Supporting Information

Ruthenium-Catalyzed Conversion of sp^3 C–O Bonds in Ethers to C–C Bonds Using Triarylboroxins

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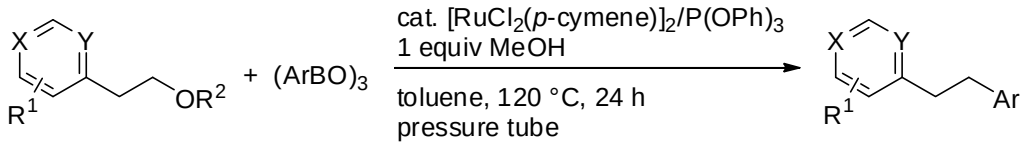
General Information

^{1}H, ^{13}C{^{1}H}, and ^{19}F NMR spectra were recorded on JEOL ECX-400 spectrometer. Chemical shifts in ^{1}H and ^{13}C{^{1}H} NMR spectra were reported in ppm relative to residual solvent peaks such as chloroform (δ 7.26 for ^{1}H, and δ 77.00 for ^{13}C), toluene (δ 2.09 for ^{1}H), and DMSO (δ 2.50 for ^{1}H, and δ 39.52 for ^{13}C), or internal reference, tetramethylsilane (δ 0.00 for ^{1}H and ^{13}C). Chemical shifts in ^{19}F NMR spectra were reported in ppm relative to an external reference, $CFCl_3$. IR spectra were recorded on a JASCO FT/IR-410 or FT/IR-4200 infrared spectrometer. GC analyses were performed using a CBP-10 capillary column (25 m × 0.22 mm, film thickness 0.25 μm). ESI- and APCI-MS were performed on a JEOL JMS-T100LCS. Flash chromatography was carried out with Kanto Chemical silica gel 60N. Toluene and $P(OPh)_3$ were distilled from Na/benzophenone ketyl and Drierite®, respectively. Triarylboroxins were prepared in similar ways to the method used for **5e** described below. Dry THF and MeOH was purchased from Kanto Chemical Co., Inc. and Nacalai Tesque, Inc., respectively and used without further purification. $[RuCl_2(p\text{-cymene})]_2$ was prepared by a literature method.[1]

General Procedure A for the Ruthenium-Catalyzed Arylation

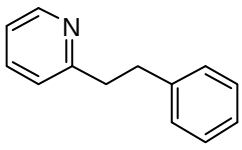


In a glove box, $[RuCl_2(p\text{-cymene})]_2$ (15.3 mg, 0.025 mmol), $(ArBO)_3$ (0.33 mmol), and a magnetic stirring bar were placed in a 20 mL pressure-tube, and then toluene (0.5 mL), $P(OPh)_3$ (13.0 μL, 0.05 mmol), alkyl ether (0.5 mmol), and MeOH (20.2 μL, 0.5 mmol) were added in this order. The mixture was heated in an oil bath at 120 °C for 24 h. The resulting mixture was diluted with dichloromethane (2 mL) and methanol (2 mL), and analyzed by GC and GC-MS. After removal of the volatile materials by rotary evaporation, the arylation product was isolated by silica gel column chromatography, followed by Kugelrohr distillation in some cases.

General Procedure B for the Ruthenium-Catalyzed Arylation

General Procedure B is the same as General Procedure A except that 0.05 mmol of $[RuCl_2(p\text{-cymene})]_2$ and 0.10 mmol of $P(OPh)_3$ were used for the reaction.

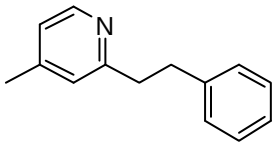
2-Methyl-4-(2-phenylethyl)pyridine (2aa)



2aa

General procedure B was followed with 2-(2-methoxyethyl)pyridine (**1a**, 68.6 mg) and triphenylboroxin (**5a**, 103 mg). Column chromatography (4:1 hexane/EtOAc) afforded **2aa** as a pale yellow oil (55.0 mg, 60%). ^{1}H NMR spectroscopic data are in good agreement with those reported in literature.[2]

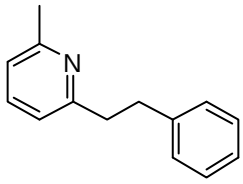
2-Methyl-4-(2-phenylethyl)pyridine (2ba)



2ba

General procedure B was followed with 2-(2-methoxyethyl)-4-methylpyridine (**1b**, 75.6 mg) and triphenylboroxin (**5a**, 103 mg). Column chromatography (4:1 hexane/EtOAc) afforded **2ba** as a pale yellow oil (52.9 mg, 54%). ^{1}H NMR spectroscopic data are in good agreement with those reported in literature.[3]

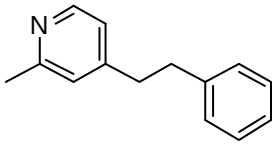
2-Methyl-4-(2-phenylethyl)pyridine (2ca)



2ca

General procedure B was followed with 2-(2-methoxyethyl)-6-methylpyridine (**1c**, 75.6 mg) and triphenylboroxin (**5a**, 103 mg). Column chromatography (4:1 hexane/EtOAc) afforded **2ca** as a pale yellow oil (37.9 mg, 38%). ^{1}H and ^{13}C NMR spectroscopic data are in good agreement with those reported in literature.[4]

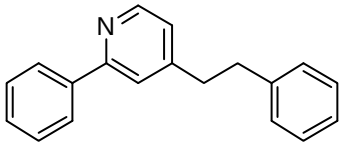
2-Methyl-4-(2-phenylethyl)pyridine (2da)



2da

General procedure A was followed with 4-(2-methoxyethyl)-2-methylpyridine (**1d**, 75.6 mg) and triphenylboroxin (**5a**, 103 mg). Column chromatography (3:1 hexane/EtOAc) afforded **2da** as a colorless oil (93.5 mg, 95%): ^{1}H NMR ($CDCl_3$) δ 2.49 (s, 3H, Ar*CH*$_3$), 2.81-2.92 (m, 4H, Ar*CH*$_2$–), 6.86 (m, 1H, Ar*H*), 6.93 (s, 1H, Ar*H*), 7.12-7.28 (m, 5H, Ar*H*), 8.34 (d, *J* = 5.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 24.3, 36.6, 37.1, 121.0, 123.4, 126.2, 128.4, 128.5, 140.9, 149.0, 150.8, 158.3; IR (neat) 3027 w, 2925 m, 2859, 1604 s, 1561 m, 1496 w, 1453 m, 1408 w, 819 w, 751 w, 699 m cm^{-1}; HRMS (ESI) calcd for $[M+H]^+$ ($C_{14}H_{16}N$) *m*/*z* 198.12827. Found 198.12847.

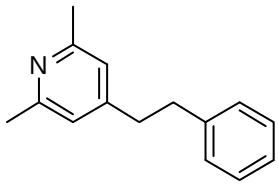
2-Phenyl- 4-(2-phenylethyl)pyridine (2ea)



2ea

General procedure B was followed with 4-(2-methoxyethyl)-2-phenylpyridine (**1e**, 107 mg) and triphenylboroxin (**5a**, 103 mg). Column chromatography (9:1 hexane/EtOAc) and Kugelrohr distillation afforded **2ea** as a pale yellow oil (68.3 mg, 52%). ^{1}H NMR ($CDCl_3$) δ 2.99 (s , 4H, Ar*CH*$_2$–), 7.04 (d, *J* = 4.9 Hz, 1H, Ar*H*), 7.16-7.33 (m, 5H, Ar*H*), 7.38-7.51 (m, 4H, Ar*H*), 7.92-7.96 (m, 2H, Ar*H*), 8.57 (d, *J* = 4.9 Hz, 1H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 36.7, 37.3, 120.9, 122.4, 126.3, 126.9, 128.5, 128.5, 128.7, 128.8, 139.5, 140.7, 149.6, 151.2, 157.5; IR (neat) 3085 w, 3061 m, 3027 m, 2927 m, 2859 w, 1599 s, 1555 s, 1494 m, 1475 m, 1446 s, 1405 m, 1300 w, 1188 m, 1162 w, 1075 w, 1028 w, 961 m, 839 w, 779 w, 752 m, 741 m, 697 s, 669 w, 637 w, 589 w cm^{-1}; HRMS (ESI) calcd for $[M+H]^+$ ($C_{19}H_{18}N$) *m*/*z* 260.14392. Found 260.14317.

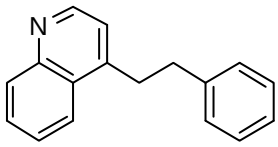
2,6-Dimethyl-4-(2-phenylethyl)pyridine (2fa)



2fa

General procedure B was followed with 2,6-dimethyl-4-(2-methoxyethyl)pyridine (**1f**, 82.6 mg) and triphenylboroxin (**5a**, 103 mg). Column chromatography (4:1 hexane/EtOAc) afforded **2fa** as a pale yellow oil (46.7 mg, 44%). ^{1}H NMR spectroscopic data are in good agreement with those reported in literature.[4]

4-(2-Phenylethyl)quinoline (2ga)

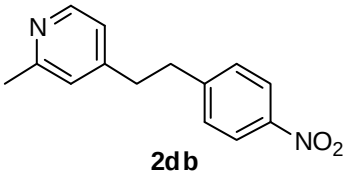


2ga

General procedure B was followed with 4-(2-methoxyethyl)quinoline (**1g**, 93.6 mg) and triphenylboroxin (**5a**, 103 mg). Column chromatography (4:1 hexane/EtOAc) afforded **2ga** as a colorless powder (49.9 mg, 43%). M.p. 96-97 °C. ^{1}H NMR ($CDCl_3$) δ 3.05-3.12 (m, 2H, Ph*CH*$_2$–), 3.36-3.44 (m, 2H, Ar*CH*$_2$–), 7.18-7.33 (m, 6H, Ar*H*), 7.56-7.74 (m, 2H, Ar*H*), 8.07-8.15 (m, 2H, Ar*H*), 8.79 (d, *J* = 4.5 Hz, 1H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 34.1, 36.2, 120.9, 123.4, 126.3, 126.4, 127.4, 128.4, 128.5, 129.1, 130.3, 141.0, 147.4, 148.3, 150.2; IR (KBr) 3025 w, 2955 w, 2928 w, 1593 s, 1509 w, 1491

w, 1455 w, 1426 w, 1414 w, 1160 w, 865 w, 848 s, 772 m, 754 s, 742 s, 704 s cm^{-1}; HRMS (ESI) calcd for $[M+H]^+$ ($C_{17}H_{16}N$) *m*/*z* 234.12827. Found 234.12945.

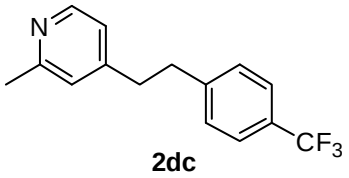
2-Methyl-4-[2-(4-nitrophenyl)ethyl]pyridine (2db)



2db

General procedure A was followed with 4-(2-methoxyethyl)-2-methylpyridine (**1d**, 75.6 mg) and tris(4-nitrophenyl)boroxin (**5b**, 147 mg). Column chromatography (3:1 hexane/EtOAc) afforded **2db** as a yellow oil (107 mg, 88%). ^{1}H NMR ($CDCl_3$) δ 2.52 (s, 3H, Ar*CH*$_3$), 2.89-2.93 (m, 2H, Ar*CH*$_2$–), 3.02-3.06 (m, 2H, Ar*CH*$_2$–), 6.87 (d, *J* = 5.2 Hz, 1H, Ar*H*), 6.94 (s, 1H, Ar*H*), 7.30 (d, *J* = 8.6 Hz, 2H, Ar*H*), 8.14 (d, *J* = 8.6 Hz, 2H, Ar*H*), 8.39 (d, *J* = 5.2 Hz, 1H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 24.4, 36.3, 36.4, 120.9, 123.3, 123.8, 129.3, 146.6, 148.5, 149.2, 149.6, 158.6; IR (neat) 3387 w br, 3077 m, 3055 m, 3012 m, 2928 m, 2859 m, 2451 w, 1926 w, 1605 s, 1562 s, 1514 s, 1450 m, 1407 m, 1345 s, 1180 w, 1110 s, 1038 w, 1016 m, 997 w, 929 w, 884 w, 856 s, 767 w, 750 m, 698 m, 658 w cm^{-1}; HRMS (ESI) calcd for $[M+H]^+$ ($C_{14}H_{15}N_2O_2$) *m*/*z* 243.11335. Found 243.11372.

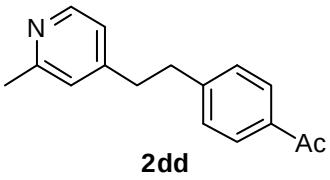
2-Methyl-4-[2-{4-(trifluoromethyl)phenyl}ethyl]pyridine (2dc)



2dc

General procedure A was followed with 4-(2-methoxyethyl)-2-methylpyridine (**1d**, 75.6 mg) and tris(4-trifluoromethylphenyl)boroxin (**5c**, 170 mg). Column chromatography (3:1 hexane/EtOAc) afforded **2dc** as a yellow oil (123 mg, 93%). ^{1}H NMR ($CDCl_3$) δ 2.52 (s, 3H, Ar*CH*$_3$), 2.86-3.00 (m, 4H, Ar*CH*$_2$–), 6.87-6.89 (m, 1H, Ar*H*), 6.94 (s, 1H, Ar*H*), 7.25 (d, *J* = 7.9 Hz, 2H, Ar*H*), 7.54 (d, *J* = 7.9 Hz, 2H, Ar*H*), 8.38 (d, *J* = 5.2 Hz, 1H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 24.4, 36.4, 36.6, 120.9, 123.4, 125.4, 125.4, 128.7, 144.9, 149.2, 150.1, 158.5; ^{19}F NMR ($CDCl_3$) δ –62.3; IR (neat) 2928 w, 1605 s, 1562 w, 1417 w, 1325 s, 1164 s, 1124 s, 1067 s, 1019 m, 836 m cm^{-1}; HRMS (ESI) calcd for $[M+H]^+$ ($C_{15}H_{15}NF_3$) *m*/*z* 266.11566. Found 266.11794.

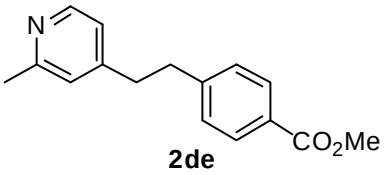
4-[2-(4-Acetylphenyl)ethyl]-2-methylpyridine (2dd)



2dd

General procedure A was followed with 4-(2-methoxyethyl)-2-methylpyridine (**1d**, 75.6 mg) and tris(4-acethylphenyl)boroxin (**5d**, 145 mg). Column chromatography (4:1 hexane/EtOAc) afforded **2dd** as and pale yellow oil (114 mg, 95%). ^{1}H NMR ($CDCl_3$) δ 2.52 (s, 3H, C(O)*CH*$_3$), 2.59 (s, 3H, Ar*CH*$_3$), 2.87-3.03 (m, 4H, Ar*CH*$_2$–), 6.88 (d, *J* = 5.2 Hz, 1H, Ar*H*), 6.95 (s, 1H, Ar*H*), 7.24 (d, *J* = 8.1 Hz, 2H, Ar*H*), 7.88 (d, *J* = 8.1 Hz, 2H, Ar*H*), 8.38 (d, *J* = 5.2 Hz, 1H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 24.3, 26.6, 36.5, 36.5, 120.9, 123.4, 128.6, 128.6, 135.4, 146.5, 149.1, 150.1, 158.4, 197.8; IR (neat) 3346 w br, 3006 m, 2926 m, 2862 w, 1677 s, 1605 s, 1562 s, 1480 w, 1412 s, 1358 s, 1302 m, 1269 s, 1183 s, 1114 w, 1018 m, 997 w, 957 m, 929 w, 883 w, 832 s, 694 w, 665 w, 614 m, 595 s, 567 m cm^{-1}; HRMS (ESI) calcd for $[M+H]^+$ ($C_{16}H_{18}NO$) *m*/*z* 240.13884. Found 240.13859.

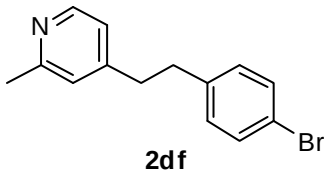
Methyl 4-[2-(2-methyl-4-pyridinyl)ethyl]benzoate (2de)



2de

General procedure A was followed with 4-(2-methoxyethyl)-2-methylpyridine (**1d**, 75.6 mg) and tris(4-methoxycarbonylphenyl)boroxin (**5e**, 242 mg, 0.5 mmol). Column chromatography (3:1 hexane/EtOAc) and Kugelrohr distillation afforded **2de** as a yellow solid (90.6 mg, 71%): M.p. 59-60 °C; ^{1}H NMR ($CDCl_3$) δ 2.50 (s, 3H, Ar*CH*$_3$), 2.85-2.98 (m, 4H, Ar*CH*$_2$–), 3.89 (s, 3H, –C(=O)O*CH*$_3$), 6.86 (d, *J* = 5.2 Hz, 1H, Ar*H*), 6.93 (s, 1H, Ar*H*), 7.20 (d, *J* = 8.5 Hz, 2H, Ar*H*), 7.94 (d, *J* = 8.5 Hz, 2H, Ar*H*), 8.35 (d, *J* = 5.2 Hz, 1H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 24.4, 36.6, 36.6, 52.1, 120.9, 123.4, 128.3, 128.5, 129.8, 146.2, 149.1, 150.2, 158.4, 167.0; IR (KBr) 3038 w, 3006 w, 2951 w, 2927 w, 2863 w, 1717 s, 1606 s, 1556 w, 1487 w, 1434 m, 1414 m, 1286 s, 1175 m, 1109 s, 1098 m, 1021 m, 995 w, 958 w, 928 w, 848 m, 830 m, 805 w, 767 m, 735 w, 702 m, 657 w, 584 w, 561 w, 543 w cm^{1}; HRMS (ESI) calcd for $[M+H]^+$ ($C_{16}H_{18}NO_2$) *m*/*z* 256.13375. Found 256.13354.

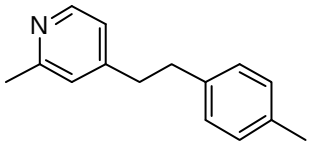
4-[2-(4-Bromophenyl)ethyl]-2-methylpyridine (2df)



2df

General procedure A was followed with 4-(2-methoxyethyl)-2-methylpyridine (**1d**, 75.6 mg) and tris(4-bromophenyl)boroxin (**5f**, 181 mg). Column chromatography (3:1 hexane/EtOAc) afforded **2df** as a pale yellow oil (125 mg, 91%): ^{1}H NMR ($CDCl_3$) δ 2.52 (s, 3H, Ar*CH*$_3$), 2.80-2.90 (m, 4H, Ar*CH*$_2$–), 6.87 (d, *J* = 4.9 Hz, 1H, Ar*H*), 6.94 (s, 1H, Ar*H*), 6.99-7.03 (m, 2H, Ar*H*), 7.38-7.41 (m, 2H, Ar*H*), 8.37 (d, *J* = 4.9 Hz, 1H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 24.4, 36.0, 36.8, 120.0, 121.0, 123.4, 130.1, 131.5, 139.7, 149.1, 150.2, 158.4; IR (neat) 3011 w, 2925 m, 2861 w, 1605 s, 1562 m, 1488 s, 1452 m, 1444 m, 1403 m, 1296 w, 1190 w, 1098 w, 1072 m, 1011 s, 928 w, 881 w, 828 m, 770 w, 651 w cm^{-1}; HRMS (ESI) calcd for $[M+H]^+$ ($C_{14}H_{15}NBr$) *m*/*z* 276.03879. Found 276.03728.

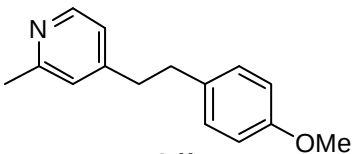
2-Methyl-4-[2-(4-methylphenyl)ethyl]pyridine (2dg)



2dg

General procedure A was followed with 4-(2-methoxyethyl)-2-methylpyridine (**1d**, 75.6 mg) and tris(4-methylphenyl)boroxin (**5g**, 117 mg). Column chromatography (3:1 hexane/EtOAc) afforded **2dg** as a colorless oil (102 mg, 97%). ^{1}H NMR ($CDCl_3$) δ 2.33 (s, 3H, Ar*CH*$_3$), 2.52 (s, 3H, Ar*CH*$_3$), 2.82-2.91 (m, 4H, Ar*CH*$_2$–), 6.89-6.91 (m, 1H, Ar*H*), 6.97 (s, 1H, Ar*H*), 7.04-7.11 (m, 4H, Ar*H*), 8.37 (d, *J* = 5.2 Hz, 1H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 21.0, 24.3, 36.2, 37.2, 121.0, 123.5, 128.3, 129.1, 135.7, 137.8, 149.0, 151.0, 158.2; IR (neat) 3048 w, 3009 w, 2923 m, 2859 w, 1604 s, 1562 w, 1515 m, 1450 w, 1444 w, 1408 w, 1296 w, 828 m, 808 m cm^{-1}; HRMS (ESI) calcd for $[M+H]^+$ ($C_{15}H_{18}N$) *m*/*z* 212.14392. Found 212.14449.

4-[2-(4-Methoxyphenyl)ethyl]-2-methylpyridine (2dh)

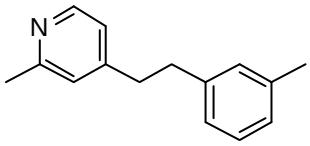


2dh

General procedure A was followed with 4-(2-methoxyethyl)-2-methylpyridine (**1d**, 75.6 mg) and tris(4-methoxyphenyl)boroxin (**5h**, 133 mg). Column chromatography (3:1 hexane/EtOAc) afforded **2dh** as a pale

yellow oil (58.3 mg, 51%). ^{1}H NMR ($CDCl_3$) δ 2.51 (s, 3H, Ar*CH*$_3$), 2.80-2.89 (m, 4H, Ar*CH*$_2$–), 3.79 (s, 3H, –O*CH*$_3$), 6.80-6.84 (m, 2H, Ar*H*), 6.88 (d, *J* = 4.7 Hz, 1H, Ar*H*), 6.95 (s, 1H, Ar*H*), 7.04-7.08 (m, 2H, Ar*H*), 8.36 (d, *J* = 5.1 Hz, 1H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 24.3, 35.8, 37.3, 55.3, 113.8, 121.1, 123.5, 129.3, 133.0, 149.0, 150.9, 158.0, 158.2; IR (neat) 3006 m, 2931 m, 2858 w, 2835 w, 1605 s, 1562 m, 1513 s, 1453 m, 1408 w, 1300 m, 1247 s, 1178 m, 1105 w, 1037 s, 997 w, 880 w, 831 s, 743 w, 697 w cm^{-1}; HRMS (ESI) calcd for $[M+H]^+$ ($C_{15}H_{18}NO$) *m*/*z* 228.13884. Found 228.13921.

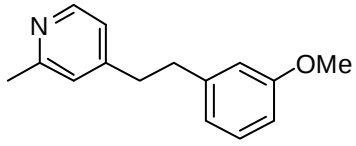
2-Methyl-4-[2-(3-methylphenyl)ethyl]pyridine (2di)



2di

General procedure A was followed with 4-(2-methoxyethyl)-2-methylpyridine (**1d**, 75.6 mg) and tris(3-methylphenyl)boroxin (**5i**, 117 mg). Column chromatography (3:1 hexane/EtOAc) afforded **2di** as a colorless oil (101 mg, 96%). ^{1}H NMR ($CDCl_3$) δ 2.33 (s, 3H, Ar*CH*$_3$), 2.52 (s, 3H, Ar*CH*$_3$), 2.87 (s, 4H, Ar*CH*$_2$–), 6.90-7.04 (m, 5H, Ar*H*), 7.18 (t, *J* = 7.5 Hz, 1H, Ar*H*), 8.37 (d, *J* = 4.9 Hz, 1H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 21.4, 24.3, 36.6, 37.1, 121.0, 123.5, 125.3, 126.9, 128.3, 129.2, 138.0, 140.8, 148.9, 151.0, 168.2; IR (neat) 3012 m, 2923 n, 2860 m, 1606 s, 1562 m, 1485 m, 1452 m, 1408 m, 1296 w, 1038 w, 997 w, 883 w, 832 m, 792 m, 778 m, 699 m cm^{-1}; HRMS (ESI) calcd for $[M+H]^+$ ($C_{15}H_{18}N$) *m*/*z* 212.14392. Found 212.14414.

4-[2-(3-Methoxyphenyl)ethyl]-2-methylpyridine (2dj)

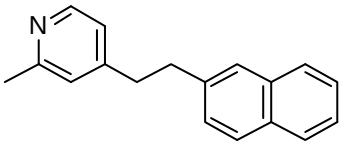


2dj

General procedure A was followed with 4-(2-methoxyethyl)-2-methylpyridine (**1d**, 75.6 mg) and tris(3-methoxyphenyl)boroxin (**5j**, 133 mg). Column chromatography (3:1 hexane/EtOAc) and Kugelrohr distillation afforded **2dj** as a pale yellow oil (98.9 mg, 87%). ^{1}H NMR ($CDCl_3$) δ 2.52 (s, 3H, Ar*CH*$_3$), 2.84-2.92 (m, 4H, Ar*CH*$_2$–), 3.78 (s, 3H, –O*CH*$_3$), 6.70-6.77 (m, 3H, Ar*H*), 6.89-6.91 (m, 1H, Ar*H*), 6.97 (s, 1H, Ar*H*), 7.20 (t, *J* = 7.8 Hz, 1H, Ar*H*), 8.37 (d, *J* = 5.2 Hz, 1H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 24.4, 36.6, 36.9, 55.1, 111.4, 114.2, 120.8, 121.0, 123.4, 129.4, 142.5, 149.0, 150.7, 158.3, 159.7; IR (neat) 3388 w, 3006 m, 2938 m, 2860 w, 2835

m, 1604 s, 1585 s, 1561 m, 1490 s, 1454 s, 1440 s, 1408 m, 1260 s, 1190 w, 1153 s, 1152 m, 996 w, 920 w, 874 w, 833 w, 788 m, 696 m cm^{-1}; HRMS (ESI) calcd for $[M+H]^+$ ($C_{15}H_{18}NO$) *m*/*z* 228.13884. Found 228.13890.

2-Methyl-4-[2-(2-naphthyl)ethyl]pyridine (2dl)



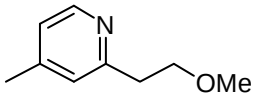
2dl

General procedure A was followed with 4-(2-methoxyethyl)-2-methylpyridine (**1d**, 75.6 mg) and tris(2-naphthyl)boroxin (**5l**, 152 mg). Column chromatography (3:1 hexane/EtOAc) afforded **2dl** as a yellow solid (113 mg, 91%). M.p. 61-62 °C. ^{1}H NMR ($CDCl_3$) δ 2.52 (s, 3H, Ar*CH*$_3$), 2.94-2.98 (m, 2H, Ar*CH*$_2$–), 3.06-3.10 (m, 2H, Ar*CH*$_2$–), 6.91-6.93 (m, 1H, Ar*H*), 6.99 (s, 1H, Ar*H*), 7.31 (dd, 1H, *J* = 8.4, 1.7 Hz, Ar*H*), 7.41-7.49 (m, 2H, Ar*H*), 7.59 (s, 1H, Ar*H*), 7.76-7.84 (m, 3H, Ar*H*), 8.37 (d, *J* = 4.7 Hz, 1H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 24.3, 36.8, 36.9, 121.0, 123.5, 125.4, 126.0, 126.5, 127.1, 127.4, 127.6, 128.0, 132.1, 133.5, 138.4, 149.0, 150.7, 158.3; IR (neat) 3386 w br, 3051 m, 3013 m, 2925 m, 2858 m, 1605 s, 1561 m, 1508 m, 1453 m, 1408 m, 1371 w, 1296 w, 1271 w, 1168 w, 1125 w, 1017 w, 997 w, 960 w, 928 w, 892 m, 855 m, 819 s, 747 s, 650 w, 625 w, cm^{-1}; HRMS (ESI) calcd for $[M+H]^+$ ($C_{18}H_{18}N$) *m*/*z* 248.14392. Found 248.14442.

General Procedure C for Synthesis of 2-(2-Methoxyethyl)pyridines

A THF solution of a pyridine derivative in a three-necked flask was cooled to –78 °C, and a hexane solution of 1.1 equiv of BuLi was added dropwise through a dropping funnel. After the completion of the addition, the mixture was stirred for 1 h at –78 °C. Then, a THF solution of 1.5 equiv of MOMCl was added dropwise to the resulting mixture through the dropping funnel. The mixture was gradually warmed to rt and stirred for 12 h. A saturated aqueous solution of $NaHCO_3$ was added to the reaction mixture, which was then extracted three times with Et_2O. The combined organic layers were washed with brine and dried over Na_2SO_4. After removal of volatile materials by rotary evaporation, the crude material was purified by silica gel column chromatography and Kugelrohr distillation.

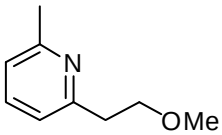
2-(2-Methoxyethyl)-4-methylpyridine (1b)



1b

General Procedure C was followed 2,4-dimethylpyridine (3.21 g). Column chromatography (1:1 hexane/EtOAc) and Kugelrohr distillation afforded **1b** as a colorless oil (1.99 g, 44%): ^{1}H NMR ($CDCl_3$) δ 2.32 (s, 3H, Ar*CH*$_3$), 3.01 (t, *J* = 6.7 Hz, 2H, Ar*CH*$_2$-), 3.35 (s, 3H, –O*CH*$_3$), 3.76 (t, *J* = 6.7 Hz, 2H, ArCH$_2$*CH*$_2$–), 6.94 (d, *J* = 4.9 Hz, 1H, Ar*H*), 7.02 (s, 1H, Ar*H*), 8.39 (d, *J* = 4.9 Hz, 1H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 21.0, 38.4, 58.7, 72.0, 122.4, 124.4, 147.4, 149.1, 158.9; IR (neat) 2925 m, 2876 w, 2824 w, 1606 s, 1563 w, 1480 w, 1449 w, 1379 w, 1191 w, 1118 s, 820 w cm^{-1}; HRMS (APCI) calcd for $[M+H]^+$ ($C_9H_{14}NO$) *m*/*z* 152.10754. Found 152.10752.

2-(2-Methoxyethyl)-6-methylpyridine (1c)



1c

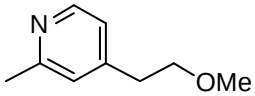
General Procedure C was followed with 2,6-dimethylpyridine (3.21 g). Silica gel column chromatography (4:1 hexane/EtOAc), and Kugelrohr distillation afforded **1c** as a colorless oil (903 mg, 20%): ^{1}H NMR ($CDCl_3$) δ 2.53 (s, 3H, Ar*CH*$_3$), 3.02 (t, *J* = 6.7 Hz, 2H, Ar*CH*$_2$-), 3.35 (s, 3H, –O*CH*$_3$), 3.75 (t, *J* = 6.7 Hz, 2H, ArCH$_2$*CH*$_2$–), 6.98 (d, *J* = 7.6 Hz, 1H, Ar*H*), 7.01 (d, *J* = 7.6 Hz, 1H, Ar*H*), 7.48 (t, *J* = 7.6 Hz, 1H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 24.5, 38.7, 58.7, 72.2, 120.3, 120.9, 136.5, 157.9, 158.5; IR (neat) 2925 m, 2875 m, 1592 s, 1579 s, 1459 s, 1376 w, 1190 w, 1154 w, 1117 s, 780 w cm^{-1}; HRMS (APCI) calcd for $[M+H]^+$ ($C_9H_{14}NO$) *m*/*z* 152.10754. Found 152.10730.

General Procedure D for Synthesis of 4-(2-Alkoxyethyl)pyridines

A THF solution of a pyridine derivative in a three-necked flask was cooled to –78 °C, and a THF solution of 1.1 equiv of LDA, prepared separately, was added dropwise through a cannula. After the completion of the addition, the mixture was stirred for 1 h at –78 °C. Then, the resulting mixture was added dropwise to a THF solution of 1.5 equiv of MOMCl (or ethoxymethyl chloride) at –78 °C through a cannula. The mixture was gradually warmed to rt and stirred for 3-24 h. A saturated aqueous solution of $NaHCO_3$ was added to the reaction mixture, which was then extracted three times with Et_2O. The combined

organic layers were washed with brine and dried over Na_2SO_4. After removal of volatile materials by rotary evaporation, the crude material was purified by silica gel column chromatography and Kugelrohr distillation.

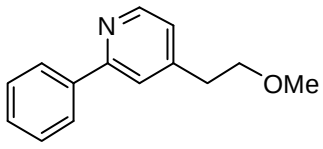
4-(2-Methoxyethyl)-2-methylpyridine (1d)



1d

General Procedure D was followed with 2,4-dimethylpyridine (3.21 g). Column chromatography (2:1 hexane/EtOAc) and Kugelrohr distillation afforded **1d** as a colorless oil (1.42 g, 31%). ^{1}H NMR ($CDCl_3$) δ 2.52 (s, 3H, Ar*CH*$_3$), 2.83 (t, *J* = 6.4 Hz, 2H, Ar*CH*$_2$-), 3.35 (s, 3H, –O*CH*$_3$), 3.61 (t, *J* = 6.4 Hz, 2H, ArCH$_2$*CH*$_2$–), 6.96 (d, *J* = 4.8 Hz, 1H, Ar*H*), 7.02 (s, 1H, Ar*H*), 8.38 (d, *J* = 4.8 Hz, 1H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 24.4, 35.5, 58.8, 72.3, 121.3, 123.8, 148.4, 149.1, 158.3; IR (neat) 3395 m br, 2983 w, 2926 m, 2875 m, 2827 w, 1607 s, 1562 m, 1481 w, 1450 w, 1409 w, 1383 w, 1214 w, 1190 w, 1116 s, 999 w, 970 w, 841 w, 620 w cm^{-1}; HRMS (ESI) calcd for $[M+H]^+$ ($C_9H_{14}NO$) *m*/*z* 152.10754. Found 152.10708.

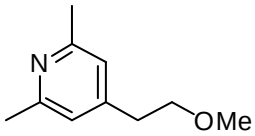
4-(2-Methoxyethyl)-2-phenylpyridine (1e)



1e

General Procedure D was followed with 4-methyl-2-phenylpyridine (1.69 g). Column chromatography (9:1 hexane/EtOAc) and Kugelrohr distillation afforded **1e** as a pale yellow oil (977 mg, 46%). ^{1}H NMR ($CDCl_3$) δ 2.94 (t, *J* = 6.6 Hz, 2H, Ar*CH*$_2$–), 3.37 (s, 3H, –O*CH*$_3$), 3.68 (t, *J* = 6.6 Hz, 2H, ArCH$_2$*CH*$_2$–), 7.11-7.12 (m, 1H, Ar*H*), 7.38-7.49 (m, 3H, Ar*H*), 7.59-7.60 (m, 1H, Ar*H*), 7.96-7.99 (m, 2H, Ar*H*), 8.58-8.60 (m, Ar*H*, 1H); ^{13}C NMR ($CDCl_3$) δ 35.8, 58.8, 72.3, 121.2, 122.7, 127.0, 128.7, 128.9, 139.5, 148.9, 149.6, 157.6; IR (neat) 3051 w, 2984 w, 2925 m, 2873 m, 2826 m, 1603 s, 1581 m, 1556 s, 1476 s, 1446 s, 1405 s, 1382 m, 1214 w, 1192 w, 1115 s, 1074 w, 1028 w, 991 w, 970 w, 843 w, 777 s, 735 m, 696 s, 637 m cm^{-1}; HRMS (ESI) calcd for $[M+H]^+$ ($C_{14}H_{16}NO$) *m*/*z* 214.12319. Found 214.12344.

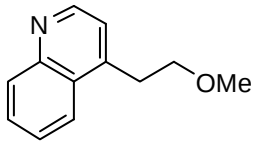
2,6-Dimethyl-4-(2-methoxyethyl)pyridine (1f)



1f

General Procedure D was followed with 2,4,6-trimethylpyridine (3.64 g). Column chromatography (3:1 hexane/EtOAc) and Kugelrohr distillation afforded **1f** as a colorless oil (187 mg, 4%). ^{1}H NMR ($CDCl_3$) δ 2.49 (s, 6H, Ar*CH*$_3$), 2.78 (t, *J* = 6.7 Hz, 2H, Ar*CH*$_2$–), 3.35 (s, 3H, –O*CH*$_3$), 3.60 (t, *J* = 6.7 Hz, 2H, ArCH$_2$*CH*$_2$–), 6.82 (s, 2H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 24.3, 35.4, 58.7, 72.3, 120.7, 148.5, 157.6; IR (neat) 3402 w br, 2986 w, 2925 m, 2873 m, 2827 w, 1610 s, 1569 s, 1437 m, 1383 m, 1220 w, 1192 w, 1116 s, 1032 w, 1003 w, 969 w, 858 w cm^{-1}; HRMS (ESI) calcd for $[M+H]^+$ ($C_{10}H_{16}NO$) *m*/*z* 166.12319. Found 166.12351.

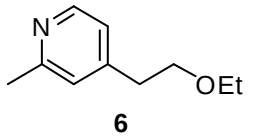
4-(2-Methoxyethyl)quinoline (1g)



1g

General Procedure D was followed with 4-methylquinoline (4.30 g). Column chromatography (2:1 hexane/EtOAc) and Kugelrohr distillation afforded **1g** as a pale yellow oil (1.15 g, 20%). ^{1}H NMR ($CDCl_3$) δ 3.36 (t, *J* = 6.7 Hz, 2H, Ar*CH*$_2$–), 3.38 (s, 3H, –O*CH*$_3$), 3.77 (t, *J* = 7.0 Hz, 2H, ArCH$_2$*CH*$_2$–), 7.29 (d, *J* = 4.4 Hz, 1H, Ar*H*), 7.57 (ddd, *J* = 8.5, 6.7, 1.3 Hz, 1H, Ar*H*), 7.71 (ddd, *J* = 8.5, 6.7, 1.3 Hz, 1H, Ar*H*), 8.04-8.07 (m, 1H, Ar*H*), 8.10-8.13 (m, 1H, Ar*H*), 8.82 (d, *J* = 4.5 Hz, 1H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 32.3, 58.8, 71.8, 121.4, 123.4, 126.4, 127.7, 129.1, 130.3, 144.9, 148.3, 150.1; IR (neat) 3394 w br, 3035 w, 2980 m, 2927 m, 2875 m, 2827 m, 1615 w, 1593 s, 1570 m, 1510 s, 1463 m, 1425 w, 1393 w, 1310 w, 1240 w, 1191 w, 1114 s, 1069 w, 1019 w, 996 w, 965 w, 848 m, 814 m, 762 s, 604 w cm^{-1}; HRMS (ESI) calcd for $[M+H]^+$ ($C_{12}H_{14}NO$) *m*/*z* 188.10754. Found 188.10843.

4-(2-Ethoxyethyl)-2-methylpyridine (6)

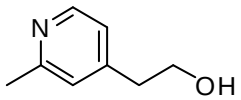


6

General Procedure D was followed with 2,4-dimethylpyridine (1.07 g) and (chloromethoxy)ethane as an electrophile. Column chromatography (3:1 hexane/EtOAc) and Kugelrohr distillation afforded **6** as a colorless oil (376 mg, 23%). ^{1}H NMR ($CDCl_3$) δ 1.91 (t, *J* = 7.0 Hz, 3H,

–OCH_2CH_3), 2.52 (s, 3H, ArCH_3), 2.83 (t, J = 7.0 Hz, 2H, ArCH_2–), 3.49 (q, J = 7.0 Hz, 2H, –$OCH_2$$CH_3$), 3.64 (t, J = 7.0 Hz, 2H, $ArCH_2CH_2$–), 6.96 (d, J = 5.1 Hz, 1H, ArH), 7.02 (s, 1H, ArH), 8.38 (d, J = 5.1 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$):δ 15.1, 24.3, 35.6, 66.4, 70.2, 121.3, 123.8, 148.5, 149.0, 158.2; IR (neat): 2976 m, 2935 m, 2866 m, 1606 s, 1561 w, 1483 w, 1445 w, 1406 w, 1377 w, 1354 w, 1110 s, 837 w, 620 w cm^{-1}; HRMS (ESI): Calcd for $[M+H]^+$ ($C_{10}H_{16}NO$) m/z 166.12319. Found 166.12306.

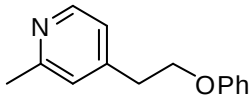
2-(2-Methyl-4-pyridinyl)ethanol (7)



7

A 500 mL three-necked flask equipped with a reflux condenser and a dropping funnel was charged with $LiAlH_4$ (0.95g, 25 mmol) and Et_2O (150 mL). A solution of methyl (2-methyl-4-pyridinyl)acetate (4.13 g, 25 mmol) in Et_2O (50 mL) was added dropwise through the dropping funnel at 0 °C. The mixture was warmed to rt and stirred for 3 h. Water (100 mL) was poured into the reaction mixture, and the resulting mixture was filtered through a pad of Celite®. The filtrate was extracted three times with Et_2O and three times with CH_2Cl_2. The combined organic layers were washed with brine and dried over Na_2SO_4. After removal of volatile materials by rotary evaporation, the crude material was purified by Kugelrohr distillation to afford **7** as an orange oil (2.36 g, 69%): ^{1}H NMR ($CDCl_3$) δ 2.47 (s, 3H, ArCH_3), 2.79 (t, J = 6.4 Hz, 2H, ArCH_2–), 3.87 (t, J = 6.4 Hz, 2H, $ArCH_2CH_2$–), 6.93-6.95 (m, 1H, ArH), 7.00 (s, 1H, ArH), 8.26 (d, J = 5.2 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$):δ 24.1, 38.6, 62.3, 121.5, 124.1, 148.7, 148.8, 158.1; IR (neat) 3238 s br, 2925 s, 2870 s, 1610 s, 1561 m, 1444 m, 1410 m, 1297 w, 1168 w, 1056 s, 1006 m, 831 m, 621 w cm^{-1}; HRMS (ESI) calcd for $[M+H]^+$ ($C_8H_{12}NO$) m/z 138.09189. Found 138.09213.

2-Methyl-4-(2-phenoxyethyl)pyridine (8)

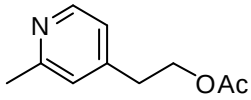


8

A 100 mL Schlenk flask was charged with 2-(2-methyl-4-pyridinyl)ethanol (**7**, 0.69 g, 5 mmol), phenol (0.52 g, 5.5 mmol), PPh_3 (1.57 g, 6 mmol), and THF (15 mL). A toluene solution of DEAD (*ca.* 2.2 mol/L, 2.95 mL, 6.5 mmol) was added at 0 °C and stirred for 3 h at rt. The resulting mixture was concentrated and purified by silica gel column

chromatography (9:1 hexane/EtOAc) and Kugelrohr distillation to afford **8** as a colorless oil (469 mg, 44%). ^{1}H NMR ($CDCl_3$) δ 2.54 (s, 3H, Ar*CH*$_3$), 3.05 (t, *J* = 6.6 Hz, 2H, Ar*CH*$_2$–), 4.19 (t, *J* = 6.6 Hz, 2H, ArCH$_2$*CH*$_2$–), 6.87-7.30 (m, 7H, Ar*H*), 8.41 (d, *J* = 4.9 Hz, 1H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 24.4, 35.0, 67.2, 114.5, 121.0, 121.4, 123.8, 129.5, 147.6, 149.2, 158.4, 158.5; IR (neat) 3063 w, 3040 w, 3013 w, 2951 w, 2926 w, 2873 w, 1599 s, 1587 m, 1562 w, 1498 s, 1474 m, 1410 w, 1388 w, 1292 w, 1244 s, 1173 w, 1080 w, 1039 m, 837 w, 757 s, 692 m cm^{-1}; HRMS (ESI) calcd for $[M+H]^+$ ($C_{14}H_{16}NO$) *m*/*z* 214.12319. Found 214.12273.

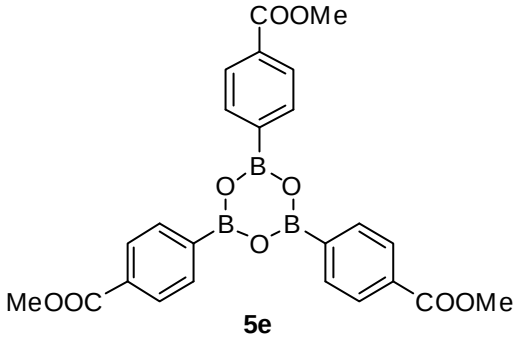
2-(2-Methyl-4-pyridinyl)ethyl acetate (9)



9

To a CH_2Cl_2 (30 mL) solution of 2-(2-methyl-4-pyridinyl)ethanol (**7**, 0.69 g, 5 mmol) in a 100 mL round bottom flask was added Ac_2O (0.94 mL, 10 mmol), Et_3N (2.08 mL, 15 mmol), and DMAP (61.1 mg, 0.5 mmol) at 0 °C, and the mixture was stirred for 1 h. A saturated aqueous solution of $NaHCO_3$ was poured into the resulting mixture, and extracted three times with EtOAc. The combined organic layers were washed with brine and dried over Na_2SO_4. After removal of volatile materials by rotary evaporation, the crude material was purified by silica gel column chromatography (1:1 hexane/EtOAc), and Kugelrohr distillation to afford **9** as a colorless oil (372 mg, 41%). ^{1}H NMR ($CDCl_3$) δ 2.04 (s, 3H, –C(=O)*CH*$_3$), 2.54 (s, 3H, Ar*CH*$_3$), 2.89 (t, *J* = 6.8 Hz, 2H, Ar*CH*$_2$–), 4.29 (t, *J* = 6.8 Hz, 2H, ArCH$_2$*CH*$_2$–), 6.94-6.96 (m, 1H, Ar*H*), 7.01 (s, 1H, Ar*H*), 8.41 (d, *J* = 5.16 Hz, 1H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 20.9, 24.4, 34.3, 63.6, 121.2, 123.6, 147.1, 149.2, 158.5, 170.9; IR (neat) 2960 w, 1738 s, 1607 s, 1563 w, 1441 w, 1410 w, 1384 m, 1365 m, 1235 s, 1038 s, 836 w, 669 w, 606 w cm^{-1}; HRMS (ESI) calcd for $[M+H]^+$ ($C_{10}H_{14}NO_2$) *m*/*z* 180.10245. Found 180.10280.

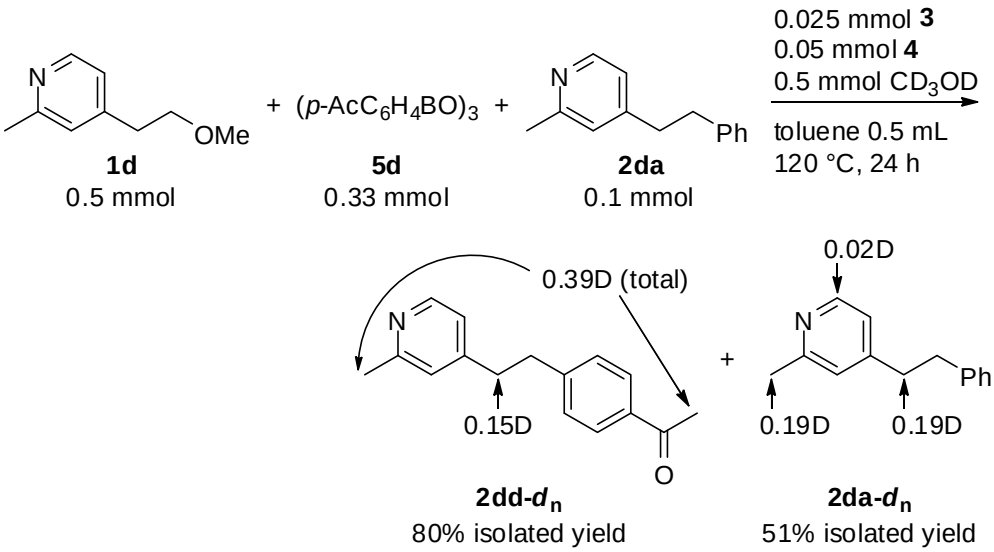
Tris(4-carbomethoxyphenyl)boroxin (5e)



5e

A 100 mL Schlenk flask connected to a trap filled with conc. H_2SO_4 (10 mL) was charged with (4-carbomethoxyphenyl)boronic acid (3.0 g, 16.7 mmol) and heated under vacuum (0.5 mmHg) at 100 °C for 10 h to afford **5e** as a colorless powder (2.3 g, 85%). ^{1}H NMR ($(CD_3)_2SO$) δ 3.86 (s, 9H, C(O)O*CH*$_3$), 7.97-8.03 (m, 12H, Ar*H*); ^{13}C NMR ($(CD_3)_2SO$) δ 52.1, 128.2, 130.5, 133.7, 143.8, 166.6.

Additional Deuterium-Labeling Experiments



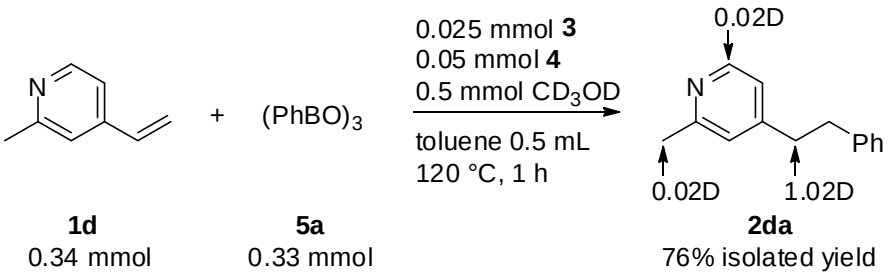
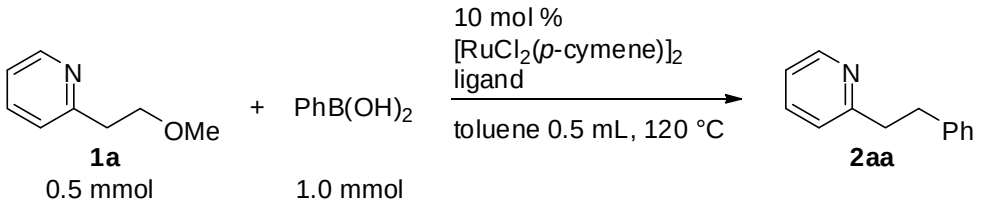


Table S1. Screening of Phosphorus Ligands.



1a 0.5 mmol — 1.0 mmol — **2aa**

entry	ligand	mol %	GC yield
1	PPh_3	20	16%
2	P(*o*-MeC_6H_4)$_3$	20	2%
3	P(*m*-MeC_6H_4)$_3$	20	9%
4	P(*p*-MeC_6H_4)$_3$	20	7%
5	P(*p*-$MeOC_6H_4$)$_3$	20	8%
6	$PPh(C_6F_5)_2$	20	4%
7	$PPhCy_2$	20	1%
8	PCy_3	20	2%
9	PEt_3	20	nd
10	P(2-furyl)$_3$	20	15%
11	$P(OMe)_3$	20	3%
12	$P(OEt)_3$	20	2%
13	$P(OPh)_3$	20	25%
14	$P(OPh)_3$	40	4%
15	$P(OPh)_3$	60	2%

References

1) Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233.
2) Lautens, M.; Roy, A.; Fukuoka, K.; Fagnou, K.; Martin-Matute, B. *J. Am. Chem. Soc.* **2001**, *123*, 5358.
3) Kawasuji, T.; Yoshinaga, T.; Sato, A.; Yodo, M.; Fujiwara, T.; Kiyama, R. *Bioorg. Med. Chem.* **2006**, *14*, 8430.
4) Compagnon, P.-L.; Kimny, T.; Gasquez, F. *Bull. Soc. Chim. Belg.* **1981**, *90*, 803.

2da
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2
4
6
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2.830
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2.852
2.862
2.873
2.884
2.889
2.892
2.905
2.917
4.000
2.951
0.951
0.951
5.095
0.950
6.860
6.861
6.863
6.864
6.874
6.876
6.877
6.932
7.120
7.122
7.133
7.139
7.141
7.143
7.158
7.161
7.174
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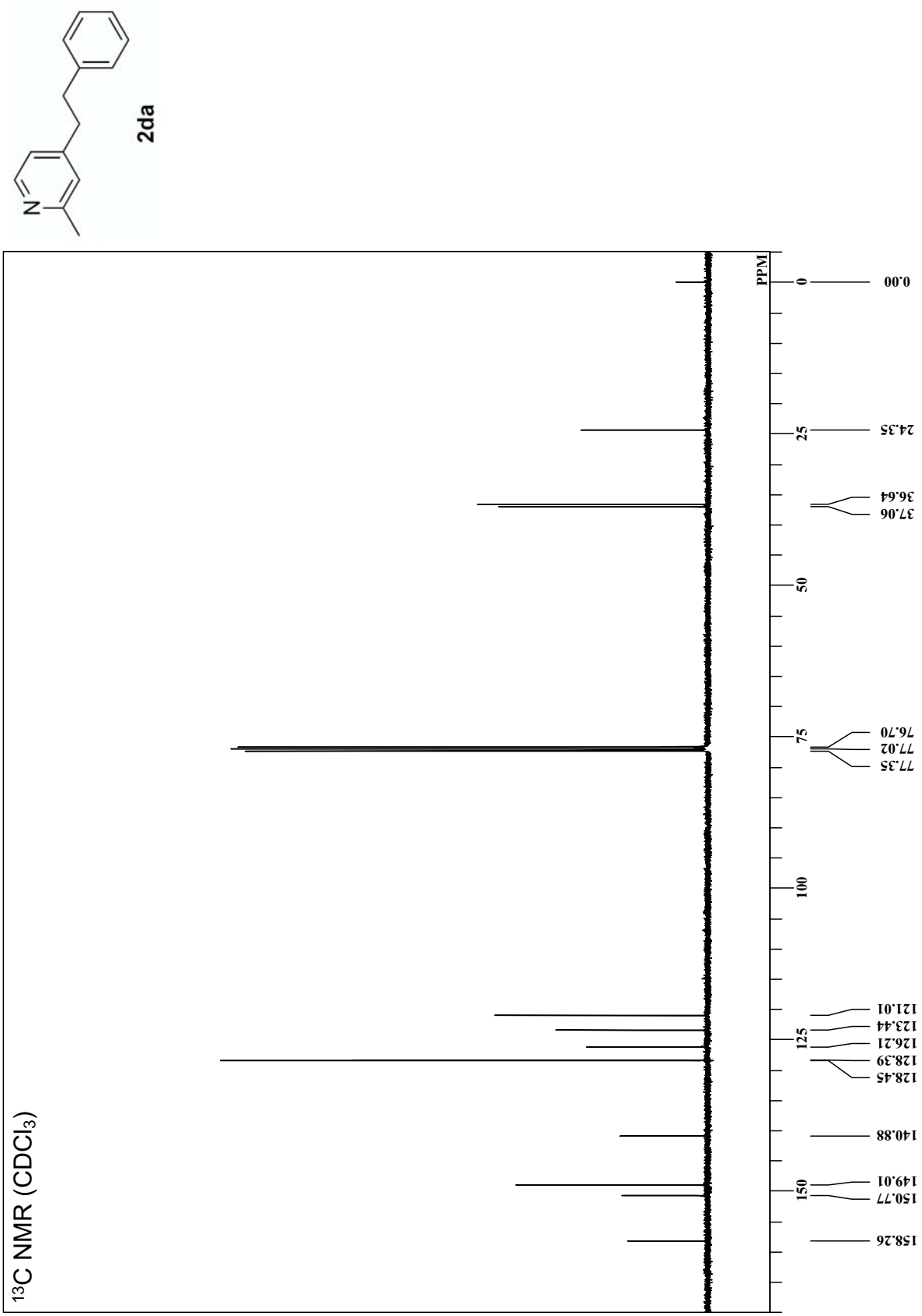
8.348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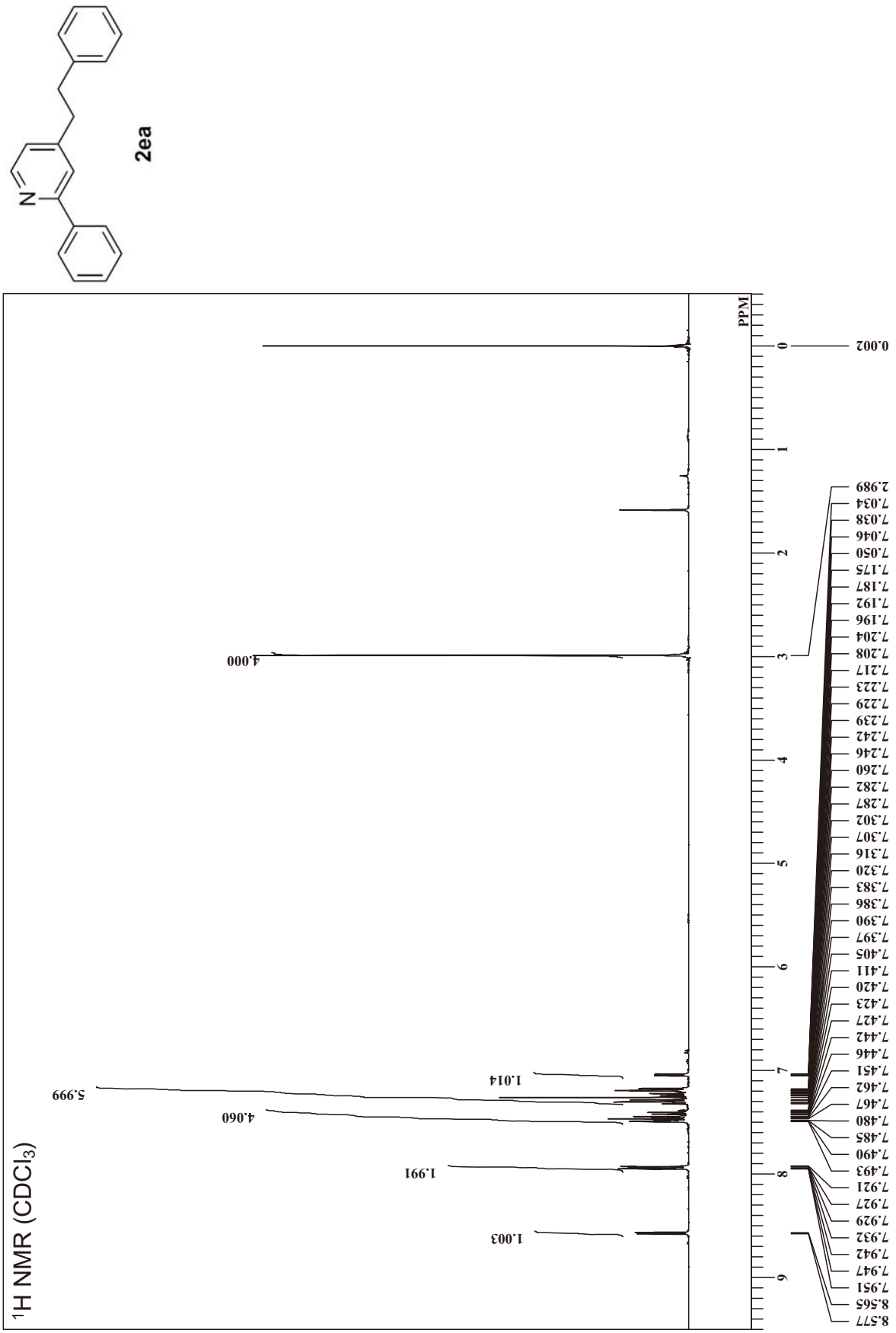
149.01
150.77
158.26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7.217
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7.246
7.260
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7.287
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7.307
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7.397
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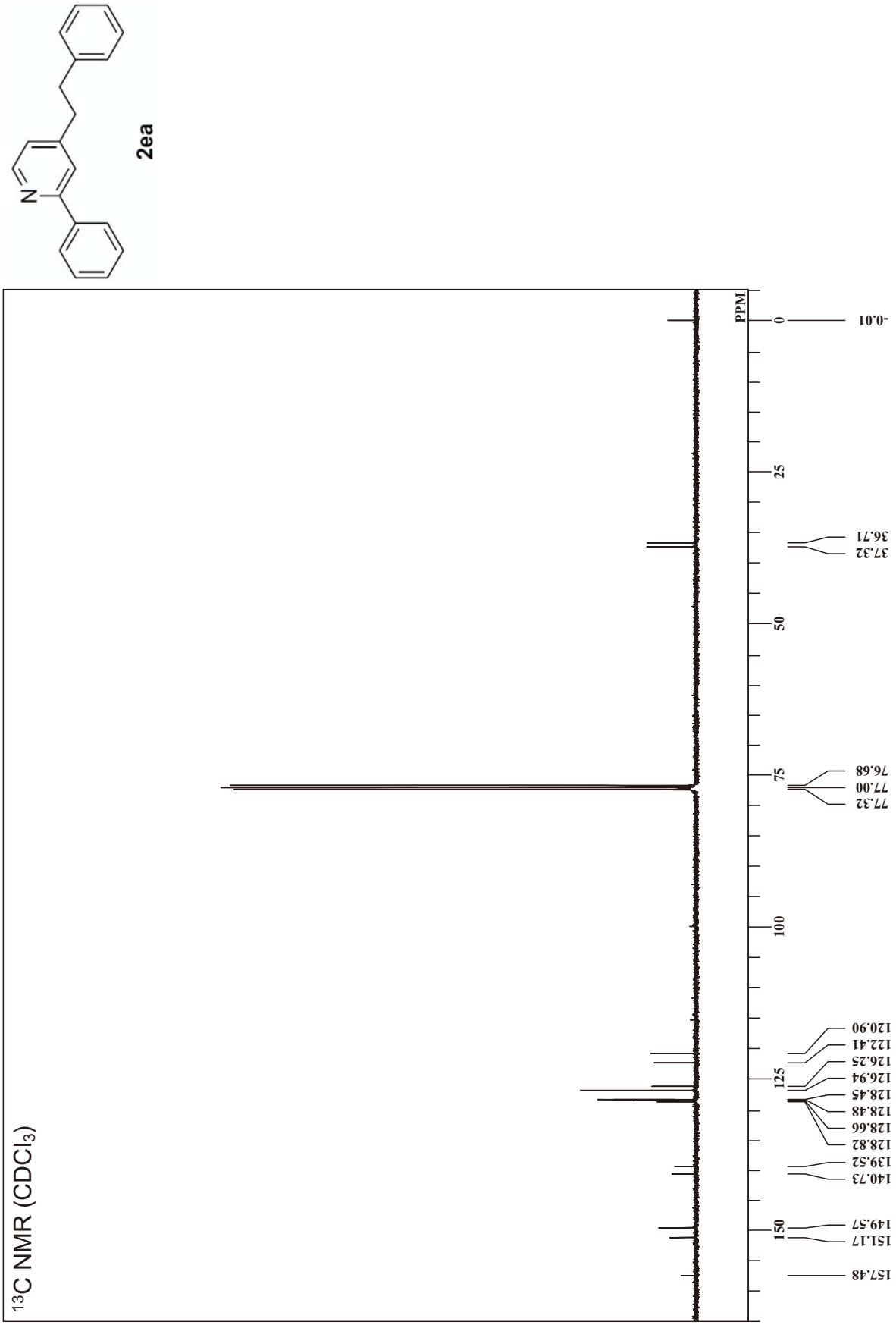
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75
100
125
150
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76.68
77.00
77.32
120.90
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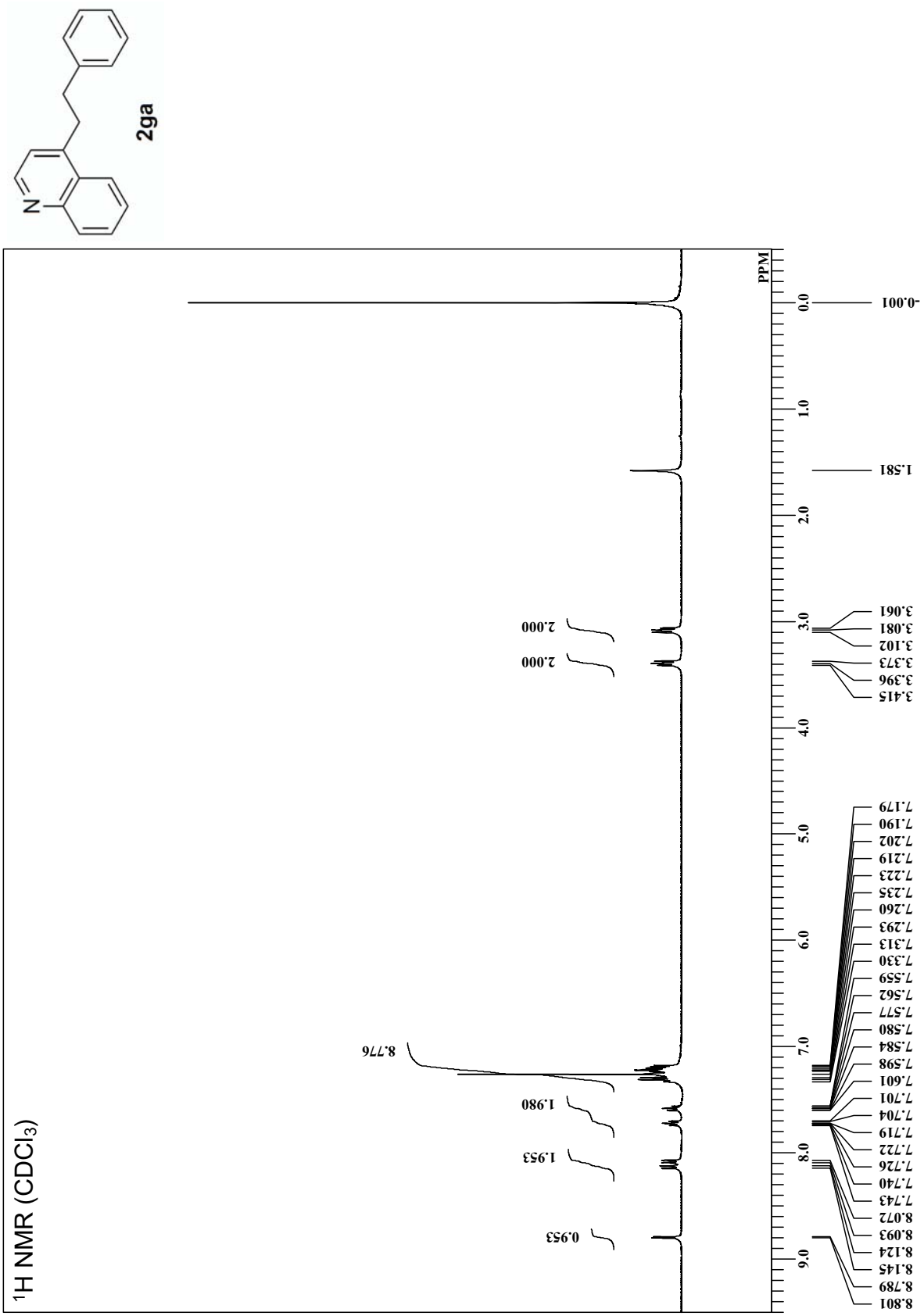
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3.081
3.102
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2.000
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7.202
7.219
7.223
7.235
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7.577
7.580
7.584
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7.701
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7.722
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7.740
7.743
8.072
8.093
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8.145
8.789
8.801

2ga
N
^{13}C NMR ($CDCl_3$)
PPM
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25
50
75
100
125
150
34.06
36.15
76.68
77.00
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120.87
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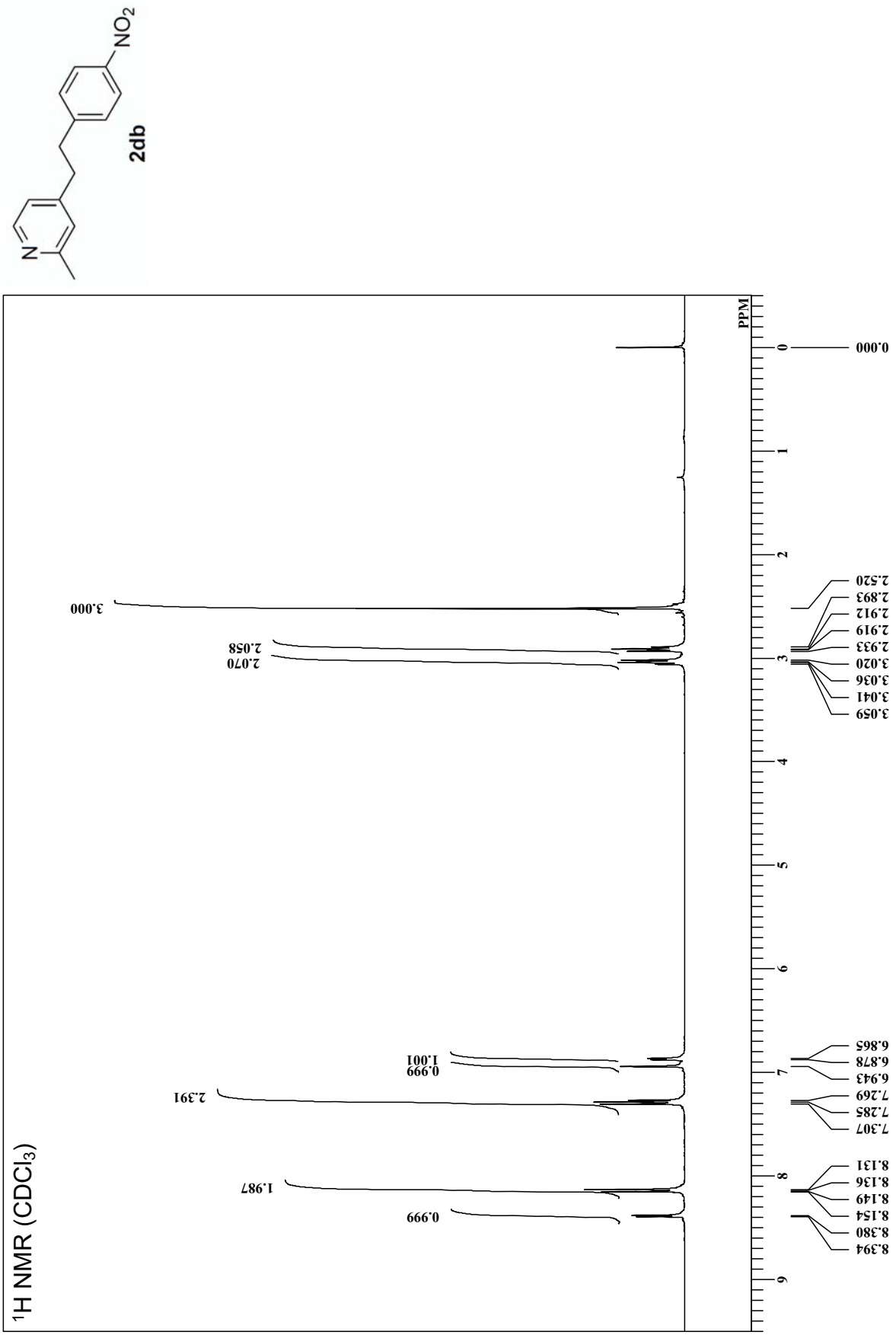
150.19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2.070
2.058
3.000
0.999
1.001
2.391
1.987
0.999
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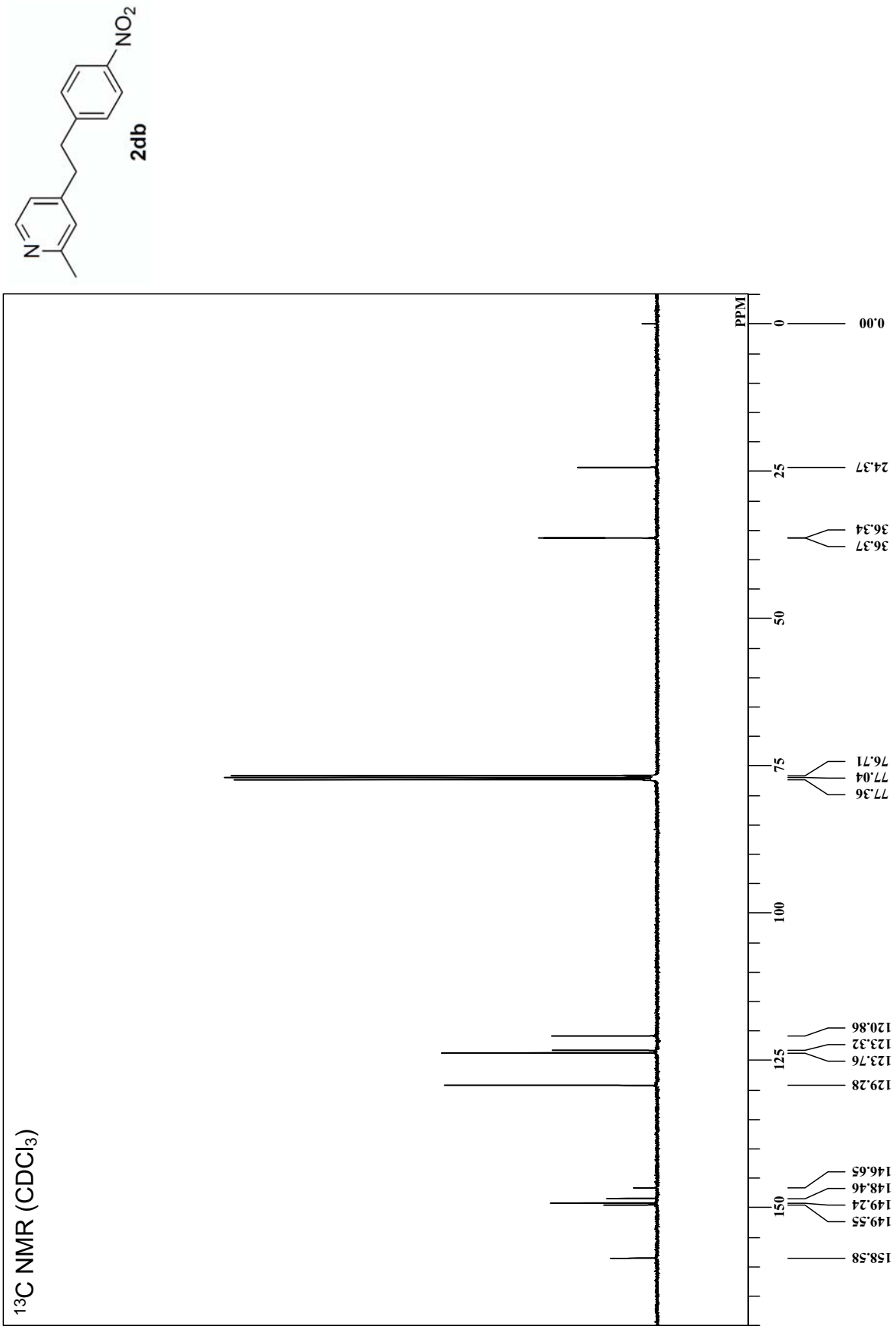
8.154
8.380
8.394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25
50
75
100
125
150
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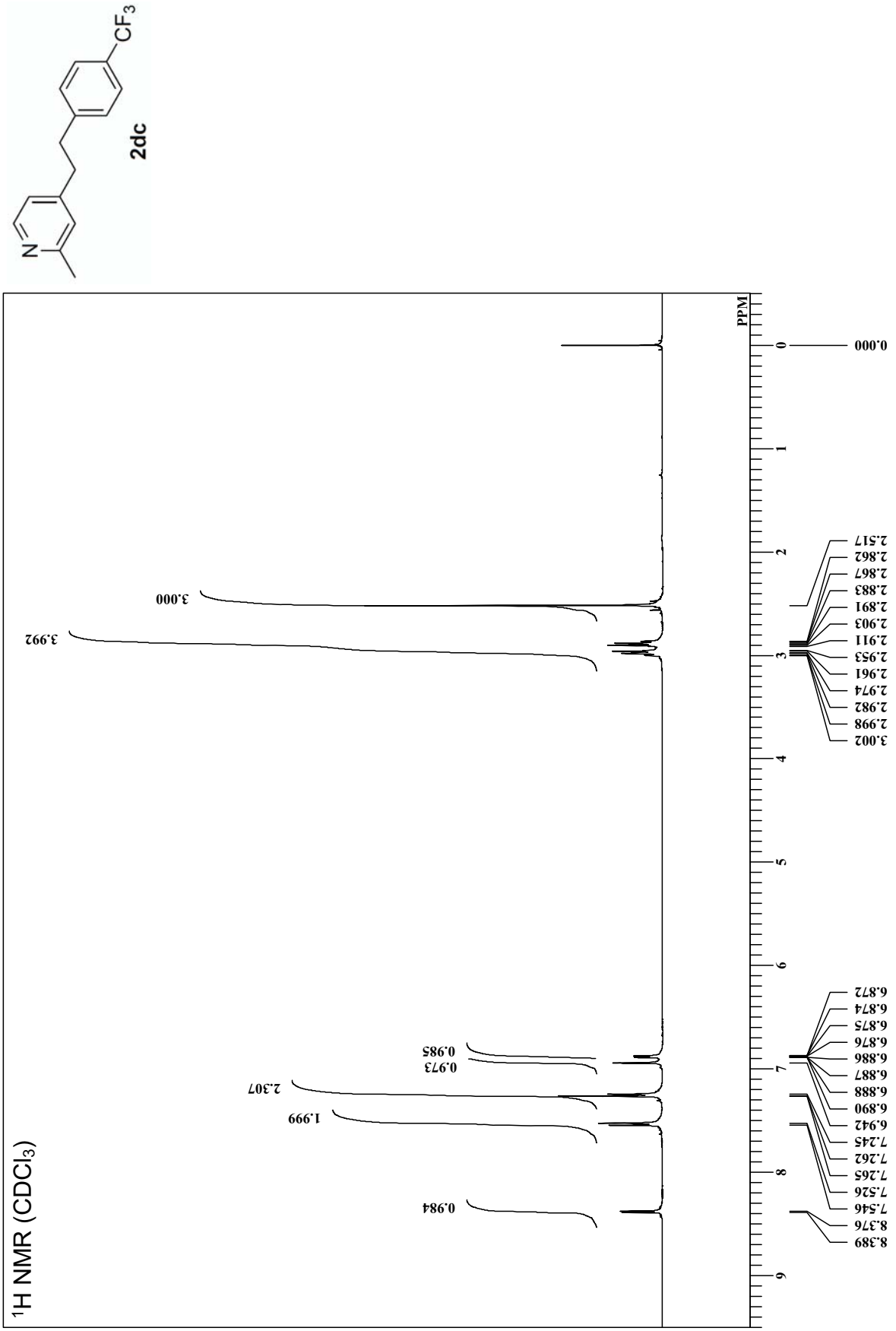
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2.911
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2.974
2.982
2.998
3.002
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6.874
6.875
6.876
6.886
6.887
6.888
6.890
6.942
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7.262
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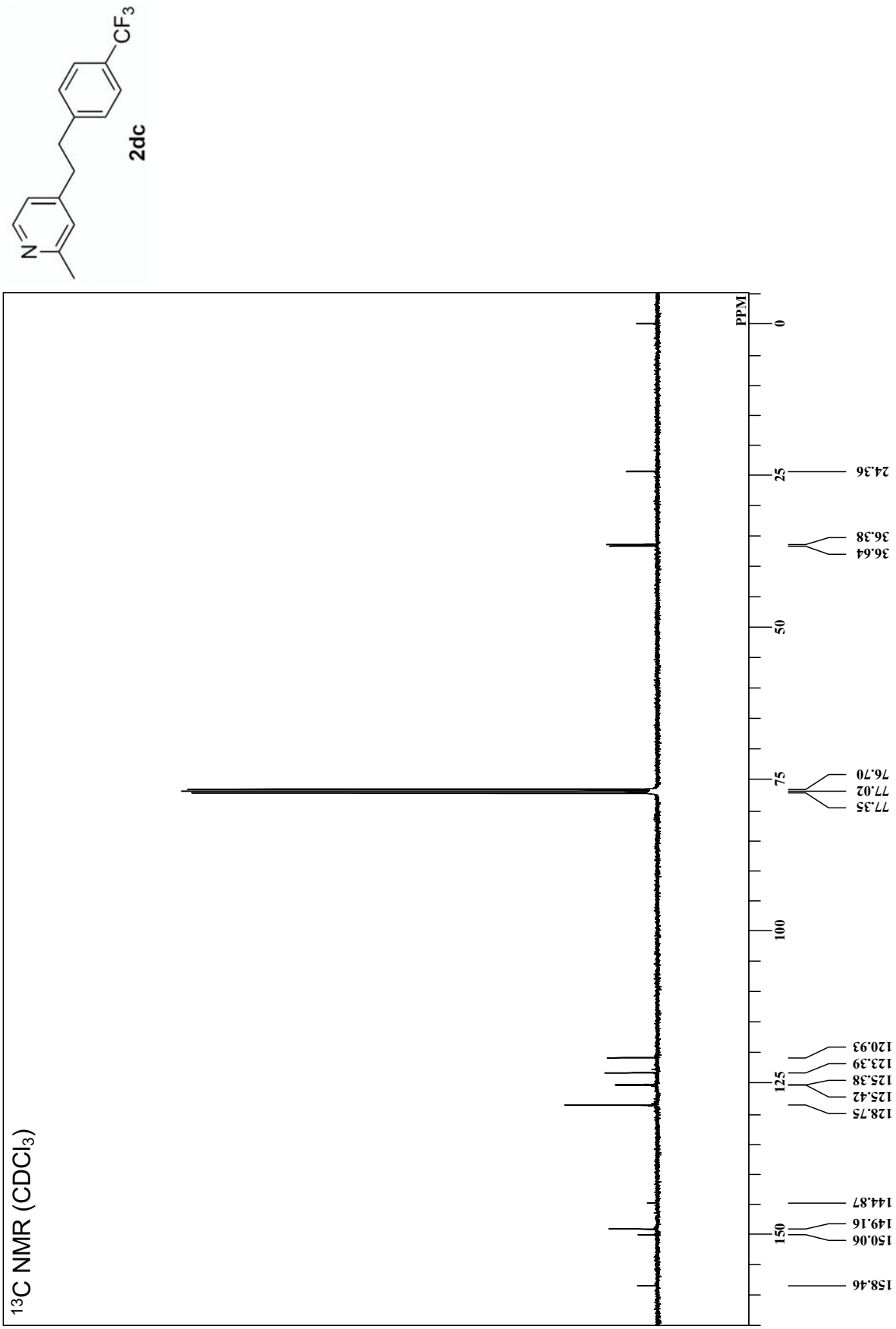
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25
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75
100
125
150
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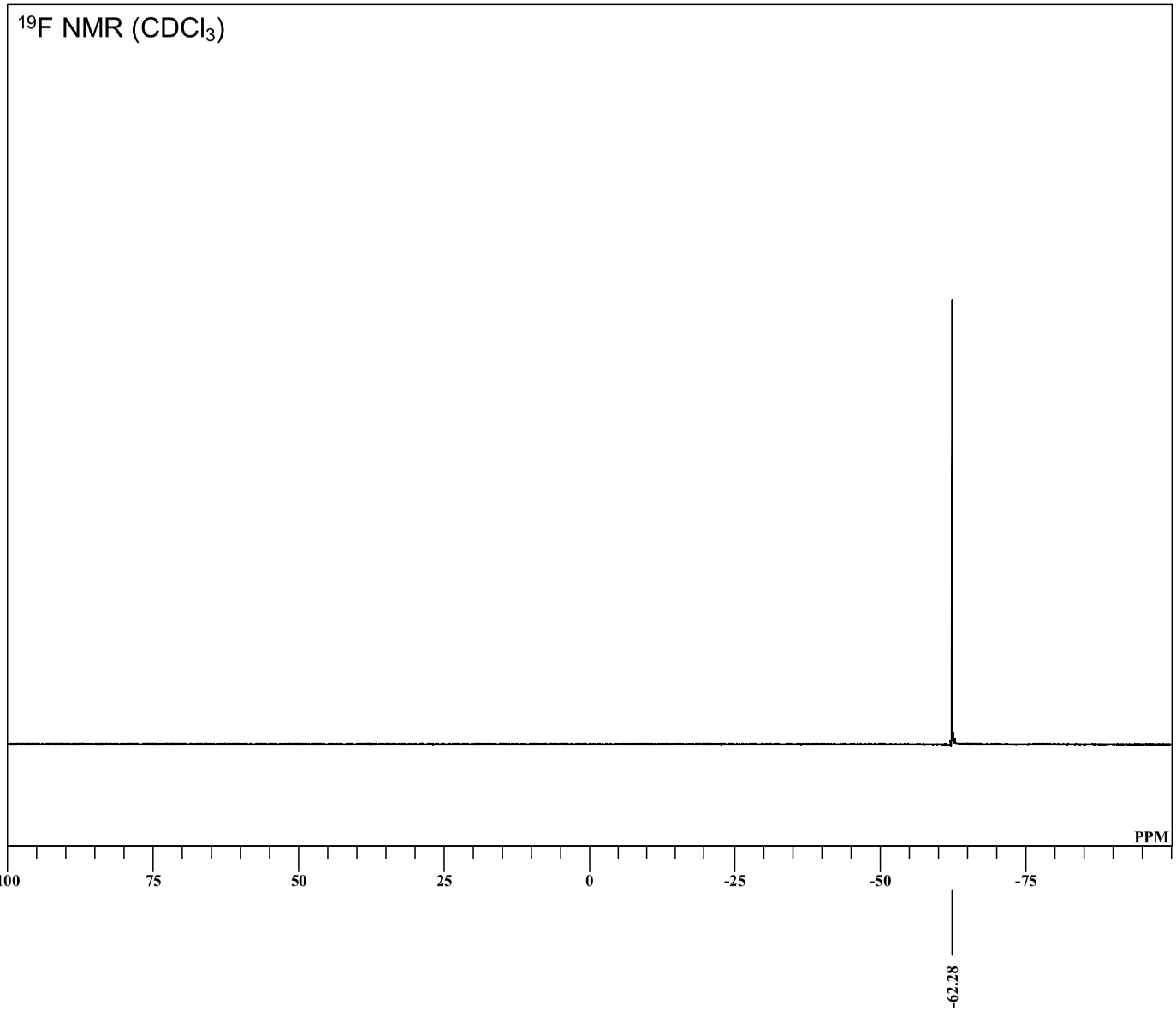

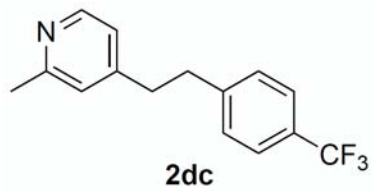

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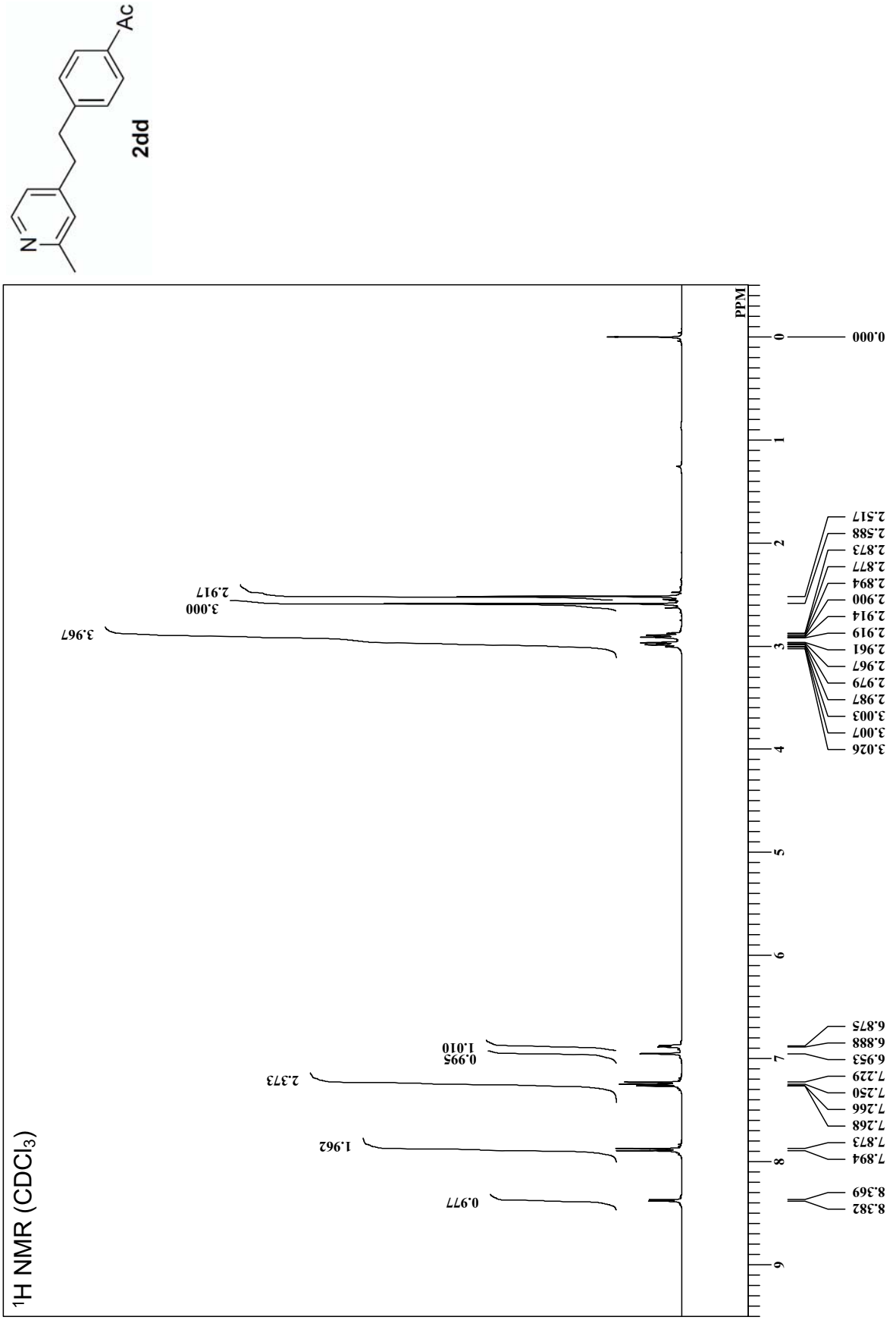
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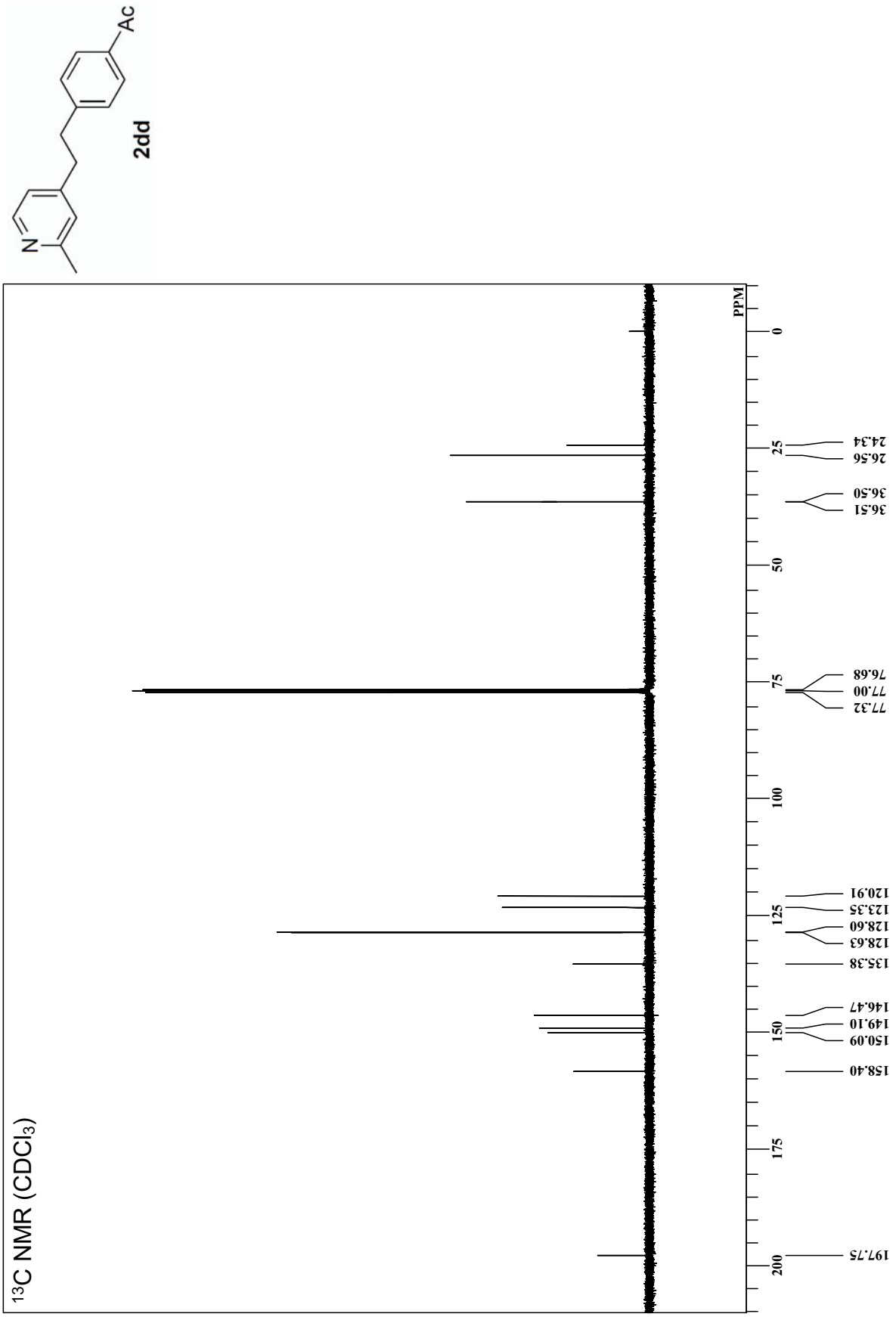
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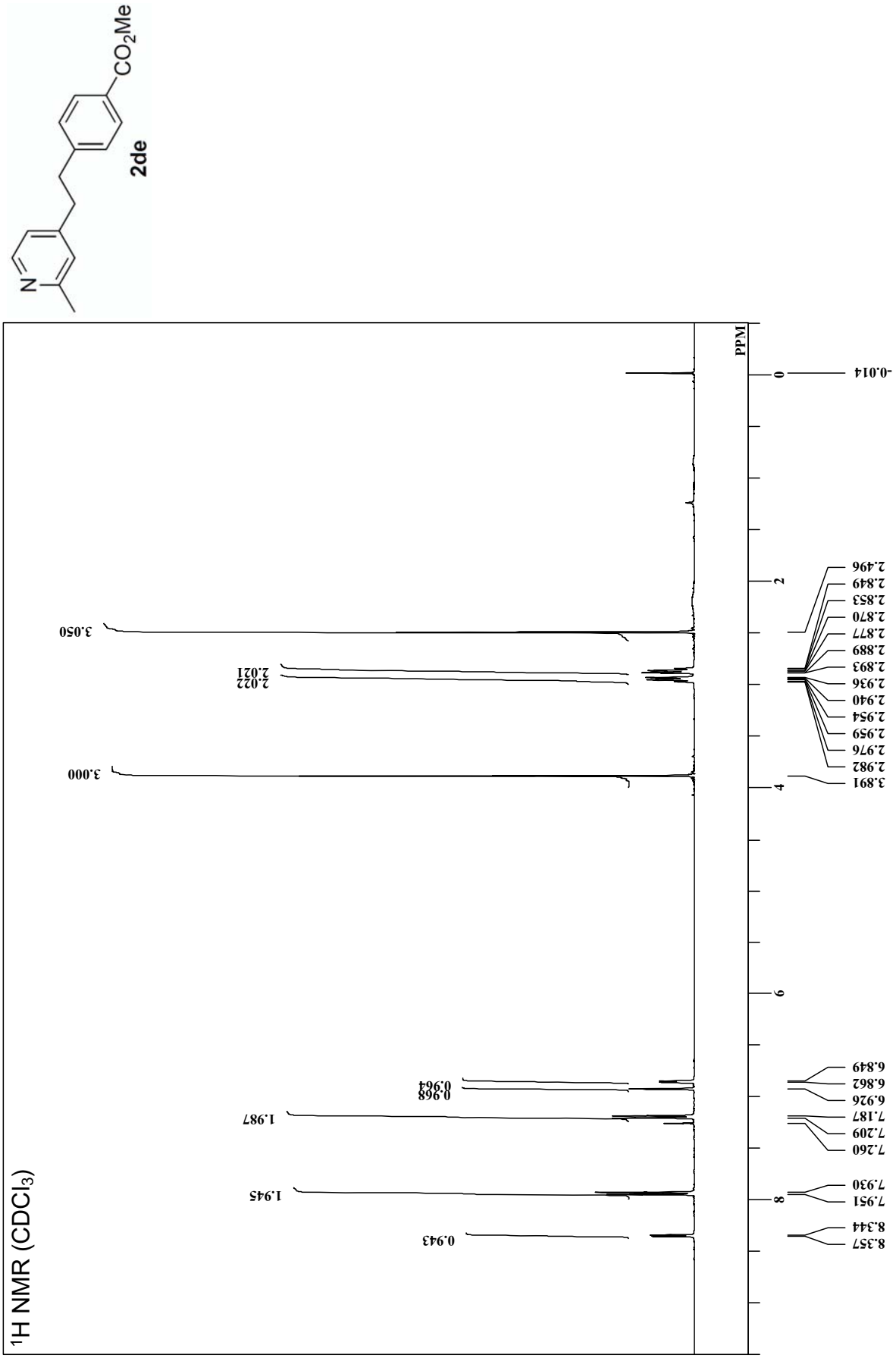
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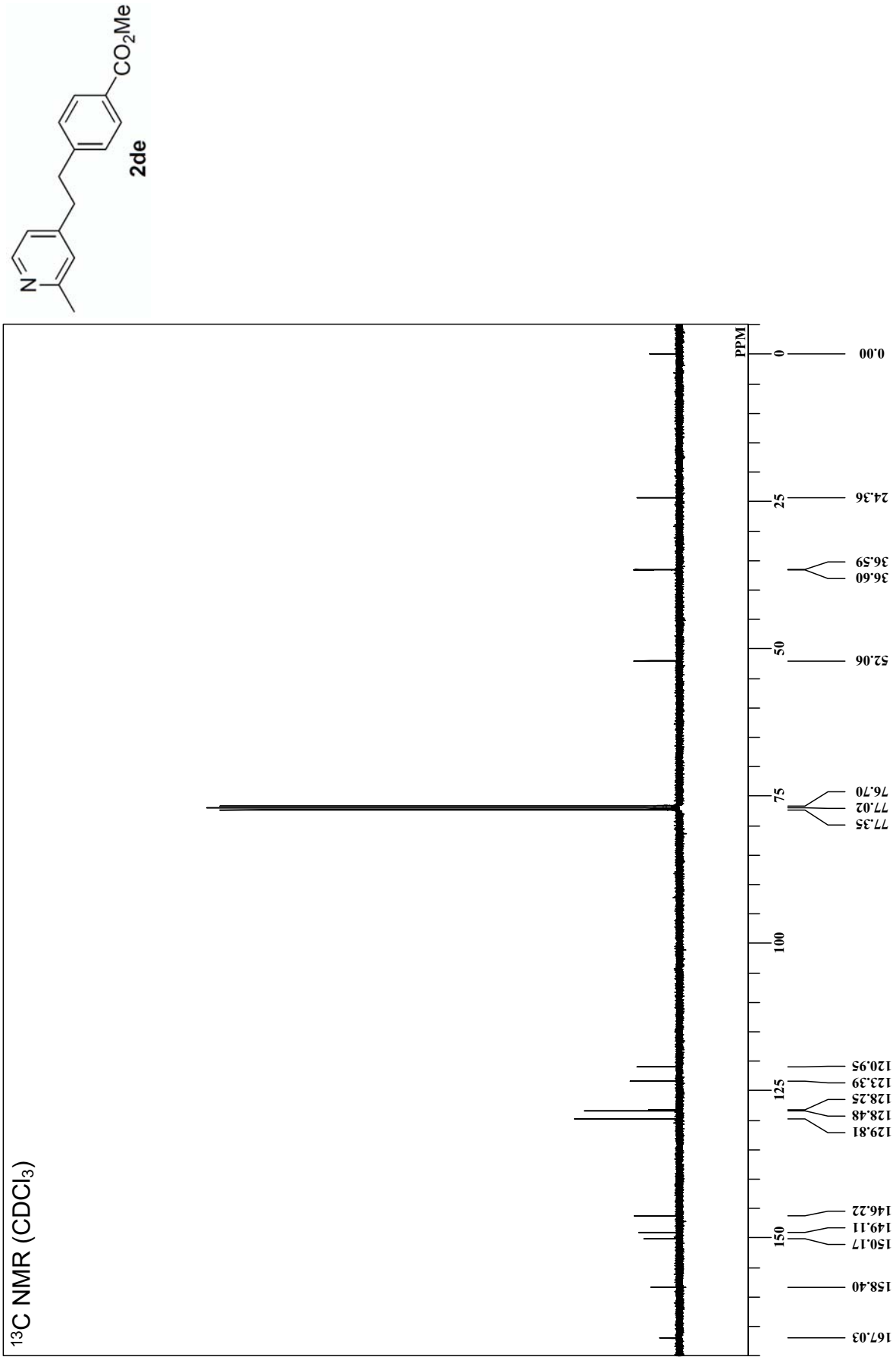
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146.22
149.11
150.17
158.40
167.03

Br
N
2df
^{1}H NMR ($CDCl_3$)
PPM
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0.959
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3.927
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2.857
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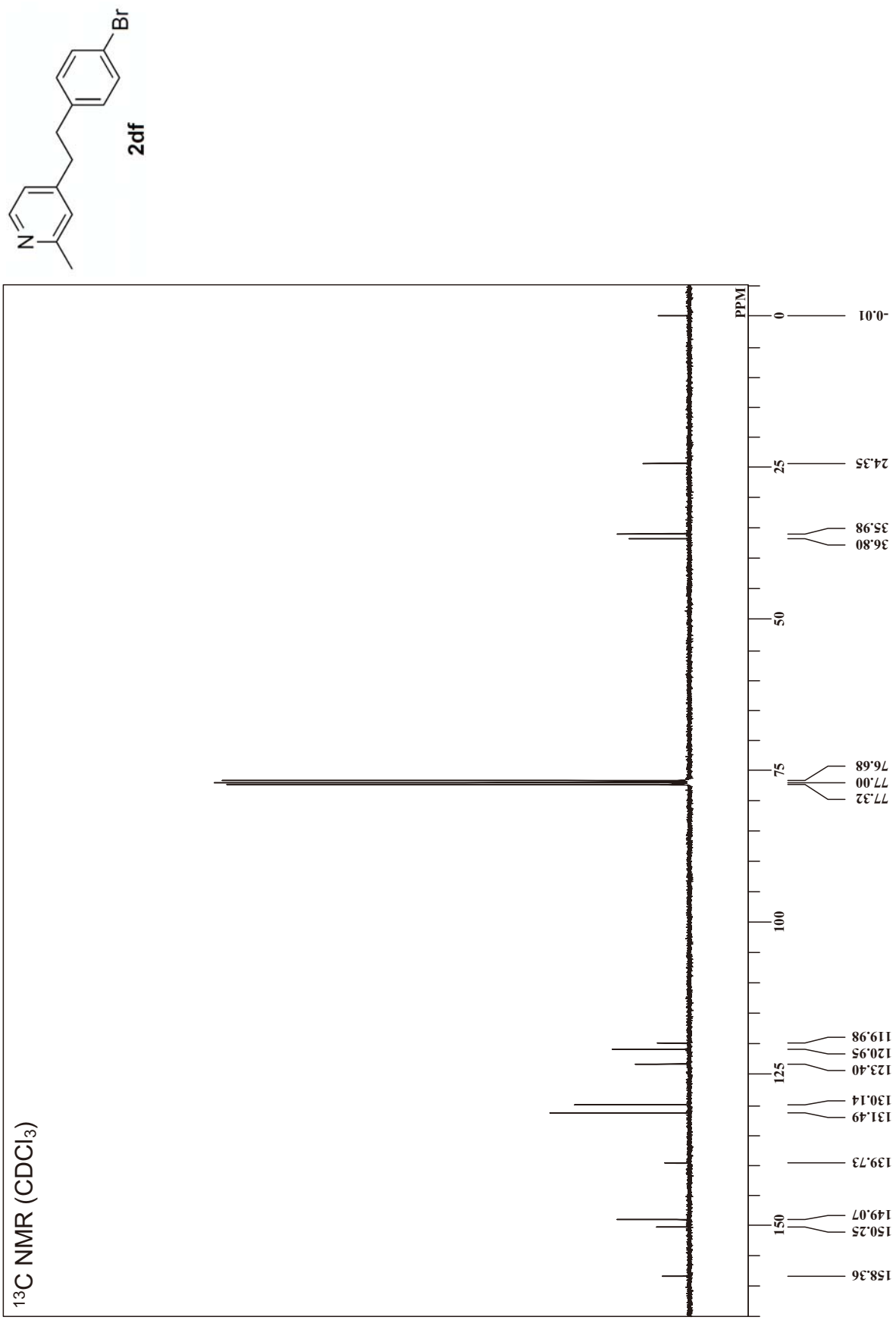
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131.49
139.73
149.07
150.25
158.36

2dg
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6.969
7.041
7.061
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7.260
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2dg
N
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PPM
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25
50
75
100
125
150
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36.19
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77.02
77.35
121.03
123.47
128.25
129.13
135.69
137.82
148.96
150.96
158.22

OMe
2dh
N
^{1}H NMR ($CDCl_3$)
PPM
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4
6
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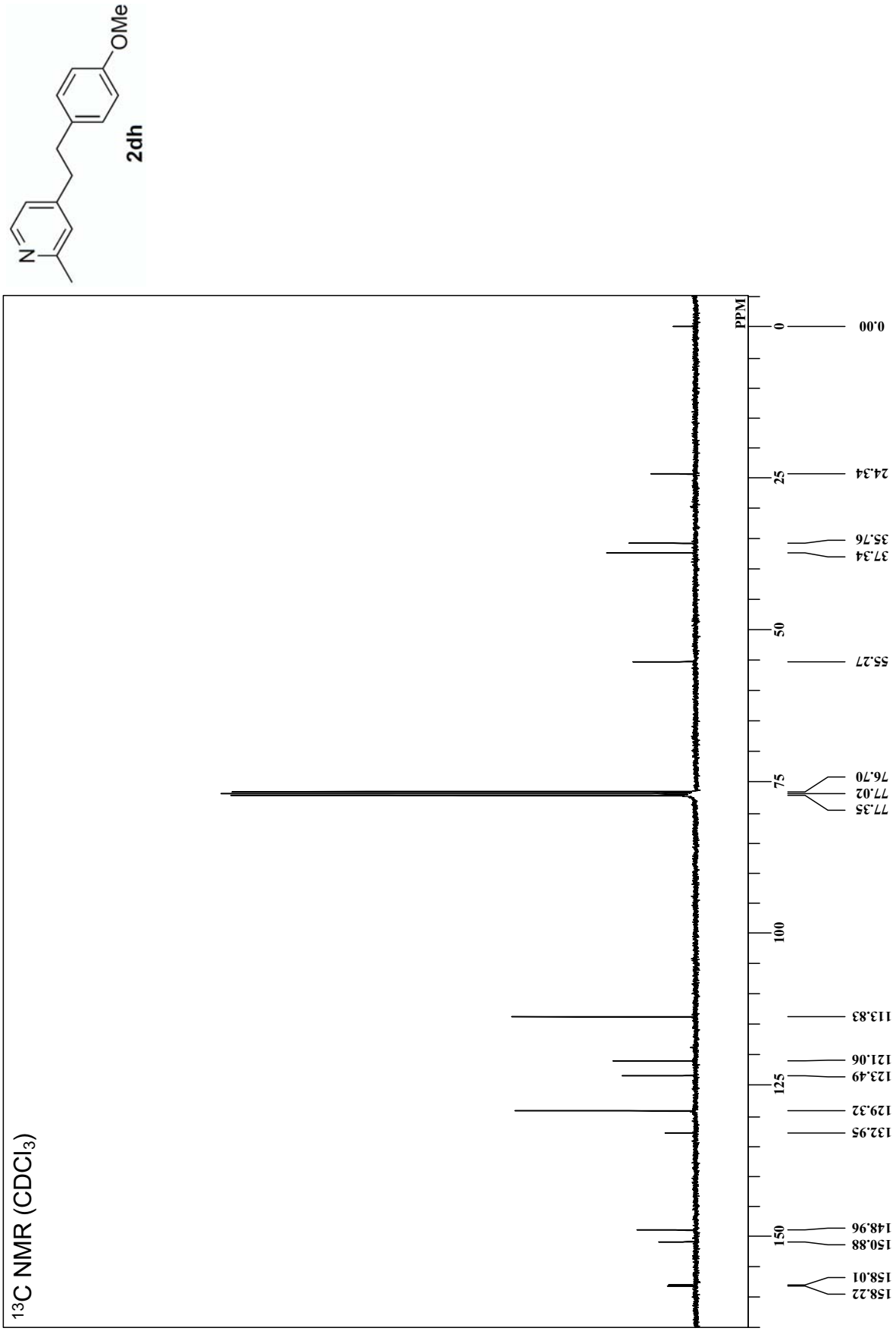
OMe
2dh
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150
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37.34
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77.02
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113.83
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123.49
129.32
132.95
148.96
150.88
158.01
158.22

2di
^{1}H NMR ($CDCl_3$)
PPM
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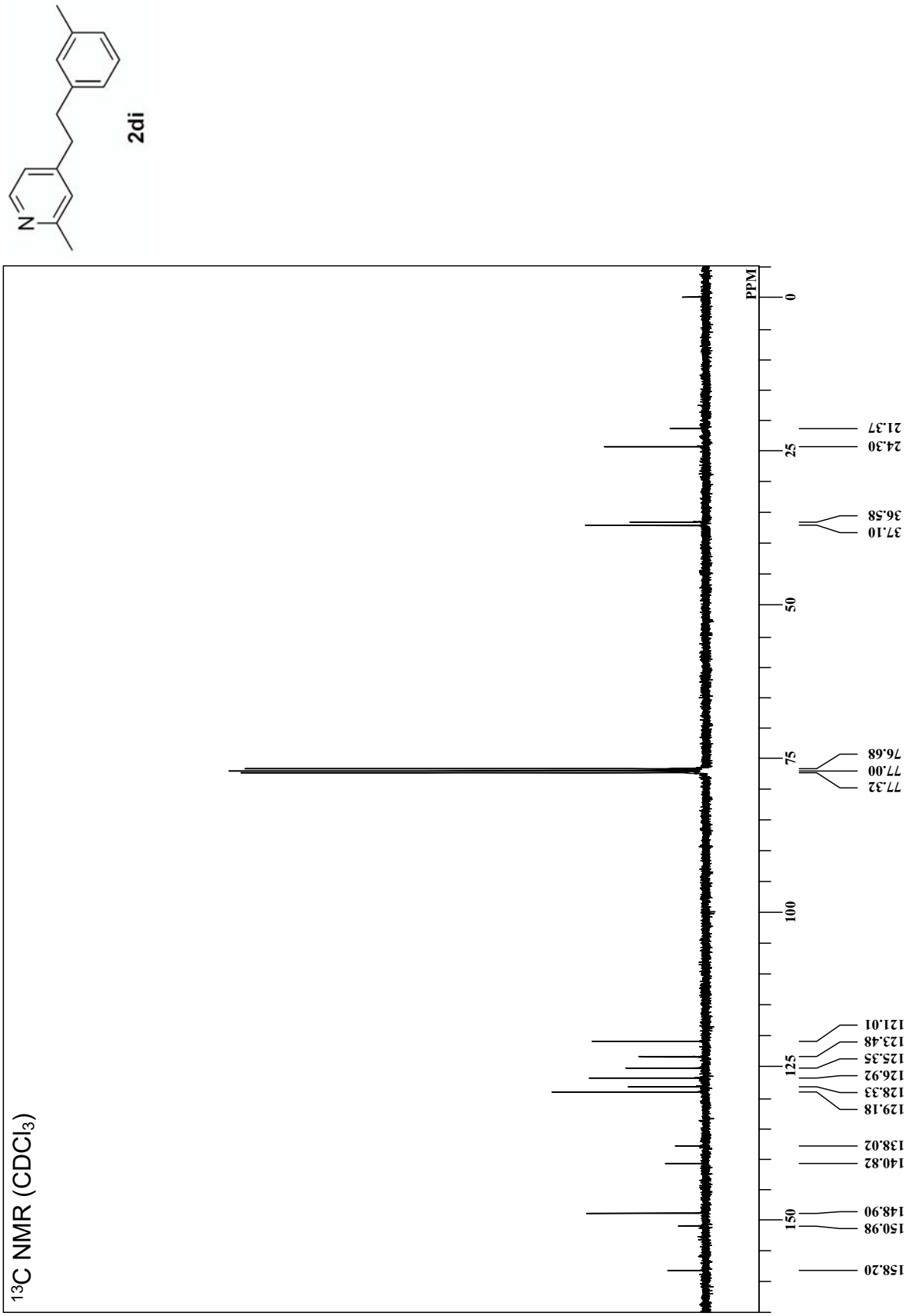
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PPM
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25
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75
100
125
150
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148.90
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77.00
76.68
37.10
36.58
24.30
21.37

OMe
2dj
N
^{1}H NMR ($CDCl_3$)
PPM
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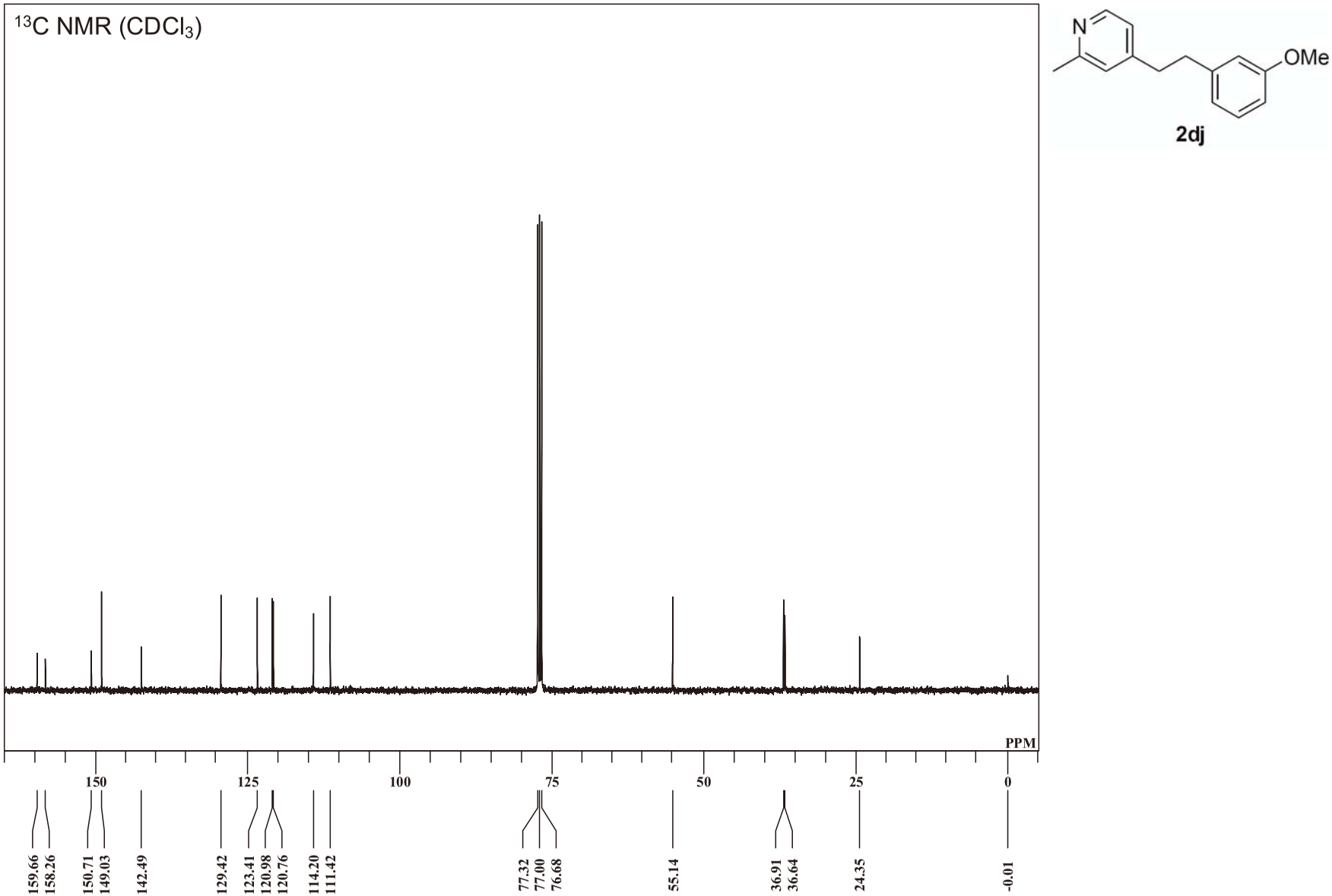
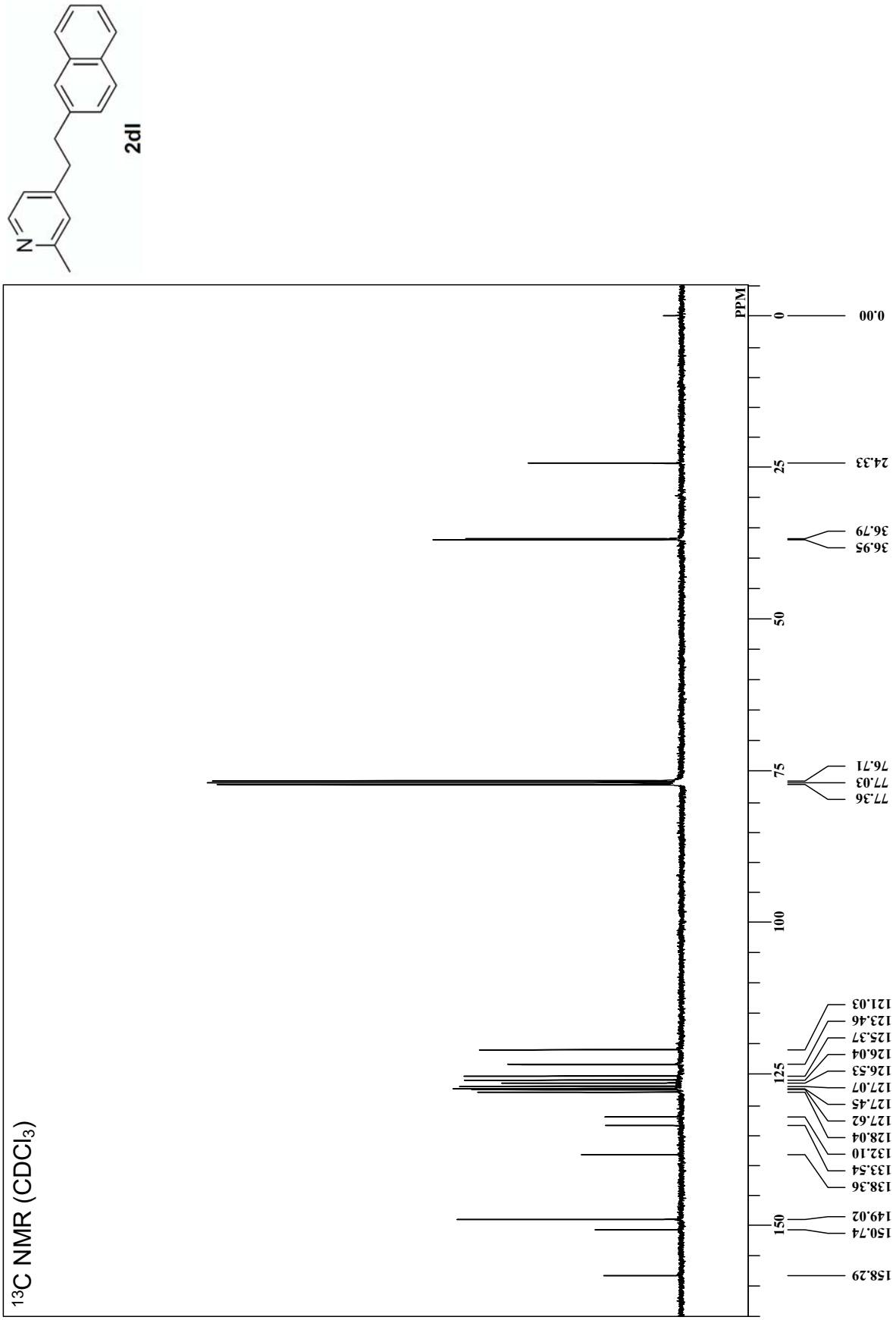
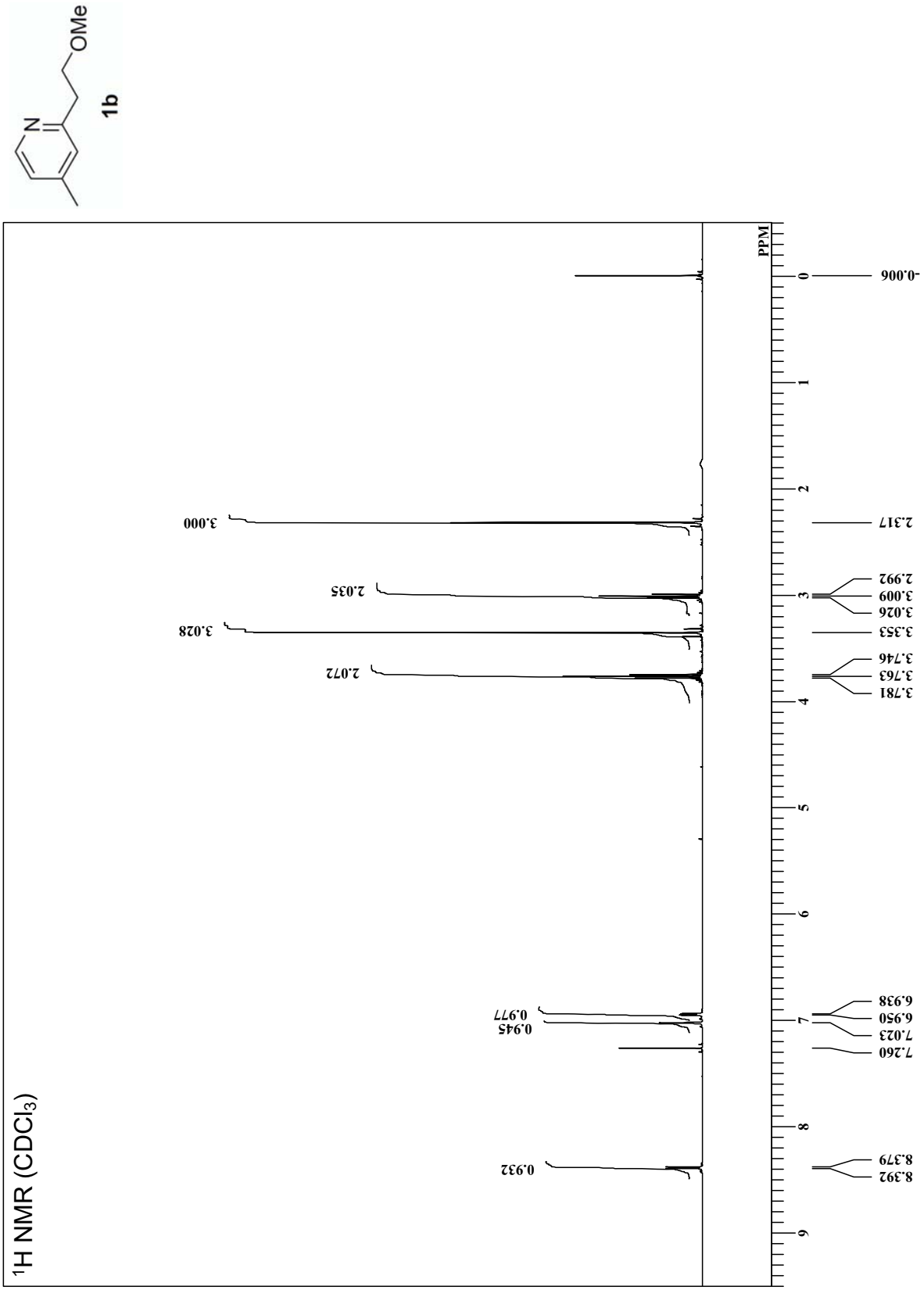
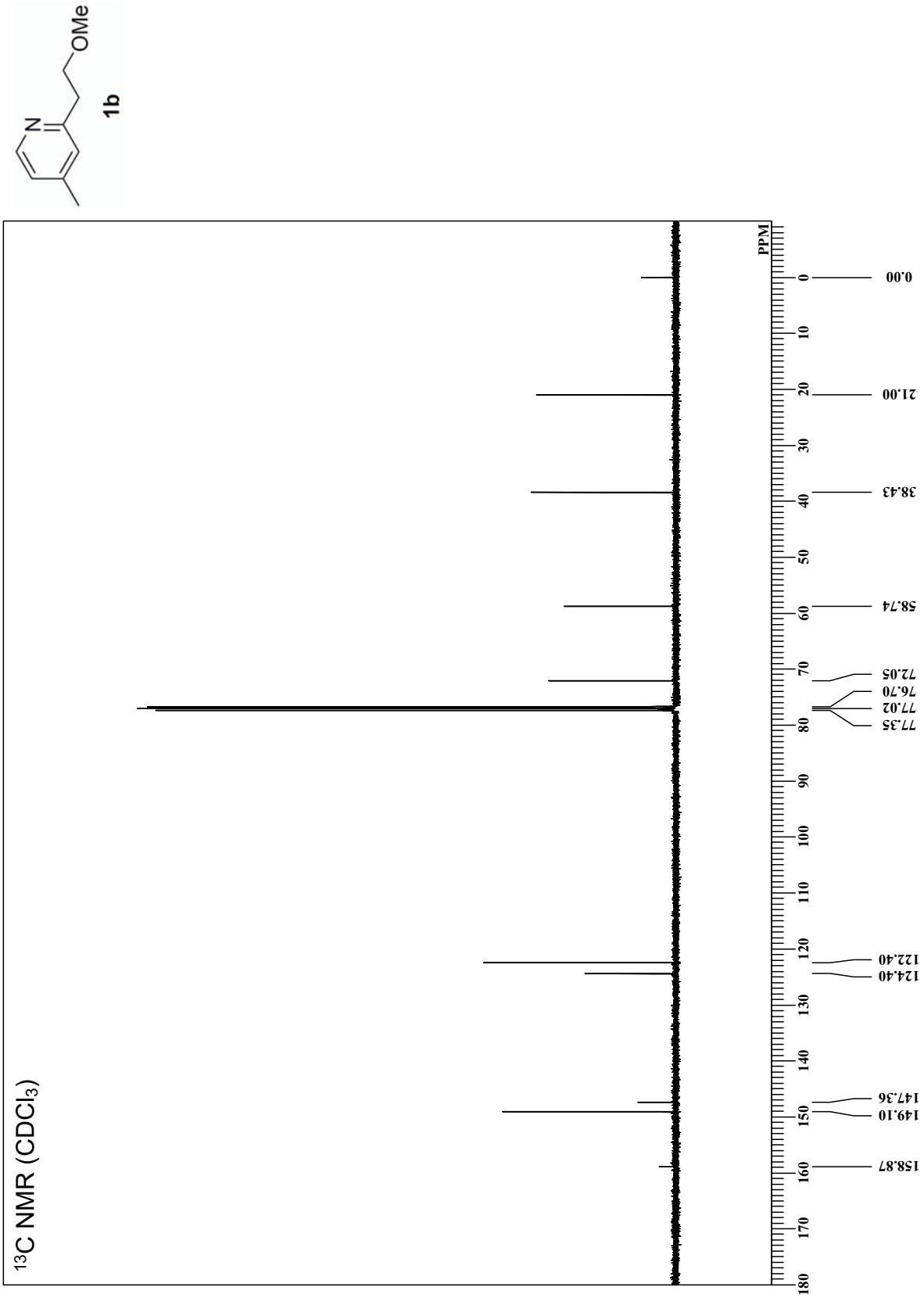
7.203
7.223
7.260
8.365
8.379
0.995
0.977
1.018
1.013
2.962
2.994
3.947
3.000


13C NMR (CDCl3)
N
OMe
2dj
PPM
150
125
100
75
50
25
0
159.66
158.26
150.71
149.03
142.49
129.42
123.41
120.98
120.76
114.20
111.42
77.32
77.00
76.68
55.14
36.91
36.64
24.35
-0.01

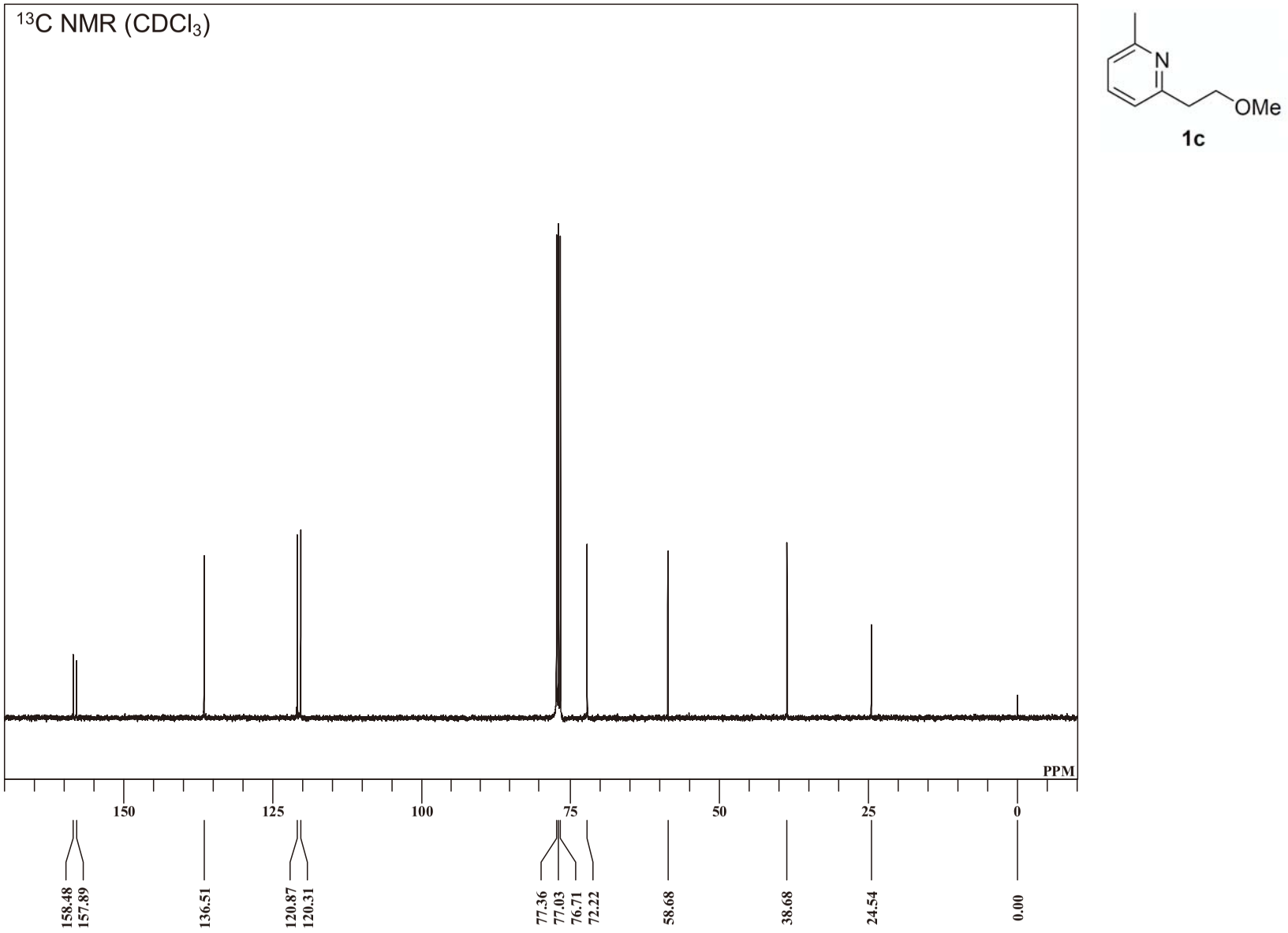
2dl
N
^{1}H NMR (CDCl$_3$)
PPM
0
2
4
6
8
0.011
2.519
2.942
2.962
2.970
2.983
3.061
3.076
3.084
3.100
6.913
6.915
6.916
6.927
6.930
6.993
7.260
7.296
7.300
7.317
7.321
7.416
7.420
7.434
7.438
7.440
7.444
7.451
7.458
7.464
7.468
7.482
7.486
7.591
7.755
7.763
7.765
7.772
7.779
7.792
7.804
7.809
7.826
7.836
8.368
8.380
0.980
2.976
0.955
1.949
0.948
0.919
0.935
3.000
1.970
1.948

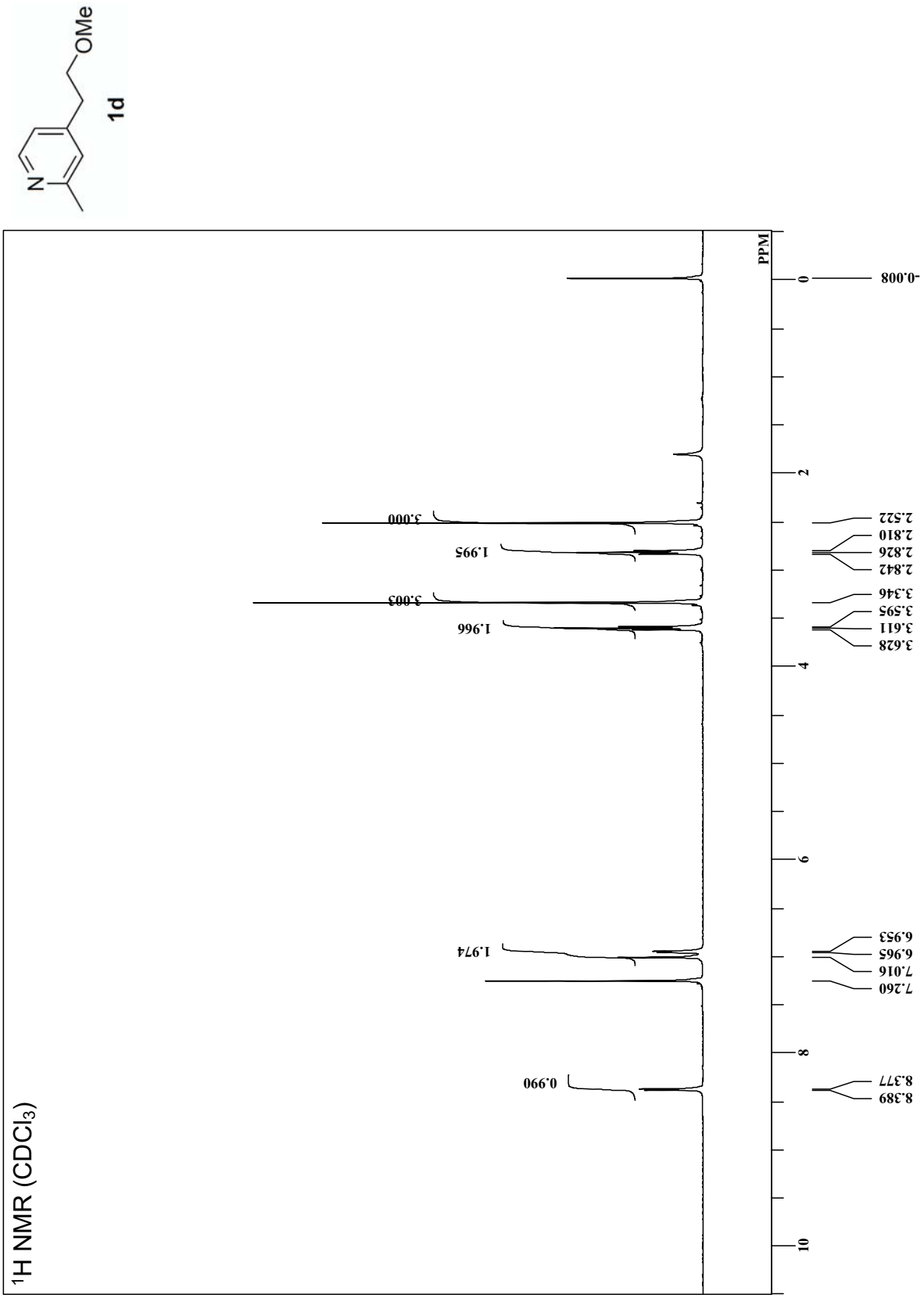

2dl
N
^{13}C NMR ($CDCl_3$)
PPM
0
25
50
75
100
125
150
0.00
24.33
36.79
36.95
76.71
77.03
77.36
121.03
123.46
125.37
126.04
126.53
127.07
127.45
127.62
128.04
132.10
133.54
138.36
149.02
150.74
158.29

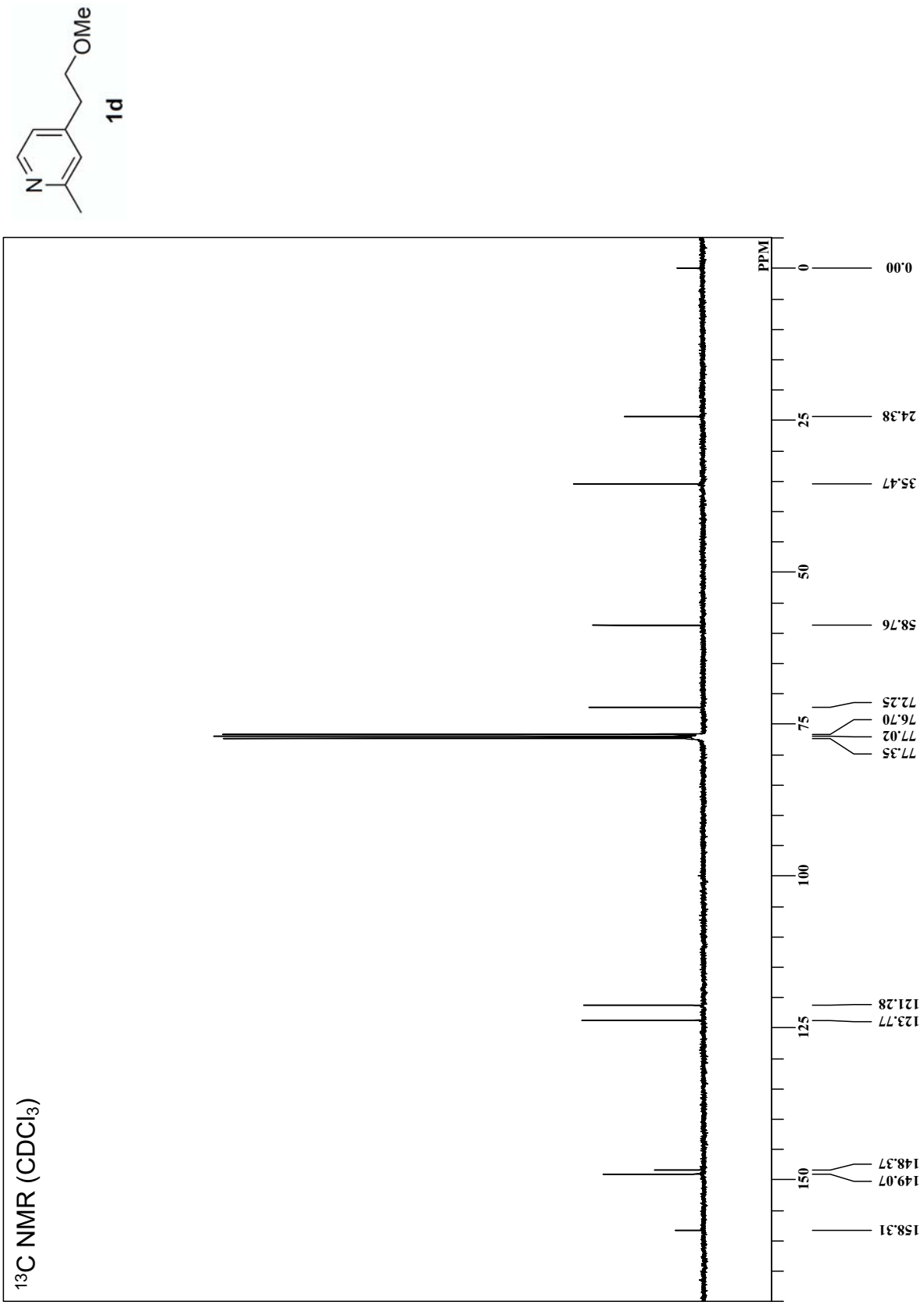

1b
OMe
N
^{1}H NMR ($CDCl_3$)
PPM
-0.006
2.317
2.992
3.009
3.026
3.353
3.746
3.763
3.781
6.938
6.950
7.023
7.260
8.379
8.392
0.932
0.945
0.977
2.072
3.028
2.035
3.000

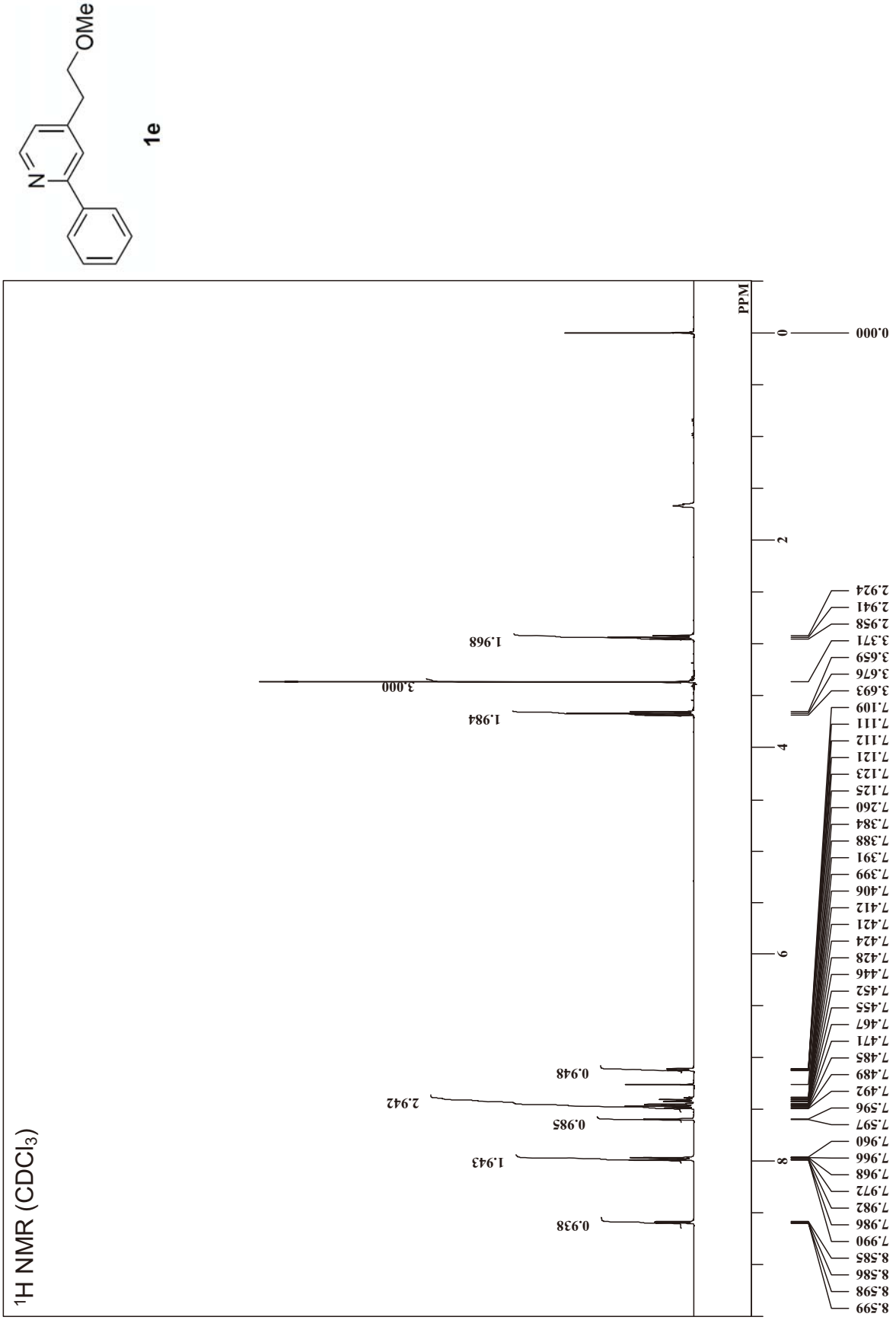

OMe
1b
N
^{13}C NMR ($CDCl_3$)
PPM
0.00
21.00
38.43
58.74
72.05
76.70
77.02
77.35
122.40
124.40
147.36
149.10
158.87

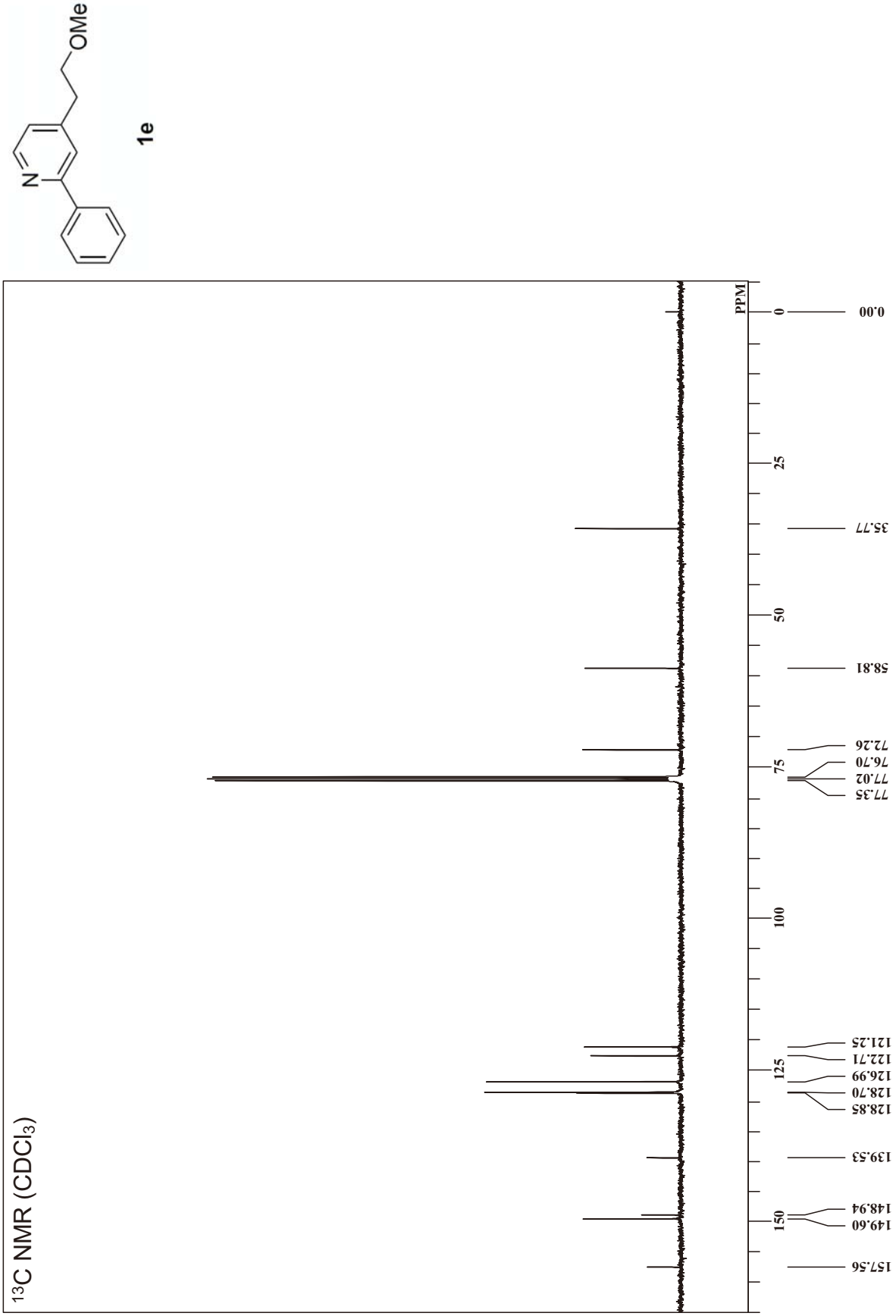
OMe
1c
N
^{1}H NMR ($CDCl_3$)
PPM
0
2
4
6
8
-0.003
2.530
3.006
3.023
3.040
3.350
3.728
3.746
3.763
6.973
6.993
7.000
7.019
7.260
7.465
7.485
7.504
1.000
1.981
2.067
3.107
2.042
3.002

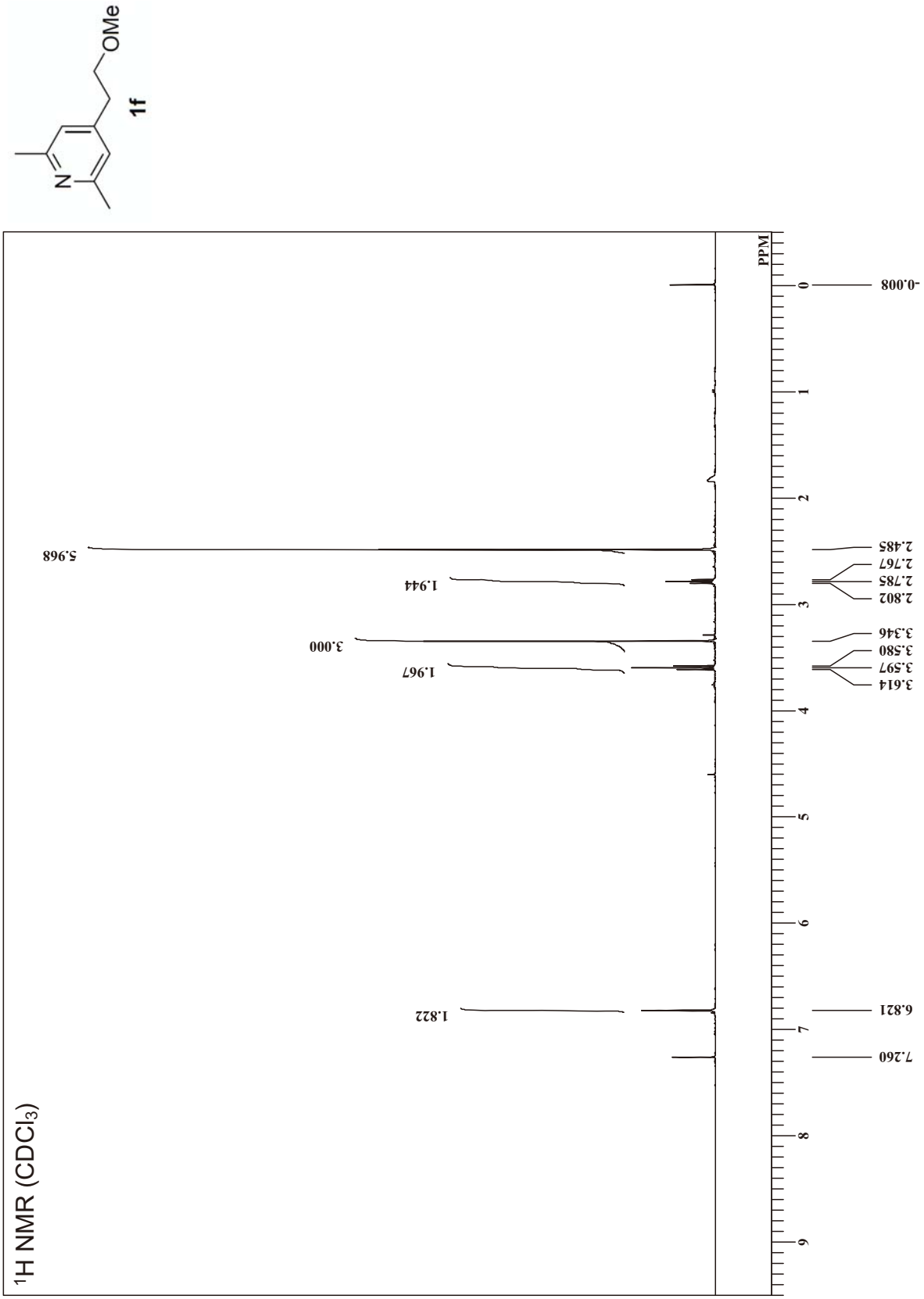

13C NMR (CDCl3)
N
OMe
1c
PPM
150
125
100
75
50
25
0
158.48
157.89
136.51
120.87
120.31
77.36
77.03
76.71
72.22
58.68
38.68
24.54
0.00

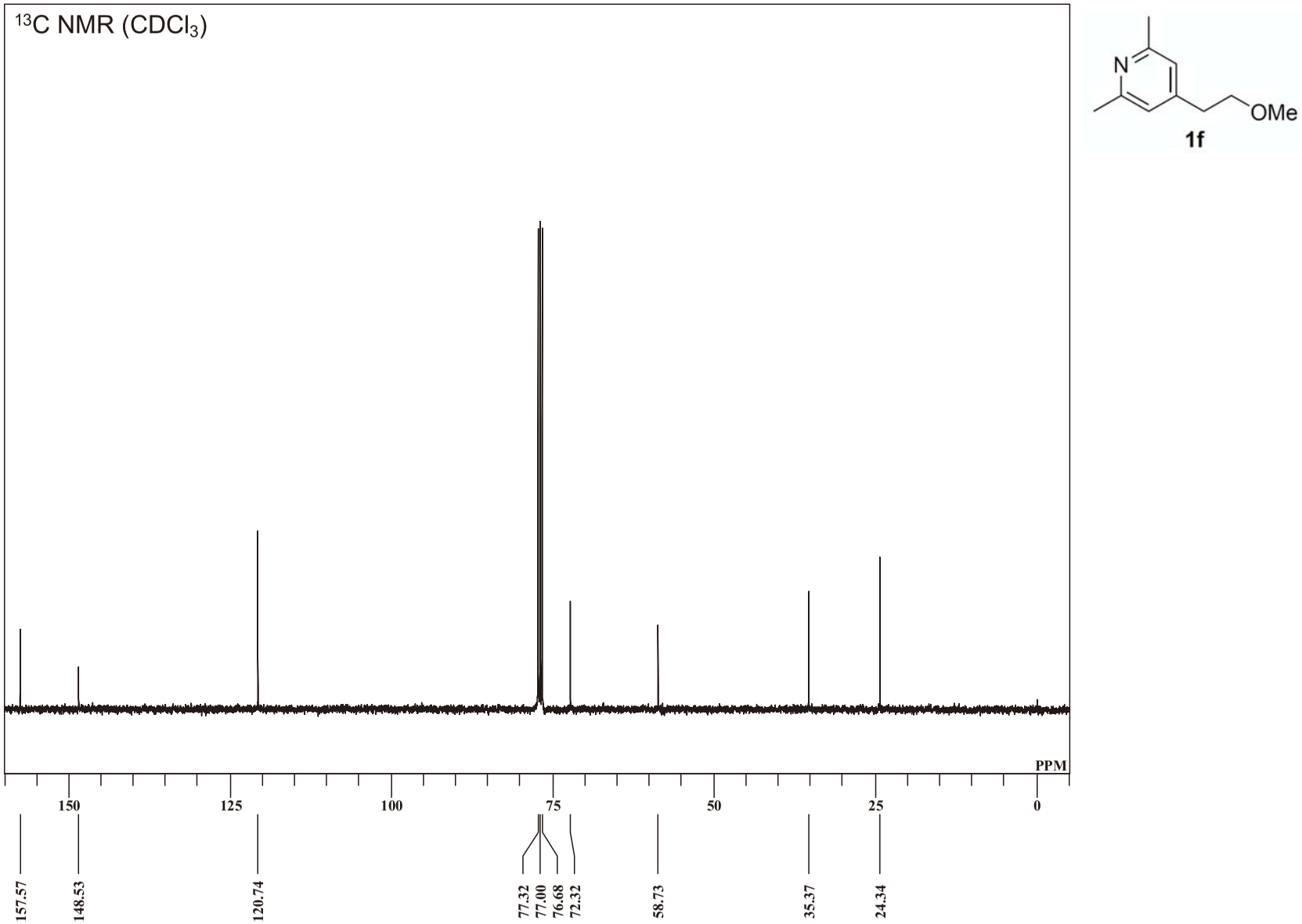

1d
OMe
N
^{1}H NMR ($CDCl_3$)
PPM
10
8
6
4
2
0
-0.008
2.522
2.810
2.826
2.842
3.346
3.595
3.611
3.628
6.953
6.965
7.016
7.260
8.377
8.389
0.990
1.974
3.003
1.966
1.995
3.000


OMe
1d
N
^{13}C NMR ($CDCl_3$)
PPM
0
25
50
75
100
125
150
0.00
24.38
35.47
58.76
72.25
76.70
77.02
77.35
121.28
123.77
148.37
149.07
158.31

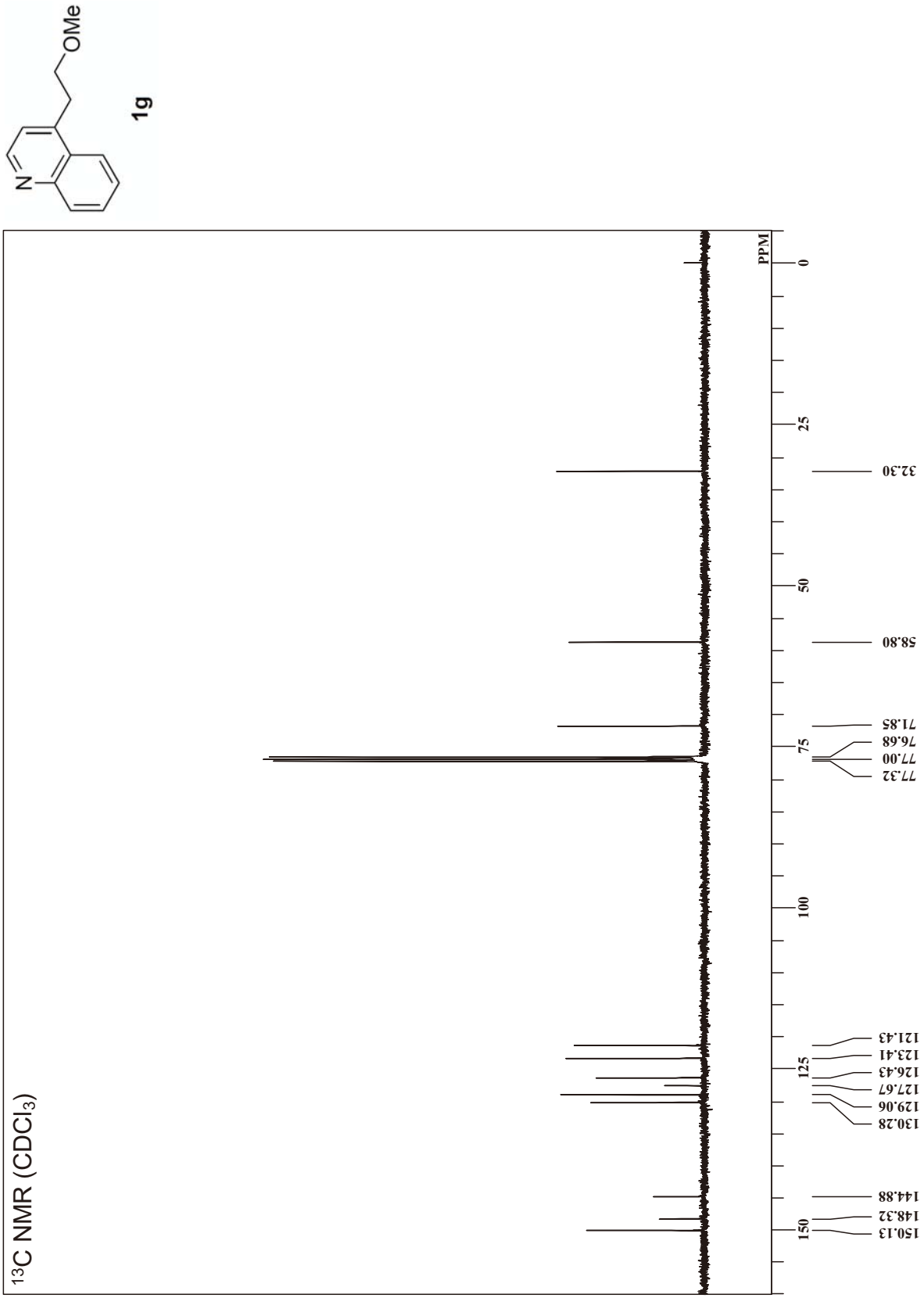

OMe
N
1e
^{1}H NMR ($CDCl_3$)
PPM
0.000
2.924
2.941
2.958
3.371
3.659
3.676
3.693
7.109
7.111
7.112
7.121
7.123
7.125
7.260
7.384
7.388
7.391
7.399
7.406
7.412
7.421
7.424
7.428
7.446
7.452
7.455
7.467
7.471
7.485
7.489
7.492
7.596
7.597
7.960
7.966
7.968
7.972
7.982
7.986
7.990
8.585
8.586
8.598
8.599
0.938
1.943
0.985
2.942
0.948
3.000
1.984
1.968


OMe
N
1e
^{13}C NMR ($CDCl_3$)
PPM
0
25
50
75
100
125
150
0.00
35.77
58.81
72.26
76.70
77.02
77.35
121.25
122.71
126.99
128.70
128.85
139.53
148.94
149.60
157.56

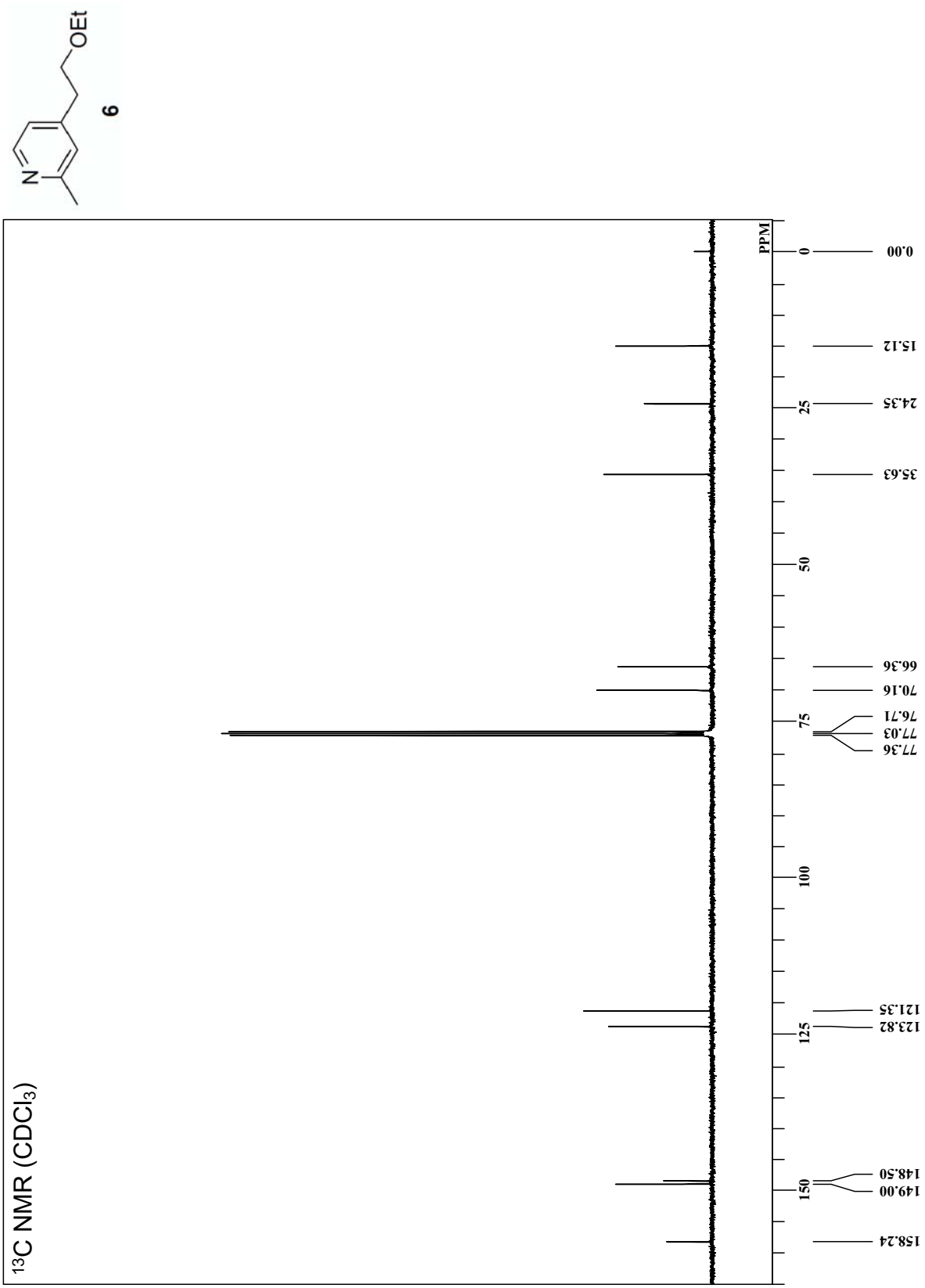

1f
OMe
N
^{1}H NMR ($CDCl_3$)
PPM
-0.008
7.260
6.821
3.614
3.597
3.580
3.346
2.802
2.785
2.767
2.485
5.968
1.944
3.000
1.967
1.822


13C NMR (CDCl3)
N
OMe
1f
PPM
150
125
100
75
50
25
0
157.57
148.53
120.74
77.32
77.00
76.68
72.32
58.73
35.37
24.34

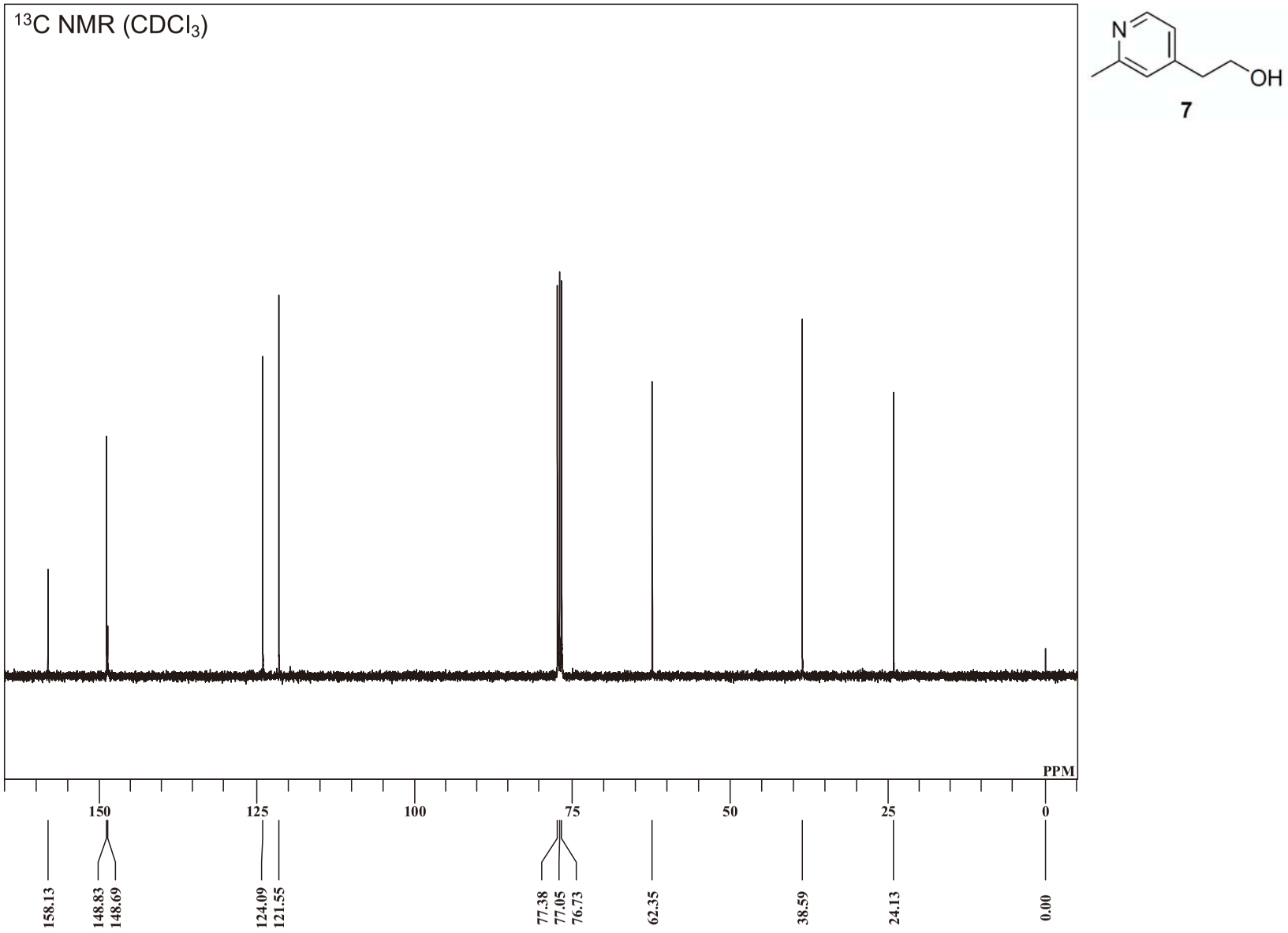
OMe
1g
N
^{1}H NMR ($CDCl_3$)
PPM
0
2
4
6
8
-0.005
3.342
3.360
3.376
3.748
3.766
3.783
4.965
2.000
0.885
0.901
0.915
1.939
0.861
7.260
7.285
7.297
7.548
7.552
7.566
7.569
7.573
7.587
7.590
7.686
7.689
7.703
7.707
7.711
7.724
7.728
8.041
8.044
8.063
8.065
8.105
8.107
8.127
8.129
8.817
8.828


OMe
N
1g
^{13}C NMR ($CDCl_3$)
PPM
0
25
50
75
100
125
150
32.30
58.80
71.85
76.68
77.00
77.32
121.43
123.41
126.43
127.67
129.06
130.28
144.88
148.32
150.13

OEt
N
6
^{1}H NMR ($CDCl_3$)
PPM
0
2
4
6
8
-0.005
1.172
1.191
1.208
2.521
2.813
2.830
2.848
3.465
3.483
3.500
3.518
3.621
3.639
3.656
6.958
6.971
7.020
7.260
8.370
8.383
0.936
0.961
0.976
1.978
2.021
2.025
2.928
3.000

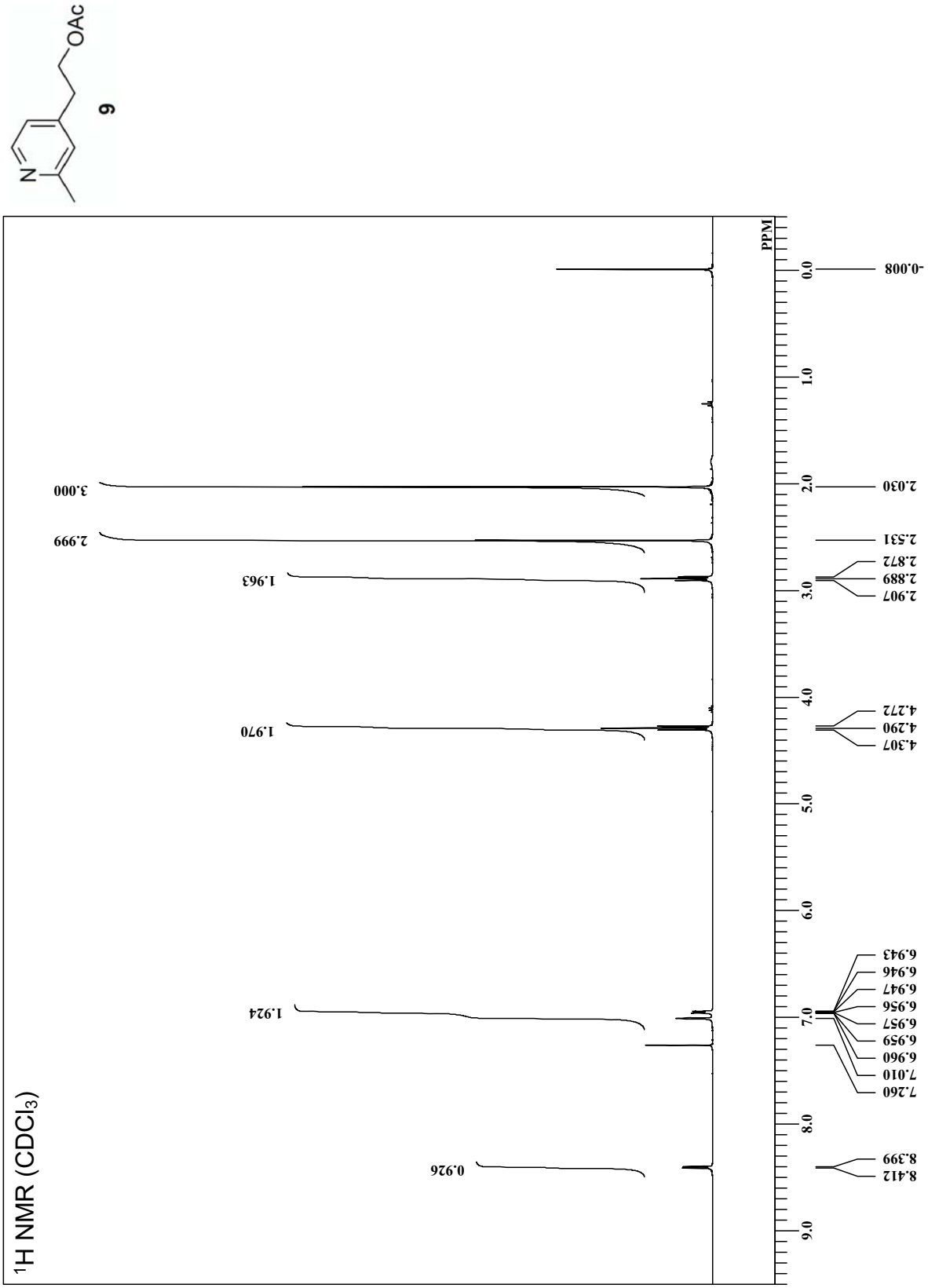

OEt
6
N
^{13}C NMR ($CDCl_3$)
PPM
0
25
50
75
100
125
150
0.00
15.12
24.35
35.63
66.36
70.16
76.71
77.03
77.36
121.35
123.82
148.50
149.00
158.24

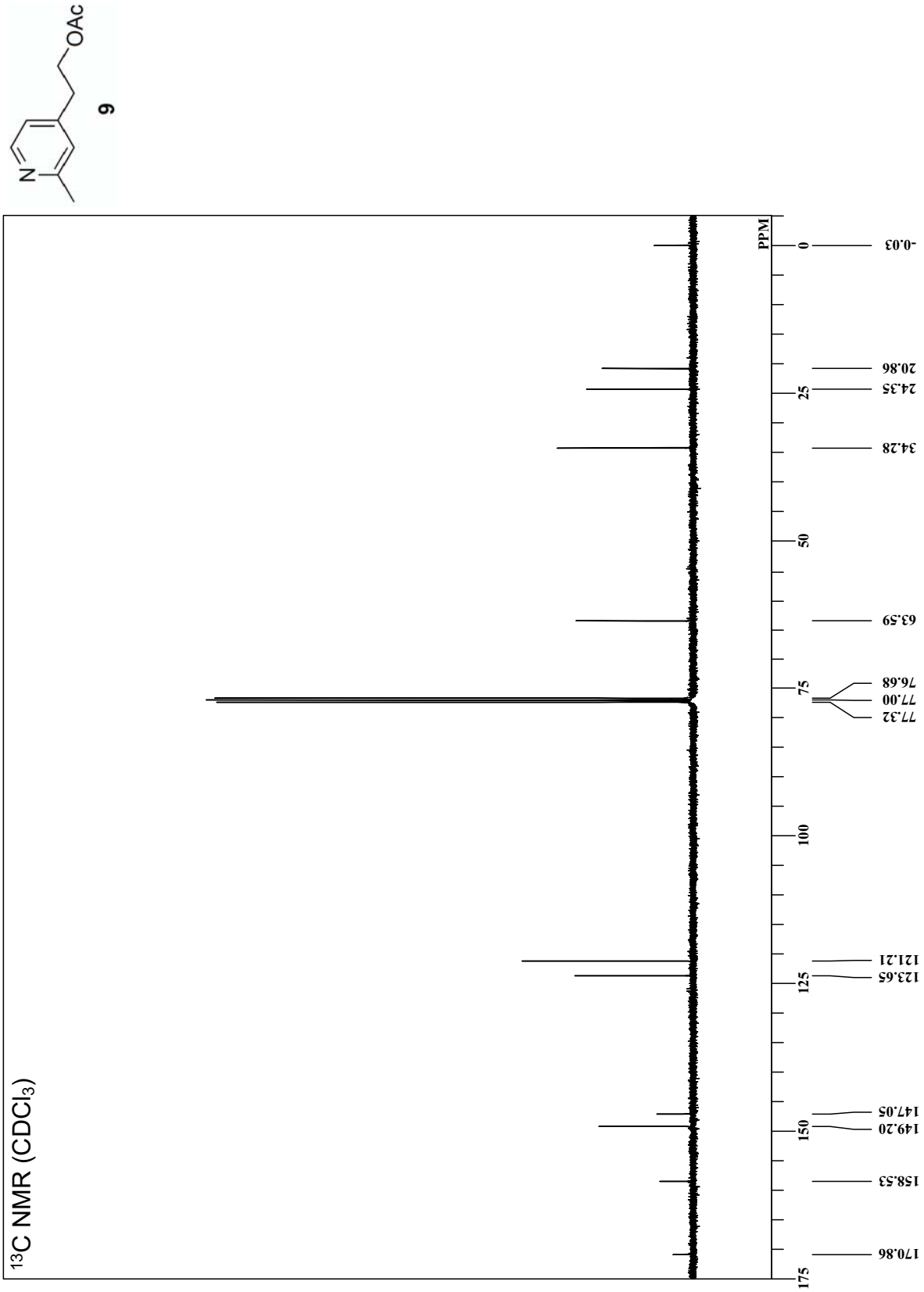
7
^{1}H NMR ($CDCl_3$)
PPM
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
-0.018
2.467
2.777
2.794
2.810
3.088
3.856
3.873
3.889
6.930
6.931
6.933
6.934
6.943
6.944
6.946
6.947
7.003
7.260
8.249
8.262
0.997
1.960
1.995
1.175
1.959
3.000


13C NMR (CDCl3)
N
OH
7
PPM
150
125
100
75
50
25
0
158.13
148.83
148.69
124.09
121.55
77.38
77.05
76.73
62.35
38.59
24.13
0.00

OPh
N
8
^{1}H NMR ($CDCl_3$)
PPM
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
-0.001
0.947
2.357
4.980
3.000
1.984
1.955
2.540
3.030
3.047
3.064
4.175
4.192
4.209
6.869
6.875
6.878
6.883
6.892
6.897
6.900
6.906
6.932
6.934
6.937
6.951
6.953
6.956
6.969
6.972
6.975
7.019
7.020
7.022
7.023
7.030
7.031
7.033
7.034
7.036
7.084
7.259
7.260
7.279
7.282
7.296
7.299
7.301
8.408
8.421

OPh
N
8
^{13}C NMR ($CDCl_3$)
PPM
0
25
50
75
100
125
150
158.50
158.43
149.16
147.63
129.49
123.81
121.37
120.99
114.52
77.32
77.00
76.68
67.22
35.01
24.38


OAc
9
N
^{1}H NMR ($CDCl_3$)
PPM
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
-0.008
2.030
2.531
2.872
2.889
2.907
4.272
4.290
4.307
6.943
6.946
6.947
6.956
6.957
6.959
6.960
7.010
7.260
8.399
8.412
0.926
1.924
1.970
1.963
2.999
3.000


OAc
N
9
^{13}C NMR ($CDCl_3$)
PPM
0
25
50
75
100
125
150
175
-0.03
20.86
24.35
34.28
63.59
76.68
77.00
77.32
121.21
123.65
147.05
149.20
158.53
170.86