

Supplementary Material

Insertion of chiral carbenoids into pinanediol boronic esters

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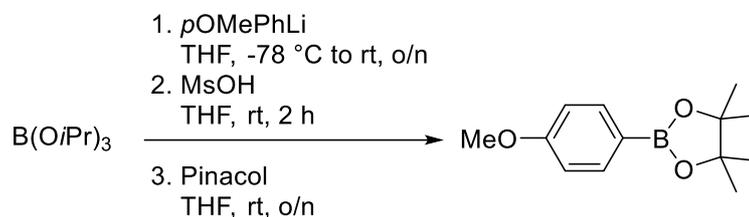
General Information

All reactions with non-aqueous media or reagents were performed under argon atmosphere using dried solvents and Schlenk-line techniques. Commercially available solvents and reagents were used as received without additional purification unless stated otherwise. These were obtained from *Abcr GmbH*, *Fisher Scientific*, *Carbolution GmbH*, *Fluorochem*, *Sigma Aldrich*, and *TCl*. Deuterated NMR solvents were received from *Deutero GmbH*. Grignard reagents were titrated using salicylaldehyde phenylhydrazone, following the method presented by Love and Jones.¹ Organolithium reagents were titrated using *N*-benzylbenzamide. THF, Et₂O and dichloromethane were dried with solvent purifier *SPS 5* by *MBRAUN*. Diisopropyl amine was dried over CaH₂ and distilled under Ar atmosphere. CPME and CHCl₃ were dried over 4 Å molecular sieves and stored under Ar atmosphere. Technical grade cyclohexane was distilled at 200 mbar and 40 °C and used for flash column chromatography. For determination of yield by internal Standard, 3% v/v solution of dichloromethane or CPME in CDCl₃ were used. Solvents were removed on a rotary evaporator under reduced pressure at 40 °C, if not stated otherwise. For thin-layer chromatography (TLC), *Polygram SIL G/UV254* silica plates from *Macherey-Nagel* were used. Spot visualization was performed using 254 and 365 nm or KMnO₄ stain. Flash-chromatography was carried out by using silica gel *MN 60 M* (0.04–0.063 mm) from *Macherey-Nagel*. High-resolution electrospray (ESI) mass spectra were measured on a *Bruker maXis 4G* spectrometer with data processing *Bruker Data Analysis* software. FT-IR spectra were measured using a *Jasco FT/IR-4600* spectrometer. NMR spectra were measured on a *Bruker AVNEO400* (¹H: 400 MHz, ¹³C: 101 MHz) spectrometer. All measurements were performed at room temperature, ¹³C-NMR spectra were recorded with proton decoupling. Spectra are given with frequency, solvent. Chemical shifts are given in parts per million (ppm). Coupling constants *J* are given in Hertz (Hz). The undeuterated residue of the solvent served as internal standard. For the assignment of ¹H-NMR, following abbreviations are used: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), m (multiplet), bs (broad singlet), dd (doublet of doublet), sxt (sextet), hpt (heptet), ddd (doublet of doublet of doublet). For the complete assignment of ¹H-NMR and ¹³C-NMR signals, 2D spectra such as HSQC, HMBC and COSY were employed. For ¹³C-NMR, the carbon atom adjacent to boron is unobservable due to carbon-boron spin-spin coupling and partially relaxed scalar coupling between boron and carbon.² All raw-data were processed and analyzed by using the *Bruker TopSpin 4.4.0 software*.

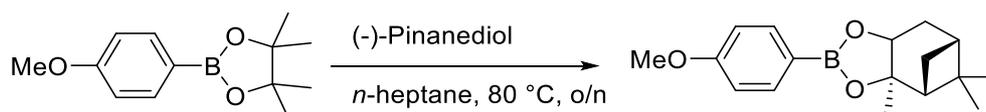
Synthesis of the miscellaneous Compounds

Preparation of general compounds

p-Anisyl(-)-pinanediol boronic ester

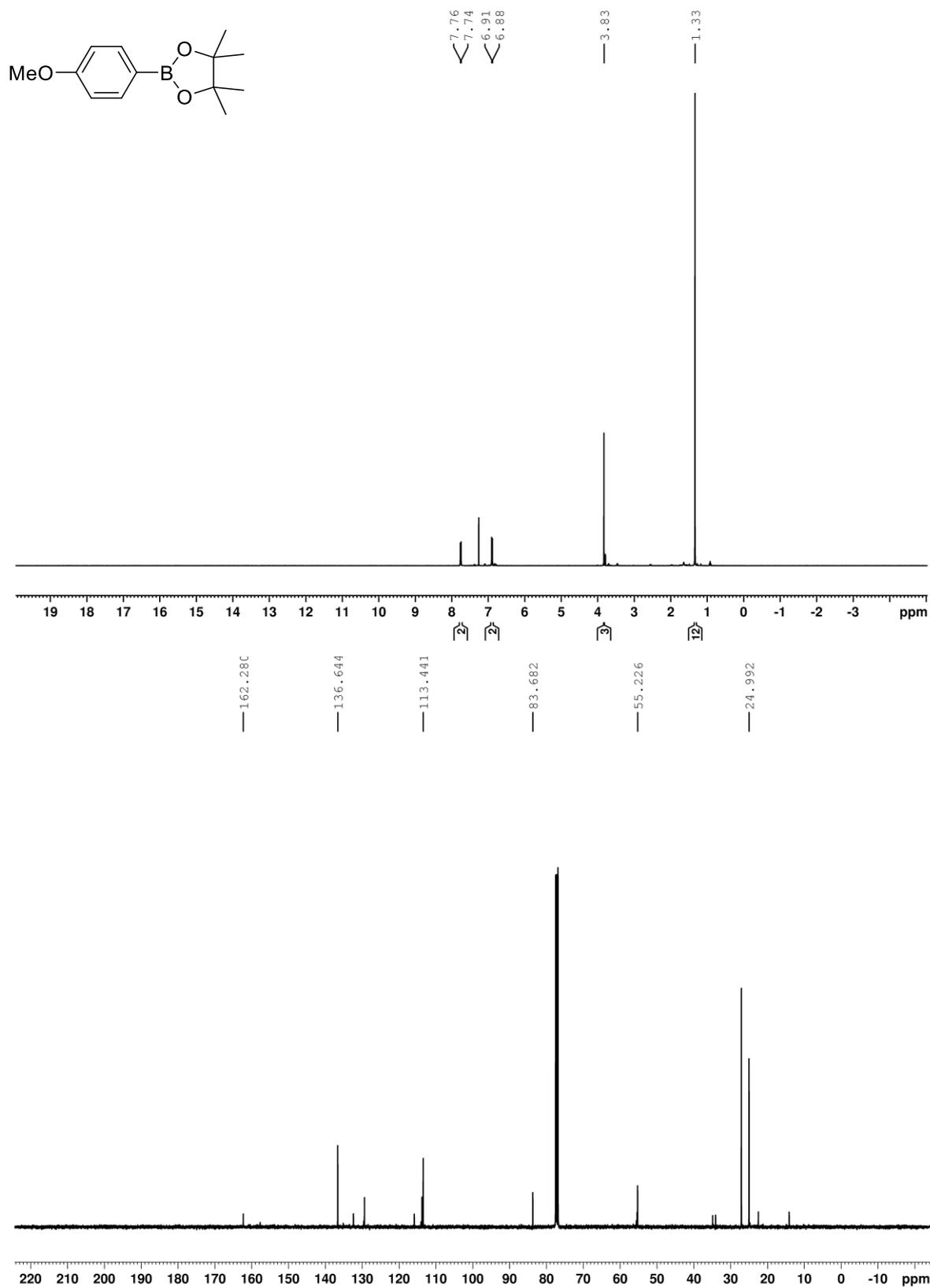


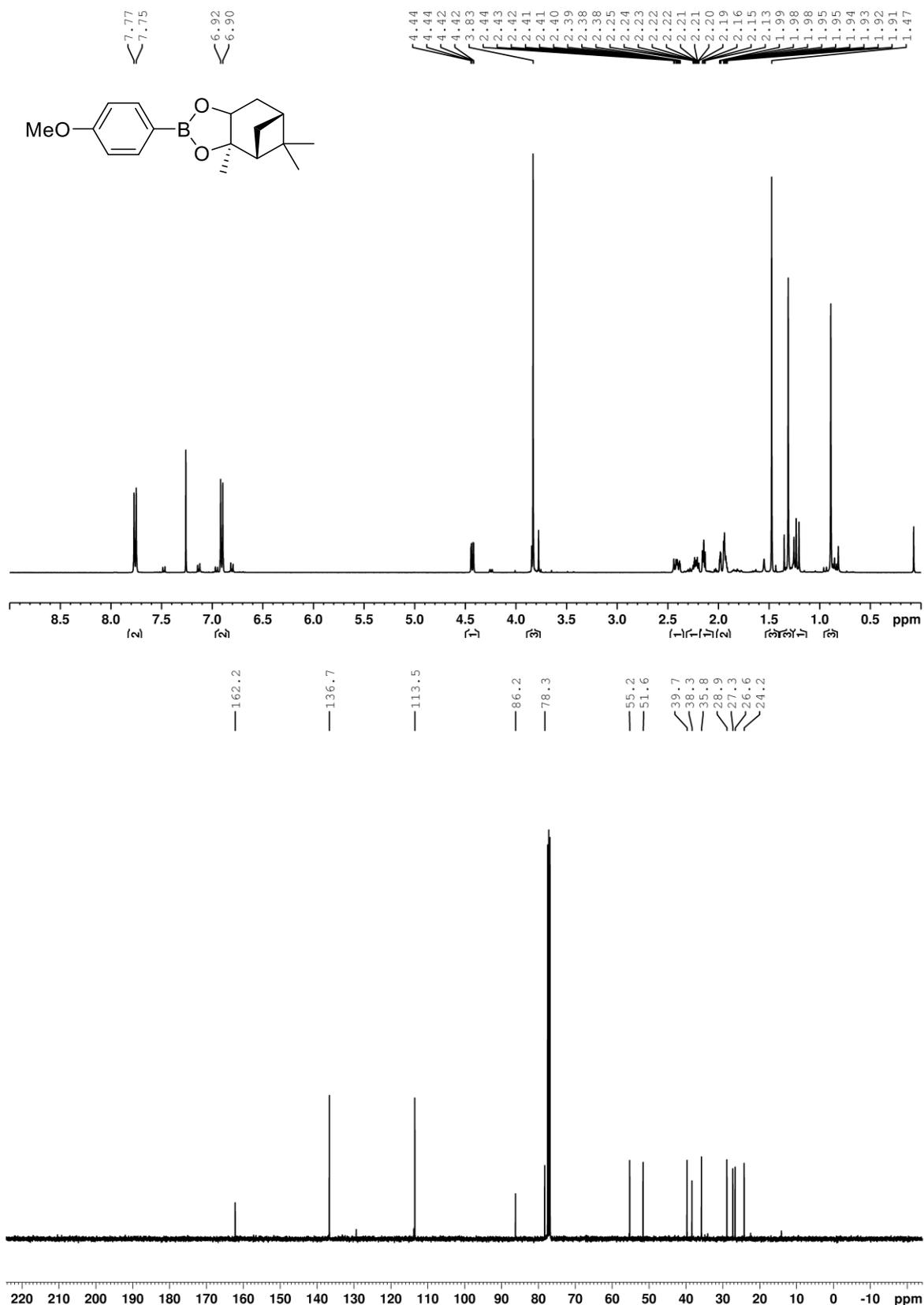
Bromoanisole (9.78 mL, 63.8 mmol, 1.20 eq.) was dissolved in THF (1.2 M) and cooled to -78 °C, before *n*-BuLi (24.9 mL, 58.5 mmol, 1.1 eq., 2.35 M in hexane) was added dropwise through a dropping funnel. The resulting mixture was stirred for 0.5 h at the same temperature before it was added to a 2 M solution of triisopropyl borate (12.3 mL, 53.2 mmol, 1.0 eq.) in THF at -78 °C. The resulting mixture was stirred for 2 h at the same temperature and then for 16 h (overnight) at rt. The mixture was cooled to at 0 °C and methanesulfonic acid (5.55 mL, 106 mmol, 2.0 eq.) was added. Then the mixture stirred for 2 h at rt. Pinacol (6.28 g, 53.2 mmol, 1.0 eq.) was added and the mixture was stirred at rt for 16 h (overnight). The reaction mixture was concentrated under reduced pressure, filtered through a pad of celite and washed with excess Et₂O. The filtrate was washed once with 1 M aq. NaOH. The organic layer was dried over MgSO₄, filtered and concentrated under reduced pressure. The crude product was used for next reaction without further purification. ¹H-NMR (400 MHz, CDCl₃): δ = 7.76–7.74 (m, 2H), 6.91–6.88 (m, 2H), 3.83 (s, 3H), 1.33 (s, 12H) ppm. ¹³C-NMR (100 MHz, CDCl₃): δ = 162.3, 136.6, 113.4, 83.7, 55.2, 25.0 ppm. NMR data complies with published data.³

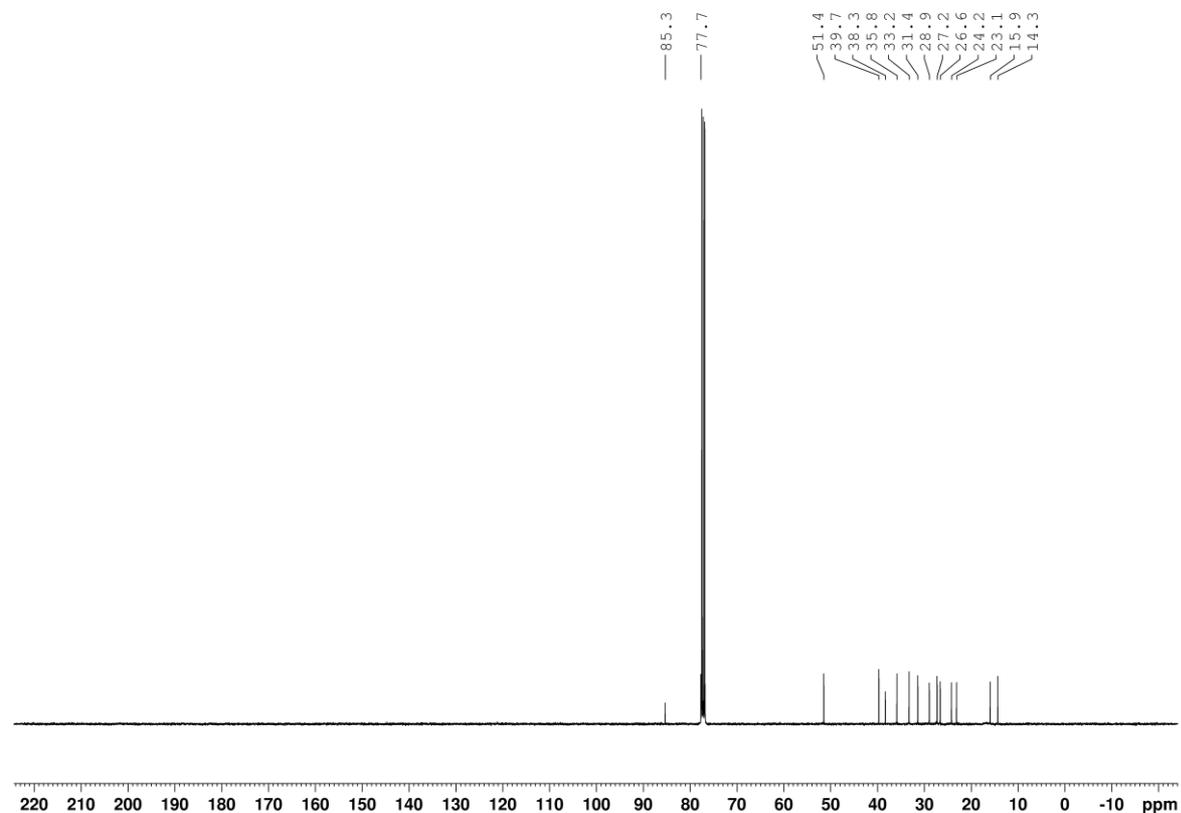
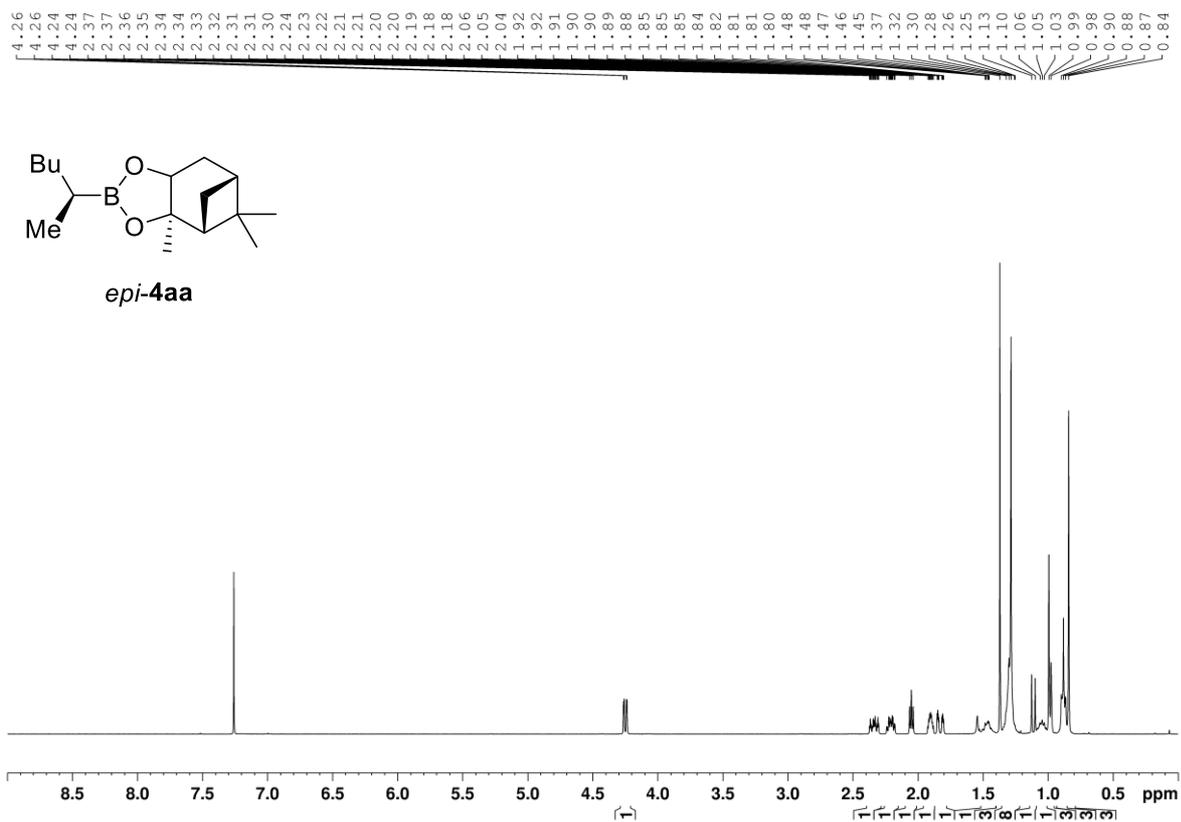


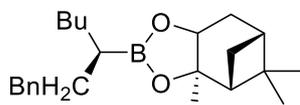
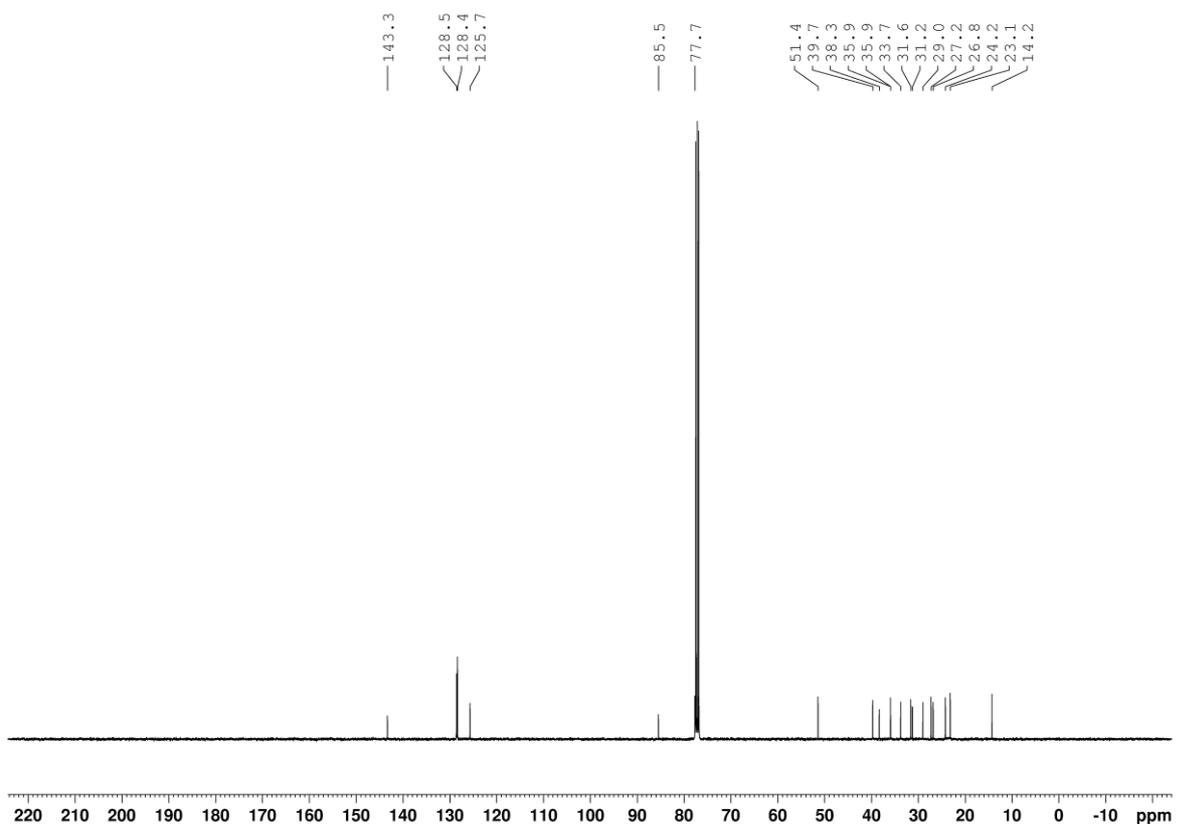
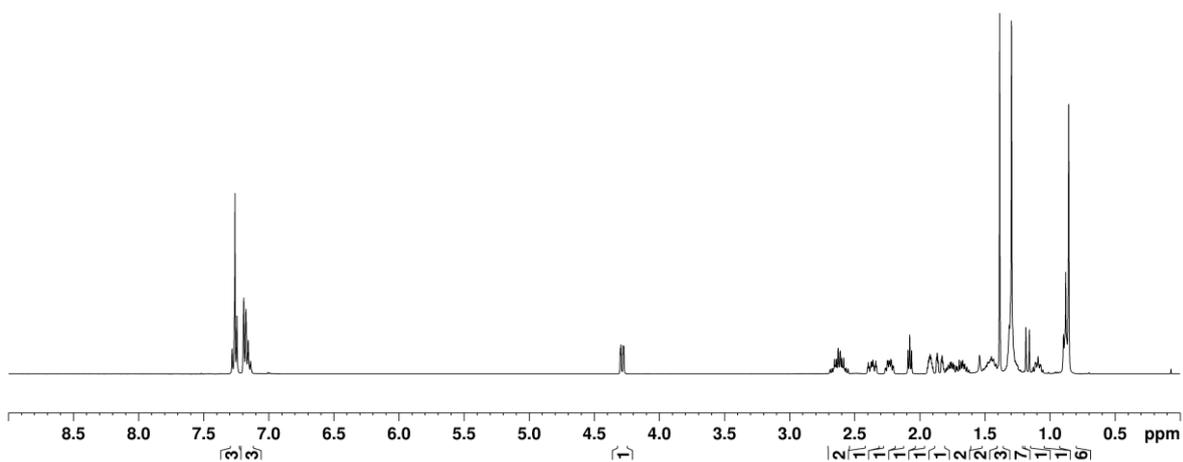
Crude pinacol ester (1.50 g, 6.41 mmol, 1.0 eq.) and (-)-pinanediol (1.09 g, 6.41 mmol, 1.0 eq.) in 64 mL *n*-heptane (0.1 M) was stirred at 80 °C overnight. Upon completion (TLC), the organic layer was washed three times with water. The organic layer was dried over MgSO₄, filtered over silica, washed with excess pentane and concentrated under reduced pressure to furnish the product in a quantitative yield. ¹H-NMR (400 MHz, CDCl₃): δ = 7.78–7.74 (m, 2H), 6.92–6.89 (m, 2H), 4.43 (dd, *J* = 8.76, 1.89 Hz, 1H), 2.45–2.38 (m, 1H), 2.25–2.19 (m, 1H), 2.15 (t, *J* = 5.52 Hz, 1H), 1.99–1.91 (m, 2H), 1.47 (s, 3H), 1.31 (s, 3H), 1.22 (d, *J* = 10.86 Hz, 1H), 0.90–0.87 (m, 3H) ppm. ¹³C-NMR (100 MHz, CDCl₃): δ = 162.2, 136.7, 113.5, 86.2, 78.3, 55.2, 51.6, 39.7, 38.3, 35.8, 28.9, 27.3, 26.6, 24.2 ppm. NMR data complies with published data.⁴

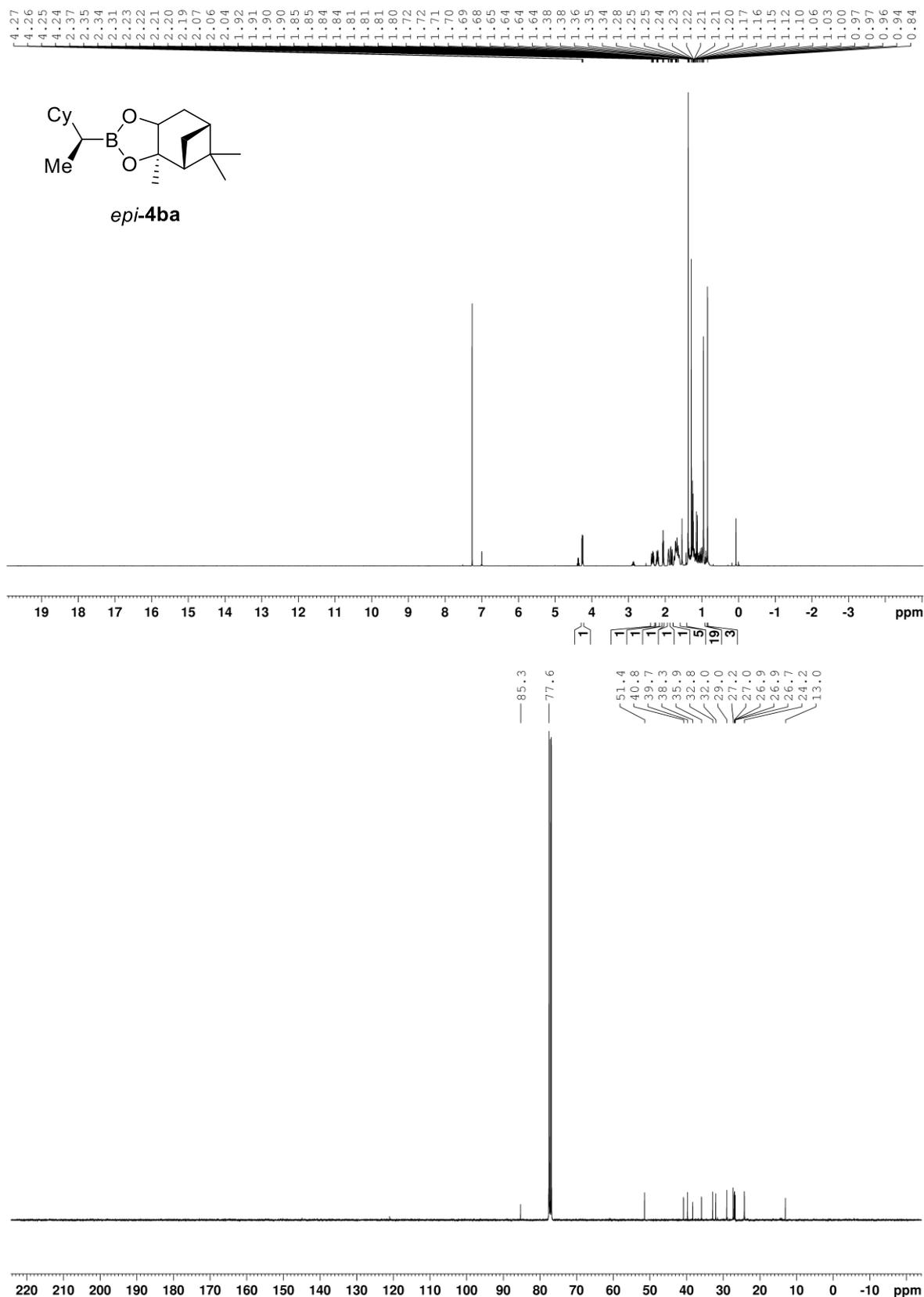
Spectra

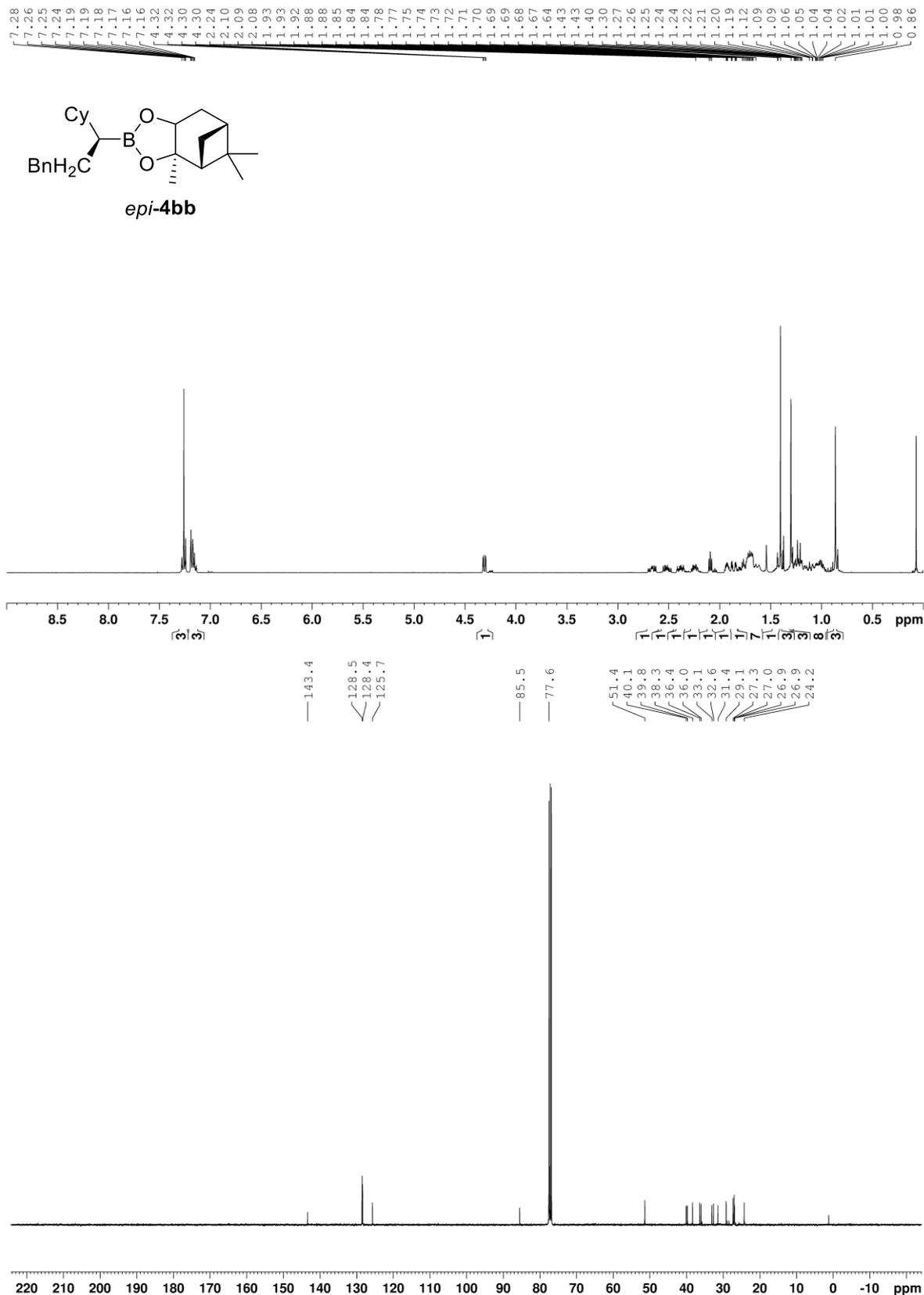


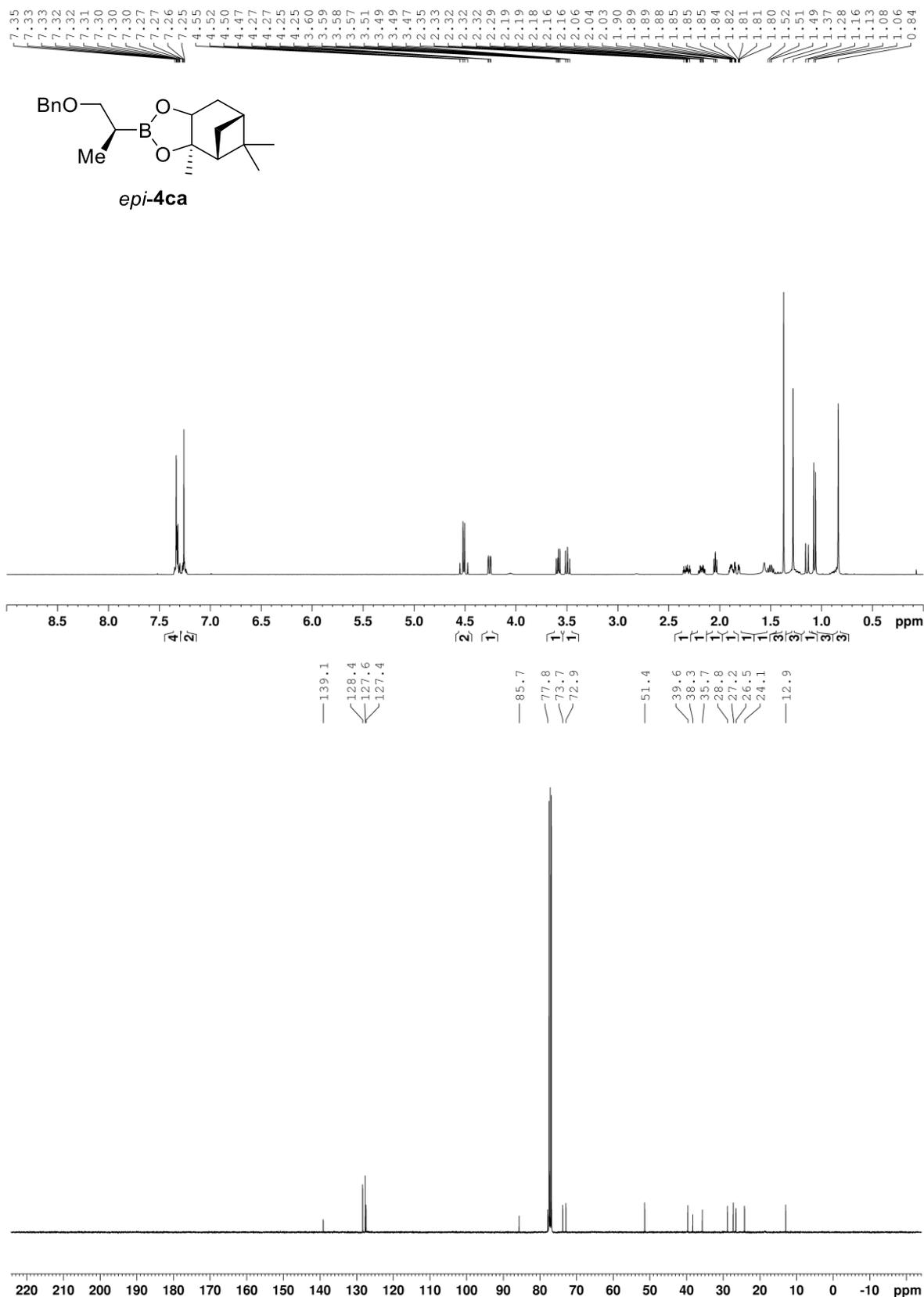


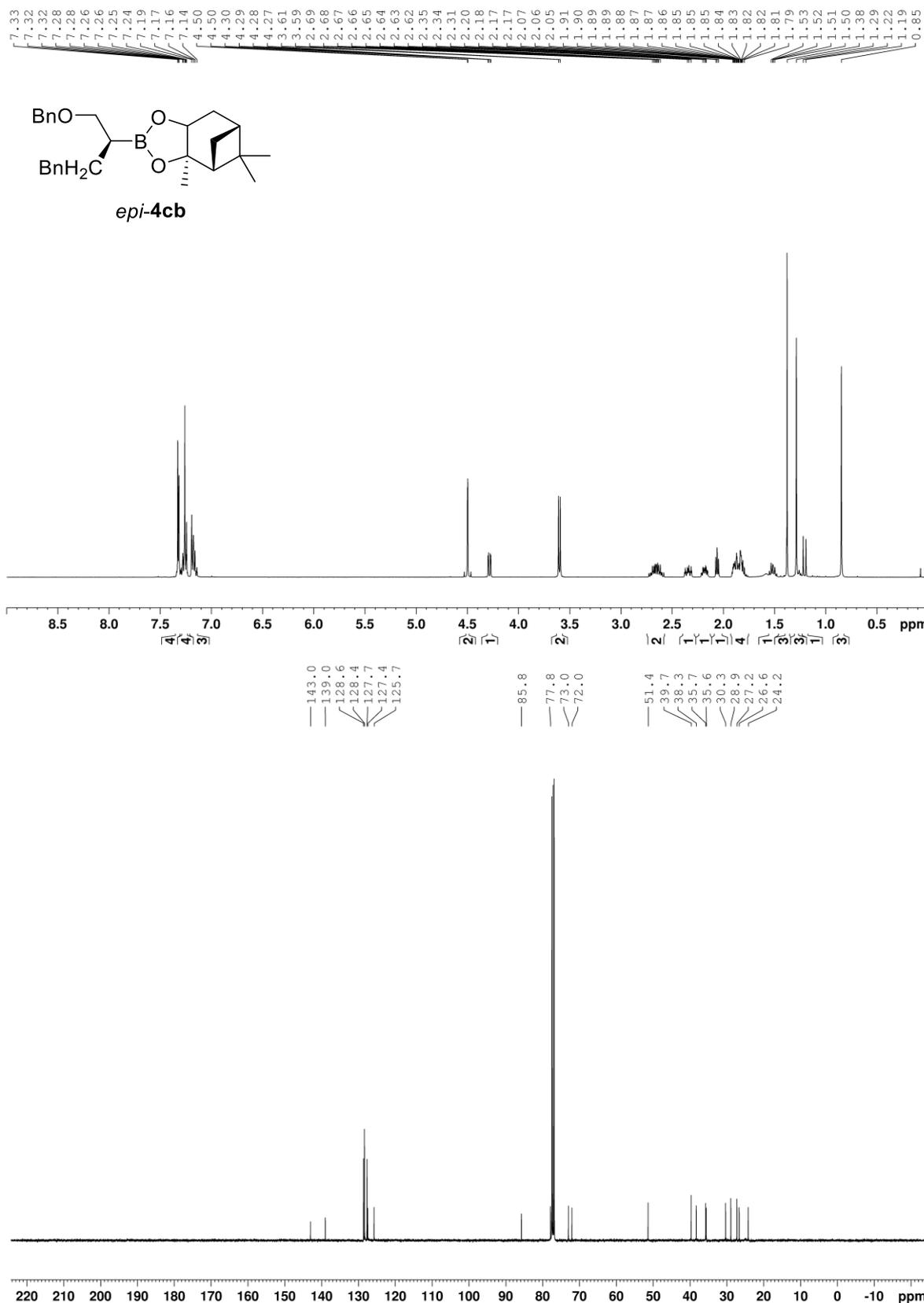


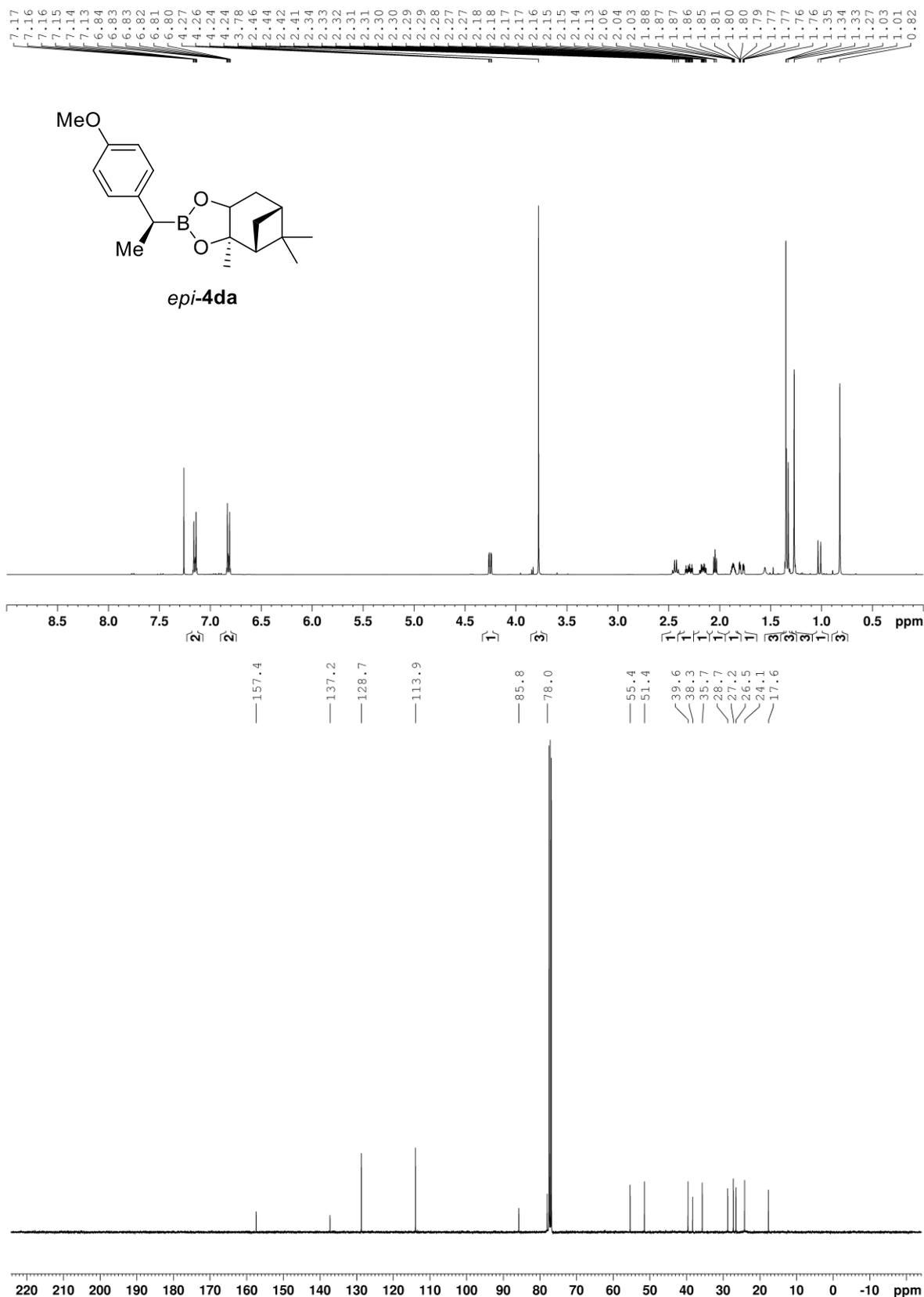
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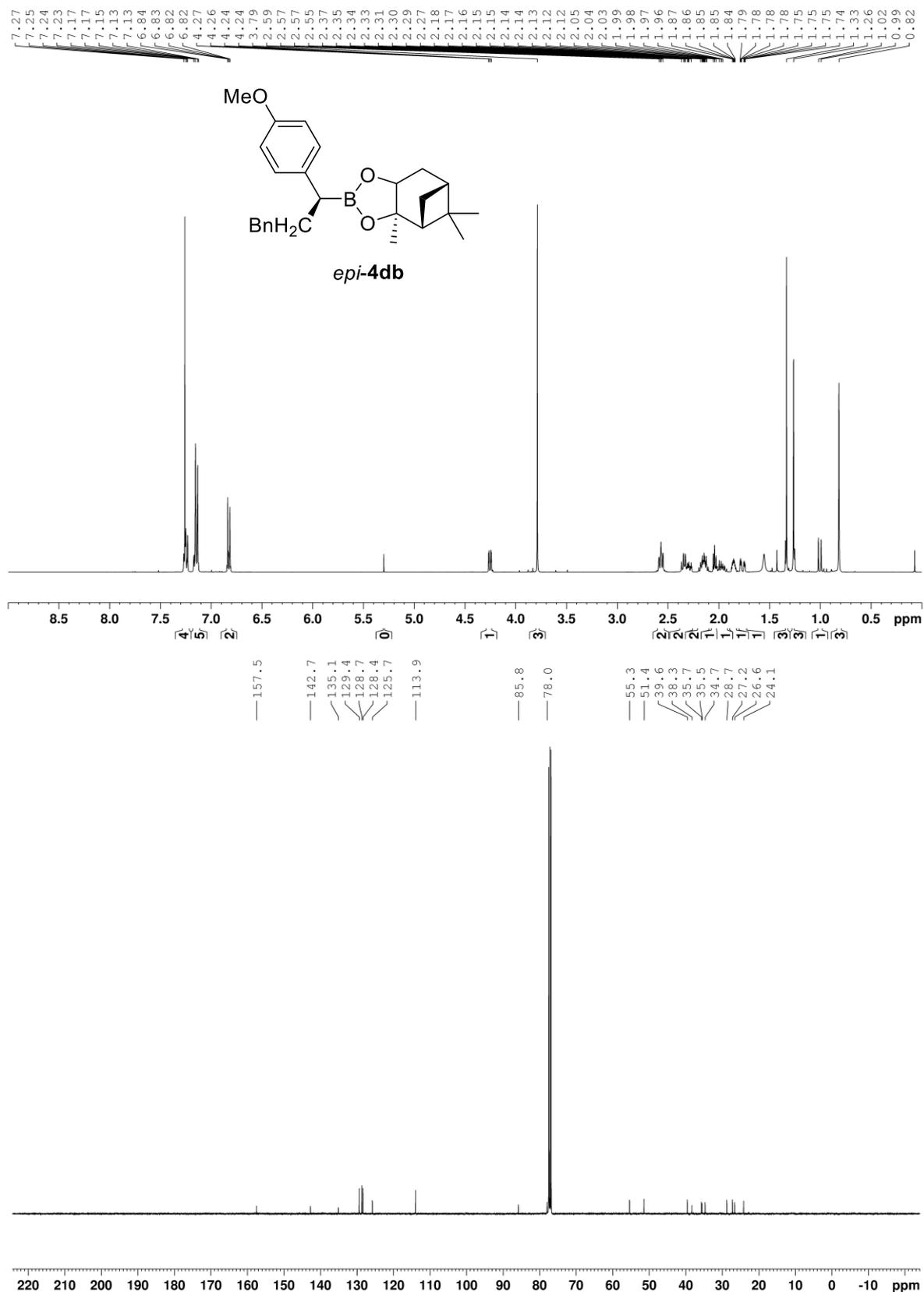


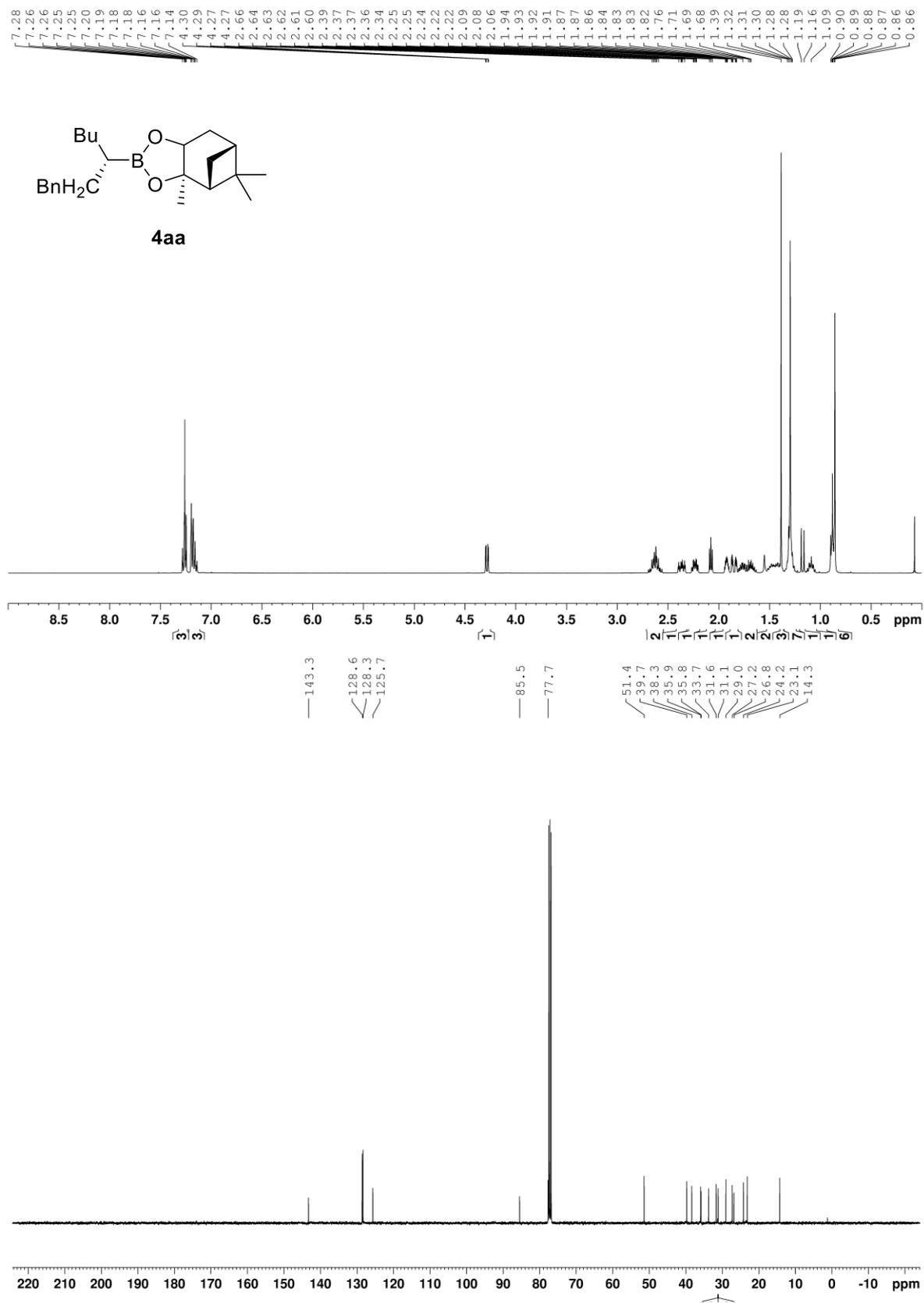


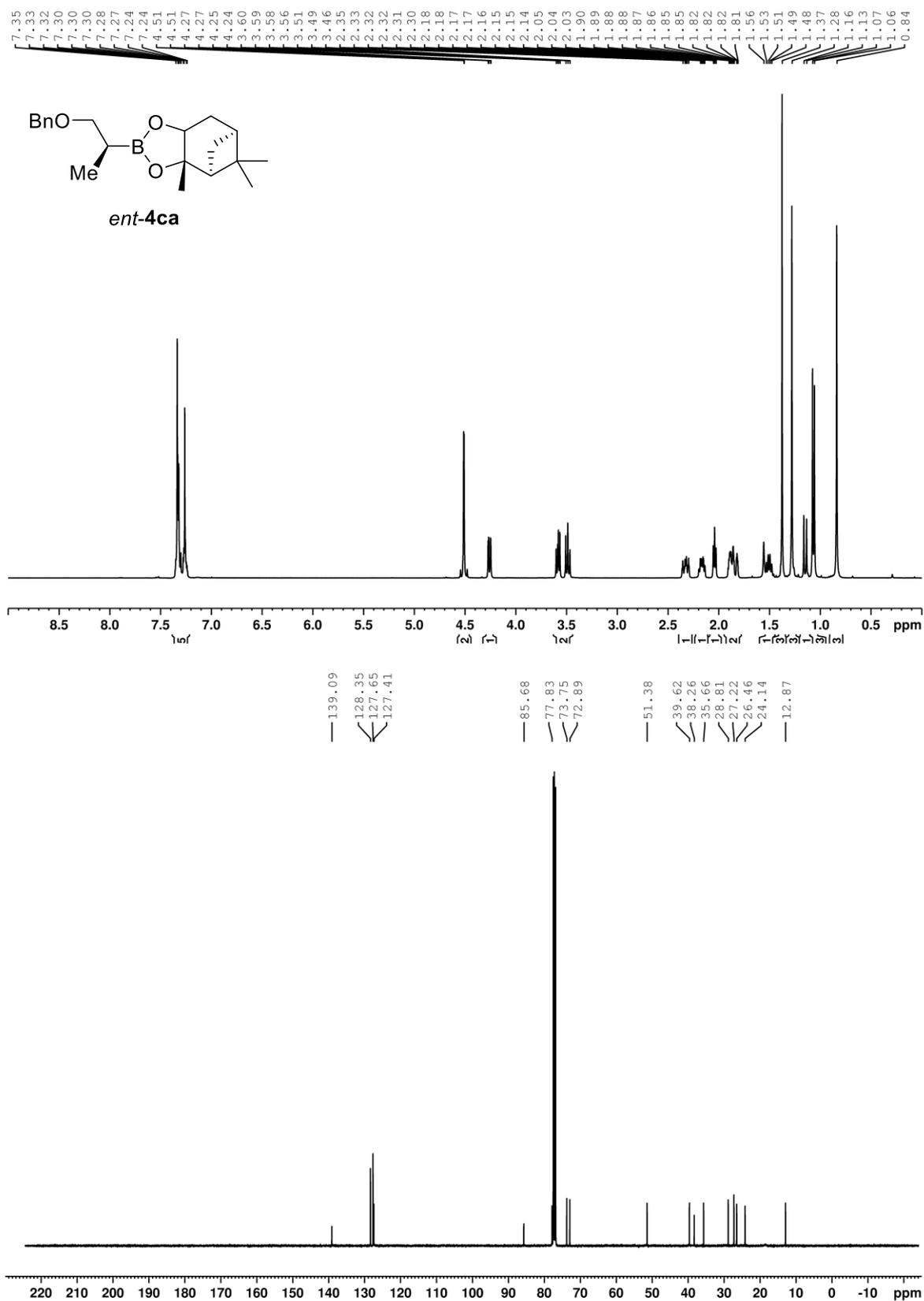


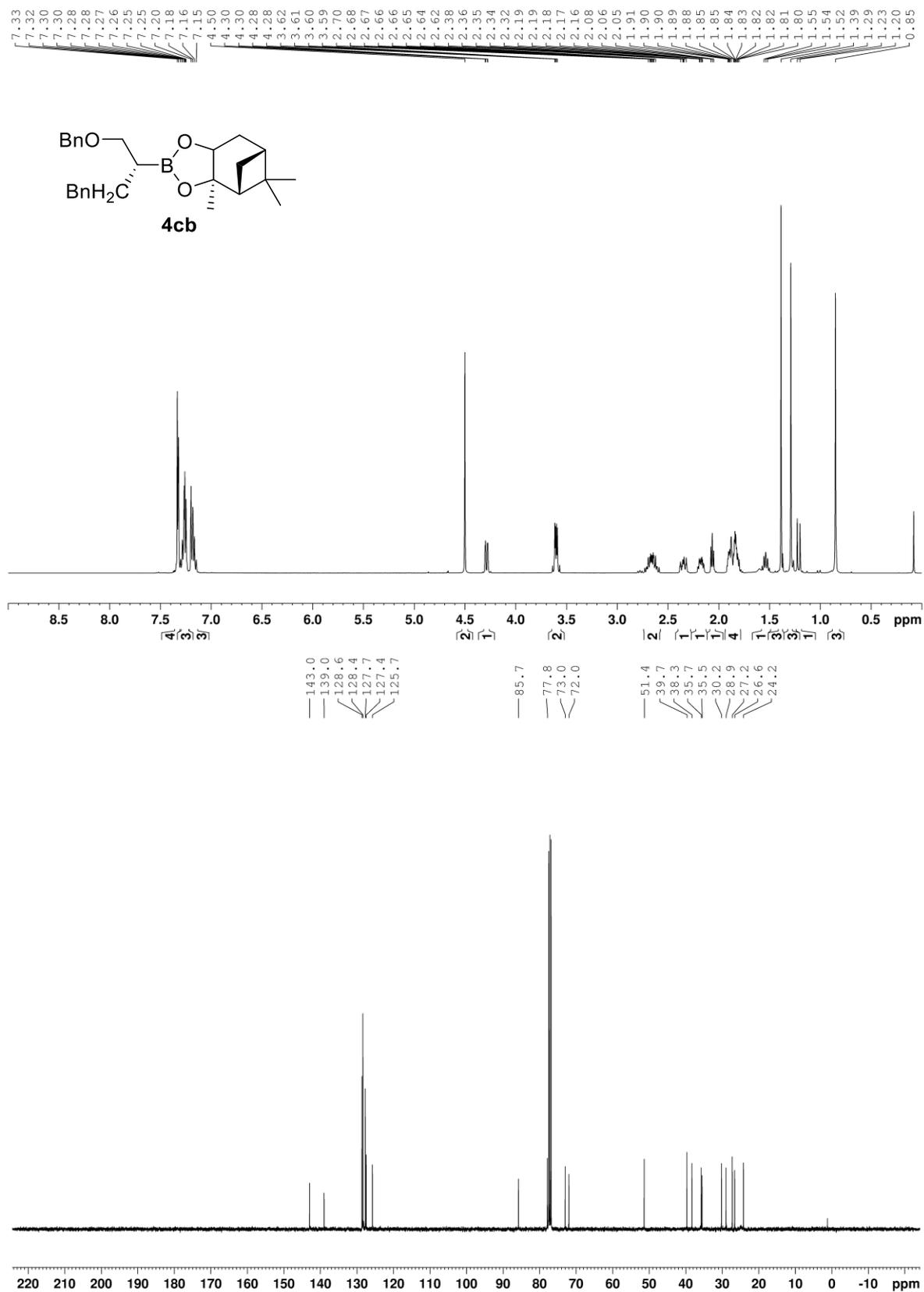


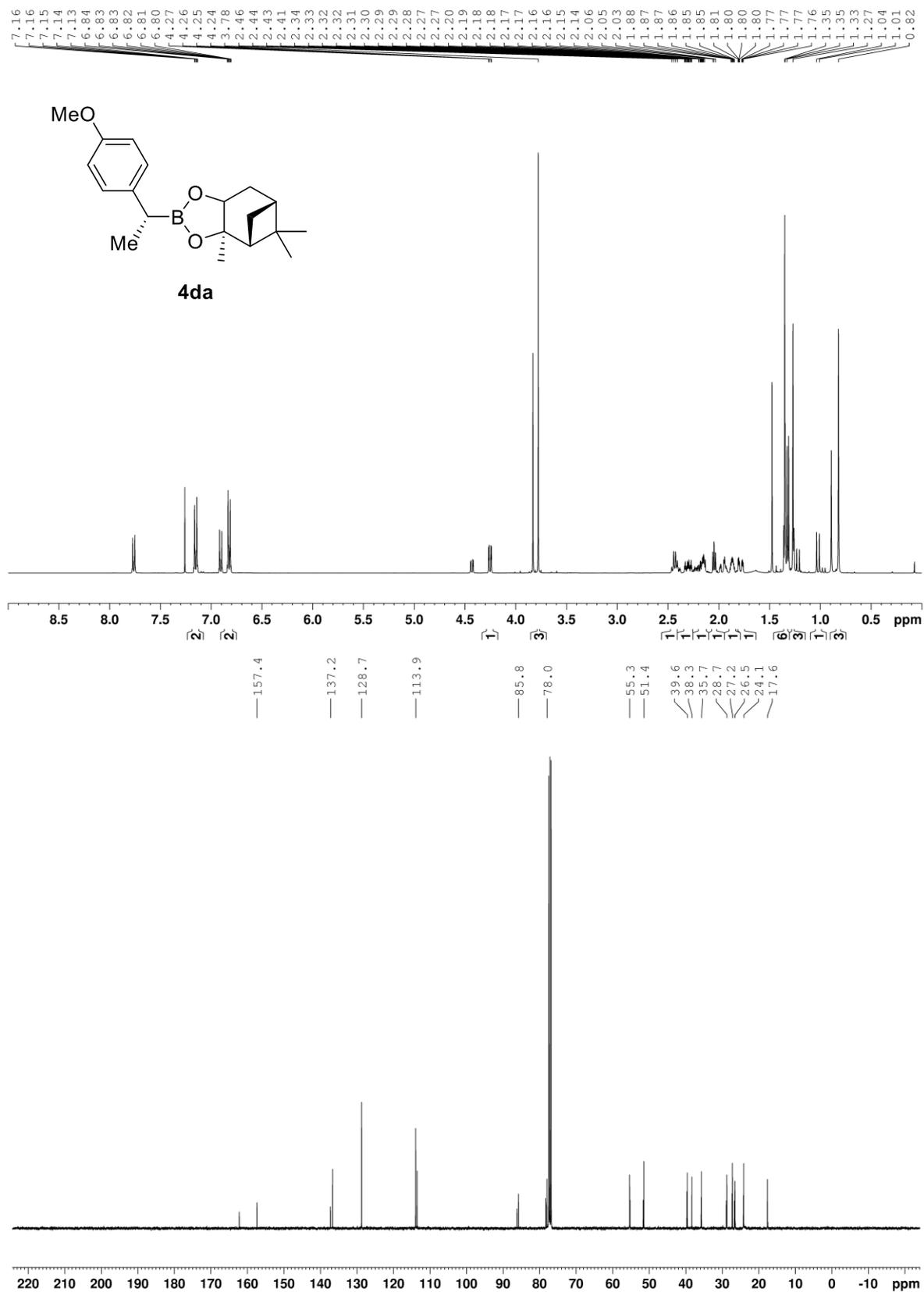


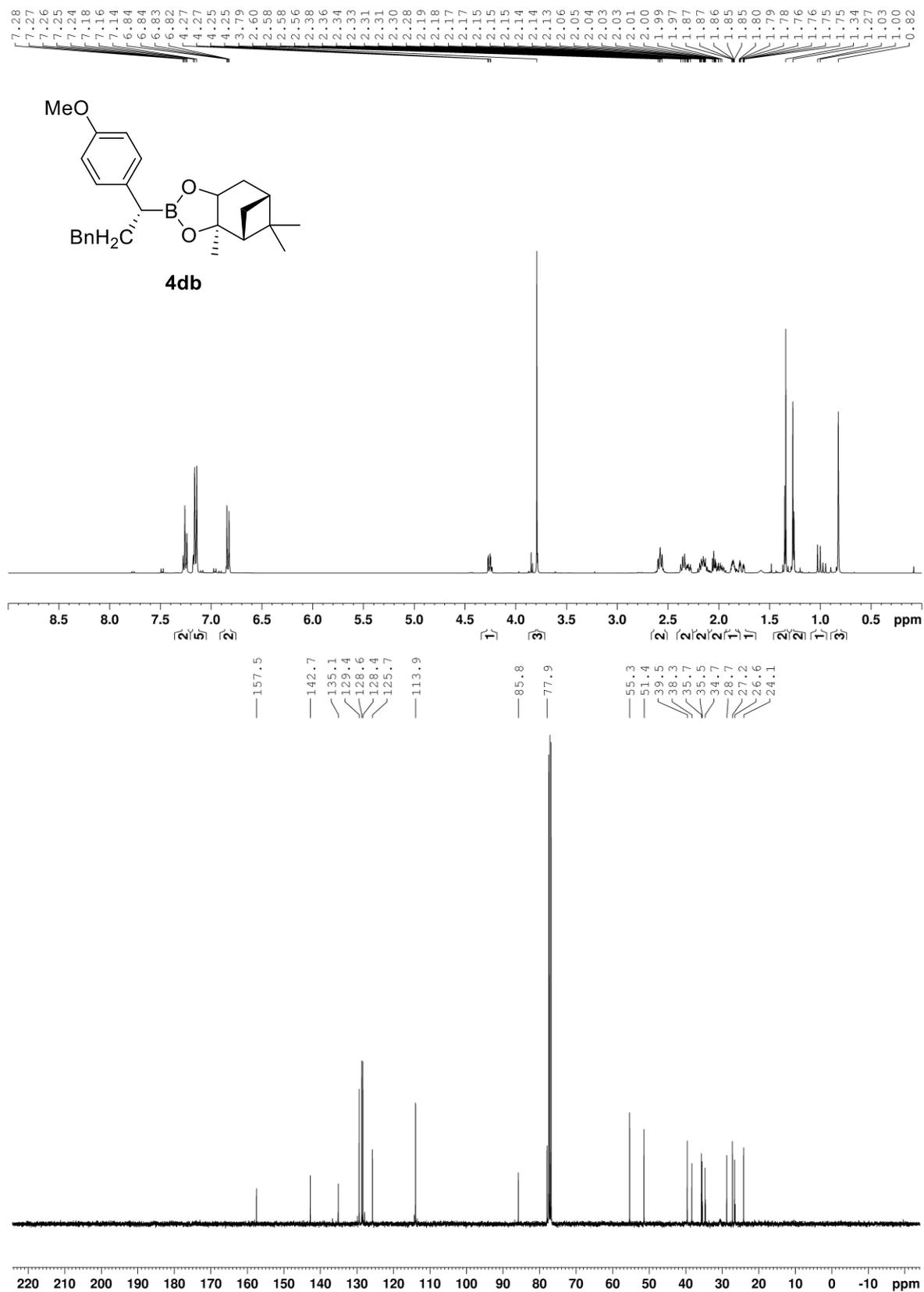


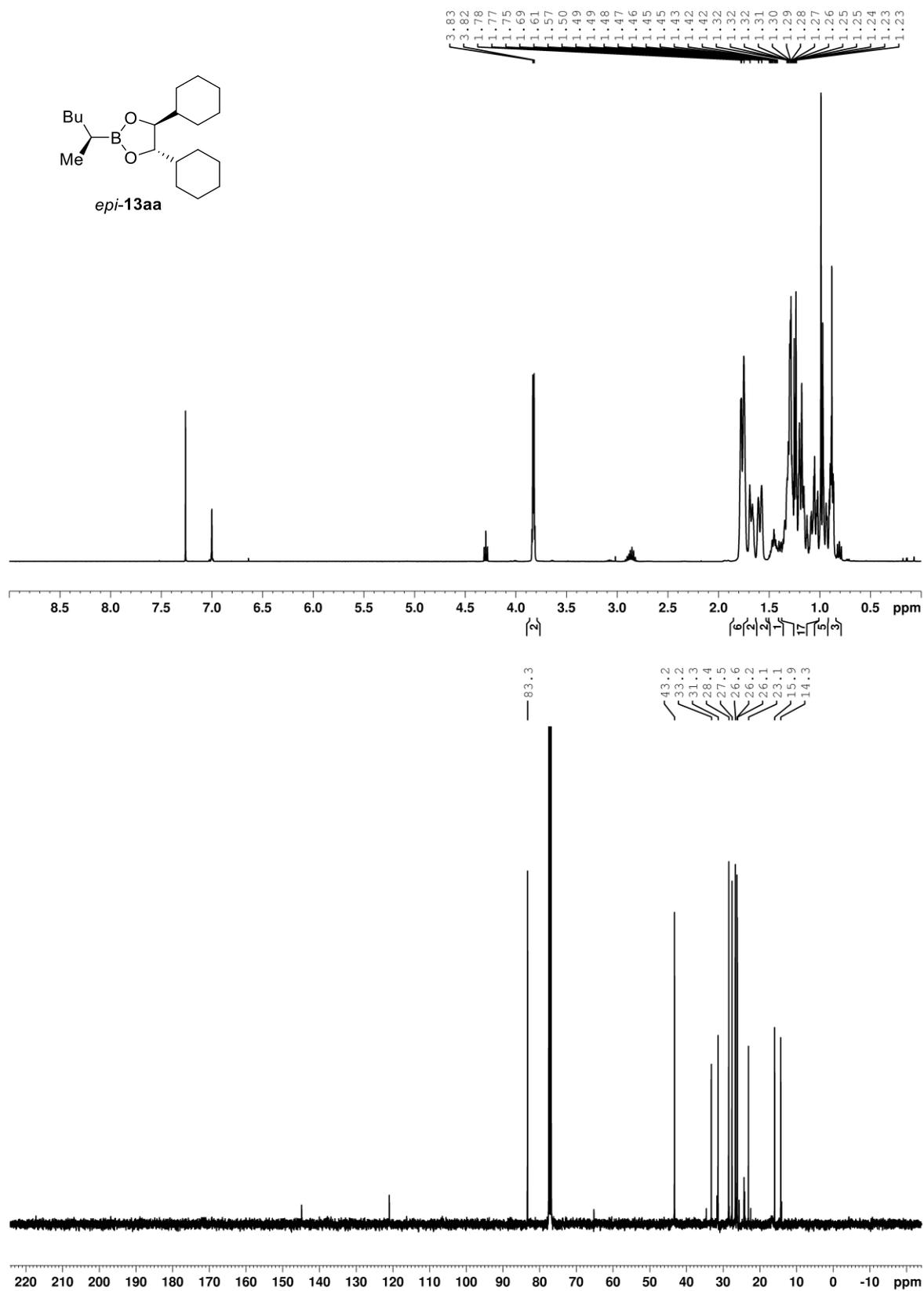


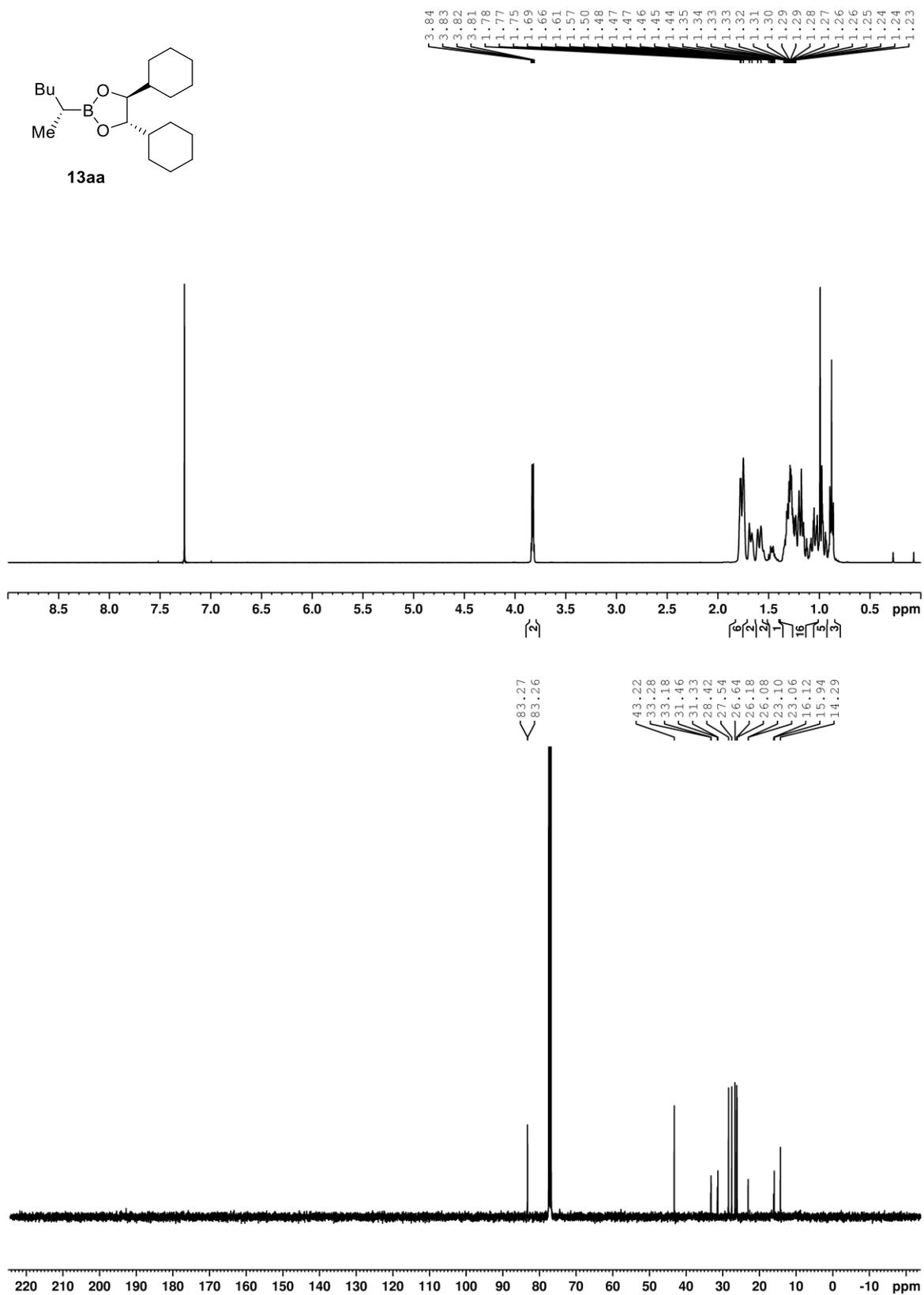


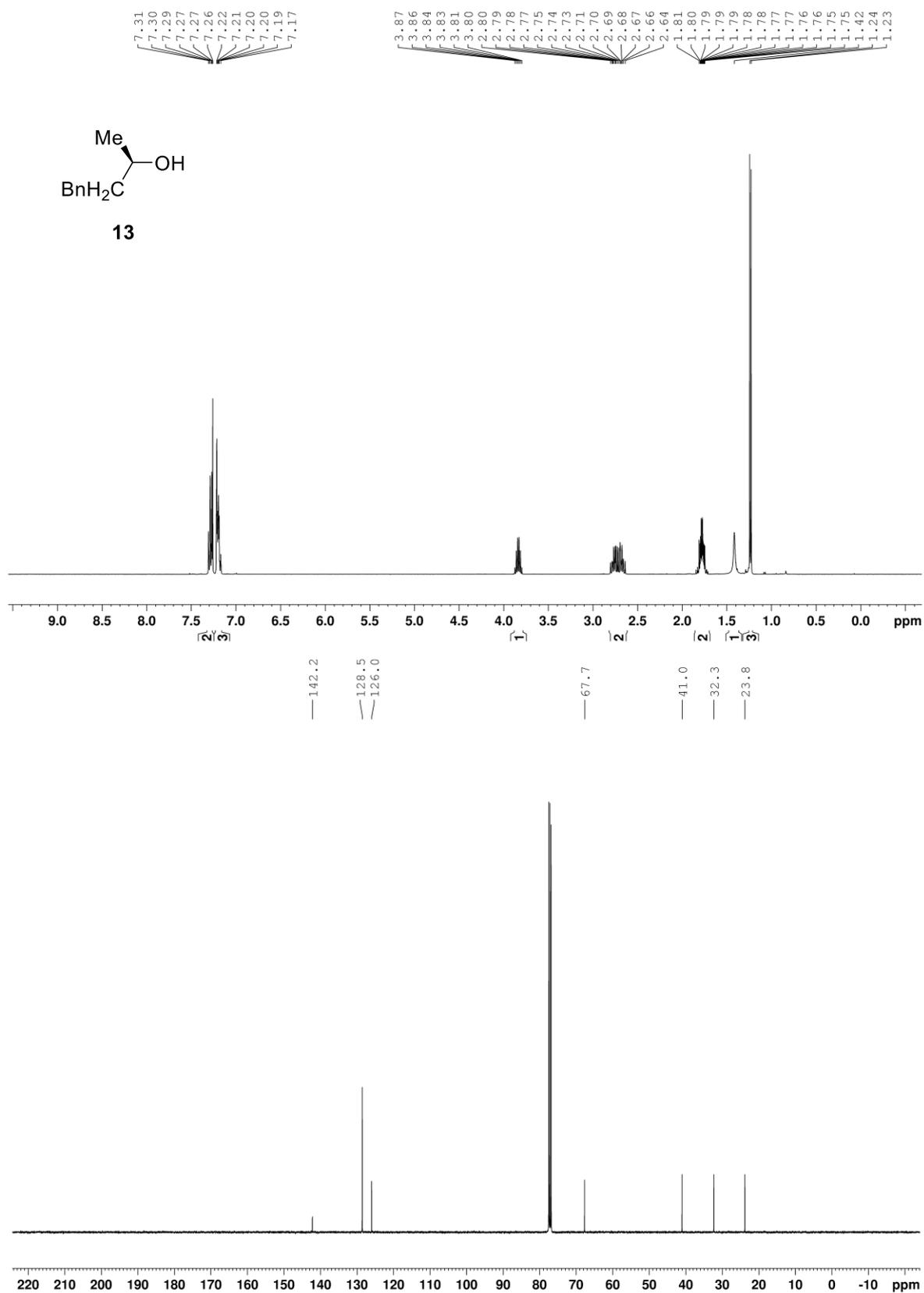


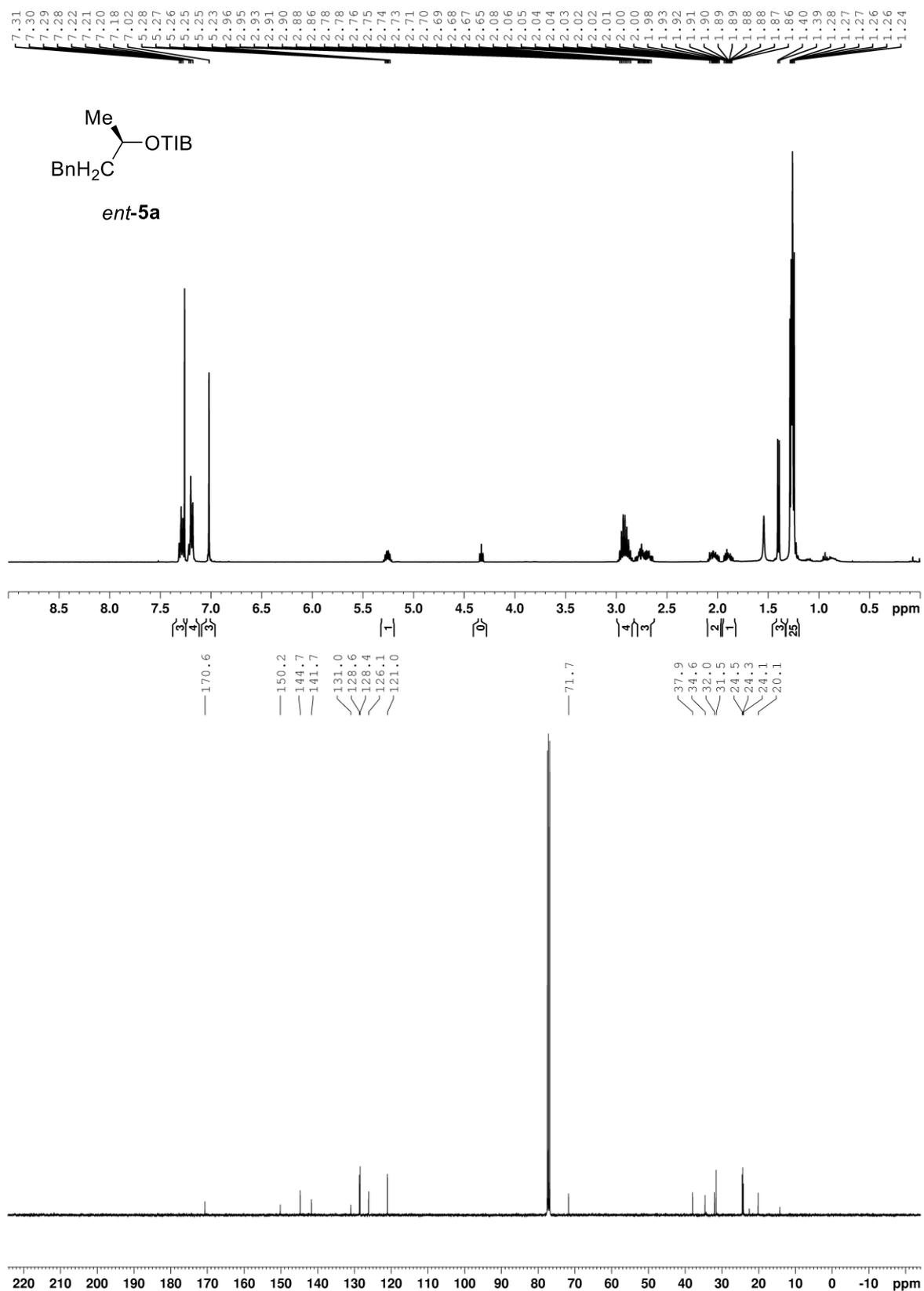


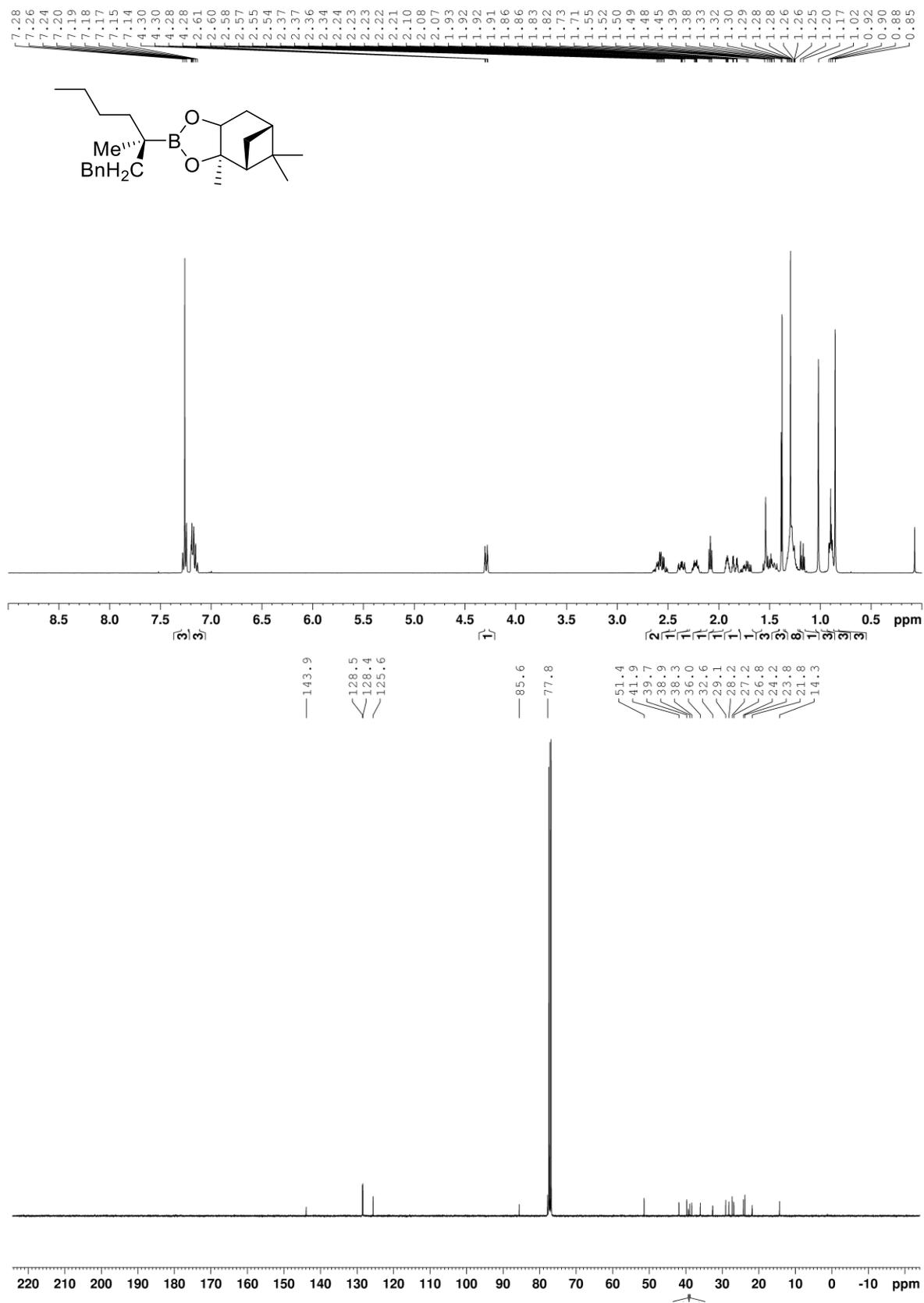


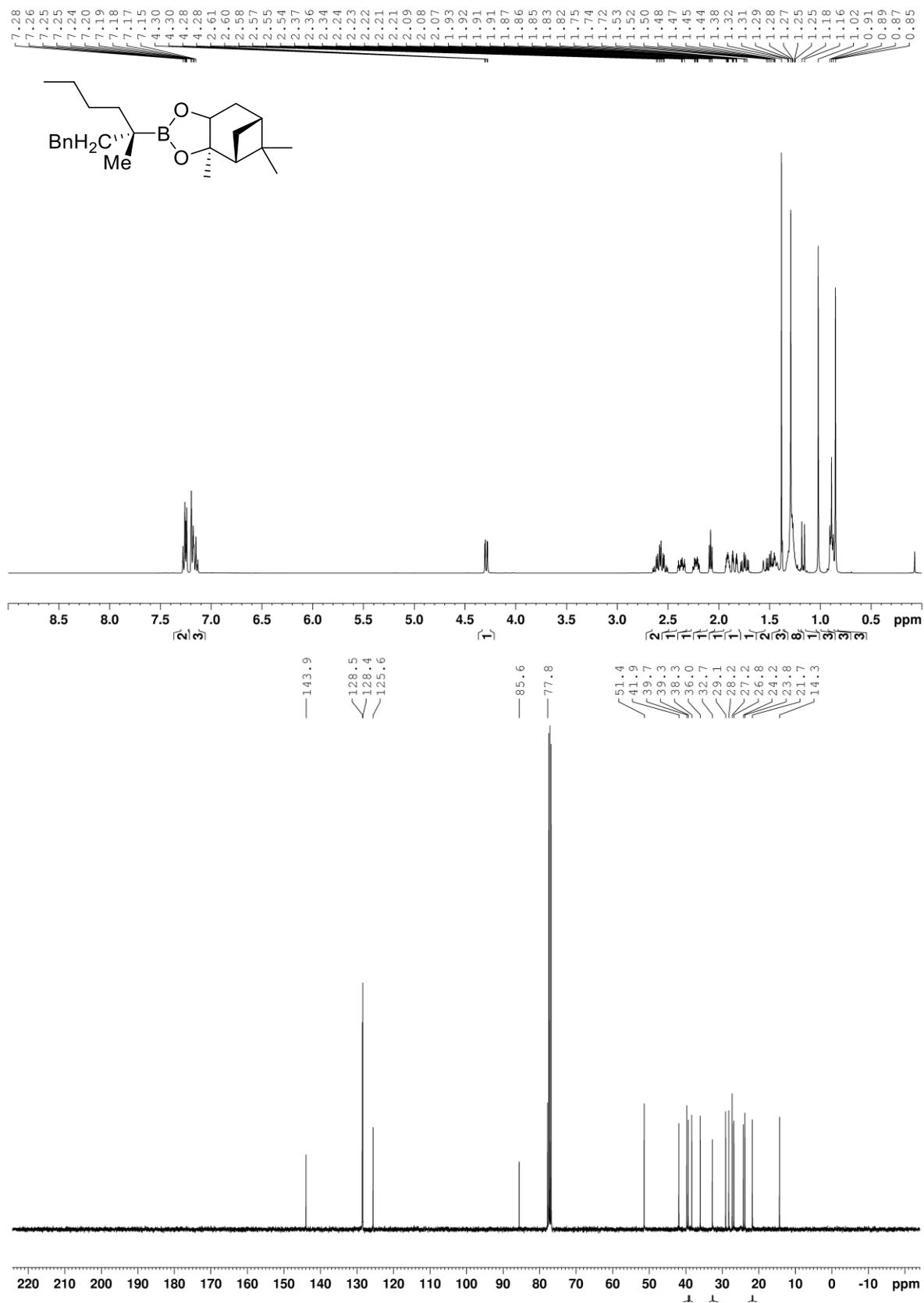




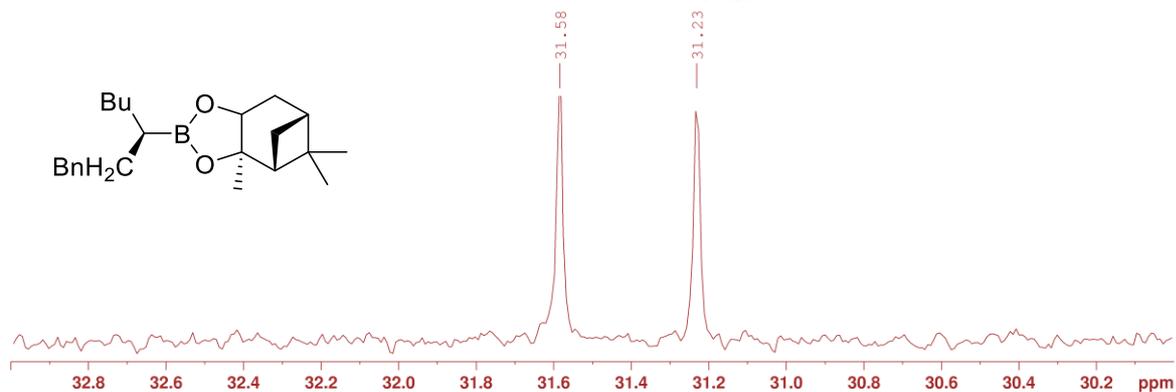
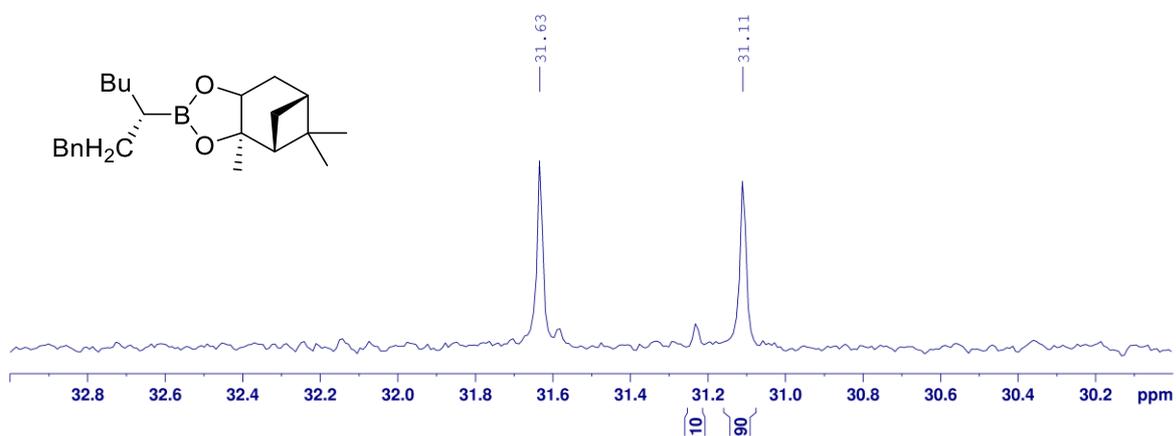
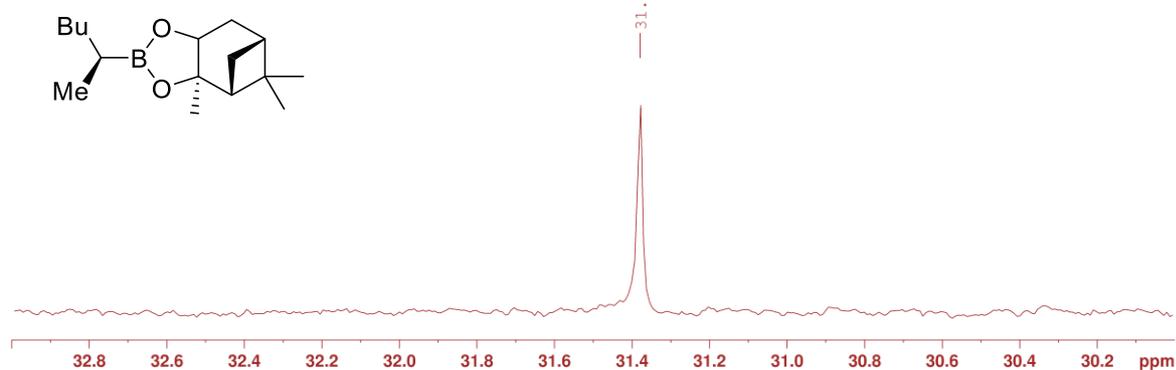
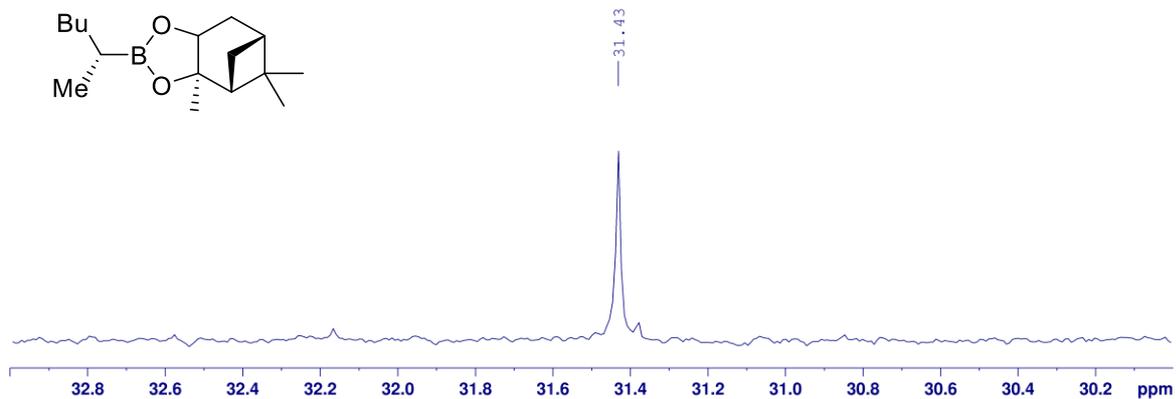


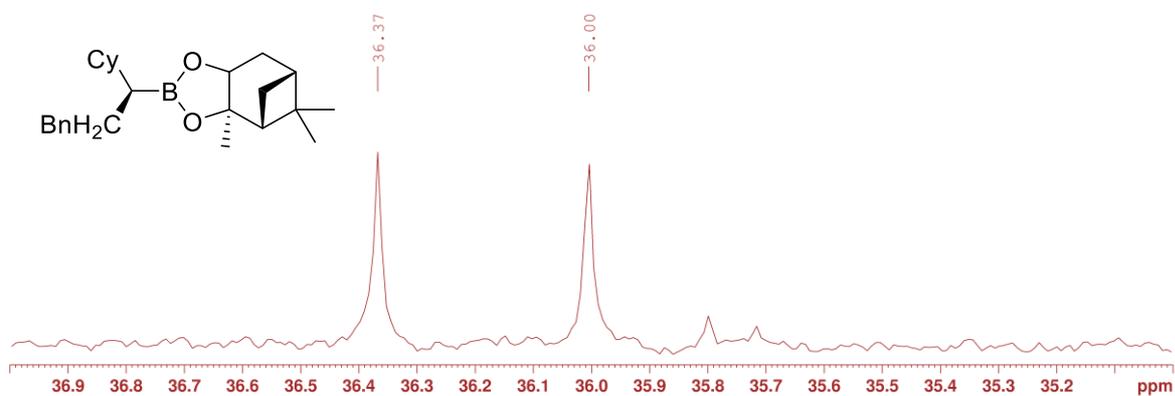
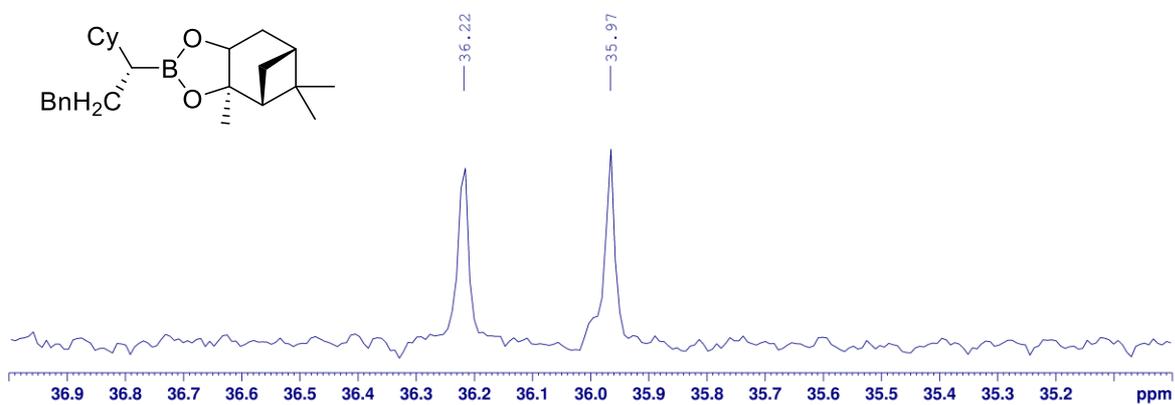
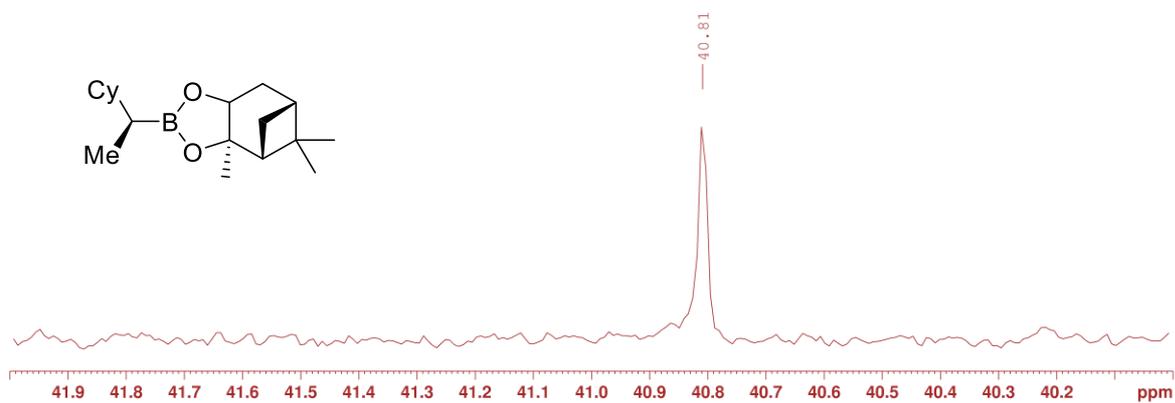
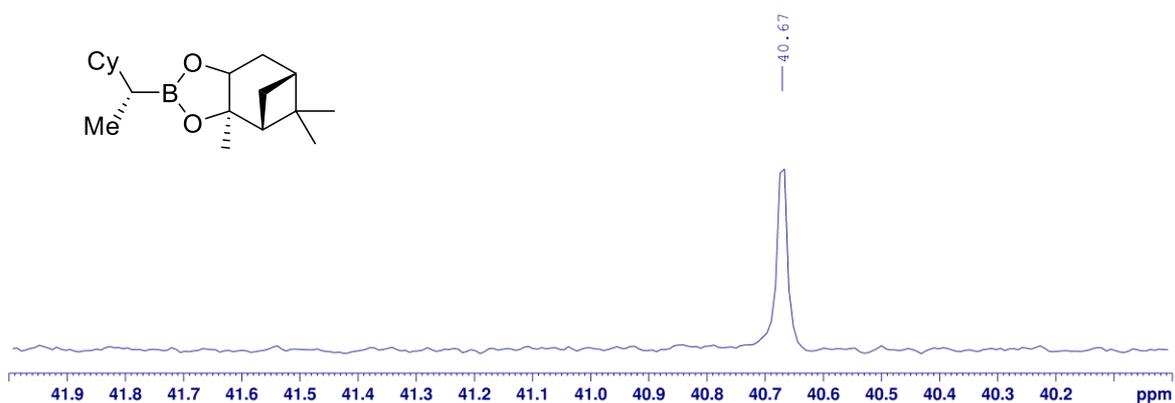


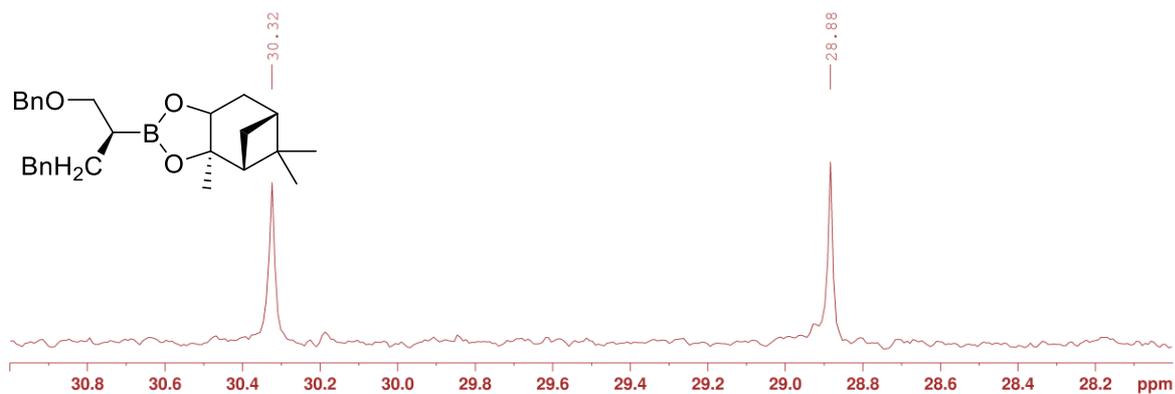
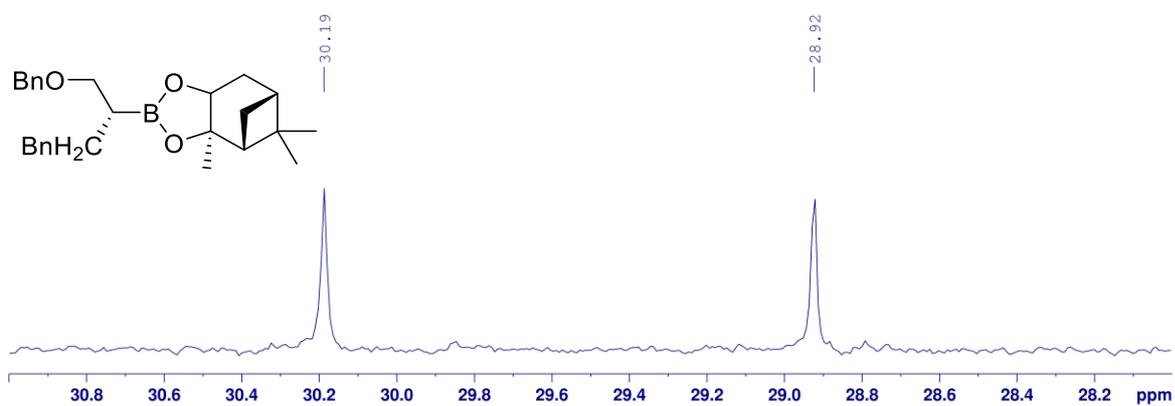
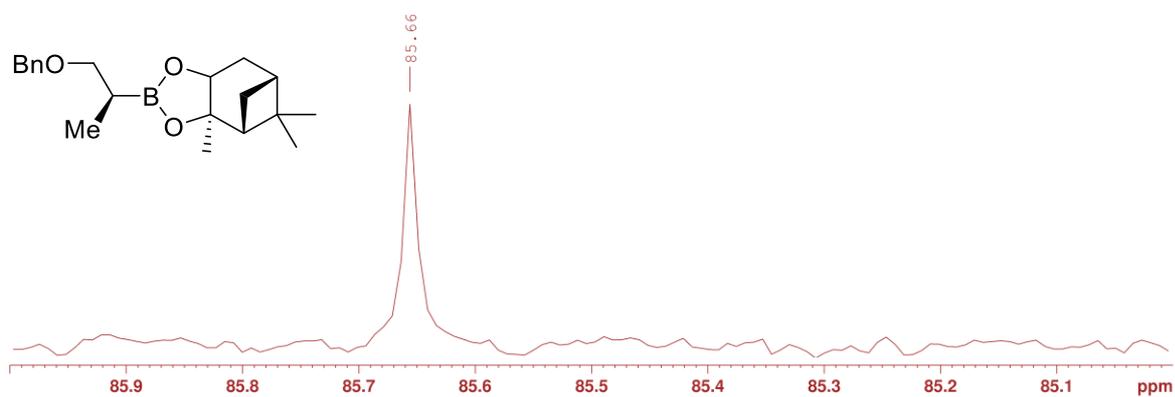
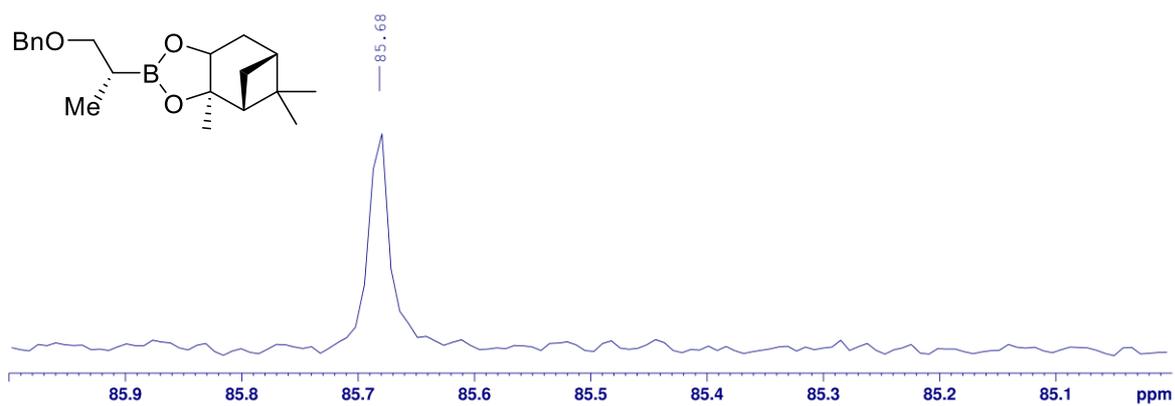


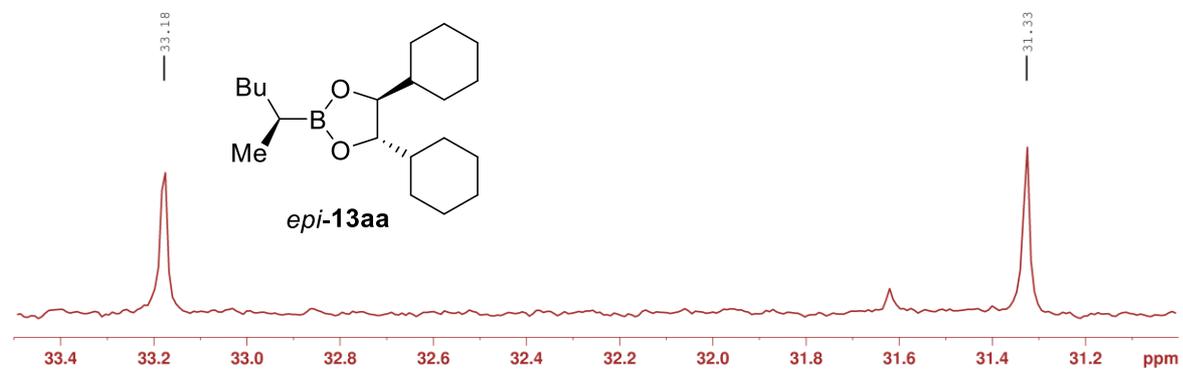
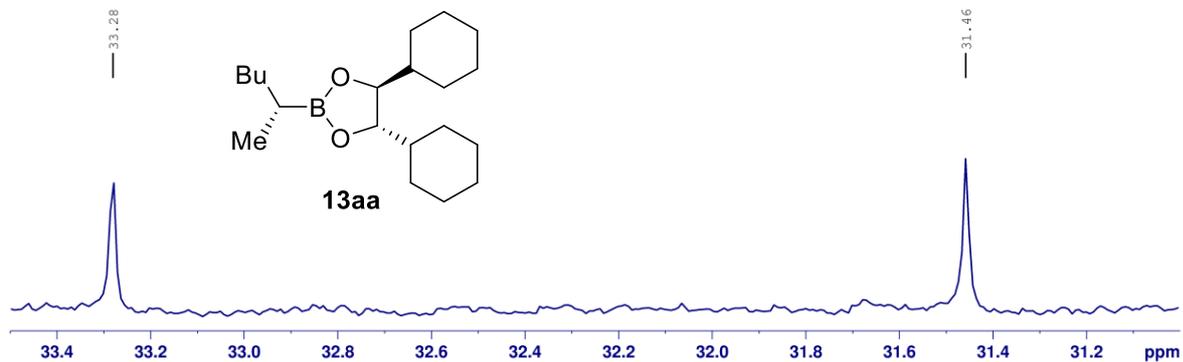
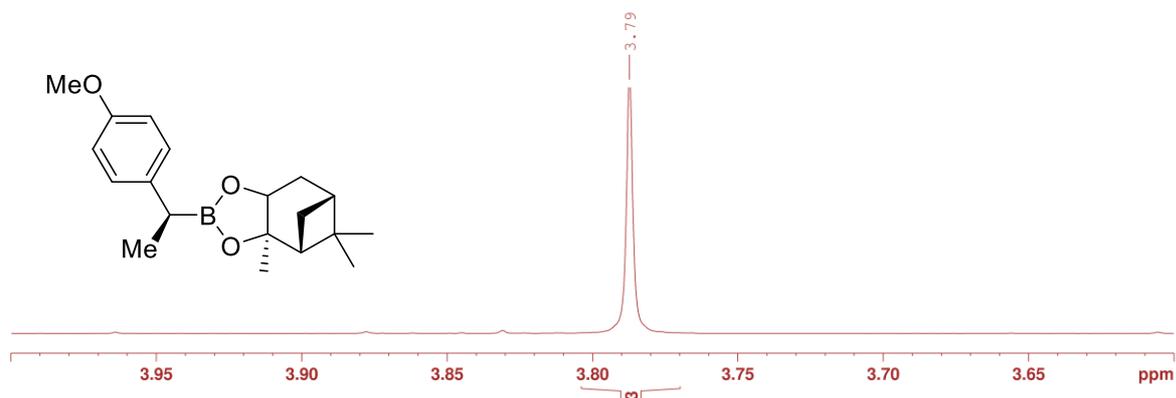
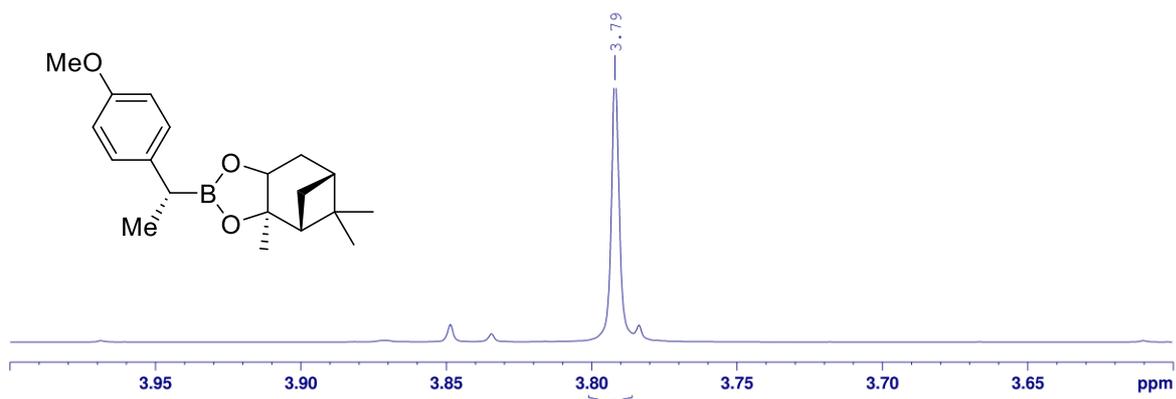


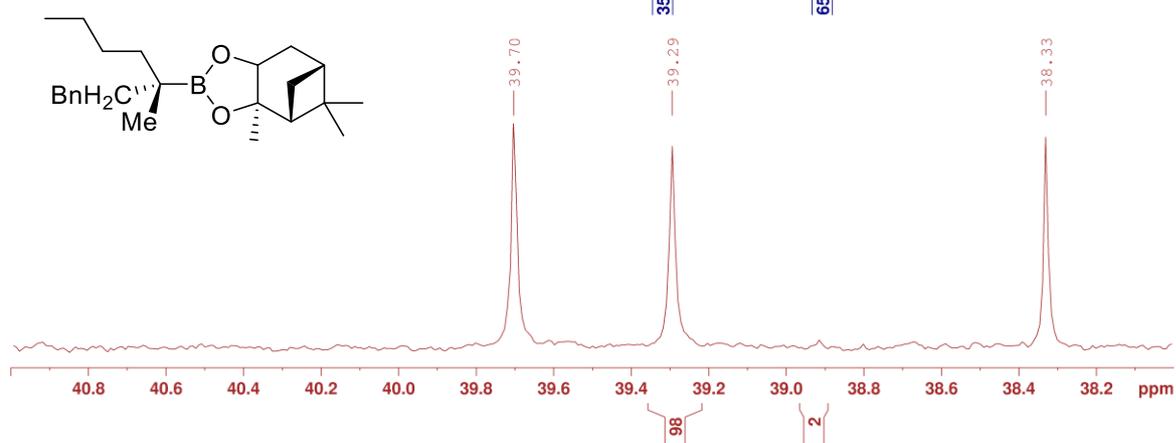
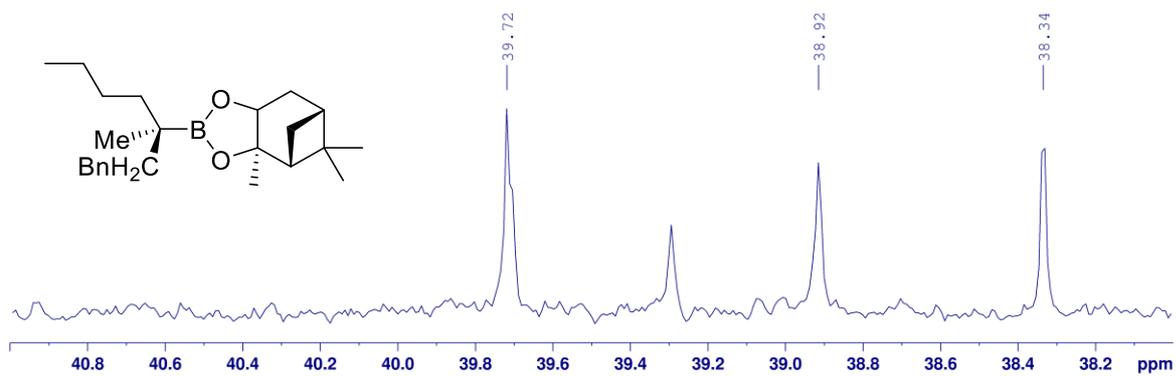
Spectra for determination of diastereomeric ratio











References

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