Supporting Information

Cross-Coupling of Mesylated Phenol Derivatives with Potassium Alkoxymethyltrifluoroborates

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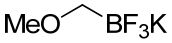
General Considerations

All reactions were carried out under an argon atmosphere. $PdCl_2(COD)$, dippf and K_3PO_4 were used as received. Both solvents and deionized water were degassed with argon each time prior to use. Standard benchtop techniques were employed for handling air-sensitive reagents. Melting points (°C) are uncorrected. NMR spectra were recorded on a 500, 400, or 300 MHz spectrometer. Data are presented as follows: chemical shift (ppm), multiplicity (*s* = singlet, *d* = doublet, *t* = triplet, *m* = multiplet, *br* = broad), coupling constant *J* (Hz) and integration. Analytical thin-layer chromatography (TLC) was performed on TLC silica or alumina gel plates (0.25 mm) precoated with a fluorescent indicator. Standard flash chromatography procedures were followed using 32–63 μm silica gel or 60-325 mesh basic alumina. Visualization was effected with ultraviolet light or cerium ammonium molybdate.

General Experimental Procedures

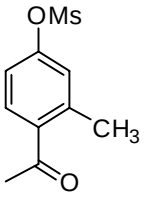
Procedure A:



(Potassium Methoxymethyltrifluoroborate (2a) is used as an example)

To KH powder (481 mg, 12.0 mmol) weighed in the glove box was added dry THF (20 mL). Freshly distilled methanol (384 mg, 12.0 mmol) was added dropwise to the suspension via syringe at 0 °C under argon. The mixture was stirred for 10 min at 0 °C and then allowed to warm to rt for 30 min. Potassium chloromethyltrifluoroborate (624 mg, 4.00 mmol) was added to the mixture in one portion at 0 °C. The reaction mixture was stirred at 50 °C overnight (unless otherwise specified). The mixture was quenched by adding 4.5 M KHF_2 (1.8 mL, 8.0 mmol). The mixture was left to stir at rt for 1 h, and then the suspension was concentrated and dried under vacuum. The dried solids were triturated with hot acetone and filtered to remove inorganic salts (unless otherwise specified). The resulting solution was concentrated until the trifluoroborate was minimally soluble in acetone, and chloroform was used to precipitate the product. After drying *in vacuo*, **2a** was obtained in 54% yield (331 mg) as a white solid. mp 152-153 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 3.20 (s, 3H), 2.63 (s, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 60.9; ^{19}F NMR (470.8 MHz, acetone-d_6) δ -146.5; ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 2.4; FT-IR (neat) 2824, 1049, 1005 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_2H_5BF_3O^-$ $(M-K)^-$ 113.0382, found 113.0386.

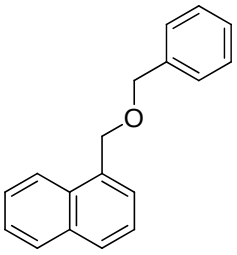
Procedure B:



(4-Acetyl-3-methylphenyl methanesulfonate is used as an example)

To a stirred solution of 1-(4-hydroxy-2-methylphenyl)ethanone (1.00 g, 6.70 mmol) in a mixture of CH_2Cl_2/pyridine (35 mL/9 mL) cooled to 0 °C was slowly added CH_3SO_2Cl (1.15 g, 10.1 mmol). The reaction mixture was allowed to warm to rt and stirred for 12-48 h. The reaction mixture was then quenched with saturated aqueous NH_4Cl (25 mL) followed by extraction with CH_2Cl_2 (3 x 30 mL). The combined extracts were washed with 3N HCl aq. (3 x 30 mL), saturated aqueous NaCl (3 x 30 mL) and then dried ($MgSO_4$). The solvent was concentrated and the product was purified by silica gel column chromatography (elution with hexanes/EtOAc 80:20) to yield 4-acetyl-3-methylphenyl methanesulfonate in 74% yield (1.12 g) as a white powder. mp: 53-55 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.5 Hz, 1H), 7.20 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.16 (d, *J* = 2.1 Hz, 1H), 3.18 (s, 3H), 2.58 (s, 3H), 2.55 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.4, 150.9, 141.7, 136.8, 131.4, 125.2, 119.2, 38.0, 29.8, 21.8; FT-IR (neat) 1670, 1364, 1182, 1125, 1151; HRMS (ESI) *m*/*z* calcd. for $C_{10}H_{11}O_4S$ $(M-H)^-$ 227.0374, found 237.0378.

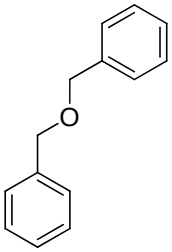
Procedure C:



(1-(Benzyloxymethyl)naphthalene (3b) is used as an example)

A Biotage microwave vial was charged with $PdCl_2$(COD) (2.1 mg, 7.5 μmol), dippf (6.3 mg, 15 μmol), **1** (55.5 mg, 0.25 mmol), **2b** (68.4 mg, 0.33 mmol) and K_3PO_4 (382 mg, 1.80 mmol) (unless otherwise specified). The test tube was sealed with a cap lined with a disposable Teflon septum, evacuated under vacuum, and purged with argon three times. A mixture of *t*-BuOH/H_2O (1.25 mL/1.25 mL) was added under argon. The reaction mixture was heated to 110 °C for 20 h before cooling to rt. The reaction mixture was extracted with EtOAc (3 x 2 mL) and then dried ($MgSO_4$). The solvent was removed *in vacuo,* and the crude product was purified by preparative silica gel chromatography (elution with hexanes/ CH_2Cl_2 80:20) to yield **3b** in 82% yield (50.8 mg) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.1 Hz, 1H), 7.88 (dd, *J* = 7.1, 1.7 Hz, 1H); 7.83 (d, *J* = 8.1 Hz, 1H), 7.56-7.50 (m, 3H), 7.47-7.44 (m, 1H), 7.41-7.36 (m, 4H), 7.33-7.29 (m, 1H), 5.03 (s, 2H), 4.64 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4, 133.9, 133.9, 132.0, 128.8, 128.7, 128.6, 128.1, 127.8, 126.7, 126.4, 125.9, 125.4, 124.2, 72.3, 70.8; FT-IR (neat) 2848, 1450, 1362, 1093, 1070 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{18}H_{16}ONa$ $(M+Na)^+$ 271.1101, found 271.1099.

Procedure D:

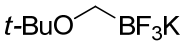


(((Oxybis(methylene))dibenzene (4a) is used as an example)

A Biotage microwave vial was charged with (2'-amino-[1,1'-biphenyl]-2-yl)palladium(II) chloride dimer (7.7 mg, 12 µmol), dippf (10.5 mg, 25.0 µmol), phenyl methanesulfonate (43.0 mg, 0.25 mmol), potassium benzyloxymethyltrifluoroborate (68.4 mg, 0.33 mmol) and K_3PO_4 (212 mg, 1.00 mmol). The test tube was sealed with a cap lined with a disposable Teflon septum, evacuated under vacuum, and purged with argon three times. A mixture of *t*-BuOH/H_2O (1.25 mL/1.25 mL) was added under argon. The reaction mixture was heated to 110 °C for 20 h before cooling to rt. The reaction mixture was extracted with EtOAc (3 x 2 mL) and then dried ($MgSO_4$). The solvent was removed *in vacuo,* and the crude product was purified by basic alumina chromatography (elution with hexanes/ ethyl acetate 95:5) to yield **4a** in 92% yield (45.3 mg) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.37 (m, 8H), 7.34-7.31 (m, 2H), 4.96 (s, 4H).
^{1}H NMR is comparable to the literature.[1]

1- Synthesis of Potassium Alkoxymethyltrifluoroborates Starting from the Potassium Chloromethyltrifluoroborate

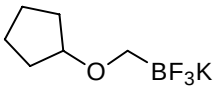
The compounds **2b**, **2e** and **2g** were prepared according to the procedure previously described.[2]



Potassium *tert*-Butoxymethyltrifluoroborate (2c)

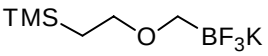
Potassium chloromethyltrifluoroborate (624 mg, 4.00 mmol) was added in one portion to *t*-BuOK (1.35 g, 12.0 mmol) in THF (20 mL) at 0 °C. The reaction mixture was stirred at rt for 24 h. The mixture was quenched by adding 4.5 M KHF_2 (1.8 mL, 8.0 mmol). The mixture was left to stir at rt for 1 h, and then suspension was concentrated and dried under vacuum. The product was purified by continnous Soxhlet extraction in a Soxhlet apparatus overnight with acetone. The resulting solution was concentrated to half volume and cooled to 0° C to precipitate the product. After filtering and drying *in vacuo*, **2c** was obtained in 75% yield (585.7 mg) as a white solid. mp > 250 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 2.29 (q, J = 5.4 Hz, 2H), 1.01 (s, 9H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 70.8, 27.2; ^{19}F NMR (470.8 MHz, DMSO-d_6) δ -140.9; ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 2.7; FT-IR (neat) 1114, 1000 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_5H_{11}BF_3O^-$ $(M\text{-}K)^-$ 155.0851, found 155.0855.

[1] Molander, G. A.; Canturk, B. *Org. Lett.* **2008**, *10*, 2135-2138.
[2] Molander, G. A.; Colombel V.; Braz V. A. *Org. Lett.* **2011**, *7*, 1852-1855.



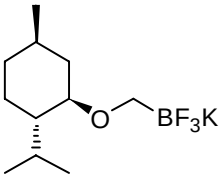
Potassium (Cyclopentyloxymethyl)trifluoroborate (2d)

Following procedure A, the reaction was carried out with cyclopentanol (1.03 g, 12.0 mmol) for 24 h at rt to obtain **2d** (193.6 mg, 23%) as a white solid after precipitation with cold acetone. mp > 250 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 3.57 (s, 1H), 2.40 (s, 2H), 1.55-1.24 (m, 8H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 82.6, 31.6, 23.3; ^{19}F NMR (470.8 MHz, DMSO-d_6) δ -141.0; ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 3.0; FT-IR (neat) 1380, 1065, 1011 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_6H_{11}BF_3O^-$ (M-K)$^-$ 167.0853, found 167.0855.



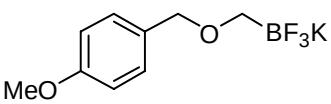
Potassium (2-(Trimethylsilyl)ethoxy)methyltrifluoroborate (2f)

Following procedure A, the reaction was carried out with trimethylsilylethanol (1.42 g, 12.0 mmol) to obtain **2f** (641.5 mg, 67%) as a white solid after Soxhlet extraction with acetone overnight and precipitation in cold acetone. mp (decomposition) 240-242 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 3.22 (t, *J* = 8.3 Hz, 2H), 2.42 (q, *J* = 5.1 Hz, 2H), 0.79 (t, *J* = 8.3 Hz, 2H), -0.02 (s, 9H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 69.8, 18.1, -1.2; ^{19}F NMR (470.8 MHz, DMSO-d_6) δ -141.1; ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 2.8; FT-IR (neat) 1106, 1011 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_6H_{15}BF_3OSi^-$ (M-K)$^-$ 199.0945, found 199.0937.



Potassium (((1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl)oxy)methyltrifluoroborate (2h)

Following procedure A, the reaction was carried out with (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexanol (1.87 g, 12.0 mmol) to obtain **2h** (703.8 mg, 64%) as a white solid after Soxhlet extraction with acetone overnight and precipitation in cold acetone. mp > 250 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 2.74-2.65 (m, 2H), 2.28-2.18 (m, 2H), 2.08-2.06 (m, 1H), 1.59-1.57 (m, 1H), 1.50-1.47 (m, 1H), 1.29-1.21 (m, 1H), 1.03-0.98 (m, 1H), 0.93-0.88 (m, 1H), 0.86 (d, *J* = 6.8 Hz, 3H), 0.81 (d, *J* = 7.1 Hz, 3H), 0.79-0.74 (m, 1H), 0.70 (d, *J* = 6.8 Hz, 3H), 0.61-0.54 (m, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 80.3, 48.1, 39.9, 34.6, 31.1, 24.9, 23.2, 22.5, 21.0, 16.5; ^{19}F NMR (470.8 MHz, DMSO-d_6) δ -141.2; ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 2.7; FT-IR (neat) 1450, 1047, 1024 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{11}H_{21}BF_3O^-$ (M-K)$^-$ 237.1645, found 237.1638; $[\alpha]^{20}_D$ = -0.20 (c=0.30 in MeOH).

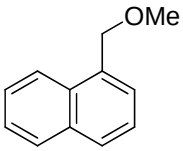


Potassium (4-Methoxybenzyloxy)methyltrifluoroborate (2i)

Following procedure A, the reaction was carried out with *p*-methoxybenzyl alcohol (1.66 g, 12.0 mmol) to obtain **2i** (606.0 mg, 59%) as a white solid after Soxhlet extraction with acetone overnight and precipitation in cold acetone. mp 197-199 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ

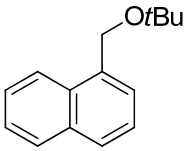
7.18 (d, *J* = 8.3 Hz, 2H), 6.86 (d, *J* = 8.3 Hz, 2H), 4.19 (s, 2H), 3.73 (s, 3H), 2.54-2.53 (m, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 158.5, 132.6, 129.2, 113.6, 74.9, 55.4; ^{19}F NMR (470.8 MHz, DMSO-d_6) δ -141.4; ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 2.3; FT-IR (neat) 1452, 1112, 1027 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_9H_{11}BF_3O_2^-$ $(M-K)^-$ 219.0804, found 219.0805.

2- Synthesis of 1-(Alkoxymethyl)naphthalenes



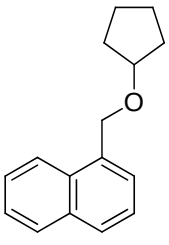
1-(Methoxymethyl)naphthalene (3a)

Following procedure C, the reaction was carried out with **1** (55.5 mg, 0.25 mmol) and **2a** (50.2 mg, 0.33 mmol), $PdCl_2$(COD) (3.6 mg, 12 μmol) and dippf (10.5 mg, 25.0 μmol) to obtain **3a** (30.5 mg, 71%) after 4 h as a yellow oil after preparative silica gel chromatography (elution with hexanes/EtOAc 92:8). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.3 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.83 (d, *J* = 8.3 Hz, 1H), 7.57-7.50 (m, 3H), 7.46-7.43 (m, 1H), 4.93 (s, 2H), 3.47 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.9, 133.8, 131.9, 128.8, 128.7, 126.6, 126.3, 125.9, 125.3, 124.1, 73.3, 58.3; FT-IR (neat) 1166, 1099 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{11}H_9O$ $(M-Me)^+$ 157.0647, found 157.0653.



1-(*tert*-Butoxymethyl)naphthalene (3c)

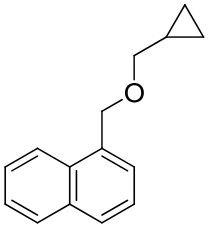
Following procedure C, the reaction was carried out with **1** (55.5 mg, 0.25 mmol) and **2c** (64.0 mg, 0.33 mmol) to obtain **3c** (46.4 mg, 87%) as a yellow oil after preparative silica gel chromatography (elution with hexanes/EtOAc 92:8). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.60 (d, *J* = 6.8 Hz, 1H), 7.56-7.45 (m, 3H), 4.93 (s, 2H), 1.42 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.3, 133.9, 131.8, 128.7, 128.1, 126.0, 125.9, 125.6, 123.9, 73.8, 62.5, 27.9; FT-IR (neat) 1194, 1100 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{15}H_{18}ONa$ $(M+Na)^+$ 237.1250, found 237.1255.



1-((Cyclopentyloxy)methyl)naphthalene (3d)

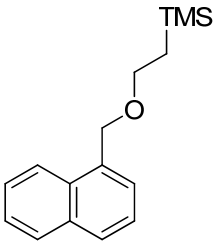
Following procedure C, the reaction was carried out with **1** (55.5 mg, 0.25 mmol) and **2d** (68.0 mg, 0.33 mmol) to obtain **3d** (43.2 mg, 76%) as a yellow oil after silica gel column chromatography (elution with CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.56-7.49 (m, 3H), 7.46-7.43

(m, 1H), 4.94 (s, 2H), 4.14-4.10 (m, 1H), 1.83-1.76 (m, 6H), 1.59-1.55 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.5, 133.9, 131.9, 128.6, 128.4, 126.3, 126.1, 125.8, 125.4, 124.2, 81.3, 69.4, 32.4, 23.8; FT-IR (neat) 1105, 1086 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{16}H_{18}ONa$ $(M+Na)^+$ 249.1267, found 249.1255.



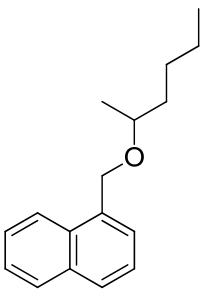
1-((Cyclopropylmethoxy)methyl)naphthalene (3e)

Following procedure C, the reaction was carried out with **1** (55.5 mg, 0.25 mmol) and **2e** (63.4 mg, 0.33 mmol) to obtain **3e** (47.7 mg, 90%) as a yellow oil after preparative silica gel chromatography (elution with hexanes/CH_2Cl_2 90:10). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 8.3 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.57-7.50 (m, 3H), 7.46-7.43 (m, 1H), 5.00 (s, 2H), 3.41 (d, *J* = 6.8 Hz, 2H), 1.20-1.13 (m, 1H), 0.59-0.53 (m, 2H), 0.26-0.23 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.1, 133.9, 131.9, 128.6, 128.6, 126.5, 126.2, 125.8, 125.3, 124.2, 75.1, 71.2, 10.8, 3.2; FT-IR (neat) 1090, 1073 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{15}H_{16}ONa$ $(M+Na)^+$ 235.1091, found 235.1099.



Trimethyl(2-(naphthalen-1-ylmethoxy)ethyl)silane (3f)

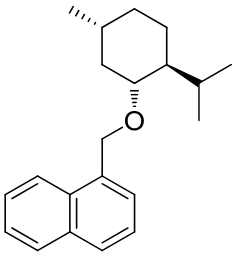
Following procedure C, the reaction was carried out with **1** (55.5 mg, 0.25 mmol) and **2f** (78.6 mg, 0.33 mmol) to obtain **3f** (58.7 mg, 91%) as a yellow oil after silica gel column chromatography (elution with hexanes/CH_2Cl_2 50:50). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.3 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 8.3 Hz, 1H), 7.57-7.50 (m, 3H), 7.48-7.45 (m, 1H), 4.97 (s, 2H), 3.71 (t, *J* = 8.3 Hz, 2H), 1.08 (t, *J* = 8.3 Hz, 2H), 0.05 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.3, 133.8, 131.8, 128.6, 128.5, 126.2, 126.2, 125.8, 125.4, 124.1, 70.9, 67.9, 18.4, -1.2; FT-IR (neat) 1248, 1091, 1073 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{16}H_{22}OSiNa$ $(M+Na)^+$ 281.1346, found 281.1338.



1-((Hexan-2-yloxy)methyl)naphthalene (3g)

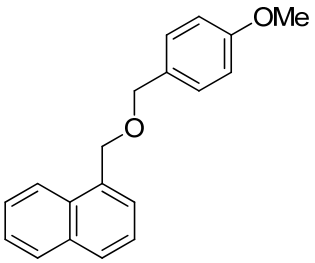
Following procedure C, the reaction was carried out with **1** (55.5 mg, 0.25 mmol) and **2g** (73.3 mg, 0.33 mmol) to obtain **3g** (48.0 mg, 79%) as a yellow oil after preparative silica gel chromatography (elution with hexanes/CH_2Cl_2 90:10). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.3 Hz, 1H), 7.88 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.82 (d, *J* = 8.3 Hz, 1H), 7.57-7.50 (m, 3H), 7.47-7.44 (m, 1H), 4.99 (AB system, J_{AB}=11.7 Hz, δ_A=5.05, δ_B=4.92, 2H), 3.63 (sextuplet, *J* = 6.1 Hz, 1H), 1.71-1.64 (m, 1H), 1.53-1.46 (m, 1H), 1.44-1.37 (m, 1H),

1.36-1.29 (m, 3H), 1.28 (d, J = 6.1 Hz, 3H), 0.90 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.7, 133.9, 131.9, 128.6, 128.5, 126.4, 126.1, 125.8, 125.4, 124.3, 75.1, 68.9, 36.6, 27.9, 22.9, 19.8, 14.2; FT-IR (neat) 2930, 2853, 1086, 1066 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{17}H_{22}ONa$ $(M+Na)^+$ 265.1569, found 265.1568.



1-((((1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl)oxy)methyl)naphthalene (3h)

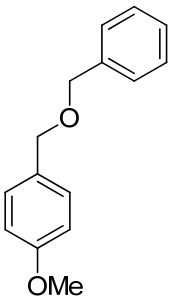
Following procedure C, the reaction was carried out with **1** (55.5 mg, 0.25 mmol) and **2h** (91.1 mg, 0.33 mmol) to obtain **3h** (48.0 mg, 65%) as a white solid after silica gel column chromatography (elution with hexanes/CH_2Cl_2 90:10). Following procedure D, the reaction was carried out with **1** (55.5 mg, 0.25 mmol) and **2h** (91.1 mg, 0.33 mmol) to obtain **3h** (53.4 mg, 72%) as a white solid after silica gel column chromatography (elution with hexanes/CH_2Cl_2 90:10). mp 44-46 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, J = 8.3 Hz, 1H), 7.87 (dd, J = 7.8, 1.5 Hz, 1H), 7.81 (d, J = 8.3 Hz, 1H), 7.55-7.48 (m, 3H), 7.45 (dd, J = 8.3, 7.1 Hz, 1H), 4.99 (AB system, J_{AB}=11.7 Hz, δ_A=5.16, δ_B=4.83, 2H), 3.27 (td, J = 10.5, 4.2 Hz, 1H), 2.36-2.32 (m, 1H), 2.29-2.23 (m, 1H), 1.71-1.62 (m, 2H), 1.45-1.37 (m, 1H), 1.35-1.28 (m, 1H), 1.04-0.99 (m, 1H), 0.98 (d, J = 6.6 Hz, 3H), 0.95-0.88 (m, 2H), 0.86 (d, J = 7.1 Hz, 3H), 0.60 (d, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.7, 133.9, 132.0, 128.6, 128.6, 126.6, 126.1, 125.8, 125.4, 124.4, 78.7, 68.7, 48.5, 40.4, 34.8, 31.8, 25.4, 23.3, 22.6, 21.2, 15.9; FT-IR (neat) 2863, 1458, 1088, 1052 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{21}H_{28}ONa$ $(M+Na)^+$ 319.2046, found 319.2038; $[\alpha]^{20}_D$ = -0.32 (c=0.30 in MeOH).



1-(((4-Methoxybenzyl)oxy)methyl)naphthalene (3i)

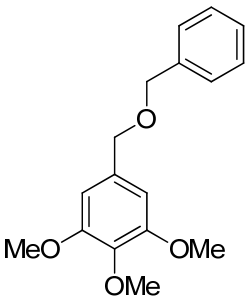
Following procedure C, the reaction was carried out with **1** (55.5 mg, 0.25 mmol) and **2i** (85.2 mg, 0.33 mmol) to obtain **3i** (56.7 mg, 82%) as a colorless oil after silica gel column chromatography (elution with hexanes/EtOAc 92:8). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, J = 8.1 Hz, 1H), 7.89 (d, J = 8.3 Hz, 1H), 7.84 (d, J = 8.1 Hz, 1H), 7.57-7.51 (m, 3H), 7.48-7.45 (m, 1H), 7.33 (d, J = 8.3 Hz, 2H), 6.92 (d, J = 8.3 Hz, 2H), 5.00 (s, 2H), 4.58 (s, 2H), 3.83 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.4, 134.0, 132.0, 130.5, 129.7, 128.8, 128.7, 126.8, 126.3, 125.9, 125.4, 124.3, 114.0, 72.0, 70.5, 55.5; FT-IR (neat) 1251, 1174, 1089, 1035 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{19}H_{18}O_2Na$ $(M+Na)^+$ 301.1204, found 301.1198.

3- Synthesis of 1-((Benzyloxy)methyl)aryl Compounds



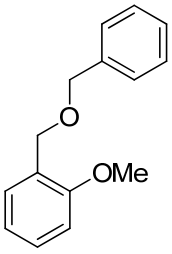
1-((Benzyloxy)methyl)-4-methoxybenzene (4b)

Following procedure D, the reaction was carried out with 4-methoxyphenyl methanesulfonate (50.5 mg, 0.25 mmol) and **2b** (68.4 mg, 0.33 mmol) to obtain **4b** (34.3 mg, 60%) as a yellow oil after silica gel column chromatography (elution with hexanes/CH_2Cl_2 60:40). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.36 (m, 4H), 7.32-7.30 (m, 3H), 6.91 (d, J = 8.8 Hz, 2H), 4.55 (s, 2H), 4.51 (s, 2H), 3.82 (s, 3H). ^{1}H NMR is comparable to the literature.[1]



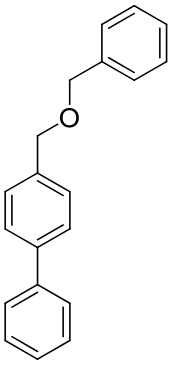
5-((Benzyloxy)methyl)-1,2,3-trimethoxybenzene (4c)

Following procedure D, the reaction was carried out with 3,4,5-trimethoxyphenyl methanesulfonate (65.5 mg, 0.25 mmol) and **2b** (68.4 mg, 0.33 mmol) to obtain **4c** (56.5 mg, 78%) as a yellow oil after basic alumina column chromatography (elution with hexanes/EtOAc 85:15). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.36 (m, 4H), 7.32-7.29 (m, 1H), 6.60 (s, 2H), 4.57 (s, 2H), 4.50 (s, 2H), 3.86 (s, 6H), 3.85 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.4, 138.3, 137.5, 134.1, 128.5, 128.0, 127.8, 104.8, 72.4, 72.3, 60.9, 56.2; FT-IR (neat) 1591, 1456, 1234, 1126 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{17}H_{20}O_4Na$ $(M+Na)^+$ 311.1259, found 311.1273.



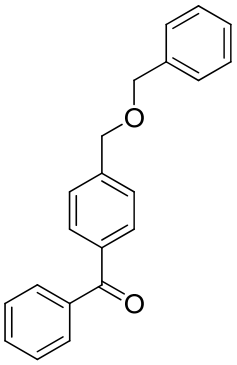
1-((Benzyloxy)methyl)-2-methoxybenzene (4d)

Following procedure D, the reaction was carried out with 2-methoxyphenyl methanesulfonate (50.5 mg, 0.25 mmol) and **2b** (68.4 mg, 0.33 mmol) to obtain **4d** (36.6 mg, 64%) as a colorless oil after preparative silica gel column chromatography (elution with hexanes/EtOAc 95:5). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45-7.40 (m, 3H), 7.38-7.35 (m, 2H), 7.31-7.26 (m, 2H), 6.98 (d, J = 8.1 Hz, 1H), 6.89 (d, J = 8.1 Hz, 1H), 4.63 (s, 4H), 3.84 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.3, 138.8, 129.1, 128.8, 128.5, 127.9, 127.7, 126.9, 120.6, 110.3, 72.6, 67.2, 55.5; FT-IR (neat) 1494, 1242, 1091, 1029 cm^{-1}; HRMS (ESI) m/z calcd. for $C_{15}H_{16}O_2Na$ $(M+Na)^+$ 251.1048, found 251.1058.



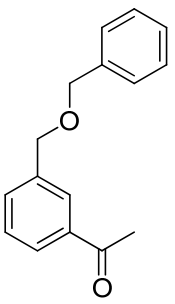
4-((Benzyloxy)methyl)-1,1'-biphenyl (4e)

Following procedure D, the reaction was carried out with [1,1'-biphenyl]-4-yl methanesulfonate (62.0 mg, 0.25 mmol) and **2b** (68.4 mg, 0.33 mmol) to obtain **4e** (53.0 mg, 77%) as a colorless oil after basic alumina column chromatography (elution with hexanes/CH_2Cl_2 80:20). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63-7.61 (m, 4H), 7.48-7.31 (m, 10H), 4.63 (s, 2H), 4.62 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.1, 140.8, 138.4, 137.5, 128.9, 128.6, 128.4, 128.0, 127.8, 127.4, 127.4, 127.3, 72.3, 72.0; FT-IR (neat) 1488, 1452, 1093, 1074 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{20}H_{18}O$ $(M)^{+\cdot}$ 274.1358, found 274.1354.



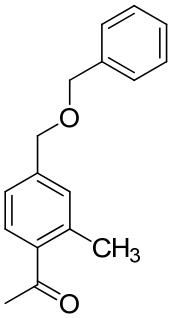
(4-((Benzyloxy)methyl)phenyl)(phenyl)methanone (4f)

Following procedure D, the reaction was carried out with 4-benzoylphenyl methanesulfonate (69.0 mg, 0.25 mmol) and **2b** (68.4 mg, 0.33 mmol) to obtain **4f** (41.9 mg, 55%) as a yellow oil after basic alumina column chromatography (elution with hexanes/EtOAc 95:5). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81-7.80 (m, 4H), 7.59-7.58 (m, 1H), 7.50-7.47 (m, 4H), 7.39-7.36 (m, 4H), 7.33-7.30 (m, 1H), 4.65 (s, 2H), 4.62 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.4, 143.1, 137.8, 137.6, 136.8, 132.3, 130.2, 129.9, 128.4, 128.2, 127.7, 127.2, 72.5, 71.4; FT-IR (neat) 1656, 1277, 1092, 1070 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{21}H_{19}O_2$ $(M+H)^+$ 303.1385, found 303.1382.



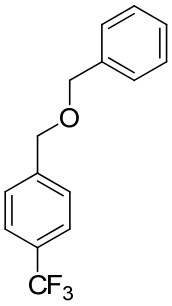
1-(3-((Benzyloxy)methyl)phenyl)ethanone (4g)

Following procedure D, the reaction was carried out with 3-acetylphenyl methanesulfonate (53.5 mg, 0.25 mmol) and **2b** (68.4 mg, 0.33 mmol) to obtain **4g** (39.5 mg, 67%) as a yellow oil after basic alumina column chromatography (elution with hexanes/CH_2Cl_2 60:40). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.38-7.37 (m, 4H), 7.32-7.30 (m, 1H), 4.61 (s, 2H), 4.59 (s, 2H), 2.62 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.3, 139.1, 138.1, 137.4, 132.6, 128.9, 128.6, 128.0, 128.0, 127.8, 127.7, 72.6, 71.8, 26.9; FT-IR (neat) 1684, 1275, 1074 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{16}H_{17}O_2$ $(M+H)^+$ 241.1229, found 241.1237.



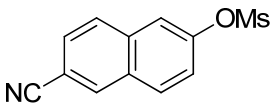
1-(4-((Benzyloxy)methyl)-2-methylphenyl)ethanone (4h)

Following procedure D, the reaction was carried out with 4-acetyl-3-methylphenyl methanesulfonate (57.0 mg, 0.25 mmol) and **2b** (68.4 mg, 0.33 mmol) to obtain **4h** (44.8 mg, 71%) as a colorless oil after basic alumina column chromatography (elution with hexanes/EtOAc 95:5). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, J = 7.9 Hz, 1H), 7.38-7.37 (m, 4H), 7.33-7.31 (m, 1H), 7.25-7.24 (m, 2H), 4.58 (s, 2H), 4.56 (s, 2H), 2.58 (s, 3H), 2.54 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.2, 142.0, 138.8, 137.9, 136.7, 131.0, 129.7, 128.4, 127.7, 124.6, 72.4, 71.3, 29.4, 21.7; FT-IR (neat) 1681, 1252, 1096 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{17}H_{19}O_2$ $(M+H)^+$ 255.1385, found 255.1389.



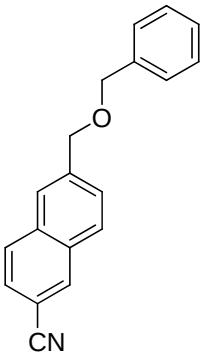
1-((Benzyloxy)methyl)-4-(trifluoromethyl)benzene (4i)

Following procedure D, the reaction was carried out with 4-trifluoromethylphenyl methanesulfonate (60.0 mg, 0.25 mmol) and **2b** (68.4 mg, 0.33 mmol) to obtain **4i** (45.8 mg, 69%) as a yellow oil after preparative silica gel chromatography (elution with hexanes/EtOAc 90:10). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, J = 7.9 Hz, 2H), 7.49 (d, J = 7.9 Hz, 2H), 7.38-7.37 (m, 4H), 7.33-7.32 (m, 1H), 4.62 (s, 2H), 4.60 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.6, 138.0, 130.0 (q, ^{2}J = 32.7 Hz, 1C), 128.6, 128.0, 127.9, 127.8, 125.5 (q, ^{3}J = 3.6 Hz, 1C), 124.3 (q, ^{1}J = 271.6 Hz, 1C), 72.7, 71.4; FT-IR (neat) 1326, 1153, 1112, 1067 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{15}H_{13}F_2O$ $(M-F)^+$ 247.0934, found 247.0925.



6-Cyanonaphthalen-2-yl methanesulfonate

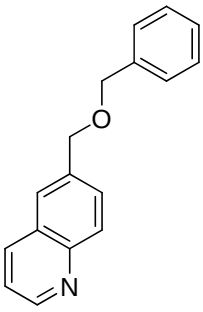
Following procedure B, the reaction was carried out with 6-hydroxy-2-naphthonitrile (1.0 g, 5.9 mmol) to obtain 6-cyanonaphthalen-2-yl methanesulfonate (1.17 g, 91%) as an orange solid without further purification. mp 115-117 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.98 (d, J = 8.8 Hz, 1H), 7.94 (d, J = 8.5 Hz, 1H), 7.83 (d, J = 2.2 Hz, 1H), 7.68 (d, J = 8.5 Hz, 1H), 7.54 (dd, J = 8.8, 2.2 Hz, 1H), 3.25 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.0, 135.3, 134.1, 131.1, 131.0, 129.4, 127.8, 123.0, 119.8, 118.9, 110.4, 38.2; FT-IR (neat) 2230, 1359, 1174 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{12}H_8NO_3S$ $(M-H)^-$ 246.0225, found 246.0215.



6-((Benzyloxy)methyl)-2-naphthonitrile (4j)

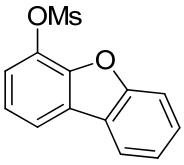
Following procedure D, the reaction was carried out with 6-cyanonaphthalen-2-yl methanesulfonate (61.8 mg, 0.25 mmol) and **2b** (68.4 mg, 0.33 mmol) to obtain **4j** (31.2 mg, 46%) as a yellow amorphous solid after basic alumina column chromatography (elution with hexanes/EtOAc 90:10). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.92-7.89 (m, 3H), 7.62 (dt, *J* = 8.6, 1.5 Hz, 2H), 7.43-7.38 (m, 4H), 7.36-7.34 (m, 1H), 4.76 (s, 2H), 4.66 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.8, 138.0, 134.8, 134.1, 131.9, 129.3, 128.8, 128.7, 128.0, 128.0, 127.5, 126.8, 126.3, 119.4, 109.4, 72.8, 71.8; FT-IR (neat) 2217, 1259, 1075, 1018 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{19}H_{16}NO$ $(M+H)^+$ 274.1232, found 274.1231.

4- Synthesis of 1-((Benzyloxy)methyl)heteroaryl Compounds



6-((Benzyloxy)methyl)quinoline (5a)

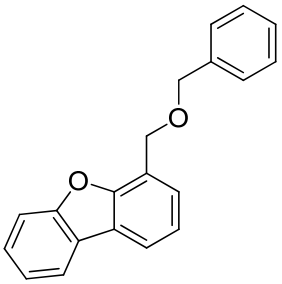
Following procedure D, the reaction was carried out with quinolin-6-yl methanesulfonate (55.8 mg, 0.25 mmol), (2'-amino-[1,1'-biphenyl]-2-yl)palladium(II) chloride dimer (4.6 mg, 7.5 µmol) and dippf (6.3 mg, 15 µmol) to obtain **5a** (50.6 mg, 81%) as a yellow oil after basic alumina column chromatography (elution with hexanes/EtOAc 70:30). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.91-8.90 (m, 1H), 8.14 (d, *J* = 7.9 Hz, 1H), 8.11 (d, *J* = 8.8 Hz, 1H), 7.81 (s, 1H), 7.72 (dd, *J* = 8.8, 1.7 Hz, 1H), 7.40-7.32 (m, 6H), 4.75 (s, 2H), 4.64 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.5, 148.1, 138.2, 136.9, 136.2, 129.8, 129.4, 128.6, 128.3, 128.0, 128.0, 126.2, 121.4, 72.6, 71.9; FT-IR (neat) 2853, 1501, 1092, 1075 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{17}H_{16}NO$ $(M+H)^+$ 250.1232, found 250.1229.



Dibenzo[b,d]furan-4-yl methanesulfonate

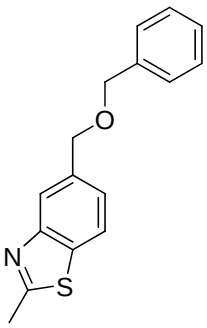
Following procedure B, the reaction was carried out with dibenzo[b,d]furan-4-ol (138 mg, 0.75 mmol) to obtain dibenzo[b,d]furan-4-yl methanesulfonate (150.9 mg, 77%) as an off-white powder without further purification. mp 80-82 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.7 Hz, 1H), 7.88 (d, *J* = 7.7 Hz, 1H), 7.61 (d, *J* = 8.3 Hz, 1H), 7.52-7.49 (m, 1H), 7.45 (d, *J* = 8.3 Hz, 1H), 7.41-7.34 (m, 2H), 3.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.5, 147.3,

134.2, 128.2, 127.5, 123.8, 123.8, 123.7, 121.7, 121.2, 119.8, 112.2, 38.6; FT-IR (neat) 1331, 1197, 1171, 1074 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{13}H_9O_4S$ $(M-H)^-$ 261.0222, found 261.0231.



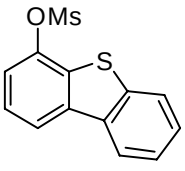
4-((Benzyloxy)methyl)dibenzo[b,d]furan (5b)

Following procedure D, the reaction was carried out with dibenzo[b,d]furan-4-yl methanesulfonate (65.5 mg, 0.25 mmol), (2'-amino-[1,1'-biphenyl]-2-yl)palladium(II) chloride dimer (4.6 mg, 7.5 μmol) and dippf (6.3 mg, 15 μmol) to obtain **5b** (49.9 mg, 69%) as a yellow oil after preparative basic alumina chromatography (elution with hexanes/CH_2Cl_2 90:10). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.5 Hz, 1H), 7.92 (d, *J* = 7.5 Hz, 1H), 7.62 (d, *J* = 8.3 Hz, 1H), 7.57 (d, *J* = 7.3 Hz, 1H), 7.50-7.45 (m, 3H), 7.41-7.32 (m, 5H), 5.00 (s, 2H), 4.71 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.3, 154.4, 138.4, 128.6, 128.0, 127.9, 127.3, 127.1, 124.4, 124.4, 123.0, 122.9, 122.5, 120.9, 120.3, 112.0, 72.6, 66.8; FT-IR (neat) 2879, 1452, 1192, 1124, 1102, 1065 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{20}H_{16}O_2$ $(M)^+$ 288.1150, found 288.1154.



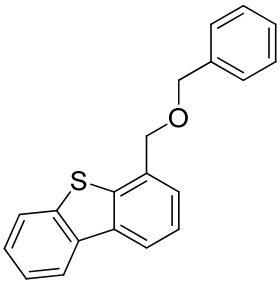
5-((Benzyloxy)methyl)-2-methylbenzo[d]thiazole (5c)

Following procedure D, the reaction was carried out with 2-methylbenzo[d]thiazol-5-yl methanesulfonate (60.8 mg, 0.25 mmol) to obtain **5c** (30.7 mg, 46%) as a yellow oil after preparative silica gel chromatography (elution with hexanes/EtOAc 80:20). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.80 (d, *J* = 8.3 Hz, 1H), 7.40-7.35 (m, 5H), 7.31-7.29 (m, 1H), 4.69 (s, 2H), 4.59 (s, 2H), 2.84 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.6, 153.7, 138.3, 136.7, 135.0, 128.6, 128.0, 127.8, 124.8, 121.7, 121.5, 72.2, 72.0, 20.3; FT-IR (neat) 2853, 1454, 1421, 1173, 1092, 1068 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{16}H_{16}NOS$ $(M+H)^+$ 270.0953, found 270.0944.



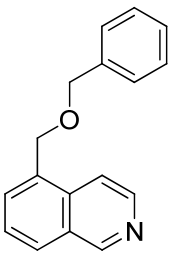
Dibenzo[b,d]thiophen-4-yl Methanesulfonate

Following procedure B, the reaction was carried out with dibenzo[b,d]furan-4-ol (600 mg, 3.00 mmol) to obtain dibenzo[b,d]thiophen-4-yl methanesulfonate (697.6 mg, 84%) as an orange powder after silica gel column chromatography (elution with hexanes/CH_2Cl_2 50:50). mp 93-95 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18-8.16 (m, 1H), 8.11-8.10 (m, 1H), 7.89-7.87 (m, 1H), 7.52-7.50 (m, 4H), 3.26 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.4, 139.2, 138.8, 135.3, 132.3, 127.8, 126.0, 125.2, 123.1, 122.3, 120.5, 120.1, 38.7; FT-IR (neat) 1346, 1176 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{13}H_9O_3S_2$ $(M-H)^-$ 276.9993, found 276.9989.



4-((Benzyloxy)methyl)dibenzo[b,d]thiophene (5d)

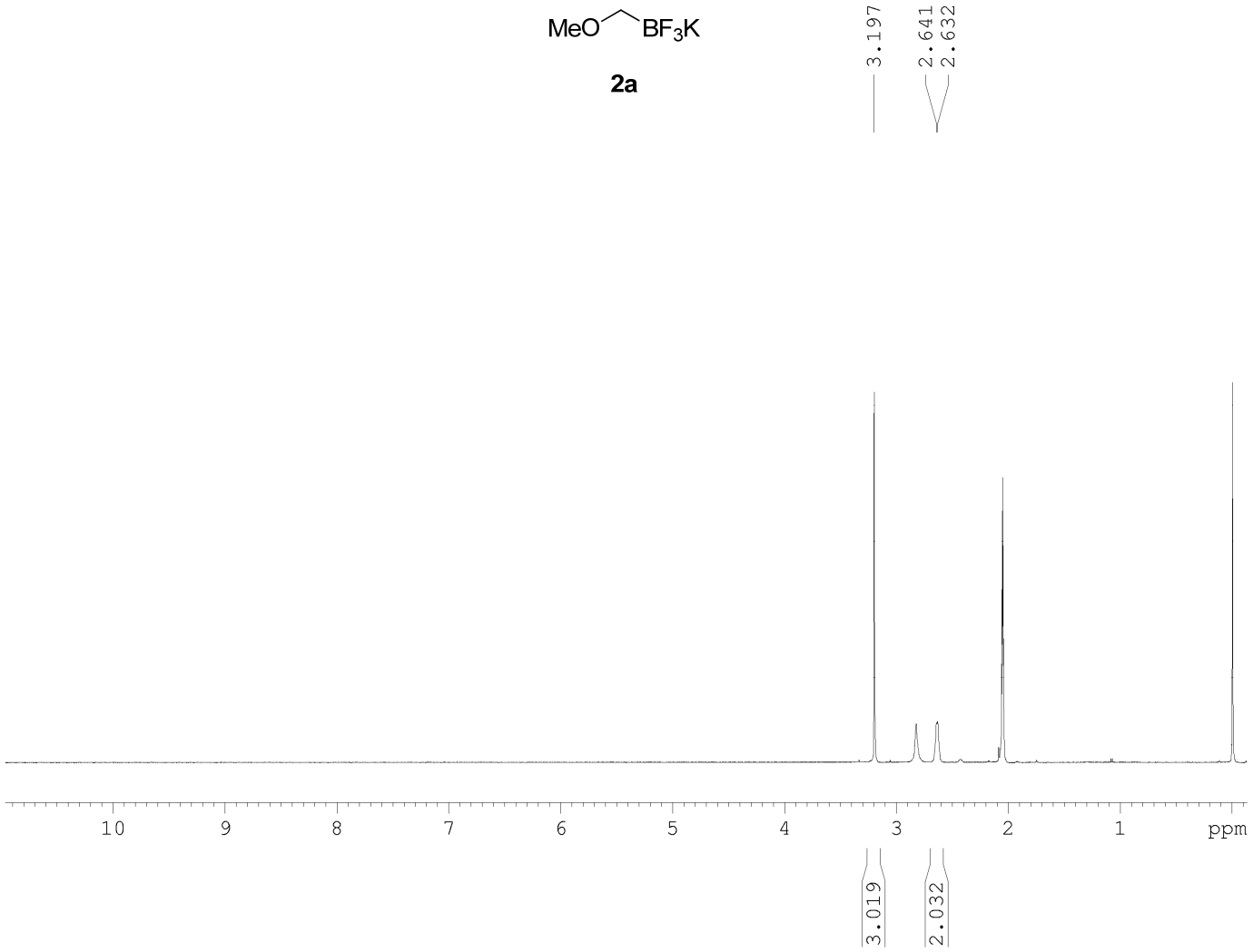
Following procedure D, the reaction was carried out with dibenzo[b,d]furan-4-yl methanesulfonate (69.5 mg, 0.25 mmol), (2'-amino-[1,1'-biphenyl]-2-yl)palladium(II) chloride dimer (4.6 mg, 7.5 µmol) and dippf (6.3 mg, 15 µmol) to obtain **5d** (51.6 mg, 68%) as a yellow oil after basic alumina gel column chromatography (elution with hexanes/EtOAc 90:10). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20-8.18 (m, 1H), 8.15-8.14 (m, 1H), 7.92-7.90 (m, 1H), 7.50-7.44 (m, 6H), 7.41-7.38 (m, 2H), 7.35-7.32 (m, 1H), 4.88 (s, 2H), 4.65 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.7, 138.2, 137.9, 136.1, 135.4, 132.5, 128.4, 127.9, 127.7, 126.7, 125.9, 124.4, 124.3, 122.7, 121.6, 121.0, 72.3, 71.2; FT-IR (neat) 2858, 1444, 1114, 1101, 1073 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{20}H_{17}OS$ $(M+H)^+$ 304.0922, found 304.0919.



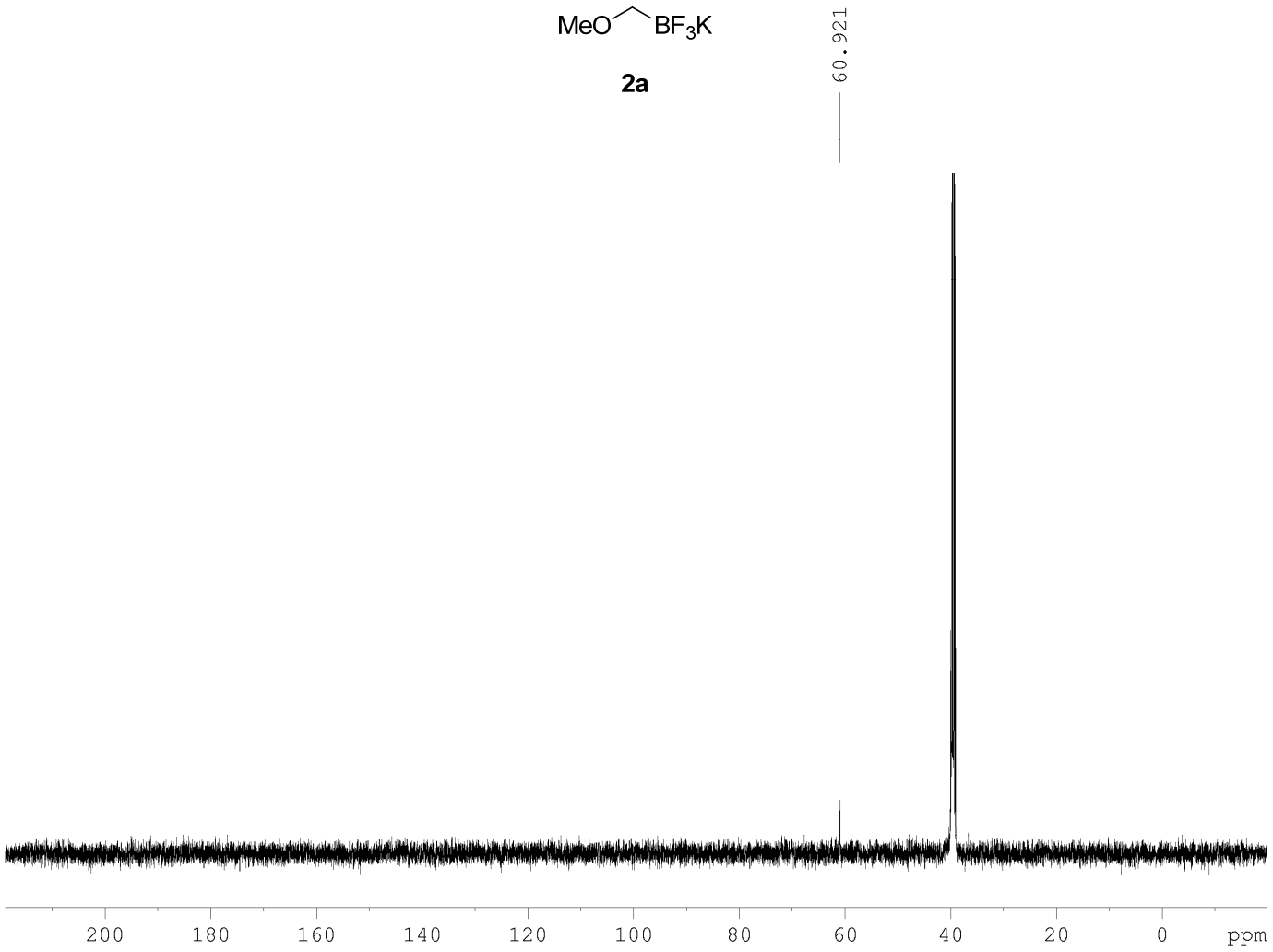
5-((Benzyloxy)methyl)isoquinoline (5e)

Following procedure D, the reaction was carried out with isoquinolin-5-yl methanesulfonate (55.8 mg, 0.25 mmol), (2'-amino-[1,1'-biphenyl]-2-yl)palladium(II) chloride dimer (4.6 mg, 7.5 µmol) and dippf (6.3 mg, 15 µmol) to obtain **5e** (35.8 mg, 57%) as a yellow oil after basic alumina column chromatography (elution with hexanes/EtOAc 85:15). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.28 (s, 1H), 8.57 (d, *J* = 5.9 Hz, 1H), 7.95 (d, *J* = 8.3 Hz, 1H), 7.88 (d, *J* = 5.9 Hz, 1H), 7.74 (d, *J* = 7.1 Hz, 1H), 7.60-7.57 (m, 1H), 7.39-7.38 (m, 4H), 7.34-7.32 (m, 1H), 4.98 (s, 2H), 4.65 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.9, 143.3, 137.8, 134.4, 133.1, 130.4, 128.8, 128.4, 127.9, 127.8, 127.8, 126.6, 116.9, 72.4, 69.6; FT-IR (neat) 2853, 1454, 1097, 1071 cm^{-1}; HRMS (ESI) *m*/*z* calcd. for $C_{17}H_{16}NO$ $(M+H)^+$ 250.1232, found 250.1223.

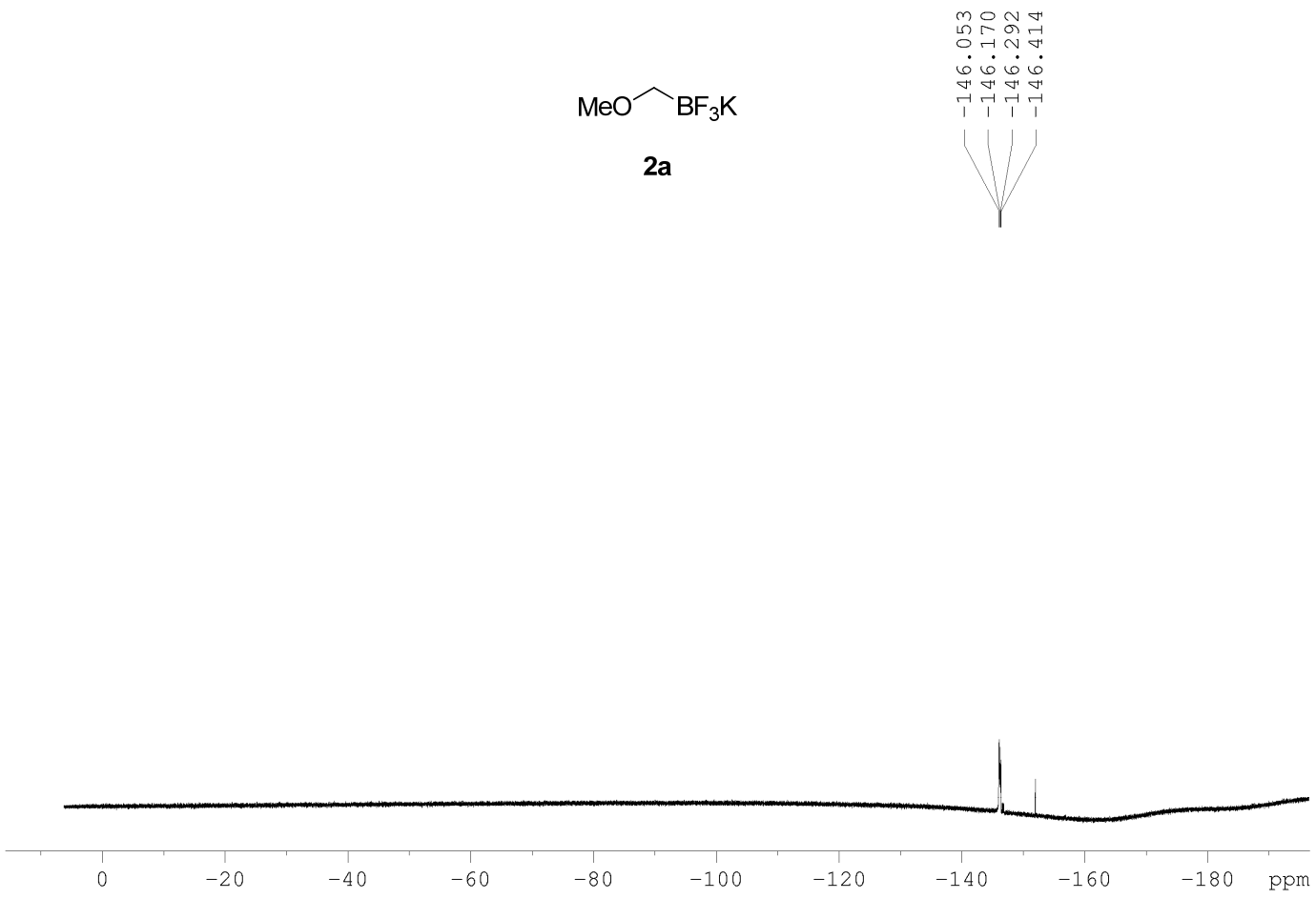
NMR Spectra



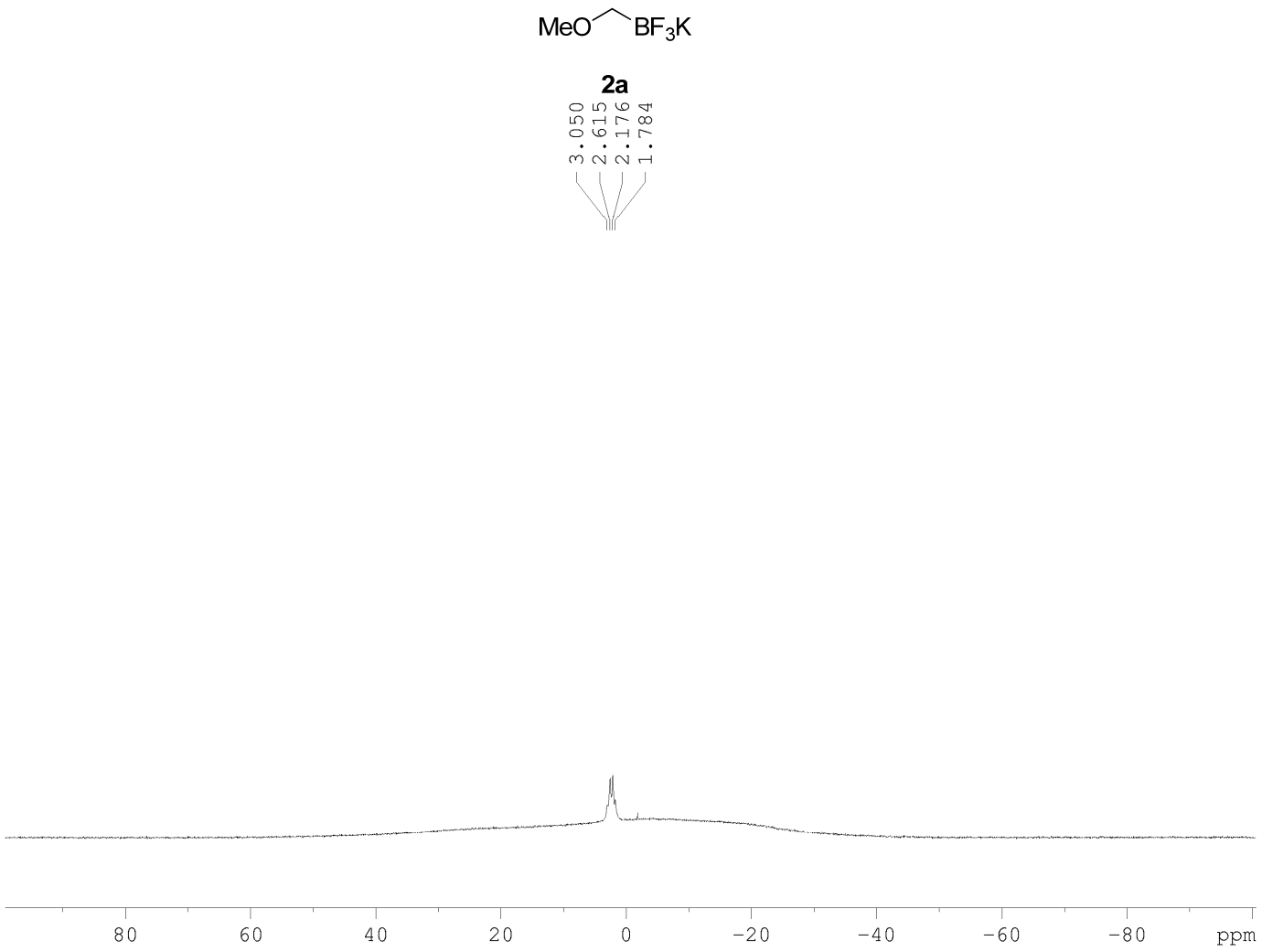
^{1}H NMR (500 MHz, acetone-d_6) Spectrum of potassium methoxymethyltrifluoroborate **2a** (Table 2, entry 1)



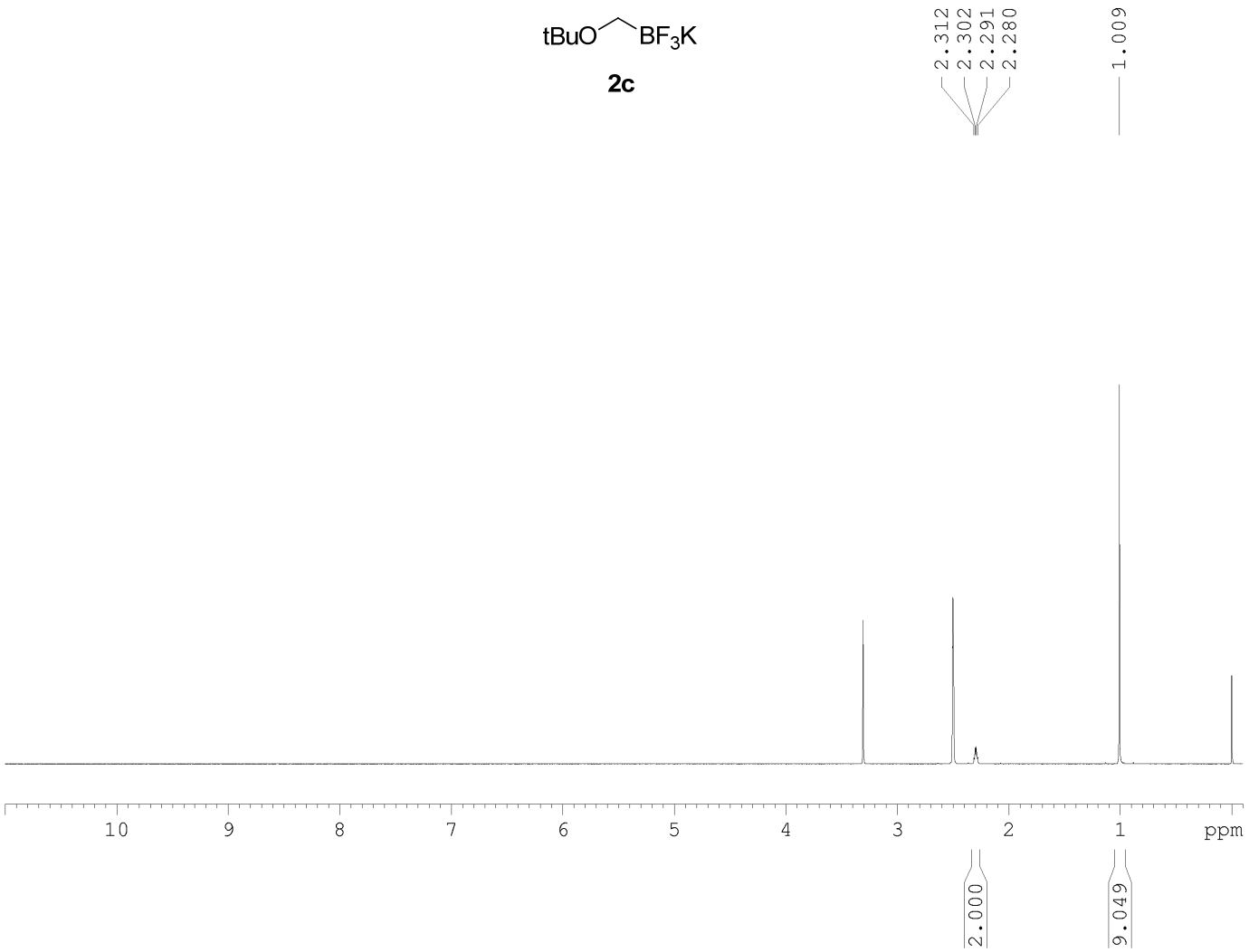
^{13}C NMR (125 MHz, DMSO-d_6) Spectrum of potassium methoxymethyltrifluoroborate **2a** (Table 2, entry 1)



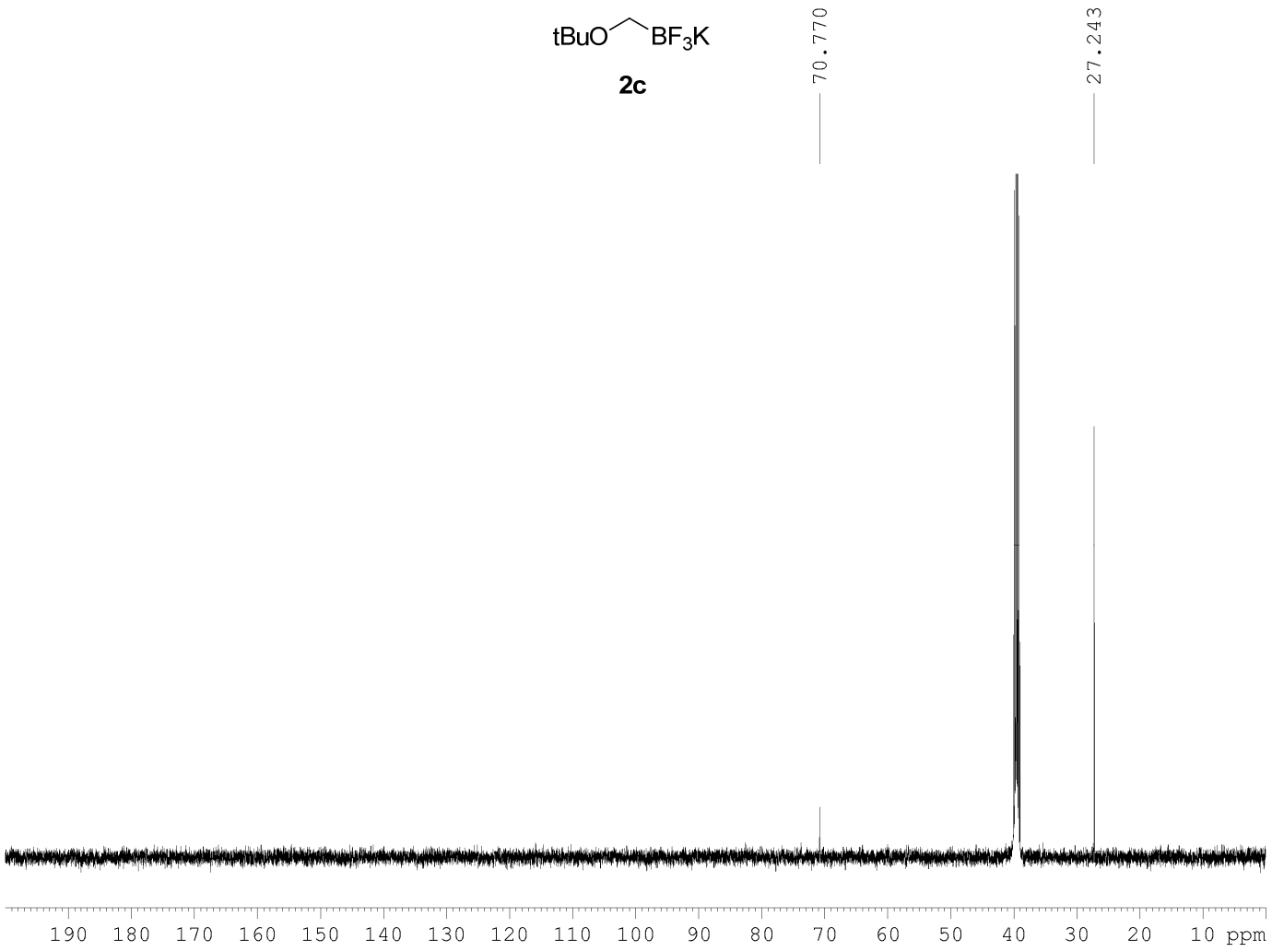
^{19}F NMR (470.8 MHz, acetone-d_6) Spectrum of potassium methoxymethyltrifluoroborate **2a** (Table 2, entry 1)



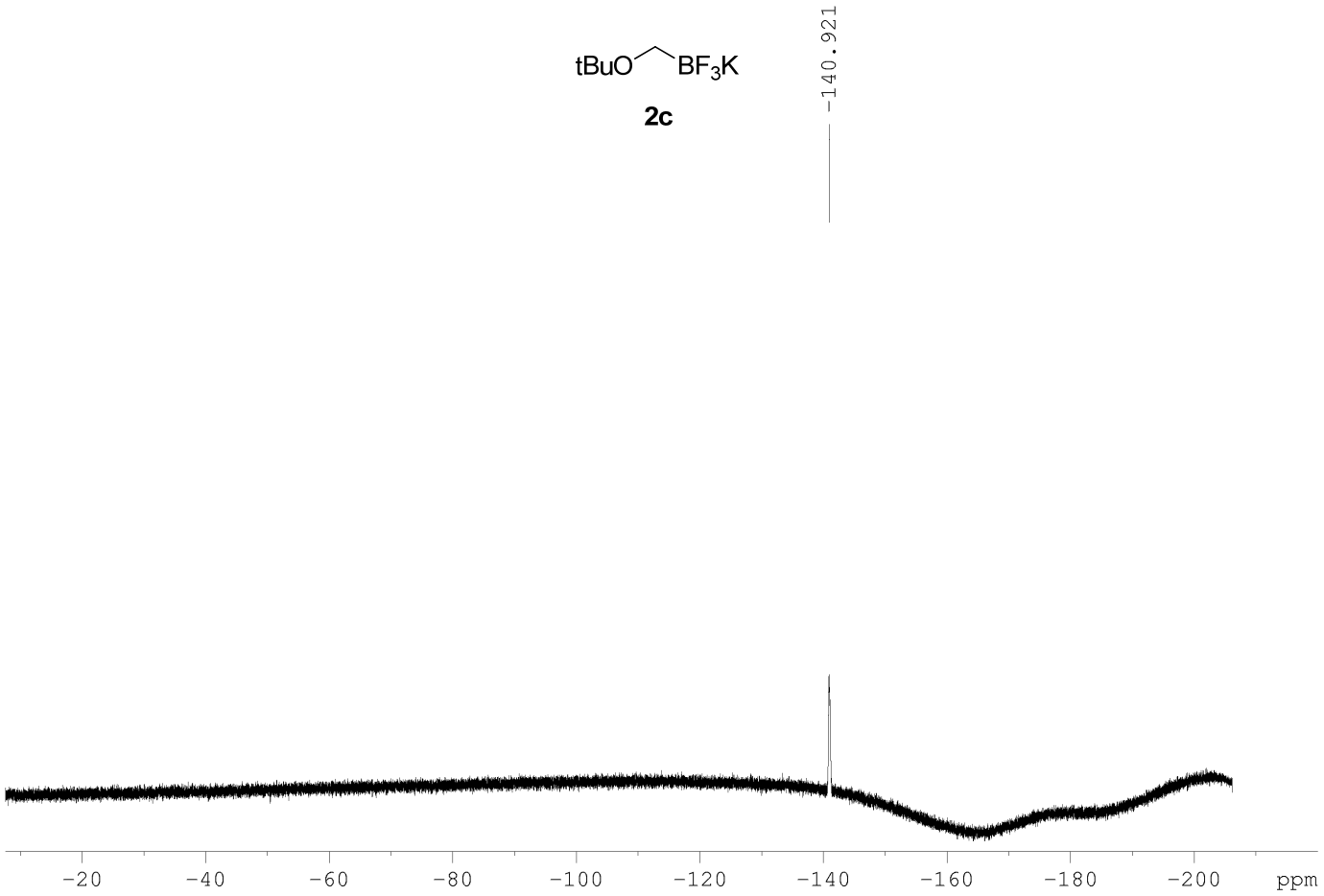
^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of potassium methoxymethyltrifluoroborate **2a** (Table 2, entry 1)



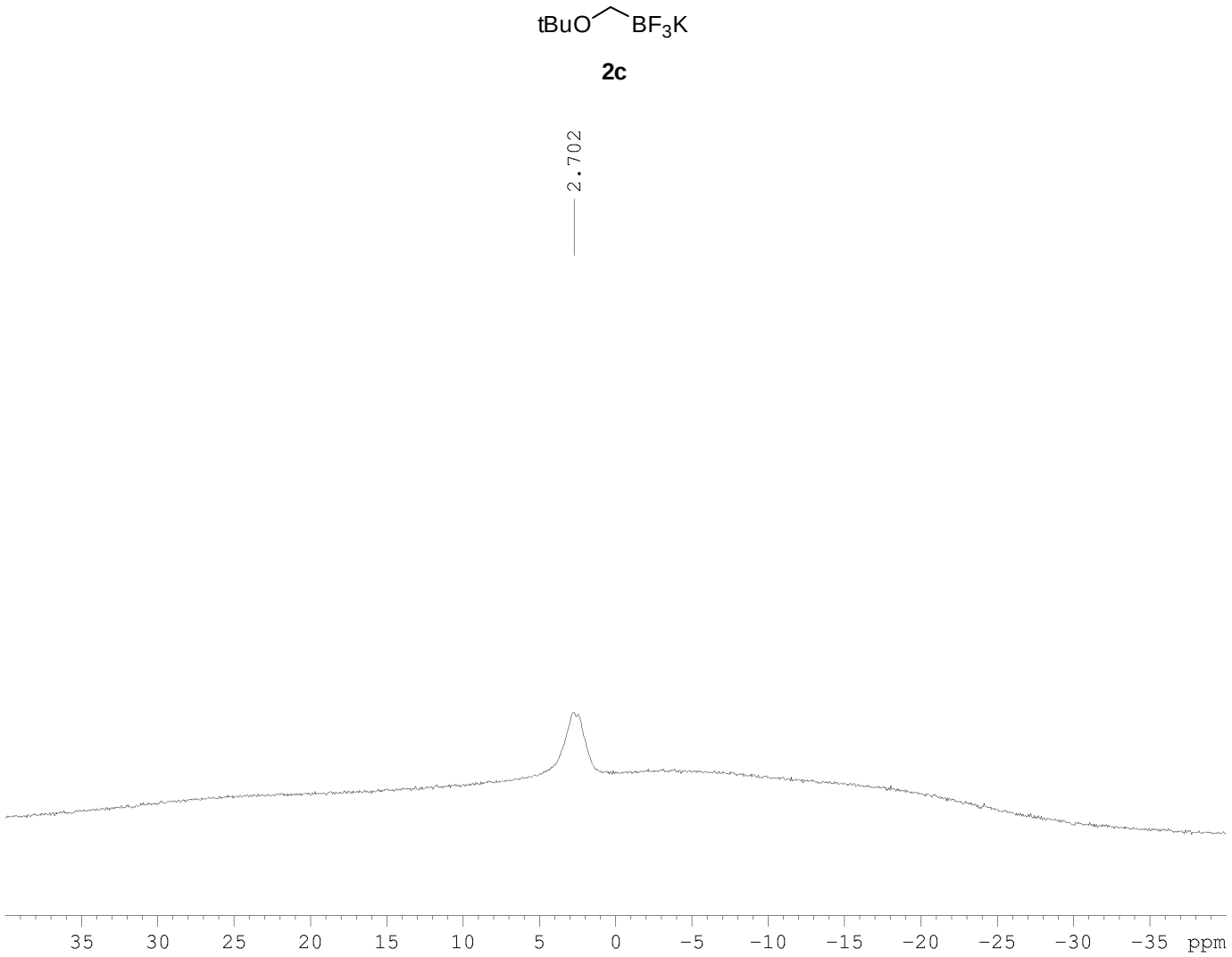
^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of potassium *tert*-butoxymethyltrifluoroborate **2c** (Table 2, entry 3)



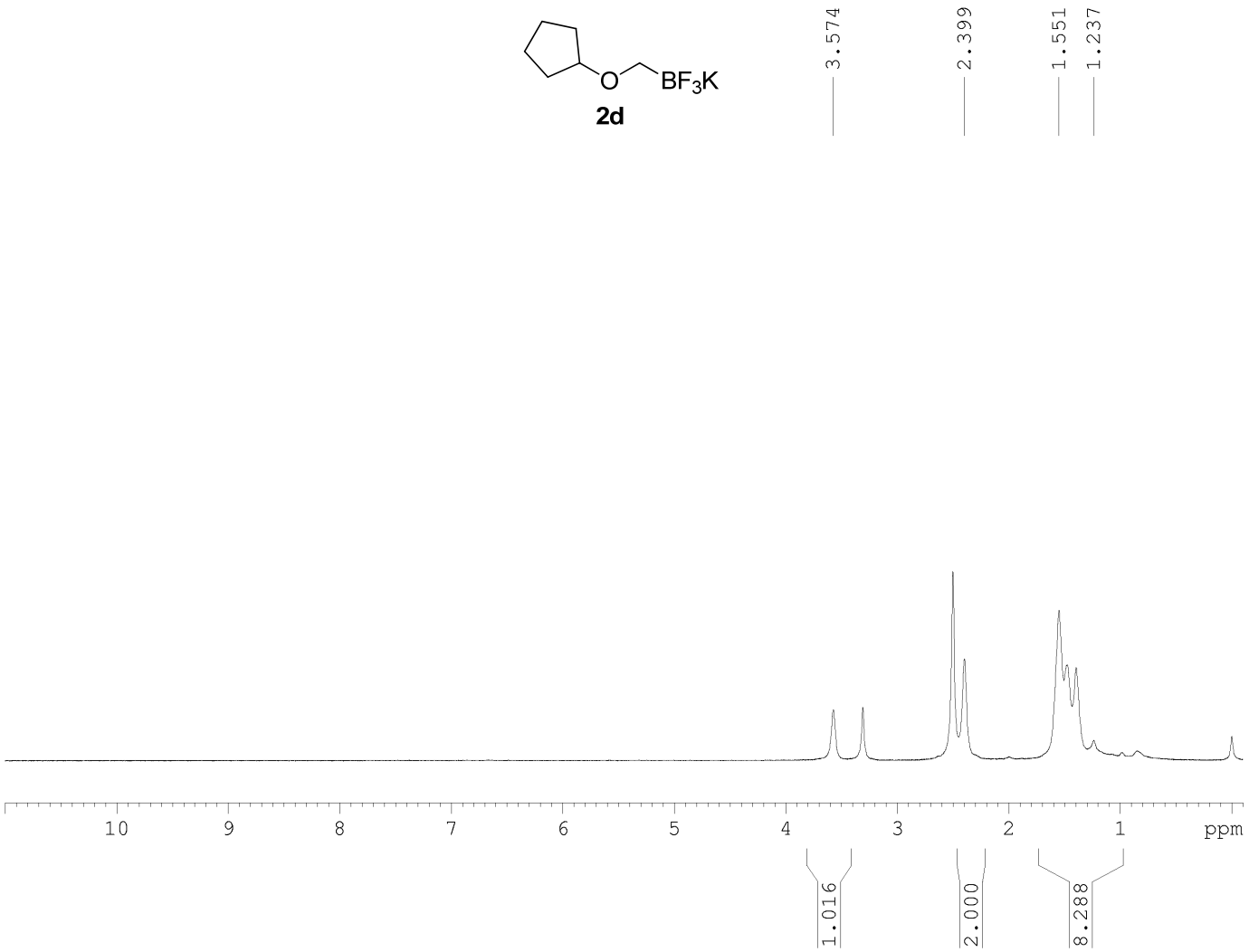
^{13}C NMR (125 MHz, DMSO-d_6) Spectrum of potassium *tert*-butoxymethyltrifluoroborate **2c** (Table 2, entry 3)



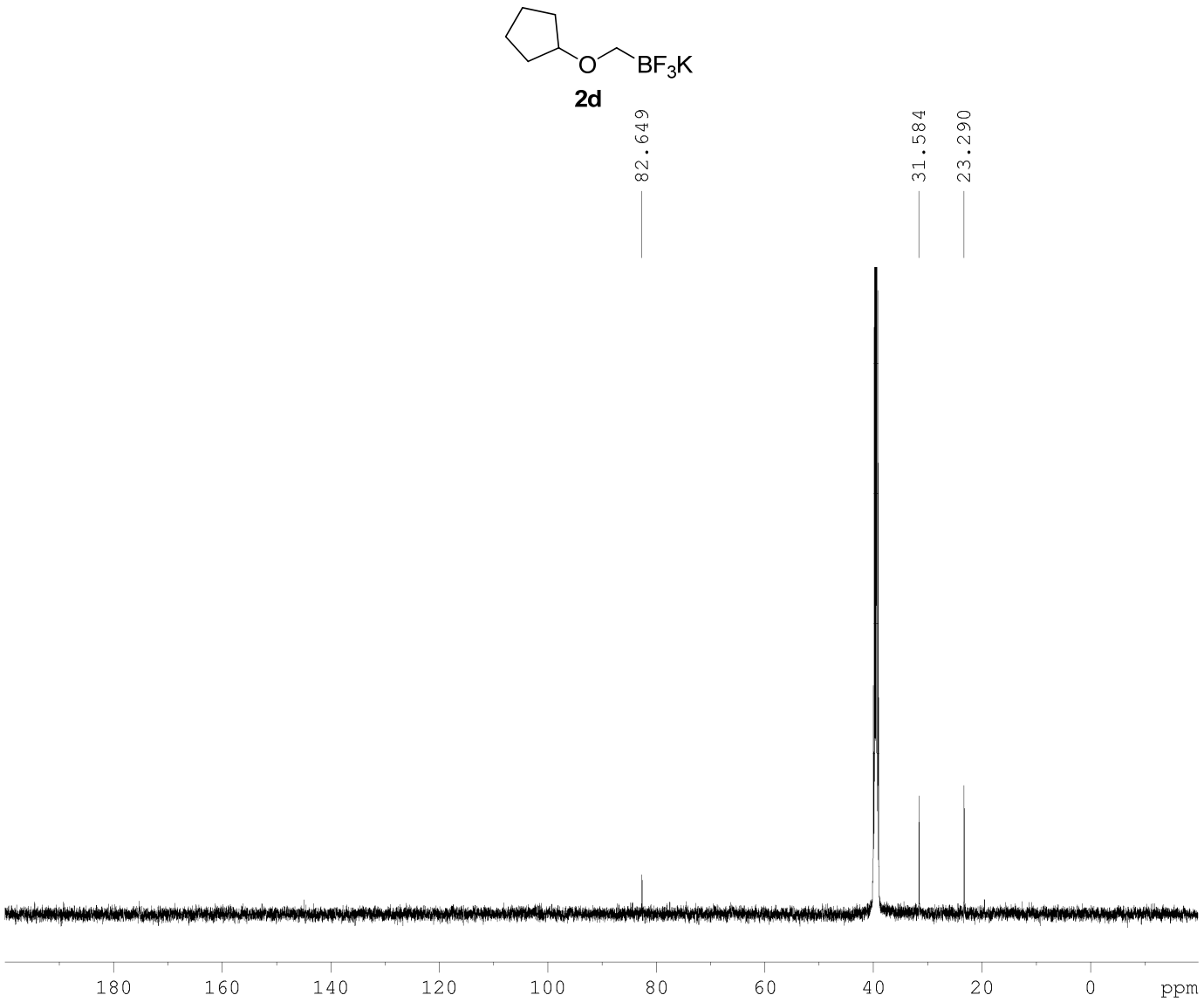
^{19}F NMR (470.8 MHz, DMSO-d_6) Spectrum of potassium *tert*-butoxymethyltrifluoroborate **2c** (Table 2, entry 3)



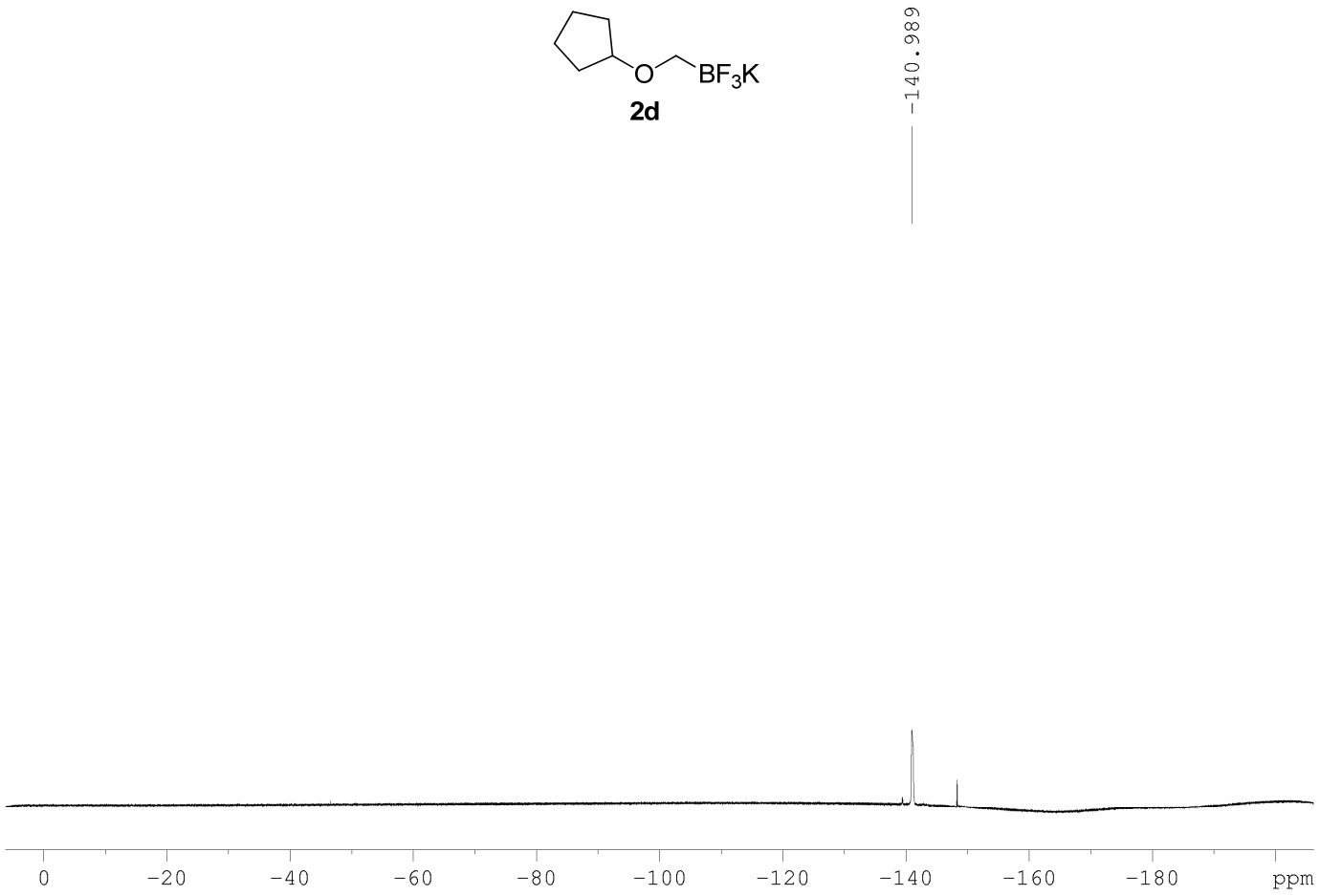
^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of potassium *tert*-butoxymethyltrifluoroborate **2c** (Table 2, entry 3)



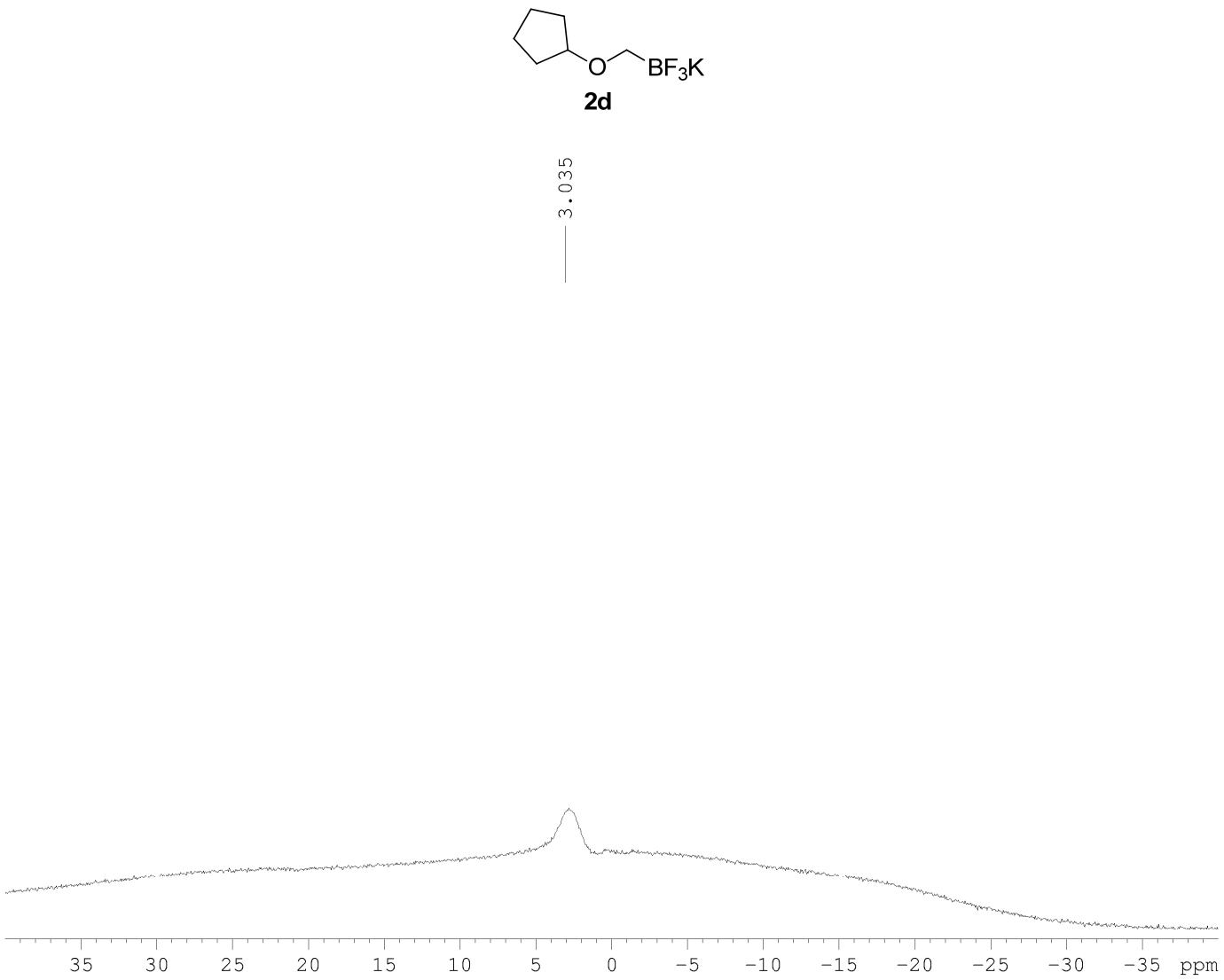
^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of potassium (cyclopentyloxymethyl)trifluoroborate **2d** (Table 2, entry 4)



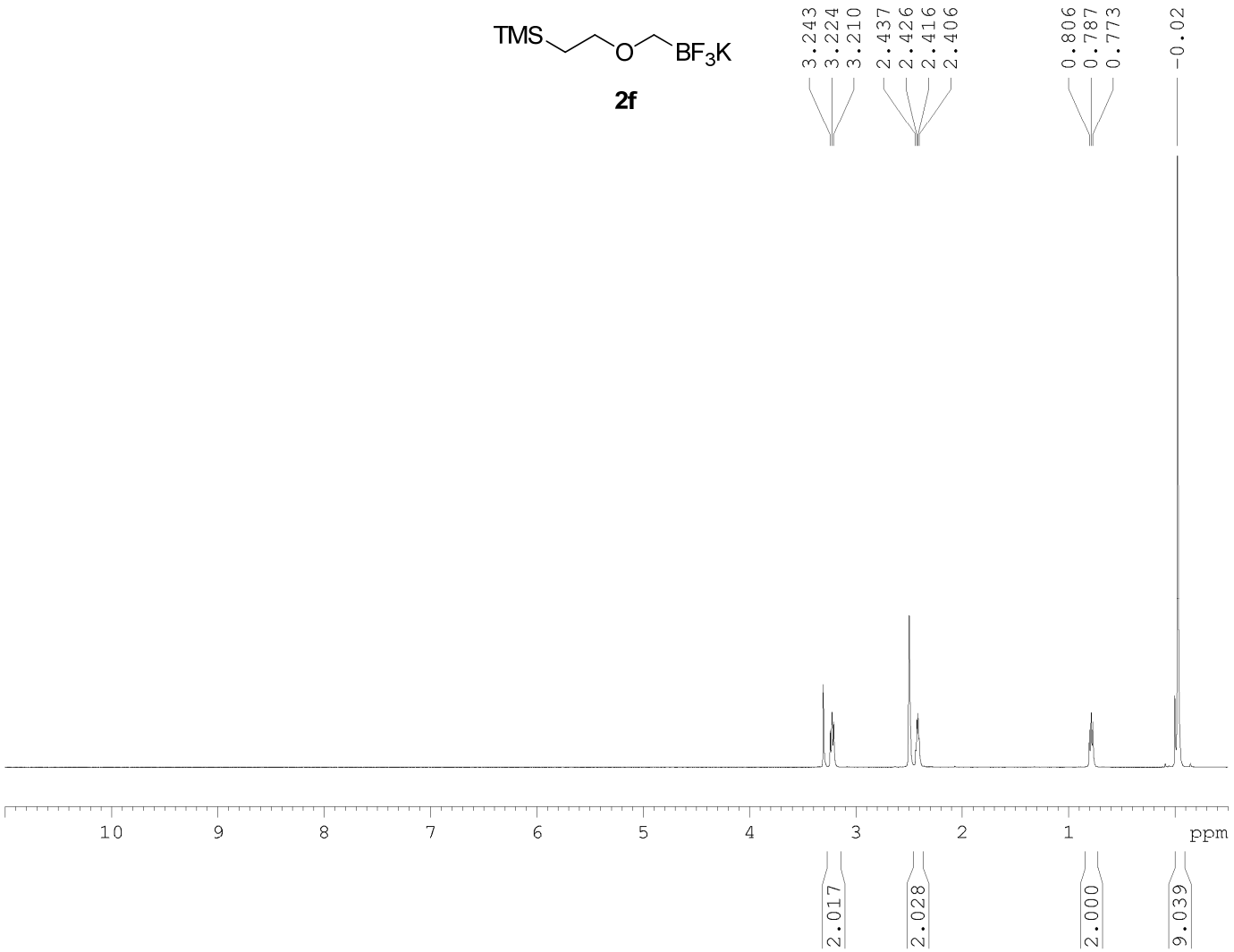
^{13}C NMR (125 MHz, DMSO-d_6) Spectrum of potassium (cyclopentyloxymethyl)trifluoroborate **2d** (Table 2, entry 4)



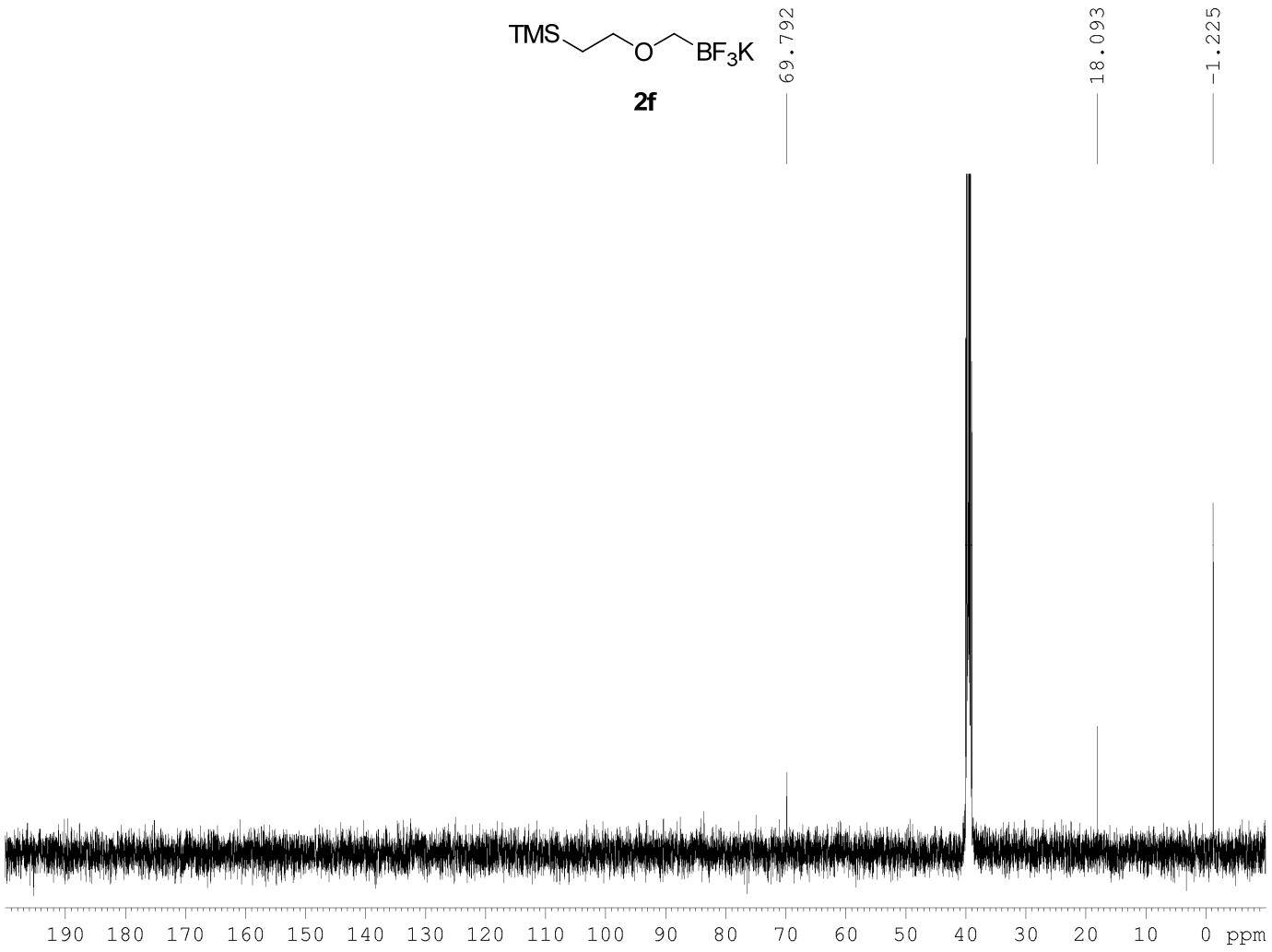
^{19}F NMR (470.8 MHz, DMSO-d_6) Spectrum of potassium (cyclopentyloxymethyl)trifluoroborate **2d** (Table 2, entry 4)



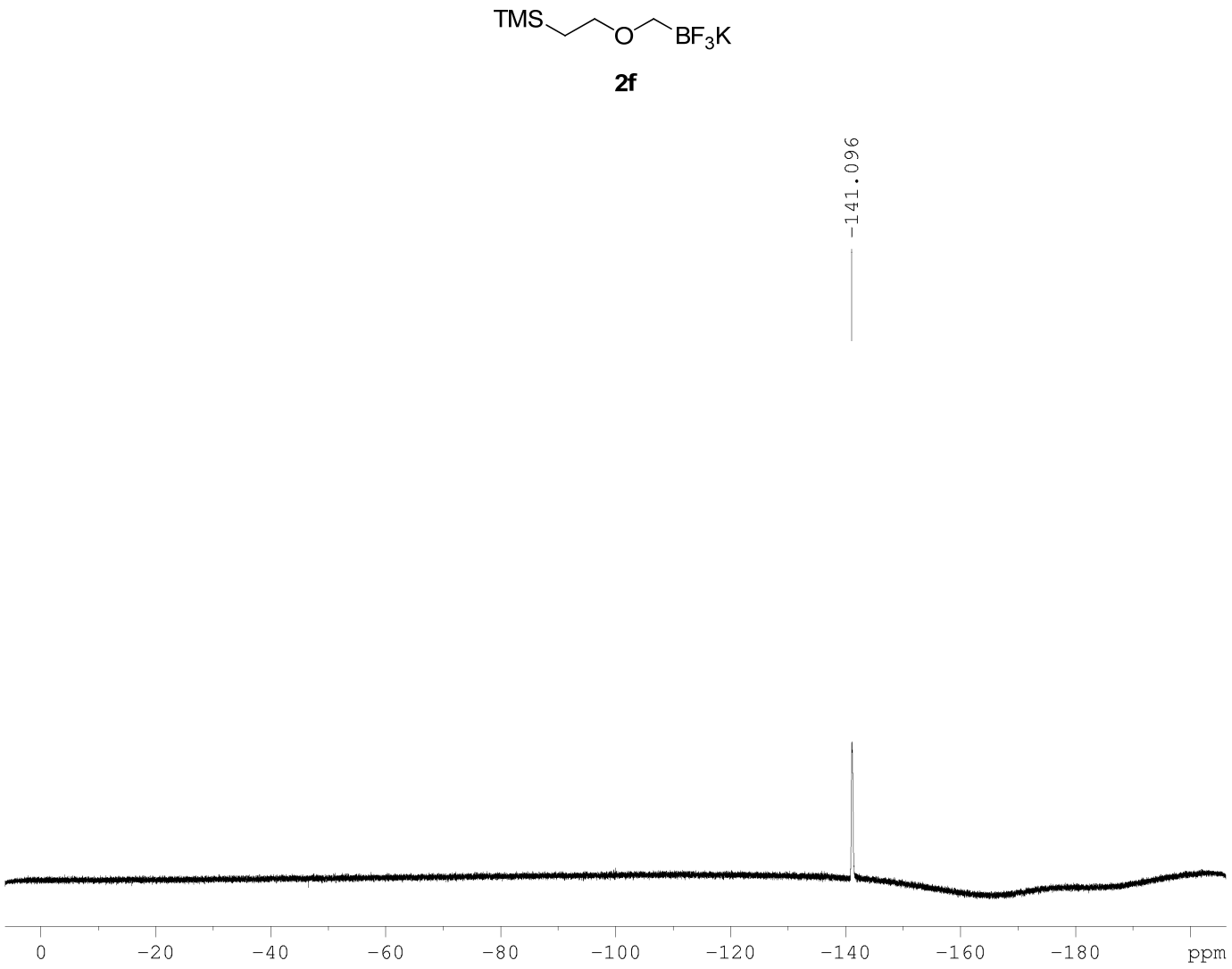
^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of potassium (cyclopentyloxymethyl)trifluoroborate **2d** (Table 2, entry 4)



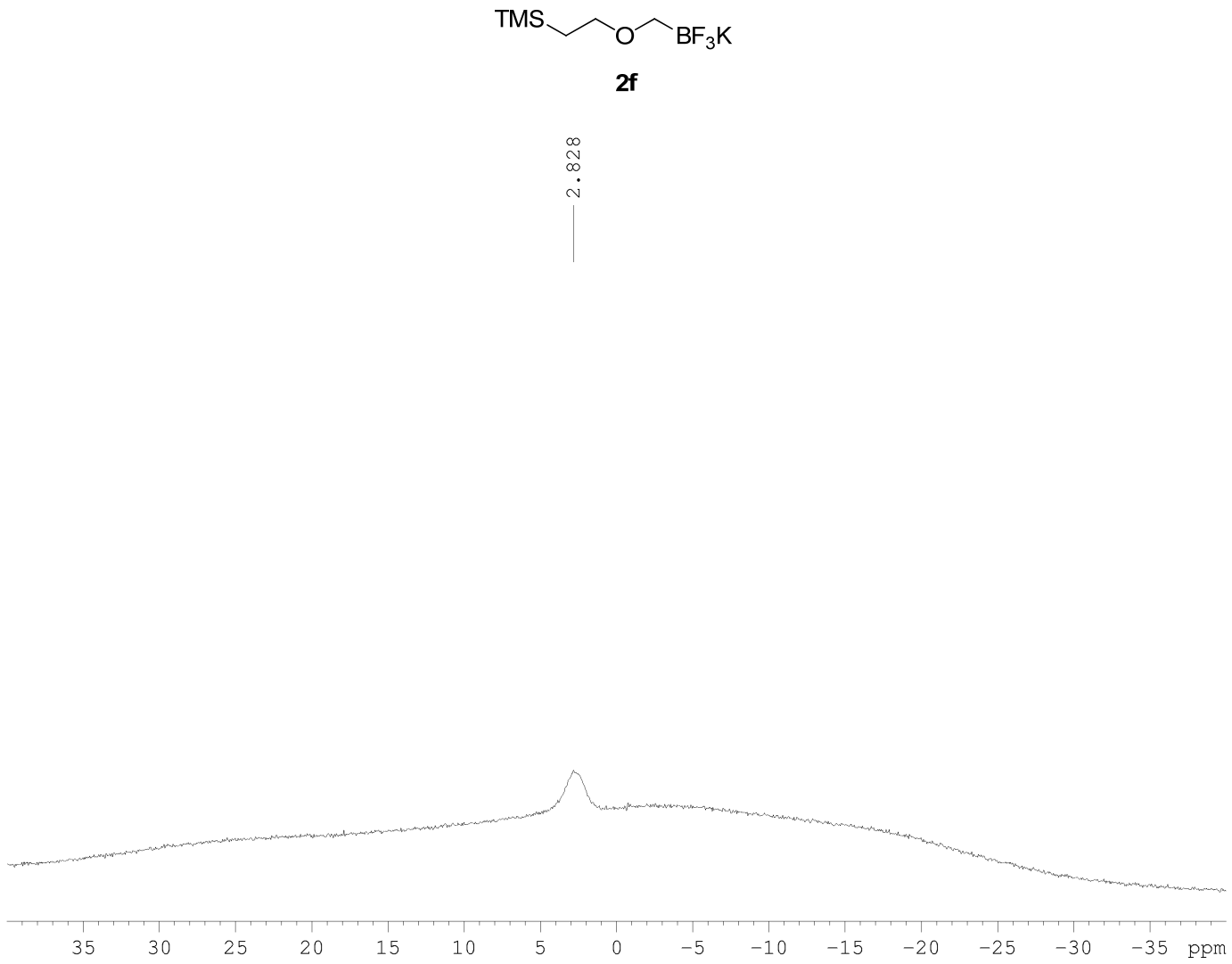
^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of potassium (2-(trimethylsilyl)ethoxy)methyltrifluoroborate **2f** (Table 2, entry 6)



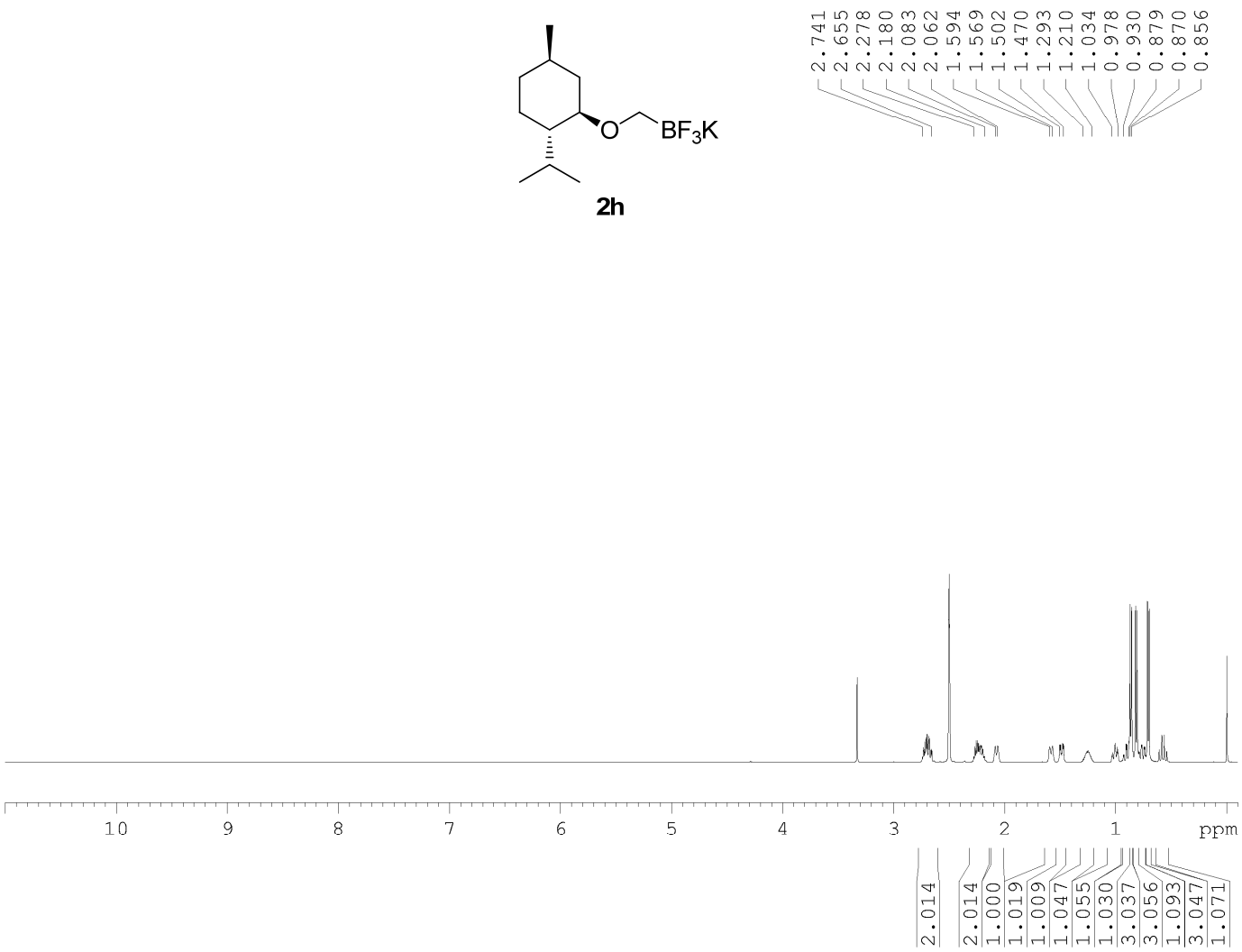
^{13}C NMR (125 MHz, DMSO-d_6) Spectrum of potassium (2-(trimethylsilyl)ethoxy)methyltrifluoroborate **2f** (Table 2, entry 6)



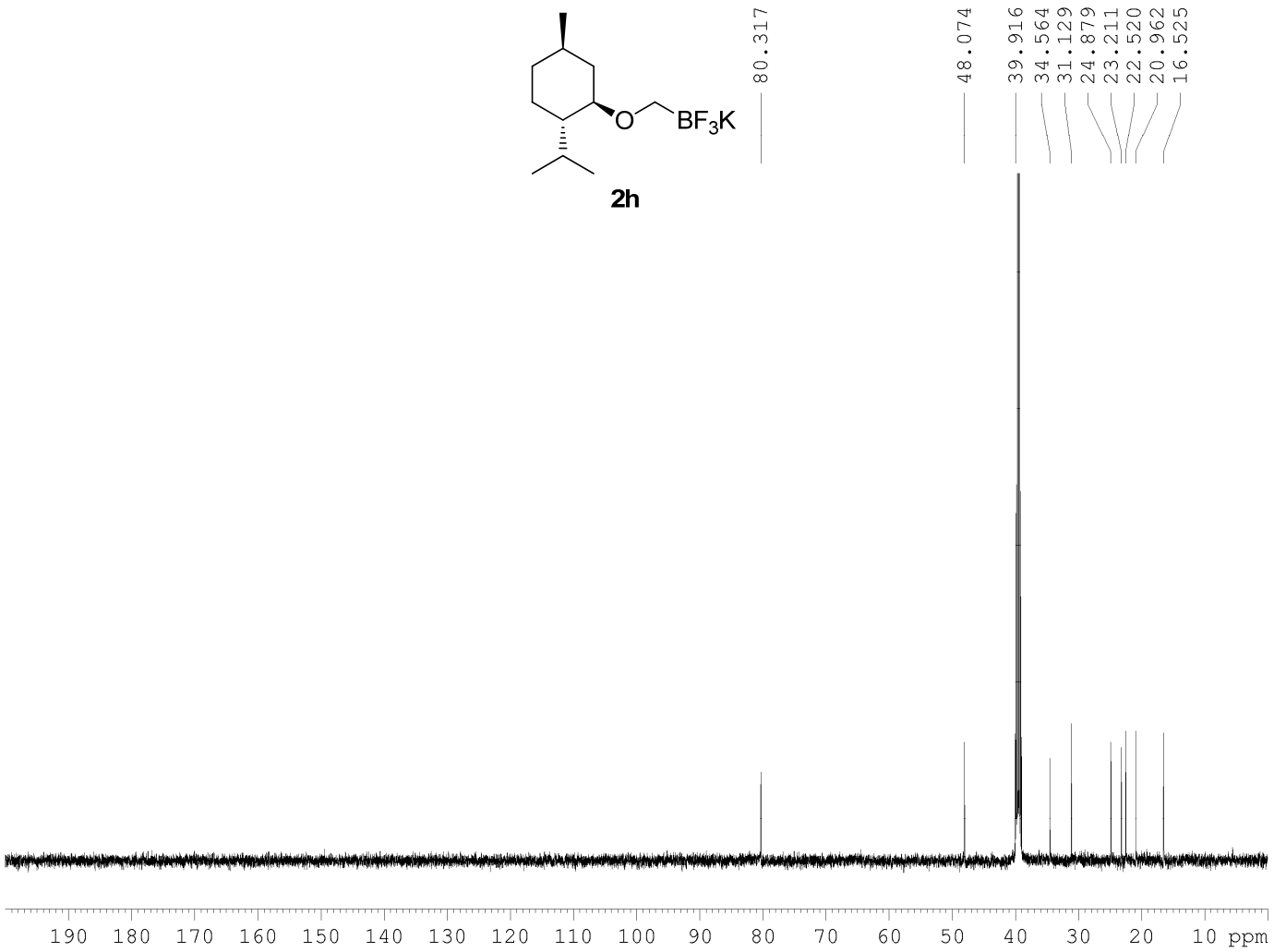
^{19}F NMR (470.8 MHz, DMSO-d_6) Spectrum of potassium (2-(trimethylsilyl)ethoxy)methyltrifluoroborate **2f** (Table 2, entry 6)



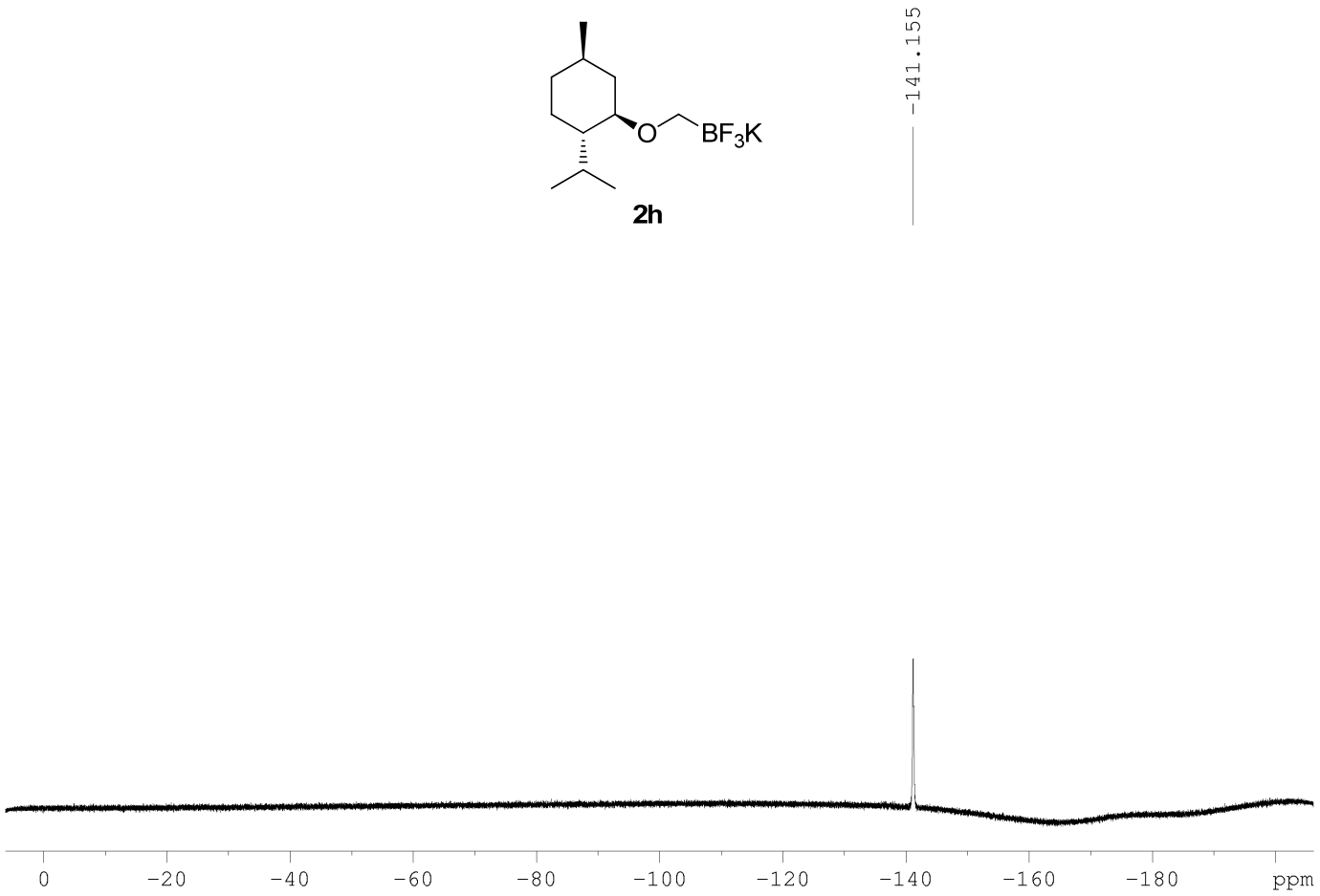
^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of potassium (2-(trimethylsilyl)ethoxy)methyltrifluoroborate **2f** (Table 2, entry 6)



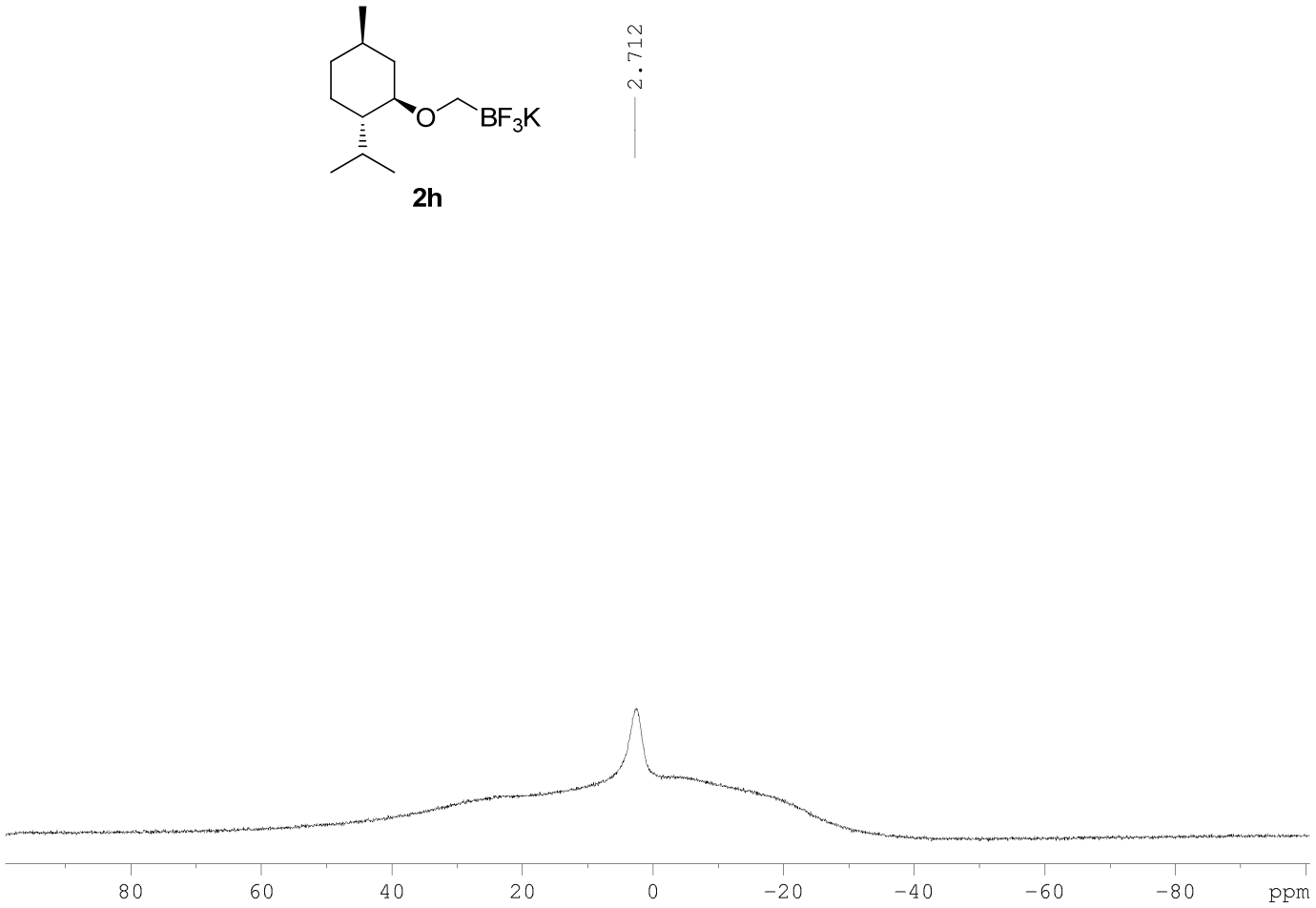
^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of potassium (((1*R*,2*S*,5R)-2-isopropyl-5-methylcyclohexyl)oxy)methyltrifluoroborate **2h** (Table 2, entry 8)



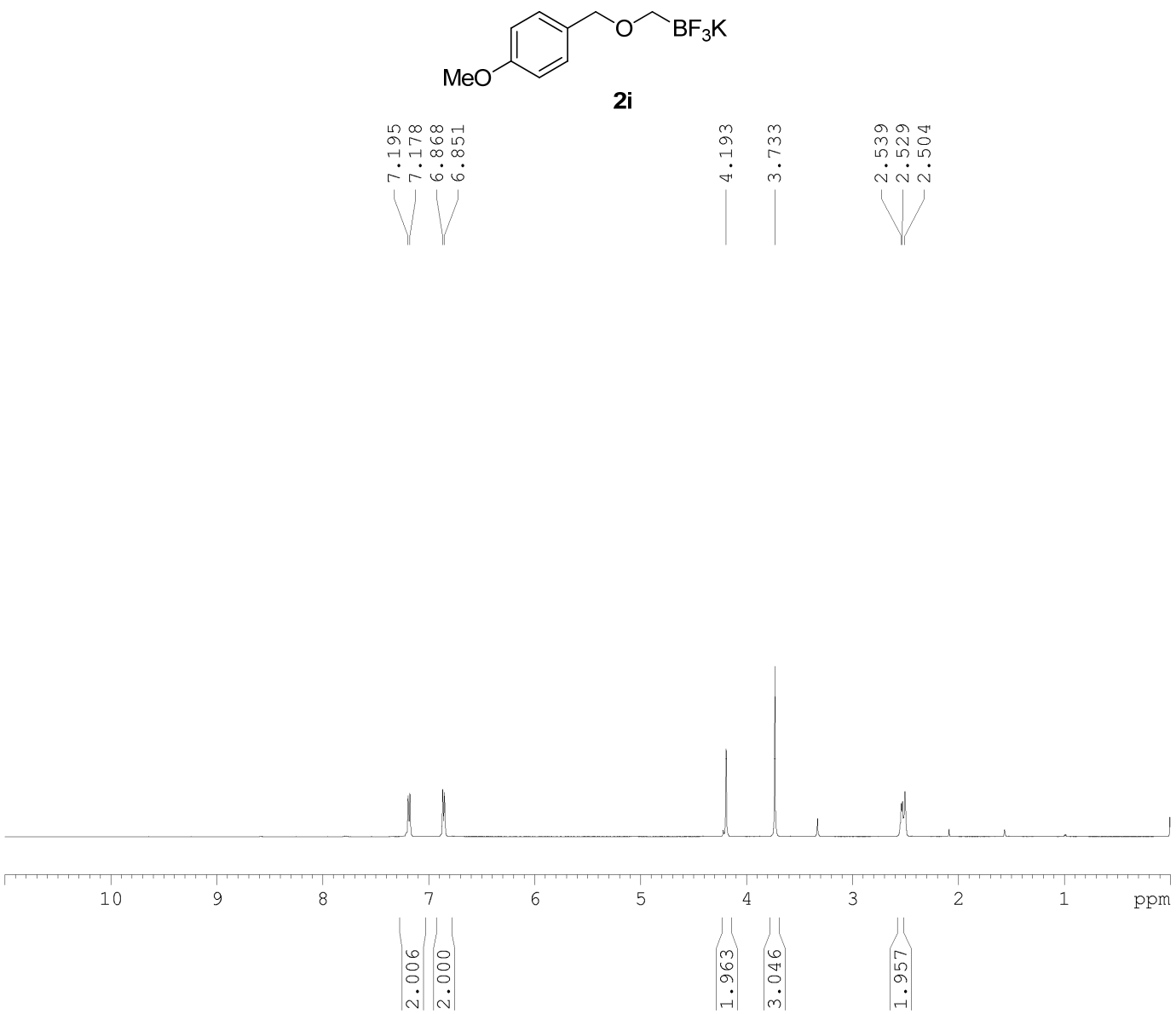
^{13}C NMR (125 MHz, DMSO-d_6) Spectrum of potassium (((1*R*,2*S*,5R)-2-isopropyl-5-methylcyclohexyl)oxy)methyltrifluoroborate **2h** (Table 2, entry 8)



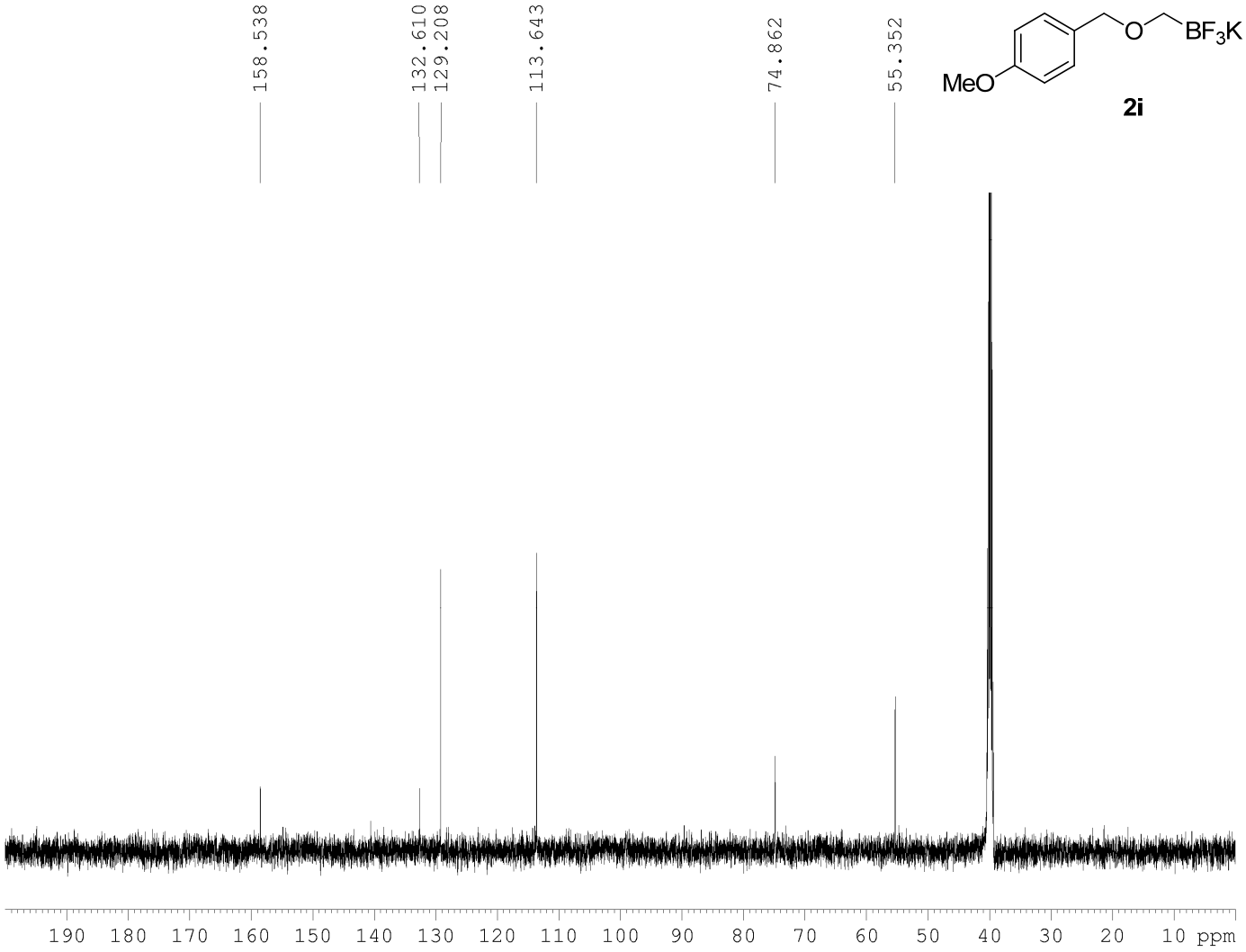
^{19}F NMR (470.8 MHz, DMSO-d_6) Spectrum of potassium (((1*R*,2*S*,5*S*)-2-isopropyl-5-methylcyclohexyl)oxy)methyltrifluoroborate **2h** (Table 2, entry 8)



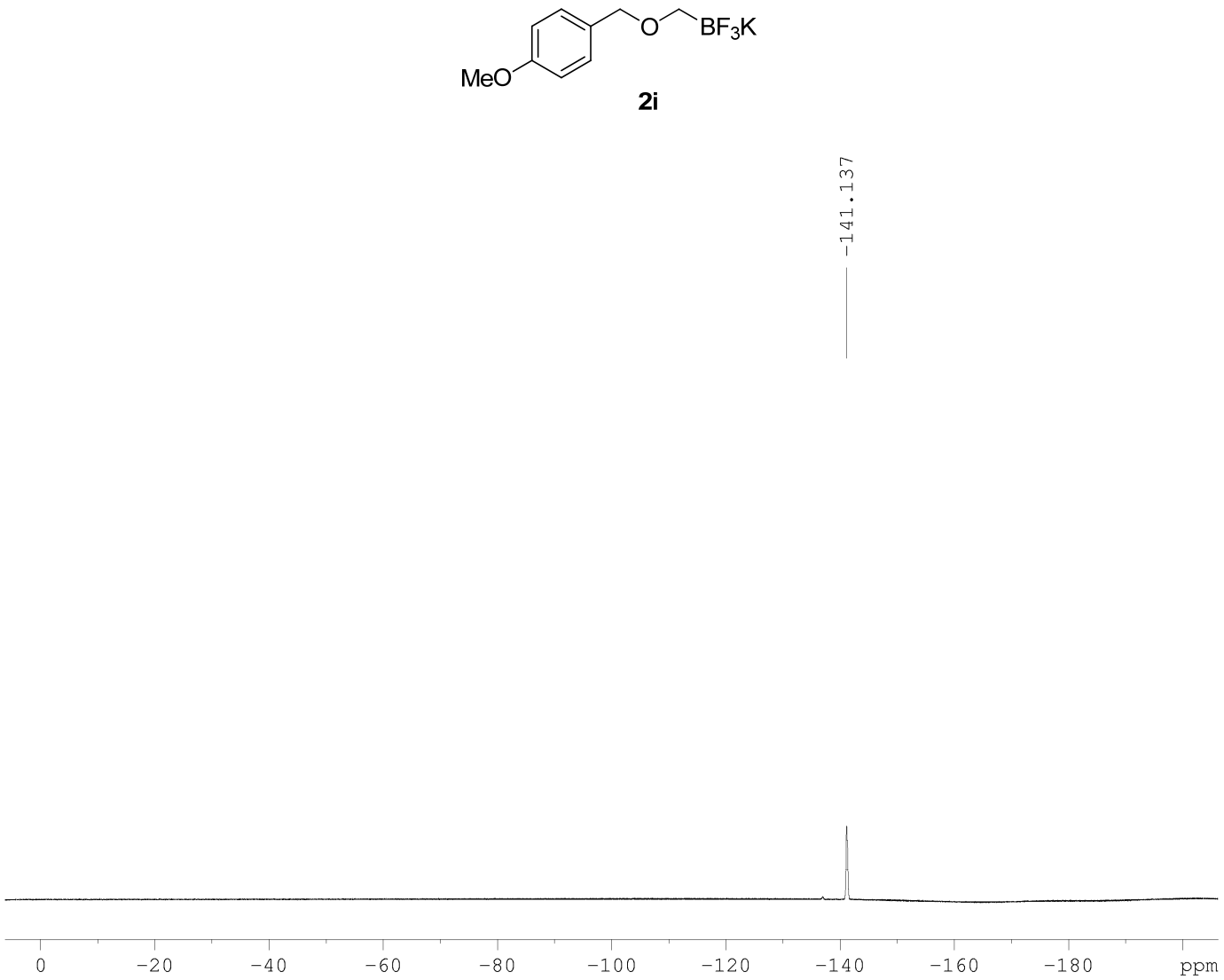
^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of potassium (((1*R*,2*S*,5*S*)-2-isopropyl-5-methylcyclohexyl)oxy)methyltrifluoroborate **2h** (Table 2, entry 8)



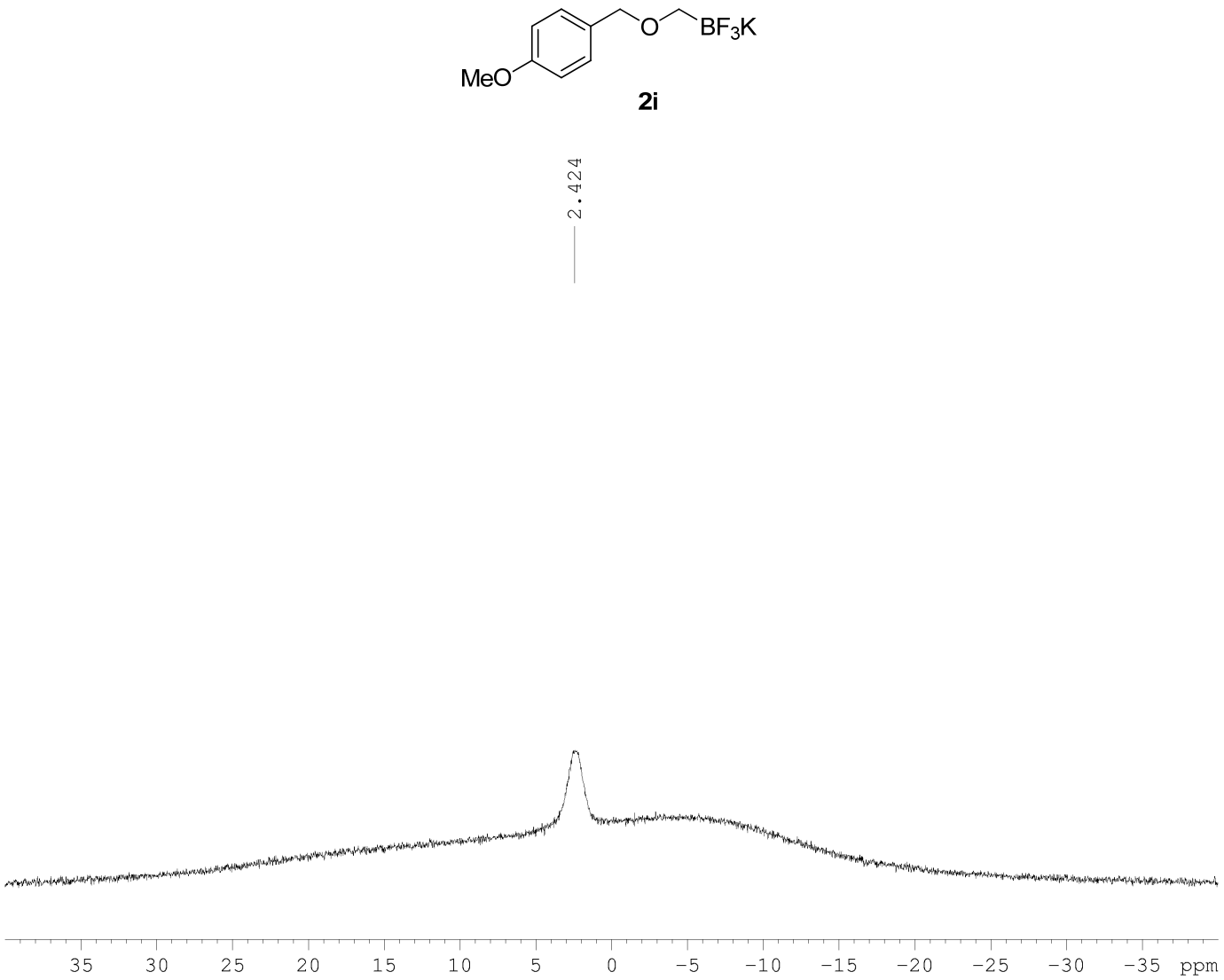
^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of potassium (4-methoxybenzyloxy)methyltrifluoroborate **2i** (Table 2, entry 9)



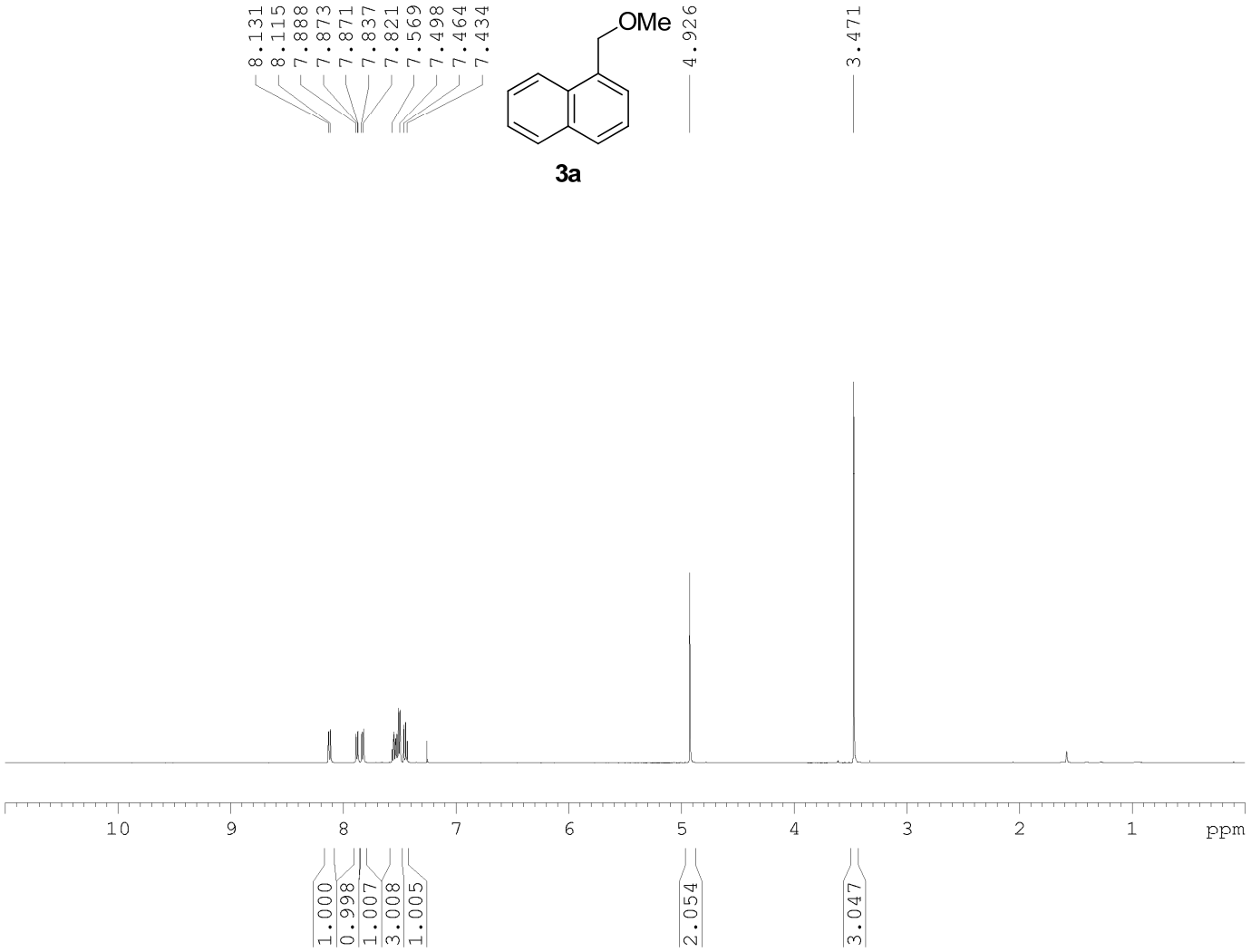
^{13}C NMR (125 MHz, DMSO-d_6) Spectrum of potassium (4-methoxybenzyloxy)methyltrifluoroborate **2i** (Table 2, entry 9)



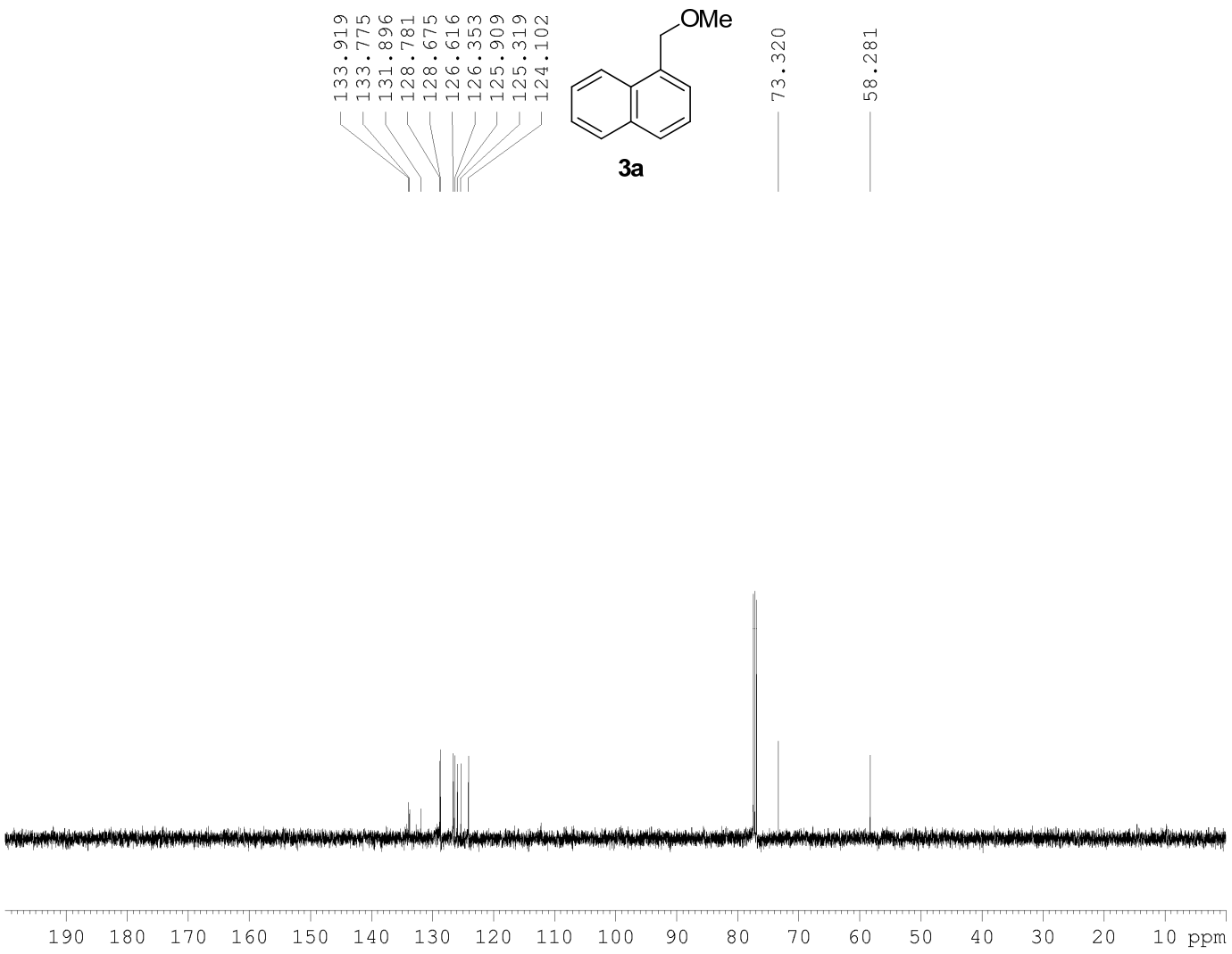
^{19}F NMR (470.8 MHz, DMSO-d_6) Spectrum of potassium (4-methoxybenzyloxy)methyltrifluoroborate **2i** (Table 2, entry 9)



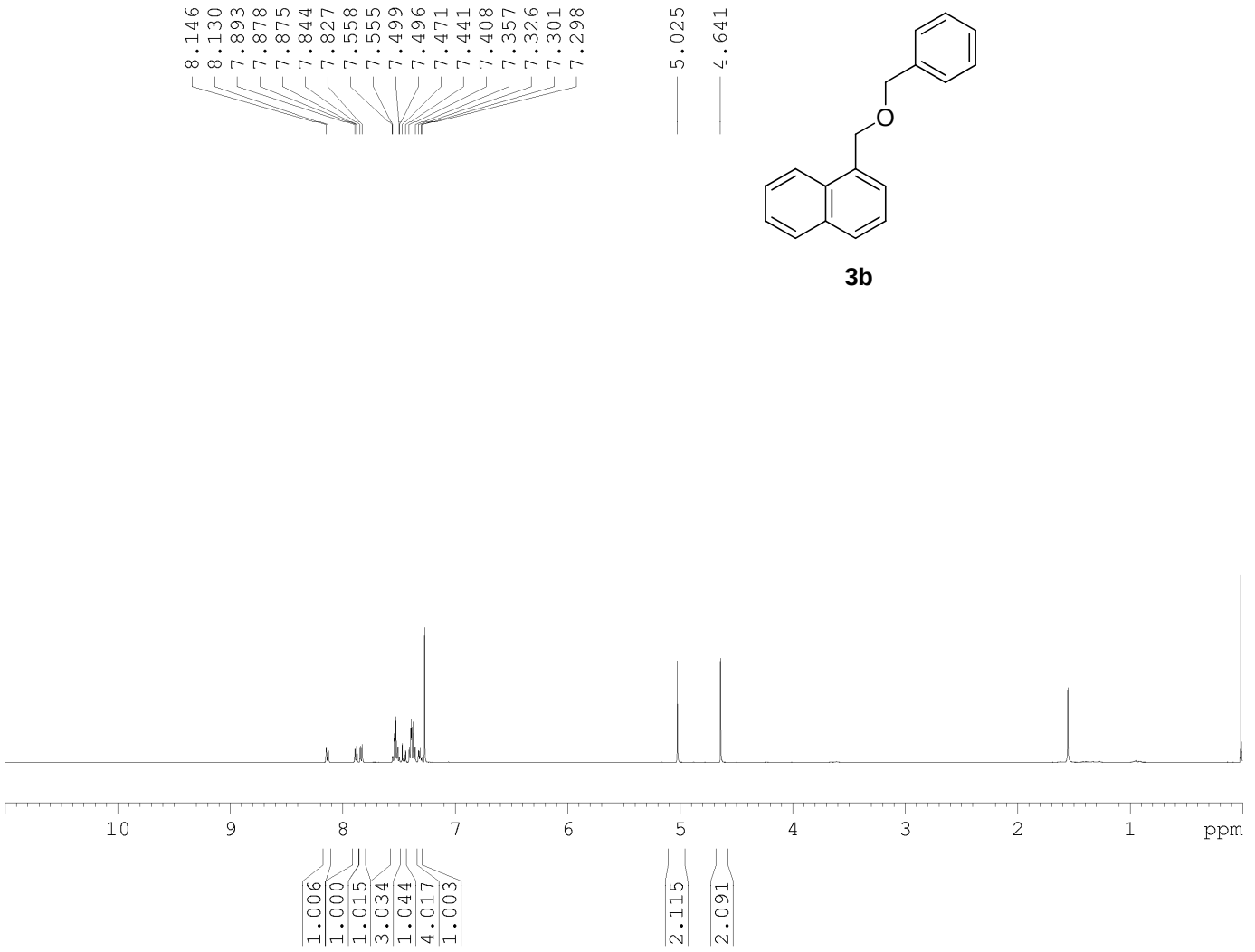
^{11}B NMR (128.4 MHz, DMSO-d_6) Spectrum of potassium (4-methoxybenzyloxy)methyltrifluoroborate **2i** (Table 2, entry 9)



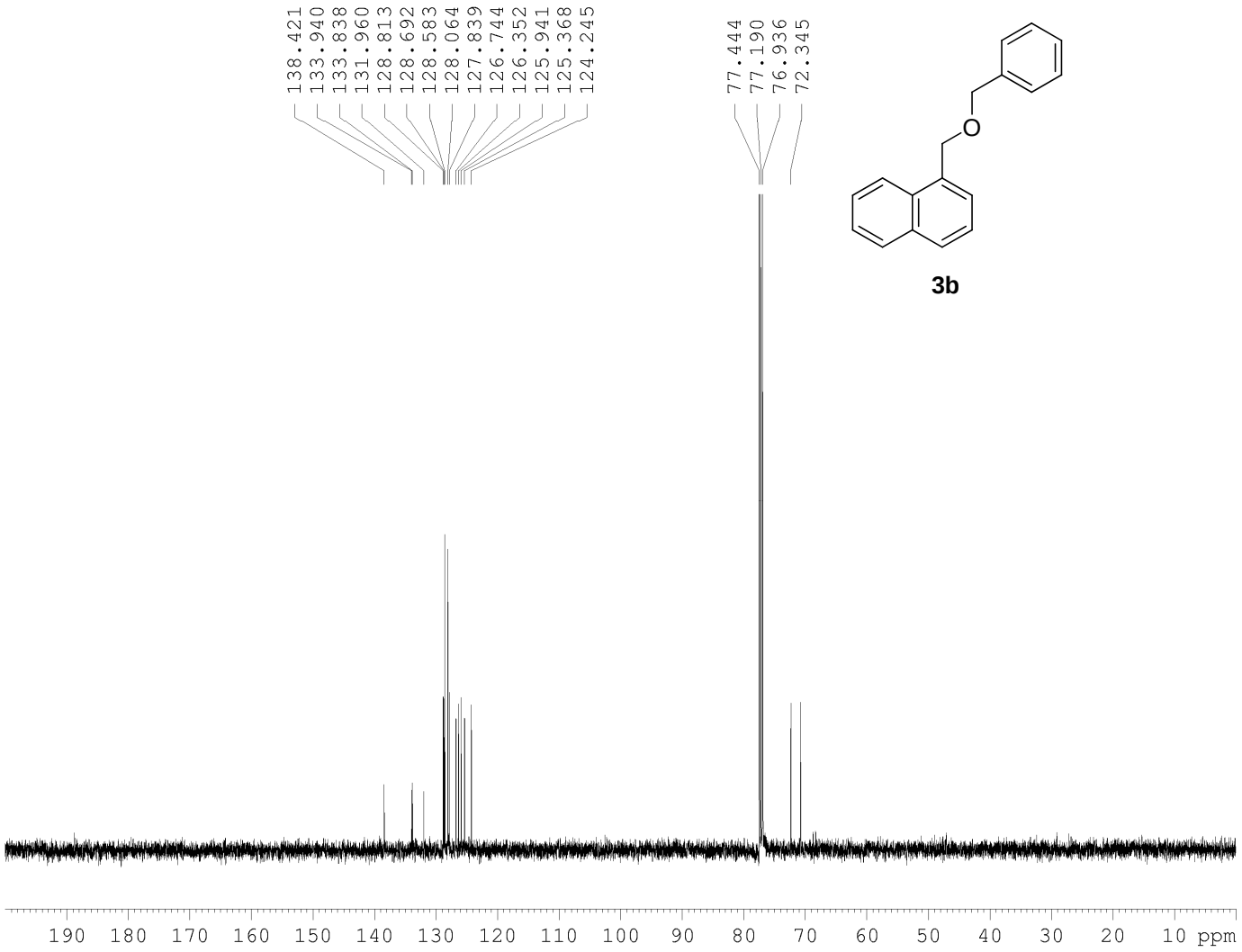
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-(methoxymethyl)naphthalene **3a** (Table 2, entry 1)



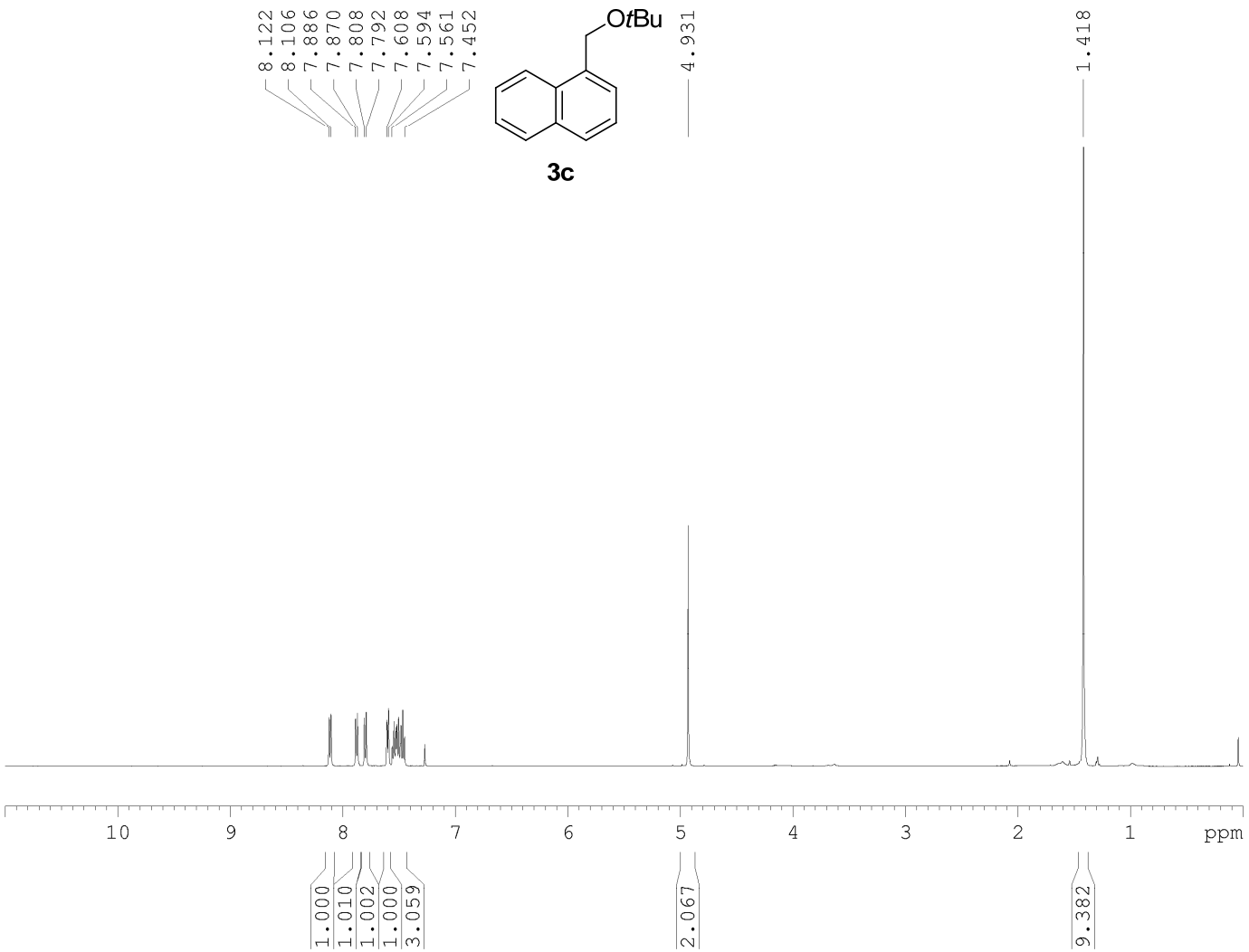
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 1-(methoxymethyl)naphthalene **3a** (Table 2, entry 1)



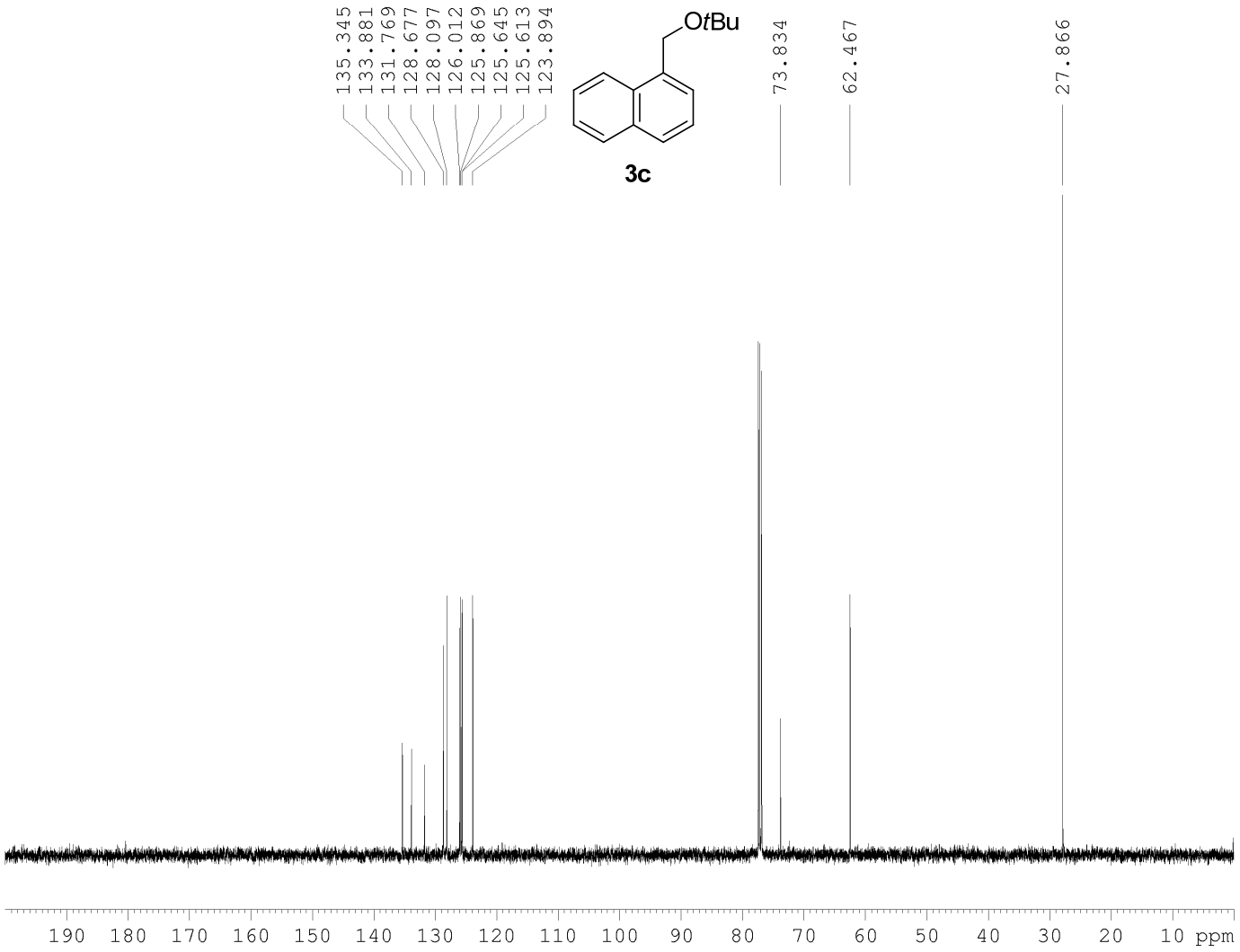
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of (1-(benzyloxymethyl)naphthalene **3b** (Table 2, entry 2)



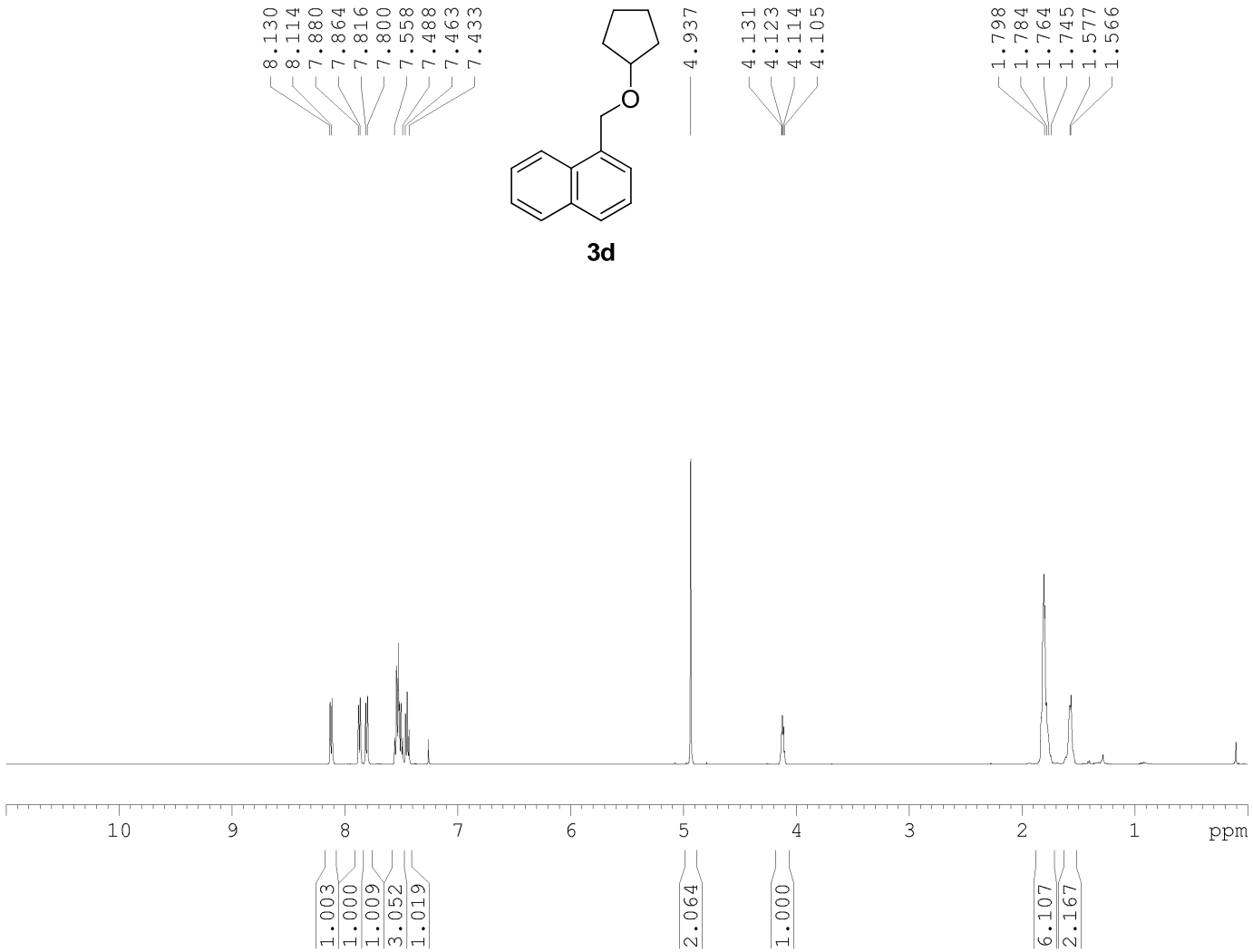
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of (1-(benzyloxymethyl)naphthalene **3b** (Table 2, entry 2)



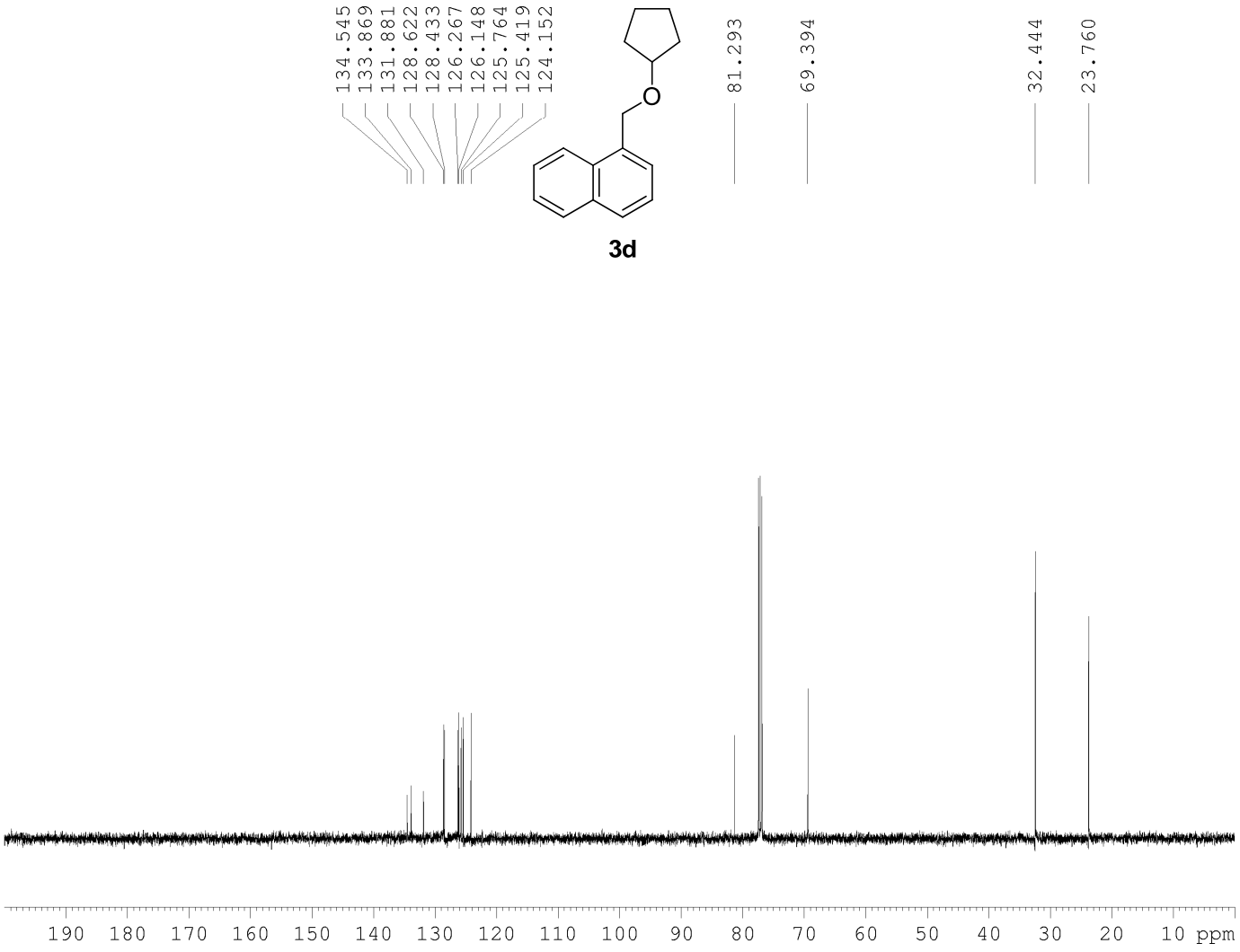
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-(*tert*-butoxymethyl)naphthalene **3c** (Table 2, entry 3)



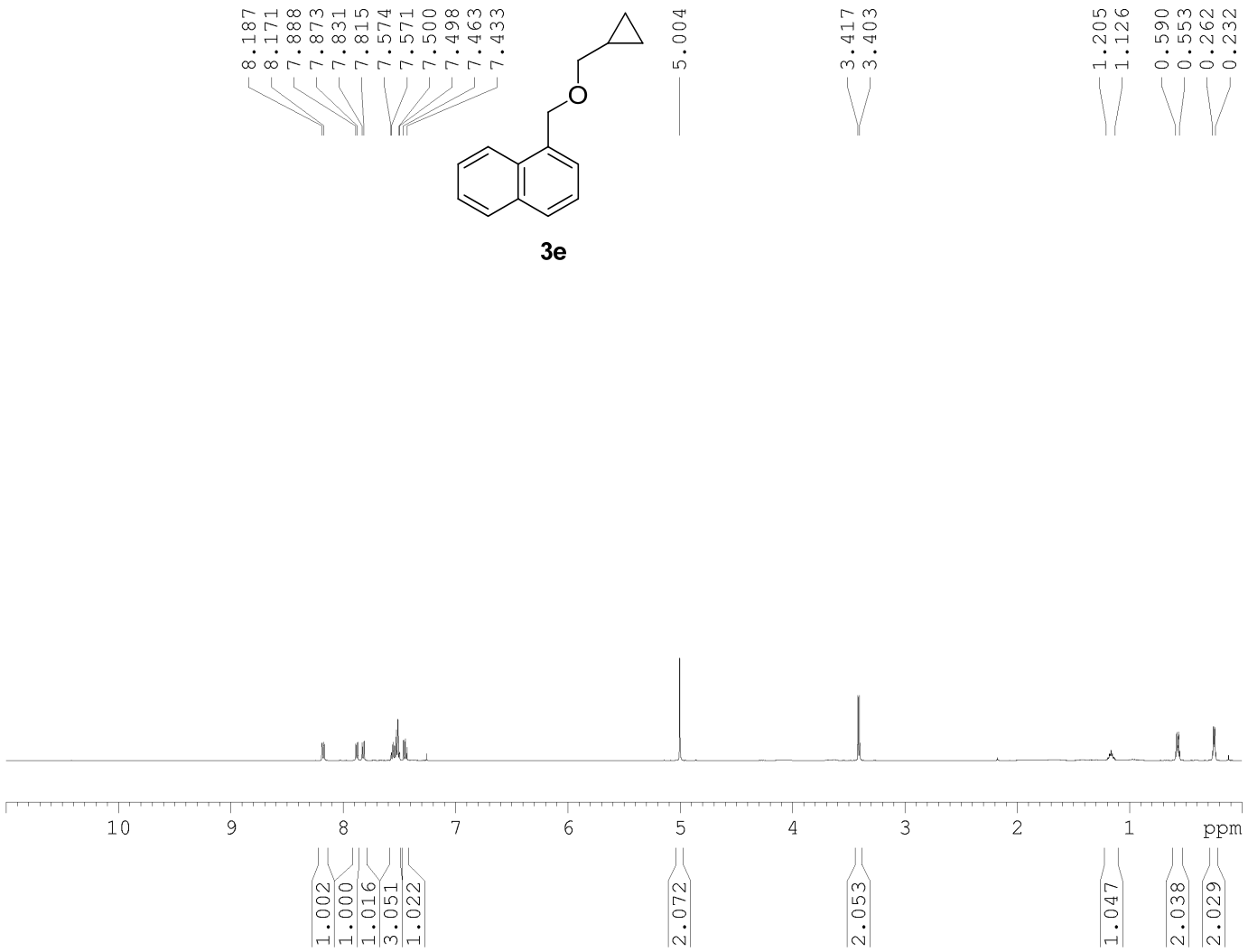
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 1-(*tert*-butoxymethyl)naphthalene **3c** (Table 2, entry 3)



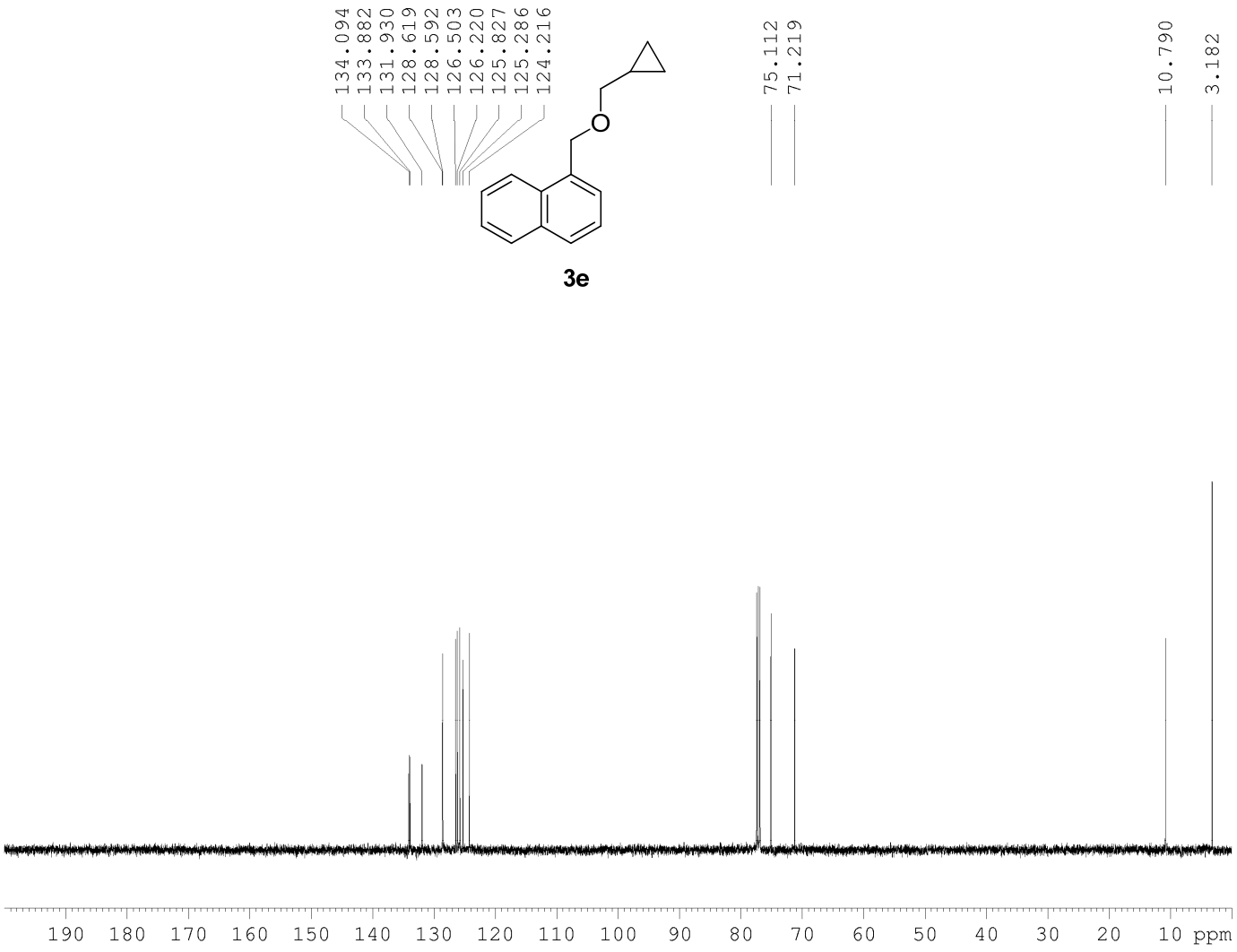
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-((cyclopentyloxy)methyl)naphthalene **3d** (Table 2, entry 4)



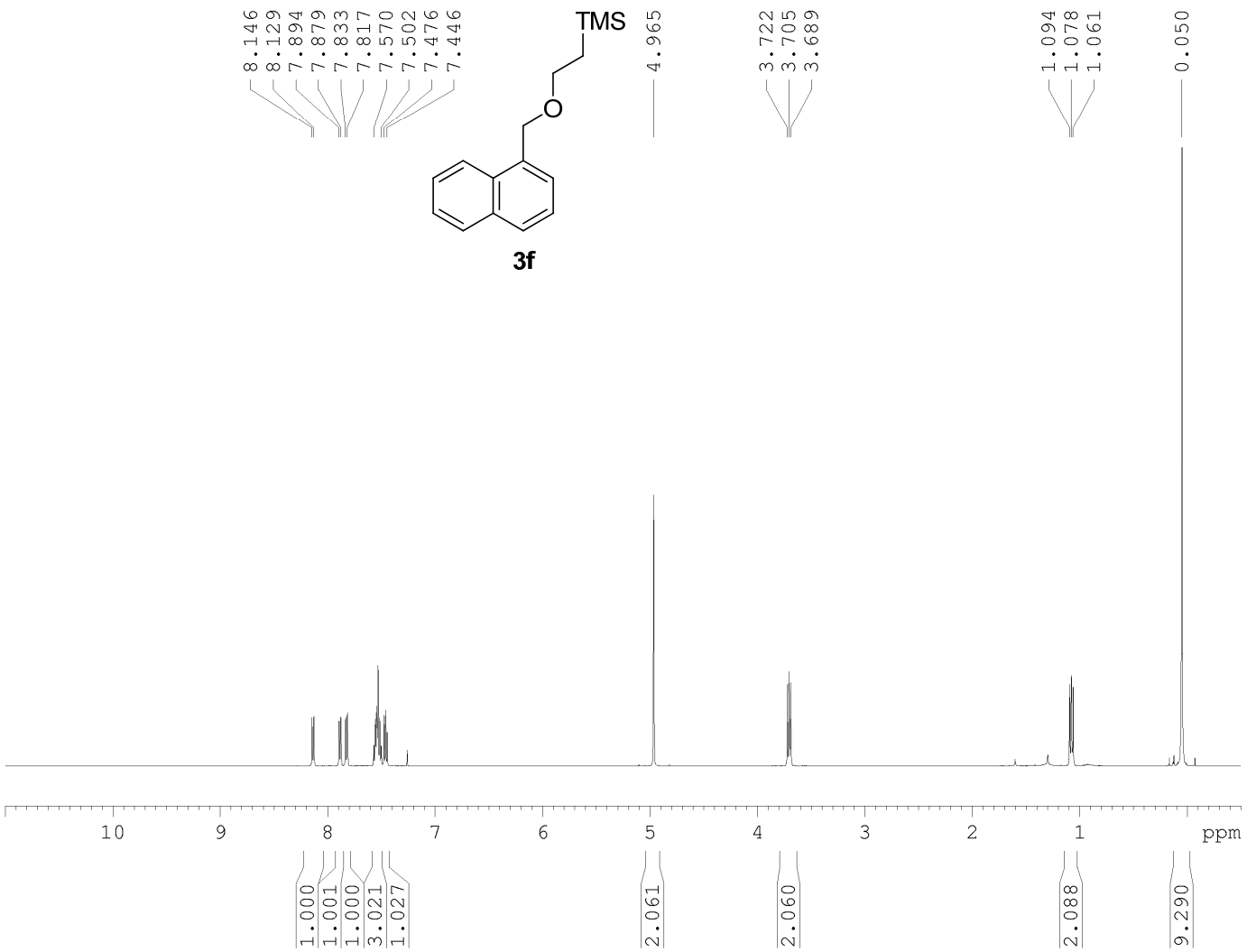
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 1-((cyclopentyloxy)methyl)naphthalene **3d** (Table 2, entry 4)



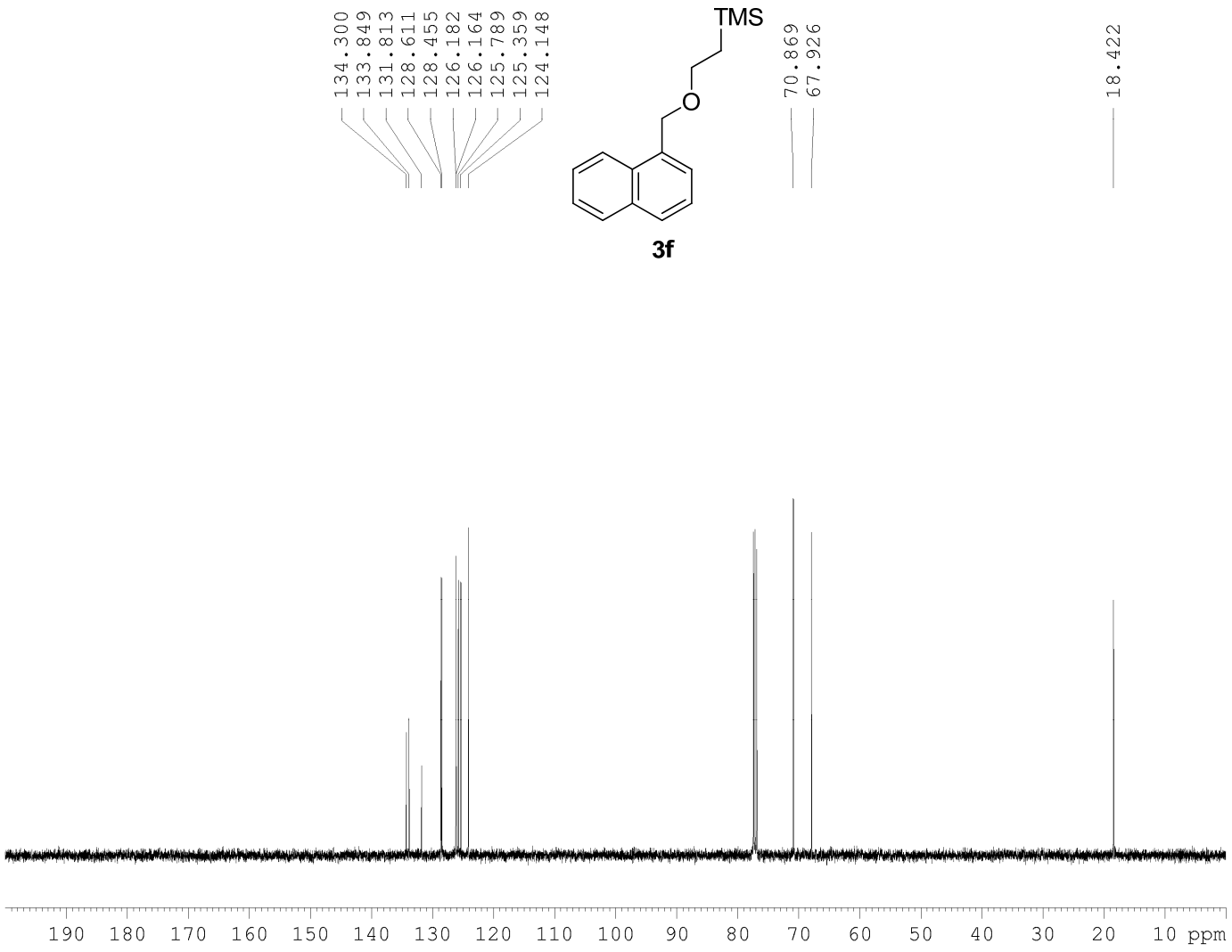
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-((cyclopropylmethoxy)methyl)naphthalene **3e** (Table 2, entry 5)



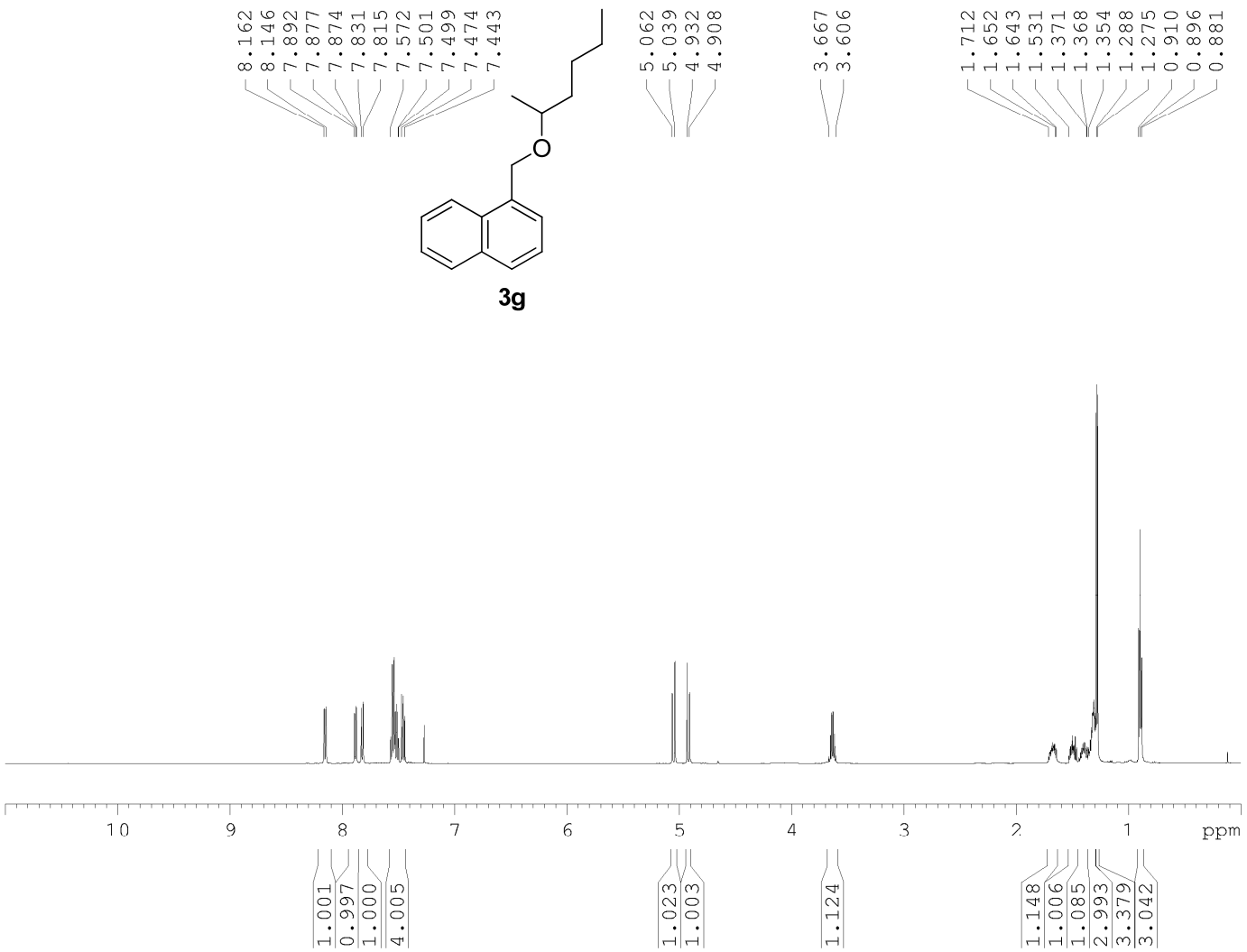
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 1-((cyclopropylmethoxy)methyl)naphthalene **3e** (Table 2, entry 5)



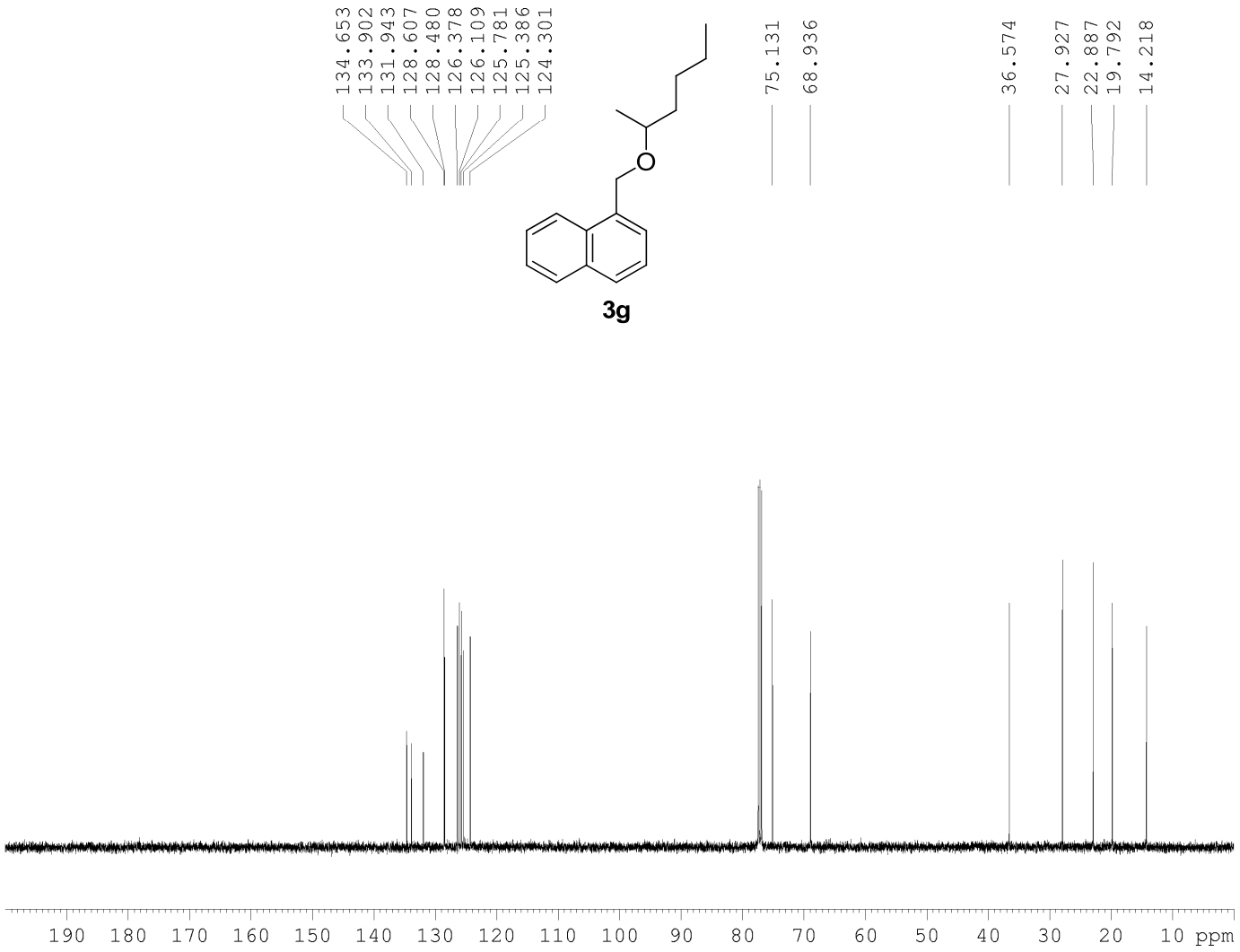
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of trimethyl(2-(naphthalen-1-ylmethoxy)ethyl)silane **3f** (Table 2, entry 6)



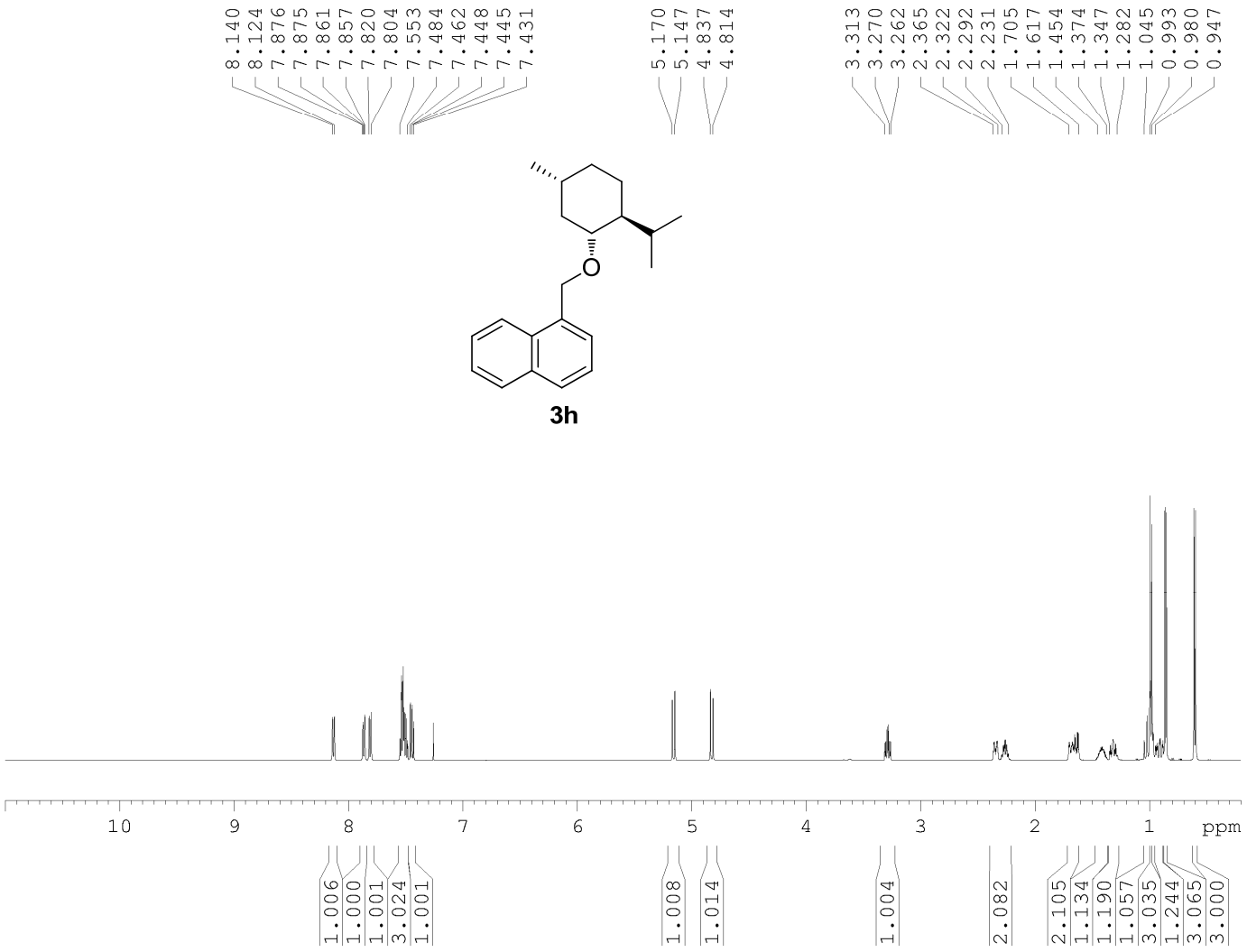
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of trimethyl(2-(naphthalen-1-ylmethoxy)ethyl)silane **3f** (Table 2, entry 6)



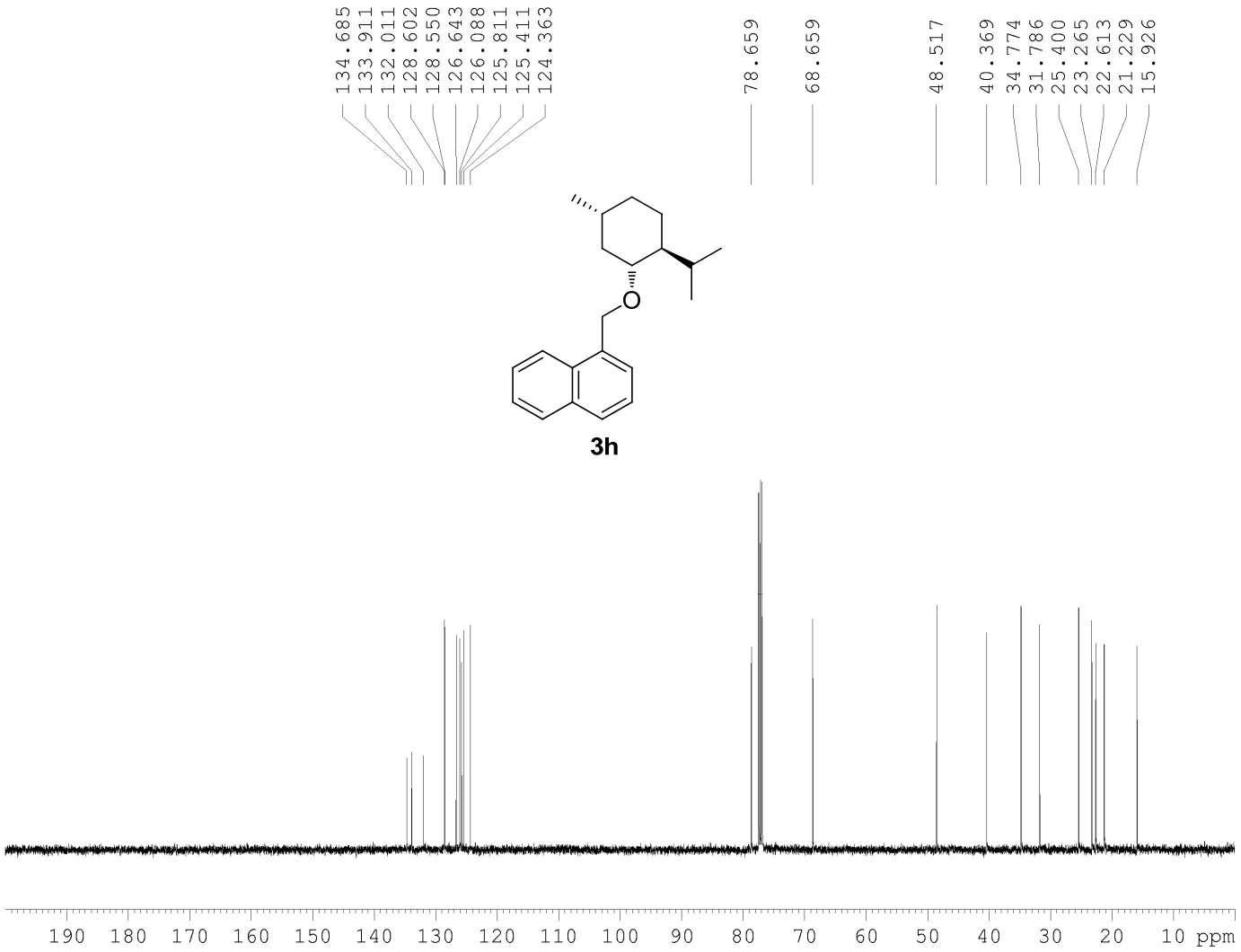
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-((hexan-2-yloxy)methyl)naphthalene **3g** (Table 2, entry 7)



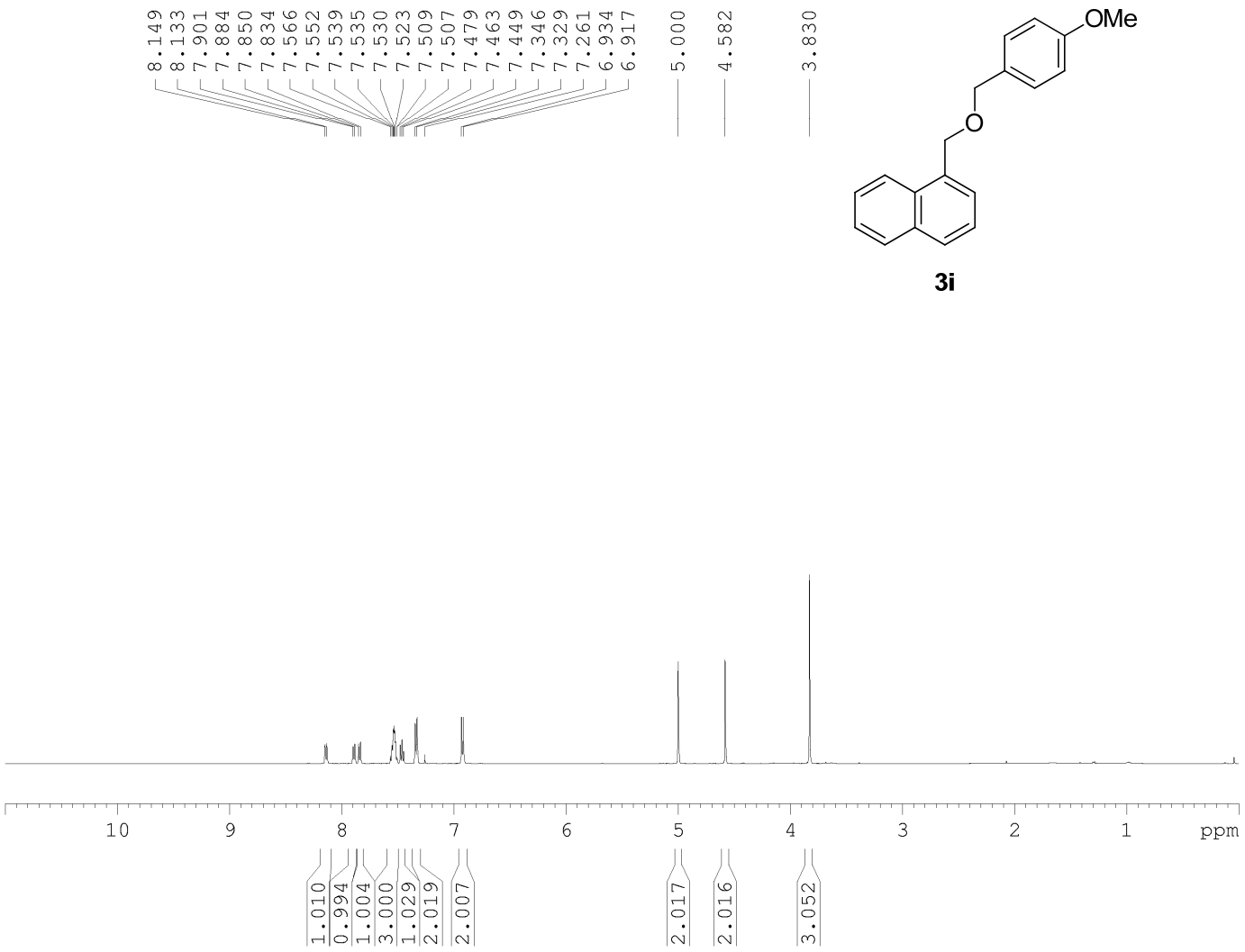
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of Spectrum of 1-((hexan-2-yloxy)methyl)naphthalene **3g** (Table 2, entry 7)



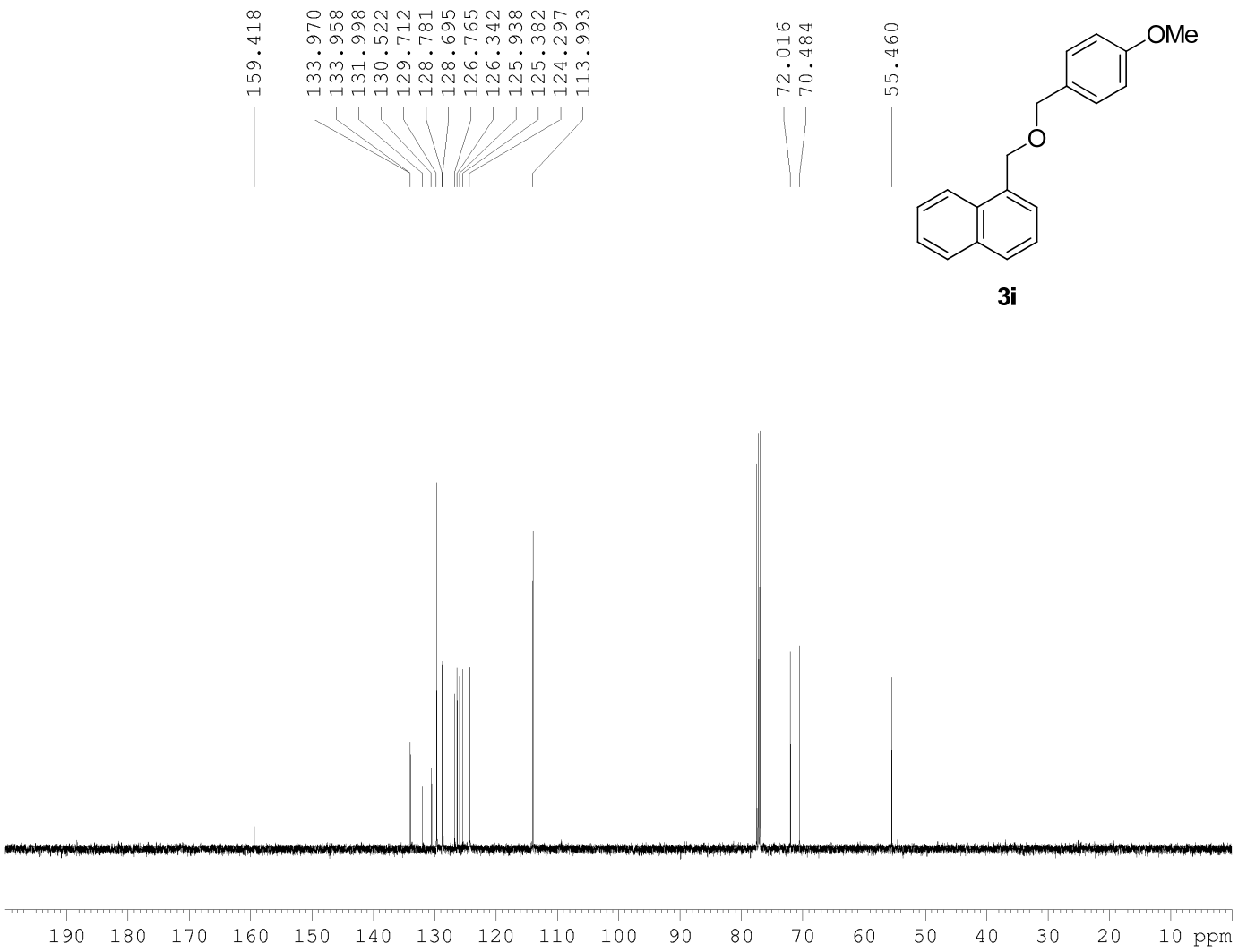
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-((((1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl)oxy)methyl)naphthalene **3h** (Table 2, entry 8)



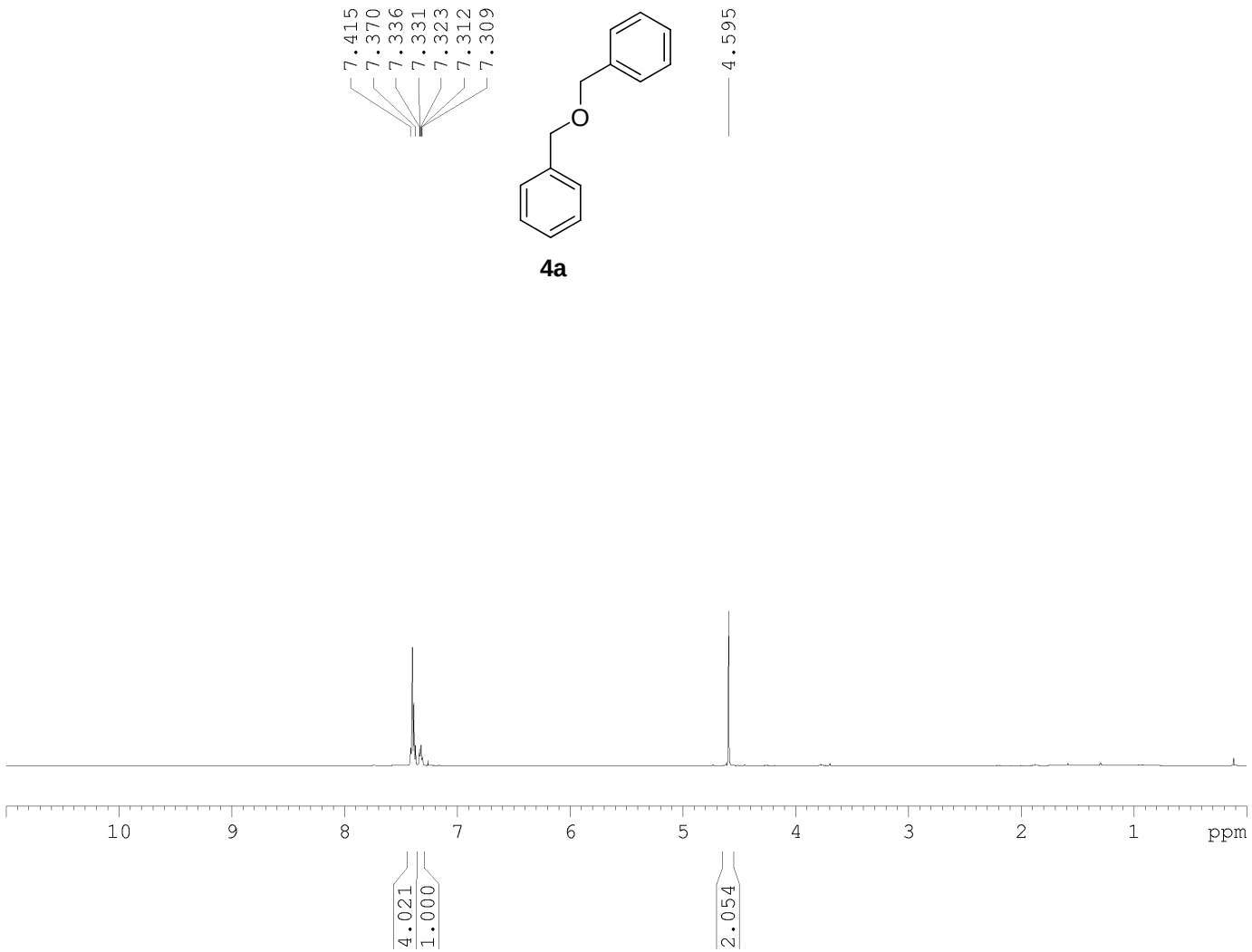
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 1-((((1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl)oxy)methyl)naphthalene **3h** (Table 2, entry 8)



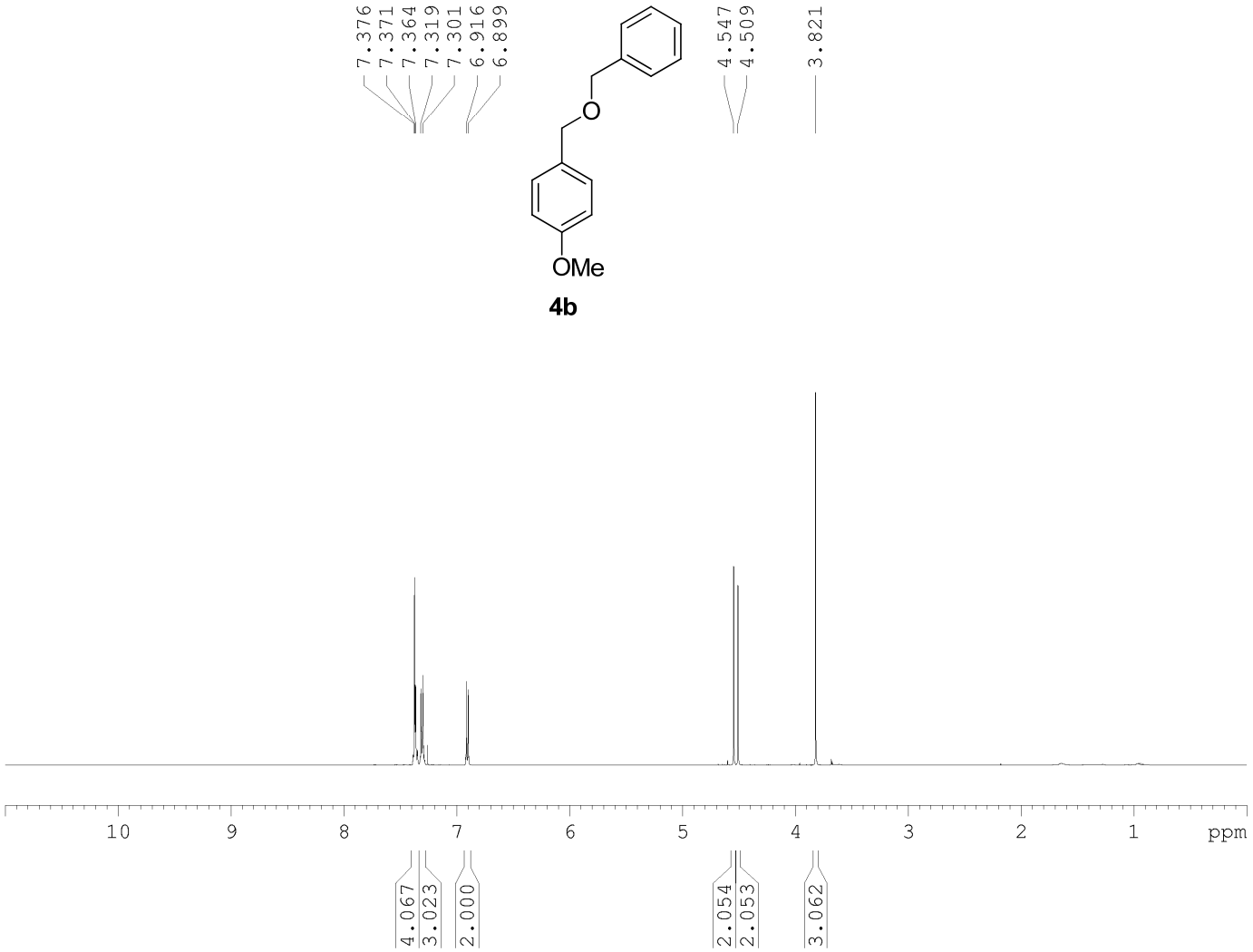
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-(((4-methoxybenzyl)oxy)methyl)naphthalene **3i** (Table 2, entry 9)



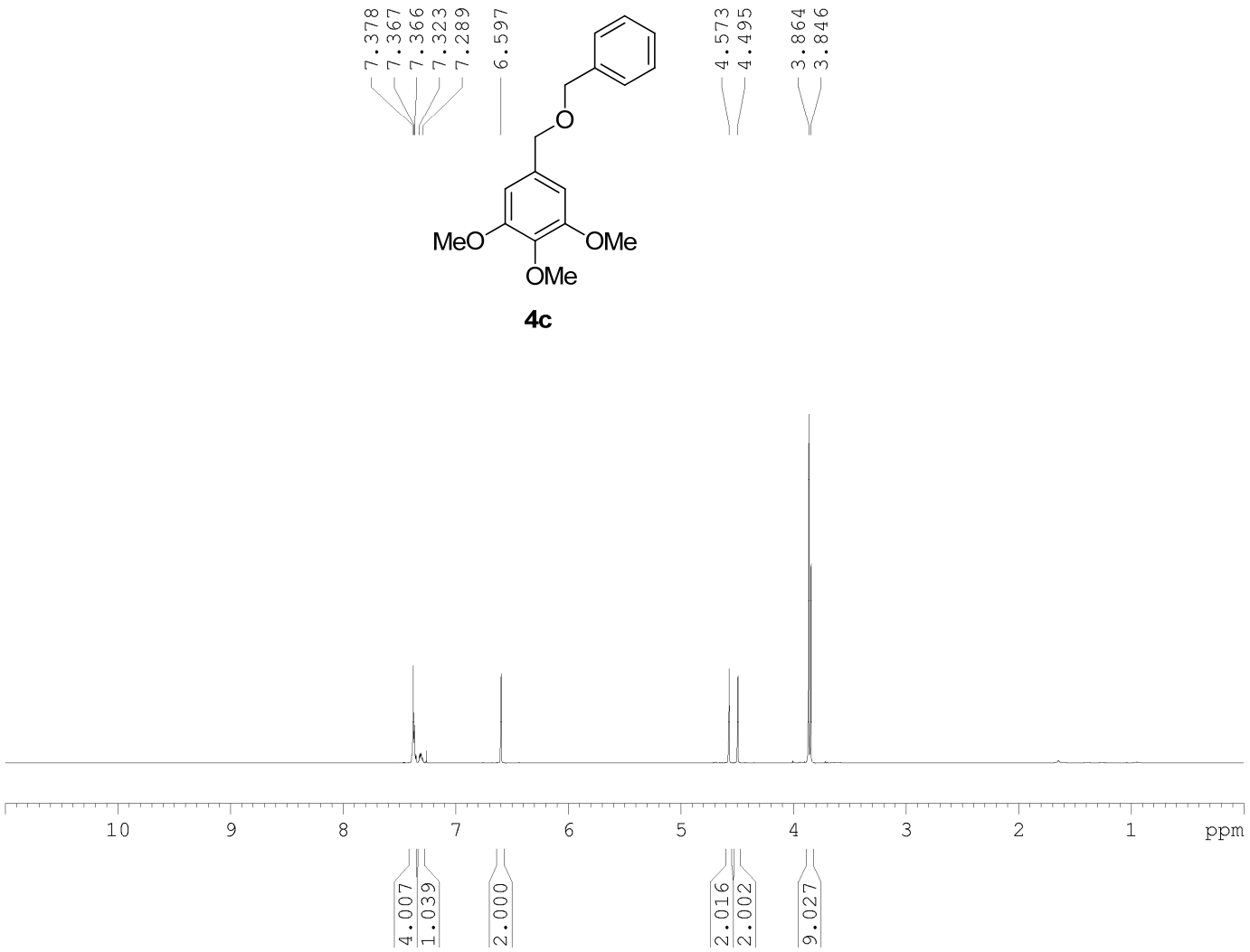
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 1-(((4-methoxybenzyl)oxy)methyl)naphthalene **3i** (Table 2, entry 9)



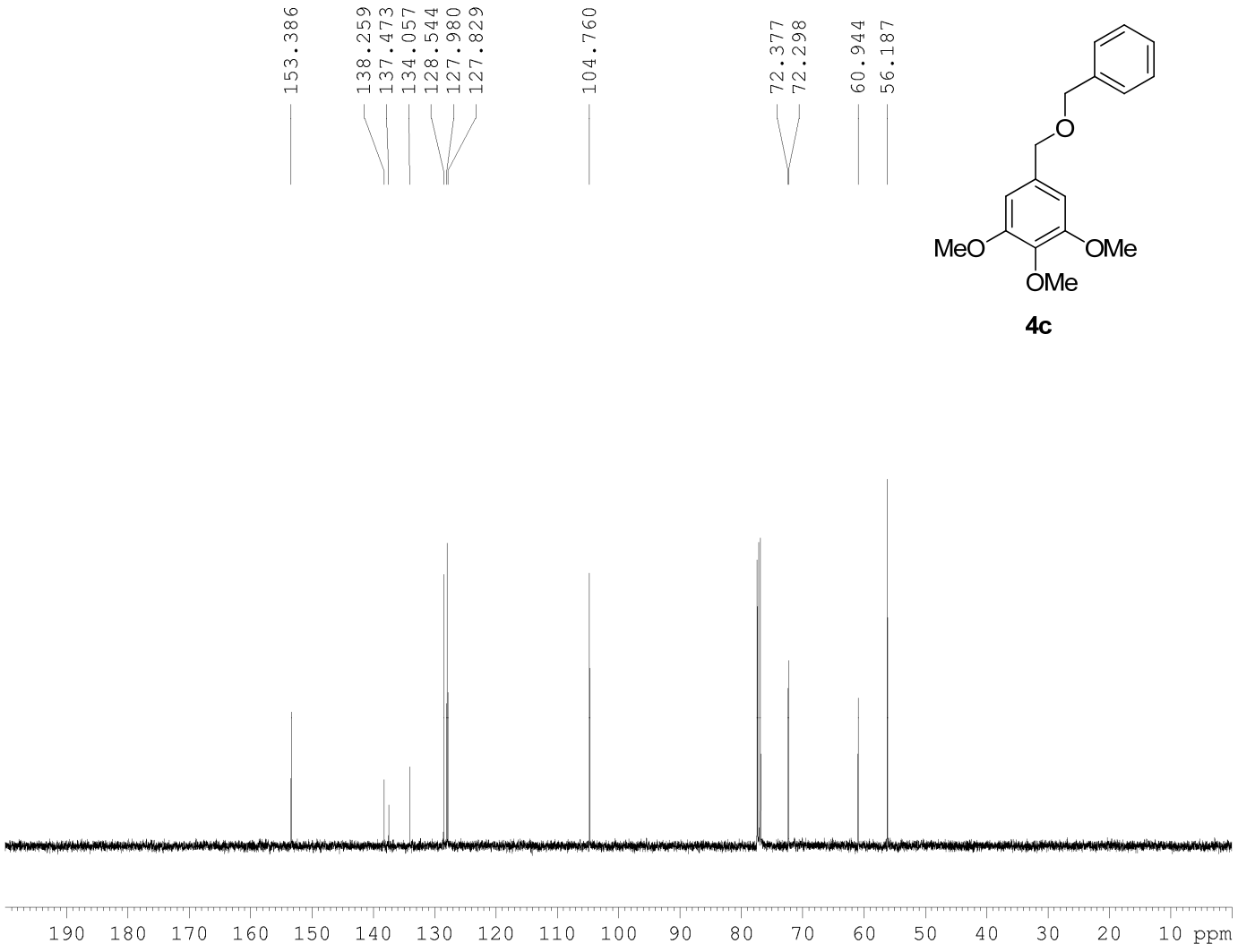
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of oxybis(methylene))dibenzene **4a** (Table 3, entry 1)



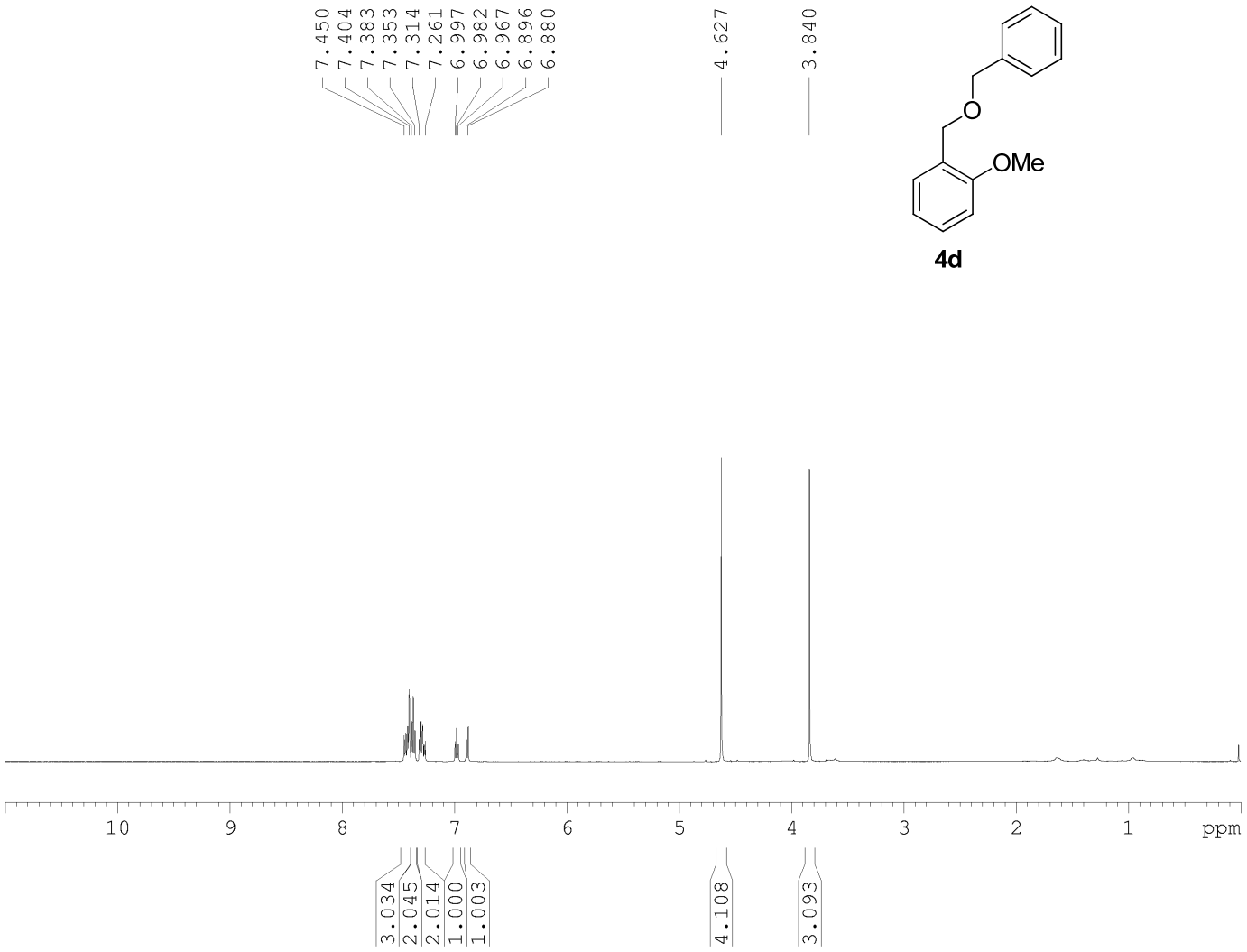
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-((benzyloxy)methyl)-4-methoxybenzene **4b** (Table 3, entry 2)



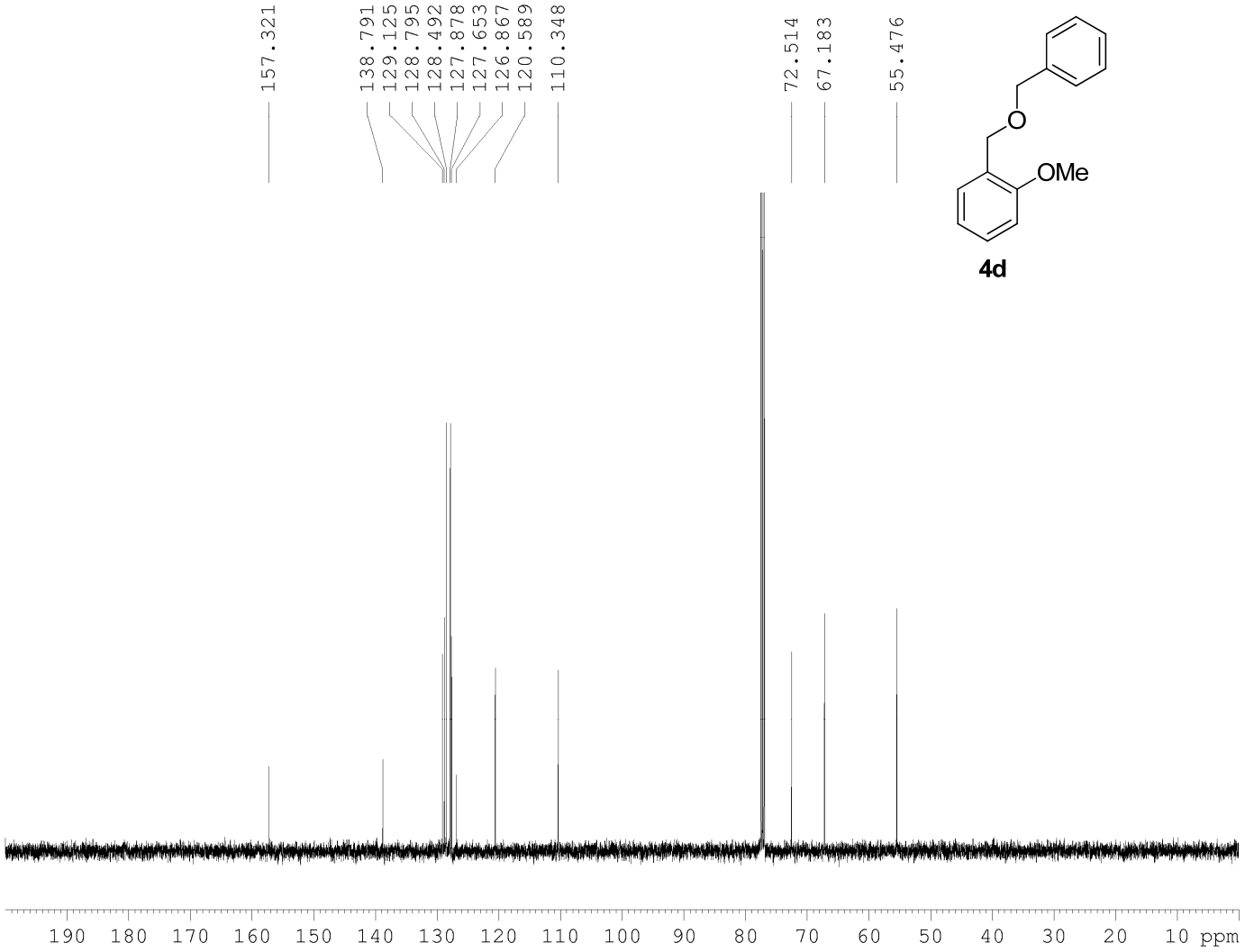
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 5-((benzyloxy)methyl)-1,2,3-trimethoxybenzene **4c** (Table 3, entry 3)



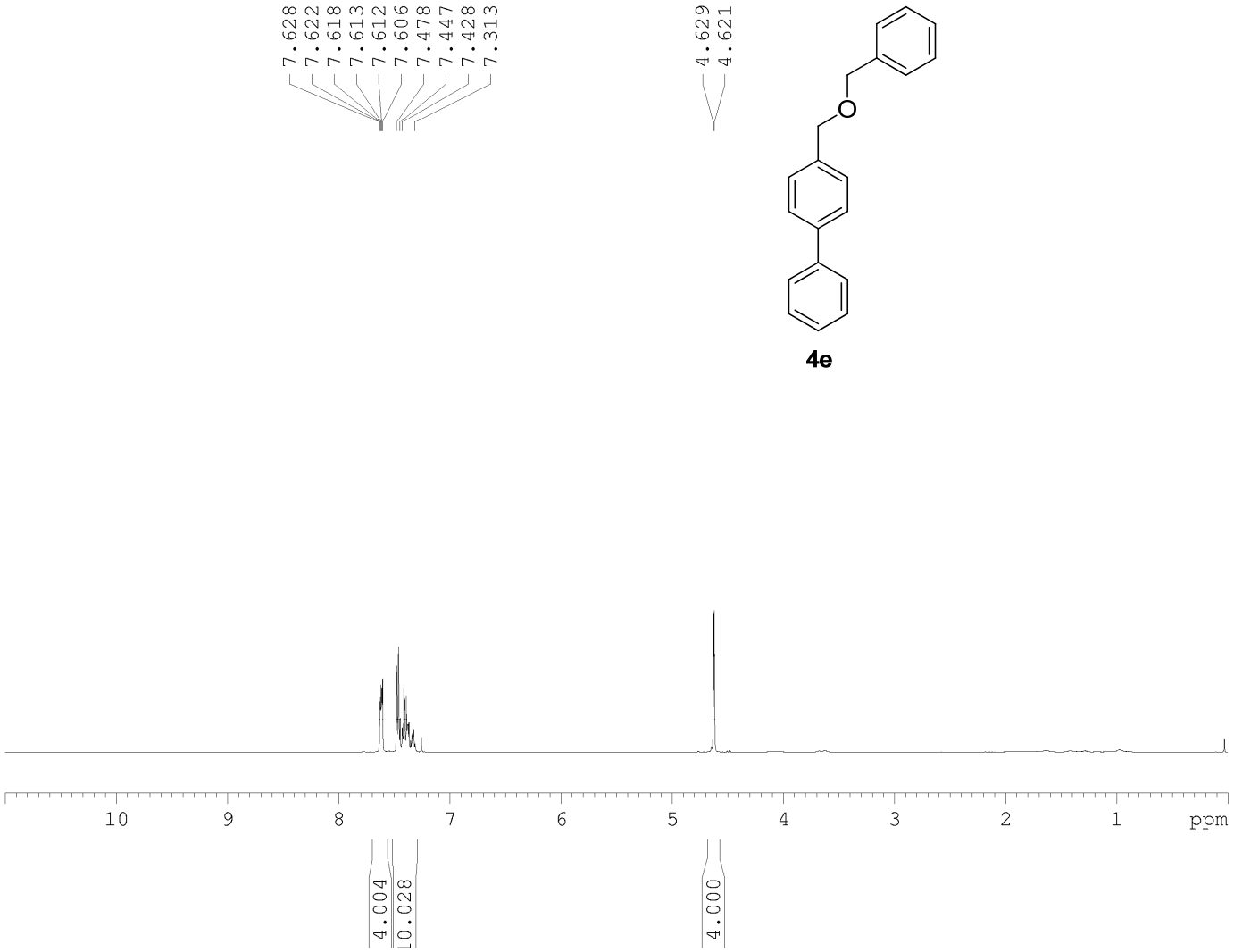
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 5-((benzyloxy)methyl)-1,2,3-trimethoxybenzene **4c** (Table 3, entry 3)



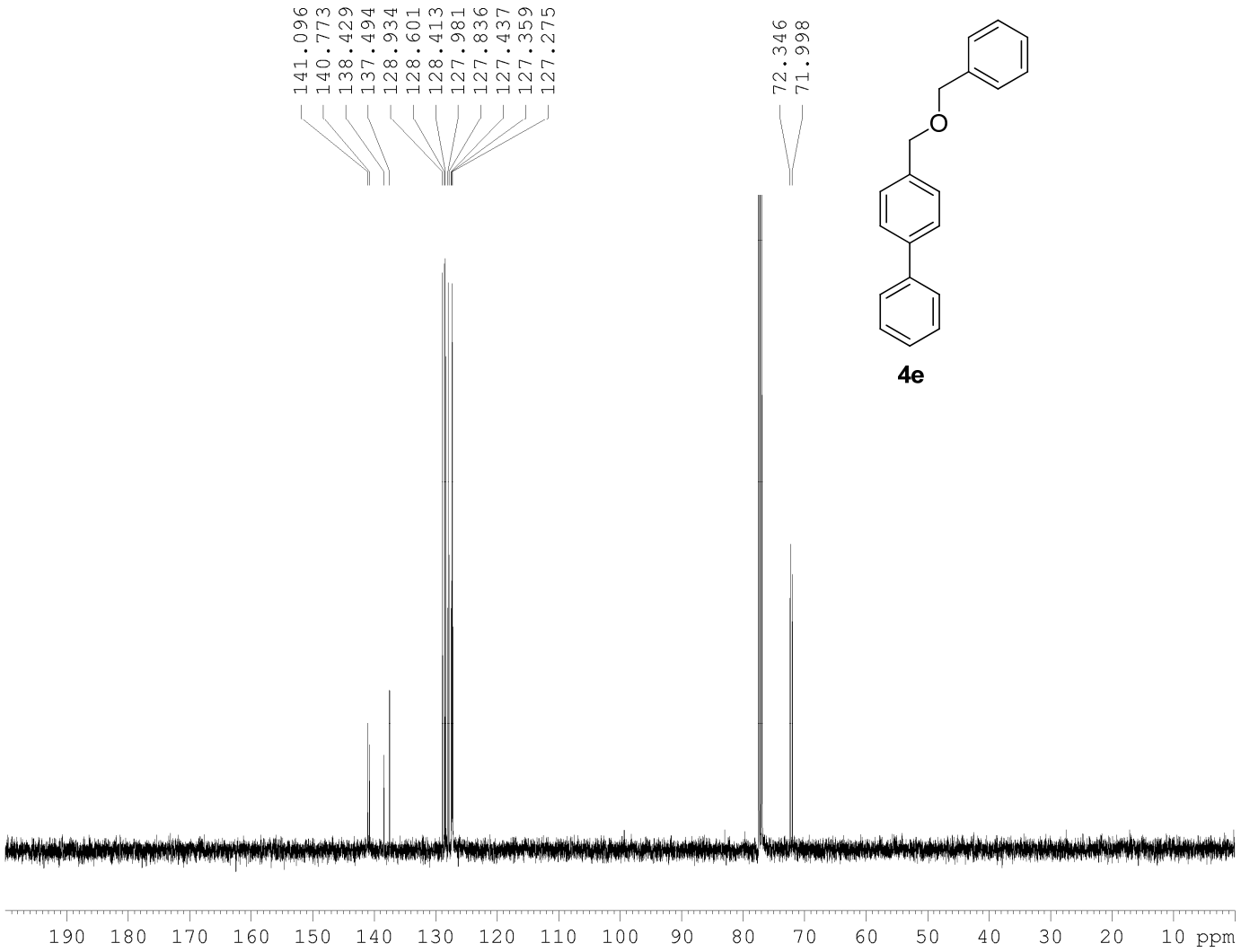
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-((benzyloxy)methyl)-2-methoxybenzene **4d** (Table 3, entry 4)



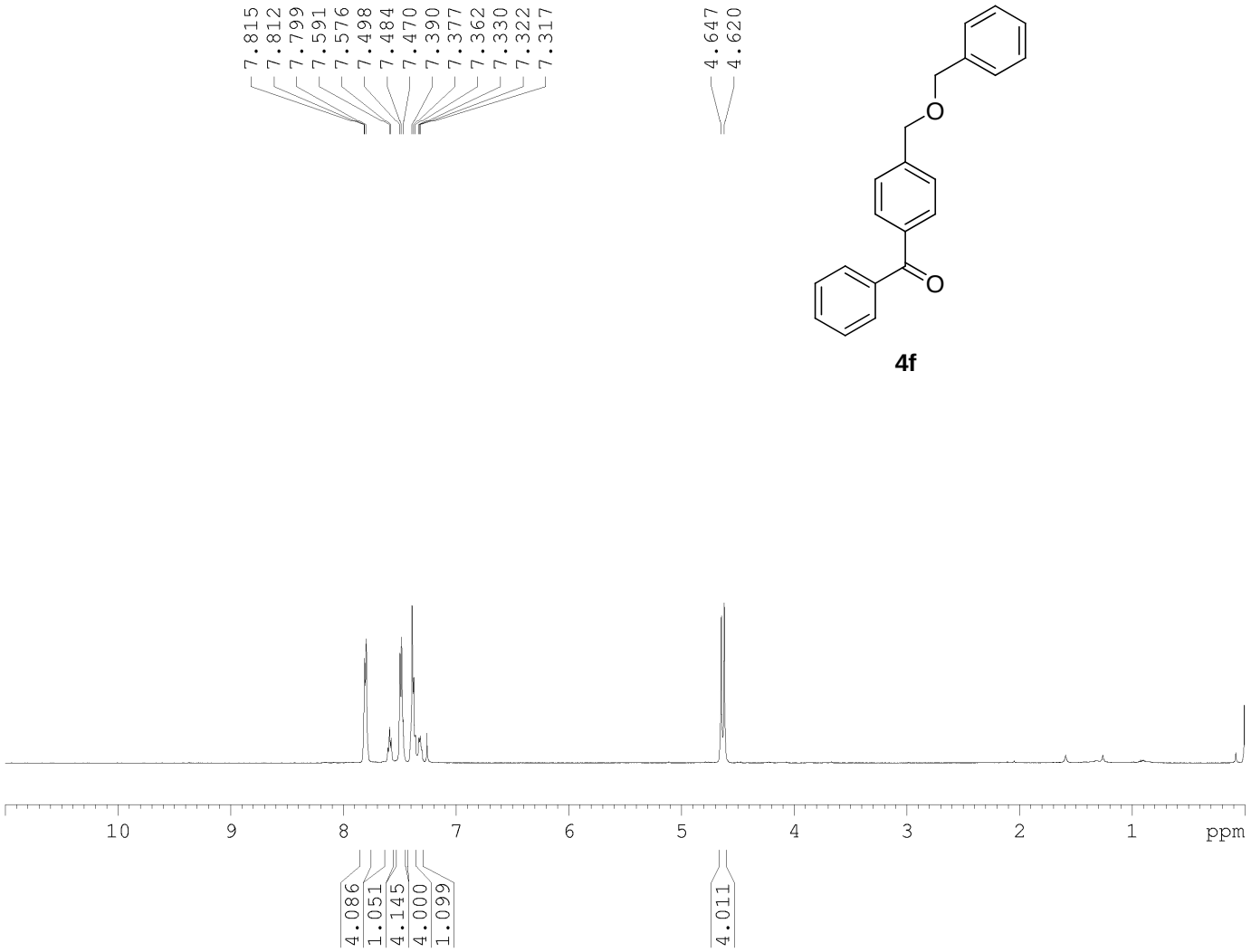
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 1-((benzyloxy)methyl)-2-methoxybenzene **4d** (Table 3, entry 4)



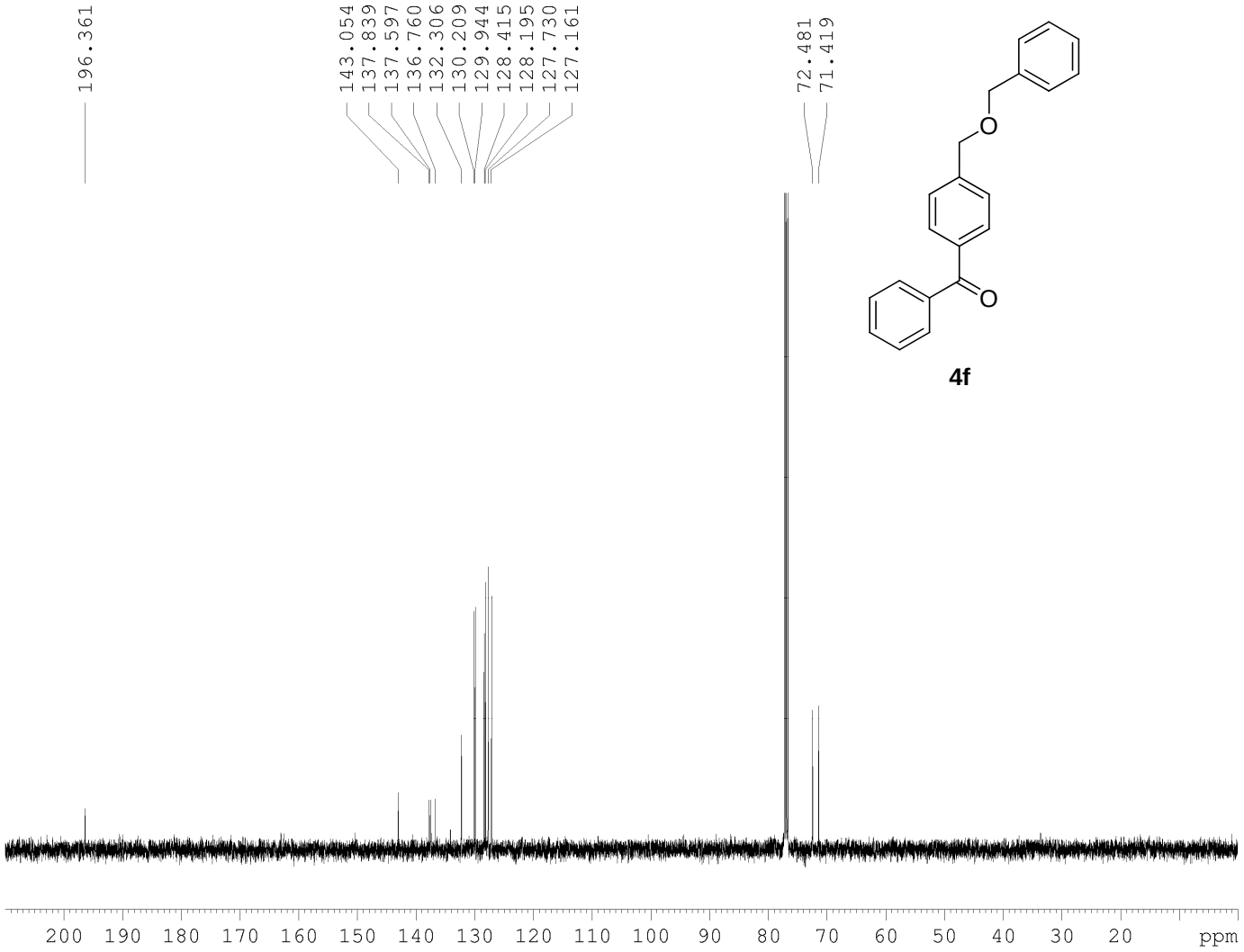
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 4-((benzyloxy)methyl)-1,1'-biphenyl **4e** (Table 3, entry 5)



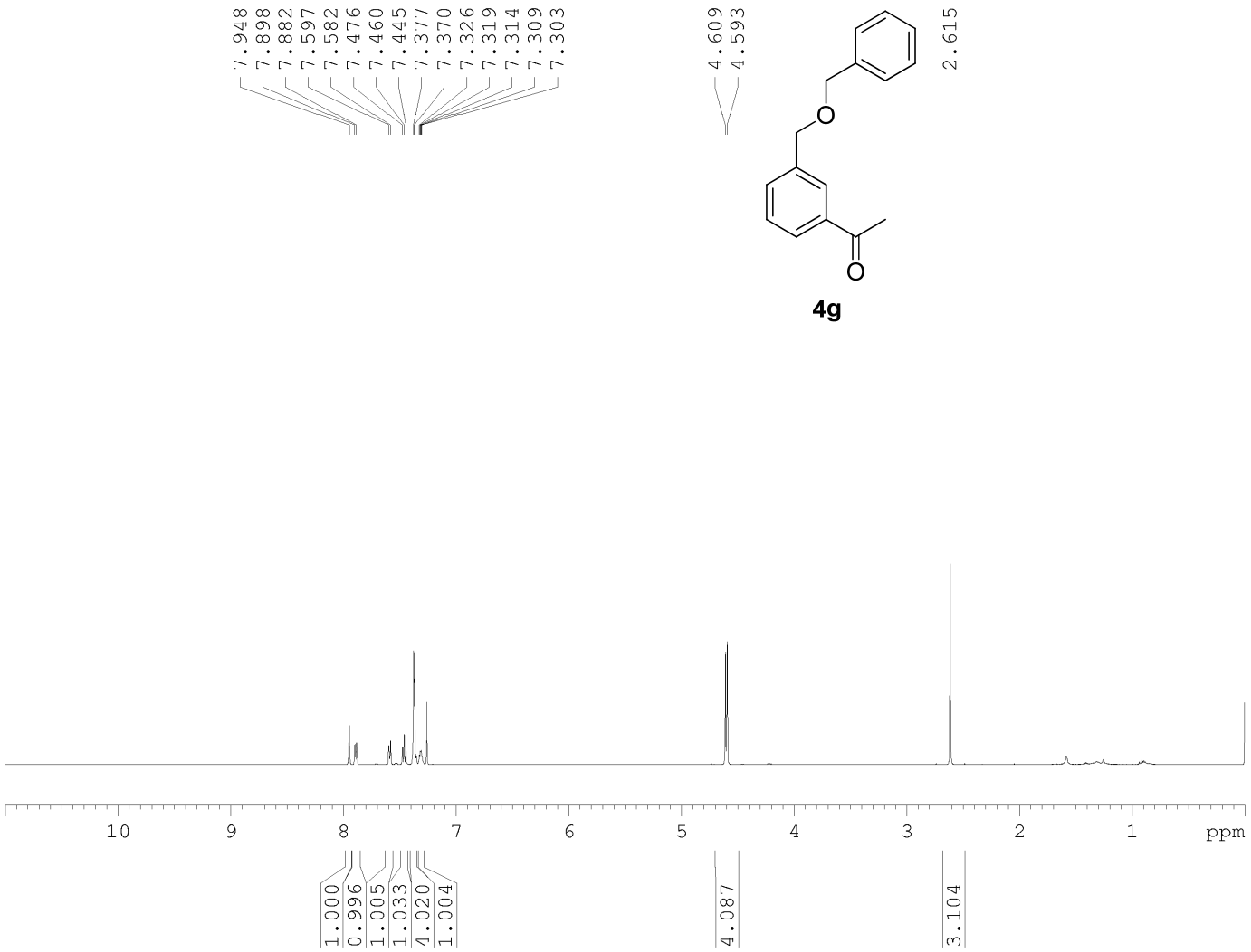
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 4-((benzyloxy)methyl)-1,1'-biphenyl **4e** (Table 3, entry 5)



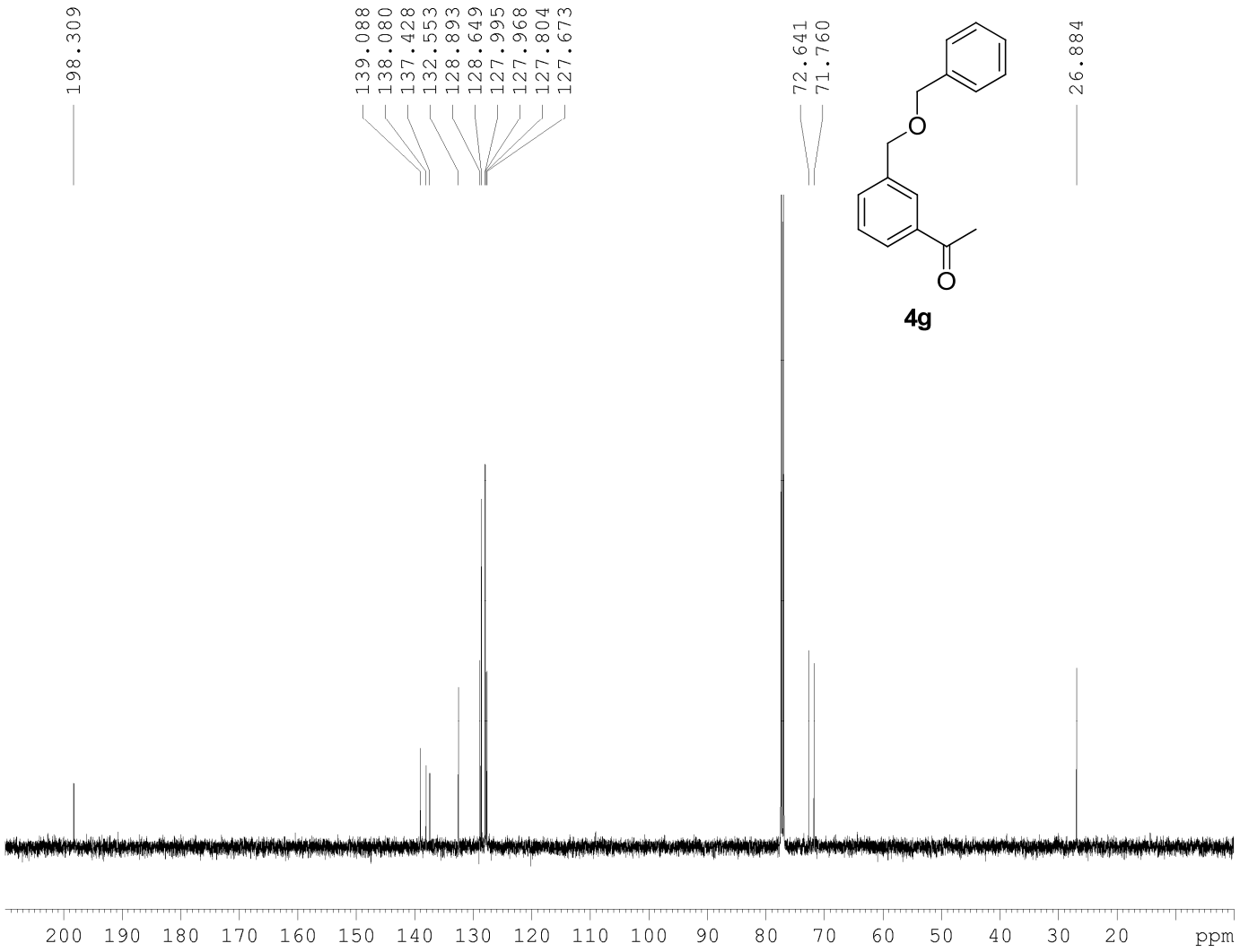
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of (4-((benzyloxy)methyl)phenyl)(phenyl)methanone **4f** (Table 3, entry 6)



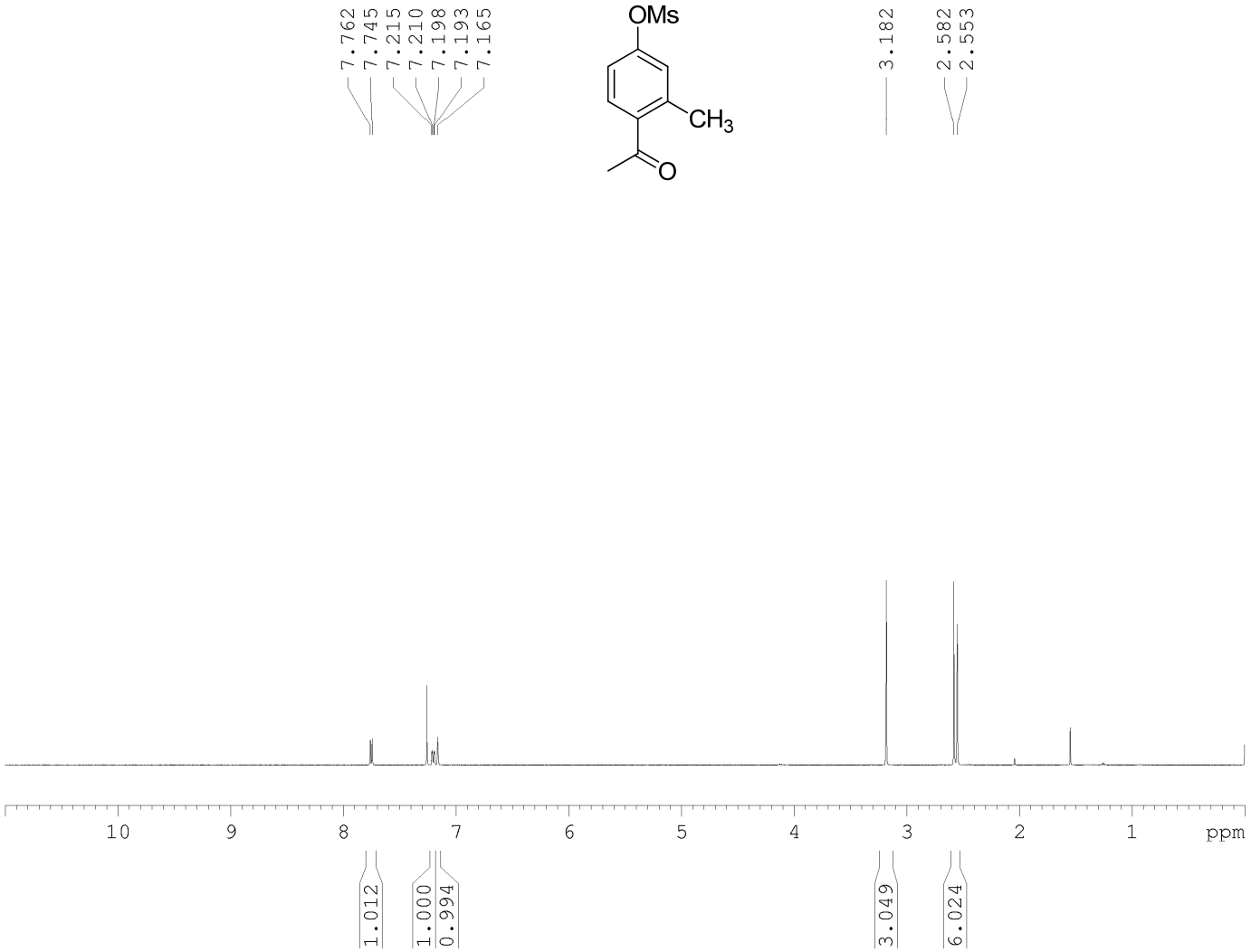
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of (4-((benzyloxy)methyl)phenyl)(phenyl)methanone **4f** (Table 3, entry 6)



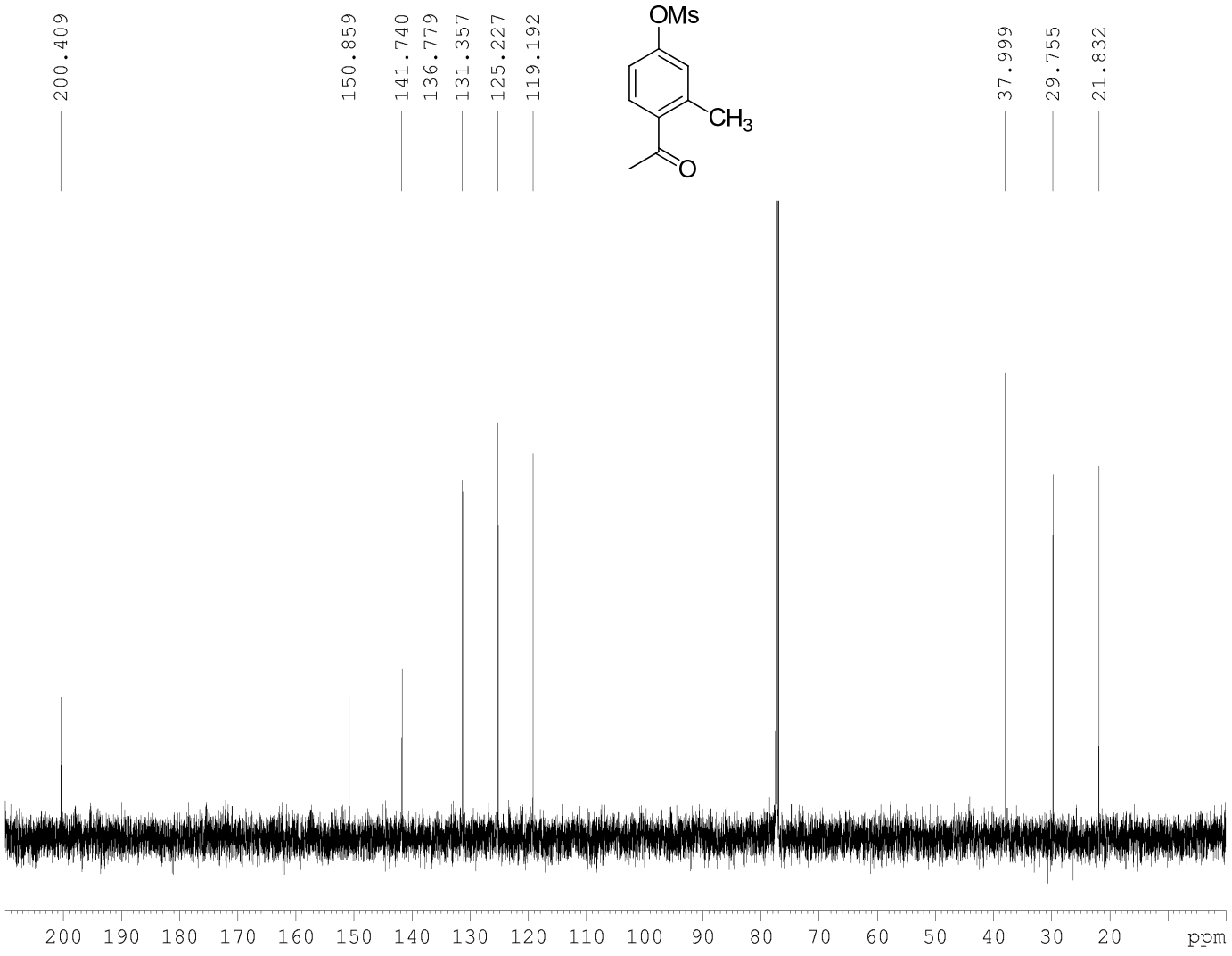
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-(3-((benzyloxy)methyl)phenyl)ethanone **4g** (Table 3, entry 7)



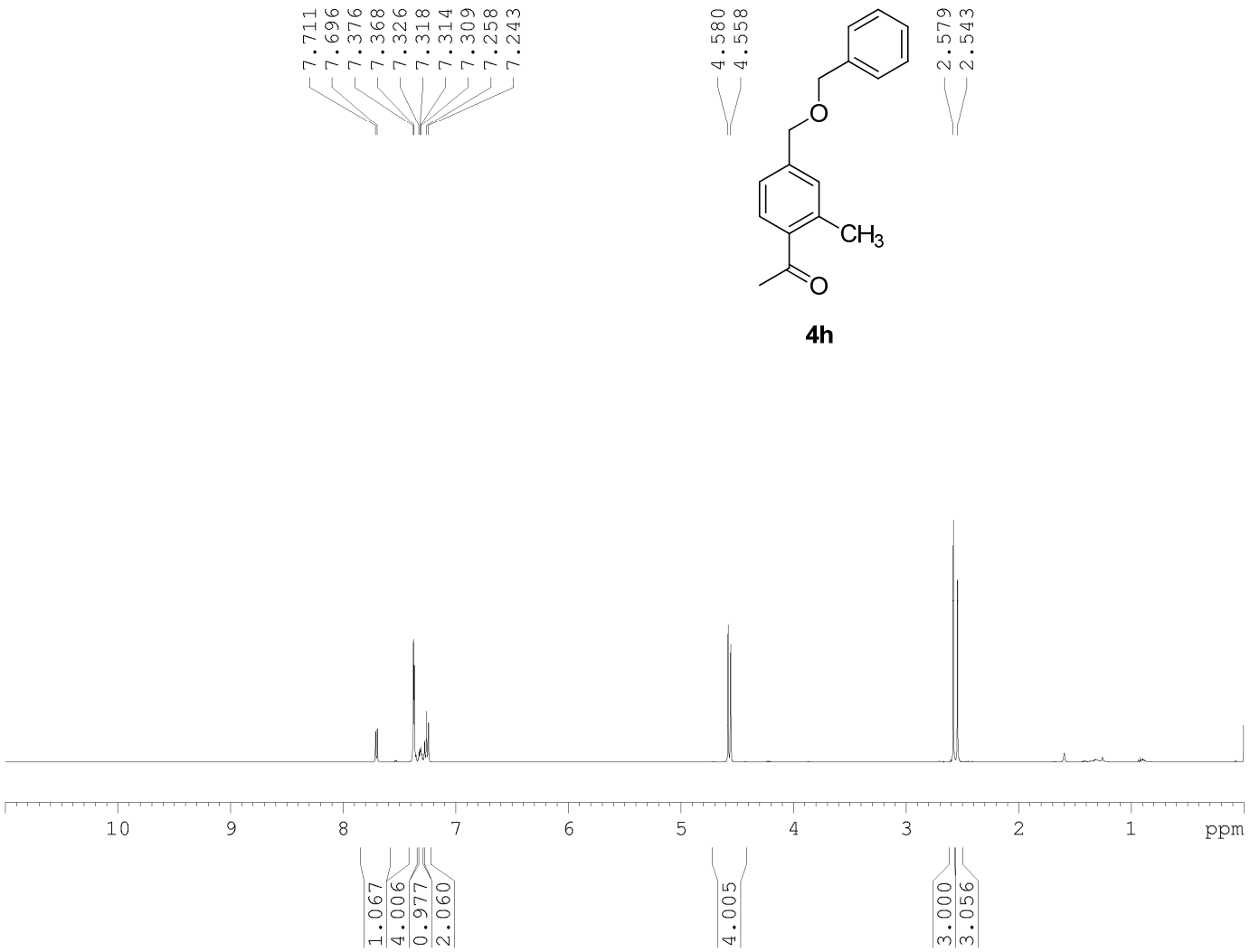
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 1-(3-((benzyloxy)methyl)phenyl)ethanone **4g** (Table 3, entry 7)



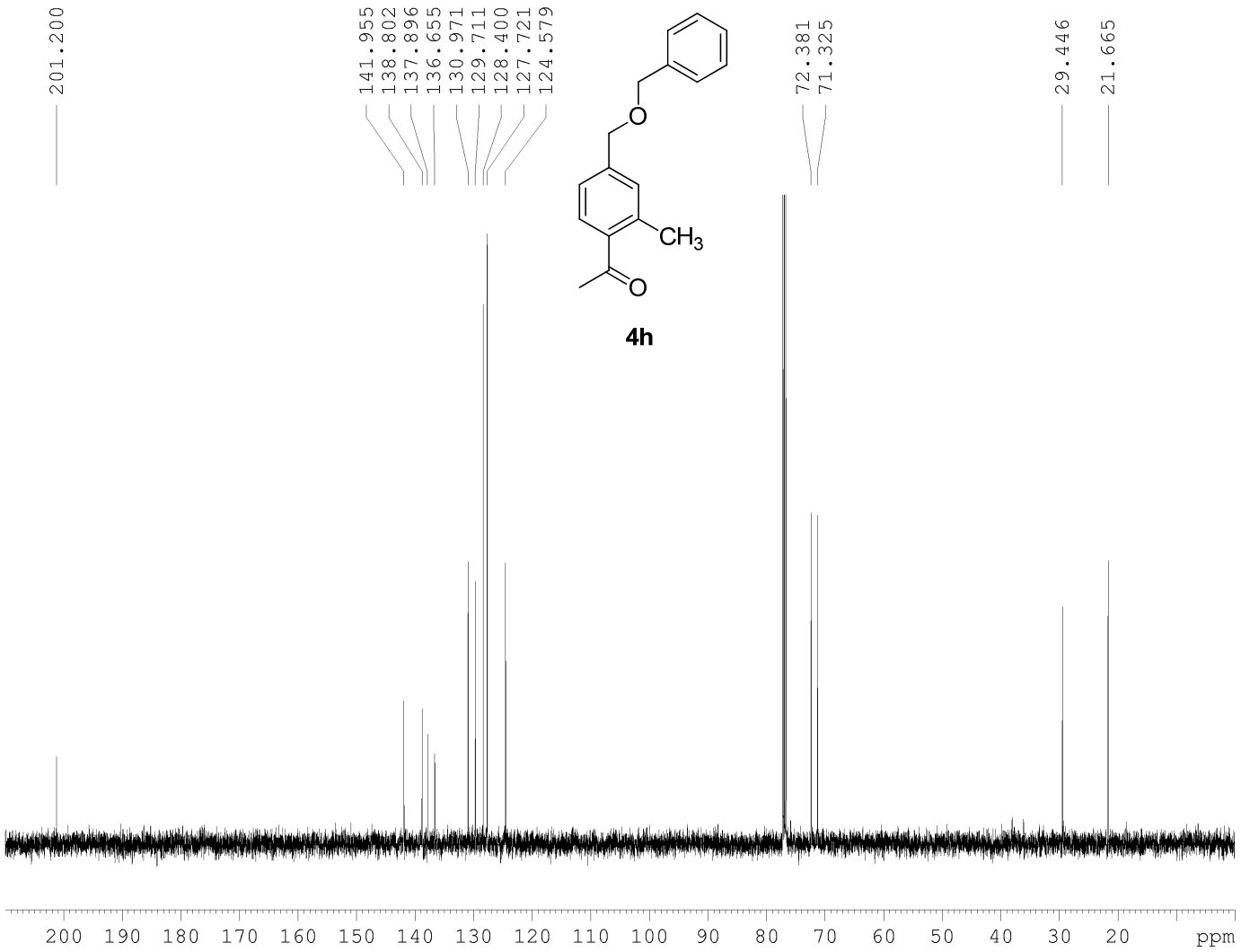
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 4-Acetyl-3-methylphenyl methanesulfonate



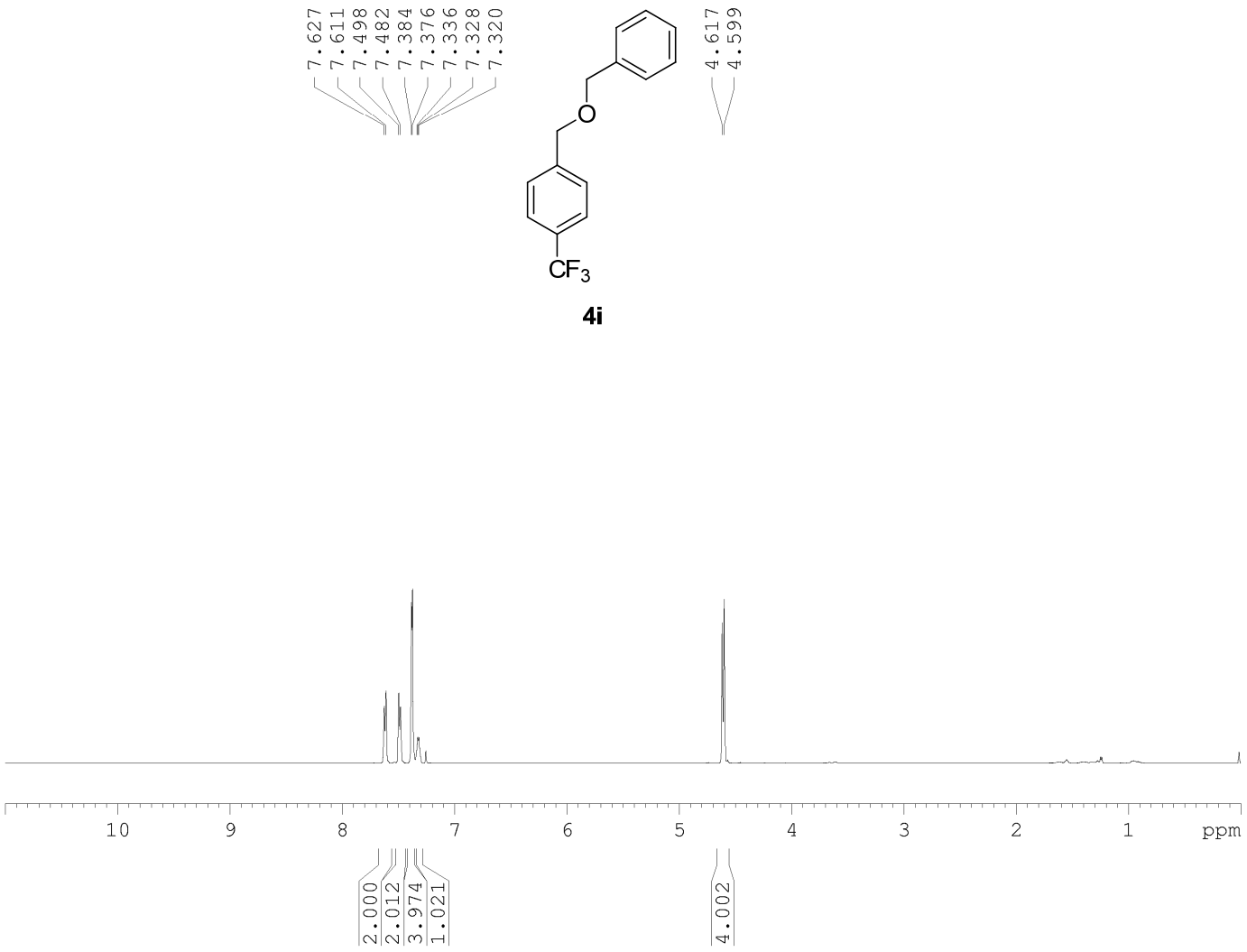
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 4-Acetyl-3-methylphenyl methanesulfonate



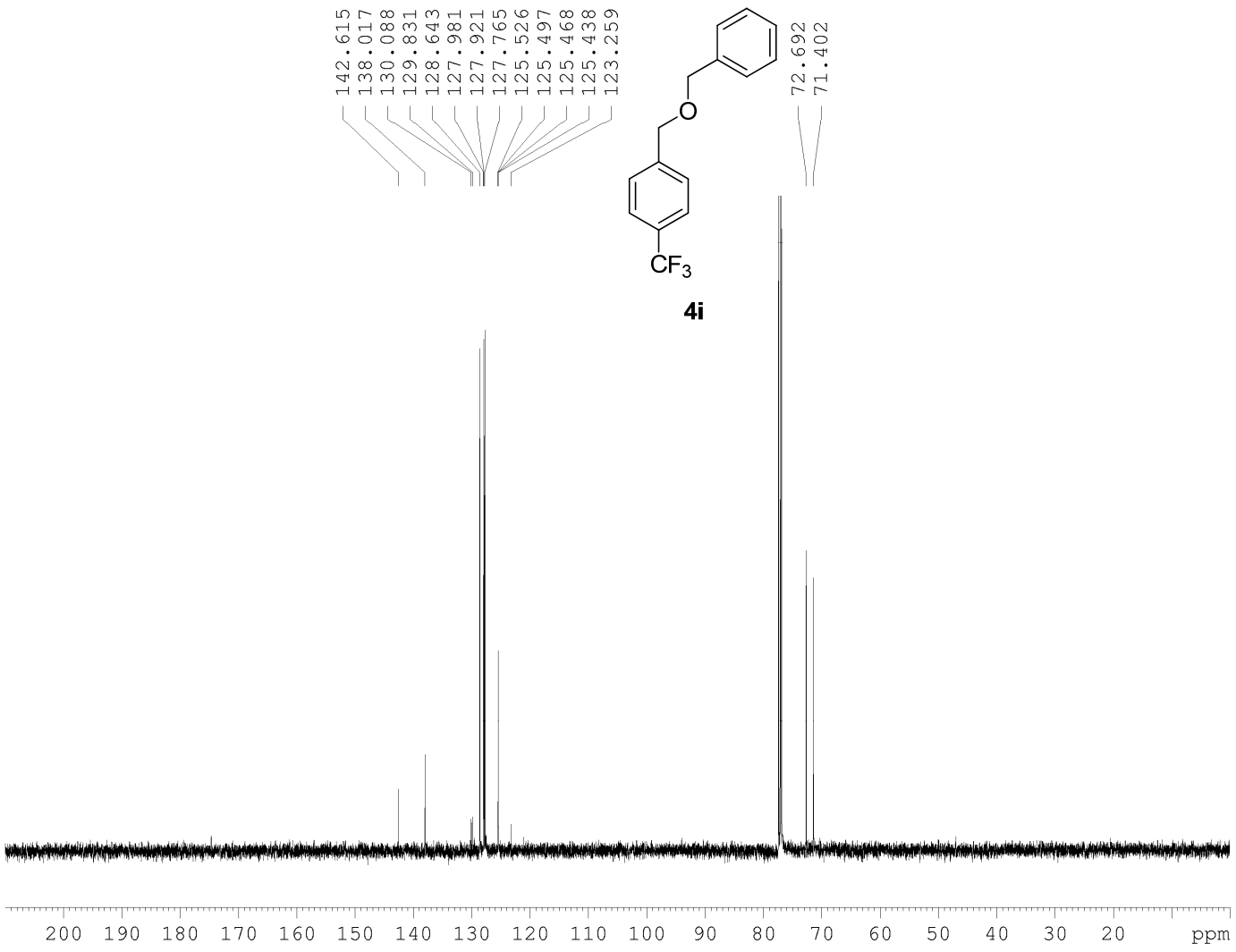
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-(4-((benzyloxy)methyl)-2-methylphenyl)ethanone **4h** (Table 3, entry 8)



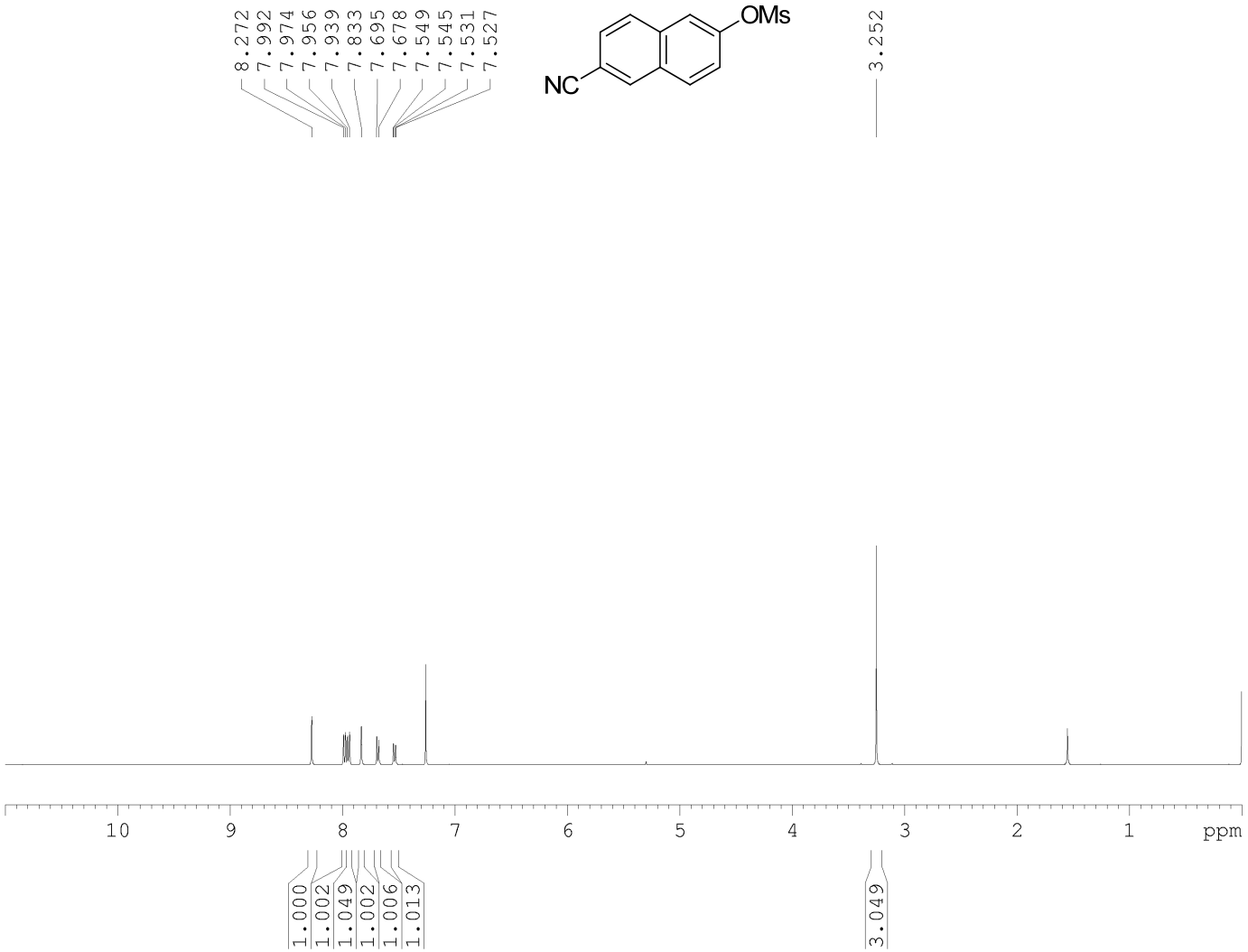
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 1-(4-((benzyloxy)methyl)-2-methylphenyl)ethanone **4h** (Table 3, entry 8)



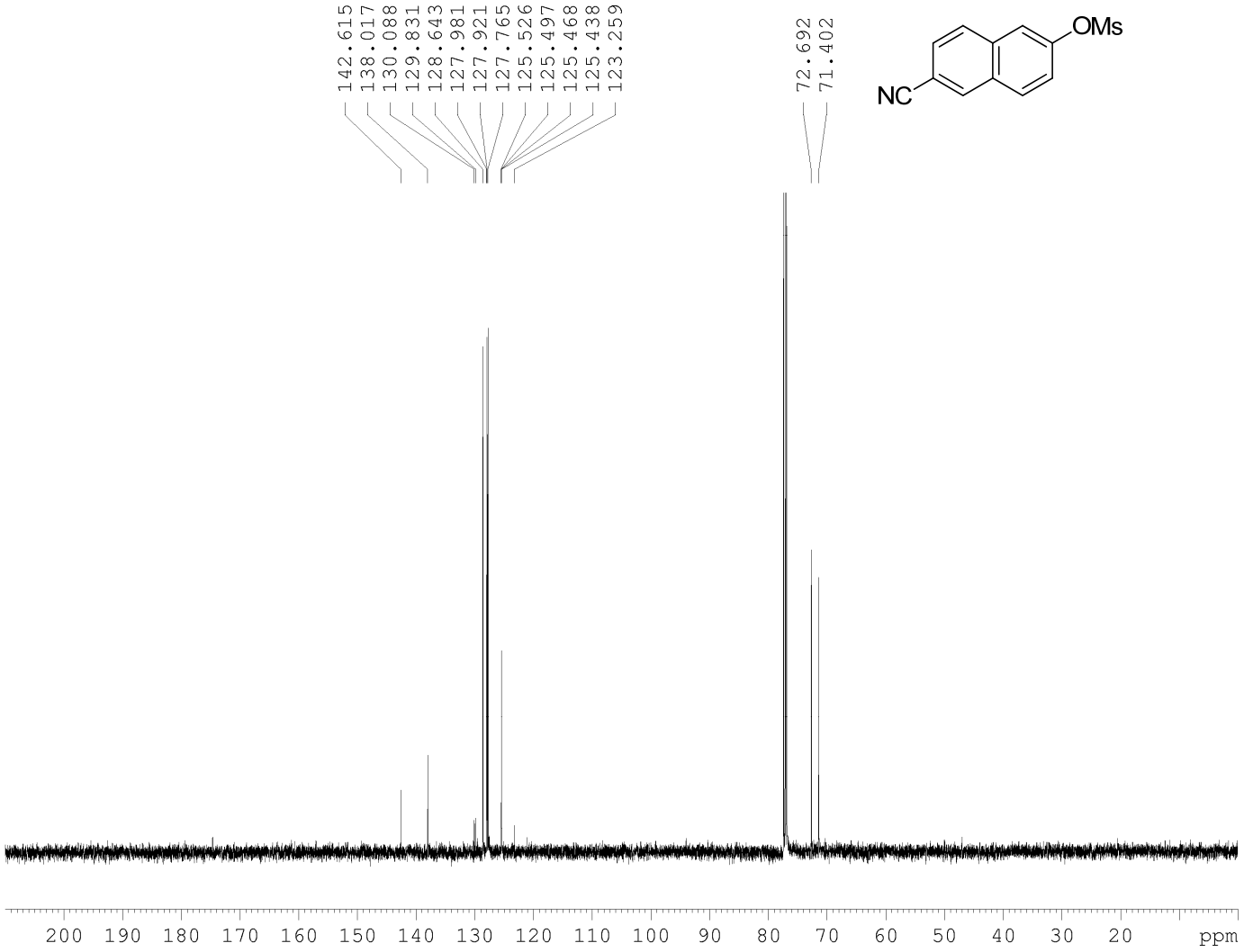
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 1-((benzyloxy)methyl)-4-(trifluoromethyl)benzene **4i** (Table 3, entry 9)



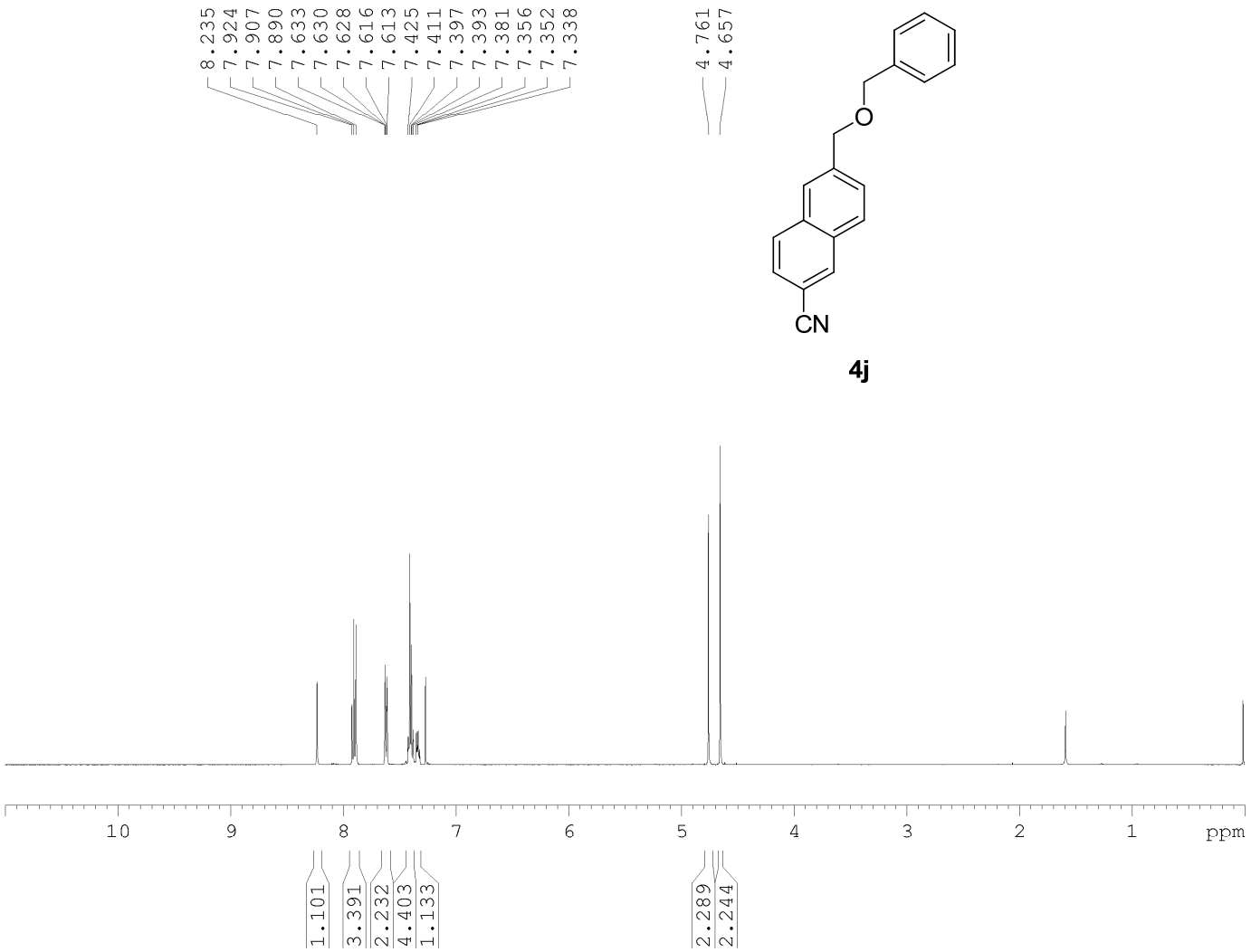
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 1-((benzyloxy)methyl)-4-(trifluoromethyl)benzene **4i** (Table 3, entry 9)



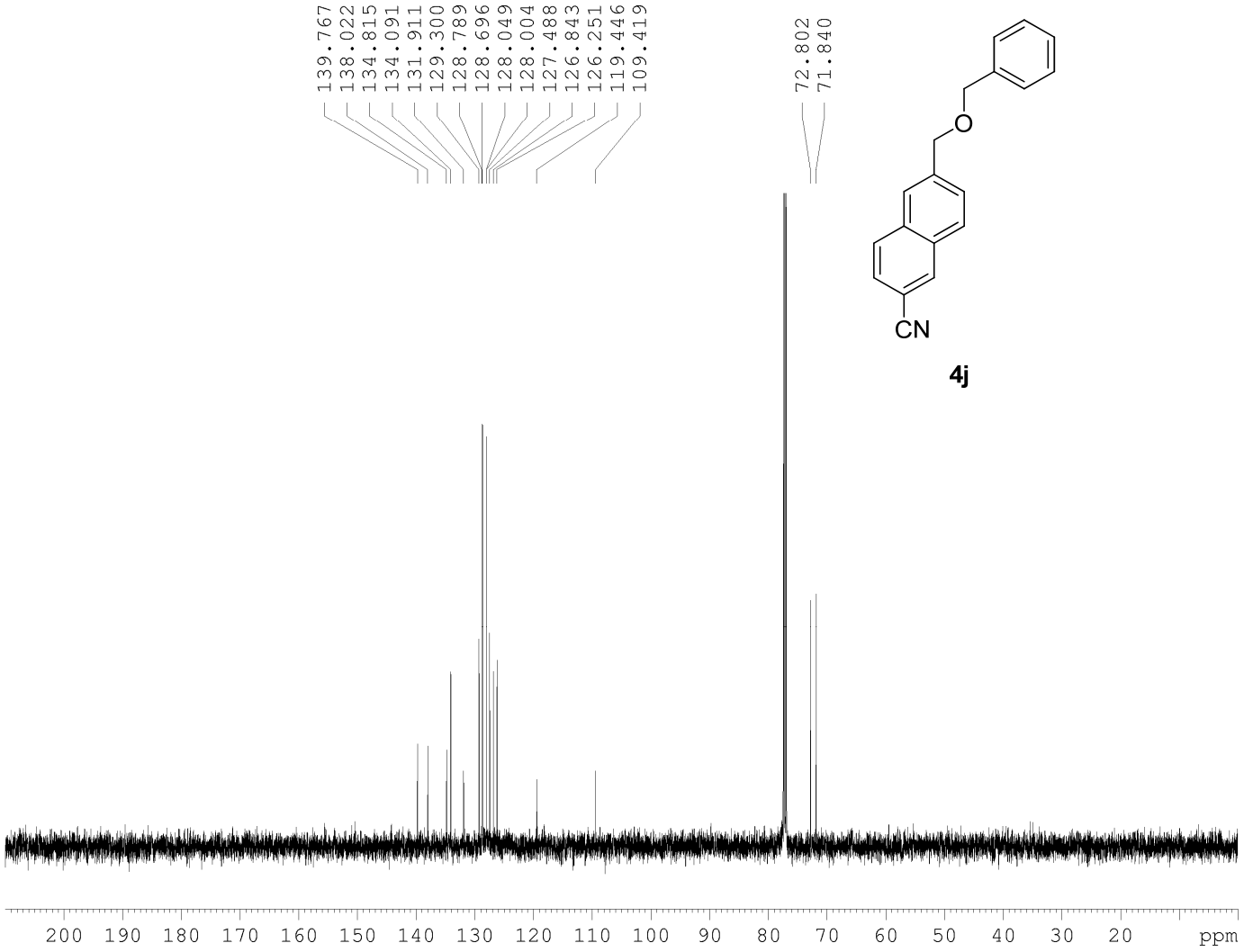
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 6-cyanonaphthalen-2-yl methanesulfonate



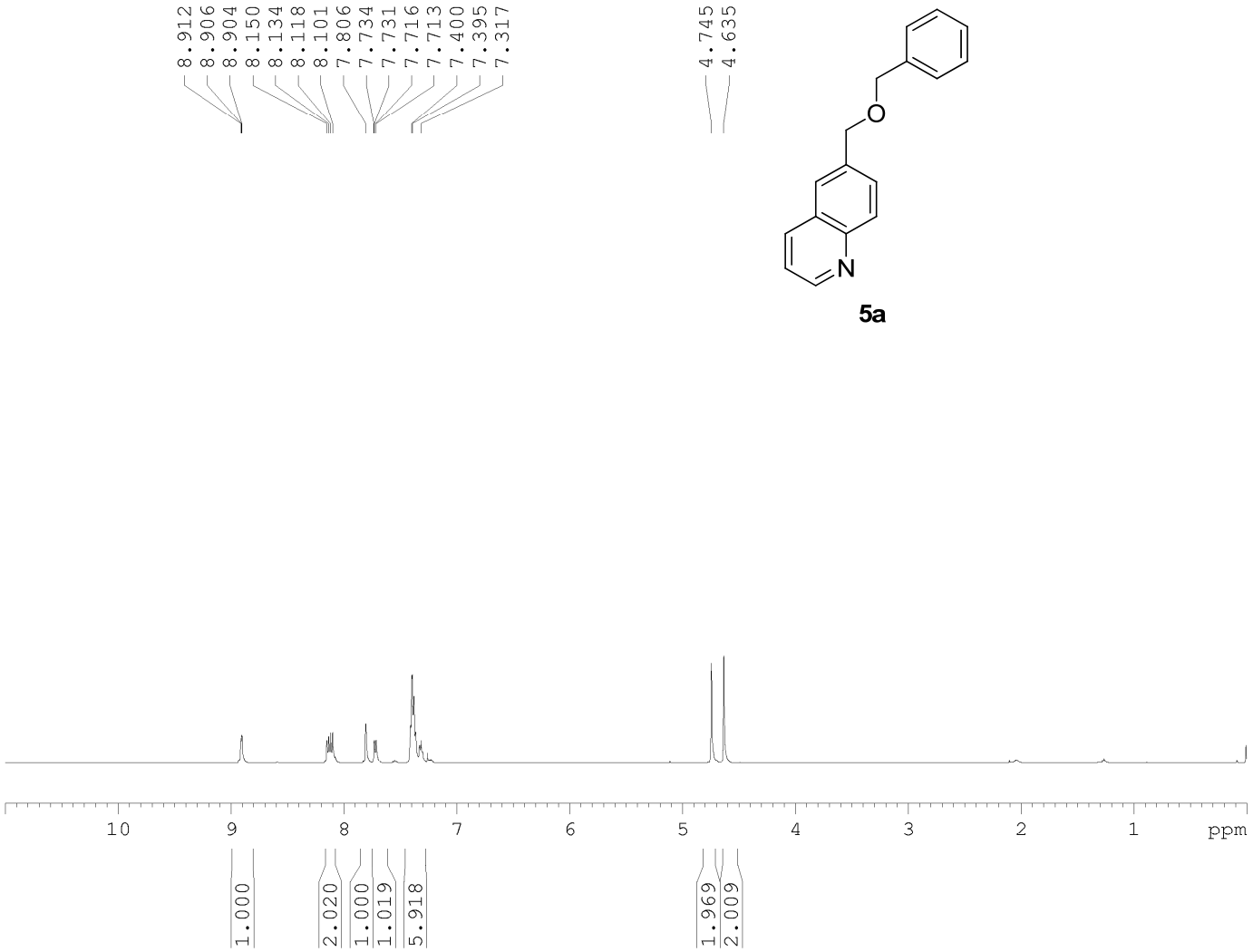
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 6-cyanonaphthalen-2-yl methanesulfonate



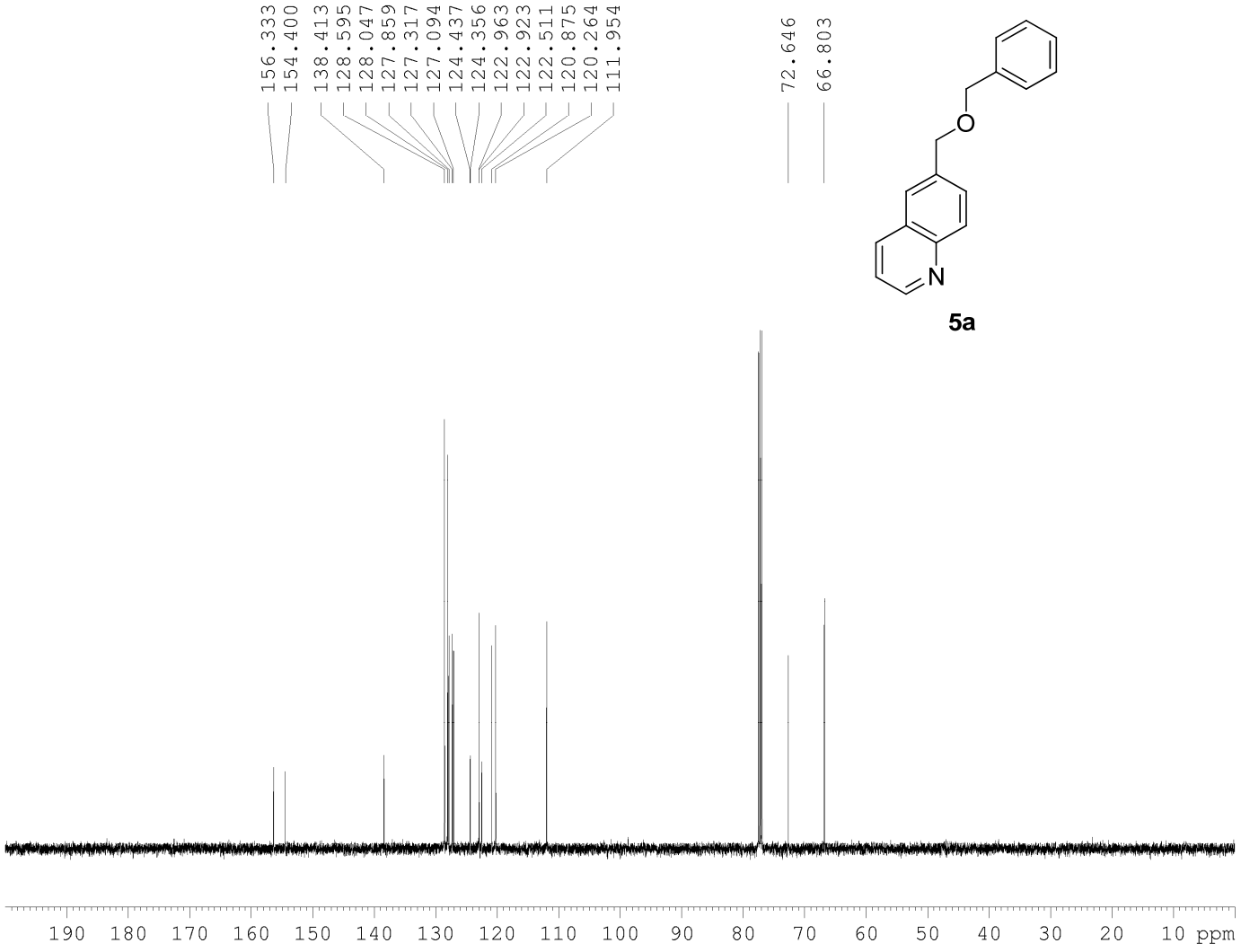
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 6-((benzyloxy)methyl)-2-naphthonitrile **4j** (Table 3, entry 11)



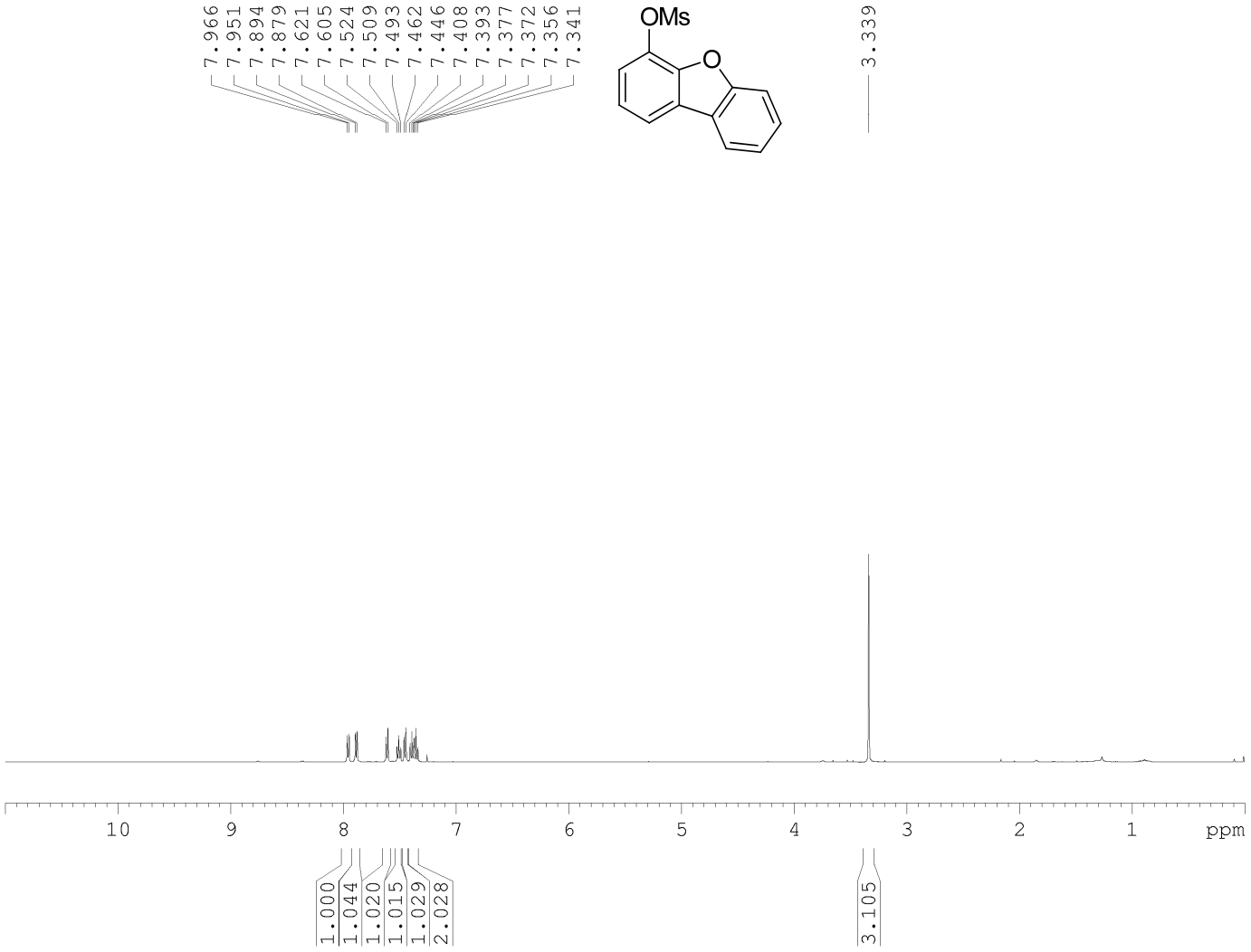
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 6-((benzyloxy)methyl)-2-naphthonitrile **4j** (Table 3, entry 11)



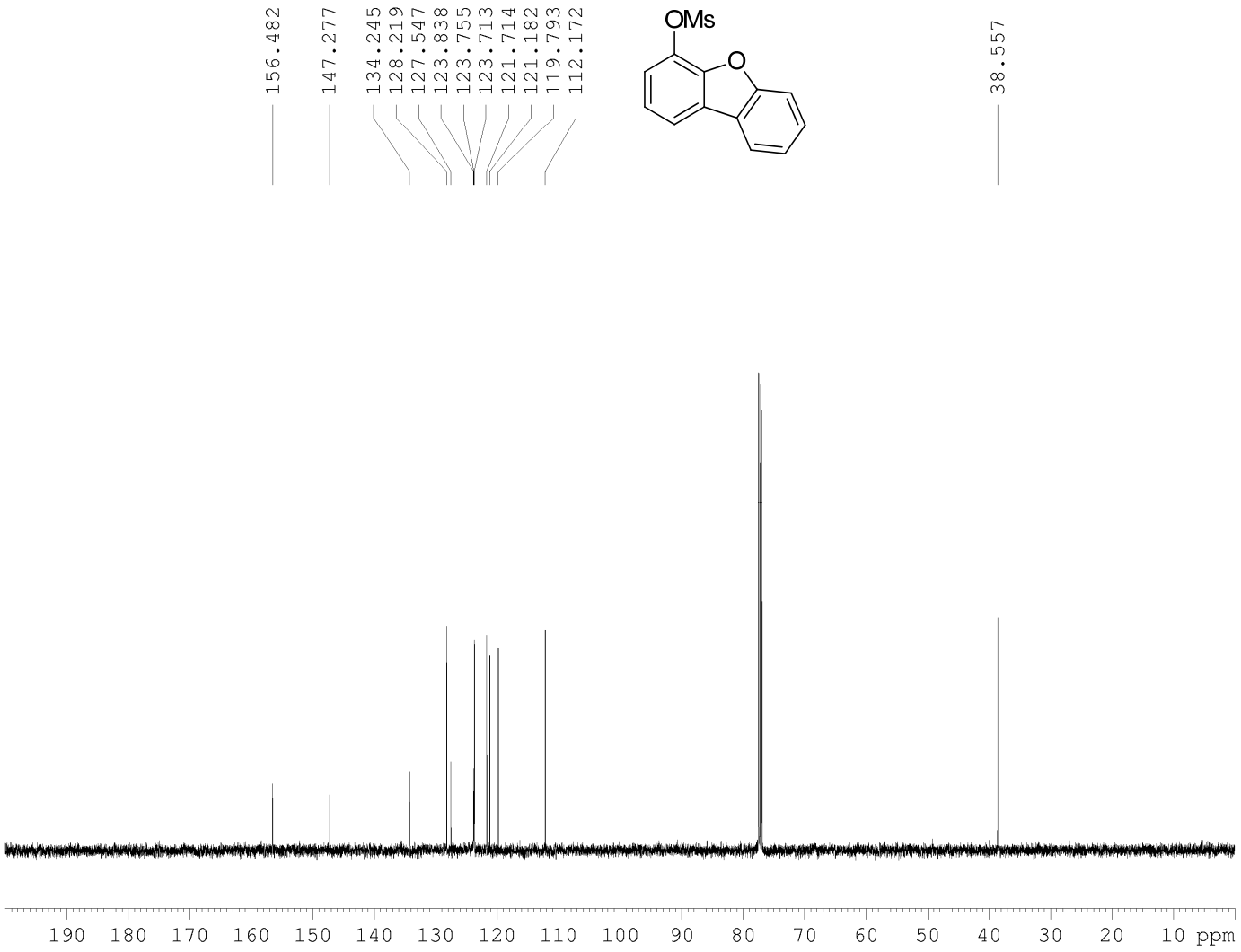
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 6-((benzyloxy)methyl)quinoline **5a** (Table 4, entry 1)



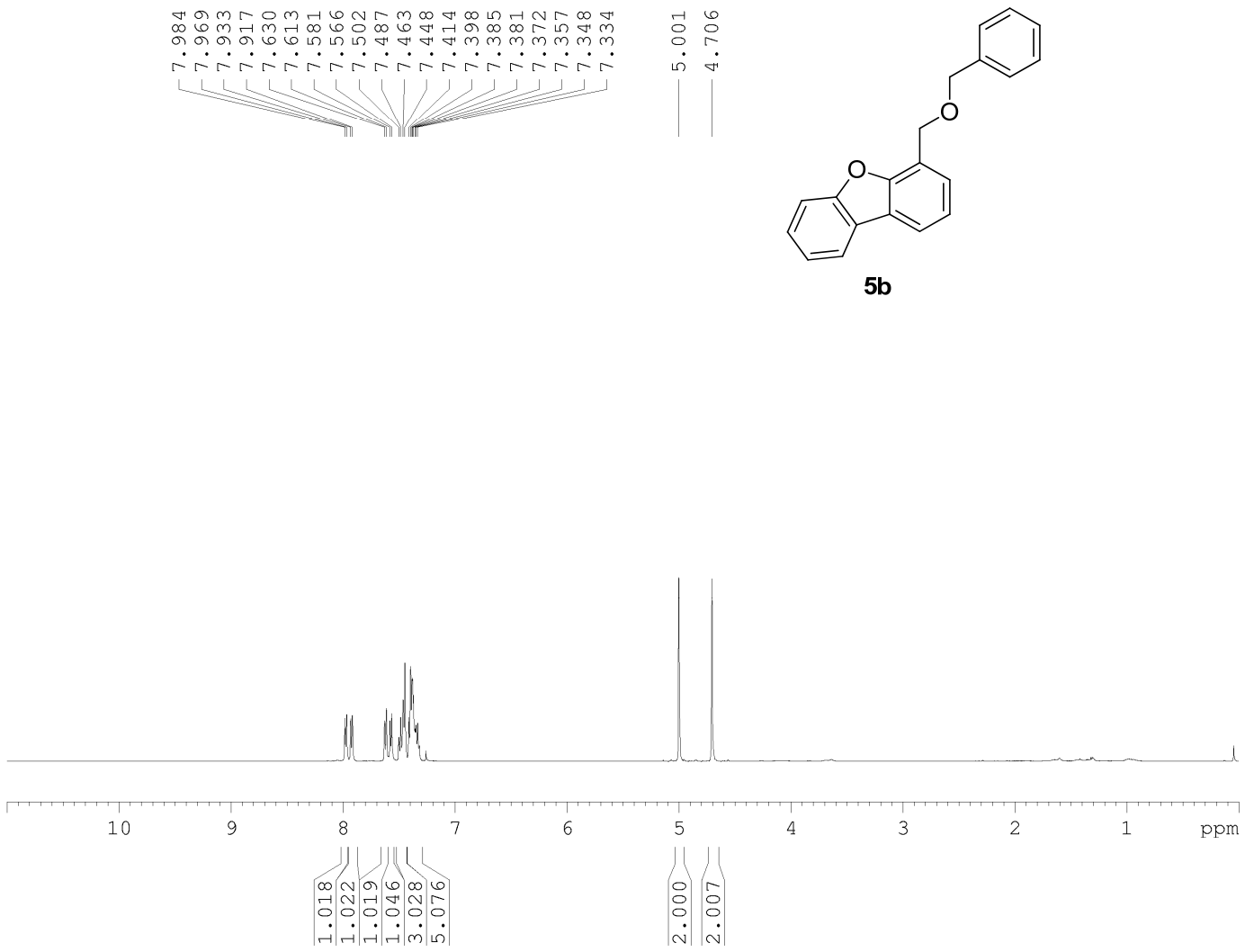
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 6-((benzyloxy)methyl)quinoline **5a** (Table 4, entry 1)



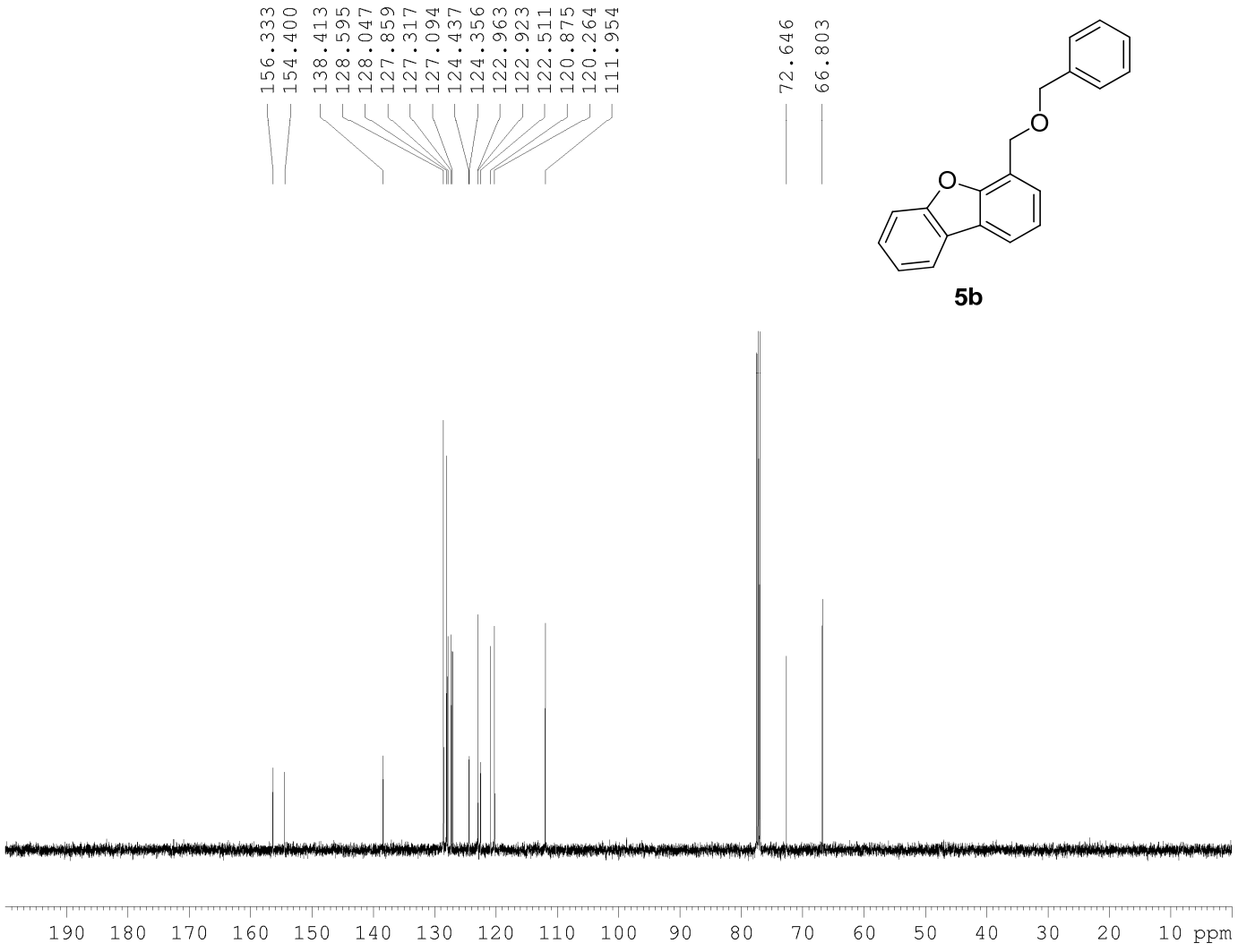
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of dibenzo[b,d]furan-4-yl methanesulfonate



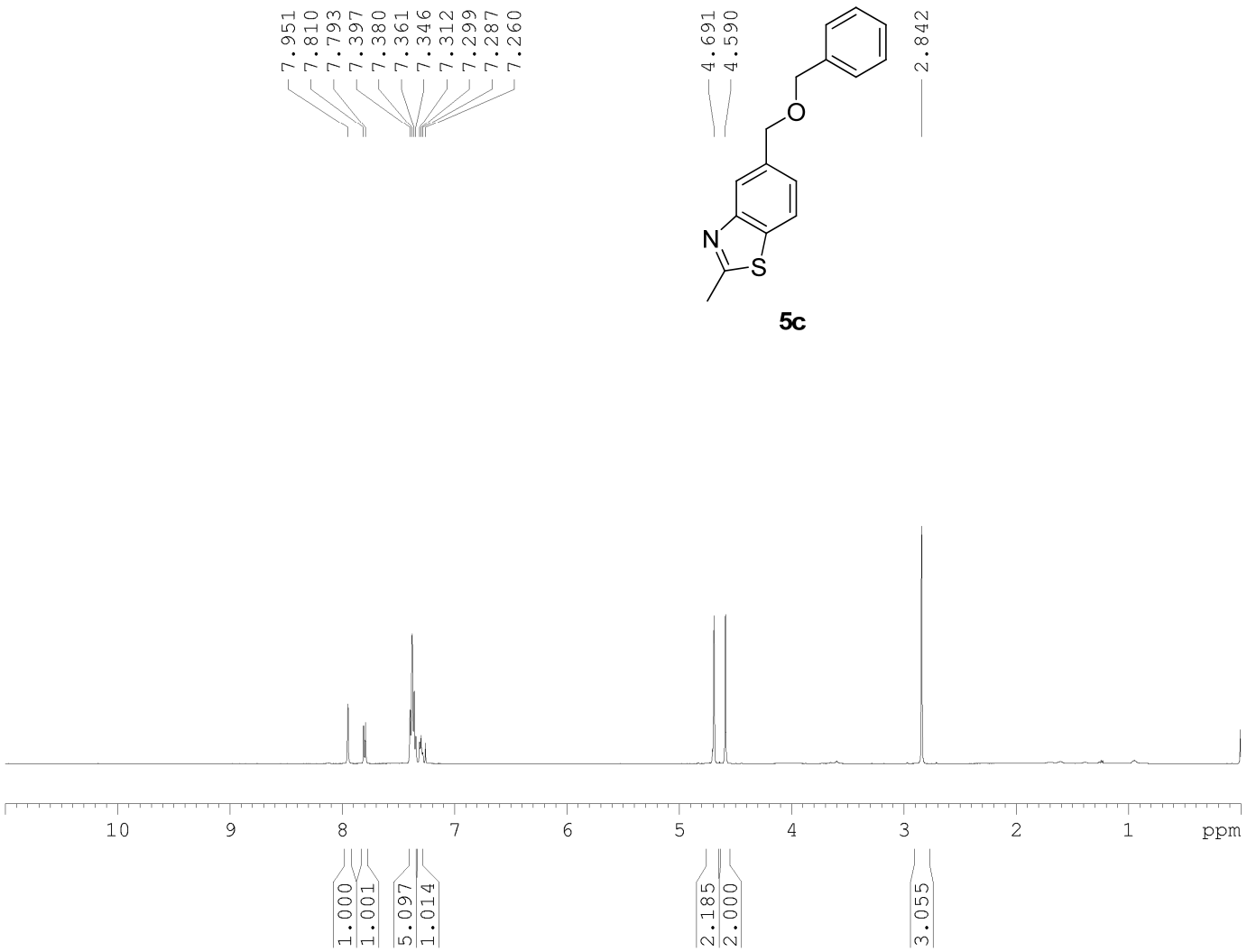
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of dibenzo[b,d]furan-4-yl methanesulfonate



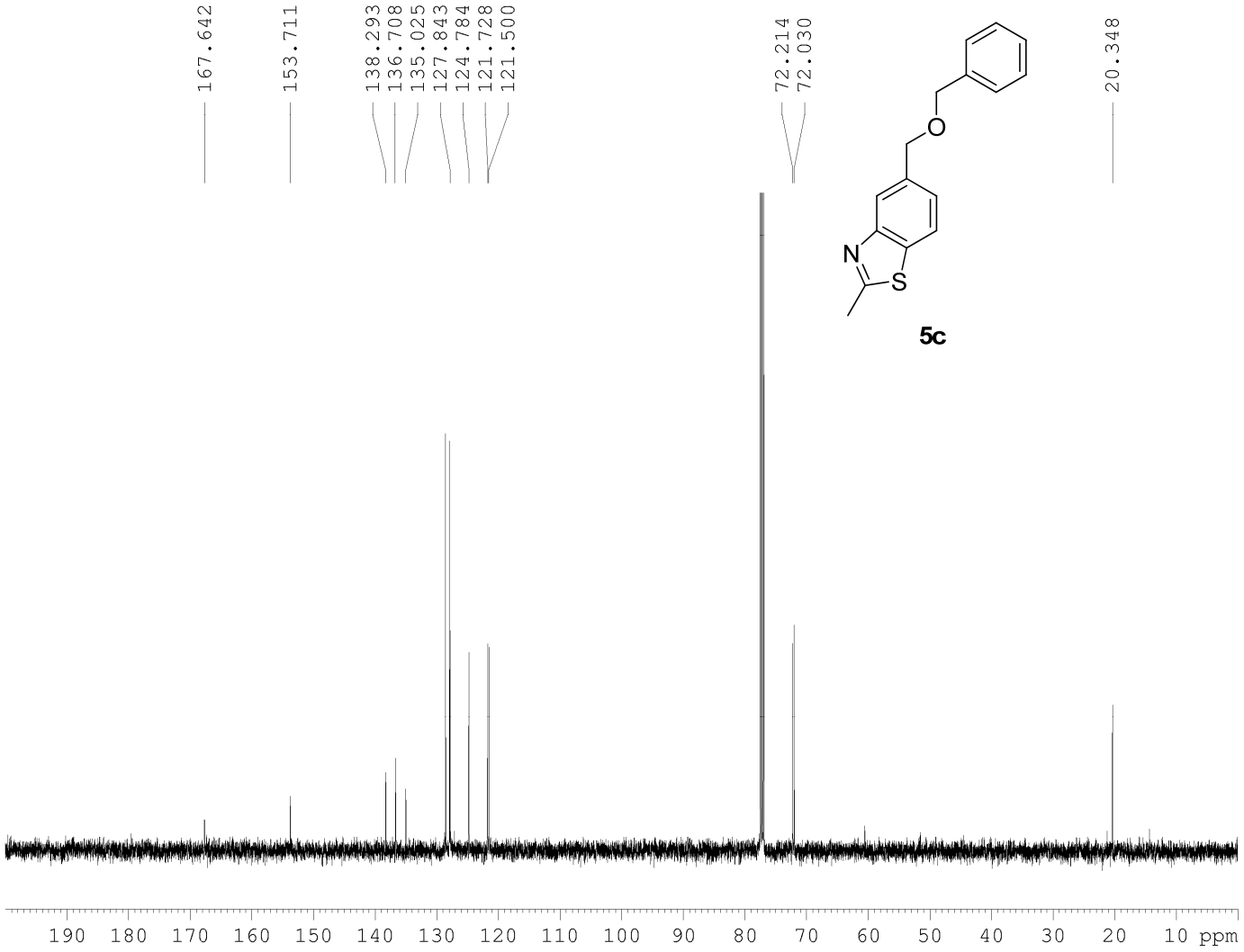
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 4-((benzyloxy)methyl)dibenzo[b,d]furan **5b** (Table 4, entry 2)



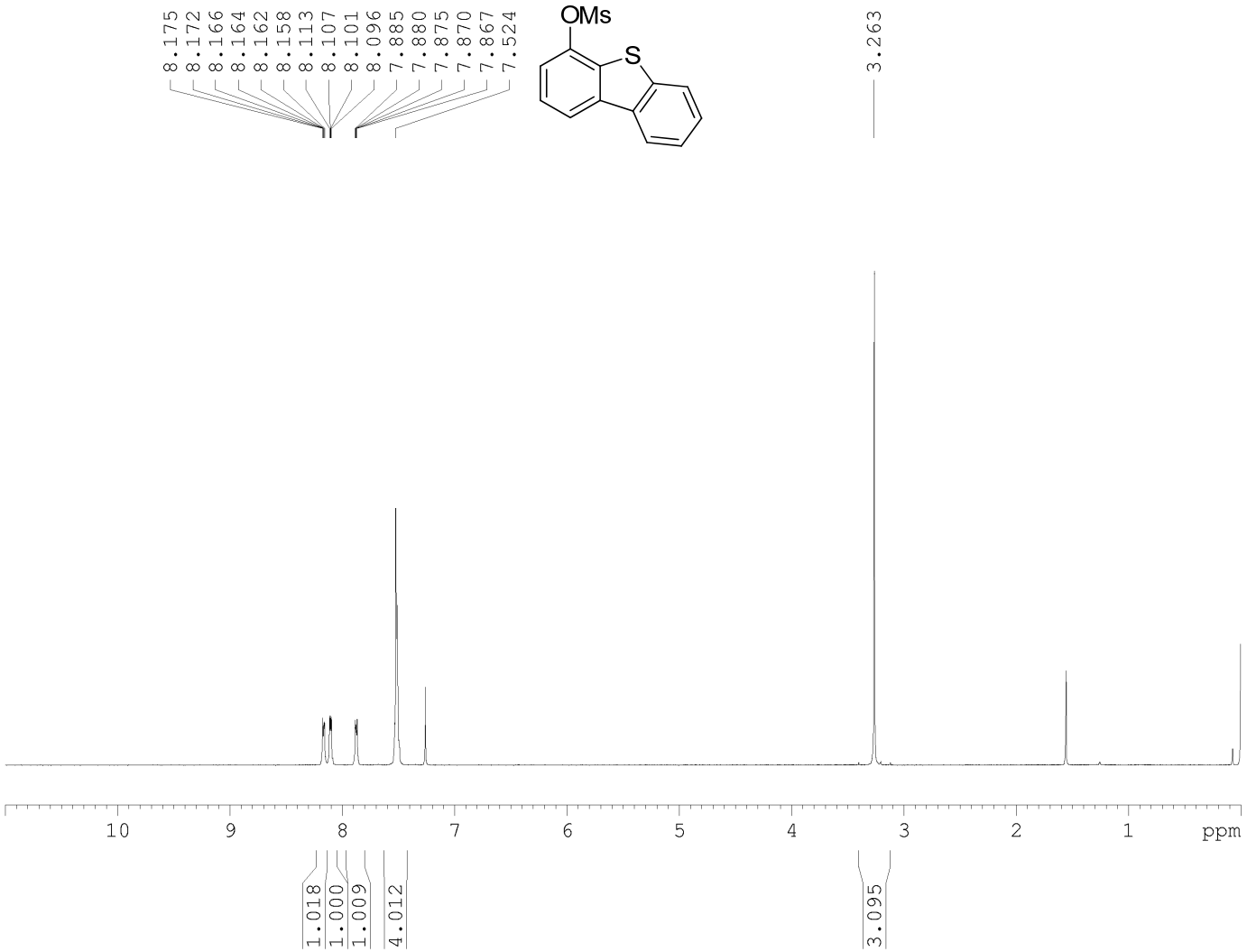
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 4-((benzyloxy)methyl)dibenzo[b,d]furan **5b** (Table 4, entry 2)



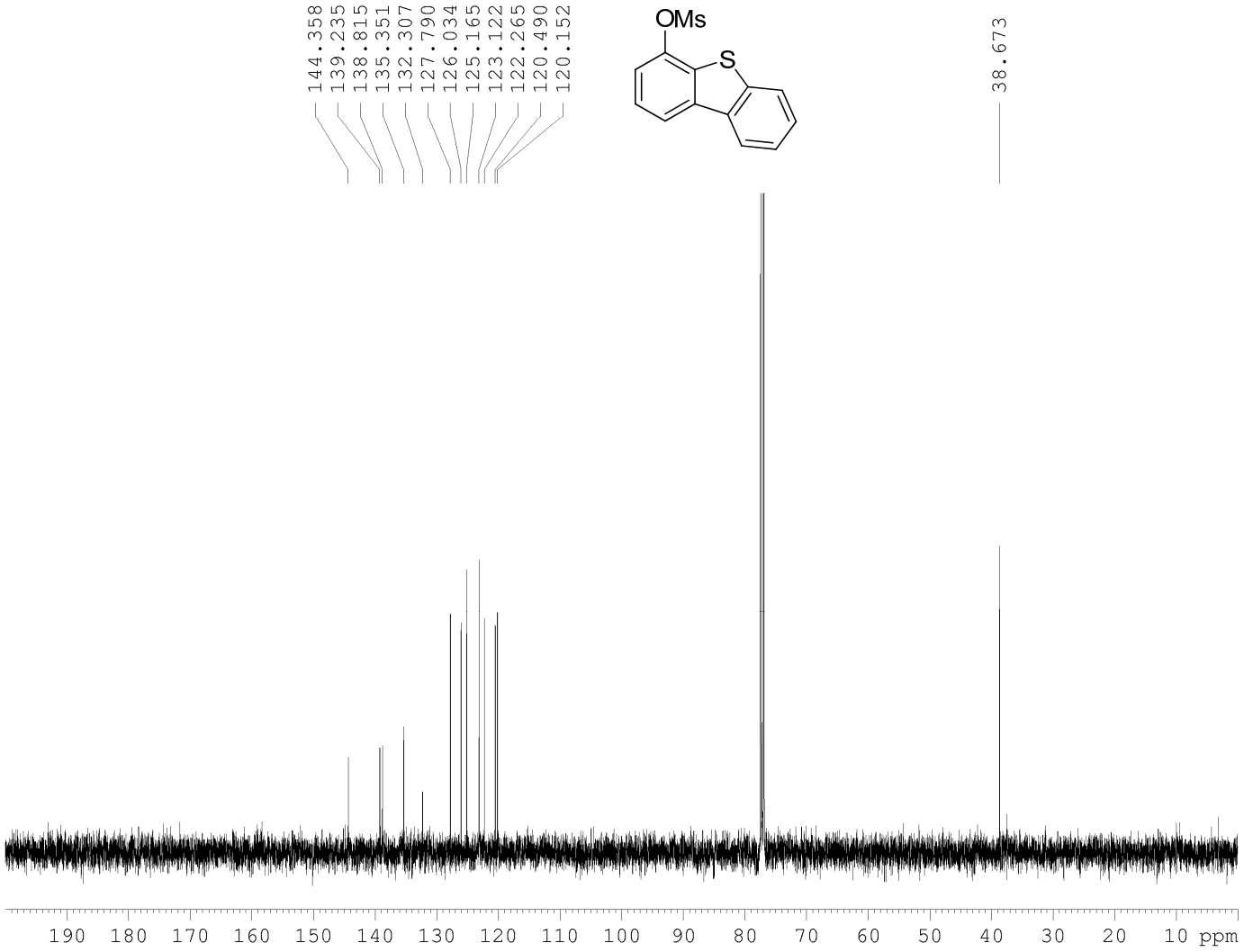
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 5-((benzyloxy)methyl)-2-methylbenzo[d]thiazole **5c** (Table 4, entry 3)



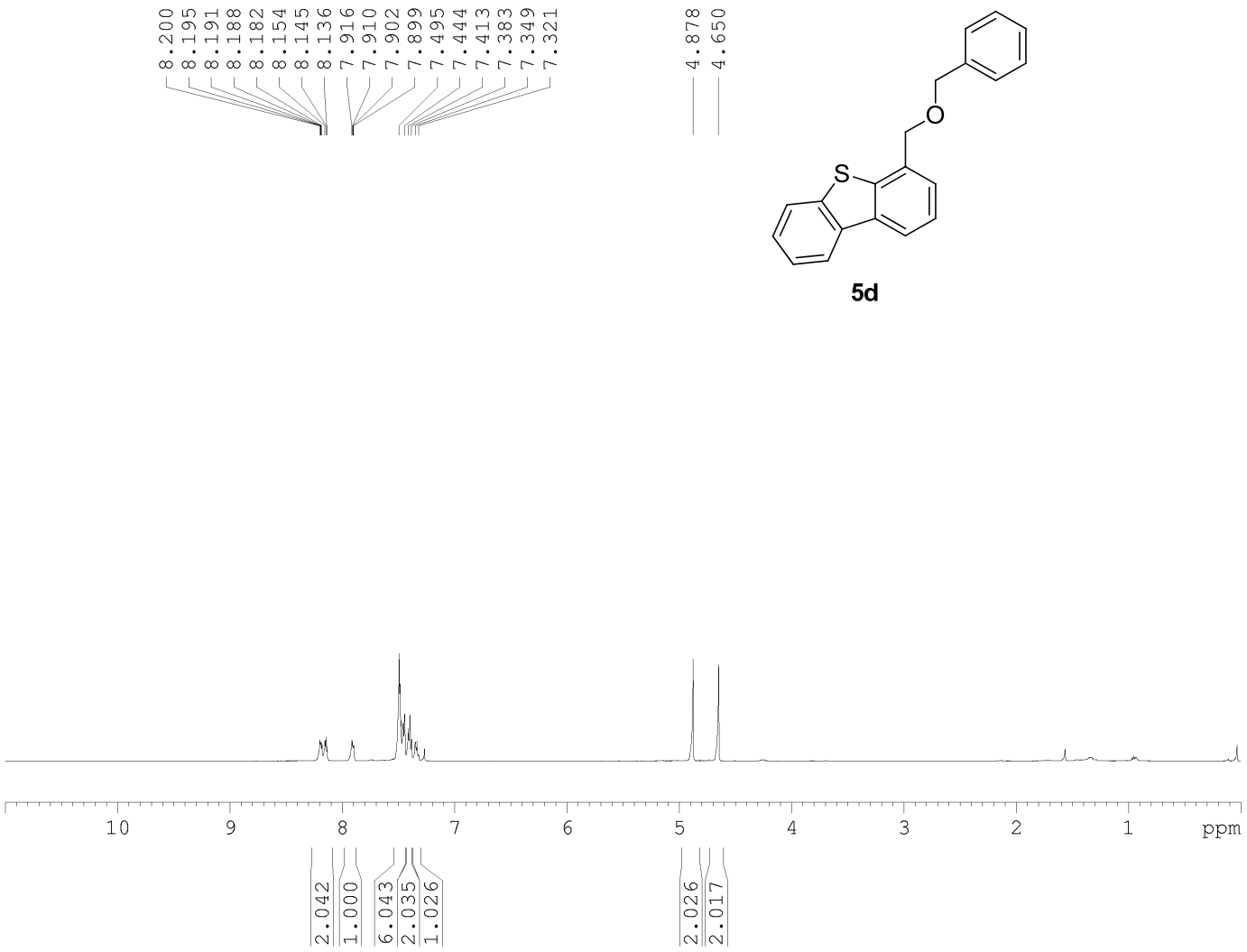
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 5-((benzyloxy)methyl)-2-methylbenzo[d]thiazole **5c** (Table 4, entry 3)



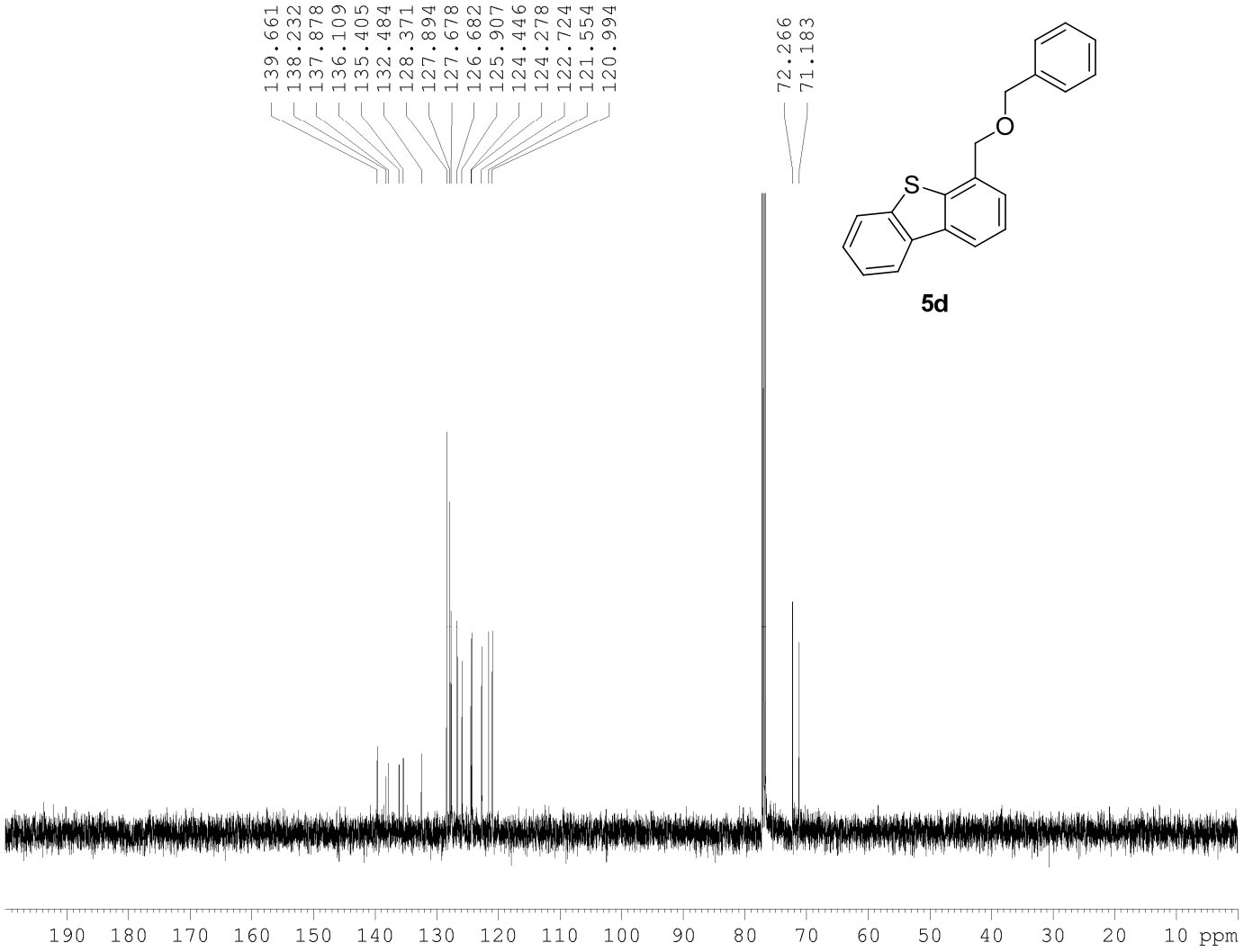
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of dibenzo[b,d]thiophen-4-yl methanesulfonate



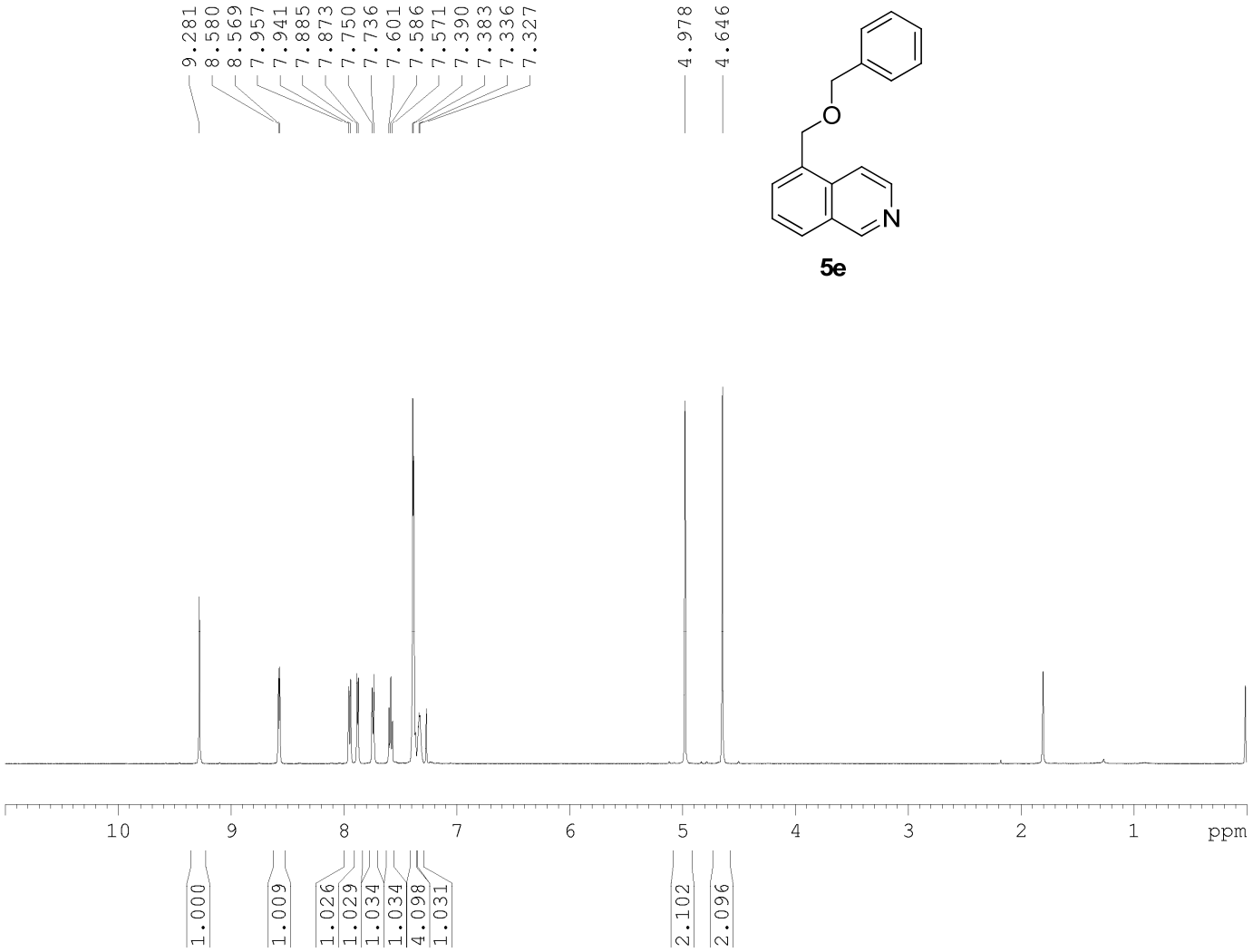
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of dibenzo[b,d]thiophen-4-yl methanesulfonate



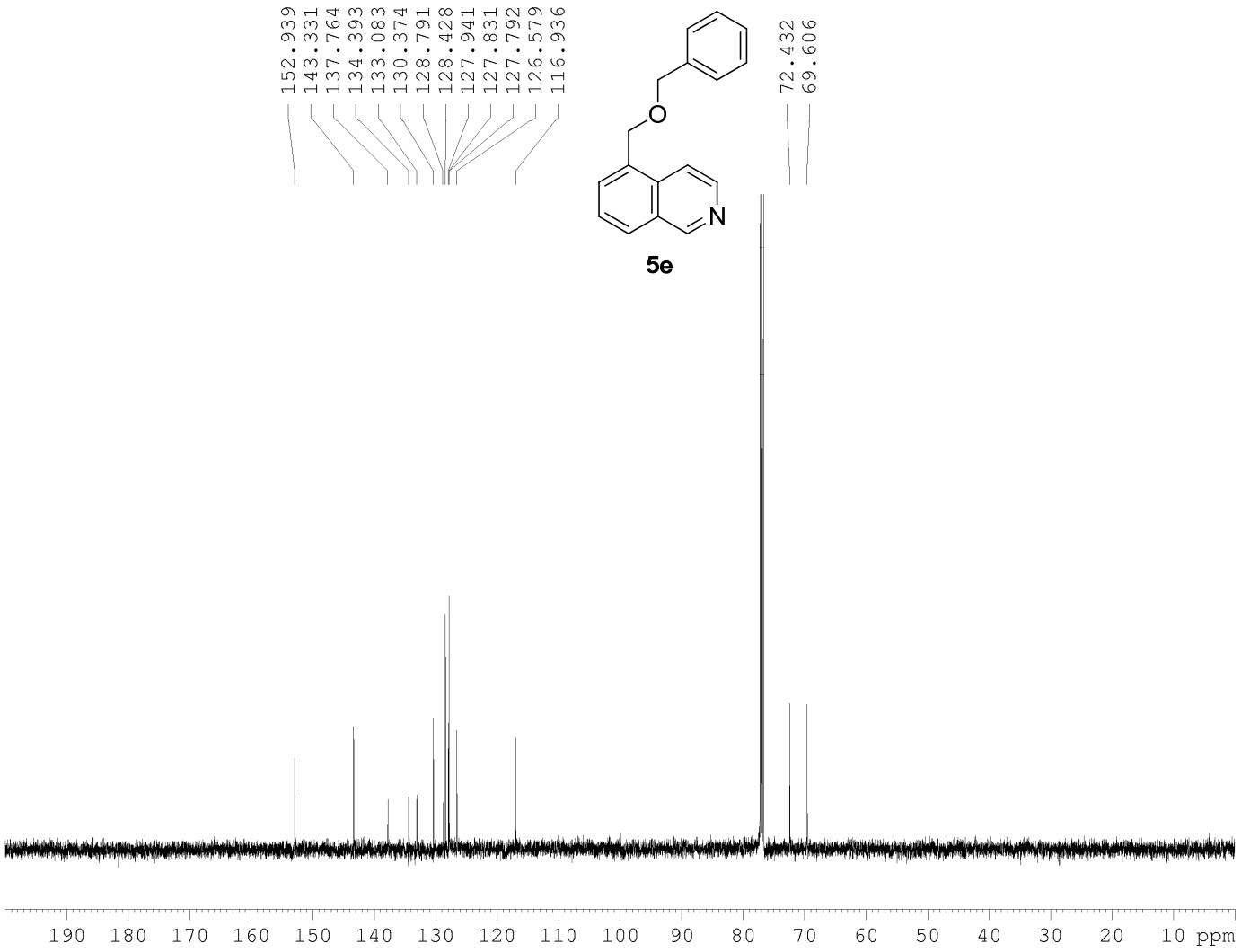
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 4-((benzyloxy)methyl)dibenzo[b,d]thiophene **5d** (Table 4, entry 4)



^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 4-((benzyloxy)methyl)dibenzo[b,d]thiophene **5d** (Table 4, entry 4)



^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 5-((benzyloxy)methyl)isoquinoline **5e** (Table 4, entry 5)



^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 5-((benzyloxy)methyl)isoquinoline **5e** (Table 4, entry 5)