Supporting Information for:

Ruthenium-Catalyzed Hydroarylation of Methylenecyclopropanes: Mild C–H Bond Functionalization with Conservation of Cyclopropane Rings

Sergei I. Kozhushkov, Dmitry S. Yufit, and Lutz Ackermann*

Institut für Organische und Biomolekulare Chemie der Georg-August-Universität Göttingen, Tammannstrasse 2, 37077 Göttingen (Germany)

Department of Chemistry, University of Durham, Durham, South Rd., DH1 3LE (UK)

Lutz.Ackermann@chemie.uni-goettingen.de

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Crystal Structure Analysis: Crystals suitable for X-ray diffractometry of compounds **13b** and **14** were obtained by slow evaporation of their solutions in hexane/Et_2O, crystals of compound **13a** –from MeOH/H_2O. The single crystal X-ray data for compounds **13a**,**b** and **14** were collected on a Bruker SMART-CCD 6000 diffractometer (ω-scan, 0.3°/frame) at 120.0(2)K using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). All structures were solved by direct method and refined by full-matrix least squares on F^2 for all data using SHELXTL software. All non-hydrogen atoms were refined with anisotropic displacement parameters, H-atoms were located on the difference map and refined isotropically.[6]

Crystal data for 13a: $C_{17}H_{17}N$ (M = 235.32), monoclinic, space group C 2/c, a = 26.4525(8), b = 7.1388(2), c = 14.1311(5) Å, β = 97.23(1)°, V = 2647.3(1) Å^3, F(000) = 1008, Z = 8, D_c = 1.181 mg m^{-3}, μ = 0.07 mm^{-1}. 15667 reflections (1.55 ≤ θ ≤ 29.0°) were collected yielding 3521 unique data (R_{merg} = 0.082). Final $wR_2(F^2)$ = 0.1496 for all data (231 refined parameters), conventional $R(F)$ = 0.0483 for 2302 reflections with I ≥ 2σ, GOF = 1.002.

Crystal data for 13b: $C_{18}H_{19}NO$ (M = 265.34), monoclinic, space group P 2_1/n, a = 9.5688(3), b = 14.4070(5), c = 10.4322(4) Å, β = 90.2170(10), V = 1438.15(9) Å^3, F(000) =

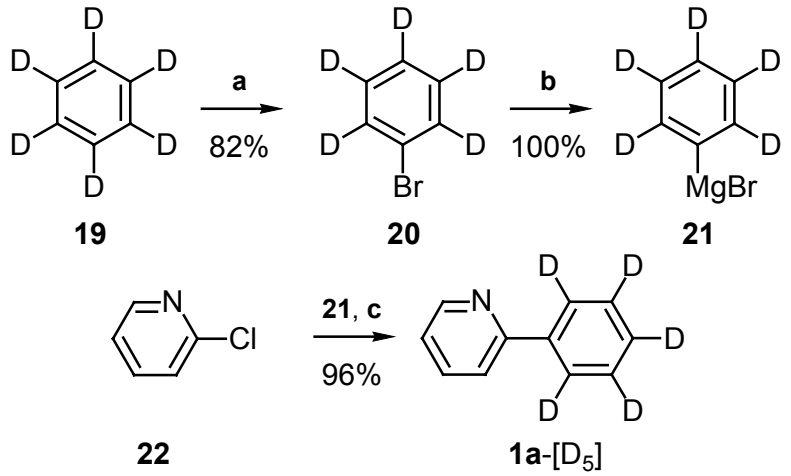
568, Z = 4, D_c = 1.225 mg m^{-3}, μ = 0.075 mm^{-1}. 16491 reflections (2.41 ≤ θ ≤ 28.0°) were collected yielding 3486 unique data (R_{merg} = 0.0558. Final $wR_2(F^2)$ = 0.0756 for all data (257 refined parameters), conventional $R(F)$ = 0.0366 for 3486 reflections with I ≥ 2σ, GOF = 1.012.

Crystal data for 14: $C_{23}H_{25}N$ (M = 315.44), monoclinic, space group C 2/c, a = 26.601(2), b = 7.0525(5), c = 22.606(1) Å, β = 121.03(1)°, V = 3634.0(4) Å^3, F(000) = 1360, Z = 8, D_c = 1.153 mg m^{-3}, μ = 0.07 mm^{-1}. 17592 reflections (1.79 ≤ θ ≤ 25.99°) were collected yielding 3568 unique data (R_{merg} = 0.131). Final $wR_2(F^2)$ = 0.1496 for all data (317 refined parameters), conventional $R(F)$ = 0.0547 for 2143 reflections with I ≥ 2σ, GOF = 0.980.

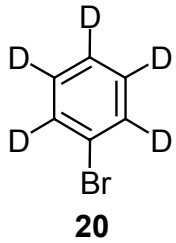
Molecules of **13a**,**b** and **14** do not contain any abnormal bond lengths. Short intramolecular C–H···N contacts between tertiary hydrogen atoms of bicyclopropyl moieties and nitrogen atoms of pyridine rings, which might be regarded as weak hydrogen bonds, were found in all molecules (2.543 in **13a** , 2.716 in **13b**, 2.447 and 2.704 Å in **14**, respectively). The conformations of these molecules in the crystals is a result of energetic compromises between these C–H···N closecontacts, conjugation effects, intramolecular van der Waals interactions between hydrogen atoms and crystal packing effects. Thus, the angles between planes of the pyridine and the benzene moieties in more sterically congested **13b** (79.4°) and **14** (71.7°) are bigger than in compound **13a** with just one bicyclopropyl fragment (55.1°), and the same holds true, but in less extent, for the angles between planes of the benzene ring and the adjacent three-membered ring of the bicyclopropyl core in **13b** (122.6°), in **14** (123.8 and 120.3°) and in **13a** (118.4°). The bicyclopropyl moieties in both compounds adopts typical[7] *gauche* (*synclinal*) conformation with dihedral angles between each two neighboring cyclopropanes of φ = 56.9 and 50.5° (**14**) or φ = –60.1° (**13a**) and –52.7° (**13b**). Broadening of methylene carbons signals in ^{13}C NMR spectrum of the compound **14** (see below) indicates the increased rotation barrier for bicyclopropyl moieties in the solution as well. In all crystal structures the molecules are linked by a number of C–H···π interactions between aromatic rings and various C–H fragments with the shortest C–H···C distances of 2.764, 2.941 and 2.779 Å in **13a**, **13b** and **14**, respectively.

Synthetic Procedures and Characterization Data. General aspects: 2-Phenylmethylenecyclopropane (**2**),[1] bicyclopropylidene (**12**),[2] methylenespiropentane (**23**),[3] and $[RuCl_2(cod)]_n$[4] were prepared according to previously published procedures. 2-(Pentadeuteriophenyl)pyridine (**1a**-[D_5]) was synthesized from C_6D_6 as indicated below adopting previously published procedures.[5] All other chemicals were used as commercially available. All operations in anhydrous solvents were performed under argon in flame-dried glassware. THF and 1,4-dioxane were dried by distillation from sodium benzophenone ketyl, NMP and DMF –from CaH_2. Organic extracts were dried over $MgSO_4$. TLC analyses were performed on precoated sheets, 0.25 mm Sil G/UV_{254} (Macherey-Nagel). Silica gel grade 60 (230–400 mesh) (Merck) was used for column chromatography. NMR spectra of solutions in $CDCl_3$ were recorded on a Bruker AM 250 (250 MHz for ^1H and 62.9 MHz for ^{13}C NMR) instrument. Multiplicities were determined by DEPT (Distortionless Enhancement by Polarization Transfer) measurements. Chemical shifts refer to $\delta_{TMS} = 0.00$ according to the chemical shifts of residual $CHCl_3$ signals.

Synthesis of 2-(pentadeuteriophenyl)pyridine (1a-[D_5]).



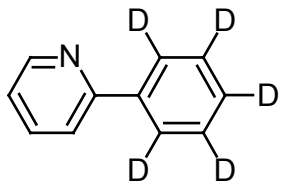
Scheme 1. Synthesis of 2-(pentadeuteriophenyl)pyridine (**1a**-[D_5]). Reagents and conditions: a) $NaBrO_3$, H_2SO_4, H_2O, 0–20 °C, 12 h; b) Mg, THF, 20–65 °C, 2 h; c) $Pd(dba)_2$ (5 mol%), dppf (5 mol%), THF, –40 to 20 °C, 12 h.



20

1-Bromopentadeuteriobenzene (20) was prepared adopting a published procedure[5a] and using $NaBrO_3$ instead of $KBrO_3$. To a vigorously stirred solution of sulfuric acid (16.65 g, 9.05 mL) in H_2O (33.3 mL), deuteriobenzene (**19**) (4.21 g, 4.43 mL, 50 mmol) was added in one portion

at 0 °C. Thereafter, $NaBrO_3$ (8.299 g, 55.0 mmol) was added in two portions with an interval of 1 h at the same temperature. The reaction mixture was stirred for an additional 10 h at ambient temperature, poured into ice-cold water (100 mL) and extracted with *n*-pentane (3 × 40 mL). The combined extracts were washed with ice-cold water (2 × 50 mL), sat. aq. $NaHCO_3$ solution (2 × 50 mL), brine (40 mL), and dried. *n*-Pentane was carefully evaporated through a 40 × 2-cm column packed with glass helices, and the residue was "bulb-to-bulb" distilled at 45 °C (0.1 Torr) into a cold (–78 °C) trap to give 6.614 g (82%) of pure **20** as a colorless liquid. ^{1}H NMR (250 MHz, $CDCl_3$): no signals; ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 131.0 (t, *J* = 25.3 Hz, 2 CD), 129.4 (t, *J* = 24.5 Hz, 2 CD), 126.3 (t, *J* = 24.5 Hz, CD), 122.2 ppm (CBr).

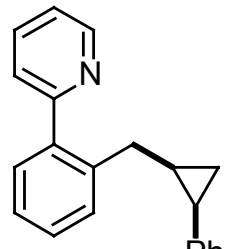


1a-[D_5]

2-(Pentadeuteriophenyl)pyridine (1a-[D_5]):[5b] Grignard reagent **21** was prepared from **20** (6.0 g, 37.03 mmol) and magnesium turnings (960 mg, 40 mmol) in anhydrous THF (30 mL) in virtually quantitative yield (20–65 °C, 2 h). A second flask was charged with $Pd(dba)_2$[8] (725 mg, 1.25 mmol, 5 mol%), dppf (675 mg, 1.25 mmol, 5 mol%), anhydrous THF (75 mL), and the resulting mixture was stirred at ambient temperature for 20 min. 2-Chloropyridine (**22**) (2.838 g, 2.35 mL, 25.0 mmol) was added in one portion, the reaction mixture was stirred at ambient temperature for 0.5 h and cooled to –40 °C. Under stirring, the Grignard reagent **21** was added dropwise via syringe at this temperature over a period of 1 h, the reaction mixture was stirred for an additional 11 h at ambient temperature, poured into ice-cold mixture of sat. aq. NH_4Cl solution (100 mL) with sat. aq. NH_4OH solution (10 mL) and extracted with diethyl ether (3 × 60 mL). The combined extracts were washed with brine (50 mL), dried and concentrated under reduced pressure. Column chromatography of the residue (6.650 g) on silica gel (180 g of silica gel, column 35 × 4 cm, hexane/Et_2O 5:2, R_f = 0.28) afforded **1a**-[D_5] (3.851 g, 96%) as a slightly yellow oil, ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.70 (ddd, *J* = 0.3, 1.4, 4.8 Hz, 1 H; Py-H), 7.80–7.71 (m, 2 H; Py-H), 7.25–7.21 ppm (m, 1 H; Py-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 156.9 (C), 149.2 (CH), 138.8 (C), 136.3 (CH), 128.0 (t, *J* = 24.0 Hz, CD), 127.8 (t, *J* = 24.5 Hz, 2 CD), 126.1 (t, *J* = 24.5 Hz, 2 CD), 121.7 (CH), 120.1 ppm (CH); HRMS calcd for $C_{11}H_4D_5N$: $(M + 1)^+$ = 161.1127; found: 161.1122.

Ruthenium-catalyzed hydroarylation of methylenecyclopropanes 2 and 12 with 2-phenylpyridines 1a, 1b, and 1a-[D_5] General procedure (GP) 1

A flame-dried 10-mL Schlenk flask was cooled under argon and charged with respective arene derivative **1a**,**b**, or **1a**-[D_5] (1–2 mmol) in anhydrous dioxane (3 mL), $[RuCl_2(cod)]_n$ (5 mol%) and L (10 mol%). After stirring at ambient temperature for 0.5 h, alkene **2** or **14** was added in three equal portions (16, and 32 h), while the reaction mixture was stirred for 48 h at 120 °C. After cooling to ambient temperature, the reaction mixture was poured into sat. aq. $NaHCO_3$ solution (50 mL) and extracted with Et_2O (3 × 40 mL). The combined extracts were washed with brine (40 mL), dried and concentrated under reduced pressure. The products were isolated by column chromatography of the residue on silica gel (50 g of silica gel, column 25 × 2.5 cm, hexane/Et_2O 20:1→5:1 for **1a** or 20:1→5:2 for **1b**.



3a

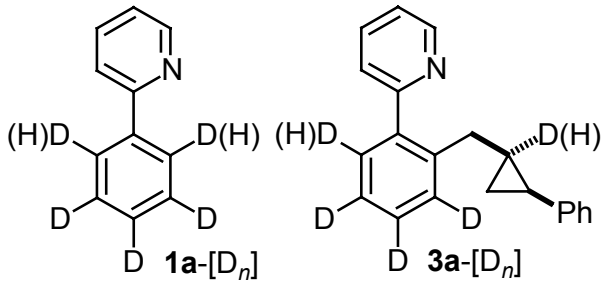
2-{[2-(*cis*-2-Phenylcyclopropyl)methyl]phenyl}pyridine (3a):

a) Column chromatography of the residue obtained from 2-phenylpyridine (**1a**), (225.0 mg, 1.45 mmol), **2** (566.2 mg, 596 µL, 4.35 mmol), $[RuCl_2(cod)]_n$ (20.3 mg, 72.5 µmol) and dicyclohexyl-(2',4',6'-triisopropylbiphenyl-2-yl)phosphane (**11**) (69.1 mg, 0.145 mmol) in anhydrous dioxane (3 mL) according to GP1 afforded recovered **1** (86.9 mg, 39%, R_f = 0.16 in hexane/Et_2O 5:1) and **3** (219.4 mg, 53%, R_f = 0.10 in hexane/Et_2O 5:1) as slightly yellow oils; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.65 (ddd, *J* = 0.8, 1.5, 4.8 Hz, 1 H; Py-H), 7.70 (td, *J* = 1.8, 7.8 Hz, 1 H; Ar-H), 7.32–7.14 (m, 9 H; Ar-H), 7.06 (d, *J* = 1.8, 4.3 Hz, 2 H; Ph-H), 2.56 (dd, *J* = 6.0, 15.0 Hz, 1 H; CH_2), 2.32 (dd, *J* = 8.3, 15.0 Hz, 1 H; CH_2), 2.12 (ddd, *J* = 5.8, 8.5, 8.8 Hz, 1 H; cPr-CH), 1.31–1.18 (m, 1 H; cPr-CH), 0.89 (ddd, *J* = 5.3, 8.5, 8.5 Hz, 1 H; cPr-CH_2), 0.59 ppm (ddd, *J* = 5.3, 5.8, 8.5 Hz, 1 H; cPr-CH_2); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 160.1 (C), 148.9 (CH), 140.2 (C), 139.8 (C), 139.0 (C), 135.9 (CH), 129.6 (CH), 129.5 (CH), 128.7 (2 CH), 128.1 (CH), 127.7 (2 CH), 125.7 (CH), 125.5 (CH), 124.1 (CH), 121.4 (CH), 31.1 (CH_2), 21.4 (CH), 20.1 (CH), 9.6 ppm (CH_2); HRMS calcd for $C_{21}H_{19}N$: $(M + 1)^+$ = 286.1491; found: 286.1488.

b) Column chromatography of the residue obtained from **1a** (182.0 mg, 1.173 mmol), **2** (458.1 mg, 482.2 µL, 3.519 mmol), $[RuCl_2(cod)]_n$ (16.4 mg, 58.6 µmol) and P(*o*-biphenyl)(*t*Bu)$_2$ (**10**) (35.0 mg, 0.1173 mmol) in anhydrous dioxane (3 mL) according to GP1 afforded recovered **1a** (96.5 mg, 53%) and **3a** (152.8 mg, 46%) as slightly yellow oils.

c) Column chromatography of the residue obtained from **1a** (303.9 mg, 1.958 mmol), **2** (382.3

mg, 402 µL, 2.937 mmol), $[RuCl_2(cod)]_n$ (27.8 mg, 100 µmol) and dicyclohexyl-(2',4',6'-triisopropylbiphenyl-2-yl)phosphane (**11**) (95.3 mg, 0.2 mmol) in anhydrous NMP (3 mL) according to GP1 afforded recovered **1a** (121.7.8 mg, 40%) and **3a** (301.5 mg, 54%) as slightly yellow oils.

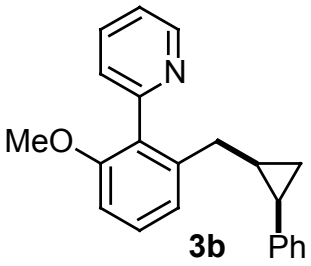


Oligodeuterio-2-{[2-(*cis*-2-phenylcyclopropyl)methyl]phenyl}pyridine (3a-[D_n]) and 1a-[D_4]: a) Column chromatography of the residue obtained from **1a**-[D_5] (189.6 mg, 1.183 mmol), **2** (616.1 mg, 648.5 µL, 4.733 mmol), $[RuCl_2(cod)]_n$ (16.5 mg, 59.1 µmol) and P(*o*-biphenyl)(*t*Bu)$_2$ (**10**) (33.5 mg, 0.118 mmol) in anhydrous dioxane (3 mL) according to GP1 (48 h heating) afforded **1a**-[D_4] (45.1 mg, 24%, R_f = 0.16 in hexane/Et_2O 5:1) and **3a**-[D_n] (221.1 mg, 65%, R_f = 0.10 in hexane/Et_2O 5:1) as slightly yellow oils. **1a**-[D_4]: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.70 (dt, *J* = 1.3, 4.8 Hz, 1 H; Py-H), 7.99 (s, 1 H; Ph-H), 7.80–7.71 (m, 2 H; Py-H), 7.25–7.20 ppm (m, 1 H; Py-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 157.4 (C), 149.6 (CH), 139.2 (C), 136.7 (CH), 128.7 (t, *J* = 24.5 Hz, CD), 128.3 (t, *J* = 24.5 Hz, CD), 128.1 (t, *J* = 24.5 Hz, CD), 126.7 (CH), 126.1 (t, *J* = 24.5 Hz, 2 CD), 122.0 (CH), 120.5 ppm (CH); MS (ESI): *m/z*: 160.2 (100) $[M+1]^+$. **3a**-[D_n]: MS (ESI): mixture of three components: **3a**-[D_5] ($C_{21}H_{14}D_5N$, *m/z*: 291.19, $[M+1]^+$, 47%), **3a**-[D_4] ($C_{21}H_{15}D_4N$, *m/z*: 290.18, $[M+1]^+$, 36%), and **3**-[D_3] ($C_{21}H_{16}D_3N$, *m/z*: 291.19, $[M+1]^+$, 17%). This is in line with the relative intensity of the resonance of cyclopropane CH moiety in the ^{1}H NMR spectrum. ^{1}H NMR (250 MHz, $CDCl_3$; **3a**-[D_n]): δ = 8.65 (dm, *J* = 4.8 Hz, 1 H; Py-H), 7.70 (td, *J* = 1.8, 7.8 Hz, 1 H; Ar-H), 7.32–7.14 (m, ca. 5.2 H; Ar-H), 7.06 (d, *J* = 1.8, 4.3 Hz, 2 H; Ph-H), 2.56 (dm, *J* = 15.0 Hz, 1 H; CH_2), 2.32 (dm, *J* = 15.0 Hz, 1 H; CH_2), 2.17–2.08 (m, 1 H; cPr-CH), 1.31–1.18 (m, ca. 0.5 H; cPr-CH and cPr-CD), 0.95–0.85 (m, Hz, 1 H; cPr-CH_2), 0.63–0.57 ppm (m, 1 H; cPr-CH_2); ^{13}C NMR (62.9 MHz, $CDCl_3$; major component **3a**-[D_5]): δ = 160.0 (C), 148.9 (CH), 140.0 (C), 139.7 (C), 138.9 (C), 135.9 (CH), 128.8 (2 CH), 127.6 (2 CH), 125.4 (CH), 124.0 (CH), 121.4 (CH), 30.8 (CH_2), 21.2 (CH), 19.8 (m, CD), 9.4 ppm (CH_2). Triplets of four CD fragment are overlapped between 129 and 126 ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$; clearly observable signals of the second major component **3**-[D_4]): δ = 31.0 (CH_2), 21.3 (CH), 20.1 (CH), 9.5 ppm (CH_2).

b) Column chromatography of the residue obtained from **1a**-[D_5] (239.2 mg, 1.493 mmol), **2**

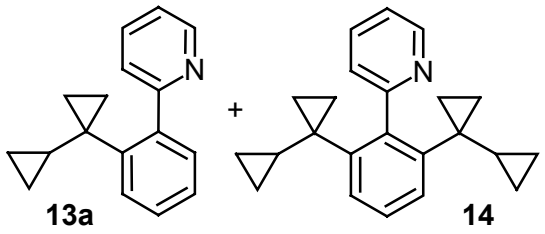
(291.5 mg, 306.8 μL, 2.239 mmol), $[RuCl_2(cod)]_n$ (20.9 mg, 74.6 μmol) and dicyclohexyl-(2',4',6'-triisopropylbiphenyl-2-yl)phosphane (**11**) (71.2 mg, 0.149 mmol) in anhydrous dioxane (3 mL) according to GP1 (12 h heating) afforded **1a**-$[D_n]$ (132.8 mg, 56%) and **3a**-$[D_n]$ (108.5 mg, 25%) as slightly yellow oils. In this experiment, however, **1a**-$[D_n]$ contained only 0.46 H in both *ortho*-positions and, according to its MS (ESI) spectra, was a mixture of **1a**-$[D_5]$ (54%), **1a**-$[D_4]$ (34%) and **1a**-$[D_3]$ (12%).

c) Column chromatography of the residue obtained from **1a** (237.5 mg, 1.530 mmol), **2** (597.6 mg, 529.0 μL, 4.591 mmol), $[RuCl_2(cod)]_n$ (21.4 mg, 76.5 μmol) and dicyclohexyl-(2',4',6'-triisopropylbiphenyl-2-yl)phosphane (**11**) (72.9 mg, 0.153 mmol) in anhydrous DMF-$[D_7]$ according to GP1 (48 h heating) afforded **1a** (71.1 mg, 30%) and **3a** (236.0 mg, 54%) as slightly yellow oils. Neither **1a** nor **3a** contained deuterium label.



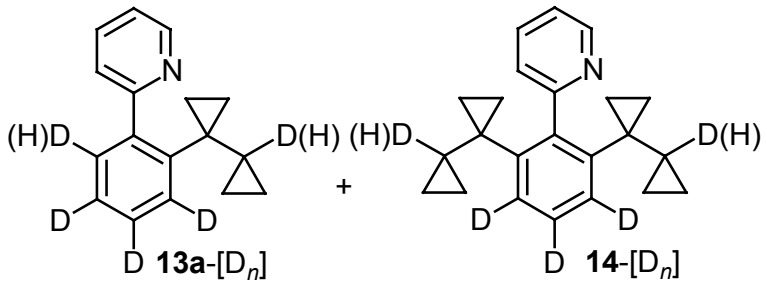
3b

2-{[2-Methoxy-6-(*cis*-2-phenylcyclopropyl)methyl]phenyl}-pyridine (3b): Column chromatography of the residue obtained from 2-(2-methoxyphenyl)pyridine (**1b**), (299.4 mg, 1.616 mmol), **2** (315.6 mg, 332.2 μL, 2.425 mmol), $[RuCl_2(cod)]_n$ (22.6 mg, 80.8 μmol) and dicyclohexyl-(2',4',6'-triisopropylbiphenyl-2-yl)phosphane (**11**) (77.0 mg, 0.162 mmol) in anhydrous dioxane (3 mL) according to GP1 afforded recovered **1b** (53.9 mg, 18%, R_f = 0.15 in hexane/Et_2O 5:2) and **3a** (399.5 mg, 78%, R_f = 0.10 in hexane/Et_2O 5:2) as slightly yellow oils; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.68 (dq, *J* = 0.9, 5.0 Hz, 1 H; Py-H), 7.69 (td, *J* = 1.8, 7.6 Hz, 1 H; Py-H), 7.33–7.08 (m, 6 H; Ar-H), 6.99 (dm, *J* = 8.0 Hz, 2 H; Ph-H), 6.81 (dd, *J* = 1.3, 8.8 Hz, 2 H; Ph-H), 2.28 (dd, *J* = 6.0, 15.0 Hz, 1 H; CH_2), 2.09 (ddd, *J* = 6.1, 8.5, 8.5 Hz, 1 H; cPr-CH), 1.93 (dd, *J* = 8.8, 15.0 Hz, 1 H; CH_2), 1.29–1.18 (m, 1 H; cPr-CH), 0.88 (ddd, *J* = 6.0, 7.5, 8.5 Hz, 1 H; cPr-CH_2), 0.56 ppm (q, *J* = 6.0 Hz, 1 H; cPr-CH_2); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 156.9 (C), 156.7 (C), 149.1 (CH), 141.8 (C), 138.9 (C), 135.5 (CH), 129.4 (C), 128.7 (CH), 128.6 (2 CH), 127.6 (2 CH), 121.5 (CH), 121.4 (CH), 108.3 (CH), 55.5 (OCH_3), 31.1 (CH_2), 21.3 (CH), 19.8 (CH), 9.5 ppm (CH_2); HRMS calcd for $C_{22}H_{21}NO$: $(M + 1)^+$ = 316.1623; found: 316.1618.



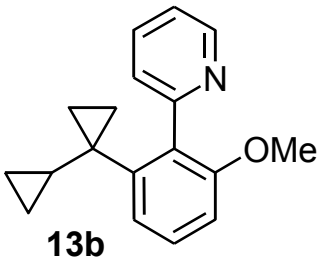
2-[(2-Bicyclopropyl-1-yl)phenyl]pyridine (13a) and 2-[2,6-bis(bicyclopropyl-1-yl)-phenyl]pyridine (14): a) Column chromatography of the residue obtained from **1a** (187.0 mg, 1.205 mmol), bicyclopropylidene (**12**) (289.6 mg, 339.2 μL, 3.615 mmol), $[RuCl_2(cod)]_n$ (16.9 mg, 60.2 μmol) and dicyclohexyl-(2',4',6'-triisopropylbiphenyl-2-yl)phosphane (**11**) (57.4 mg, 0.1205 mmol) according to GP1 (48 h heating) afforded **14** (226.8 mg, 60%, R_f = 0.30 in hexane/Et_2O 5:1) and **13a** (94.4 mg, 33%, R_f = 0.13 in hexane/Et_2O 5:1) as slightly yellow oils. Compounds **13a** and **14** solidified upon standing at –20 °C overnight. **13a**: colorless solid, m.p. 43–45 °C (MeOH/H_2O); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.69 (dq, *J* = 0.9, 4.8 Hz, 1 H; Py-H), 7.99 (dm, *J* = 8.3 Hz, 1 H; Ph-H), 7.72 (tm, *J* = 7.4 Hz, 1 H; Py-H), 7.57 (dm, *J* = 6.8 Hz, 1 H; Py-H), 7.51–7.21 (m, 4 H; Ar-H), 1.43–1.36 (m, 1 H; cPr-CH), 0.41–0.31 (m, 6 H; 3 cPr-CH_2), 0.09 ppm (q, *J* = 5.3 Hz, 2 H; cPr-CH_2); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 160.2 (C), 148.8 (CH), 143.8 (C), 141.3 (C), 135.2 (CH), 131.7 (CH), 129.8 (CH), 127.9 (CH), 126.1 (CH), 124.2 (CH), 121.3 (CH), 24.8 (C), 18.7 (CH), 11.6 (2 CH_2), 3.1 ppm (2 CH_2). **14**: colorless solid, m.p. 92 °C (hexane/Et_2O); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.70 (dq, *J* = 1.0, 4.8 Hz, 1 H; Py-H), 7.74 (td, *J* = 1.6, 7.8 Hz, 1 H; Py-H), 7.45 (dt, *J* = 1.0, 7.8 Hz, 1 H; Py-H), 7.30–7.25 (m, 4 H; Ar-H), 1.31–1.22 (m, 2 H; cPr-CH), 0.51–0.45 (m, 4 H; 2 cPr-CH_2), 0.23–0.14 (m, 8 H; 4 cPr-CH_2), –0.04 to –0.10 ppm (m, 4 H; 2 cPr-CH_2); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 159.5 (C), 148.2 (CH), 144.4 (2 C), 142.5 (C), 134.6 (CH), 129.8 (2 CH), 127.8 (CH), 126.2 (CH), 121.5 (CH), 25.5 (2 C), 18.3 (2 CH), 11.3 (broad, 2 CH_2), 10.3 (broad, 2 CH_2), 3.3 (broad, 2 CH_2), 3.0 ppm (broad, 2 CH_2). The structures of the compounds **13a** and **14** were proved by X-ray crystal structure analysis.[6]

b) Column chromatography of the residue obtained from **1a** (201.4 mg, 1.298 mmol), **12** (312.0 mg, 365.3 μL, 3.894 mmol), $[RuCl_2(cod)]_n$ (18.2 mg, 64.8 μmol) and P(*o*-biphenyl)(*t*Bu)$_2$ (**10**) (38.7 mg, 129.8 μmol) according to GP1 (48 h heating) afforded **14** (115.1 mg, 28%, R_f = 0.30 in hexane/Et_2O 5:1), recovered **1a** (18.1 mg, 9%, R_f = 0.16 in hexane/Et_2O 5:1) and **13a** (200.0 mg, 65%, R_f = 0.13) as slightly yellow oils.



Oligodeuterated 2-[(2-bicyclopropyl-1-yl)phenyl]-pyridine (5-[D$_n$]), 2-[2,6-bis(bicyclopropyl-1-yl)-phenyl]pyridine (6-[D$_n$]) and 2-(oligodeuteriophenyl)pyridine (1a-[D$_n$]): Column chromatography of the residue obtained from **1a**-[D_5] (228.1 mg, 1.423 mmol), **14** (456.2 mg, 534.2 µL, 5.694 mmol), [$RuCl_2$(cod)]$_n$ (19.9 mg, 71.1 µmol) and P(*o*-biphenyl)(*t*Bu)$_2$ (10) (42.5 mg, 142.3 µmol) according to GP1 (48 h heating) afforded **16**-[D_n] (137.2 mg, 30%, R_f = 0.30 in hexane/Et_2O 5:1), **1a**-[D_n] (18.1 mg, 8%, R_f = 0.16 in hexane/Et_2O 5:1) and **13a**-[D_n] (157.8 mg, 46%, R_f = 0.13 in hexane/Et_2O 5:1) as slightly yellow oils. **13a**-[D_n]: MS (ESI): mixture of three components, **13a**-[D_5] ($C_{17}H_{12}D_5N$, *m/z*: 241.1748, [*M*+1]$^+$, 62%), **13a**-[D_4] ($C_{17}H_{13}D_4N$, *m/z*: 240.1686, [*M*+1]$^+$, 33%), and **13a**-[D_3] ($C_{17}H_{14}D_3N$, *m/z*: 239.1623, [*M*+1]$^+$, 5%). This corresponds to the relative intensity of the resonance of cyclopropane CH moiety in the ^{1}H NMR spectrum. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.69 (dq, *J* = 0.8, 4.8 Hz, 1 H; Py-H), 8.00 (s, 0.06 H, Ar-H), 7.75 (td, *J* = 2.0, 7.8 Hz, 1 H; Py-H), 7.57 (dd, *J* = 1.3, 6.8 Hz, 1 H; Py-H), 7.25 (dd, *J* = 1.3, 7.5 Hz, 1 H; Py-H), 1.45–1.34 (m, ca. 0.4 H; cPr-CH and cPr-CD), 0.41–0.26 (m, 6 H; 3 cPr-CH_2), 0.11–0.06 ppm (m, 2 H; cPr-CH_2); ^{13}C NMR (62.9 MHz, $CDCl_3$; major component **13a**-[D_5]): δ = 160.2 (C), 148.7 (CH), 143.7 (C), 141.2 (C), 135.2 (CH), 131.8 (t, *J* = 18.8 Hz, CD), 129.1 (t, *J* = 20.0 Hz, CD), 127.5 (t, *J* = 20.0 Hz, CD), 125.8 (t, *J* = 20.0 Hz, CD), 124.2 (CH), 121.3 (CH), 24.6 (C), 18.3 (t, *J* = 24.5 Hz, CD), 11.6 (2 CH_2), 3.0 ppm (2 CH_2). ^{13}C NMR (62.9 MHz, $CDCl_3$; clearly observable signals of the second major component **13a**-[D_4]): δ = 24.7 (C), 18.7 (CH), 11.6 (2 CH_2), 3.1 ppm (2 CH_2). **14**-[D_n]: MS (ESI) spectrum of this compound disclosed this to be a mixture of three components, i. e. **14**-[D_5] ($C_{23}H_{20}D_5N$, *m/z*: 321.2383, [*M*+1]$^+$, 25%), **14**-[D_4] ($C_{23}H_{21}D_4N$, *m/z*: 320.3216, [*M*+1]$^+$, 49%), and **14**-[D_3] ($C_{13}H_{22}D_3N$, *m/z*: 319.2253, [*M*+1]$^+$, 26%). This is in line with the relative intensity of the signal of cyclopropane CH moiety in the ^{1}H NMR spectrum. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.70 (dq, *J* = 0.9, 4.8 Hz, 1 H; Py-H), 7.74 (td, *J* = 1.8, 7.8 Hz, 1 H; Py-H), 7.44 (d, *J* = 1.0, 7.8 Hz, 1 H; Py-H), 7.27 (td, *J* = 1.3, 5.0 Hz, 1 H; Py-H), 1.33–1.18 (m, ca. 1 H; cPr-CH and cPr-CD), 0.50–0.44 (m, 4 H; 2 cPr-CH_2), 0.22–0.07 (m, 8 H; 4 cPr-CH_2), –0.06 to –0.11 ppm (m, 4 H; 2 cPr-CH_2); ^{13}C

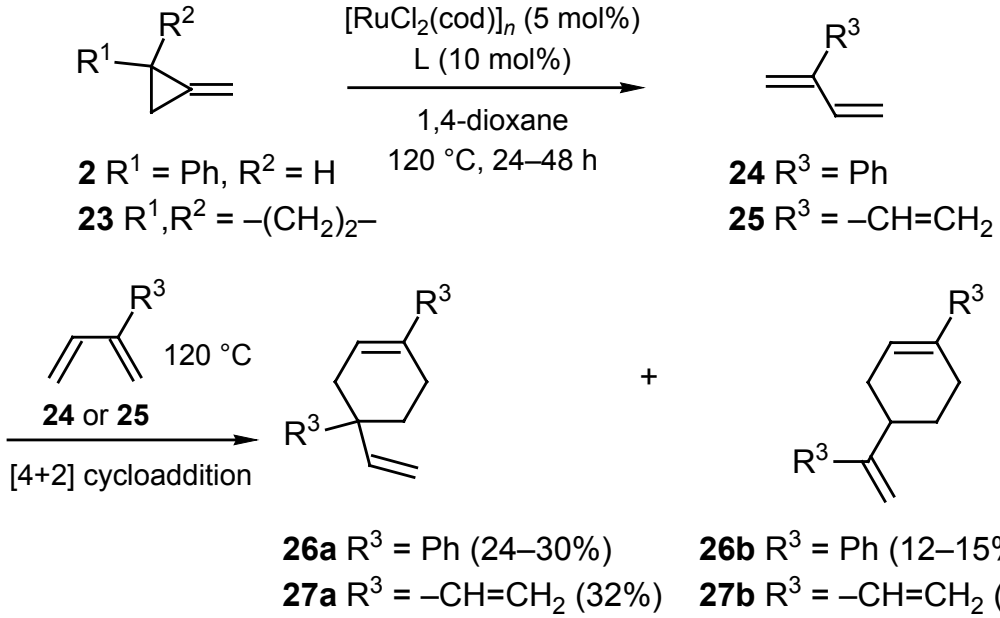
NMR (62.9 MHz, $CDCl_3$; major component **14**-[D_4]): δ = 159.4 (C), 148.1 (CH), 144.2 (2 C), 142.4 (C), 134.5 (CH), 129.3 (t, *J* = 23.8 Hz, 2 CD), 126.9 (t, *J* = 28.0 Hz, CD), 126.1 (CH), 121.4 (CH), 25.4 (C), 25.3 (C), 18.2 (CH), 17.8 (t, *J* = 24.5 Hz, CD), 11.3 (broad, 2 CH_2), 10.2 (broad, 2 CH_2), 3.2 (broad, 2 CH_2), 3.0 ppm (broad, 2 CH_2).



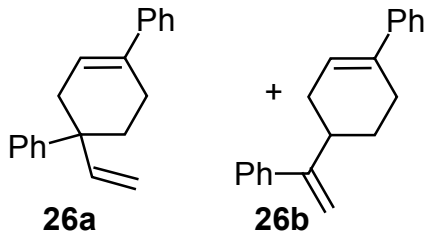
13b

2-[(2-Bicyclopropyl-1-yl)-6-methoxy-phenyl]pyridine (13b): Column chromatography of the residue obtained from 2-(2-methoxyphenyl)pyridine (**1b**), (281.3 mg, 1.519 mmol), **12** (182.5 mg, 213.7 μL, 2.278 mmol), $[RuCl_2(cod)]_n$ (21.3 mg, 75.9 μmol) and **11** (72.4 mg, 0.152 mmol) in anhydrous dioxane (3 mL) according to GP1 afforded **13b** (341.9 mg, 85%, R_f = 0.17 in hexane/Et_2O 5:2) as slightly yellow oil, which solidified upon standing at 0 °C °C overnight. **13b**: colorless solid, m.p. 96–98 °C (hexane/Et_2O); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.71 (ddd, *J* = 0.8, 1.8, 4.8 Hz, 1 H; Py-H), 7.73 (td, *J* = 1.8, 7.6 Hz, 1 H; Py-H), 7.34 (dd, *J* = 0.8, 8.8 Hz, 1 H; Py-H), 7.29–7.22 (m, 2 H; Ar-H), 7.00 (dd, *J* = 0.8, 7.8 Hz, 1 H; Py-H), 6.85 (dd, *J* = 0.8, 8.3 Hz, 1 H; Ar-H), 3.69 (s, 1 H; OMe), 0.47–0.49 (m ½ AA'BB', 2 H; cPr-CH_2), 0.28–0.22 (m ½ AA'BB', 2 H; cPr-CH_2), 0.20–0.16 (m ½ AA'BB', 2 H; cPr-CH_2), –0.02 to –0.08 (m ½ AA'BB', 2 H; cPr-CH_2); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 157.1 (C), 156.9 (C), 148.7 (CH), 145.9 (C), 135.0 (CH), 130.9 (C), 128.6 (CH), 125.7 (CH), 123.7 (CH), 121.4 (CH), 55.5 (OCH_3), 25.1 (C), 18.1 (CH), 10.6 (2 CH_2), 3.0 ppm (2 CH_2). The structures of the compound **13b** was proved by X-ray crystal structure analysis.[6]

Competitive ring opening reactions of 2-phenylmethylenecyclopropane (2) and methylenespiropentane (23) followed by Diels-Alder [4+2] cycloaddition.



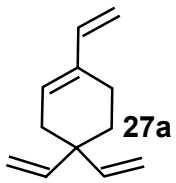
Scheme 2. Competitive reactions of 2-phenylmethylenecyclopropane (**2**) and methylenespiropentane (**23**) upon hydroarylation under ruthenium catalysis at 120 °C in dioxane.[9]



1,4-Diphenyl-4-vinylcyclohex-1-ene (26a)[10] **and 1-phenyl-4-(1-phenylvinyl)cyclohex-1-ene (26b)**:[11] a) Column chromatography (50 g of silica gel, column 25 × 2.5 cm, eluted with hexane, than with hexane/Et_2O 20:1→5:1) of the residue obtained from **1a** (188.2 mg, 1.213 mmol), **2** (473.7 mg, 499 μL, 3.639 mmol), $[RuCl_2(cod)]_n$ (17.0 mg, 60.6 μmol) and *rac*-BINAP (**5**) (75.5 mg, 121.2 μmol) according to GP1 (48 h heating) afforded a non-separable 2:1 mixture of **26a** and **26b** (170.1 mg, 36%, R_f = 0.23 in hexane) as a colorless oil, and recovered **1** (194.4 mg, 97%, R_f = 0.16 in hexane/Et_2O 5:1). **26a**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.42–7.22 (m, 10 H; Ph-H), 6.24–6.21 (m, 1 H; =CH), 5.96 (dd, *J* = 10.5, 17.3 Hz, 1 H; =CH), 5.13–5.00 (m, 2 H; $=CH_2$), 2.60–2.54 (m, 2 H; CH_2), 2.28–2.15 (m, 2 H; CH_2), 2.15–2.06 ppm (m, 2 H; CH_2); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 146.3 (C), 145.1 (CH), 141.7 (C), 136.1 (C), 128.2 (2 CH), 128.0 (2 CH), 126.6 (CH), 126.5 (2 CH), 124.9 (2 CH), 122.6 (CH), 112.2 (CH_2), 43.0 (C), 36.0 (CH_2), 32.0 (CH_2), 25.0 ppm (CH_2). This spectrum was identical to the previously published one.[10] **26b**: ^{1}H NMR (250 MHz, $CDCl_3$): δ

= 7.42–7.22 (m, 10 H; Ph-H), 6.15–6.14 (m, 1 H; =CH), 5.27–5.24 (m, 2 H; =CH_2), 2.95–2.85 (m, 1 H; CH), 2.53–2.38 (m, 2 H; CH_2), 2.28–2.06 ppm (m, 4 H; 2 CH_2); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 155.9 (C), 153.4 (C), 142.4 (C), 141.9 (C), 127.2 (CH), 125.9 (2 CH), 125.0 (2 CH), 123.9 (2 CH), 122.1 (CH), 110.8 (CH_2), 37.7 (CH), 32.1 (CH_2), 28.3 (CH_2), 27.8 ppm (CH_2). Several signals of aromatic CH fragments are overlapped with the signals of hydrocarbon **26a**.

a) Column chromatography of the residue obtained from **1a** (162.8 mg, 1.050 mmol), **2** (410.1 mg, 431.6 μL, 3.150 mmol), $[RuCl_2(cod)]_n$ (14.7 mg, 52.4 μmol) and dppf (**6**) (58.2 mg, 104.8 μmol) according to GP1 (48 h heating) afforded a non-separable 2:1 mixture of **29a** and **29a** (184.6 mg, 45%) and recovered **1a** (156.0 mg, 96%).



1,4,4-Trivinylcyclohexene (27a):[12] Column chromatography (50 g of silica gel, column 25 × 2.5 cm, eluted with hexane, than with hexane/Et_2O 20:1→5:1) of the residue obtained from **1a** (331.0 mg, 2.133 mmol), **24** (512.7 mg, 603 μL, 6.399 mmol), $[RuCl_2(cod)]_n$ (29.9 mg, 106.6 μmol) and P(*o*-biphenyl)(*t*Bu)$_2$ (**10**) (63.6 mg, 213.2 μmol) according to GP1 (24 h heating; all quantity of **27** was added in one portion) afforded **27a** (164.5 mg, 32%, R_f = 0.38 in hexane) as a colorless oil and recovered **1a** (314.6 mg, 95%, R_f = 0.16 in hexane/Et_2O 5:1). **27a**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.34 (dd, *J* = 10.8, 17.8 Hz, 1 H; =CH), 5.77 (dd, *J* = 10.8, 17.8 Hz, 2 H; 2 =CH), 5.75–5.73 (m, 1 H; =CH), 5.08–4.88 (m, 6 H; 3 =CH_2), 2.21 (br. s, 2 H; CH_2), 2.14 (tq, *J* = 1.8, 6.4 Hz, 2 H; CH_2), 1.69 ppm (t, *J* = 6.4 Hz, 2 H; CH_2); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 144.1 (2 CH), 139.5 (CH), 135.4 (C), 112.6 (2 CH_2), 110.2 (CH2), 41.9 (C), 34.4 (CH_2), 31.3 (CH_2), 21.2 ppm (CH_2). These spectra correspond to the previously published ones (measured in C_6D_6).[12]

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(6) CCDC-678126 (**13a**), -688765 (**13b**) and -678125 (**14**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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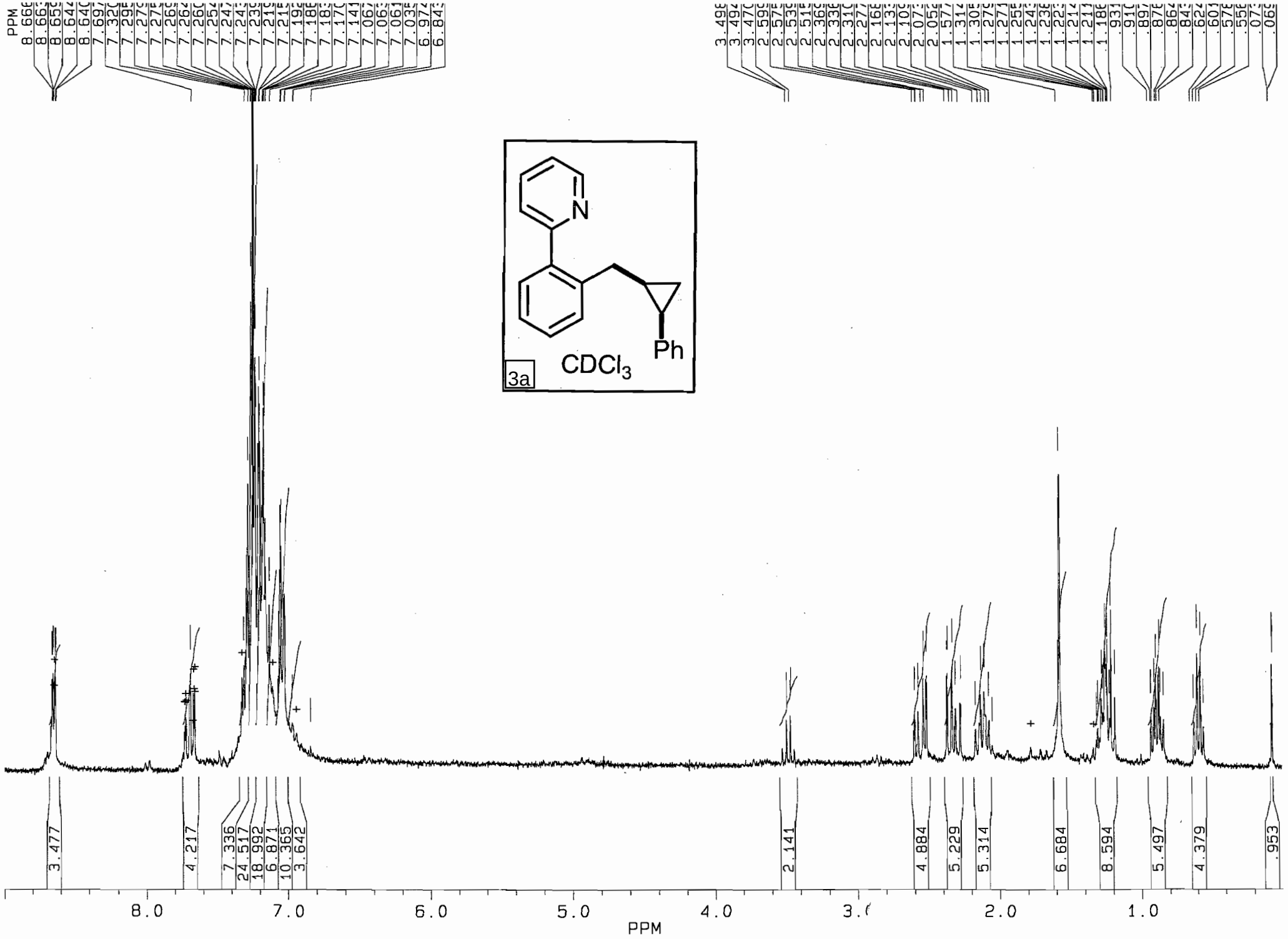
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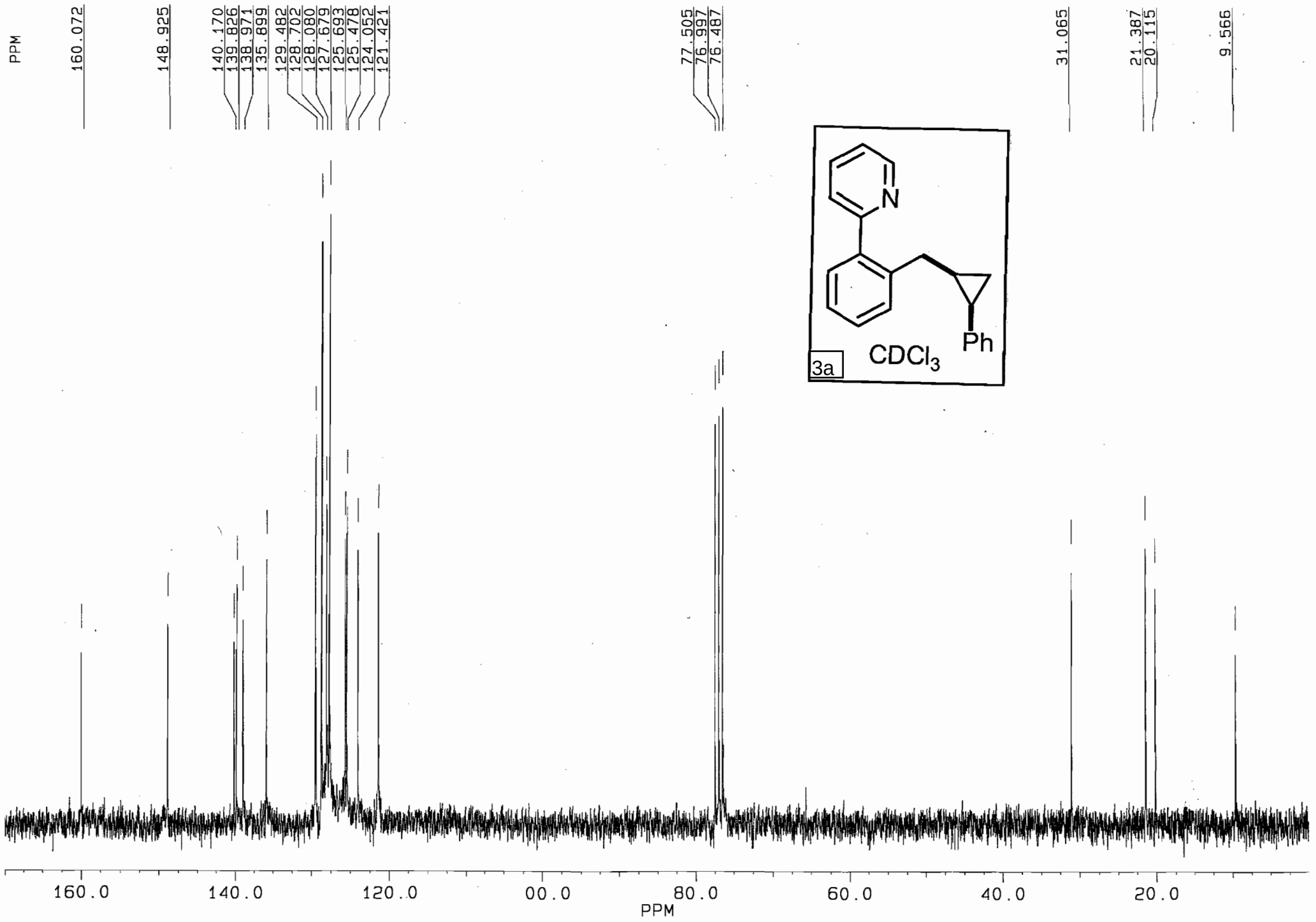
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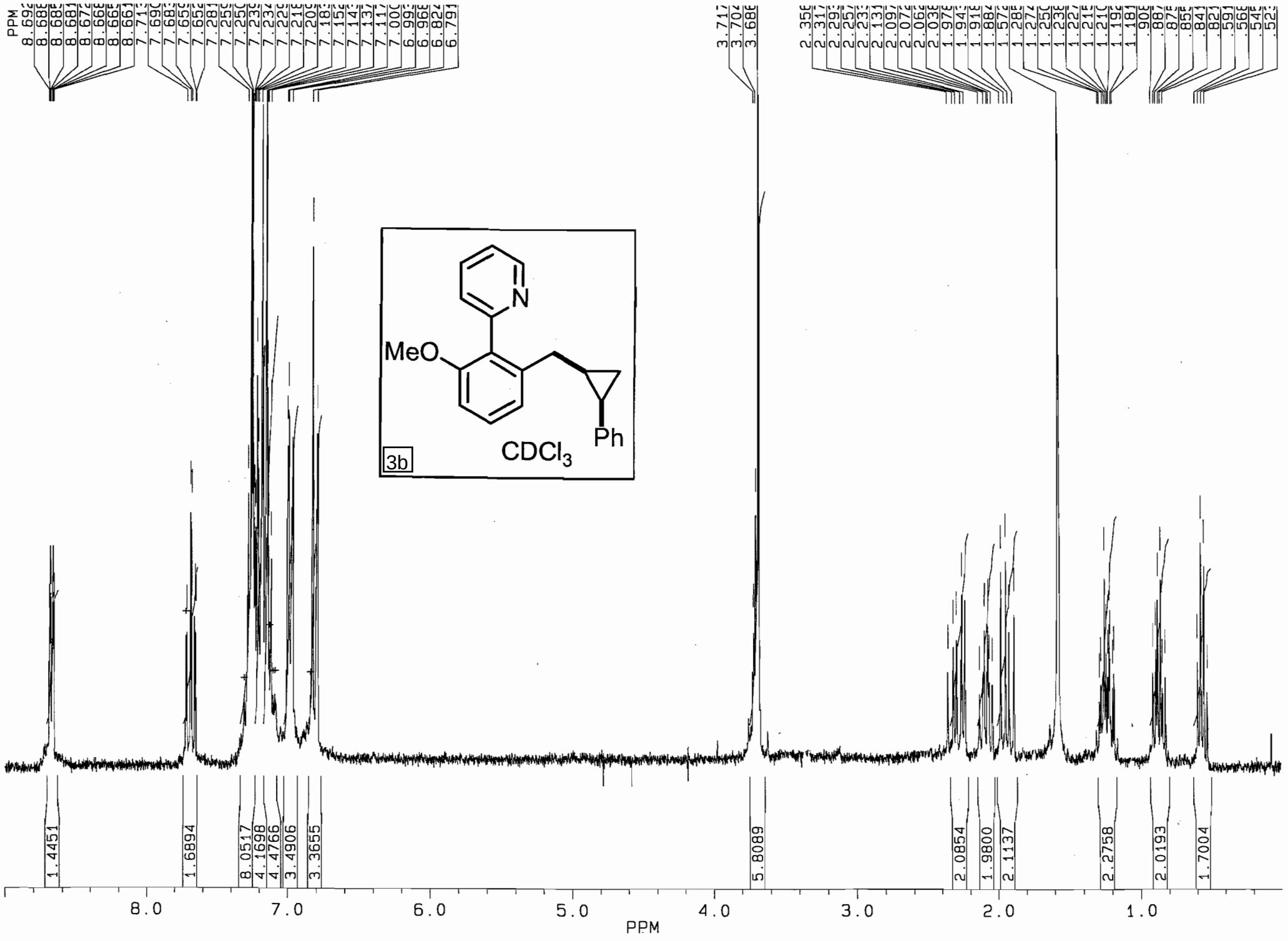
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PPM
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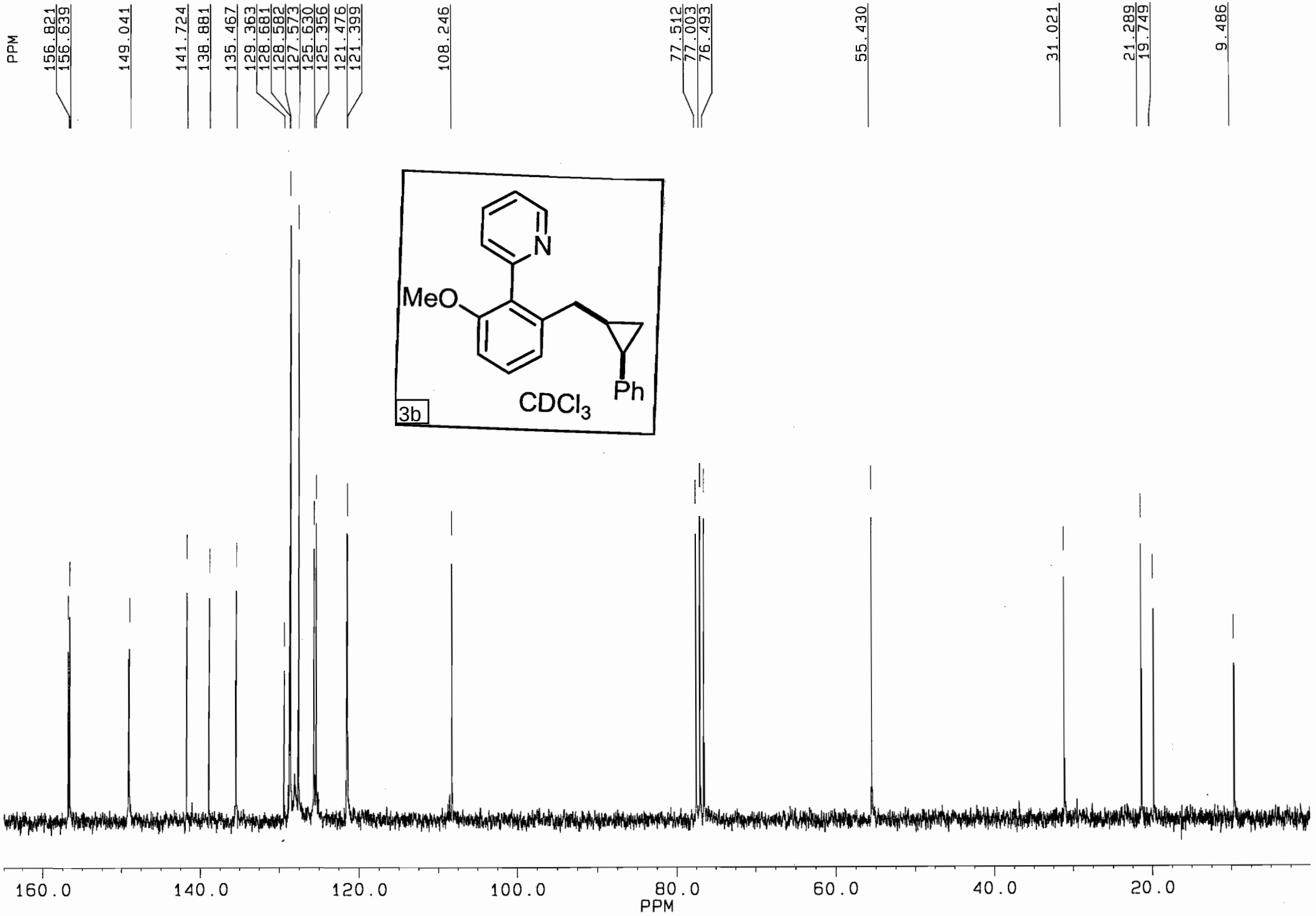
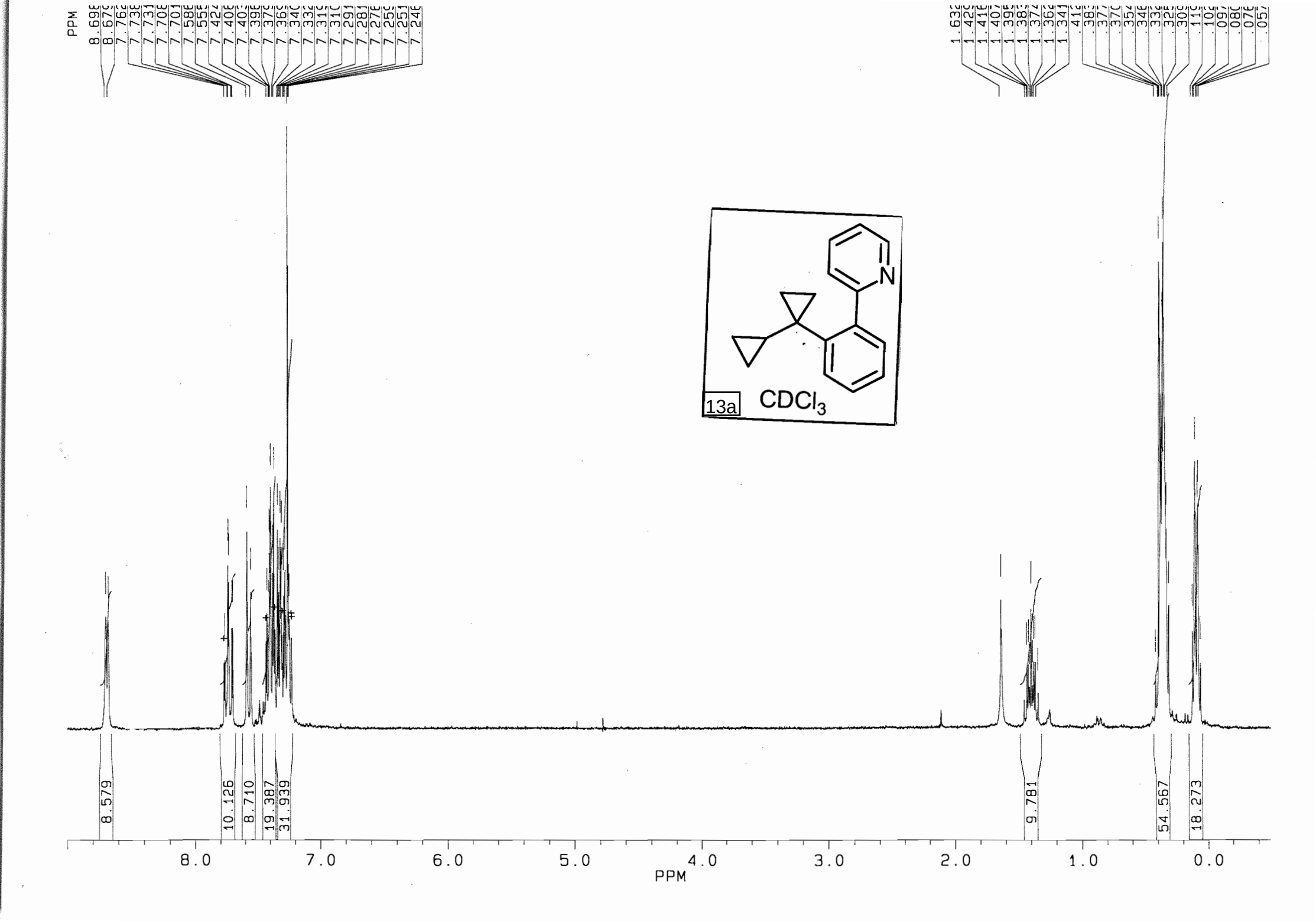
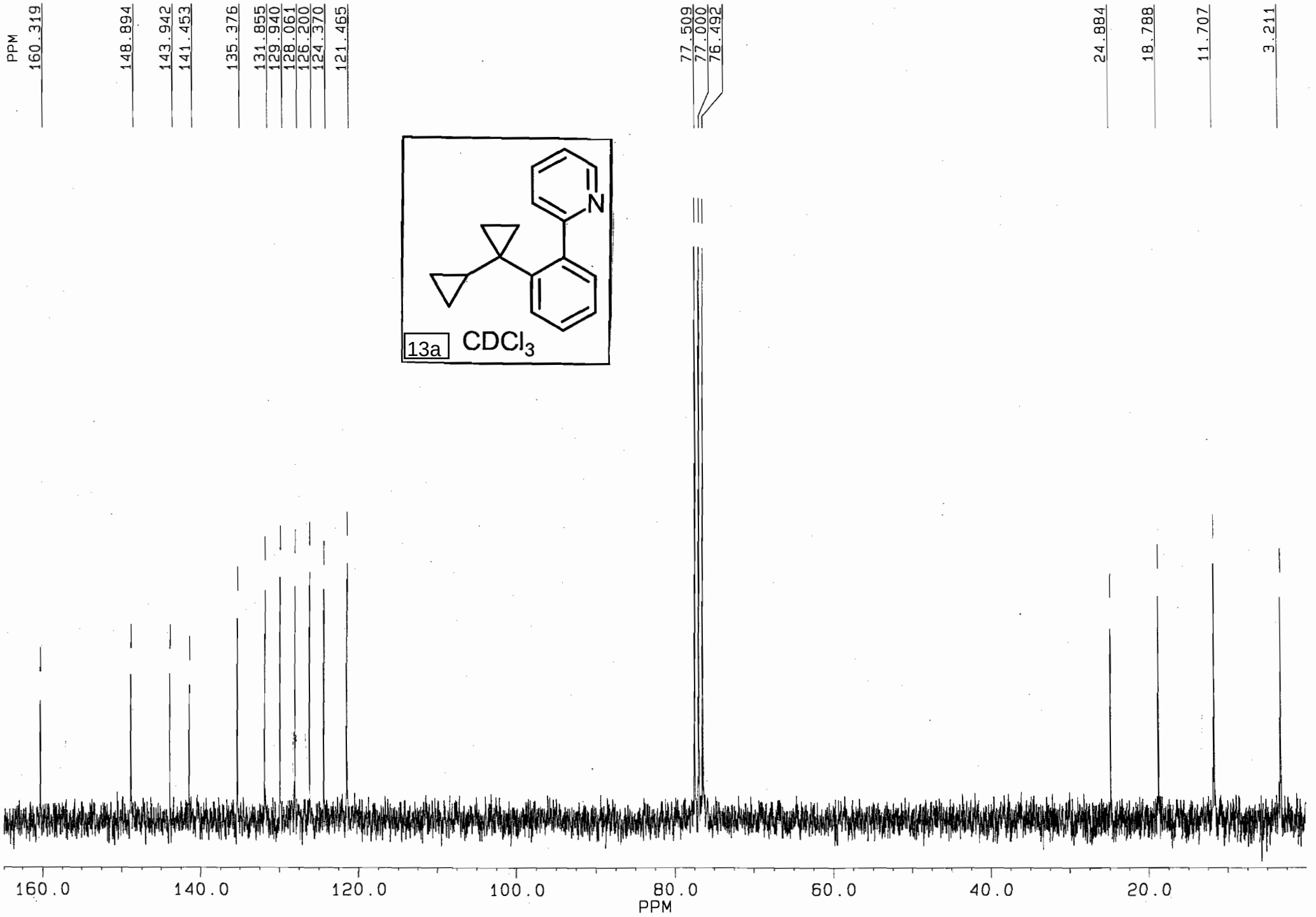
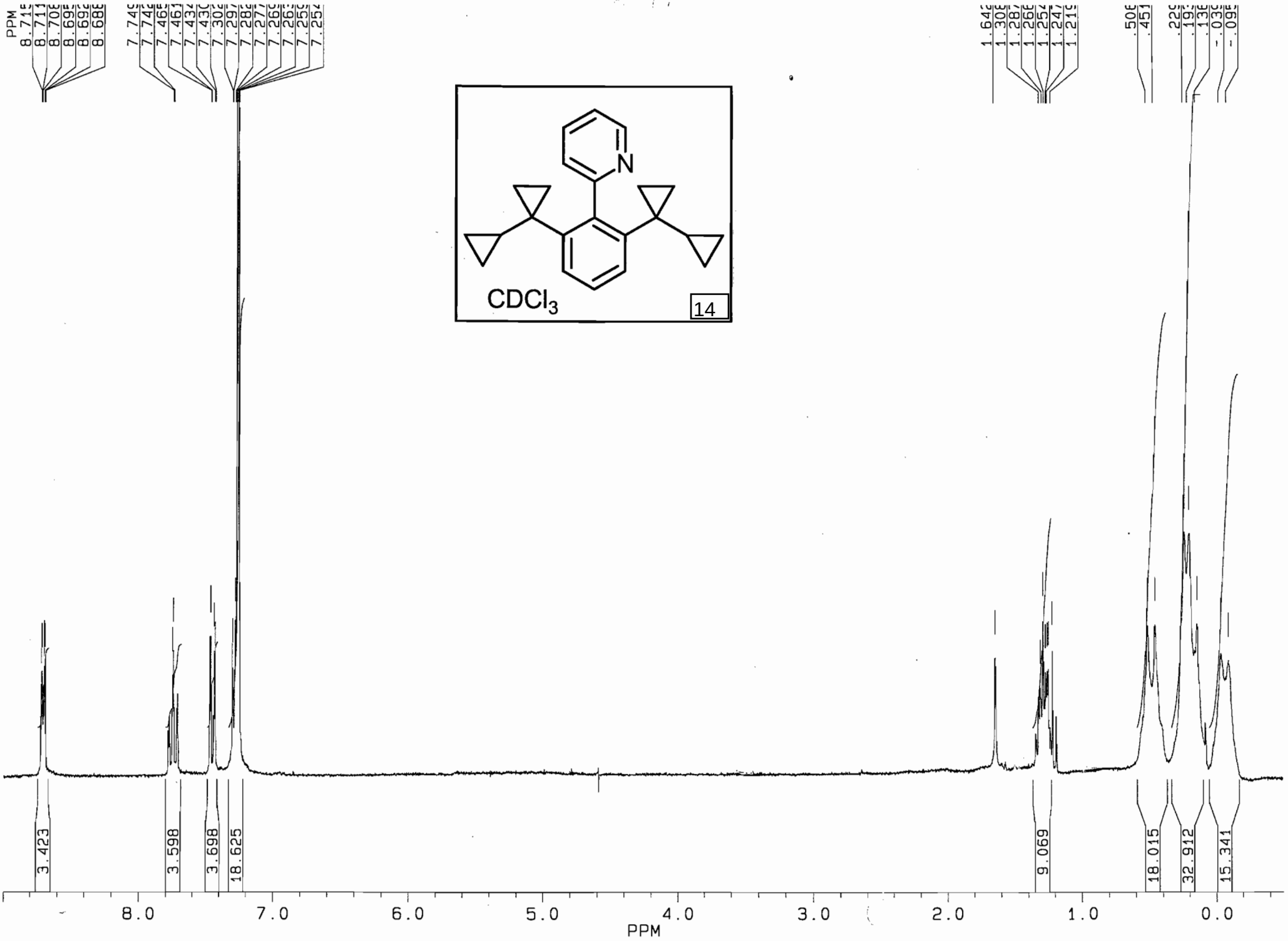
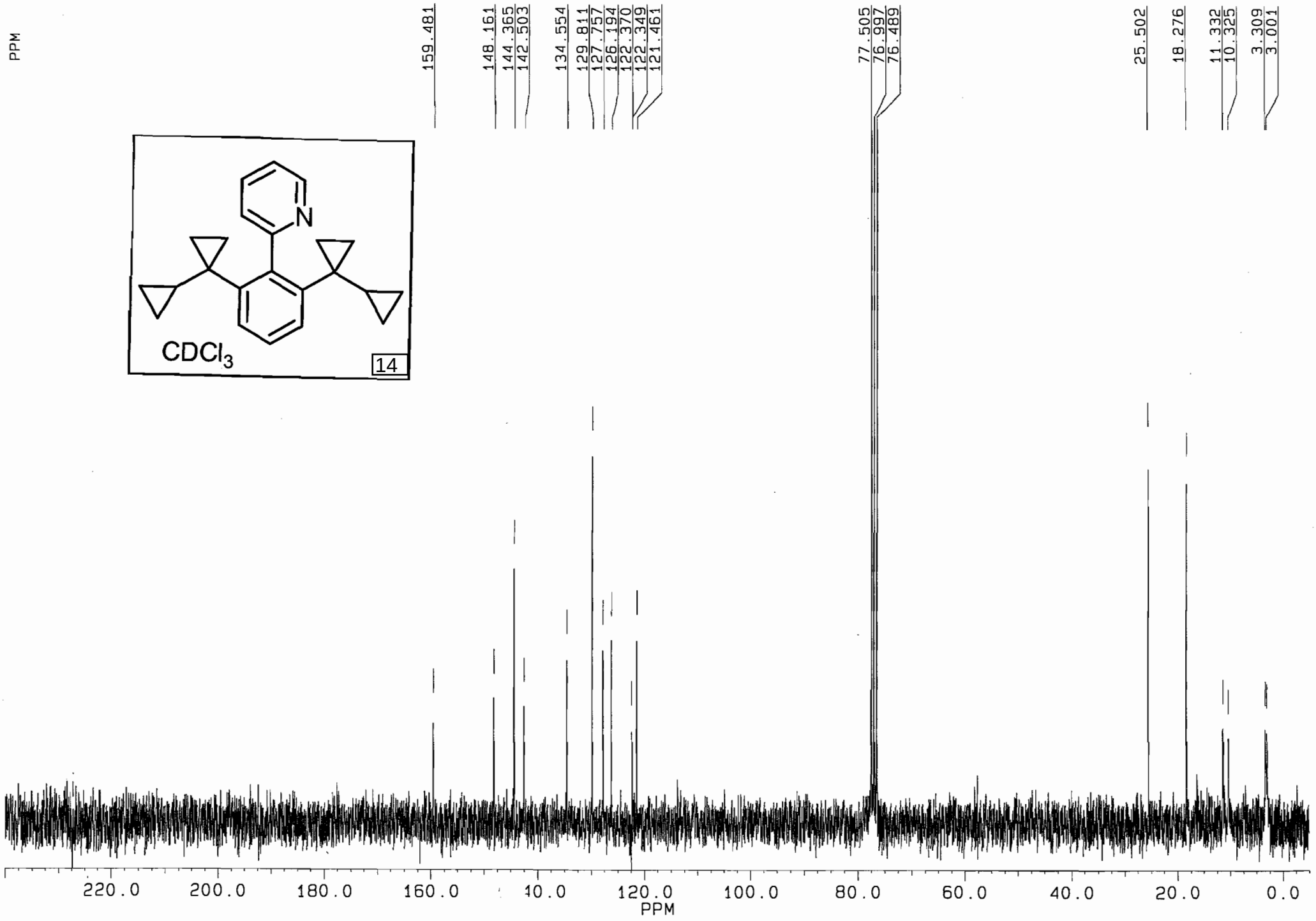
7.0
6.0
5.0
4.0
3.0
2.0
1.0
1.4451
1.6894
8.0517
4.1698
4.4766
3.4906
3.3655
5.8089
2.0854
1.9800
2.1137
2.2758
2.0193
1.7004

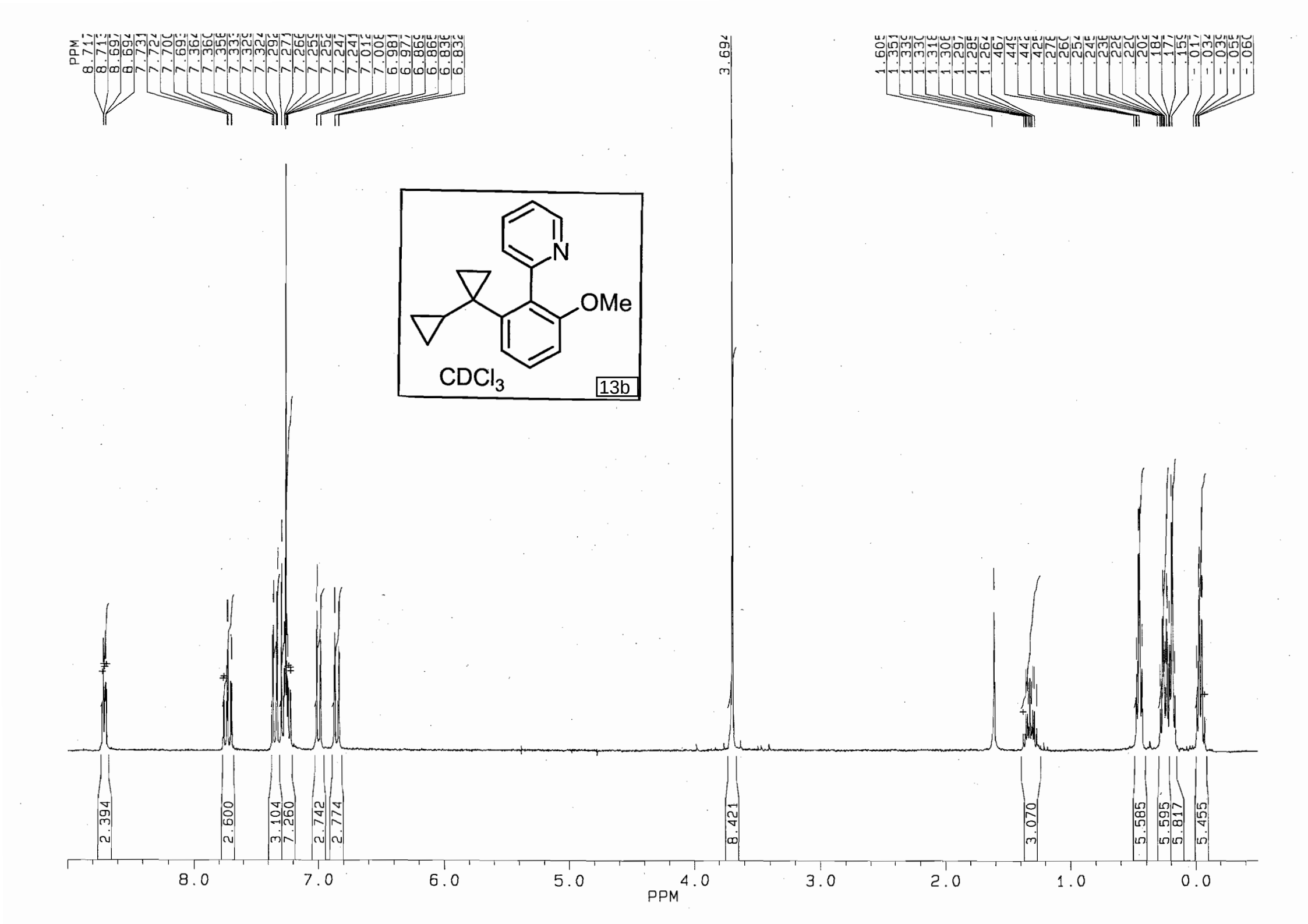

PPM
156.821
156.639
149.041
141.724
138.881
135.467
129.363
128.681
128.582
127.573
125.630
125.356
121.476
121.399
108.246
77.512
77.003
76.493
55.430
31.021
21.289
19.749
9.486
MeO
N
Ph
CDCl3
3b
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
PPM

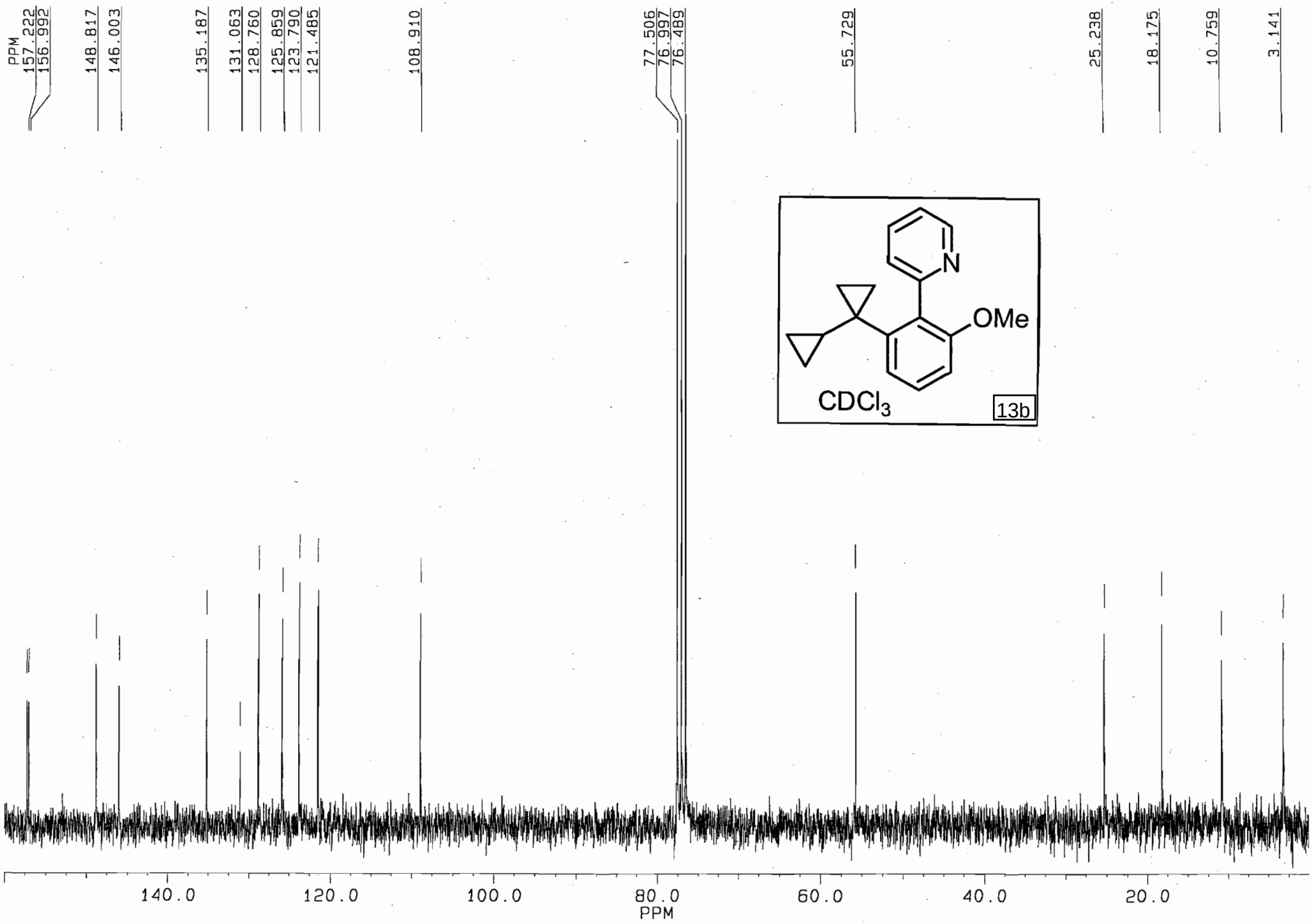

13a
CDCl3
N
PPM
8.579
10.126
8.710
19.387
31.939
9.781
54.567
18.273
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

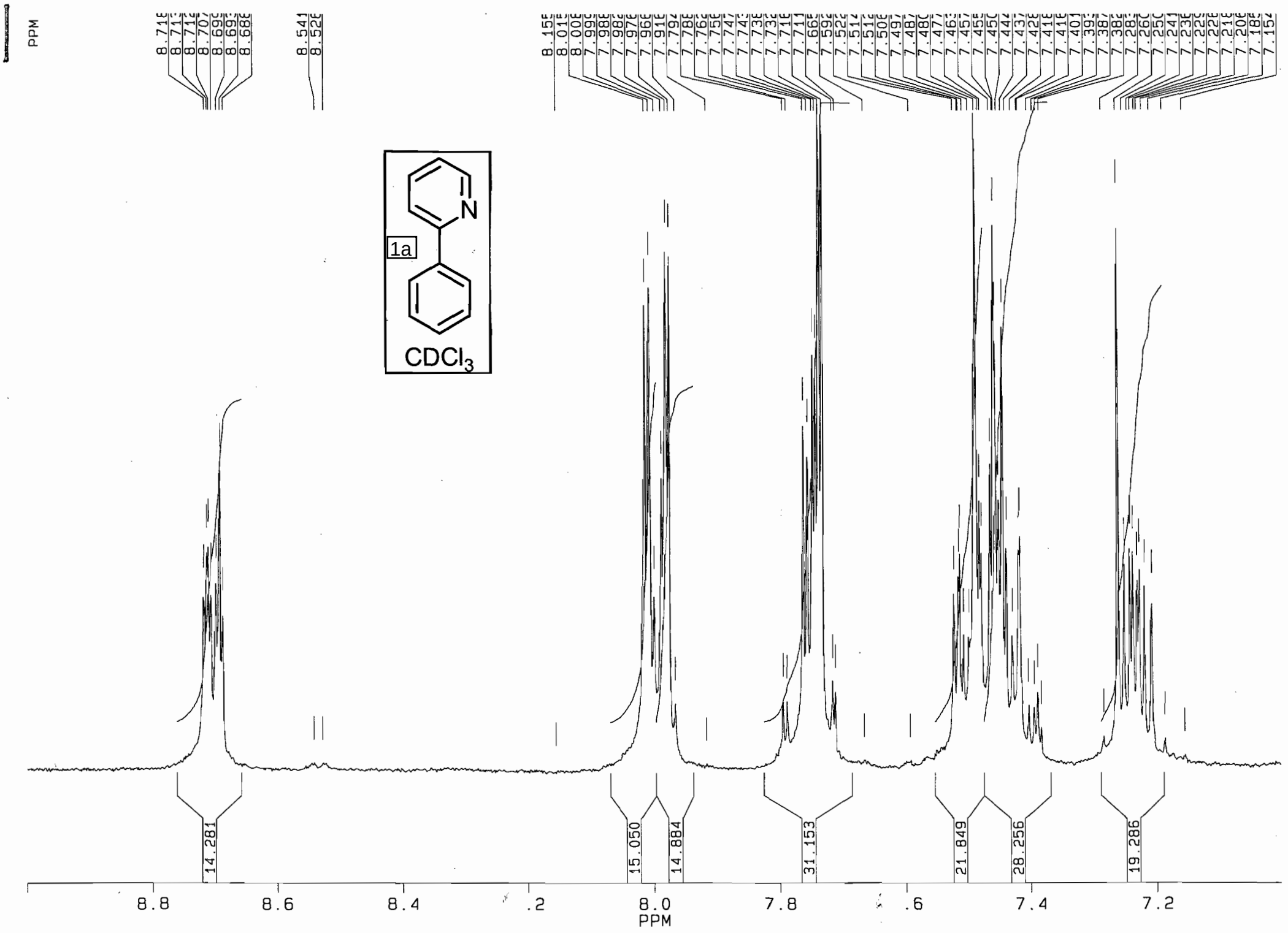

PPM
160.319
148.894
143.942
141.453
135.376
131.855
129.940
128.061
126.200
124.370
121.465
77.509
77.000
76.492
24.884
18.788
11.707
3.211
N
13a
CDCl3
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
PPM

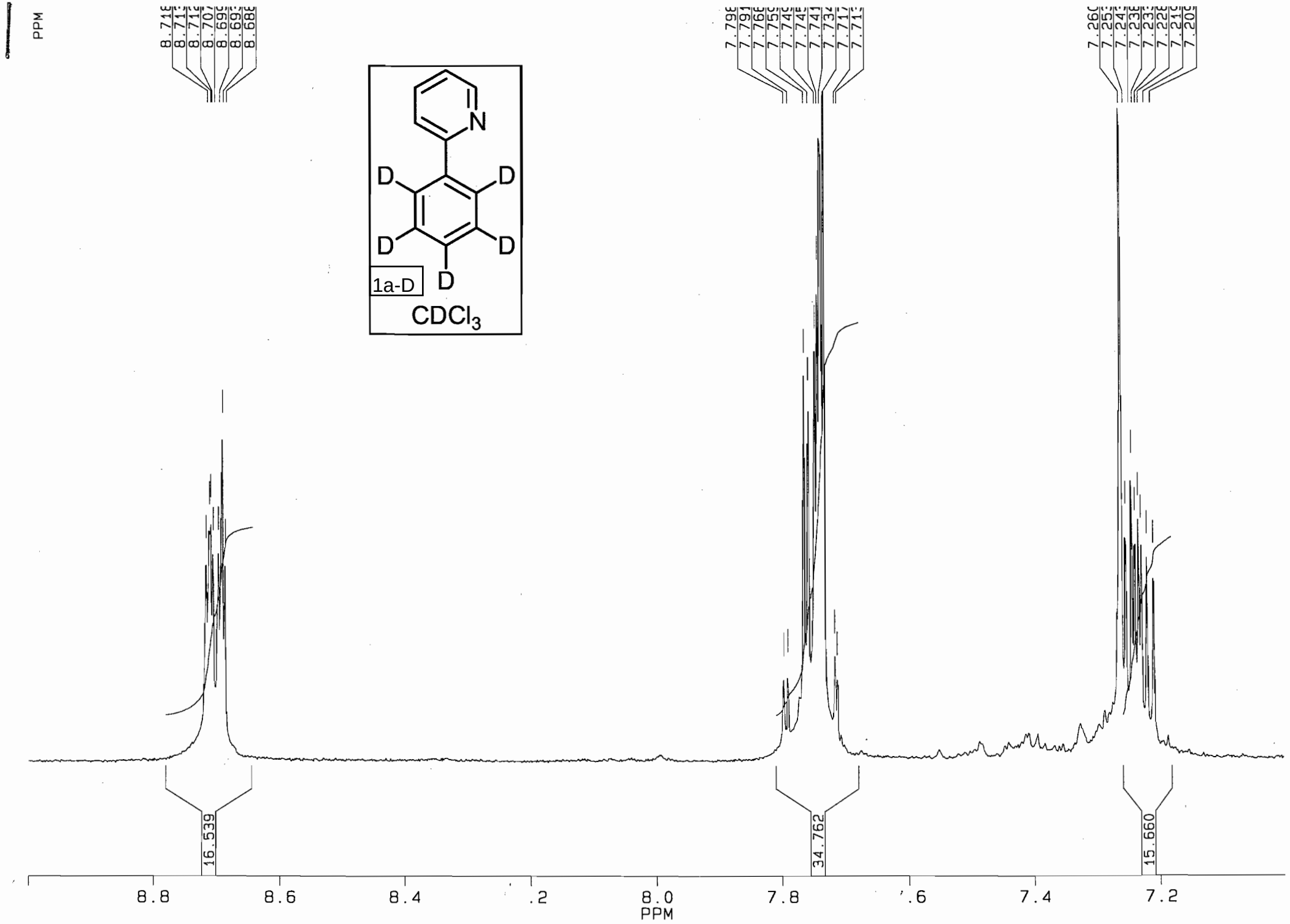

PPM
8.711
8.708
8.695
8.692
8.688
7.746
7.744
7.465
7.461
7.434
7.430
7.302
7.297
7.282
7.277
7.265
7.255
7.254
1.642
1.308
1.287
1.266
1.254
1.247
1.215
.506
.451
.225
.193
.138
-.033
-.098
N
CDCl3
14
3.423
3.598
3.698
18.625
9.069
18.015
32.912
15.341
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM

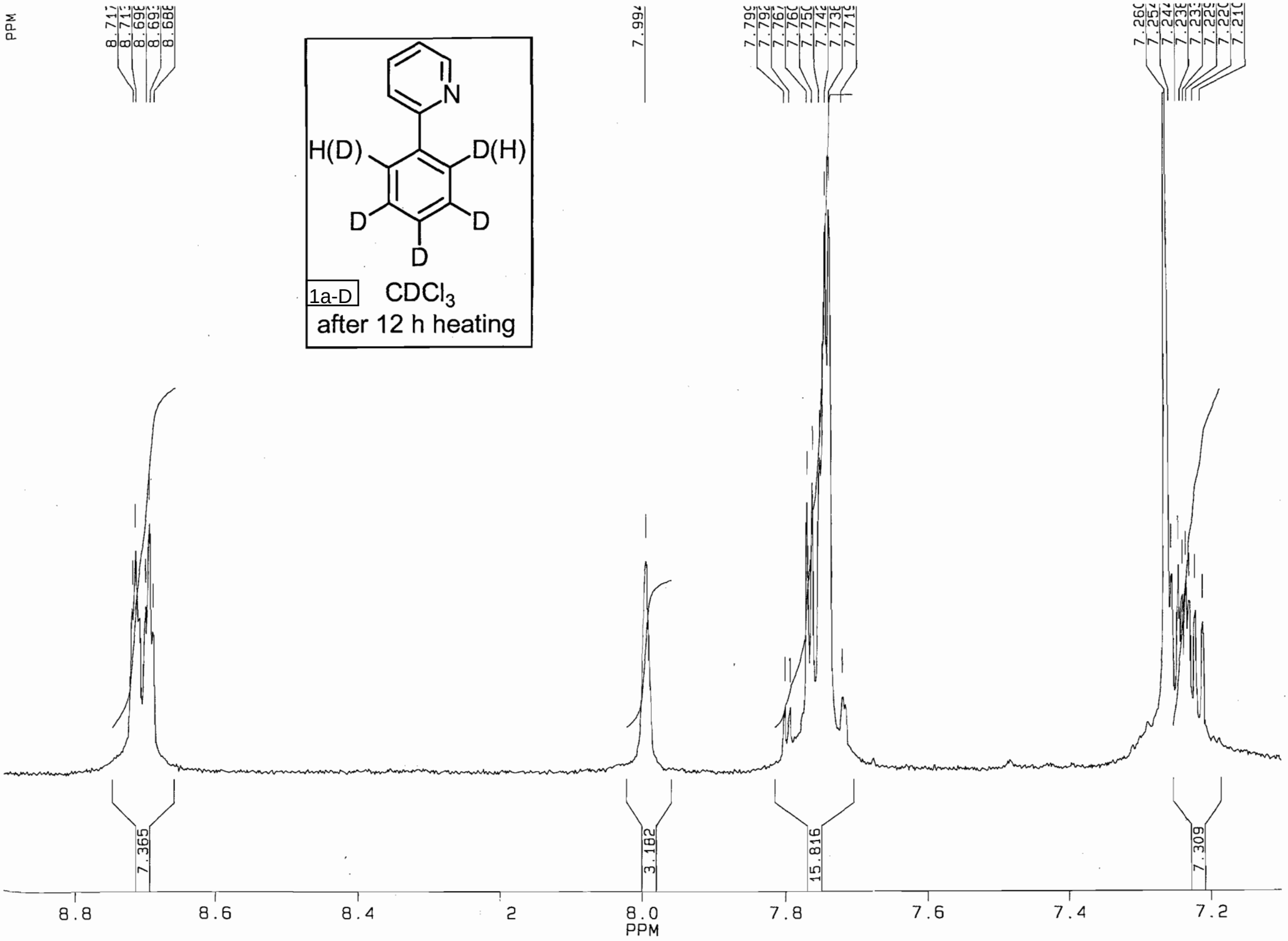

PPM
159.481
148.161
144.365
142.503
134.554
129.811
127.757
126.194
122.370
122.349
121.461
77.505
76.997
76.489
25.502
18.276
11.332
10.325
3.309
3.001
N
CDCl3
14
220.0
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0
PPM

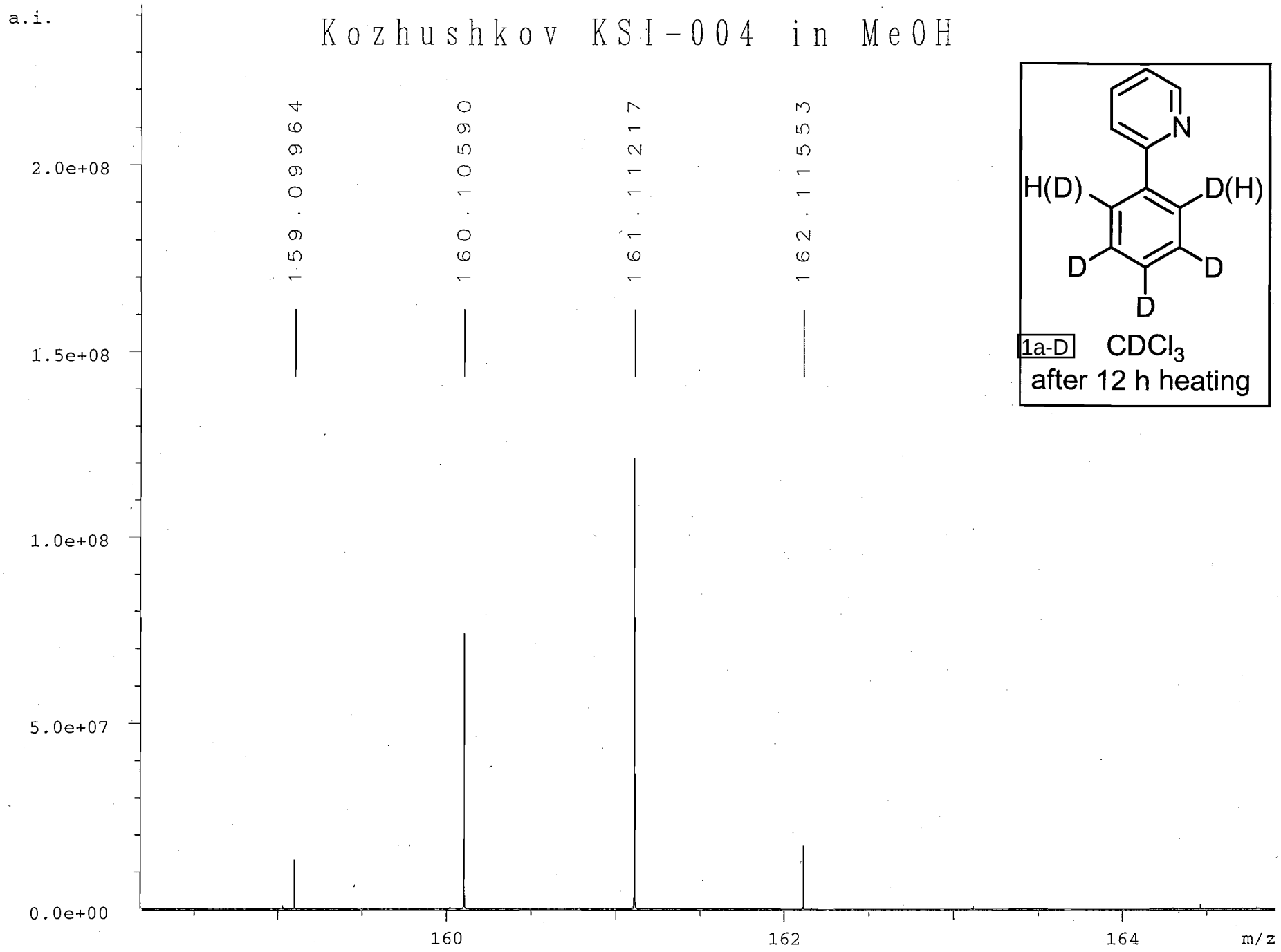

N
OMe
CDCl3
13b
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
2.394
2.600
3.104
7.260
2.742
2.774
8.421
3.070
5.585
5.595
5.817
5.455

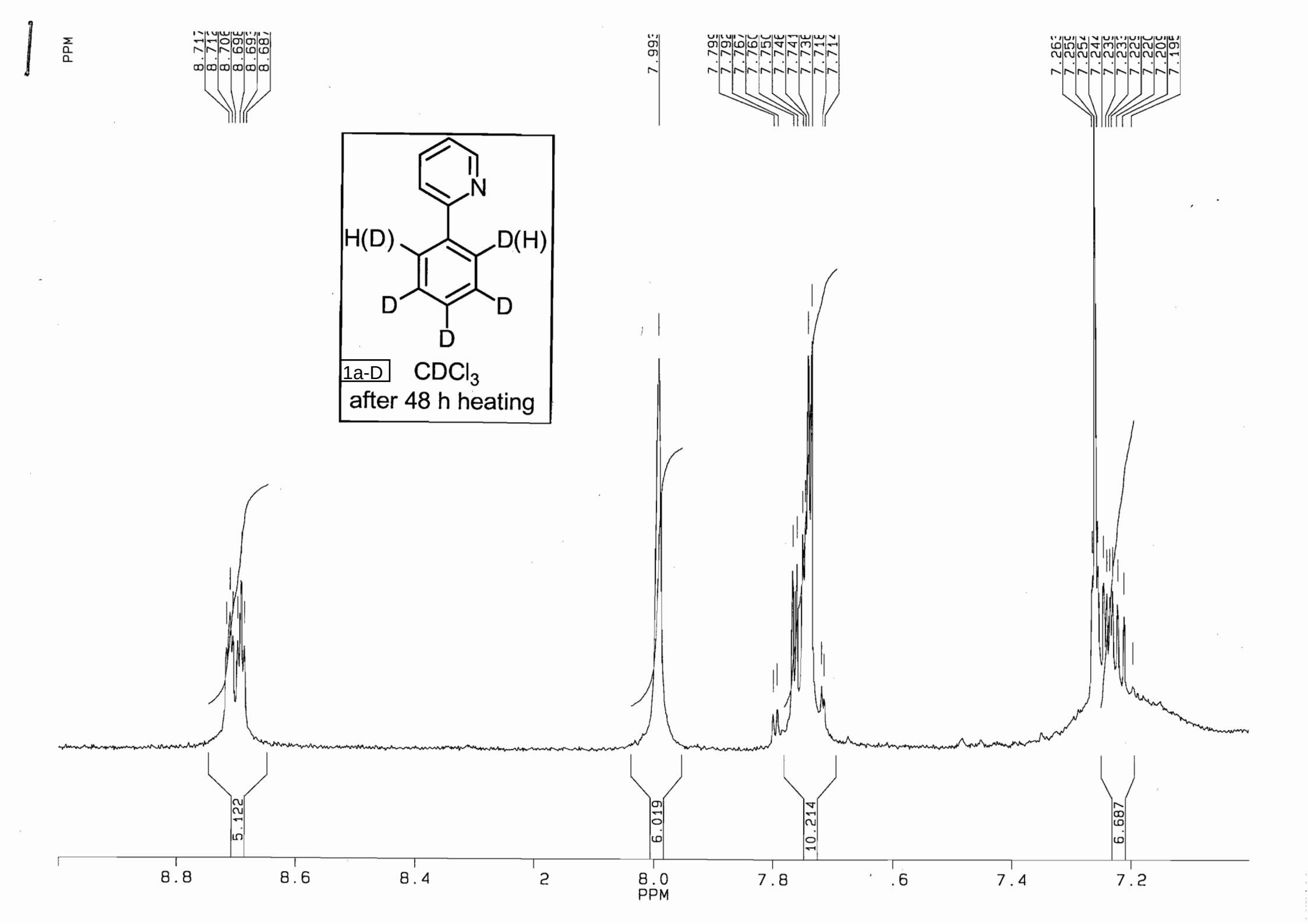

PPM
157.222
156.992
148.817
146.003
135.187
131.063
128.760
125.859
123.790
121.485
108.910
77.506
76.997
76.489
55.729
25.238
18.175
10.759
3.141
N
OMe
CDCl3
13b
140.0
120.0
100.0
80.0
60.0
40.0
20.0
PPM

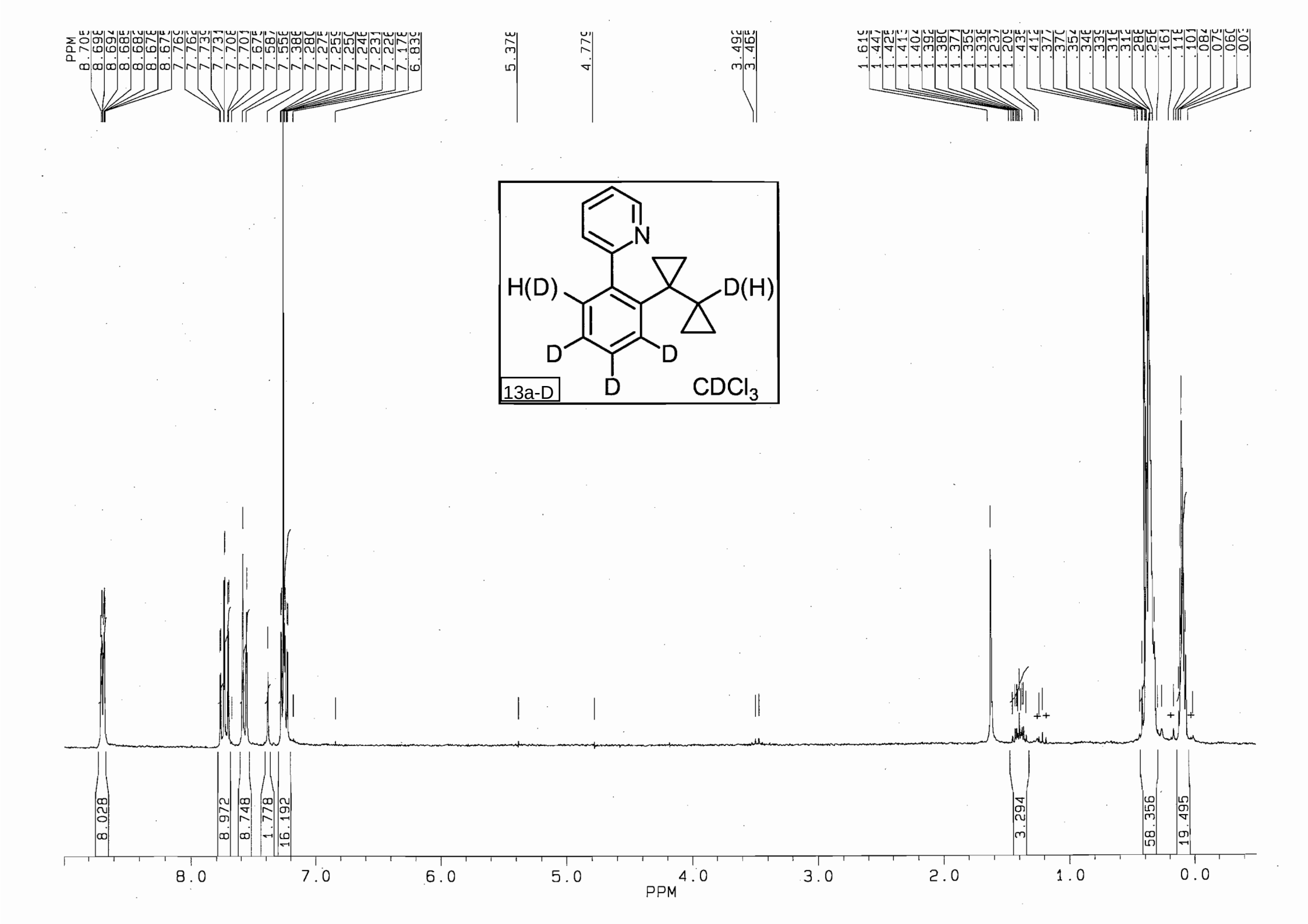

PPM
8.718
8.715
8.714
8.707
8.695
8.693
8.688
8.541
8.528
8.155
8.015
8.008
7.998
7.988
7.982
7.978
7.966
7.918
7.794
7.788
7.762
7.758
7.747
7.743
7.738
7.732
7.718
7.711
7.668
7.596
7.522
7.514
7.512
7.508
7.497
7.487
7.480
7.477
7.463
7.457
7.455
7.450
7.444
7.437
7.428
7.418
7.415
7.401
7.393
7.387
7.382
7.283
7.260
7.250
7.241
7.238
7.225
7.222
7.218
7.208
7.185
7.154
1a
N
CDCl3
14.281
15.050
14.884
31.153
21.849
28.256
19.286
8.8
8.6
8.4
.2
8.0
7.8
.6
7.4
7.2
PPM

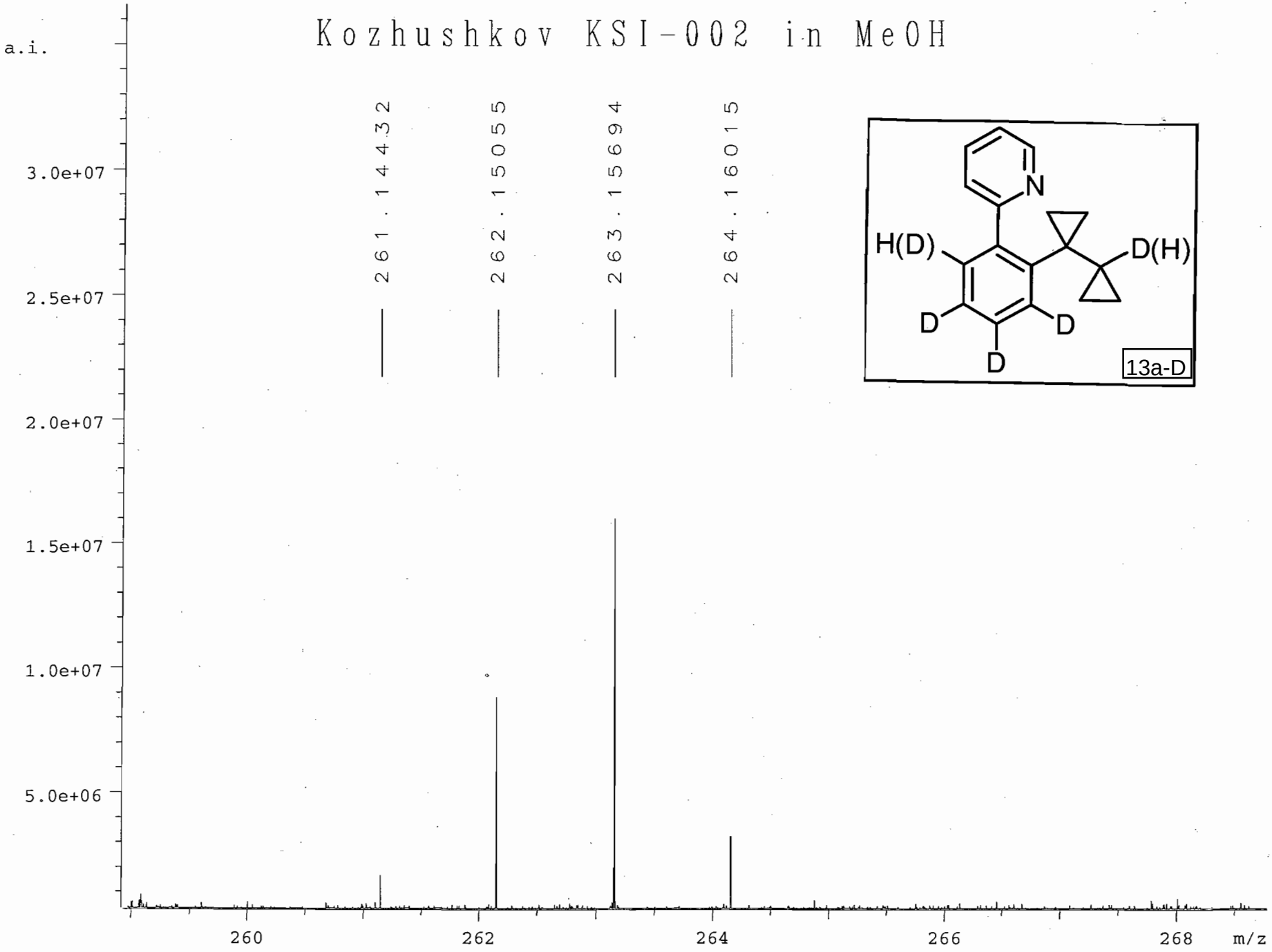

PPM
8.718
8.712
8.707
8.695
8.693
8.688
7.798
7.791
7.768
7.755
7.745
7.741
7.734
7.717
7.713
7.260
7.253
7.243
7.238
7.233
7.228
7.216
7.209
N
D
D
D
D
D
1a-D
CDCl3
16.539
34.762
15.660
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
PPM

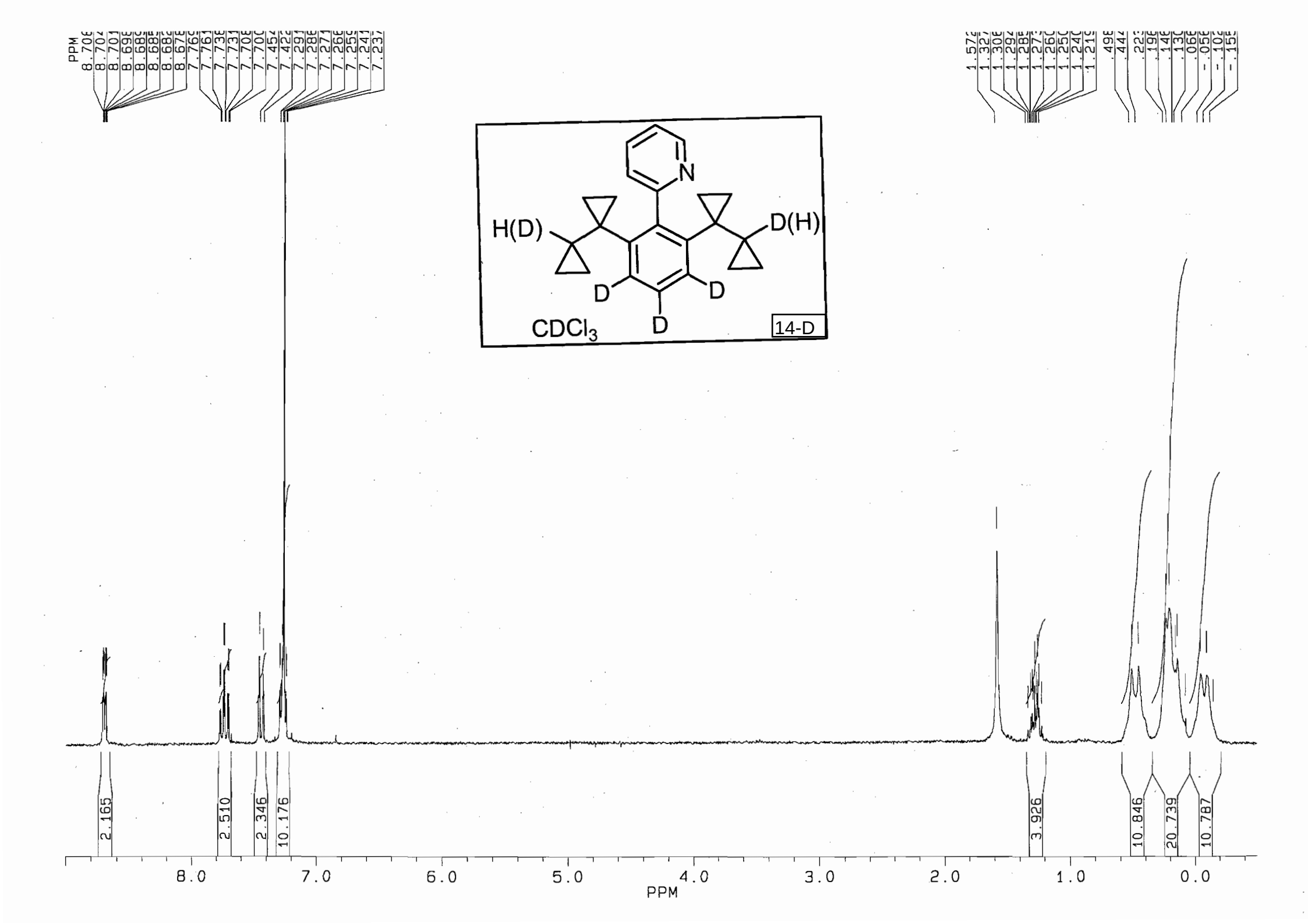

PPM
8.717
8.713
8.698
8.693
8.688
7.994
7.795
7.792
7.767
7.760
7.750
7.742
7.738
7.719
7.260
7.254
7.244
7.238
7.233
7.225
7.220
7.210
N
H(D)
D(H)
D
D
D
1a-D
CDCl3
after 12 h heating
7.365
3.182
15.816
7.309
8.8
8.6
8.4
2
8.0
7.8
7.6
7.4
7.2
PPM

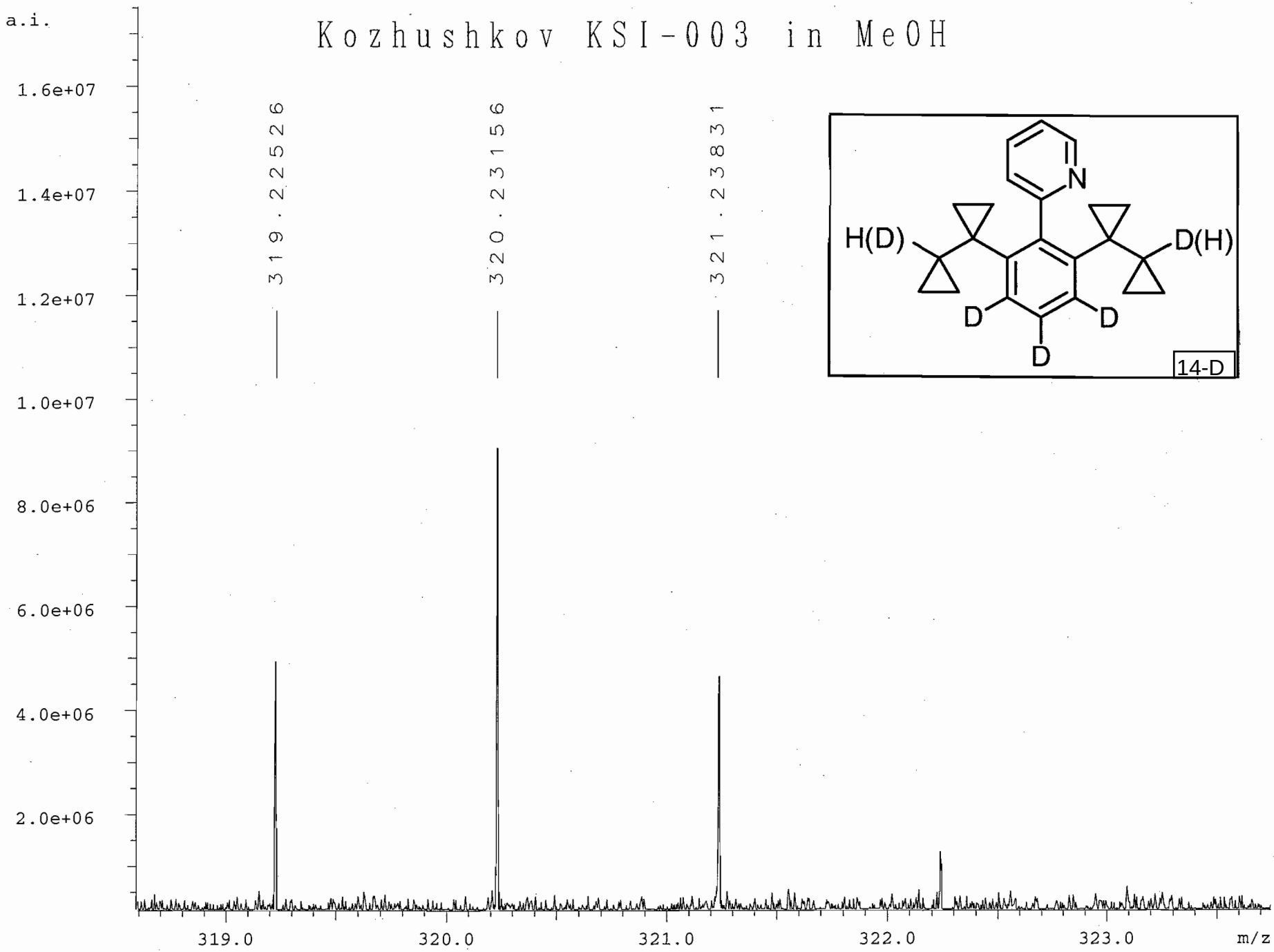

Kozhushkov KSI-004 in MeOH
a.i.
159.09964
160.10590
161.11217
162.11553
2.0e+08
1.5e+08
1.0e+08
5.0e+07
0.0e+00
160
162
164
m/z
H(D)
D(H)
D
D
D
N
1a-D
CDCl3
after 12 h heating
/Data/esi/kozhushkov080410a/1/pdata/1 Administrator Thu Apr 10 16:08:44 2008

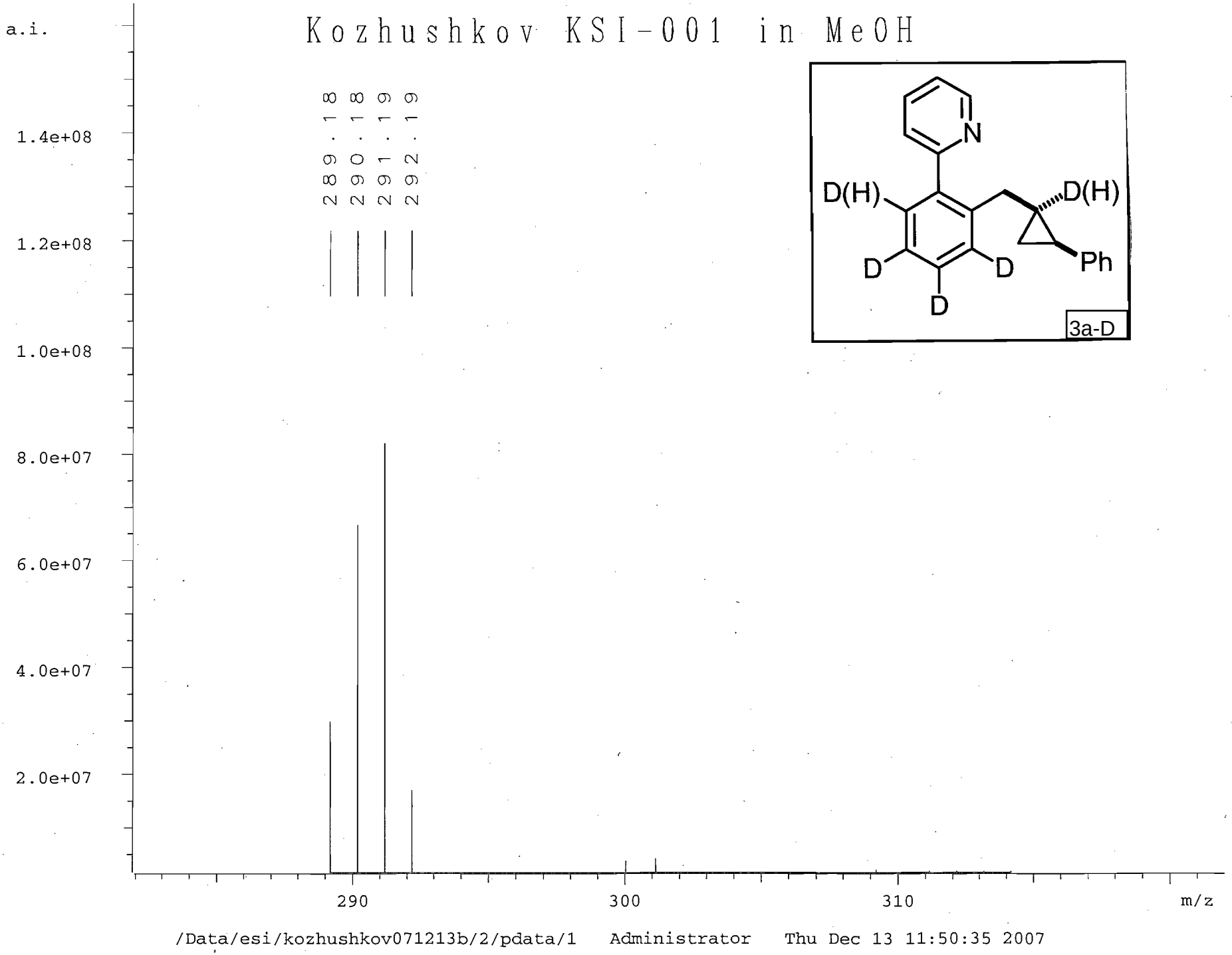

PPM
8.717
8.712
8.708
8.698
8.693
8.687
7.993
7.799
7.792
7.767
7.760
7.750
7.748
7.741
7.736
7.718
7.714
7.263
7.259
7.254
7.242
7.235
7.231
7.225
7.220
7.205
7.195
H(D)
D(H)
D
D
D
1a-D
CDCl3
after 48 h heating
5.122
6.019
10.214
6.687
8.8
8.6
8.4
2
8.0
7.8
.6
7.4
7.2
PPM


PPM
8.028
8.972
8.748
1.778
16.192
3.294
58.356
19.495
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM
N
H(D)
D(H)
D
D
D
13a-D
CDCl3


Kozhushkov KSI-002 in MeOH
a.i.
261.14432
262.15055
263.15694
264.16015
3.0e+07
2.5e+07
2.0e+07
1.5e+07
1.0e+07
5.0e+06
260
262
264
266
268
m/z
H(D)
D(H)
D
D
D
N
13a-D
/Data/esi/kozhushkov071213a/2/pdata/1 Administrator Thu Dec 13 11:42:45 2007


H(D)
D(H)
D
D
D
N
CDCl3
14-D
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
2.165
2.510
2.346
10.176
3.926
10.846
20.739
10.787


Kozhushkov KSI-003 in MeOH
a.i.
1.6e+07
1.4e+07
1.2e+07
1.0e+07
8.0e+06
6.0e+06
4.0e+06
2.0e+06
319.22526
320.23156
321.23831
H(D)
D(H)
D
D
D
N
14-D
319.0
320.0
321.0
322.0
323.0
m/z
/Data/esi/kozhushkov071213c/4/pdata/1 Administrator Thu Dec 13 12:07:33 2007


Kozhushkov KSI-001 in MeOH
a.i.
289.18
290.18
291.19
292.19
1.4e+08
1.2e+08
1.0e+08
8.0e+07
6.0e+07
4.0e+07
2.0e+07
290
300
310
m/z
D(H)
D(H)
N
D
D
D
Ph
3a-D
/Data/esi/kozhushkov071213b/2/pdata/1 Administrator Thu Dec 13 11:50:35 2007