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Supporting Information

Intramolecular Asymmetric Cyclopropanation Using Air Stable Alkylboronic Esters

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General information

Techniques

Unless otherwise stated, all reactions were performed under positive nitrogen pressure in oven- or flame dried glassware. To reach –78 °C, a bath of dry ice in acetone was used. To reach –100 °C, a slush bath of ethanol cooled with liquid nitrogen was used. Thin layer chromatography (TLC) was performed on *Macherey-Nagel* glass backed 0.25 mm silica gel 60 with fluorescent indicator UV 60. Visualization under UV light (254 nm) or by staining with a solution of potassium permanganate [$KMnO_4$ (3 g), K_2CO_3 (20 g) and NaOH 5% (3 mL) in H_2O (300 mL)] or Ceric Ammonium Molybdate [$(NH_4)_2MoO_4$ (15.0 g), $Ce(SO_4)_2$ (0.5 g), H_2O (90 mL), conc. H_2SO_4 (10 mL) and subsequent heating. Flash column chromatography (FC) was performed using Macherey-Nagel Silica 60, 0.04– 0.063 mm.

Material

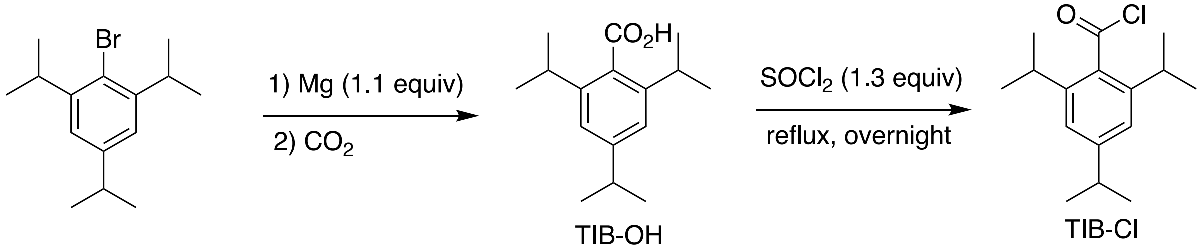
Et_2O, toluene, benzene, CH_2Cl_2, and THF were filtered over aluminum oxide under positive argon pressure. α,α,α-Trifluorotoluene (TFT) was filtered over a column of aluminum oxide and stored over 3Å molecular sieves. Solvents for extractions and flash column chromatography were of technical grade and distilled prior to use. All reagents and chemicals were commercial and used without further purification, unless otherwise stated.

Instrumentation

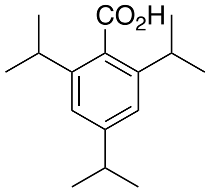
^{1}H, ^{13}C, and ^{11}B spectra were recorded on a Bruker Avance IIIHD-300 spectrometer. Some spectra were recorded on either a Bruker Avance IIIHD-400 or a Bruker Avance II-400 spectrometer. Chemical shifts (δ) are reported in ppm using the residual solvent signal or $Si(CH_3)_4$ as a standard. Coupling constants (*J*) are reported in Hz. Following abbreviations were used for the multiplicities: singlet (s), doublet (d), triplet (t), quartet (q), pentuplet (p), multiplet (m). The carbon α to the boron atom is sometimes not visible due to quadrupolar coupling. Infrared spectra were recorded on a Jasco FT-IR-460 plus spectrometer equipped with a Specac MKII Golden Gate Single Reflection Diamond ATR system. Only prominent peaks are reported (in cm^{-1}). GC analyses were performed using a Thermo Electron trace GC ULTRA fitted with a Macherey-Nagel Optima delta-3-0.25 µm capillary column (20 m, 0.25 mm). Gas carrier: He 1.4 mL/min; injector: 220 °C split mode; detector: FID 280 °C, H_2 35 mL/min, air 350 mL/min. GC yields were determined using dodecane as an internal standard. HPLC was performed using an Agilent Technologies 1260 Infinity. HRMS analysis were performed on a Thermo Scientific LTQ Orbitrap XL mass spectrometer using ESI and NSI mode. Melting points were measured on a Büchi B-545 melting point apparatus. Specific rotation $[\alpha]_D^{20}$ was measured on a Schmidt + Haensch Polartronic H 532 at 589 nm and corrected to c = 1.

Reagents and additives

Preparation of 2,4,6-triisopropylbenzoyl chloride (TIB-Cl)



2,4,6-Triisopropylbenzoic acid (TIB-OH)

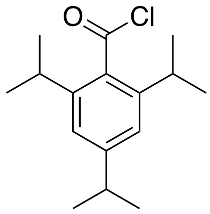


$C_{16}H_{24}O_2$
MW: 248.3660

Magnesium turnings (3.16 g, 130 mmol, 1.30 equiv) and a small crystal of I_2 were added to a flask fitted with a pressure equalizing addition funnel. Dry THF (5 mL) was added to cover the turnings. To start the reaction, a few drops of ethylene dibromide were added, and the reaction mixture was gently heated. Once bubbles were observed indicating the reaction had started, a solution of 2-bromo-1,3,5-triisopropyl-benzene (28.3 g, 100 mmol, 1.00 equiv) in dry THF (100 mL) was added *via* the addition funnel at such a rate that the reaction was sustaining a gentle reflux due to its exothermicity. Once the reaction was complete, it was cooled down to −78 °C. Carbon dioxide was bubbled through the reaction mixture (exothermic reaction). After 40 min at −78 °C the reaction was complete. The reaction mixture was allowed to reach rt and it was carefully quenched with 4 M HCl (100 mL). The phases were separated, and the aqueous phase was extracted with Et_2O (3 × 30 mL). The Organic phases were washed with sat. aq. NH_4Cl (30 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give crude TIB-OH as a white solid. The crude product was recrystallized from heptane to give 2,4,6-triisopropylbenzoic acid TIB-OH (21 g, 85%) as a white crystalline solid.

^1H NMR (300 MHz, $CDCl_3$) δ 7.04 (s, 2H), 3.05 (hept, J = 6.9 Hz, 2H), 2.90 (hept, J = 6.9 Hz, 1H), 1.27 (m, 18H). ^{13}C NMR (75 MHz, C_6D_6) δ 176.9, 150.5, 145.2, 130.0, 121.0, 34.5, 31.8, 24.0, 23.7. Mp: 187.8−189 °C. Analytical data are in accordance with the literature.[1]

2,4,6-Triisopropylbenzoyl chloride (TIB-Cl)



$C_{16}H_{23}ClO$
MW: 266.8090

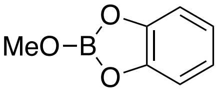
To 2,4,6-triisopropylbenzoic acid (12.4 g, 50.0 mmol, 1.00 equiv) was added thionyl chloride (5.00 mL, 68.5 mmol, 1.37 equiv) and the reaction was heated to 80 °C (reflux) overnight. After cooling down, the resulting solid was dissolved in Et_2O, washed successively with 0.1M NaOH (10 mL) and with saturated aq. NH_4Cl (10 mL). The organic phase was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Residual water was co-evaporated with benzene to give 2,4,6-triisopropylbenzoyl chloride TIB-Cl (13.1 g, 98%) as a yellowish solid.

To distinguish the chloride from the acid, ^{13}C NMR is best suited.

^1H NMR is possible but should be performed in benzene d_6 as this results in a bigger difference in chemical shift. ^1H NMR (300 MHz, C_6D_6) δ 7.08 (s, 2H), 3.30 (hept, J = 6.8 Hz, 2H), 2.73 (hept, J = 7.0 Hz, 1H), 1.25 (d, *J* = 6.8 Hz, 12H), 1.17 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.3, 151.7, 143.2, 135.4, 121.5, 34.6, 31.6, 24.1, 24.0. Mp: 78−79.7 °C. Analytical data are in accordance with the literature.[2]

Additives for transesterification

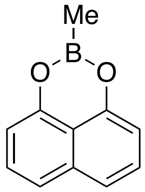
2-Methoxybenzo[*d*][1,3,2]dioxaborole (MeOBact)



$C_7H_7BO_3$
MW: 149.9400

2-methoxybenzo[d][1,3,2]dioxaborole was synthesized according to the literature procedure.[3]

3-Methyl-2,4-dioxa-3-boratricyclo[7.3.1.05,13]trideca-1(13),5,7,9,11-pentaene (MeBnap)

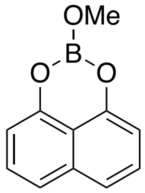


$C_{11}H_9BO_2$
MW: 184.0010

To a solution of 2,4,6-trimethyl-1,3,5,2,4,6-trioxatriborinane (0.14 mL, 1.0 mmol, 1.0 equiv) in pentane (5 mL), was added naphthalene-1,8-diol (481 mg, 3.00 mmol, 3.00 equiv). The resulting reaction mixture was stirred at rt for 2 h. The reaction mixture was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give MeBnap (431 mg, 78%) as a pink crystalline solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44–7.28 (m, 4H), 6.84 (dd, *J* = 7.2, 1.2 Hz, 2H), 0.61 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.7 (Cq_{Ar}), 135.1 (Cq_{Ar}), 127.9 ($2\times CH_{Ar}$), 121.0 ($2\times CH_{Ar}$), 109.2 ($2\times CH_{Ar}$), CH_3 signal not observed. ^{11}B NMR (96 MHz, $CDCl_3$) δ 32.65. Mp: 78.5–79.0 °C. IR (cm^{-1}): 2364, 2329, 1637, 1607, 1585, 1407, 1379, 1362, 1343, 1261, 1222, 1044, 887, 814, 753, 666, 628.

3-Methoxy-2,4-dioxa-3-boratricyclo[7.3.1.05,13]trideca-1(13),5,7,9,11-pentaene (MeOBnap)

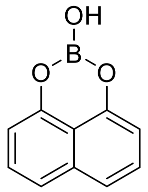


$C_{11}H_9BO_3$
MW: 200.0000

The titled product was prepared following a reported procedure.[4] Trimethyl borate (2.10 mL, 18.7 mmol, 3.00 equiv) was added to a solution of naphthalene-1,8-diol (1.00 g, 6.24 mmol, 1.00 equiv) in CH_2Cl_2 (10 mL) and the resulting reaction mixture was stirred at rt for 18 h. The reaction mixture was then concentrated under reduced pressure and the crude product was purified by kugelrohr distillation (120 °C, 5×10^{-2} mbar) to give MeOBnap (686 mg, 55%) as a crystalline yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.33 (dd, *J* = 8.4, 7.2 Hz, 2H), 6.87 (dd, *J* = 7.2, 1.2 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.7, 135.1, 127.7, 120.8, 116.1, 109.5, 51.9 (CH_3). ^{11}B NMR (96 MHz, $CDCl_3$) δ 19.0. Mp: 82.1−83.5 °C. Analytical data are in accordance with the literature.[4]

3-Hydroxy-2,4-dioxa-3-boratricyclo[7.3.1.05,13]trideca-1(13),5,7,9,11-pentaene (HOBnap)

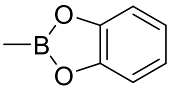


$C_{10}H_7BO_3$
185.97 g/mol

The titled product was prepared following a reported procedure.[4] Boric acid (386 mg, 6.24 mmol, 1.00 equiv) was added to a solution of naphthalene-1,8-diol (1.00 g, 6.24 mmol, 1.00 equiv) in MeCN (50 mL) and the resulting reaction mixture was stirred at 80 °C for 1.5 h. The reaction mixture was then allowed to reach rt and concentrated under reduced pressure. The residue was then re-dissolved in toluene (20 mL) and the solution was filtered through a plug of Na_2SO_4. Toluene was removed under reduced pressure to give the crude solid. Recrystallisation from heptanes/toluene (7:3) gave HOBnap (928 mg, 80%) as a white crystalline solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (dd, J = 8.4, 1.1 Hz, 1H), 7.34 (dd, J = 8.4, 7.2 Hz, 1H), 6.87 (dd, J = 7.3, 1.1 Hz, 1H), 4.19 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.6, 135.2, 127.9 (2×CH_{Ar}), 121.1 (2×CH_{Ar}), 116.2, 109.7 (2×CH_{Ar}). ^{11}B NMR (96 MHz, $CDCl_3$) δ 19.40. Mp: 221.9–223.3 °C. Analytical data are in accordance with the literature.[4]

2-Methyl-1,3,2-benzodioxaborole (MeBcat)

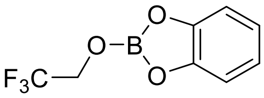


$C_7H_7BO_2$
133.94 g/mol

The titled product was prepared following a reported procedure.[5] Catechol (3.30 g, 3.00 mmol, 3.00 equiv.) was added to a solution of 2,4,6-trimethyl-1,3,5,2,4,6-trioxatriborinane (1.40 mL, 10.0 mmol, 1.00 equiv.) in pentane (40 mL) and the resulting reaction mixture was stirred until all solid was dissolved. The formed water was removed using a syringe and the organic phase was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give MeBcat (3.6 g, 90%) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24–7.18 (m, 2H), 7.10–7.04 (m, 2H), 0.80 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.4 (2×Cq_{Ar}), 122.6 (2×CH_{Ar}), 112.3 (2×CH_{Ar}). ^{11}B NMR (96 MHz, $CDCl_3$) δ 35.39. Analytical data are in accordance with the literature.[5]

2-(2,2,2-Trifluoroethoxy)-1,3,2-benzodioxaborole (CF_3CH_2OBcat)



$C_8H_6BF_3O_3$
217.94 g/mol

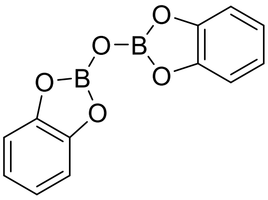
Catecholborane (1.06 mL, 10.0 mmol, 1.00 equiv) was added dropwise to a solution of 2,2,2-trifluoroethanol (0.73 mL, 10.0 mmol, 1.00 equiv) in dry, degassed benzene (10 mL), leading to hydrogen evolution. The reaction was stirred for 2h at rt and the solvent was removed under reduced pressure to give CF_3CH_2OBcat as a clear liquid. *This compound proved to be very sensitive, and it could not be exposed to ambient air. IR and HRMS data could not be measured.* ^{1}*H and* ^{19}*F NMR spectra showed signals in a 5.5 :1 ratio and the* ^{11}*B spectra shows two peaks (with one major one). It is suspected that the product may form dimers.*

Major product: ^{1}H NMR (300 MHz, C_6D_6) δ 6.89–6.82 (m, 2H), 6.78–6.67 (m, 2H), 3.76 (q, J = 8.4 Hz, 2H). ^{13}C NMR (75 MHz, C_6D_6) δ 147.9 (bs, Cq_{Ar}), 128.6 (2×CH_{Ar}), 123.7 (q, J = 278 Hz, $\underline{C}F_3$), 122.9 (2×CH_{Ar}), 112.6 (bs), 63.04 (q, J = 36.7 Hz, $\underline{C}H_2CF_3$). ^{11}B NMR (96 MHz, C_6D_6) δ 23.18. ^{19}F NMR (282 MHz, C_6D_6) δ –76.23 (t, J = 8.3 Hz).

Minor product (characteristic signals): ^{1}H NMR (300 MHz, C_6D_6) δ 3.60 (q, J = 8.4 Hz).

^{11}B NMR (96 MHz, C_6D_6) δ 17.33. ^{19}F NMR (282 MHz, C_6D_6) δ –76.47 (t, J = 8.7 Hz).

2-(1,3,2-Benzodioxaborol-2-yloxy)-1,3,2-benzodioxaborole (O(Bcat)$_2$)

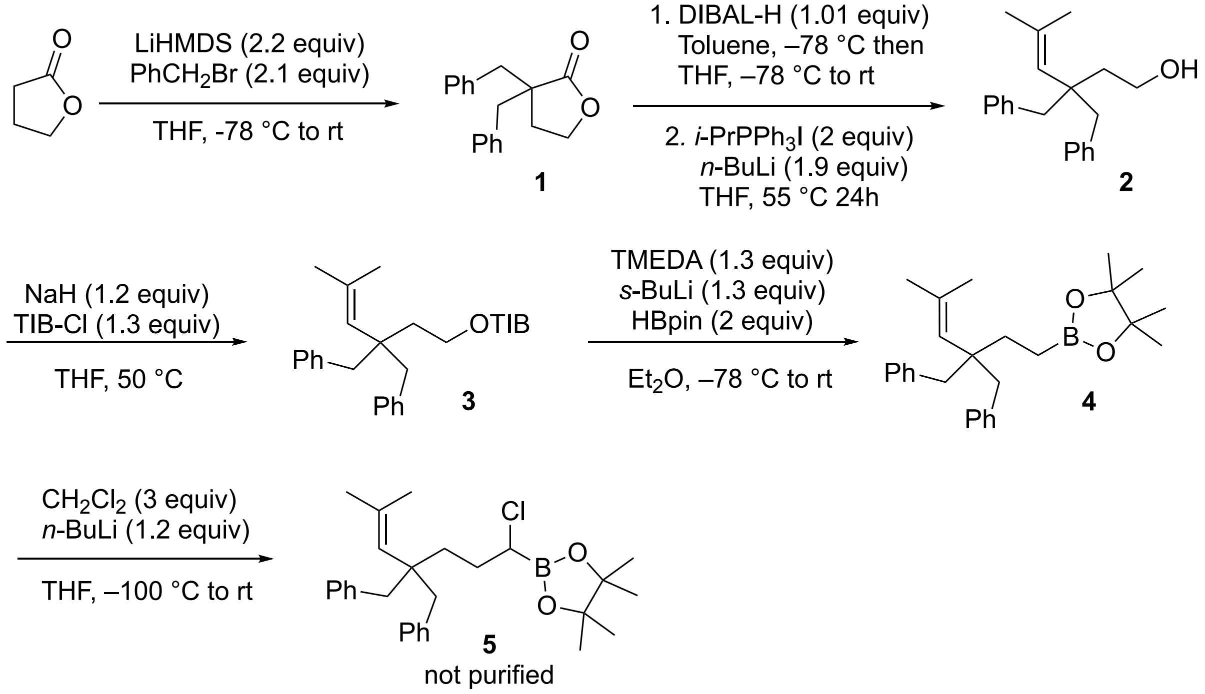


$C_{12}H_8B_2O_5$
253.81 g/mol

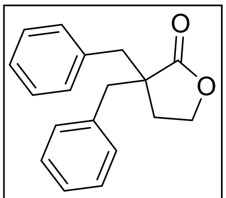
Catechol was recrystallized from toluene ca. (100 g / 600 mL) prior to use. The titled product was prepared following a reported procedure.[6] Catechol (22.0 g, 200 mmol, 1.00 equiv), boric acid (12.4g, 200 mmol, 1.00 equiv) and benzene (100 mL) were added to a flask fitted with a Dean-Stark apparatus. The reaction was refluxed until no more water was liberated (ca. 9 mL). Benzene was removed under reduced pressure to give a crude white solid. The crude product was purified by kugelrohr distillation (200 °C, 2×10^{-1} mBar) to give O(Bcat)$_2$ (14.5 g, 57%) as a white, crystalline solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25–7.20 (m, 4H), 7.13–7.07 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.7, 123.1, 112.7. ^{11}B NMR (96 MHz, $CDCl_3$) δ 22.45. Mp: 147−147.9 °C. Analytical data are in accordance with the literature.[6]

Synthesis of acyclic precursors 4 and 5



3,3-Dibenzyldihydrofuran-2(3H)-one (1)

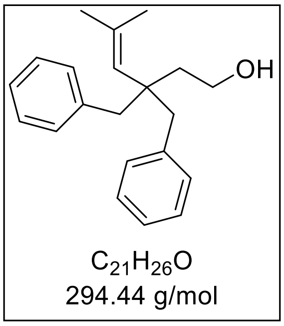


$C_{18}H_{18}O_2$
266.34 g/mol

The titled product was prepared following a procedure adapted from the literature.[7] To a solution of LiHMDS (100 mL, 100 mmol, 2.20 equiv, 1 M in THF) was added at −78 °C a solution of tetrahydrofuran-2-one (3.40 mL, 45.0 mmol, 1.00 equiv) in THF (10 mL). The resulting reaction mixture was stirred for 10 min at −78 °C then benzyl bromide (11.2 mL, 94.5 mmol, 2.10 equiv) was added dropwise (slowly). The reaction mixture was allowed to reach rt and was stirred for 2 h at rt. The reaction was quenched with water and the aqueous phase was extracted with Et_2O (3 × 50 mL). The organic phases were washed with brine (1 ×50 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give a crude yellow solid. The crude product was recrystallized from heptanes (500 mL) to give **1** as off-white crystals (10.91 g, 91%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40–7.23 (m, 10H), 3.39 (t, *J* = 7.4 Hz, 2H), 3.23 (d, *J* = 13.4 Hz, 2H), 2.81 (d, *J* = 13.4 Hz, 2H), 2.18 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.2 (C=O), 136.6 (Cq_{Ar}), 130.3 (2×CH_{Ar}), 128.7 (2×CH_{Ar}), 127.3 (CH_{Ar}), 65.4, 49.9, 44.0, 29.2. Mp: 135.6–136.3 °C. Analytical data are in accordance with the literature.[7]

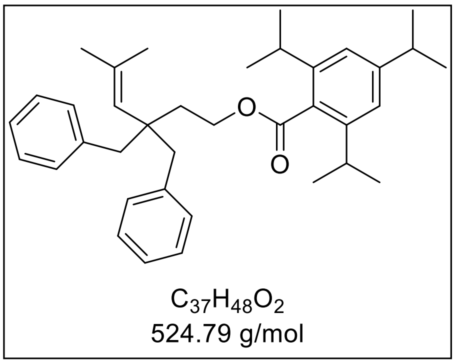
3,3-Dibenzyl-5-methyl-hex-4-en-1-ol (2)



DIBAL-H (40.4 mL, 1 M in toluene, 40.4 mmol, 1.01 equiv) was added slowly to a suspension of 3,3-dibenzyltetrahydrofuran-2-one **1** (10.6 g, 40.0 mmol, 1.00 equiv) in dry toluene (200 mL) at −78 °C *(the internal temperature should not exceed −70 °C).* The reaction mixture was stirred at −78 °C until no starting material was observed (TLC monitoring). The reaction mixture clears up once it is close to being complete (approximately after 1.5 h). Dry THF (80 mL) was added at −78 °C and the dry ice bath was removed (*It is important not to let the reaction mixture warm up without additional THF as this leads to reduction of the lactol)*.

Simultaneously, in a second reaction flask, *n*-BuLi (31.2 mL, 2.5 M in hexane, 78.0 mmol 1.95 equiv) was slowly added at 0 °C to a suspension of isopropyl(triphenyl)phosphonium iodide (34.6 g, 80.0 mmol, 2.00 equiv) in THF (150 mL). Upon addition, the reaction mixture turned deep red. The reaction mixture was allowed to reach rt and stirred for 1 h. The previously prepared solution of aluminium lactolate was added to the ylide via cannula. The reaction vessel, in which the aluminium lactolate was prepared, was washed with additional dry THF (50 mL). The resulting reaction mixture was stirred overnight at 55 °C. The reaction mixture was quenched with 0.5 M HCl (200 mL), and the phases were separated. The aqueous phase was extracted with Et_2O (3 × 150 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated to give the crude product. The crude product was purified by FC on silica gel (pentane/Et_2O 7:3) to give **2** (10.0 g, 85%) as a clear oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26–7.13 (m, 10H), 5.06–5.04 (m, 1H), 3.70 (dt, J = 7.7, 5.1 Hz, 2H), 2.80 (d, *J* = 13.5 Hz, 2H), 2.72 (d, *J* = 13.5 Hz, 2H), 1.78–1.73 (m, 3H), 1.71 (d, *J* = 1.4 Hz, 3H), 1.40 (d, *J* = 1.3 Hz, 3H), 1.13 (t, *J* = 5.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.7, 133.3, 131.0, 129.5, 127.9, 126.2, 77.6, 77.2, 76.7, 60.1, 46.0, 43.2, 39.1, 28.7, 19.4. IR (cm^{-1}): 3303, 3024, 2922, 1599, 1495, 1452, 1181, 1075, 1031, 998, 911, 832. HRMS (ESI): Calculated for $C_{21}H_{26}ONa$ $[M+Na]^+$: 317.1876; found: 317.1877

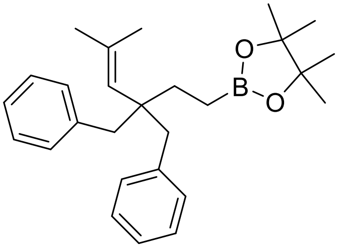
(3,3-Dibenzyl-5-methyl-hex-4-enyl) 2,4,6-triisopropylbenzoate (3)



NaH (1.45 g, 34.7 mmol, 55% in mineral oil, 1.20 equiv) was added to a solution of 3,3-dibenzyl-5-methyl-hex-4-en-1-ol 2 (8.60 g, 28.9 mmol, 1.00 equiv) in THF (30 mL). The resulting reaction mixture was stirred for 1 h at rt, then TIB-Cl (8.49 g, 8.68 mmol, 1.20 equiv) was added and the reaction mixture was heated at 55 °C and stirred at this temperature overnight. The reaction mixture was quenched with water (30 mL) and stirred for 2 h to hydrolyze unreacted TIB-Cl. The phases were separated, and the aqueous phase was extracted with Et_2O (3 × 20 mL). The combined organic phases were washed with brine (30 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give a yellow oil. The crude product was purified by FC on silica gel (heptanes/toluene 7:3 to 6:4) to give **3** (12.4 g, 82%) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37–7.09 (m, 10H), 6.98 (s, 2H), 5.09–5.07 (m, 1H), 4.44–4.34 (m, 2H), 2.92–2.76 (m, 3H), 2.85 (d, *J* = 13.5 Hz, 2H), 2.76 (d, *J* = 13.5 Hz, 2H), 1.97–1.83 (m, 2H), 1.73 (d, *J* = 1.4 Hz, 3H), 1.33 (d, *J* = 1.3 Hz, 3H), 1.23 (d, *J* = 7.0 Hz, 6H), 1.21 (d, *J* = 6.9 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.0, 150.2, 144.8, 138.4, 133.8, 131.4, 130.8, 128.6, 127.9, 126.3, 121.0, 62.6, 46.1, 43.1, 34.6, 34.3, 31.6, 28.7, 24.3, 24.1, 19.2. IR (cm^{-1}): 2959, 2926, 2869,1800, 1723, 1605, 1456, 1384, 1362, 1249, 1137, 1101, 1072, 966, 876, 749, 700. HRMS (ESI): Calculated for $C_{37}H_{48}O_2Na$ [M+Na]$^+$: 547.3547; found: 547.3528.

2-(3,3-Dibenzyl-5-methyl-hex-4-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4)

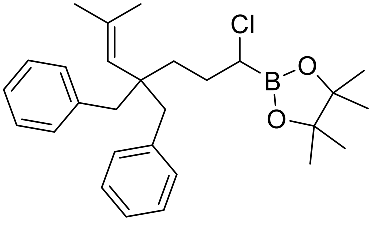


$C_{27}H_{37}BO_2$
404.40 g/mol

The titled product was prepared following a procedure adapted from the literature.[8] TMEDA (2.34 mL, 15.6 mmol, 1.30 equiv) was added to a solution of (3,3-dibenzyl-5-methyl-hex-4-enyl) 4-ethyl-2,6-diisopropyl-benzoate **3** (6.36 mg, 12.0 mmol, 1.00 equiv) in dry Et_2O (100 mL). The solution was cooled to −78 °C and *s*-BuLi (11.1 mL, 15.6 mmol, 1.4 M in cyclohexane, 1.30 equiv) was added slowly. The reaction mixture was stirred at −78 °C for 1 h and a solution of pinacolborane (3.48 mL, 24.0 mmol, 2.00 equiv) in dry Et_2O (18 mL) was then added. The resulting reaction mixture was stirred at −78 °C for 1 h, then allowed to reach rt and stirred overnight. The reaction mixture was carefully quenched with saturated aq. $NaHCO_3$ (50 mL) and the phases were separated. The aqueous phase was extracted with Et_2O (2 × 30 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by FC on silica gel (heptane/toluene 6:4 to 3:7) to give **4** (3.4 g, 71%) as a clear oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28–7.12 (m, 10H), 4.94–4.93 (m, 1H), 2.81 (d, *J* = 13.5 Hz, 2H), 2.71 (d, *J* = 13.5 Hz, 2H), 1.69 (d, *J* = 1.4 Hz, 3H), 1.56–1.48 (m, 2H), 1.45 (d, *J* = 1.3 Hz, 3H), 1.22 (s, 12H), 0.91–0.79 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.4, 132.4, 131.1, 130.0, 127.7, 125.8, 83.0, 44.8, 44.2, 29.9, 28.7, 24.9, 19.5. ^{11}B NMR (96 MHz, $CDCl_3$) δ 34.31. IR (cm^{-1}): 3027, 2975, 2925, 2868, 1453, 1369, 1315, 1144, 1077, 1031, 967, 884, 848, 750, 726, 697. HRMS (ESI): Calculated for $C_{27}H_{38}O_2B$ [M+H]$^+$: 405.2959; found: 405.2948.

2-(4,4-Dibenzyl-1-chloro-6-methyl-hept-5-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5)[9,10]



$C_{28}H_{38}BClO_2$
452.87 g/mol

To a solution of dry CH_2Cl_2 (0.38 mL, 6.0 mmol, 3.0 equiv.) in THF (12 mL) was added slowly *n*-BuLi (0.96 mL, 2.5 M in hexane, 2.40 mmol, 1.20 equiv) at a temperature that should not exceed −100 °C. The resulting reaction mixture was stirred at below −100 °C for 30 min and a solution of 2-(3,3-dibenzyl-5-methyl-hex-4-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **4** (816 mg, 2.00 mmol, 1.00 equiv) in dry THF (4 mL) was then added. The resulting reaction mixture was allowed to reach rt and stirred for 20 h. Dry toluene (10 mL) was added, and the solvent were removed under reduced pressure. The residue was re-dissolved in toluene and filtered through a syringe filter. The filtrate was concentrated under reduced pressure to give **5** (860 mg, 95%, crude) that was used in the next step without further purification. *Purification by FC was not possible due to the unstable nature of this molecule.*

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29–7.12 (m, 10H), 5.00–4.99 (m, 1H), 3.31 (t, *J* = 7.4 Hz, 1H), 2.84 (d, *J* = 13.5 Hz, 1H), 2.83 (d, *J* = 13.5 Hz, 1H), 2.73 (d, *J* = 13.5 Hz, 1H), 2.71 (d, *J* = 13.5 Hz, 1H), 1.96 (dt, *J* = 9.6, 7.5 Hz, 2H), 1.71 (d, *J* = 1.4 Hz, 3H), 1.53–1.44 (m, 2H), 1.41 (d, *J* = 1.3 Hz, 3H), 1.21 (s, 6H), 1.21 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.90, 138.86, 133.0, 131.06, 131.04, 129.8, 127.83, 127.78, 126.06, 126.02, 84.5, 45.1, 43.9, 33.9, 29.6, 28.7, 24.74, 24.68, 19.5. ^{11}B NMR (96 MHz, $CDCl_3$) δ 32.72.

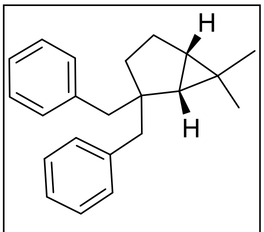
Intramolecular cyclopropanation

Thermal intramolecular cyclopropanation

Preparative cyclopropanation

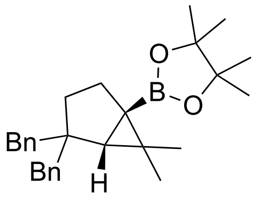
(±)-(1*SR*,5*SR*)-2,2-Dibenzyl-6,6-dimethylbicyclo[3.1.0]hexane ((±)-6) and 2-((1*SR*,5*SR*)-4,4-dibenzyl-6,6-dimethylbicyclo[3.1.0]hexan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((±)-7)

To a solution of dry CH_2Cl_2 (0.35 mL, 5.4 mmol) in THF (10 mL) was added slowly *n*-BuLi (0.87 mL, 2.5 M in hexane, 2.2 mmol) at such a rate that the internal temperature did not exceed −100 °C. The resulting reaction mixture was stirred below −100 °C for 30 min and a solution of 2-(3,3-dibenzyl-5-methyl-hex-4-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **4** (730 mg, 1.81 mmol) in dry THF (4 mL) was then added. The resulting reaction mixture was allowed to reach rt and stirred for 5 h. The solvents were removed under reduced pressure and toluene (20 mL), resulting in the precipitation of LiCl. The supernatant was transferred via cannula to a reaction flask containing potassium benzoate (265 mg, 1.8 mmol) and the reaction mixture was heated at 140 °C overnight (closed vessel). After cooling down, the solid residue was filtered off and the remaining solution was concentrated under reduced pressure. The residue was purified by FC (heptane/EtOAc 100:1 to 30:1)to give (±)-**6** (368 mg, 1.27 mmol, 70% yield) as alear liquid that solidified in the fridge. A second fraction containing (±)-**7** (9 mg, 0.18 mmol, 10% yield) was also isolated. Recrystallization from hexane/Et_2O gave single crystals of (±)-**7** suitable for X-ray diffraction analysis.



$C_{22}H_{26}$
290.45 g/mol

(±)-**6**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35–7.13 (m, 10H), 2.85 (d, *J* = 13.1 Hz, 1H), 2.71 (d, *J* = 13.1 Hz, 1H), 2.62 (d, *J* = 12.9 Hz, 1H), 2.45 (d, *J* = 12.9 Hz, 1H), 1.80–1.69 (m, 1H), 1.44–1.24 (m, 2H), 1.21 (s, 3H), 1.01 (s, 3H), 0.91–0.73 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.7 (Cq_{Ar}), 140.0 (Cq_{Ar}), 130.8 (2×CH_{Ar}), 130.5 (2×CH_{Ar}), 128.0 (2×CH_{Ar}), 127.7 (2×CH_{Ar}), 126.0 (CH_{Ar}), 125.8 (CH_{Ar}), 49.7, 48.0, 45.7, 39.7, 36.9, 31.5, 29.5, 25.1, 20.5, 17.3. Mp: 46.8–47.7 °C. IR (cm^{-1}): 3021, 2999, 2943, 2913, 2859, 1602, 1494, 1452, 1373, 1186, 1126, 1076, 1031, 778, 754, 738, 702, 639. HRMS (ESI): Calculated for $C_{22}H_{27}$ $[M+H]^+$: 291.2107, found: 291.2108.



$C_{28}H_{37}BO_2$
416.41

(±)-**7**: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.35 – 7.14 (m, 10H), 2.93 – 2.69 (m, 2H), 2.63 – 2.46 (m, 2H), 1.83 – 1.69 (m, 1H), 1.58 – 1.25 (m, 4H), 1.21 (s, 6H), 1.17 (s, 3H), 1.13 (d, *J* = 3.4 Hz, 9H); ^{11}B NMR (96 MHz, CD_2Cl_2) δ 34.15; ^{13}C NMR (75 MHz, CD_2Cl_2) δ 141.11, 140.18, 131.41, 131.03, 128.35, 128.31, 126.34, 126.21, 83.26, 50.70, 48.09, 46.25, 45.25, 36.75, 27.77, 27.48, 26.92, 25.99, 24.76, 18.83; HRMS (ESI-Orbitrap) *m/z* calculated for $C_{28}H_{38}O_2B$ $[M+H]^+$: 417.2959, found: 417.2951.

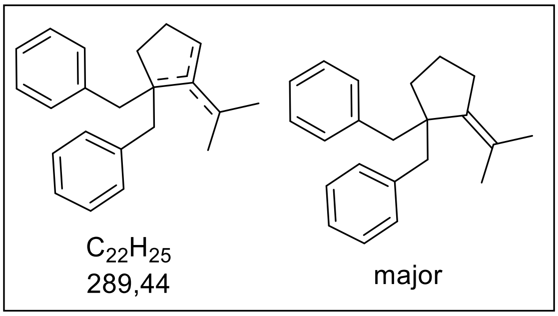
Transesterification mediated intramolecular cyclopropanation

Effect of additives

Procedure to test additives

To a solution of 2-(4,4-dibenzyl-1-chloro-6-methyl-hept-5-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **5** (226 mg, 0.5 mmol) in the respective solvent (5 mL), the addititives were added. The reaction mixture was stirred at 70 °C for 20 h, cooled down to rt and concentrated under reduced pressure. The crude product was purified by FC on silica gel (pentane).

Reaction of 6 with HCl: ((2-(propan-2-ylidene)cyclopentane-1,1-diyl)bis(methylene))dibenzene (8)



A suspension of (±)-(1*SR*,5*SR*)-2,2-dibenzyl-6,6-dimethylbicyclo[3.1.0]hexane ((±)-**6**) (73 mg, 0.25 mmol) in HCl (2.5 mL, 3 M in methanol) was heated to reflux for 6 h. The reaction mixture was treated with saturated aq. $NaHCO_3$ (5 mL) and the phases were separated. The aqueous phase was extracted with Et_2O (2 × 5 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by FC on silica gel (pentane) to give a mixture of olefinic products **8** that could not be separated.

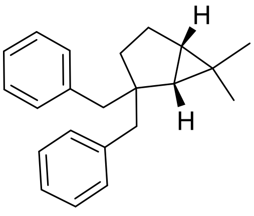
Characteristic NMR signals of major isomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.07 (m), 3.16 (d, *J* = 13.3 Hz, 2H), 2.78 – 2.69 (m, 2H), 1.98 (t, *J* = 1.9 Hz, 3H), 1.94 – 1.88 (m, 2H), 1.70 (s, 3H), 1.61 (t, *J* = 7.0 Hz, 2H), 0.95 (t, *J* = 7.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.9, 122.9, 50.8, 44.8, 36.6, 34.4, 23.7, 22.3, 21.3.

Preparative cyclopropanation

(±)-(1*SR*,5*SR*)-2,2-Dibenzyl-6,6-dimethylbicyclo[3.1.0]hexane ((±)-6) and 4,4-dibenzyl-7-hydroxy-2-methylheptan-3-one (9)

To a solution of dry CH_2Cl_2 (0.39 mL, 6.0 mmol) in THF (15 mL) was added slowly *n*-BuLi (0.96 mL, 2.5 M in hexane, 2.40 mmol) at such a rate that the internal temperature did not exceed −100 °C. The resulting reaction mixture was stirred below −100 °C for 30 min and a solution of 2-(3,3-dibenzyl-5-methyl-hex-4-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **4** (810 mg, 2.00 mmol) in dry THF (5 mL)

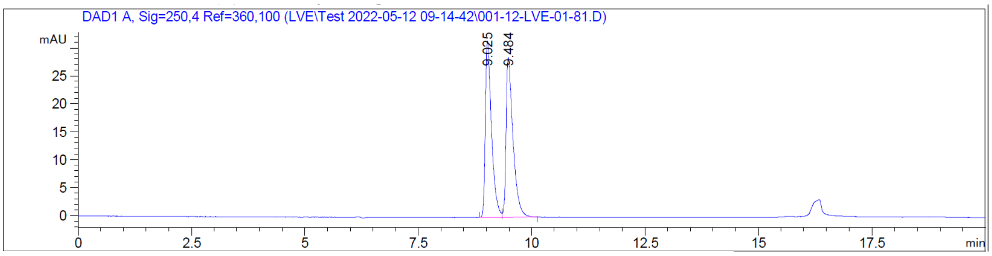


$C_{22}H_{26}$
290.45 g/mol

was then added. The resulting reaction mixture was allowed to reach rt and stirred for 5 h. The solvents were removed under reduced pressure and the residue was re-dissolved in TFT (20 mL), resulting in the precipitation of the LiCl. The solution was then transferred via cannula to a reaction flask containing $O(Bcat)_2$ (1.02 g, 4.00 mmol), removing LiCl from the reaction mixture, and the resulting reaction mixture was stirred at 70 °C for 20 h. The reaction mixture was then cooled down to rt and concentrated under reduced pressure. The crude product was purified by FC on silica gel (pentane) to give the desired (±)-6 containing some olefinic impurities that could be removed by ozonolysis.

Ozonolysis: Product (±)-**6**, contaminated with olefinic impurities, was dissolved $MeOH/CH_2Cl_2$ (6 mL, 1:5) and the reaction mixture cooled to −78 °C. Ozone was bubbled through the solution until the colour of the reaction mixture turned light blue. Nitrogen was then bubbled through for 15 min to remove the excess of ozone and $NaBH_4$ (76 mg, 2.0 mmol) was carefully added at –78 °C. The reaction mixture was allowed to reach rt and stirred at this temperature for 3 h. The reaction mixture was then quenched with water (2 mL), followed by saturated aq. $NaHCO_3$ (2 mL). The phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (2 × 5 mL). The combined organic phases were washed with saturated aq. NH_4Cl (5 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by FC on silica gel (pentane/Et_2O 100:0 to 70:30) to give **6** (314 mg, 54%) as a clear oil, which crystallized in the fridge. A second fraction provided hydroxyketone **9** (71 mg, 11%) as a clear oil.

(±)-**6**: Identical to the product describe above under thermal conditions. The enantiomeric ratio ((1*S*,5*S*)/(1*R*,5*R*) 50:50) was determined by chiral HPLC: CHIRALPAK IB-3; 100% hexane; 0.7 mL/min; λ= 210 nm



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Signal 1: DAD1 A, Sig=250,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   9.025 BV    0.1397  299.26758   31.53886  49.6019
   2   9.484 VB    0.1563  304.07098   28.53767  50.3981

Totals :                   603.33856   60.07653
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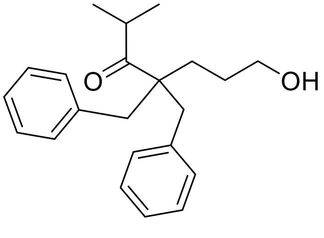


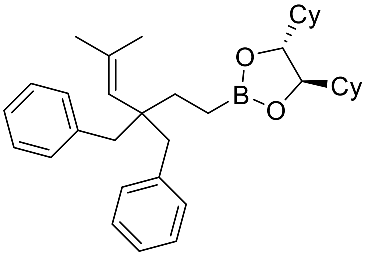
$C_{22}H_{28}O_2$
324.46 g/mol

9: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.14 (m, 6H), 7.09–7.05 (m, 4H), 3.67 (t, *J* = 6.4 Hz, 2H), 3.08 (d, *J* = 14.0 Hz, 2H), 2.93 (d, *J* = 14.0 Hz, 2H), 2.68 (hept, *J* = 6.8 Hz, 1H), 1.87–1.79 (m, 2H), 1.74–1.68 (m, 2H), 1.59 (bs, 1H), 0.72 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 219.2 (C=O), 137.7 (2×Cq_{Ar}), 130.5 (4×CH_{Ar}), 128.3 (4×CH_{Ar}), 126.6 (2×CH_{Ar}), 63.2 (CH_2), 57.4 (Cq), 41.2 (2×CH_2), 35.7 (CH), 27.9 (CH_2), 27.8 (CH_2), 19.3 (2×CH_3). HRMS (ESI): Calculated for $C_{22}H_{29}O_2$ $[M+H]^+$: 325.2164, found 325.2173.

Asymmetric intramolecular cyclopropanation: chiral auxiliary approach

Reactions starting from (+)-10

(+)-(4*R*,5*R*)-4,5-Dicyclohexyl-2-(3,3-dibenzyl-5-methyl-hex-4-enyl)-1,3,2-dioxaborolane ((+)-10)[11–13]

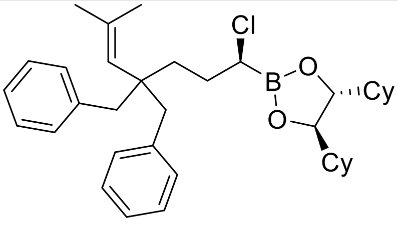


$C_{35}H_{49}BO_2$
512.59 g/mol

(1*R*,2*R*)-1,2-Dicyclohexylethane-1,2-diol (835 mg, 3.70 mmol, 1.20 equiv) and saturated aq. $NaHCO_3$ (0.9 mL) were added to a solution of 2-(3,3-dibenzyl-5-methyl-hex-4-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **5** (1.26 g, 3.07 mmol, 1.00 equiv) in THF (6 mL). The resulting reaction mixture was stirred overnight at rt. The reaction mixture was dried with Na_2SO_4, filtered, and concentrated under reduced pressure to give crude **10** as a clear oil. The crude product was purified by FC on silica gel (heptanes/toluene 8:2 to 7:3) to give (+)-**10** (1.1g, 72%) as a clear oil. The product contained some residual heptanes.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30–7.12 (m, 10H), 4.96–4.94 (m, 1H), 3.84–3.79 (m, 2H), 2.83 (d, *J* = 13.4 Hz, 1H), 2.83 (d, *J* = 13.5 Hz, 1H), 2.72 (d, *J* = 13.4 Hz, 2H), 1.79–1.58 (m, 9H), 1.71 (d, *J* = 1.4 Hz, 3H), 1.58–1.52 (m, 5H), 1.44 (d, *J* = 1.3 Hz, 3H), 1.38–0.85 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.3, 132.4, 131.1, 129.9, 129.2, 127.7, 125.8, 125.4, 83.4, 44.8, 44.3, 43.1, 30.2, 28.7, 28.5, 27.5, 26.6, 26.2, 26.1, 21.6, 19.5. ^{11}B NMR (96 MHz, $CDCl_3$) δ 33.61. $[\alpha]_D^{20}$ = +26 (c = 1.00, CH_2Cl_2). IR (cm^{-1}): 2922, 2851, 1495, 1450, 1390, 1361, 1309, 1232, 1171, 1076, 1030, 1017, 981, 890, 831, 749. HRMS (ESI): Calculated for $C_{35}H_{50}O_2B$ $[M+H]^+$: 513.3898, found: 513.3886.

(4*R*,5*R*)-4,5-Dicyclohexyl-2-((*S*)-4,4-dibenzyl-1-chloro-6-methylhept-5-en-1-yl)-1,3,2-dioxaborolane ((***S***)-11)[13–15]

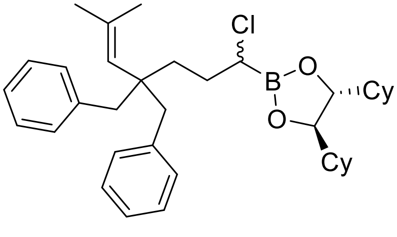


$C_{36}H_{50}BClO_2$
561.05 g/mol

To a solution of CH_2Cl_2 (0.17 mL, 2.70 mmol, 1.50 equiv.) in dry THF (15 mL) at –100 °C was added slowly *n*-BuLi (0.79 mL, 2.5 M in hexane, 2.00 mmol, 1.10 equiv) at such a rate that the internal temperature never exceeded –100 °C. The resulting reaction mixture was then stirred below–100 °C for 30 min and a solution of (4*R*,5*R*)-4,5-dicyclohexyl-2-(3,3-dibenzyl-5-methyl-hex-4-enyl)-1,3,2-dioxaborolane **10** (940 mg, 1.80 mmol, 1.00 equiv) in dry THF (5 mL) was the added. The resulting reaction mixture was stirred below −100 °C for 15 min then anhydrous $ZnCl_2$ (417 mg, 3.00 mmol, 1.70 equiv) was added in one portion. The resulting reaction mixture was stirred for 14 h at rt. Pentane (5 mL) was added, and the reaction mixture was carefully quenched with saturated aq. NH_4Cl (5 mL), followed by water (5 mL). The phases were separated, and the aqueous phase was extracted with pentane (2 × 10 mL). The combined organic phases were dried over Na_2SO_4 and filtered. Toluene (5 mL) was added (to remove residual THF) and the mixture was concentrated under reduced pressure. The resulting residue was re-dissolved in pentane (10 mL), which resulted in a slightly turbid solution. This solution was filtered through a syringe filter and concentrated to give **11**. The compound could not be purified by FC due to its instability on silica. *Since this compound is not stable for HPLC, the dr was determined via quantitative ^{13}C-NMR. Only peaks for one diastereoisomer were observed (vide infra).*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.10 (m, 10H), 5.00–4.98 (m, 1H), 3.92–3.88 (m, 2H), 3.31 (t, J = 7.5 Hz, 1H), 2.84 (d, J = 13.5 Hz, 1H), 2.82 (d, J = 13.4 Hz, 1H), 2.75 (d, J = 13.4 Hz, 1H), 2.69 (d, J = 13.5 Hz, 1H), 2.06–1.88 (m, 2H), 1.80–1.50 (m, 12H), 1.71 (d, J = 1.3 Hz, 3H), 1.47–0.88 (m, 12H), 1.40 (d, J = 1.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.87 (Cq_{Ar}), 138.83 (Cq_{Ar}), 132.9 (Cq), 131.1 (4×CH_{Ar}), 129.8 (=*C*H), 127.79 (2×CH_{Ar}), 127.75 (2×CH_{Ar}), 126.05 (CH_{Ar}), 126.01 (CH_{Ar}), 84.2 (2×CH), 45.3 (CH_2), 45.1 (CH_2), 44.0 (C_q), 42.9 (2×CH), 34.2 (CH_2), 29.8 (CH_2), 28.7 (CH_3), 28.3 (2×CH_2), 27.4 (2×CH_2), 26.5 (CH_2), 26.1 (CH_2), 25.98 (2×CH_2), 25.96 (2×CH_2), 19.5 (CH_3). ^{11}B NMR (96 MHz, $CDCl_3$) δ 31.25.

(4*R*,5*R*)-4,5-Dicyclohexyl-2-((*RS*)-4,4-dibenzyl-1-chloro-6-methylhept-5-en-1-yl)-1,3,2-dioxaborolane ((*RS*)-11)

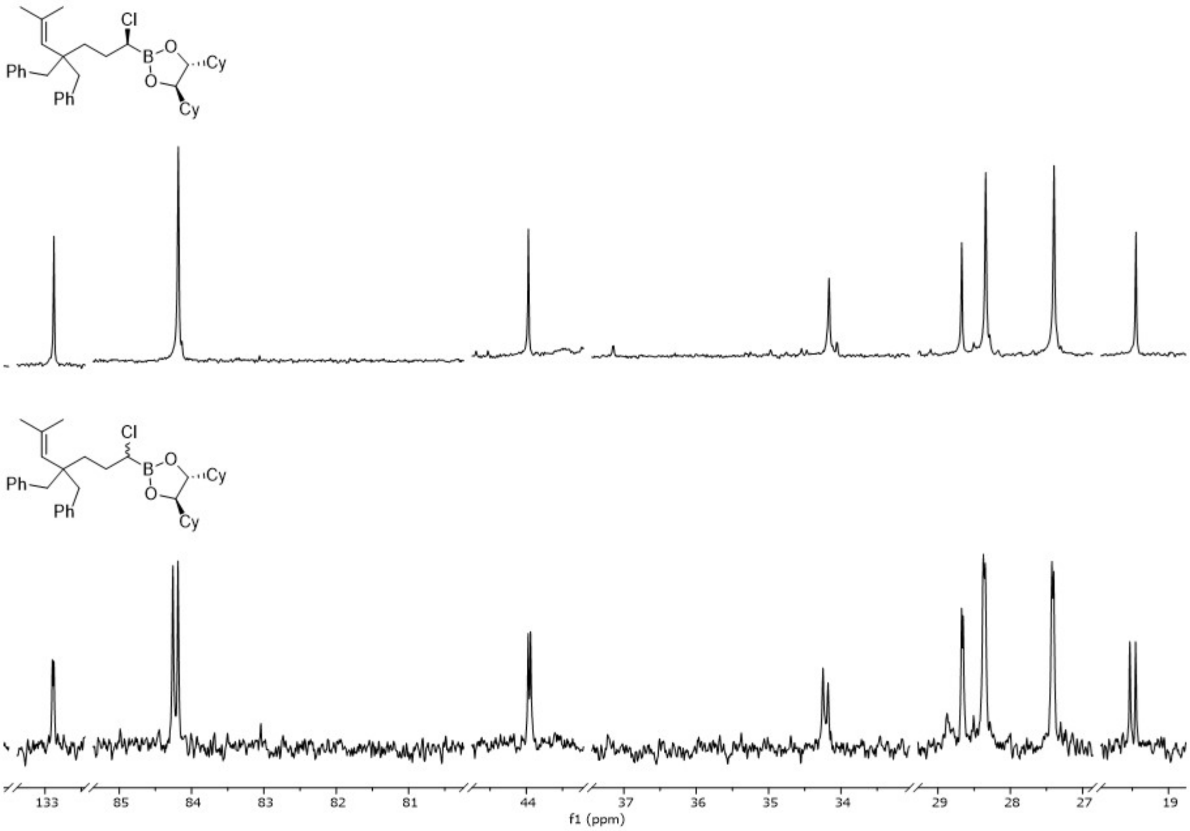


$C_{36}H_{50}BClO_2$
561.05 g/mol

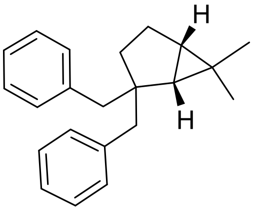
To a solution of racemic **5** (41.0 mg, 0.10 mmol, 1.00 equiv) in $CDCl_3$ (1.5 mL) was added (1*R*,2*R*)-1,2-dicyclohexylethane-1,2-diol (23.0 mg, 0.10 mmol, 1.00 equiv). The resulting reaction mixture was stirred at 60 °C for 6 h. The reaction mixture was cooled to rt, concentrated under reduced pressure to a volume of 0.5 mL and filtered through a syringe filter into an NMR tube. The crude mixture (*RS*)-**11** is as anticipated a 1:1 mixture of diastereomer. It was used without further purification for the intramolecular cyclopropanation step.

^{1}H NMR (300 MHz, $CDCl_3$, characteristic signals) δ 3.37 (t, J = 7.3 Hz, 1H), 3.31 (t, J = 7.6 Hz, 1H), 1.71 (d, J = 1.2 Hz, 3H), 1.42 (d, J = 1.3 Hz, 3H), 1.40 (d, J = 1.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.94, 138.88, 138.84, 132.90, 132.88, 131.05, 131.02, 130.99, 129.77, 127.84, 127.80, 127.76, 126.08, 126.05, 126.01, 84.26, 84.19, 45.29, 45.26, 45.19, 45.12, 43.97, 43.94, 42.93, 34.25, 34.18, 29.82, 29.74, 29.65, 28.67, 28.65, 28.37, 28.34, 27.43, 27.40, 26.58, 26.53, 26.33, 26.20, 26.07, 25.95, 25.00, 19.53, 19.45. ^{11}B NMR (96 MHz, $CDCl_3$) δ 31.8.

Selected ^{13}C signals of (*S*)-**11** (top) and a (*R*S)-**11** (bottom):



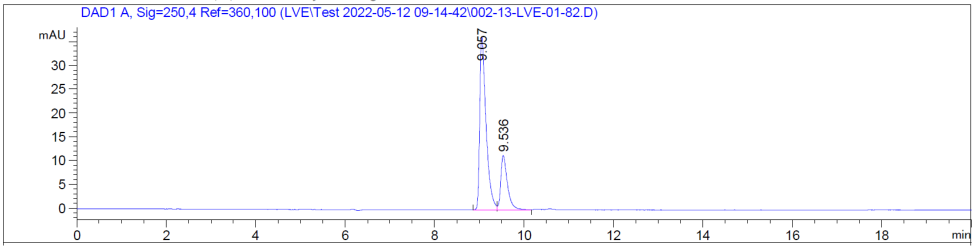
(+)-(1*S*,5*S*)-2,2-dibenzyl-6,6-dimethylbicyclo[3.1.0]hexane ((+)-6):



$C_{22}H_{26}$
290.45 g/mol

To a solution of CH_2Cl_2 (0.17 mL, 2.70 mmol, 1.50 equiv.) in dry THF (15 mL) at –100 °C was added slowly *n*-BuLi (0.79 mL, 2.5 M in hexane, 2.00 mmol, 1.10 equiv) at such a rate that the internal temperature never exceeded –100 °C. The resulting reaction mixture was then stirred below−100 °C for 30 min and a solution of (4*R*,5*R*)-4,5-dicyclohexyl-2-(3,3-dibenzyl-5-methyl-hex-4-enyl)-1,3,2-dioxaborolane **10** (940 mg, 1.80 mmol) in dry THF (5 mL) was the added. The resulting reaction mixture was stirred below −100 °C for 15 min then anhydrous $ZnCl_2$ (417 mg, 3.00 mmol, 1.70 equiv) was added in one portion. The resulting reaction mixture was stirred for 14 h at rt. Pentane (5 mL) was added, and the reaction mixture was carefully quenched with saturated aq. NH_4Cl (5 mL), followed by water (5 mL). The phases were separated, and the aqueous phase was extracted with pentane (2 × 10 mL). The combined organic phases were dried over Na_2SO_4 and filtered. Toluene (5 mL) was added (to remove residual THF) and the mixture was concentrated under reduced pressure. The resulting residue was re-dissolved in pentane (10 mL), which resulted in a slightly turbid solution. This solution was filtered through a syringe filter and concentrated to give the α-chloroboronic ester intermediate (*S*)-**11**. The resulting residue was re-dissolved in dry TFT (20 mL) and $O(Bcat)_2$ (914 mg, 3.60 mmol) was added. The resulting reaction mixture was stirred at 70 °C for 24 h. The reaction mixture was then cooled down to rt and concentrated under reduced pressure. The crude product was purified by FC on silica gel (pentane) to give (+)-**6** as a clear oil, contaminated with olefinic impurities. Removal of the impurities was achieved by ozonolysis, in analogy to the procedure for racemic (±)-**6**. The crude product was purified by FC on silica gel (pentane) to give (+)-**6** (209 mg, 40%, 77:23 er) as a clear oil, which crystallized in the fridge. (+)-**6**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35–7.13 (m, 10H), 2.85 (d, *J* = 13.1 Hz, 1H), 2.71 (d, *J* = 13.1 Hz, 1H), 2.62 (d, *J* = 12.9 Hz, 1H), 2.45 (d, *J* = 12.9 Hz, 1H), 1.80–1.69 (m, 1H), 1.44–1.24 (m, 2H), 1.21 (s, 3H), 1.01 (s, 3H), 0.91–0.73 (m, 3H). Mp: 41.0–42.1 °C. $[\alpha]_D^{20}$ = +36.76 (c = 1, CH_2Cl_2). The other physical data are in accordance with those of racemic compound (±)-**6**.

The absolute configuration of the major enantiomer was assigned by analogy to the configuration of enantioenriched (+)-**(14)**. The enantiomeric ratio ((1*S*,5*S*)/(1*R*,5*R*) 75:25) was determined by chiral HPLC: CHIRALPAK IB-3; 100% hexane; 0.7 mL/min; λ= 210 nm



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Signal 1: DAD1 A, Sig=250,4 Ref=360,100

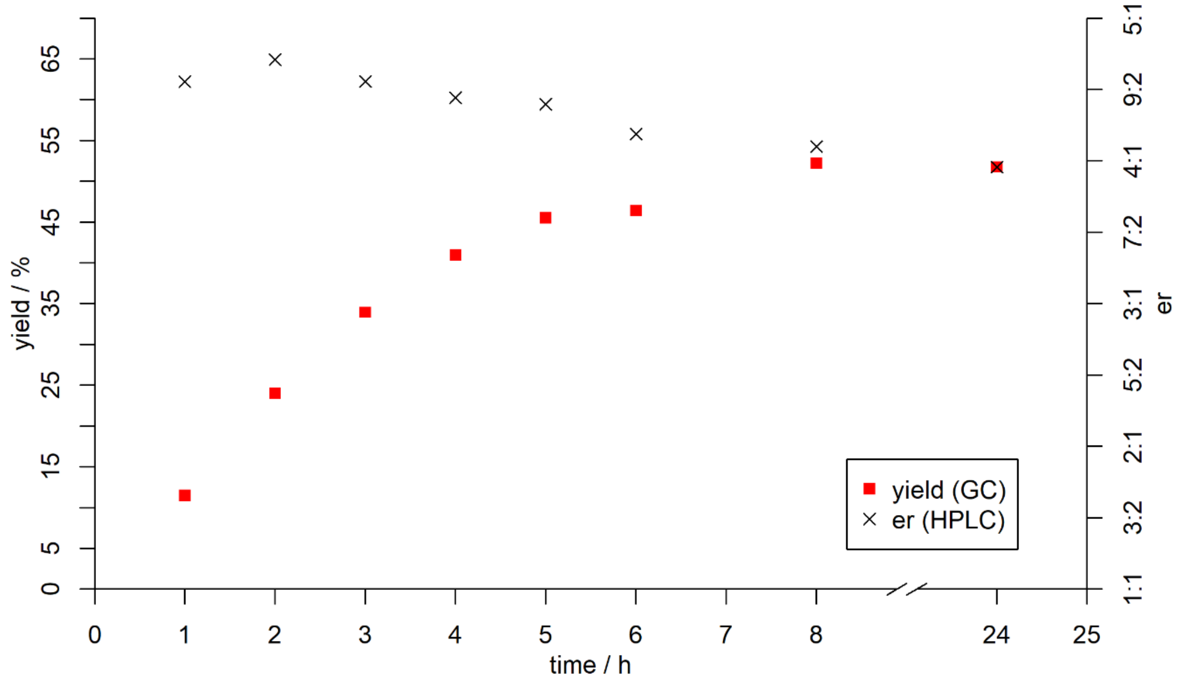
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   9.057 BV    0.1465  358.13477   36.48118  75.3935
   2   9.536 VB    0.1517  116.88588   11.39551  24.6065

Totals :                   475.02065   47.87670
```

Enantioenriched (+)-**(6)** was suspended in methanol. CH_2Cl_2 was added until all solid dissolved. Slow evaporation of CH_2Cl_2 at 4 °C gave crystals suitable for X-ray analysis. Due to low anomalous scattering the absolute configuration of the single crystal could not be determined.

Monitoring of the enantiomeric ratio during the reaction:

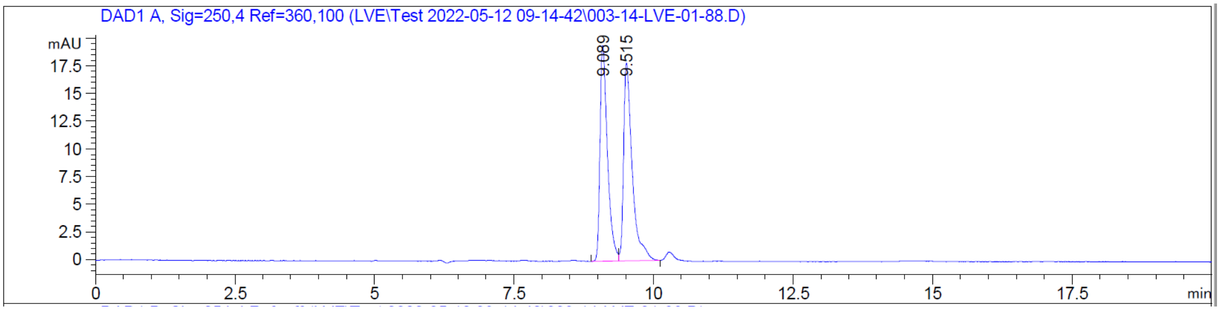
During the first 6 h of the cyclopropanation, an aliquot was taken from the reaction mixture every hour, then after 8 h and finally after 24 h. The aliquot was diluted with hexane. The enantiomeric ratio was determined by chiral HPLC and the yield was determined by GC using dodecane as an internal standard. HPLC Conditions: CHIRALPAK IB-3; 100% hexane; 0.7 mL/min; λ= 210 nm



Experiment with (RS)-11 leading to racemic 6

To a solution of (4*R*,5*R*)-4,5-dicyclohexyl-2-((*RS*)-4,4-dibenzyl-1-chloro-6-methylhept-5-en-1-yl)-1,3,2-dioxaborolane ((*RS*)-**11**) (561mg, 1 mmol) in dry TFT (10 mL), O(Bcat)$_2$ (508 mg, 2.00 mmol) was added. The resulting reaction mixture was stirred at 70 °C for 24 h. The reaction mixture was then cooled down to rt and concentrated under reduced pressure. The crude product was purified by FC on silica gel (pentane) to give (+)-**6** as a clear oil, contaminated with olefinic impurities. Removal of the impurities was achieved by ozonolysis, in analogy to the procedure for racemic (±)-**6**. The crude product was purified by FC on silica gel (pentane) to give **6** (91 mg, 31%, er 50:50) as a clear oil, which crystallized in the fridge.

The enantiomeric ratio ((1*S*,5*S*)/(1*R*,5*R*) 1:1) was determined by chiral HPLC: CHIRALPAK IB-3; 100% hexane; 0.7 mL/min; λ= 210 nm



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Signal 1: DAD1 A, Sig=250,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.089 BV    0.1385  181.30550   19.48752  48.4507
   2   9.515 VB    0.1576  192.90077   17.92152  51.5493

Totals :                   374.20627   37.40904
```
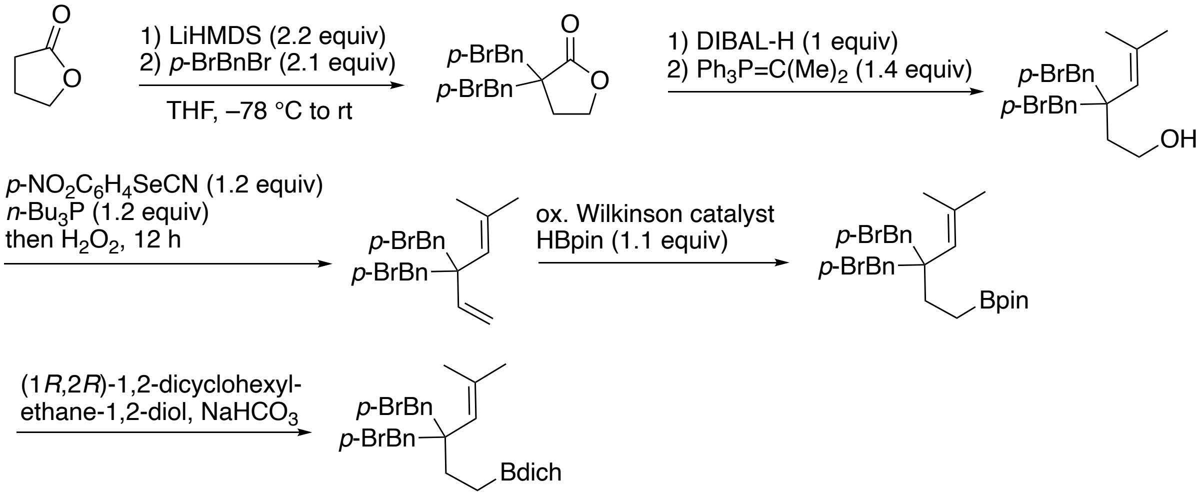
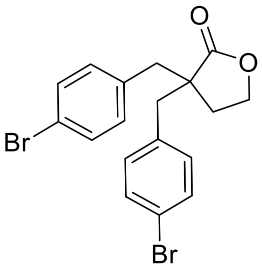

Reaction starting from (+)-12



12

3,3-Bis(4-bromobenzyl)dihydrofuran-2(3*H*)-one

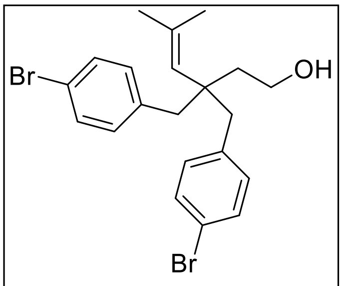


$C_{18}H_{16}Br_2O_2$
424.13

To a solution of LiHMDS (100 mL, 100 mmol, 2.20 equiv, 1 M in THF) at −78 °C was added dropwise a solution of tetrahydrofuran-2-one (3.40 mL, 45.0 mmol, 1.00 equiv) in THF (5 mL). The resulting mixture was stirred for 10 min at −78 °C and a solution of 1-bromo-4-(bromomethyl)benzene (10.5 g, 25.9 mmol, 2.10 equiv) in THF (10 mL) was added slowly. The reaction mixture was allowed to reach rt and was stirred at rt for 2 h. The reaction mixture was quenched with water and the aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were washed with brine (50 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was recrystallized from heptane/toluene (200/50 mL) to give the titled product as white crystals (7.00 g, 83%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40–7.40 (m, 4H), 7.13–7.03 (d, *J* = 8.4 Hz, 4H), 3.46 (t, *J* = 7.4 Hz, 2H), 3.13 (d, *J* = 13.5 Hz, 2H), 2.72 (d, *J* = 13.5 Hz, 2H), 2.11 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.3, 131.9, 121.6, 65.3, 49.7, 43.2, 29.0. Mp: 160.7–161.6 °C. IR (cm^{-1}): 3037, 2985, 2916, 1752, 1486, 1449, 1408, 1381, 1226, 1163, 1124, 1101, 1070, 1027, 1011, 960, 882, 815, 730, 711, 678, 652, 615. HRMS (ESI): Calculated for $C_{18}H_{17}O_2Br_2$ $[M+H]^+$: 422.9590, found 422.9584.

3,3-Bis(4-bromobenzyl)-5-methylhex-4-en-1-ol



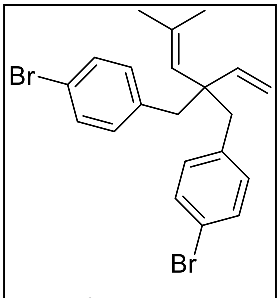
$C_{21}H_{24}Br_2O$
452.23

DIBAL-H (16.7 mL, 1 M in toluene, 16.7 mmol, 1.01 equiv) was added slowly to a suspension of 3,3-bis[(4-bromophenyl) methyl]tetrahydrofuran-2-one (7.00 g, 16.5 mmol, 1.00 equiv) in dry toluene (80 mL) at −78 °C. *The internal temperature should never exceed −70 °C.* The reaction mixture was stirred at −78 °C until no starting material was observed (TLC monitoring). The reaction mixture clears up once it is close to being complete, (ca. 1.5 h). Dry THF (30 mL) was added at −78 °C and the dry ice bath was removed. *It is important that the reaction mixture does not warm up without the additional THF as this leads to reduction of the aluminium lactolate*. In a separate reaction vessel, *n*-BuLi (9.2 mL, 2.5 M in hexane, 23.1 mmol 1.4

equiv) was slowly added at 0 °C to a suspension of isopropyl(triphenyl)phosphonium iodide (10.7 g, 24.8 mmol, 1.50 equiv) in THF (60 mL). Upon he addition the reaction mixture turned deep red. The reaction was allowed to reach rt and was stirred for 1 h at this temperature. The previously prepared solution of aluminium lactolate was added to the ylide via cannula. The reaction vessel of the lactol was washed with dry THF (20 mL). The resulting reaction mixture was stirred overnight at 55 °C. The reaction mixture was quenched with 0.5 M HCl (100 mL) and the phases were separated. The aqueous phase was extracted with Et_2O (3 × 50 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by FC on silica gel (pentane/Et_2O 7:3) to give 3,3-bis(4-bromobenzyl)-5-methylhex-4-en-1-ol (5.9 g, 79%) as a clear oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40–7.35 (m, 4H), 7.07–6.96 (m, 4H), 5.01–4.97 (m, 1H), 3.71 (dt, J = 7.6, 4.9 Hz, 2H), 2.75 (d, J = 13.6 Hz, 2H), 2.67 (d, J = 13.6 Hz, 2H), 1.722 (t, J = 7.6 Hz, 2H), 1.720 (d, J = 1.1 Hz, 3H), 1.44 (d, J = 1.1 Hz, 3H), 1.16 (t, J = 5.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.4 (2Cq_{Ar}), 133.9 (Cq), 132.6 (4×CH_{Ar}), 131.0 (4×CH_{Ar}), 128.9 (CH), 120.3 (CH), 59.9 (CH_2), 45.1 (2×CH_2), 43.0 (Cq), 38.9 (CH_2), 28.7 (CH_3), 19.6 (CH_3). IR (cm^{-1}): 3333, 2968, 1486, 1444, 1403, 1108, 1071, 1036, 1010, 839, 800, 720, 656.

4,4'-(2-(2-Methylprop-1-en-1-yl)-2-vinylpropane-1,3-diyl)bis(bromobenzene)

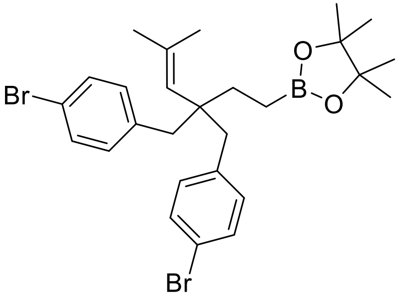


$C_{21}H_{22}Br_2$
434.22

To a solution of 3,3-bis[(4-bromophenyl)methyl]-5-methyl-hex-4-en-1-ol (2.4 g, 5.20 mmol, 1.00 equiv) and (2-nitrophenyl) selenocyanate (1.44 g, 6.36 mmol, 1.20 equiv) in THF (25mL) was added tri-*n*-butylphosphine (1.57 mL, 6.36 mmol, 1.20 equiv) at rt. The reaction mixture was stirred at rt for 2 h, then solid $NaHCO_3$ (534 mg, 6.36 mmol, 1.20 equiv) was added and the reaction mixture was cooled to 0 °C. H_2O_2 (3 mL, 30%) was added *carefully* and the reaction was stirred overnight at rt. Water was added and the phases were separated. The aqueous phase was extracted with Et_2O (3 × 10 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by FC on silica gel (pentane) to give 4,4'-(2-(2-methylprop-1-en-1-yl)-2-vinylpropane-1,3-diyl)bis(bromobenzene) (2.10 g, 91%) as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37–7.32 (m, 4H), 7.03–6.95 (m, 4H), 5.77 (dd, J = 17.7, 10.9 Hz, 1H), 5.14 (dd, J = 10.9, 1.0 Hz, 1H), 5.06–5.03 (m, 1H), 4.98 (dd, J = 17.7, 1.0 Hz, 1H), 2.80–2.70 (m, 4H), 1.68 (d, J = 1.2 Hz, 3H), 1.52 (d, J = 1.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.1, 137.4, 135.3, 132.9, 130.8, 120.2, 113.5, 46.3, 45.8, 27.6, 19.9. Mp: 112.0-112.7 °C. IR (cm^{-1}): 2975, 2941, 2921, 2360, 1895, 1626, 1483, 1440, 1401, 1213, 1069, 1010, 914, 848, 796, 747, 725, 685, 644. HRMS (EI): Calculated for $C_{21}H_{22}Br_2$ $[M]^{+\cdot}$: 432.0083, found 432.0081.

2-(3,3-Bis(4-bromobenzyl)-5-methylhex-4-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

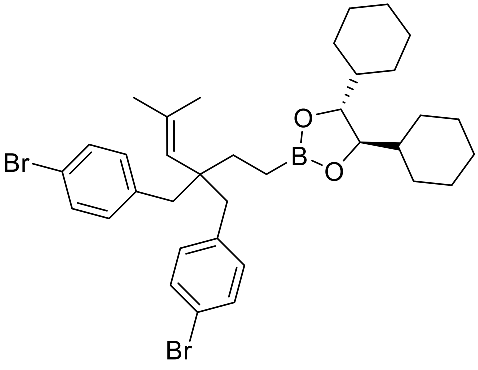


$C_{27}H_{35}BBr_2O_2$
562.19

The titled product was prepared following a procedure adapted from the literature.[16] Oxidized Wilkinson's catalyst (45.2 mg, 2 mol%) was added to a solution of 1-bromo-4-[2-[(4-bromophenyl)methyl]-4-methyl-2-vinyl-pent-3-enyl]benzene (1.06 g, 2.44 mmol, 1.00 equiv) in dry THF (10 ml). 4,4,5,5-Tetramethyl-1,3,2-dioxaborolane (0.43 ml, 2.93 mmol, 1.20 equiv) was added dropwise and the reaction mixture was stirred at 50°C for 4 h. The reaction mixture was cooled to rt, then carefully quenched with saturated aq. $NaHCO_3$ (4 mL). The phases were separated and the aqueous phase was extracted with Et_2O (3 × 5 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by FC on silica gel (pentane/Et_2O 100:2) to give the product (2.00 g, 86%) as a clear oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.32 (m, 4H), 7.02–6.98 (m, 4H), 4.87–4.84 (m, 1H), 2.73 (d, J = 13.6 Hz, 2H), 2.63 (d, J = 13.6 Hz, 2H), 1.69 (d, J = 1.1 Hz, 3H), 1.48 (d, J = 1.0 Hz, 3H), 1.47–1.43 (m, 2H), 1.22 (s, 12H), 0.84–0.78 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0 (2×Cq_{Ar}), 133.1 (Cq), 132.6 (4×CH_{Ar}), 130.8 (4×CH_{Ar}), 129.5 (=CH), 120.0 (2×Cq_{Ar}), 83.1 (2×Cq), 44.6 (Cq), 43.4 (CH_2, 2 C), 29.8 (CH_2), 28.6 (CH_3), 24.9 (4×CH_3), 19.6 (CH_3). IR (cm^{-1}): 2975, 2926, 2863, 1487, 1446, 1368, 1317, 1143, 1072, 1010, 966, 883, 847, 742. HRMS: Not found.

(+)-(4*R*,5*R*)-2-(3,3-Bis(4-bromobenzyl)-5-methylhex-4-en-1-yl)-4,5-dicyclohexyl-1,3,2-dioxaborolane ((+)-12)

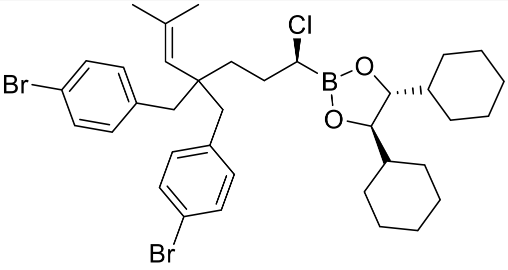


$C_{35}H_{47}BBr_2O_2$
670.38

To a solution of 2-[3,3-bis[(4-bromophenyl)methyl]-5-methyl-hex-4-enyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.00 g, 1.78 mmol, 1.00 equiv) in THF (5 mL), were added (1*R*,2*R*)-1,2-dicyclohexylethane-1,2-diol (483 mg, 2.13 mmol, 1.20 equiv) and saturated aq. $NaHCO_3$ (0.5 mL). The resulting reaction mixture was stirred overnight at rt. The reaction mixture was dried with Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by FC on silica gel (pentane/Et_2O 100:1) to give (+)-**12** (1.06 g, 89%) as a clear oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (d, J = 8.3 Hz, 4H), 7.00 (d, J = 8.3 Hz, 4H), 4.87 (bs, 1H), 3.83–3.79 (m, 2H), 2.75 (d, J = 13.6 Hz, 1H), 2.74 (d, J = 13.6 Hz, 1H), 2.64 (d, J = 13.5 Hz, 2H), 1.82–0.80 (m, 26H), 1.70 (s, 3H), 1.47 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.0, 133.1, 132.6, 130.8, 129.4, 120.0, 83.4, 44.6, 43.5, 43.1, 30.1, 28.7, 28.5, 27.5, 26.6, 26.2, 26.0, 19.6. ^{11}B NMR (96 MHz, $CDCl_3$) δ 34.6. $[\alpha]_D^{20}$ = +12.8 (c = 1.00, $CHCl_3$). IR (cm^{-1}): 2923, 2850, 1487, 1447, 1361, 1233, 1072, 1011, 492, 409. HRMS (ESI): Calculated for $C_{35}H_{48}O_2BBr_2$ $[M+H]^+$: 669.2109, found 669.2124.

(4*R*,5*R*)-2-((*S*)-4,4-bis(4-bromobenzyl)-1-chloro-6-methylhept-5-en-1-yl)-4,5-dicyclohexyl-1,3,2-dioxaborolane (13)

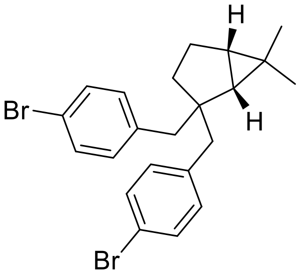


$C_{36}H_{48}BBr_2ClO_2$
718.85

To a solution of CH_2Cl_2 (0.29 mL, 4.50 mmol, 3.00 equiv.) in dry THF (10 mL) at –100 °C was added slowly *n*-BuLi (0.72 mL, 2.5 M in hexane, 1.80 mmol, 1.20 equiv) at such a rate that the internal temperature never exceeded –100 °C. The resulting reaction mixture was then stirred below−100 °C for 30 min and a solution of (+)-(4*R*,5*R*)-2-(3,3-Bis(4-bromobenzyl)-5-methylhex-4-en-1-yl)-4,5-dicyclohexyl-1,3,2-dioxaborolane ((+)-**12** (1.01 g, 1.50 mmol, 1.00 equiv) in dry THF (5 mL) was the added. The resulting reaction mixture was stirred below −100 °C for 15 min then anhydrous $ZnCl_2$ (307 mg, 4.50 mmol, 1.50 equiv) was added in one portion. The resulting reaction mixture was stirred for 14 h at rt. Pentane (5 mL) was added, and the reaction mixture was carefully quenched with saturated aq. NH_4Cl (5 mL), followed by water (5 mL). The phases were separated, and the aqueous phase was extracted with pentane (2 × 10 mL). The combined organic phases were dried over Na_2SO_4 and filtered. Toluene (5 mL) was added (to remove residual THF) and the mixture was concentrated under reduced pressure. The resulting residue was re-dissolved in pentane (10 mL), which resulted in a slightly turbid solution. This solution was filtered through a syringe filter and concentrated to give **13**. The compound could not be purified by FC due to its instability on silica.

^{1}H NMR (300 MHz, CDCl3) δ 7.37 – 7.34 (m, 4H), 7.03 – 6.99 (m, 4H), 4.90 (s, 1H), 3.89 – 3.88(m, 2H), 3.31 (t, J = 7.3 Hz, 1H), 2.83 – 2.51, 2.05 – 1.82 (m, 3H), 1.81 – 1.64 (m, 19H), 1.58 (d, *J* = 12.9 Hz, 4H), 1.49 – 1.42 (m, 5H), 1.41 – 1.11 (m, 14H), 1.09 – 0.85 (m, 5H); ^{11}B NMR (96 MHz, CDCl3) δ 28.2; ^{13}C NMR (75 MHz, CDCl3) δ 137.6, 133.5, 132.6, 131.0, 130.9, 129.4, 120.2, 84.2, 77.6, 77.2, 76.7, 44.4, 44.2, 43.8, 42.9, 34.0, 29.7, 28.7, 28.3, 27.4, 26.5, 26.1, 26.0, 19.6

(±)-(1*SR* 5*SR*)-2,2-Bis(4-bromobenzyl)-6,6-dimethylbicyclo[3.1.0]hexane ((±)-14)

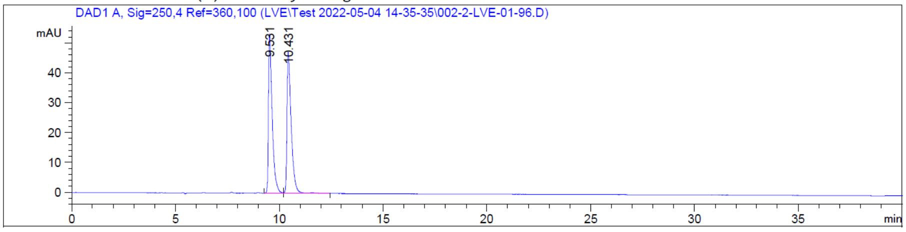


$C_{22}H_{24}Br_2$
448.24

Racemic (±)-**14** was prepared according to the transesterification procedure used for (±)-**6** starting from 2-[3,3-bis[(4-bromophenyl)methyl]-5-methyl-hex-4-enyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (281 mg, 0.50 mmol). The crude product was purified by FC on silica gel (pentane) to give (±)-**14** (115 mg, 51%) as a white crystalline solid.

^{1}H NMR (300 MHz, $CDCl_3$) *δ* 7.43 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 8.3 Hz, 2H), 7.01 (d, *J* = 8.3 Hz, 2H), 2.79 (d, *J* = 13.2 Hz, 1H), 2.63 (d, *J* = 13.2 Hz, 1H), 2.53 (d, *J* = 12.9 Hz, 1H), 2.35 (d, *J* = 12.9 Hz, 1H), 1.75–1.64 (m, 1H), 1.47–1.28 (m, 2H), 1.20 (s, 3H), 1.00 (s, 3H), 0.80–0.70 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.4 (CqAr), 138.7 (CqAr), 132.3 (2×CHAr), 132.1 (2×CHAr), 131.1 (2×CHAr), 130.8 (2×CHAr), 120.04 (CHAr), 120.0 (CHAr), 49.6 (Cq), 47.4 (CH_2), 45.2 (CH_2), 39.4, 36.9 (CH_2), 31.6, 29.4, 25.2 (CH_2), 20.5 (Cq), 17.3. M.p.: 76.0–78.5 °C. IR (cm^{-1}): 3001, 2916, 2860, 1895, 1590, 1484, 1402, 1373, 1071, 1011, 840, 818, 795, 766, 725, 653, 633. HRMS (EI): Calculated for $C_{22}H_{2}4Br_{2}$ $[M]^{+\cdot}$: 446.0239, found 446.0236.

The enantiomeric ratio ((1*S*,5*S*)/(1*R*,5*R*) 50:50) was determined by chiral HPLC: CHIRALPAK IB-3; 100% hexane; 0.7 mL/min; λ= 250 nm



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Signal 1: DAD1 A, Sig=250,4 Ref=360,100

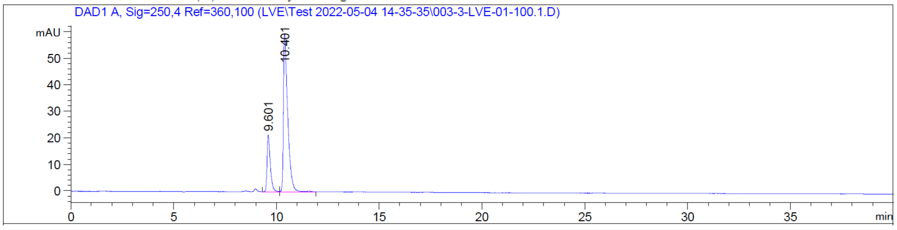
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   9.531 BV    0.1838  665.23822   53.21461  49.7663
   2  10.431 VV R  0.2070  671.48639   47.26289  50.2337

Totals :                  1336.72461  100.47751
```

(+)-(1*S*,5*S*)-2,2-Bis(4-bromobenzyl)-6,6-dimethylbicyclo[3.1.0]hexane (+)-(14):

Enantioenriched (+)-**(14)** was prepared according to the procedure used for (+)-**6**, from (+)-**12** (900 mg, 1.25 mmol). The crude product was purified by FC on silica gel (pentane) to give (+)-**14** (340 mg, 60%) as a white crystalline solid.

$[\alpha]_D^{20}$ = +43.51 (c = 1.00, $CHCl_3$). Mp: 99.9–101.0 °C. The other physical data are in accordance with the racemic compound (±)-**14**. The enantiomeric ratio ((1*S*,5*S*)/(1*R*,5*R*) 78:22) was determined by chiral HPLC: CHIRALPAK IB-3; 100% hexane; 0.7 mL/min; λ= 250 nm.



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Signal 1: DAD1 A, Sig=250,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   9.601 BV    0.1641  236.49538   21.53980  21.5973
   2  10.401 VV R  0.2055  858.52649   59.56324  78.4027

Totals :                  1095.02187   81.10304
```
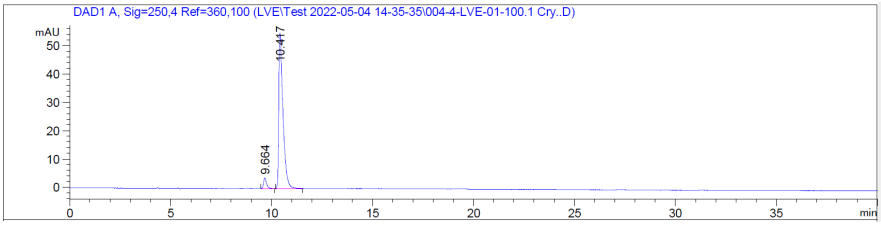

Single crystal X-ray crystallography:

Enantioenriched (+)-**(14)** was suspended in methanol. CH_2Cl_2 was added until all solid dissolved. Slow evaporation of CH_2Cl_2 at 4 °C gave crystals suitable for X-ray analysis. A single crystal of sufficient size was selected and cut in two pieces using a razor blade. One piece was used for the diffraction experiment and the enantiomeric purity (er 95:5) of the second piece was determined by HPLC.



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Signal 1: DAD1 A, Sig=250,4 Ref=360,100

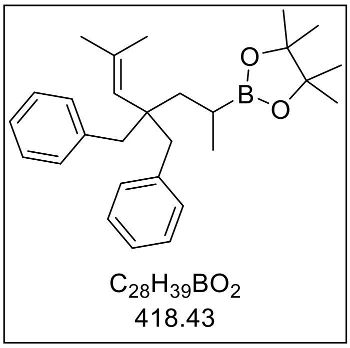
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.664 BB    0.1486   37.64204    3.70429   4.6350
   2  10.417 BB    0.2020  774.48767   54.74879  95.3650

Totals :                   812.12971   58.45308
```

Asymmetric intramolecular cyclopropanation: substrate control

Preparation of (*S*)-15

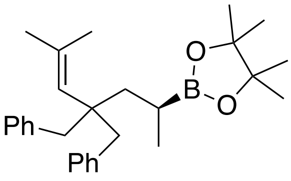
(±)-2-(4,4-Dibenzyl-6-methylhept-5-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((±)-15)



The titled compound was prepared according to reported procedure.[17] To a solution of (3,3-dibenzyl-5-methyl-hex-4-enyl) 4-ethyl-2,6-diisopropyl-benzoate (1.33 g, 2.50 mmol, 1.00 equiv.) and TMEDA (0.49 mL, 2.25 mmol, 1.30 equiv.) in dry Et_2O (10 mL) was added slowly *s*-BuLi (2.12 mL, 2.75 mmol, 1.3 M in cyclohexane/hexane 92:8, 1.30 equiv.) at −78 °C. The color of the reaction mixture turned to deep red. The reaction mixture was stirred at −78 °C for 4 h then 2,4,4,5,5-pentamethyl-1,3,2-dioxaborolane (0.83 mL, 5.00 mmol, 2.00 equiv.) was added. The resulting mixture was stirred at −78 °C for 1 h and then refluxed overnight. The reaction was carefully quenched with saturated aq. $NaHCO_3$ (10 mL) and the phases were separated. The aqueous phase was extracted with Et_2O (2 ×10 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by FC on silica gel (pentane/Et_2O 100:0.5 to 100:1) to give (±)-**15** (710 mg, 68%) as a clear oil.

^1H NMR (300 MHz, $CDCl_3$) δ 7.26–7.10 (m, 10H), 5.13–5.09 (m, 1H), 2.84 (d, J = 13.1 Hz, 1H), 2.78 (d, J = 13.5 Hz, 1H), 2.68 (d, J = 13.3 Hz, 2H), 1.87 (dd, J = 14.0, 10.3 Hz, 1H), 1.67 (d, J = 1.1 Hz, 3H), 1.43 (dd, J = 14.0, 2.6 Hz, 1H), 1.39 (d, J = 1.1 Hz, 3H), 1.30–1.16 (m, 1H), 1.22 (s, 12H), 0.95 (d, J = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.4 (Cq), 132.2 (Cq), 131.2 (2×CH_{Ar}), 131.1 (2×CH_{Ar}), 129.2 (CH_{Ar}), 127.8 (2×CH_{Ar}), 127.6 (2×CH_{Ar}), 125.9 (=CH), 125.8 (CH_{Ar}), 83.1 (Cq), 45.1 (CH_2), 45.0 (CH_2), 44.7 (Cq), 41.8 (CH_2), 28.9 (CH_3), 24.90 (2×CH_3), 24.86 (2×CH_3), 19.6 (CH_3), 17.9 (CH_3). ^{11}B NMR (96 MHz, $CDCl_3$) δ 33.9. IR (cm^{-1}): 2976, 2925, 2867, 1495, 1454, 1381, 1312, 1142, 1032, 967, 909, 862, 732, 687, 579, 473. HRMS (ESI): Calculated for $C_{28}H_{40}O_2B$ $[M+H]^+$: 419.3127, found 419.3127

(*S*)-2-(4,4-dibenzyl-6-methylhept-5-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((*S*)-15)

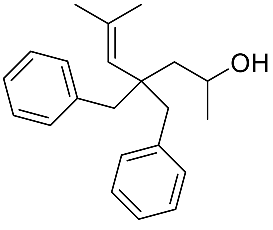


$C_{28}H_{39}BO_2$
MW: 418.4280

To a solution of (3,3-dibenzyl-5-methyl-hex-4-enyl) 4-ethyl-2,6-diisopropyl-benzoate (1.33 g, 2.50 mmol, 1.00 equiv) and (−)-sparteine (0.69 mL, 3.00 mmol, 1.20 equiv.) in dry Et_2O (10 mL) at –78 °C was added slowly *s*-BuLi (2.12 mL, 1.3 M in cyclohexane/hexane 92:8, 2.75 mmol, 1.30 equiv.). The color of the reaction mixture turned to deep red. The reaction mixture was stirred at −78 °C for 4 h then 2,4,4,5,5-pentamethyl-1,3,2-dioxaborolane (0.83 mL, 5.00 mmol, 2.00 equiv.) was added. The resulting mixture was stirred at −78 °C for 1 h and then refluxed overnight. The reaction was carefully quenched with sat. aq. $NaHCO_3$ (10 mL) and the phases were separated. The aqueous phase was extracted with Et_2O (2 × 10 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by FC on silica gel (pentane/Et_2O 100:0.5 to 100:1) to give (*S*)-**15** (409 mg, 39%, er = 76:24) as a clear oil. The absolute configuration of the major enantiomer was assigned by analogy to literature precedents.[17]

^1H NMR (300 MHz, $CDCl_3$) δ 7.26–7.10 (m, 10H), 5.13–5.09 (m, 1H), 2.84 (d, *J* = 13.1 Hz, 1H), 2.78 (d, *J* = 13.5 Hz, 1H), 2.68 (d, *J* = 13.3 Hz, 2H), 1.87 (dd, *J* = 14.0, 10.3 Hz, 1H), 1.67 (d, *J* = 1.1 Hz, 3H), 1.43 (dd, *J* = 14.0, 2.6 Hz, 1H), 1.39 (d, *J* = 1.1 Hz, 3H), 1.30–1.16 (m, 1H), 1.22 (s, 12H), 0.95 (d, *J* = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.4 (Cq), 132.2 (Cq), 131.2 (2×CH_{Ar}), 131.1 (2×CH_{Ar}), 129.2 (CH_{Ar}), 127.8 (2×CH_{Ar}), 127.6 (2×CH_{Ar}), 125.9 (=CH), 125.8 (CH_{Ar}), 83.1 (Cq), 45.1 (CH_2), 45.0 (CH_2), 44.7 (Cq), 41.8 (CH_2), 28.9 (CH_3), 24.90 (2×CH_3), 24.86 (2×CH_3), 19.6 (CH_3), 17.9 (CH_3). ^{11}B NMR (96 MHz, $CDCl_3$) δ 33.9. IR (cm^{-1}): 2976, 2925, 2867, 1495, 1454, 1381, 1312, 1142, 1032, 967, 909, 862, 732, 687, 579, 473.

(±)-4,4-Dibenzyl-6-methylhept-5-en-2-ol ((±)-16)

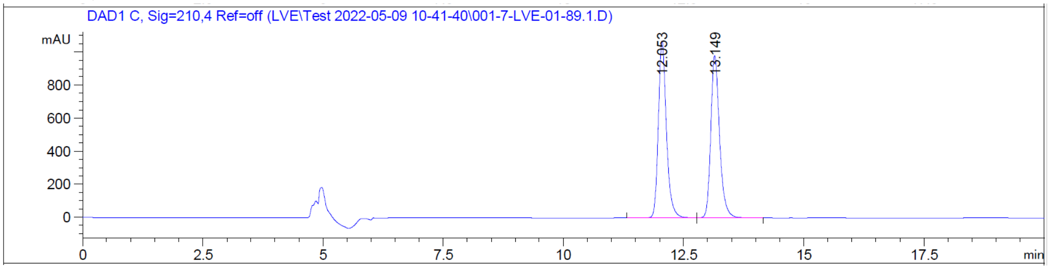


$C_{22}H_{28}O$
308.47

To a solution of (±)-**15** (20 mg, 48 µmol) in THF (2 mL) were added NaOH (2 mL, 2 M) and H_2O_2 (1 mL, 30%) at 0 °C. The reaction mixture was stirred at rt for 3 h, then quenched with saturated aq. $NaHCO_3$ (3 mL). The phases were separated, and the aqueous phase was extracted with Et_2O (3 × 5 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by FC on silica gel (pentane/Et_2O 8:2) to give (±)-**16** (13 mg, 90%) as a clear oil.

^1H NMR (300 MHz, $CDCl_3$) δ 7.29–7.13 (m, 10H), 5.31–5.27 (m, 1H), 4.17 (ddq, *J* = 9.0, 6.3, 3.2 Hz, 1H), 2.93 (s, 2H), 2.87 (s, 2H), 2.00 (d, *J* = 2.9 Hz, 1H), 1.76 (d, *J* = 14.8, 9.0 Hz, 1H), 1.75 (d, *J* = 1.2 Hz, 3H), 1.59–1.50 (m, 1H), 1.53 (d, *J* = 1.1 Hz, 3H), 1.14 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.9 (Cq_{Ar}), 138.8 (Cq_{Ar}), 134.2 (Cq), 131.17 (2×CH_{Ar}), 131.15 (2×CH_{Ar}), 130.5 (=CH), 127.93 (2×CH_{Ar}), 127.88 (2×CH_{Ar}), 126.2 (CH_{Ar}), 126.1 (CH_{Ar}), 65.8 (CH), 45.7 (CH_2), 45.4 (CH_2), 45.0 (CH_2), 43.5 (Cq), 28.8 (CH_3), 24.9 (CH_3), 20.0 (CH_3). IR (cm^{-1}): 3443, 3026, 2965, 2925, 1601, 1495, 1452, 1370, 1116, 1075, 1030, 948, 845, 746, 724;

The enantiomeric ratio was determined by chiral HPLC: CHIRALPAK IB-3; 3% *i*-PrOH in hexane; 0.7 mL/min; λ= 210 nm



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Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.053 BB    0.1791 1.25864e4  1071.38330  50.1664
   2  13.149 BB    0.1932 1.25029e4   984.38715  49.8336

Totals :                  2.50893e4  2055.77045
```
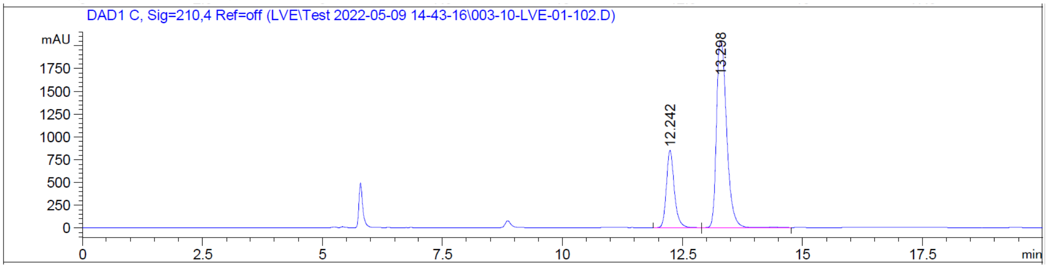

(−)-(*S*)-4,4-Dibenzyl-6-methylhept-5-en-2-ol ((−)-16)

The reaction was repeated with enantioenriched (*S*)-**15** (10 mg, 24 μmol)under the same conditions used to prepare (±)-**16**. The crude product was purified by FC on silica gel (pentane/Et_2O 8:2) to give (−)-**16** (7 mg, 96%) as a clear oil.

The enantiomeric ratio (*S/R* 76:24) was determined by chiral HPLC: CHIRALPAK IB-3; 3% *i*-PrOH in hexane; 0.7 mL/min; λ= 210 nm



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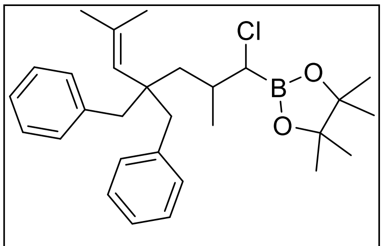
Signal 3: DAD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.242 BB    0.1742 9730.05762  845.92578  24.3283
   2  13.298 BV R  0.2274 3.02647e4  2049.94312  75.6717

Totals :                  3.99948e4  2895.86890
```

Intramolecular cyclopropanation

(±)-2-(4,4-Dibenzyl-1-chloro-2,6-dimethylhept-5-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (17)



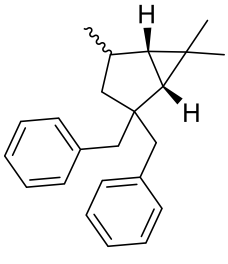
$C_{29}H_{40}BClO_2$
466.90

To a solution of dry CH_2Cl_2 (0.19 mL, 3.0 mmol, 3.0 equiv.) in THF (6 mL) was added slowly *n*-BuLi (0.48 mL, 2.5 M in hexane, 1.20 mmol, 1.20 equiv) at a temperature that should not exceed −100 °C. The resulting reaction mixture was stirred at below −100 °C for 30 min and a solution of (±)-**15** (418 mg, 1.00 mmol, 1.00 equiv, er = 76:24) in dry THF (2 mL) was then added. The resulting reaction mixture was allowed to reach rt and stirred for 20 h. Dry toluene (10 mL) was added, and the solvent were removed under reduced pressure. The residue was re-dissolved in toluene and filtered through a syringe filter. The filtrate was concentrated under reduced pressure to give **17** (420 mg, 90%, crude, dr = ca. 80:20).

Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.12 (m, 10H), 5.21–5.17 (m, 1H), 3.38 (d, J = 5.4 Hz, 1H), 2.92–2.80 (m, 4H), 2.32–2.20 (m, 1H), 1.72 (d, J = 1.4 Hz, 3H), 1.63 (dd, J = 14.5, 3.9 Hz, 1H), 1.57–1.47 (m, 1H), 1.54 (d, J = 1.5 Hz, 3H), 1.22 (s, 12H), 1.10 (d, J = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2 (Cq_{Ar}), 139.1 (Cq_{Ar}), 132.1 (Cq), 131.1 (2×CH_{Ar}), 131.0 (2×CH_{Ar}), 130.6 (=CH), 127.9 (2×CH_{Ar}), 127.8 (2×CH_{Ar}), 126.0 (2×CH_{Ar}), 84.3 (2×Cq), 45.2 (CH_2), 44.9 (CH_2), 44.0 (Cq), 43.0 (CH_2), 34.8 (CH), 28.9 (CH_3), 24.80 (2×CH_3), 24.76 (2×CH_3), 20.0 (CH_3), 18.9 (CH_3). ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.1.

Minor isomer (characteristic signals): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.43 (d, J = 3.9 Hz, 1H), 1.05 (d, J = 6.7 Hz, 3H). ^{11}B NMR (128 MHz, $CDCl_3$) δ 22.4.

(±)-2,2-Dibenzyl-4,6,6-trimethylbicyclo[3.1.0]hexane ((±)-18)



$C_{23}H_{28}$
304.48

Compound (±)-**18** was prepared according to according to the transesterification procedure used for (±)-**6** starting from (±)-**15** (476 mg, 1.00 mmol). The cyclopropanation step was slightly modified by running the reaction at 90 °C instead of 70 °C. The crude product was purified by FC on silica gel (pentane) to give (±)-**18** (107 mg, 35%, *endo/exo* 86:14, determined by GC using achiral stationary phase) was obtained as a clear oil.

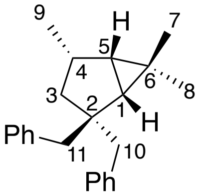
Endo-**18**: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.27–7.06 (m, 10H), 2.81 (d, J = 13.2 Hz, 1H), 2.60 (d, J = 13.2 Hz, 1H), 2.50 (d, J = 13.0 Hz, 1H), 2.38 (d, J = 13.0 Hz, 1H), 1.75 (dd, J = 13.6, 9.2 Hz, 1H), 1.36 (s, 3H), 1.34–1.26 (m, 1H), 1.13 (dd, J = 13.8, 10.9 Hz, 1H), 0.92 (s, 3H), 0.77 (d, J = 7.0 Hz, 3H), 0.76 (dd, J = 6.8, 1.1 Hz, 1H), 0.69 (dd, J = 6.6, 5.5 Hz, 1H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 140.4 (Cq_{Ar}), 139.9 (Cq_{Ar}), 130.4 (2×CH_{Ar}), 130.2 (2×CH_{Ar}), 127.6 (2×CH_{Ar}), 127.4 (2×CH_{Ar}), 125.6 (CH_{Ar}), 125.5 (CH_{Ar}), 49.5 (Cq), 47.3 (CH_2), 44.7 (CH_2), 44.1 (CH_2), 39.5 (CH), 36.1 (CH), 34.1 (CH), 29.9 (CH_3), 21.4 (Cq), 19.4 (CH_3), 16.8 (CH_3). IR (cm^{-1}): 3025, 2951, 2869, 2359, 2342, 1941, 1873, 1802, 1692, 1493, 1453, 1373, 742, 696. HRMS (EI): Calculated for $C_{23}H_{28}$ $[M]^{+\bullet}$: 304.2186, found 304.2184.

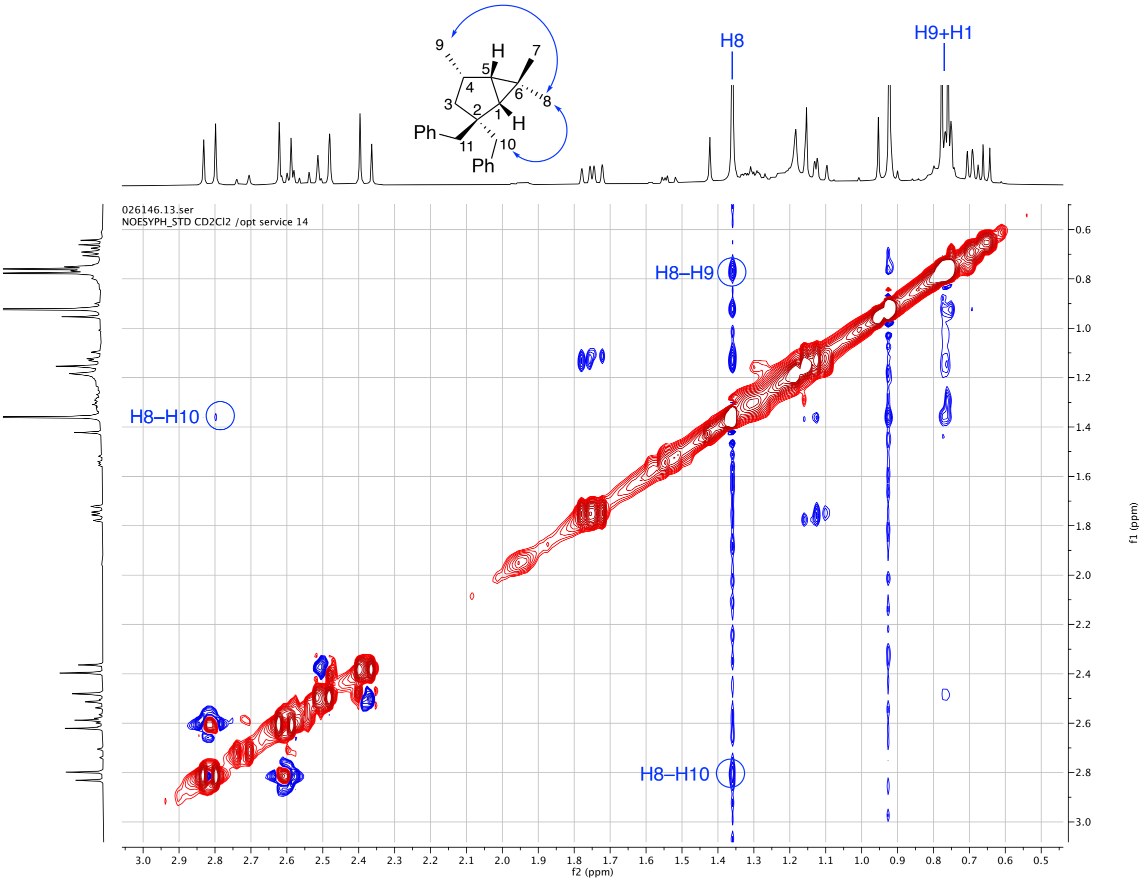
Exo-**18** (characteristic signals): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.29–7.03 (m, 10H), 2.72 (d, J = 13.8 Hz, 1H), 2.60 (d, J = 13.5 Hz, 1H), 2.58 (d, J = 13.7 Hz, 1H), 2.52 (d, J = 13.5 Hz, 1H), 2.02–1.87 (m, 1H), 1.57

(dd, *J* = 14.7, 3.1 Hz, 1H), 1.51 (dd, *J* = 14.7, 8.9 Hz, 1H), 0.65 (d, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2) *δ* 140.6 (Cq_{Ar}), 139.8 (Cq_{Ar}), 131.2, 127.7, 127.6, 125.6, 49.7 (Cq), 47.0 (CH_2), 45.0 (CH_2), 43.5 (CH_2), 41.7 (CH), 37.7 (CH), 32.9 (CH), 28.5 (CH_3), 22.3 (CH_3), 20.2 (Cq), 17.1 (CH_3).

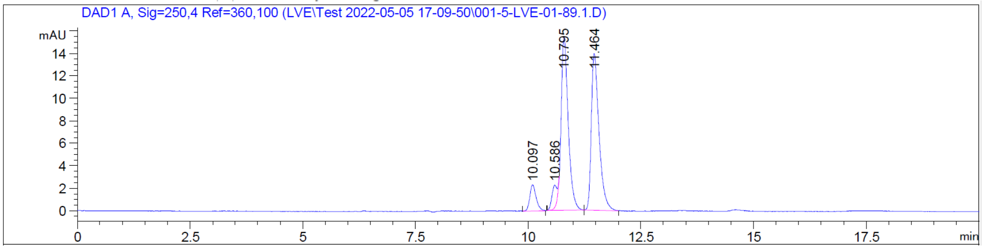
NMR assignment for the major *endo* diastereoisomer of **18**: Correlation NOESY between H8 and H9, and between H8 and H10.

Position	δ ^{1}H / ppm	δ ^{13}C / ppm
1	0.76	39.5
2	-	49.5
3	1.75 and 1.13	44.1
4	1.34–1.26	34.1
5	0.69	36.1
6	-	21.4
7	0.92	29.9
8	1.36	19.4
9	0.77	16.8
10	2.81; 2.60	44.7
11	2.50; 2.38	47.3





The enantiomeric ratio (1:1) was confirmed by chiral HPLC: CHIRALPAK IB-3; 100% hexane; 0.55 mL/min; λ= 250 nm.



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Signal 1: DAD1 A, Sig=250,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  10.097 BB    0.1412   22.77281    2.32591   6.0604
   2  10.586 BV E  0.1140   15.30182    2.00672   4.0722
   3  10.795 VB R  0.1669  172.15685   15.45731  45.8155
   4  11.464 BB    0.1773  165.52985   13.96389  44.0519

Totals :                   375.76133   33.75383
```
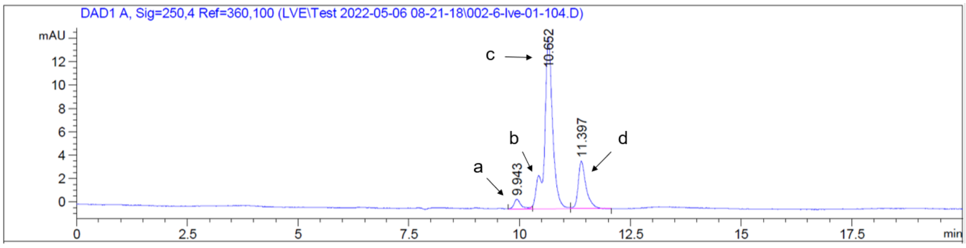

Enantioenriched (1*S*,4*S*,5*S*)- and (1R,4S,5R)-2,2-Dibenzyl-4,6,6-trimethylbicyclo[3.1.0]hexane (18)

The reaction was repeated with enantioenriched (*S*)-**15** (300 mg, 0.71 mmol) under the conditions reported for (±)-**18**. It afforded **18** (86 mg, 40% yield) as an unseparable *endo/exo* 86:14 mixture. The enantiomeric purity of *endo*-**18** (76:24) and *exo*-**18** (75:25) was determined by HPLC: CHIRALPAK IB-3; 100% hexane; 0.55 mL/min; λ= 250 nm.



```
Signal 1: DAD1 A, Sig=250,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   9.943 BV E  0.1623    8.91718 8.23776e-1   3.5538
   2  10.652 VV R  0.1912  191.10242   14.74224  76.1599
   3  11.397 VB    0.1856   50.90293    4.07757  20.2863

Totals :                   250.92253   19.64358
```

The diastereomeric ratio (dr = 86:14) was determined by GC analysis on achiral stationary phase. Unfortunately, no baseline separation of all four species could be achieved using chiral HPLC. Two peaks (**b** and **c**, see chromatogram above) were overlapping. Based on the change in the relative area% with respect to that measured for the racemic mixture, the integration of peak **d** (significantly higher than the expected sum for the two enantiomers of the minor diastereomer, ie 14.26 based on GC analysis) peaks **c** and **d** could be assigned to the two enantiomers of the major diastereomers. Peaks **a** and **b** correspond to the two enantiomers of the minor diastereomer. With that information in hand, together with the diastereomeric ratio determined separately by achiral GC analysis, one can determine the integration for peaks **b** and **c**, respectively (see below). The enantiomeric ratio of the product is ca. 75:25, in agreement with the er measured for alcohol **16.**

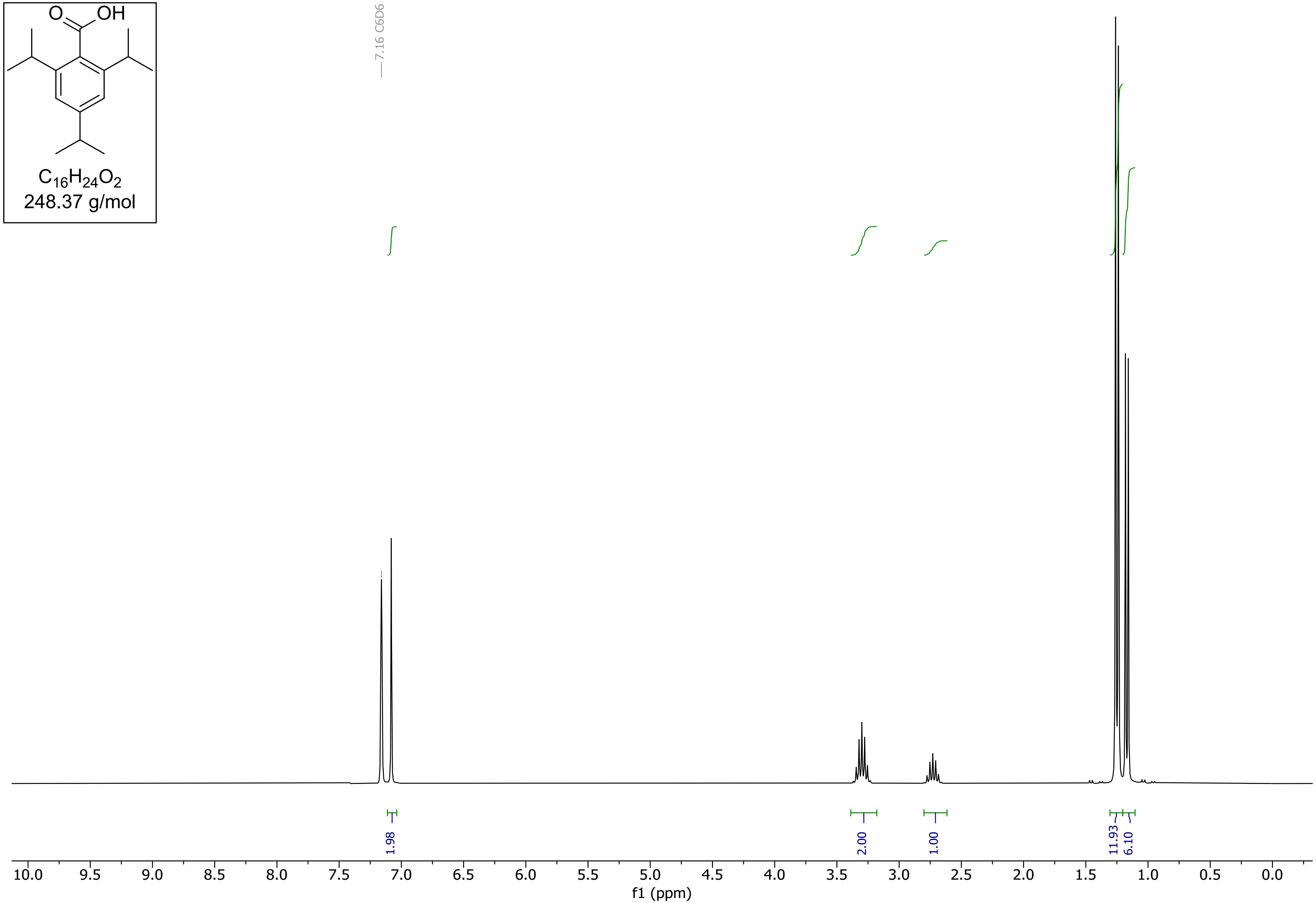
GC : a + b = 14.26; c + d = 85.47. HPLC: a = 3.55; b + c = 76.16; d = 20.29

Calculated values: b = 14.26 – 3.55 = 10.71; c = 85.47 – 20.29 = 65.16; er (minor) = 75:25; er (major) = 76:24.

References

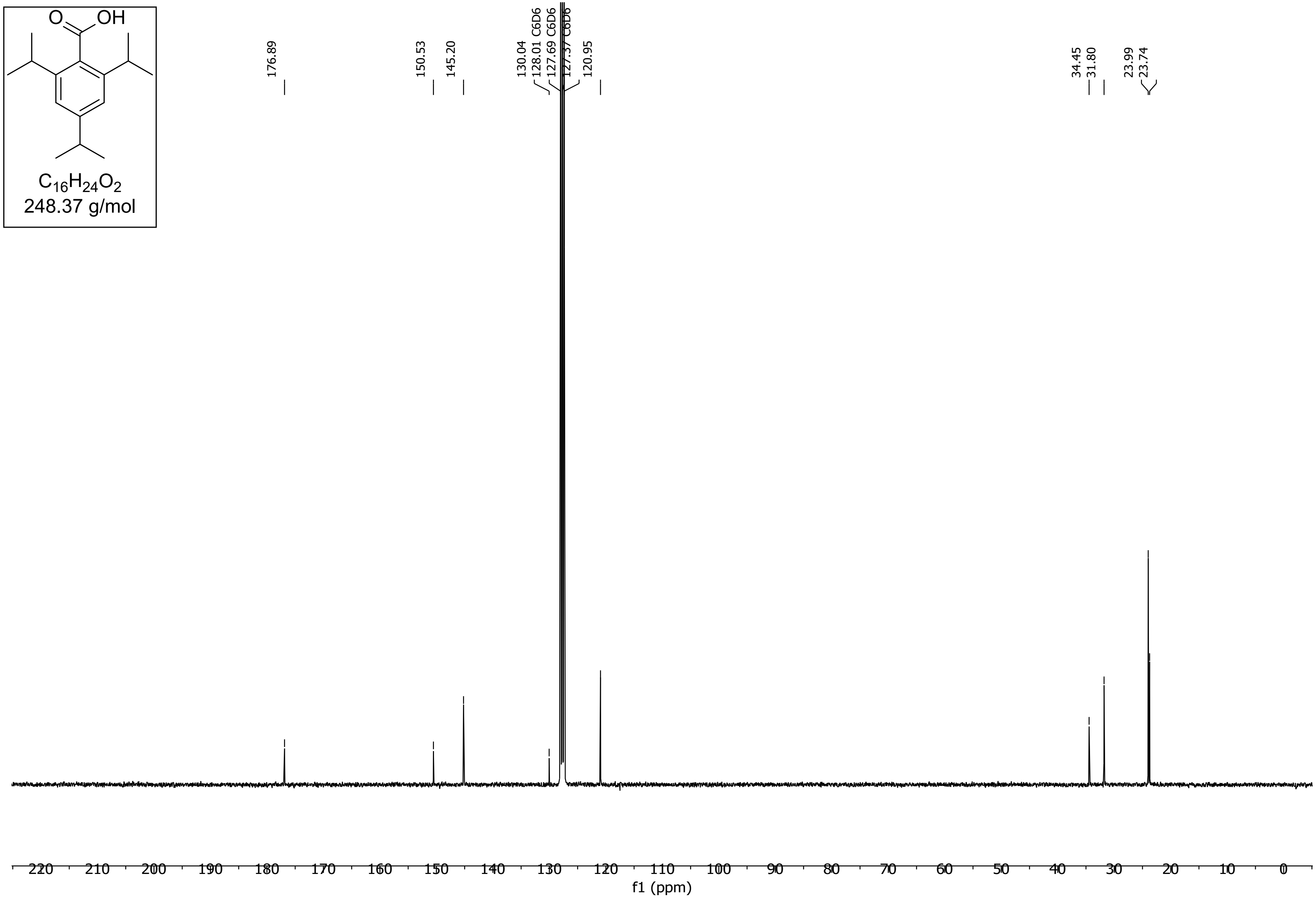
(1) Beak, P.; Carter, L. G. J. Org. Chem. **1981**, *46*, 2363.
(2) Leibfritz, D. Chem. Ber. **1975**, *108*, 3014.
(3) André-Joyaux, E.; Kuzovlev, A.; Tappin, N. D. C.; Renaud, P. Angew. Chem. Int. Ed. **2020**, *59*, 13859.
(4) Manankandayalage, C. P.; Unruh, D. K.; Krempner, C. Dalton Trans. **2020**, *49*, 4834.
(5) Ishida, K.; Yamazaki, H.; Hagiwara, C.; Abe, M.; Kusama, H. Chem. – Eur. J. **2020**, *26*, 1249.
(6) Lang, A.; Knizek, J.; Nöth, H.; Schur, S.; Thomann, M. Z. Für Anorg. Allg. Chem. **1997**, *623*, 901.
(7) Miao, L.; Haque, I.; Manzoni, M. R.; Tham, W. S.; Chemler, S. R. Org. Lett. **2010**, *12*, 4739.
(8) Roesner, S.; Brown, C. A.; Mohiti, M.; Pulis, A. P.; Rasappan, R.; Blair, D. J.; Essafi, S.; Leonori, D.; Aggarwal, V. K. Chem. Commun. **2014**, *50*, 4053.
(9) Matteson, D. S.; Majumdar, D. J. Am. Chem. Soc. **1980**, *102*, 7588.
(10) Matteson, D. S.; Majumdar, D. Organometallics **1983**, *2*, 1529.
(11) Hoffmann, R. W.; Ditrich, K.; Köster, G.; Stürmer, R. Chem. Ber. **1989**, *122*, 1783.
(12) Matteson, D. S.; Man, H. W. J. Org. Chem. **1993**, *58*, 6545.
(13) Matteson, D. S.; Man, H.-W.; Ho, O. C. J. Am. Chem. Soc. **1996**, *118*, 4560.
(14) Matteson, D. S.; Sadhu, K. M. J. Am. Chem. Soc. **1983**, *105*, 2077.
(15) Matteson, D. S. Tetrahedron **1998**, *54*, 10555.
(16) Xu, G.; Renaud, P. Angew. Chem. Int. Ed. **2016**, *55*, 3657.
(17) Larouche-Gauthier, R.; Fletcher, C. J.; Couto, I.; Aggarwal, V. K. Chem. Commun. **2011**, *47*, 12592.

^{1}H NMR (300 MHz, C_6D_6)
2,4,6-Triisopropylbenzoic acid

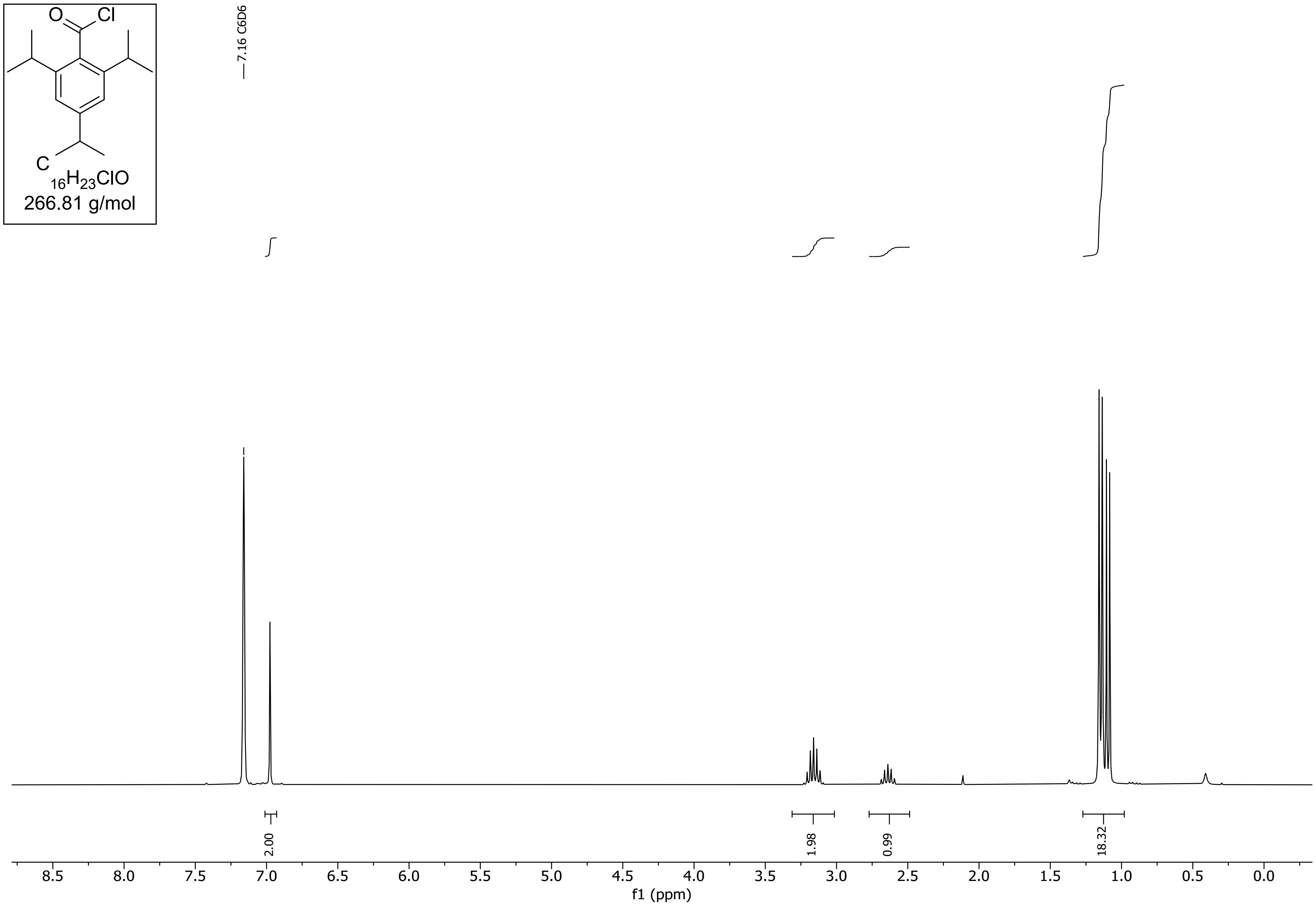


$C_{16}H_{24}O_2$
248.37 g/mol

^{13}C NMR (75 MHz, C_6D_6)
2,4,6-Triisopropylbenzoic acid

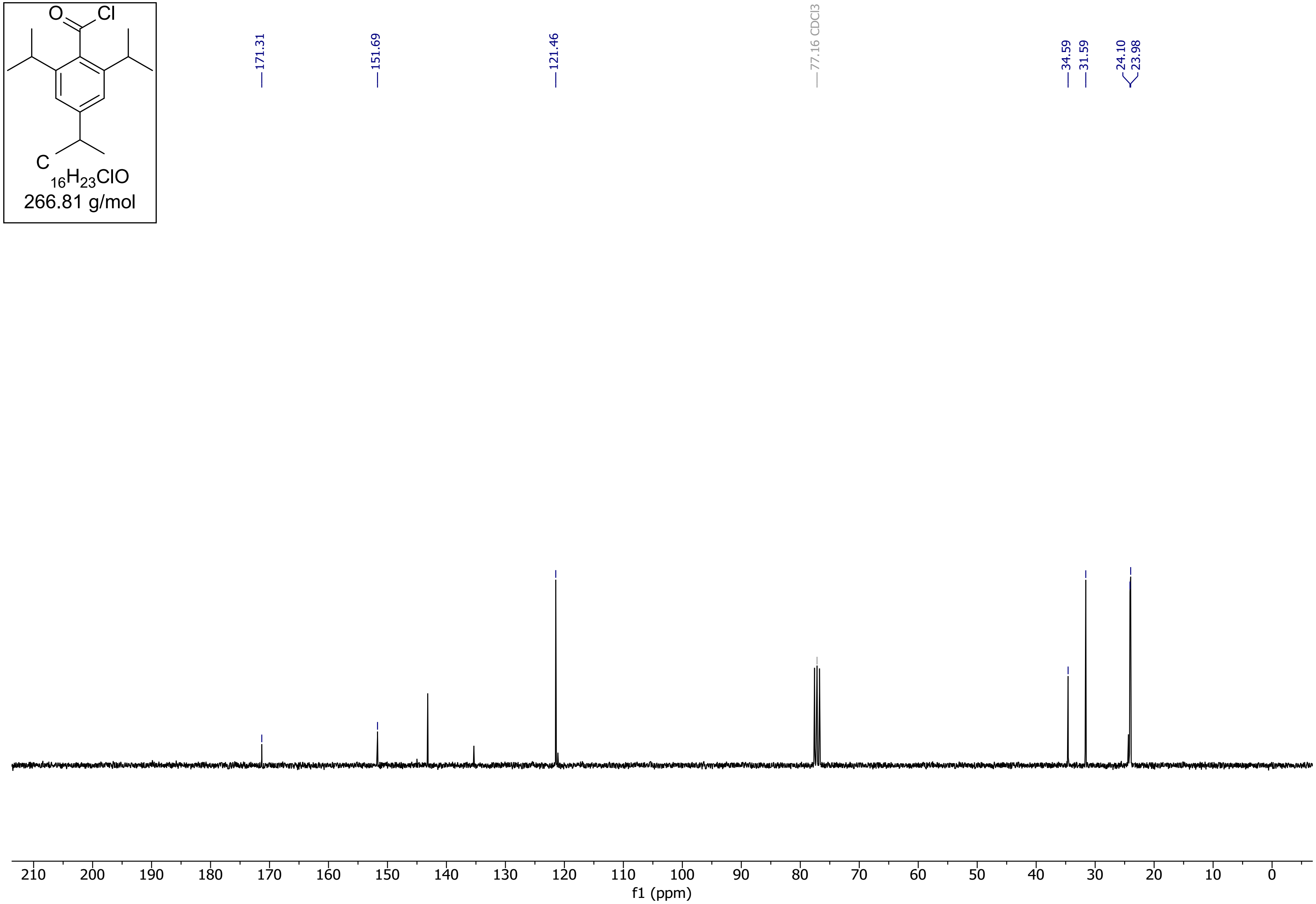


^{1}H NMR (300 MHz, C_6D_6)
2,4,6-Triisopropylbenzoyl chloride



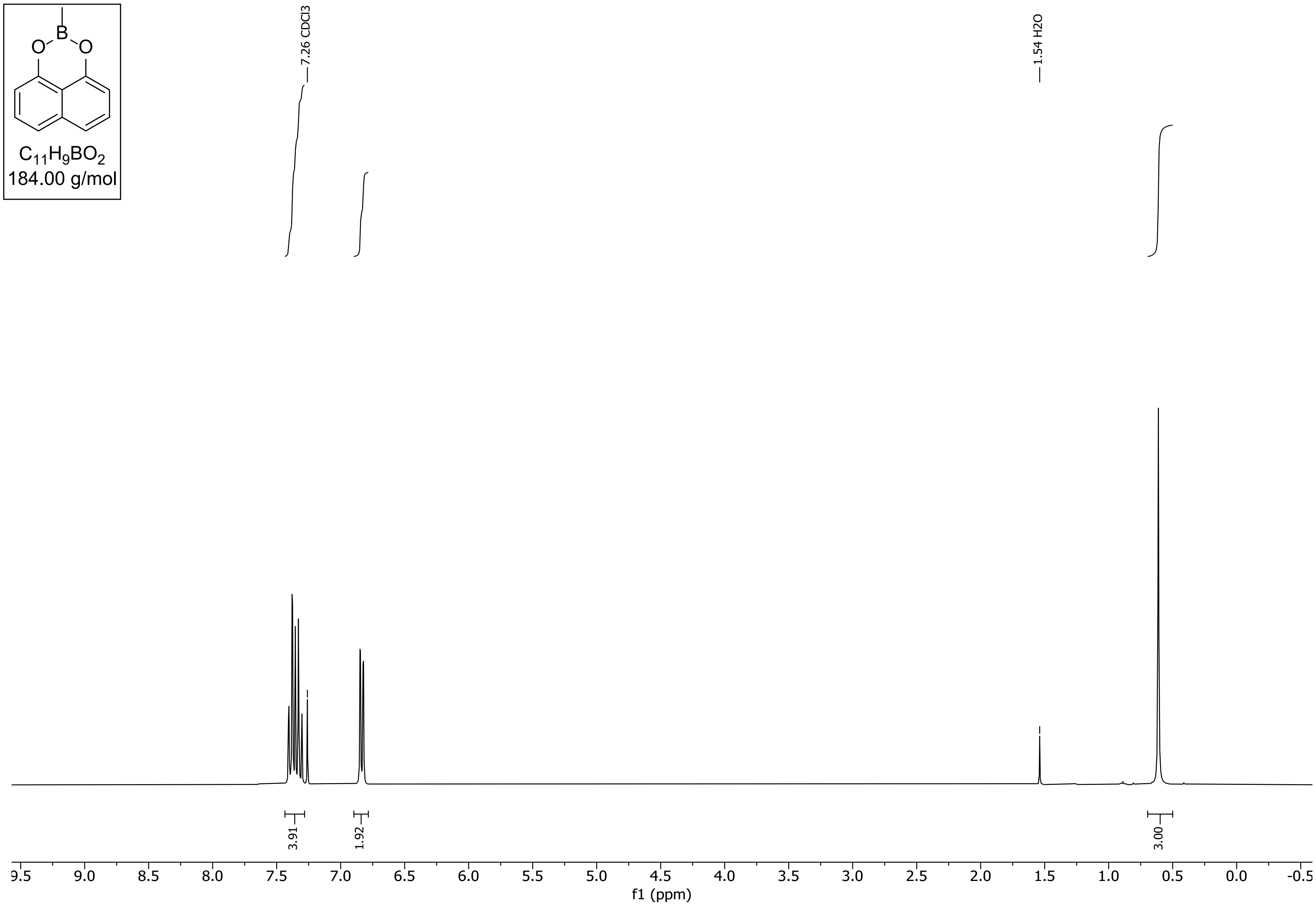
$C_{16}H_{23}ClO$
266.81 g/mol

^{13}C NMR (75 MHz, C_6D_6)
2,4,6-Triisopropylbenzoyl chloride



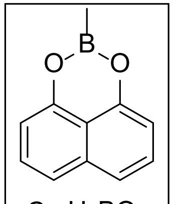
$C_{16}H_{23}ClO$
266.81 g/mol

^{1}H NMR (300 MHz, $CDCl_3$)
3-Methyl-2,4-dioxa-3-boratricyclo[7.3.1.05,13]trideca-1(13),5,7,9,11-pentaene



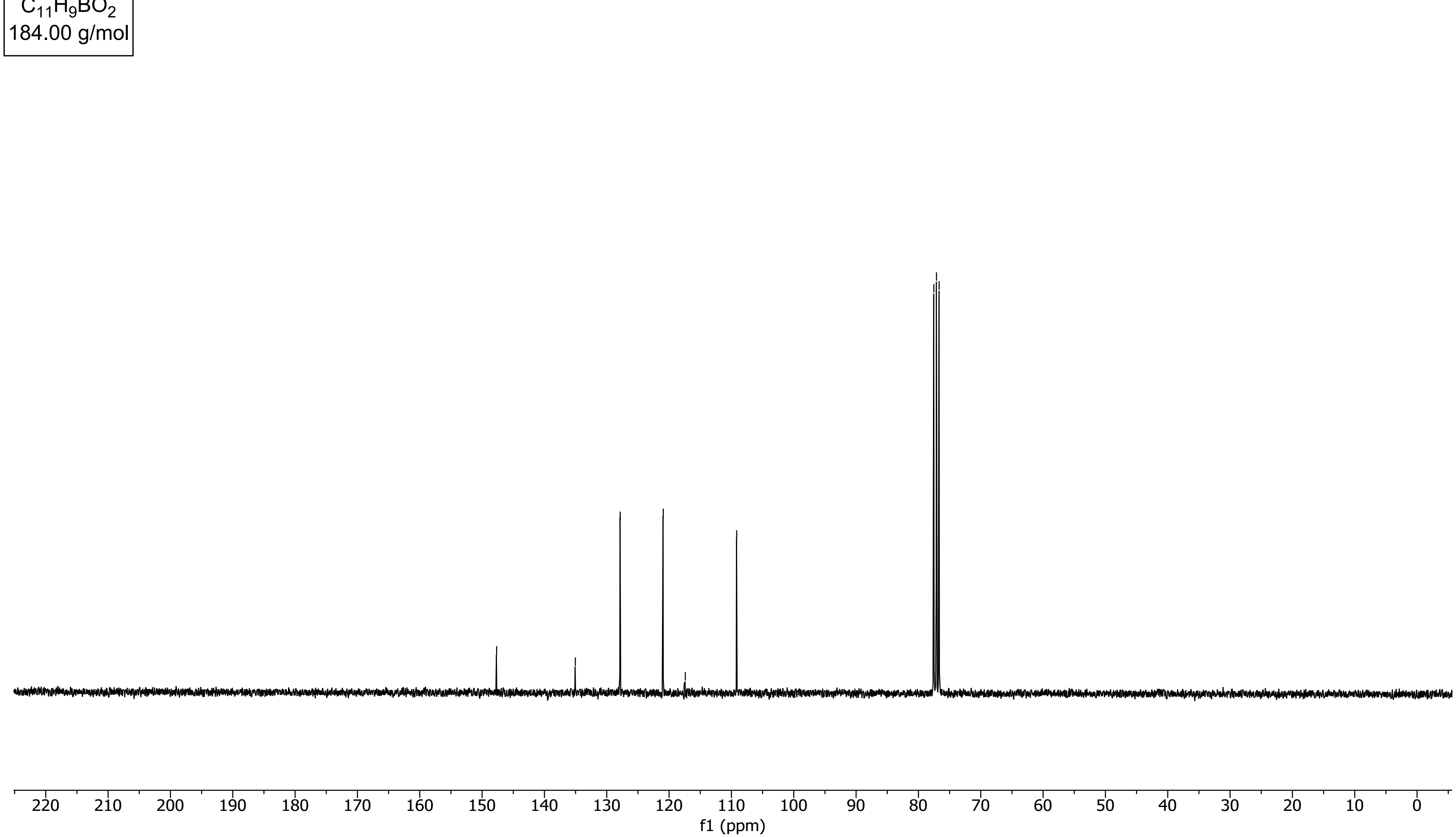
^{13}C NMR (75 MHz, $CDCl_3$)

3-Methyl-2,4-dioxa-3-boratricyclo[7.3.1.05,13]trideca-1(13),5,7,9,11-pentaene

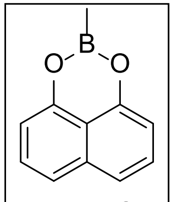


$C_{11}H_9BO_2$

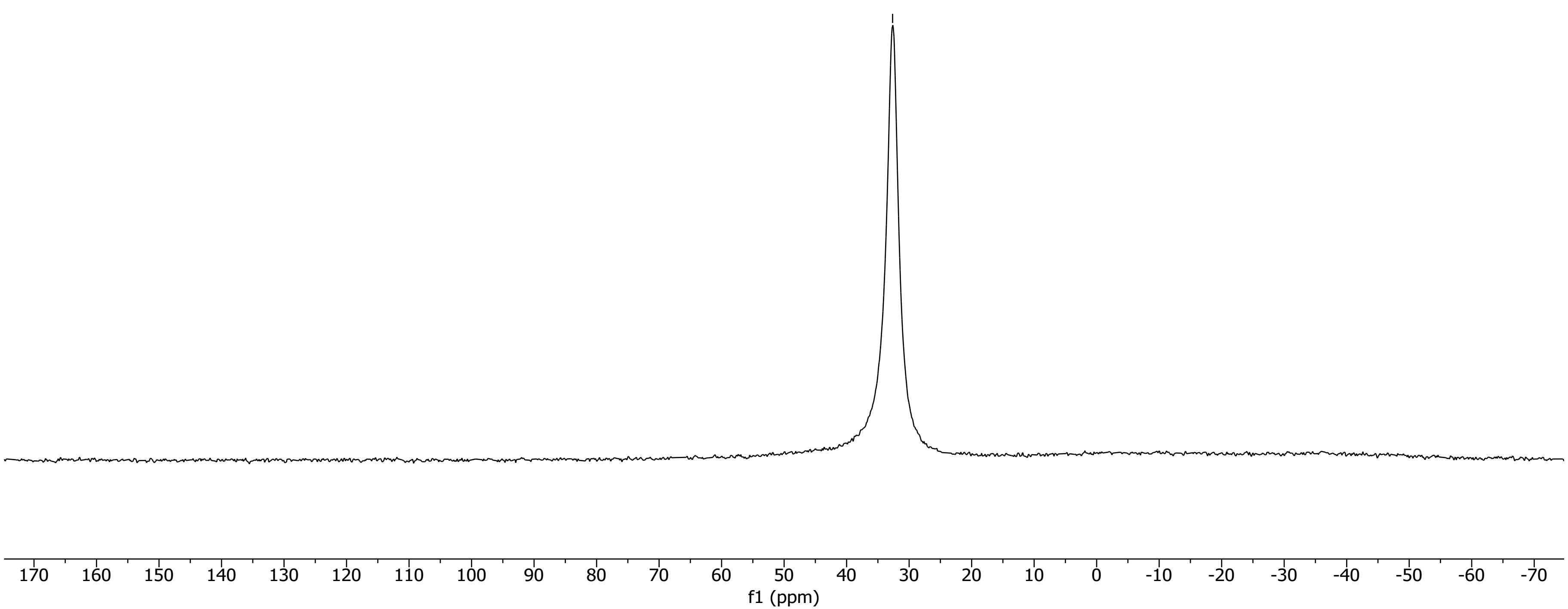
184.00 g/mol



^{11}B NMR (96 MHz, $CDCl_3$)
3-Methyl-2,4-dioxa-3-boratricyclo[7.3.1.05,13]trideca-1(13),5,7,9,11-pentaene



$C_{11}H_9BO_2$
184.00 g/mol



^{1}H NMR (300 MHz, $CDCl_3$)

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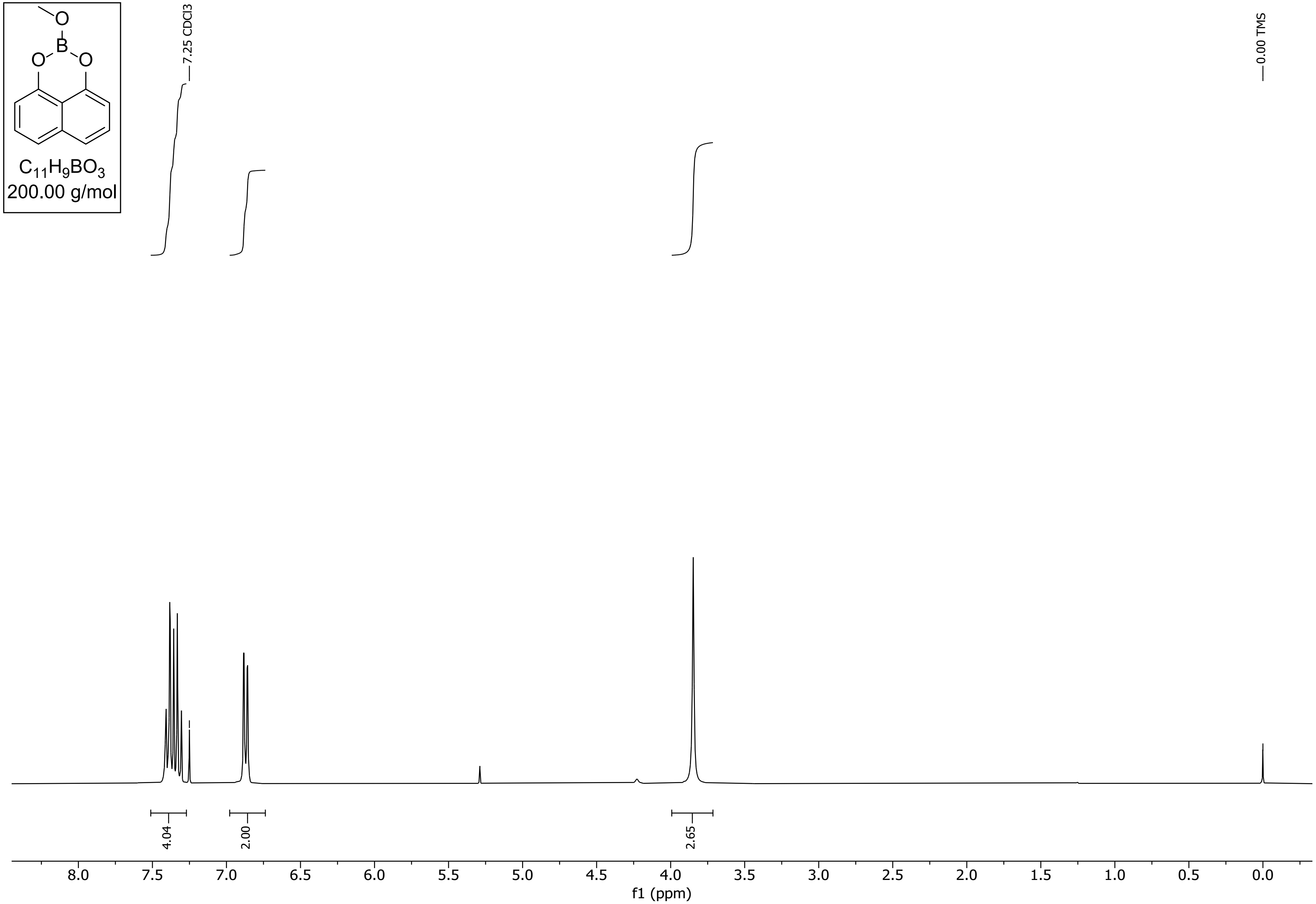
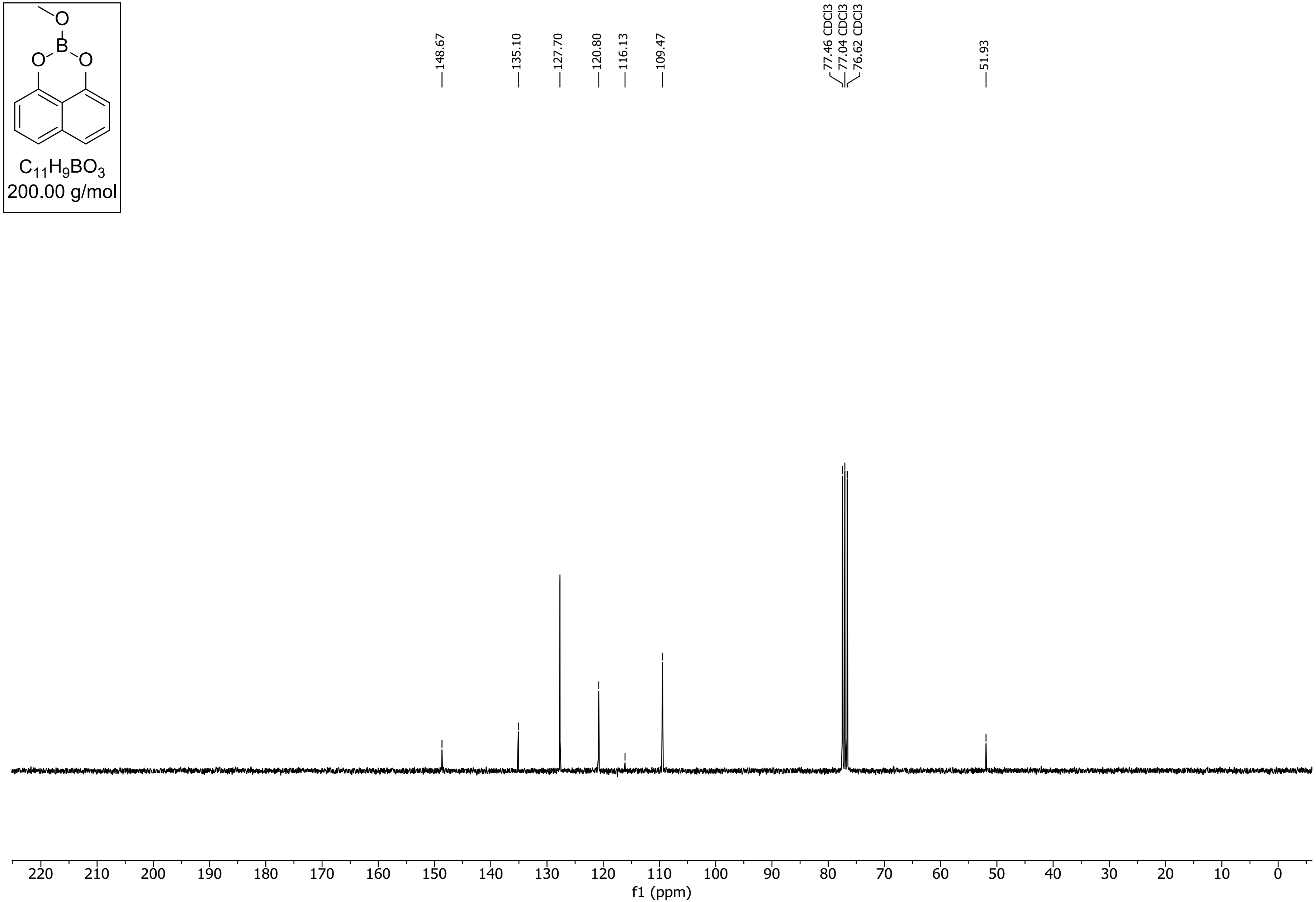
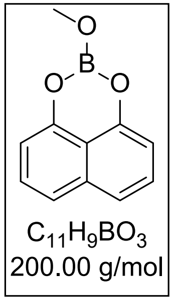


^{13}C NMR (75 MHz, CDCl$_3$)
3-Methoxy-2,4-dioxa-3-boratricyclo[7.3.1.05,13]trideca-1(13),5,7,9,11-pentaene

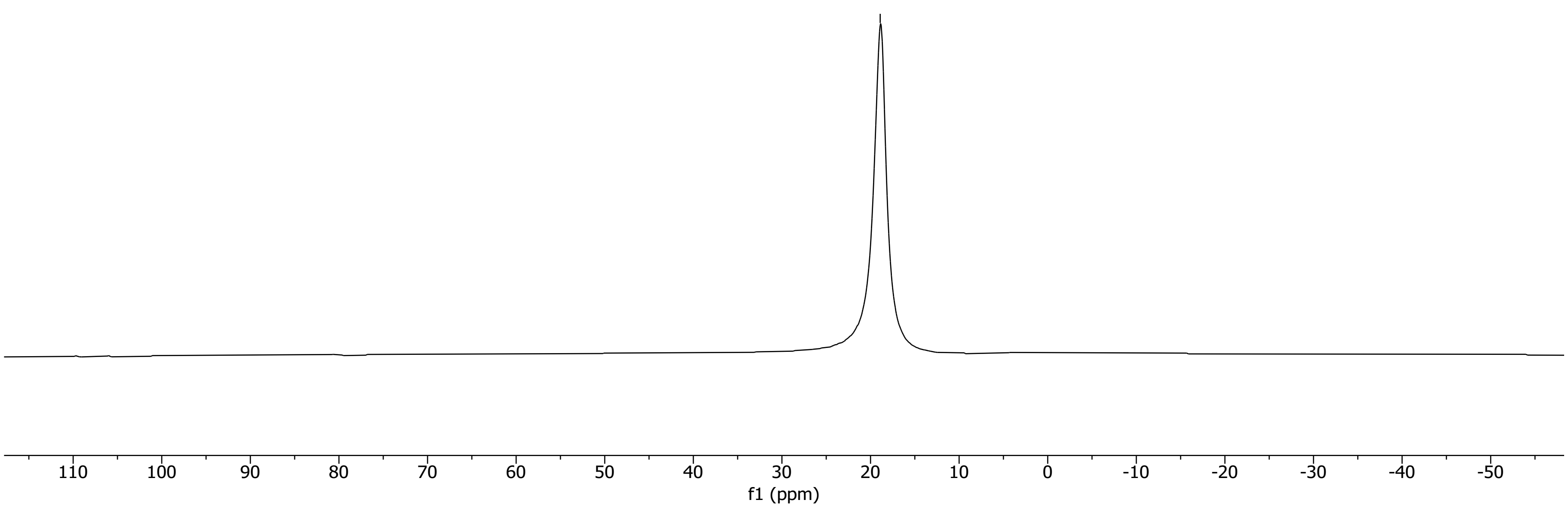


$C_{11}H_9BO_3$
200.00 g/mol

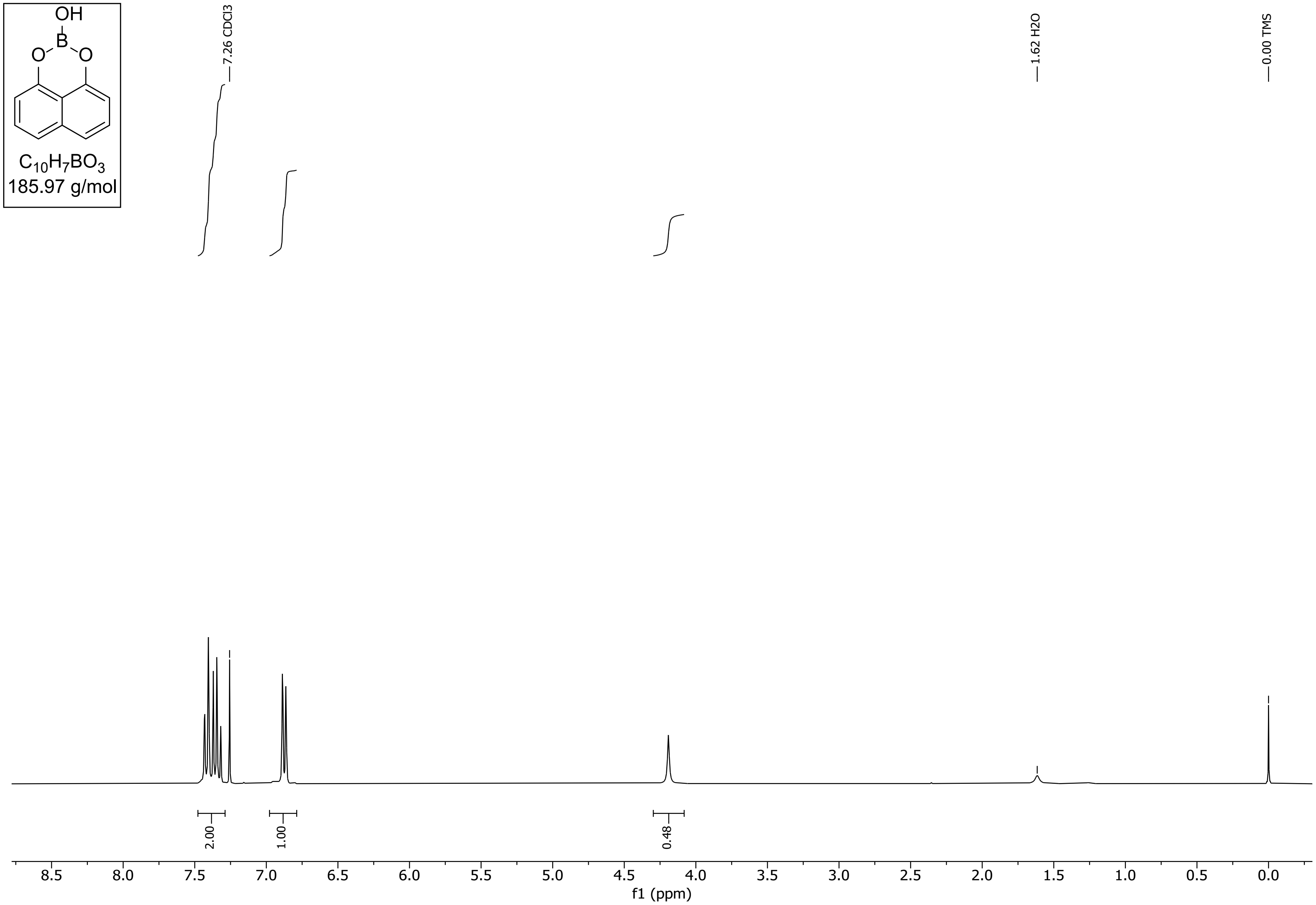
^{11}B NMR (96 MHz, $CDCl_3$)
3-Methoxy-2,4-dioxa-3-boratricyclo[7.3.1.05,13]trideca-1(13),5,7,9,11-pentaene



$C_{11}H_9BO_3$
200.00 g/mol

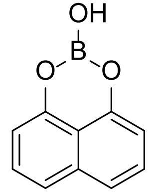


^{1}H NMR (300 MHz, $CDCl_3$)
3-Methyl-2,4-dioxa-3-boratricyclo[7.3.1.05,13]trideca-1(13),5,7,9,11-pentaene



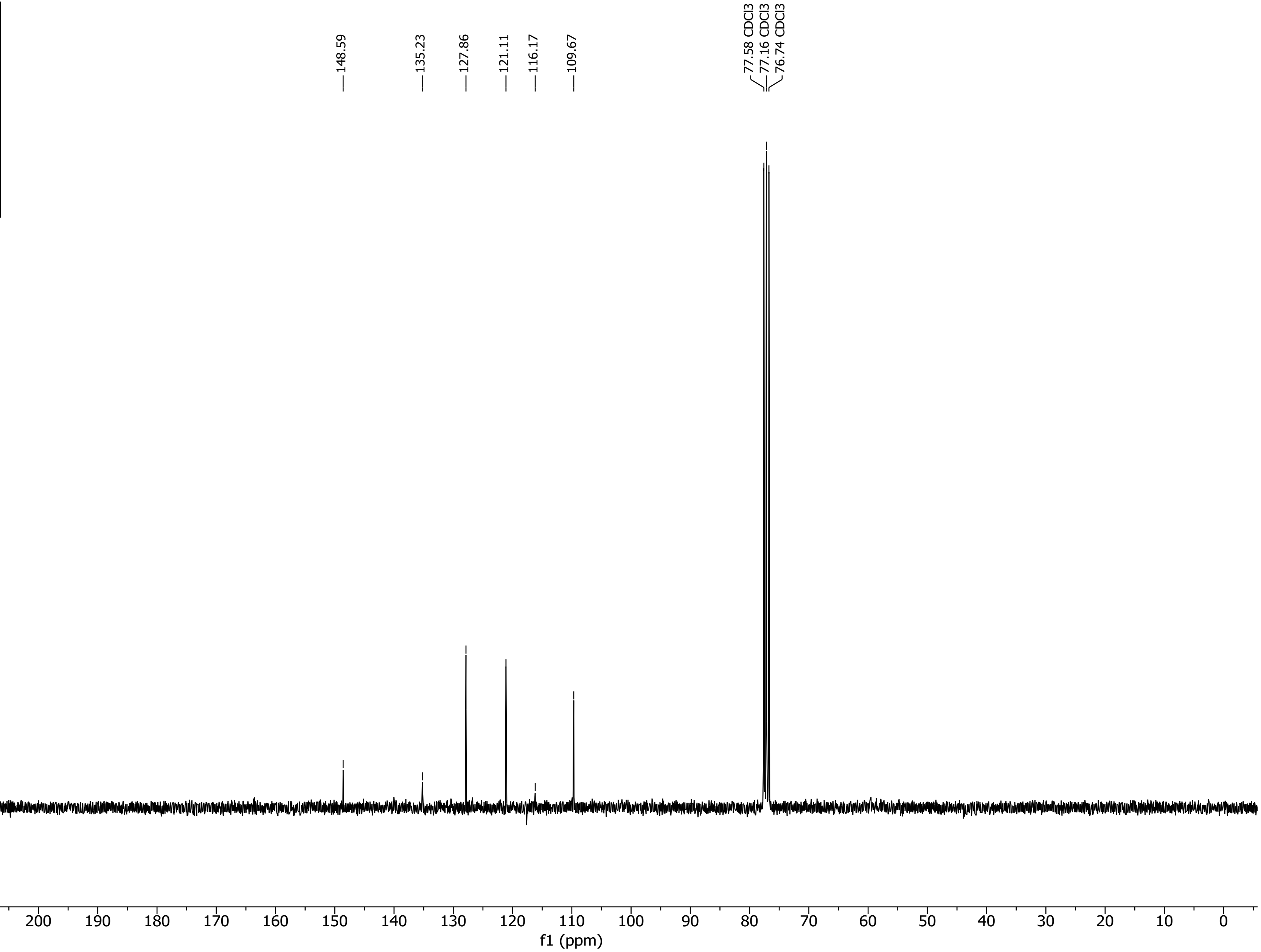
^{13}C NMR (75 MHz, $CDCl_3$)

3-Methyl-2,4-dioxa-3-boratricyclo[7.3.1.05,13]trideca-1(13),5,7,9,11-pentaene

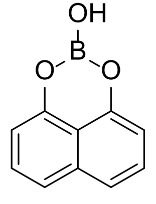


$C_{10}H_7BO_3$

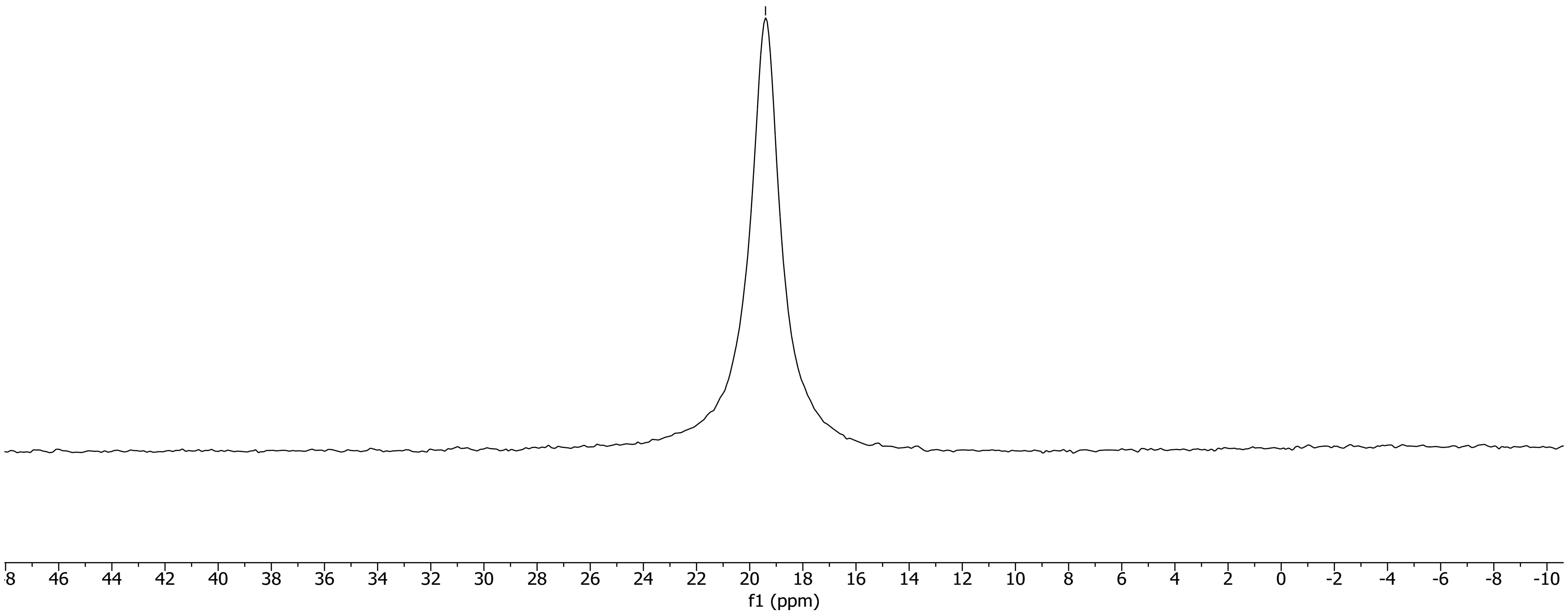
185.97 g/mol



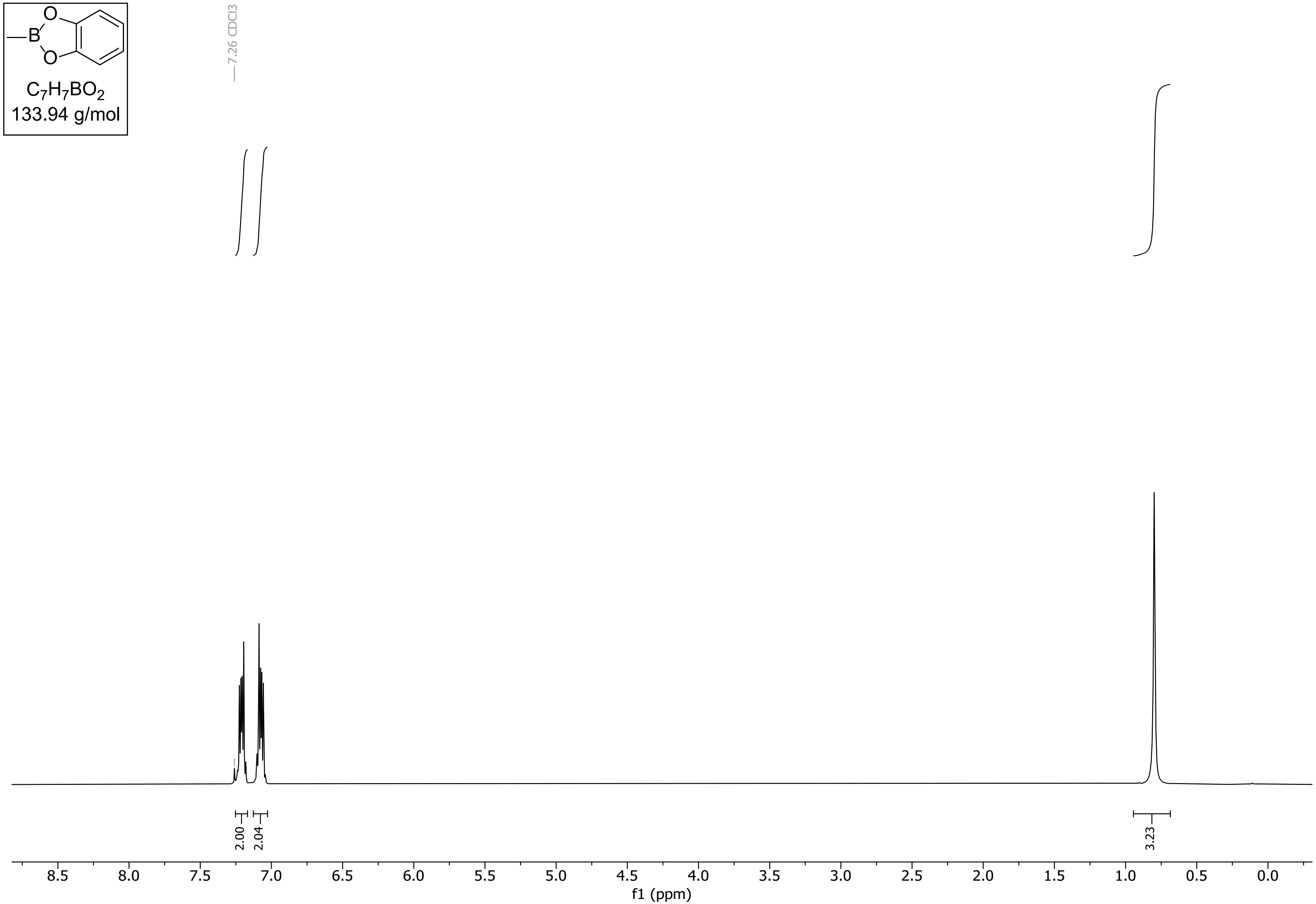
^{11}B NMR (96 MHz, $CDCl_3$)
3-Methyl-2,4-dioxa-3-boratricyclo[7.3.1.05,13]trideca-1(13),5,7,9,11-pentaene



$C_{10}H_7BO_3$
185.97 g/mol

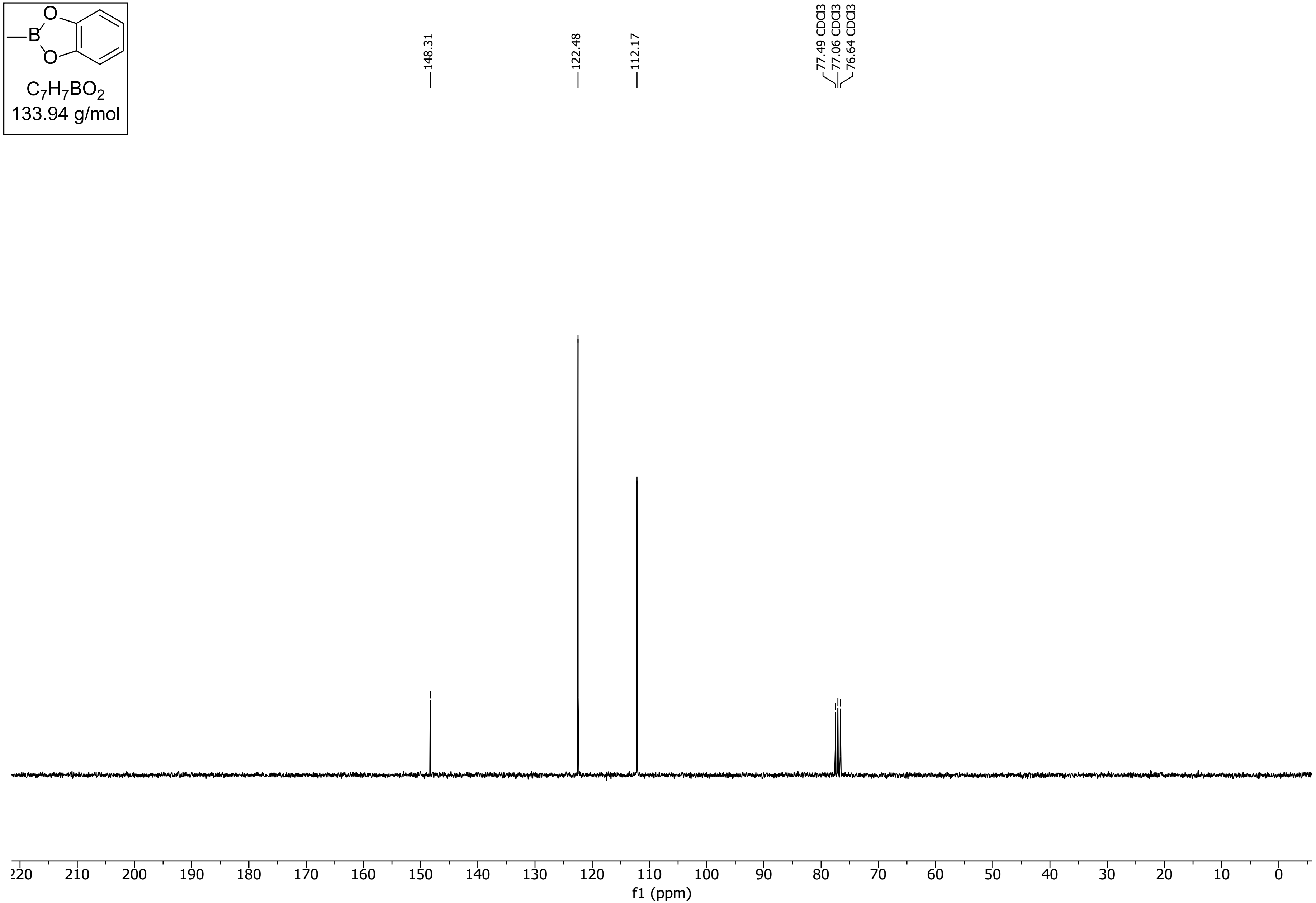


^1H NMR (300 MHz, $CDCl_3$)
2-Methyl-1,3,2-benzodioxaborole

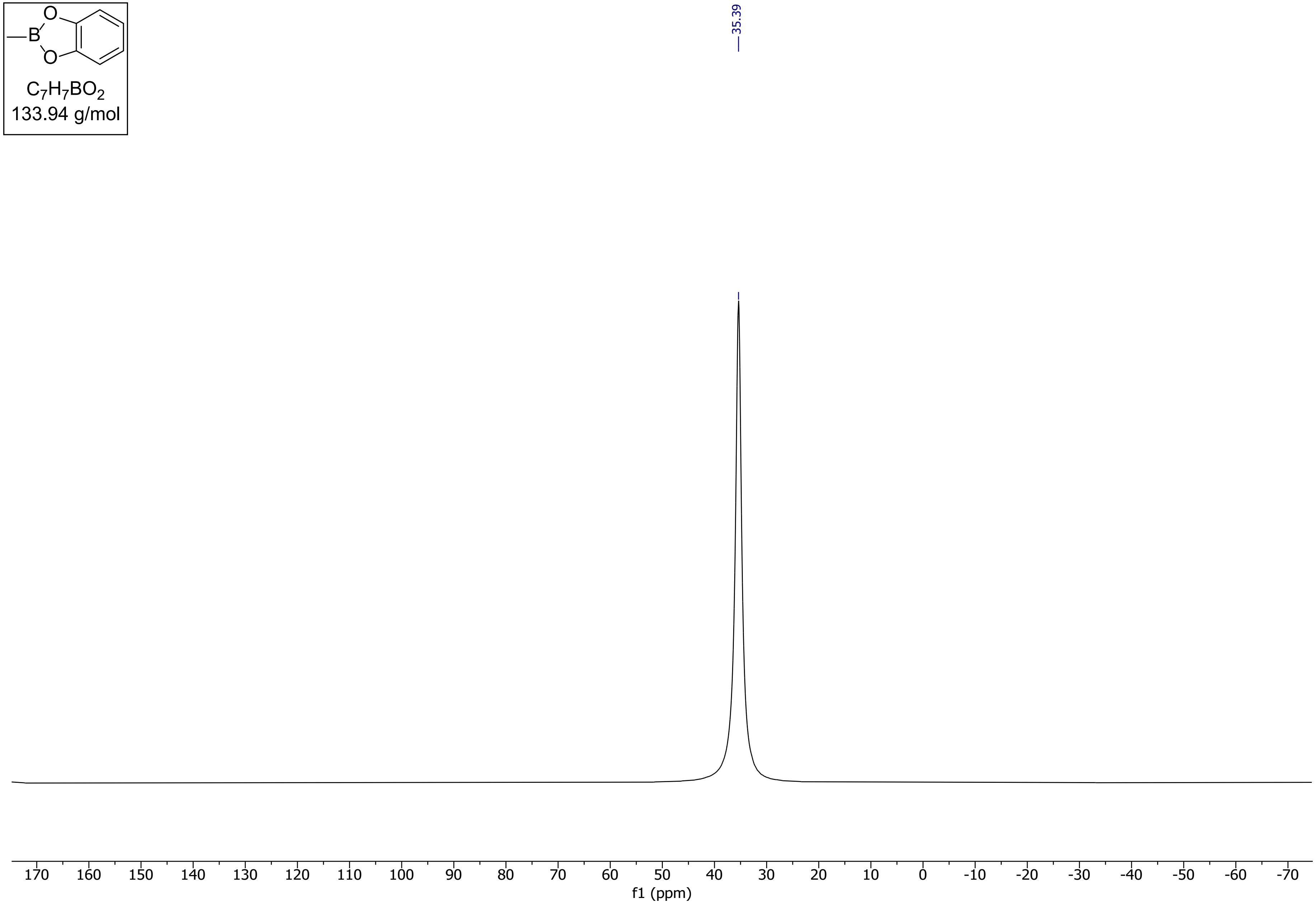


$C_7H_7BO_2$
133.94 g/mol

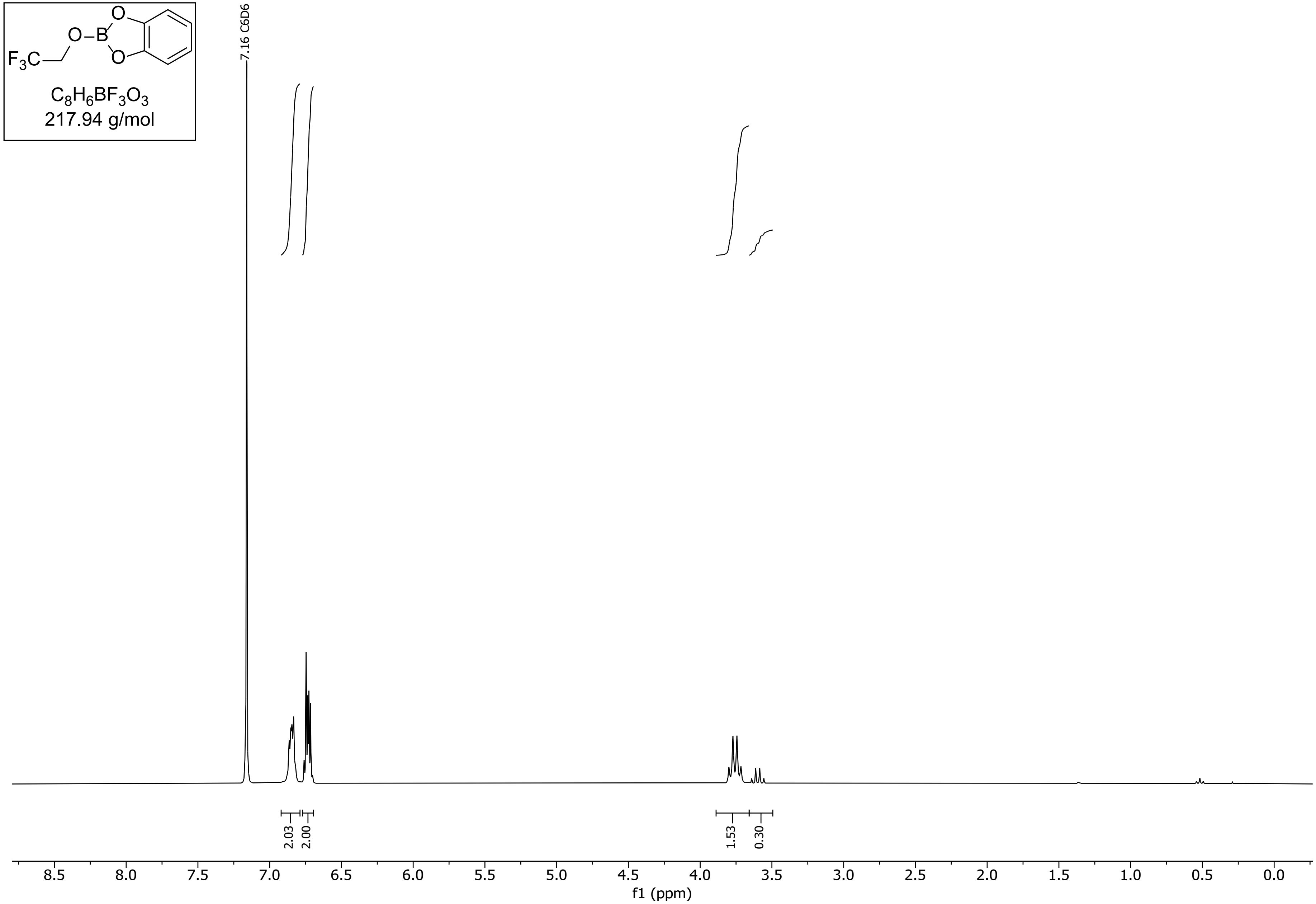
^{13}C NMR (75 MHz, $CDCl_3$)
2-Methyl-1,3,2-benzodioxaborole



^{11}B NMR (96 MHz, $CDCl_3$)
2-Methyl-1,3,2-benzodioxaborole

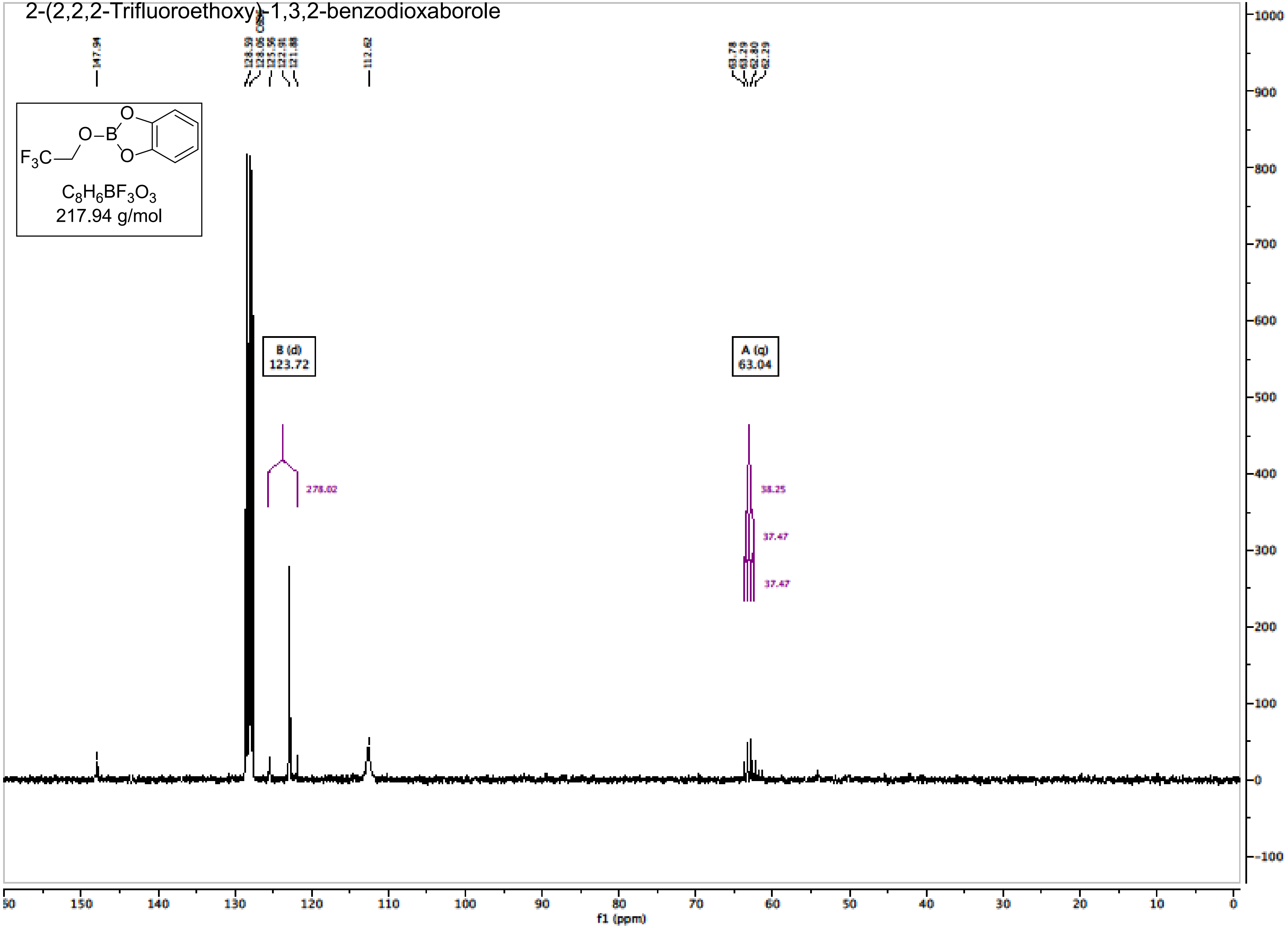


^{1}H NMR (300 MHz, $CDCl_3$)
2-(2,2,2-Trifluoroethoxy)-1,3,2-benzodioxaborole

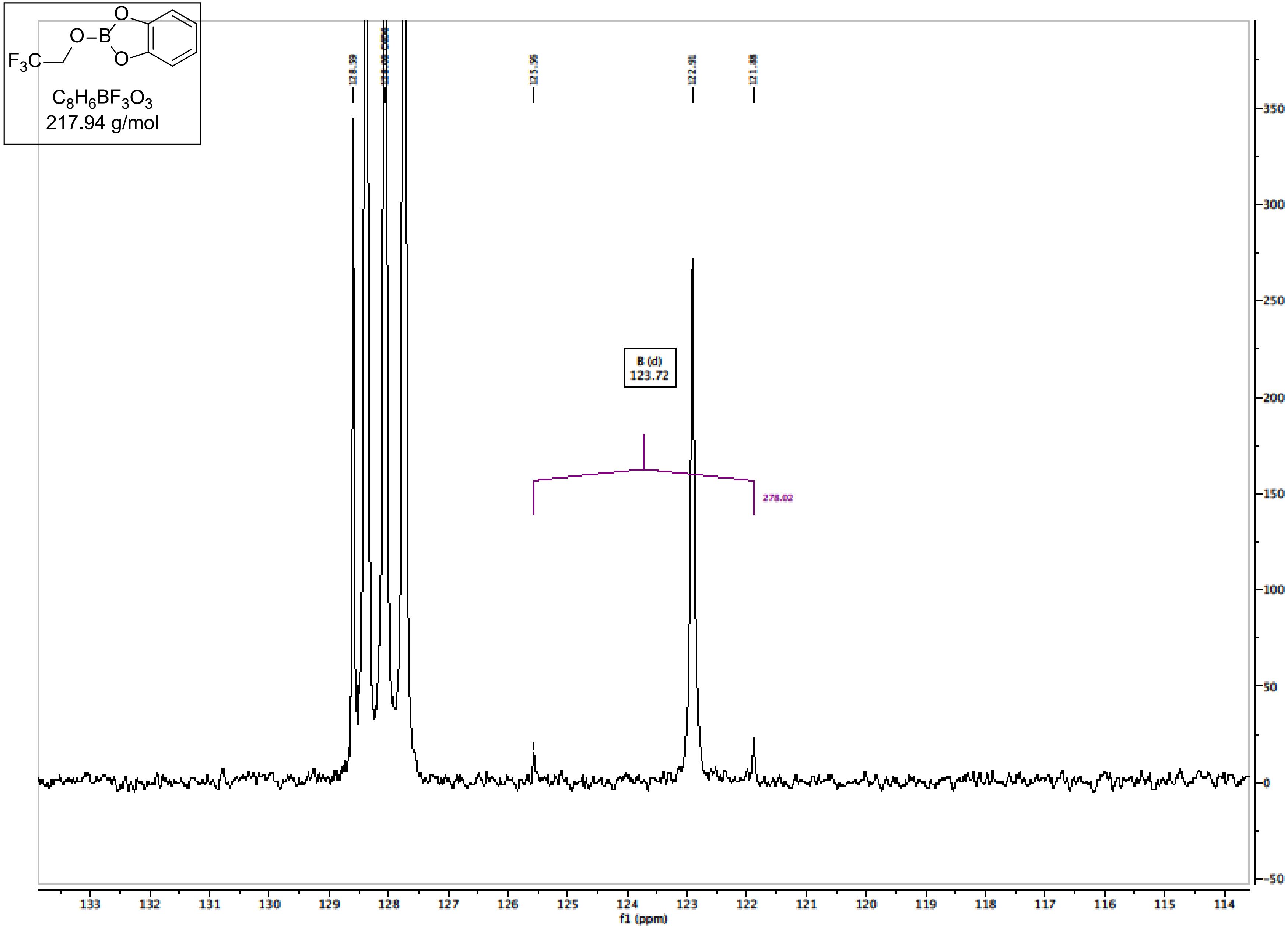


$C_8H_6BF_3O_3$
217.94 g/mol

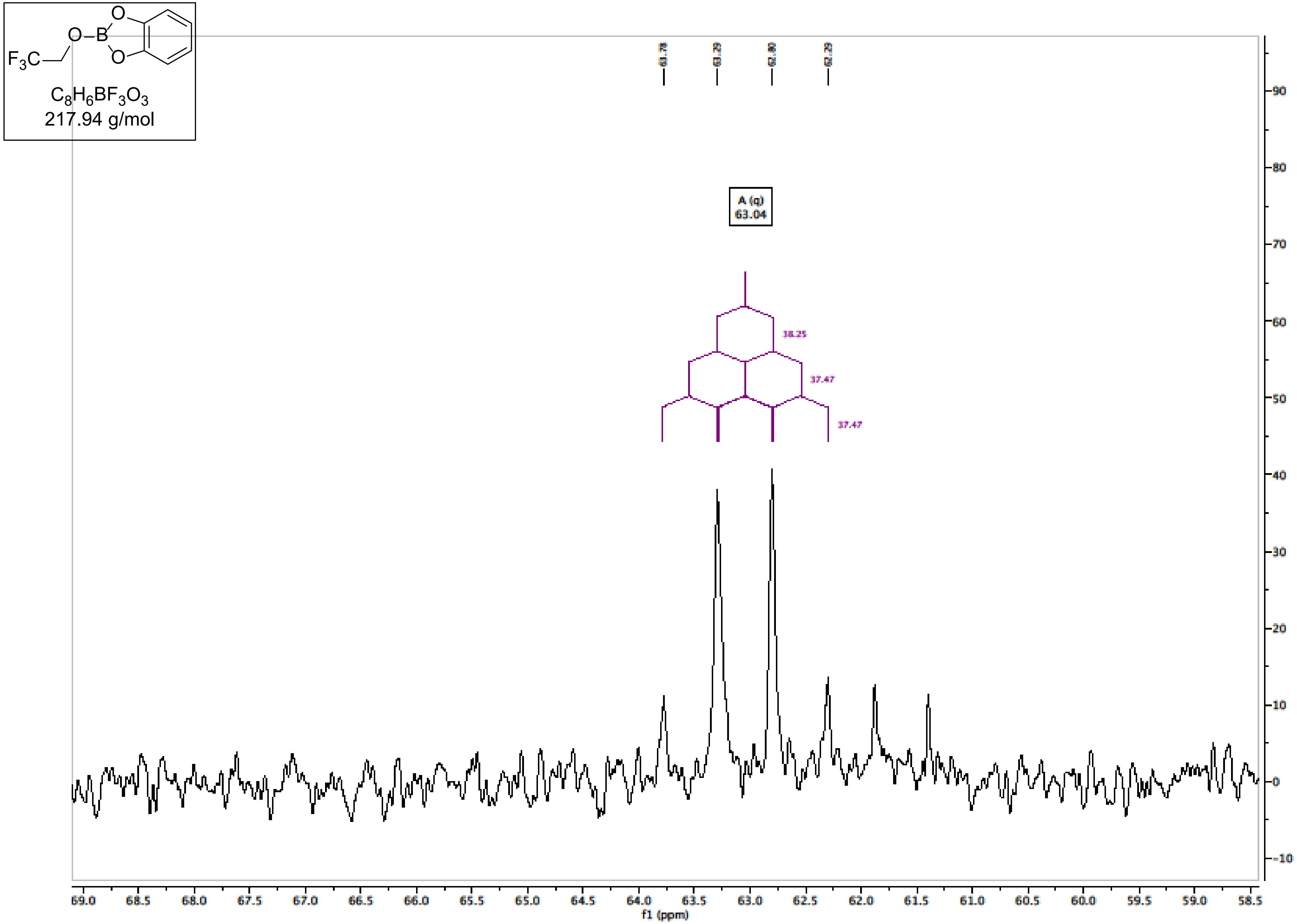
^{13}C NMR (75 MHz, $CDCl_3$)
2-(2,2,2-Trifluoroethoxy)-1,3,2-benzodioxaborole



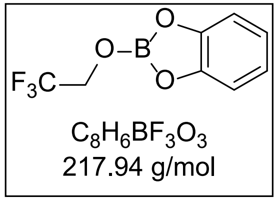
^{13}C NMR (75 MHz, $CDCl_3$)
2-(2,2,2-Trifluoroethoxy)-1,3,2-benzodioxaborole

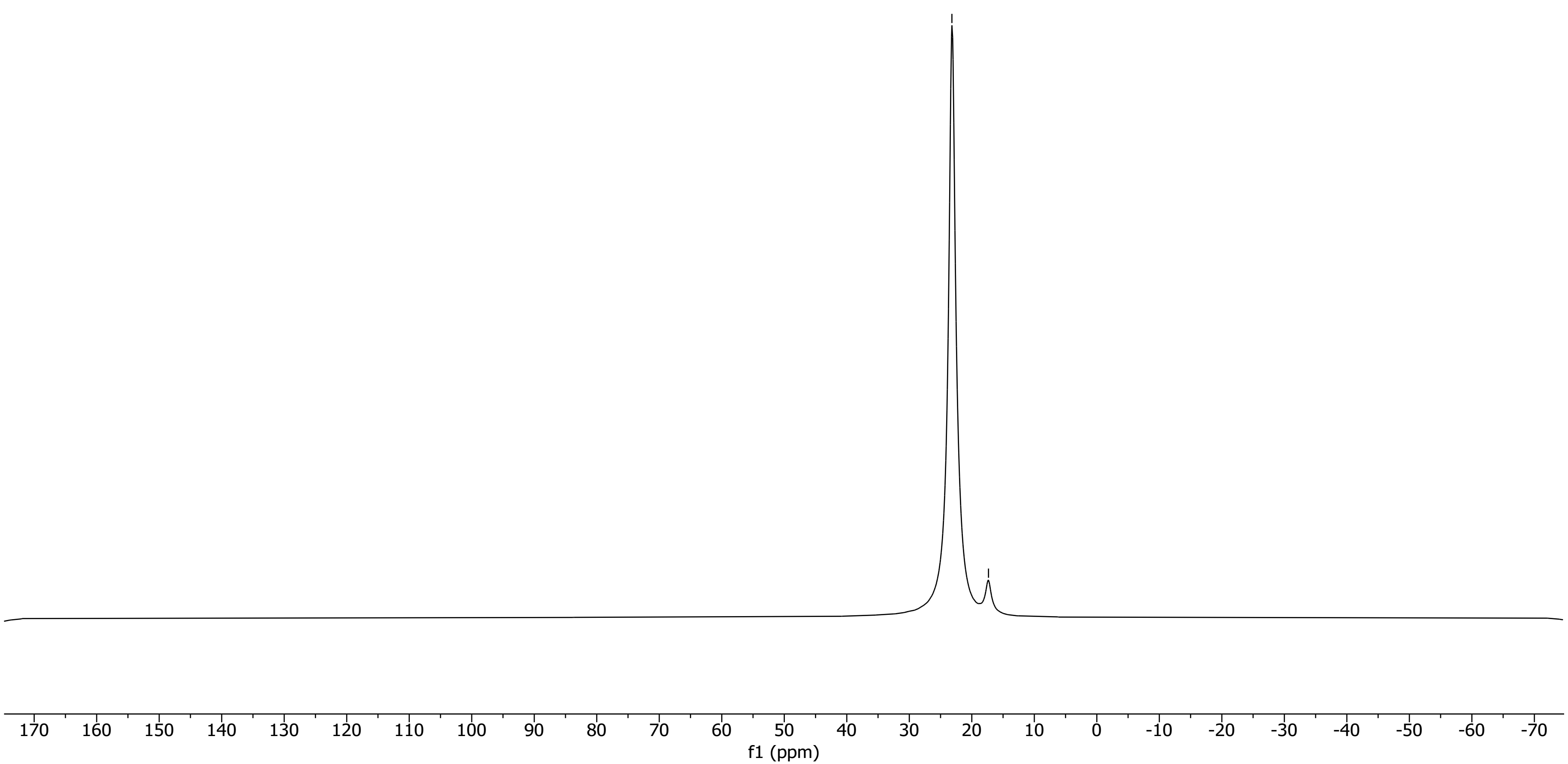


^{13}C NMR (75 MHz, $CDCl_3$)
2-(2,2,2-Trifluoroethoxy)-1,3,2-benzodioxaborole

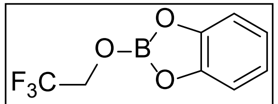


^{11}B NMR (96 MHz, $CDCl_3$)
2-(2,2,2-Trifluoroethoxy)-1,3,2-benzodioxaborole

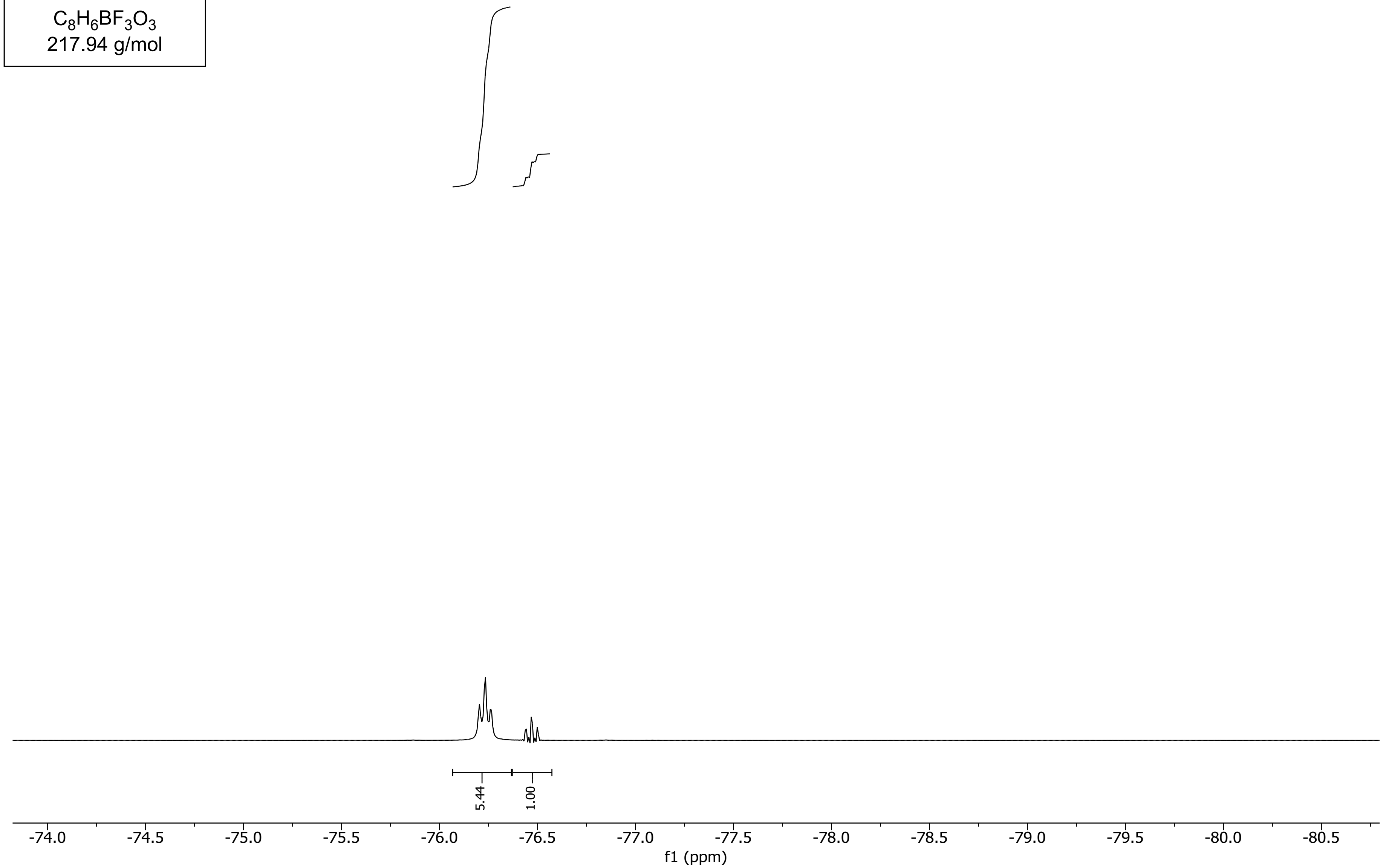




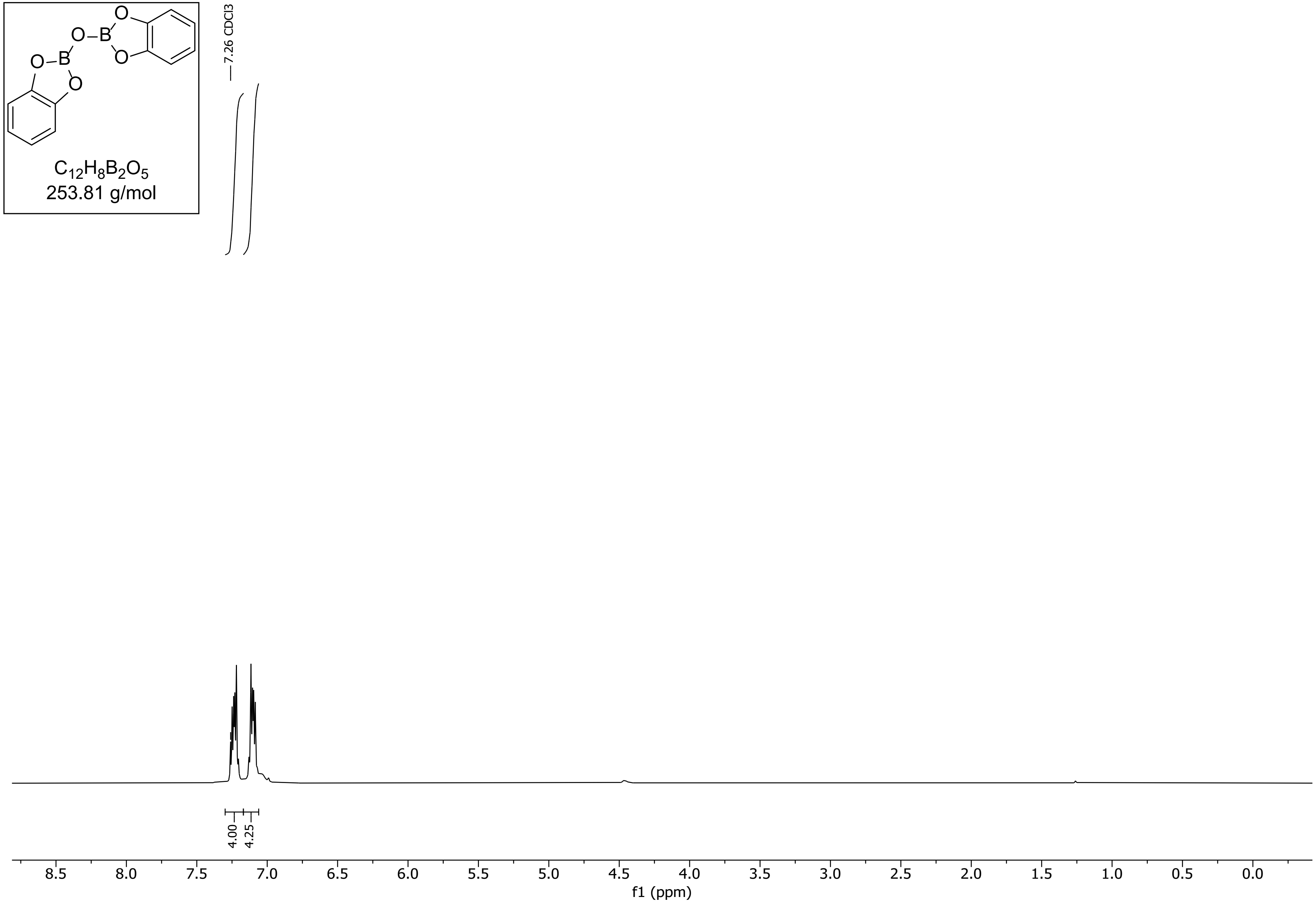
^{19}F NMR (282 MHz, $CDCl_3$)
2-(2,2,2-Trifluoroethoxy)-1,3,2-benzodioxaborole



$C_8H_6BF_3O_3$
217.94 g/mol

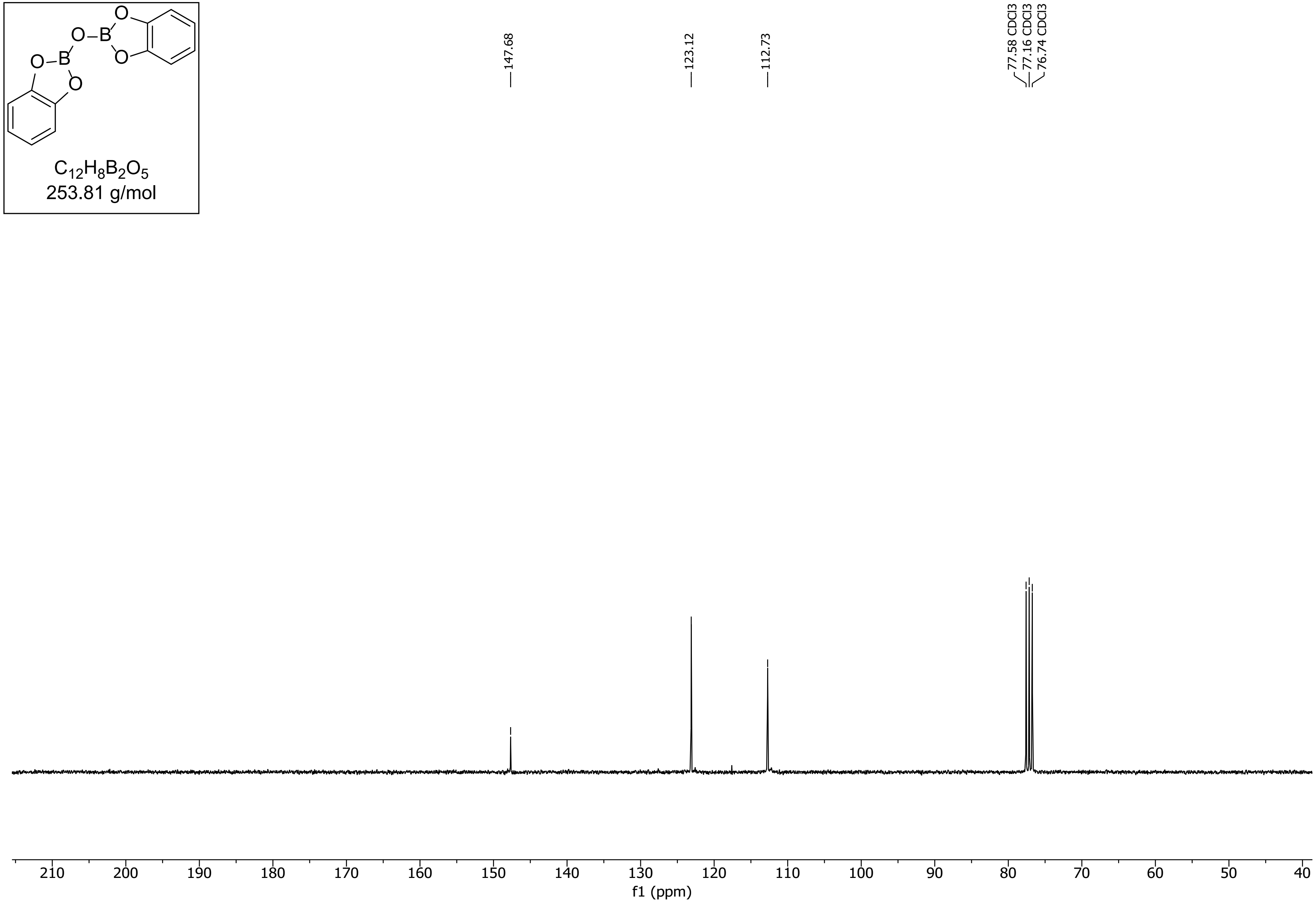


^{1}H NMR (300 MHz, CDCl$_3$)
2-(1,3,2-Benzodioxaborol-2-yloxy)-1,3,2-benzodioxaborole



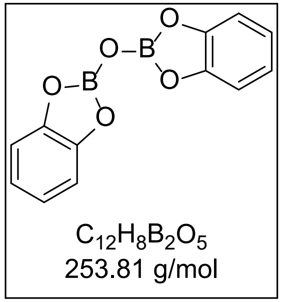
$C_{12}H_8B_2O_5$
253.81 g/mol

^{13}C NMR (75 MHz, $CDCl_3$)
2-(1,3,2-Benzodioxaborol-2-yloxy)-1,3,2-benzodioxaborole

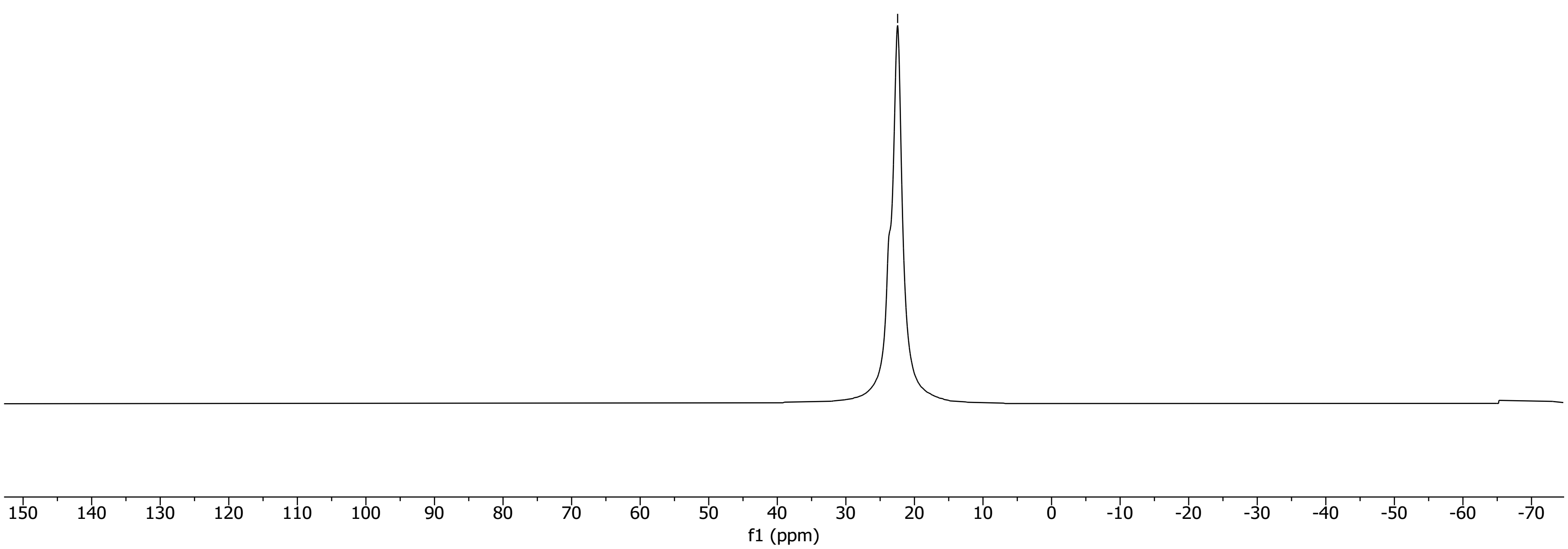


$C_{12}H_8B_2O_5$
253.81 g/mol

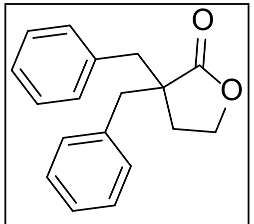
^{11}B NMR (96 MHz, $CDCl_3$)
2-(1,3,2-Benzodioxaborol-2-yloxy)-1,3,2-benzodioxaborole



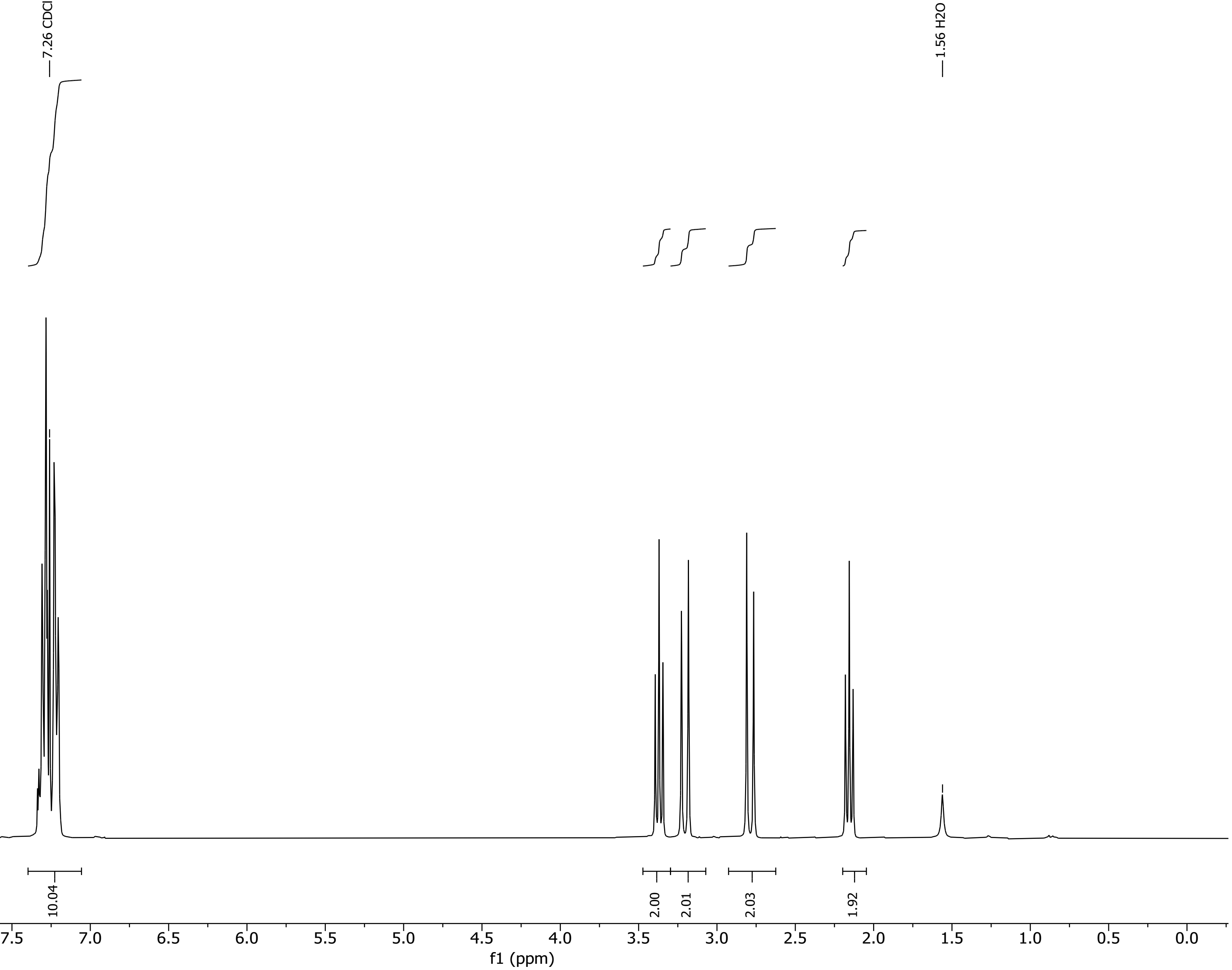
$C_{12}H_8B_2O_5$
253.81 g/mol



^{1}H NMR (300 MHz, $CDCl_3$)
3,3-Dibenzyldihydrofuran-2(3H)-one (**1**)

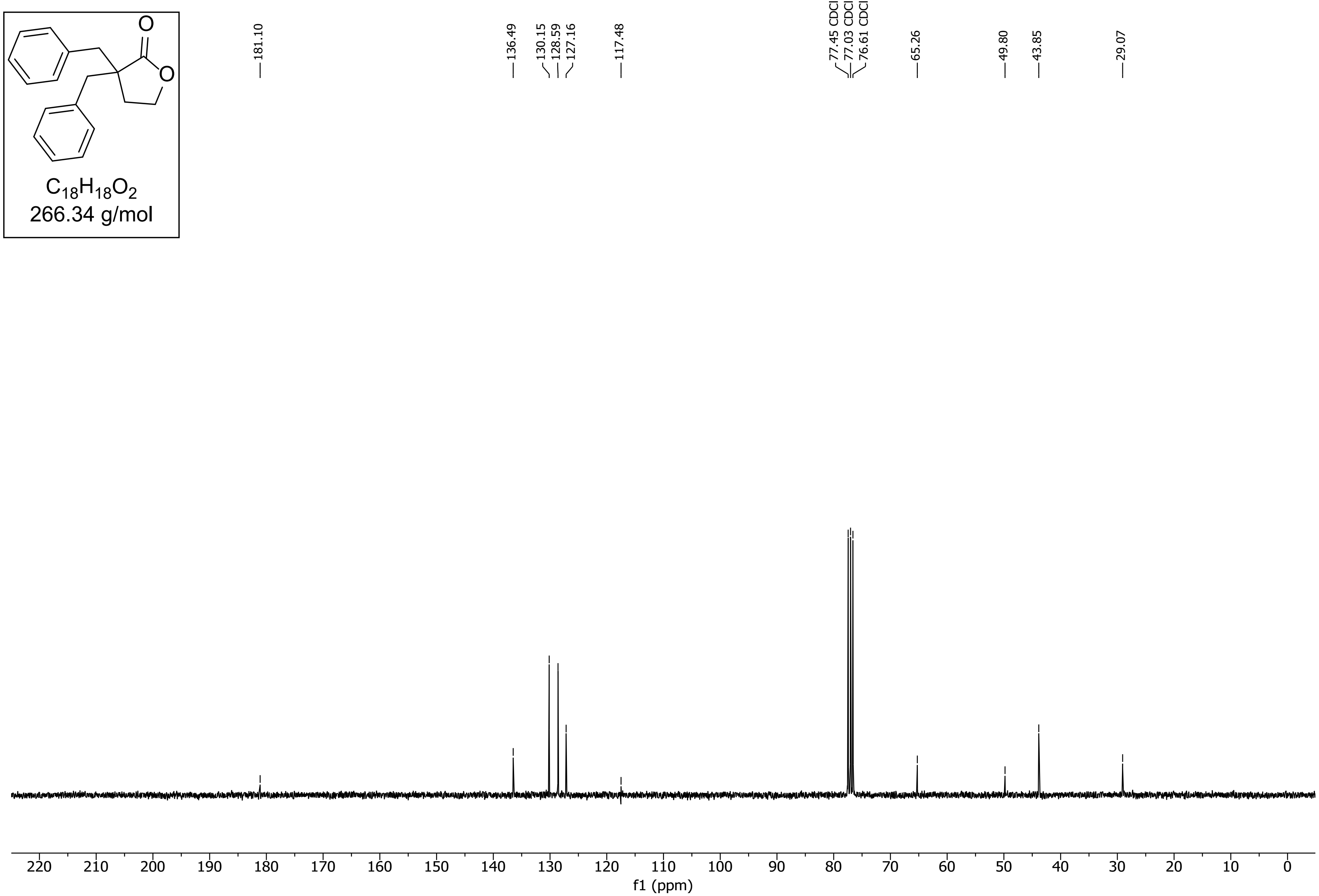


$C_{18}H_{18}O_2$
266.34 g/mol



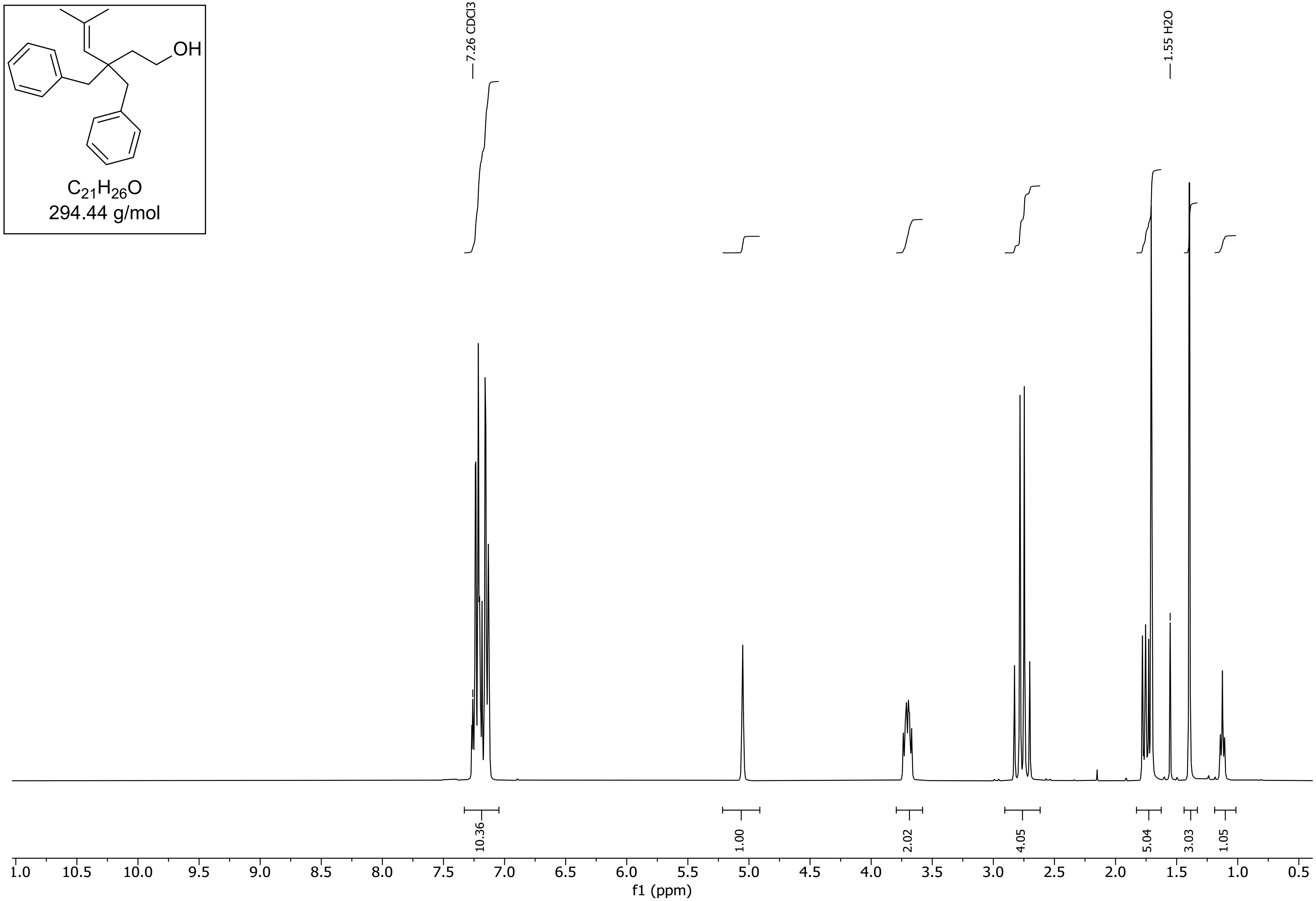
^{13}C NMR (75 MHz, $CDCl_3$)

3,3-Dibenzyldihydrofuran-2(3H)-one (**1**)

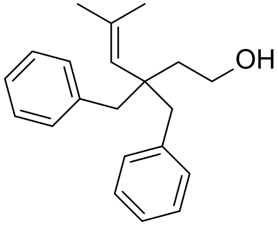


$C_{18}H_{18}O_2$
266.34 g/mol

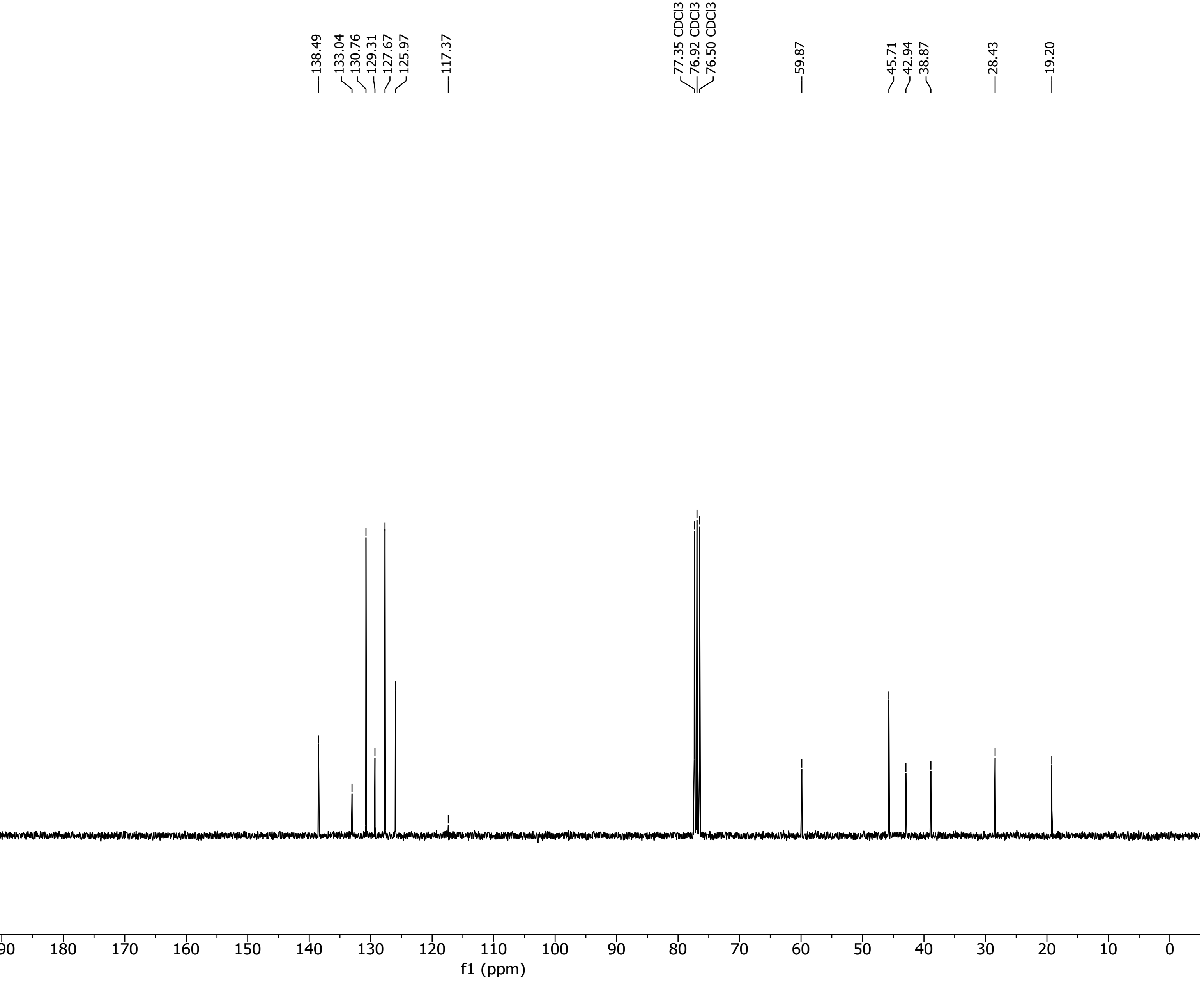
^{1}H NMR (300 MHz, $CDCl_3$)
3,3-Dibenzyl-5-methyl-hex-4-en-1-ol (**2**)



^{13}C NMR (75 MHz, $CDCl_3$)
3,3-Dibenzyl-5-methyl-hex-4-en-1-ol (**2**)

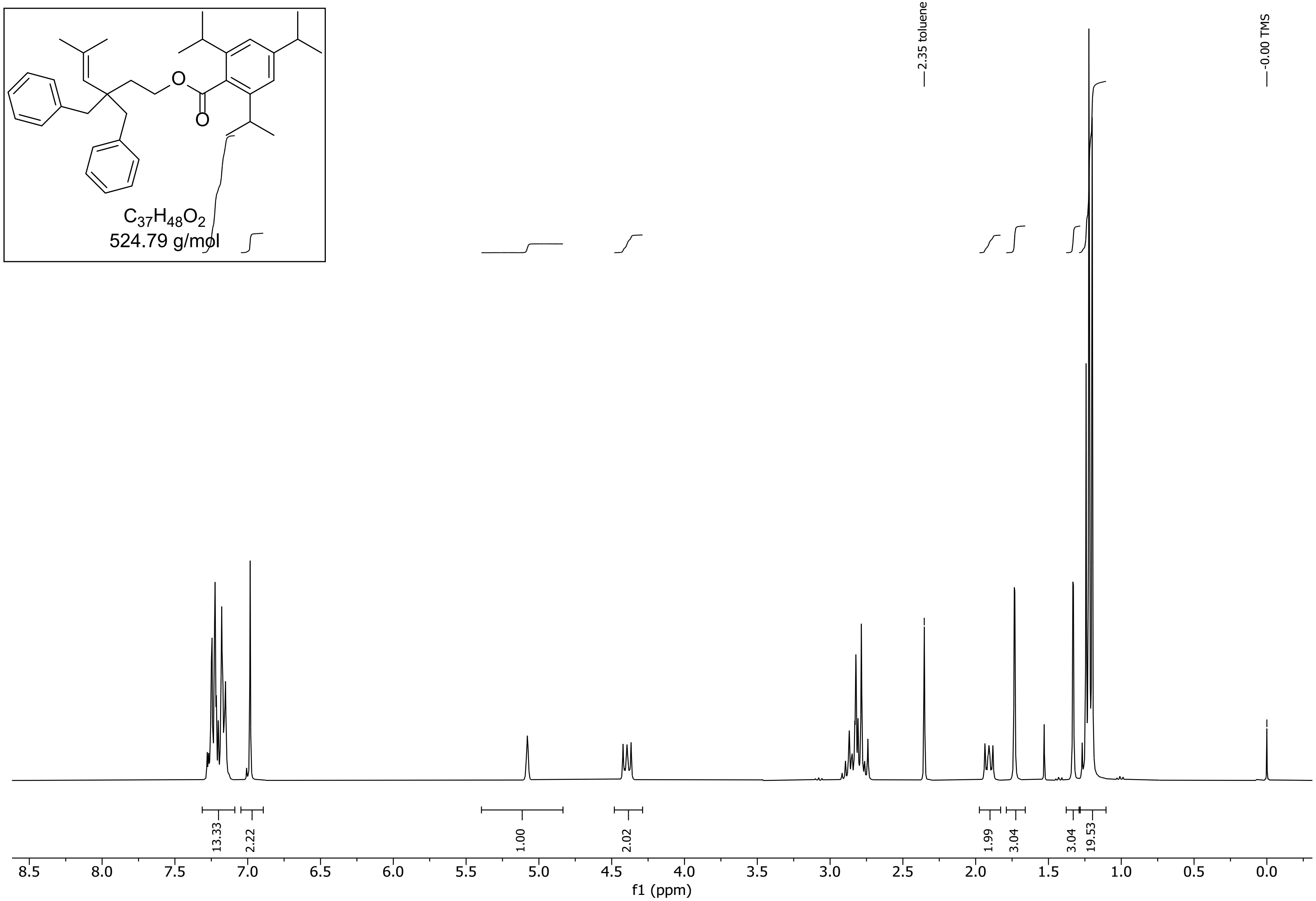


$C_{21}H_{26}O$
294.44 g/mol

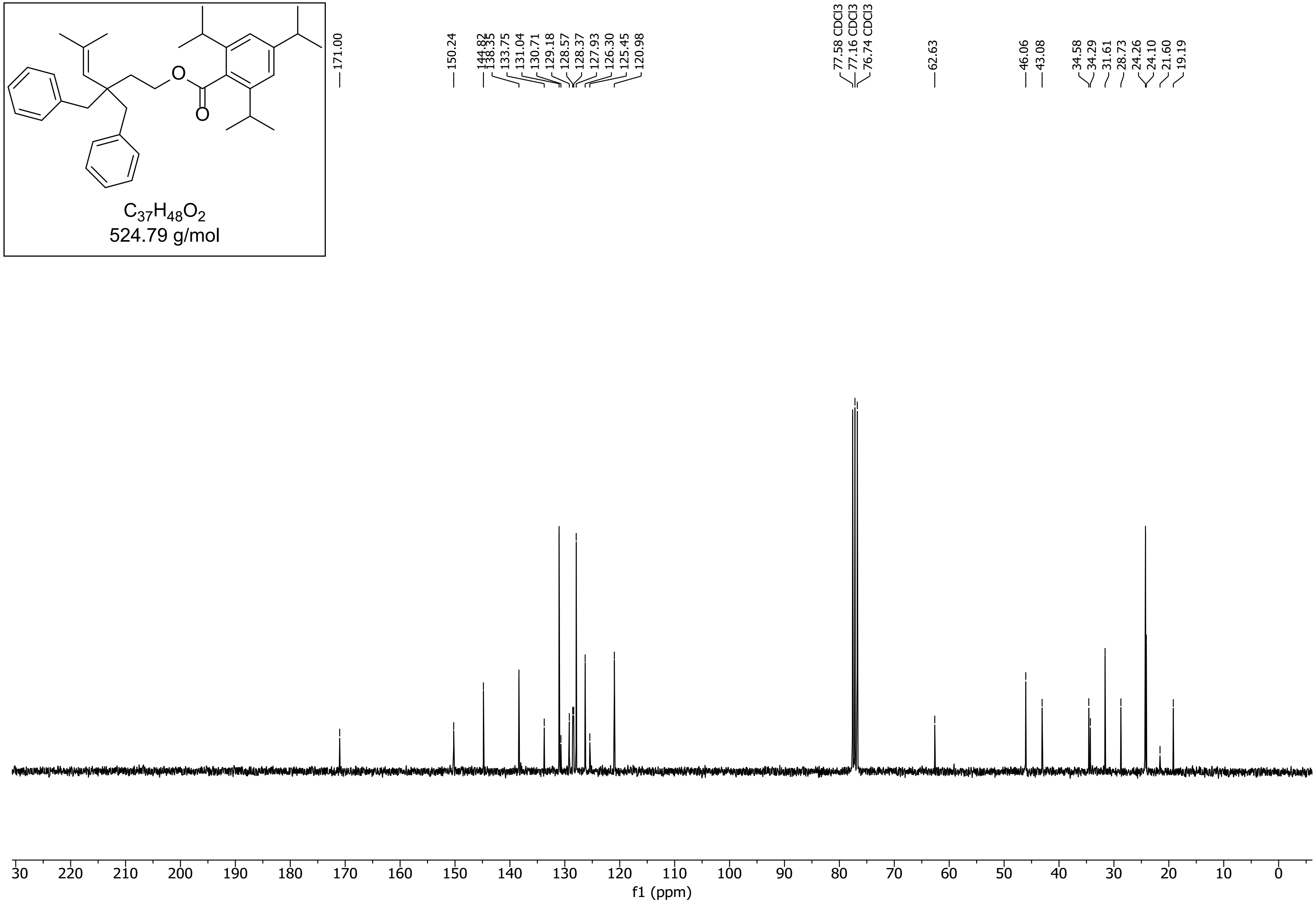


^{1}H NMR (300 MHz, CDCl$_3$)

(3,3-Dibenzyl-5-methyl-hex-4-enyl) 2,4,6-triisopropylbenzoate (**3**)

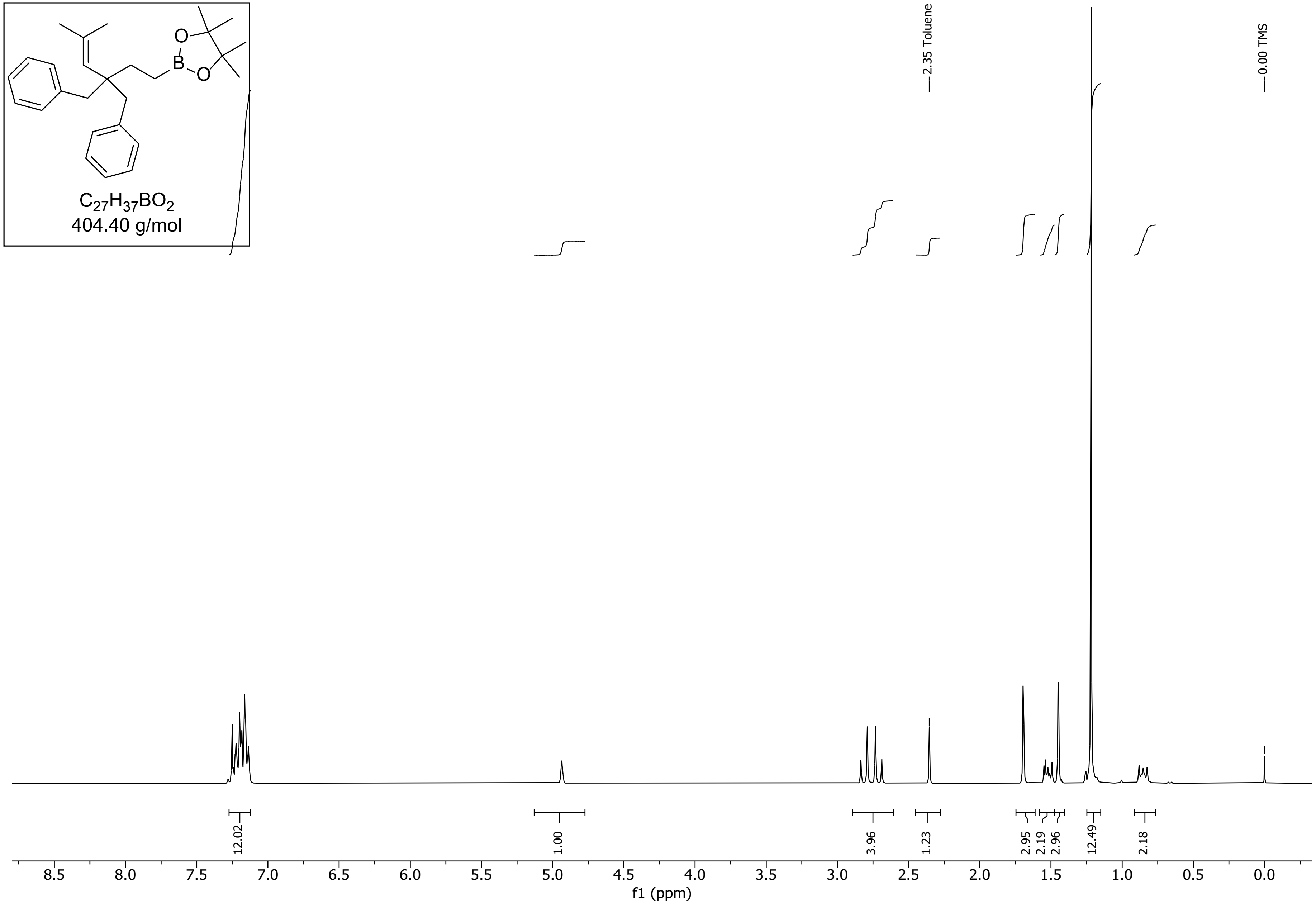


^{13}C NMR (75 MHz, $CDCl_3$)
(3,3-Dibenzyl-5-methyl-hex-4-enyl) 2,4,6-triisopropylbenzoate (**3**)



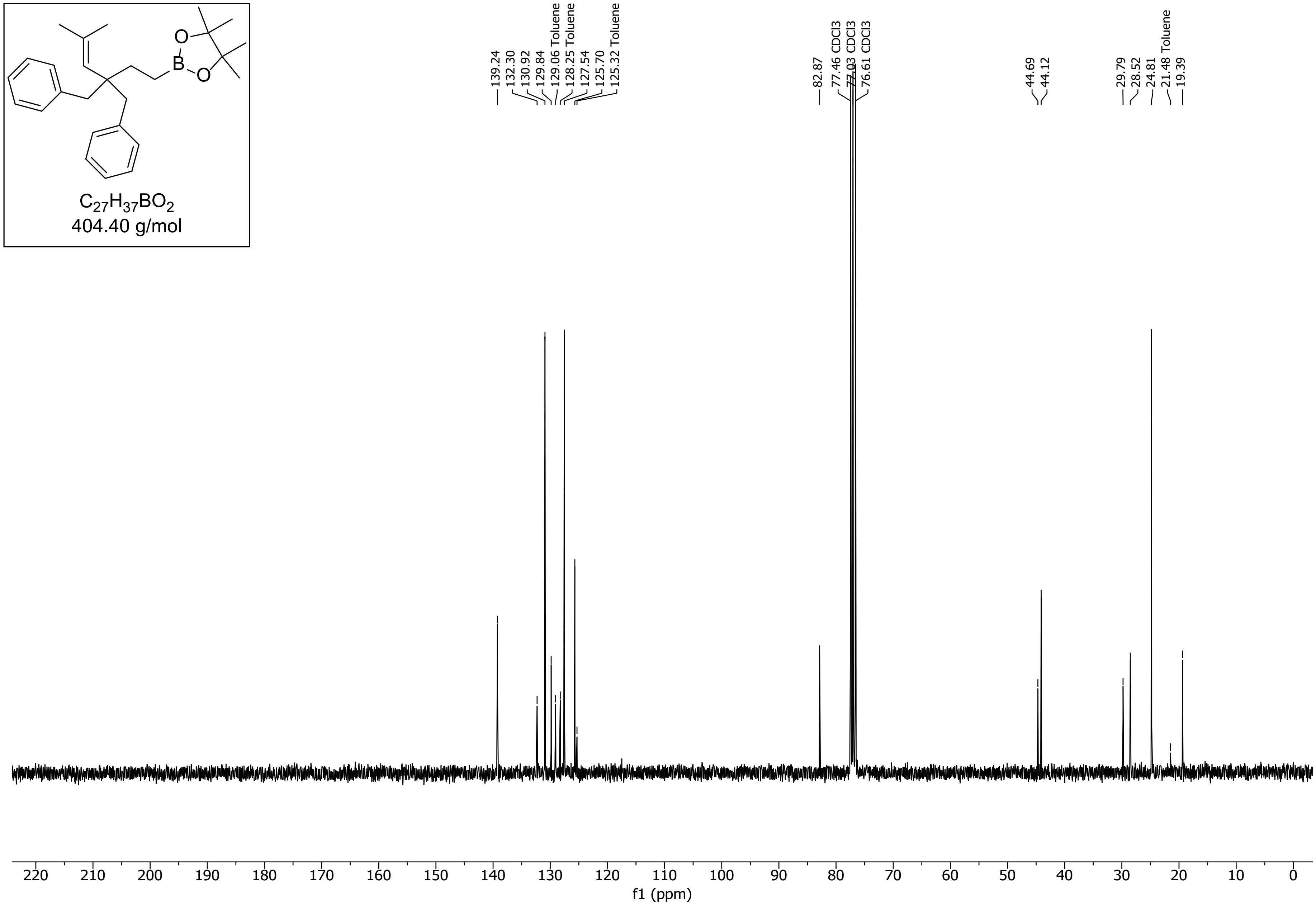
$C_{37}H_{48}O_2$
524.79 g/mol

^{1}H NMR (300 MHz, $CDCl_3$)
2-(3,3-Dibenzyl-5-methyl-hex-4-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4**)

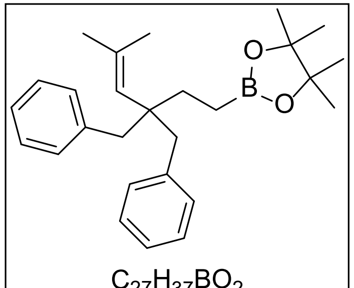


^{13}C NMR (75 MHz, $CDCl_3$)
2-(3,3-Dibenzyl-5-methyl-hex-4-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4**)

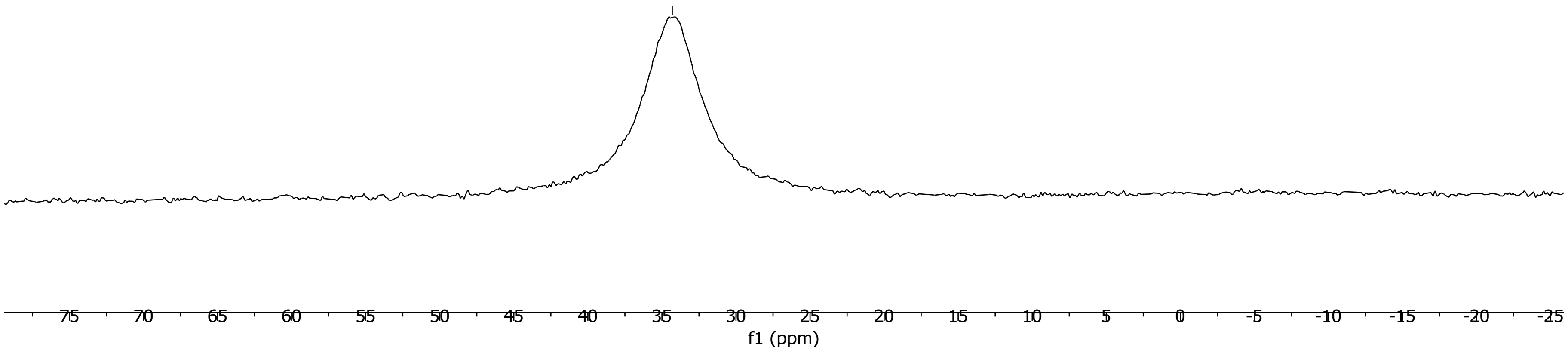
$C_{27}H_{37}BO_2$
404.40 g/mol



^{11}B NMR (96 MHz, $CDCl_3$)
2-(3,3-Dibenzyl-5-methyl-hex-4-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4**)

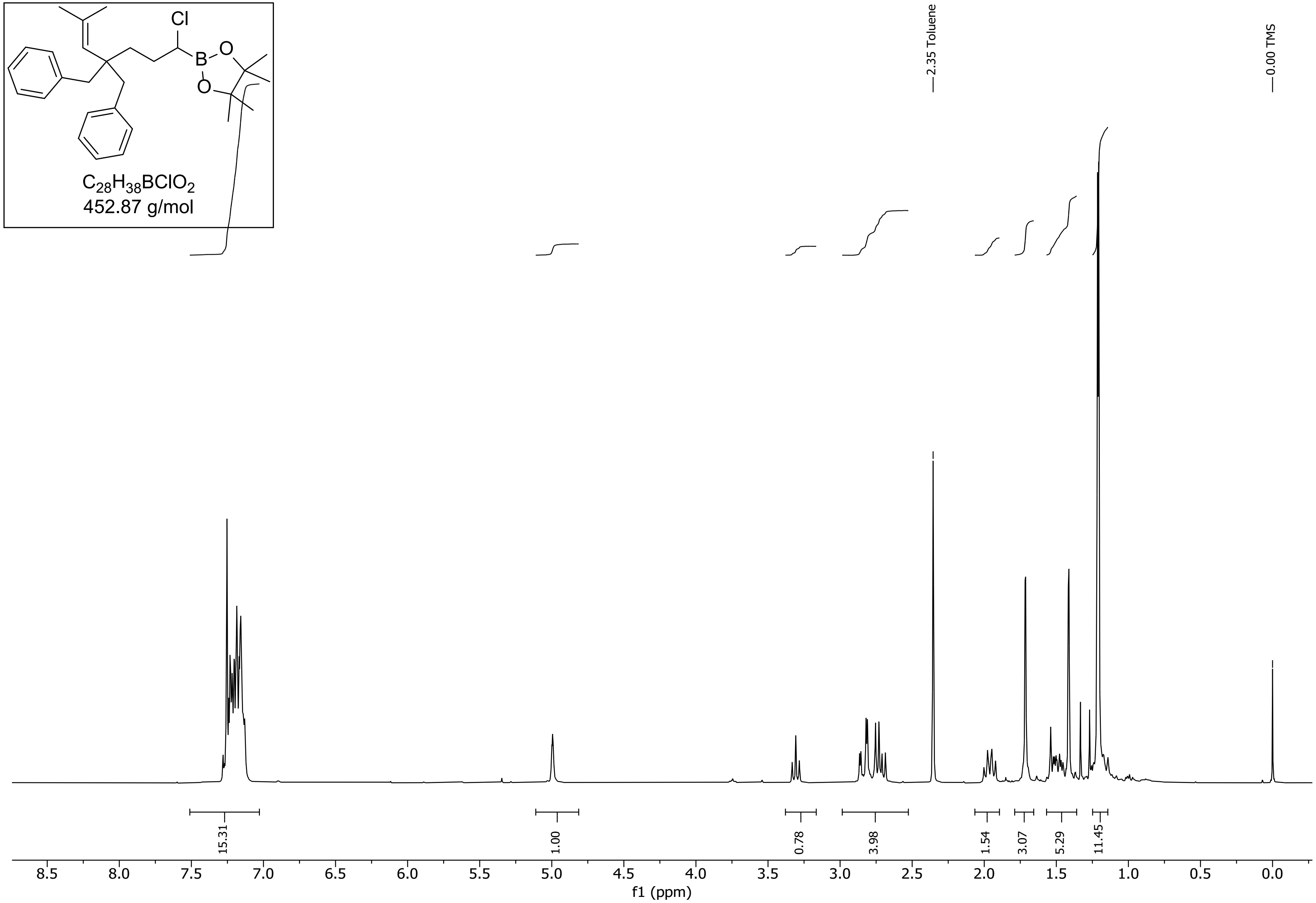


$C_{27}H_{37}BO_2$
404.40 g/mol

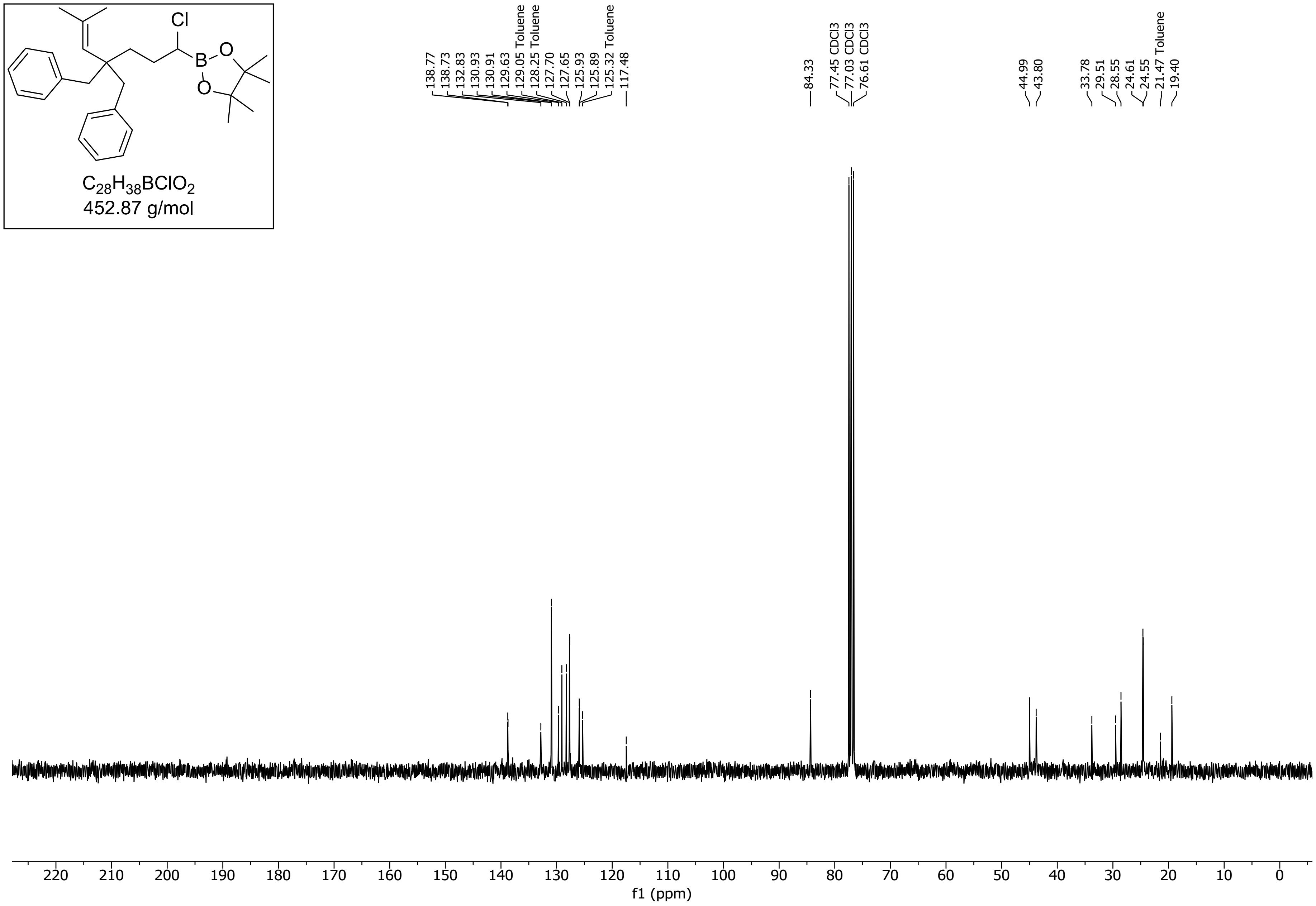


^1H NMR (300 MHz, $CDCl_3$)

2-(4,4-Dibenzyl-1-chloro-6-methyl-hept-5-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5**)

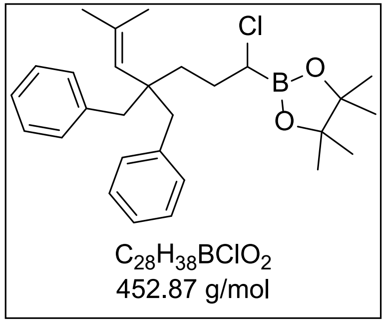


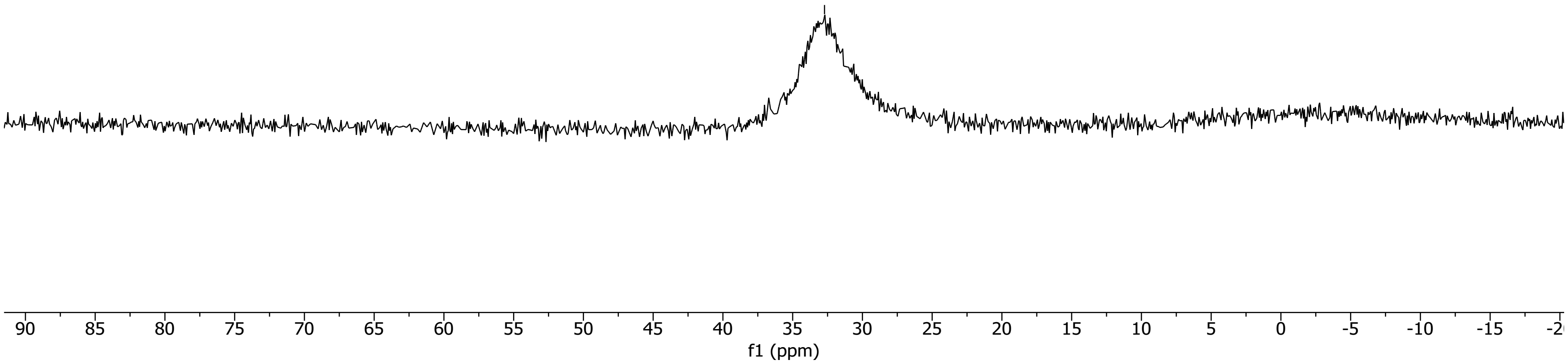
^{13}C NMR (75 MHz, $CDCl_3$)
2-(4,4-Dibenzyl-1-chloro-6-methyl-hept-5-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5**)



^{11}B NMR (96 MHz, $CDCl_3$)

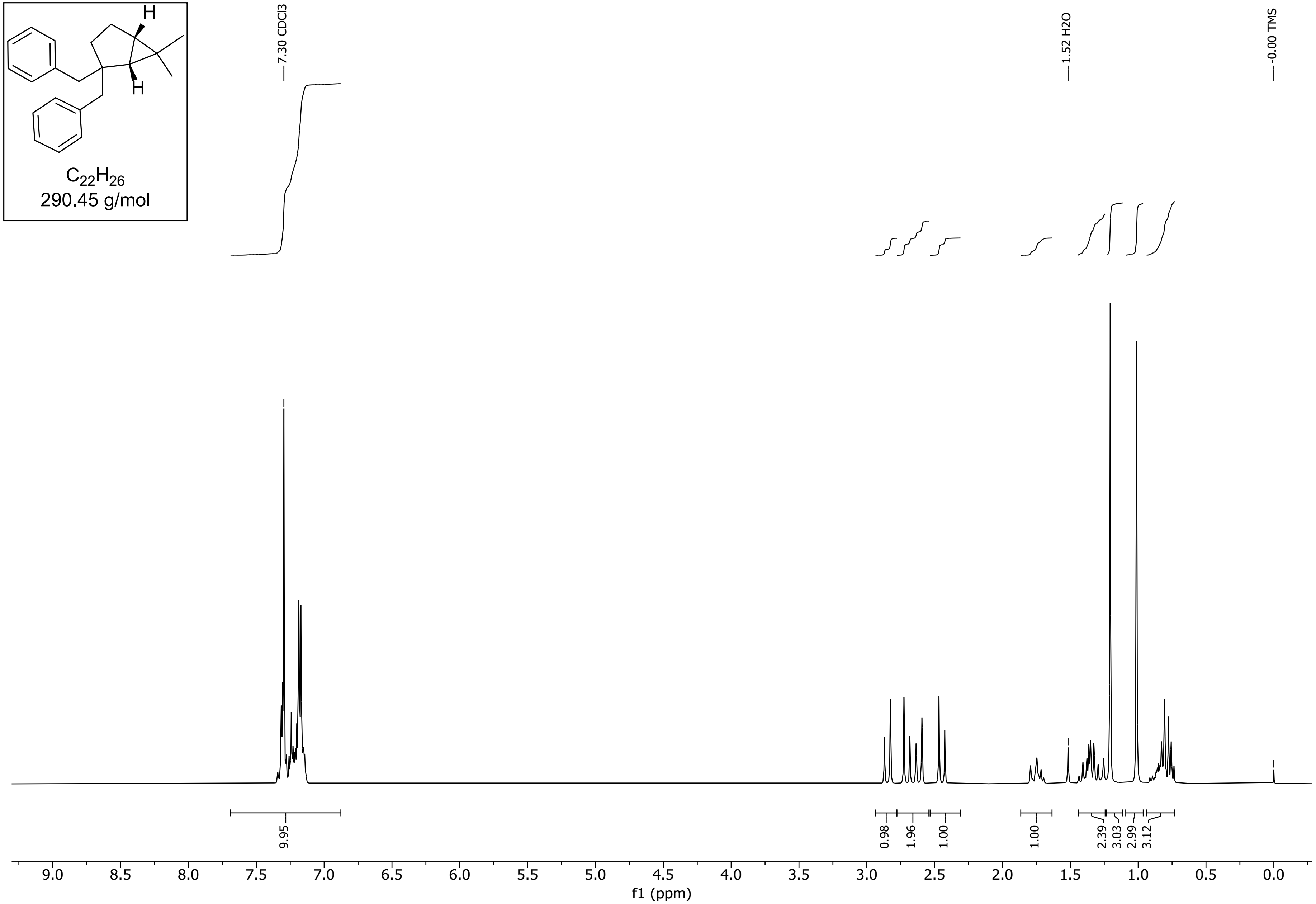
2-(4,4-Dibenzyl-1-chloro-6-methyl-hept-5-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5**)





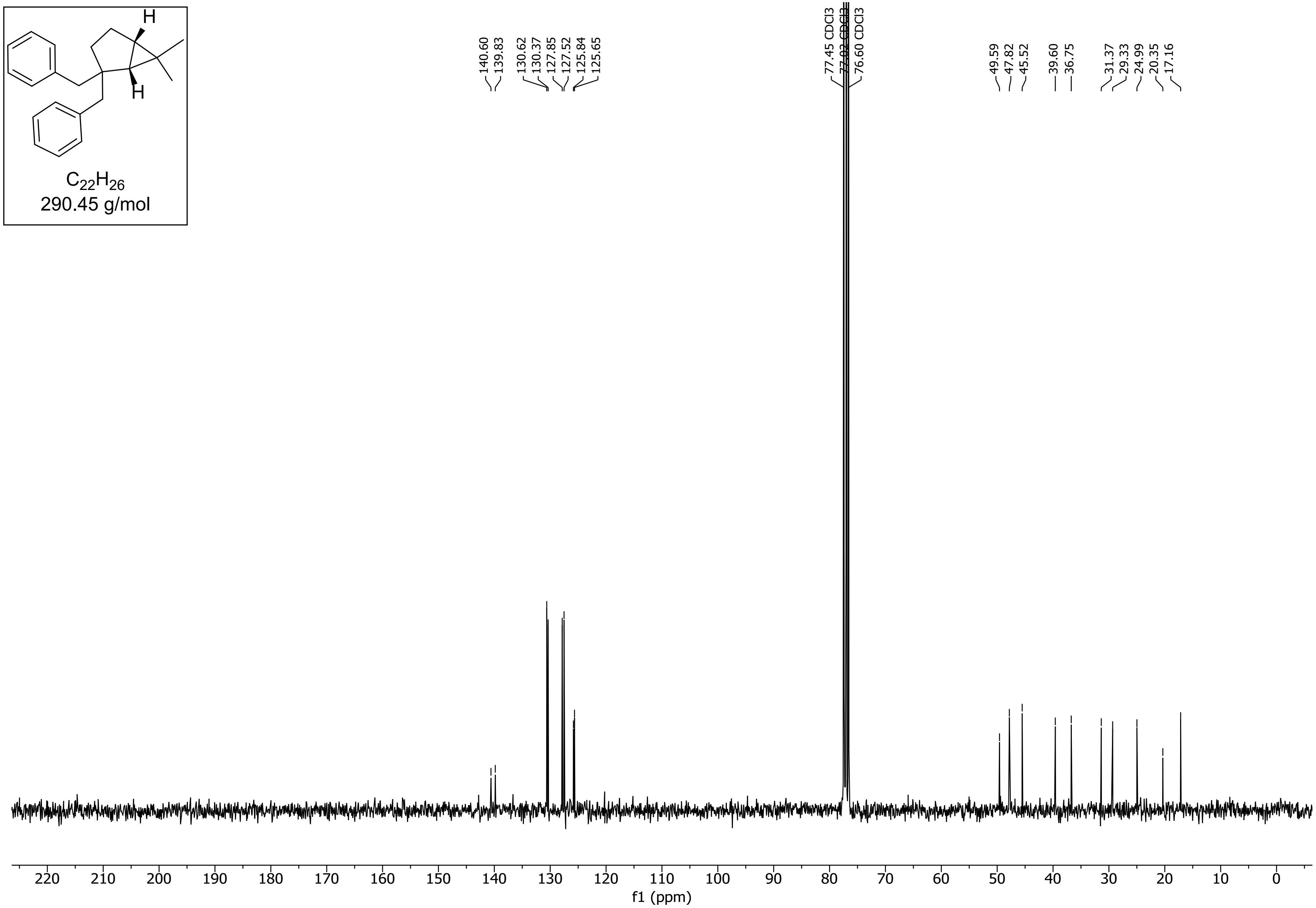
^{1}H NMR (300 MHz, $CDCl_3$)

2,2-Dibenzyl-6,6-dimethyl-bicyclo[3.1.0]hexane (**6**)



^{13}C NMR (75 MHz, $CDCl_3$)

2,2-Dibenzyl-6,6-dimethyl-bicyclo[3.1.0]hexane (**6**)

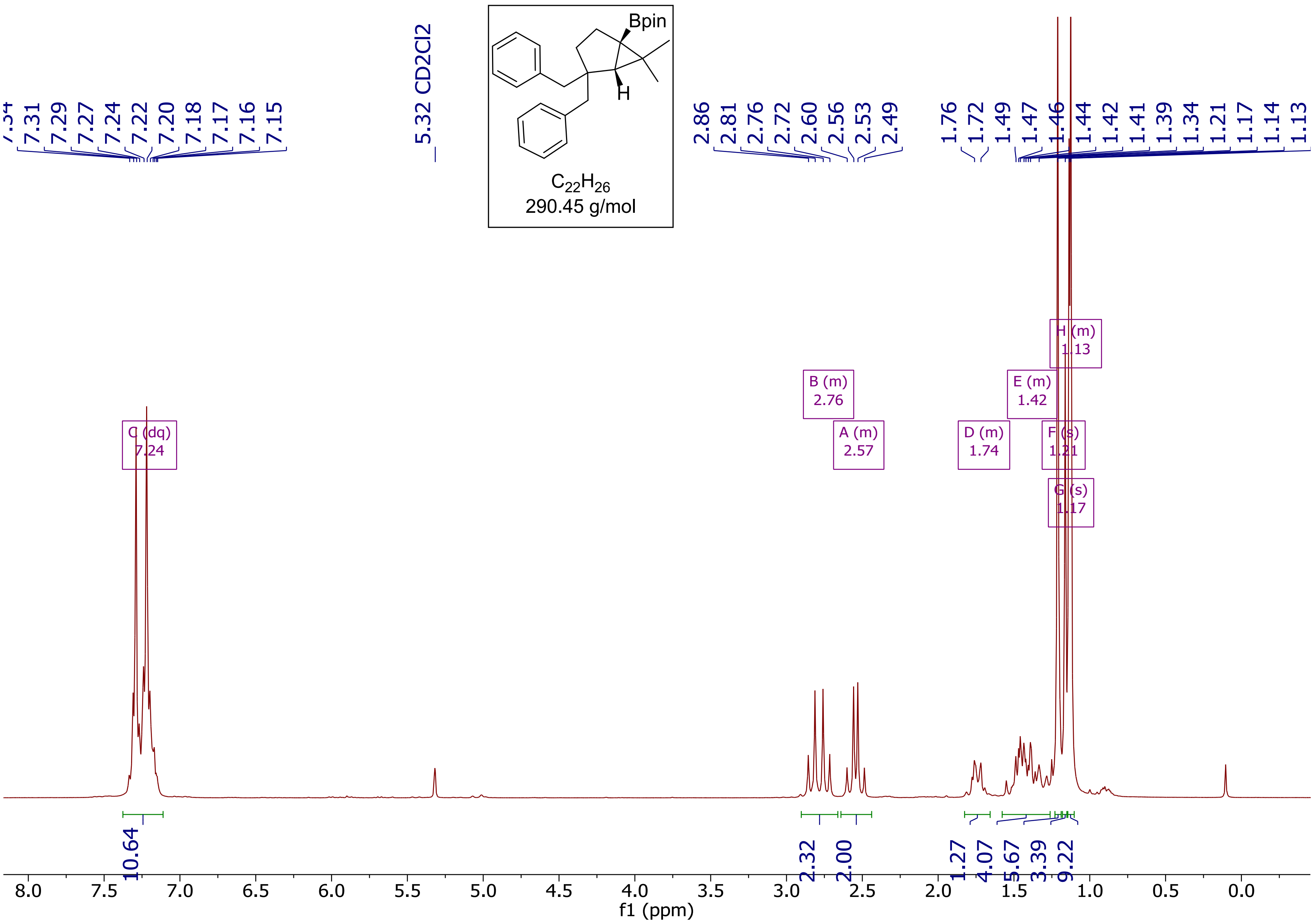


$C_{22}H_{26}$

290.45 g/mol

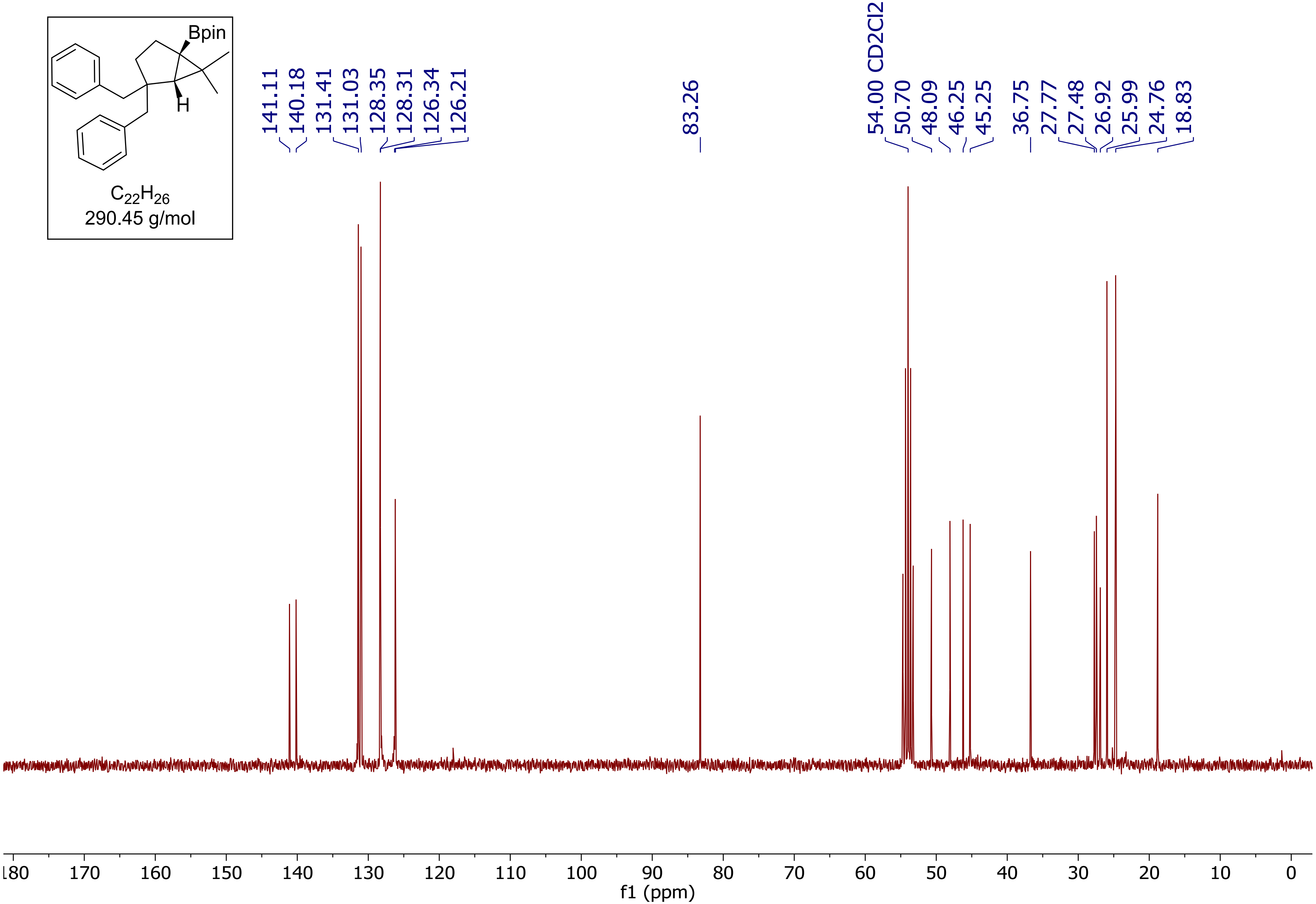
^{1}H NMR (300 MHz, $CDCl_3$)

2-(4,4-Dibenzyl-6,6-dimethylbicyclo[3.1.0]hexan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**7**)

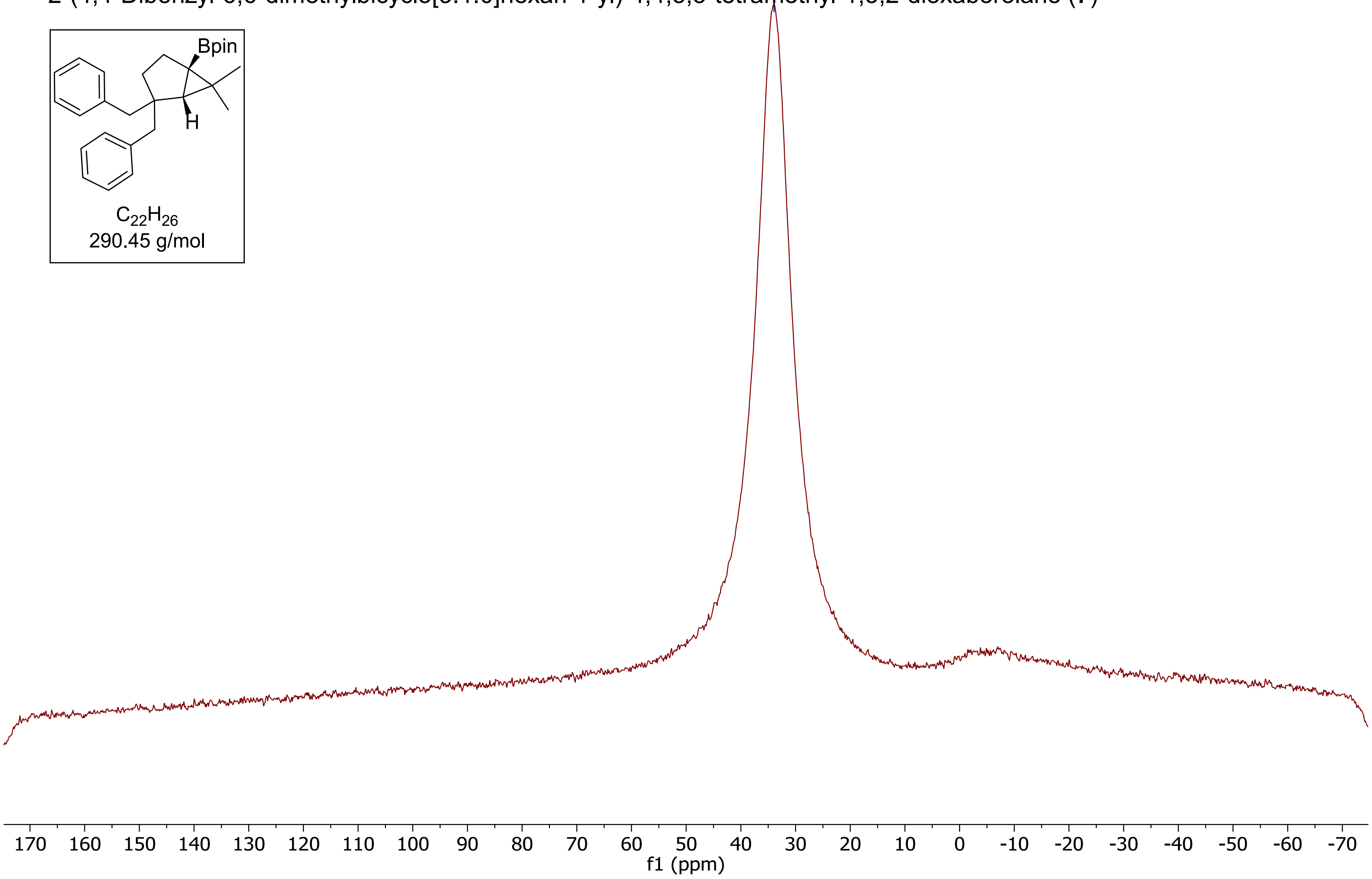


^{13}C NMR (75 MHz, $CDCl_3$)
2-(4,4-Dibenzyl-6,6-dimethylbicyclo[3.1.0]hexan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**7**)

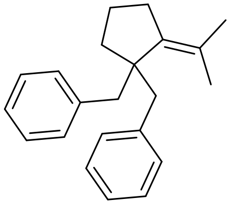
$C_{22}H_{26}$
290.45 g/mol



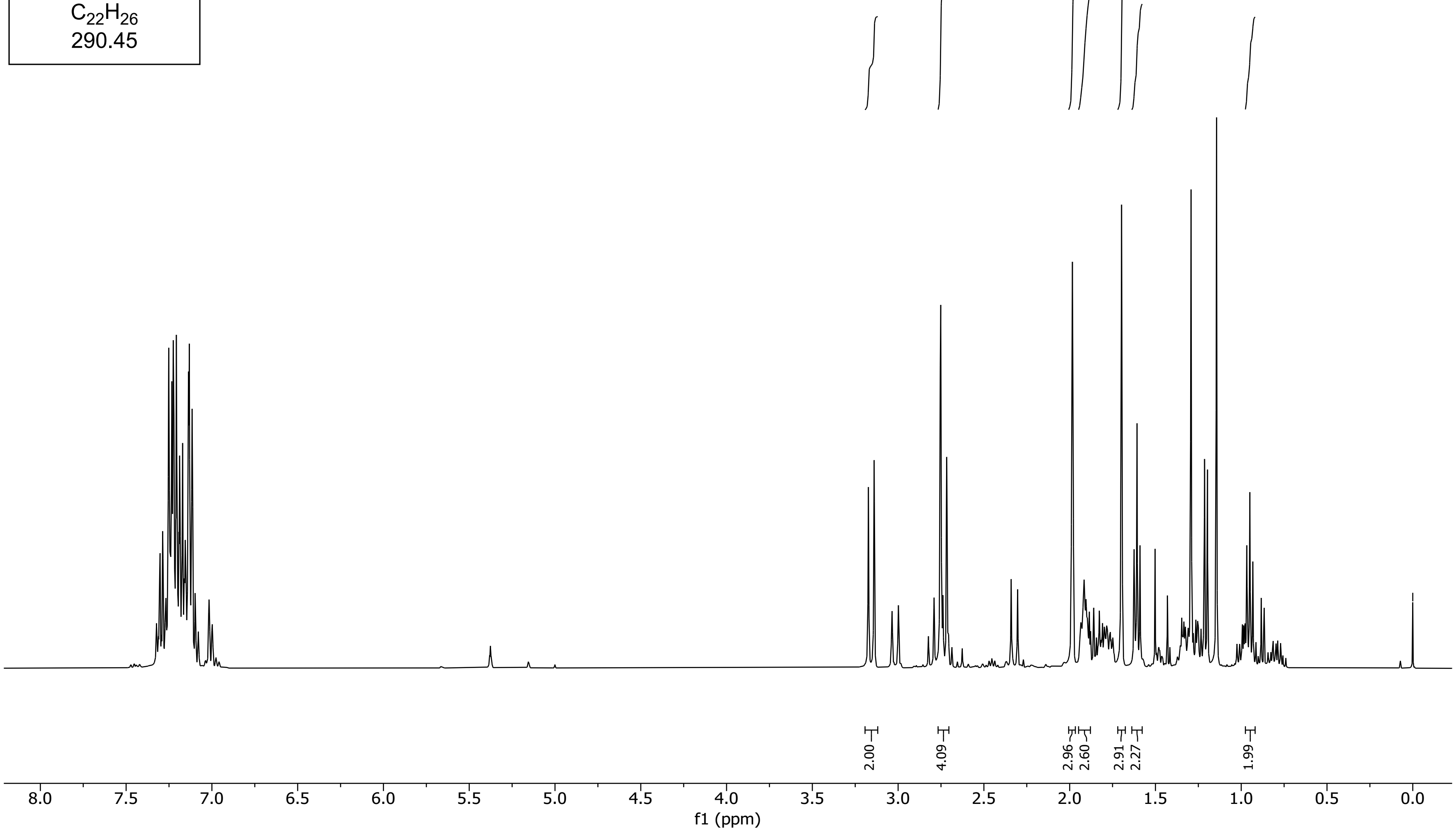
^{11}B NMR (96 MHz, $CDCl_3$)
2-(4,4-Dibenzyl-6,6-dimethylbicyclo[3.1.0]hexan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**7**)



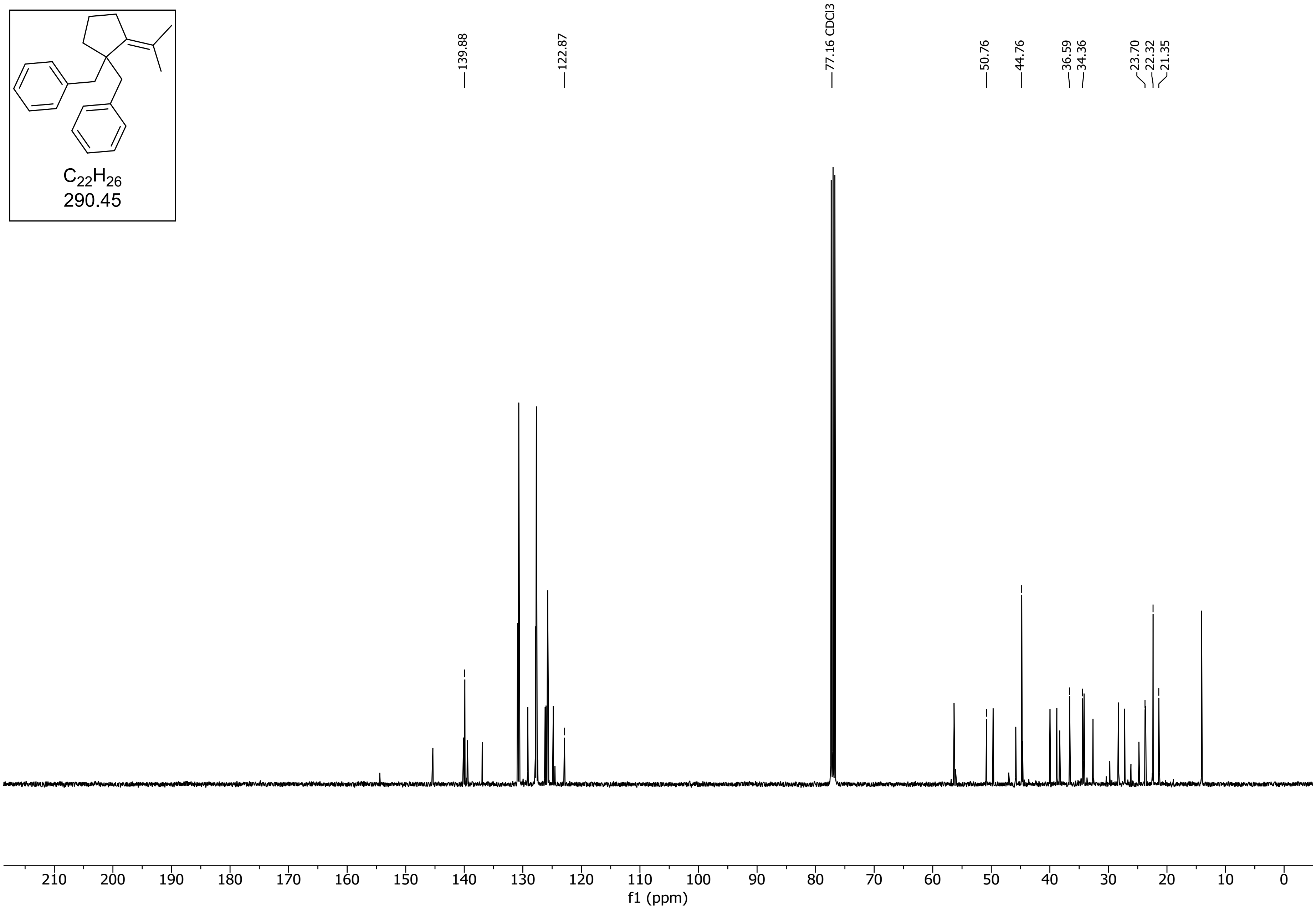
^{1}H NMR (400 MHz, $CDCl_3$)
2,2-Bis(4-bromobenzyl)-6,6-dimethylbicyclo[3.1.0]hexane (**8**)



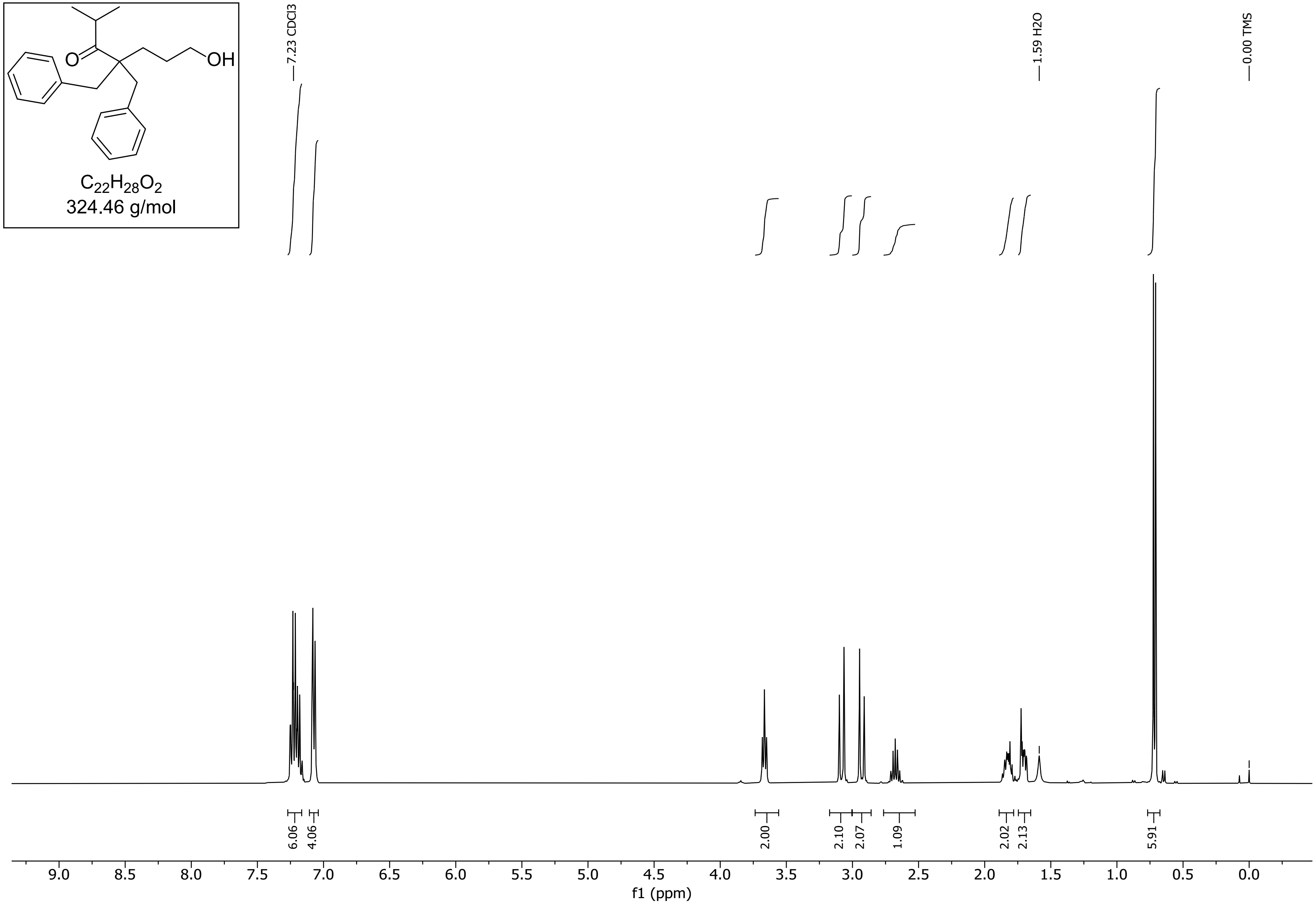
$C_{22}H_{26}$
290.45



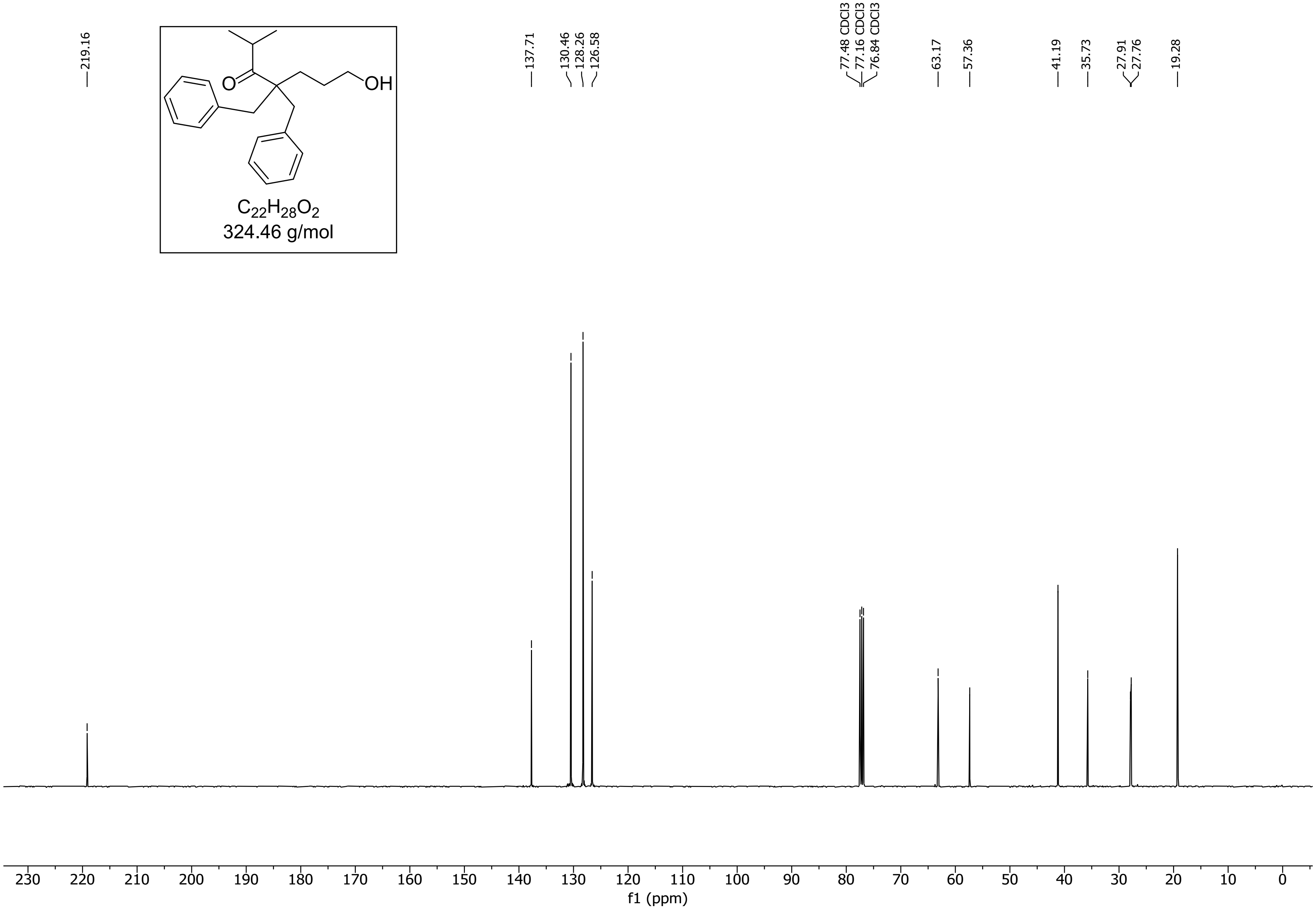
^{13}C NMR (101 MHz, $CDCl_3$)
2,2-Bis(4-bromobenzyl)-6,6-dimethylbicyclo[3.1.0]hexane (**8**)



^{1}H NMR (400 MHz, $CDCl_3$)
4,4-Dibenzyl-6-hydroxy-2-methylhexan-3-one (**9**)

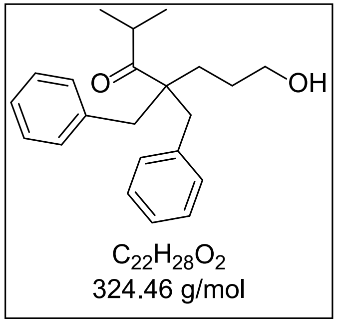


^{13}C NMR (101 MHz, CDCl$_3$)
4,4-Dibenzyl-6-hydroxy-2-methylhexan-3-one (**9**)

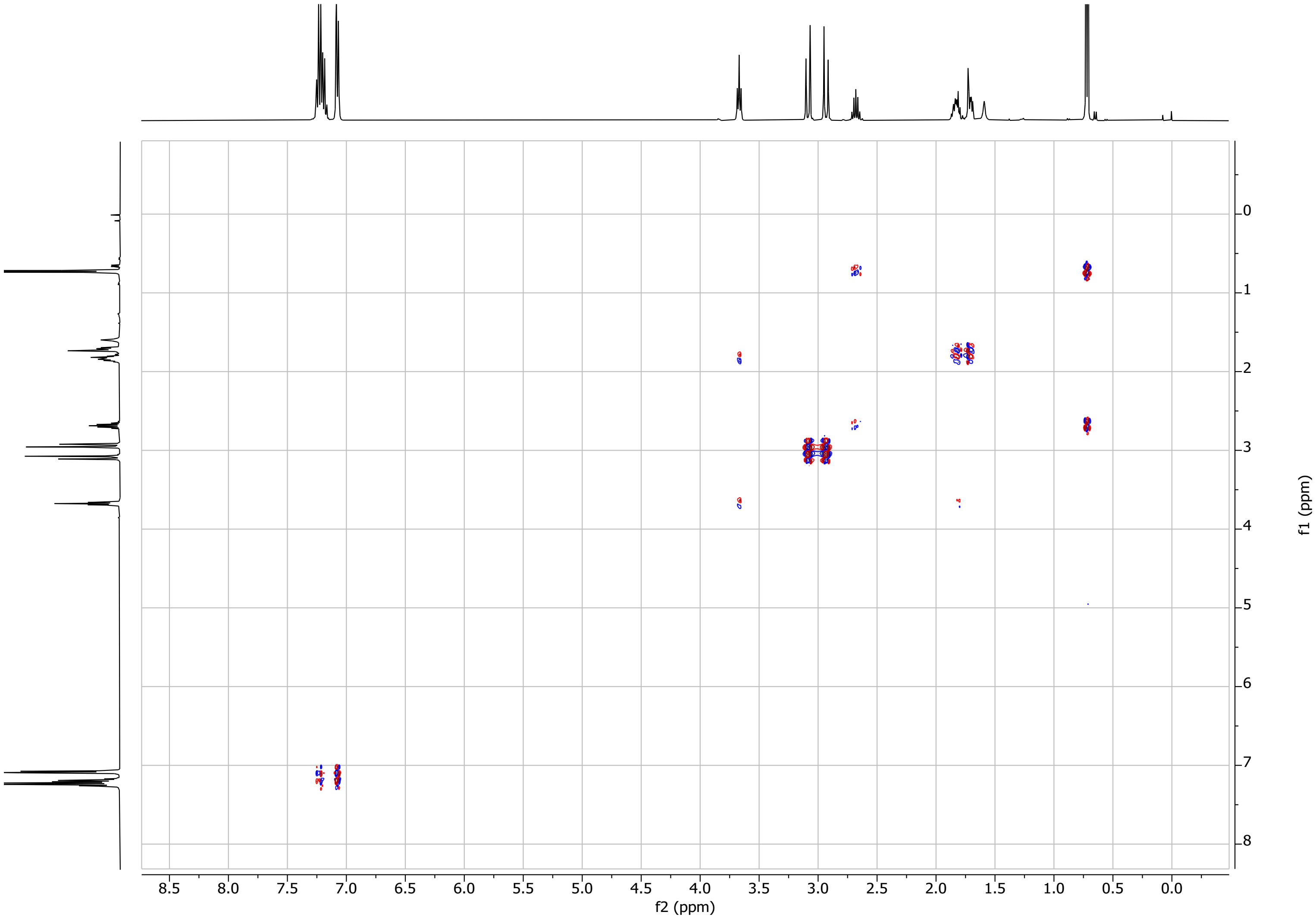


$C_{22}H_{28}O_2$
324.46 g/mol

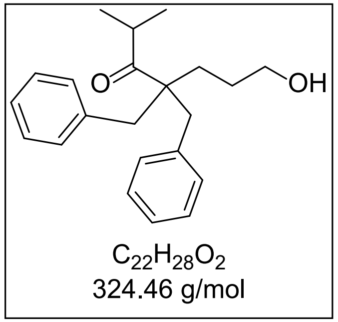
^1H, ^1H-COSY (400 MHz, $CDCl_3$)
4,4-Dibenzyl-6-hydroxy-2-methylhexan-3-one (**9**)



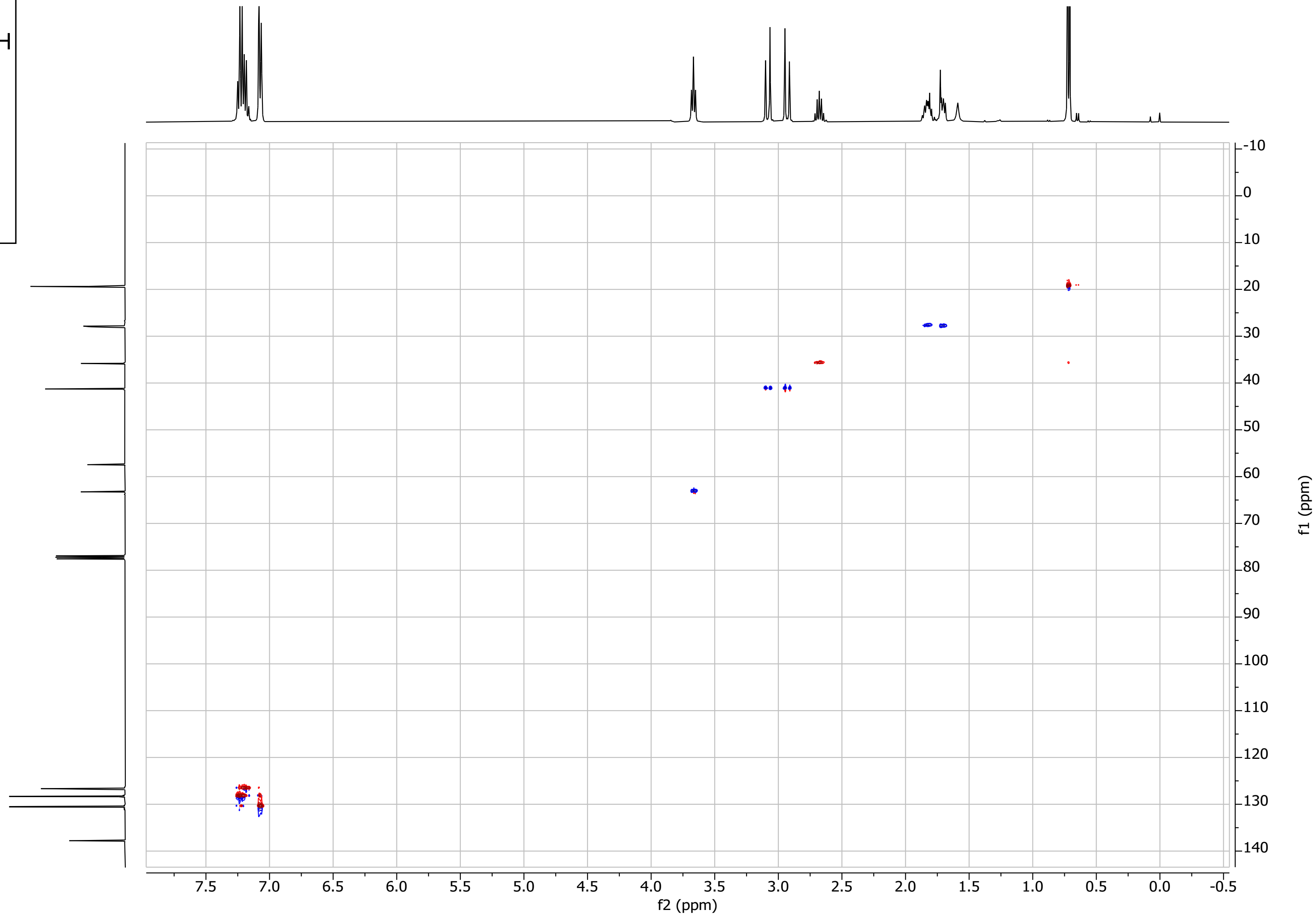
$C_{22}H_{28}O_2$
324.46 g/mol



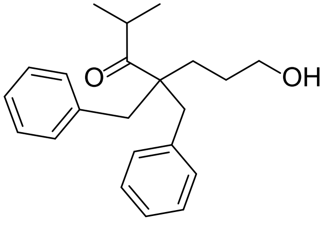
^{1}H, ^{13}C-HSQC (400 MHz, $CDCl_3$)
4,4-Dibenzyl-6-hydroxy-2-methylhexan-3-one (**9**)



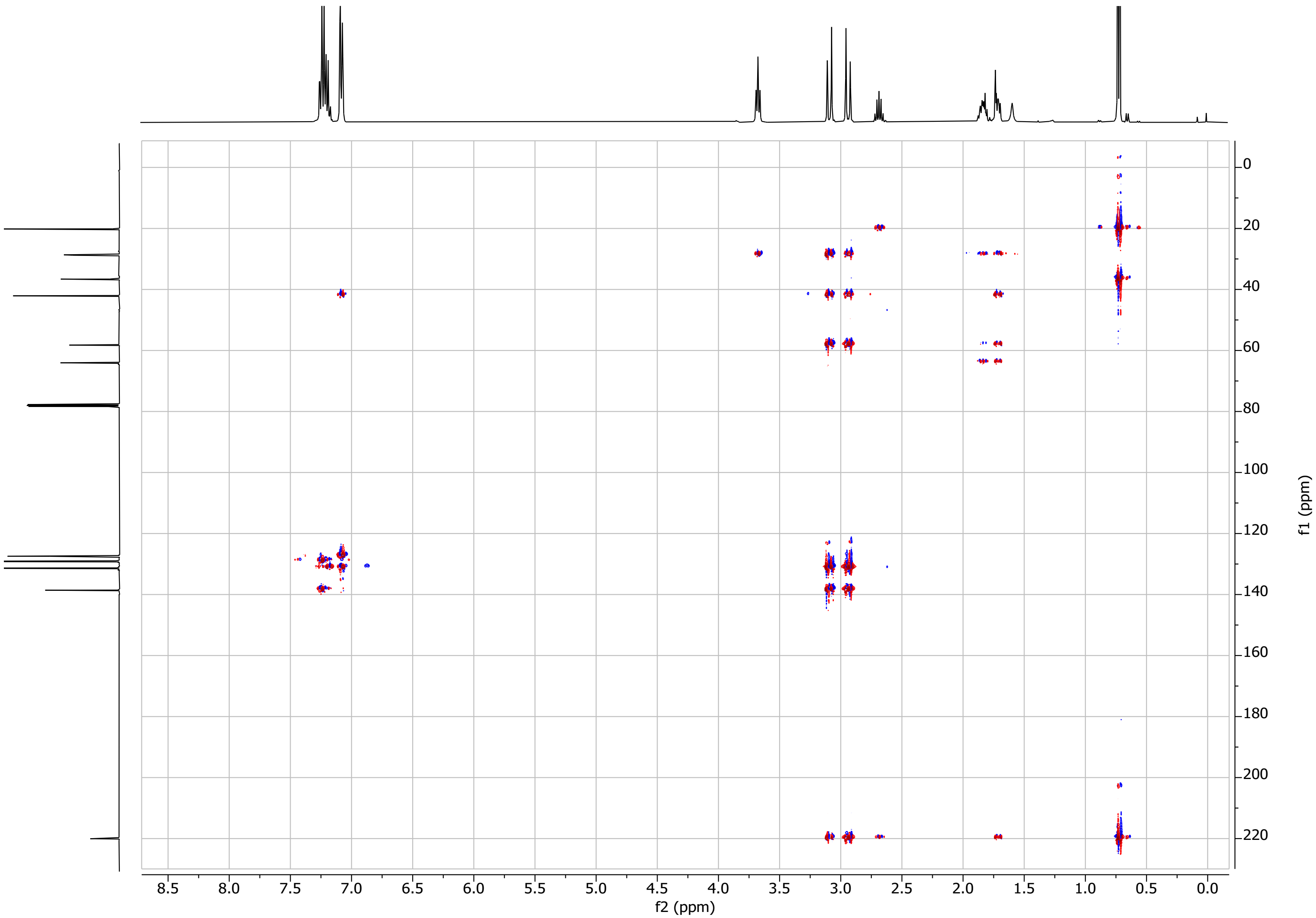
$C_{22}H_{28}O_2$
324.46 g/mol



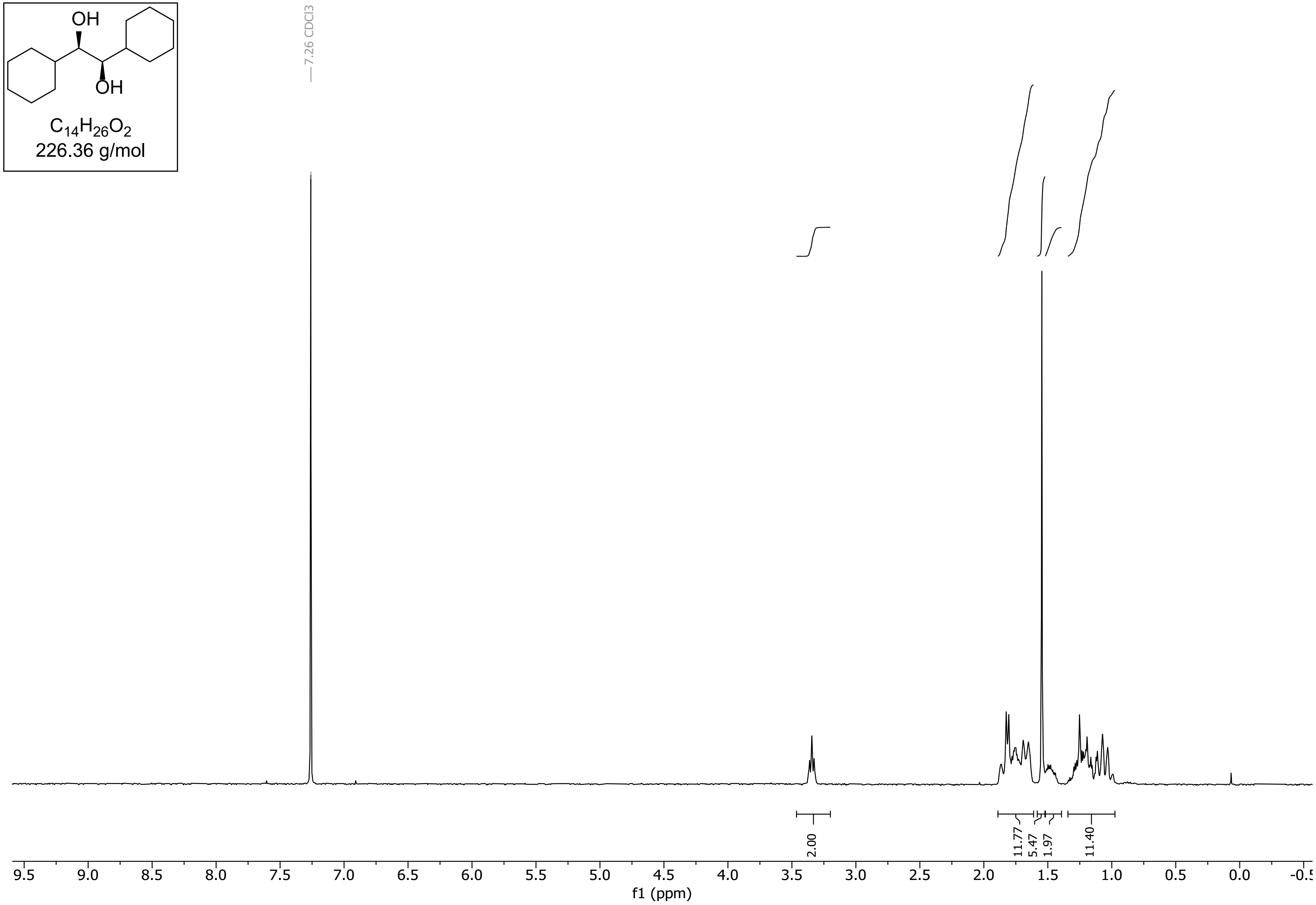
^{1}H, ^{13}C-HMBC (400 MHz, $CDCl_3$)
4,4-Dibenzyl-6-hydroxy-2-methylhexan-3-one (**9**)



$C_{22}H_{28}O_2$
324.46 g/mol

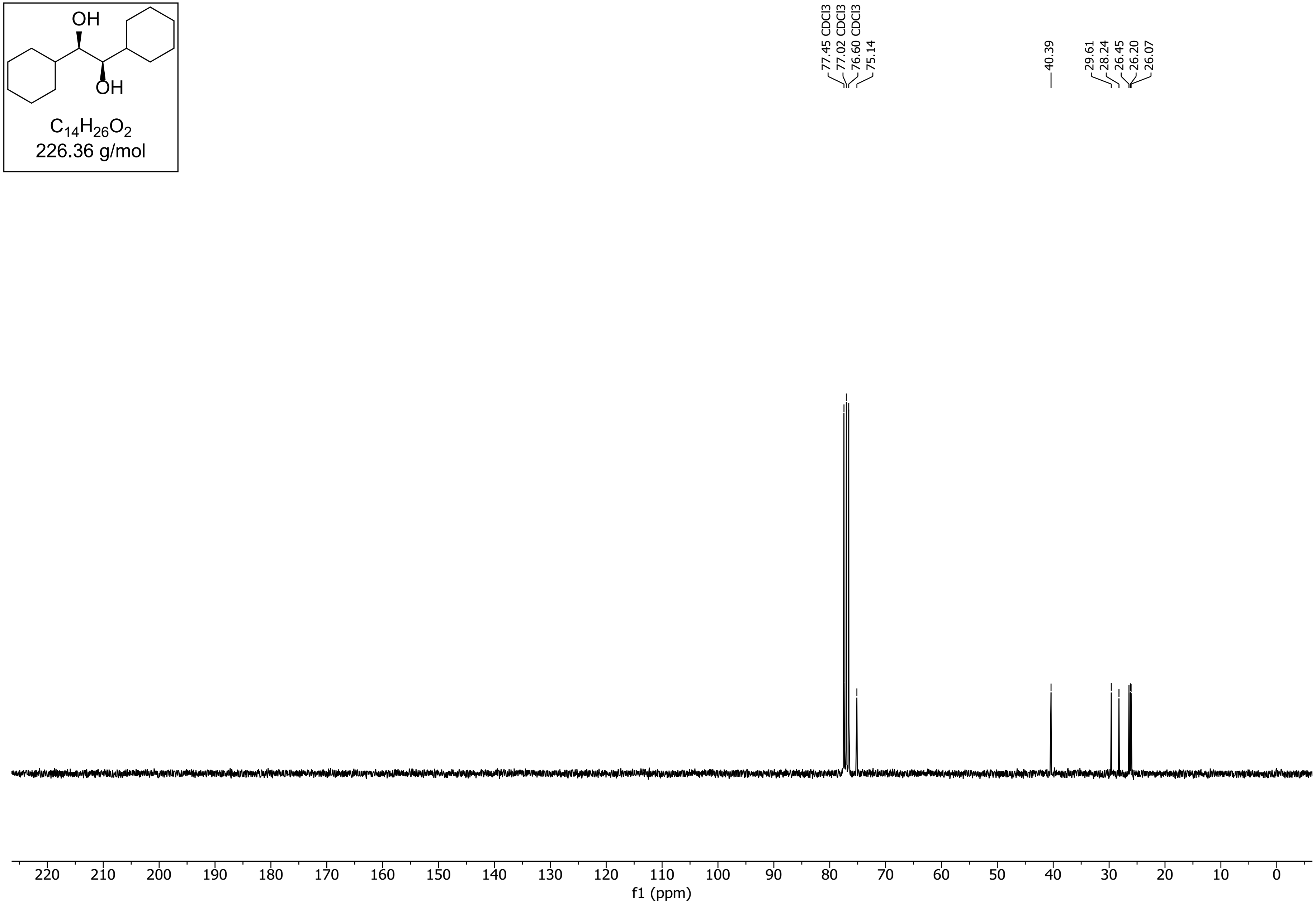


^{1}H NMR (300 MHz, $CDCl_3$)
(1R,2R)-1,2-Dicyclohexylethane-1,2-diol



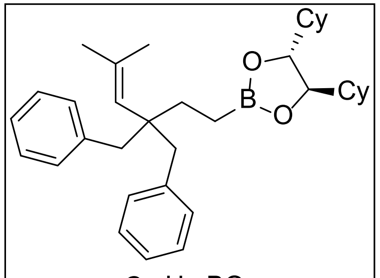
$C_{14}H_{26}O_2$
226.36 g/mol

^{13}C NMR (75 MHz, $CDCl_3$)
(1R,2R)-1,2-Dicyclohexylethane-1,2-diol

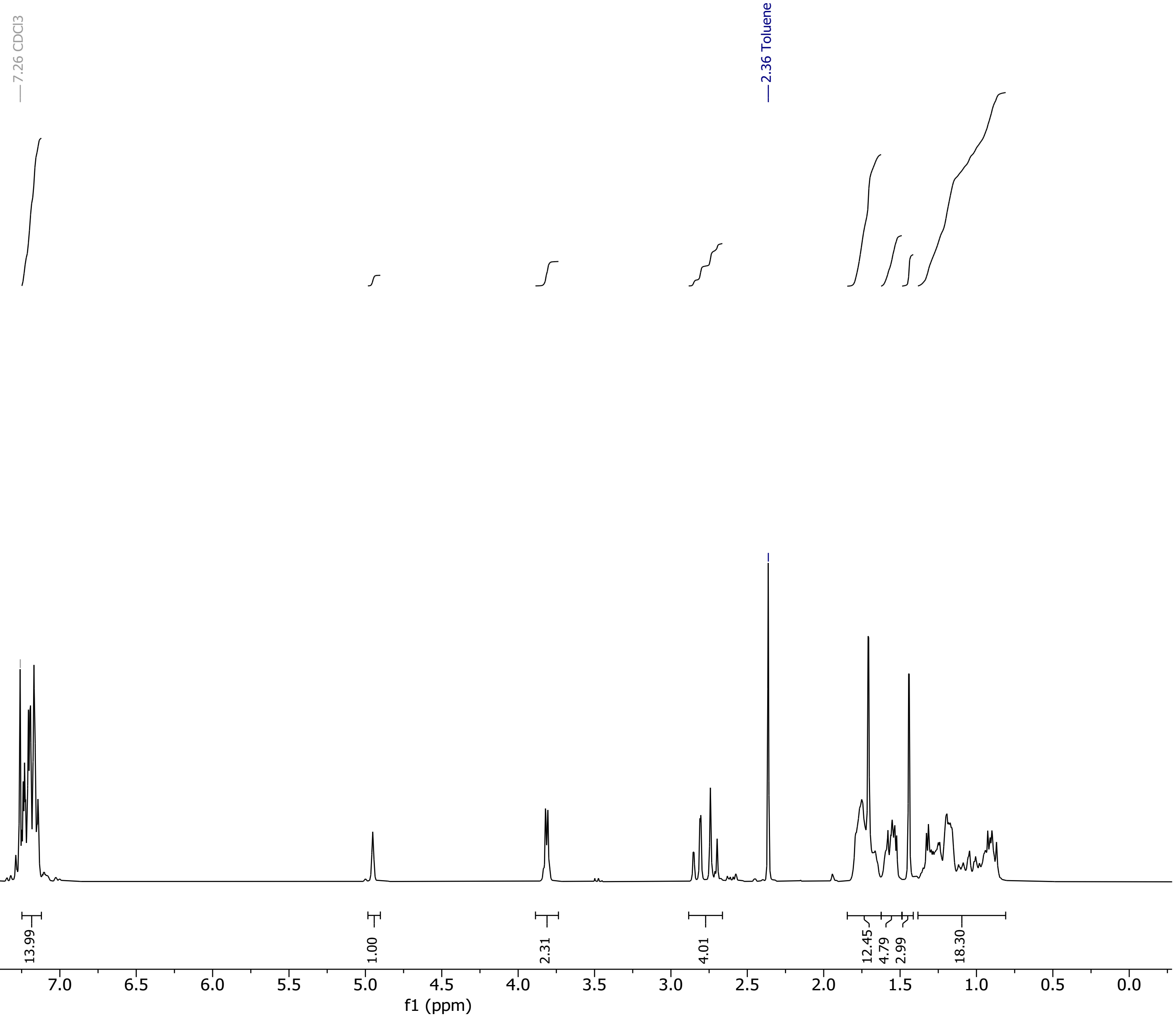


^{1}H NMR (300 MHz, $CDCl_3$)

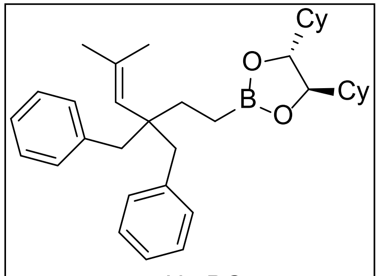
(4R,5R)-4,5-Dicyclohexyl-2-(3,3-dibenzyl-5-methyl-hex-4-enyl)-1,3,2-dioxaborolane (**10**)



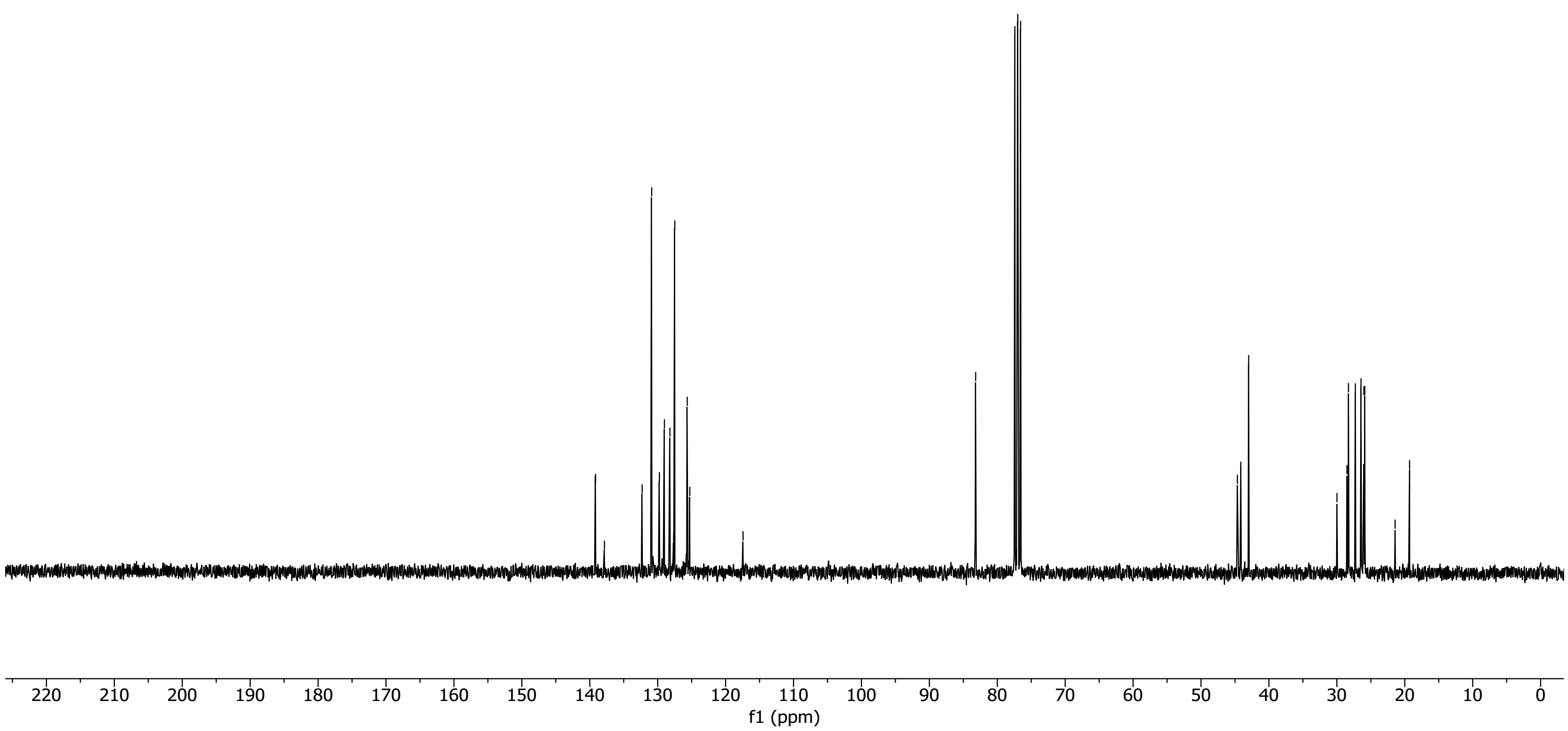
$C_{35}H_{49}BO_2$
512.59 g/mol



^{13}C NMR (75 MHz, CDCl$_3$)
(4R,5R)-4,5-Dicyclohexyl-2-(3,3-dibenzyl-5-methyl-hex-4-enyl)-1,3,2-dioxaborolane (**10**)

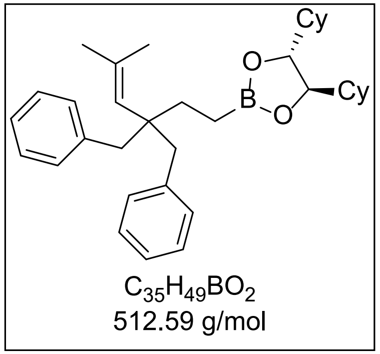


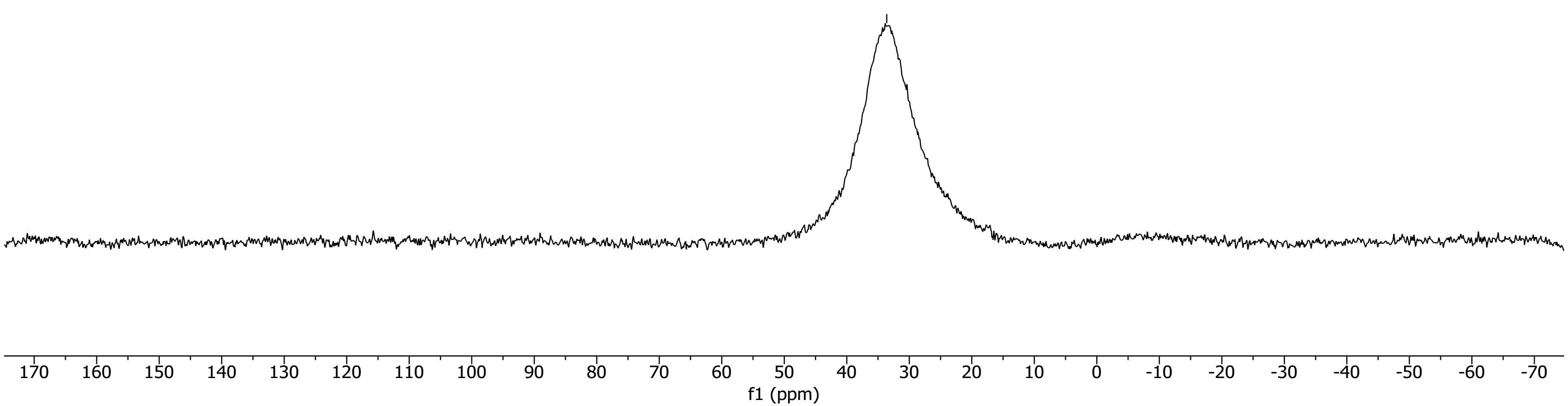
$C_{35}H_{49}BO_2$
512.59 g/mol



^{11}B NMR (96 MHz, $CDCl_3$)

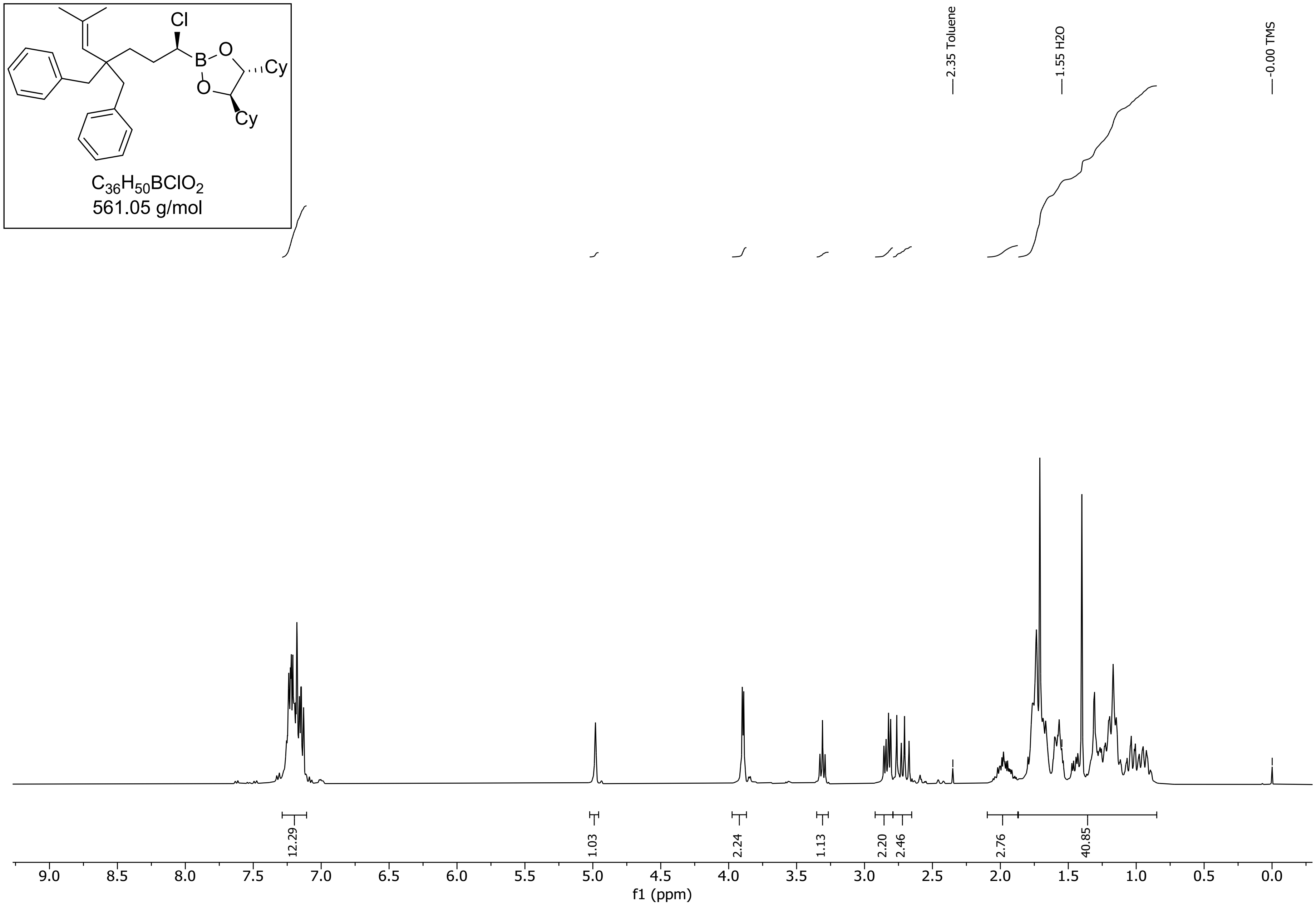
(4R,5R)-4,5-Dicyclohexyl-2-(3,3-dibenzyl-5-methyl-hex-4-enyl)-1,3,2-dioxaborolane (**10**)





^{1}H NMR (400 MHz, $CDCl_3$)

(4R,5R)-4,5-Dicyclohexyl-2-((S)-4,4-dibenzyl-1-chloro-6-methylhept-5-en-1-yl)-1,3,2-dioxaborolane ((S)-**11**)

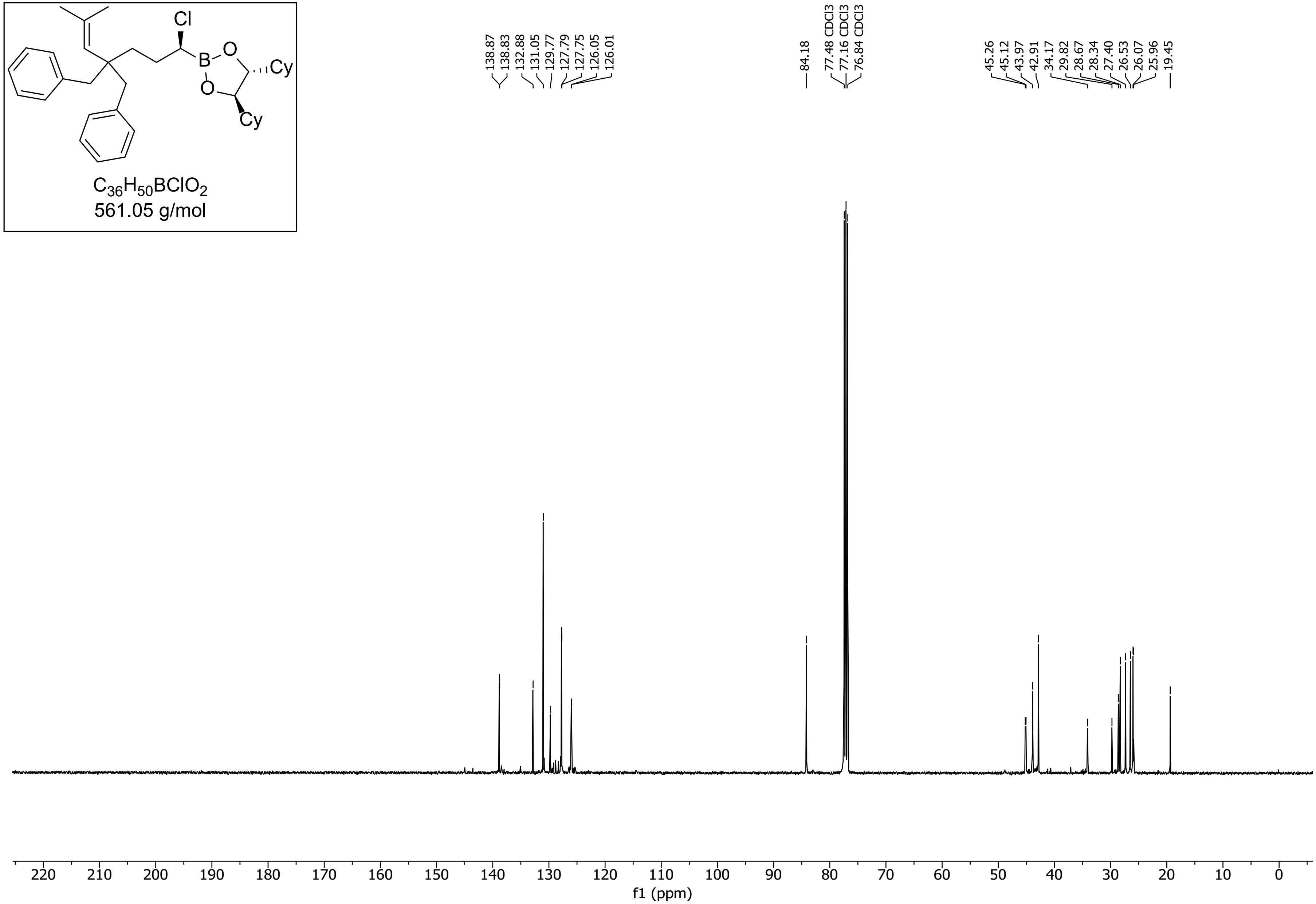


$C_{36}H_{50}BClO_2$

561.05 g/mol

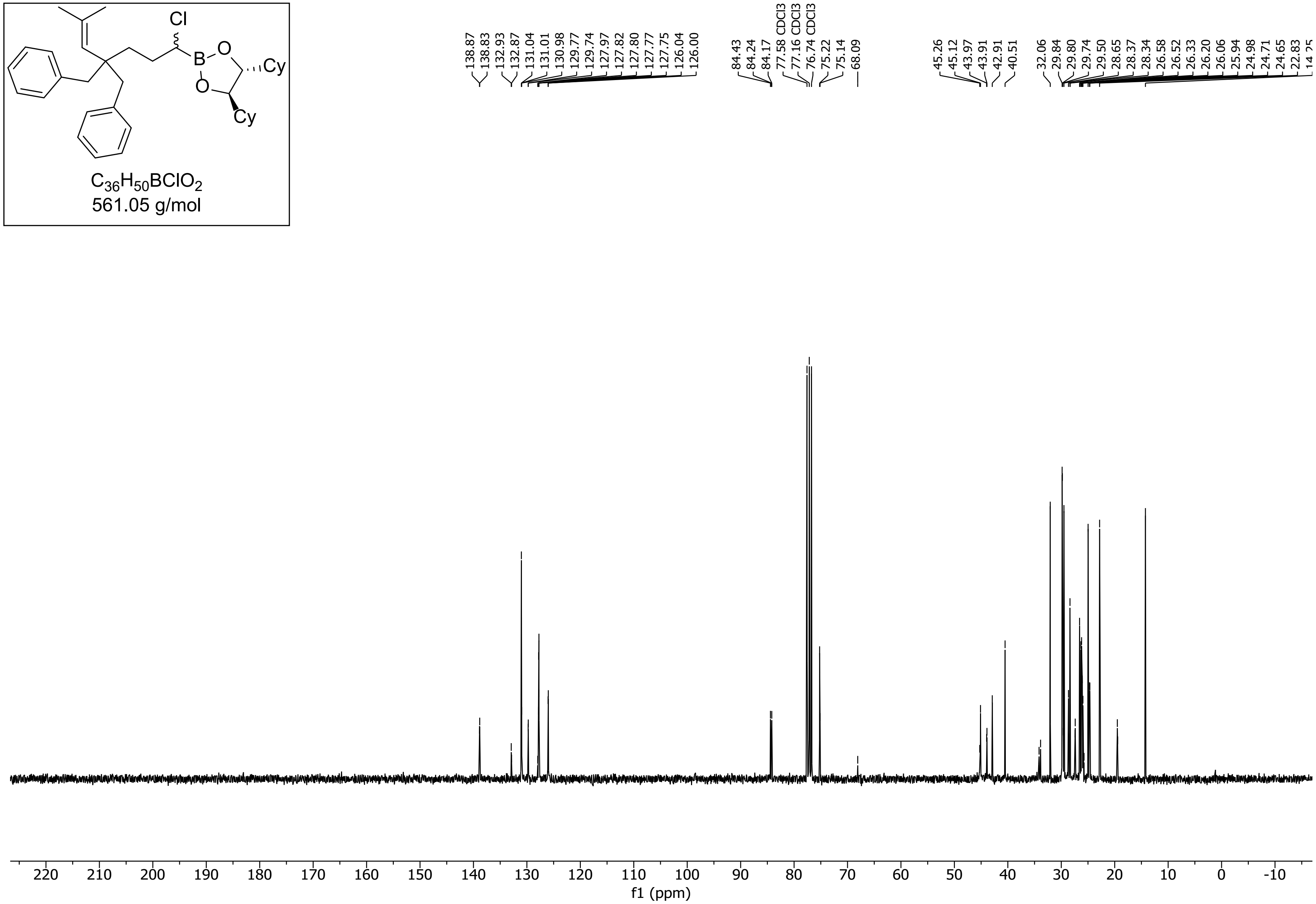
^{13}C NMR (101 MHz, CDCl$_3$)

(4R,5R)-4,5-Dicyclohexyl-2-((S)-4,4-dibenzyl-1-chloro-6-methylhept-5-en-1-yl)-1,3,2-dioxaborolane ((S)-**11**)



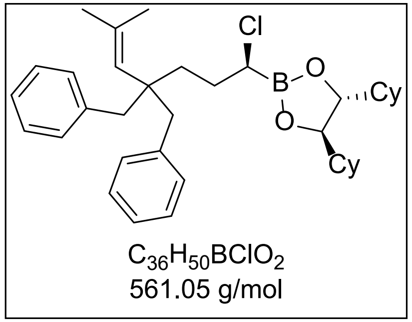
$C_{36}H_{50}BClO_2$
561.05 g/mol

^{13}C NMR (75 MHz, $CDCl_3$)
(4R,5R)-4,5-Dicyclohexyl-2-(4,4-dibenzyl-1-chloro-6-methylhept-5-en-1-yl)-1,3,2-dioxaborolane

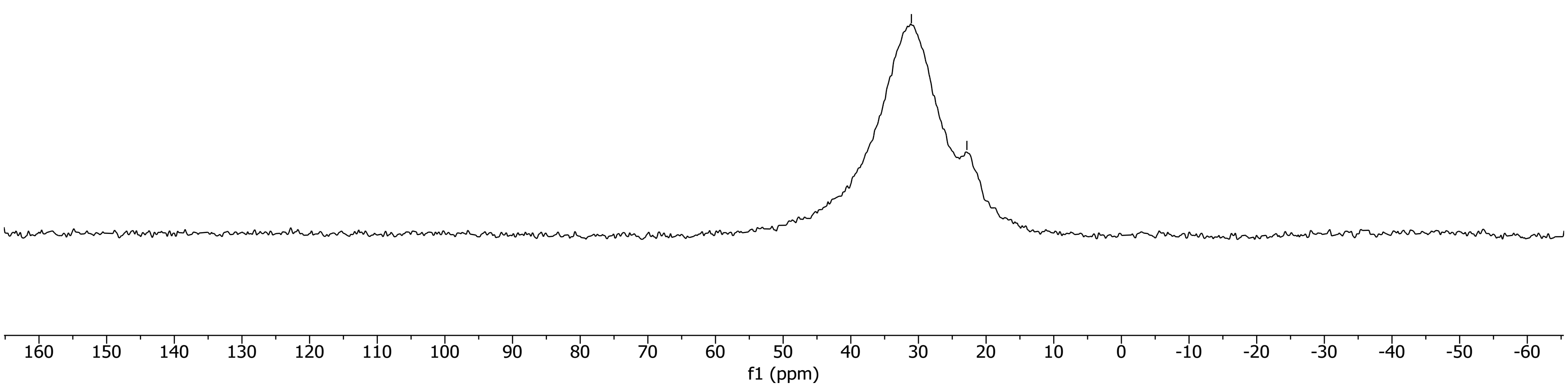


$C_{36}H_{50}BClO_2$
561.05 g/mol

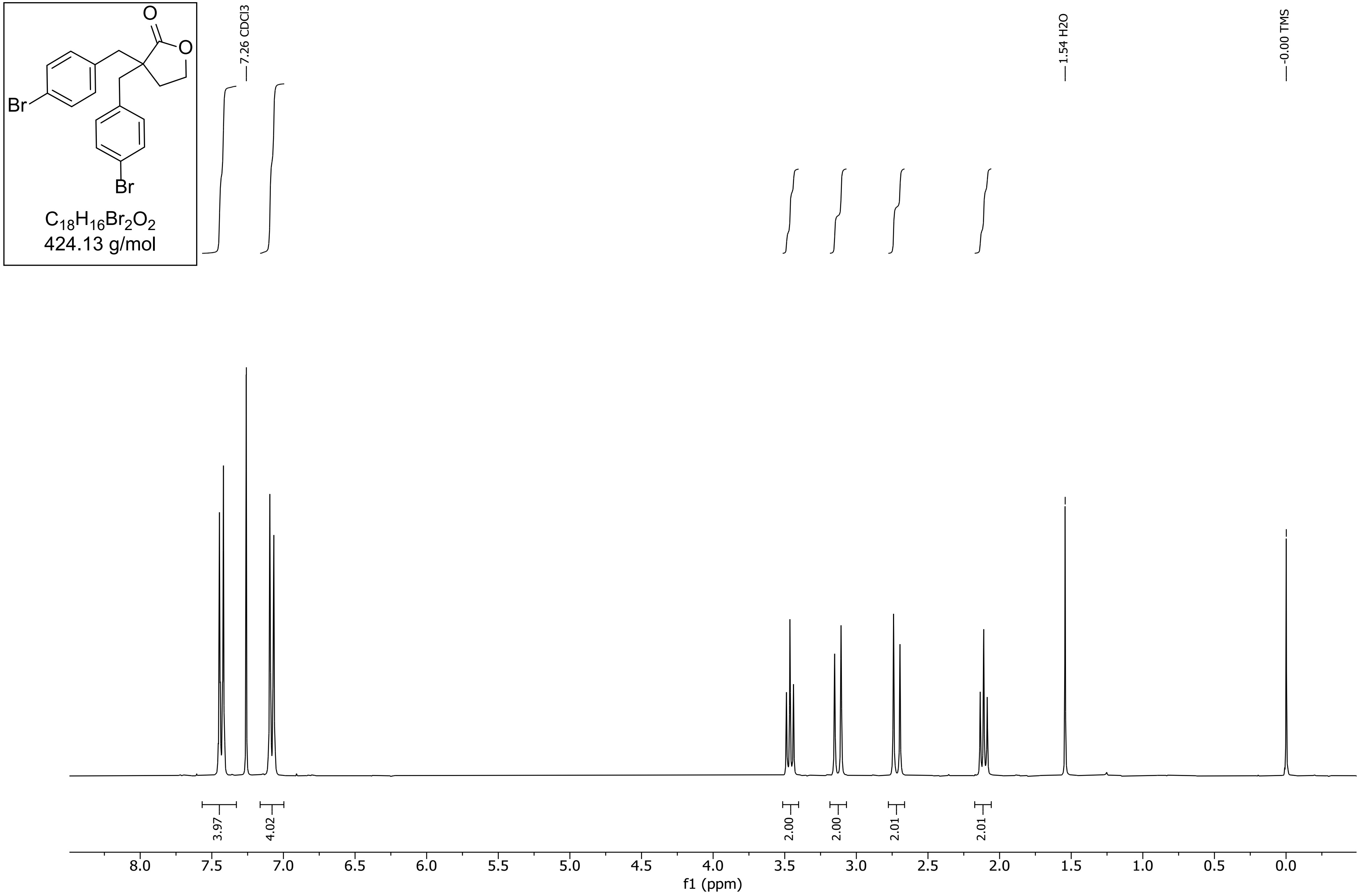
^{11}B NMR (96 MHz, $CDCl_3$)
(4R,5R)-4,5-Dicyclohexyl-2-((S)-4,4-dibenzyl-1-chloro-6-methylhept-5-en-1-yl)-1,3,2-dioxaborolane ((S)-**11**)



$C_{36}H_{50}BClO_2$
561.05 g/mol

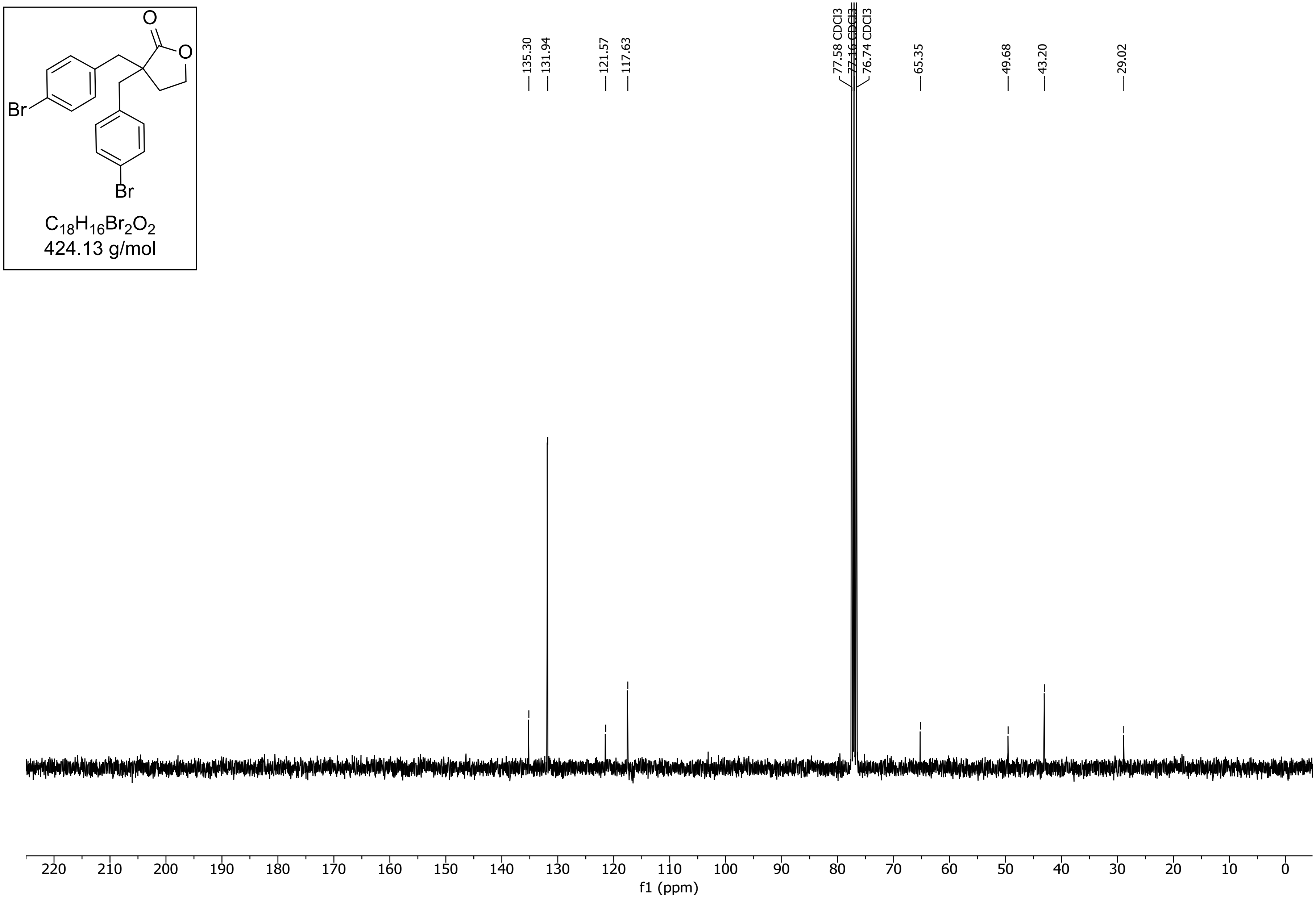


^{1}H NMR (300 MHz, $CDCl_3$)
3,3-bis(4-bromobenzyl)dihydrofuran-2(3H)-one



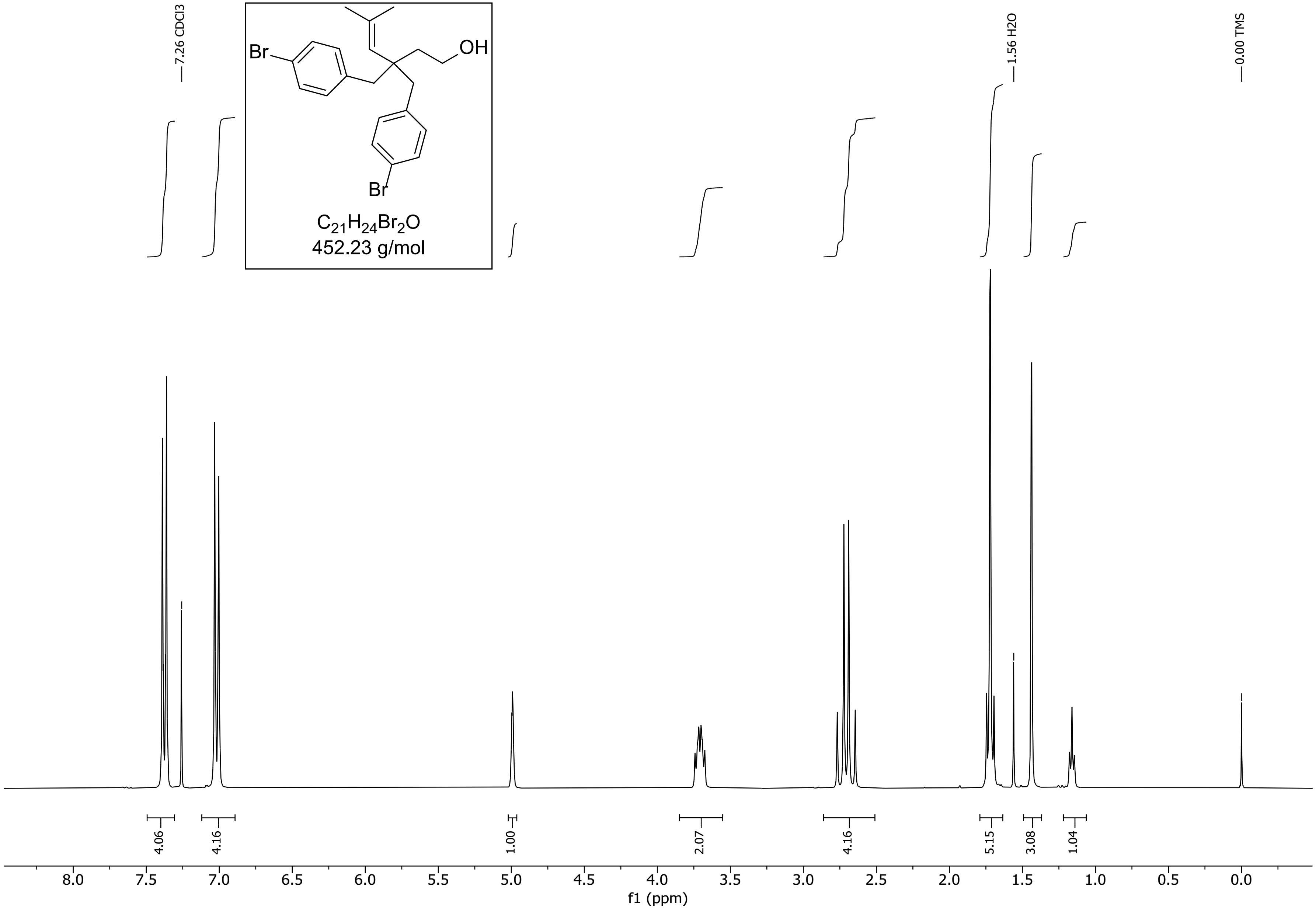
$C_{18}H_{16}Br_2O_2$
424.13 g/mol

^{13}C NMR (75 MHz, $CDCl_3$)
3,3-bis(4-bromobenzyl)dihydrofuran-2(3H)-one

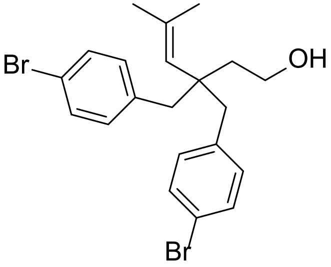


$C_{18}H_{16}Br_2O_2$
424.13 g/mol

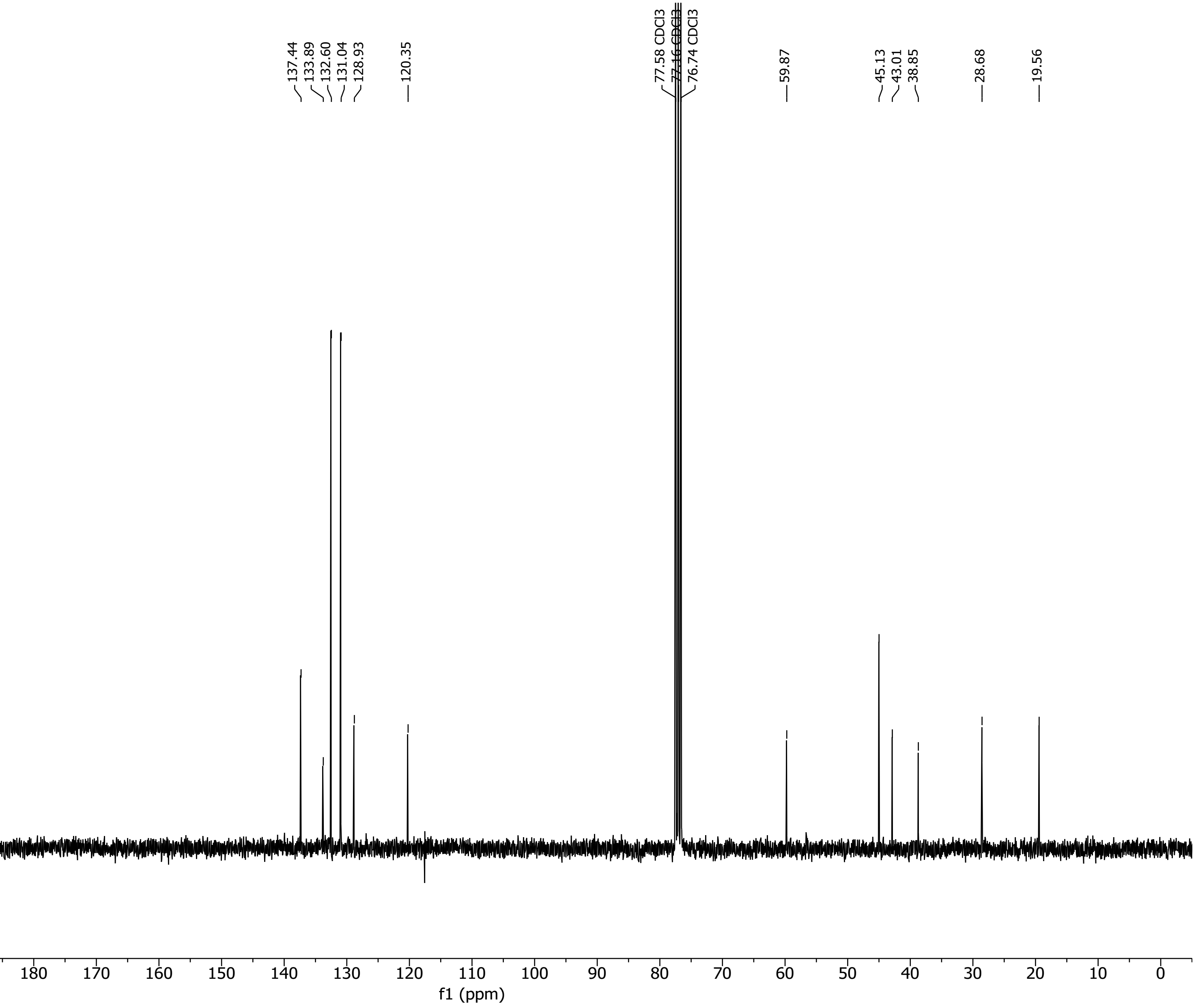
^{1}H NMR (300 MHz, $CDCl_3$)
3,3-bis(4-bromobenzyl)-5-methylhex-4-en-1-ol



^{13}C NMR (75 MHz, $CDCl_3$)
3,3-bis(4-bromobenzyl)-5-methylhex-4-en-1-ol

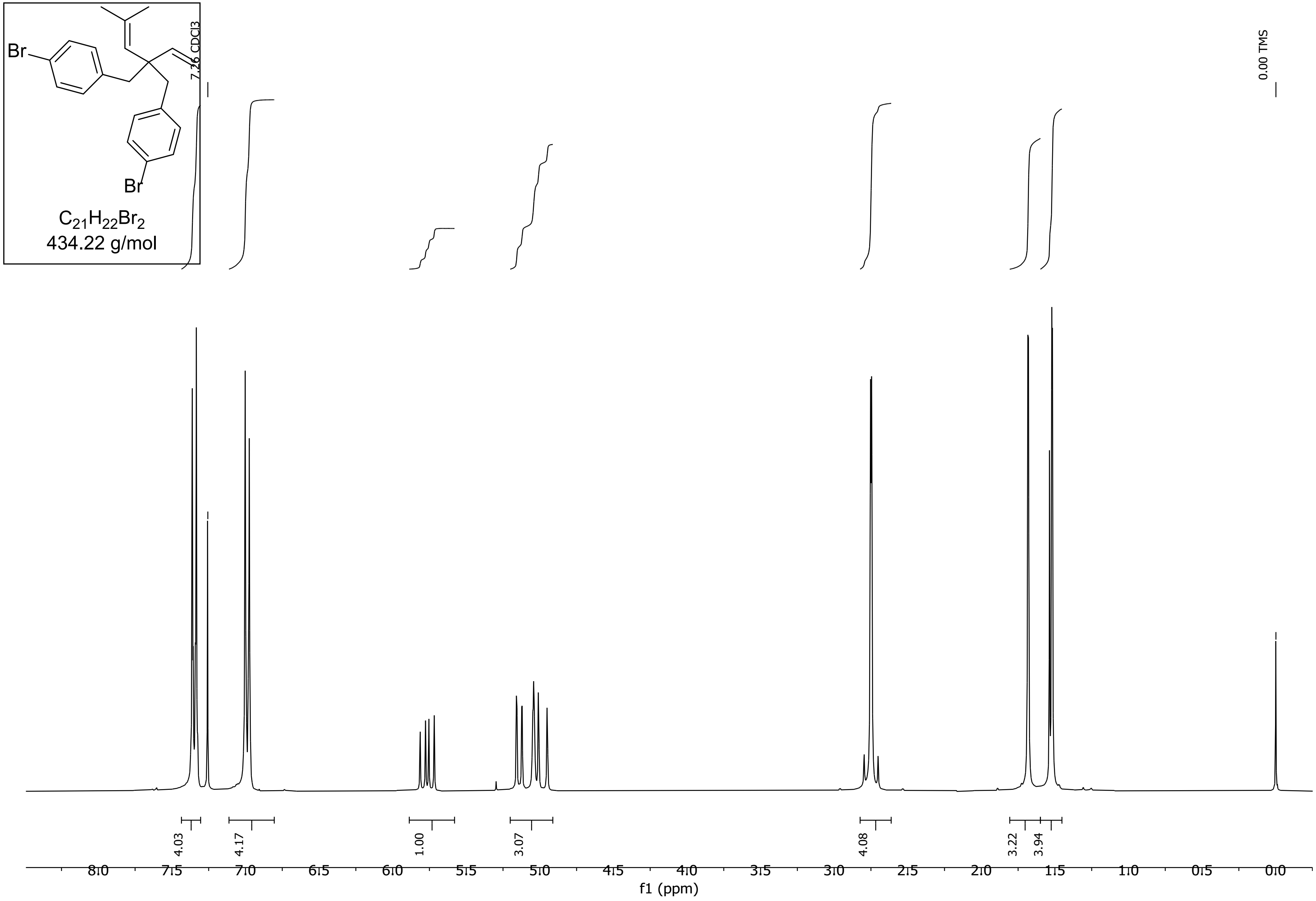


$C_{21}H_{24}Br_2O$
452.23 g/mol



^{1}H NMR (300 MHz, $CDCl_3$)

4,4'-(2-(2-methylprop-1-en-1-yl)-2-vinylpropane-1,3-diyl)bis(bromobenzene)

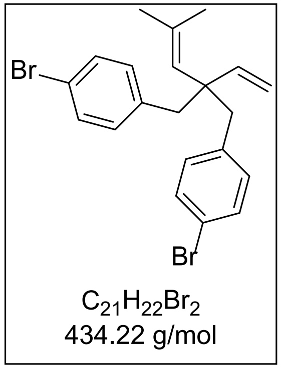


$C_{21}H_{22}Br_2$

434.22 g/mol

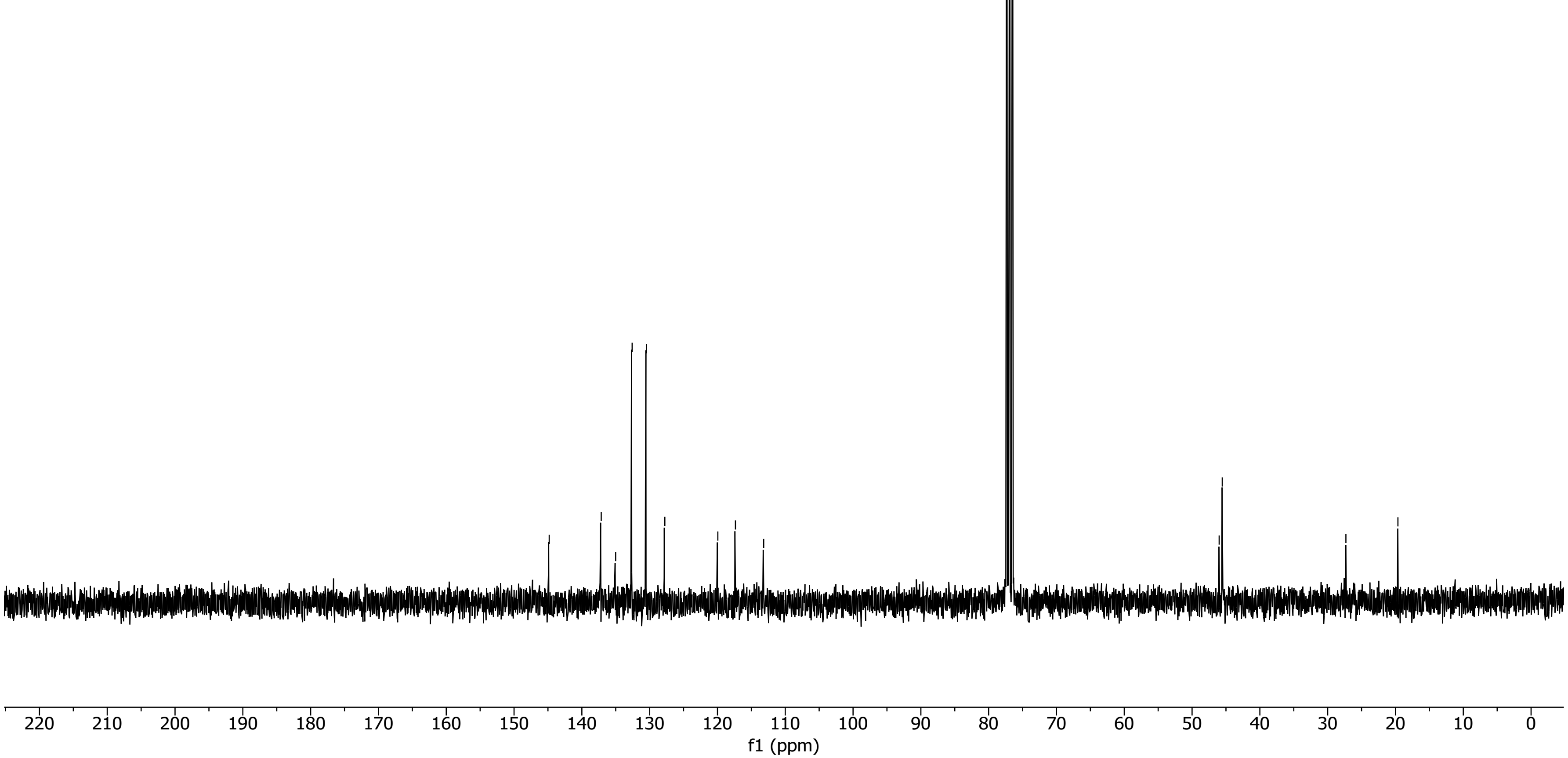
^{13}C NMR (75 MHz, CDCl$_3$)

4,4'-(2-(2-methylprop-1-en-1-yl)-2-vinylpropane-1,3-diyl)bis(bromobenzene)



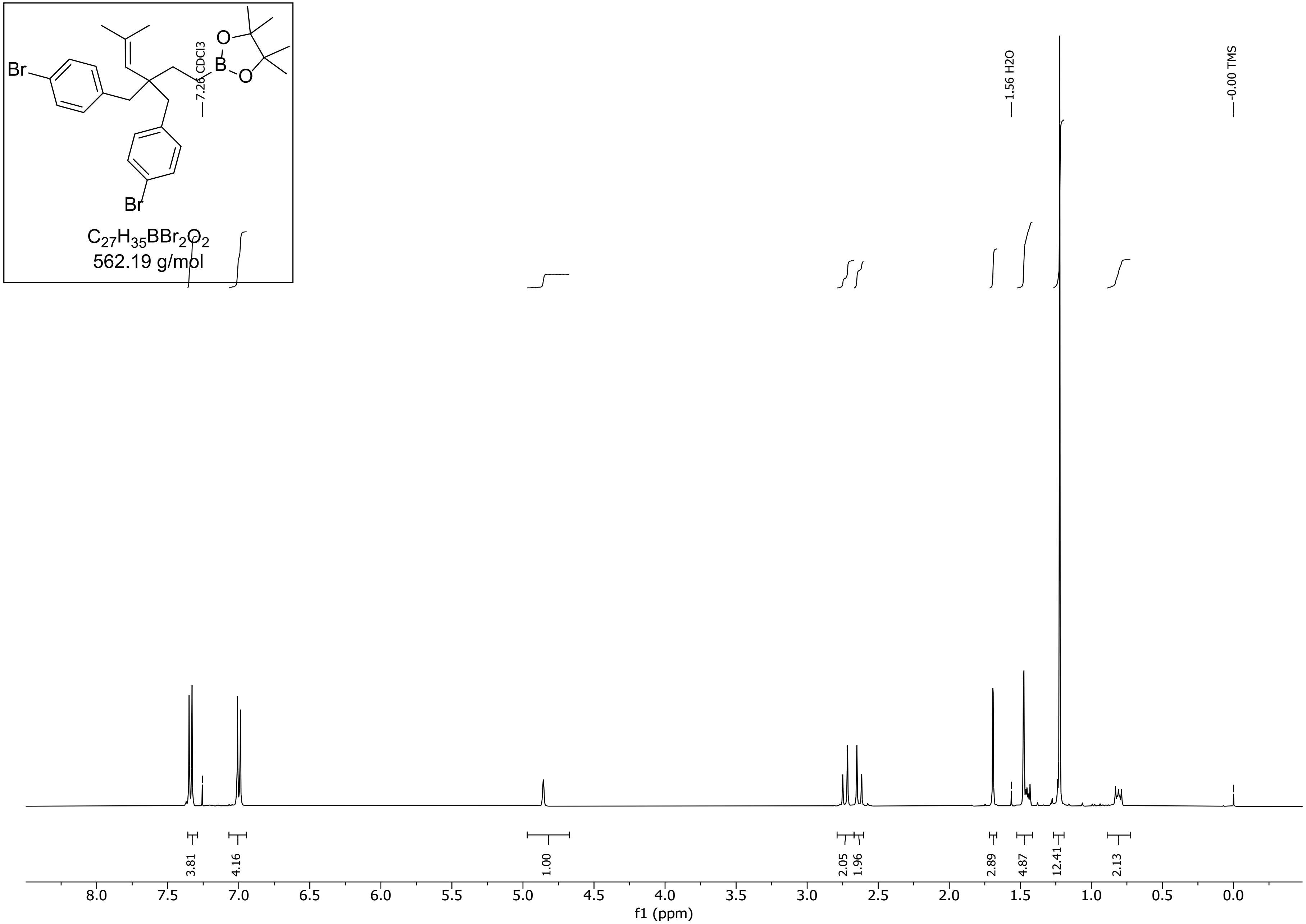
$C_{21}H_{22}Br_2$

434.22 g/mol

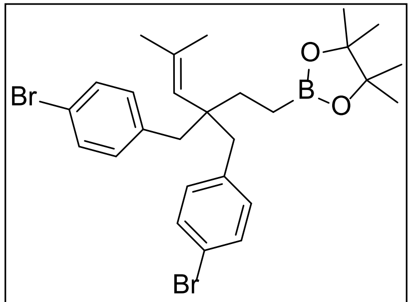


^{1}H NMR (400 MHz, $CDCl_3$)

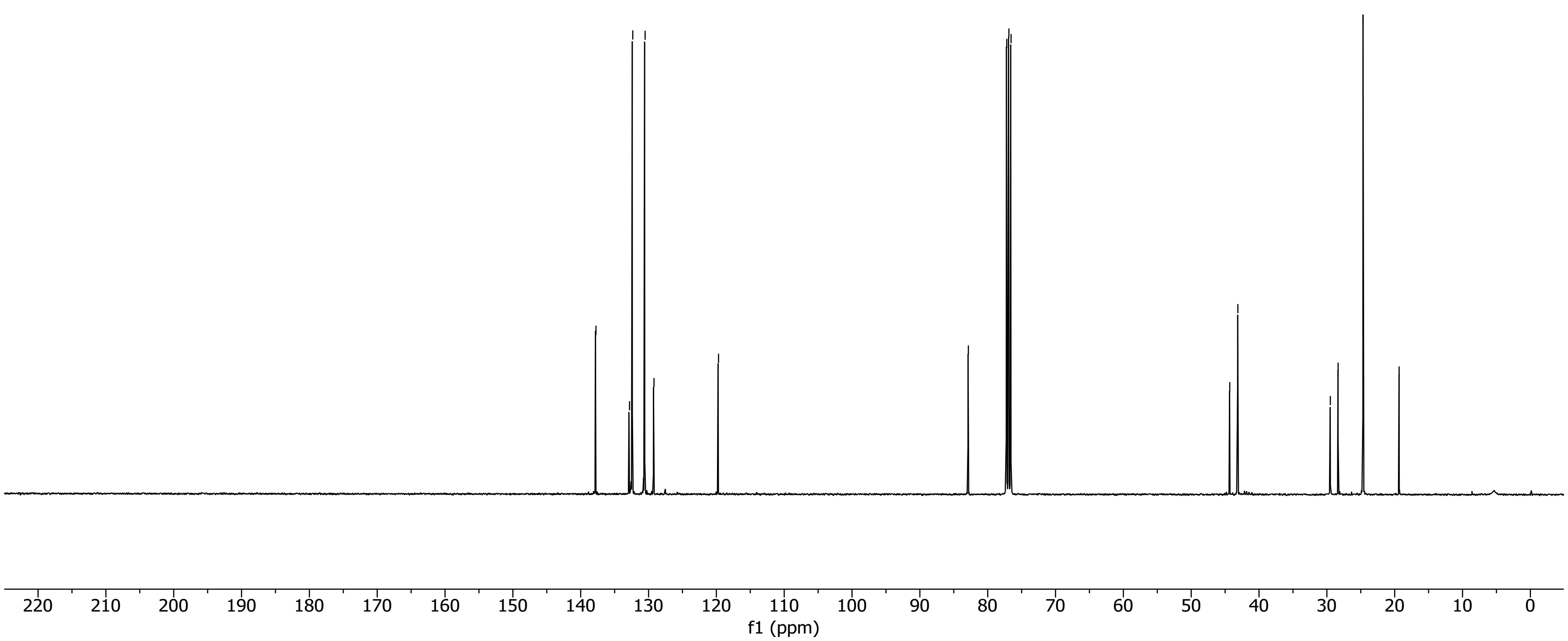
2-(3,3-bis(4-bromobenzyl)-5-methylhex-4-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



^{13}C NMR (101 MHz, CDCl$_3$)
2-(3,3-bis(4-bromobenzyl)-5-methylhex-4-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

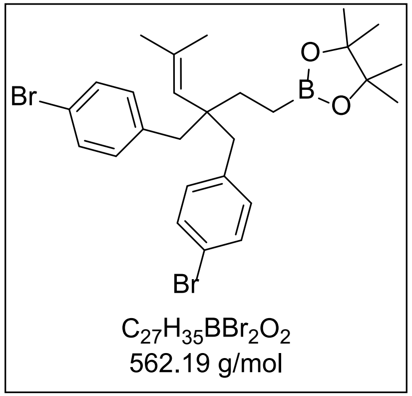


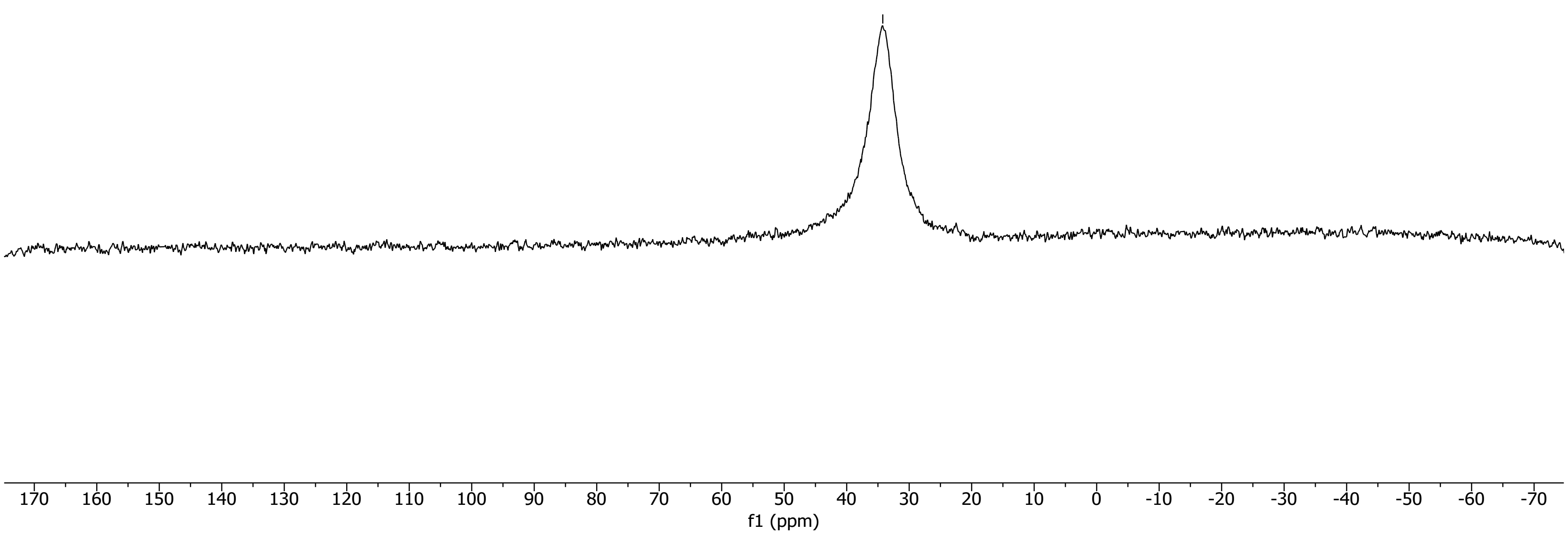
$C_{27}H_{35}BBr_2O_2$
562.19 g/mol



^{11}B NMR (96 MHz, $CDCl_3$)

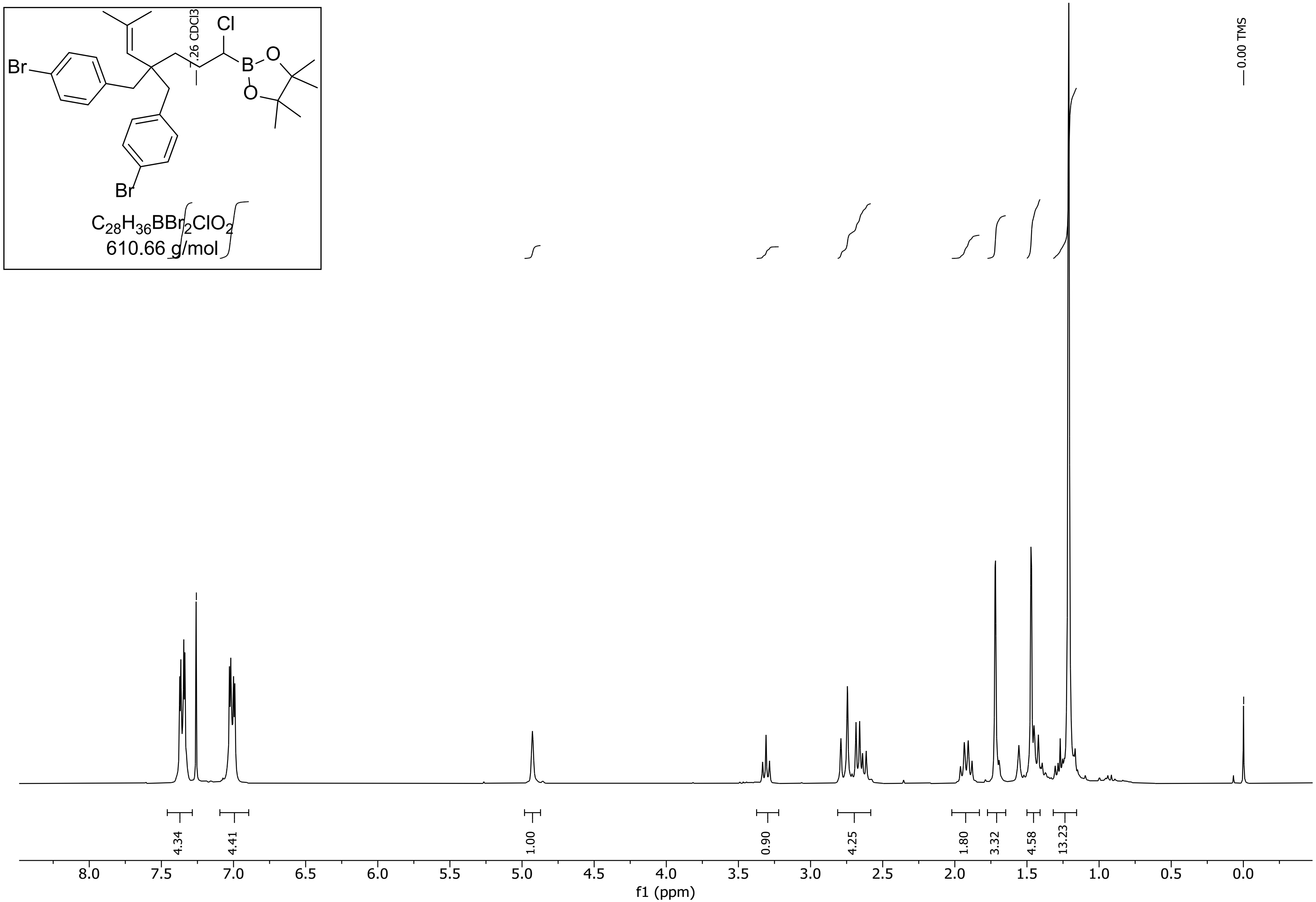
2-(3,3-bis(4-bromobenzyl)-5-methylhex-4-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane





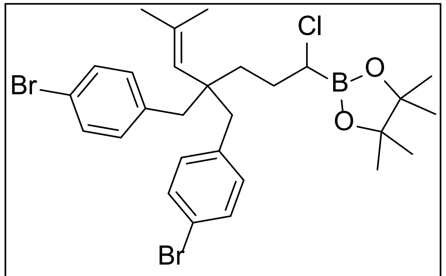
^{1}H NMR (300 MHz, $CDCl_3$)

2-(4,4-bis(4-bromobenzyl)-1-chloro-6-methylhept-5-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

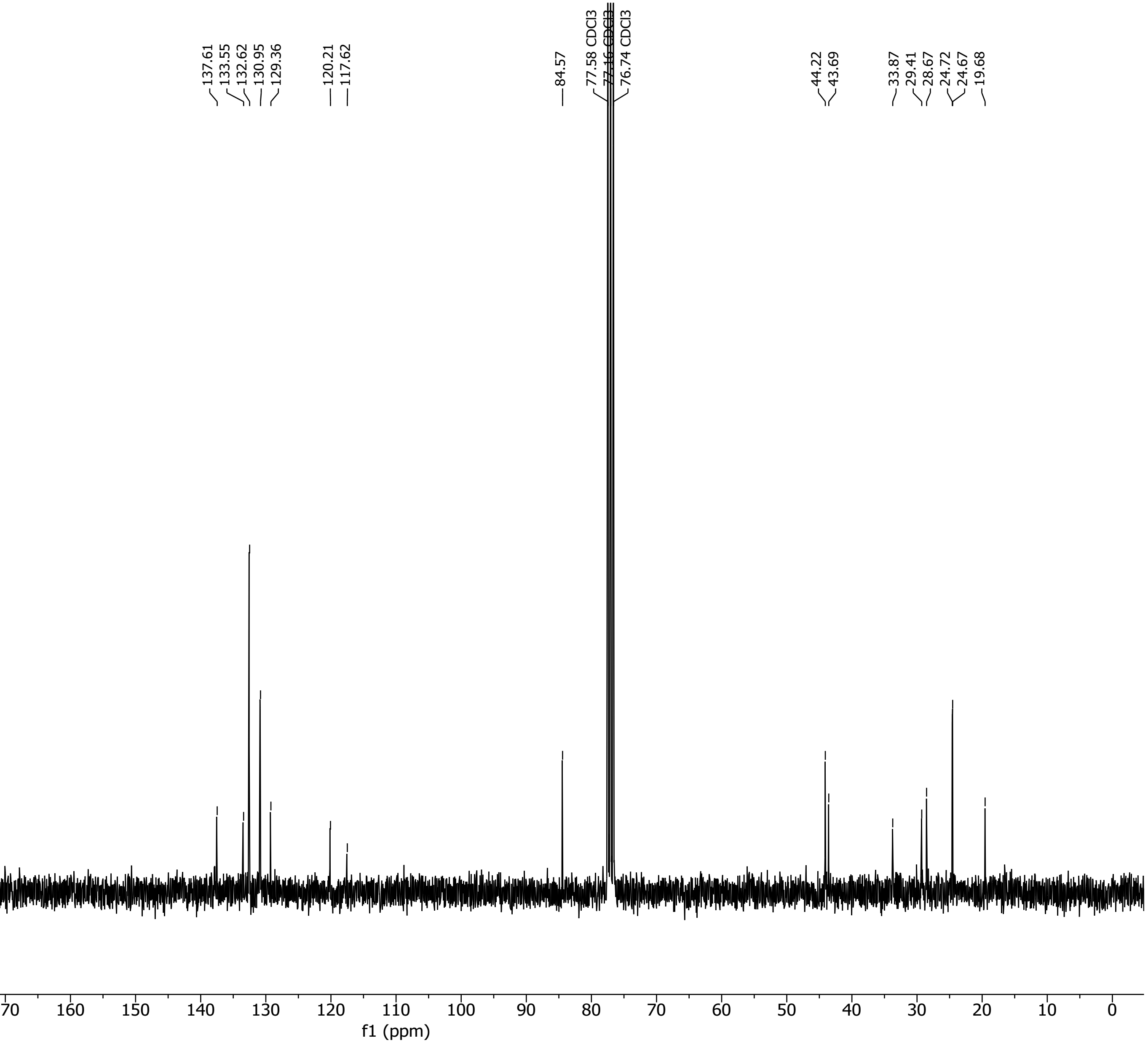


^{13}C NMR (75 MHz, $CDCl_3$)

2-(4,4-bis(4-bromobenzyl)-1-chloro-6-methylhept-5-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

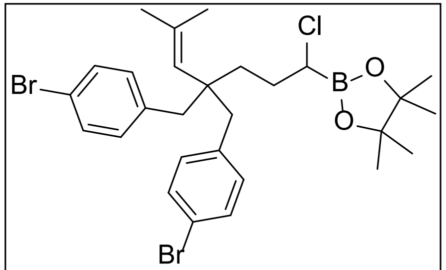


$C_{28}H_{36}BBr_2ClO_2$
610.66 g/mol

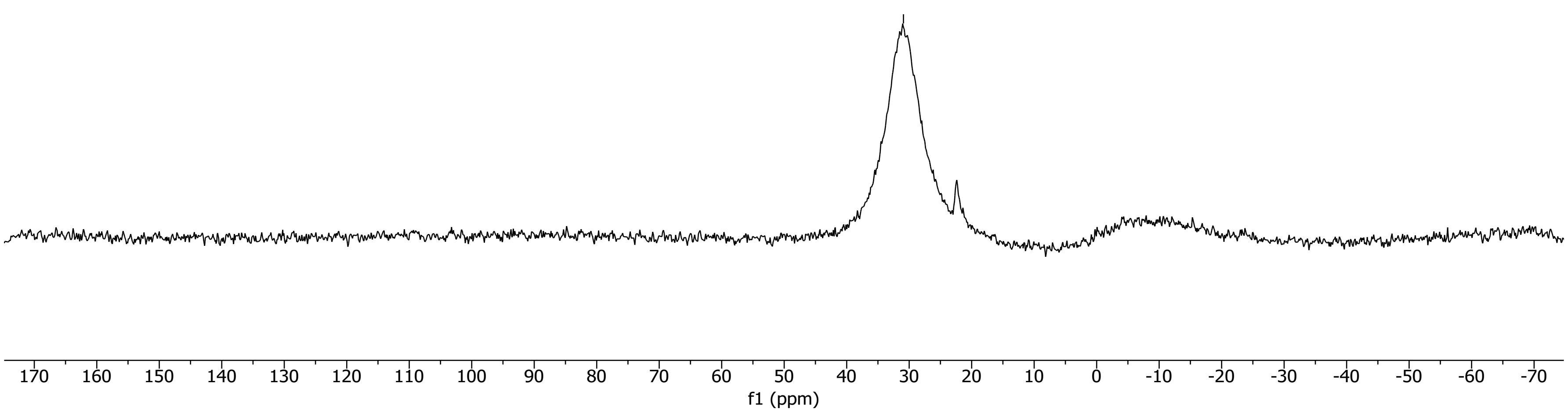


^{11}B NMR (96 MHz, $CDCl_3$)

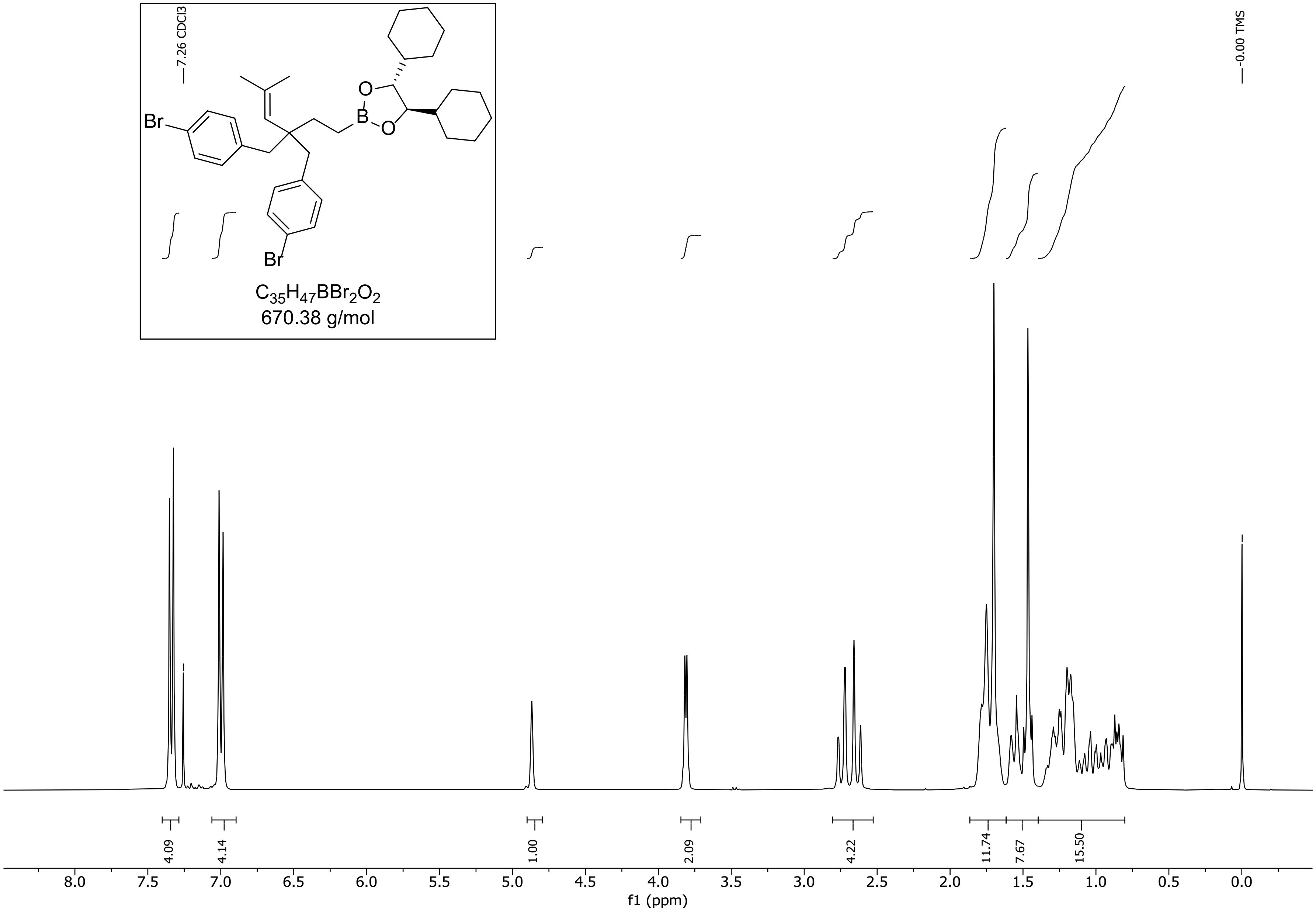
2-(4,4-bis(4-bromobenzyl)-1-chloro-6-methylhept-5-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



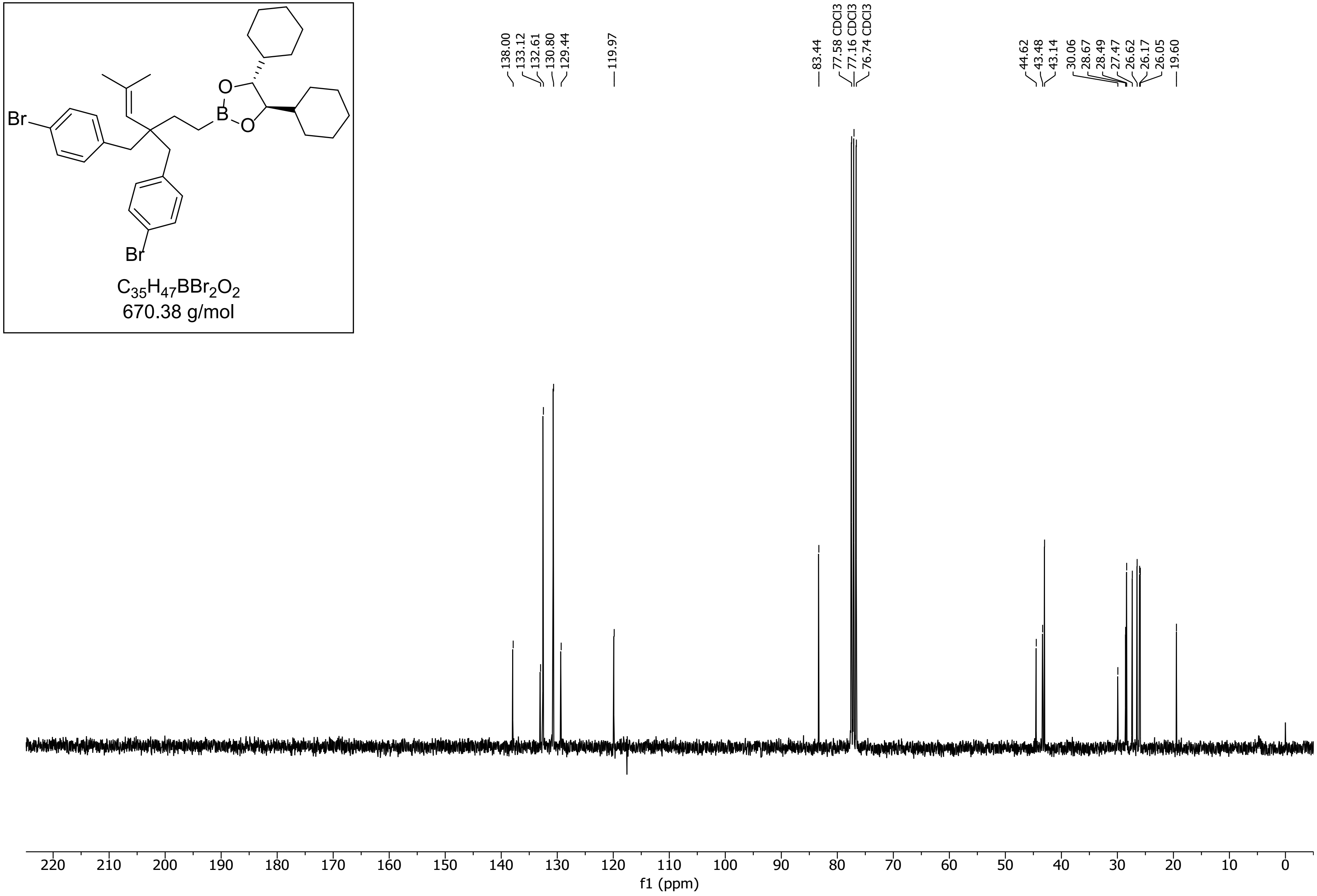
$C_{28}H_{36}BBr_2ClO_2$
610.66 g/mol



^{1}H NMR (300 MHz, $CDCl_3$)
(4R,5R)-2-(3,3-Bis(4-bromobenzyl)-5-methylhex-4-en-1-yl)-4,5-dicyclohexyl-1,3,2-dioxaborolane (**12**)

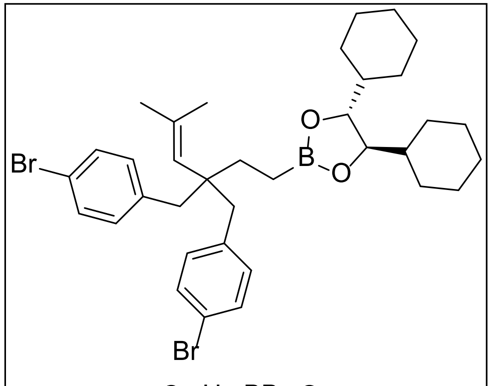


^{13}C NMR (75 MHz, $CDCl_3$)
(4R,5R)-2-(3,3-Bis(4-bromobenzyl)-5-methylhex-4-en-1-yl)-4,5-dicyclohexyl-1,3,2-dioxaborolane (**12**)

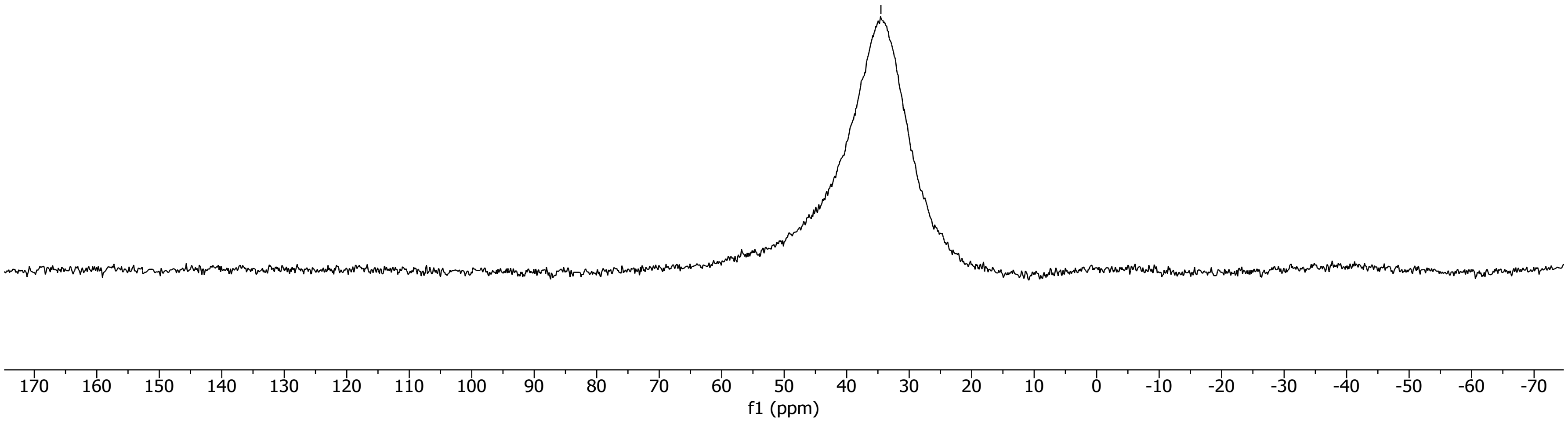


$C_{35}H_{47}BBr_2O_2$
670.38 g/mol

^{11}B NMR (96 MHz, $CDCl_3$)
(4R,5R)-2-(3,3-Bis(4-bromobenzyl)-5-methylhex-4-en-1-yl)-4,5-dicyclohexyl-1,3,2-dioxaborolane (**12**)

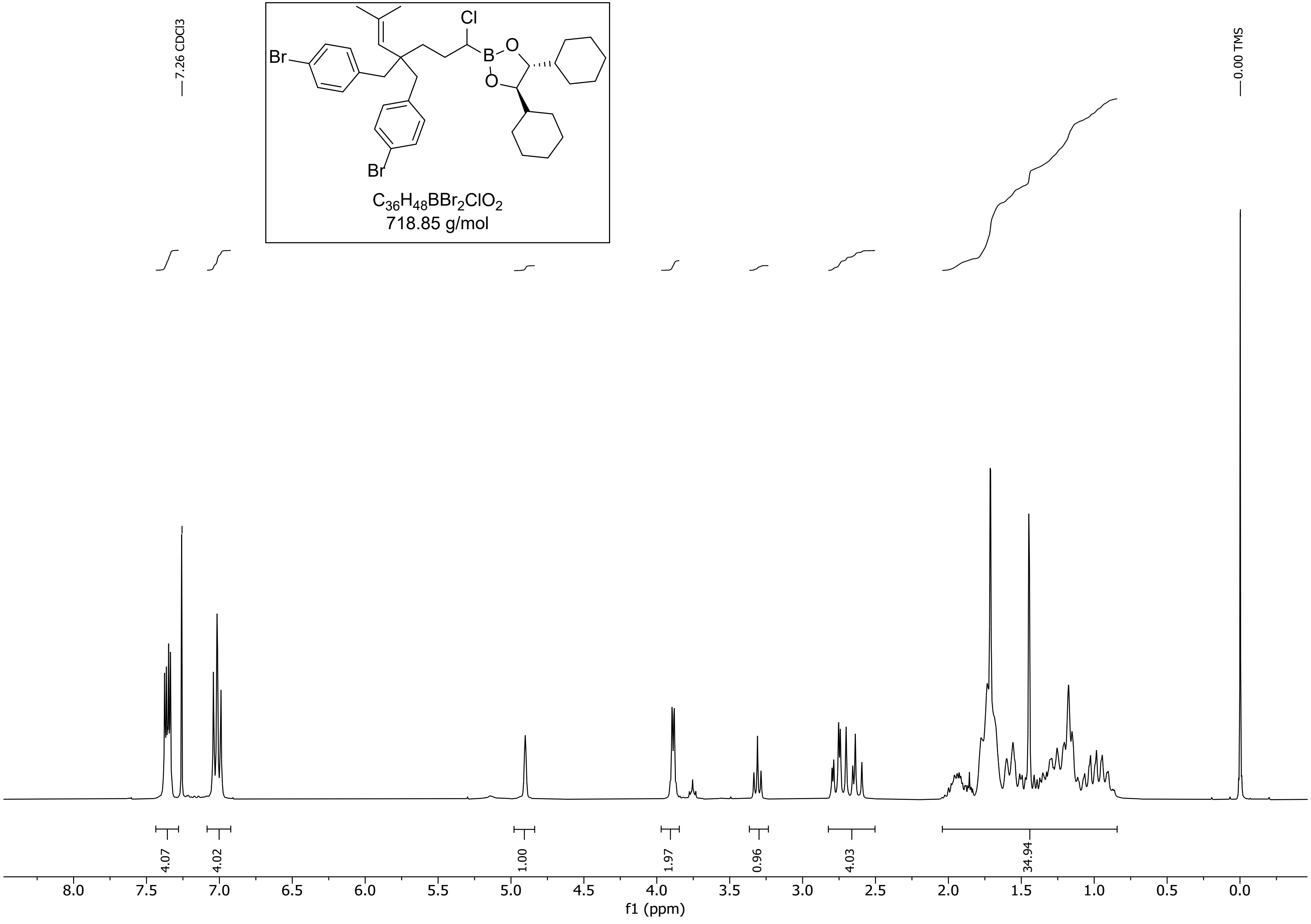


$C_{35}H_{47}BBr_2O_2$
670.38 g/mol

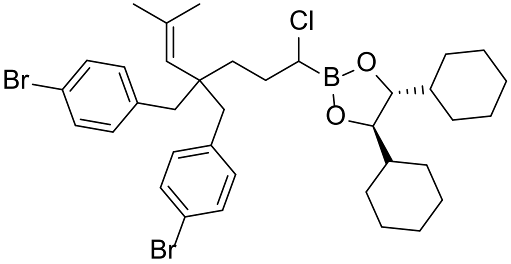


^{1}H NMR (300 MHz, $CDCl_3$)

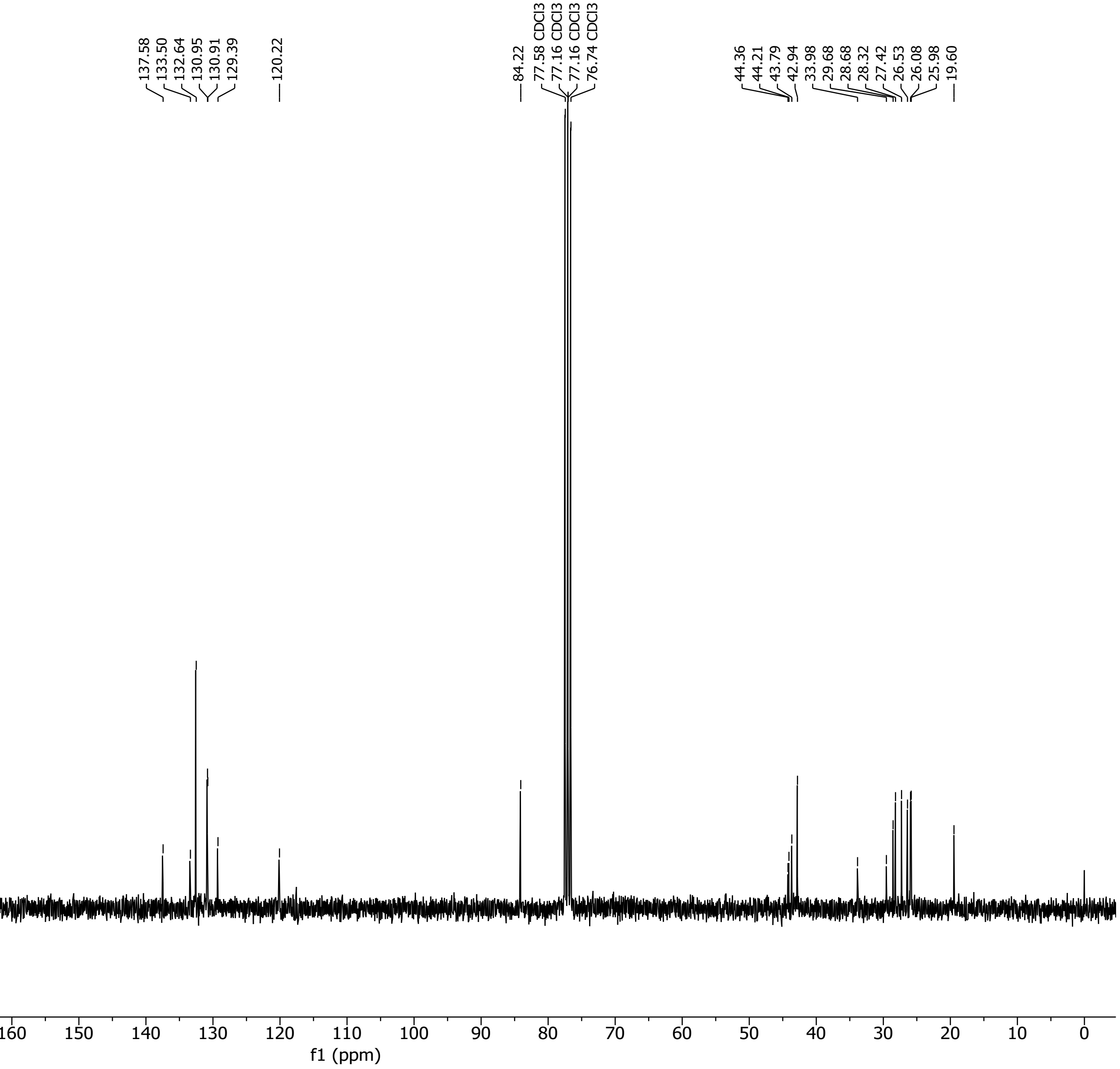
(4R,5R)-2-(4,4-Bis(4-bromobenzyl)-1-chloro-6-methylhept-5-en-1-yl)-4,5-dicyclohexyl-1,3,2-dioxaborolane (**13**)



^{13}C NMR (75 MHz, $CDCl_3$)
(4R,5R)-2-(4,4-Bis(4-bromobenzyl)-1-chloro-6-methylhept-5-en-1-yl)-4,5-dicyclohexyl-1,3,2-dioxaborolane (**13**)

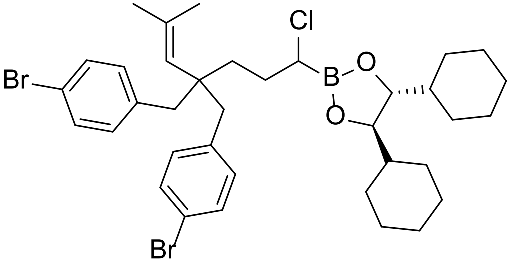


$C_{36}H_{48}BBr_2ClO_2$
718.85 g/mol

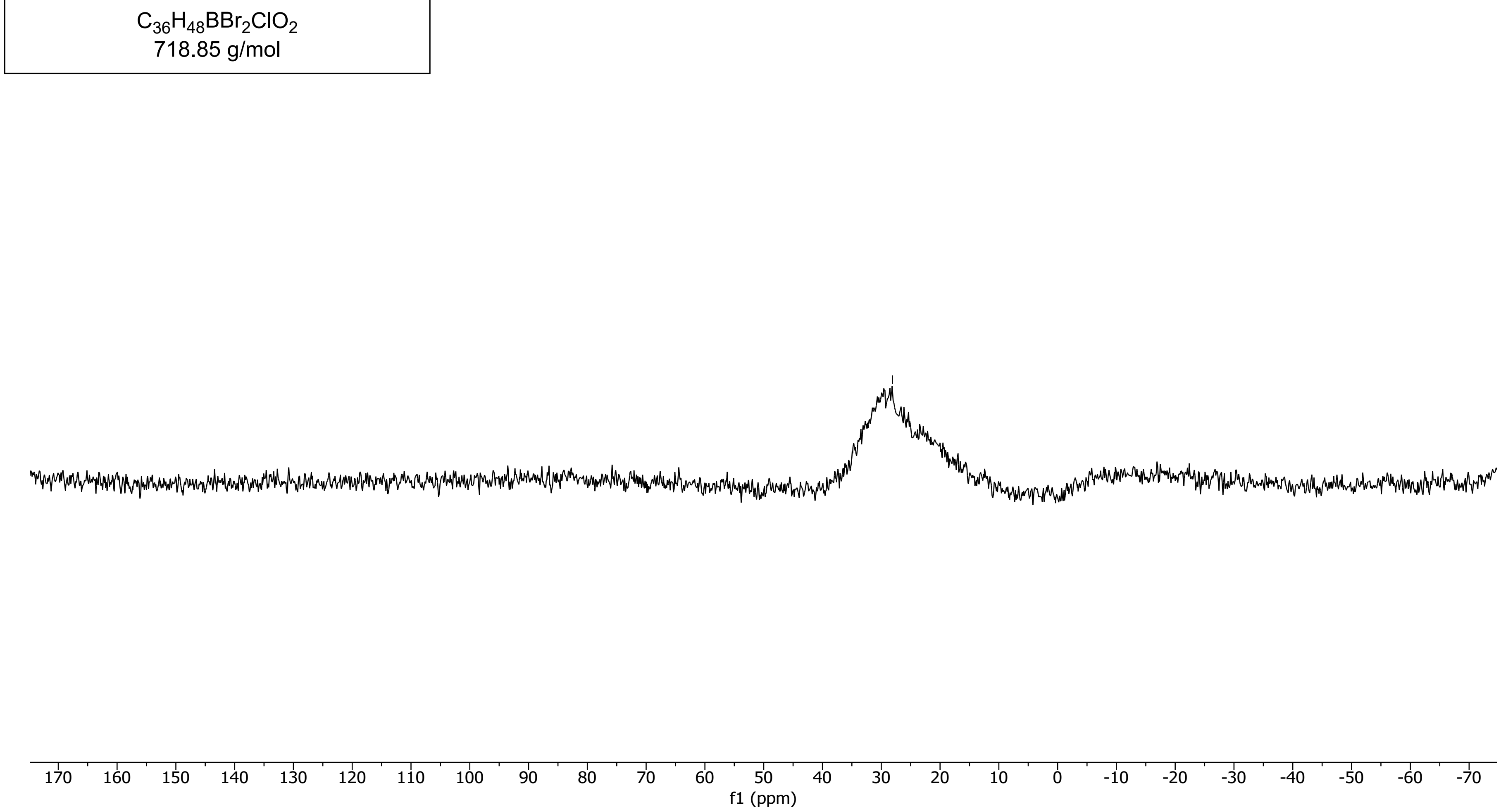


^{11}B NMR (96 MHz, CDCl$_3$)

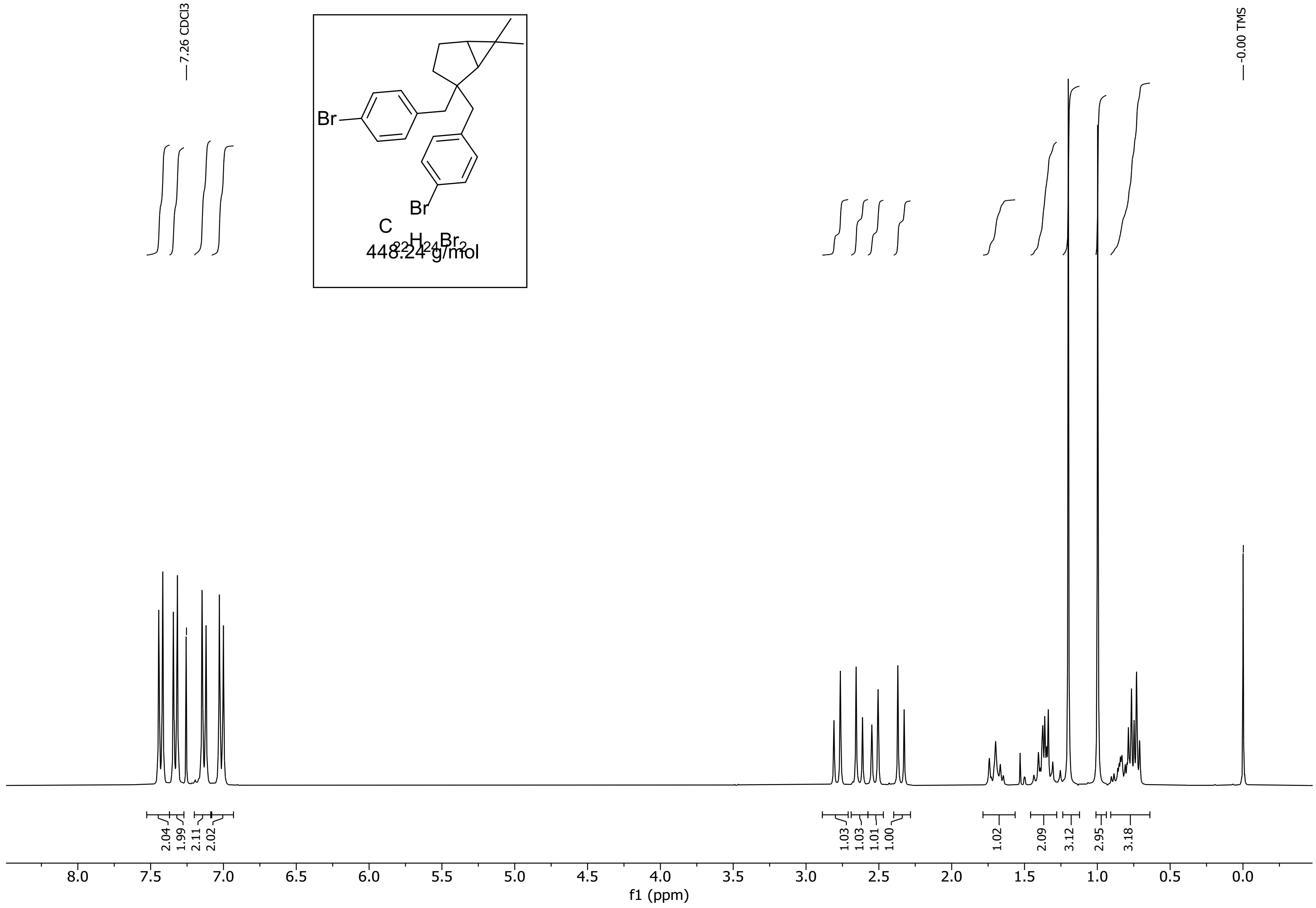
(4R,5R)-2-(4,4-Bis(4-bromobenzyl)-1-chloro-6-methylhept-5-en-1-yl)-4,5-dicyclohexyl-1,3,2-dioxaborolane (**13**)



$C_{36}H_{48}BBr_2ClO_2$
718.85 g/mol

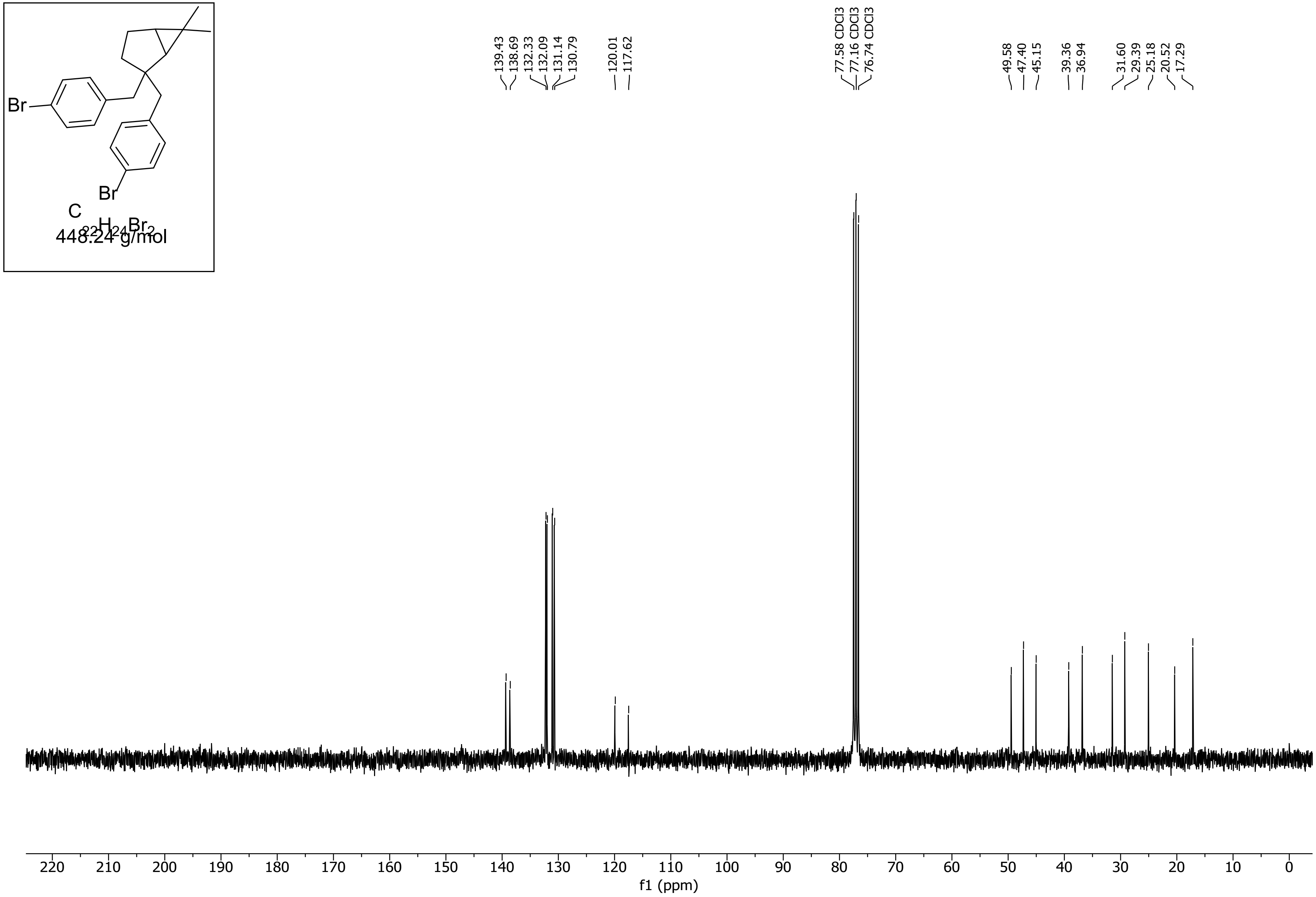


^{1}H NMR (300 MHz, $CDCl_3$)
2,2-Bis(4-bromobenzyl)-6,6-dimethylbicyclo[3.1.0]hexane (**14**)



^{13}C NMR (75 MHz, $CDCl_3$)

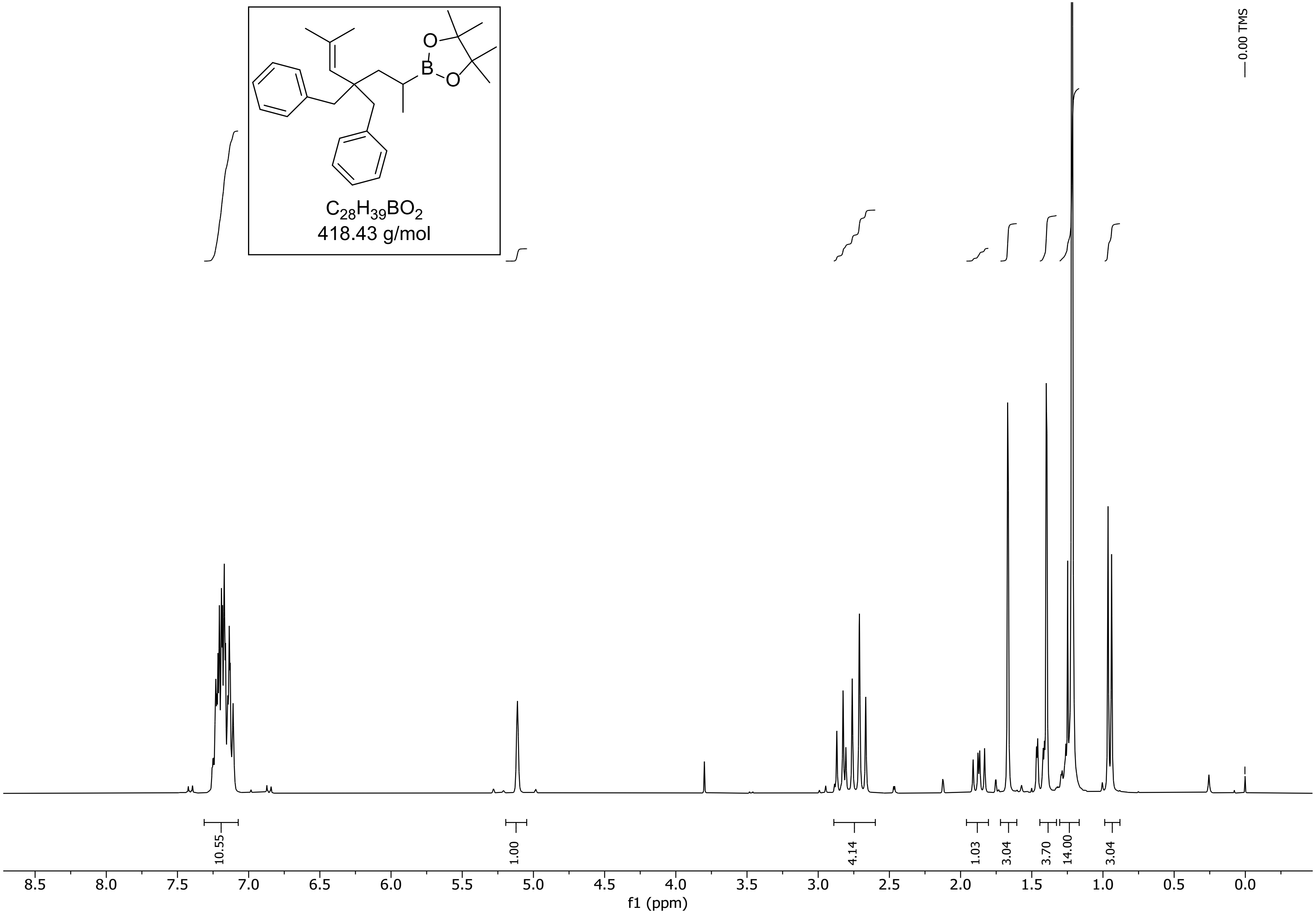
2,2-Bis(4-bromobenzyl)-6,6-dimethylbicyclo[3.1.0]hexane (**14**)



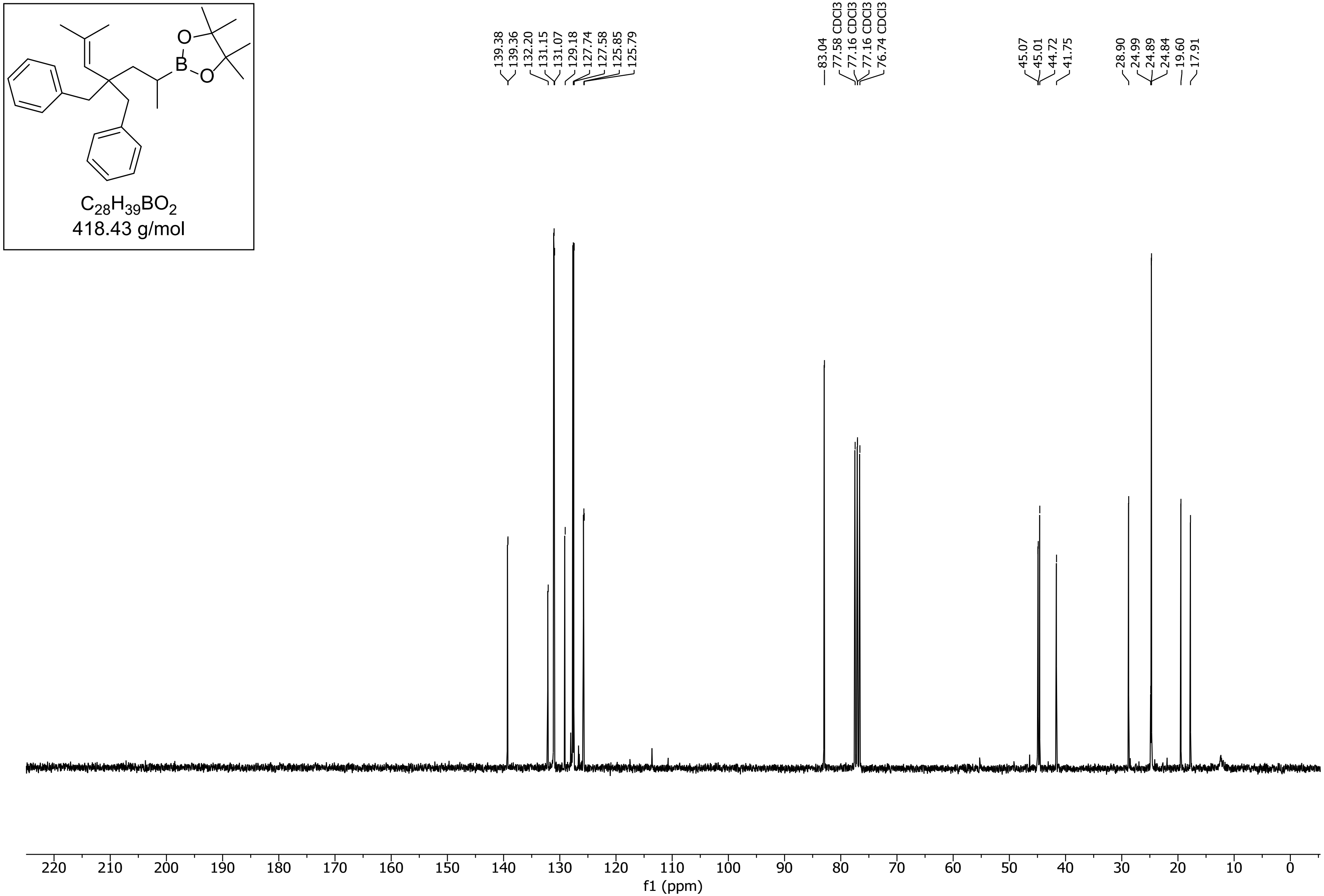
^{1}H NMR (300 MHz, $CDCl_3$)

2-(4,4-Dibenzyl-6-methylhept-5-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**15**)

$C_{28}H_{39}BO_2$
418.43 g/mol



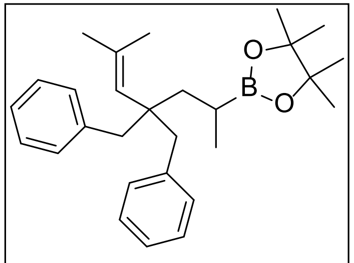
^{13}C NMR (75 MHz, CDCl$_3$)
2-(4,4-Dibenzyl-6-methylhept-5-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**15**)



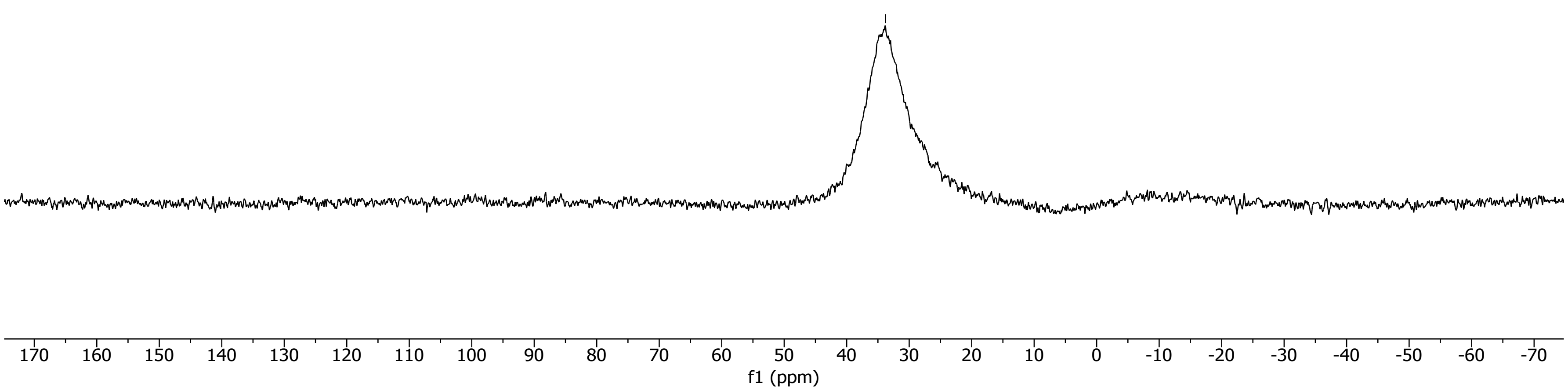
$C_{28}H_{39}BO_2$

418.43 g/mol

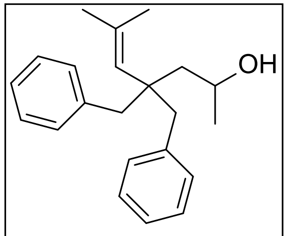
^{11}B NMR (96 MHz, $CDCl_3$)
2-(4,4-Dibenzyl-6-methylhept-5-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**15**)



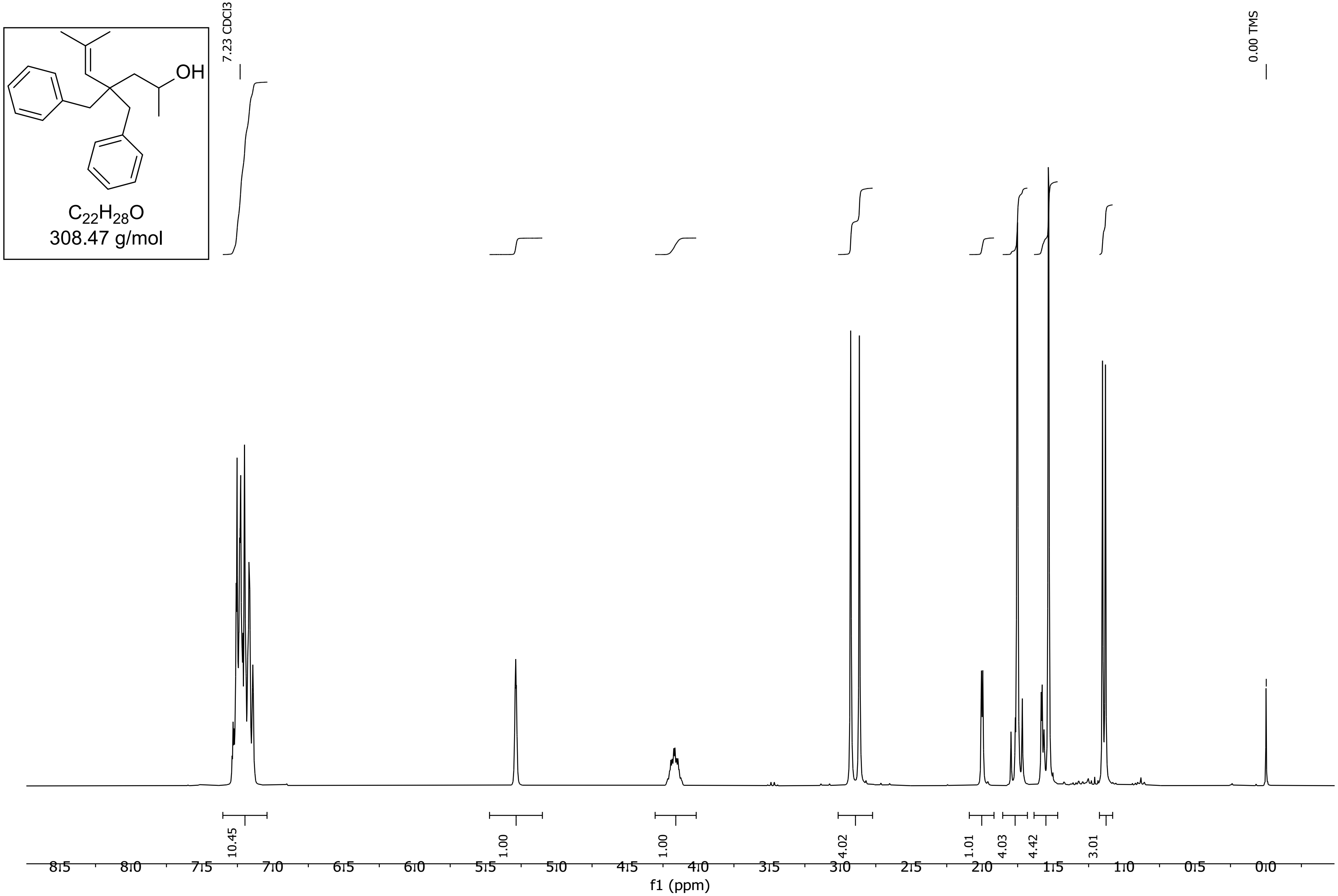
$C_{28}H_{39}BO_2$
418.43 g/mol



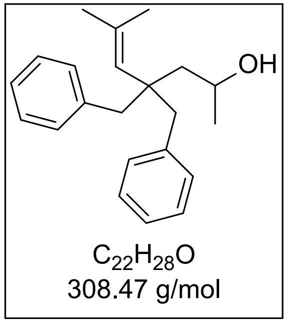
^{1}H NMR (300 MHz, $CDCl_3$)
4,4-Dibenzyl-6-methylhept-5-en-2-ol (**16**)



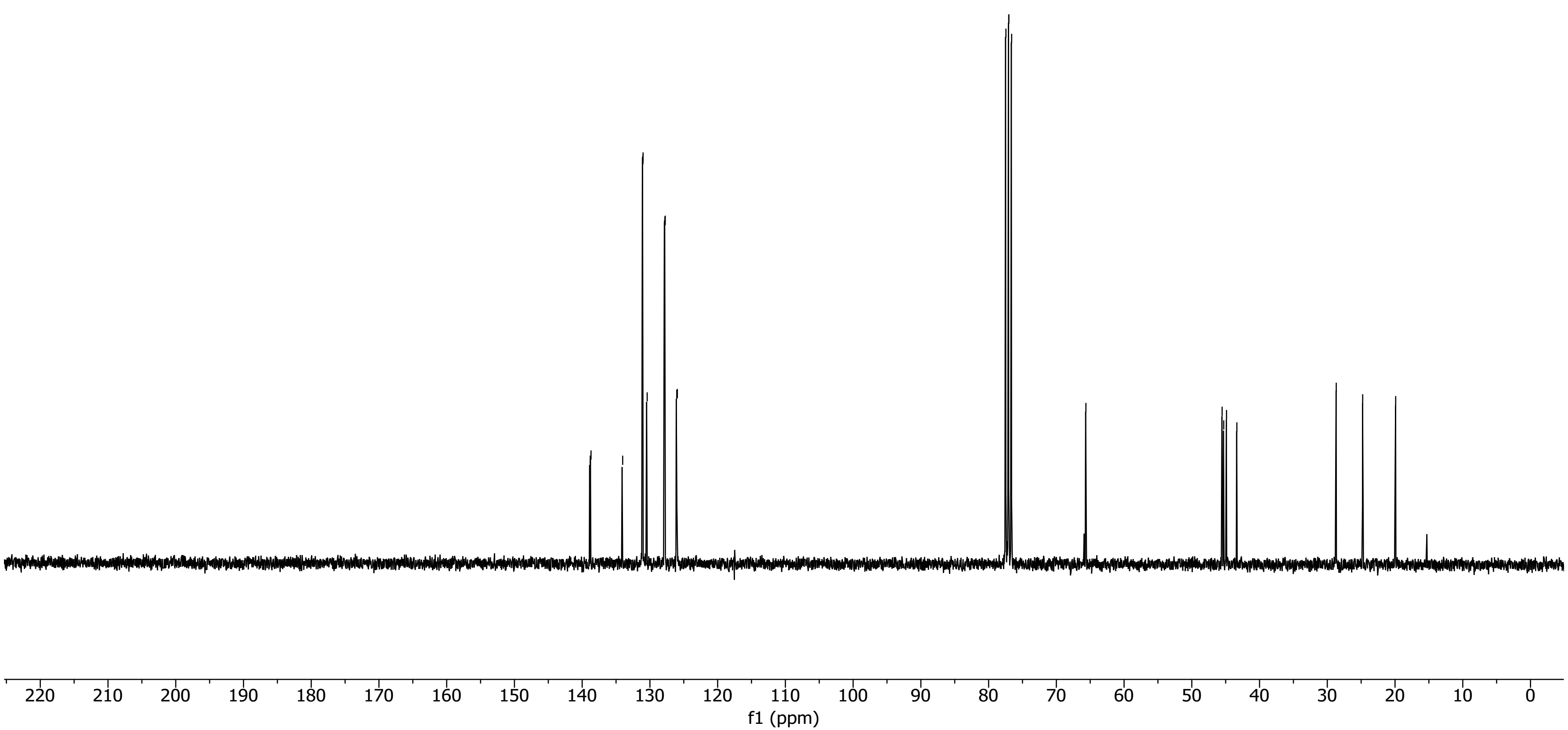
$C_{22}H_{28}O$
308.47 g/mol



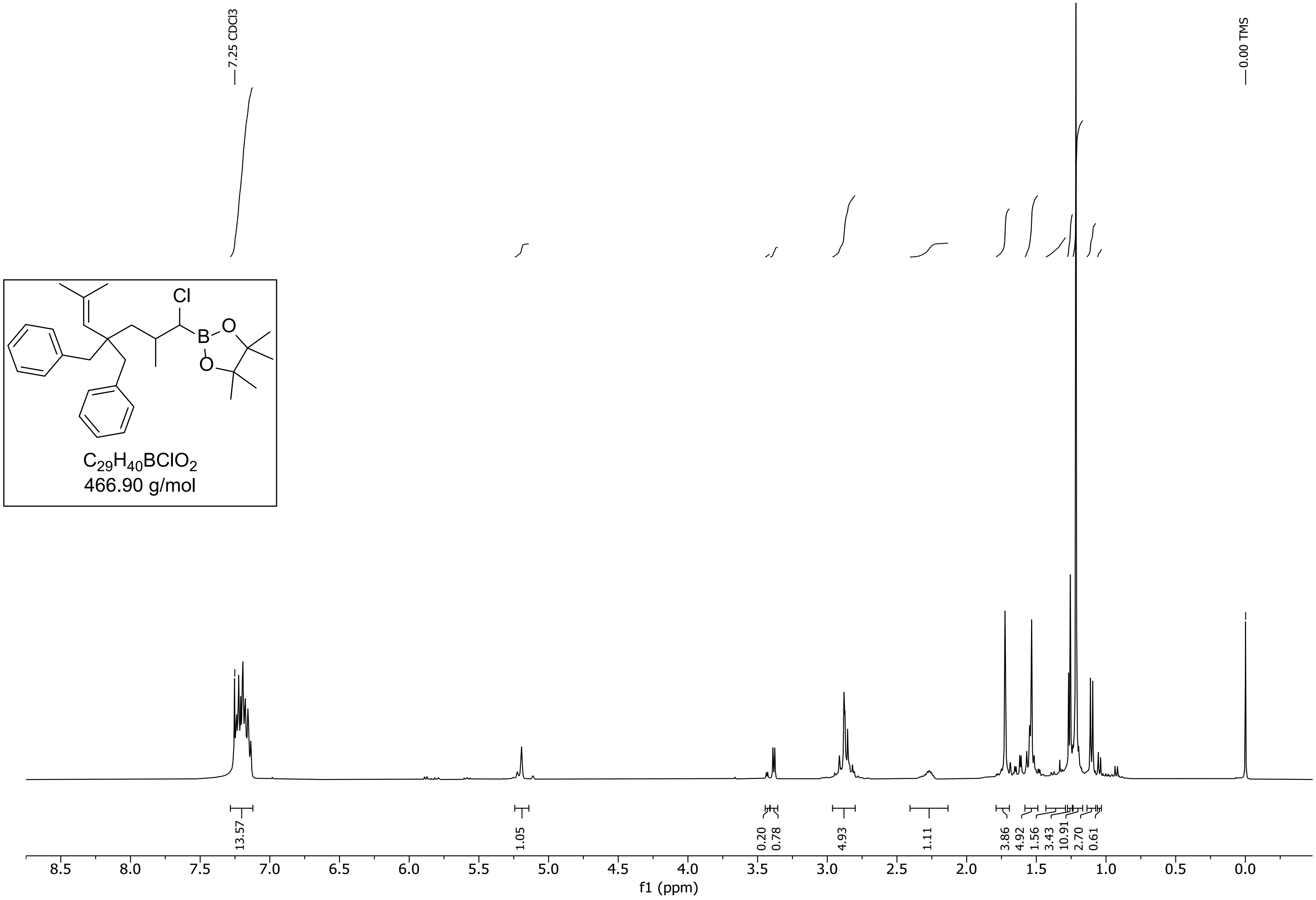
^{13}C NMR (75 MHz, CDCl$_3$)
4,4-Dibenzyl-6-methylhept-5-en-2-ol (**16**)



$C_{22}H_{28}O$
308.47 g/mol

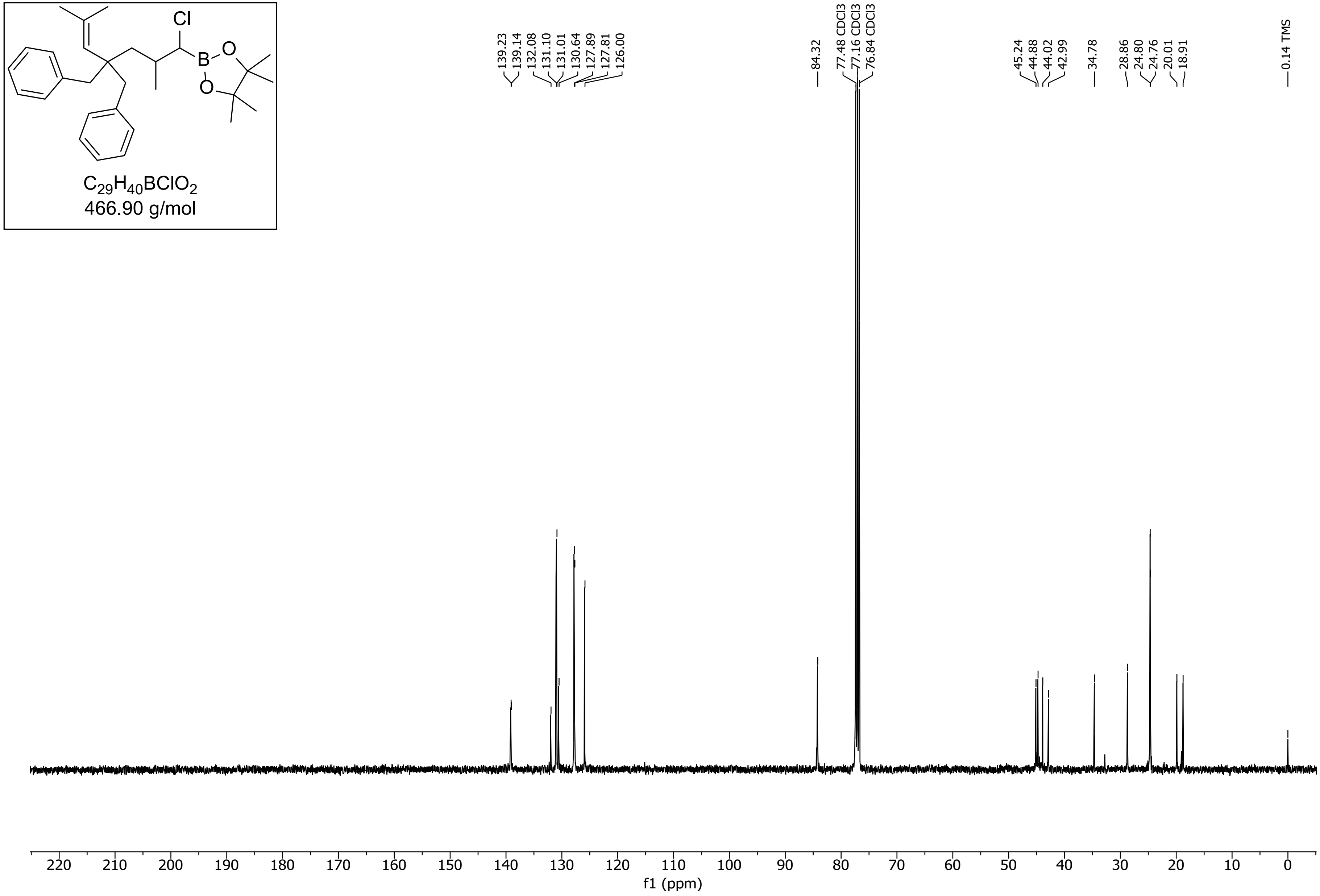


^{1}H NMR (400 MHz, CDCl$_3$)
2-(4,4-Dibenzyl-1-chloro-2,6-dimethylhept-5-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**17**)



^{13}C NMR (101 MHz, $CDCl_3$)

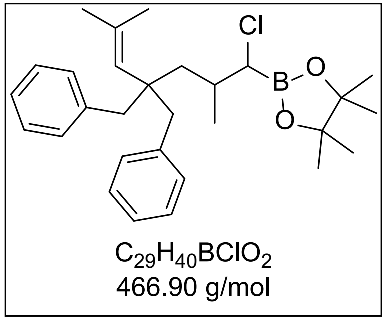
2-(4,4-Dibenzyl-1-chloro-2,6-dimethylhept-5-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**17**)

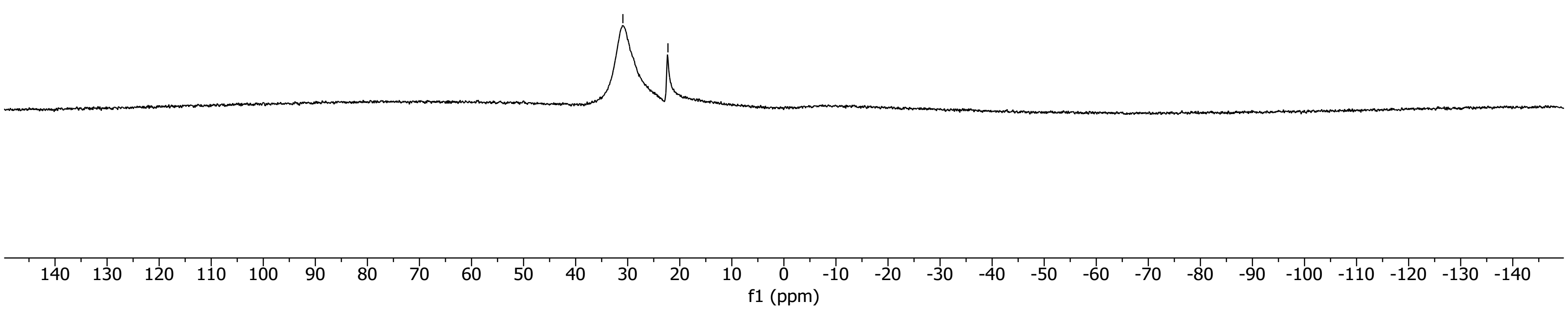


$C_{29}H_{40}BClO_2$
466.90 g/mol

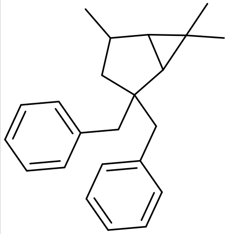
^{11}B NMR (128 MHz, $CDCl_3$)

2-(4,4-Dibenzyl-1-chloro-2,6-dimethylhept-5-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**17**)

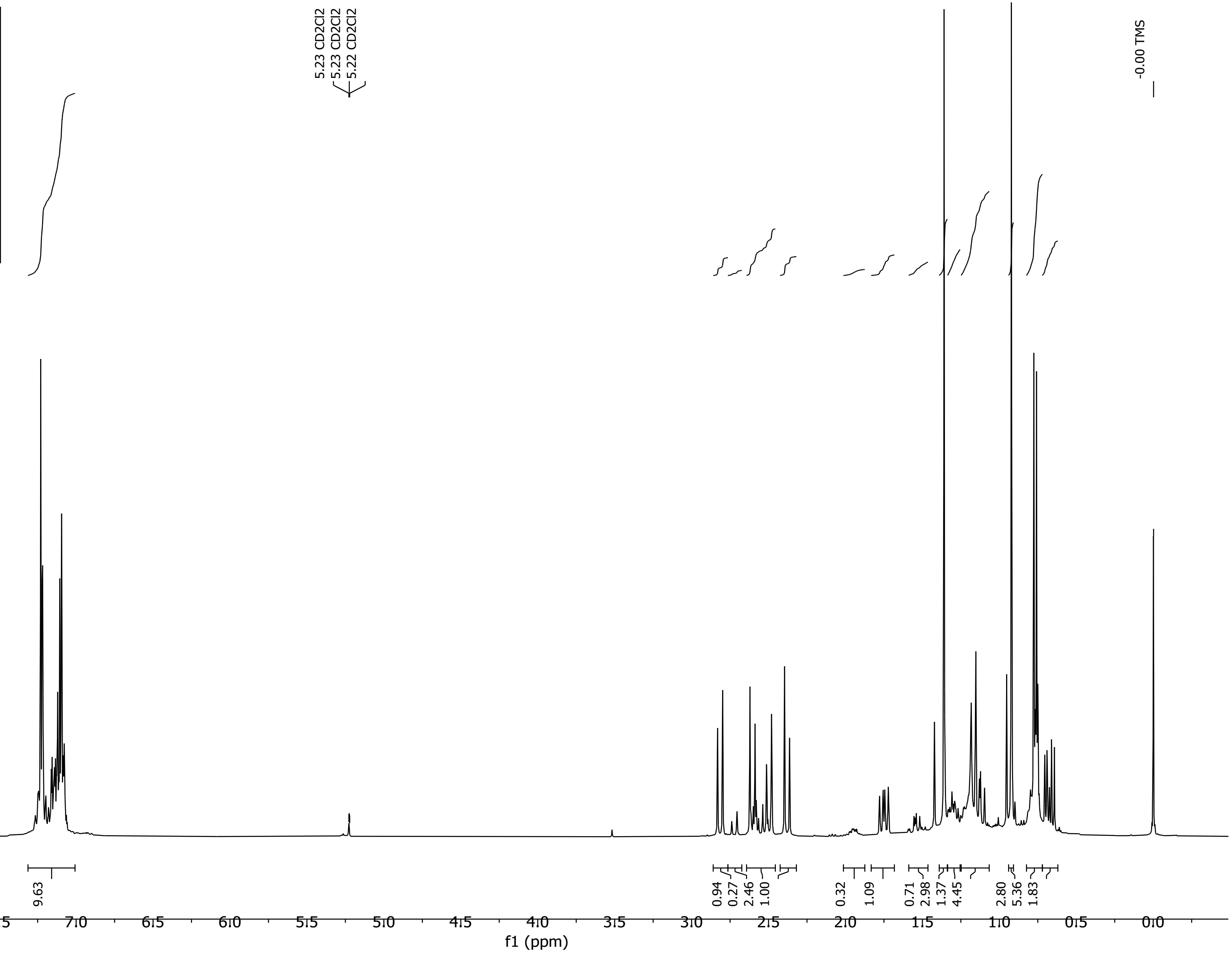




^{1}H NMR (400 MHz, CD_2Cl_2)
2,2-Dibenzyl-4,6,6-trimethylbicyclo[3.1.0]hexane (**18**)

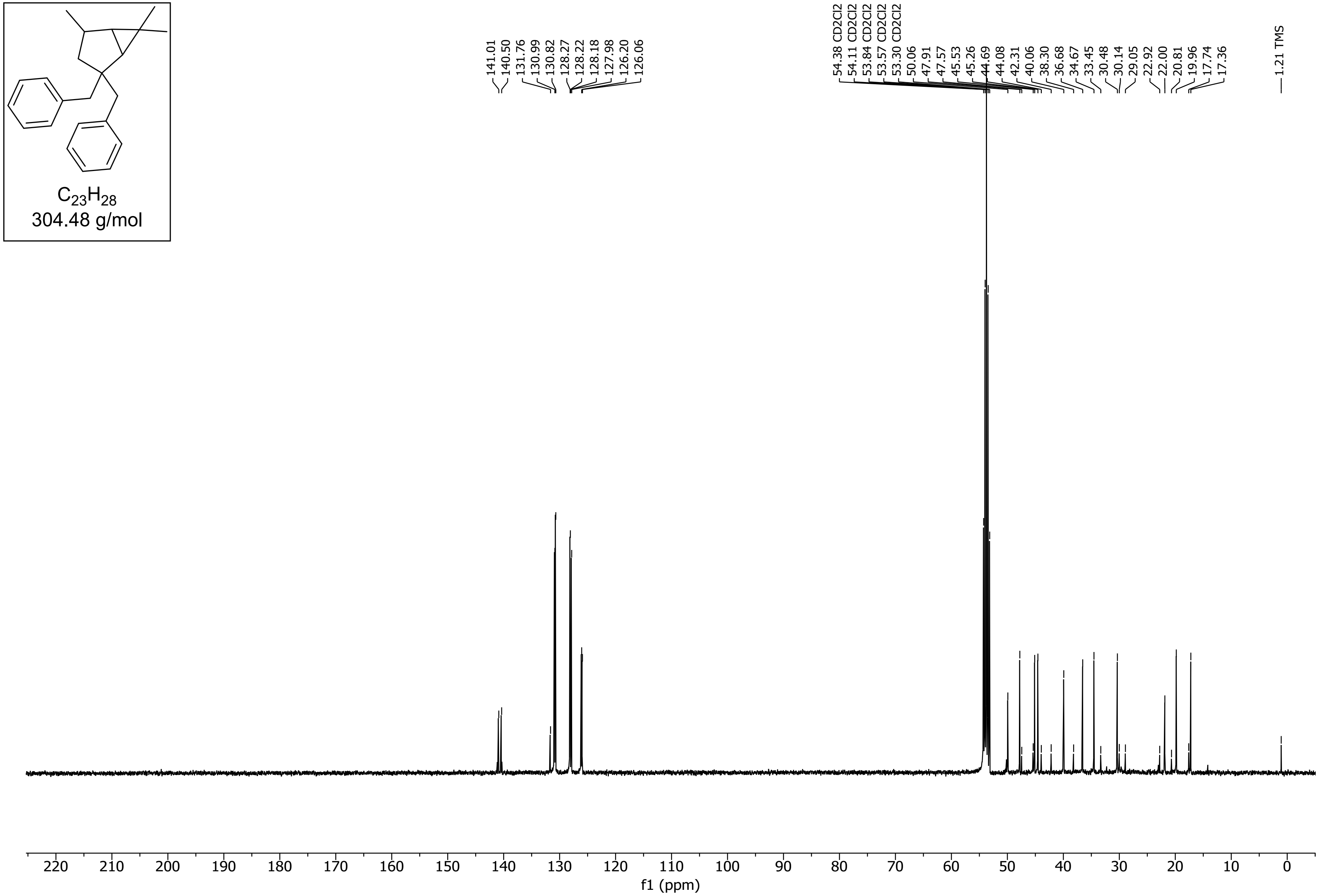


$C_{23}H_{28}$
304.48 g/mol



^{13}C NMR (101 MHz, CD$_2$Cl$_2$)

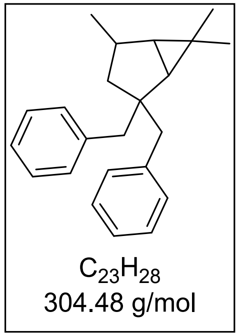
2,2-Dibenzyl-4,6,6-trimethylbicyclo[3.1.0]hexane (**18**)

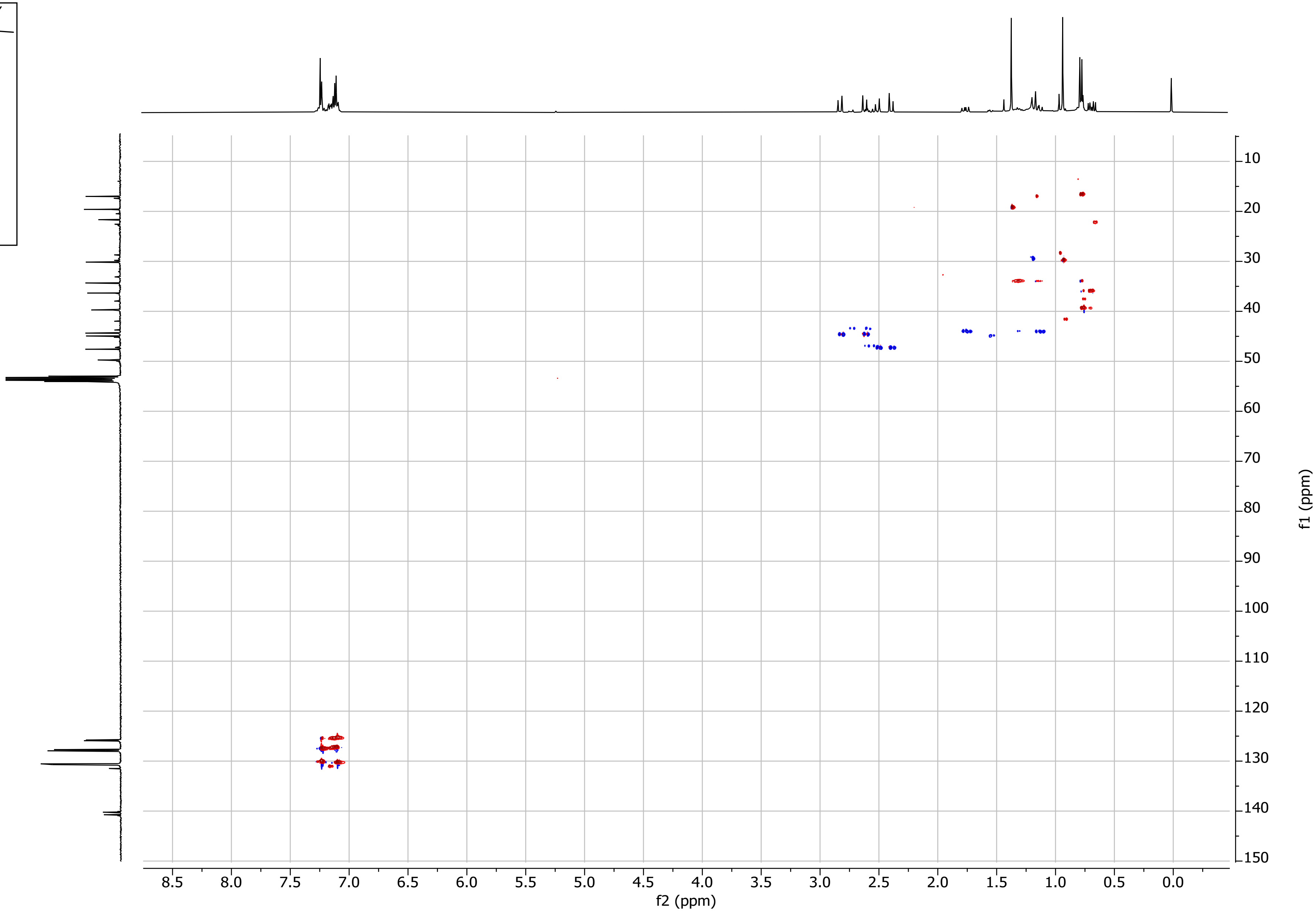


$C_{23}H_{28}$

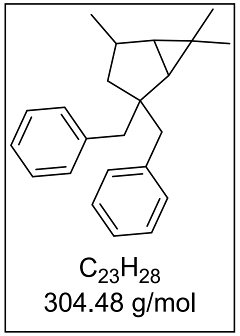
304.48 g/mol

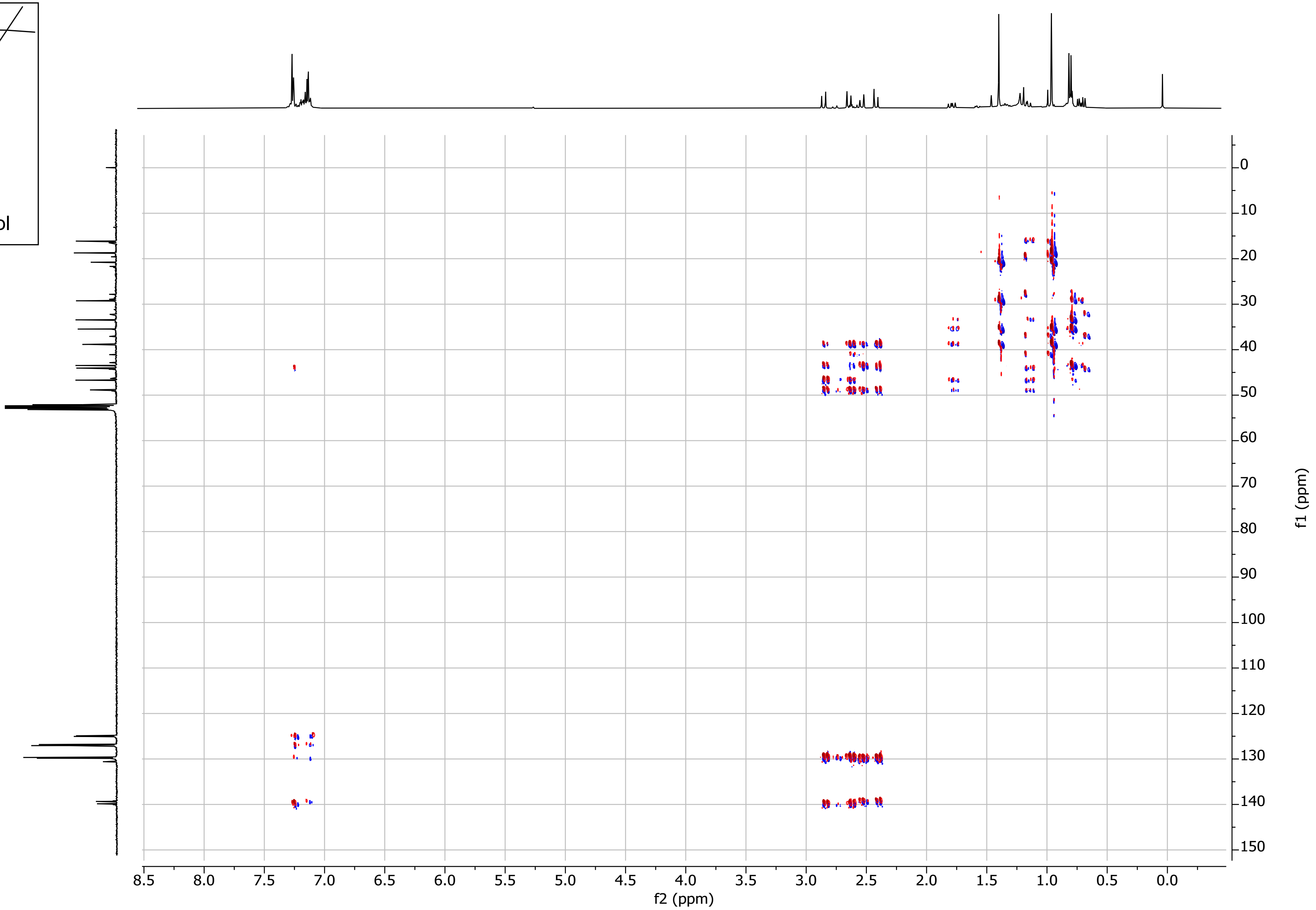
^{1}H, ^{13}C-HSQC (400 MHz, CD_2Cl_2)
2,2-Dibenzyl-4,6,6-trimethylbicyclo[3.1.0]hexane (**18**)


$C_{23}H_{28}$
304.48 g/mol

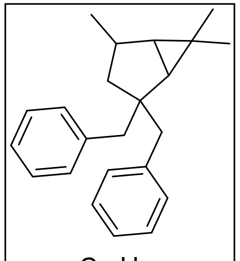


^{1}H, ^{13}C-HMBC (400 MHz, CD_2Cl_2)
2,2-Dibenzyl-4,6,6-trimethylbicyclo[3.1.0]hexane (**18**)





^1H, ^1H NOESY (400 MHz, CD_2Cl_2)
2,2-Dibenzyl-4,6,6-trimethylbicyclo[3.1.0]hexane (**18**)



$C_{23}H_{28}$
304.48 g/mol