Photoredox Cross-Coupling: Ir/Ni Dual Catalysis for the Synthesis of Benzylic Ethers

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Supporting Information

General considerations

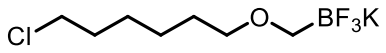
All reactions were carried out under an inert atmosphere of nitrogen or argon unless otherwise noted. Dioxane (99.9%, extra dry) and dimethyl acetamide (purity, extra dry) were used as received. K_2HPO_4 was used as received. $IrCl_3 \cdot xH_2O$, and $NiCl_2$•dme were purchased from commercial sources. All other reagents were purchased commercially and used as received. Photoredox reactions were irradiated with two to three standard 26 W compact fluorescent light bulbs. Melting points (°C) are uncorrected. NMR spectra were recorded on a 500 or 400 MHz spectrometer. ^{19}F NMR chemical shifts were referenced to external $CFCl_3$ (0.0 ppm). ^{11}B NMR spectra were obtained on a spectrometer equipped with the appropriate decoupling accessories. All ^{11}B NMR chemical shifts were referenced to an external $BF_3 \cdot OEt_2$ (0.0 ppm) with a negative sign indicating an upfield shift. Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant *J* (Hz) and integration. The ^{13}C signal of the carbon bonded to boron was not observed in some cases due to quadrupolar relaxation.

Synthesis of α-alkoxymethyltrifluoroborates:

Most potassium α-alkoxymethyltrifluoroborates were purchased commercially. In cases where the desired potassium organotrifluoroborate was unavailable, the corresponding alcohol derivative was converted to the trifluoroborate by the following procedure.

General procedure for α-alkoxymethyltrifluoroborate synthesis:

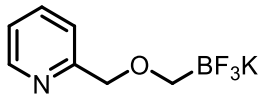
NaH (96 mg, 4 mmol) was added to a 50 mL 2-neck round-bottom-flask and purged with N_2 three times. The content was diluted with dry THF (10 mL) and precursor alcohol (4.0 mmol) was then added dropwise to the reaction mixture at 0 °C under N_2. After stirring for 15 min at 0 °C, the temperature was increased to rt and further stirred for 30 min. Bromomethyltrifluoroborate (267 mg, 1.33 mmol) was added in one portion to the suspension at 0 °C, and the reaction was stirred at rt for 3 h. The reaction was quenched by adding 4.5 M KHF_2 (pH 6, ~ 4.5 mL). The final mixture was stirred for 30 min and then concentrated and dried overnight under high vacuum to remove trace solvent. The crude residue was suspended in hot acetone (3 x 50 mL) and filtered. The filtrate was concentrated to a minimal volume (5 – 10 mL) and Et_2O (~150 mL) was added to precipitate. The white precipitate was isolated by filtration, washing with hexanes (~30 mL) and CH_2Cl_2 (~30 mL), to give the desired trifluoroborate in good yield.



S1

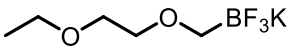
Potassium (((6-Chlorohexyl)oxy)methyl)trifluoroborate (S1): Obtained as a white solid (296 mg, 87%). mp = 177-181 °C, ^1H NMR (DMSO, 500 MHz): 3.60-3.58 (m, 2H), 3.15-3.14 (m, 2H), 2.46-2.45 (m, 2H), 1.69-1.66 (m, 2H), 1.41-1.40 (m, 2H), 1.34-1.33 (m, 2H), 1.25-1.24 (m, 2H), ^{13}C NMR (DMSO, 126 MHz) δ 73.9, 46.0, 32.6, 29.9, 26.9, 25.7, ^{19}F NMR (DMSO, 471 MHz) δ -141.5, ^{11}B NMR (DMSO, 128 MHz) δ 3.1, IR: ν = 2936, 2856, 1444, 1402, 1353, 1230, 1221,

1068, 1008, 961, 920, 804, 732 cm^{-1}, HRMS (ESI) m/z calc. for $C_7H_{14}BClF_3O$ (M^-) 217.0767, found 217.0773.



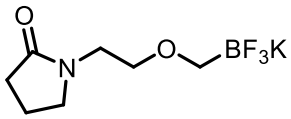
S2

Potassium ((Pyridin-2-ylmethoxy)methyl)trifluoroborate (S2): Obtained as a white solid (213 mg, 70%), mp = 162-164 ºC, ^{1}H NMR (DMSO, 500 MHz) δ 8.45-8.44 (m, 1H), 7.74 (t, *J* = 7.5 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.25 – 7.14 (m, 1H), 4.35 (s, 2H), 2.62 (s, 2H), ^{13}C NMR (DMSO, 126 MHz) δ 160.7, 149.2, 136.9, 122.5, 121.5, 76.4, ^{19}F NMR (DMSO, 471 MHz) δ -141.4, ^{11}B NMR (DMSO, 128 MHz) δ 3.2, IR: ν = 3773, 2834, 1593, 1435, 1352, 1304, 1234, 1121, 1060, 1022, 985, 918, 801 cm^{-1}, HRMS (ESI) m/z calc. for $C_7H_8BF_3NO$ (M^-) 190.0657, found 190.0653.



S3

Potassium ((2-Ethoxyethoxy)methyl)trifluoroborate (S3): Obtained as a colorless oil, 5 mmol scale (610 mg, 58%), ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ ^{1}H NMR (acetone-d_6, 500 MHz,) δ 3.58 – 3.50 (m, 4H), 3.49-3.46 (m, 2H), 2.80 (s, 2H), 1.16 (t, *J* = 7.0 Hz, 3H), ^{13}C NMR (acetone-d_6, 126 MHz) δ 72.9, 69.2, 66.0, 14.4, ^{19}F NMR (acetone-d_6, 471 MHz) δ -145.0, ^{11}B NMR (acetone-d_6, 128 MHz) δ -4.8, IR: ν = 3606, 3054, 2977, 2870, 2305, 1712, 1608, 1447, 1265, 1072, 735 cm^{-1}, HRMS (ESI) m/z calc. for $C_5H_{11}BF_3O_2$ (M^-) 171.0804, found 171.0806.



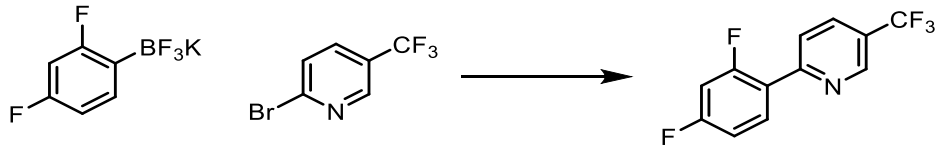
S4

Potassium ((Methoxy)methyl)pyrrolidin-2-onetrifluoroborate (S4): Obtained as a white solid (256 mg, 82%), mp = 120-123 ºC ^{1}H NMR (DMSO, 500 MHz) δ 3.36-3.35 (m, 4H), 3.25 (s, 4H), 2.18-2.16 (m, 2H), 1.88-1.87 (m, 2H), ^{13}C NMR (DMSO, 126 MHz) δ 174.5, 71.0, 47.5, 42.3, 30.8, 17.8, ^{19}F NMR (DMSO, 471 MHz) δ 141.8, ^{11}B NMR (DMSO, 128 MHz) δ 3.3, IR: ν = 3053, 2987, 2305, 1669, 1422, 1265, 1071, 895, 739, 705 cm^{-1}, HRMS (ESI) m/z calc. for $C_7H_{12}BF_3NO_2$ (M^-) 210.0913, found 210.0914.

Synthesis of photocatalyst 1

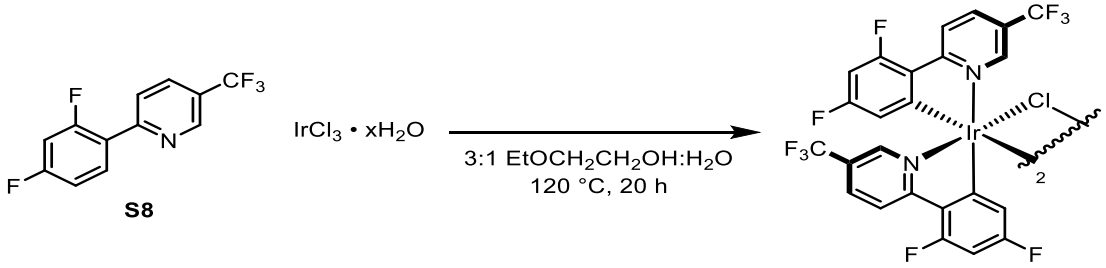
The synthesis of photocatalyst **1** has been documented in literature reports and fully included in our previous reports, but to aid the practicing chemist, all details are included here as well.[1] The procedures below have proven the most reliable in our experience.

[1] Tellis, J. C.; Primer, D. N.; Molander, G. A. *Science*, **2014**, *345*, 433.



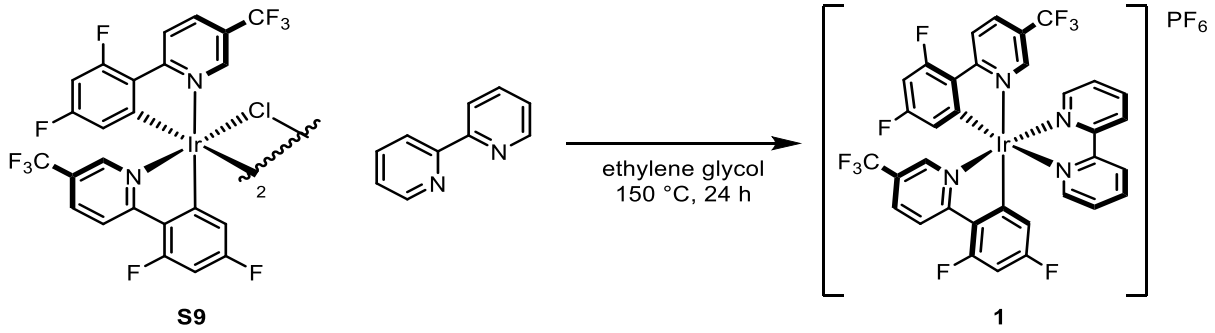
S5 **S6** **S7**

To a large vial equipped with a magnetic stir bar was added **S5** (3.3 g, 15 mmol), **S6** (2.26 g, 10 mmol), anhyd K_2CO_3 (6.9 g, 50 mmol), and $Pd(PPh_3)_4$ (1.16 g, 1 mmol). The vial was sealed tightly with a Teflon-coated septum cap and evacuated and purged with N_2 three times. The contents were dissolved in THF (32 mL) and degassed H_2O (16 mL), then stirred at 80 °C for 24 h. After cooling to rt, the reaction mixture was diluted with H_2O and extracted three times with CH_2Cl_2 (3 x 60 mL). The combined organic layers were dried ($MgSO_4$), filtered, concentrated under reduced pressure, and purified by silica gel column chromatography, eluting with 5% EtOAc in hexanes to afford ligand **S7** as a white solid (2.54 g, 98%). mp = 55-58 °C.
A small amount of PPh_3 was usually observed after column chromatography (<5 mol %), which did not interfere with subsequent reactions.



S8 **S9**

To a 20 mL round-bottom flask equipped with a magnetic stir bar was added ligand **S8** (428 mg, 1.65 mmol) and $IrCl_3$ hydrate (224 mg, 0.75 mmol). The flask was equipped with a cold water condenser and evacuated and purged with N_2 five times. The contents were suspended in rigorously degassed ethoxy ethanol (9 mL) and H_2O (3 mL) and then heated with stirring to 120 °C for 20 h, during which time a yellow precipitate was observed to form. After cooling to rt, the precipitate was collected by vacuum filtration. The filter cake was washed copiously with H_2O (~75 mL) and hexanes (~30 mL) to afford iridium μ-Cl-dimer **S9** as a fine yellow powder (84%). mp >250 °C. Characterization data for this compound matched that reported in the literature.[2]



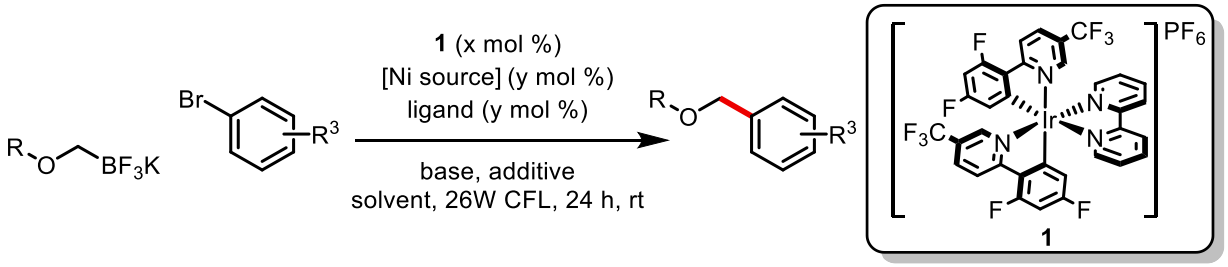
S9 **1**

To a 15 mL round-bottom flask equipped with a magnetic stir bar was added iridium dimer **S9** (130 mg, 0.087 mmol) and 2,2'-bipyridine (32 mg, 0.21 mmol). The flask was attached to a reflux

[2] Lowry, M. S.; Goldsmith, J. I.; Slinker, J. D.; Rohl, R.; Pascal, R. A.; Malliaras, G. G.; Bernhard, S. *Chem. Mater.* **2005**, *17*, 5712.

condenser, and the contents were placed under an inert atmosphere by three evacuation/purge cycles. The reaction components were dissolved in degassed ethylene glycol (6 mL) and heated with stirring at 150 °C for 24 h. Upon cooling to rt, the reaction mixture was diluted with deionized H_2O and transferred to a separatory funnel. The aqueous phase was washed three times with hexanes, then drained into an Erlenmeyer flask and heated to ~85 °C for 5-15 min to remove residual hexanes. Upon cooling to rt, an aq soln of NH_4PF_6 (10 mL, 0.1 g/mL) was added, resulting in the formation of a fine yellow precipitate that was isolated by vacuum filtration and then washing with H_2O (20 mL) and hexanes (15 mL). The solid was dried under high vacuum to remove residual H_2O and then dissolved in acetone and recrystallized by vapor diffusion with hexane to yield **1** as large yellow crystals (172 mg, 88%). mp = 199-202 °C. Characterization data for this compound matched that reported in the literature.[3]

Selected reaction optimization studies



A 1:1 ratio of Ni source and ligand were dissolved in THF in a 1 gram reaction vial equipped with a Teflon coated magnetic stir bar. After stirring about 10 min, the solvent was removed *in vacuo*. Other solid additives were weighed into the vials. The vials were then brought into the glovebox where a stock solution of aryl bromide (0.1 mmol), alkoxymethyltrifluoroborate, Ir catalyst **1**, and internal standard were then added by syringe and stirred for 24 h in front of a single 26 W CFL at an ambient temperature of ~35^0 C. Reactions were analyzed using GC and compared within sets by crude product to internal standard (P/IS) ratios. Note: P/IS can only be compared within each table; fresh stock solutions were prepared for each screen.

[3] Hanss, D.; Freys, J. C.; Bernardinelli, G.; Wenger, O. S. *Eur. J. Inorg. Chem.* **2009**, *2009*, 4850.

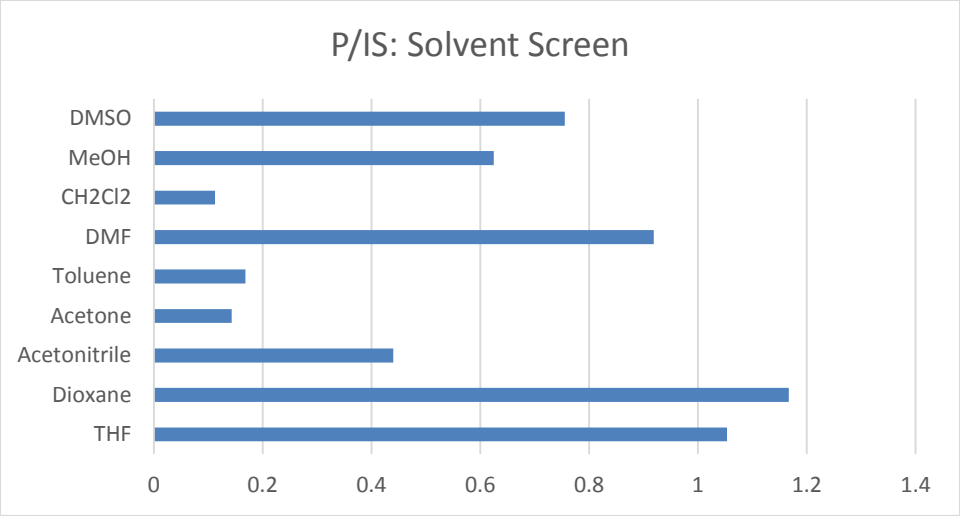


Figure S1: Comparison of Solvents
Conditions: 0.1 mmol Ph-Br, 1.2 equiv R-BF_3K, 2.0 % $Ir(dFCF_3ppy)_2bpy•PF_6$, 5.0 % $NiCl_2$•dme/dtbbpy, 0.05 M in solvent

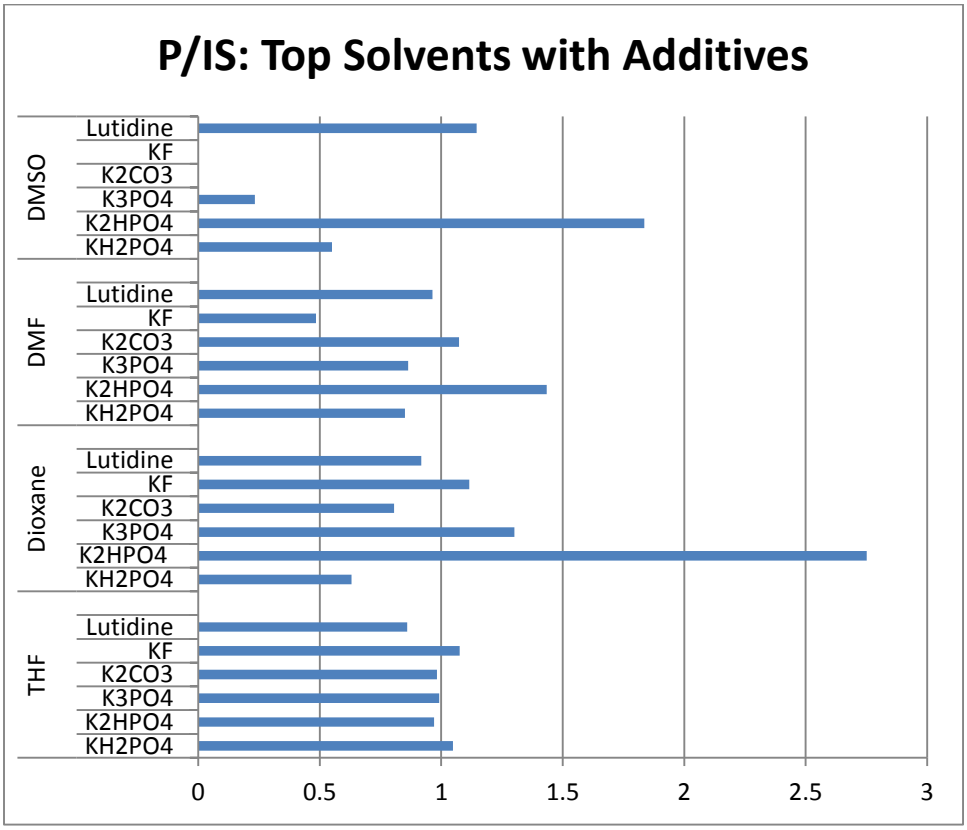


Figure S2: Comparison of Solvents and Bases
Conditions: 0.1 mmol Ph-Br, 1.2 equiv R-BF_3K, 2.0 % $Ir(dFCF_3ppy)_2bpy•PF_6$, 5.0 % $NiCl_2$•dme/dtbbpy, 1.0 equiv base, 0.05 M in solvent

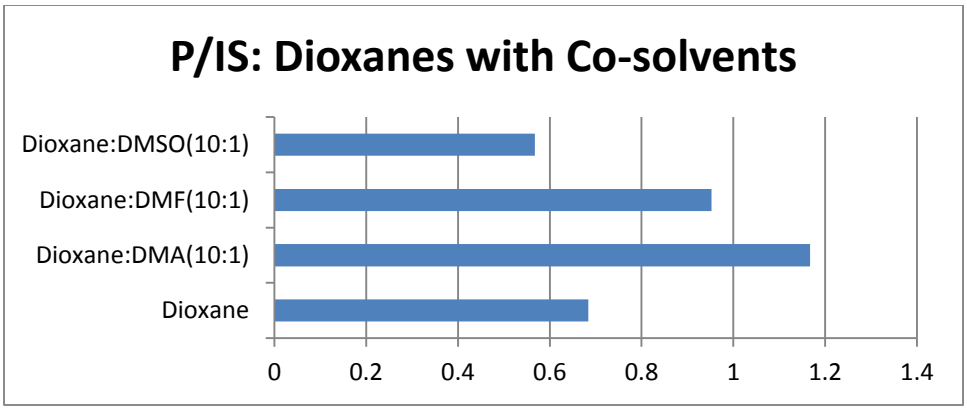


Figure S3: Comparison of Solvent Mixtures
Conditions: 0.1 mmol Ph-Br, 1.2 equiv R-BF_3K, 2.0 % $Ir(dFCF_3ppy)_2bpy•PF_6$, 5.0 % $NiCl_2$•dme/dtbbpy, 1.0 equiv K_2HPO_4, 0.05 M in solvent

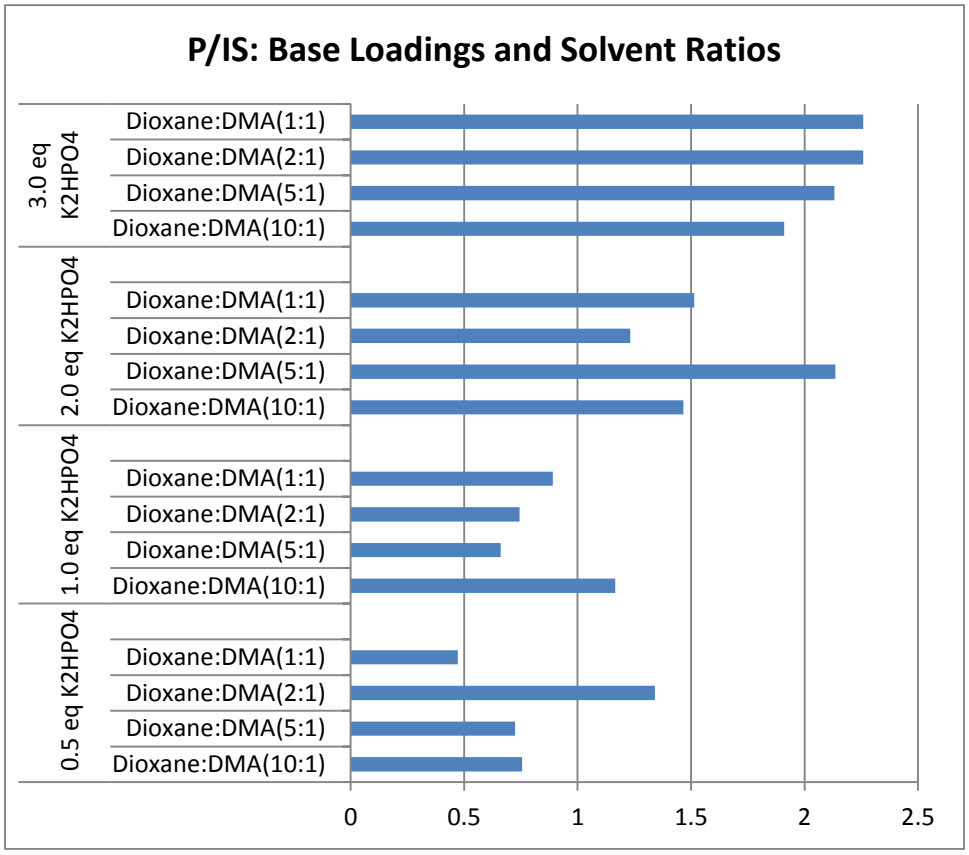


Figure S4: Comparison of Solvent Mixture and Base Ratios
Conditions: 0.1 mmol Ph-Br, 1.2 equiv R-BF_3K, 2.0 % $Ir(dFCF_3ppy)_2bpy•PF_6$, 5.0 % $NiCl_2$•dme/dtbbpy, 0.05 M in solvent

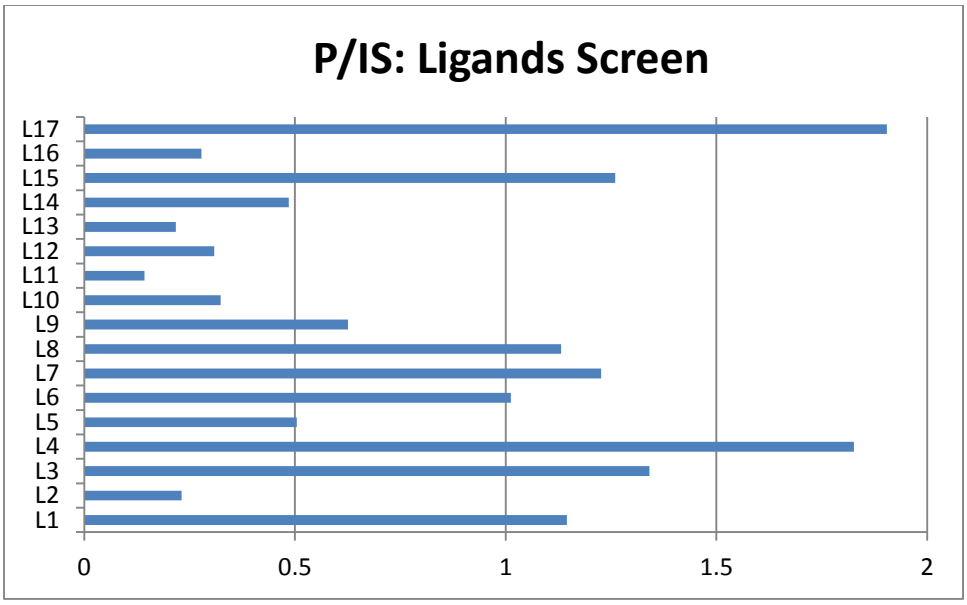
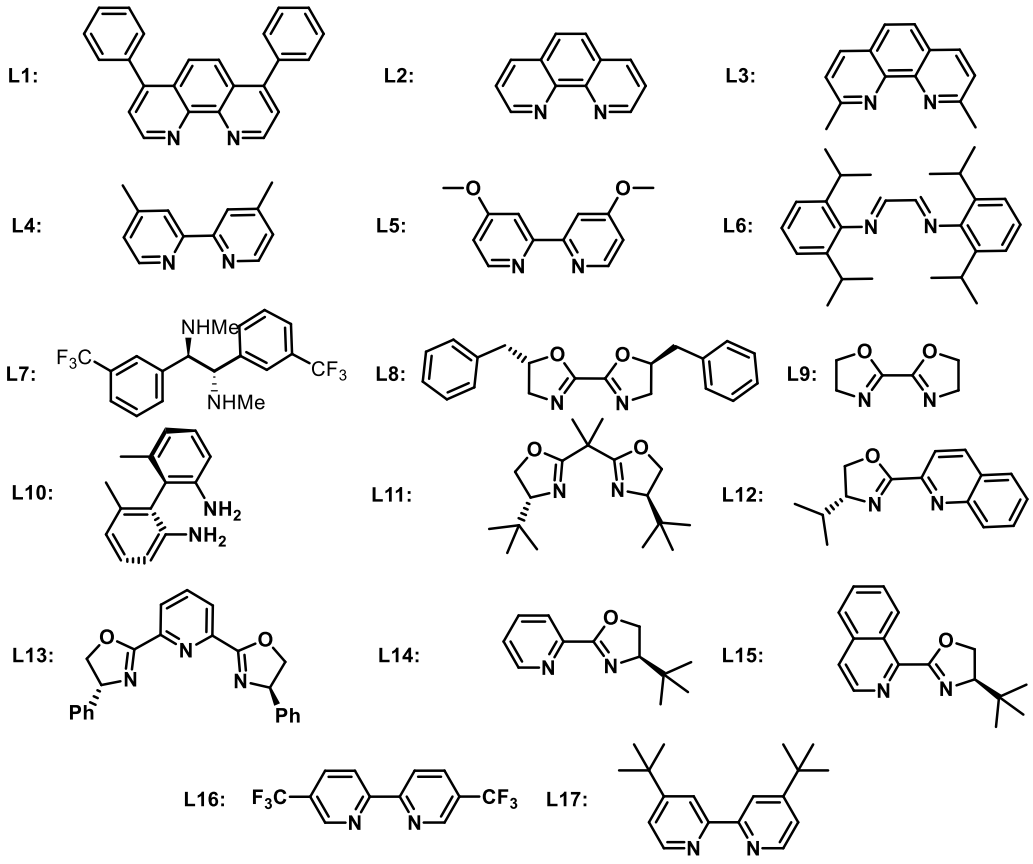


Figure S5: Comparison of Ligands
Conditions: 0.1 mmol Ph-Br, 1.2 equiv R-BF_3K, 2.0 % $Ir(dFCF_3ppy)_2bpy•PF_6$, 5.0 % $NiCl_2$•dme/ligand, 3.0 equiv K_2HPO_4, 0.05 M in solvent



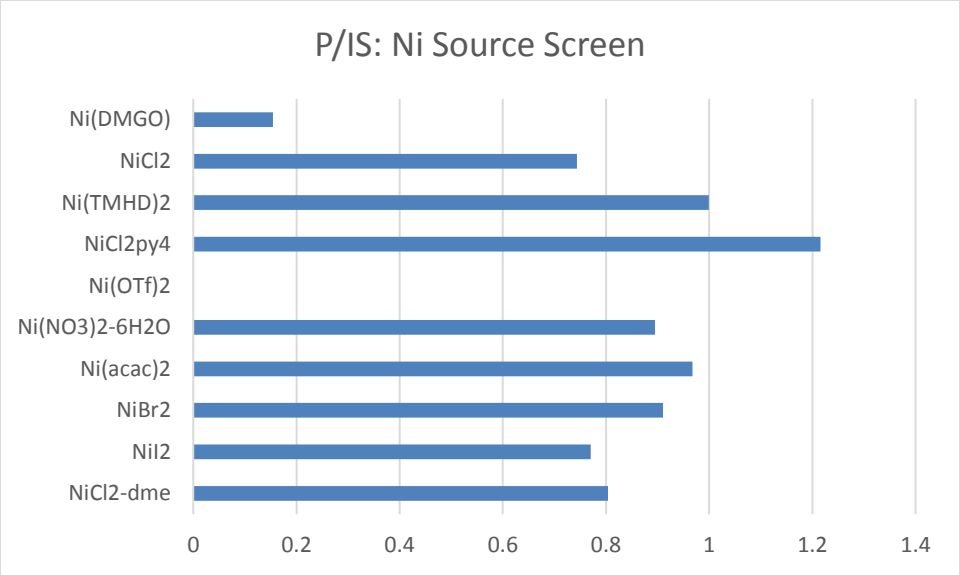


Figure S6: Comparison of Ni Sources
Conditions: 0.1 mmol Ph-Br, 1.2 equiv R-BF_3K, 2.0 % $Ir(dFCF_3ppy)_2bpy•PF_6$, 5.0 % Ni source / dtbbpy, 3.0 equiv K_2HPO_4, 0.05 M in solvent

Ni(DMGO) = Nickel(II) Dimethylglyoxime; $Ni(TMHD)_2$ = Nickel(II) bis(2,2,6,6-tetramethyl-3,5-heptanedionate); $NiCl_2py_4$ = Nickel(II) chloride tetrapyridine

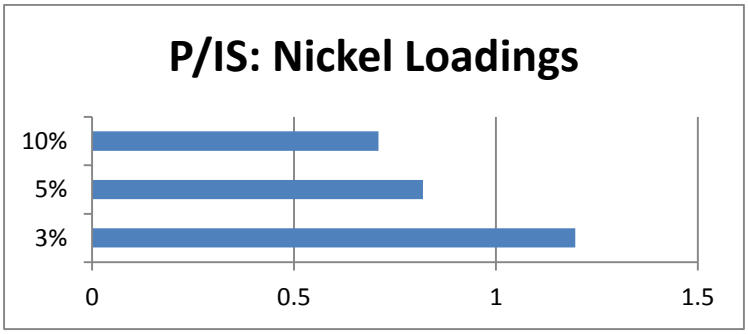
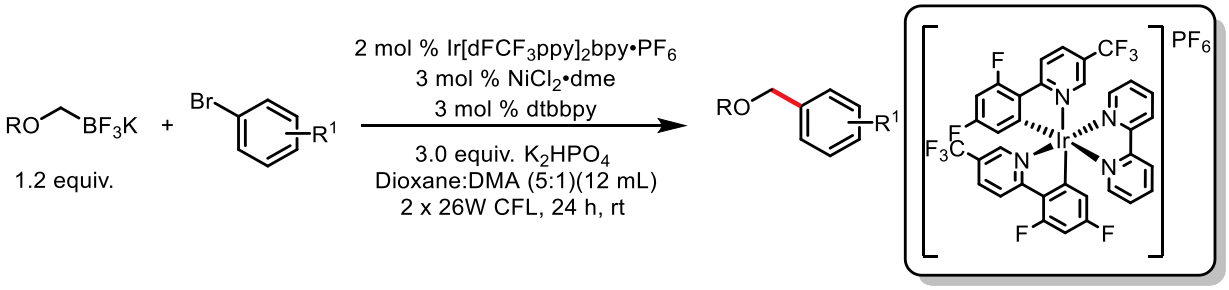


Figure S7: Comparison of $NiCl_2$•dme/dtbbpy loadings
Conditions: 0.1 mmol Ph-Br, 1.2 equiv R-BF_3K, 2.0 % $Ir(dFCF_3ppy)_2bpy•PF_6$, 3.0 equiv K_2HPO_4, 0.05 M in solvent

General procedure for photoredox cross-coupling reactions



4,4'-di-*tert*-Butyl-2,2'-bipyridine (4.0 mg, 0.015 mmol) and $NiCl_2$•dme (3.3 mg, 0.015 mmol) were weighed into a 20 mL oven-dried, long, thin (~20 mL) glass vial. Approximately 1 mL of dry, degassed THF was added and the mixture was heated briefly until obtaining a pale green solution. The solvent was then removed under vacuum to yield a ligated nickel complex that was pale evergreen color. Next, aryl bromide (0.5 mmol, 1 equiv) (liquid aryl bromides were added with solvent), alkoxymethyltrifluoroborate (0.6 mmol, 1.2 equiv), $Ir[dFCF_3ppy]_2(bpy)•PF_6$ **1** (10.1 mg, 0.02 mmol) and K_2HPO_4 (261 mg, 1.5 mmol) were added sequentially. Afterwards, the tube was sealed and subsequently purged and evacuated four times. Dioxane/DMA (5:1) (12 mL) was next added under inert atmosphere. The resulting mixture was stirred for 24 h approximately 4 cm away from two 26 W fluorescent light bulbs while a fan was blown across the reaction setup to maintain an ambient temperature of 24 ^oC. The crude reaction mixture was filtered through a cylindrical plug of Celite and rinsed with CH_2Cl_2 and EtOAc (10-20 mL). The resulting solution was concentrated, and the residue was purified by column chromatography on silica gel, eluting with EtOAc and hexanes, to obtain products in pure form.

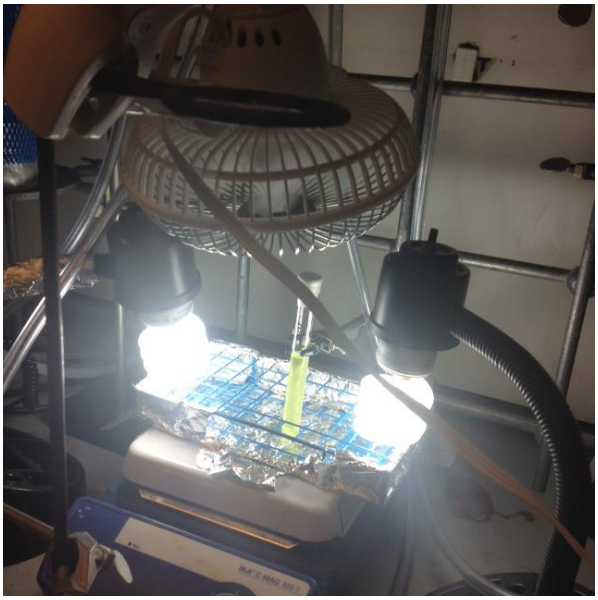


Fig S8: Photoredox cross-coupling reaction set-up (0.5 mmol scale)

Gram scale reaction: To a ~125 mL long, thin-walled vacuum flask equipped with a Teflon-coated magnetic stir bar was added $NiCl_2$•dme (16.5 mg, 0.075 mmol, 0.015 equiv) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (20 mg, 0.075, 0.015 equiv), and 5.0 mL of THF. The vial was capped, and the resulting suspension was heated briefly with a heat gun until the nickel and ligand were fully solubilized, yielding a pale green solution. The solvent was then removed under vacuum to give a fine coating of the ligated nickel complex (pale evergreen in color). Once fully evacuated, 1-(4-bromophenyl)ethan-1-one (1.000 g, 5.025 mmol, 1.00 equiv), potassium (benzyloxy)methyltrifluoroborate (1.37 g, 6.03 mmol, 1.20 equiv), $Ir[dFCF_3ppy]_2(bpy)$•PF_6 **1** (53 mg, 0.0525 mmol, 0.01 equiv), and K_2HPO_4 (2.6 g, 15.07 mmol, 3.0 equiv) was added. The vial was then capped with a rubber septum and purged and evacuated four times. Under inert atmosphere, dioxane (92 mL) and DMA (18 mL) was introduced. The vial containing all the reagents was further sealed with parafilm and stirred vigorously (a small vortex should be observed toward the top of the reaction mixture) for 48 h approximately 4 cm away from three 26 W fluorescent light bulbs. A fan was blown across the reaction setup to maintain an ambient temperature around 24 ºC. After completion, the crude reaction mixture was filtered through an approximately 4 cm x 2 cm cylindrical plug of Celite, washing with EtOAc (40 mL). The resulting solution was concentrated, and the residue was purified by column chromatography on silica gel, eluting with EtOAc and hexanes, to obtain product in pure form.

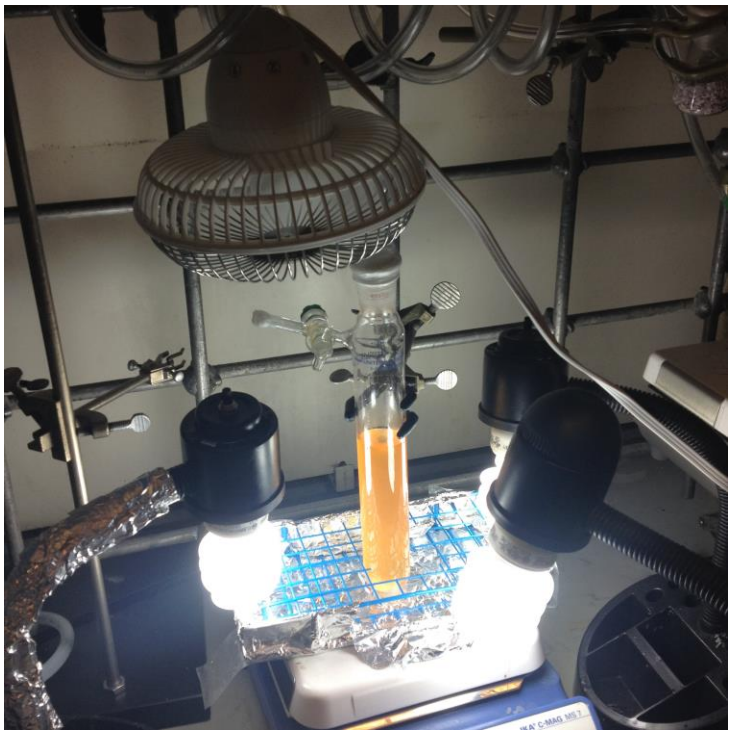
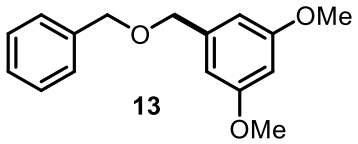


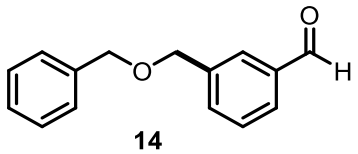
Fig S9: Gram scale photoredox cross-coupling reaction set-up (4.65 mmol)

Compound Characterization Data



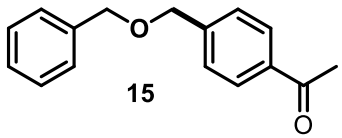
13

1-((Benzyloxy)methyl)-3,5-dimethoxybenzene (13): Obtained as a colorless oil (111 mg, 86%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.42-7.37 (m, 4H), 7.34-7.33 (m, 1H), 6.59 (s, 2H), 6.45 (s, 1H), 4.59 (s, 2H), 4.55 (s, 2H), 3.82 (s, 6H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 161.1, 141.0, 138.4, 128.6, 128.0, 127.8, 105.6, 99.9, 72.3, 72.2, 55.5, IR: ν = 2838, 1597, 1455, 1430, 1358, 1320, 1204, 1153, 1098, 1065, 1055, 833, 737, 698 cm^{-1}; HRMS (ESI) m/z calc. for $C_{16}H_{18}O_3Na$ (M+Na) 281.1154, found 281.1162.



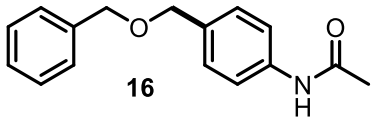
14

3-((Benzyloxy)methyl)benzaldehyde (14): Obtained as a semi solid (97 mg, 86%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.03 (s, 1H), 7.89 (s, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.41 – 7.35 (m, 4H), 7.33-7.31 (m, 1H), 4.63 (s, 2H), 4.61 (s, 2H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 192.4, 139.7, 138.0, 136.7, 133.7, 129.3, 129.1, 128.9, 128.7, 128.0, 128.0, 72.7, 71.5, IR: ν = 2856, 1694, 1606, 1590, 1453, 1285, 1203, 1099, 1072, 1028, 750, 697 cm^{-1}; HRMS (ESI) m/z calc. for $C_{15}H_{14}O_2Na$ (M+Na) 249.0891, found 249.0896.



15

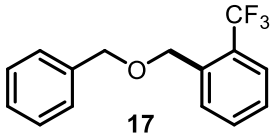
1-(4-(Benzyloxy)methyl)phenyl)ethan-1-one (15): Obtained as a colorless oil (114 mg, 95%) On gram scale with 1% Ir cat. **1** and 1.5% $NiCl_2$**.**dme/dtbbpy (868 mg, 72% yield), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.40 – 7.35 (m, 4H), 7.33-7.30 (m, 1H), 4.62 (s, 2H), 4.60 (s, 2H), 2.60 (s, 3H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 197.9, 144.0, 138.1, 136.6, 128.7, 128.6, 128.0, 127.9, 127.6, 72.7, 71.6, 26.8, IR: ν = 2919, 2851, 1682, 1609, 1413, 1358, 1267, 1092, 1073, 1016, 957, 820, 699 cm^{-1}; HRMS (ESI) m/z calc. for $C_{16}H_{16}O_2Na$ (M+Na) 263.1048, found 263.1035.



16

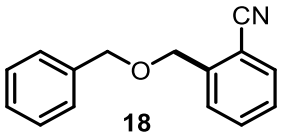
***N*-((4-(Benzyloxy)methyl)phenyl)acetamide (16):** Obtained as a white solid (108 mg, 85%), mp = 84-85 °C, ^{1}H NMR ($CDCl_3$, 500 MHz): 8.06 (s, 1H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.45 – 7.26 (m, 7H), 4.54 (s, 2H), 4.51 (s, 2H), 2.12 (s, 3H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 169.0, 138.3, 137.7, 134.2, 128.7, 128.5, 127.9, 127.8, 120.1, 72.2, 71.8, 24.5, IR: ν = 3309, 2866, 2342, 1614, 1611,

1555, 1544, 1517, 1358, 1326, 1270, 1091, 1073, 824, 730 cm^{-1}; HRMS (ESI) m/z calc. for $C_{16}H_{17}NO_2Na$ (M+Na) 278.1157, found 278.1147.



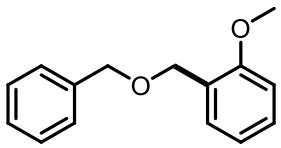
17

1-(Benzyloxy)methyl)-2-(trifluoromethyl)benzene (17): Obtained as a colorless oil (112 mg, 84%), ^1H NMR ($CDCl_3$, 500 MHz): δ 7.80 (d, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.59 (m, 1H), 7.42-7.39 (m, 5H), 7.35-7.32 (m, 1H), 4.81 (s, 2H), 4.66 (s, 2H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 138.1, 137.3, 132.1, 129.1, 128.6, 127.9, 127.9, 127.5, 125.8 (q, *J* = 5.7 Hz), 124.6 (q, *J* = 273.6 Hz), 73.0, 68.4 (q, *J* = 2.7 Hz), ^{19}F NMR (471 MHz, $CDCl_3$) δ -59.97, IR: ν = 2854, 1451, 1365, 1314, 1163, 1117, 1059, 1038, 769, 697 cm^{-1}; HRMS (ESI) m/z calc. for $C_{15}H_{14}F_3O$ (M+H) 267.0997, found 267.0992.



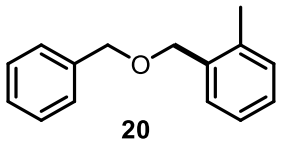
18

2-((Benzyloxy)methyl)benzonitrile (18): Obtained as a colorless oil (105 mg, 94%), ^1H NMR ($CDCl_3$, 500 MHz): δ 7.66-7.58 (m, 3H), 7.43-7.37 (m, 5H), 7.34-7.31 (m, 1H), 4.76 (s, 2H), 4.67 (s, 2H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 142.2, 137.8, 133.0, 132.9, 128.8, 128.7, 128.2, 128.1, 128.1, 117.5, 111.7, 73.37, 70.0, IR: ν = 2919, 2850, 2225, 1600, 1453, 13612, 1214, 1111, 1075, 763, 738, 698 cm^{-1}; HRMS (ESI) m/z calc. for $C_{15}H_{14}NO$ (M+H) 224.1075, found 224.1077.



19

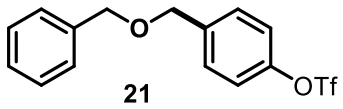
1-((Benzyloxy)methyl)-2-methoxybenzene (19): Obtained as a colorless oil (49 mg, 43%), ^1H NMR ($CDCl_3$, 500 MHz): δ 7.48 – 7.36 (m, 5H), 7.33-7.27 (m, 2H), 7.01-6.98 (m, 1H), 6.91-6.89 (m, 1H), 4.64 (s, 4H), 3.85 (s, 3H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 157.1, 138.5, 128.9, 128.6, 128.3, 127.7, 127.4, 126.6, 120.4, 110.1, 72.3, 66.9, 55.2, IR: ν = 3865, 2838, 1603, 1494, 1464, 1361, 1244, 1092, 1029, 753 cm^{-1}; HRMS (ESI) m/z calc. for $C_{15}H_{16}O_2$ (M+) 228.1150, found 228.1143.



20

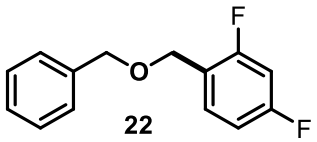
1-((Benzyloxy)methyl)-2-methylbenzene (20): Obtained as a colorless oil (77 mg, 73%), ^1H NMR ($CDCl_3$, 500 MHz): δ 7.41-7.37 (m, 5H), 7.34-7.32 (m, 1H), 7.26 – 7.18 (m, 3H), 4.61 (s, 2H), 4.59 (s, 2H), 2.37 (s, 3H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 138.3, 136.7, 136.0, 130.2, 128.6, 128.3, 127.8, 127.7, 127.6, 125.7, 72.2, 70.5, 18.8, IR: ν = 3029, 2855, 1605, 1495, 1454, 1358,

1213, 1090, 1072, 742, 697 cm^{-1}; HRMS (ESI) m/z calc. for $C_{15}H_{15}O$ (M-H) 211.1123, found 211.1129.



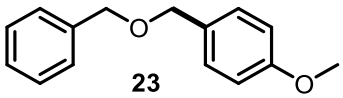
21

4-((Benzyloxy)methyl)phenyl trifluoromethanesulfonate (21): Obtained as a colorless oil (160 mg, 92%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.48-7.26 (m, 2H), 7.41-7.38 (m, 4H), 7.36-7.33 (m, 1H), 7.31-7.27 (m, 2H), 4.62 (s, 2H), 4.59 (s, 2H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 149.0, 139.2, 138.0, 129.4, 128.7, 128.0, 128.0, 121.4, 119.0 (q, *J* = 320.8 Hz), 72.8, 71.1, ^{19}F NMR (471 MHz, $CDCl_3$) δ -72.76, IR: ν = 2853, 1501, 1422, 1249, 1210, 1139, 1094, 1017, 887, 697 cm^{-1}; HRMS (ESI) m/z calc. for $C_{15}H_{13}F_3O_4SNa$ (M+Na) 369.0384, found 369.0383.



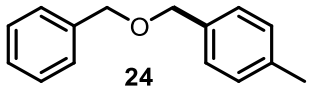
22

1-((Benzyloxy)methyl)-2,4-difluorobenzene (22): Obtained as a colorless oil (71 mg, 61%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.45-7.41 (m, 1H), 7.39 – 7.35 (m, 4H), 7.31-7.30 (m, 1H), 6.91 – 6.85 (m, 1H), 6.84 – 6.78 (m, 1H), 4.59 (s, 2H), 4.58 (s, 2H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 162.8 (dd, *J* = 220.7, 12.1 Hz), 160.9 (dd, *J* = 221.8, 12.2 Hz) 138.1, 131.2 (dd, *J* = 9.7, 5.6 Hz), 128.6, 127.9, 121.5 (dd, *J* = 15.3, 3.5 Hz), 111.3 (dd, *J* = 21.0, 3.6 Hz), 103.8 (dd, *J* = 25.4, 25.4 Hz), 72.7, 65.3 (d, *J* = 3.4 Hz), ^{19}F NMR ($CDCl_3$, 471 MHz): δ -110.9 (d, *J* = 7.4 Hz), -114.6 (d, *J* = 7.4 Hz), IR: ν = 2864, 1620, 1606, 1505, 1454, 1430, 1277, 1139, 1101, 1072, 1029, 962, 849, 735, 697 cm^{-1}; HRMS (ESI) m/z calc. for $C_{14}H_{12}F_2O$ (M+) 234.0856, found 234.0857.



23

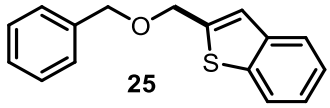
1-((Benzyloxy)methyl)-4-methoxybenzene (23): Obtained as a colorless oil (60 mg, 52%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.41 – 7.35 (m, 4H), 7.32 (m, 3H), 6.92 (d, *J* = 8.6 Hz, 2H), 4.56 (s, 2H), 4.52 (s, 2H), 3.83 (s, 3H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 159.1, 138.3, 130.3, 129.4, 128.3, 127.7, 127.5, 113.7, 71.7, 71.6, 55.2, IR: ν = 3893, 2853, 1652, 1513, 1454, 1360, 1302, 1247, 1172, 1088, 1071, 1034, 822, 737, 697 cm^{-1}; HRMS (ESI) m/z calc. for $C_{15}H_{16}O_2$ (M+) 228.1150, found 228.1155.



24

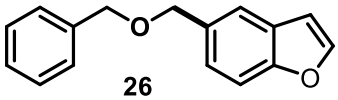
1-((Benzyloxy)methyl)-4-methylbenzene (24): Obtained as a colorless oil (66 mg, 62%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.46 – 7.38 (m, 4H), 7.36-7.33 (m, 3H), 7.23-7.22 (m, 2H), 4.60 (s, 2H), 4.58 (s, 2H), 2.41 (s, 3H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 138.3, 137.3, 135.2, 129.1, 128.3, 127.9, 127.7, 127.5, 71.9, 71.8, 21.2, IR: ν = 3028, 2854, 1615, 1516, 1496, 1453, 1359, 1204,

1092, 1073, 1028, 803, 735, 697 cm^{-1}; HRMS (ESI) m/z calc. for $C_{15}H_{15}O$ (M-H) 211.1123, found 211.1124.



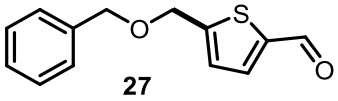
25

2-((Benzyloxy)methyl)benzo[b]thiophene (25): Obtained as a white solid, mp = 51-53 ^oC (98 mg, 77%), ^1H NMR ($CDCl_3$, 500 MHz): δ 7.87 (d, *J* = 7.3 Hz, 1H), 7.78 (d, *J* = 7.2 Hz, 1H), 7.45 – 7.31 (m, 7H), 7.26 (s, 1H), 4.85 (s, 2H), 4.65 (s, 2H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 142.2, 140.2, 139.4, 137.7, 128.4, 127.9, 127.8, 126.3, 124.2, 123.4, 122.6, 122.4, 71.8, 67.2, IR: ν = 3031, 2923, 2851, 1496, 1455, 1355, 1140, 1129, 1086, 1070, 1061, 841, 746, 727, 696 cm^{-1}; HRMS (ESI) m/z calc. for $C_{16}H_{14}OSNa$ (M+Na) 277.0663, found 277.0673.



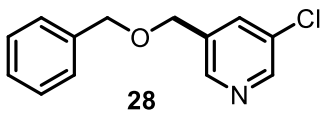
26

5-((Benzyloxy)methyl)benzofuran (26): Obtained as a colorless oil (86 mg, 72%), ^1H NMR ($CDCl_3$, 500 MHz): δ 7.65-7.64 (m, 2H), 7.53-7.51 (m, 1H), 7.46 – 7.37 (m, 4H), 7.36 – 7.29 (m, 2H), 6.79-6.78 (m, 1H), 4.68 (s, 2H), 4.61 (s, 2H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 154.8, 145.5, 138.5, 133.0, 128.6, 128.0, 127.8, 127.7, 124.7, 120.9, 111.4, 106.8, 72.5, 72.1, IR: ν = 2854, 1538, 1496, 1469, 1453, 1444, 1362, 1264, 1126, 1108, 1089, 1070, 1031, 884, 760, 734 cm^{-1}; HRMS (ESI) m/z calc. for $C_{16}H_{14}O_2Na$ (M+Na) 261.0891, found 261.0899.



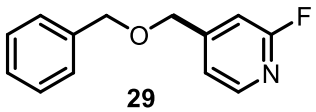
27

5-((Benzyloxy)methyl)thiophene-2-carbaldehyde (27): Obtained as a colorless oil (65 mg, 56%), ^1H NMR ($CDCl_3$, 500 MHz): 9.87 (s, 1H), 7.66 (d, *J* = 3.8 Hz, 1H), 7.37 (d, *J* = 4.4 Hz, 4H), 7.34 – 7.26 (m, 1H), 7.09 (d, *J* = 3.7 Hz, 1H), 4.73 (s, 2H), 4.61 (s, 2H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 183.1, 152.6, 143.5, 137.5, 136.6, 128.7, 128.2, 128.0, 126.6, 72.7, 66.9, IR: ν = 2854, 1713, 1668, 1464, 1454, 1359, 1227, 1206, 1086, 816, 738, 698 cm^{-1}; HRMS (ESI) m/z calc. for $C_{13}H_{12}O_2SNa$ (M+Na) 255.0456, found 255.0462.



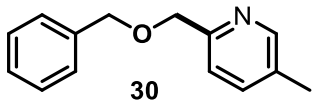
28

1-((Benzyloxy)methyl)-3-chlorobenzene (28): Obtained as a colorless oil (75 mg, 64%), ^1H NMR ($CDCl_3$, 500 MHz): δ 8.52 (m, 1H), 8.46 (s, 1H), 7.73 (s, 1H), 7.38 (m, 4H), 7.34 (m, 1H), 4.61 (s, 2H), 4.56 (s, 2H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 147.9, 146.6, 137.3, 135.1, 134.9, 132.0, 128.5, 127.9, 127.7, 72.7, 68.6, IR: ν = 2921, 1566, 1336, 1265, 1165, 1059, 1035, 911, 732, cm^{-1}; HRMS (ESI) m/z calc. for $C_{13}H_{13}ClNO$ (M+H) 234.0686, found 234.0685.



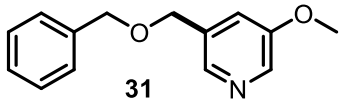
29

4-((Benzyloxy)methyl)-2-fluoropyridine (**29)**: Obtained as a colorless oil (102 mg, 94%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.17 (d, *J* = 5.1 Hz, 1H), 7.39-7.38 (m, 4H), 7.35-7.32 (m, 1H), 7.15-7.14 (m, 1H), 6.97 (s, 1H), 4.63 (s, 2H), 4.59 (s, 2H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 165.0, 163.1, 153.7 (d, *J* = 7.6 Hz), 147.5 (d, *J* = 15.1 Hz), 137.3, 128.5, 127.8 (d, *J* = 32.9 Hz), 119.2 (d, *J* = 4.1 Hz), 107.2 (d, *J* = 38.2 Hz), 72.9, 69.7 (d, *J* = 2.9 Hz), ^{19}F NMR (471 MHz, $CDCl_3$) δ -68.1, IR: ν = 2858,1615, 1570, 1453, 1411, 1359, 1277, 1148, 1097, 958, 830, 737, 698 cm^{-1}; HRMS (ESI) m/z calc. for $C_{13}H_{13}FNO$ (M+H) 218.0981, found 218.0977.



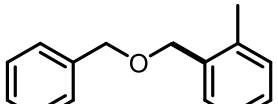
30

2-((Benzyloxy)methyl)-5-methylpyridine (30): Obtained as a colorless oil (91 mg, 86%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.40 (s, 1H), 7.51-7.49 (m, 1H), 7.40-7.34 (m, 5H), 7.31-7.29 (m, 1H), 4.67 (s, 2H), 4.64 (s, 2H), 2.33 (s, 3H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 155.4, 149.4, 138.0, 137.1, 131.7, 128.3, 127.7, 127.6, 121.0, 73.0, 72.7, 18.1, IR: ν = 2922, 2855, 1603, 1573, 1490, 1454, 1356, 1099, 1030, 824, 734, 698 cm^{-1}; HRMS (ESI) m/z calc. for $C_{14}H_{15}NONa$ (M+Na) 236.1051, found 236.1062.



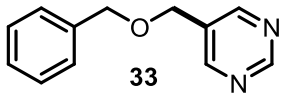
31

3-((Benzyloxy)methyl)-5-methoxypyridine (31): Obtained as a colorless oil (87 mg, 76%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.25-8.24 (m, 1H), 8.18 (s, 1H), 7.37-7.36 (m, 4H), 7.34 – 7.28 (m, 1H), 7.24 (s, 1H), 4.58 (s, 2H), 4.55 (s, 2H), 3.85 (s, 3H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 155.9, 141.4, 137.9, 137.3, 134.5, 128.7, 128.0, 128.0, 119.7, 72.7, 69.4, 55.7, IR: ν = 2840, 1591, 1468, 1429, 1287, 1192, 1178, 1097, 1051, 865, 740, 701 cm^{-1}; HRMS (ESI) m/z calc. for $C_{14}H_{16}NO_2$ (M+H) 230.1181, found 230.1185.



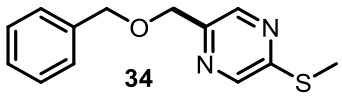
32

3-((Benzyloxy)methyl)-4-methylpyridine (32): Obtained as a colorless oil (90 mg, 85%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.48 (s, 1H), 8.41 (d, *J* = 4.9 Hz, 1H), 7.35-7.32 (m, 4H), 7.29 (dd, *J* = 8.6, 4.2 Hz, 1H), 7.07 (d, *J* = 4.9 Hz, 1H), 4.55 (s, 2H), 4.53 (s, 2H), 2.33 (s, 3H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 150.0, 149.6, 146.7, 138.0, 132.0, 128.6, 128.0, 127.9, 125.4, 72.7, 68.3, 18.5, IR: ν = 3052, 2861, 1597, 1559, 1506, 1496, 1456, 1362, 1265, 1076, 738 cm^{-1}, HRMS (ESI) m/z calc. for $C_{14}H_{16}NO$ (M+H) 214.1232, found 214.1230.



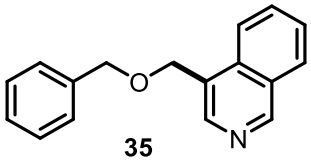
33

5-((Benzyloxy)methyl)pyrimidine (33): Obtained as a colorless oil (82 mg, 82%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.14 (s, 1H), 8.71 (s, 2H), 7.38 – 7.33 (m, 4H), 7.31-7.39 (m, 1H), 4.60 (s, 2H), 4.53 (s, 2H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 158.3, 156.4, 137.4, 131.7, 128.7, 128.2, 128.0, 73.1, 67.3, IR: ν = 2917, 2851, 1722, 1564, 1410, 1271, 1164, 1109, 1092, 1074, 728 cm^{-1}; HRMS (ESI) m/z calc. for $C_{12}H_{13}N_2O$ (M+H) 201.1028, found 201.1027.



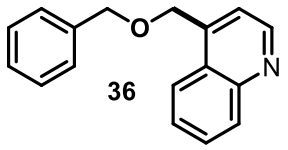
34

2-((Benzyloxy)methyl)-5-(methylthio)pyrazine (34): Obtained as a colorless oil (103 mg, 84%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.52-8.51 (m, 1H), 8.41-8.40 (m, 1H), 7.40 – 7.33 (m, 4H), 7.31-7.29 (m, 1H), 4.65 (s, 2H), 4.64 (s, 2H), 2.56 (s, 3H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 156.3, 148.0, 142.9, 142.4, 137.8, 128.6, 128.0, 128.0, 73.1, 71.0, 12.8, IR: ν = 3030, 2856, 1497, 1463, 1357, 1317, 1116, 1023, 736, 698 cm^{-1}; HRMS (ESI) m/z calc. for $C_{13}H_{15}N_2OS$ (M+H) 247.0905, found 247.0903.



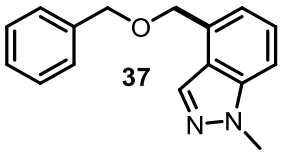
35

4-((Benzyloxy)methyl)isoquinoline (35): Obtained as a colorless oil (89 mg, 72%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.24 (s, 1H), 8.52 (s, 1H), 8.13 (d, *J* = 8.3 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.75-7.72 (m, 1H), 7.63-7.61 (m, 1H), 7.39 – 7.34 (m, 4H), 7.33 – 7.28 (m, 1H), 4.95 (s, 2H), 4.62 (s, 2H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 153.6, 143.3, 138.0, 134.9, 130.8, 128.7, 128.3, 128.1, 128.0, 127.4, 127.0, 123.6, 72.5, 68.4, IR: ν = 3053, 2985, 2861, 2305, 1624, 1420, 1362, 1265, 1075, 896, 738, 703 cm^{-1}, HRMS (ESI) m/z calc. for $C_{17}H_{16}NO$ (M+H) 250.1232, found 250.1235.



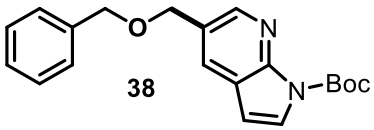
36

4-((Benzyloxy)methyl)quinoline (36): Obtained as a semisolid (116 mg, 93%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.91 (d, *J* = 4.2 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.73-7.71 (m, 1H), 7.60-7.51 (m, 2H), 7.39 (m, 4H), 7.33 (m, 1H), 5.01 (s, 2H), 4.68 (s, 2H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 150.3, 148.0, 143.5, 137.6, 130.1, 129.1, 128.5, 127.8, 127.7, 126.5, 126.1, 123.1, 119.4, 72.8, 68.5, IR: ν = 2863, 1712, 1596, 1510, 1453, 1352, 1242, 1109, 852, 758, 737 cm^{-1}; HRMS (ESI) m/z calc. for $C_{17}H_{16}NO$ (M+H) 250.1232, found 250.1238.



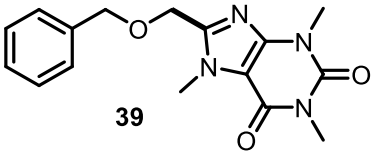
37

4-((Benzyloxy)methyl)-1-methyl-1H-indazole (37): Obtained as a colorless oil (92 mg, 73%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.12 (s, 1H), 7.42 – 7.34 (m, 6H), 7.33-7.30 (m, 1H), 7.14 (d, *J* = 5.8 Hz, 1H), 4.90 (s, 2H), 4.61 (s, 2H), 4.10 (s, 3H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 140.1, 138.0, 131.8, 131.6, 128.4, 127.8, 127.6, 126.0, 122.8, 119.4, 108.5, 72.2, 70.3, 35.5 , IR: ν = 2854, 2358, 2340, 1611, 1453, 1354, 1275, 1162, 1093, 1074, 980, 781, 735, 698 cm^{-1}; HRMS (ESI) m/z calc. for $C_{16}H_{16}N_2ONa$ (M+Na) 275.1160, found 275.1161.



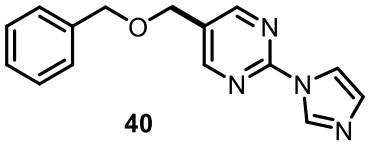
38

(*tert*-Butyl 5-(Benzyloxy)methyl)-1H-pyrrolo[2,3-b]pyridine-1-carboxylate (38): Obtained as a colorless oil (98 mg, 58%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.47 (d, *J* = 1.9 Hz, 1H), 7.90 (d, *J* = 1.9 Hz, 1H), 7.64 (d, *J* = 4.0 Hz, 1H), 7.35 (d, *J* = 4.3 Hz, 4H), 7.30-7.28 (m, 1H), 6.48 (d, *J* = 4.1 Hz, 1H), 4.65 (s, 2H), 4.55 (s, 2H), 1.66 (s, 9H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 148.3, 148.0, 145.3, 138.1, 129.0, 128.6, 128.0, 127.9, 127.2, 123.1, 104.6, 84.2, 72.2, 70.0, 28.2, IR: ν = 2860, 1753, 1729, 1532, 1477, 1392, 1370, 1318, 1254, 1159, 1092, 1028, 734 cm^{-1}; HRMS (ESI) m/z calc. for $C_{20}H_{23}N_2O_3$ (M+H) 339.1725, found 339.1719.



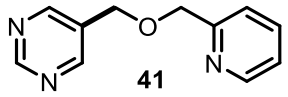
39

8-((Benzyloxy)methyl)-1,3,7-trimethyl-3,7-dihydro-1H-purine-2,6-dione (39): Obtained as a white solid, mp = 124-125 ^{o}C (146 mg, 93%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.37 – 7.23 (m, 5H), 4.62 (s, 2H), 4.55 (s, 2H), 3.94 (s, 3H), 3.53 (s, 3H), 3.36 (s, 3H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 155.5, 151.7, 149.3, 147.5, 137.0, 128.7, 128.3, 128.2, 108.6, 73.2, 63.7, 32.4, 29.8, 28.1, IR: ν = 3055, 2359, 2343, 1705, 1660, 1544, 1457, 1265, 1073, 849, 738, 703 cm^{-1}, HRMS (ESI) m/z calc. for $C_{16}H_{19}N_4O_3$ (M+H) 315.1457, found 315.1457.



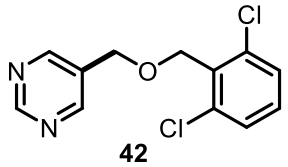
40

5-((benzyloxy)methyl)-2-(1H-imidazol-1-yl)pyrimidine (40): Obtained as a white solid, mp = 59-61 ^{o}C (111 mg, 83%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.68 – 8.59 (m, 3H), 7.89 (s, 1H), 7.42 – 7.30 (m, 5H), 7.17 (s, 1H), 4.60 (s, 2H), 4.52 (s, 2H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 158.9, 158.3, 154.5, 137.3, 130.9, 129.3, 128.8, 128.3, 128.0, 119.1, 73.1, 66.8, IR: ν = 3051, 2925, 2859, 2305, 1700, 1573, 1476, 1454, 1266, 1097, 1052, 981, 737 cm^{-1}, HRMS (ESI) m/z calc. for $C_{15}H_{15}N_4O$ (M+H) 267.1246, found 267.1247.



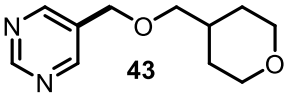
41

5-((Pyridin-2-ylmethoxy)methyl)pyrimidine (41): Obtained as a white solid, mp = 38-39 ºC (71 mg, 71%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.13 (s, 1H), 8.73 (s, 2H), 8.54-8.53 (m, 1H), 7.70-7.68 (m, 1H), 7.42-7.40 (m, 1H), 7.23 – 7.15 (m, 1H), 4.71 (s, 2H), 4.64 (s, 2H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 158.4, 157.5, 156.4, 149.4, 137.0, 131.4, 122.9, 121.7, 74.0, 68.1, IR: ν = 2858, 1718, 1590, 1564, 1439, 1412, 1111, 1046, 1029, 764, 729 cm^{-1}; HRMS (ESI) m/z calc. for $C_{11}H_{11}N_3ONa$ (M+Na) 224.0800, found 224.0807.



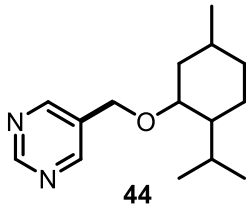
42

5-(((2,6-Dichlorobenzyl)oxy)methyl)pyrimidine (42): Obtained as a white solid, mp = 77-78 ºC (95 mg, 71%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.13 (s, 1H), 8.74 (s, 2H), 7.32-7.30 (m, 2H), 7.20-7.17 (m, 1H), 4.86 (s, 2H), 4.62 (s, 2H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 158.4, 156.4, 137.0, 132.8, 131.5, 130.5, 128.6, 67.9, 67.5, IR: ν = 2923, 2853, 1184, 1565, 1436, 1407, 1104, 1090, 1080, 941, 792, 760, 729 cm^{-1}; HRMS (ESI) m/z calc. for $C_{12}H_{11}Cl_2N_2O$ (M+H) 269.0248, found 269.0248.



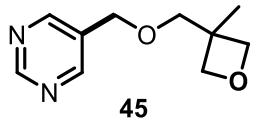
43

5-((Tetrahydro-2H-pyran-4-yl)methoxy)methyl)pyrimidine (43): Obtained as a colorless oil (61 mg, 58%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.14 (s, 1H), 8.69 (s, 2H), 4.50 (s, 2H), 3.98 – 3.92 (m, 2H), 3.44 – 3.30 (m, 4H), 1.93 – 1.83 (m, 1H), 1.68 – 1.60 (m, 2H), 1.41 – 1.28 (m, 2H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 158.3, 156.2, 131.8, 76.2, 68.4, 67.7, 35.6, 30.0, IR: ν = 2918, 2847, 1728, 1564, 1442, 1407, 1288, 1237, 1148, 1111, 1091, 728 cm^{-1}; HRMS (ESI) m/z calc. for $C_{11}H_{17}N_2O_2$ (M+H) 209.1290, found 209.1287.



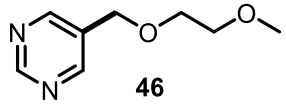
44

5-(((1*S*)-2-Isopropylcyclohexyl)oxy)methyl)pyrimidine (44): Obtained as a colorless oil (78 mg, 63%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.11 (s, 1H), 8.69 (s, 2H), 4.66 (d, *J* = 12.1 Hz, 1H), 4.37 (d, *J* = 12.1 Hz, 1H), 3.20-3.15 (m, 1H), 2.24 – 2.09 (m, 2H), 1.66-1.60 (m, 2H), 1.37-1.33 (m, 1H), 1.29-1.24 (m, 1H), 0.93-0.80 (m, 9H), 0.71 (d, *J* = 7.0 Hz, 3H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 158.1, 156.3, 132.5, 79.9, 65.7, 48.3, 40.3, 34.5, 31.6, 25.8, 23.4, 22.4, 21.0, 16.2, IR: ν = 3354, 2959, 2871, 1565, 1453, 1410, 1370, 1161, 1110, 953, 727 cm^{-1}; HRMS (ESI) m/z calc. for $C_{15}H_{25}N_2O$ (M+H) 249.1967, found 249.1978.



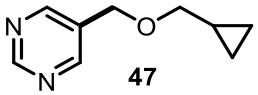
45

5-(((2-Methyloxetan-2-yl)methoxy)methyl)pyrimidine (45): Obtained as a colorless oil (72 mg, 74%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.13 (s, 1H), 8.69 (s, 2H), 4.56 (s, 2H), 4.47 (d, *J* = 5.6 Hz, 2H), 4.34-4.33 (m, 2H), 3.56 (s, 2H), 1.29 (s, 3H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 158.2, 156.1, 131.4, 79.9, 76.2, 68.6, 39.9, 21.3, IR: ν = 2868, 1729, 1584, 1564, 1407, 1290, 1111, 1093, 1045, 977, 833, 727 cm^{-1}; HRMS (ESI) m/z calc. for $C_{10}H_{15}N_2O_2$ (M+H) 195.1134, found 195.1133.



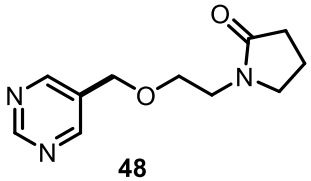
46

5-((2-Methoxyethoxy)methyl)pyrimidine (46): Obtained as a colorless oil (80 mg, 95%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.09 (s, 1H), 8.68 (s, 2H), 4.54 (s, 2H), 3.69-3.67 (m, 2H), 3.58-3.57 (m, 2H), 3.33 (s, 3H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 158.2, 156.4, 131.6, 72.0, 70.4, 68.6, 59.2, IR: ν = 3420, 2894, 1628, 1568, 1410, 1111, 1092, 847, 727, 630 cm^{-1}; HRMS (ESI) m/z calc. for $C_8H_{12}N_2O_2Na$ (M+Na) 191.0796, found 191.0799.



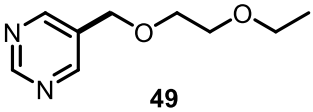
47

5-((Cyclopropylmethoxy)methyl)pyrimidine (47): Obtained as a colorless oil (45 mg, 55%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.14 (s, 1H), 8.72 (s, 2H), 4.54 (s, 2H), 3.37 (d, *J* = 6.9 Hz, 2H), 1.14 – 1.04 (m, 1H), 0.59 – 0.52 (m, 2H), 0.23-0.20 (m, 2H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 158.0, 156.1, 131.7, 75.7, 67.6, 10.3, 3.0, IR: ν = 2858, 1586, 1564, 1440, 1409, 1376, 1110, 1089, 1045, 728 cm^{-1}; HRMS (ESI) m/z calc. for $C_9H_{13}N_2O$ (M+H) 165.1028, found 165.1026.



48

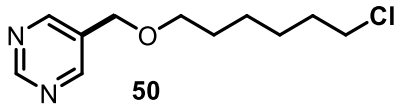
1-(2-(Pyrimidin-5-ylmethoxy)ethyl)pyrrolidin-2-one (48): Obtained as a colorless oil (74 mg, 67%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.12 (s, 1H), 8.66 (s, 2H), 4.50 (s, 2H), 3.65-3.63 (m, 2H), 3.50-3.48 (m, 2H), 3.45-4.42 (m, 2H), 2.35-2.42 (m, 2H), 2.02-1.94 (m, 2H),^{13}C NMR ($CDCl_3$, 126 MHz): δ 175.4, 158.3, 156.2, 131.4, 69.2, 68.2, 48.7, 42.4, 30.9, 18.2, IR: ν = 2923, 2870, 2239, 1677, 1566, 1408, 1289, 1115, 912, 728 cm^{-1}, HRMS (ESI) m/z calc. for $C_{11}H_{15}N_3O_2Na$ (M+Na) 244.1062, found 244.1059.



49

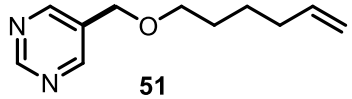
5-((2-Ethoxyethoxy)methyl)pyrimidine (49): Obtained as a colorless oil (55 mg, 60%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.11 (s, 1H), 8.70 (s, 2H), 4.57 (s, 2H), 3.66-3.64 (m, 2H), 3.60-3.58 (m, 2H), 3.49 (q, *J* = 7.0 Hz, 2H), 1.18 (t, *J* = 7.0 Hz, 3H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 158.0,

156.1, 131.4, 70.3, 69.7, 68.4, 66.7, 15.0, IR: ν = 3053, 2980, 2873, 2306, 1734, 1565, 1410, 1265, 1110, 896, 739 cm^{-1}, HRMS (ESI) m/z calc. for $C_9H_{14}N_2O_2Na$ (M+Na) 205.0953, found 205.0958.



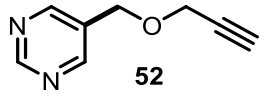
50

5-((5-Chloropentyl)oxy)methyl)pyrimidine (50): Obtained as a colorless oil (90 mg, 79%), ^1H NMR ($CDCl_3$, 500 MHz): δ 9.10 (s, 1H), 8.67 (s, 2H), 4.47 (s, 2H), 3.50-3.46 (m, 4H), 1.76-1.70 (m, 2H), 1.63-1.57 (m, 2H), 1.45-1.35 (m, 4H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 158.2, 156.2, 131.9, 71.1, 68.2, 45.1, 32.6, 29.6, 26.7, 25.5, IR: ν = 2934, 2860, 1727, 1564, 1440, 1406, 1112, 1095, 727 cm^{-1}; HRMS (ESI) m/z calc. for $C_{11}H_{18}ClN_2O$ (M+H) 229.1108, found 229.1112.



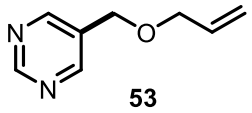
51

5-((Hex-5-en-1-yloxy)methyl)pyrimidine (51): Obtained as a colorless oil (67 mg, 70%), ^1H NMR ($CDCl_3$, 500 MHz): δ 9.13 (s, 1H), 8.69 (s, 2H), 5.82 – 5.72 (m, 1H), 5.00-4.91 (m, 2H), 4.49 (s, 2H), 3.52-3.49 (m, 2H), 2.12 – 2.02 (m, 2H), 1.69 – 1.57 (m, 2H), 1.52 – 1.41 (m, 2H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 158.2, 156.2, 138.6, 131.9, 114.8, 71.2, 68.2, 33.6, 29.1, 25.5, IR: ν = 3391, 2968, 2934, 2861, 1731, 1643, 1565, 1408, 1112, 1099, 952, 910, 728 cm^{-1}; HRMS (ESI) m/z calc. for $C_{11}H_{17}N_2O$ (M+H) 193.1341, found 193.1345.



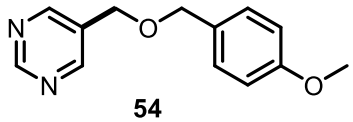
52

5-((Prop-2-yn-1-yloxy)methyl)pyrimidine (52): Obtained as a white semi-solid (58 mg, 78%), ^1H NMR ($CDCl_3$, 500 MHz): δ 9.15 (s, 1H), 8.72 (s, 2H), 4.61 (s, 2H), 4.23 (s, 2H), 2.51 (s, 1H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 158.5, 156.5, 131.0, 78.8, 75.8, 66.8, 58.1, IR: ν = 3276, 1566, 1444, 1409, 1388, 1276, 1233, 1164, 1107, 1091, 1046, 724 cm^{-1}; HRMS (ESI) m/z calc. for $C_8H_9N_2O$ (M+H) 149.0715, found 149.0712.



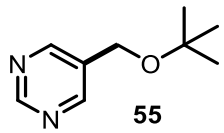
53

5-((Allyloxy)methyl)pyrimidine (53): Obtained as a colorless oil (57 mg, 76%), ^1H NMR ($CDCl_3$, 500 MHz): δ 9.11 (s, 1H), 8.69 (s, 2H), 5.96 – 5.83 (m, 1H), 5.30-5.20 (m, 2H), 4.49 (s, 2H), 4.04 (d, *J* = 5.6 Hz, 2H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 158.3, 156.3, 134.0, 131.7, 118.1, 72.0, 67.3, IR: ν = 3050, 2982, 2858, 1588, 1564, 1410, 1267, 1086, 931, 737 cm^{-1}, HRMS (ESI) m/z calc. for $C_8H_{11}N_2O$ (M+H) 151.0871, found 151.0867.



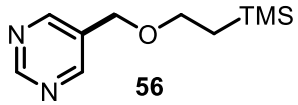
54

5-(((4-Methoxybenzyl)oxy)methyl)pyrimidine (54): Obtained as a colorless oil (71 mg, 62%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.19 (s, 1H), 8.76 (s, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 6.92 (d, *J* = 8.5 Hz, 2H), 4.57 (s, 2H), 4.54 (s, 2H), 3.83 (s, 3H),^{13}C NMR ($CDCl_3$, 126 MHz): δ 159.7, 158.3, 156.4, 132.0, 129.7, 129.4, 114.1, 72.8, 67.0, 55.4, IR: ν = 3047, 2859, 1613, 1586, 1564, 1514, 1441, 1410, 1302, 1249, 1174, 1082, 1034, 820, 728 cm^{-1}, HRMS (ESI) m/z calc. for $C_{13}H_{15}N_2O_2$ (M+H) 231.1134, found 231.1126.



55

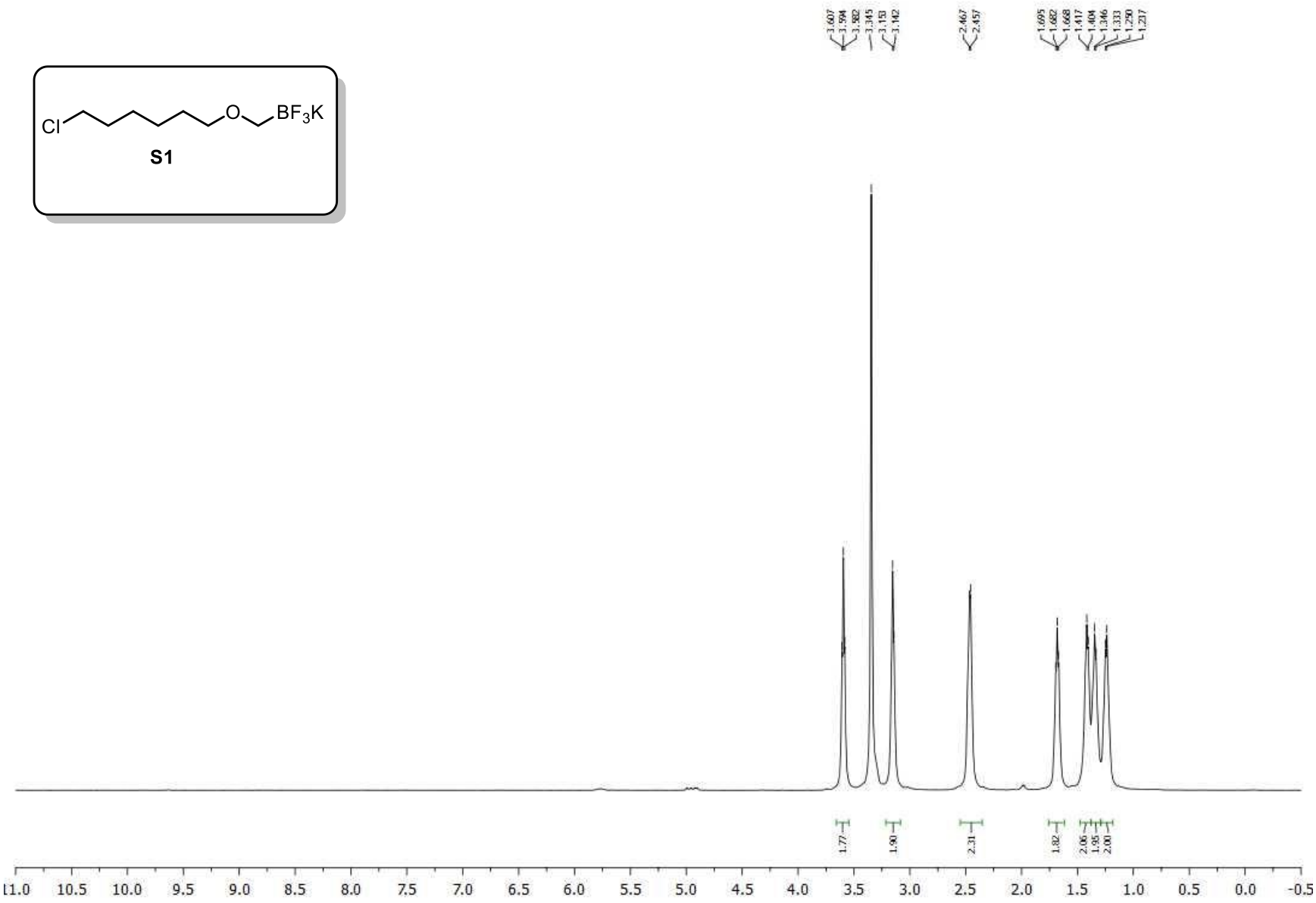
5-(*Tert*-butoxymethyl)pyrimidine (55): Obtained as a colorless oil (59 mg, 71%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.09 (s, 1H), 8.67 (s, 2H), 4.43 (s, 2H), 1.27 (s, 9H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 157.9, 156.1, 133.0, 74.3, 59.7, 27.6, IR: ν = 2974, 2359, 2341, 1723, 1564, 1490, 1392, 1365, 1197, 1082, 877, 727 cm^{-1}; HRMS (ESI) m/z calc. for $C_9H_{15}N_2O$ (M+H) 167.1184, found 167.1183.



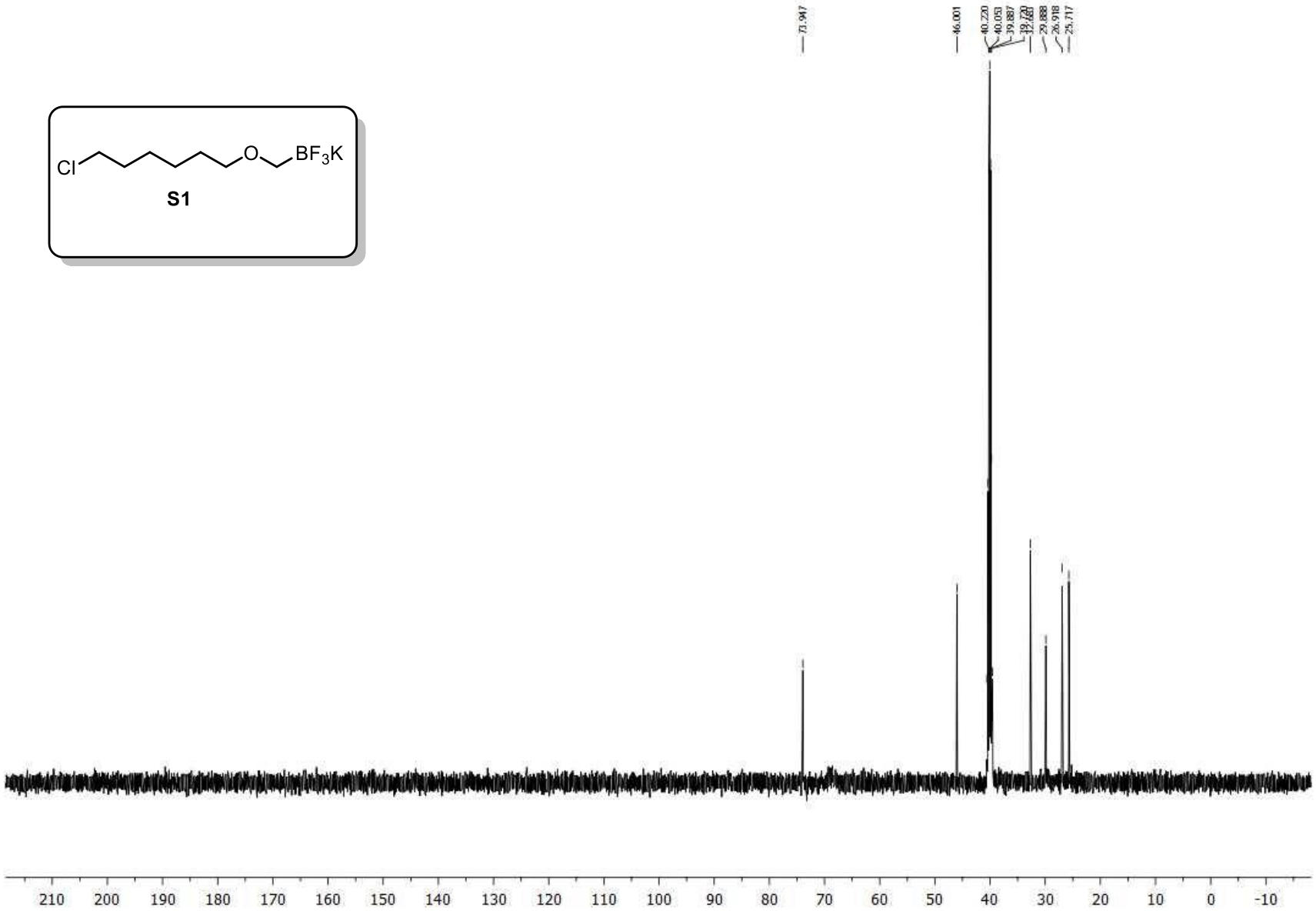
56

5-(2-(Trimethylsilyl)ethoxy)methyl)pyrimidine (56): Obtained as a colorless oil (85 mg, 81%), ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.09 (s, 1H), 8.67 (s, 2H), 4.45 (s, 2H), 3.57 (dd, *J* = 11.1, 5.2 Hz, 2H), 0.95 (dd, *J* = 11.1, 5.42 Hz, 2H), -0.03 (s, 9H), ^{13}C NMR ($CDCl_3$, 126 MHz): δ 158.1, 156.2, 132.0, 68.7, 67.6, 18.3, -1.3, IR: ν = 2953, 1563, 1409, 1360, 1249, 1182, 1110, 1087, 859, 836, 727 cm^{-1}; HRMS (ESI) m/z calc. for $C_{10}H_{18}N_2OSiNa$ (M+Na) 233.1079, found 233.1076.

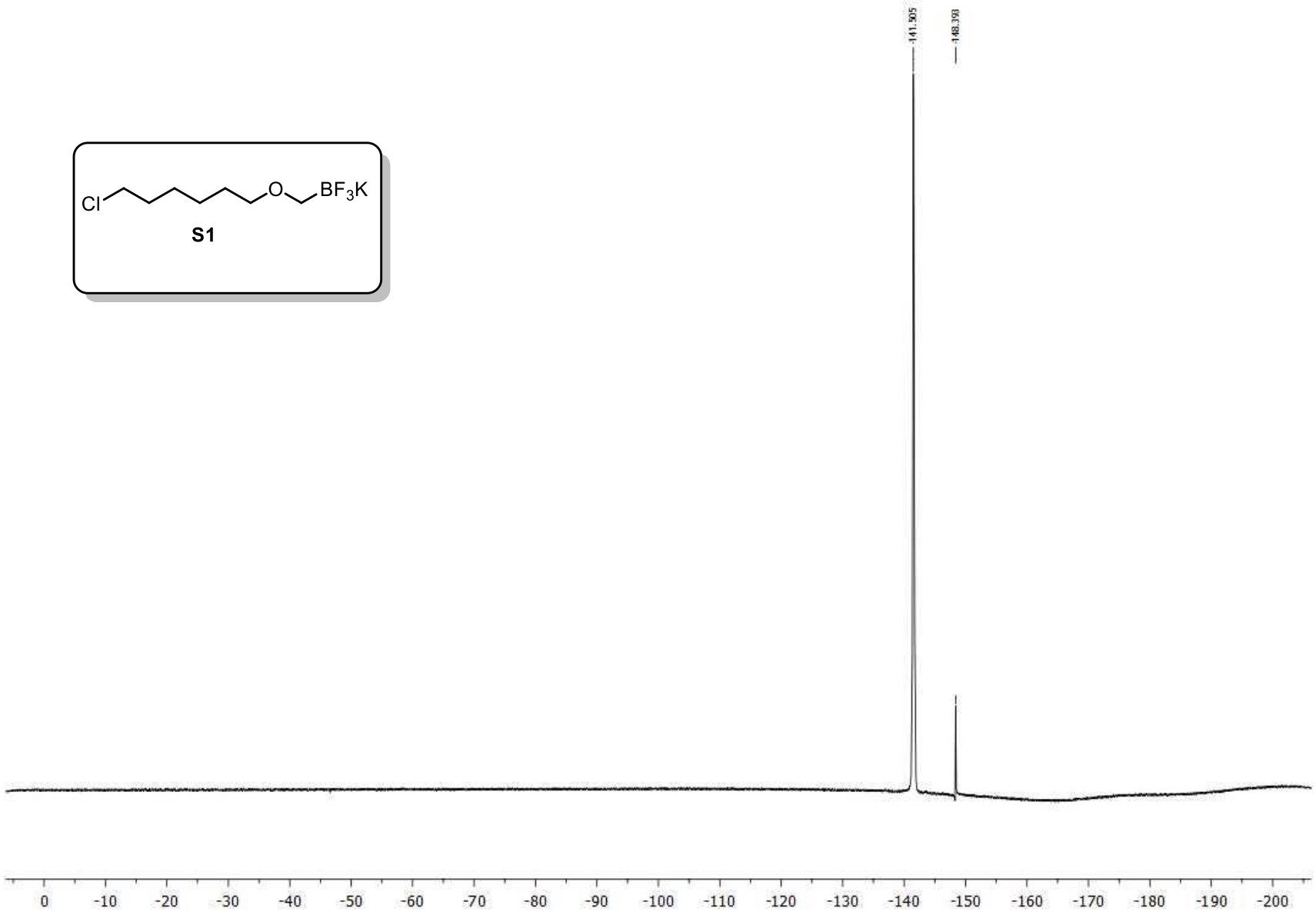
^{1}H NMR (DMSO-d_6, 500 MHz) spectrum of Potassium (((6-(chlorohexyl)oxy)methyl)trifluoroborate (**S1**)



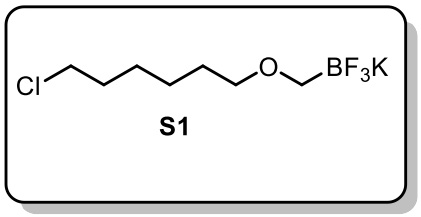
^{13}C NMR (DMSO-d_6, 126 MHz) spectrum of Potassium (((6-chlorohexyl)oxy)methyl)trifluoroborate (**S1**)



^{19}F NMR (DMSO-d_6, 471 MHz) spectrum of Potassium (((6-chlorohexyl)oxy)methyl)trifluoroborate (**S1**)

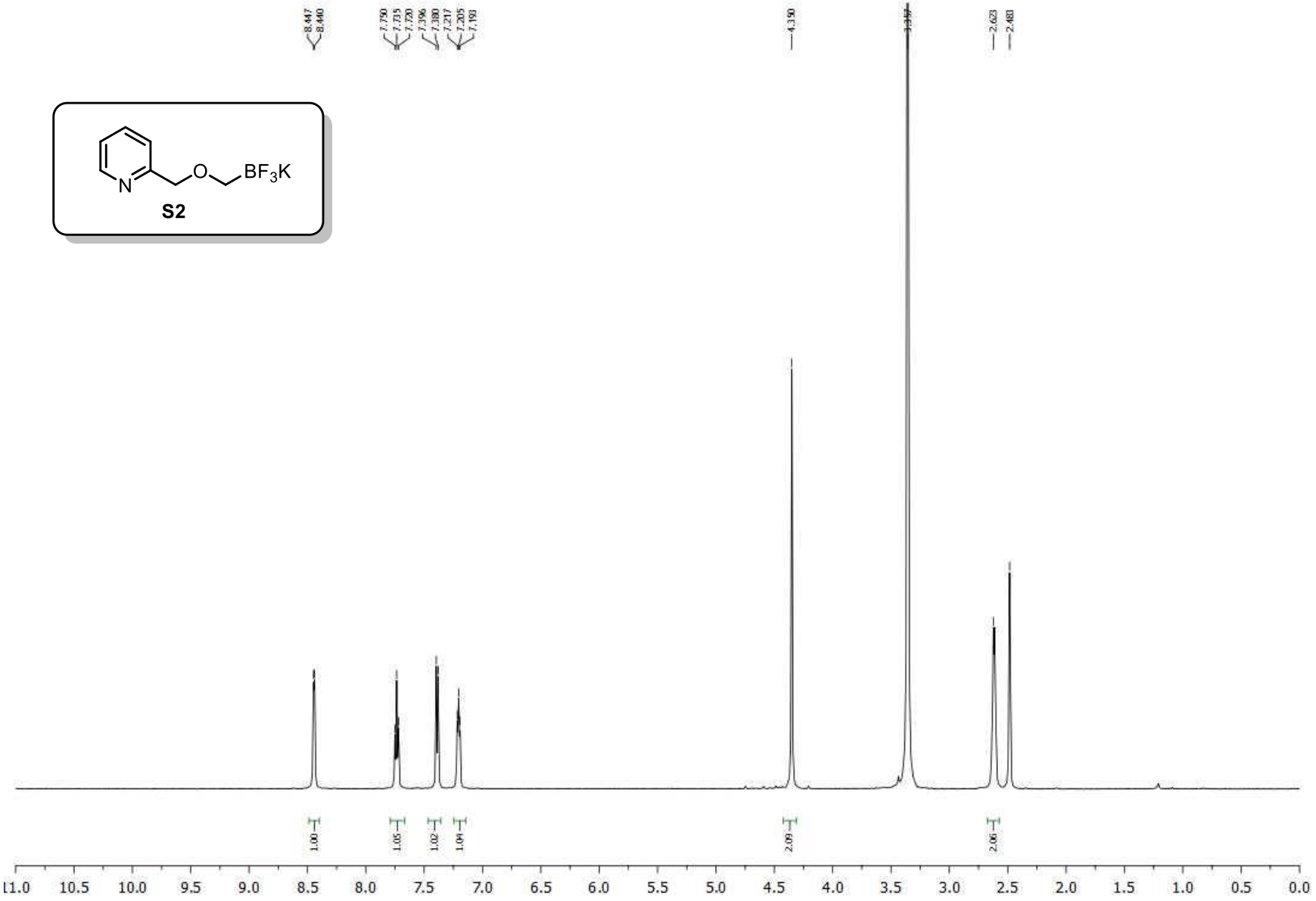


^{11}B NMR (DMSO-d_6, 128 MHz) spectrum of Potassium (((6-chlorohexyl)oxy)methyl)trifluoroborate (**S1**)

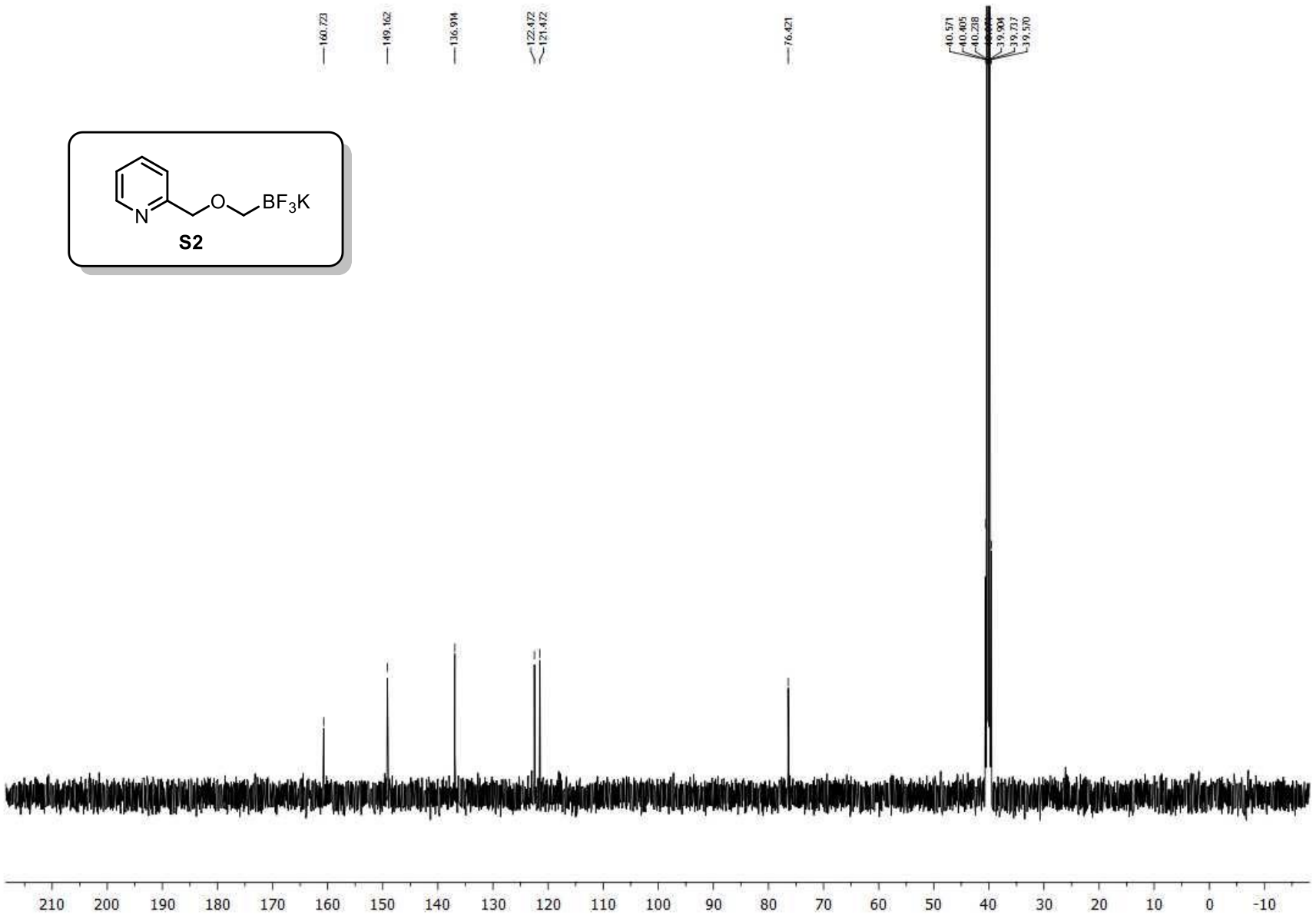


S1

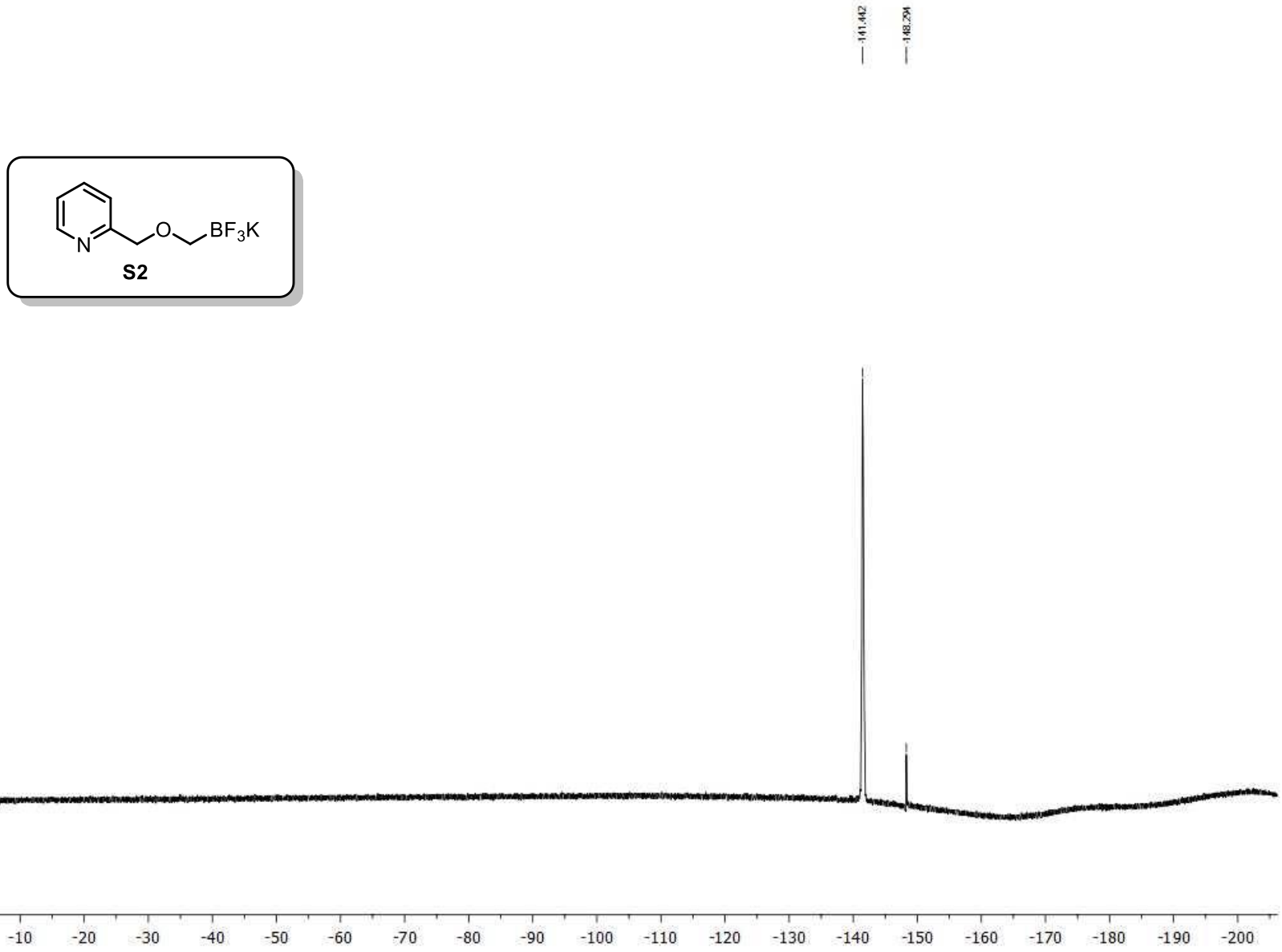
^{1}H NMR (DMSO-d_6, 500 MHz) spectrum of Potassium ((pyridin-2-ylmethoxy)methyl)trifluoroborate (**S2**)



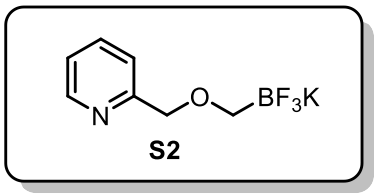
^{13}C NMR (DMSO-d_6, 126 MHz) spectrum of Potassium ((pyridin-2-ylmethoxy)methyl)trifluoroborate (**S2**)



^{19}F NMR (DMSO-d_6, 471 MHz) spectrum of Potassium ((pyridin-2-ylmethoxy)methyl)trifluoroborate (**S2**)

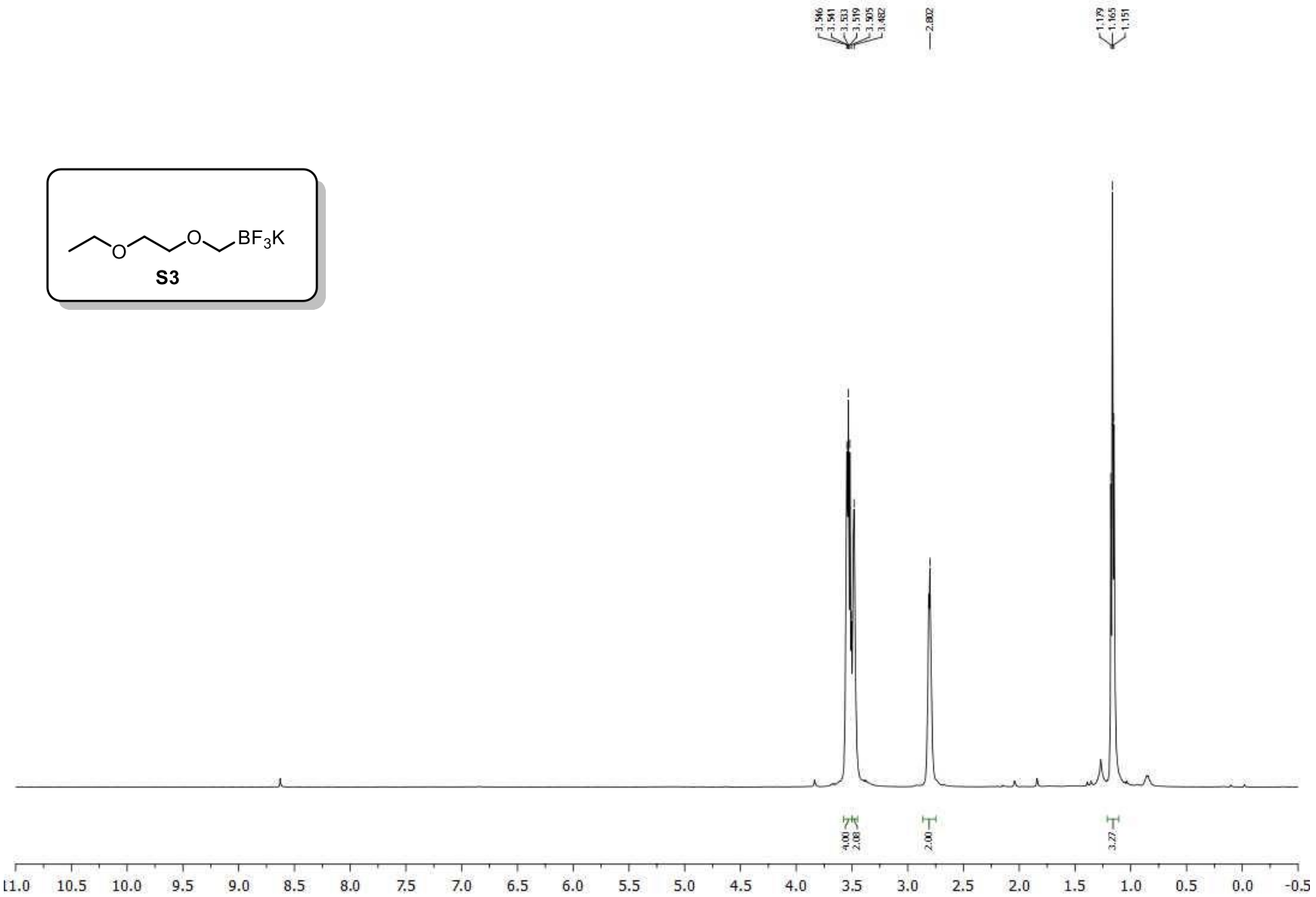


^{11}B NMR (DMSO-d_6, 128 MHz) spectrum of Potassium ((pyridin-2-ylmethoxy)methyl)trifluoroborate (**S2**)

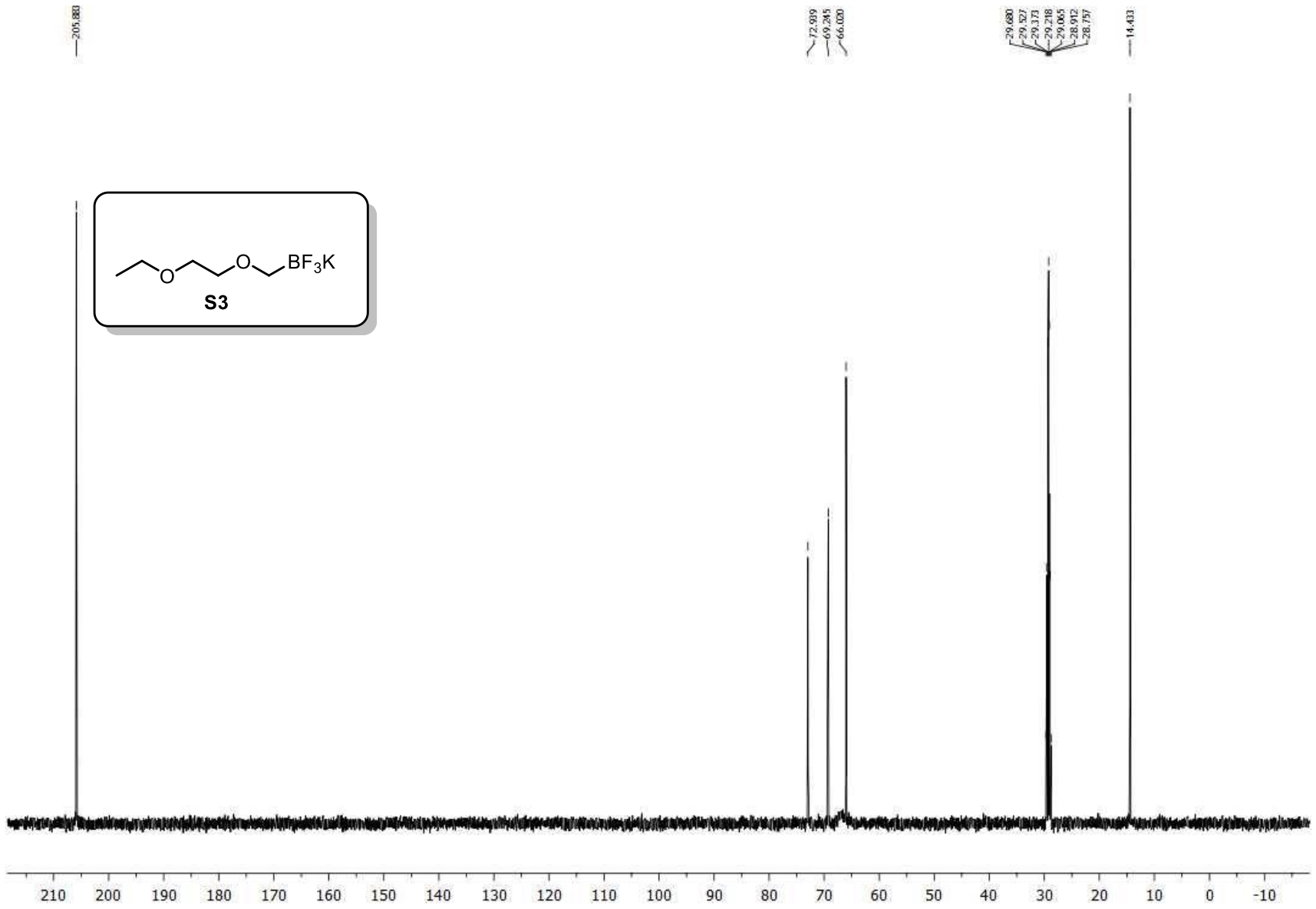


S2

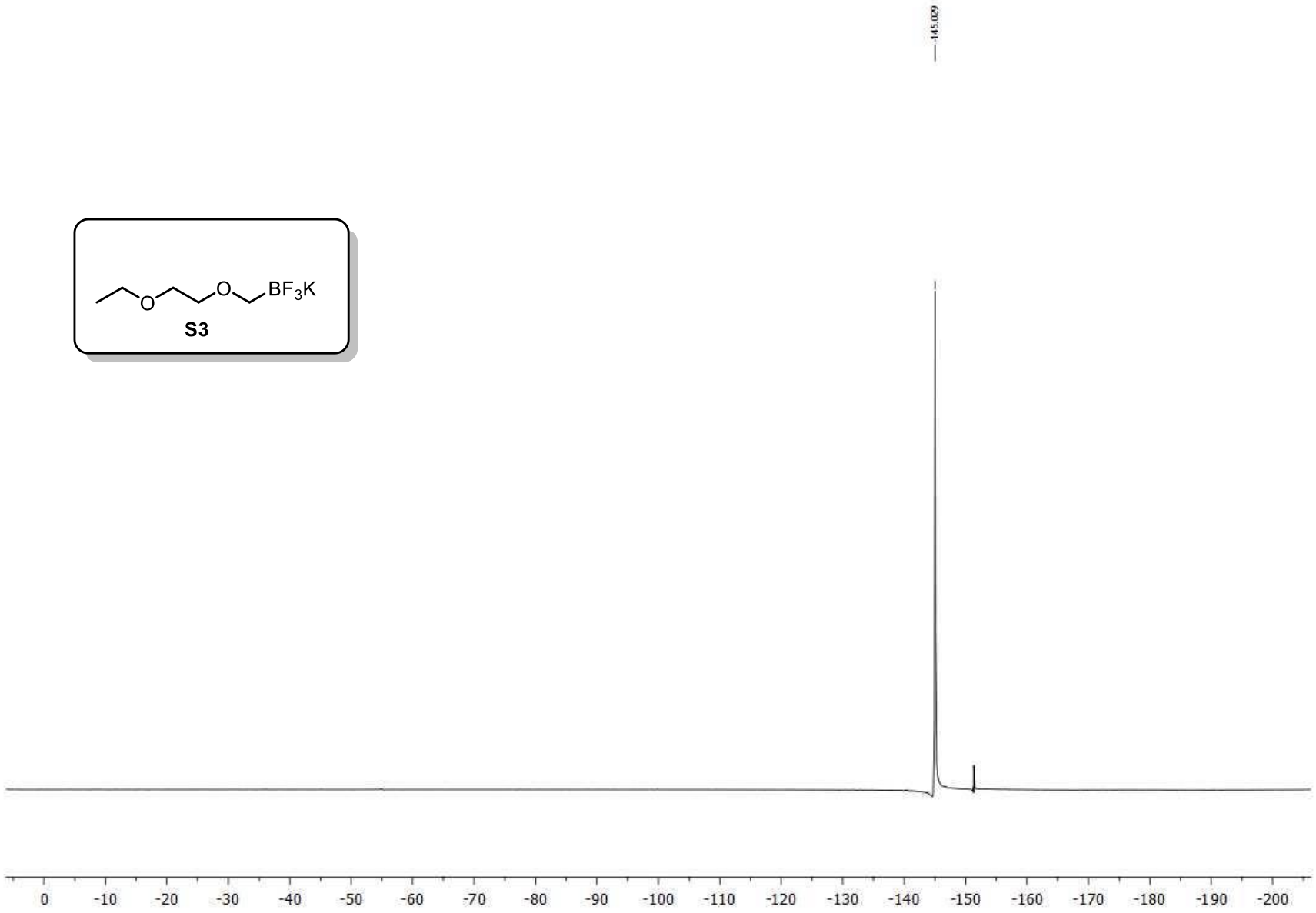
^{1}H NMR (acetone-d_6, 500 MHz) spectrum of Potassium ((2-ethoxyethoxy)methyl)trifluoroborate (**S3**)



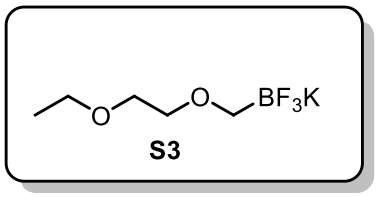
^{13}C NMR (acetone-d_6, 126 MHz) spectrum of Potassium ((2-ethoxyethoxy)methyl)trifluoroborate (**S3**)



^{19}F NMR (acetone-d_6, 471 MHz) spectrum of Potassium ((2-ethoxyethoxy)methyl)trifluoroborate (**S3**)

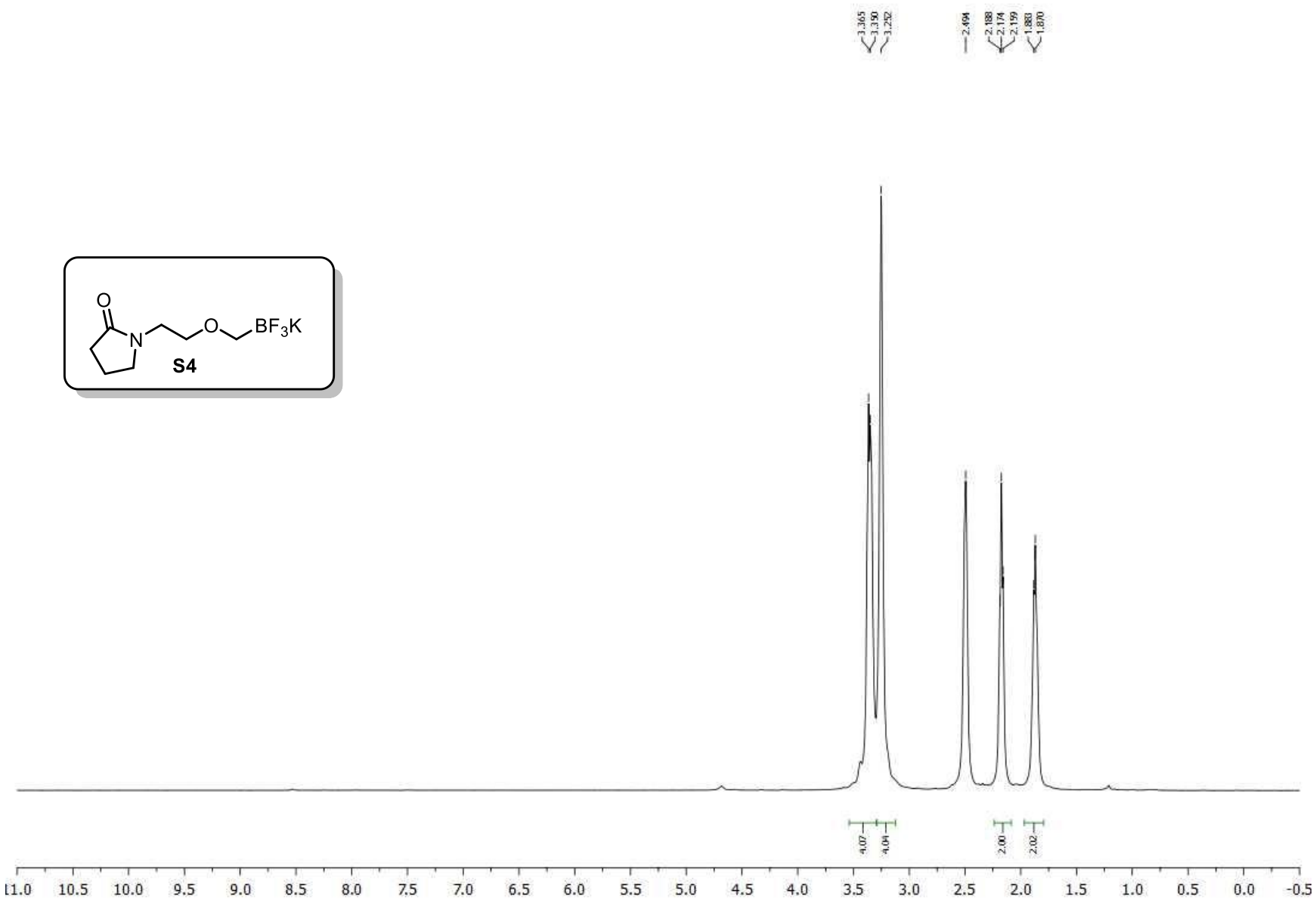


^{11}B NMR (acetone-d_6, 128 MHz) spectrum of Potassium ((2-ethoxyethoxy)methyl)trifluoroborate (**S3**)

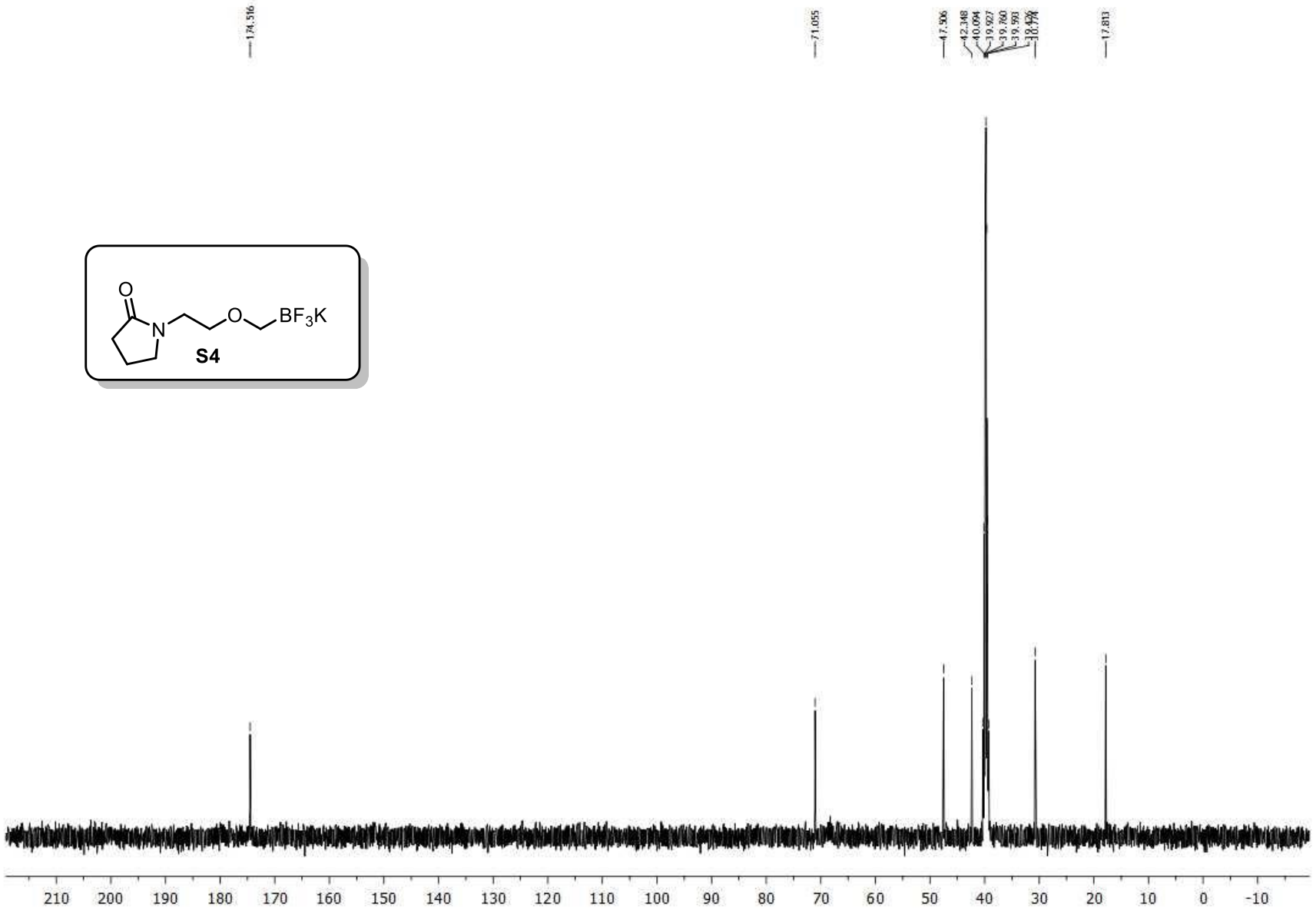


S3

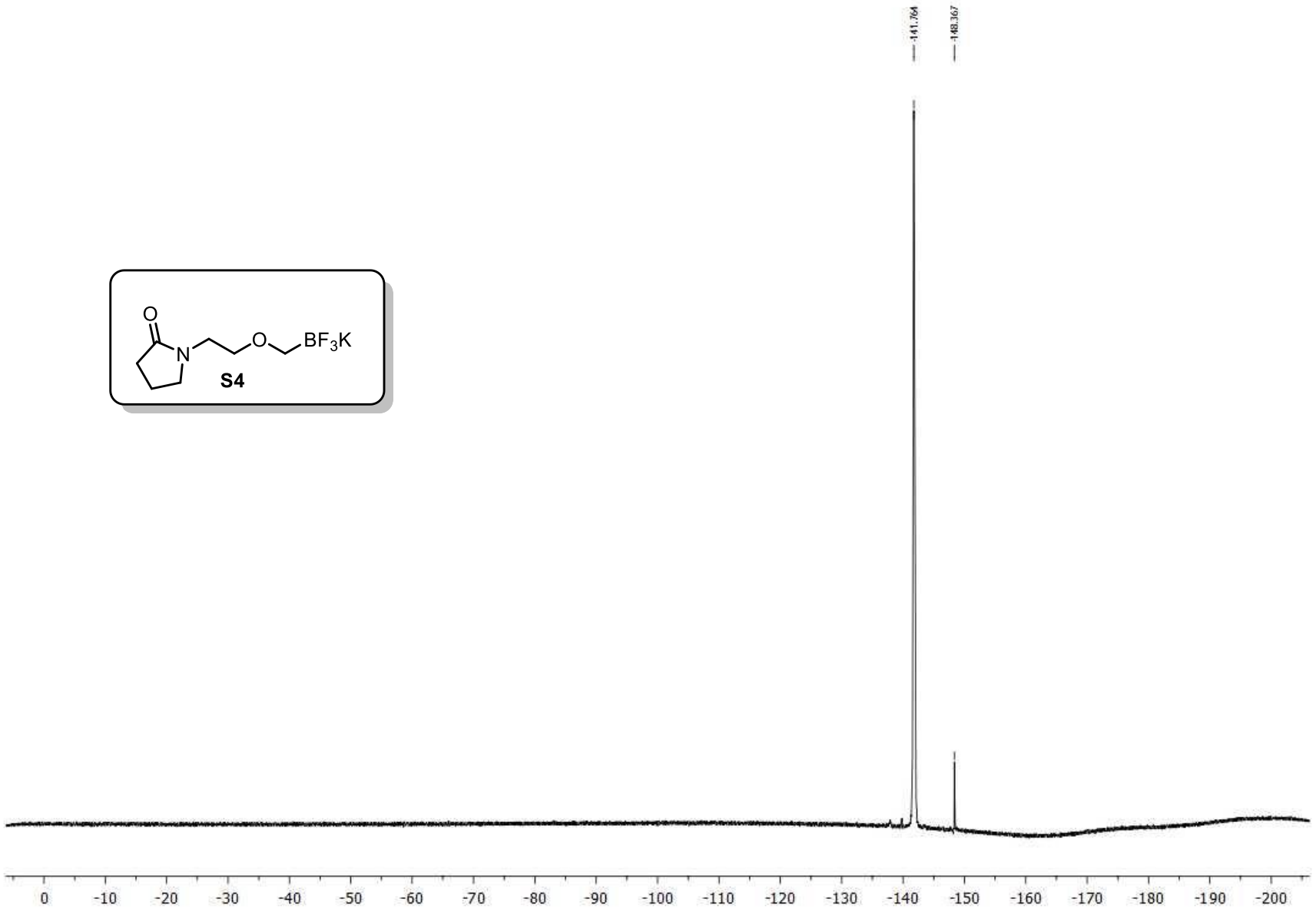
^{1}H NMR (DMSO-d_6, 500 MHz) spectrum of Potassium ((methoxy)methyl)pyrrolidin-2-onetrifluoroborate (**S4**)



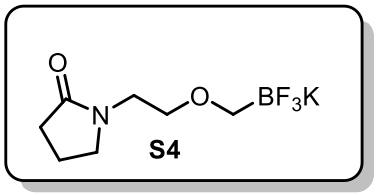
^{13}C NMR (DMSO-d_6, 126 MHz) spectrum of Potassium ((methoxy)methyl)pyrrolidin-2-onetrifluoroborate (**S4**)



^{19}F NMR (DMSO-d_6, 471 MHz) spectrum of Potassium ((methoxy)methyl)pyrrolidin-2-onetrifluoroborate (**S4**)

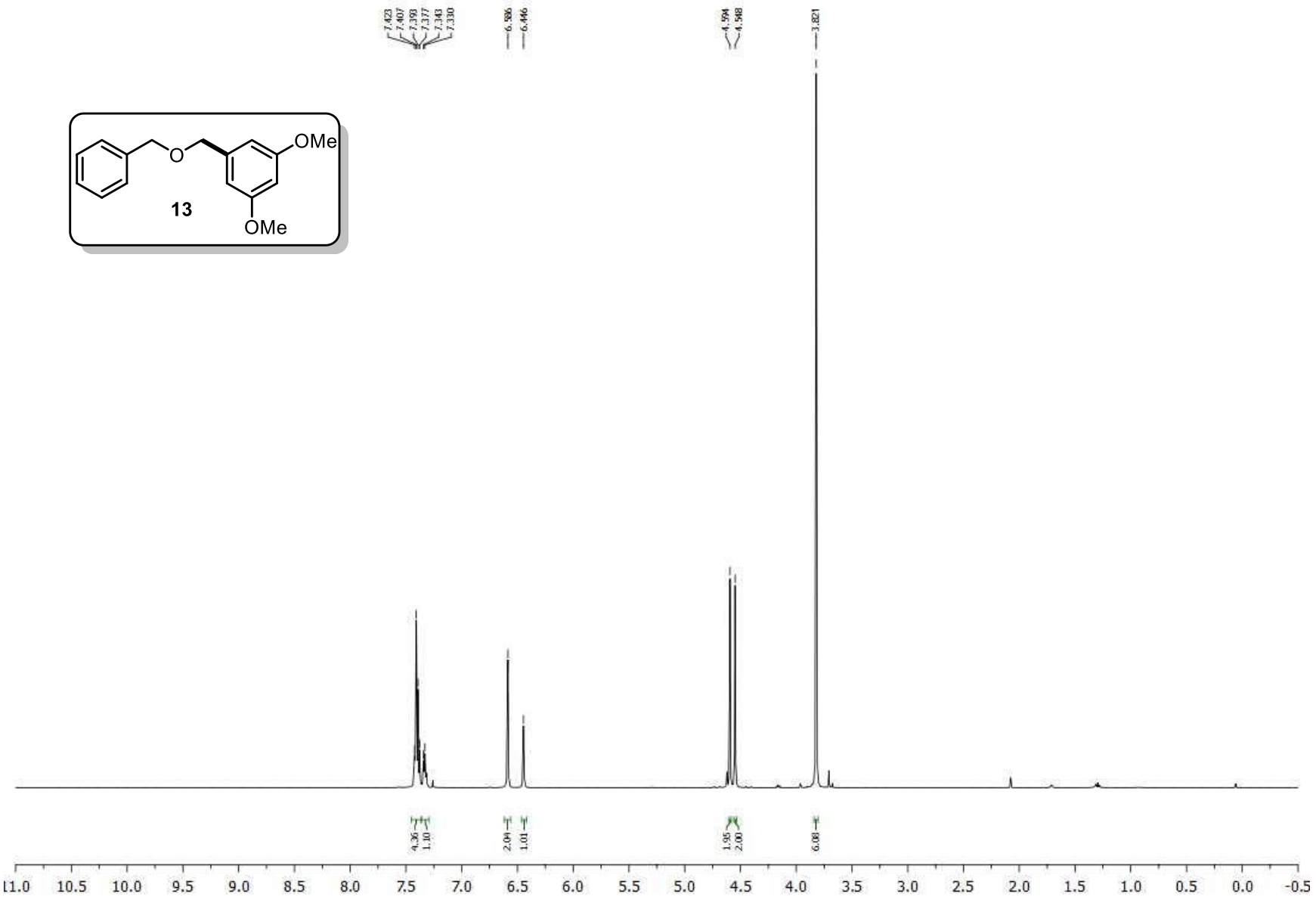


^{11}B NMR (DMSO-d_6, 128 MHz) spectrum of Potassium ((methoxy)methyl)pyrrolidin-2-onetrifluoroborate (**S4**)

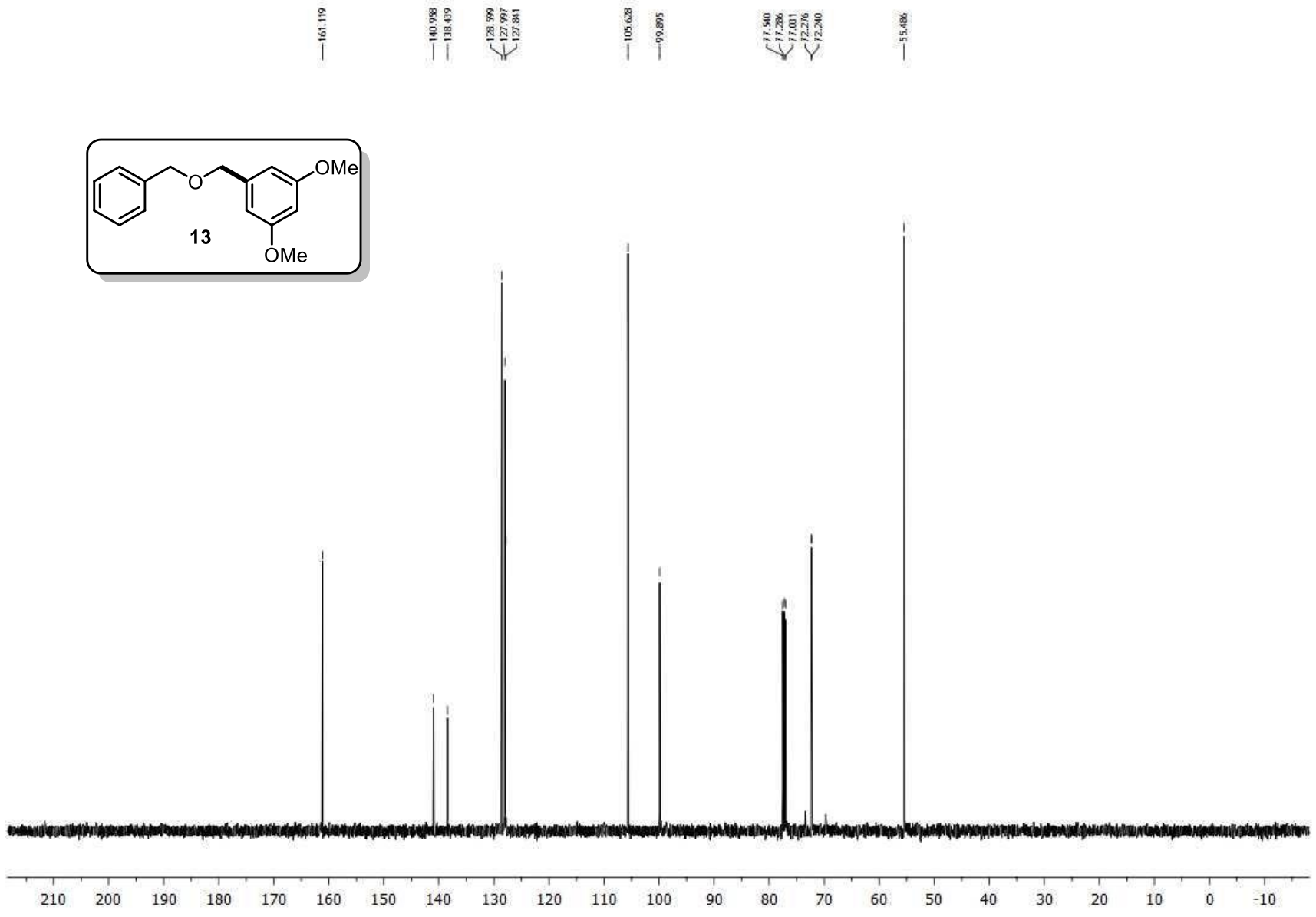


S4

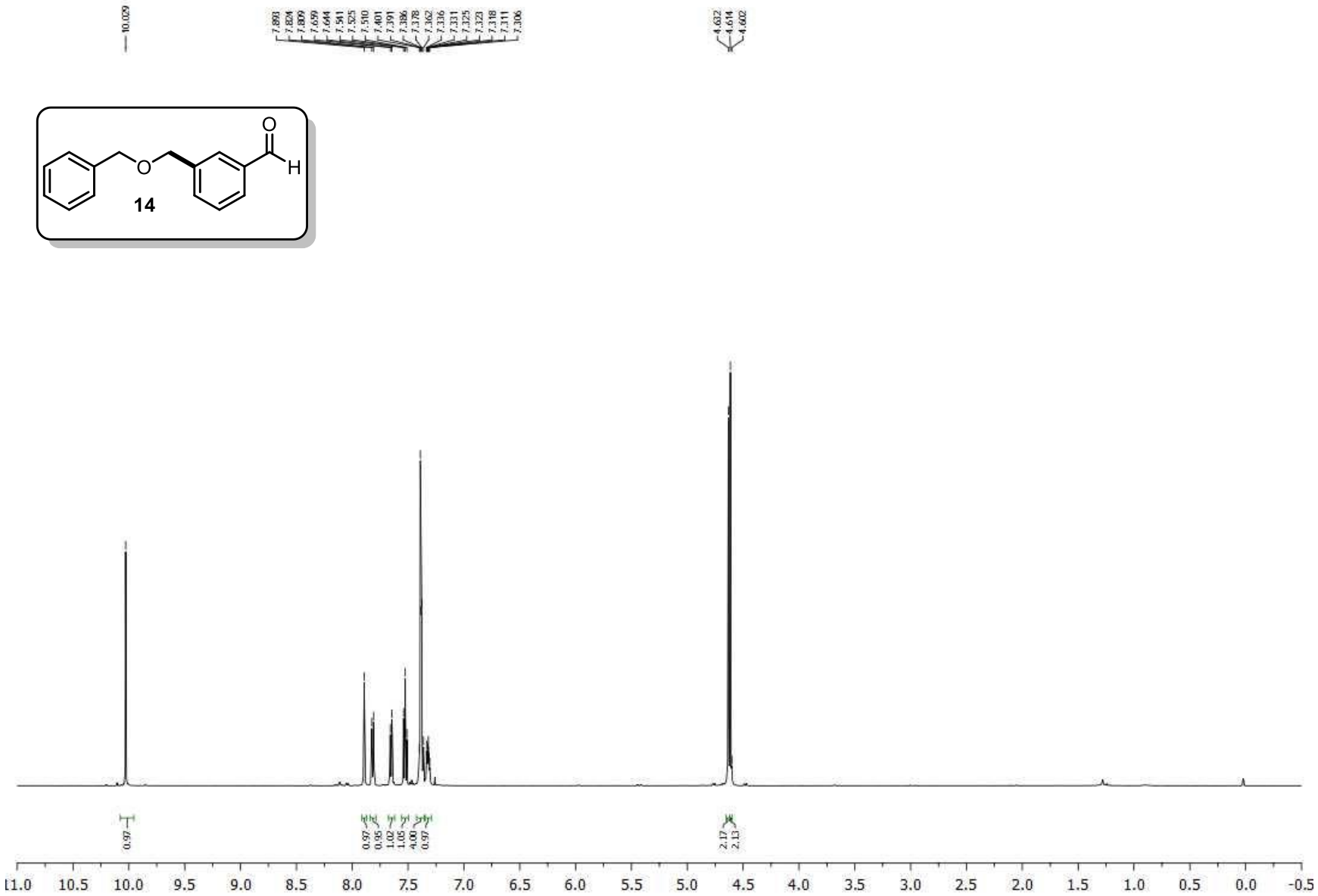
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 1-((benzyloxy)methyl)-3,5-dimethoxybenzene (**13**)



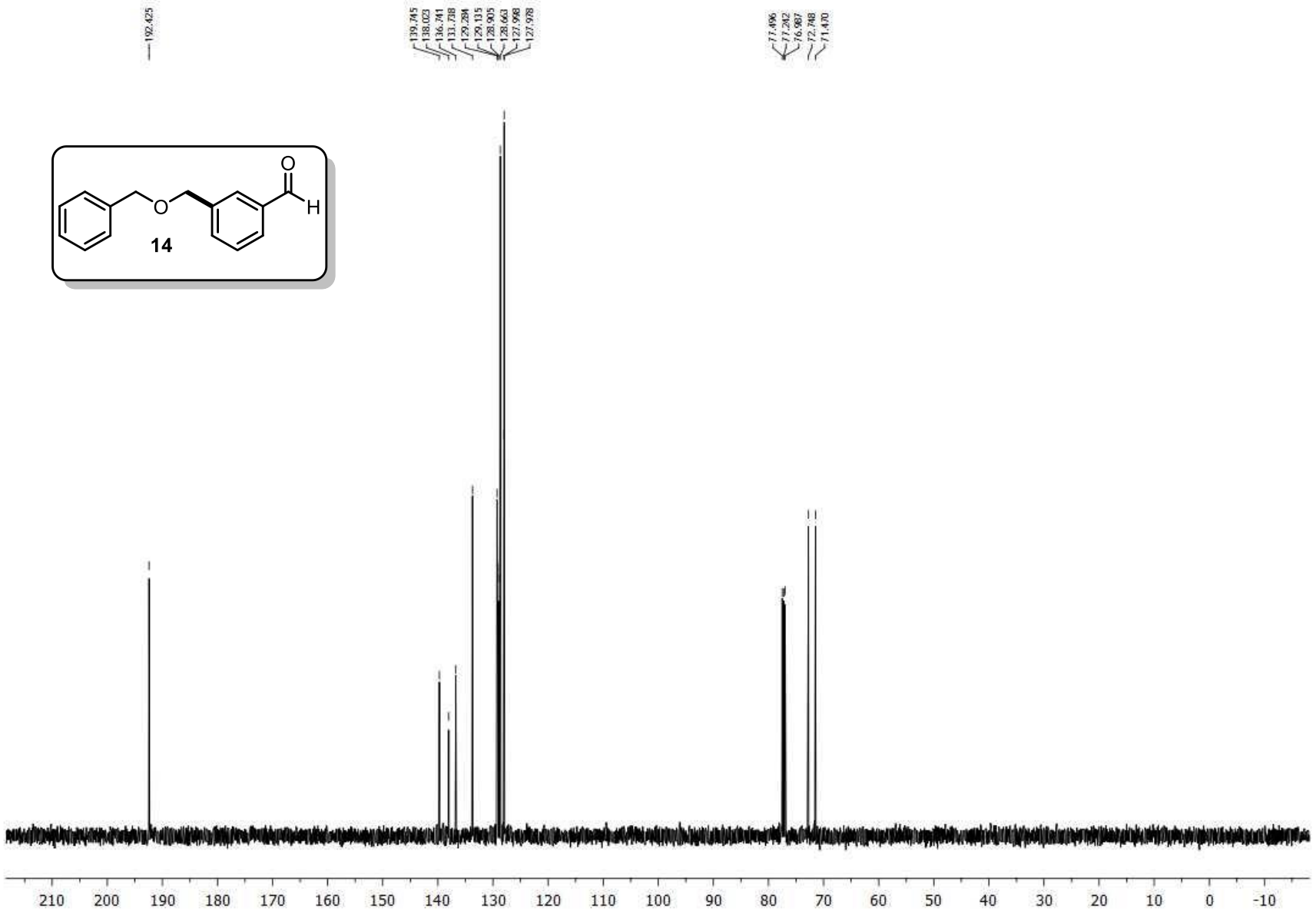
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 1-((benzyloxy)methyl)-3,5-dimethoxybenzene (**13**)



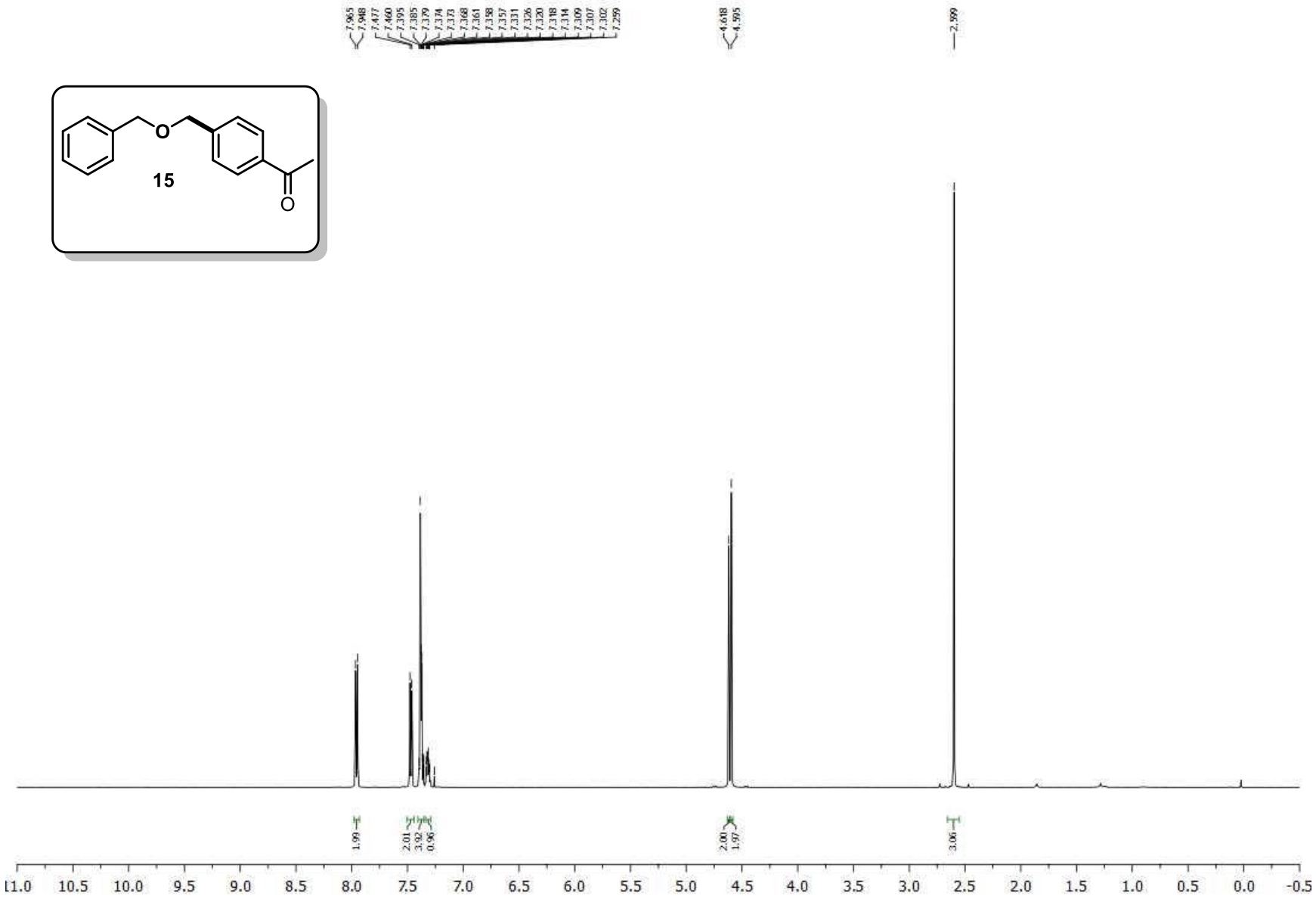
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 3-((benzyloxy)methyl)benzaldehyde (**14**)



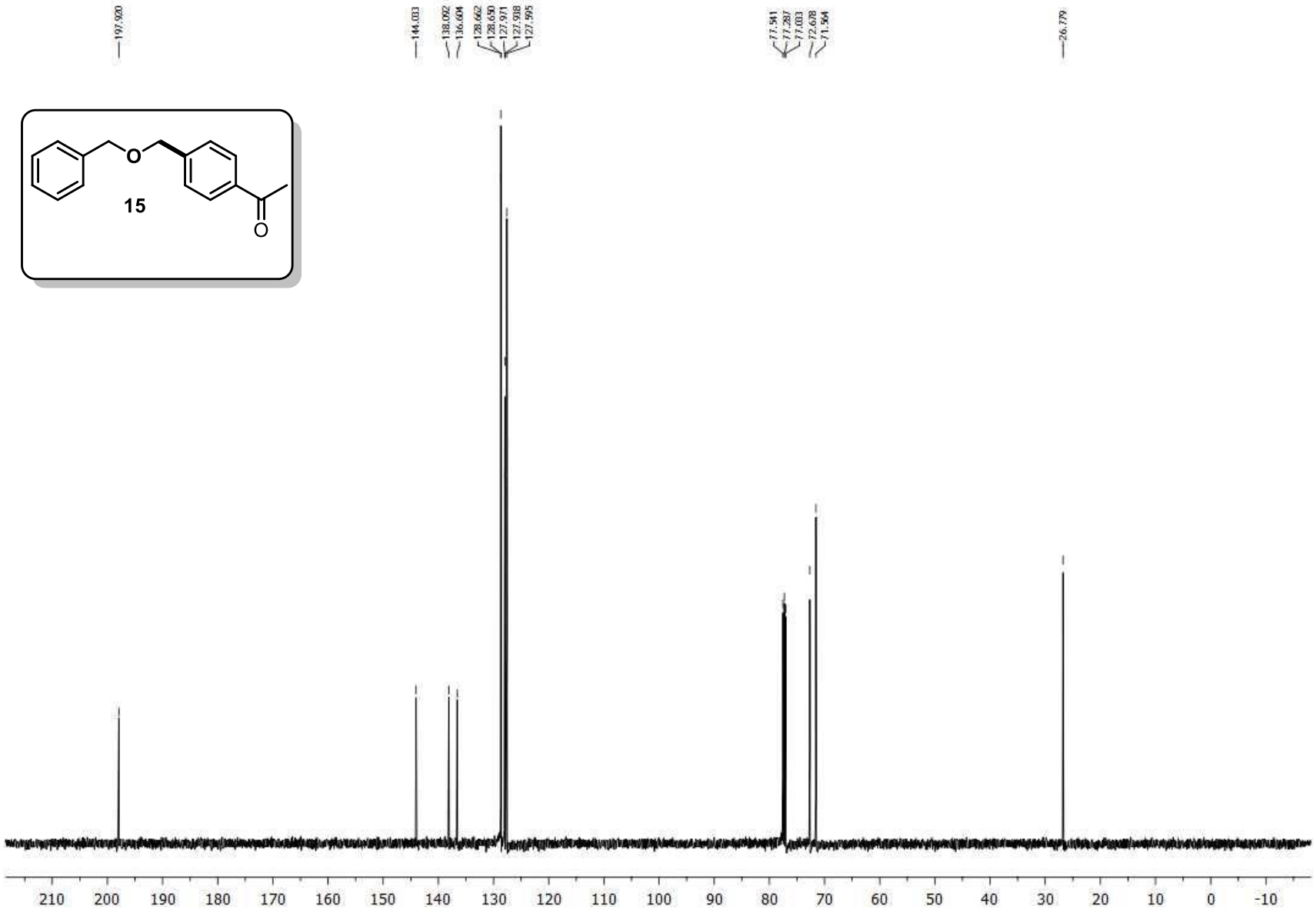
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 3-((benzyloxy)methyl)benzaldehyde (**14**)



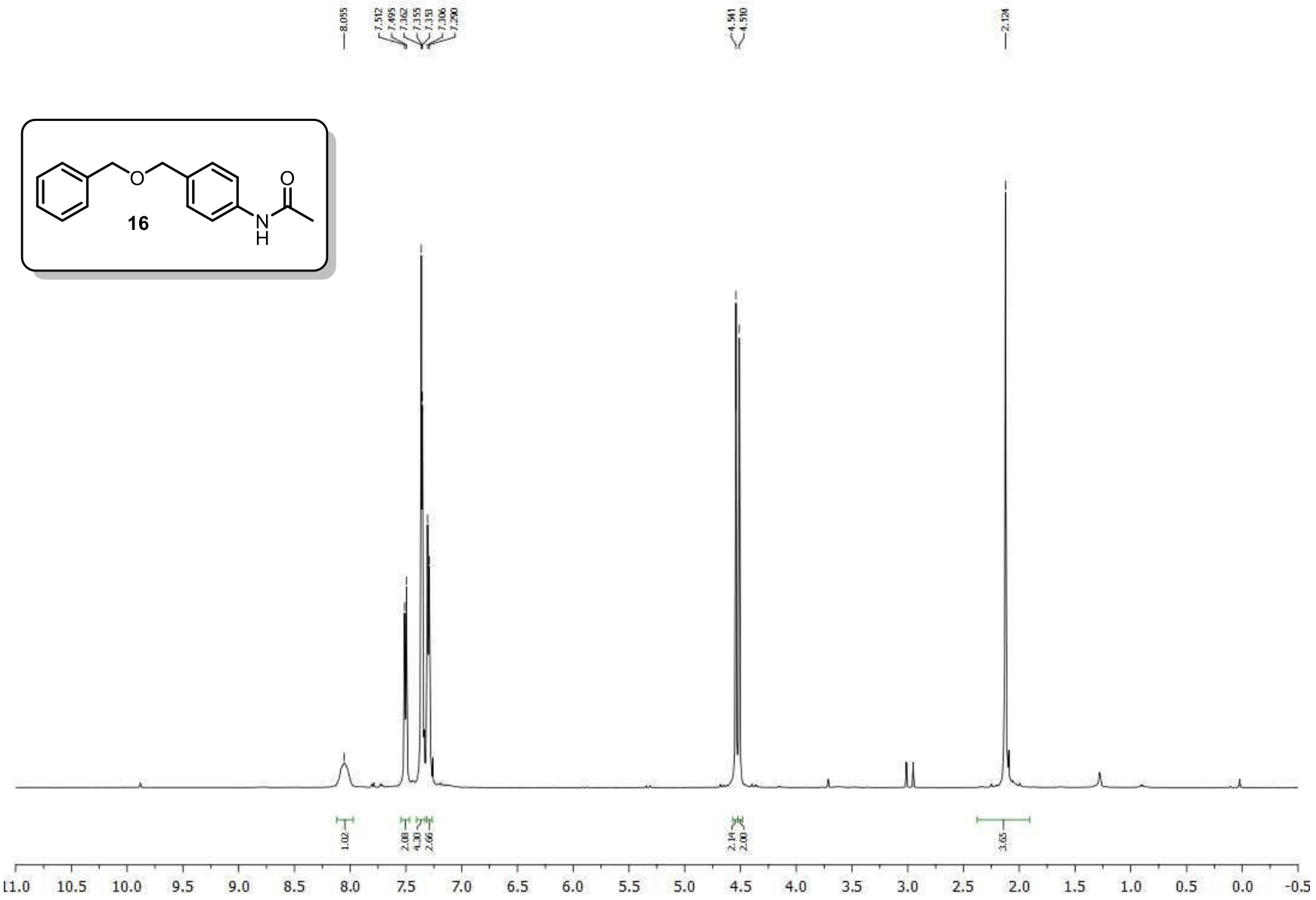
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 1-(4-(benzyloxy)methyl)phenyl)ethan-1-one (**15**)



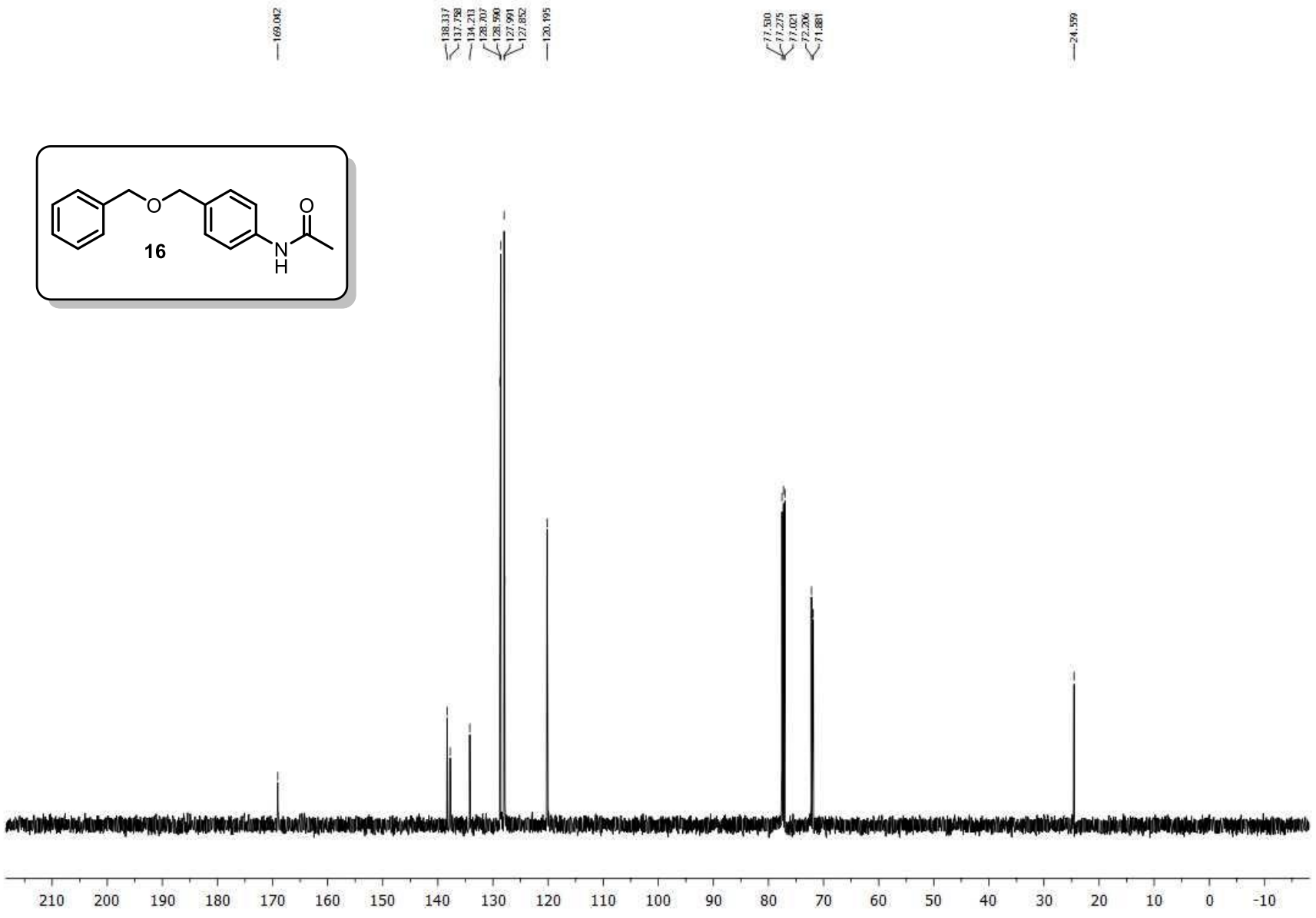
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 1-(4-(benzyloxy)methyl)phenyl)ethan-1-one (**15**)



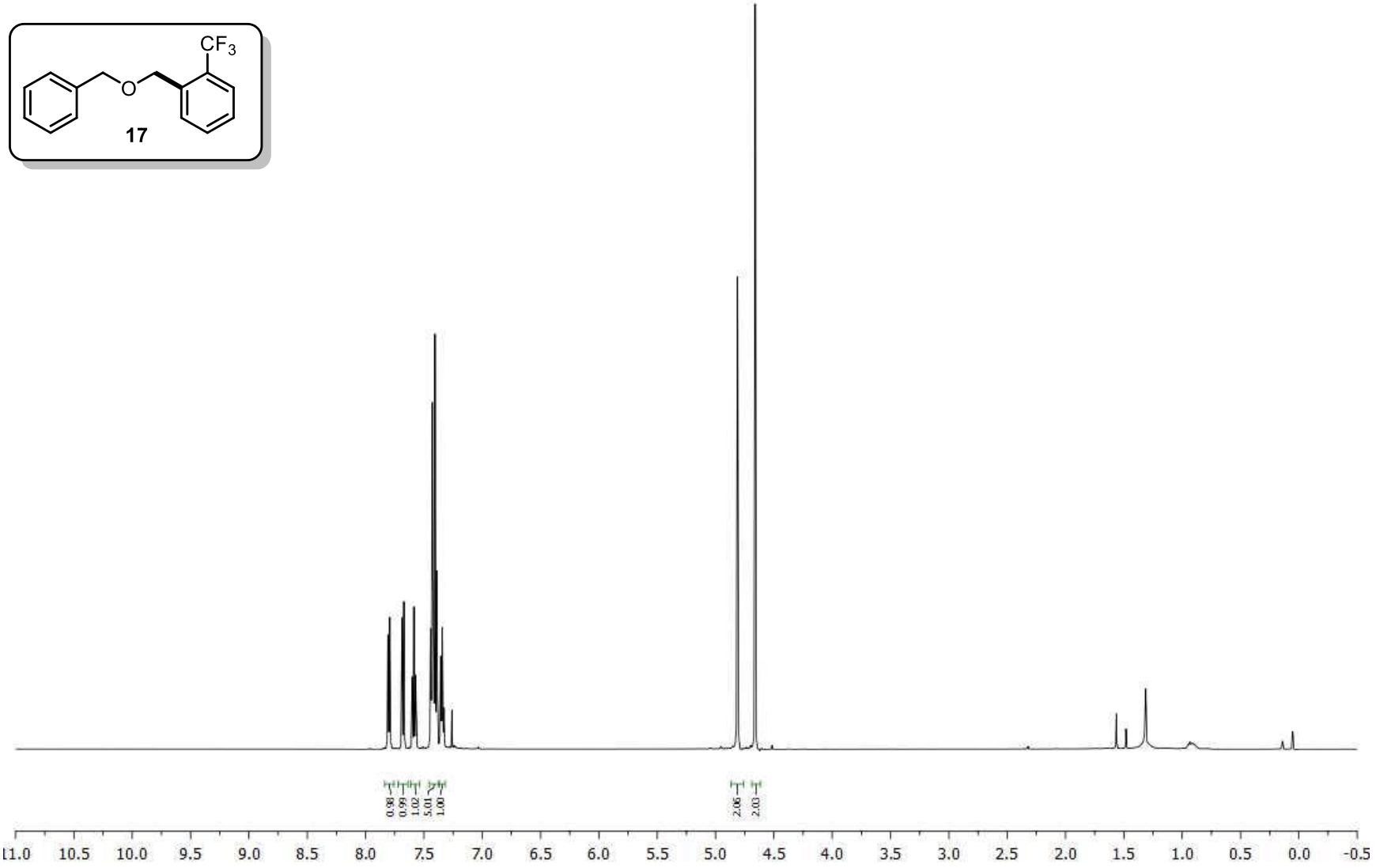
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of *N*-((4-(benzyloxy)methyl)phenyl)acetamide (**16**)



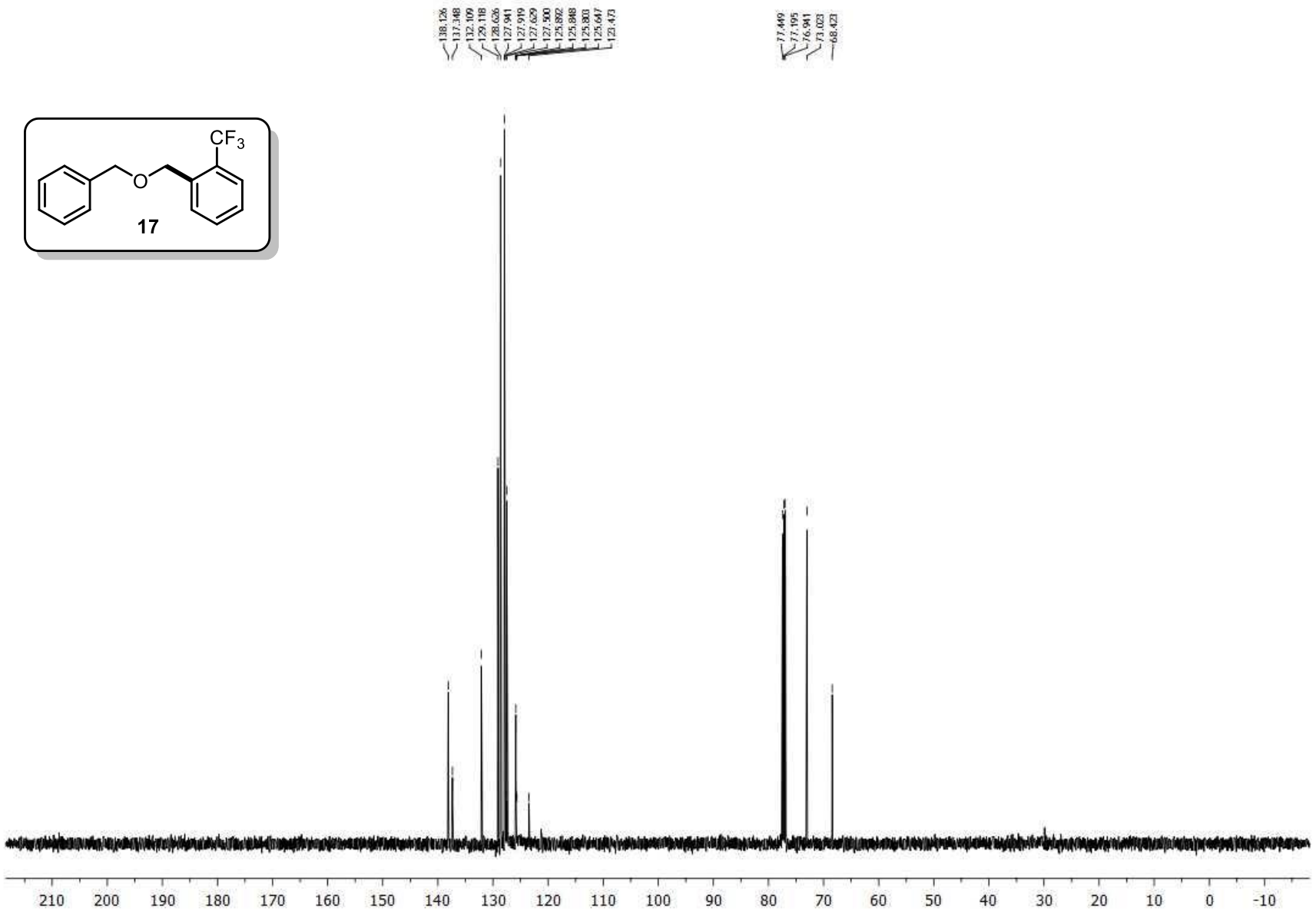
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of *N*-((4-(benzyloxy)methyl)phenyl)acetamide (**16**)



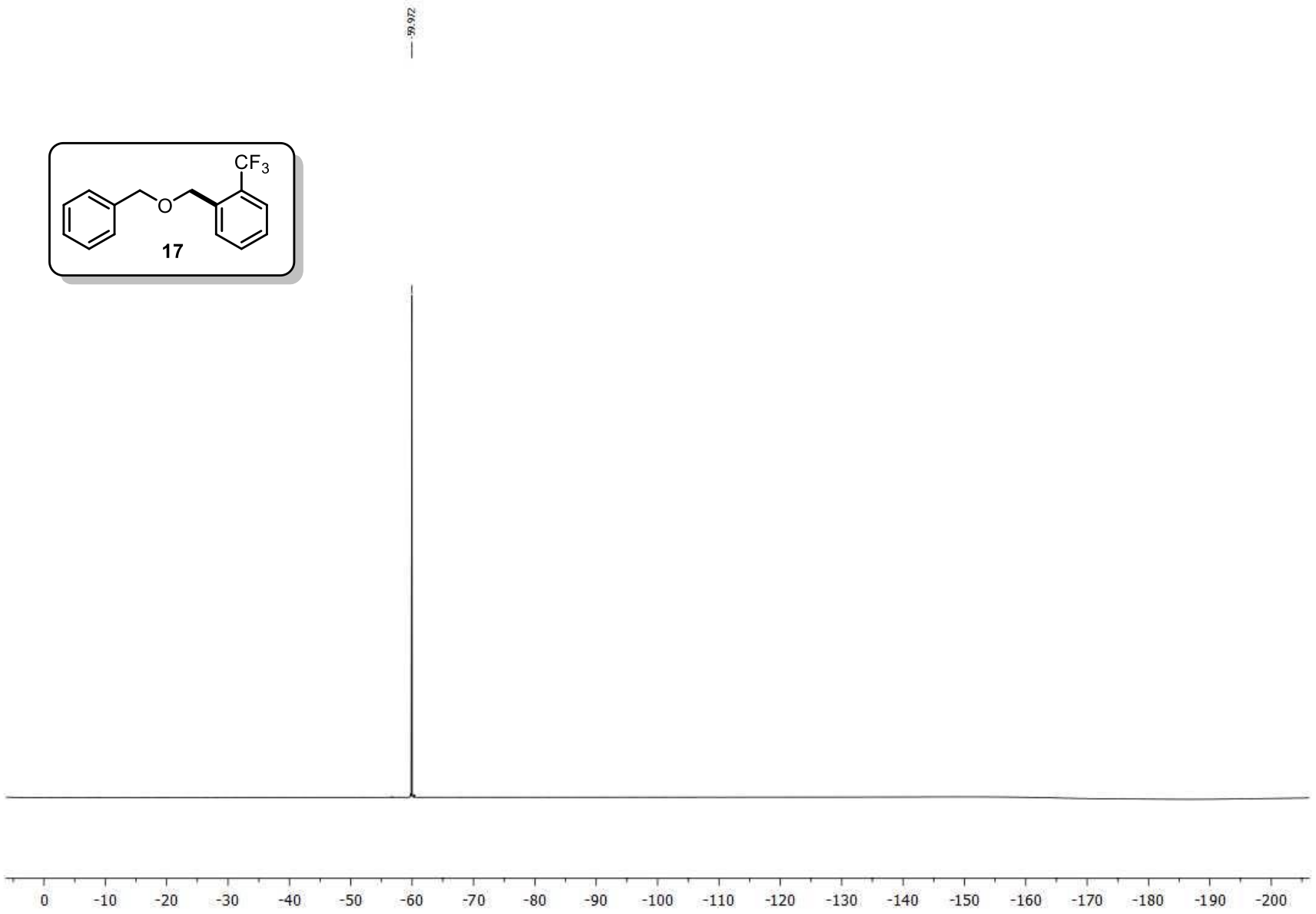
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 1-(benzyloxy)methyl)-2-(trifluoromethyl)benzene (**17**)



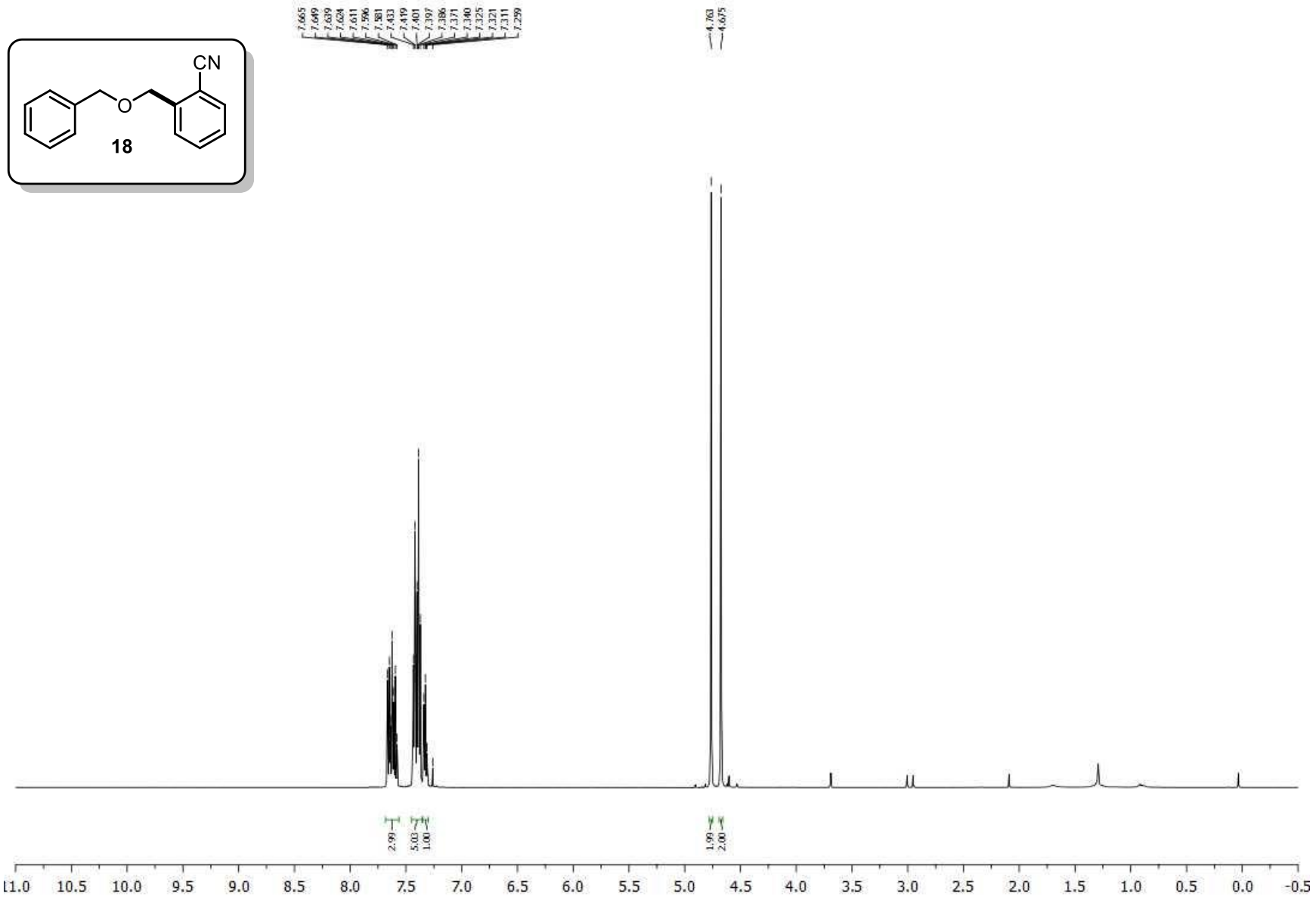
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 1-(benzyloxy)methyl)-2-(trifluoromethyl)benzene (**17**)



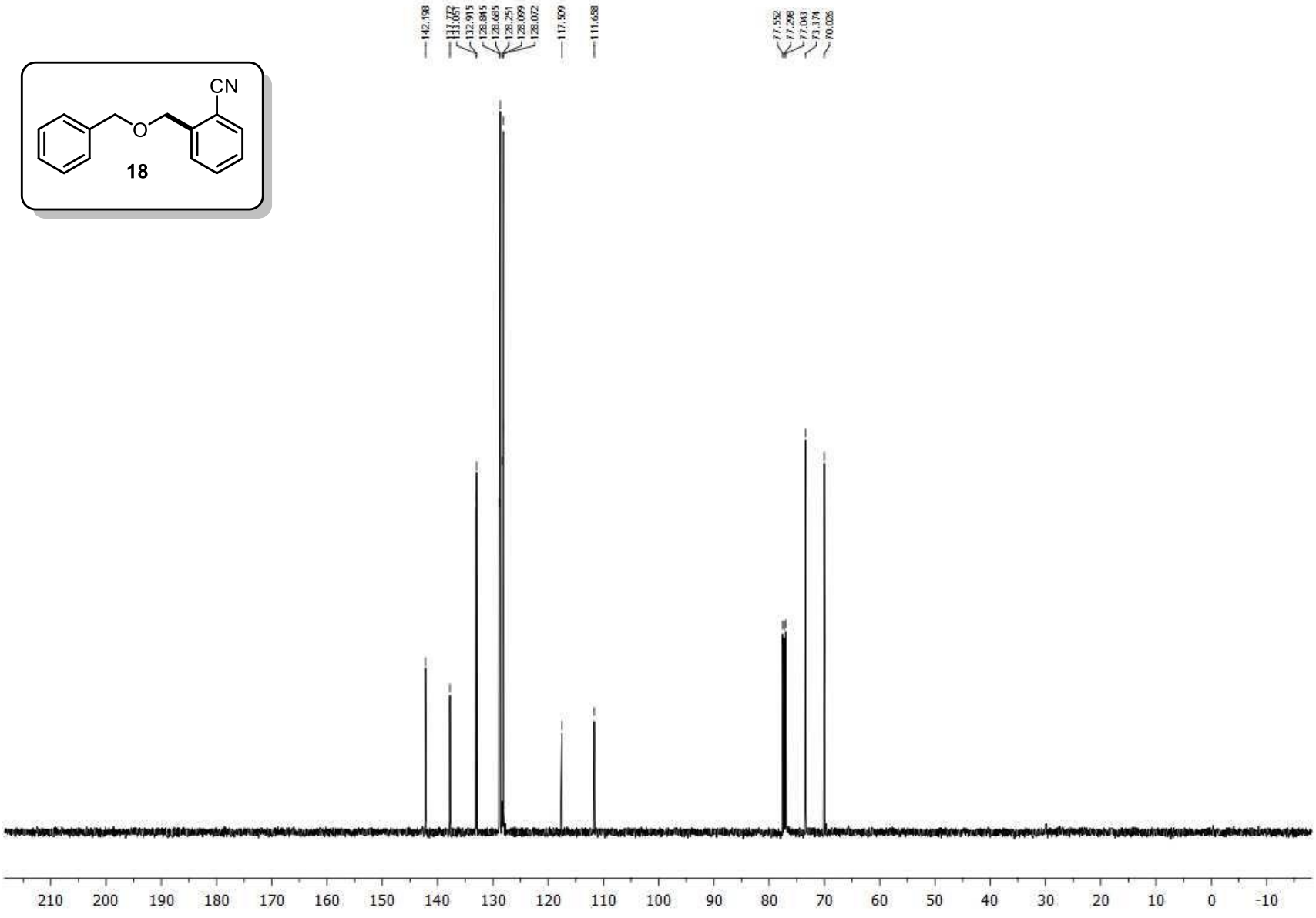
^{19}F NMR ($CDCl_3$, 471 MHz) spectrum of 1-(benzyloxy)methyl)-2-(trifluoromethyl)benzene (**17**)



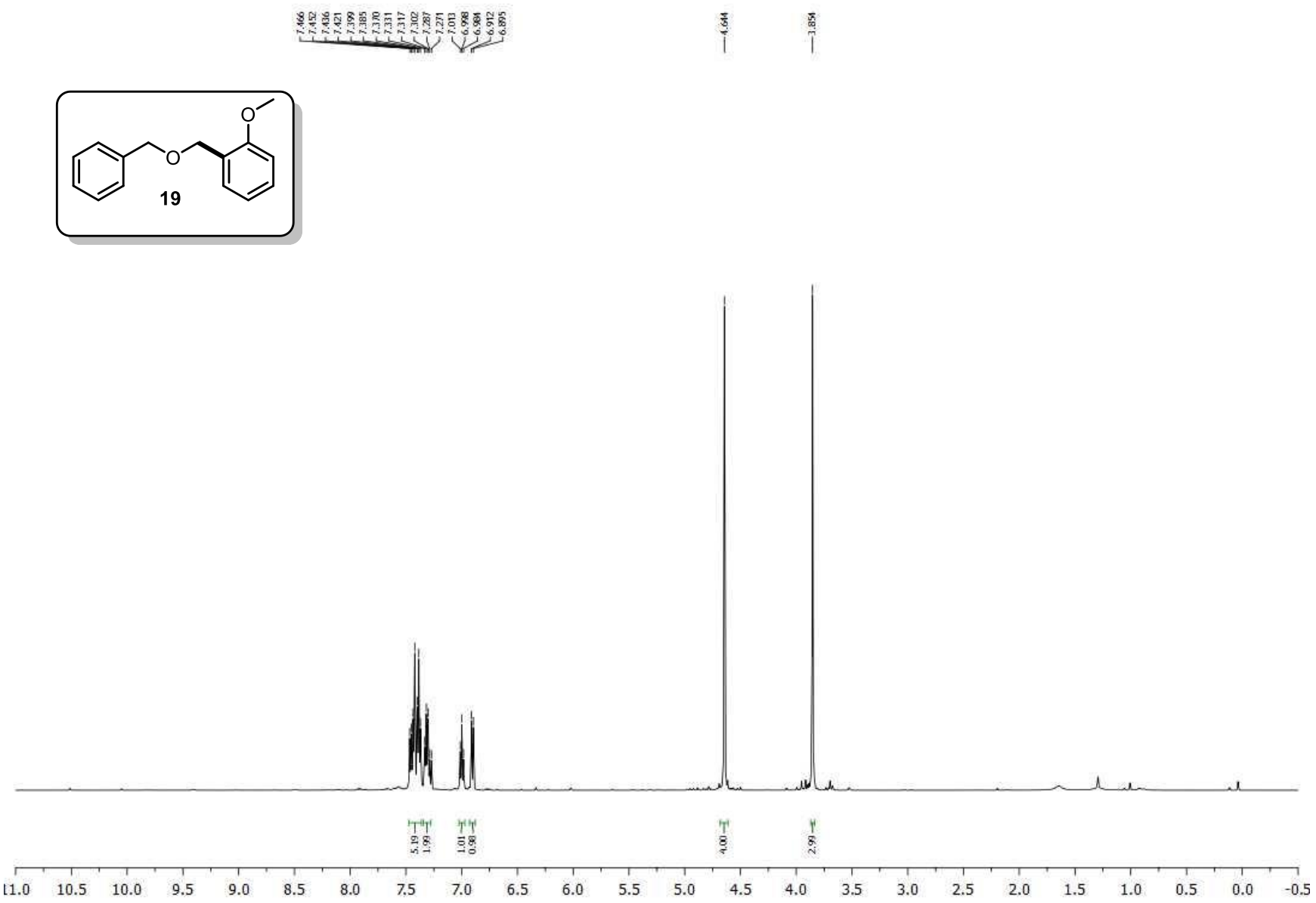
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 2-((benzyloxy)methyl)benzonitrile (**18**)



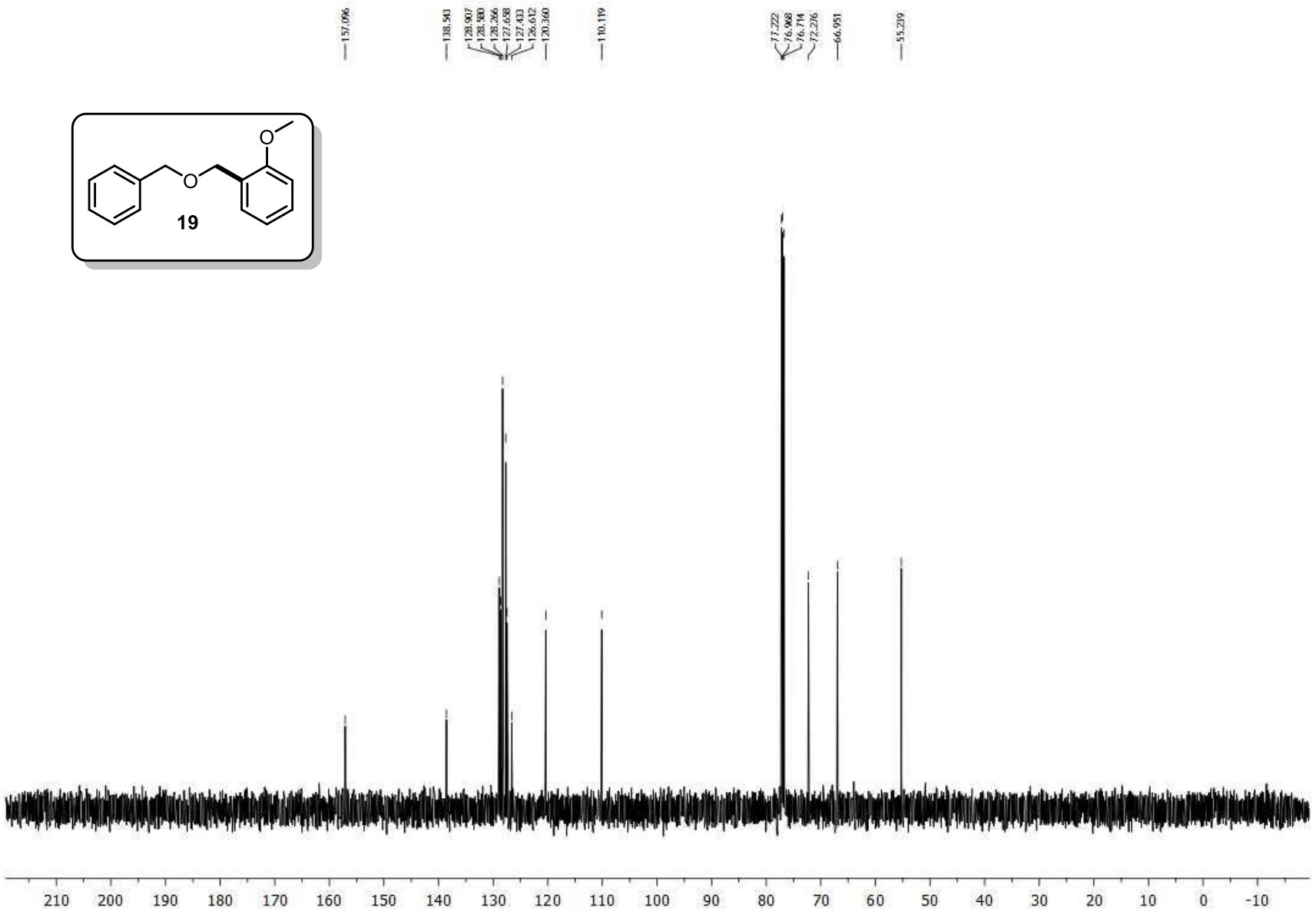
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 2-((benzyloxy)methyl)benzonitrile (**18**)



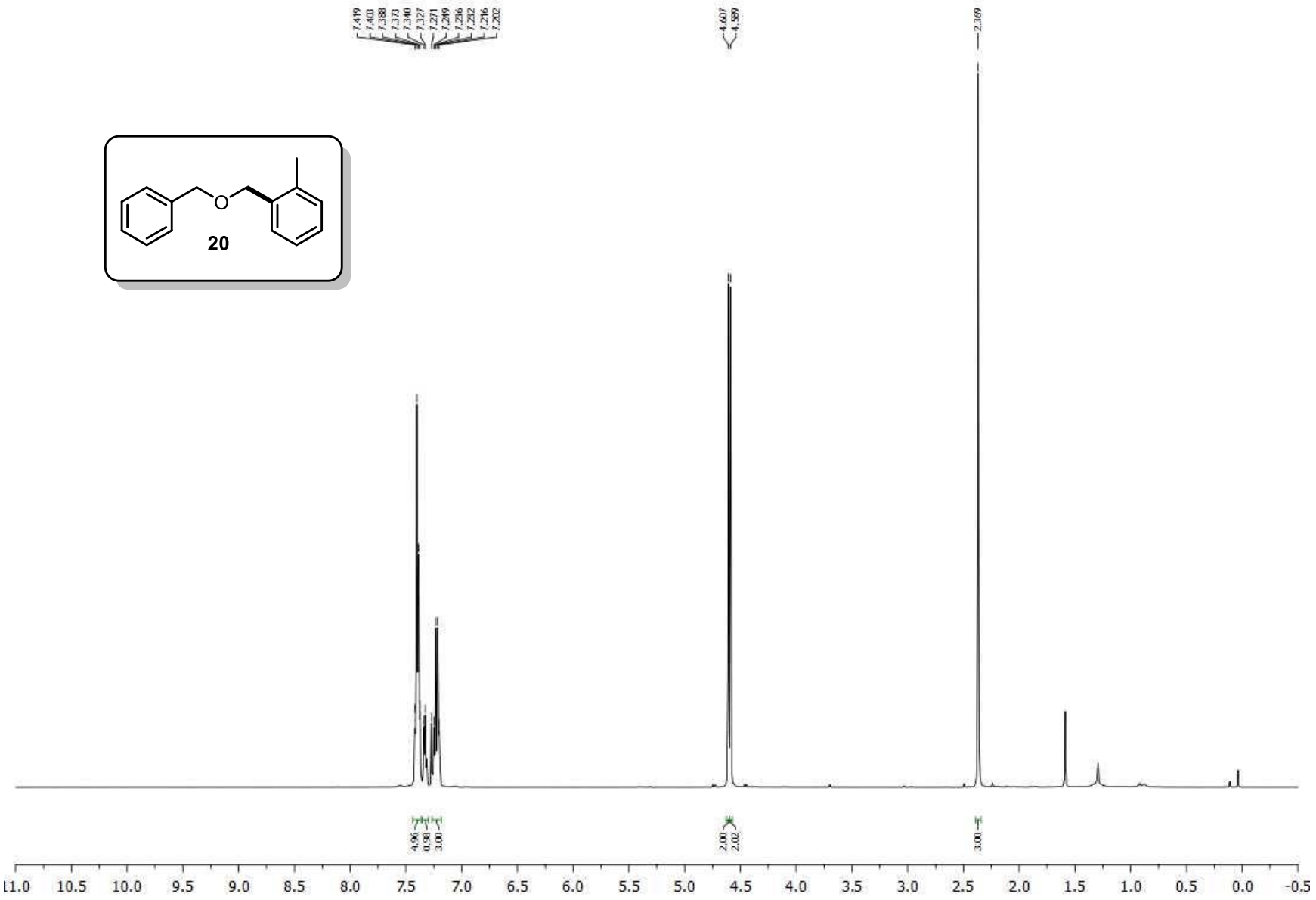
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 1-((benzyloxy)methyl)-2-methoxybenzene (**19**)



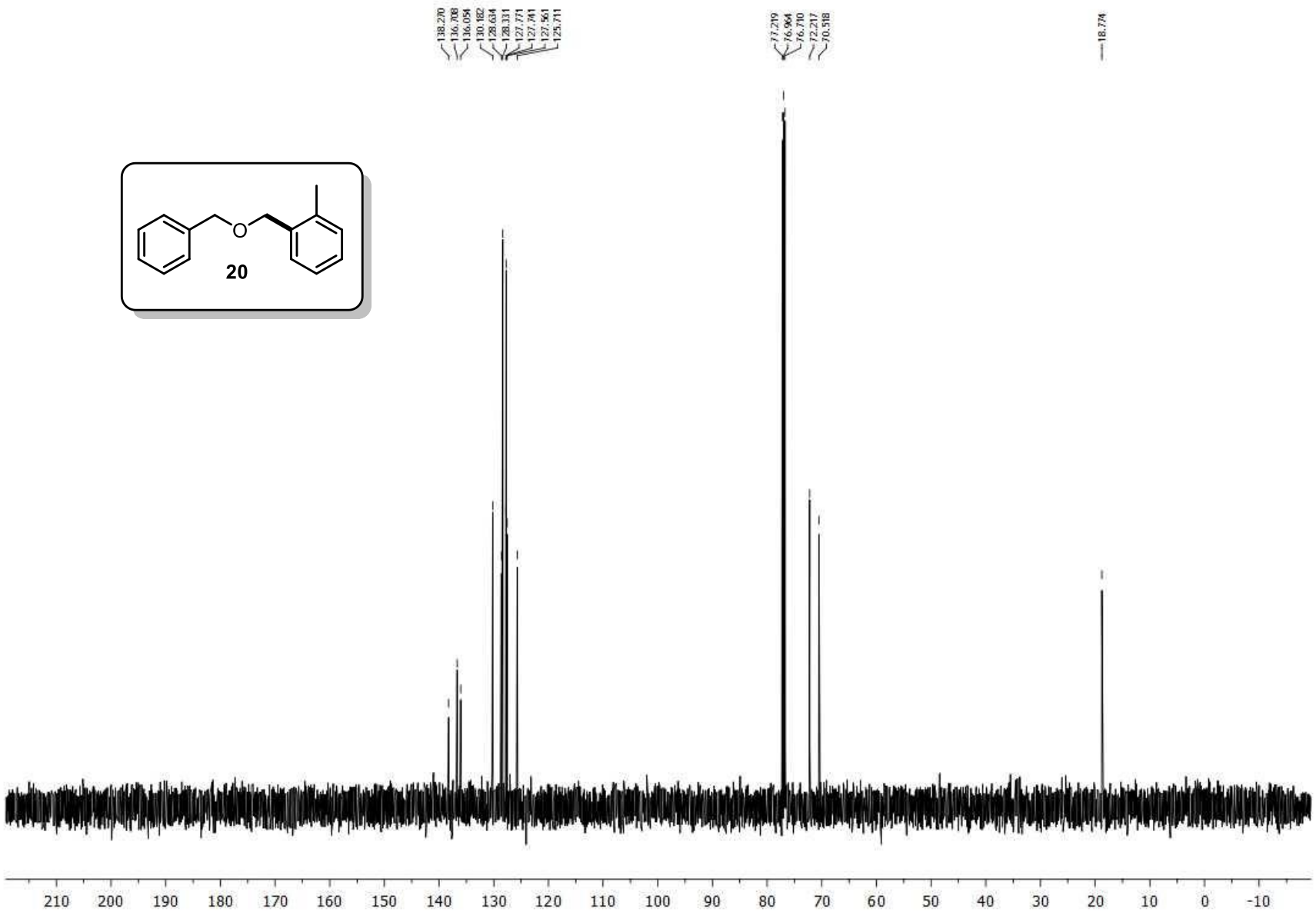
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 1-((benzyloxy)methyl)-2-methoxybenzene (**19**)



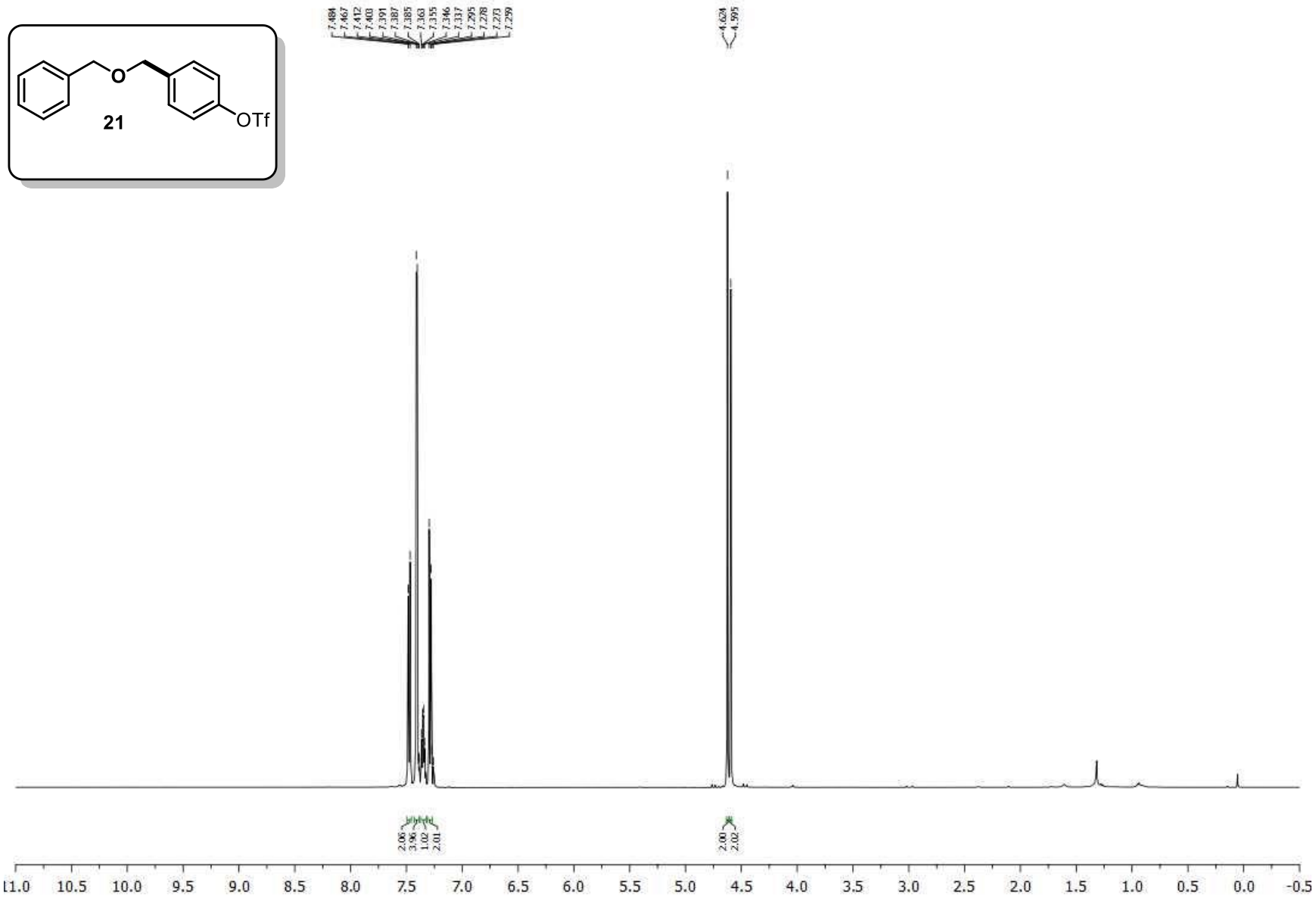
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 1-((benzyloxy)methyl)-2-methylbenzene (**20**)



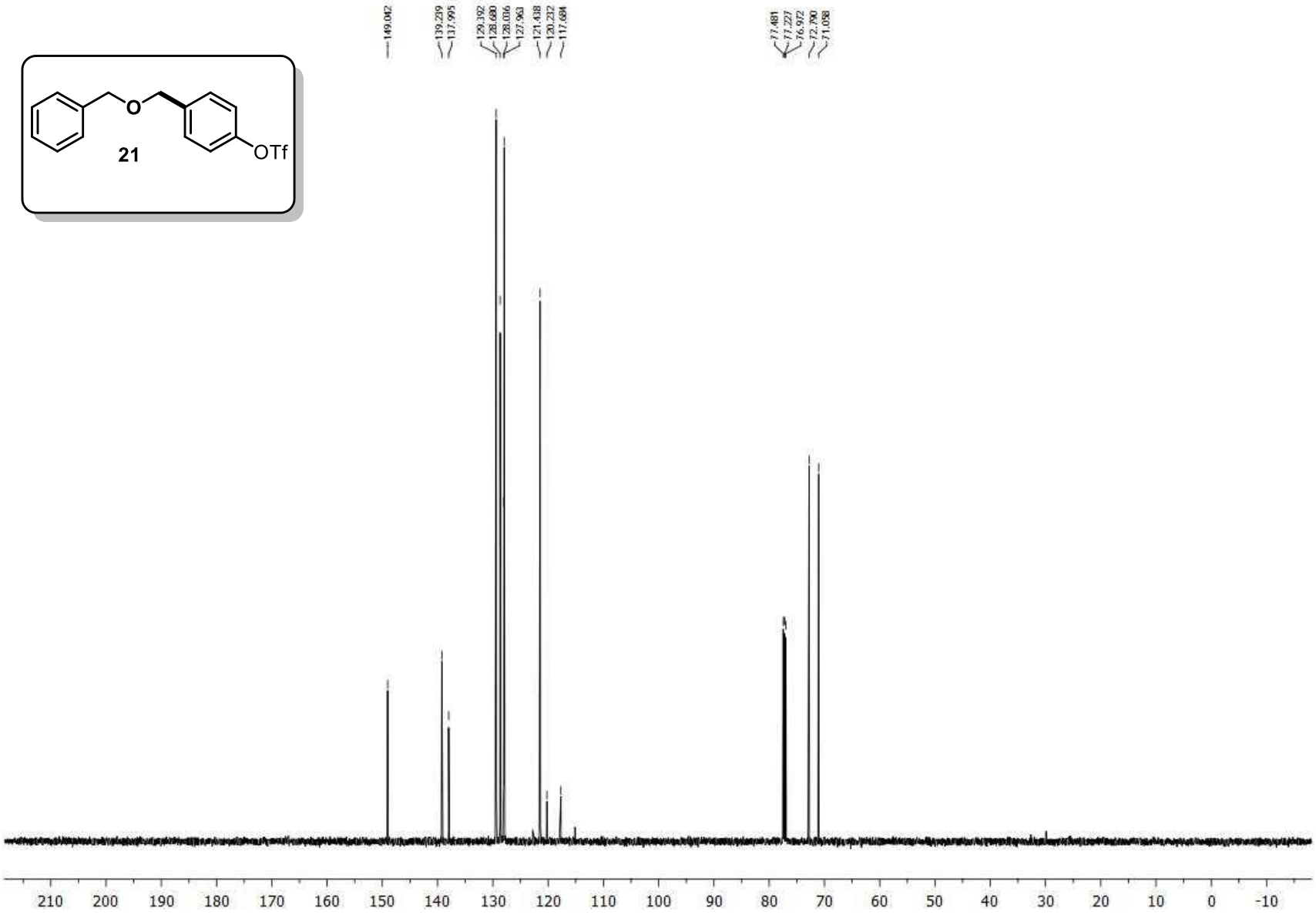
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 1-((benzyloxy)methyl)-2-methylbenzene (**20**)



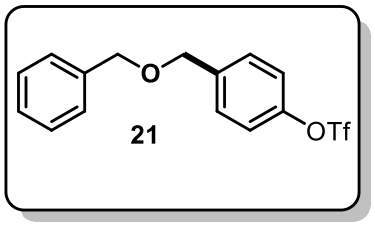
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 4-((benzyloxy)methyl)phenyl trifluoromethanesulfonate (**21**)



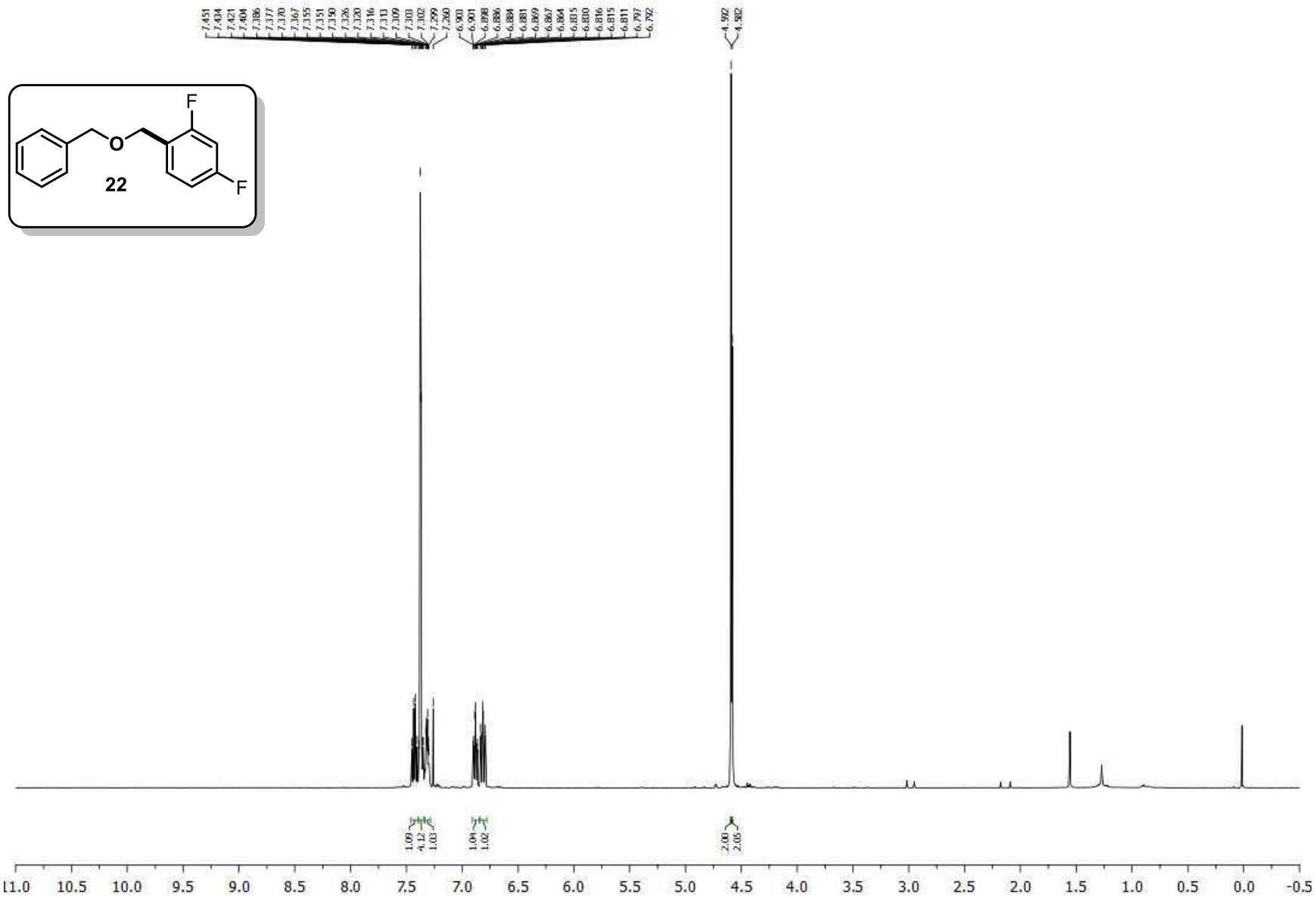
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 4-((benzyloxy)methyl)phenyl trifluoromethanesulfonate (**21**)



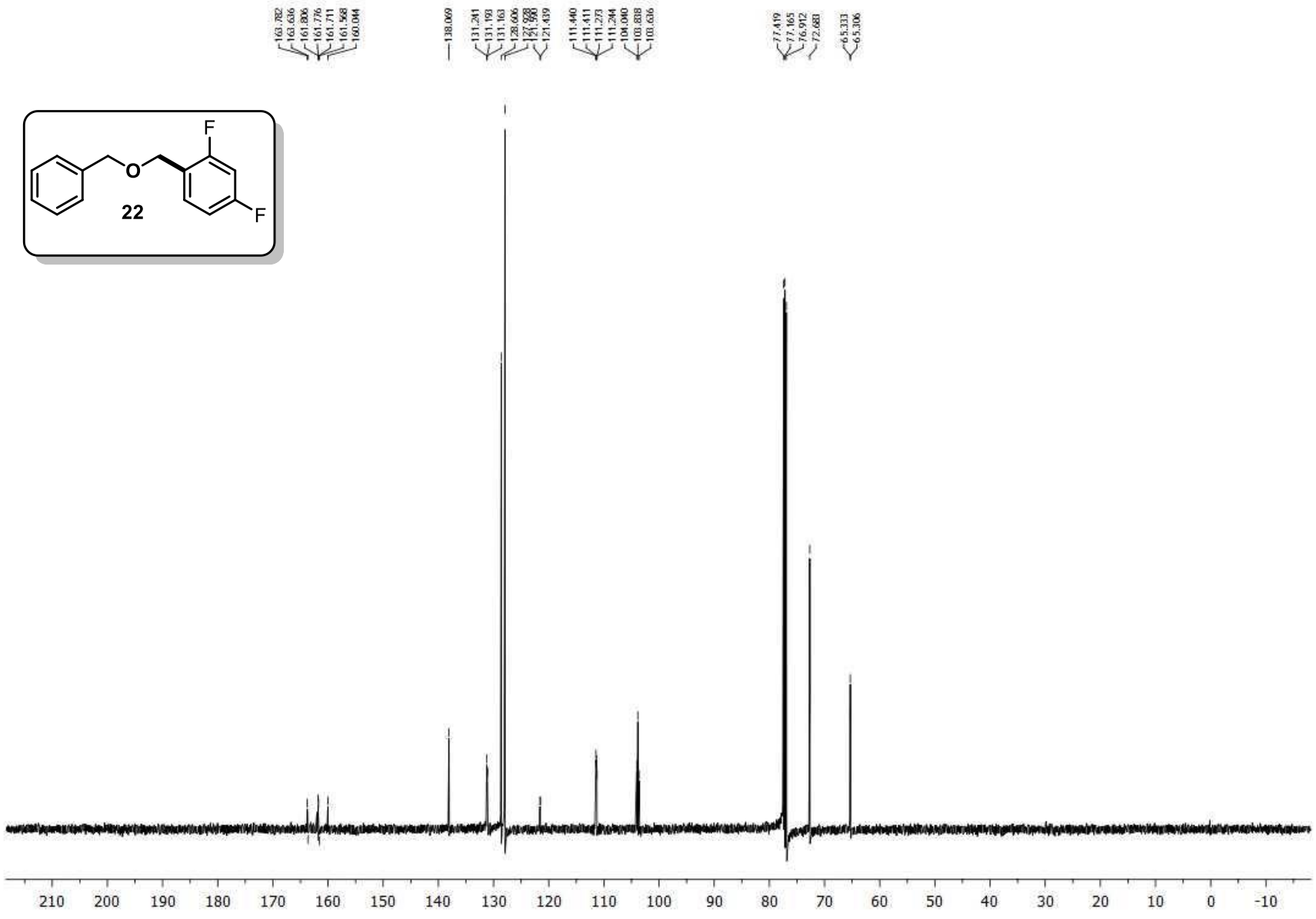
^{19}F NMR ($CDCl_3$, 471 MHz) spectrum of 4-((benzyloxy)methyl)phenyl trifluoromethanesulfonate (**21**)



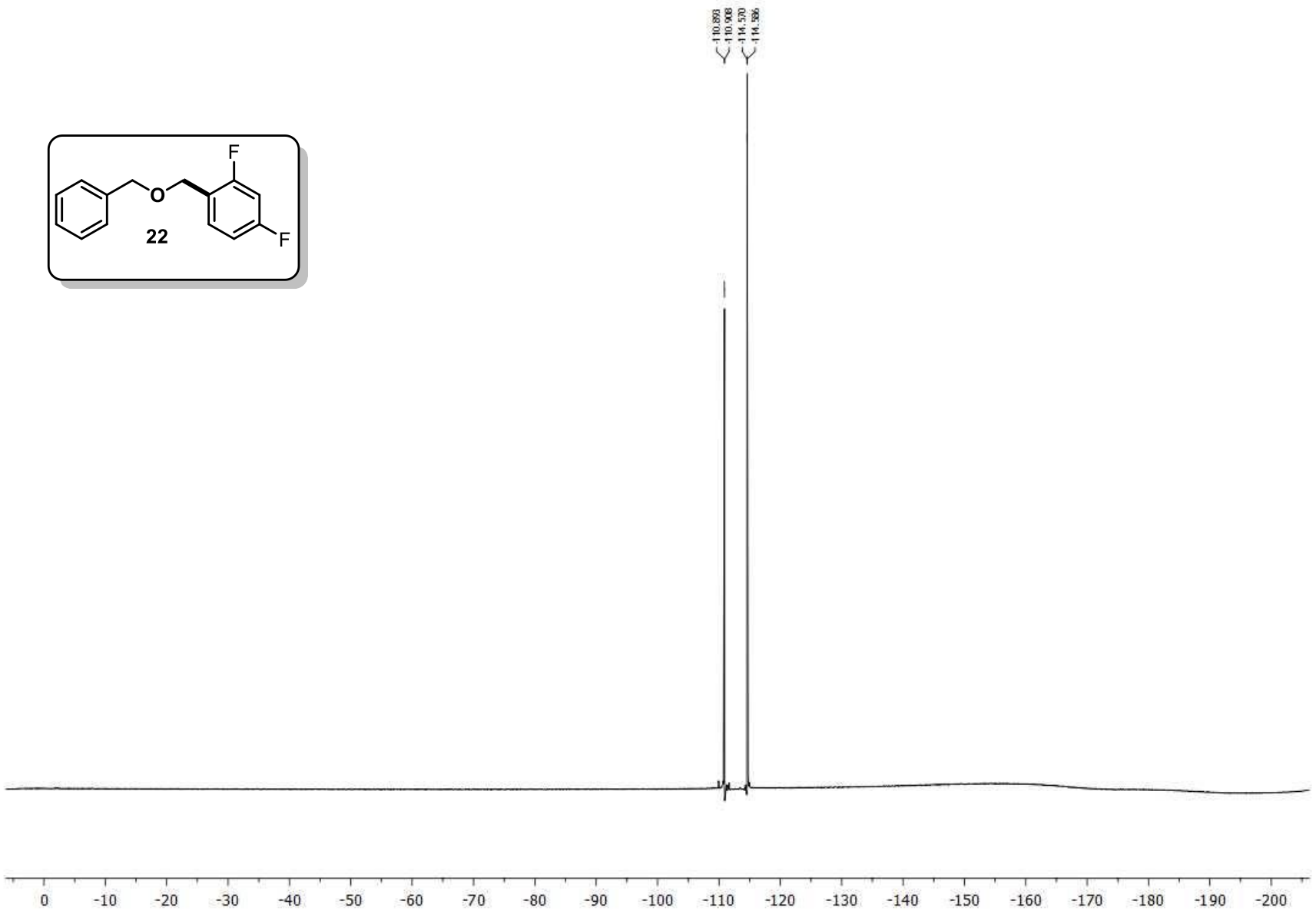
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 1-((benzyloxy)methyl)-2,4-difluorobenzene (**22**)



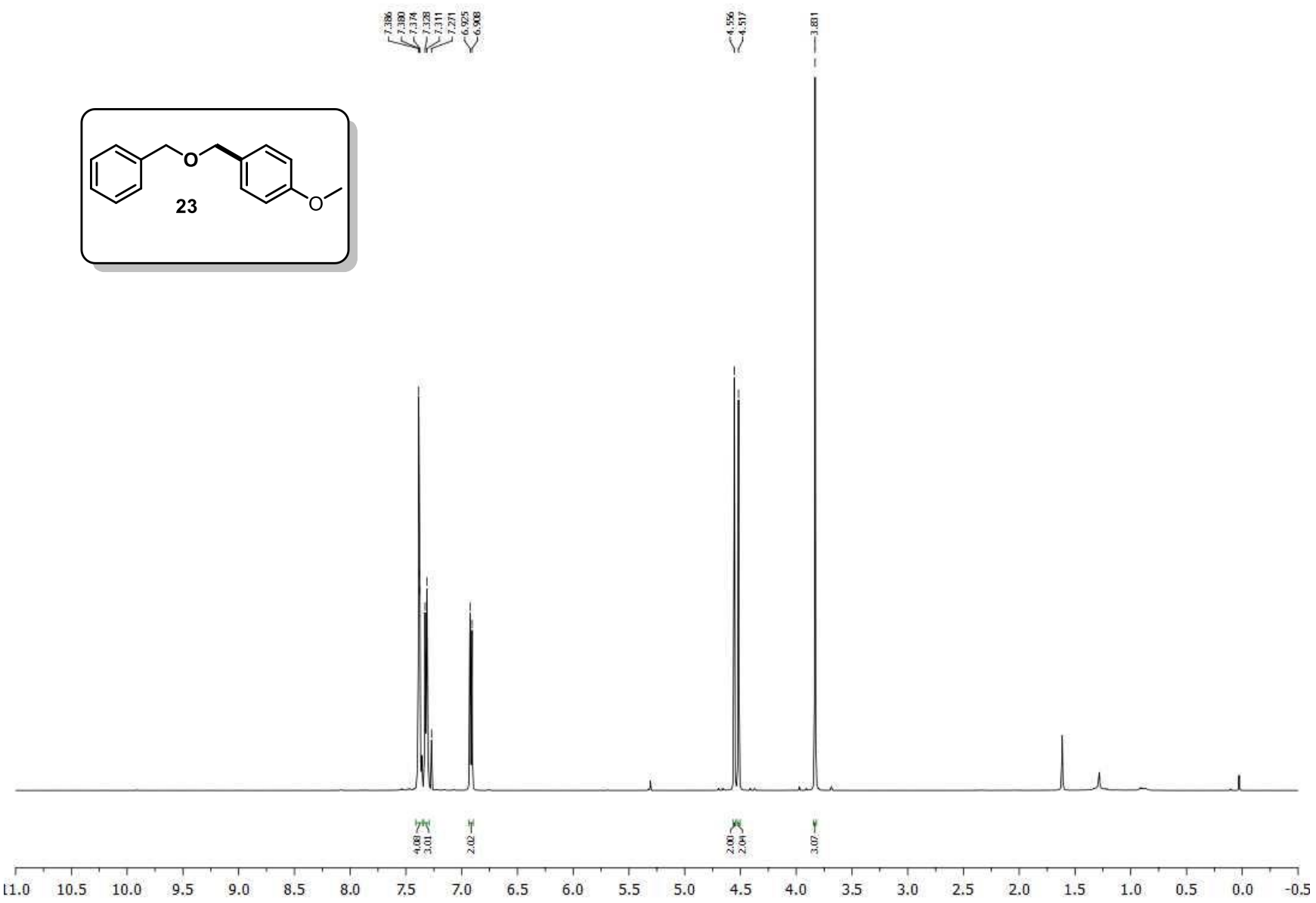
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 1-((benzyloxy)methyl)-2,4-difluorobenzene (**22**)



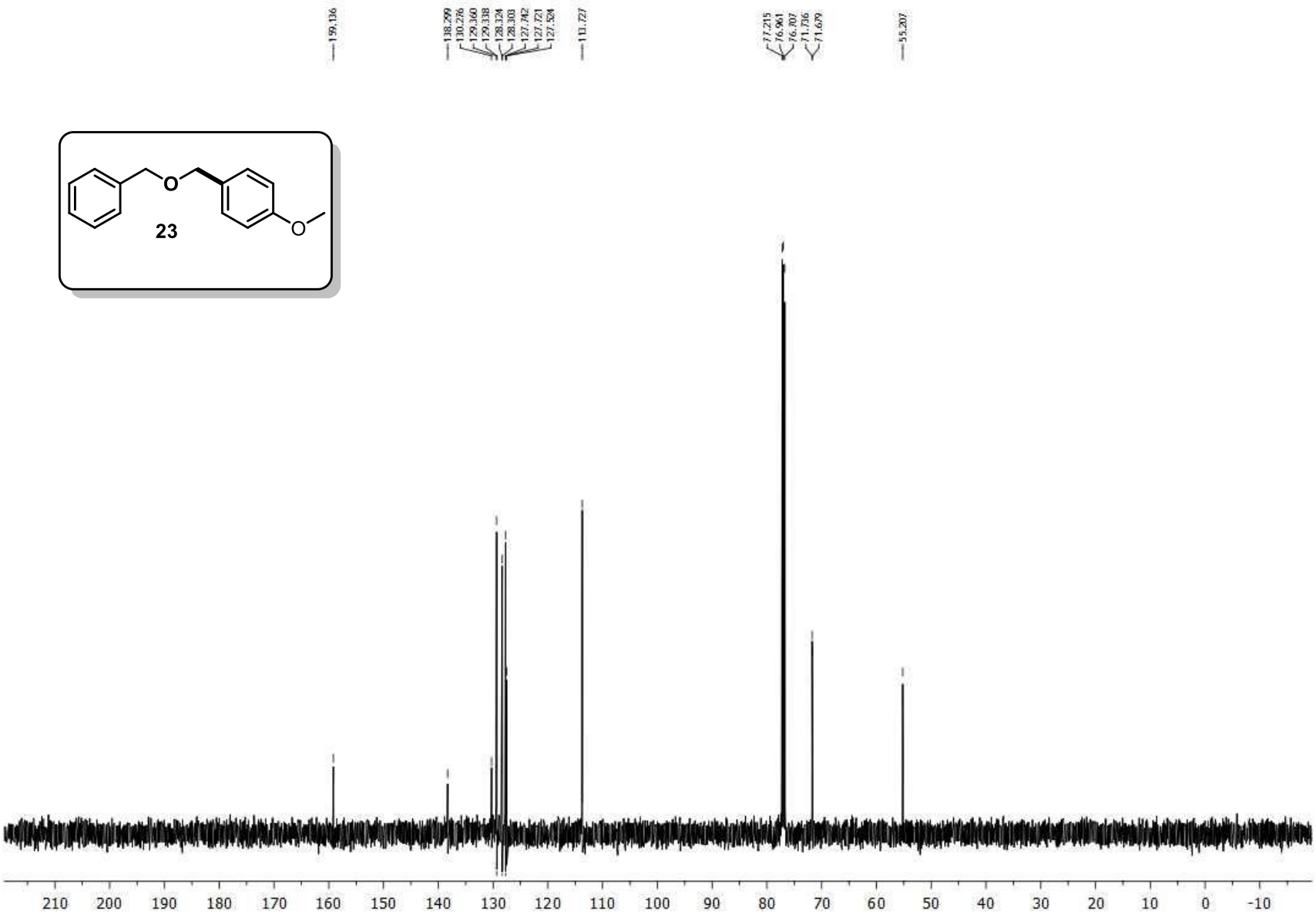
^{19}F NMR ($CDCl_3$, 471 MHz) spectrum of 1-((benzyloxy)methyl)-2,4-difluorobenzene (**22**)



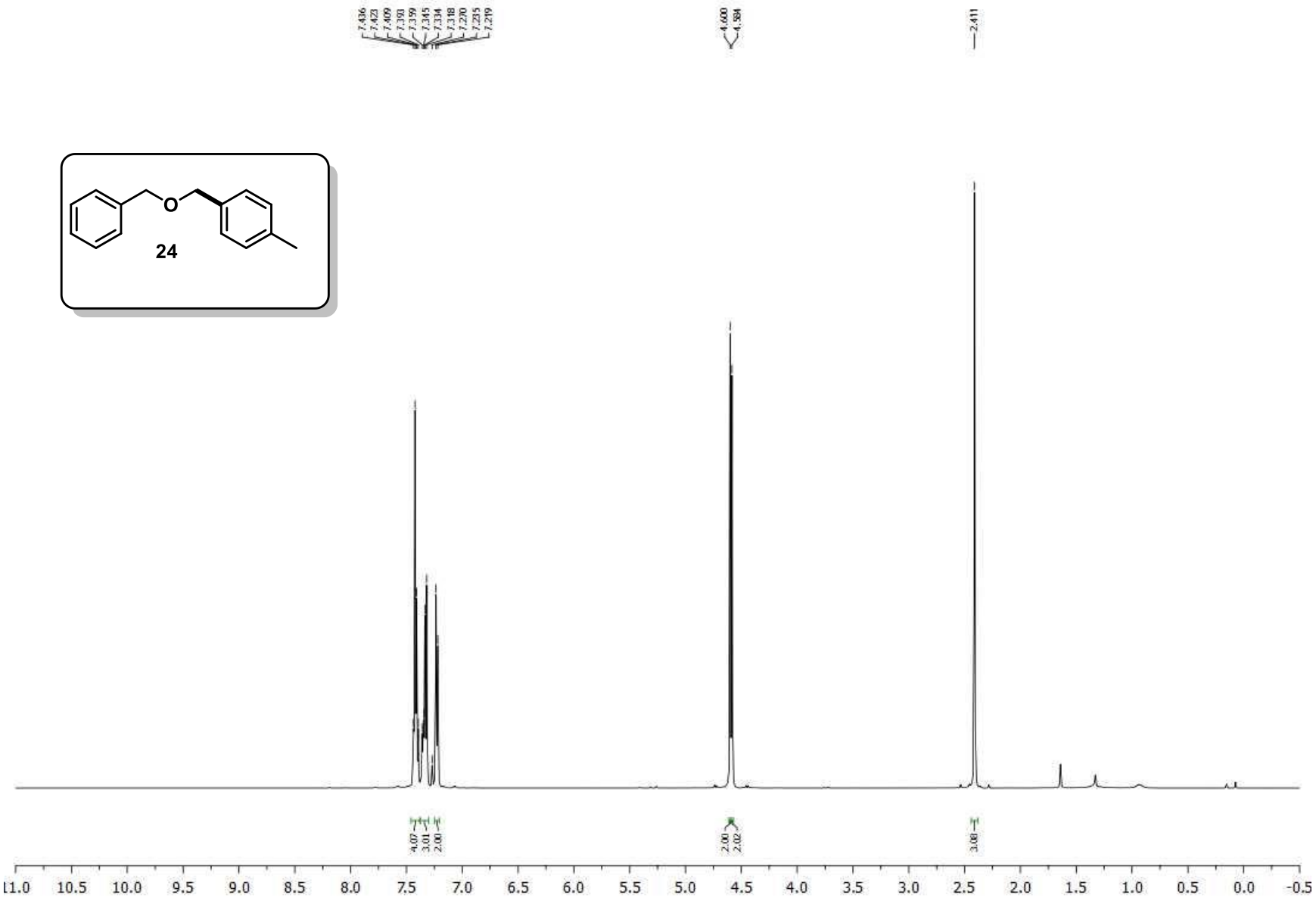
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 1-((benzyloxy)methyl)-4-methoxybenzene (**23**)



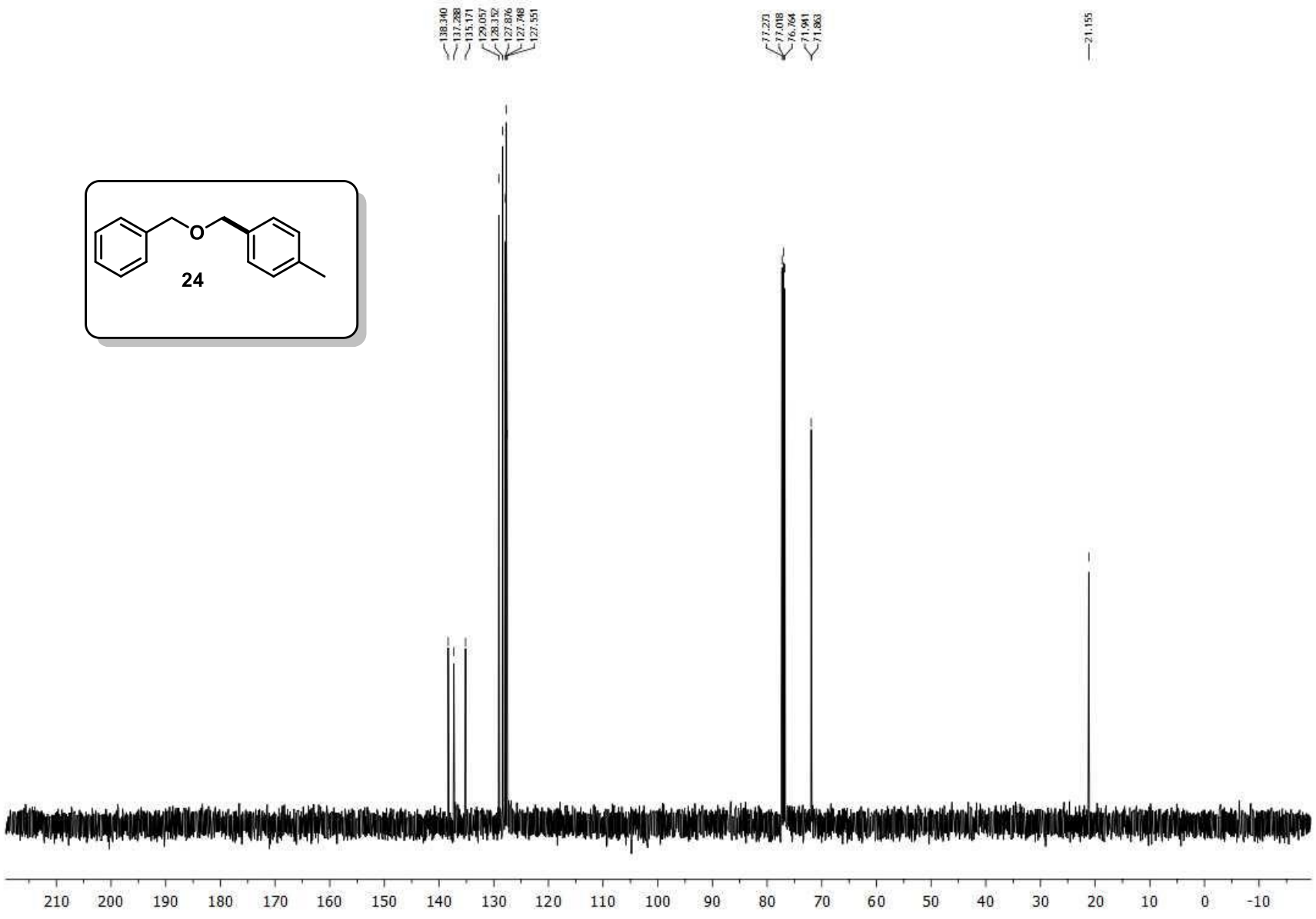
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 1-((benzyloxy)methyl)-4-methoxybenzene (**23**)



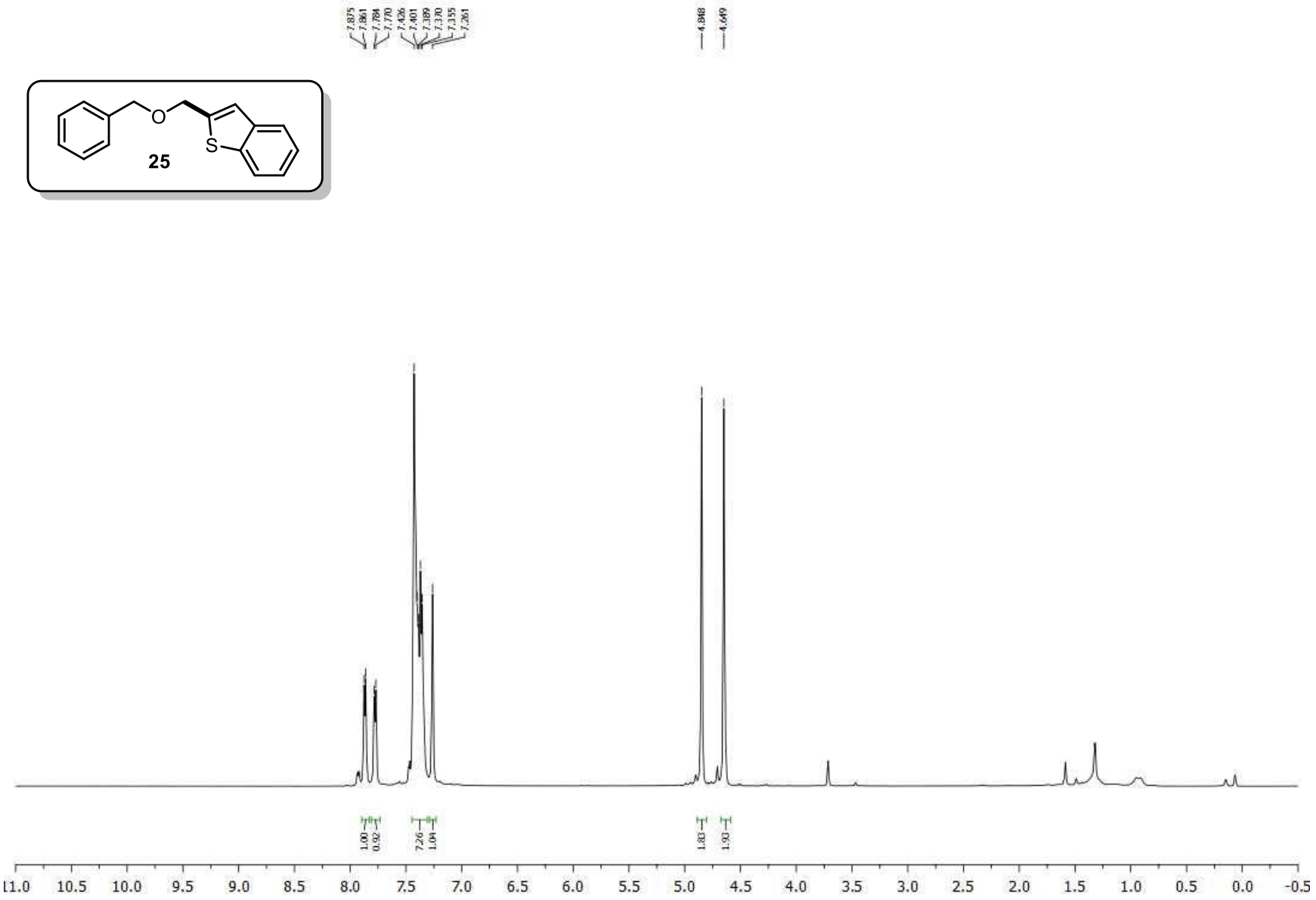
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 1-((benzyloxy)methyl)-4-methylbenzene (**24**)



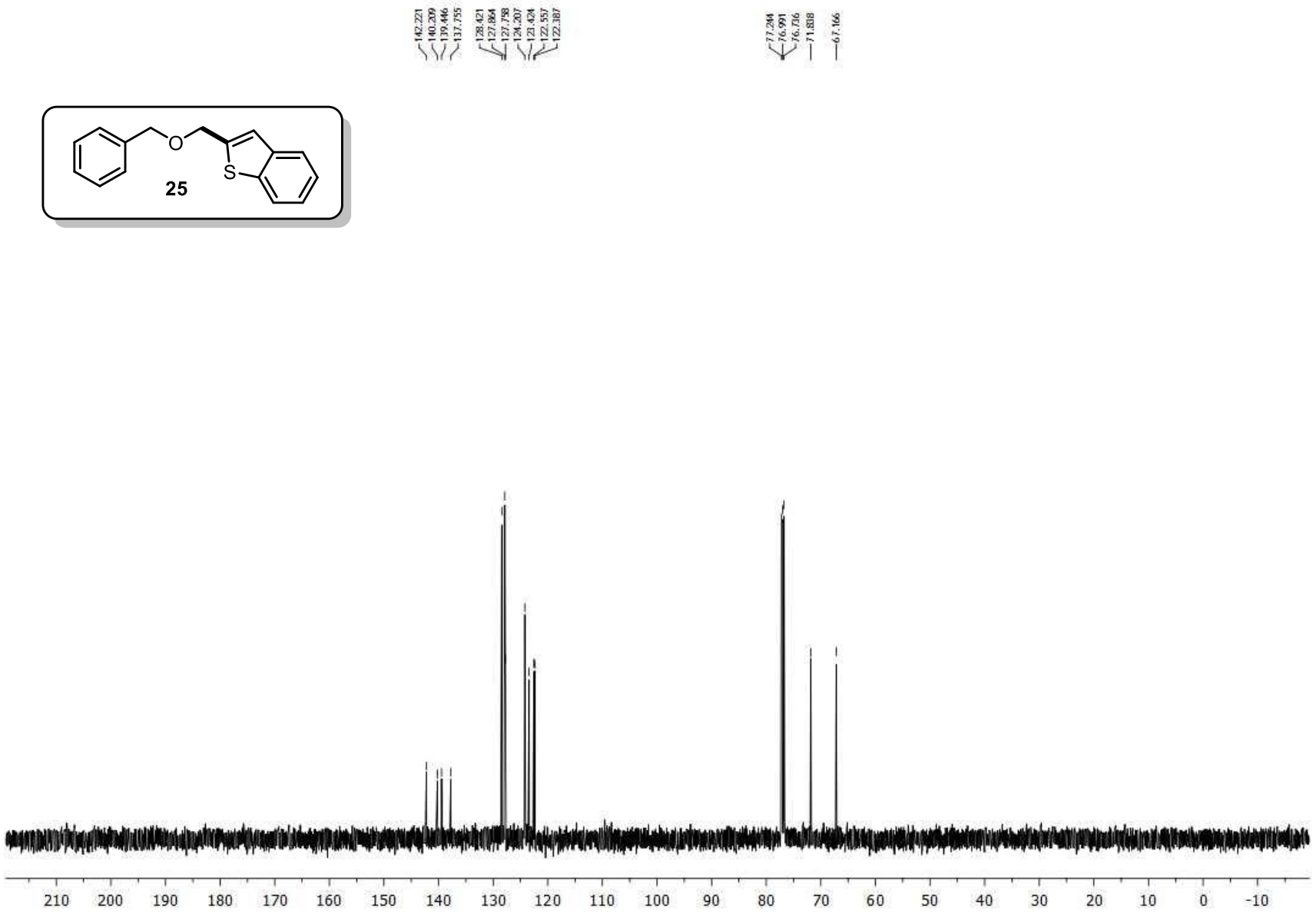
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 1-((benzyloxy)methyl)-4-methylbenzene (**24**)



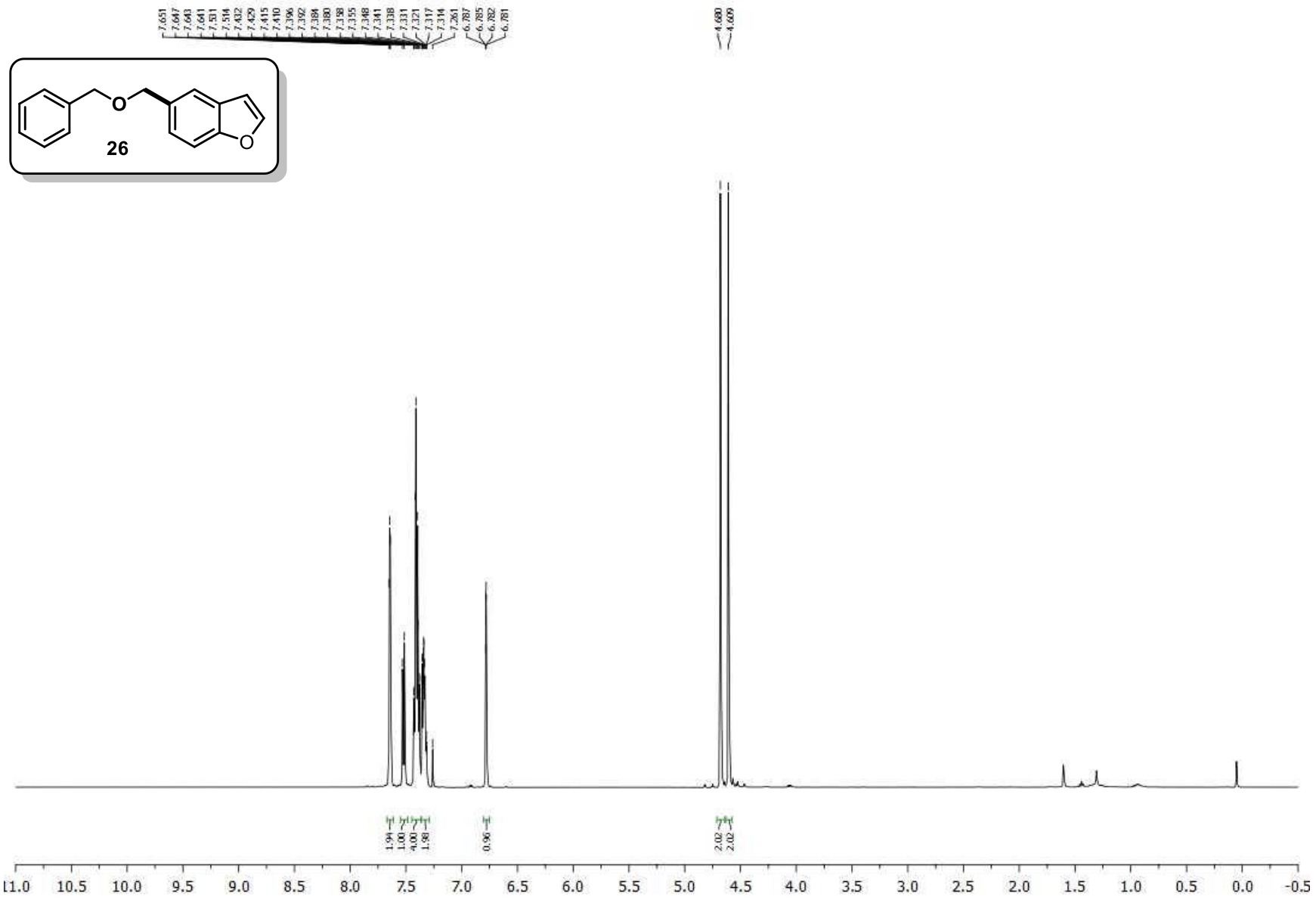
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 2-((benzyloxy)methyl)benzo[b]thiophene (**25**)



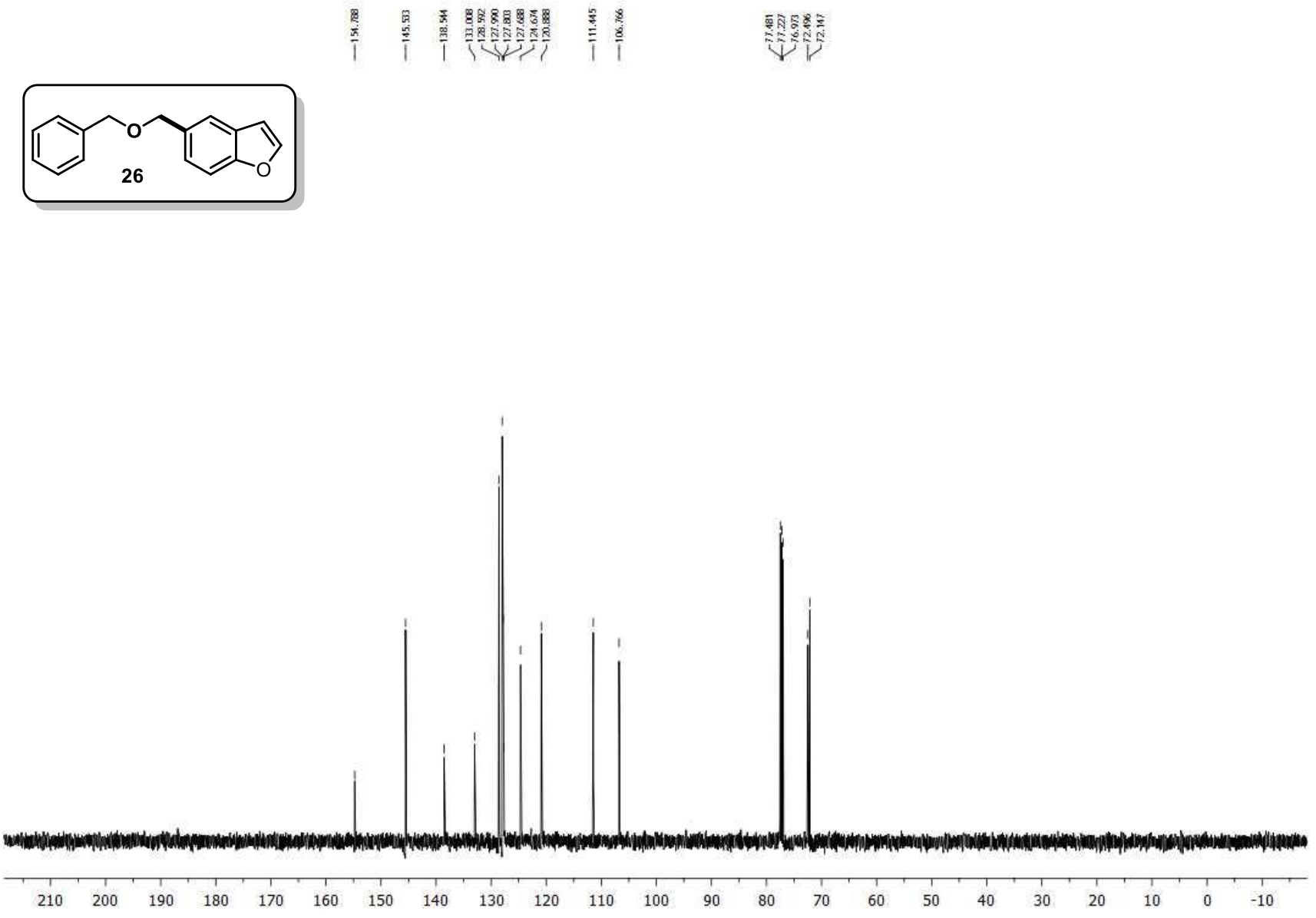
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 2-((benzyloxy)methyl)benzo[b]thiophene (**25**)



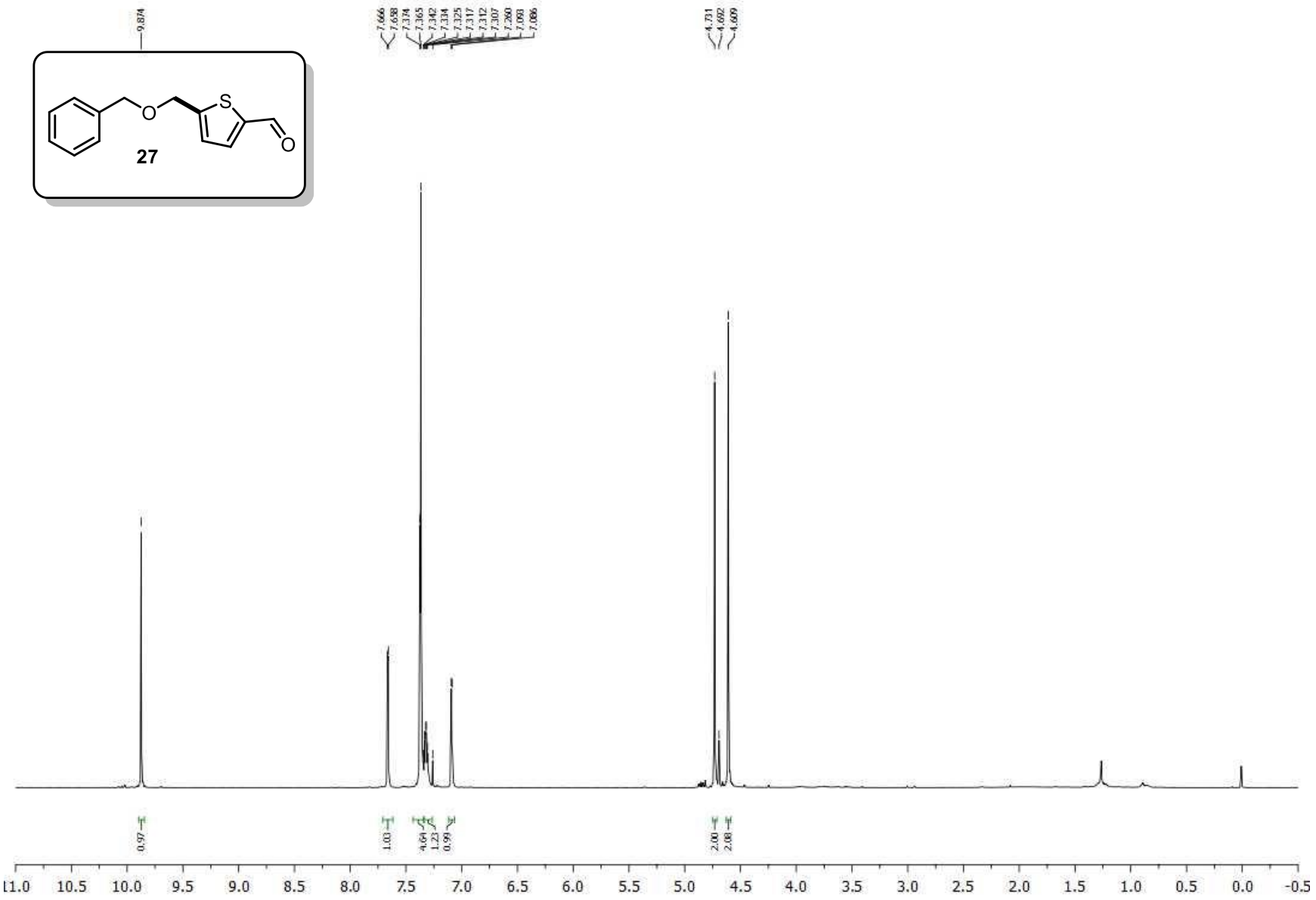
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 5-((benzyloxy)methyl)benzofuran (**26**)



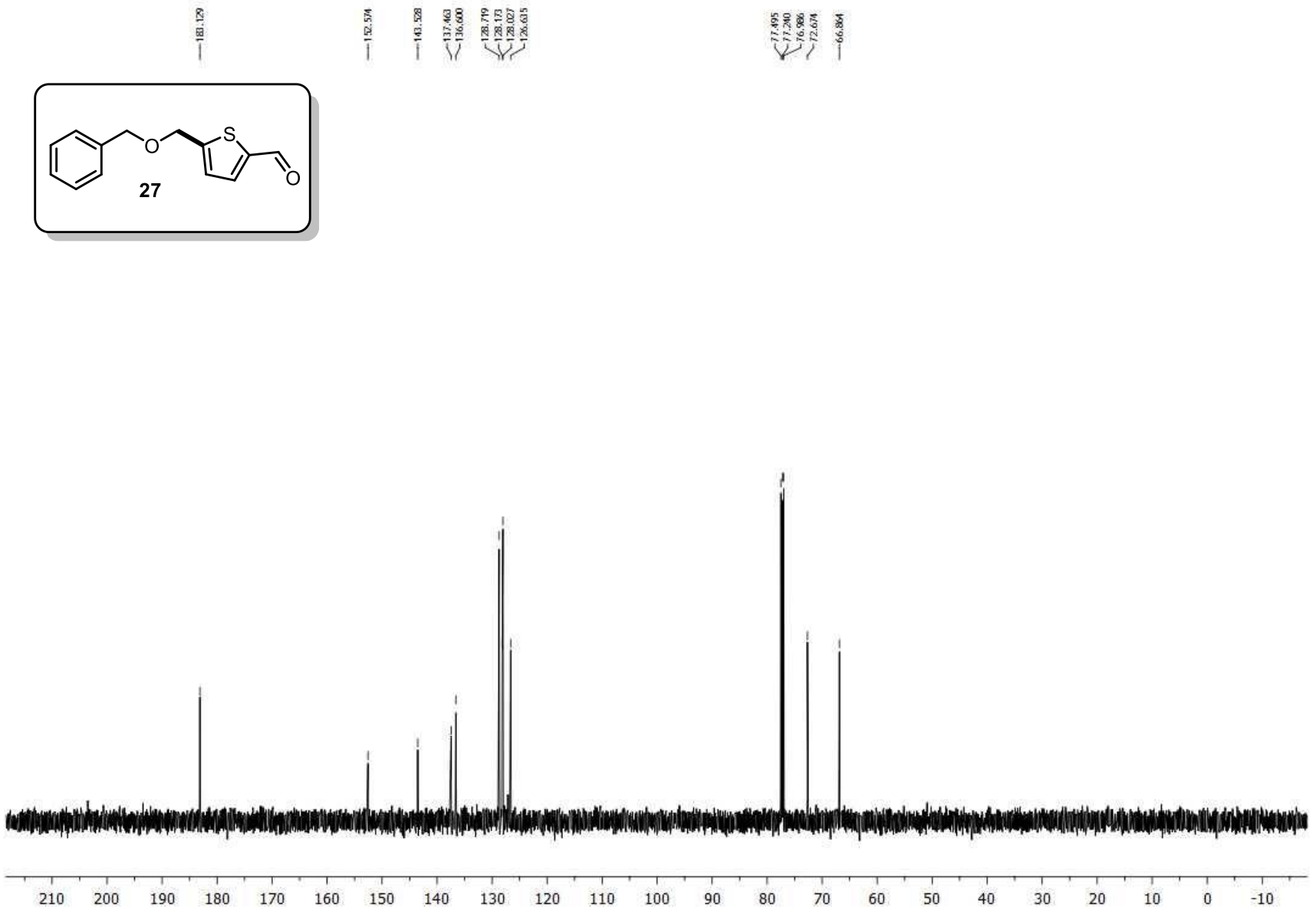
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 5-((benzyloxy)methyl)benzofuran (**26**)



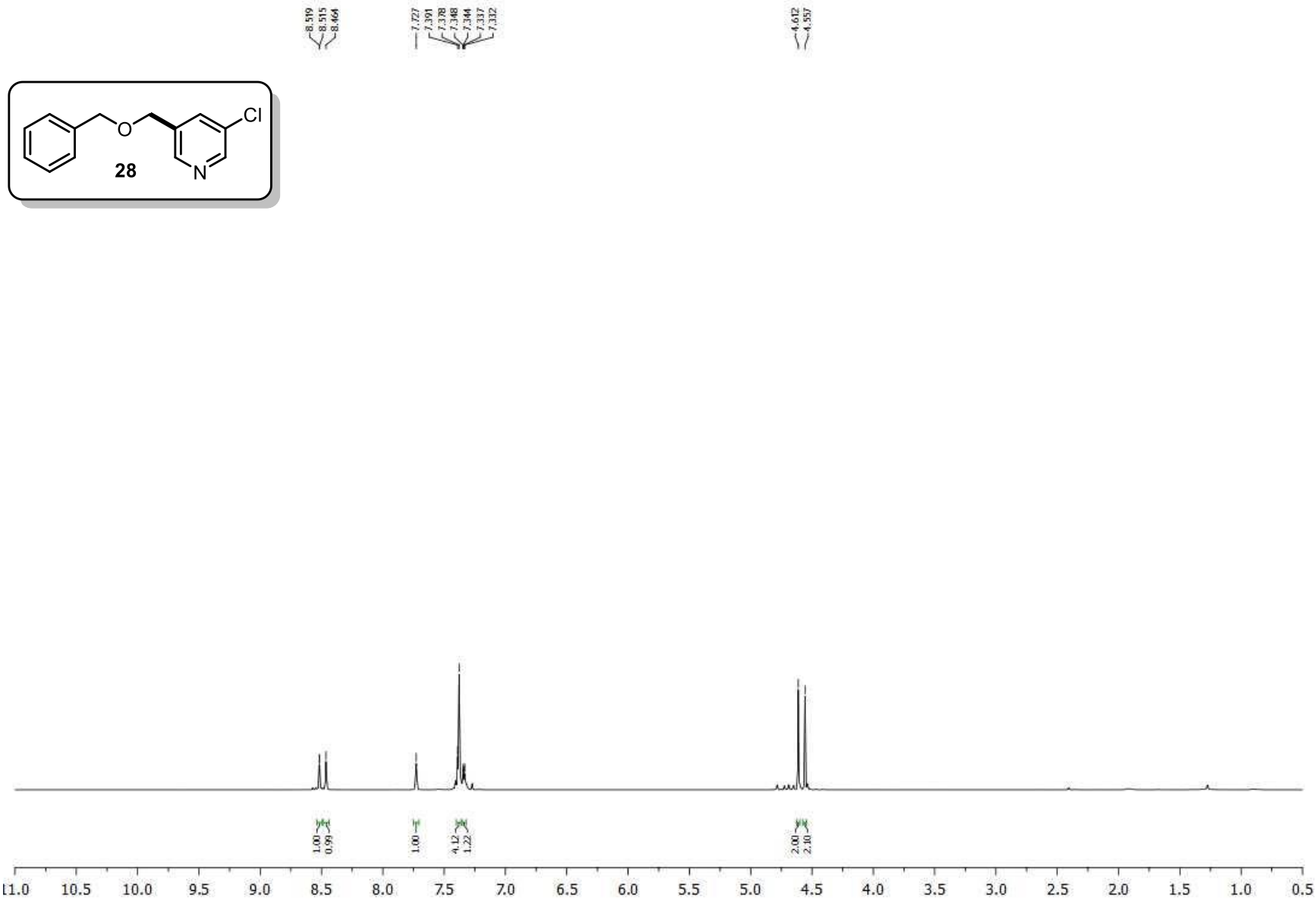
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 5-((benzyloxy)methyl)thiophene-2-carbaldehyde (**27**)



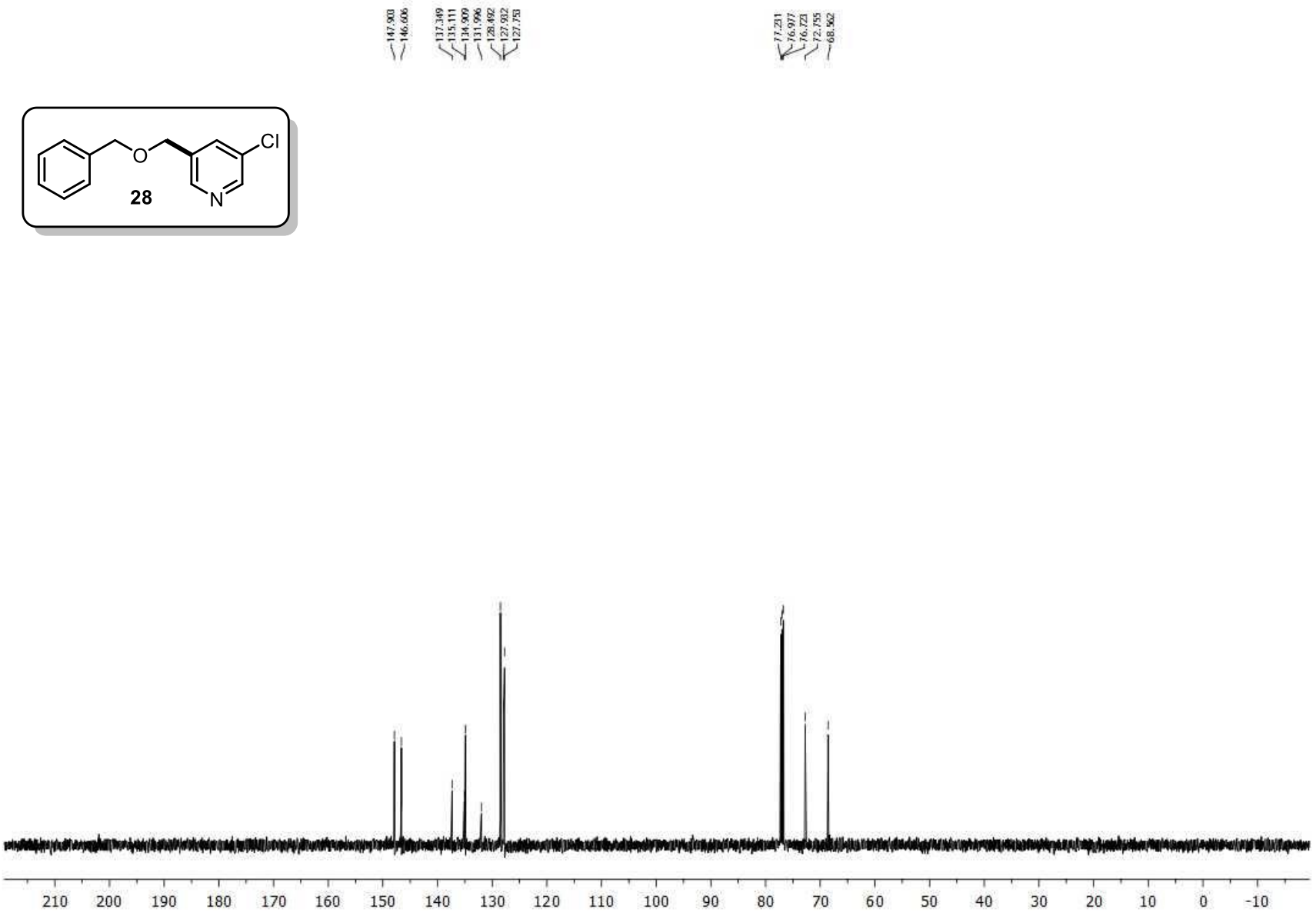
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 5-((benzyloxy)methyl)thiophene-2-carbaldehyde (**27**)



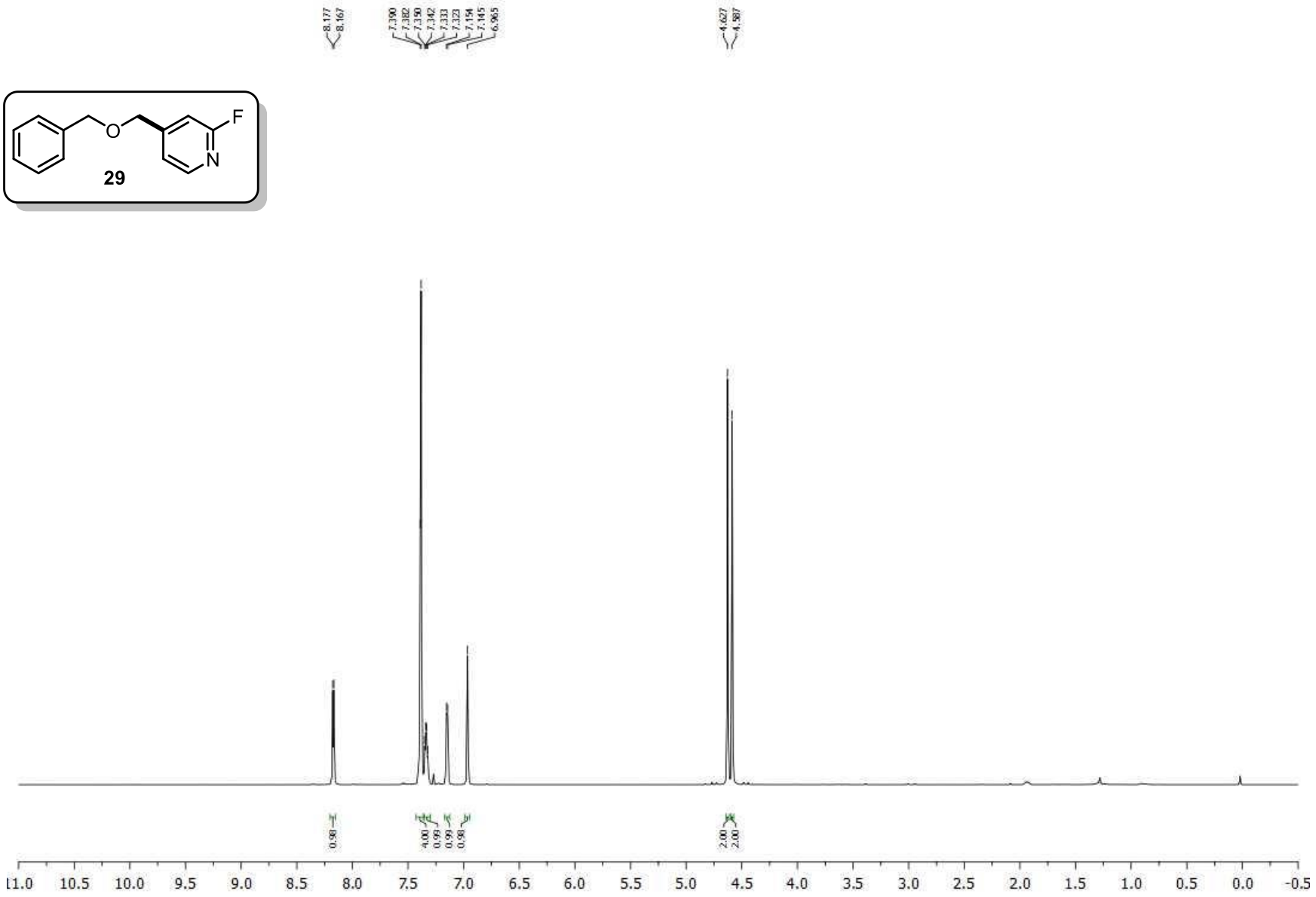
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 1-((benzyloxy)methyl)-3-chlorobenzene (**28**)



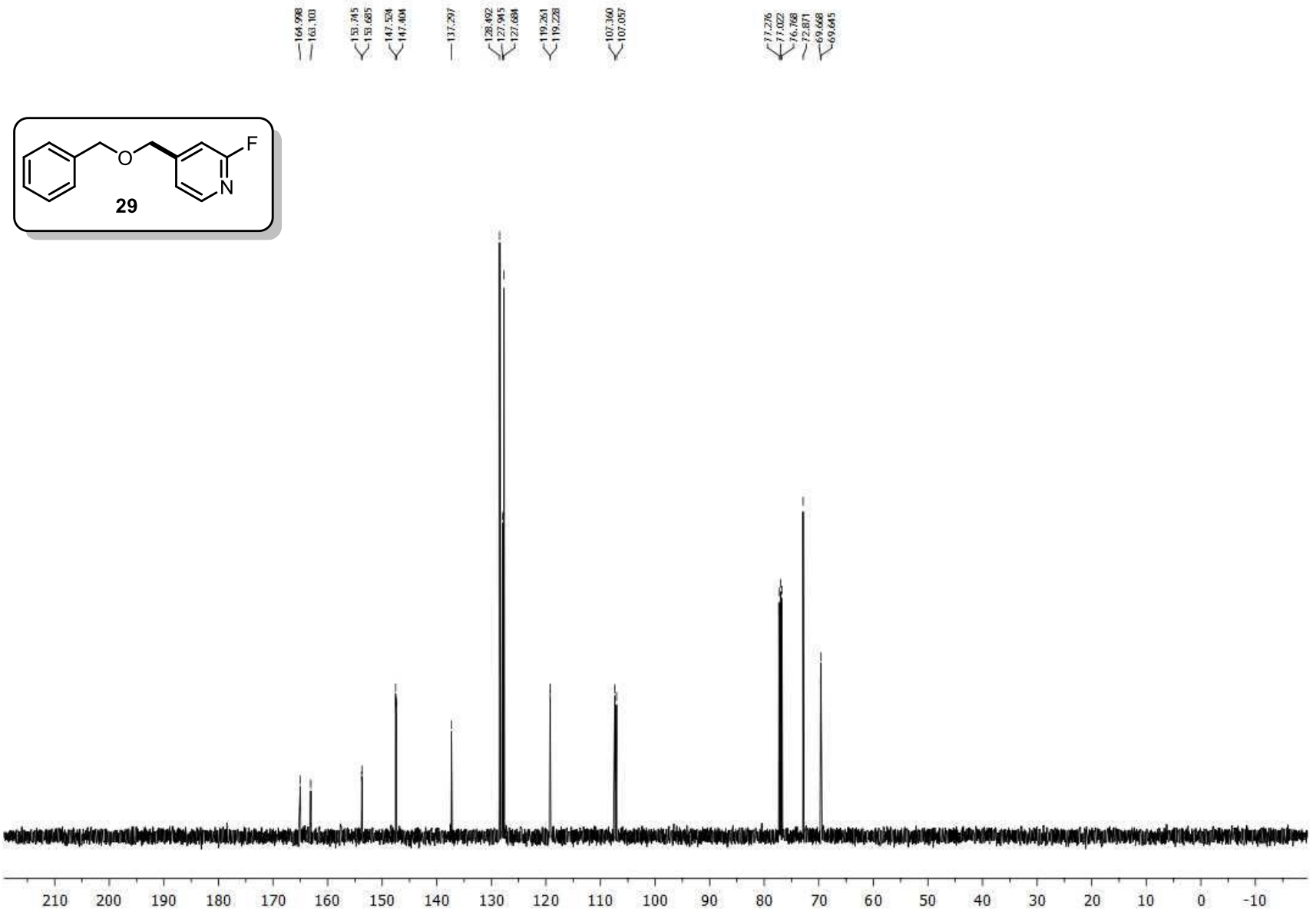
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 1-((benzyloxy)methyl)-3-chlorobenzene (**28**)



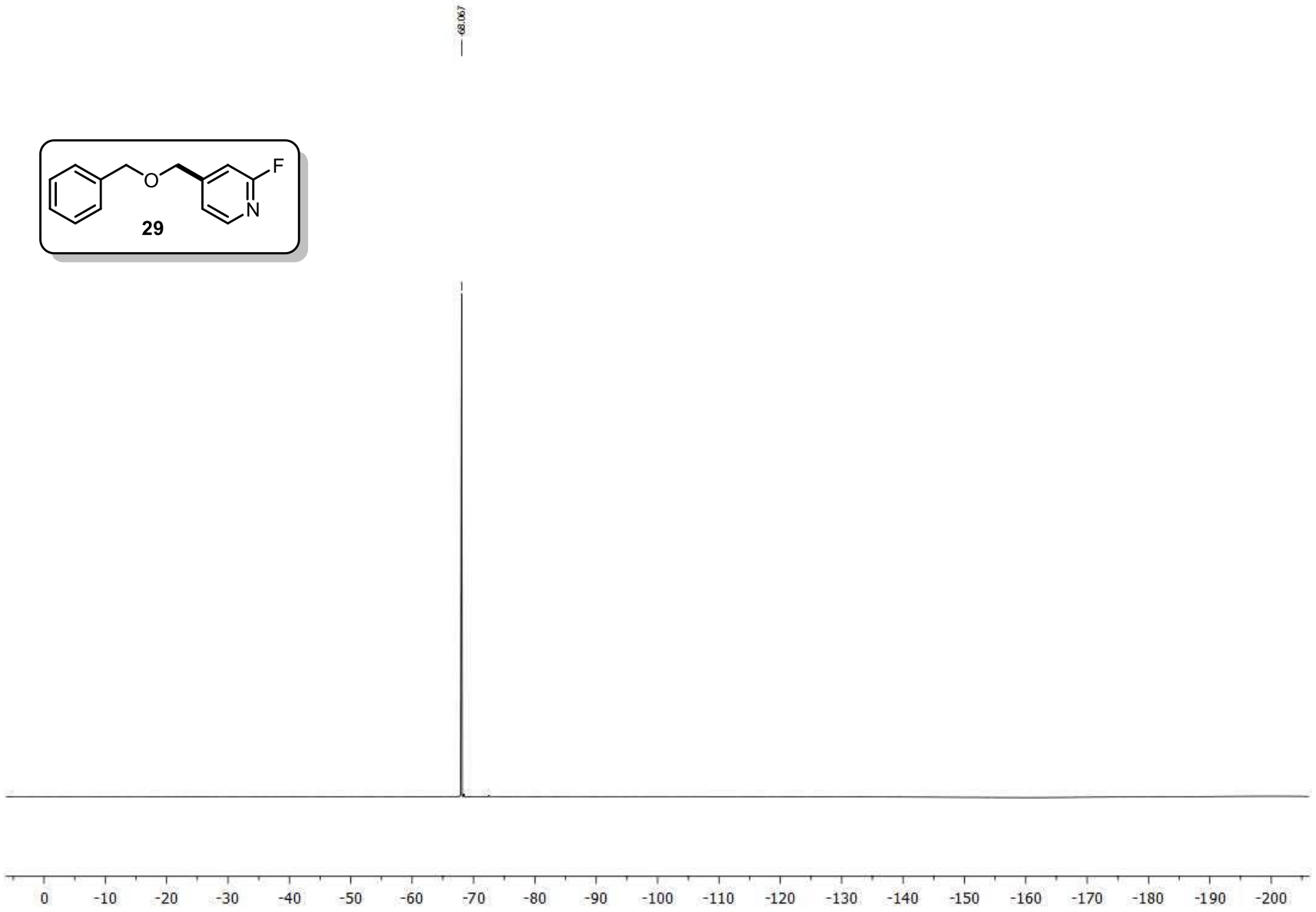
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 4-((benzyloxy)methyl)-2-fluoropyridine (**29**)



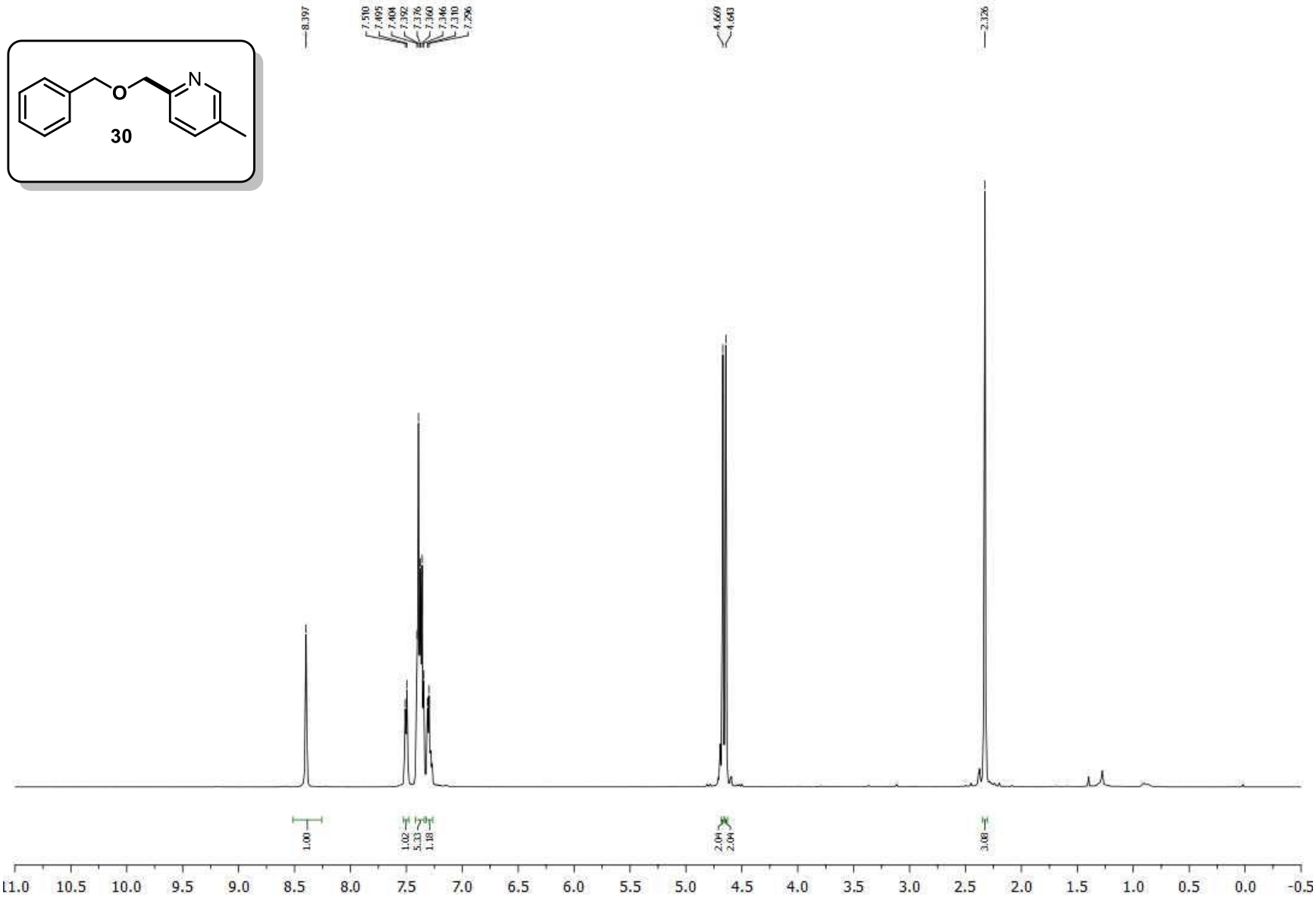
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 4-((benzyloxy)methyl)-2-fluoropyridine (**29**)



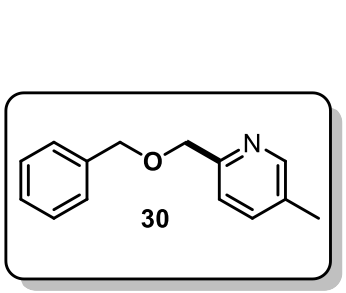
^{19}F NMR ($CDCl_3$, 471 MHz) spectrum of 4-((benzyloxy)methyl)-2-fluoropyridine (**29**)



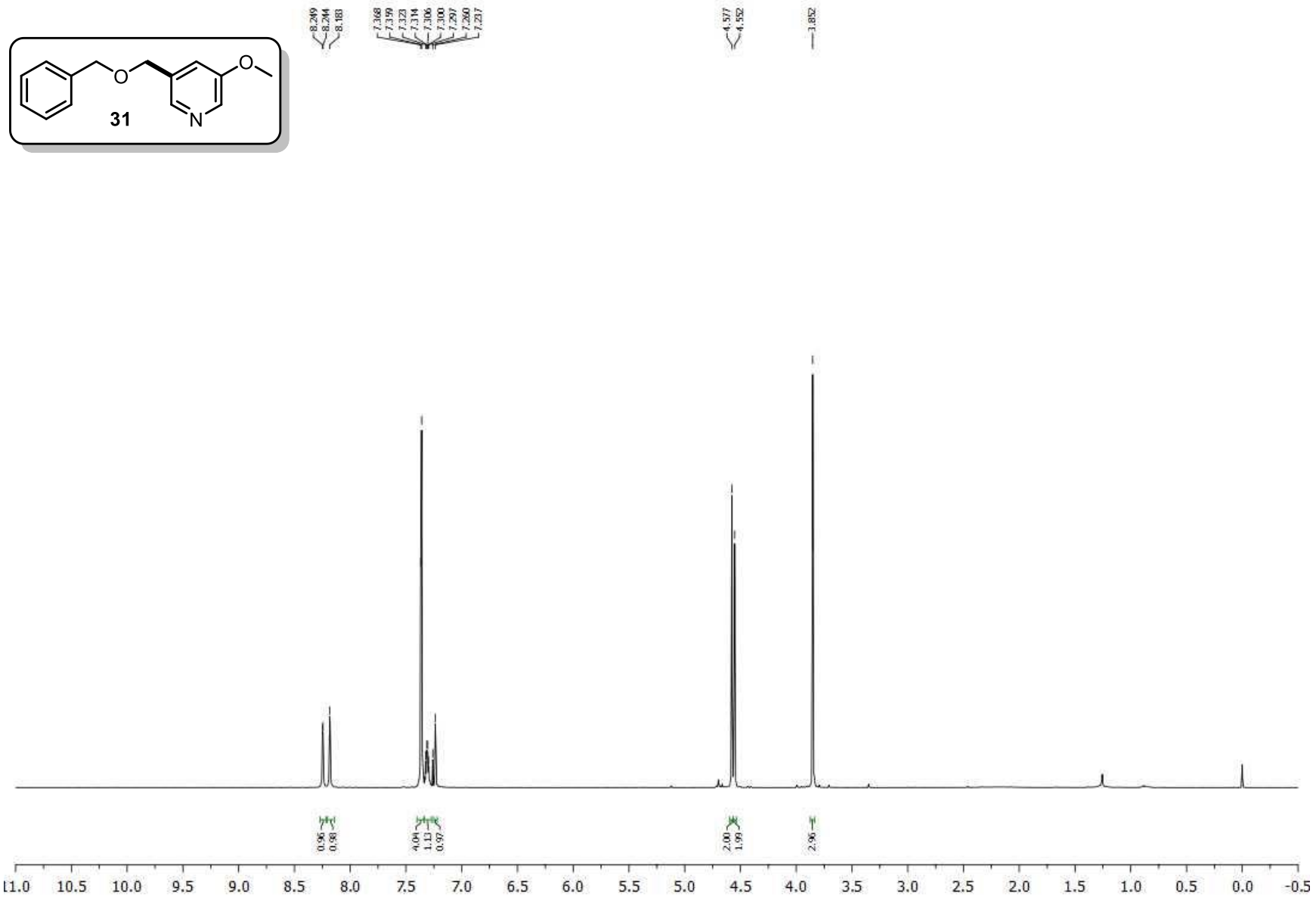
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 2-((benzyloxy)methyl)-5-methylpyridine (**30**)



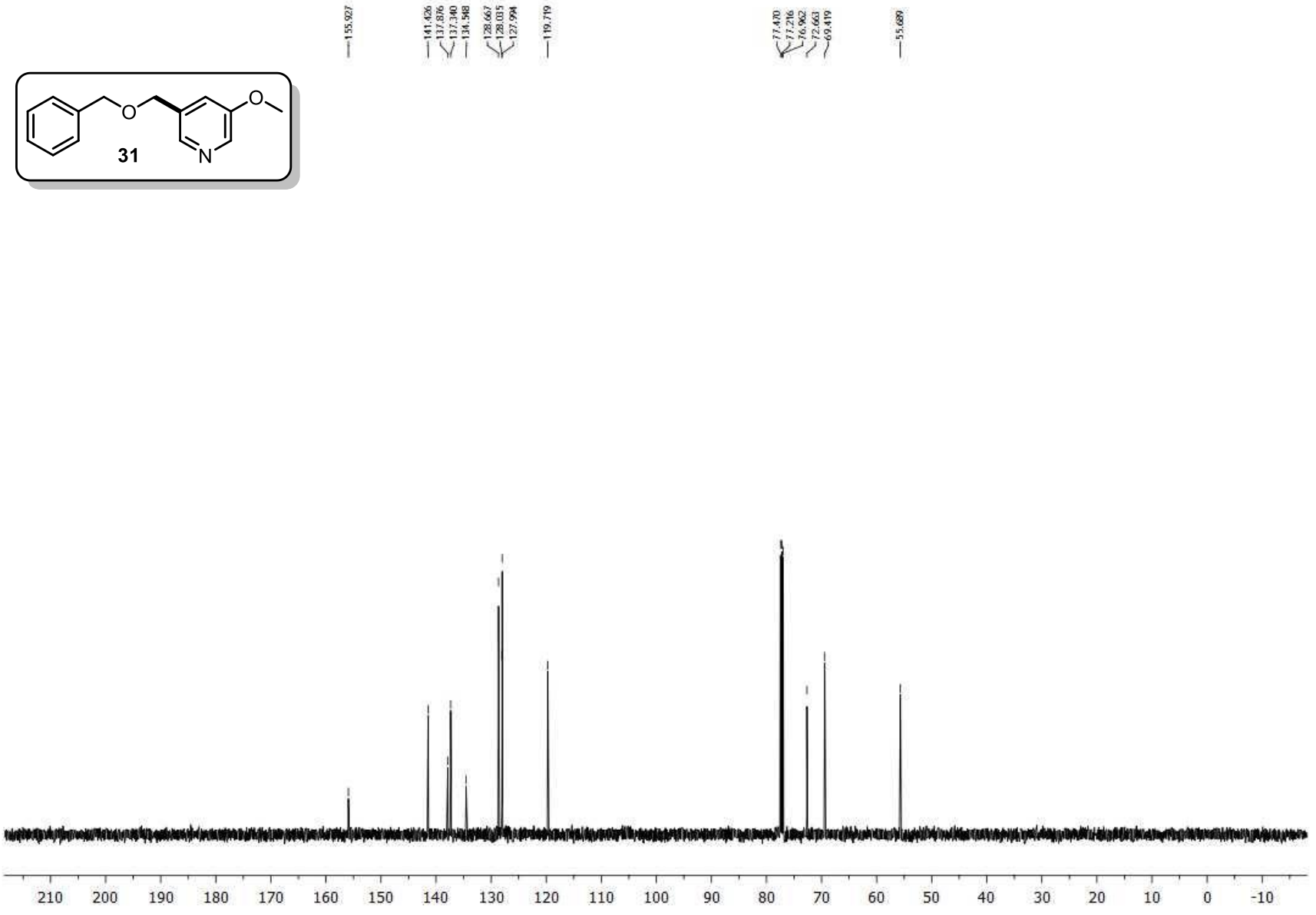
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 2-((benzyloxy)methyl)-5-methylpyridine (**30**)



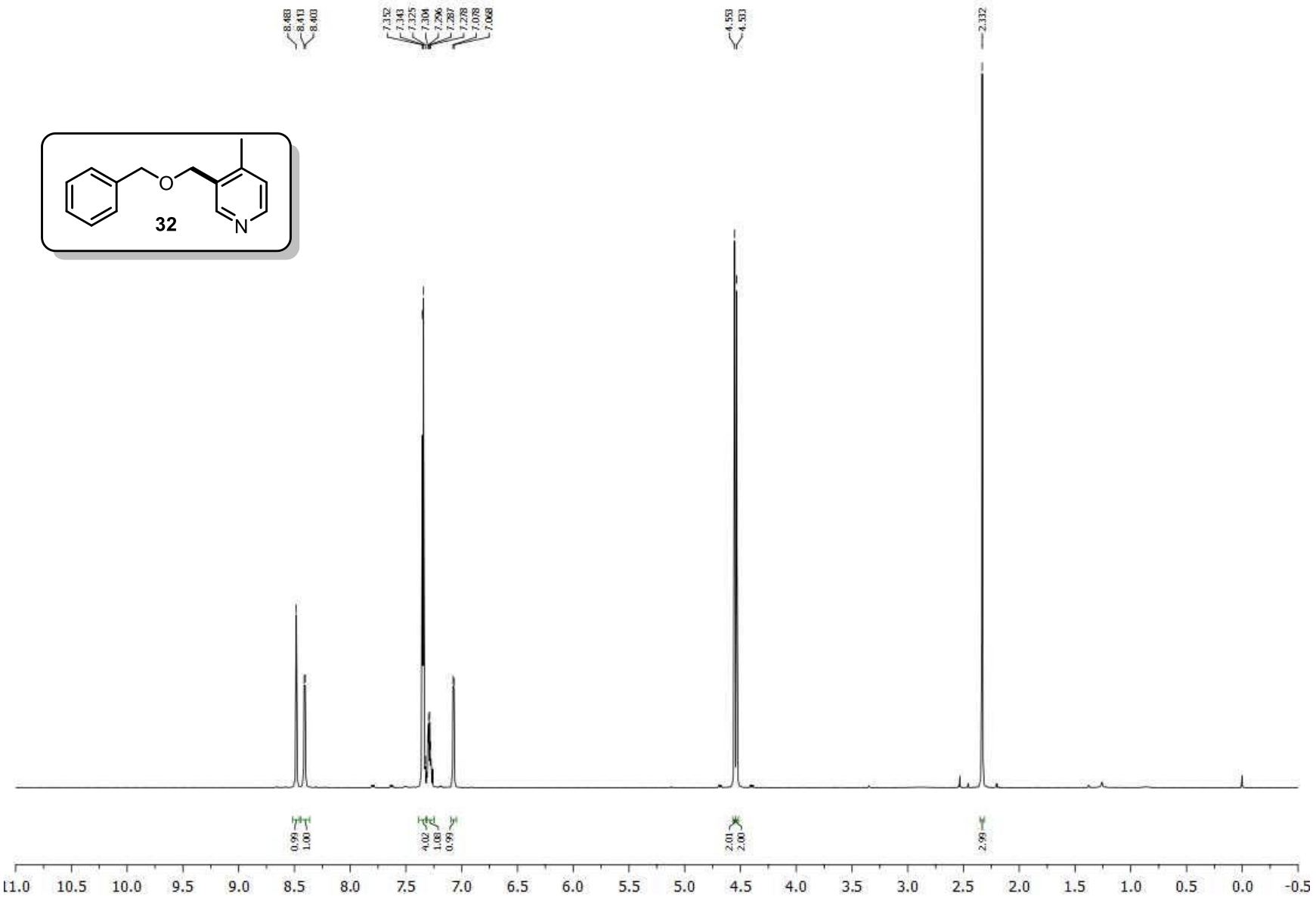
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 3-((benzyloxy)methyl)-5-methoxypyridine (**31**)



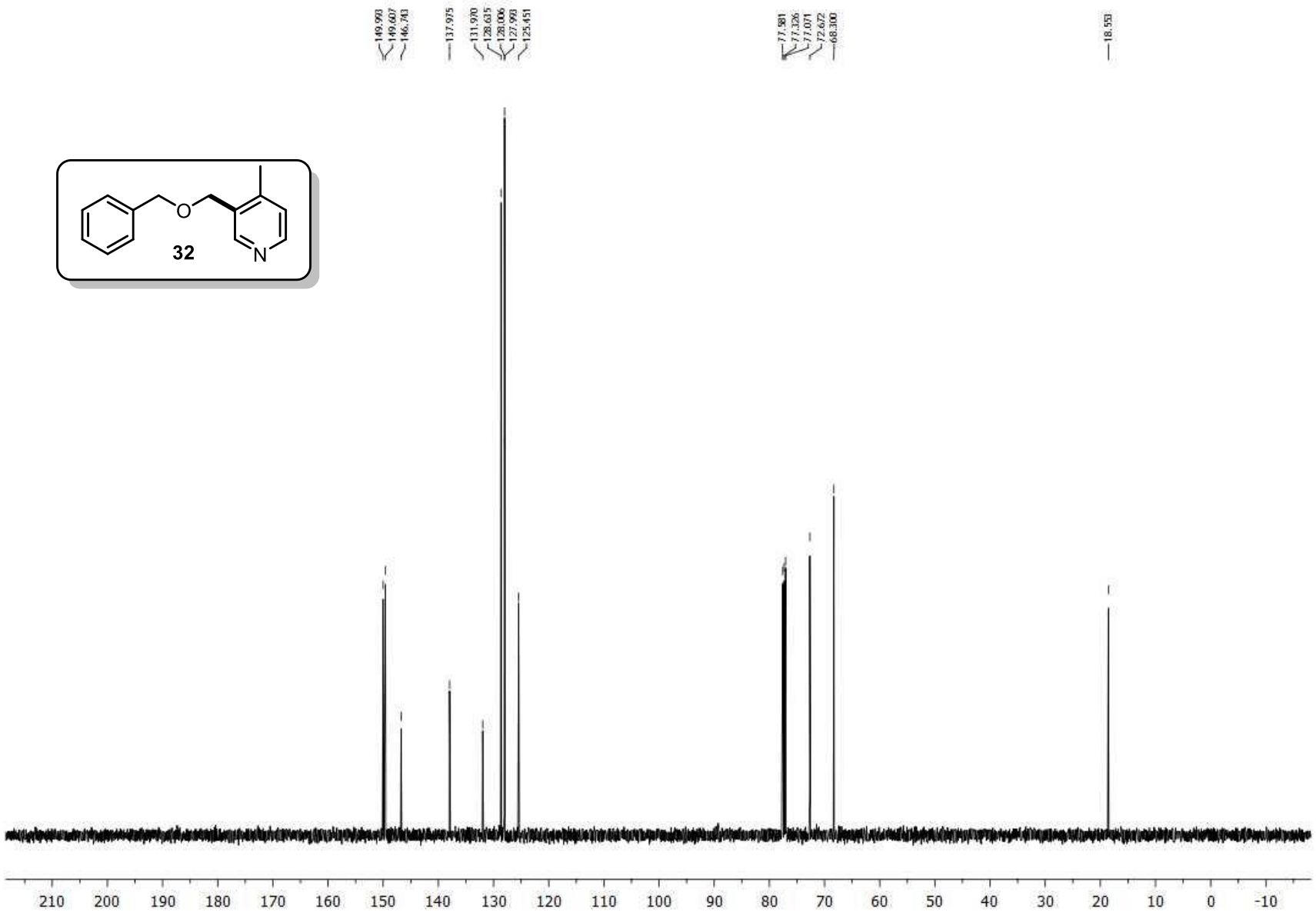
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 3-((benzyloxy)methyl)-5-methoxypyridine (**31**)



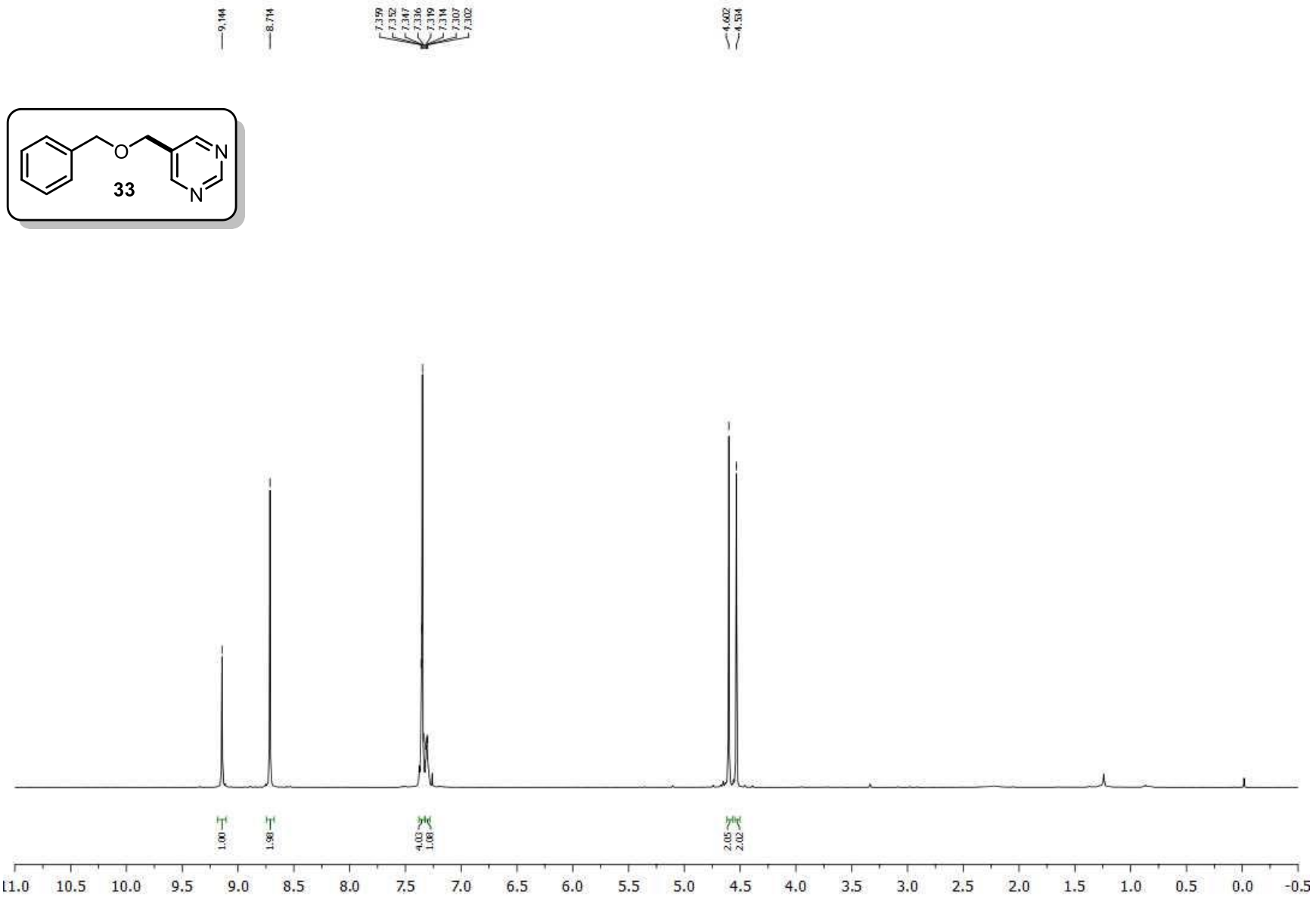
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 3-((benzyloxy)methyl)-4-methylpyridine (**32**)



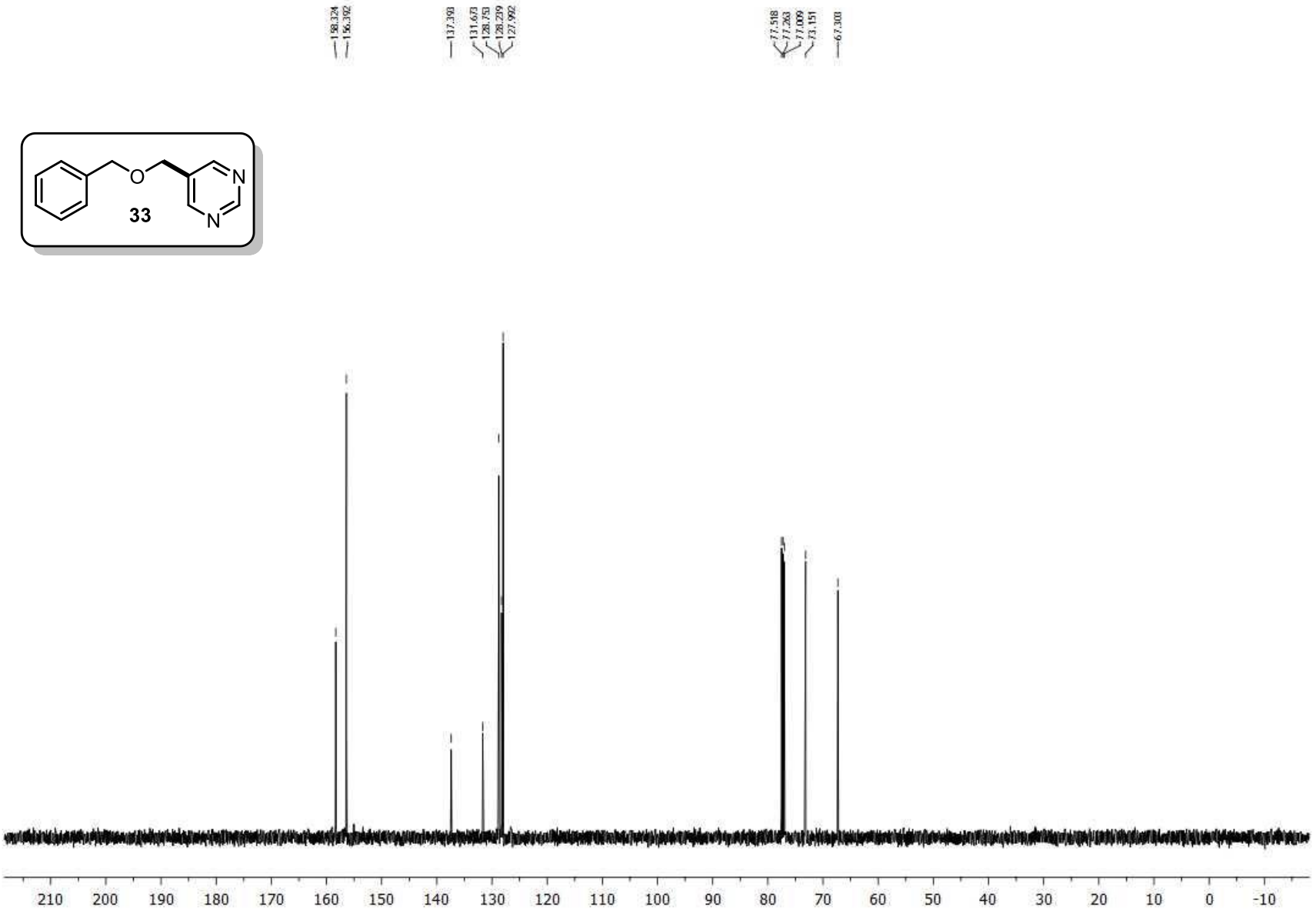
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 3-((benzyloxy)methyl)-4-methylpyridine (**32**)



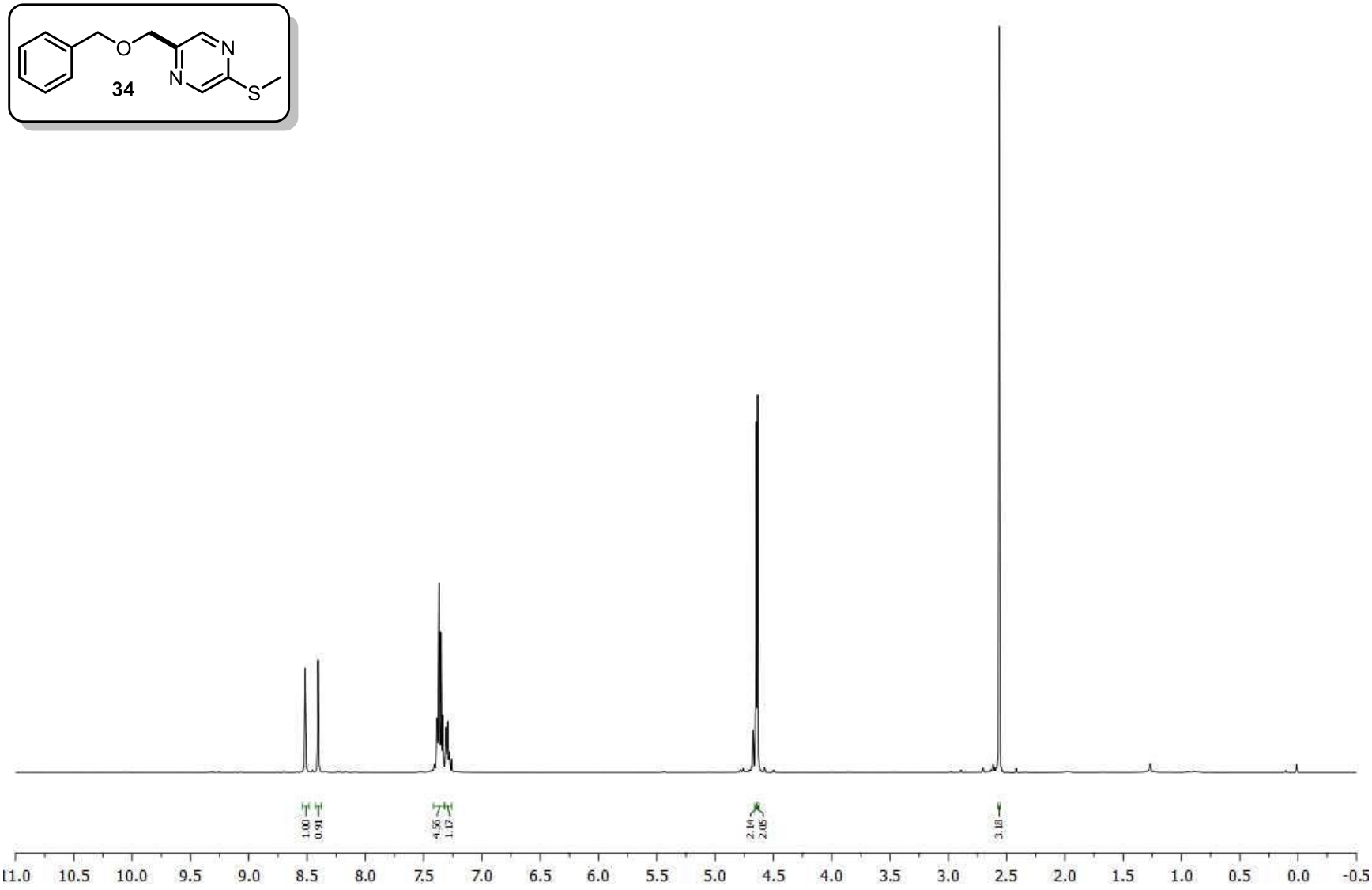
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 5-((benzyloxy)methyl)pyrimidine (**33**)



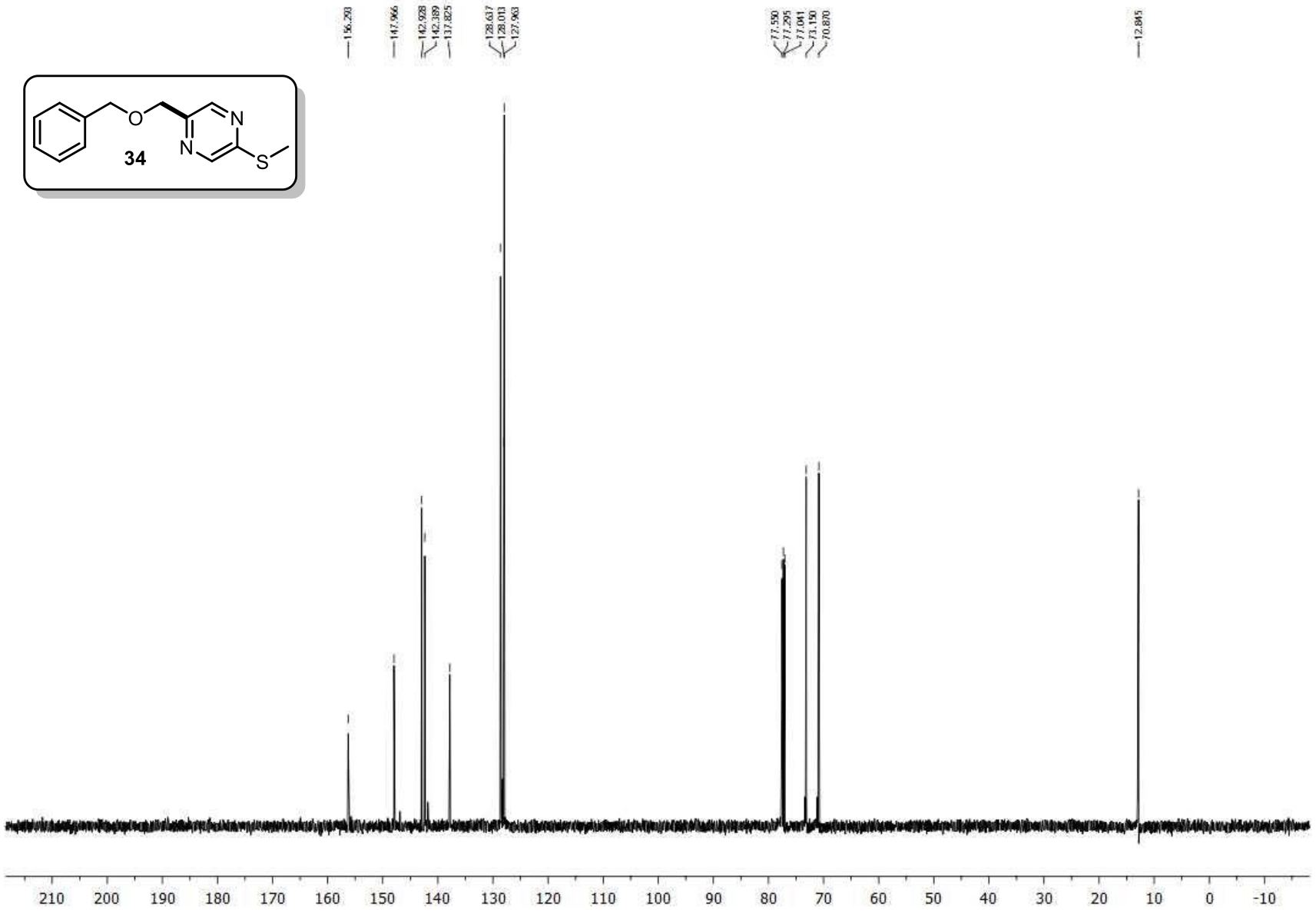
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 5-((benzyloxy)methyl)pyrimidine (**33**)



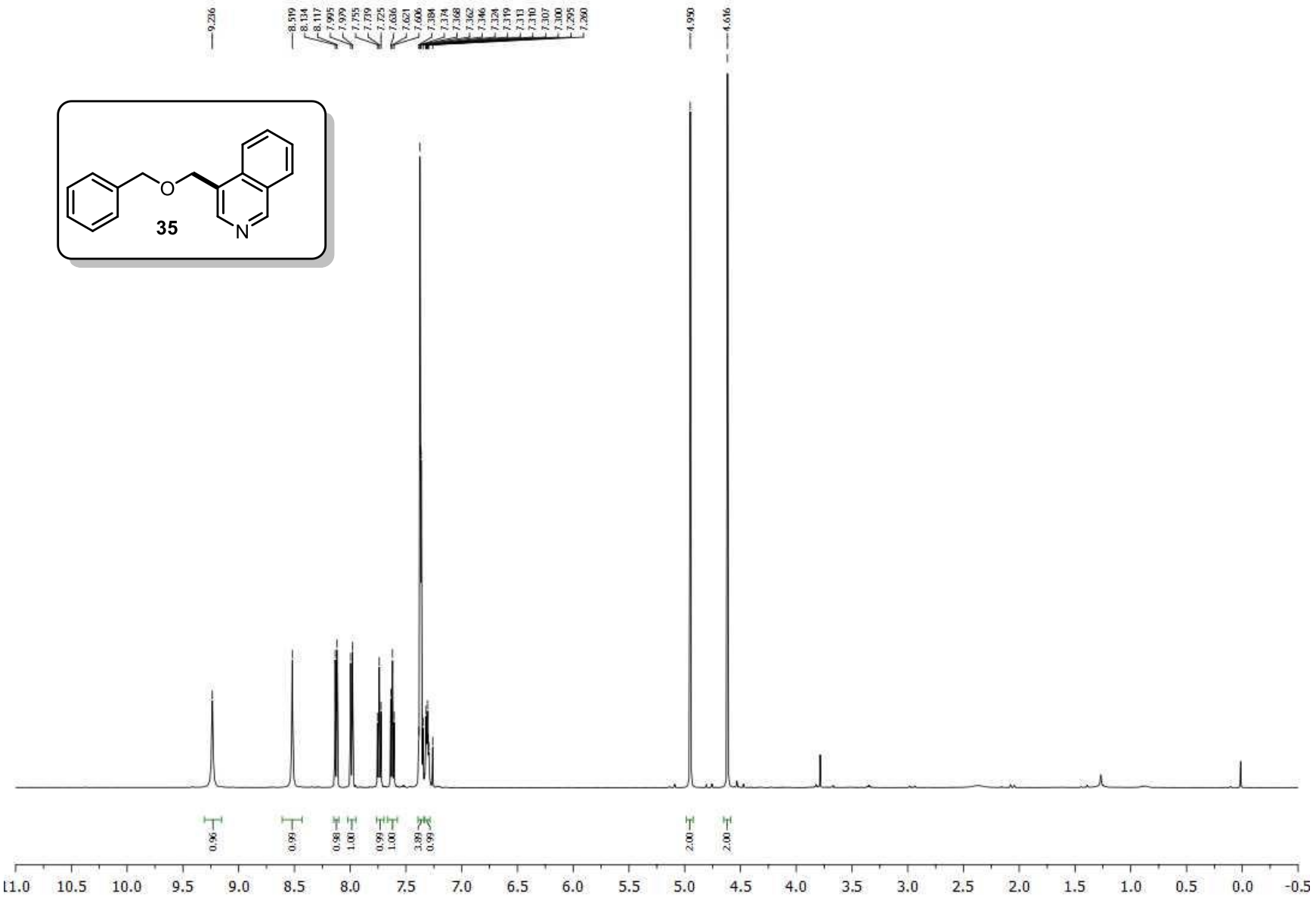
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 2-((benzyloxy)methyl)-5-(methylthio)pyrazine (**34**)



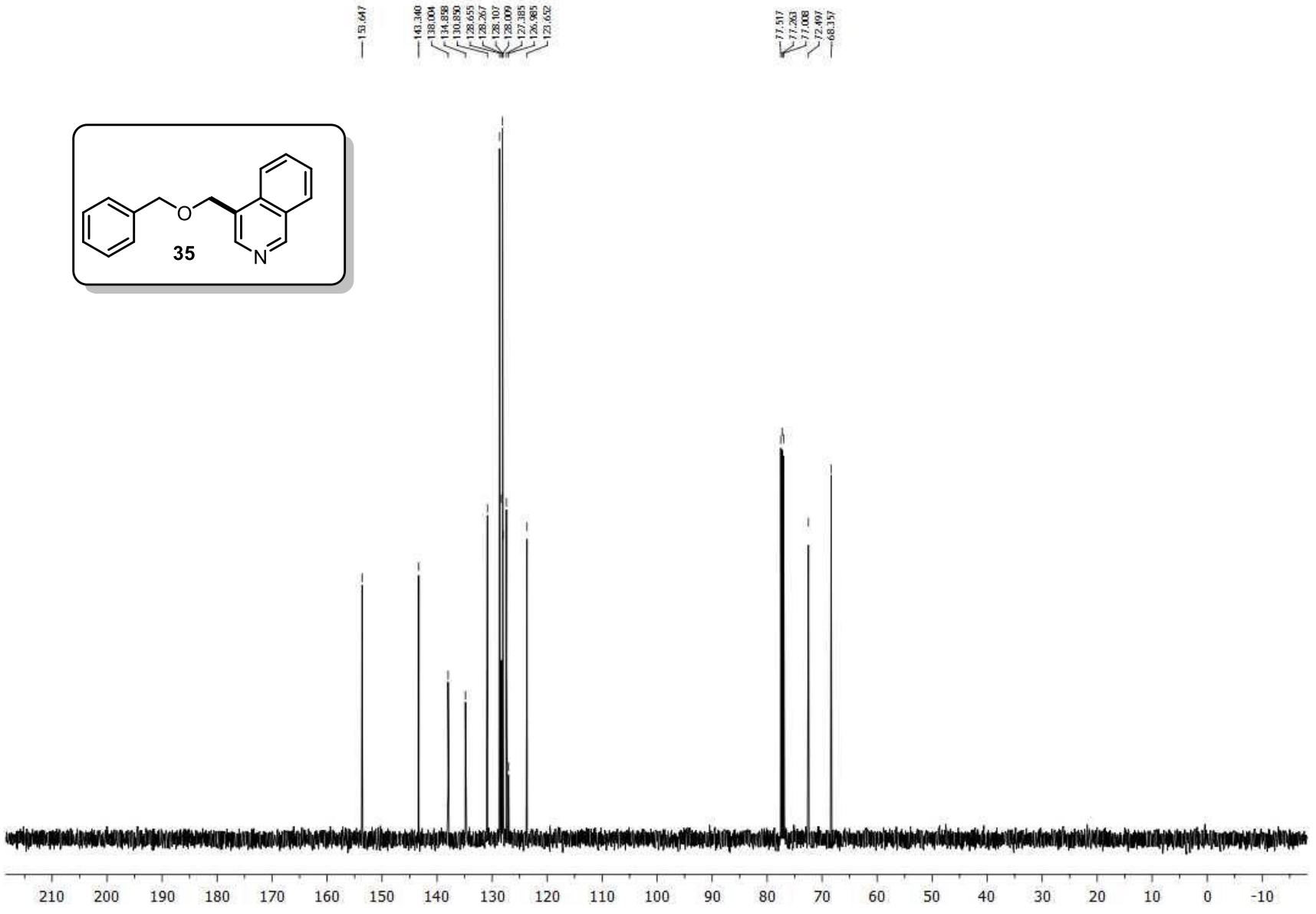
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 2-((benzyloxy)methyl)-5-(methylthio)pyrazine (**34**)



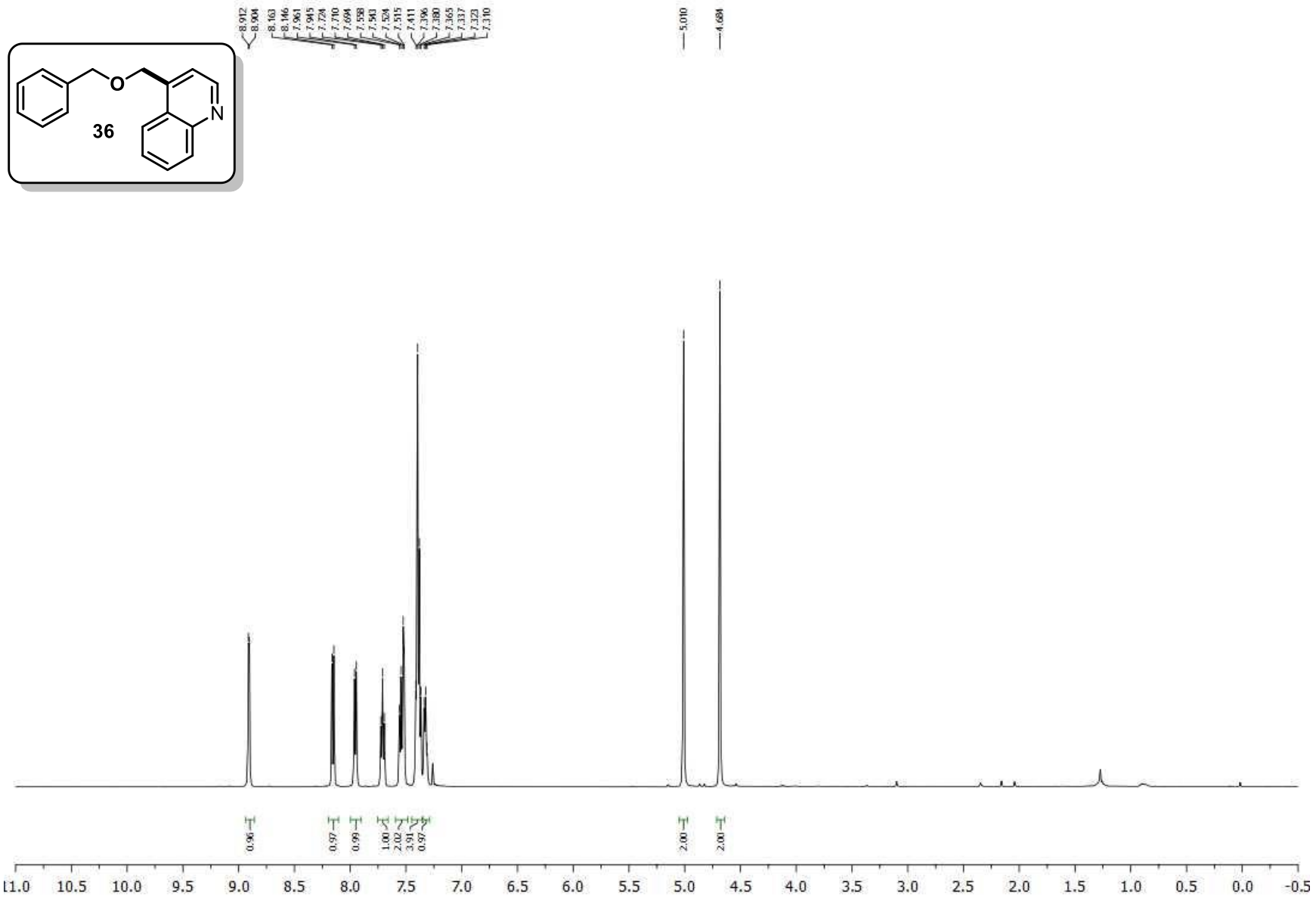
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 4-((benzyloxy)methyl)isoquinoline (**35**)



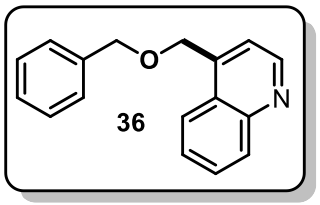
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 4-((benzyloxy)methyl)isoquinoline (**35**)



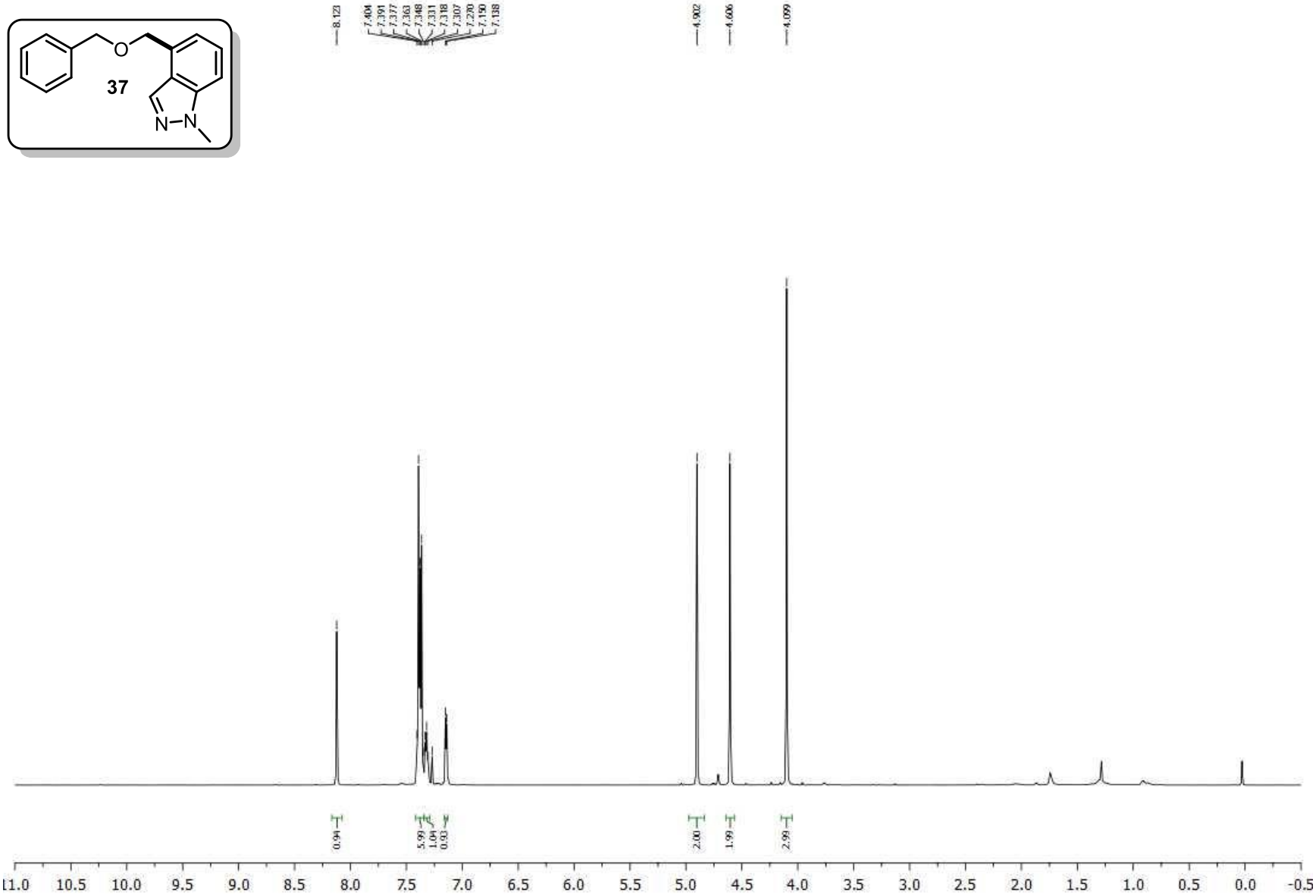
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 4-((benzyloxy)methyl)quinoline (**36**)



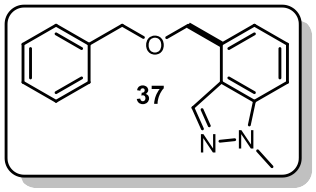
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 4-((benzyloxy)methyl)quinoline (**36**)



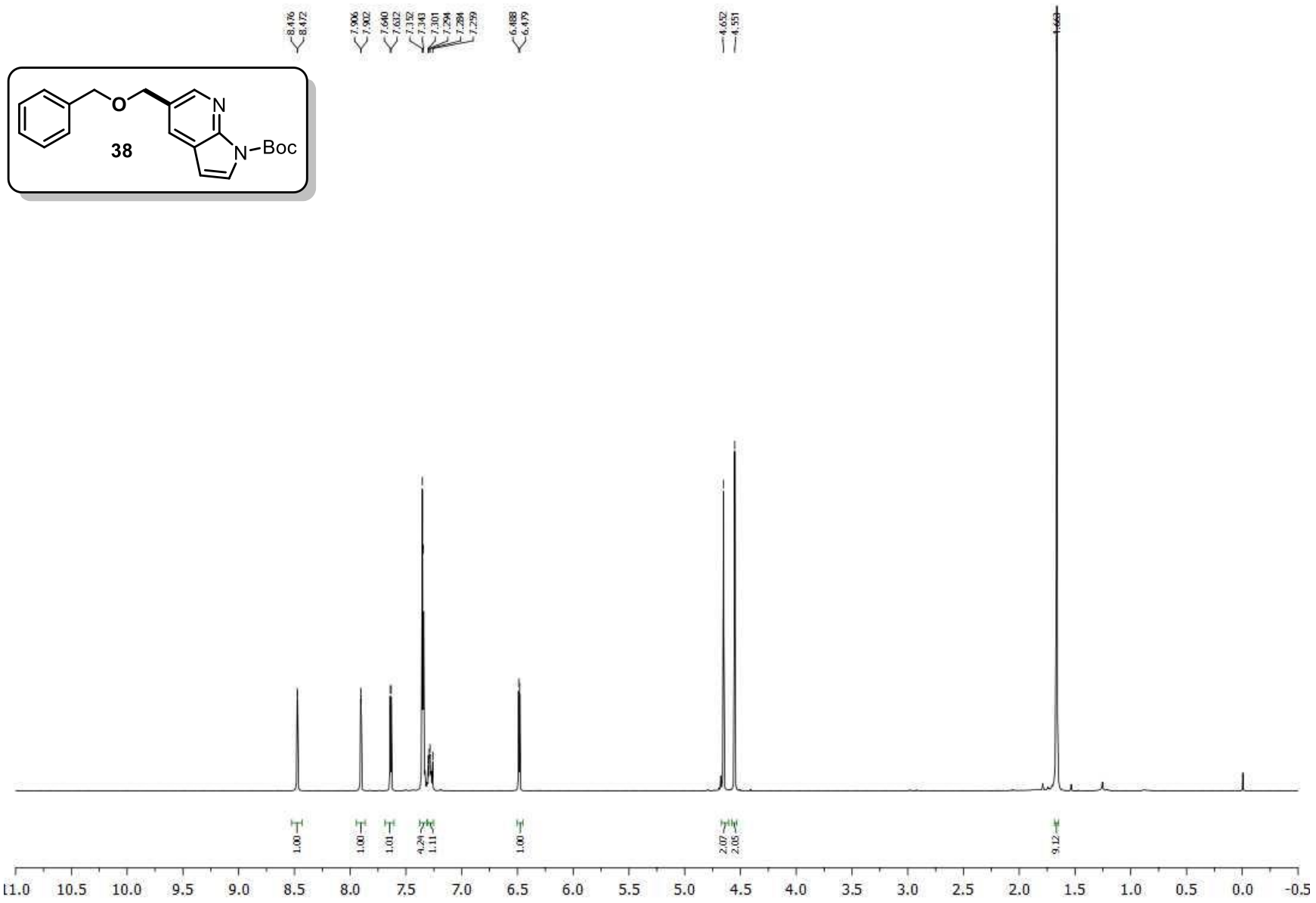
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 4-((benzyloxy)methyl)-1-methyl-1H-indazole (**37**)



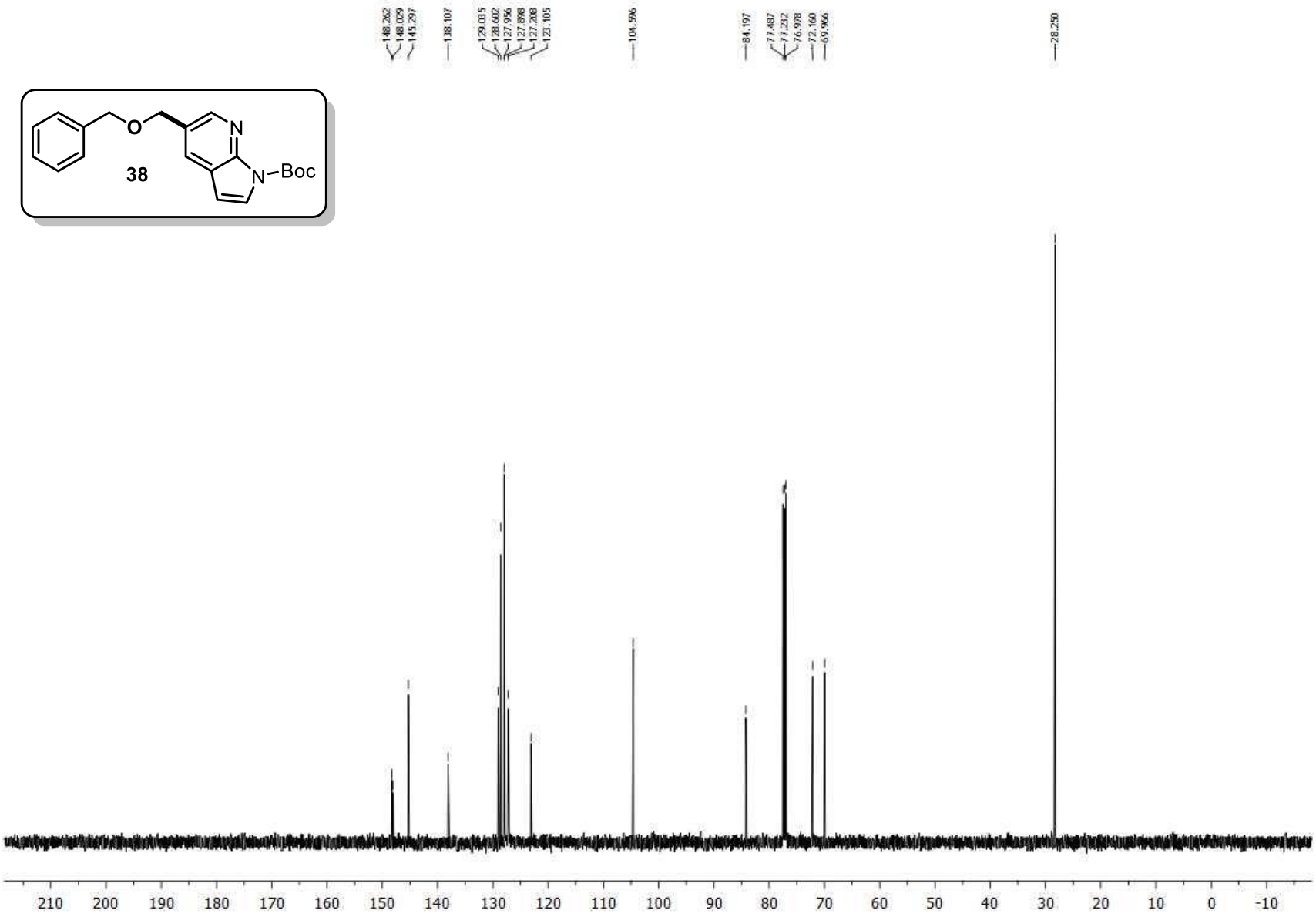
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 4-((benzyloxy)methyl)-1-methyl-1H-indazole (**37**)



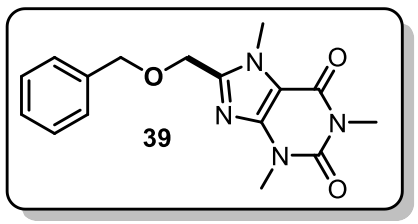
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of (*tert*-butyl 5-(benzyloxy)methyl)-1H-pyrrolo[2,3-b]pyridine-1-carboxylate (**38**)



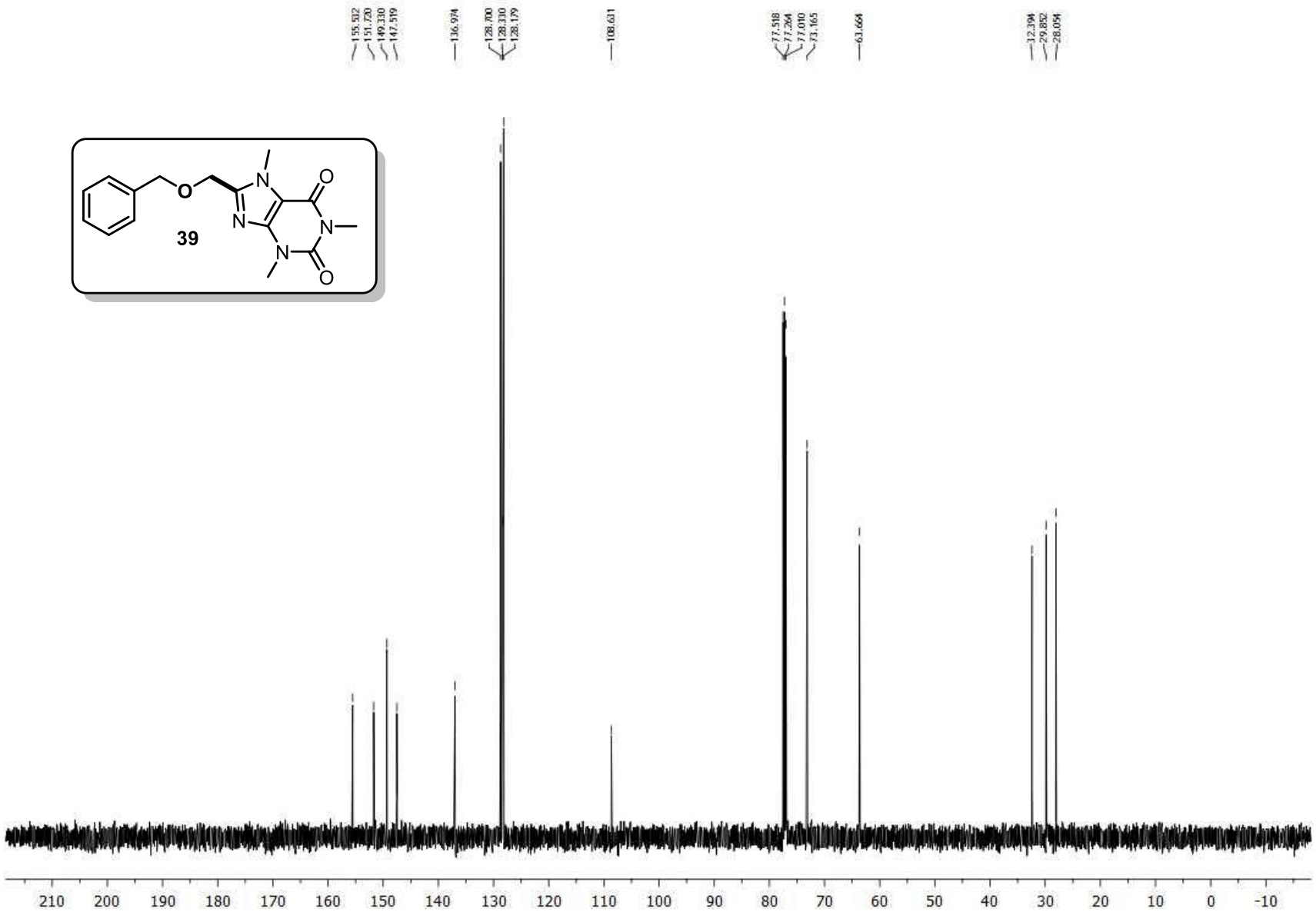
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of (*tert*-butyl 5-(benzyloxy)methyl)-1H-pyrrolo[2,3-b]pyridine-1-carboxylate (**38**)



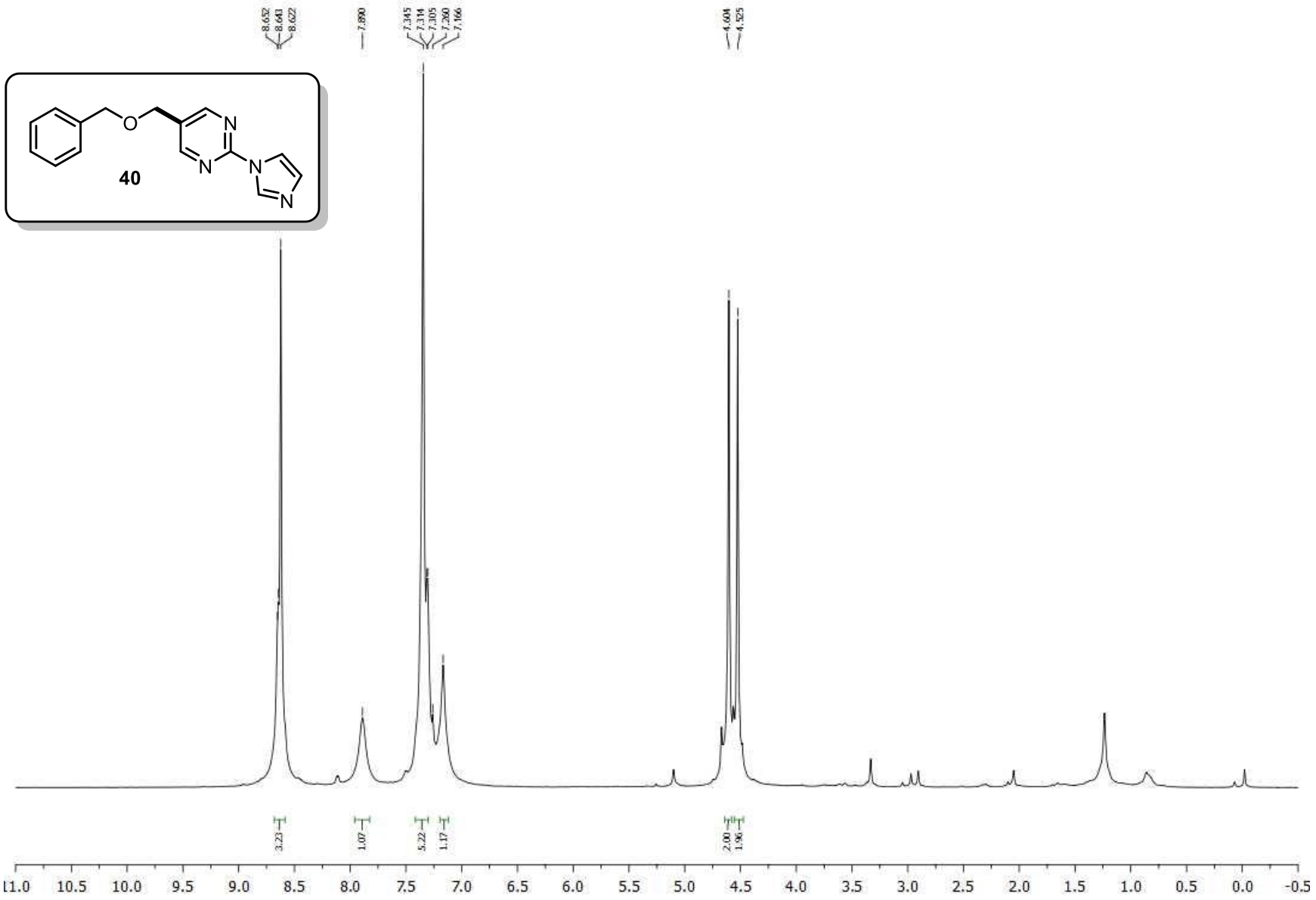
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 8-((benzyloxy)methyl)-1,3,7-trimethyl-3,7-dihydro-1H-purine-2,6-dione (**39**)



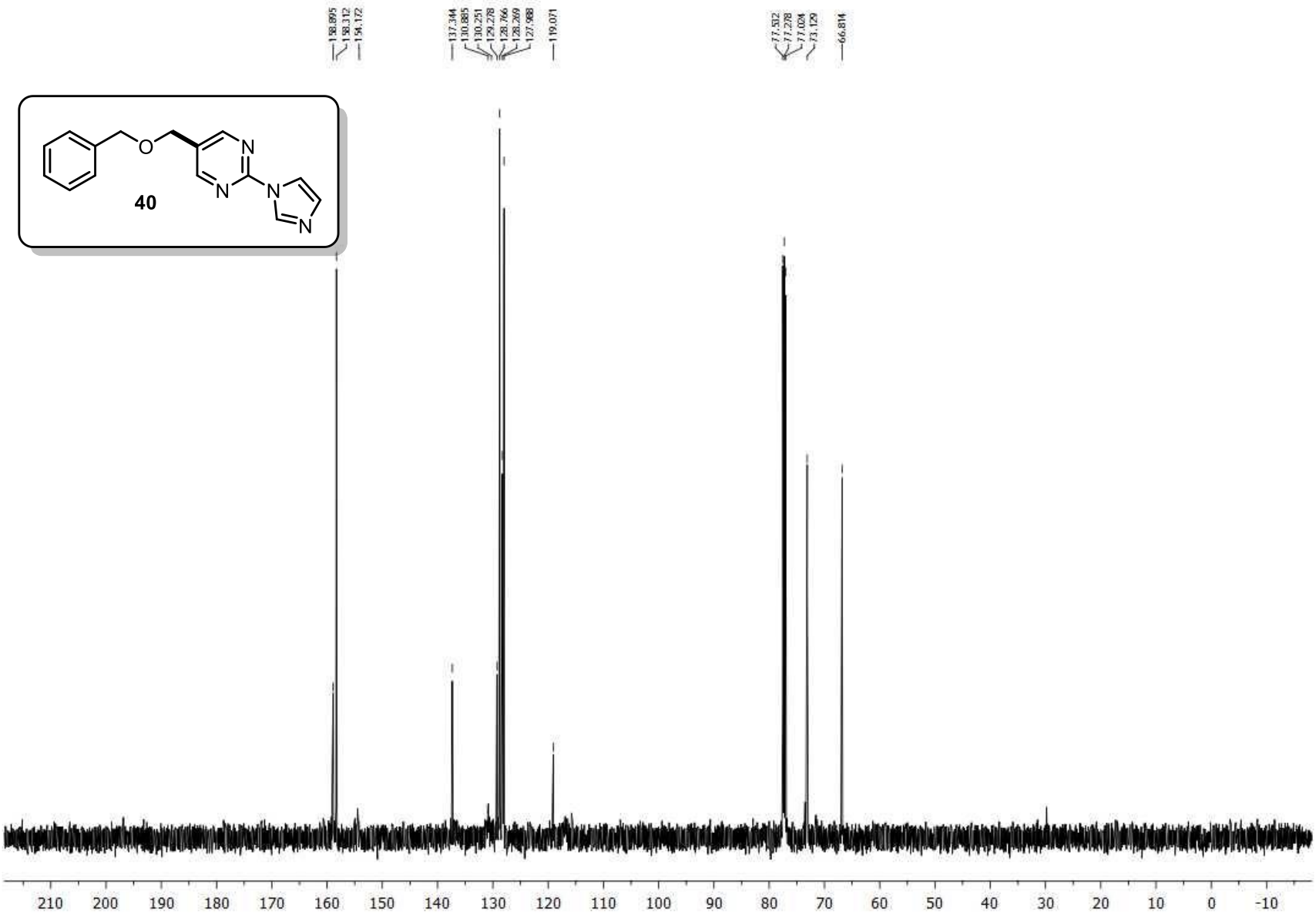
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 8-((benzyloxy)methyl)-1,3,7-trimethyl-3,7-dihydro-1H-purine-2,6-dione (**39**)



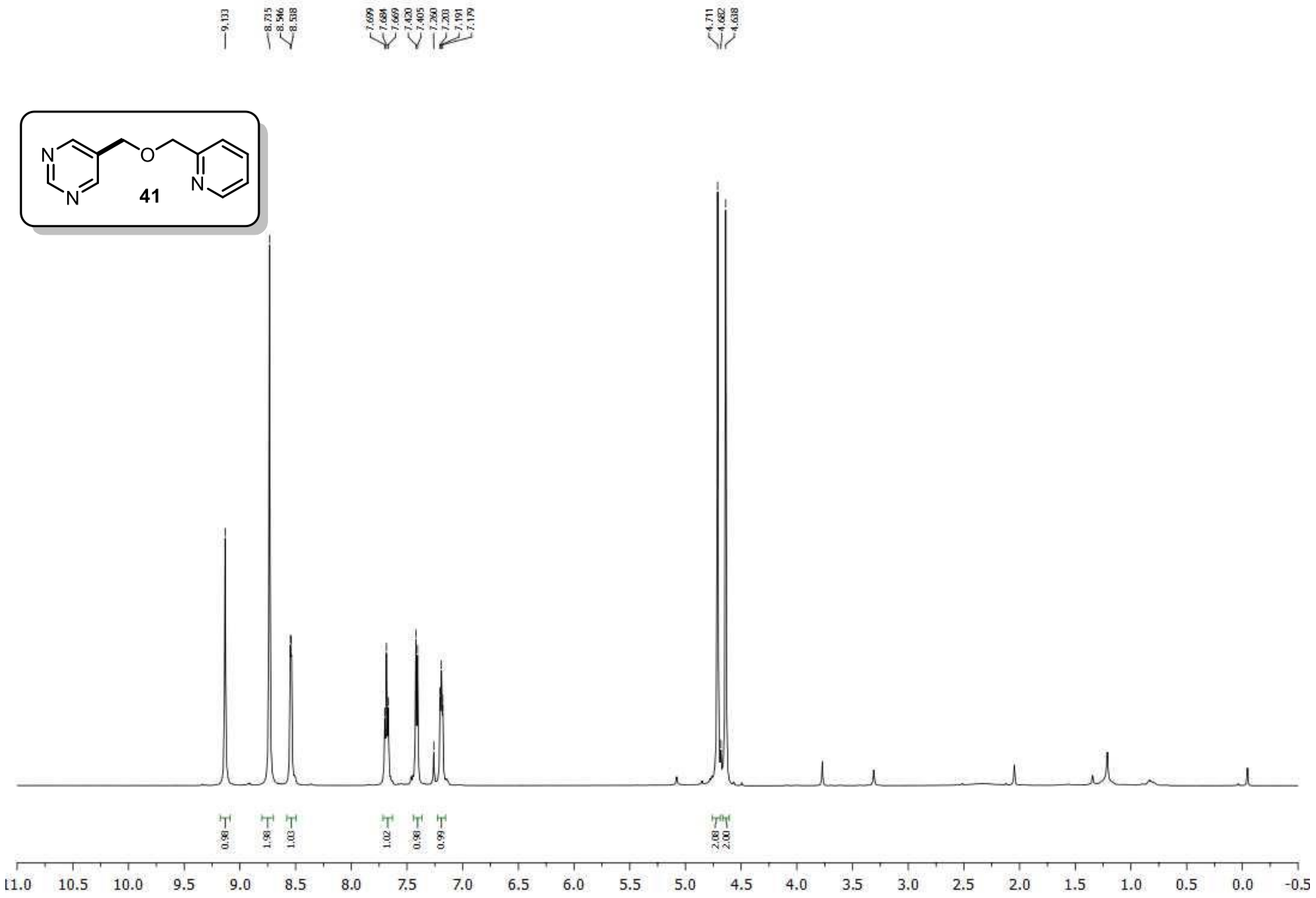
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 5-((benzyloxy)methyl)-2-(1H-imidazol-1-yl)pyrimidine (**40**)



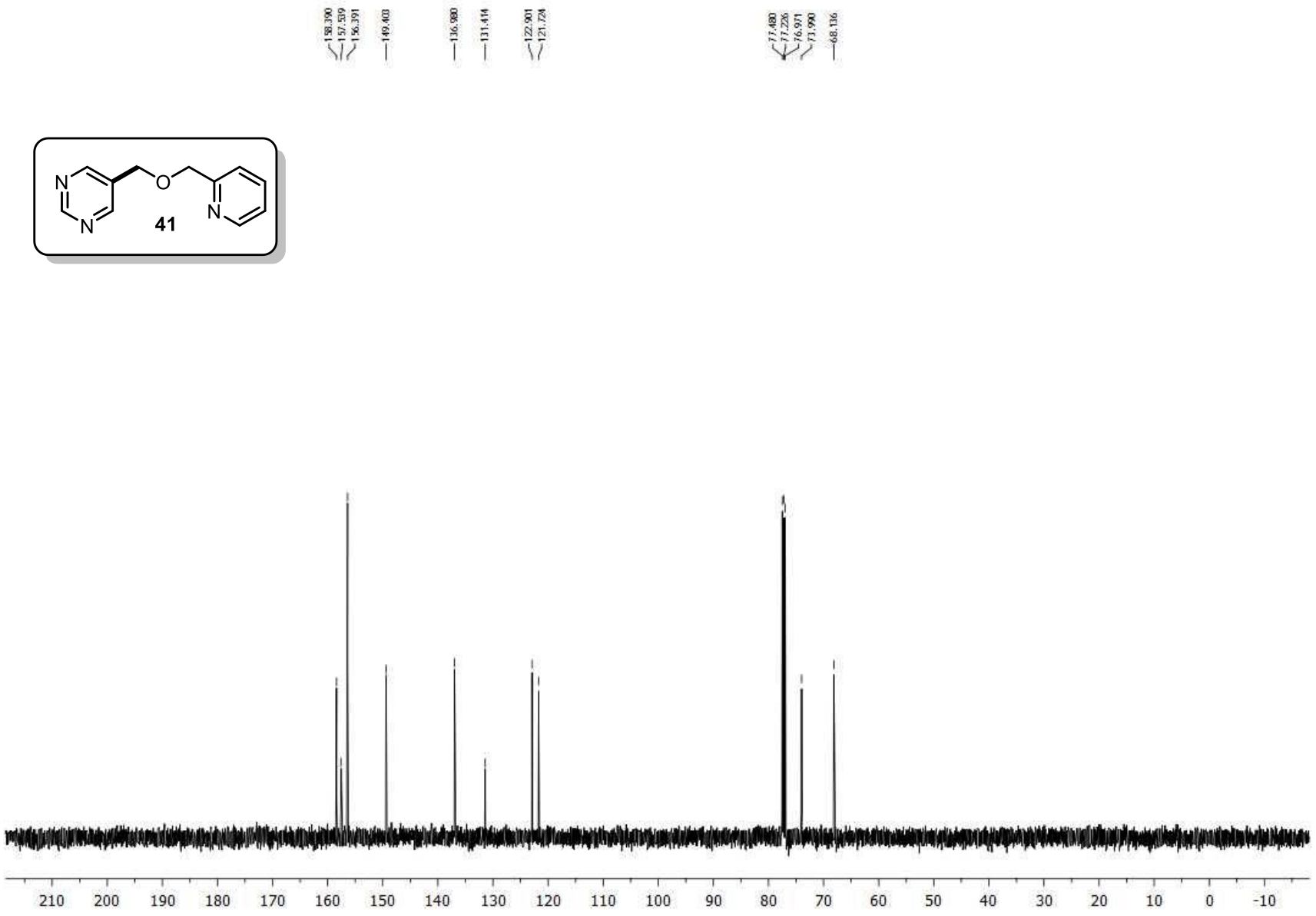
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 5-((benzyloxy)methyl)-2-(1H-imidazol-1-yl)pyrimidine (**40**)



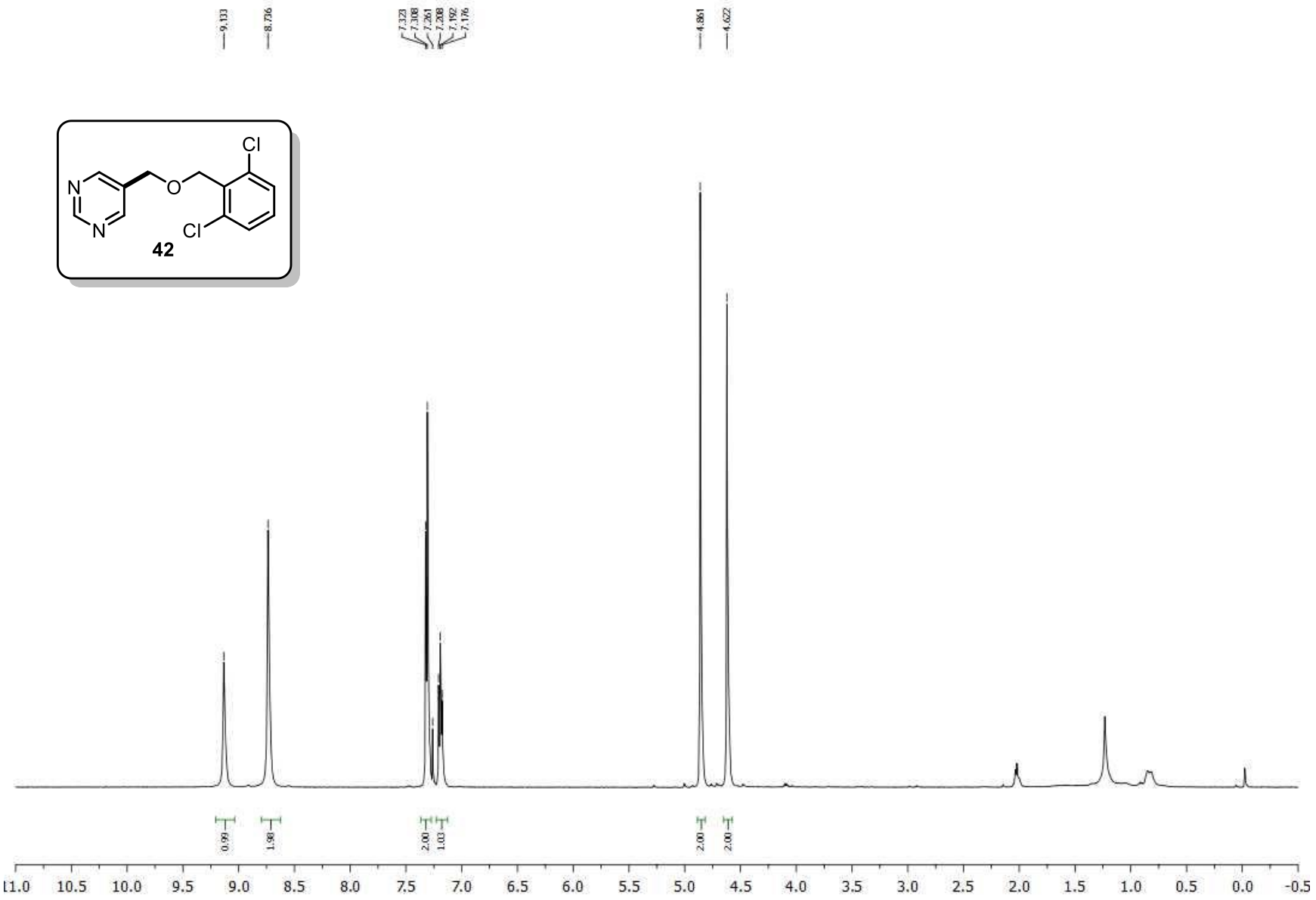
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 5-((pyridin-2-ylmethoxy)methyl)pyrimidine (**41**)



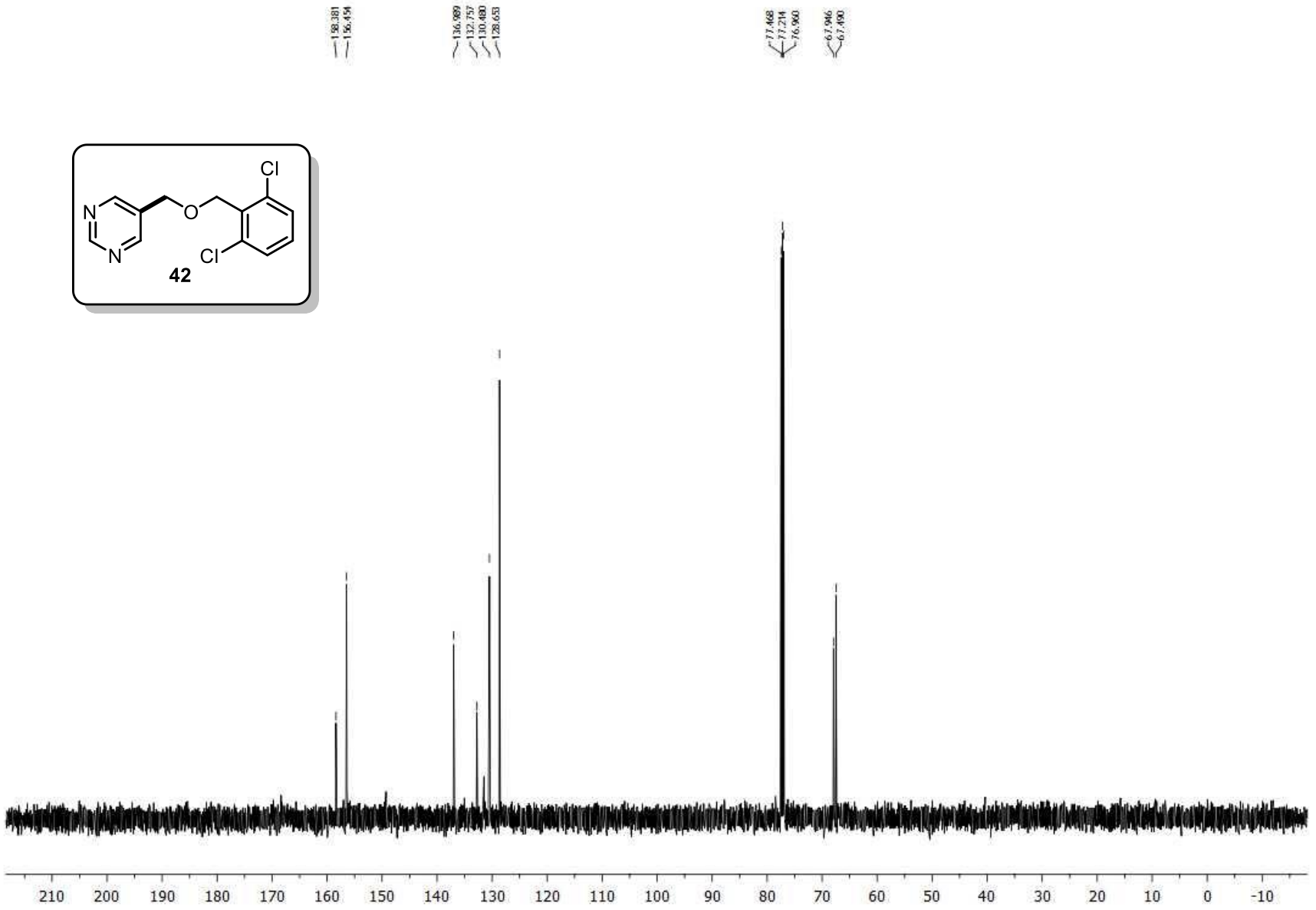
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 5-((pyridin-2-ylmethoxy)methyl)pyrimidine (**41**)



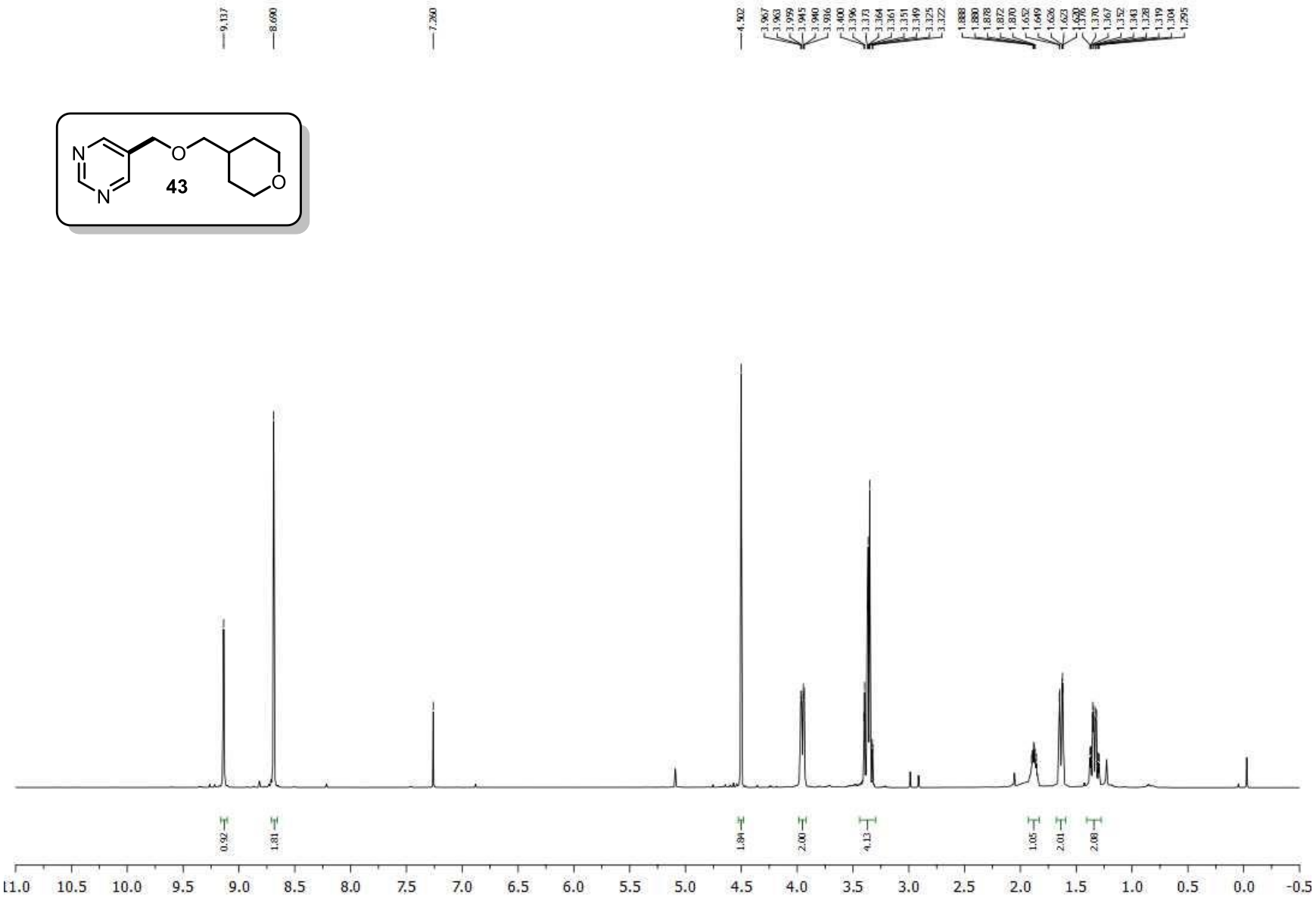
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 5-(((2,6-dichlorobenzyl)oxy)methyl)pyrimidine (**42**)



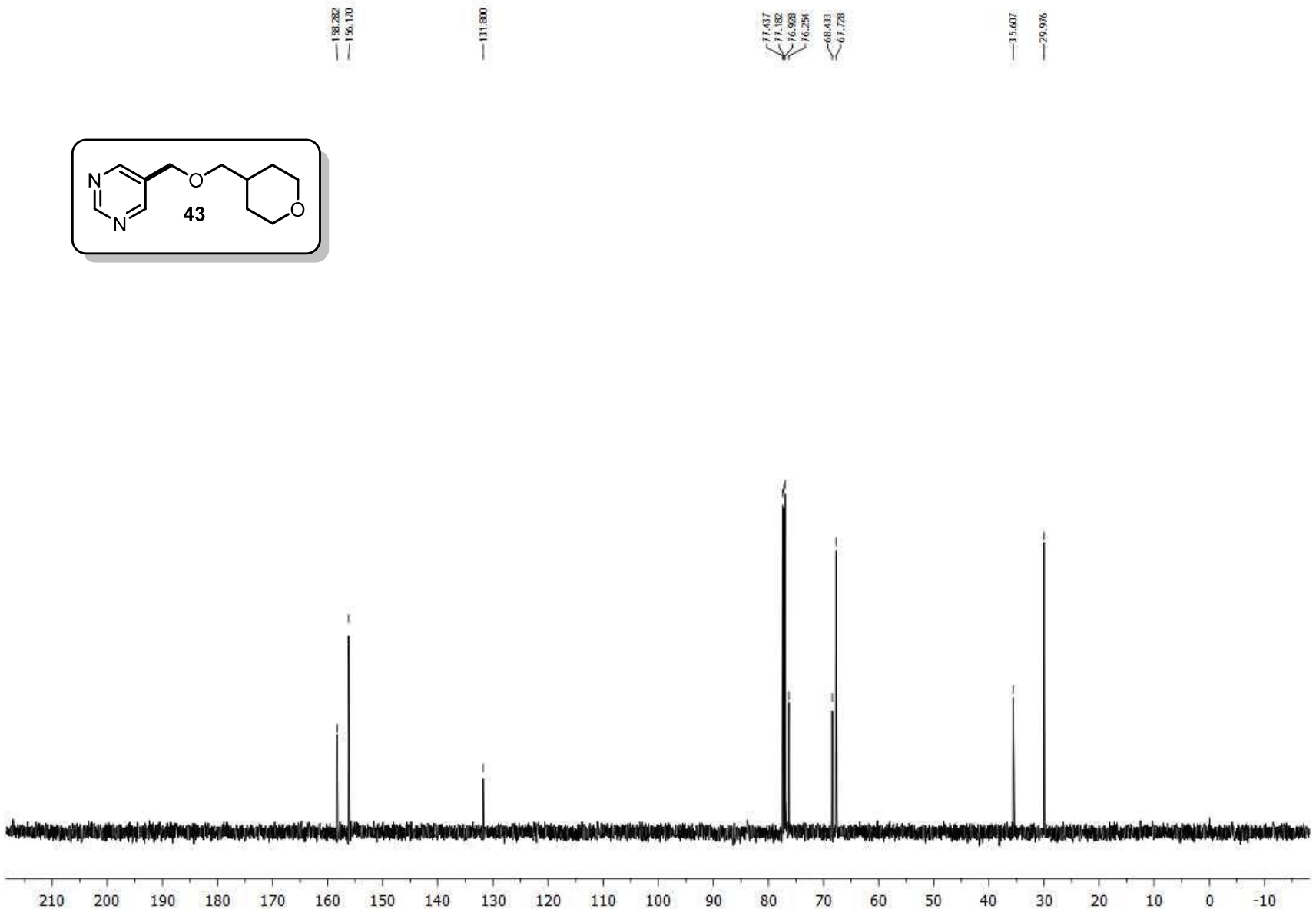
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 5-(((2,6-dichlorobenzyl)oxy)methyl)pyrimidine (**42**)



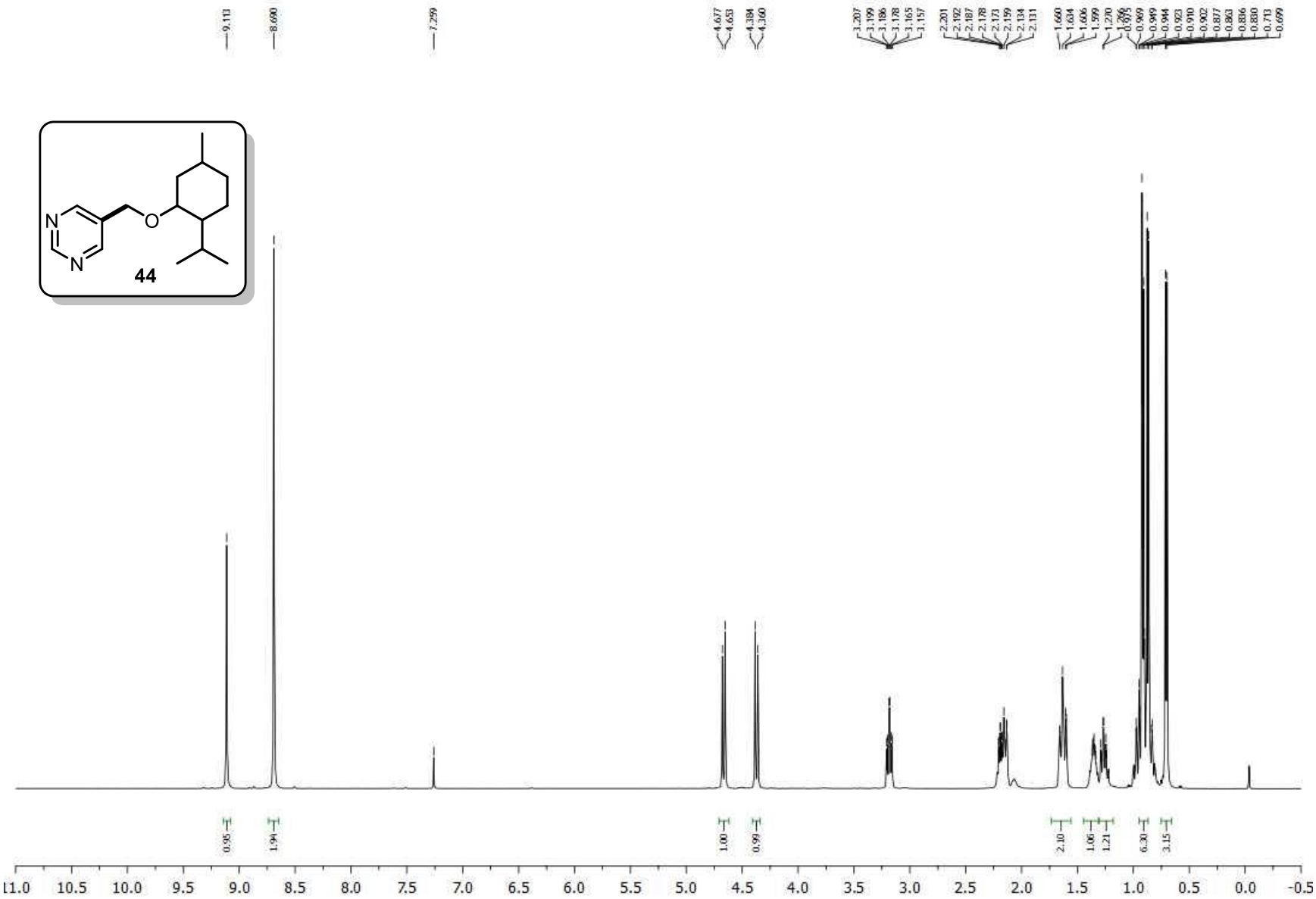
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 5-((tetrahydro-2H-pyran-4-yl)methoxy)methyl)pyrimidine (**43**)



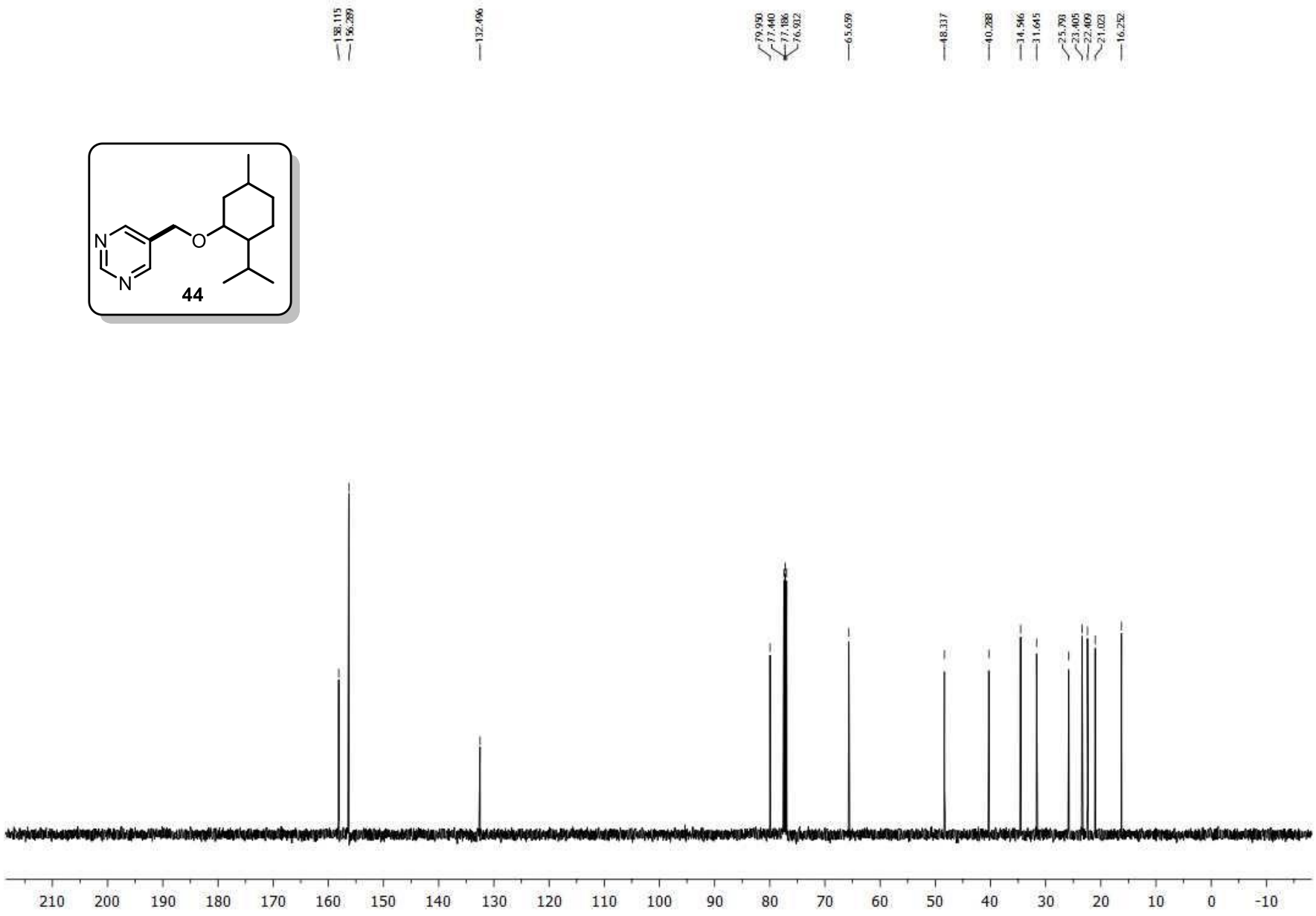
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 5-((tetrahydro-2H-pyran-4-yl)methoxy)methyl)pyrimidine (**43**)



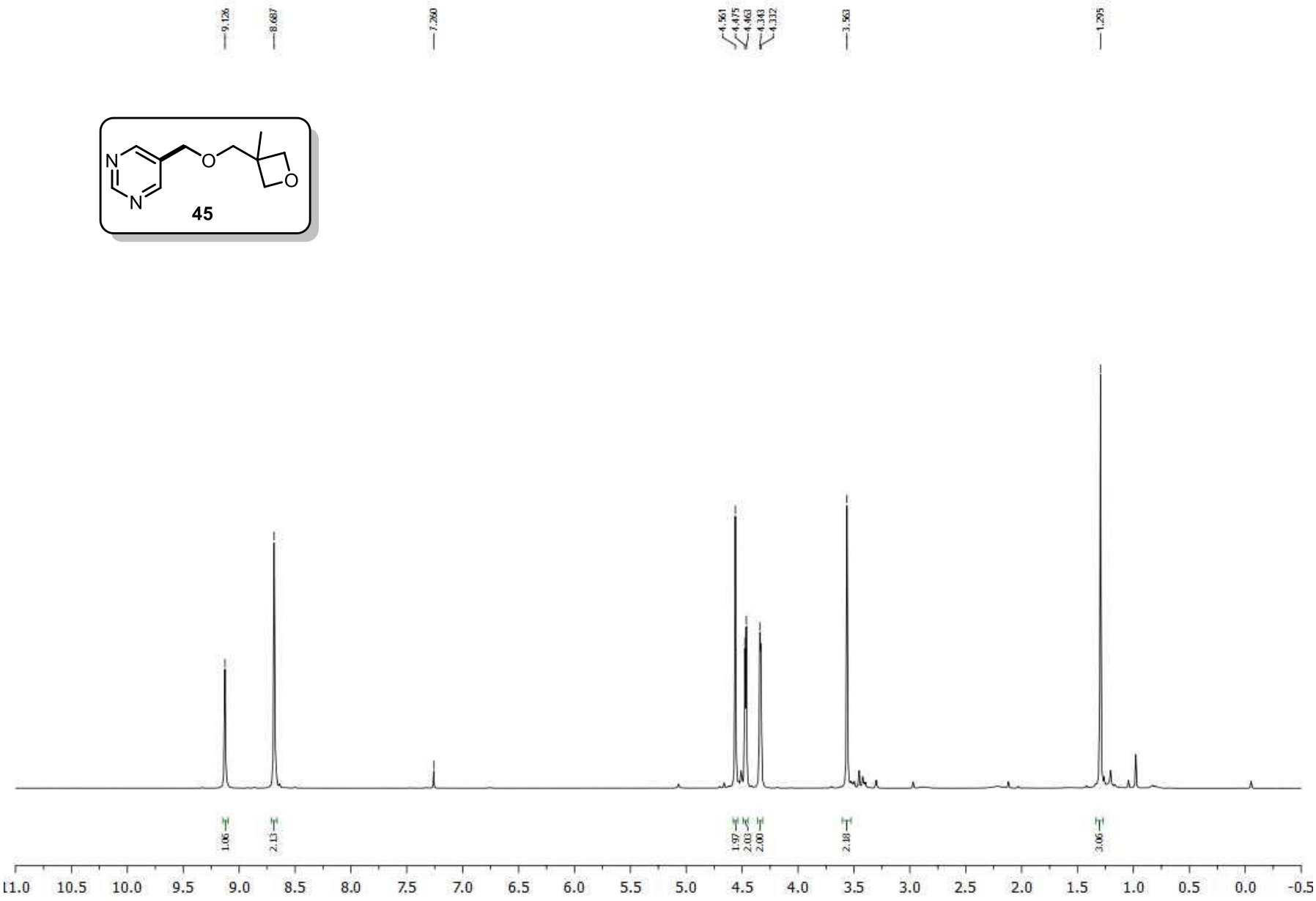
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 5-(((1*S*)-2-isopropylcyclohexyl)oxy)methyl)pyrimidine (**44**)



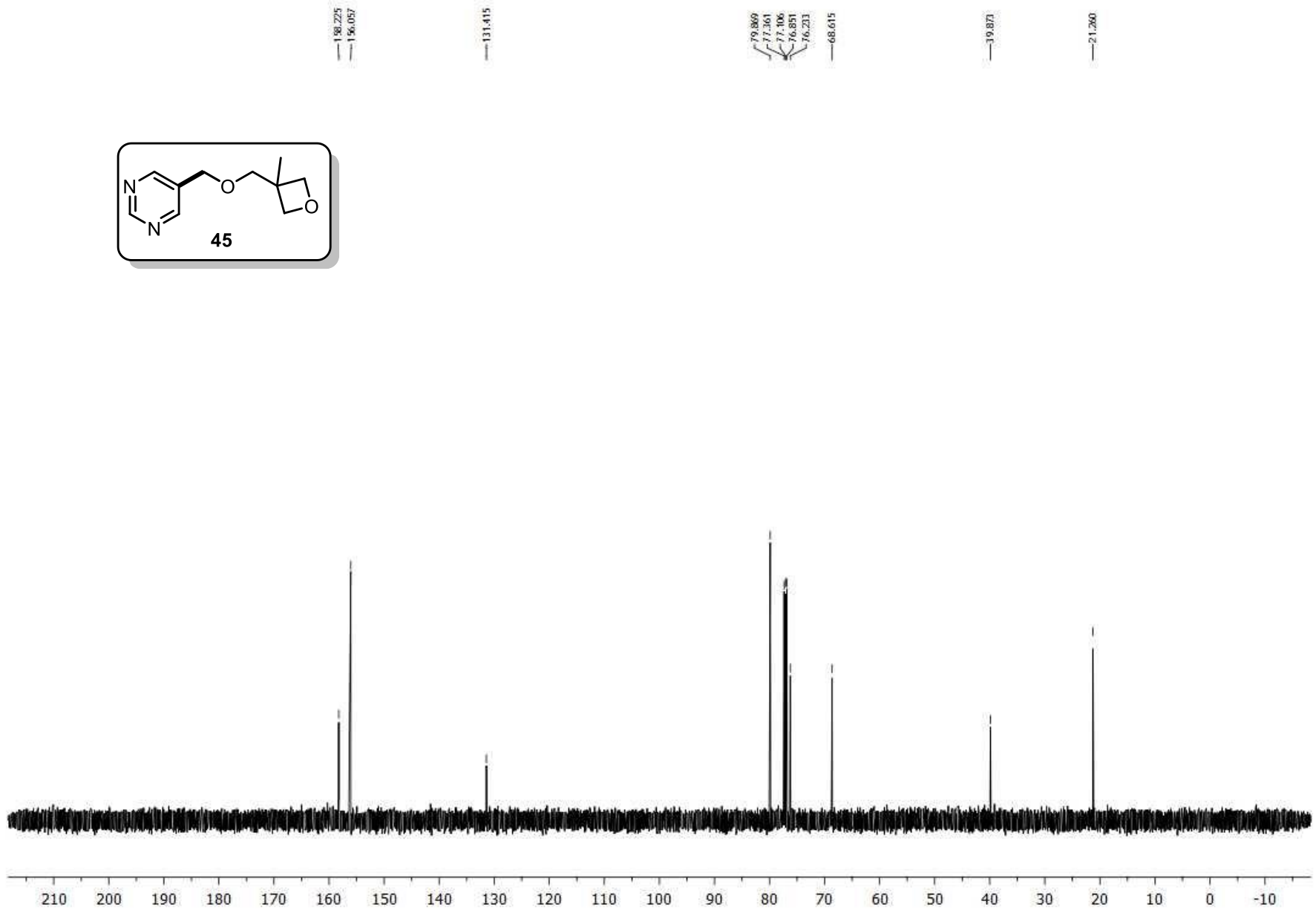
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 5-(((1*S*)-2-isopropylcyclohexyl)oxy)methyl)pyrimidine (**44**)



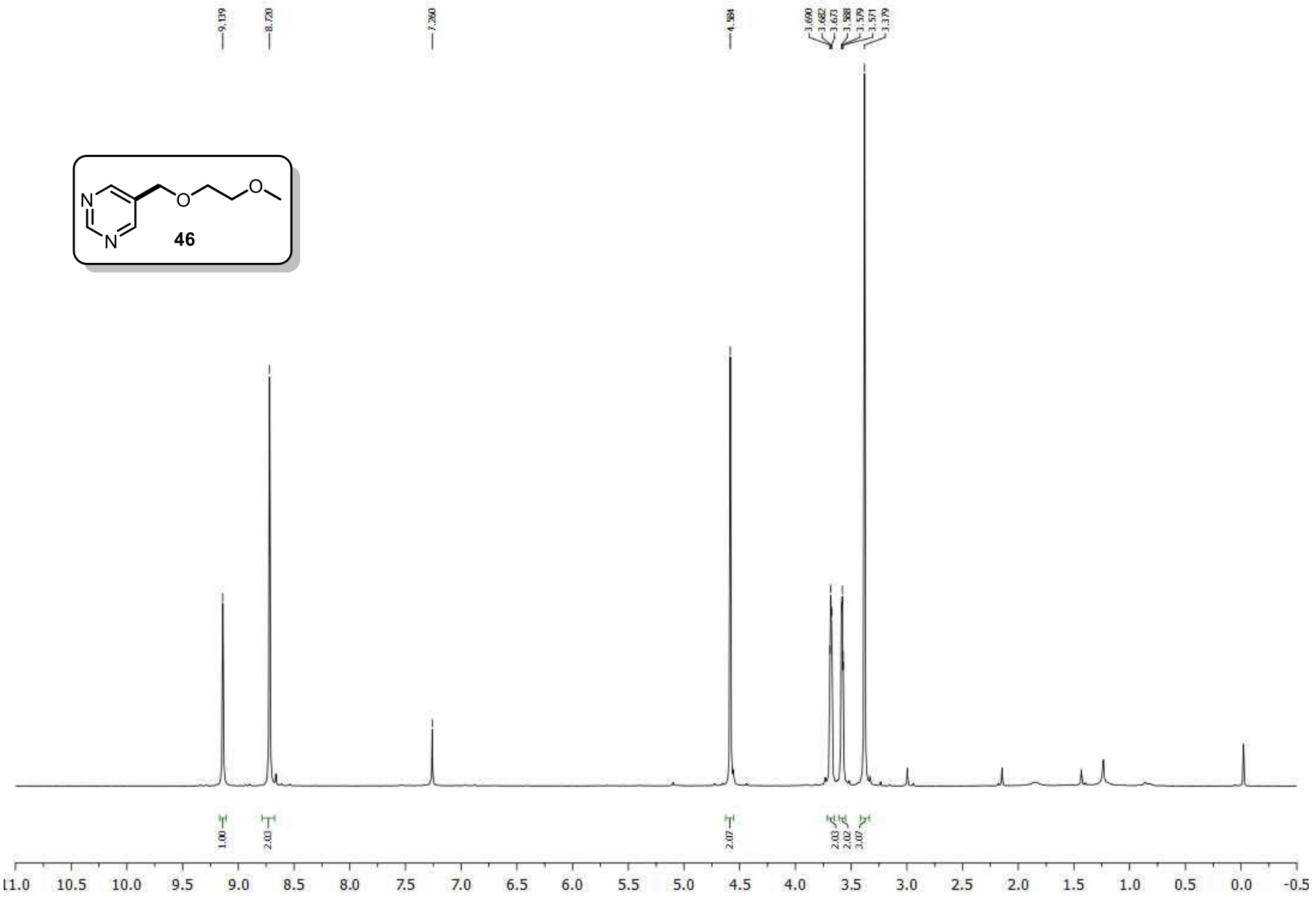
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 5-(((2-methyloxetan-2-yl)methoxy)methyl)pyrimidine (**45**)



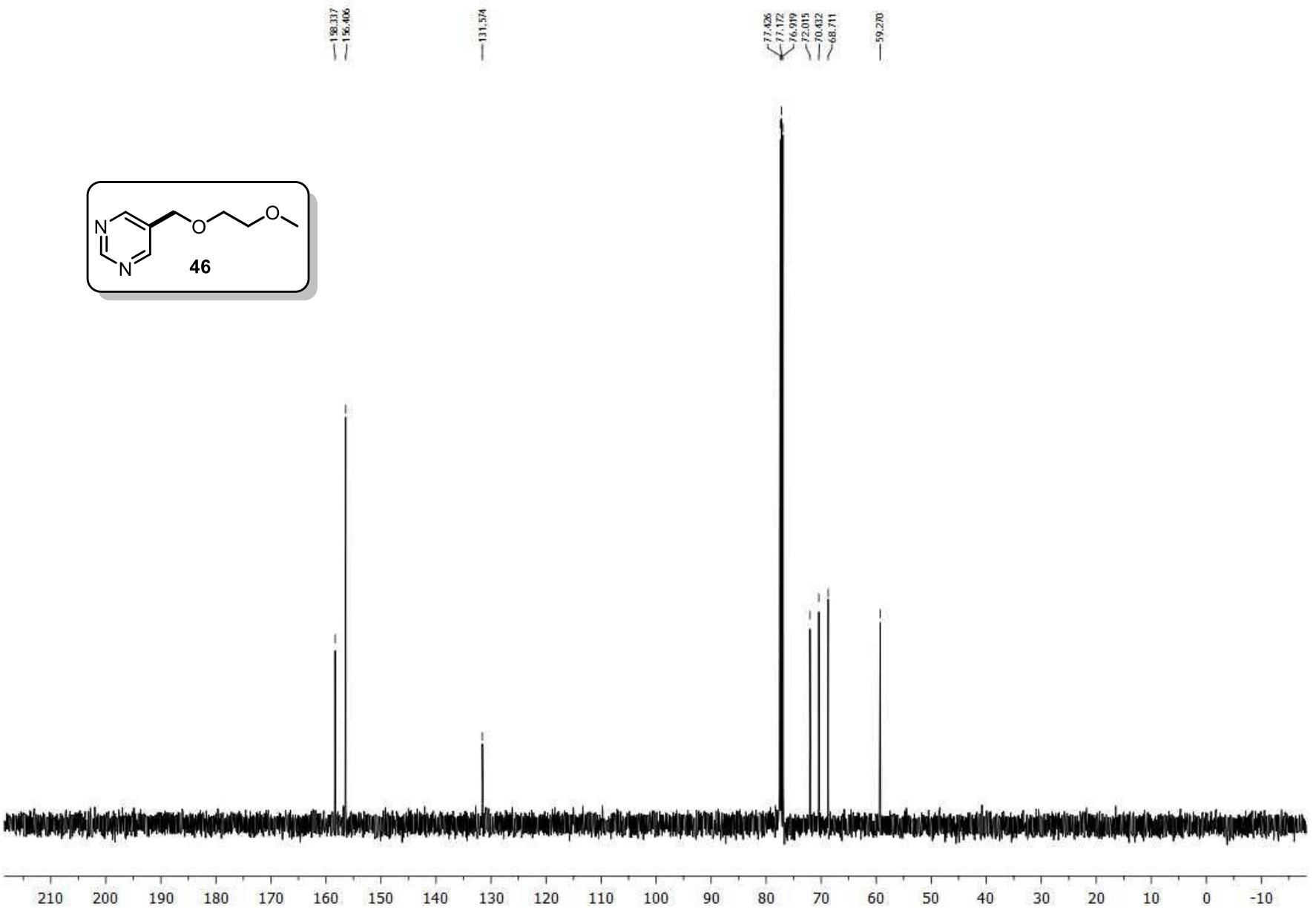
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 5-(((2-methyloxetan-2-yl)methoxy)methyl)pyrimidine (**45**)



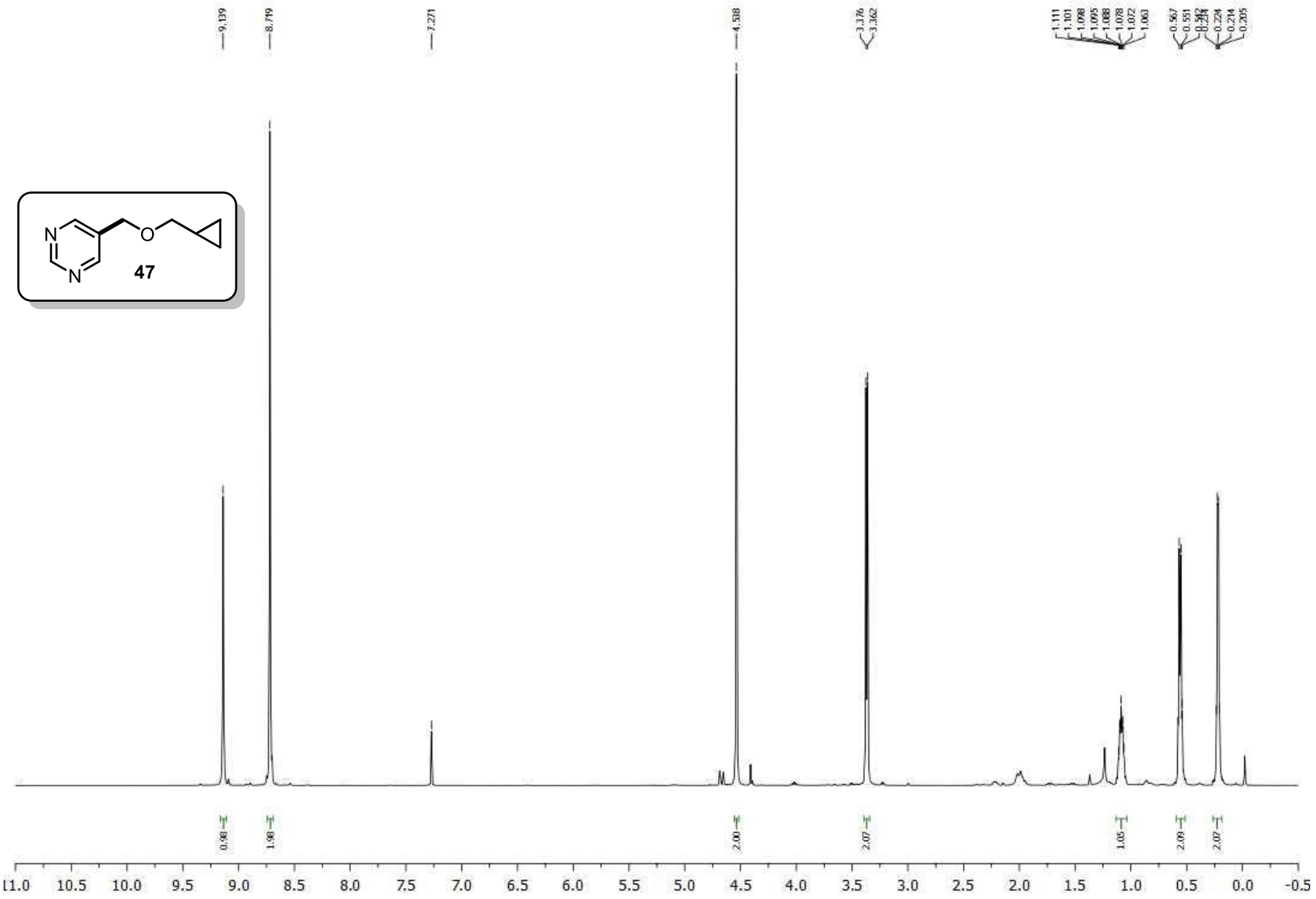
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 5-((2-methoxyethoxy)methyl)pyrimidine (**46**)



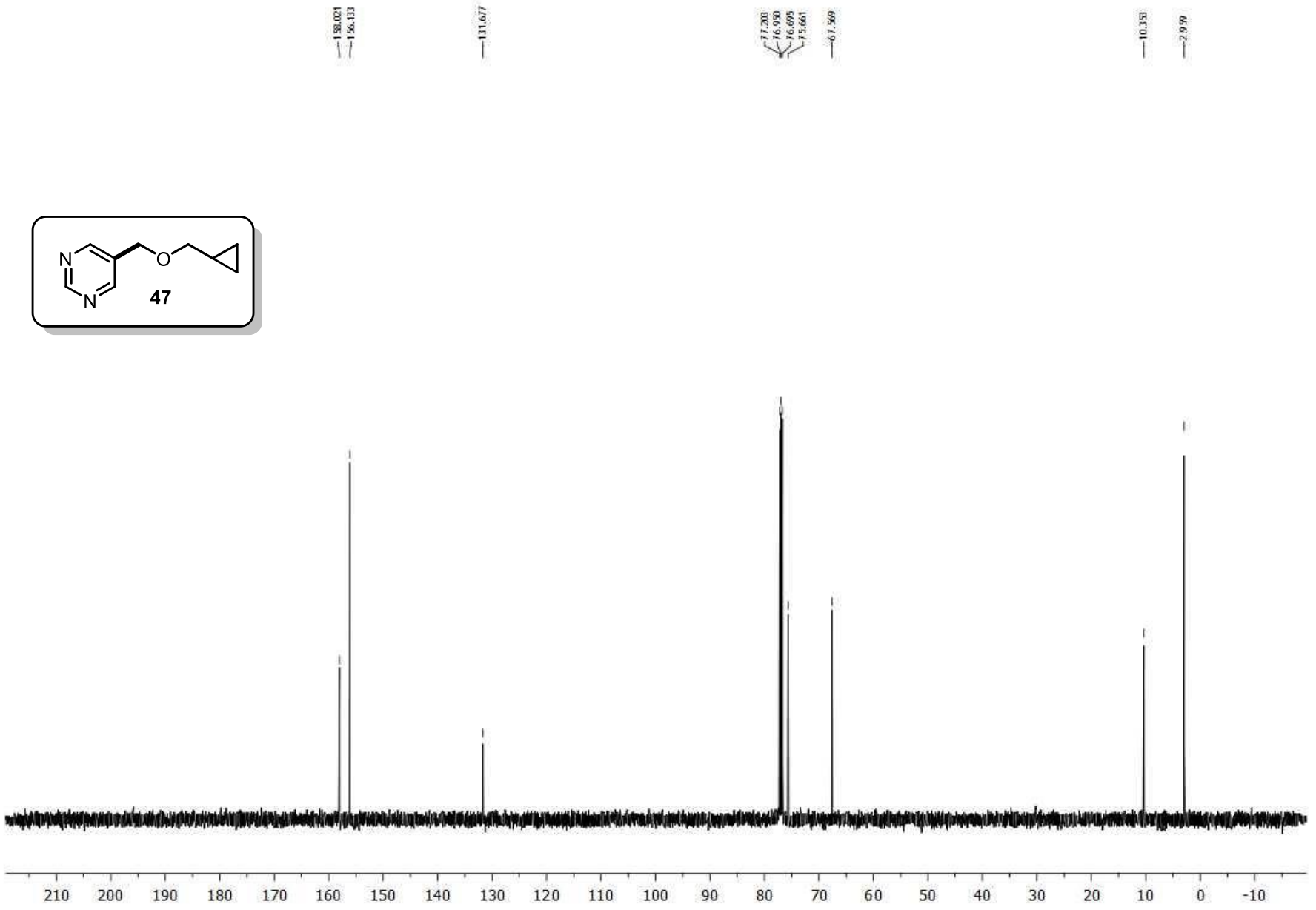
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 5-((2-methoxyethoxy)methyl)pyrimidine (**46**)



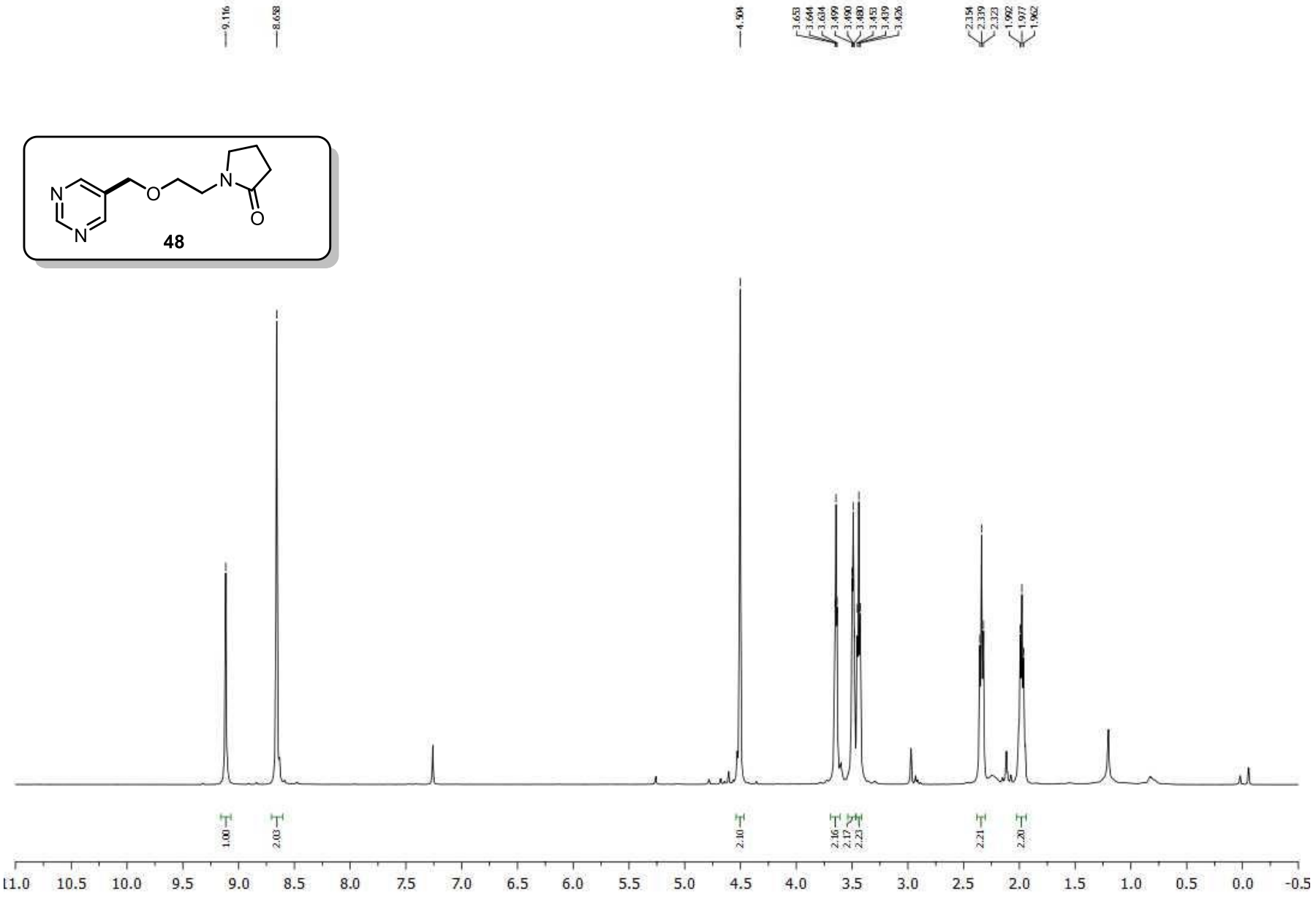
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 5-((cyclopropylmethoxy)methyl)pyrimidine (**47**)



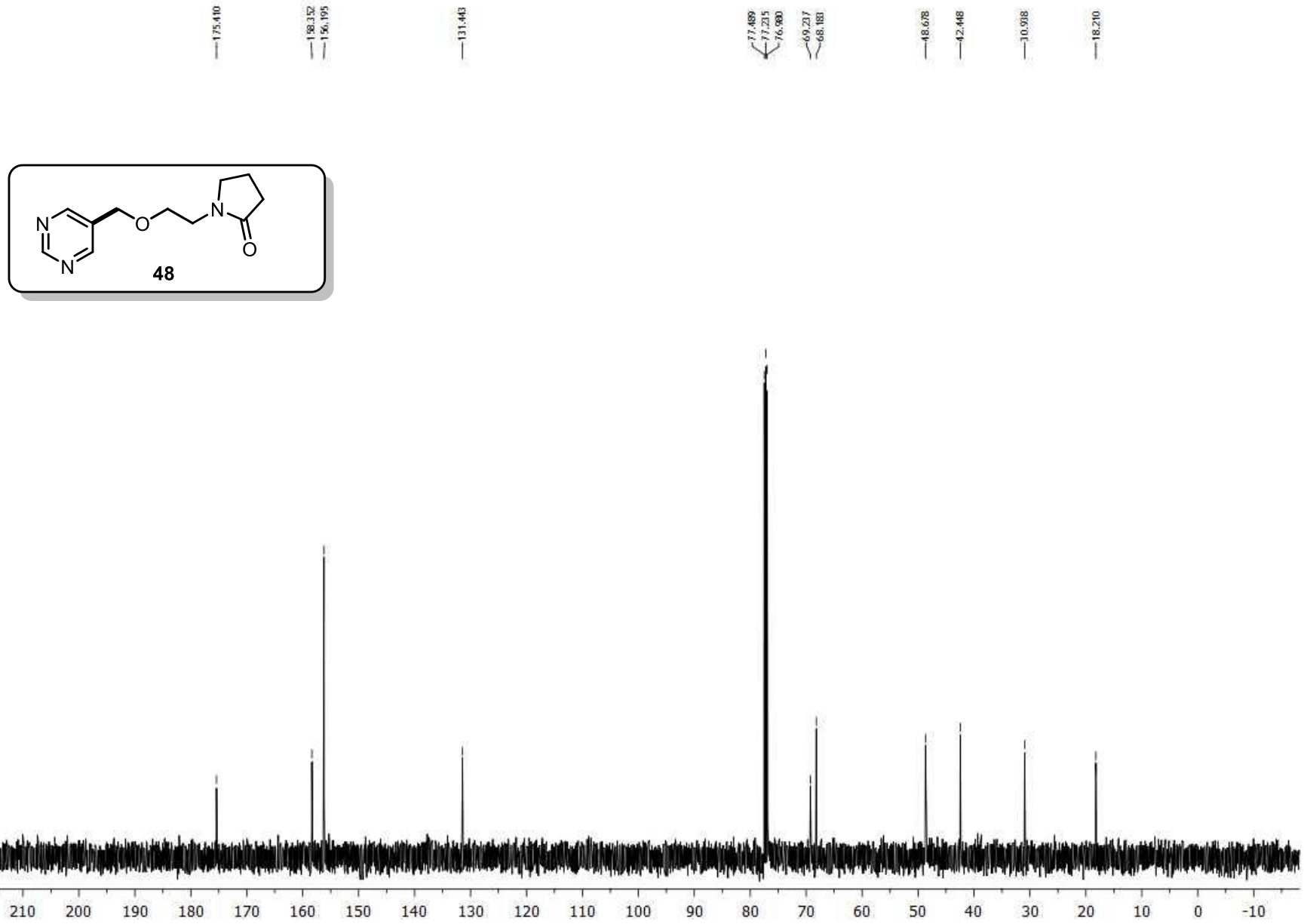
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 5-((cyclopropylmethoxy)methyl)pyrimidine (**47**)



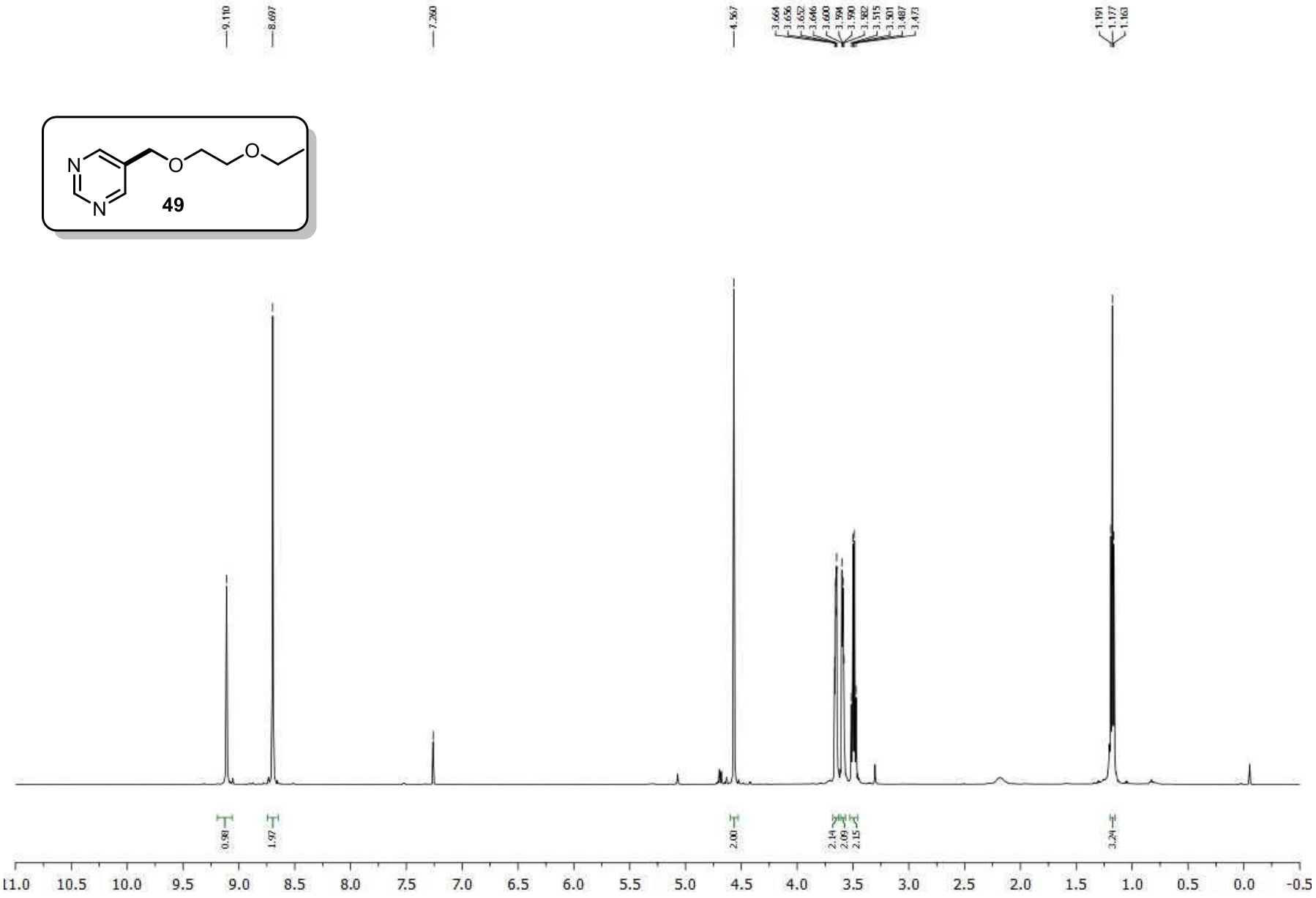
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 1-(2-(pyrimidin-5-ylmethoxy)ethyl)pyrrolidin-2-one (**48**)



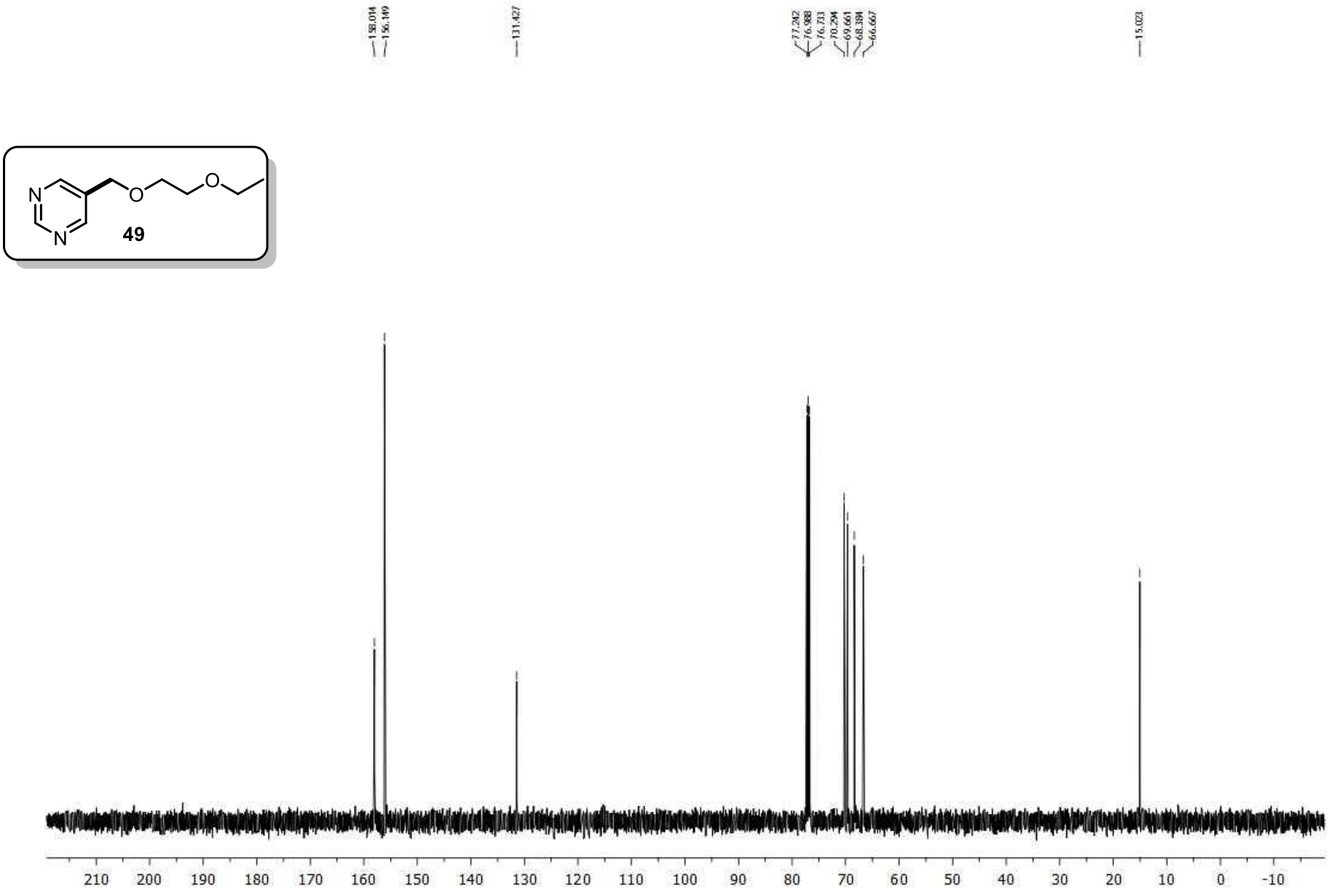
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 1-(2-(pyrimidin-5-ylmethoxy)ethyl)pyrrolidin-2-one (**48**)



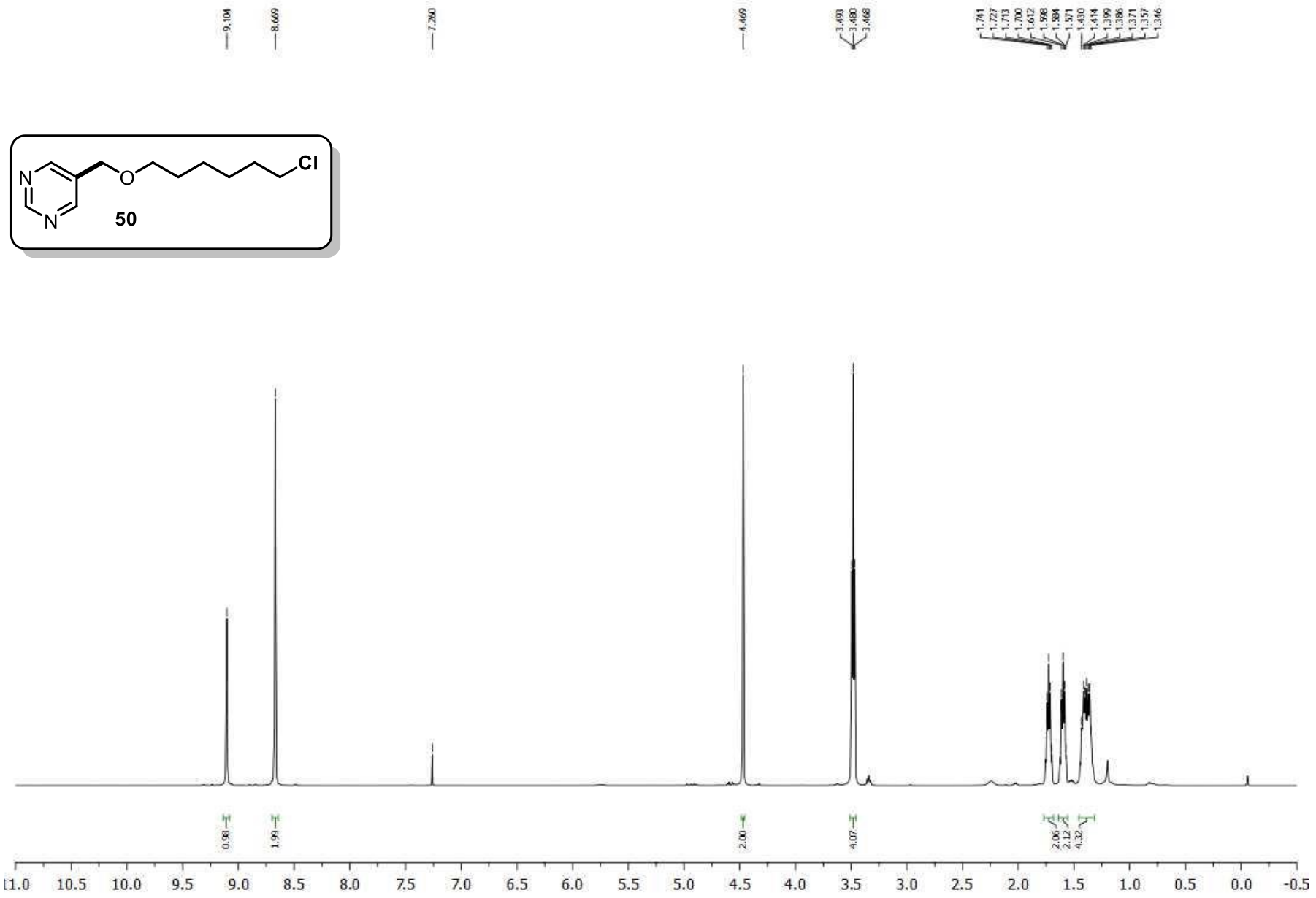
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 5-((2-ethoxyethoxy)methyl)pyrimidine (**49**)



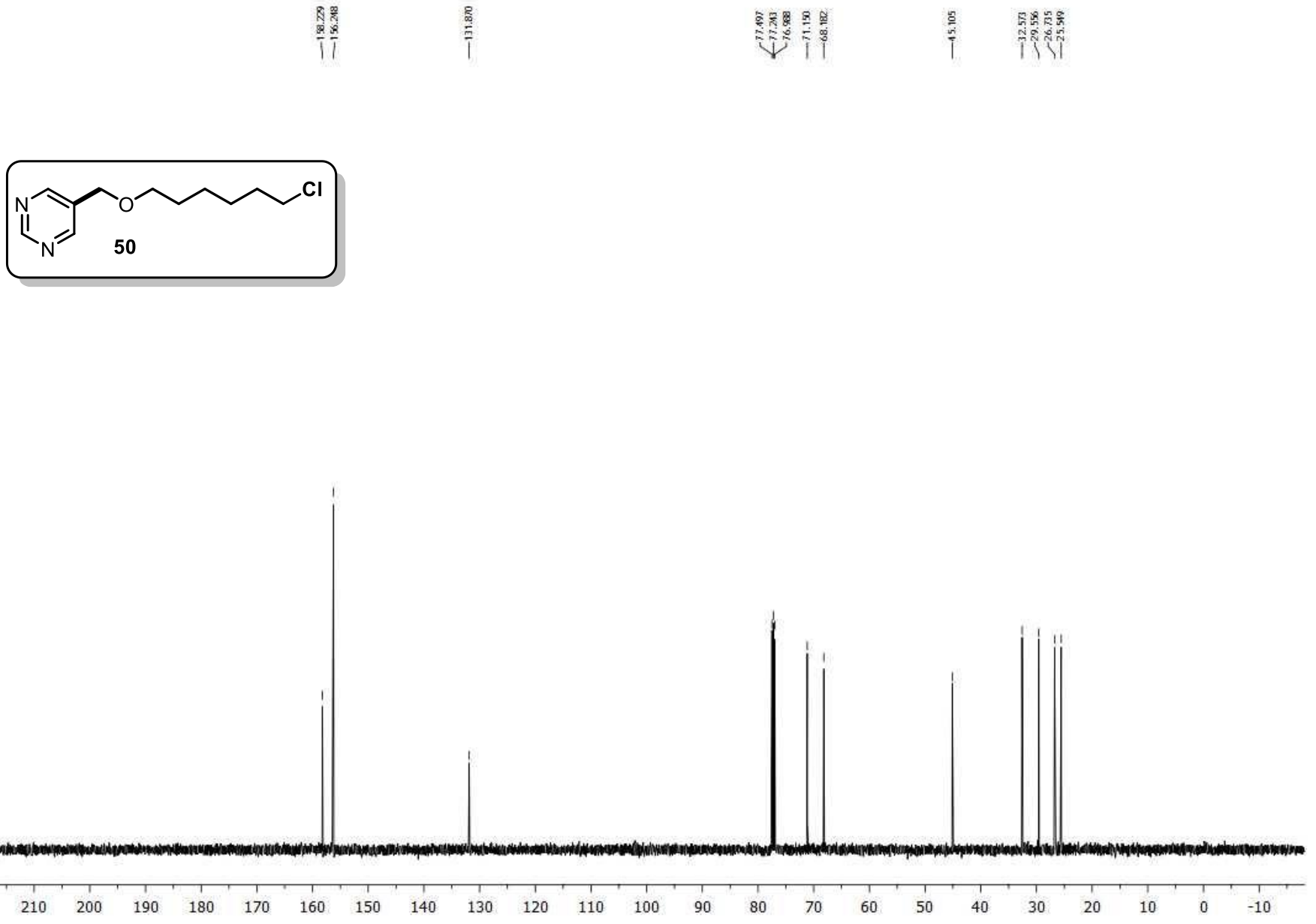
^{13}C NMR ($CDCl_3$, 500 MHz) spectrum of 5-((2-ethoxyethoxy)methyl)pyrimidine (**49**)



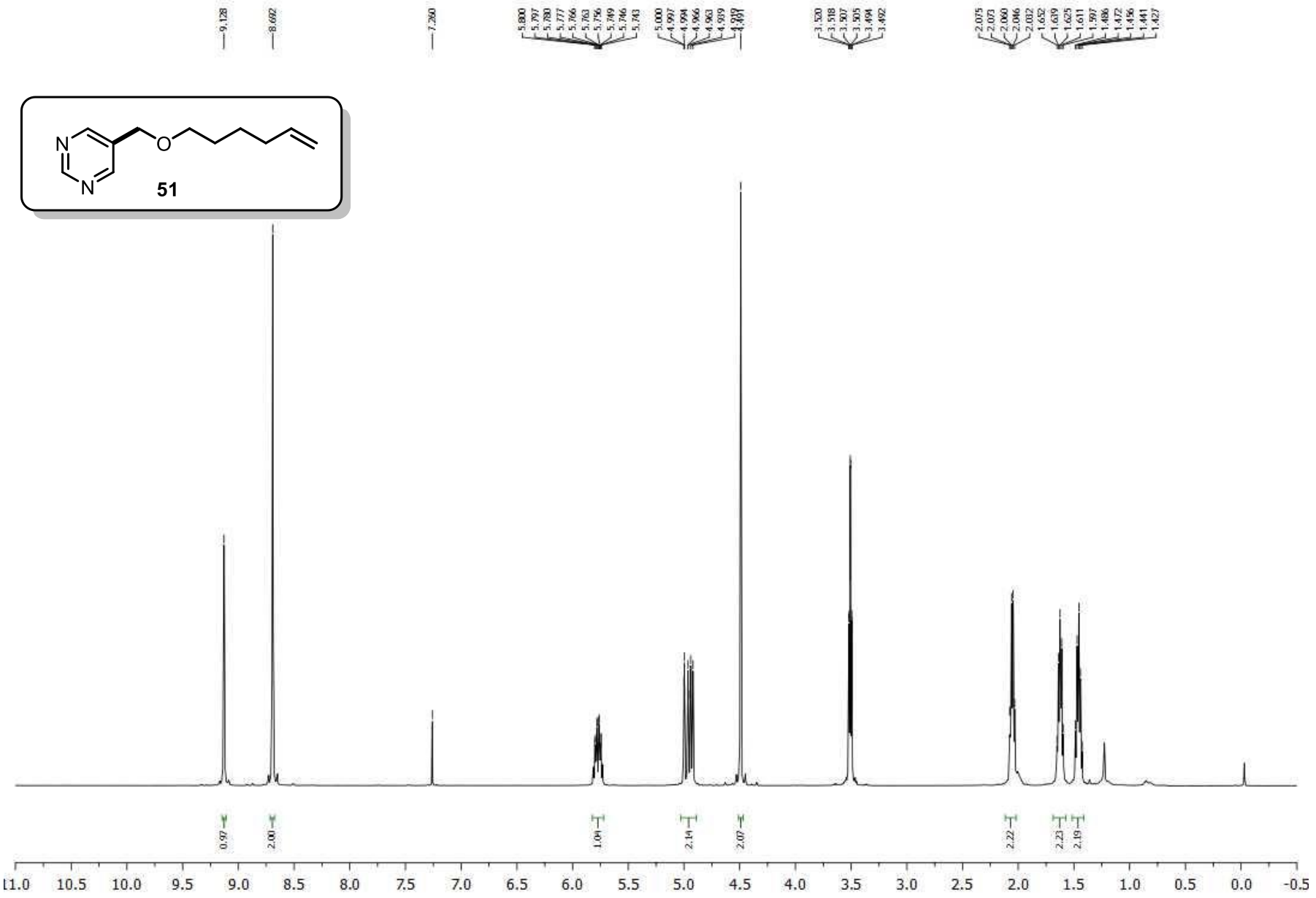
^{1}H NMR ($CDCl_3$, 126 MHz) spectrum of 5-((5-chloropentyl)oxy)methyl)pyrimidine (**50)**



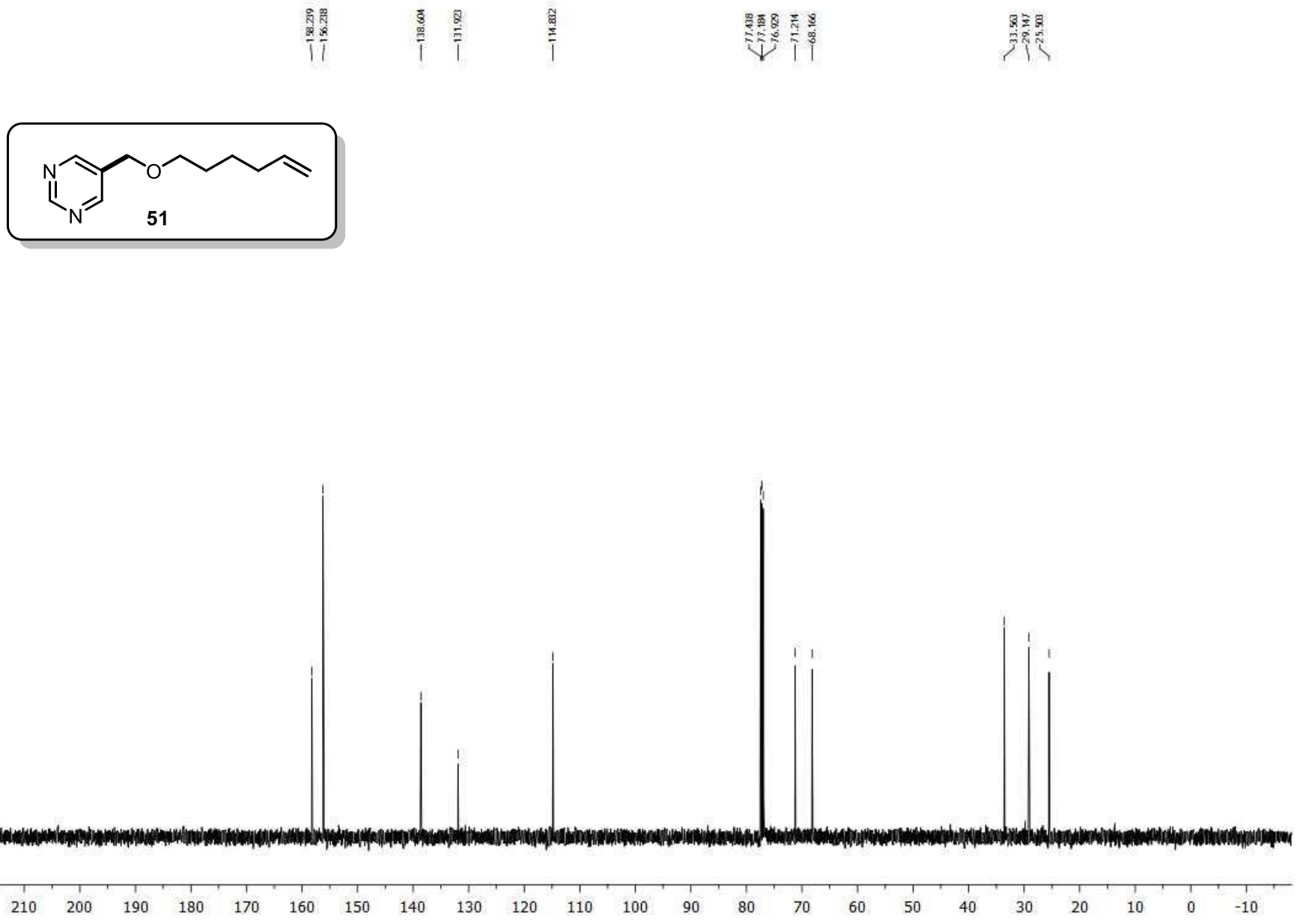
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 5-((5-chloropentyl)oxy)methyl)pyrimidine (**50**)



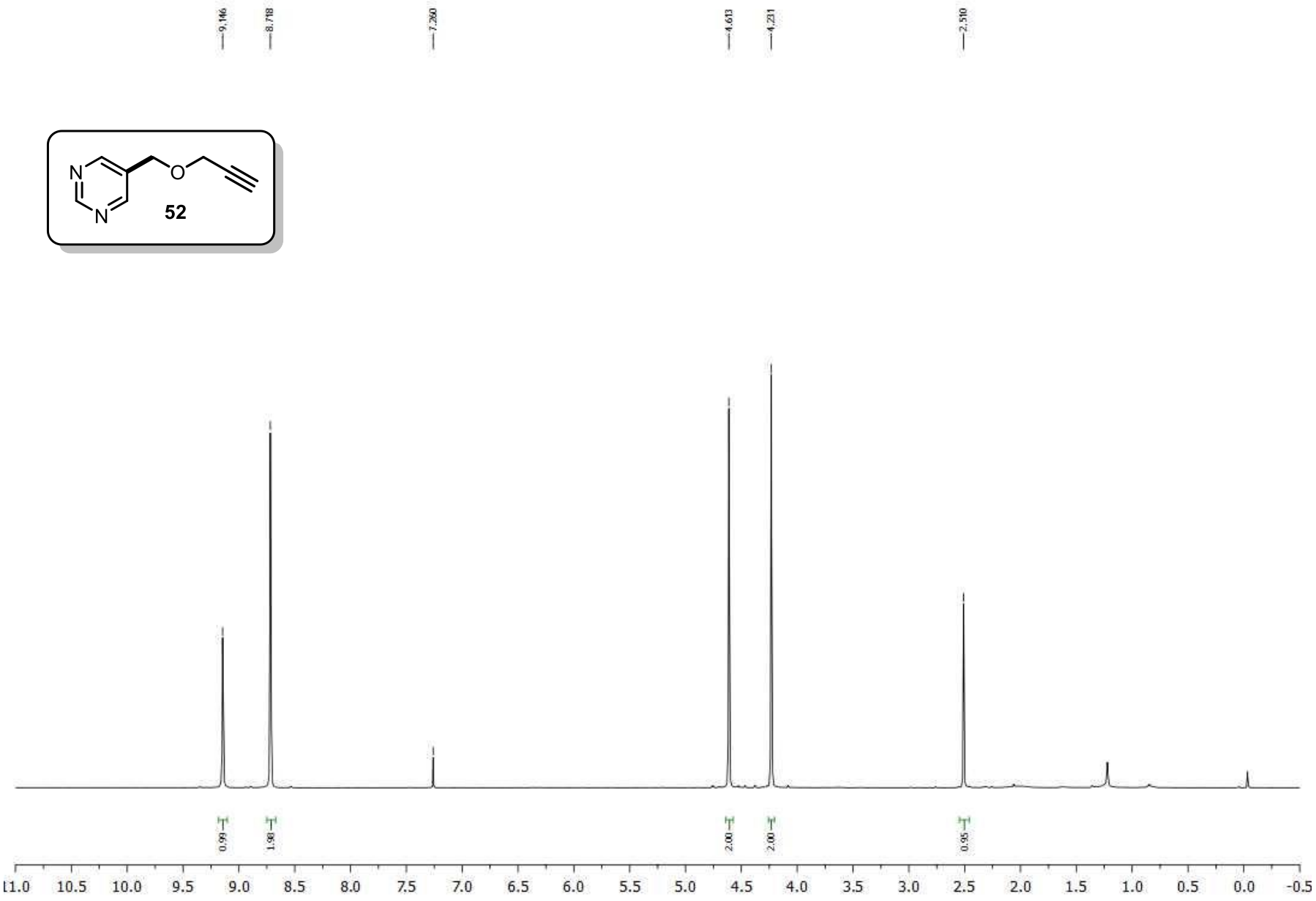
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 5-((hex-5-en-1-yloxy)methyl)pyrimidine (**51**)



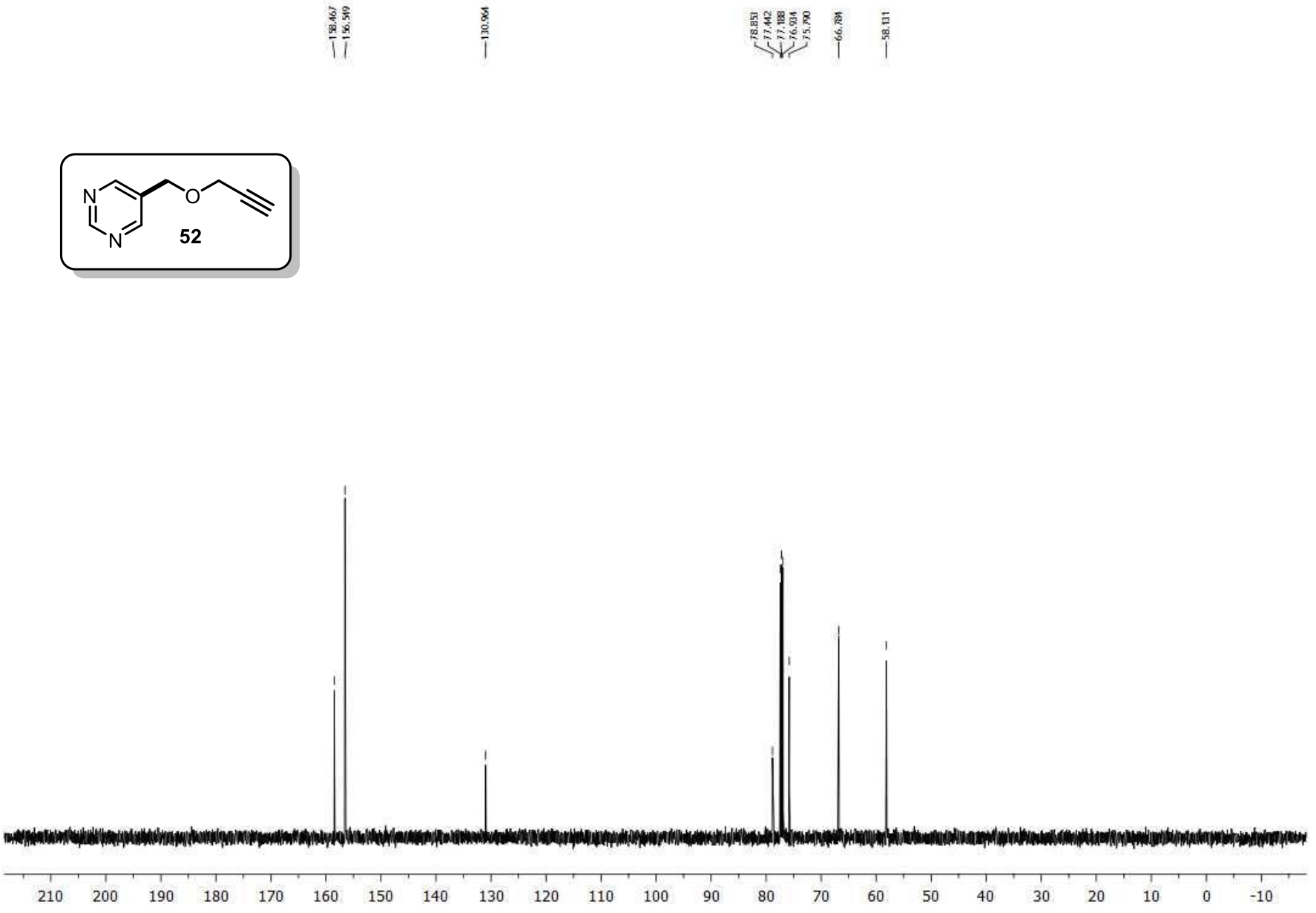
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 5-((hex-5-en-1-yloxy)methyl)pyrimidine (**51**)



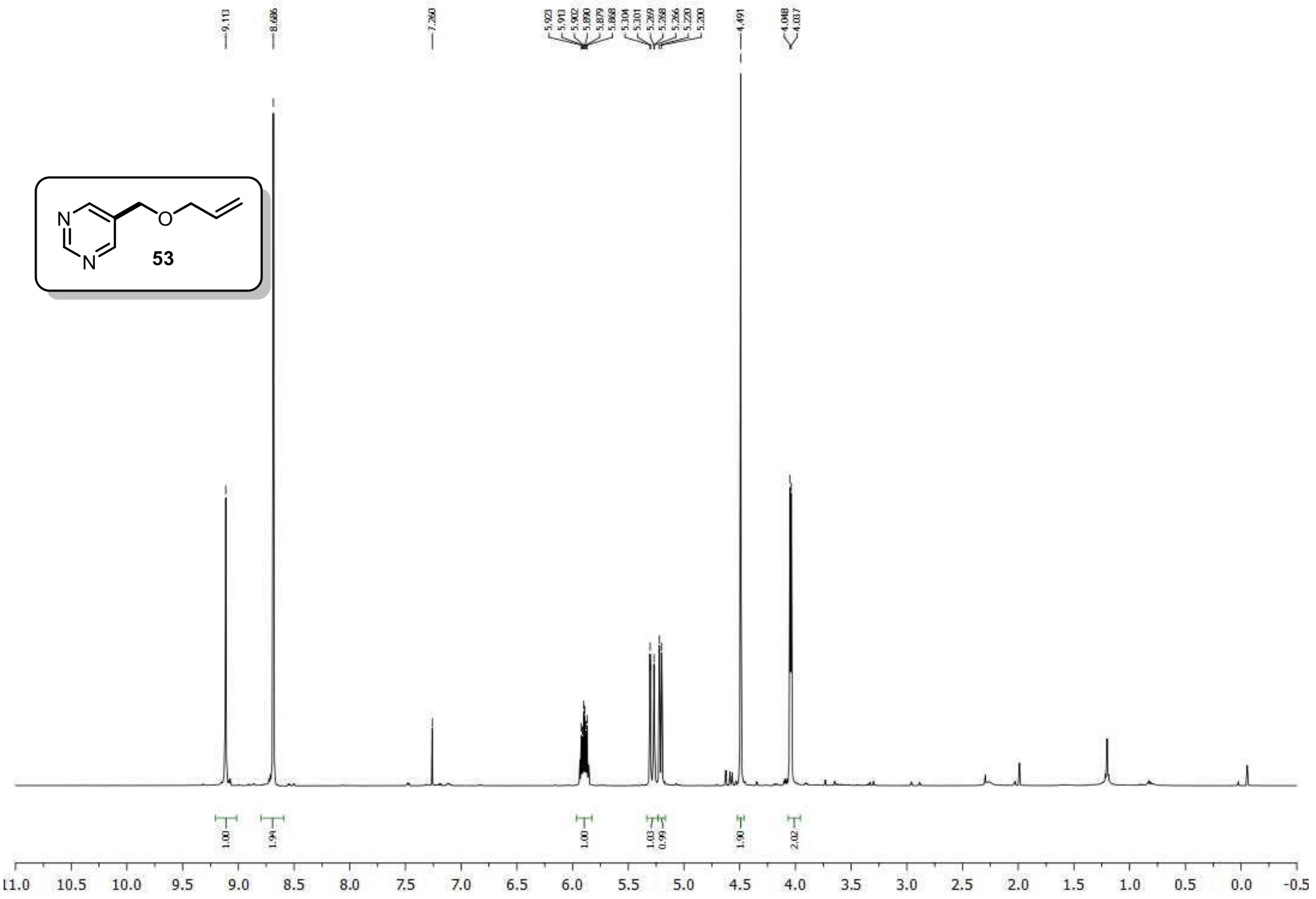
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 5-((prop-2-yn-1-yloxy)methyl)pyrimidine (**52**)



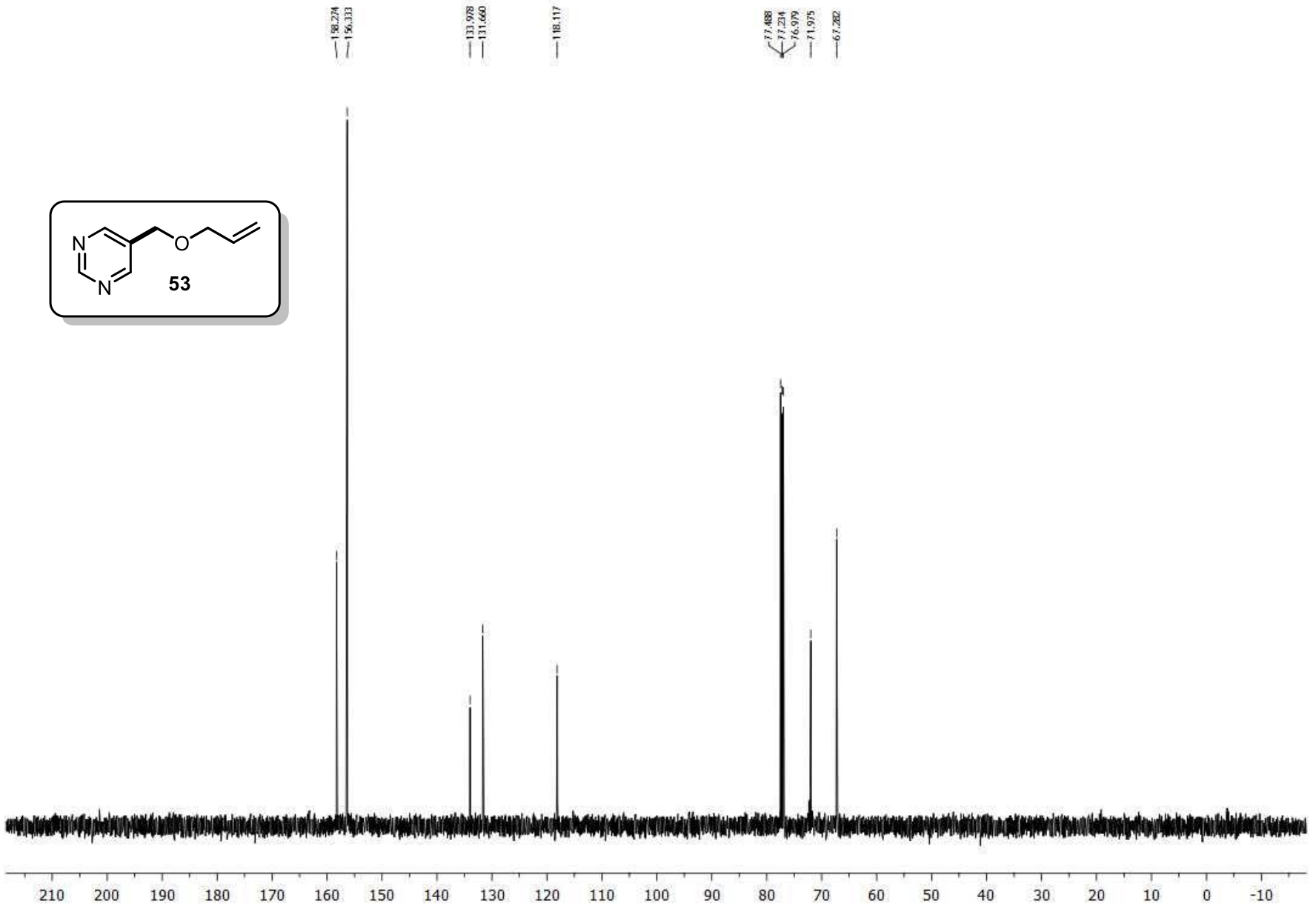
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 5-((prop-2-yn-1-yloxy)methyl)pyrimidine (**52**)



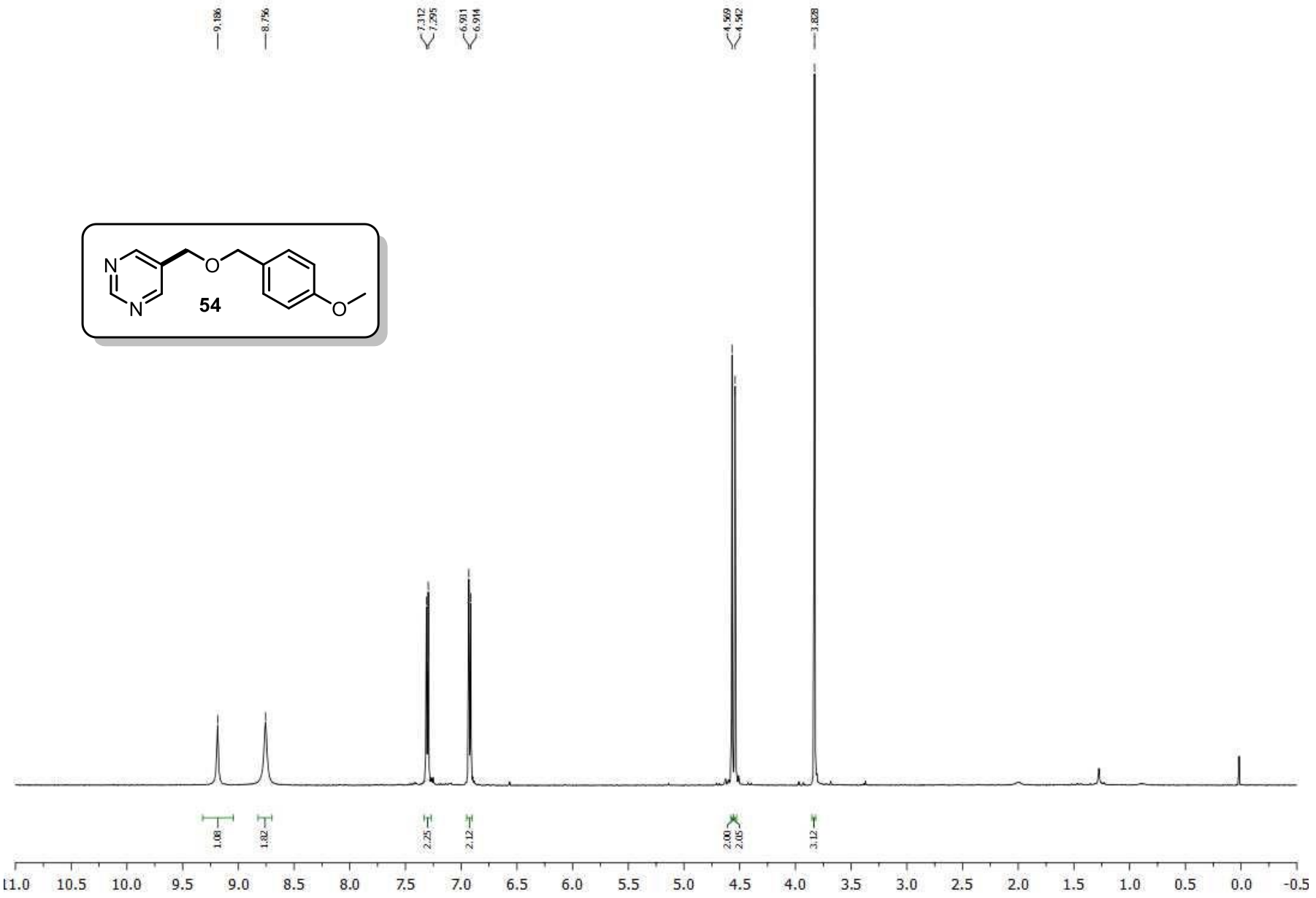
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 5-((allyloxy)methyl)pyrimidine (**53**)



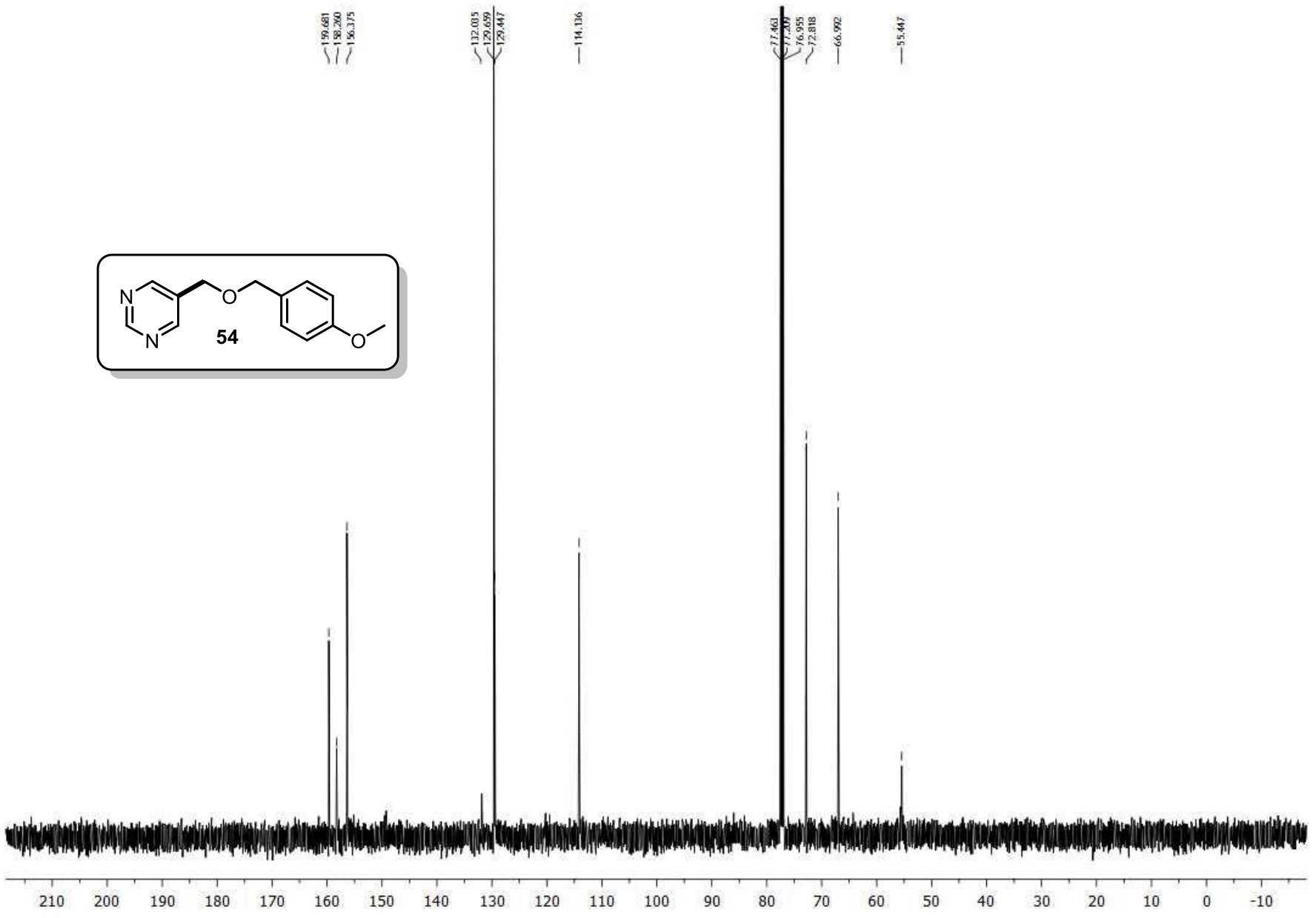
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 5-((allyloxy)methyl)pyrimidine (**53**)



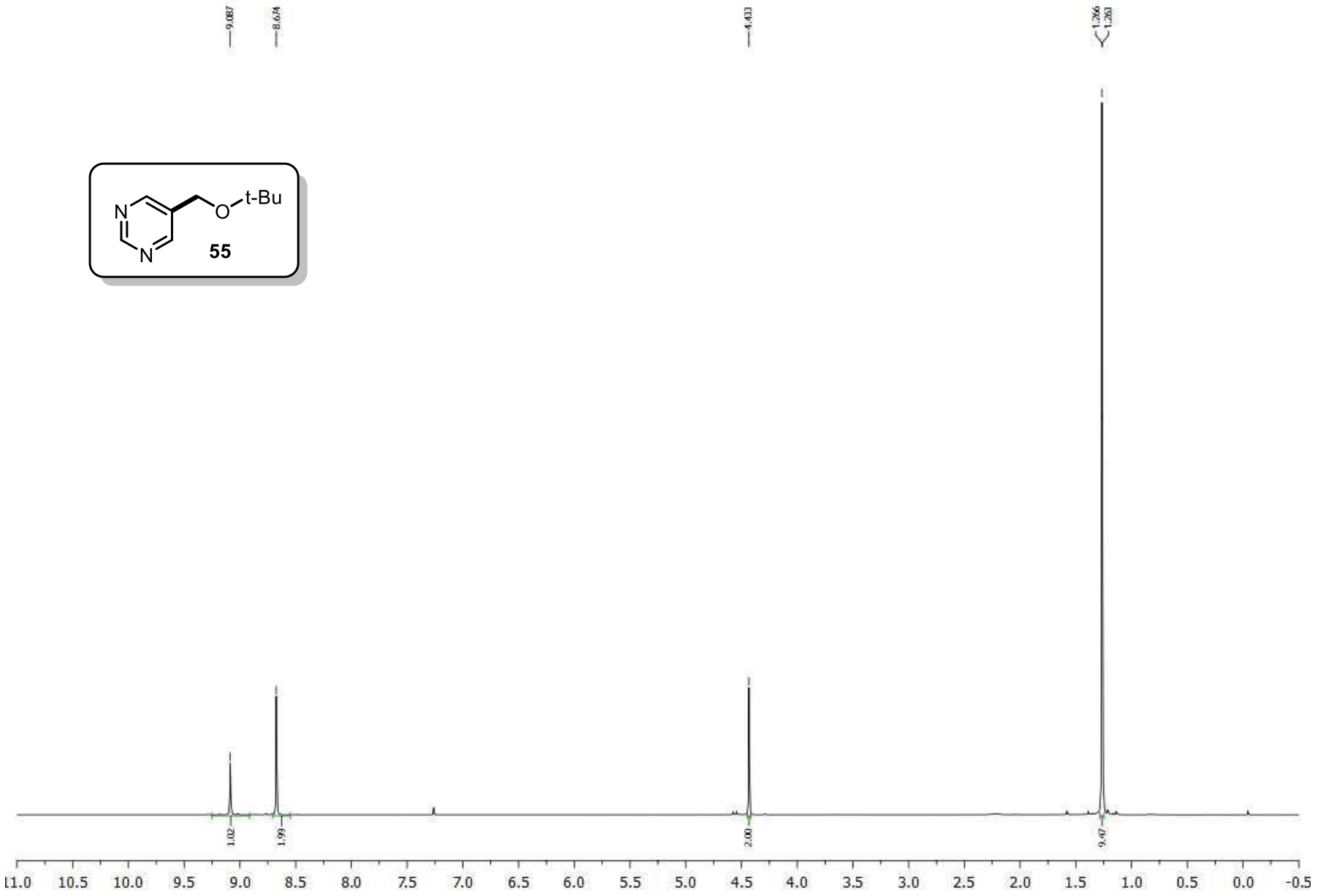
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 5-(((4-methoxybenzyl)oxy)methyl)pyrimidine (**54**)



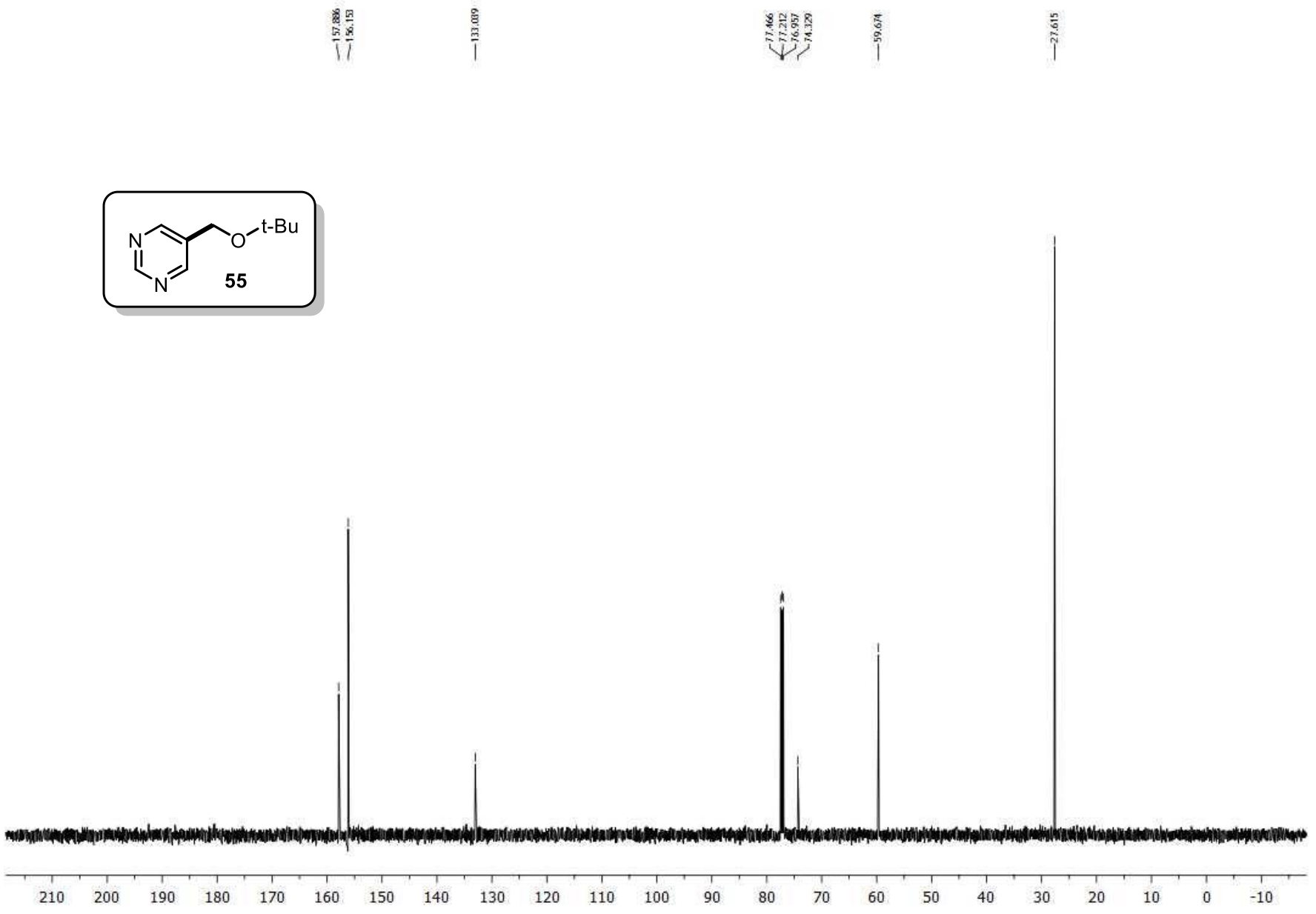
^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 5-(((4-methoxybenzyl)oxy)methyl)pyrimidine (**54**)



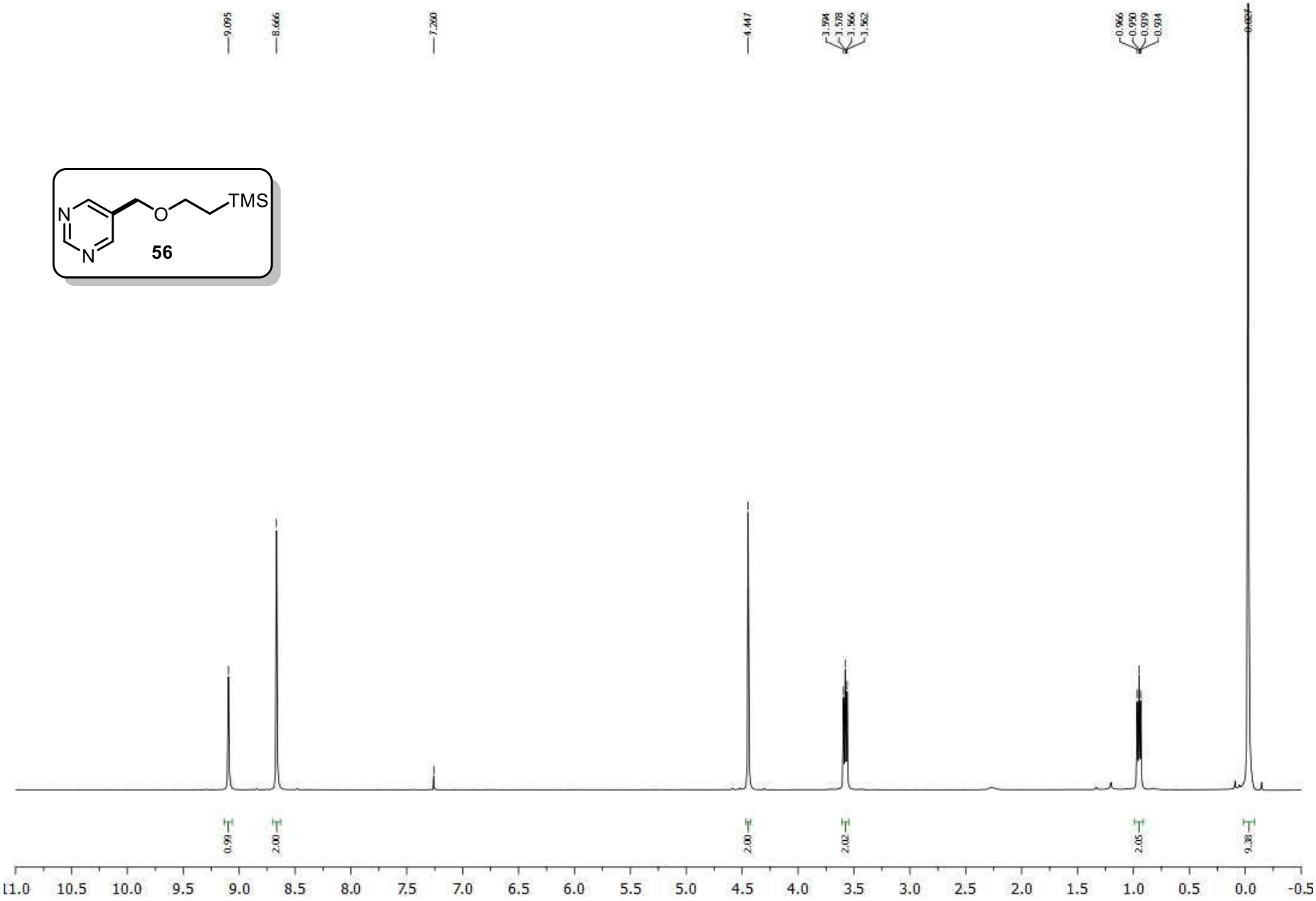
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 5-(*tert*-butoxymethyl)pyrimidine (**55**)



^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 5-(*tert*-butoxymethyl)pyrimidine (**55**)



^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 5-(2-(trimethylsilyl)ethoxy)methyl)pyrimidine (**56**)



^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 5-(2-(trimethylsilyl)ethoxy)methyl)pyrimidine (**56**)