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Supplementary Materials for

Single-electron transmetalation in organoboron cross-coupling by photoredox/nickel dual catalysis

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Single-Electron Transmetalation in Organoboron Cross-Coupling by Photoredox/Nickel Dual Catalysis

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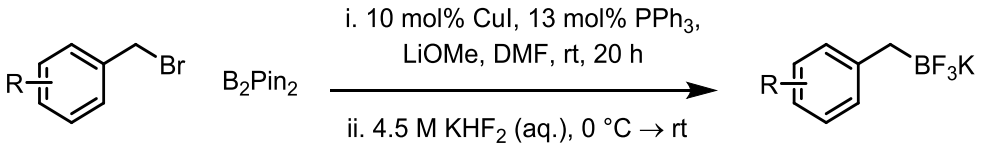
Supplementary Material

General considerations

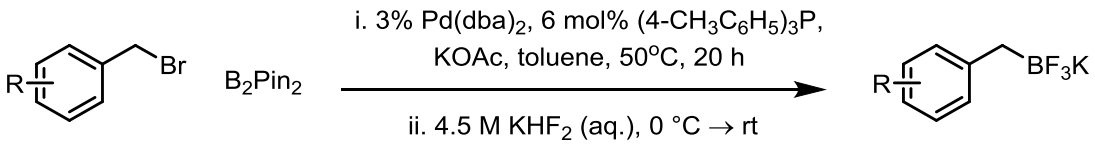
All reactions were carried out under an inert atmosphere of nitrogen or argon unless otherwise noted. Acetone (99.9%, extra dry), methanol (99.8% extra dry), and DMF (99.8%, anhydrous) were used as received. 2,6-Lutidine (>99%, purified by redistillation) was used without further purification (high purity lutidine was found to be important for reproducibly obtaining high yields. Commercially redistilled lutidine or lutidine distilled from $AlCl_3$ and stored under N_2 gave similar results). CuI, $IrCl_3 \cdot xH_2O$, and $Ni(COD)_2$ were from commercial sources. Potassium benzyltrifluoroborate was purchased or prepared using a published procedure (*30*). Potassium (1-(benzyloxy)-3-phenylpropyl)trifluoroborate and potassium trifluoro(1-phenylethyl)borate were prepared according to published procedures (*31*, *38*). All other reagents were purchased commercially and used as received. Photoredox reactions were irradiated with a standard 26W compact fluorescent light bulb. Stereoconvergent cross-couplings were irradiated with blue LED light strips (~425 nm). 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, dd = doublet of doublets, m = multiplet, br = broad), 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.

General procedure A for synthesis of benzylic trifluoroborates



According to an unoptimized procedure derived from that reported by Liu and coworkers (*39*), to a flame-dried 20 mL vial was added benzylic bromide (5 mmol) and triphenylphosphine (173 mg, 0.66 mmol). The vial was taken into a glovebox and CuI (95 mg, 0.5 mmol), LiOMe (380 mg, 10 mmol, 2 equiv), and bis(pinacolato)diboron (1.93 g, 7.6 mmol, 1.52 equiv) were added. The vial was sealed with a Teflon lined silicone septum, DMF was added, and the mixture was stirred vigorously under inert atmosphere at room temperature for 20 h. The resultant brown, viscous mixture was filtered through a pad of silica gel, washing with EtOAc (60–100 mL). The filtrate was diluted with MeOH (HPLC grade, ~50 mL), cooled to 0 °C. Then sat. aq. KHF_2 (9 mL, 40.5 mmol, 8.1 equiv) was added dropwise over 15 to 30 min, and the soln was allowed to warm to rt. The resultant suspension was concentrated under reduced pressure. Pinacol and H_2O were azeotropically removed by suspension in toluene (100–150 mL) followed by rotary evaporation. The remaining solid was dried under high vacuum and then suspended in hot acetone (3 x 100 mL) and filtered. The filtrate was concentrated to a minimal volume (5–20 mL) and hexane (~200 mL) was added to yield a white precipitate. The precipitate was isolated by filtration, washing with hexane (~30 mL) and CH_2Cl_2 (~30 mL) to afford the desired benzylic trifluoroborate.

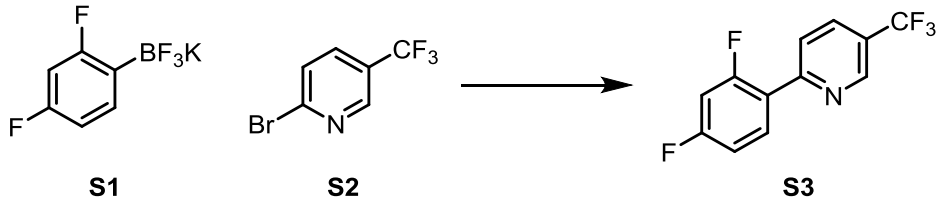
General procedure B for synthesis of benzylic trifluoroborates



According to an unoptimized procedure derived from that reported by Miyaura and coworkers (*40*), to a flame dried 100 mL round bottom flask equipped with a stir bar was added benzylic bromide (5 mmol), KOAc (736 mg, 7.5 mmol), and $(4\text{-}MeC_6H_4)_3P$ (91 mg, 0.30 mmol). The flask was taken into the glovebox and $Pd(dba)_2$ (86 mg, 0.15 mmol) and bis(pinacolato)diboron (1.40 g, 5.5 mmol) were added. The flask was sealed with a rubber septum, toluene was added (30 mL), and the mixture was stirred vigorously under inert atmosphere for 20 h. The resultant yellow-brown mixture was concentrated to near dryness and then diluted with MeOH (HPLC grade, 20 mL), cooled to 0 ^oC, and sat. KHF_2 (9 mL, 40.5 mmol, 8.1 equiv.) was added dropwise by an addition funnel under inert atmosphere during 30 min. The resulting suspension was concentrated under reduced pressure. Pinacol and H_2O were azeotropically removed by suspension in toluene (100-150 mL) followed by rotary evaporation. The remaining solid was dried under high vacuum and then suspended in hot acetone (3 x 100 mL) and filtered. The filtrate was concentrated to a minimal volume (5 – 20 mL) and hexane (~200 mL) was added to yield a white precipitate. The precipitate was isolated by filtration, washing with hexanes (~30 mL) and CH_2Cl_2 (~30 mL), to afford the desired benzylic trifluoroborate.

Synthesis of photocatalyst 4

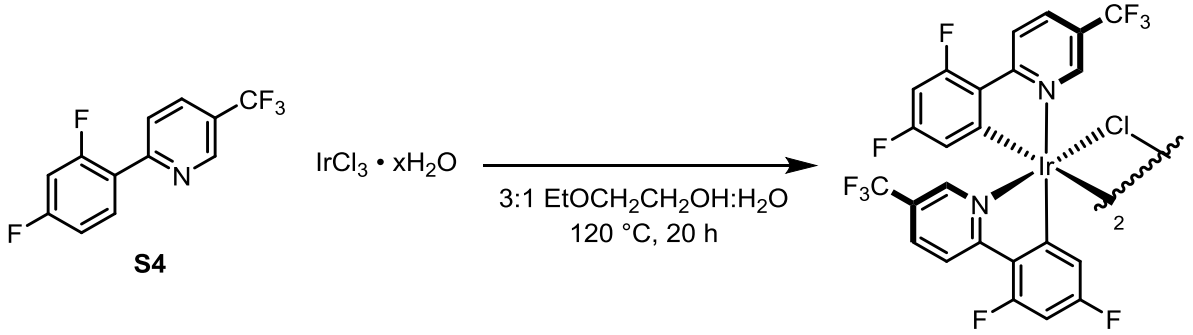
The synthesis of photocatalyst **4** has been documented in literature reports, though never compiled in one location. In an effort to aid the practicing chemist, the procedures found to be most effective in our hands are compiled below. Alternatively, the 4,4'-di-*tert*-butyl bipyridine derivative of **4** is commercially available.



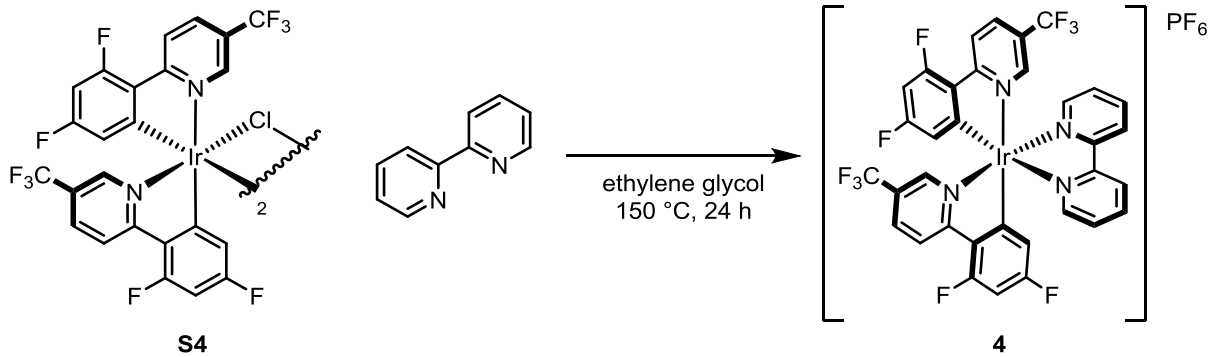
S1 **S2** **S3**

To a large vial equipped with a magnetic stir bar was added **S1** (3.3 g, 15 mmol), **S2** (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 **S3** as white solid (2.54 g, 98%). Mp = 55-58 °C.
A small amount of triphenylphosphine was usually observed after column chromatography (<5 mol %) which did not interfere with subsequent reactions.
^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.96 (s, 1H), 8.12-8.07 (m, 1H), 7.98 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.90 (d, *J* = 8.5 Hz, 1H), 7.06-7.02 (m, 1H), 6.97-6.92 (m, 1H)
^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 163.8 (dd, *J* = 253.1, 12.5 Hz), 161.1 (dd, *J* = 253.5, 12.0 Hz), 155.8, 133.8 (d, *J* = 3.1 Hz), 132.6 (dd, *J* = 9.7, 4.0 Hz), 128.6 (d, *J* = 6.9 Hz), 125.2 (q, *J* = 33.1 Hz), 123.70 (q, *J* = 272.2 Hz), 123.68 (d, *J* = 10.9 Hz), 122.5 (dd, *J* = 11.2, 3.8 Hz), 112.3 (dd, *J* = 21.1, 3.5 Hz), 104.7 (dd, *J* = 26.0, 26.0 Hz)
^{19}F NMR ($CDCl_3$, 470.8 MHz): δ = -62.3, -107.1 (d, *J* = 8.5 Hz), 112.0 (d, *J* = 8.5 Hz)
IR: ν = 2925, 2337, 1601, 1321, 1119, 1058 cm^{-1}
HRMS: (ESI) m/z calc. for $C_{12}H_7NF_5$ (M+H) 259.0499, found 259.0421

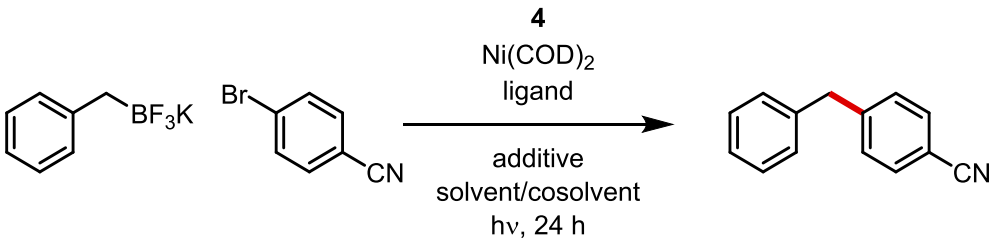


To a 20 mL round-bottom flask equipped with a magnetic stir bar was added ligand **S4** (428 mg, 1.65 mmol) and $IrCl_3$ hydrate (224 mg, 0.75 mmol). The flask was equipped with a cold water condenser and evacuated and purged with N_2 five times. The contents were suspended in rigorously degassed ethoxyethanol (9 mL) and water (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 **S5** as a fine yellow powder (84%). Mp = >250 °C. Characterization data for this compound matched that reported in the literature (*23*).



To a 15 mL round-bottom flask equipped with a magnetic stir bar was added iridium dimer **S4** (130 mg, 0.087 mmol) and 2,2'-bipyridine (32 mg, 0.21 mmol). The flask was attached to a reflux 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, 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 pentane to yield **4** as large yellow crystals (172 mg, 88%). Mp = 199-202 °C. Characterization data for this compound matched that reported in the literature (*41*).

Selected reaction optimization studies



Procedure for reaction screening at 0.01 or 0.05 mmol scale: To a reaction vial equipped with a Teflon coated magnetic stir bar in a glovebox was added a soln of $Ni(COD)_2$ and ligand [1:1 $Ni(COD)_2$:ligand] dissolved in THF. The solvent was removed *in vacuo* under an inert atmosphere, then a soln of potassium benzyltrifluoroborate (1 equiv), 4-bromobenzonitrile (1 equiv), and 4,4'-di-*tert*-butylbiphenyl (0.1 equiv) in solvent was added, followed by a soln of photocatalyst **4**. If desired, an alcoholic cosolvent or amine base was added before the vial was sealed and stirred over blue LED lights. After 24 h the reactions were opened to air, diluted with acetonitrile, and analyzed by reversed phase analytical HPLC using product:internal standard (4,4'-di-*tert*-butylbiphenyl) ratios as a qualitative assessment of reaction yield.

Solvent	Cosolvent	Additive
MeCN	MeOH	2,6-lutidine
MeCN	MeOH	None
MeCN	None	None
acetone	MeOH	2,6-lutidine
acetone	MeOH	None
Acetone	None	None

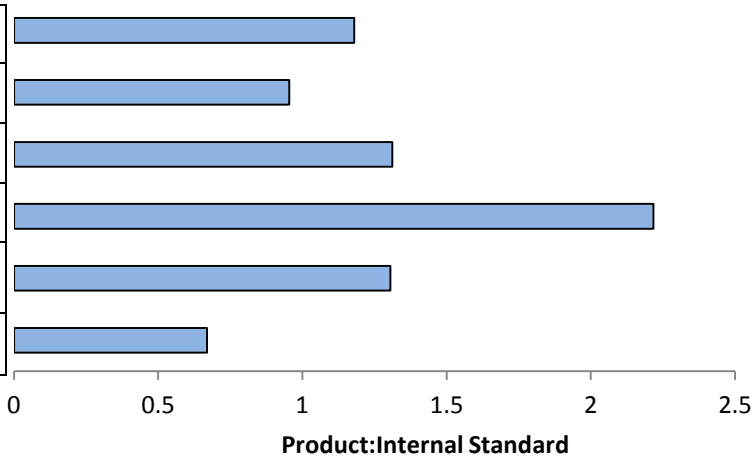


Fig S1: Conditions: 2 mol % **4**, 10 mol % $Ni(COD)_2$, 10 mol % 2,2'-bipyridine, 0.1 M, 24 h, 0.01 mmol

Ligand
prolinol
terpyridine
4,4'-di-*tert*-butyl bipyridine
2,2'-bipyridine

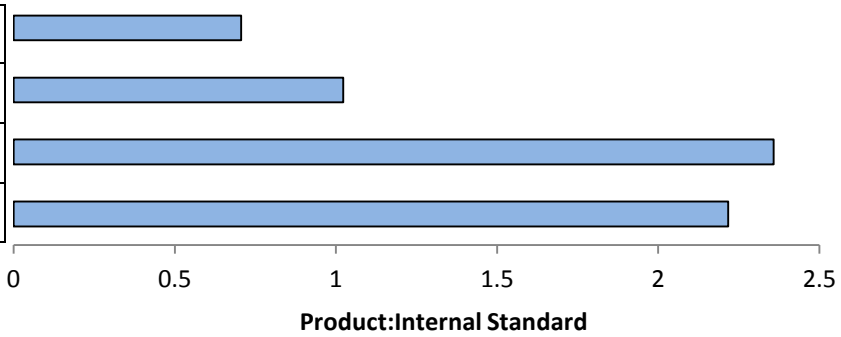


Fig S2: Conditions: 2 mol % **4**, 10 mol % $Ni(COD)_2$, 10 mol % ligand, 10:1 acetone/MeOH, 2 equiv 2,6-lutidine, 0.1 M, 24 h, 0.01 mmol

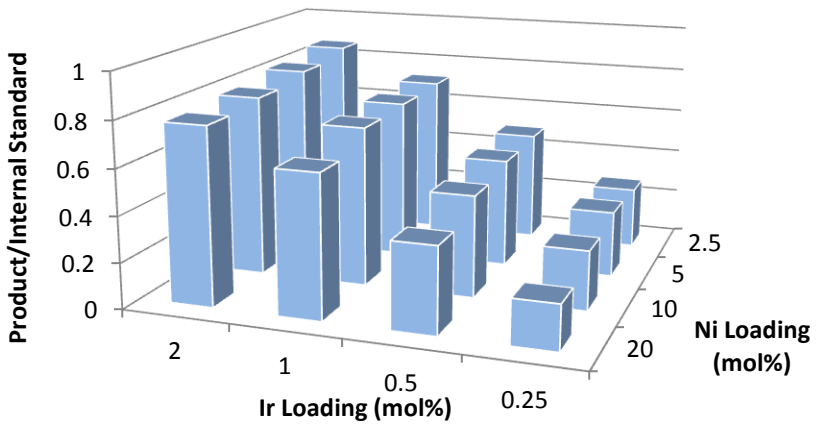


Fig S3: Conditions: 1:1 $Ni(COD)_2$/dtbbpy, 10:1 acetone/MeOH, 2 equiv 2,6-lutidine, 0.1 M, 24h, 0.05 mmol

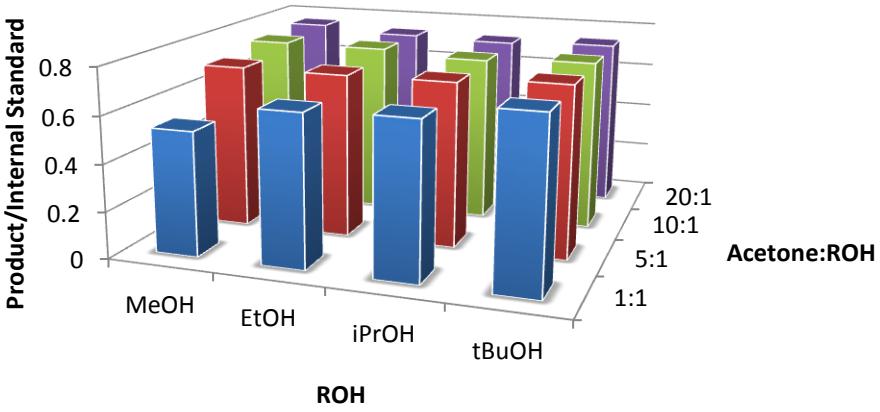
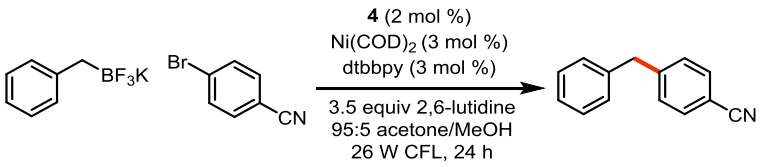


Fig S4: Conditions: 1 mol % **4**, 5 mol % $Ni(COD)_2$, 5 mol % dtbbpy, 10:1 acetone/alcohol, 2 equiv 2,6-lutidine, 0.1 M, 24 h, 0.05 mmol

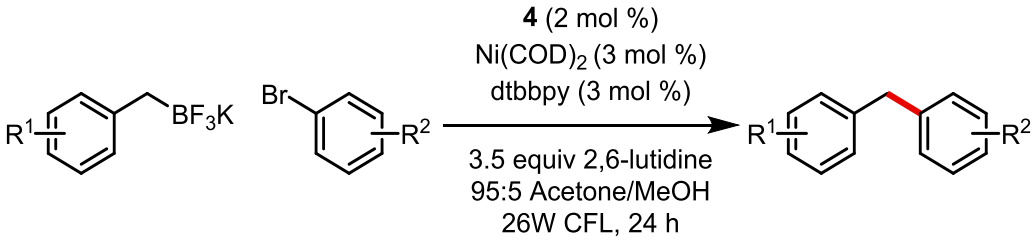


Variation from Standard Condition	Yield [a]
None	80
Photocatalyst omitted	0
$Ni(COD)_2$/dtbbpy omitted	0
No light	0
Ligand omitted	45
Lutidine omitted	43
MeOH omitted	75

Reactions performed on 0.05 mmol scale; [a] Yield determined by calibrated HPLC analysis

Fig S5: Conditions: 2 mol% **4**, 3 mol % $Ni(COD)_2$, 3 mol % dtbbpy, 95:5 acetone/methanol, 3.5 equiv 2,6-lutidine, 0.1 M, 24 h, 0.05 mmol

General procedure for photoredox cross-coupling reactions



To a two dram (8 mL) borosilicate glass vial equipped with a Teflon-coated magnetic stir bar was added aryl bromide (0.5 mmol, 1 equiv) (liquid aryl bromides were added with solvent), benzylic trifluoroborate (0.6 mmol, 1.2 equiv), $Ir[dFCF_3ppy]_2(bpy)PF_6$ **4** (10 mg, 0.01 mmol), and 4,4'-di-*tert*-butyl-2,2'-bipyridine (4.0 mg, 0.015 mmol). The vial was taken into a glovebox and $Ni(COD)_2$ (4.1 mg, 0.015 mmol) was added. The vial was sealed with a plastic screw cap containing a Teflon-lined silicone septum, removed from the glovebox, and evacuated and purged with inert gas three times. Under inert atmosphere was introduced successively acetone (4.75 mL), methanol (0.25 mL), and 2,6-lutidine (202 µL, 1.75 mmol, 3.5 equiv). The vial was sealed with Teflon ribbon, electrical tape, and parafilm and stirred for 24 hours approximately 3 cm from a 26 W fluorescent light bulb. The crude reaction mixture was filtered through an approximately 2 cm x 2 cm cylindrical plug of Celite, washing with EtOAc (30–50 mL). The residue was purified by column chromatography on silica gel, eluting with EtOAc and hexanes, to obtain products in pure form.

Fig S6: Photoredox cross-coupling reaction set-up (0.5 mmol scale)

Gram scale reaction: To a ~75 mL Schlenk flask equipped with a Teflon-coated magnetic stir bar was added 4-bromobenzonitrile (1.000 g, 5.49 mmol, 1 equiv), benzyl trifluoroborate (1.306 g, 6.59 mmol, 1.2 equiv), $Ir[dFCF_3ppy]_2(bpy)PF_6$ **4** (55.0 mg, 0.055 mmol, 0.01 equiv), and 4,4'-di-*tert*-butyl-2,2'-bipyridine (22.0 mg, 0.082 mmol, 0.015 equiv). The flask was taken into the glovebox and $Ni(COD)_2$ (22.5 mg, 0.082 mmol, 0.015 equiv) was added. The flask was sealed and under an inert atmosphere, acetone (47.5 mL), methanol (2.5 mL), and 2,6-lutidine (2.24 mL, 19.2 mmol, 3.5 equiv) were added successively. The reaction was stirred ~5 cm from two 26 watt compact fluorescent light bulbs for 24 h. After filtration though Celite, the residue was purified by column chromatography on silica gel, eluting with EtOAc and hexanes, to obtain the product in pure form.

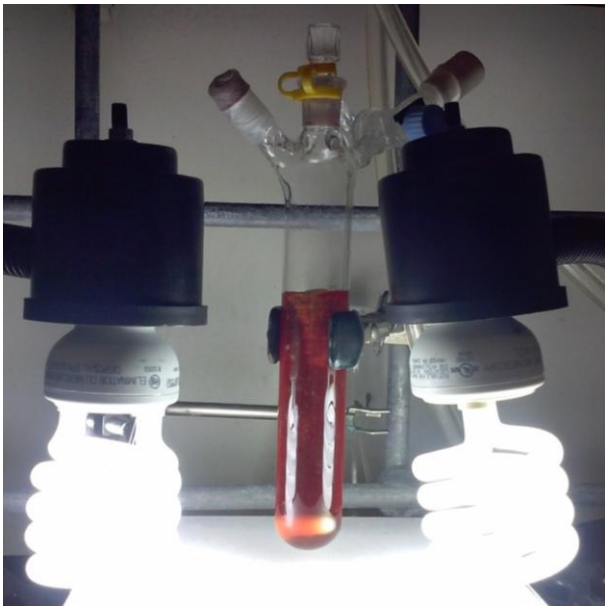
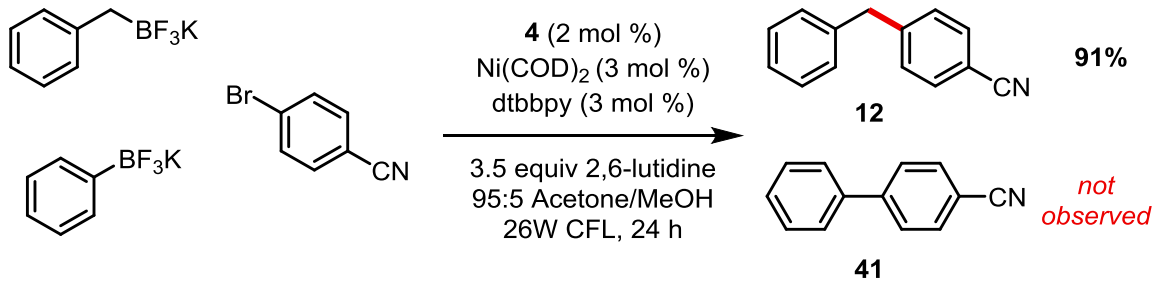


Fig S7: Gram scale photoredox cross-coupling reaction set-up (5.5 mmol)

Benzyl-aryl competition experiment details



The reaction was performed according to the general procedure for photoredox cross-coupling at 0.5 mmol scale using 1.2 equiv $BnBF_3K$ and 1.2 equiv $PhBF_3K$. The crude reaction was analyzed by reversed phase analytical HPLC. A product standard for biaryl **41** was synthesized according to a literature procedure (*42*). After workup and purification according to the general procedure, diarylmethane product **12** was isolated in 91% yield (88 mg).

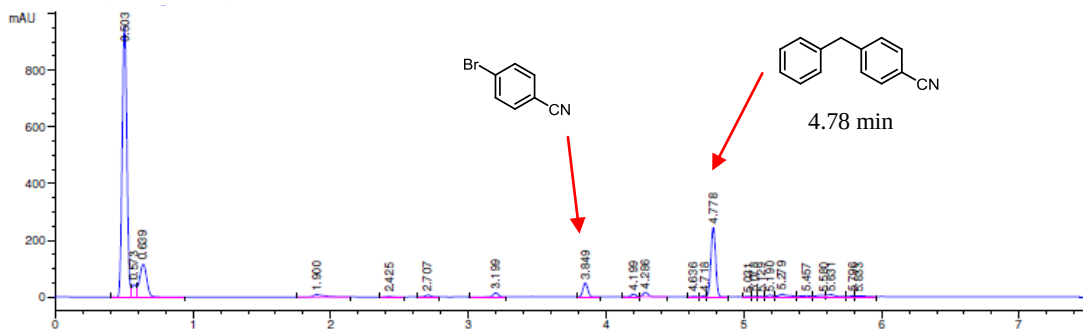


Fig S8: Crude HPLC chromatogram for benzyl-aryl competition experiment under photoredox cross-coupling conditions.

A traditional Suzuki-Miyaura cross-coupling was performed for comparison of the product distribution in the photoredox cross-coupling to that of a cross-coupling employing a traditional transmetalation. The reaction was performed on 0.2 mmol scale using 1.2 equiv $BnBF_3K$, 1.2 equiv $PhBF_3K$, and 1 mol % $Pd(OAc)_2$. The crude reaction mixture was analyzed by reversed phase analytical HPLC.

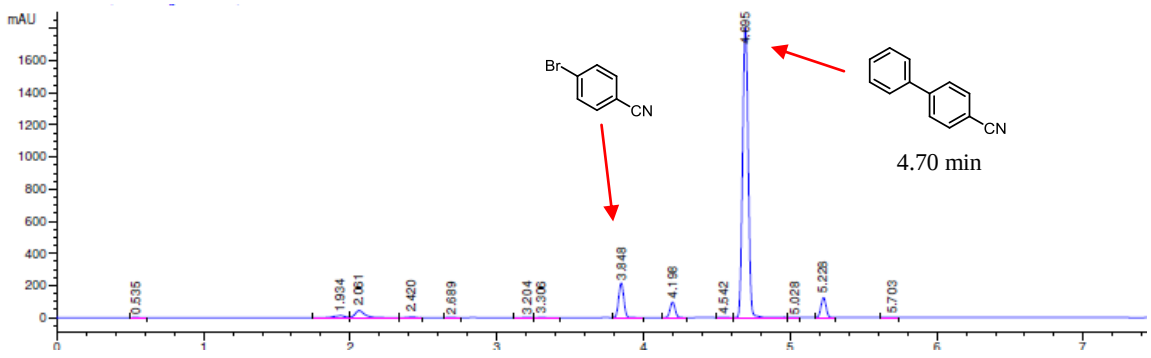
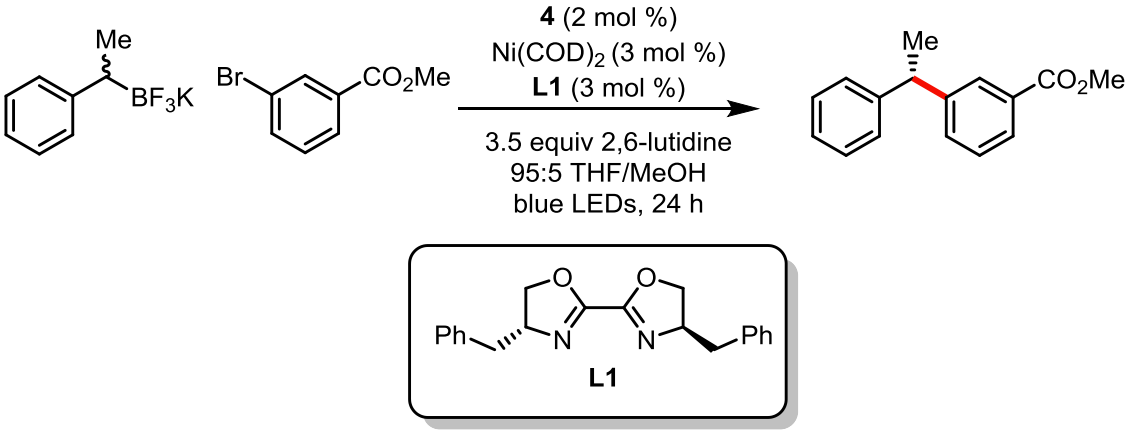


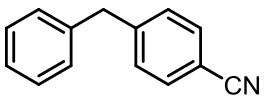
Fig S9: Crude HPLC chromatogram for benzyl-aryl competition experiment under conventional Suzuki-Miyaura cross-coupling conditions

Procedure for stereoconvergent cross-coupling



To a two dram (8 mL) borosilicate glass vial equipped with a Teflon-coated magnetic stir bar was added methyl 3-bromobenzoate (108 mg, 0.5 mmol, 1 equiv), potassium trifluoro(1-phenylethyl)borate (127 mg, 0.6 mmol, 1.2 equiv), $Ir[dFCF_3ppy]_2(bpy)PF_6$ **4** (10 mg, 0.01 mmol), and **L1** (4.8 mg, 0.015 mmol). The vial was taken into a glovebox and $Ni(COD)_2$ (4.1 mg, 0.015 mmol) was added. The vial was sealed with a plastic screw cap containing a Teflon-lined silicone septum, removed from the glovebox, and evacuated and purged with inert gas three times. Under inert atmosphere THF (4.75 mL), MeOH (0.25 mL), and 2,6-lutidine (202 μL, 1.75 mmol, 3.5 equiv) were introduced successively. The vial was sealed with Teflon ribbon, electrical tape, and parafilm and stirred for 24 h in a crystallization dish surrounded by blue LED lights. The crude reaction mixture was filtered through an approximately 2 cm x 2 cm cylindrical plug of Celite, washing with EtOAc (30–50 mL). The residue was purified by column chromatography on silica gel, eluting with EtOAc and hexanes, to obtain product in pure form.

Compound Characterization Data



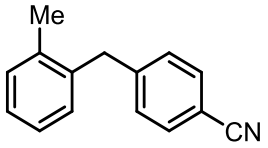
12

4-Benzylbenzonitrile (12): obtained as a white crystalline solid (86 mg, 89%); gram scale (1029 mg, 97%), Mp = 47-50 °C

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.57 (d, *J* = 8.5 Hz, 2H), 7.25-7.32 (m, 5H), 7.17 (d, *J* = 7.5 Hz, 2H), 4.04 (s, 2H)

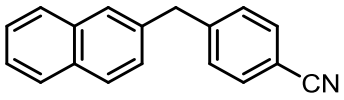
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 146.9, 139.5. 132.4, 129.8, 129.1, 128.9, 126.8, 119.1, 110.2, 42.1

Characterization data matched that reported in the literature (*43*).



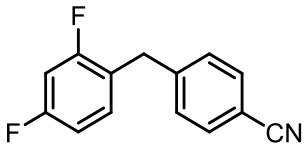
13

4-(2-Methylbenzyl)benzonitrile (13): obtained as a white solid (85 mg, 82%), Mp = 50-52 °C
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.57 (d, *J* = 8.5 Hz, 2H), 7.26-7.21 (m, 5H), 7.13-7.12 (m, 1H), 4.07 (s, 2H), 2.24 (s, 3H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 146.2, 137.2, 136.5, 132.2, 130.5, 130.0 129.3, 127.0, 126.2, 118.9, 109.9, 39.5, 19.6
Characterization data matched that reported in the literature (*44*).



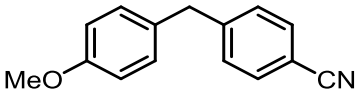
14

4-(Naphthalen-2-ylmethyl)benzonitrile (**14)**: obtained as a white solid (121 mg, 99%), Mp = 105-110 °C
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.83-7.77 (m, 3H), 7.62 (s, 1H), 7.58 (m, 2H), 7.48 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.27-7.25 (m, 1H), 4.20 (s, 2H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 146.5, 136.8, 133.6, 132.3, 129.7, 128.5, 127.7, 127.5, 127.4, 126.3, 125.8, 119.0, 110.1, 42.1
Characterization data matched that reported in the literature (*45*).



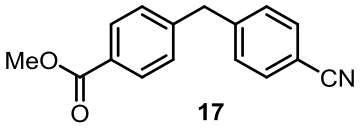
15

4-(2,4-Difluorobenzyl)benzonitrile (15): obtained as a white crystalline solid (80 mg, 70%), Mp = 63-65 °C
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.59 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.13-7.11 (m, 1H), 6.86-6.82 (m, 2H), 4.02 (s, 2H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 162.3 (dd, *J* = 148.6, 11.8 Hz), 160.3 (dd, *J* = 148.9, 11.8 Hz), 145.1, 132.3, 131.5 (dd, *J* = 9.7, 6.2 Hz), 129.3, 122.2 (dd, *J* = 12.5, 3.6 Hz), 118.7, 111.4 (dd, *J* = 21.1, 3.8 Hz), 110.3, 104.0 (dd, *J* = 25.5, 25.5 Hz)
^{19}F NMR ($CDCl_3$, 470.8 MHz): δ = -111.7, -113.0
IR: ν = 2225, 1604, 1500, 1269, 1136, 968, 852 cm^{-1}
HRMS: (ESI) m/z calc. for $C_{14}H_{10}NF_2$ (M+H) 230.0781, found 230.0772



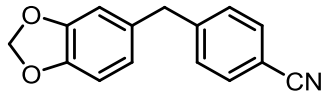
16

4-(4-Methoxybenzyl)benzonitrile (16): obtained as a white solid (105 mg, 94%), Mp = 48-50 °C
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.56 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 7.5 Hz, 2H), 7.07 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 3.97 (s, 2H), 3.79 (s, 3H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 158.5, 147.4, 132.4, 131.6, 130.1, 129.7, 119.2, 114.3, 110.0, 55.4, 41.2
Characterization data matched that reported in the literature (*46*).



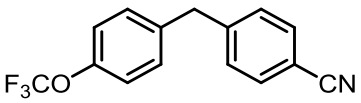
17

Methyl 4-(4-Cyanobenzyl)benzoate (17): obtained as a colorless oil (94 mg, 75%)
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.97 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 4.08 (s, 2H), 3.89 (s, 3H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 167.0, 145.8, 144.7, 132.6, 130.2, 129.8, 129.1, 128.8, 119.0, 110.5, 52.3, 42.0
Characterization data matched that reported in the literature (*44*).



18

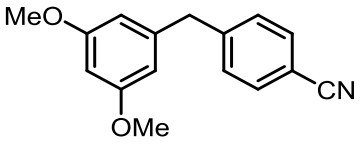
4-(Benzo[d][1,3]dioxol-5-ylmethyl)benzonitrile (**18)**: obtained as a white crystalline solid (115 mg, 97%) , Mp = 106-108 °C
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.56 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.75 (d, *J* = 8.0 Hz, 1H), 6.64-6.61 (m, 2H), 5.92 (s, 2H), 3.93 (s, 2H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 148.1, 147.0, 146.5, 133.2, 132.4, 129.6, 122.1, 119.1, 110.2, 109.5, 108.6, 101.2, 41.8
IR: ν = 2920, 2362, 2226, 1604, 1491, 1254, 1038, 927, 816 cm^{-1}
HRMS: (ESI) m/z calc. for $C_{15}H_{12}NO_2$ (M+H) 238.0868, found 238.0860



19

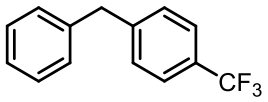
4-(4-(Trifluoromethoxy)benzyl)benzonitrile (**19)**: obtained as a colorless oil (106 mg, 76%)
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.58 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.19-7.15 (m, 4H), 4.04 (s, 2H)

^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 147.9, 145.9, 138.0, 132.3, 130.1, 129.5, 121.2, 120.4 (q, *J* = 257.3 Hz), 118.7, 110.3, 41.1
^{19}F NMR ($CDCl_3$, 470.8 MHz): δ = -57.9
IR: ν = 2920, 2228, 1608, 1508, 1257, 1222, 1161, 1020, 921, 811 cm^{-1}
HRMS (ESI) m/z calc. for $C_{15}H_{11}NOF_3$ (M+H) 178.0793, found 178.0795



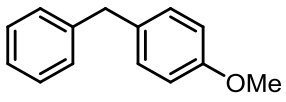
20

4-(3,5-Dimethoxybenzyl)benzonitrile (**20)**: obtained as a colorless oil (108 mg, 86%)
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.57 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.34 (s, 1H), 6.30 (s, 2H), 3.95 (s, 2H,), 3.76 (s, 6H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 161.2, 146.5, 141.7, 132.4, 129.7, 119.1, 110.2, 107.4, 98.4, 55.4, 42.3
IR: ν = 2937, 2838, 2358, 2227, 1594, 1461, 1430, 1205, 1156, 1065, 822 cm^{-1}
HRMS (ESI) m/z calc. for $C_{16}H_{16}NO_2$ (M+H) 254.1181, found 254.1182



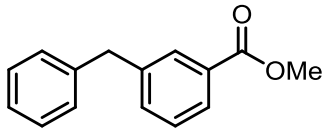
21

1-Benzyl-4-(trifluoromethyl)benzene (**21)**: obtained as a colorless oil (93 mg, 79%)
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.52 (d, *J* = 8.0 Hz, 2H), 7.30-7.26 (m, 4H), 7.22-7.19 (m, 1H), 7.16 (d, *J* = 7.5 Hz, 2H), 4.01 (s, 2H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 145.4, 140.2, 129.4, 129.1, 128.9, 128.7 (q, *J* = 32.2 Hz), 126.7, 125.6 (q, *J* = 3.9 Hz), 123.4, 41.9
^{19}F NMR ($CDCl_3$, 470.8 MHz): δ = -62.3
Characterization data matched that reported in the literature (*48*).



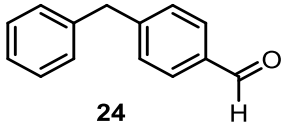
22

1-Benzyl-4-methoxybenzene (22): obtained as a colorless oil (74 mg, 75%)
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.31-7.28 (m, 2H), 7.22-7.19 (m, 3H), 7.12 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 3.95 (s, 2H), 3.80 (s, 3H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 158.1, 141.7, 133.4, 130.0, 129.0. 128.5, 126.1, 114.0, 55.4, 41.2
Characterization data matched that reported in the literature (*49*).



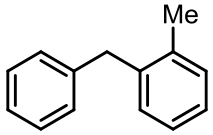
23

Methyl 3-Benzylbenzoate (**23)**: obtained as a pale yellow oil (102 mg, 90%)
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.93-7.89 (m, 2H), 7.40-7.35 (m, 2H), 7.32-7.30 (m, 2H), 7.24-7.20 (m, 3H), 4.04 (s, 2H), 3.91 (s, 3H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 167.3, 141.6, 140.7, 133.7, 130.5, 130.2, 129.0, 128.8, 128.7, 127.6, 126.5, 52.3, 41.9
Characterization data matched that reported in the literature (*50*).



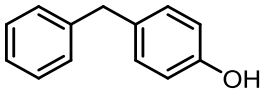
24

4-Benzylbenzaldehyde (24): obtained as a colorless oil (79 mg, 81%)
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 9.98 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.31 (dd, *J* = 7.5, 7.0 Hz, 2H), 7.24 (t, *J* = 7.0 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 2H), 4.06 (s, 2H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 192.1, 148.6, 139.9, 134.8, 130.2, 129.7, 129.1, 128.8, 126.7, 42.2.
Characterization data matched that reported in the literature (*29*).



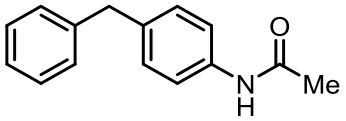
25

1-Benzyl-2-methylbenzene (**25)**: obtained as a colorless oil (51 mg, 56%)
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.30-7.27 (m, 2H), 7.21-7.11 (m, 7H), 4.01 (s, 2H) 2.26 (s, 3H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 140.6, 139.1, 136.8, 130.5, 130.2, 129.0, 128.6, 126.7, 126.2, 126.1, 39.7, 19.9
Characterization data matched that reported in the literature (*51*).



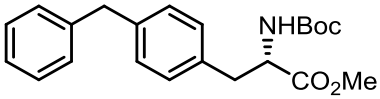
26

4-Benzylphenol (**26)**: obtained as a white solid (58 mg, 63%), Mp = 80-82 °C
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.32-7.29 (m, 2H), 7.23-7.18 (m, 3H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.76 (d, *J* = 8.0 Hz, 2H) 4.84 (s, 1H), 3.93 (s, 2H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 153.9, 141.7, 133.6, 130.3, 129.0, 128.6, 126.2, 115.5, 41.2
Characterization data matched that reported in the literature (*53*).



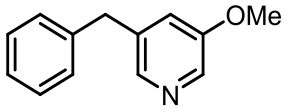
27

***N*-(4-Benzylphenyl)acetamide (27):** obtained as a white solid (107 mg, 96%), Mp = 117-119 °C
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.40 (d, *J* = 8.5 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.21-7.13 (m, 5H), 3.94 (s, 2H), 2.16 (s, 3H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): (* denotes minor rotamer) δ = 168.8, 141.0, 137.1, 136.0, 131.7*, 129.3, 129.0, 128.4, 126.0, 121.5*, 120.3, 41.3, 24.3
IR: ν = 3249, 3186, 3120, 2898, 2362, 1659, 1604, 1552, 1511, 1410, 1322, 1271, 850, 731 cm^{-1}
HRMS (ESI) m/z calc. for $C_{15}H_{16}NO$ (M+H) 226.1232, found 226.1235



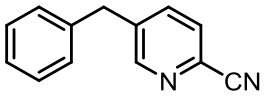
28

Methyl (*S*)-3-(4-Benzylphenyl)-2-((*tert*-butoxycarbonyl)amino)propanoate (28) obtained as a yellow oil after purification by preparatory reverse phase high pressure liquid chromatography (19 x 100 mm Waters XBridge Prep BHE130 C18 column, 10% → 90% MeCN/H_2O, 20 mL/min flow rate) (116 mg, 63%)
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.30-7.27 (m, 2H), 7.22-7.17 (m, 3H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 4.96 (d, *J* = 7.5 Hz, 1H), 4.57 (dd, *J* = 14.0, 6.0 Hz, 1H), 3.95 (s, 2H), 3.71 (s, 3H), 3.10-2.99 (m, 2H), 1.41 (s, 9H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 172.4, 155.2, 141.0, 139.0, 133.8, 129.5, 129.2, 129.0, 128.5, 126.2, 100.0, 79.9, 54.5, 52.2, 41.6, 38.0, 28.4
IR: ν = 3363, 2978, 2362, 1745, 1715, 1494, 1366, 1166 cm^{-1}
HRMS (ESI) m/z calc. for $C_{22}H_{27}NO_4Na$ (M+Na) 392.1838, found 392.1822
Chiral SFC (ChiralPak AD-H column: 10% MeOH in CO_2, 5.0 mL/min) t_r = 2.017 (major peak)



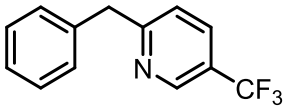
29

3-Benzyl-5-methoxypyridine (**29**): obtained as a dark yellow oil (74 mg, 75%)
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.17 (s, 1H), 8.13 (s, 1H), 7.31-7.28 (m, 2H), 7.23-7.17 (m, 3H), 6.97 (s, 1H), 3.96 (s, 2H), 3.80 (s, 3H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 147.9, 145.9, 138.0, 132.3, 130.1, 129.5, 121.2, 120.4 (q, *J* = 257.3 Hz), 118.7, 110.3, 41.1
IR: ν = 3027, 2940, 2838, 1586, 1426, 1281, 1184, 1156, 1051, 843, 718, 669 cm^{-1}
HRMS (ESI) m/z calc. for $C_{13}H_{14}NO$ (M+H) 200.1075, found 200.1066



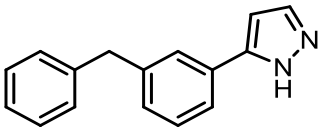
30

5-Benzylpicolinonitrile (30): obtained as a colorless oil (87 mg, 90%)
^{1}H NMR: ($CDCl_3$, 500 MHz): δ = 8.60 (s, 1H), 7.60 (m, 2H), 7.33 (dd, *J* = 7.0, 7.0 Hz, 2H), 7.27 (m, 1H), 7.16 (d, *J* = 7.0 Hz, 2H), 4.06 (s, 2H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 151.7, 141.1, 138.3, 137.2, 131.8, 129.2, 129.1, 128.4, 127.2, 117.5, 39.2
IR: ν = 3027, 2920, 2851, 2362, 2234, 1586, 1566, 1496, 1470, 1454, 1392, 1027, 741, 706 cm^{-1}
HRMS (ESI) m/z calc. for $C_{13}H_{11}N_2$ (M+H) 195.0922, found 195.0924



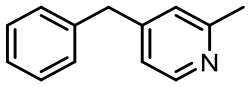
31

2-Benzyl-5-(trifluoromethyl)pyridine (**31)**: obtained as a colorless oil (77 mg, 65%)
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.84 (s, 1H), 7.82 (d, *J* = 7.0 Hz, 1H), 7.34-7.32 (m, 2H), 7.28-7.24 (m, 4H), 4.25 (s, 2H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 165.2, 146.5 (d, *J* = 3.5 Hz), 138.6, 133.8, 129.3, 129.0, 127.0, 124.6 (q, *J* = 33.2), 123.9 (q, *J* = 271.9), 122.9, 44.8
^{19}F NMR ($CDCl_3$, 470.8 MHz): δ = -62.3
IR: ν = 3030, 2360, 1605, 1495, 1322, 1327, 1124, 1017, 735 cm^{-1}
HRMS (ESI) m/z calc. for $C_{13}H_{11}F_3N$ (M+H) 208.0844, found 208.0842



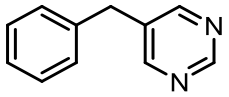
32

5-(3-Benzylphenyl)-1H-pyrazole (32): obtained as a white solid (76 mg, 65%), Mp = 78-79 °C
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 11.46 (br s, 1H), 7.63 (s, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 2 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.31-7.27 (m, 2H), 7.22-7.19 (m, 3H), 7.16 (d, *J* = 7.5 Hz, 2H), 6.58 (d, *J* = 1.5 Hz, 1H), 4.01 (s, 2H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 141.8, 141.0, 133.3, 132.4, 129.10, 129.09, 128.9, 128.7, 126.5, 126.3, 125.9, 123.8, 102.9, 42.1
IR: ν = 3166, 3068, 2919, 2850, 1559, 1494, 1472, 1452, 1357, 1052, 822, 771, 706 cm^{-1}
HRMS (ESI) m/z calc. for $C_{16}H_{15}N_2$ (M+H) 235.1235, found 235.1235



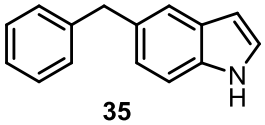
33

4-Benzyl-2-methylpyridine (33): obtained as a light yellow oil (52 mg, 57%)
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.38 (d, *J* = 5.0 Hz, 1H), 7.32 (m, 2H), 7.25 (m, 1 H), 7.17 (d, *J* = 7.0 Hz, 2H), 6.97 (s, 1H), 6.91 (d, *J* = 5.0 Hz, 1H), 3.92 (s, 2H), 2.51 (s, 3H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 158.6, 150.4, 149.3, 139.3, 129.2, 128.8, 126.7, 123.8, 121.5, 41.4, 24.5
IR: ν = 3027, 2923, 2358, 1600, 1558, 1495, 1453, 734, 699 cm^{-1}
HRMS (ESI) m/z calc. for $C_{13}H_{14}N$ (M+H) 184.1126, found 184.1117



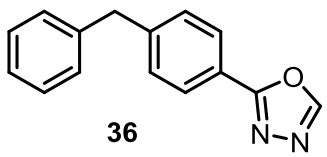
34

5-Benzylpyrimidine (**34)**: obtained as yellow crystals (82 mg, 96%), Mp = 45-47 °C
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 9.07 (s, 1H), 8.57 (s, 2H), 7.33-7.30 (m, 2H) 7.25-7.22 (m, 2H) 7.17-7.15 (m, 2H), 3.95 (s, 2H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 157.15, 157.08, 138.4, 134.4, 129.1, 128.9, 127.1, 36.7
IR: ν = 3032, 2916, 2850, 1560, 1408, 1230, 1100, 987, 924, 749, 729 cm^{-1}
HRMS (ESI) m/z calc. for $C_{11}H_{11}N_2$ (M+H) 171.0922, found 171.0919



35

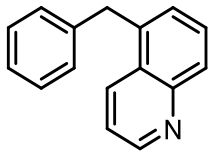
5-Benzyl-1H-indole (35): obtained in pure form as a white solid (57 mg, 55%), Mp = 40-42 °C, and as a mixture with aryl bromide starting material [30 mg (mass of mixture), 18% (based on ^{1}H NMR purity analysis)]
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.99 (br s, 1H), 7.50 (s, 1H), 7.33-7.21 (m, 6H), 7.16 (d, *J* = 2.5 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.52 (s, 1H), 4.13 (s, 2H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 142.3, 134.4, 132.5, 128.9, 128.3, 128.1, 125.8, 124.3, 123.5, 120.6, 110.9, 102.4, 42.0
IR: ν = 3401, 2923, 2853, 2358, 1453, 1338, 1090, 1028, 762, 730, 699 cm^{-1}
HRMS (ESI) m/z calc. for $C_{15}H_{14}N$ (M+H) 208.1126, found 208.1135



36

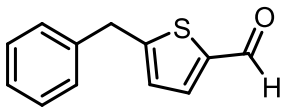
2-(4-Benzylphenyl)-1,3,4-oxadiazole (36): obtained as a yellow solid (85 mg, 72%), Mp = 71-73 °C

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.43 (s, 1H), 8.00 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 7.5 Hz, 2H), 7.25-7.19 (m, 3H), 4.06 (s, 2H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 164.9, 152.6, 145.8, 140.1, 129.8, 129.1, 128.8, 127.4, 126.6, 121.5, 42.0
IR: ν = 2924, 2854, 1614, 1493, 1094, 1065, 865, 712 cm^{-1}
HRMS (ESI) m/z calc. for $C_{15}H_{13}N_2O$ (M+H) 237.1028, found 237.1034



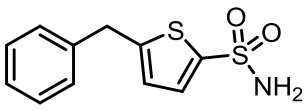
37

5-Benzylquinoline (37): obtained as a white solid (64 mg, 58%), Mp = 80-81 °C
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.90 (dd, *J* = 4, 1.5 Hz, 1H), 8.30 (d, *J* = 8.5 Hz, 1H), 8.04 (d, *J* = 8.5 Hz, 1H), 7.67 (dd, *J* = 8.4, 7.2 Hz, 1H), 7.61-7.24 (m, 4H), 7.13 (m, 3H), 4.45 (s, 2H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 149.9, 148.8, 140.0, 137.0, 132.5, 129.1, 128.5, 127.7, 127.1, 126.2, 120.8, 38.4
Characterization data matched that reported in the literature (*52*).



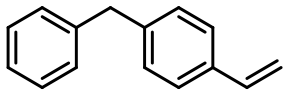
38

5-Benzylthiophene-2-carbaldehyde (38): obtained as a colorless oil (55 mg, 54%)
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 9.81 (s, 1H), 7.60 (d, *J* = 3.5 Hz, 1H), 7.35-7.32 (m, 2H), 7.28-7.24 (m, 3H), 6.90 (d, *J* = 3.5 Hz, 1H), 4.19 (s, 2H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 182.8, 155.9, 142.6, 138.9, 137.0, 129.0, 128.8, 127.2, 126.8, 37.0
Characterization data matched that reported in the literature (*53*).



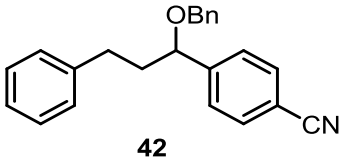
39

5-Benzylthiophene-2-sulfonamide (39): obtained as a white solid (71 mg, 56%), Mp =89-90 °C
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.78 (d, *J* = 3.5 Hz, 1H), 7.34 (m, 2H), 7.29-7.23 (m, 3 H), 6.76 (d, *J* = 3.5 Hz, 1H), 4.93 (s, 2H), 4.15 (s, 2H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 152.1, 140.8, 138.9, 132.1, 129.0, 128.8, 127.3, 125.5, 36.5
IR: ν = 3382, 3276, 3109, 2918, 1566, 1443, 1330, 1163, 1142, 1020, 908, 704 cm^{-1}
HRMS (ESI) m/z calc. for $C_{11}H_{10}NO_2S_2$ (M-H) 252.0153, found 252.0164



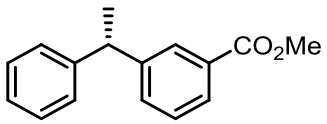
40

1-Benzyl-4-vinylbenzene (40): obtained as a colorless oil (59 mg, 61%)
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.38-7.27 (m, 4H), 7.23–7.18 (m, 5H), 6.73 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.74 (d, *J* = 17.5, 1H), 5.23 (d, *J* = 11.0, 1H), 4.01 (s, 2H)22
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 140.9, 140.7, 136.5, 135.5, 129.0, 128.8, 128.4, 126.3, 126.0, 113.1, 41.6
Characterization data matched that reported in the literature (*51*).



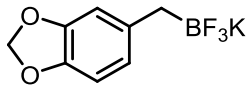
42

4-(1-(benzyloxy)-3-phenylpropyl)benzonitrile (42): prepared using the general procedure for primary benzyl cross-couplings, obtained as a colorless oil (106 mg, 65%)
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.67 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.40-7.37 (m, 2H), 7.34-7.32 (m, 3H), 7.30-7.26 (m, 2H), 7.22-7.18 (m, 1H), 7.14 (d, *J* = 7.5 Hz, 2H), 4.46 (d, *J* = 11.5 Hz, 1H), 4.38 (dd, *J* = 8.5, 4.5 Hz, 1H), 4.29 (d, *J* = 11.5 Hz, 1H), 2.83-2.77 (m, 1H), 2.72-2.67 (m, 1H), 2.19-2.14 (m, 1H), 1.97-1.92 (m, 1H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 148.2, 141.3, 137.9, 132.4, 128.5, 128.40, 128.38, 127.78, 127.76, 127.3, 125.9, 118.8, 111.4, 79.8, 71.0, 39.8, 31.8
IR: ν = 3028, 2924, 2228, 1607, 1496, 1094, 853, 698, 737 cm^{-1}
HRMS (ESI) m/z calc. 328.1701 for (M+H), found 328.1709



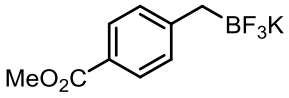
45

Methyl 3-(1-Phenylethyl)benzoate (45): obtained as a colorless oil (62 mg, 52%)
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.96 (m, 1H), 7.87 (m, 1H), 7.41-7.28 (m, 4H), 7.22-7.18 (m, 3H), 4.21 (q, *J* = 7.5 Hz, 1H), 3.90 (s, 3H), 1.67 (d, *J* = 7.5 Hz, 3H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 167.4, 146.9, 145.9, 132.5, 130.4, 128.8, 128.64, 128.61, 127.7, 127.6, 126.4, 52.2, 44.8, 21.9
$[\alpha_D]^{25}$ = -4.4 ($CDCl_3$, c = 1.0 mg/mL)
Chiral SFC (ChiralPak OJ-H column: 5% iPrOH in CO_2, 2.0 mL/min) t_r = 8.37 (minor peak) t_r = 9.17 (major peak) Absolute configuration of the major enantiomer was assigned as (*S*) based on literature data (*54*).
Characterization data matched that reported in the literature (*54*).



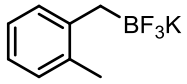
S5

Potassium (Benzo[d][1,3]dioxol-5-ylmethyl)trifluoroborate (S5): prepared following general procedure A, obtained as a white solid (498 mg, 41%), Mp = 258 °C (dec.)
^{1}H NMR (acetone-d_6, 500 MHz): δ = 6.65 (s, 1H), 6.54-6.50 (m, 2H), 5.79 (s, 2H), 1.55 (br s, 2H)
^{13}C NMR (DMSO-d_6, 125.8 MHz): δ = 146.8, 143.1, 141.2, 121.2, 109.8, 107.7, 100.3
^{19}F NMR (acetone-d_6, 282.4 MHz): δ = -136.3 (q, *J* = 70.6 Hz)
^{11}B NMR (acetone-d_6, 128.4 MHz): δ = 4.12 (q, *J* = 50.2 Hz)
IR: ν = 3067, 1482, 1436, 1230, 1040, 960, 775, 630 cm^{-1}
HRMS (ESI) m/z calc. for $C_8H_7O_2BF_3$ (M-) 203.0491, found 203.0486



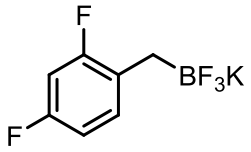
S6

Potassium Trifluoro(4-(methoxycarbonyl)benzyl)borate (S6): prepared following general procedure B, obtained as a white solid (706 mg, 55%), Mp = 205°C (dec.)
^{1}H NMR (acetone-d_6, 500 MHz): δ = 7.73 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 3.81 (s, 3H), 1.75 (br s, 2H)
^{13}C NMR (acetone-d_6, 125.8 MHz): δ = 166.9, 153.7, 128.5, 128.3, 124.3, 50.7
^{19}F NMR (acetone-d_6, 470.8 MHz): δ = -140.7 (q, *J* = 55.6 Hz)
^{11}B NMR (acetone-d_6, 128.4 MHz): δ = 4.70 (q, *J* = 57.9 Hz)
IR: ν = 3038, 1690, 1607, 1444, 1293, 1233, 1056, 993, 959, 782, 720, 642
HRMS: (ESI) m/z calc. for $C_9H_9O_2BF_3$ (M-) 217.0648, found 217.0647



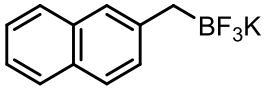
S7

Potassium Trifluoro(2-methylbenzyl)borate (S7): prepared following general procedure A, obtained as a white solid (850 mg, 80%), Mp = 230 °C (dec.)
^{1}H NMR (acetone-d_6, 500 MHz): δ = 7.05 (d, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 7.5 Hz, 1H), 6.90-6.87 (m, 1H), 6.81-6.78 (m, 1H), 2.24 (s, 3H), 1.66 (br s, 2H)
^{13}C NMR (acetone-d_6, 125.8 MHz): δ = 145.0, 135.3, 129.4, 129.0, 124.8, 122.5, 19.9
^{19}F NMR (acetone-d_6, 470.8 MHz): δ = -138.3
^{11}B NMR (acetone-d_6, 128.4 MHz): δ = 5.27 (q, *J* = 51.0 Hz)
IR: ν = 2941, 1488, 1228, 1049, 975, 781, 734, 636 cm^{-1}
HRMS (ESI) m/z calc. for $C_8H_9BF_3$ (M-) 173.0749, found 173.0753



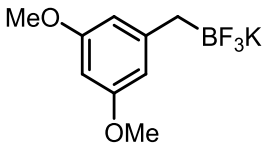
S8

Potassium (2,4-Difluorobenzyl)trifluoroborate (S8): prepared following general procedure A, obtained as a white solid (422 mg, 36%), Mp = 225-227 °C
^{1}H NMR (acetone-d_6, 500 MHz): δ = 7.23 (q, *J* = 7.5 Hz, 1H), 6.70-6.66 (m, 2H), 1.59 (br s, 2H)
^{13}C NMR (acetone-d_6, 125.8 MHz): δ = 160.7 (dd, *J* = 131, 11 Hz), 158.8 (dd, *J* = 129, 11 Hz), 131.7 (t, *J* = 8 Hz), 128.0 (d, *J* = 17 Hz), 109.7 (dd, *J* = 20, 3 Hz), 102.0 (dd, *J* = 28, 25 Hz), 18.5
^{19}F NMR (acetone-d_6, 470.8 MHz): δ = -114.9, -119.4, -139.9
^{11}B NMR (acetone-d_6, 128.4 MHz): δ = 4.98
IR: ν = 2928, 1622, 1601, 1504, 1253, 1087, 1071, 986, 949, 846 cm^{-1}
HRMS (ESI) m/z calc. for $C_7H_5BF_5$ (M-) 195.0404, found 195.0402



S9

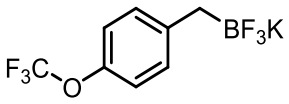
Potassium Trifluoro(naphthalen-2-ylmethyl)borate (S9): prepared following general procedure A, obtained as a white solid (323 mg, 26%), Mp: 199-202 °C
^{1}H NMR (acetone-d_6, 500 MHz): δ = 7.70 (d, *J* = 8.1 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.49 (s, 1H), 7.38 (d, *J* = 8.5 Hz, 1H), 7.35-7.28 (m, 1H), 7.27-7.21 (m, 1H), 1.81 (br s, 2H)
^{13}C NMR (acetone-d_6, 125.8 MHz): δ = 144.0, 134.0, 130.9, 129.4, 127.3, 126.8, 126.3, 125.4, 124.9, 123.3
^{19}F NMR (acetone-d_6, 470.8 MHz): δ = -139.1
^{11}B NMR (acetone-d_6, 128.4 MHz): δ = 5.34
IR: ν = 3054, 2891, 1631, 1597, 1505, 1239, 1074, 953, 746
HRMS (ESI) m/z calc. for $C_{11}H_9BF_3$ (M-) 209.0749, found 209.0749



S10

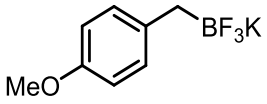
Potassium (3,5-Dimethoxybenzyl)trifluoroborate (S10): prepared following general procedure A, obtained as a white solid (809 mg, 63%), Mp: 220-222 °C
^{1}H NMR (DMSO-d_6, 500 MHz): δ = 6.16 (s, 2H), 6.02 (s, 1H), 3.64 (s, 6H), 1.40 (br s, 2H)
^{13}C NMR (DMSO-d_6, 125.8 MHz): δ = 159.4, 149.3, 106.7, 94.5, 54.6
^{19}F NMR (DMSO-d_6, 470.8 MHz): δ = -136.3

^{11}B NMR (DMSO-d_6, 128.4 MHz): δ = 4.20
IR: ν = 2837, 1614, 1588, 1315, 1240, 1156, 1147, 1068, 978, 934 cm^{-1}
HRMS (ESI) m/z calc. for $C_9H_{11}BF_3O_2$ (M-) 219.0804, found 219.0812



S11

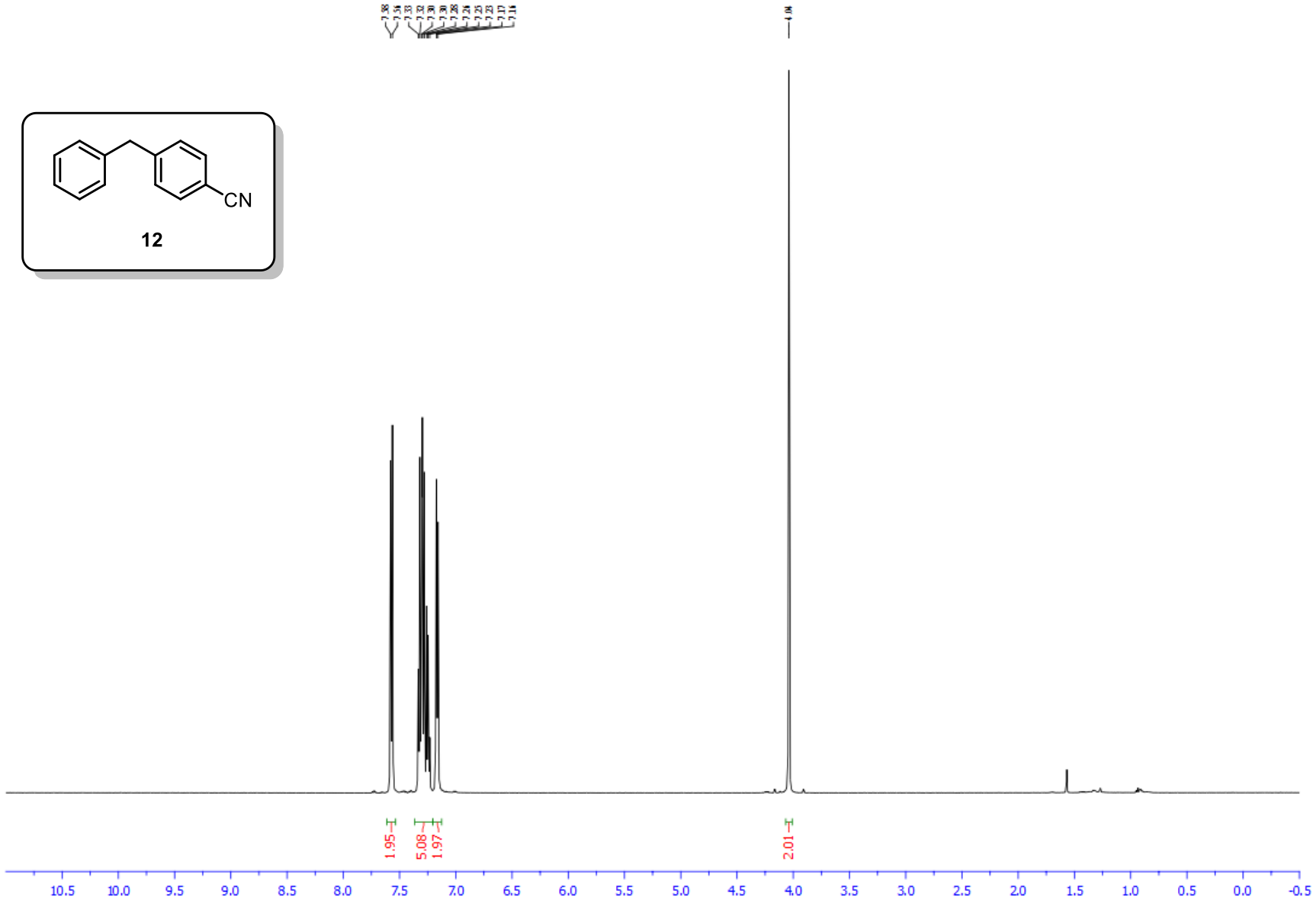
Potassium (3,5-Dimethoxybenzyl)trifluoroborate (S11): reaction performed on 3 mmol scale according to general procedure A, obtained as a white solid (466 mg, 55%), Mp = 165-168 °C
^{1}H NMR (acetone-d_6, 500 MHz): δ = 7.16 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 1.66 (br s, 2H)
^{13}C NMR (acetone-d_6, 125.8 MHz): δ = 146.7, 145.0, 130.0, 120.9 (q, *J* = 253 Hz), 119.8
^{19}F NMR (acetone-d_6, 470.8 MHz): δ = -59.0, -141.0 (q, *J* = 62 Hz)
^{11}B NMR (acetone-d_6, 128.4 MHz): δ = 4.88
Characterization data matched that reported in the literature (*38*).



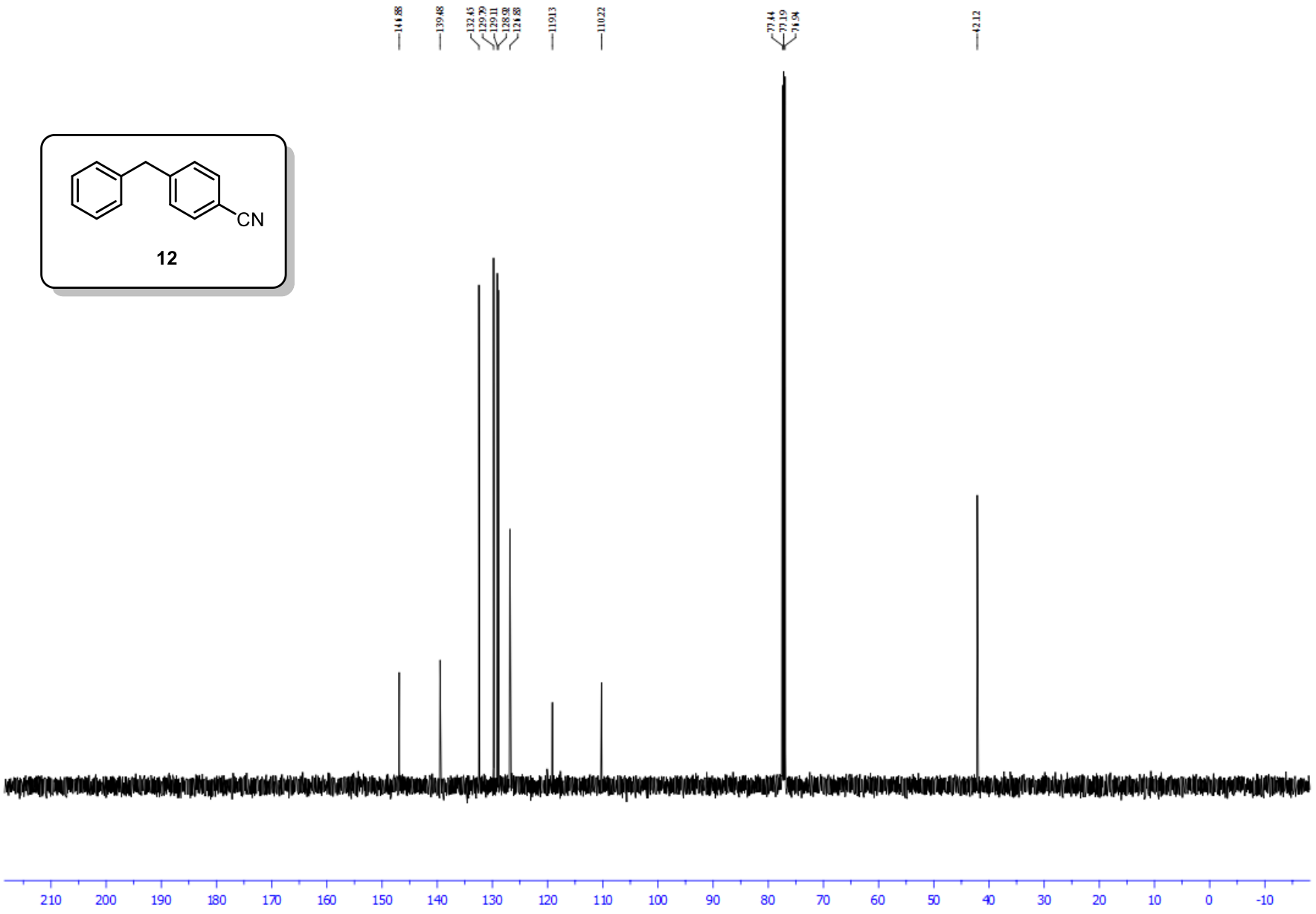
S12

Potassium Trifluoro(4-methoxybenzyl)borate (S12): prepared following general procedure A, obtained as a white solid (403 mg, 35%), Mp = 162-165 °C
^{1}H NMR (acetone-d_6, 500 MHz): δ = 7.01 (d, *J* = 8.0 Hz, 2H), 6.64 (d, *J* = 8.0 Hz, 2H), 3.68 (s, 3H), 1.56 (br s, 2H)
^{13}C NMR (acetone-d_6, 125.8 MHz): δ = 156.4, 138.0, 129.8, 113.3, 54.9
^{19}F NMR (acetone-d_6, 470.8 MHz): δ = -140.7 (q, *J* = 58.9 Hz)
^{11}B NMR (acetone-d_6, 128.4 MHz): δ = 5.14
Characterization data matched that reported in the literature (*28*).

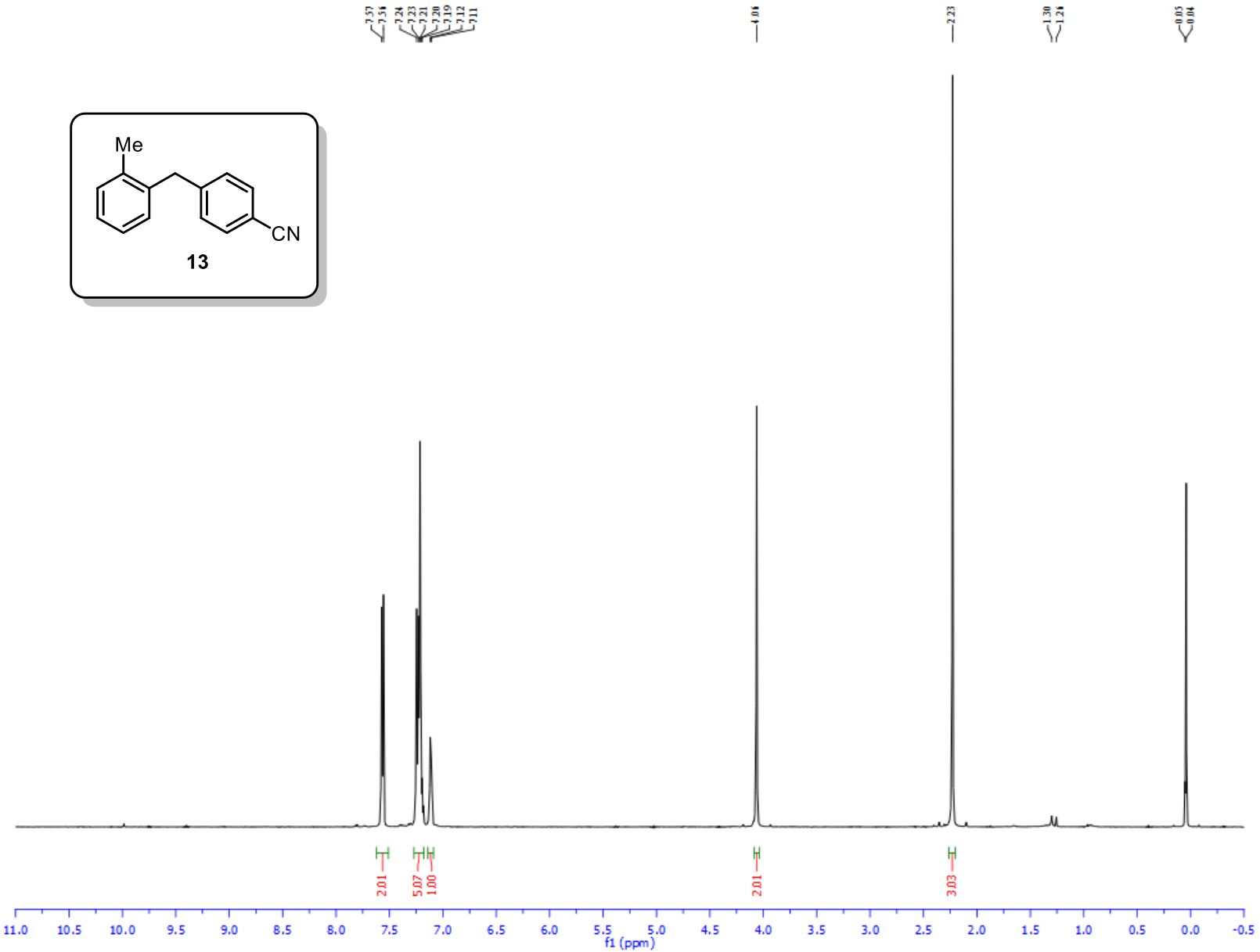
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 4-benzylbenzonitrile (**12**)



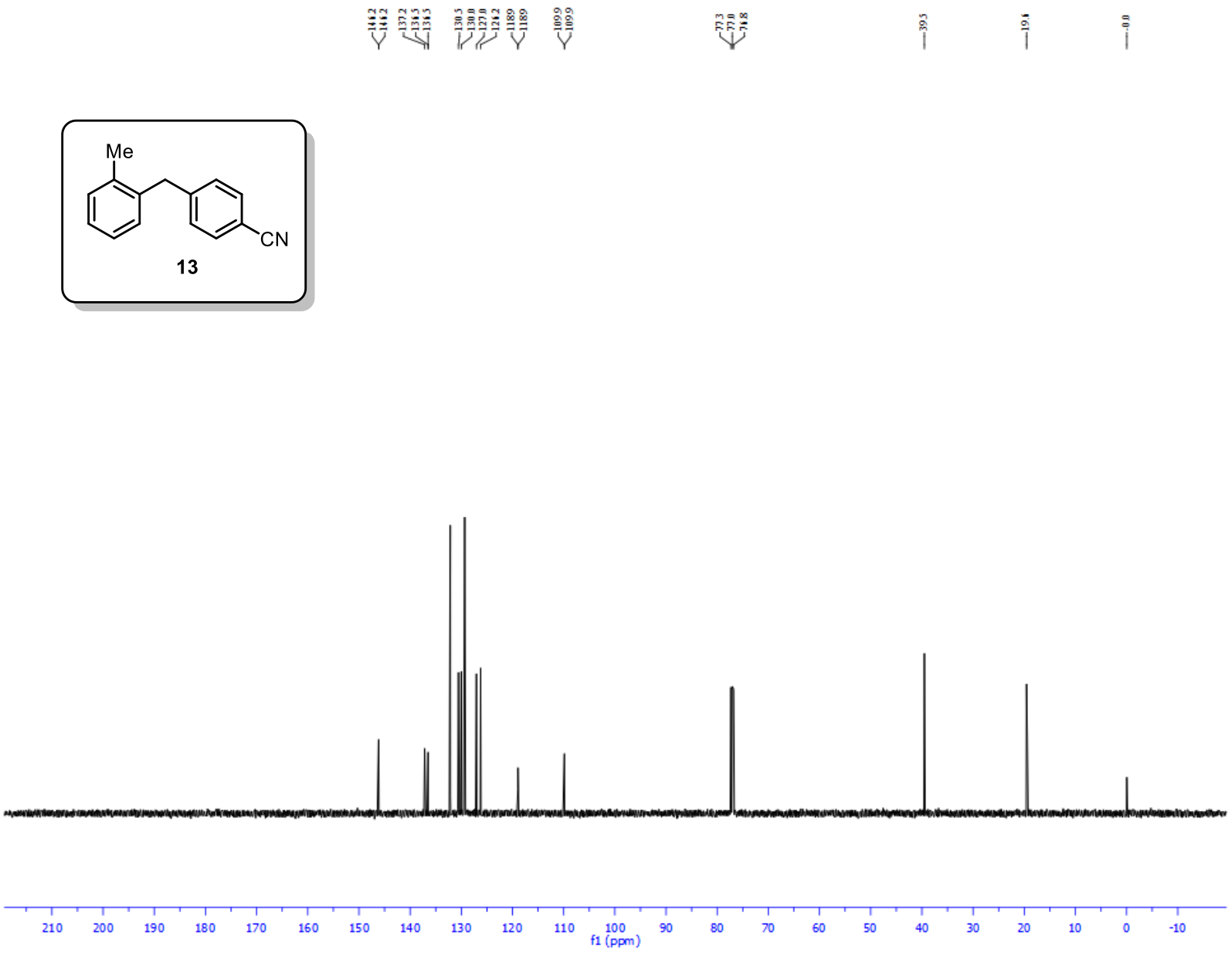
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 4-benzylbenzonitrile (**12**)



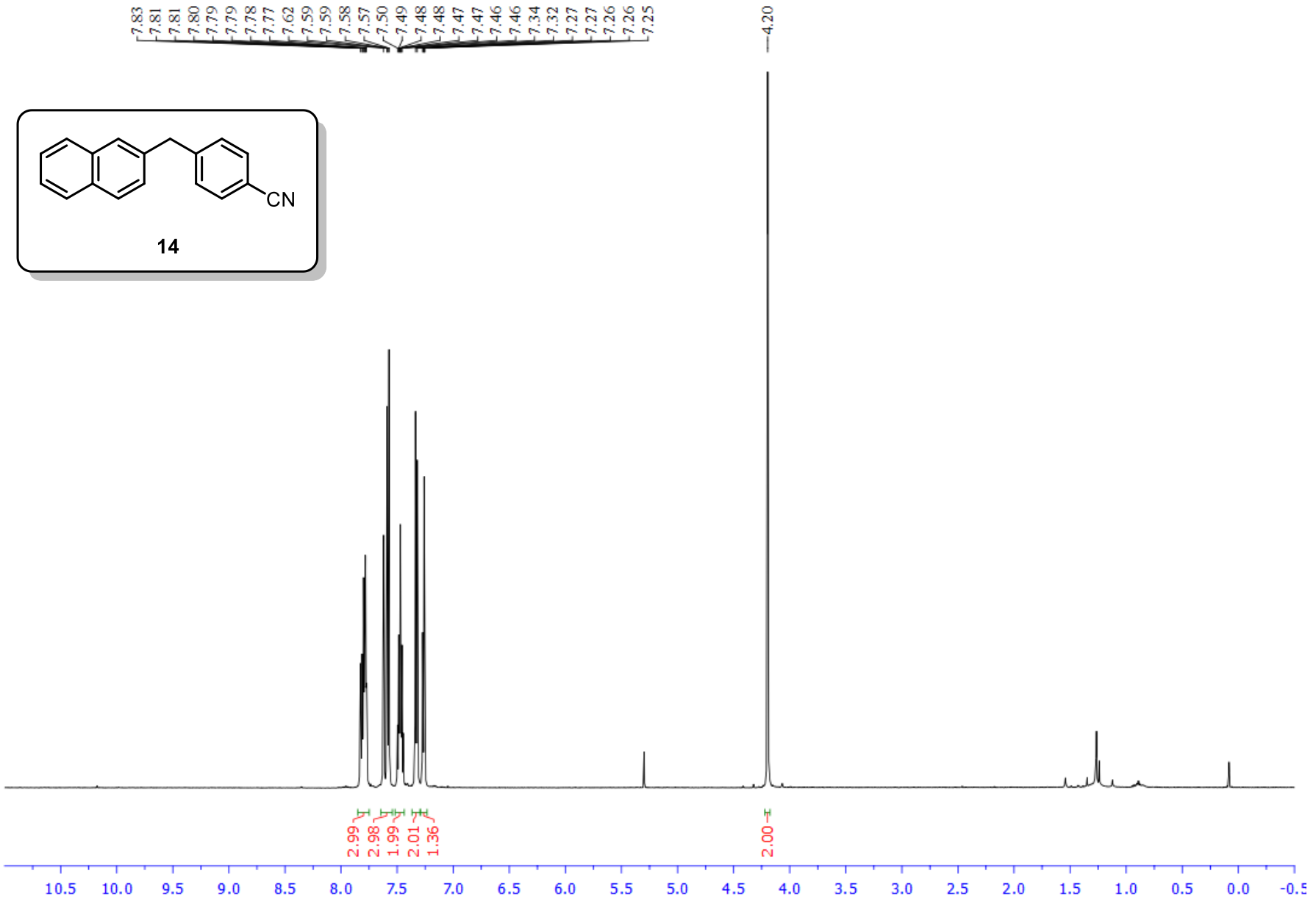
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 4-(2-methylbenzyl)benzonitrile (**13**)



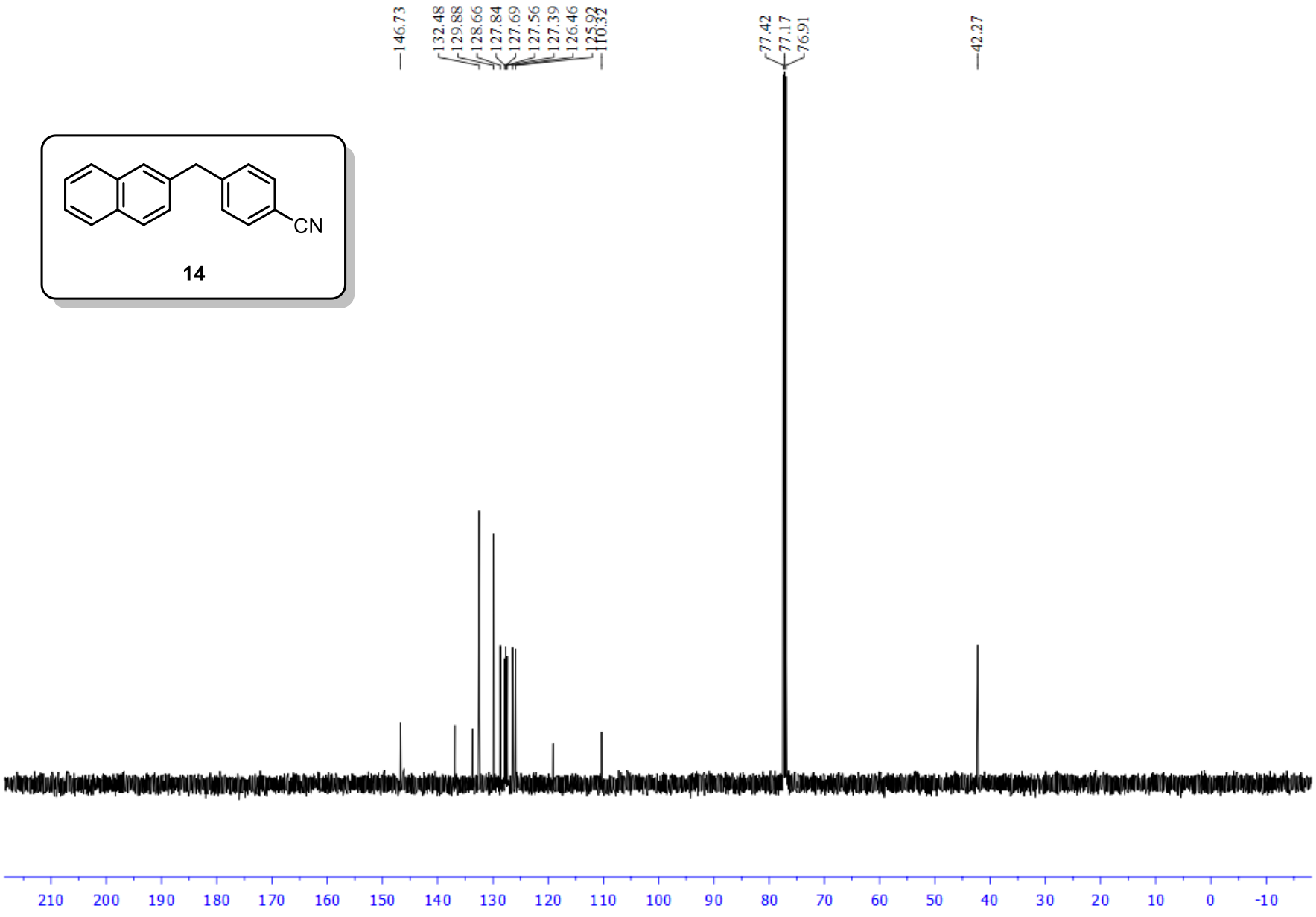
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 4-(2-methylbenzyl)benzonitrile (**13**)



^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 4-(naphthalen-2-ylmethyl)benzonitrile (**14**)

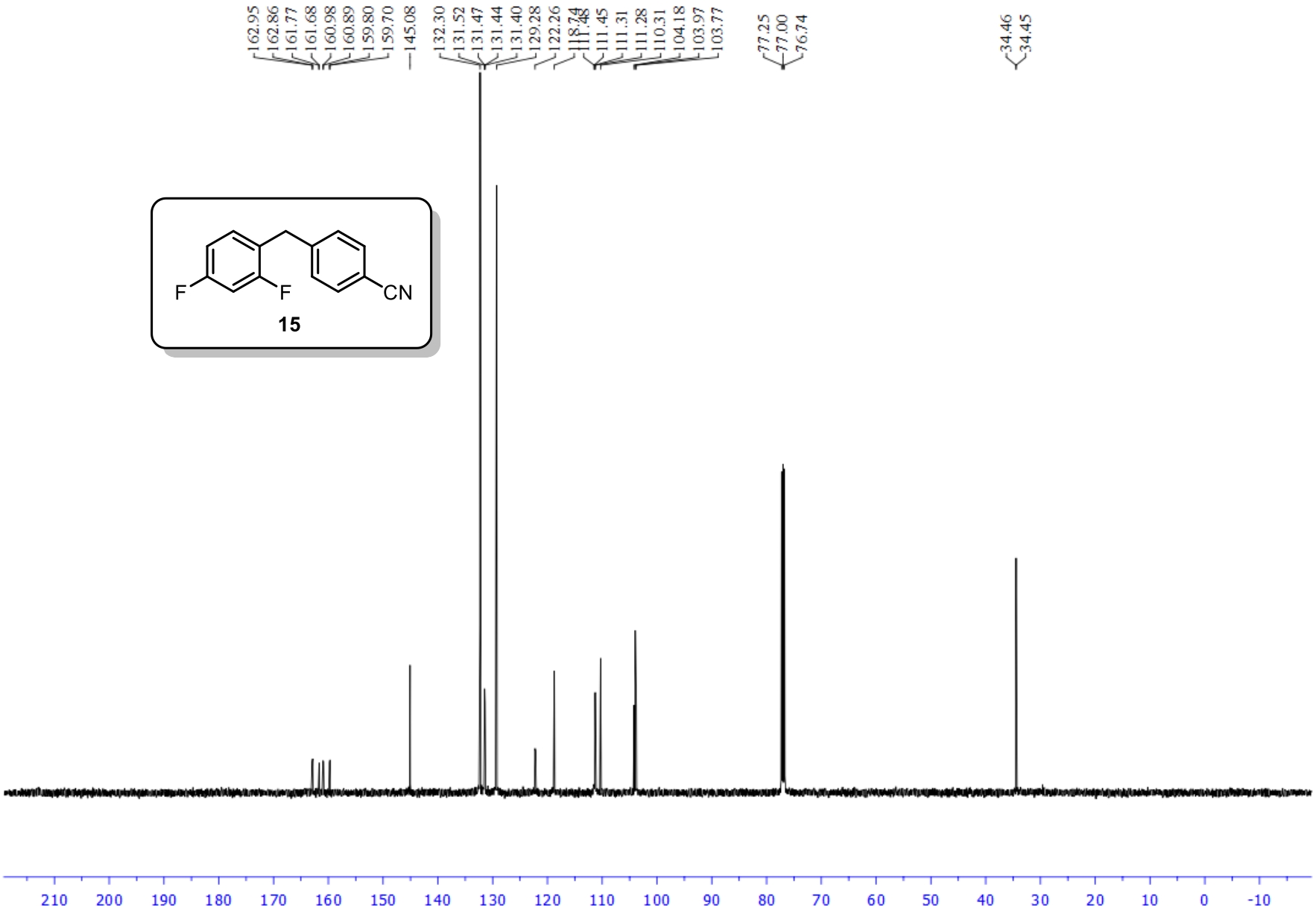


^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 4-(naphthalen-2-ylmethyl)benzonitrile (**14**)



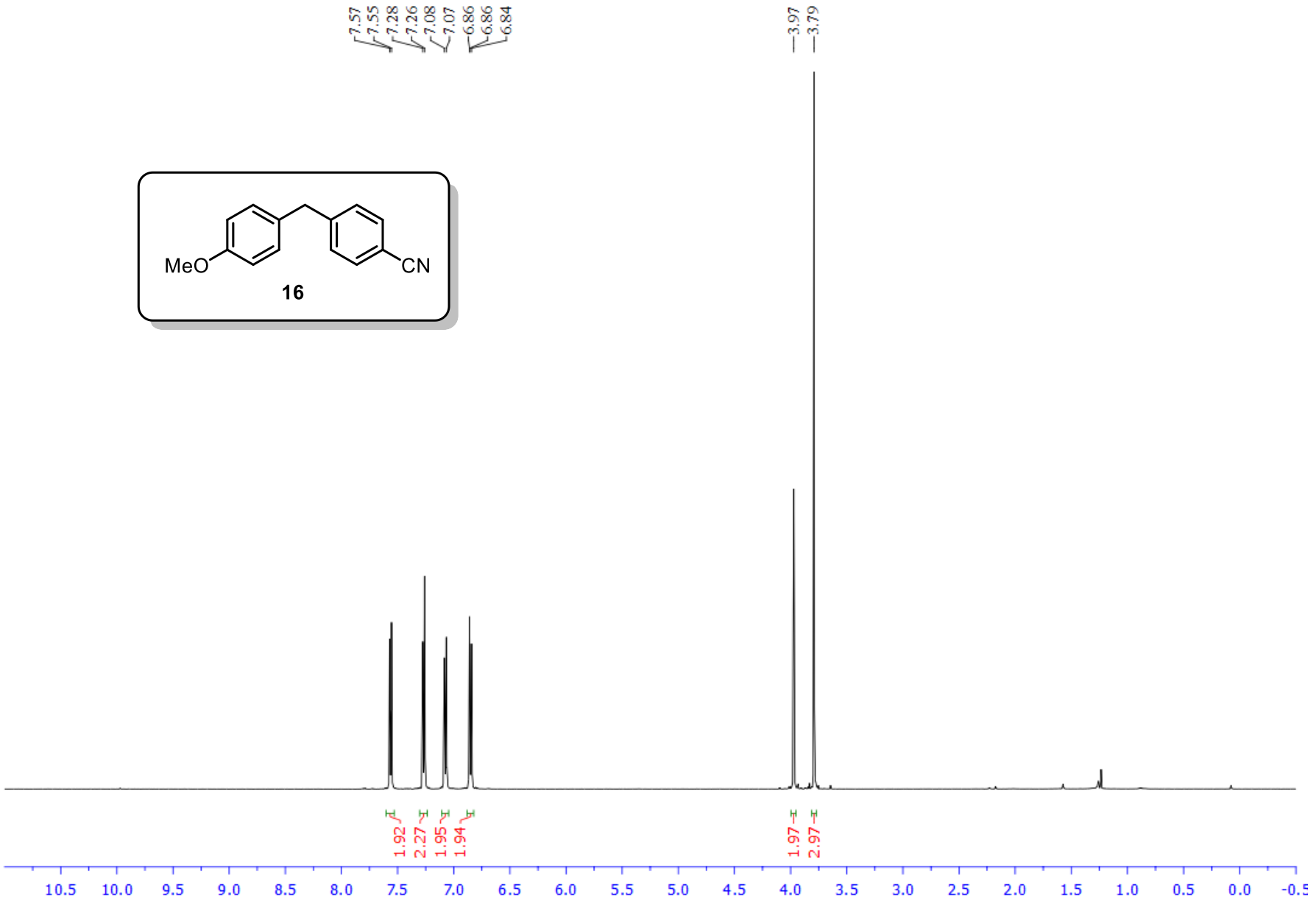
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 4-(2,4-difluorobenzyl)benzonitrile (**15**)

^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 4-(2,4-difluorobenzyl)benzonitrile (**15**)

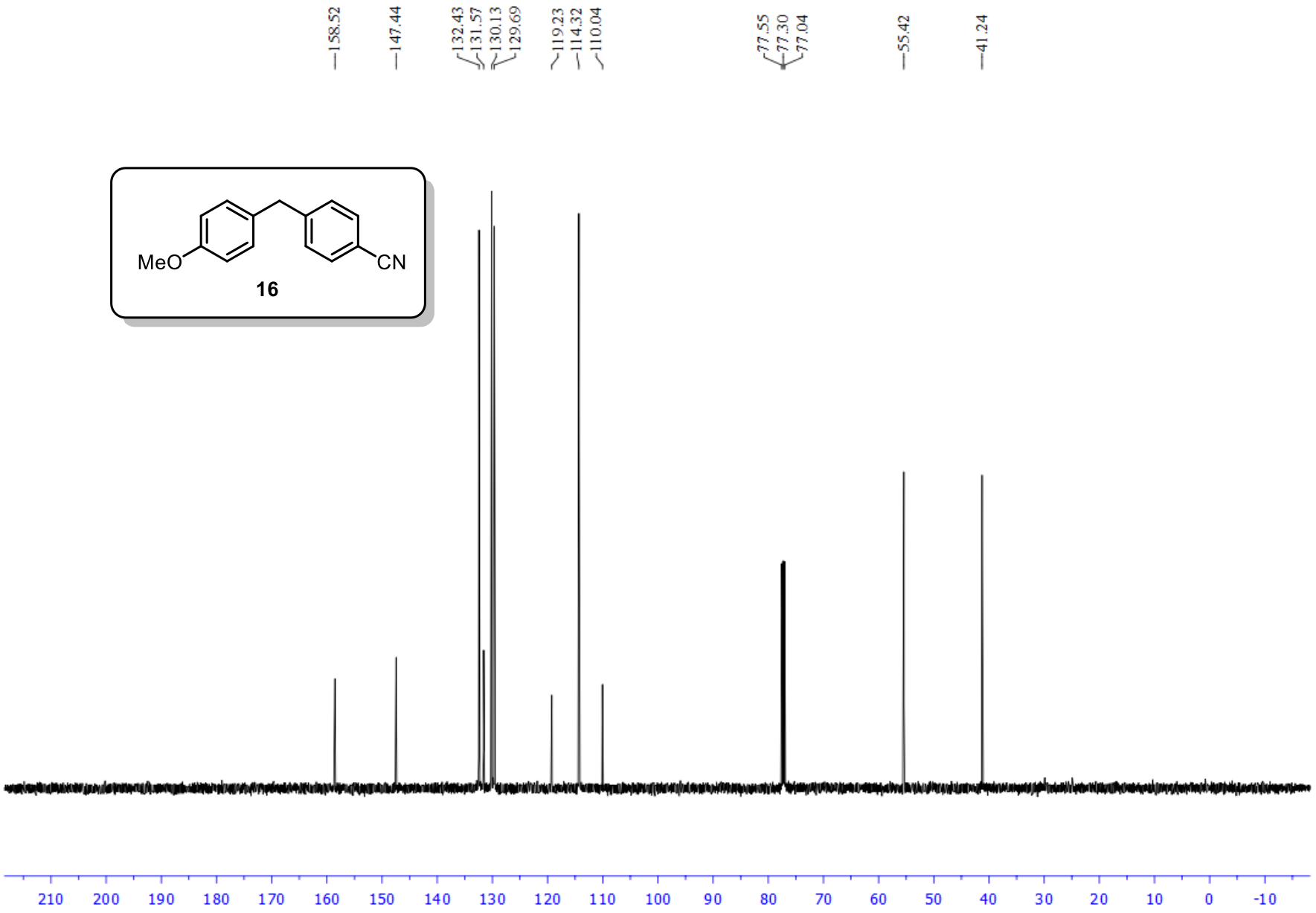


^{19}F NMR ($CDCl_3$, 470.8 MHz) spectrum of 4-(2,4-difluorobenzyl)benzonitrile (**15**)

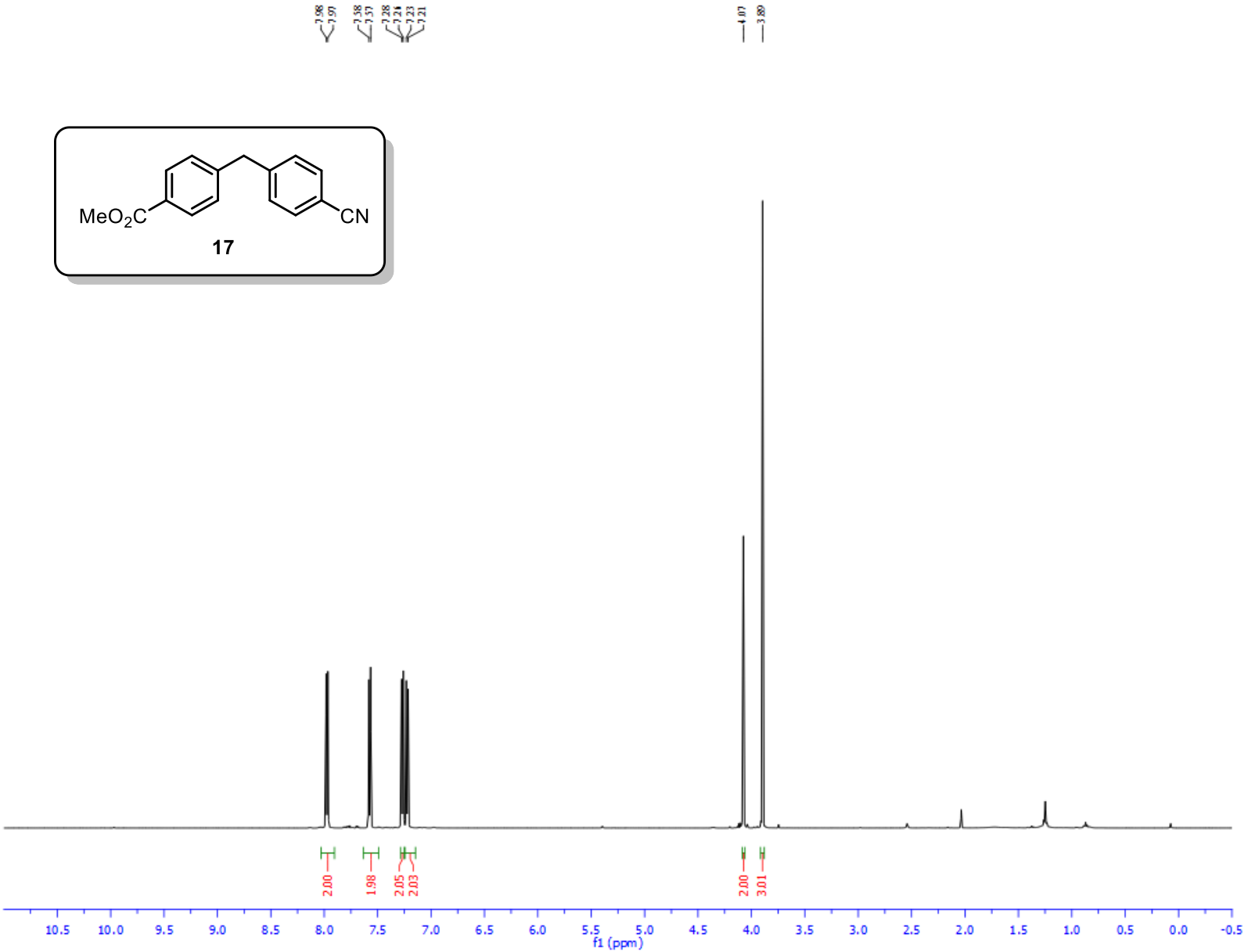
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 4-(4-methoxybenzyl)benzonitrile (**16**)



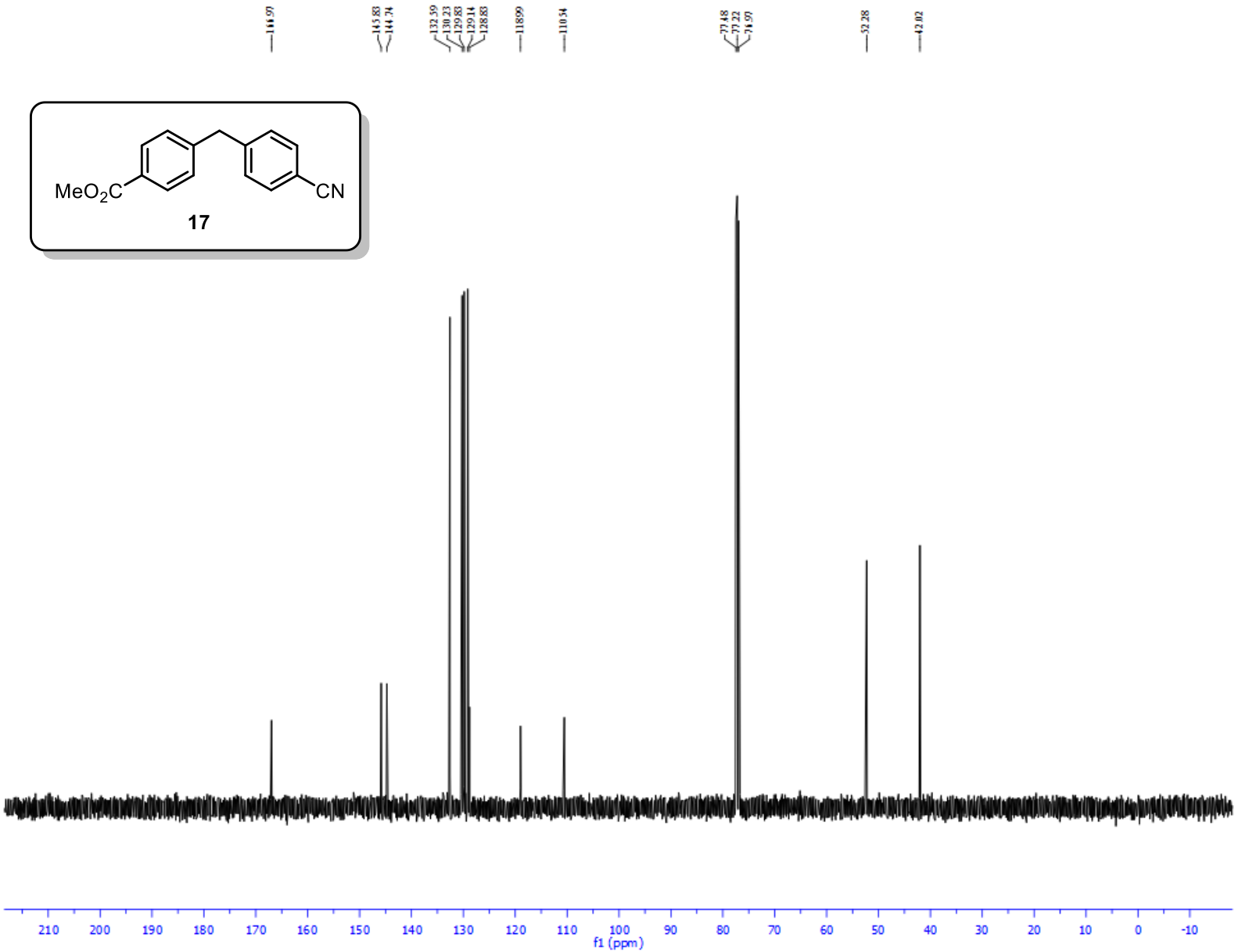
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 4-(4-methoxybenzyl)benzonitrile (**16**)



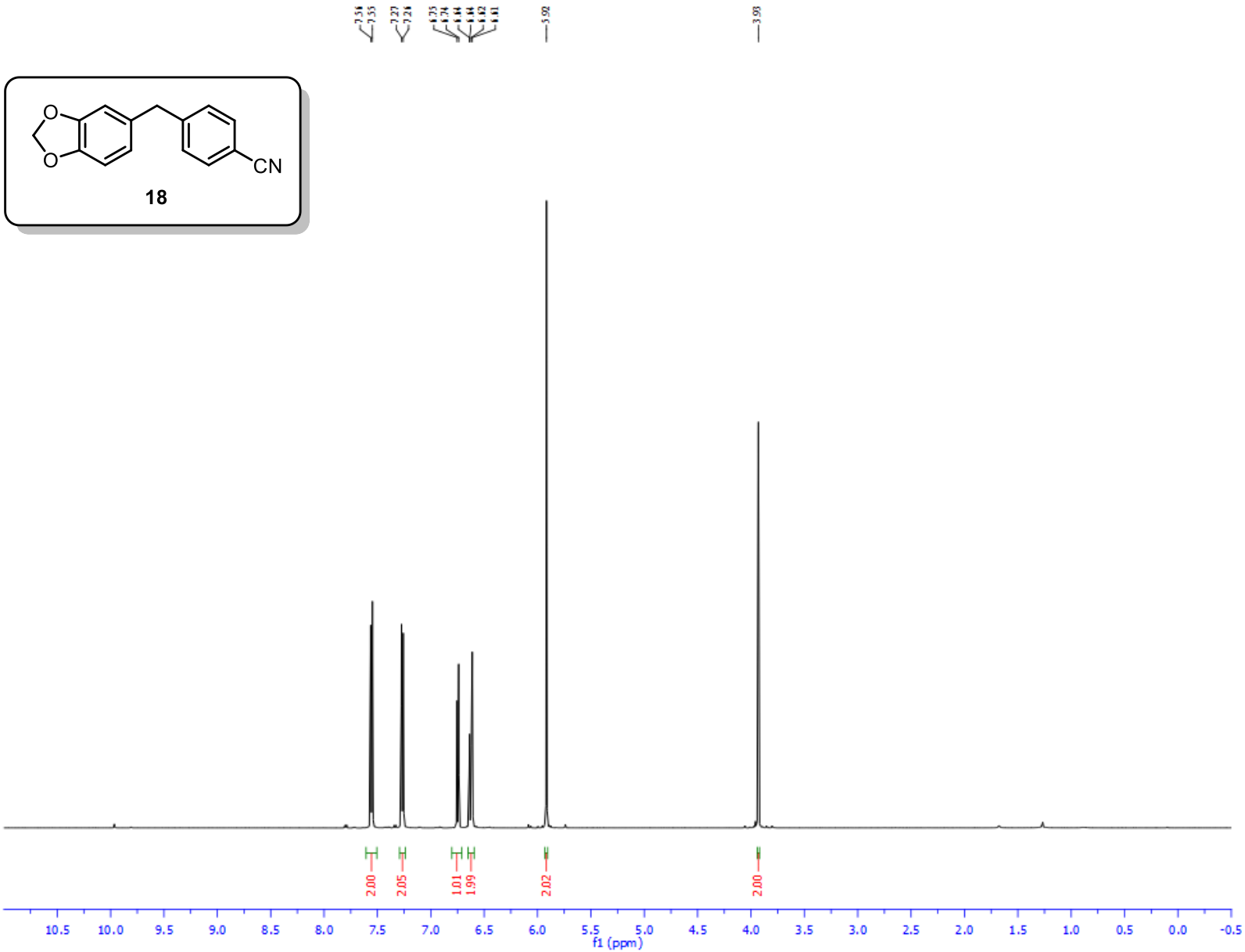
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of methyl 4-(4-cyanobenzyl)benzoate (**17**)



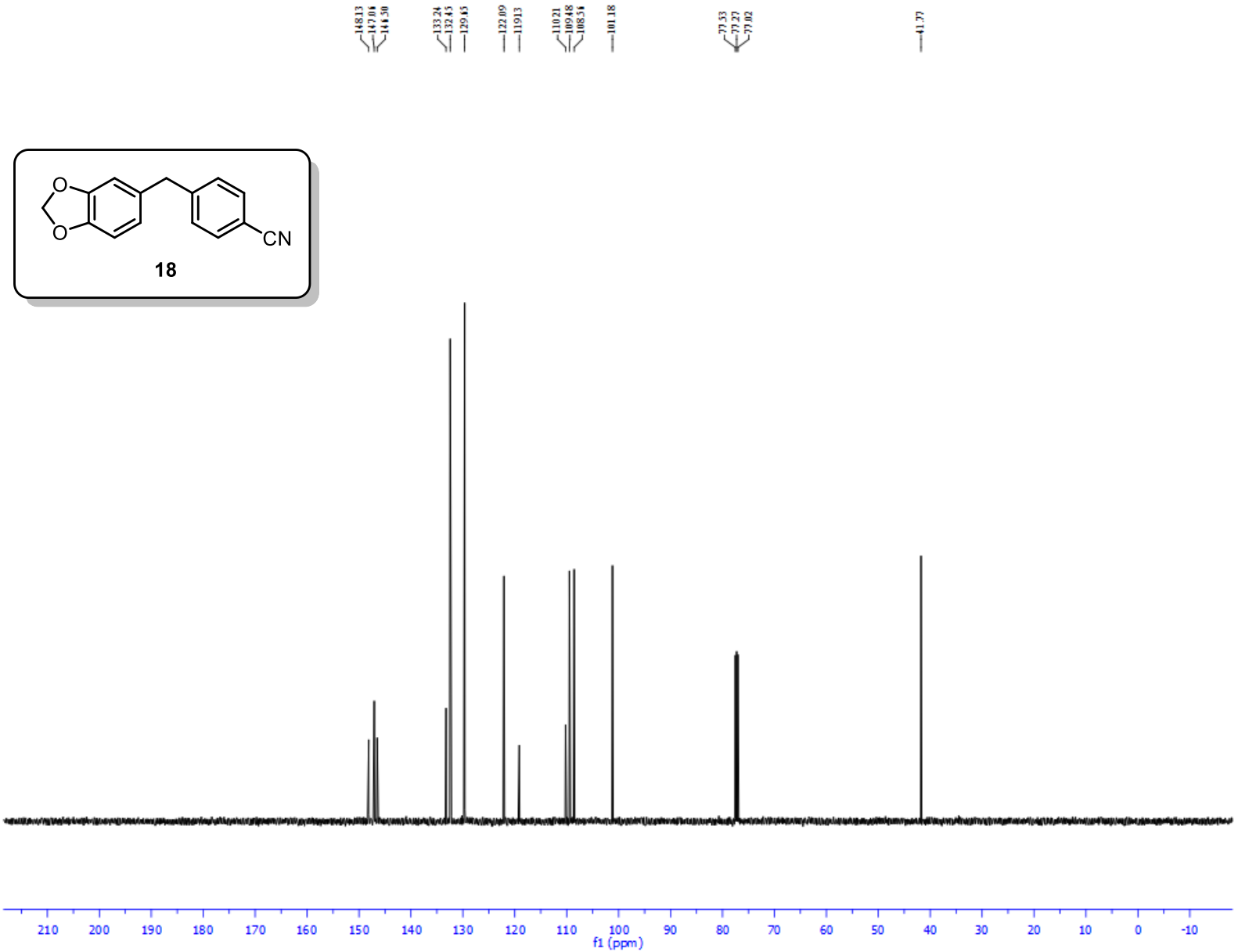
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of methyl 4-(4-cyanobenzyl)benzoate (**17**)



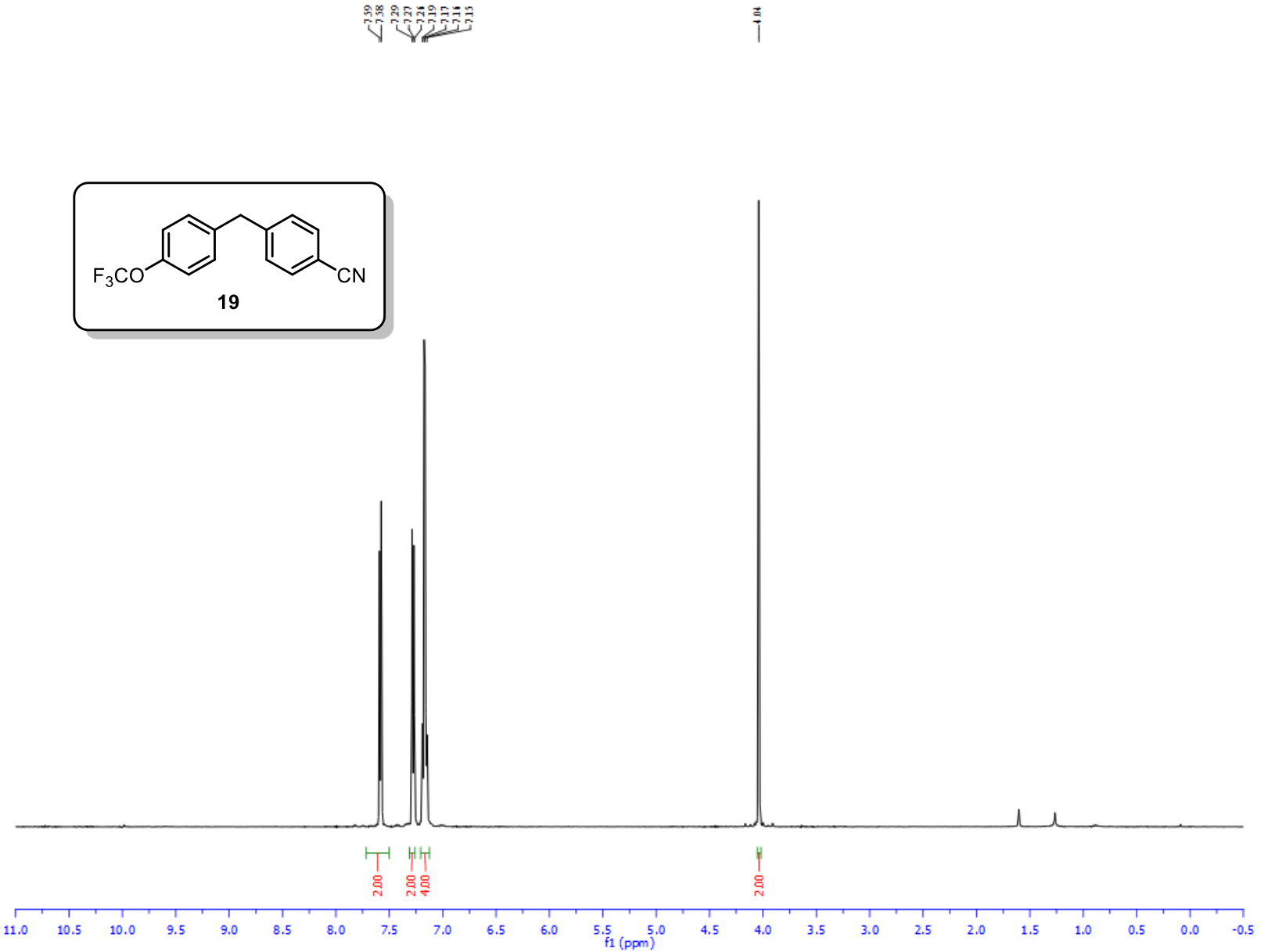
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 4-(benzo[d][1,3]dioxol-5-ylmethyl)benzonitrile (**18**)



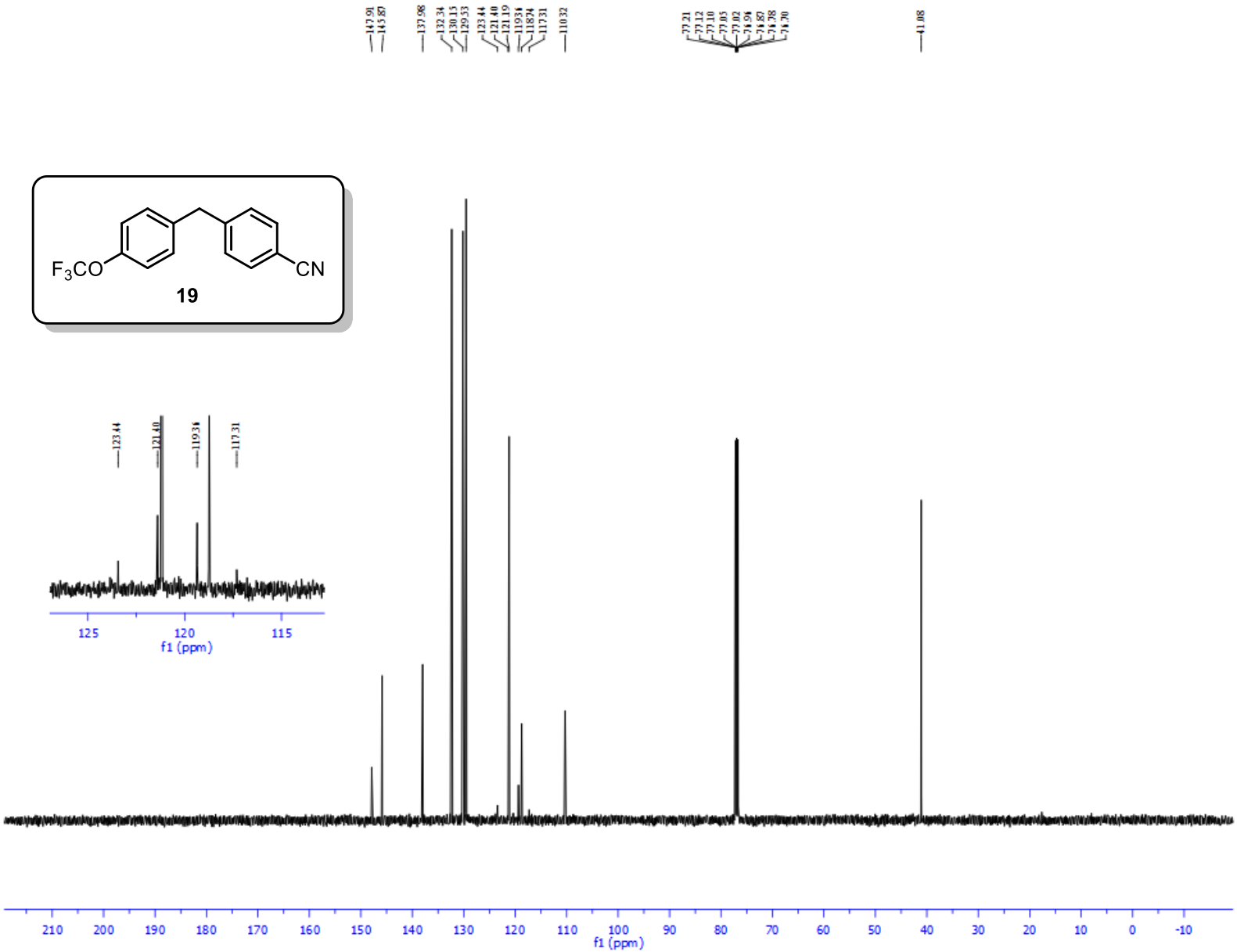
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 4-(benzo[d][1,3]dioxol-5-ylmethyl)benzonitrile (**18**)



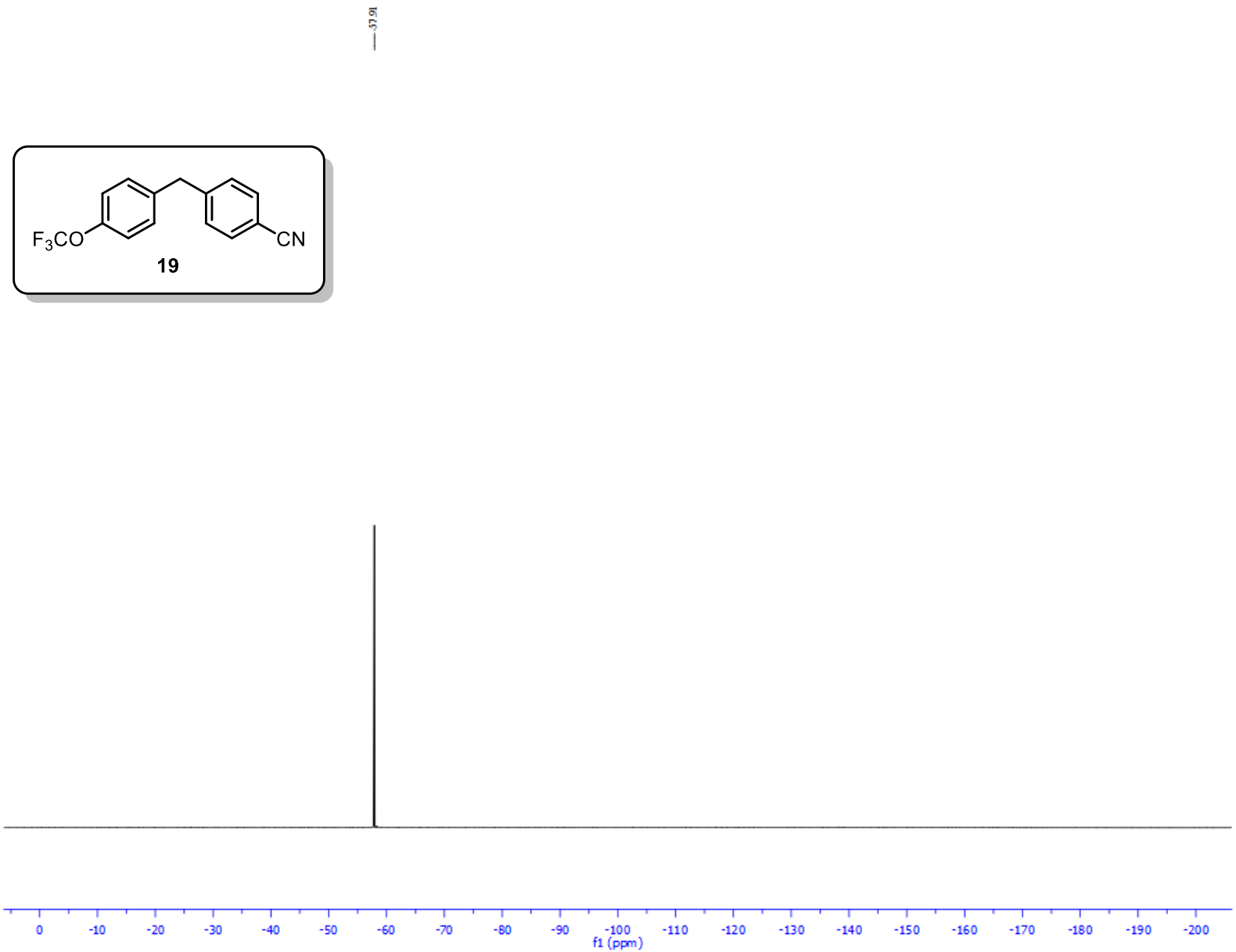
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 4-(4-(trifluoromethoxy)benzyl)benzonitrile (**19**)



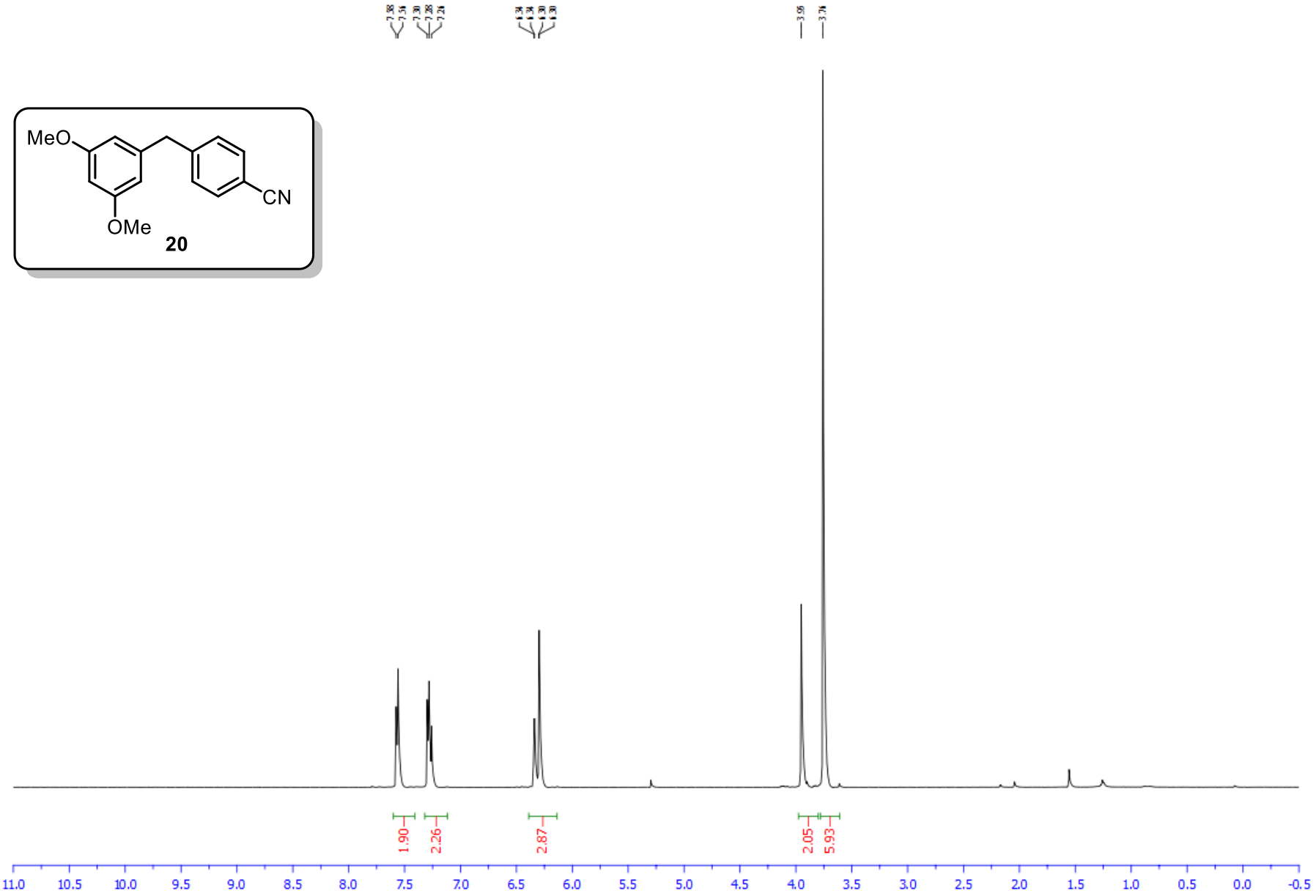
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 4-(4-(trifluoromethoxy)benzyl)benzonitrile (**19**)



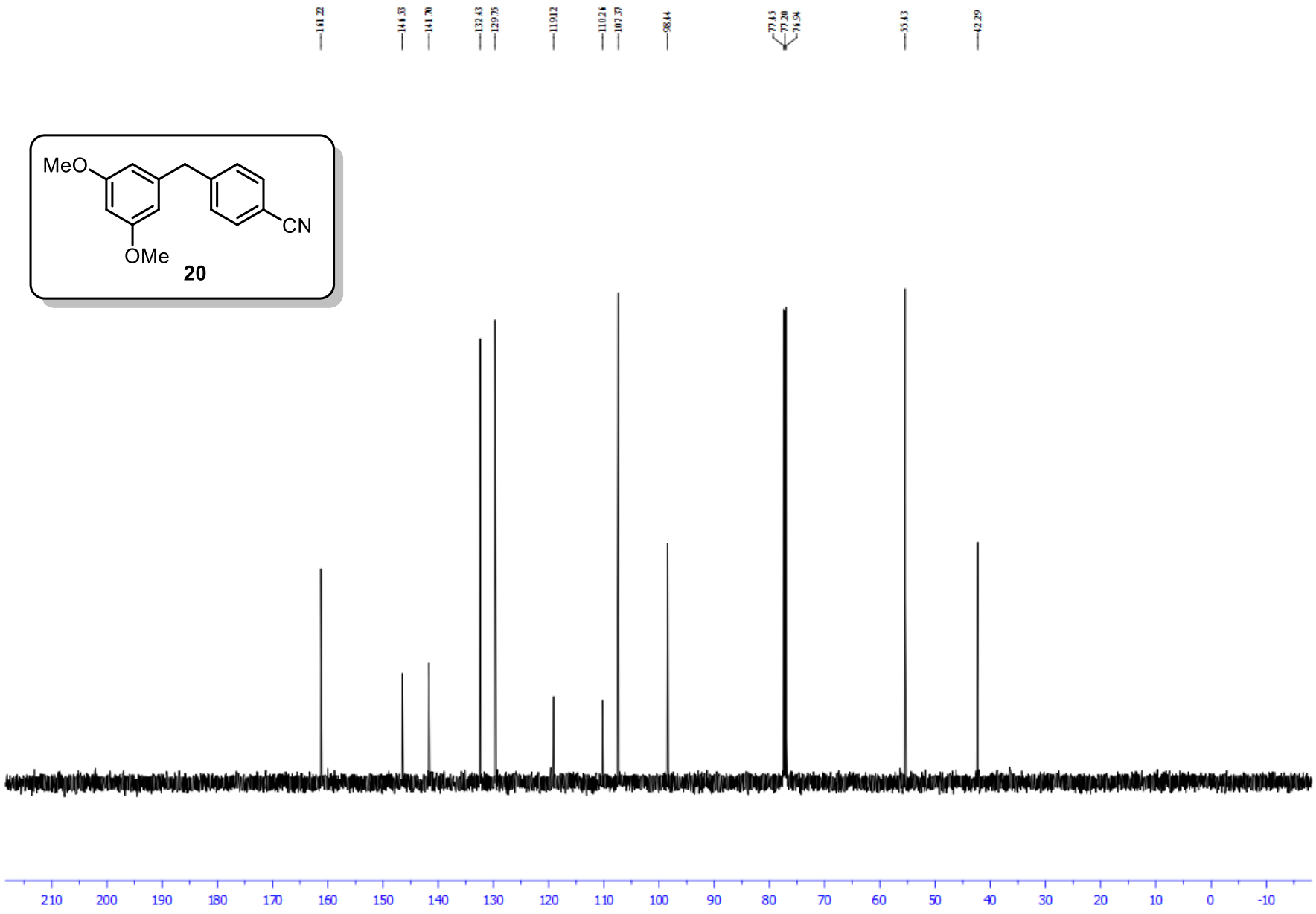
^{19}F NMR ($CDCl_3$, 470.8 MHz) spectrum of 4-(4-(trifluoromethoxy)benzyl)benzonitrile (**19**)



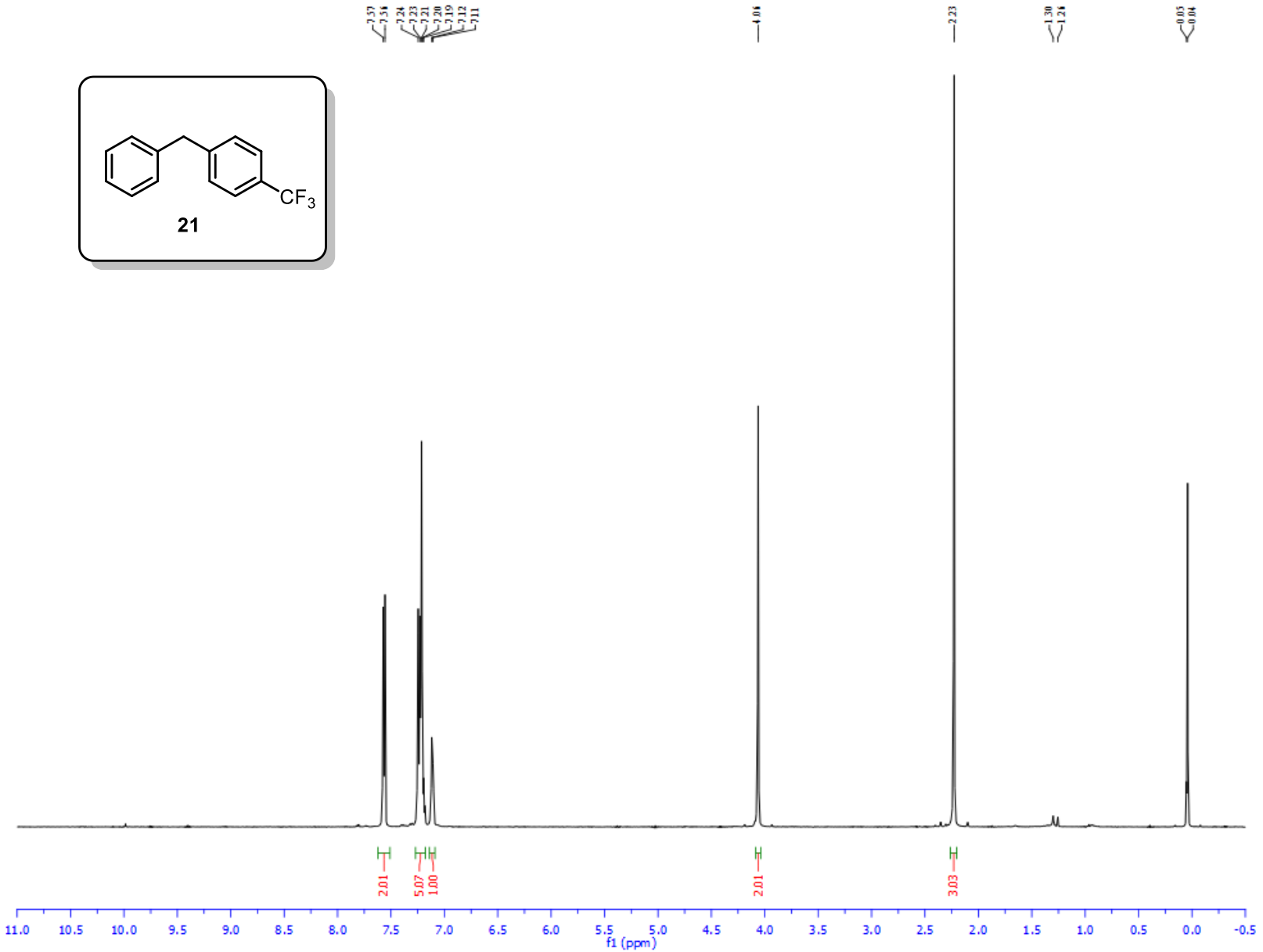
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 4-(3,5-dimethoxybenzyl)benzonitrile (**20**)



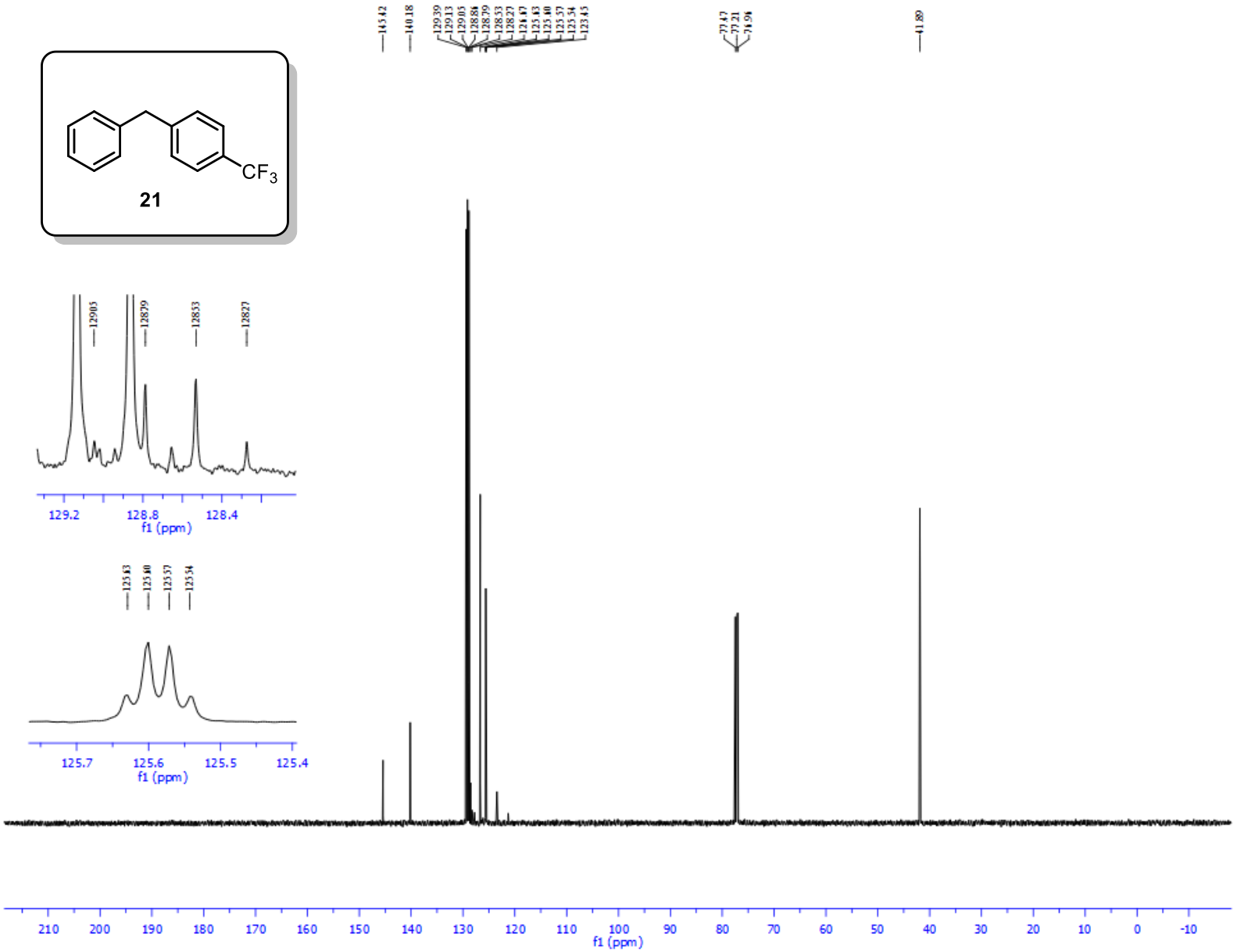
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 4-(3,5-dimethoxybenzyl)benzonitrile (**20**)



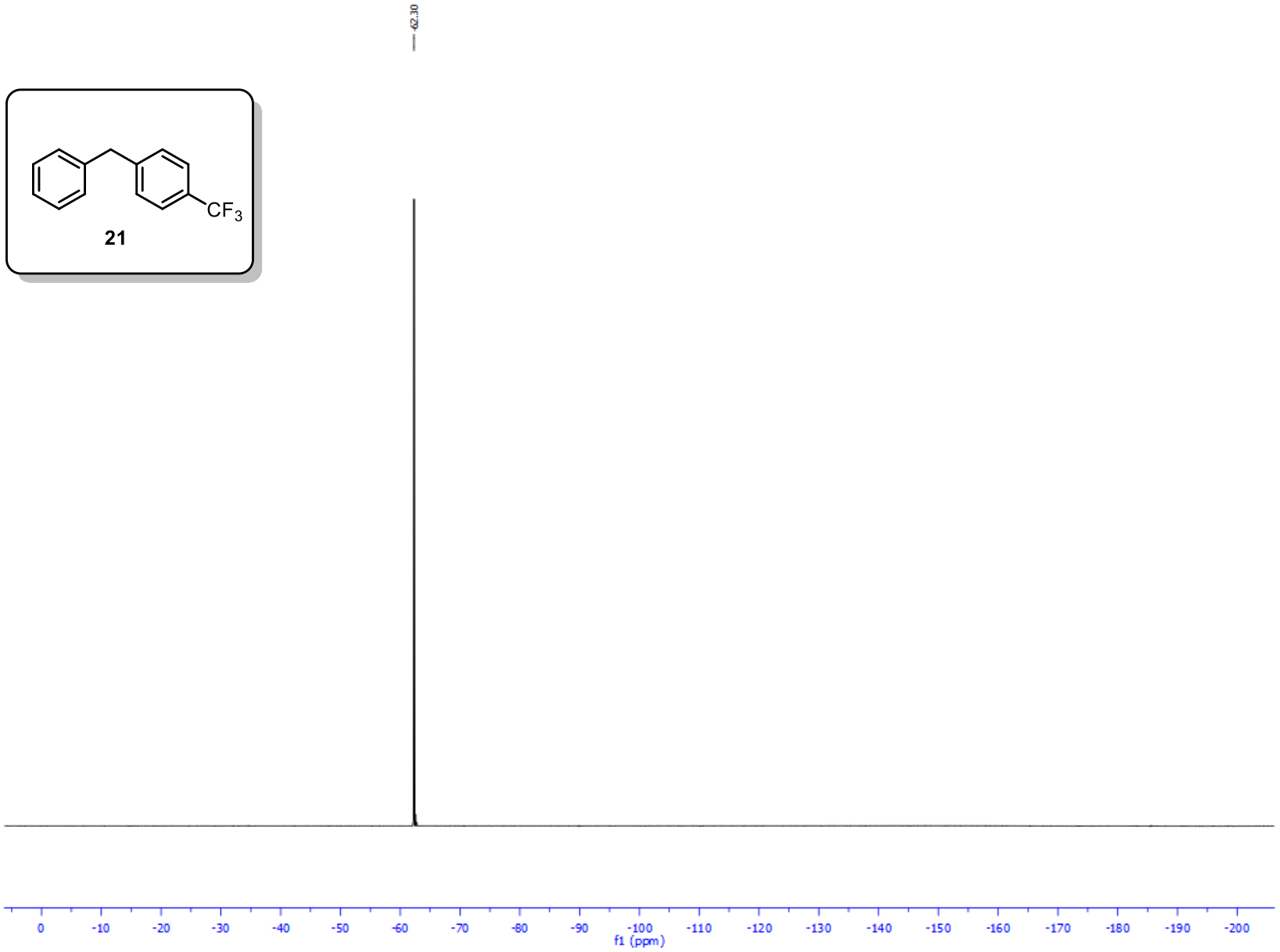
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 1-benzyl-4-(trifluoromethyl)benzene (**21**)



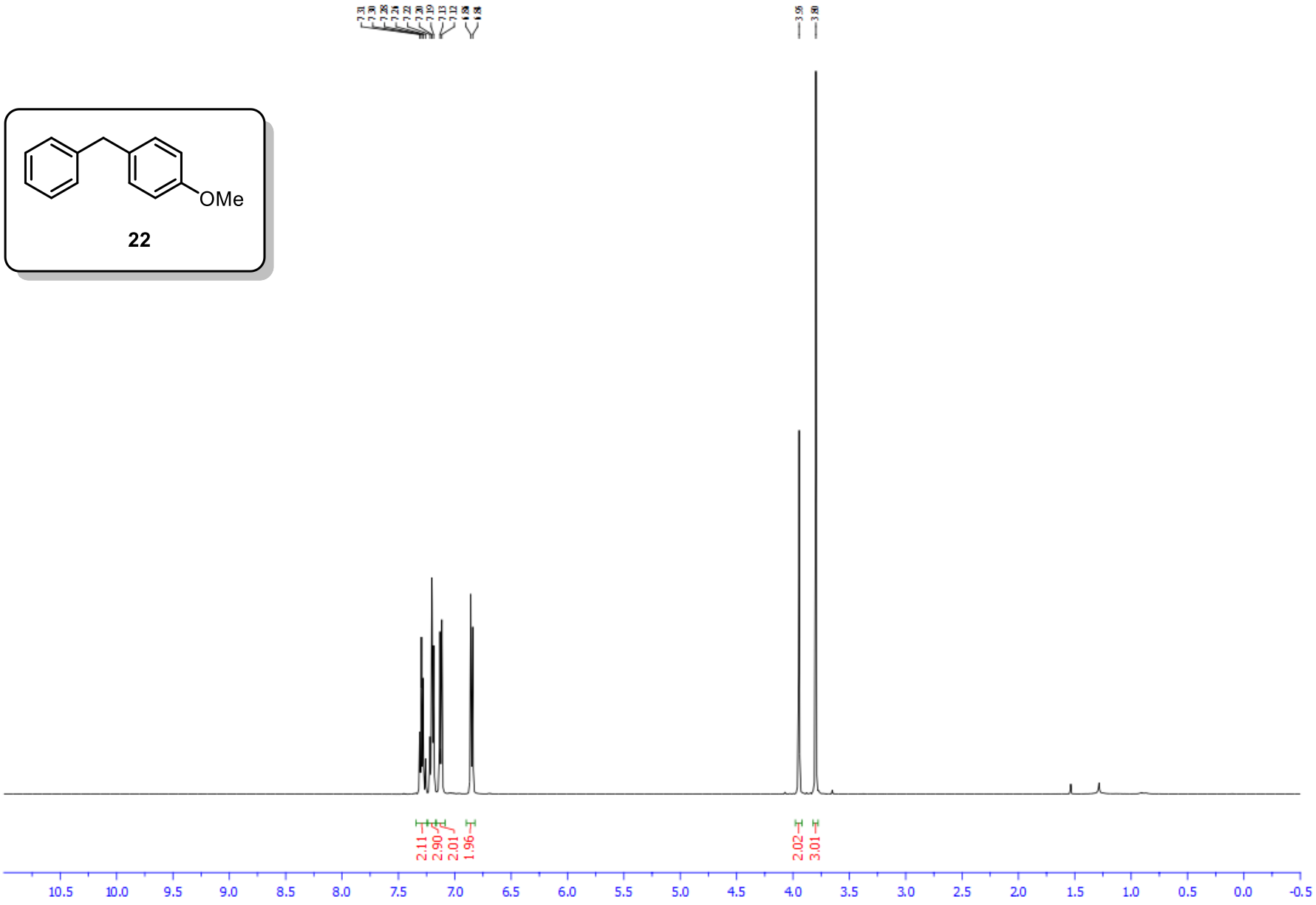
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 1-benzyl-4-(trifluoromethyl)benzene (**21**)



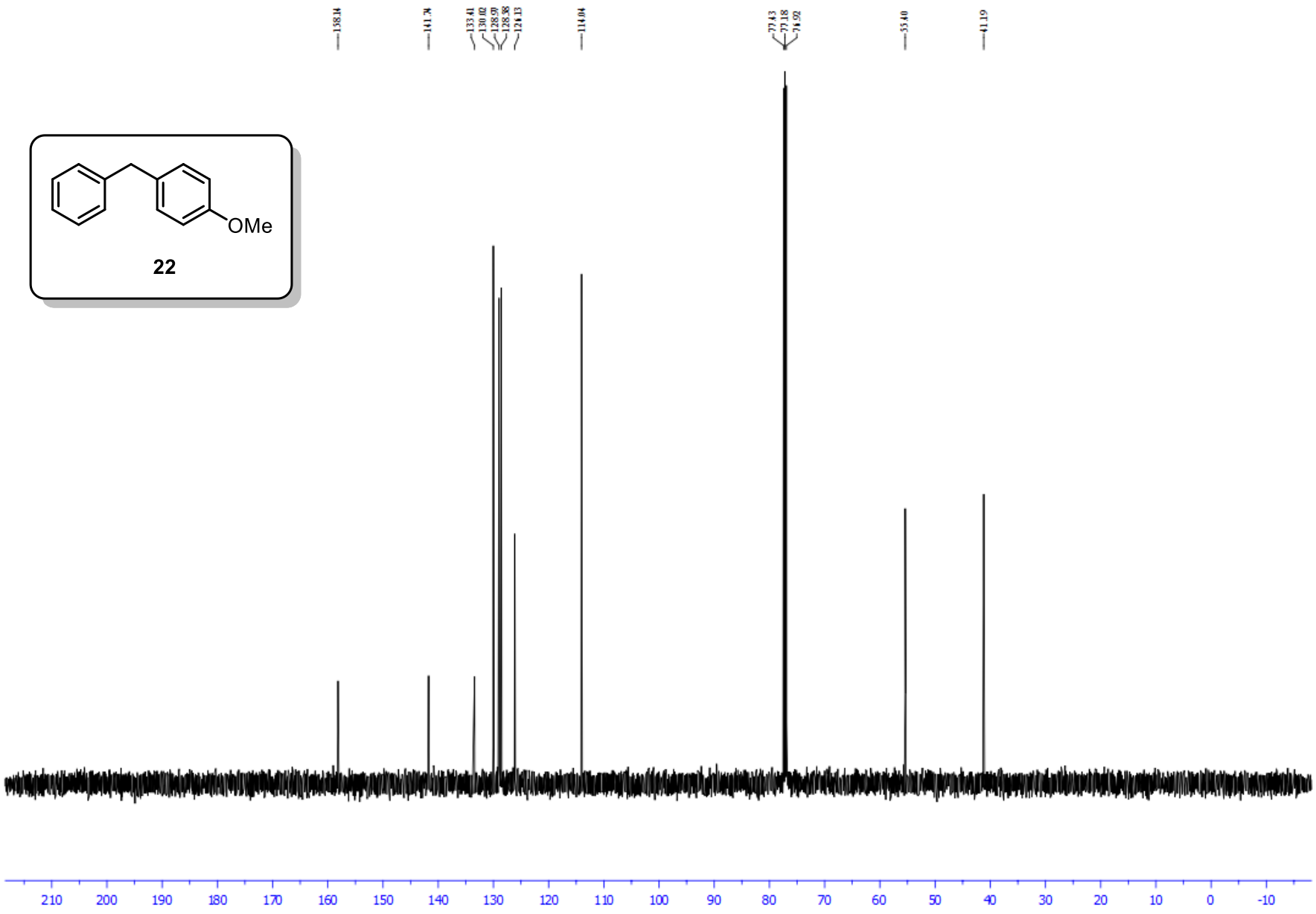
^{19}F NMR ($CDCl_3$, 470.8 MHz) spectrum of 1-benzyl-4-(trifluoromethyl)benzene (**21**)



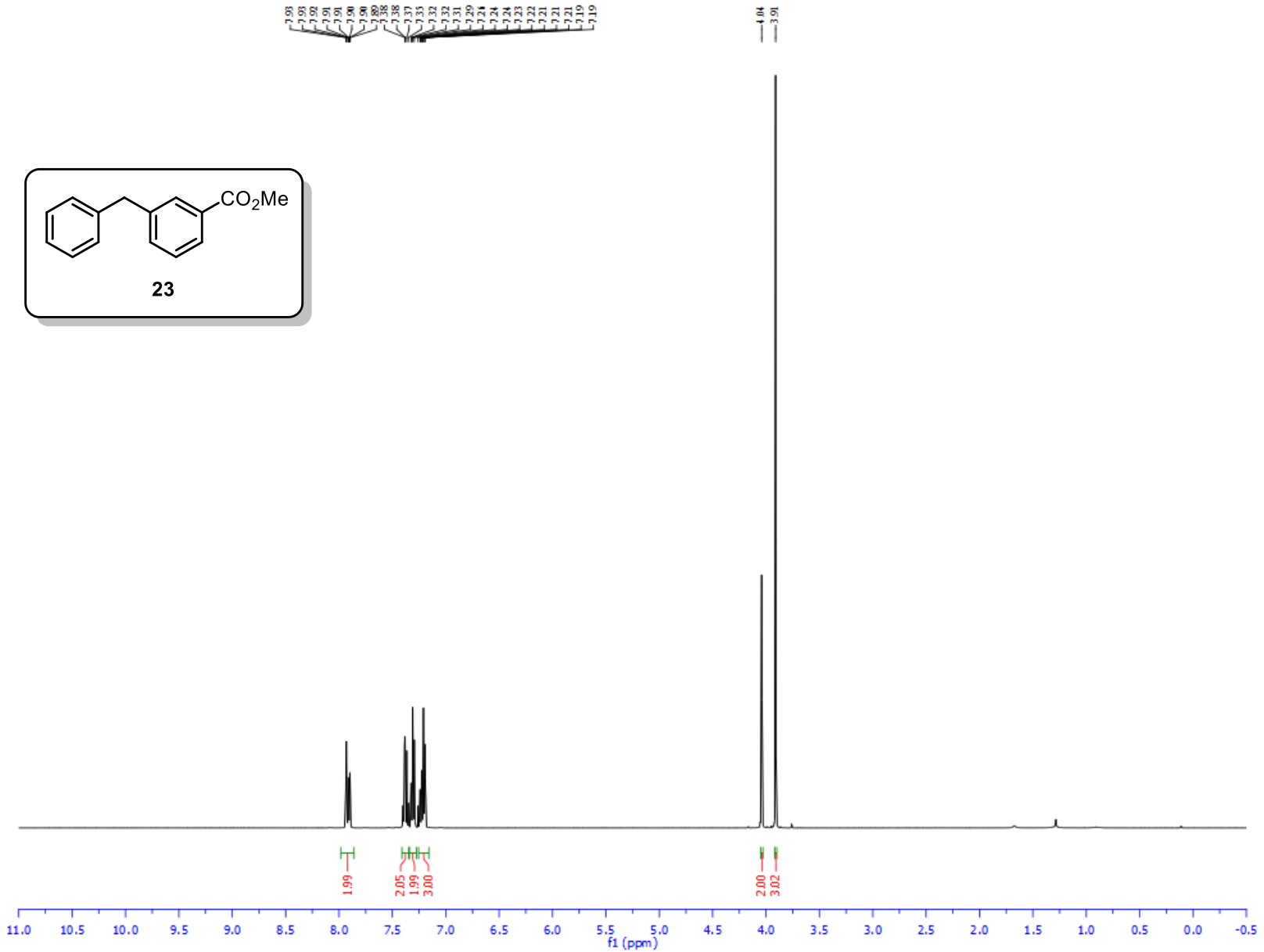
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 1-benzyl-4-methoxybenzene (**22**)



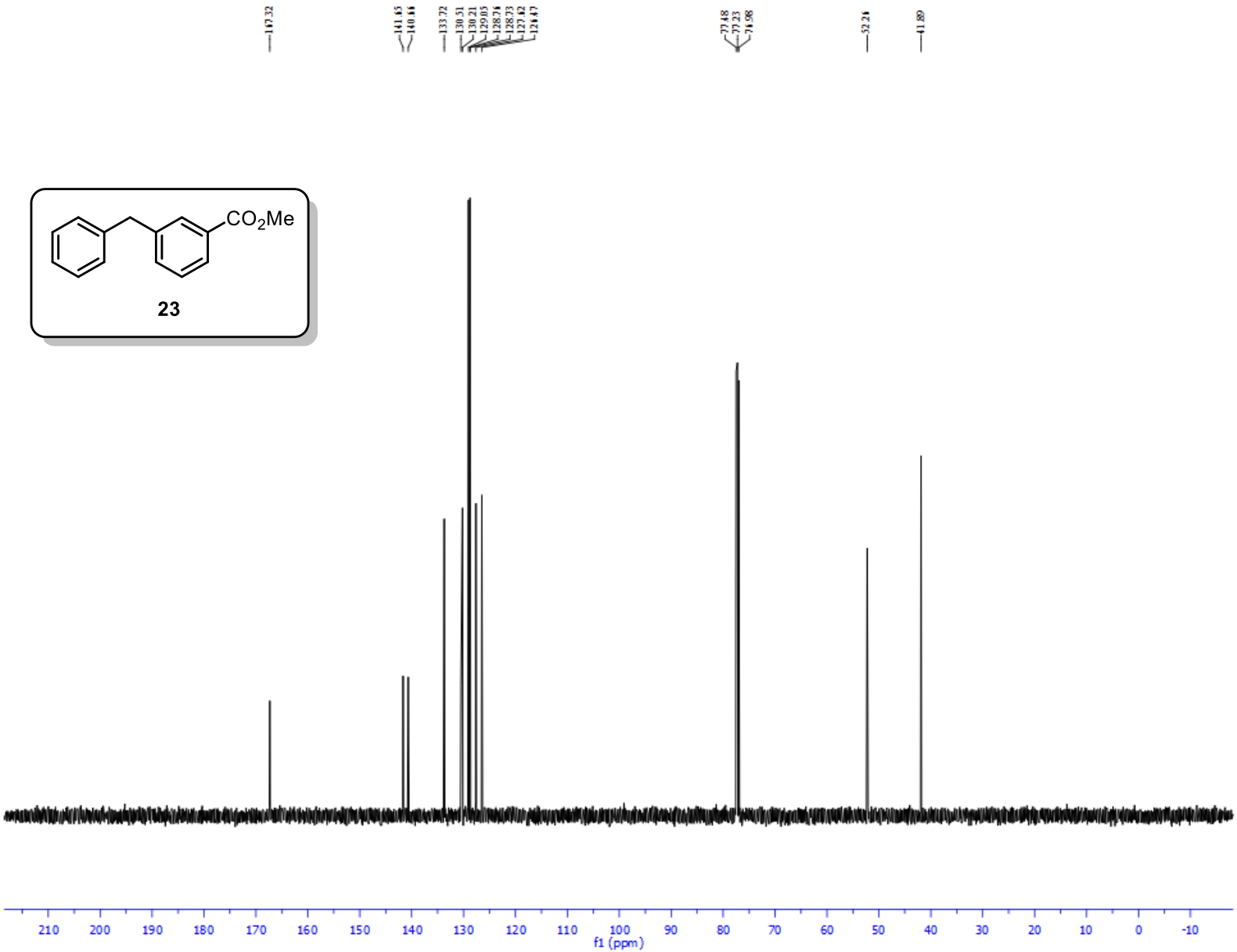
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 1-benzyl-4-methoxybenzene (**22**)



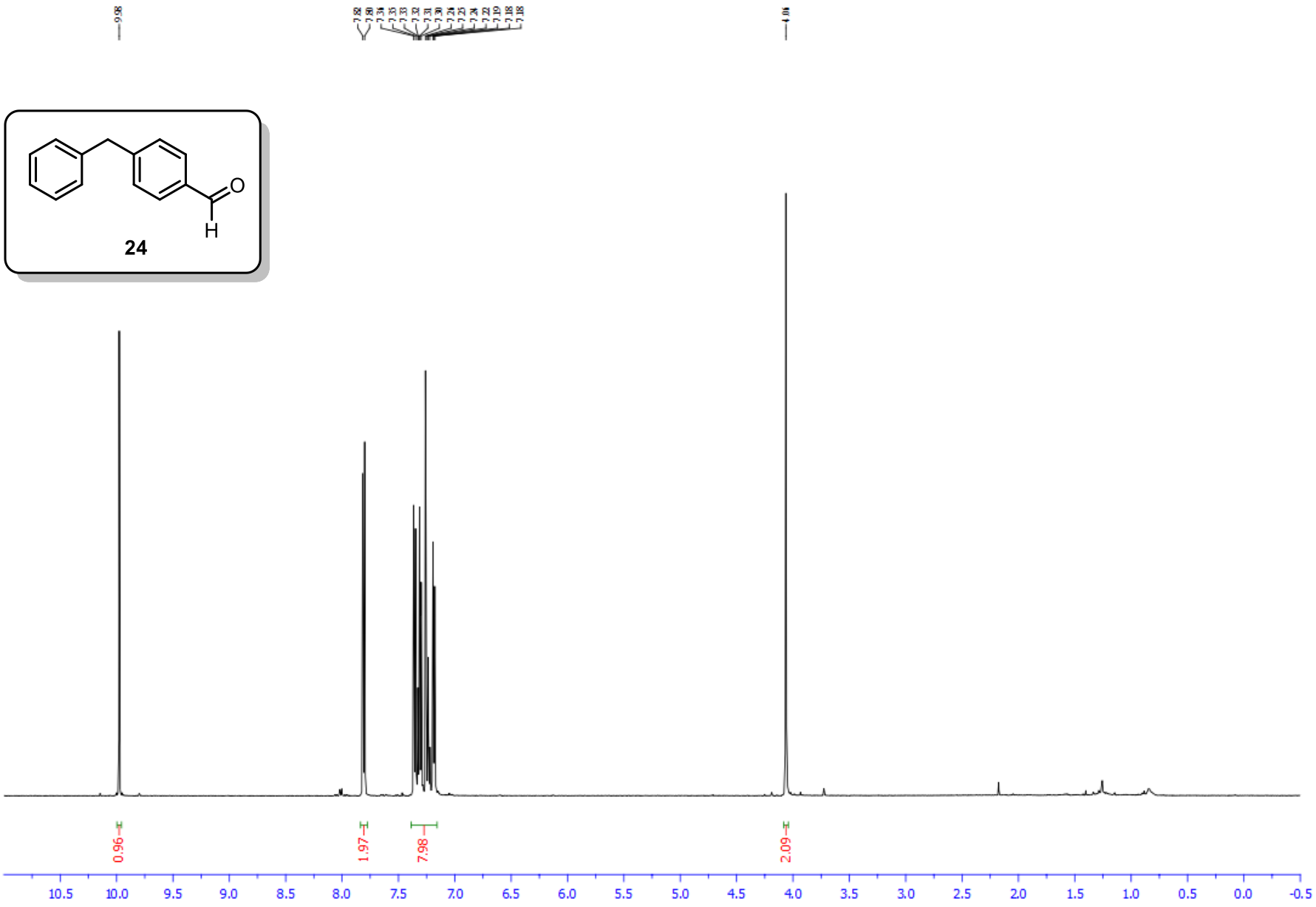
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of methyl 3-benzylbenzoate (23)



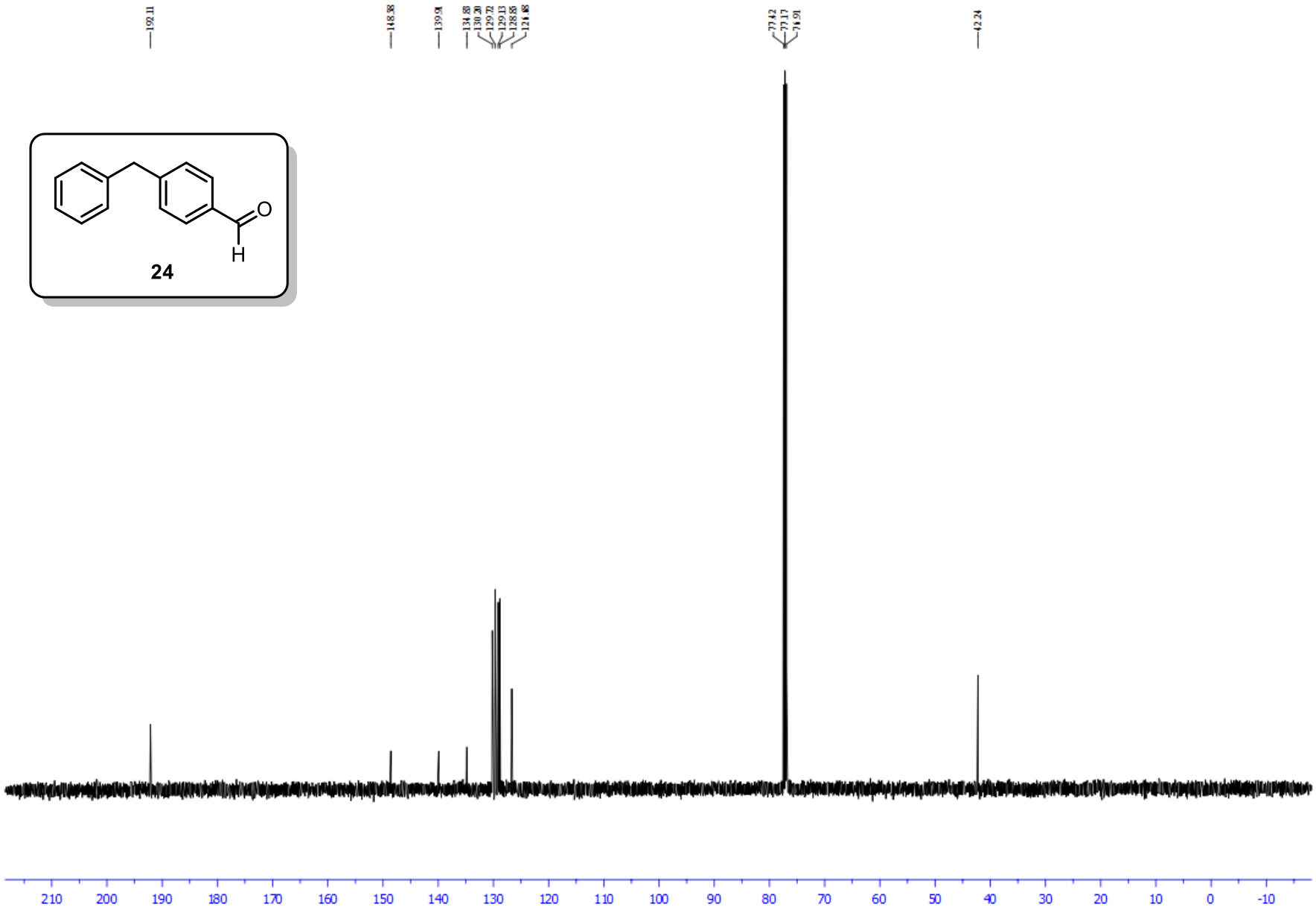
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of methyl 3-benzylbenzoate (**23**)



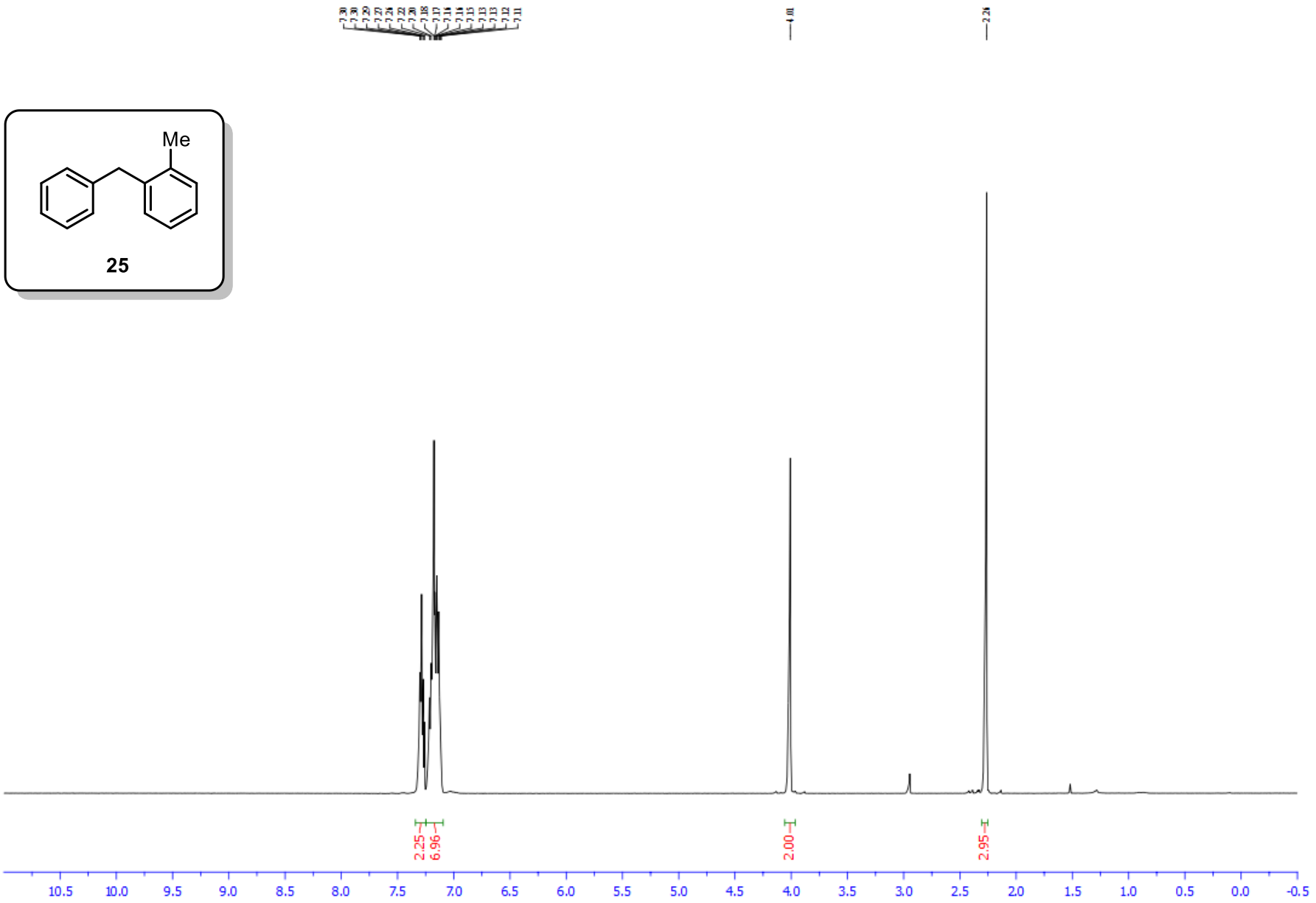
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 4-benzylbenzaldehyde (**24**)



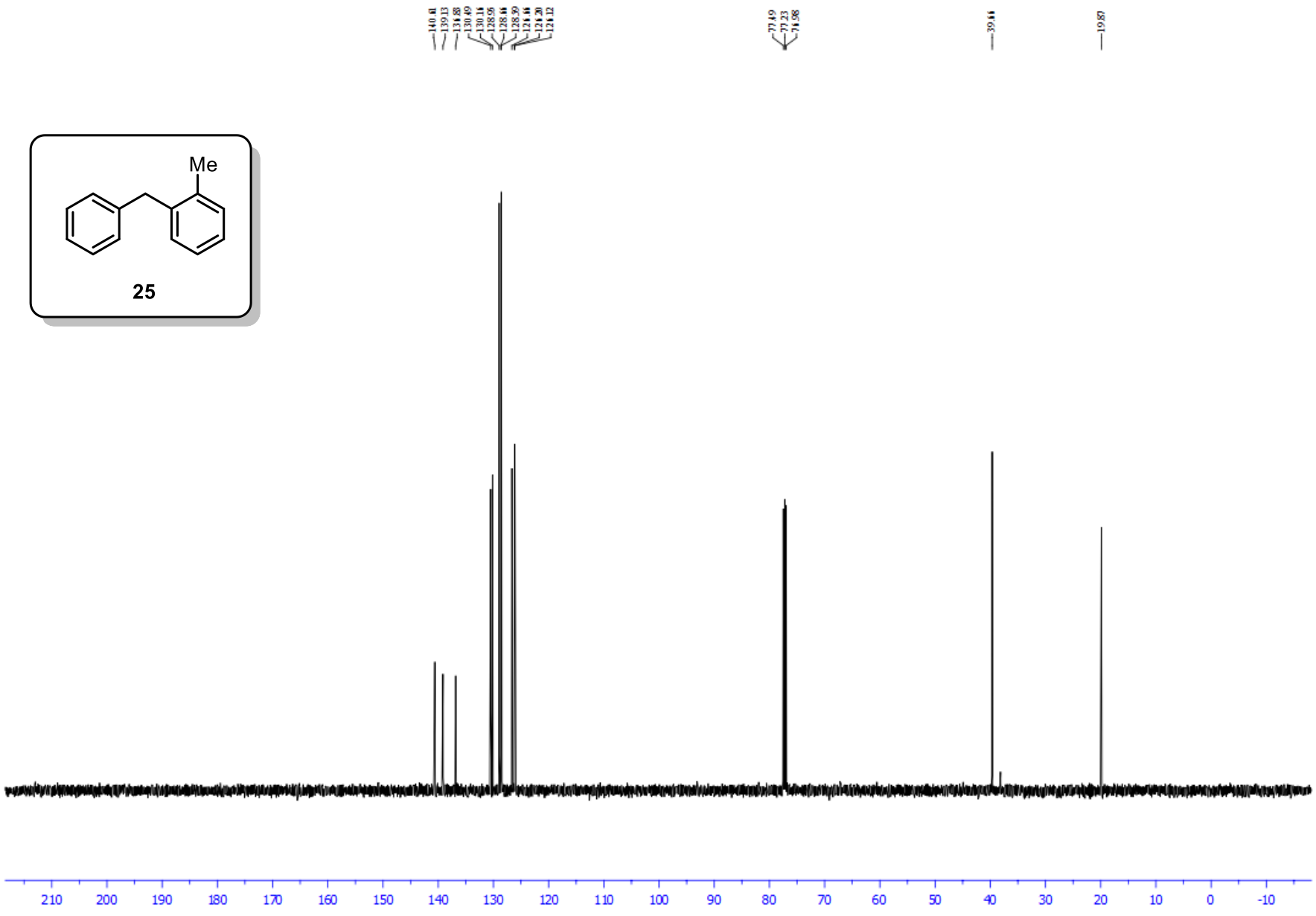
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 4-benzylbenzaldehyde (**24)**



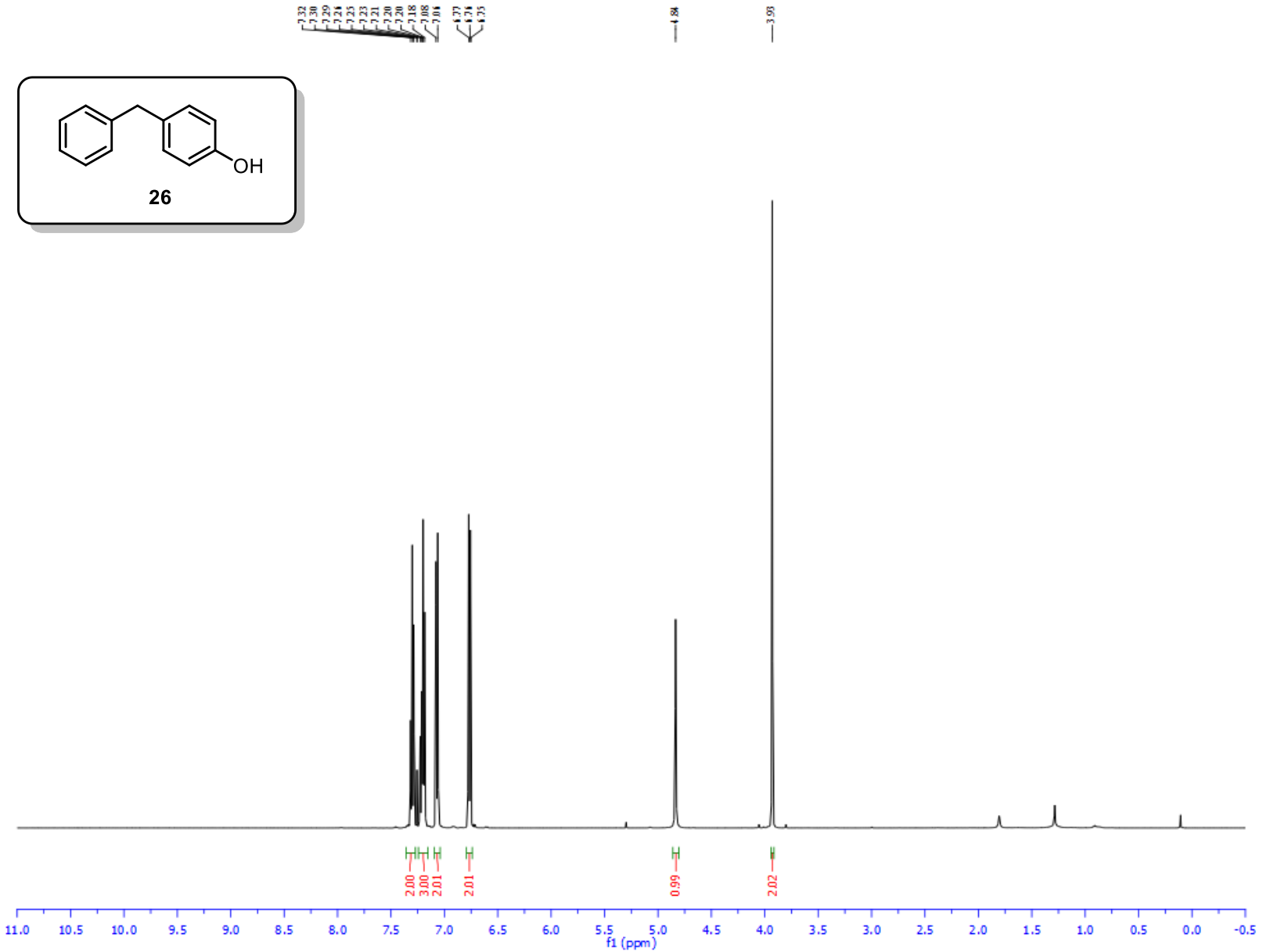
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 1-benzyl-2-methylbenzene (**25**)



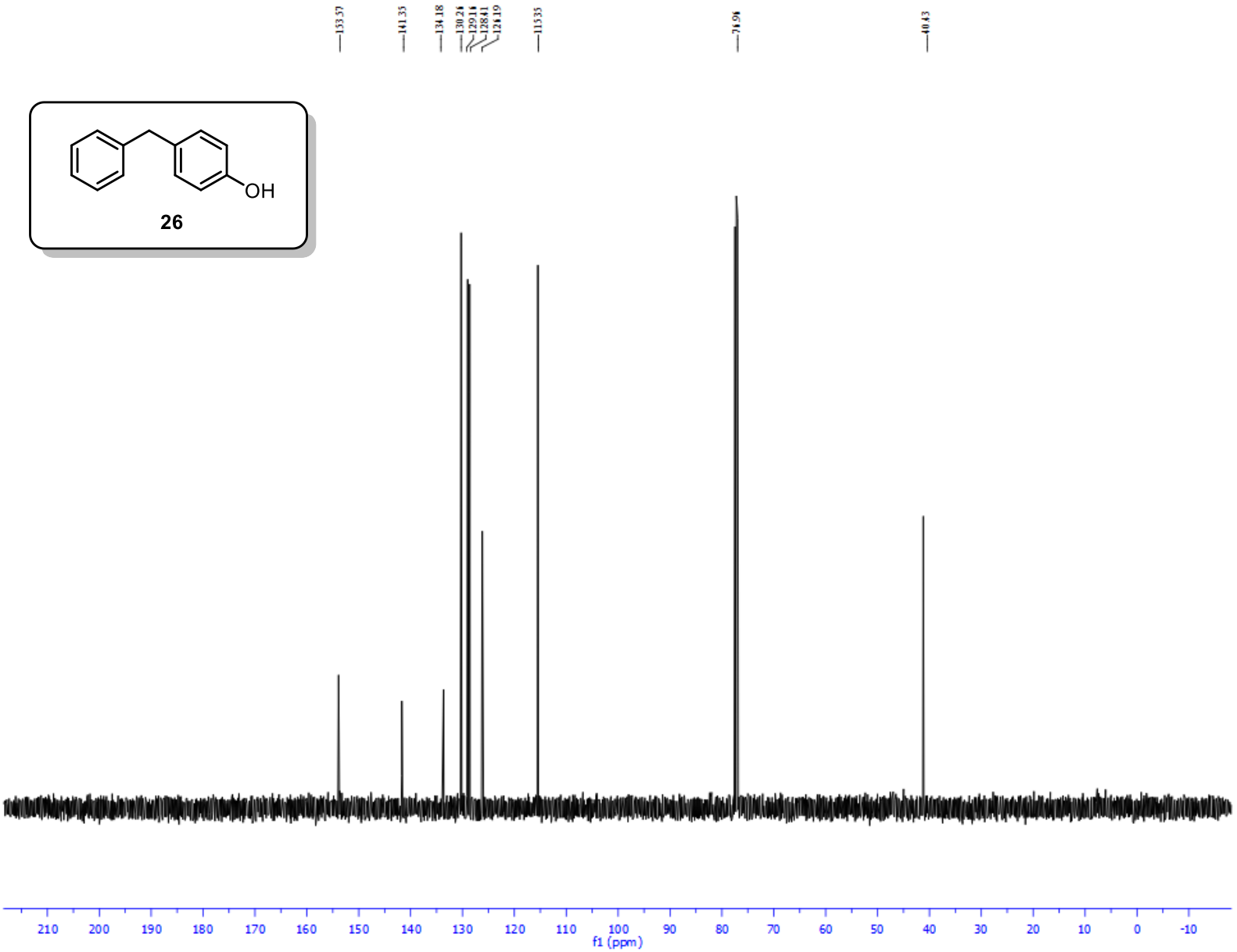
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 1-benzyl-2-methylbenzene (**25**)



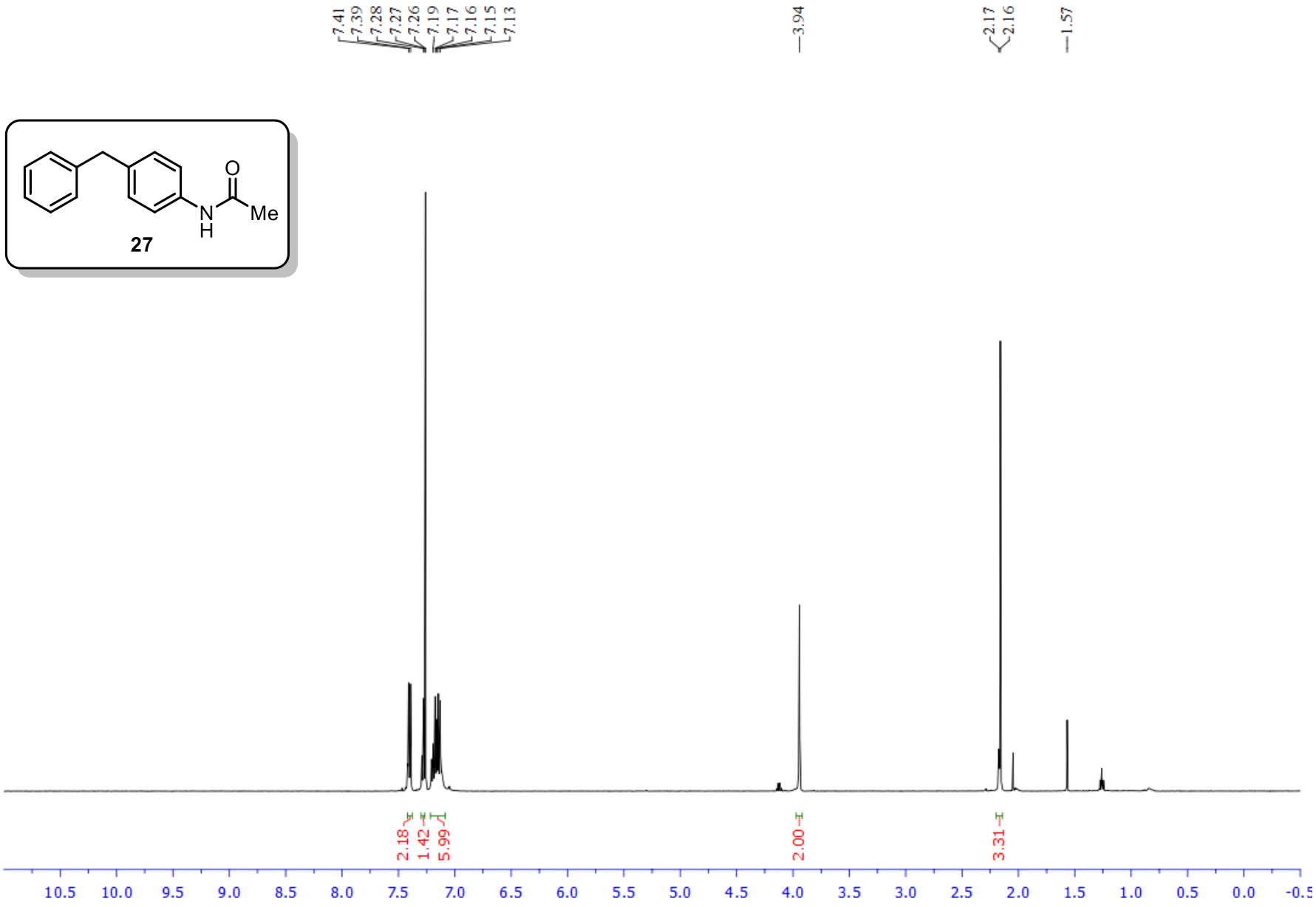
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 4-benzylphenol (**26**)



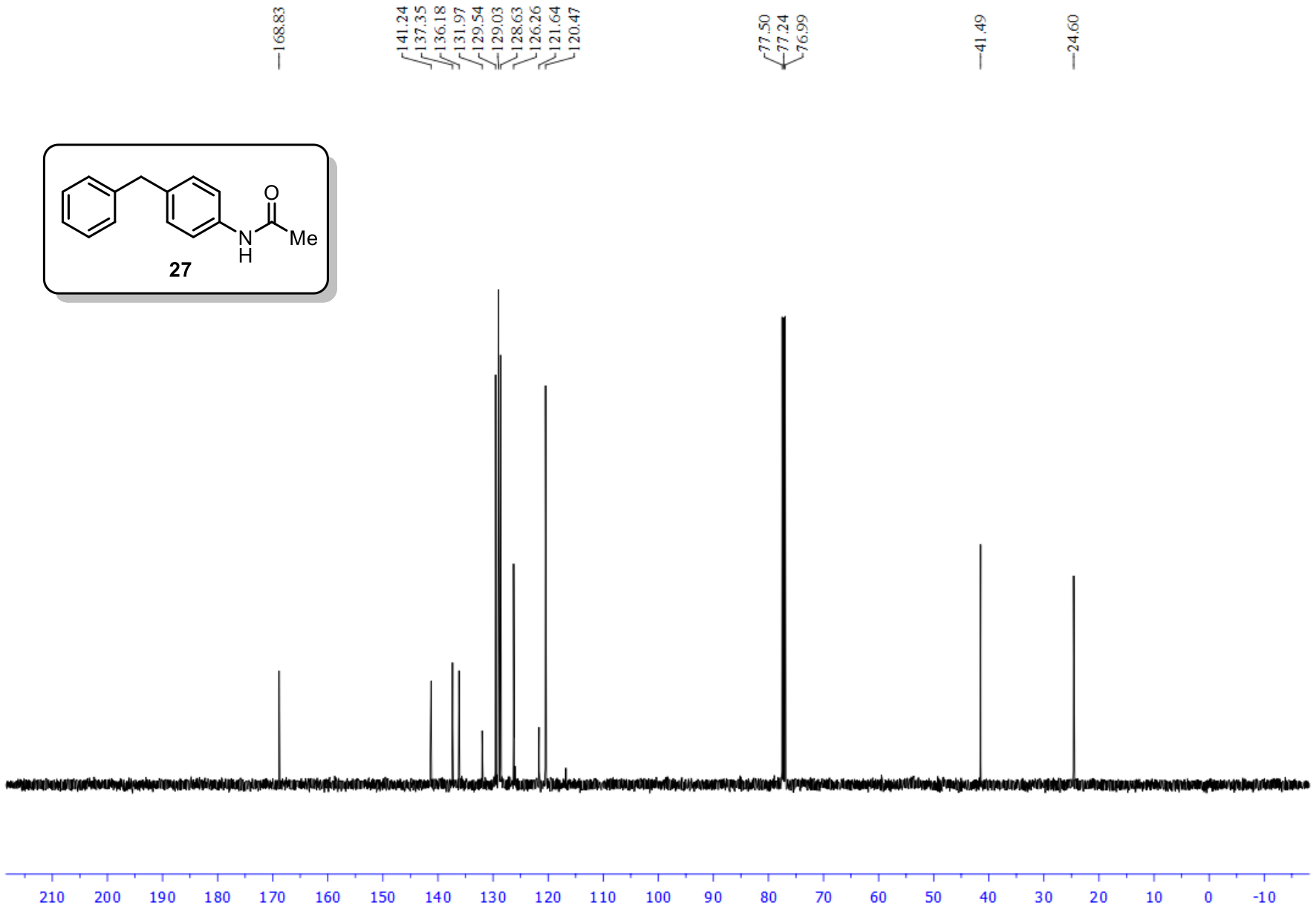
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 4-benzylphenol (**26**)



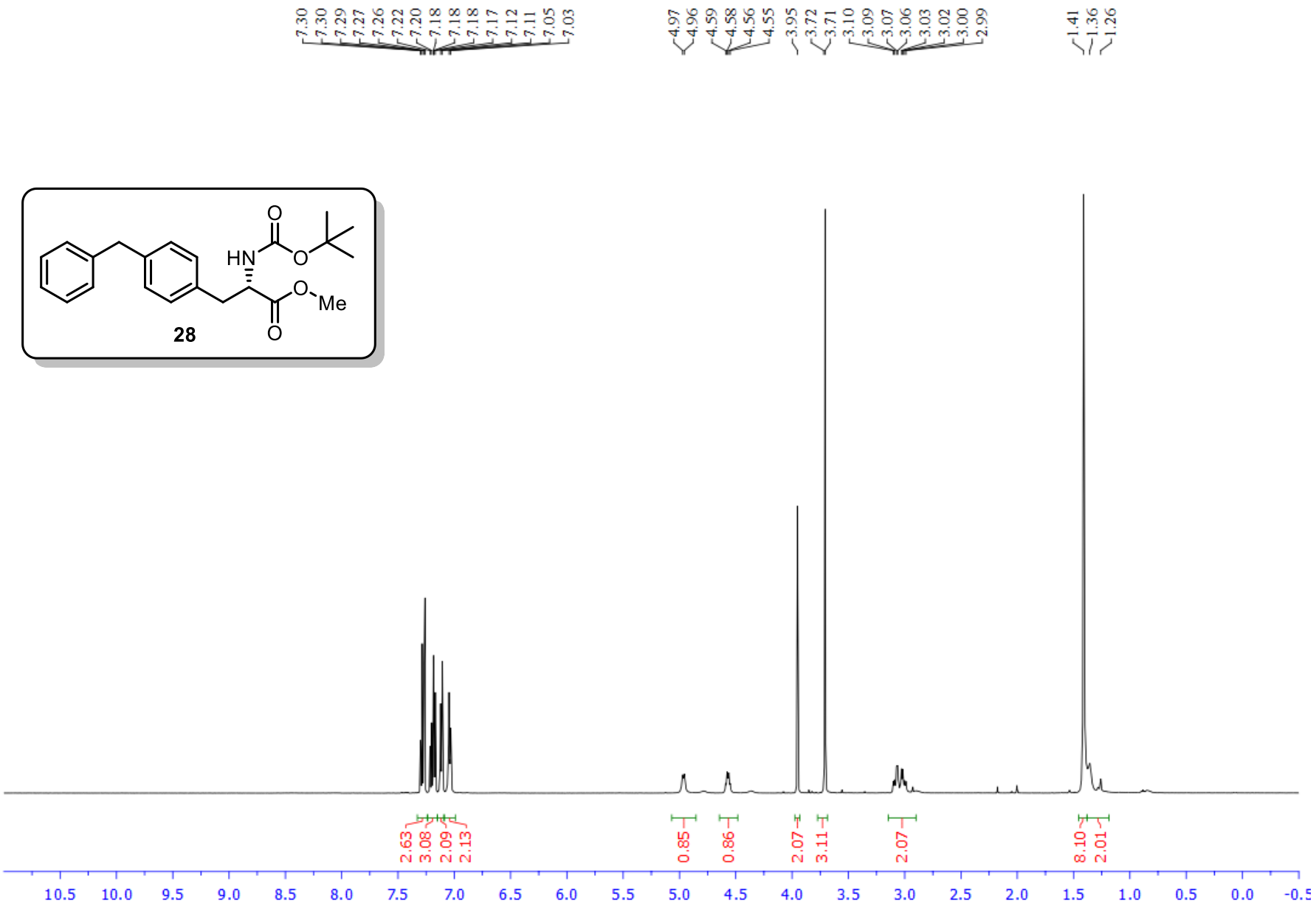
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of N-(4-benzylphenyl)acetamide (**27**)



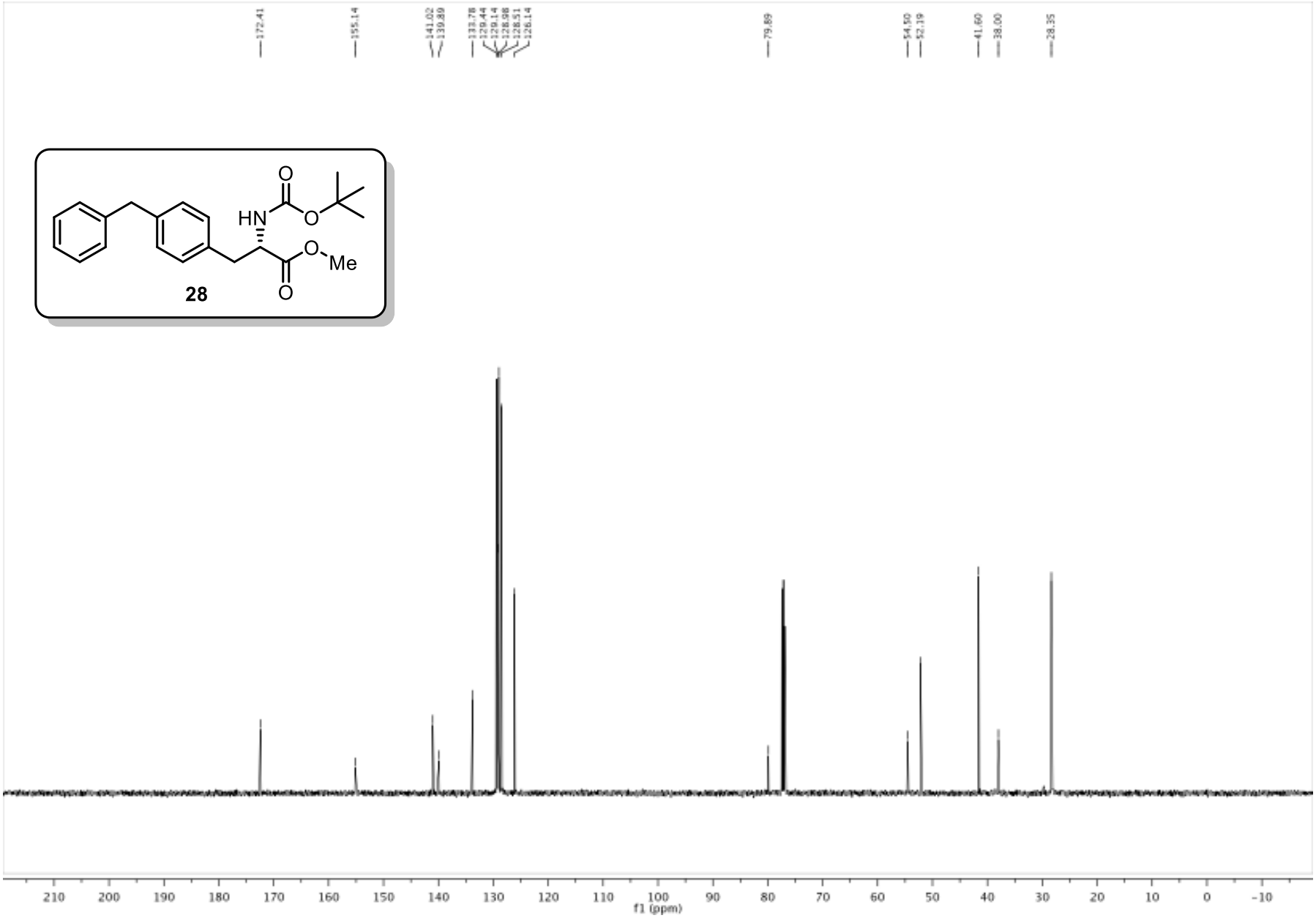
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of N-(4-benzylphenyl)acetamide (**27**)



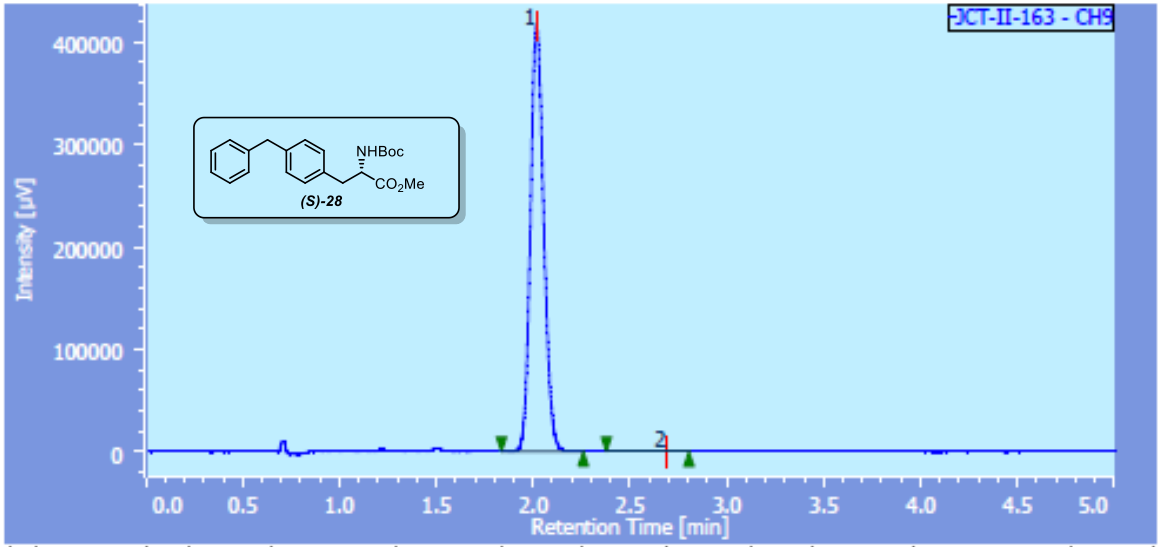
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of methyl (S)-3-(4-benzylphenyl)-2-((tert-butoxycarbonyl)amino)propanoate (**28**)



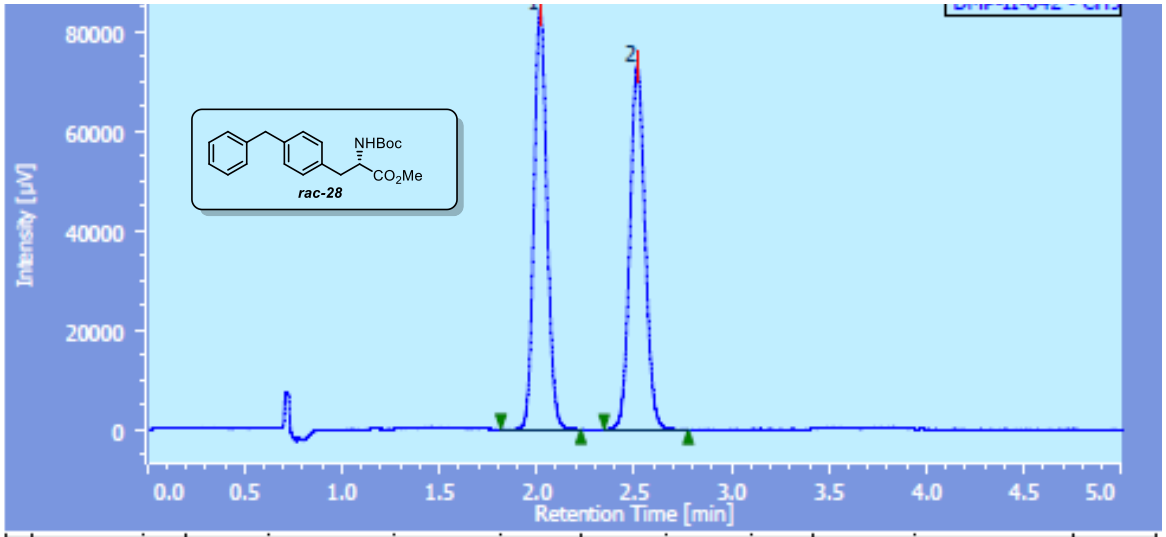
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of methyl (S)-3-(4-benzylphenyl)-2-((tert-butoxycarbonyl)amino)propanoate (**28**)



Chiral SFC (AD-H column: 10% MeOH in CO_2, 5.0 mL/min) spectrum of methyl (S)-3-(4-benzylphenyl)-2-((tert-butoxycarbonyl)amino)propanoate (**28**)

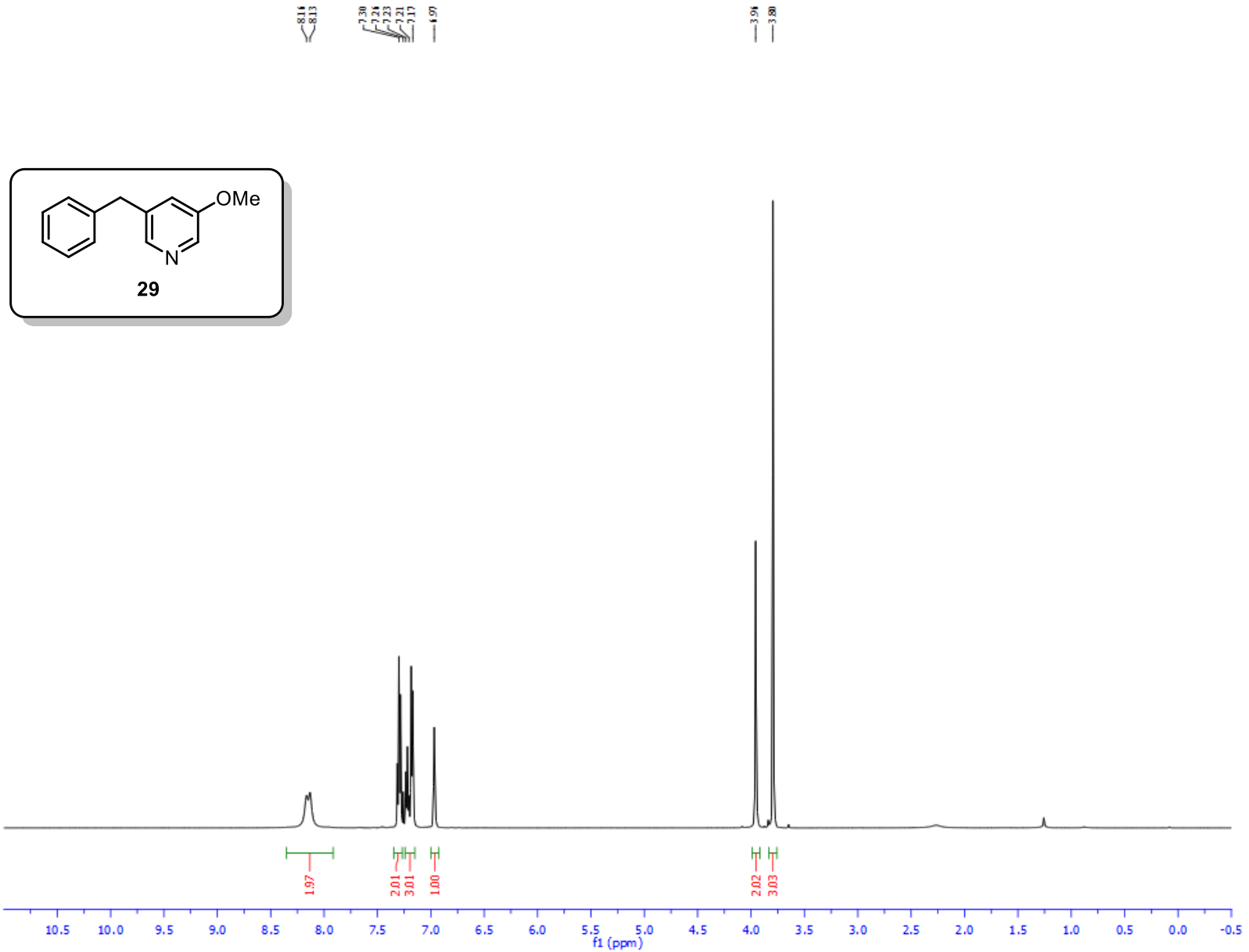


#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	2.017	1990759	415797	99.989	99.987	N/A	4157	2.055	1.155	
2	Unknown	9	2.687	217	52	0.011	0.013	N/A	413	N/A	0.563	

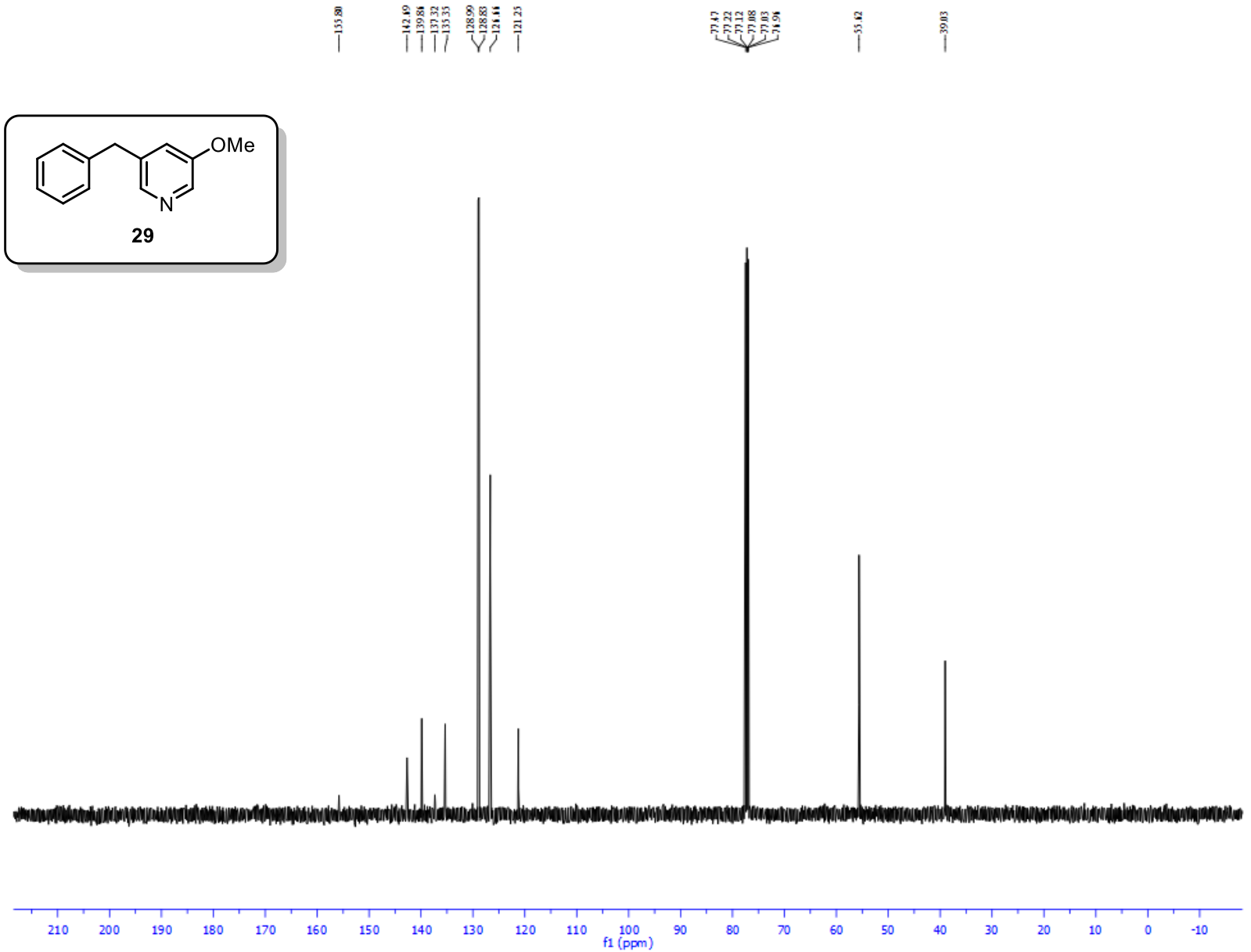


#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	2.017	389750	84111	49.711	53.568	N/A	4427	3.805	1.112	
2	Unknown	9	2.515	394276	72906	50.289	46.432	N/A	5062	N/A	1.072	

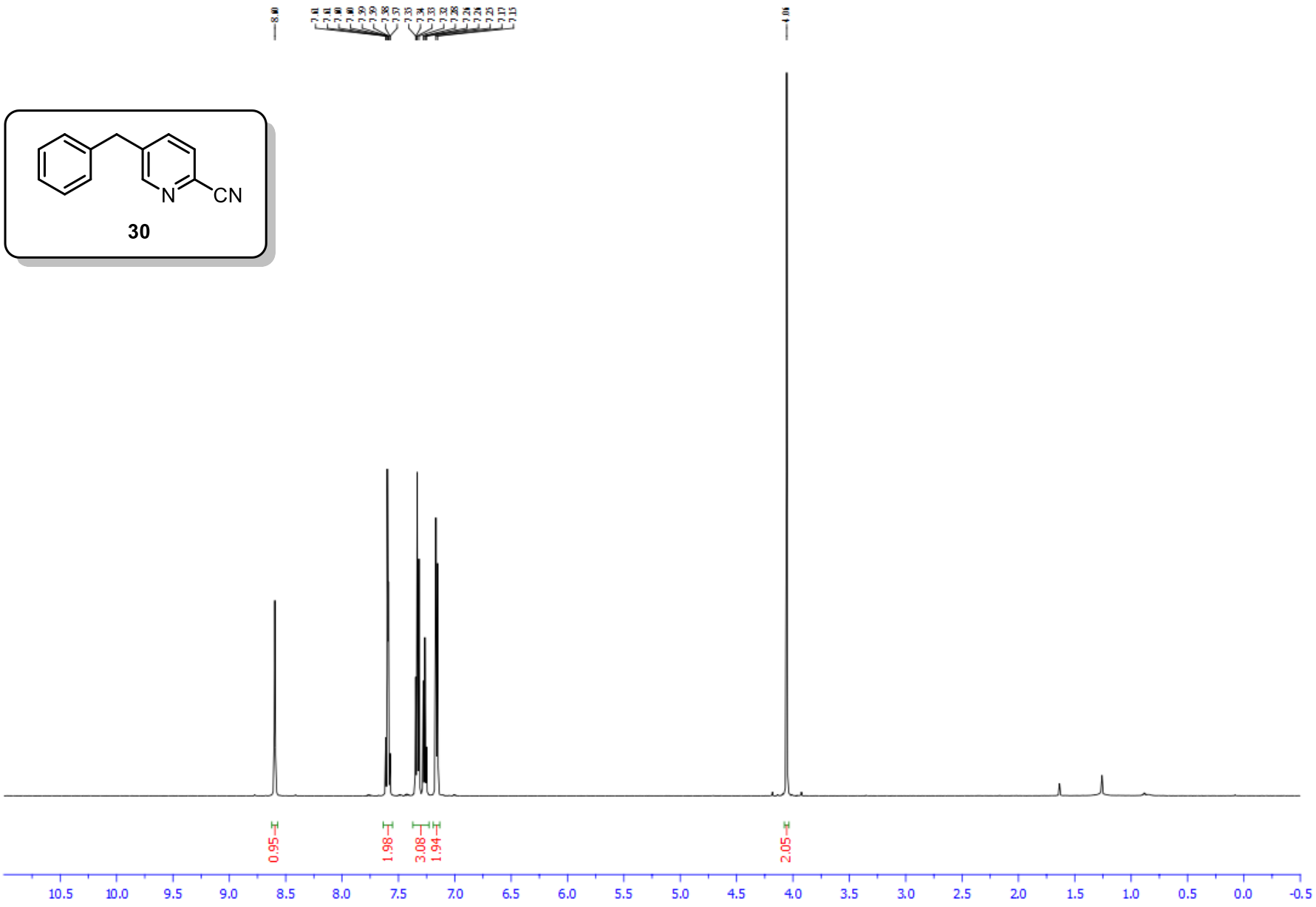
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 3-benzyl-5-methoxypyridine (**29**)



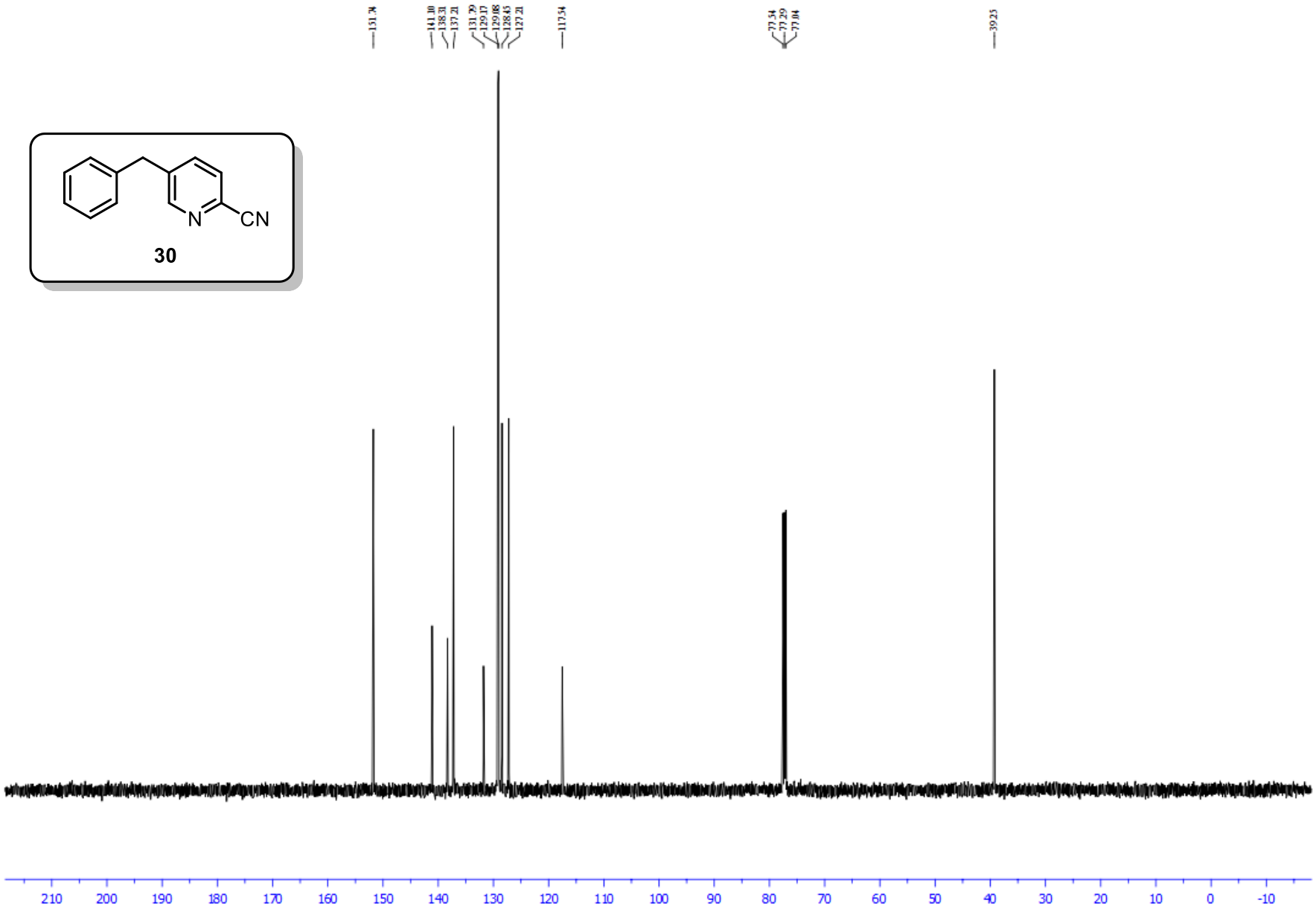
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 3-benzyl-5-methoxypyridine (**29**)



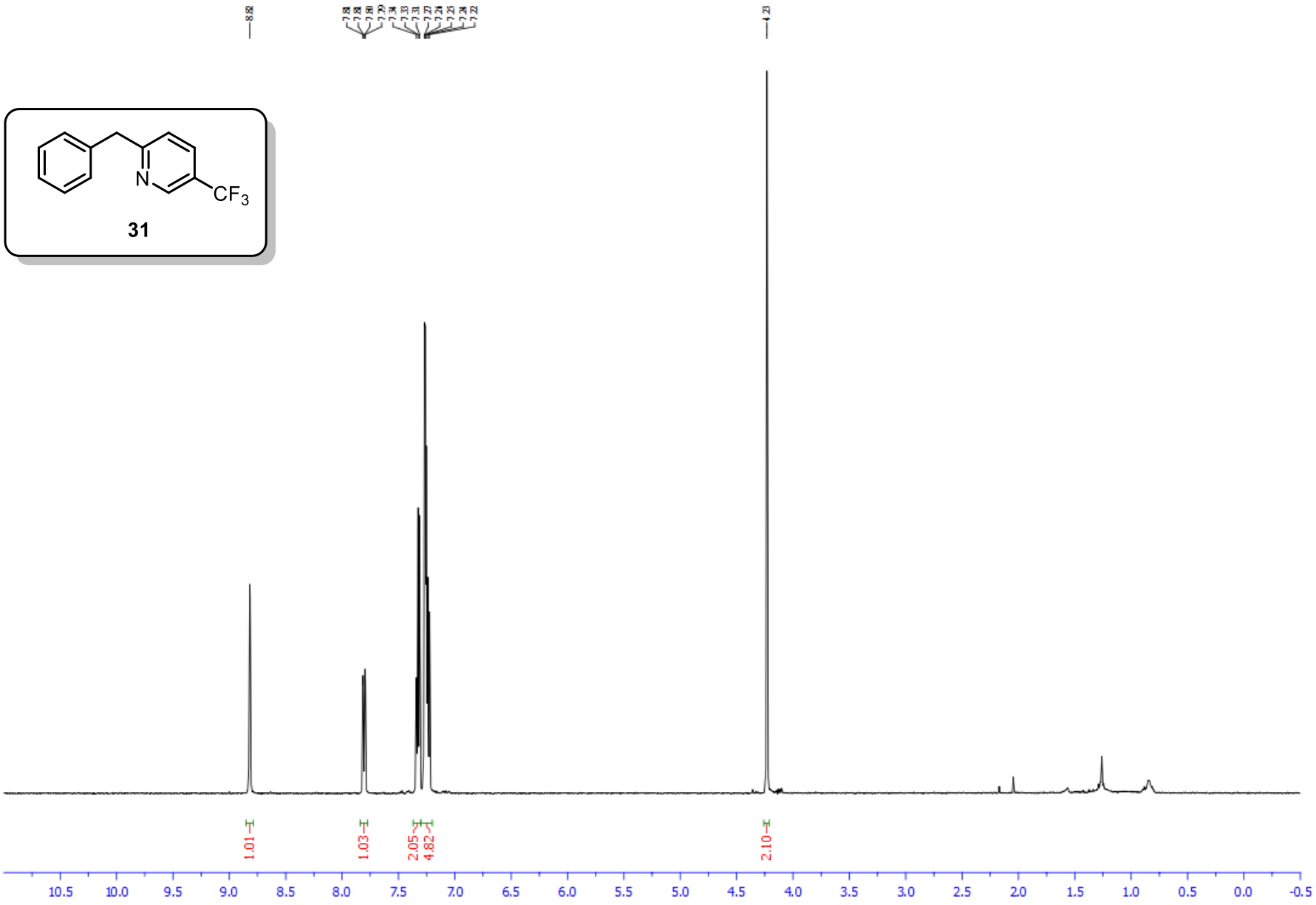
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 5-benzylpicolinonitrile (**30**)



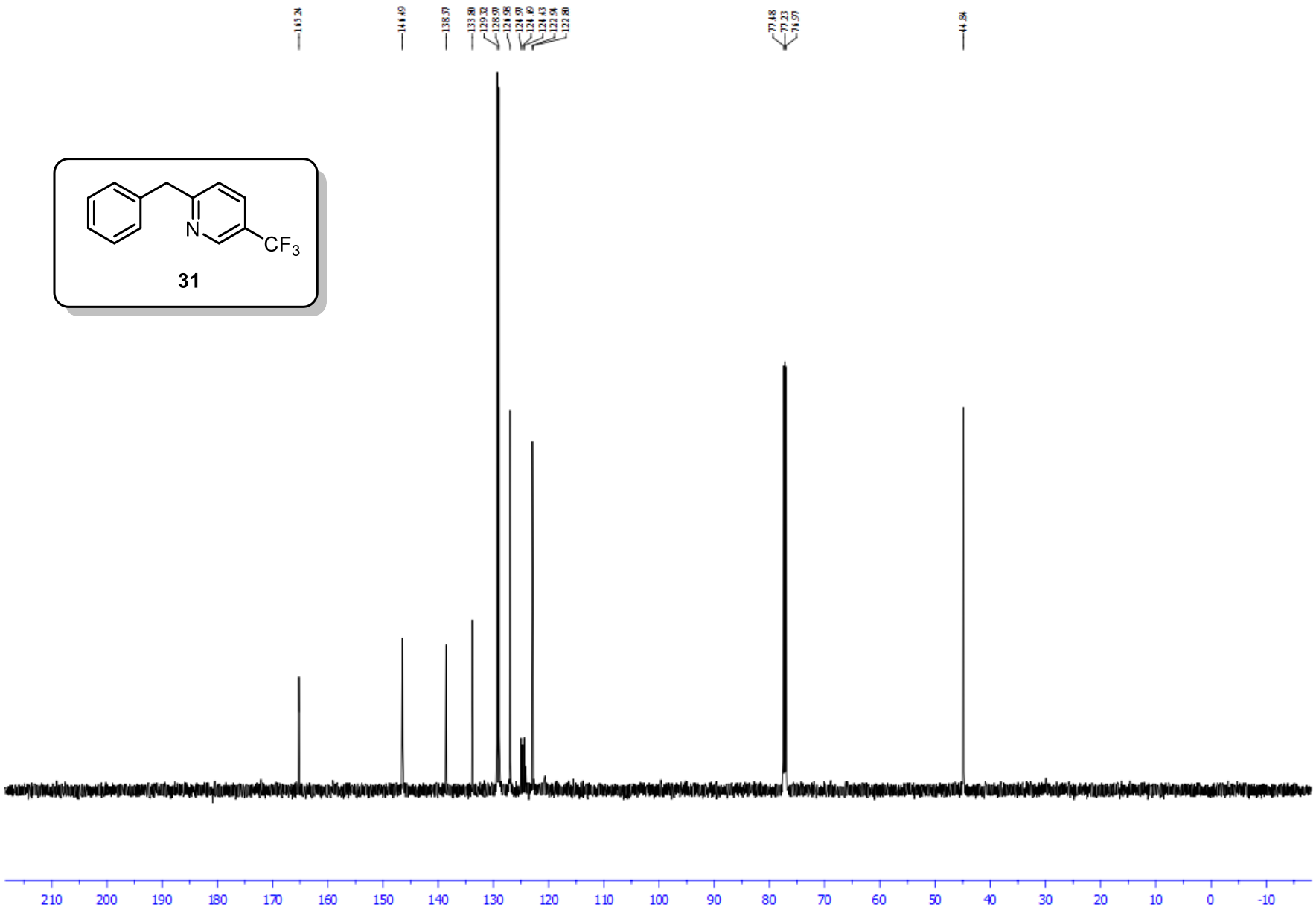
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 5-benzylpicolinonitrile (**30**)



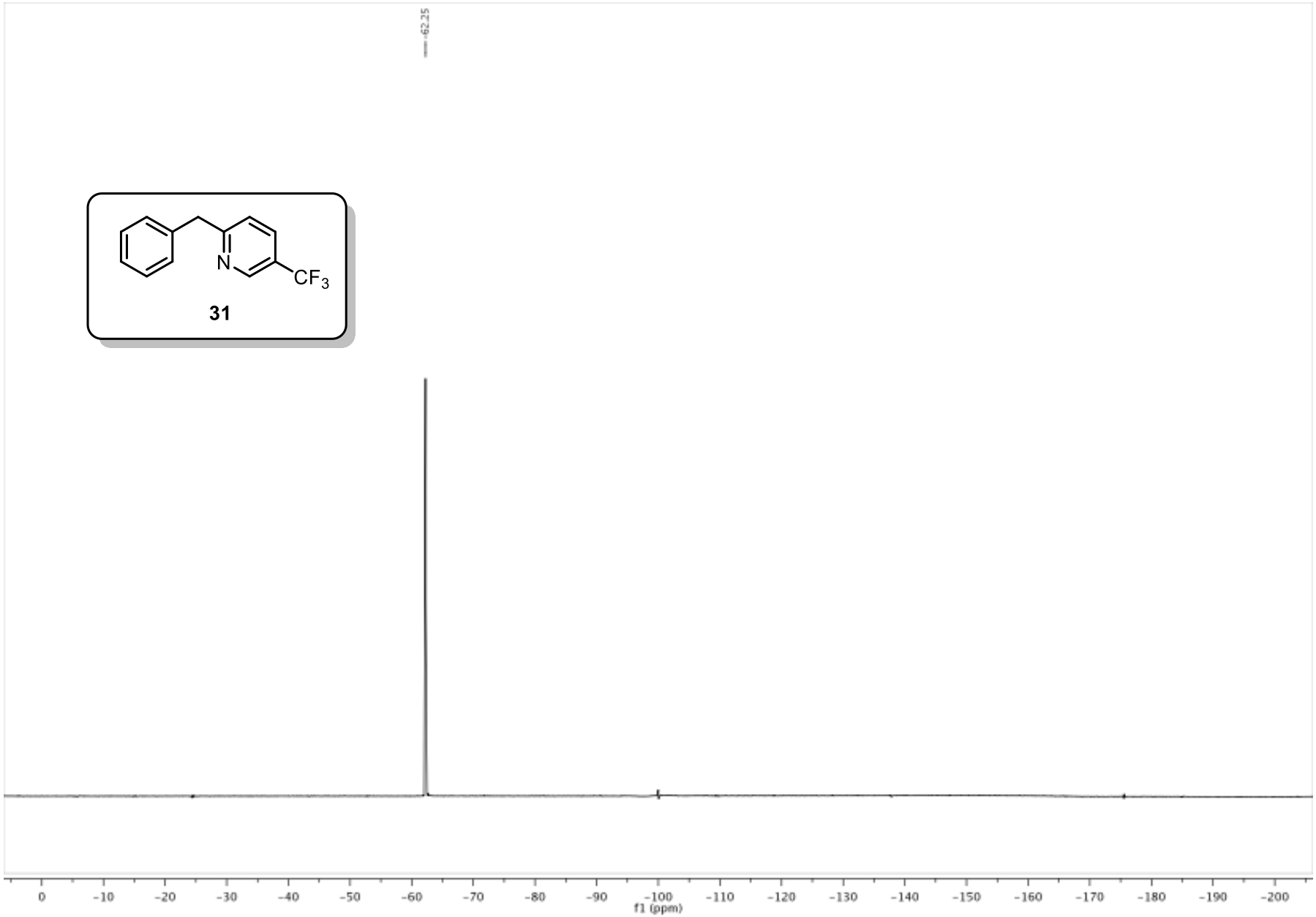
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 2-benzyl-5-(trifluoromethyl)pyridine (**31**)



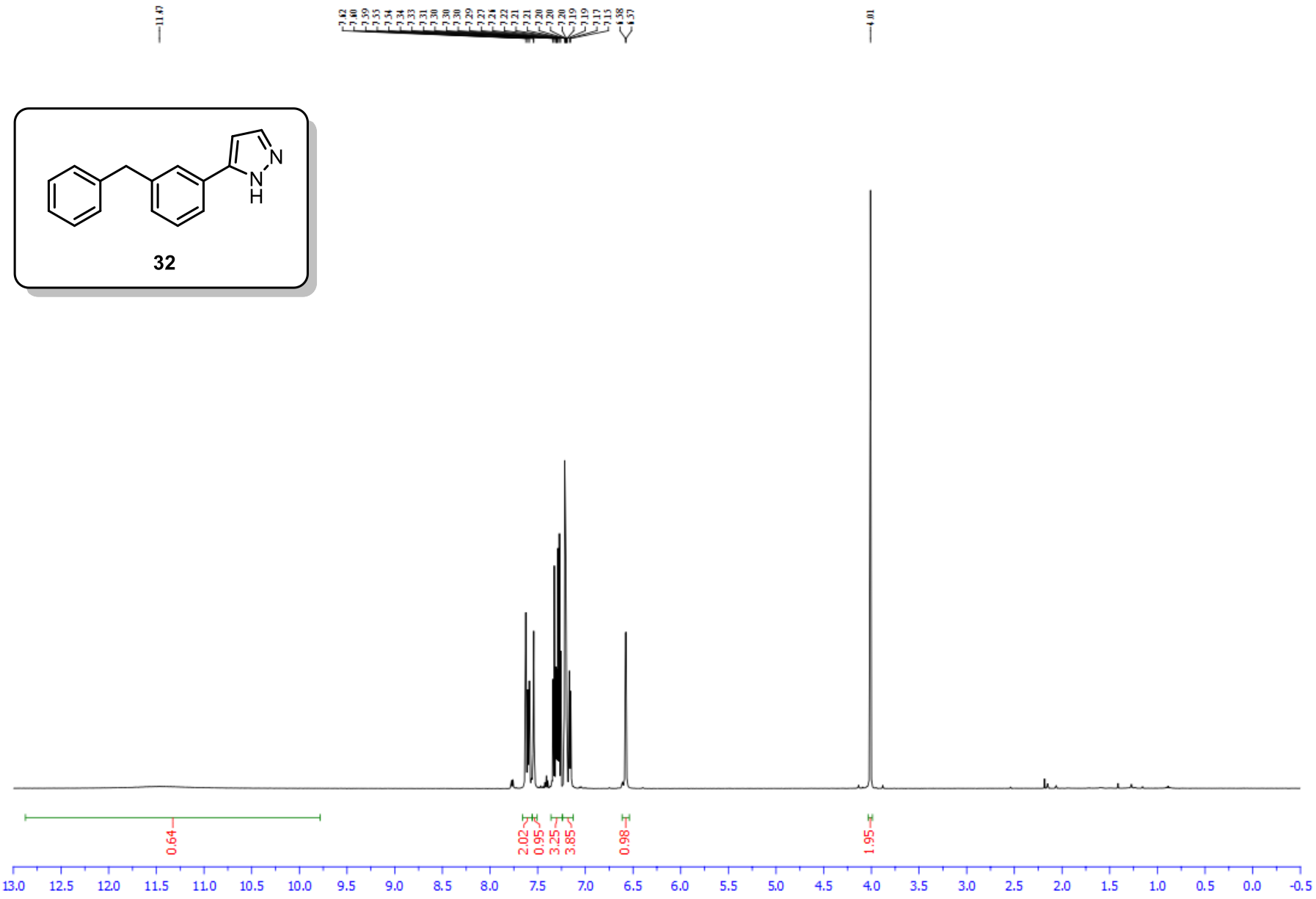
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 2-benzyl-5-(trifluoromethyl)pyridine (**31**)



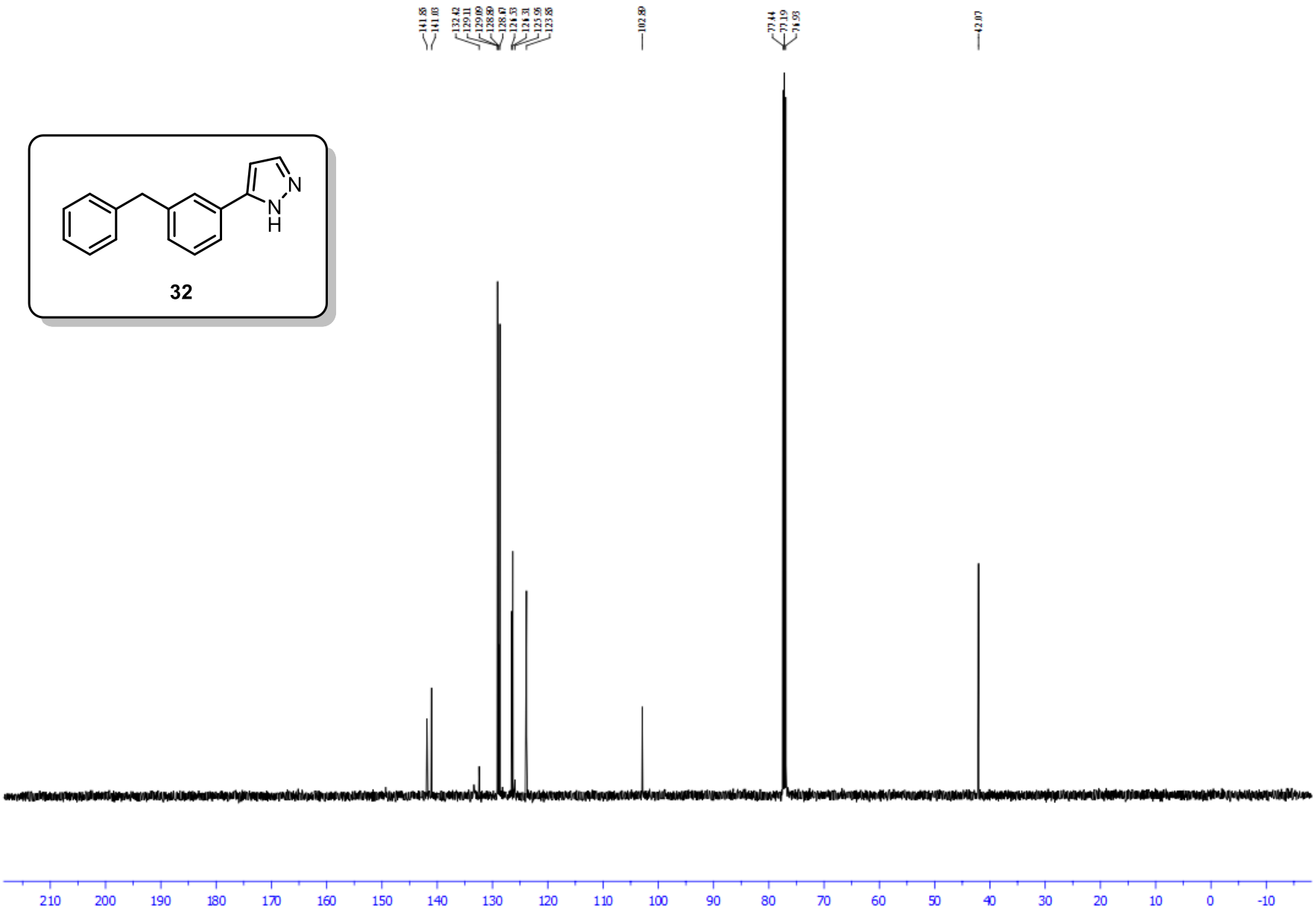
^{19}F NMR ($CDCl_3$, 470.8 MHz) spectrum of 2-benzyl-5-(trifluoromethyl)pyridine (**31**)



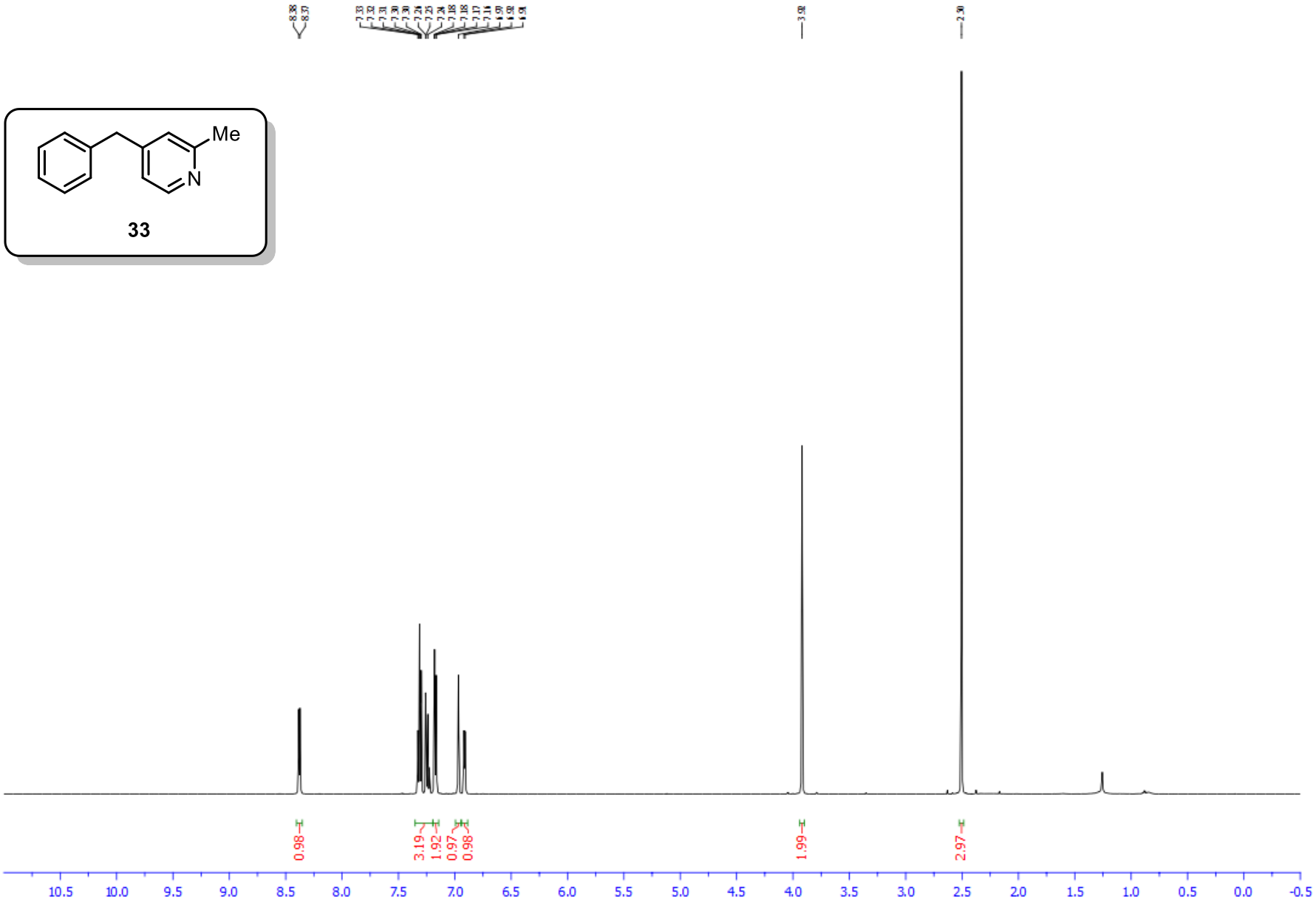
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 5-(3-benzylphenyl)-1H-pyrazole (**32**)



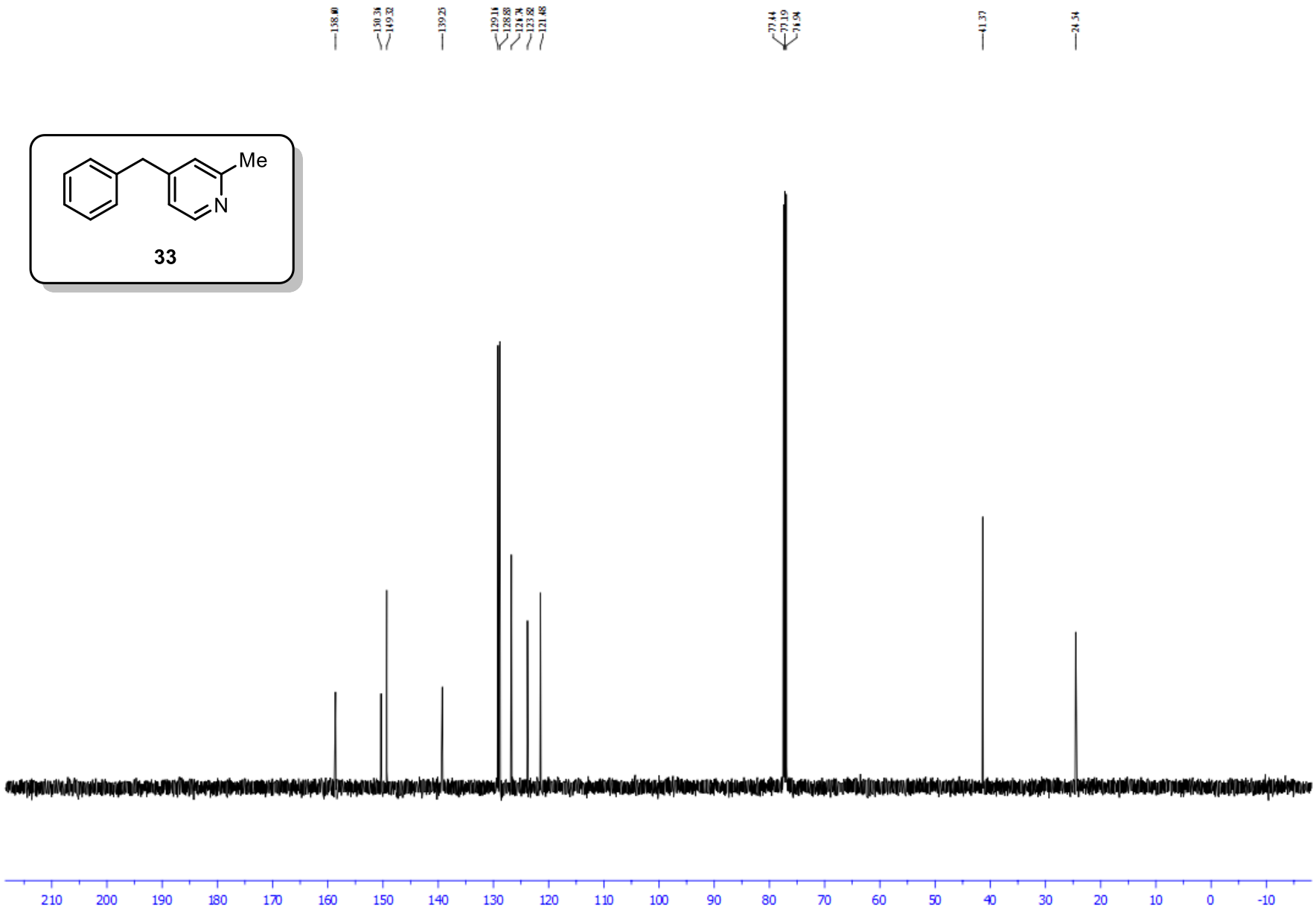
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 5-(3-benzylphenyl)-1H-pyrazole (**32**)



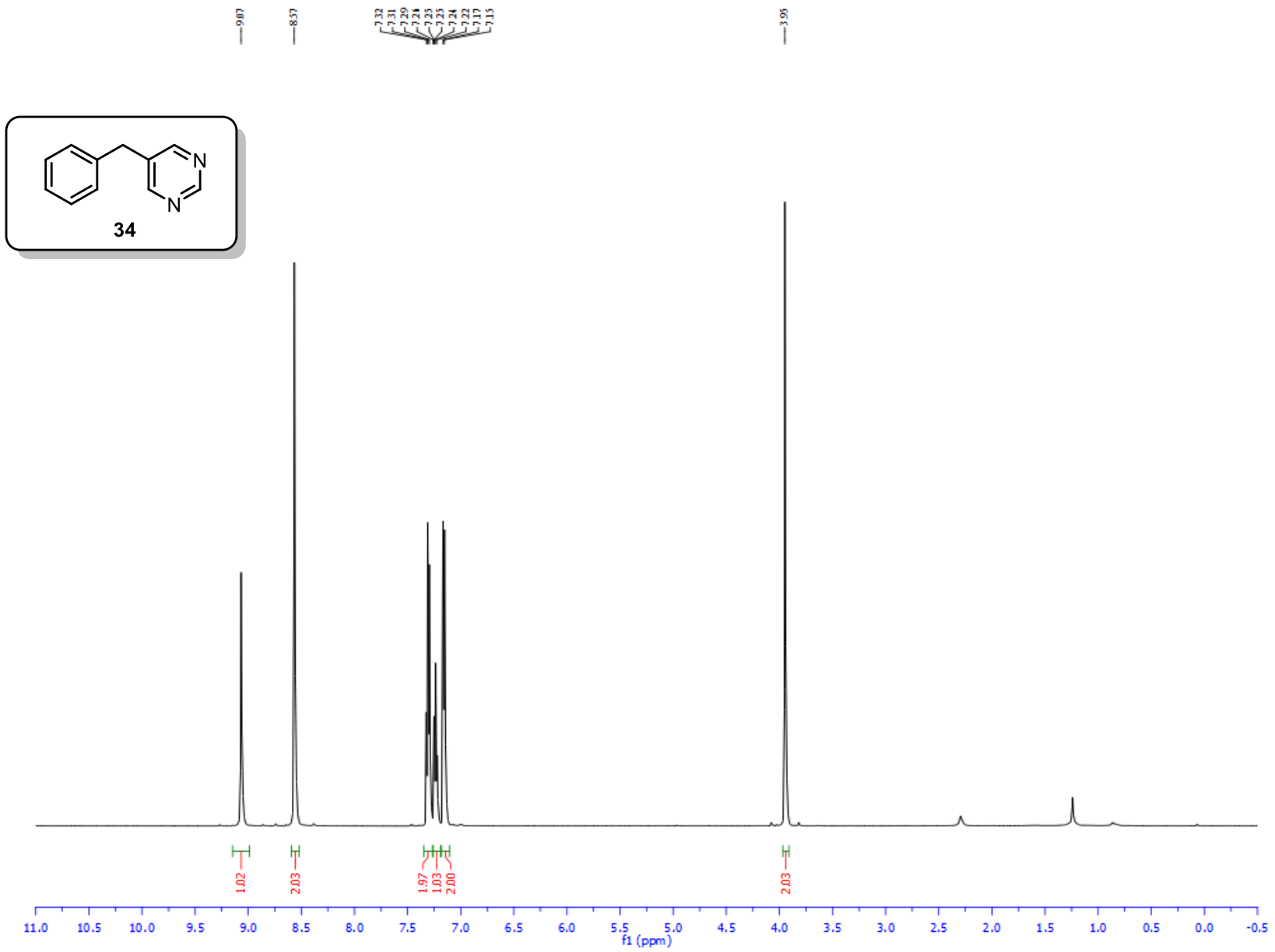
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 4-benzyl-2-methylpyridine (**33**)



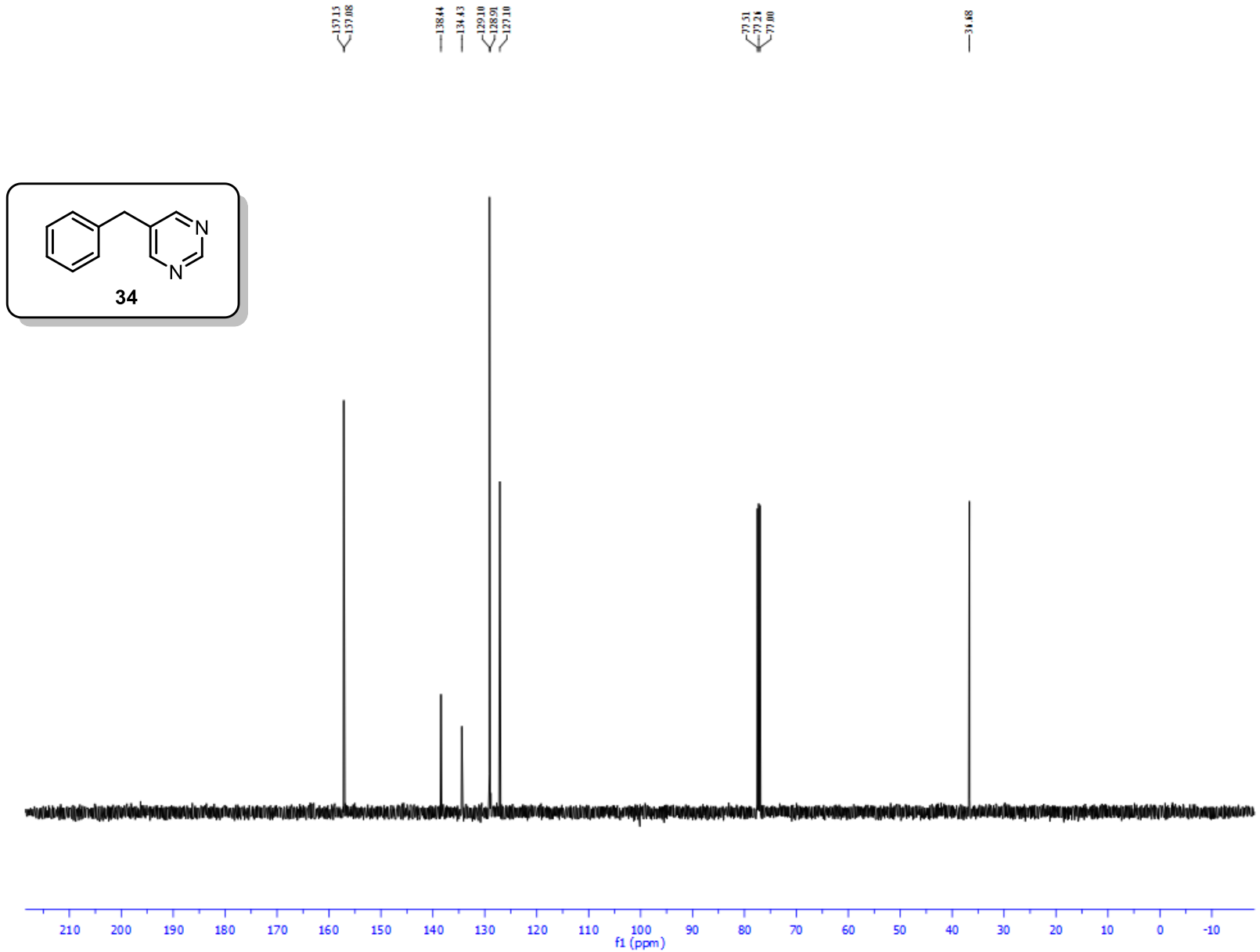
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 4-benzyl-2-methylpyridine (**33)**



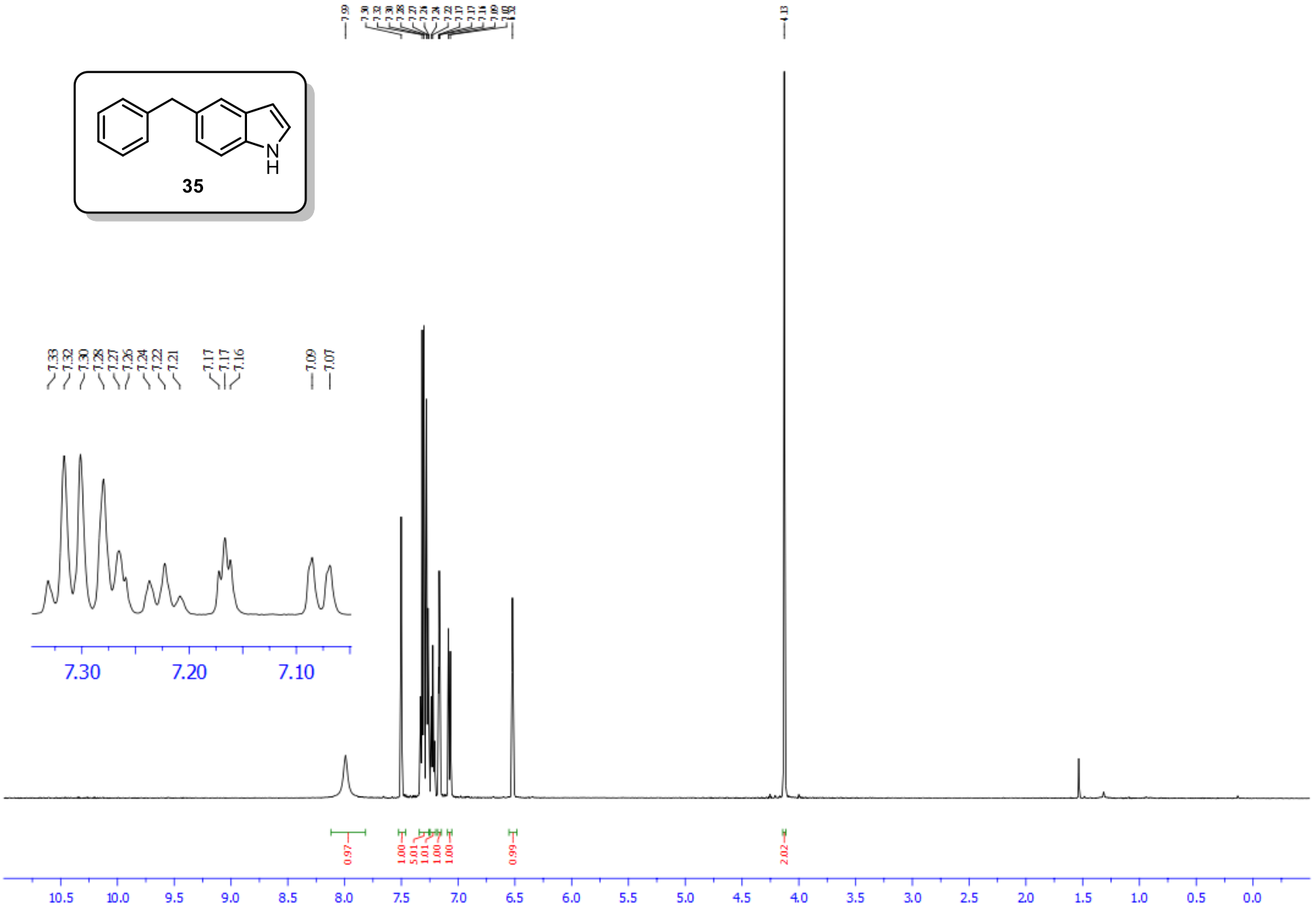
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 5-benzylpyrimidine (**34**)



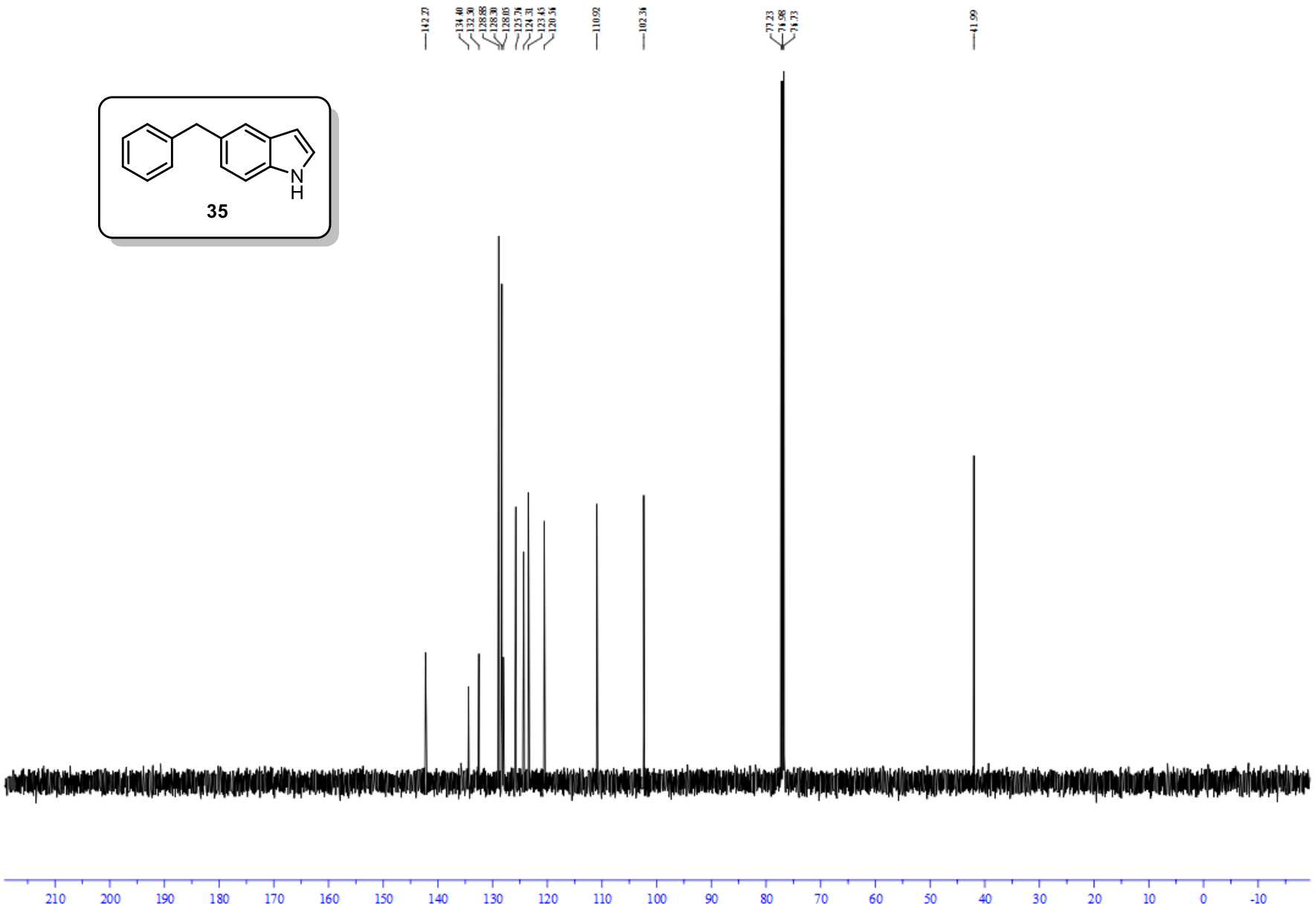
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 5-benzylpyrimidine (**34**)



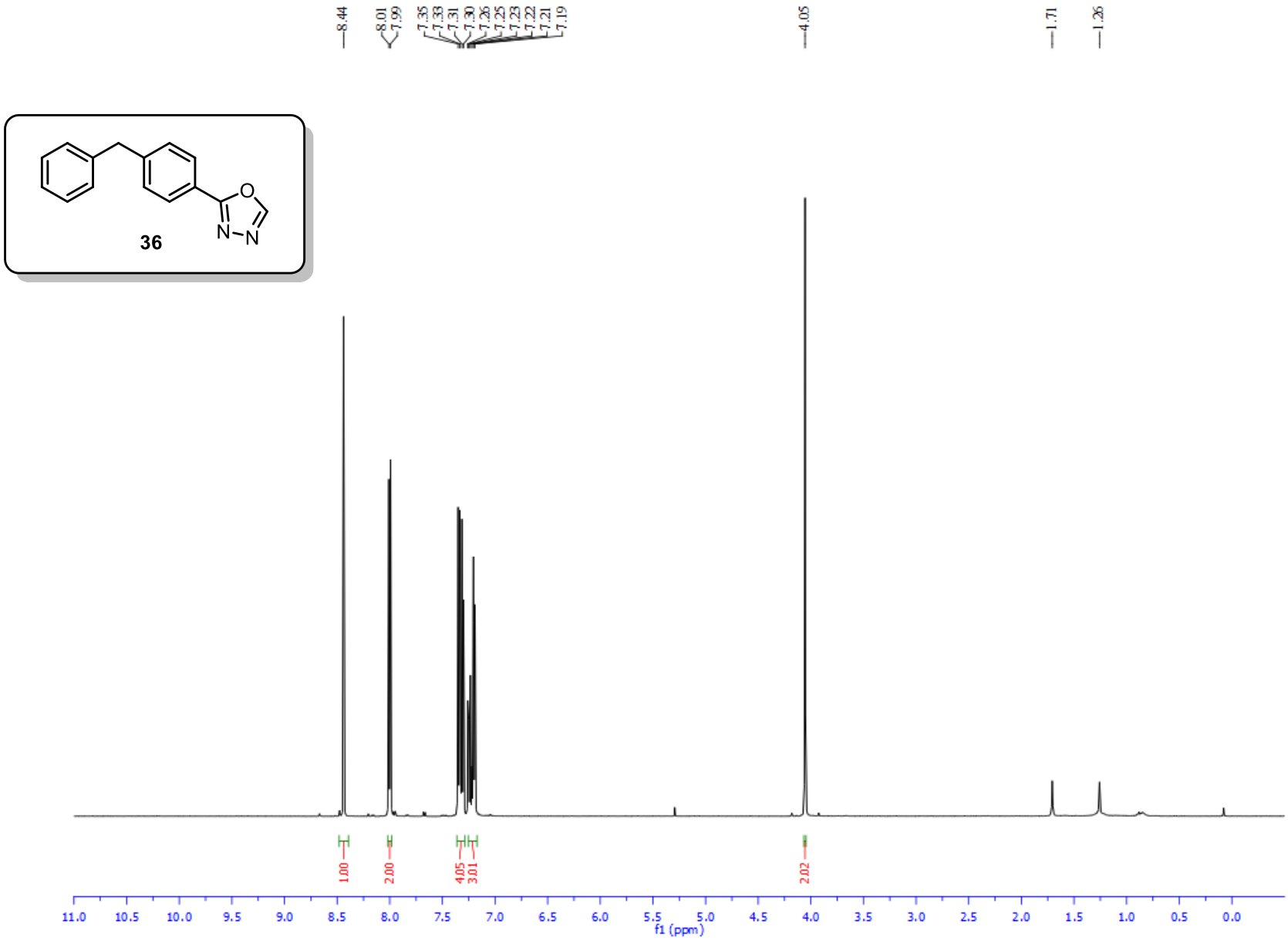
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 5-benzyl-1H-indole (**35**)



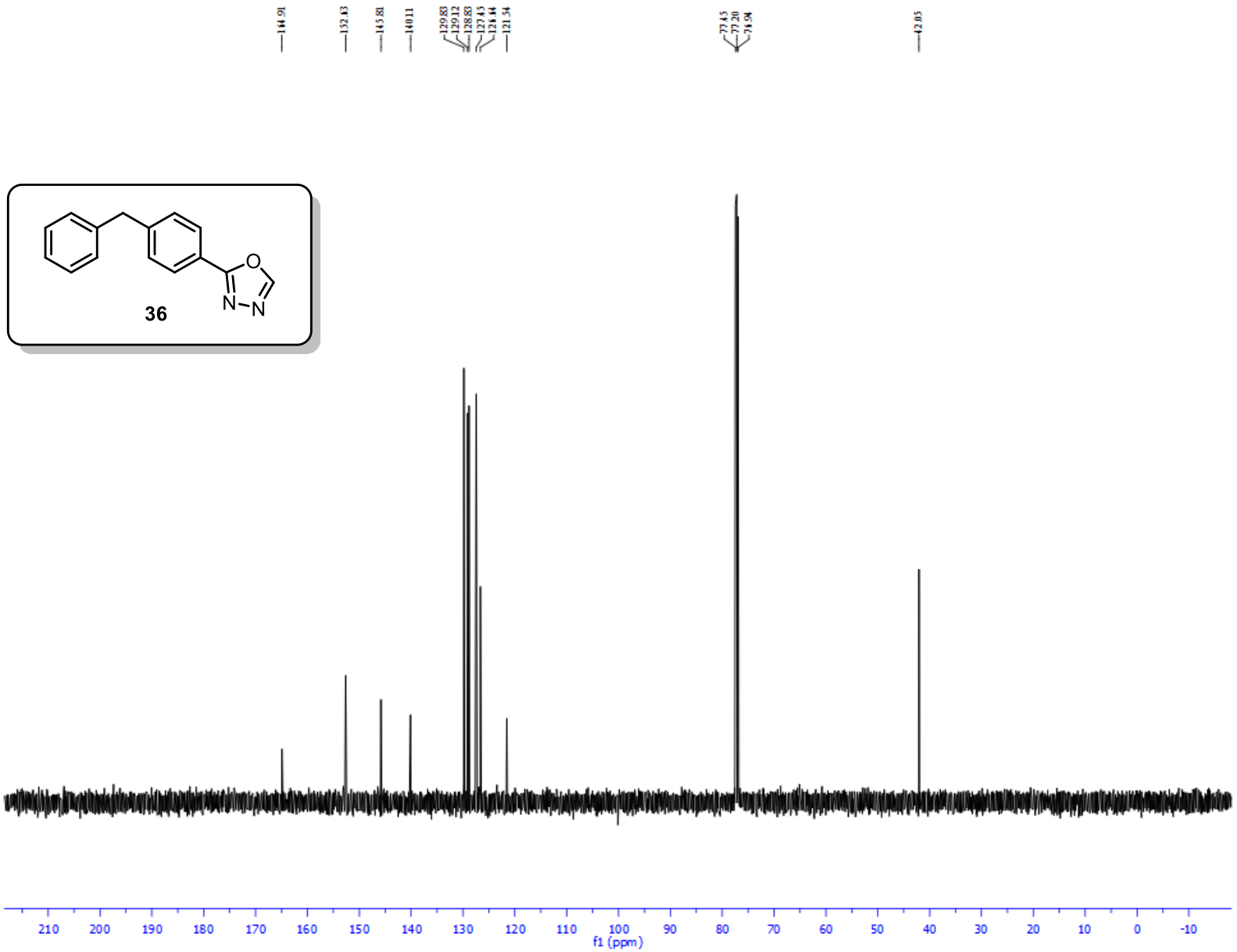
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 5-benzyl-1H-indole (**35**)



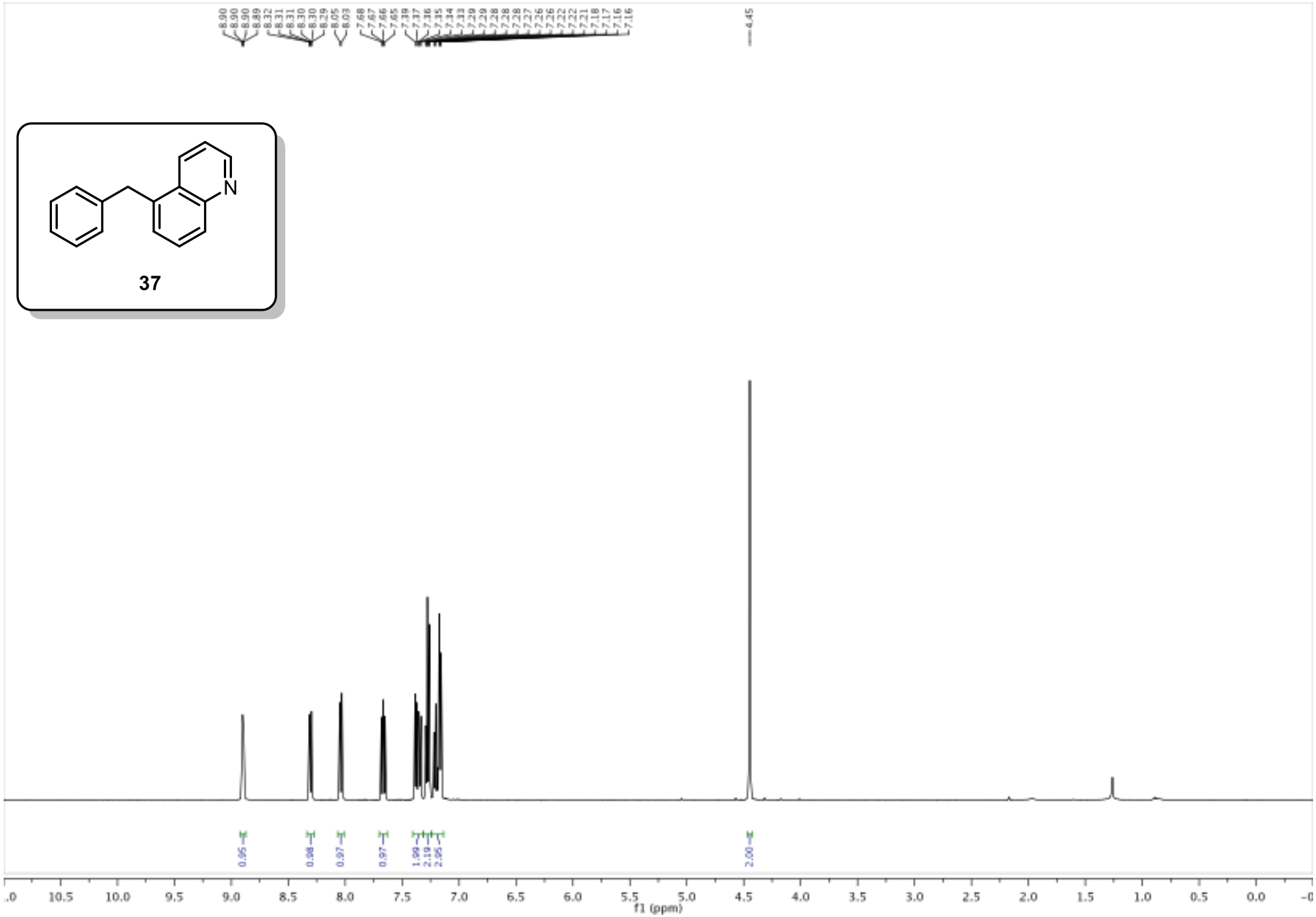
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 2-(4-benzylphenyl)-1,3,4-oxadiazole (**36**)



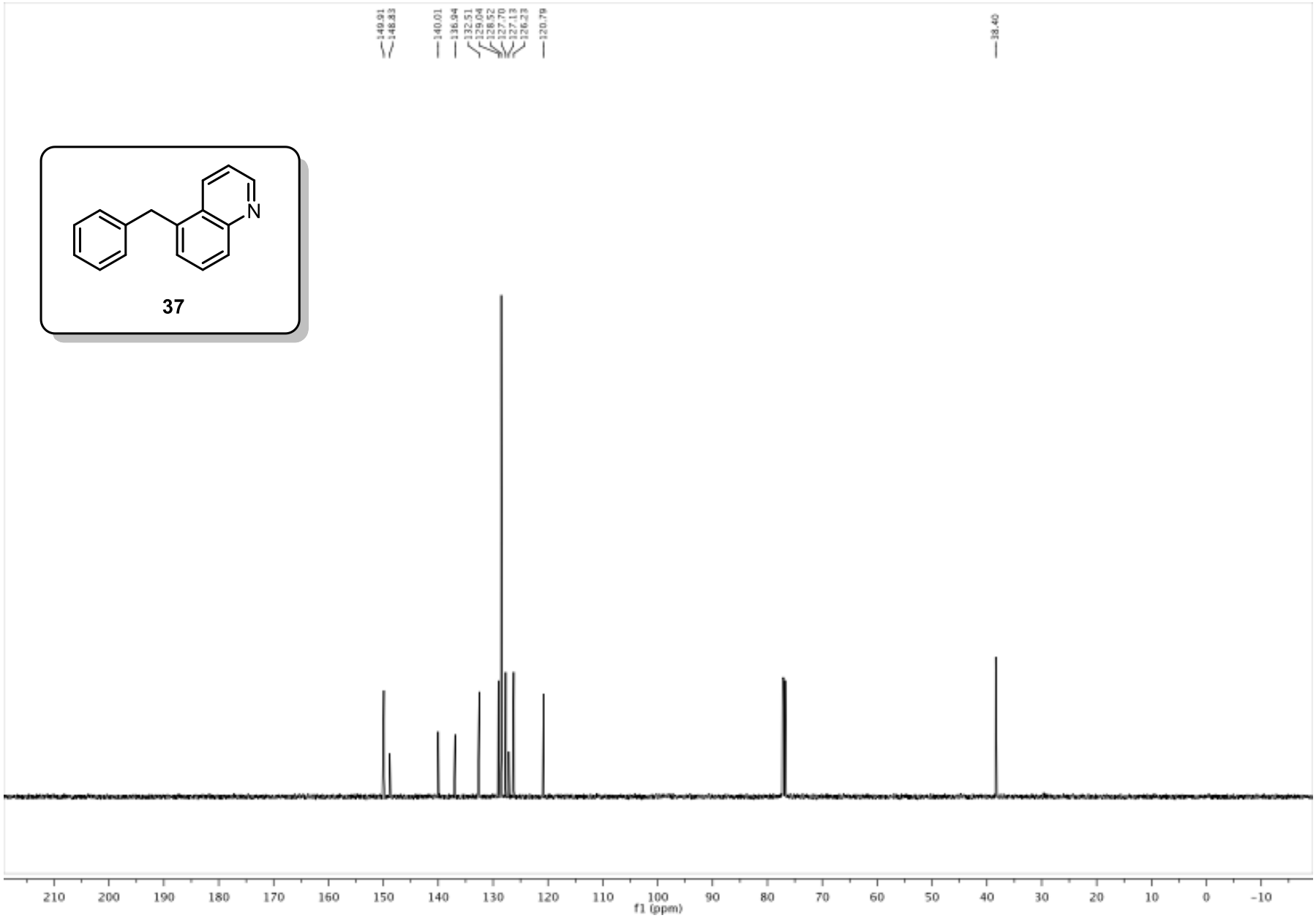
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 2-(4-benzylphenyl)-1,3,4-oxadiazole (**36**)



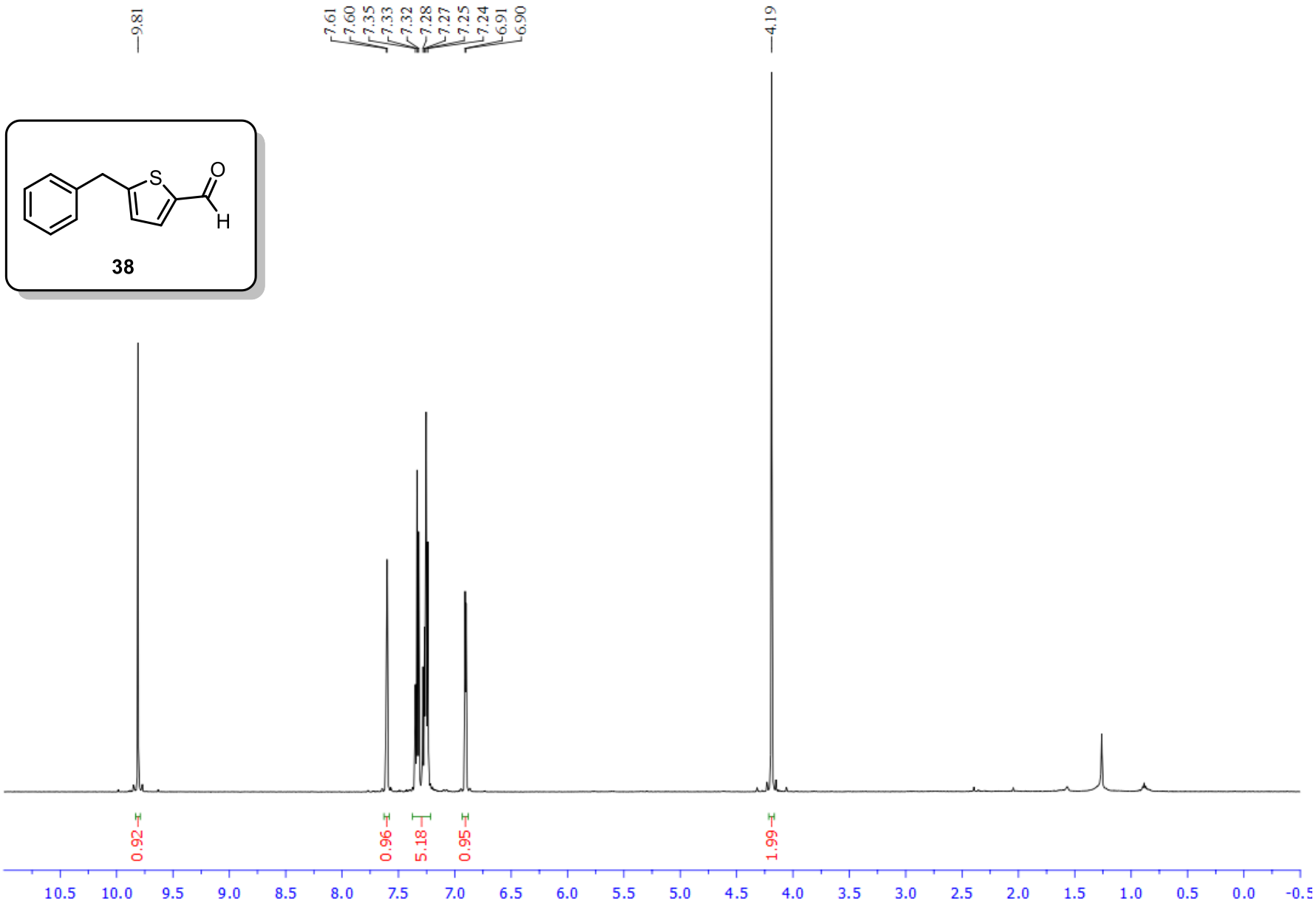
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 5-benzylquinoline (**37**)



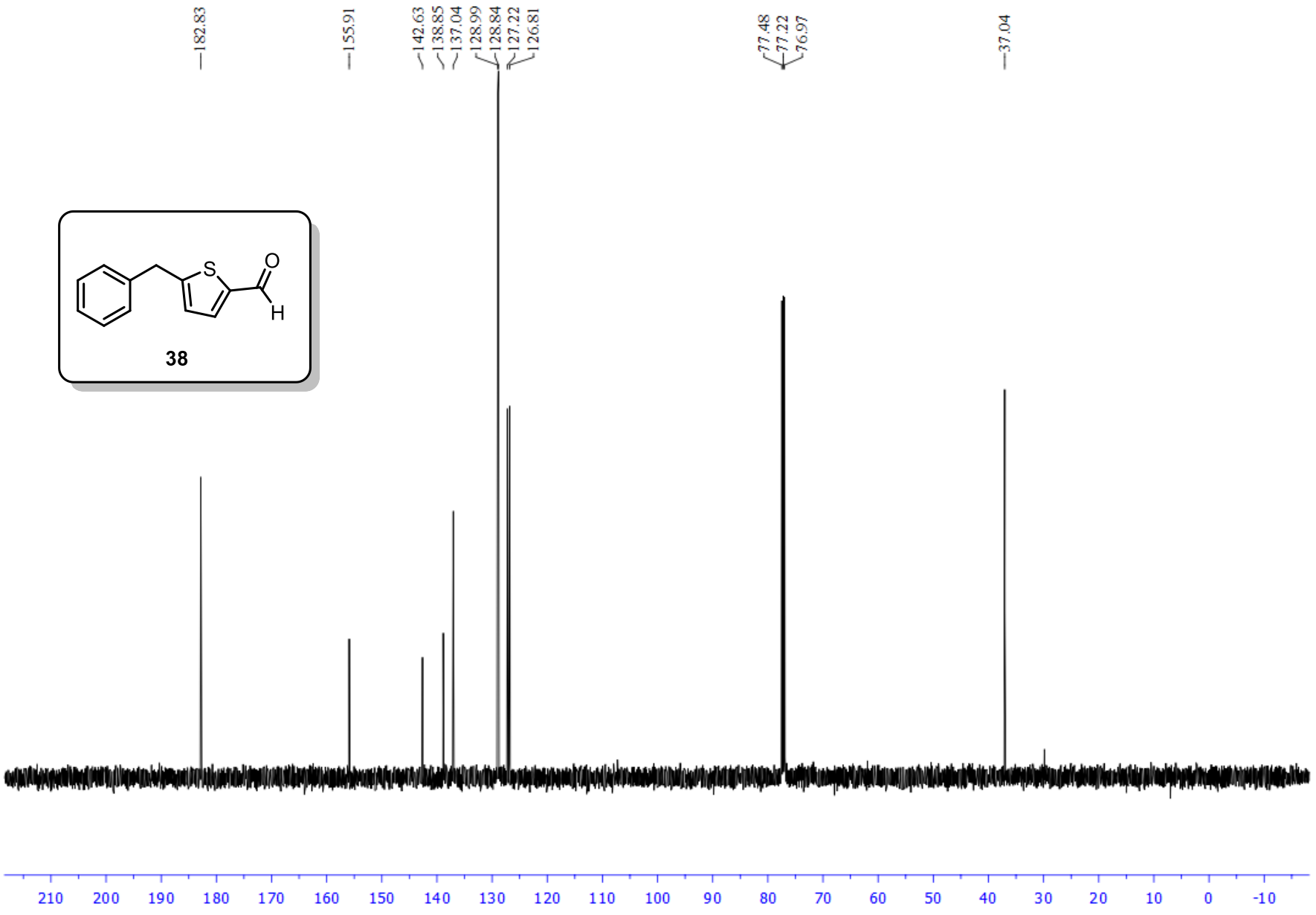
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 5-benzylquinoline (**37**)



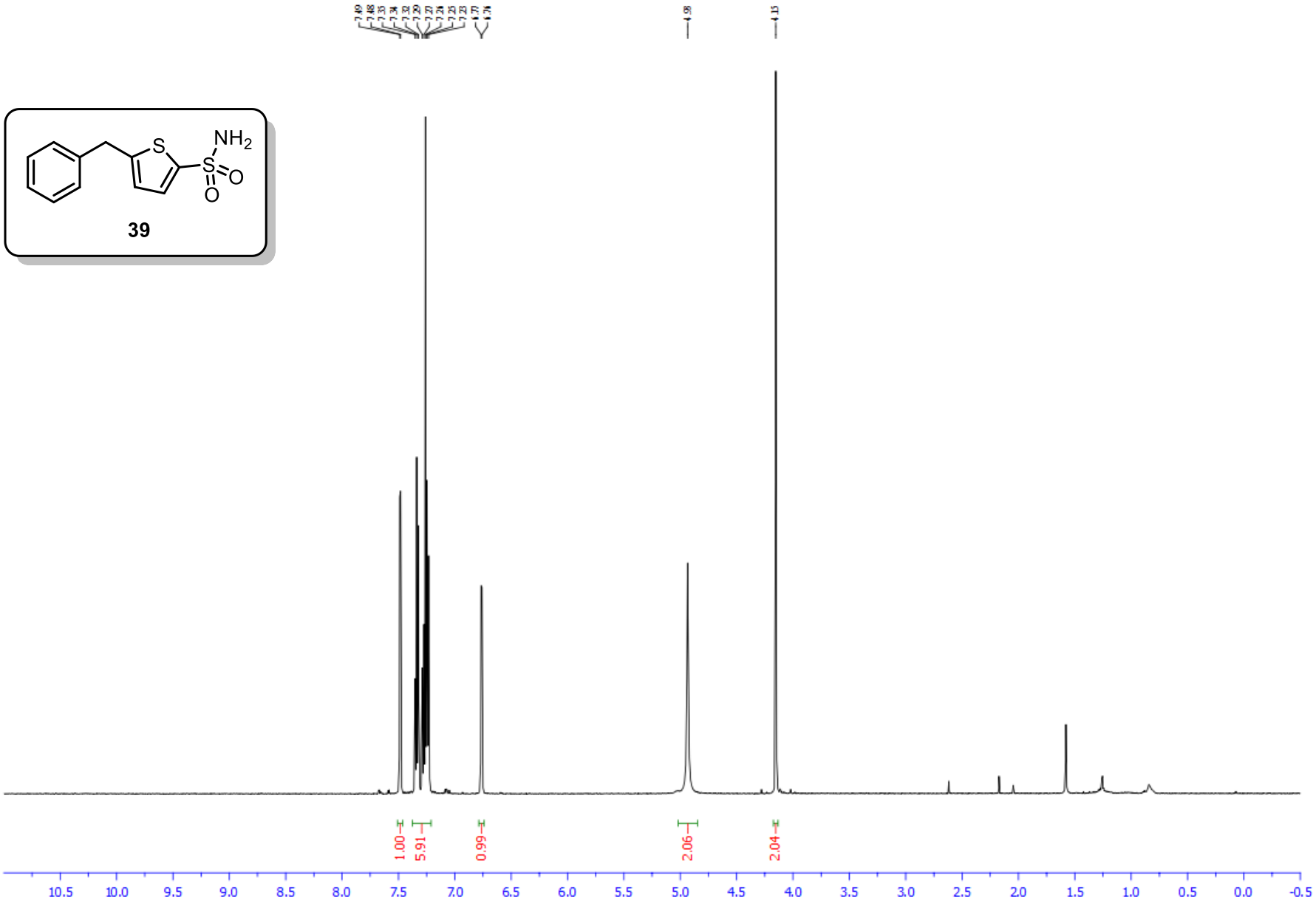
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 5-benzylthiophene-2-carbaldehyde (**38**)



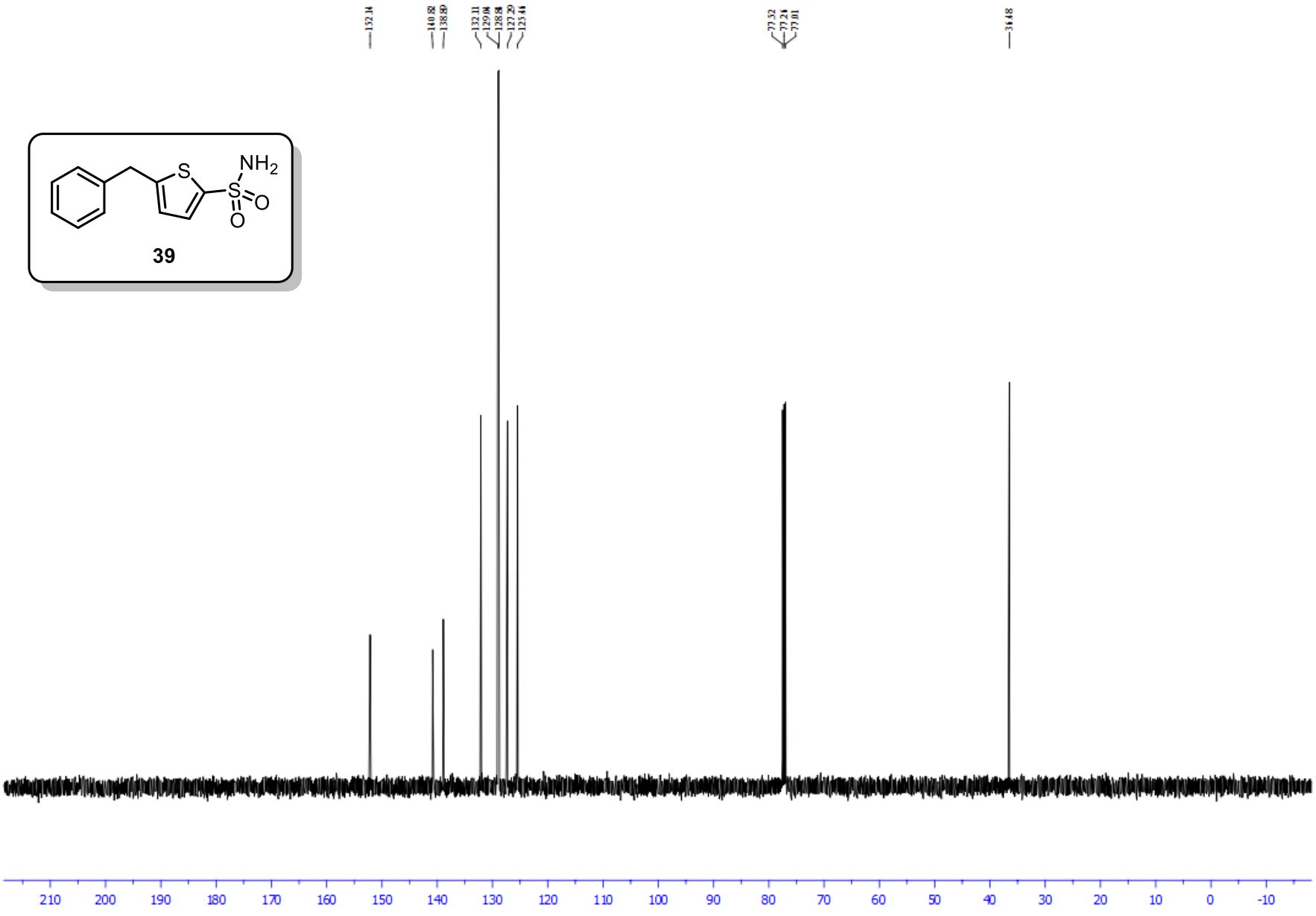
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 5-benzylthiophene-2-carbaldehyde (**38**)



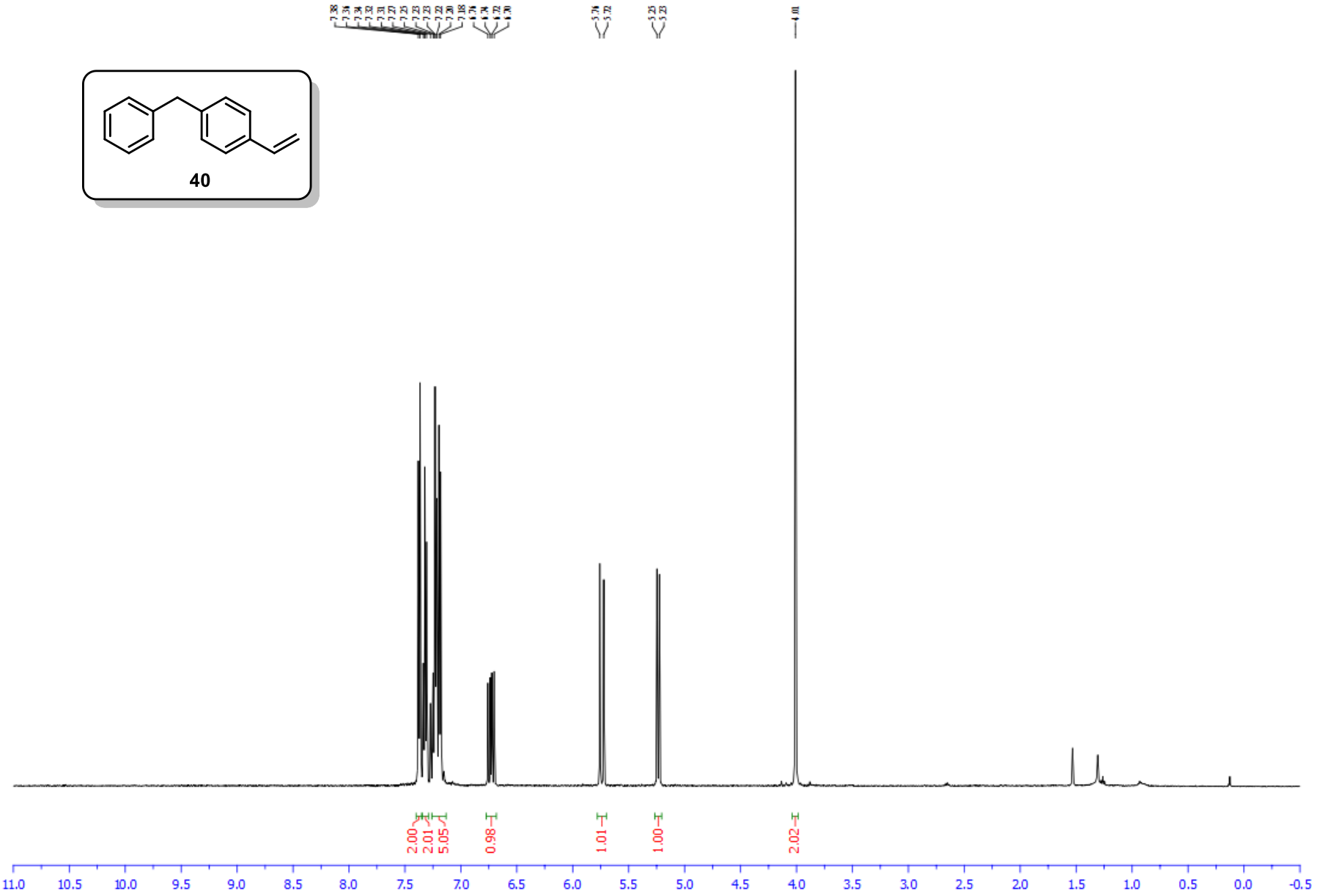
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 5-benzylthiophene-2-sulfonamide (**39**)



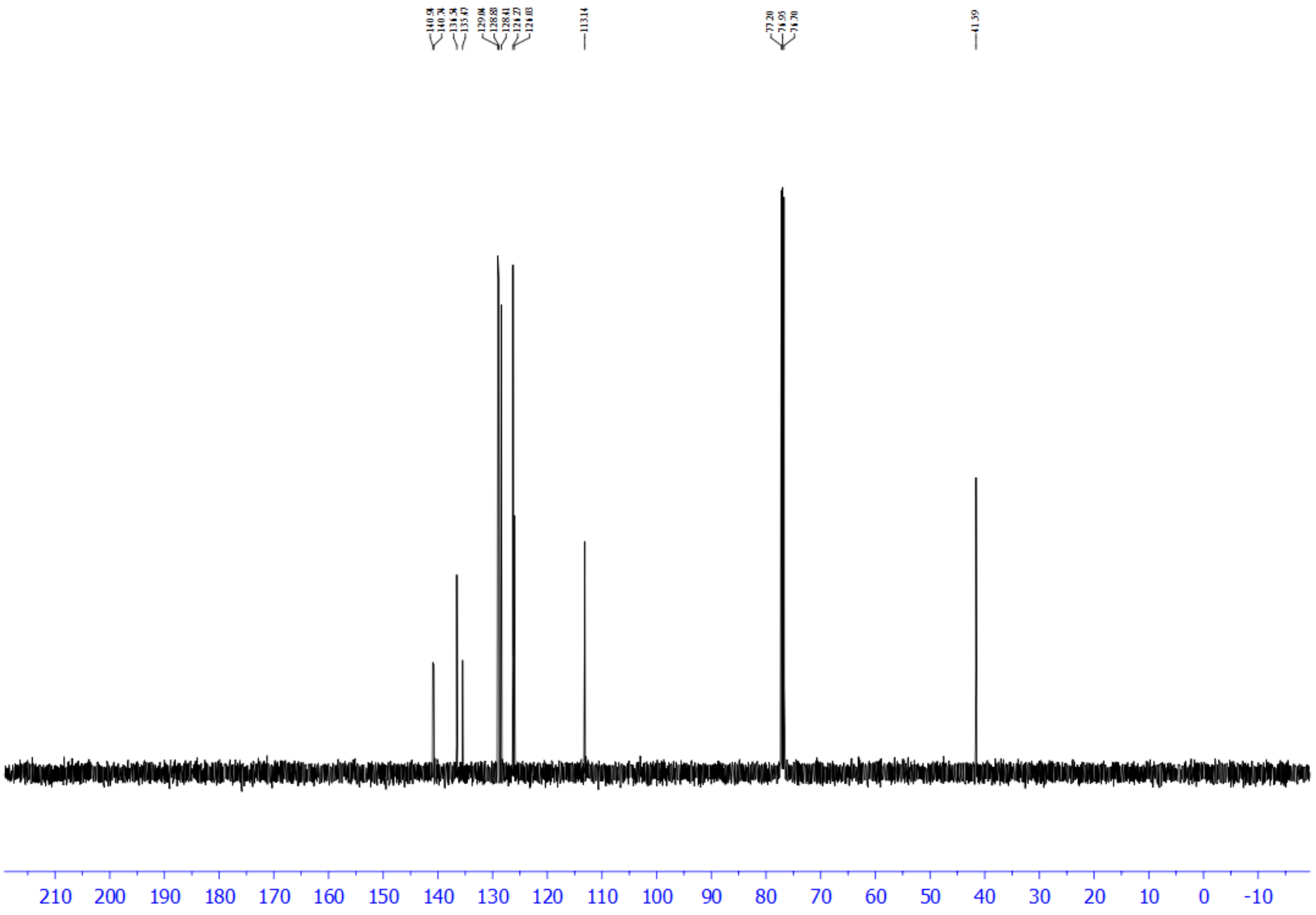
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 5-benzylthiophene-2-sulfonamide (**39**)



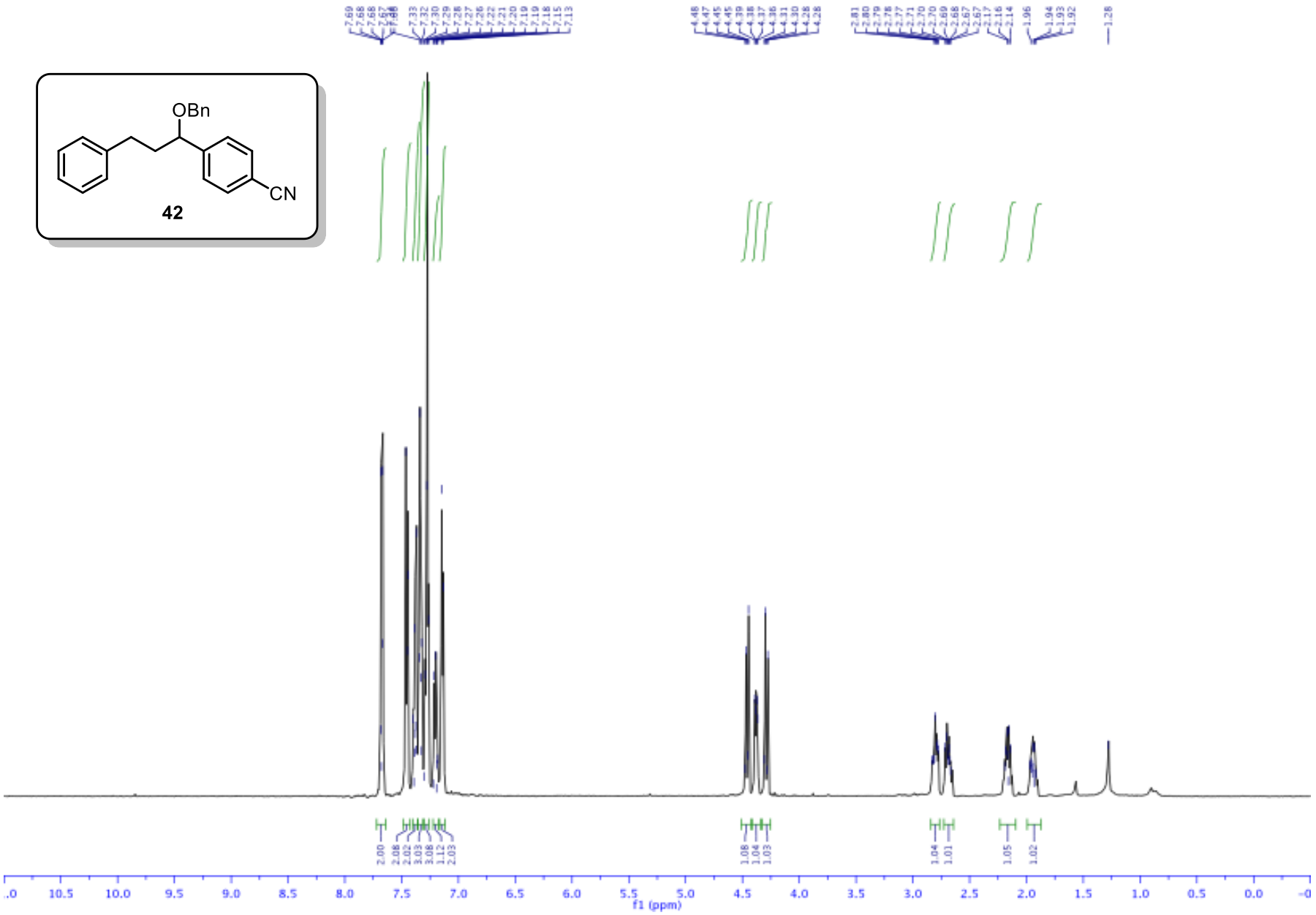
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 1-benzyl-4-vinylbenzene (**40**)



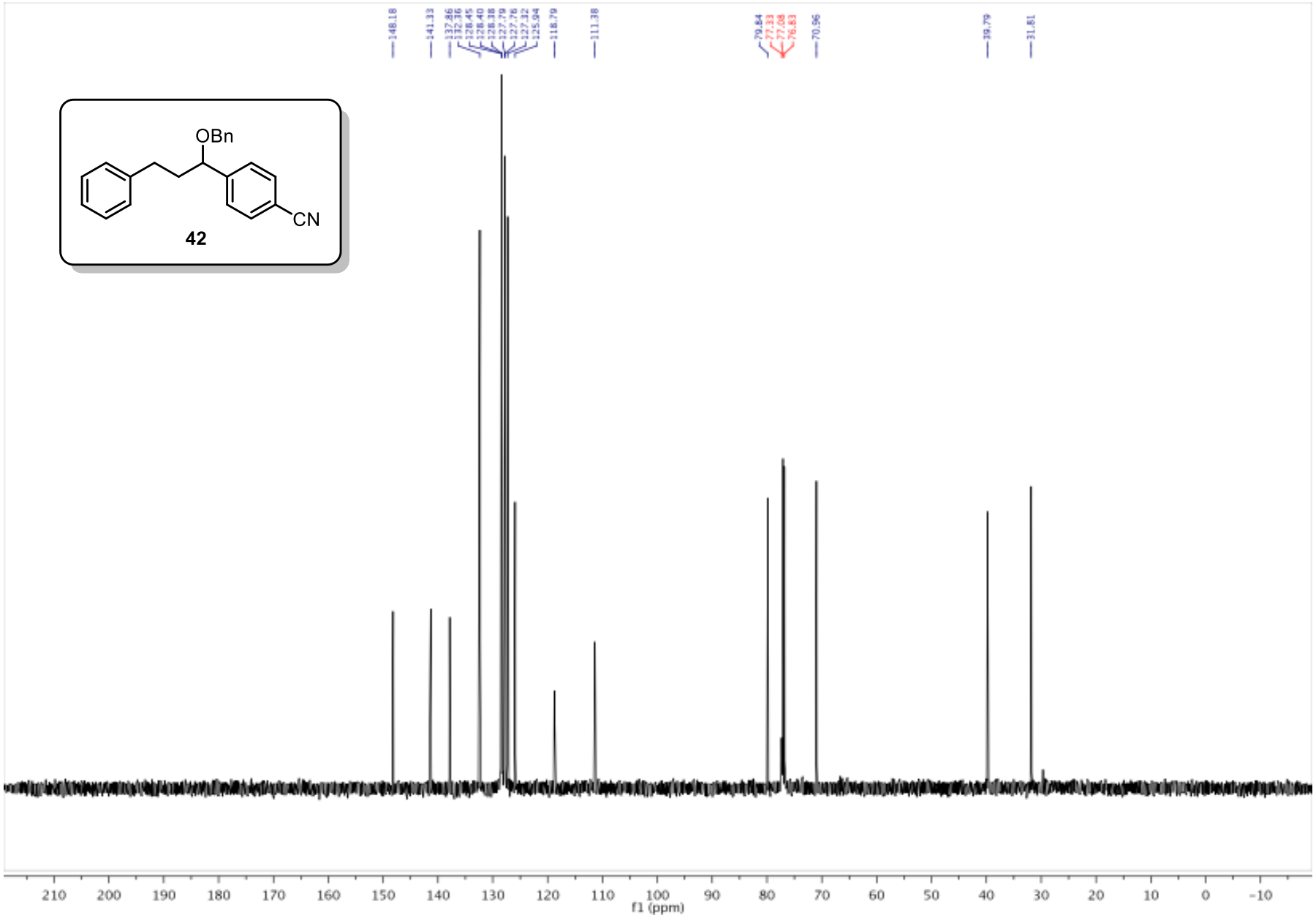
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 1-benzyl-4-vinylbenzene (**40**)



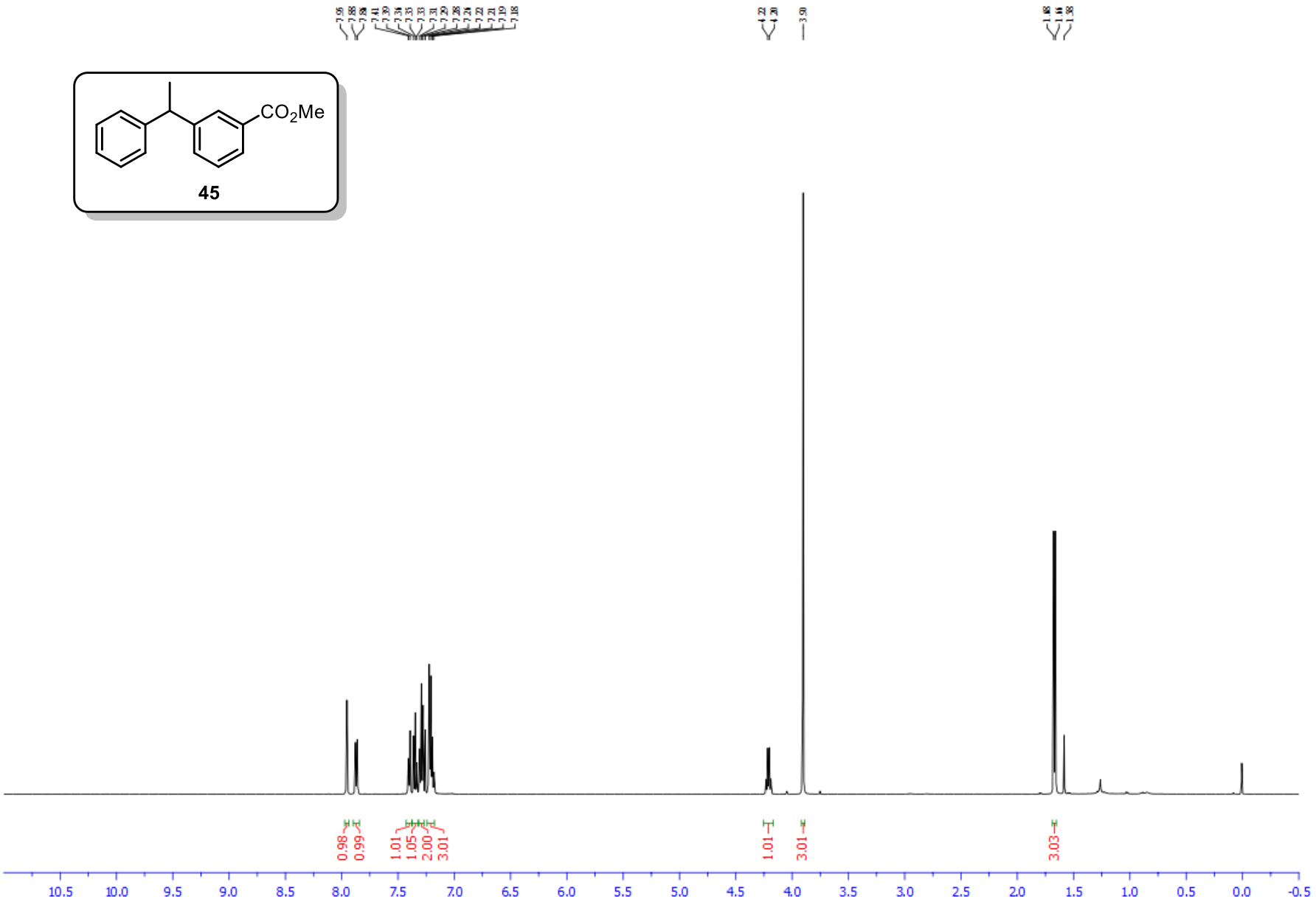
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 4-(1-(benzyloxy)-3-phenylpropyl)benzonitrile **(42)**



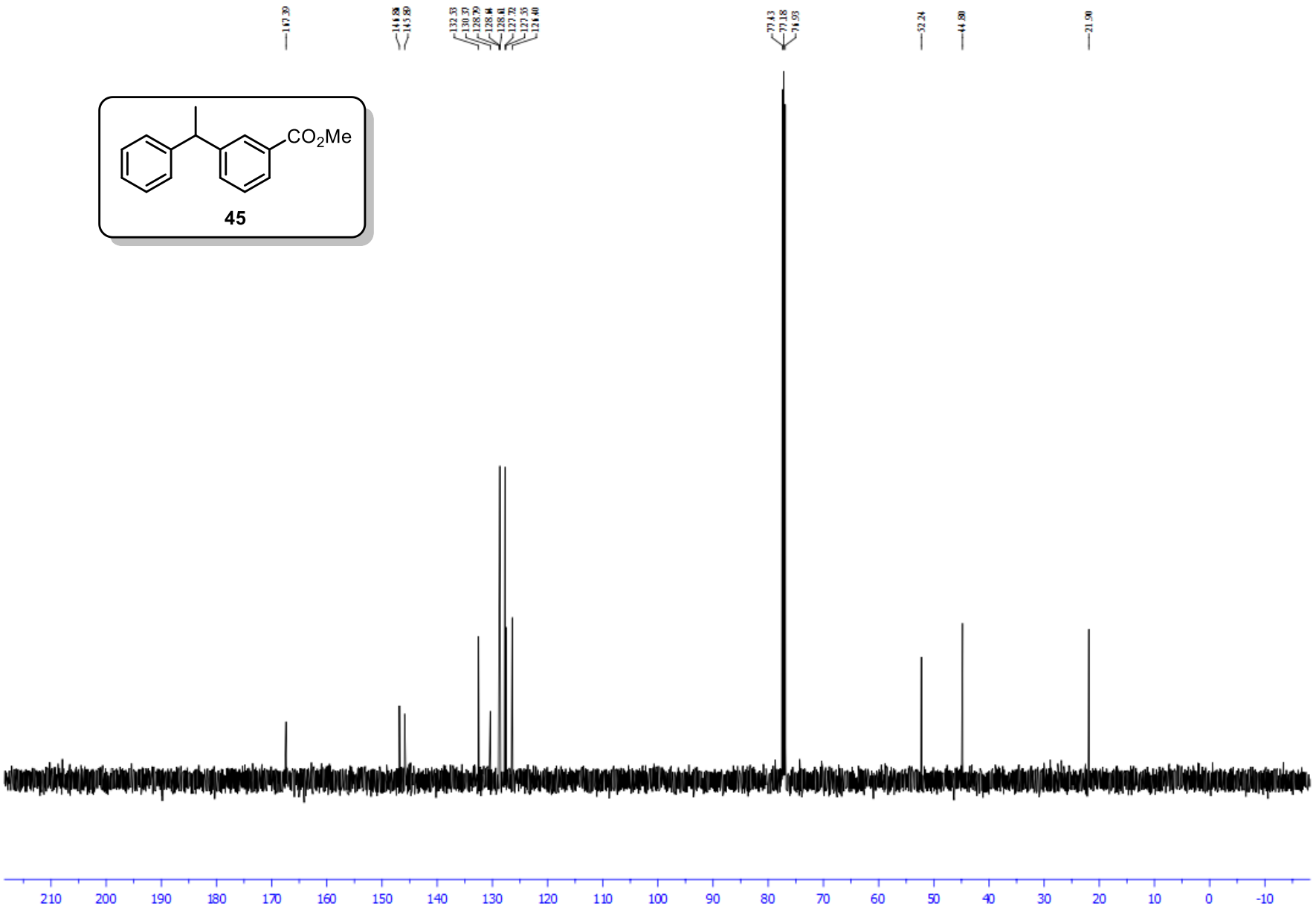
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 4-(1-(benzyloxy)-3-phenylpropyl)benzonitrile **(42)**



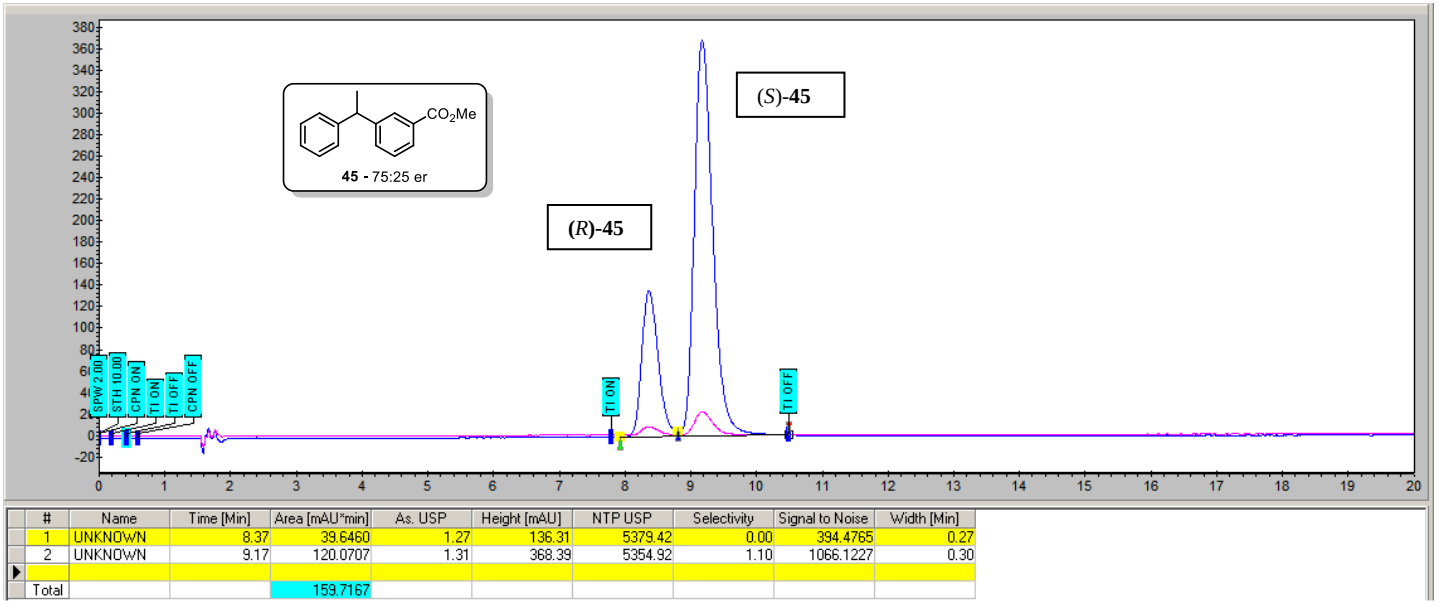
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of methyl 3-(1-phenylethyl)benzoate (**45**)



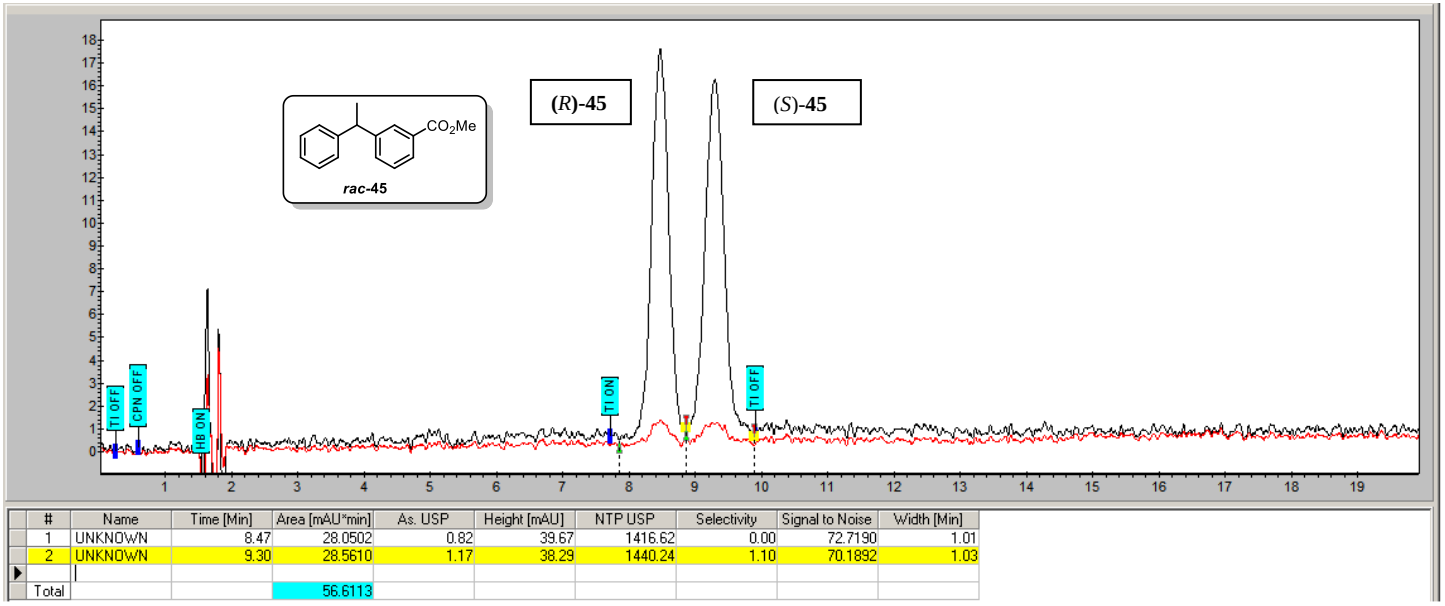
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of methyl 3-(1-phenylethyl)benzoate (**45**)



Chiral SFC (OJ-H column: 5% iPrOH in CO_2, 2.0 mL/min) chromatograms of methyl 3-(1-phenylethyl)benzoate (**45**)

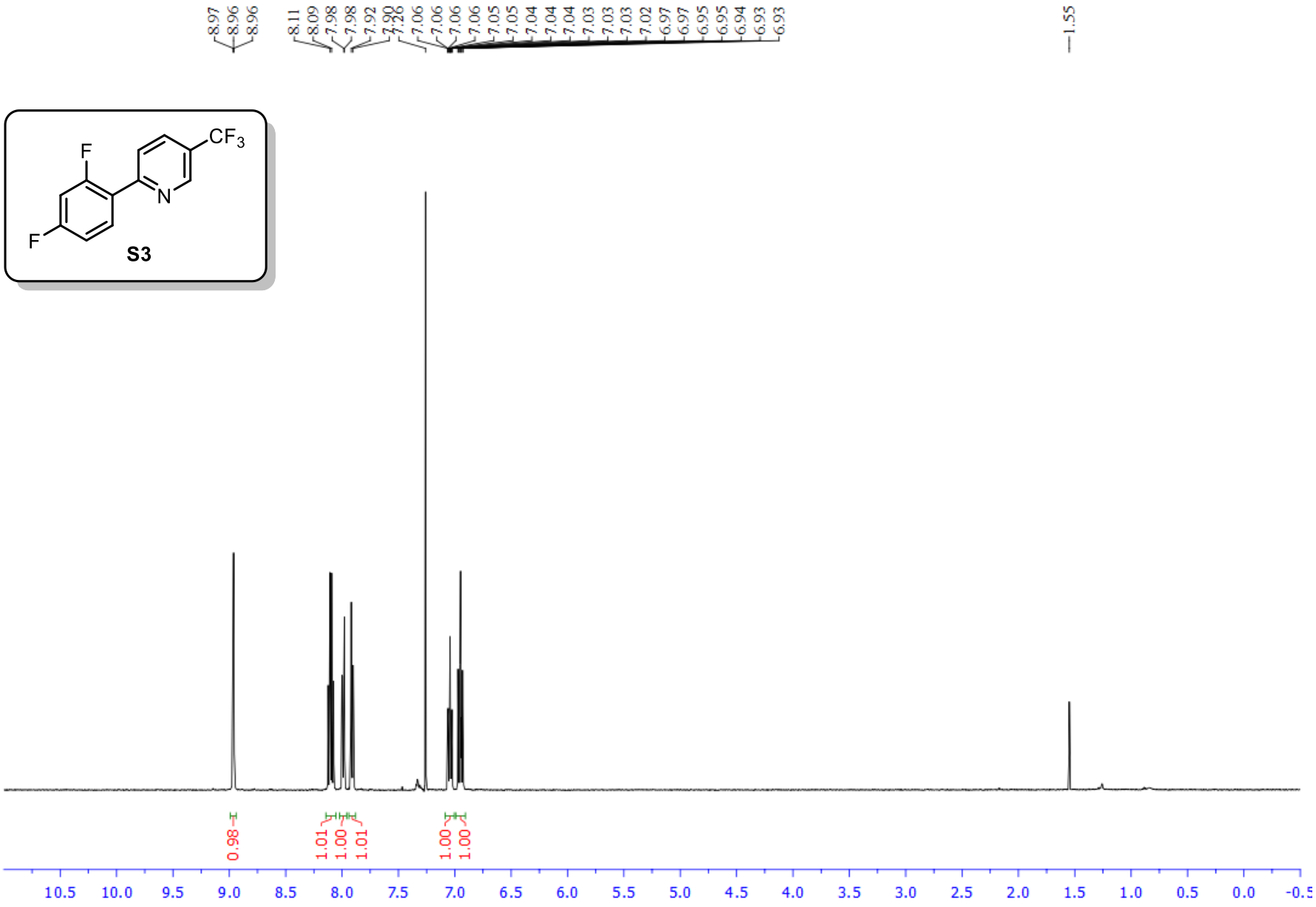


#	Name	Time [Min]	Area [mAU*min]	As. USP	Height [mAU]	NTP USP	Selectivity	Signal to Noise	Width [Min]
1	UNKNOWN	8.37	39.6460	1.27	136.31	5379.42	0.00	394.4765	0.27
2	UNKNOWN	9.17	120.0707	1.31	368.39	5354.92	1.10	1066.1227	0.30
Total			159.7167						

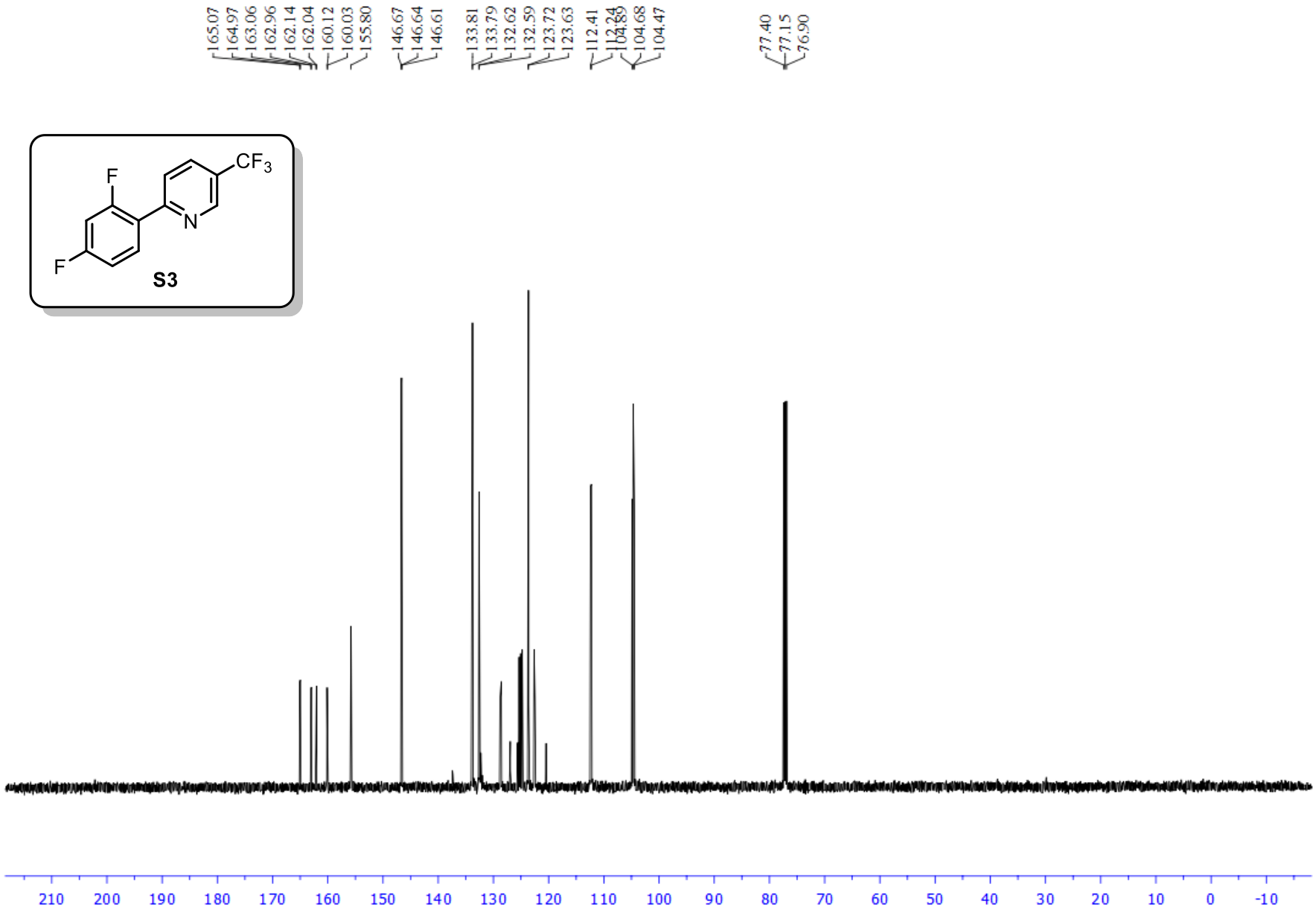


#	Name	Time [Min]	Area [mAU*min]	As. USP	Height [mAU]	NTP USP	Selectivity	Signal to Noise	Width [Min]
1	UNKNOWN	8.47	28.0502	0.82	39.67	1416.62	0.00	72.7190	1.01
2	UNKNOWN	9.30	28.5610	1.17	38.29	1440.24	1.10	70.1892	1.03
Total			56.6113						

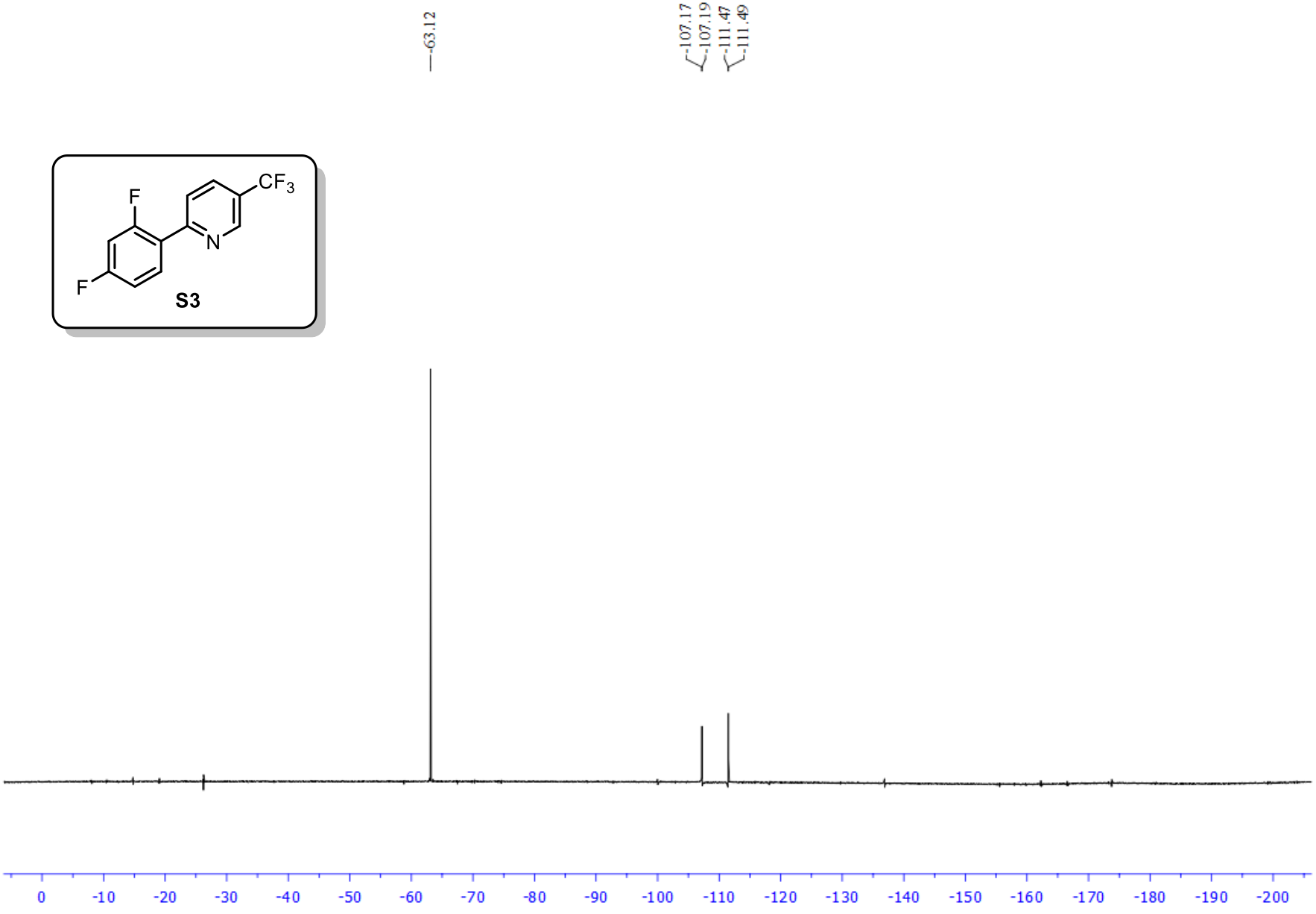
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 2-(2,4-difluorophenyl)-5-(trifluoromethyl)pyridine (**S3**)



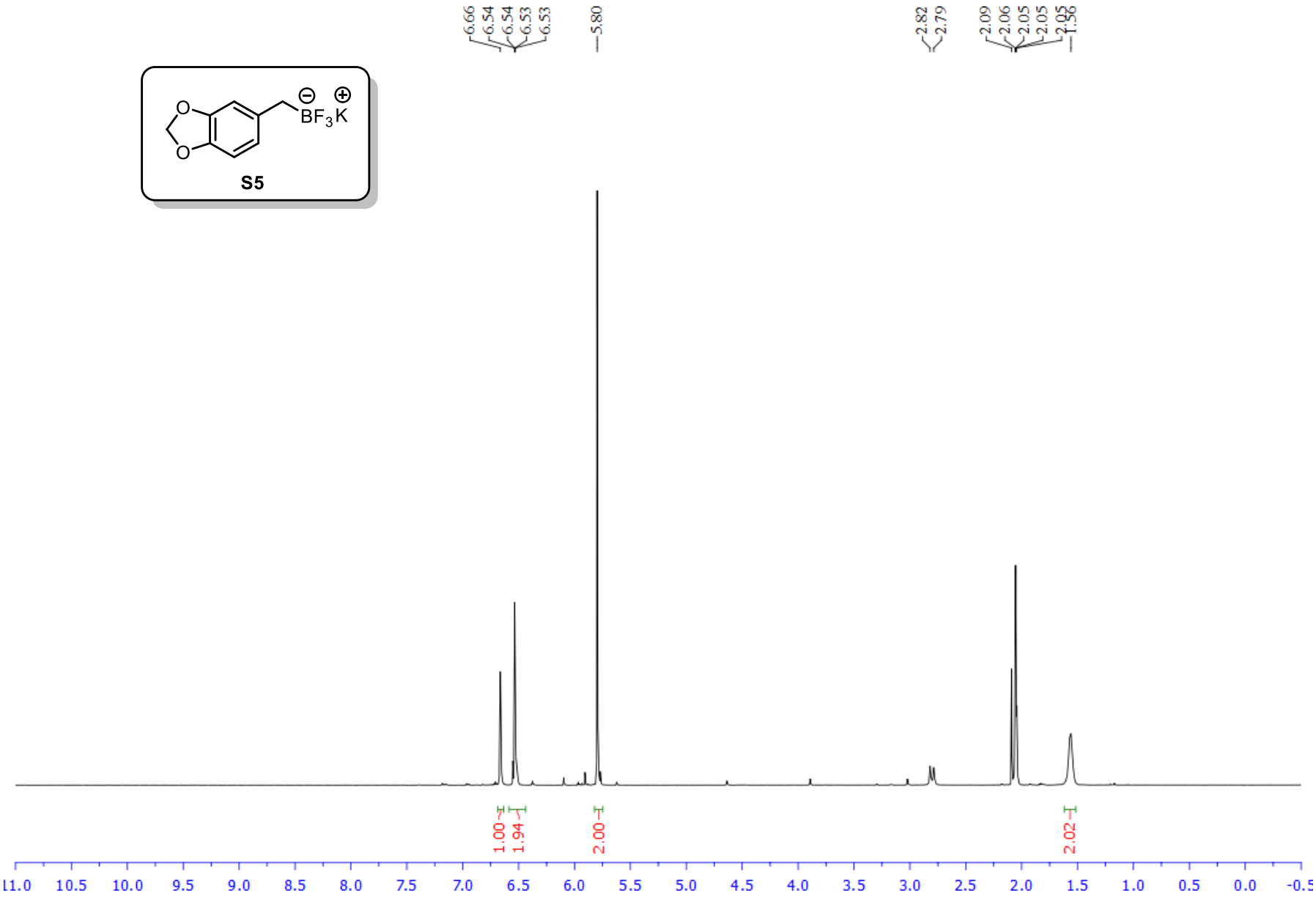
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 2-(2,4-difluorophenyl)-5-(trifluoromethyl)pyridine (**S3**)



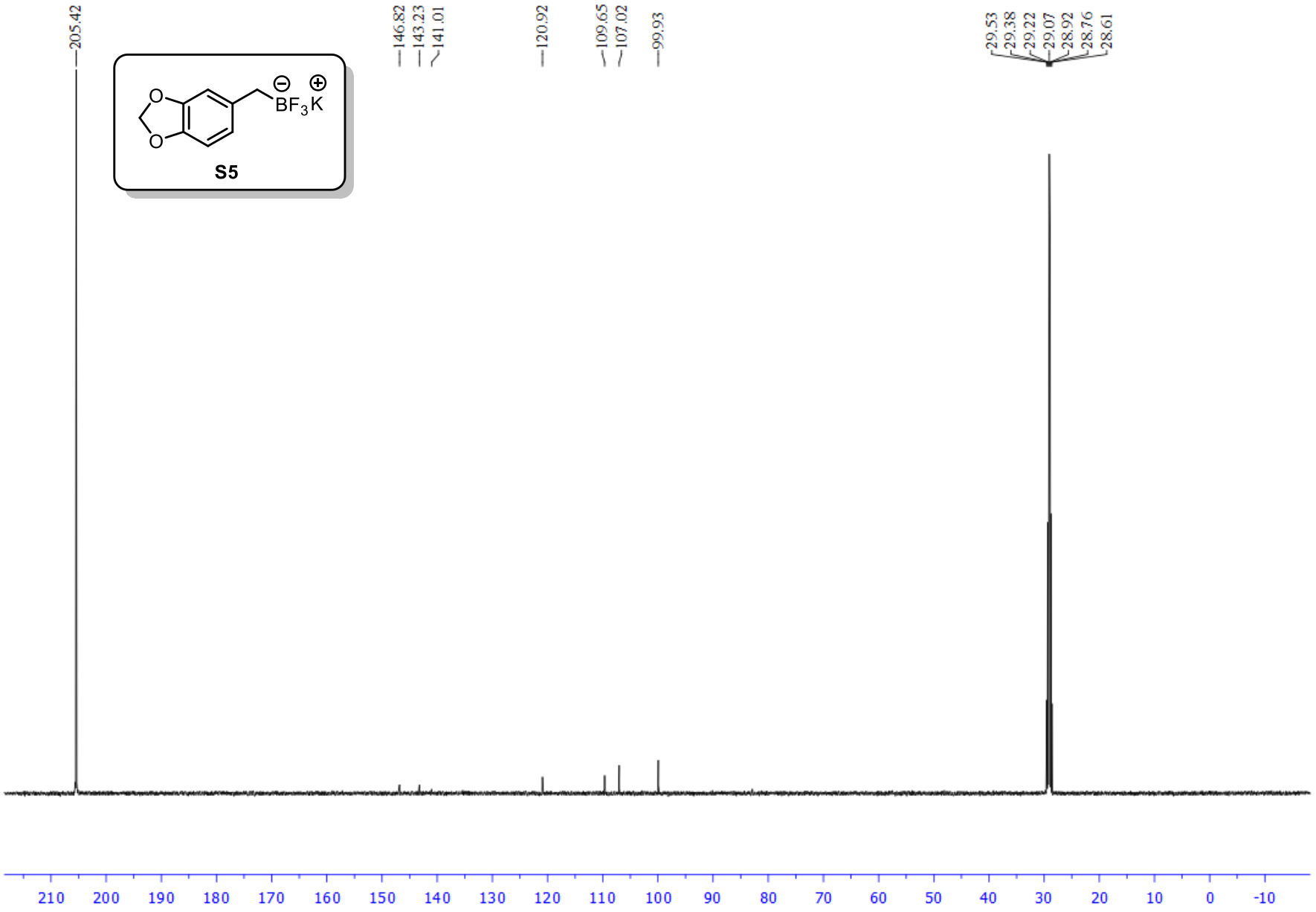
^{19}F NMR ($CDCl_3$, 470.8 MHz) spectrum of 2-(2,4-difluorophenyl)-5-(trifluoromethyl)pyridine (**S3**)



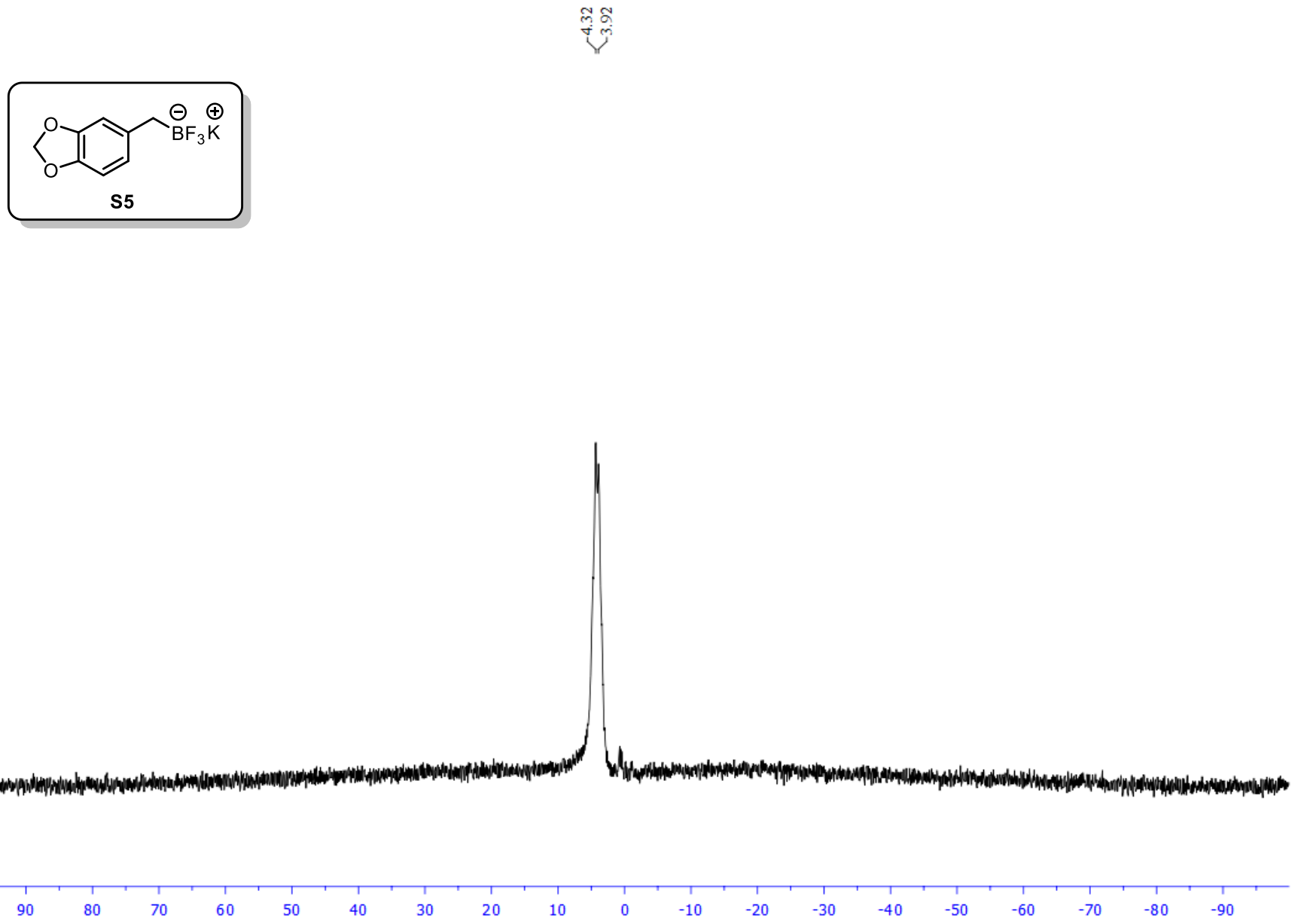
^{1}H NMR (acetone-d^{6}, 500 MHz) spectrum of potassium (benzo[d][1,3]dioxol-5-ylmethyl)trifluoroborate (**S5**)



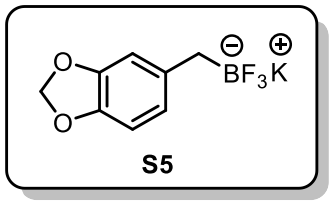
^{13}C NMR (acetone-d^{6}, 125.8 MHz) spectrum of potassium (benzo[d][1,3]dioxol-5-ylmethyl)trifluoroborate (**S5**)



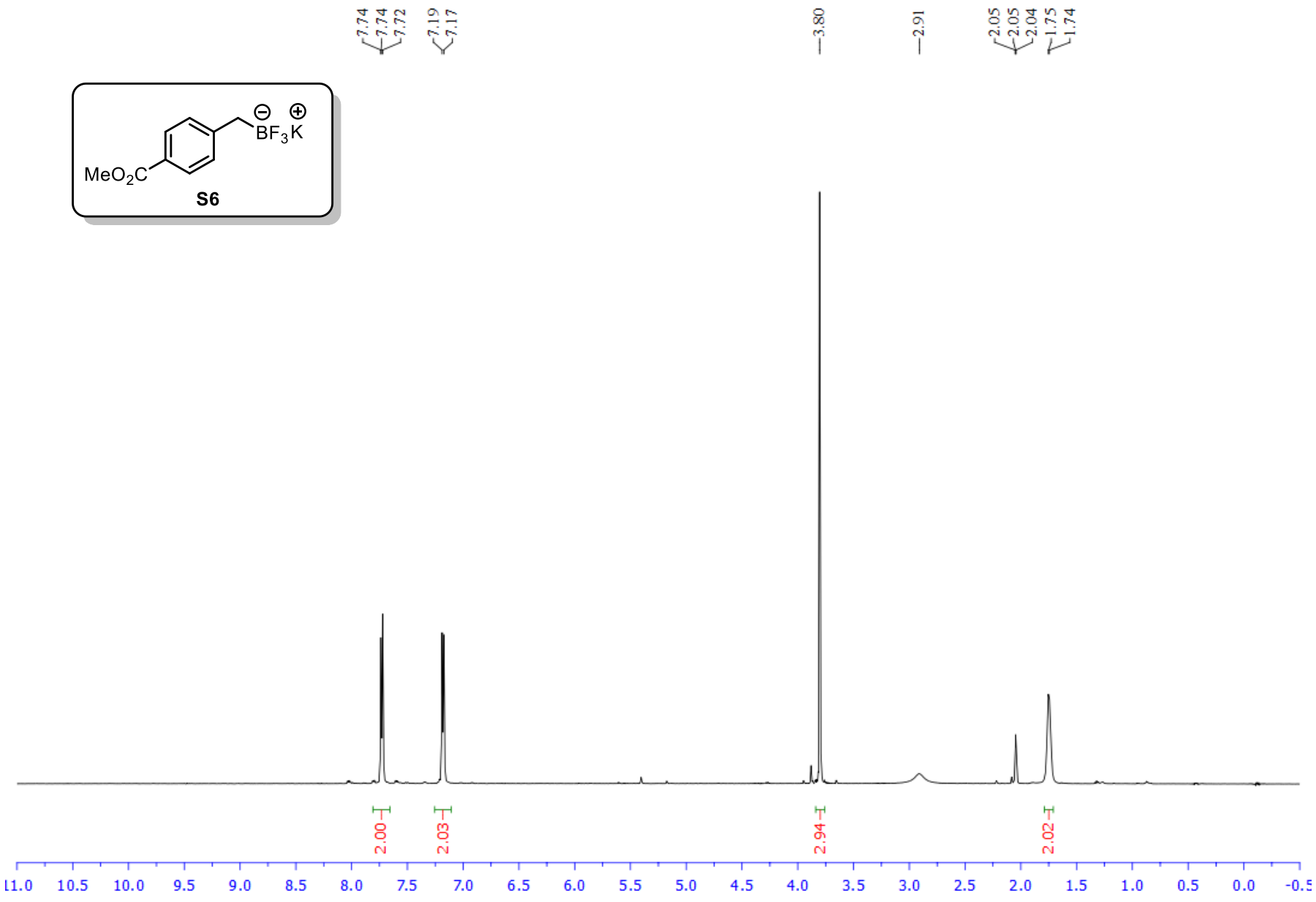
^{11}B NMR (acetone-d^{6}, 128.4 MHz) spectrum of potassium (benzo[d][1,3]dioxol-5-ylmethyl)trifluoroborate (**S5**)



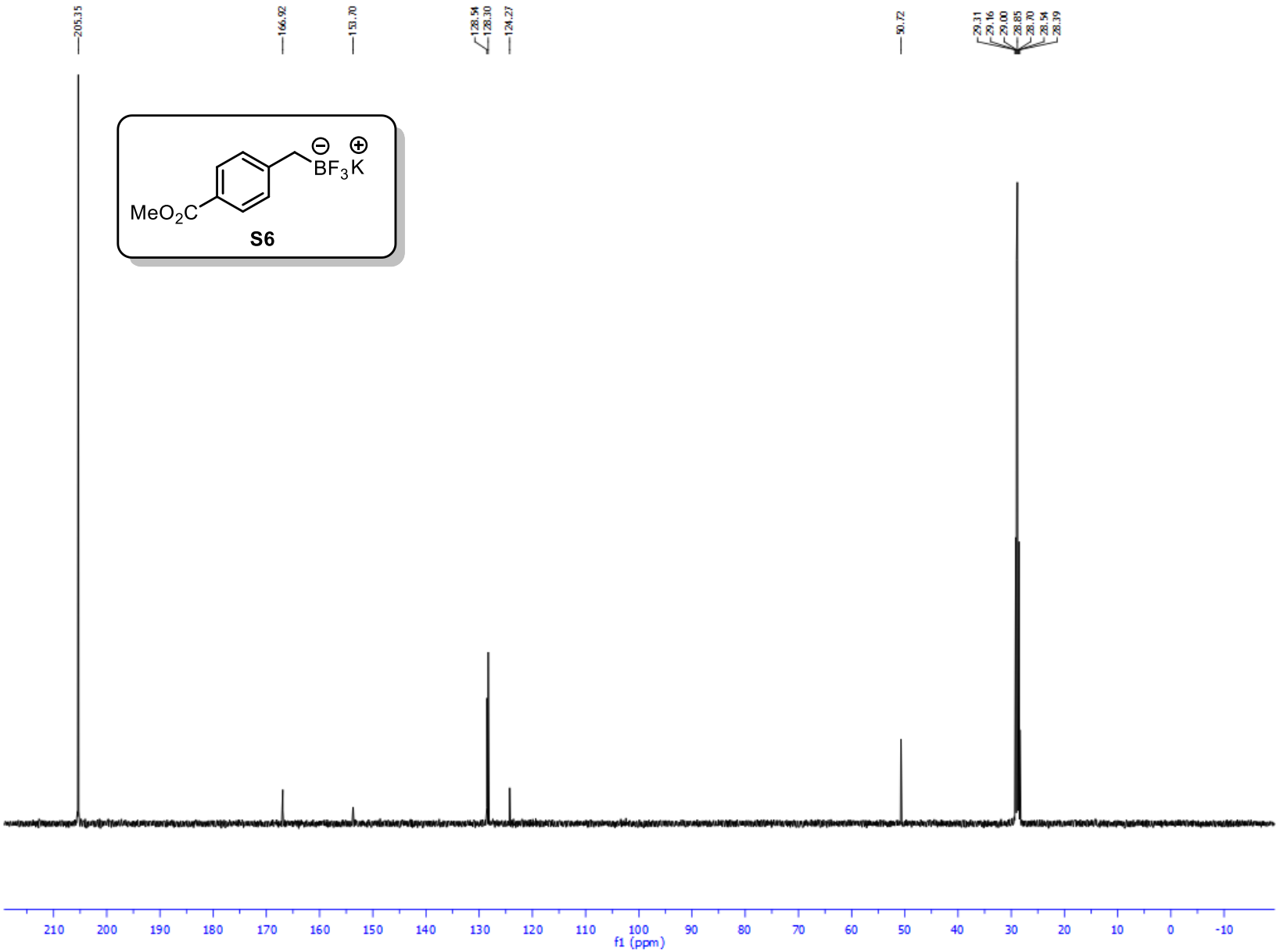
^{19}F NMR (acetone-d^6, 282.4 MHz) spectrum of potassium (benzo[d][1,3]dioxol-5-ylmethyl)trifluoroborate (**S5**)



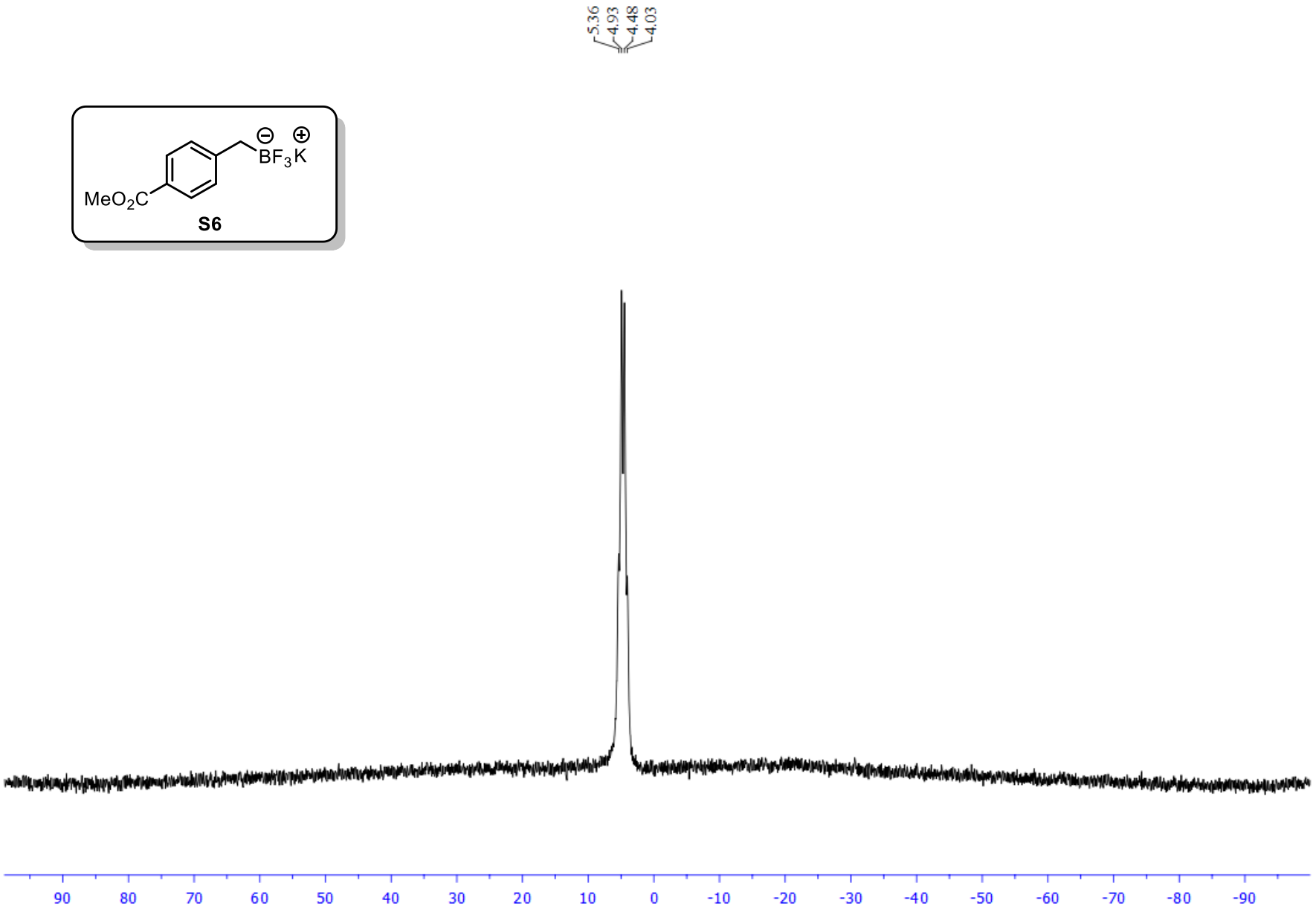
^{1}H NMR (acetone-d^{6}, 500 MHz) spectrum potassium trifluoro(4-(methoxycarbonyl)benzyl)borate (**S6**)



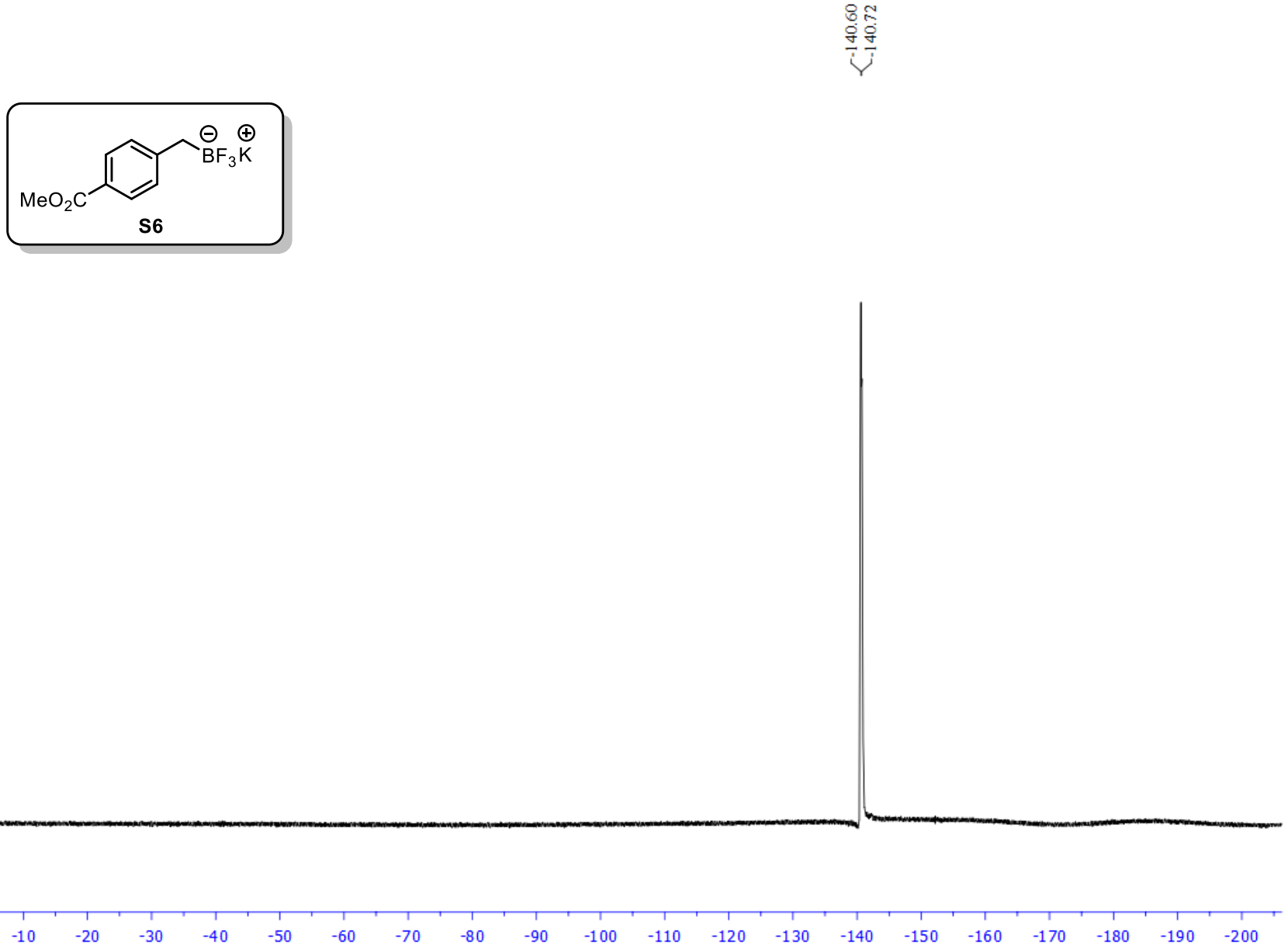
^{13}C NMR (acetone-d^{6}, 125.8 MHz) spectrum potassium trifluoro(4-(methoxycarbonyl)benzyl)borate (**S6**)



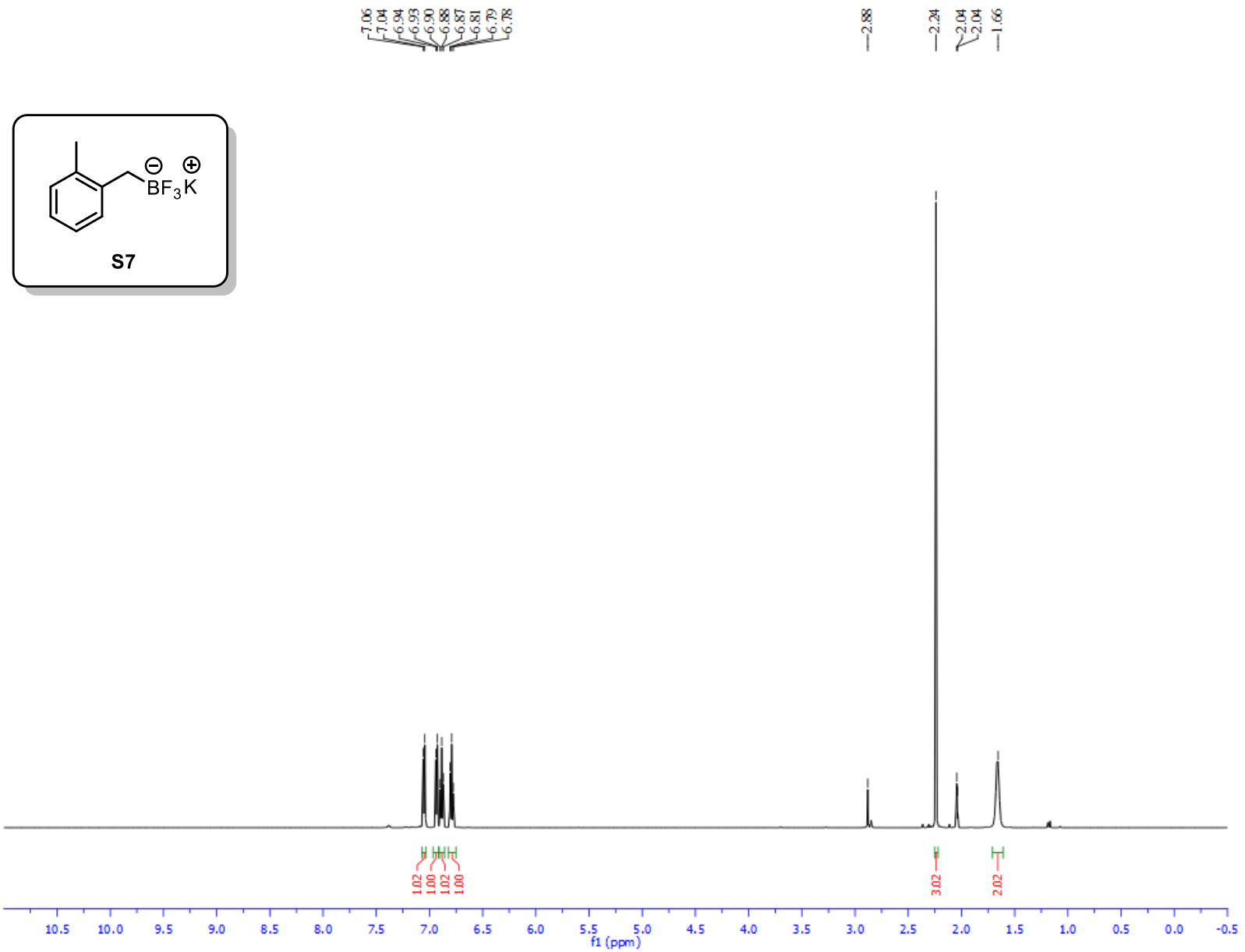
^{11}B NMR (acetone-d^{6}, 128.4 MHz) spectrum potassium trifluoro(4-(methoxycarbonyl)benzyl)borate (**S6**)



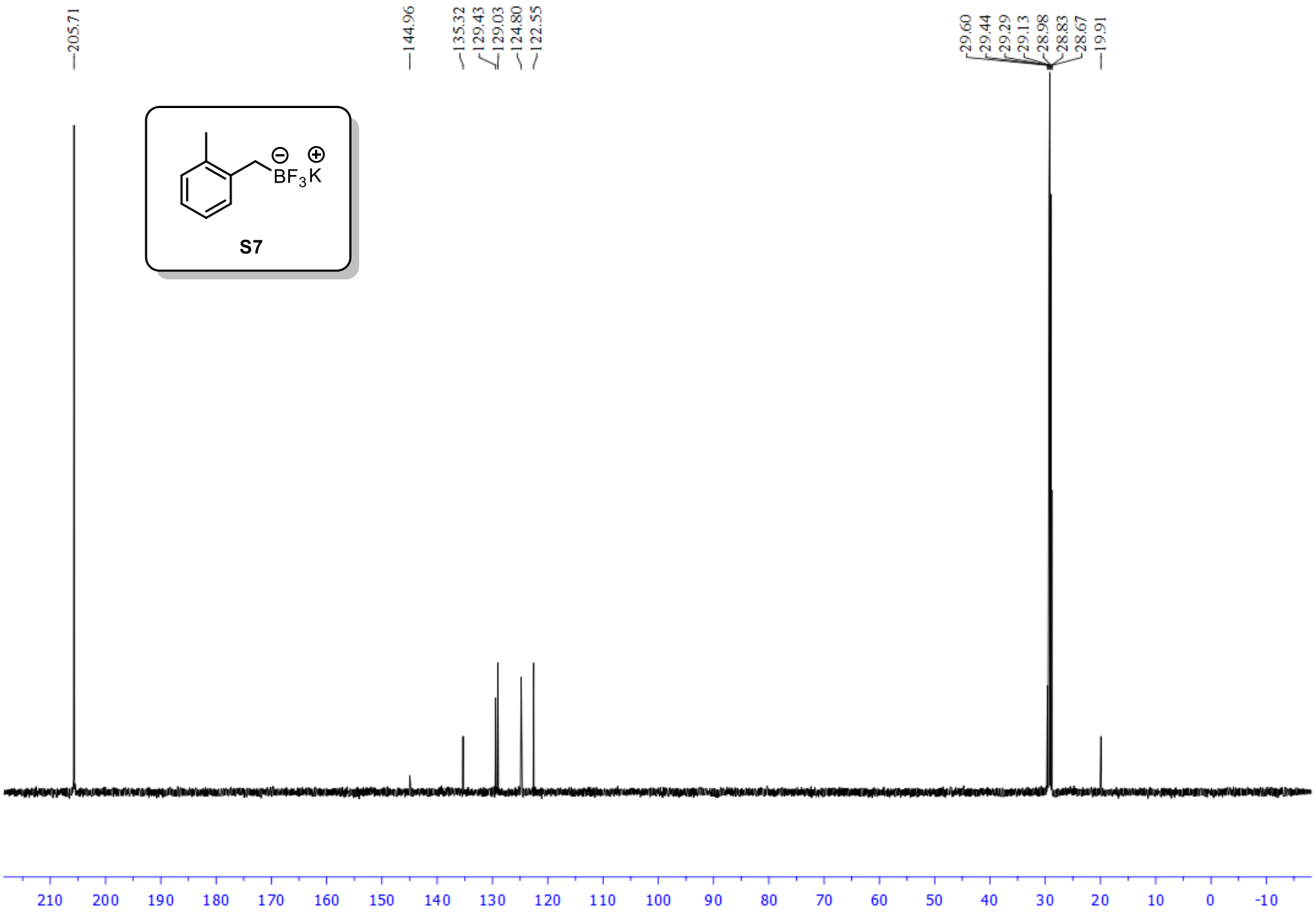
^{19}F NMR (acetone-d^{6}, 470.8 MHz) spectrum potassium trifluoro(4-(methoxycarbonyl)benzyl)borate (**S6**)



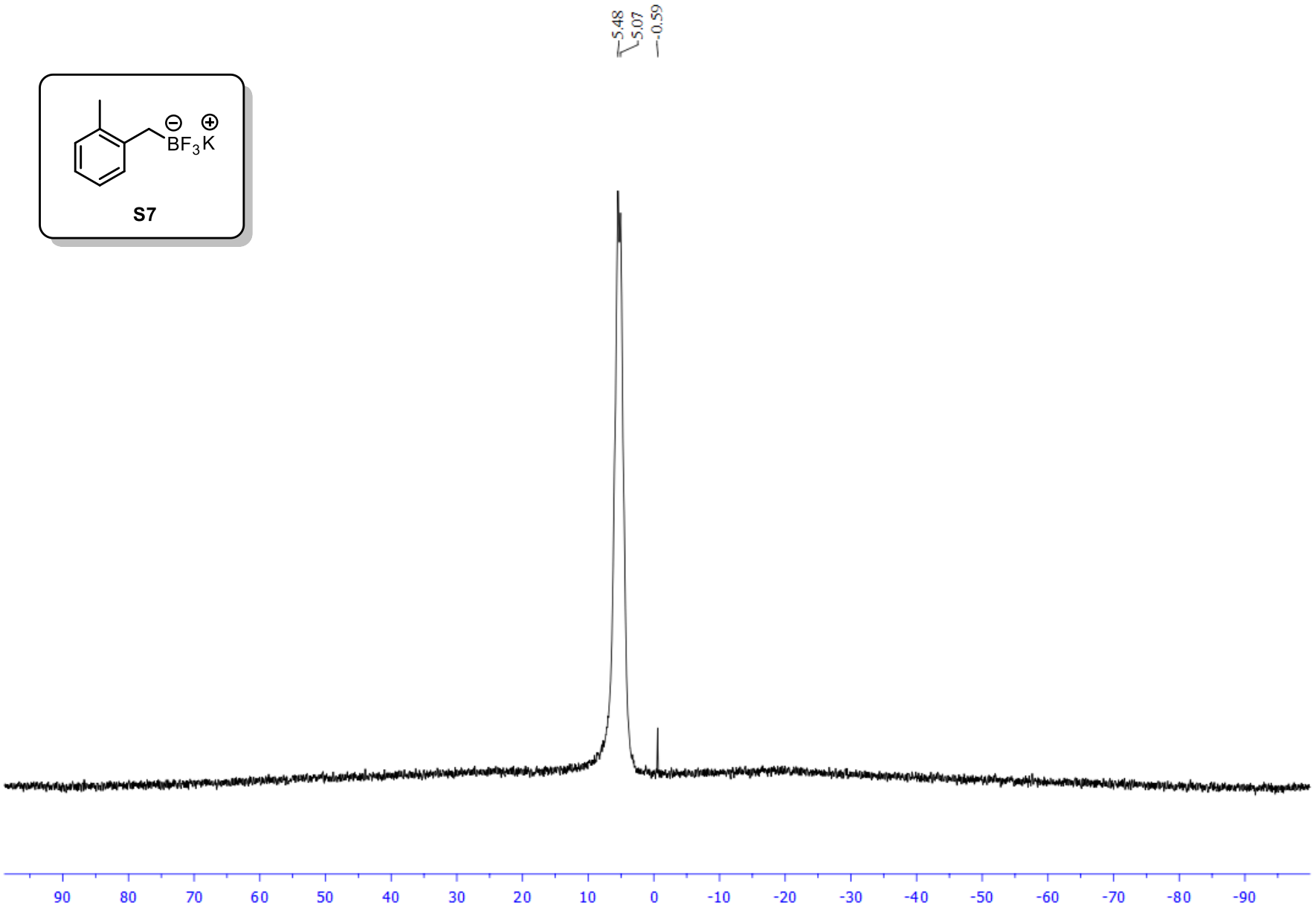
^{1}H NMR (acetone-d^{6}, 500 MHz) spectrum of potassium trifluoro(2-methylbenzyl)borate (**S7**)



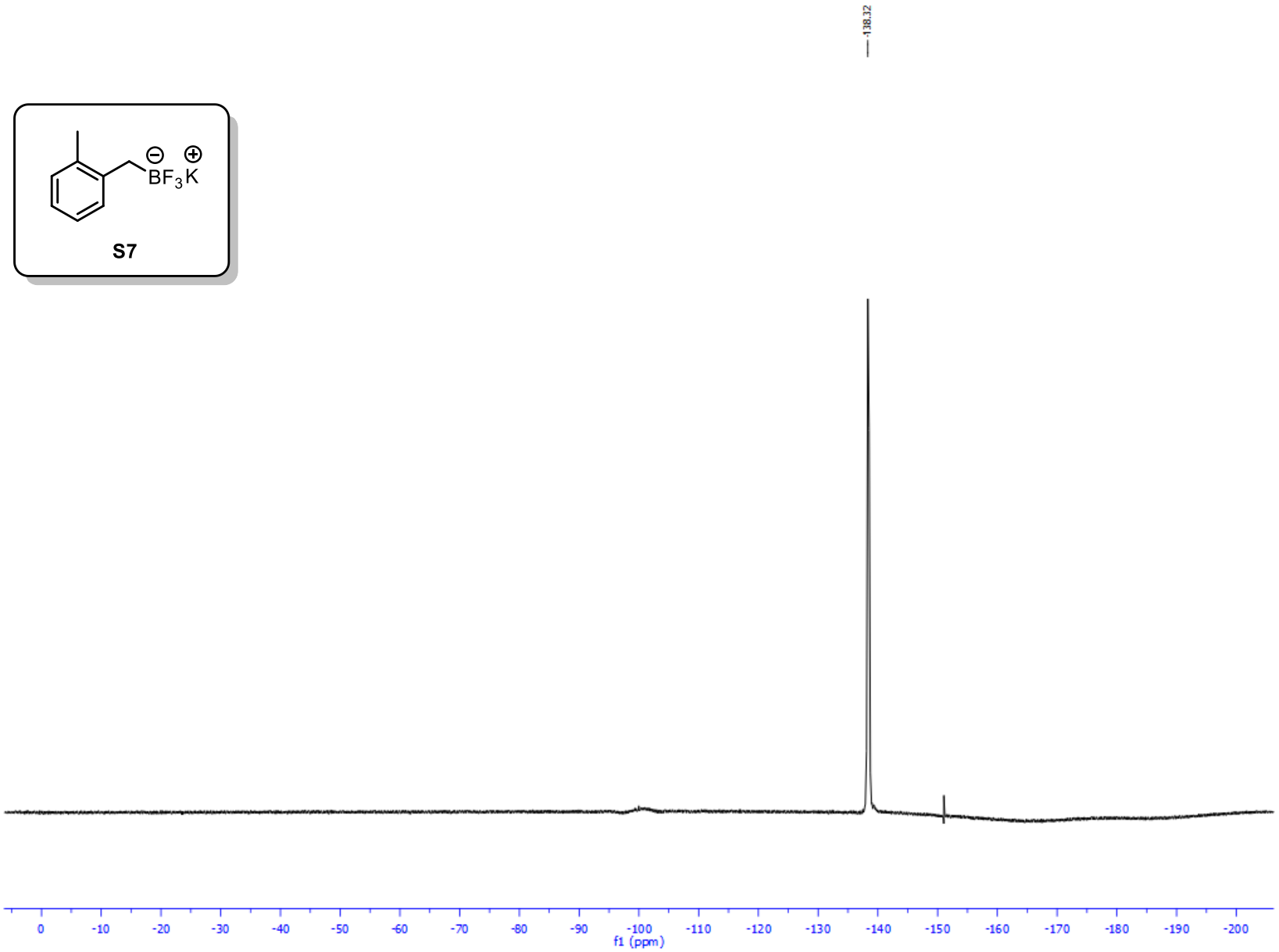
^{13}C NMR (acetone-d^{6}, 125.8 MHz) spectrum of potassium trifluoro(2-methylbenzyl)borate (**S7**)



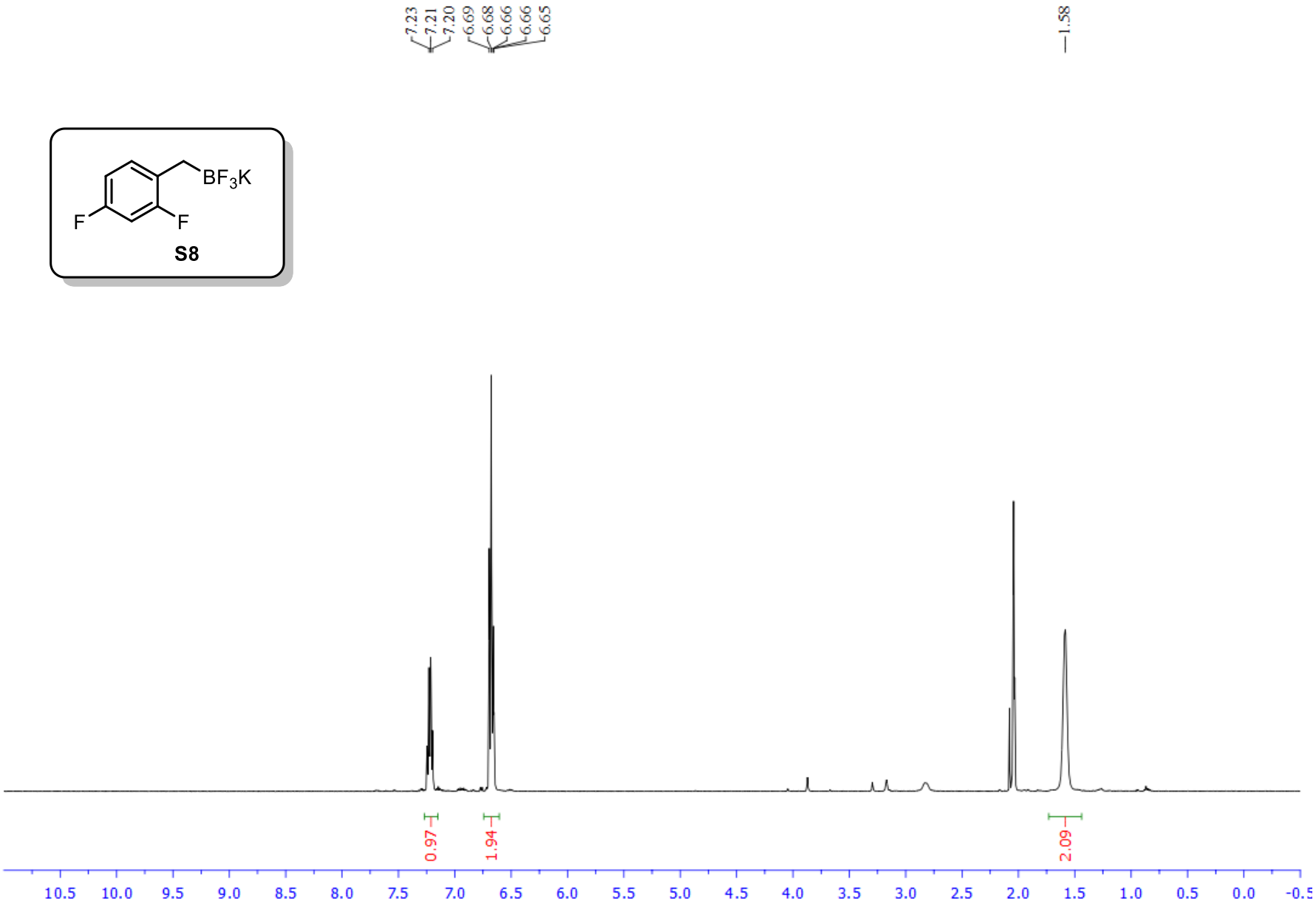
^{11}B NMR (acetone-d^{6}, 128.4 MHz) spectrum of potassium trifluoro(2-methylbenzyl)borate **(S7)**



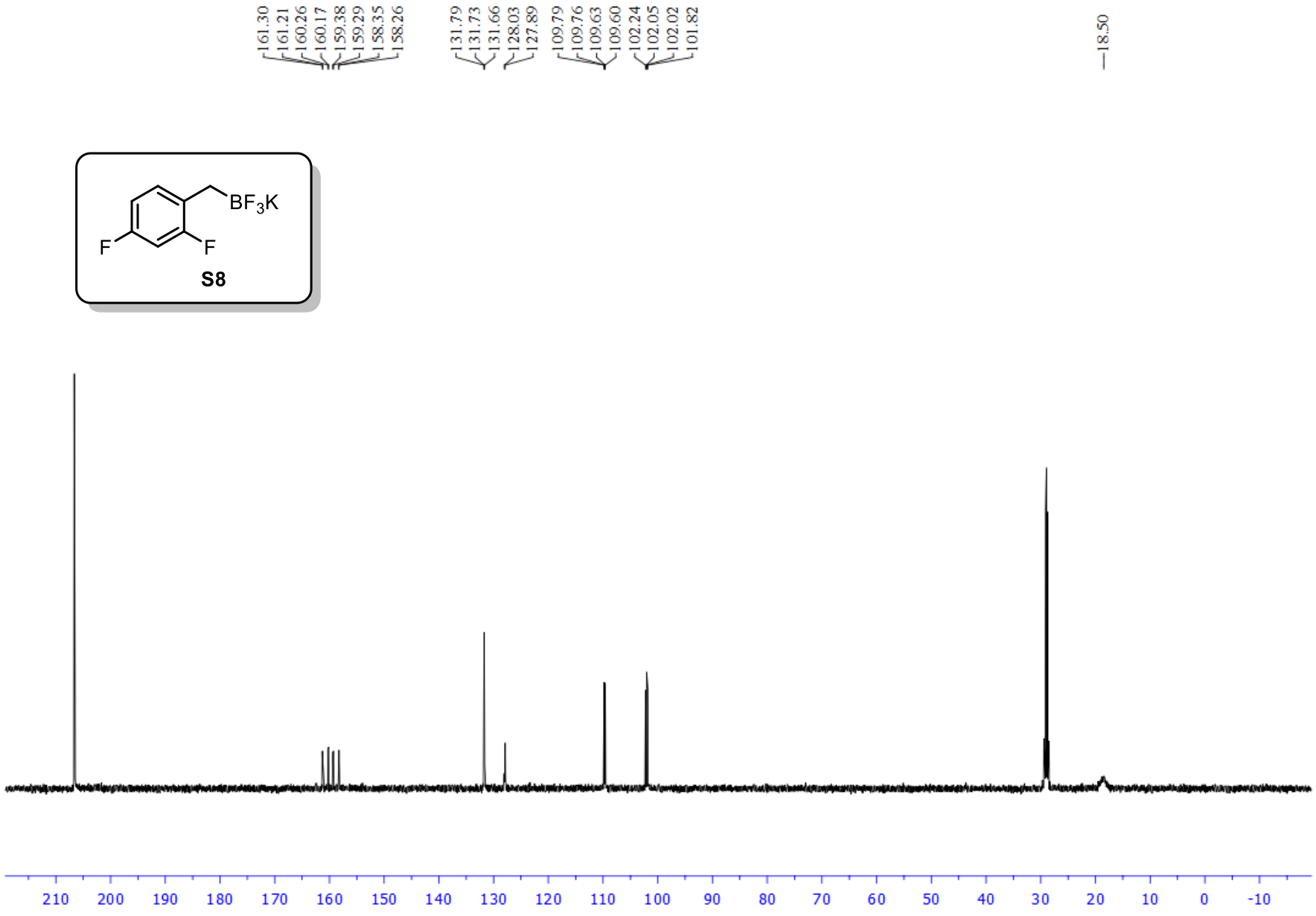
^{19}F NMR (acetone-d^{6}, 470.8 MHz) spectrum of potassium trifluoro(2-methylbenzyl)borate (**S7)**



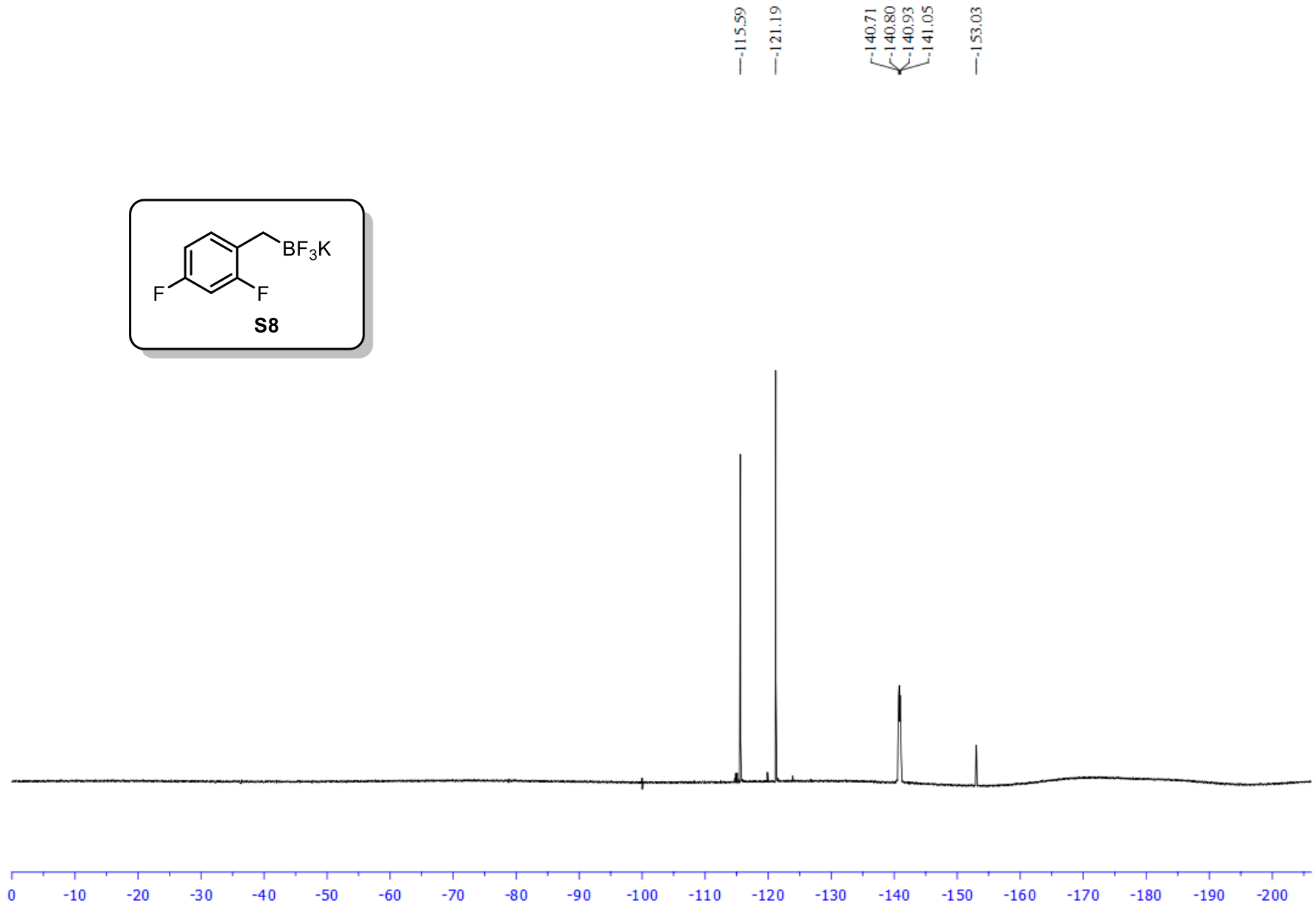
^{1}H NMR (acetone-d^{6}, 500 MHz) spectrum of potassium (2,4-difluorobenzyl)trifluoroborate (**S8**)



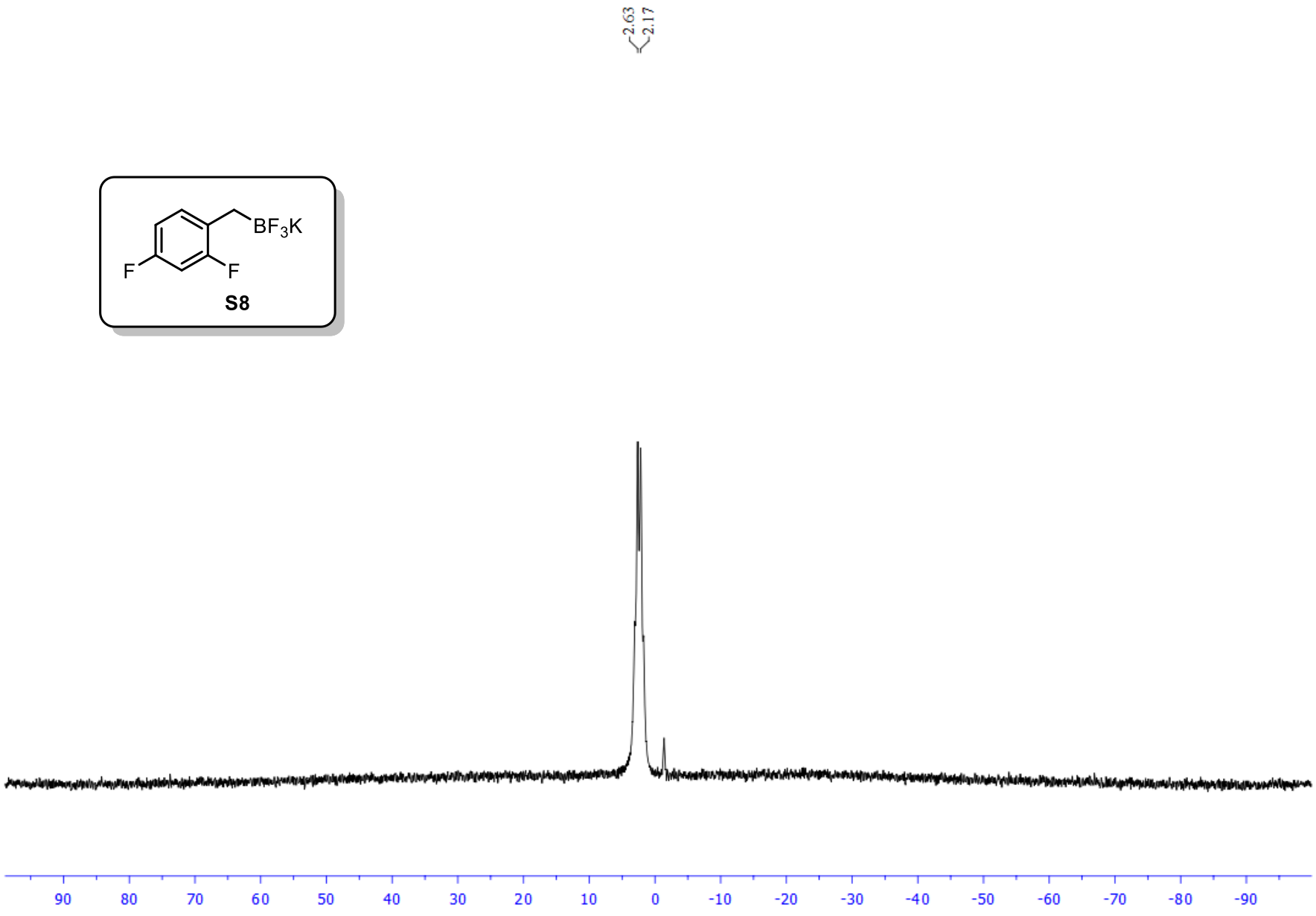
^{13}C NMR (acetone-d^{6}, 125.8 MHz) spectrum of potassium (2,4-difluorobenzyl)trifluoroborate (**S8**)



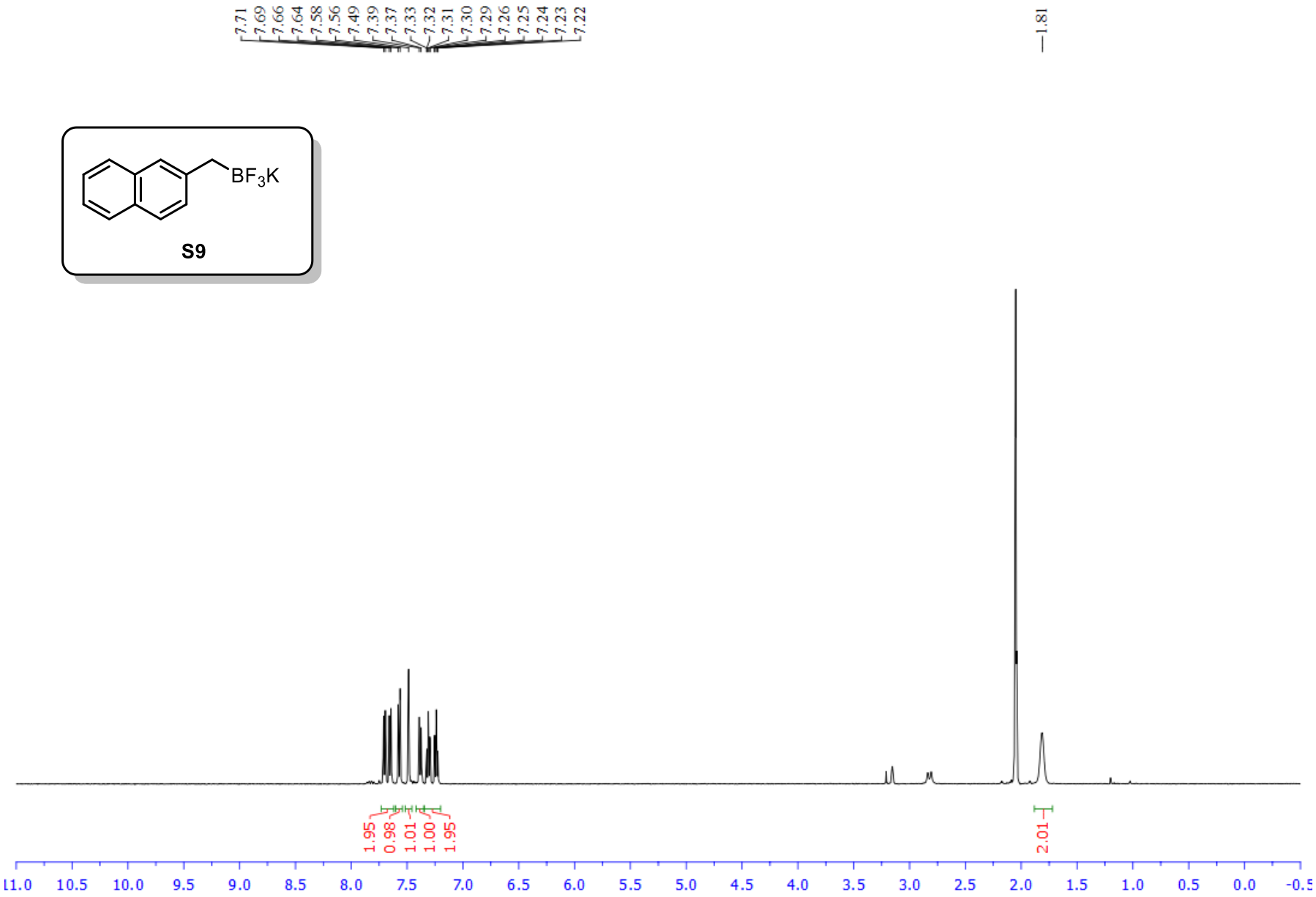
^{19}F NMR (acetone-d^{6}, 470.8 MHz) spectrum of potassium (2,4-difluorobenzyl)trifluoroborate (**S8**)



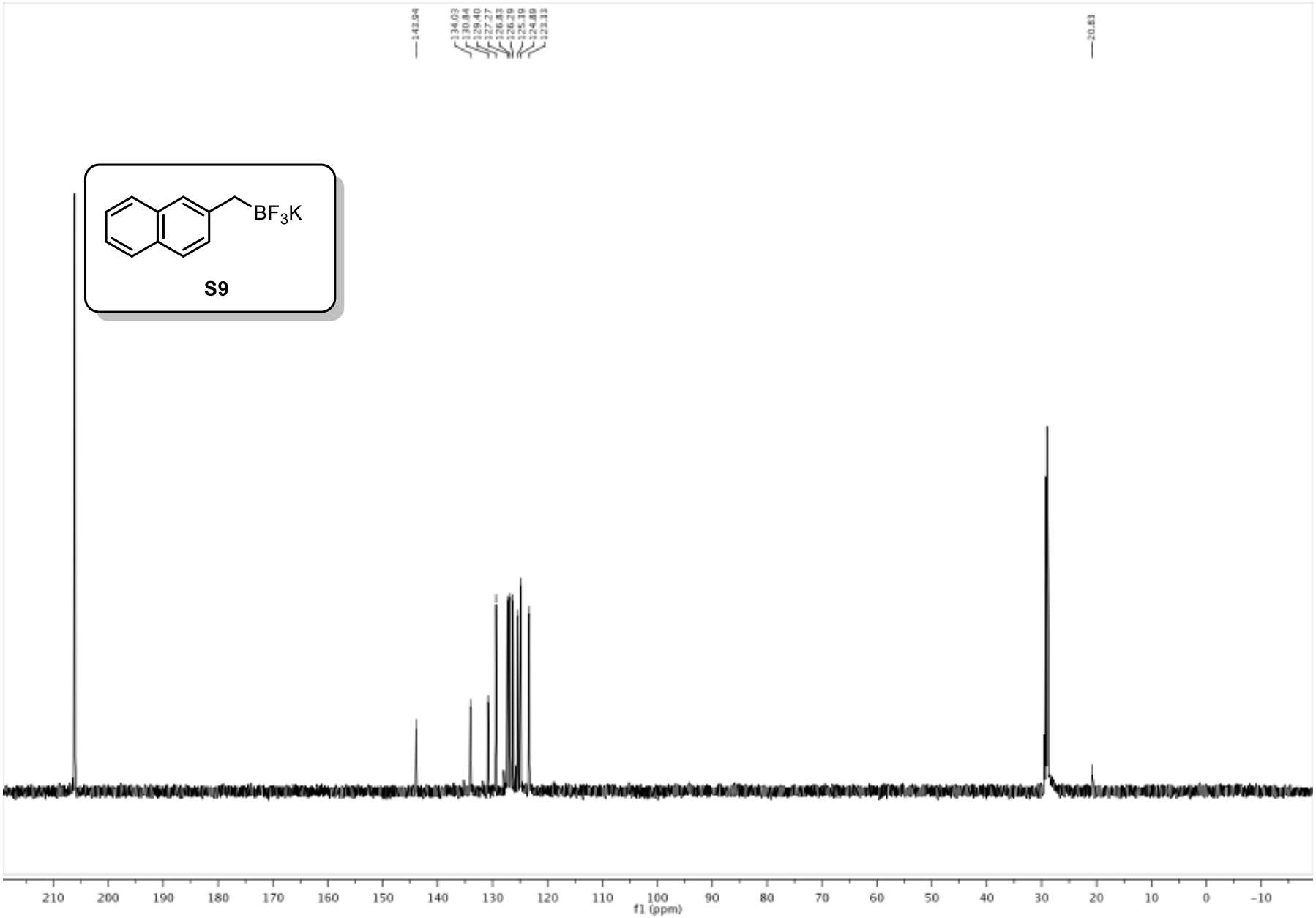
^{11}B NMR (acetone-d^{6}, 128.4 MHz) spectrum of potassium (2,4-difluorobenzyl)trifluoroborate (**S8**)



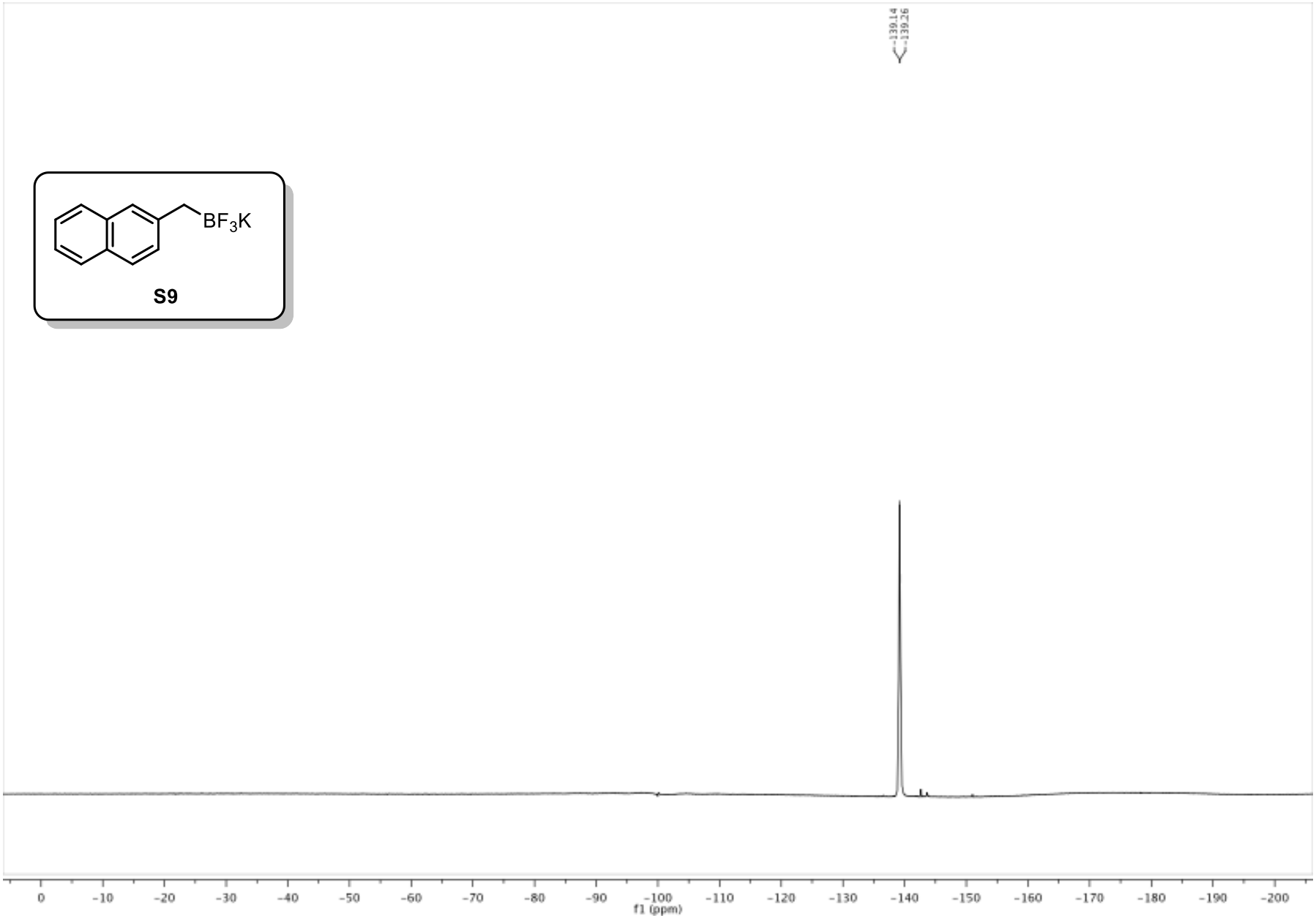
^{1}H NMR (acetone-d^{6}, 500 MHz) spectrum of potassium trifluoro(naphthalen-2-ylmethyl)borate (**S9**)



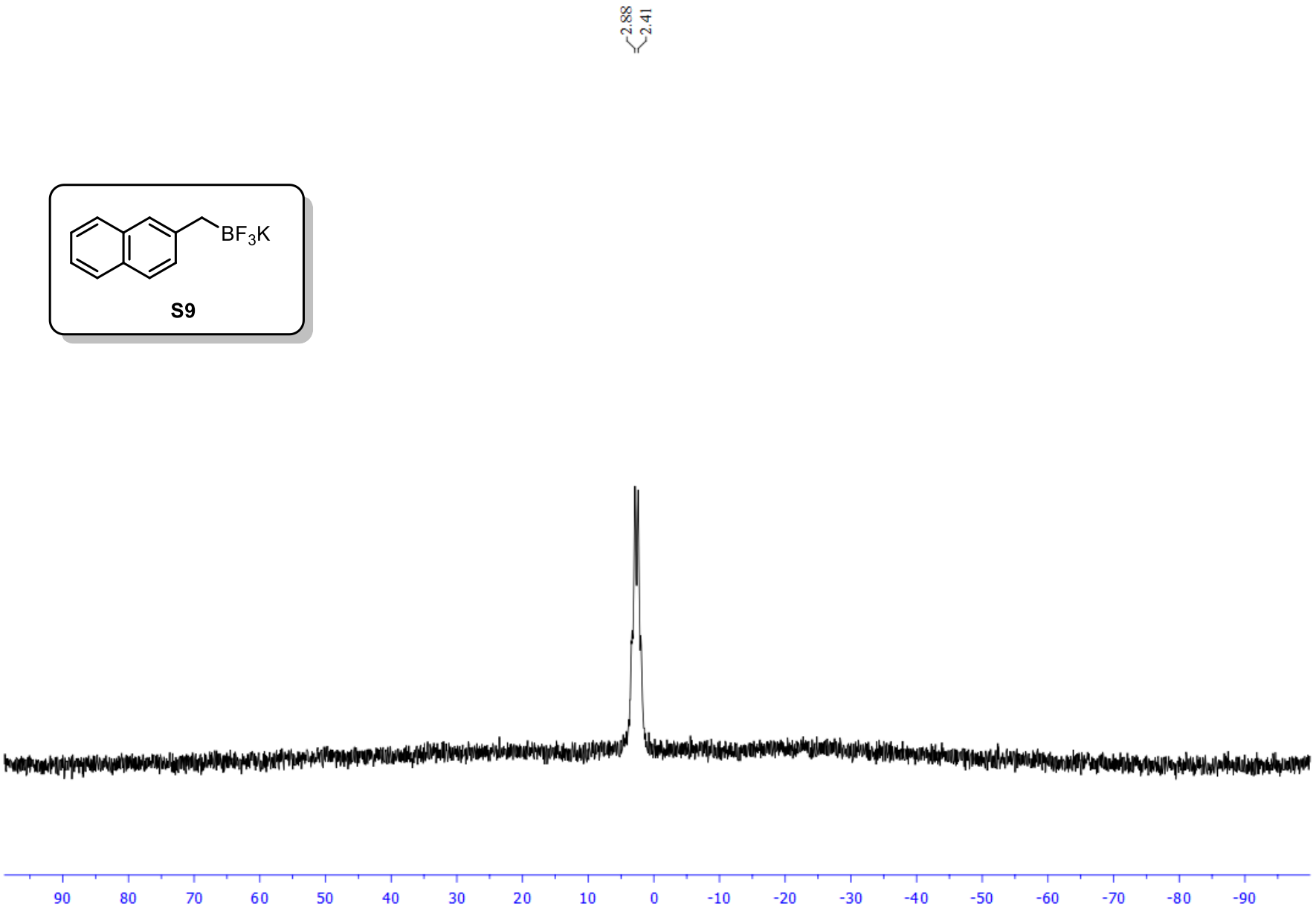
^{13}C NMR (acetone-d^{6}, 125.8 MHz) spectrum of potassium trifluoro(naphthalen-2-ylmethyl)borate (**S9**)



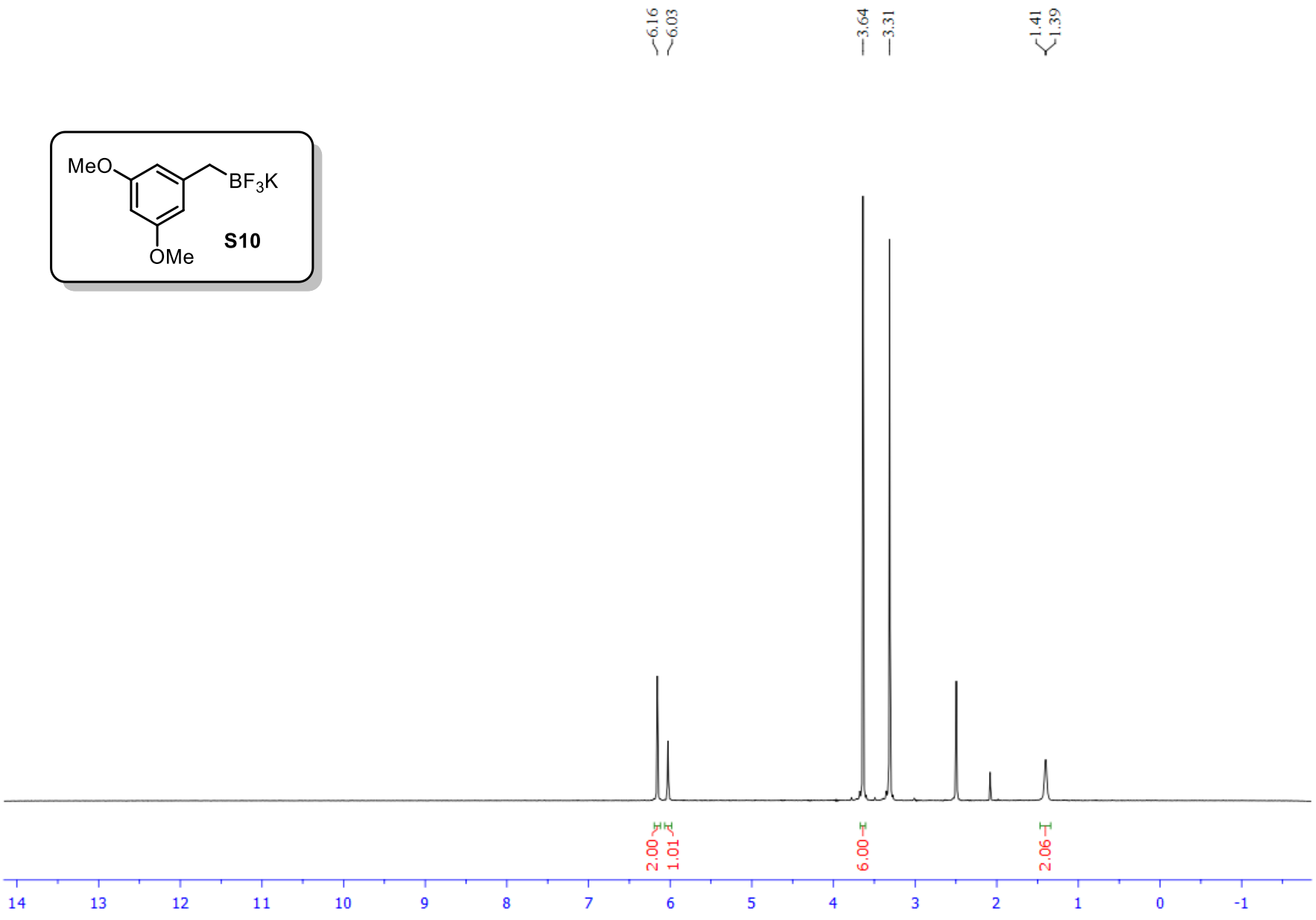
^{19}F NMR (acetone-d^{6}, 470.8 MHz) spectrum of potassium trifluoro(naphthalen-2-ylmethyl)borate (**S9**)



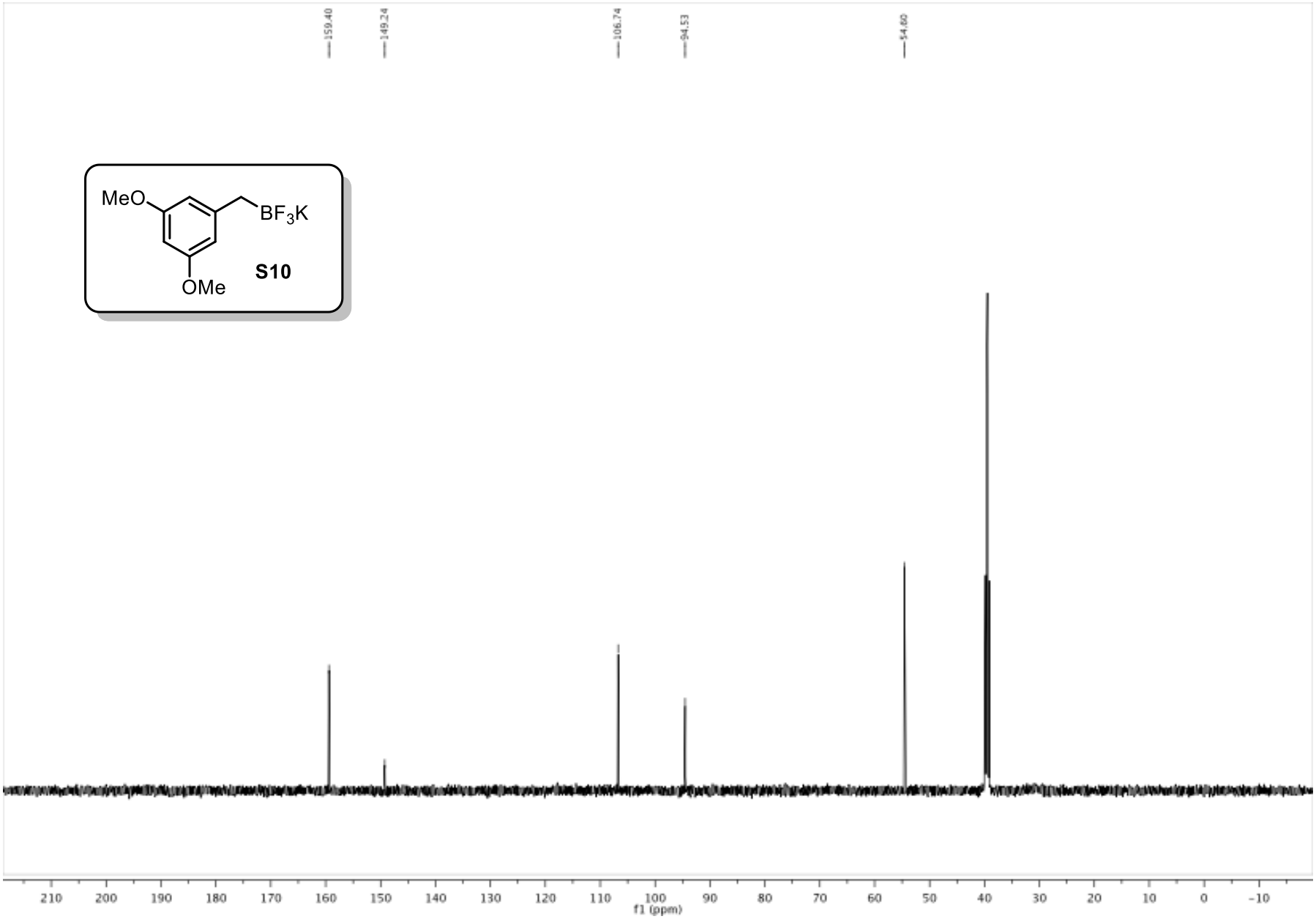
^{11}B NMR (acetone-d^{6}, 128.4 MHz) spectrum of potassium trifluoro(naphthalen-2-ylmethyl)borate (**S9**)



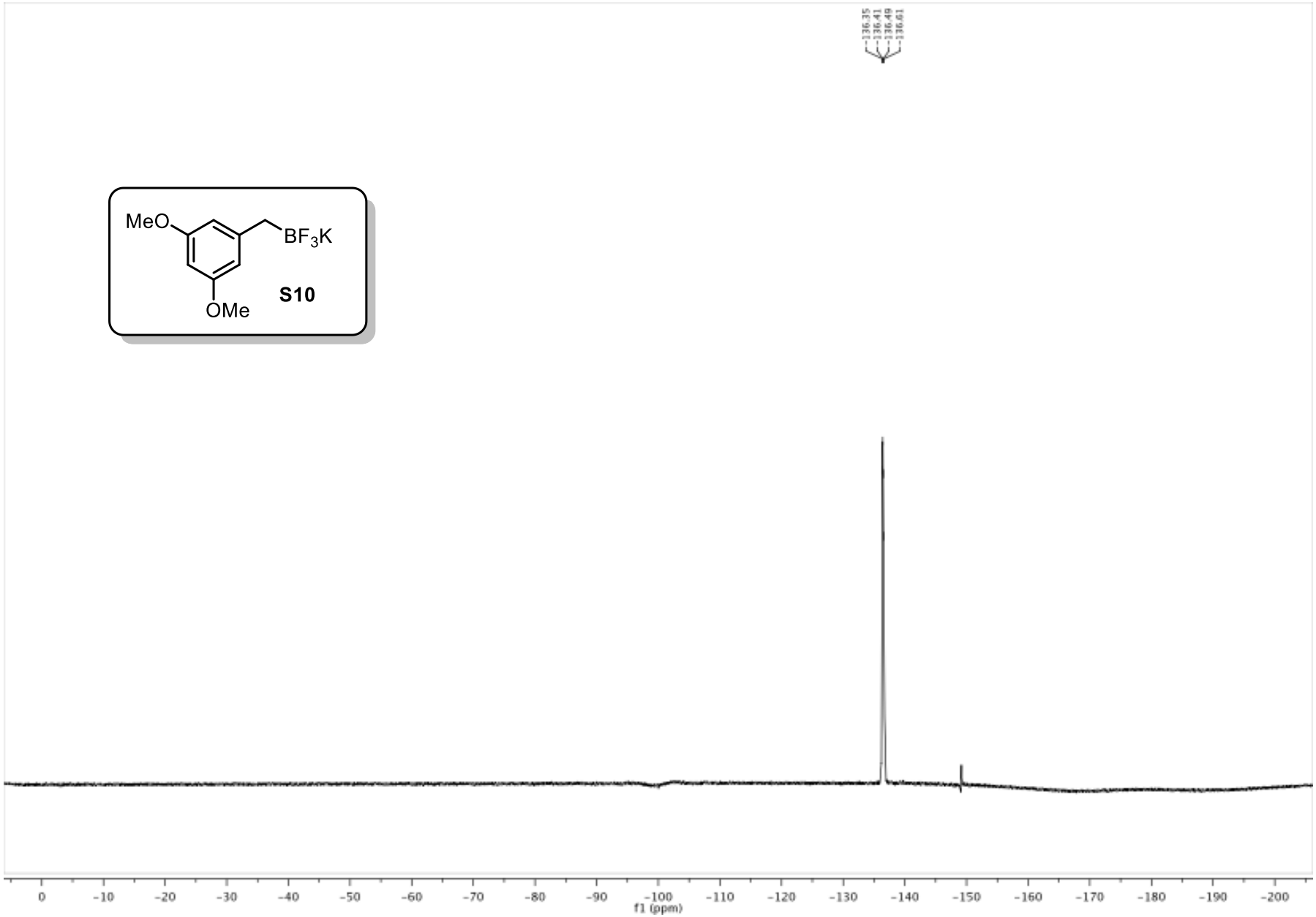
^{1}H NMR (DMSO-d^{6}, 500 MHz) spectrum of potassium (3,5-dimethoxybenzyl)trifluoroborate (**S10**)



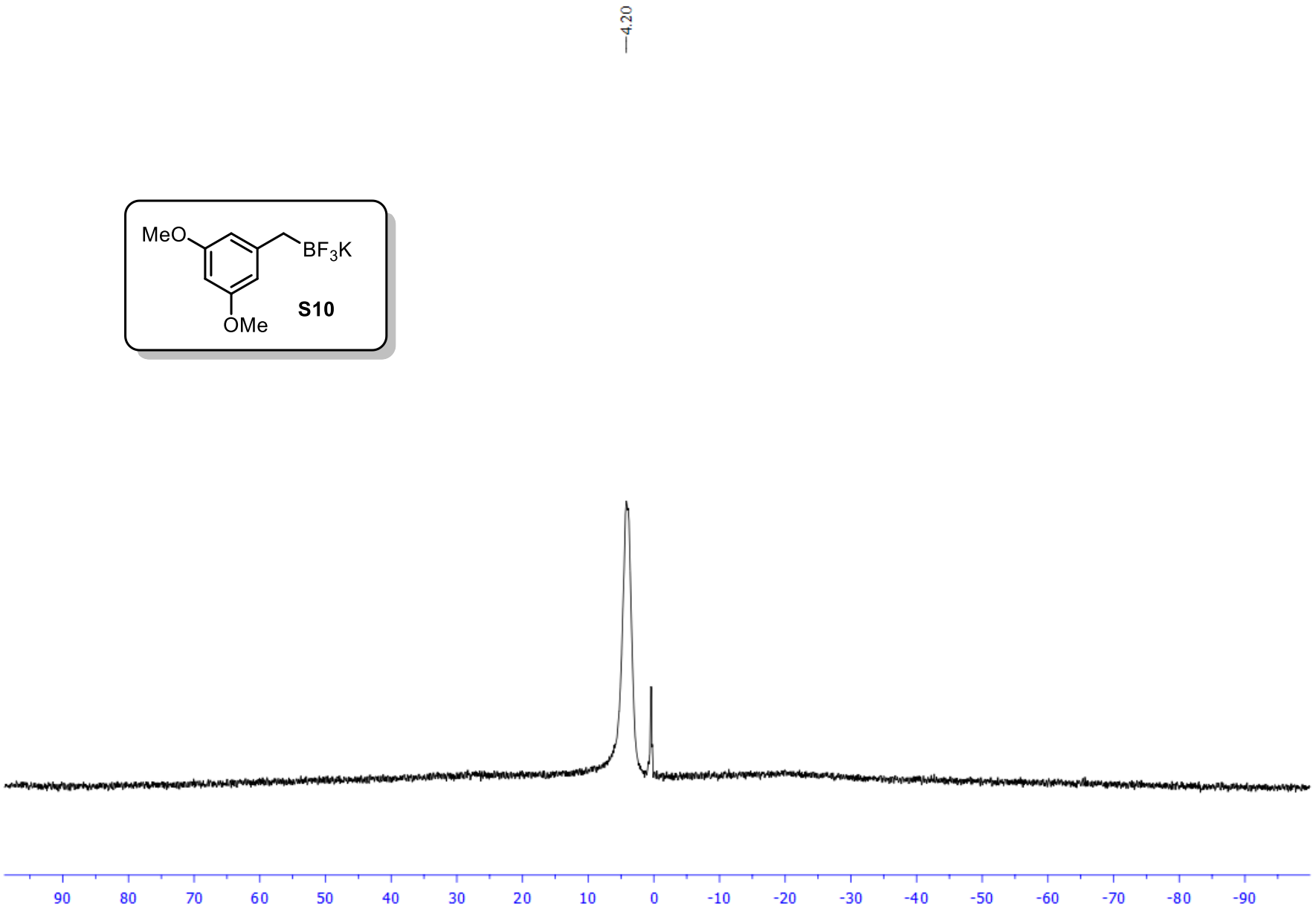
^{13}C NMR (DMSO-d^{6}, 125.8 MHz) spectrum of potassium (3,5-dimethoxybenzyl)trifluoroborate (**S10**)



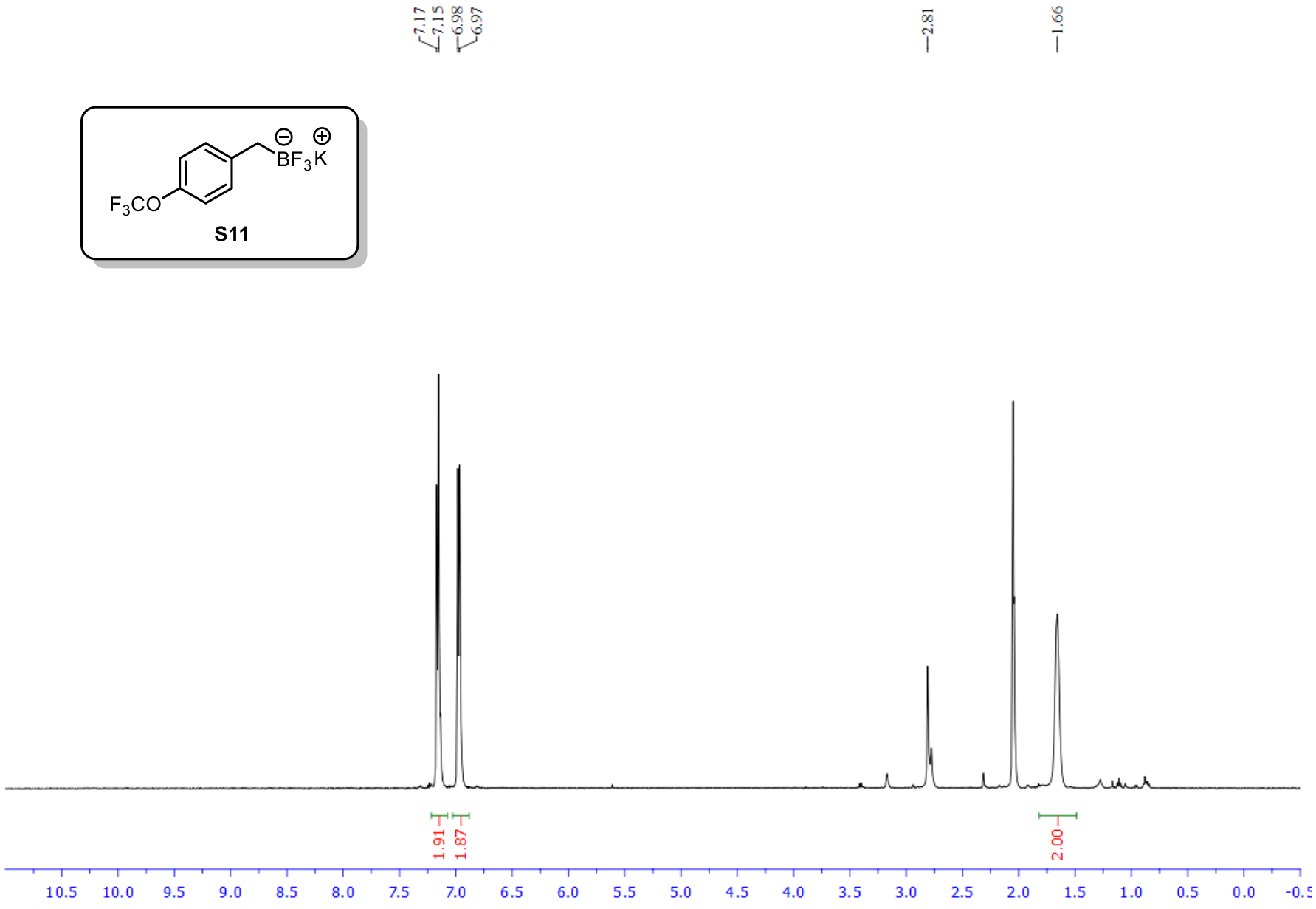
^{19}F NMR (DMSO-d^6, 470.8 MHz) spectrum of potassium (3,5-dimethoxybenzyl)trifluoroborate (**S10**)



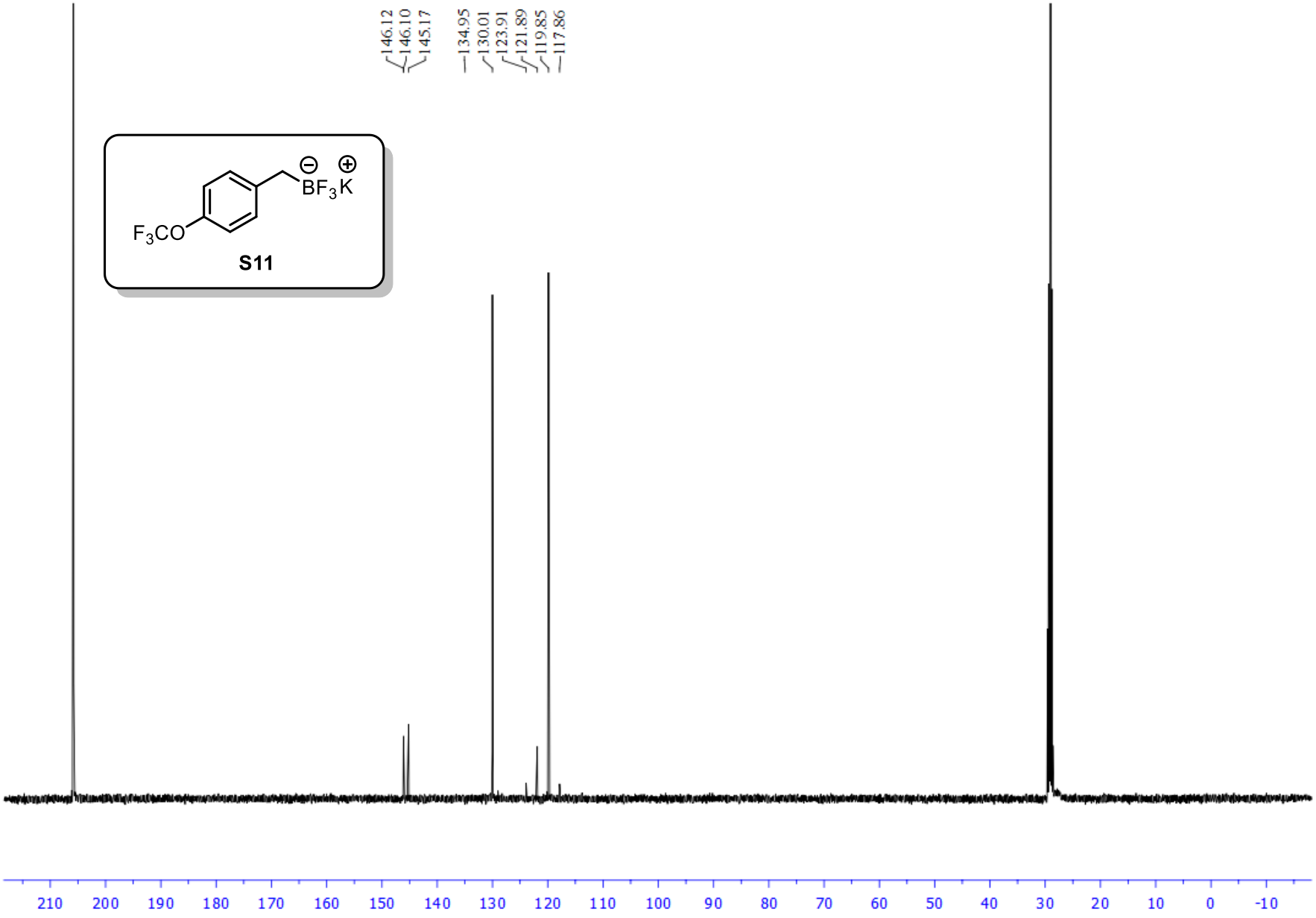
^{11}B NMR (DMSO-d^{6}, 128.4 MHz) spectrum of potassium (3,5-dimethoxybenzyl)trifluoroborate (**S10**)



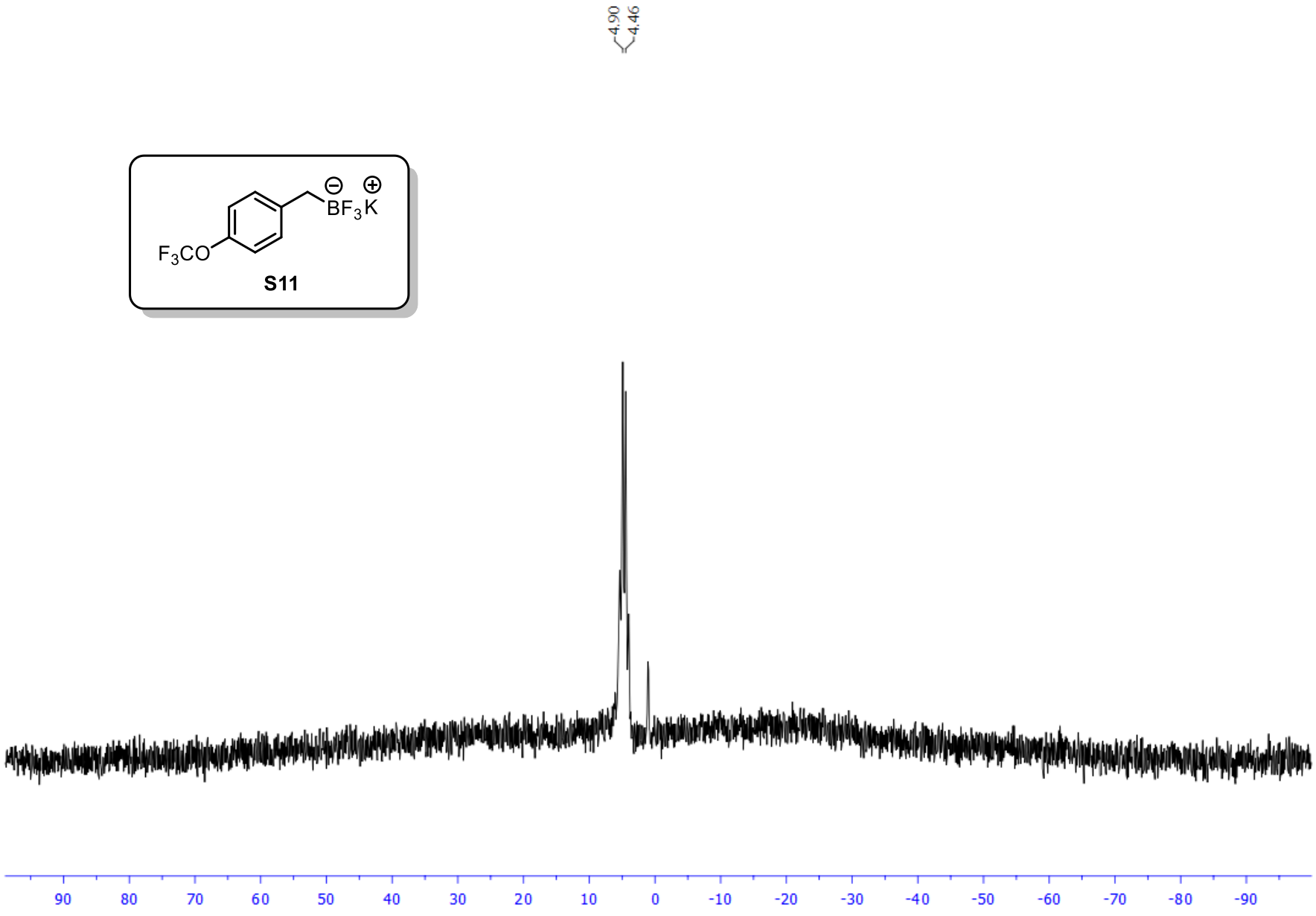
^{1}H NMR (acetone-d^{6}, 500 MHz) spectrum of potassium trifluoro(4-(trifluoromethoxy)benzyl)borate (**S11**)



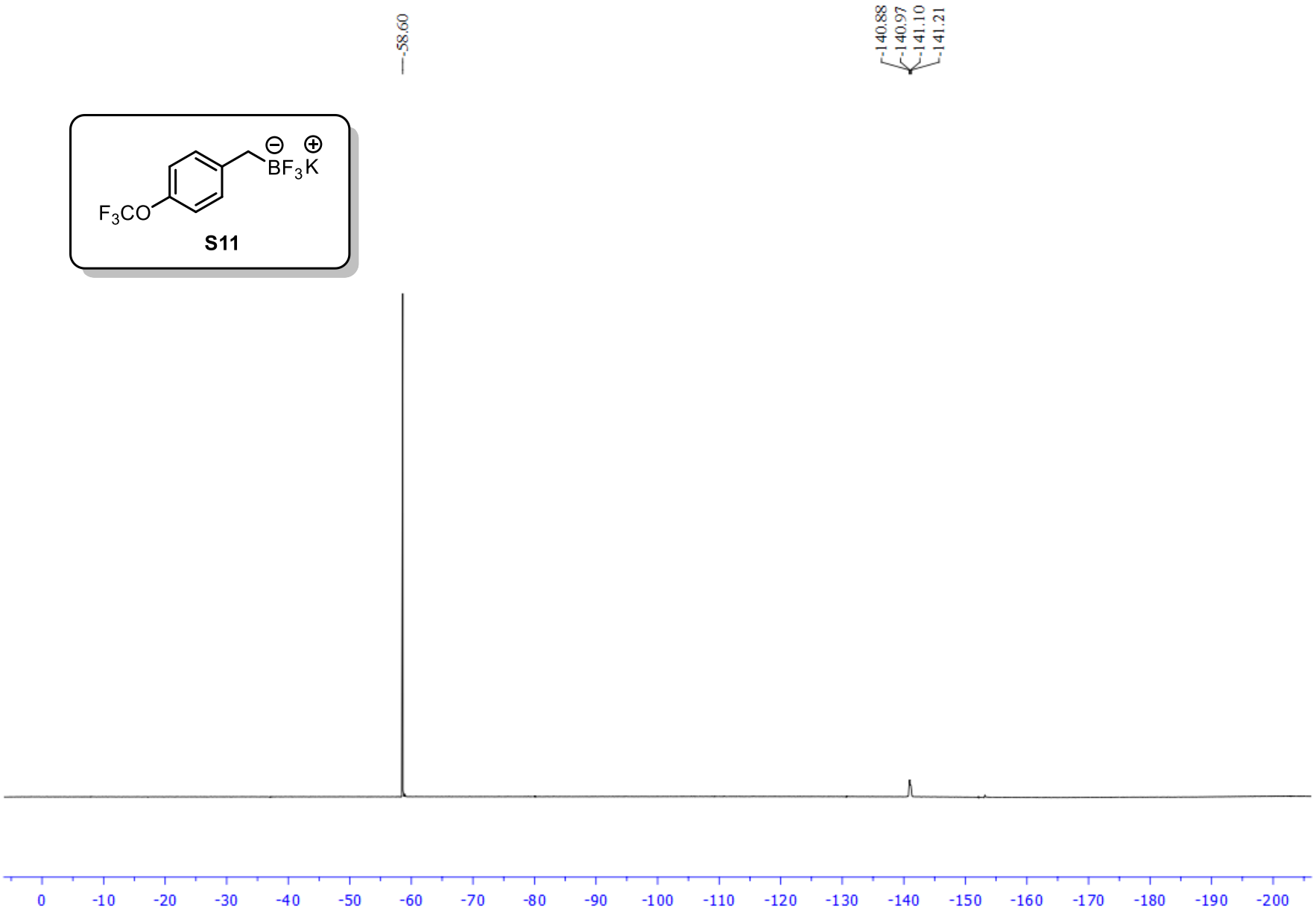
^{13}C NMR (acetone-d^{6}, 125.8 MHz) spectrum of potassium trifluoro(4-(trifluoromethoxy)benzyl)borate (**S11**)



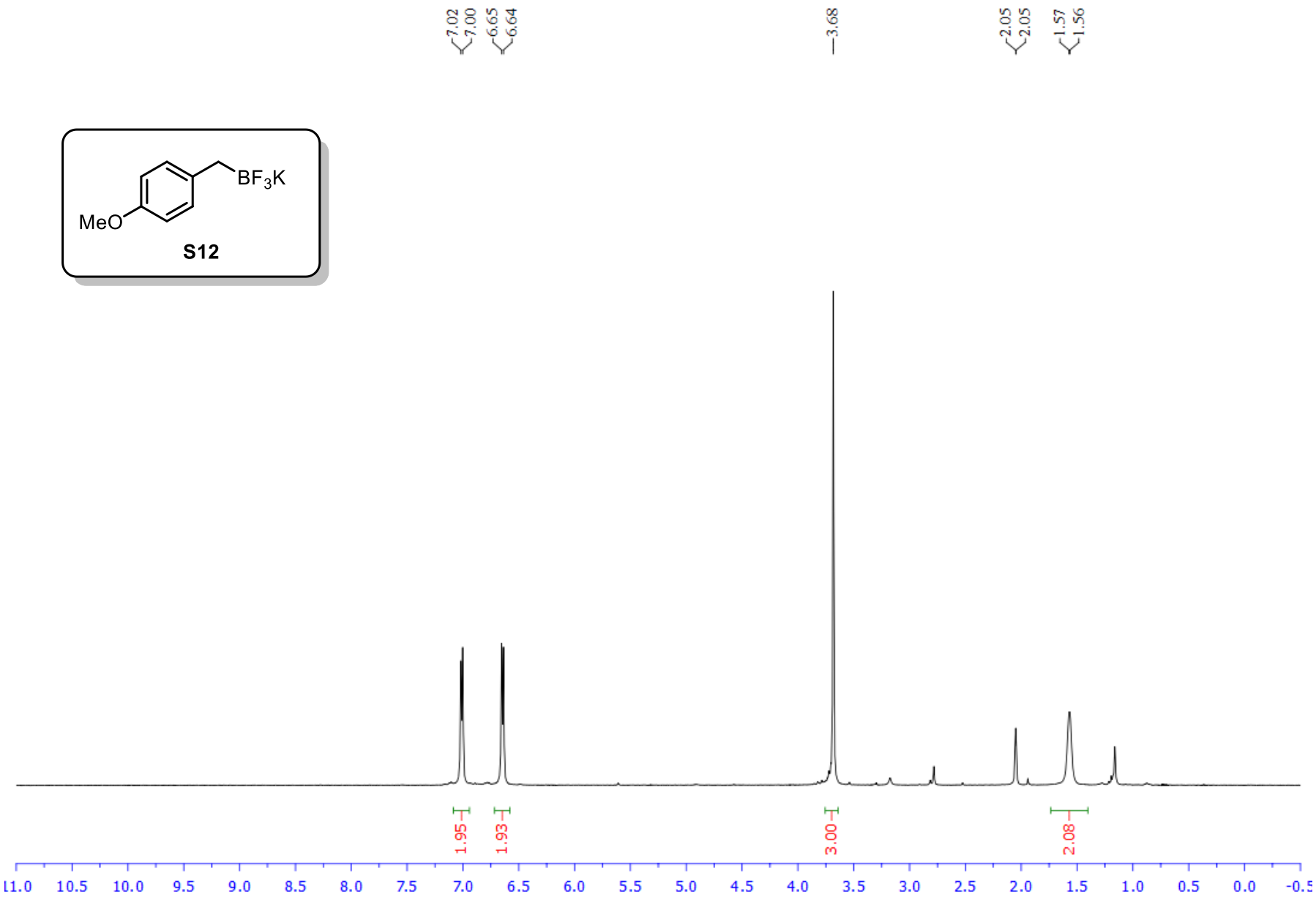
^{11}B NMR (acetone-d^{6}, 128.4 MHz) spectrum of potassium trifluoro(4-(trifluoromethoxy)benzyl)borate (**S11**)



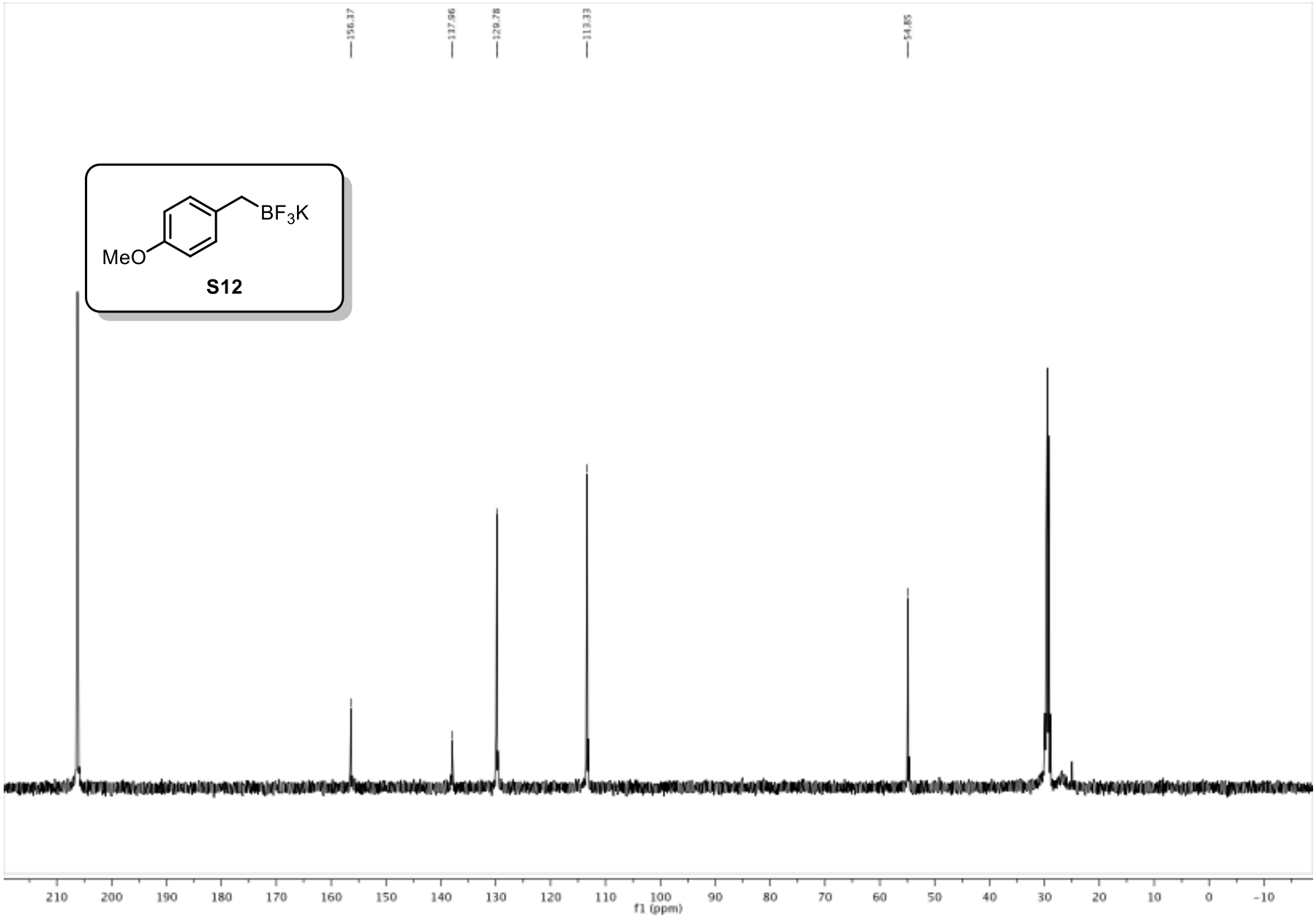
^{19}F NMR (acetone-d^{6}, 470.8 MHz) spectrum of potassium trifluoro(4-(trifluoromethoxy)benzyl)borate (**S11**)



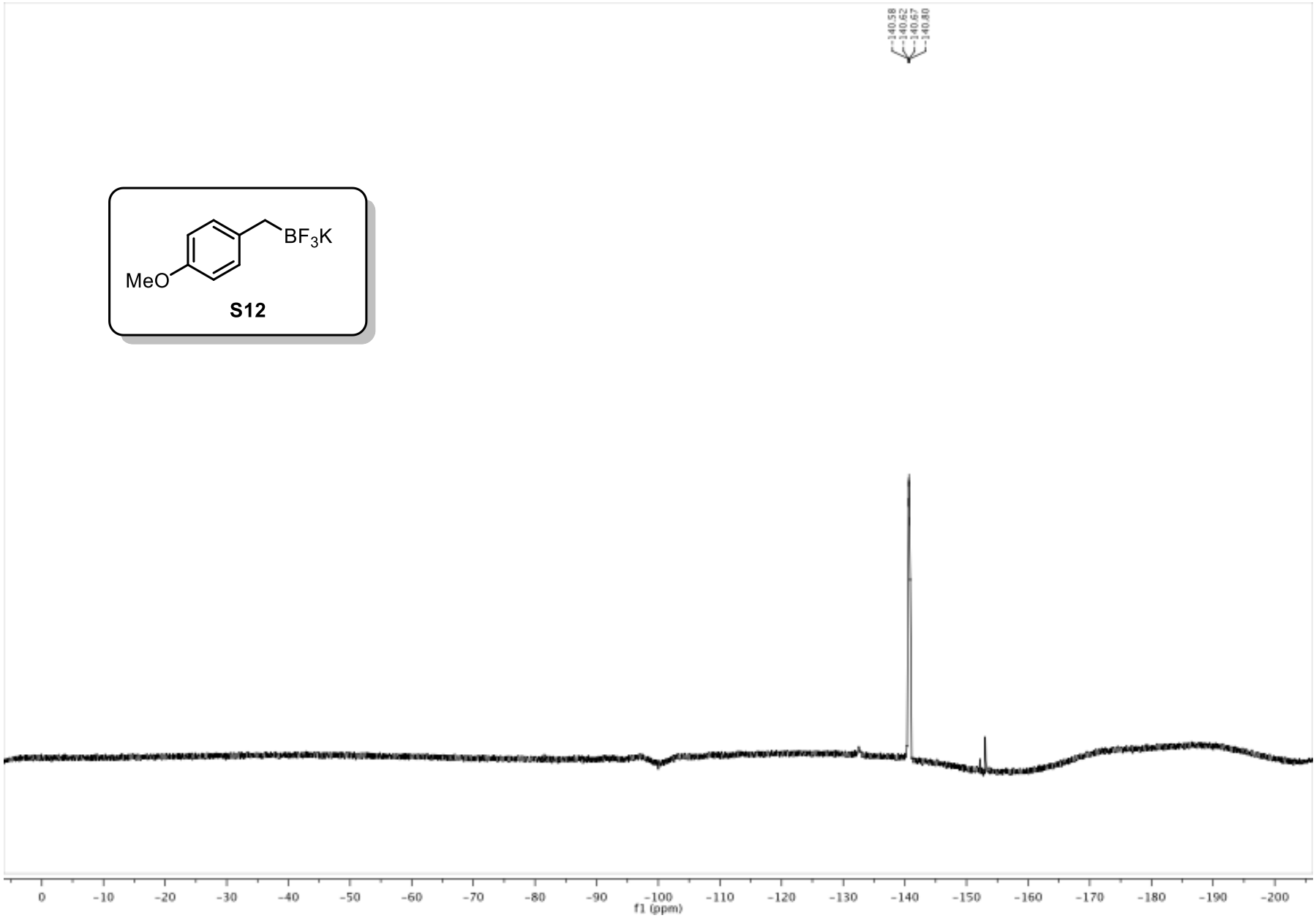
^{1}H NMR (acetone-d^{6}, 500 MHz) spectrum of potassium trifluoro(4-methoxybenzyl)borate (**S12**)



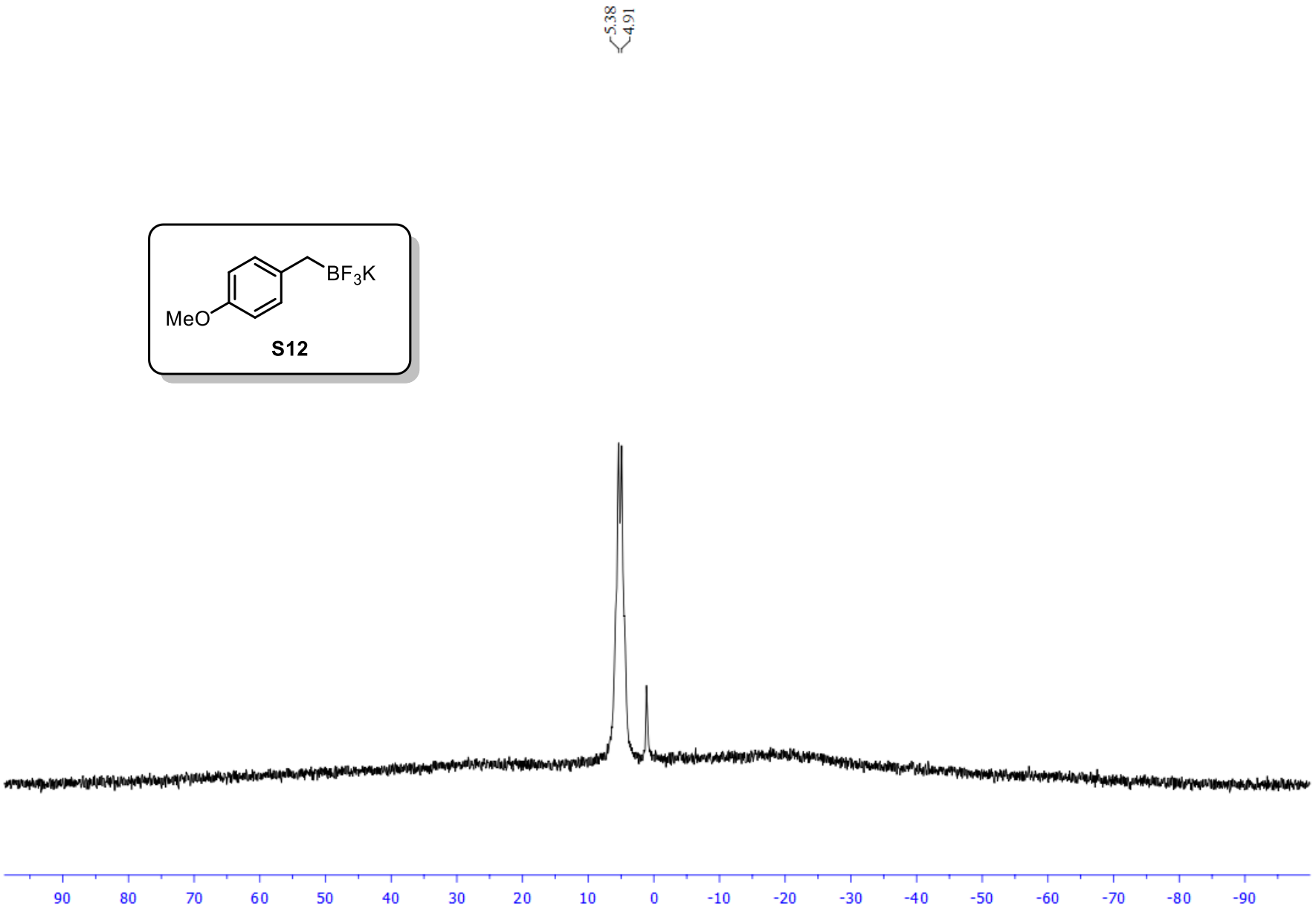
^{13}C NMR (acetone-d^{6}, 125.8 MHz) spectrum of potassium trifluoro(4-methoxybenzyl)borate (**S12**)



^{19}F NMR (acetone-d^{6}, 470.8 MHz) spectrum of potassium trifluoro(4-methoxybenzyl)borate (**S12**)



^{11}B NMR (acetone-d^{6}, 128.4 MHz) spectrum of potassium trifluoro(4-methoxybenzyl)borate (**S12**)



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