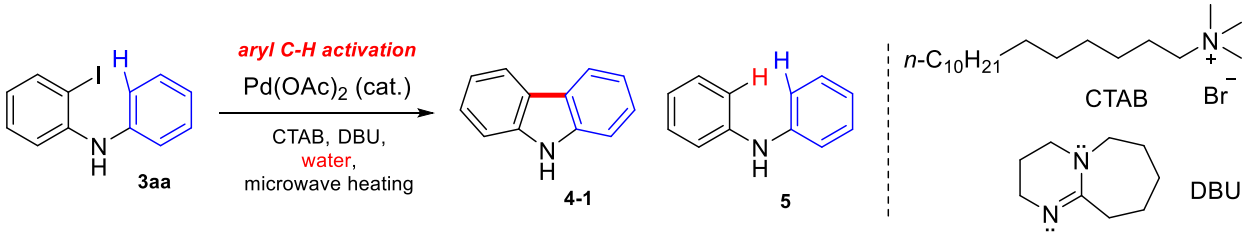


Figure S1. (a) Mass spectrum of DBU hydrolyzed compound, and (b-e) ^{1}H NMR spectra of **3aa**, **4-1**, **5**, and reaction mixture of **3aa**.

Table S1. Optimization of reactions for Pd-catalyzed intramolecular aryl C–H activation of 2-iodo-*N*-phenylaniline **3aa** in water to give carbazole **4-1**.[a]



a. Reactions with variable concentration of CTAB under microwave-assisted conditions.

Entry	*[Pd] (mol%)*	*Base (equiv.)*	*Surfactant (equiv.)*	*Temperature (°C)*	*Time (h)*	*Yield of **4-1+5** (%)*[b] ***(4-1:5)***
1	$Pd(OAc)_2$ (5)	DBU (2)	CTAB (0.1)	100	1 h	99
2	$Pd(OAc)_2$ (5)	DBU (2)	CTAB (1)	100	1 h	99
3	$Pd(OAc)_2$ (5)	DBU (2)	CTAB (0.5)	100	1 h	99
4	$Pd(OAc)_2$ (5)	DBU (2)	CTAB (0.02)	100	1 h	70 (1:0.1)

b. Reactions with variable concentration of DBU under microwave-assisted conditions.

Entry	*[Pd] (mol%)*	*Base (equiv.)*	*Surfactant (equiv.)*	*Temperature (°C)*	*Time (h)*	*Yield of **4-1** (%)*[b]
1	$Pd(OAc)_2$ (5)	DBU (2)	CTAB (0.1)	100	1 h	99
2	$Pd(OAc)_2$ (5)	DBU (3)	CTAB (0.1)	100	1 h	99
3	$Pd(OAc)_2$ (5)	DBU (1)	CTAB (0.1)	100	1 h	81
4	$Pd(OAc)_2$ (5)	DBU (1)	CTAB (0.1)	100	1.5 h	82
5	$Pd(OAc)_2$ (5)	-	CTAB (0.1)	100	1.5 h	0

c. Reactions with variable reaction time under microwave-assisted conditions.

Entry	*[Pd] (mol%)*	*Base (equiv.)*	*Surfactant (equiv.)*	*Temperature (°C)*	*Time (min)*	*Yield of **4-1** (%)*[b]
1	$Pd(OAc)_2$ (5)	DBU (2)	CTAB (0.1)	100	20	40
2	$Pd(OAc)_2$ (5)	DBU (2)	CTAB (0.1)	100	30	60
3	$Pd(OAc)_2$ (5)	DBU (2)	CTAB (0.1)	100	40	70
4	$Pd(OAc)_2$ (5)	DBU (2)	CTAB (0.1)	100	50	91
5	$Pd(OAc)_2$ (5)	DBU (2)	CTAB (0.1)	100	60	99
6	$Pd(OAc)_2$ (5)	DBU (2)	CTAB (0.1)	100	70	99
7	$Pd(OAc)_2$ (5)	DBU (2)	CTAB (0.1)	100	80	98
8	$Pd(OAc)_2$ (5)	DBU (2)	CTAB (0.1)	100	90	99
9	$Pd(OAc)_2$ (5)	DBU (2)	CTAB (0.1)	100	120	98

d. Reactions with variable reaction temperature under microwave-assisted conditions.

Entry	*[Pd] (mol%)*	*Base (equiv.)*	*Surfactant (equiv.)*	*Time (min)*	*Temperature (°C)*	*Yield of **4-1** (%)*[b]
1	$Pd(OAc)_2$ (5)	DBU (2)	CTAB (0.1)	60	70	15
2	$Pd(OAc)_2$ (5)	DBU (2)	CTAB (0.1)	60	80	35
3	$Pd(OAc)_2$ (5)	DBU (2)	CTAB (0.1)	60	90	85
4	$Pd(OAc)_2$ (5)	DBU (2)	CTAB (0.1)	60	100	99
5	$Pd(OAc)_2$ (5)	DBU (2)	CTAB (0.1)	60	110	98
6	$Pd(OAc)_2$ (5)	DBU (2)	CTAB (0.1)	60	120	99
7	$Pd(OAc)_2$ (5)	DBU (2)	CTAB (0.1)	60	130	98
8	$Pd(OAc)_2$ (5)	DBU (2)	CTAB (0.1)	60	140	98

[a] **Reaction conditions: 3aa** (0.4 mmol, 1 equiv), $Pd(OAc)_2$, CTAB and DBU in 1 ml water under MW (60 W) at different temperature for 60 min in a capped vial in a microwave reactor. [b] Isolated yields of carbazole **4-1** from silica gel column, and diphenylamine **5**.

Dynamic light scattering (DLS) study: DLS study performed on Malvern instrument UK, Zetasizer Nano S. Model No: Zen 6000.

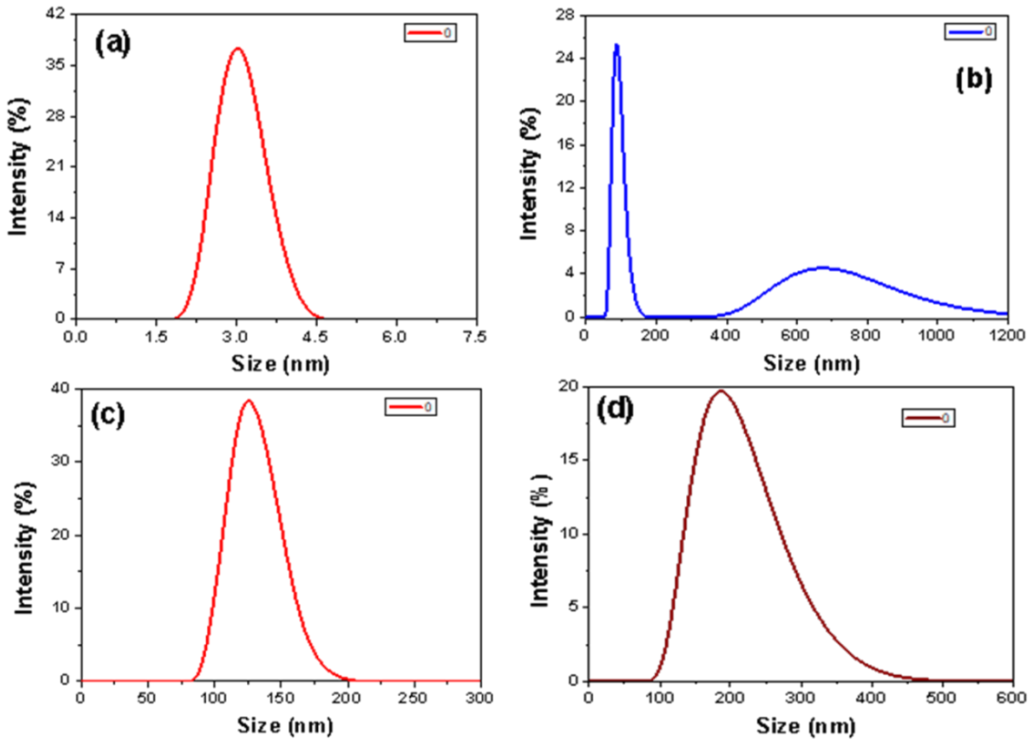


Figure S2. Plots of DLS data of (a) $Pd(OAc)_2$/CTAB in water at room temperature. (b) $Pd(OAc)_2$/CTAB in water after microwave-assisted heating at 100 ºC for 15 min (60 W). (c) $Pd(OAc)_2$/CTAB/DBU in water after microwave-

assisted heating at 100 °C for 15 min (60 W). (d) Recovered aqueous part of the reaction mixture from **3aa**/Pd(OAc)$_2$/CTAB/DBU, after microwave-assisted heating at 100 °C for 60 min (60W).

In order to confirm CTAB micelles' stability, dynamic light scattering (DLS) data of the aqueous Pd(OAc)$_2$/CTAB combination have been collected under different conditions (Figure S2). There DLS data of aqueous Pd(OAc)$_2$-CTAB mixture at room temperature showed formation of particles having dimension around 3 nm corresponding to the formation of CTAB micelles (Figure S2a). Upon microwave-assisted heating at 100 °C, size of the Pd nanoparticles surrounding CTAB micelles with solvent shells having hydrodynamic diameter around ~ 100 nm, along with some bigger particles with size around 700 nm were observed (Figure S2b). In presence of DBU, the particle size was found to decrease with more or less uniform distribution with dimension around 125 nm (Figure S2c). Size of the particles observed from the recovered aqueous part of carbazole (**4-1**) forming reaction mixture of 2-iodo-*N*-phenylaniline **3aa**, was found around 200 nm (Figure S2d). The observed larger particle size hints at the association of CTAB micelles to the in situ generated palladium nanoparticles (PdNPs). Thus similarity in particle size and their distribution observed from the Pd(OAc)$_2$-CTAB-DBU system and the recovered aqueous part of the reactions mixture hints at the stability of CTAB micelles under the reaction conditions.

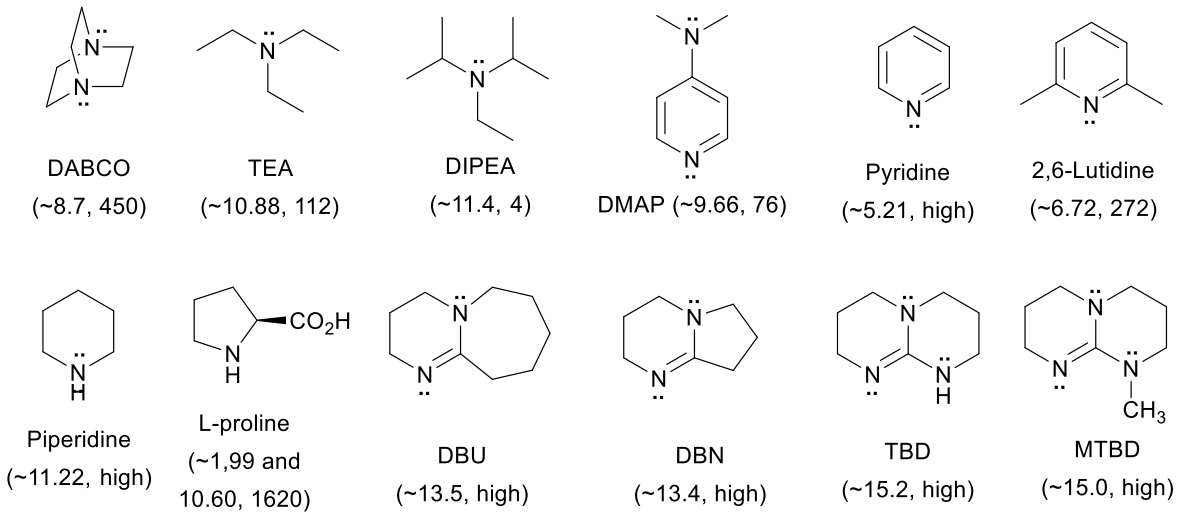
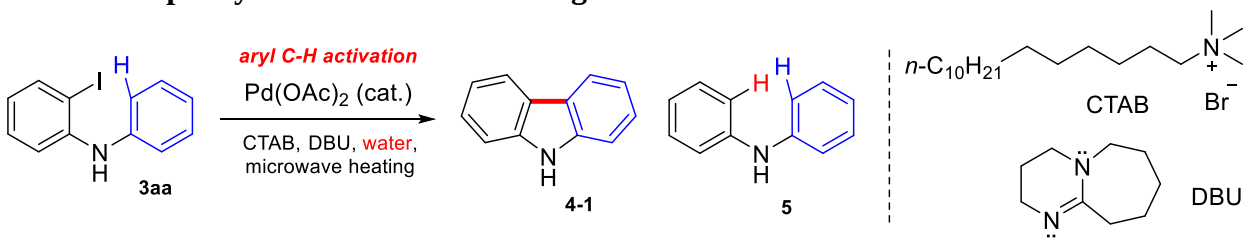


Figure S3. Structure of few organic bases with the pK_a values of their conjugate acids in water at 25 °C, and their solubility (g/L) in water at 20-25 °C.

4. Kinetic study: Control experiments on Pd-catalyzed intramolecular aryl C–H activation of 2-iodo-*N*-phenylaniline 3aa in water to give carbazole 4-1.



4.1 Calculation of molar extinction coefficient (ε_{max}) value of carbazole (4-1) from absorbance in methanol (Spectroscopic grade MeOH).

Stock solution of 2-iodo-*N*-phenylaniline (**3aa**) was prepared by dissolving 2.9 mg (0.01 mmol) in 0.5 ml MeOH (spectroscopic grade). Using this stock solutions absorbance of **3aa** was measured to find out its λ_{max} value in MeOH (Figure S4a). Stock solution of diphenylamine (**5**) was prepared by dissolving 1.7 mg (0.01 mmol) in 0.5 ml MeOH, and its absorbance of **5** was measured to find out its λ_{max} value in MeOH (Figure S4b).

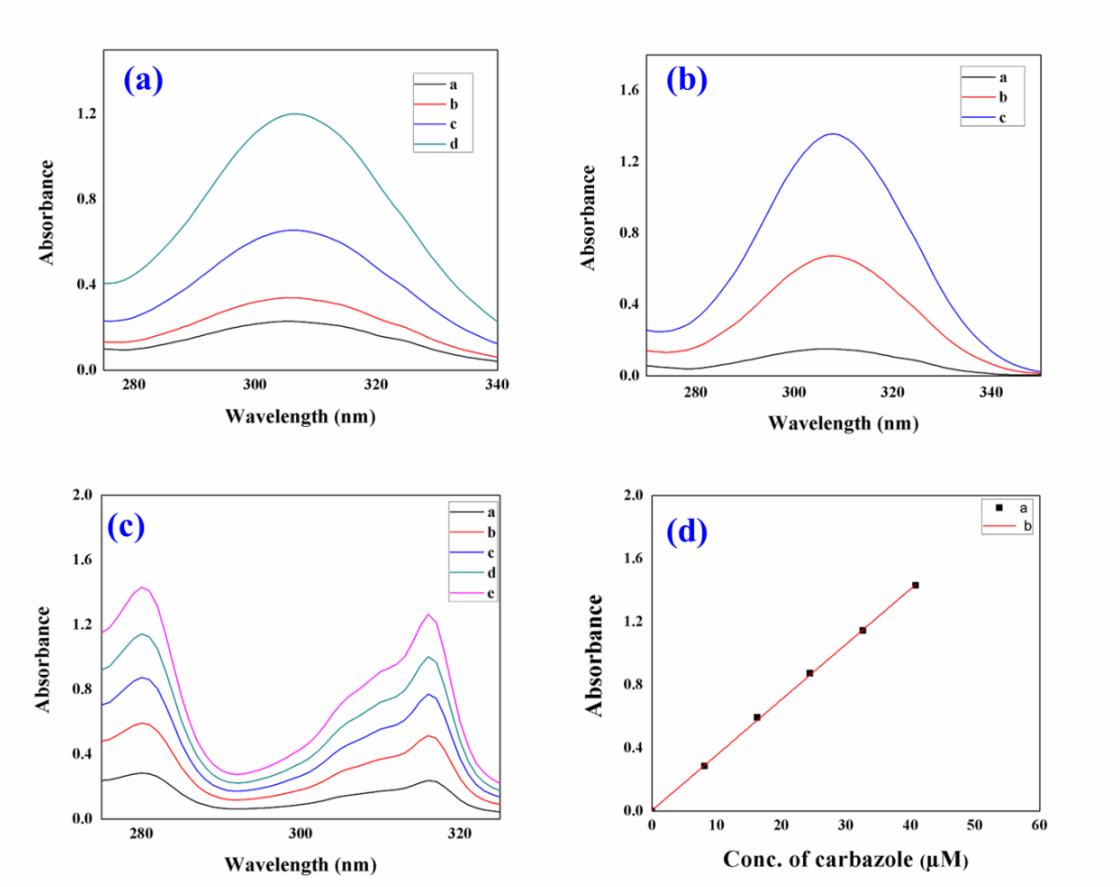


Figure S4. (a) Absorbance vs Wavelength plot of 2-iodo-*N*-phenylaniline (**3aa**), and there λ_{max} was found at 306 nm in MeOH. (b) Absorbance vs Wavelength plot of diphenylamine **5**, and there λ_{max} was found at 307 nm in MeOH. (c) Absorbance vs Wavelength plot of carbazole (**4-1**), and there are two main absorption peaks (λ_{max}) were observed at 281 and 316 nm. (d) Absorbance vs concentration plot of carbazole (**4-1**).

Stock solution of carbazole **4-1** was prepared by dissolving 1.7 mg (0.01 mmol) in 0.5 ml MeOH. Thus, concentration of stock solution of carbazole [**4-1**] was 0.0204×10^3 mmol/L. Concentration of 1μL stock solution of carbazole in 2.5 ml MeOH (in UV cuvette) was 8.134×10^{-6} M (8.13 μM). Using this stock solutions absorbance of carbazole (**4-1**) was measured to find out its λ_{max} value in MeOH (Figure S4c). There two main peaks for carbazole were observed at 281 nm and 316 nm. The peak at λ_{max} 281 nm was chosen for absorbance measurement of carbazole **4-1** as other peaks at higher wavelength were present in the region of the peak of 2-iodo-*N*-phenylaniline **3aa** at λ_{max} 306 nm. From the slope of absorbance vs concentration plot of carbazole **4-1** (Figure S4d), molar extinction coefficient (ε_{max}) of carbazole **4-1** was found 35,340 M^{-1} cm^{-1} (Table S2a).

Table S2. Absorbance of carbazole (**4-1**) at λ_{max} 281 nm with known concentration in MeOH.

Entry	Volume of stock solution of carbazole (**4-1**) taken	Concentration of carbazole (**4-1**) in μM (10^{-6} M)	Absorbance (at λ_{max} 281 nm)	Molar extinction coefficient (ε_{max} in M^{-1} cm^{-1}) from slope of the Absorbance vs Concentration of carbazole (**4-1**) plot
1	1 μL	8.13 μM	0.284	35,340
2	2 μL	16.26 μM	0.592	
3	3 μL	24.39 μM	0.872	
4	4 μL	32.52 μM	1.143	
5	5 μL	40.65 μM	1.430	

Molar extinction coefficient (ε_{max}) = slope of Absorbance vs Conc. plot = 0.03534×10^6 = 35,340 M^{-1} cm^{-1}

4.2 Determination of rate constant value (k):

4.2.1 Control experiments for the synthesis of carbazole 4-1 under micellar conditions (with addition of CTAB) under microwave.

Reactions were conducted following the optimized conditions (Entry 12, Table 1, in the Manuscript) for 10 min to 60 min run time under microwave-assisted heating conditions at 100 °C (60 W), using 2-iodo-*N*-phenylaniline **3aa** (32.5 mg, 0.1101 mmol), CTAB (0.1 equiv.), $Pd(OAc)_2$ (4 mol%) and DBU (2 equiv.) in a capped microwave vial (10 ml) containing a stir bar, deionized water (0.5 ml). The reaction mixture was cooled to room temperature, diluted with 8.5 ml MeOH (spectroscopic grade). Then absorbance of the solutions obtained from each reaction were measured, and from the observed absorbance values at λ_{max} 281 nm (Figure S5a**)**, concentrations of product (carbazole, **4-1**) were

calculated (Table S3). Then concentration of carbazole (**4-1**) vs reaction time plot was drawn (Figure S5a**)**, which showed exponential curve passing through the origin indicating pseudo first order reaction. Concentration of 2-iodo-*N*-phenylaniline (**3aa**) vs reaction time plot was also drawn (Figure S5c). There after we have drawn ln(conc. of carbazole) vs time plot (Figure S5d**)**, that showed a linear plot with a slope 0.012 min^{-1} or 2.0×10^{-4} s^{-1}. Thus the rate constant (k) of the reaction was found 2.0×10^{-4} s^{-1}, at 100 ºC.

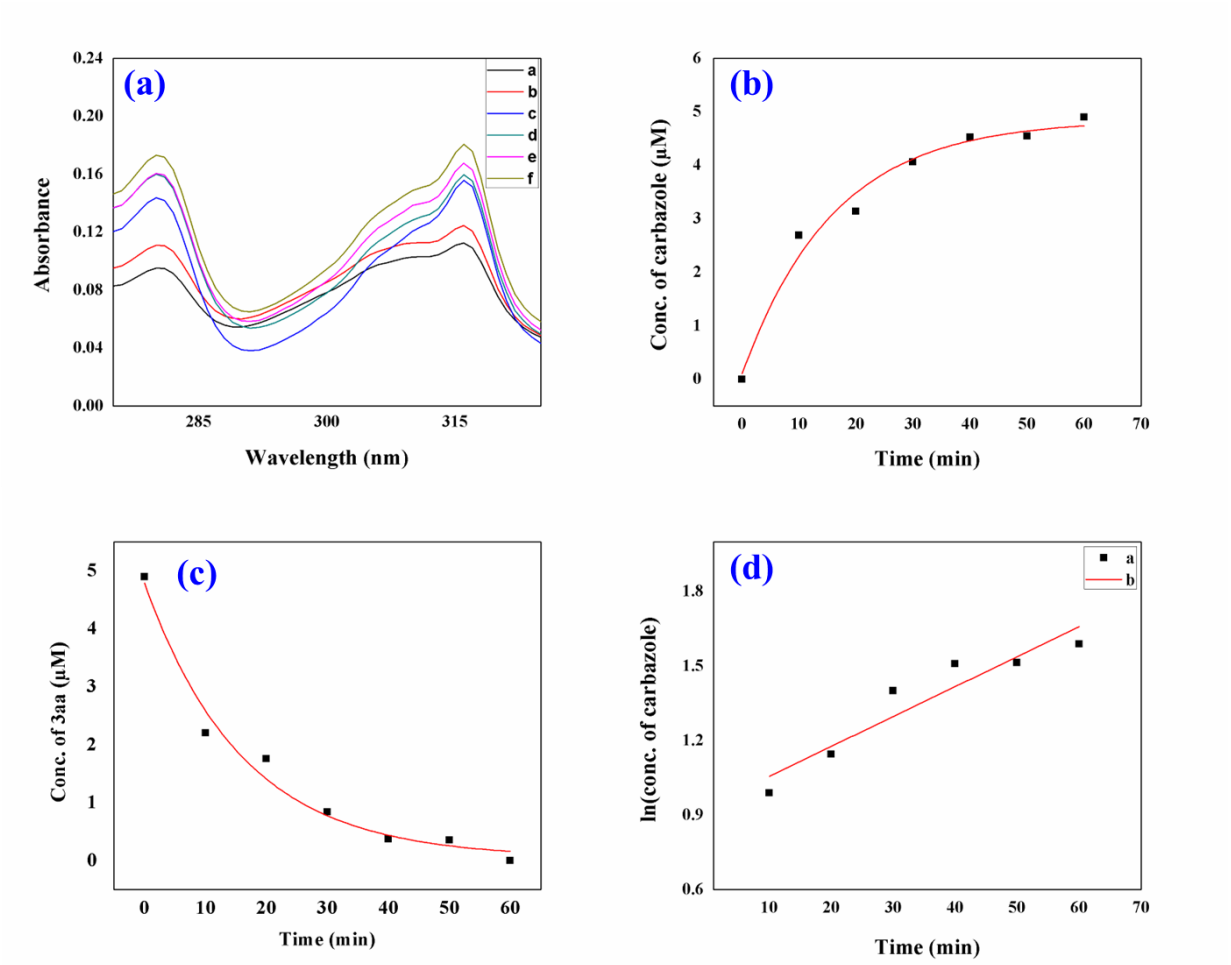


Figure S5. (a) Absorbance vs Wavelength plots of carbazole (**4-1**) of the reaction mixtures (reaction time 10 min to 60 min) in presence of CTAB. (b) Conc. of carbazole (**4-1**) vs reaction time plot. (c) Conc. Of 2-iodo-*N*-phenylaniline (**3aa**) vs reaction time plot. (d) ln (Conc. of carbazole, **4-1**) vs reaction time plot.

Initial concentration of 2-iodo-*N*-phenylaniline (**3aa**): c = 32.5 mg/295.12 = 0.1101 mmol in 9 ml solution. Thus, 0.1101 mmol/ 9×10^{-3} lit = 12.236 mmol/lit = 12.236×10^{-3} mol/lit. So, 1 lit solution contains 12.236×10^{-3} mole. 1 µL = 10^{-6} lit contains = 12.236×10^{-3} mole $\times10^{-6}$ = 12.236×10^{-9} mole. Now, 1 µL of it was added to 2.5 ml MeOH in UV cuvette. So, 2.5 ml = 2.5×10^{-3} lit solution contained 12.236×10^{-9} mole **3aa**, and 1 lit contains 12.236×10^{-9} / 2.5×10^{-3} = 4.894×10^{-6} mole of **3aa** (4.894 µM).

Table S3a. Concentrations of carbazole (**4-1**) obtained from Absorbance vs Wavelength plots of the reaction mixtures with run time 10 min to 60 min, under Micellar conditions.

Entry	Reaction time (Vol. of solution taken 2 µL)	Absorbance at λ_{max} 281 nm	Concentration of product carbazole (**4-1**) at λ_{max} 281 nm [c = [**4-1**]/ε_{max}] (ε_{max} = 35,340 M^{-1} cm^{-1})	Initial concentration of 2-iodo-*N*-phenylaniline (**3aa)**	Yield of carbazole **4-1** (from UV-Vis) [**4-1**]/[**3aa**] × 100%	ln [Conc. of carbazole]
1	0 min	0.0	0.0	4.894 µM	0 (0)	-
2	10 min	0.0951	2.691 µM	4.894 µM	53%	0.989
3	20 min	0.1110	3.140 µM	4.894 µM	64%	1.144
5	30 min	0.1437	4.067 µM	4.894 µM	83%	1.400
6	40 min	0.1599	4.524 µM	4.894 µM	92 %	1.509
5	50 min	0.1605	4.541 µM	4.894 µM	93%	1.513
6	60 min	0.1731	4.869 µM	4.894 µM	100%	1.588

Rate constant (k) = slope of ln(conc. of carbazole) vs time plot = 0.012 min^{-1} = 2.0 × 10^{-4} s^{-1}.

4.2.2 Control experiments for synthesis of carbazole 4-1 without addition of CTAB, under microwave.

Two reactions were conducted following the optimized conditions, however without addition of CTAB for 30 min and 60 min run times under microwave-assisted heating conditions at 100 °C (60 W), using 2-iodo-*N*-phenylaniline **3aa** (32.5 mg, 0.1101 mmol), $Pd(OAc)_2$ (4 mol%) and DBU (2 equiv.) in a capped microwave vial (10 ml) containing a stir bar, deionized water (0.5 ml). The reaction mixture was cooled to room temperature, and diluted with 8.5 ml MeOH (spectroscopic grade).

Then absorbance of the solutions obtained from each reaction were measured, and from the observed absorbance values at λ_{max} 281 nm (Figure S6a**)**, concentrations of product (carbazole, **4-1**) were calculated (Table S3b). Then

concentrations of carbazole (**4-1**) vs reaction time plot was drawn (Figure S6b). Here yields of carbazoles were found less than the reactions which were performed with the addition of CTAB.

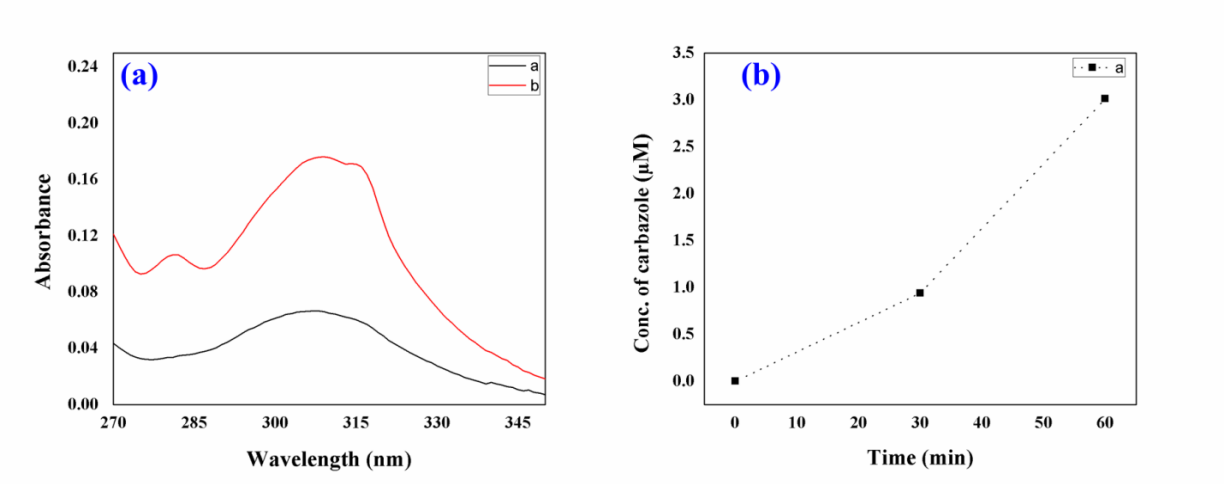


Figure S6. (a) Absorbance vs Wavelength plots of carbazole (**4-1**) of the reaction mixtures of 30 min and 60 min run time, in absence of CTAB. (b) Conc. of carbazole (**4-1**) vs reaction time plot.

Table S3b. Concentrations of carbazole (**4-1**) obtained from Absorbance vs Wavelength plots of the reaction mixtures of 30 min and 60 min run time, in absence of CTAB.

Entry	Reaction time (Vol. of solution taken 2 μL)	Absorbance at λ_{max} 281 nm	Concentration of product carbazole (**4-1**) at λ_{max} 281 nm [c = [**4-1**]/ε_{max}] (ε_{max} = 35,340)	Initial concentration of 2-iodo-*N*-phenylaniline (**3aa**)	Yield of carbazole **4-1** (from UV-Vis) [**4-1**]/[**3aa**] × 100%
1	0 min	0.0	0.0	4.894 μM	0%
2	30 min	0.0335	0.947 μM	4.894 μM	19%
3	60 min	0.1065	3.013 μM	4.894 μM	62%

Table S3c. Yields carbazole **4-1** under different conditions.

Entry	Reaction conditions	UV-Vis yield of carbazole **4-1** (Isolated yield of **4-1**) (%)
1	**3aa**, $Pd(OAc)_2$, CTAB, DBU, MW, 100 ^oC, 60 min	100 (99)
2	**3aa**, $Pd(OAc)_2$, DBU, water, MW, 100 ^oC, 60 min (Without CTAB)	62 (36% **4-1**, and 14% **5**)
3	**3aa**, $Pd(OAc)_2$, CTAB, MW, 100 ^oC, 60 min (without DBU)	0 (0)
4	**3aa**, $Pd(OAc)_2$, DBU, CTAB, 100 ^oC, 60 min (Conventional heating in an oil bath)	0 (0)
5	**3aa**, $Pd(OAc)_2$, DBU, CTAB, 100 ^oC, 24 h (Conventional heating in an oil bath)	not checked (60)
6	**3aa**, $Pd(OAc)_2$, DBU, CTAB, 140 ^oC, 24 h (Conventional heating in an oil bath)	not checked (93)

5.1 Preparation of palladium nanoparticles (PdNPs) catalysts 1 and 2.

To a light brown suspension of $Pd(OAc)_2$ (3.6 mg, 0.016 mmol) in deionized water (1.0 ml) in a microwave vial (10 ml), CTAB (14.6 mg, 0.04 mmol) was added at room temperature followed by N_2 gas purging for 2 minutes to give a chocolate brown suspension (Figure S7, vial a,b). Then DBU (121.8 mg, 0.8 mmol) was added to the chocolate brown suspension at room temperature. The chocolate brown suspension turned to a colorless clear solution (Figure S7, vial c). Then after purging N_2 gas for 2 minutes at room temperature the clear solution was heated under microwave irradiation in a capped vial at 100 ^oC for 15 min (60 W). That resulted in the formation of black colloidal matter (Figure S7, vial d). After cooling to room temperature, it was centrifuged (at 21000 RCF, 25 ^oC) for 30 min. The supernatant was removed by a syringe, and deionized water (1 ml), was added to the blackish residue. It was again centrifuged (at 21000 RCF, 25 ^oC) for 30 min, then supernatant was removed by a syringe, and the blackish residue was collected on a clean watch glass for drying on a hot air oven (>100 ^oC) for 72 h to get the Pd catalyst for characterization study (PdNPs catalyst 1).

In order to compare the characterization data as well as reaction efficiency of the catalysts, Pd catalyst was also prepared without adding DBU. There the chocolate brown suspension of $Pd(OAc)_2$ and CTAB in water (Figure S7, vial b) was heated under microwave irradiation in a capped vial at 100 ^oC for 15 min (60 W) to get another black colloidal matter (Figure S7, vial e). After cooling to room temperature, it was centrifuged (at 21000 RCF, 25 ^oC) for 30 min. The supernatant was removed by a syringe, and deionized water (1 ml), was added to the blackish residue. It was again centrifuged (at 21000 RCF, 25 ^oC) for 30 min, then supernatant was removed by a syringe, and the blackish residue was collected on a clean watch glass for drying on a hot air oven (>100 ^oC) for 72 h to get the Pd catalyst 2 (PdNPs catalyst 2) for characterization study.

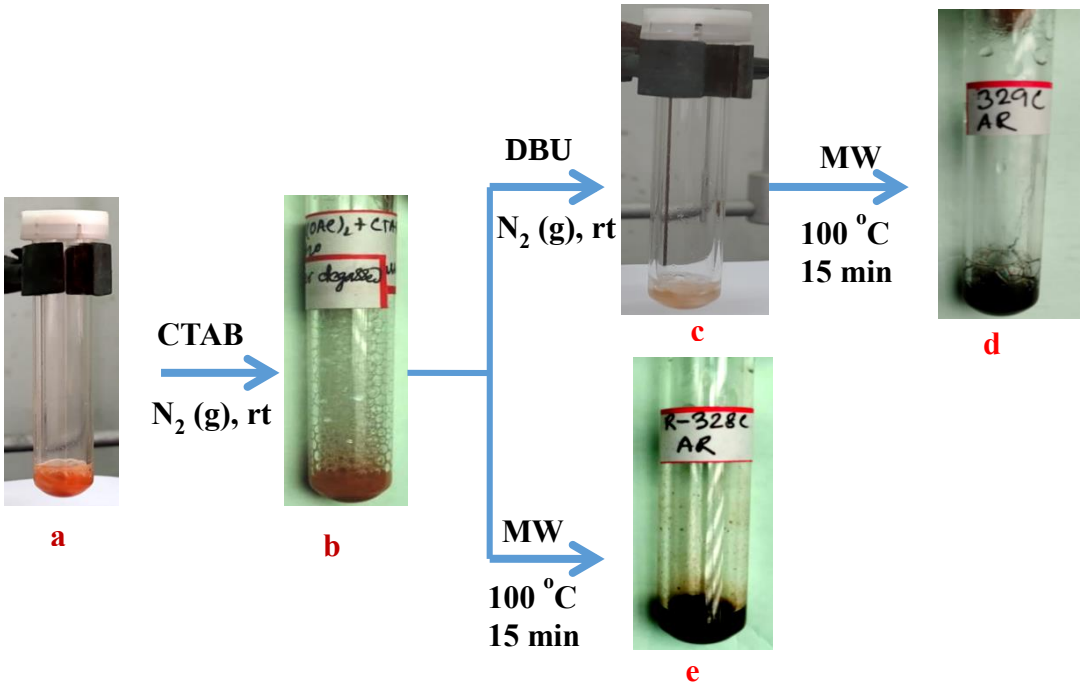
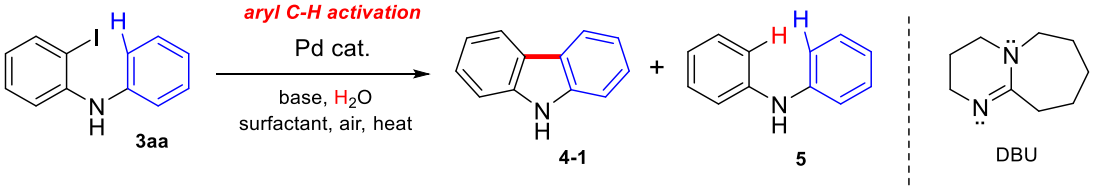


Figure S7. Preparation of PdNPs catalysts 1 and 2: (a) $Pd(OAc)_2$ in water at room temperature, (b) Chocolate brown suspension of $Pd(OAc)_2$ and CTAB in water under N_2 gas purging at room temperature, (c) Colorless clear solution after addition of DBU at room temperature, (d) Colloidal matter of PdNPs catalyst 1 after microwave irradiation (MW) at 100 °C (60 W) for 15 min. (e) Colloidal matter of PdNPs catalyst 2 after microwave irradiation (MW) at 100 °C (60 W) for 15 min.

5.2 Screening of PdNPs catalysts 1 and 2 for the optimization reactions of 3aa to give 4-1.

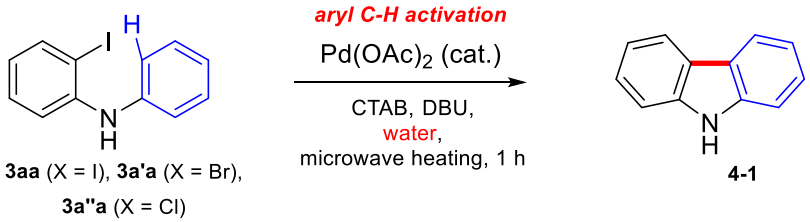
Table S4. Optimization of Pd-catalyzed intramolecular aryl C–H activation of **3aa** in water to give **4-1**[a]



Entry	[Pd] (mol%)	Base (equiv)	Surfactant (equiv)	Temp (°C), Mode, Time	Yield % (**4-1**:**5**)[b]
1	$Pd(OAc)_2$ (4)	DBU (2)	CTAB (0.1)	100, MW, 1 h	99
2[c]	Pd catalyst 1 (aq.)	-	-	100, MW, 1 h	90
3[d]	Pd catalyst 1 (s)	-	-	100, MW, 1 h	55
4[d]	Pd catalyst 1 (s)	DBU (2)	-	100, MW, 1 h	65
5[d]	Pd catalyst 1 (s)	DBU (2)	CTAB (0.1)	100, MW, 1 h	75
6[e]	Pd catalyst 2 (aq)	-	-	100, MW, 1 h	20 (1:0.2)
7[f]	Pd catalyst 2 (s)	-	-	100, MW, 1 h	10 (1:0.4)
8[f]	Pd catalyst 2 (s)	DBU (2)	CTAB (0.1)	100, MW, 1 h	40 (1:0.2)

[a]**Reaction conditions: 3aa** (0.4 mmol, 1 equiv.), Pd salt, surfactant, base, water (1 ml), heat (in a capped vial in a microwave reactor, 60 W). [b] Isolated yields. [c] Reaction using the aqueous part of separately prepared Pd catalyst using $Pd(OAc)_2$ (4 mol%), CTAB (0.04 mmol) and DBU (0.8 mmol) in 1.0 ml water under MW at 100 °C. [d] Reaction using isolated black residue of the Pd catalyst prepared from $Pd(OAc)_2$ (4 mol%), CTAB (0.04 mmol) and DBU (0.8 mmol) in 1.0 ml water under MW at 100 °C (Pd catalyst 1). [e] Reaction using the aqueous part of separately prepared Pd catalyst using $Pd(OAc)_2$ (4 mol%) and CTAB (0.04 mmol) in 1.0 ml water under MW at 100 °C. [f] Reaction using isolated black residue of the Pd catalyst prepared from $Pd(OAc)_2$ (4 mol%) and CTAB (0.04 mmol) in 1.0 ml water under MW at 100 °C (Pd catalyst 2).

Table S5. Screening of Pd-catalyzed intramolecular aryl C–H activation reactions of 2-iodo-*N*-phenylaniline **3aa**, 2-bromo-*N*-phenylaniline **3a'a**, and 2-chloro-*N*-phenylaniline **3a"a**, under microwave-assisted conditions in water to give carbazole **4-1**.[a]



Entry	*Reactant*	*[Pd] (mol%)*	*Base (equiv.)*	*Surfactant (equiv.)*	*Temperature (°C)*	*Yield of **4-1** (%)*[b]
1	**3aa**	$Pd(OAc)_2$ (4)	DBU (2)	CTAB (0.1)	70	15
2	**3aa**	$Pd(OAc)_2$ (4)	DBU (2)	CTAB (0.1)	80	35
3	**3aa**	$Pd(OAc)_2$ (4)	DBU (2)	CTAB (0.1)	90	85
4	**3aa**	$Pd(OAc)_2$ (4)	DBU (2)	CTAB (0.1)	100	99
5	**3aa**	$Pd(OAc)_2$ (4)	DBU (2)	CTAB (0.1)	110	98
6	**3aa**	$Pd(OAc)_2$ (4)	DBU (2)	CTAB (0.1)	120	99
7	**3aa**	$Pd(OAc)_2$ (4)	DBU (2)	CTAB (0.1)	130	98
8	**3aa**	$Pd(OAc)_2$ (4)	DBU (2)	CTAB (0.1)	140	99
9	**3a'a**	$Pd(OAc)_2$ (4)	DBU (2)	CTAB (0.1)	100	5
10	**3a'a**	$Pd(OAc)_2$ (4)	DBU (2)	CTAB (0.1)	120	25
11	**3a'a**	$Pd(OAc)_2$ (4)	DBU (2)	CTAB (0.1)	130	50
12	**3a'a**	$Pd(OAc)_2$ (4)	DBU (2)	CTAB (0.1)	140	90
13	**3a'a**	$Pd(OAc)_2$ (4)	DBU (2)	CTAB (0.1)	150	92
14	**3a"a**	$Pd(OAc)_2$ (4)	DBU (2)	CTAB (0.1)	100	0
15	**3a"a**	$Pd(OAc)_2$ (4)	DBU (2)	CTAB (0.1)	140	0
16	**3a"a**	$Pd(OAc)_2$ (4)	DBU (2)	CTAB (0.1)	150	0

[a]**Reaction conditions: 3aa/3a'a/3a"a** (0.4 mmol, 1 equiv.), $Pd(OAc)_2$, CTAB and DBU in 1 ml water under MW (60 W) at different temperatures for 1 h in a capped vial in a microwave reactor. [b] Isolated yields of **4-1**.

6.1 Typical procedure for the preparation of carbazole 4-1 *via* PdNPs-catalyzed aryl C–H activation of 2-iodo-*N*-phenylaniline 3aa under microwave-assisted heating in water.

To a mixture of 2-iodo-*N*-phenylaniline **3aa** (118 mg, 0.4 mmol), CTAB (15 mg, 0.04 mmol, 0.1 equiv.) and $Pd(OAc)_2$ (3.6 mg, 0.016 mmol, 4 mol%) in a microwave vial (10 ml) containing a stir bar, deionized water (1 ml) was added at room temperature. The mixture turned into a brown suspension. The vial was closed with a septum, and N_2 (g) was purged into it for 2 to 3 minutes to make the micelles of CTAB. Then DBU (120 μl, 122 mg, 0.8 mmol, 2.0 equiv.) was added to it by a syringe, and N_2 (g) was purged into it for 2 minutes at room temperature. The brown suspension became a colorless clear solution with the addition of DBU. The reaction vial was sealed with a plastic microwave septum replacing the previous septum. The capped reaction vial was submitted to a microwave reactor for microwave irradiation at 100 °C (60 W) for 1 h. The reaction mixture was cooled to room temperature, transferred into a centrifuge tube with the addition of ethyl acetate-hexane mixture (1 ml, 3:1 v/v), and centrifuged (at 21000 RCF, 25 °C) for 15 min. Then organic layer was collected by syringe, again ethyl acetate-hexane mixture (1 ml, 3:1 v/v) was added to the aqueous part in the centrifuge tube, and the mixture was centrifuged (at 21000 RCF, 25 °C) for 15 min. The aqueous and organic parts were collected separately by syringe, and the aqueous layer recovered from this reaction was saved for further use (for the next catalytic reaction of the same substrate). The combined organic part was washed with water (2 ml) followed by brine solution (2 ml), dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The crude product was purified through a silica gel (100-200 mesh) column using hexane/ethyl acetate mixtures (90:10) as the eluent to yield 9*H*-carbazole **4-1** (66.2 mg, 99%) as white solid.

Carbazoles derivatives **4-2** to **4-43** were prepared similarly from the respective 2-iodo-*N*-arylanilines **3** (Scheme S1).

6.2 TON (Turnover number) and TOF (Turnover frequency) calculations.

TON = [(Amount of reactant in mmol) / (Amount of catalyst in mmol)] × yield of product

= [0.4/0.016] × 0.99 = 24.75

TOF = TON value/reaction time

= 24.75/1 h = 24.75 h^{-1}

6.3 Recycling studies and E-factor calculation.

2-Iodo-*N*-phenylaniline **3aa** (118 mg, 0.4 mmol) was added to the recovered aqueous part collected from the previous reaction, in a microwave vial (10 ml). Then CTAB (8 mg, 0.02 mmol, 0.05 equiv., in 0.2 ml water) and DBU (60 μl, 61 mg, 0.4 mmol, 1 equiv.) were added to it by a syringe, and N_2 (g) was purged into it for 2 minutes at room temperature. The reaction vial was sealed with a plastic microwave septum replacing the previous septum. The capped reaction vial with a stir bar was submitted to microwave reactor for microwave irradiation at 100 °C (60 W) for 1 h. Then reaction mixture was cooled to room temperature, transferred into a centrifuge tube with the addition of ethyl acetate-hexane mixture (1 ml, 3:1 v/v), and centrifuged (at 21000 RCF, 25 °C) for 15 min. It was done for two times (with the addition of ethyl acetate-hexane mixture (1 ml, 3:1 v/v)). Both the aqueous and organic parts were collected

separately. Product carbazole **4-1** was collected from the combined organic part, similarly as described in the typical procedure. The collected aqueous part containing the recovered Pd catalyst was used for successive recycling experiments by repeating the same procedure, only additional amount of CTAB (8 mg, in 0.2 ml water) and DBU (61 mg) were added to each recycling experiment (see Table S6).

Table S6. Recyclability of PdNPs catalyst in the reaction of **3aa** to give carbazole **4-1**.

Number of cycles	1	2	3	4	5
Yields of **4-1** (amount)	99% (66.2 mg)	96% (64.2 mg)	92% (61.5 mg)	90% (60.2 mg)	85% (56.8 mg)

E-factor = (Amount of organic waste in mg) / (Amount of product carbazole in mg)

= (Mass of all reactants and reagents taken – Mass of product obtained)/(Mass of product obtained)

= [(258.6-66.2)+(258.6-64.2)+(258.6-61.5)+(258.6-60.2)+(258.6-56.8)] mg /

(66.2+64.2+61.5+60.2+56.8) mg

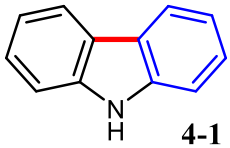
= (192.4 + 194.4 + 197.1 + 198.4 + 201.8) mg / 308.9 mg

= 984.1 mg / 308.9 mg

= 3.18

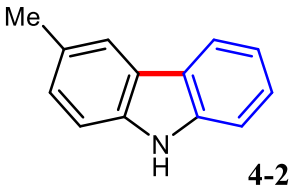
[Mass of all reactants and reagents taken = (118 + 15 + 3.6 + 122) mg = 258.6 mg]

6.4 Characterization data of carbazoles 4-1 to 4-43, and diphenylamine 5.

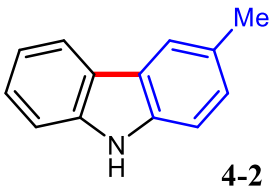


4-1

9*H*-Carbazole (4-1)[1]: White solid (66.2 mg, 99%); mp: 244-246 °C (ref.[1,2] 243.5-246 °C); ^{1}H NMR (400 MHz, DMSO-D_6): δ = 11.24 (brs, 1H, N–H), 8.10 (d, J = 7.7 Hz, 2H, Ar–H), 7.48 (d, J = 8.1 Hz, 2H, Ar–H), 7.37 (t, J = 7.3 Hz, 2H, Ar–H), 7.15 (t, J = 7.4 Hz, 2H, Ar–H) ppm; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.08 (d, J = 8.0 Hz, 2H, Ar–H), 8.01 (brs, 1H, N–H), 7.43-7.39 (m, 4H, Ar–H), 7.24-7.21 (m, 2H, Ar–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.70 (2C), 126.04 (2CH), 123.58 (2C), 120.54 (2CH), 119.66 (2CH), 110.78 (2 CH) ppm; IR (ATR): $\tilde{\nu}$ = 3415 (N–H), 3051, 1625, 1449, 1138, 927, 720 cm^{-1}; LCMS (ESI): *m/z* calcd. for $[C_{12}H_9N+H]^+$: 168.08, found: 168.30. This compound was known.[1,2] TON 24.75.

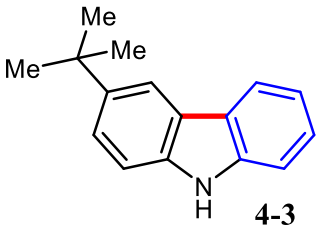


4-2
from **3ba**



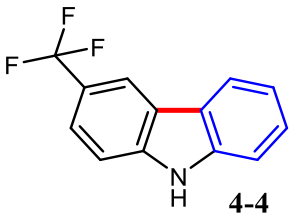
4-2
from **3ab**

3-Methyl-9*H*-carbazole (4-2)[1,2]**:** Carbazole **4-2** was prepared according to the typical procedure from compound **3ba** or **3ab** (124 mg, 0.4 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (95:5). Off-white solid (69 mg, 95% from **3ba** and 71 mg, 98% from **3ab**); mp: 202-204 °C (ref.[1,2] 206-208 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.03 (d, J = 7.5 Hz, 1H, Ar–H), 7.91 (brs, 1H, N–H), 7.86 (s, 1H, Ar–H), 7.39-7.38 (m, 2H, Ar–H), 7.31 (d, J = 8.0 Hz, 1H, Ar–H), 7.24-7.18 (m, 2H, Ar–H), 2.52 (s, 3H, Ar–CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.83 (C), 137.73 (C), 128.76 (C), 127.18 (CH), 125.65 (CH), 123.55 (C), 123.26 (C), 120.25 (2CH), 119.23 (CH), 110.55 (CH), 110.24 (CH), 21.44 (-CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3401 (N–H), 2916, 1458, 1333, 1226, 1171, 1028, 928, 886, 804, 727 cm^{-1}; LCMS (ESI): *m/z* calcd. for $[C_{13}H_{11}N+H]^+$: 182.09, found: 182.10. TON 23.75 from **3ba** and 24.5 from **3ab**.



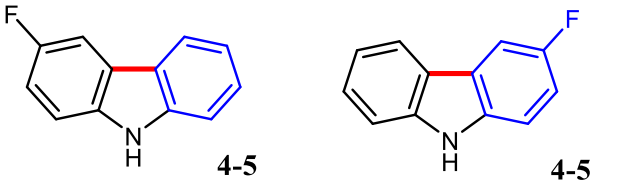
4-3

3-(*tert*-Butyl)-9*H*-carbazole (4-3)[3]**:** It was prepared according to the typical procedure from compound **3ca** (140 mg, 0.4 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (95:5). White solid (87 mg, 98%); mp: 150-152 °C (ref.[3a] 150-152 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.08 (d, J = 6.0 Hz, 2H, Ar–H), 7.91 (brs, 1H, N–H), 7.48 (dt, J = 8.7, 1.4 Hz, 1H, Ar–H), 7.38 (dd, J = 3.8, 1.4 Hz, 2H, Ar–H), 7.34 (d, J = 8.5 Hz, 1H, Ar–H), 7.35-7.20 (m, 1H, Ar–H), 1.44 (s, 9H, $C(CH_3)_3$) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.42 (C), 139.85 (C), 137.51 (C), 125.52 (CH), 123.80 (CH), 123.54 (C), 122.99 (C), 120.11 (CH), 119.16 (CH), 116.33 (CH), 110.52 (CH), 110.02 (CH), 34.67 (C), 31.97 (CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3419 (N–H), 3058, 2954, 2857, 1712, 1605, 1498, 1480, 1391, 1294, 1258, 1143, 1089, 885, 751 cm^{-1}; HRMS (ESI): *m/z* calcd. for $[C_{16}H_{16}N\text{-}H]^+$: 222.1283, found: 222.1287. TON 24.5.



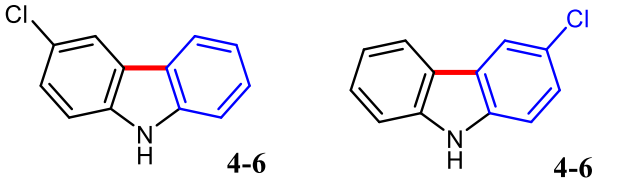
4-4

3-(Trifluoromethyl)-9*H*-carbazole (4-4)[4]**:** It was prepared according to the typical procedure from compound **3da** (145 mg, 0.4 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (90:10). Off white solid (89 mg, 95%); mp: 164-166 ºC (Ref.[4] 163.5-164.5 ºC); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.34 (s,1H, Ar–H), 8.26 (brs, 1H, N–H), 8.11 (d, J = 7.8 Hz, 1H, Ar–H), 7.66 (dd, J = 8.5, 1.9 Hz, 1H, Ar–H), 7.50-7.46 (m, 3H, A–-H), 7.30 (ddd, J = 7.9, 5.4, 2.6 Hz, 1H, Ar–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.38 (C), 139.89 (C), 126.82 (CH), 126.27 (C), 124.11 (C), 122.89 (d, J_{CF} = 13.1 Hz, C), 122.67 (q, J_{CF} = 3.5 Hz, CH), 121.74 (q, J_{CF} = 31.8 Hz, C), 120.58 (CH), 120.29 (CH), 117.92 (q, J_{CF} = 8.0, 4.0, Hz CH), 110.93 (CH), 110.62 (CH) ppm; IR (ATR): $\tilde{\nu}$ = 3352 (N–H), 3050, 2368, 1675, 1569, 1518, 1348, 1270, 1150, 935, 806, 735, 614 cm^{-1}; HRMS (ESI): *m/z* calcd. for $[C_{13}H_7F_3N\text{-}H]^+$: 234.0531, found: 234.0534. TON 23.75.



4-5 from **3ea** **4-5** from **3ac**

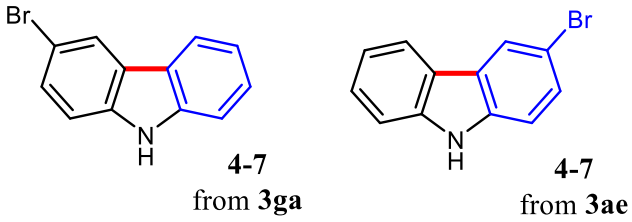
3-Fluoro-9*H*-carbazole (4-5)[1,2]**:** Carbazole **4-5** was prepared according to the typical procedure from **3ea** or **3ac** (125 mg, 0.4 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (95:5). Off-white solid (73 mg, 99% from **3ea** and 72 mg, 97% from **3ac**); mp: 206-208 ºC (ref.[1,2] 201.1-203.4 ºC); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.01 (dd, J = 8.0, 0.5 Hz, 1H, Ar–H), 7.98 (brs, 1H, N–H), 7.71 (dd, J = 8.5, 2.5 Hz, 1H, Ar–H), 7.44-7.39 (m, 2H, Ar–H), 7.32 (dd, J = 8.5, 4.0 Hz, 1H, Ar–H), 7.21 (ddd, J = 8.0, 5.5, 2.5 Hz, 1H, Ar–H), 7.14 (td, J = 9.0, 2.5 Hz, 1H, Ar–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.04 (d, J_{CF} = 235.7 Hz, C), 140.75 (C), 135.97 (C), 126.64 (CH), 124.13 (d, J_{CF} = 9.5 Hz, C), 123.33 (d, J_{CF} = 3.6 Hz, C), 120.76 (CH), 119.69 (CH), 113.83 (d, J_{CF} = 25.1 Hz, CH), 111.30 (d, J_{CF} = 9.1 Hz, CH), 111.06 (CH), 106.21 (d, J_{CF} = 23.6 Hz, CH) ppm; IR (ATR): $\tilde{\nu}$ = 3415 (N–H), 3053, 1936, 1896, 1585, 1456, 1275, 1165, 864, 805, 744 cm^{-1}; LCMS (ESI): *m/z* calcd. for $[C_{12}H_8FN\text{-}H]^+$: 184.05, found: 184.10. TON 24.75 from **3ea** and 24.25 from **3ac**.



4-6 from **3fa** **4-6** from **3ad**

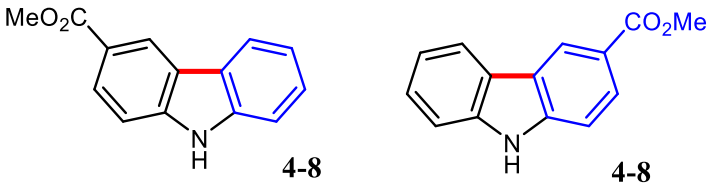
3-Chloro-9*H*-carbazole (4-6)[1,2]**:** Carbazole **4-6** was prepared according to the typical procedure from **3fa** or **3ad** (132 mg, 0.4 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (95:5). White solid (78 mg, 97% from **3fa** and 77 mg, 95% from **3ad**); mp: 202-204 ºC (ref.[1,2] 198-200 ºC); ^{1}H NMR (500 MHz, CD_3OD): δ = 8.00 (s, 1H, Ar–H), 7.99 (d, J = 1.5 Hz, 1H, Ar–H), 7.43 (d, J = 8.0 Hz, 1H, Ar–H), 7.38-7.36 (m, 2H, Ar–H), 7.30 (dd, J = 8.5, 2.0 Hz, 1H, Ar–H), 7.14 (t, J = 8.0 Hz, 1H, Ar–H) ppm; ^{13}C NMR (125 MHz, CD_3OD):

δ = 141.98 (C), 139.67 (C), 127.21 (CH), 126.37 (CH), 125.44 (C), 125.04 (C), 123.35 (C), 121.12 (CH), 120.51 (CH), 119.99 (CH), 112.77 (CH), 111.95 (CH) ppm; IR (ATR): $\tilde{\nu}$ = 3400 (N–H), 3049, 2313, 1436, 1333, 1270, 928, 744 cm^{-1}; LCMS (ESI): *m/z* calcd. for $[C_{12}H_8ClN\text{-}H]^+$: 200.02, found: 200.00. TON 24.25 from **3fa** and 23.75 from **3ad**.



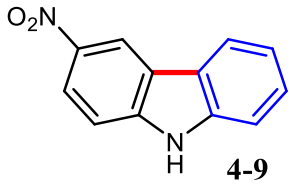
4-7 from **3ga** **4-7** from **3ae**

3-Bromo-9*H*-carbazole (4-7)[1,2]**:** Carbazole **4-7** was prepared according to the typical procedure from **3ga** or **3ae** (150 mg, 0.4 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (95:5). White solid (89 mg, 91% from **3ga**, and 89 mg, 90% from **3ae**); mp: 194-196 °C (ref.[1,2] 193-195 °C); ^{1}H NMR (500 MHz, acetone-d_6): δ = 10.52 (brs, 1H, residual N–H), 8.28 (t, *J* = 1.0 Hz, 1H, Ar–H), 8.15 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.53 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.49-7.48 (m, 2H, Ar–H), 7.42 (td, *J* = 8.0, 1.0 Hz, 1H, Ar–H), 7.20 (td, *J* = 8.0, 1.0 Hz, 1H, Ar–H) ppm; ^{13}C NMR (125 MHz, acetone-d_6): δ = 141.33 (C), 139.55 (C), 128.93 (CH), 127.30 (CH), 125.92 (C), 125.88 (C), 123.60 (CH), 122.93 (C), 121.31 (CH), 120.15 (CH), 113.50 (CH), 111.97 (C) ppm; IR (ATR): $\tilde{\nu}$ = 3401 (N–H), 2923, 1599, 1444, 1270, 1055, 879, 745 cm^{-1}; LCMS (ESI): *m/z* calcd. for $[C_{12}H_8BrN\text{-}H]^+$: 243.97, found: 244.00. TON 22.75 from **3ga** and 22.5 from **3ae**.



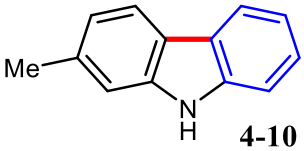
4-8 from **3ha** **4-8** from **3af**

Methyl 9*H*-carbazole-3-carboxylate (4-8)[1,5]**:** Carbazole **4-8** was prepared according to the typical procedure from compound **3ha** or **3af** (141 mg, 0.4 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (85:15). White solid (82 mg, 91% yield from **3ha**, and 81 mg, 90% from **3af**); mp: 174-176 °C (ref.[5] 168-170 °C); ^{1}H NMR (250 MHz, acetone-d_6): δ = 10.79 (brs, 1H, residual N–H), 8.82 (d, *J* = 1.5 Hz, 1H, Ar–H), 8.24 (d, *J* = 7.7 Hz, 1H, Ar–H), 8.08 (dd, *J* = 8.5, 1.5 Hz, 1H, Ar–H), 7.58 (dd, *J* = 8.7, 1.2 Hz, 2H, Ar–H), 7.46 (td, *J* = 7.7, 1.2 Hz, 1H, Ar–H), 7.26 (td, *J* = 7.7, 1.2 Hz, 1H, Ar–H), 3.91 (s, 3H, -CH_3) ppm; ^{13}C NMR (62.5 MHz, acetone-d_6): δ = 167.94 (C=O), 143.60 (C), 141.43 (C), 127.79 (CH), 127.27 (CH), 123.87 (C), 123.66 (C), 123.22 (CH), 121.71 (C), 121.28 (CH), 120.64 (CH), 112.10 (CH), 111.35 (CH), 51.99 (CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3325 (N–H), 2982, 1684 (C=O), 1626, 1602, 1431, 1333, 1292, 1260, 1099, 977, 825, 722 cm^{-1}; LCMS (ESI): *m/z* calcd. for $[C_{14}H_{11}NO_2\text{+H}]^+$: 226.08, found: 226.10. TON 22.75 from **3ha** and 22.5 from **3af**.



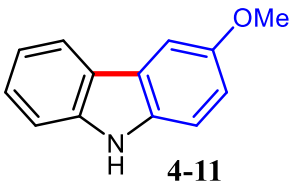
4-9

3-Nitro-9*H*-carbazole (4-9)[1,2]**:** Carbazole **4-9** was prepared according to the typical procedure from compound **3ia** (136 mg, 0.4 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (90:10). Yellow solid (81 mg, 95% yield); mp: 212-214 °C (ref.[1,2] 214-216 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.99 (d, J = 2.0 Hz, 1H, Ar–H), 8.45 (brs, 1H, N–H), 8.34 (dd, J = 9.0, 2.0 Hz, 1H, Ar–H), 8.13 (d, J = 8.0 Hz, 1H, Ar–H), 7.53-7.48 (m, 2H, Ar–H), 7.45 (d, J = 9.0 Hz, 1H Ar–H), 7.34 (td, J = 8.0, 2.0 Hz, 1H, Ar–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.72 (C), 141.31 (C), 140.48 (C), 127.64 (CH), 123.21 (C), 123.17 (C), 121.81 (CH), 121.22 (CH), 121.00 (CH), 117.35 (CH), 111.37 (CH), 110.27 (CH) ppm; IR (ATR): $\tilde{\nu}$ = 3327 (N–H), 2917, 1603, 1524, 1455 (N–O), 1279, 1192, 1083, 813, 720 cm^{-1}; LCMS (ESI): *m/z* calcd. for $[C_{12}H_8N_2O_2+H]^+$: 213.06, found: 213.10. TON 23.75.



4-10

2-Methyl-9*H*-carbazole (4-10) [1,6]**:** Carbazole **4-10** was prepared according to the typical procedure from **3ja** (124 mg, 0.4 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (90:10). White solid (67 mg, 93%); mp: 258-260 °C (ref.[6] 261-262 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.02 (d, J = 8.0 Hz, 1H, Ar–H), 7.94 (d, J = 8.0 Hz, 1H, Ar–H), 7.89 (brs, 1H, residual N–H), 7.38-7.36 (m, 2H, Ar–H), 7.20 (td, J = 8.0, 2.0 Hz, 2H, Ar–H), 7.05 (dd, J = 8.0, 1.0 Hz, 1H, Ar–H), 2.52 (s, 3H, CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.19 (C), 139.70 (C), 136.23 (C), 125.49 (CH), 123.69 (C), 121.29 (C), 121.21 (CH), 120.21 (2 CH), 119.56 (CH), 110.94 (CH), 110.68 (CH), 22.26 (CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3396 (N–H), 2915, 1923, 1886, 1605, 1460, 1437, 1326, 1243, 1148, 1016, 864, 806, 744 cm^{-1}; LCMS (ESI): *m/z* calcd. for $[C_{13}H_{11}N+H]^+$: 182.09, found: 182.10. TON 23.25.

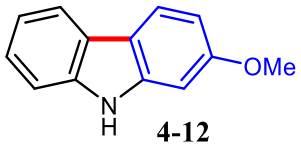


4-11

3-Methoxy-9*H*-carbazole (4-11)[1,2]**:** Carbazole **4-11** was prepared according to the typical procedure from compound **3ag** (130 mg, 0.4 mmol), and purified by column chromatography on silica gel (100-200 mesh), eluting with hexane/ethyl acetate (90:10). Off-white solid (75 mg, 95% yield); mp: 146-148 °C (ref.[2] 149-151 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.03 (d, J = 8.0 Hz, 1H, Ar–H), 7.90 (brs, 1H, N–H), 7.55 (d, J = 2.5 Hz, 1H, Ar–H), 7.40-7.39 (m,

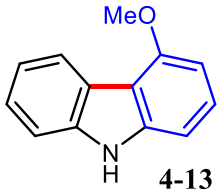
2H, Ar–H), 7.33 (d, *J* = 9.0 Hz, 1H, Ar–H), 7.20 (ddd, *J* = 8.0, 5.5, 2.5 Hz, 1H, Ar–H), 7.06 (dd, *J* = 8.5, 2.5 Hz, 1H, Ar–H), 3.93 (s, 3H, -CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.95 (C), 140.30 (C), 134.39 (C), 125.80 (CH), 123.83 (C), 123.40 (C), 120.25 (CH), 119.07 (CH), 115.08 (CH), 111.27 (CH), 110.73 (CH), 103.24 (CH), 56.10 (-CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3397 (N–H), 2919, 1624, 1585, 1458, 1332, 1283, 1171, 817, 747 cm^{-1}; LCMS (ESI): *m/z* calcd. for $[C_{13}H_{11}NO+H]^+$: 198.09, found: 198.10. TON 23.75.

According to the typical procedure, reaction of **3ah** (130 mg, 0.4 mmol) produced a mixture of 2-methoxy-9*H*-carbazole (**4-12**, 24 mg, 30%) and 4-methoxy-9*H*-carbazole (**4-13**, 49 mg, 62%). Carbazoles **4-12** and **4-13** were collected separately during column chromatography on silica gel, eluting with hexane/ethyl acetate (90:10), from the earlier fractions and later fractions, respectively. Ratio of 2-methoxy-9*H*-carbazole (**4-12**) and 4-methoxy-9*H*-carbazole (**4-13**) was found 0.48:1 (C2:C4), from ^{1}H NMR spectrum of the reaction mixture. Combined yield 92% and TON 23.0.



4-12

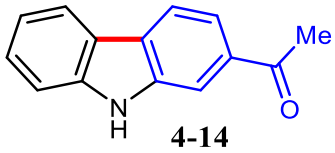
2-Methoxy-9*H*-carbazole (4-12)[1,7]**:** White solid (24 mg, 30%); mp: 234-236 °C (ref.[7] 234 °C); ^{1}H NMR (250 MHz, acetone-d_6): δ = 10.22 (brs, 1H, residual N–H), 8.02 (s, 1H, Ar–H), 7.98 (d, *J* = 8.5 Hz, 1H, Ar–H), 7.46 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.30 (td, *J* =7.5, 1.0 Hz, 1H, Ar–H), 7.14 (t, *J* = 7.5 Hz, 1H, Ar–H), 7.05 (d, *J* = 2.5 Hz, 1H, Ar–H), 6.82 (dd, *J* = 8.5, 2.0 Hz, 1H, Ar–H), 3.88 (s, 3H,-CH_3) ppm; ^{13}C NMR (62.5 MHz, acetone-d_6): δ = 159.18 (C), 141.34 (C), 139.99 (C), 124.15 (CH), 123.30 (C), 120.69 (CH), 119.11 (CH), 118.81 (CH), 116.80 (C), 110.45 (CH), 107.89 (CH), 94.43 (CH), 54.83 (-CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3388 (N–H), 2932, 1600, 1583, 1508, 1455, 1442, 1308, 1262, 1098, 783 cm^{-1}; LCMS (ESI): *m/z* calcd. for $[C_{13}H_{11}NO+H]^+$: 198.09, found: 198.10.



4-13

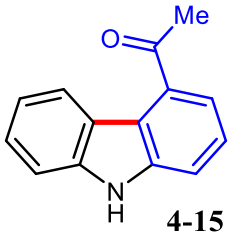
4-Methoxy-9*H*-carbazole (4-13)[1,7]**:** White solid (49 mg, 62%); mp: 136-138 °C (ref.[7] 135 °C); ^{1}H NMR (500 MHz, acetone-d_6): δ = 8.25 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.49 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.35 (td, *J* = 8.0, 1.0 Hz, 1H, Ar–H), 7.32 (d, *J* = 8.5 Hz, 1H, Ar–H), 7.17 (t, *J* = 8.0 Hz, 1H, Ar–H), 7.12 (d, *J* = 8.0 Hz, 1H, Ar–H), 6.73 (d, *J* = 7.5 Hz, 1H, Ar–H), 4.08 (s, 3H, -CH_3) ppm; ^{13}C NMR (125 MHz, acetone-d_6): δ = 156.35 (C), 141.47 (C), 139.28 (C), 126.41 (CH), 124.47 (CH), 122.67 (CH), 122.53 (C), 118.73 (CH), 112.40 (C), 110.09 (CH), 103.74 (CH), 99.93 (CH), 54.79 (-CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3389 (N–H), 2932, 1602, 1583, 1507, 1455, 1436, 1310, 1265, 754 cm^{-1}; LCMS (ESI): *m/z* calcd. for $[C_{13}H_{11}NO+H]^+$: 198.09, found: 198.00.

According to the typical procedure, reaction of **3ai** (135 mg, 0.4 mmol), produced a mixture of 2-acetylcarbazole (**4-14**, 13 mg, 16%) and 4-acetylcarbazole (**4-15**, 60 mg, 72%). Carbazoles **4-14** and **4-15** were collected separately during column chromatography on silica gel, eluting with hexane/ethyl acetate (85:15), from the later fractions and earlier fractions respectively. Ratio of 2-acetylcarbazole (**4-14**) and 4-acetylcarbazole (**4-15**) was found 0.23:1 (C2:C4), from ^{1}H NMR spectrum of the reaction mixture. Combined yield 88% and TON 22.0.



4-14

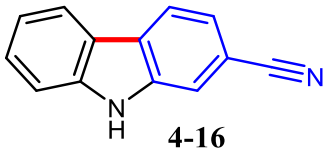
2-Acetylcarbazole (4-14) [1,7,8]**:** Pale yellow solid (13 mg, 16%); mp: 230-232 °C (ref.[8] 232-234 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.24 (brs, 1H, N–H), 8.11 (t, J = 8.0 Hz, 3H, Ar–H), 7.86 (dd, J = 8.0, 1.0 Hz, 1H, Ar–H), 7.51-7.47 (m, 2H, Ar–H), 7.29-7.26 (m, 1H, Ar–H), 2.71 (s, 3H, CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 198.43 (C=O), 141.24 (C), 139.27 (C), 135.01 (2C), 127.62 (CH), 127.52 (CH), 122.74 (C), 121.42 (CH), 120.28 (2CH), 111.19 (CH), 111.10 (CH), 27.17 (CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3317 (N–H), 2921, 1660 (C=O), 1605, 1498, 1440, 1351, 1312, 1258, 1015, 822, 749 cm^{-1}; LCMS (ESI): *m/z* calcd. for $[C_{14}H_{11}NO\text{-}H]^+$: 208.07, found: 208.10.



4-15

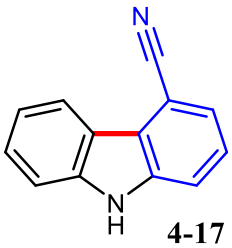
4-Acetylcarbazole (4-15)[8]**:** Pale yellow solid (60 mg, 72%); mp: 126-128 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.74 (d, J = 8.2 Hz, 1H, Ar–H), 8.29 (brs, 1H, N–H), 7.67 (d, J = 7.5 Hz, 1H, Ar–H), 7.60 (d, J = 7.5 Hz, 1H, Ar–H), 7.48-7.41 (m, 3H, Ar–H), 7.25 (dt, J = 8.2, 1.6 Hz, 1H, Ar–H), 2.80 (s, 3H, CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 201.30 (C=O), 140.39 (C), 140.26 (C), 134.05 (C), 126.95 (CH), 125.52 (CH), 124.72 (CH), 122.17 (C), 121.90 (CH), 120.52 (C), 119.78 (CH), 114.90 (CH), 110.30 (CH), 29.17 (CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3245 (N–H), 1664 (C=O), 1602, 1559, 1507, 1458, 1399, 1324, 1268, 1229, 1175, 1116, 992, 792, 722 cm^{-1}; LCMS (ESI): *m/z* calcd. for $[C_{14}H_{11}NO\text{-}H]^+$: 208.07, found: 208.00.

According to the typical procedure, reaction of **3aj** (128 mg, 0.4 mmol), produced a mixture of 9*H*-carbazole-2-carbonitrile (**4-16**, 19 mg, 25%) and 9*H*-carbazole-4-carbonitrile (**4-17**, 35 mg, 45%). Carbazoles **4-16** and **4-17** were collected separately during column chromatography on silica gel, eluting with hexane/ethyl acetate (85:15), from the earlier and later fractions, respectively. Ratio of 9*H*-carbazole-2-carbonitrile (**4-16**) and 9*H*-carbazole-4-carbonitrile (**4-17**) was found 0.62:1 (C2:C4), from ^{1}H NMR spectrum of the reaction mixture. Combined yield 70% and TON 17.5.



4-16

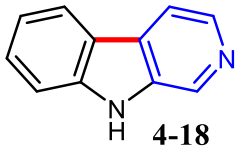
9*H*-Carbazole-2-carbonitrile (4-16)[1,9]**:** Off-white solid (19 mg, 25% yield); mp: 124-126 ºC (ref.[10] 120-122 ºC). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.28 (brs, 1H, N–H), 8.14 (d, *J* = 8.0 Hz, 1H, Ar–H), 8.11 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.75 (s, 1H Ar–H), 7.52-7.49 (m, 3H, Ar–H), 7.29 (t, *J* = 8.0 Hz, 1H, Ar–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.79 (C), 138.53 (C), 128.16 (CH), 127.12 (C), 123.06 (CH), 122.46 (C), 121.42 (CH), 121.24 (CH), 120.77 (CH), 120.28 (CN), 114.98 (CH), 111.34 (CH), 108.51 (C) ppm; IR (ATR): $\tilde{\nu}$ = 3257 (N–H), 2222 (CN), 1631, 1559, 1507, 1451, 1341, 1327, 1244, 861, 740 cm^{-1}; LCMS (ESI): *m/z* calcd. for $[C_{13}H_8N_2\text{-}H]^+$: 191.06, found: 191.00.



4-17

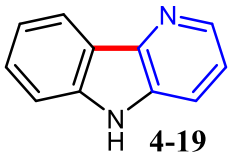
9*H*-Carbazole-4-carbonitrile (4-17)[1,10]**:** White solid (35 mg, 45%); mp: 158-160 ºC (ref.[11] 156-158 ºC). ^{1}H NMR (500 MHz, acetone-d_6): δ = 8.52 (d, *J* = 7.5 Hz, 1H, Ar–H), 7.90 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.66 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.63 (d, *J* = 7.5 Hz, 1H, Ar–H), 7.59 (d, *J* = 7.5 Hz, 1H; Ar–H), 7.56 (d, *J* = 7.5 Hz, 1H, Ar–H), 7.35 (t, *J* = 7.5 Hz, 1H, Ar–H) ppm; ^{13}C NMR (125 MHz, acetone-d_6): δ = 140.68 (C), 139.90 (C), 127.39 (CH), 125.36 (CH), 123.84 (CH), 122.79 (C), 120.90 (CH), 120.77 (C), 119.78 (CH), 118.42 (CN), 115.74 (CH), 111.46 (CH), 103.42 (C) ppm; IR (ATR): $\tilde{\nu}$ = 3318 (N–H), 2982, 2924, 2222 (C–N), 1602, 1506, 1459, 1323, 1228, 786, 713 cm^{-1}; LCMS (ESI): *m/z* calcd. for $[C_{13}H_8N_2\text{-}H]^+$: 191.06, found: 191.10.

According to the typical procedure, reaction of **3ak** (118 mg, 0.4 mmol), produced a mixture of β-Carboline or 9*H*-pyrido[3,4-*b*]indole (**4-18**, 3 mg, 4%) and δ-Carboline or 5*H*-pyrido[3,2-*b*]indole (**4-19**, 50 mg, 75%). Carbazoles **4-18** and **4-19** were collected separately during column chromatography on silica gel, eluting with hexane/ethyl acetate (70:30), from the earlier and later fractions, respectively. Ratio of 9*H*-pyrido[3,4-*b*]indole (**4-18**) and 5*H*-pyrido[3,2-*b*]indole (**4-19**) was found 0.02:1 (C2:C4), from LCMS spectrum of the reaction mixture. Combined yield 79% and TON 19.75.



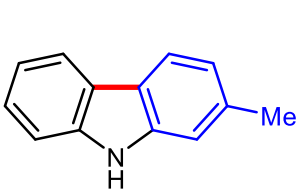
4-18

9*H*-β-Carboline or 9*H*-pyrido[3,4-*b*]indole (4-18)[1]**:** Carbazole **4-18** was prepared from **3ak** (118 mg, 0.4 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (70:30). Yellow solid (3 mg, 4%); mp: 196-198 ºC (ref.[1] 199-200 ºC); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.11 (brs, 1H; residual NH), 8.59 (d, *J*= 8.0 Hz, 1H, Ar–H), 8.41 (d, *J*= 8.0 Hz, 1H, Ar–H), 7.79 (d, *J*= 8.0 Hz, 1H, Ar–H), 7.56-7.50 (m, 2H, Ar–H), 7.37-7.30 (m, 2H, Ar–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.78 (C), 141.42 (CH), 140.56 (C), 133.17 (C), 128.07 (CH), 122.02 (C), 120.97 (CH), 120.44 (CH), 120.14 (CH), 118.16 (CH), 111.31 (CH) ppm; HRMS (ESI): *m/z* [*M*+H]$^+$ calcd. for $[C_{11}H_8N_2+H]^+$: 169.0766, found: 169.0776.

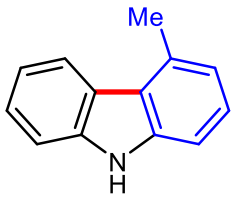


4-19

δ-Carboline or 5*H*-pyrido[3,2-*b*]indole (4-19)[3b]**:** Pale yellow solid (50 mg, 75%); mp: 140-142 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.57 (brs, 1H, N–H), 9.02 (s, 1H, Ar–H), 8.48 (d, *J*= 4.0 Hz, 1H, Ar–H), 8.16 (d, *J* = 8 Hz, 1H, Ar–H)), 8.02 (d, *J*= 4 Hz, 1H, Ar–H), 7.59-7.58 (m, 2H, Ar–H), 7.36-7.31(m, 1H, Ar–H) ppm; ^{3}C NMR (125 MHz, $CDCl_3$): δ = 140.92 (C), 137.92 (CH), 136.02 (C), 133.01 (CH), 129.46 (C), 128.86 (CH), 121.86 (CH), 121.28 (C), 120.25 (CH), 114.96 (CH), 111.84 (CH); HRMS (ESI): *m/z* [*M*+H]$^+$ calcd. for $[C_{11}H_8N_2+H]^+$: 169.0766, found: 169.0752.

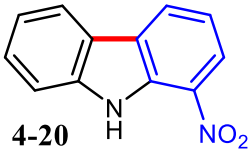


4-10
from **3al**



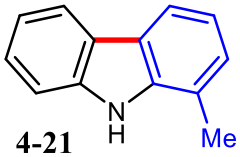
4-Methyl-isomer
(not found)

2-Methyl-9*H*-carbazole (4-10)[1,6]**:** Off-white solid (65 mg, 90% from **3al**); mp: 202-204 ºC (ref.[1,2] 206-208 ºC); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 7.7 Hz, 1H, Ar–H), 7.93 (d, *J* = 7.7 Hz, 2H, Ar–H), 7.40-7.34 (m, 2H, Ar–H), 7.22-7.18 (m, 2H, Ar–H) 7.05 (d, *J* = 7.9 Hz, 1H, Ar–H), 2.51 (s, 3H, -CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.98 (C), 139.49 (C), 136.03 (C), 125.28 (CH), 123.47 (C), 121.07 (CH), 121.00 (CH), 120.00 (2CH), 119.34 (CH), 110.74 (CH), 110.48 (CH), 22.06 (CH_3) ppm; LCMS (ESI): *m/z* calcd. for $[C_{13}H_{11}N+H]^+$: 182.09, found: 182.10. TON 22.5.



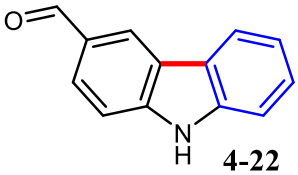
4-20

1-Nitro-9*H*-carbazole (4-20)[1,11]**:** Carbazole **4-20** was prepared according to the typical procedure from compound **3am** (136 mg, 0.4 mmol) and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (95:5). Yellow solid (68 mg, 80% yield); mp: 188-190 °C (ref.[12] 186-188 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.98 (brs, 1H, N–H), 8.33 (d, *J* = 7.5 Hz, 1H, Ar–H), 8.31 (dd, *J* = 8.0, 1.0 Hz, 1H, Ar–H), 8.08 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.56-7.50 (m, 2H, Ar–H), 7.33 (td, *J* = 8.0, 1.5 Hz, 1H, Ar–H), 7.28 (t, *J* = 8.0 Hz, 1H, Ar–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.77 (C), 133.73 (C), 132.17 (C), 127.72 (CH), 127.47 (C, CH), 122.25 (C), 121.96 (CH), 121.29 (CH), 120.69 (CH), 118.75 (CH), 111.65 (CH) ppm; IR (ATR): $\tilde{\nu}$ = 3409 (N–H), 2920, 1490, 1458 (N=O), 1330, 1204, 1066, 804, 725 cm^{-1}; LCMS (ESI) *m/z* [M-H]$^{+}$ calcd. for [$C_{12}H_8N_2O_2$-H]$^{+}$: 211.0507, found: 211.0496. TON 20.0



4-21

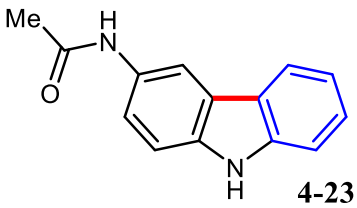
1-Methyl-9*H*-carbazole (4-21)[1,12]**:** Carbazole **4-21** was prepared according to the typical procedure from compound **3an** (124 mg, 0.4 mmol) and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (95:5). Off-white solid (65 mg, 90%); mp: 124-126 °C (ref.[13] 123.5-124.5 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 7.5 Hz, 1H, Ar–H), 7.98 (brs, 1H, residual N–H), 7.93 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.47 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.41 (t, *J* = 7.5 Hz, 1H, Ar–H), 7.24-7.21 (m, 2H, Ar–H), 7.16 (t, *J* = 7.5 Hz, 1H, Ar–H), 2.58 (s, 3H, -CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.37 (C), 138.82 (C), 126.38 (CH), 125.65 (CH), 123.83 (C), 122.80 (C), 120.46 (CH), 119.69 (C), 119.55 (CH), 119.45 (CH), 117.92 (CH), 110.66 (CH), 16.89 (CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3405, 2960, 2850, 1615, 1457, 1325, 1230, 1120, 750 cm^{-1}; LCMS (ESI): *m/z* calcd. for [$C_{13}H_{11}$N+H]$^{+}$: 182.09; found: 182.20. TON 22.5



4-22

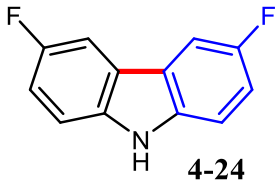
9*H*-Carbazole-3-carbaldehyd (4-23)[5,13]**:** Carbazole **4-23** was prepared from **3ba-1** (129 mg, 0.4 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (85:15). Pale yellow solid (73 mg, 93%); mp: 156-158 °C (Ref. [5] 158-159 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ= 10.10 (s, 1H, -CHO), 8.60 (d, *J* = 1.0, Hz, 1H,

Ar–H), 8.55 (brs, 1 H, N–H), 8.13 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.96 (dd, *J* = 8.5, 1.5 Hz, 1H, Ar–H), 7.51 (d, *J* = 8.5 Hz, 1H, Ar–H), 7.50-7.49 (m, 2H, Ar–H), 7.34-7.31 (m, 1H, Ar–H); ^{13}C NMR (125 MHz, $CDCl_3$): δ= 191.99 (C=O), 143.29 (C), 139.96 (C), 129.05 (CH), 127.32 (CH), 126.95 (CH), 124.09 (C), 123.53 (C), 123.19 (C), 120.74 (CH), 120.70 (CH), 111.13 (CH), 110.94 (CH) ppm; IR (ATR): $\tilde{\nu}$ = 3248, 2826, 1668 (C=O), 1619, 1496, 1333, 1297, 1118, 1006, 895, 740 cm^{-1}; LCMS (ESI): *m/z* calcd. for $C_{13}H_9NO+H]^+$: 196.07, found: 196.20. TON 23.25.



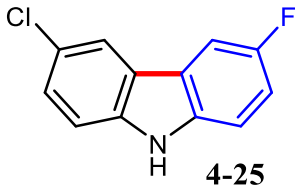
4-23

***N*-(9*H*-carbazol-3-yl)acetamide (4-23):** Carbazole **4-23** was prepared from **3ia-1** (141 mg, 0.4 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (85:15). Grey solid (81 mg, 90%); mp: 166-168 ºC; ^{1}H NMR (500 MHz, CD_3CN): δ = 9.30 (brs, 1H, N–H), 8.37 (brs, 1H, N–H), 8.32 (s, 1H, Ar–H), 8.04 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.49-7.38 (m, 4H, Ar–H), 7.17 (td, *J* = 7.5, 0.5 Hz, 1H, Ar–H), 2.09 (s, 3H, -CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.33 (C), 141.49 (C), 137.64 (C), 132.27 (C), 126.86 (CH), 123.81 (C), 123.74 (C), 121.15 (CH), 120.30 (CH), 119.87 (CH), 112.52 (CH), 112.00 (CH), 111.83 (CH), 24.26 (CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3413, 3231, 3060, 2921, 2850, 1643 (C=O), 1540, 1453, 1369, 1239, 1183, 1002, 877, 752 cm^{-1}; HRMS (ESI): *m/z* calcd. for $[C_{14}H_{12}N_2O+H]^+$: 225.1028, found: 225.1019. TON 22.5.



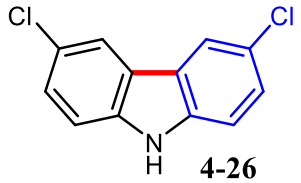
4-24

3,6-Difluoro-9*H*-carbazole (4-24)[14]**:** Carbazole **4-24** was prepared according to the typical procedure from compound **3ec** (132 mg, 0.4 mmol) and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (90:10). White solid (79 mg, 97%); mp: 198-200 ºC (ref.[15] 198-200 ºC); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.97 (s, brs, 1H, N–H), 7.65 (dd, *J* = 9.0, 3.0 Hz, 2H, Ar–H), 7.33 (dd, *J* = 8.5, 4.0 Hz, 2H, Ar–H), 7.19-7.15 (m, 2H, Ar–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.29 (d, J_{CF} = 234.6 Hz, 2C), 136.75 (2C), 123.49 (q, J_{CF} = 5.3 Hz, 2C), 114.36 (d, J_{CF} = 25.3 Hz, 2CH), 111.45 (d, J_{CF} = 9.0 Hz, 2CH), 106.09 (d, J_{CF} = 23.3 Hz, 2CH) ppm; IR (ATR): $\tilde{\nu}$ = 3420 (N–H), 3090, 2922, 1863, 1736, 1578, 1464, 1293, 1271, 1240, 1183, 1135, 1013, 948, 807, 715, 593 cm^{-1}; LCMS (ESI): *m/z* calcd. for $[C_{12}H_7F_2N+H]^+$: 204.06; found: 204.20. TON 24.25.



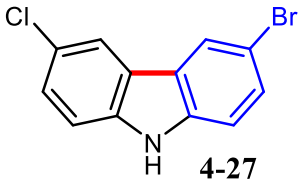
4-25

3-Chloro-6-fluoro-9*H*-carbazole (4-25)[15]**:** Carbazole **4-25** was prepared according to the typical procedure from compound **3fc** (139 mg, 0.4 mmol) and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (90:10). White solid (83 mg, 95%); mp: 230-232 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.05 (brs, 1H, N–H), 7.97 (s, 1H, Ar–H), 7.66 (dd, *J* = 8.9, 2.5 Hz, 1H, Ar–H), 7.39-7.34 (m, 3H, Ar–H), 7.18 (td, *J* = 9.0, 2.5 Hz, 1H, Ar–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.55 (d, J_{CF} = 234.6, Hz, C), 138.72 (C), 136.27 (C), 126.56 (CH), 124.94 (C), 124.22 (d, J_{CF} = 4.5 Hz, C), 122.98 (d, *J* = 9.8 Hz, C), 120.26 (CH), 114.51 (d, J_{CF} = 25.2 Hz, CH), 111.85 (CH), 111.45 (d, J_{CF} = 9.0 Hz, CH), 106.14 (d, J_{CF} = 25.5 Hz, CH) ppm; IR (ATR): $\tilde{\nu}$ = 3425 (N–H), 3095, 2929, 1854, 1732, 1606, 1570, 1468, 1428, 1291, 1275, 1231, 1140, 1000, 930, 845, 728 cm^{-1}; LCMS (ESI): *m/z* calcd. for $[C_{12}H_7ClFN+H]^+$: 220.03, found: 220.20. TON 23.75.



4-26

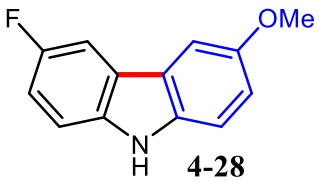
3,6-Dichloro-9*H*-carbazole (4-26)[14]**:** Carbazole **4-26** was prepared according to the typical procedure from compound **3fd** (146 mg, 0.4 mmol) and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (90:10). Off-white solid (87 mg, 92%); mp: 202-204 ºC (ref.[15] 202.0-202.5 ºC). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.10 (brs, 1H, N–H), 7.97 (s, 2H, Ar–H), 7.40-7.34 (m, 4H, Ar–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.22 (2C), 126.68 (2CH), 125.31 (2C), 123.64 (2C), 120.22 (2CH), 111.80 (2CH) ppm; IR (ATR): $\tilde{\nu}$ = 3425 (N–H), 3095, 2925, 1732, 1606, 1570, 1468, 1428, 1275, 1140, 1001, 845, 803, 769, 728, 603 cm^{-1}; LCMS (ESI): *m/z* calcd. for $[C_{12}H_7Cl_2N+H]^+$: 236.00; found: 236.30. TON 23.0



4-27

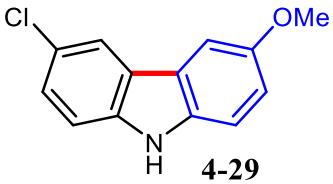
3-Bromo-6-chloro-9*H*-carbazole (4-27)[1]**:** Carbazole **4-27** was prepared according to the typical procedure from **3fe** (163 mg, 0.4 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (90:10). Off-white solid (101 mg, 90%); mp: 188-190 ºC (ref.[1] 188-190 ºC); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.11 (s, 1H, Ar–H), 8.09 (brs, 1H, residual N–H), 7.95 (s, 1H, Ar–H), 7.50 (dd, *J* = 8.5, 2.0 Hz, 1H, Ar–H), 7.37 (dd, *J* = 8.5, 2.0

Hz, 1H, Ar–H), 7.32 (d, J = 8.5 Hz, 1H, Ar–H), 7.28 (d, J = 8.5 Hz, 1H, Ar–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.80 (C), 138.29 (C), 129.51 (CH), 126.95 (CH), 125.64 (C), 124.50 (C), 123.75 (C), 123.50 (CH), 120.45 (CH), 112.81 (C), 112.47 (CH), 112.00 (CH) ppm; IR (ATR): $\tilde{\nu}$ = 3406 (N–H), 2918, 2849, 2358, 1684, 1653, 1559, 1507, 1436, 1287, 1071, 1020, 967, 869, 804 cm^{-1}; LCMS (ESI): *m/z* calcd. for $[C_{12}H_7BrClN\text{-}H]^+$: 277.93, found: 277.90. TON 22.5



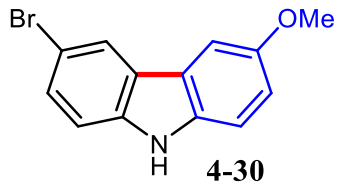
4-28

3-Fluoro-6-methoxy-9*H*-carbazole (4-28)[1]**:** Carbazole **4-28** was prepared according to the typical procedure from compound **3eg** (137 mg, 0.4 mmol) and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (85:15). White solid (85 mg, 99% yield); mp: 136-138 ºC (ref.[1] 136-138 ºC); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.85 (brs, 1H, N–H), 7.66 (dd, J = 9.0, 2.5 Hz, 1H, Ar–H), 7.47 (d, J = 2.5 Hz, 1H, Ar–H), 7.31 (d, J = 8.5 Hz, 1H, Ar–H), 7.30 (dd, J = 9.0, 4.0 Hz, 1H, Ar–H), 7.13 (td, J = 9.0, 2.5 Hz, 1H, Ar–H), 7.08 (dd, J = 9.0, 2.5 Hz, 1H, Ar–H), 3.91 (s, 3H, -CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.25 (d, J_{CF} = 235.2 Hz; C), 153.87 (C), 136.57 (C), 135.46 (C), 123.82 (d, J_{CF} = 9.5 Hz; C), 123.51 (d, J_{CF} = 4.1 Hz; C), 115.97 (CH), 113.63 (d, J_{CF} = 25.4 Hz; CH), 111.64 (CH), 111.27 (d, J_{CF} = 9.1 Hz; CH), 105.80 (d, J_{CF} = 23.6 Hz; CH), 103.07 (CH), 56.07 (CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3416 (N–H), 2982, 1577, 1495, 1462, 1200, 1145, 1025, 942, 843, 806, 781 cm^{-1}; LCMS (ESI): *m/z* calcd. for $[C_{13}H_{10}FNO\text{-}H]^+$: 214.06, found: 214.00. TON 24.75



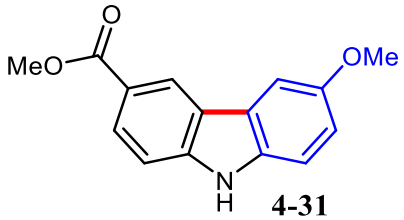
4-29

3-Chloro-6-methoxy-9*H*-carbazole (4-29)[1]**:** Carbazole **4-29** was prepared according to the typical procedure from **3fg** (144 mg, 0.4 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (85:15). White solid (86 mg, 93%); mp: 162-164 ºC (ref.[1] 162-164 ºC); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.98 (d, J = 2.0 Hz, 1H, Ar–H), 7.90 (brs, 1H, N–H), 7.48 (d, J = 2.5 Hz, 1H, Ar–H), 7.34-7.25 (m, 3H, Ar–H), 7.08 (dd, J = 9.0, 2.5 Hz, 1H, Ar–H), 3.91 (s, 3H, -CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.12 (C), 138.48 (C), 134.90 (C), 125.85 (CH), 124.53 (2C), 122.94 (C), 119.96 (CH), 116.04 (CH), 111.68 (CH), 111.58 (CH), 103.04 (CH), 56.04 (CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3413 (N–H), 2960, 1490, 1450, 1227, 1167, 1030, 838, 809, 735 cm^{-1}; LCMS (ESI): *m/z* calcd. for $[C_{13}H_{10}ClNO\text{-}H]^+$: 230.03, found: 230.00. TON 23.25.



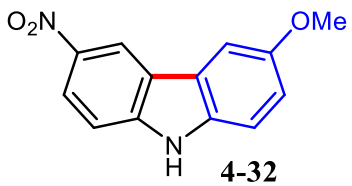
4-30

3-Bromo-6-methoxy-9*H*-carbazole (4-30)[1]**:** Carbazole **4-30** was prepared according to the typical procedure from **3gg** (162 mg, 0.4 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (85:15). White solid (99 mg, 90%); mp: 132-134 ºC (ref.[1] 132-134 ºC); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 2.0 Hz, 1H, Ar–H), 7.91 (brs, 1H, N–H), 7.46 (t, *J* = 2.5 Hz, 1H, Ar–H), 7.44 (d, *J* = 2.0 Hz, 1H, Ar–H), 7.31 (d, *J* = 9.0 Hz, 1H, Ar–H), 7.26 (d, *J* = 8.5 Hz, 1H, Ar–H), 7.07 (dd, *J* = 9.0, 2.5 Hz, 1H, Ar–H), 3.90 (s, 3H, -CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.20 (C), 138.81 (C), 134.72 (C), 128.46 (CH), 125.19 (C), 123.02 (CH), 122.84 (C), 116.12 (CH), 112.16 (CH), 111.82 (C), 111.58 (CH), 103.04 (CH), 56.05 (CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3385 (N–H), 2922, 2363, 1839, 1576, 1462, 1436, 1274, 1202, 1165, 1030, 906, 874, 789 cm^{-1}; LCMS (ESI): *m/z* calcd. for $[C_{13}H_{10}BrNO\text{-}H]^+$: 273.98, found: 274.00. TON 22.5.



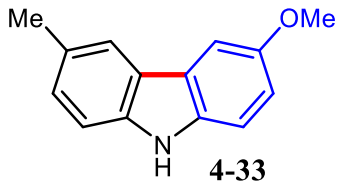
4-31

Methyl 6-methoxy-9*H*-carbazole-3-carboxylate (4-31)[1,5]**:** Carbazole **4-31** was prepared according to the typical procedure from compound **3hg** (153 mg, 0.4 mmol) and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (80:20). White solid (85 mg, 83% yield); mp: 146-148 ºC (ref.[5] 147-149 ºC); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.77 (d, *J* = 1.0 Hz, 1H, Ar–H), 8.17 (brs, 1H, N–H), 8.11 (dd, *J* = 8.5, 2.0 Hz, 1H, Ar–H), 7.60 (d, *J* = 2.5 Hz, 1H, Ar–H), 7.40 (d, *J* = 8.5 Hz, 1H, Ar–H), 7.35 (d, *J* = 9.0 Hz, 1H, Ar–H), 7.10 (dd, *J* = 9.0, 2.5 Hz, 1H, Ar–H), 3.97 (s, 3H, -CH_3), 3.93 (s, 3H, -CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.87 (C=O), 154.56 (C), 142.92 (C), 134.65 (C), 127.34 (CH), 123.89 (C), 123.14 (C), 122.93 (CH), 121.04 (C), 115.98 (CH), 111.65 (CH), 110.25 (CH), 103.24 (CH), 56.02 (CH_3), 51.94 (CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3301 (N–H), 2951, 2828, 1701 (C=O), 1604, 1472, 1430, 1265, 1033, 801, 722 cm^{-1}; LCMS (ESI): *m/z* calcd. for $[C_{15}H_{13}NO_3+H]^+$: 256.09, found: 256.00. TON 20.75.



4-32

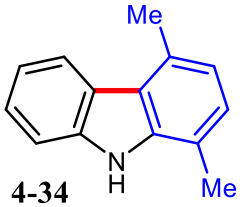
3-Nitro-6-methoxy-9*H*-carbazole (4-32)[1]**:** Carbazole **4-32** was prepared according to the typical procedure from **3ig** (148 mg, 0.4 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (85:15). Yellow solid (88 mg, 91%); mp: 180-182 °C (ref.[1] 132-134 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.96 (d, *J* = 2.0 Hz, 1H, Ar–H), 8.31 (dd, *J* = 9.0, 2.0 Hz, 1H, Ar–H, and 1H, residual N–H), 7.58 (d, *J* = 2.5 Hz, 1H, Ar–H), 7.41 (d, *J* = 9.0 Hz, 1H, Ar–H), 7.39 (d, *J* = 9.0 Hz, 1H, Ar–H), 7.14 (dd, *J* = 8.5, 2.5 Hz, 1H, Ar–H), 3.93 (s, 3H, -CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.29 (C), 143.45 (C), 141.14 (C), 135.32 (C), 123.97 (C), 123.29 (C), 121.83 (CH), 117.61 (CH), 117.37 (CH), 112.37 (CH), 110.56 (CH), 103.51 (CH), 56.23 ppm (CH_3); IR (ATR): $\tilde{\nu}$ = 3346 (N–H), 2825, 1636, 1609, 1590, 1491, 1478 (N=O), 1294, 1197, 1170, 1077, 1035, 725 cm^{-1}; LCMS (ESI): *m/z* calcd. for $[C_{13}H_{10}N_2O_3\text{-}H]^+$: 241.06, found: 241.00. TON 22.75.



4-33

3-Methoxy-6-methyl-9*H*-carbazole (4-33, Glycozoline**):** Carbazole **4-33** was prepared according to the typical procedure from **3bg** (136 mg, 0.4 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (95:5). Off-white solid (80 mg, 95%); mp: 180-182 °C (ref.[15] 181-182 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.82 (s, 1H, Ar–H), 7.79 (brs, 1H, N–H), 7.52 (s, 1H, Ar–H), 7.29-7.20 (m, 3H, Ar–H), 7.03 (dd, *J* = 8.5, 2.0 Hz, 1H, Ar–H), 3.91 (s, 3H, -OCH_3), 2.51 (s, 3H, Ar–CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.70 (C), 138.52 (C), 134.72 (C), 128.31 (C), 127.16 (CH), 123.62 (C), 123.50 (C), 120.11 (CH), 114.85 (CH), 111.25 (CH), 111.40 (CH), 103.05 (CH), 56.05 (-OCH_3), 21.41 (CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3325 (N–H), 2928, 2831, 1710, 1605, 1560, 1470, 1255, 1040, 800 cm^{-1}; LCMS (ESI): *m/z* calcd. for $[C_{14}H_{13}ON+H]^+$: 212.10; found: 212.20. TON 23.75.

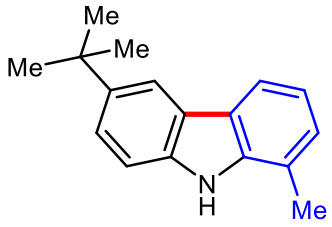
Gram-scale reaction of 3bg: Following the general procedure under microwave-assisted heating condition in water, reaction of 2-iodo-*N*-(4-methoxyphenyl)-4-methylaniline **3bg** (1.0 g, 2.95 mmol) was done with the addition of $Pd(OAc)_2$ (26.5 mg, 0.118 mmol), CTAB (108 mg, 0.295 mmol), DBU (900 mg, 5.9 mmol), and water (7 ml) in a microwave vial. The reaction was performed under the optimized condition at 100 °C for 60 min. Product 3-methoxy-6-methyl-9*H*-carbazole **4-33** (505 mg, 81% yield, off-white solid) was collected through column chromatography on silica gel, eluting with hexane/ethyl acetate (95:5).



4-34

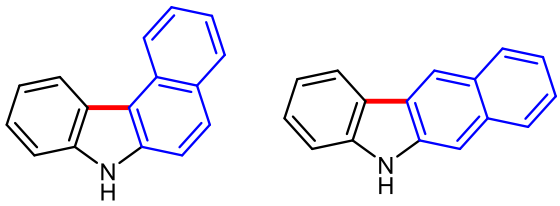
1,4-Dimethyl-9H-carbazole (4-34)[16]: Carbazole **4-34** was prepared according to the typical procedure from **3ao** (129 mg, 0.4 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (95:5).

Brown solid (69 mg, 88%); mp: 178-180 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.17 (d, J = 8.0, 1H, Ar–H), 7.99 (brs, 1H, N–H), 7.48 (d, J = 8.0 Hz, 1H, Ar–H), 7.41 (t, J = 7.5 Hz, 1H, Ar–H), 7.26-7.23 (m, 1H, Ar–H), 7.13 (d, J = 7.3 Hz, 1H, Ar–H), 6.93 (d, J = 7.1 Hz, 1H, Ar–H), 2.85 (s, 3H, Ar–CH_3), 2.53 (s, 3H, Ar–CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.34 (C), 138.73 (C), 130.84 (C), 126.13 (CH), 125.01 (CH), 124.47 (C), 122.56 (CH), 121.35 (C), 120.85 (CH), 119.39 (CH), 116.94 (C), 110.44 (CH), 20.51 (CH_3), 16.59 (CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3430 (N–H), 3045, 2953, 1590, 1550, 1460, 1380, 1300, 158, 1120, 1039, 1008, 892, 733 cm^{-1}; LCMS (ESI): *m/z* calcd. for $[C_{14}H_{13}N+H]^+$: 196.11, found: 196.20. TON 22.0.



4-35

6-(*tert*-Butyl)-1-methyl-9*H*-carbazole (4-35): Carbazole **4-35** was prepared according to the typical procedure from **3cn** (146 mg, 0.4 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (95:5). Off-white solid (71 mg, 75%); mp: 134-136 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.05 (s, 1H, Ar–H), 7.92 (d, J = 8.0 Hz, 1H, Ar–H), 7.86 (brs, 1H, N–H), 7.47 (d, J = 8.0 Hz, 1H, Ar–H), 7.39 (d, J = 8.5 Hz, 1H, Ar–H), 7.20 (d, J = 8.0 Hz, 1H, Ar–H), 7.14 (t, J = 7.5 Hz, 1H, Ar–H), 2.55 (s, 3H, Ar–CH_3), 1.44 (s, 9H, Ar–C $(CH_3)_3$) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.47 (C), 139.25 (C), 137.48 (C), 126.12 (CH), 123.64 (CH), 123.54 (C), 123.06 (C), 119.60 (C), 119.30 (CH), 117.74 (CH), 116.49 (CH), 110.11 (CH), 34.67 (C), 31.99 (Ar–$C(CH_3)_3$), 16.89 (-CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3344 (N–H), 2825, 1636, 1609, 1590, 1491, 1294, 800 cm^{-1}; HRMS (ESI): *m/z* calcd. for $[C_{17}H_{19}N-H]^+$: 236.1439; found: 236.1436. TON 18.75.

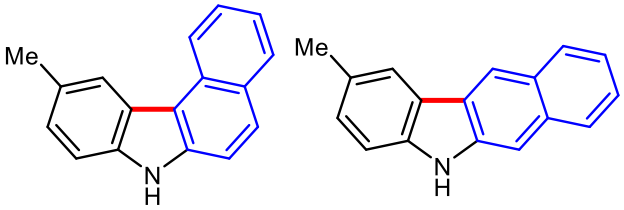


4-36 Linear isomer of **4-36**

(**4-36** : Linear isomer of **4-36** = 1 : 0)

7*H*-benzo[*c*]carbazole (4-36)[17]**:** According to the typical procedure, reaction of **3ap** (138 mg, 0.4 mmol), produced 7*H*-benzo[*c*]carbazole (**4-36**) exclusively, without any 5*H*-benzo[*b*]carbazole[4] (linear isomer of **4-36**). Carbazole **4-36** was purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (90:10). Off-white solid (69 mg, 80%); mp: 134-136 °C (ref.[18] 133-134 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.78 (d, J = 8.0 Hz, 1H, Ar–H), 8.57 (d, J = 7.5 Hz, 1H, Ar–H) 8.42 (brs, 1H, N–H), 8.00 (d, J = 7.5 Hz, 1H, Ar–H), 7.86 (d, J = 8.0 Hz, 1H, Ar–H), 7.70-7.69 (m, 1H, Ar–H), 7.63-7.56 (m, 2H, Ar–H), 7.49-7.44 (m, 2H, Ar–H), 7.40-7.37 (m, 1H, Ar–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.41 (C), 137.03 (C), 129.90 (2C), 129.18 (CH), 127.41 (CH), 126.85 (CH), 124.32

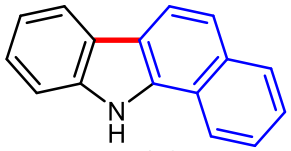
(CH), 123.99 (C), 123.24 (CH), 122.98 (CH), 122.03 (CH), 120.22 (CH), 115.45 (C), 112.55 (CH), 111.10 (CH) ppm; IR (ATR): $\tilde{\nu}$ = 3356 (N–H), 2925, 1870, 1478, 1270, 1130, 1077, 801 cm^{-1}; LCMS (ESI): *m/z* calcd. for $[C_{16}H_{11}N\text{-}H]^+$: 216.08, found: 216.20. TON 20.0.



4-37 Linear isomer of **4-37**

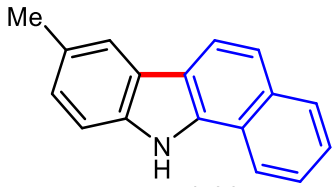
(**4-37** : Linear isomer of **4-37** = 1 : 0)

10-Methyl-7*H*-benzo[*c*]carbazole(4-37)[18]**:** According to the typical procedure, reaction of **3bp** (144 mg, 0.4 mmol), produced 10-methyl-7*H*-benzo[*c*]carbazole (**4-37**) exclusively, without any 2-methyl-5*H*-benzo[*b*]carbazole (linear isomer of **4-37**). Carbazole **4-37** was purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (90:10). Off-white solid (72 mg, 78%); mp: 180-182 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.77 (d, *J* = 8.5 Hz, 1H, Ar–H), 8.35 (s, 1H, Ar–H), 8.33 (brs, 1H, N–H), 7.99 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.83 (d, *J* = 8.5 Hz, 1H, Ar–H), 7.70 (t, *J* = 7.0 Hz, 1H, Ar–H), 7.60 (d, *J* = 8.5 Hz, 1H, Ar–H), 7.48-7.45 (m, 2H, Ar–H), 7.28 (d, *J* = 8.0 Hz, 1H, Ar–H), 2.63 (s, 3H, -CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.29 (C), 136.67 (C), 129.98 (C), 129.49 (2C), 129.13 (CH), 127.18 (CH), 126.74 (CH), 125.74 (CH), 124.20 (C), 123.26 (CH), 122.84 (CH), 121.96 (CH), 115.19 (C), 112.62 (CH), 110.71 (CH), 21.82 (CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3466 (N–H), 2895, 1696, 1545, 1265, 1150, 1035, 825 cm^{-1}; LCMS (ESI): *m/z* calcd. for $[C_{17}H_{13}N\text{-}H]^+$: 230.09, found: 230.20. TON 19.5.



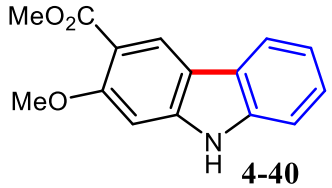
4-38

11*H*-benzo[*a*]carbazole (4-38)[19]**:** Carbazole **4-38** was prepared according to the typical procedure from **3aq** (138 mg, 0.4 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (90:10). Brown solid (73 mg, 84%); mp: 226-228 °C (Ref:[20] 224-226 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.79 (brs, 1H, N–H), 8.15-8.12 (m, 3H, Ar–H), 8.01 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.66 (d, *J* = 8.5 Hz, 1H, Ar–H), 7.61-7.58 (m, 2H, Ar–H), 7.53 (t, *J* = 7.5 Hz, 1H, Ar–H), 7.44 (t, *J* = 7.0 Hz, 1H, Ar–H), 7.31 (t, *J* = 7.0 Hz, 1H, Ar–H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.46 (C), 134.87 (C), 132.43 (C), 129.06 (CH), 125.57 (CH), 125.23 (CH), 124.88 (CH), 124.19 (C), 121.09 (C), 120.47 (CH), 120.22 (CH), 119.99 (CH), 119.92 (CH), 119.34 (CH), 118.44 (C), 111.04 (CH) ppm; IR (ATR): $\tilde{\nu}$ = 3415 (N–H), 3035, 1625, 1605, 1197, 995, 720 cm^{-1}; LCMS (ESI): *m/z* calcd. for $C_{16}H_{11}N\text{-}H]^+$: 216.09, found: 216.20. TON 21.0.



4-39

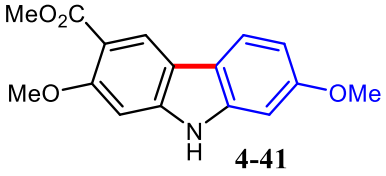
8-Methyl-11*H*-benzo[*a*]carbazole (4-39)[19]**:** Carbazole **4-39** was prepared according to the typical procedure from **3bq** (144 mg, 0.4 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (90:10). Off-white solid (75 mg, 81%); mp: 250-252 ºC (Ref:[20] 250-252 ºC). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.69 (brs, 1H, N–H), 8.12-8.09 (m, 2H, Ar–H), 8.00 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.92 (s, 1H, Ar–H), 7.64 (d, *J* = 8.5 Hz, 1H, Ar–H), 7.58 (td, *J* = 7.0, 1.0 Hz, 1H, Ar–H), 7.52 (td, *J* = 7.0, 1.0 Hz, 1H, Ar–H), 7.48 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.27 (d, *J* = 1.0 Hz, 1H, Ar–H), 2.56 (s, 3H, Ar–CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 136.72 (C), 135.11 (C), 132.35 (C), 129.32 (C), 129.02 (CH), 126.30 (CH), 125.46 (CH), 125.09 (CH), 124.36 (C), 121.13 (C), 120.44 (CH), 119.96 (CH), 119.74 (CH), 119.33 (CH), 118.23 (C), 110.67 (CH), 21.55 (CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3471 (N–H), 3095, 1605, 1490, 1000, 815 cm^{-1}; LCMS (ESI): *m/z* calcd. for $[C_{17}H_{13}N+H]^+$: 232.11, found: 232.20. TON 20.25.



4-40

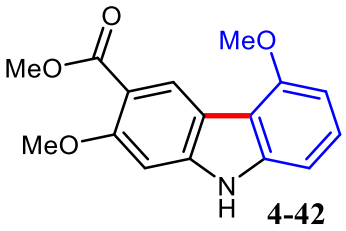
Clausine L (4-40)[1,20]**:** Carbazole **4-40** was prepared from **3ka** (153 mg, 0.4 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (80:20). White solid (84 mg, 82%); mp: 170-172 ºC (ref.[21] 172-173 ºC); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.52 (s, 1H; Ar–H), 8.14 (brs, 1H; N–H), 7.92 (d, *J*= 7.5 Hz, 1H; Ar–H), 7.32-7.28 (m, 2H; Ar–H), 7.19-7.15 (m, 1H; Ar–H), 6.84 (s, 1H; Ar–H), 3.87 (s, 6H; 2-CH_3) ppm ; ^{13}C NMR (125 MHz, $CDCl_3$): δ= 167.24 (C=O), 159.49 (C), 143.50 (C), 140.06 (C), 125.60 (CH), 125.16 (CH), 123.71 (C), 120.62 (CH), 120.08 (CH), 116.70 (C), 112.82 (C), 110.81 (CH), 93.80 (CH), 56.51 (CH_3), 52.08 ppm (CH_3); IR (ATR): $\tilde{\nu}$ = 3297 (N–H), 2920, 1690 (C=O), 1634, 1608, 1572, 1458, 1353, 1230, 1076, 727 cm^{-1}; LCMS (ESI): *m/z* [*M*-H]$^+$ calcd. for $C_{15}H_{13}NO_3$: 254.08, found: 254.00. TON 20.5.

According to the typical procedure, reaction of **3kh** (165 mg, 0.4 mmol), produced a mixture of clausine H (**4-41**, 36 mg, 31%) and methyl 2,5-dimethoxy-9*H*-carbazole-3-carboxylate (**4-42**, 51 mg, 45%). Carbazoles **4-41** and **4-42** were collected separately during column chromatography on silica gel, eluting with hexane/ethyl acetate (85:15 to 80:20), from the later fractions and earlier fractions, respectively. Combined yield 76% and TON 19.0.



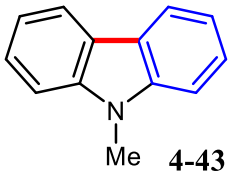
4-41

Clausine H (4-41)[1,21]**:** Carbazole **4-41** was prepared from **3kh** (165 mg, 0.4 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (80:20) and collected from the later fractions. White solid (36 mg, 31%); mp: 190-192 °C (ref.[22] 191-192 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ= 8.46 (s, 1H; Ar–H), 8.08 (brs, 1H, N–H), 7.83 (d, *J*= 8.0 Hz, 1H, Ar–H), 6.86-6.83 (m, 3H; Ar–H), 3.92 (s, 3H, -CH_3), 3.91 (s, 3H, -CH_3), 3.86 (s, 3H, -CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ= 167.31 (C=O), 158.97 (C), 158.71 (C), 143.57 (C), 141.38 (C), 124.10 (CH), 120.77 (CH), 117.45 (C), 116.91 (C), 112.69 (C), 108.83 (CH), 95.55 (CH), 93.98 (CH), 56.56 (CH_3), 55.90 (CH_3), 52.04 (CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3286 (N–H), 2837, 1696 (C=O), 1616, 1573, 1457, 1436, 1275, 1185, 1085, 796, 726 cm^{-1}; LCMS (ESI): *m/z* calcd. for $[C_{16}H_{15}NO_4+H]^+$: 286.10, found: 286.20.



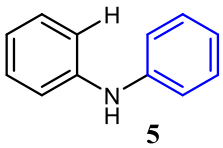
4-42

Methyl 2,5-dimethoxy-9*H*-carbazole-3-carboxylate (4-42) [1]**:** Carbazole **4-42** was prepared from **3kh** (165 mg, 0.4 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (80:20) and collected from the earlier fractions. Off-white solid (51 mg, 45%); mp: 176-178 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ= 8.67 (s, 1H; Ar–H), 8.03 (brs, 1H, N–H), 7.23 (t, *J*= 8.5 Hz, 1H, Ar–H), 6.95 (d, *J*= 8.0 Hz, 1H, Ar–H), 6.85 (s, 1H, Ar–H), 6.64 (d, *J*= 8.0 Hz, 1H, Ar–H), 4.00 (s, 3H, -CH_3), 3.90 (s, 3H, -CH_3), 3.87 (s, 3H; CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ= 167.44 (C=O), 158.82 (C), 155.91 (C), 142.65 (C), 141.38 (C), 127.44 (CH), 126.57 (CH), 116.11 (C), 113.17 (C), 112.87 (C), 103.71 (CH), 101.66 (CH), 93.44 (CH), 56.53 (CH_3), 55.66 (CH_3), 52.02 (CH_3) ppm; IR (ATR): $\tilde{\nu}$ = 3339 (N–H), 2923, 2852, 1669 (C=O), 1609, 1463, 1431, 1332, 1256, 1097, 744 cm^{-1}; LCMS (ESI): *m/z* calcd. for $[C_{16}H_{15}NO_4+H]^+$: 286.10, found: 286.10.



4-43

9-Methyl-9*H*-carbazole (4-43)[1]**:** Carbazole **4-43** was prepared from **3aa-1** (124 mg, 0.4 mmol), and purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (97:3). White solid (67 mg, 92%); mp: 90-92 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.14 (d, *J* = 7.5 Hz, 2H, Ar–H), 7.55-7.42 (m, 4H, Ar–H), 7.28 (dd, *J* = 7.7, 1.2 Hz, 2H, Ar–H), 3.89 (s, 3H, CH_3) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 141.00 (2C), 125.68 (2CH), 122.77 (2C), 120.31 (2CH), 118.83 (2CH), 108.43 (2CH), 29.09 (CH_3) ppm; IR (ATR): $\tilde{\nu}$=3051, 2927, 2359, 1628, 1597, 1493, 1450, 1323, 1246, 1128, 1058, 922, 850, 771, 743 cm^{-1}; LCMS (ESI): *m/z* calcd. for $[C_{13}H_{11}N+H]^+$: 182.09, found: 182.10. TON 23.0.



5

Diphenylamine (5): Off-white solid; mp: 52-54 °C; ^{1}H NMR (400 MHz, DMSO-D_6): δ = 8.14 (brs, 1H, N–H), 7.22 (t, J = 8.0 Hz, 4H, Ar–H), 7.06 (d, J = 7.7 Hz, 4H, Ar–H), 6.81 (t, J = 7.3 Hz, 2H, Ar–H) ppm; LCMS m/z [M+H]$^+$ calcd for $C_{12}H_{12}N$: 170.09, found: 170.20.

7. Analytical techniques for the characterization of PdNPs catalysts 1 and 2.

7.1 FTIR (Fourier Transform Infrared Spectroscopy) studies:

FTIR spectra (Figure S8) were recorded with a Shimadzu FTIR spectrometer IR Affinity-1S using the ATR (Attenuated Total Reflectance) method. Powder of the solid samples (CTAB, $Pd(OAc)_2$, PdNPs 1, and PdNPs 2) were used to collect their IR spectra. IR spectrum of DBU was collect as neat (liquid) sample.

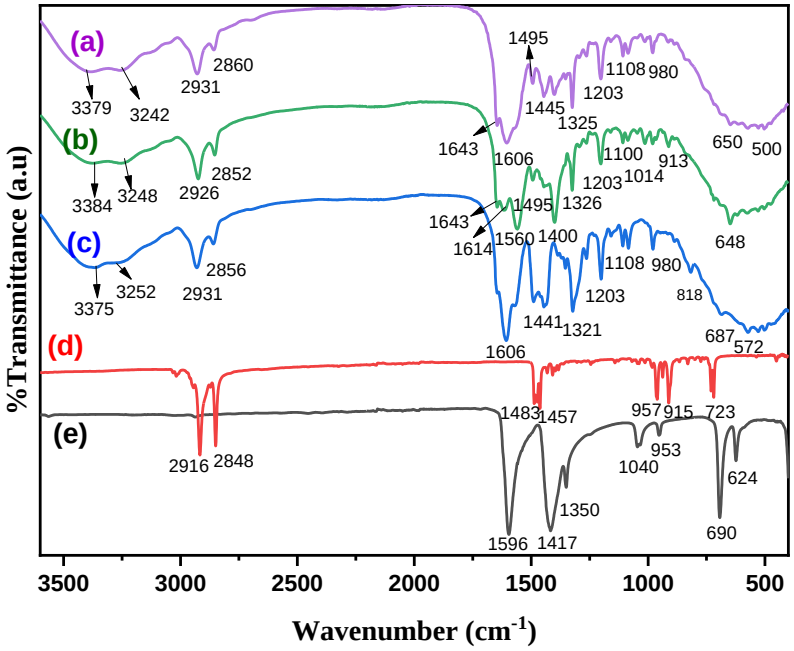


Figure S8. FTIR spectra of (a) PdNPs catalyst 1 ($Pd(OAc)_2$+CTAB+DBU), (b) PdNPs catalyst 2 ($Pd(OAc)_2$+CTAB), (c) DBU, (d) CTAB and (e) $Pd(OAc)_2$.

The FTIR spectrum of Pd catalyst 2 showed shifting of the characteristic vibration peaks of $Pd(OAc)_2$ and CTAB. Peaks of $Pd(OAc)_2$ at 1596 ($\tilde{\nu}_{as}$) and 1350 ($\tilde{\nu}_s$) cm^{-1} due to the stretching vibrations of C=O, and a sharp peak at 1417 cm^{-1} due to the ionized carboxylate group,[22a] were found to shift at 1560, 1326 and 1400 cm^{-1} respectively, in catalyst

2 (Figure S8b). Also the shift of the C–H scissoring vibrations of H–C–N^+ of CTAB molecules[22b] from 1483–1457 cm^{-1} to 1495–1460 cm^{-1}, and disappearance of the peak at 690 cm^{-1} for Pd–O bond[22c] of $Pd(OAc)_2$ in catalyst 2 hinted at significant interactions of CTAB with $Pd(OAc)_2$. In the FTIR spectrum of catalyst 1 (Figure S8a), shift of the vibrational peaks respective to the catalyst 2 as well as DBU,[22d] and appearance of the peaks at 1643 (C=N^+), 1606 (C=N), 1560, 1445, 1400 and 1325 cm^{-1}, indicated at Pd(DBU) complex formation. The appearance of new peaks in the region 650 to 500 cm^{-1} with the disappearance of the sharp peak at 690 cm^{-1} for the Pd–O vibration of $Pd(OAc)_2$ indicated the formation of Pd(0) nanostructures[22b] with the displacement of acetate groups, and revealed the binding interaction of DBU and CTAB to PdNPs via Pd–N linkage.

7.2 UV-Vis (Ultraviolet-visible) studies:

UV-Vis absorption experiments were done on a Shimadzu UV/Vis spectrophotometer at 25±0.1 ºC in a quartz cuvette of 1.00 cm path length. Dilute solution of samples ($Pd(OAc)_2$, PdNPs 1, and PdNPs 2) were used to collect their UV-Vis spectra (Figure S9).

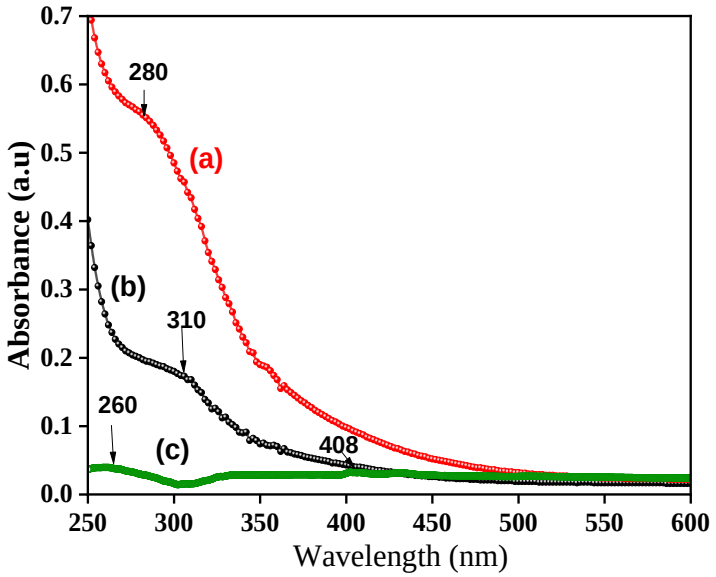


Figure S9. UV-Vis absorption spectra of (a) PdNPs catalyst 1, (b) PdNPs catalyst 2, and (c) $Pd(OAc)_2$.

In the UV-Vis spectrum of Pd catalyst 2 (Figure S9b), the appearance of a shoulder at 310 nm with the disappearance of the characteristic peaks of $Pd(OAc)_2$ at 260 and 408 nm,[23] indicated the interaction of CTAB with $Pd(OAc)_2$. The appearance of a shoulder at 280 nm for the colloidal suspension of Pd catalyst 1 (Figure S9a) with the disappearance of the above peaks hinted at the coordination of DBU to the Pd center, and complete reduction of Pd(II) species to nanosized Pd(0) species[24] under microwave-assisted heating. The shift of peak positions from 310 nm to 280 nm indicated at smaller nano-sized Pd(0) species formation in presence of DBU under microwave-assisted heating.

7.3 PXRD (Powdered X-ray diffraction) studies:

The PXRD study was done by Bruker D8 Advance X-ray diffractometer using Cu-Kα (λ = 1.5418 Å) radiation. Powder of the solid samples (PdNPs 1, and PdNPs 2) were used to collect their PXRD data.

Williamson-Hall Equation:

$$\beta\, cos\theta \;=\; 4\varepsilon\, sin\theta \;+\; \frac{K\lambda}{D}$$

Where, β represents FWHM (Full width half maxima) of each XRD peak (radian),

θ is the Bragg's angle, λ is the wavelength of the radiation; 0.154 in nm, K is constant value;

0.9D represents crystallite size of the material in nm, ε describes lattice strain of the material.

When, we plotted **βcosθ** versus **4sinθ**, we got the lattice strain from the slope and crystallite size component from the intercept (Figure S10).

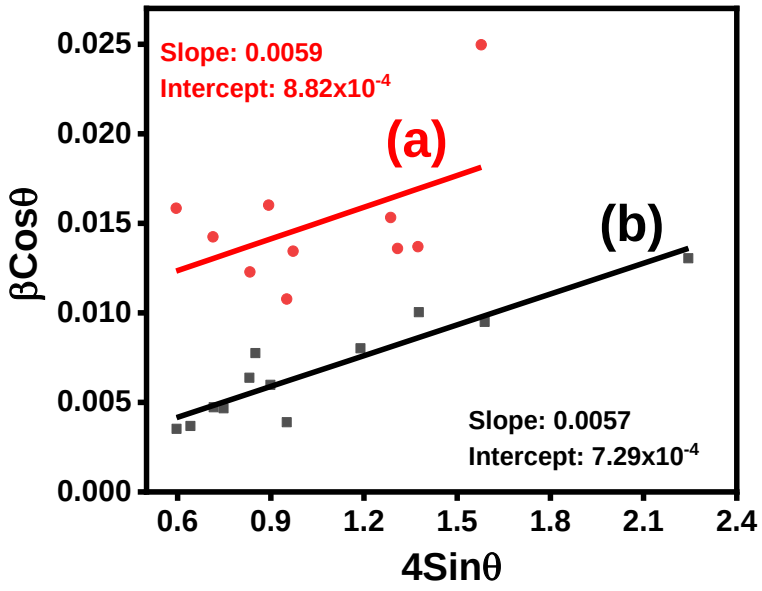


Figure S10. Williamson-Hall plot of (a) PdNPs catalyst 1 and (b) PdNPs catalyst 2.

Table S6. Calculation details of Williamson-Hall plot for PdNPs 1 [$Pd(OAc)_2$+CTAB+DBU]

Peak (2θ)	FWHM	Size	Average Size	Radians (2θ)	Radians of FWHM	βcosθ	4sinθ	Slope	Intercept
17.12	0.918	6.55	7.23	0.15	0.016	0.0158	0.5955	0.0059	8.82E-4
20.56	0.8295	7.29		0.18	0.014	0.0142	0.7141		
24.03	0.71961	8.45		0.21	0.012	0.0122	0.8327		
25.80	0.9413	6.48		0.22	0.016	0.0160	0.8931		
27.52	0.6352	9.64		0.24	0.011	0.0107	0.9515		
28.13	0.794	7.72		0.24	0.014	0.0134	0.9720		
37.50	0.9272	6.78		0.32	0.016	0.0153	1.285		
38.18	0.824	7.64		0.33	0.014	0.0135	1.3082		
40.16	0.8353	7.58		0.35	0.014	0.0136	1.3736		
46.45	1.5566	4.16		0.40	0.027	0.0249	1.5775		

Table S7. Calculation details of Williamson-Hall plot for PdNPs 2 [$Pd(OAc)_2$+CTAB]

Peak (2θ)	FWHM	Size	Average Size	Radians (2θ)	Radians of FWHM	βcosθ	4sinθ	Slope	Intercept
17.17	0.2040	39.35	24.23	0.15	0.0031	0.0035	0.5969	0.00573	7.297E-4
18.46	0.2134	37.68		0.16	0.0034	0.0037	0.6415		
20.62	0.2753	29.32		0.18	0.0048	0.0047	0.7160		
21.55	0.2724	29.67		0.19	0.004	0.0047	0.7479		
23.99	0.3734	21.74		0.21	0.0065	0.0064	0.8313		
24.55	0.4543	17.88		0.21	0.0079	0.0077	0.8506		
25.97	0.3518	23.17		0.22	0.0061	0.006	0.8989		
27.52	0.2296	35.60		0.24	0.0040	0.0038	0.9514		
34.58	0.4810	17.29		0.3	0.0083	0.0080	1.1889		
40.26	0.6125	13.81		0.35	0.0107	0.0100	1.3765		
46.8	0.5929	14.6		0.41	0.0103	0.0095	1.5885		
68.26	0.9029	10.62		0.60	0.016	0.013	2.2442		

7.4 FE-SEM (Field Emission Scanning Electron Microscopy) studies:

The FE-SEM images were collected by QUANTA FEG 250, and Carl Zeiss Sigma SUPRA 55VP instruments at 10 KV. The sample solution in dichloromethane (DCM) was drop-casted onto a silicon wafer, and it was vacuum-dried

in a desiccator. In addition the Figure 4 in the manuscript, more FESEM images of PdNPs catalyst 1 and catalyst 2 are given here in Figure S11a,b, and Figure S11c,d., respectively.

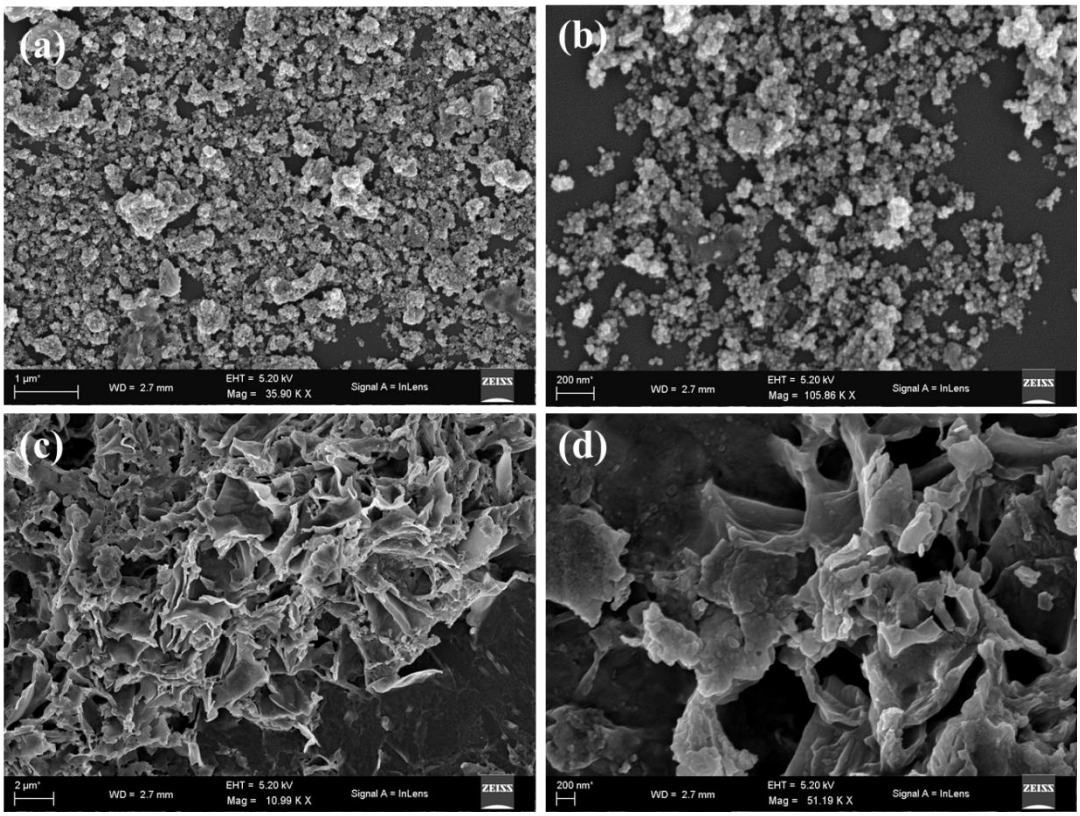


Figure S11. (a,b) FESEM images of PdNPs catalyst 1, and (c,d) FESEM images of PdNPs catalyst 2.

7.5 HR-TEM (High-Resolution Transmission Electron Microscopy) studies:

High-resolution transmission electron microscopy (HR-TEM) images were collected from JEOL, JEM-2100F instrument, operating at an accelerating voltage of 200 kV. The EDS mapping related to this was recorded using the same instrument. Samples for TEM measurements were prepared by dispersing a 2 mg of the catalyst (PdNPs 1, and PdNPs 2) in 2-propanol in the ultrasonic bath, and then placing a drop of suspension on a copper grid coated with carbon film. Transmission electron microscopy (TEM) images of the recovered Pd catalysts were recorded by JEOL JEM-2100F microscope, operating at an accelerating voltage of 200 kV equipped with an Oxford EDX attachment. The sample solution in dichloromethane (DCM) was drop-casted onto a 200-mesh copper carbon-coated grid and vacuum-dried under in a desiccator. HRTEM images of PdNPs catalyst 2 are given in Figure S12.

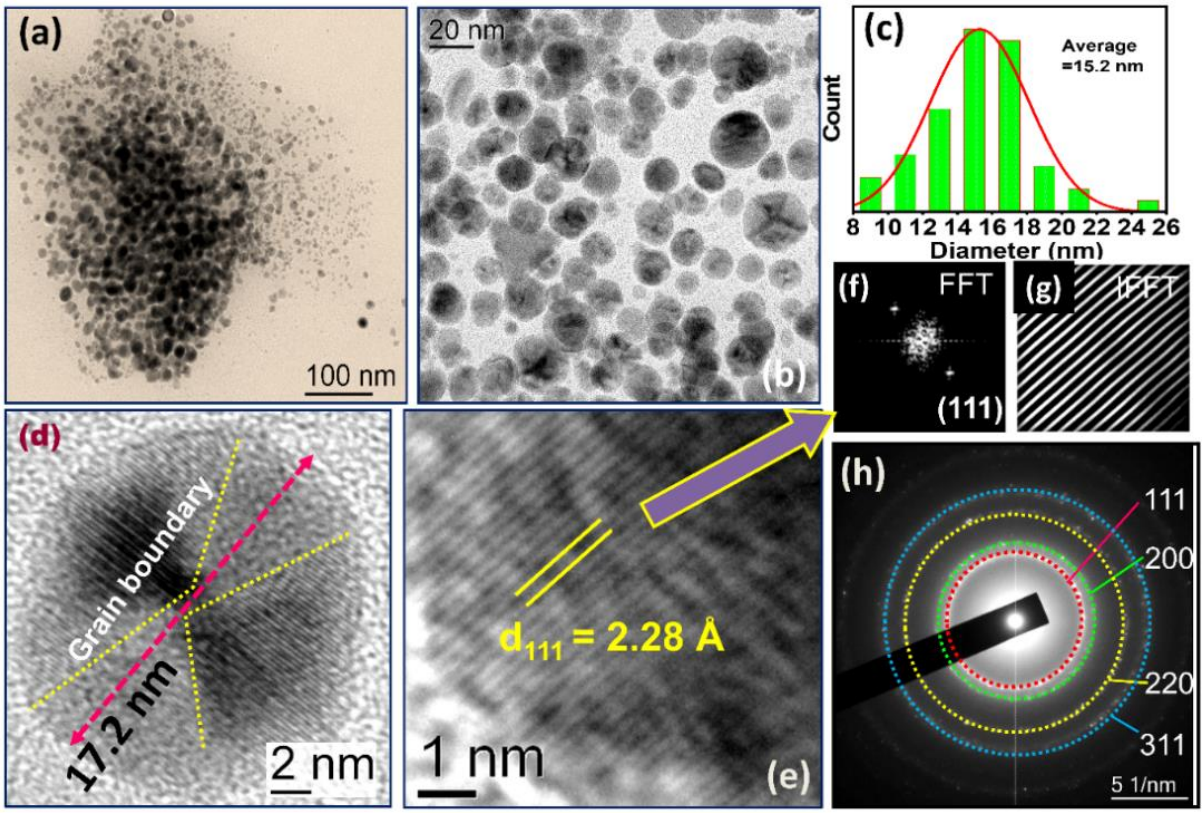


Figure S12. (a,b) TEM and HRTEM images of PdNPs catalyst 2, (c) Corresponding particle size distribution plot, (d) Particle showing grain boundary, (e-g) HRTEM image showing (111) plane and corresponding FFT and IFFT patterns of (111) plane, and (h) SAED pattern.

7.6 Energy dispersive X-ray (EDX) analysis:

Energy dispersive X-ray (EDX) analysis was done to prove the nanostructure, identify the chemical elements and determine their concentrations in the PdNPs catalyst 1. Energy dispersive X-ray (EDX) image corresponding to the PdNPs catalyst 1 of an average dimensions *ca* 8.2 nm indicated that the PdNPs were well distributed on the surface (Figure S13). Thus, it hinted that DBU - the organic base as well as ligand, played a key role in enhancing the dispersibility of the PdNPs. Homogeneous distribution of palladium (Pd) and carbon (C) was noticed in the structure of the nanopowder, and the absence of impurities confirmed the purity of the PdNPs catalyst 1.

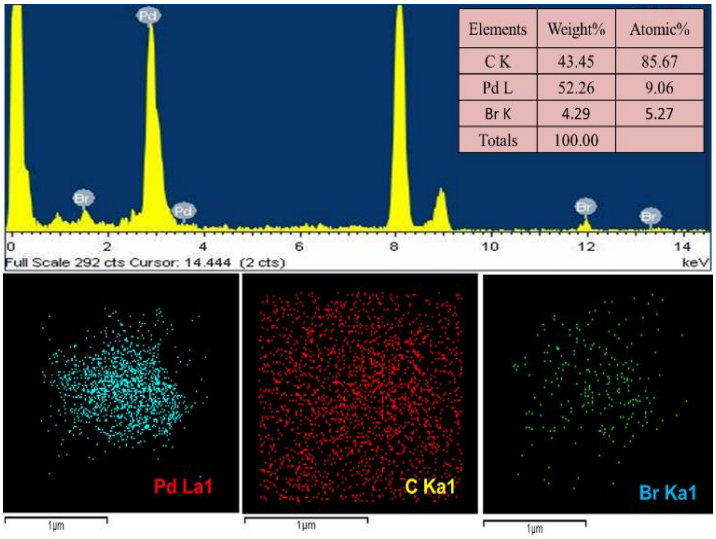


Figure S13. EDX images of PdNPs catalyst 1.

7.7 X-ray Photoelectron Spectroscopy (XPS) analysis:

To evaluate the oxidation states of palladium present the in situ generated Pd nanoparticle catalysts 1 and 2, X-ray Photoelectron Spectroscopy (XPS) data analysis were collected. There in case of Pd catalyst 1, presence of peaks at 340.1 and 334.7 eV with relative intensity ~2:3, indicated electron transitions from Pd(0) $3d_{3/2}$ and Pd(0) $3d_{5/2}$. Whereas, in case of Pd catalyst 2, along with the peaks at 340.6 and 335.3 eV, due to electron transitions from Pd(0) $3d_{3/2}$ and Pd(0) $3d_{5/2}$, appearance of two more intense peaks at 342.5 and 337.2 eV having relative intensity ~2:3, indicated electron transition from Pd(II) $3d_{3/2}$ and Pd(II) $3d_{5/2}$ (Figure 6, in manuscript). Thus the PdNPs catalyst 1 contained almost 100% Pd(0), whereas Pd catalyst 2 contained a mixture of Pd(II) (~70%) and Pd(0) (~30%) with a ratio ~2.3:1. Hence, here DBU is acting as a reducing agent to reduce the Pd(II) species to Pd(0) species.

Analysis of the XPS survey plots of Pd catalysts 1 and 2 (Figure S14), showed a peak near 402.4 eV due to the presence of quaternary N in catalyst 2. However, intensity of that peak was fund to decreases with shifting its position to lower energy (at 401.7 eV) in catalyst 1. And there appearance of peaks at 397.7 eV (for C-N), 399.3 eV (for C=N) and 400.3 eV (for C=N-C), suggested binding of BDU to Pd(0) via C=N-Pd coordinate linkage in catalyst 1. And micelles of CTAB stabilizes the Pd(0) nanoparticles in water medium through ion-dipole interactions with its polar heads.

Compared to Pd catalyst 2, intensity of peaks corresponding to Pd 3p, Pd 3d and O 1s increases, whereas intensity of peak for C 1s decreases in Pd catalyst 1. Peaks corresponding to Br 3d and 3p which are present in catalyst 2, are absent in catalyst 1. Peaks at 532.6 eV (for C=O) and 533.2 eV (for C-O-Pd) indicates the presence of some palladium(II) acetate in catalyst 2. On the other hand, appearance of peaks at 533.5 eV (for COOH) and 531.4 eV (for C-OH) in catalyst 1, indicates the displacement of those acetate group by DBU to generate Pd(0) and acetic acid molecules, which react with basic DBU.The peaks at 286.2 eV (for C-O/C-N) and 284.8 eV (for C-C) of C 1s are due to the presence of CTAB and acetate group in catalyst 2.

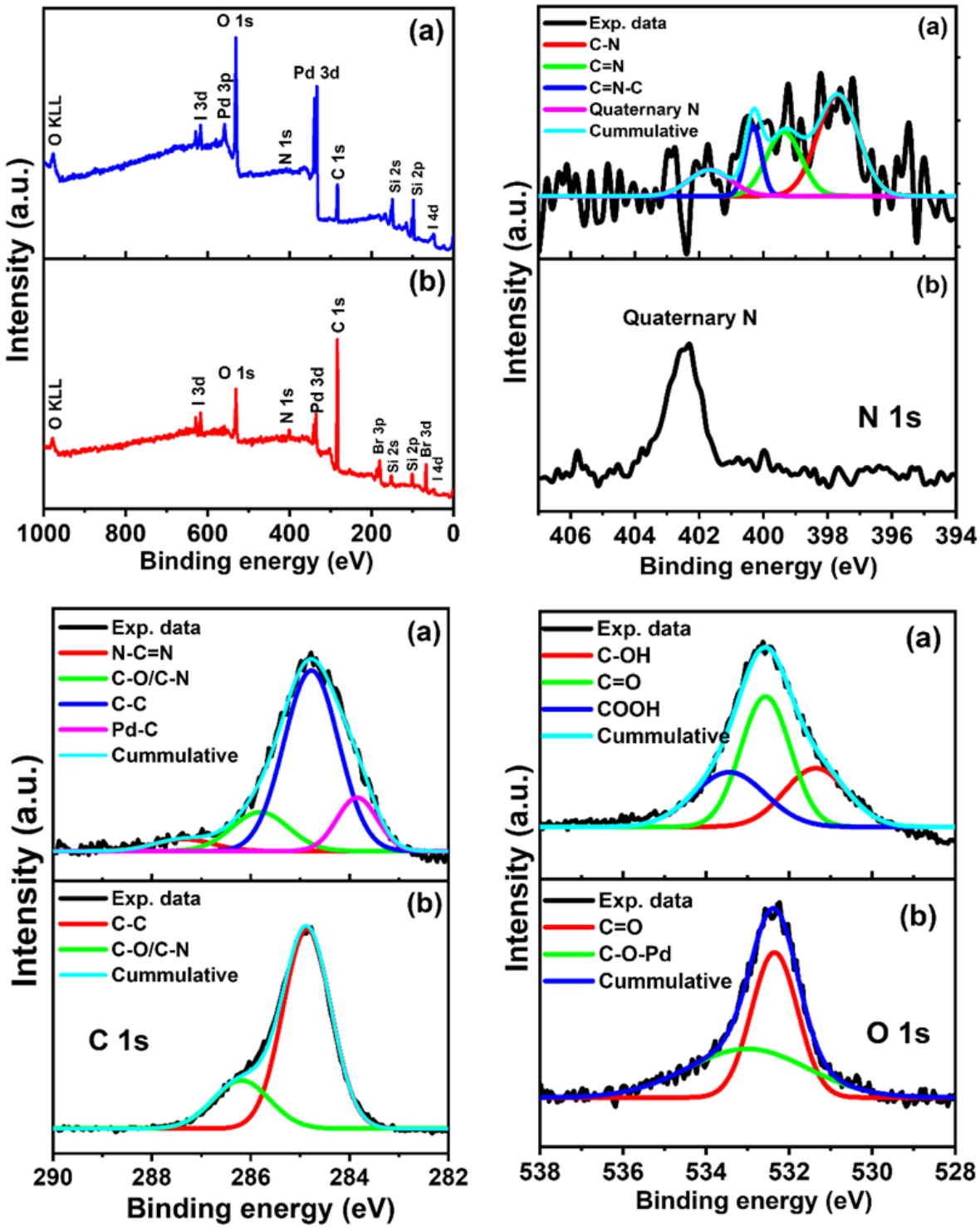


Figure S14. XPS data of (a) Pd catalyst 1 (collected from $Pd(OAc)_2$+CTAB+DBU), and (b) Pd catalyst 2 (collected from $Pd(OAc)_2$+CTAB).

7.8 Single crystal X-ray diffraction (SCXRD) analysis:

SCXRD data were collected with Mo Kα radiation by a Bruker APEX-2 CCD diffractometer. The data were processed using the Bruker SAINT package. The structure solution and refinement were performed by SHELX97.

Isolated solid Pd catalyst 2 (collected from $Pd(OAc)_2$ + CTAB) was found crystalline in nature. For crystallization it was dissolved in DCM, and allowed for slow evaporation. Its single crystal XRD data showed presence of $Pd(II)Br_4.(CTAB)_2$ crystals (Figure S15).

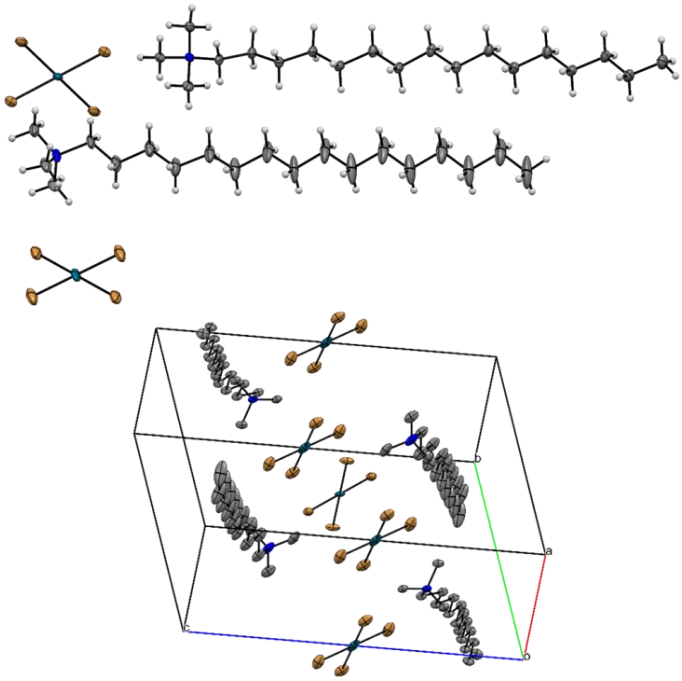


Figure S15. Single crystal structure of Pd catalyst 2, with ORTEP representation showing thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Color: Deep blue (N), Yellow (Br) and Sky blue (Pd).

SCXRD data of Pd catalyst 2:

CCDC No.	2495048
Identification code	SB_JA_61
Empirical formula	$C_{19}H_{42}Br_2NPd_{0.5}$
Formula weight	497.55
Temperature/K	101.00
Crystal system	triclinic
Space group	P-1
a/Å	8.8718(10)
b/Å	13.5374(15)
c/Å	19.143(2)

α/°	84.934(4)
β/°	82.326(4)
γ/°	88.275(4)
Volume/Å^3	2269.2(4)
Z	4
ρ_{calc}g/cm^3	1.456
μ/mm^{-1}	3.956
F(000)	1024.0
Crystal size/mm^3	0.8 × 0.5 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.858 to 50.046
Index ranges	-10 ≤ h ≤ 10, -16 ≤ k ≤ 16, -22 ≤ l ≤ 22
Reflections collected	57238
Independent reflections	8014 [R_{int} = 0.0711, R_{sigma} = 0.0492]
Data/restraints/parameters	8014/302/418
Goodness-of-fit on F^2	1.023
Final R indexes [I>=2σ (I)]	R_1 = 0.0484, wR_2 = 0.1196
Final R indexes [all data]	R_1 = 0.0689, wR_2 = 0.1357
Largest diff. peak/hole / e Å^{-3}	2.15/-1.17

Isolated Pd catalyst 2 was found crystalline in nature, and its single crystal XRD data showed presence of Pd(II)Br_4.$(CTAB)_2$ unit (Figure S15). Thus, there are ionic bonds between the anionic Pd(II) species and ammonium ions of CTAB in Pd catalyst 2. However, the Pd catalyst 1 was found amorphous in nature, and it was difficult to confirm the nature of the Pd–N linkage, at this stage. Thus, there may be coordinate linkage between the Pd(0) and DBU, a neutral amidine ligand, for generating a tetrahedral $Pd(DBU)_4$ complex, via Pd–N=C bonds in Pd(0) catalyst 1 (Figure S16).

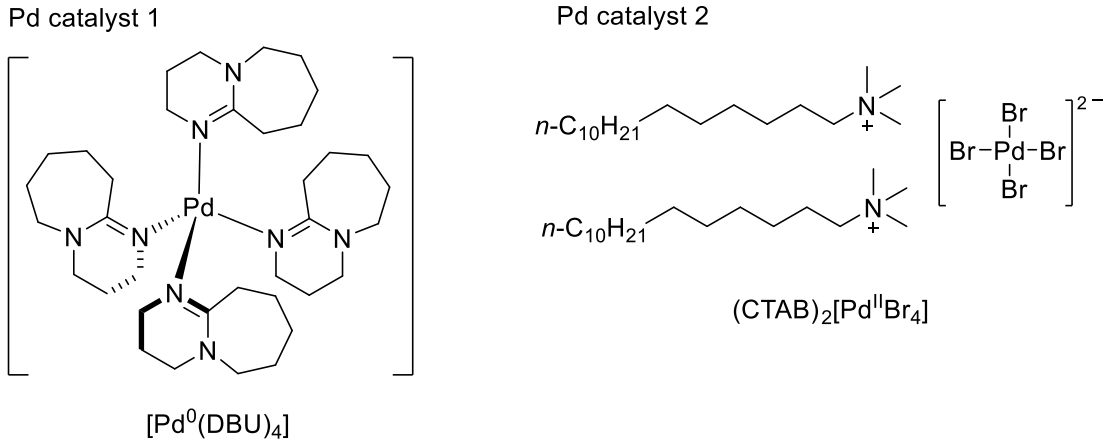


Figure S16. Possible Pd–N linkages of DBU and CTAB ligands to Pd in catalyst 1 and catalyst 2.

7.9 Analytical data of the recovered Pd catalysts: FESEM micrographs of recovered PdNPs catalyst (after 3rd recycling reaction) are given in Figure S17. XPS data and TEM images of recovered PdNPs catalyst are given in Figure S18 and Figure S19, respectively.

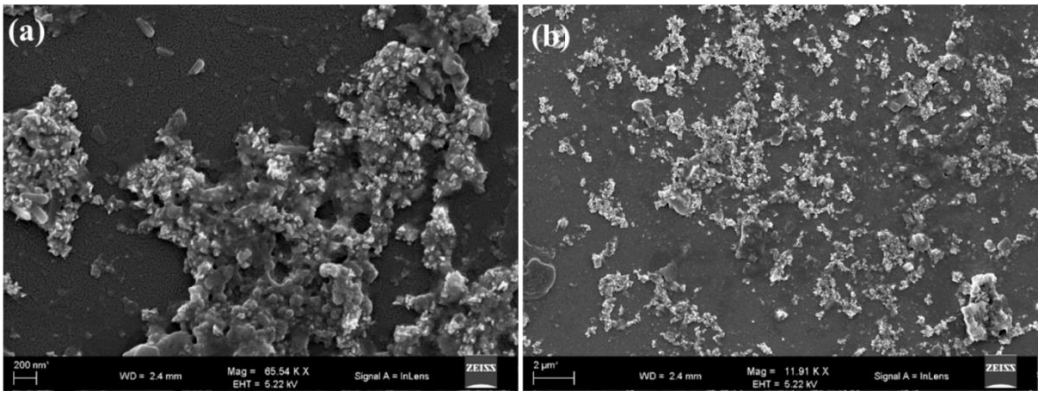


Figure S17. FESEM micrographs of recovered PdNPs catalyst after 3rd recycling reaction.

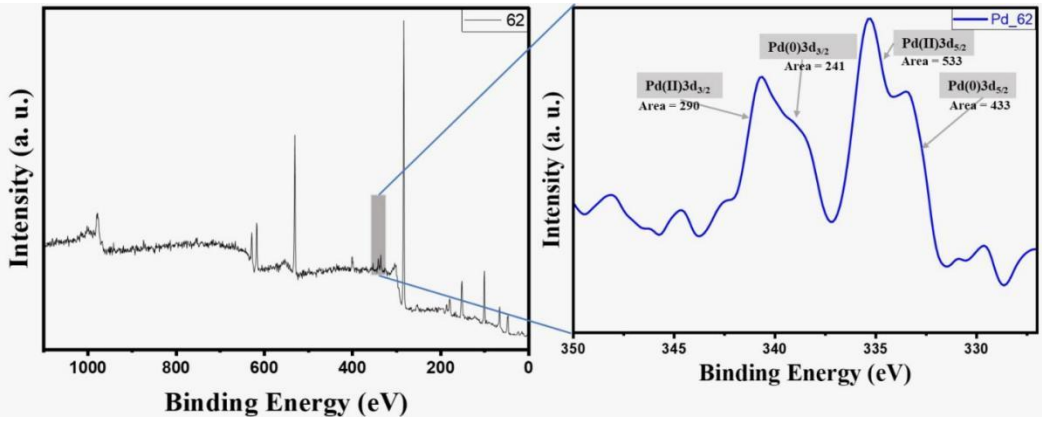


Figure S18. XPS data of recovered PdNPs catalyst after 3rd recycling reaction.

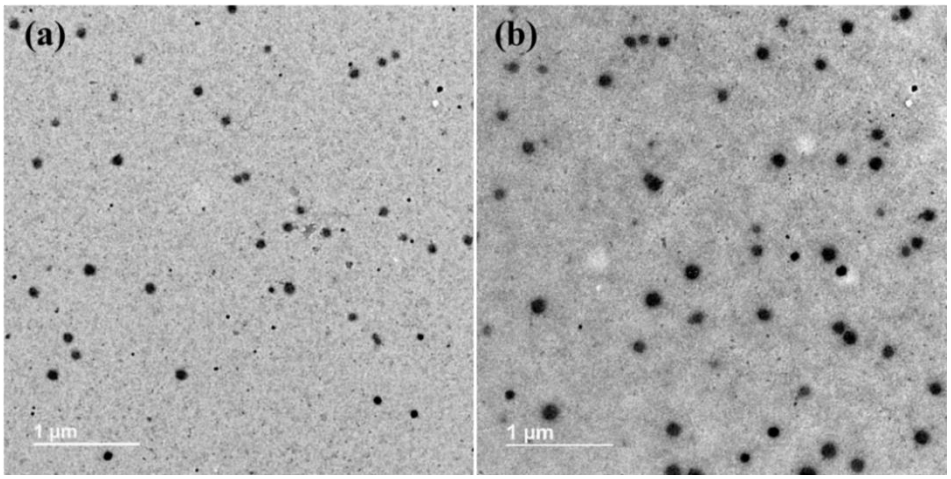


Figure S19. TEM images of recovered PdNPs catalysts (a) after 1st recycling (size ~50 nm), and (b) after 3rd recycling (size ~80 nm) reactions.

8. References:

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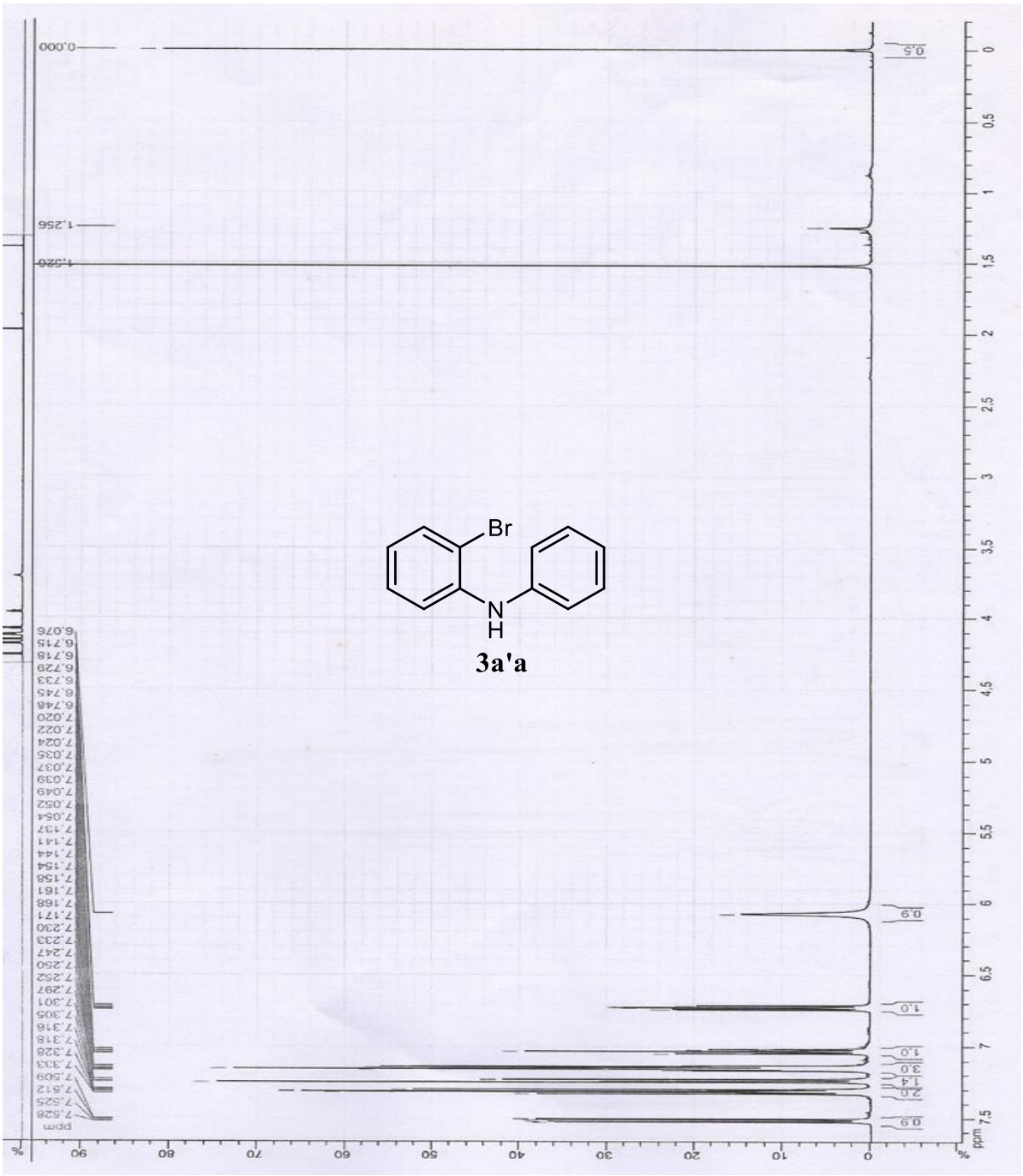
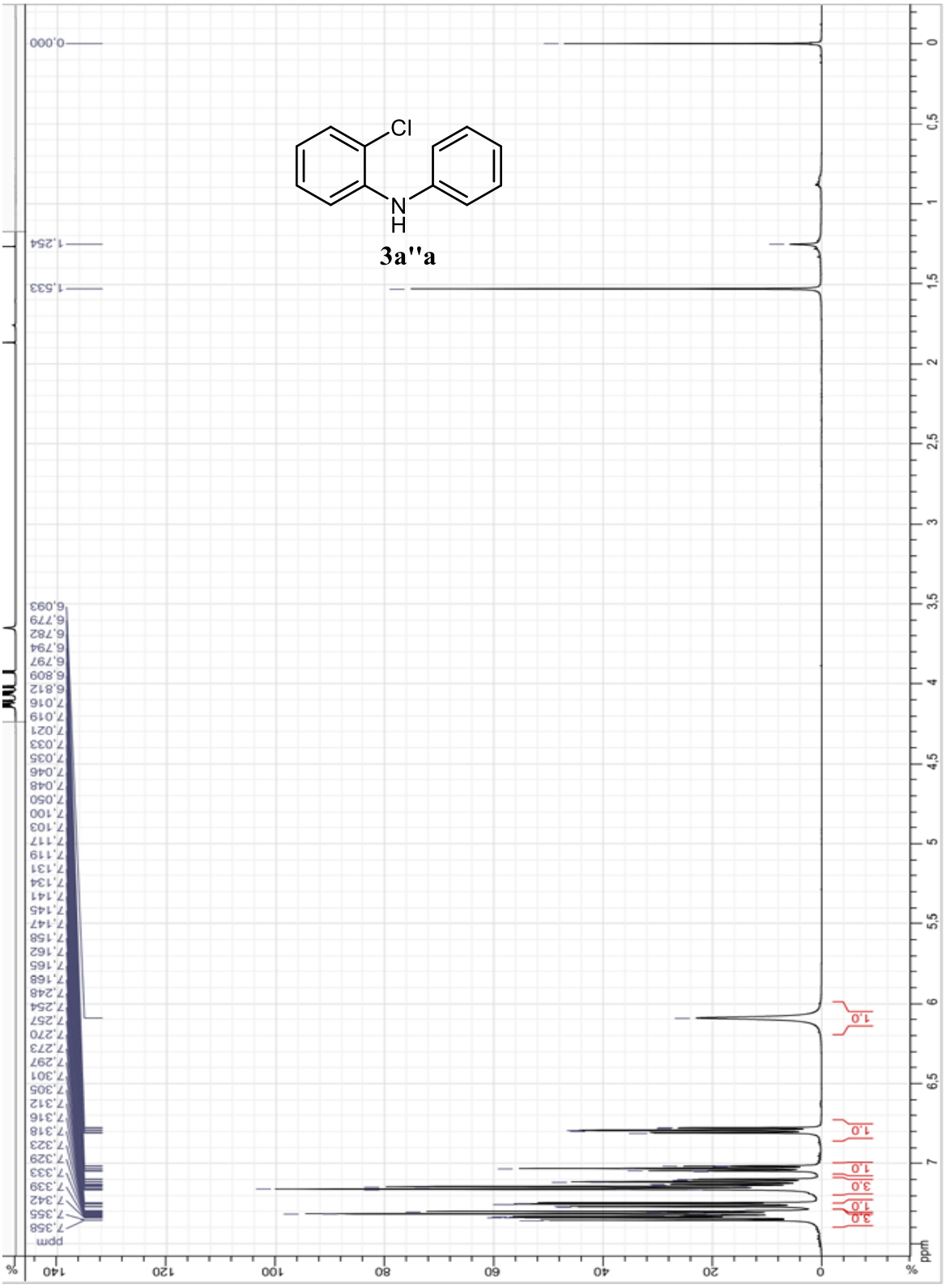
9.1 ^{1}H NMR and ^{13}C NMR spectra of 2-halo-*N*-arylanilines 3: ^{1}H NMR spectra of 2-iodo-*N*-arylanilines (**3a'a**, **3a"a**, **3ba**, **3ca**, **3ea**, **3fa**, **3ga**, **3ha**, **3ia**, **3ja**, **3ab**, **3ac**, **3ae**, **3af**, **3ag**, **3ah**, **3ai**, **3aj**, **3ak**, **3am**, **3fe**, **3eg**, **3fg**, **3gg**, **3hg**, **3ig**, **3ap**, **3aq**, **3bq**, **3ka**, **3ka** and **3aa-1**); and ^{1}H NMR and ^{13}C NMR spectra of 2-iodo-*N*-arylanilines (**3da**, **3da**, **3al**, **3an**, **3ao**, **3ec**, **3fc**, **3fd**, **3bg**, **3cn**, **3ap**, **3bp**, **3ba-1** and **3ia-1**) are given here.

^{1}H NMR spectrum of 2-iodo-*N*-phenylaniline (**3aa**) in $CDCl_3$ is given at page S24 (Figure S1b).

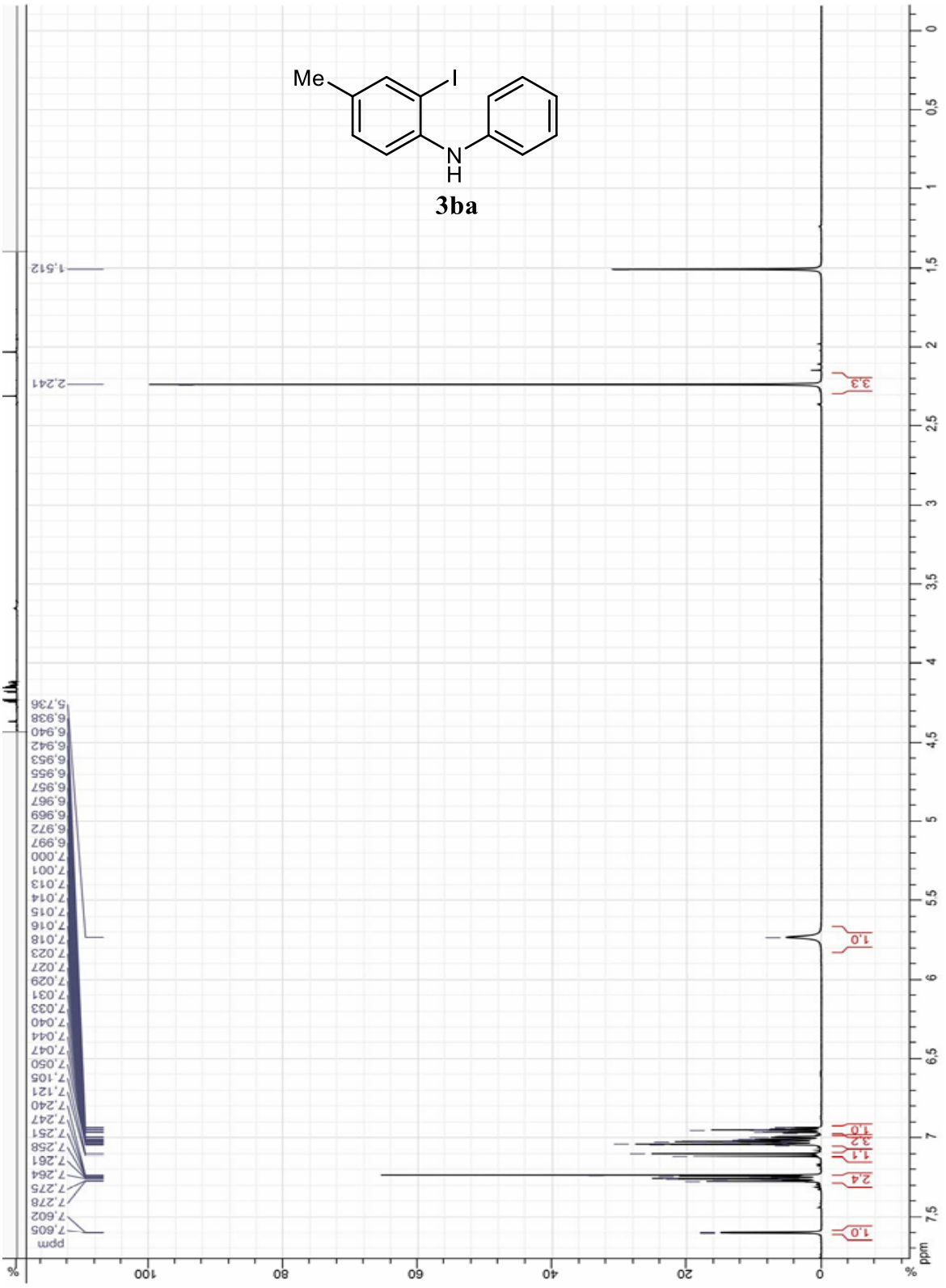
^{1}H NMR spectrum of 2-bromo-*N*-phenylaniline (**3a'a**) in $CDCl_3$.



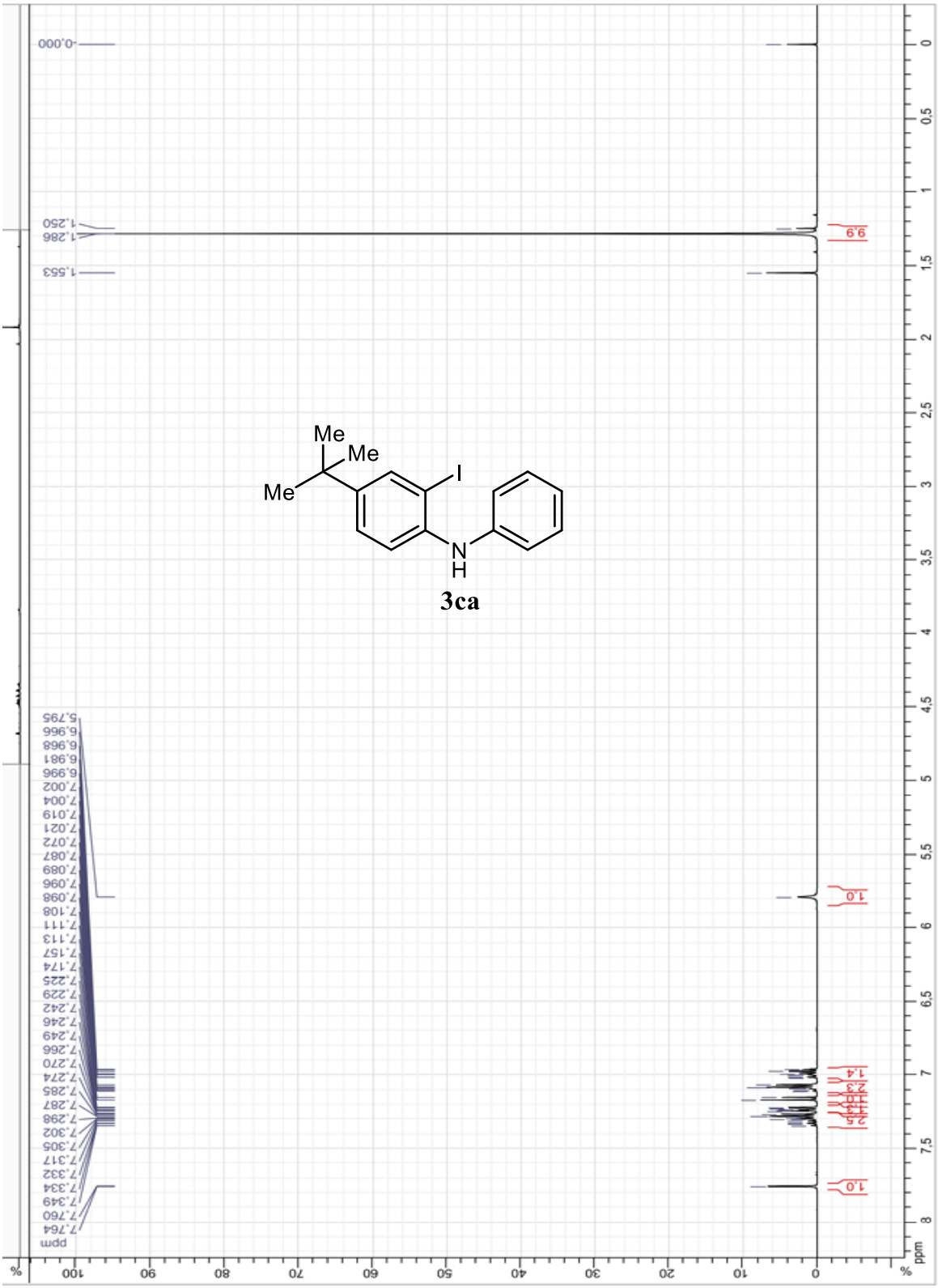
^{1}H NMR spectrum of 2-chloro-*N*-phenylaniline (**3a”a**) in $CDCl_3$



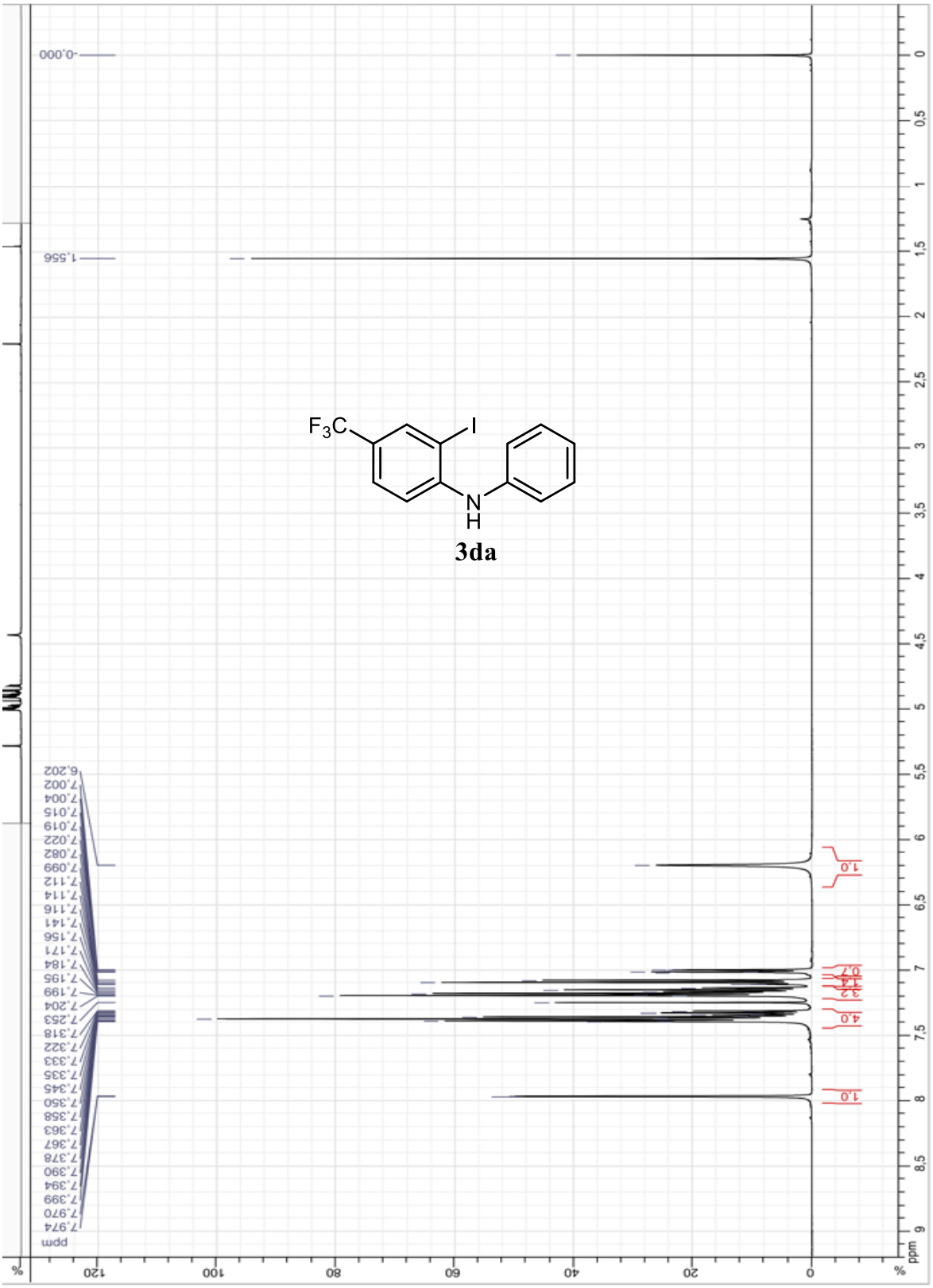
^{1}H NMR spectrum of 2-iodo-4-methyl-*N*-phenylaniline (**3ba**) in $CDCl_3$

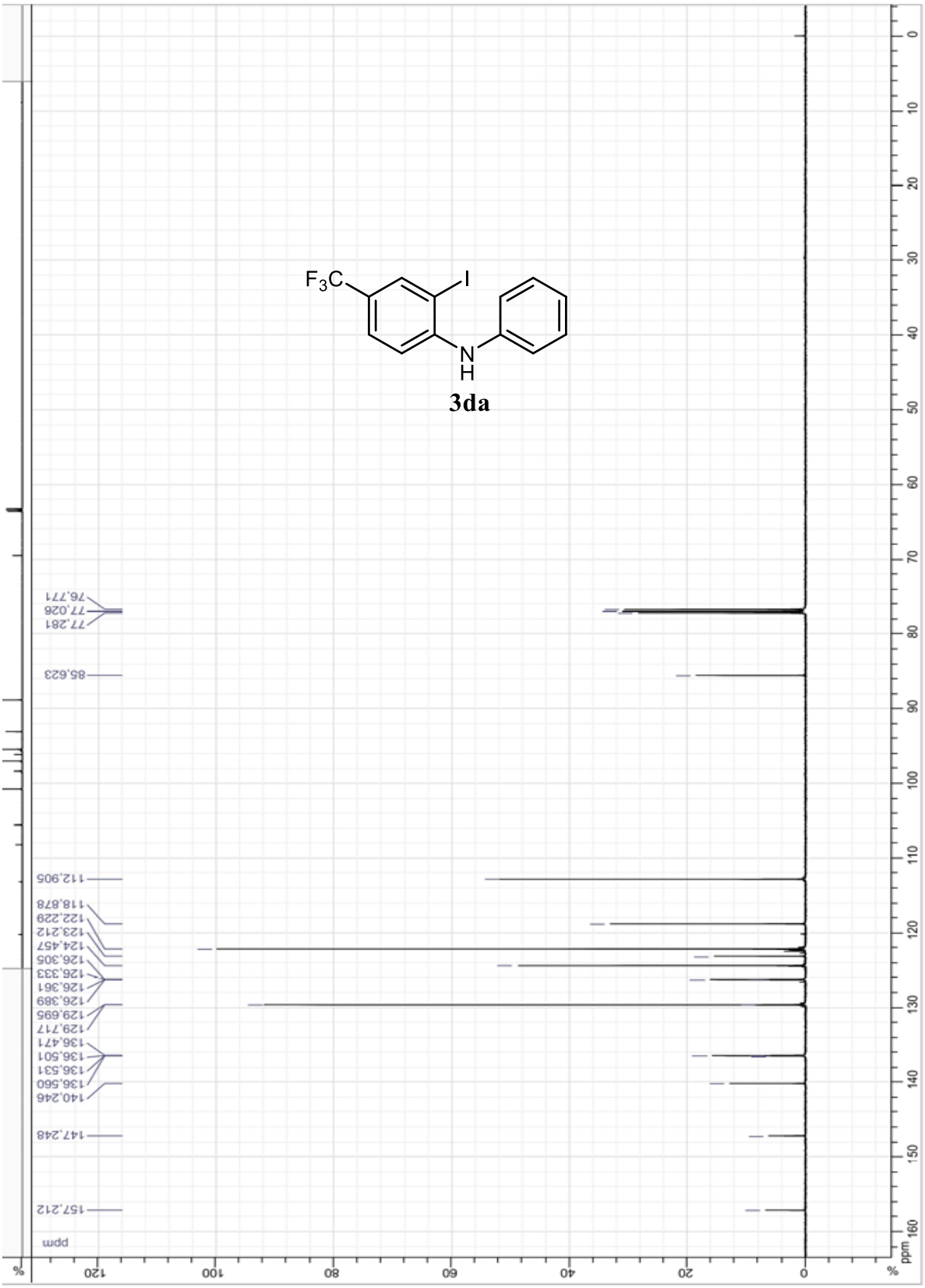


^{1}H NMR spectrum of 4-(*tert*-butyl)-2-iodo-*N*-phenylaniline (**3ca**) in $CDCl_3$

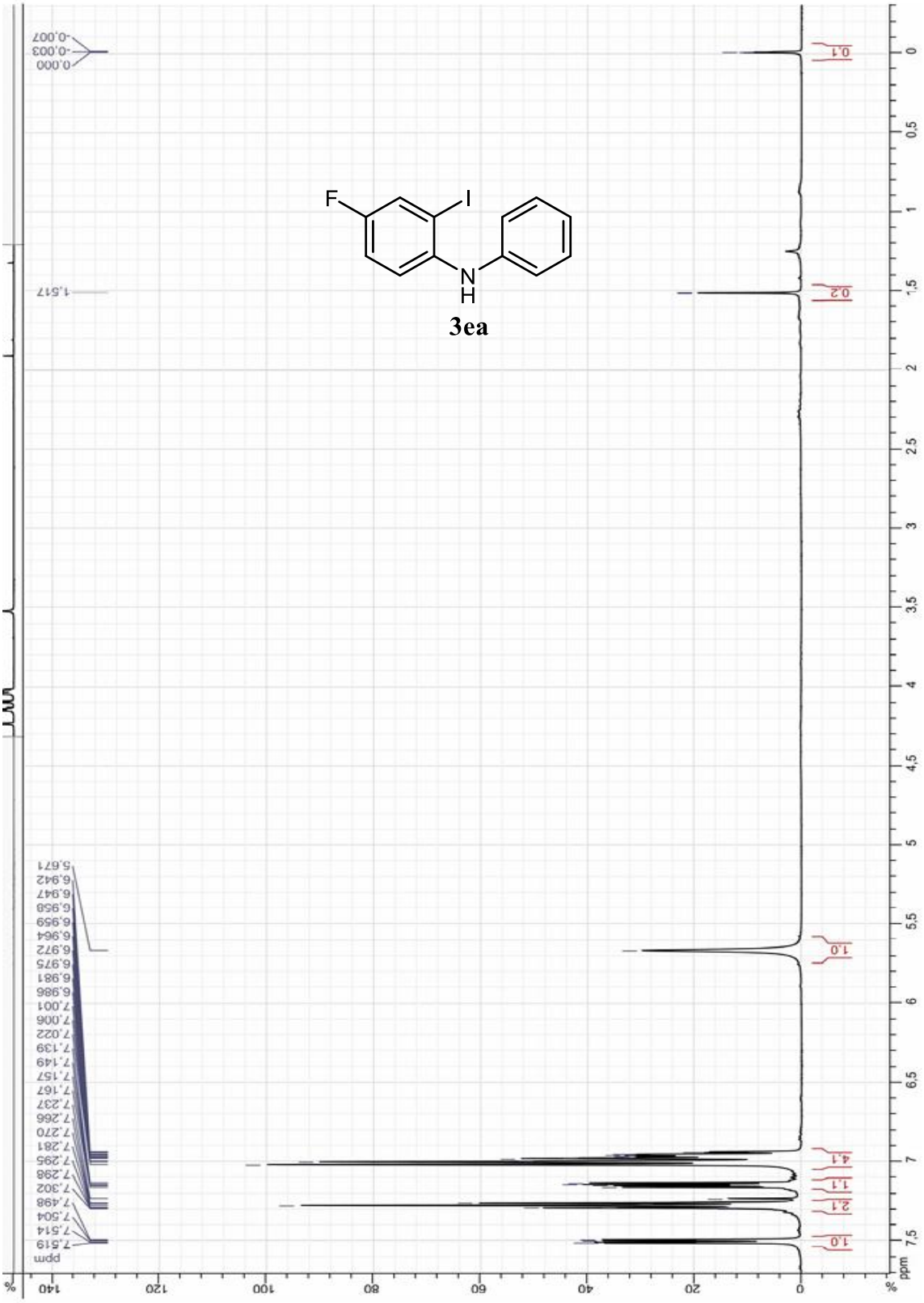


^{1}H NMR and ^{13}C spectra of 2-iodo-*N*-phenyl-4-(trifluoromethyl)aniline (**3da**) in $CDCl_3$

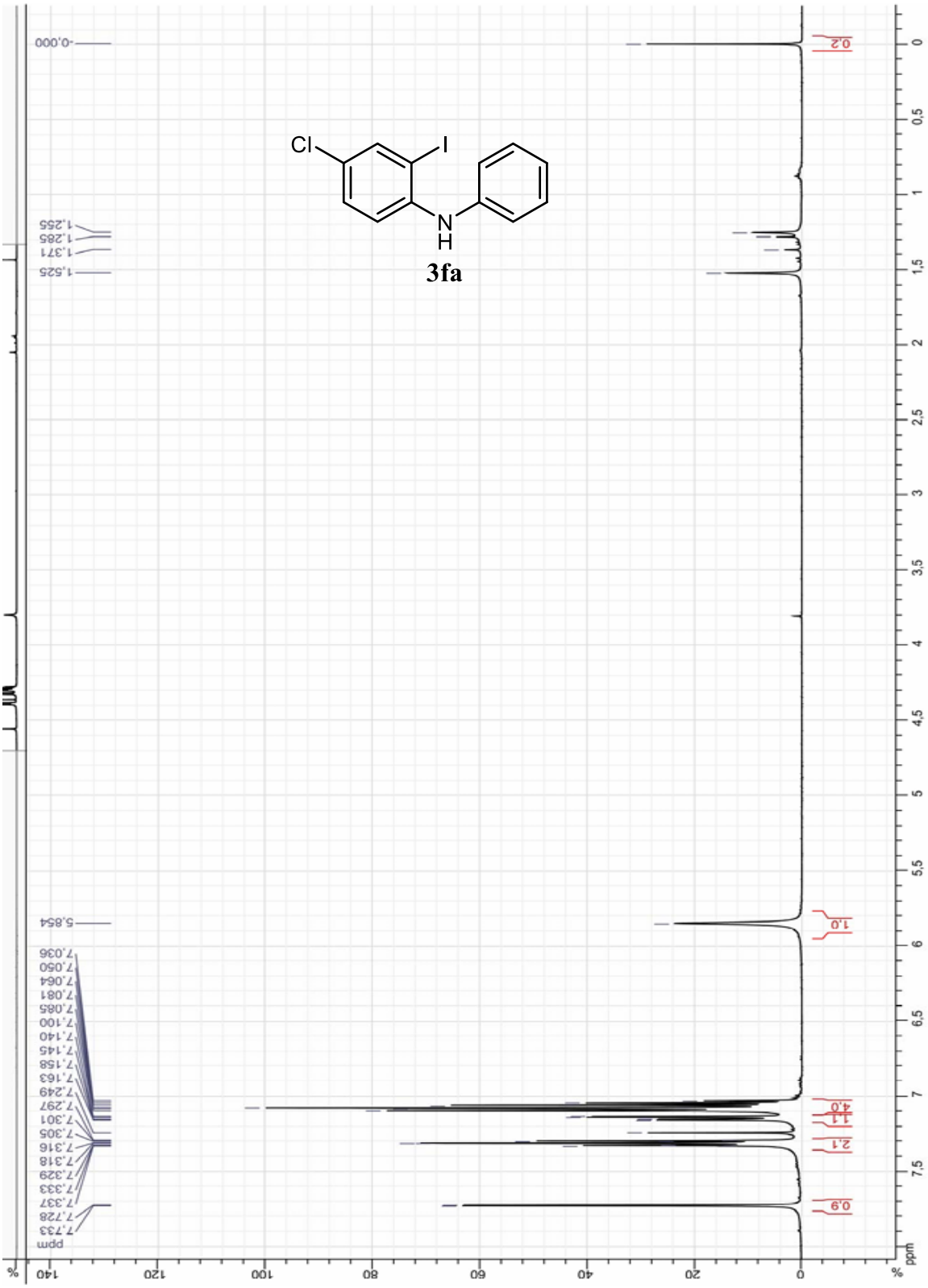



F3C
I
N
H
3da
157.212
147.248
140.246
136.560
136.531
136.501
136.471
129.717
129.695
126.389
126.361
126.333
126.305
124.457
123.212
122.229
118.878
112.905
85.623
77.281
77.026
76.771
ppm

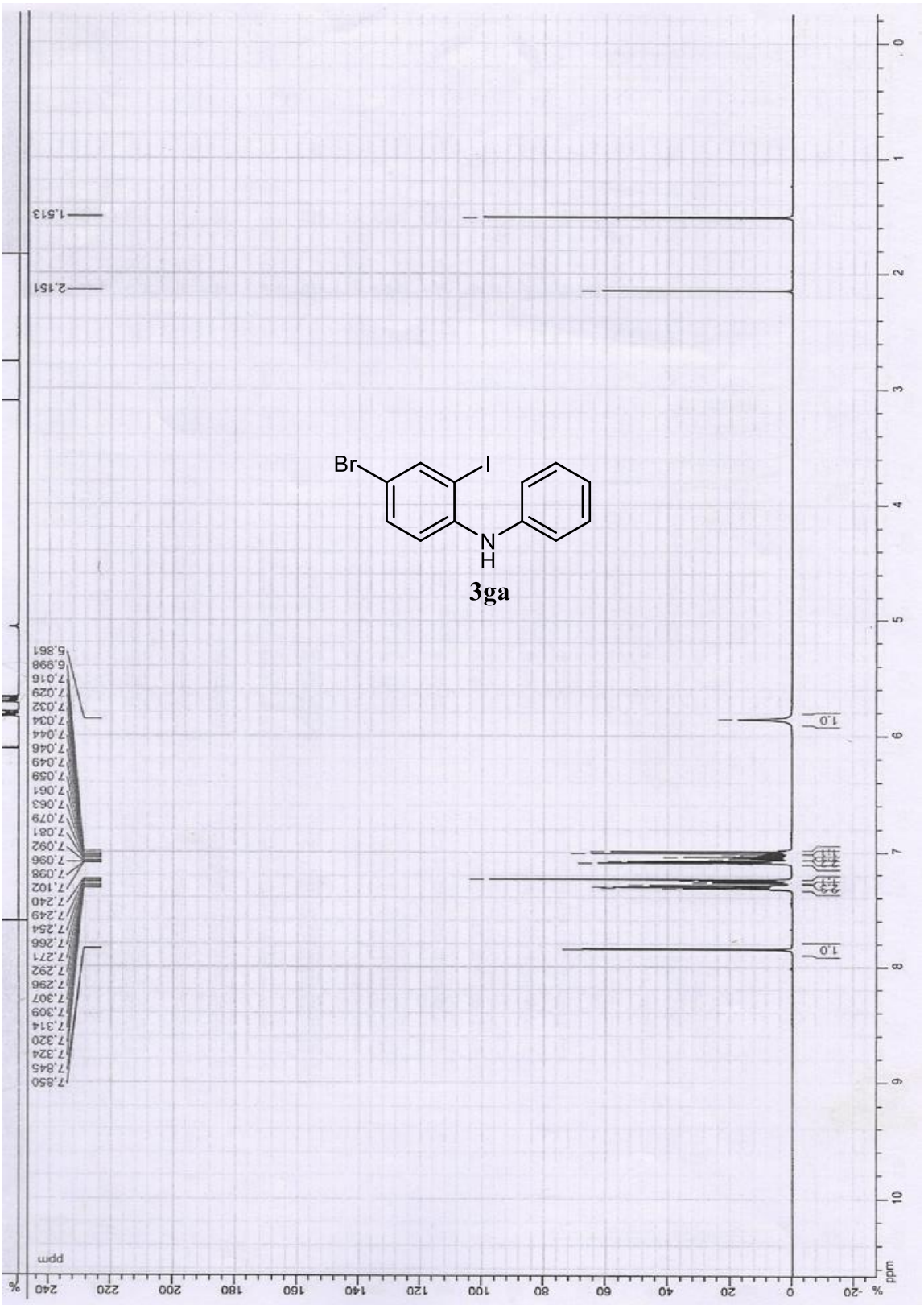
^{1}H NMR spectrum of 4-fluoro-2-iodo-*N*-phenylaniline (**3ea**) in $CDCl_3$



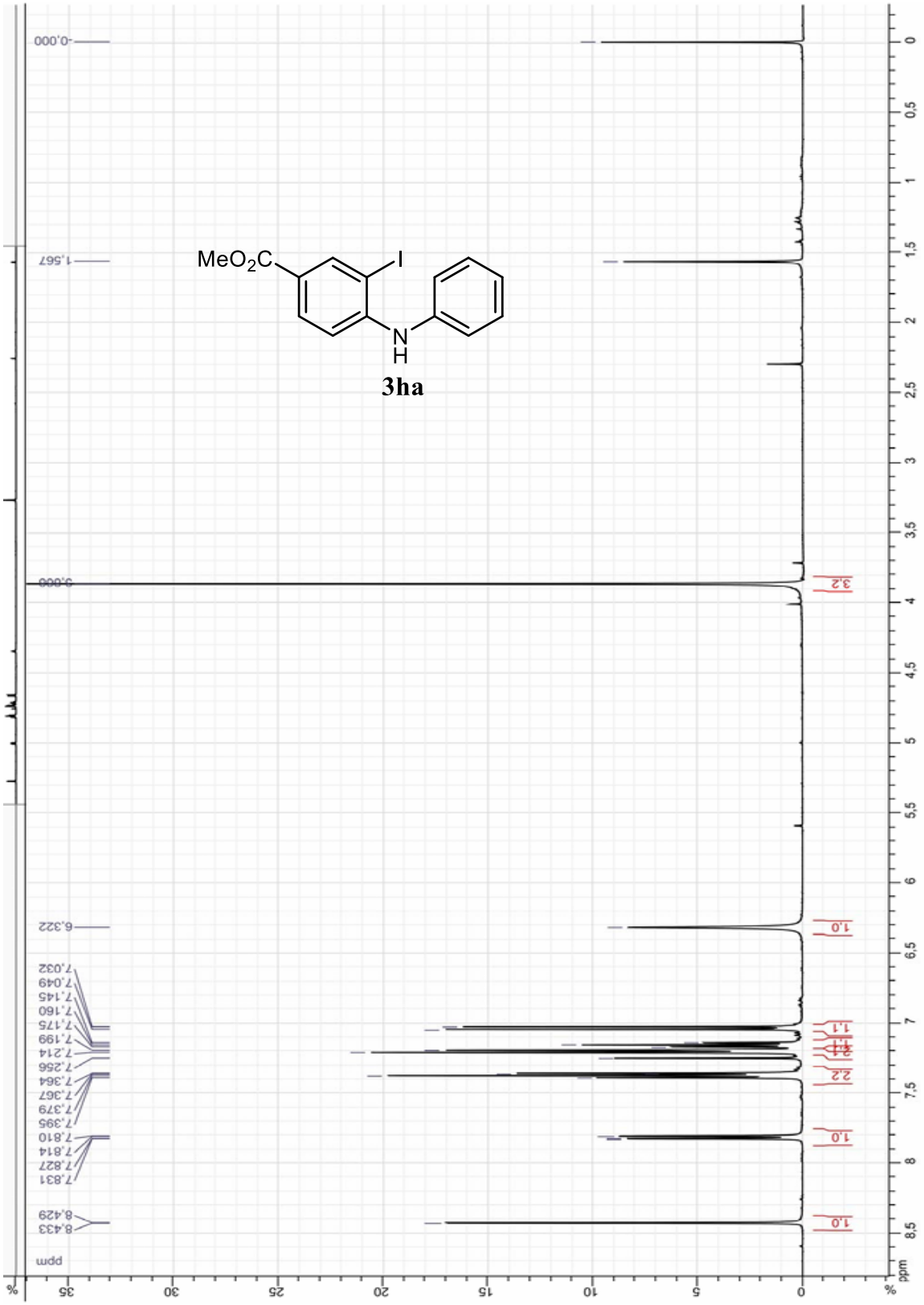
^{1}H NMR spectrum of 4-chloro-2-iodo-*N*-phenylaniline (**3fa**) in $CDCl_3$



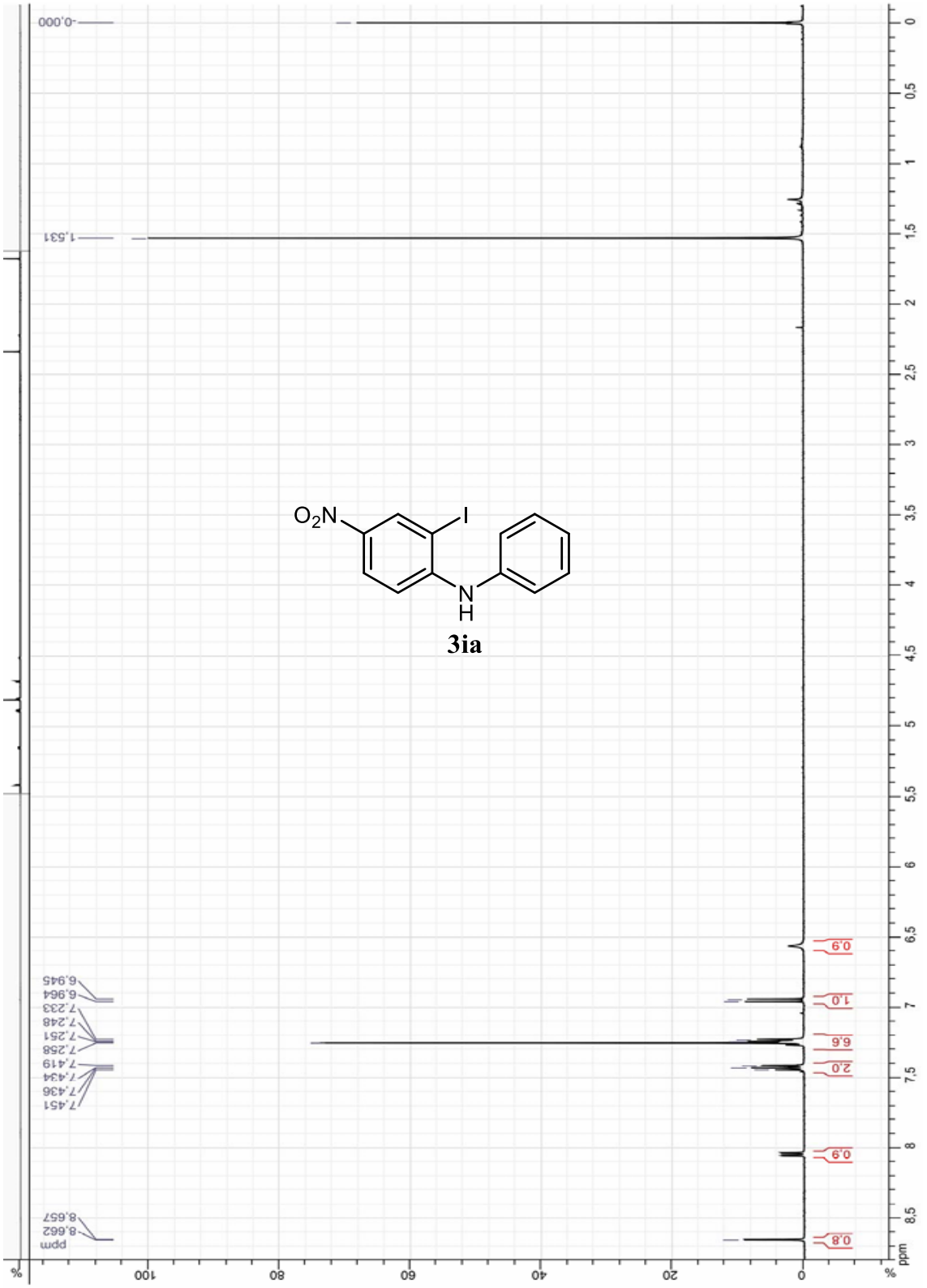
[1]H NMR spectrum of 4-bromo-2-iodo-*N*-phenylaniline (**3ga**) in $CDCl_3$



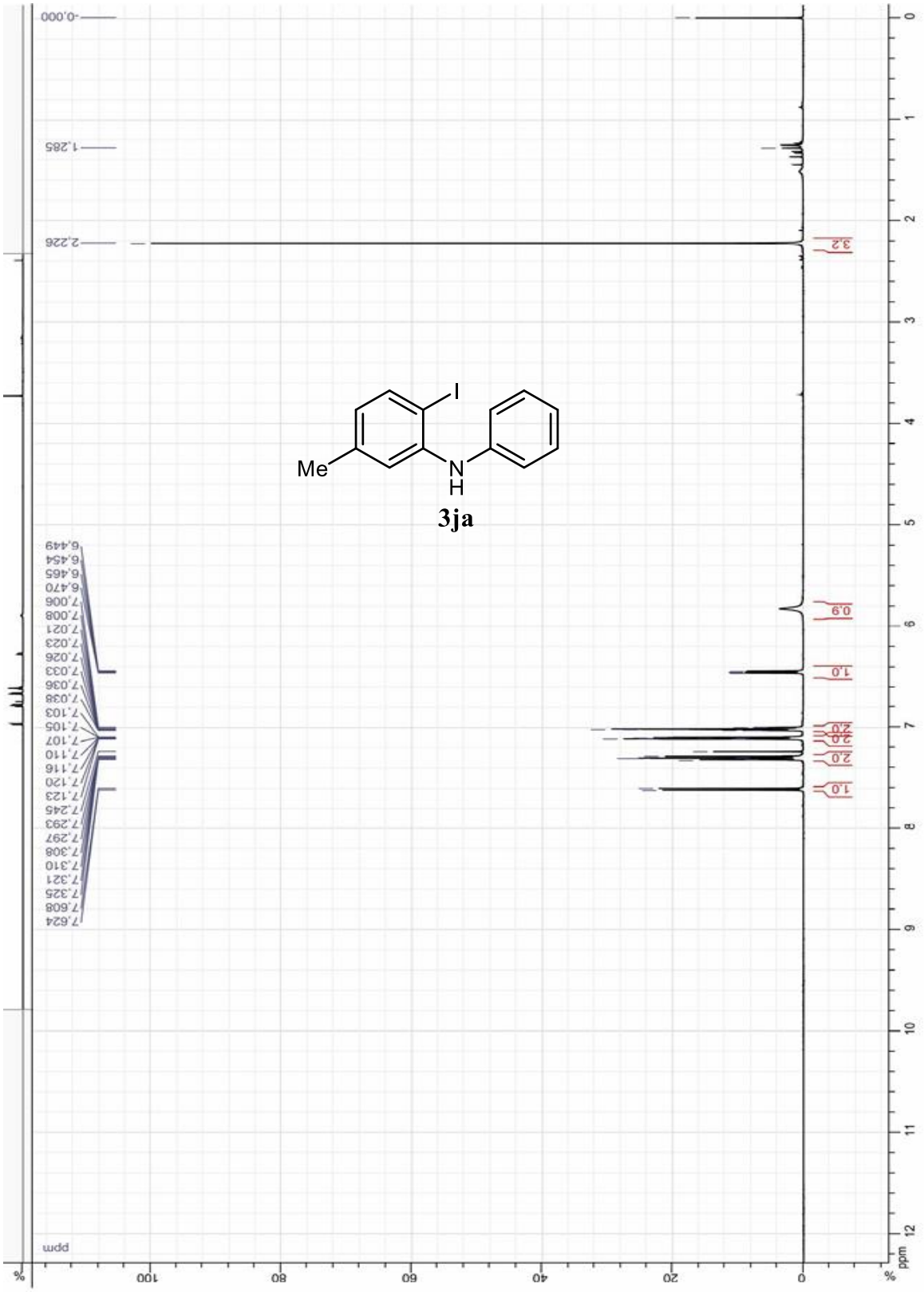
^{1}H NMR spectrum of methyl 3-iodo-4-(phenylamino)benzoate (**3ha**) in $CDCl_3$



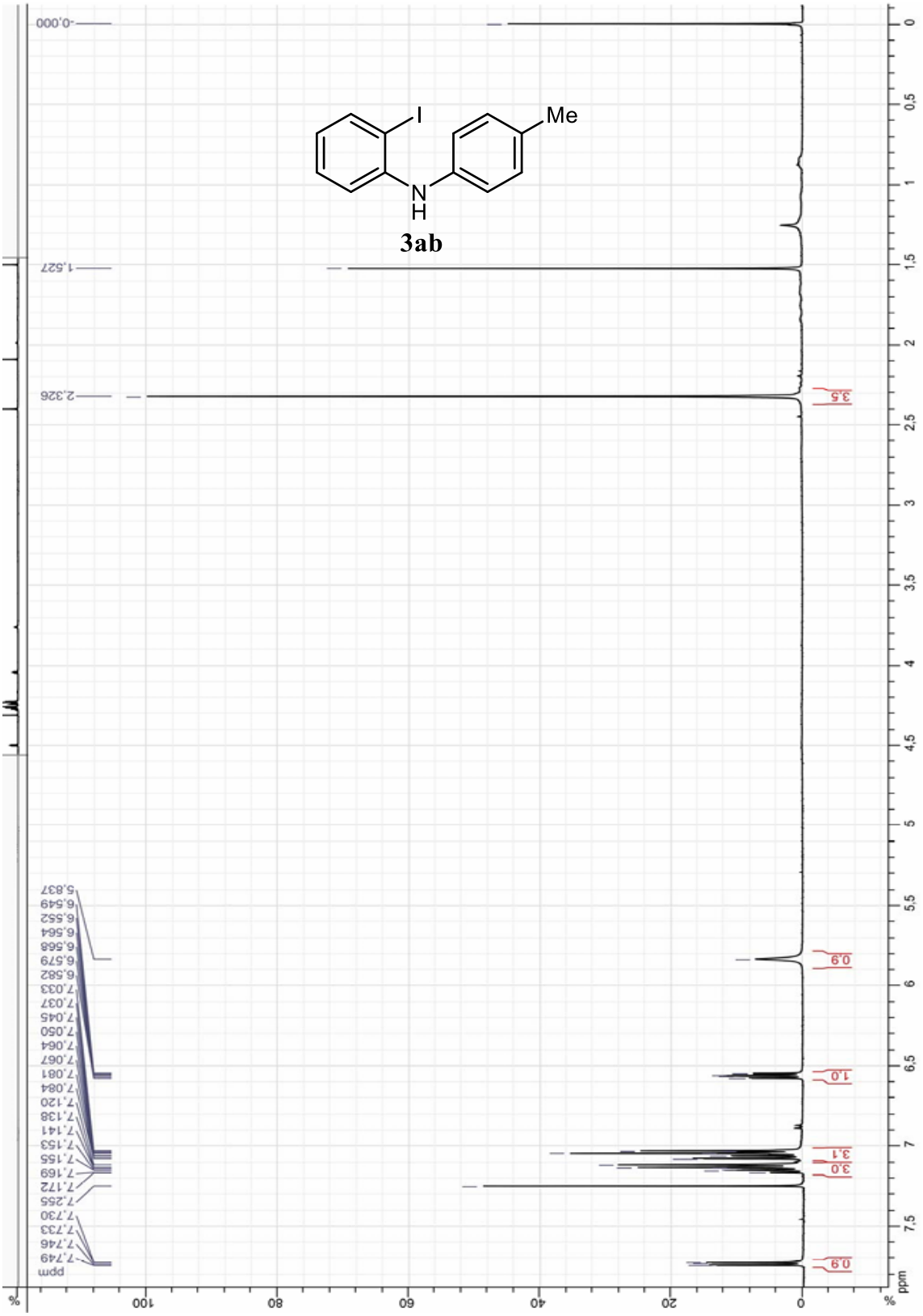
^{1}H NMR spectrum of 2-iodo-4-nitro-*N*-phenylaniline (**3ia**) in $CDCl_3$



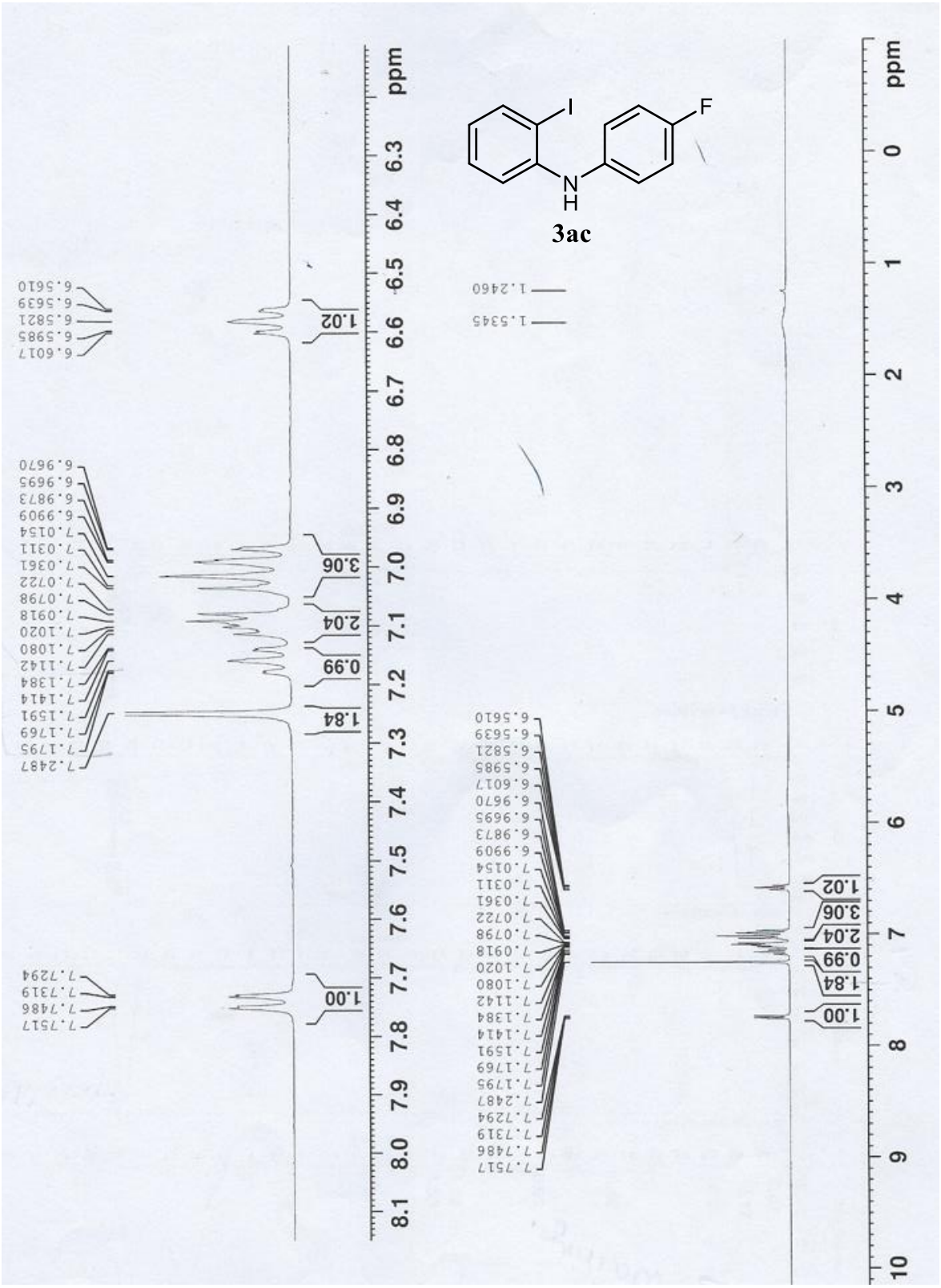
^{1}H NMR spectrum of 2-iodo-5-methyl-*N*-phenylaniline (**3ja**) in $CDCl_3$



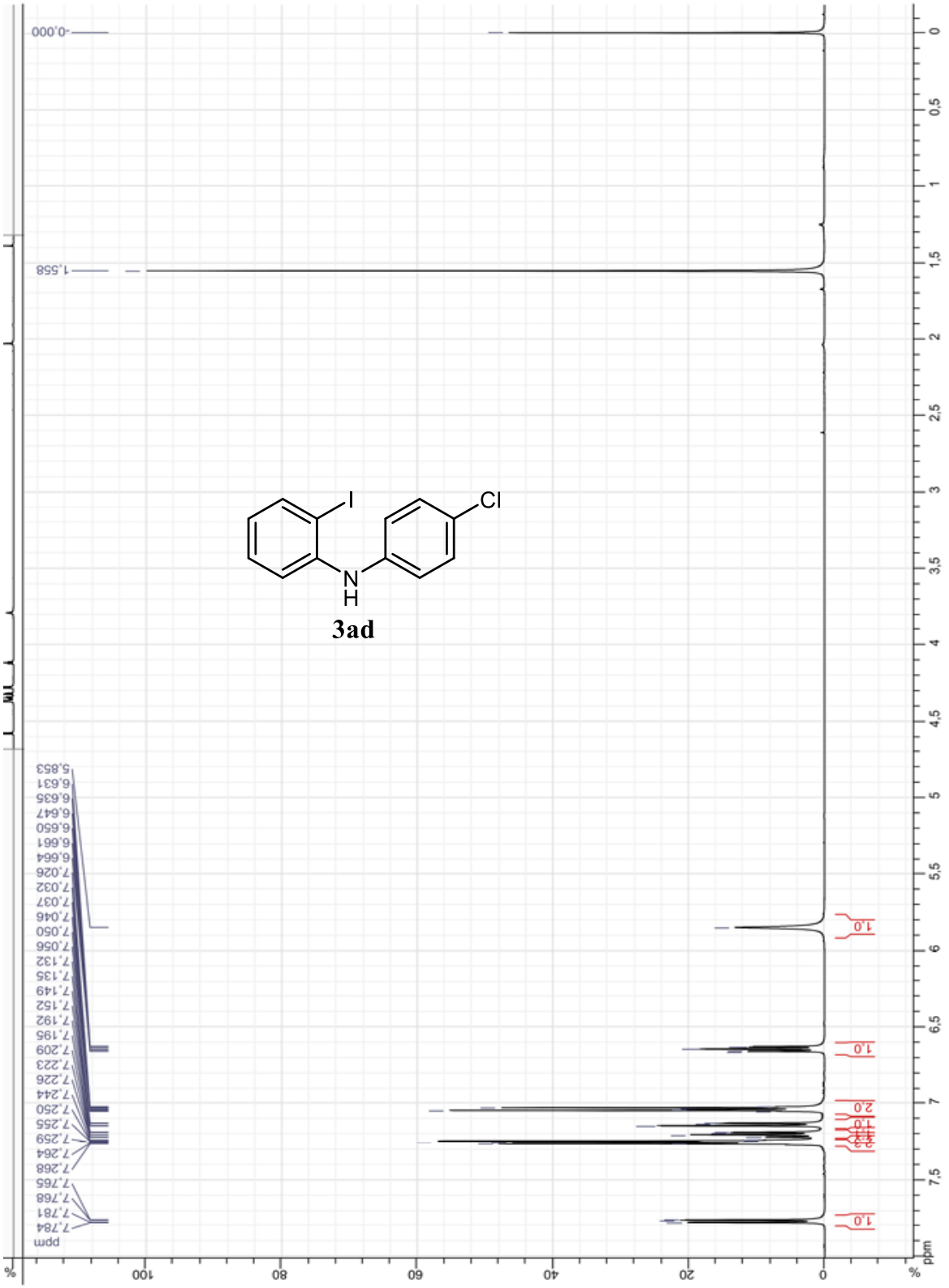
^{1}H NMR spectra of 2-Iodo-*N*-(*p*-tolyl)aniline (**3ab**) in $CDCl_3$

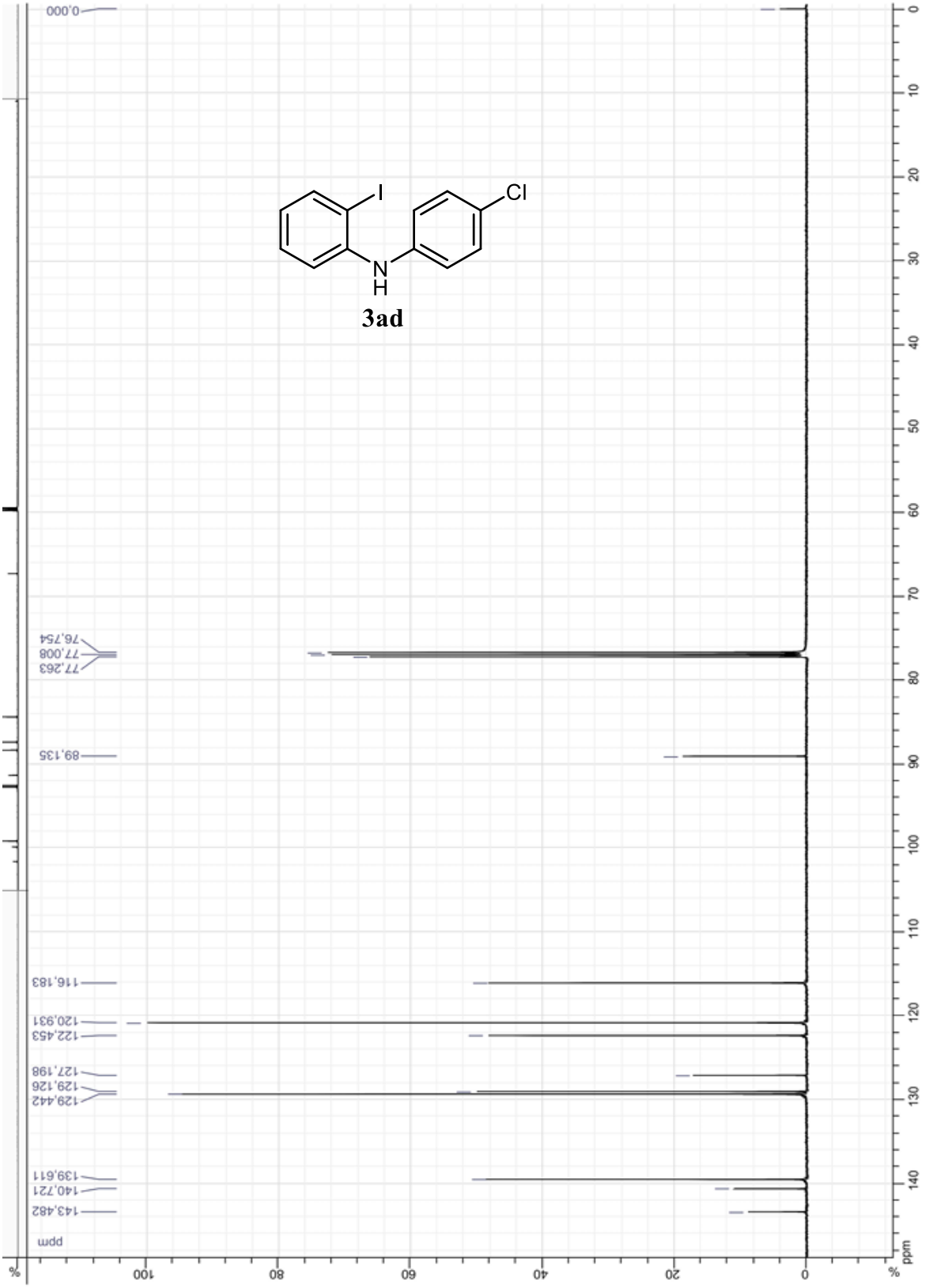


^{1}H NMR spectrum of *N*-(4-fluorophenyl)-2-iodoaniline (**3ac**) in $CDCl_3$



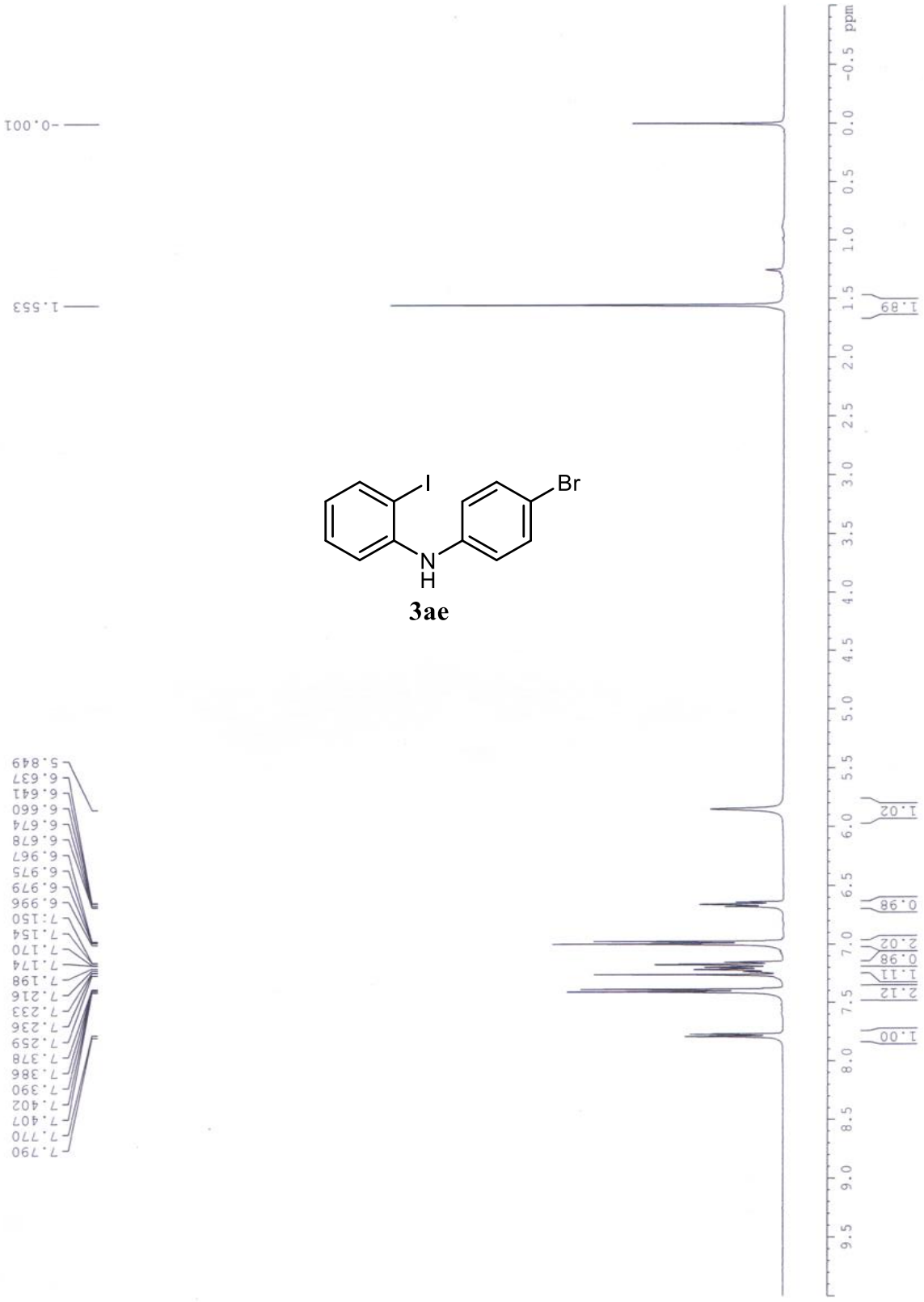
^{1}H NMR and ^{13}C spectra of *N*-(4-chlorophenyl)-2-iodoaniline (**3ad**) in $CDCl_3$



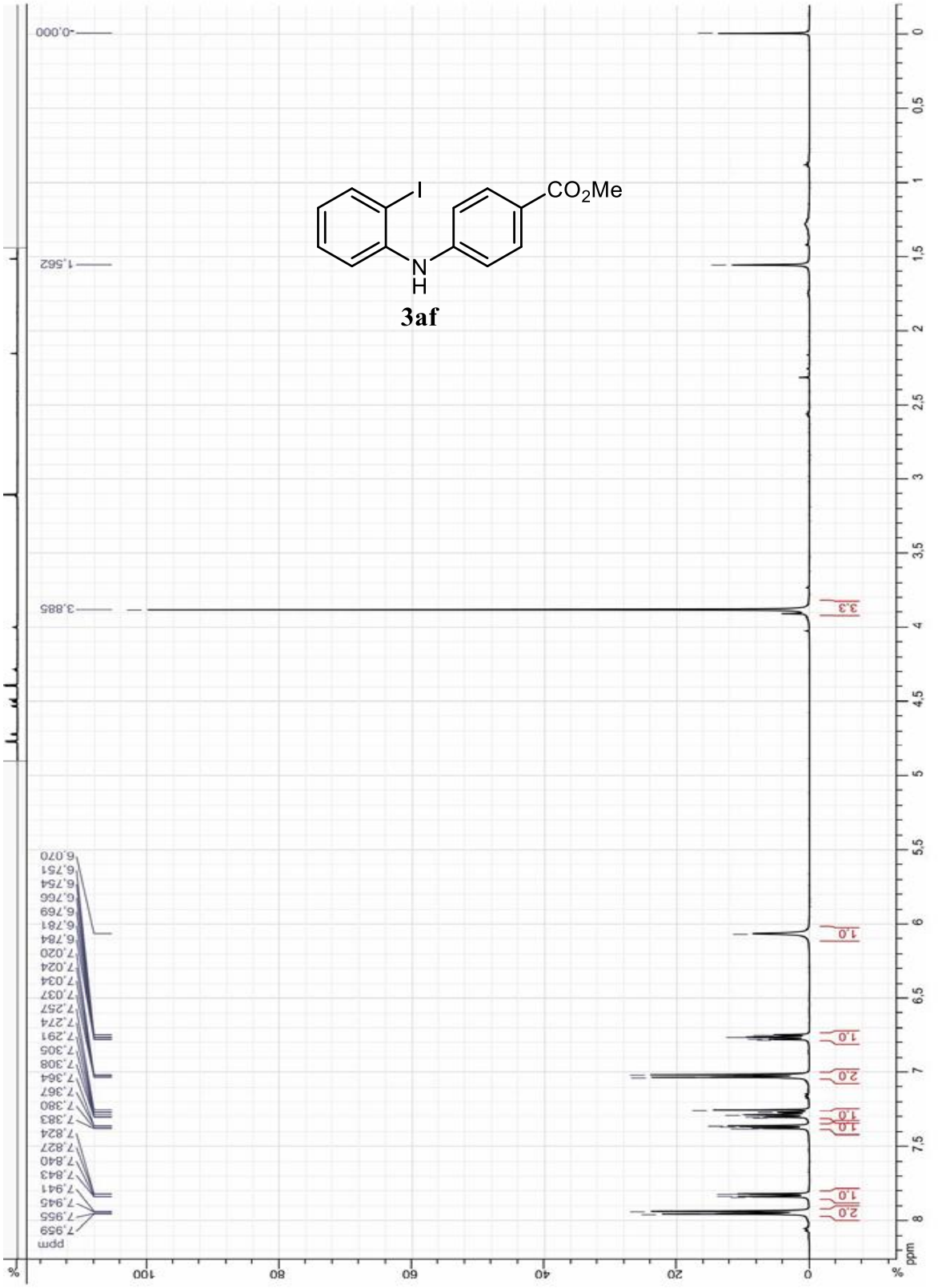

I
Cl
N
H
0.000
76.754
77.008
77.263
89.135
116.183
120.931
122.453
127.198
129.126
129.442
139.611
140.721
143.482
ppm

3ad

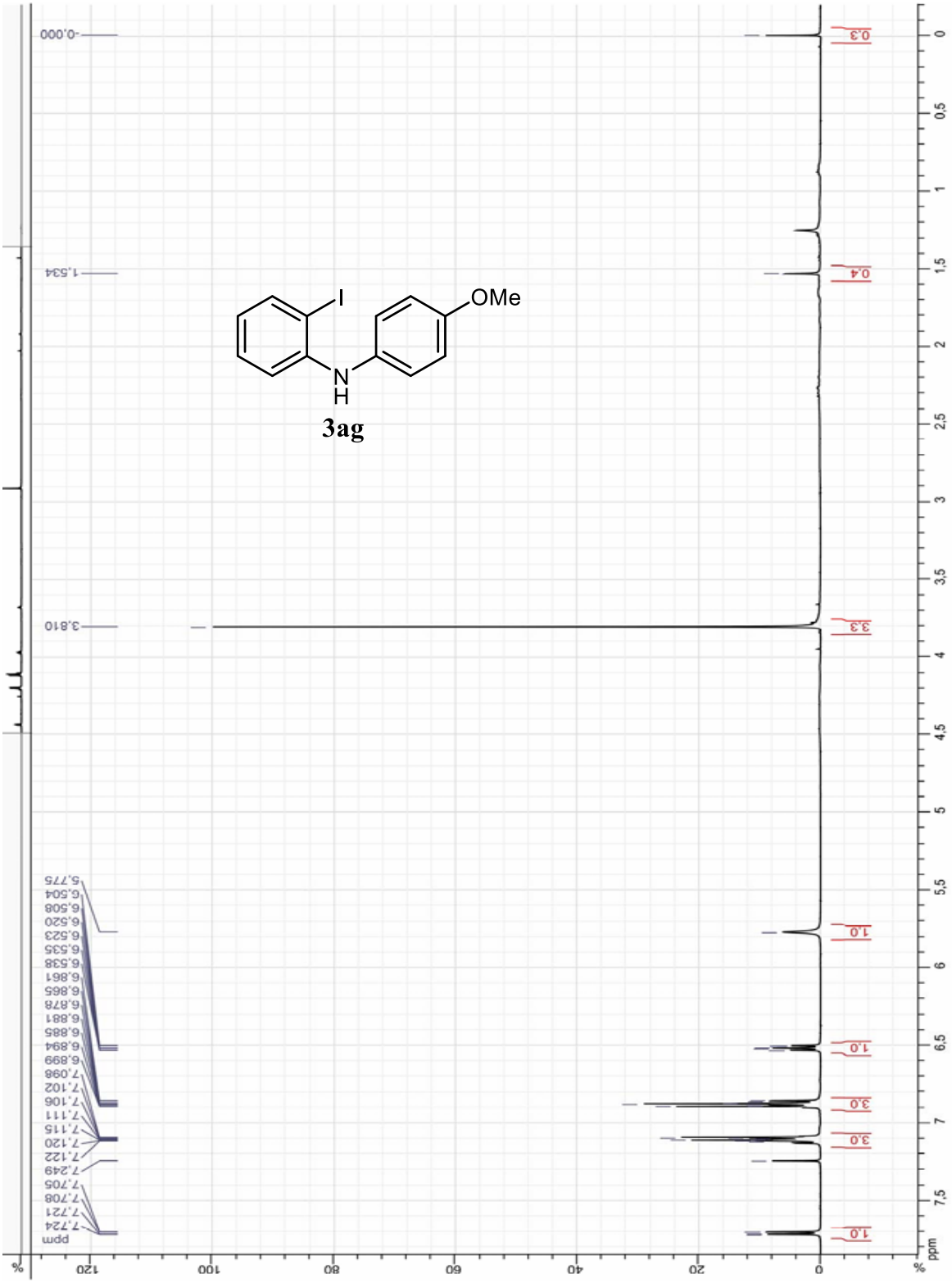
^{1}H NMR spectrum of *N*-(4-bromophenyl)-2-iodoaniline (**3ae**) in $CDCl_3$



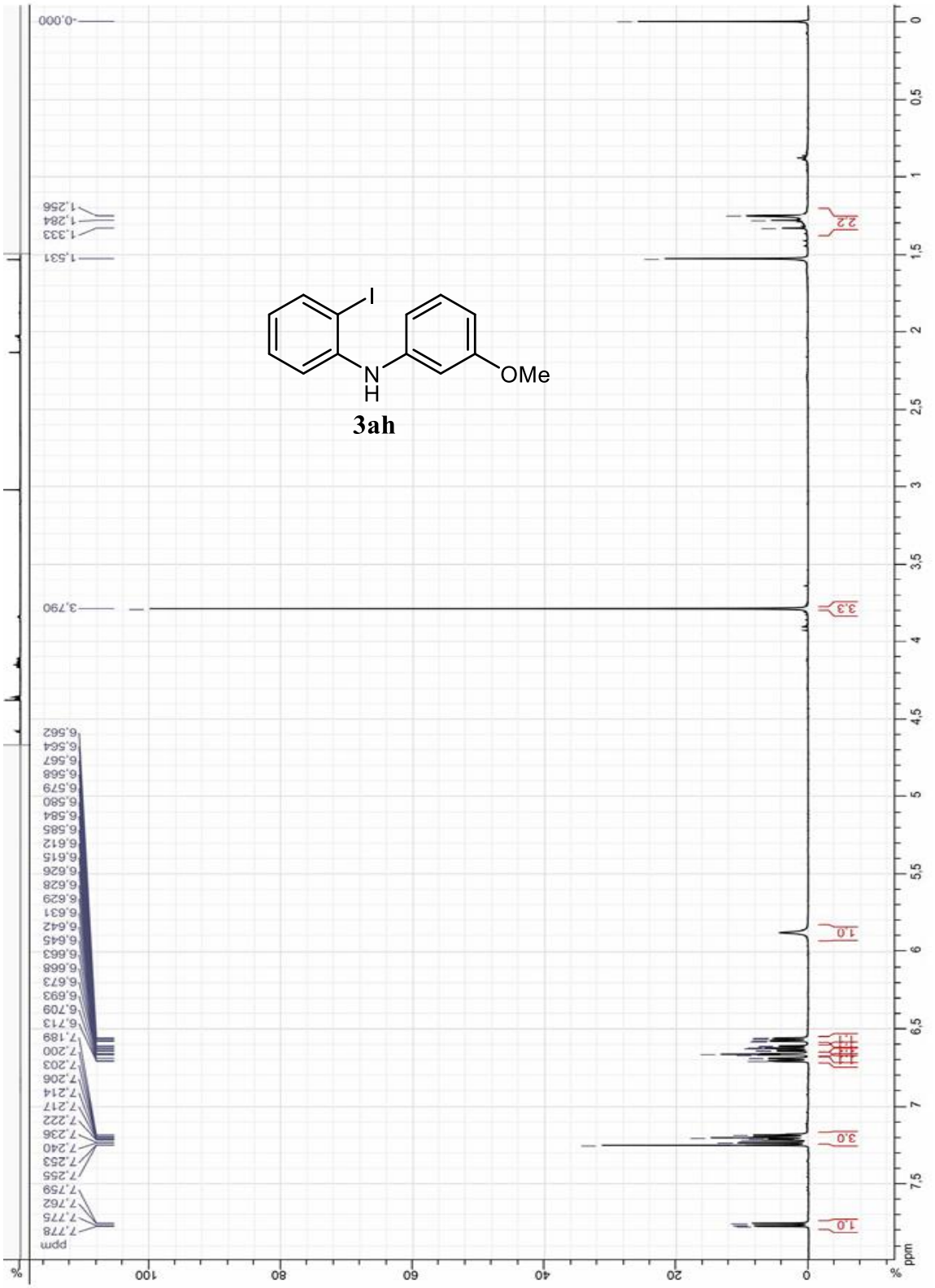
^{1}H NMR spectrum of methyl 4-((2-iodophenyl)amino)benzoate (**3af**) in $CDCl_3$



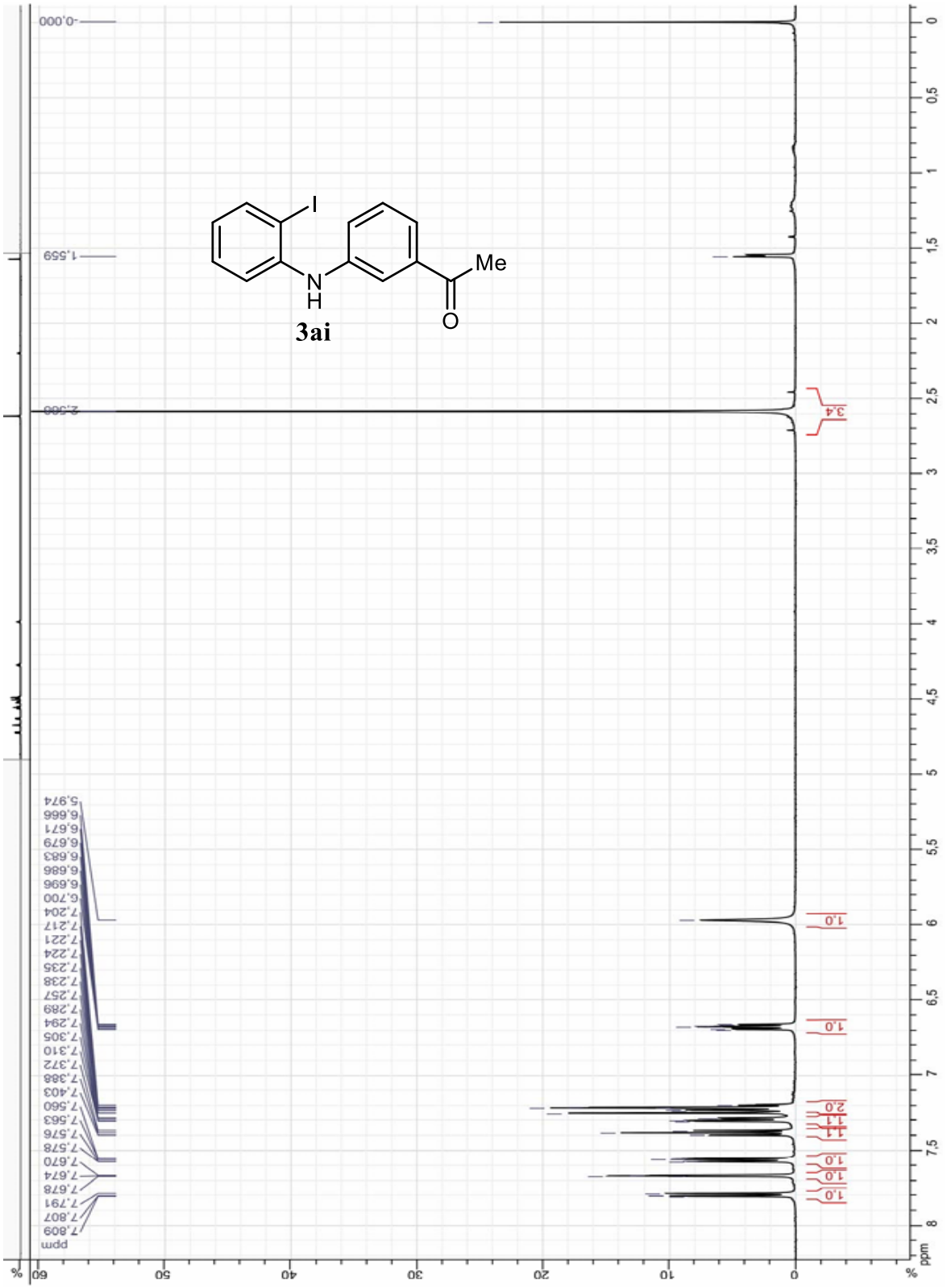
^{1}H NMR spectrum of 2-iodo-*N*-(4-methoxylphenyl)aniline (**3ag**) in $CDCl_3$



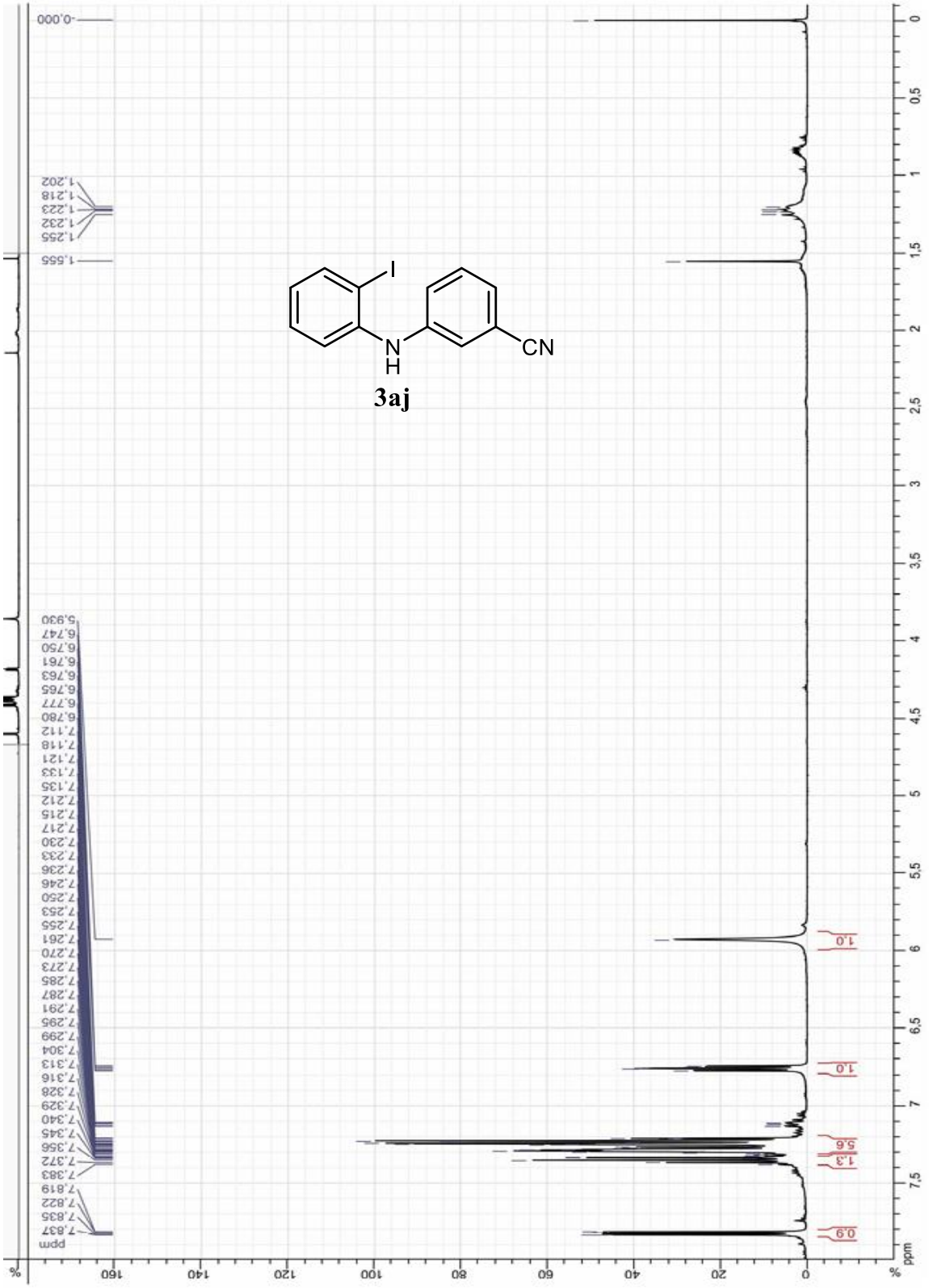
^{1}H NMR spectrum of 2-iodo-*N*-(3-methoxylphenyl)aniline (**3ah**) in $CDCl_3$



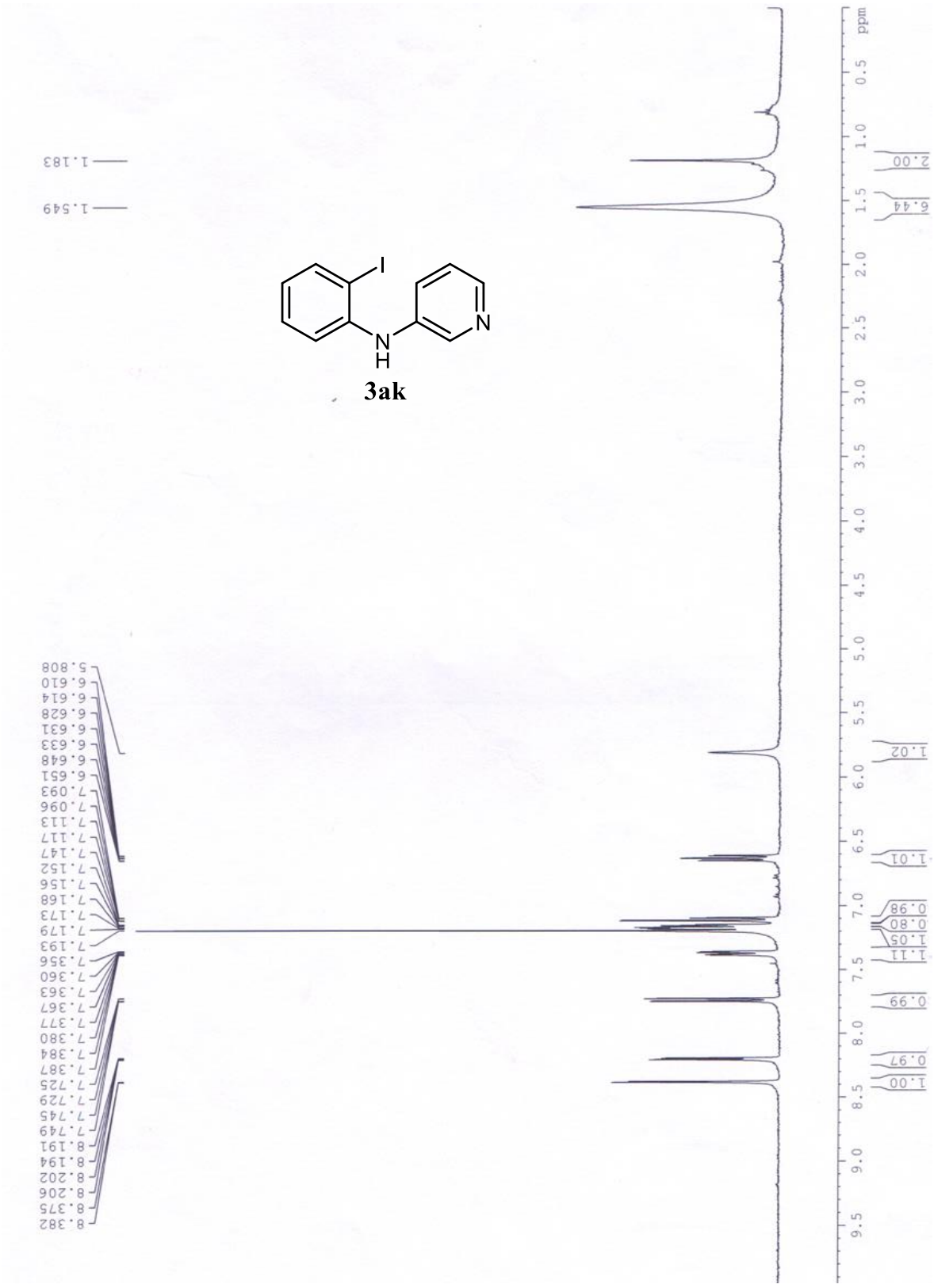
^{1}H NMR spectra of 2-iodo-*N*-(3-acetylphenyl)aniline (**3ai**) in $CDCl_3$



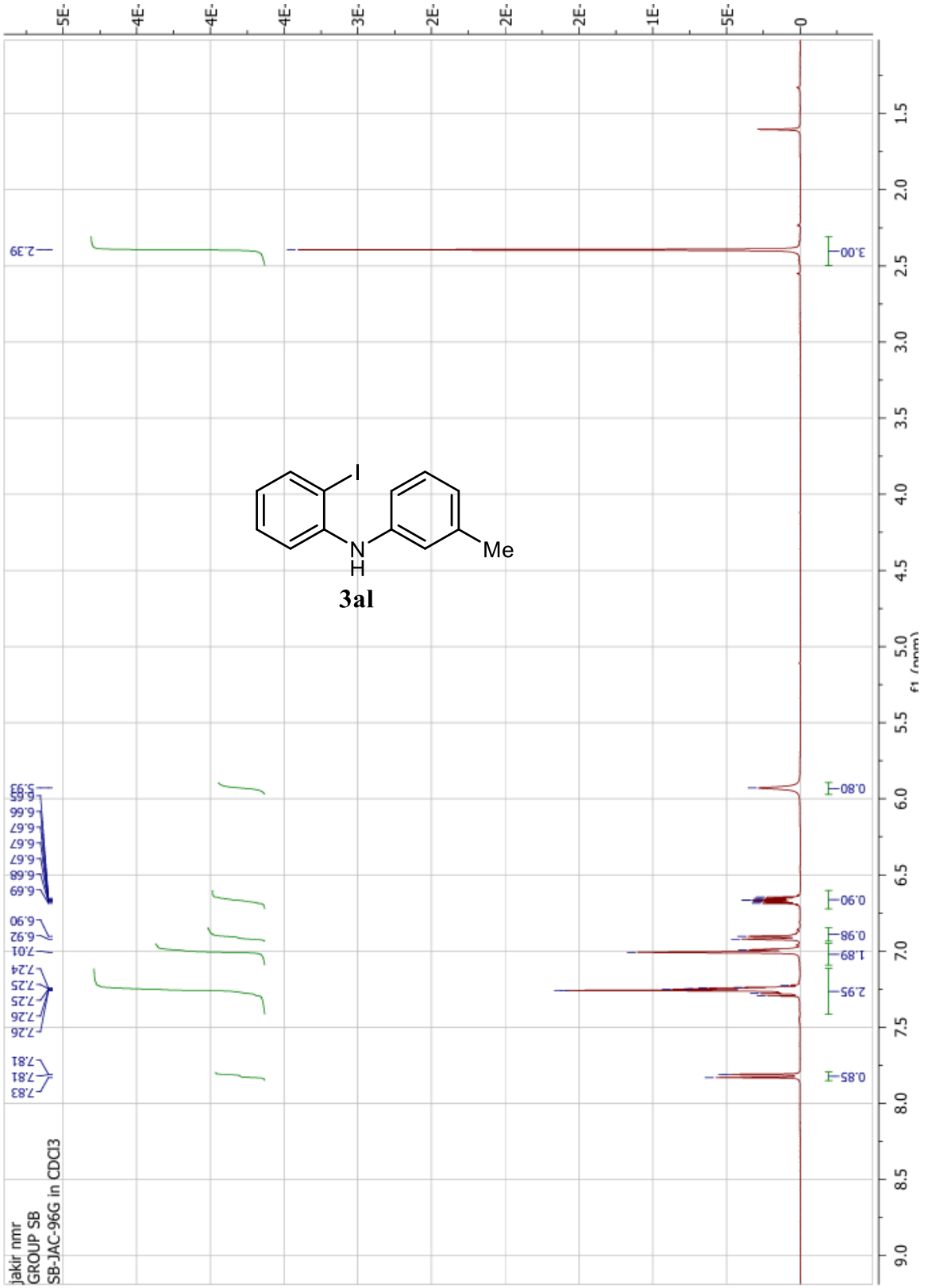
^{1}H NMR spectra of 2-iodo-*N*-(3-cyanophenyl)aniline (**3aj**) in $CDCl_3$

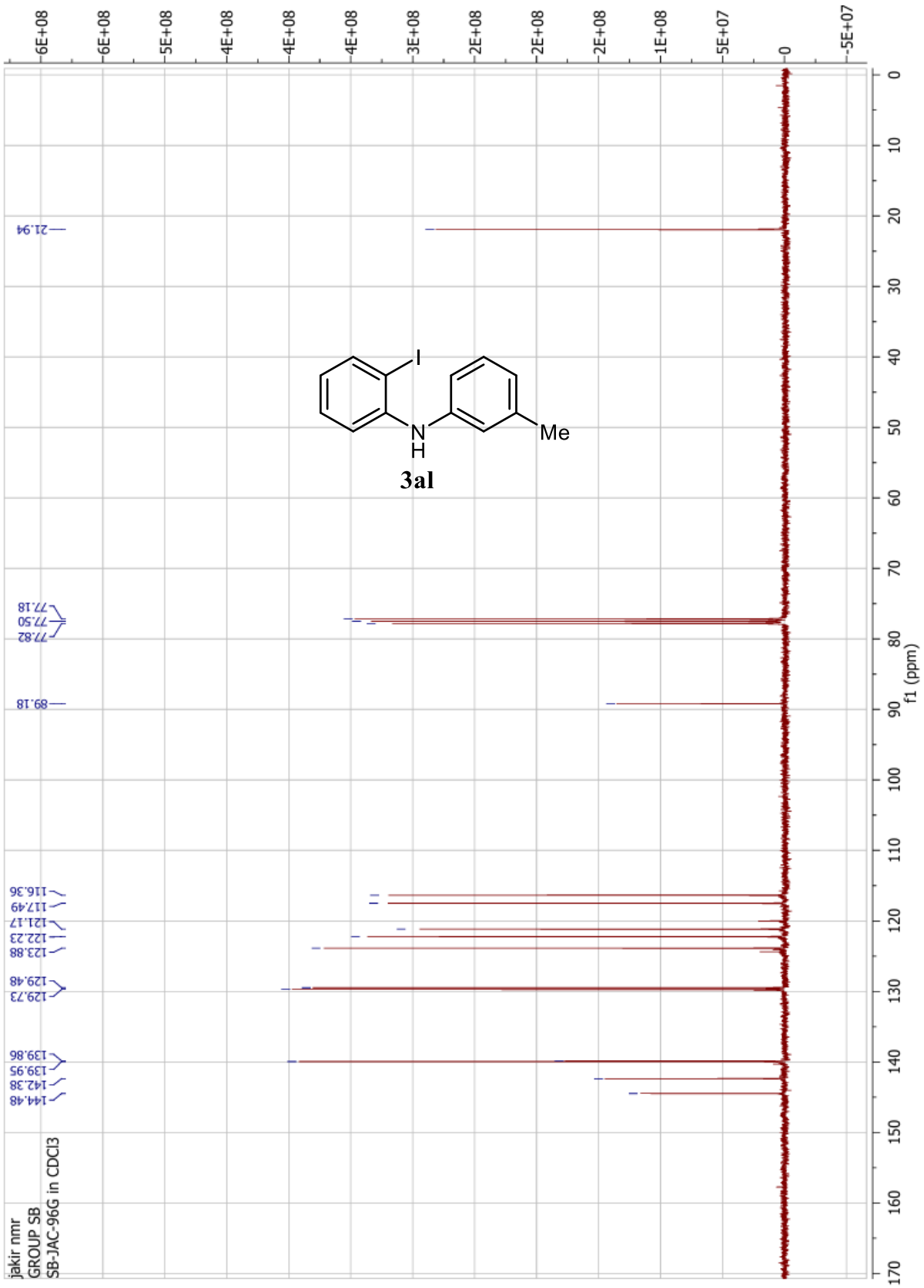


^{1}H NMR spectrum of *N*-(2-iodophenyl)pyridin-3-amine (**3ak**) in $CDCl_3$

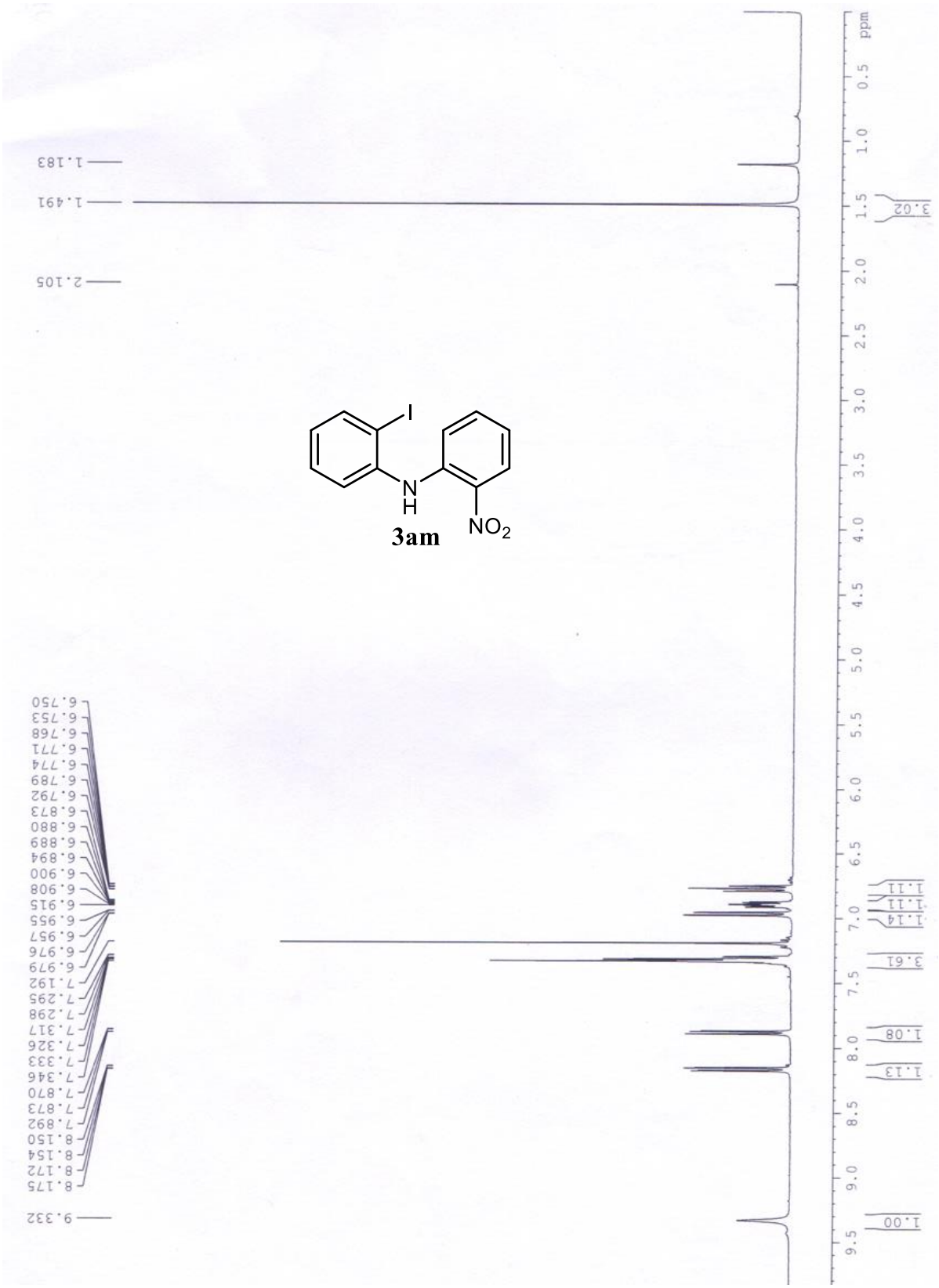


^{1}H NMR and ^{13}C spectra of 2-iodo-*N*-(*m*-tolyl)aniline (**3al**) in $CDCl_3$

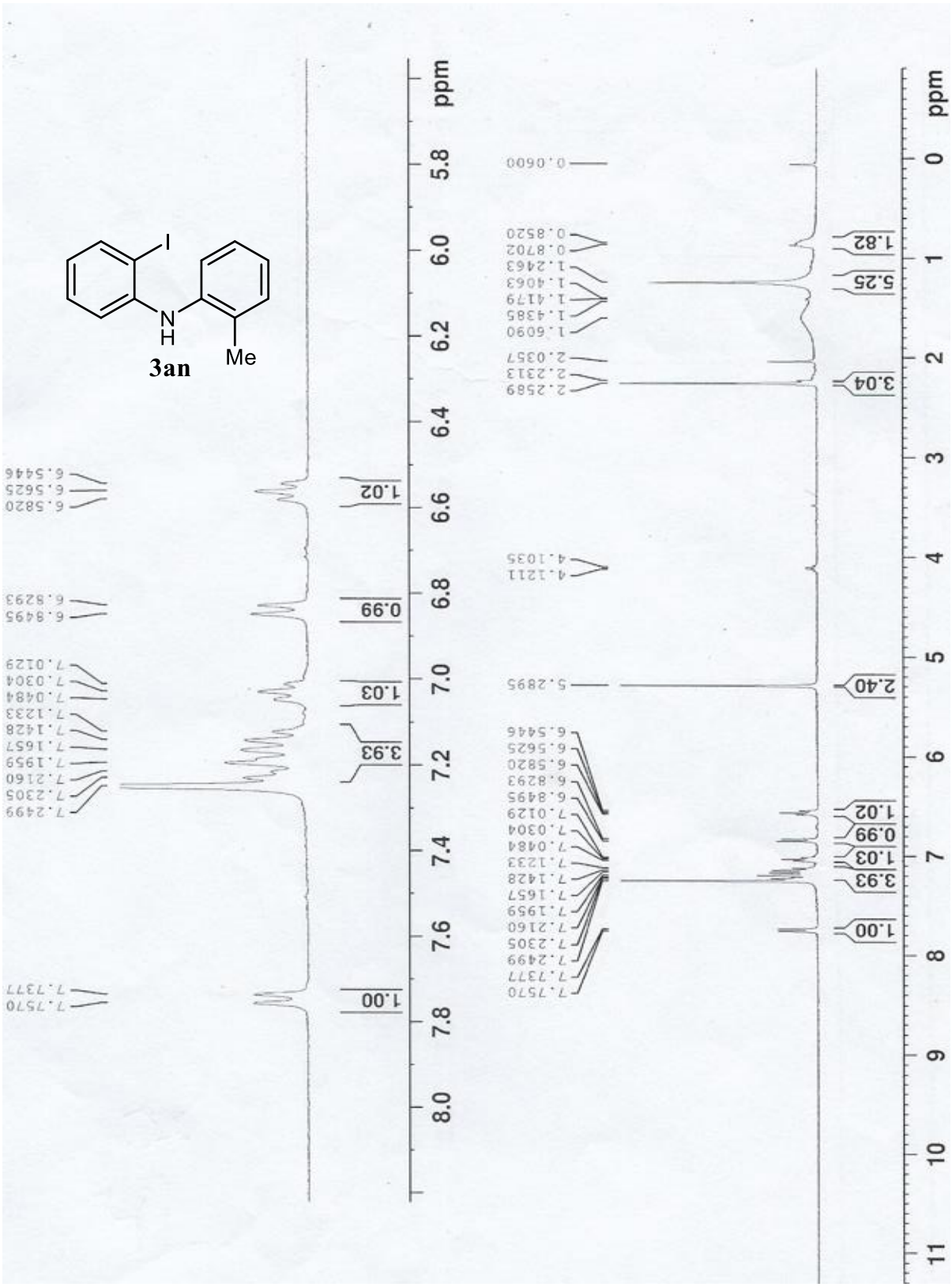


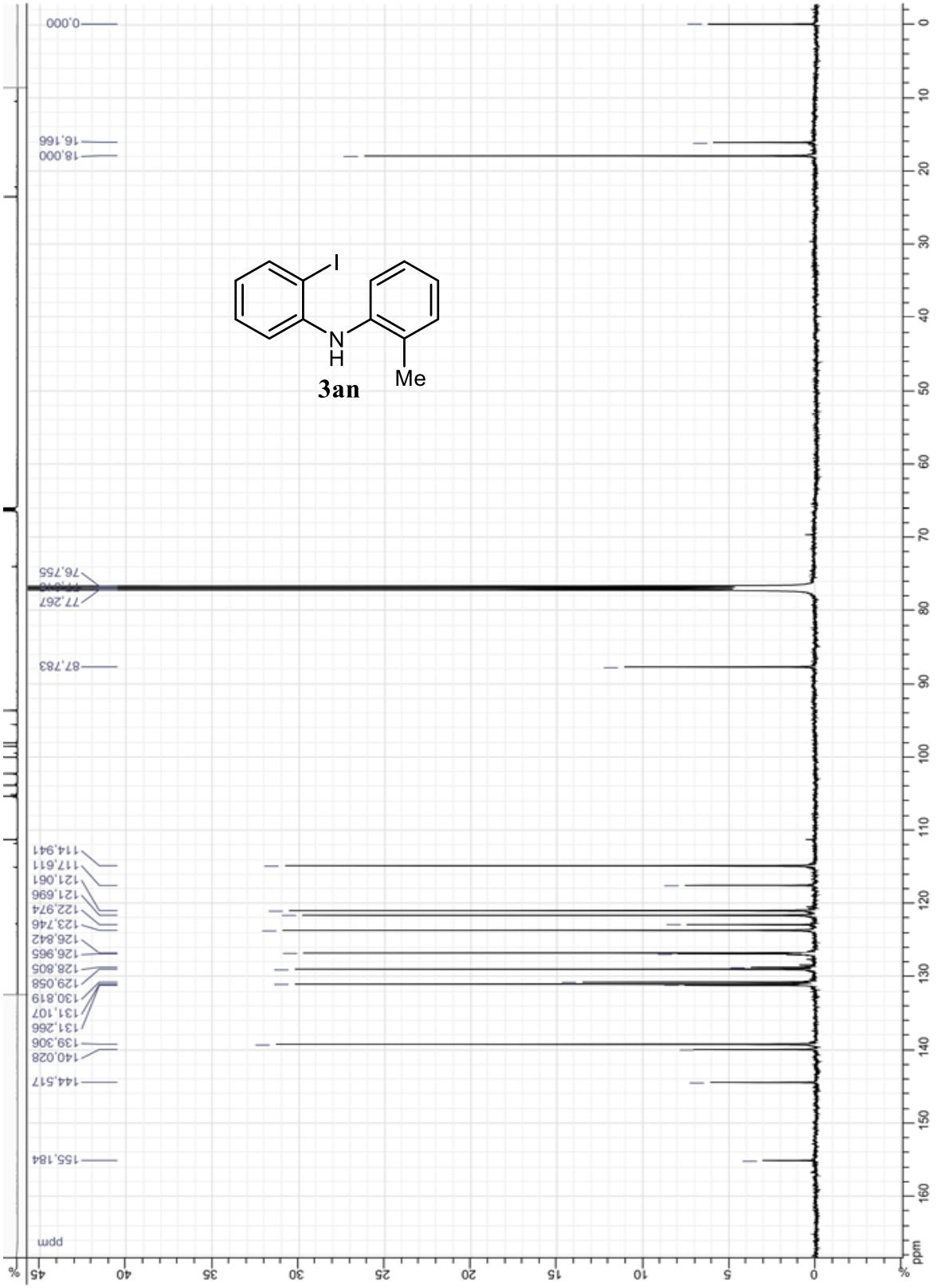

jakir nmr
GROUP SB
SB-JAC-96G in CDCl3
144.48
142.38
139.95
139.86
129.73
129.48
123.88
122.23
121.17
117.49
116.36
89.18
77.82
77.50
77.18
21.94
I
N
H
Me
3al
f1 (ppm)

^{1}H NMR spectrum of 2-iodo-*N*-(2-nitrophenyl)aniline (**3am**) in $CDCl_3$

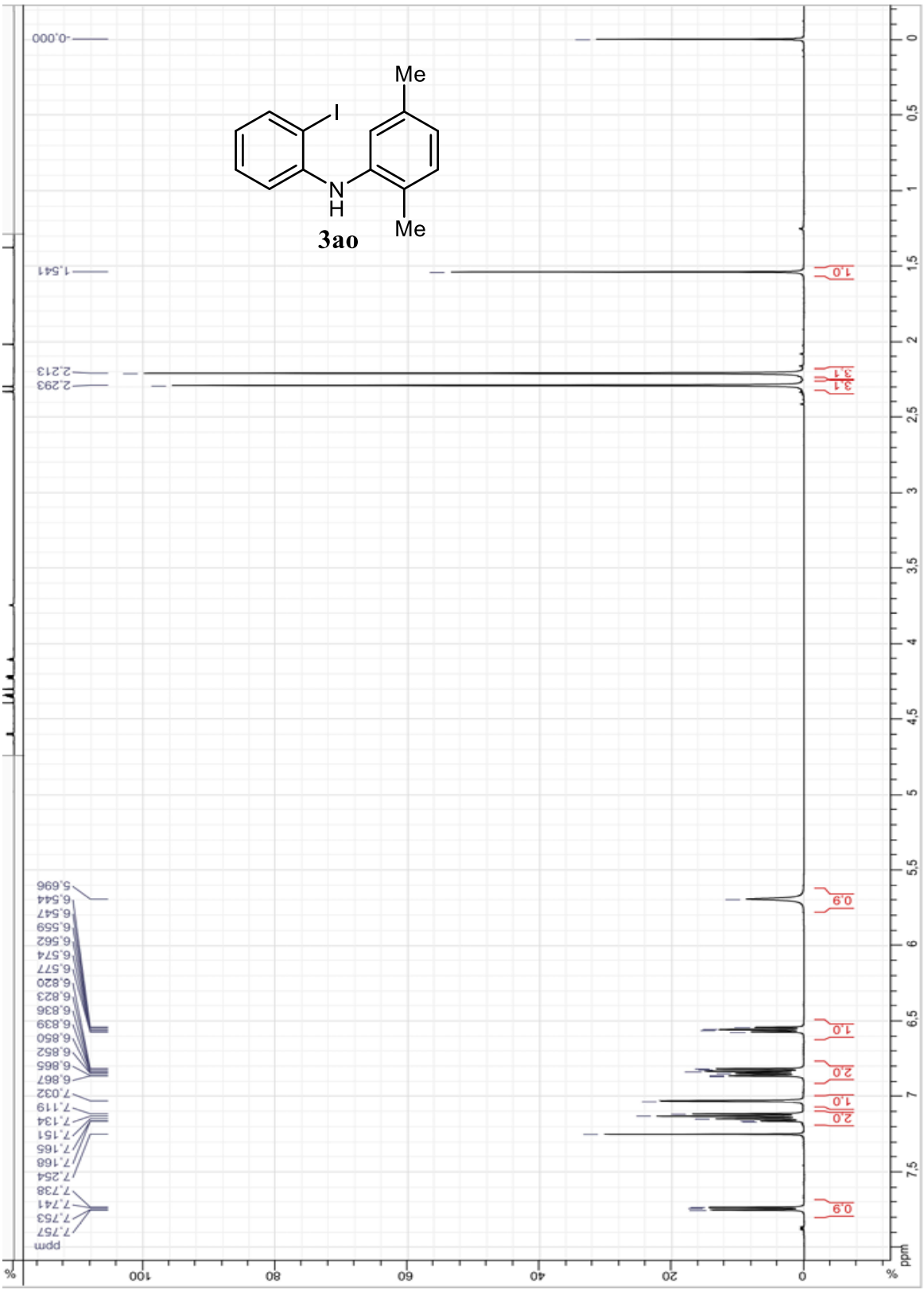


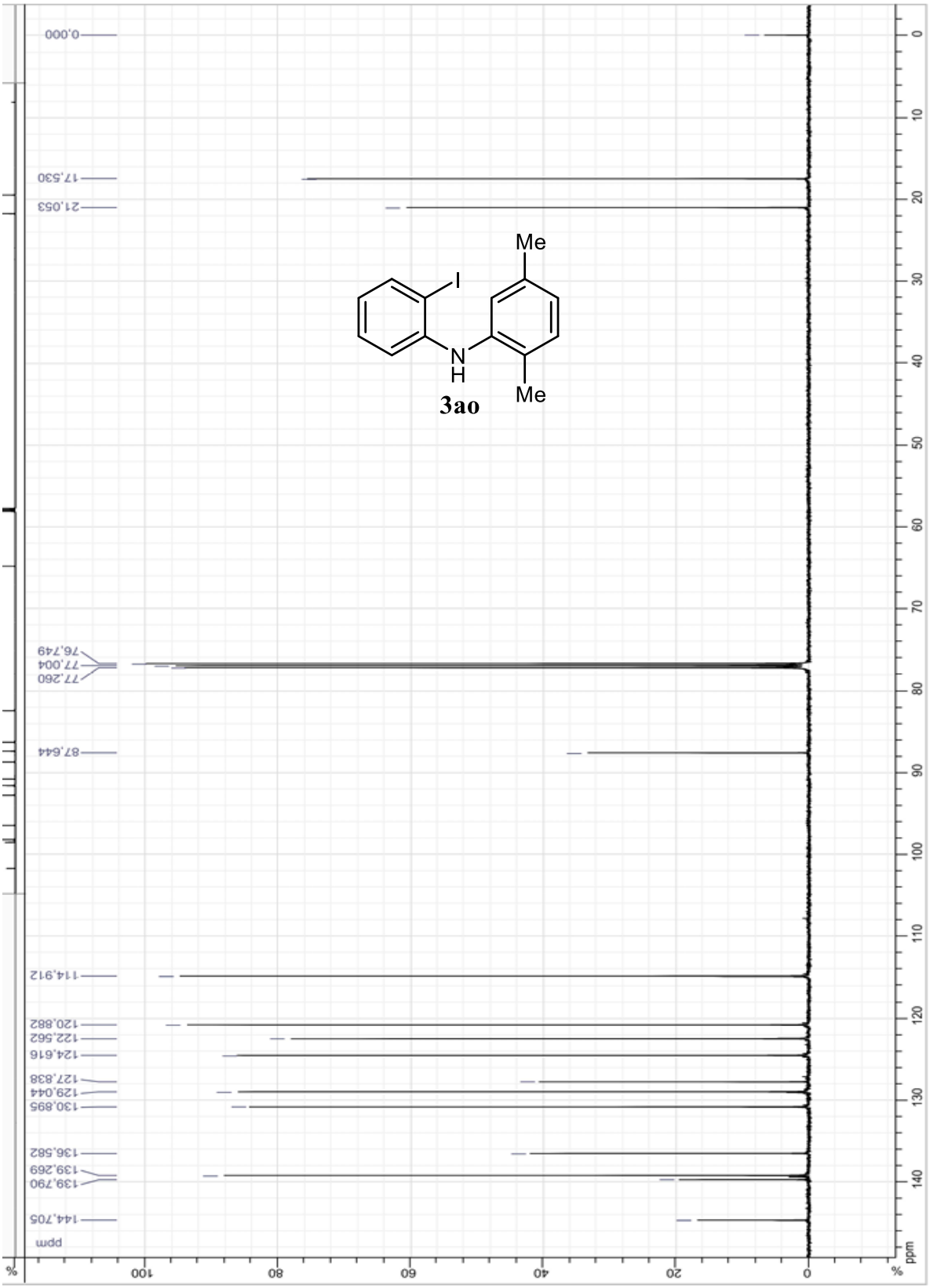
^{1}H NMR and ^{13}C spectra of 2-iodo-*N*-(*o*-tolyl)aniline (**3an**) in $CDCl_3$



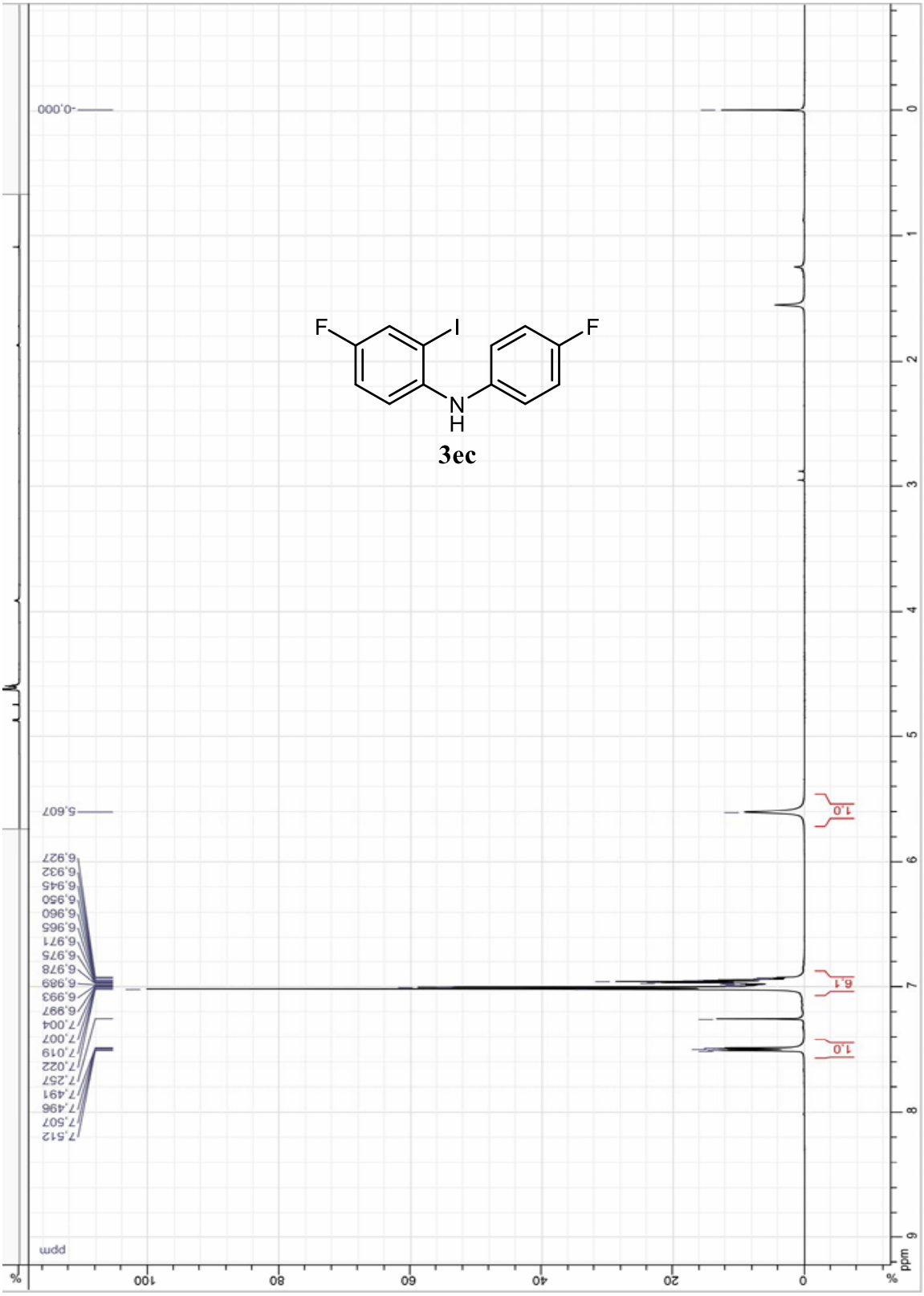

I
N
H
Me
3an
0.000
16.166
18.000
76.755
77.267
87.783
114.941
117.611
121.061
121.696
122.974
123.746
126.842
126.965
128.805
129.058
130.819
131.107
131.266
139.306
140.028
144.517
155.184
ppm

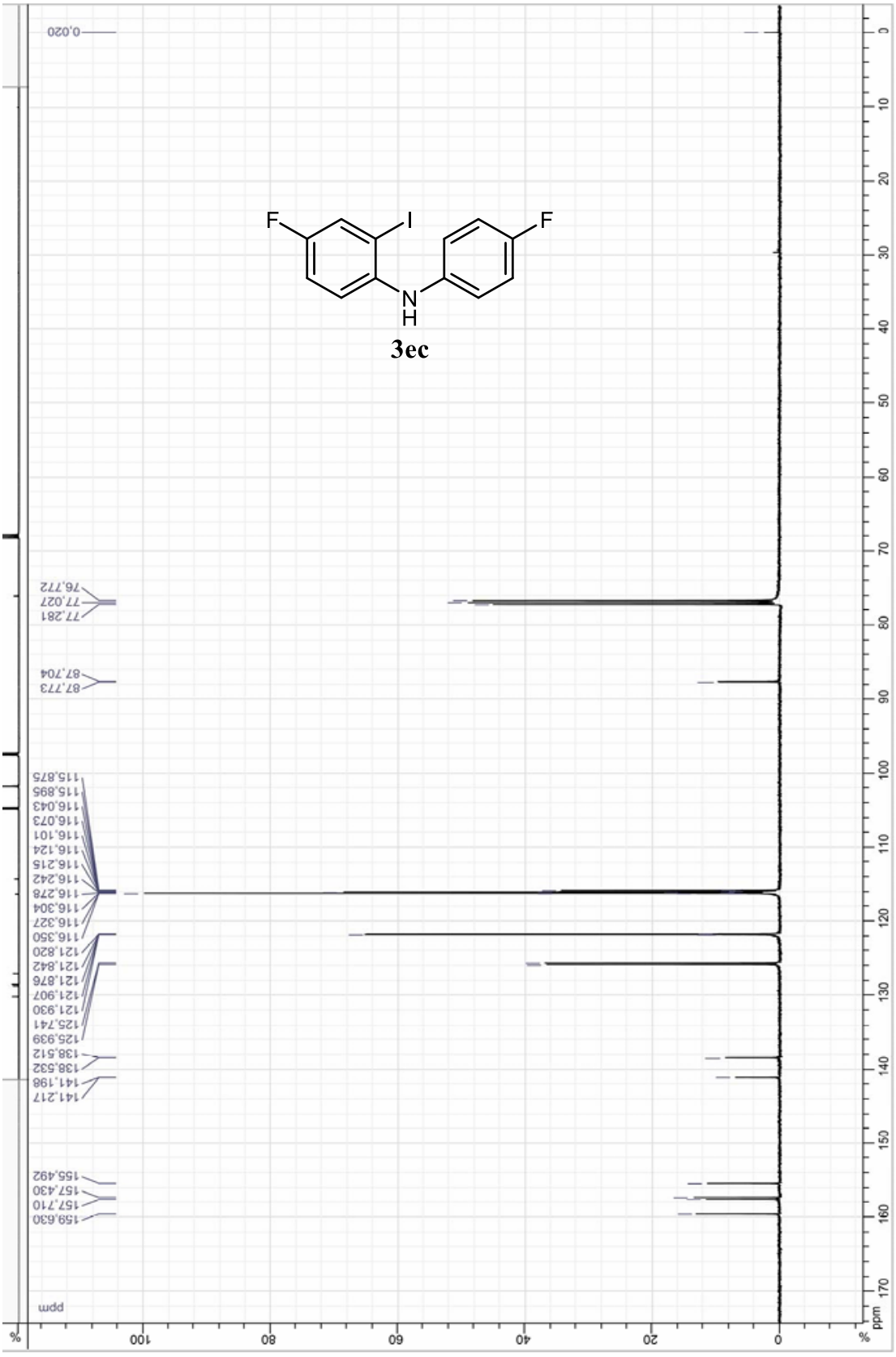
^{1}H NMR and ^{13}C spectra of *N*-(2-iodophenyl)-2,5-dimethylaniline (**3ao**) in $CDCl_3$



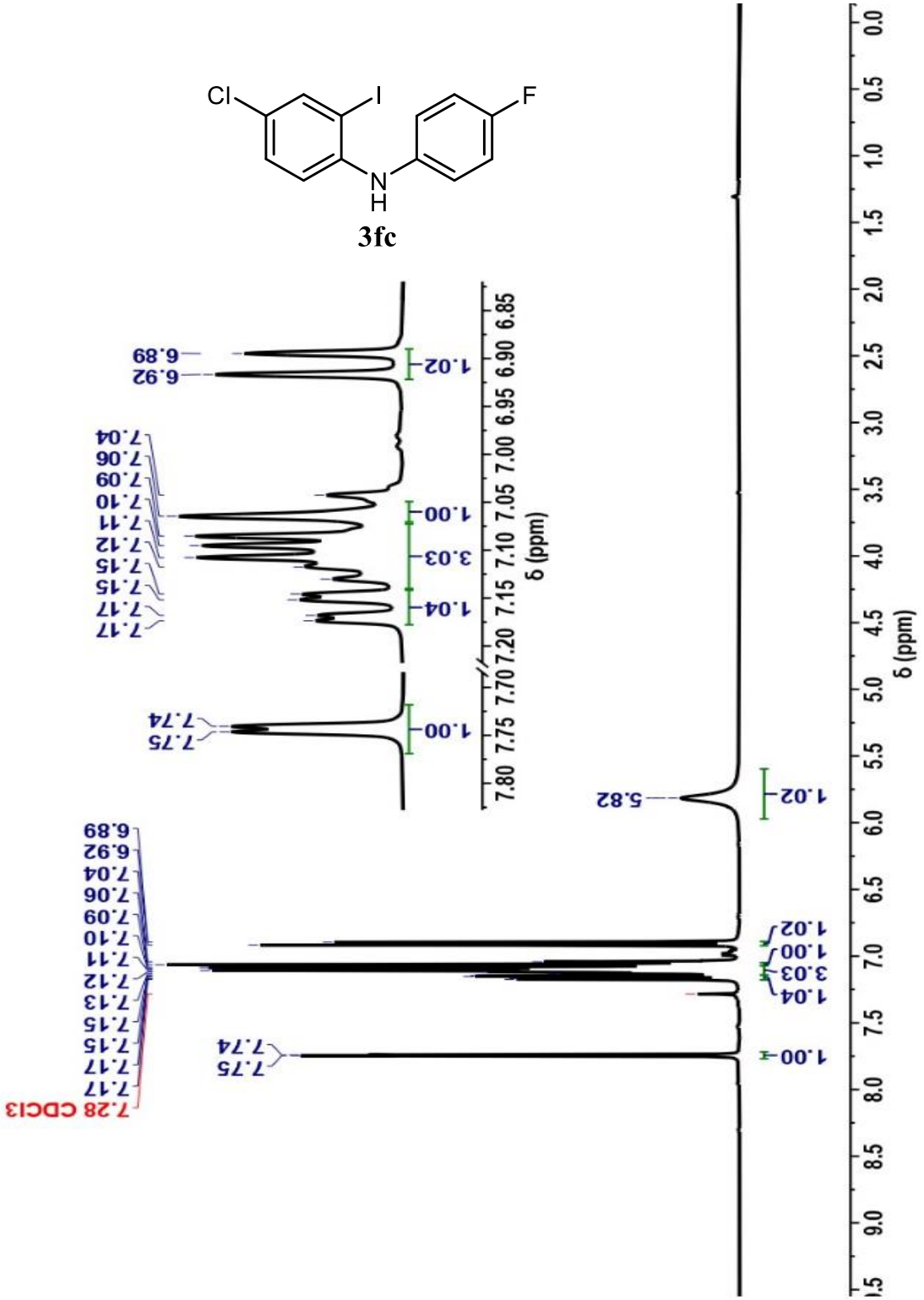

0.000
17.530
21.053
76.749
77.004
77.260
87.644
114.912
120.882
122.562
124.616
127.838
129.044
130.895
136.582
139.269
139.790
144.705
ppm
Me
I
N
H
Me
3ao

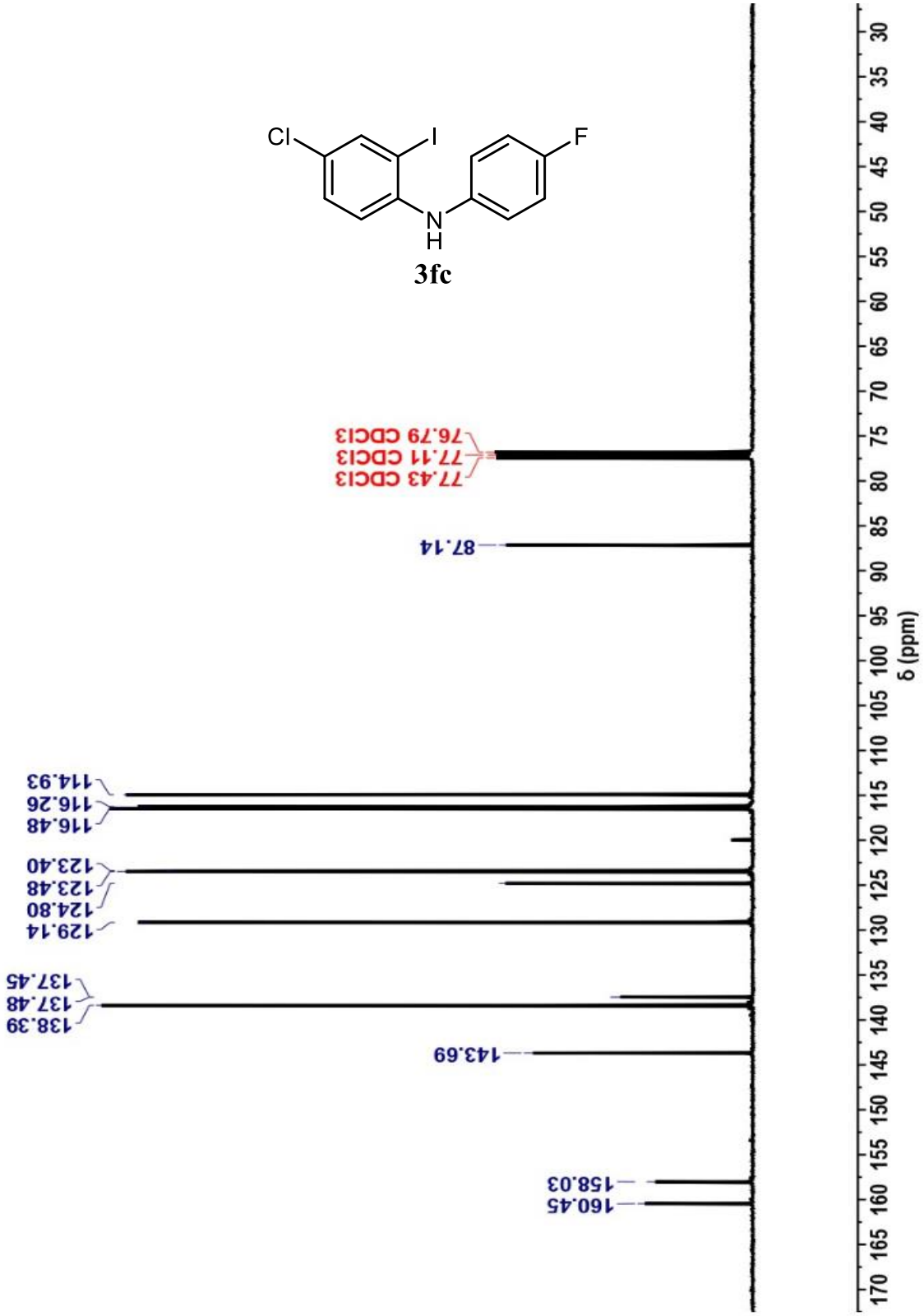
^{1}H NMR and ^{13}C spectra of 4-fluoro-*N*-(4-fluorophenyl)-2-iodoaniline (**3ec**) in $CDCl_3$



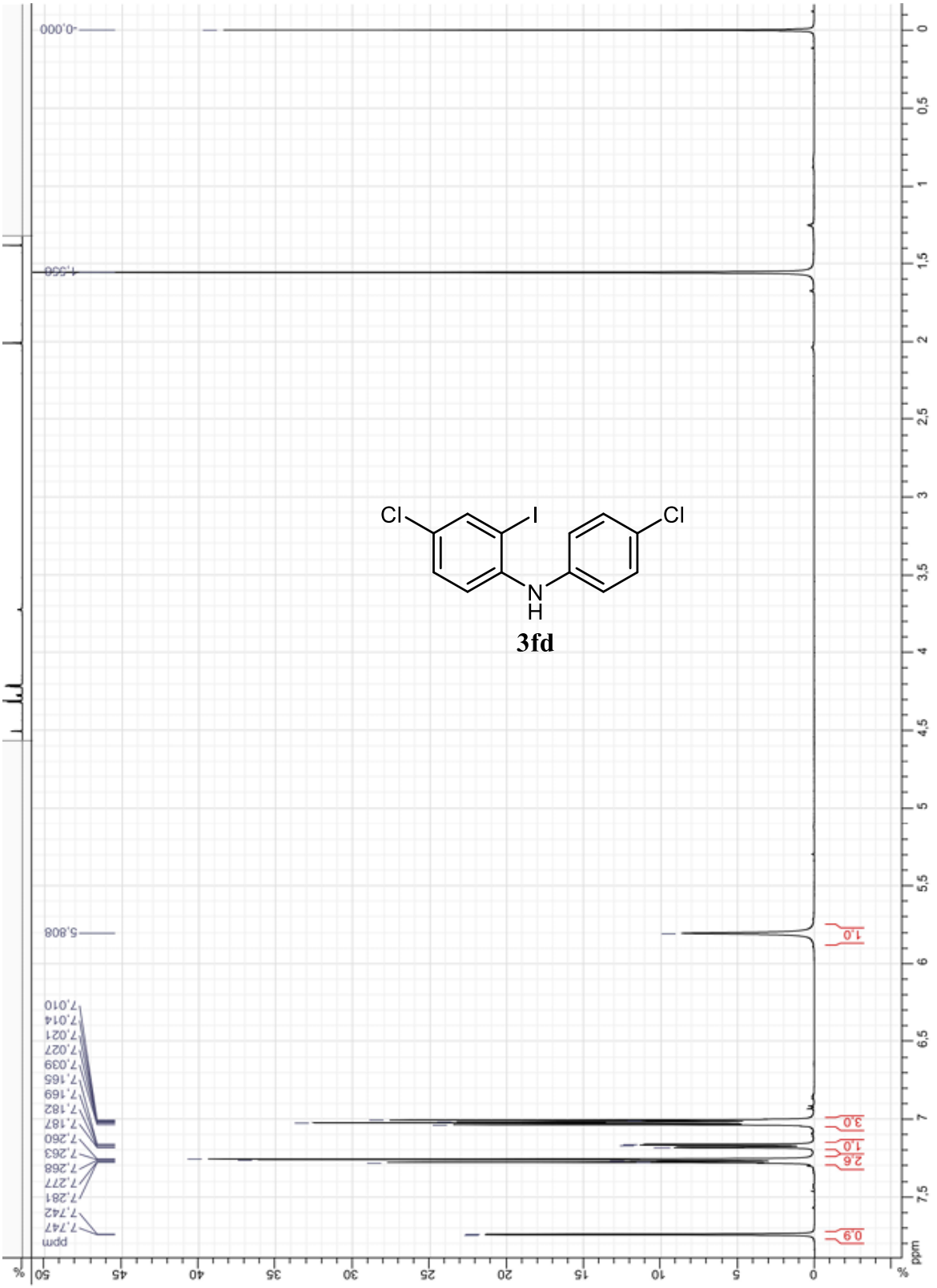

F
I
F
N
H
3ec

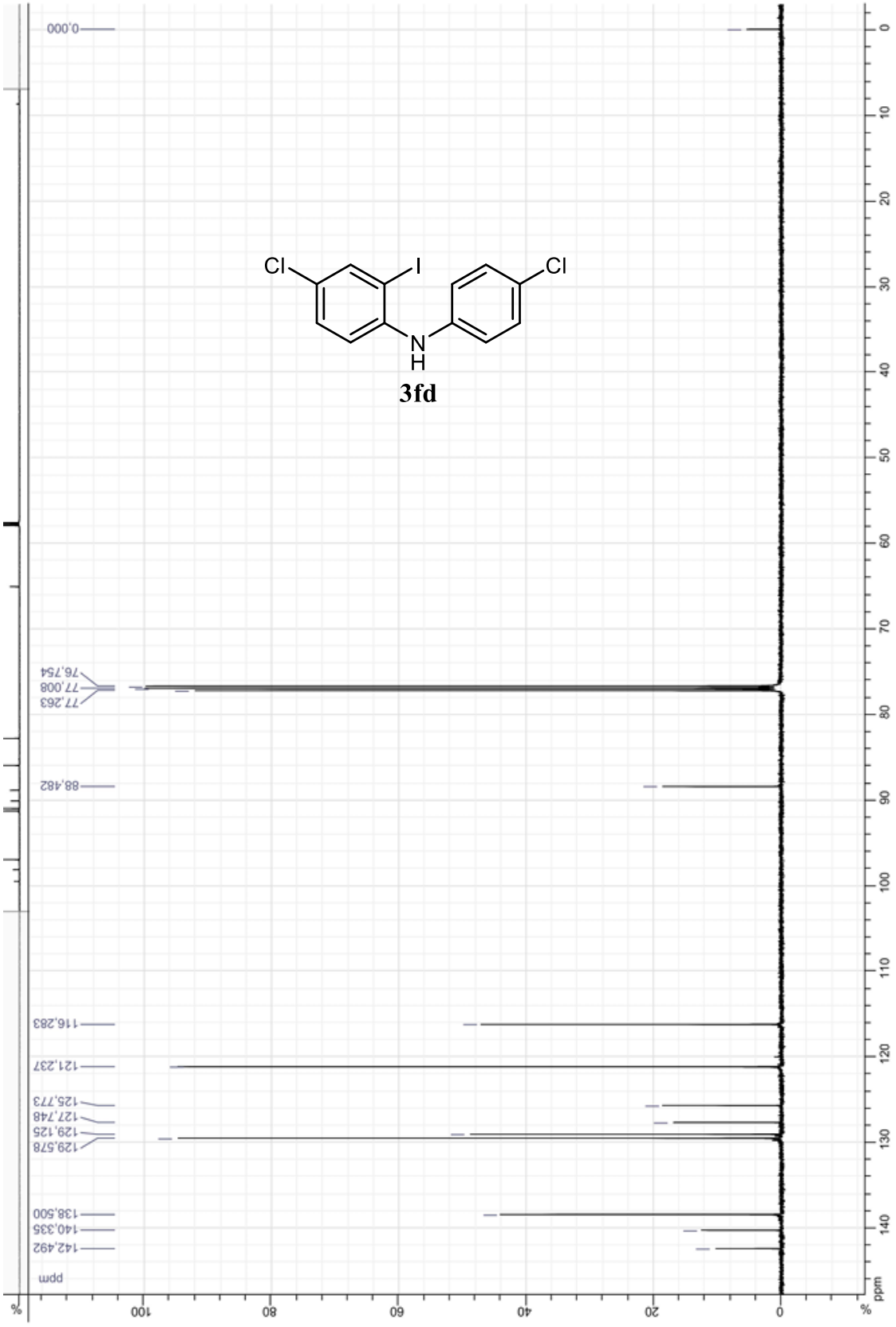
^{1}H NMR and ^{13}C spectra of 4-chloro-*N*-(4-fluorophenyl)-2-iodoaniline (**3fc**) in $CDCl_3$




Cl
I
F
N
H
3fc
77.43 CDCl3
77.11 CDCl3
76.79 CDCl3
87.14
114.93
116.26
116.48
123.40
123.48
124.80
129.14
137.45
137.48
138.39
143.69
158.03
160.45
δ (ppm)

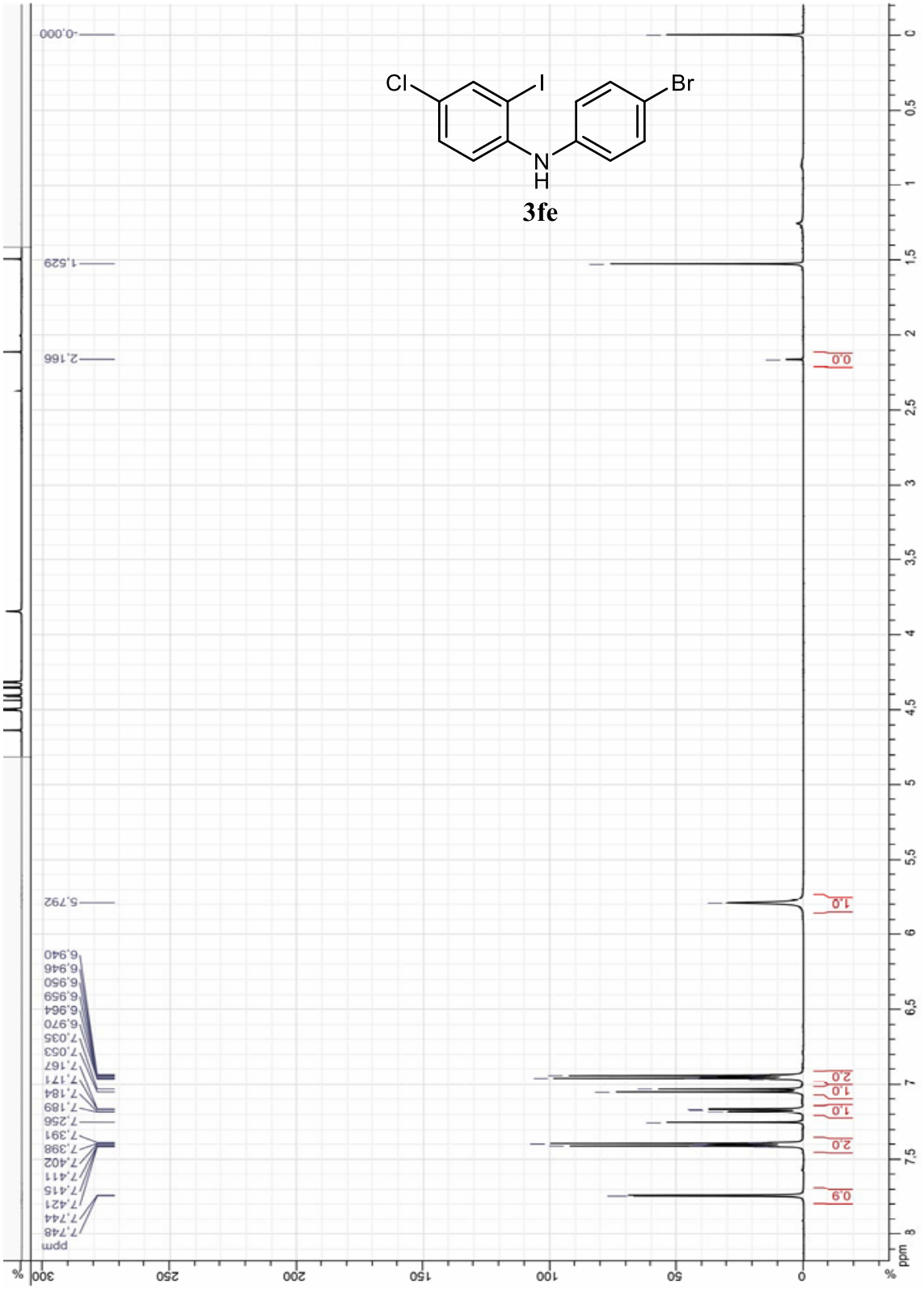
^{1}H NMR and ^{13}C spectra of 4-chloro-*N*-(4-chlorophenyl)-2-iodoaniline (**3fd**) in $CDCl_3$



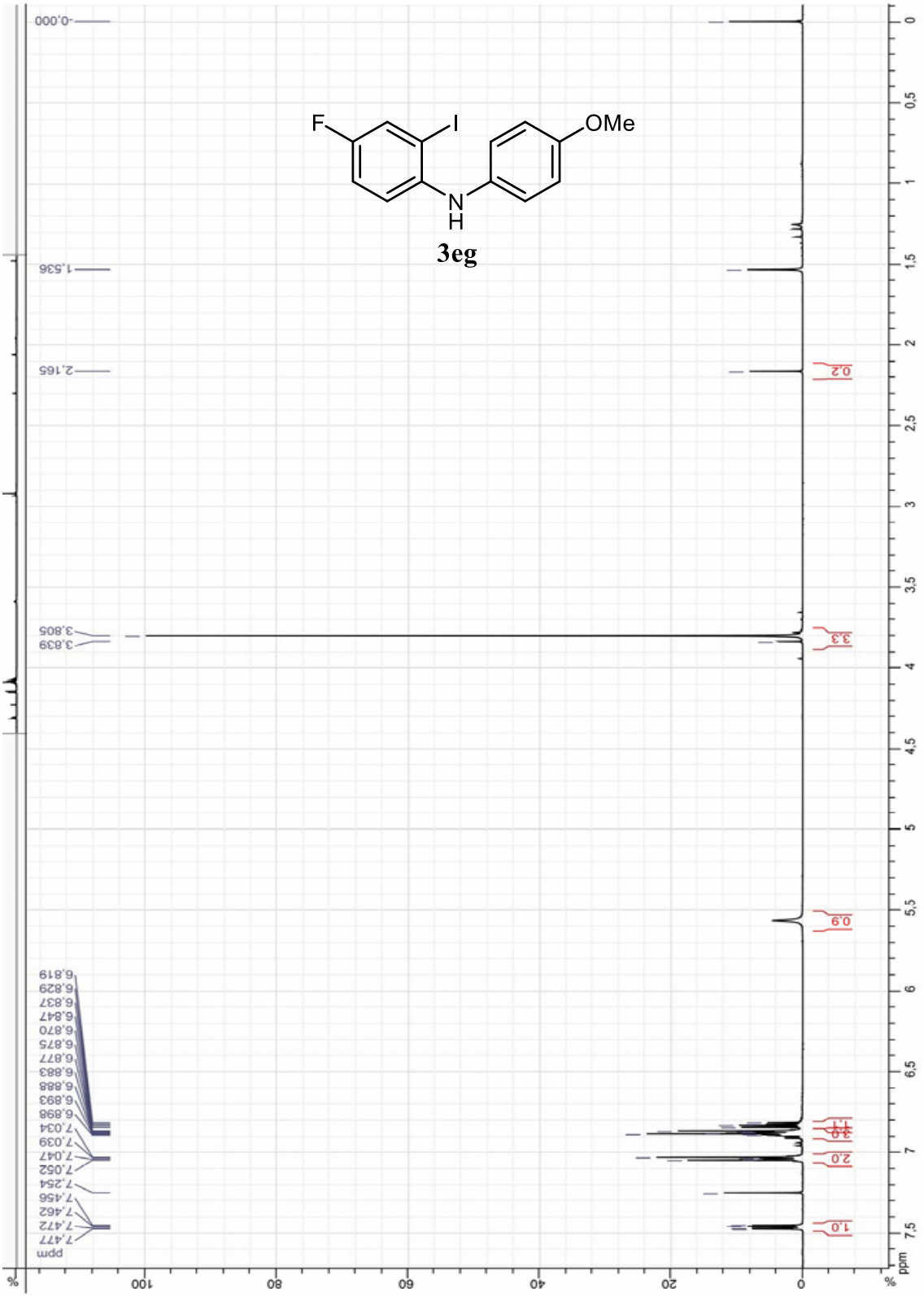

Cl
I
Cl
N
H
0.000
76.754
77.008
77.263
88.482
116.283
121.237
125.773
127.748
129.125
129.578
138.500
140.335
142.492
ppm

3fd

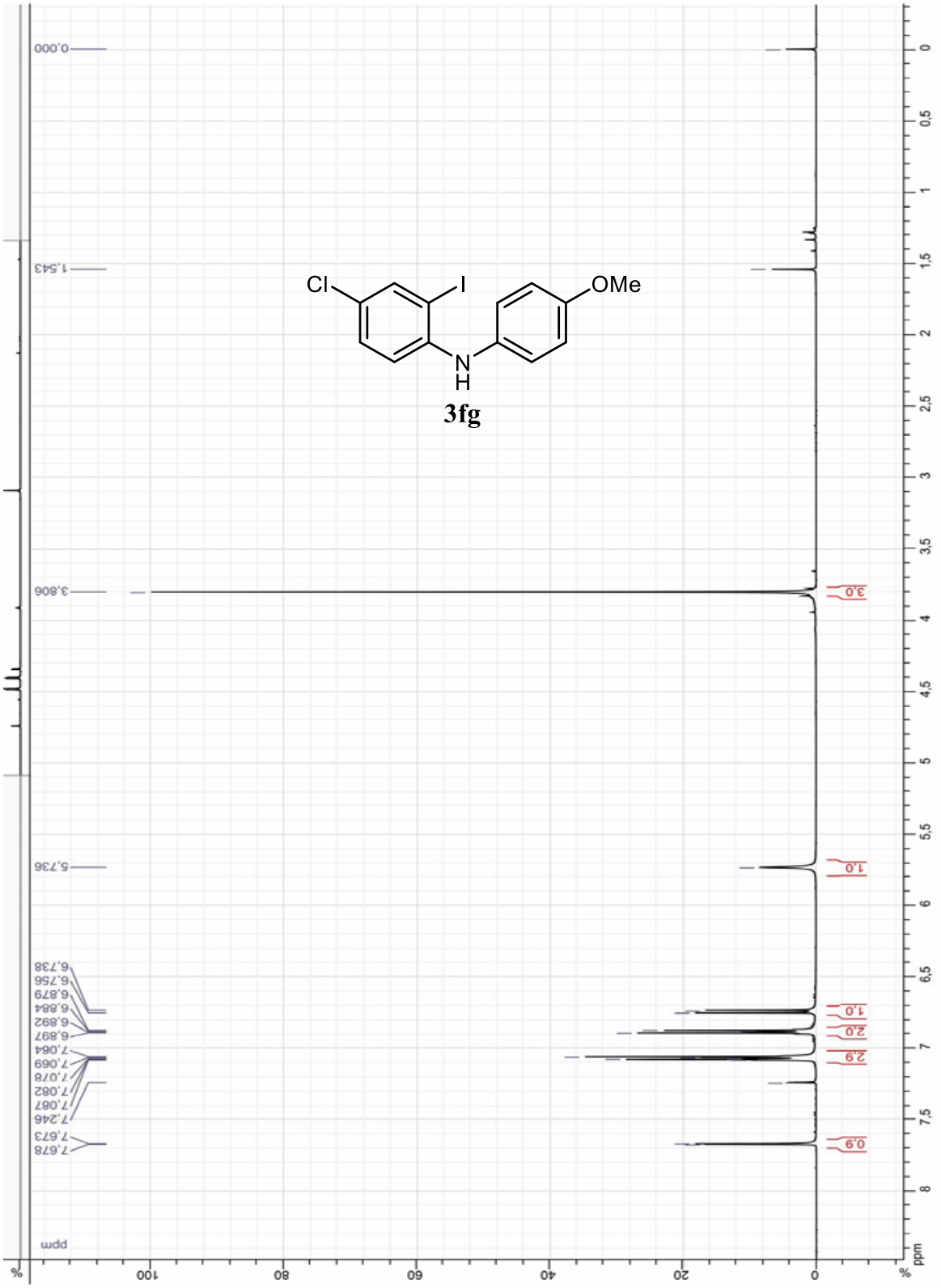
^{1}H NMR spectrum of 4-chloro-2-iodo-*N*-(4-bromophenyl)aniline (**3fe**) in $CDCl_3$



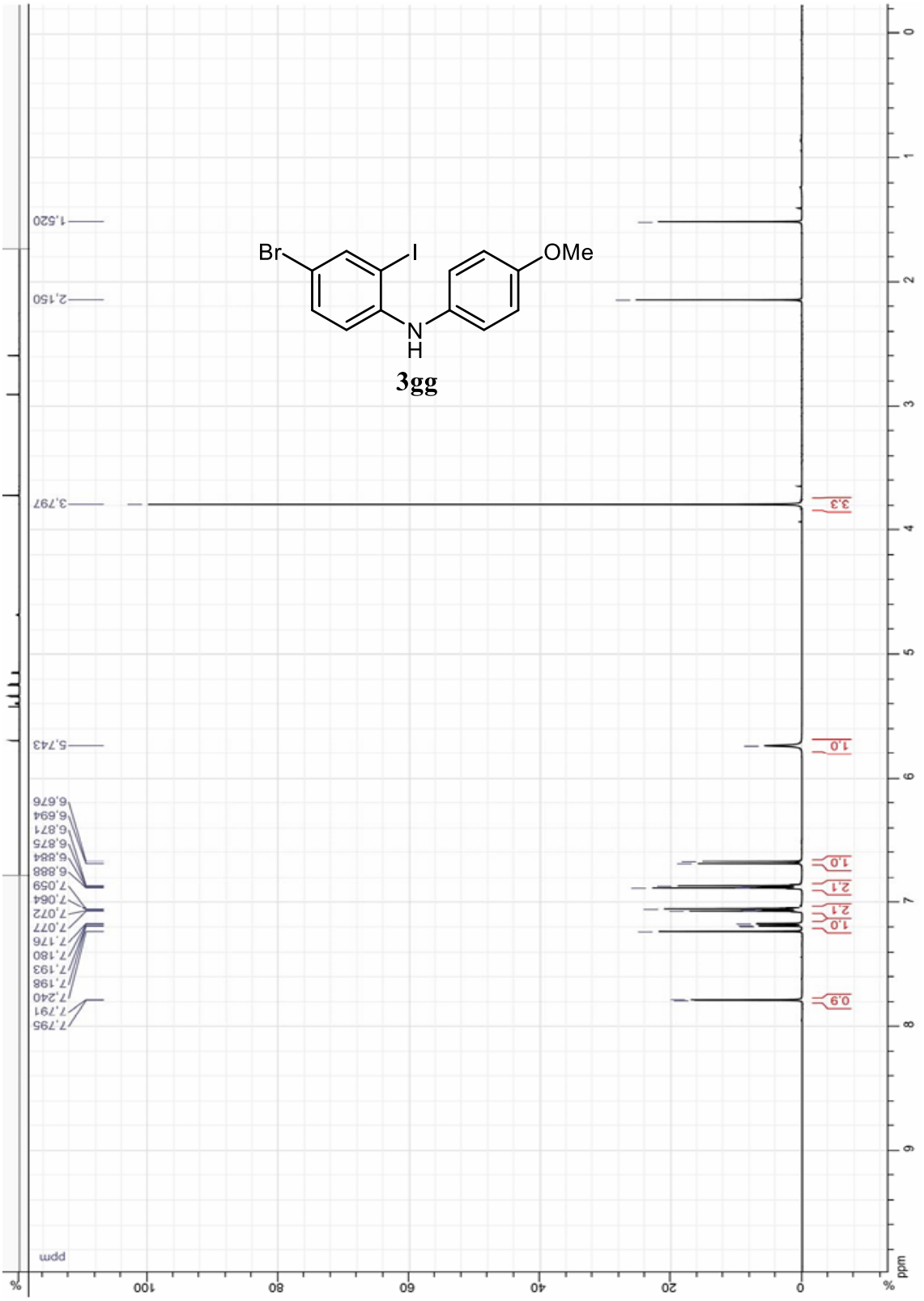
^{1}H NMR spectrum of 4-fluoro-2-iodo-*N*-(4-methoxyphenyl)aniline (**3eg**) in $CDCl_3$



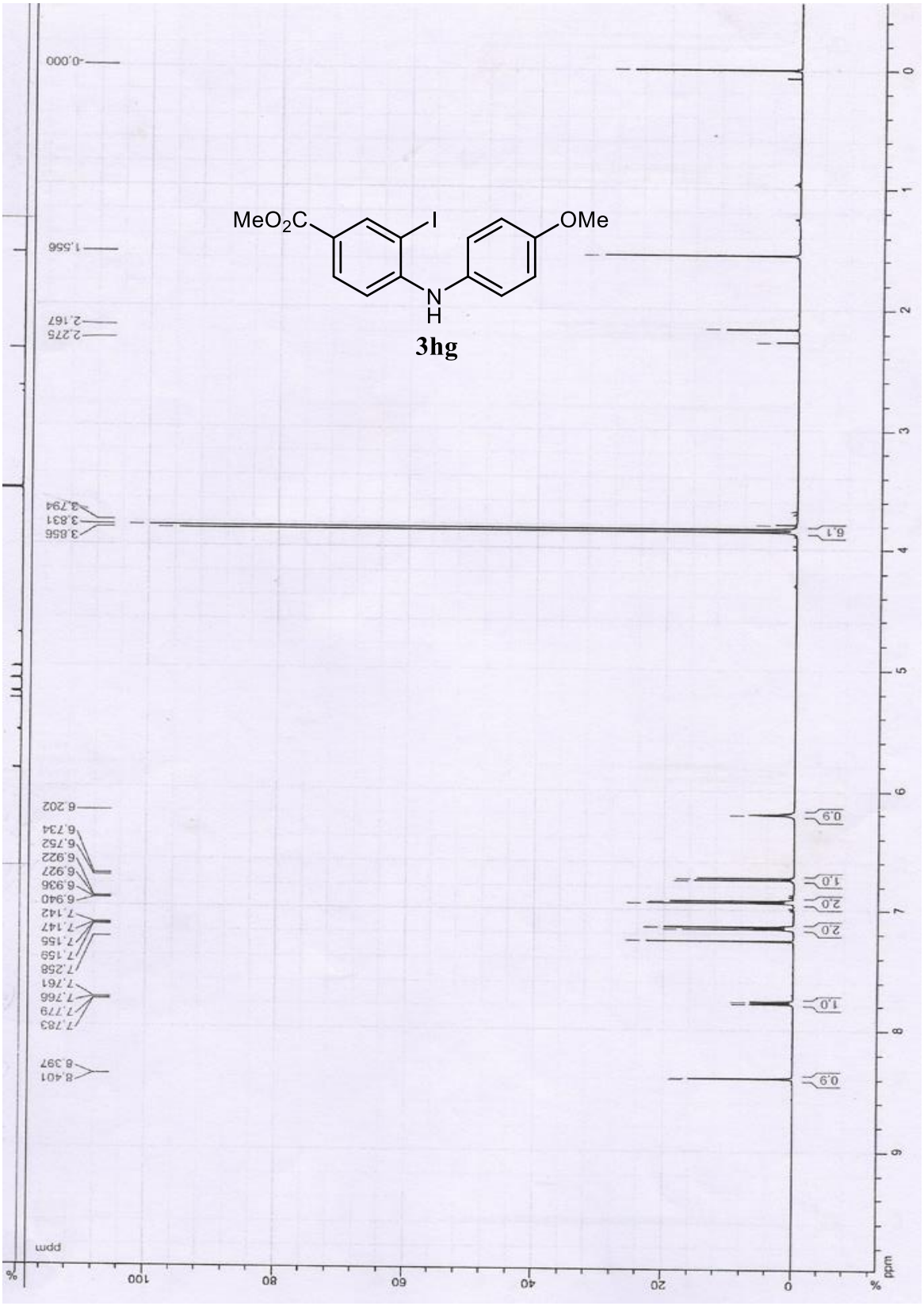
^{1}H NMR spectrum of 4-chloro-2-iodo-*N*-(4-methoxylphenyl)aniline (**3fg**) in $CDCl_3$



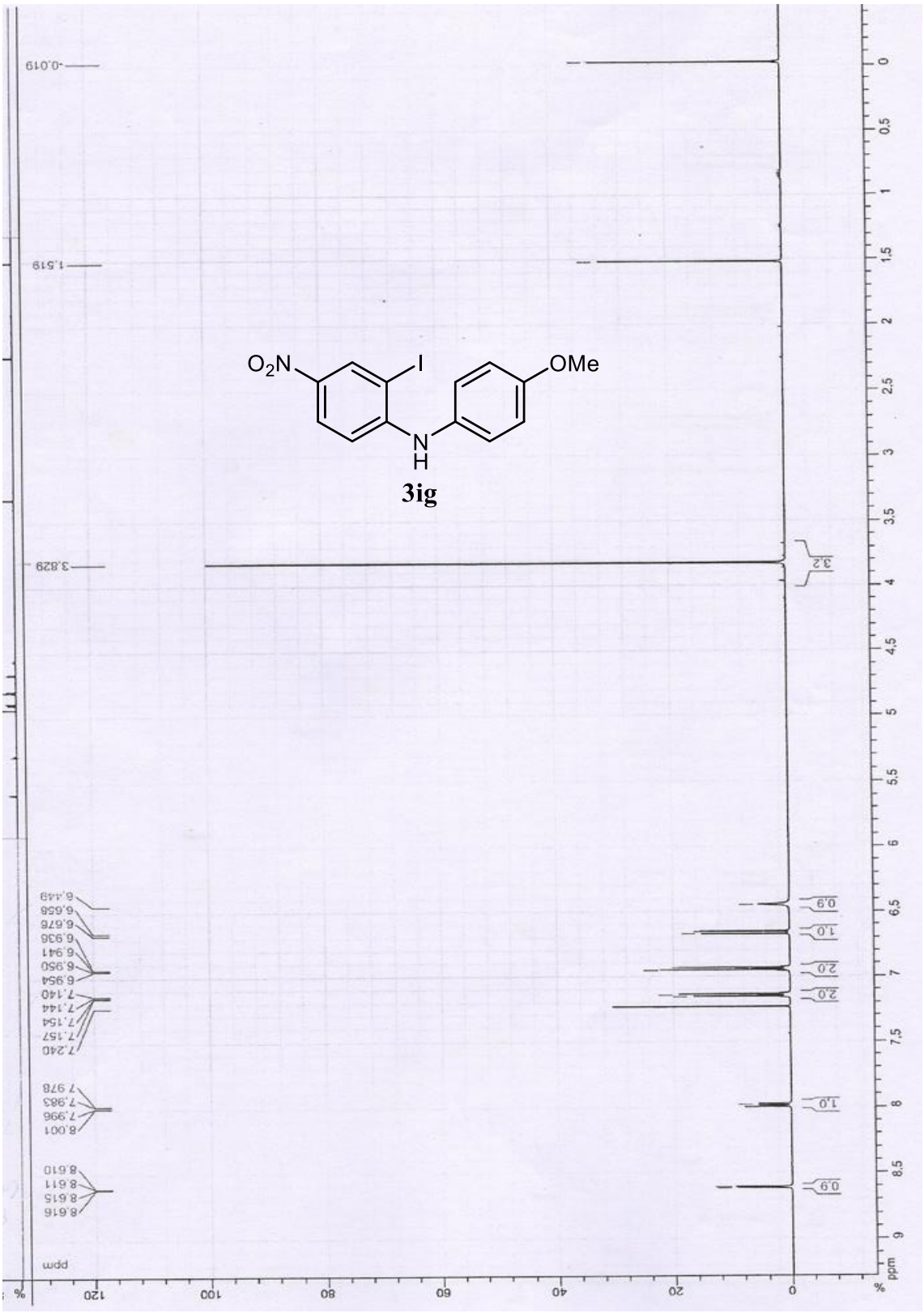
^{1}H NMR spectrum of 4-bromo-2-iodo-*N*-(4-methoxylphenyl)aniline (**3gg**) in $CDCl_3$



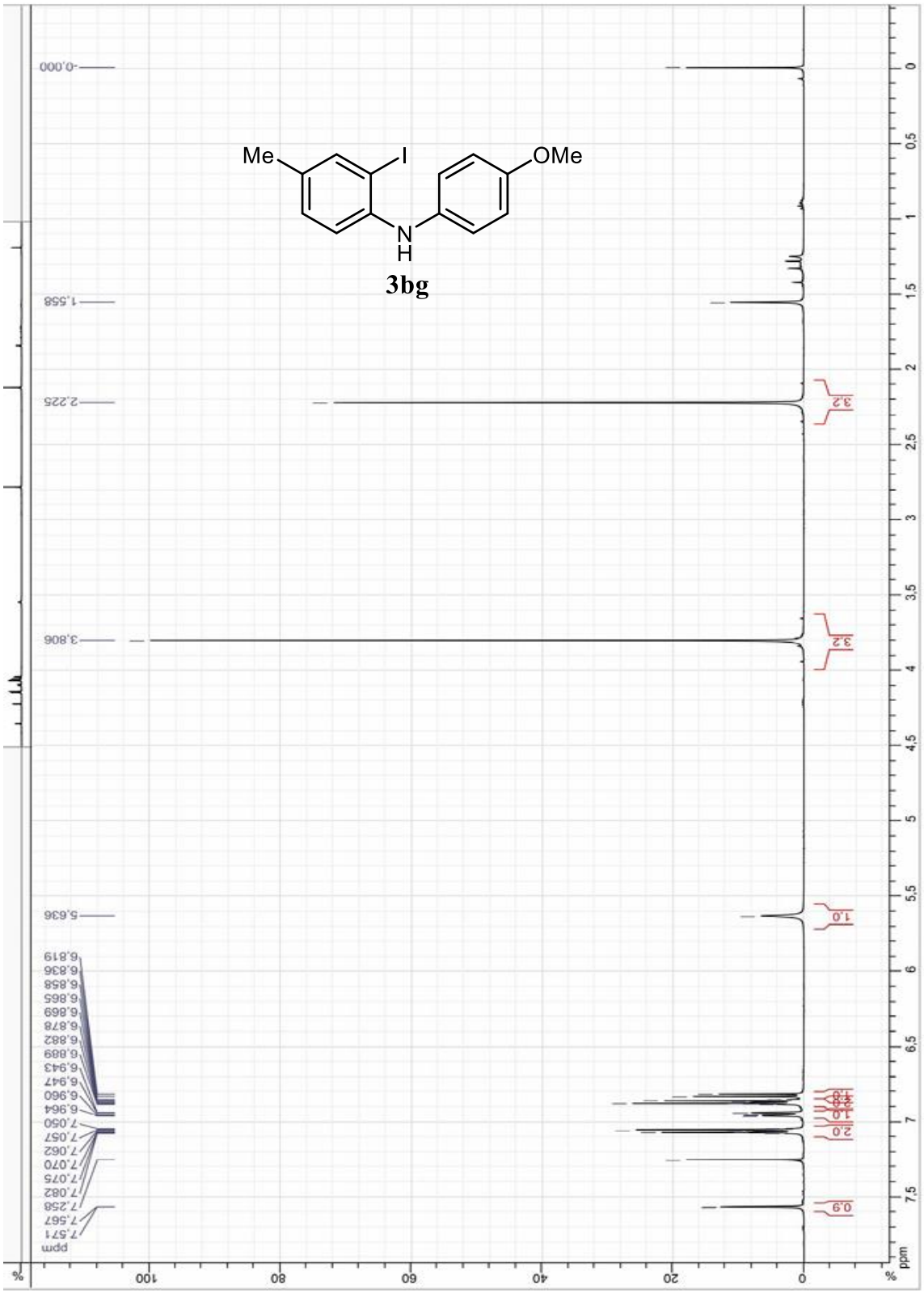
^{1}H NMR spectra of methyl 3-iodo-4-((4-methoxyphenyl)amino)benzoate (**3hg**) in $CDCl_3$

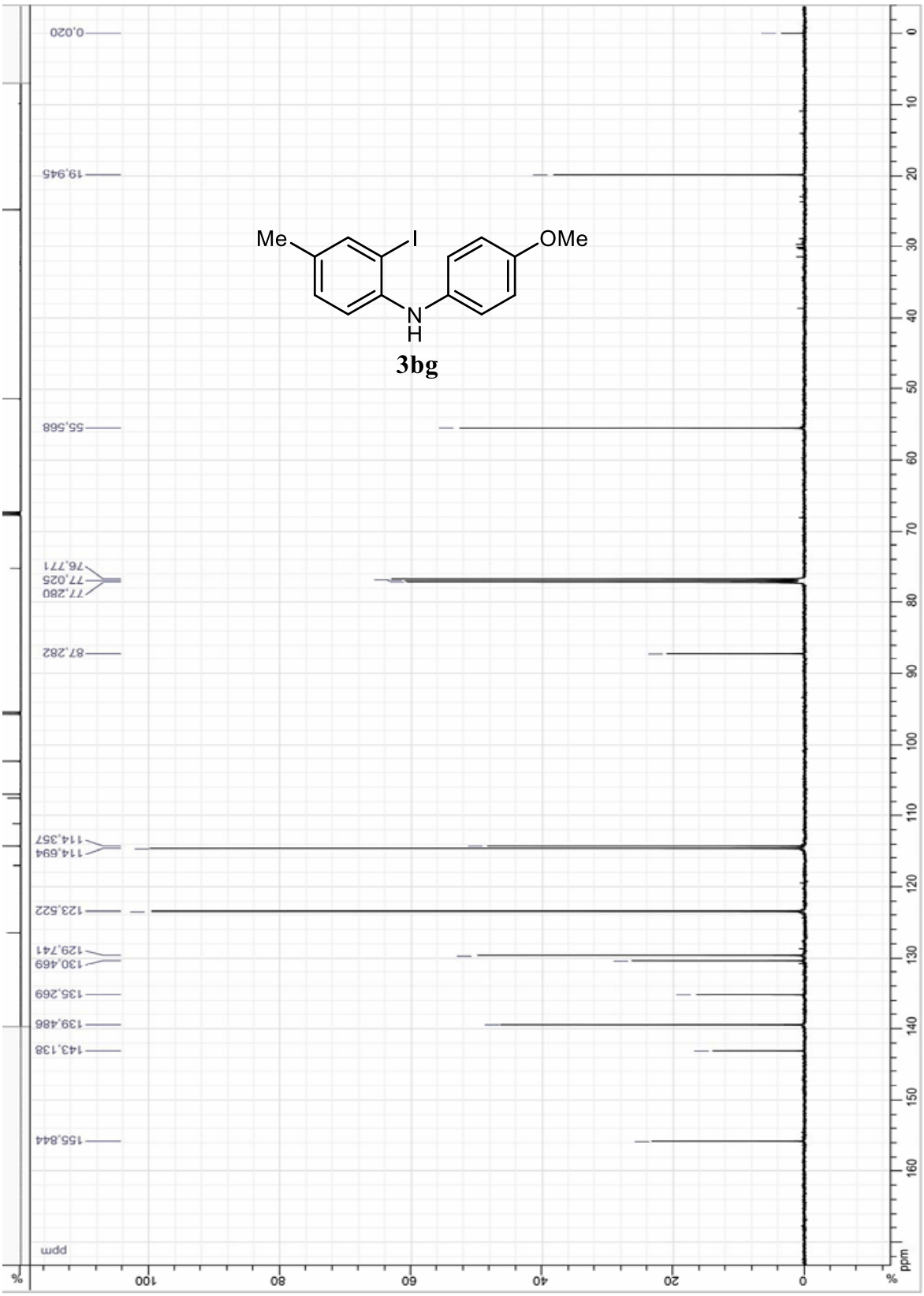


^{1}H NMR spectra of methyl 4-nitro-2-iodo-*N*-(4-methoxylphenyl)aniline (**3ig**) in $CDCl_3$

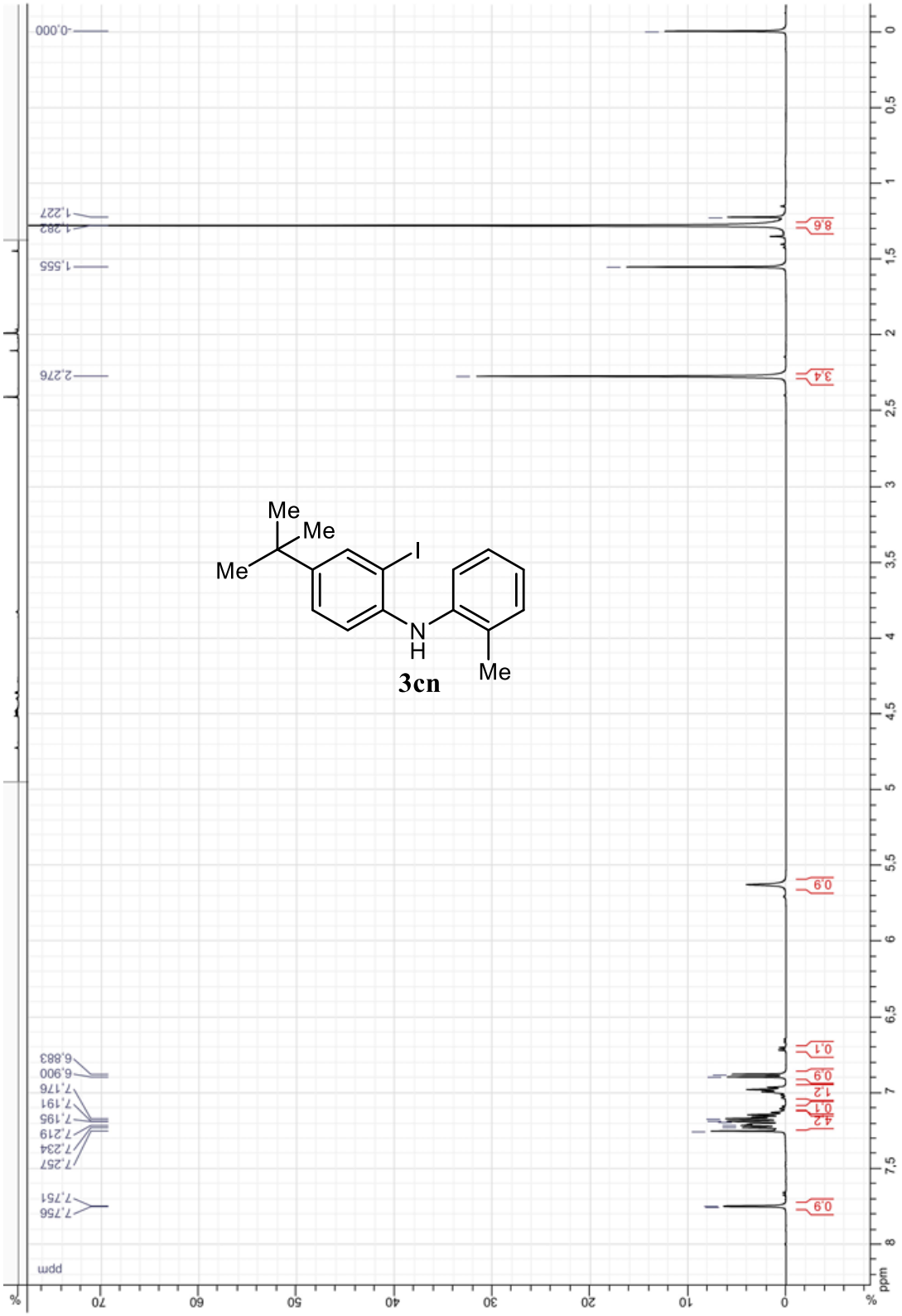


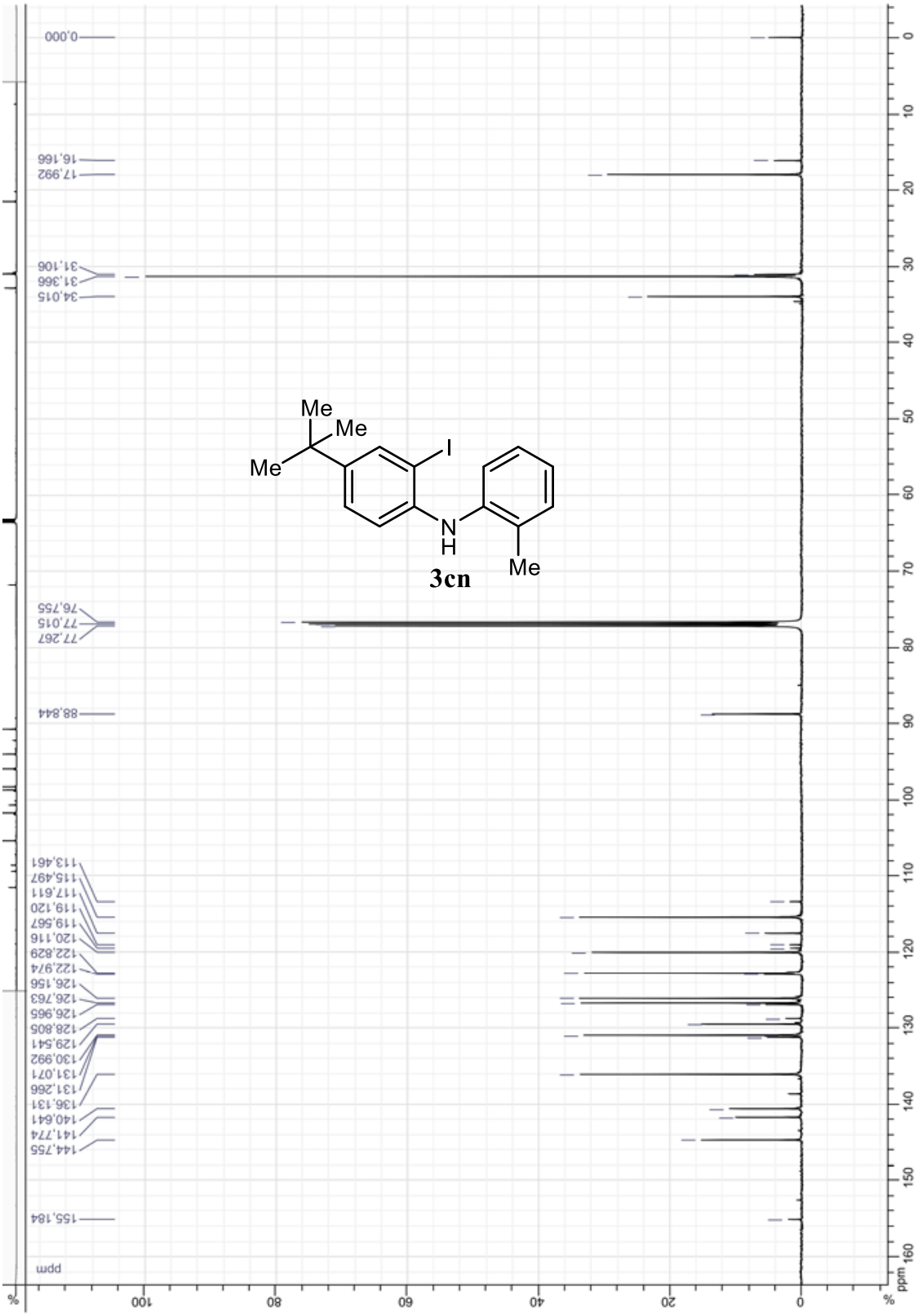
^{1}H NMR and ^{13}C NMR spectra of 2-iodo-*N*-(4-methoxyphenyl)-4-methylaniline (**3bg**) in $CDCl_3$



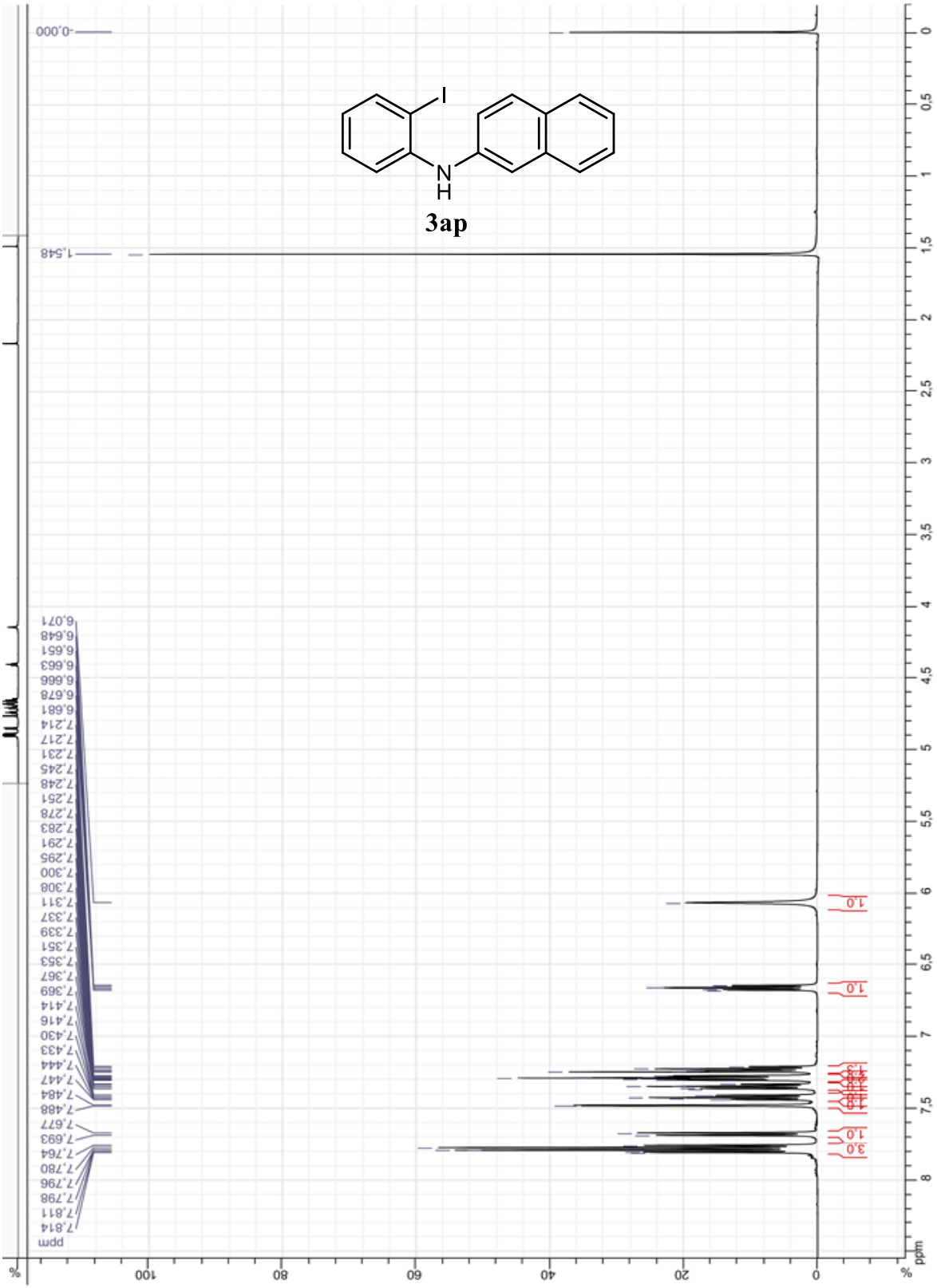

Me
I
OMe
N
H
3bg
0.020
19.945
55.568
76.771
77.025
77.280
87.282
114.357
114.694
123.522
129.741
130.469
135.269
139.486
143.138
155.844
ppm

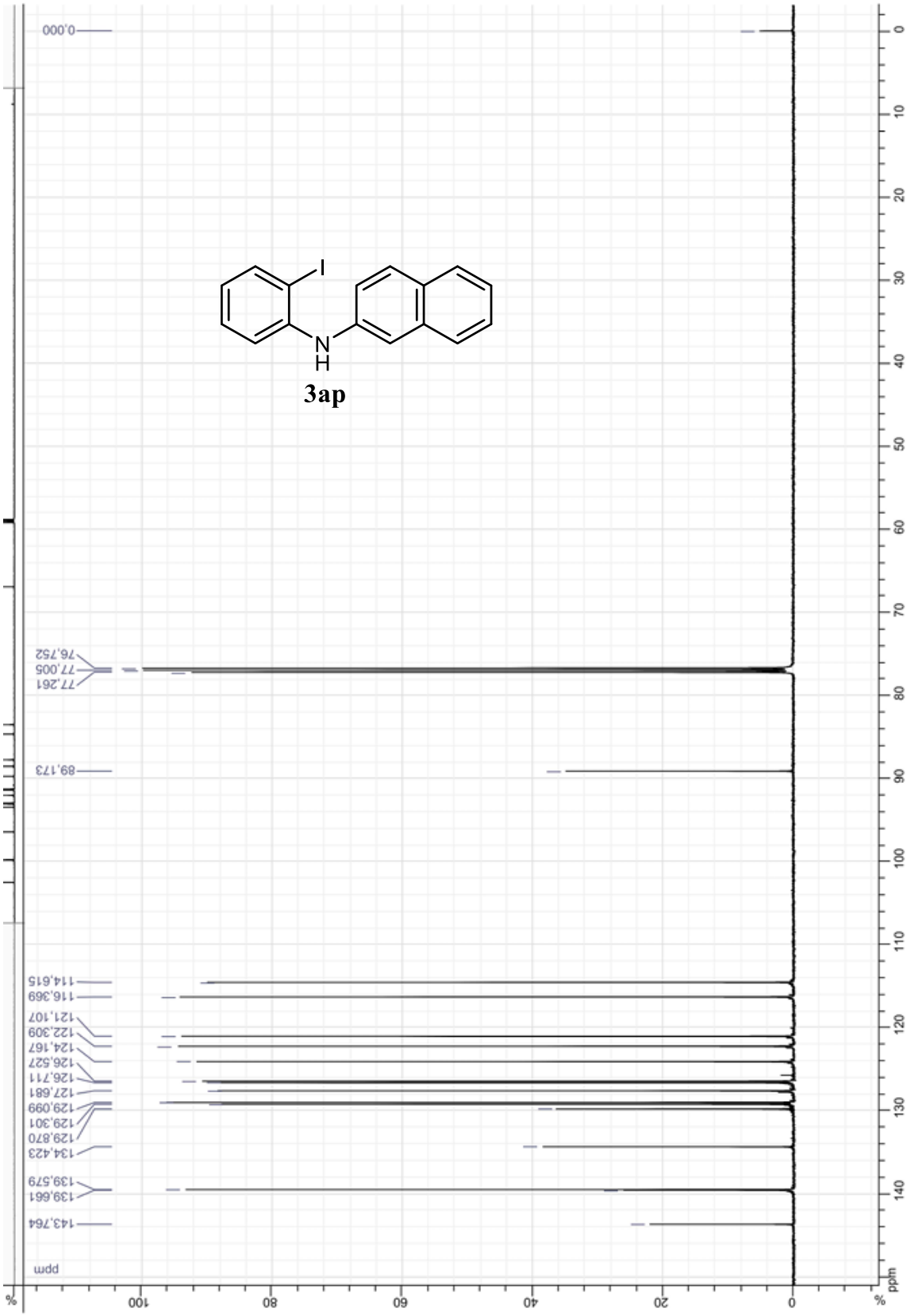
^{1}H NMR and ^{13}C NMR spectra of 4-(*tert*-butyl)-2-iodo-*N*-(*o*-tolyl)aniline (**3cn**) in $CDCl_3$



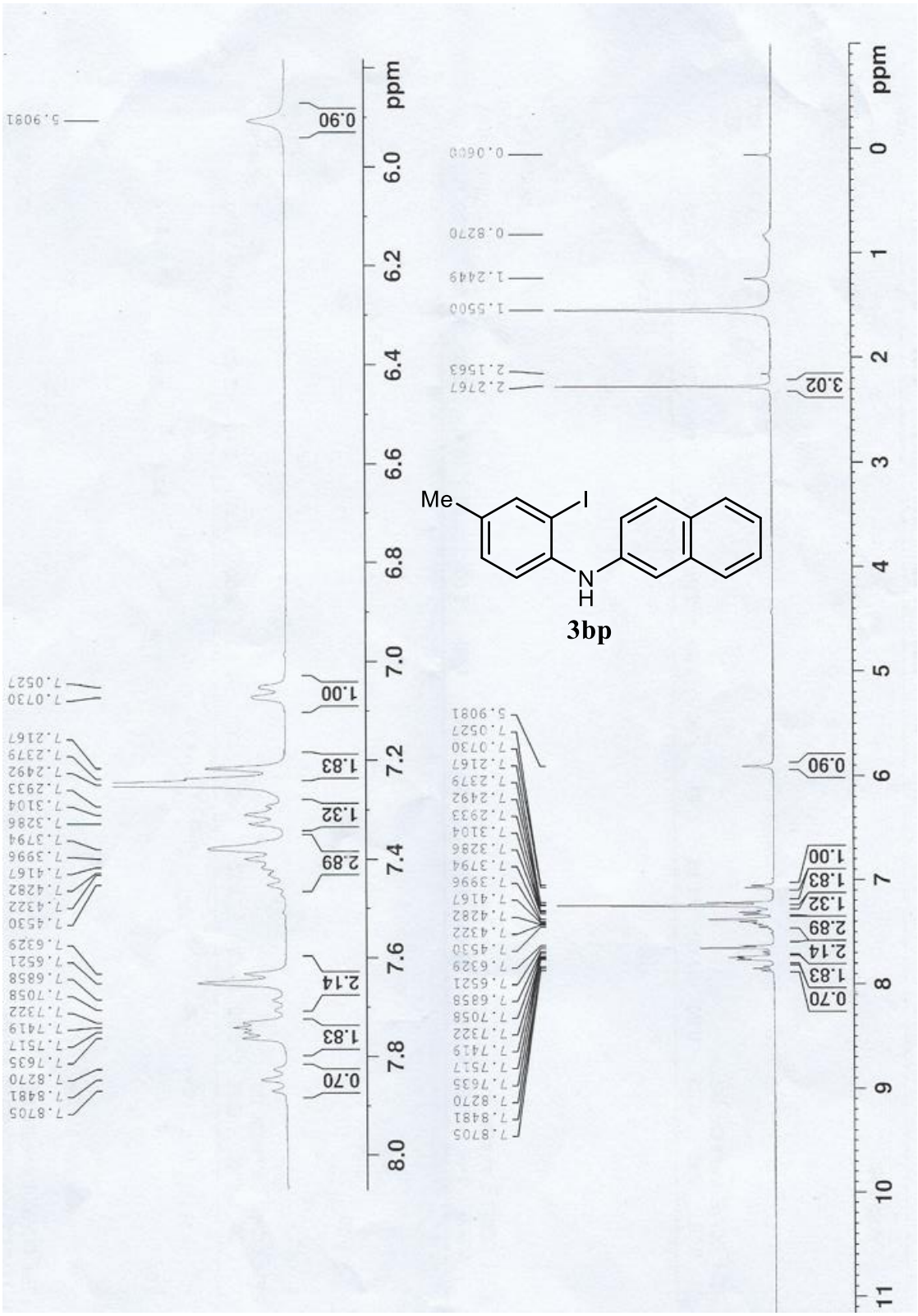

Me
Me
Me
I
N
H
Me
3cn
0.000
16.166
17.992
31.106
31.366
34.015
76.755
77.015
77.267
88.844
113.461
115.497
117.611
119.120
119.567
120.116
122.829
122.974
126.156
126.763
126.965
128.805
129.541
130.992
131.071
131.266
136.131
140.641
141.774
144.755
155.184
ppm

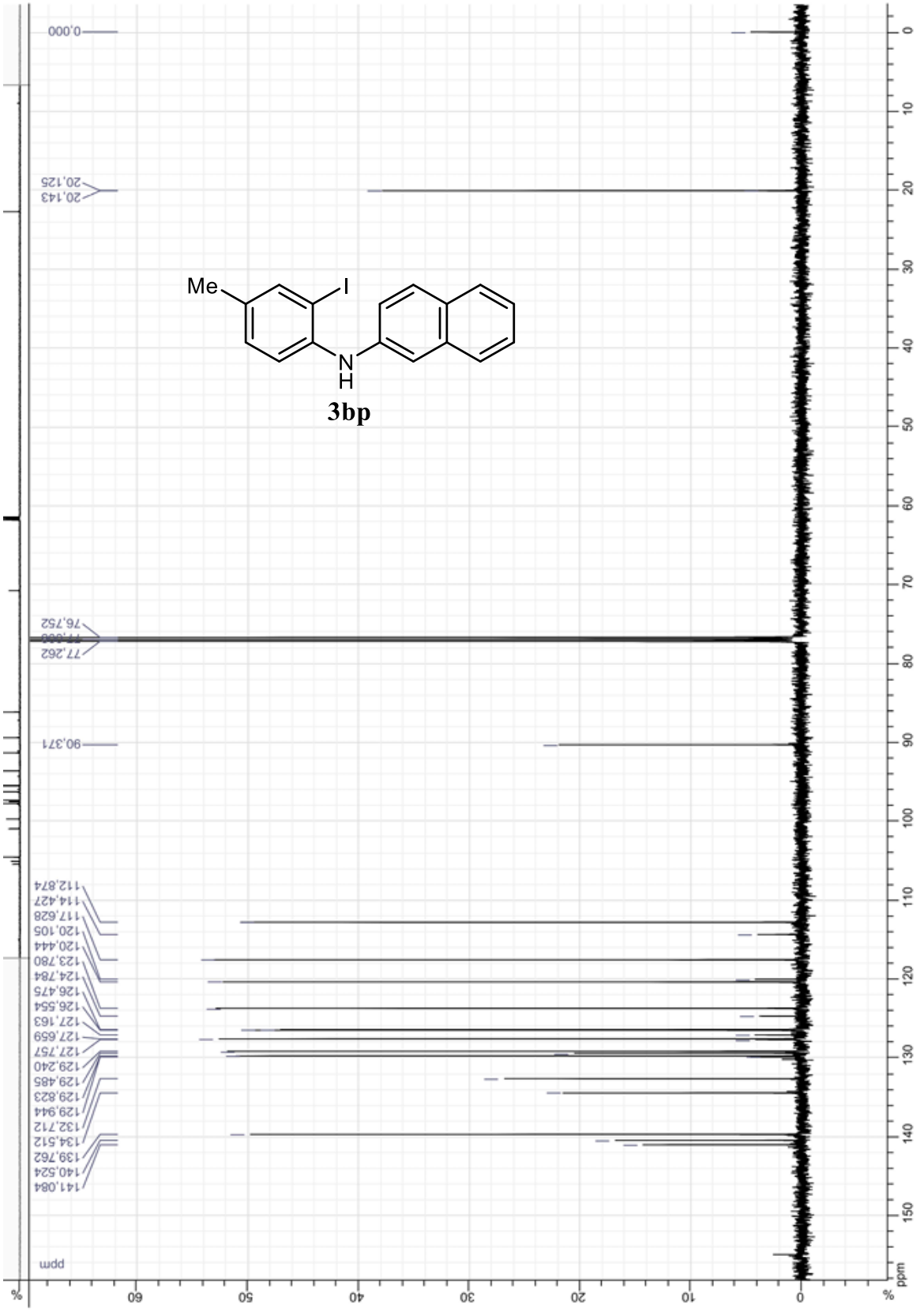
^{1}H NMR and ^{13}C NMR spectra of *N*-(2-iodophenyl)naphthalen-2-amine (**3ap**) in $CDCl_3$



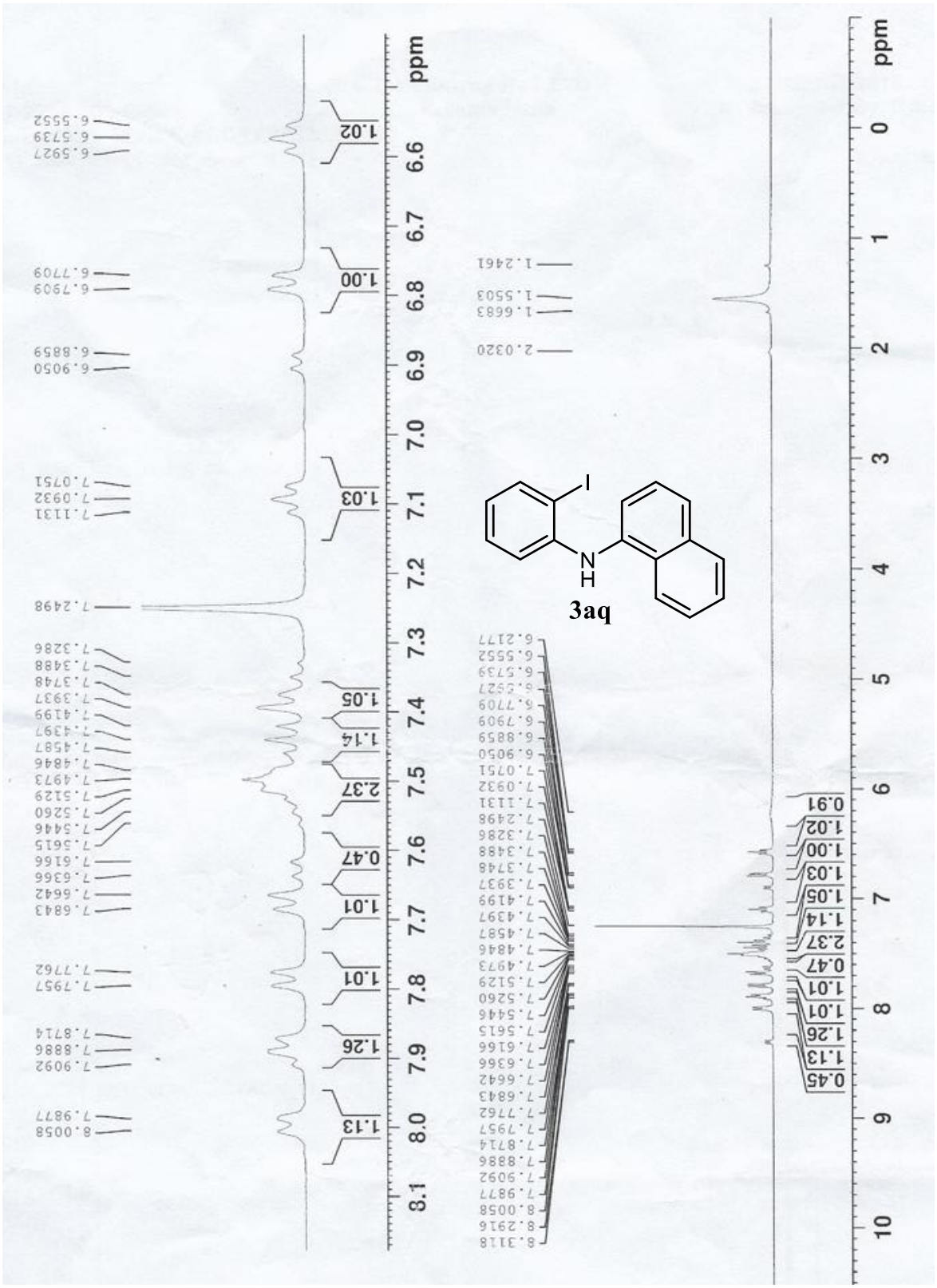

I
N
H
3ap
0.000
76.752
77.005
77.261
89.173
114.615
116.369
121.107
122.309
124.167
126.527
126.711
127.681
129.099
129.301
129.870
134.423
139.579
139.661
143.764
ppm

^{1}H NMR and ^{13}C NMR spectra of *N*-(2-iodo-4-methylphenyl)naphthalen-2-amine (**3bp**) in $CDCl_3$

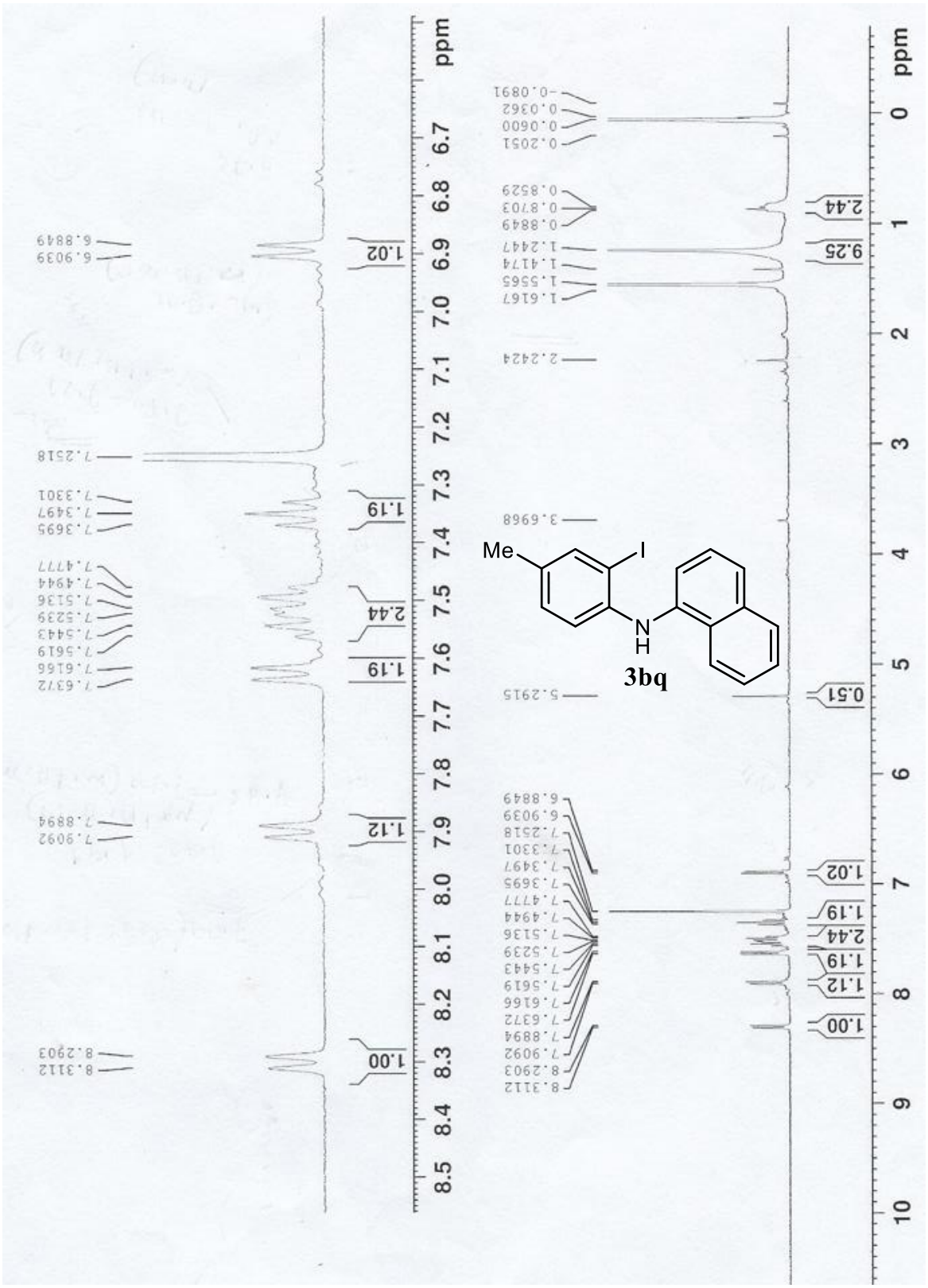



Me
I
N
H
3bp

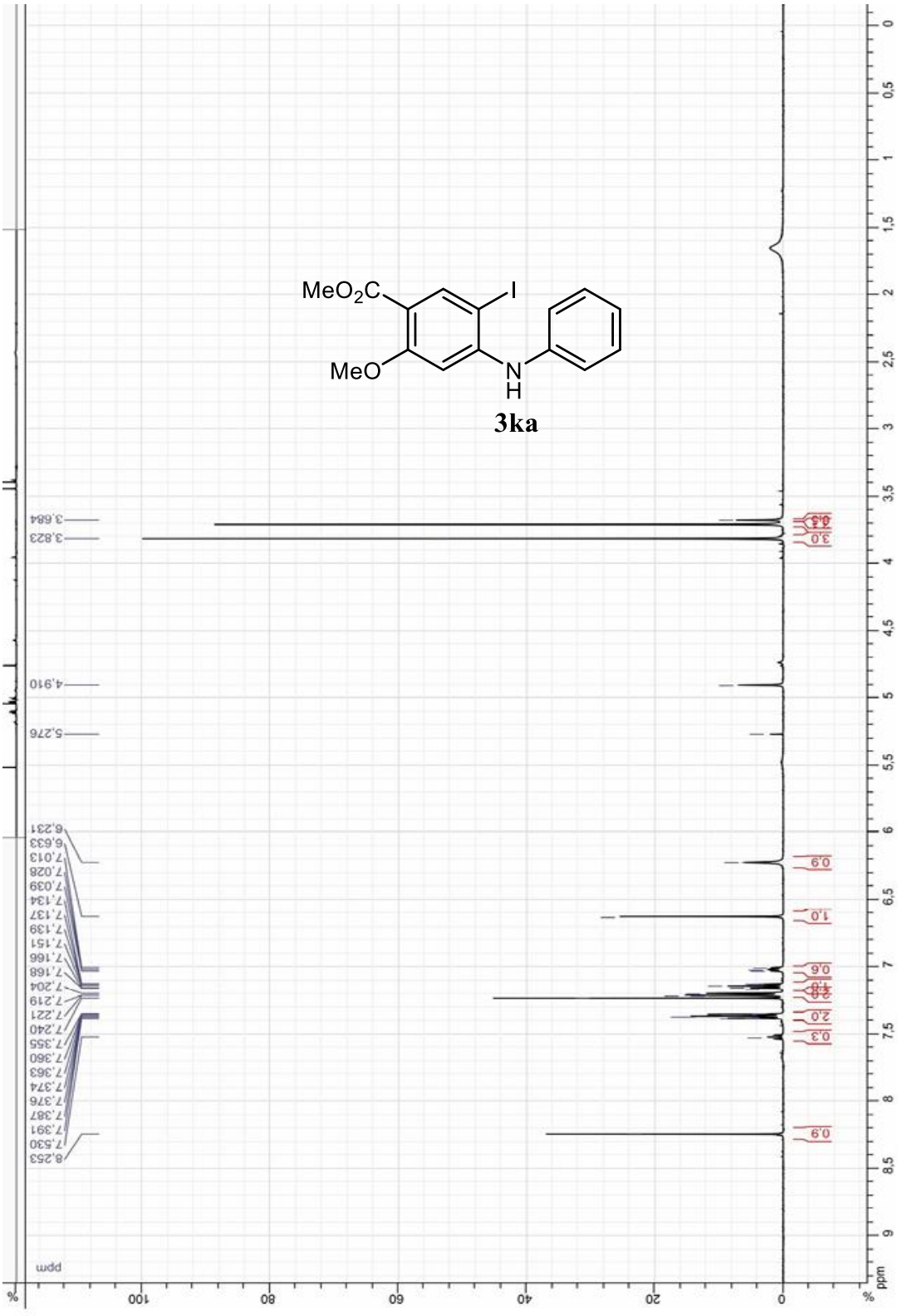
^{1}H NMR spectrum of *N*-(2-iodophenyl)naphthalen-1-amine (**3aq**) in $CDCl_3$



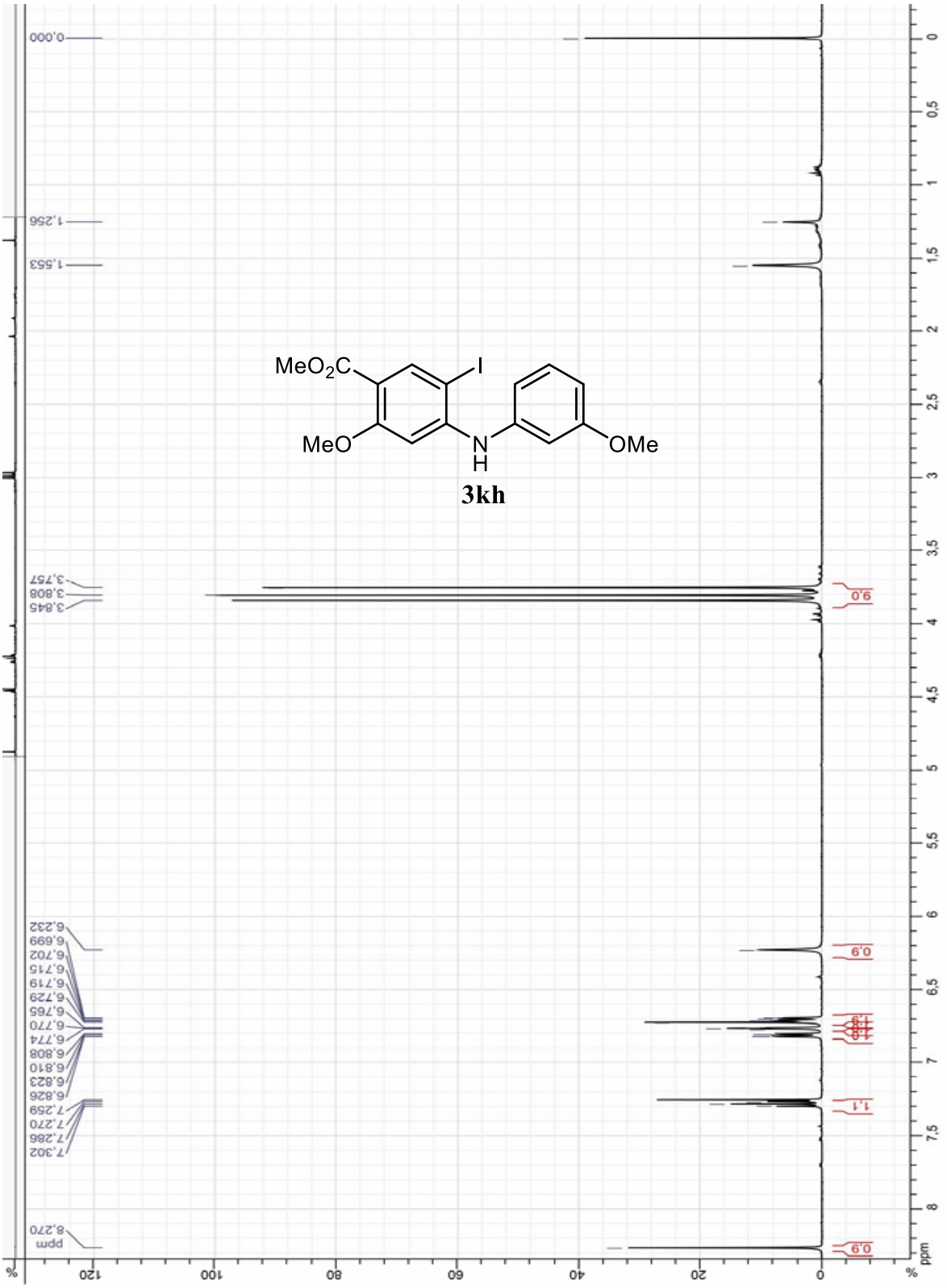
^{1}H NMR spectrum of *N*-(2-iodo-4-methylphenyl)naphthalen-1-amine (**3bq**) in $CDCl_3$



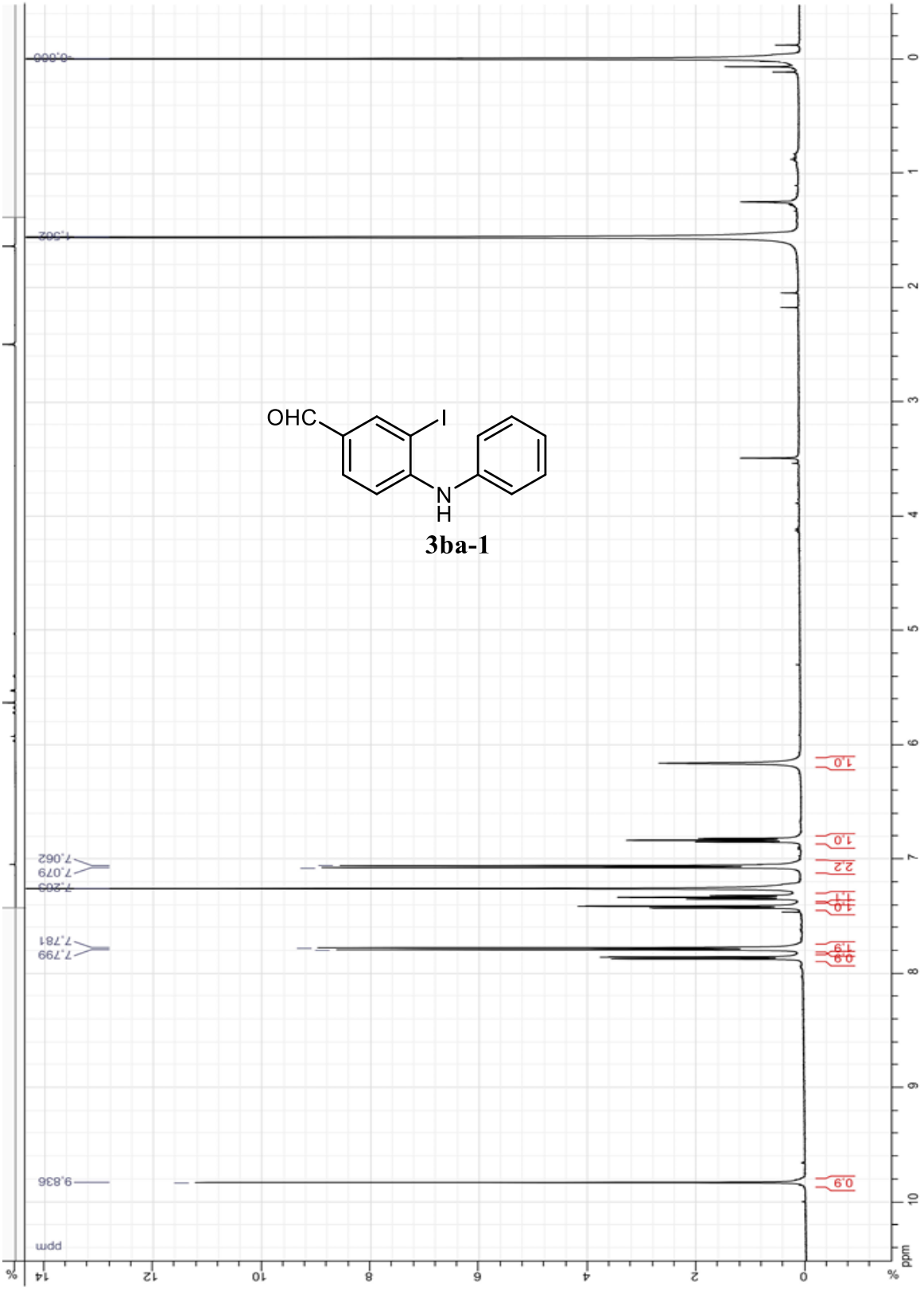
^{1}H NMR spectrum of methyl 5-iodo-2-methoxy-4-(phenylamino)benzoate (**3ka**) in $CDCl_3$

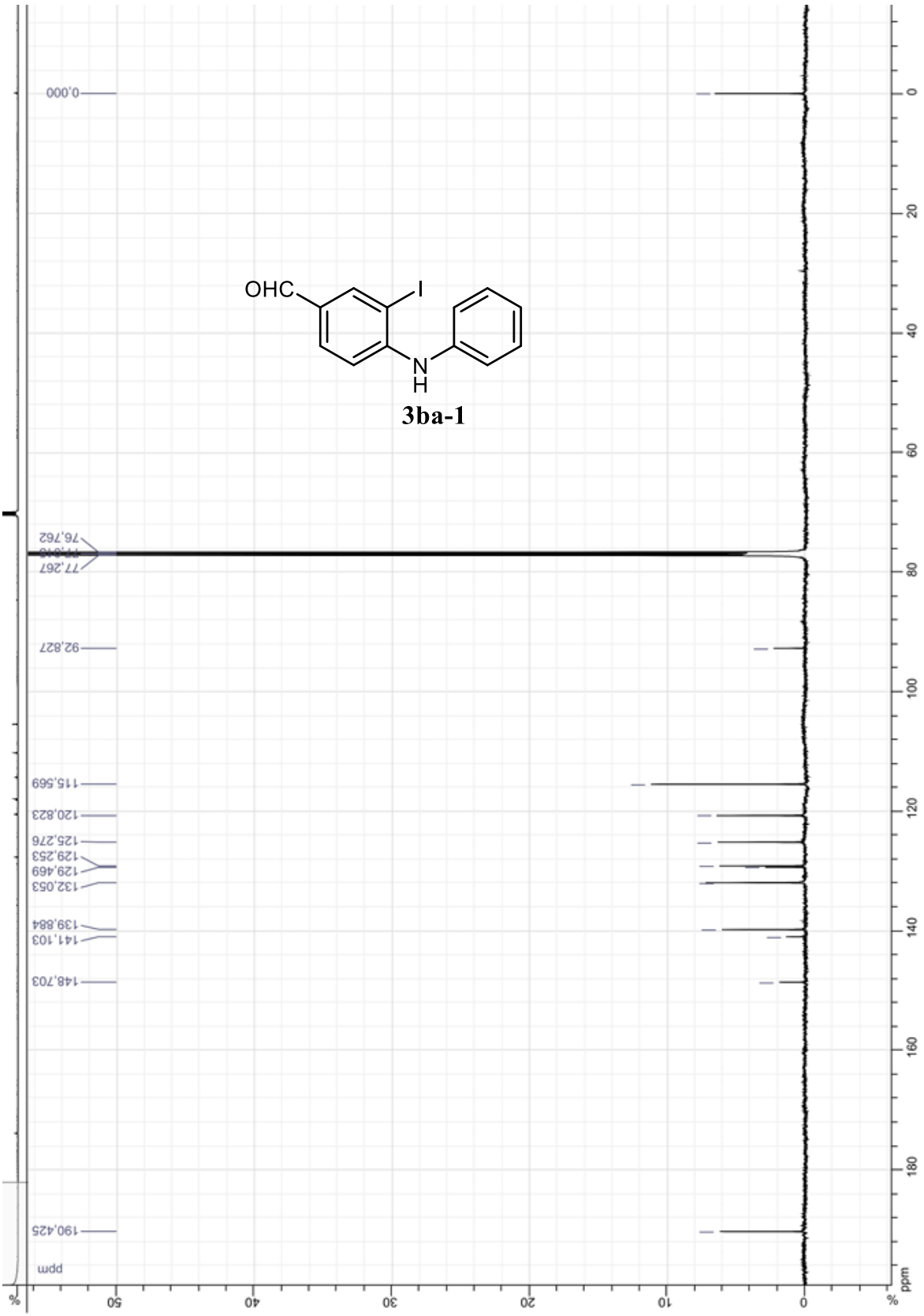


^{1}H NMR spectrum of methyl 5-iodo-2-methoxy-4-((3-methoxyphenyl)amino)benzoate (**3kh**) in $CDCl_3$



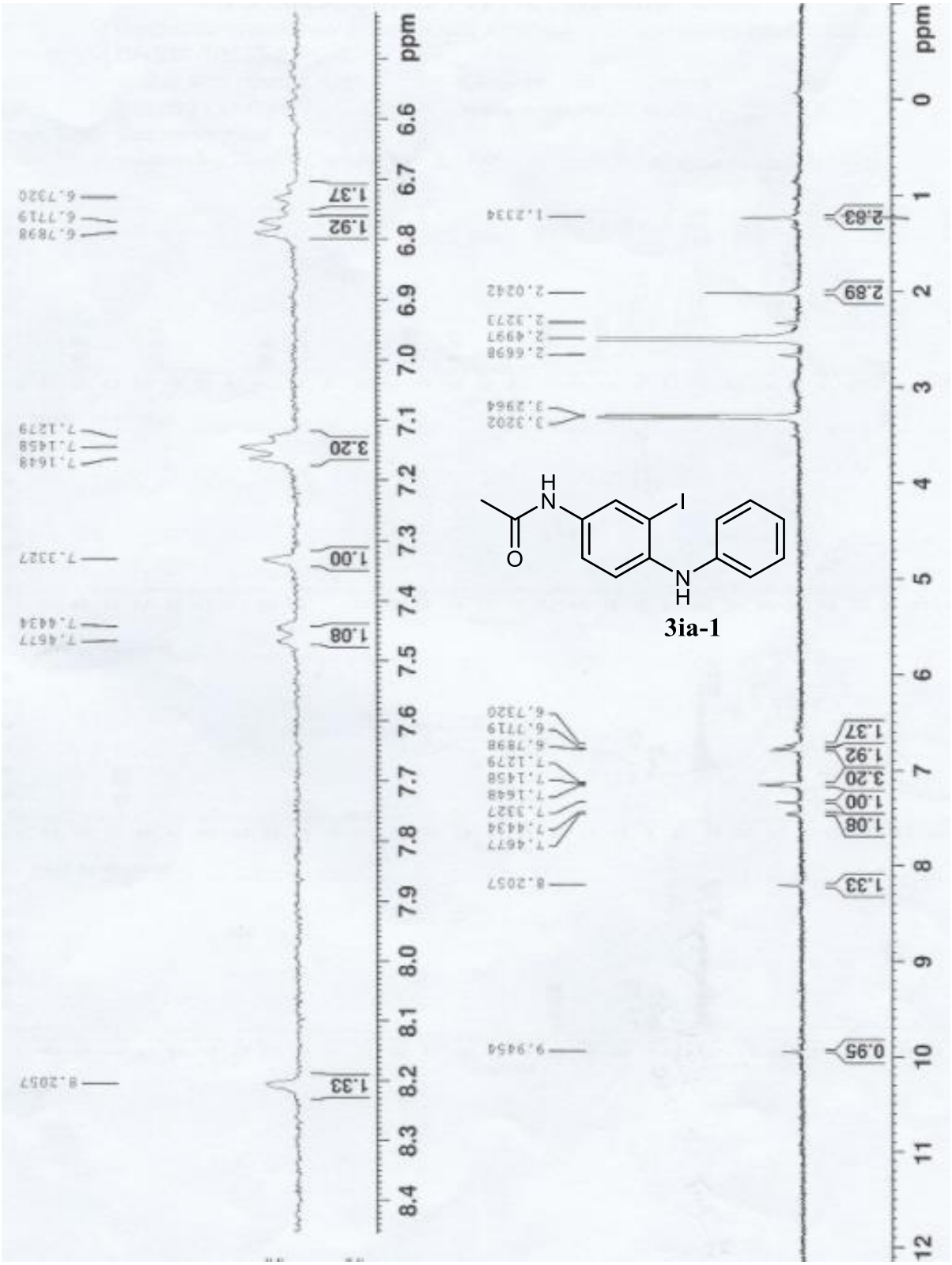
^{1}H NMR and ^{13}C NMR spectra of 4-((2-iodophenyl)amino)benzaldehyde (**3ba-1**) in $CDCl_3$

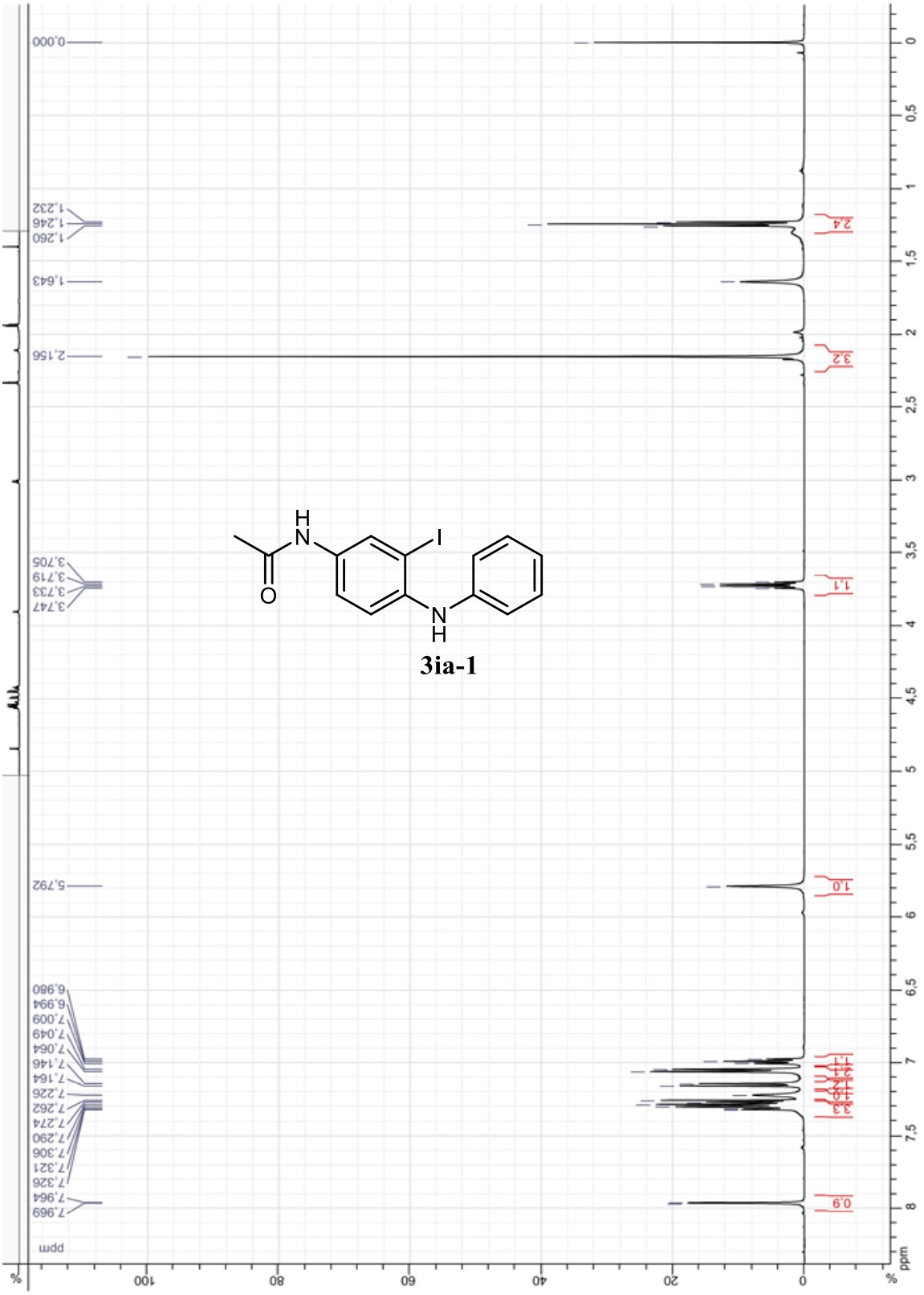



OHC
I
N
H
0.000
76.762
77.019
77.267
92.827
115.569
120.823
125.276
129.253
129.469
132.053
139.884
141.103
148.703
190.425
ppm
%
ppm

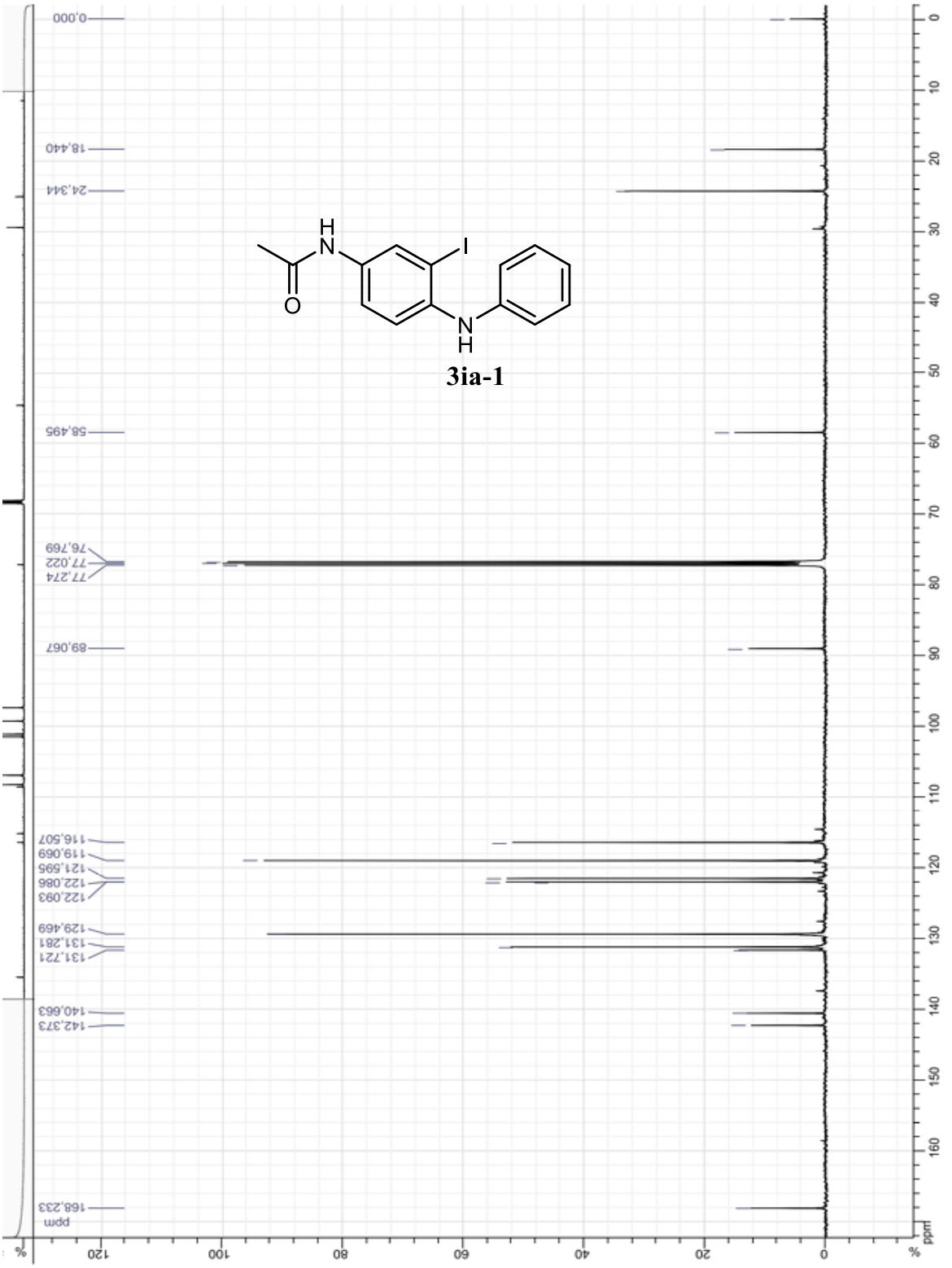
3ba-1

^{1}H NMR and ^{13}C NMR spectra of *N*-(3-iodo-4-(phenylamino)phenyl)acetamide (**3ia-1**) in DMSO-D_6 and $CDCl_3$





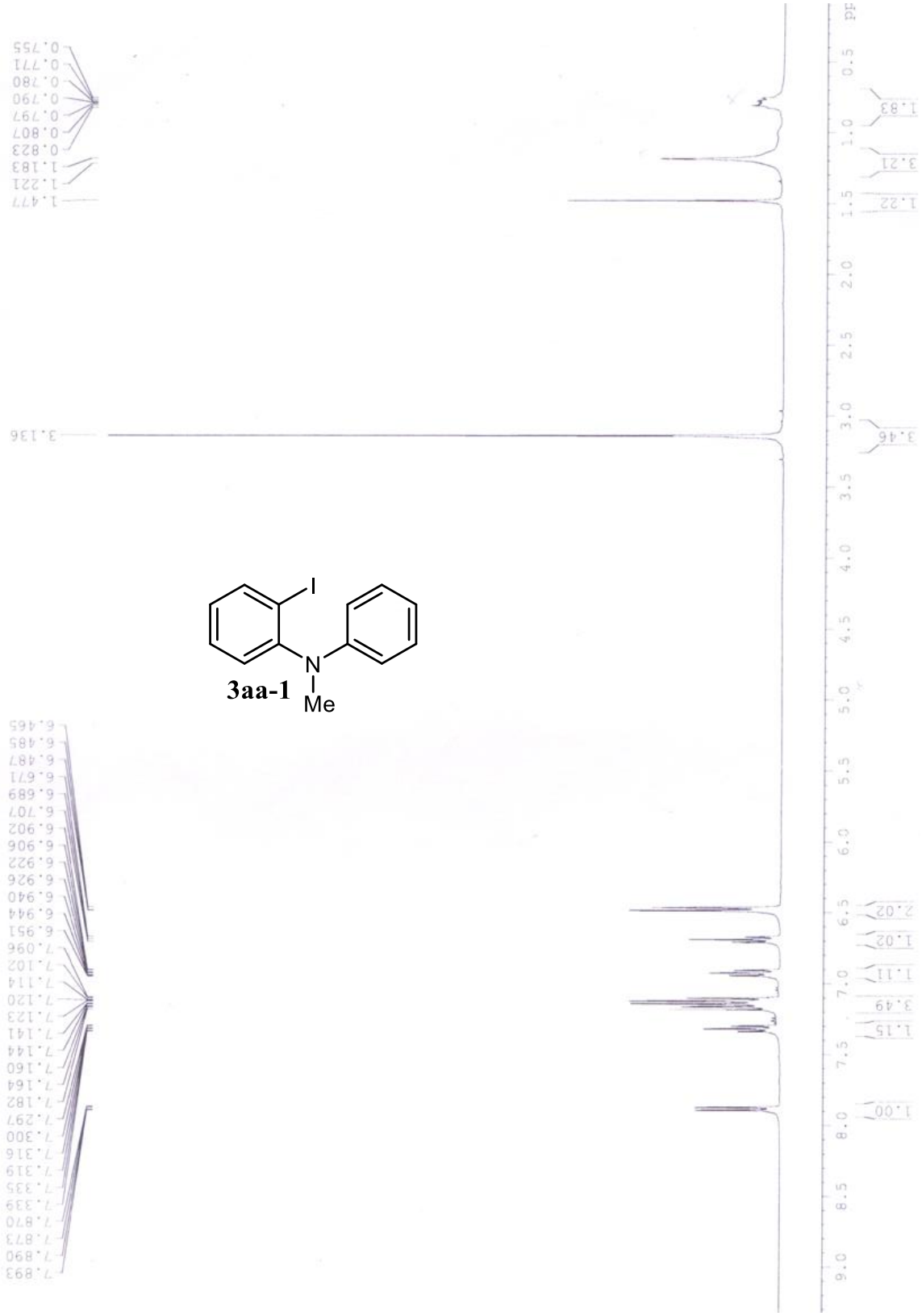
[Peaks at 1.25 (t) and 3.72 (q) are due to residual ethanol]



3ia-1

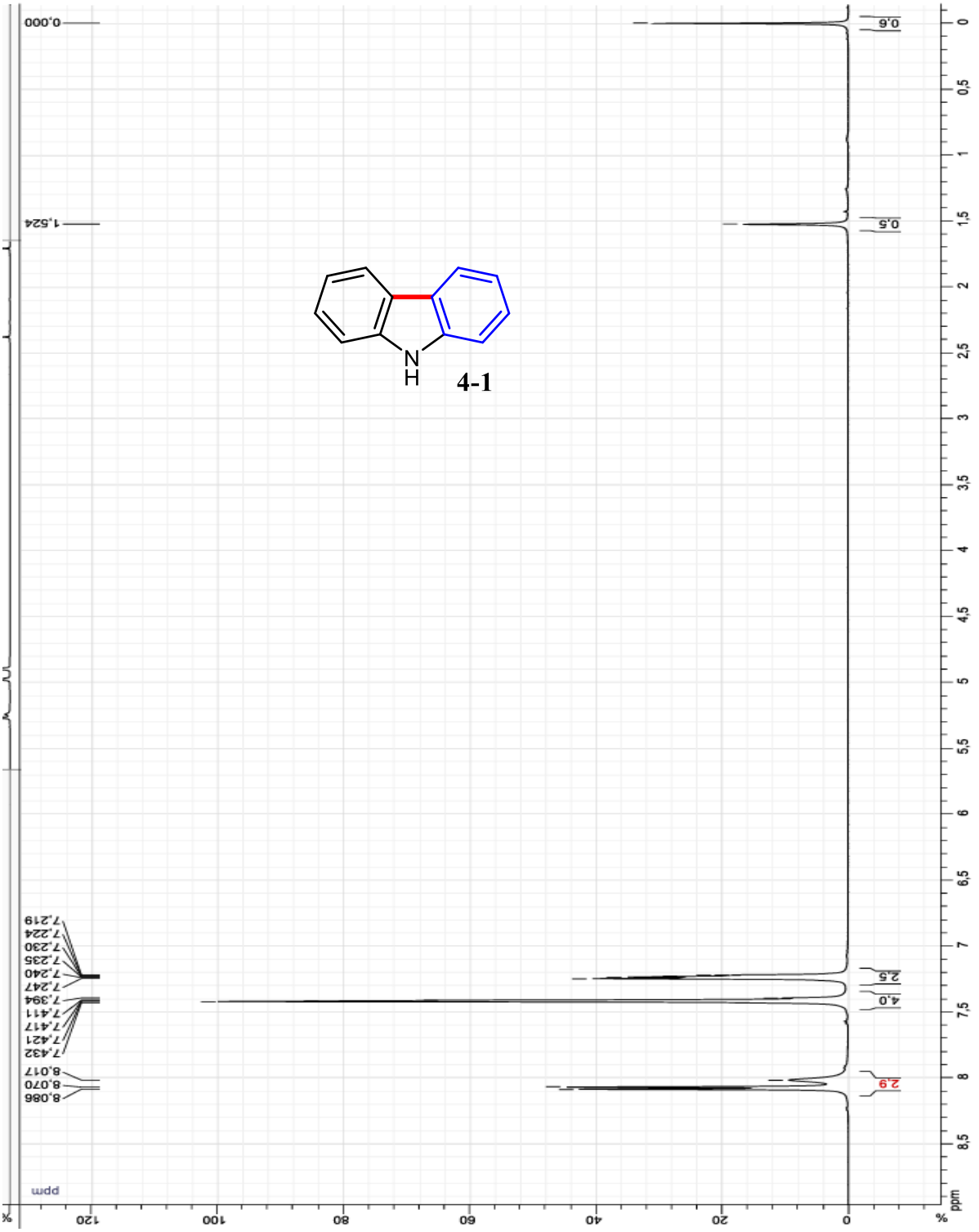
[Peaks at 18.4 and 58.4 are due to residual ethanol]

^{1}H NMR spectrum of 2-iodo-*N*-methyl-*N*-phenylaniline (**3aa-1**) in $CDCl_3$

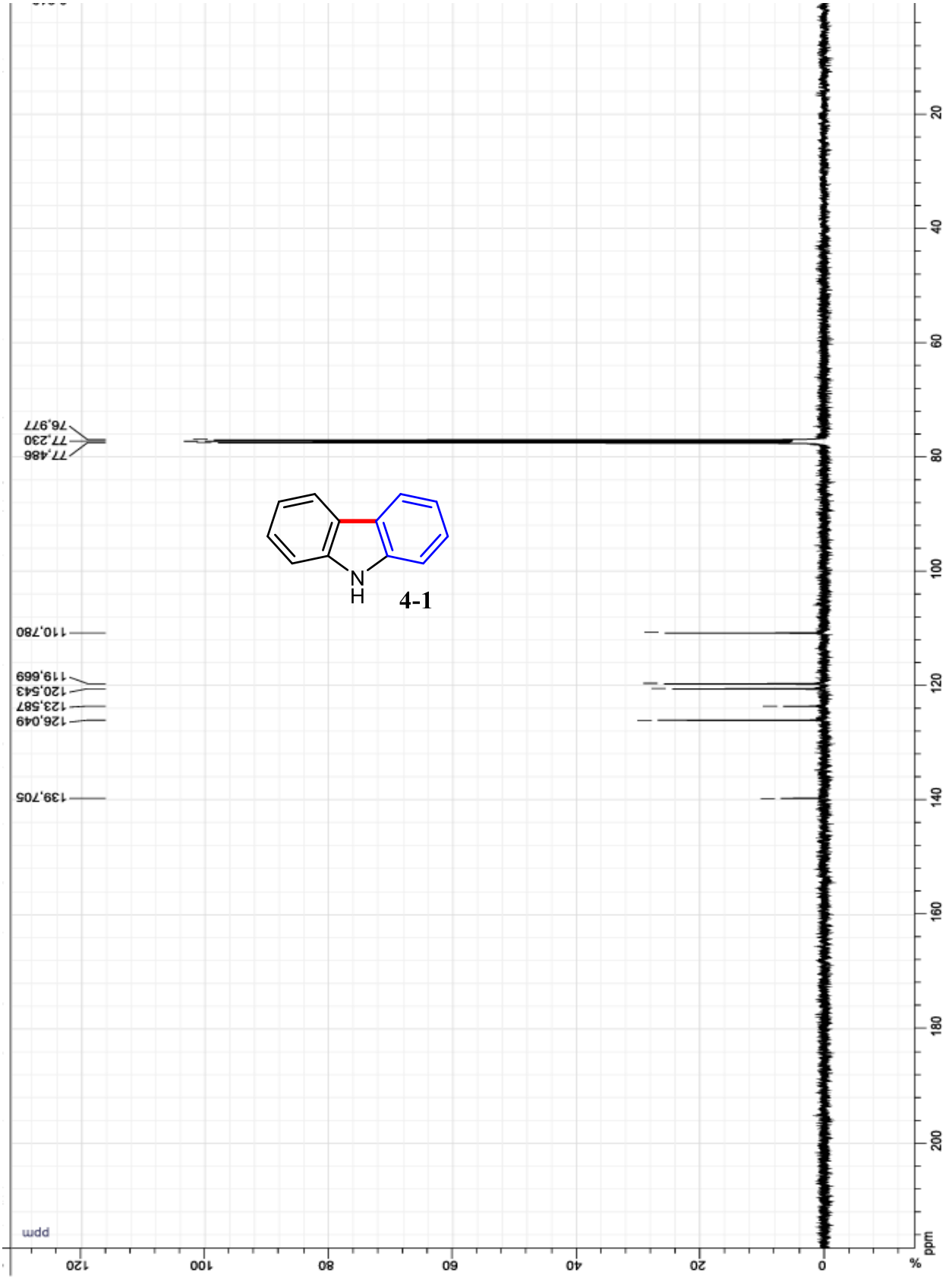


9.2 ^{1}H NMR and ^{13}C NMR spectra of carbazoles 4-1 to 4-43.

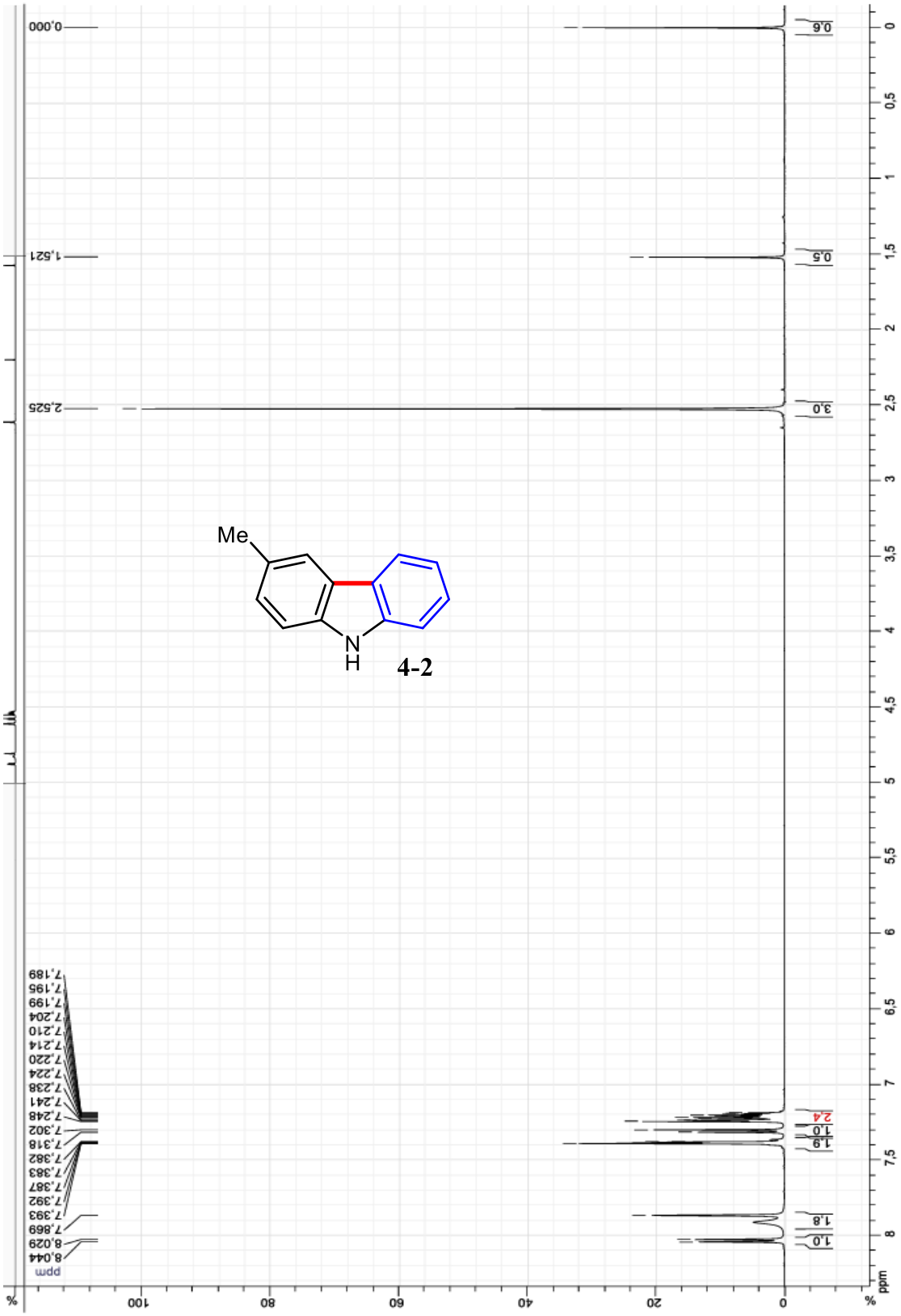
^{1}H NMR and ^{13}C NMR spectra of 9*H*-carbazole (**4-1**) in $CDCl_3$



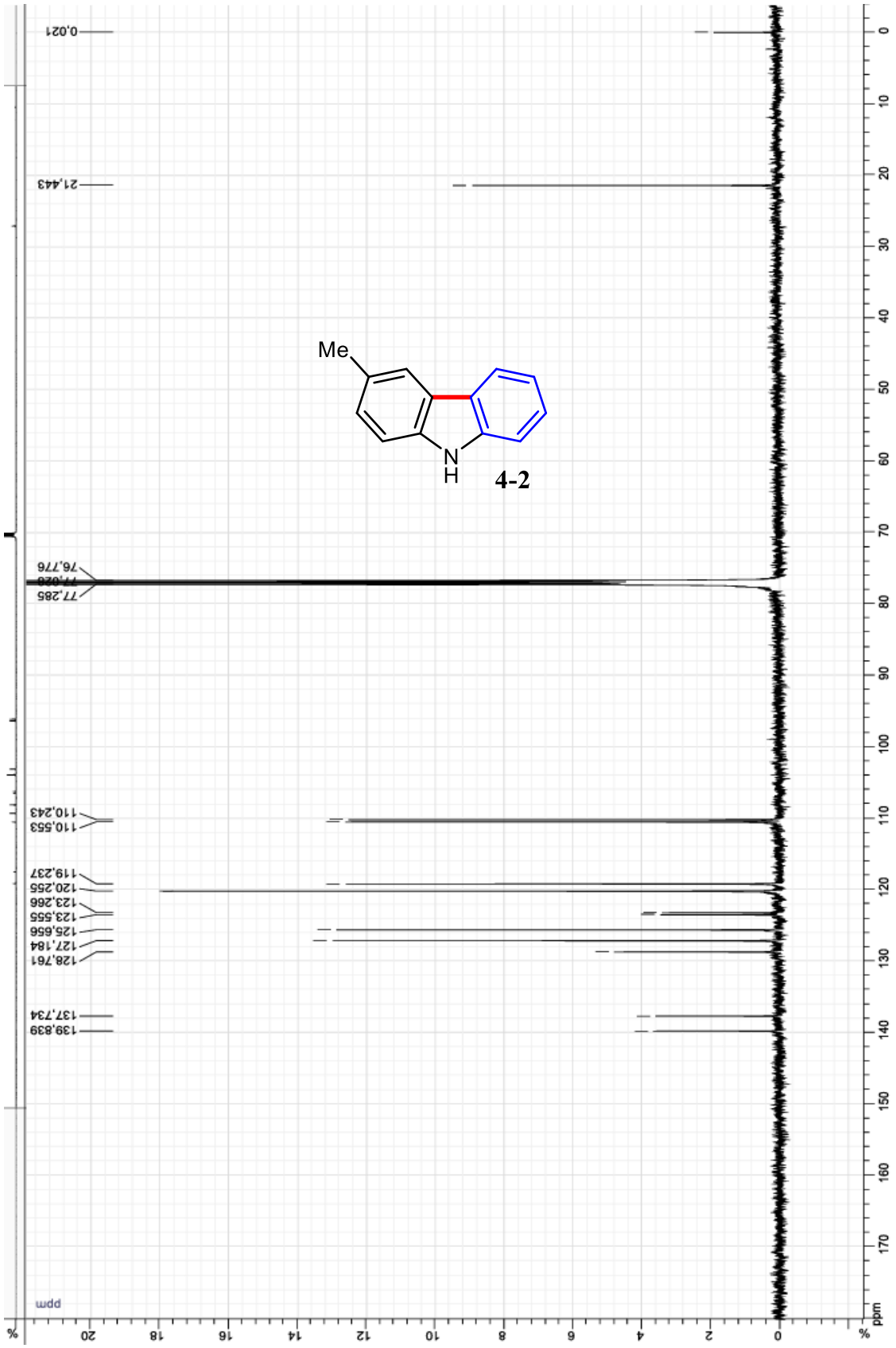
4-1


77,486
77,230
76,977
110,780
119,669
120,543
123,587
126,049
139,705
N
H
4-1
ppm

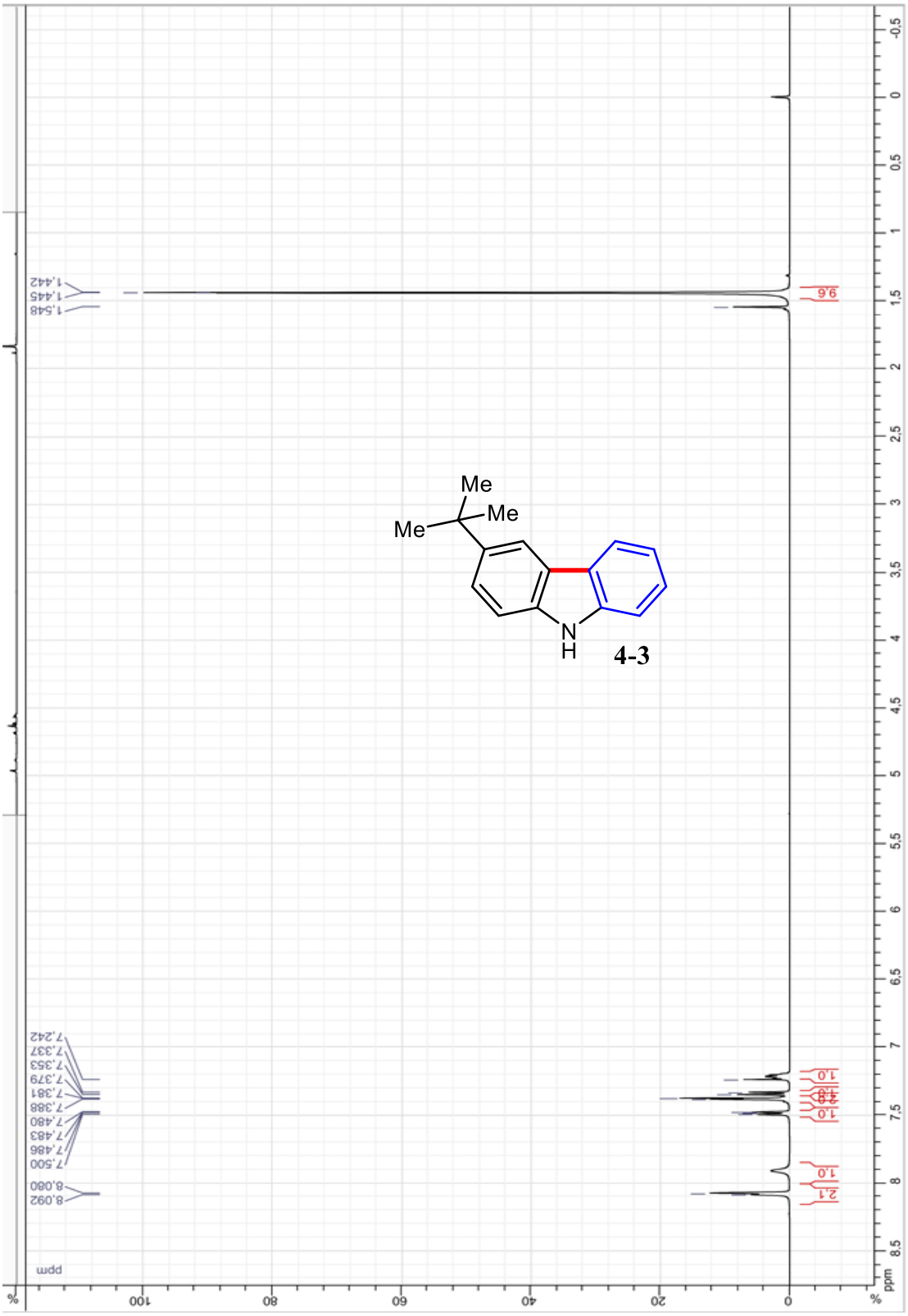
^{1}H NMR and ^{13}C NMR spectra of 3-methyl-9*H*-carbazole (**4-2**) in $CDCl_3$

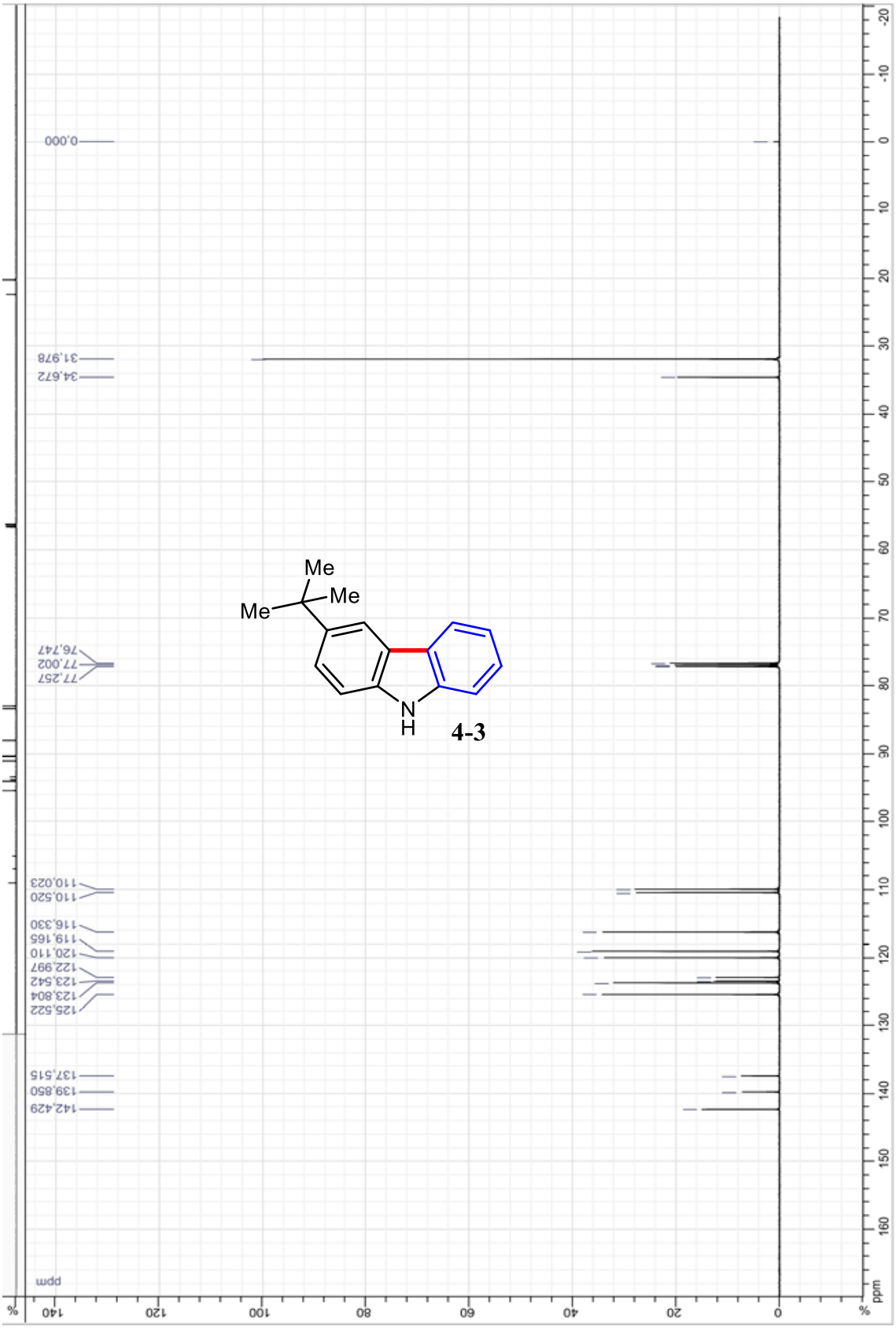


1.

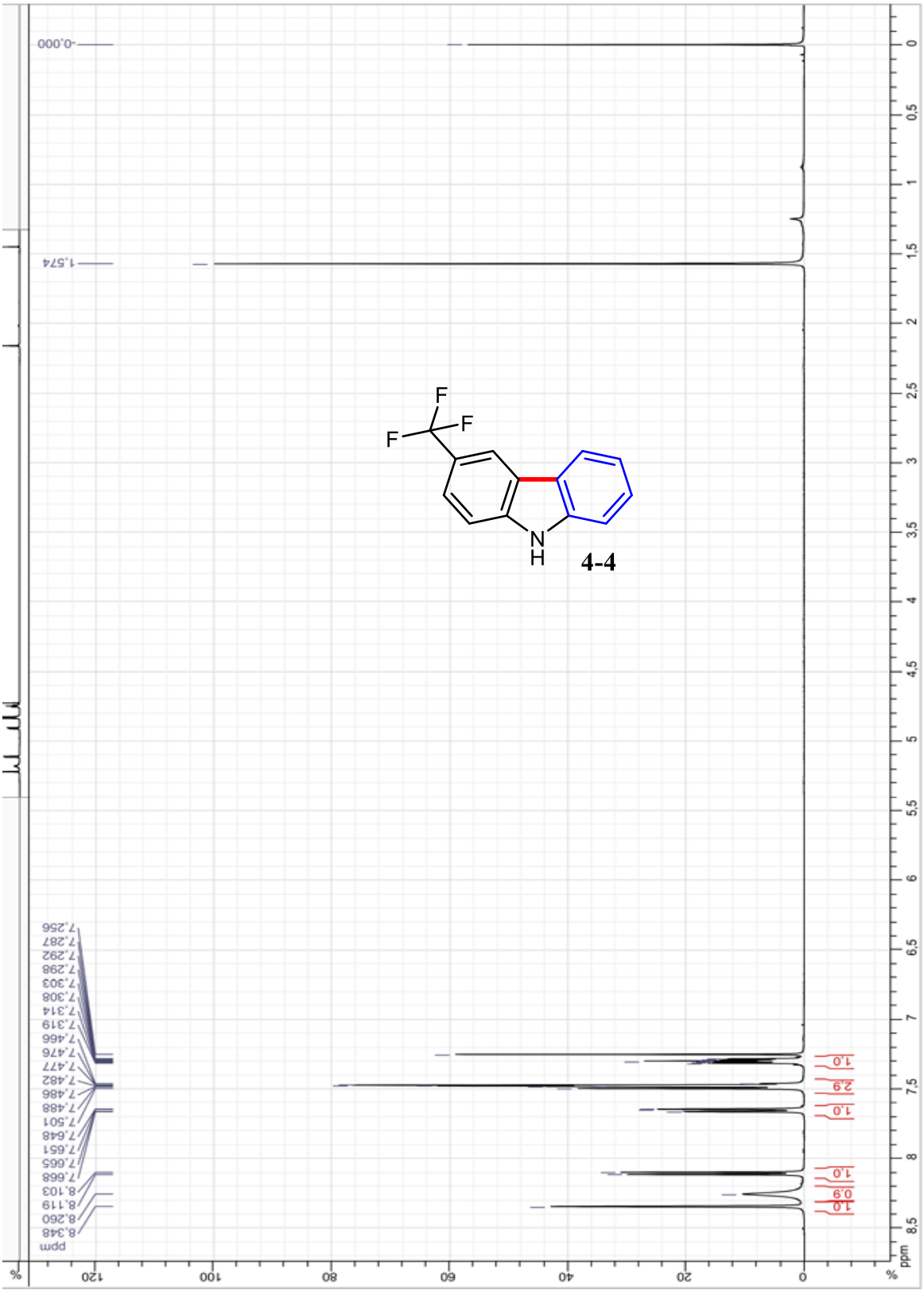

0.021
21.443
77.285
76.776
110.243
110.553
119.237
120.255
123.266
123.555
126.656
127.184
128.761
137.734
139.839
Me
N
H
4-2
ppm

^{1}H NMR and ^{13}C NMR spectra of 3-(*tert*-butyl)-9*H*-carbazole (**4-3**) in $CDCl_3$

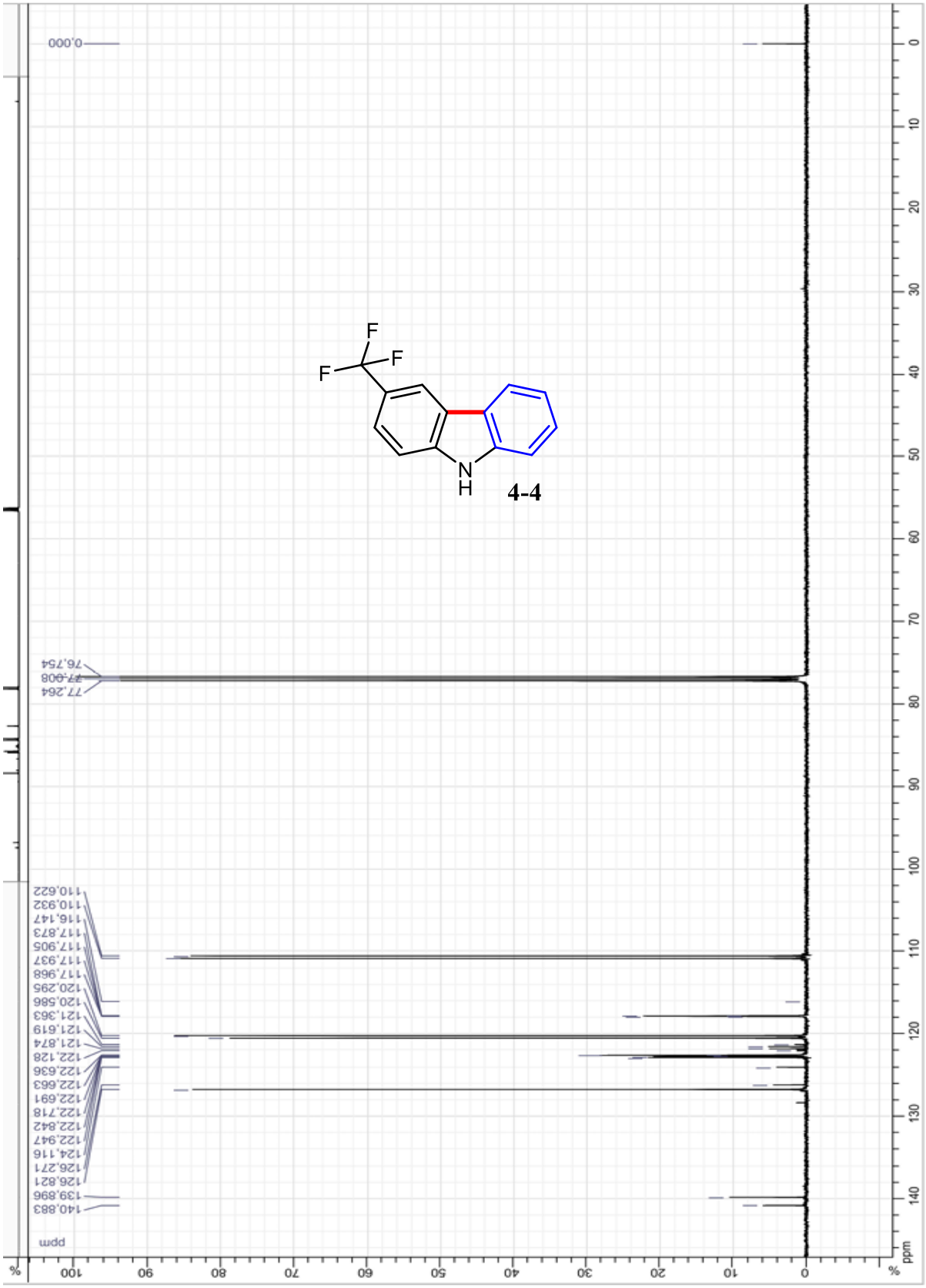



0.000
31.978
34.672
76.747
77.002
77.257
110.023
110.520
116.330
119.165
120.110
122.997
123.542
123.804
125.522
137.515
139.850
142.429
Me
Me
Me
N
H
4-3
ppm

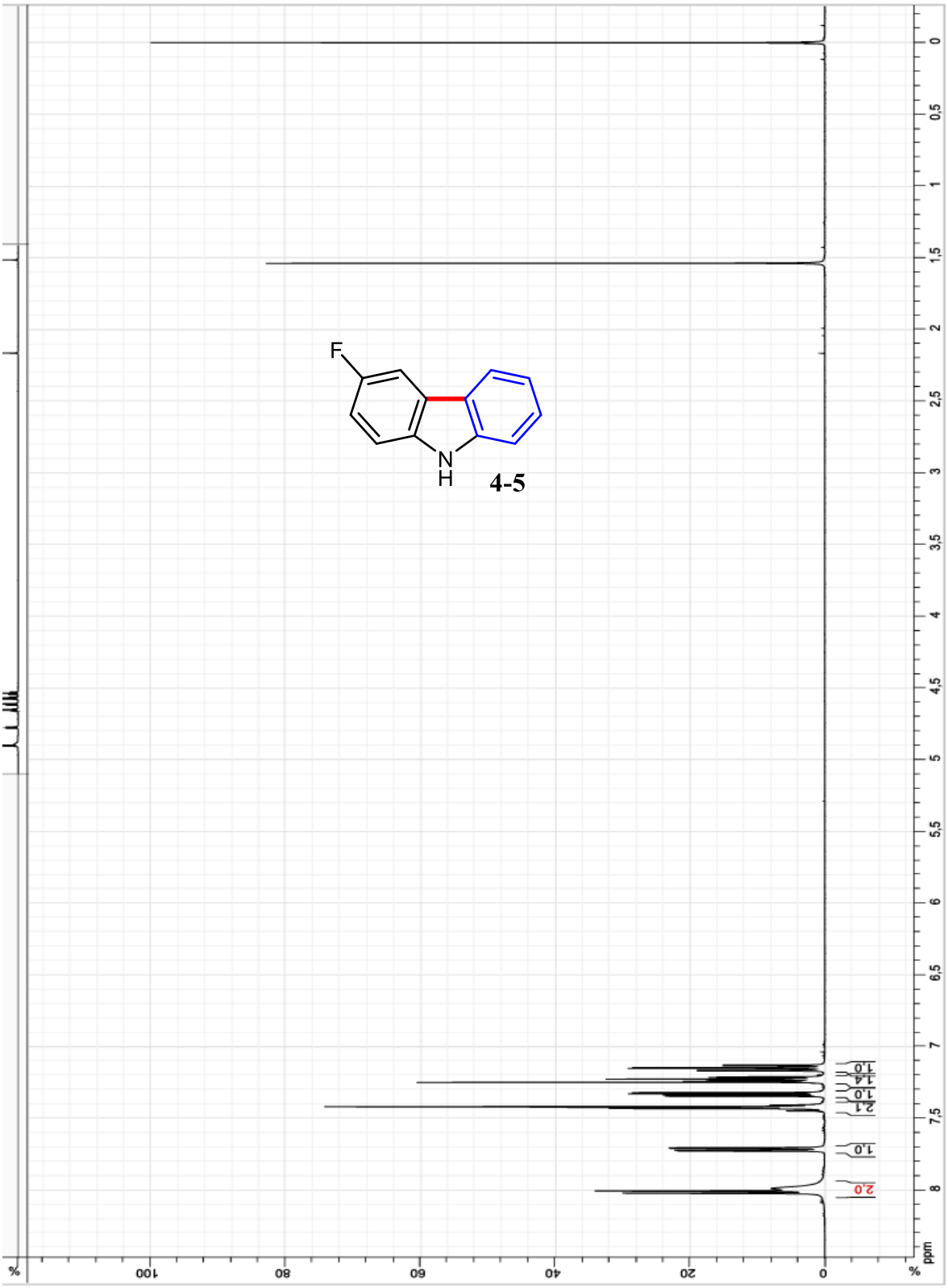
^{1}H NMR and ^{13}C NMR spectra of 3-(trifluoromethyl)-9*H*-carbazole (**4-4**) in $CDCl_3$

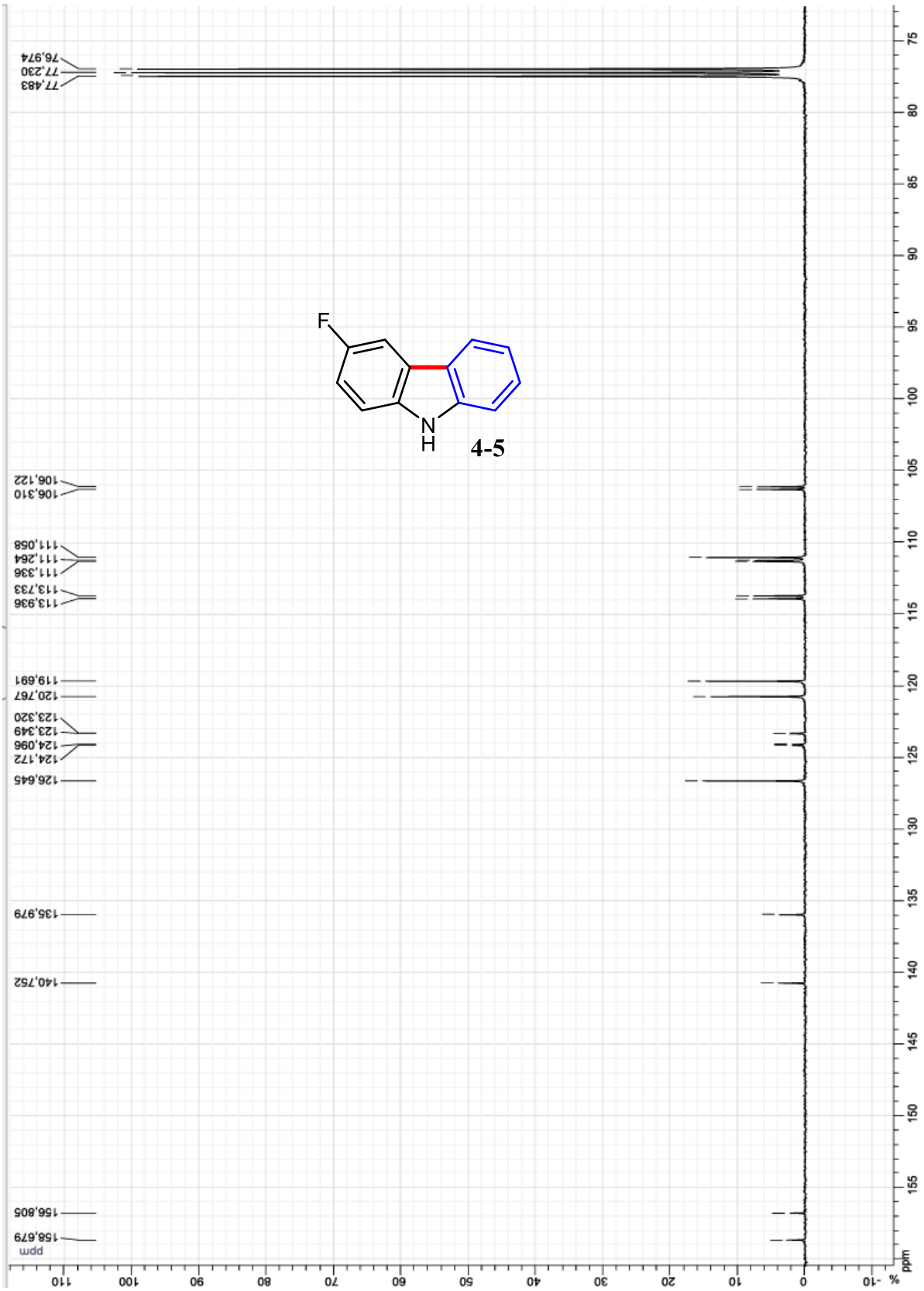


1.

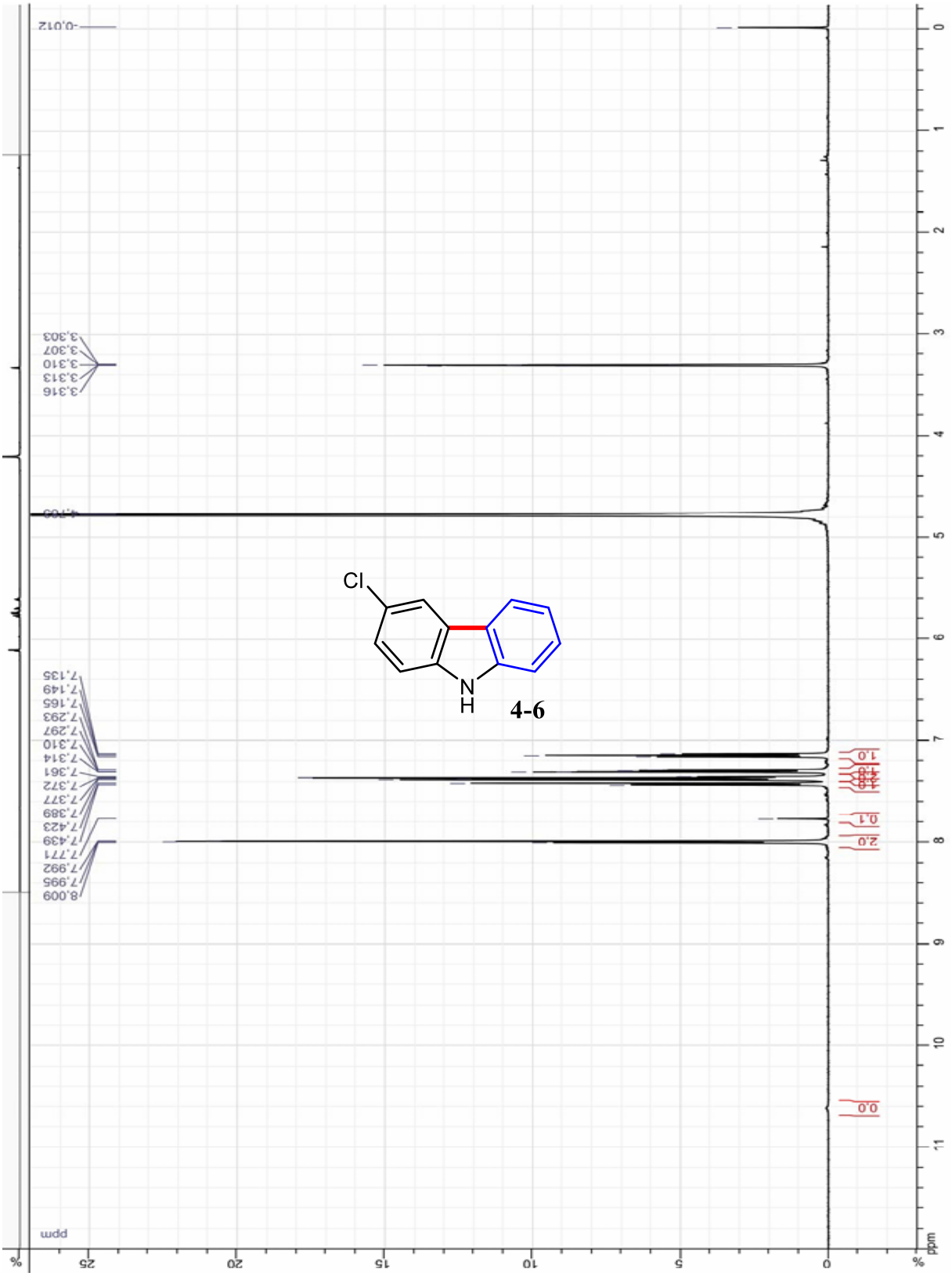

F
F
F
N
H
4-4

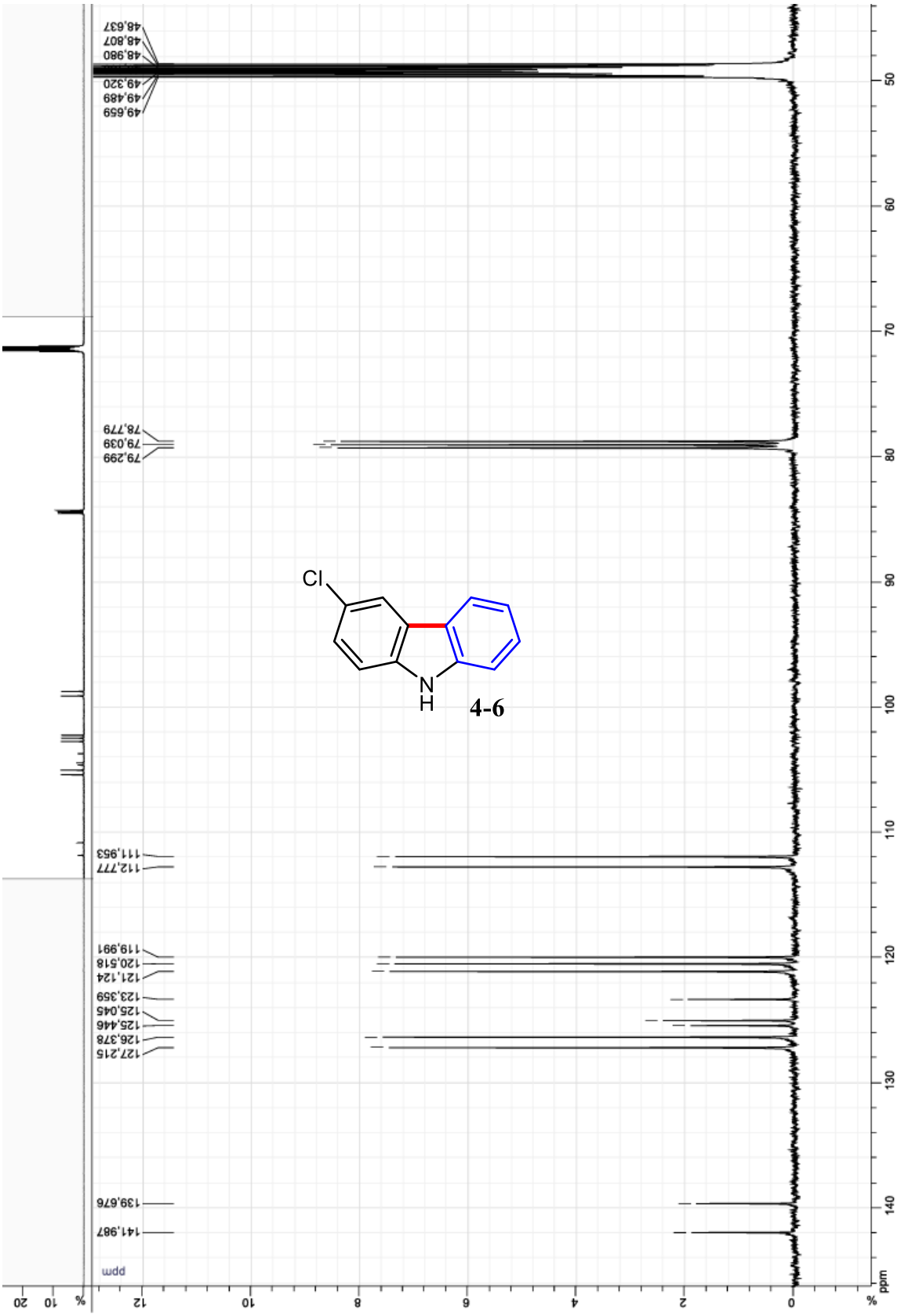
^{1}H NMR and ^{13}C NMR spectra of 3-fluoro-9*H*-carbazole (**4-5**) in $CDCl_3$



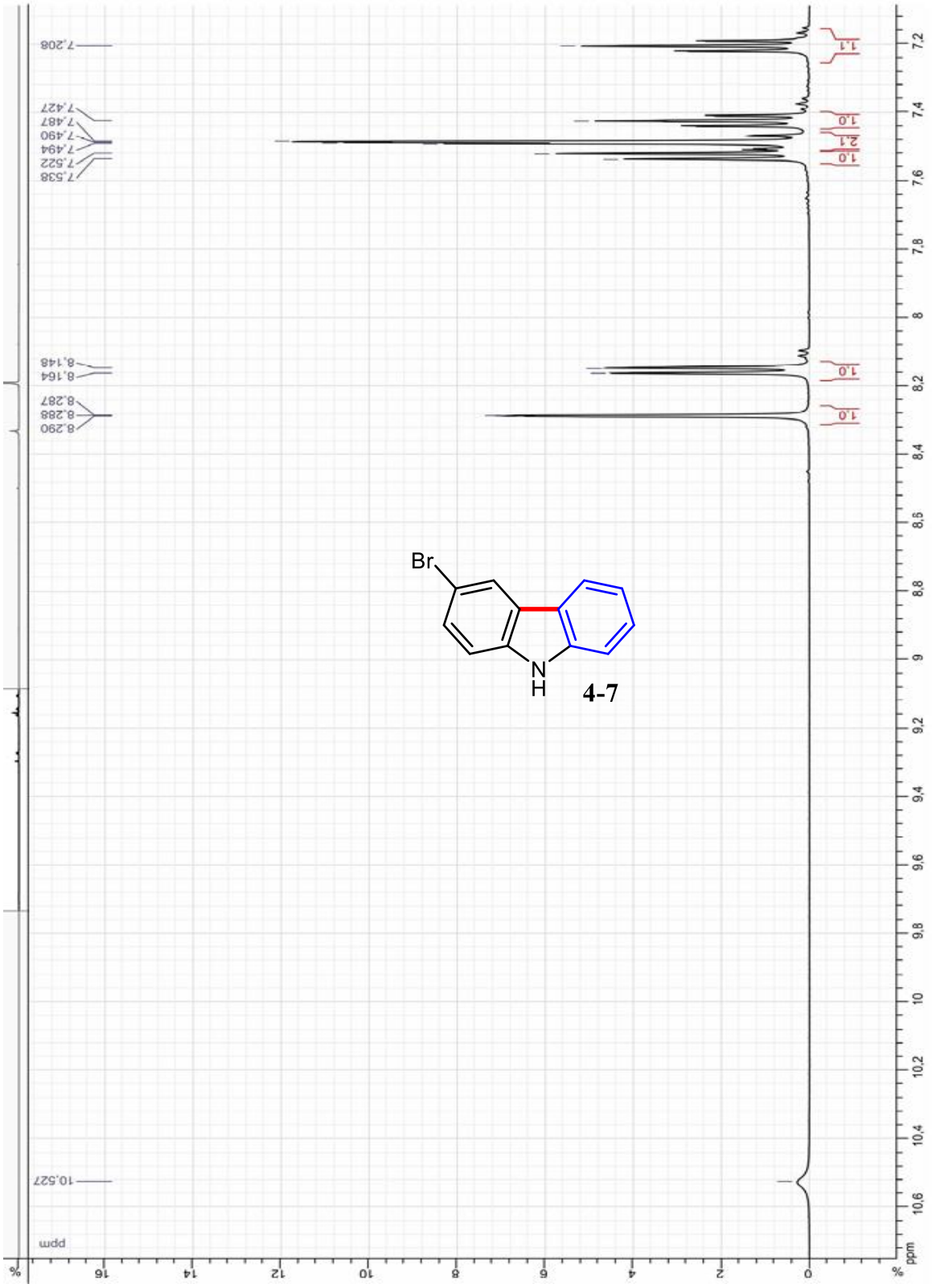

F
N
H
4-5
76.974
77.230
77.483
106.122
106.310
111.058
111.264
111.336
113.733
113.936
119.691
120.767
123.320
123.349
124.096
124.172
126.645
135.979
140.752
156.805
158.679
ppm

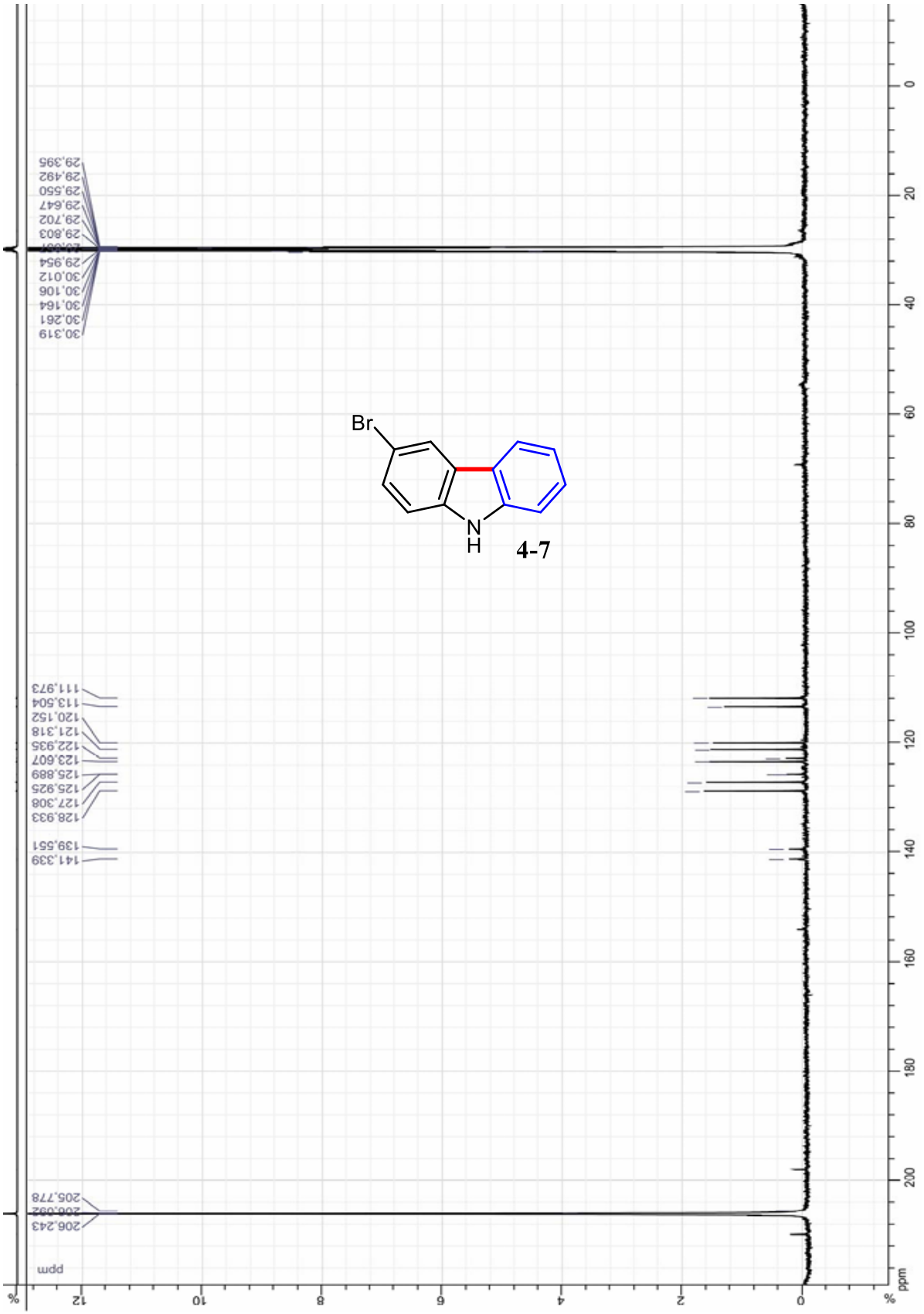
^{1}H NMR and ^{13}C NMR spectra of 3-chloro-9*H*-carbazole (**4-6**) in MeOD



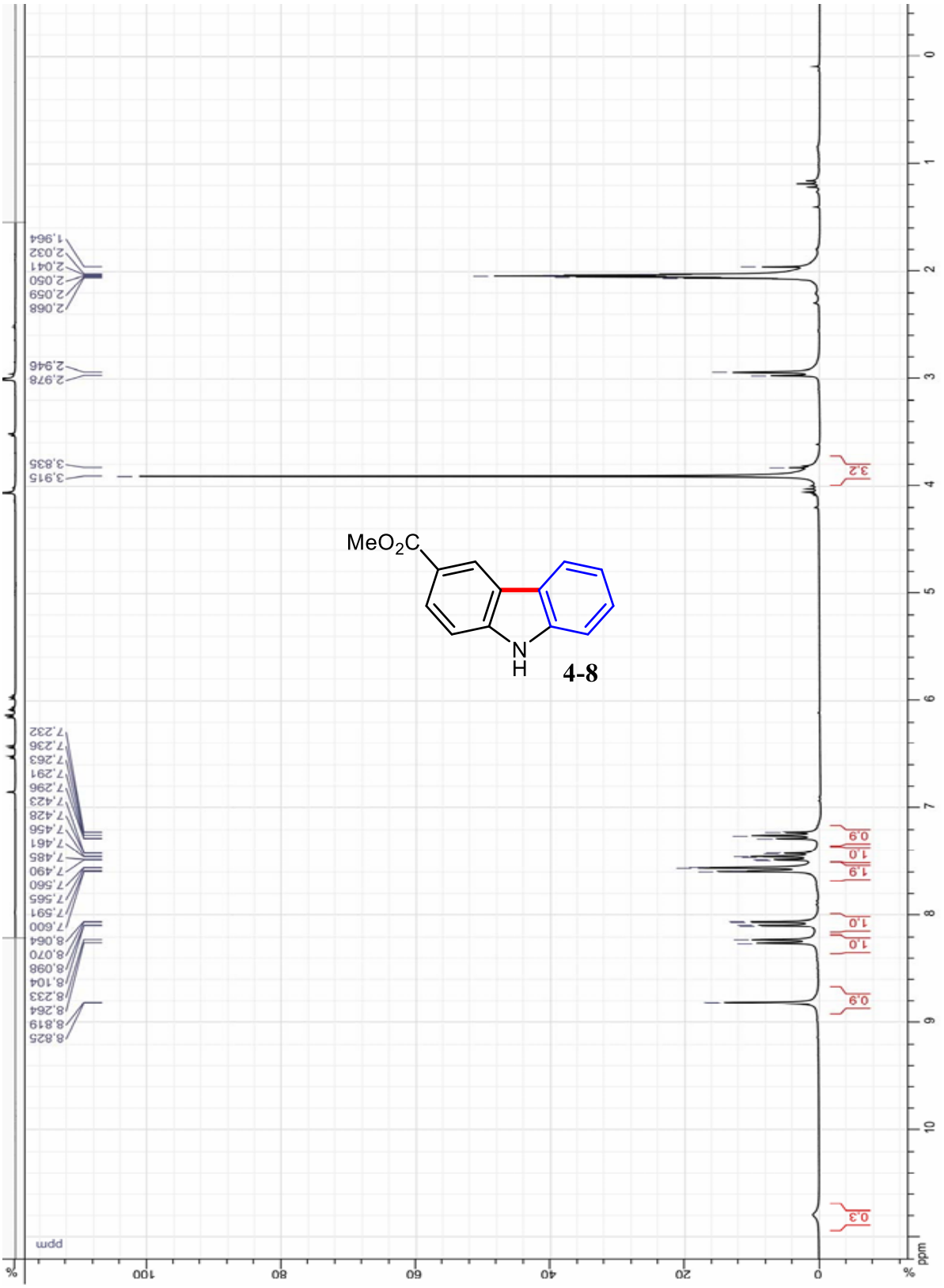

48.637
48.807
48.980
49.320
49.489
49.659
78.779
79.039
79.299
Cl
N
H
4-6
111.953
112.777
119.991
120.518
121.124
123.359
125.045
125.446
126.378
127.215
139.676
141.987
ppm

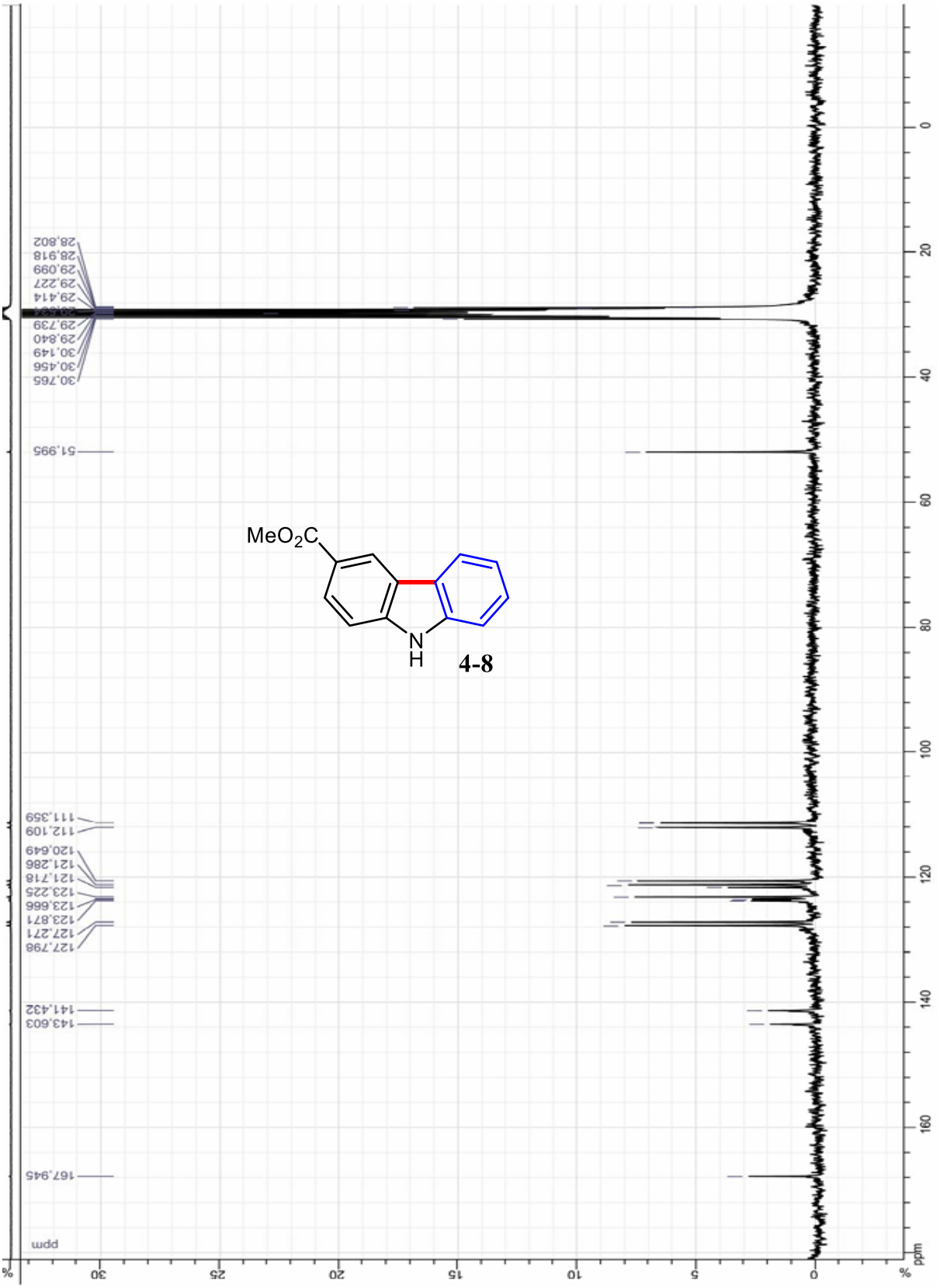
^{1}H NMR and ^{13}C NMR spectra of 3-bromo-9*H*-carbazole (**4-7**) in Acetone-D_6



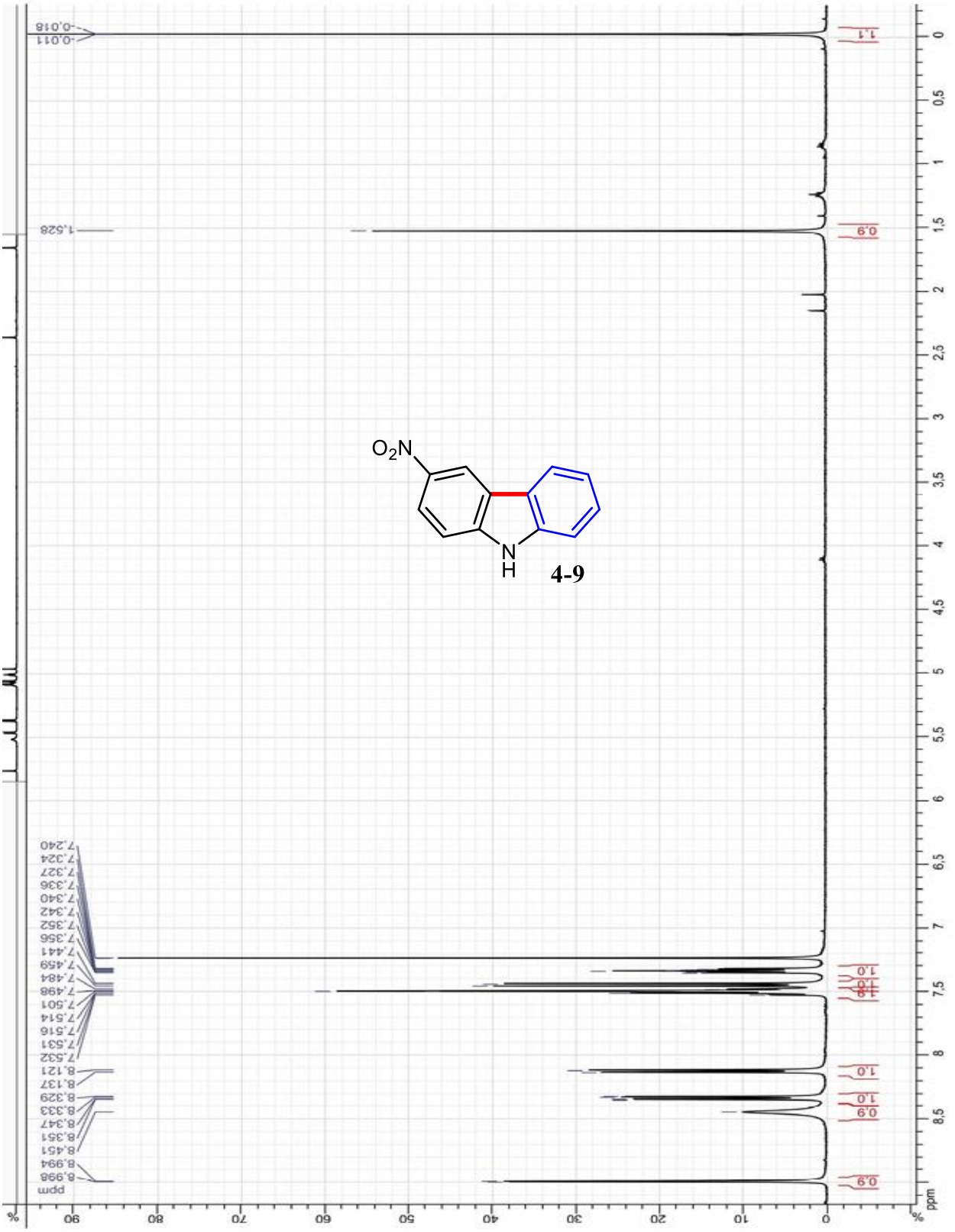

Br
N
H
4-7

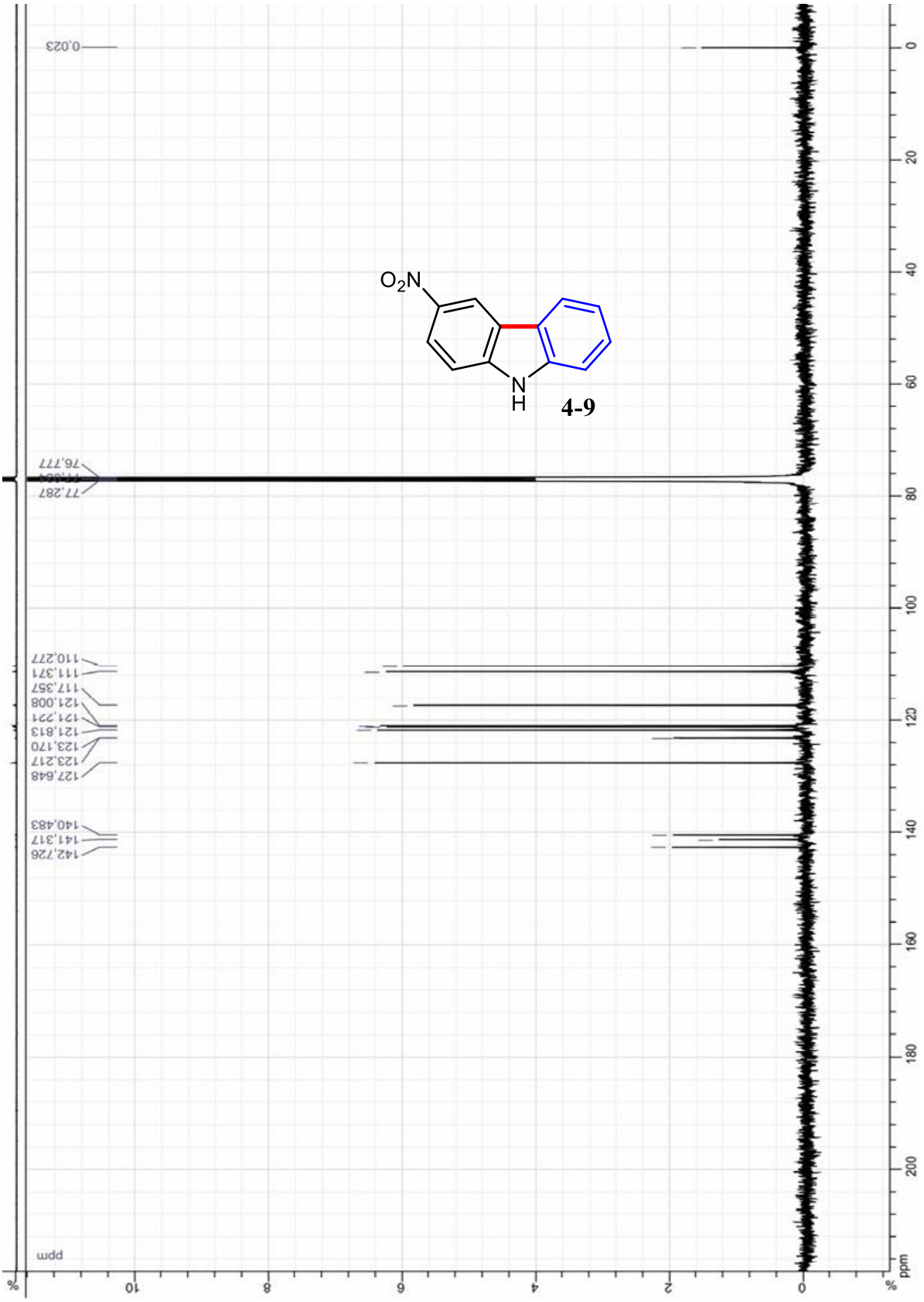
^{1}H NMR and ^{13}C NMR spectra of methyl 9*H*-carbazole-3-carboxylate (**4-8**) in Acetone-D_6



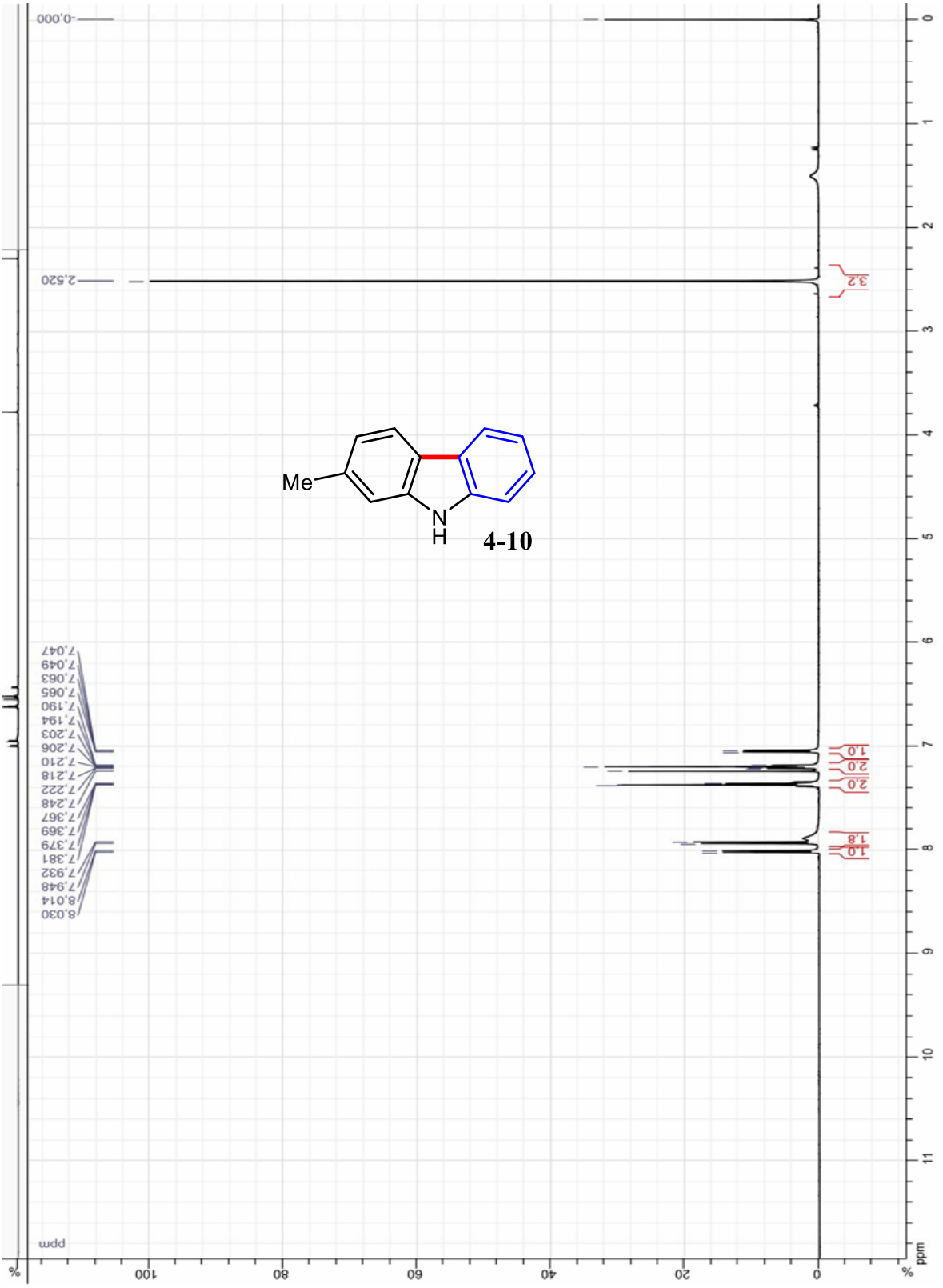

MeO2C
N
H
4-8

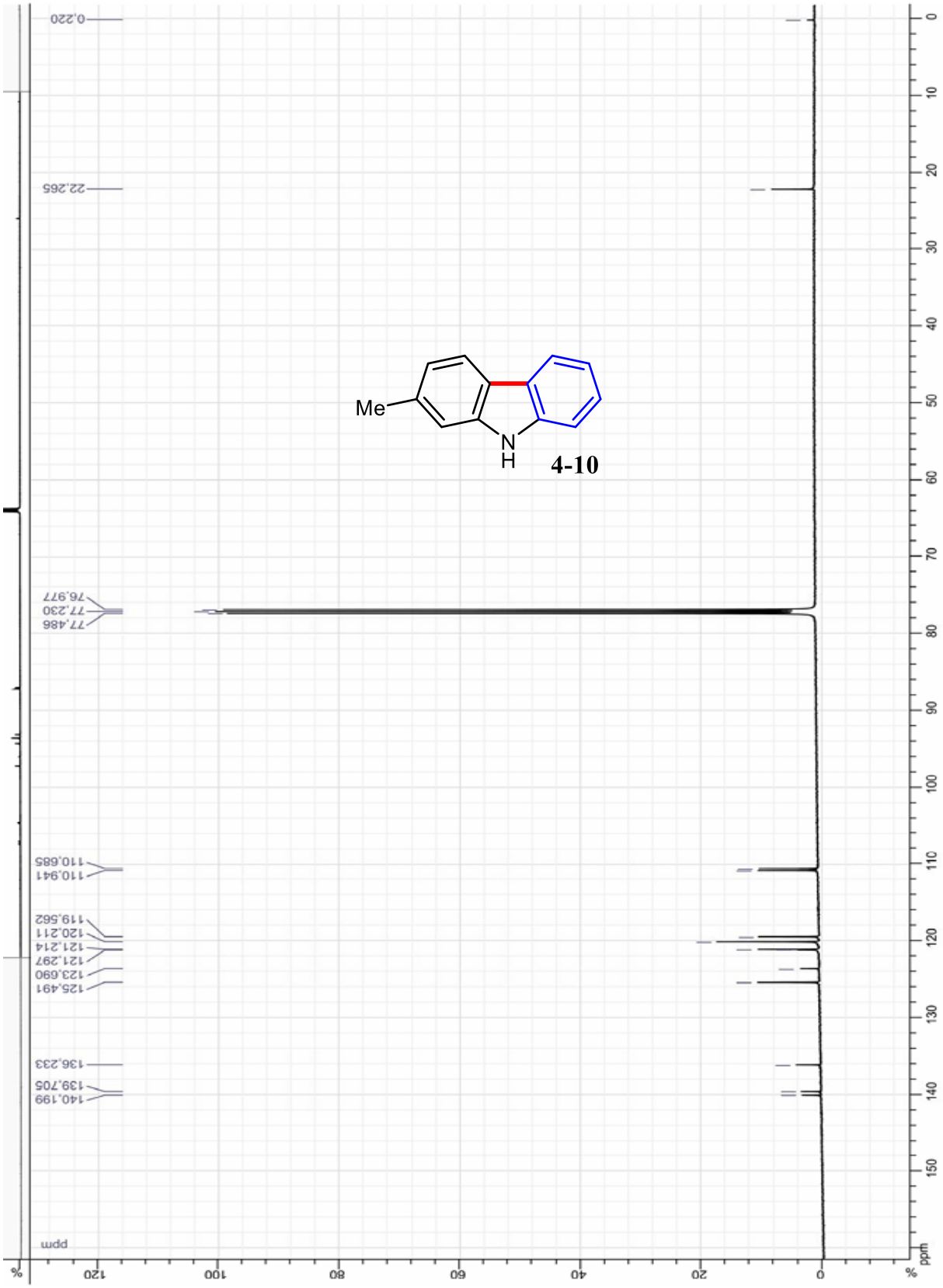
^{1}H NMR and ^{13}C NMR spectra of 3-nitro-9*H*-carbazole (**4-9**) in $CDCl_3$



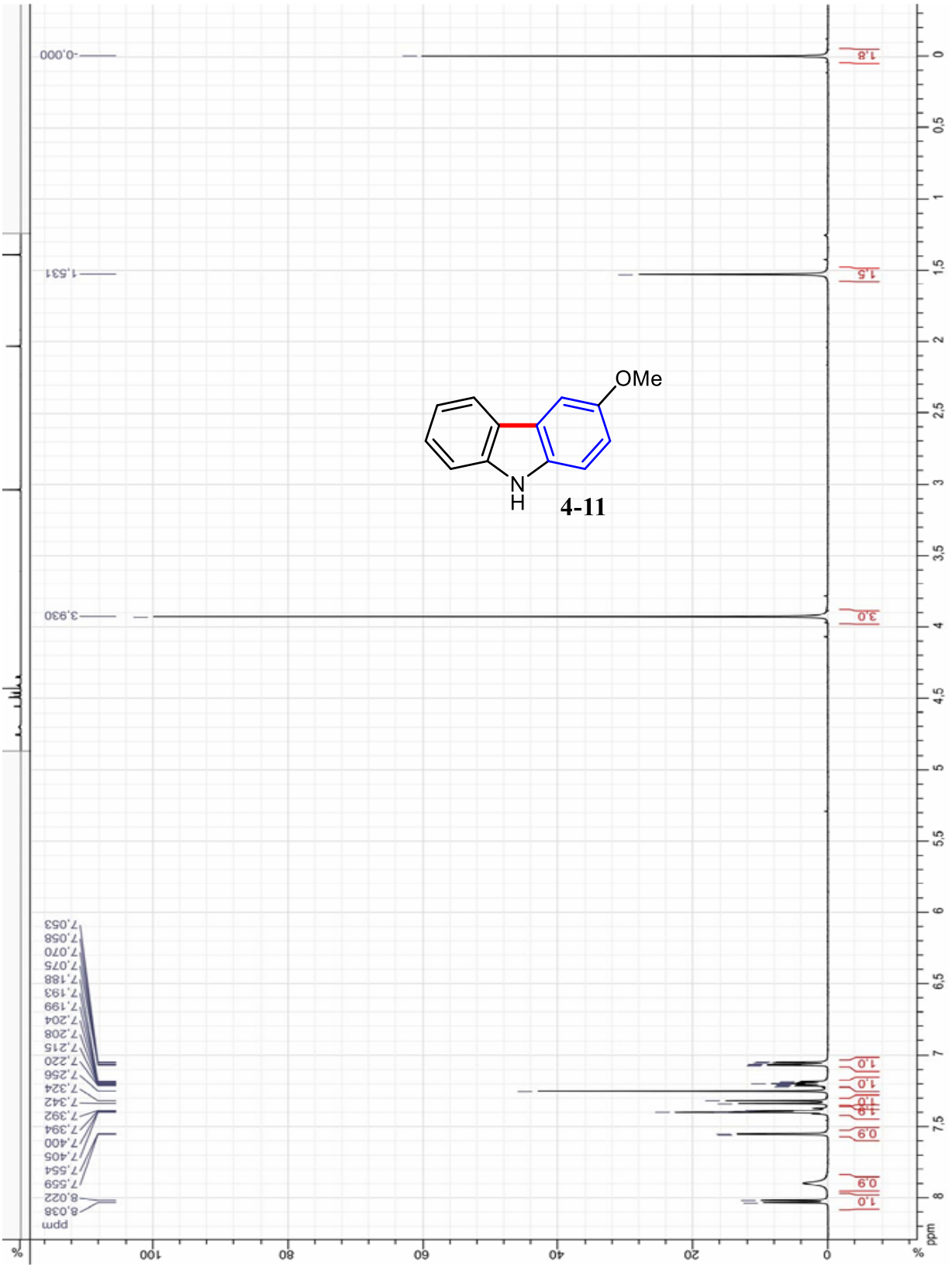

O2N
N
H
4-9
0.023
76.777
77.287
110.277
111.371
117.357
121.008
121.221
121.813
123.170
123.217
127.648
140.483
141.317
142.726
ppm

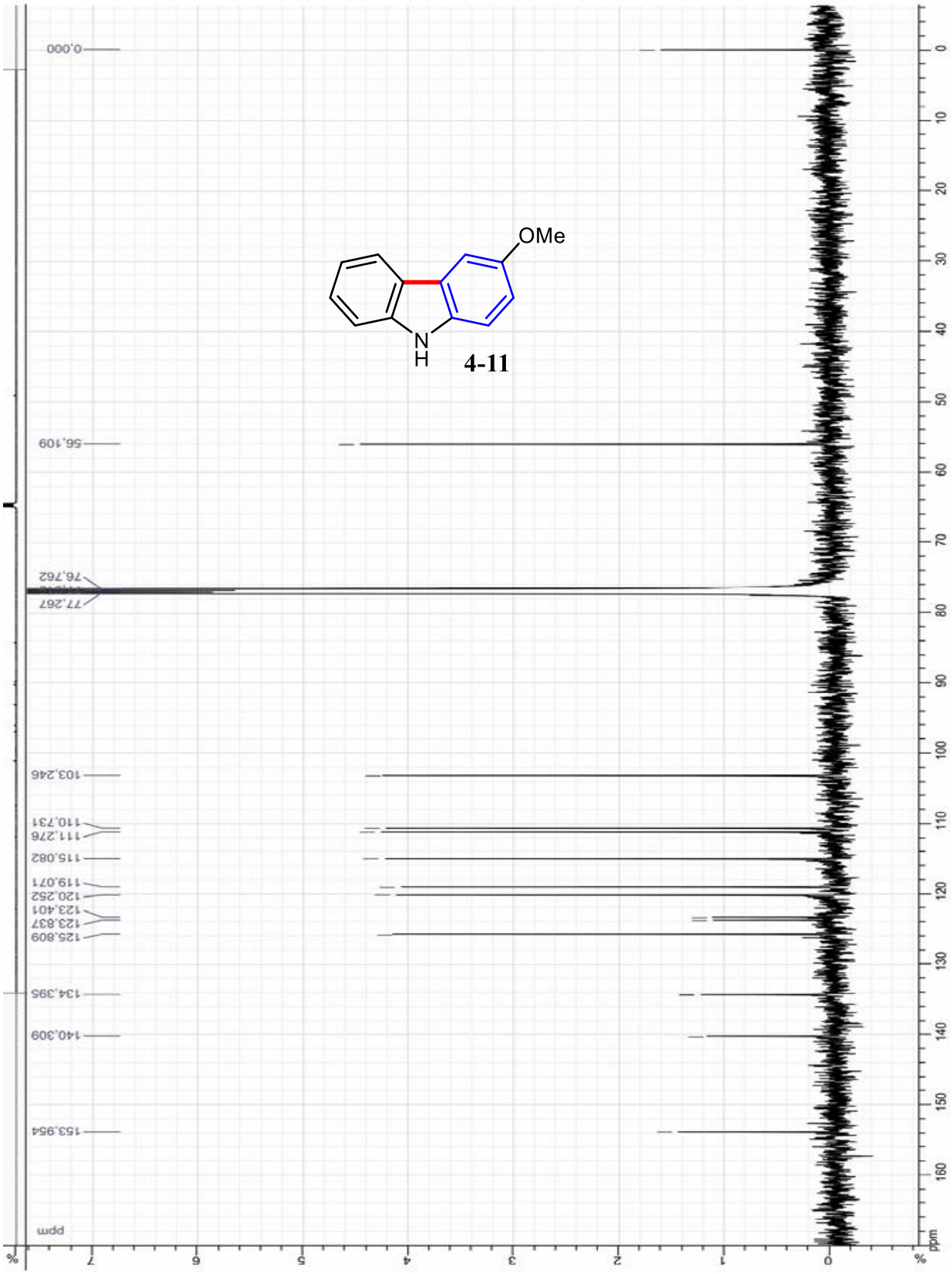
^{1}H NMR and ^{13}C NMR spectra of 2-methyl-9*H*-carbazole (**4-10**) in $CDCl_3$



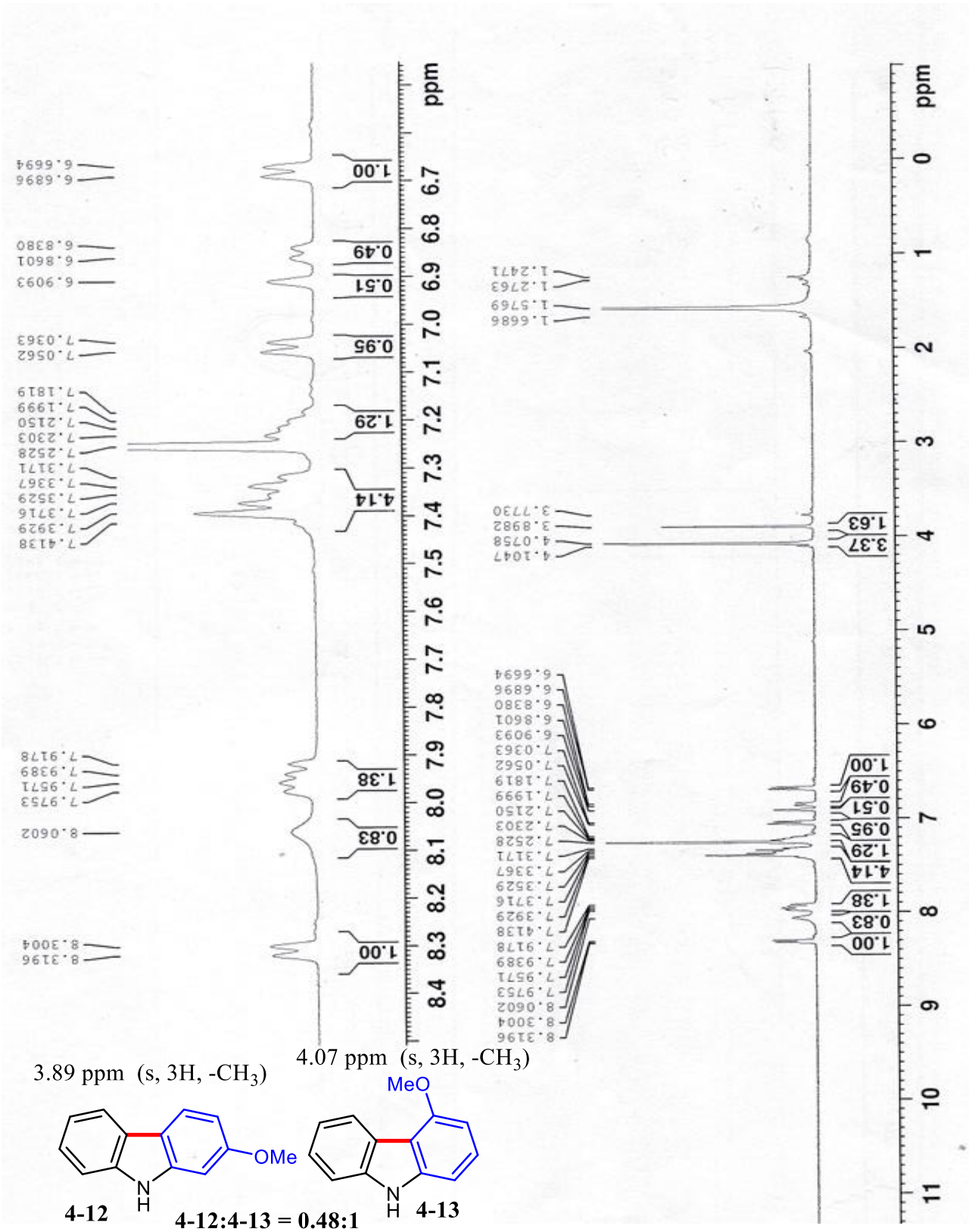

Me
N
H
4-10
0.220
22.265
76.977
77.230
77.486
110.685
110.941
119.562
120.211
121.214
121.297
123.690
125.491
136.233
139.705
140.199
ppm

^{1}H NMR and ^{13}C NMR spectra of 3-methoxy-9*H*-carbazole (**4-11**) in $CDCl_3$

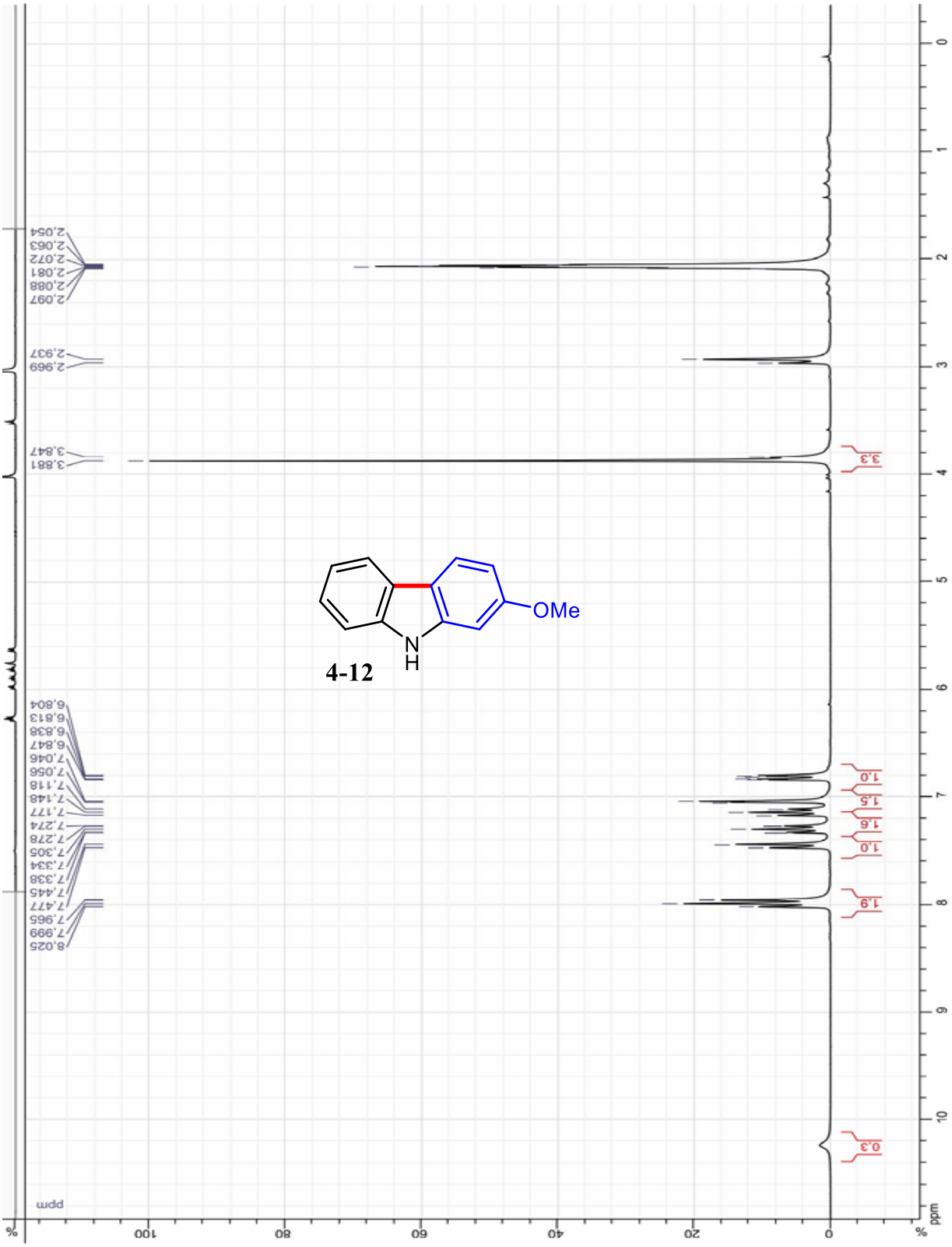


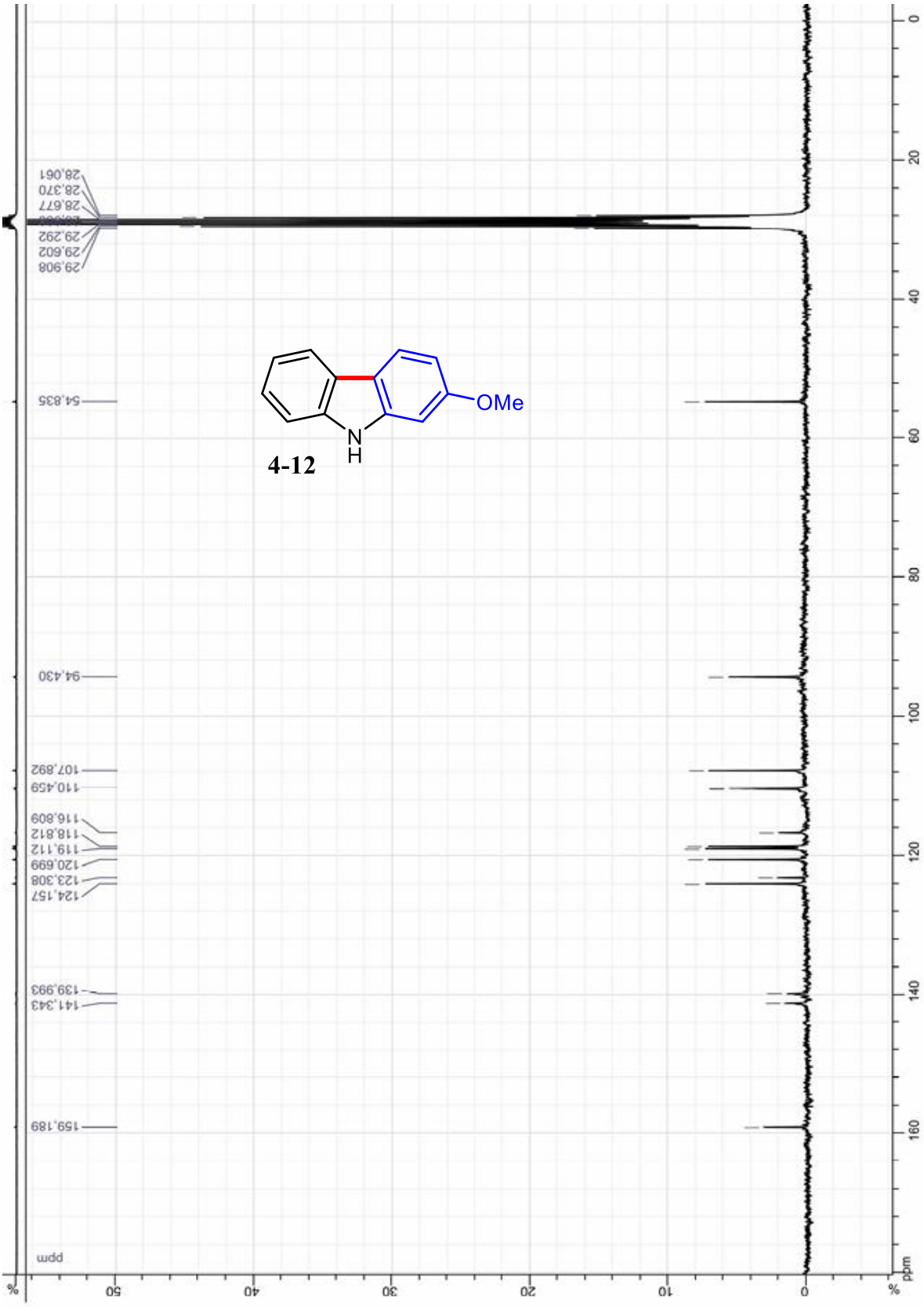

OMe
N
H
4-11
0.000
56.109
76.762
77.267
103.246
110.731
111.276
115.082
119.071
120.252
123.401
123.837
125.809
134.395
140.309
153.954
ppm

^{1}H NMR spectrum of the reaction mixture of **3ah** to get regioisomeric ratio (C2:C4) of **4-12** and **4-13** in $CDCl_3$



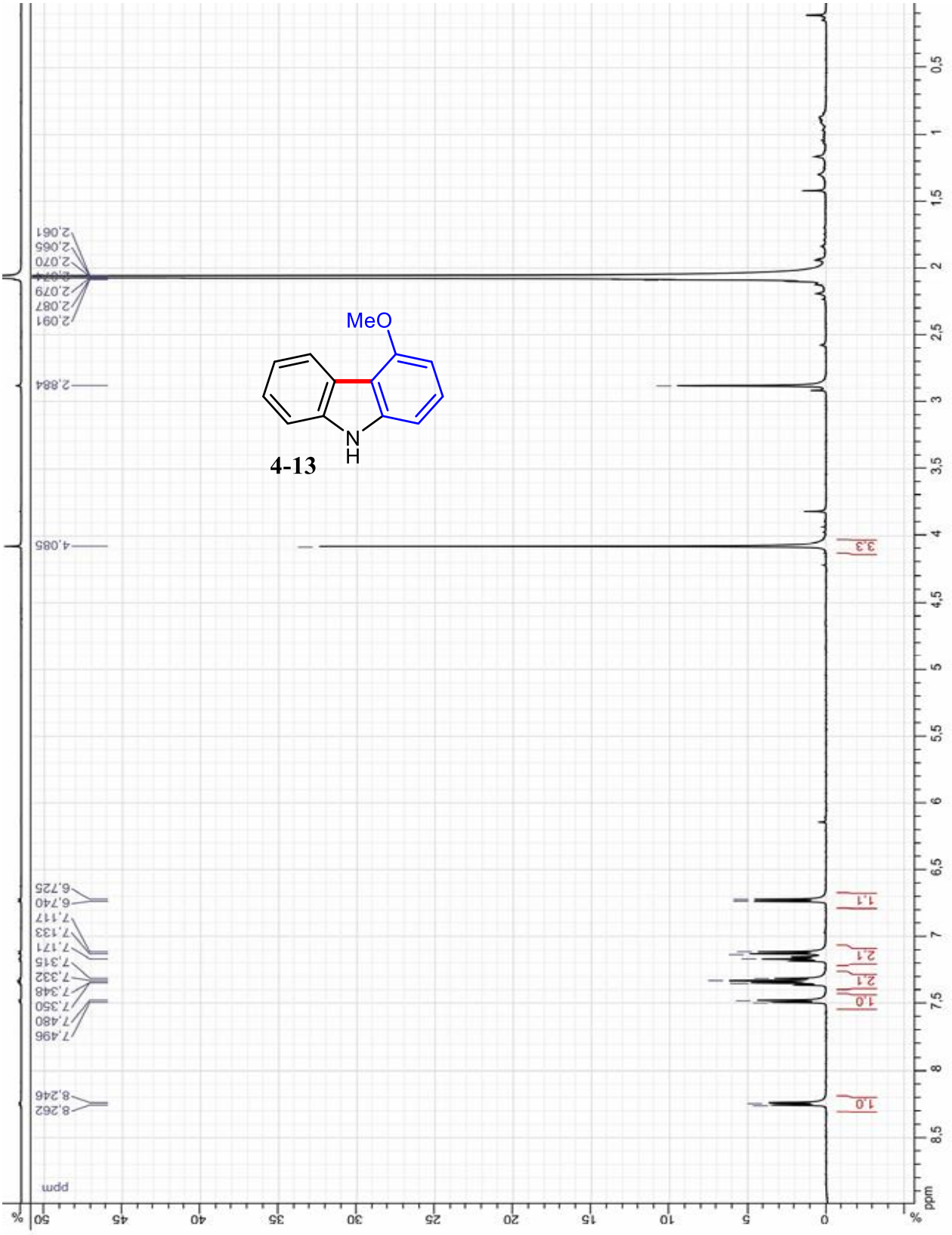
^{1}H NMR and ^{13}C NMR spectra of 2-methoxy-9*H*-carbazole (**4-12**) in Acetone-D_6

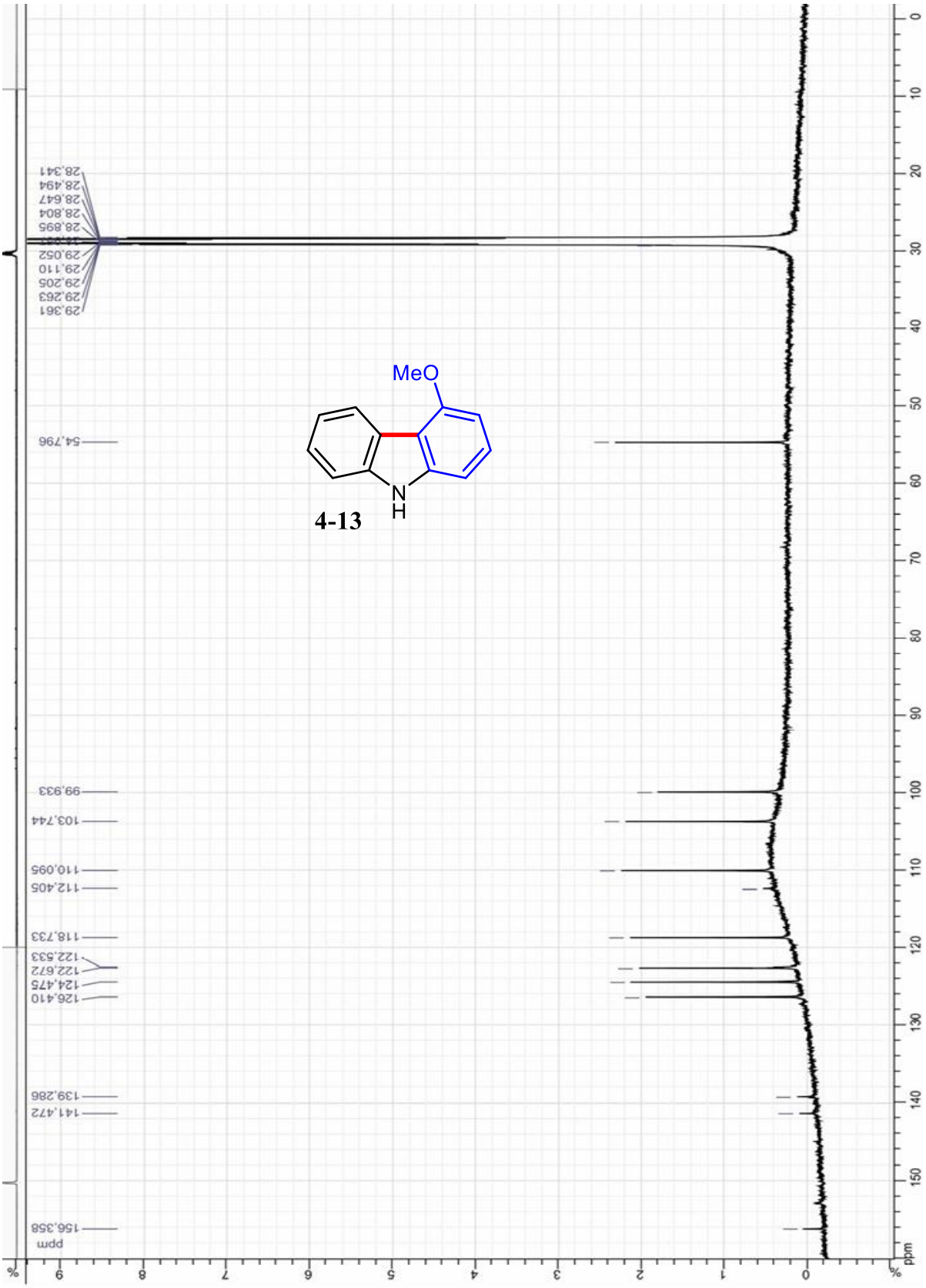



28.061
28.370
28.677
29.292
29.602
29.908
54.835
94.430
107.892
110.459
116.809
118.812
119.112
120.699
123.308
124.157
139.993
141.343
159.189
ppm
0
20
40
60
80
100
120
140
160
OMe
N
H

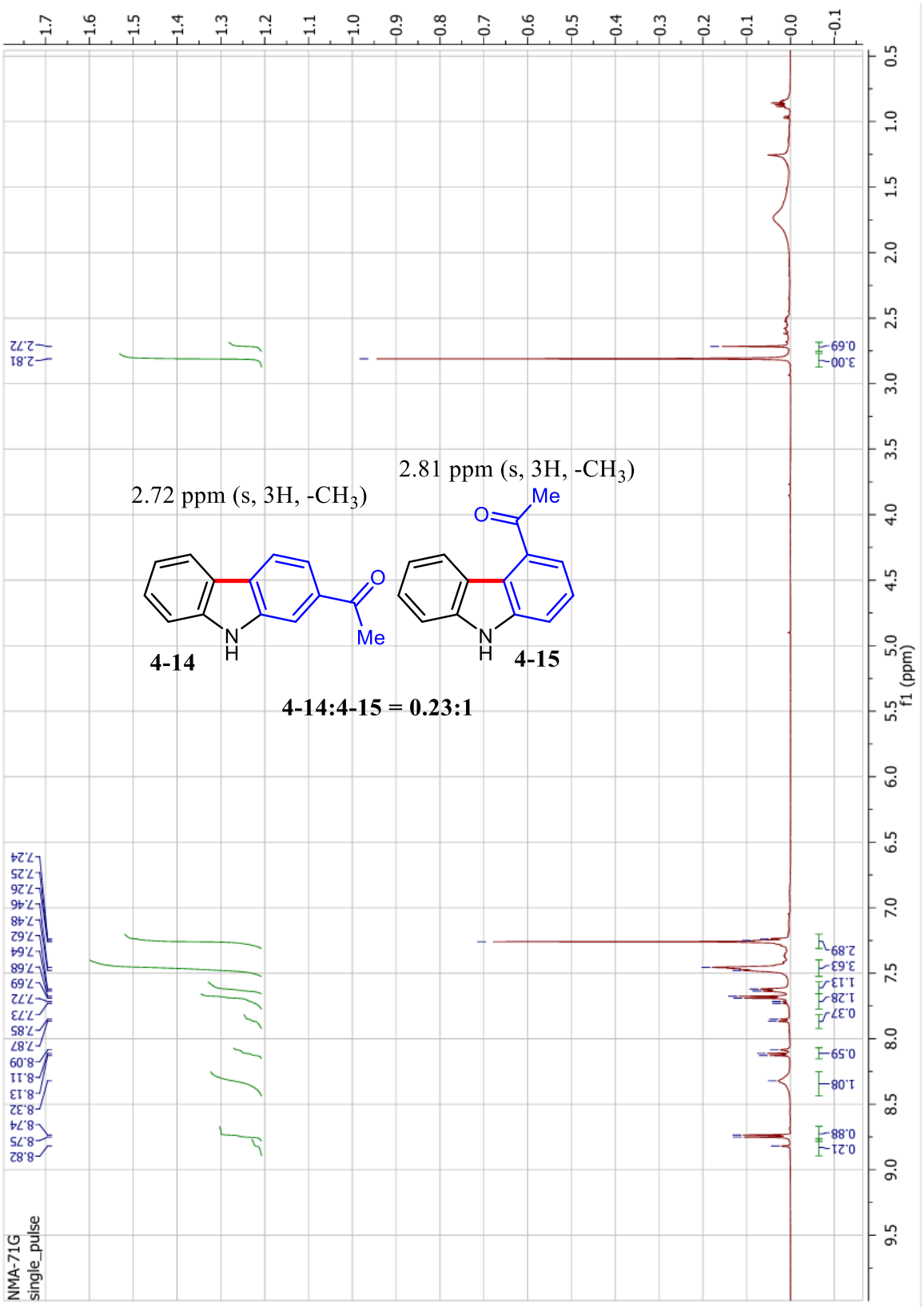
4-12

^{1}H NMR and ^{13}C NMR spectra of 4-methoxy-9*H*-carbazole (**4-13**) in Acetone-D_6

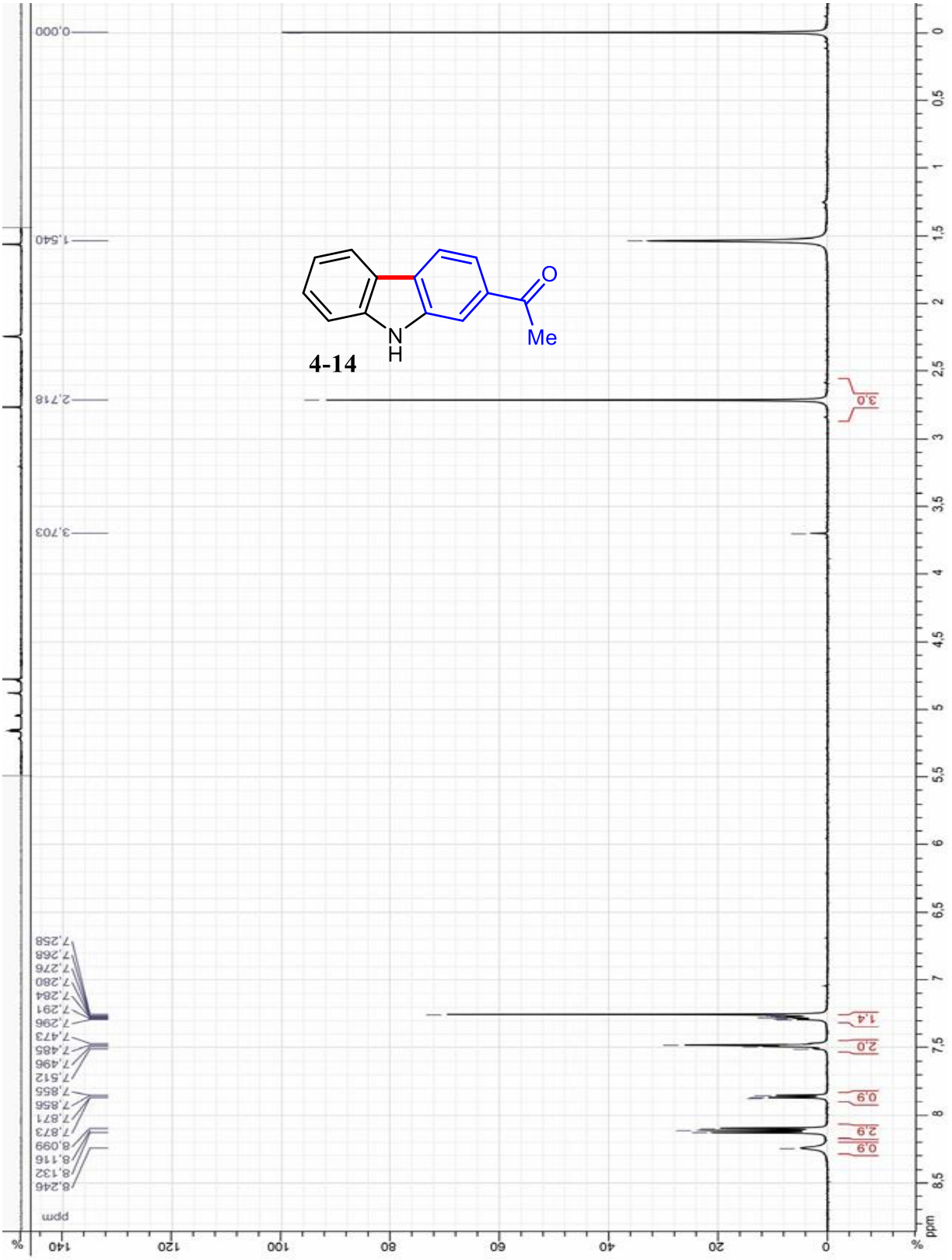


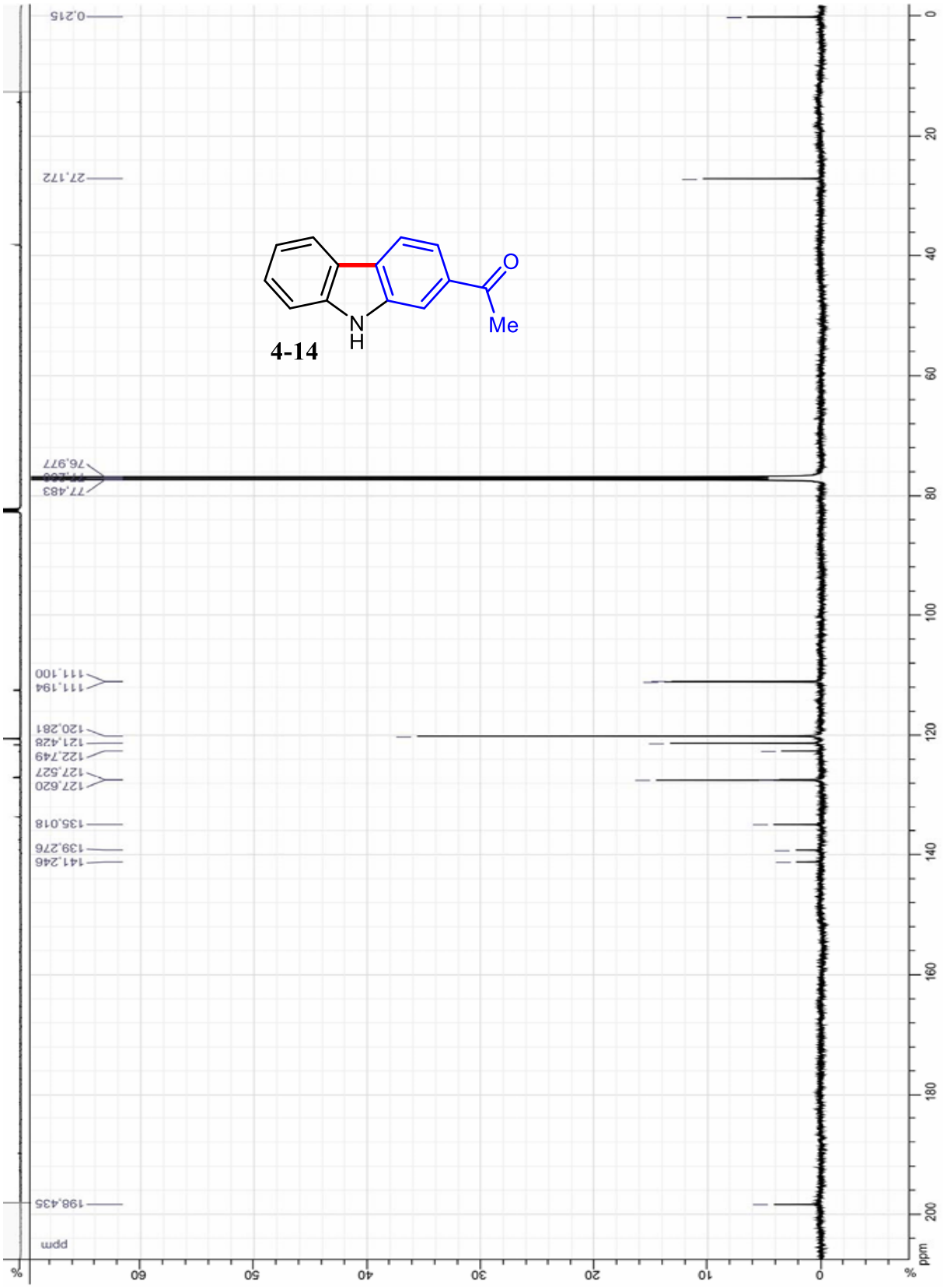

MeO
N
H
4-13
28.341
28.494
28.647
28.804
28.895
29.052
29.110
29.205
29.263
29.361
54.796
99.933
103.744
110.095
112.405
118.733
122.533
122.672
124.475
126.410
139.286
141.472
156.358
ppm

^{1}H NMR spectrum of the reaction mixture of **3ai** to get regioisomeric ratio (C2:C4) of **4-14** and **4-15** in $CDCl_3$

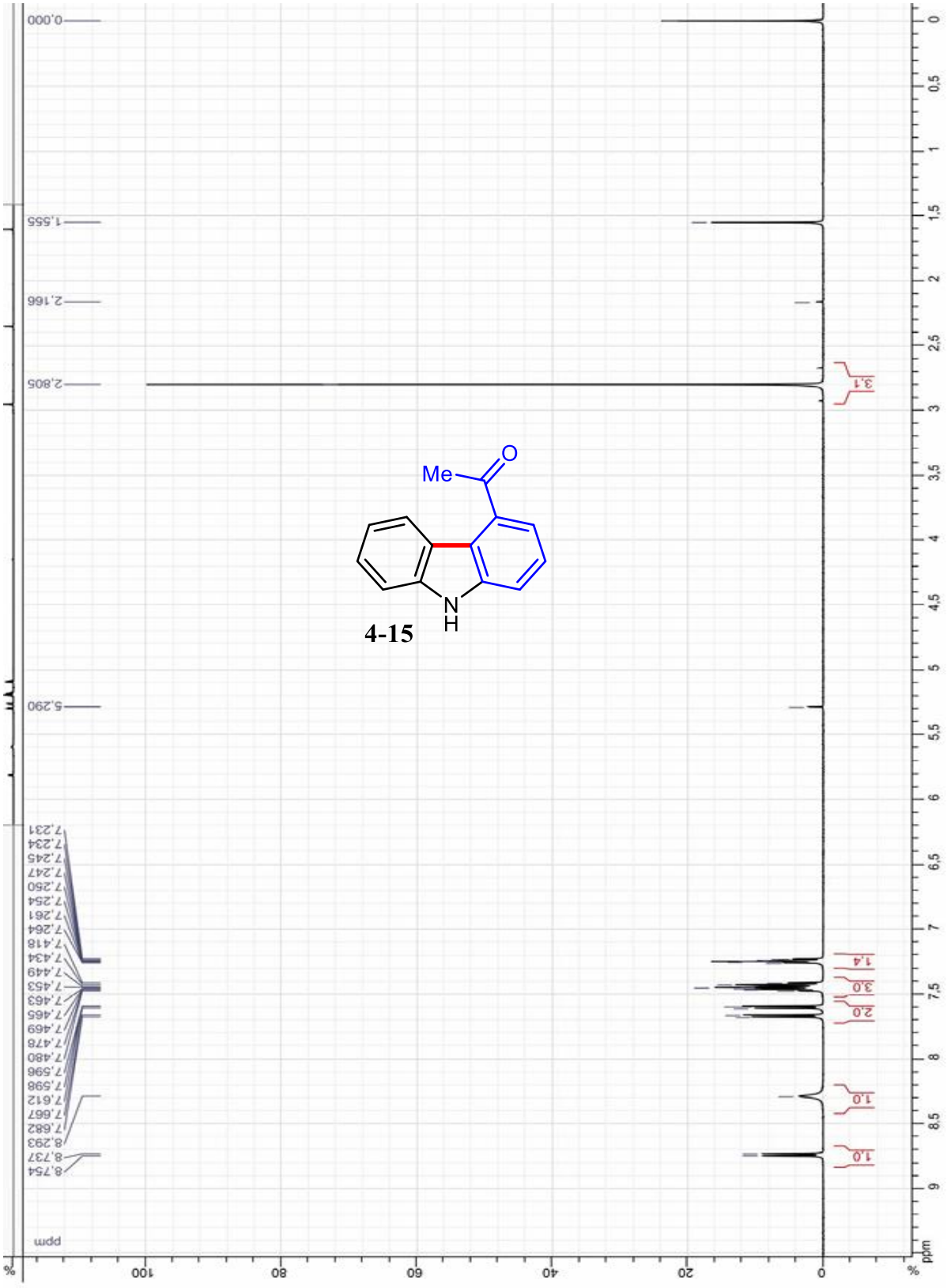


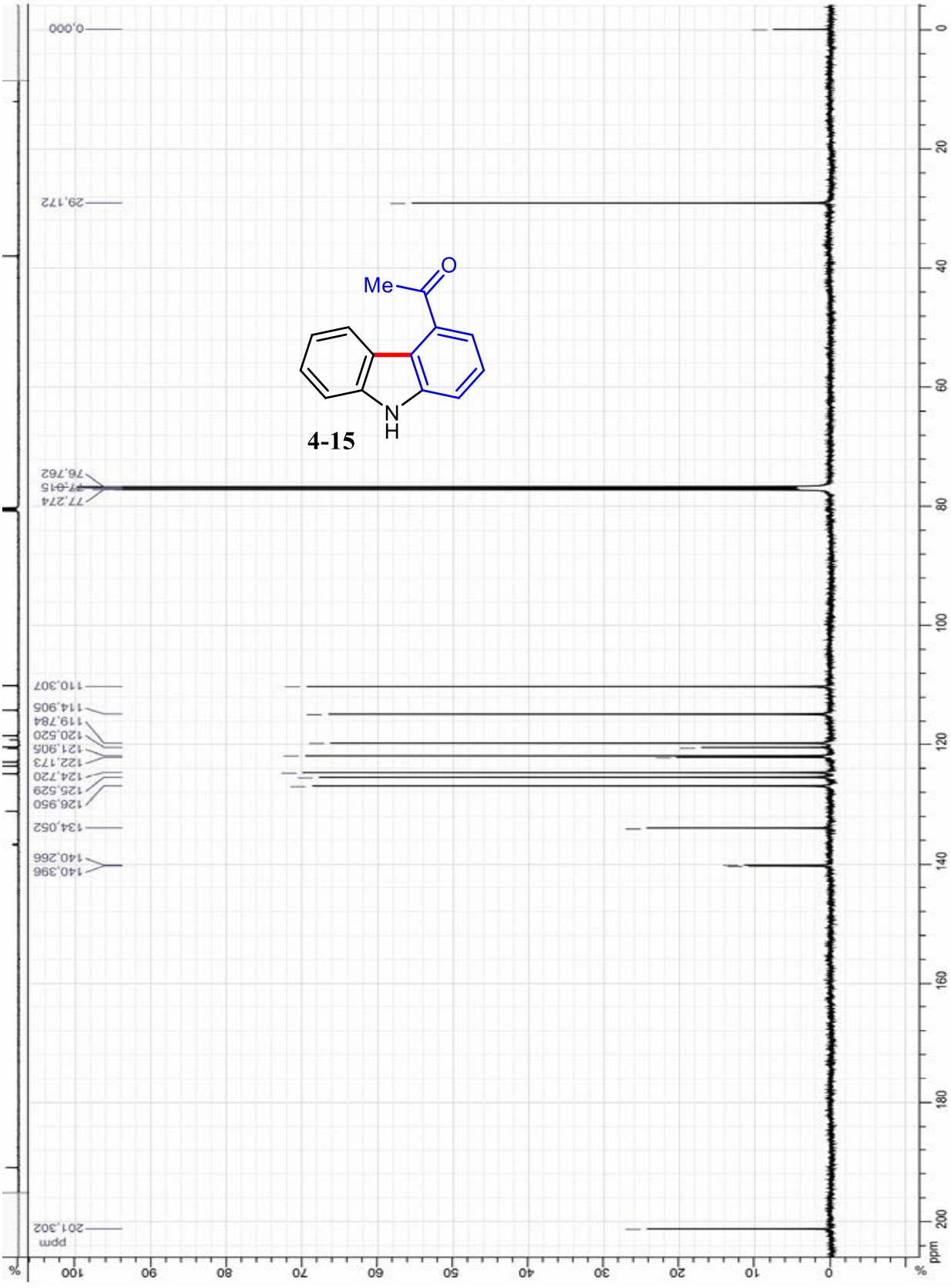
^{1}H NMR and ^{13}C NMR spectra of 1-(9*H*-carbazol-2-yl)ethan-1-one (**4-14**) in $CDCl_3$



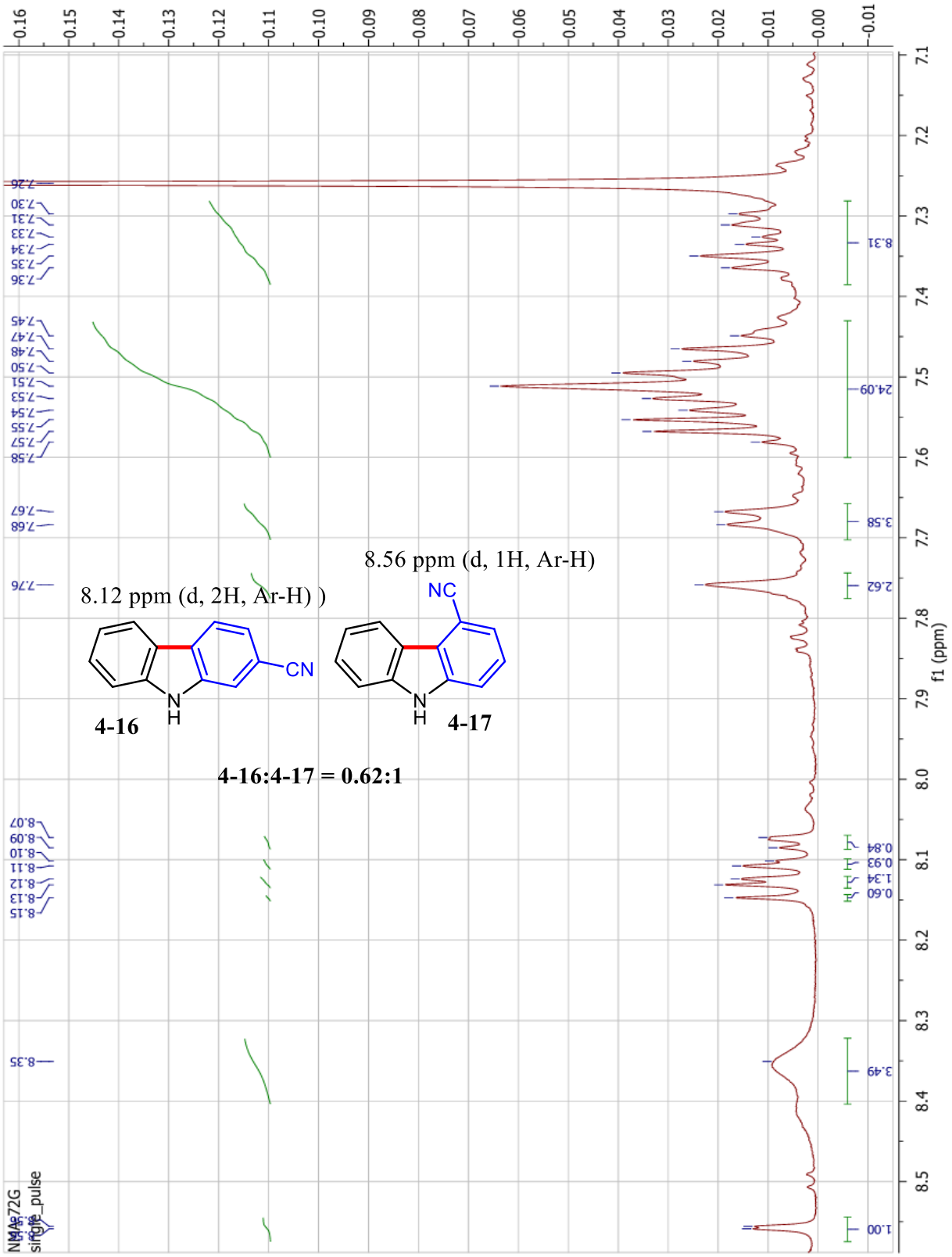

O
Me
N
H
4-14
0.215
27.172
76.977
77.283
111.100
111.194
120.281
121.428
122.749
127.527
127.620
135.018
139.276
141.246
198.435
ppm

^{1}H NMR and ^{13}C NMR spectra of 1-(9*H*-carbazol-4-yl)ethan-1-one (**4-15**) in $CDCl_3$

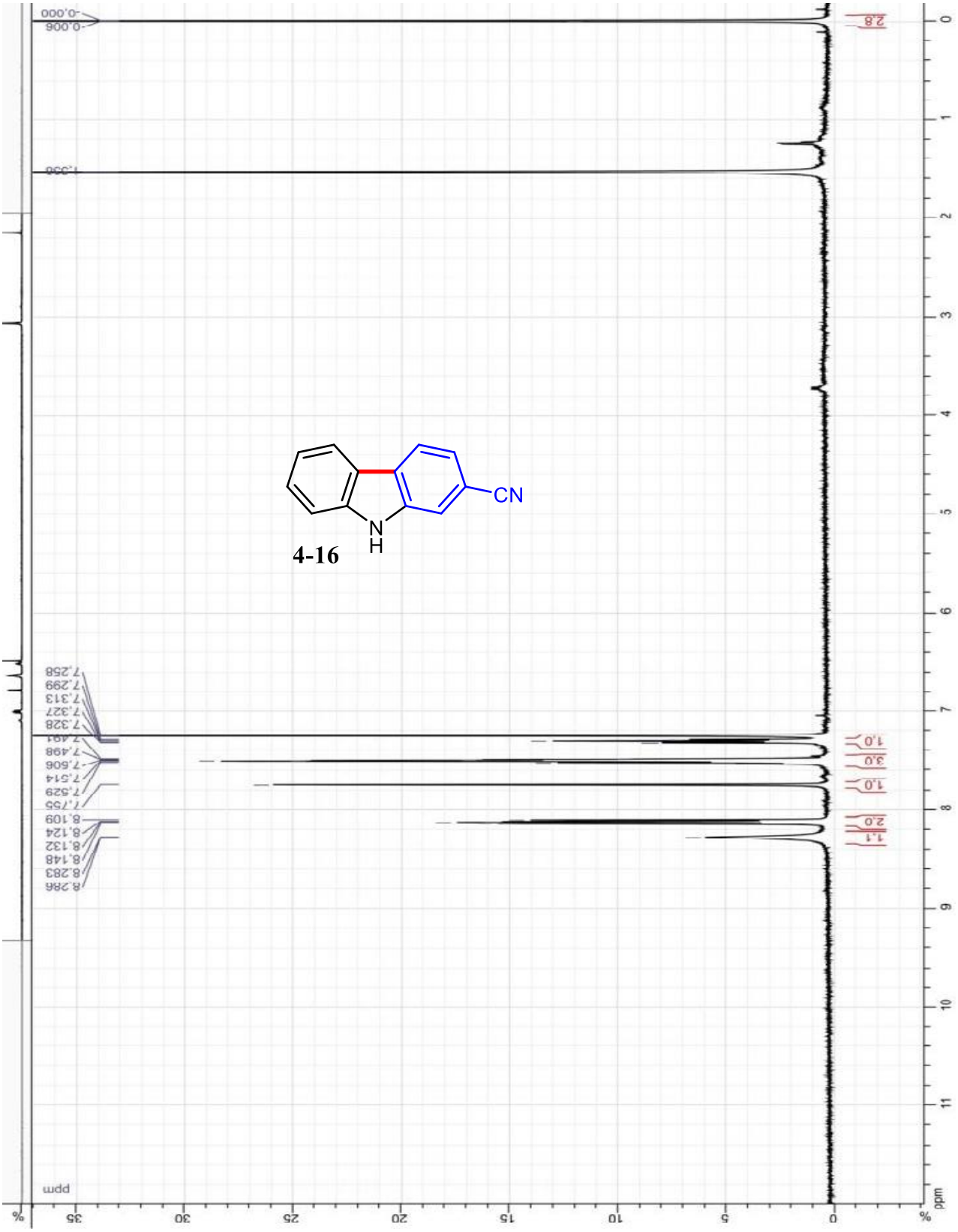


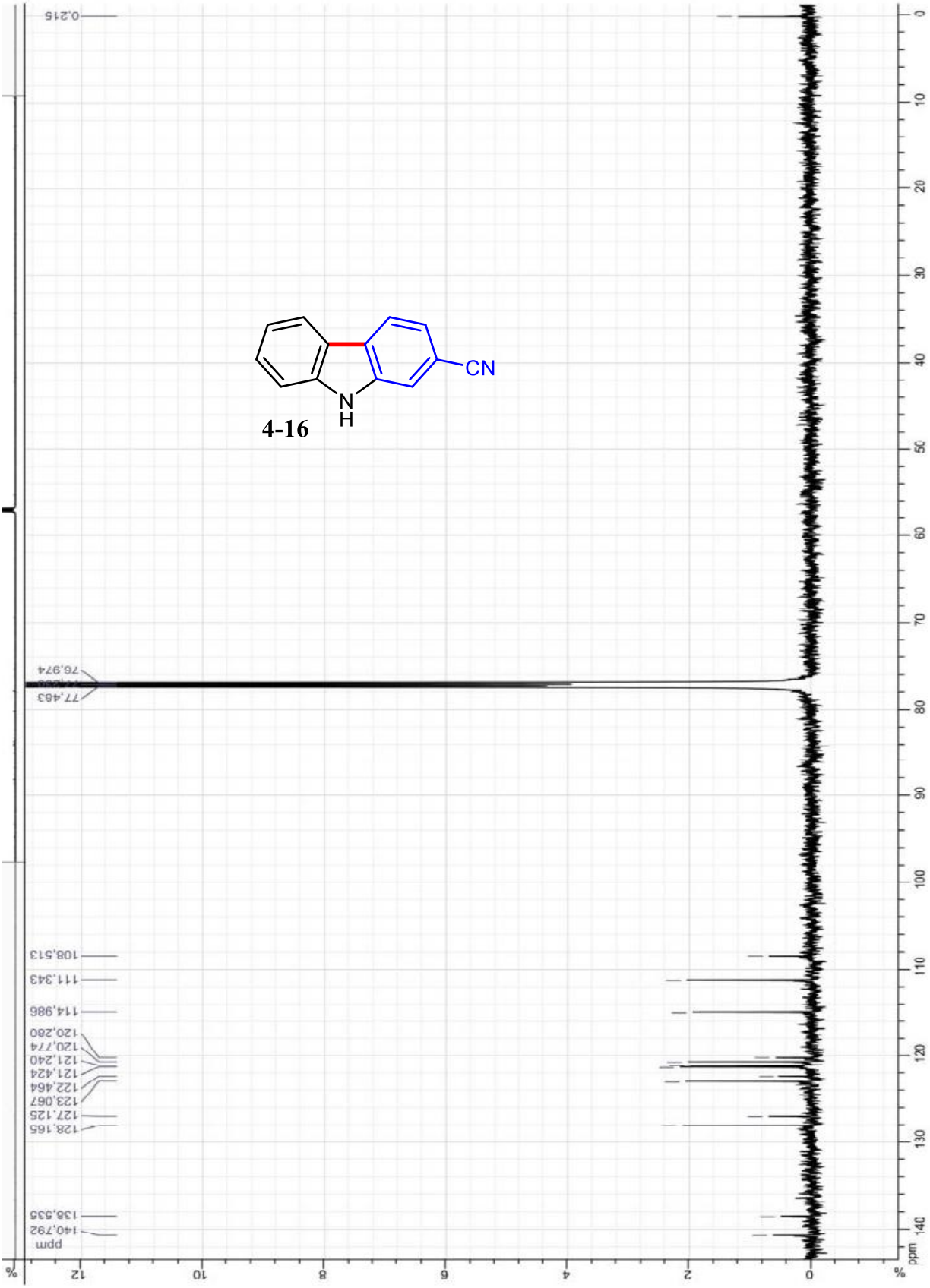

Me
O
N
H
4-15
0.000
29.172
76.762
77.274
110.307
114.905
119.784
120.520
121.905
122.173
124.720
125.529
126.950
134.052
140.266
140.396
201.302
ppm

^{1}H NMR spectrum of the reaction mixture of **3aj** to get regioisomeric ratio (C2:C4) of **4-1** and **4-17** in $CDCl_3$

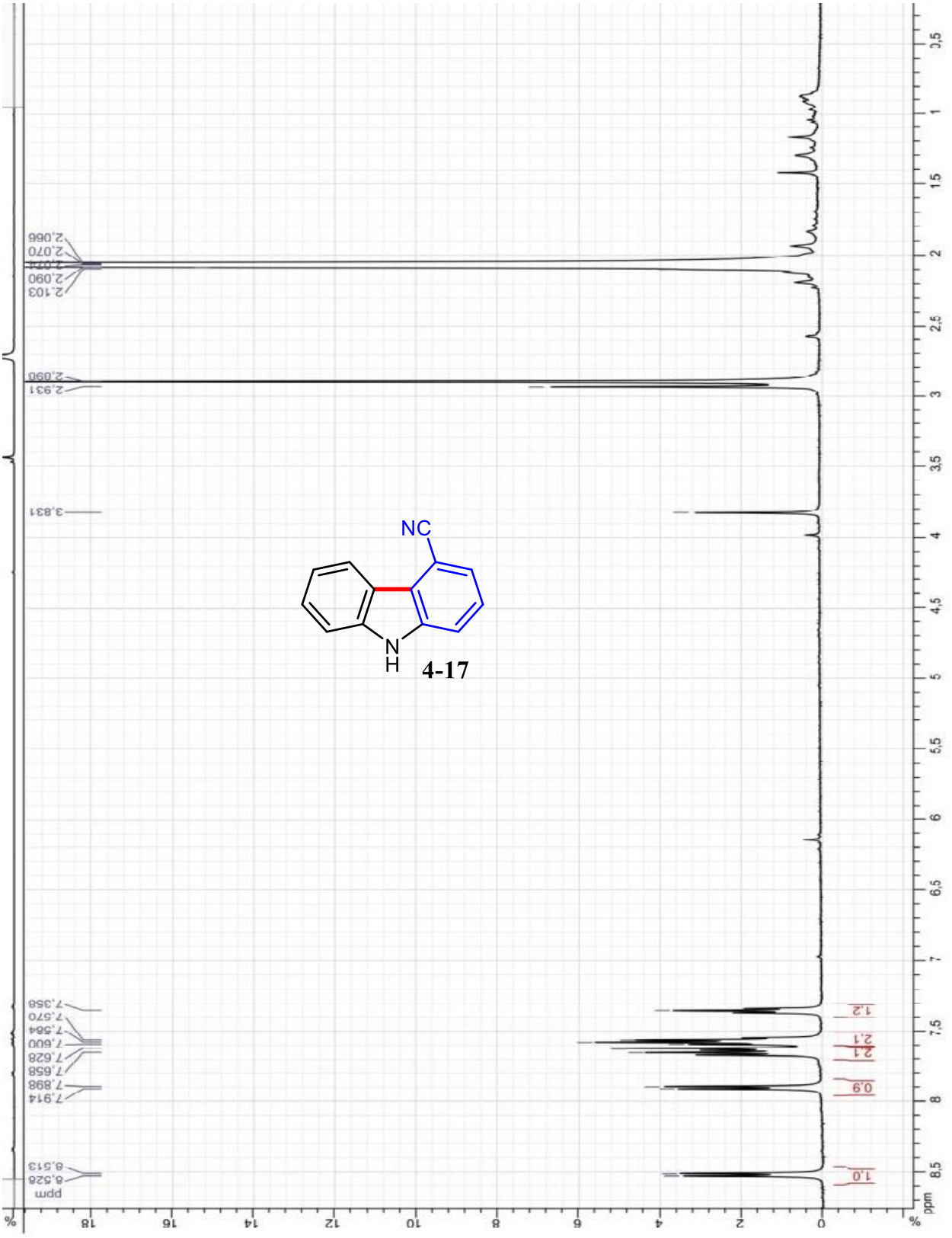


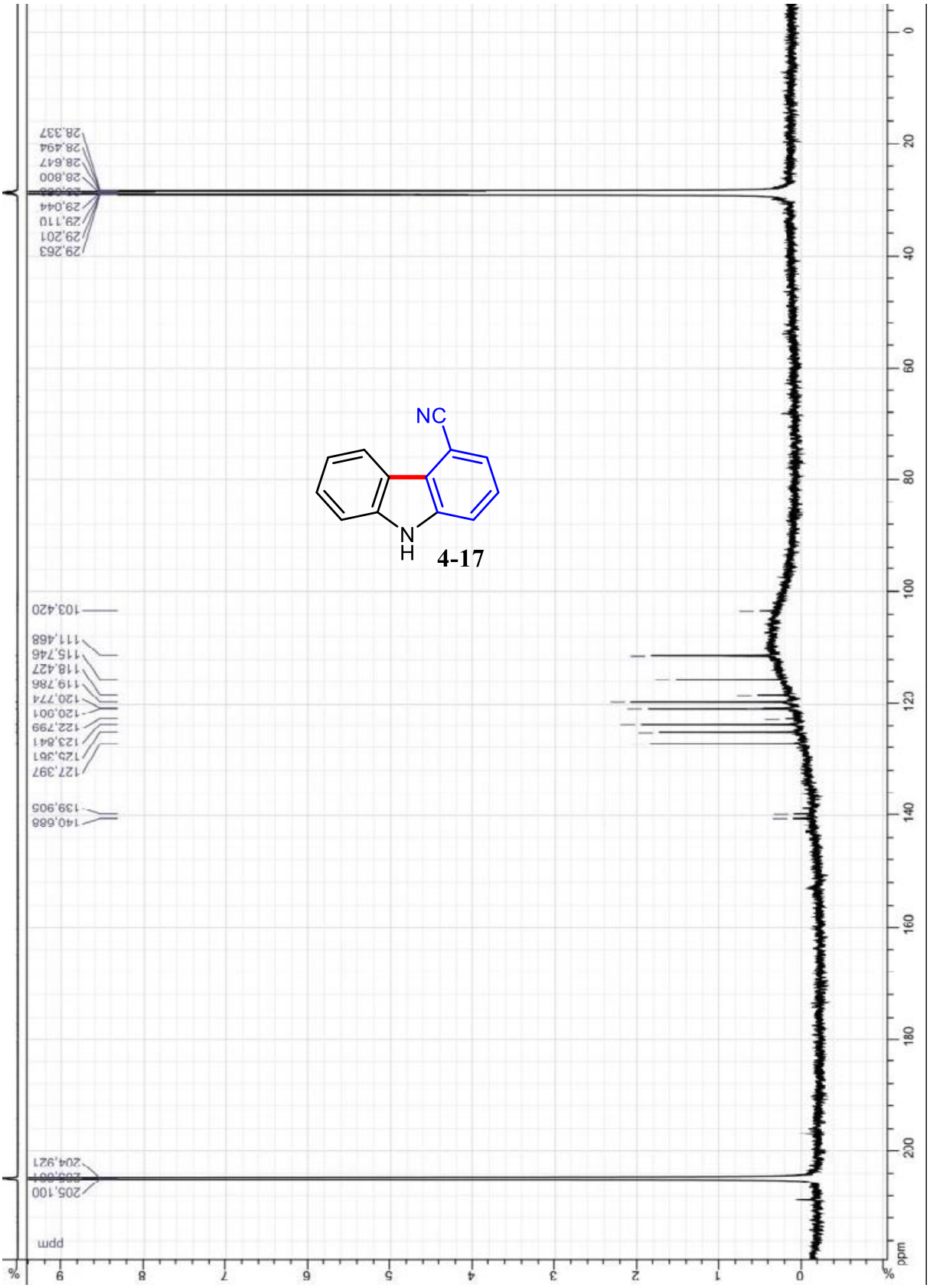
^{1}H NMR and ^{13}C NMR spectra of 9*H*-carbazole-2-carbonitrile (**4-16**) in $CDCl_3$



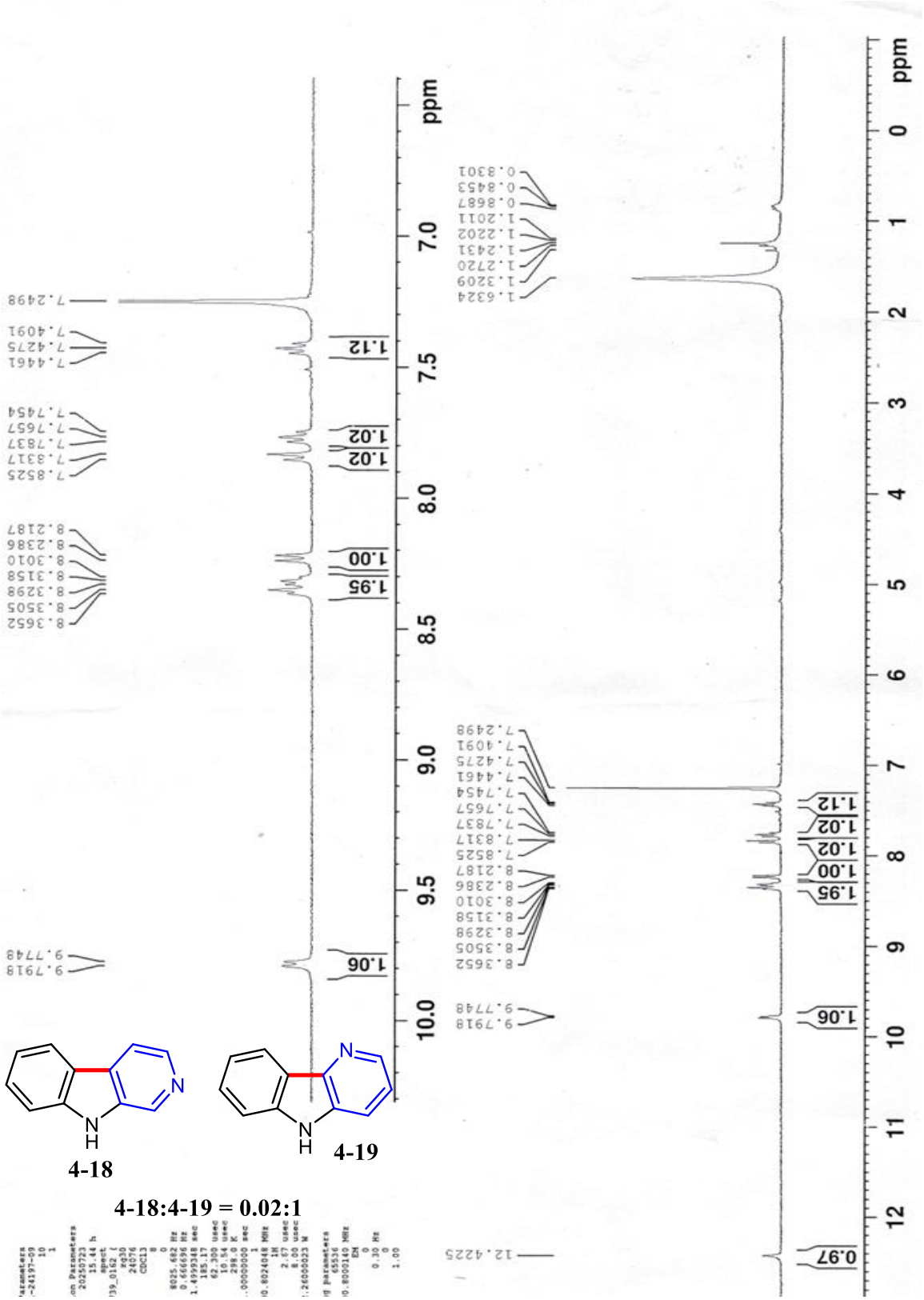

CN
N
H
4-16

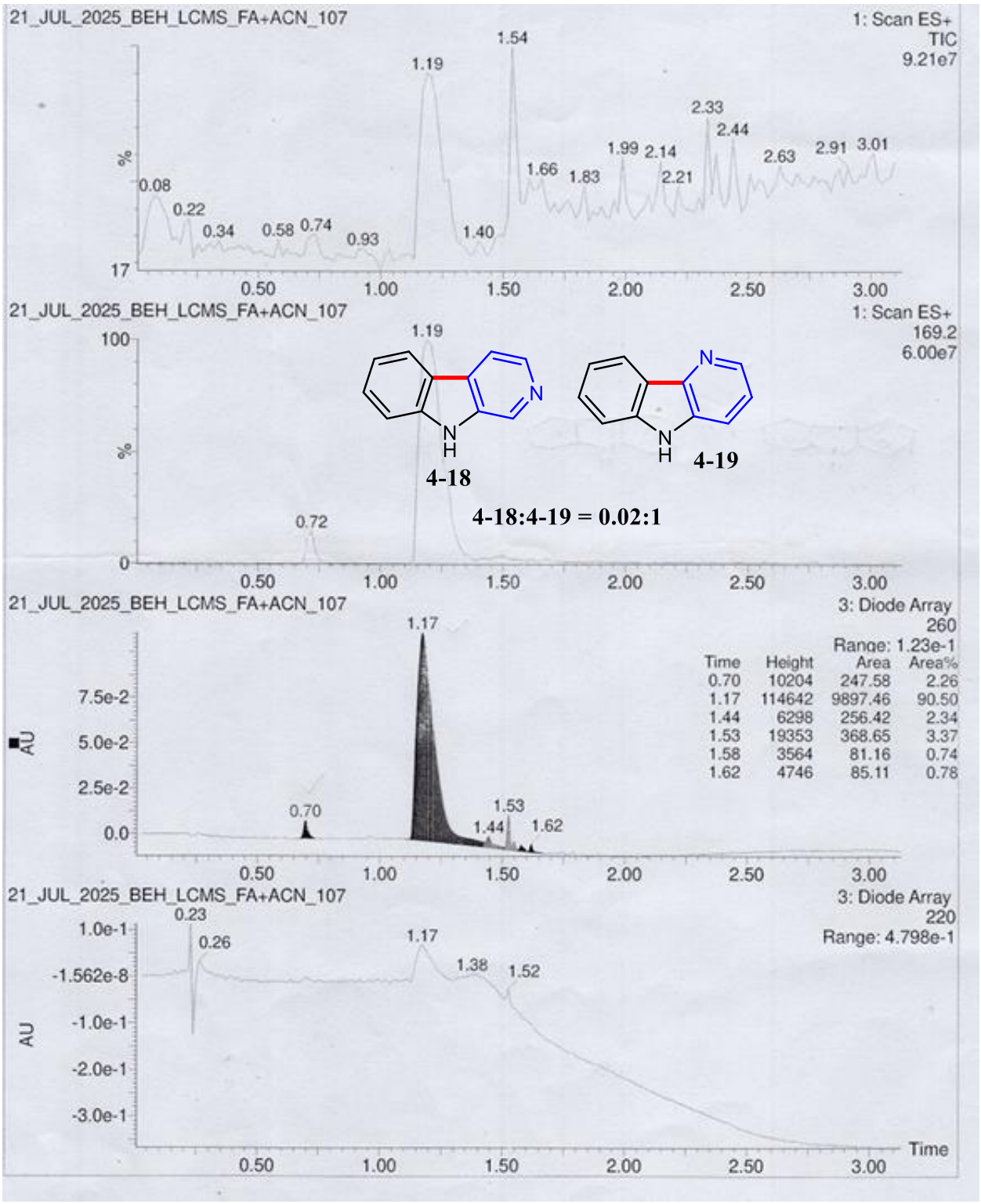
^{1}H NMR and ^{13}C NMR spectra of 9*H*-carbazole-2-carbonitrile (**4-17**) in Acetone-D_6

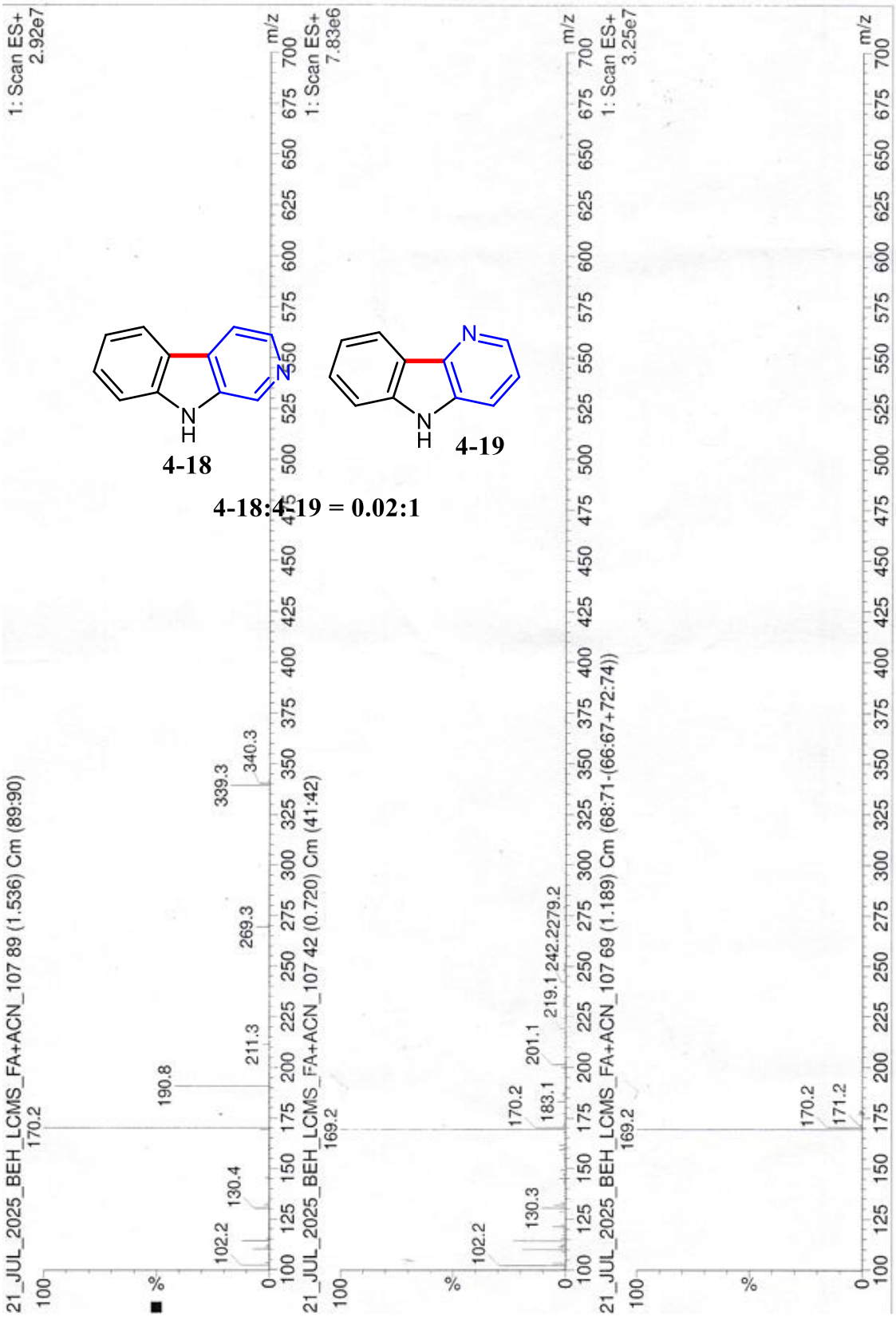



NC
N
H
4-17
28.337
28.494
28.647
28.800
29.044
29.110
29.201
29.263
103.420
111.468
115.746
118.427
119.786
120.774
120.901
122.799
123.841
125.361
127.397
139.905
140.666
205.100
ppm

^{1}H NMR ($CDCl_3$) and LCMS data of the reaction mixture of **3ak** to get regioisomeric ratio (C2:C4) of **4-18** and **4-19**.




21_JUL_2025_BEH_LCMS_FA+ACN_107
1: Scan ES+
TIC
9.21e7
1.54
1.19
2.33
2.44
1.99
2.14
2.63
2.91
3.01
1.66
1.83
2.21
0.08
0.22
0.34
0.58
0.74
0.93
1.40
%
17
0.50
1.00
1.50
2.00
2.50
3.00
21_JUL_2025_BEH_LCMS_FA+ACN_107
1: Scan ES+
169.2
6.00e7
100
1.19
%
0
0.72
4-18
4-19
4-18:4-19 = 0.02:1
21_JUL_2025_BEH_LCMS_FA+ACN_107
3: Diode Array
260
Range: 1.23e-1
1.17
Time Height Area Area%
0.70 10204 247.58 2.26
1.17 114642 9897.46 90.50
1.44 6298 256.42 2.34
1.53 19353 368.65 3.37
1.58 3564 81.16 0.74
1.62 4746 85.11 0.78
7.5e-2
5.0e-2
2.5e-2
AU
0.0
0.70
1.53
1.44
1.62
21_JUL_2025_BEH_LCMS_FA+ACN_107
3: Diode Array
220
Range: 4.798e-1
0.23
0.26
1.17
1.38
1.52
1.0e-1
-1.562e-8
-1.0e-1
-2.0e-1
-3.0e-1
AU
Time

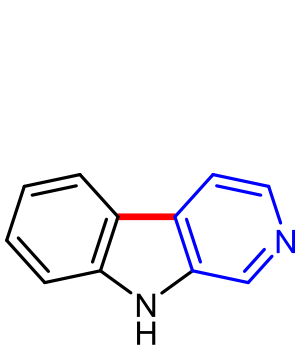


4-18

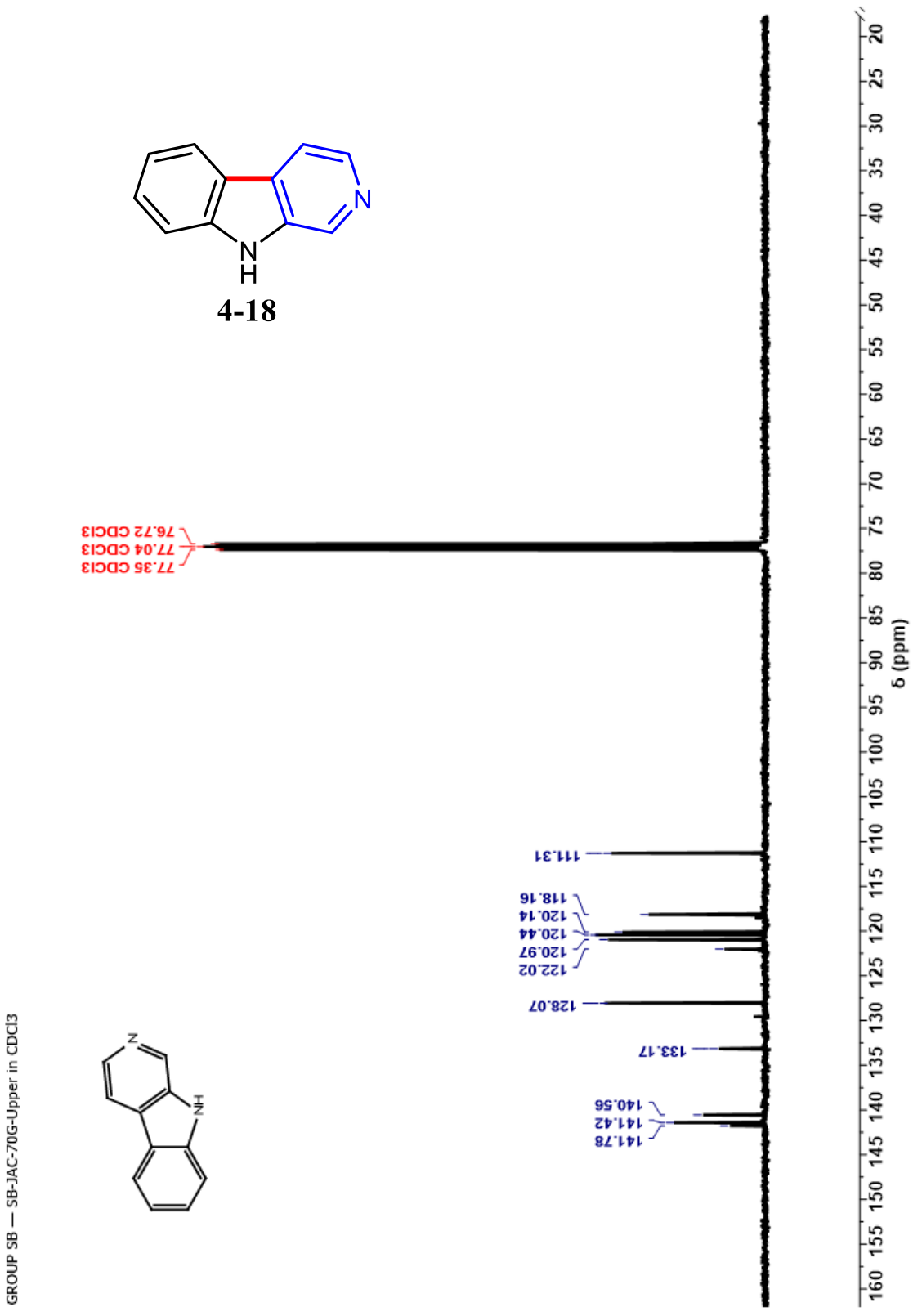
4-19

4-18:4-19 = 0.02:1

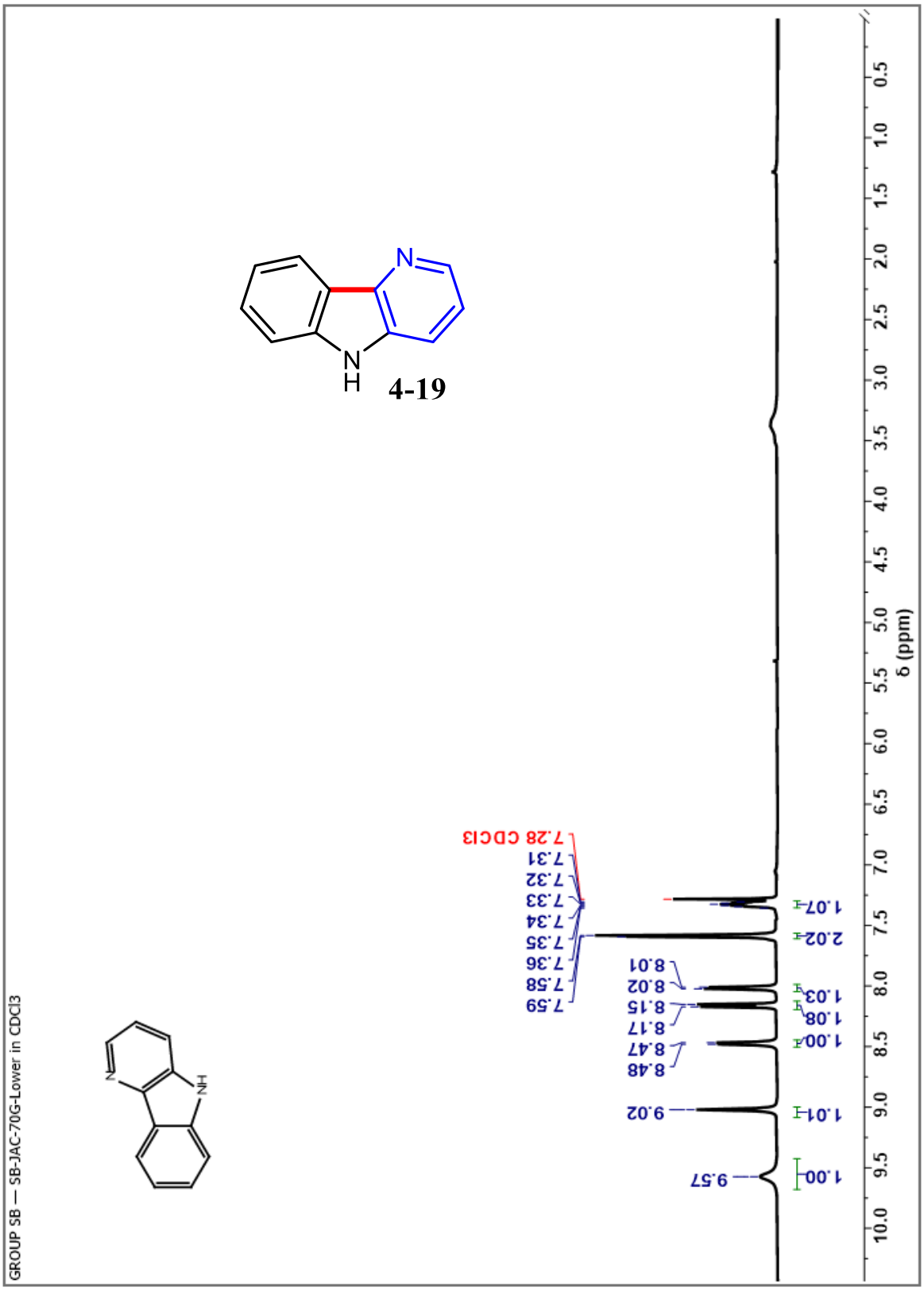
^{1}H NMR and ^{13}C NMR spectra of 9*H*-pyrido[3,4-*b*]indole (**4-18**) in $CDCl_3$

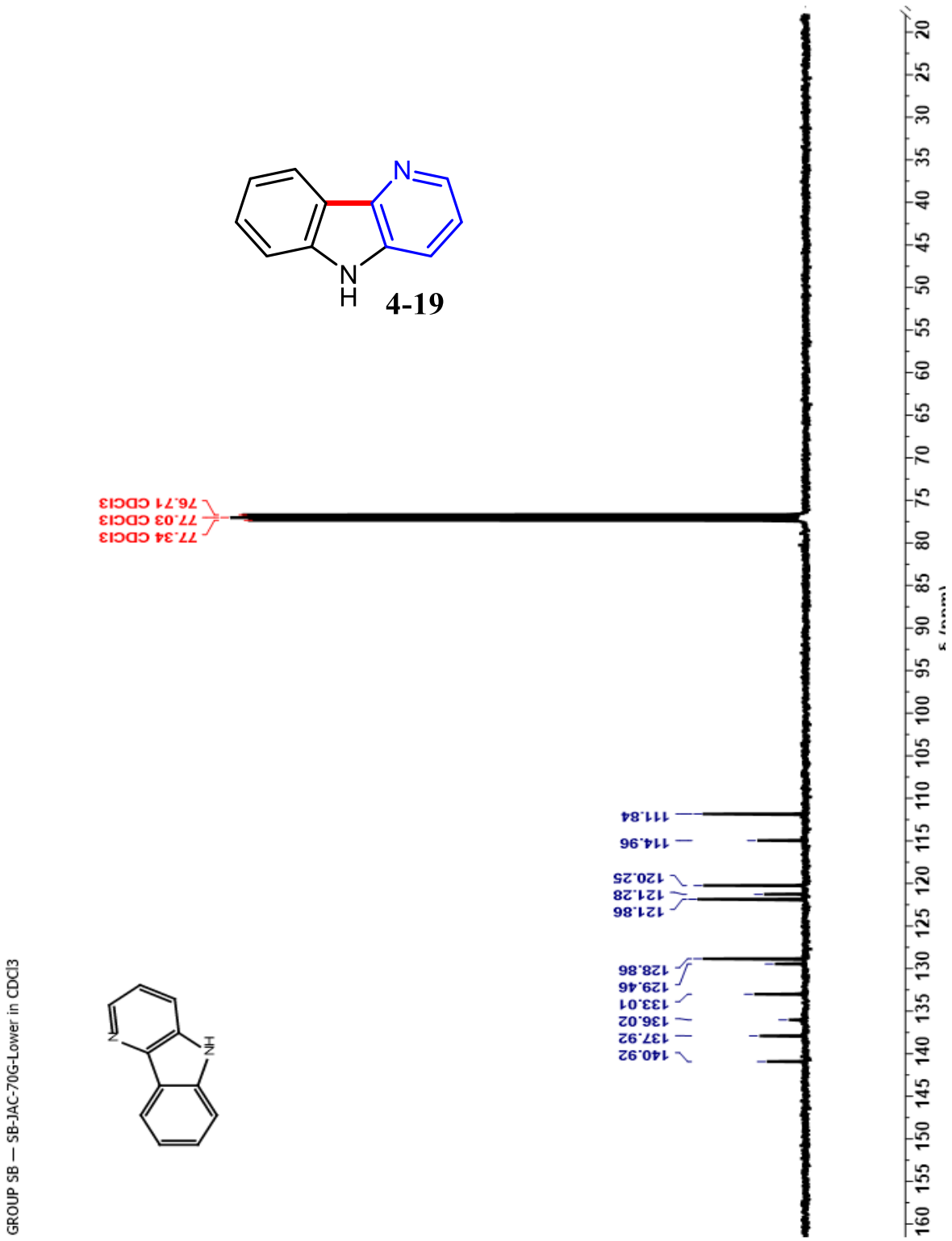


4-18

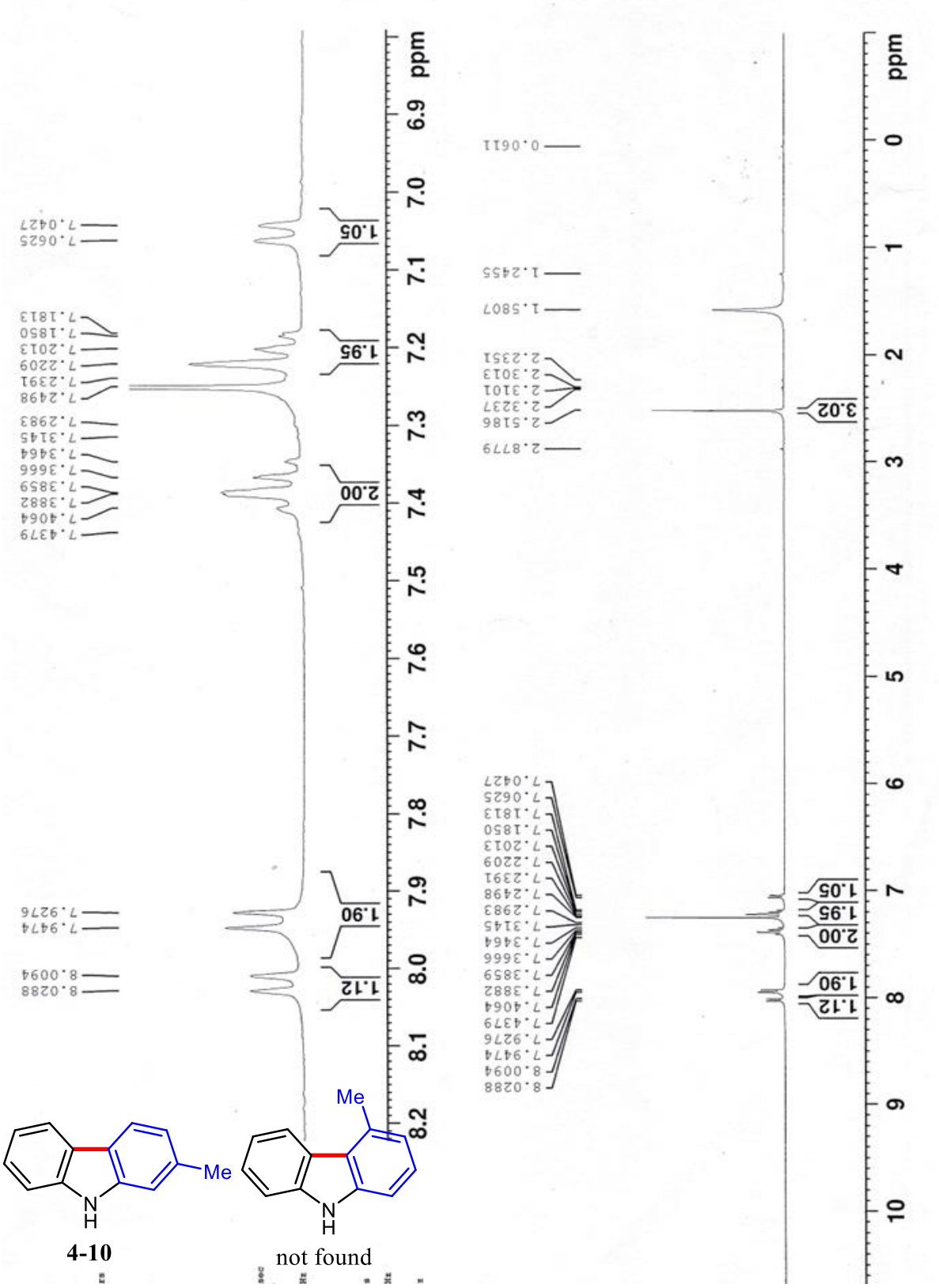

4-18
GROUP SB — SB-JAC-70G-Upper in CDCl3
δ (ppm)
77.35 CDCl3
77.04 CDCl3
76.72 CDCl3
111.31
118.16
120.14
120.44
120.97
122.02
128.07
133.17
140.56
141.42
141.78

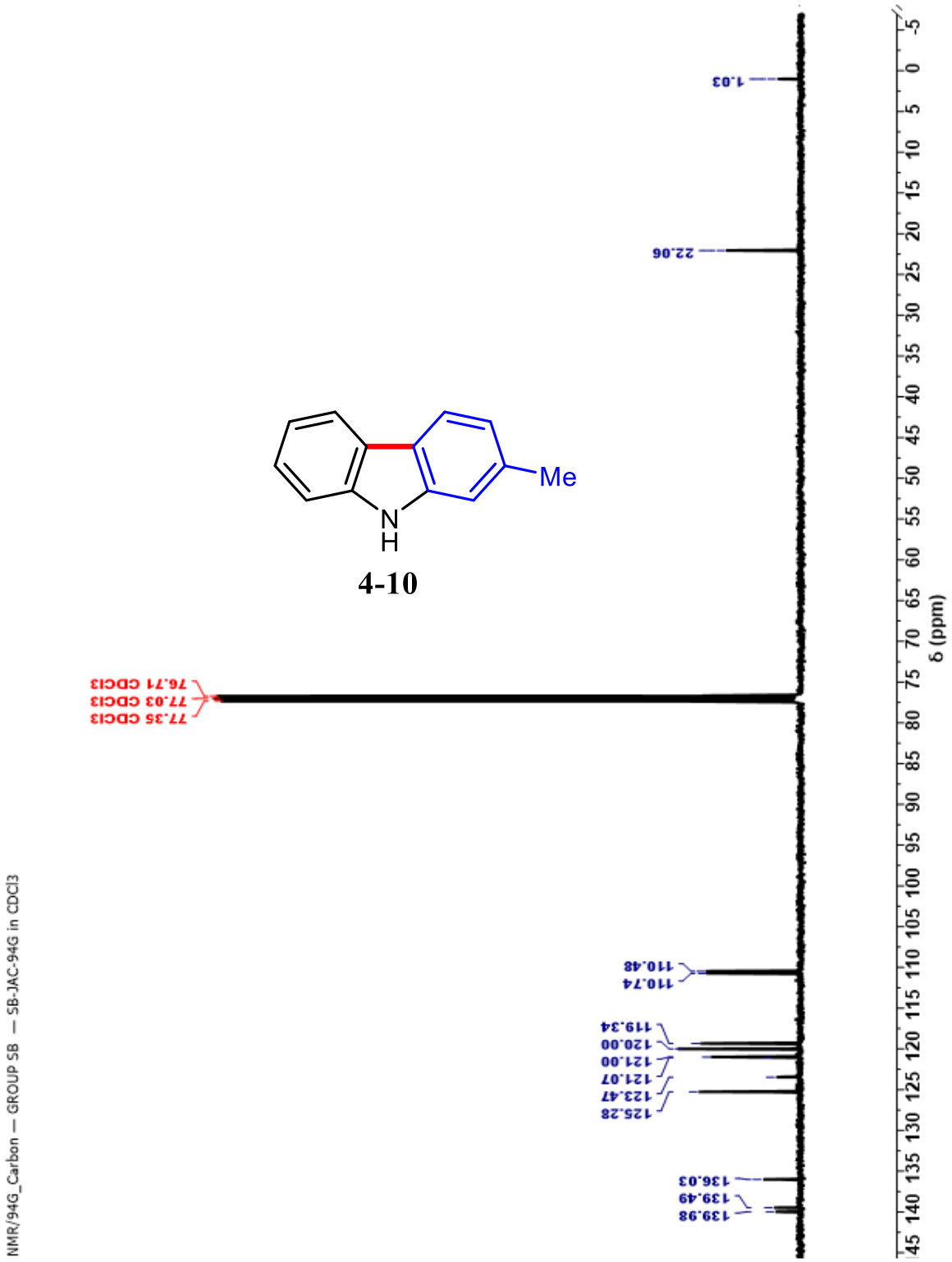
^{1}H NMR and ^{13}C NMR spectra of 5*H*-pyrido[3,2-*b*]indole (**4-19**) in $CDCl_3$



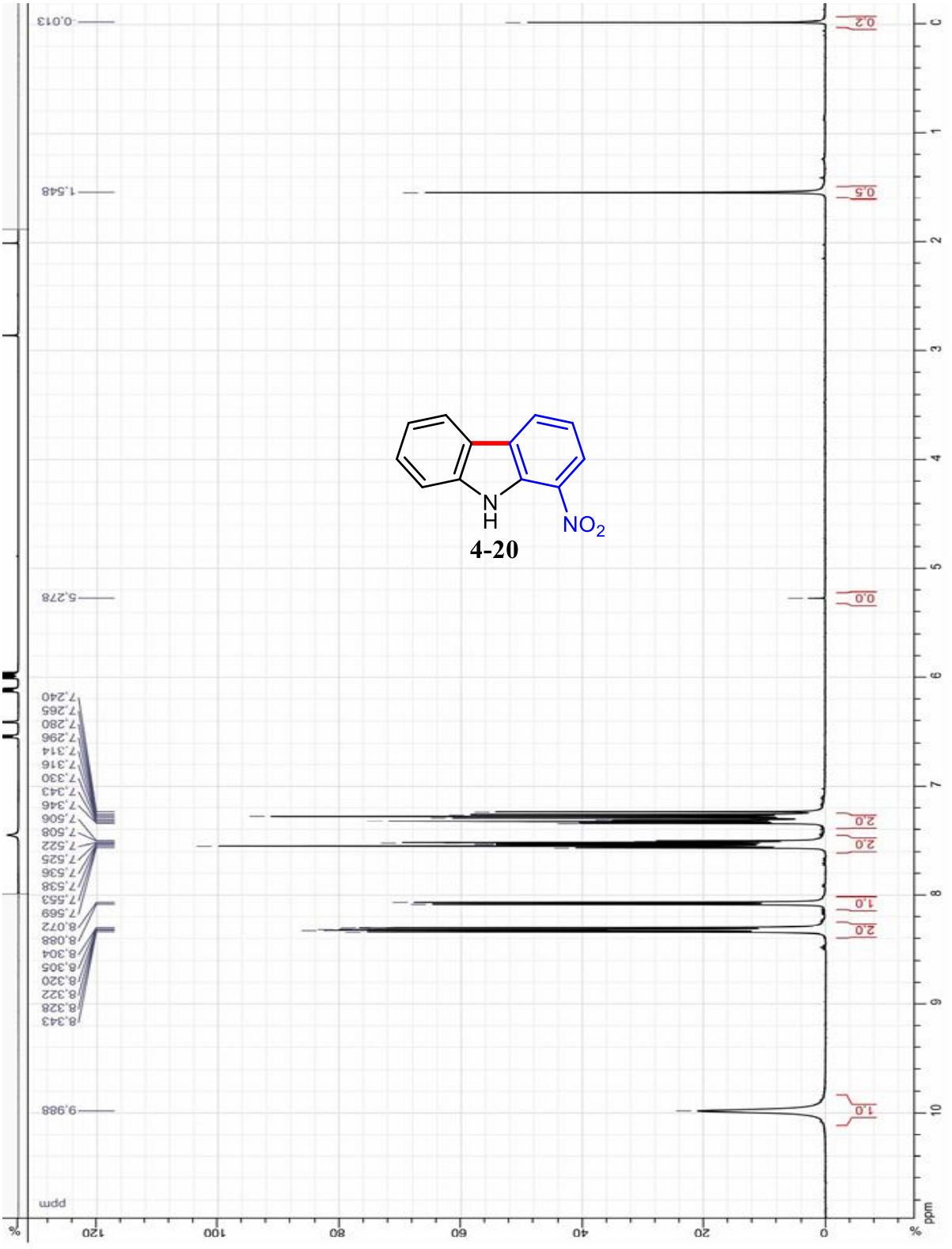

GROUP SB — SB-JAC-70G-Lower in CDCl3
4-19
N
H
N
H
77.34 CDCl3
77.03 CDCl3
76.71 CDCl3
111.84
114.96
120.25
121.28
121.86
128.86
129.46
133.01
136.02
137.92
140.92
f1 (ppm)

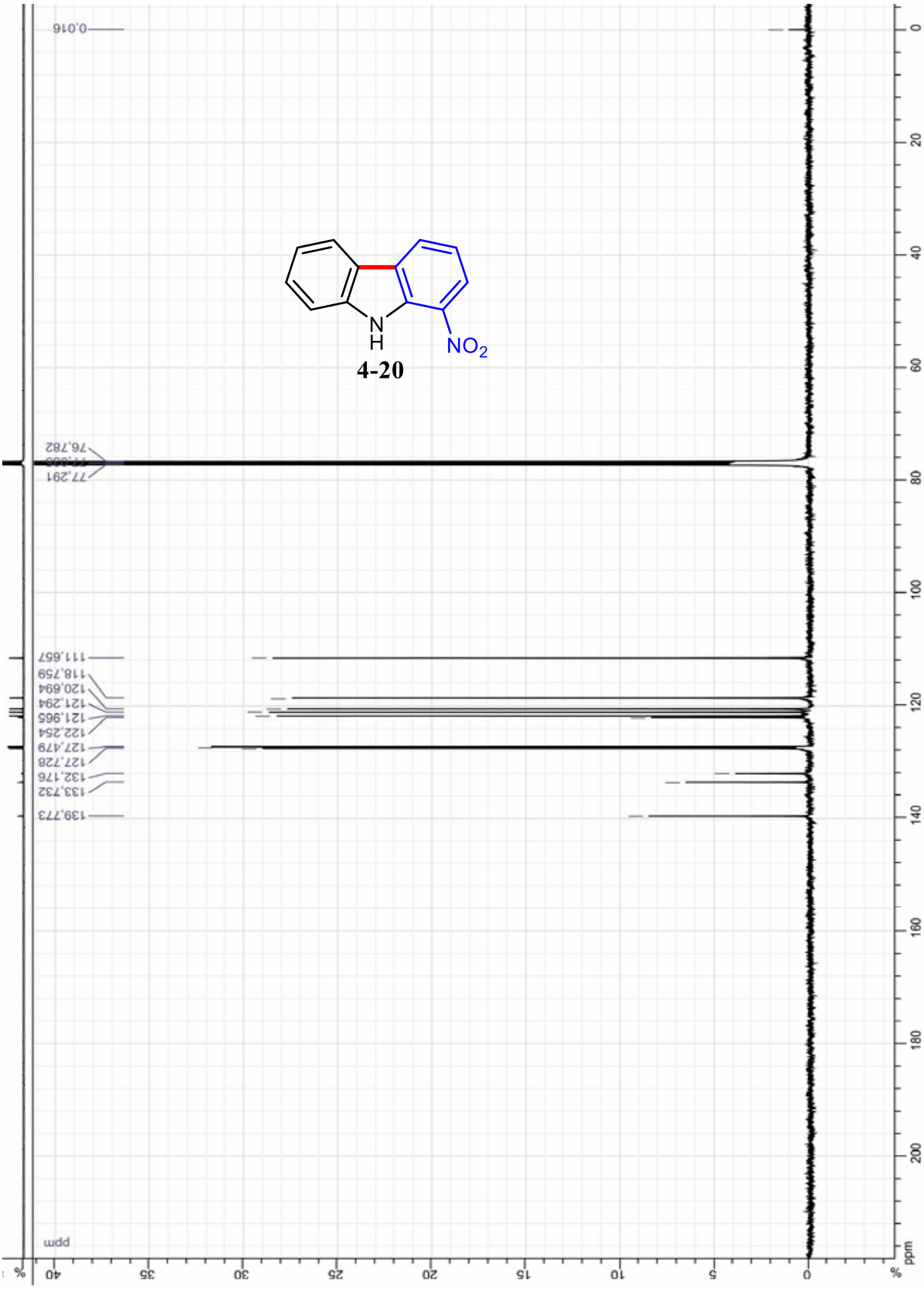
[1]H NMR and 13C NMR spectra of 2-methyl-9*H*-carbazole (**4-10**) (from the reaction of **3al**) in $CDCl_3$




NMR/94G_Carbon — GROUP SB — SB-JAC-94G in CDCl3
Me
N
H
4-10
δ (ppm)
1.03
22.06
76.71 CDCl3
77.03 CDCl3
77.35 CDCl3
110.48
110.74
119.34
120.00
121.00
121.07
123.47
125.28
136.03
139.49
139.98

^{1}H NMR and 13C NMR spectra of 1-nitro-9*H*-carbazole (**4-20**) in $CDCl_3$

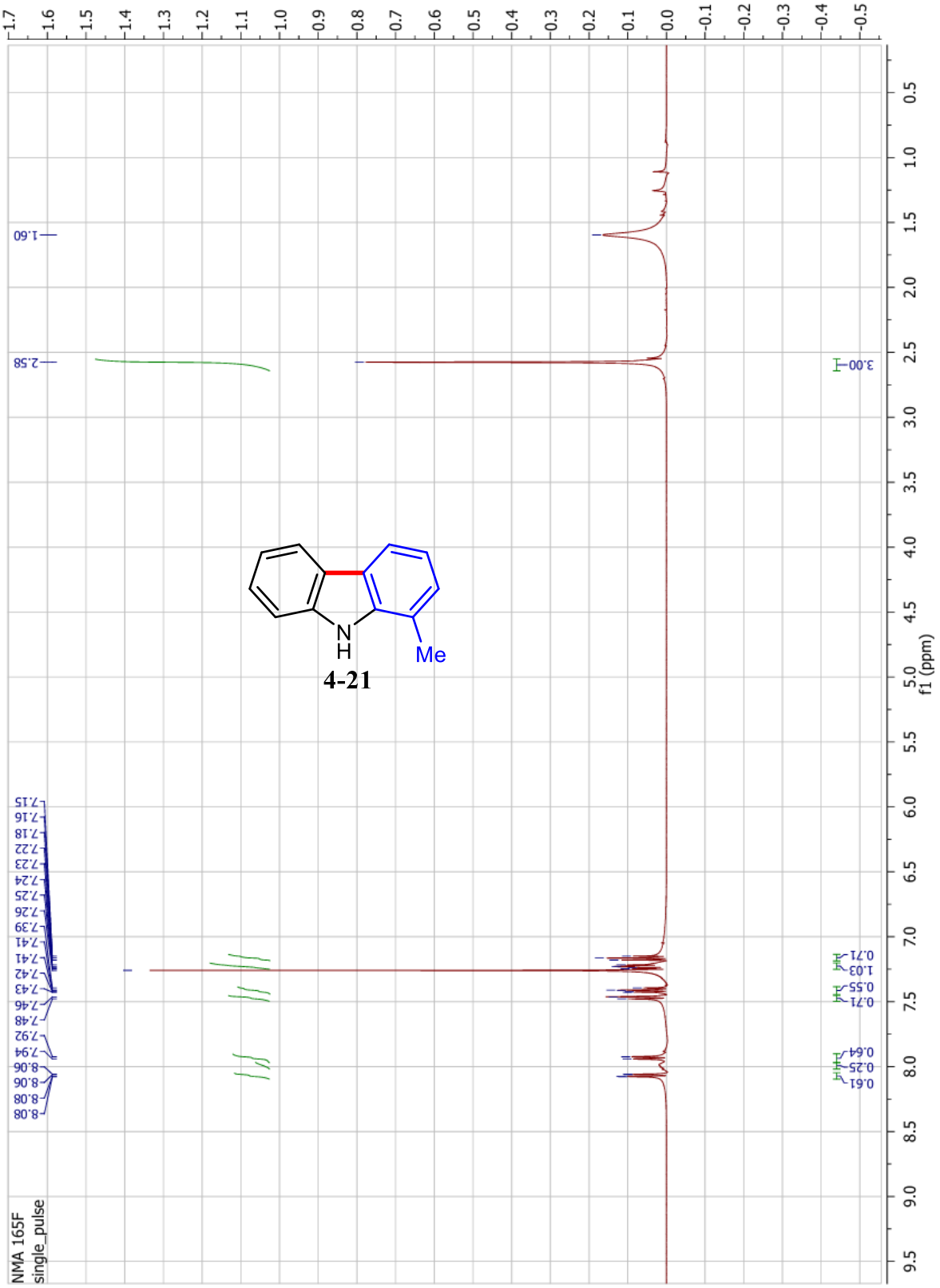


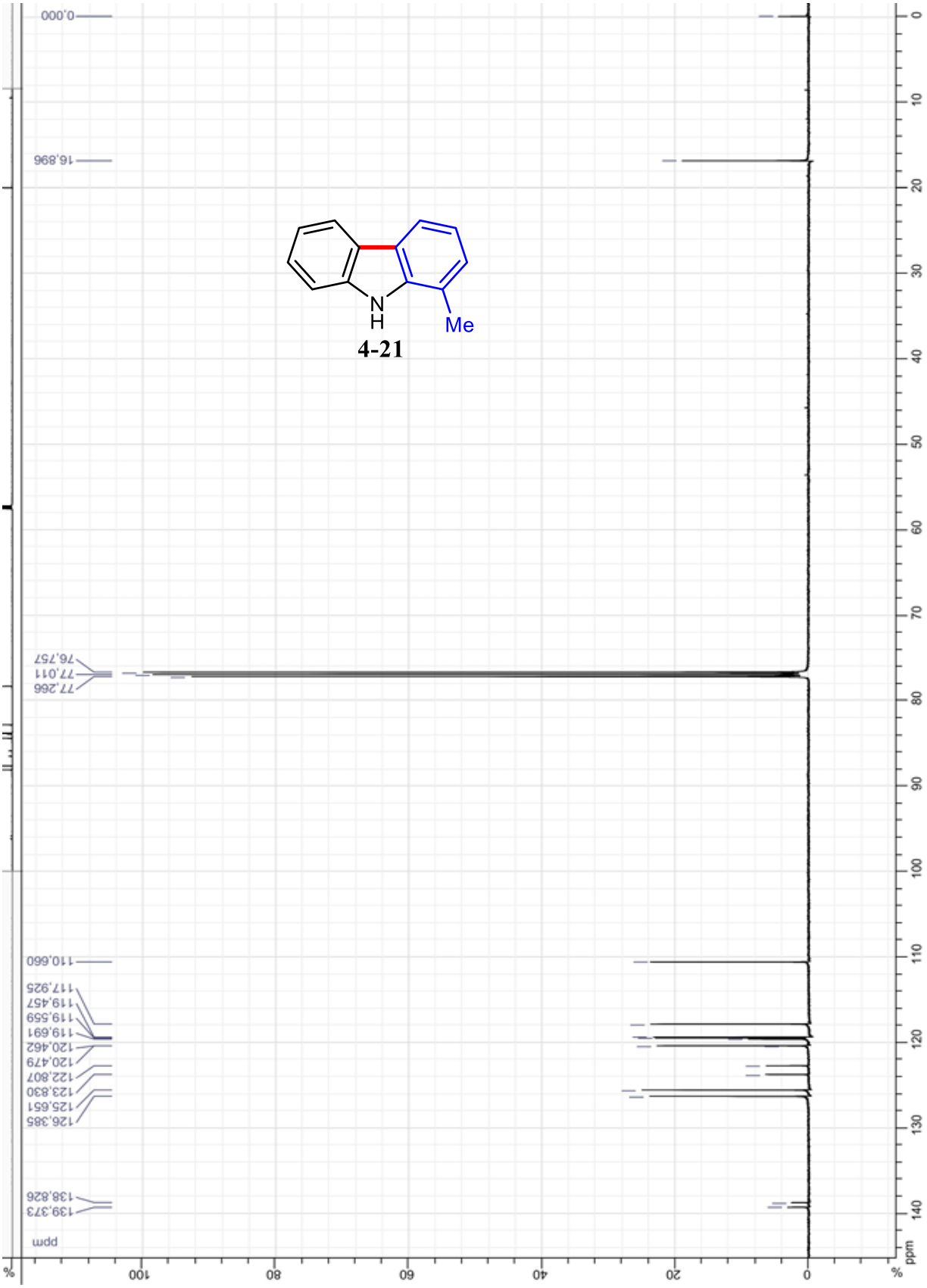

0.016
76.782
77.291
111.657
118.759
120.694
121.294
121.965
122.254
127.479
127.728
132.176
133.732
139.773
ppm

N
H
NO2

4-20

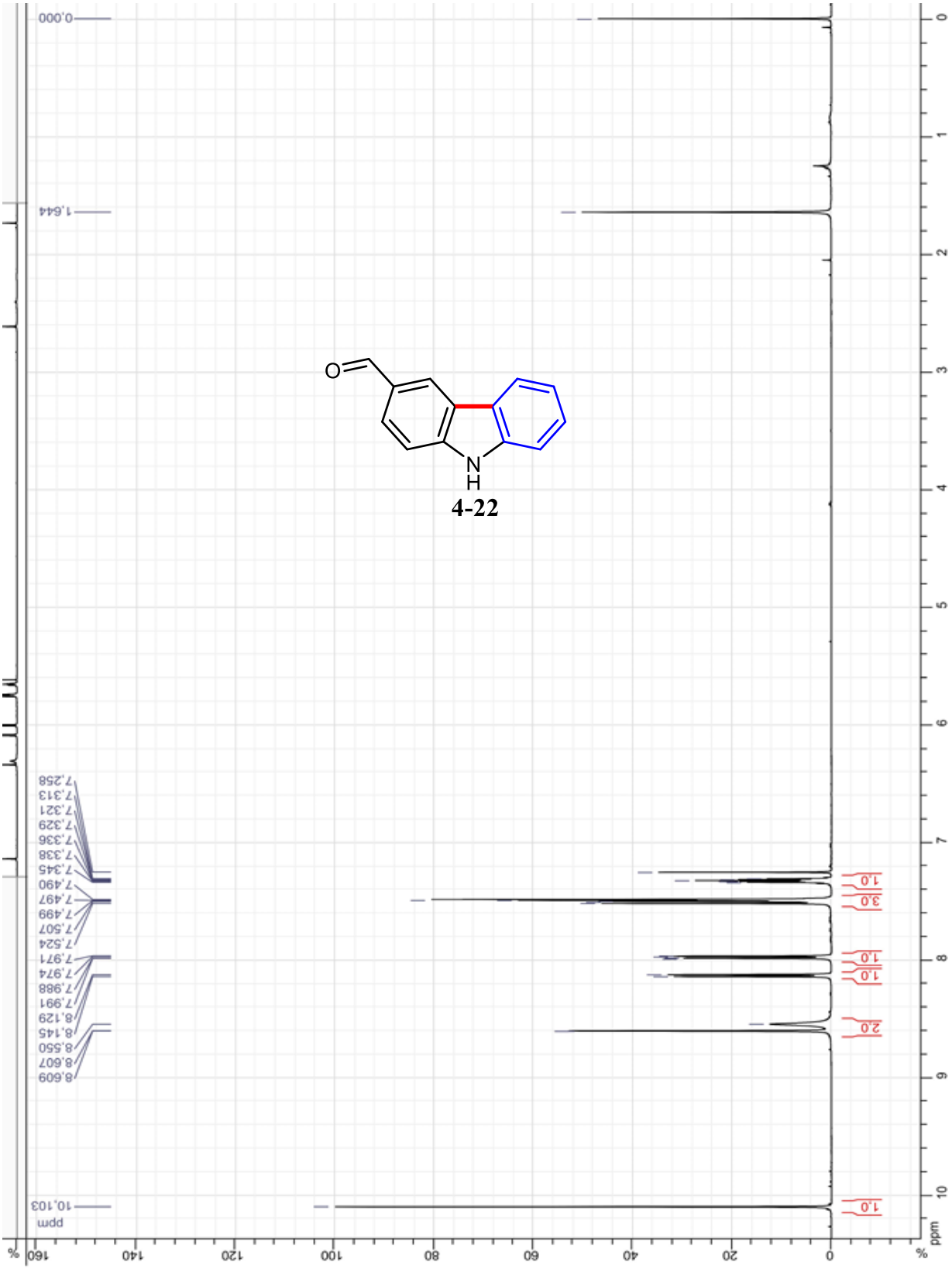
^{1}H NMR and ^{13}C NMR spectra of 1-methyl-9*H*-carbazole (**4-21**) in $CDCl_3$



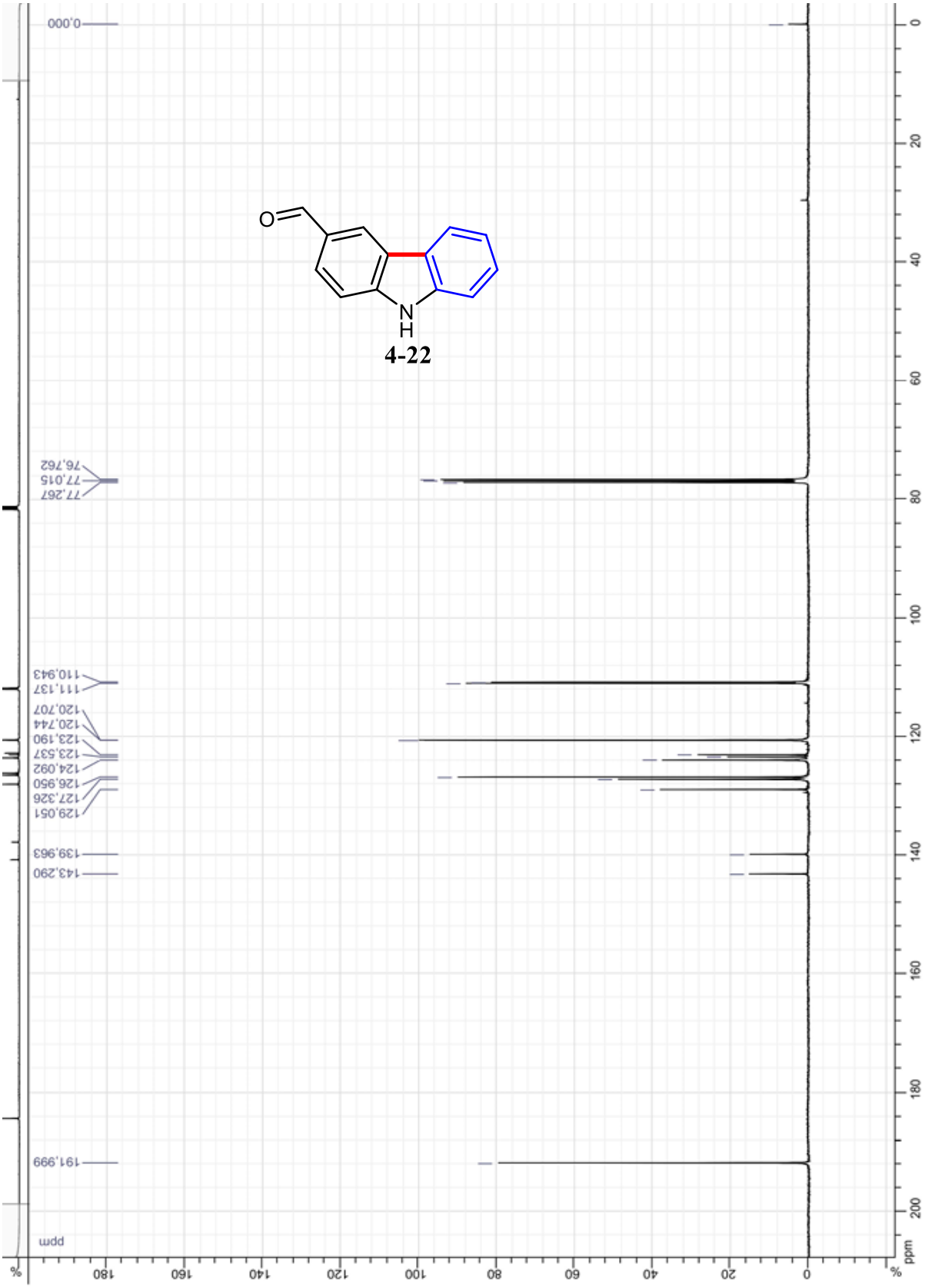

0.000
16.896
76.757
77.011
77.266
110.660
117.925
119.457
119.559
119.691
120.462
120.479
122.807
123.830
125.651
126.385
138.826
139.373
ppm
Me
N
H

4-21

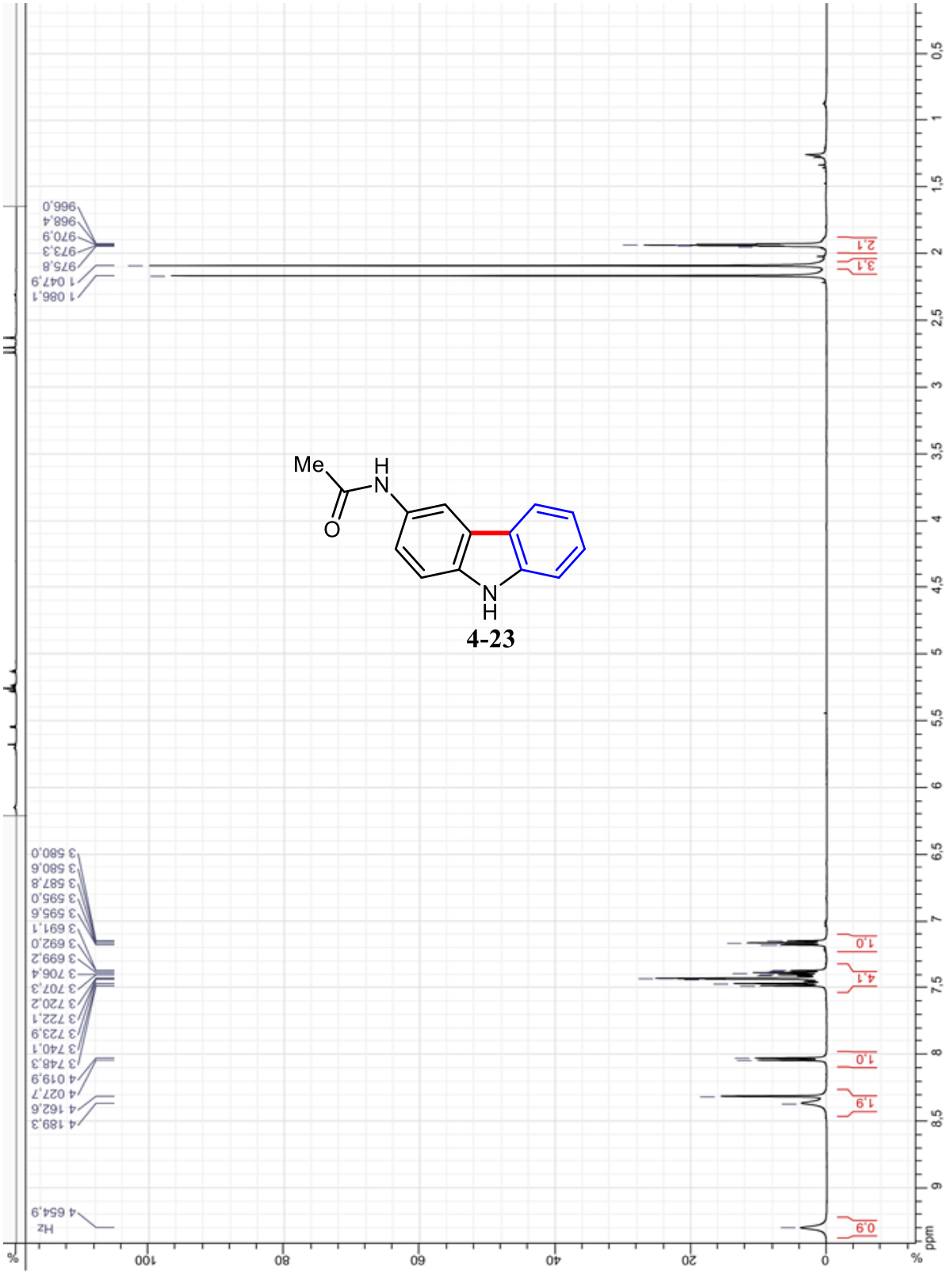
^{1}H NMR and ^{13}C NMR spectra of 9*H*-carbazole-3-carbaldehyde (**4-22**) in $CDCl_3$

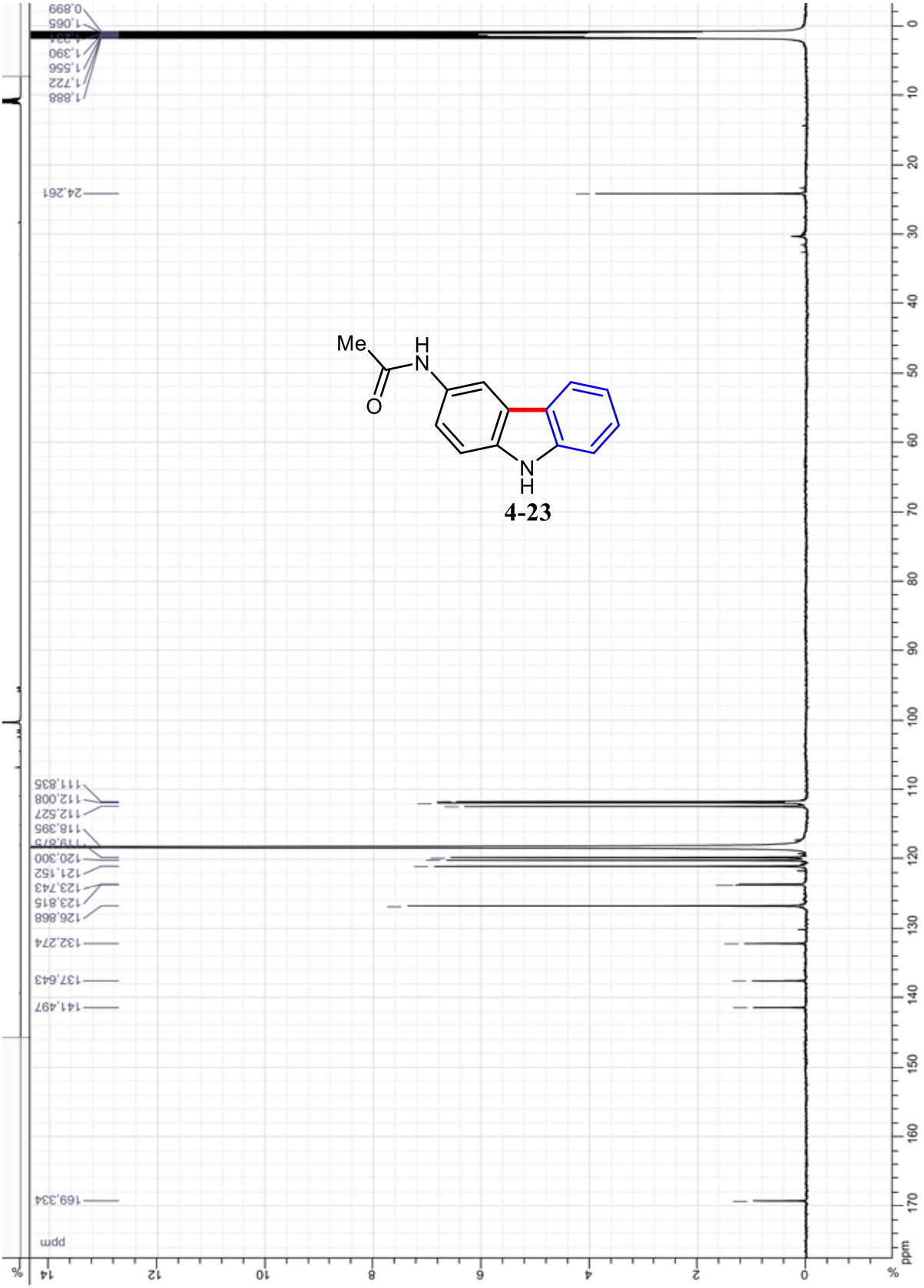


4-22

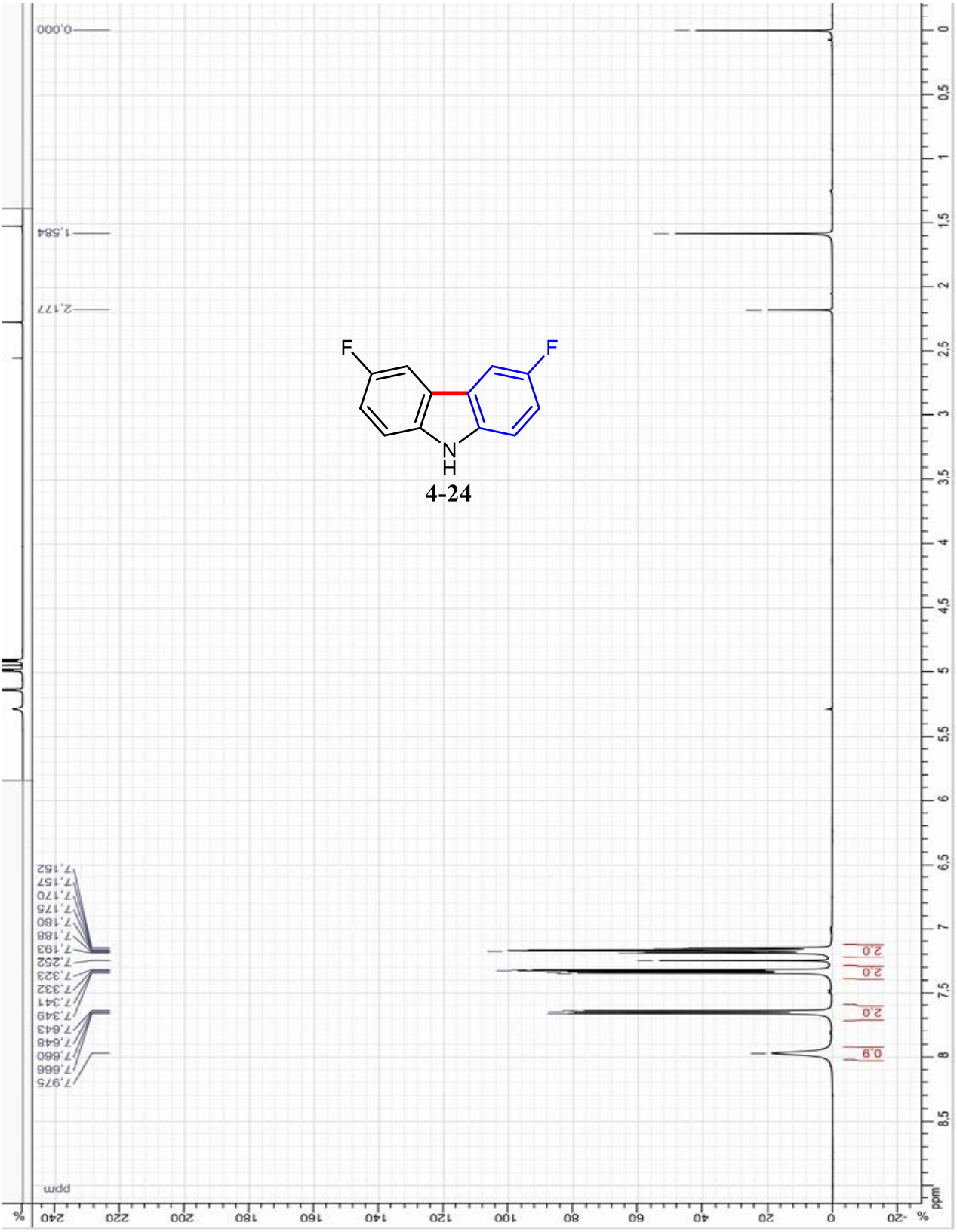

O
N
H
4-22
0.000
76.762
77.015
77.267
110.943
111.137
120.707
120.744
123.190
123.537
124.092
126.950
127.326
129.051
139.963
143.290
191.999
ppm

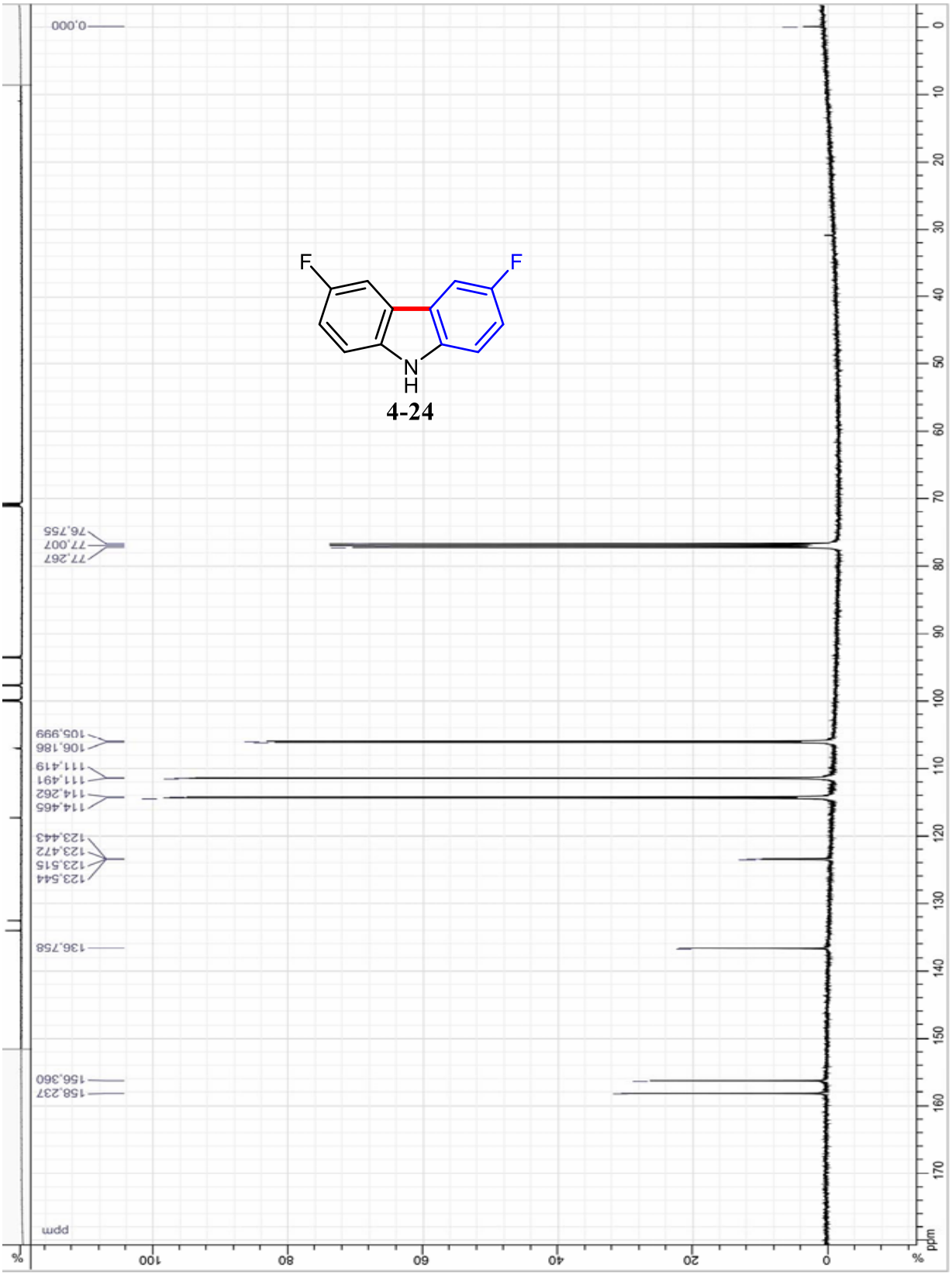
^{1}H NMR and ^{13}C NMR spectra of *N*-(9*H*-carbazol-3-yl)acetamide (**4-23**) in CD_3CN



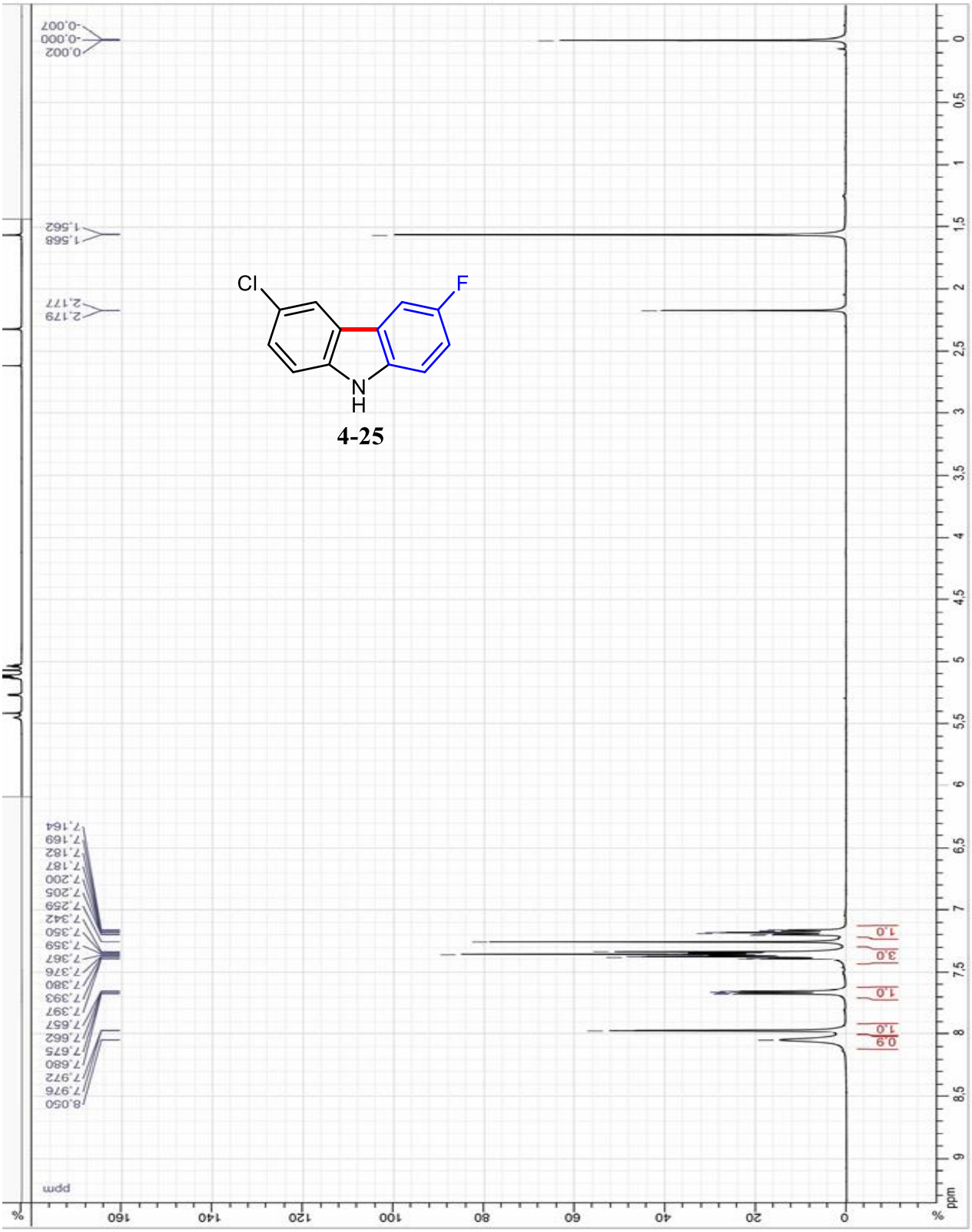

Me
H
N
O
N
H
4-23

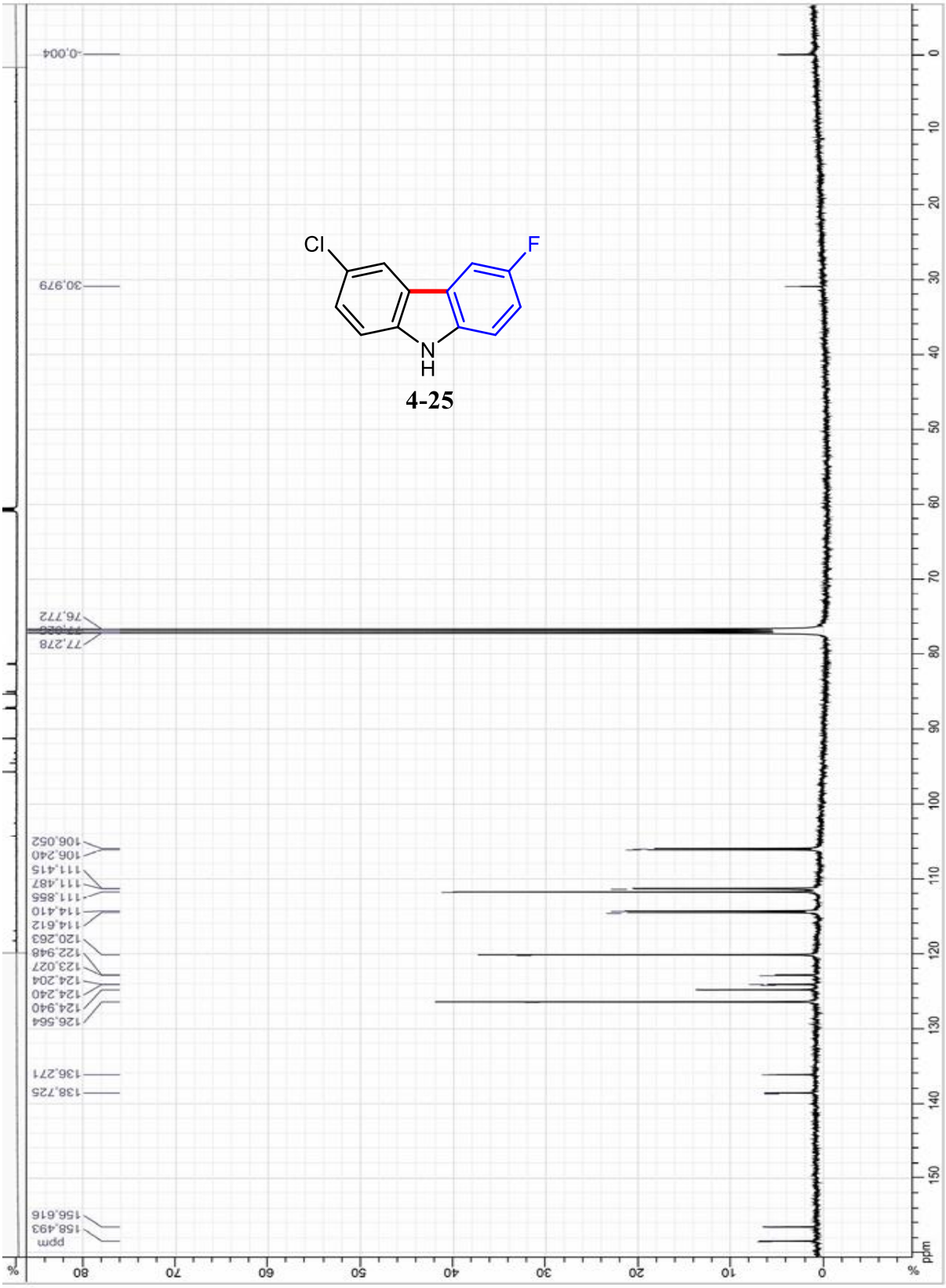
^{1}H NMR and ^{13}C NMR spectra of 3,6-difluoro-9*H*-carbazole (**4-24**) in $CDCl_3$



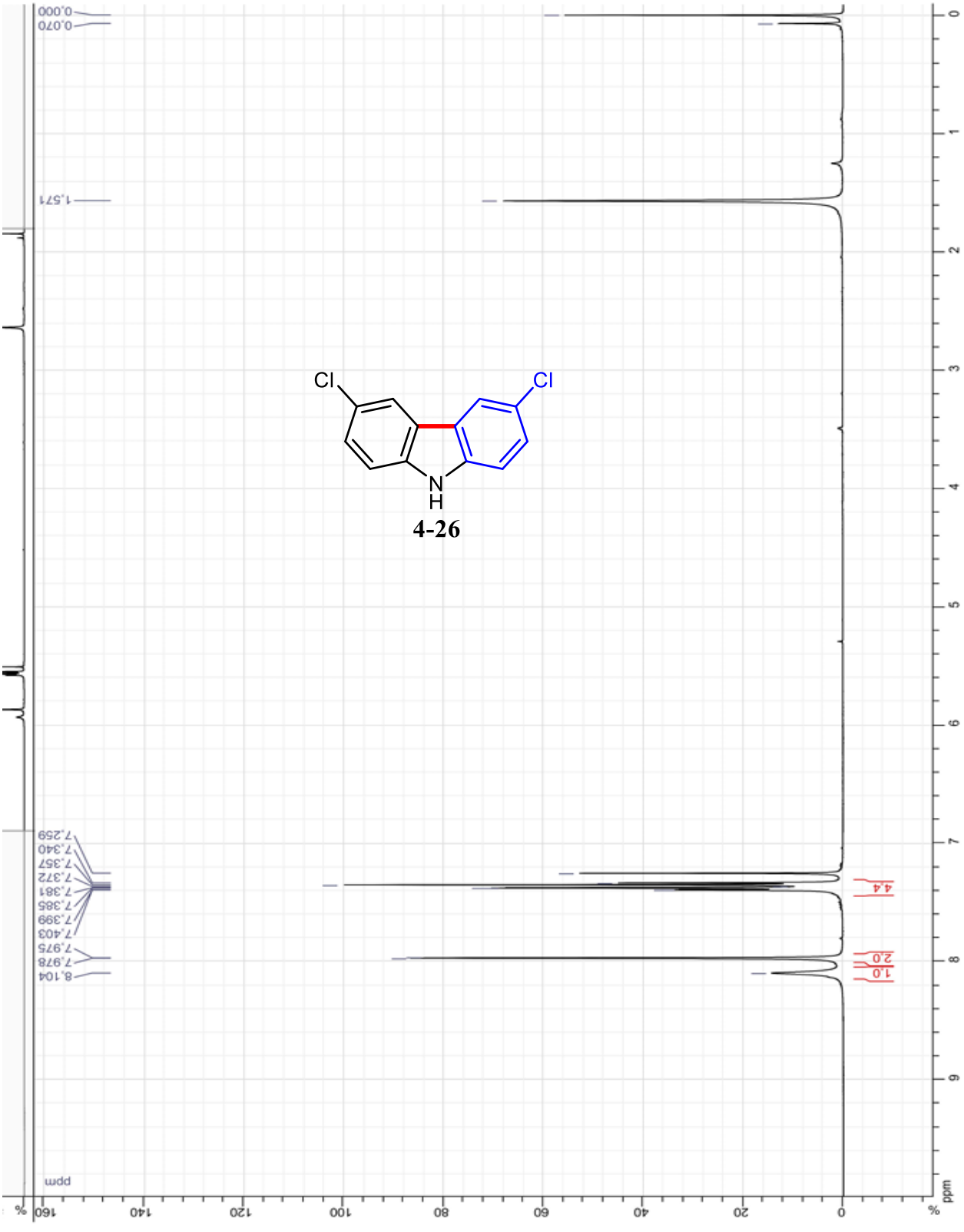

F
F
N
H
4-24
0.000
76.755
77.007
77.267
105.999
106.186
111.419
111.491
114.262
114.465
123.443
123.472
123.515
123.544
136.758
156.360
158.237
ppm

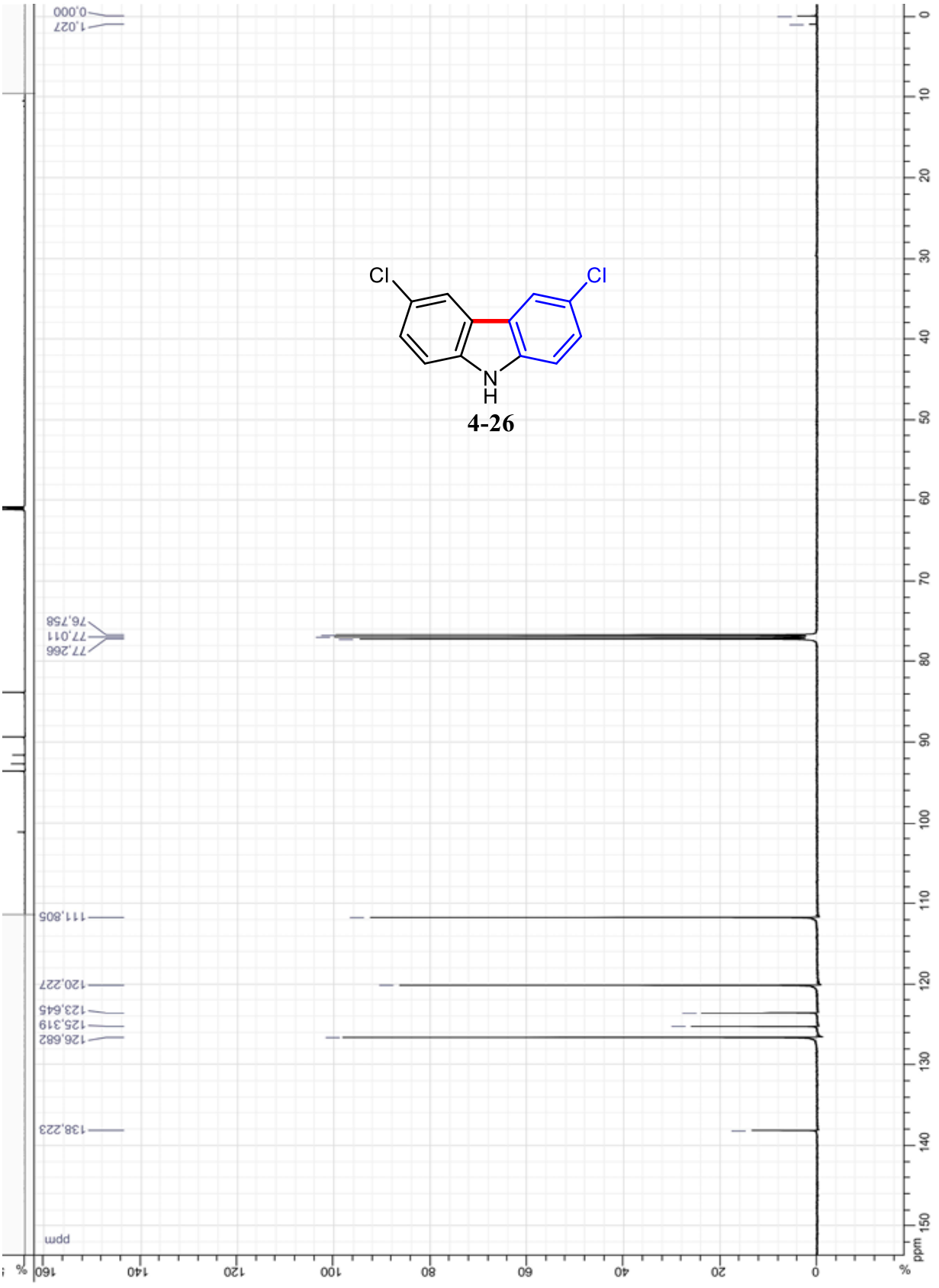
^{1}H NMR and ^{13}C NMR spectra of 3-chloro-6-fluoro-9*H*-carbazole **(4-25)** in $CDCl_3$



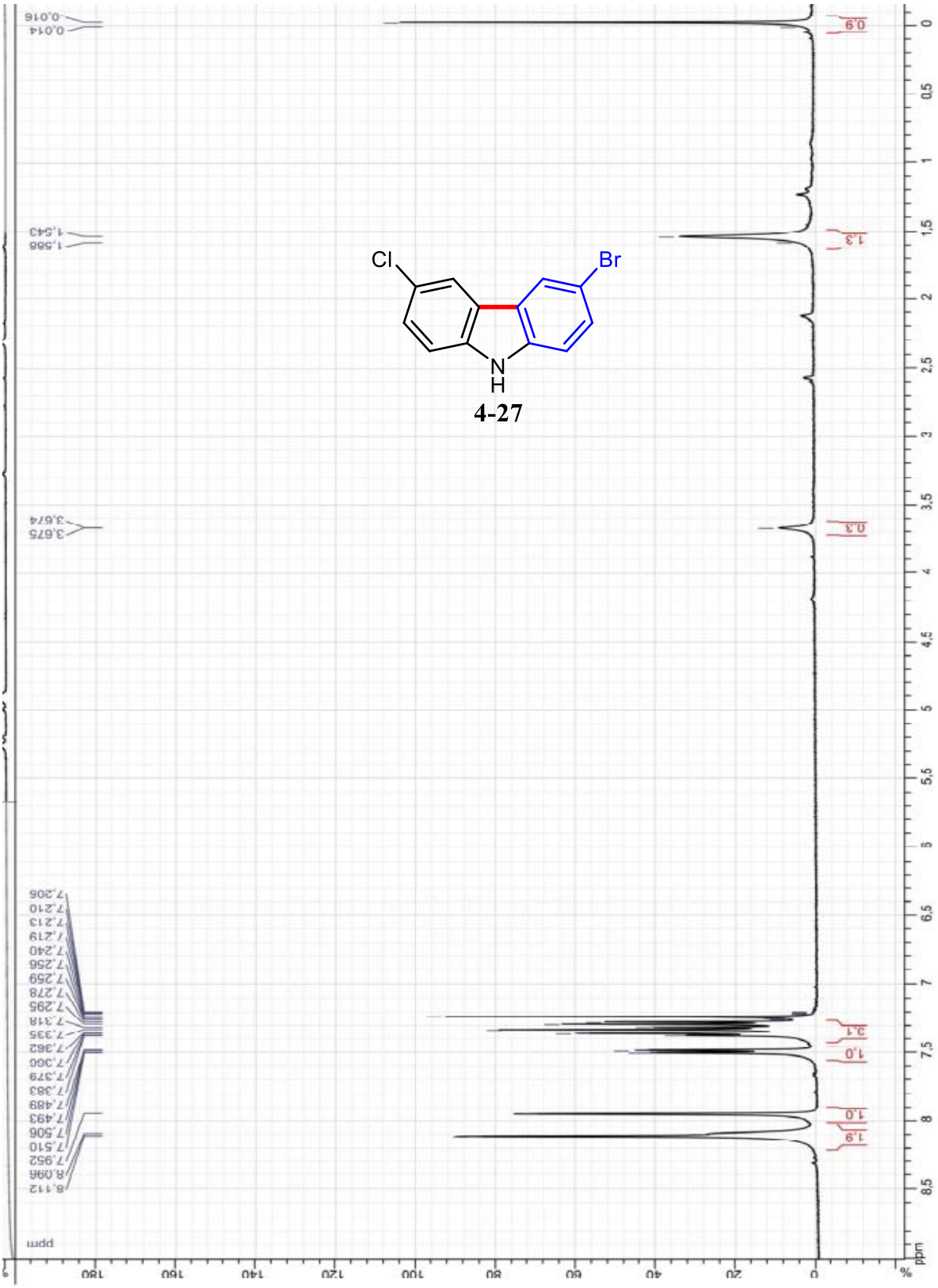

Cl
F
N
H
4-25
-0.004
30.979
76.772
77.278
106.052
106.240
111.415
111.487
111.855
114.410
114.612
120.263
122.948
123.027
124.204
124.240
124.940
126.564
136.271
138.725
156.616
158.493
ppm
%
80
70
60
50
40
30
20
10
0
ppm

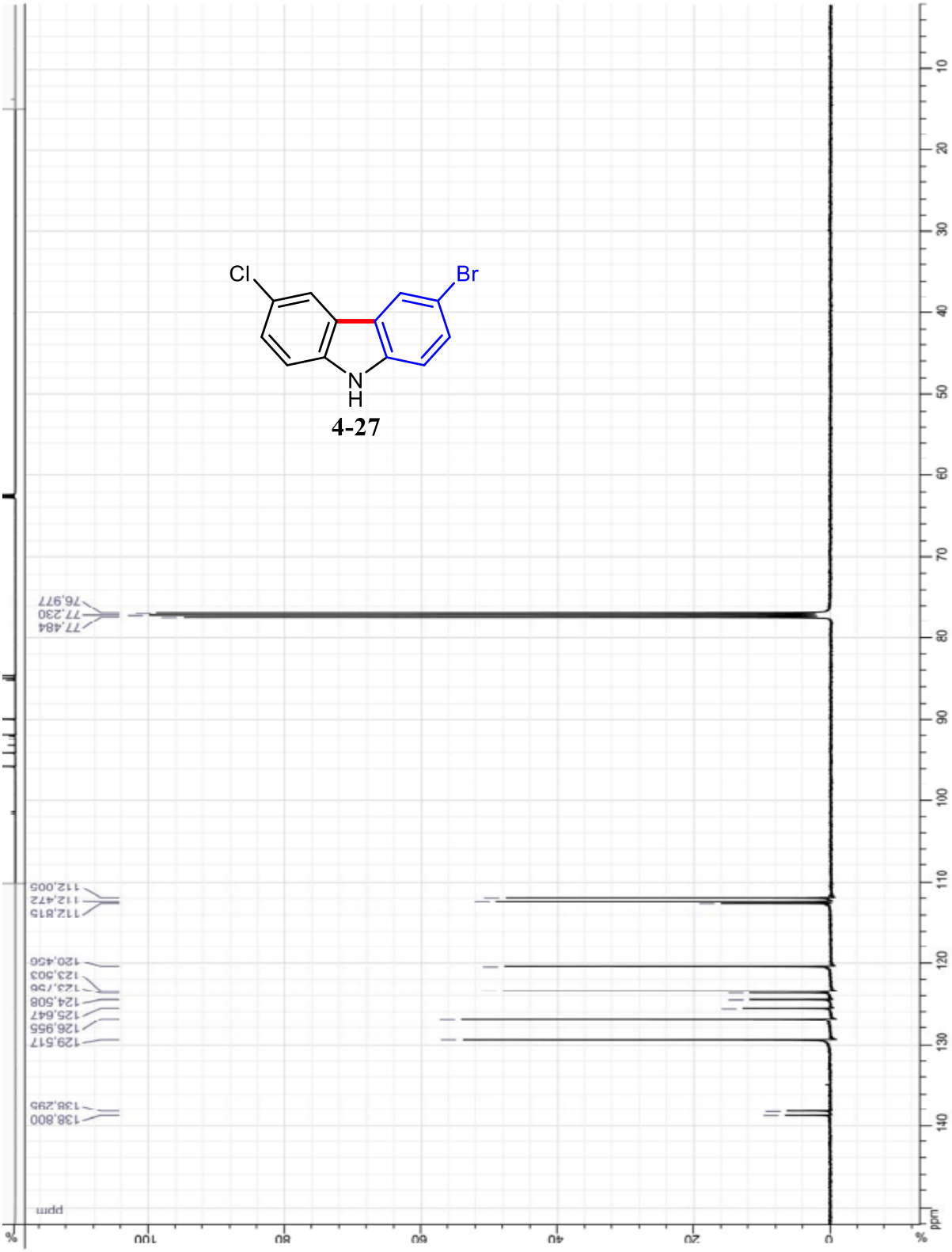
^{1}H NMR and ^{13}C NMR spectra of 3,6-dichloro-9*H*-carbazole (**4-26**) in $CDCl_3$



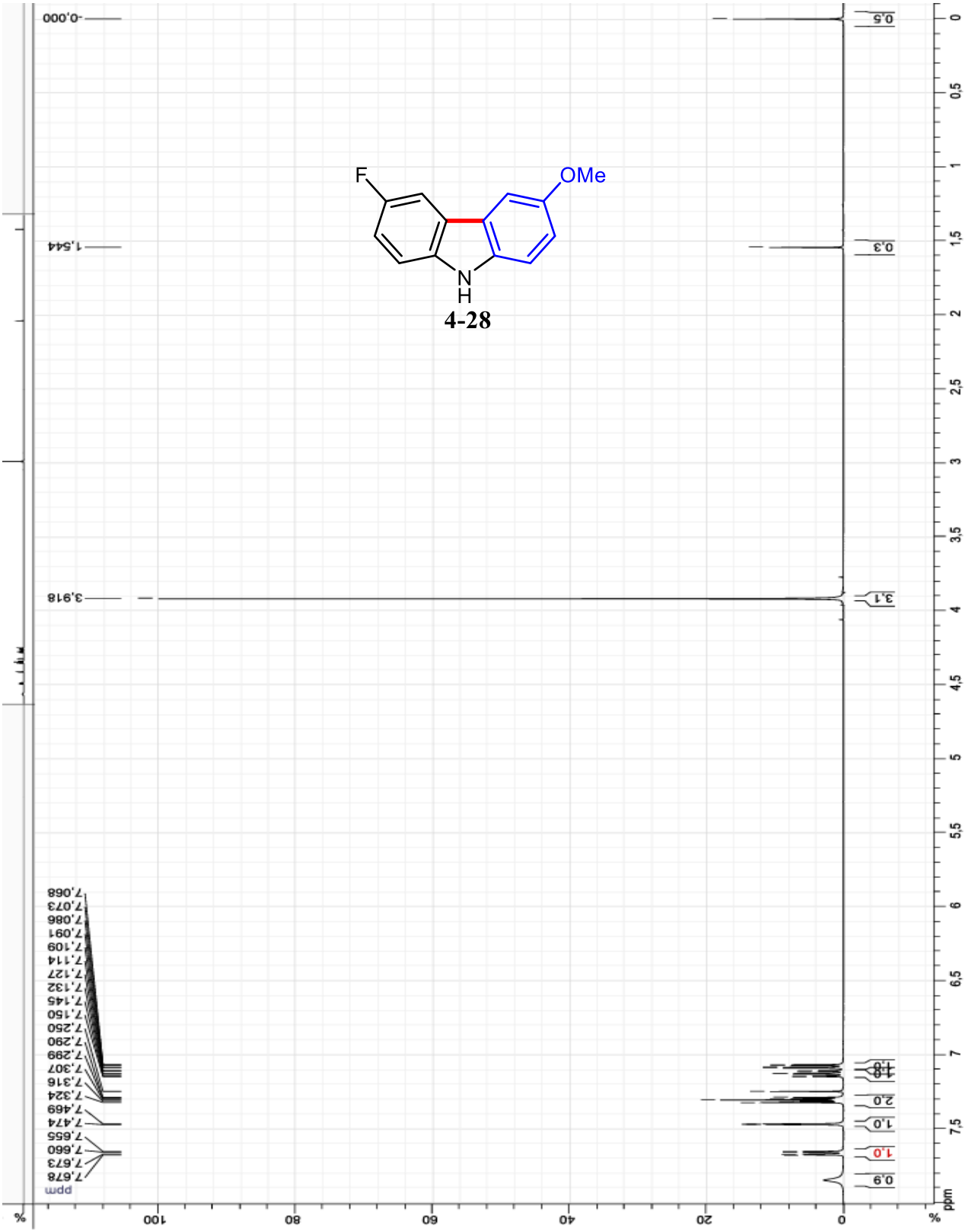

Cl
Cl
N
H
4-26
0.000
1.027
76.758
77.011
77.266
111.805
120.227
123.645
125.319
126.682
138.223
ppm

^{1}H NMR and ^{13}C NMR spectra of 3-bromo-6-chloro-9*H*-carbazole (**4-27**) in $CDCl_3$

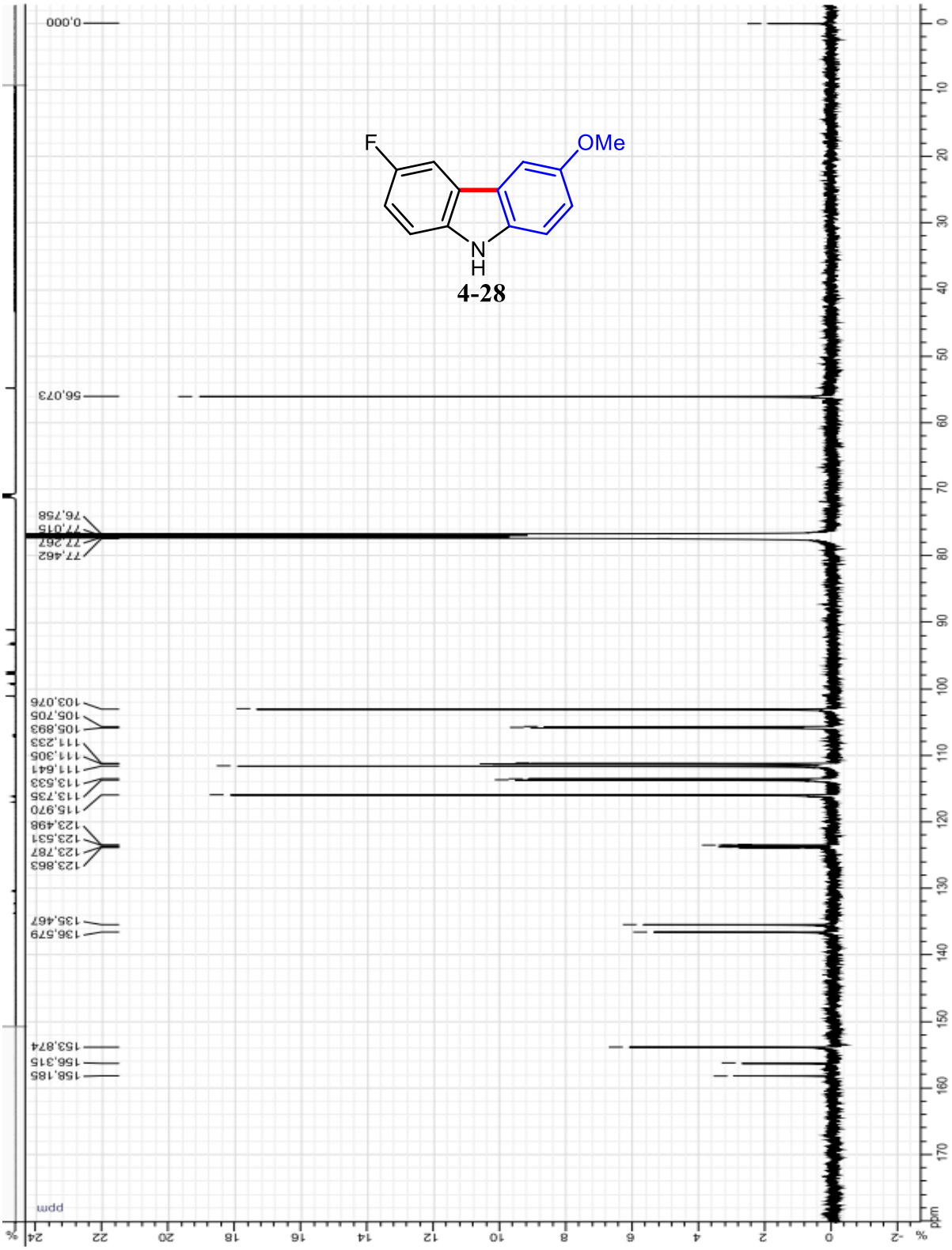


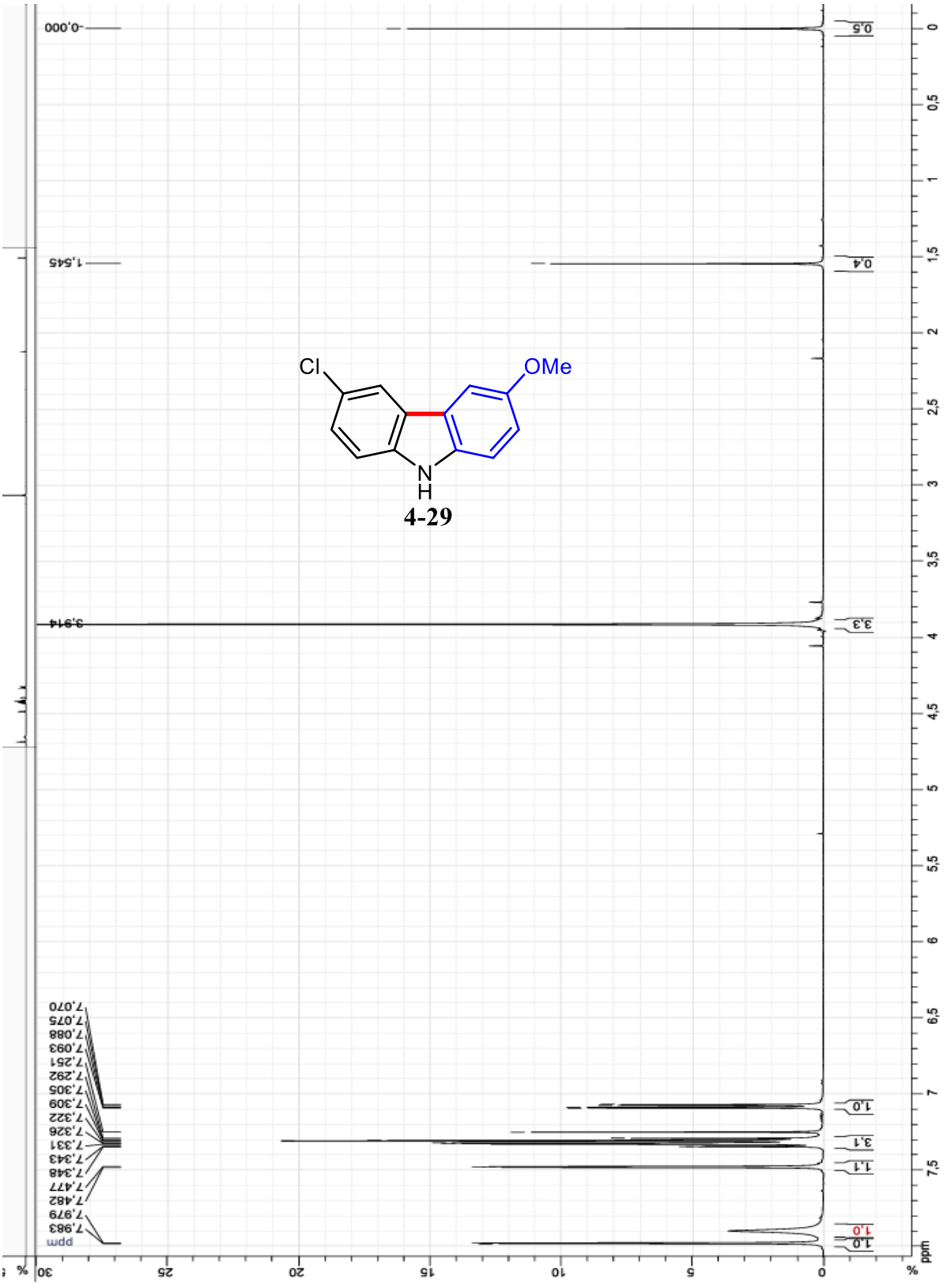

Cl
Br
N
H
4-27
77.484
77.230
76.977
112.815
112.472
112.005
120.456
123.503
123.796
124.508
125.647
126.955
129.517
138.295
138.800
ppm

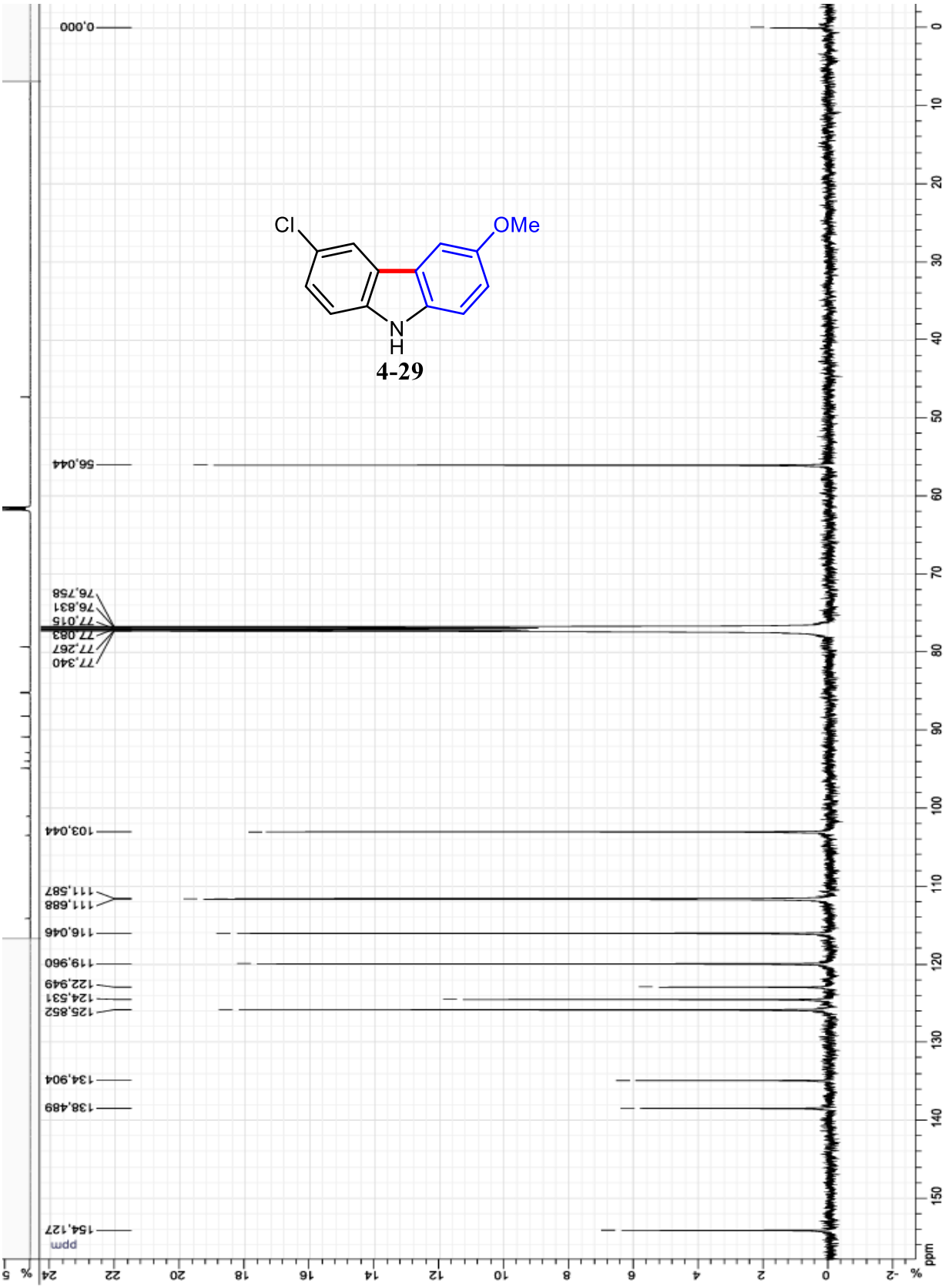
^{1}H NMR and ^{13}C NMR spectra of 3-fluoro-6-methoxy-9*H*-carbazole (**4-28**) in $CDCl_3$



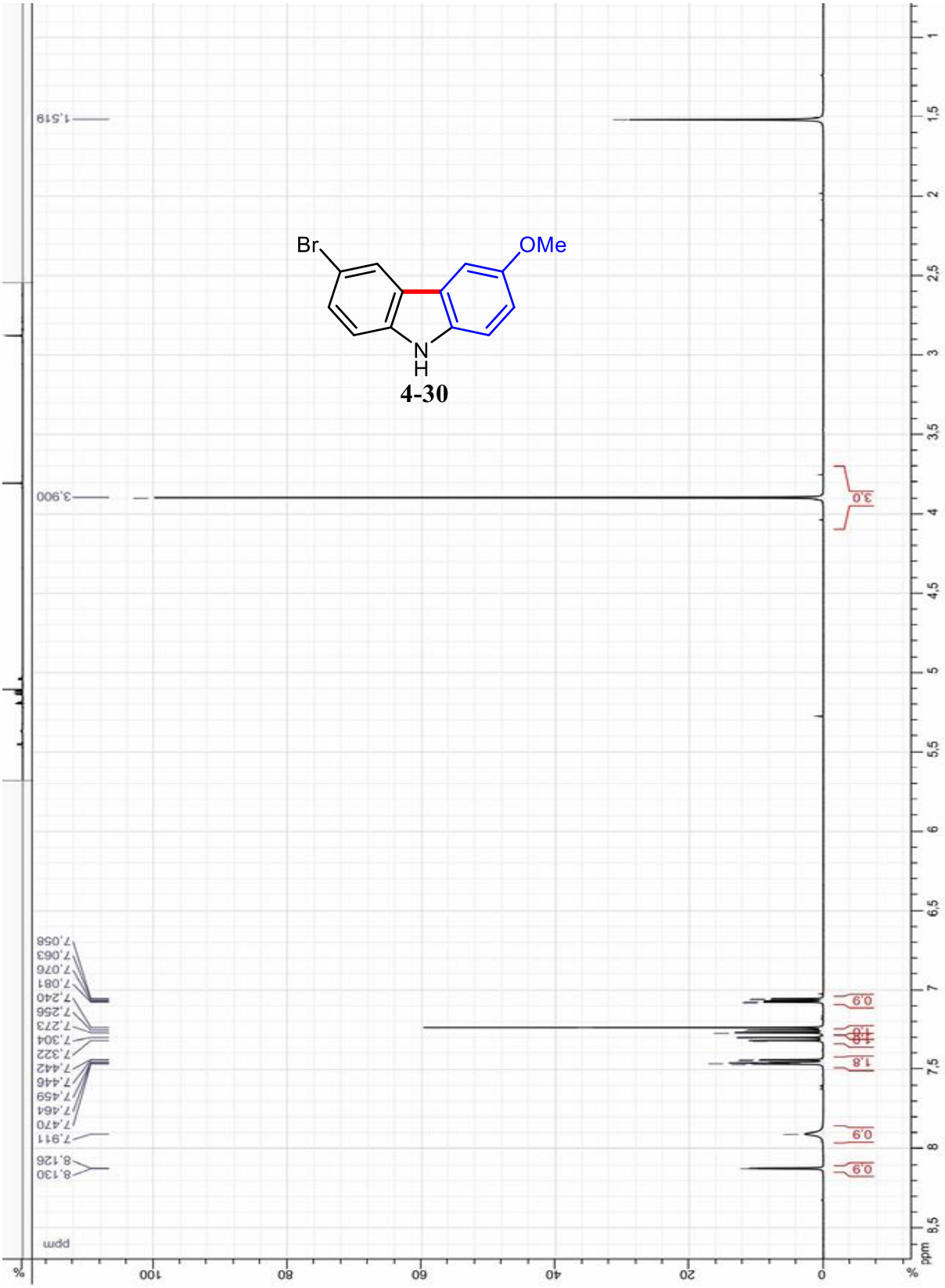
^{1}H NMR and ^{13}C NMR spectra of 3-chloro-6-methoxy-9*H*-carbazole (**4-29**) in $CDCl_3$

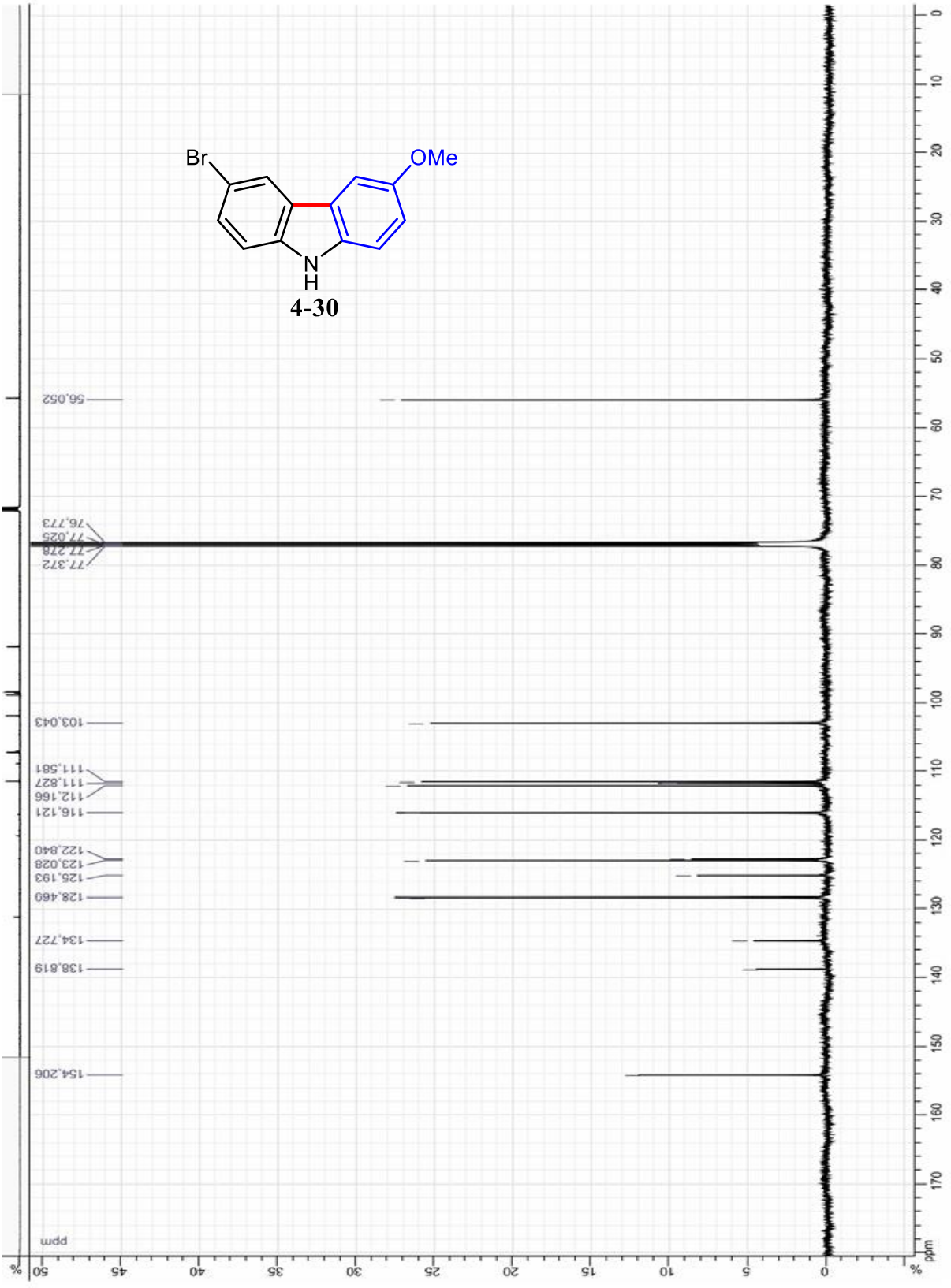



Cl
OMe
N
H
4-29

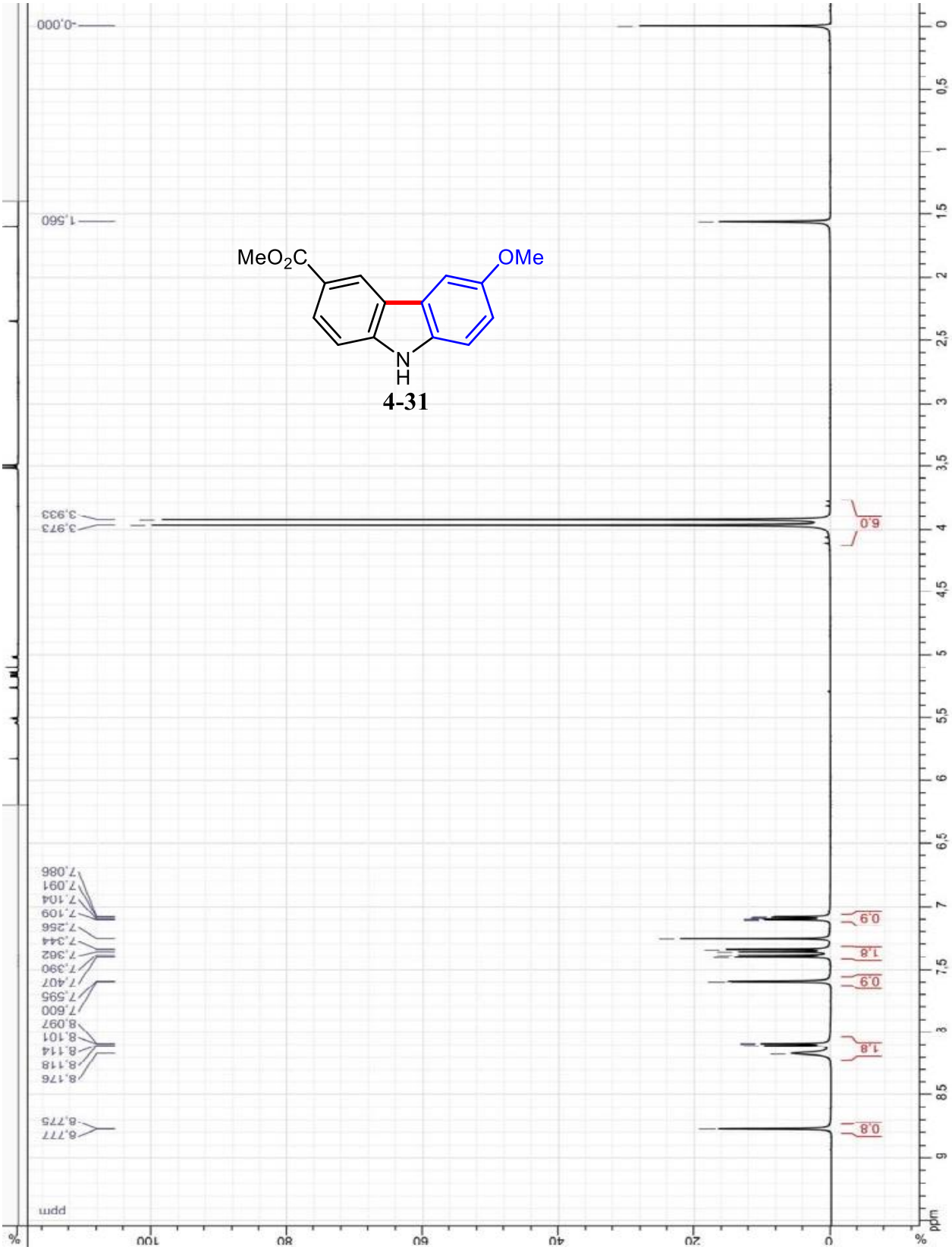

Cl
OMe
N
H
4-29
0.000
56.044
76.758
76.831
77.015
77.083
77.267
77.340
103.044
111.587
111.688
116.046
119.960
122.949
124.531
125.852
134.904
138.489
154.127
ppm

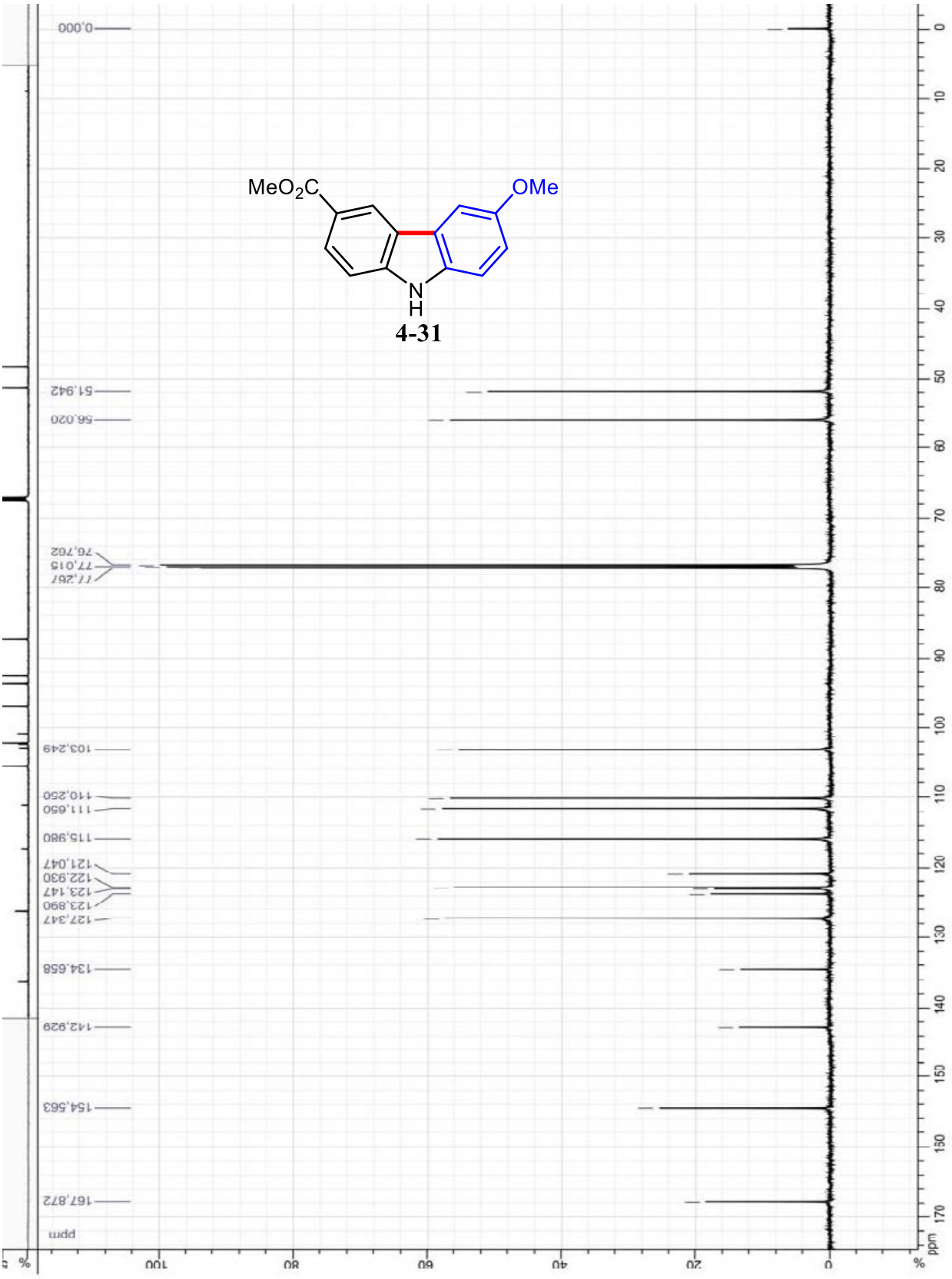
^{1}H NMR and ^{13}C NMR spectra of 3-bromo-6-methoxy-9*H*-carbazole (**4-30**) in $CDCl_3$



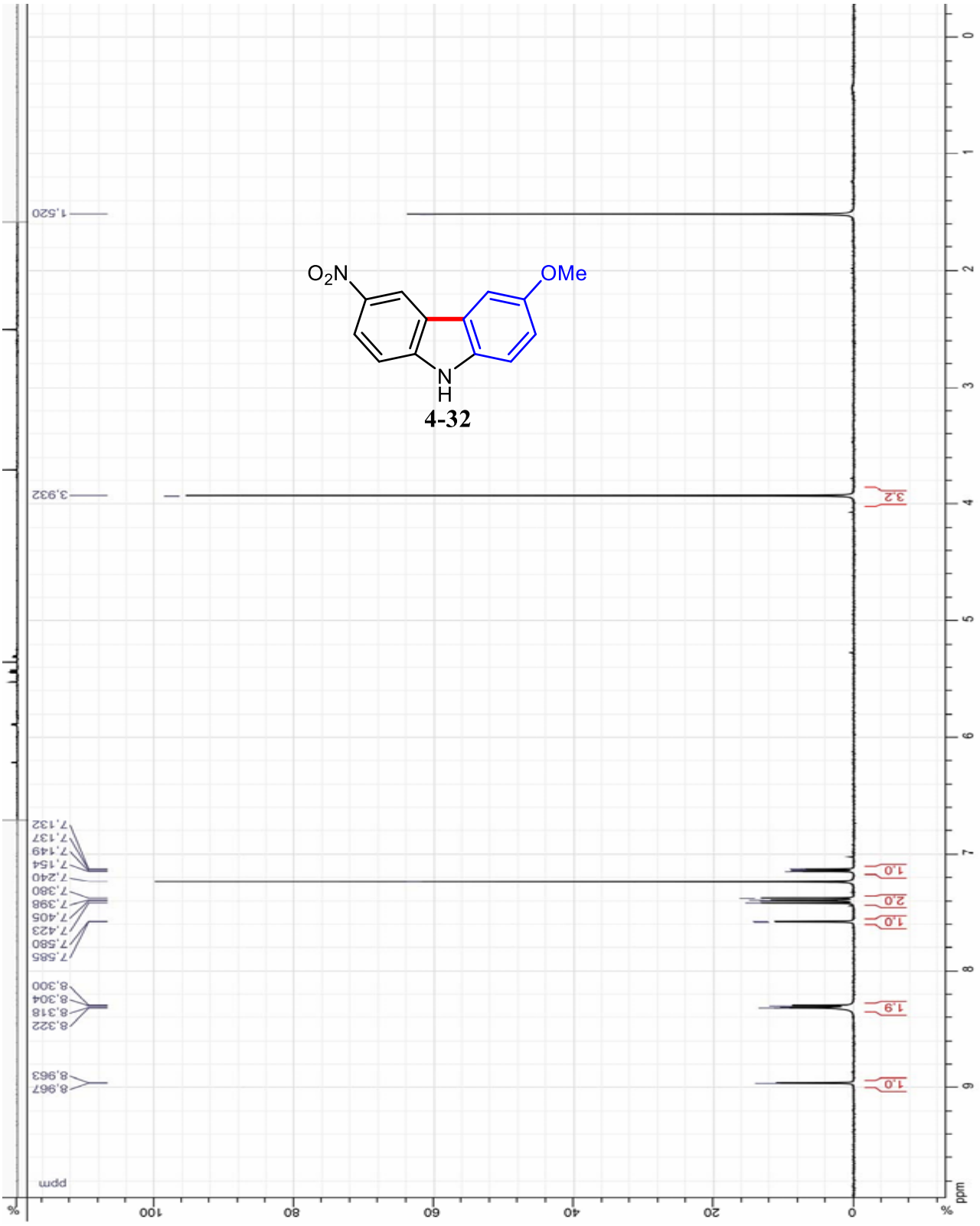

Br
OMe
N
H
4-30
56.052
76.773
77.025
77.278
77.372
103.043
111.581
111.827
112.166
116.121
122.840
123.028
125.193
128.469
134.727
138.819
154.206
ppm

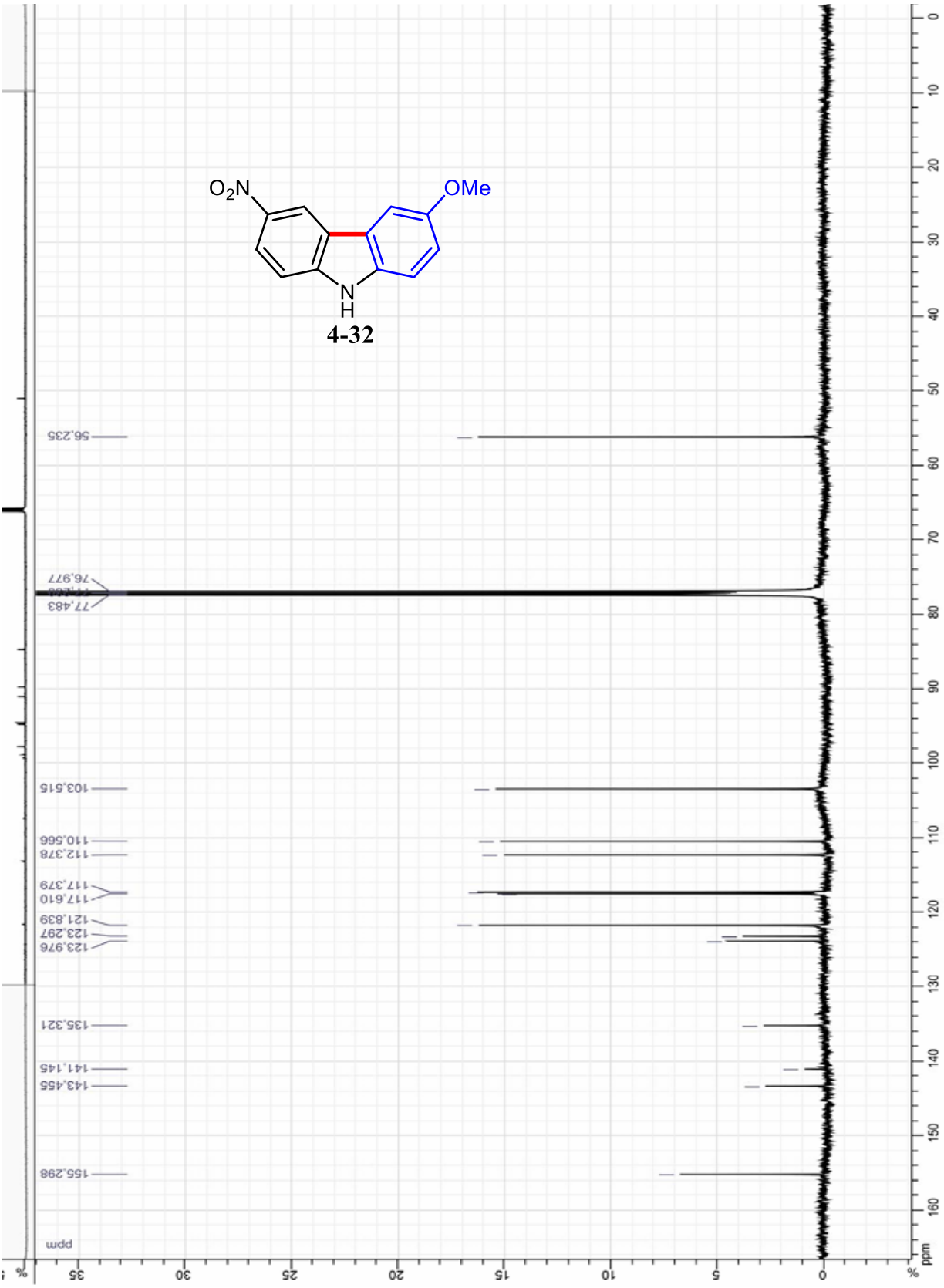
^{1}H NMR and ^{13}C NMR spectra of methyl 6-methoxy-9*H*-carbazole-3-carboxylate (**4-31**) in $CDCl_3$



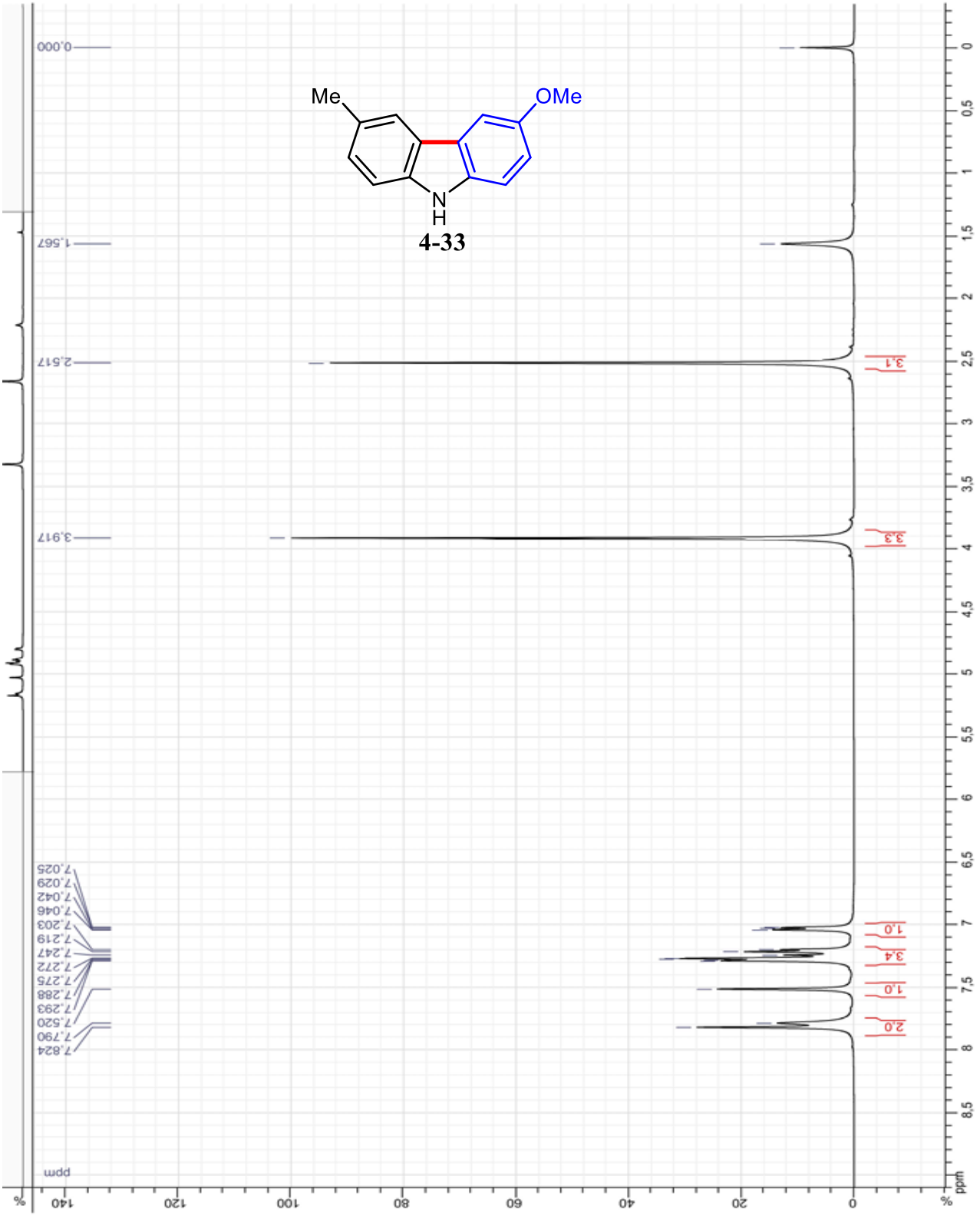

MeO2C
OMe
N
H
4-31
0.000
51.942
56.020
76.762
77.013
77.267
103.249
110.250
111.650
115.980
121.047
122.930
123.147
123.890
127.347
134.658
142.929
154.563
167.872
ppm

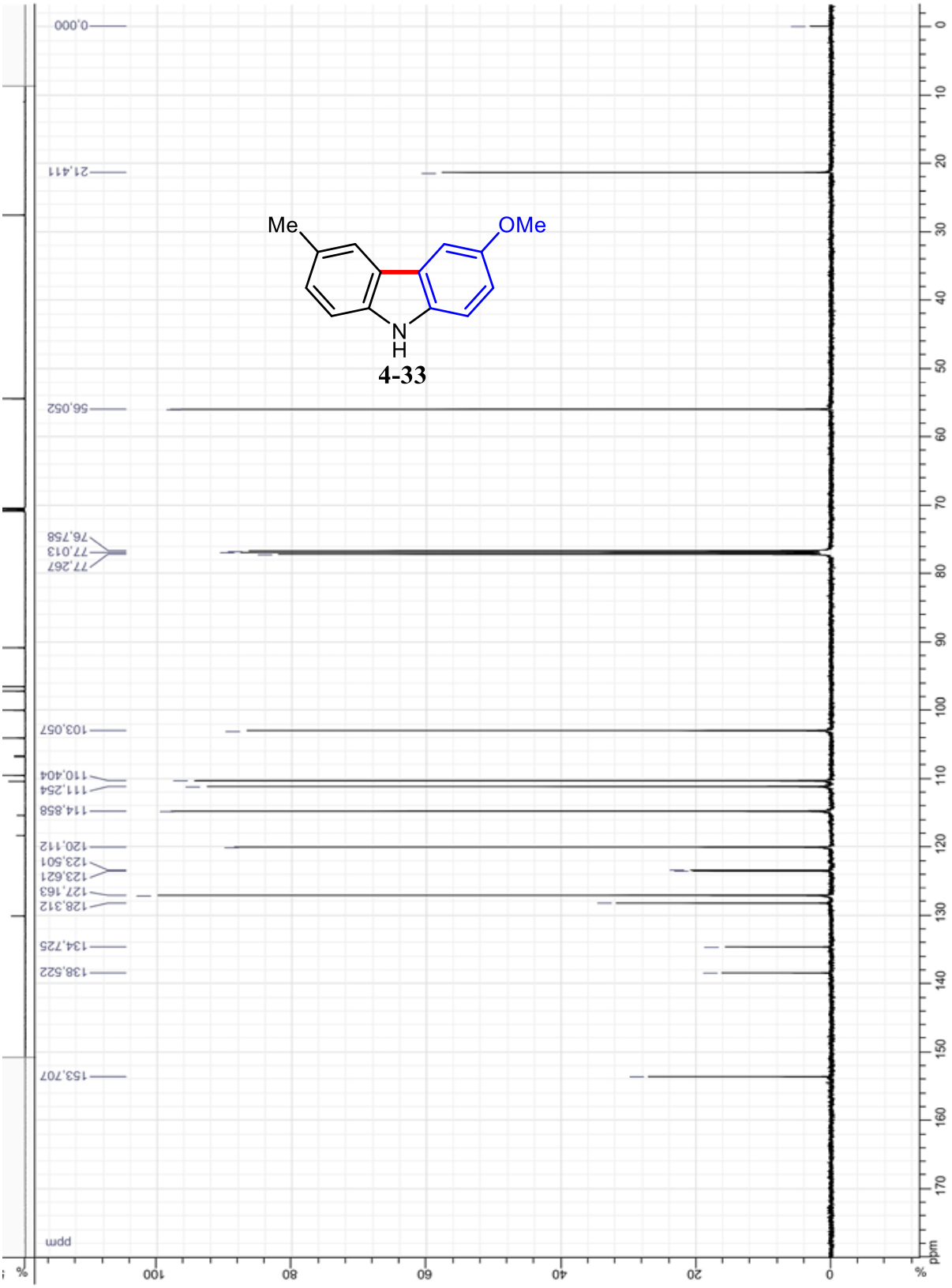
^{1}H NMR and ^{13}C NMR spectra of 3-methoxy-6-nitro-9*H*-carbazole (**4-32**) in $CDCl_3$



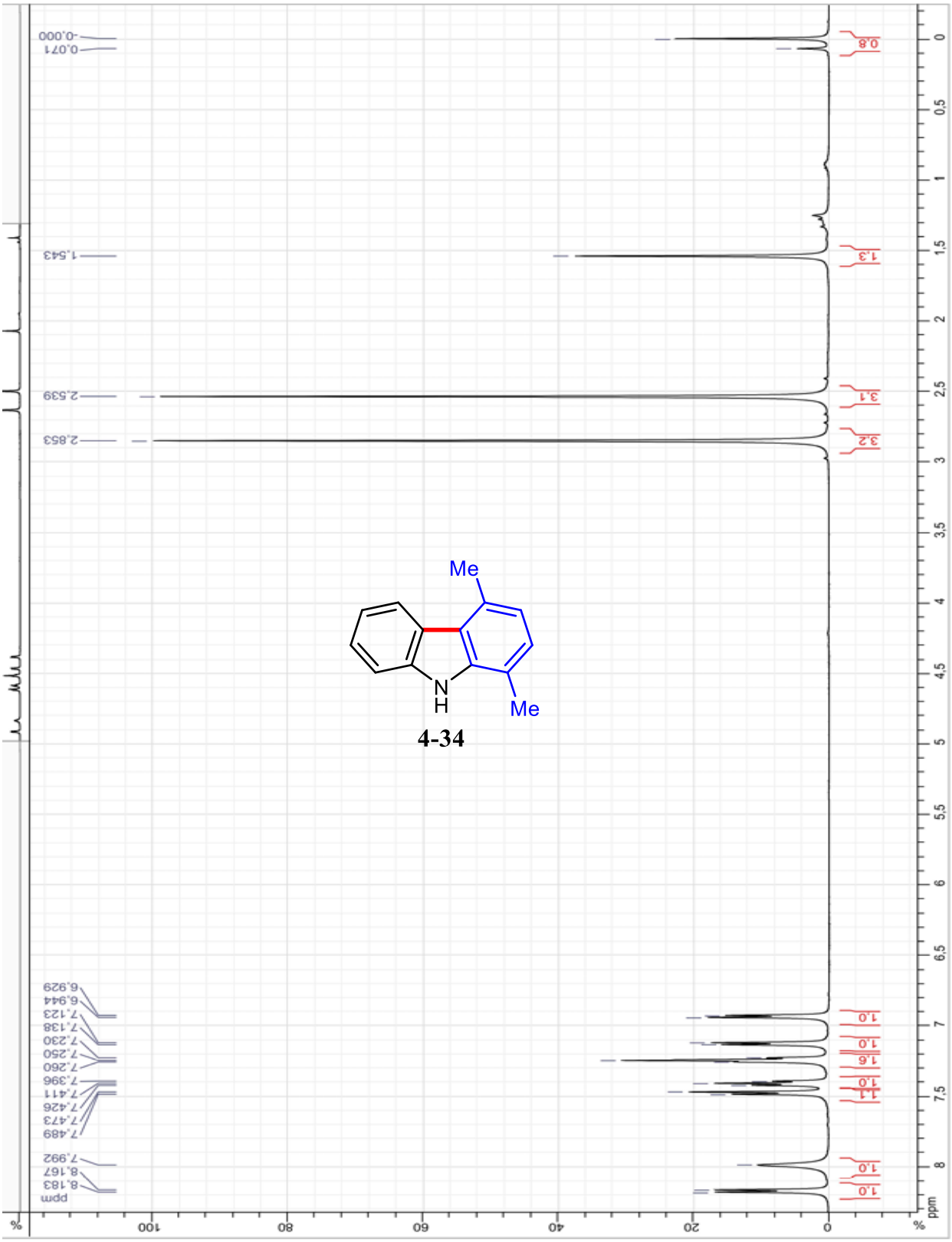

O2N
OMe
N
H
4-32
56.235
76.977
77.483
103.515
110.566
112.378
117.379
117.610
121.839
123.297
123.976
135.321
141.145
143.455
155.298
ppm

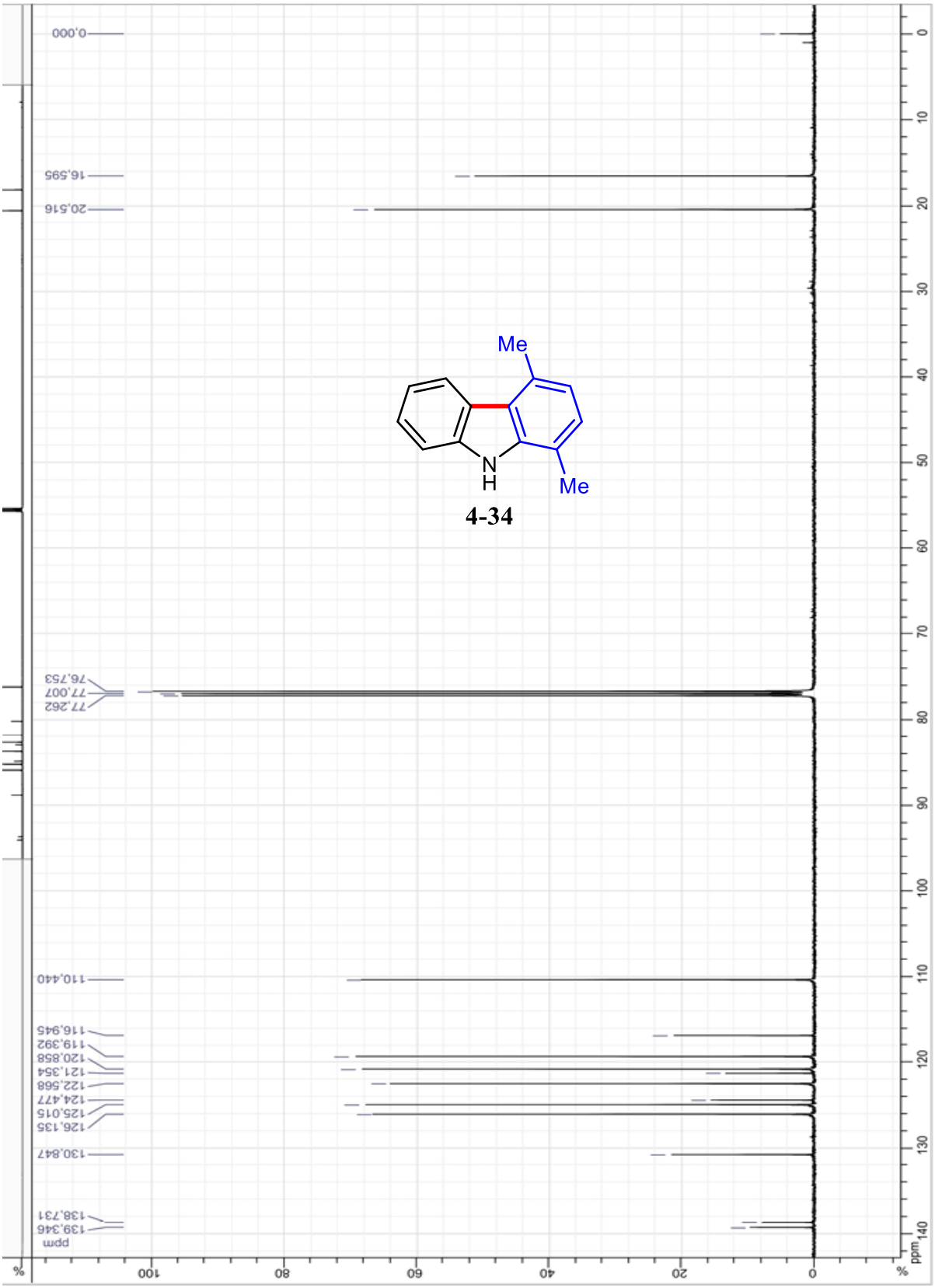
^{1}H NMR and ^{13}C NMR spectra of 3-methoxy-6-methyl-9*H*-carbazole **(4-33**, Glycozoline) in $CDCl_3$




Me
OMe
N
H
4-33
0.000
21.411
56.052
76.758
77.013
77.267
103.057
110.404
111.254
114.858
120.112
123.501
123.621
127.163
128.312
134.725
138.522
153.707
ppm

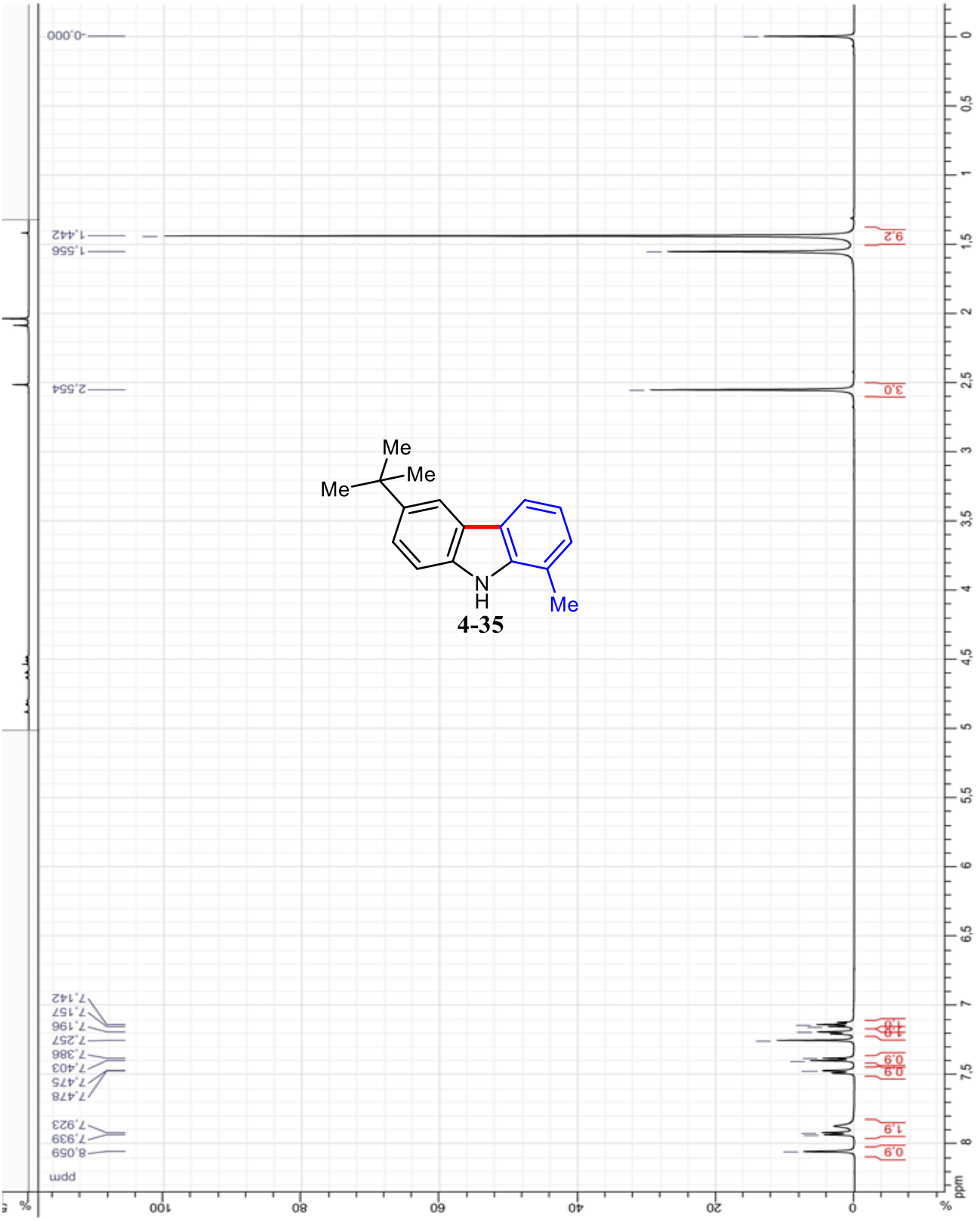
^{1}H NMR and ^{13}C NMR spectra of 1,4-dimethyl-9*H*-carbazole (**4-34**) in $CDCl_3$

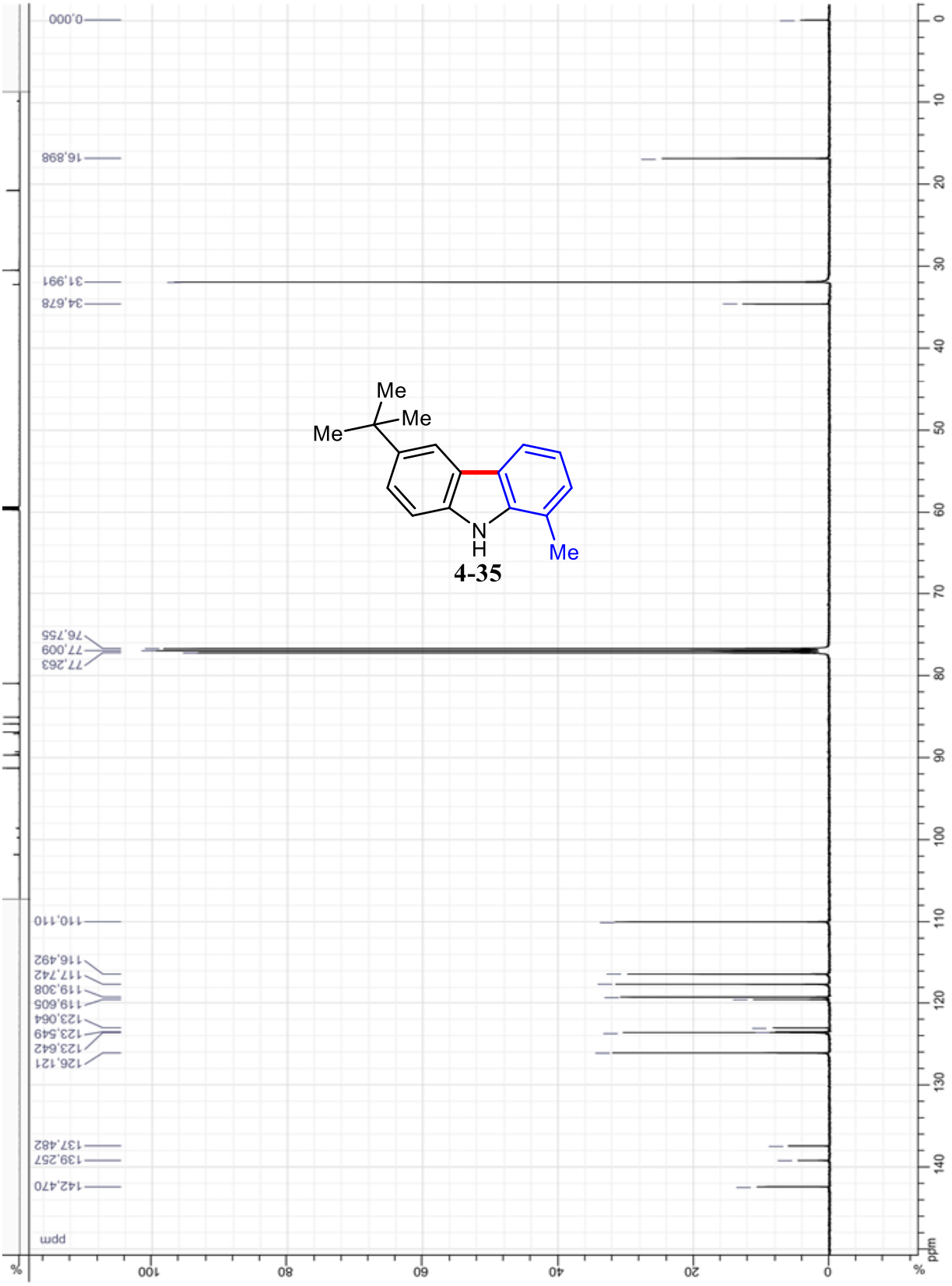



0.000
16.595
20.516
77.262
77.007
76.753
110.440
116.945
119.392
120.858
121.354
122.568
124.477
125.015
126.135
130.847
138.731
139.346
ppm
Me
N
H
Me

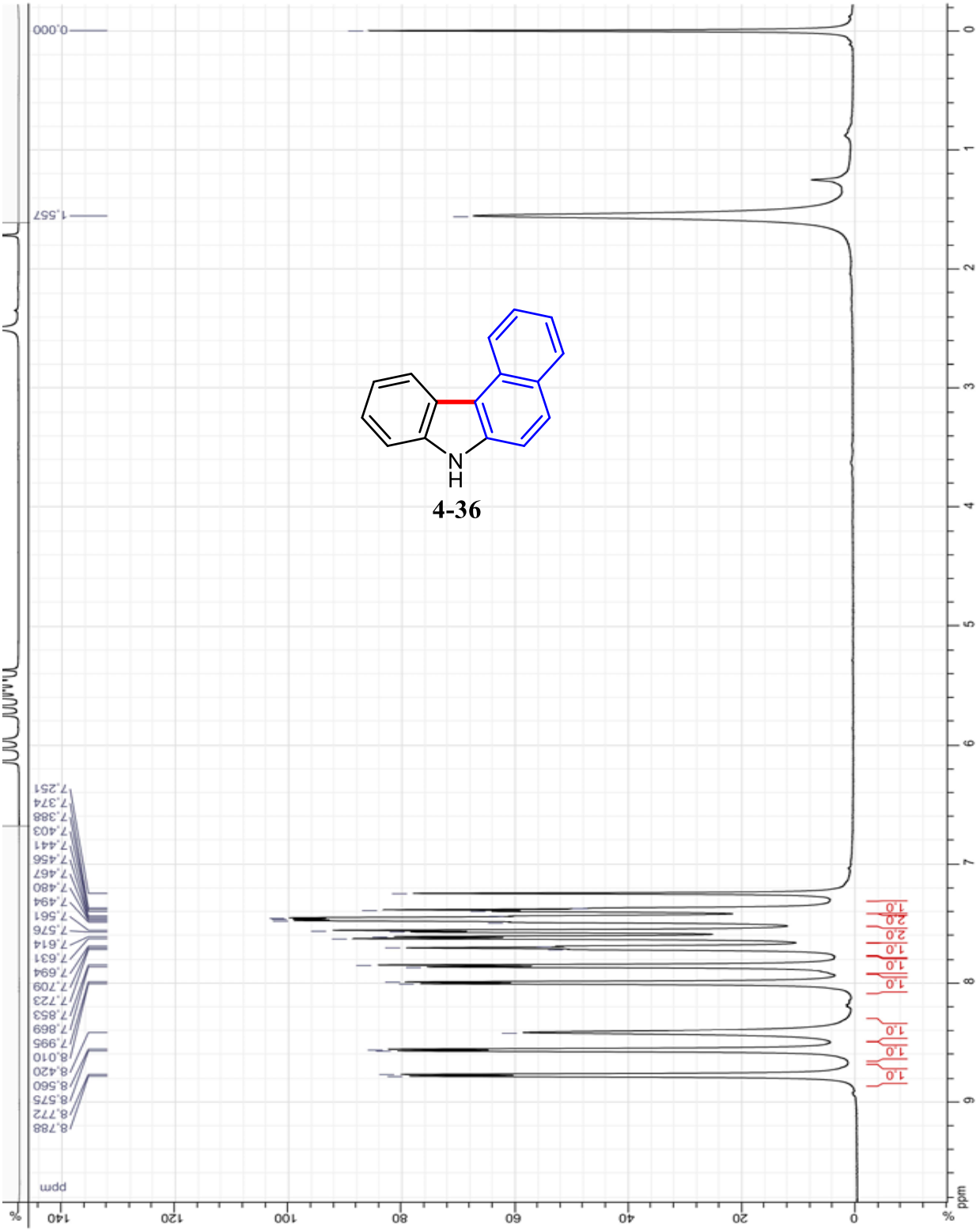
4-34

^{1}H NMR and ^{13}C NMR spectra of 6-(*tert*-butyl)-1-methyl-9*H*-carbazole (**4-35**) in $CDCl_3$

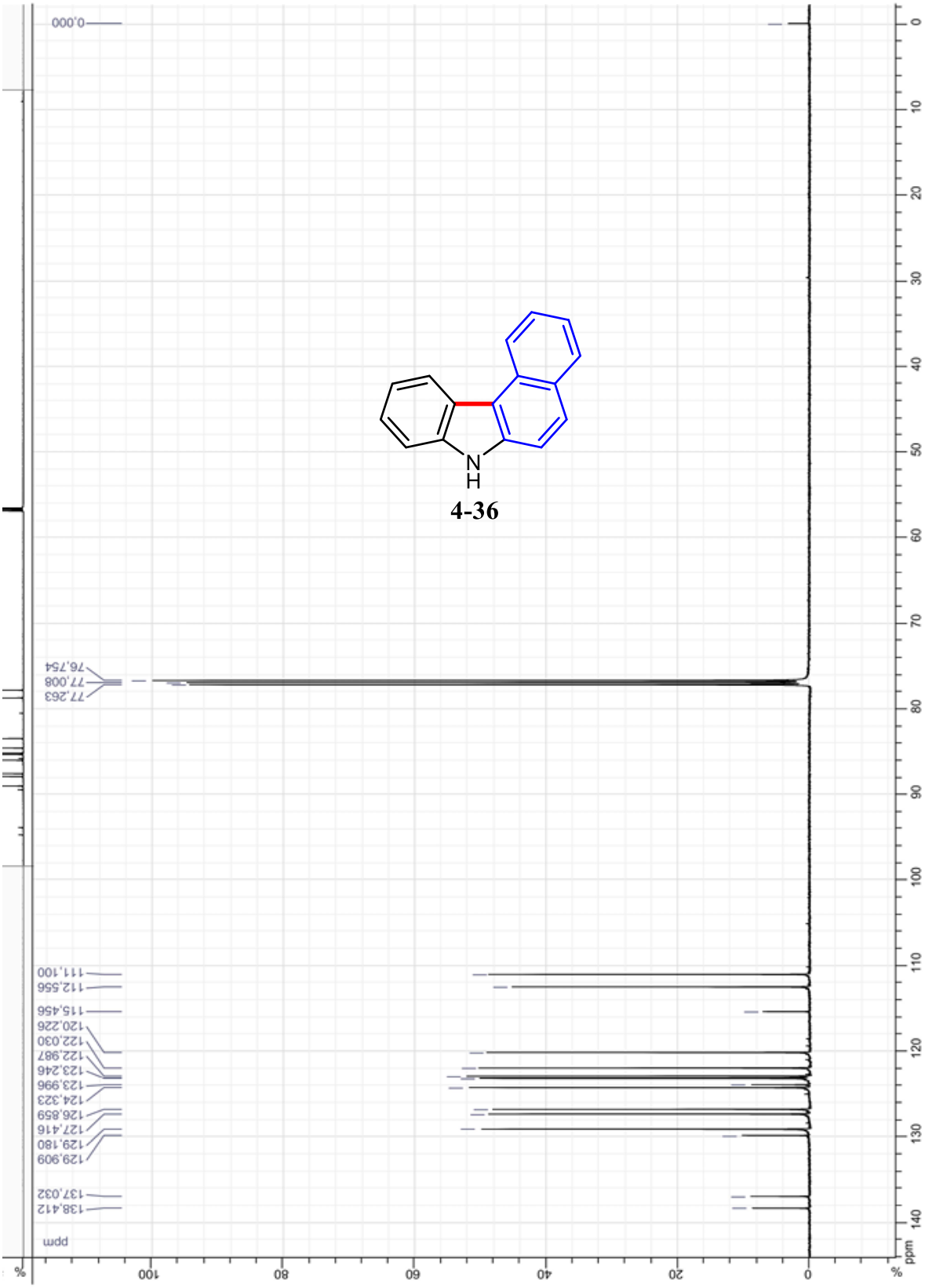



0.000
16.898
31.991
34.678
77.263
77.009
76.755
110.110
116.492
117.742
119.308
119.605
123.064
123.549
123.642
126.121
137.482
139.257
142.470
ppm
Me
Me
Me
N
H
Me
4-35

^{1}H NMR and ^{13}C NMR spectra of 7*H*-benzo[*c*]carbazole (**4-36**) in DMSO-D_6

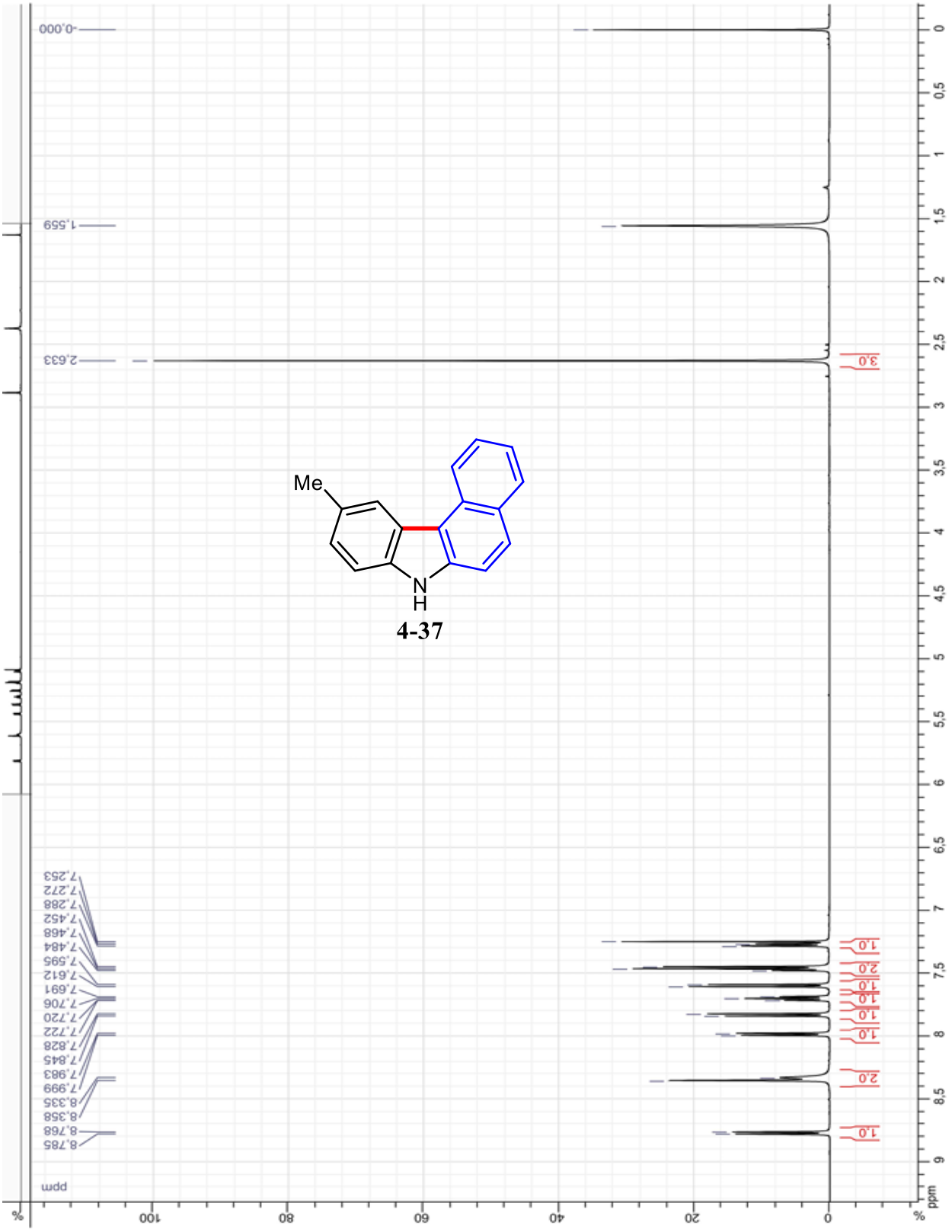


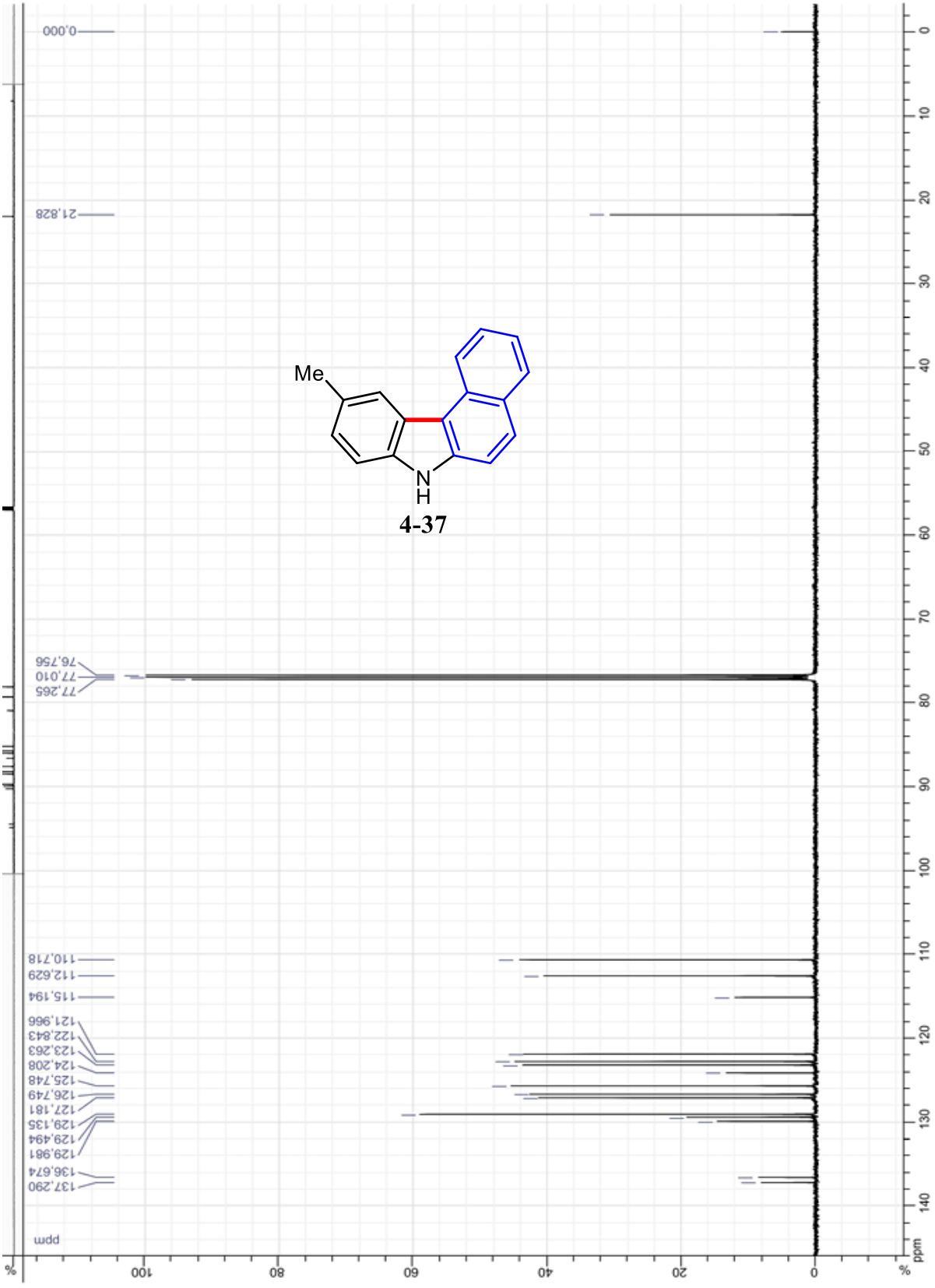
4-36


0.000
77.263
77.008
76.754
111.100
112.556
115.456
120.226
122.030
122.987
123.246
123.996
124.323
126.859
127.416
129.180
129.909
137.032
138.412
ppm
%
100
80
60
40
20
0
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
N
H

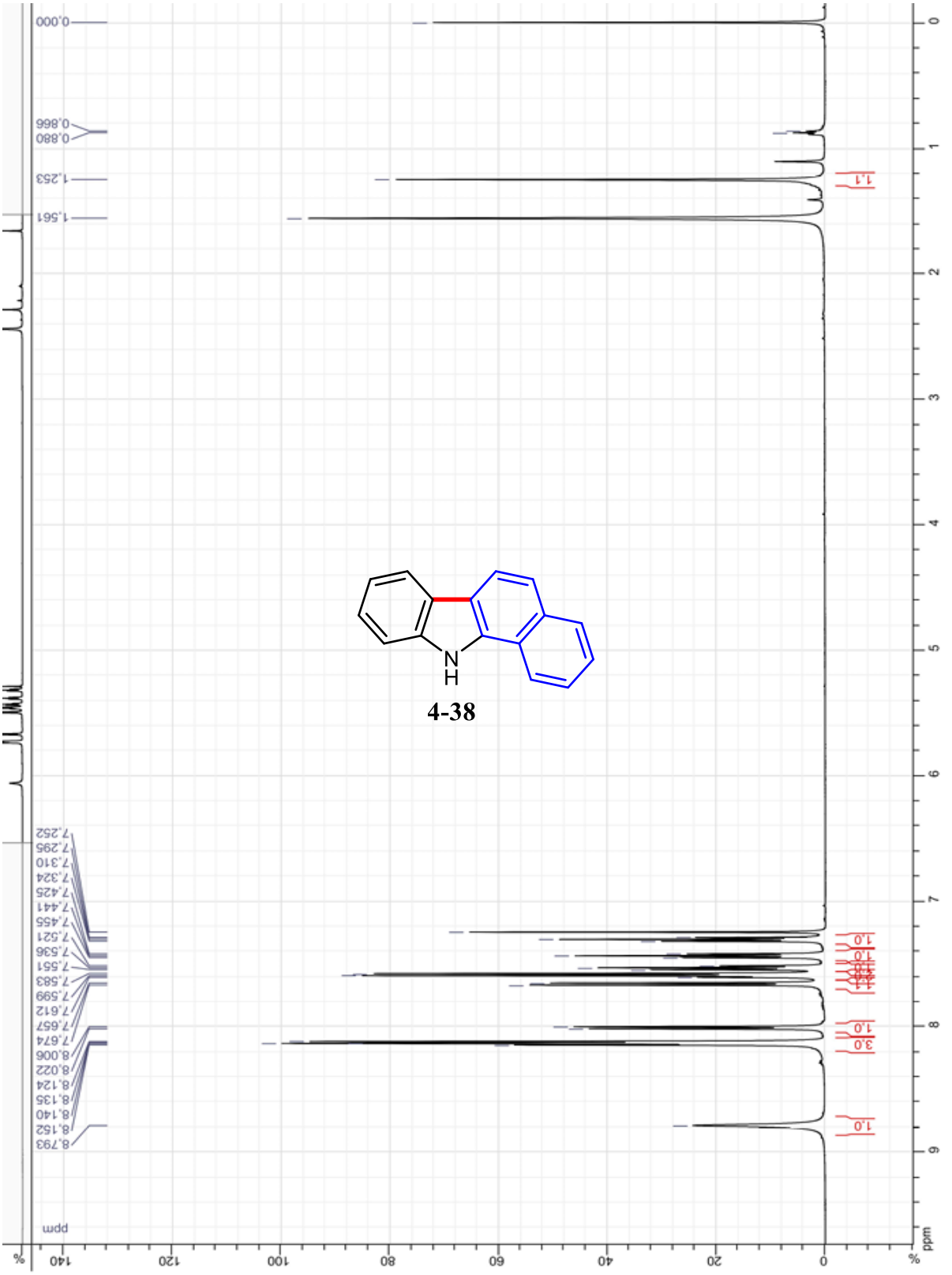
4-36

^{1}H NMR and ^{13}C NMR spectra of 10-methyl-7*H*-benzo[*c*]carbazole (**4-37**) in DMSO-D_6

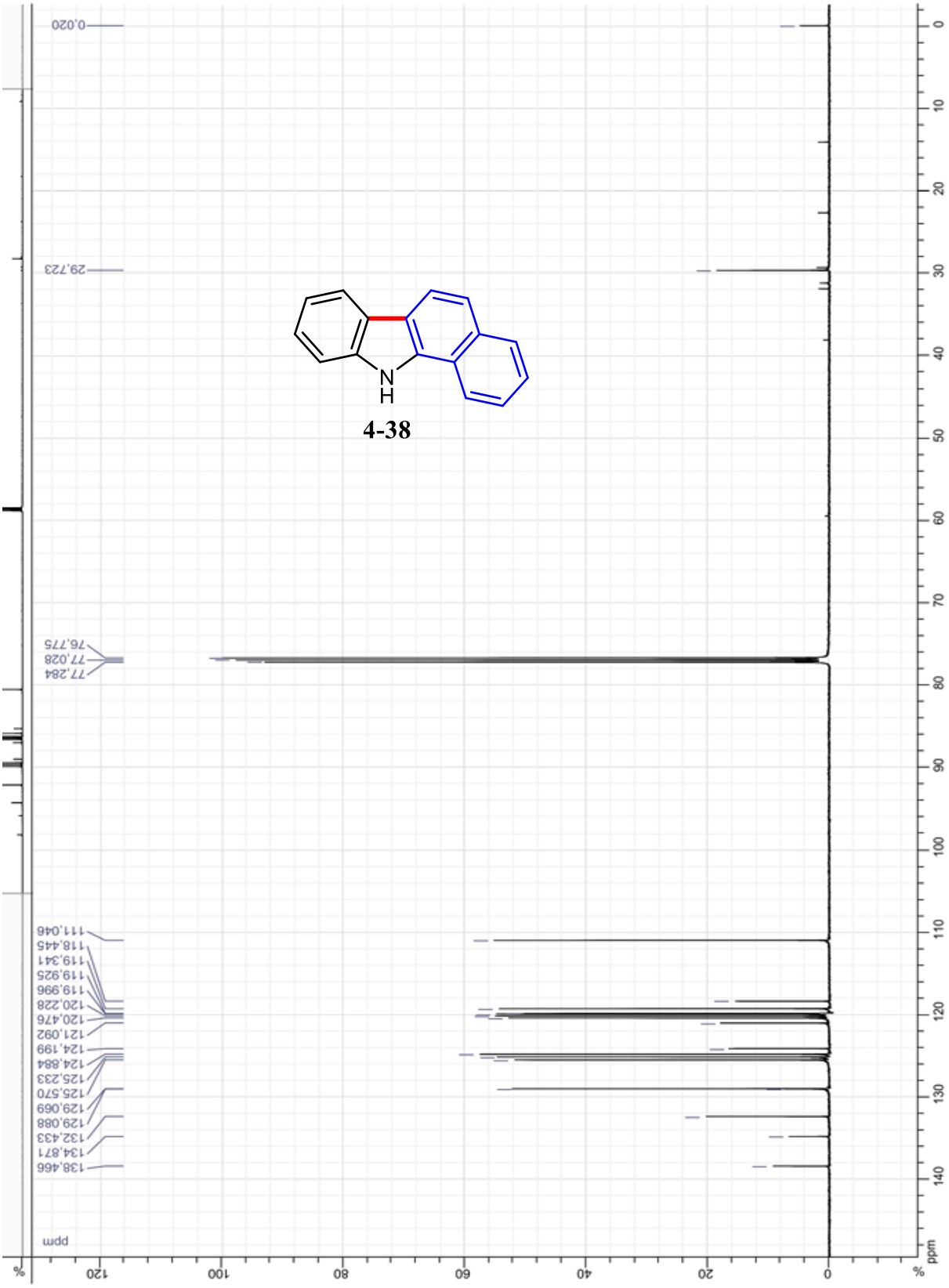



Me
N
H
4-37
0.000
21.828
76.756
77.010
77.265
110.718
112.629
115.194
121.966
122.843
123.263
124.208
125.748
126.749
127.181
129.135
129.494
129.981
136.674
137.290
ppm

^{1}H NMR and ^{13}C NMR spectra of 11*H*-benzo[*a*]carbazole (**4-38**) in $CDCl_3$

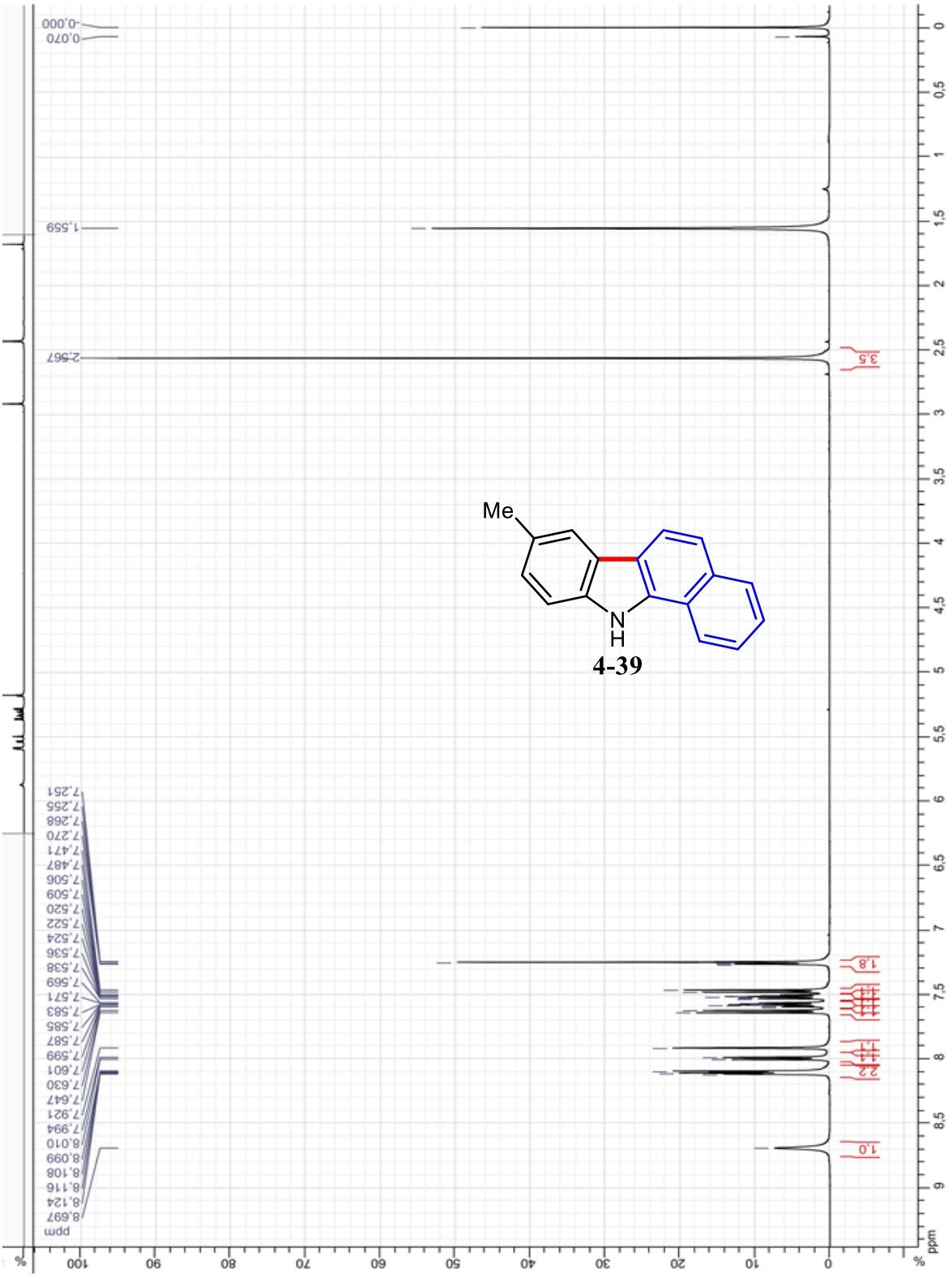


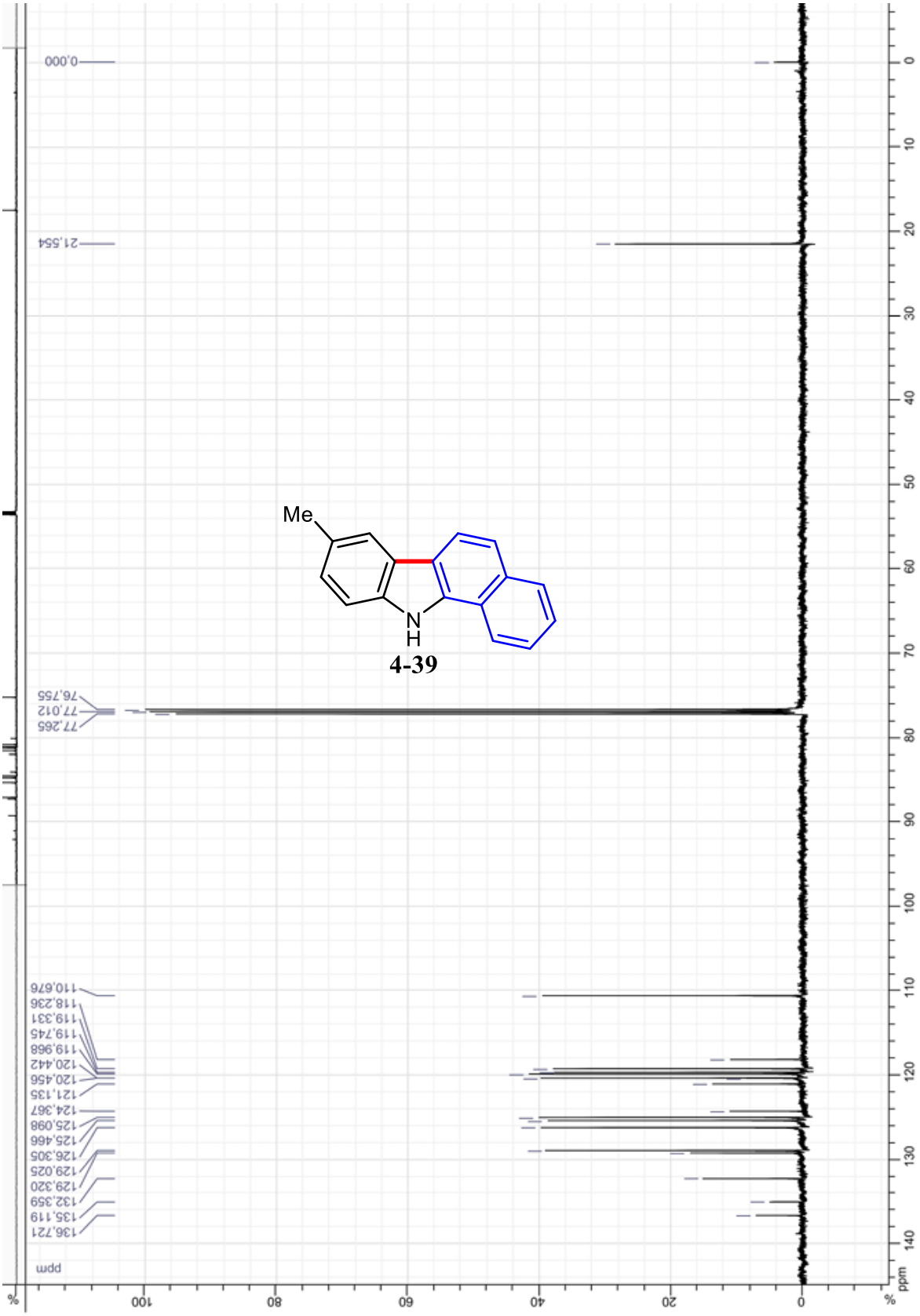
4-38


0.020
29.723
76.775
77.028
77.284
111.046
118.445
119.341
119.925
119.996
120.228
120.476
121.092
124.199
124.884
125.233
125.570
129.069
129.088
132.433
134.871
138.466
ppm
%
120
100
80
60
40
20
0
%
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140

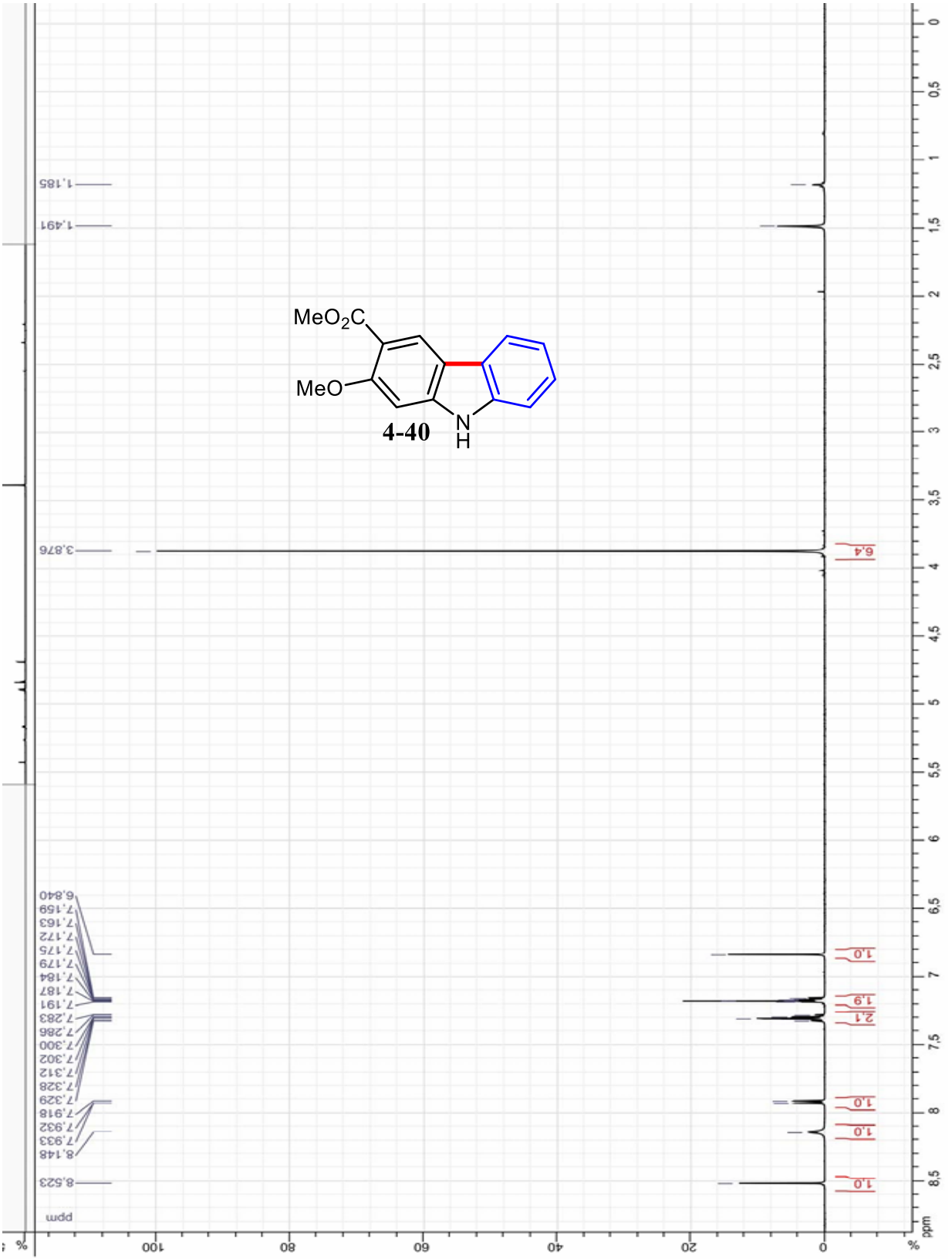
4-38

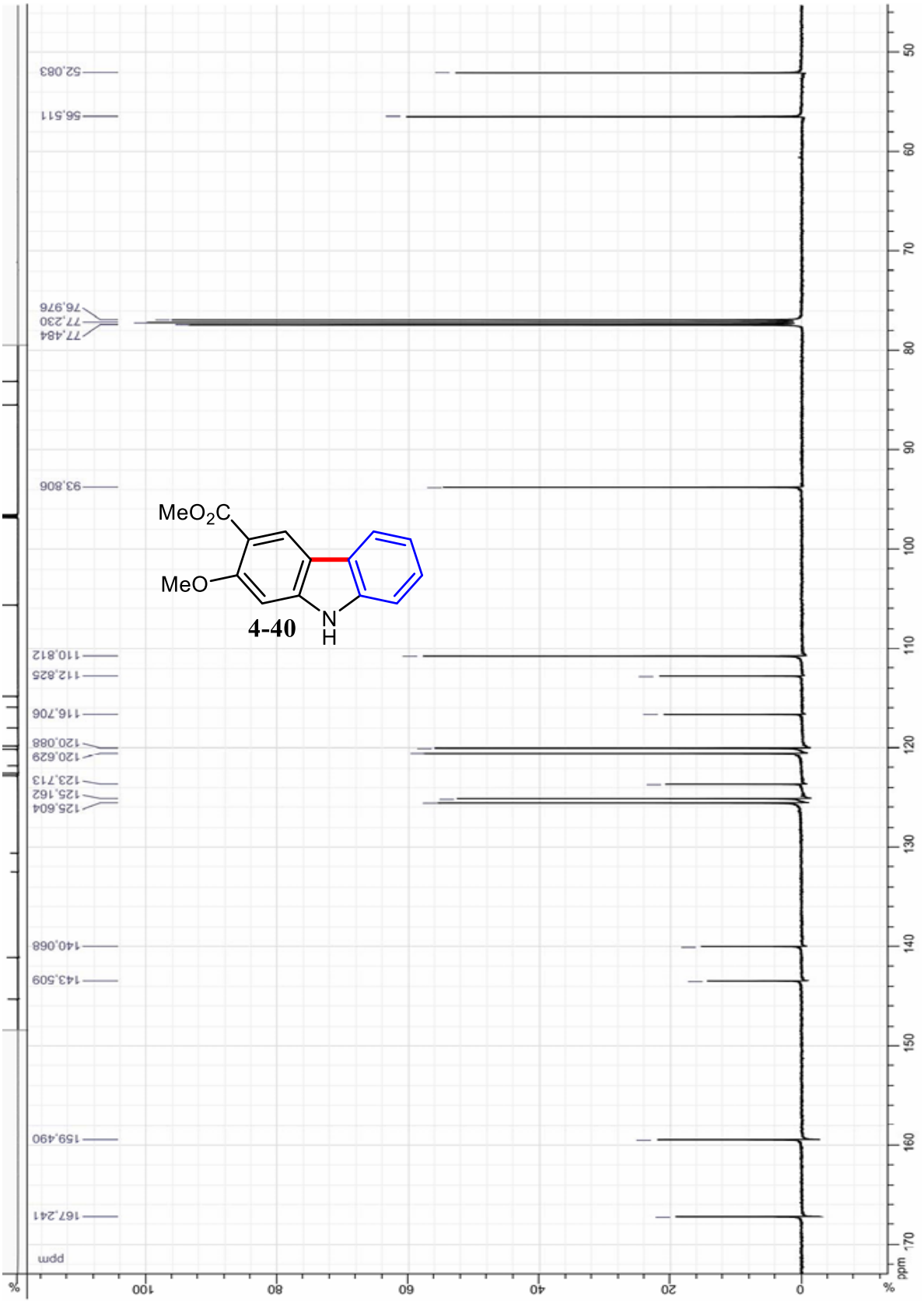
^{1}H NMR and ^{13}C NMR spectra of 8-methyl-11*H*-benzo[*a*]carbazole (**4-39**) in $CDCl_3$



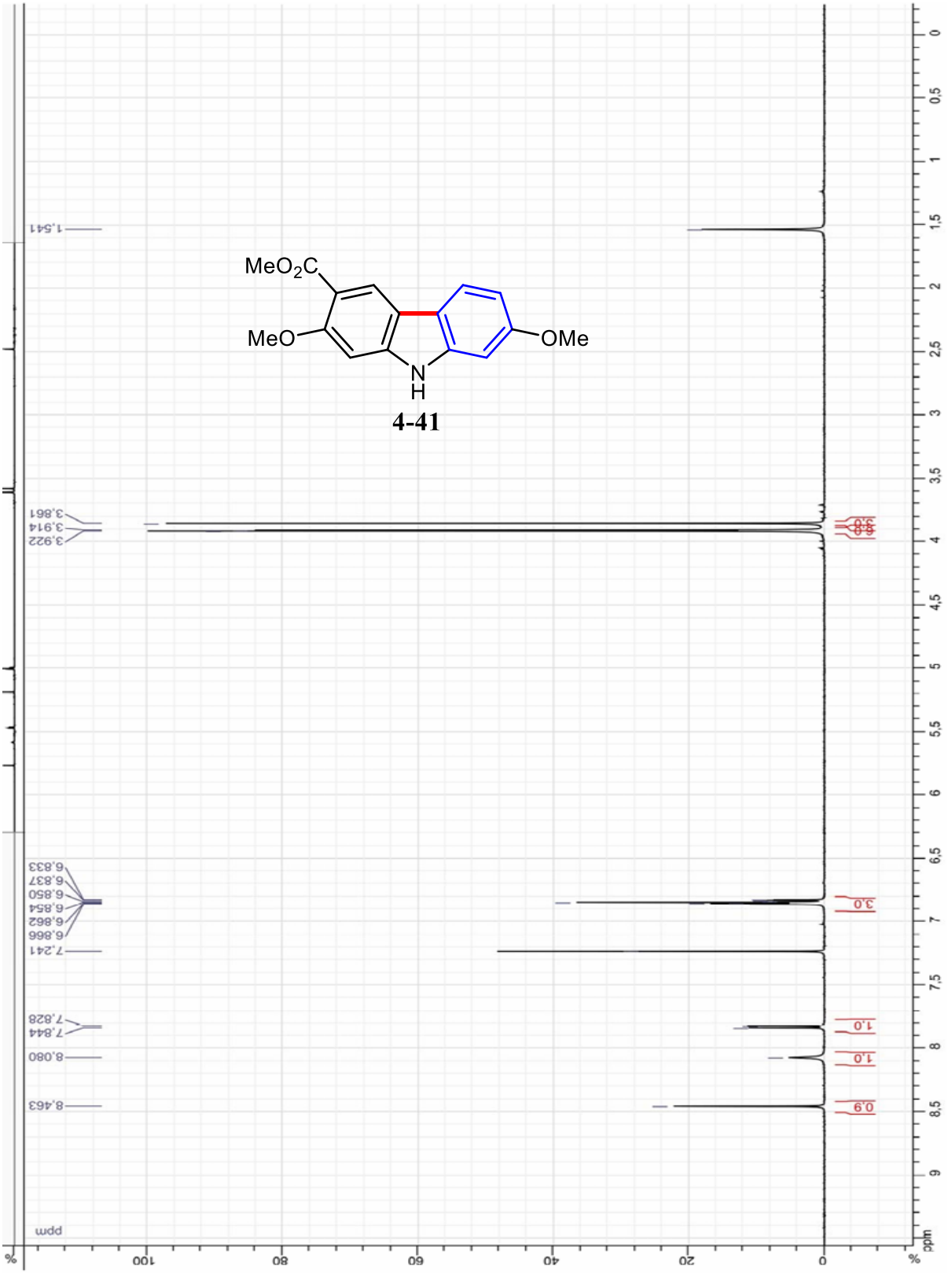

Me
N
H
4-39
0.000
21.554
76.755
77.012
77.265
110.676
118.236
119.331
119.745
119.968
120.442
120.456
121.135
124.367
125.098
125.466
126.305
129.025
129.320
132.359
135.119
136.721
ppm

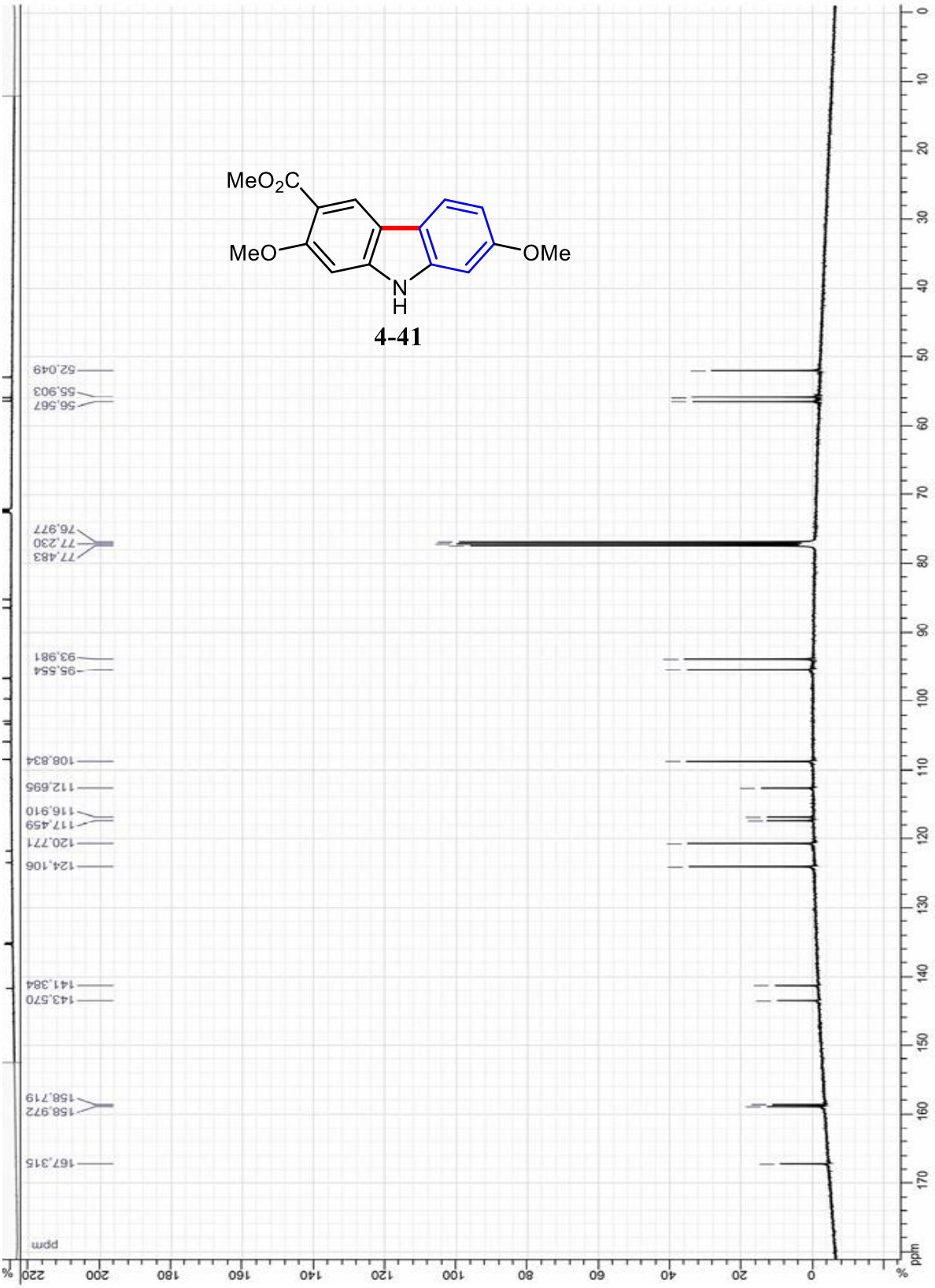
^{1}H NMR and ^{13}C NMR spectra of methyl 2-methoxy-9*H*-carbazole-3-carboxylate (**4-40**) in $CDCl_3$



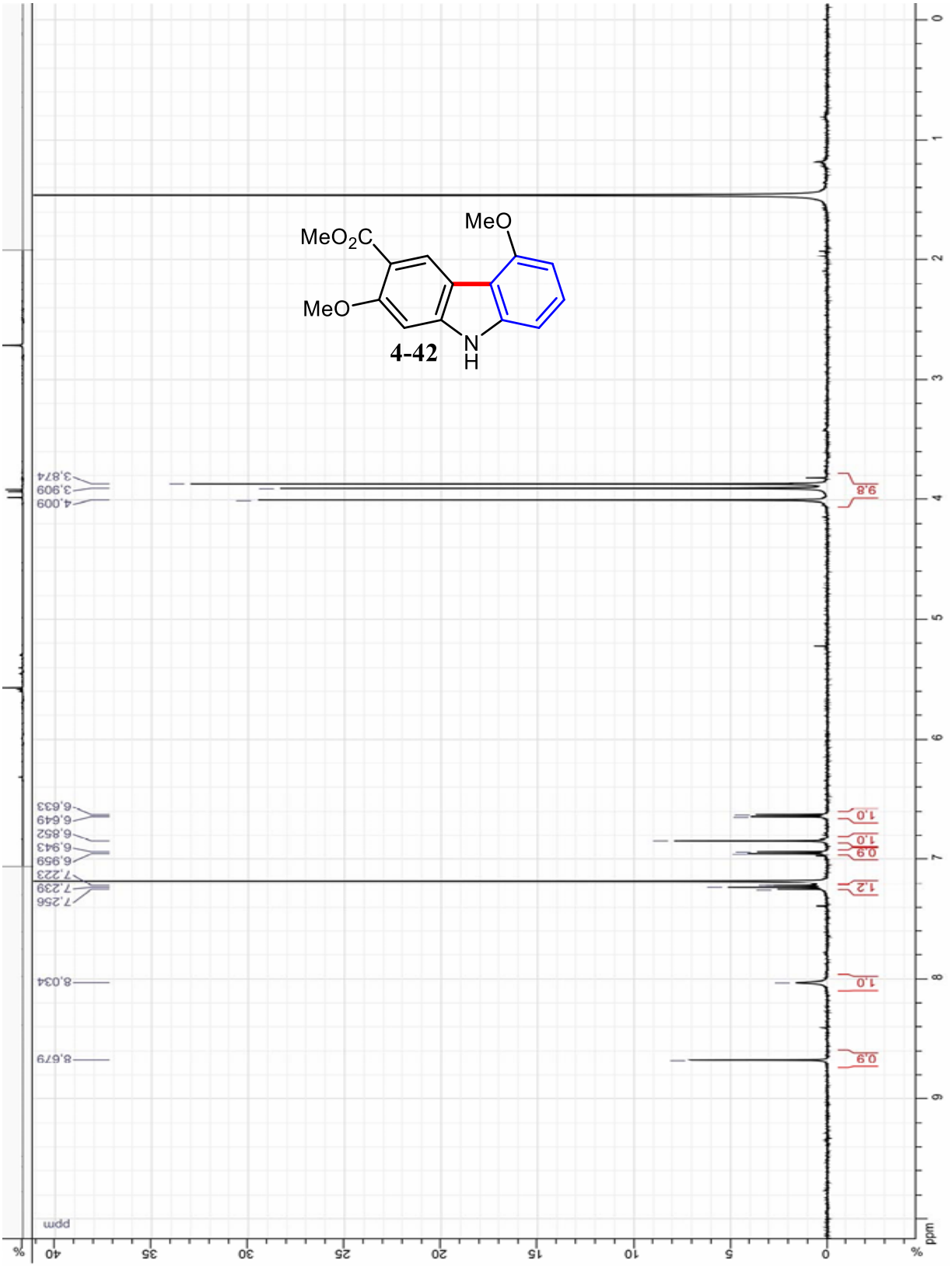

MeO2C
MeO
N
H
4-40
52.083
56.511
76.976
77.230
77.484
93.806
110.812
112.825
116.706
120.088
120.629
123.713
125.162
125.604
140.068
143.509
159.490
167.241
ppm

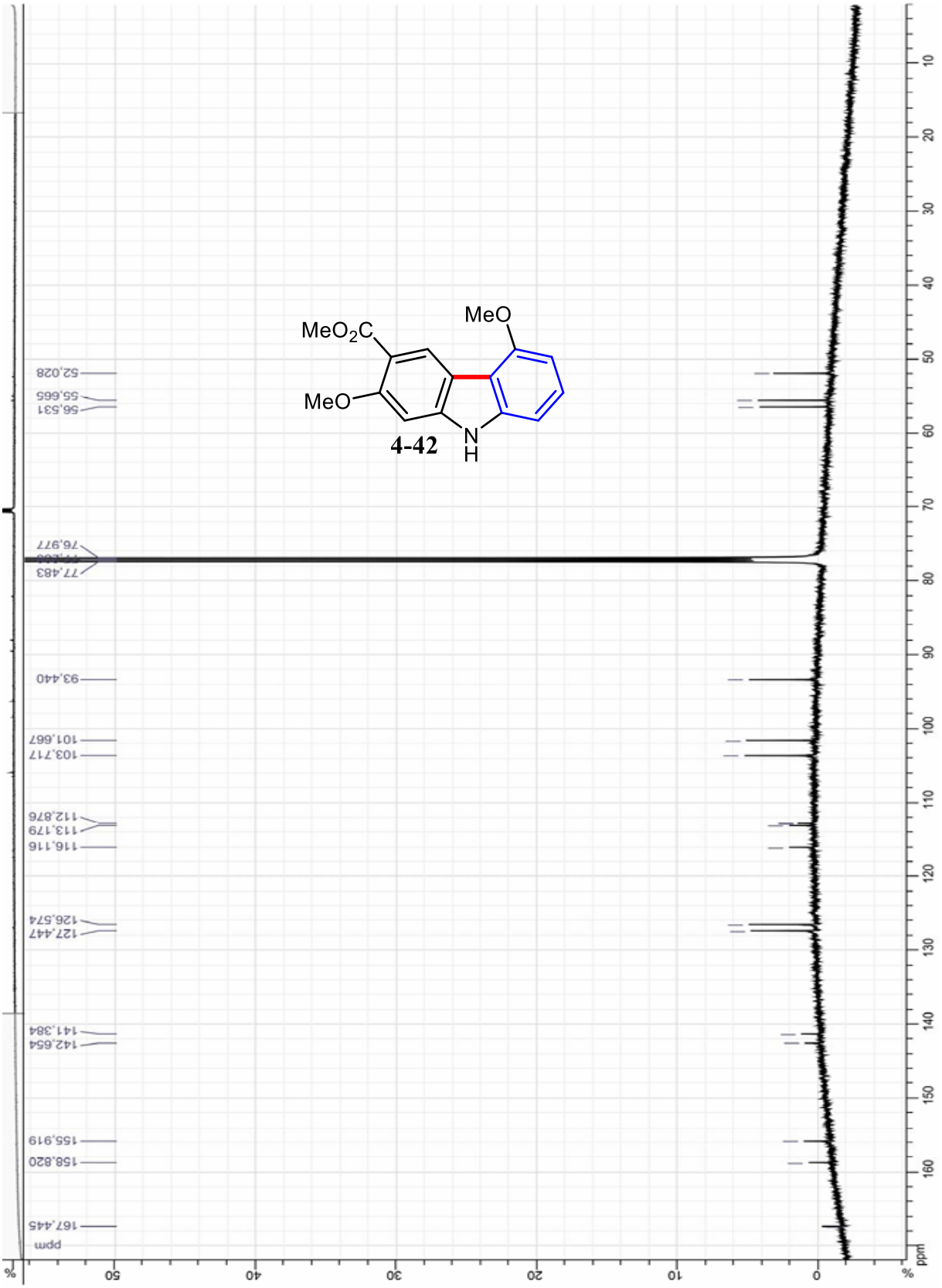
^{1}H NMR and ^{13}C NMR spectra of methyl 2,7-dimethoxy-9*H*-carbazole-3-carboxylate (**4-41**) in $CDCl_3$



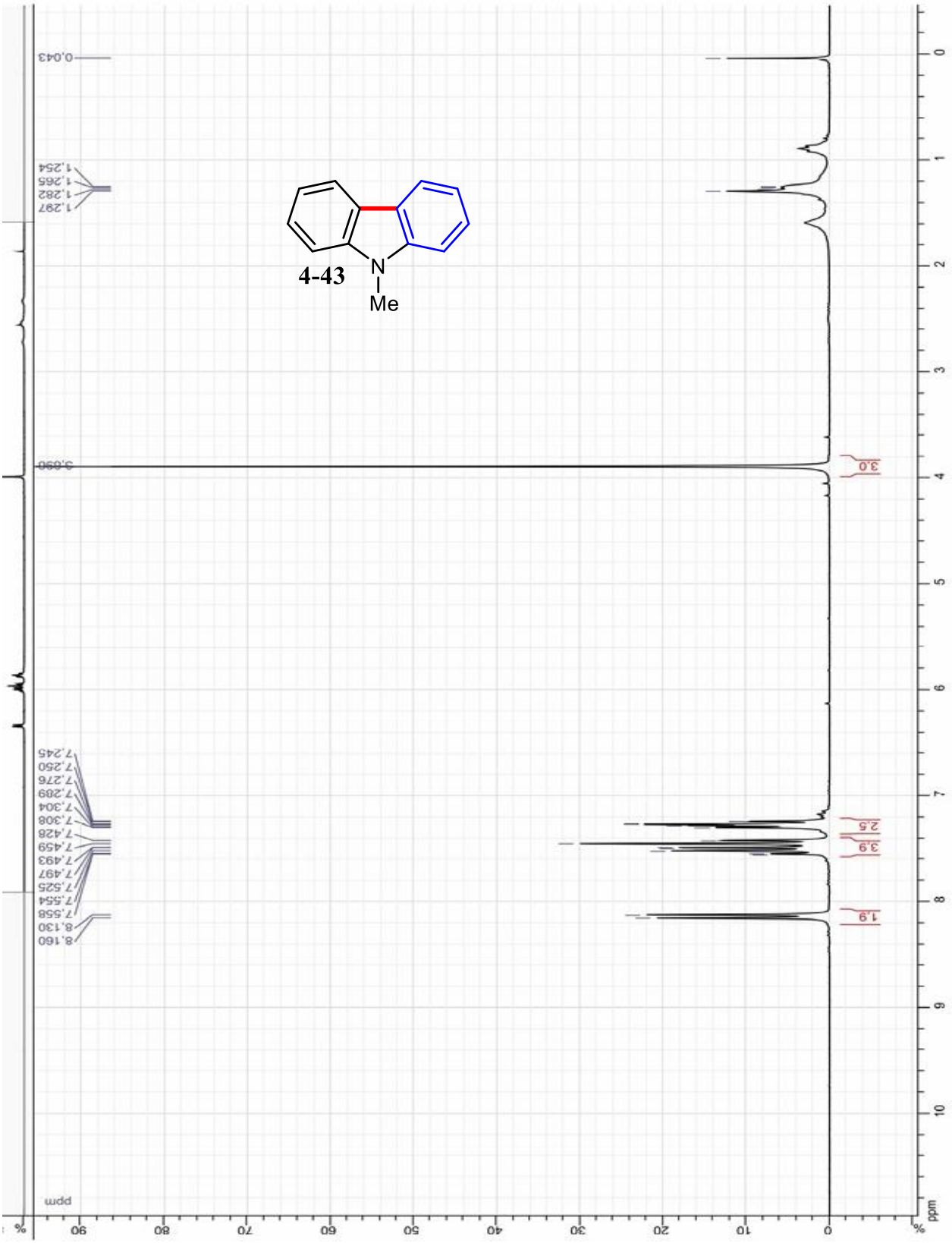

MeO2C
MeO
OMe
N
H
4-41
52.049
55.903
56.567
76.977
77.230
77.483
93.981
95.554
108.834
112.695
116.910
117.459
120.771
124.106
141.384
143.570
158.719
158.972
167.315
ppm

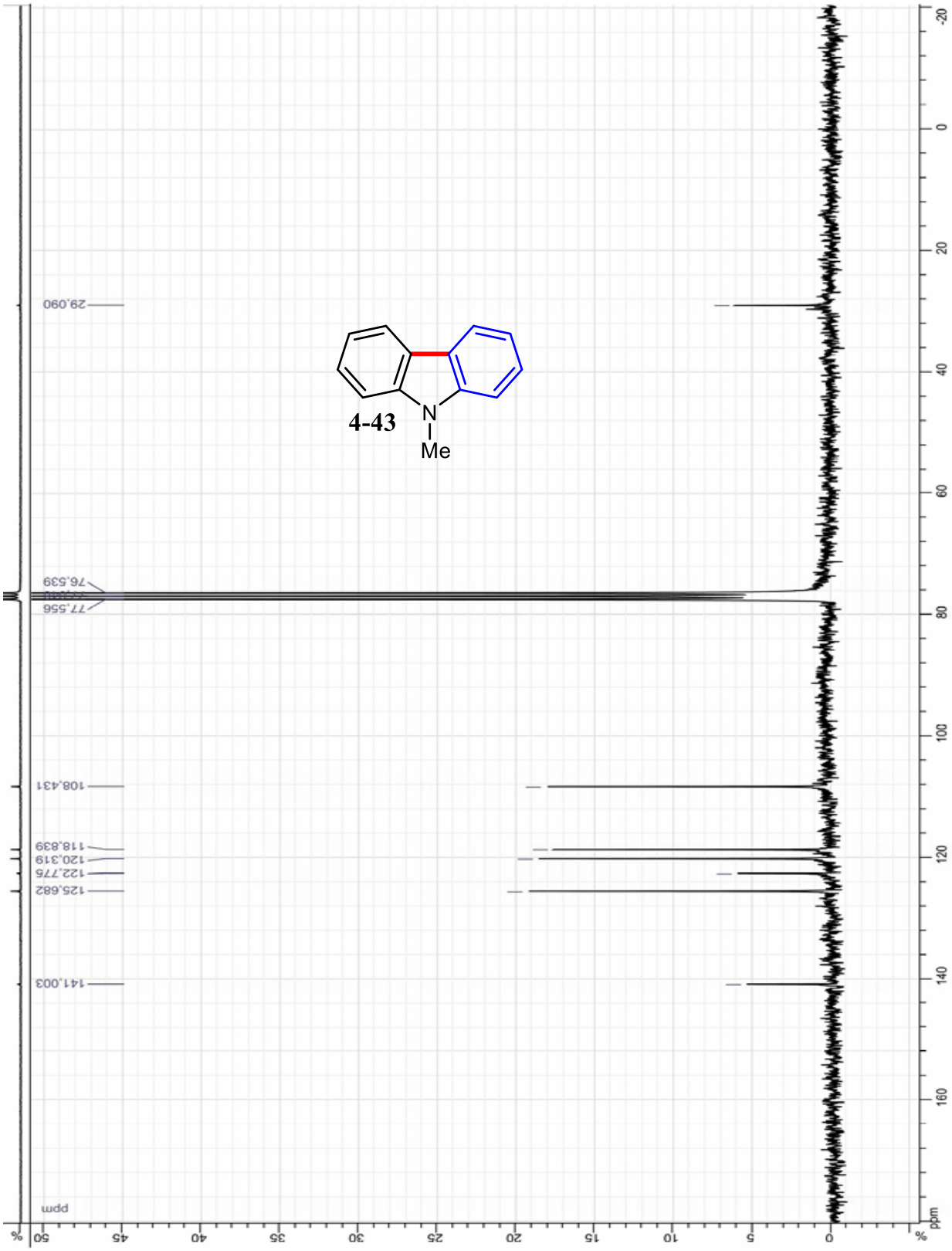
^{1}H NMR and ^{13}C NMR spectra of methyl 2,5-dimethoxy-9*H*-carbazole-3-carboxylate (**4-42**) in $CDCl_3$



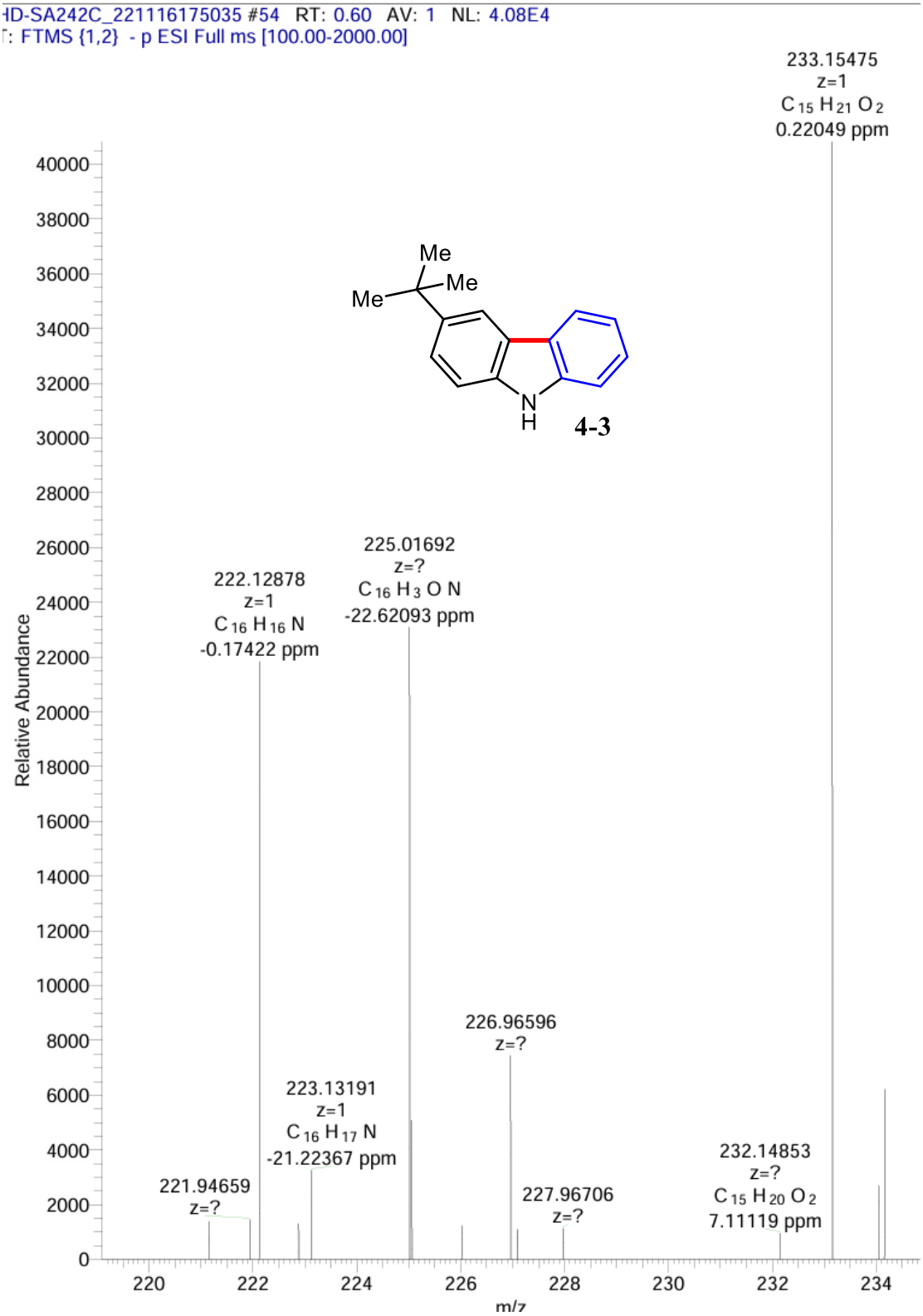

MeO2C
MeO
MeO
N
H
4-42
52.028
55.665
56.531
76.977
77.483
93.440
101.667
103.717
112.876
113.179
116.116
126.574
127.447
141.384
142.654
155.919
158.820
167.445
ppm
%
ppm

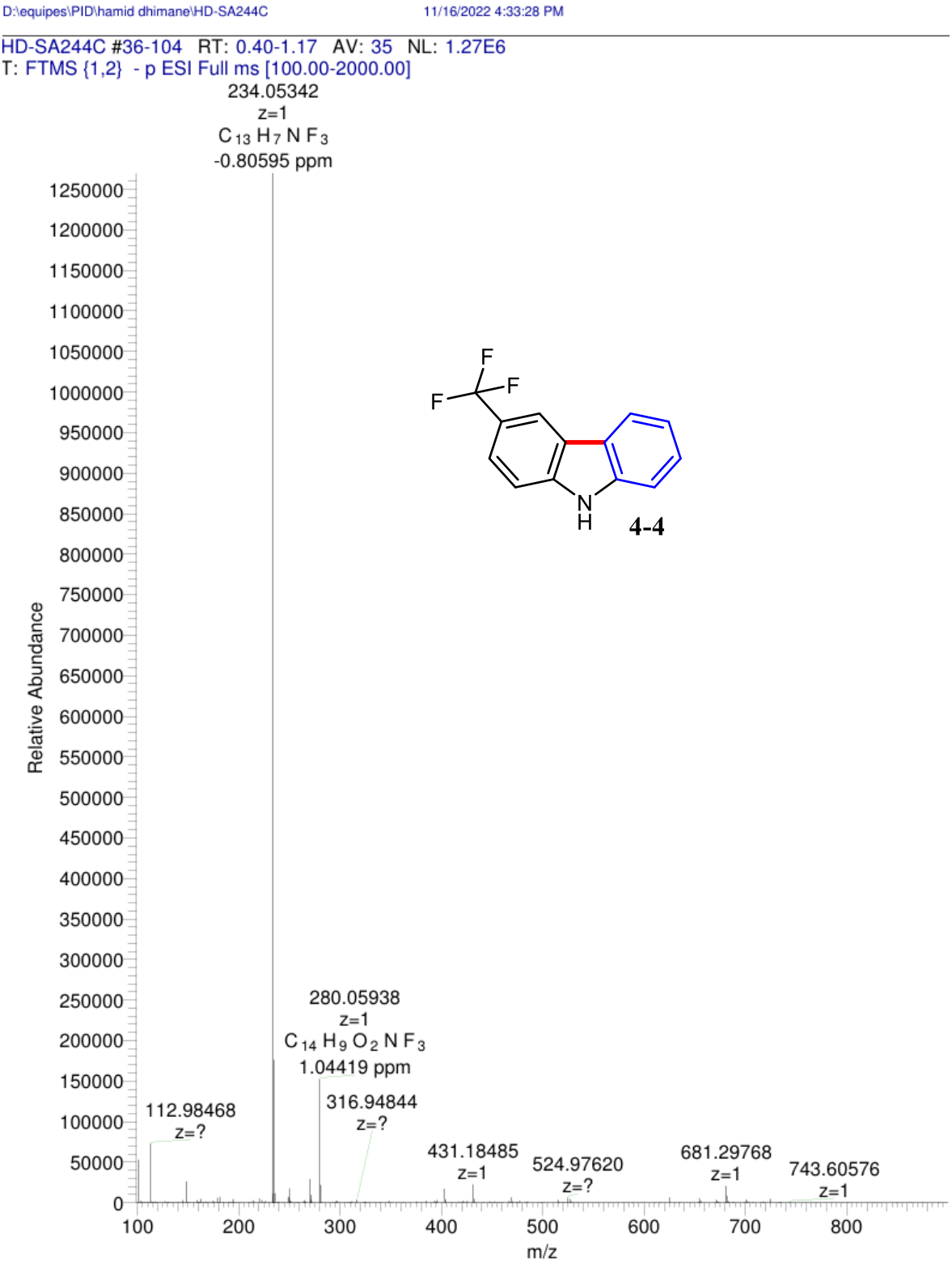
^{1}H NMR and ^{13}C NMR spectra of 9-methyl-9*H*-carbazole (**4-43**) in $CDCl_3$

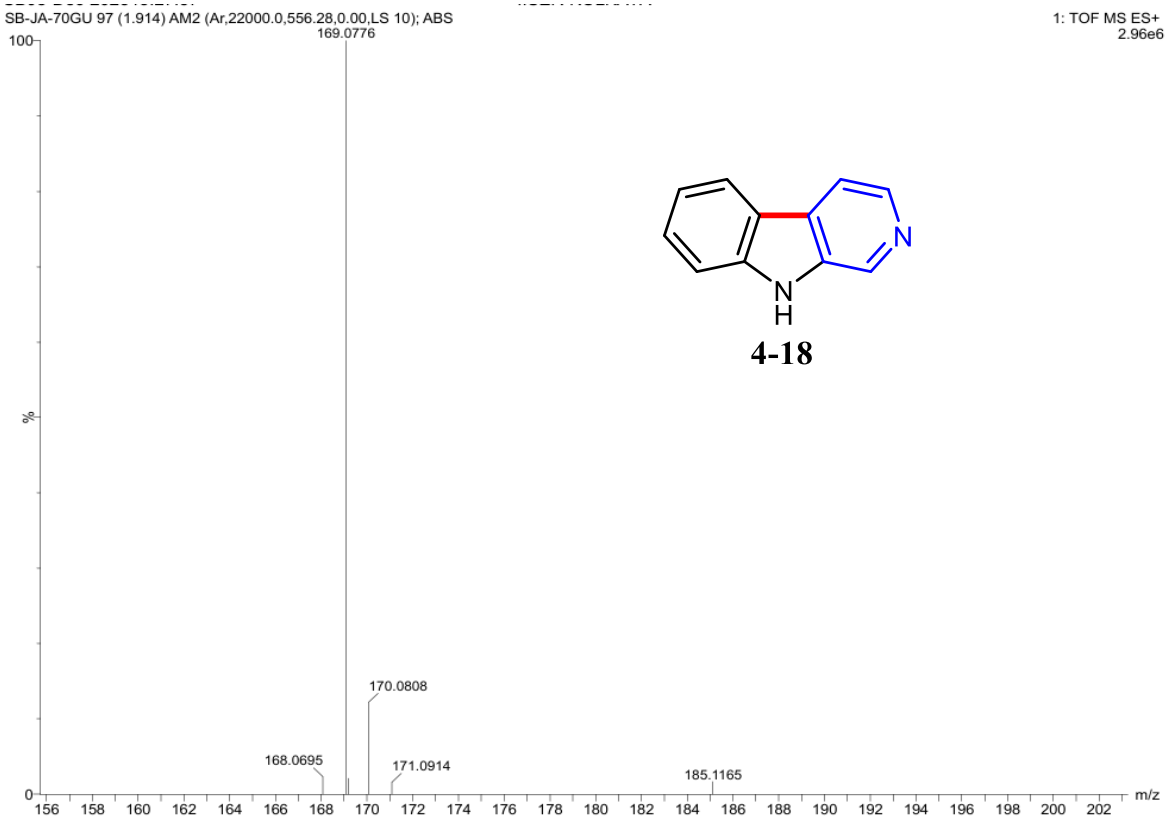



4-43
N
Me
29.090
76.539
77.556
108.431
118.839
120.319
122.776
125.682
141.003
ppm

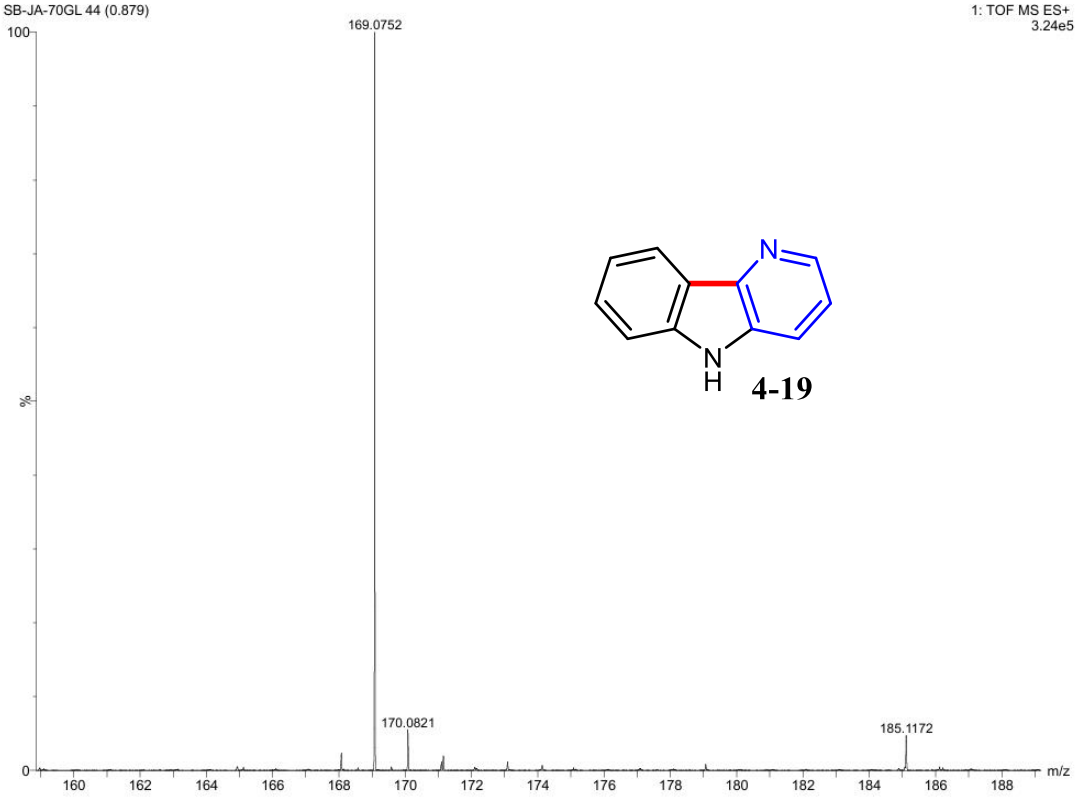
9.3 HRMS spectra of carbazoles 4-3, 4-4, 4-18, 4-19, 4-23 and 4-35.



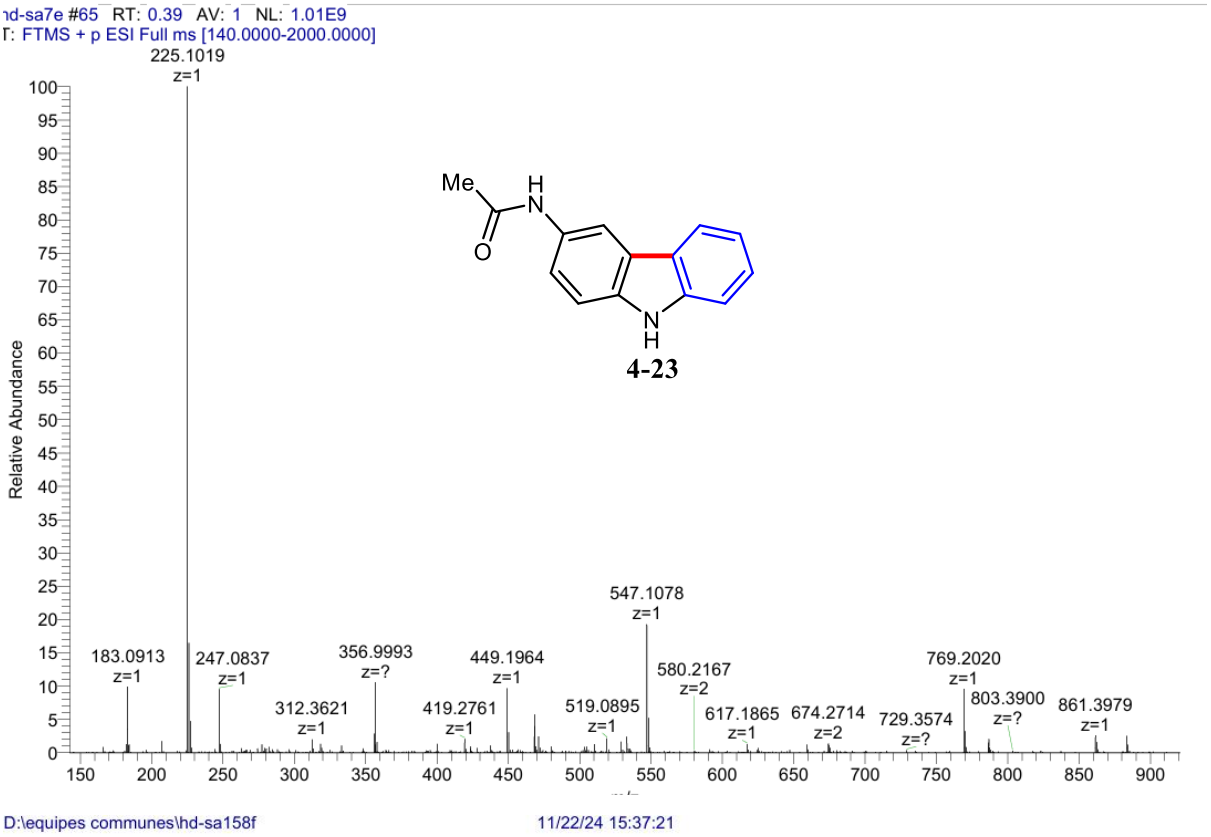

D:\equipes\PID\hamid dhimane\HD-SA244C 11/16/2022 4:33:28 PM
HD-SA244C #36-104 RT: 0.40-1.17 AV: 35 NL: 1.27E6
T: FTMS {1,2} - p ESI Full ms [100.00-2000.00]
234.05342
z=1
C 13 H 7 N F 3
-0.80595 ppm
280.05938
z=1
C 14 H 9 O 2 N F 3
1.04419 ppm
112.98468
z=?
316.94844
z=?
431.18485
z=1
524.97620
z=?
681.29768
z=1
743.60576
z=1
Relative Abundance
m/z
F
F
F
N
H
4-4

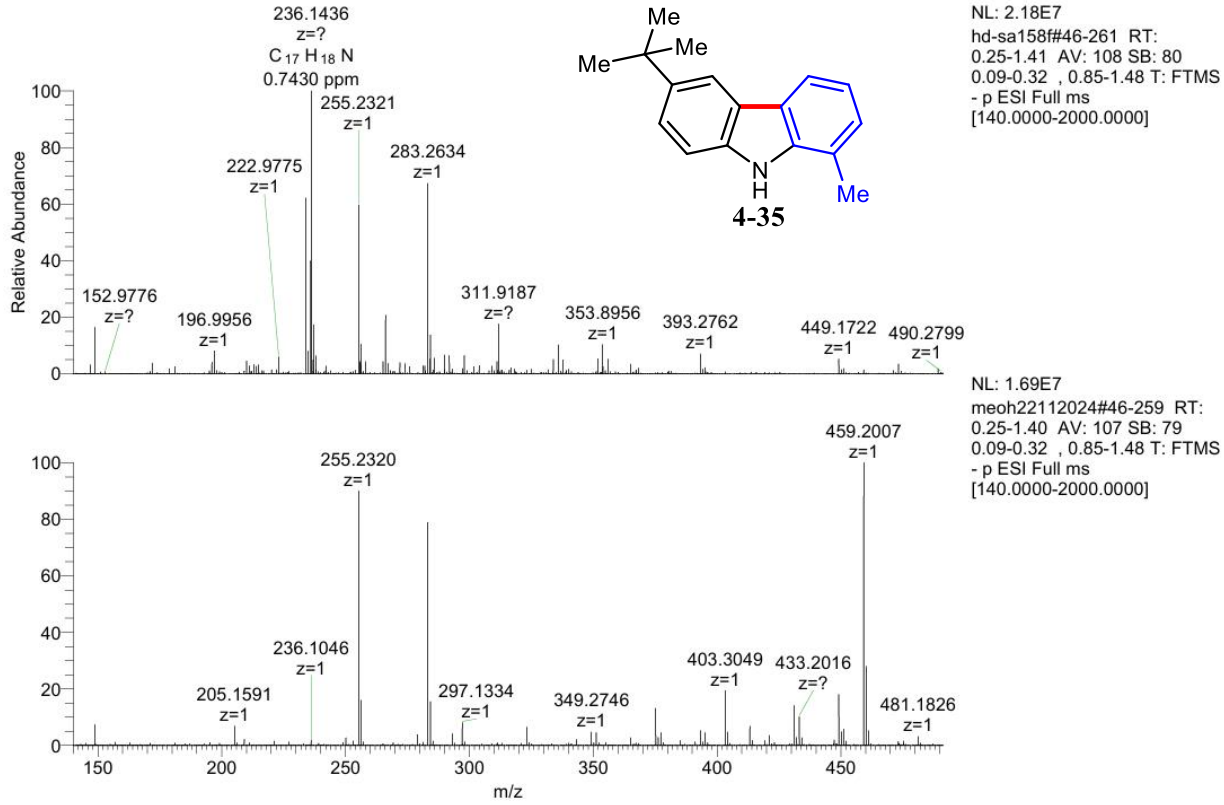

SB-JA-70GU 97 (1.914) AM2 (Ar,22000.0,556.28,0.00,LS 10); ABS
1: TOF MS ES+
2.96e6
169.0776
170.0808
168.0695
171.0914
185.1165
%
m/z

4-18


SB-JA-70GL 44 (0.879)
1: TOF MS ES+
3.24e5
169.0752
170.0821
185.1172
%
m/z

4-19


hd-sa7e #65 RT: 0.39 AV: 1 NL: 1.01E9
T: FTMS + p ESI Full ms [140.0000-2000.0000]
Me
H
N
O
N
H
4-23
Relative Abundance
225.1019 z=1
547.1078 z=1
183.0913 z=1
247.0837 z=1
356.9993 z=?
449.1964 z=1
580.2167 z=2
769.2020 z=1
312.3621 z=1
419.2761 z=1
519.0895 z=1
617.1865 z=1
674.2714 z=2
729.3574 z=?
803.3900 z=?
861.3979 z=1
D:\equipes communes\hd-sa158f
11/22/24 15:37:21


236.1436
z=?
C 17 H 18 N
0.7430 ppm
Me
Me
Me
N
H
Me
4-35
NL: 2.18E7
hd-sa158f#46-261 RT:
0.25-1.41 AV: 108 SB: 80
0.09-0.32 , 0.85-1.48 T: FTMS
- p ESI Full ms
[140.0000-2000.0000]
Relative Abundance
255.2321 z=1
222.9775 z=1
283.2634 z=1
152.9776 z=?
196.9956 z=1
311.9187 z=?
353.8956 z=1
393.2762 z=1
449.1722 z=1
490.2799 z=1
NL: 1.69E7
meoh22112024#46-259 RT:
0.25-1.40 AV: 107 SB: 79
0.09-0.32 , 0.85-1.48 T: FTMS
- p ESI Full ms
[140.0000-2000.0000]
459.2007 z=1
255.2320 z=1
236.1046 z=1
205.1591 z=1
297.1334 z=1
349.2746 z=1
403.3049 z=1
433.2016 z=?
481.1826 z=1
m/z