Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Synthesis of Di-, Tri- and Tetracyclopropylhydrazines

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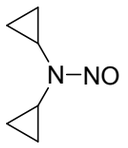
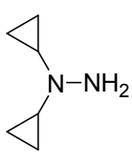
General Information. NMR spectroscopic data were recorded with a Bruker Avance 400 spectrometer (400.13 MHz for ^{1}H, 100.61 MHz for ^{13}C, respectively) in $CDCl_3$, C_6D_6, or DMSO-d_6 and were referenced to the residual solvent proton (δ_H = 7.26, 7.16 ppm) and carbon (δ_C = 77.16, 128.06 or 39.52 ppm) signals. DEPT spectra were used for the assignment of carbon atoms signals. IR spectra were registered on Bruker Tensor 27 FT-IR spectrometer. Melting points were determined with a Stuart SMP30 instrument. High-resolution mass spectra were recorded with a Bruker Maxis HRMS-ESI-qTOF spectrometer (electrospray ionization mode). Column chromatography was performed on silica gel Merck 60. TLC monitoring was performed on Alugram SIL G/UV_{254} plates (Macherey-Nagel).

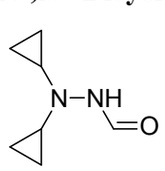
***N*-Nitrosodicyclopropylamine 7**. A solution of sodium nitrite (0.35 g, 5.1 mmol) in 2 mL of water was added dropwise to a solution of dicyclopropylamine hydrochloride (0.67 g, 5.0 mmol) in 5 mL water covered with 5 mL of ether. After that one drop of conc. HCl was added. After stirring at room temperature for 2 hours reaction mixture was extracted with ether (3*10 mL). Extracts were dried with K_2CO_3 and concentrated under reduced pressure yielding compound **7** (0.51 g, 81 %) as yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz)**:** δ 0.80-1.10 (m, 8H, 4 CH_2), 3.04-3.09 (m, 2H, 2 CH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 5.2 (2 CH_2), 6.0 (2 CH_2), 29.5 (CH), 32.4 (CH); HRMS (ESI) calcd for $C_6H_{11}N_2O$ $[M+H]^+$ 127.0866, found 127.0867.



1,1-Dicyclopropylhydrazine 3. A suspension of $LiAlH_4$ (0.28 g, 7.4 mmol) in dry ether (20 mL) was cooled to 4 °C and treated dropwise with the solution of *N*-nitrosodicyclopropylamine (0.47 g, 3.7 mmol) in dry ether (10 mL). After stirring overnight at room temperature, the excess hydride was destroyed by addition of water (2 mL). The suspension was filtered and the precipitate was washed with ether (3*3 mL). Combined extracts were dried (K_2CO_3) and ether was evaporated under reduced pressure, thus affording 1,1-dicyclopropylhydrazine (0.34 g, 82 %) pure according NMR spectra as yellowish oil. ^{1}H NMR ($CDCl_3$, 400 MHz)**:** δ 0.49-0.51 (m, 8H, 4 CH_2), 2.02-2.08 (m, 2H, 2 CH), 3.24 (br s, 2H, NH_2); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 5.7 (CH_2), 41.4 (CH); HRMS (ESI) calcd for $C_6H_{13}N_2$ $[M+H]^+$ 113.1073, found 113.1069.



***N',N'*-Dicyclopropylformic hydrazide 8.** A mixture of N,N-dicyclopropylhydrazine (300 mg, 2.68 mmol) and methyl formate (1 mL) was stirred for 3 days at r.t. To the residue obtained by evaporation of the solvent under reduced pressure hexane (1 mL) was added and left overnight at 4-5 °C. Obtained crystals were filtered and washed with cold hexane (2*0.5 mL) affording **8** (278 mg, 74 %) which melted at r.t. giving yellow oil. NMR spectra demonstrate the existence of two rotamers in solution in ratio ~5:1, because of restricted rotation about amide C-N bond. ^{1}H NMR ($CDCl_3$, 400 MHz)**:** δ 0.49-0.59 (m, 8H, 4 CH_2), 2.31-2.36 and 2.6-2.7 (m, 1.6H and 0.3H, NCH), 7.07 (br. s, 0.2H, NH) and 7.52

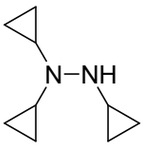


(br. d, *J*≈10 Hz, 0.8H, NH), 7.96 and 7.97 (s and d, *J*=11 Hz, 1H, CH=O); ^{13}C NMR ($CDCl_3$, 100 MHz); δ 6.1 (CH_2), 6.5 (CH_2), 38.5 (CH), 39.6 (CH), 159.2 (CH=O), 165.8 (CH=O); HRMS (ESI) calcd for $C_7H_{11}N_2ONa$ $[M+Na]^+$ 163.0842, found 163.0846.

***N*-Benzyl-*N′*,*N′*-dicyclopropylformic hydrazide 9.** A mixture of hydrazide **8** (0.22 g, 1.57 mmol), finely powdered sodium hydroxide (0.22 g, 5.5 mmol), potassium carbonate (0.13 g), and tetra-*n*-butylammonium hydrogen sulfate (53 mg) in benzene (2 mL) was stirred vigorously at 35-40 °C for 30 min. The resulted slurry was heated to 60°C and a solution of benzyl chloride (0.2 g, 1.58 mmol) in benzene (1 mL) was added dropwise. Stirring was continued for 4 h at 60-70 °C. The mixture was cooled to room temperature, filtered and the solid was washed with benzene (2 mL). Combined benzene solution was washed with water (2*2 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel yielding **9** (293 mg, 81 %) as light yellow oil. ^{13}C NMR spectrum demonstrates broadening of methylene cyclopropyl signal that might be caused by restricted rotation about N-N bond of tetrasubstituted hydrazine what makes methylene groups diastereotopic one. ^{1}H NMR ($CDCl_3$, 400 MHz)**:** δ 0.42 (br. s 8H, 4 CH_2), 2.29-2.35 (m, 2H, 2 NCH), 4.79 (s, 2H, Ph$\underline{CH_2}$), 7.22-7.25 (m, 1H, H^p), 7.28-7.32 (m, 2H, H^m), 7.38-7.40 (m, 2H, H^o), 8.06 (s, 1H, CH=O); ^{13}C NMR ($CDCl_3$, 100 MHz); δ 7.6 (br, 4CH_2), 36.7 (2CH), 44.1 (CH_2Ph), 127.4 (C^p) 128.3 (2CH), 128.5 (2CH), 138.1 (C^i) 165.3 (CH=O); HRMS (ESI) calcd for $C_{14}H_{19}N_2O$ $[M+H]^+$ 231.1492, found 231.1488.

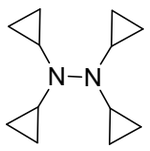
1-Benzyl-1,2,2-tricyclopropylhydrazine 10. A vigorously stirred solution of *N*-benzyl-*N′*,*N′*-dicyclopropylformic hydrazide **9** (300 mg, 1.3 mmol) and (*i*-PrO)$_3$TiMe (0.38 g, 1.6 mmol) in anhydrous THF (3 mL) was treated with the solution of ethylmagnesium bromide (prepared by slow addition of EtBr (0.2 mL, 2.7 mmol) in ether (1.5 mL) to Mg (62 mg, 2.6 mmol) in ether (0.5 mL)) within 20 s (the color of the reaction mixture changed to brown-black and the temperature rose to about 45°C), and the resulted mixture was stirred at r.t. overnight. The reaction was then quenched by addition of H_2O (1 mL), stirred until a colorless precipitate had formed (1 h), filtered, and the filter cake was washed with Et_2O (2*2 mL). The filtrate was dried over K_2CO_3 and the solvents were evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane) yielding **10** (186 mg, 59 %) as yellowish oil. ^{1}H NMR ($CDCl_3$, 400 MHz)**:** δ 0.37-0.45 (m, 12H, 6 CH_2), 2.34-2.41 (m, 2H, 2 NCH), 2.43-2.49 (m, 1H, NCH), 3.99 (s, 2H, Ph$\underline{CH_2}$), 7.21-7.29 (m, 5H, Ph), ^{13}C NMR ($CDCl_3$, 100 MHz); δ 6.2 (4CH_2), 7.1 (2CH_2), 34.1 (CH), 34.6 (2CH) , 59.2 (Ph$\underline{CH_2}$), 126.5 (C^p), 127.7 (2CH), 129.6 (2CH), 141.0 (C^i). HRMS (ESI) calcd for $C_{16}H_{23}N_2$ $[M+H]^+$ 243.1856, found 243.1863

Tricyclopropylhydrazine 4. A solution of 1-benzyl-1,2,2-tricyclopropylhydrazine **10** (150 mg, 0.62 mmol) in 5 mL of hexane was hydrogenated over 20 mg of 10% Pd on charcoal at



atmospheric pressure. After reaction completion the mixture was filtered from the catalyst through Celite. The catalyst was washed with 10 mL of hexane and the combined solutions was acidified by addition of ethereal solution of HCl, and the solvent was evaporated under reduced pressure. The residue was dissolved in 5 mL of water, and pH adjusted to 11-12 by slow addition of aqueous 10 % NaOH than extracted with ether (3*5 mL). Combined extracts were dried (K_2CO_3) and ether was evaporated under reduced pressure (~100 torr) at r.t., thus affording tricyclopropylhydrazine (94 mg, 87 %) as yellowish oil. ^{1}H NMR ($CDCl_3$, 400 MHz)**:** δ 0.41-0.66 (m, 12H, 6 CH_2), 2.17-2.22 (m, 2H, N-1-CH), 2.53-2.58 (m, 1H, N-2-CH), 2.98 (br.s, 1H, NH), ^{13}C NMR ($CDCl_3$, 100 MHz); δ 5.7 ($4CH_2$), 6.5 ($2CH_2$), 29.5 (CH), 39.0 (2CH); HRMS (ESI) calcd for $C_9H_{17}N_2$ $[M+H]^+$ 153.1386, found 153.1394.

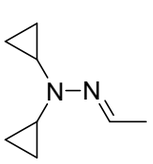
Tetracyclopropylhydrazine 5. To a mixture of 1,1-dicyclopropylhydrazine **3** (1 mmol, 112 mg)**,** acetic acid (20 mmol, 1.2 g) and molecular sieves in 5 mL of methanol cyclopropanone



ethyl trimethylsilyl acetal (6 mmol, 1,04 g) and $NaBH_3CN$ (9 mmol, 0.57 g) were added. After stirring at 60 °C for 6 hours reaction mixture was filtered and the filtrate was concentrated under reduced pressure. The residue was dissolved in 10 mL water, acidified with 10 % HCl to pH 1-2 and extracted with ether (2*5 mL) to remove byproducts. The pH of aqueous layer was adjusted to 4 by addition of aqueous 10 % NaOH than extracted with ether (3*5 mL). These extracts were dried (Na_2SO_4) and ether was evaporated under reduced pressure, thus affording tetracyclopropylhydrazine (98 mg, 51 %) as yellowish oil. The reaction of hydrazine with 12 eq of cyclopropanone ethyl trimethylsilyl acetal and 18 eq of $NaBH_3CN$ for 10 hours gave the desired product **5** in 17 % yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.43-0.45 (m, 16H, 8 CH_2), 2.45-2.50 (m, 4H, 4 CH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 6.5 (CH_2), 34.6 (CH); HRMS (ESI) calcd for $C_{12}H_{20}N_2$ $[M+H]^+$ 193.1699, found 193.1700.

General procedure for reaction of 1,1-dicyclopropylhydrazine with aldehydes. A suspension of $MgSO_4$ (150 mg) in solution of 1,1-dicyclopropylhydrazine (112 mg, 1 mmol) and aldehyde (1 mmol) in ether (2 mL) was stirred at room temperature for 6 hours. After reaction completion suspension was filtered off and the solid was washed with ether (2 x 4 mL). Combined washings were concentrated under reduced pressure. The crude product was purified by column chromatography (hexane:EA).

Acetaldehyde dicyclopropylhydrazone 15a: freshly distilled aldehyde was used; yield 105 mg,



76 %. Colorless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz)**:** δ 0.58-0.67 (m, 8H, 4 H_2), 1.93 (d, *J*=5.2 Hz, 3H, CH_3), 2.16-2.21 (m, 2H, NCH), 7.43 (q, *J*=5.2 Hz, 1H, CH=N); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 6.0 (4 CH_2), 19.2 (CH_3), 35.6 (2 NCH),

138.2 (CH=N); HRMS (ESI) calcd for $C_8H_{15}N_2$ $[M+H]^+$ 139.1230, found 139.1227.

Benzaldehyde dicyclopropylhydrazone 15b. yield 168 mg, 84 %. Light yellow oil. IR (neat) ν, (cm^{-1}): 3090, 3060, 3014 ($\nu_{CH\square}$), 2953, 2852, 1591, 1562, 1492, 1447, 1026($\nu_{\square}$). ^1H NMR ($CDCl_3$, 400 MHz)**:** δ 0.74-0.83 (m, 8H, 4 CH_2), 2.45-2.50 (m, 2H, NCH), 7.23 (m, 1H, H^p,Ph), 7.33 (m, 2H, H^m,Ph), 7.60 (m, 2H, H^o,Ph), 7.95 (s, 1H, CH=N); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 6.0 (CH_2), 34.9 (CH), 126.1 (2CH), 127.7 (C^p), 128.6 (2CH), 135.3 (CH=N), 137.0 (C^i); HRMS (ESI) calcd for $C_{13}H_{17}N_2$ $[M+H]^+$ 201.1386, found 201.1387.

3,4-Dimethoxybenzaldehyde dicyclopropylhydrazone 15c: yield 231 mg, 89 %. Colorless crystals; mp 87.5-88.0 °C. IR (KBr pellet) ν (cm^{-1}): 3092, 3013 ($\nu_{\square CH}$), 2951, 2902, 2839, 1602, 1570, 1514, 1462, 1260 (s, $\nu_{C\text{-}O}$), 1137, 1070, 1022 ($\nu_{\square}$). ^1H NMR (C_6D_6, 400 MHz)**:** δ 0.49-0.54 (m, 4H), 0.74-0.79 (m, 4H), 2.24-2.29 (m, 2H, NCH), 3.40 (s, 3H, CH_3), 3.47 (s, 3H, CH_3), 6.65 (d, J=8.2 Hz, 1H, H^5,Ph), 7.20 (dd, J=8.2 Hz, J=1.6 Hz, 1H, H^6,Ph), 7.60 (d, J=1.6 Hz, 1H, H^2,Ph), 8.05 (s, 1H, CH=N); ^{13}C NMR (C_6D_6, 100 MHz): δ 6.3 (CH_2), 35.3 (NCH), 55.5 (CH_3), 55.6 (CH_3), 109.3 (C-2), 112.0 (C-5), 120.3 (C-6), 131.0 (C-1), 135.8 (CH=N), 150.4 ($\underline{C}_{ar}$-O), 150.6 ($\underline{C}_{ar}$-O); HRMS (ESI) calcd for $C_{15}H_{21}N_2O_2$ $[M+H]^+$ 261.1598, found 261.1598.

Acetone dicyclopropylhydrazone 15d. 1,1-Dicyclopropylhydrazine (112 mg, 1 mmol) in dry acetone (0.5 mL) was refluxed for 3 hours. After that reaction mixture was concentrated under reduces pressure giving acetone dicyclopropylhydrazone (138 mg, 91 %) as light yellow oil (pure according NMR). ^1H NMR ($CDCl_3$, 400 MHz): δ 0.34-0.44 (m, 8H, 4 CH_2), 1.82 (s, 3H, CH_3), 1.97 (s, 3H, CH_3), 2.27-2.34 (m, 2H, N-CH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 4.7 (CH_2), 19.3 (CH_3), 25.1 (CH_3), 38.9 (CH), 168.9 (C=N); HRMS (ESI) calcd for $C_9H_{17}N_2$ $[M+H]^+$ 153.1386, found 153.1385.

Acetophenone dicyclopropylhydrazone 15e. To a solution of 1,1-dicyclopropylhydrazine (112 mg, 1 mmol) and acetophenone (120 mg, 1 mmol) in benzene (3 mL) was added catalytic amount of PTSA and the mixture was refluxed for 6 hours. After reaction completion solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (hexane:EA), affording acetophenone dicyclopropylhydrazone (154 mg, 72 %) as light yellow oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 0.46-0.52 (m, 8H, 4 CH_2), 2.26 (s, 3H, CH_3), 2.47-2.54 (m, 2H, N-CH), 7.37-7.41 (m, 3H, $H^{m,p}$), 7.78-7.80 (m, 2H, H^o); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 4.8 (CH_2), 16.9 (CH_3), 39.1 (CH), 127.1 (2CH), 128.4 (2CH), 129.7 (C^p), 139.2 (C^i), 167.2 (C=N); HRMS (ESI) calcd for $C_{14}H_{19}N_2$ $[M+H]^+$ 215.1543, found 215.1544.

General procedure for preparation of *N,N*-dicyclopropyl-*N'*-acylhydrazines. A solution of acyl chloride (1 mmol) in ether (1 mL) was added dropwise at 4 °C to a mixture of 1,1-dicyclopropylhydrazine (112 mg, 1 mmol) and Et_3N (101 mg) in ether (7 mL). After stirring for 2 h at room temperature, the suspension was filtered and the solid was washed with ether. The solvent was evaporated under reduced pressure, and the residue was purified by column chromatography giving acylhydrazines (hexane:EA).

***N',N'*-Dicyclopropylacetohydrazide 16a:** yield 125 mg, 81 %, colorless crystals; mp 125.3-126.2 °C. IR (KBr) ν (cm^{-1}): 3241 (s, ν_{NH}), 3072 ($\nu_{\square CH2}$), 3013($\nu_{\square CH}$), 2960, 2931, 2835, 1660 (s, $\nu_{C=O}$), 1552, 1025($\nu_{\square}$). NMR spectra demonstrate the existence of two rotamers in solution in ratio ~3:2, because of restricted rotation about amide C-N bond. ^1H NMR ($CDCl_3$, 400 MHz): δ 0.46-0.56 (m, 8H, 4 CH_2), 1.91 (s, 3H, CH_3), 2.26-2.32 and 2.63-2.69 (m, 1.2H and 0.8H, 2 CH), 6.94 and 7.01 (br. s, 0.6H and 0.4H, NH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 5.7 (CH_2), 6.0 (CH_2), 19.4 (CH_3), 21.8 (CH_3), 38.3 (CH), 40.1 (CH), 168.5 (C=O), 174.3 (C=O); HRMS (ESI) calcd for $C_8H_{15}N_2O$ $[M+H]^+$ 155.1179, found 155.1179.

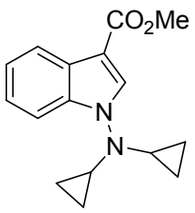
***N',N'*-Dicyclopropylbenzohydrazide 16b:** yield 160 mg, 74%, colorless crystals; mp 159.4-159.9 °C. IR (KBr) ν (cm^{-1}): 3221 (s, ν_{NH}), 3077, 3056, 3007 ($\nu_{\square CH}$), 2960, 2831, 1651 (s, $\nu_{C=O}$), 1537, 1026($\nu_{\square}$). ^1H NMR ($CDCl_3$, 400 MHz)**:** δ 0.50-0.64 (m, 8H, 4 CH_2), 2.87-2.89 (m, 2H, 2 NCH), 7.41 (m, 2H, H^m), 7.49 (m, 1H, H^p), 7.56 (br s, 1H, NH), 7.75 (m, 2H, H^o); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 6.2 (CH_2), 38.1 (CH), 127.2 (2CH), 128.7 (2CH), 131.6 (C^p), 134.3 (C^i), 166.4 (C=O); HRMS (ESI) calcd for $C_{13}H_{17}N_2O$ $[M+H]^+$ 217.1335, found 217.1336.

Methyl 2-(2-bromophenyl)-3-(2,2-dicyclopropylhydrazino)acrylate 18. Mixture of 1,1-dicyclopropylhydrazine (112 mg, 1 mmol) and methyl 2-(2-bromophenyl)-3-hydroxyacrylate (256 mg, 1 mmol) in 1.5 mL of MeOH was stirred at r.t. for 4 h, the solvent was evaporated and residue was purified by column chromatography (hexane:EA) affording **18** (304 mg, 87 %) as a mixture of (*Z*:*E*)-isomers =3:1, colorless oil.

(*Z*)-18: ^1H NMR ($CDCl_3$, 400 MHz)**:** δ 0.52-0.58 (m, 8H, 4 CH_2), 2.28-2.41 (m, 2H, 2 NCH), 3.66 (s, 3H, CH_3), 6.76 (d, *J*=11 Hz, 1H, CH), 7.06-7.10 (m, 1H, H), 7.22-7.24 (m, 2H, H), 7.56-7.58 (m, 1H, H), 9.07 (d, *J*=11 Hz, 1H, NH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 6.2 (CH_2, br), 40.0 (CH), 50.9 (CH_3), 95.3 (C), 127.0 (C), 127.1 (CH), 128.1 (CH), 132.7 (CH), 133.0 (CH), 138.7 (C), 153.9 (CH), 169.5 (C=O); HRMS (ESI) calcd for $C_{16}H_{20}BrN_2O_2$ $[M+H]^+$ 351.0703, found 351.0695.

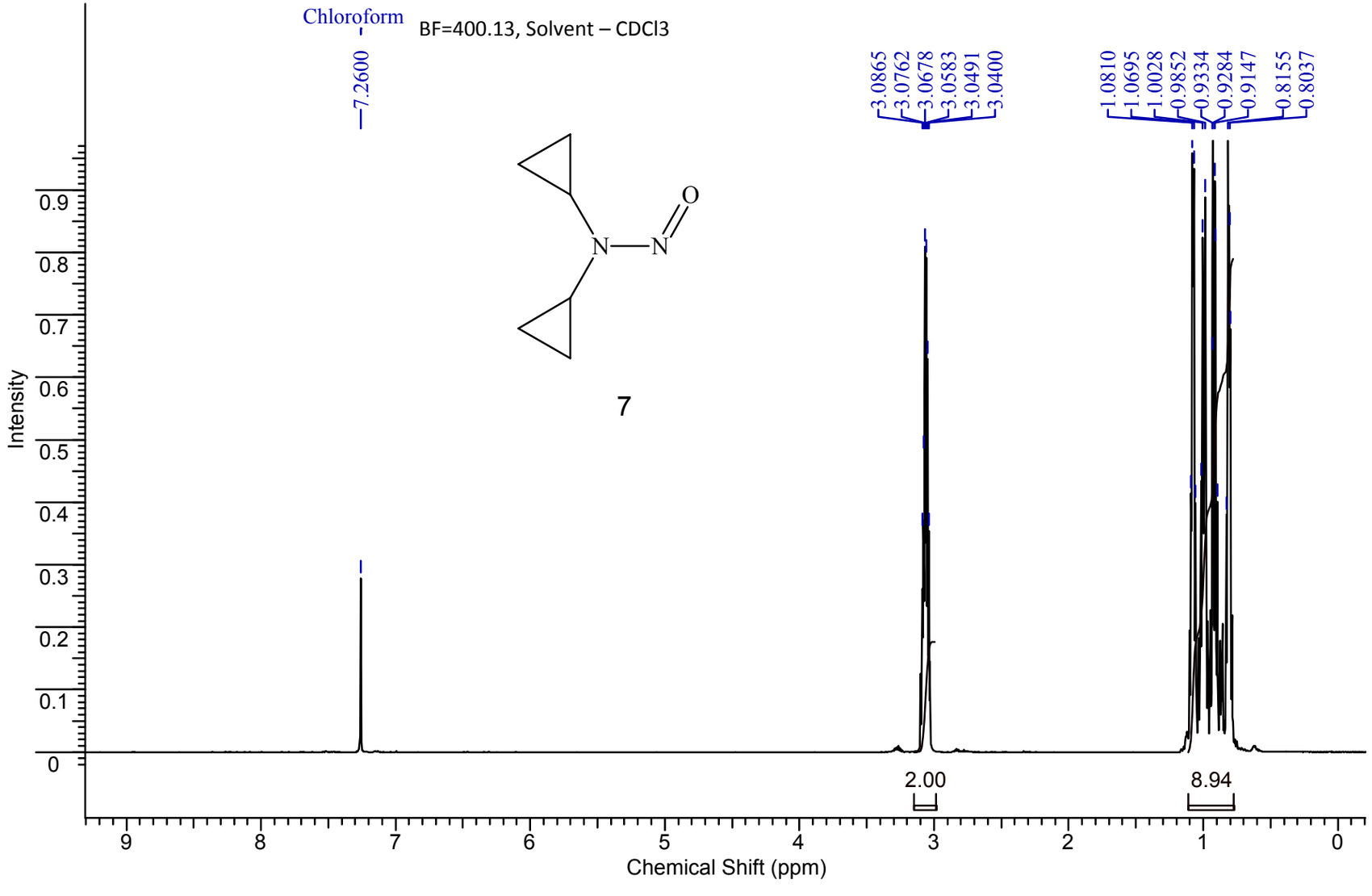
(*E*)-18: ^{1}H NMR ($CDCl_3$, 400 MHz)**:** δ 0.52-0.58 (m, 8H, 4 CH_2), 2.16-2.21 (m, 2H, 2 NCH), 3.65 (s, 3H, CH_3), 5.35 (d, *J*=11.9 Hz, 1H, NH), 7.16-7.20 (m, 1H, H), 7.23-7.26 (m, 1H, H), 7.32-7.36 (m, 1H, H), 7.58 (d, *J*=11.9 Hz, 1H, CH), 7.65-7.67 (m, 1H, CH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 6.3 (CH_2), 39.9 (CH), 51.3 (CH_3), 98.6 (C), 126.2 (C), 127.9 (CH), 129.1 (CH), 133.1 (CH), 133.3 (CH), 135.7 (C), 148.4 (CH), 168.1 (C=O); HRMS (ESI) calcd for $C_{16}H_{20}BrN_2O_2$ $[M+H]^+$ 351.0703, found 351.0695.

Methyl 1-(dicyclopropylamino)-1H-indole-3-carboxylate 17. To a solution of **18** (210 mg, 0.6



mmol) in DMF (3 mL) was added CuI (5.7 mg, 0.03 mmol) and anhydrous K_3PO_4 (0.254 g, 1.2 mmol). The reaction mixture was heated at 85 °C (bath temperature) for 2 h, cooled to r.t., poured into 10 mL of water and extracted with ether (3*5 mL). Extracts were dried with Na_2SO_4, the solvent was evaporated and residue was purified by column chromatography (hexane:EA) affording **17** (104 mg, 64 %) as colorless crystal. M.p. 121.2-122.6 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.56-0.62 (m, 8H, 4 CH_2), 2.92-2.97 (m, 2H, 2 CH), 3.93 (s, 3H, CH_3), 7.23-7.26 (m, 2H, CH), 7.37-7.40 (m, 1H, CH), 8.13 (s, 1H, CH), 8.13-8.17 (m, 1H, CH); ^{13}C NMR ($CDCl_3$, 100 MHz, 296 K): δ 6.7 (CH_2, br), 39.1 (CH), 51.2 (CH_3), 105.9 (C), 110.3 (CH), 121.5 (CH), 122.1 (CH), 123.1 (CH), 124.2 (C), 130.7 (CH), 136.9 (C), 165.6 (C=O); HRMS (ESI) calcd for $C_{16}H_{19}N_2O_2$ $[M+H]^+$ 271.1441, found 271.1447.

^{13}C NMR spectrum of **17** measured at room temperature in $CDCl_3$ shows a broad signal of cyclopropyl CH_2 groups at δ 6.7 ppm. It might be caused by restricted rotation of either ester group (around C-C bond) or dicyclopropylamino group (around N-N bond) that should cause the diastereotopicity of methylene groups in each cyclopropyl substituent. It was confirmed by getting spectra of **17** in DMSO-d_6 upon heating that led to coalescence of this signal into a sharp singlet at 80 °C (see the corresponding spectra below).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3.0865
3.0762
3.0678
3.0583
3.0491
3.0400
1.0810
1.0695
1.0028
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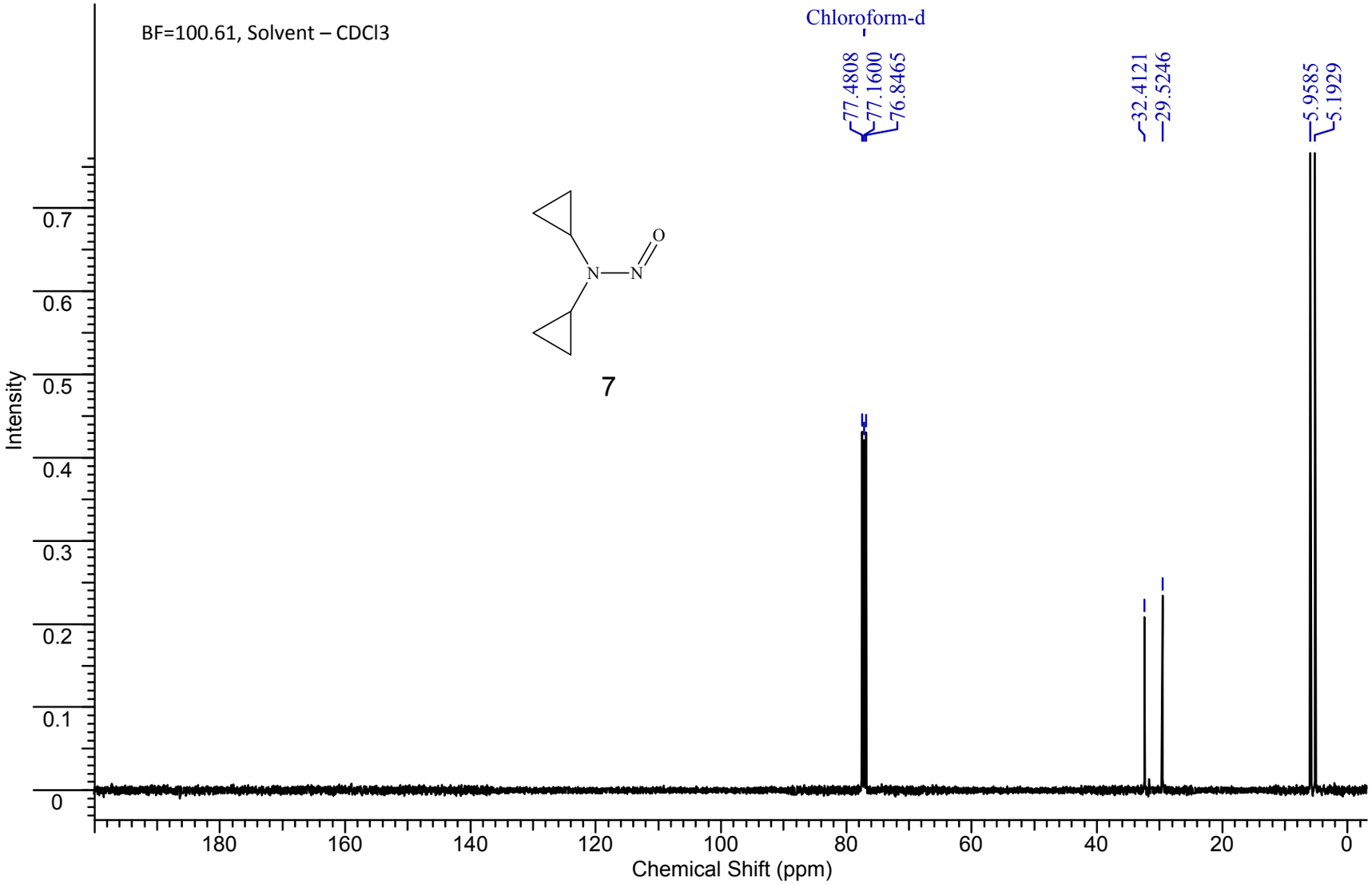
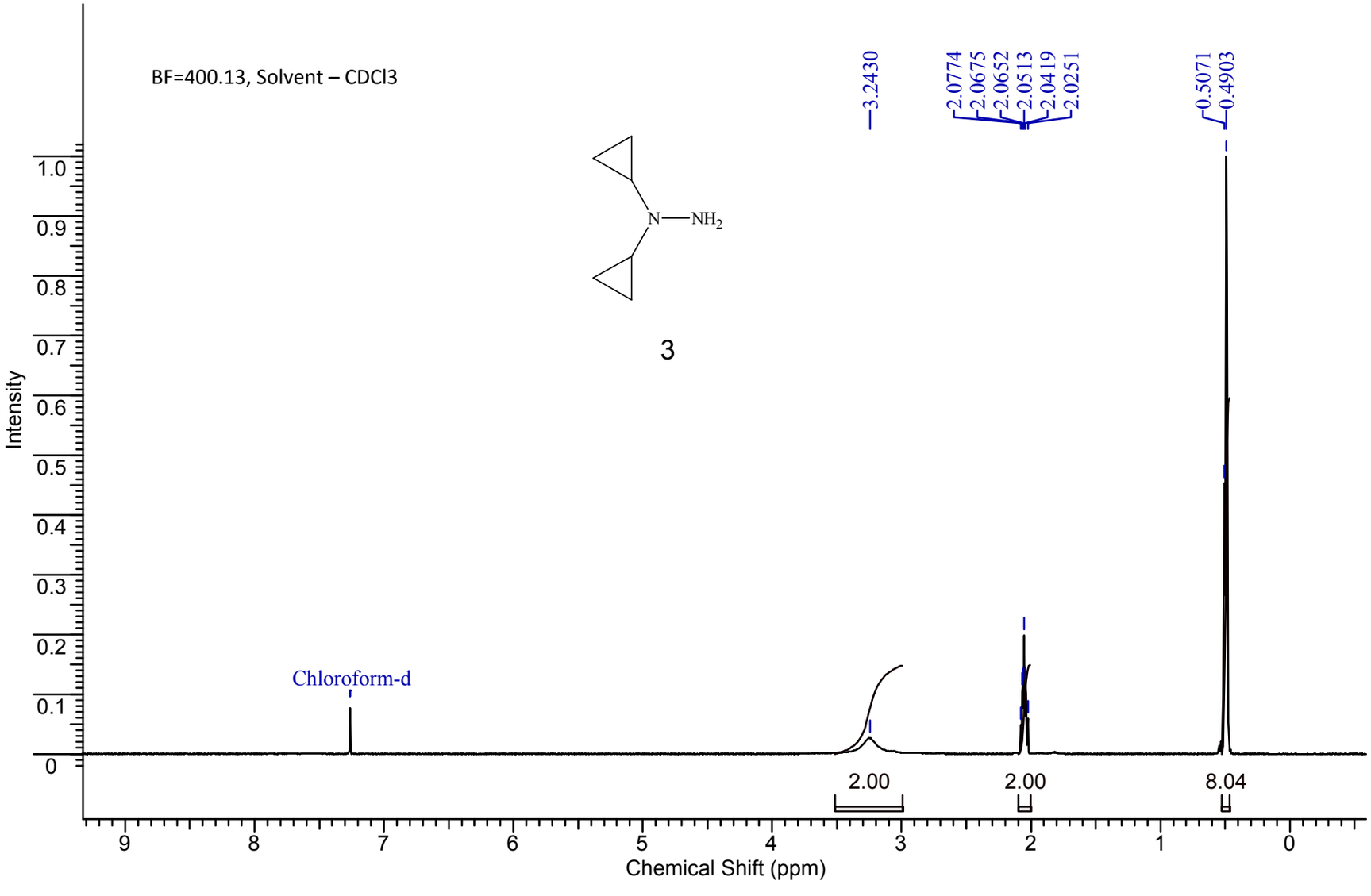
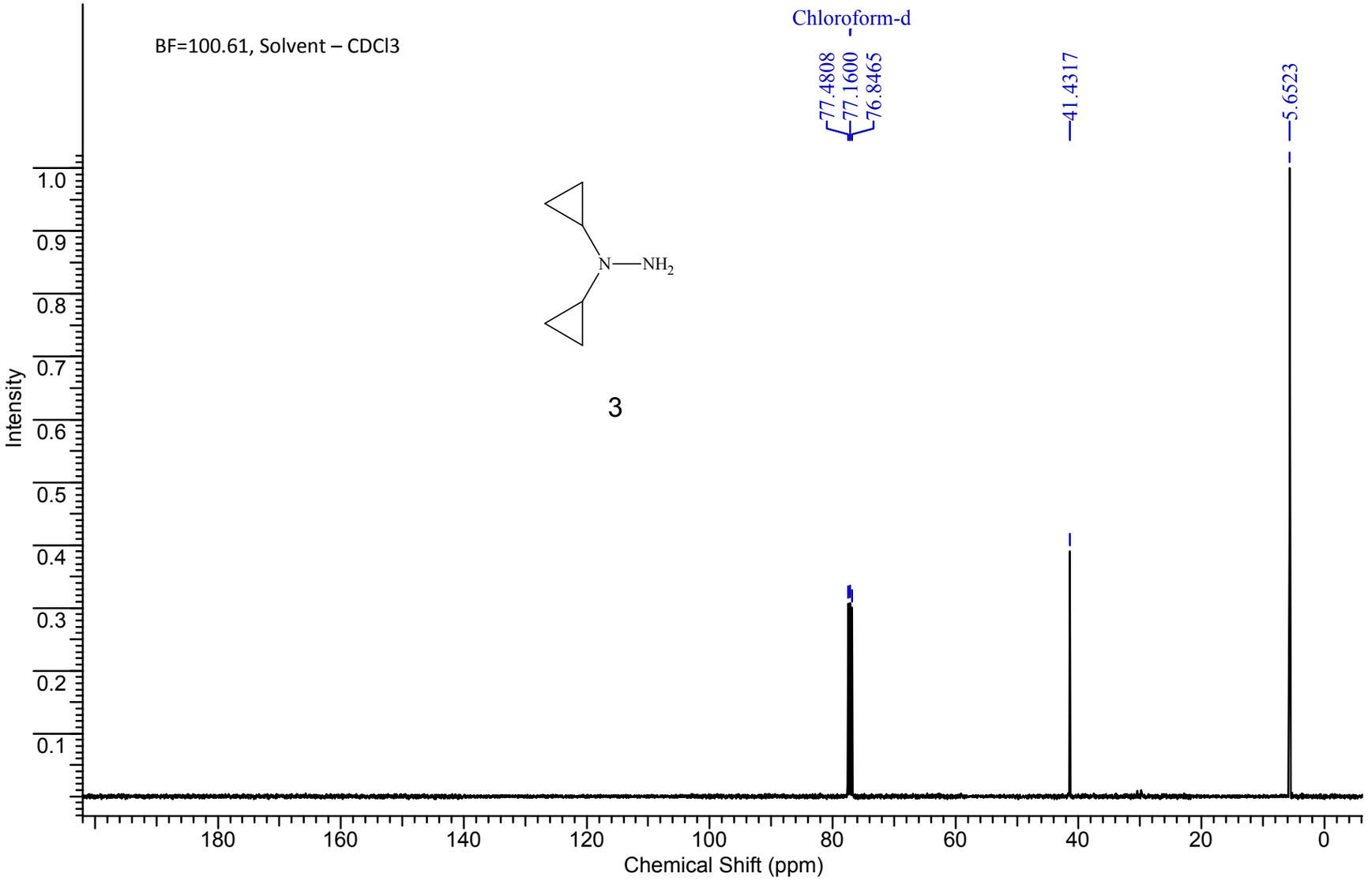
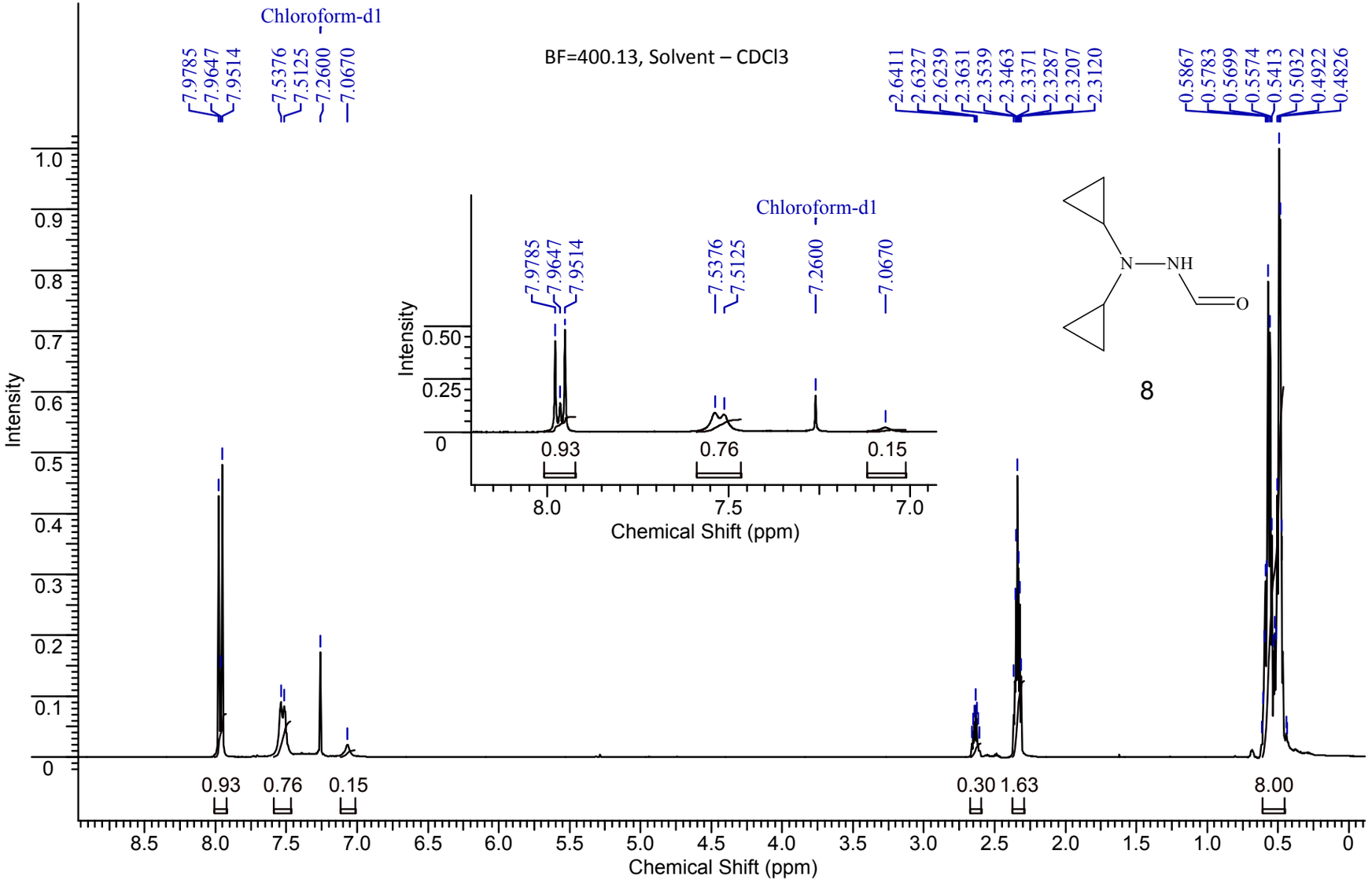
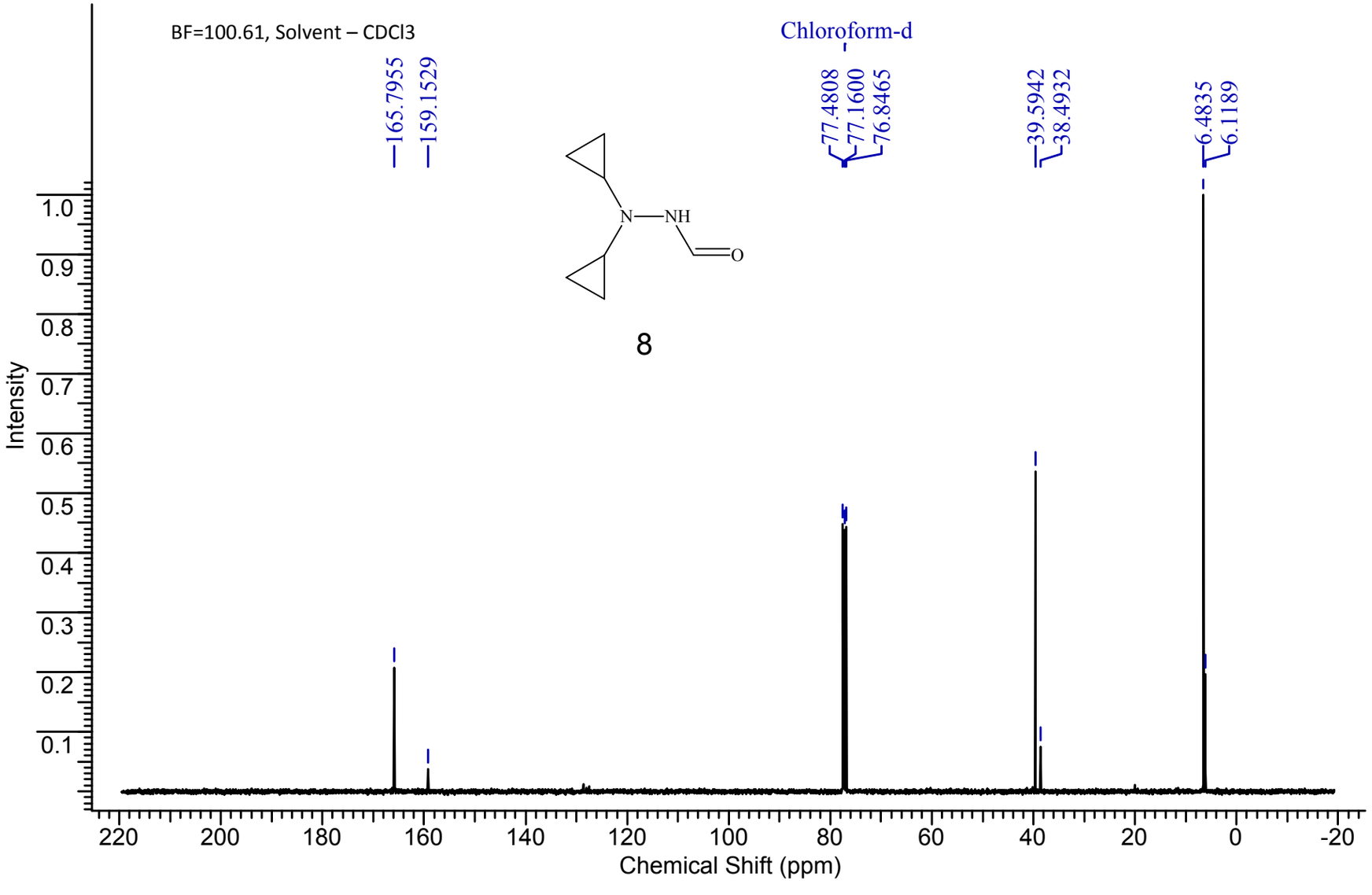
0.9334
0.9284
0.9147
0.8155
0.8037
O
N
N
7
Intensity
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
2.00
8.94
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

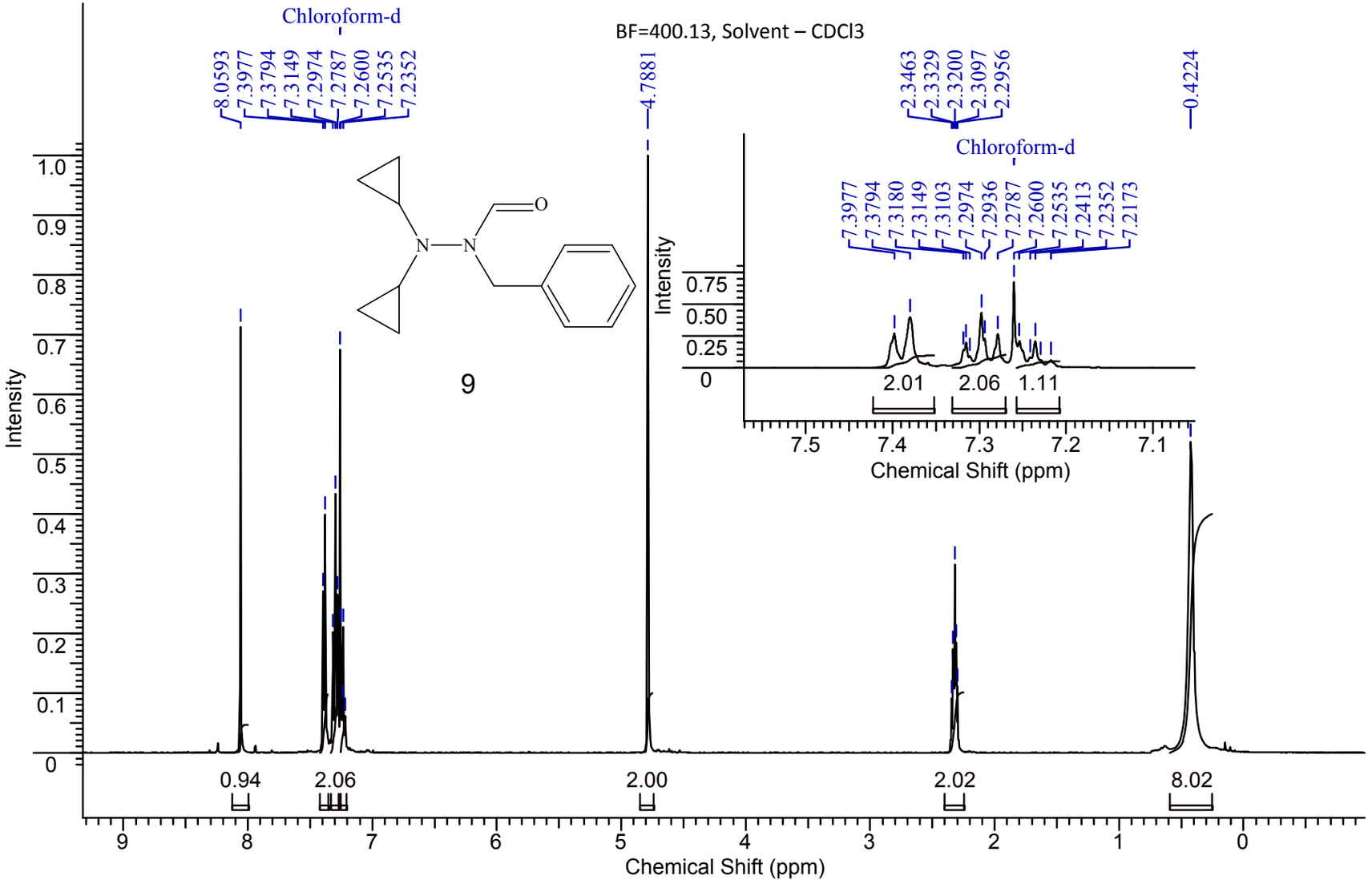

BF=100.61, Solvent – CDCl3
Chloroform-d
77.4808
77.1600
76.8465
32.4121
29.5246
5.9585
5.1929
O
N
N
7
Intensity
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

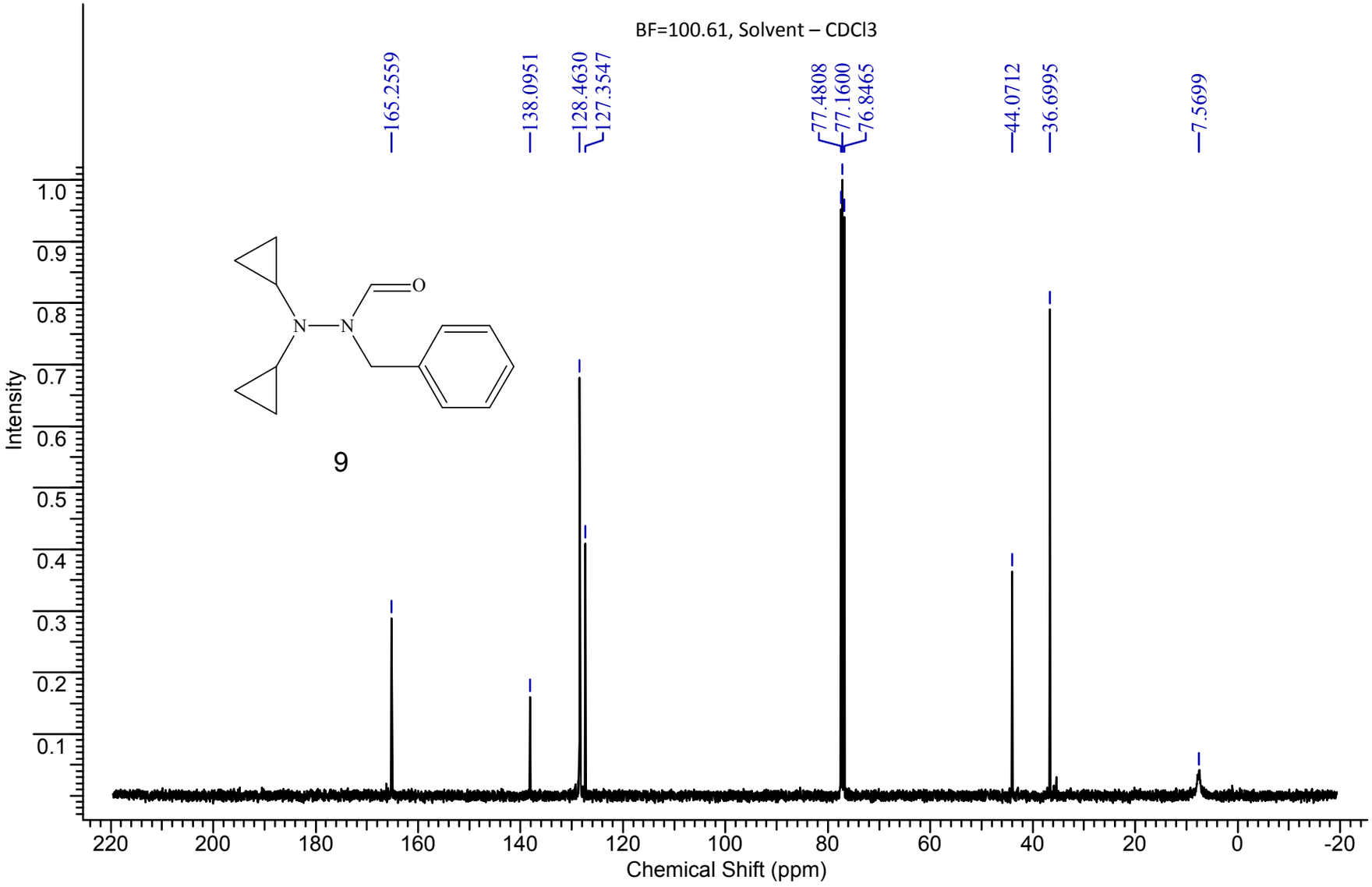

BF=400.13, Solvent – CDCl3
3.2430
2.0774
2.0675
2.0652
2.0513
2.0419
2.0251
0.5071
0.4903
N—NH2
3
Chloroform-d
2.00
2.00
8.04
Intensity
Chemical Shift (ppm)

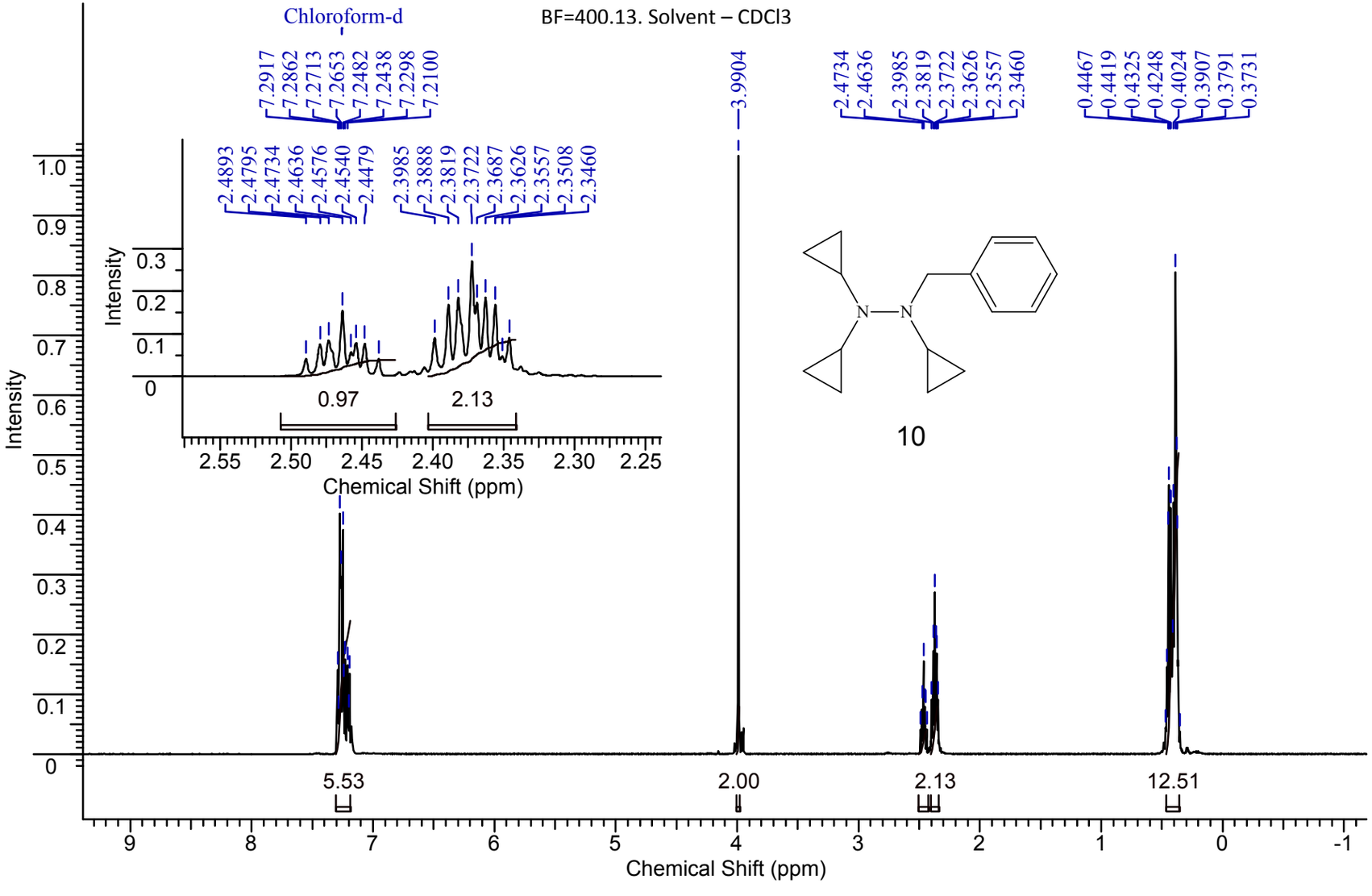

BF=100.61, Solvent – CDCl3
Chloroform-d
77.4808
77.1600
76.8465
41.4317
5.6523
N—NH2
3
Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

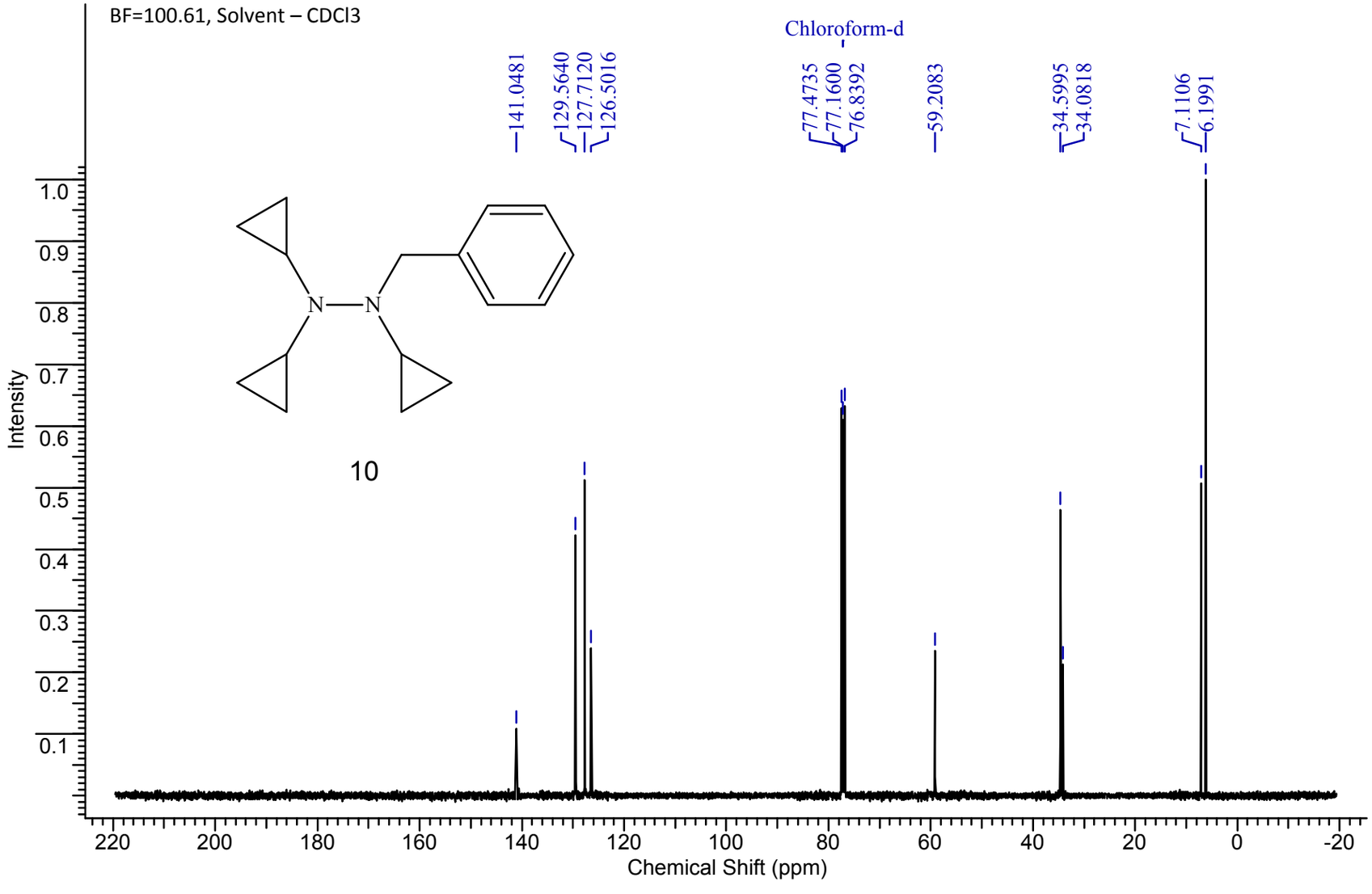

Chloroform-d1
BF=400.13, Solvent – CDCl3
7.9785
7.9647
7.9514
7.5376
7.5125
7.2600
7.0670
2.6411
2.6327
2.6239
2.3631
2.3539
2.3463
2.3371
2.3287
2.3207
2.3120
0.5867
0.5783
0.5699
0.5574
0.5413
0.5032
0.4922
0.4826
Intensity
Chemical Shift (ppm)
0.93
0.76
0.15
0.30
1.63
8.00
N
NH
O
8

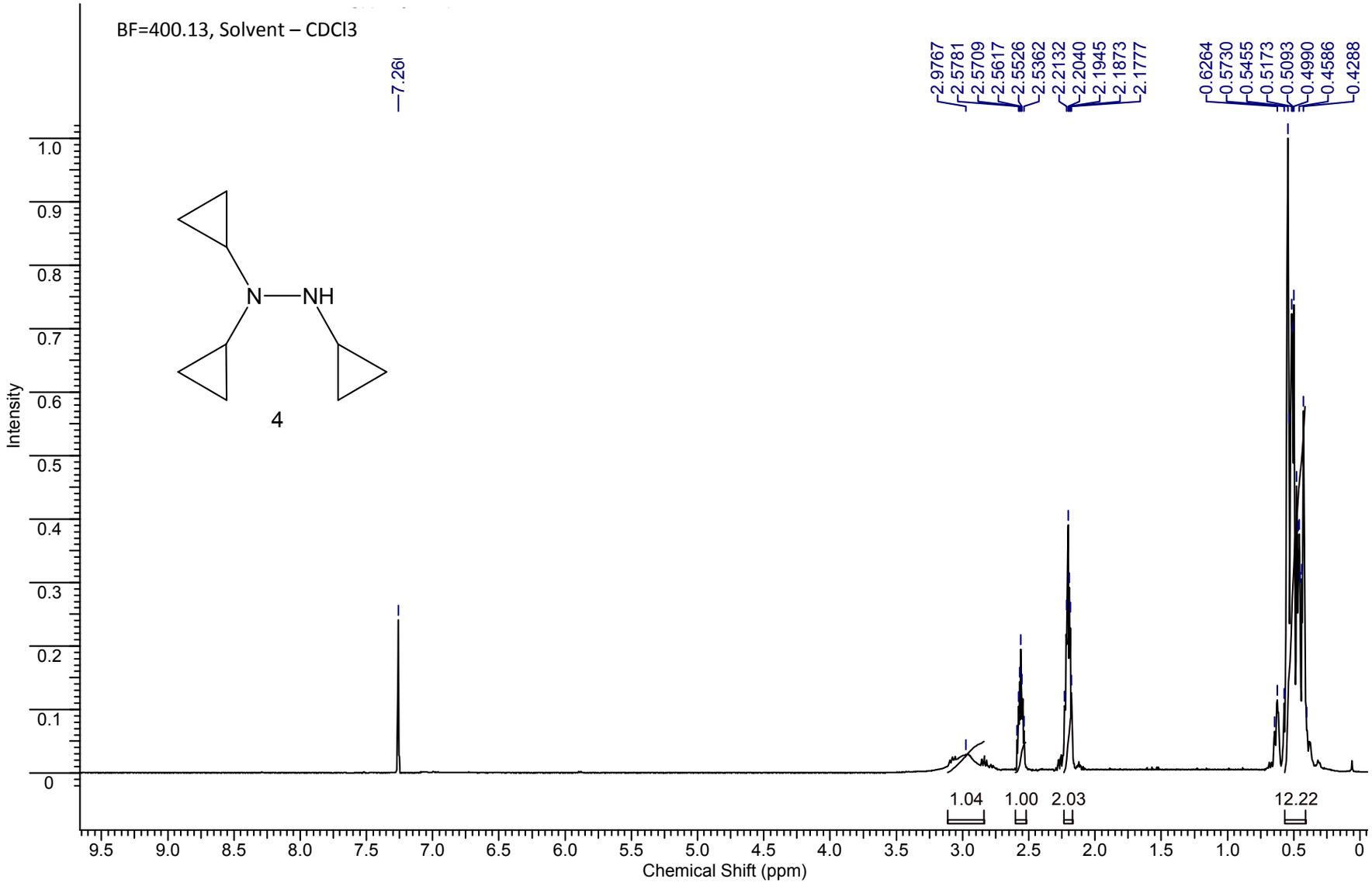

BF=100.61, Solvent – CDCl3
Chloroform-d
165.7955
159.1529
77.4808
77.1600
76.8465
39.5942
38.4932
6.4835
6.1189
N
NH
O
8
Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

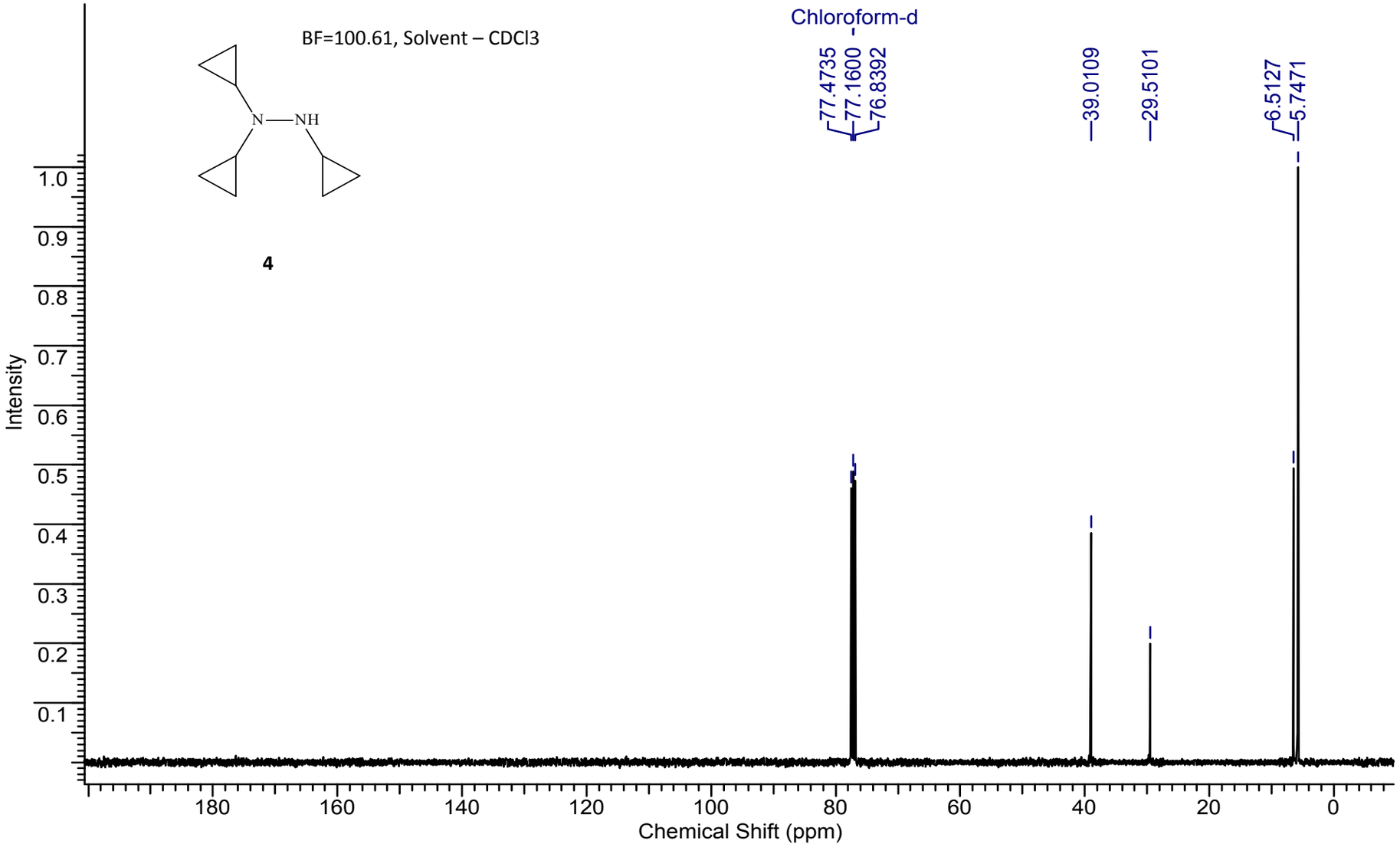

Chloroform-d
BF=400.13, Solvent – CDCl3
8.0593
7.3977
7.3794
7.3149
7.2974
7.2787
7.2600
7.2535
7.2352
4.7881
2.3463
2.3329
2.3200
2.3097
2.2956
0.4224
9
Intensity
Chemical Shift (ppm)
0.94
2.06
2.00
2.02
8.02
Chloroform-d
7.3977
7.3794
7.3180
7.3149
7.3103
7.2974
7.2936
7.2787
7.2600
7.2535
7.2413
7.2352
7.2173
2.01
2.06
1.11

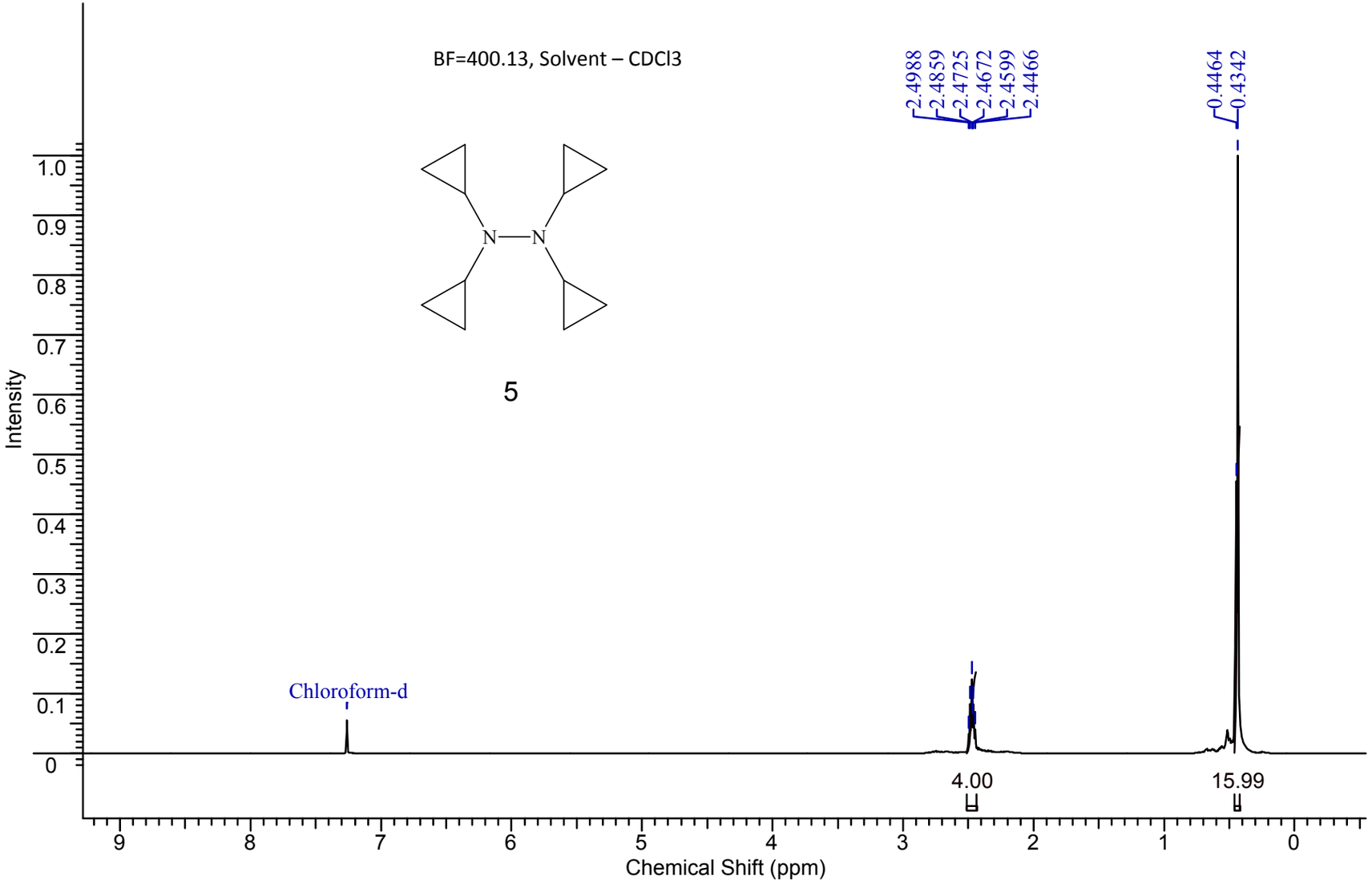

BF=100.61, Solvent – CDCl3
165.2559
138.0951
128.4630
127.3547
77.4808
77.1600
76.8465
44.0712
36.6995
7.5699
O
N
N
9
Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

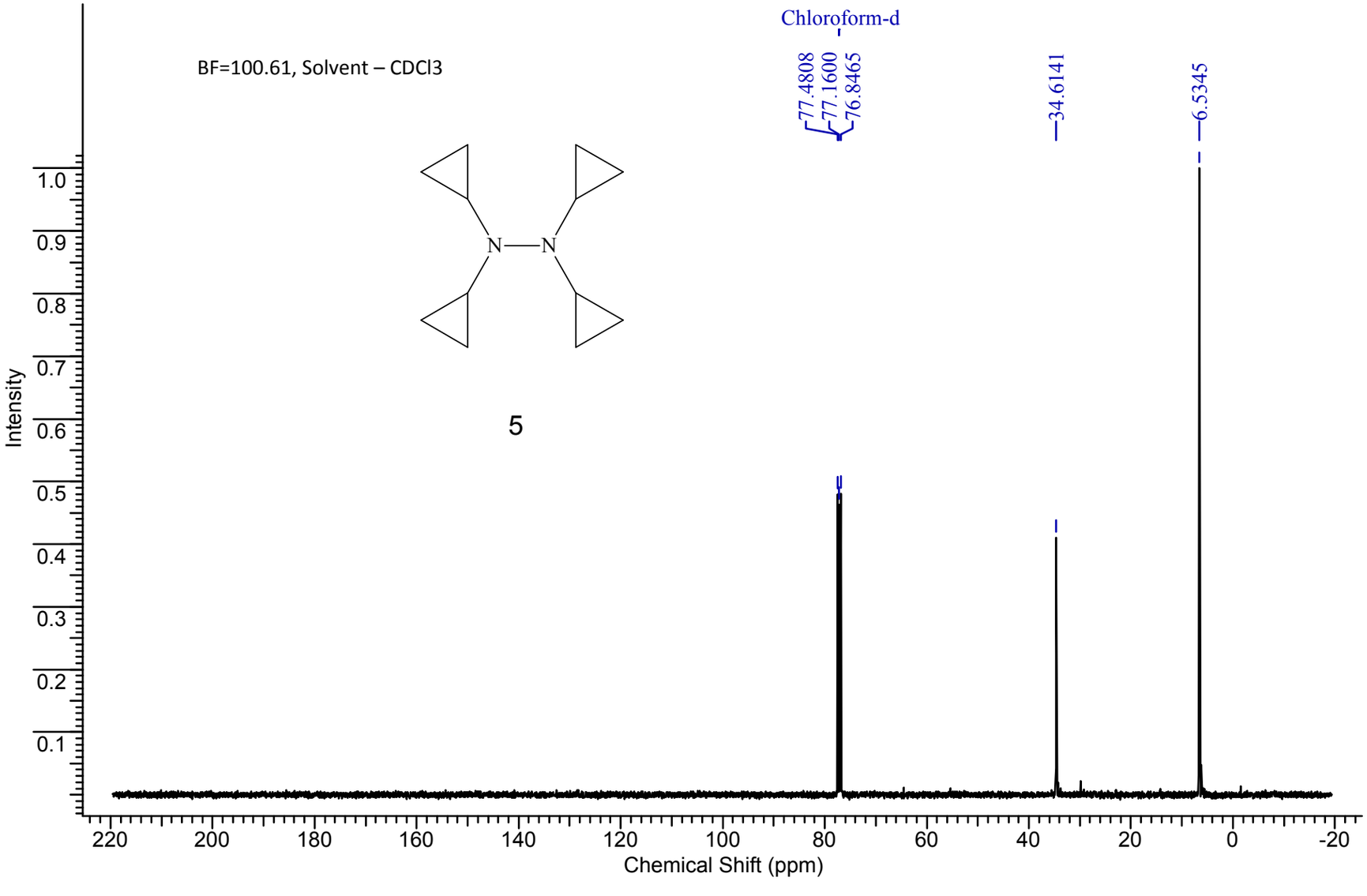

Chloroform-d
BF=400.13. Solvent – CDCl3
7.2917
7.2862
7.2713
7.2653
7.2482
7.2438
7.2298
7.2100
3.9904
2.4734
2.4636
2.3985
2.3819
2.3722
2.3626
2.3557
2.3460
0.4467
0.4419
0.4325
0.4248
0.4024
0.3907
0.3791
0.3731
2.4893
2.4795
2.4734
2.4636
2.4576
2.4540
2.4479
2.3985
2.3888
2.3819
2.3722
2.3687
2.3626
2.3557
2.3508
2.3460
Intensity
0.97
2.13
Chemical Shift (ppm)
10
Intensity
5.53
2.00
2.13
12.51
Chemical Shift (ppm)

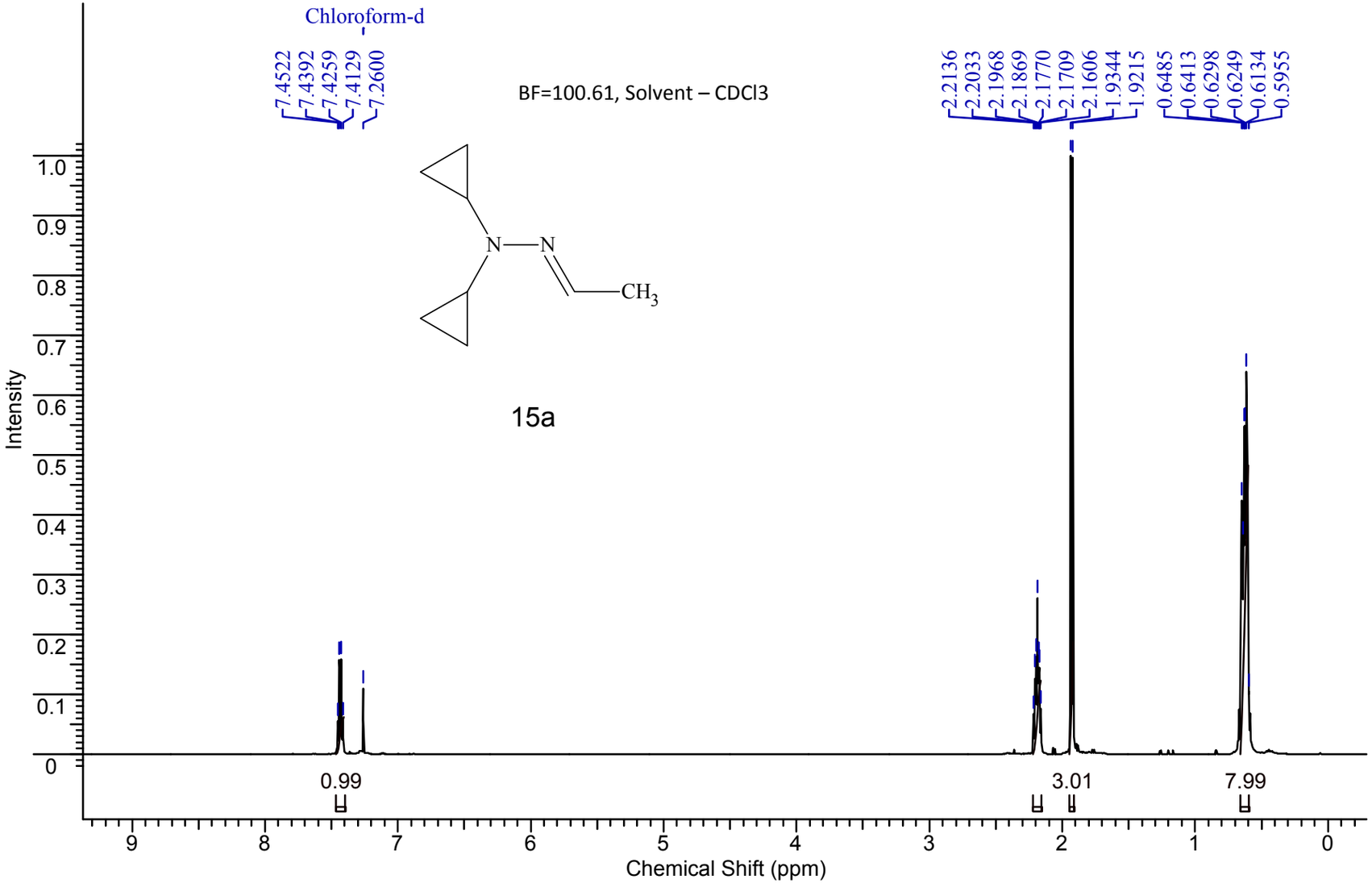

BF=100.61, Solvent – CDCl3
Chloroform-d
141.0481
129.5640
127.7120
126.5016
77.4735
77.1600
76.8392
59.2083
34.5995
34.0818
7.1106
6.1991
N
N
10
Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

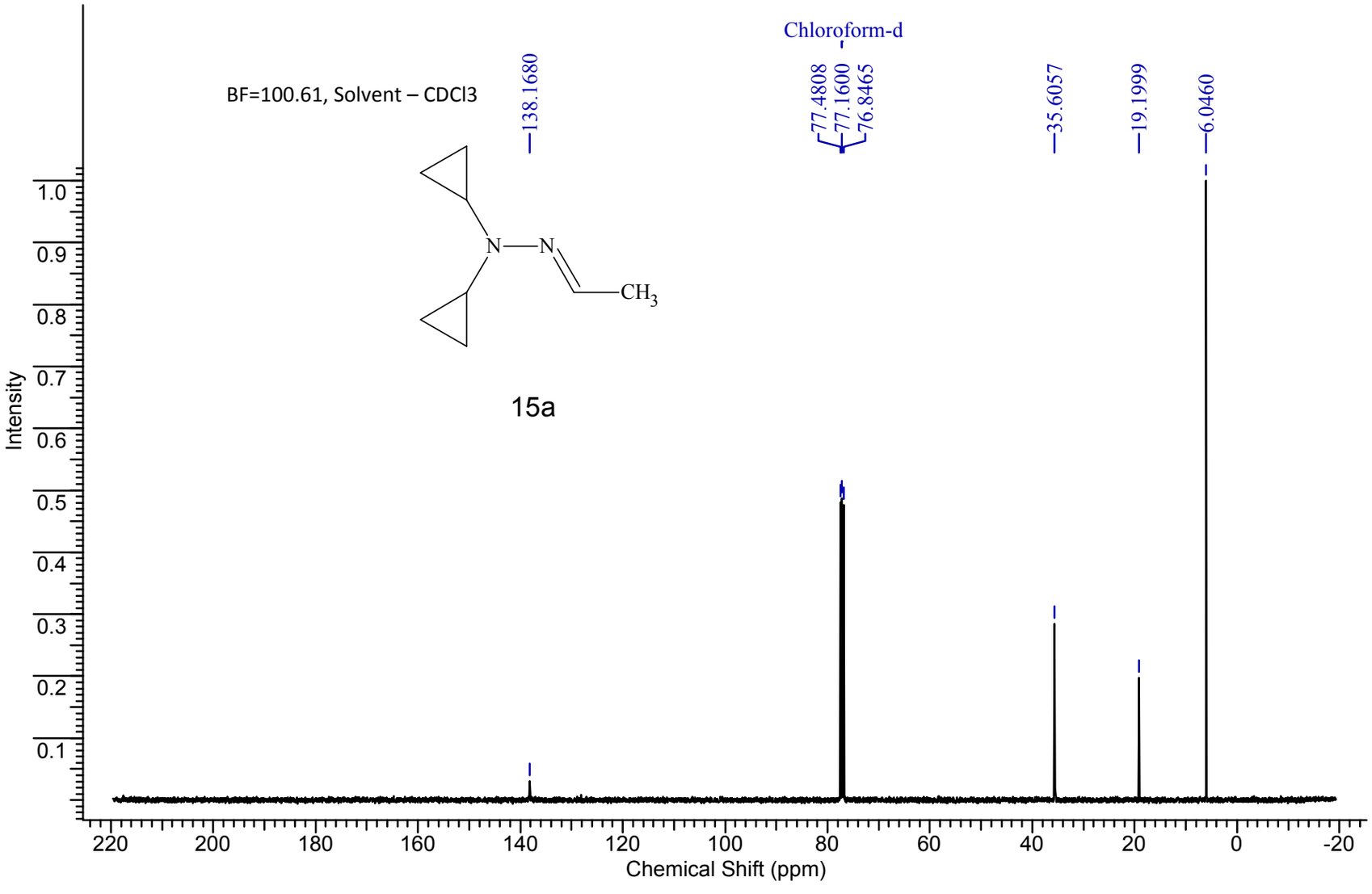

BF=400.13, Solvent – CDCl3
7.26
2.9767
2.5781
2.5709
2.5617
2.5526
2.5362
2.2132
2.2040
2.1945
2.1873
2.1777
0.6264
0.5730
0.5455
0.5173
0.5093
0.4990
0.4586
0.4288
N
NH
4
Intensity
1.04
1.00
2.03
12.22
Chemical Shift (ppm)

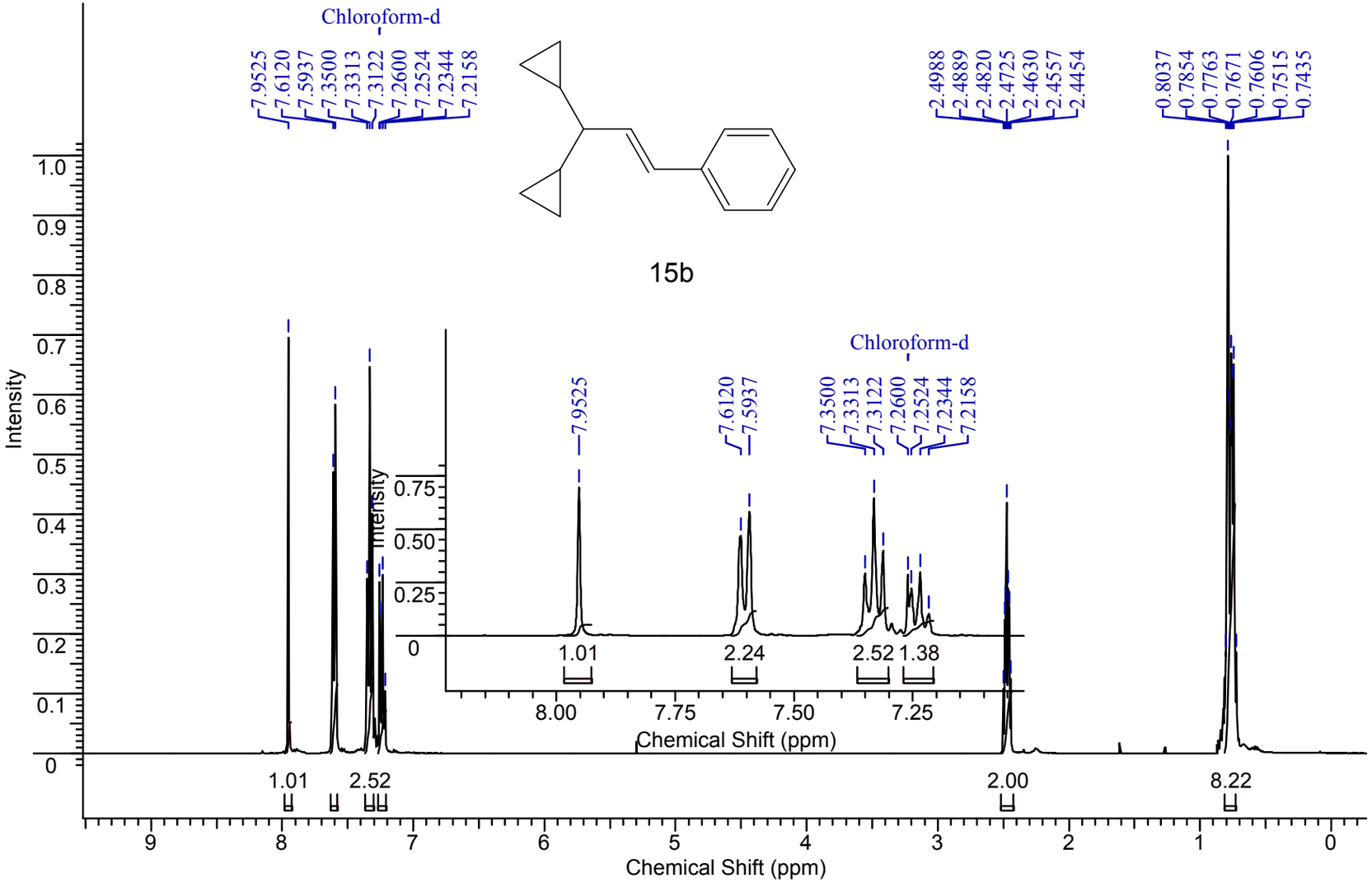

BF=100.61, Solvent – CDCl3
Chloroform-d
77.4735
77.1600
76.8392
39.0109
29.5101
6.5127
5.7471
N—NH
4
Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

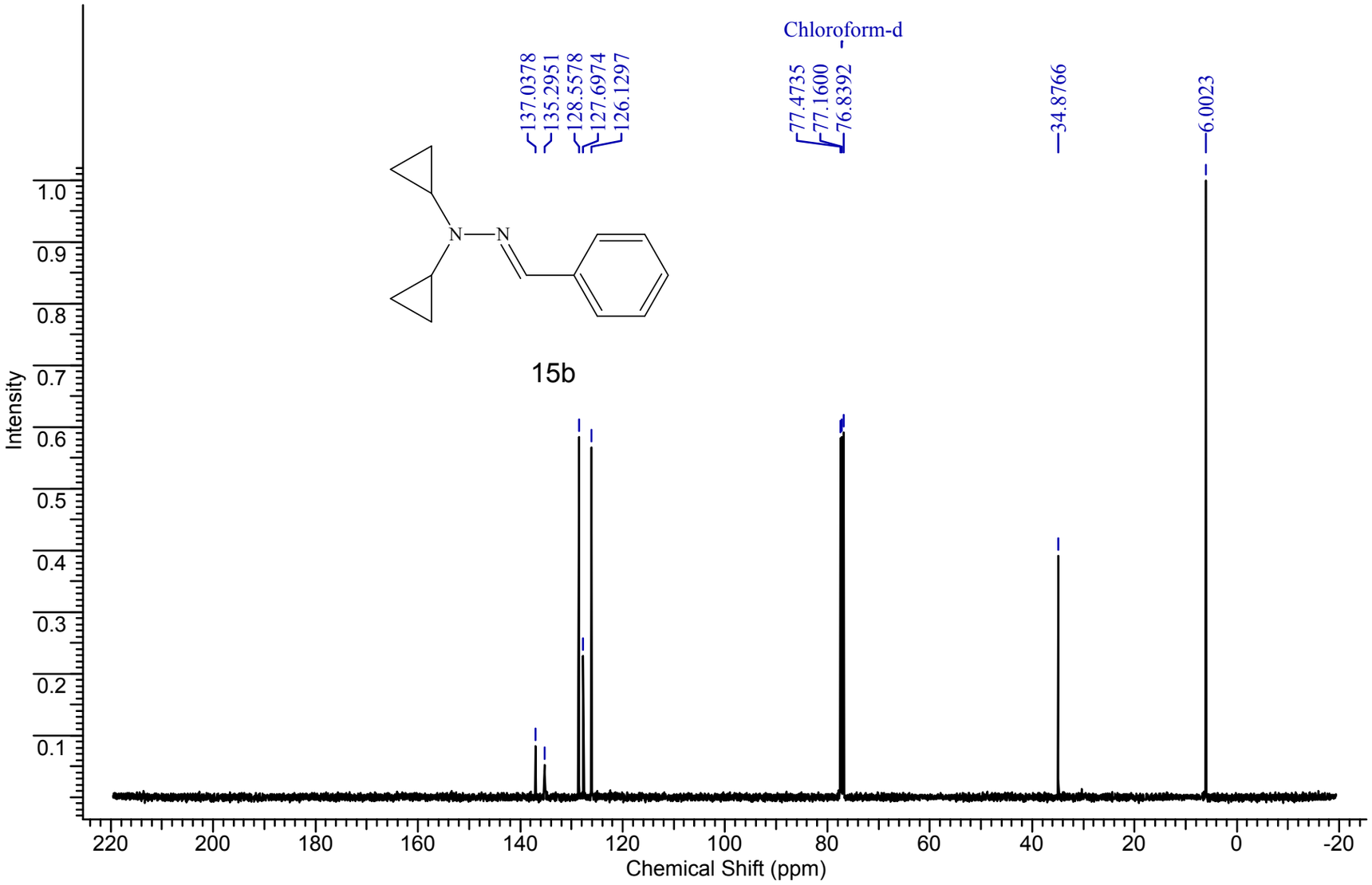

BF=400.13, Solvent – CDCl3
2.4988
2.4859
2.4725
2.4672
2.4599
2.4466
0.4464
0.4342
N
N
5
Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Chloroform-d
4.00
15.99
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

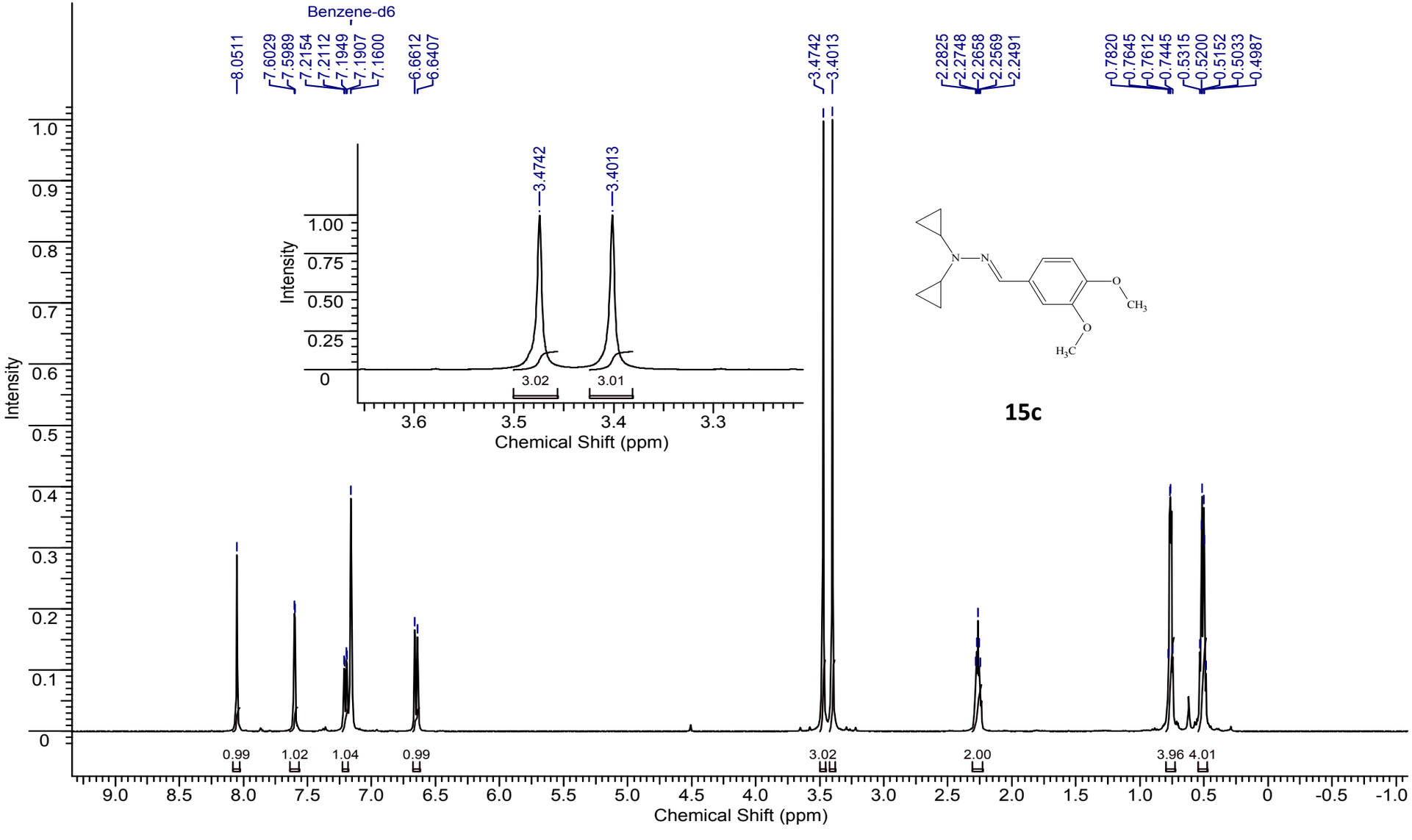

BF=100.61, Solvent – CDCl3
Chloroform-d
77.4808
77.1600
76.8465
34.6141
6.5345
N
N
5
Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

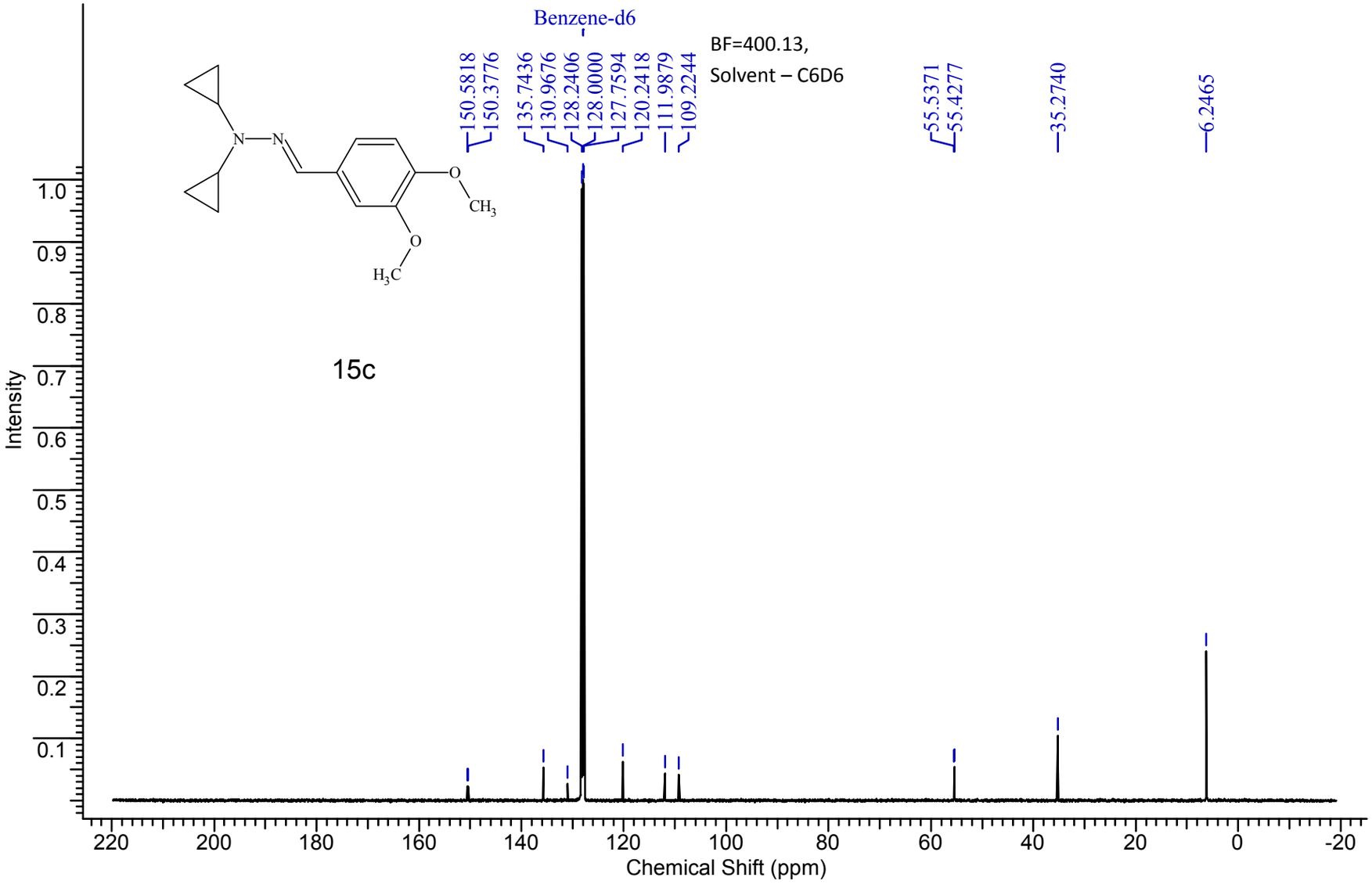

Chloroform-d
7.4522
7.4392
7.4259
7.4129
7.2600
BF=100.61, Solvent – CDCl3
2.2136
2.2033
2.1968
2.1869
2.1770
2.1709
2.1606
1.9344
1.9215
0.6485
0.6413
0.6298
0.6249
0.6134
0.5955
N
N
CH3
15a
Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0.99
3.01
7.99
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

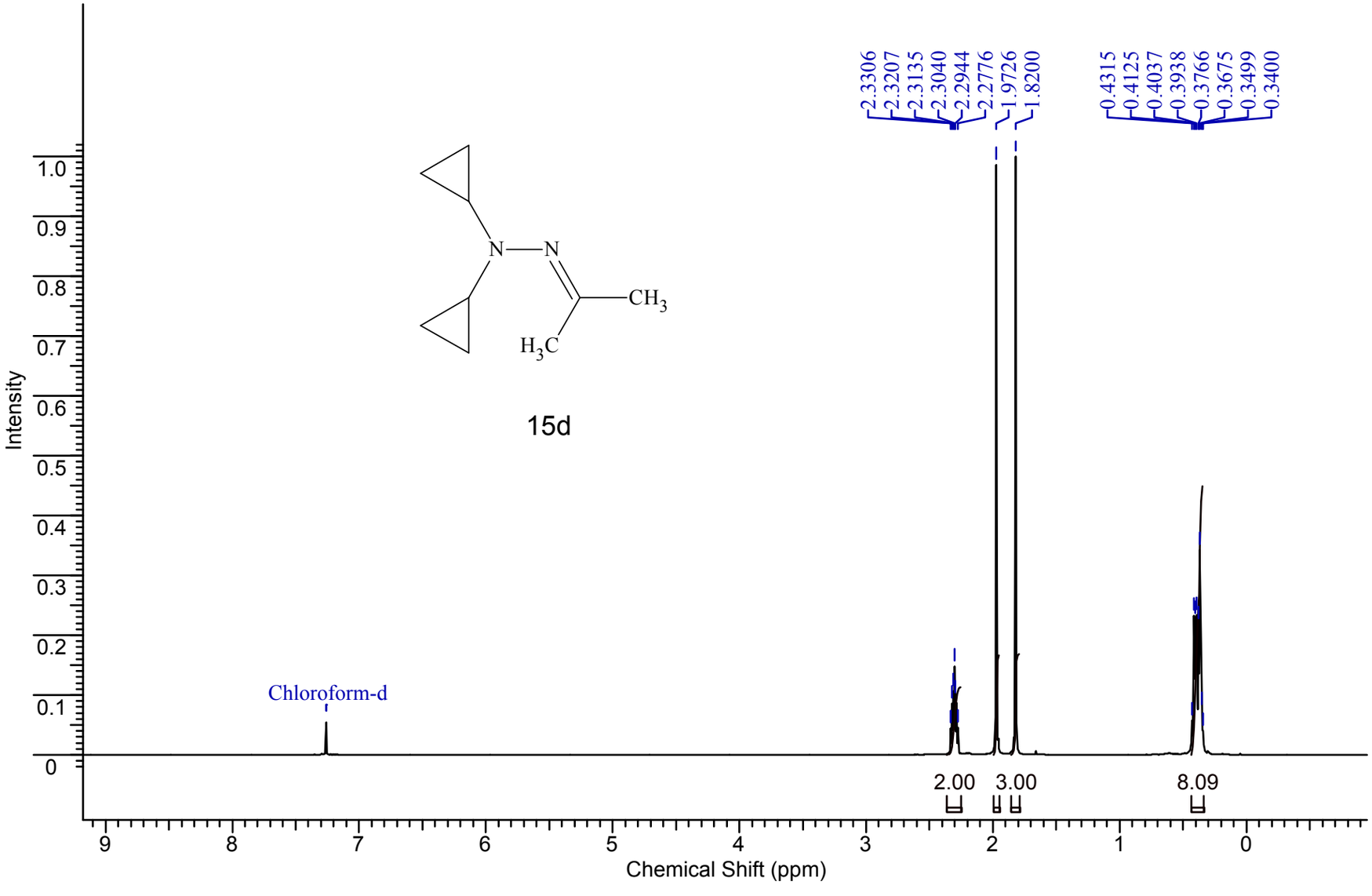

BF=100.61, Solvent – CDCl3
138.1680
Chloroform-d
77.4808
77.1600
76.8465
35.6057
19.1999
6.0460
N
N
CH3
15a
Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

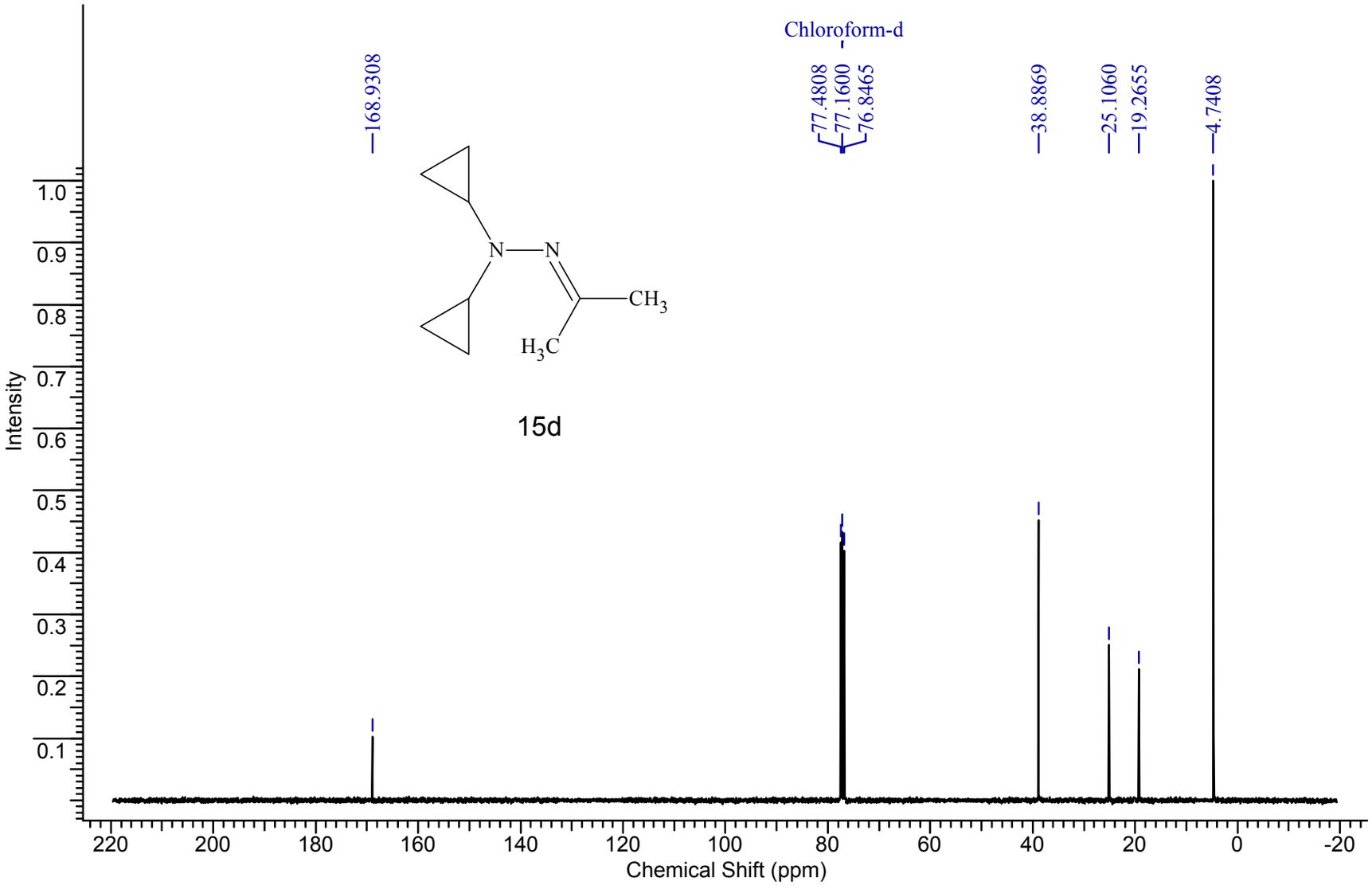

Chloroform-d
7.9525
7.6120
7.5937
7.3500
7.3313
7.3122
7.2600
7.2524
7.2344
7.2158
2.4988
2.4889
2.4820
2.4725
2.4630
2.4557
2.4454
0.8037
0.7854
0.7763
0.7671
0.7606
0.7515
0.7435
15b
Intensity
Chemical Shift (ppm)
1.01
2.52
2.00
8.22
1.01
2.24
2.52
1.38

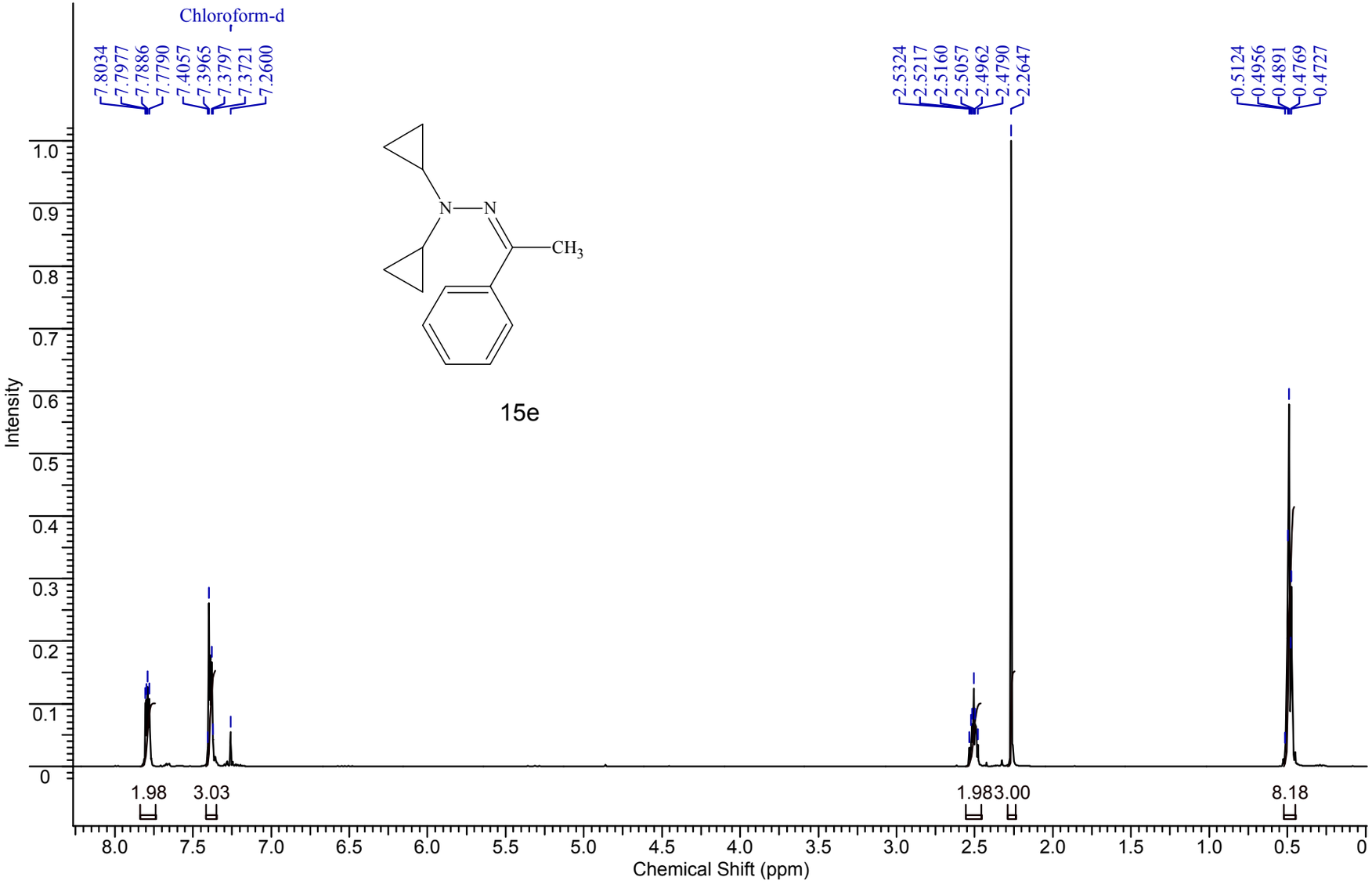

Chloroform-d
137.0378
135.2951
128.5578
127.6974
126.1297
77.4735
77.1600
76.8392
34.8766
6.0023
N
N
15b
Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

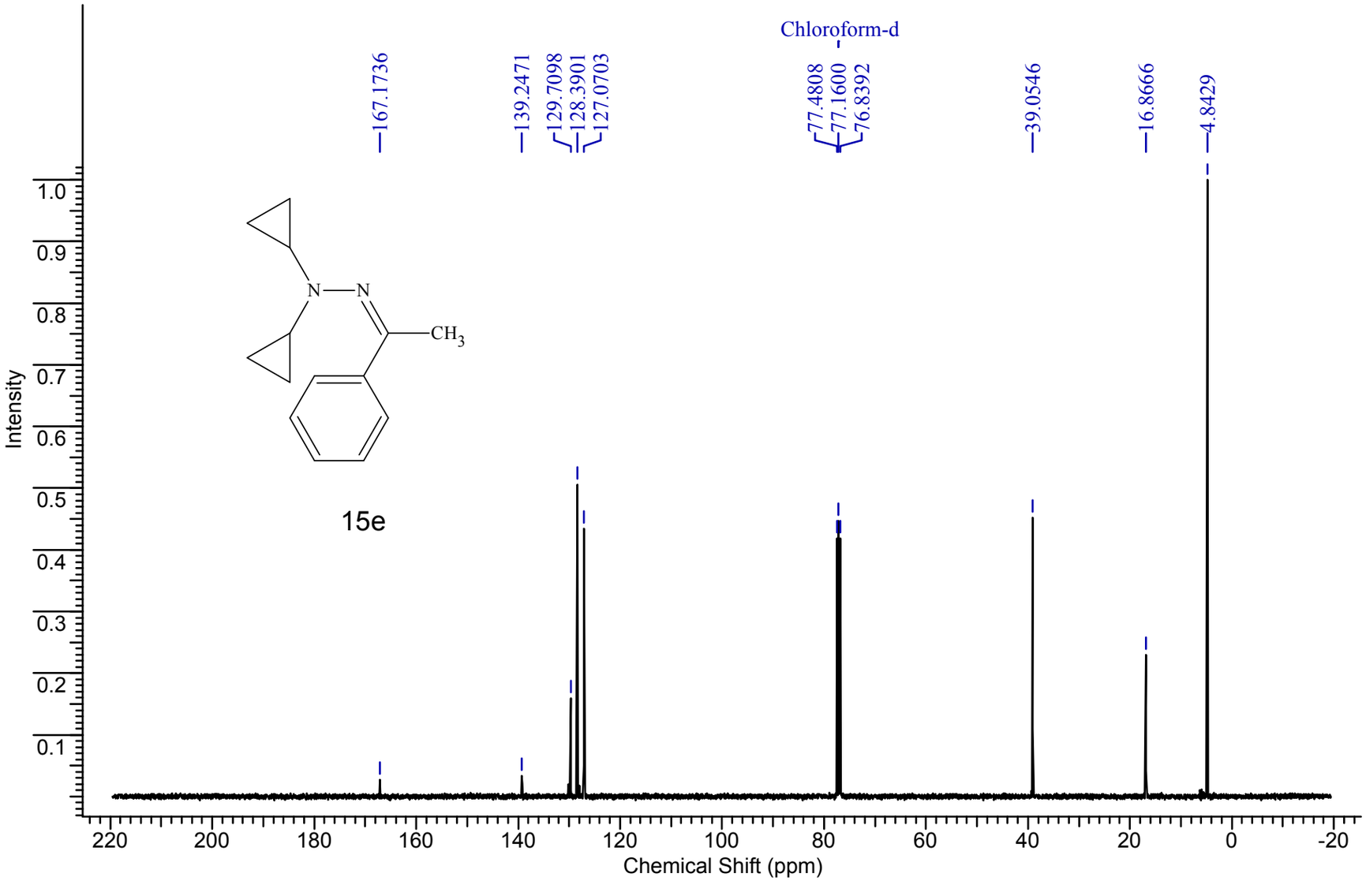

Benzene-d6
8.0511
7.6029
7.5989
7.2154
7.2112
7.1949
7.1907
7.1600
6.6612
6.6407
3.4742
3.4013
2.2825
2.2748
2.2658
2.2569
2.2491
0.7820
0.7645
0.7612
0.7445
0.5315
0.5200
0.5152
0.5033
0.4987
Intensity
Chemical Shift (ppm)
0.99
1.02
1.04
0.99
3.02
2.00
3.96
4.01
3.02
3.01
15c

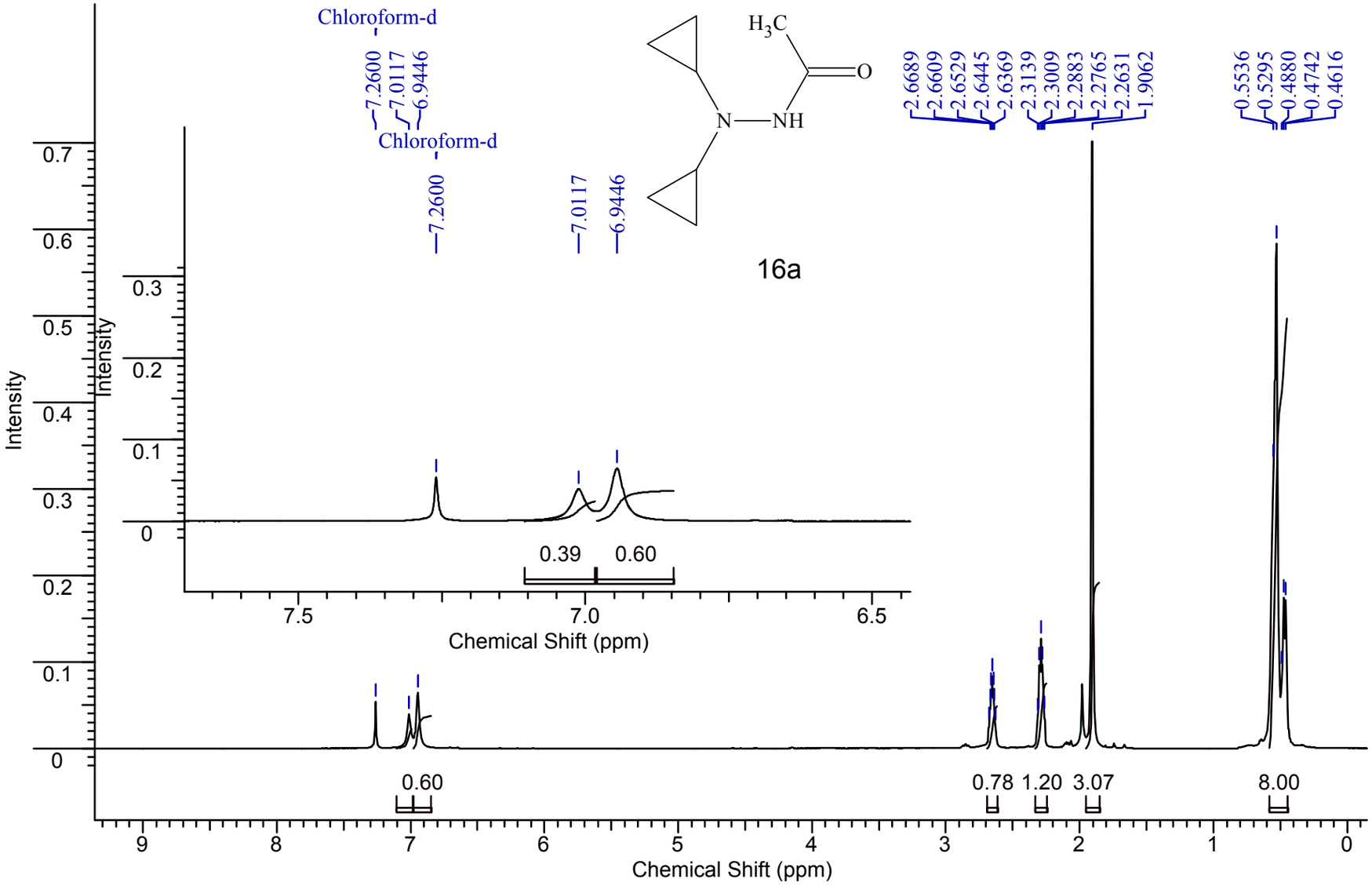

Benzene-d6
BF=400.13,
Solvent – C6D6
150.5818
150.3776
135.7436
130.9676
128.2406
128.0000
127.7594
120.2418
111.9879
109.2244
55.5371
55.4277
35.2740
6.2465
15c
Intensity
Chemical Shift (ppm)

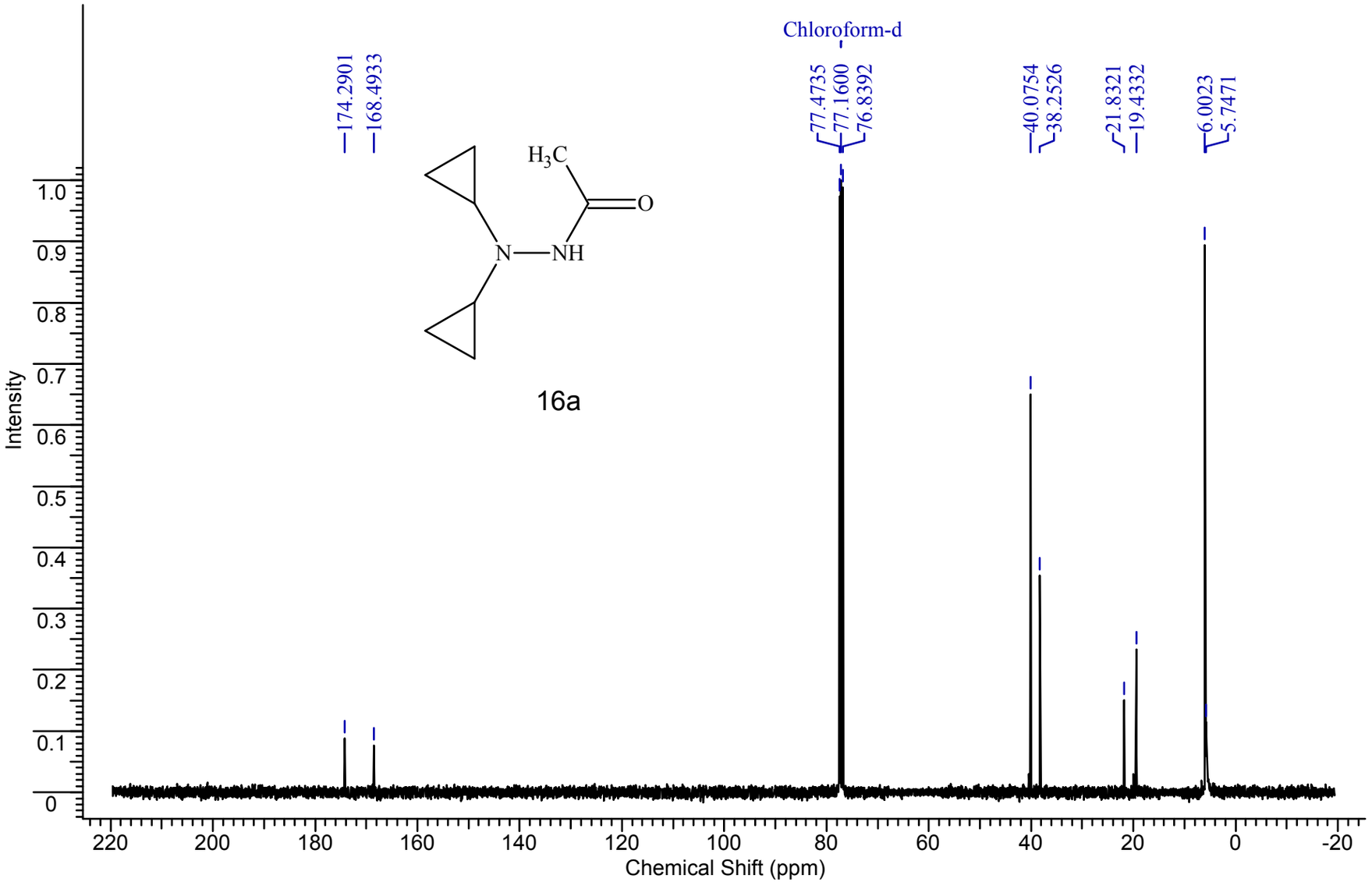

2.3306
2.3207
2.3135
2.3040
2.2944
2.2776
1.9726
1.8200
0.4315
0.4125
0.4037
0.3938
0.3766
0.3675
0.3499
0.3400
N
N
CH3
H3C
15d
Chloroform-d
2.00
3.00
8.09
Intensity
Chemical Shift (ppm)

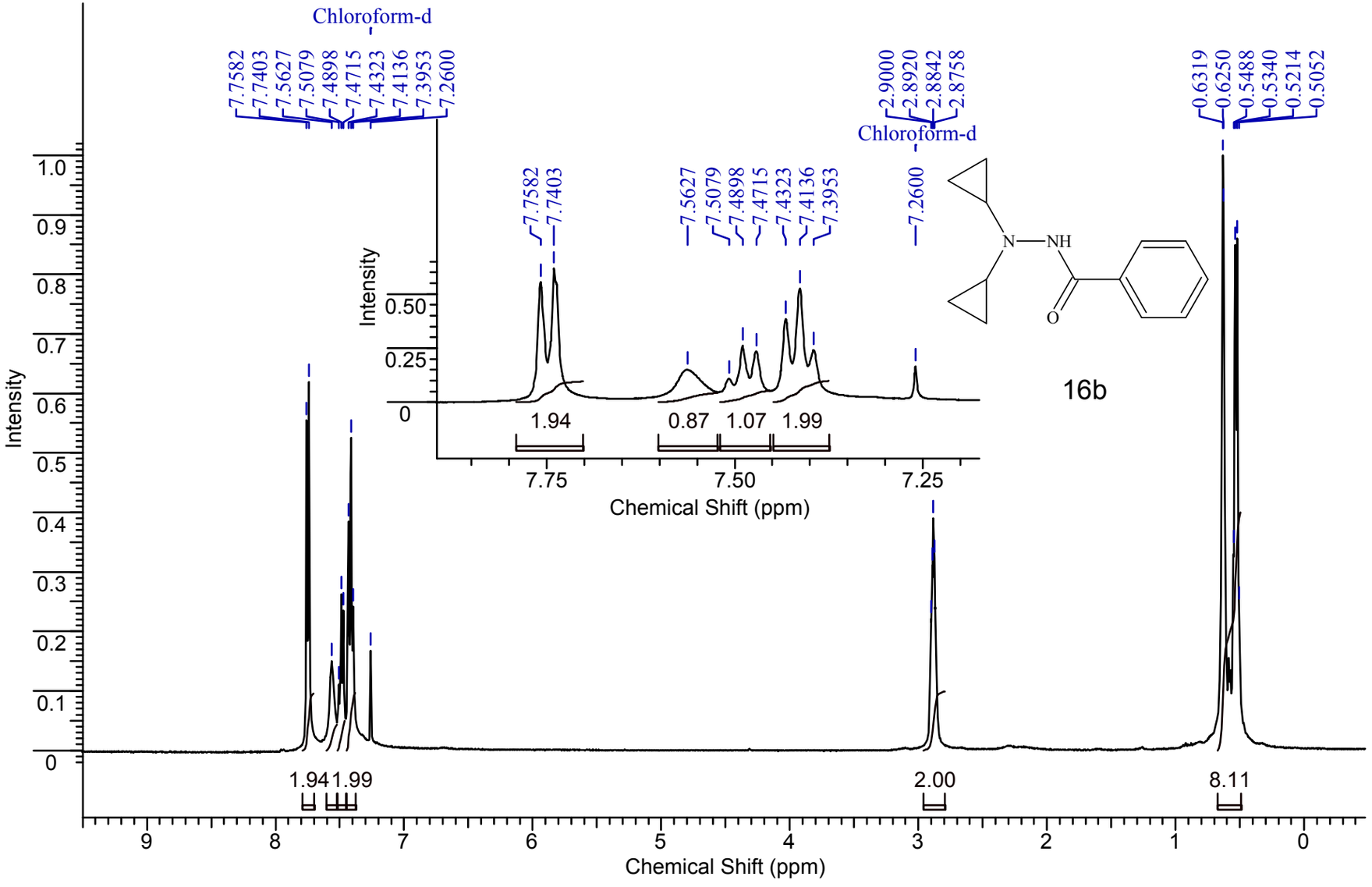

Chloroform-d
168.9308
77.4808
77.1600
76.8465
38.8869
25.1060
19.2655
4.7408
N
N
CH3
H3C
15d
Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

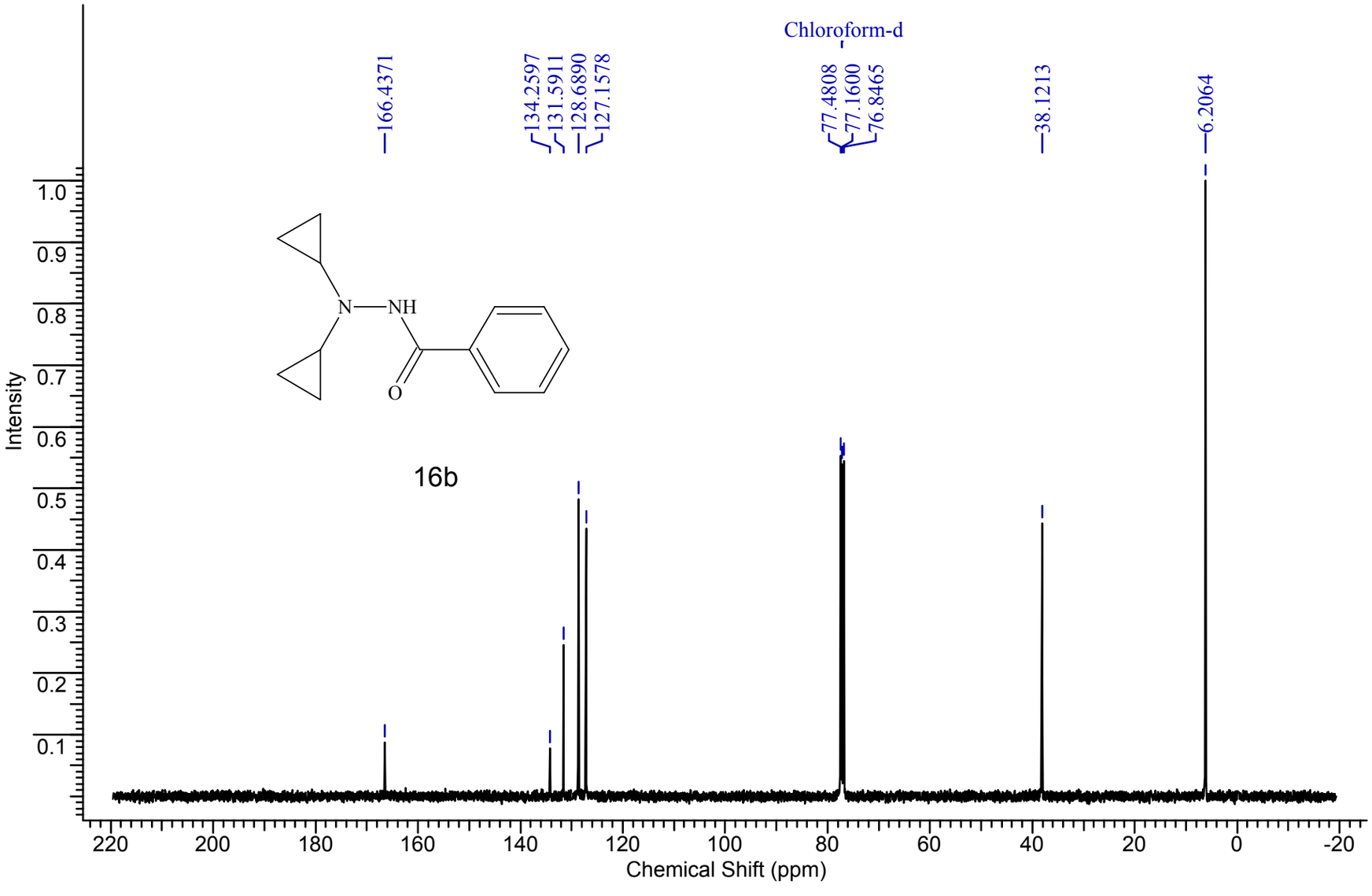

Chloroform-d
7.8034
7.7977
7.7886
7.7790
7.4057
7.3965
7.3797
7.3721
7.2600
2.5324
2.5217
2.5160
2.5057
2.4962
2.4790
2.2647
0.5124
0.4956
0.4891
0.4769
0.4727
N
N
CH3
15e
Intensity
1.98
3.03
1.98
3.00
8.18
Chemical Shift (ppm)

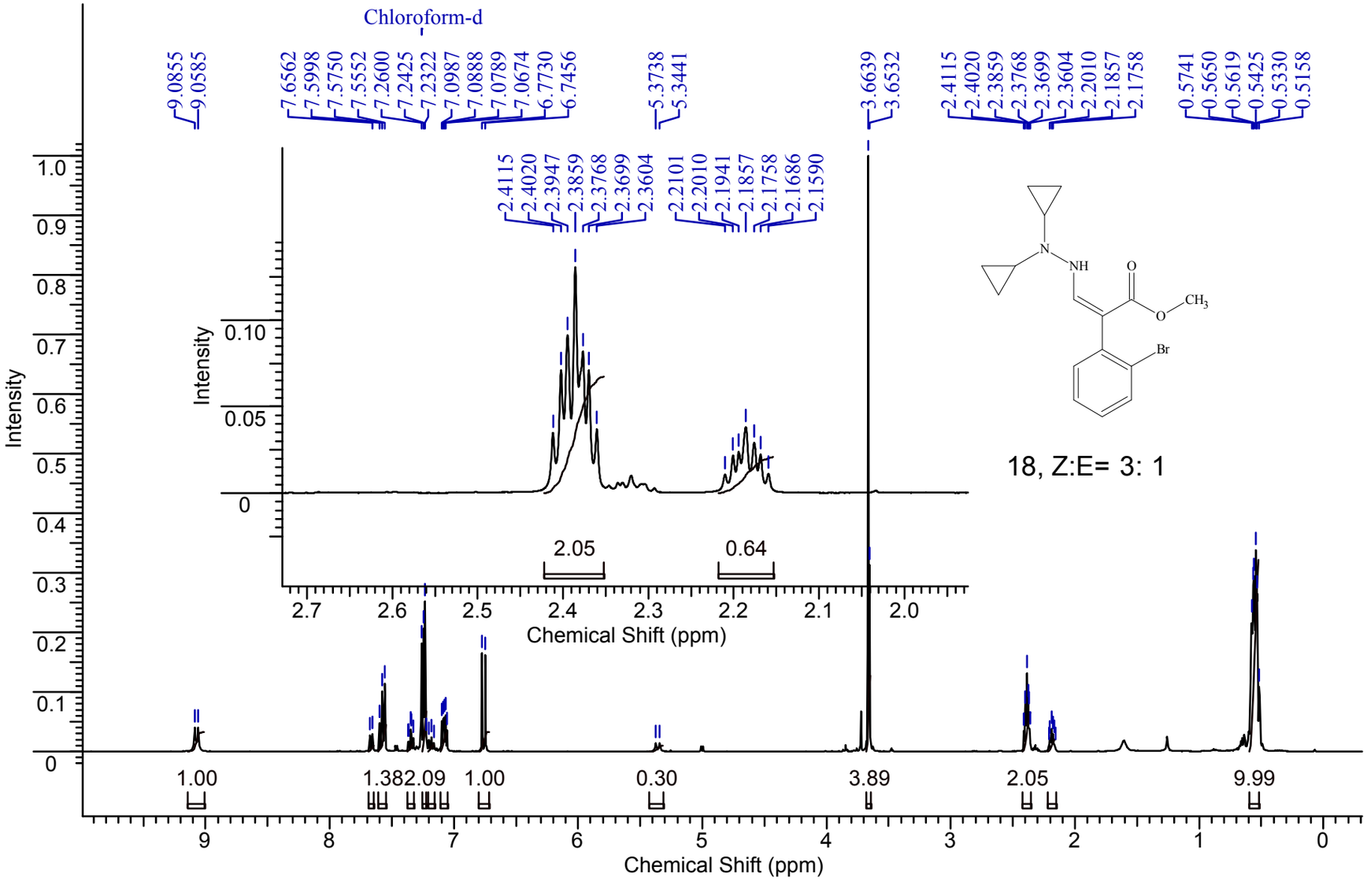

Chloroform-d
167.1736
139.2471
129.7098
128.3901
127.0703
77.4808
77.1600
76.8392
39.0546
16.8666
4.8429
Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
N
N
CH3
15e
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

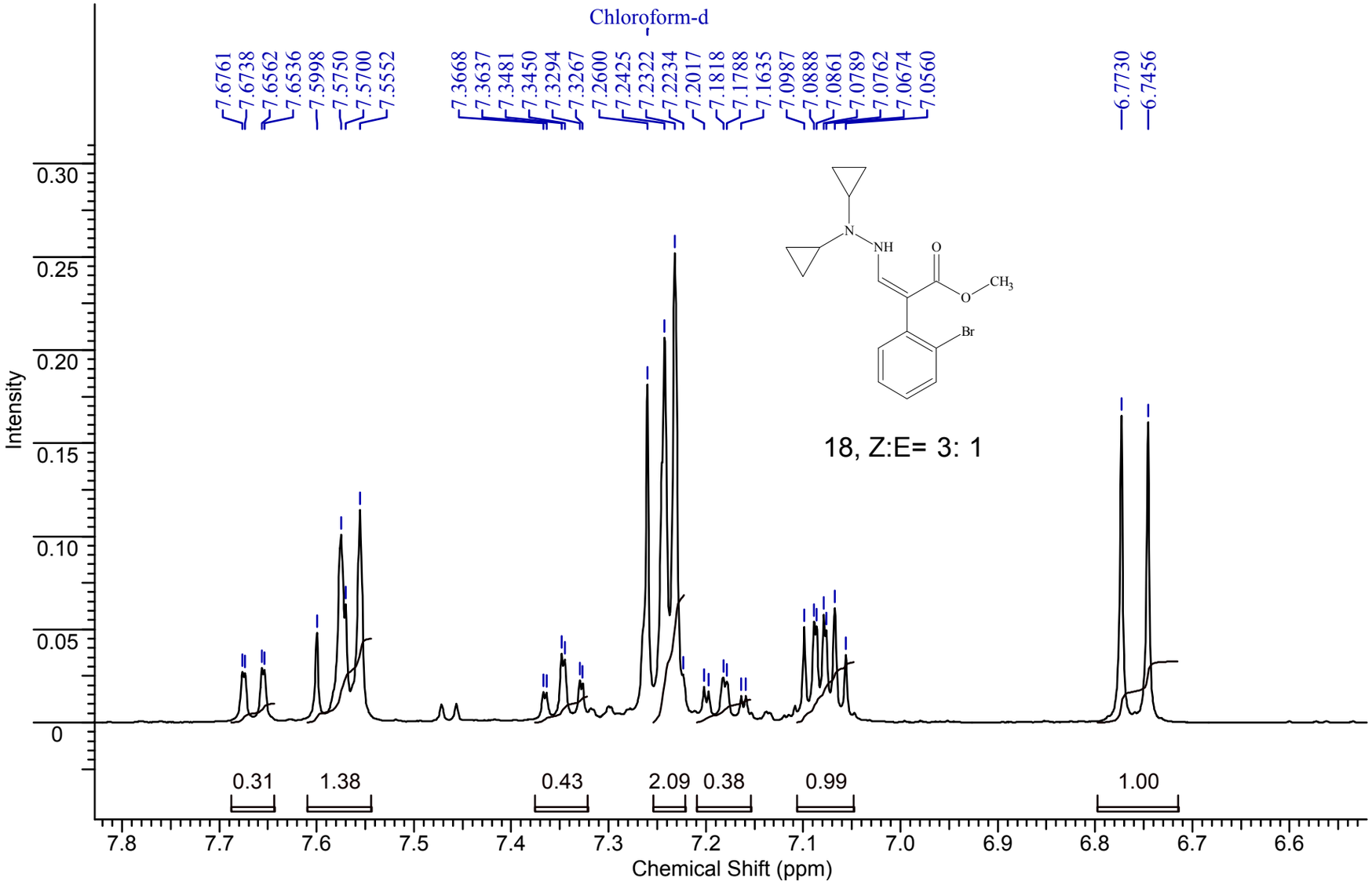

Chloroform-d
7.2600
7.0117
6.9446
Chloroform-d
7.2600
7.0117
6.9446
H3C
O
N
NH
16a
2.6689
2.6609
2.6529
2.6445
2.6369
2.3139
2.3009
2.2883
2.2765
2.2631
1.9062
0.5536
0.5295
0.4880
0.4742
0.4616
Intensity
Intensity
0.39
0.60
Chemical Shift (ppm)
0.60
0.78
1.20
3.07
8.00
Chemical Shift (ppm)

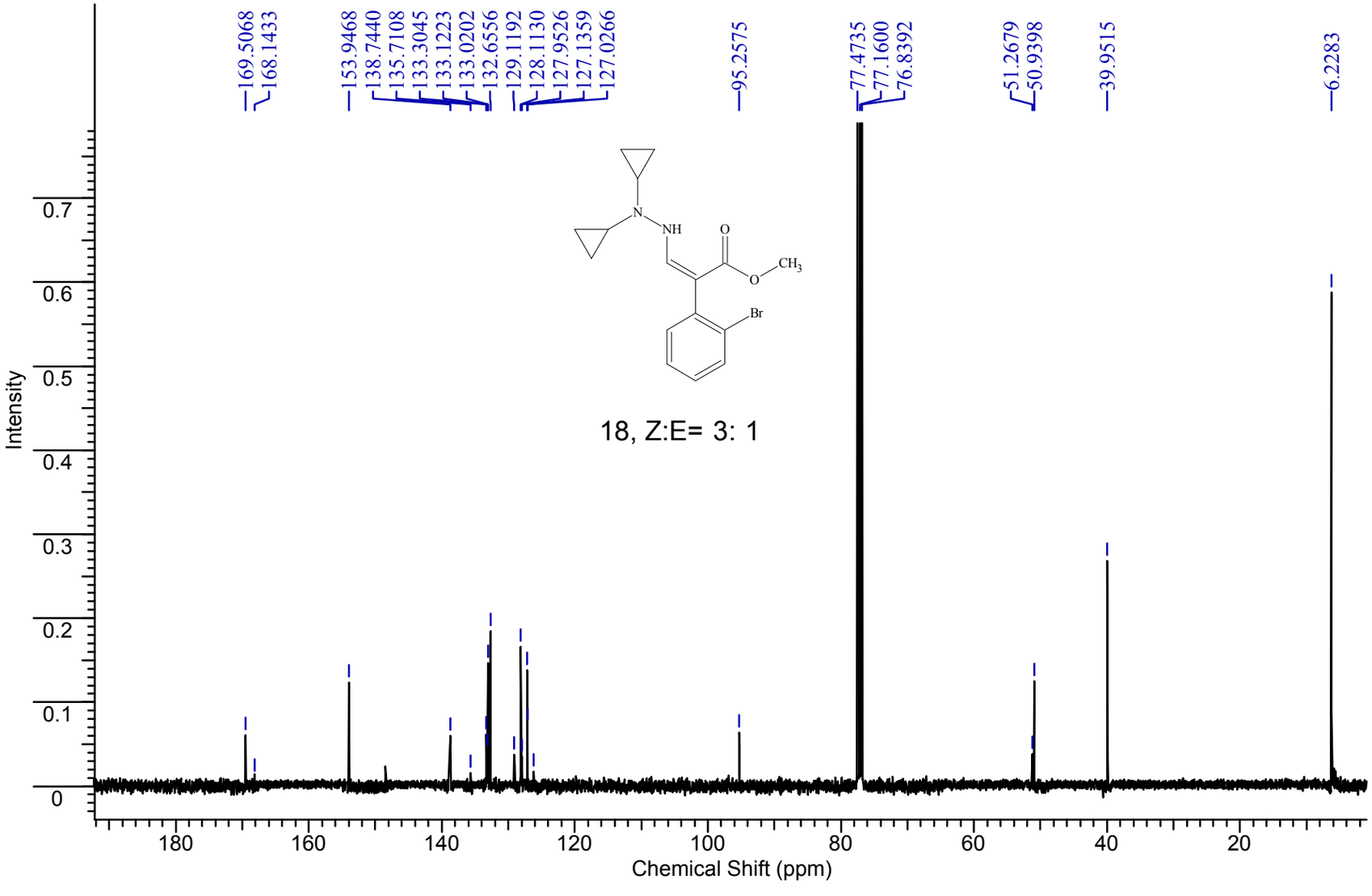

Chloroform-d
174.2901
168.4933
77.4735
77.1600
76.8392
40.0754
38.2526
21.8321
19.4332
6.0023
5.7471
H3C
O
N
NH
16a
Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

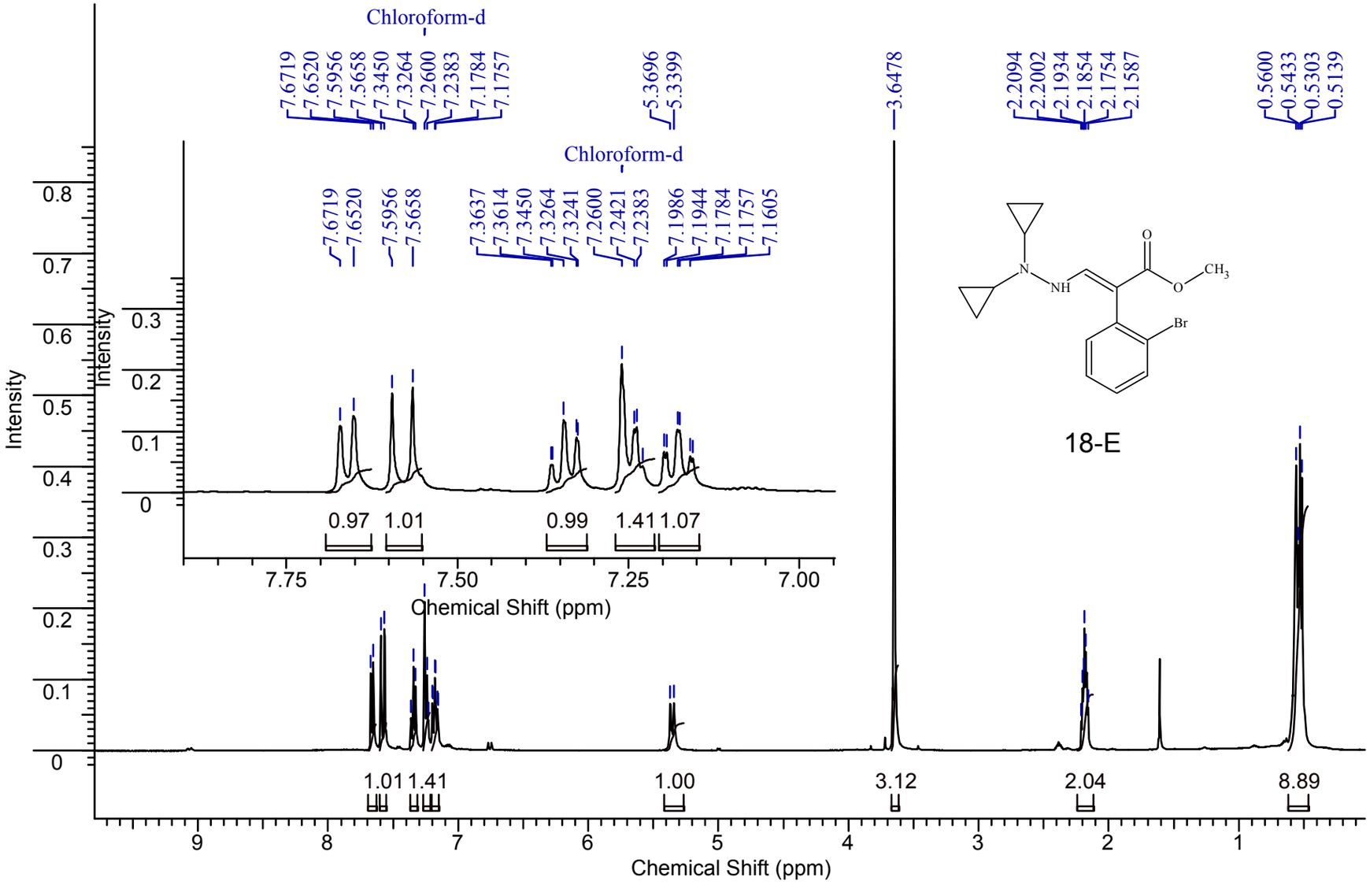

Chloroform-d
7.7582
7.7403
7.5627
7.5079
7.4898
7.4715
7.4323
7.4136
7.3953
7.2600
2.9000
2.8920
2.8842
2.8758
0.6319
0.6250
0.5488
0.5340
0.5214
0.5052
Intensity
Chemical Shift (ppm)
1.94
1.99
2.00
8.11
16b
N
NH
O
0.87
1.07

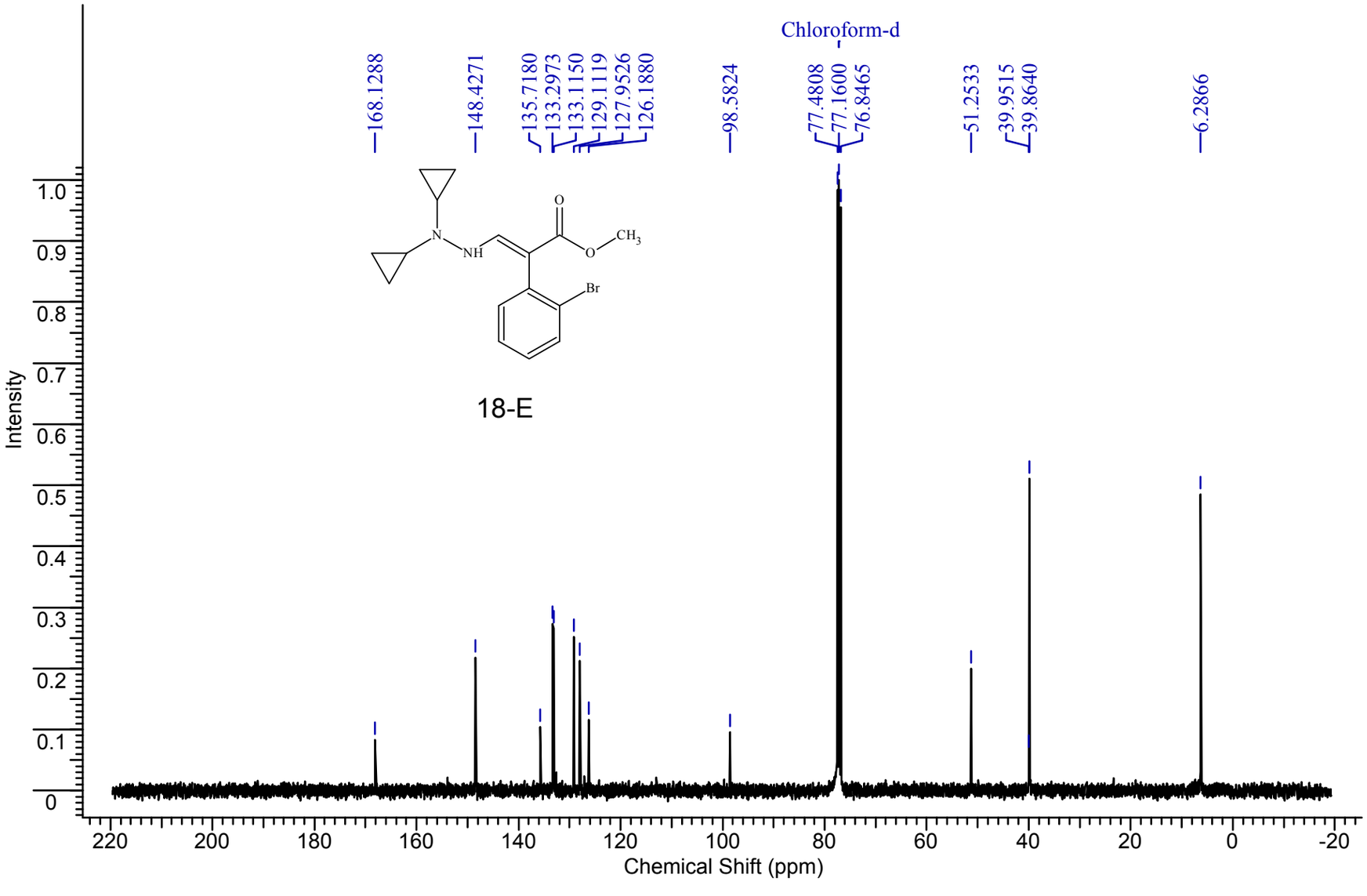

Chloroform-d
166.4371
134.2597
131.5911
128.6890
127.1578
77.4808
77.1600
76.8465
38.1213
6.2064
N
NH
O
16b
Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

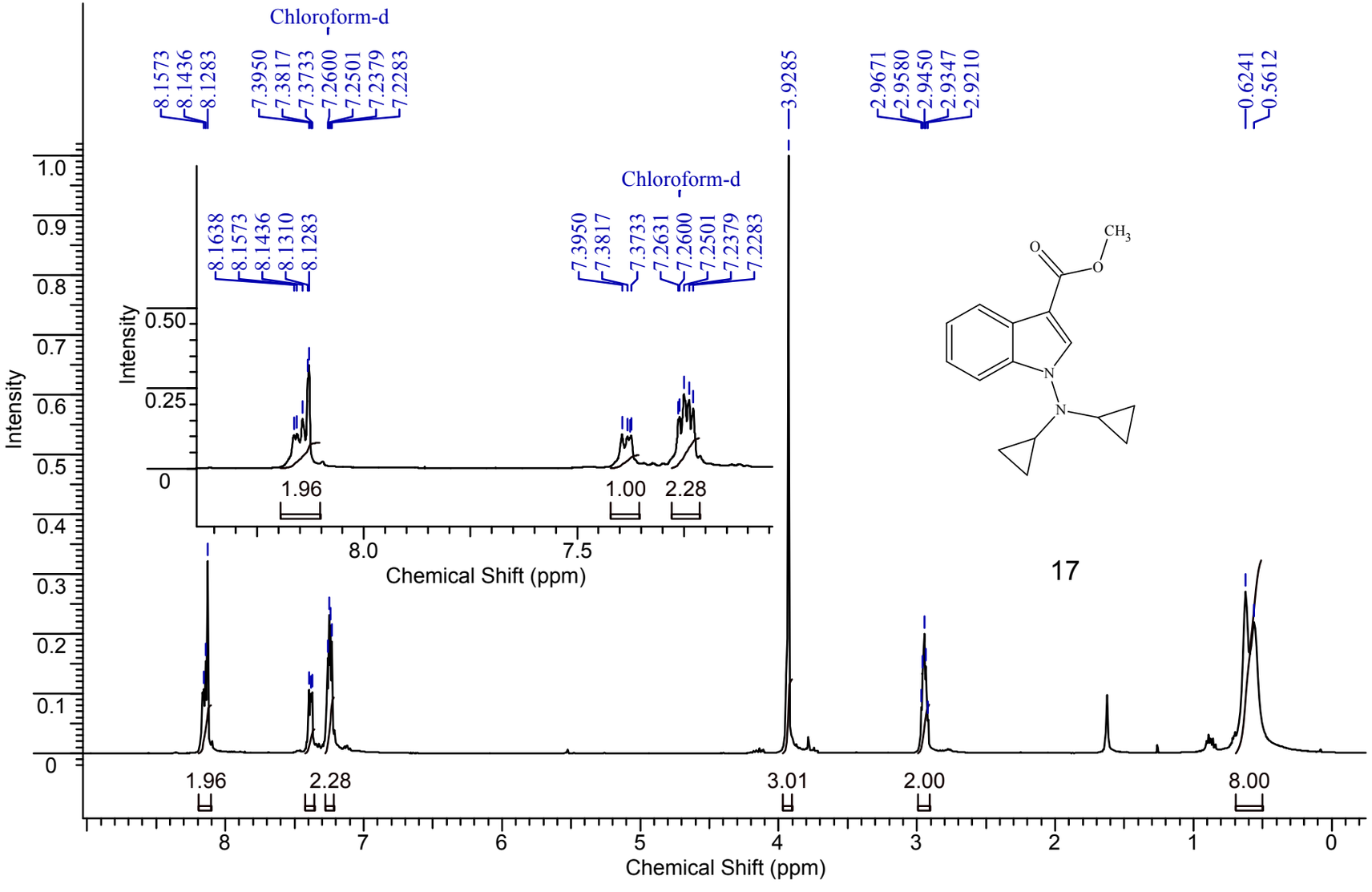

Chloroform-d
9.0855
9.0585
7.6562
7.5998
7.5750
7.5552
7.2600
7.2425
7.2322
7.0987
7.0888
7.0789
7.0674
6.7730
6.7456
5.3738
5.3441
3.6639
3.6532
2.4115
2.4020
2.3859
2.3768
2.3699
2.3604
2.2010
2.1857
2.1758
0.5741
0.5650
0.5619
0.5425
0.5330
0.5158
2.4115
2.4020
2.3947
2.3859
2.3768
2.3699
2.3604
2.2101
2.2010
2.1941
2.1857
2.1758
2.1686
2.1590
Intensity
Chemical Shift (ppm)
1.00
1.38
2.09
1.00
0.30
3.89
2.05
9.99
2.05
0.64
N
NH
O
O
CH3
Br
18, Z:E= 3: 1

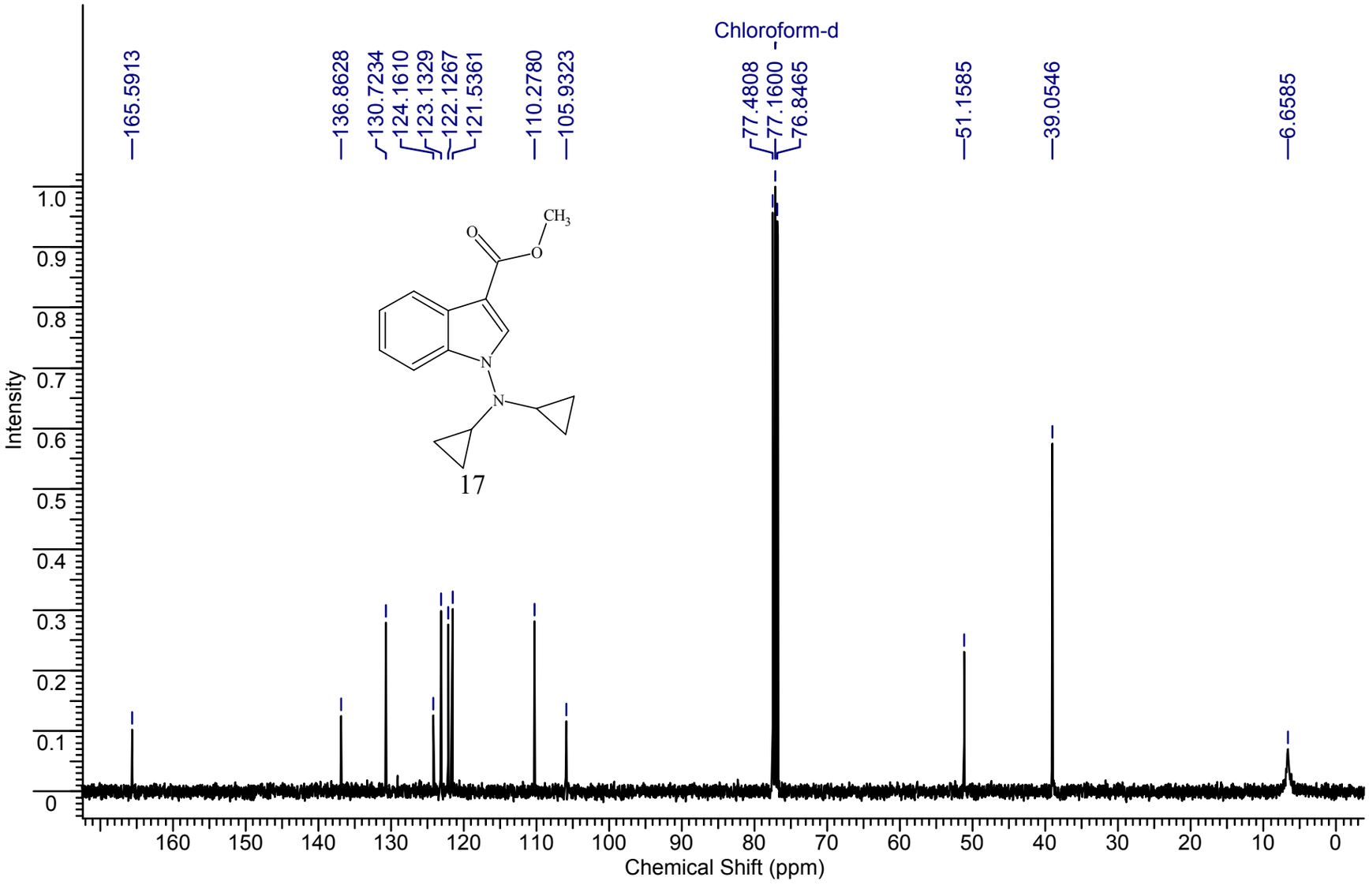

Chloroform-d
7.6761
7.6738
7.6562
7.6536
7.5998
7.5750
7.5700
7.5552
7.3668
7.3637
7.3481
7.3450
7.3294
7.3267
7.2600
7.2425
7.2322
7.2234
7.2017
7.1818
7.1788
7.1635
7.0987
7.0888
7.0861
7.0789
7.0762
7.0674
7.0560
6.7730
6.7456
N
NH
O
O
CH3
Br
18, Z:E= 3: 1
Intensity
0.30
0.25
0.20
0.15
0.10
0.05
0
0.31
1.38
0.43
2.09
0.38
0.99
1.00
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
Chemical Shift (ppm)


169.5068
168.1433
153.9468
138.7440
135.7108
133.3045
133.1223
133.0202
132.6556
129.1192
128.1130
127.9526
127.1359
127.0266
95.2575
77.4735
77.1600
76.8392
51.2679
50.9398
39.9515
6.2283
N
NH
O
O
CH3
Br
18, Z:E= 3: 1
Intensity
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
180
160
140
120
100
80
60
40
20
Chemical Shift (ppm)

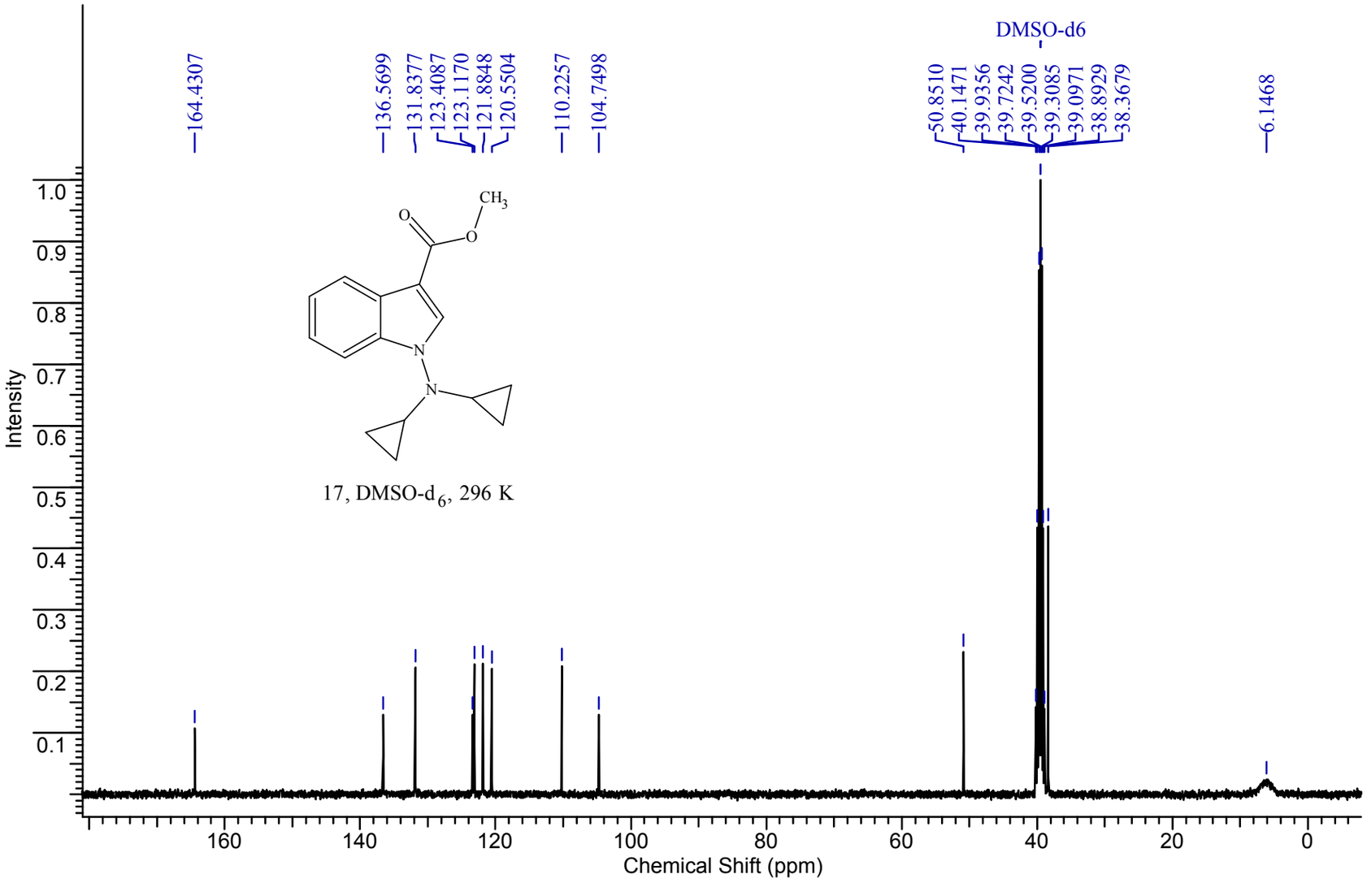

Chloroform-d
7.6719
7.6520
7.5956
7.5658
7.3450
7.3264
7.2600
7.2383
7.1784
7.1757
5.3696
5.3399
3.6478
2.2094
2.2002
2.1934
2.1854
2.1754
2.1587
0.5600
0.5433
0.5303
0.5139
Chloroform-d
7.6719
7.6520
7.5956
7.5658
7.3637
7.3614
7.3450
7.3264
7.3241
7.2600
7.2421
7.2383
7.1986
7.1944
7.1784
7.1757
7.1605
Intensity
Chemical Shift (ppm)
0.97
1.01
0.99
1.41
1.07
1.01
1.41
1.00
3.12
2.04
8.89
Chemical Shift (ppm)
O
N
NH
O
CH3
Br
18-E

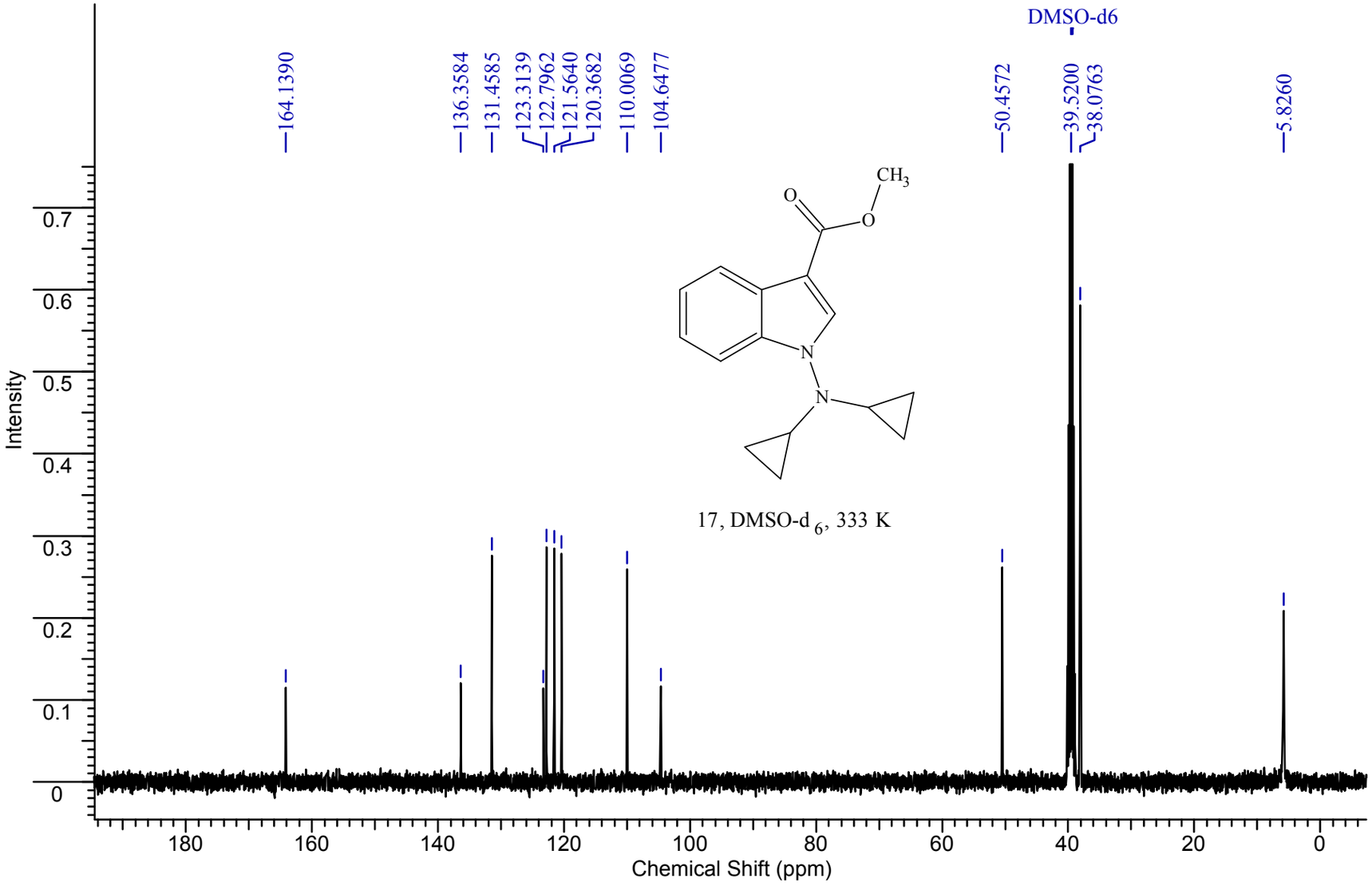

Chloroform-d
168.1288
148.4271
135.7180
133.2973
133.1150
129.1119
127.9526
126.1880
98.5824
77.4808
77.1600
76.8465
51.2533
39.9515
39.8640
6.2866
O
N
NH
O
CH3
Br
18-E
Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)


Chloroform-d
8.1573
8.1436
8.1283
7.3950
7.3817
7.3733
7.2600
7.2501
7.2379
7.2283
3.9285
2.9671
2.9580
2.9450
2.9347
2.9210
0.6241
0.5612
Chloroform-d
8.1638
8.1573
8.1436
8.1310
8.1283
7.3950
7.3817
7.3733
7.2631
7.2600
7.2501
7.2379
7.2283
Intensity
1.96
1.00
2.28
Chemical Shift (ppm)
17
1.96
2.28
3.01
2.00
8.00
Chemical Shift (ppm)

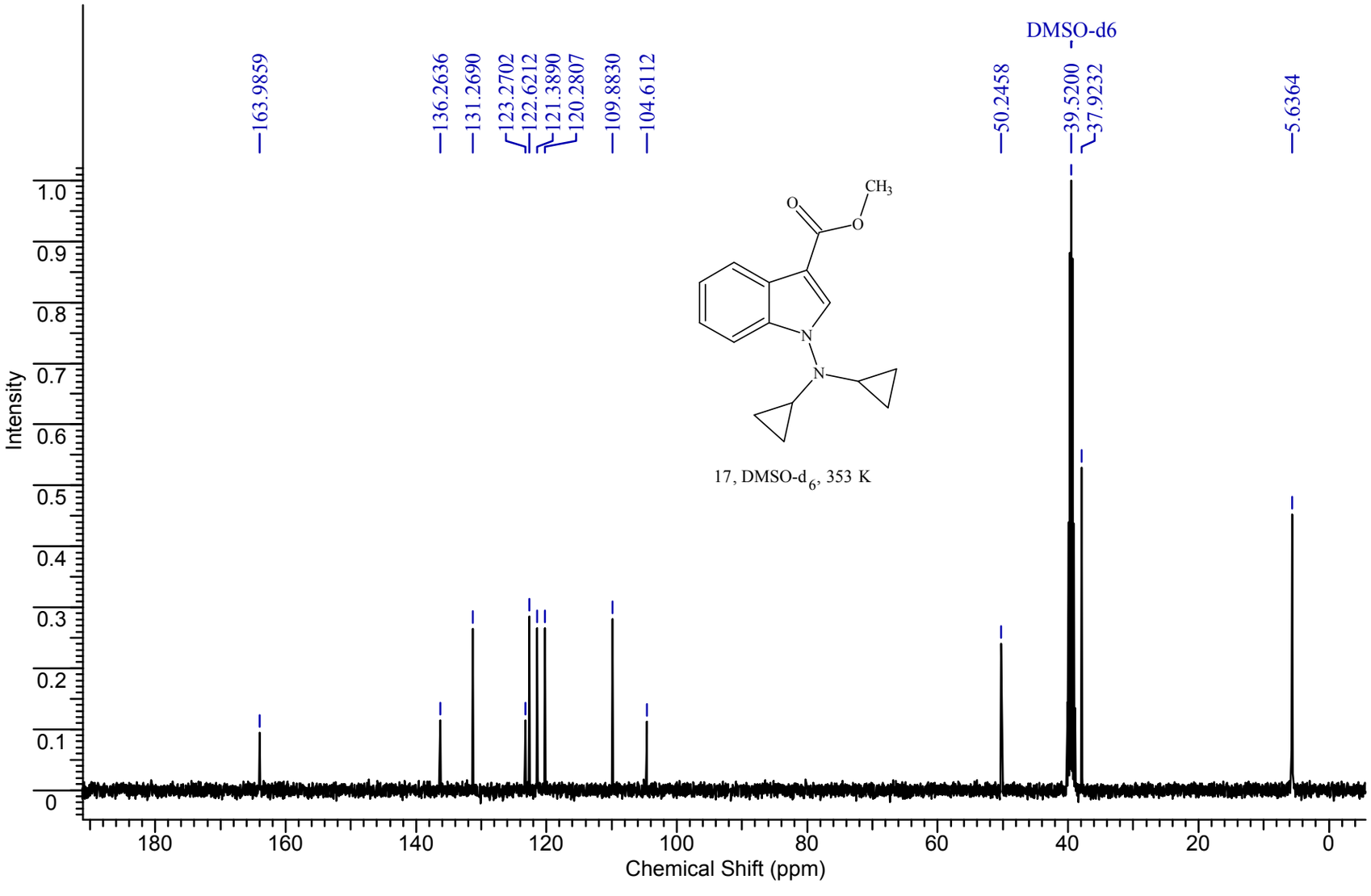

Chloroform-d
165.5913
136.8628
130.7234
124.1610
123.1329
122.1267
121.5361
110.2780
105.9323
77.4808
77.1600
76.8465
51.1585
39.0546
6.6585
Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)
O
O
CH3
N
N

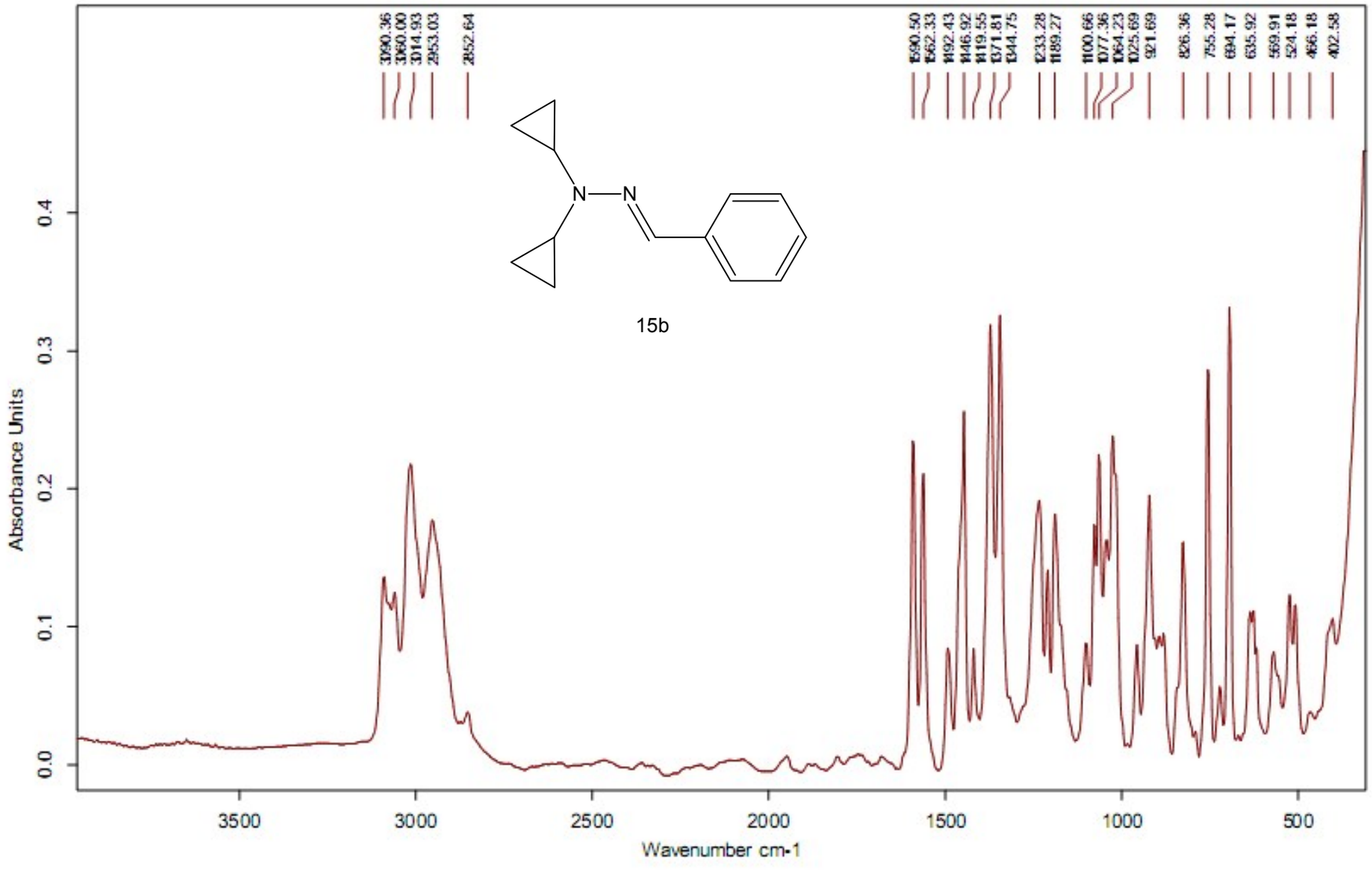
17


DMSO-d6
164.4307
136.5699
131.8377
123.4087
123.1170
121.8848
120.5504
110.2257
104.7498
50.8510
40.1471
39.9356
39.7242
39.5200
39.3085
39.0971
38.8929
38.3679
6.1468
CH3
O
O
N
N
17, DMSO-d6, 296 K
Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

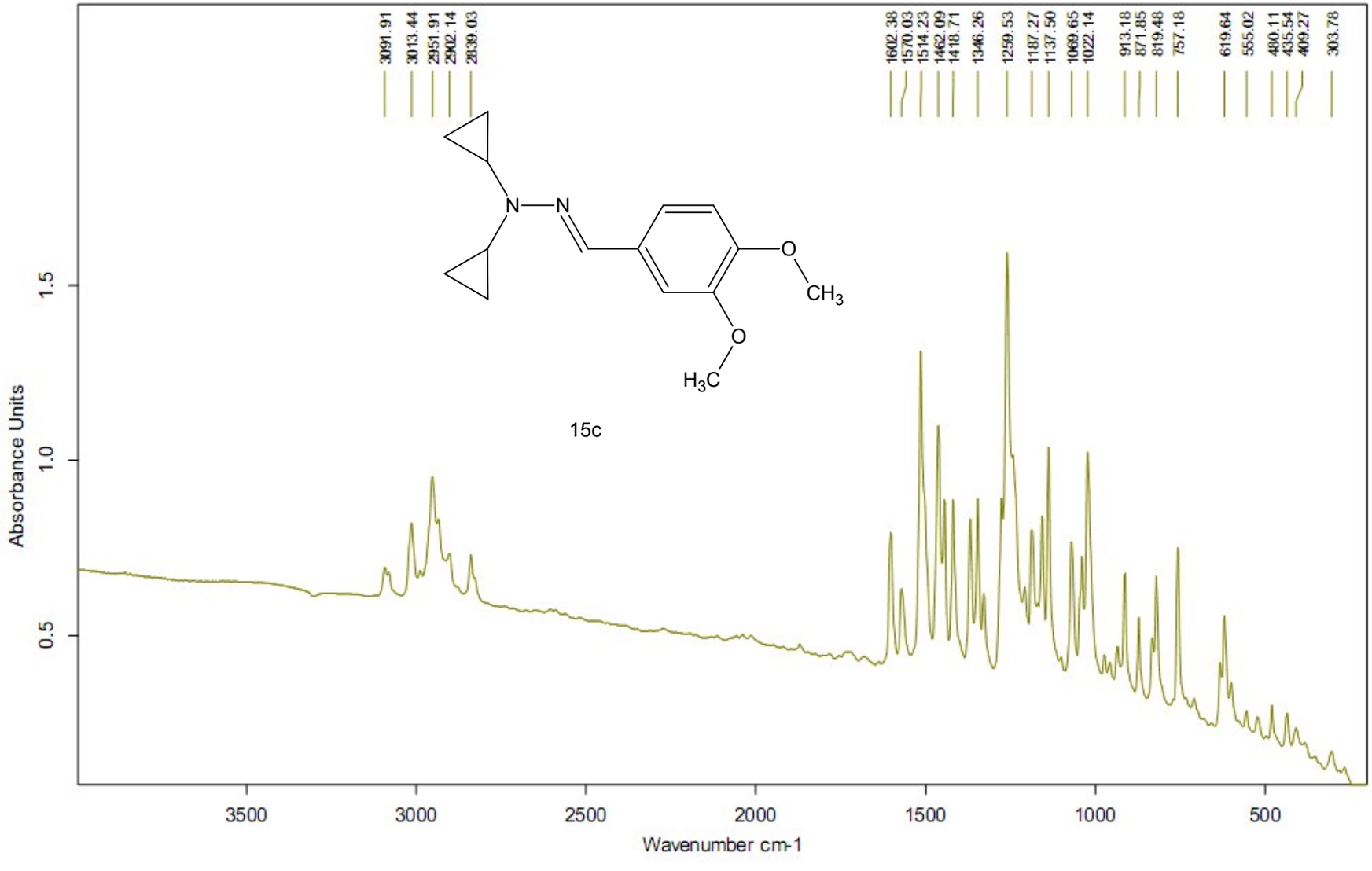


17, DMSO-d $_6$, 333 K

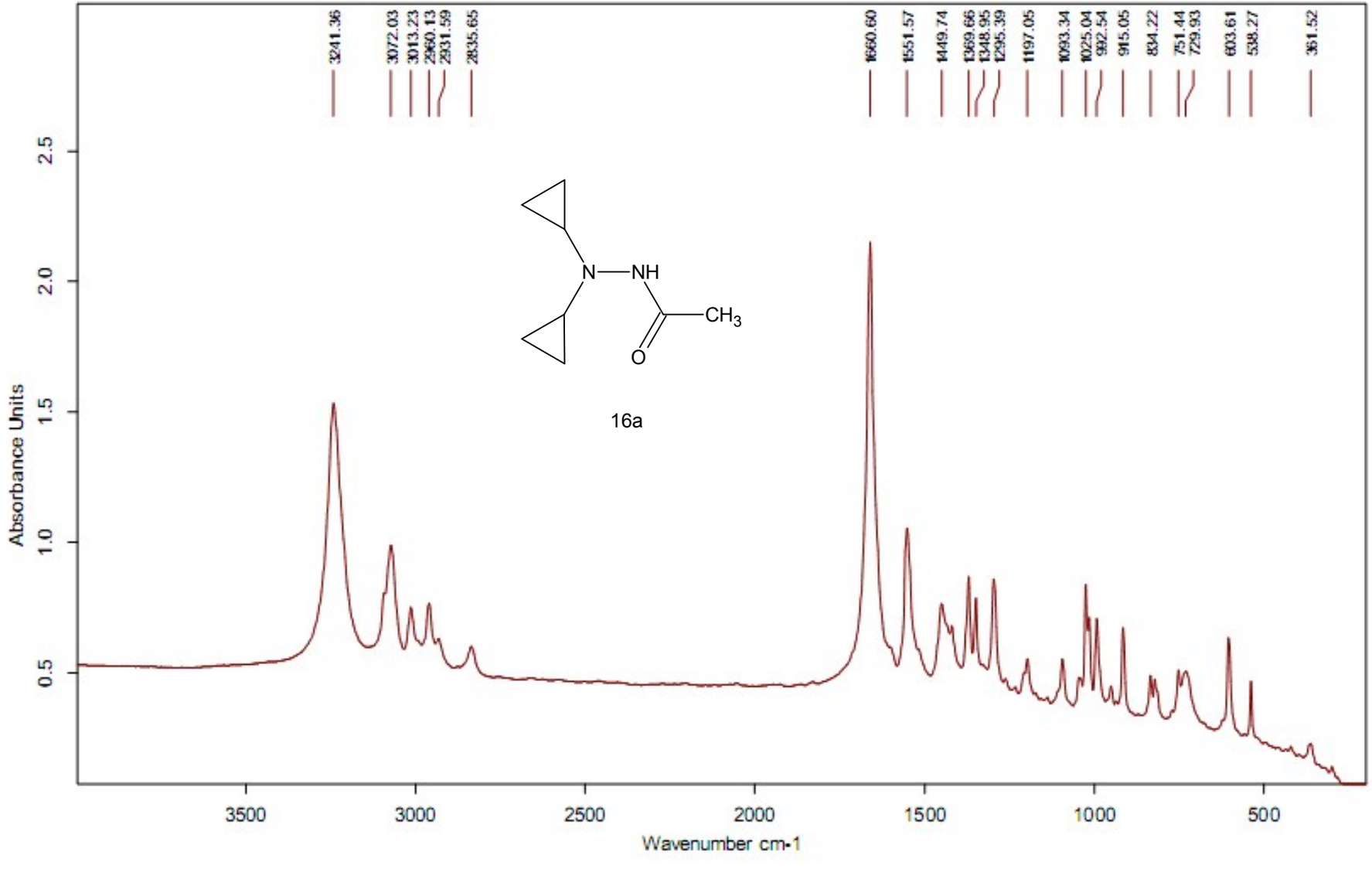

DMSO-d6
163.9859
136.2636
131.2690
123.2702
122.6212
121.3890
120.2807
109.8830
104.6112
50.2458
39.5200
37.9232
5.6364
O
O
CH3
N
N
17, DMSO-d6, 353 K
Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


3090.36
3060.00
3014.93
2953.03
2852.64
1590.50
1562.33
1492.43
1446.92
1419.55
1371.81
1344.75
1233.28
1189.27
1100.66
1077.36
1064.23
1025.69
921.69
826.36
755.28
694.17
635.92
569.91
524.18
466.18
402.58
N
N
0.0
0.1
0.2
0.3
0.4
Absorbance Units
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

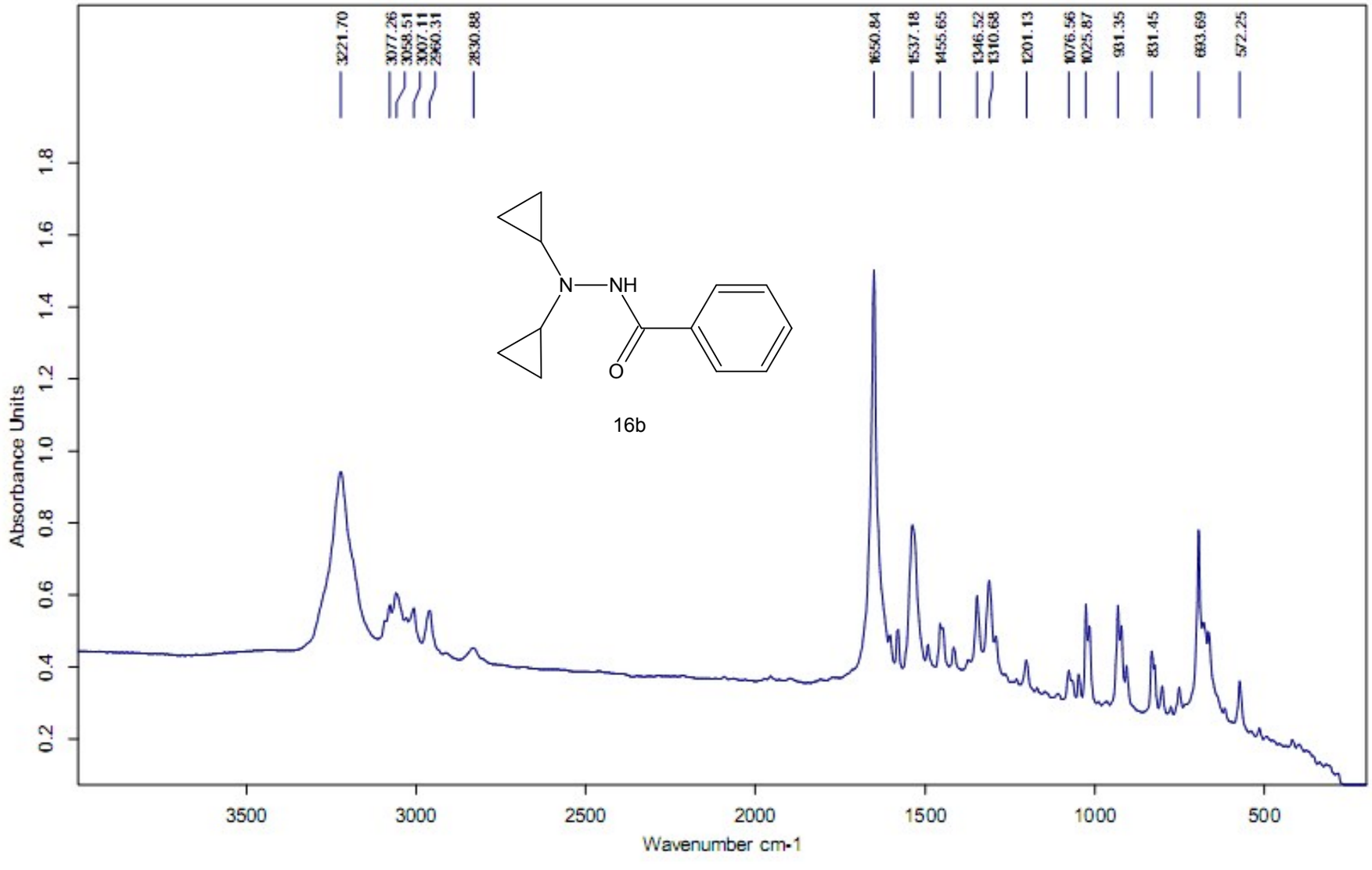
15b


3091.91
3013.44
2951.91
2902.14
2839.03
1602.38
1570.03
1514.23
1462.09
1418.71
1346.26
1259.53
1187.27
1137.50
1069.65
1022.14
913.18
871.85
819.48
757.18
619.64
555.02
480.11
435.54
409.27
303.78
N
N
O
CH3
O
H3C
Absorbance Units
0.5
1.0
1.5
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

15c


3241.36
3072.03
3013.23
2960.13
2931.59
2835.65
1660.60
1551.57
1449.74
1369.66
1348.95
1295.39
1197.05
1093.34
1025.04
992.54
915.05
834.22
751.44
729.93
603.61
538.27
361.52
N
NH
CH3
O
Absorbance Units
0.5
1.0
1.5
2.0
2.5
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

16a


3221.70
3077.26
3058.51
3007.11
2960.31
2830.88
1650.84
1537.18
1455.65
1346.52
1310.68
1201.13
1076.56
1025.87
931.35
831.45
683.69
572.25
N
NH
O
Absorbance Units
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

16b