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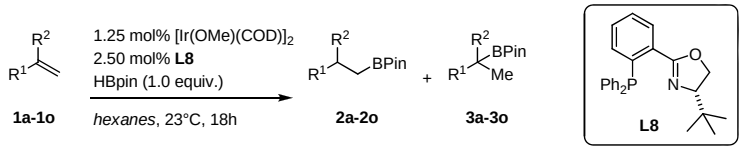
General Methods. All reactions were carried out under an inert atmosphere of argon or nitrogen using either two-manifold vacuum / inert gas lines or a M.Braun glove-box, unless otherwise noted. Solvents were dried over activated alumina columns and further degassed by three successive "freeze-pump-thaw" cycles when necessary. NMR spectra were recorded on ARX-300, AMX-400 and AMX-500 Bruker Avance spectrometers. ^{1}H and ^{13}C NMR chemical shifts are given in ppm relative to $SiMe_4$, with the solvent resonance used as internal reference. ^{31}P NMR chemical shifts are reported in ppm relative to H_3PO_4 (external standard). ^{19}F NMR chemical shifts are reported in ppm with absolute reference relative to ^{1}H. Infrared spectra were obtained on a Perkin-Elmer 1650 FT-IR spectrometer using neat samples on a diamond ATR Golden Gate sampler. Optical rotations were measured on a Perkin-Elmer 241 polarimeter equipped with a Na-lamp. The mass spectrometric data were obtained at the mass spectrometry facility of the University of Geneva (http://www.ms.unige.ch/sms). Chiral GC analyses were performed on either a HP6890 or a HP6850 gas chromatograph. HPLC analyses were performed on a Agilent 1100 Series. Commercial reagents were purchased from Aldrich, Fluka, Acros or Strem and used without further purification, unless otherwise noted. Liquid reagents were transferred with stainless steel syringes or cannula. Flash chromatography was performed using silica gel 60 (230–400 mesh ASTM) from Fluka.

$IrCl_3.(H_2O)x$ was generously provided by Johnson-Matthey. $[Ir(COD)(OMe)]_2$,[1] $[Ir(COD)(O\textit{i}\text{-Pr})]_2$,[1] $[Ir(COD)(O\textit{t}\text{-Bu})]_2$,[1] $[Ir(COD)(OPh)]_2$,[1] ligands **L7-L10**,[2] and DBpin[3] were prepared according to literature procedures. All 1,1-disubstituted olefins were either commercially available and used without any further purification (**1a**, **1c**) or were synthesized by Wittig olefination of the corresponding ketones following reported procedures (**1b**, **1d-o**).[4] Spectroscopic data were in good agreement with the literature.

General procedure for the iridium-catalyzed asymmetric hydroboration of terminal olefins

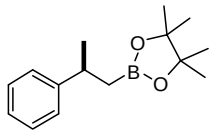


In a 10 mL Schlenck tube, ligand **L8** (9.7 mg; $2.5.10^{-5}$ mol) and $[Ir(OMe)(COD)]_2$ (8.4 mg; $2.5.10^{-5}$ mol) are dissolved in 2 mL of anhydrous hexanes and stirred for 10 minutes at room temperature. The slightly turbid orange solution is cooled to 0°C and 130 µL of α-methylstyrene (1.0 mmol) are slowly added. After 5 minutes, 150 µL of pinacolborane (1.0 mmol) are added drop-wise. The solution immediately turns yellow and becomes homogeneous. The ice bath is removed and the reaction stirred at room temperature. After 18 hours, the volatiles are evaporated* and the crude mixture is purified by column chromatography (SiO_2; Et_2O/cycloghexane (9:1)) to give a pale yellow oil.**

* NMR yields and regioselectivities were assessed before purification using an internal standard.
** **2d** solidifies upon standing in a -35°C freezer but the enantiomeric purity could not be improved by iterative recrystallization attempts.

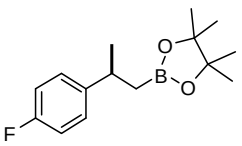
The enantiomeric excesses were determined after oxidation of the pinacolborane derivatives to the corresponding alcohols according to the protocol described for **5d** (vide infra). The absolute configuration was assigned by analogy with that of an authentic sample of 2-phenylpropanol, a racemic sample and the oxidation product of **2a** after an asymmetric catalytic experiment. The HPLC instrument used being not thermostated, in some instances, there is a time difference between the analysis of the racemate and the catalytic run. In such cases, a co-injection of both samples was performed to secure the analysis.

(*S*)-4,4,5,5-tetramethyl-2-(2-phenylpropyl)-1,3,2-dioxaborolane (2a)



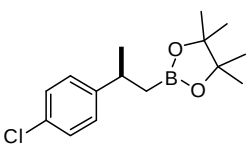
^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.22 (m, 4H), 7.20 – 7.10 (m, 1H), 3.06 (dd, J = 14.7, 7.3 Hz, 1H), 1.30 (d, J = 6.9 Hz, 3H), 1.19 – 1.11 (bm, 14H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.24, 128.23, 126.68, 125.74, 83.00, 35.88, 25.01, 24.82, 24.74, 21.30. **IR (neat)** ν 2977.3, 1365.8, 1342.3, 1319.9, 1143.2, 968.3, 846.4, 760.3, 698.4 cm^{-1}. **$[\alpha]_D^{23}$** (CH_2Cl_2, 1.0) -11.7. **EI HRMS** m/z $[M]^+$ $C_{15}H_{23}BO_2$ calculated: 246.1791; found: 246.1793.

(*S*)-2-(2-(4-fluorophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2b)



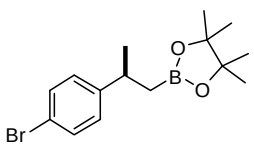
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.15 (m, 2H), 6.98 – 6.90 (m, 2H), 3.03 (m, 1H), 1.25 (d, J = 6.9 Hz, 3H), 1.15 (bs, 14H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 161.10 (d, J_{CF} = 242.7 Hz), 144.80 (d, J_{CF} = 3.3 Hz), 127.97 (d, J_{CF} = 7.5 Hz), 114.80 (d, J_{CF} = 20.8 Hz), 83.03, 35.19, 25.17, 24.75, 24.71, 21.24. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -118.04. **IR (neat)** ν 2977.9, 2927.4, 1509.3, 1365.2, 1321.4, 1221.9, 1143.1, 968.4, 846.9, 831.6 cm^{-1}. **$[\alpha]_D^{23}$** (CH_2Cl_2, 1.0) -9.0. **EI HRMS** m/z $[M]^+$ $C_{15}H_{22}BFO_2$ calculated: 264.1701; found: 264.1697.

(*S*)-2-(2-(4-chlorophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2c)



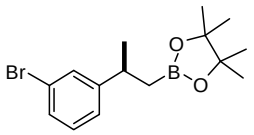
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 8.6 Hz, 2H), 7.16 (d, J = 8.5 Hz, 2H), 3.01 (m, 1H), 1.25 (d, J = 6.9 Hz, 3H), 1.15 (bs, 12H), 1.12 (bd, J = 7.8 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.66, 131.22, 128.24, 128.05, 82.97, 35.30, 24.75, 24.71, 21.19. **IR (neat)** ν 2977.8, 2927.9, 1492.4, 1365.1, 1320.7, 1143.0, 1093.0, 1012.6, 968.1, 846.7, 825.3 cm^{-1}. **$[\alpha]_D^{23}$** (CH_2Cl_2, 1.0) -17.9. **EI HRMS** m/z $[M]^+$ $C_{15}H_{22}BClO_2$ calculated: 280.1401; found: 280.1404.

(*S*)-2-(2-(4-bromophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2d)



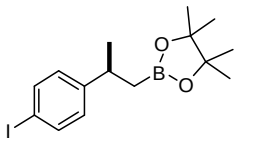
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 11.0 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 3.00 (m, 1H), 1.25 (d, J = 6.9 Hz, 3H), 1.16 (bs, 12H), 1.12 (bd, J = 7.8 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 148.21, 131.21, 128.50, 119.26, 83.08, 35.36, 24.79, 24.74, 21.10. **IR (neat)** ν 2977.0, 1488.7, 1364.3, 1320.3, 1142.5, 1008.9, 968.0, 846.6, 821.2 cm^{-1}. **$[\alpha]_D^{23}$** (CH_2Cl_2, 1.0) -18.4. **EI HRMS** m/z $[M]^+$ $C_{15}H_{22}BBrO_2$ calculated: 324.0896; found: 324.0897.

(*S*)-2-(2-(3-bromophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2e)



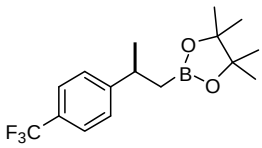
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.26 (dt, J = 7.5, 1.6 Hz, 1H), 7.13 (m, 2H), 3.00 (m, 1H), 1.26 (d, J = 6.9 Hz, 3H), 1.15 (s, 12H), 1.12 (d, J = 7.8 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 151.57, 130.00, 129.84, 128.78, 125.32, 122.26, 83.07, 35.66, 24.80, 24.76, 24.63, 21.33. **IR (neat)** ν 2977.9, 1478.1, 1365.6, 1319.6, 1143.1, 996.8, 968.2, 845.9, 779.5, 695.1 cm^{-1}. **$[\alpha]_D^{23}$** (CH_2Cl_2, 1.0) -11.5. **EI HRMS** m/z $[M]^+$ $C_{15}H_{22}BBrO_2$ calculated: 324.0896; found: 324.0890

(*S*)-2-(2-(4-iodophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2f)



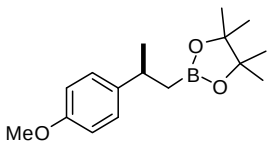
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.3 Hz, 2H), 6.99 (d, J = 8.4 Hz, 2H), 2.98 (m, 1H), 1.24 (d, J = 6.9 Hz, 3H), 1.16 (bs, 12H), 1.11 (bd, J = 8.0 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 148.92, 137.22, 128.90, 90.68, 83.08, 35.43, 24.85, 24.80, 21.12. **IR (neat)** ν 2975.8, 2924.9, 1484.9, 1364.3, 1320.2, 1142.5, 1004.4, 967.9, 846.6, 817.6 cm^{-1}. **$[\alpha]_D^{23}$** (CH_2Cl_2, 1.0) -7.7. **EI HRMS** m/z $[M]^+$ $C_{15}H_{22}BIO_2$ calculated: 372.0758; found: 372.0756

(*S*)-4,4,5,5-tetramethyl-2-(2-(4-(trifluoromethyl)phenyl)propyl)-1,3,2-dioxaborolane (2g)



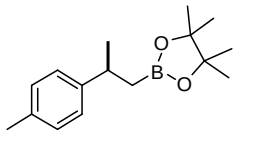
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 3.10 (m, 1H), 1.29 (d, J = 6.9 Hz, 3H), 1.15 (s, 14H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 153.32, 128.05, (q, J = 3.7 Hz), 127.00, 125.12 (q, J = 32.2 Hz), 83.12, 35.76, 24.67, 24.61, 24.58, 21.11. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.26. **IR (neat)** ν 2979.02929.3, 1368.1, 1322.0, 1162.7, 1143.1, 1120.9, 1068.0, 1015.7, 968.1, 837.8, 734.9 cm^{-1}. **$[\alpha]_D^{23}$** (CH_2Cl_2, 1.0) -11.0. **EI HRMS** m/z $[M]^+$ $C_{16}H_{22}BF_3O_2$ calculated: 314.1665; found: 314.1664.

(*S*)-2-(2-(4-methoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2h)



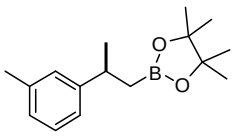
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, J = 8.5 Hz, 2H), 6.83 (d, J = 8.6 Hz, 2H), 3.78 (s, 3H), 3.01 (m, 1H), 1.26 (d, J = 6.9 Hz, 3H), 1.18 (s, 14H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.62, 141.48, 127.50, 113.56, 83.00, 55.26, 35.03, 25.20, 24.82, 24.75, 21.42. **IR (neat)** ν 2976.9, 1611.7, 1512.0, 1364.2, 1321.4, 1244.4, 1177.9, 1142.9, 828.0 cm^{-1}. **$[\alpha]_D^{23}$** (CH_2Cl_2, 1.0) -11.2. **EI HRMS** m/z $[M]^+$ $C_{16}H_{25}BO_3$ calculated: 276.1897; found: 276.1897.

(*S*)-4,4,5,5-tetramethyl-2-(2-p-tolylpropyl)-1,3,2-dioxaborolane (2i)



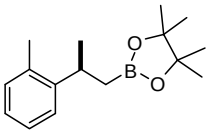
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 3.13 – 3.00 (m, 1H), 2.35 (s, 3H), 1.32 (d, J = 6.9 Hz, 3H), 1.23 (bs, 14H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.35, 135.04, 128.93, 126.52, 83.01, 35.43, 25.01, 24.87, 24.77, 21.44, 21.06. **IR (neat)** ν 3294.2, 2924.6, 2856.0, 1653.9, 1543.3, 1515.0, 1365.7, 1321.1, 1305.3, 1143.8, 1108.1, 968.8, 847.0, 813.8 cm^{-1}.**$[\alpha]_D^{23}$** (CH_2Cl_2, 1.0) -9.2**. EI HRMS** m/z $[M]^+$ $C_{16}H_{25}BO_2$ calculated: 260.1948; found: 260.1946.

(*S*)-4,4,5,5-tetramethyl-2-(2-m-tolylpropyl)-1,3,2-dioxaborolane (2j)



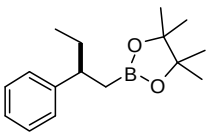
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (t, J = 7.5 Hz, 1H), 7.09 (d, J = 8.8 Hz, 2H), 7.01 (d, J = 7.4 Hz, 1H), 3.05 (m, 1H), 2.36 (s, 3H), 1.32 (d, J = 6.9 Hz, 3H), 1.21 (s, 14H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.22, 137.57, 128.17, 127.54, 126.47, 123.66, 83.02, 35.78, 24.89, 24.84, 24.75, 21.55. **IR (neat)** ν 2977.6, 2925.5, 1363.8, 1320.2, 1143.4, 968.5, 846.9, 782.1, 702.9 cm^{-1}. **$[\alpha]_D^{23}$** (CH_2Cl_2, 1.0) -8.2. **EI HRMS** m/z $[M]^+$ $C_{16}H_{25}BO_2$ calculated: 260.1948; found: 260.1949.

(*S*)-4,4,5,5-tetramethyl-2-(2-o-tolylpropyl)-1,3,2-dioxaborolane (2k)



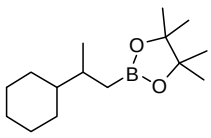
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 6.9 Hz, 1H), 7.18 (td, J = 7.7, 1.5 Hz, 1H), 7.08 (ddd, J = 11.4, 8.6, 3.8 Hz, 2H), 3.37 – 3.25 (m, 1H), 2.40 (s, 3H), 1.28 – 1.24 (d, J = 6.9 Hz, 3H), 1.16 (bs, 14H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.22, 135.01, 130.02, 126.16, 125.42, 125.23, 82.95, 30.71, 24.75, 24.66, 24.37, 20.36, 19.62. **IR (neat)** ν 2977.1, 2925.0, 1363.6, 1319.1, 1143.6, 968.4, 877.0, 846.4, 757.6, 726.7 cm^{-1}. **$[\alpha]_D^{23}$** (CH_2Cl_2, 1.0) 0.0. **EI HRMS** m/z $[M]^+$ $C_{16}H_{25}BO_2$ calculated: 260.1947; found: 260.1948.

(*S*)-4,4,5,5-tetramethyl-2-(2-phenylbutyl)-1,3,2-dioxaborolane (2l)



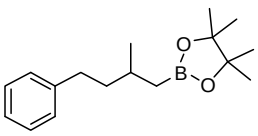
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 2H), 7.21 (m, 2H), 7.15 (t, J = 7.1 Hz, 1H), 2.83 – 2.69 (m, 1H), 1.73 – 1.54 (m, 2H), 1.30 – 1.14 (m, 3H), 1.12 (d, J = 6.5 Hz, 12H), 0.80 (t, J = 7.4 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.27, 128.05, 127.53, 125.74, 82.90, 43.33, 32.34, 24.70, 19.35, 12.29. **IR (neat)** ν2976.7, 1363.7, 1320.1, 1143.5, 966.8, 883.8, 847.0, 698.5 cm^{-1}. **$[\alpha]_D^{23}$** (CH_2Cl_2, 1.0) -4.2. **EI HRMS** m/z $[M]^+$ $C_{16}H_{25}BO_2$ calculated: 260.1948; found: 260.1946.

2-(2-cyclohexylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2n)



^{1}H NMR (400 MHz, $CDCl_3$) δ 1.73 – 1.66 (m, 3H), 1.59 (dd, J = 18.1, 10.2 Hz, 4H), 1.23 (bs, 12H), 1.20 – 1.03 (m, 4H), 1.00 – 0.88 (m, 2H), 0.85 (d, J = 6.7 Hz, 3H), 0.81 (d, J = 5.0 Hz, 1H), 0.61 (dd, J = 15.3, 9.6 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 82.79, 44.81, 34.53, 30.33, 29.18, 26.90, 26.84, 24.92, 24.72, 19.15, 16.57. **IR (neat)** ν 2977.5, 2922.8, 2851.6, 1368.7, 1312.3, 1144.8, 969.0, 847.0 cm^{-1}. **$[\alpha]_D^{23}$** (CH_2Cl_2, 1.0) 0.0. **EI HRMS** m/z $[M]^+$ $C_{15}H_{29}BO_2$ calculated: 252.2260; found: 252.2264.

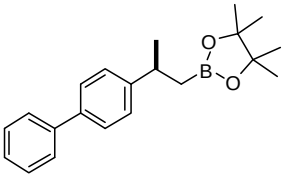
4,4,5,5-tetramethyl-2-(2-methyl-4-phenylbutyl)-1,3,2-dioxaborolane (2o)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 2H), 7.22 (dd, J = 14.0, 7.2 Hz, 3H), 2.76 – 2.59 (m, 2H), 1.92 – 1.76 (m, 1H), 1.73 – 1.52 (m, 2H), 1.30 (s, 12H), 1.06 (d, J = 6.6 Hz, 3H), 1.01 – 0.93 (m, 1H), 0.79 (dd, J = 15.4, 8.3 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.23, 128.43, 128.31, 125.56, 82.93, 41.66, 33.89, 29.48, 24.97, 24.91, 22.39, 19.87. **IR (neat)** ν 2977.6, 2926.4, 1369.1, 1313.1, 1142.7, 969.5, 846.8, 734.0, 697.6 cm^{-1}. **$[\alpha]_D^{23}$** (CH_2Cl_2, 1.0) 0.0. **EI HRMS** m/z $[M]^+$ $C_{17}H_{27}BO_2$ calculated: 274.2104; found: 274.2103.

Synthesis of (*S*)-2-(2-(biphenyl-4-yl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4d)

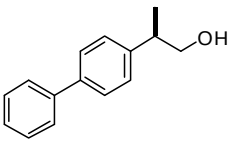
In a 25-mL Young-valved Schlenck, phenylboronic acid (558 mg, 4.58 mmol), K_3PO_4 (1.800 g, 7.83 mmol), $Pd(OAc)_2$ (59 mg, $2.61.10^{-4}$ mol), dppf (173 mg, $3.13.10^{-4}$ mmol) and **2**-(2-(4-bromophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2d**) (850 mg, 2.61 mmol) are dissolved in 10 mL of THF. The tube is sealed and the reaction vigorously stirred at 80°C for 48h. The reaction mixture is cooled down to room temperature, quenched with 3.0 mL of a saturated NH_4Cl solution, extracted with EtOAc (3 x 2 mL). The organic phases are dried over $MgSO_4$ and concentrated under vacuum. Purification by silica gel chromatography (SiO_2; Et_2O/cycloghexane (40:1)) yields a pale yellow oil (550 mg, 1.71 mmol, 65% yield).



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.59 (m, 2H), 7.54 (d, J = 8.2 Hz, 2H), 7.45 (dd, J = 10.5, 4.7 Hz, 2H), 7.35 (d, J = 8.1 Hz, 3H), 3.19 – 3.07 (m, 1H), 1.35 (d, J = 6.9 Hz, 3H), 1.20 (s, 14H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 148.49, 141.36, 138.73, 134.89, 131.38, 128.80, 127.83, 127.19, 127.05, 83.11, 35.61, 25.00, 24.82, 21.37. **IR (neat)** ν 2977.0, 2924.6, 1485.9, 1360.8, 1321.0, 1142.7, 967.8, 835.5, 764.1, 732.4, 697.0 cm^{-1}. **EIS HRMS** m/z $[M+H]^+$ $C_{21}H_{28}BO_2$ calculated: 323.2169; found: 323.2182.

Synthesis of (*S*)-2-(biphenyl-4-yl)propan-1-ol (5d)

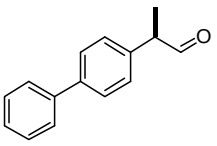
2-(2-(biphenyl-4-yl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4d**) (80 mg, $2.48.10^{-4}$ mol) are dissolved in 2 mL of dry Et_2O and placed at 0°C. NaOH (3N, 2.0 mL) and H_2O_2 (30%, 1.5 mL) are successively added. The ice bath is removed and the solution stirred at room temperature. After 2 hours, the solution is extrated twice with Et_2O (2 mL), dried over $MgSO_4$. After evaporation of the volatiles, the crude mixture is purified by column chromatography (SiO_2; Et_2O/cycloghexane (4:1)) to yield 50 mg of **5d** ($2.36.10^{-4}$ mol, 95% yield).



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (m, 4H), 7.47 (dd, J = 7.6 Hz, 2H), 7.37 (m, 3H), 3.82 – 3.70 (m, 2H), 3.12 – 2.96 (m, 1H), 1.54 (s, 1H), 1.34 (d, J = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.84, 140.97, 139.70, 128.83, 127.98, 127.44, 127.10, 109.00, 68.74, 42.18, 17.68. **IR (neat)** ν 3296.3, 2930.5, 2853.3, 1487.6, 1408.9, 1024.7, 1013.53, 1002.6, 837.0, 762.5, 727.7, 688 cm^{-1}. **ESI HRMS** m/z $[M+NH_4]^+$ $C_{15}H_{20}NO_2$ calculated: 230.1542; found: 230.1539

Synthesis of (*S*)-2-(biphenyl-4-yl)propanal (6d)

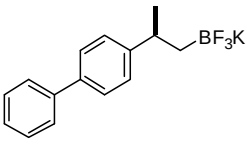
In a 5 mL round bottom flask, 30 mg of 2-(biphenyl-4-yl)propan-1-ol (**5d**) ($1.40.10^{-4}$ mol) are dissolved in 1.5 mL of dry CH_2Cl_2. To this solution, 100 mg of Dess-Martin periodinane ($2.40.10^{-4}$ mol) are added in one portion. The reaction is stirred at room temperature for 30 minutes and then quenched with 1.0 mL of a 1/1 (v:v) $Na_2S_2O_3$ (sat.)/$NaHCO_3$ (sat.) solution and stirred for an additional 10 minutes. 5 mL of CH2Cl2 are subsequently added and the mixture is filtered through a pad of Celite. The organic phases are dried over $MgSO_4$ and, after concentration under vacuum; the mixture is purified by pipette column chromatography (Et_2O/cycloghexane (4:1)) to yield 29 mg of a colorless oil ($1.38.10^{-4}$ mol, 98% yield).



^{1}H NMR (400 MHz, $CDCl_3$) δ 9.75 (s, 1H), 7.67 – 7.58 (m, 4H), 7.47 (t, J = 6.8 Hz, 2H), 7.41 – 7.35 (m, 1H), 7.31 (d, J = 8.2 Hz, 2H), 3.71 (q, J = 7.4 Hz, 1H), 1.51 (d, J = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 201.06, 140.59, 136.71, 128.89, 128.81, 127.87, 127.50, 127.13, 77.41, 77.09, 76.77, 52.73, 14.68, 1.10. **IR (neat)** ν 2971.4, 1715.9, 1485.9, 1260.4, 1031.6, 1015.4, 1005.1, 836.1, 763.2, 727.4, 689.9 cm^{-1}. **ESI (negative) HRMS** m/z $[M-H]^-$ $C_{15}H_{13}O_2$ calculated: 209.0974; found: 209.0971.

Synthesis of potassium (*S*)-(2-(biphenyl-4-yl)propyl)trifluoroborate (7d)

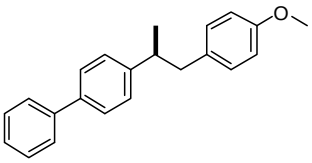
This compound was prepared according to the very detailed procedure reported by V. K. Aggarwal and coworkers.[5] The reaction was performed on a 1.0 mmol scale, 5 evaporation-dissolution cycles were necessary to azeotrope off the residual pinacol formed. **7d** was obtained quantitatively as beige solid.



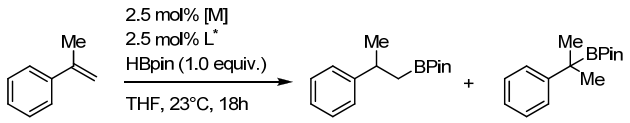
^{1}H NMR (400 MHz, CD_3CN) δ 7.62 (d, J = 8.2 Hz, 1H), 7.50 (d, J = 8.2 Hz, 1H), 7.43 (t, J = 7.5 Hz, 1H), 7.32 (d, J = 8.1 Hz, 1H), 2.91 – 2.74 (m, 1H), 1.21 (d, J = 6.9 Hz, 1H), 0.59 – 0.30 (m, 1H). **^{19}F NMR (376 MHz, CD_3CN)** δ -137.98. **IR (neat)** ν 2892.6, 1703.0, 1486.0, 1306.2, 1218.2, 1076.5, 1056.1, 911.6, 837.8, 763.9, 694.0 cm^{-1}. **ESI (negative) HRMS** m/z $[M]^-$ $C_{15}H_{15}BF_3$ calculated: 263.1235; found: 263.1224.

Synthesis of (*S*)-4-(1-(4-methoxyphenyl)propan-2-yl)biphenyl (8d)

In a 25-mL Young-valved Schlenck, K_2CO_3 (137 mg, 1.0 mmol), $Pd(OAc)_2$ (3.7 mg, $1.65.10^{-5}$ mol), RuPhos (15.4 mg, $3.30.10^{-5}$ mmol) and potassium (2-(biphenyl-4-yl)propyl)trifluoroborate (**7d**) (100 mg, $3.30.10^{-4}$ mol) are dissolved in 1 mL of toluene and 0.13 mL of water were added. 4-bromoanisole (42 µL, $3.30.10^{-4}$ mol) is added next. The tube is sealed and the reaction vigorously stirred at 80°C for 24h. The reaction mixture is cooled down to room temperature, quenched with 1.5 mL of a 1/1 (v:v) $Na_2S_2O_3$ (sat.)/$NaHCO_3$ (sat.) solution, extracted with EtOAc (3 x 2 mL). The organic phases are dried over $MgSO_4$ and concentrated under vacuum. Purification by silica gel chromatography (SiO_2; Et_2O/cycloghexane (80:1)) yields a white fluffy solid (70 mg, $2.30.10^{-4}$ mol, 70% yield).

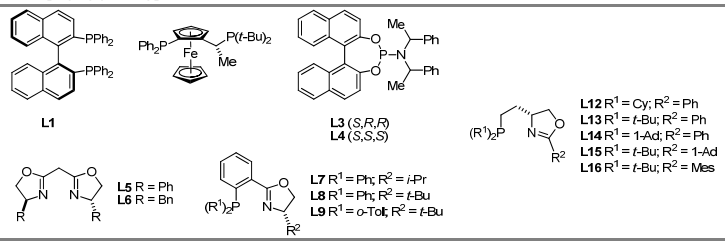


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.59 (m, 2H), 7.57 – 7.52 (m, 2H), 7.46 (t, J = 7.6 Hz, 2H), 7.35 (t, J = 7.4 Hz, 1H), 7.31 – 7.25 (m, 2H), 7.05 (d, J = 8.6 Hz, 2H), 6.82 (d, J = 8.6 Hz, 2H), 3.80 (s, 3H), 3.08 – 2.98 (m, 1H), 2.95 (dd, J = 13.4, 6.4 Hz, 1H), 2.77 (dd, J = 13.3, 8.2 Hz, 1H), 1.29 (d, J = 6.8 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.91, 146.27, 141.06, 138.93, 132.84, 130.12, 128.76, 128.22, 127.54, 127.04 (2C), 113.56, 77.40, 77.08, 76.77, 55.26, 44.15, 41.74, 21.14. **IR (neat)** ν 2956.2, 2903.9, 1608.7, 1509.5, 1487.7, 1452.2, 1246.4, 1176.6, 1111.7, 1035.8, 831.9, 753.7, 725.6, 690.2 cm^{-1}. **ESI HRMS** m/z $[M+NH_4]^+$ $C_{22}H_{26}NO$ calculated: 320.2004; found: 320.2008.

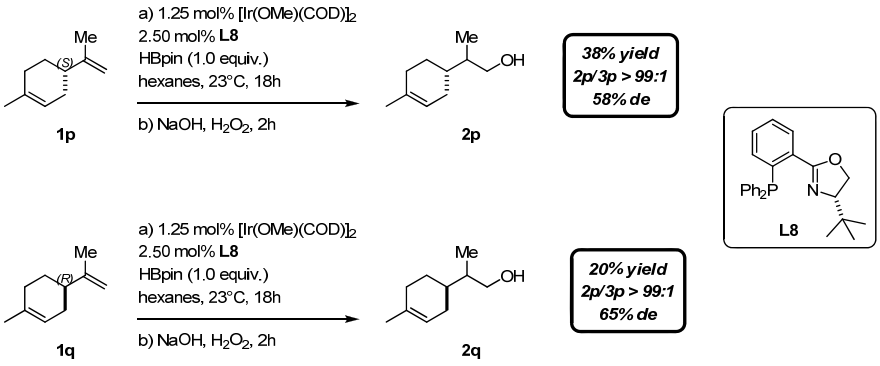


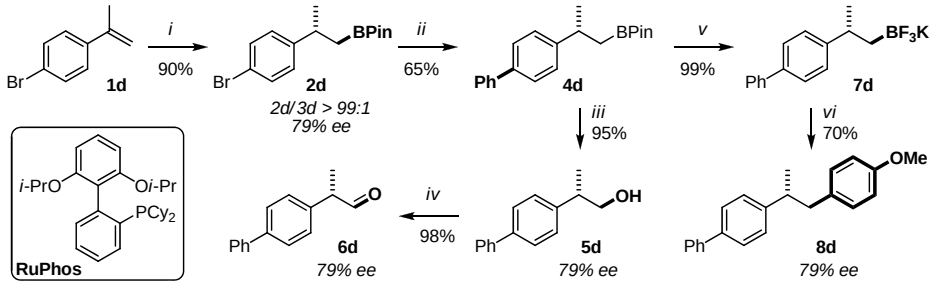
1a **2a** **3a**

Entry	L*	Metal precursor	**2a/3a**[b]	Yield [%][b]	ee [%][c]
1	**L1**	$[Ir(Cl)(COD)]_2$	*nd*	<5	*nd.*
2	**L2**	$[Ir(Cl)(COD)]_2$	*nd*	<5	*nd.*
3	**L3**	$[Ir(Cl)(COD)]_2$	>99:1	75	<5
4	**L4**	$[Ir(Cl)(COD)]_2$	>99:1	>99	<5
5	**L6**	$[[Ir(Cl)(COD)]_2$	>99:1	99	<5
6	**L7**	$[Ir(Cl)(COD)]_2$	>99:1	89	32 (*S*)
7	**L8**	**$[Ir(Cl)(COD)]_2$**	**>99:1**	**95**	**48 (*S*)**
8	**L9**	$[Ir(Cl)(COD)]_2$	>99:1	55	6 (*S*)
9	**L8**	$[Rh(Cl)(COD)]_2$	90:10	90	<5
10	**L8**	$[Ir(COD)_2]BAr_F$	*nd*	*nd*	*nd*[d]
11	**L12**	$[Ir(Cl)(COD)]_2$	>99:1	>99	9 (*S*)
12	**L13**	$[Ir(Cl)(COD)]_2$	>99:1	90	40 (*S*)
13	**L14**	$[Ir(Cl)(COD)]_2$	>99:1	50	46
14	**L15**	$[Ir(Cl)(COD)]_2$	>99:1	53	<5
15	**L16**	$[Ir(Cl)(COD)]_2$	>99:1	54	<5



Diastereoselective [hydroboration / oxidation] sequence of (*S*)- and (*R*)-limonene under optimized reaction conditions.





Scheme 1 *i*) see Table 2 entry 4 (1.0 g scale); *ii*) $Pd(OAc)_2$ (10 mol%), dppf (12 mol%), $PhB(OH)_2$ (1.5 equiv.), K_3PO_4 (3.0 equiv.), THF, 80°C, 48 h; *iii*) NaOH, H_2O_2, 23°C, 2 h; *iv*) DMP (1.7 equiv.) CH_2Cl_2, 23°C, 20 min.; *v*) KHF_2, H_2O:MeOH, 23°C, 30 min.; *vi*) $Pd(OAc)_2$ (5 mol%), RuPhos (10 mol%), 4-bromoanisole (1.0 equiv.), K_2CO_3 (3.0 equiv.), Toluene:H_2O (10:1), 80°C, 24 h.

References

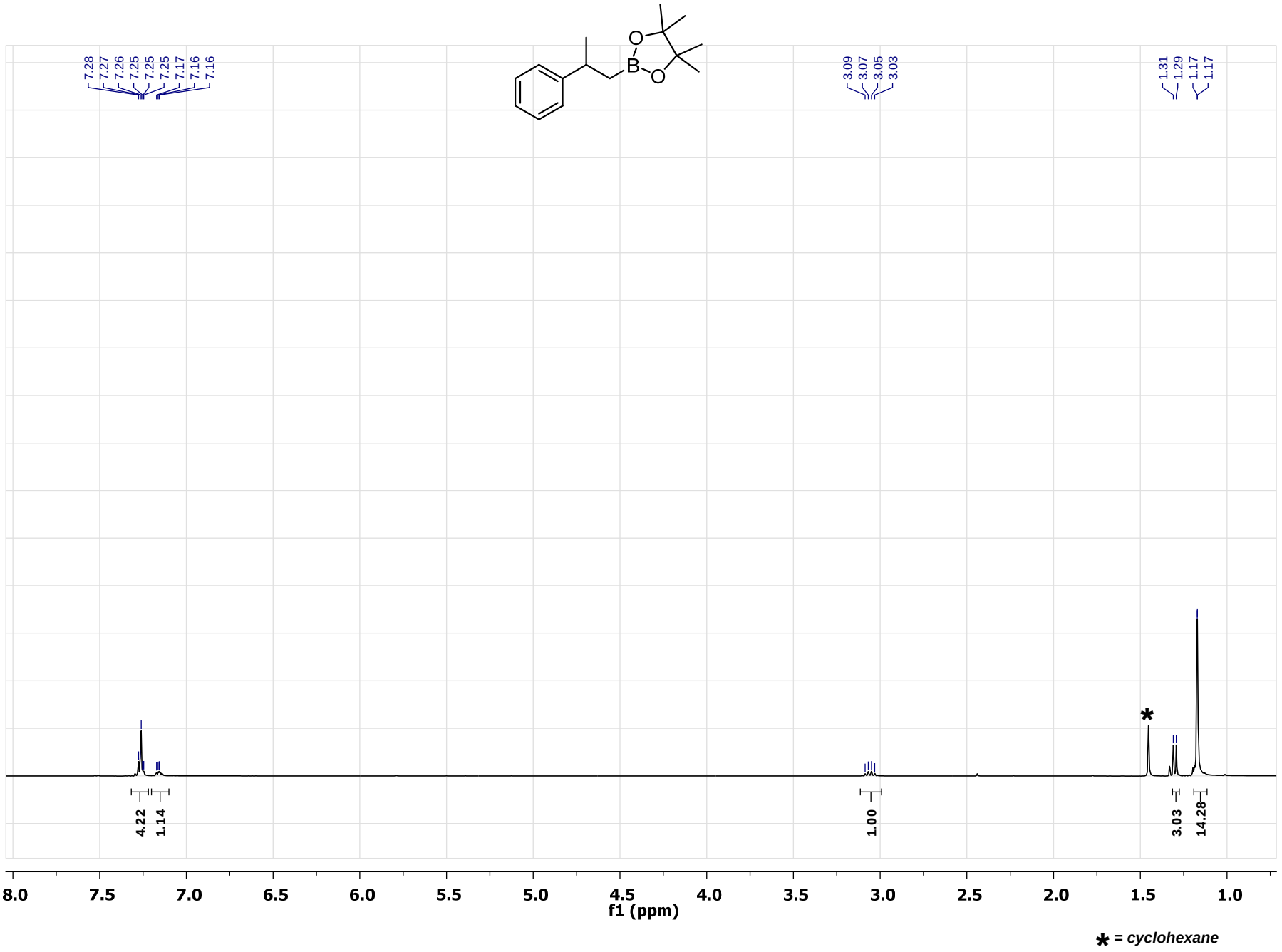
[1] L. M. Green, D. W. Meek, *Organometallics* **1989**, *8*, 659-666.

[2] M. R. Krout, J. T. Mohr, B. M. Stoltz, *Org. Synth.* **2009**, *86*, 181-193.

[3] P. L. Callaghan, R. Fernandez-Pacheco, N. Jasim, S. Lachaize, T. B. Marder, R. N. Perutz, E. Rivalta, S. Sabo-Etienne, *Chem. Commun.* **2004**, 242-243.

[4] (a) S. H. Pine, G. S. Shen, H. Hoang, *Synthesis* **1991**, 165-166; (b) S.-i. Ohsugi, K. Nishide, M. Node, *Tetrahedron* **2003**, *59*, 1859-1871.

[5] V. Bagutski, A. Ros, V. K. Aggarwal, *Tetrahedron* **2009**, *65*, 9956-9960.



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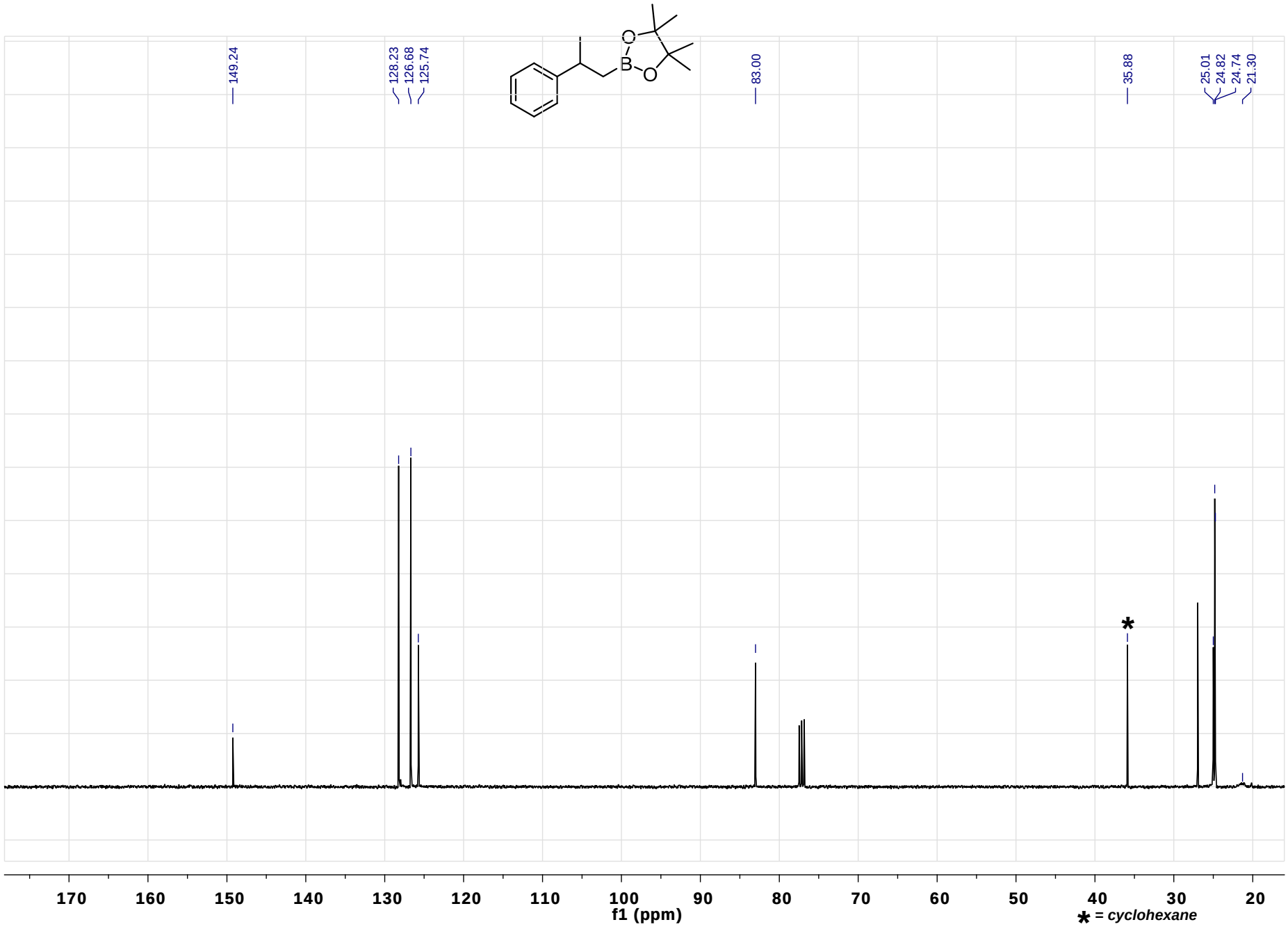
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24.74
21.30
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B
O
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140
130
120
110
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90
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50
40
30
20
f1 (ppm)
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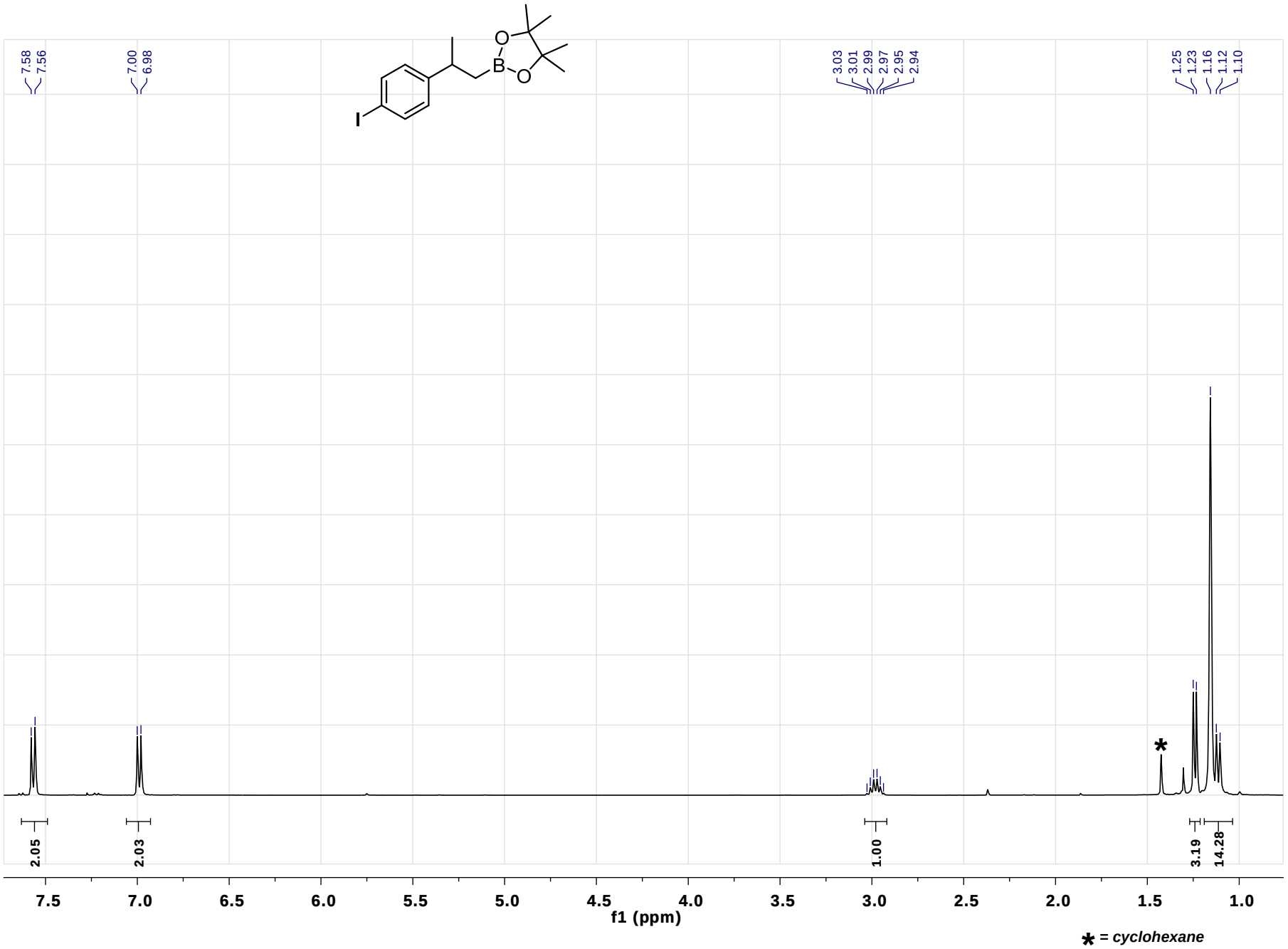
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2.94
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1.12
1.10
O
B
O
I
*
2.05
2.03
1.00
3.19
14.28
7.5
7.0
6.5
6.0
5.5
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4.0
3.5
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1.5
1.0
f1 (ppm)
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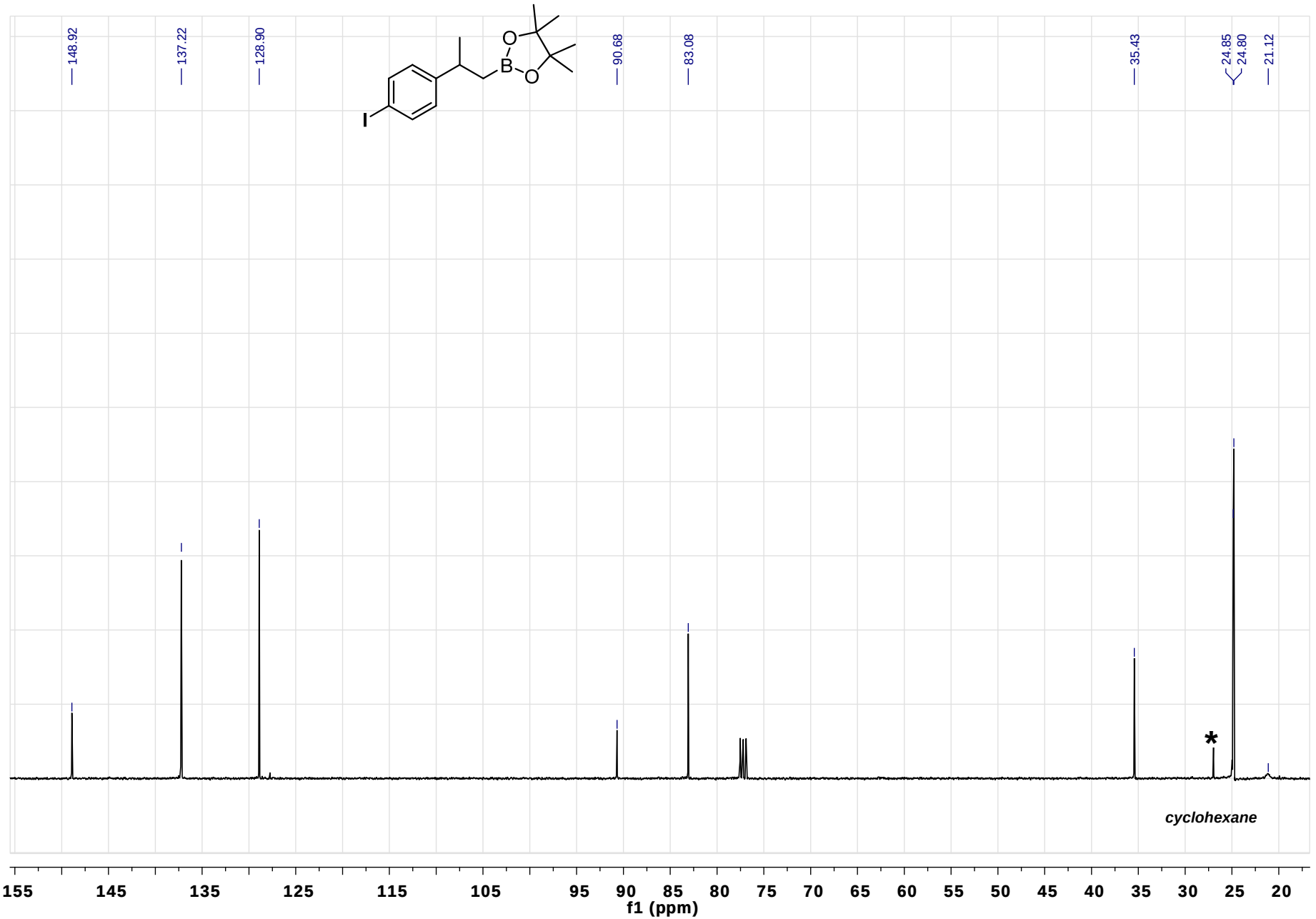
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B
O
I
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135
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45
40
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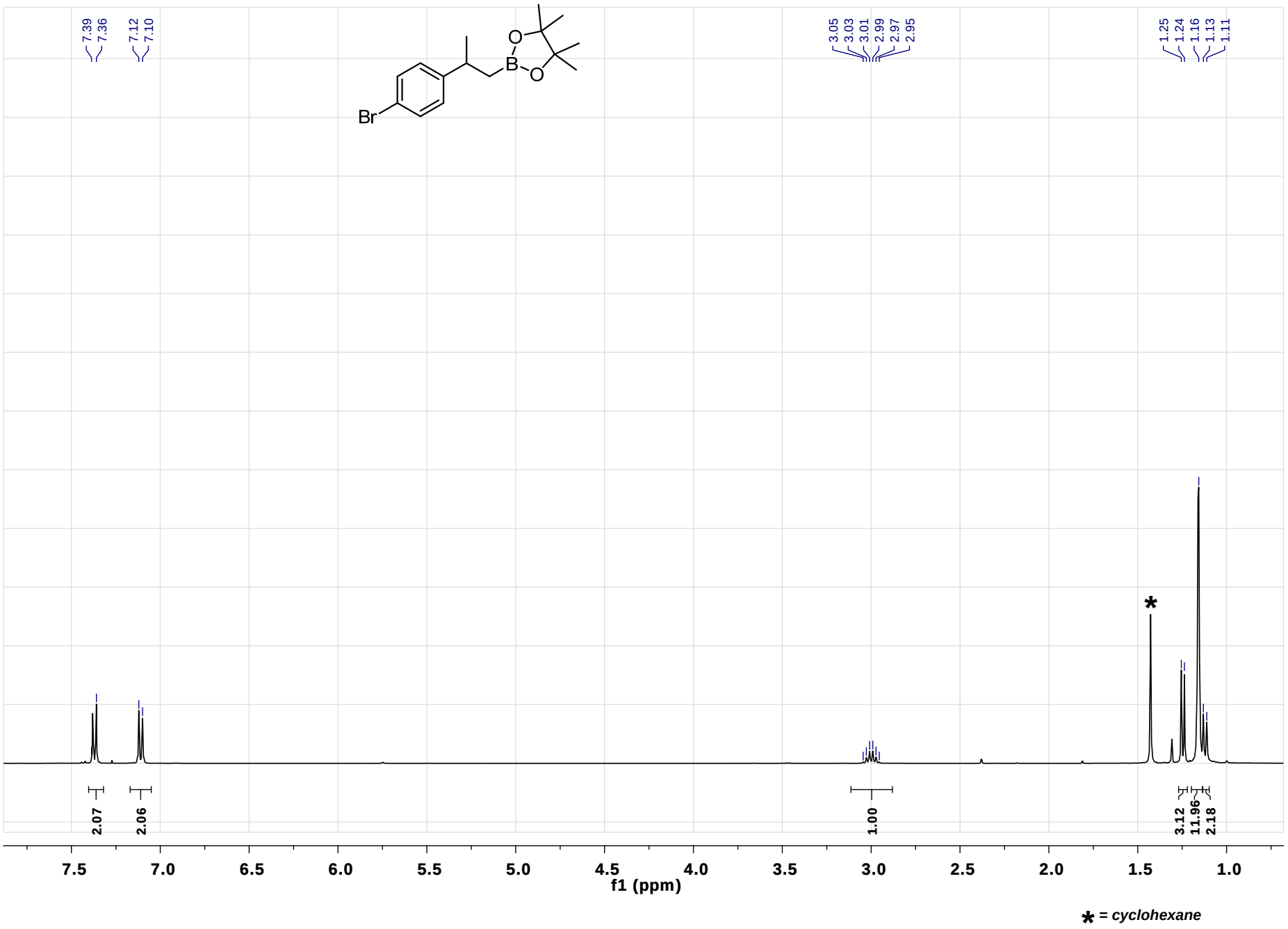
30
25
20
f1 (ppm)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3.03
3.01
2.99
2.97
2.95
1.25
1.24
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1.13
1.11
Br
O
B
O
*
2.07
2.06
1.00
3.12
11.96
2.18
7.5
7.0
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6.0
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1.5
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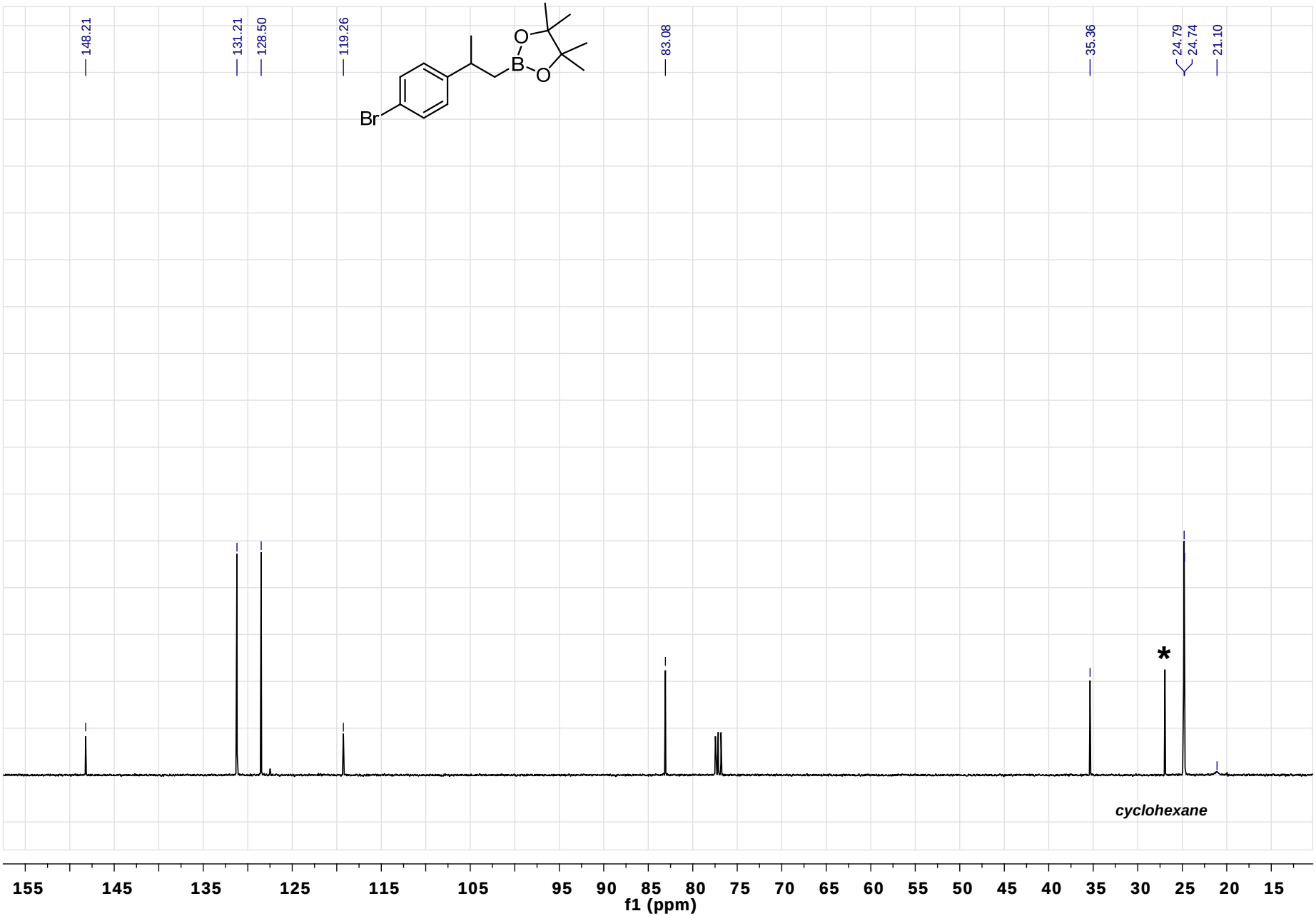
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145
135
125
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60
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40
35
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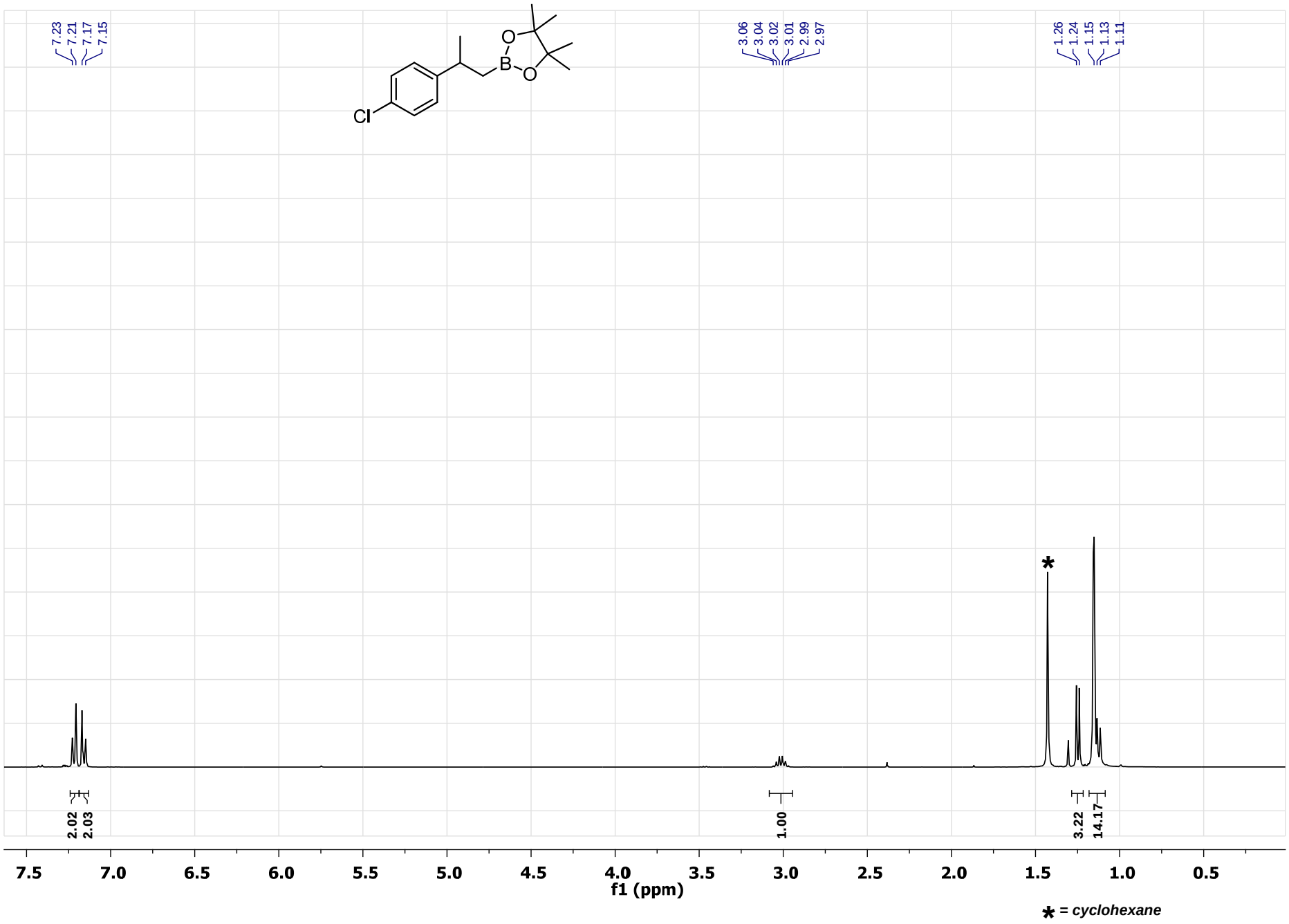
f1 (ppm)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1.13
1.11
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O
B
O
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2.03
1.00
3.22
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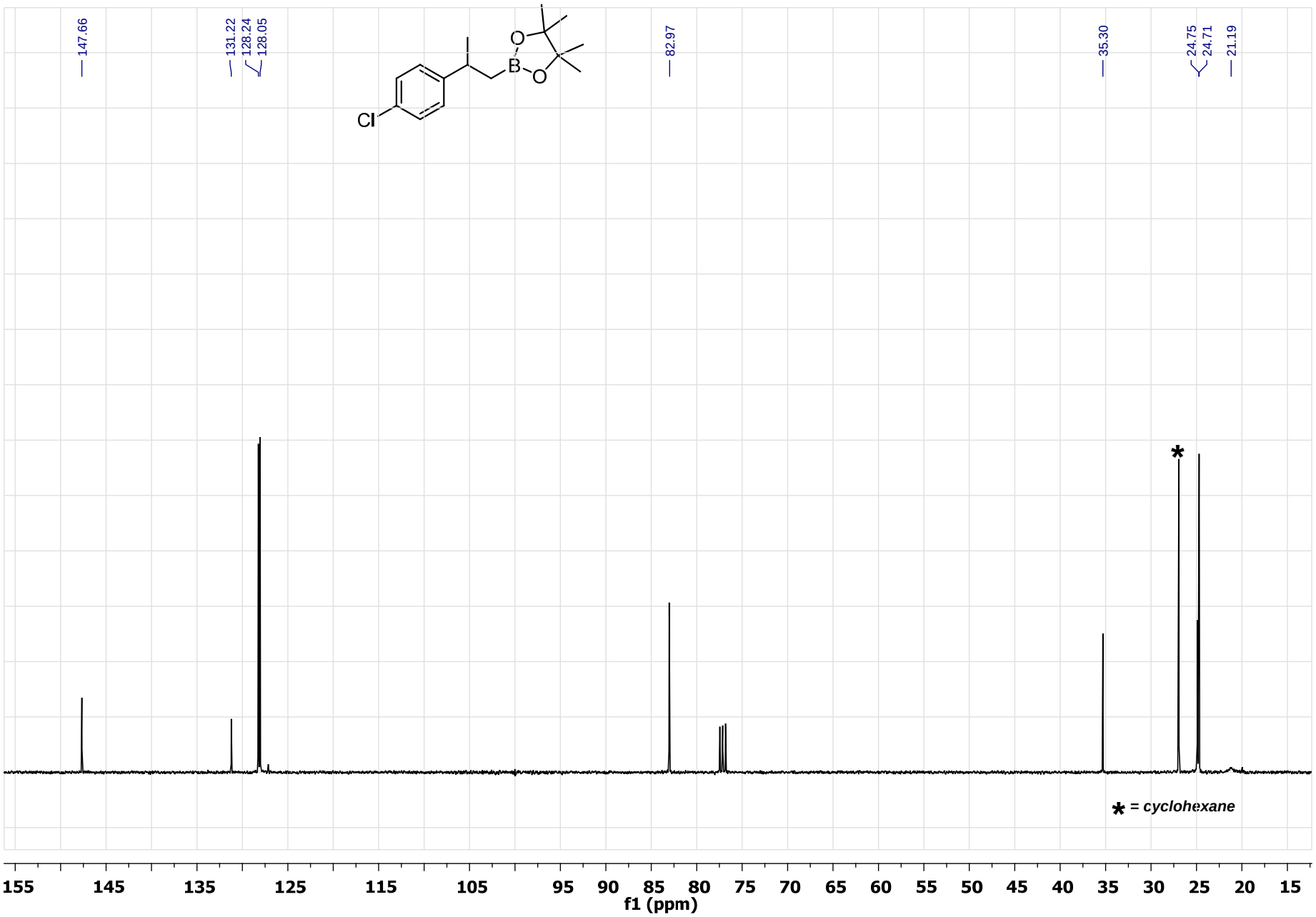
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135
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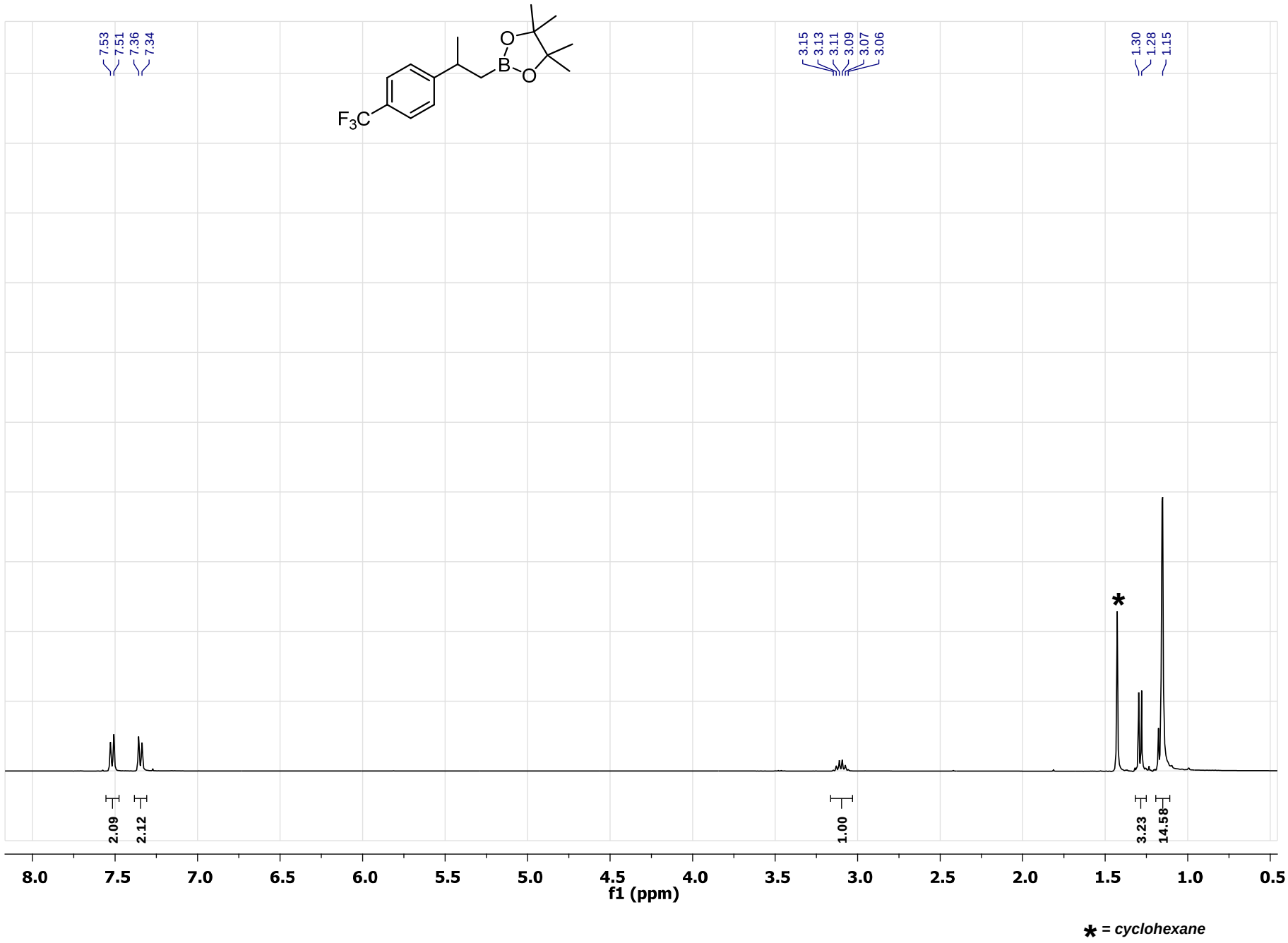
f1 (ppm)



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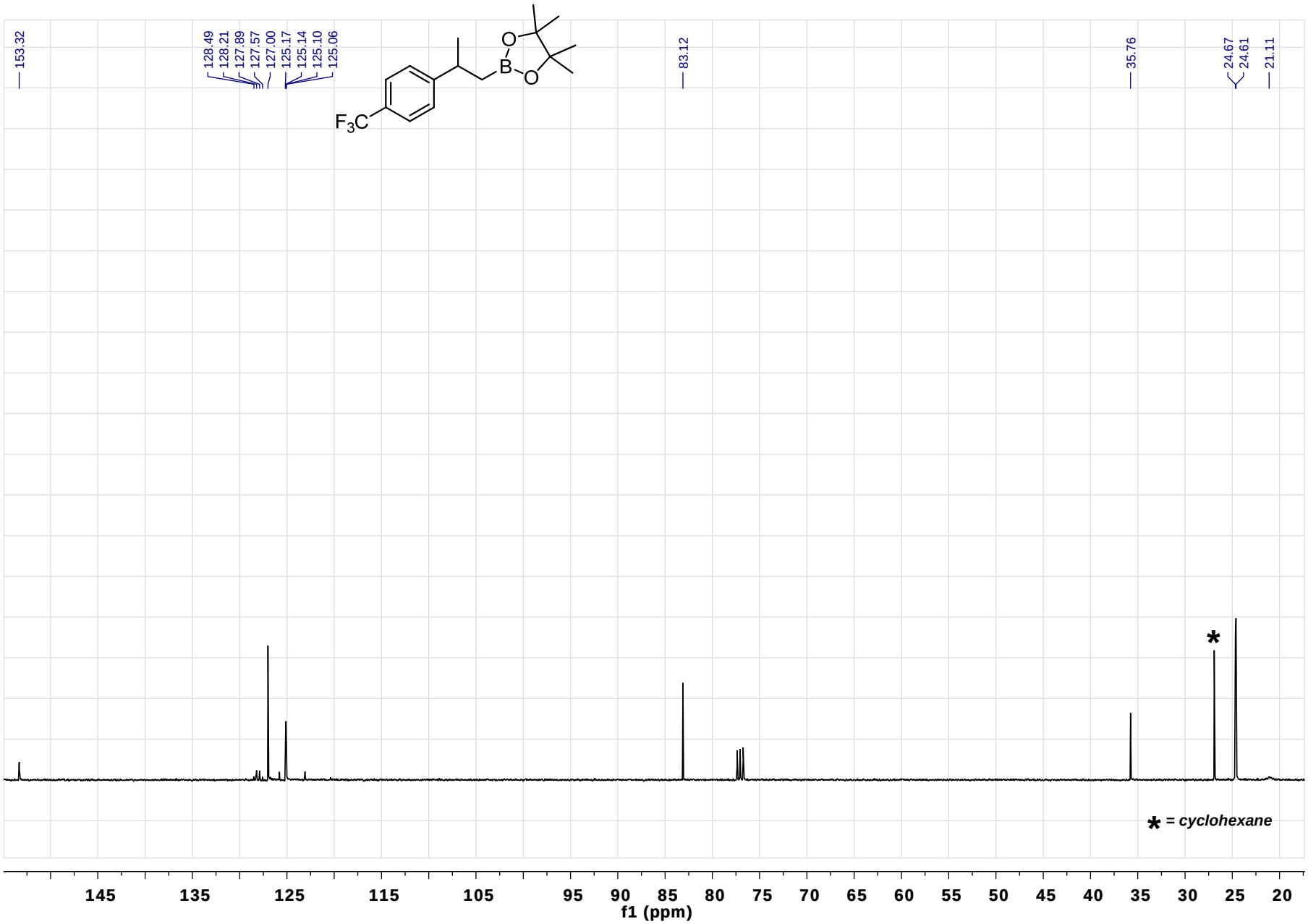
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24.61
21.11
F3C
O
B
O
*
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135
125
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45
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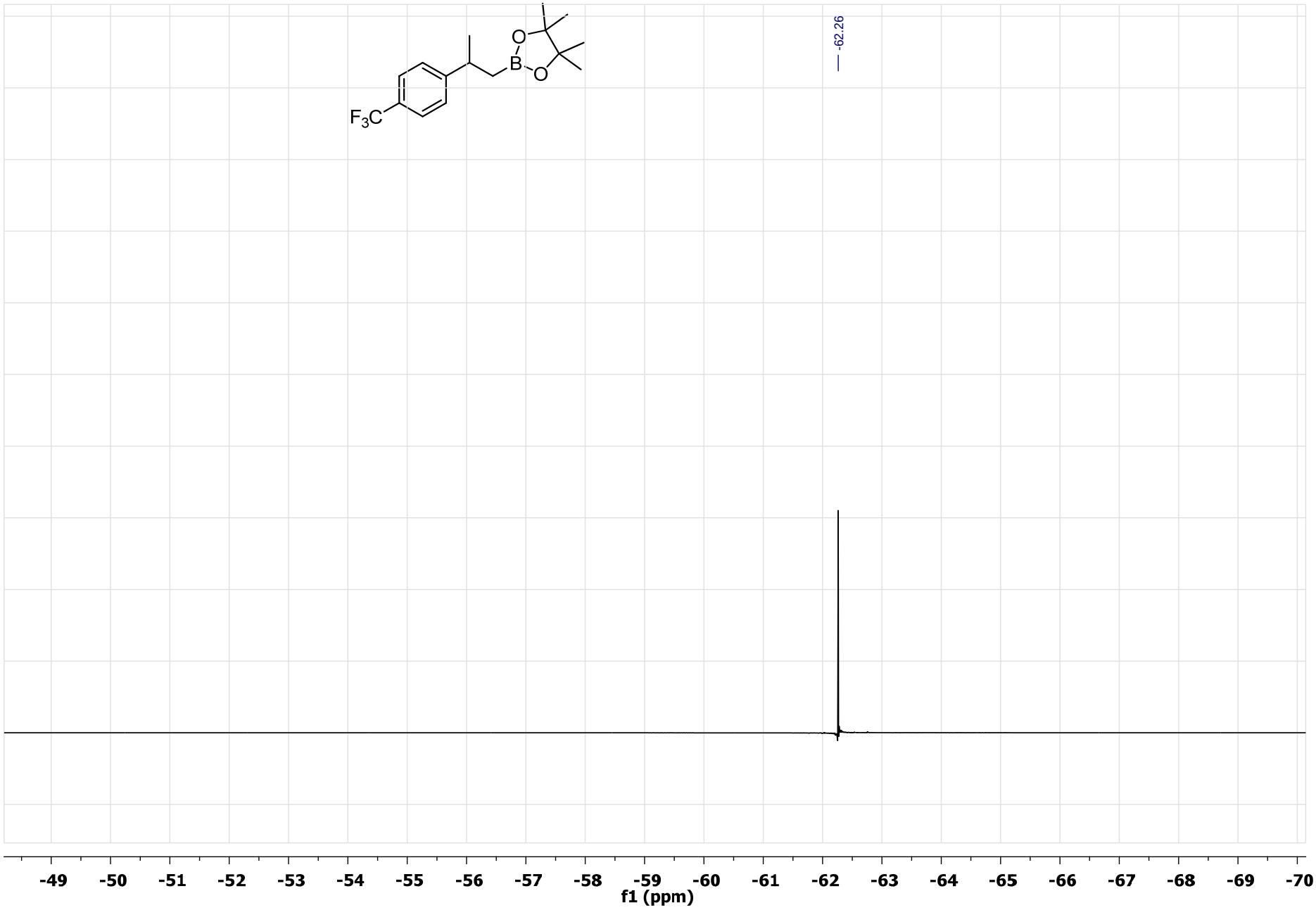
25
20
f1 (ppm)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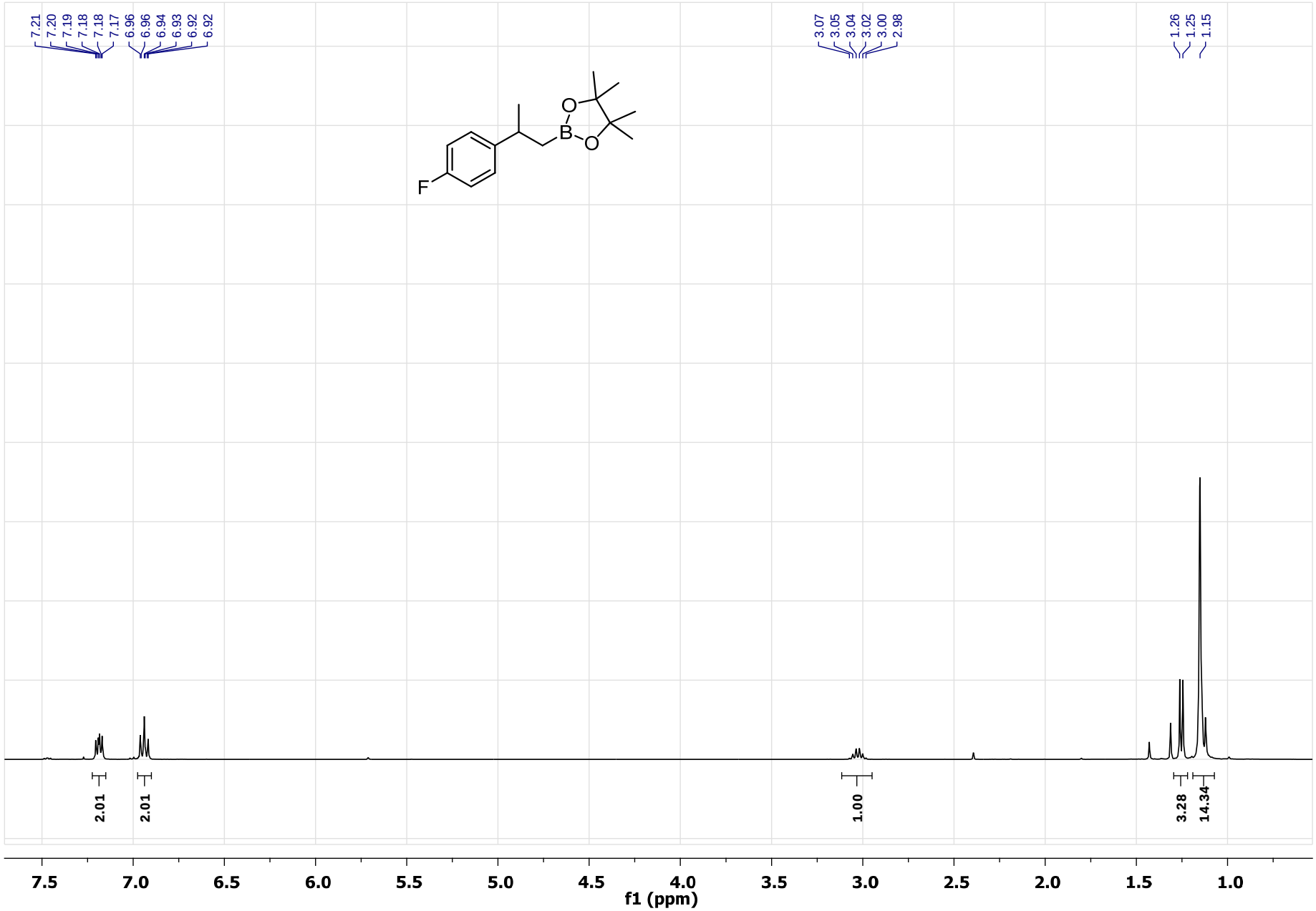
f1 (ppm)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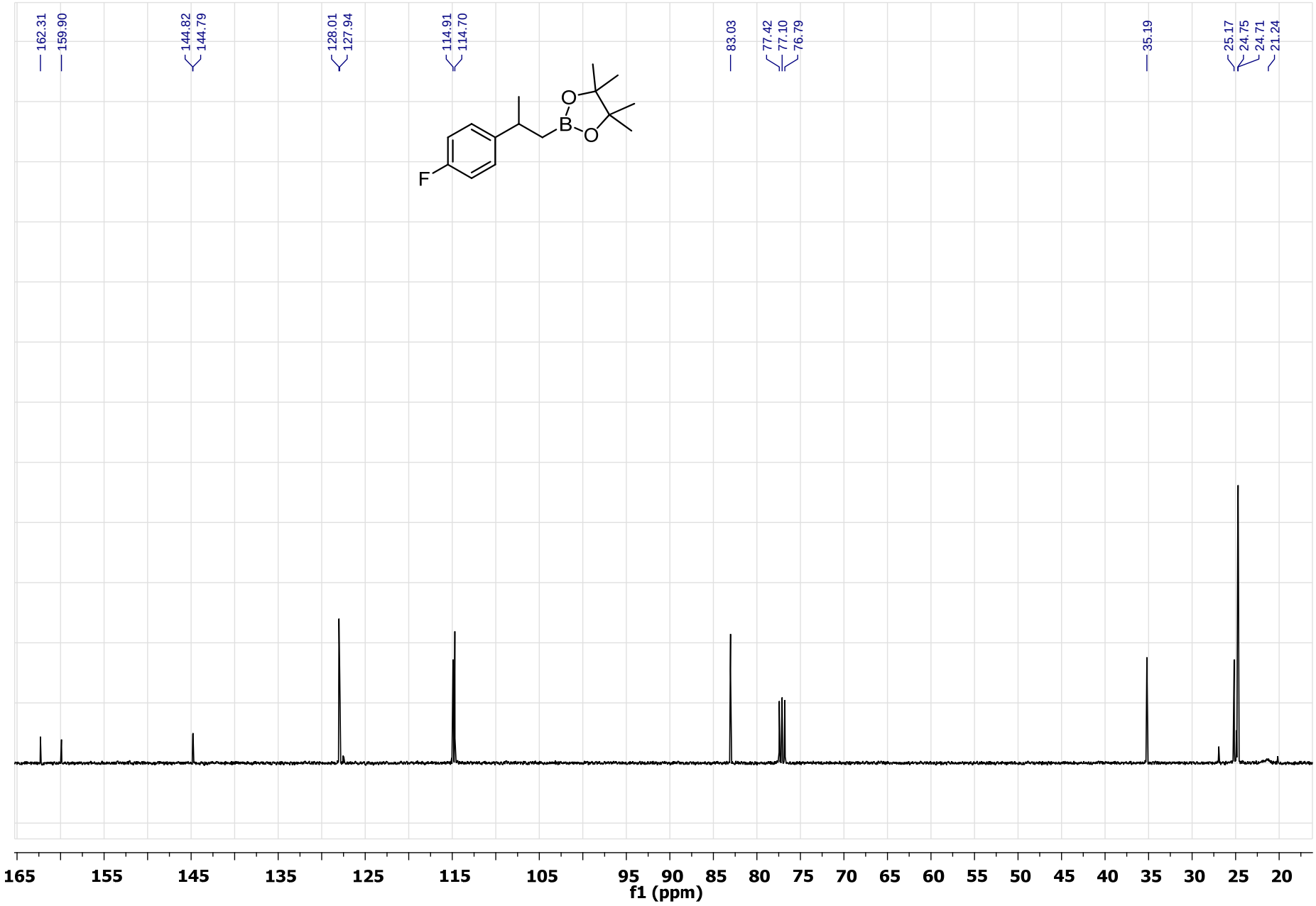
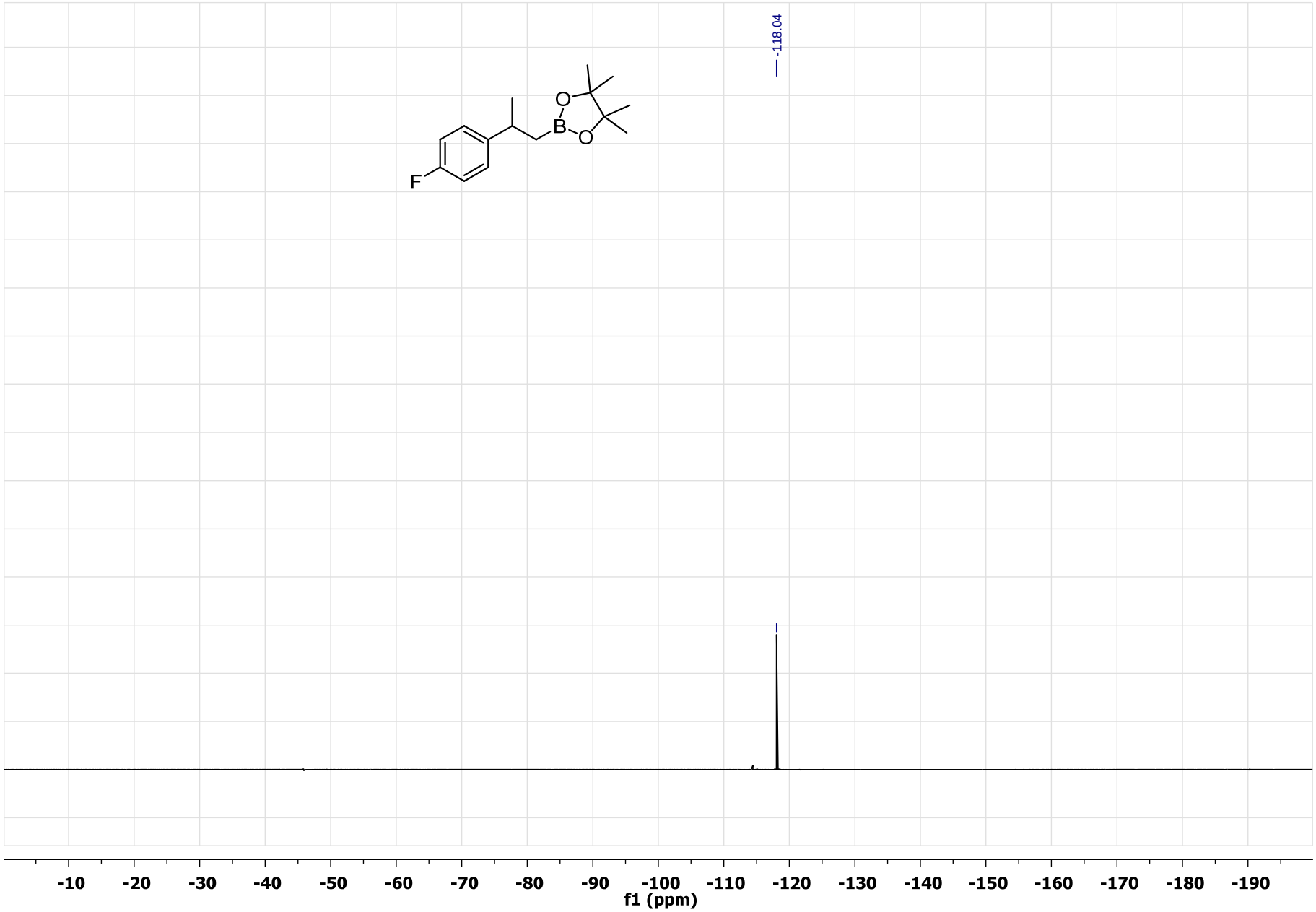
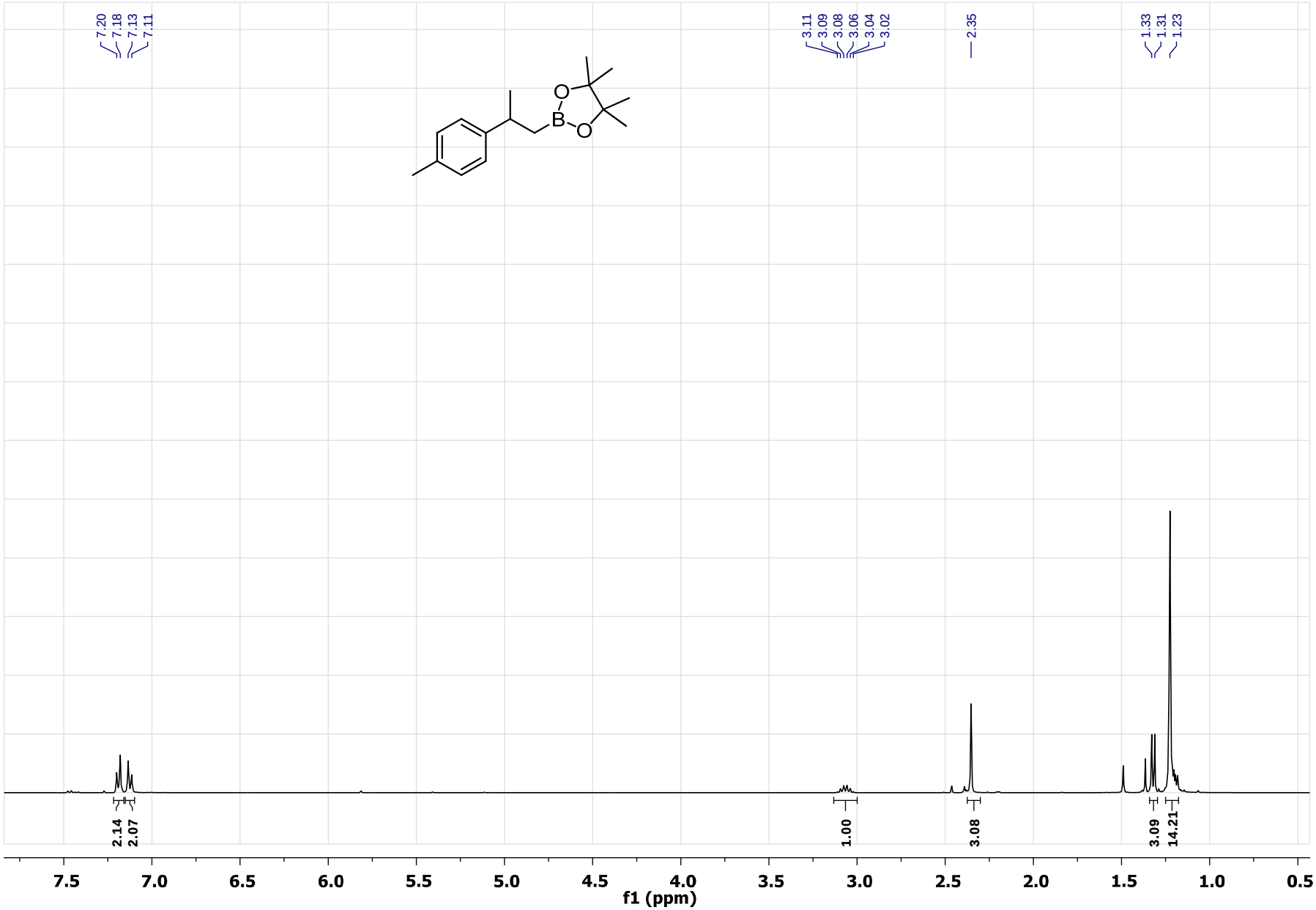
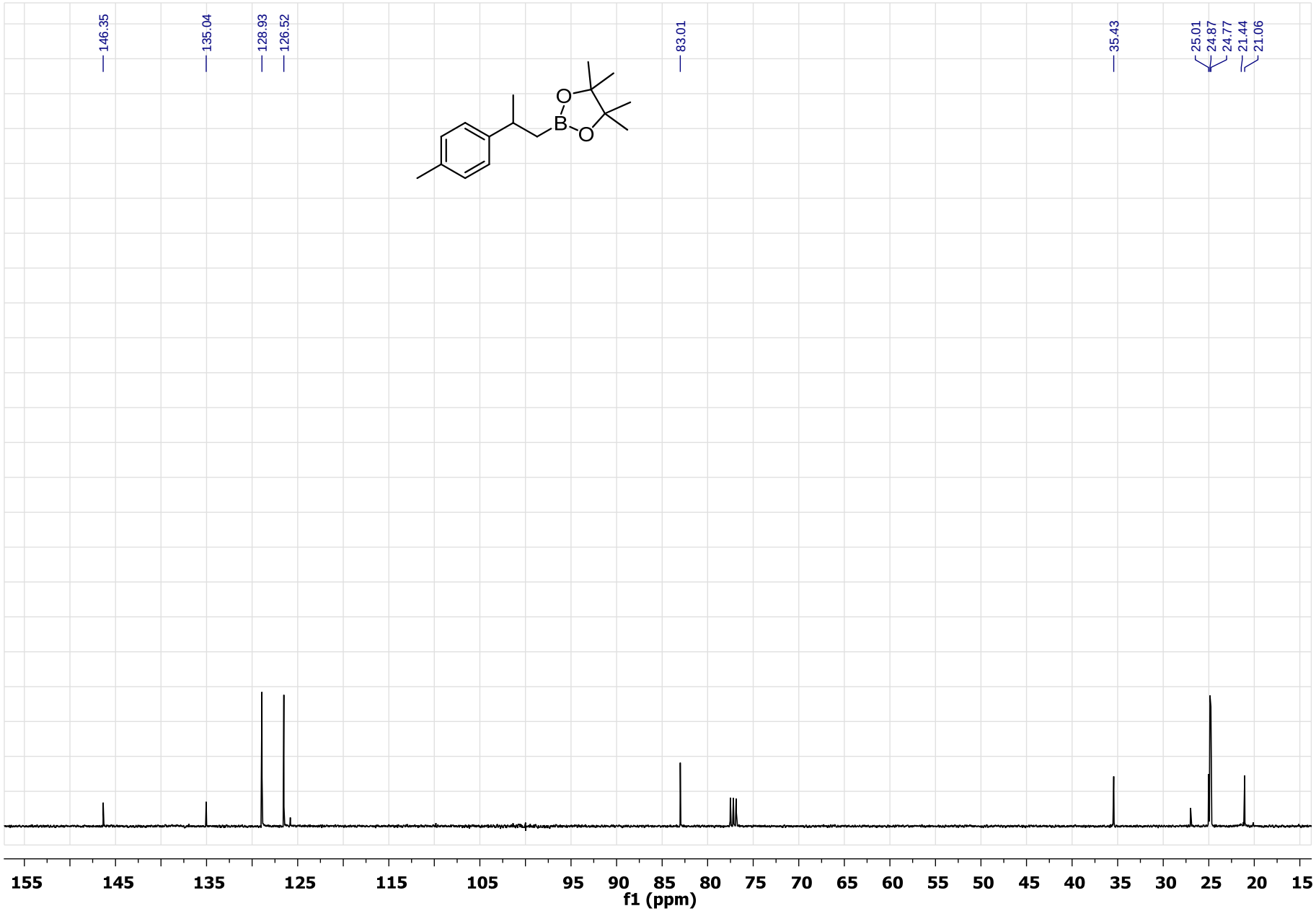
1.25
1.15
O
B
O
F
2.01
2.01
1.00
3.28
14.34
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)


162.31
159.90
144.82
144.79
128.01
127.94
114.91
114.70
83.03
77.42
77.10
76.79
35.19
25.17
24.75
24.71
21.24
O
B
O
F
165
155
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
f1 (ppm)


-118.04
F
O
B
O
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)


7.20
7.18
7.13
7.11
3.11
3.09
3.08
3.06
3.04
3.02
2.35
1.33
1.31
1.23
O
B
O
2.14
2.07
1.00
3.08
3.09
14.21
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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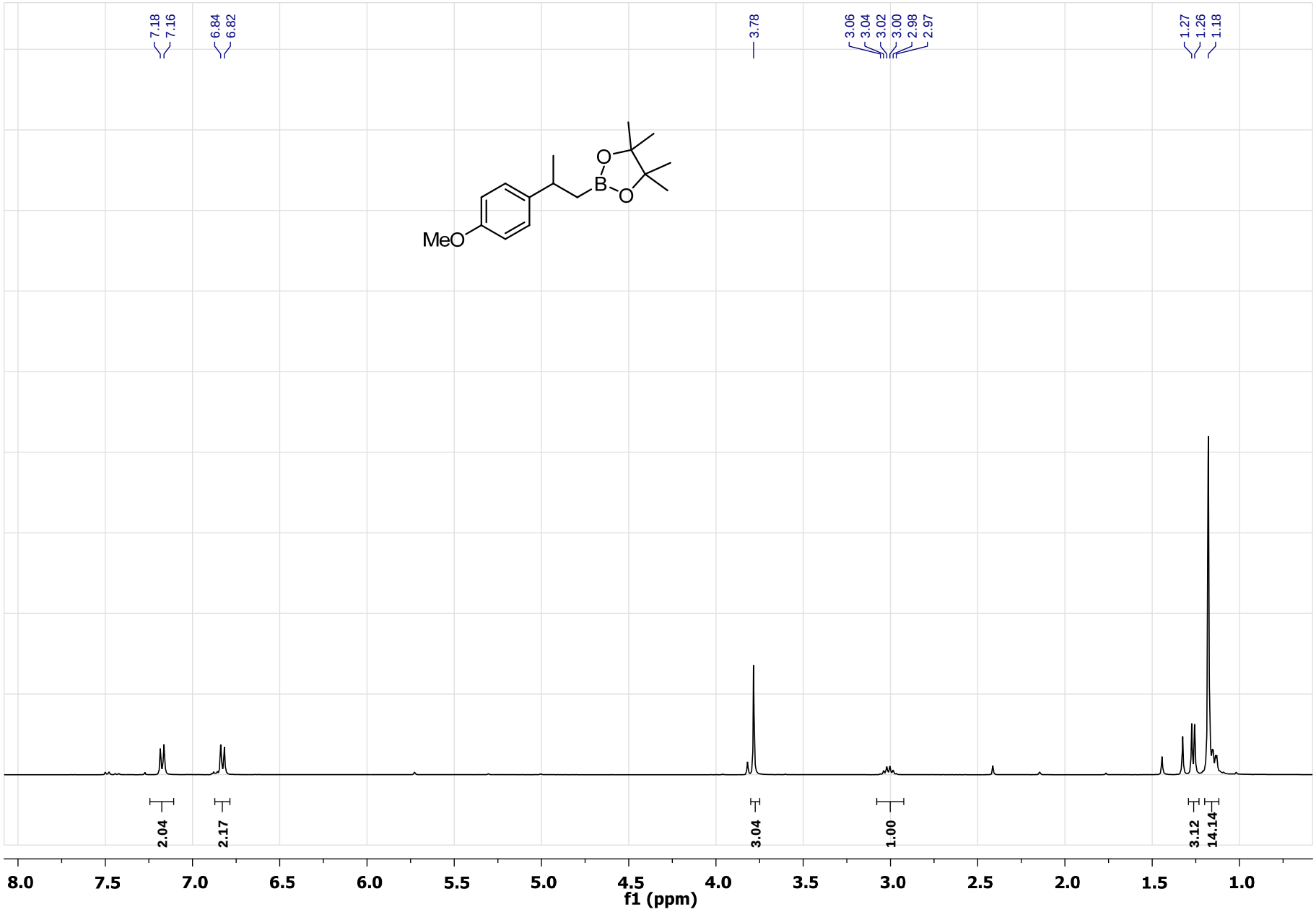
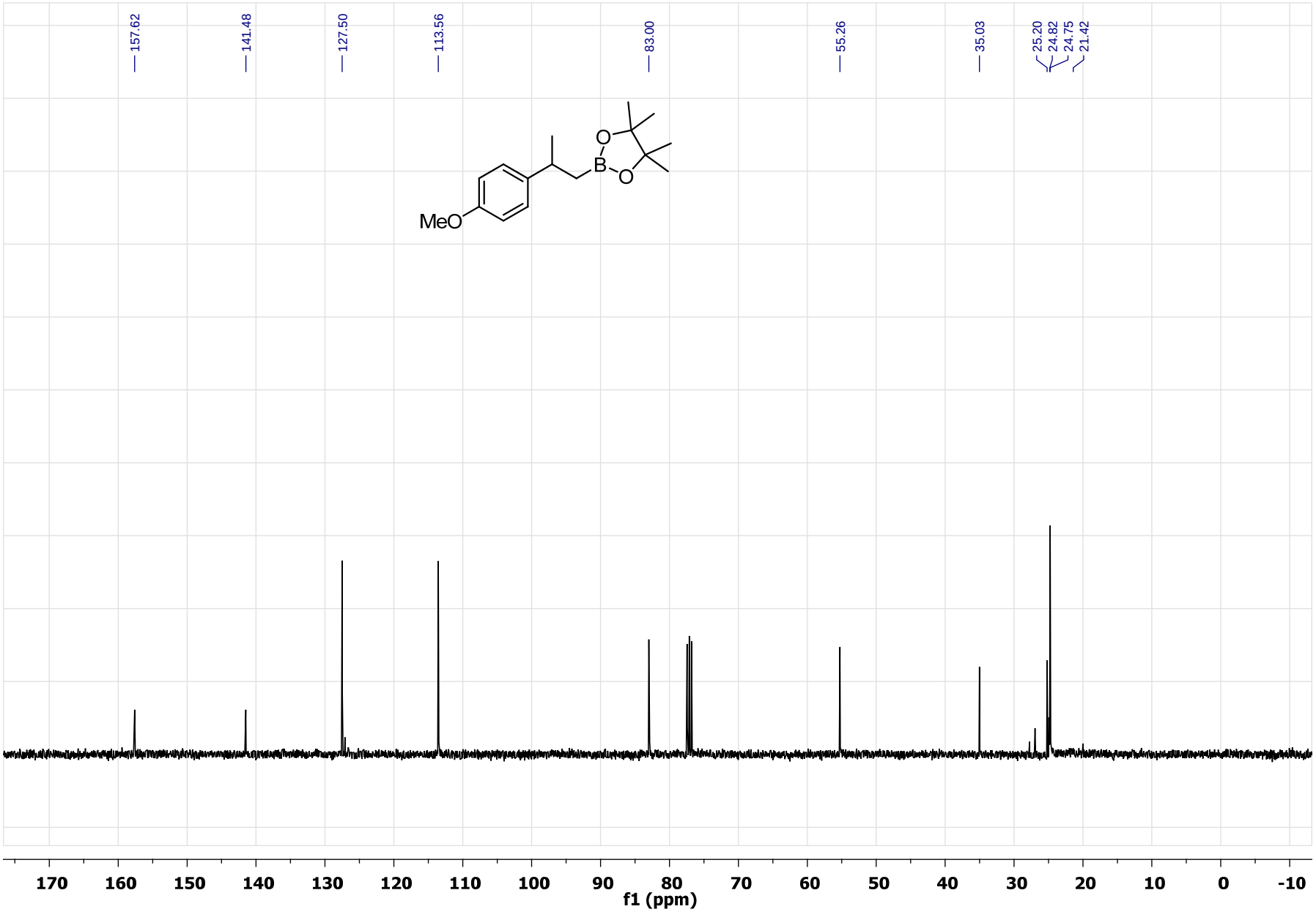
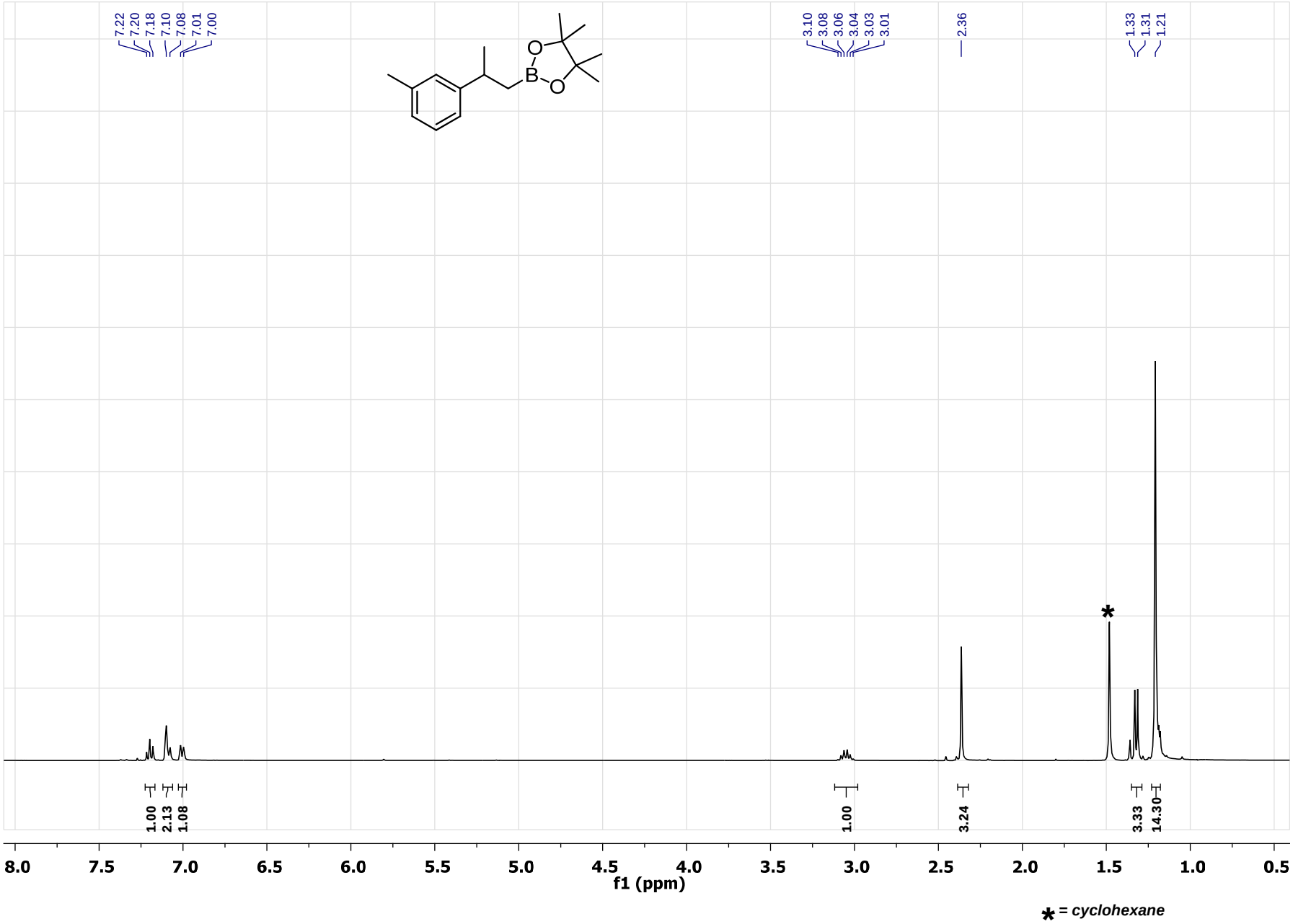
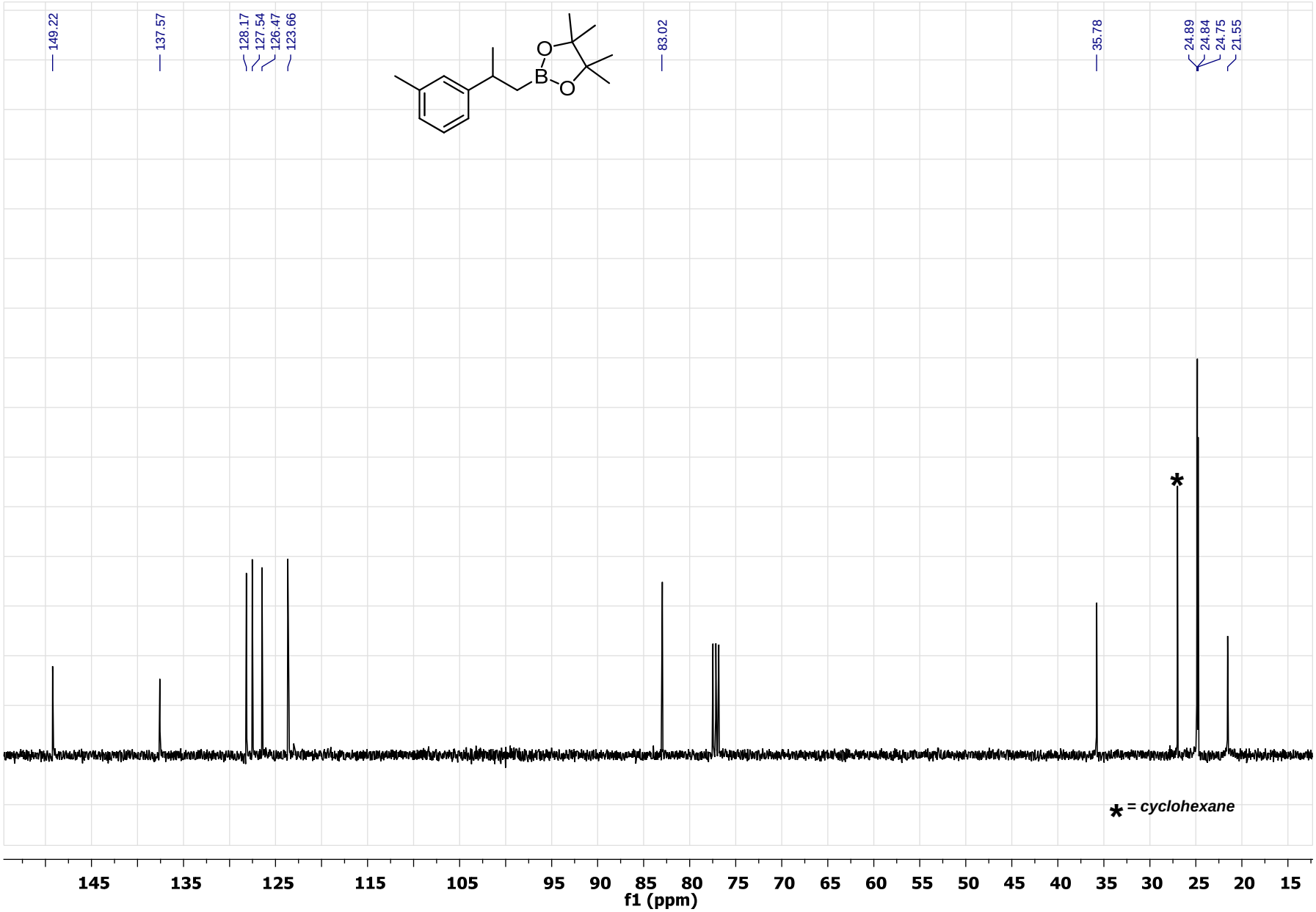
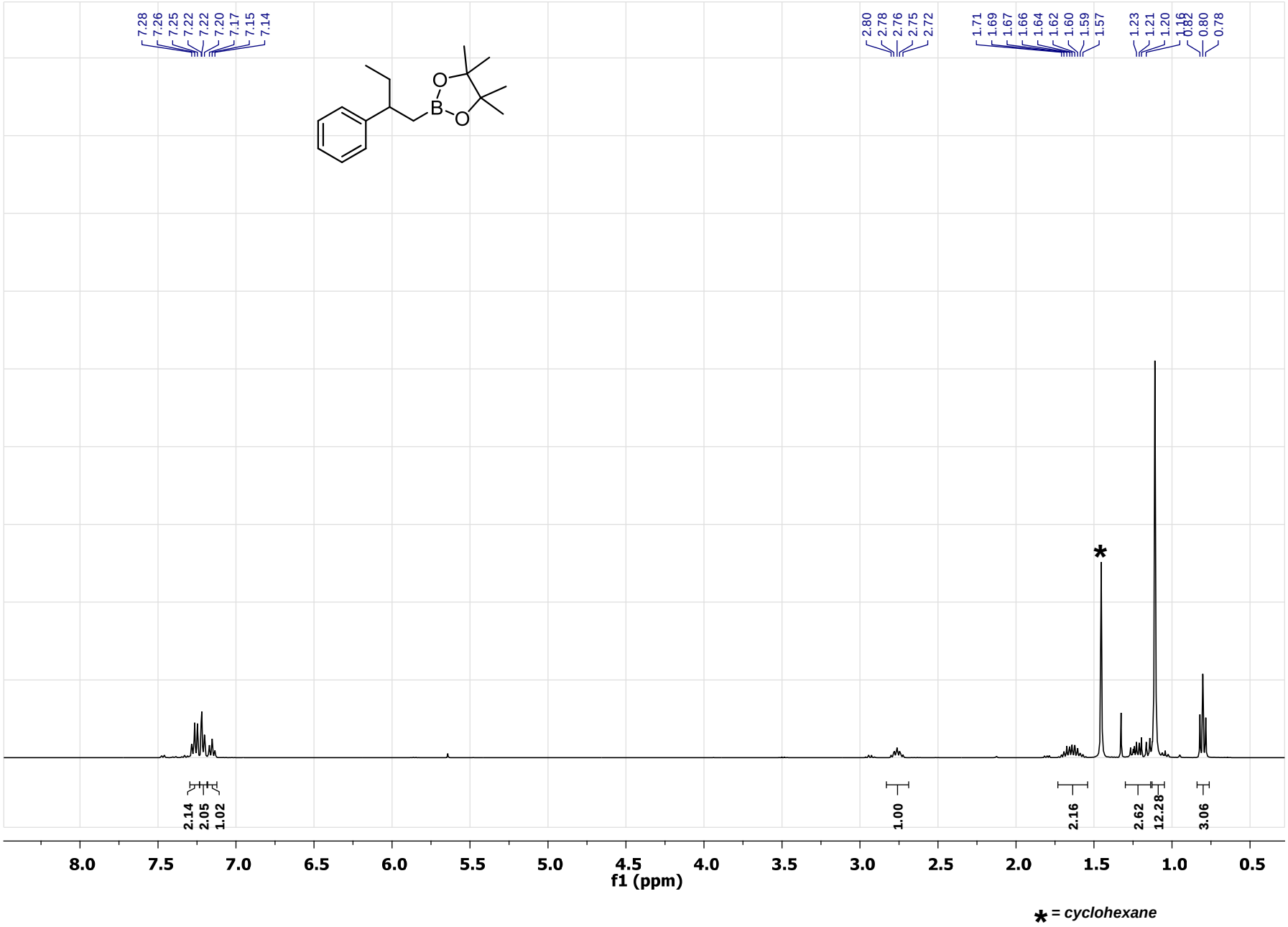
135.04
128.93
126.52
83.01
35.43
25.01
24.87
24.77
21.44
21.06
O
B
O
155
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
f1 (ppm)

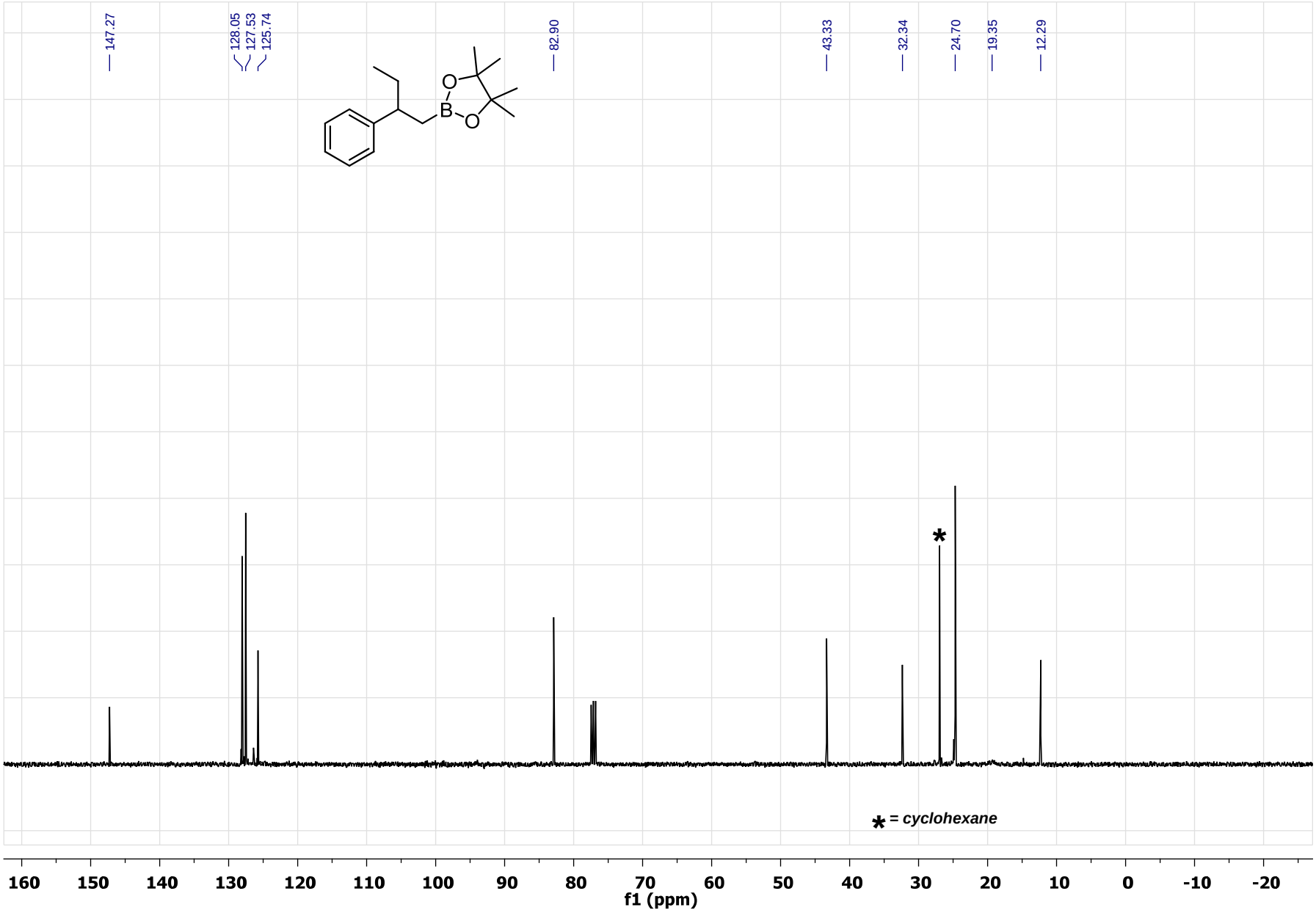

7.18
7.16
6.84
6.82
3.78
3.06
3.04
3.02
3.00
2.98
2.97
1.27
1.26
1.18
MeO
O
B
O
2.04
2.17
3.04
1.00
3.12
14.14
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

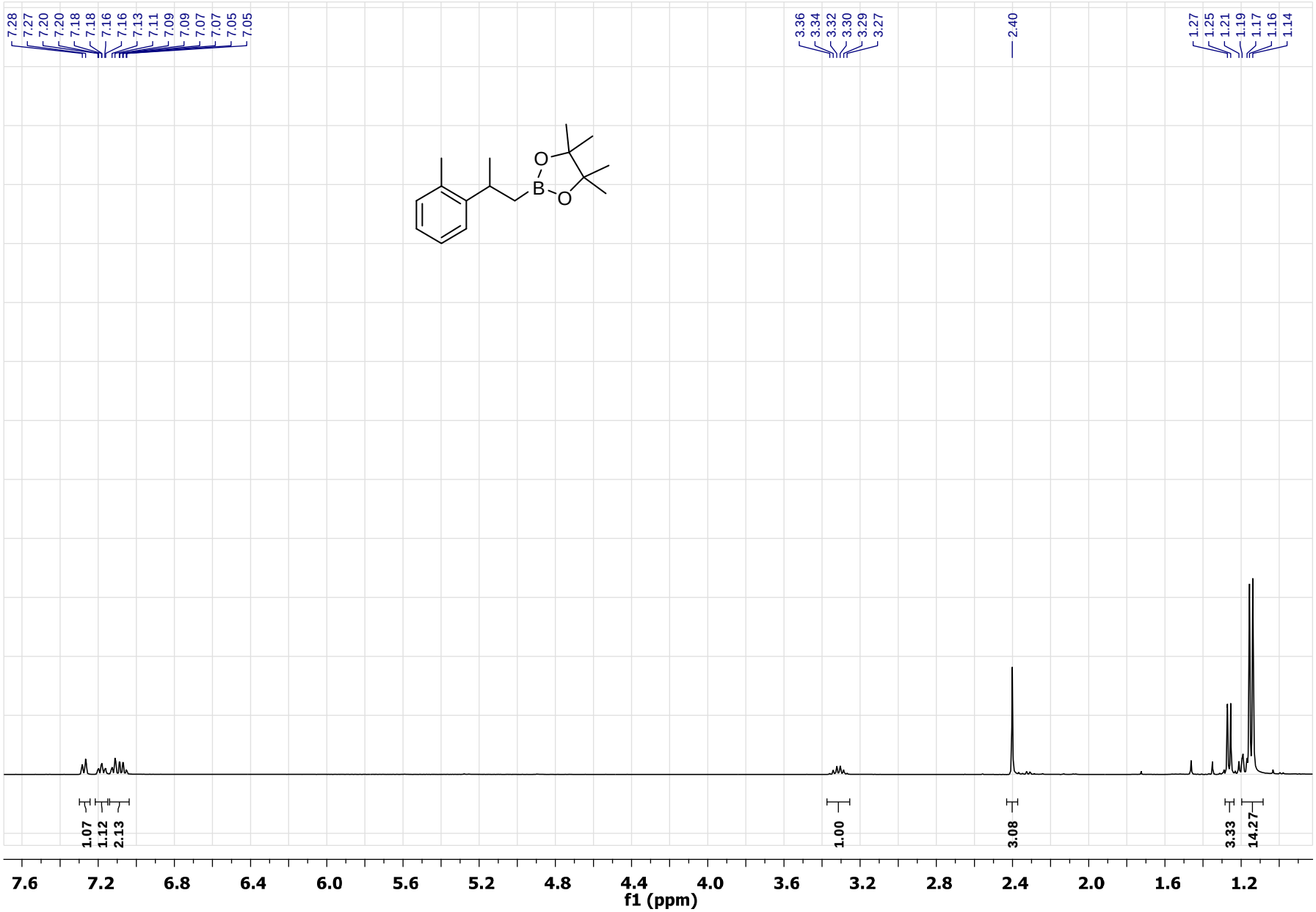

157.62
141.48
127.50
113.56
83.00
55.26
35.03
25.20
24.82
24.75
21.42
MeO
O
B
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

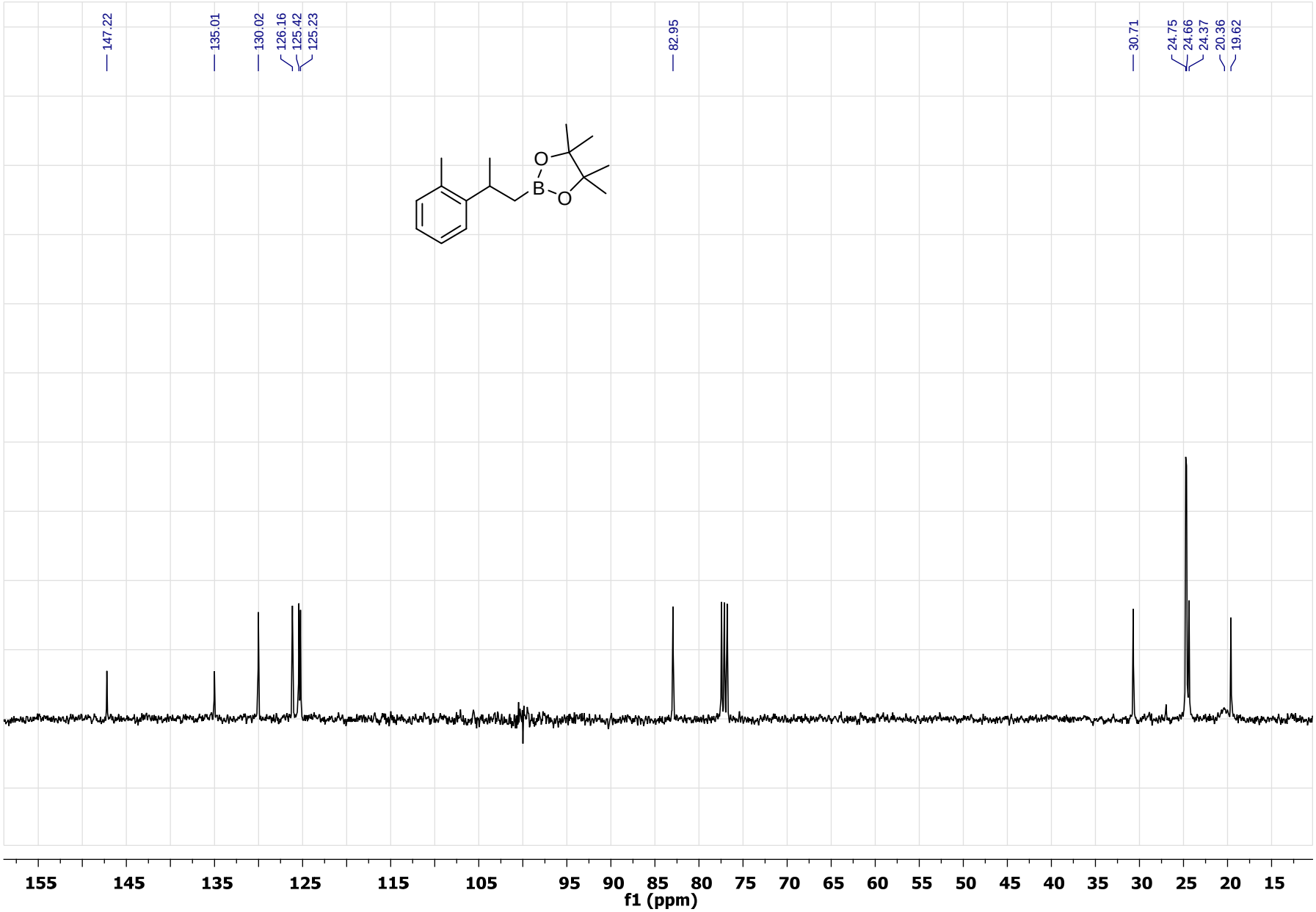

7.22
7.20
7.18
7.10
7.08
7.01
7.00
3.10
3.08
3.06
3.04
3.03
3.01
2.36
1.33
1.31
1.21
O
B
O
1.00
2.13
1.08
1.00
3.24
3.33
14.30
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
* = cyclohexane

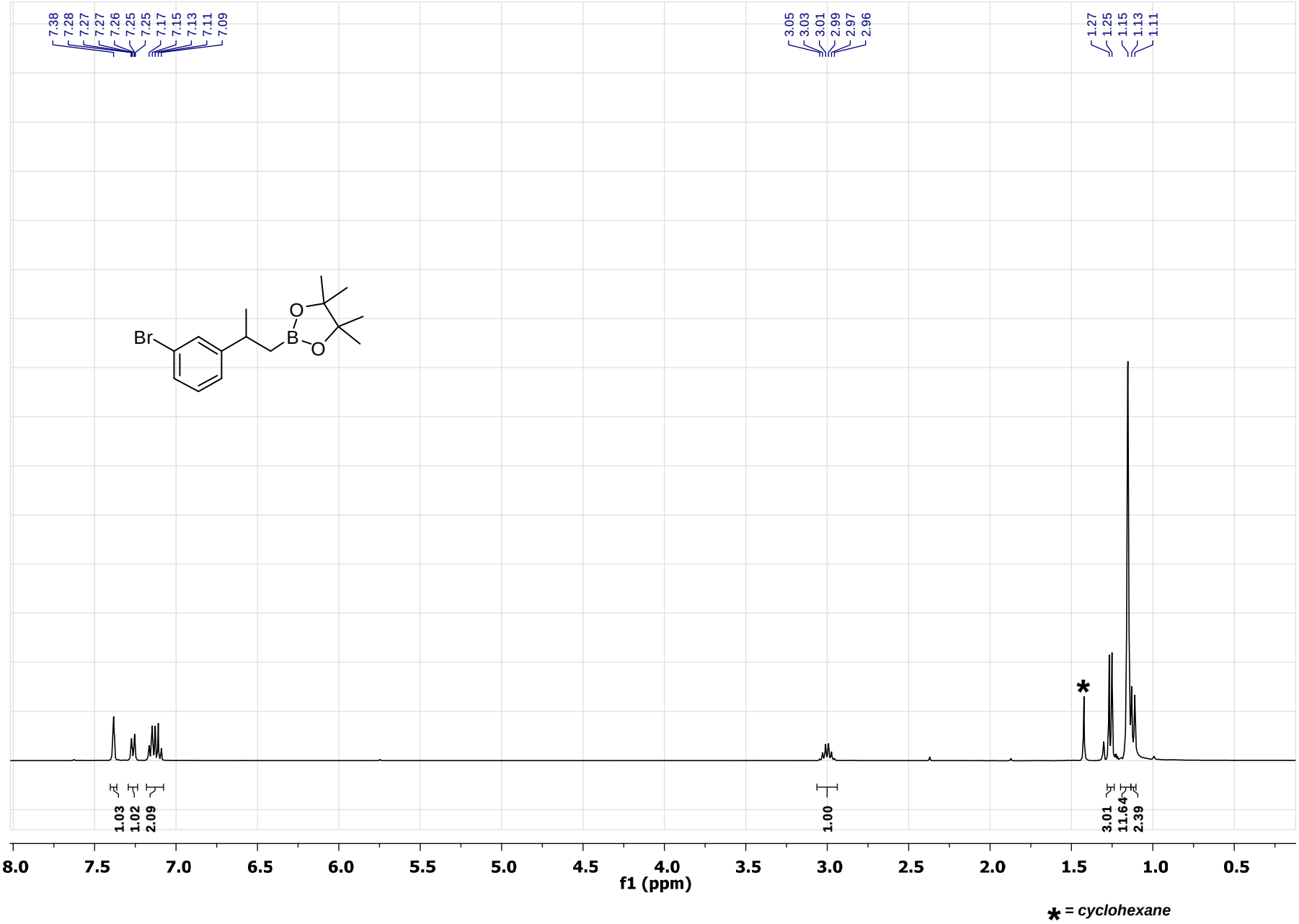

149.22
137.57
128.17
127.54
126.47
123.66
83.02
35.78
24.89
24.84
24.75
21.55
O
B
O
*
* = cyclohexane
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
f1 (ppm)

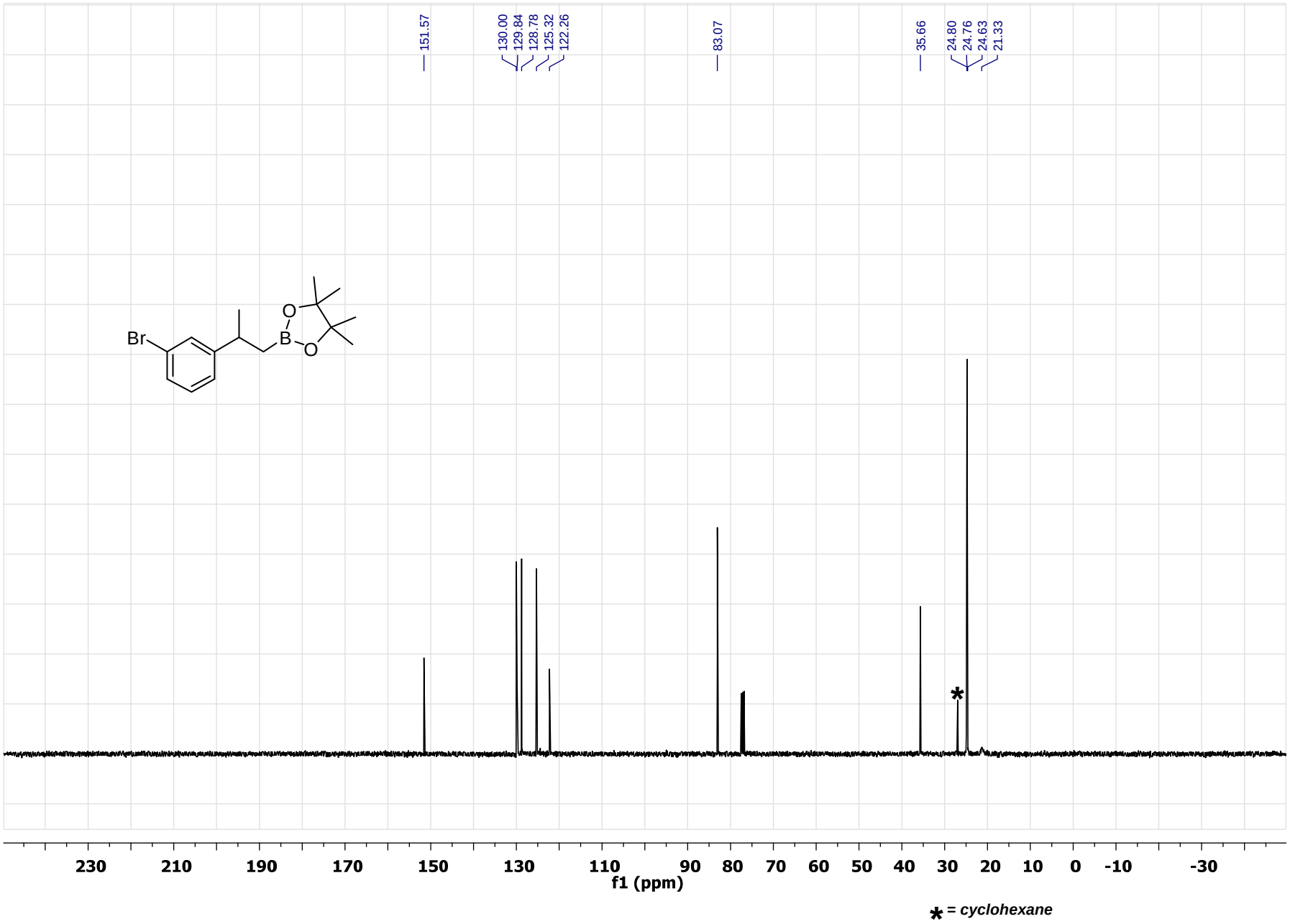

7.28
7.26
7.25
7.22
7.22
7.20
7.17
7.15
7.14
2.80
2.78
2.76
2.75
2.72
1.71
1.69
1.67
1.66
1.64
1.62
1.60
1.59
1.57
1.23
1.21
1.20
0.82
0.80
0.78
O
B
O
*
2.14
2.05
1.02
1.00
2.16
2.62
12.28
3.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
* = cyclohexane

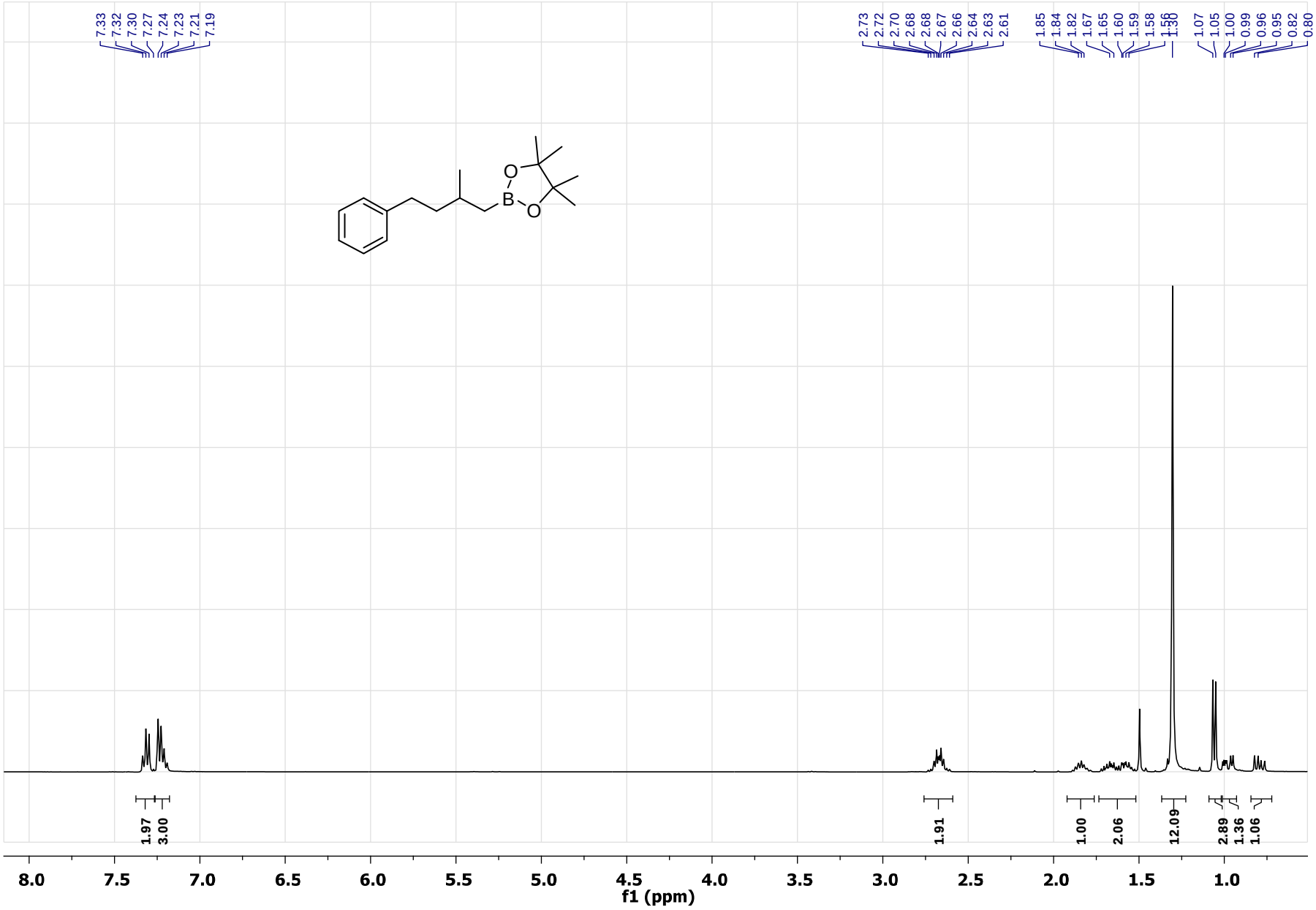

147.27
128.05
127.53
125.74
82.90
43.33
32.34
24.70
19.35
12.29
O
B
O
*
* = cyclohexane
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

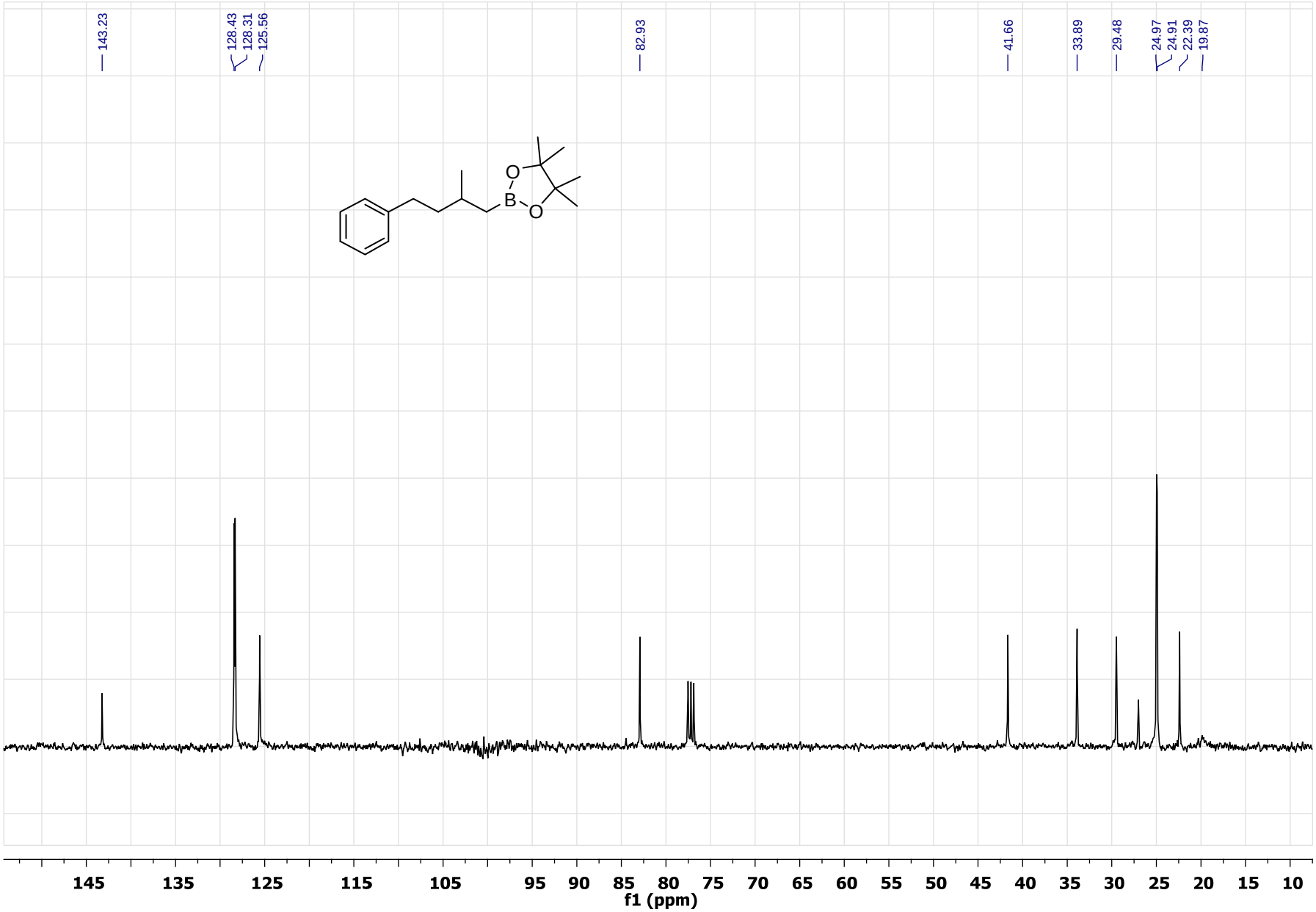

7.28
7.27
7.20
7.20
7.18
7.18
7.16
7.16
7.13
7.11
7.09
7.09
7.07
7.07
7.05
7.05
3.36
3.34
3.32
3.30
3.29
3.27
2.40
1.27
1.25
1.21
1.19
1.17
1.16
1.14
O
B
O
1.07
1.12
2.13
1.00
3.08
3.33
14.27
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
f1 (ppm)

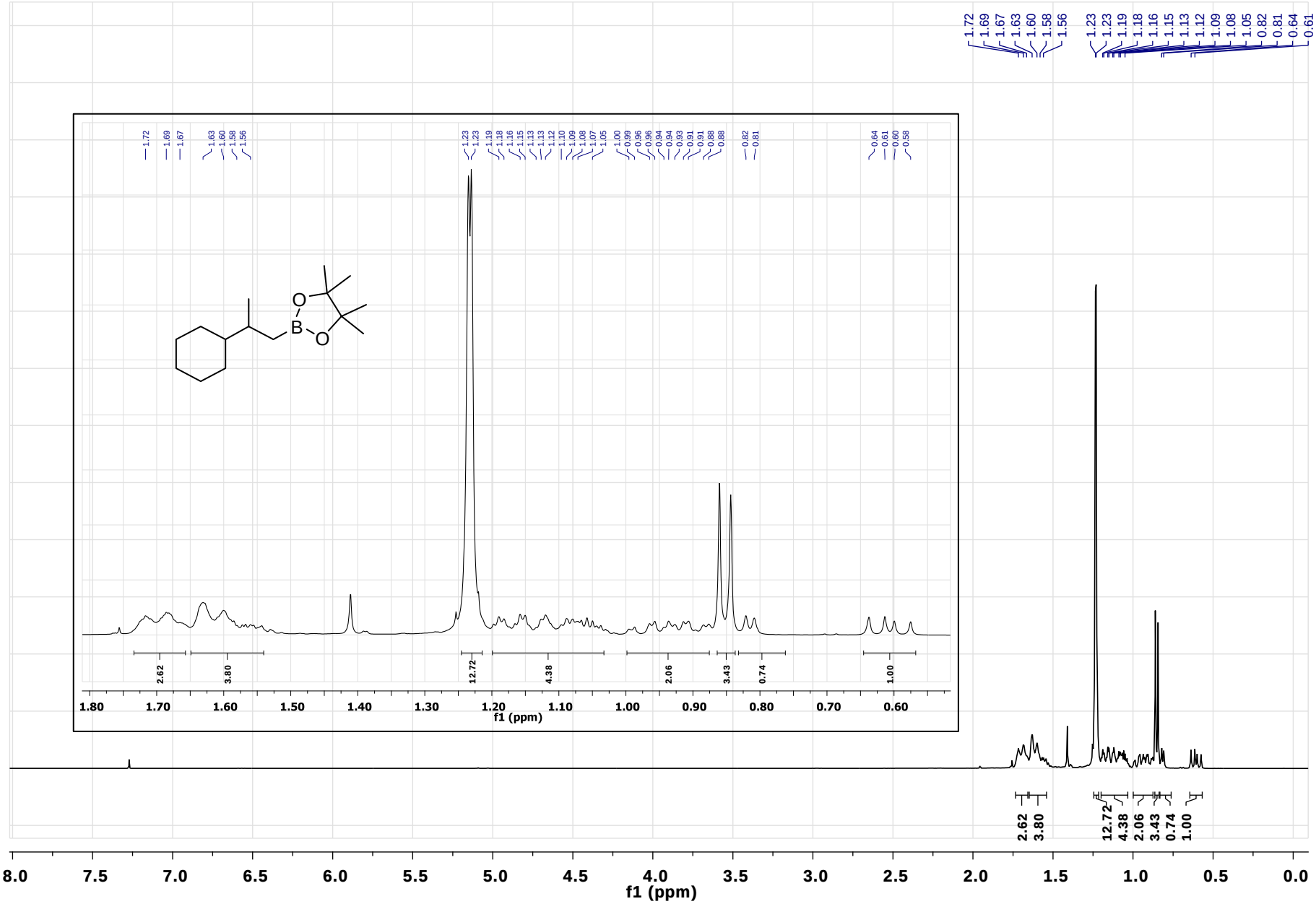

147.22
135.01
130.02
126.16
125.42
125.23
82.95
30.71
24.75
24.66
24.37
20.36
19.62
O
B
O
155
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
f1 (ppm)

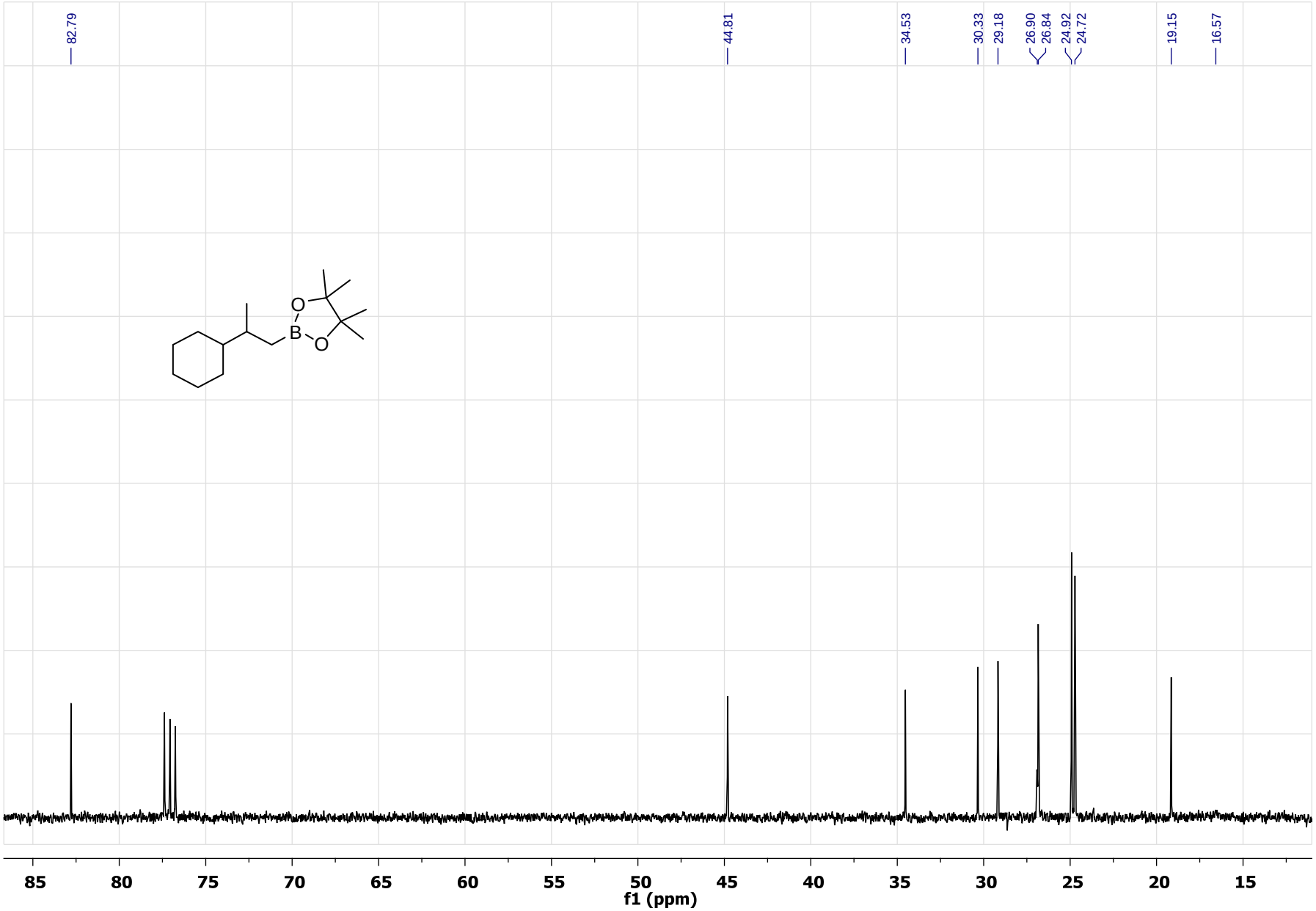

7.38
7.28
7.27
7.27
7.26
7.25
7.25
7.17
7.15
7.13
7.11
7.09
3.05
3.03
3.01
2.99
2.97
2.96
1.27
1.25
1.15
1.13
1.11
Br
O
B
O
1.03
1.02
2.09
1.00
3.01
11.64
2.39
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
* = cyclohexane

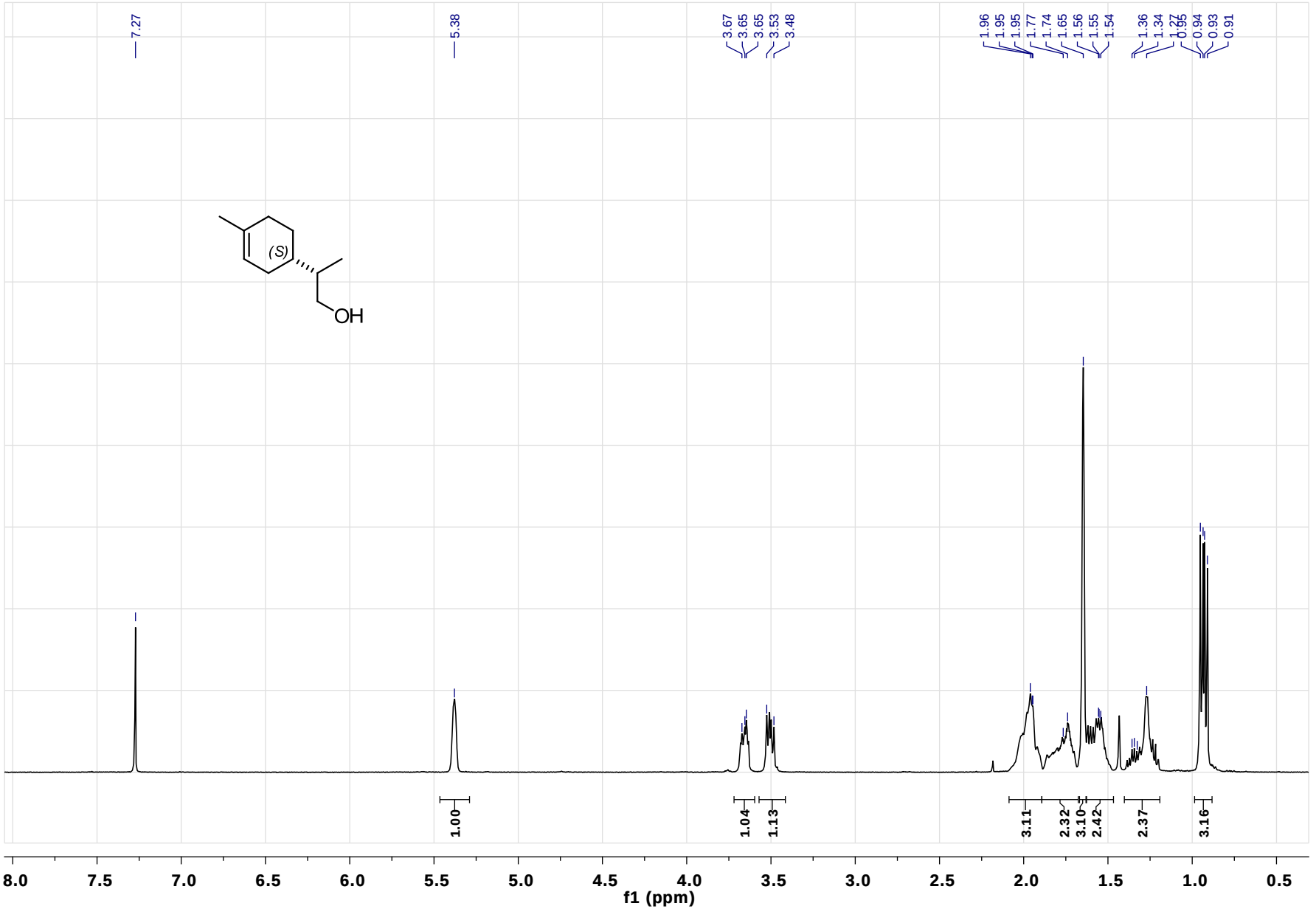

151.57
130.00
129.84
128.78
125.32
122.26
83.07
35.66
24.80
24.76
24.63
21.33
Br
O
B
O
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
f1 (ppm)
* = cyclohexane

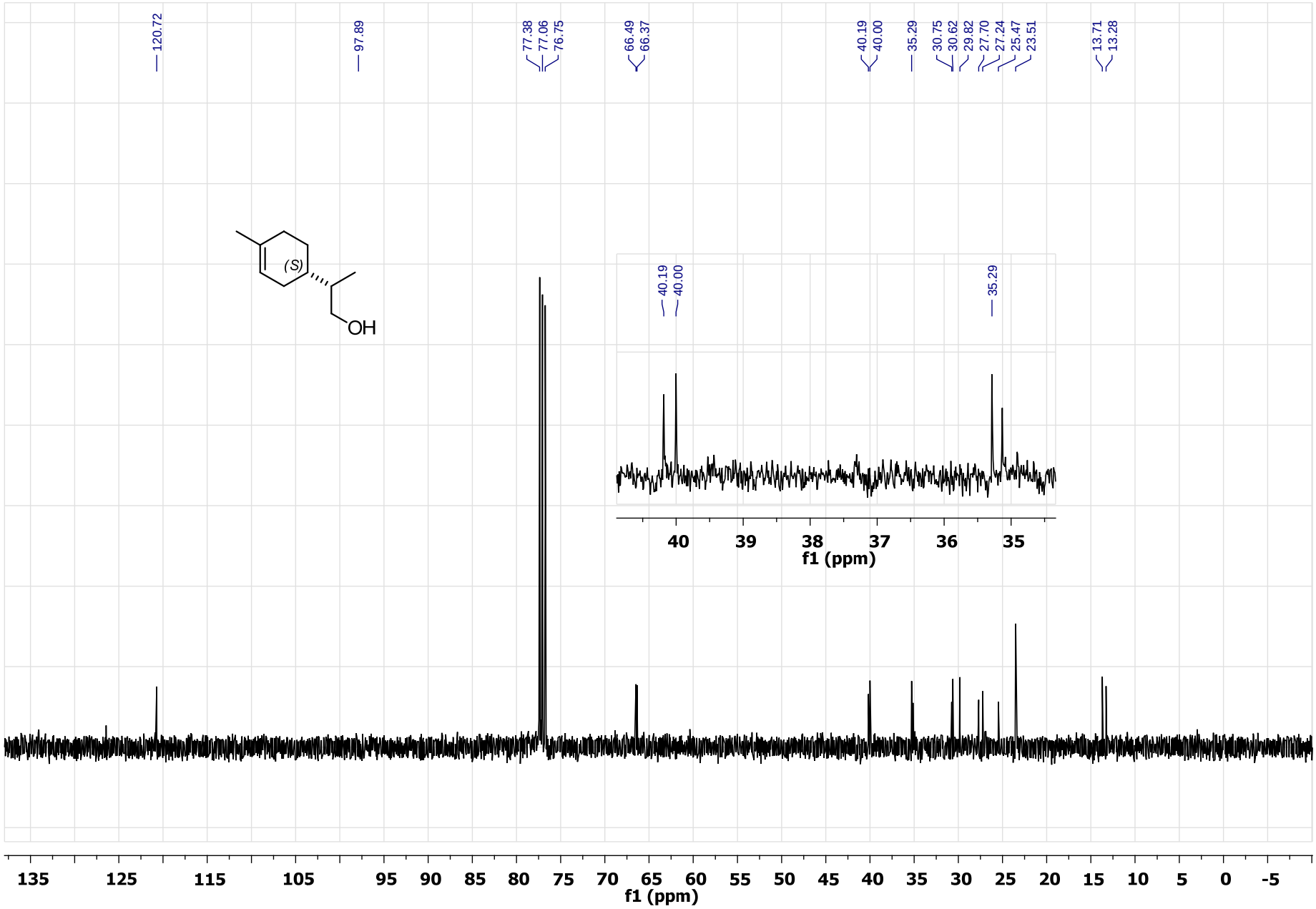

7.33
7.32
7.30
7.27
7.24
7.23
7.21
7.19
2.73
2.72
2.70
2.68
2.68
2.67
2.66
2.64
2.63
2.61
1.85
1.84
1.82
1.67
1.65
1.60
1.59
1.58
1.30
1.07
1.05
1.00
0.99
0.96
0.95
0.82
0.80
O
B
O
1.97
3.00
1.91
1.00
2.06
12.09
2.89
1.36
1.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

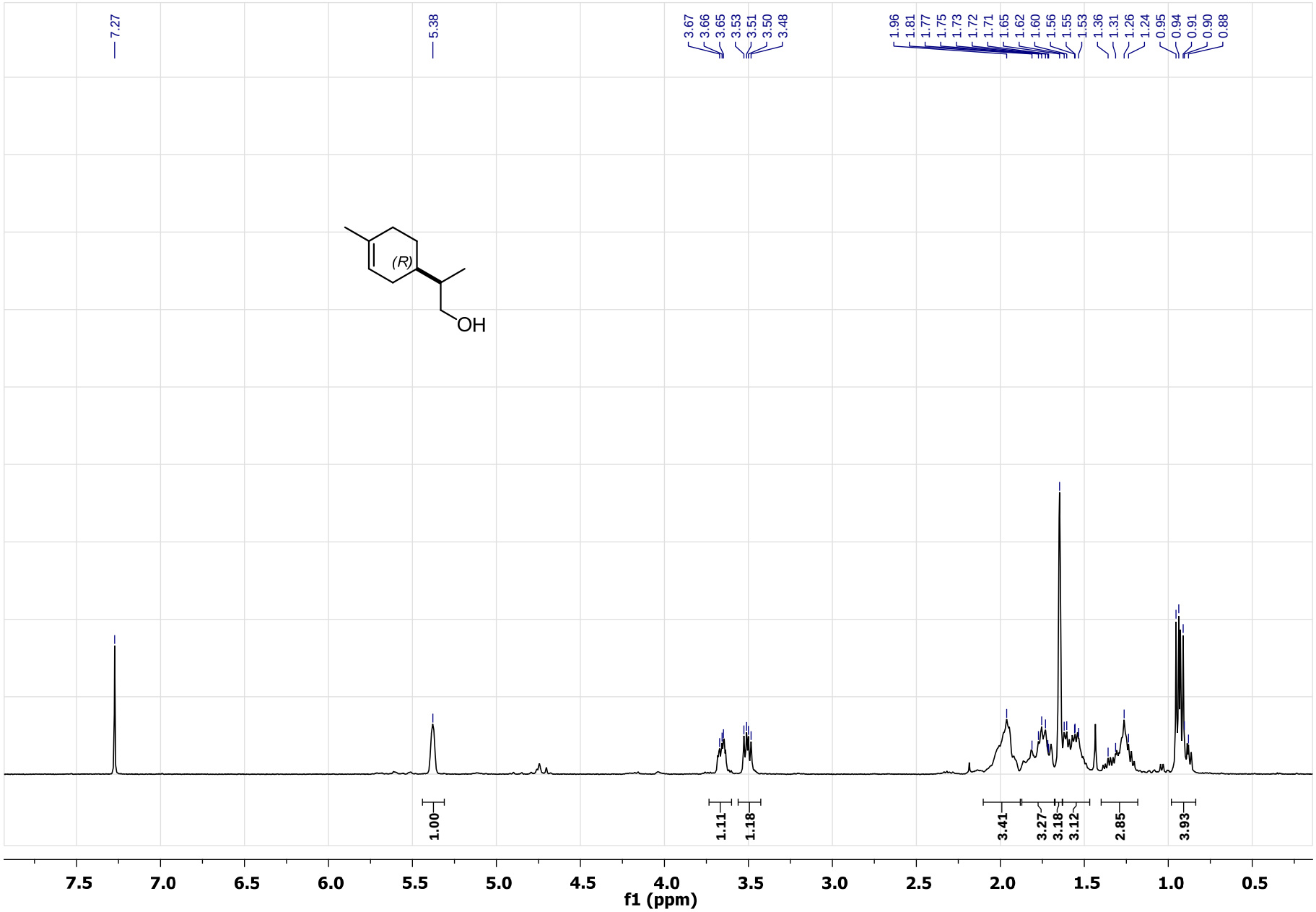

143.23
128.43
128.31
125.56
82.93
41.66
33.89
29.48
24.97
24.91
22.39
19.87
O
B
O
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
f1 (ppm)

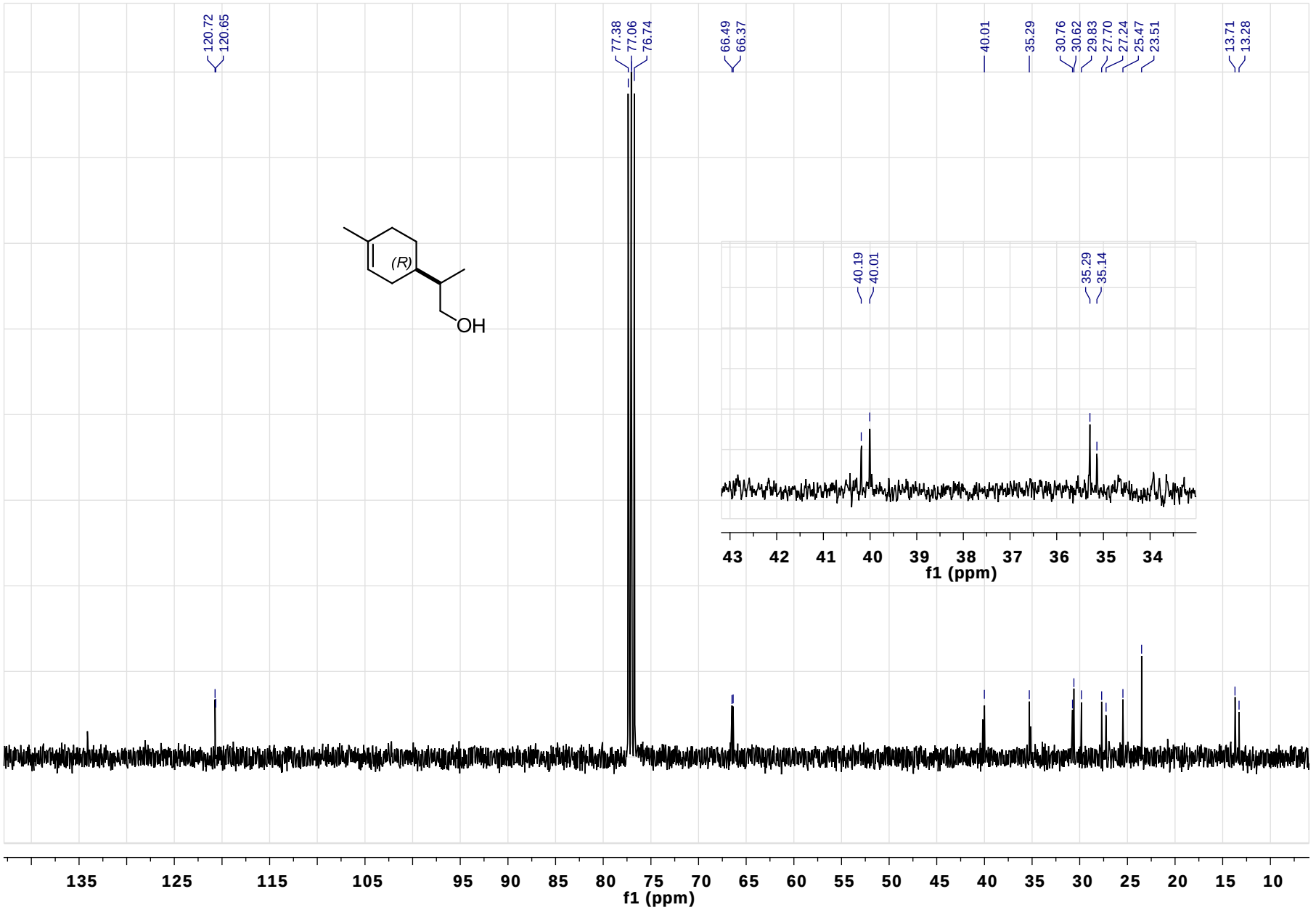

1.72
1.69
1.67
1.63
1.60
1.58
1.56
1.23
1.23
1.19
1.18
1.16
1.15
1.13
1.12
1.09
1.08
1.05
0.82
0.81
0.64
0.61
0.60
0.58
O
B
O
O
2.62
3.80
12.72
4.38
2.06
3.43
0.74
1.00
f1 (ppm)

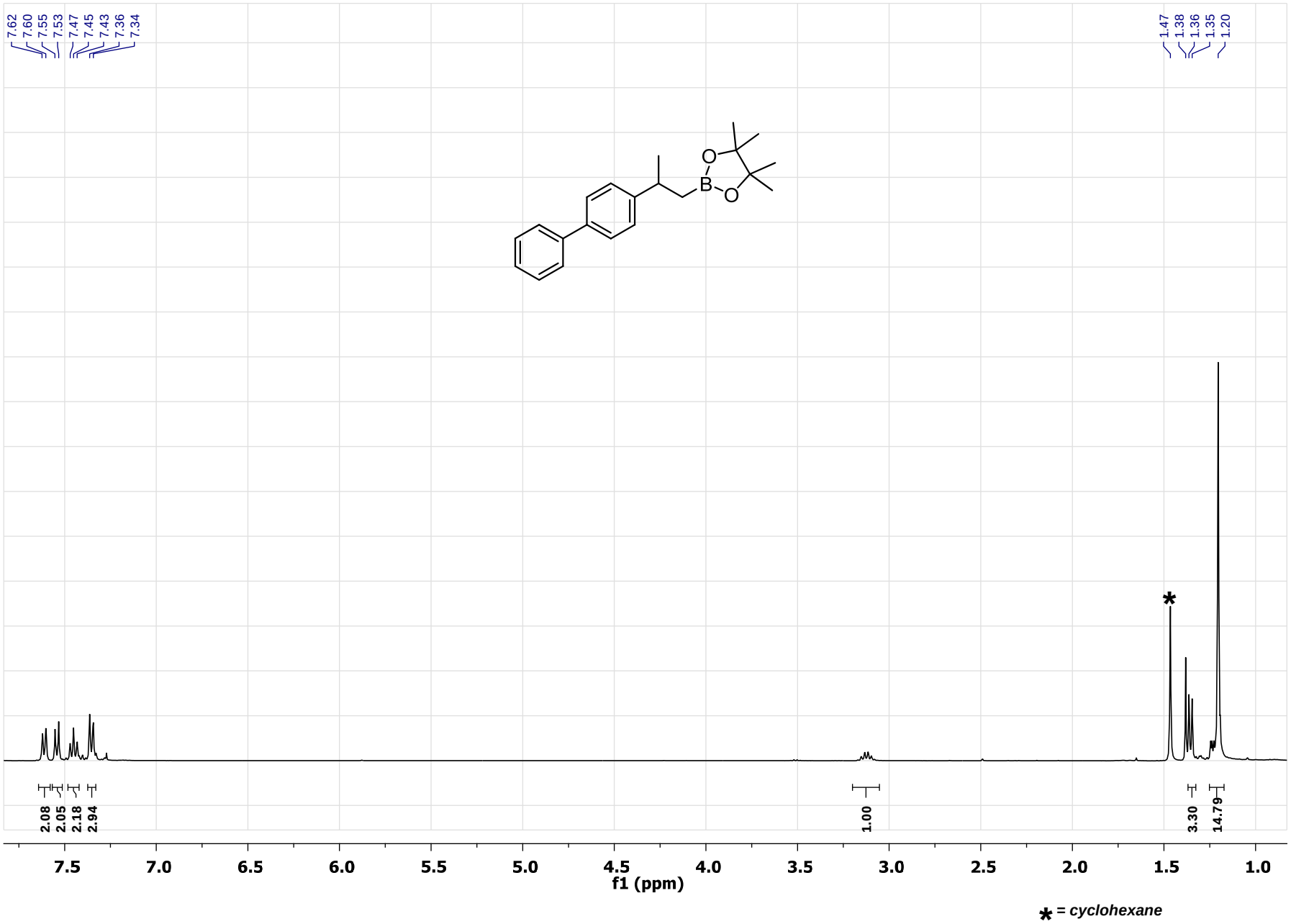

82.79
44.81
34.53
30.33
29.18
26.90
26.84
24.92
24.72
19.15
16.57
O
B
O
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
f1 (ppm)

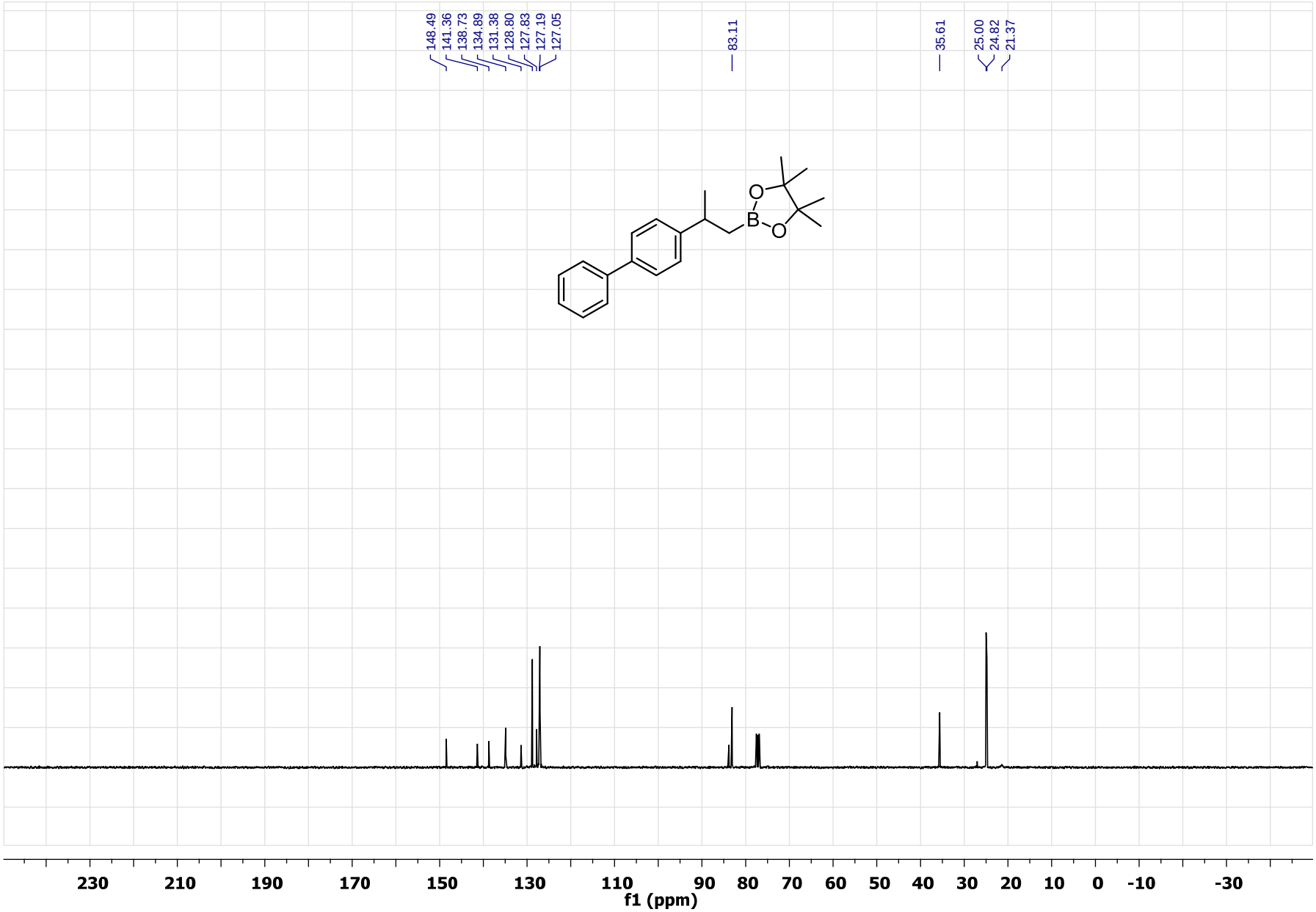

7.27
5.38
3.67
3.65
3.65
3.53
3.48
1.96
1.95
1.95
1.77
1.74
1.65
1.56
1.55
1.54
1.36
1.34
0.95
0.94
0.93
0.91
(S)
OH
1.00
1.04
1.13
3.11
2.32
3.10
2.42
2.37
3.16
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

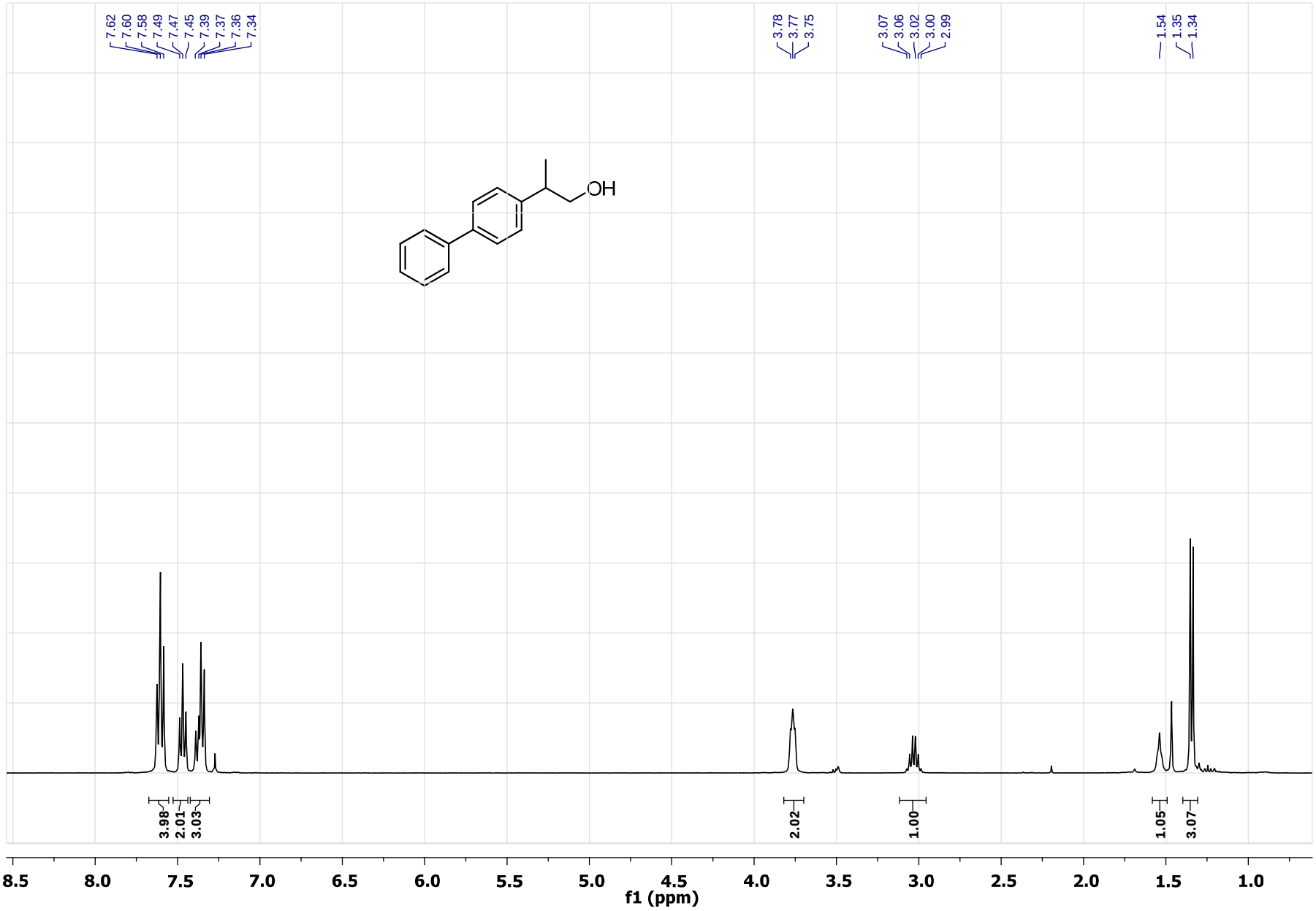

120.72
97.89
77.38
77.06
76.75
66.49
66.37
40.19
40.00
35.29
30.75
30.62
29.82
27.70
27.24
25.47
23.51
13.71
13.28
(S)
OH
40.19
40.00
35.29
40
39
38
37
36
35
f1 (ppm)
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
f1 (ppm)

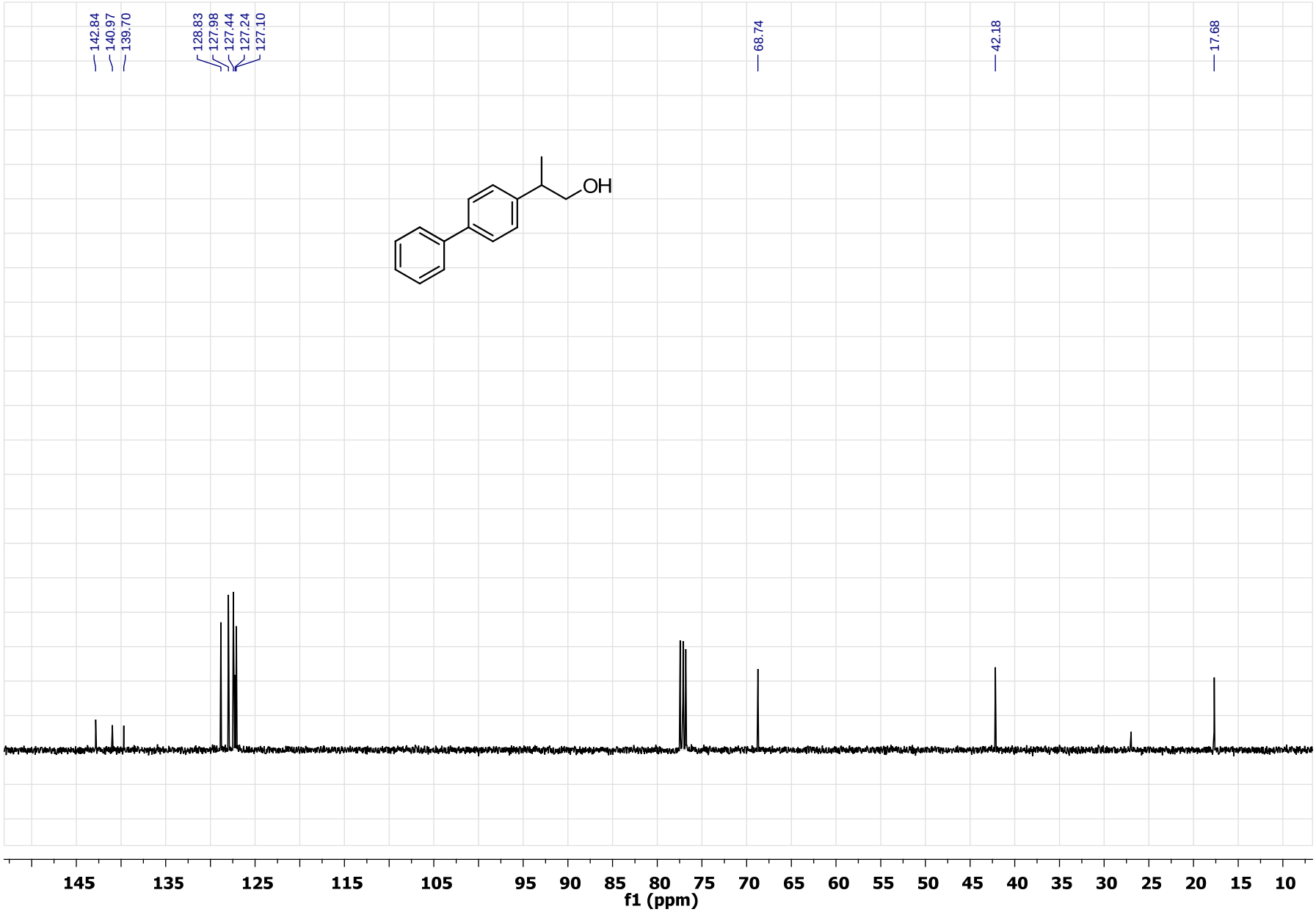

7.27
5.38
3.67
3.66
3.65
3.53
3.51
3.50
3.48
1.96
1.81
1.77
1.75
1.73
1.72
1.71
1.65
1.62
1.60
1.56
1.55
1.53
1.36
1.31
1.26
1.24
0.95
0.94
0.91
0.90
0.88
(R)
OH
1.00
1.11
1.18
3.41
3.27
3.18
3.12
2.85
3.93
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

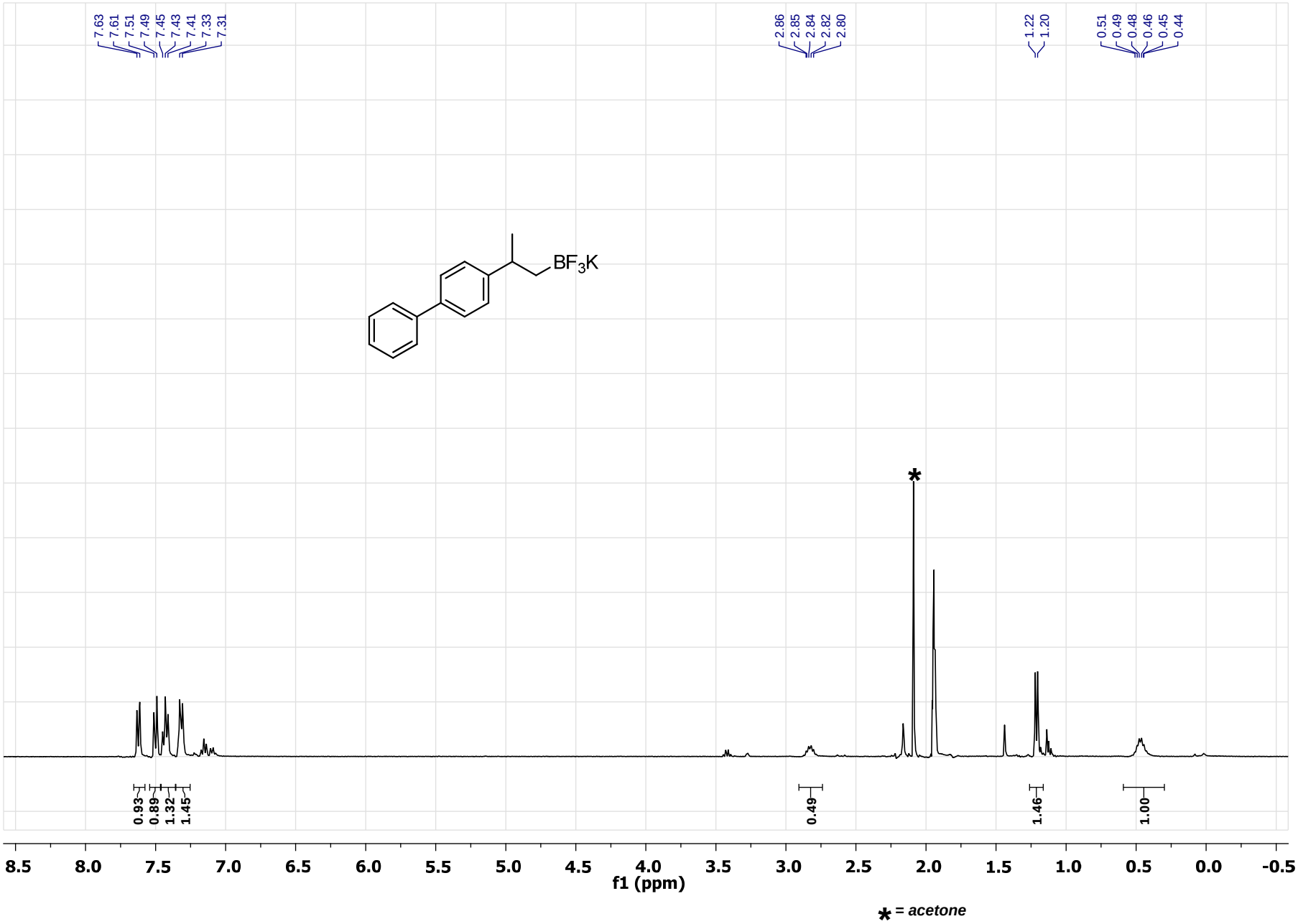

120.72
120.65
77.38
77.06
76.74
66.49
66.37
40.01
35.29
30.76
30.62
29.83
27.70
27.24
25.47
23.51
13.71
13.28
(R)
OH
40.19
40.01
35.29
35.14
43 42 41 40 39 38 37 36 35 34
f1 (ppm)
135 125 115 105 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)

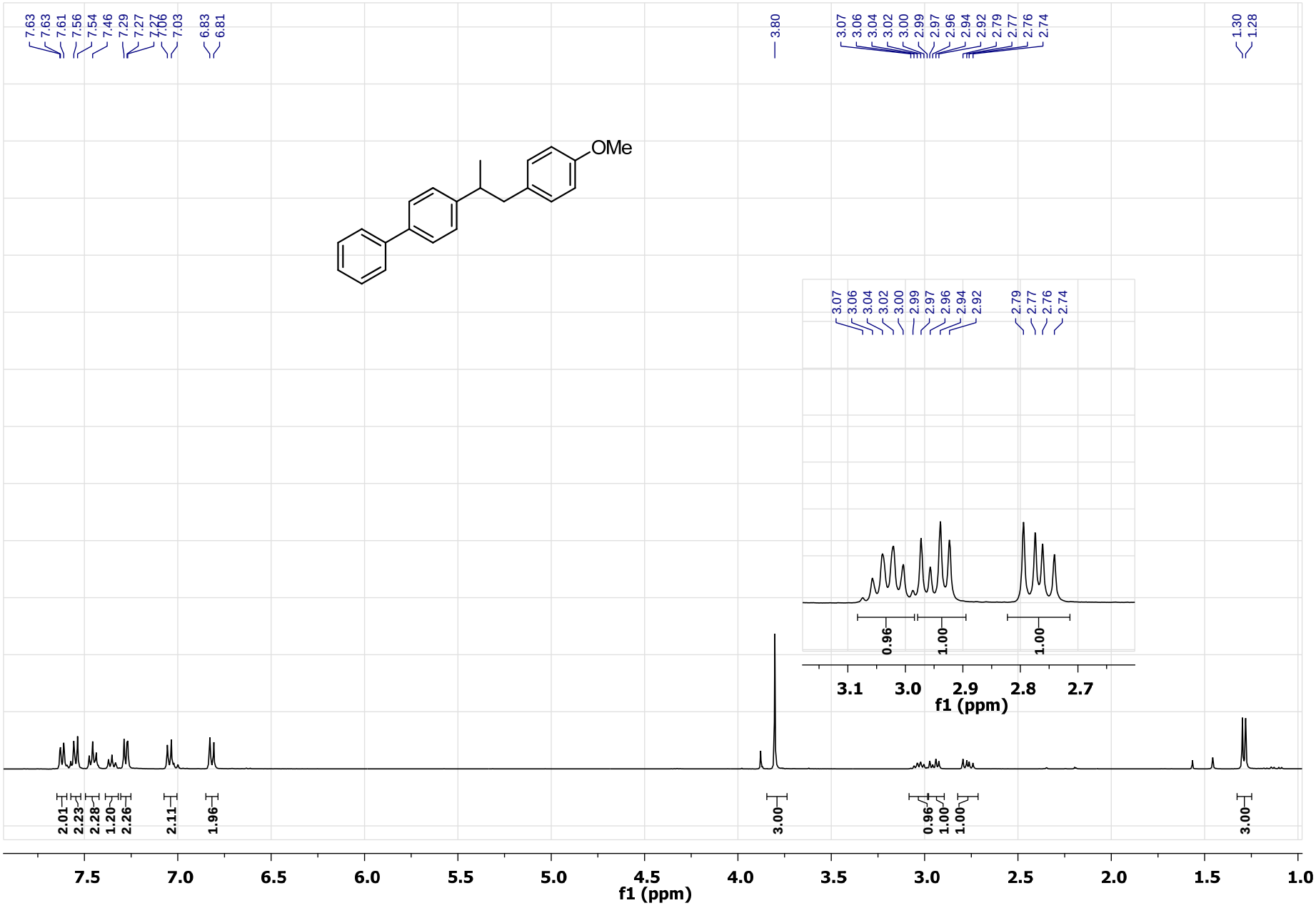

7.62
7.60
7.55
7.53
7.47
7.45
7.43
7.36
7.34
1.47
1.38
1.36
1.35
1.20
O
B
O
*
2.08
2.05
2.18
2.94
1.00
3.30
14.79
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)
* = cyclohexane

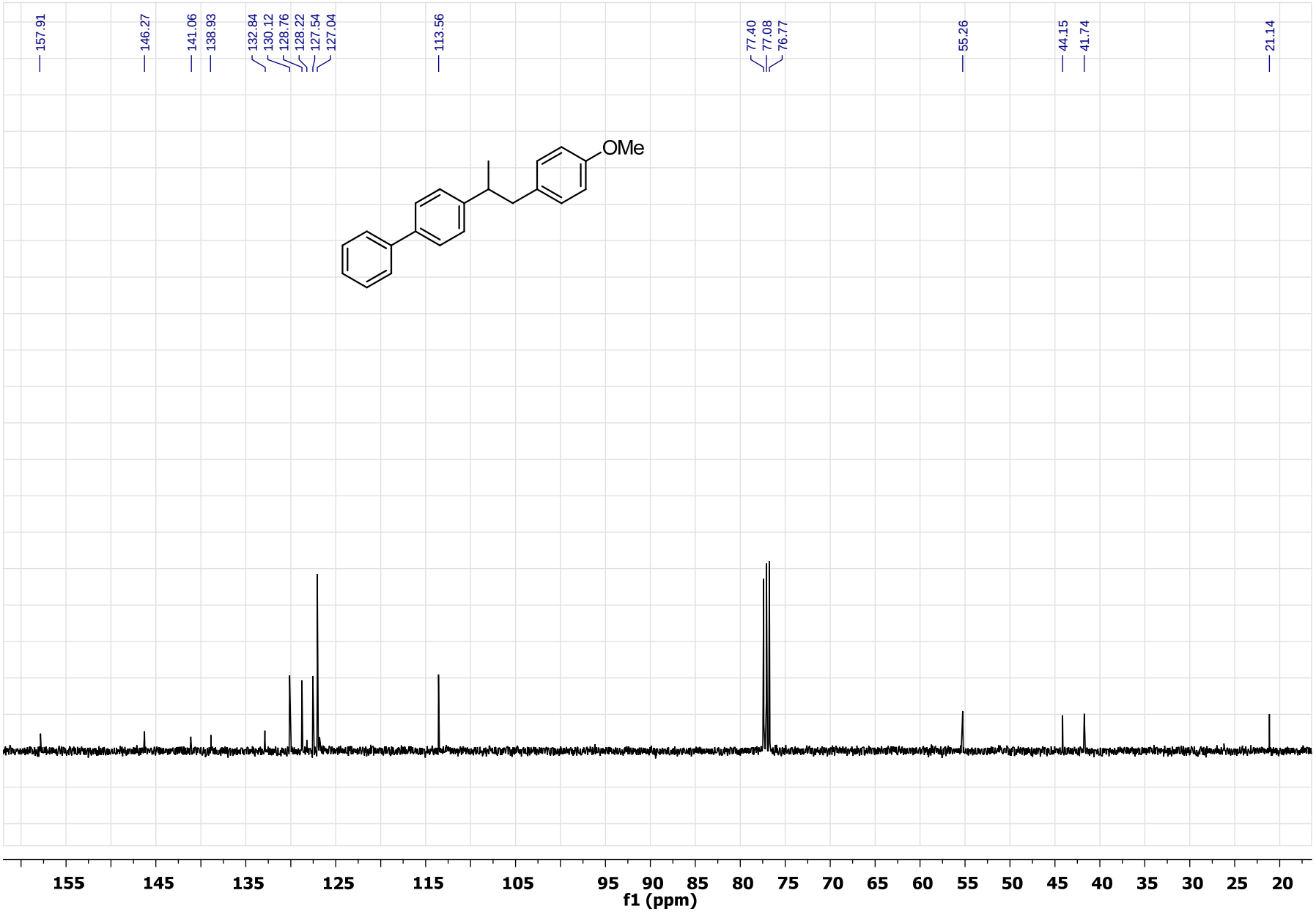

148.49
141.36
138.73
134.89
131.38
128.80
127.83
127.19
127.05
83.11
35.61
25.00
24.82
21.37
O
B
O
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
f1 (ppm)

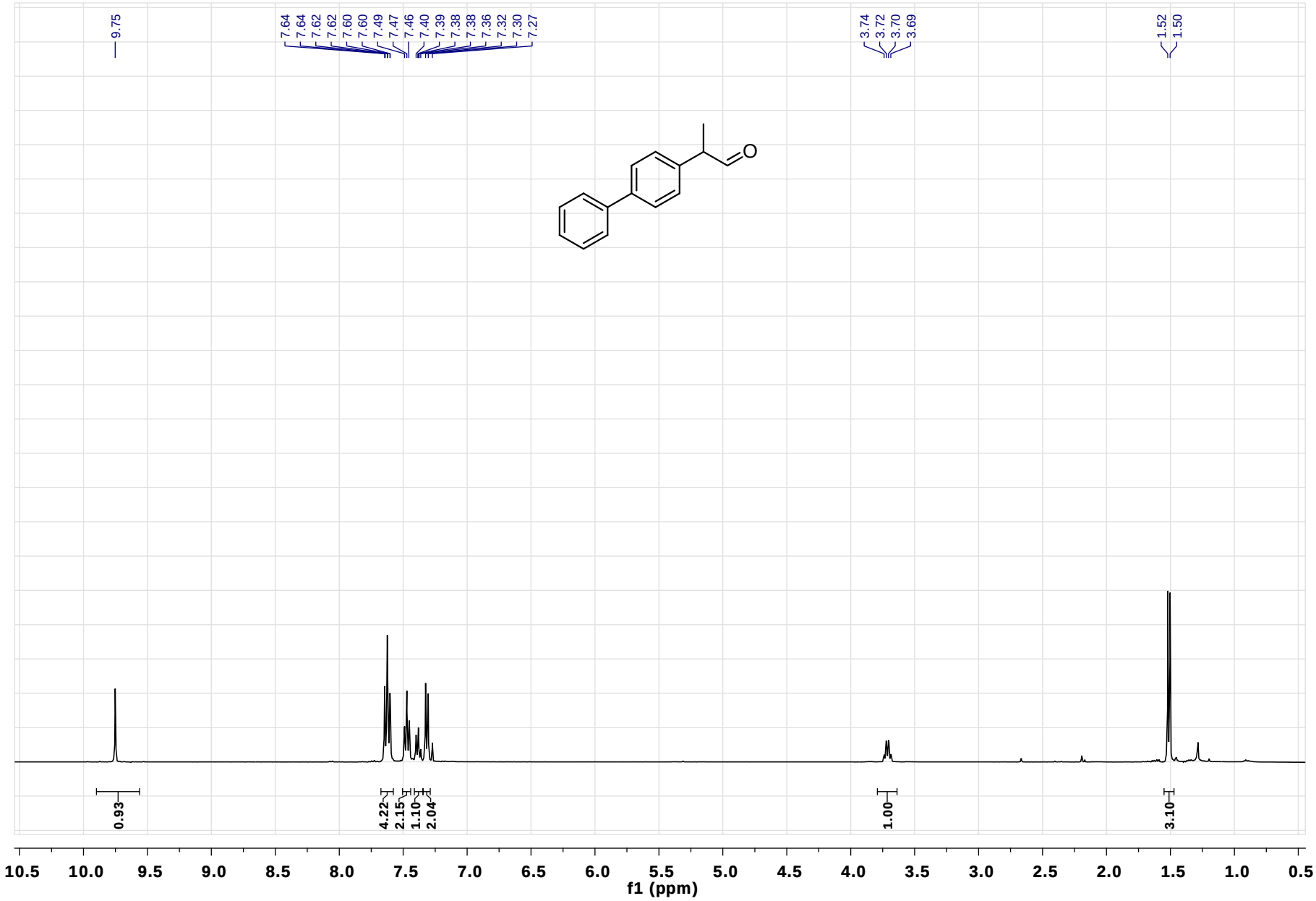

7.62
7.60
7.58
7.49
7.47
7.45
7.39
7.37
7.36
7.34
3.78
3.77
3.75
3.07
3.06
3.02
3.00
2.99
1.54
1.35
1.34
OH
3.98
2.01
3.03
2.02
1.00
1.05
3.07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

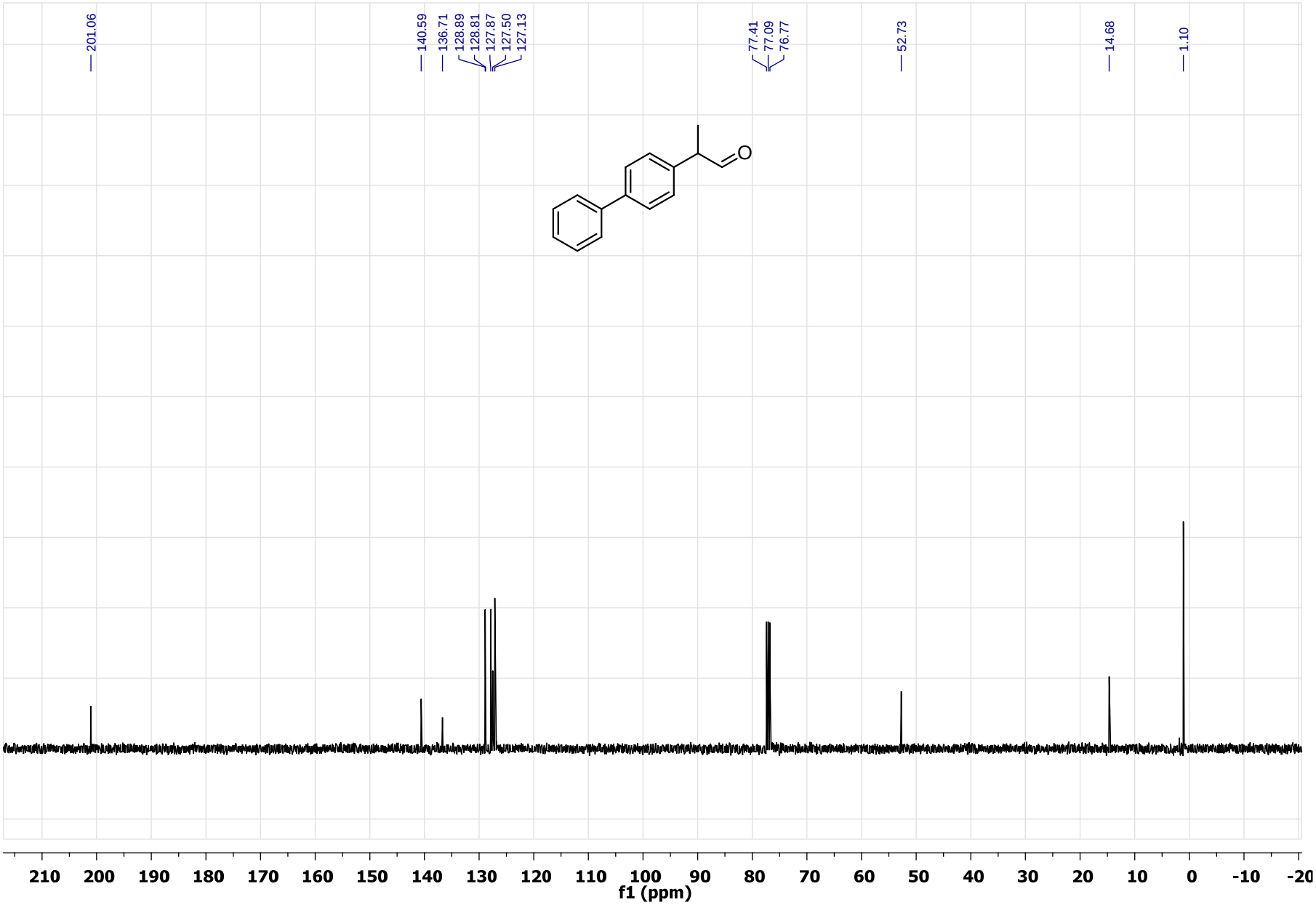

142.84
140.97
139.70
128.83
127.98
127.44
127.24
127.10
68.74
42.18
17.68
OH
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
f1 (ppm)

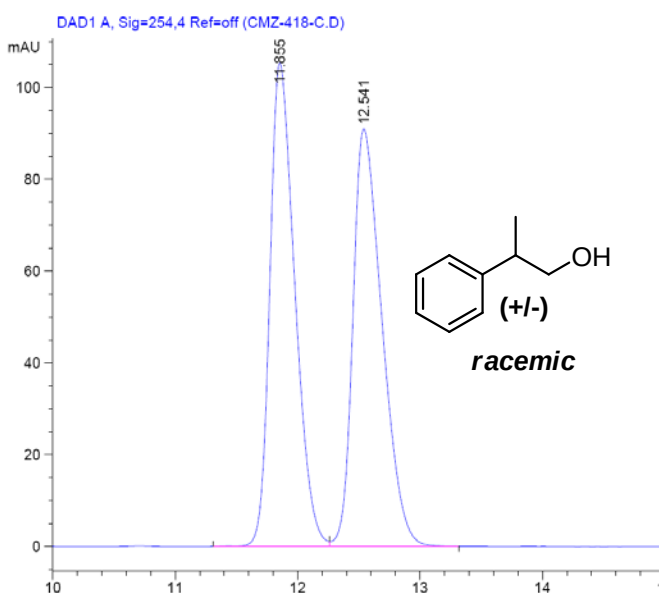

7.63
7.61
7.51
7.49
7.45
7.43
7.41
7.33
7.31
2.86
2.85
2.84
2.82
2.80
1.22
1.20
0.51
0.49
0.48
0.46
0.45
0.44
BF3K
*
0.93
0.89
1.32
1.45
0.49
1.46
1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
* = acetone

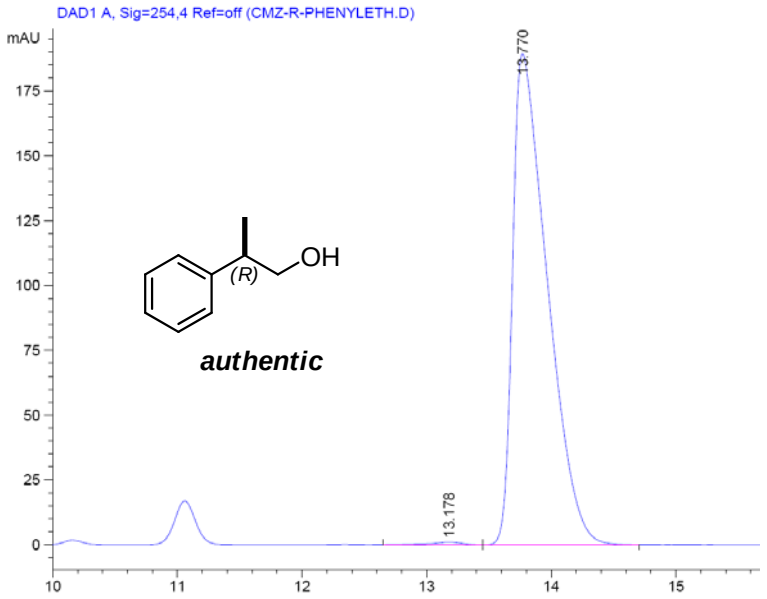

7.63
7.63
7.61
7.56
7.54
7.46
7.29
7.27
7.07
7.06
7.03
6.83
6.81
3.80
3.07
3.06
3.04
3.02
3.00
2.99
2.97
2.96
2.94
2.92
2.79
2.77
2.76
2.74
1.30
1.28
OMe
0.96
1.00
1.00
3.1
3.0
2.9
2.8
2.7
f1 (ppm)
2.01
2.23
2.28
1.20
2.26
2.11
1.96
3.00
0.96
1.00
1.00
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)


157.91
146.27
141.06
138.93
132.84
130.12
128.76
128.22
127.54
127.04
113.56
77.40
77.08
76.77
55.26
44.15
41.74
21.14
OMe
155
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
f1 (ppm)

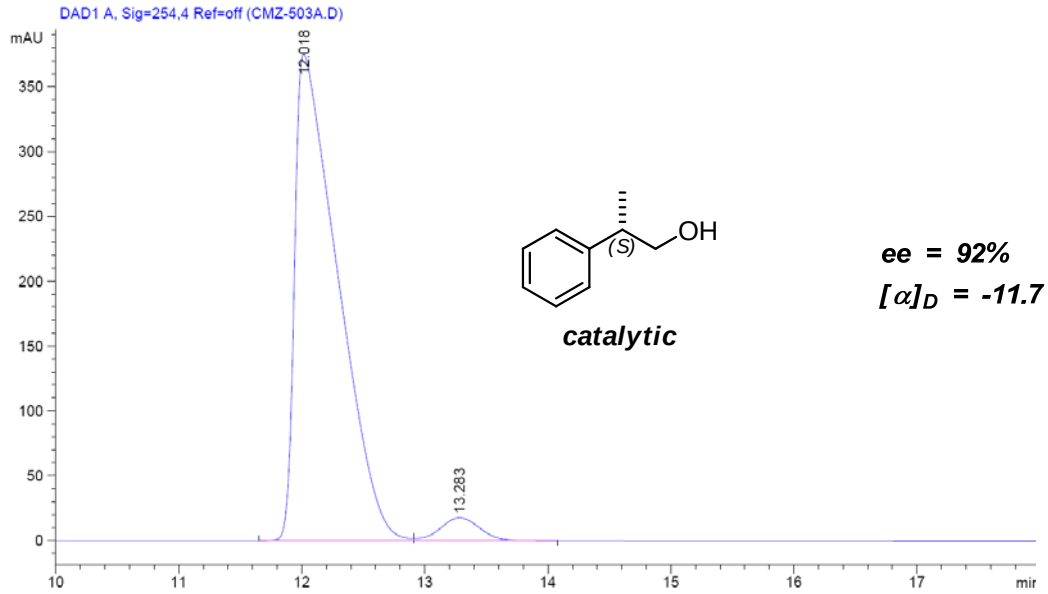

9.75
7.64
7.64
7.62
7.62
7.60
7.60
7.49
7.47
7.46
7.40
7.39
7.38
7.38
7.36
7.32
7.30
7.27
3.74
3.72
3.70
3.69
1.52
1.50
O
0.93
4.22
2.15
1.10
2.04
1.00
3.10
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


201.06
140.59
136.71
128.89
128.81
127.87
127.50
127.13
77.41
77.09
76.77
52.73
14.68
1.10
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)





HPLC conditions: *column: Chiralpak AS-H; 98/2 (Hexanes:i-PrOH); 1 mL/min; λ = 254 nm; $rt_{(R)}$ = 11.9 min., $rt_{(S)}$ = 12.5 min.*

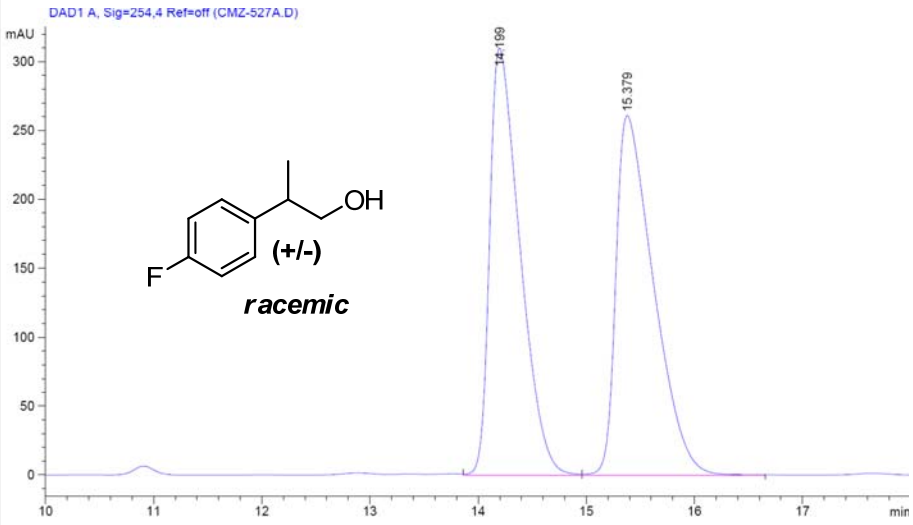


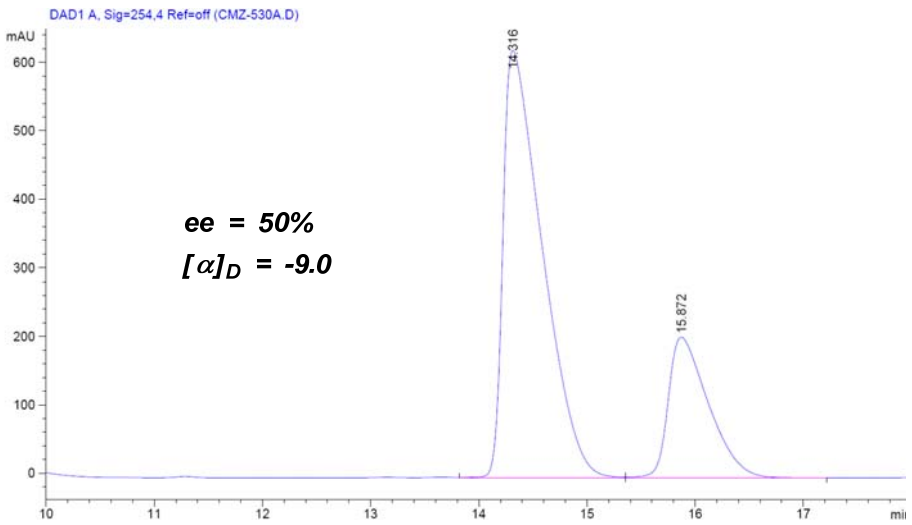
ee = 92%

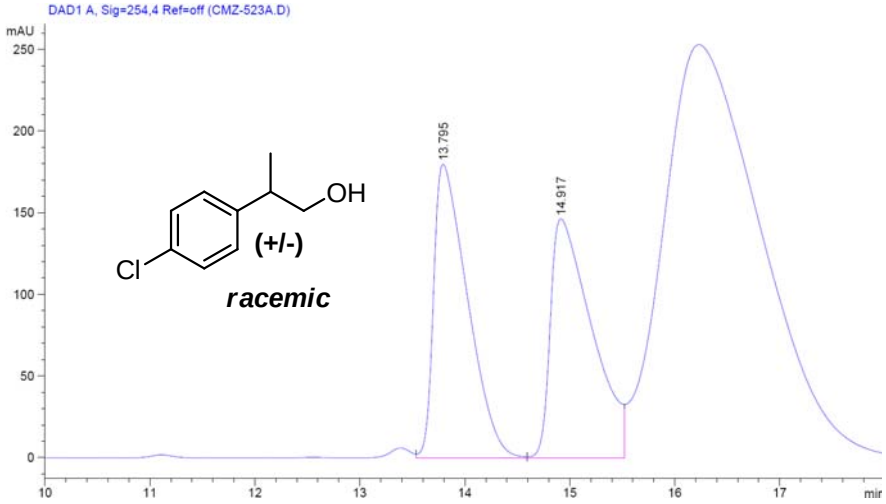
$[\alpha]_D$ = -11.7 (of 'Bpin' derivative)

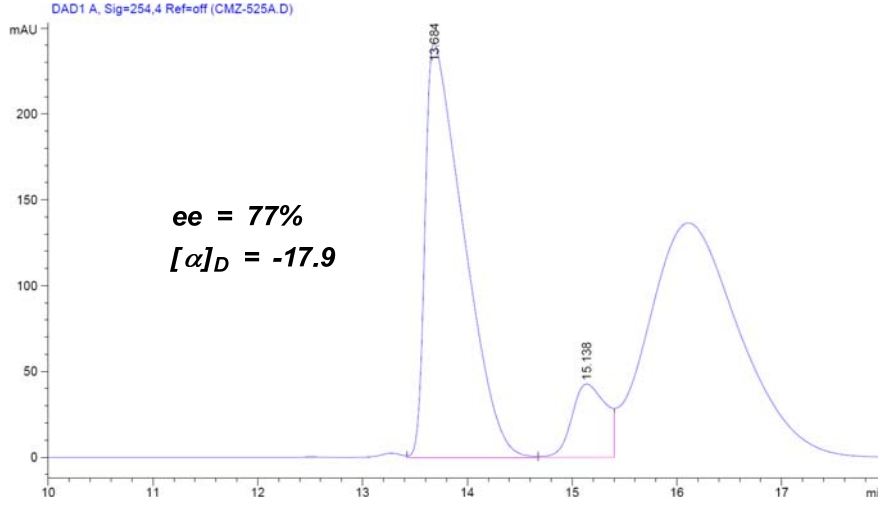
All $[\alpha]_D$ are given for the R-Bpin derivatives
See text of the SI for details

HPLC conditions: ***column: Chiralpak AS-H; 98/2 (Hexanes:i-PrOH); 1 mL/min; λ = 254 nm; $rt_{(1)}$ = 14.2 min., $rt_{(2)}$ = 15.4 min.***



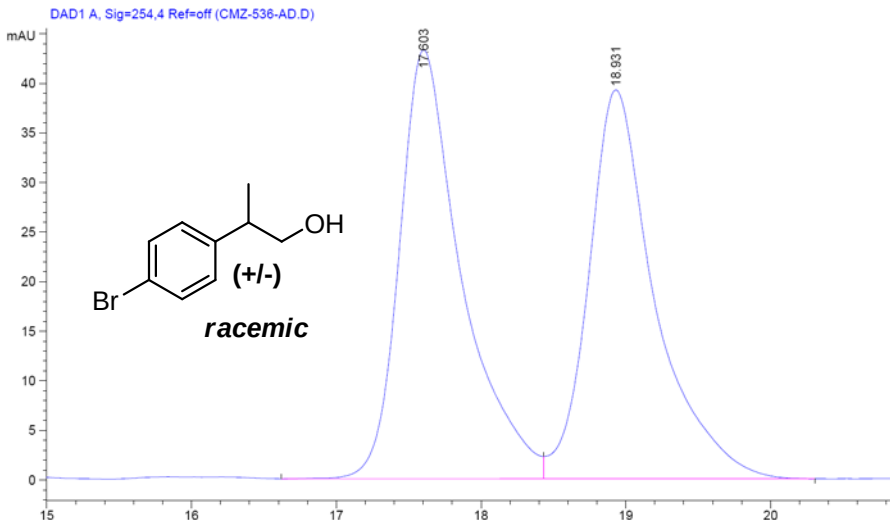


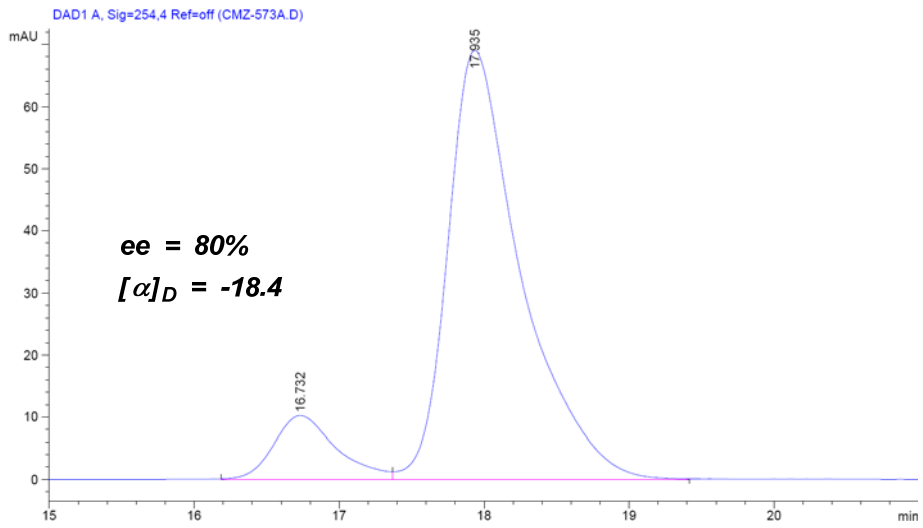


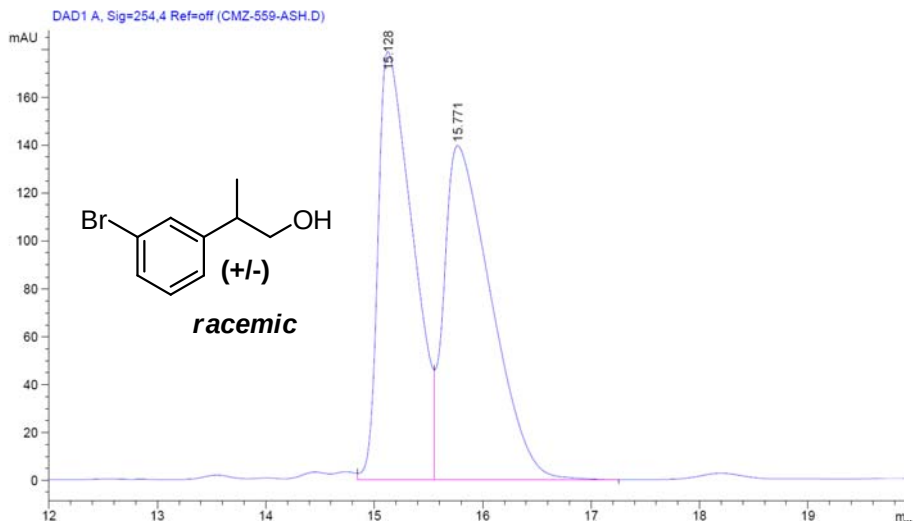


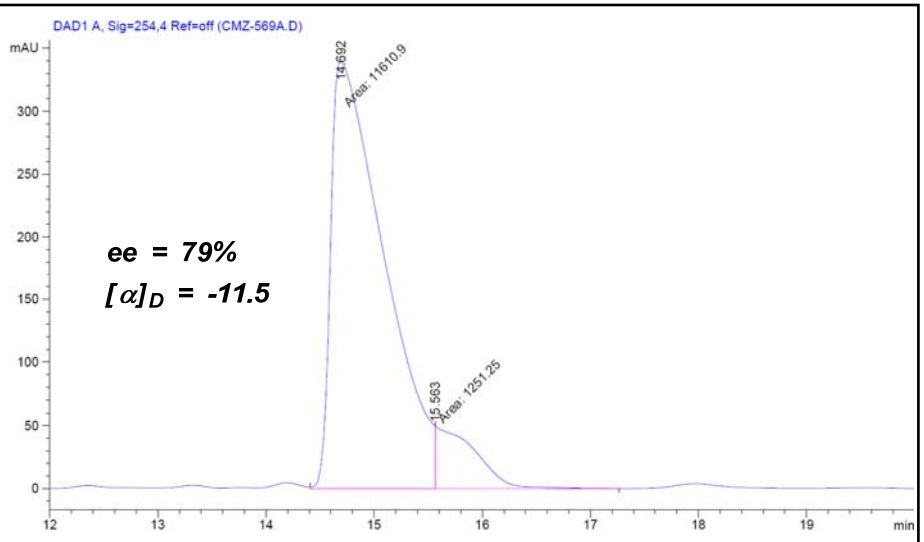
HPLC conditions: ***column: Chiralpak AS-H; 98/2 (Hexanes:i-PrOH); 1 mL/min; λ = 254 nm; $rt_{(1)}$ = 13.8 min., $rt_{(2)}$ = 14.9 min.***

HPLC conditions: ***column: Chiralpak AD; 98/2 (Hexanes:i-PrOH); 1 mL/min; λ = 254 nm; $rt_{(1)}$ = 17.6 min., $rt_{(2)}$ = 18.9 min.***



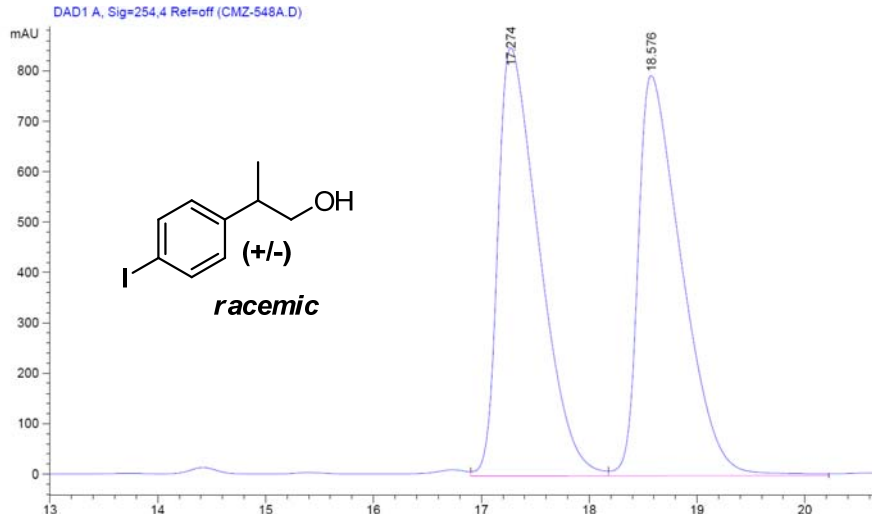


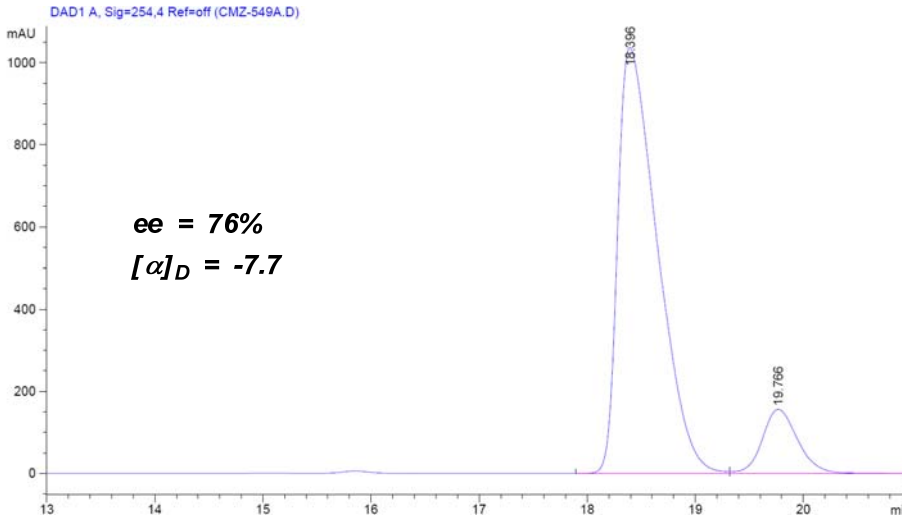


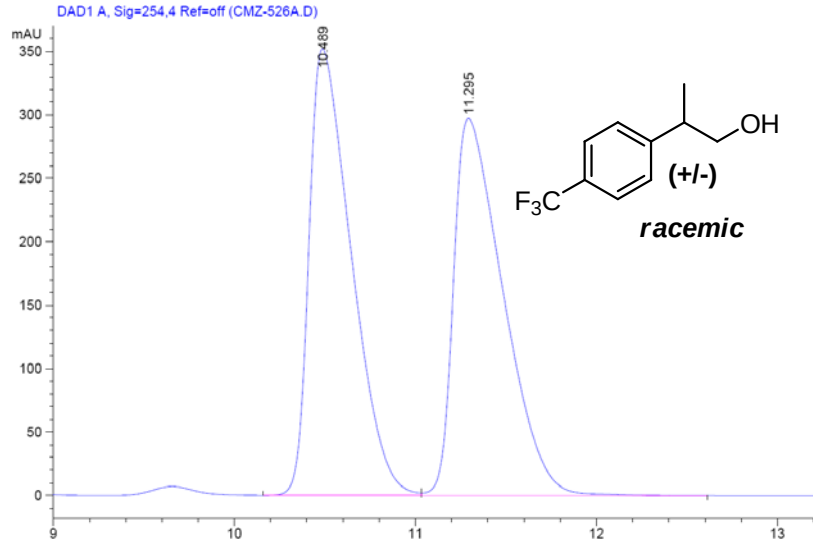


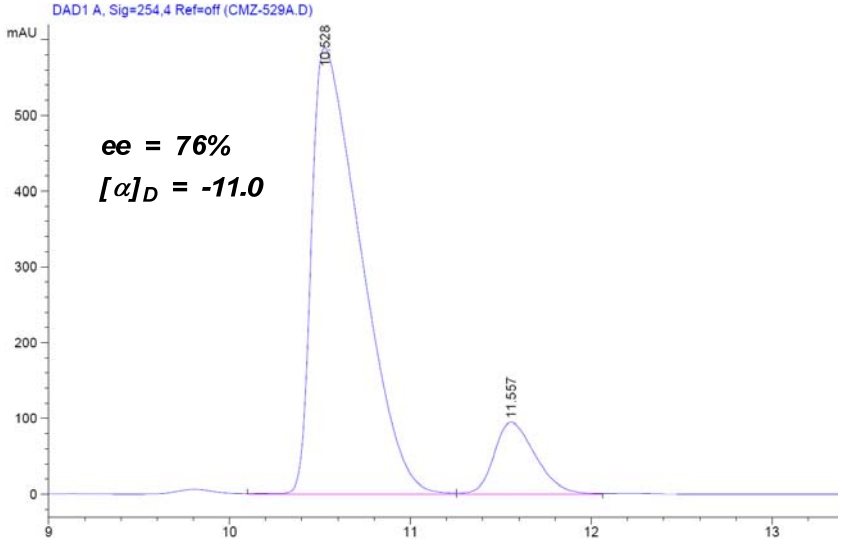
HPLC conditions: ***column: Chiralpak AS-H; 98/2 (Hexanes:i-PrOH); 1 mL/min; λ = 254 nm; $rt_{(1)}$ = 15.1 min., $rt_{(2)}$ = 15.8 min.***

HPLC conditions: ***column: Chiralpak AS-H; 98/2 (Hexanes:i-PrOH); 1 mL/min; λ = 254 nm; $rt_{(1)}$ = 17.3 min., $rt_{(2)}$ = 18.6 min.***



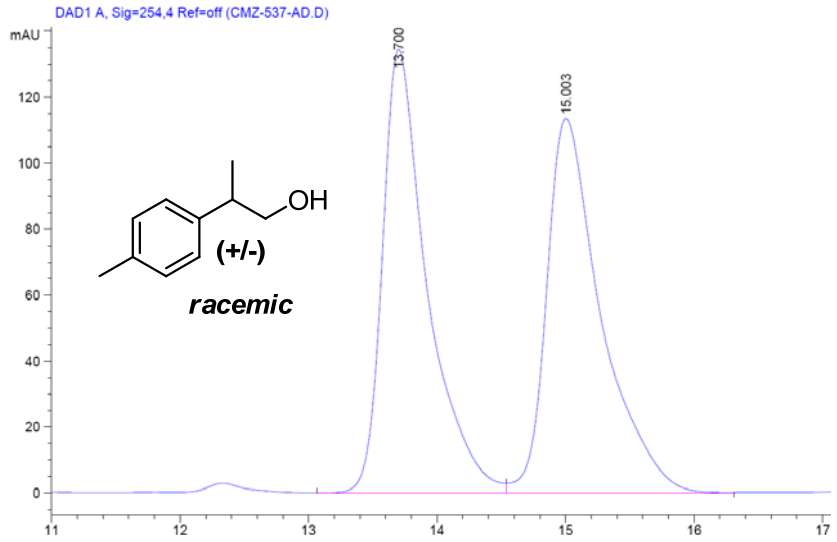


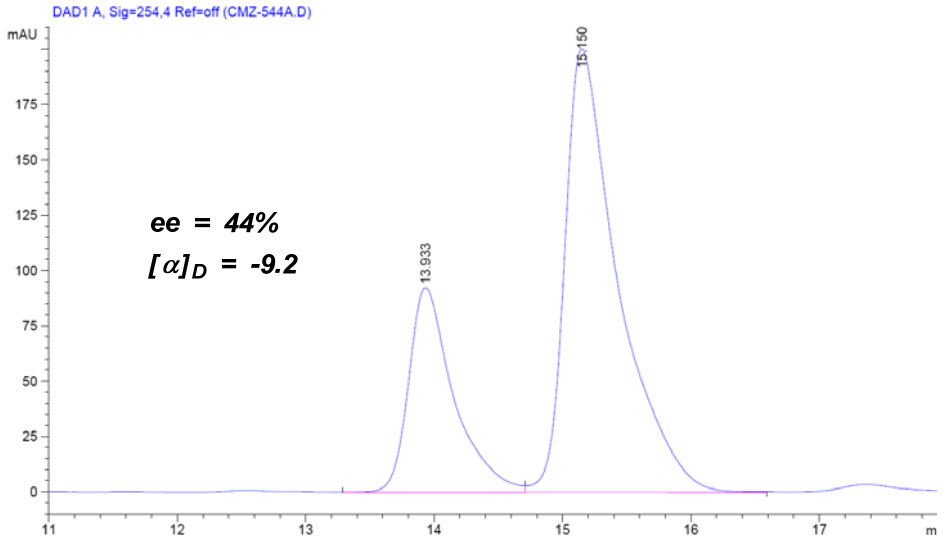


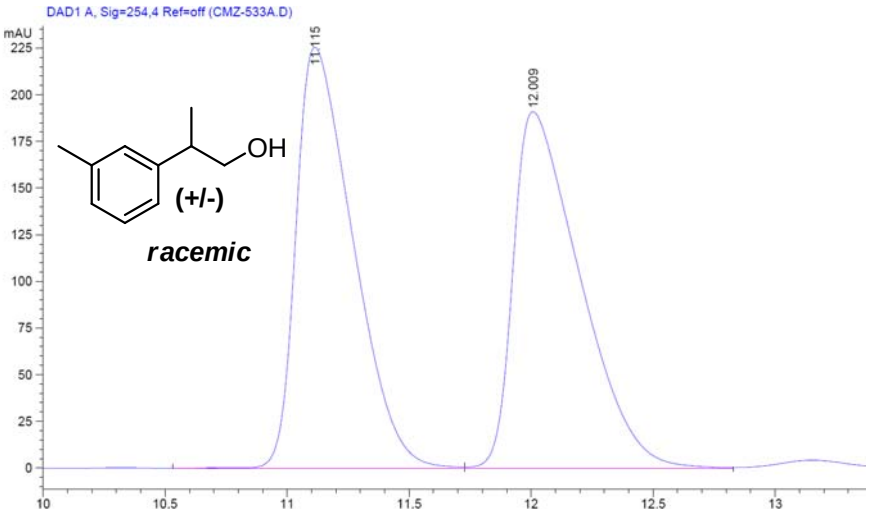


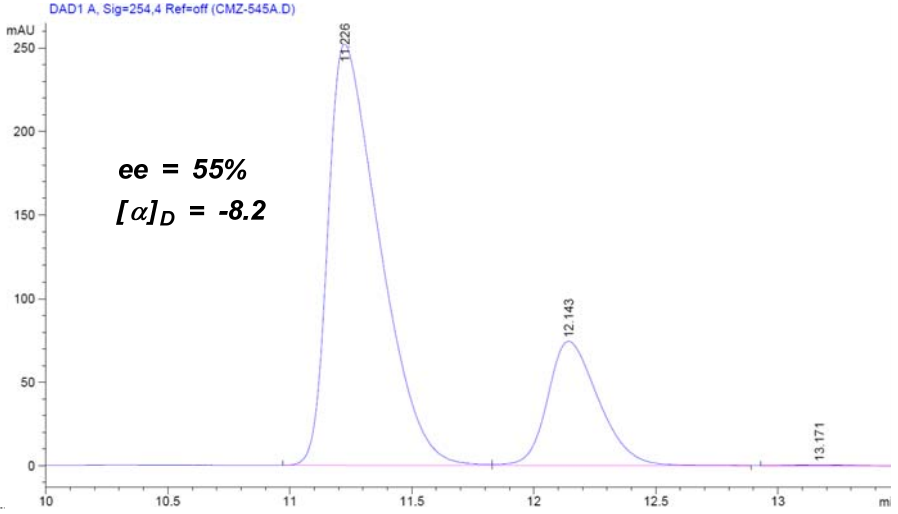
HPLC conditions: ***column: Chiralpak AS-H; 98/2 (Hexanes:i-PrOH); 1 mL/min; λ = 254 nm; $rt_{(1)}$ = 10.5 min., $rt_{(2)}$ = 11.3 min.***

HPLC conditions: ***column: Chiralpak AD; 98/2 (Hexanes:i-PrOH); 1 mL/min; λ = 254 nm; $rt_{(1)}$ = 13.7 min., $rt_{(2)}$ = 15.0 min.***



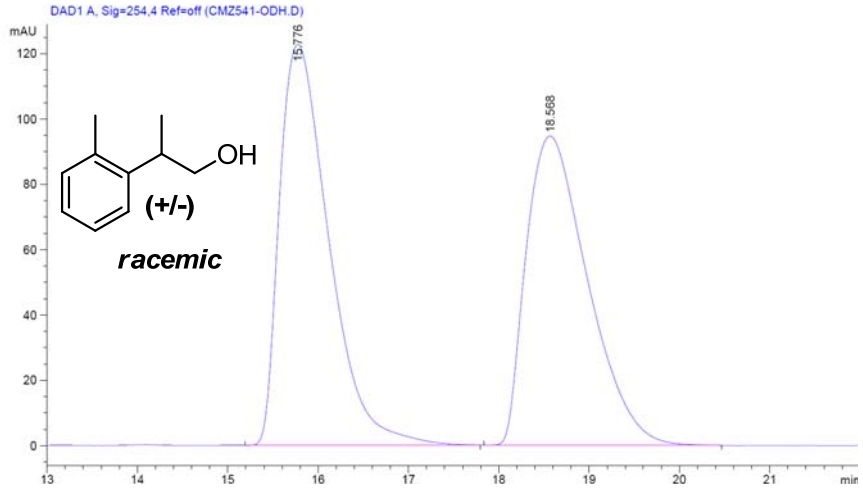




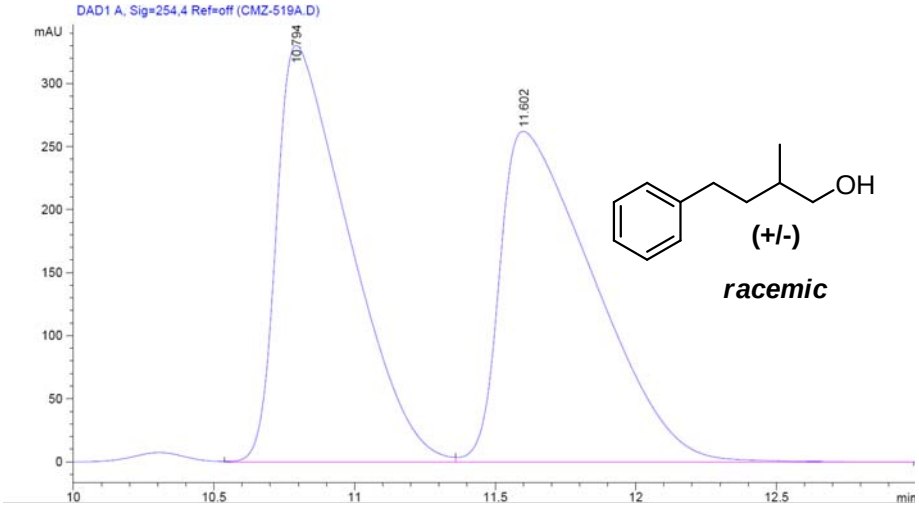


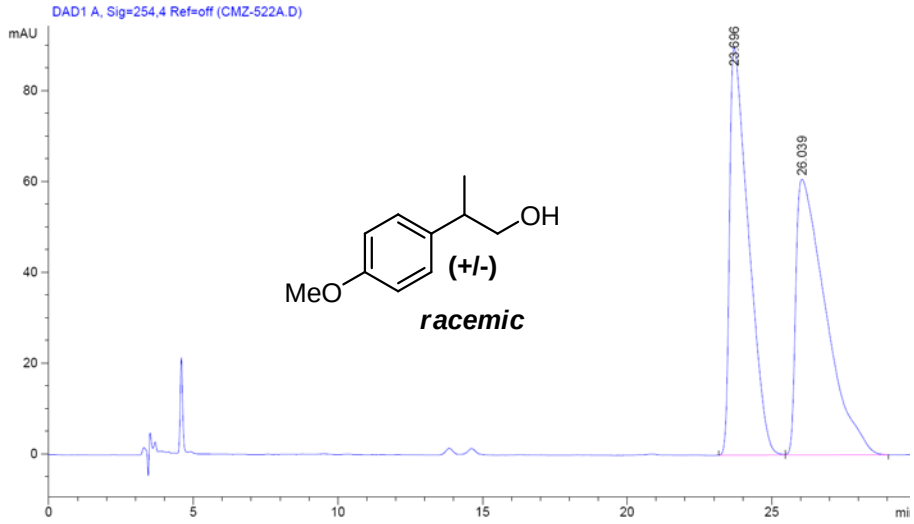
HPLC conditions: ***column: Chrialpak AS-H; 98/2 (Hexanes:i-PrOH); 1 mL/min; λ = 254 nm; $rt_{(1)}$ = 11.1 min., $rt_{(2)}$ = 12.0 min.***

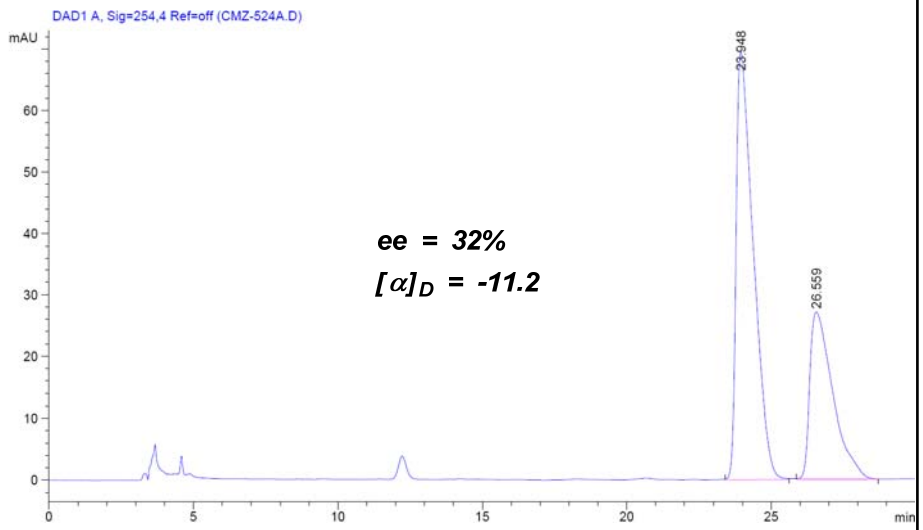
HPLC conditions: ***column: Chiralpak AD; 98/2 (Hexanes:i-PrOH); 1 mL/min; λ = 254 nm; $rt_{(1)}$ = 15.8 min., $rt_{(2)}$ = 18.6 min.***



HPLC conditions: ***column: Chiralpak AS-H; 98/2 (Hexanes:i-PrOH); 1 mL/min; λ = 254 nm; $rt_{(1)}$ = 10.8 min., $rt_{(2)}$ = 11.6 min.***

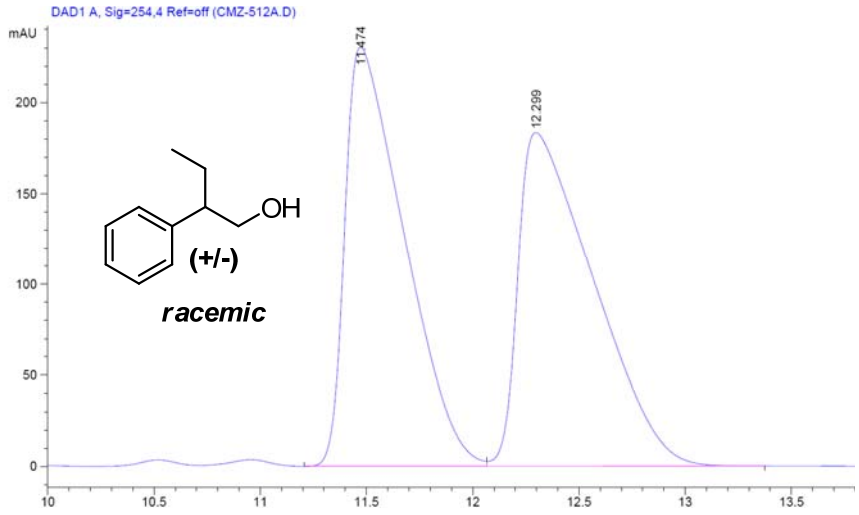


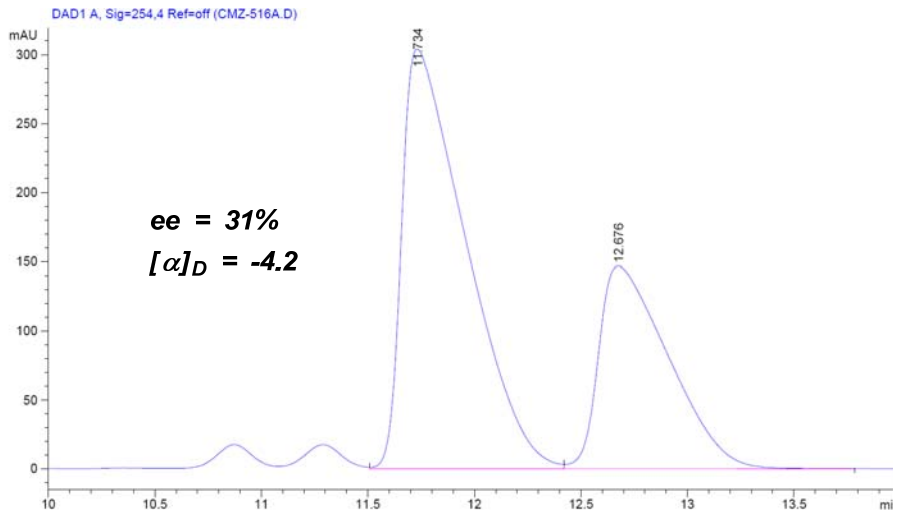


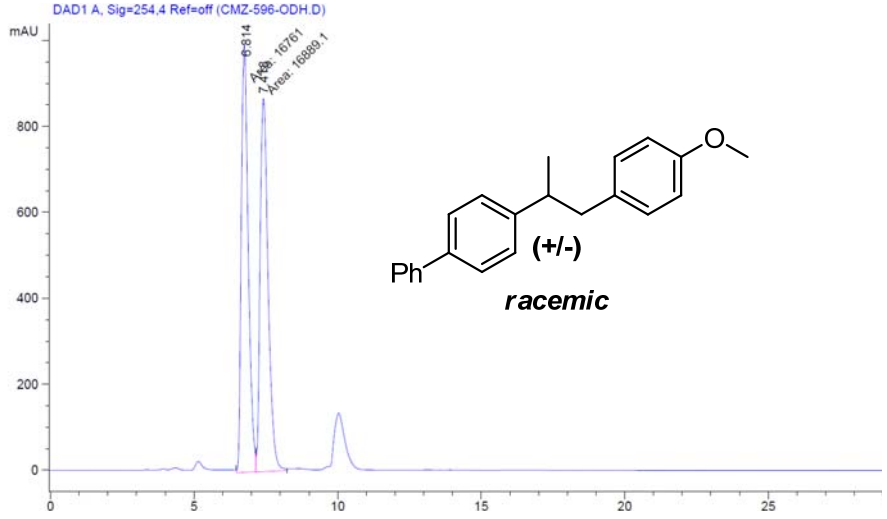


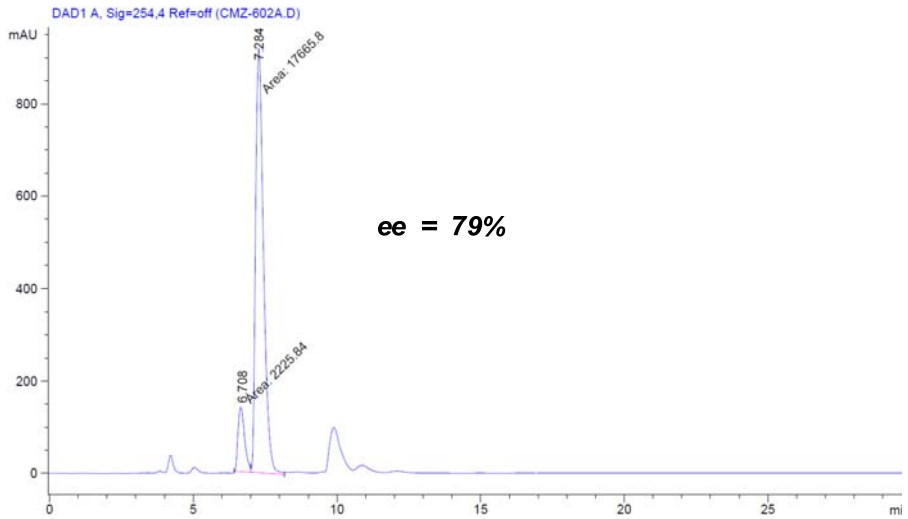
HPLC conditions: ***column: Chiralpak AS-H; 98/2 (Hexanes:i-PrOH); 1 mL/min; λ = 254 nm; $rt_{(1)}$ = 23.7 min., $rt_{(2)}$ = 26.0 min.***

HPLC conditions: ***column: Chiralpak AS-H; 98/2 (Hexanes:i-PrOH); 1 mL/min; λ = 254 nm; $rt_{(1)}$ = 11.5 min., $rt_{(2)}$ = 12.3 min.***



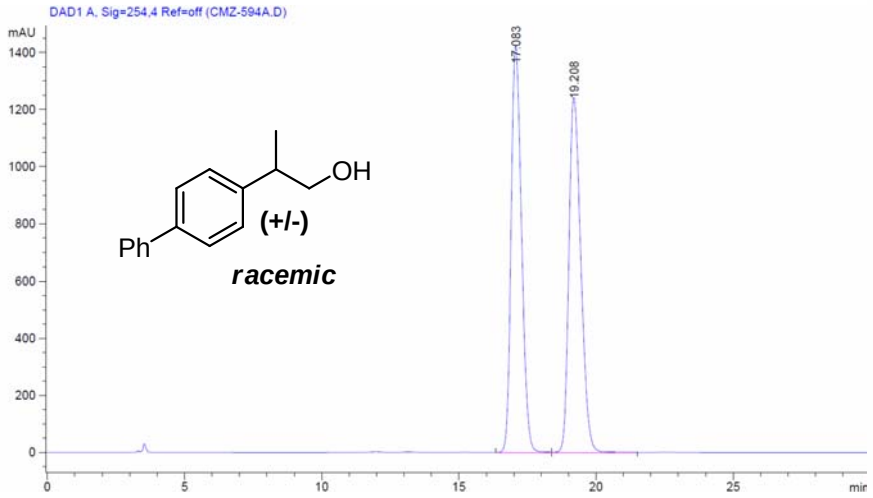


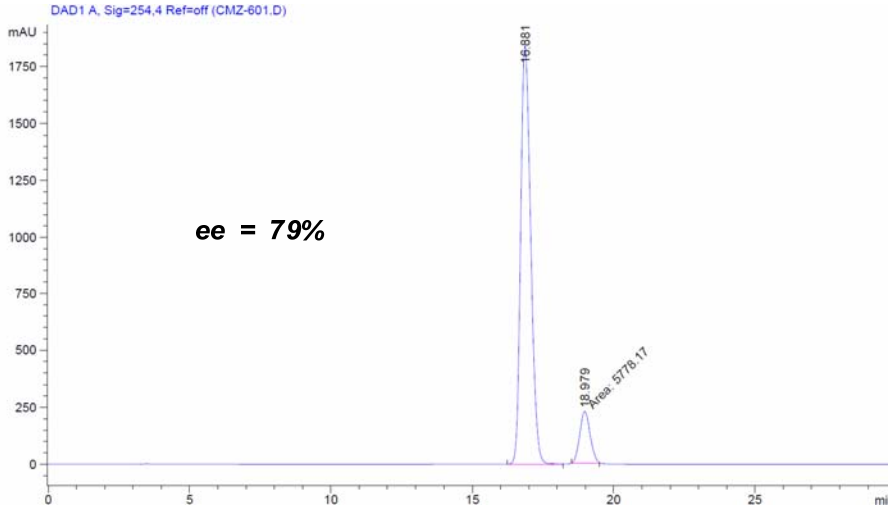


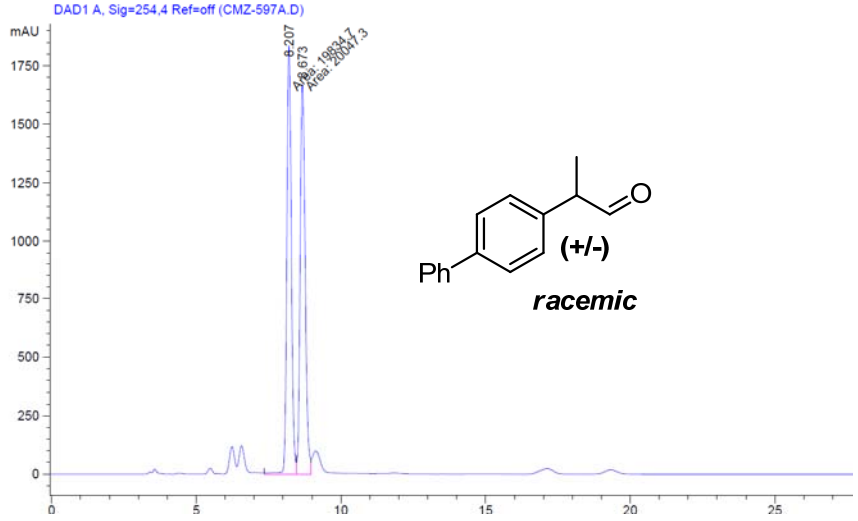


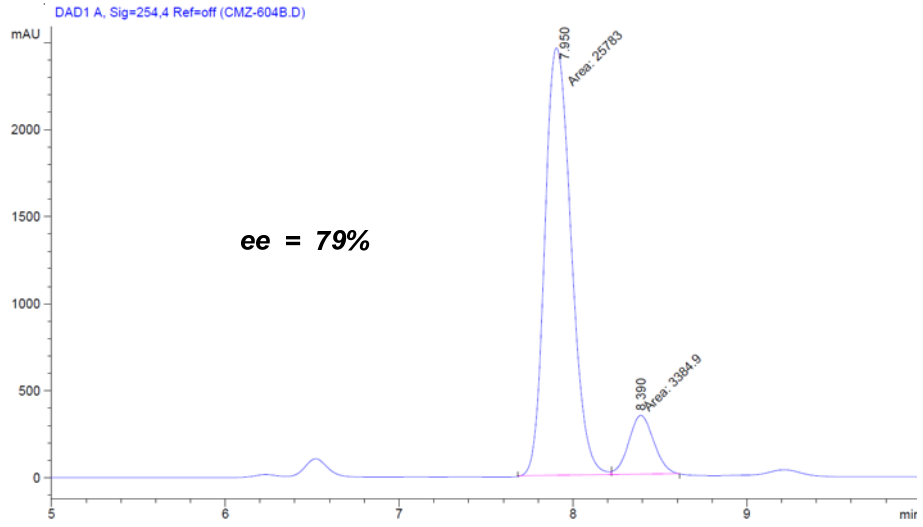
HPLC conditions: ***column: Chiralpak OD-H; 98/2 (Hexanes:i-PrOH); 1 mL/min; λ = 254 nm; $rt_{(1)}$ = 6.7 min., $rt_{(2)}$ = 7.3 min.***

HPLC conditions: ***column: Chiralpak AS-H; 98/2 (Hexanes:i-PrOH); 1 mL/min; λ = 254 nm; $rt_{(1)}$ = 16.9 min., $rt_{(2)}$ = 18.9 min.***









HPLC conditions: ***column: Chiralpak AS-H; 98/2 (Hexanes:i-PrOH); 1 mL/min; λ = 254 nm; $rt_{(1)}$ = 8.2 min., $rt_{(2)}$ = 8.7 min.***