

Construction of Azacycles by Intramolecular Amination of Organoboronates and Organobis(boronates)

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Supporting Information

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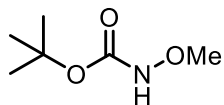
General Information

^1H NMR spectra were recorded on either a Varian Gemini-600 (600 MHz), Inova-400 (400 MHz) or Varian Inova-500 (500 MHz) spectrometer. Chemical shifts are reported in ppm with the solvent resonance as the internal standard (CDCl_3 : 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on either a Varian Gemini-600 (150 MHz) or a Varian Inova-500 (125 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard (CDCl_3 : 77.16 ppm). ^{11}B NMR spectra were recorded on a Varian Gemini-500 (128 MHz) spectrometer. Infrared (IR) spectra were recorded on a Bruker alpha-P Spectrometer. Frequencies are reported in wavenumbers (cm^{-1}) as follows: strong (s), broad (br), medium (m), and weak (w). Optical rotations were measured on a Rudolph Analytical Research Autopol IV Polarimeter. High-resolution mass spectrometry (DART+) was performed at the Mass Spectrometry Facility, Boston College, Chestnut Hill, MA. Purification was performed using forced flow (flash chromatography) on silica gel (SiO_2 , 230 x 450 Mesh) purchased from Silicycle. Thin layer chromatography (TLC) was performed on 25 μm silica gel aluminum backed plates from Silicycle. Visualization was performed using ultraviolet light (254 nm), ceric ammonium molybdate (CAM) in ethanol, basic potassium permanganate or ninhydrin and acetic acid in ethanol.

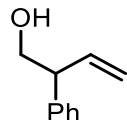
Analytical chiral supercritical fluid chromatography (SFC) was performed on a TharSFC Method Station II equipped with Waters 2998 Photodiode Array Detector with isopropanol as the modifier. HPLC measurements were carried out on a Shimadzu HPLC system.

All reactions were conducted in oven- or flame-dried glassware under an inert atmosphere of nitrogen or argon unless otherwise specified. Heated reactions are conducted in a mineral oil bath on a hot plate equipped with a temperature probe. Tetrahydrofuran (THF), diethyl ether (Et_2O), dichloromethane (DCM) and toluene were purified using Pure Solv MD-4 solvent purification system, from Innovative Technology, Inc., by passing the solvent through two activated alumina columns after purging with nitrogen. Potassium *tert*-butoxide was purchased from Oakwood Chemicals. Tris(dibenzylideneacetone)platinum(0) ($\text{Pt}(\text{dba})_3$) was synthesized following literature methods.¹ (3*aS*,8*aS*)-(+)-4,4,8,8-tetrakis(3,5-diethylphenyl)tetrahydro-2,2-dimethyl-6-phenyl-1,3-dioxolo[4,5-*e*]dioxaphosphepine ((*S,S*)-3,5-diethylphenylTADDOLPPh) was synthesized from D-(-)-tartaric acid (obtained from Sigma Aldrich) following literature methods.² All other reagents were purchased from Sigma Aldrich, Alfa Aesar, Oakwood Chemicals, Combi-Blocks, or Acros Organics and used without further purification.

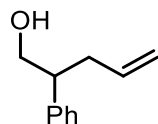
Experimental Procedures



tert-butyl methoxycarbamate (S-1) The title compound was prepared according to the procedure reported in the patent literature.³ All spectral data was in accordance with previously published results.



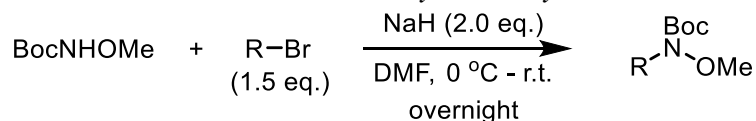
2-phenylbut-3-en-1-ol (S-2) The title compound was prepared according to the procedure reported in the literature.⁴ All spectral data was in accordance with previously published results.



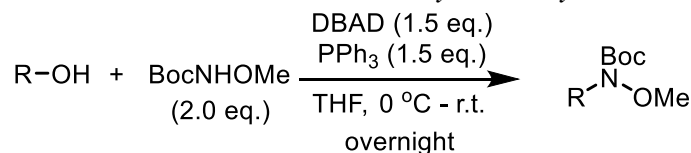
2-phenylpent-4-en-1-ol (S-3) The title compound was prepared according to the procedure reported in the literature.⁵ All spectral data was in accordance with previously published results.

I. Representative procedures for preparation of starting materials

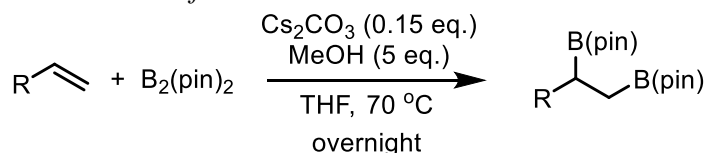
General procedure A: S_N2 substitution with tert-butyl methoxycarbamate



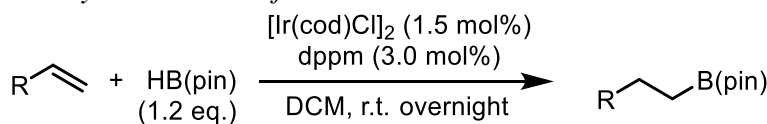
In a round bottom flask, *tert*-butyl methoxycarbamate (**S-1**) (20 mmol, 1.0 equiv.) was added dropwise carefully to a suspension of sodium hydride (40 mmol, 2.0 equiv.) in DMF (50 mL) at 0 °C. After addition was complete, the reaction was allowed to warm up to room temperature and stirred for 1 hour. The reaction was cooled down to 0 °C, and the corresponding alkyl bromide (30 mmol, 1.5 equiv.) was added to the reaction mixture, which was then warmed to room temperature and allowed to stir overnight. The reaction was quenched carefully with saturated ammonium chloride solution (20 mL), diluted with diethyl ether (100 mL), and transferred to a separatory funnel. The organic phase was washed with DI water (4 x 10 mL) and then with brine (10 mL). The organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The pure products were isolated with SiO₂ chromatography.

General procedure B: Mitsunobu reaction with tert-butyl methoxycarbamate

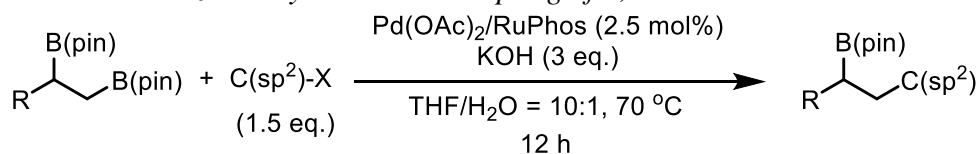
This procedure is adapted from literature.⁶ In a round bottom flask, the corresponding alcohol (10 mmol, 1.0 equiv.), triphenyl phosphine (15 mmol, 1.5 equiv.) and *tert*-butyl methoxycarbamate (**S-1**) (20 mmol, 2.0 equiv) were dissolved in THF (20 mL). The reaction mixture was cooled to 0 °C, and di-*tert*-butyl azodicarboxylate (15 mmol, 1.5 equiv.) in THF (15 mL) was added to the reaction mixture, which was then warmed to room temperature and stirred overnight. At this time, the reaction mixture was opened to the air and the solvent was removed under reduced pressure. The pure products were isolated with SiO₂ chromatography.

General procedure C: Diboration of alkenes

This procedure is adapted from literature.⁷ A round bottom flask was charged with cesium carbonate (1.5 mmol, 0.15 equiv.) and bis(pinacolato)diboron (11 mmol, 1.1 equiv.). THF (30 mL) and methanol (50 mmol, 5.0 equiv.) was added, followed by the corresponding alkene (10 mmol, 1.0 equiv.). The reaction was heated at 70 °C overnight. At this time, the reaction mixture was opened to the air and the solvent was removed under reduced pressure. The pure products were isolated with SiO₂ chromatography.

General procedure D: Hydroboration of alkenes.

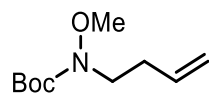
This procedure is adapted from literature.⁸ An oven-dried vial was loaded with [Ir(cod)Cl]₂ (0.015 mmol, 1.5 mol%) and bis(diphenylphosphino)methane (0.03 mmol, 3 mol%). Anhydrous DCM (4 mL) was added, followed by the corresponding alkene (1.0 mmol, 1.0 equiv.) and pinacol borane (1.2 mmol, 1.2 equiv.). The mixture was stirred at room temperature overnight, then quenched with water (2 mL), extracted with diethyl ether (3 x 10 mL) and dried over anhydrous sodium sulfate. After removal of solvent under reduced pressure, the pure products were isolated with SiO₂ chromatography.

General procedure E: Suzuki-Miyaura cross-coupling of 1,2-bisboronates

This procedure is adapted from literature.⁹ In the glovebox, an oven dried vial was charged with the corresponding 1,2-bisboronate (1.0 mmol, 1.0 equiv.), solid potassium hydroxide (3 mmol, 3

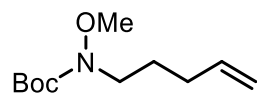
equiv.), Pd(OAc)₂/RuPhos (0.025 mmol, 2.5 mol%) as a 1:1 solution in THF (1 mL), THF (9 mL) and electrophile (1.5 mmol, 1.5 equiv.). The vial was sealed, removed from the glovebox, and H₂O (sparged with N₂ for 30 min, 1.0 mL) was added through the teflon septum cap. The vial was heated to 70 °C and stirred for 12 h. At this time, the vial was cooled down to room temperature and opened to air, and the reaction mixture was diluted with ethyl acetate and the aqueous and organic layers were separated. The aqueous layer was extracted with ethyl acetate (3 x 10 mL) and the combined organics were dried over anhydrous sodium sulfate. After removal of solvent under reduced pressure, the pure products were isolated with SiO₂ chromatography.

II. Procedures for Preparation of substrates



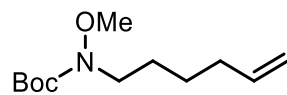
tert-butyl but-3-en-1-yl(methoxy)carbamate (20) The reaction was performed according to *General procedure A* with 4-bromobut-1-ene (3.05 mL, 30 mmol, 1.5 equiv.), *tert*-butyl methoxycarbamate (**S-1**) (2.94 g, 20 mmol, 1.0 equiv.), sodium hydride (1.07 g, 90% purity, 40 mmol, 2 equiv.) in DMF (50 mL). The compound was purified with SiO₂ chromatography (10% ethyl acetate in hexane, stain in KMnO₄) as a colorless oil (3.41 g, 85%).

¹H NMR (600 MHz, CDCl₃) δ 5.82 – 5.73 (m, 1H), 5.09 (dd, *J* = 17.1, 1.7 Hz, 1H), 5.03 (dd, *J* = 10.3, 1.7 Hz, 1H), 3.66 (s, 3H), 3.51 – 3.46 (m, 2H), 2.35 (q, *J* = 7.1, 7.0, 7.0 Hz, 2H), 1.47 (s, 9H). ¹³C NMR (151 MHz, CDCl₃) δ 156.4, 135.4, 116.8, 81.3, 62.3, 48.7, 31.6, 28.4. IR (neat) ν_{\max} 2977 (w), 2934 (w), 1727 (m), 1700 (s), 1642 (w), 1467 (w), 1436 (w), 1366 (s), 1320 (w), 1287 (w), 1252 (m), 1220 (w), 1147 (s), 1074 (m), 1034 (w), 993 (m), 914 (m), 858 (w), 837 (w), 766 (m), 630 (w), 564 (w) cm⁻¹. HRMS (DART+) for C₁₀H₂₀NO₃ [M+H]⁺: Calc'd: 202.1438, found: 202.1440.



tert-butyl methoxy(pent-4-en-1-yl)carbamate (25) The reaction was performed according to *General procedure A* with 5-bromopent-1-ene (3.55 mL, 30 mmol, 1.5 equiv.), *tert*-butyl methoxycarbamate (**S-1**) (2.94 g, 20 mmol, 1.0 equiv.), sodium hydride (1.07 g, 90% purity, 40 mmol, 2 equiv.) in DMF (50 mL). The compound was purified with SiO₂ chromatography (10% ethyl acetate in hexane, stain in KMnO₄) as a colorless oil (3.15 g, 73%).

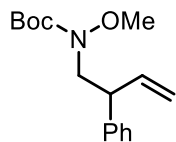
¹H NMR (600 MHz, CDCl₃) δ 5.82 – 5.72 (m, 1H), 4.99 (dq, *J* = 17.2, 1.7, 1.7, 1.7 Hz, 1H), 4.97 – 4.91 (m, 1H), 3.63 (s, 3H), 3.42 – 3.36 (m, 2H), 2.09 – 2.00 (m, 2H), 1.70 – 1.64 (m, 2H), 1.46 (s, 9H). ¹³C NMR (151 MHz, CDCl₃) δ 156.3, 137.9, 115.0, 81.1, 62.2, 48.5, 30.9, 28.4, 26.3. IR (neat) ν_{\max} 2977 (w), 2934 (w), 1725 (m), 1701 (s), 1641 (w), 1456 (w), 1438 (w), 1391 (m), 1366 (s), 1282 (m), 1253 (m), 1158 (s), 1080 (m), 992 (w), 911 (w), 852 (w), 825 (w), 765 (w), 627 (w) cm⁻¹. HRMS (DART+) for C₁₁H₂₂NO₃ [M+H]⁺: Calc'd: 216.1594, found: 216.1604.



tert-butyl hex-5-en-1-yl(methoxy)carbamate (S-4) The reaction was performed according to *General procedure A* with 6-bromohex-1-ene (4.02 mL, 30 mmol, 1.5 equiv.), *tert*-butyl methoxycarbamate (**S-1**) (2.94 g, 20 mmol, 1.0 equiv.), sodium hydride (1.07 g, 90% purity, 40 mmol, 2 equiv.) in DMF (50 mL). The compound was purified with SiO₂ chromatography (10% ethyl acetate in hexane, stain in KMnO₄) as a colorless oil (4.44 g, 97%).

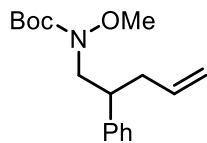
¹H NMR (600 MHz, CDCl₃) δ 5.77 – 5.67 (m, 1H), 4.94 (d, *J* = 17.2 Hz, 1H), 4.88 (d, *J* = 10.1 Hz, 1H), 3.60 (s, 3H), 3.36 (t, *J* = 7.2 Hz, 2H), 2.01 (q, *J* = 6.5 Hz, 2H), 1.59 – 1.52 (m, 2H), 1.43 (s, 9H), 1.38 – 1.30 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 156.3, 138.5, 114.6, 81.0, 62.1, 48.8, 33.4, 28.3, 26.6, 26.0. IR (neat) ν_{\max} 3076 (w), 2976 (w), 2933 (w), 2861 (w), 2816 (w), 1700 (s),

1640 (w), 1456 (w), 1437 (w), 1391 (m), 1366 (s), 1294 (w), 1253 (m), 1095 (w), 1060 (w), 992 (m), 909 (m), 859 (w), 765 (m), 632 (w) cm^{-1} . **HRMS** (DART+) for $\text{C}_{12}\text{H}_{24}\text{NO}_3$ $[\text{M}+\text{H}]^+$: Calc'd: 230.1751, found: 230.1753.

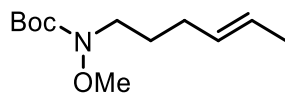


tert-butyl methoxy(2-phenylbut-3-en-1-yl)carbamate (S-5) The reaction was performed according to *General procedure B* with 2-phenylbut-3-en-1-ol (**S-2**) (1.48 g, 10 mmol, 1.0 equiv.), *tert*-butyl methoxycarbamate (**S-1**) (2.95 g, 20 mmol, 2.0 equiv), triphenyl phosphine (3.92 g, 15 mmol, 1.5 equiv.) and di-*tert*-butyl azodicarboxylate (3.45 g, 15 mmol, 1.5 equiv.) in THF (35 mL). The compound was purified with SiO_2 chromatography (10% ethyl acetate in hexane, stain in KMnO_4) as a colorless oil (1.10 g, 40%).

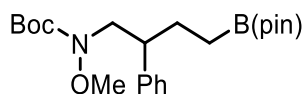
^1H NMR (600 MHz, CDCl_3) δ 7.33 – 7.27 (m, 2H), 7.25 – 7.20 (m, 3H), 6.07 – 5.98 (m, 1H), 5.15 – 5.10 (m, 2H), 3.84 – 3.75 (m, 2H), 3.74 – 3.67 (m, 1H), 3.61 (s, 3H), 1.41 (s, 9H). **^{13}C NMR** (126 MHz, CDCl_3) δ 155.9, 141.6, 139.2, 128.7, 128.2, 126.8, 116.5, 81.3, 62.1, 53.8, 47.8, 28.4. **IR** (neat) ν_{max} 2977 (w), 2932 (w), 1722 (s), 1701 (s), 1638 (w), 1601 (w), 1493 (w), 1476 (w), 1454 (w), 1391 (w), 1366 (s), 1304 (w), 1228 (w), 1165 (s), 1140 (w), 1087 (w), 1075 (w), 1032 (w), 997 (w), 917 (w), 860 (w), 754 (w), 700 (s), 542 (w) cm^{-1} . **HRMS** (DART+) for $\text{C}_{16}\text{H}_{24}\text{NO}_3$ $[\text{M}+\text{H}]^+$: Calc'd: 278.1751, found: 278.1755.



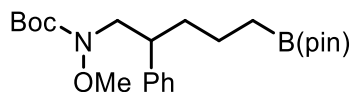
tert-butyl methoxy(2-phenylpent-4-en-1-yl)carbamate (S-6) The reaction was performed according to *General procedure B* with 2-phenylpent-4-en-1-ol (**S-3**) (1.62 g, 10 mmol, 1.0 equiv.), *tert*-butyl methoxycarbamate (**S-1**) (2.95 g, 20 mmol, 2.0 equiv), triphenyl phosphine (3.92 g, 15 mmol, 1.5 equiv.) and di-*tert*-butyl azodicarboxylate (3.45 g, 15 mmol, 1.5 equiv.) in THF (35 mL). The compound was purified with SiO_2 chromatography (10% ethyl acetate in hexane, stain in KMnO_4) as a colorless oil (1.45 g, 50%). **^1H NMR** (600 MHz, CDCl_3) δ 7.31 – 7.27 (m, 2H), 7.22 – 7.18 (m, 3H), 5.69 – 5.61 (m, 1H), 5.01 – 4.96 (m, 1H), 4.95 – 4.91 (m, 1H), 3.72 – 3.61 (m, 2H), 3.56 (s, 3H), 3.14 – 3.09 (m, 1H), 2.49 – 2.36 (m, 2H), 1.39 (s, 9H). **^{13}C NMR** (126 MHz, CDCl_3) δ 155.8, 142.3, 136.2, 128.4, 128.2, 126.6, 116.5, 81.1, 61.9, 54.1, 43.6, 37.9, 28.3. **IR** (neat) ν_{max} 2976 (w), 2931 (w), 1720 (s), 1700 (s), 1640 (w), 1603 (s), 1494 (s), 1476 (s), 1453 (m), 1438 (m), 1391 (m), 1366 (s), 1228 (m), 1162 (s), 1127 (m), 1076 (m), 1033 (w), 994 (w), 912 (m), 855 (w), 757 (m), 699 (s) cm^{-1} . **HRMS** (DART+) for $\text{C}_{17}\text{H}_{26}\text{NO}_3$ $[\text{M}+\text{H}]^+$: Calc'd: 292.1907, found: 292.1911.



tert-butyl (E)-hex-4-en-1-yl(methoxy)carbamate (29) The reaction was performed according to *General procedure B* with (E)-hex-4-en-1-ol (1.00 g, 10 mmol, 1.0 equiv.), *tert*-butyl methoxycarbamate (**S-1**) (3.93 g, 30 mmol, 3.0 equiv), triphenyl phosphine (5.23 g, 20 mmol, 2.0 equiv.) and di-*tert*-butyl azodicarboxylate (4.60 g, 20 mmol, 2.0 equiv.) in THF (35 mL). The compound was purified with SiO₂ chromatography (10% ethyl acetate in hexane, stain in KMnO₄) as a colorless oil (1.26 g, 54%). **¹H NMR** (500 MHz, CDCl₃) δ 5.49 – 5.32 (m, 2H), 3.65 (s, 3H), 3.44 – 3.35 (m, 2H), 2.06 – 1.91 (m, 2H), 1.71 – 1.57 (m, 5H), 1.47 (s, 9H). **¹³C NMR** (126 MHz, CDCl₃) δ 156.4, 130.4, 125.6, 81.1, 62.3, 48.7, 29.8, 28.4, 27.0, 18.0. **IR** (neat) ν_{\max} 2977 (w), 2935 (w), 2162 (w), 1724 (m), 1703 (s), 1456 (w), 1438 (w), 1392 (m), 1367 (s), 1280 (w), 1256 (w), 1166 (s), 966 (w) cm⁻¹. **HRMS** (DART+) for C₁₂H₂₄NO₃ [M+H]⁺: Calc'd: 230.1751, found: 230.1761.

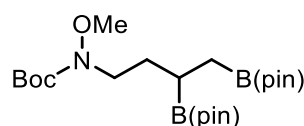


tert-butyl methoxy(2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)carbamate (S-7) The reaction was performed according to *General procedure D* with *tert*-butyl methoxy(2-phenylbut-3-en-1-yl)carbamate (**S-5**) (0.28 g, 1.0 mmol, 1.0 equiv.), [Ir(cod)Cl]₂ (10.1 mg, 0.015 mmol, 1.5 mol%), bis(diphenylphosphino)methane (11.5 mg, 0.03 mmol, 3 mol%), pinacol borane (0.17 mL, 1.2 mmol, 1.2 equiv.) in DCM (4 mL). The compound was purified with SiO₂ chromatography (10% ethyl acetate in hexane, stain with CAM) as a colorless oil (0.33 g, 82%). **¹H NMR** (600 MHz, CDCl₃) δ 7.28 – 7.22 (m, 2H), 7.20 – 7.13 (m, 3H), 3.63 (d, *J* = 7.5 Hz, 2H), 3.54 (s, 3H), 2.99 – 2.90 (m, 1H), 1.85 – 1.77 (m, 1H), 1.69 – 1.58 (m, 1H), 1.36 (s, 9H), 1.18 (s, 12H), 0.67 – 0.56 (m, 2H). **¹³C NMR** (126 MHz, CDCl₃) δ 155.8, 142.6, 128.3, 128.3, 126.4, 82.9, 80.9, 61.8, 54.6, 46.0, 28.2, 28.1, 27.8, 24.9, 24.8, 9.1. **IR** (neat) ν_{\max} 2976 (w), 2931 (w), 1720 (w), 1702 (w), 1453 (w), 1366 (s), 1318 (m), 1236 (w), 1169 (m), 1145 (s), 1093 (w), 968 (w), 859 (w), 847 (w), 757 (w), 700 (w) cm⁻¹. **HRMS** (DART+) for C₂₂H₃₇BNO₅ [M+H]⁺: Calc'd: 406.2759, found: 406.2756.



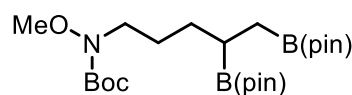
tert-butyl methoxy(2-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)carbamate (S-8) The reaction was performed according to *General procedure D* with *tert*-butyl methoxy(2-phenylpent-4-en-1-yl)carbamate (**S-6**) (0.29 g, 1.0 mmol, 1.0 equiv.), [Ir(cod)Cl]₂ (10.1 mg, 0.015 mmol, 1.5 mol%), bis(diphenylphosphino)methane (11.5 mg, 0.03 mmol, 3 mol%), pinacol borane (0.17 mL, 1.2 mmol, 1.2 equiv.) in DCM (4 mL). The compound was purified with SiO₂ chromatography (10% ethyl acetate in hexane, stain with CAM) as a colorless oil (0.30 g, 71%). **¹H NMR** (600 MHz, CDCl₃) δ 7.29 – 7.23 (m, 2H), 7.21 – 7.12 (m, 3H), 3.62 – 3.55 (m, 2H), 3.54 (s, 3H), 3.03 – 2.93 (m, 1H), 1.71 – 1.55 (m, 2H), 1.36 (s, 9H),

1.31 – 1.24 (m, 2H), 1.19 (s, 12H), 0.77 – 0.66 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 155.9, 143.0, 128.4, 128.3, 126.4, 83.0, 81.0, 61.9, 55.1, 43.9, 36.1, 28.3, 24.9, 21.9, 11.3. IR (neat) ν_{max} 2976 (w), 2931 (w), 1721 (m), 1701 (m), 1453 (w), 1366 (s), 1320 (m), 1227 (m), 1161 (m), 1143 (s), 1093 (m), 1074 (m), 1030 (w), 992 (w), 968 (m), 846 (m), 756 (m), 700 (s), 543 (w) cm^{-1} . HRMS (DART+) for $\text{C}_{23}\text{H}_{39}\text{BNO}_5$ $[\text{M}+\text{H}]^+$: Calc'd: 420.2916, found: 420.2938.



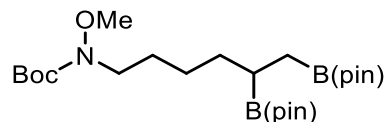
tert-butyl (3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-

yl)butyl)(methoxy)carbamate (**14**) The reaction was performed according to *General procedure C* with *tert*-butyl but-3-en-1-yl(methoxy)carbamate (**20**) (2.02 g, 10 mmol, 1.0 equiv.), bis(pinacolato)diboron (2.78 g, 11 mmol, 1.1 equiv.), cesium carbonate (0.49 g, 1.5 mmol, 0.15 equiv.), methanol (2.0 mL, 50 mmol, 5.0 equiv.) in THF (30 mL). The compound was purified with SiO_2 chromatography (10% ethyl acetate in hexane, stain with CAM) as a white solid (3.87 g, 85%). ^1H NMR (600 MHz, CDCl_3) δ 3.63 (s, 3H), 3.46 – 3.35 (m, 2H), 1.80 – 1.70 (m, 1H), 1.62 – 1.53 (m, 1H), 1.45 (s, 9H), 1.20 (s, 12H), 1.19 (s, 12H), 1.13 – 1.07 (m, 1H), 0.90 – 0.77 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 156.3, 83.0, 83.0, 80.9, 62.2, 48.8, 30.8, 28.4, 25.1, 25.0, 24.9, 24.9, 24.8, 15.9, 12.6. IR (neat) ν_{max} 2976 (m), 2931 (w), 1701 (m), 1366 (s), 1313 (s), 1235 (m), 1214 (w), 1143 (s), 1109 (w), 1087 (w), 967 (m), 860 (w), 846 (m), 765 (w), 671 (w), 578 (w) cm^{-1} . HRMS (DART+) for $\text{C}_{22}\text{H}_{44}\text{B}_2\text{NO}_7$ $[\text{M}+\text{H}]^+$: Calc'd: 456.3298, found: 456.3300. Melting point: 71–74 °C.

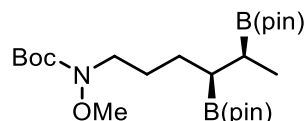


tert-butyl (4,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-

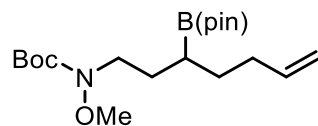
yl)pentyl)(methoxy)carbamate (**16**) The reaction was performed according to *General procedure C* with *tert*-butyl methoxy(pent-4-en-1-yl)carbamate (**25**) (2.15 g, 10 mmol, 1.0 equiv.), bis(pinacolato)diboron (2.78 g, 11 mmol, 1.1 equiv.), cesium carbonate (0.49 g, 1.5 mmol, 0.15 equiv.), methanol (2.0 mL, 50 mmol, 5.0 equiv.) in THF (30 mL). The compound was purified with SiO_2 chromatography (10% ethyl acetate in hexane, stain with CAM) as a colorless oil (3.80 g, 81%). ^1H NMR (600 MHz, CDCl_3) δ 3.61 (s, 3H), 3.38 – 3.26 (m, 2H), 1.61 – 1.52 (m, 2H), 1.46 – 1.37 (m, 10H), 1.34 – 1.23 (m, 1H), 1.17 (s, 12H), 1.17 (s, 12H), 1.12 – 1.04 (m, 1H), 0.86 – 0.72 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 156.4, 82.9, 80.9, 62.3, 49.7, 30.9, 28.4, 26.5, 25.1, 24.9, 24.9, 24.8, 24.8, 18.2, 12.7. IR (neat) ν_{max} 2976 (m), 2932 (w), 1702 (m), 1458 (w), 1366 (s), 1312 (s), 1274 (m), 1248 (m), 1214 (m), 1140 (s), 967 (m), 883 (w), 846 (m), 766 (w), 671 (w), 578 (w) cm^{-1} . HRMS (DART+) for $\text{C}_{23}\text{H}_{49}\text{B}_2\text{N}_2\text{O}_7$ $[\text{M}+\text{NH}_4]^+$: Calc'd: 487.3720, found: 487.3726.



tert-butyl (5,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)(methoxy)carbamate (18) The reaction was performed according to *General procedure C* with *tert*-butyl hex-5-en-1-yl(methoxy)carbamate (**S-4**) (2.29 g, 10 mmol, 1.0 equiv.), bis(pinacolato)diboron (2.78 g, 11 mmol, 1.1 equiv.), cesium carbonate (0.49 g, 1.5 mmol, 0.15 equiv.), methanol (2.0 mL, 50 mmol, 5.0 equiv.) in THF (30 mL). The compound was purified with SiO₂ chromatography (10% ethyl acetate in hexane, stain with CAM) as a colorless oil (3.2 g, 67%). ¹H NMR (600 MHz, CDCl₃) δ 3.63 (s, 3H), 3.39 – 3.32 (m, 2H), 1.59 – 1.52 (m, 2H), 1.46 (s, 10H), 1.33 – 1.25 (m, 3H), 1.20 (s, 24H), 1.13 – 1.04 (m, 1H), 0.87 – 0.73 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 156.5, 82.9, 82.9, 81.0, 62.4, 49.5, 33.6, 28.4, 27.5, 26.2, 25.1, 25.0, 24.9, 24.9, 24.8, 18.5, 12.7. IR (neat) ν_{max} 2976 (w), 2931 (w), 2864 (w), 1702 (m), 1366 (m), 1311 (m), 1269 (w), 1214 (w), 1140 (s), 1109 (w), 994 (w), 967 (w), 859 (w), 846 (m), 766 (w), 735 (w), 703 (w), 671 (w), 577 (w) cm⁻¹. HRMS (DART+) for C₂₄H₅₁B₂N₂O₇ [M+NH₄]⁺: Calc'd: 501.3877, found: 501.3886.

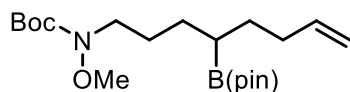


tert-butyl (rac-(4*S*,5*S*)-4,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)(methoxy)carbamate (30) The reaction was performed according to *General procedure C* with *tert*-butyl (*E*)-hex-4-en-1-yl(methoxy)carbamate (**29**) (0.23 g, 1.0 mmol, 1.0 equiv.), bis(pinacolato)diboron (0.278 g, 11 mmol, 1.1 equiv.), cesium carbonate (0.98 g, 0.3 mmol, 0.15 equiv.), methanol (0.2 mL, 5.0 mmol, 5.0 equiv.) in THF (1.5 mL). The compound was purified with SiO₂ chromatography (10% ethyl acetate in hexane, stain with CAM) as a colorless oil (0.20 g, 41%). ¹H NMR (500 MHz, CDCl₃) δ 3.62 (s, 3H), 3.35 (t, *J* = 7.0 Hz, 2H), 1.66 – 1.55 (m, 1H), 1.53 – 1.46 (m, 2H), 1.44 (s, 9H), 1.35 – 1.27 (m, 1H), 1.21 – 1.15 (m, 24H), 1.14 – 1.09 (m, 1H), 1.06 – 0.99 (m, 1H), 0.92 (d, *J* = 7.5 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 156.4, 82.9, 82.8, 80.9, 62.3, 49.9, 28.4, 27.0, 26.8, 26.0, 25.1, 25.0, 24.8, 24.7, 17.9, 14.5, 13.9. IR (neat) ν_{max} 2976 (w), 2932 (w), 1703 (w), 1459 (w), 1368 (s), 1311 (m), 1215 (w), 1142 (s), 969 (w), 858 (w) cm⁻¹. HRMS (DART+) for C₂₄H₅₁B₂N₂O₇ [M+NH₄]⁺: Calc'd: 501.3877, found: 501.3897.

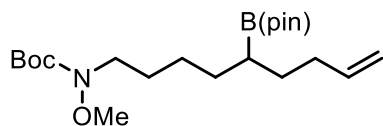


tert-butyl methoxy(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-6-en-1-yl)carbamate (S-9) The reaction was performed using a method under development in the group from *tert*-butyl (3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)(methoxy)carbamate (**14**) (0.46 g, 1 mmol) and this method will be reported separately.

The compound was purified with SiO₂ chromatography (10% ethyl acetate in hexane, stain with CAM) as a colorless oil (0.25 g, 68%). **¹H NMR** (600 MHz, CDCl₃) δ 5.84 – 5.73 (m, 1H), 5.01 – 4.95 (m, 1H), 4.94 – 4.88 (m, 1H), 3.65 (s, 3H), 3.48 – 3.35 (m, 2H), 2.13 – 1.98 (m, 1H), 1.77 – 1.69 (m, 1H), 1.69 – 1.61 (m, 1H), 1.59 – 1.50 (m, 1H), 1.48 (s, 10H), 1.23 (s, 12H), 1.04 – 0.94 (m, 1H). **¹³C NMR** (151 MHz, CDCl₃) δ 156.4, 139.1, 114.5, 83.2, 81.1, 62.3, 48.9, 33.4, 30.4, 28.5, 28.4, 25.0, 24.9. **IR** (neat) ν_{\max} 2977 (w), 2931 (w), 1726 (m), 1701 (m), 1640 (w), 1457 (w), 1380 (m), 1367 (m), 1318 (m), 1239 (m), 1160 (s), 1143 (s), 1085 (w), 995 (w), 967 (w), 909 (w), 859 (w), 765 (w), 693 (w), 670 (w), 578 (w) cm⁻¹. **HRMS** (DART+) for C₁₉H₃₇BNO₅ [M+H]⁺: Calc'd: 370.2759, found: 370.2763.

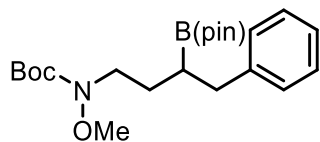


tert-butyl methoxy(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-7-en-1-yl)carbamate (S-10) The reaction was performed using a method under development in the group from *tert*-butyl (4,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)(methoxy)carbamate (**16**) (0.47 g, 1 mmol) and this method will be reported separately. The compound was purified with SiO₂ chromatography (10% ethyl acetate in hexane, stain with CAM) as a colorless oil (0.24 g, 62%). **¹H NMR** (500 MHz, CDCl₃) δ 5.83 – 5.69 (m, 1H), 4.98 – 4.91 (m, 1H), 4.90 – 4.86 (m, 1H), 3.63 (s, 3H), 3.38 – 3.33 (m, 2H), 2.08 – 1.95 (m, 2H), 1.61 – 1.53 (m, 2H), 1.54 – 1.41 (m, 10H), 1.43 – 1.28 (m, 3H), 1.20 (s, 12H), 1.02 – 0.91 (m, 1H). **¹³C NMR** (126 MHz, CDCl₃) δ 156.4, 139.2, 114.4, 83.0, 81.0, 62.3, 49.5, 33.4, 30.6, 28.4, 26.8, 24.9, 23.2. **IR** (neat) ν_{\max} 2977 (w), 2931 (w), 2857 (w), 1725 (w), 1703 (m), 1640 (w), 1458 (w), 1380 (m), 1367 (s), 1316 (m), 1254 (w), 1214 (w), 1152 (s), 1144 (s), 1083 (w), 994 (w), 967 (w), 908 (w), 856 (w), 766 (w), 690 (w), 670 (w) cm⁻¹. **HRMS** (DART+) for C₂₀H₄₂BN₂O₅ [M+NH₄]⁺: Calc'd: 401.3181, found: 401.3196.

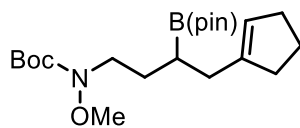


tert-butyl methoxy(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)non-8-en-1-yl)carbamate (S-11) The reaction was performed using a method under development in the group from *tert*-butyl (5,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)(methoxy)carbamate (**18**) (0.48 g, 1 mmol) and this method will be reported separately. The compound was purified with SiO₂ chromatography (10% ethyl acetate in hexane, stain with CAM) as a colorless oil (0.26 g, 65%). **¹H NMR** (600 MHz, CDCl₃) δ 5.82 – 5.73 (m, 1H), 4.96 (dd, *J* = 17.1, 1.9 Hz, 1H), 4.89 (dd, *J* = 10.2, 1.2 Hz, 1H), 3.64 (s, 3H), 3.37 (t, *J* = 7.3 Hz, 2H), 2.08 – 1.95 (m, 2H), 1.61 – 1.54 (m, 2H), 1.53 – 1.37 (m, 12H), 1.37 – 1.25 (m, 3H), 1.21 (s, 12H), 1.00 – 0.92 (m, 1H). **¹³C NMR** (151 MHz, CDCl₃) δ 156.5, 139.3, 114.3, 83.0, 81.1, 62.4, 49.3, 33.5, 31.0, 30.7, 28.4, 27.6, 26.5, 24.9. **IR** (neat) ν_{\max} 2976 (w), 2930 (w), 2856 (w), 1727 (w),

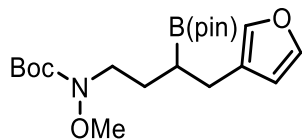
1702 (m), 1640 (w), 1458 (w), 1387 (m), 1367 (m), 1315 (w), 1234 (w), 1143 (s), 994 (w), 967 (w), 908 (w), 859 (w), 766 (w), 689 (w), 670 (w) cm^{-1} . **HRMS** (DART+) for $\text{C}_{21}\text{H}_{44}\text{BN}_2\text{O}_5$ $[\text{M}+\text{NH}_4]^+$: Calc'd: 415.3338, found: 415.3326.



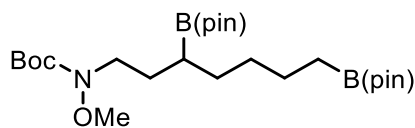
tert-butyl methoxy(4-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)carbamate (S-12) The reaction was performed according to *General procedure E* with *tert*-butyl (3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)(methoxy)carbamate (**14**) (0.46 g, 1 mmol, 1.0 equiv.), solid potassium hydroxide (0.17 g, 3 mmol, 3 equiv.), $\text{Pd}(\text{OAc})_2$ (5.6 mg, 0.025 mmol, 2.5 mol%), RuPhos (11.7 mg, 0.025 mmol, 2.5 mol%) and bromobenzene (0.24 g, 1.5 mmol, 1.5 equiv.) in THF (10 mL) and H_2O (1 mL). The compound was purified with SiO_2 chromatography (10% ethyl acetate in hexane, stain with CAM) as a colorless oil (0.24 g, 60%). **^1H NMR** (500 MHz, CDCl_3) δ 7.24 – 7.17 (m, 4H), 7.16 – 7.10 (m, 1H), 3.61 (s, 3H), 3.50 – 3.37 (m, 2H), 2.78 – 2.64 (m, 2H), 1.79 – 1.63 (m, 2H), 1.46 (s, 9H), 1.39 – 1.32 (m, 1H), 1.16 (s, 6H), 1.14 (s, 6H). **^{13}C NMR** (151 MHz, CDCl_3) δ 156.4, 142.0, 129.0, 128.2, 125.8, 83.3, 81.1, 62.4, 48.9, 37.1, 28.5, 28.3, 24.9, 24.8. **IR** (neat) ν_{max} 2976 (w), 2931 (w), 1724 (w), 1700 (m), 1454 (w), 1380 (m), 1366 (s), 1321 (m), 1242 (m), 1142 (s), 1111 (w), 967 (w), 880 (w), 747 (w), 699 (w) cm^{-1} . **HRMS** (DART+) for $\text{C}_{22}\text{H}_{37}\text{BNO}_5$ $[\text{M}+\text{H}]^+$: Calc'd: 406.2759, found: 406.2761.



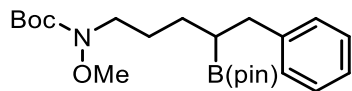
tert-butyl (4-(cyclopent-1-en-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)(methoxy)carbamate (S-13) The reaction was performed according to *General procedure E* with *tert*-butyl (3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)(methoxy)carbamate (**14**) (0.46 g, 1 mmol, 1.0 equiv.), solid potassium hydroxide (0.17 g, 3 mmol, 3 equiv.), $\text{Pd}(\text{OAc})_2$ (5.6 mg, 0.025 mmol, 2.5 mol%), RuPhos (11.7 mg, 0.025 mmol, 2.5 mol%) and 1-chlorocyclopentene (0.15 g, 1.5 mmol, 1.5 equiv.) in THF (10 mL) and H_2O (1 mL). The compound was purified with SiO_2 chromatography (10% ethyl acetate in hexane, stain with CAM) as a colorless oil (0.35 g, 89%). **^1H NMR** (600 MHz, CDCl_3) δ 5.35 (s, 1H), 3.66 (s, 3H), 3.46 – 3.37 (m, 2H), 2.28 – 2.17 (m, 5H), 2.17 – 2.11 (m, 1H), 1.86 – 1.79 (m, 2H), 1.75 – 1.61 (m, 2H), 1.48 (s, 9H), 1.26 – 1.17 (m, 13H). **^{13}C NMR** (151 MHz, CDCl_3) δ 156.4, 144.4, 124.3, 83.2, 81.1, 62.3, 49.0, 35.2, 32.6, 32.5, 28.6, 28.5, 25.0, 24.9, 23.7. **IR** (neat) ν_{max} 2976 (w), 2931 (w), 2843 (w), 1725 (w), 1701 (m), 1438 (w), 1379 (m), 1366 (m), 1321 (m), 1241 (m), 1142 (s), 1091 (w), 1061 (w), 1034 (w), 967 (w), 860 (w), 835 (w), 766 (w), 669 (w) cm^{-1} . **HRMS** (DART+) for $\text{C}_{21}\text{H}_{39}\text{BNO}_5$ $[\text{M}+\text{H}]^+$: Calc'd: 396.2916, found: 396.2913.



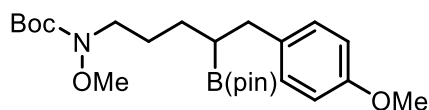
tert-butyl (4-(furan-3-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)(methoxy)carbamate (S-14) The reaction was performed according to *General procedure E* with *tert*-butyl (3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)(methoxy)carbamate (**14**) (0.46 g, 1 mmol, 1.0 equiv.), solid potassium hydroxide (0.17 g, 3 mmol, 3 equiv.), Pd(OAc)₂ (5.6 mg, 0.025 mmol, 2.5 mol%), RuPhos (11.7 mg, 0.025 mmol, 2.5 mol%), 3-bromofuran (0.22 g, 1.5 mmol, 1.5 equiv.) and LiCl (42 mg, 1.0 mmol, 1.0 equiv.) in THF (10 mL) and H₂O (1 mL). The compound was purified with SiO₂ chromatography (10% ethyl acetate in hexane, stain with CAM) as a colorless oil (0.20 g, 50%). **¹H NMR** (600 MHz, CDCl₃) δ 7.26 (s, 1H), 7.18 (s, 1H), 6.24 (s, 1H), 3.60 (s, 3H), 3.46 – 3.35 (m, 2H), 2.57 – 2.41 (m, 2H), 1.76 – 1.61 (m, 2H), 1.44 (s, 9H), 1.26 – 1.18 (m, 1H), 1.14 (s, 12H). **¹³C NMR** (151 MHz, CDCl₃) δ 156.3, 142.5, 139.4, 124.4, 111.4, 83.2, 81.0, 62.2, 48.7, 28.4, 28.2, 25.9, 24.8, 24.8. **IR** (neat) ν_{\max} 2976 (w), 2931 (w), 1698 (m), 1456 (w), 1366 (m), 1319 (m), 1241 (m), 1151 (m), 1141 (s), 1093 (w), 1063 (w), 1023 (m), 967 (w), 872 (m), 860 (w), 774 (w), 737 (w), 670 (w), 599 (m) cm⁻¹. **HRMS** (DART+) for C₂₀H₃₅BNO₆ [M+H]⁺: Calc'd: 396.2552, found: 396.2550.



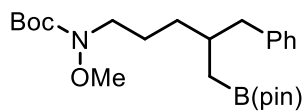
tert-butyl (3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptyl)(methoxy)carbamate (S-15) The reaction was performed according to *General procedure D* with *tert*-butyl methoxy(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-6-en-1-yl)carbamate (**S-9**) (0.37 g, 1.0 mmol, 1.0 equiv.), [Ir(cod)Cl]₂ (10.1 mg, 0.015 mmol, 1.5 mol%), bis(diphenylphosphino)methane (11.5 mg, 0.03 mmol, 3 mol%), pinacol borane (0.17 mL, 1.2 mmol, 1.2 equiv.) in DCM (4 mL). The compound was purified with SiO₂ chromatography (15% ethyl acetate in hexane, stain with CAM) as a colorless oil (0.42 g, 85%). **¹H NMR** (500 MHz, CDCl₃) δ 3.63 (s, 3H), 3.43 – 3.31 (m, 2H), 1.73 – 1.56 (m, 2H), 1.45 (s, 9H), 1.42 – 1.30 (m, 4H), 1.30 – 1.23 (m, 2H), 1.20 (s, 24H), 0.96 – 0.89 (m, 1H), 0.75 – 0.69 (m, 2H). **¹³C NMR** (126 MHz, CDCl₃) δ 156.4, 83.0, 82.9, 81.0, 62.3, 49.1, 32.0, 31.0, 28.5, 28.4, 24.9, 24.9, 24.9, 24.4. **IR** (neat) ν_{\max} 2976 (w), 2929 (w), 2860 (w), 1742 (w), 1701 (m), 1459 (w), 1367 (s), 1315 (s), 1242 (m), 1414 (m), 1144 (s), 1111 (m), 1089 (w), 1031 (w), 967 (m), 859 (w), 846 (m), 766 (w), 671 (w), 578 (w) cm⁻¹. **HRMS** (DART+) for C₂₅H₅₀B₂NO₇ [M+H]⁺: Calc'd: 498.3768, found: 498.3785.



tert-butyl methoxy(5-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)carbamate (S-16) The reaction was performed according to *General procedure E* with *tert-butyl* (4,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)(methoxy)carbamate (**16**) (0.47 g, 1 mmol, 1.0 equiv.), solid potassium hydroxide (0.17 g, 3 mmol, 3 equiv.), Pd(OAc)₂ (5.6 mg, 0.025 mmol, 2.5 mol%), RuPhos (11.7 mg, 0.025 mmol, 2.5 mol%) and bromobenzene (0.24 g, 1.5 mmol, 1.5 equiv.) in THF (10 mL) and H₂O (1 mL). The compound was purified with SiO₂ chromatography (10% ethyl acetate in hexane, stain with CAM) as a colorless oil (0.25 g, 60%). **¹H NMR** (500 MHz, CDCl₃) δ 7.24 – 7.16 (m, 4H), 7.15 – 7.10 (m, 1H), 3.63 (s, 3H), 3.37 (t, *J* = 7.3, 2H), 2.75 – 2.61 (m, 2H), 1.69 – 1.55 (m, 2H), 1.47 (s, 9H), 1.45 – 1.33 (m, 3H), 1.15 (s, 6H), 1.12 (s, 6H). **¹³C NMR** (151 MHz, CDCl₃) δ 156.5, 142.2, 129.0, 128.2, 125.8, 83.2, 81.1, 62.3, 49.6, 37.4, 28.5, 28.4, 26.8, 24.9, 24.9. **IR** (neat) ν_{\max} 2976 (w), 2931 (w), 2857 (w), 1701 (m), 1603 (w), 1454 (w), 1380 (m), 1367 (m), 1320 (m), 1270 (w), 1250 (w), 1141 (s), 1112 (w), 1033 (w), 989 (w), 968 (w), 857 (w), 748 (w), 699 (w), 579 (w) cm⁻¹. **HRMS** (DART+) for C₂₃H₄₂BN₂O₅ [M+NH₄]⁺: Calc'd: 437.3181, found: 437.3176.

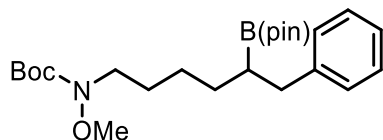


tert-butyl methoxy(5-(4-methoxyphenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)carbamate (S-17) The reaction was performed according to *General procedure E* with *tert-butyl* (4,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)(methoxy)carbamate (**16**) (0.47 g, 1 mmol, 1.0 equiv.), solid potassium hydroxide (0.17 g, 3 mmol, 3 equiv.), Pd(OAc)₂ (5.6 mg, 0.025 mmol, 2.5 mol%), RuPhos (11.7 mg, 0.025 mmol, 2.5 mol%) and 1-bromo-4-methoxybenzene (0.28 g, 1.5 mmol, 1.5 equiv.) in THF (10 mL) and H₂O (1 mL). The compound was purified with SiO₂ chromatography (12% ethyl acetate in hexane, stain with CAM) as a colorless oil (0.35 g, 79%). **¹H NMR** (500 MHz, CDCl₃) δ 7.09 (d, *J* = 8.2 Hz, 2H), 6.77 (d, *J* = 8.2 Hz, 2H), 3.75 (s, 3H), 3.63 (s, 3H), 3.37 (t, *J* = 7.3, 2H), 2.70 – 2.55 (m, 2H), 1.68 – 1.54 (m, 2H), 1.47 (s, 9H), 1.43 – 1.28 (m, 3H), 1.15 (s, 6H), 1.13 (s, 6H). **¹³C NMR** (126 MHz, CDCl₃) δ 157.8, 156.4, 134.3, 129.8, 113.6, 83.1, 81.0, 62.3, 55.3, 49.5, 36.4, 28.4, 28.3, 26.8, 26.0, 24.9, 24.8. **IR** (neat) ν_{\max} 2976 (w), 2931 (w), 2857 (w), 1700 (m), 1611 (w), 1511 (m), 1458 (w), 1366 (s), 1319 (m), 1299 (m), 1245 (s), 1140 (s), 1112 (m), 1061 (w), 1036 (m), 967 (w), 854 (m), 839 (m), 762 (w), 686 (w), 670 (w) cm⁻¹. **HRMS** (DART+) for C₂₄H₄₄BN₂O₆ [M+NH₄]⁺: Calc'd: 467.3287, found: 467.3293.



tert-butyl (4-benzyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)(methoxy)carbamate (S-18) In an oven-dried 20 mL vial, *tert-butyl* methoxy(5-

phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)carbamate (**S-16**) (0.42 g, 1.0 mmol, 1.0 equiv.) and bromochloromethane (0.20 mL, 3.0 mmol, 3.0 equiv.) were dissolved in anhydrous THF (7.5 mL). After the solution was cooled to -78 °C, *n*-butyllithium in hexane (1.6 M, 1.56 mL, 2.5 mmol, 2.5 equiv.) was added dropwise, and the reaction mixture was stirred at this temperature for 20 mins before the cooling bath was removed. The mixture was allowed to warm up to r.t. and stirred for 2 h. The reaction mixture was quenched by the addition of saturated ammonium chloride solution, extracted with ethyl acetate (3 x 20 mL), dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. compound was purified with SiO₂ chromatography (10% ethyl acetate in hexane, stain with CAM) as a colorless oil (0.35 g, 81%). The isolated compound contained 9% of unreacted starting material (**S-23**) and was used without further purification. ¹H NMR (400 MHz, CDCl₃) δ 7.26 – 7.19 (m, 2H), 7.18 – 7.11 (m, 3H), 3.62 (s, 3H), 3.33 (t, *J* = 7.3 Hz, 2H), 2.55 (d, *J* = 7.7 Hz, 2H), 1.96 – 1.85 (m, 1H), 1.72 – 1.51 (m, 2H), 1.46 (s, 9H), 1.38 – 1.26 (m, 1H), 1.21 (s, 12H), 0.76 (d, *J* = 6.0 Hz, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 156.5, 141.5, 129.5, 128.2, 128.2, 125.7, 83.0, 81.1, 62.4, 49.6, 43.1, 36.4, 33.1, 28.5, 25.0, 24.7. IR (neat) ν_{\max} 2976 (w), 2930 (w), 1701 (m), 1454 (w), 1366 (s), 1317 (m), 1248 (m), 1142 (s), 1113 (m), 1032 (w), 968 (m), 847 (m), 740 (m), 700 (m), 577 (w) cm⁻¹. HRMS (DART+) for C₂₄H₄₁BNO₅ [M+H]⁺: Calc'd: 434.3072, found: 434.3079.



tert-butyl methoxy(6-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)carbamate (S-19) The reaction was performed according to *General procedure E* with *tert*-butyl (5,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)(methoxy)carbamate (**18**) (0.48 g, 1.0 mmol, 1.0 equiv.), solid potassium hydroxide (0.17 g, 3 mmol, 3 equiv.), Pd(OAc)₂ (5.6 mg, 0.025 mmol, 2.5 mol%), RuPhos (11.7 mg, 0.025 mmol, 2.5 mol%) and bromobenzene (0.24 g, 1.5 mmol, 1.5 equiv.) in THF (10 mL) and H₂O (1 mL). The compound was purified with SiO₂ chromatography (10% ethyl acetate in hexane, stain with CAM) as a colorless oil (0.34 g, 79%). ¹H NMR (600 MHz, CDCl₃) δ 7.26 – 7.16 (m, 4H), 7.16 – 7.10 (m, 1H), 3.65 (s, 3H), 3.41 – 3.35 (m, 2H), 2.74 – 2.62 (m, 2H), 1.63 – 1.54 (m, 2H), 1.48 (s, 9H), 1.46 – 1.30 (m, 5H), 1.15 (s, 6H), 1.12 (s, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 156.5, 142.3, 129.0, 128.2, 125.7, 83.1, 81.1, 62.4, 49.3, 37.4, 31.0, 28.5, 27.6, 26.5, 24.9, 24.8. IR (neat) ν_{\max} 2976 (w), 2930 (w), 2856 (w), 1723 (w), 1701 (m), 1454 (w), 1380 (m), 1366 (m), 1319 (m), 1252 (w), 1239 (w), 1214 (w), 1142 (s), 1111 (w), 1074 (w), 1031 (w), 966 (w), 861 (m), 749 (w), 699 (m), 670 (w), 578 (w) cm⁻¹. HRMS (DART+) for C₂₄H₄₄BN₂O₅ [M+NH₄]⁺: Calc'd: 451.3338, found: 451.3351.

III. Representative Procedure of Intramolecular Amination

Intramolecular amination followed by Boc protection (Method A):

The corresponding *tert*-butyl(methoxy)carbamate substrate (0.2 mmol) was dissolved in dichloromethane (2 mL). Trifluoroacetic acid (2.0 mmol, 0.15 mL) was added dropwise. The mixture was allowed to stir at r.t. for 90 min and monitored by TLC. The mixture was quenched carefully with saturated sodium bicarbonate solution, extracted with ethyl acetate, and dried over anhydrous sodium sulfate and concentrated. The product was used without further purification.

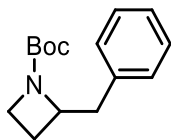
The deprotected methoxy amine substrate was transferred into an oven-dried 20 mL vial loaded with a stir bar, and brought into the glovebox. Potassium *tert*-butoxide (0.22 mmol, 24.5 mg) was added, followed by toluene (3.6 mL) and THF (0.36 mL). The vial was sealed with a PTFE screw-cap, removed from the glovebox, and heated at 110 °C (reaction time: 24 hours for azetidines, and 14 hours for pyrrolidines and piperidines). After the reaction was cooled to r.t., a solution of di-*tert*-butyl dicarbonate (0.3 mmol, 35mg) in THF (1.5 mL) was added and the mixture was allowed to stir for 3 hours. The mixture was washed with water, extracted with ethyl acetate, dried over anhydrous sodium sulfate and concentrated. The crude mixture was then purified using SiO₂ chromatography.

Intramolecular amination followed by Ts protection (Method B):

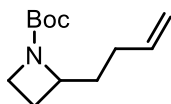
The corresponding *tert*-butyl(methoxy)carbamate substrate (0.2 mmol) was dissolved in dichloromethane (2 mL). Trifluoroacetic acid (2.0 mmol, 0.15 mL) was added dropwise. The mixture was allowed to stir at r.t. for 90 min and monitored by TLC. The mixture was quenched carefully with saturated sodium bicarbonate solution, extracted with ethyl acetate, and dried over anhydrous sodium sulfate and concentrated. The product was used without further purification.

The deprotected methoxy amine substrate was transferred into an oven-dried 20 mL vial loaded with a stir bar, and brought into the glovebox. Potassium *tert*-butoxide (0.22 mmol, 24.5 mg) was added, followed by toluene (3.6 mL) and THF (0.36 mL). The vial was sealed with a PTFE screw-cap, removed from the glovebox, and heated at 110 °C (reaction time: 24 hours for azetidines, and 14 hours for pyrrolidines and piperidines). After the reaction was cooled to r.t., a solution of tosyl chloride (0.4 mmol, 28 mg) in THF (2 mL) was added, followed by triethylamine (0.5 mmol, 0.07 mL) and the mixture was allowed to stir for 3 hours. The mixture was washed with water, extracted with ethyl acetate, dried over anhydrous sodium sulfate and concentrated. The crude mixture was then purified using SiO₂ chromatography.

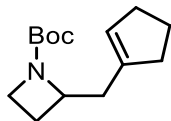
IV. Procedures and Characterization for Intramolecular Amination Product



tert-butyl 2-benzylazetidine-1-carboxylate (1) The reaction was performed according to the general procedure above (*Method A*) with *tert*-butyl methoxy(4-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)carbamate (**S-12**) (83.9 mg, 0.20 mmol, 1.0 equiv.), and potassium *tert*-butoxide (24.7 mg, 0.22 mmol, 1.1 equiv.) in toluene and THF (3.6/0.36 mL, 0.05 M) for 24 hours. The compound was purified with SiO₂ chromatography (10% ethyl acetate in hexane, stain with Ninhydrin) as a colorless oil (33.6 mg, 68%). All spectral data was in accordance with previously published results.¹⁰

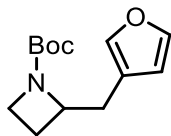


tert-butyl 2-(but-3-en-1-yl)azetidine-1-carboxylate (2) The reaction was performed according to the general procedure above (*Method A*) with *tert*-butyl methoxy(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-6-en-1-yl)carbamate (**S-9**) (73.9 mg, 0.20 mmol, 1.0 equiv.), and potassium *tert*-butoxide (24.7 mg, 0.22 mmol, 1.1 equiv.) in toluene and THF (3.6/0.36 mL, 0.05 M) for 24 hours. The compound was purified with SiO₂ chromatography (10% ethyl acetate in hexane, stain with KMnO₄) as a colorless oil (19.8 mg, 47%). ¹H NMR (500 MHz, CDCl₃) δ 5.90 – 5.74 (m, 1H), 5.02 (d, *J* = 17.1 Hz, 1H), 4.95 (d, *J* = 10.3 Hz, 1H), 4.26 – 4.15 (m, 1H), 3.88 – 3.73 (m, 2H), 2.29 – 2.19 (m, 1H), 2.13 – 2.04 (m, 2H), 2.03 – 1.93 (m, 1H), 1.88 – 1.78 (m, 1H), 1.74 – 1.64 (m, 1H), 1.43 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 156.8, 138.3, 114.7, 79.2, 61.8, 46.3, 34.8, 30.4, 29.1, 28.6, 22.1. IR (neat) ν_{max} 2928 (w), 2891 (w), 2861 (w), 2160 (m), 1701 (s), 1391 (w), 1365 (w), 1183 (w), 1135 (w), 908 (w) cm⁻¹. HRMS (DART+) for C₁₂H₂₂NO₂ [M+H]⁺: Calc'd: 212.1645, found: 212.1643.

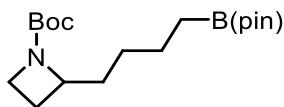


tert-butyl 2-(cyclopent-1-en-1-ylmethyl)azetidine-1-carboxylate (3) The reaction was performed according to the general procedure above (*Method A*) with *tert*-butyl (4-(cyclopent-1-en-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)(methoxy)carbamate (**S-13**) (79.0 mg, 0.20 mmol, 1.0 equiv.), and potassium *tert*-butoxide (24.7 mg, 0.22 mmol, 1.1 equiv.) in toluene and THF (3.6/0.36 mL, 0.05 M) for 24 hours. The compound was purified with SiO₂ chromatography (10% ethyl acetate in hexane, stain with KMnO₄) as a colorless oil (28.5 mg, 60%). ¹H NMR (500 MHz, CDCl₃) δ 5.32 (s, 1H), 4.34 – 4.24 (m, 1H), 3.85 – 3.72 (m, 2H), 2.72 (d, *J* = 14.6 Hz, 1H), 2.36 (dd, *J* = 14.0, 9.3 Hz, 1H), 2.31 – 2.25 (m, 2H), 2.25 – 2.19 (m, 3H), 1.89 – 1.79 (m, 3H), 1.43 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 156.5, 140.2, 125.7, 79.2,

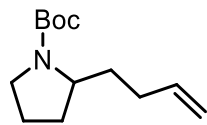
60.9, 37.0, 35.9, 32.6, 28.6, 23.5, 22.4. **IR** (neat) ν_{\max} 2929 (w), 2890 (w), 2845 (w), 1698 (s), 1478 (w), 1455 (w), 1388 (s), 1363 (s), 1254 (w), 1181 (w), 1131 (s), 1082 (w), 864 (w), 777 (w), 564 (w) cm^{-1} . **HRMS** (DART+) for $\text{C}_{14}\text{H}_{24}\text{NO}_2$ $[\text{M}+\text{H}]^+$: Calc'd: 238.1802, found: 238.1815.



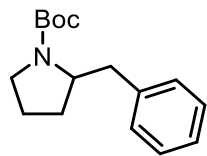
tert-butyl 2-(furan-3-ylmethyl)azetidide-1-carboxylate (4) The reaction was performed according to the general procedure above (**Method A**) with *tert*-butyl (4-(furan-3-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)(methoxy)carbamate (**S-14**) (79.1 mg, 0.20 mmol, 1.0 equiv.), and potassium *tert*-butoxide (24.7 mg, 0.22 mmol, 1.1 equiv.) in toluene and THF (3.6/0.36 mL, 0.05 M) for 24 hours. The compound was purified with SiO_2 chromatography (10% ethyl acetate in hexane, stain with CAM) as a colorless oil (31.0 mg, 66%). **^1H NMR** (600 MHz, CDCl_3) δ 7.36 (s, 1H), 7.25 (s, 1H), 6.28 (s, 1H), 4.39 – 4.33 (m, 1H), 3.82 – 3.75 (m, 1H), 3.69 – 3.62 (m, 1H), 2.91 (dd, $J = 14.3, 3.6$ Hz, 1H), 2.80 (dd, $J = 14.5, 8.2$ Hz, 1H), 2.24 – 2.09 (m, 1H), 1.90 – 1.78 (m, 1H), 1.45 (s, 9H). **^{13}C NMR** (151 MHz, CDCl_3) δ 156.4, 143.0, 140.1, 120.0, 111.7, 79.4, 61.4, 46.3, 30.0, 28.6, 21.2. **IR** (neat) ν_{\max} 2973 (w), 2927 (w), 1692 (s), 1500 (w), 1478 (w), 1455 (w), 1389 (s), 1364 (s), 1306 (w), 1254 (w), 1182 (m), 1133 (s), 1069 (w), 1022 (m), 972 (w), 947 (w), 872 (m), 770 (m), 727 (w), 600 (m), 564 (w) cm^{-1} . **HRMS** (DART+) for $\text{C}_{13}\text{H}_{20}\text{NO}_3$ $[\text{M}+\text{H}]^+$: Calc'd: 238.1438, found: 238.1430.



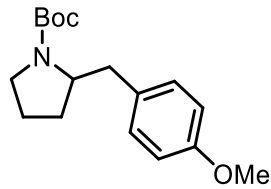
tert-butyl 2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)azetidide-1-carboxylate (5) The reaction was performed according to the general procedure above (**Method A**) with *tert*-butyl (3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptyl)(methoxy)carbamate (**S-15**) (99.5 mg, 0.20 mmol, 1.0 equiv.), and potassium *tert*-butoxide (24.7 mg, 0.22 mmol, 1.1 equiv.) in toluene and THF (3.6/0.36 mL, 0.05 M) for 24 hours. The compound was purified with SiO_2 chromatography (10% ethyl acetate in hexane, stain with CAM) as a colorless oil (37.3 mg, 55%). **^1H NMR** (400 MHz, CDCl_3) δ 4.20 – 4.10 (m, 1H), 3.84 – 3.72 (m, 2H), 2.29 – 2.14 (m, 1H), 1.92 – 1.73 (m, 2H), 1.63 – 1.52 (m, 1H), 1.46 – 1.37 (m, 11H), 1.32 – 1.25 (m, 2H), 1.23 (s, 12H), 0.77 (t, $J = 7.8$ Hz, 2H). **^{13}C NMR** (151 MHz, CDCl_3) δ 156.7, 83.0, 79.1, 62.3, 35.3, 30.5, 28.6, 27.4, 24.9, 24.2, 22.1. **^{11}B NMR** (160 MHz, CDCl_3) δ 33.9. **IR** (neat) ν_{\max} 2976 (w), 2930 (w), 2890 (w), 2860 (w), 1698 (s), 1456 (w), 1364 (s), 1317 (m), 1255 (w), 1142 (s), 968 (w), 881 (w), 846 (w), 777 (w) cm^{-1} . **HRMS** (DART+) for $\text{C}_{18}\text{H}_{35}\text{BNO}_4$ $[\text{M}+\text{H}]^+$: Calc'd: 340.2654, found: 340.2658.



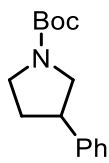
tert-butyl 2-(but-3-en-1-yl)pyrrolidine-1-carboxylate (6) The reaction was performed according to the general procedure above (*Method A*) with *tert*-butyl methoxy(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-7-en-1-yl)carbamate (**S-10**) (76.7 mg, 0.20 mmol, 1.0 equiv.), and potassium *tert*-butoxide (24.7 mg, 0.22 mmol, 1.1 equiv.) in toluene and THF (3.6/0.36 mL, 0.05 M) for 14 hours. The compound was purified with SiO₂ chromatography (10% ethyl acetate in hexane, stain with KMnO₄) as a colorless oil (24.0 mg, 53%). ¹H NMR (500 MHz, CDCl₃) δ 5.87 – 5.77 (m, 1H), 5.06 – 4.98 (m, 1H), 4.97 – 4.91 (m, 1H), 3.76 (br, 1H), 3.36 (br, 1H), 3.33 – 3.26 (m, 1H), 2.11 – 1.96 (m, 2H), 1.96 – 1.73 (m, 4H), 1.69 – 1.60 (m, 1H), 1.46 (s, 9H), 1.41 – 1.33 (m, 1H). ¹³C NMR (151 MHz, CDCl₃, rotamers) δ 154.8, 138.5, 114.6, 79.1&79.0, 57.0&56.9, 46.6&46.2, 34.0&33.4, 30.8, 29.9&29.8, 28.7, 23.9&23.2. IR (neat) ν_{max} 2972 (w), 2928 (w), 2873 (w), 1694 (s), 1641 (w), 1478 (w), 1454 (w), 1392 (m), 1365 (w), 1250 (w), 1171 (w), 1107 (w), 909 (w), 868 (w), 771 (w) cm⁻¹. HRMS (DART+) for C₁₃H₂₄NO₂ [M+H]⁺: Calc'd: 226.1802, found: 226.1805.



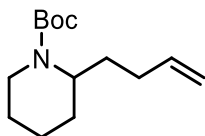
tert-butyl 2-benzylpyrrolidine-1-carboxylate (7) The reaction was performed according to the general procedure above (*Method A*) with *tert*-butyl methoxy(5-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)carbamate (**S-16**) (83.9 mg, 0.20 mmol, 1.0 equiv.), and potassium *tert*-butoxide (24.7 mg, 0.22 mmol, 1.1 equiv.) in toluene and THF (3.6/0.36 mL, 0.05 M) for 14 hours. The compound was purified with SiO₂ chromatography (10% ethyl acetate in hexane, stain with Ninhydrin) as a colorless oil (38.1 mg, 73%). All spectral data was in accordance with previously published results.¹¹



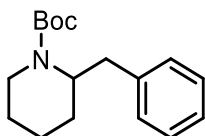
tert-butyl 2-(4-methoxybenzyl)pyrrolidine-1-carboxylate (8) The reaction was performed according to the general procedure above (*Method A*) with *tert*-butyl methoxy(5-(4-methoxyphenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)carbamate (**S-17**) (89.9 mg, 0.20 mmol, 1.0 equiv.), and potassium *tert*-butoxide (24.7 mg, 0.22 mmol, 1.1 equiv.) in toluene and THF (3.6/0.36 mL, 0.05 M) for 14 hours. The compound was purified with SiO₂ chromatography (10% ethyl acetate in hexane, stain with Ninhydrin) as a colorless oil (38.4 mg, 66%). All spectral data was in accordance with previously published results.¹¹



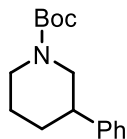
tert-butyl 3-phenylpyrrolidine-1-carboxylate (9) The reaction was performed according to the general procedure above (*Method A*) with *tert*-butyl methoxy(2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)carbamate (**S-7**) (81.6 mg, 0.20 mmol, 1.0 equiv.), and potassium *tert*-butoxide (24.7 mg, 0.22 mmol, 1.1 equiv.) in toluene and THF (3.6/0.36 mL, 0.05 M) for 14 hours. The compound was purified with SiO₂ chromatography (10% ethyl acetate in hexane, stain with Ninhydrin) as a colorless oil (39.5 mg, 80%). All spectral data was in accordance with previously published results.¹²



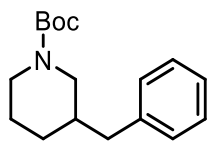
tert-butyl 2-(but-3-en-1-yl)piperidine-1-carboxylate (10) The reaction was performed according to the general procedure above (*Method A*) with *tert*-butyl methoxy(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)non-8-en-1-yl)carbamate (**S-11**) (79.5 mg, 0.20 mmol, 1.0 equiv.), and potassium *tert*-butoxide (24.7 mg, 0.22 mmol, 1.1 equiv.) in toluene and THF (3.6/0.36 mL, 0.05 M) for 14 hours. The compound was purified with SiO₂ chromatography (10% ethyl acetate in hexane, stain with KMnO₄) as a colorless oil (29.7 mg, 62%). All spectral data was in accordance with previously published results.¹³



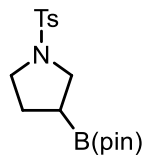
tert-butyl 2-benzylpiperidine-1-carboxylate (11) The reaction was performed according to the general procedure above (*Method A*) with *tert*-butyl methoxy(6-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)carbamate (**S-19**) (86.7 mg, 0.20 mmol, 1.0 equiv.), and potassium *tert*-butoxide (24.7 mg, 0.22 mmol, 1.1 equiv.) in toluene and THF (3.6/0.36 mL, 0.05 M) for 14 hours. The compound was purified with SiO₂ chromatography (10% ethyl acetate in hexane, stain with Ninhydrin) as a colorless oil (39.5 mg, 84%). **IR** (neat) ν_{\max} 2974 (w), 2931 (w), 2858 (w), 1686 (s), 1454 (w), 1411 (m), 1363 (m), 1270 (m), 1160 (s), 1034 (w), 871 (w), 742 (w), 700 (w) cm⁻¹. All other spectral data was in accordance with previously published results.¹⁴



tert-butyl 3-phenylpiperidine-1-carboxylate (12) The reaction was performed according to the general procedure above (*Method A*) with *tert*-butyl methoxy(2-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)carbamate (**S-8**) (83.9 mg, 0.20 mmol, 1.0 equiv.), and potassium *tert*-butoxide (24.7 mg, 0.22 mmol, 1.1 equiv.) in toluene and THF (3.6/0.36 mL, 0.05 M) for 14 hours. The compound was purified with SiO₂ chromatography (10% ethyl acetate in hexane, stain with Ninhydrin) as a colorless oil (33.2 mg, 63%). All spectral data was in accordance with previously published results.¹²

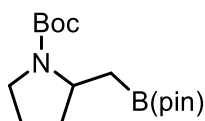


tert-butyl 3-benzylpiperidine-1-carboxylate (13) The reaction was performed according to the general procedure above (*Method A*) with *tert*-butyl (4-benzyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)(methoxy)carbamate (**S-18**) (86.7 mg, 0.20 mmol, 1.0 equiv.), and potassium *tert*-butoxide (24.7 mg, 0.22 mmol, 1.1 equiv.) in toluene and THF (3.6/0.36 mL, 0.05 M) for 14 hours. The compound was purified with SiO₂ chromatography (10% ethyl acetate in hexane, stain with Ninhydrin) as a colorless oil (46.2 mg, 84%). ¹H NMR (500 MHz, CDCl₃) δ 7.30 – 7.24 (m, 2H), 7.21 – 7.12 (m, 3H), 4.17 – 3.66 (brm, 2H), 2.78 (brs, 1H), 2.68 – 2.37 (brm, 3H), 1.79 – 1.69 (m, 2H), 1.68 – 1.57 (brm, 1H), 1.42 (s, 10H), 1.13 (brs, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 155.0, 140.1, 129.2, 128.4, 126.1, 79.3, 49.7, 44.6, 40.3, 37.8, 30.8, 28.6, 25.0. IR (neat) ν_{max} 2975 (w), 2929 (w), 2851 (w), 1688 (s), 1419 (m), 1364 (m), 1266 (m), 1240 (m), 1167 (m), 1130 (m), 886 (w), 745 (w), 700 (m) cm⁻¹. HRMS (DART+) for C₁₇H₂₆NO₂ [M+H]⁺: Calc'd: 276.1958, found: 276.1971.



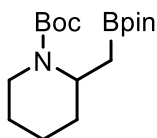
3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosylpyrrolidine (15) The reaction was performed according to the general procedure above (*Method B*) with *tert*-butyl (3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)(methoxy)carbamate (**14**) (91.0 mg, 0.20 mmol, 1.0 equiv.), and potassium *tert*-butoxide (29.2 mg, 0.26 mmol, 1.3 equiv.) in toluene and THF (3.6/0.36 mL, 0.05 M) for 24 hours. The compound was purified with SiO₂ chromatography (15% ethyl acetate in hexane, stain with CAM) as a white solid (35.8 mg, 51%). ¹H NMR (500 MHz, CDCl₃) δ 7.71 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 3.47 (t, *J* = 9.2 Hz, 1H), 3.37 – 3.27 (m, 1H), 3.19 – 3.09 (m, 2H), 2.42 (s, 3H), 1.97 – 1.87 (m, 1H), 1.75 – 1.63 (m, 1H), 1.48 – 1.38 (m, 1H), 1.18 (s, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 143.2, 134.5, 129.7, 127.7, 83.8, 50.1,

48.7, 28.0, 24.8, 24.8, 21.6. ^{11}B NMR (160 MHz, CDCl_3) δ 33.9. IR (neat) ν_{max} 2976 (w), 2929 (w), 2883 (w), 1597 (w), 1452 (w), 1382 (m), 1326 (s), 1230 (w), 1158 (s), 1142 (s), 1098 (m), 1026 (w), 1015 (w), 972 (w), 855 (w), 816 (w), 775 (w), 709 (w), 661 (s), 591 (s), 548 (s) cm^{-1} . HRMS (DART+) for $\text{C}_{17}\text{H}_{27}\text{BNO}_4\text{S}$ $[\text{M}+\text{H}]^+$: Calc'd: 352.1748, found: 352.1750. Melting point: 73-74 $^\circ\text{C}$.



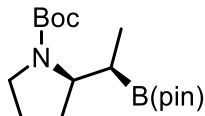
tert-butyl 2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)pyrrolidine-1-carboxylate (17)

The reaction was performed according to the general procedure above (*Method A*) with *tert*-butyl (4,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)(methoxy)carbamate (**16**) (93.9 mg, 0.20 mmol, 1.0 equiv.), and potassium *tert*-butoxide (38.2 mg, 0.34 mmol, 1.7 equiv.) in toluene and THF (0.9/0.09 mL, 0.2 M) for 24 hours. The compound was purified with SiO_2 chromatography (10% ethyl acetate in hexane, stain with CAM) as a white solid (28.6 mg, 46%). Melting point: 63-66 $^\circ\text{C}$. All spectral data was in accordance with previously published results.¹⁵



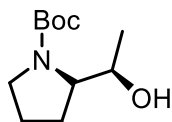
tert-butyl 2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)piperidine-1-carboxylate (19)

The reaction was performed according to the general procedure above (*Method A*) with *tert*-butyl (5,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)(methoxy)carbamate (**18**) (96.7 mg, 0.20 mmol, 1.0 equiv.), and potassium *tert*-butoxide (33.7 mg, 0.30 mmol, 1.5 equiv.) in toluene and THF (0.9/0.09 mL, 0.2 M) for 24 hours. The compound was purified with SiO_2 chromatography (10% ethyl acetate in hexane, stain with CAM) as a colorless oil (32.0 mg, 49%). ^1H NMR (600 MHz, CDCl_3) δ 4.49 (brs, 1H), 3.88 (brd, $J = 12.2$ Hz, 1H), 2.81 (t, $J = 13.3, 13.3$ Hz, 1H), 1.63 – 1.48 (m, 5H), 1.44 (s, 9H), 1.39 – 1.30 (m, 1H), 1.29 – 1.22 (m, 1H), 1.22 (s, 6H), 1.22 (s, 6H), 1.00 (dd, $J = 15.3, 5.8$ Hz, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 154.9, 83.2, 79.0, 47.8, 38.8, 30.1, 28.7, 25.9, 25.0, 24.9, 18.8. ^{11}B NMR (160 MHz, CDCl_3) δ 34.0. IR (neat) ν_{max} 2975 (w), 2930 (w), 2856 (w), 1687 (s), 1470 (w), 1447 (w), 1363 (s), 1322 (s), 1269 (m), 1253 (m), 1150 (s), 1141 (s), 1097 (w), 1068 (w), 1039 (w), 1003 (w), 968 (m), 927 (w), 872 (m), 847 (m), 769 (w) cm^{-1} . HRMS (DART+) for $\text{C}_{17}\text{H}_{33}\text{BNO}_4$ $[\text{M}+\text{H}]^+$: Calc'd: 326.2497, found: 326.2501.



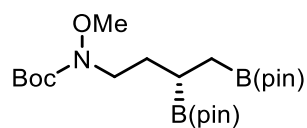
tert-butyl rac-(R)-2-((R)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)pyrrolidine-1-carboxylate (31)

The reaction was performed according to the general procedure above (**Method A**) with *tert*-butyl (*rac*-(4*S*,5*S*)-4,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)(methoxy)carbamate (**30**) (96.7 mg, 0.20 mmol, 1.0 equiv.), and potassium *tert*-butoxide (33.7 mg, 0.30 mmol, 1.5 equiv.) in toluene and THF (0.9/0.09 mL, 0.2 M) for 24 hours. The compound was purified with SiO₂ chromatography (10% ethyl acetate in hexane, stain with CAM) as a colorless oil (34.2 mg, 53%). ¹H NMR (500 MHz, CDCl₃, rotamers) δ 3.98 (brs, 1H), 3.57 (brs, 0.5 H), 3.42 (brs, 0.5 H), 3.26 – 3.12 (m, 1H), 2.06 – 1.92 (m, 1H), 1.91 – 1.73 (m, 2H), 1.73 – 1.53 (m, 2H), 1.44 (s, 9H), 1.21 (s, 12H), 0.84 (d, *J* = 7.4 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃, rotamers) δ 155.0&154.7, 83.1&82.6, 79.0, 59.3&58.4, 47.6, 29.4, 28.7, 24.9, 24.4&24.2, 21.1, 9.7, 8.5. ¹¹B NMR (160 MHz, cdcl₃) δ 33.9. IR (neat) ν_{\max} 2975 (w), 2931 (w), 2876 (w), 1692 (s), 1458 (w), 1392 (s), 1366 (s), 1317 (w), 1269 (w), 1168 (m), 1145 (m), 1107 (m), 868 (w) cm⁻¹. HRMS (DART+) for C₁₇H₃₃BNO₄ [M+H]⁺: Calc'd: 326.2497, found: 326.2505.



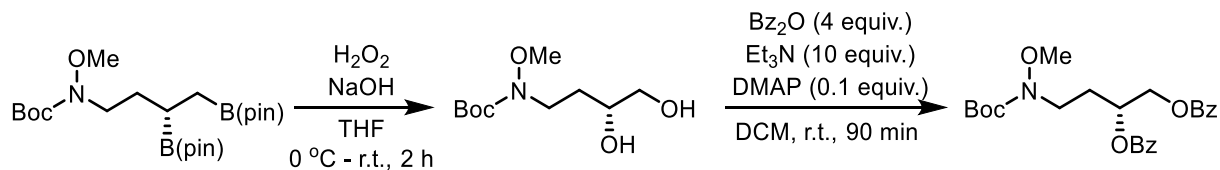
tert-butyl rac-(R)-2-((R)-1-hydroxyethyl)pyrrolidine-1-carboxylate (32) *Tert*-butyl *rac*-(*R*)-2-((*R*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)pyrrolidine-1-carboxylate (**31**) (34.2 mg, 0.105 mmol, 1.0 equiv.) was dissolved in THF (1 mL). At 0 °C, the solution was treated carefully with 3M NaOH (0.4 mL), pH 7.00 buffer solution (0.4 mL) and 30% H₂O₂ (0.2 mL). The cooling bath was removed, and the reaction was allowed to stir at r.t. for 2 hours. At this time the reaction was again cooled down to 0 °C and carefully quenched with saturated aqueous sodium thiosulfate (0.5 mL). The aqueous phase was extracted with ethyl acetate (3 x 4 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, concentrated under reduced pressure. The compound was purified with SiO₂ chromatography (40% ethyl acetate in hexane, stain with ninhydrin) as a colorless oil (18.6 mg, 82%). ¹H NMR (600 MHz, CDCl₃) δ 3.76 – 3.69 (m, 1H), 3.69 – 3.62 (m, 1H), 3.54 – 3.46 (m, 1H), 3.31 – 3.23 (m, 1H), 2.01 – 1.91 (m, 1H), 1.86 – 1.78 (m, 1H), 1.78 – 1.71 (m, 1H), 1.62 (s, 1H), 1.47 (s, 9H), 1.16 – 1.13 (m, 3H). IR (neat) ν_{\max} 3420 (br), 2974 (w), 2929 (w), 1683 (s), 1668 (s), 1456 (w), 1401 (s), 1366 (w), 1168 (m), 1106 (w). HRMS (DART+) for C₁₁H₂₂NO₃ [M+H]⁺: Calc'd: 216.1594, found: 216.1600.

V. Synthesis of Enantiomerically Enriched Compounds and Testing of Stereospecificity



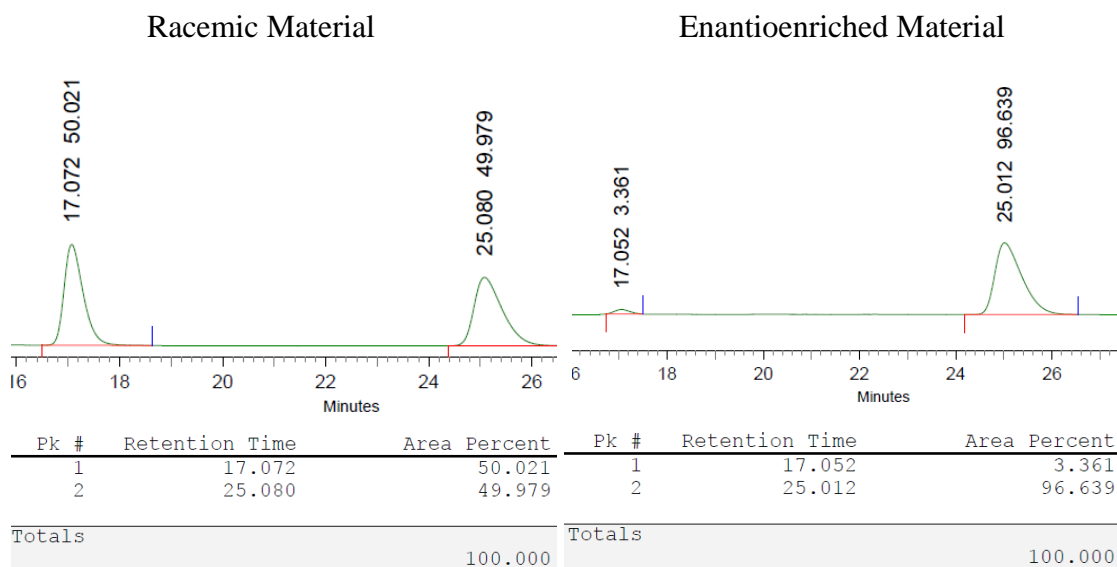
tert-butyl (S)-(3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)(methoxy)carbamate (21) The reaction was performed according to a procedure reported in the literature¹ with slight modification. In the glovebox, an oven-dried 20 mL vial was loaded with bis(pinacolato)diboron (0.28 g, 1.1 mmol, 1.1 equiv.), Pt(dba)₃ (9.0 mg, 0.01 mmol, 1.0 mol%), (*S,S*)-3,5-diethylphenylTADDOLPh (9.6 mg, 0.012 mmol, 1.2 mol%) and anhydrous THF (5 mL). The vial was sealed with a pierceable PTFE cap, taken out of the glovebox and heated at 80 °C for 20 mins. After the reaction was removed from the oil bath and cooled down to r.t., *tert*-butyl but-3-en-1-yl(methoxy)carbamate (**20**) (0.20 g, 1.0 mmol, 1.0 equiv) was added via syringe and the reaction was heated at 60 °C for 14 hours. The vial was cooled down to r.t. and opened to air. The solvent was removed under reduced pressure. The compound was purified with SiO₂ chromatography (10% ethyl acetate in hexane, stain with CAM) as a yellow oil (0.42 g, 92%). $[\alpha]_D^{20}$: +2.2 ($c = 0.89$, CHCl₃, $l = 50$ mm). All other spectral data are in accordance with the racemic compound reported above (**14**).

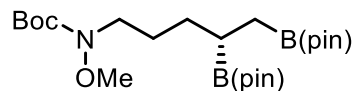
Analysis of Stereochemistry:



The compound was oxidized with hydrogen peroxide and sodium hydroxide, and the resulting diol was treated with benzoic anhydride, triethylamine and 4-dimethylaminopyridine. The resulting protected diol was compared with the racemic compound prepared using the same method from **14**.

Chiral HPLC (Chiracel IF, 10% isopropanol in hexanes, 0.8 mL/min, 35 °C, 210-290 nm), analysis of *tert*-butyl (*S*)-(3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)(methoxy)carbamate



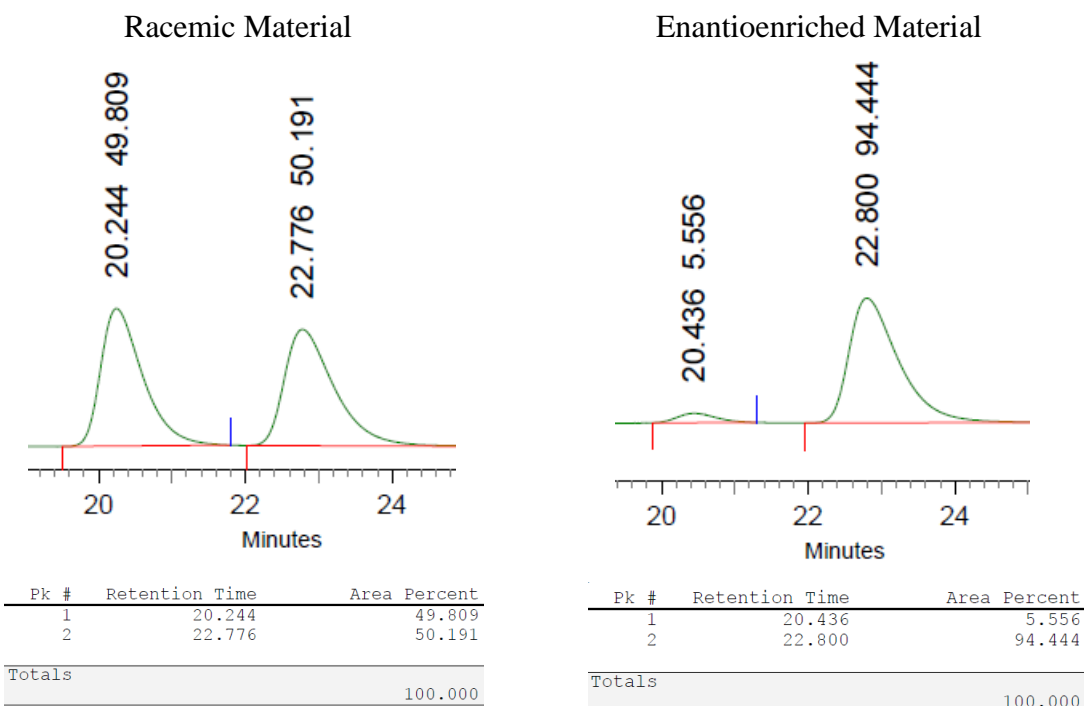


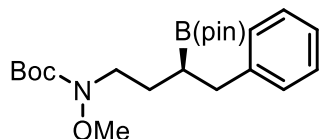
tert-butyl (S)-(4,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)(methoxy)carbamate (26) The reaction was performed using the same method as (21) with *tert*-butyl methoxy(pent-4-en-1-yl)carbamate (25) (0.22 g, 1.0 mmol, 1.0 equiv), bis(pinacolato)diboron (0.28 g, 1.1 mmol, 1.1 equiv.), Pt(dba)₃ (9.0 mg, 0.01 mmol, 1.0 mol%), (*S,S*)-3,5-diethylphenylTADDOLPPh (9.6 mg, 0.012 mmol, 1.2 mol%) and anhydrous THF (5 mL). The compound was purified with SiO₂ chromatography (10% ethyl acetate in hexane, stain with CAM) as a yellow oil (0.45 g, 96%). [α]_D²⁰: +2.3 (*c* = 1.05, CHCl₃, *l* = 50 mm). All other spectral data are in accordance with the racemic compound reported above (16).

Analysis of Stereochemistry:

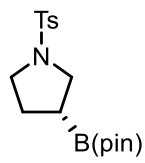
The compound was converted to the protected diol using the same method as (21). The resulting protected diol was compared with the racemic compound prepared using the same method from 16.

Chiral HPLC (Chiracel IF, 10% isopropanol in hexanes, 0.8 mL/min, 35 °C, 210-290 nm), analysis of *tert*-butyl (*S*)-(4,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)(methoxy)carbamate





tert-butyl (S)-methoxy(4-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)carbamate (23) The reaction was performed according to *General procedure E* with *tert*-butyl (S)-(3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)(methoxy)carbamate (**21**) (0.32 g, 0.7 mmol, 1.0 equiv.), solid potassium hydroxide (0.12 g, 2.1 mmol, 3 equiv.), Pd(OAc)₂ (3.9 mg, 0.018 mmol, 2.5 mol%), RuPhos (8.2 mg, 0.018 mmol, 2.5 mol%) and bromobenzene (0.16 g, 1.5 mmol, 1.5 equiv.) in THF (6 mL) and H₂O (0.6 mL). The compound was purified with SiO₂ chromatography (10% ethyl acetate in hexane, stain with CAM) as a colorless oil (0.24 g, 84%). $[\alpha]_{\text{D}}^{20}$: +5.4 ($c = 1.00$, CHCl₃, $l = 50$ mm). All other spectral data are in accordance with the racemic compound reported above (**S-12**).

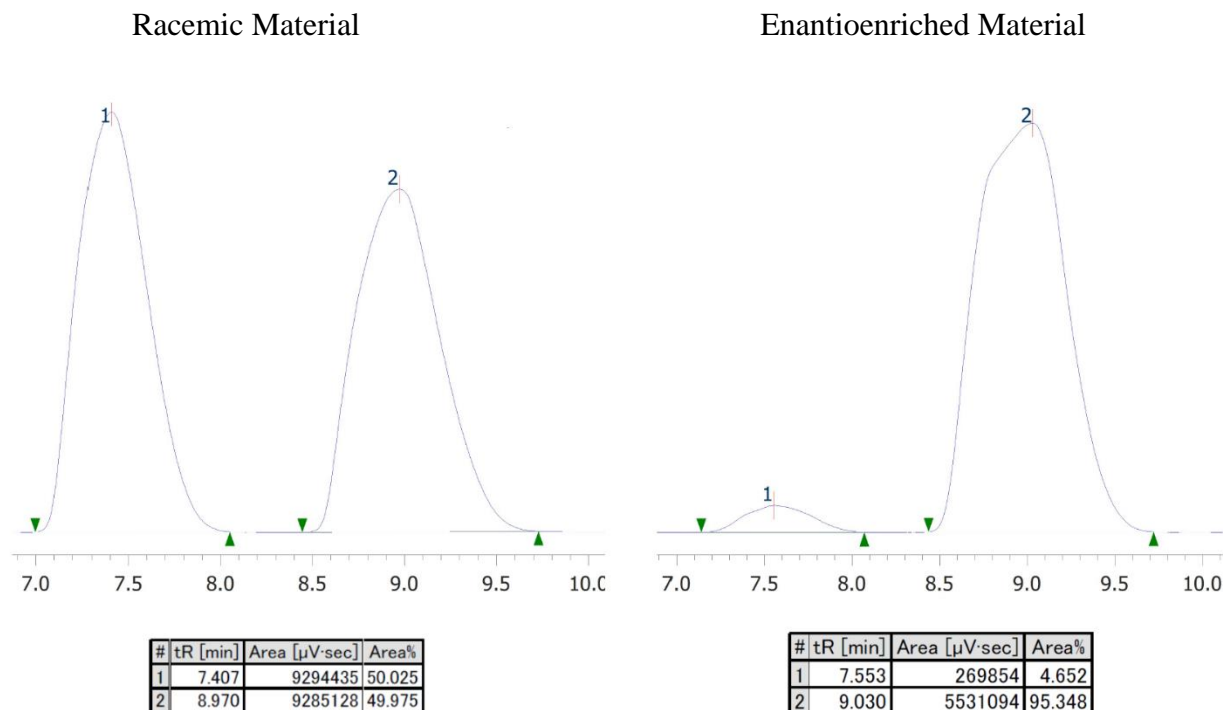


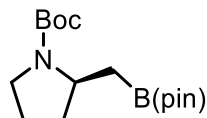
(R)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosylpyrrolidine (22) The reaction was performed according to the general procedure above (*Method B*) with *tert*-butyl (*S*)-(3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)(methoxy)carbamate (**21**) (91.0 mg, 0.20 mmol, 1.0 equiv.), and potassium *tert*-butoxide (29.2 mg, 0.26 mmol, 1.3 equiv.) in toluene and THF (3.6/0.36 mL, 0.05 M) for 24 hours. The compound was purified with SiO₂ chromatography (15% ethyl acetate in hexane, stain with CAM) as a colorless oil (37.0 mg, 54%). $[\alpha]_D^{20}$: -9.3 ($c = 0.50$, CHCl₃, $l = 50$ mm). All other spectral data are in accordance with the racemic compound reported above (**15**).

Analysis of Stereochemistry:

Enantiomeric ratio was determined in comparison to the racemic compound (**15**).

Chiral SFC (Chiracel OJ-H, 3% isopropanol, 3.0 mL/min, 35 °C, 210-290 nm), analysis of (*R*)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosylpyrrolidine





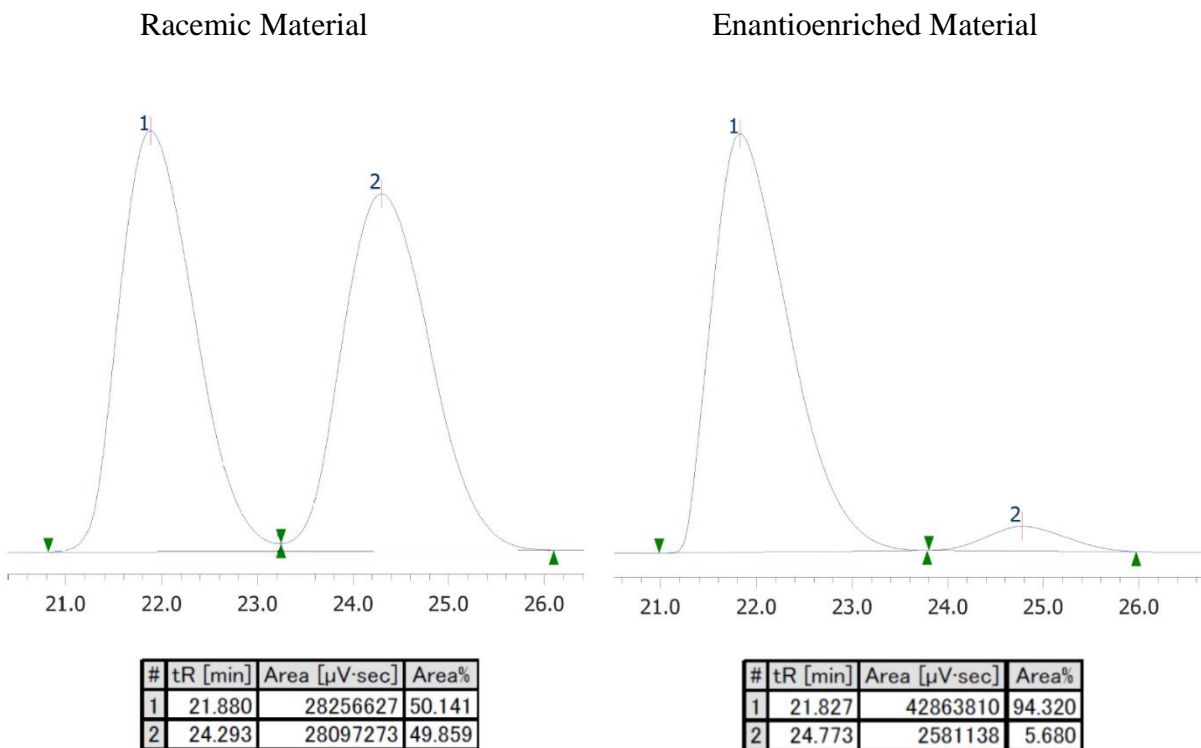
tert-butyl (S)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)pyrrolidine-1-carboxylate (27)

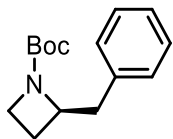
The reaction was performed according to the general procedure above (**Method A**) with *tert*-butyl (*S*)-(4,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)(methoxy)carbamate (**26**) (93.9 mg, 0.20 mmol, 1.0 equiv.), and potassium *tert*-butoxide (38.2 mg, 0.34 mmol, 1.7 equiv.) in toluene and THF (0.9/0.09 mL, 0.2 M) for 24 hours. The compound was purified with SiO₂ chromatography (10% ethyl acetate in hexane, stain with CAM) as a colorless oil (27.2 mg, 44%). $[\alpha]_D^{20}$: +18.4 ($c = 0.79$, CHCl₃, $l = 50$ mm). All other spectral data are in accordance with the racemic compound reported above (**17**).

Analysis of Stereochemistry:

Enantiomeric ratio was determined using the tosyl-protected pyrrolidine synthesized following **Method B**. Racemic compound was prepared using the same method from **16**.

Chiral SFC (Chiracel OJ-H, 3% isopropanol, 3.0 mL/min, 35 °C, 210-290 nm), analysis of (S)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)pyrrolidine-1-carboxylate



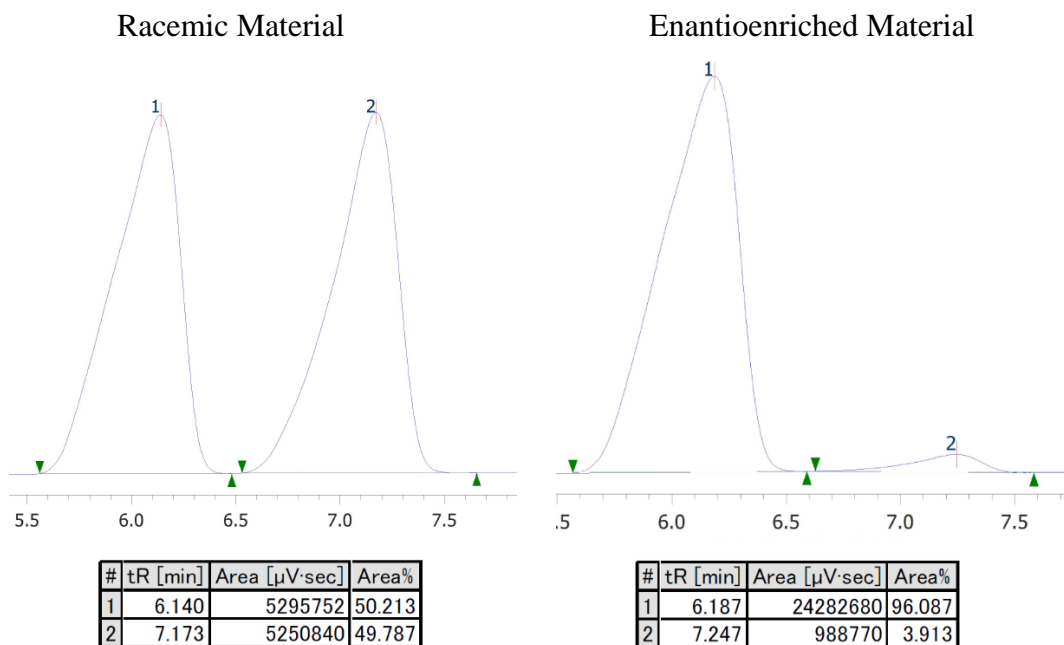


tert-butyl (S)-2-benzylazetidine-1-carboxylate (24) The reaction was performed according to the general procedure above (*Method A*) with *tert*-butyl (S)-methoxy(4-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)carbamate (**23**) (83.9 mg, 0.20 mmol, 1.0 equiv.), and potassium *tert*-butoxide (24.7 mg, 0.22 mmol, 1.1 equiv.) in toluene and THF (3.6/0.36 mL, 0.05 M) for 24 hours. The compound was purified with SiO₂ chromatography (10% ethyl acetate in hexane, stain with Ninhydrin) as a colorless oil (32.4 mg, 66%). $[\alpha]_D^{20}$: +90.0 ($c = 0.50$, CHCl₃, $l = 50$ mm).

Analysis of Stereochemistry:

Enantiomeric ratio was determined in comparison to the racemic compound ().

Chiral SFC (Chiracel OJ-H, 5% isopropanol, 1.0 mL/min, 35 °C, 210-290 nm), analysis of *tert*-butyl (S)-2-benzylazetidine-1-carboxylate

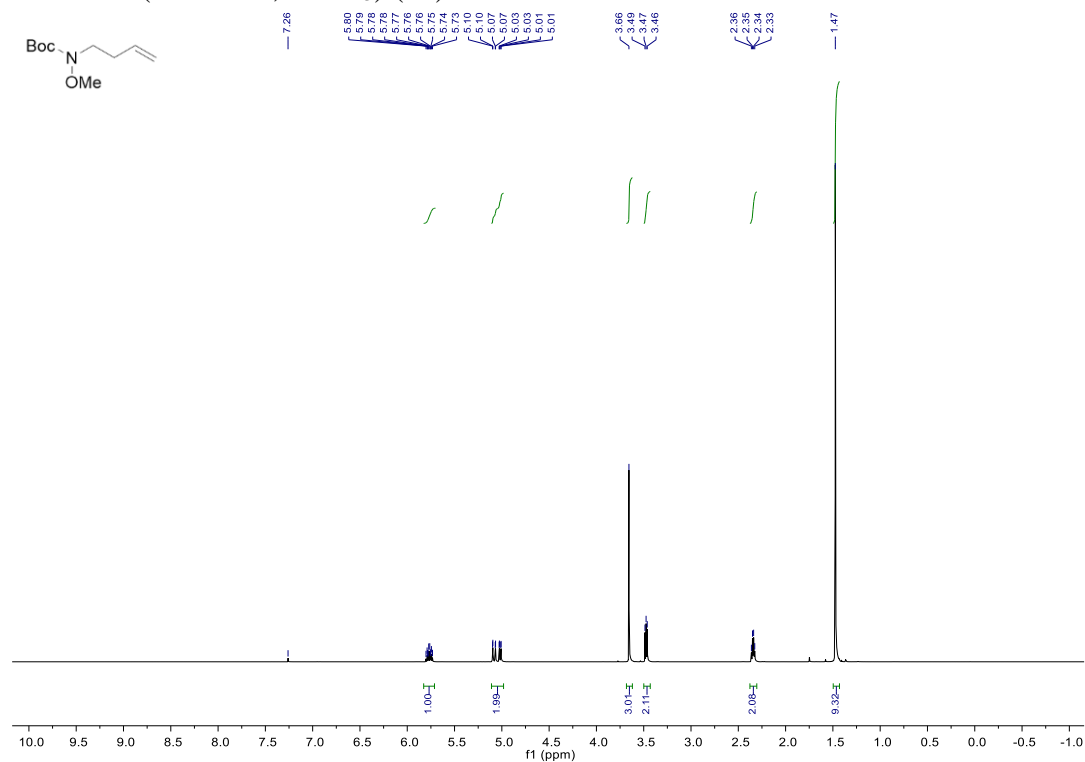


References:

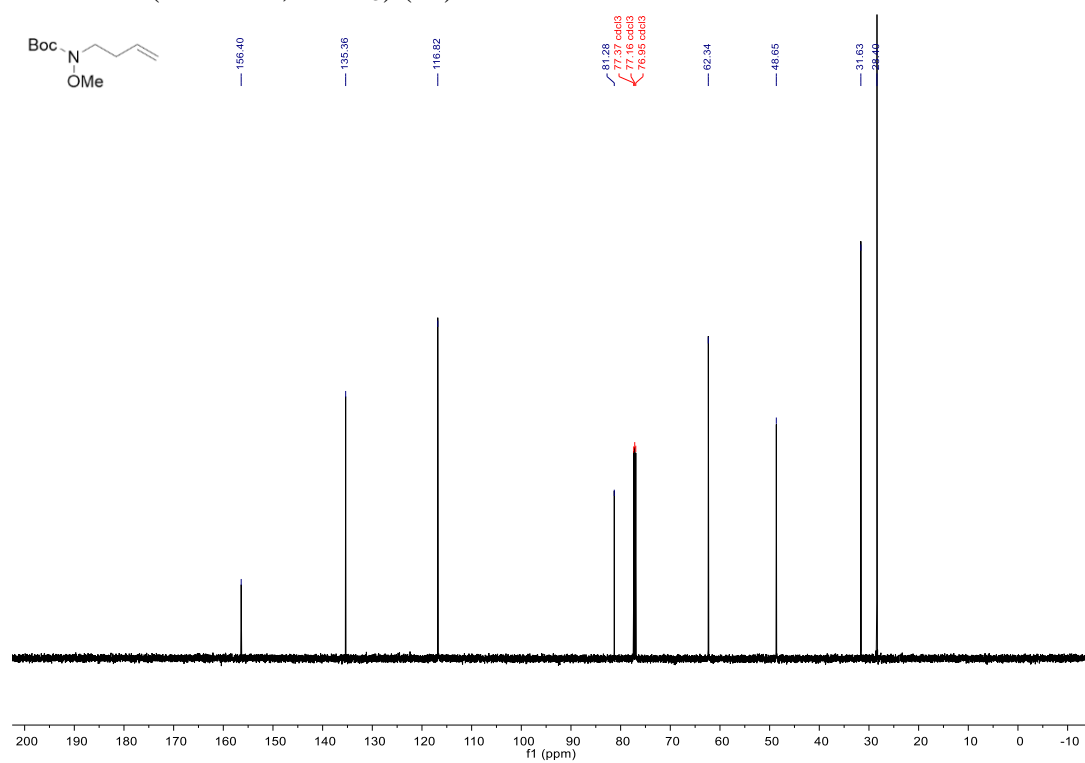
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Spectral data

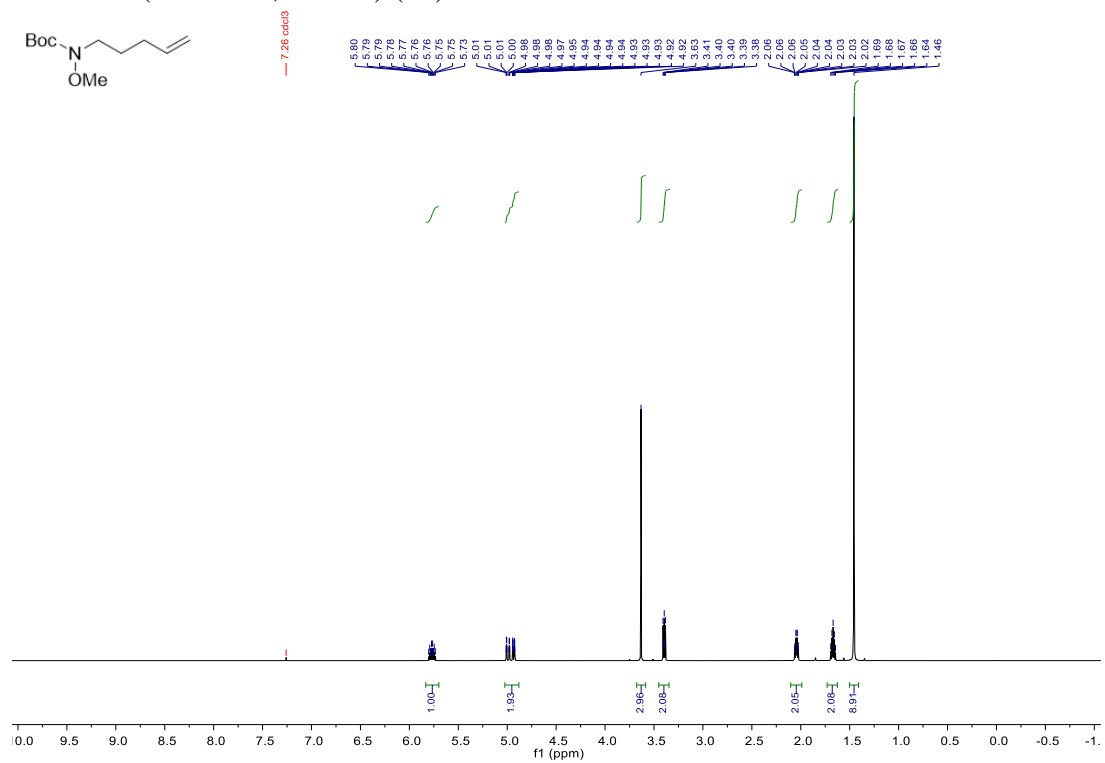
¹H NMR (600 MHz, CDCl₃) (20)



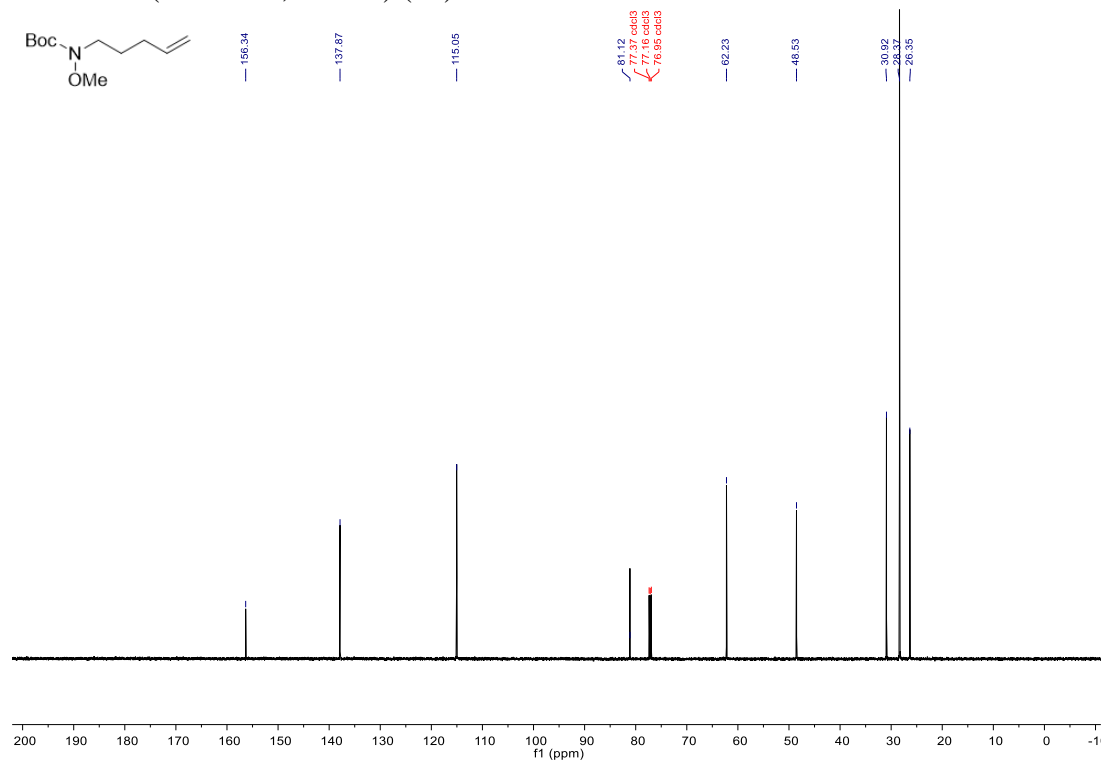
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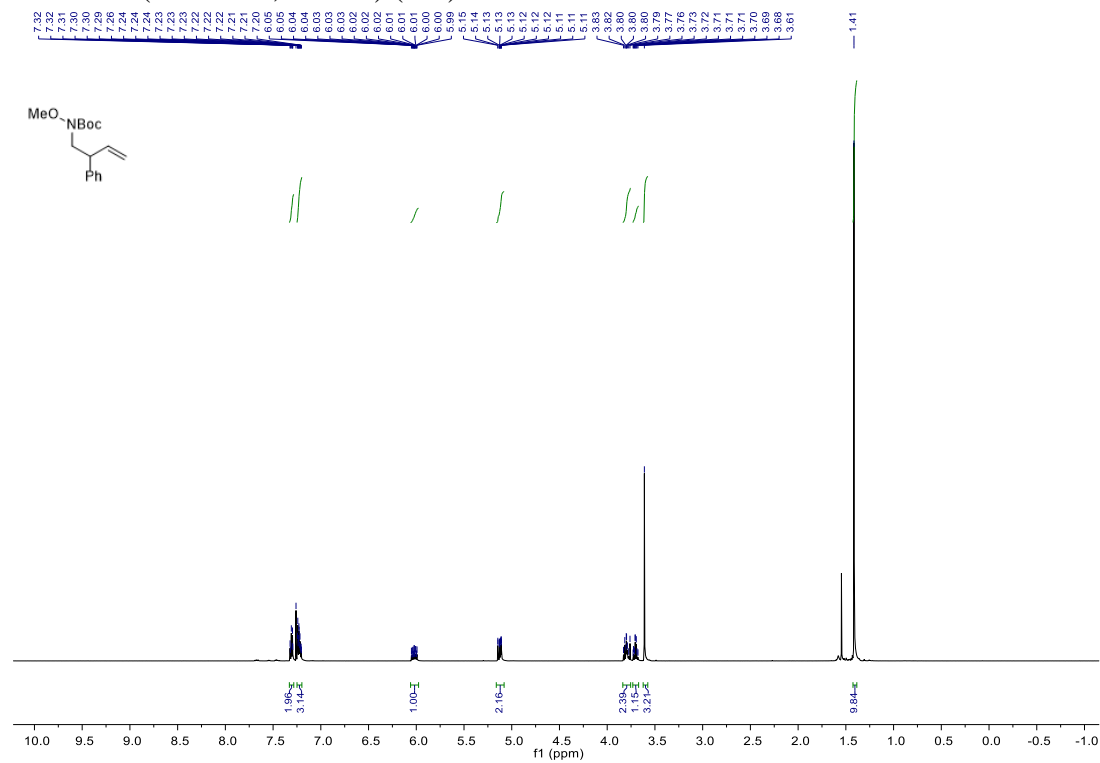
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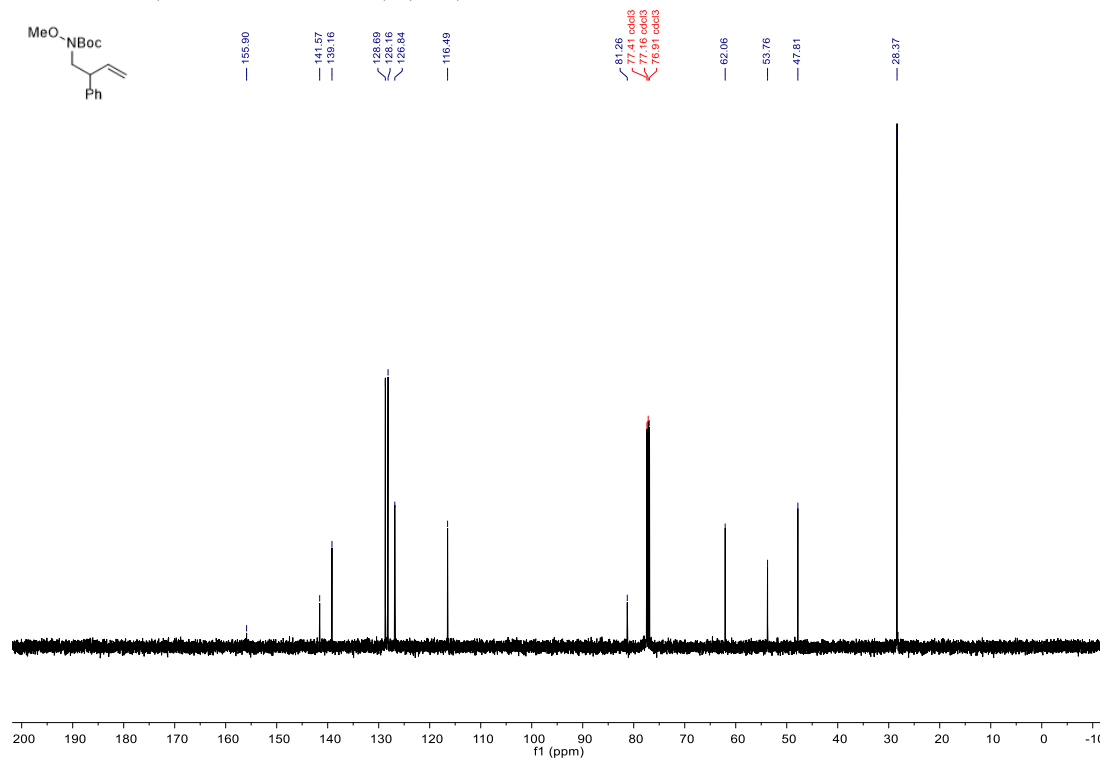
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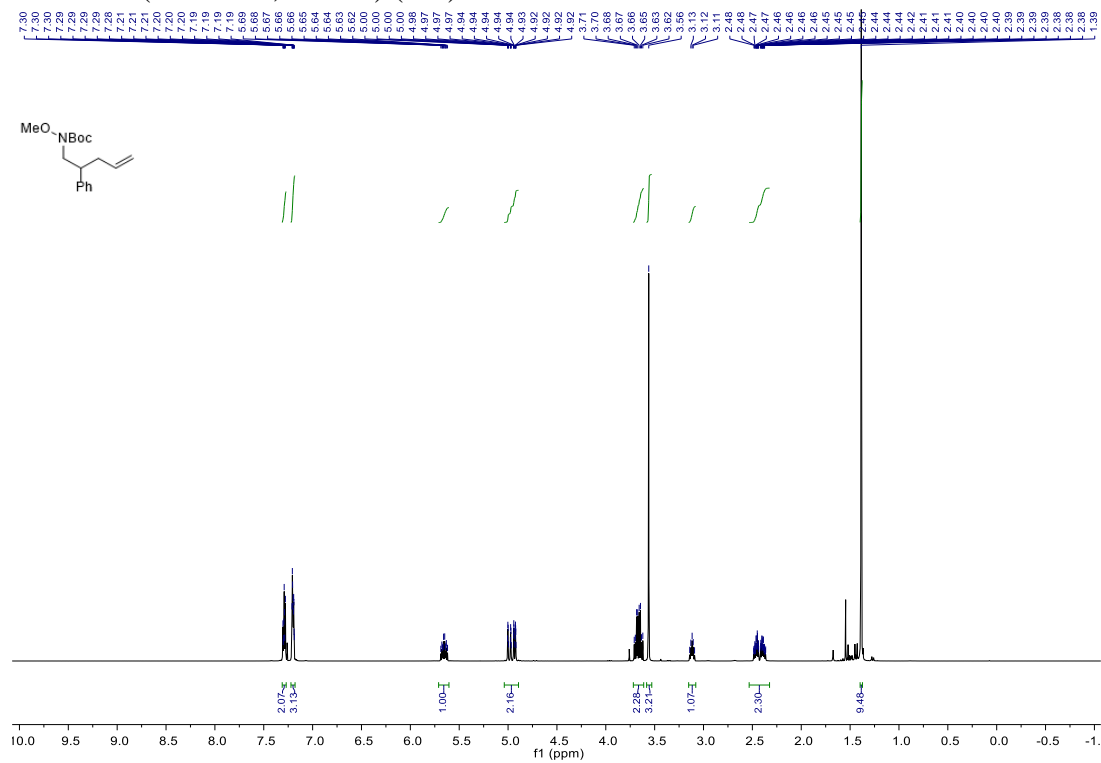
¹H NMR (600 MHz, CDCl₃) (S-5)



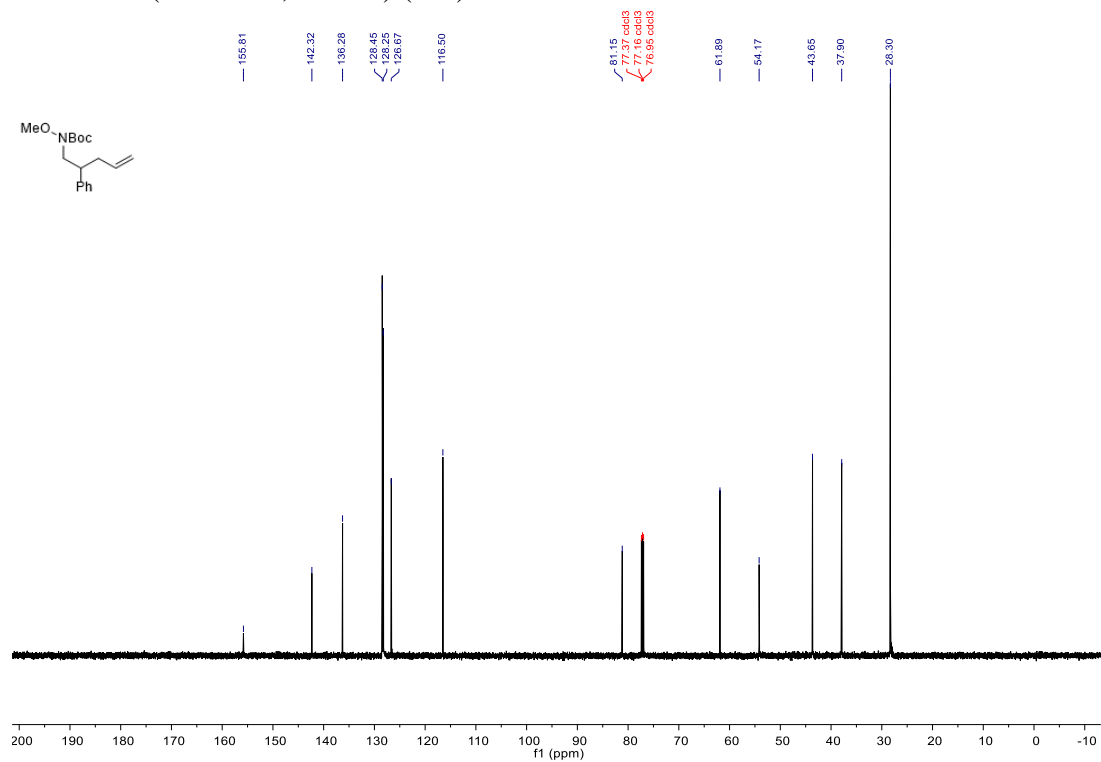
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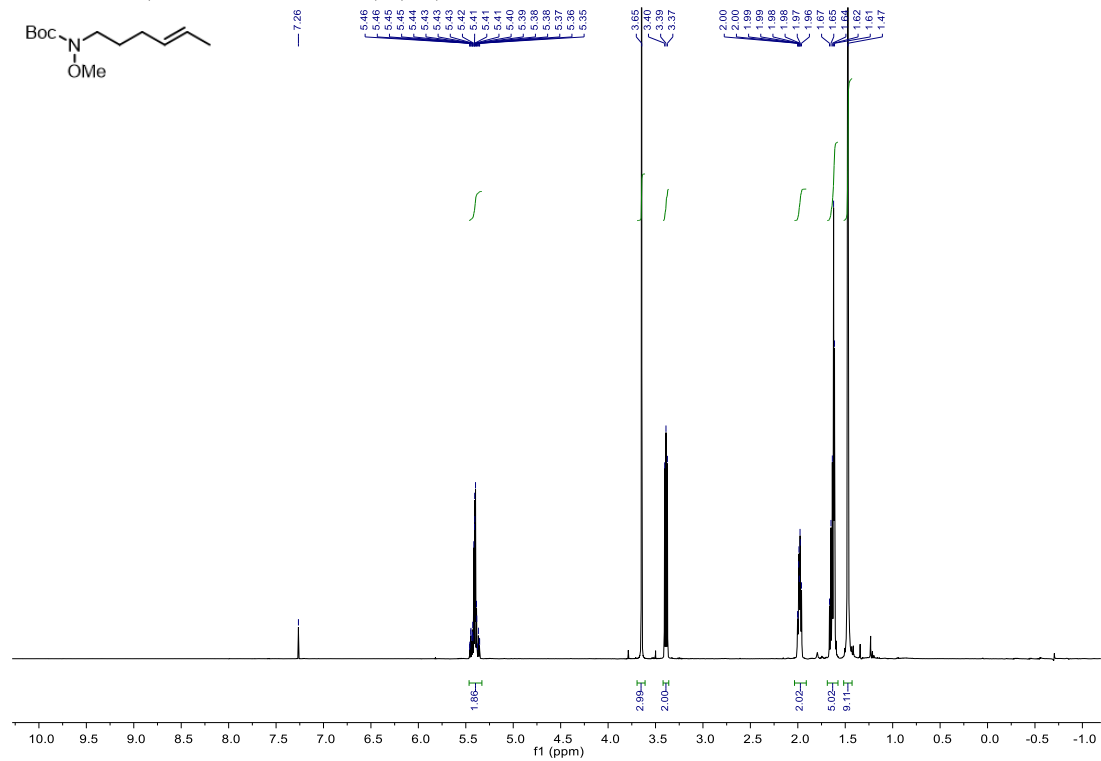
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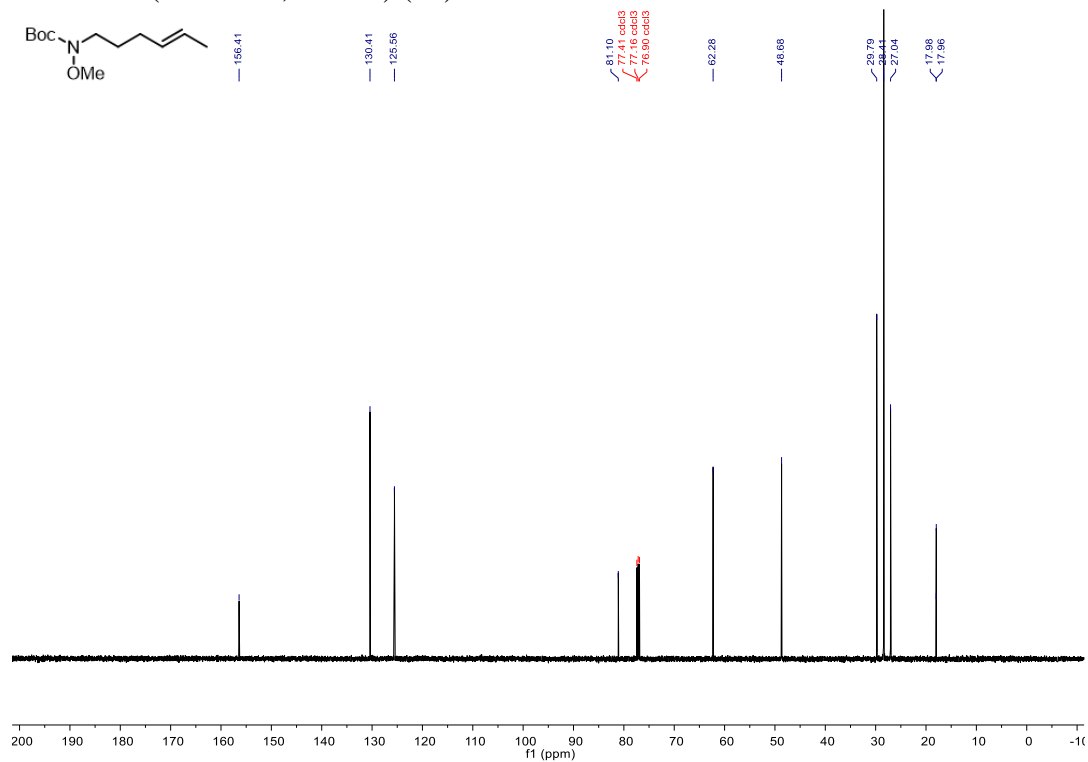
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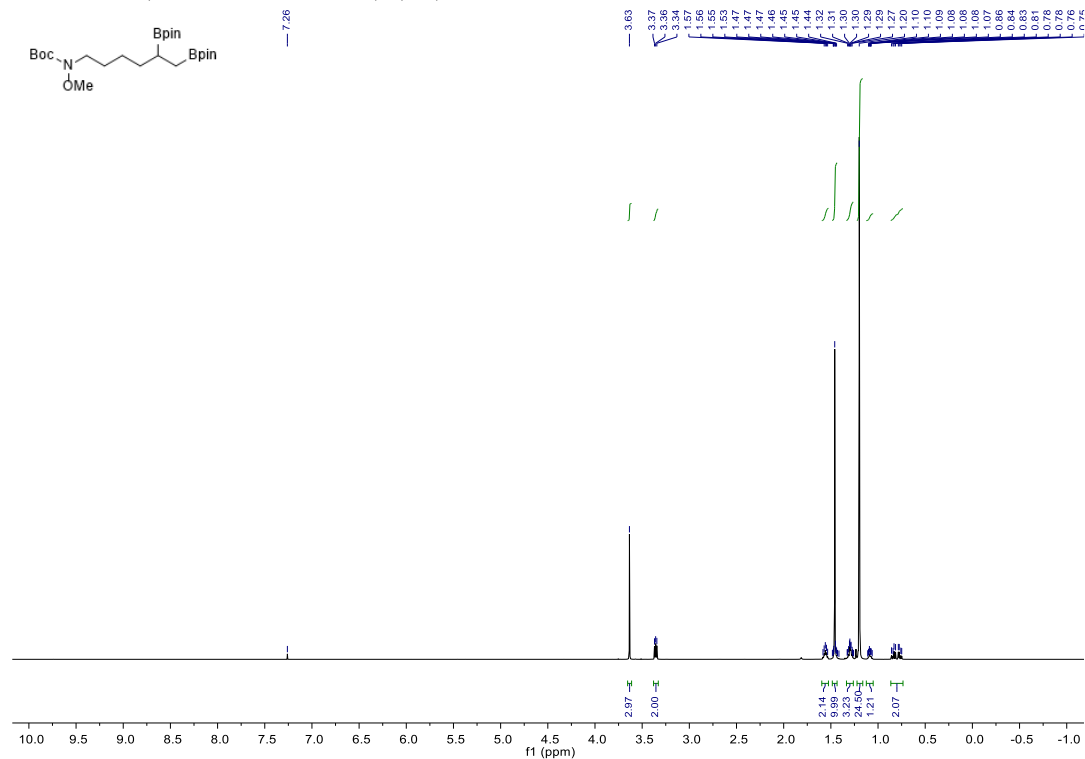
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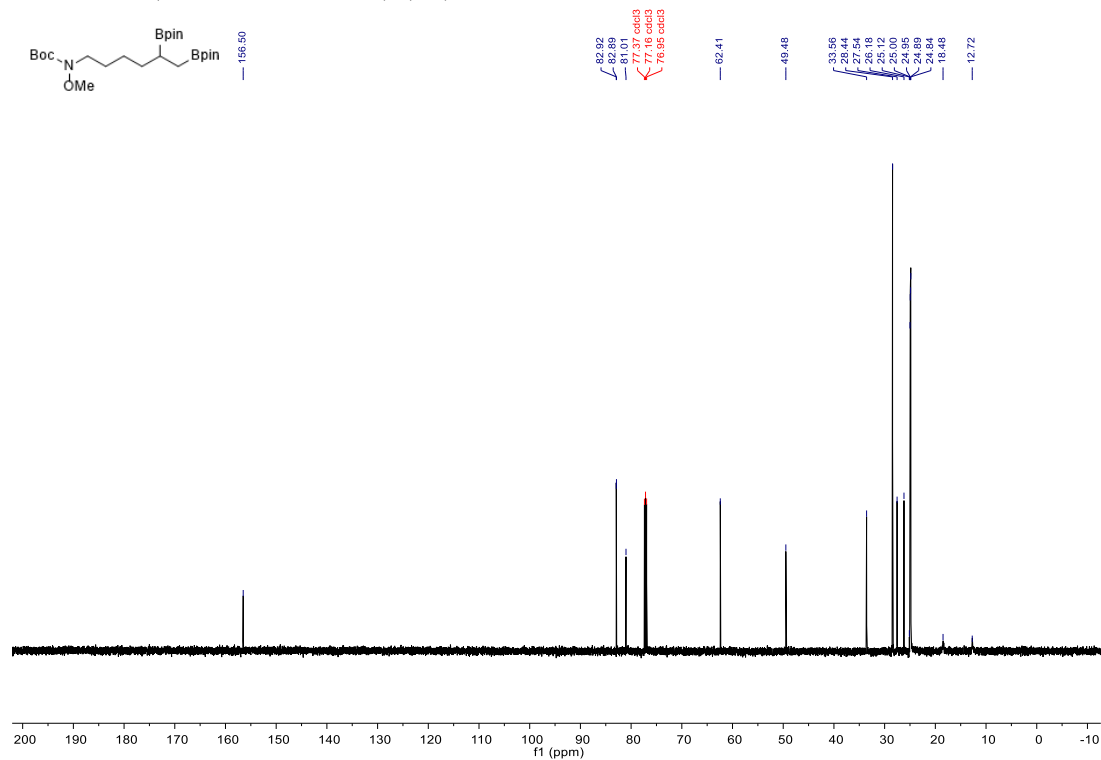
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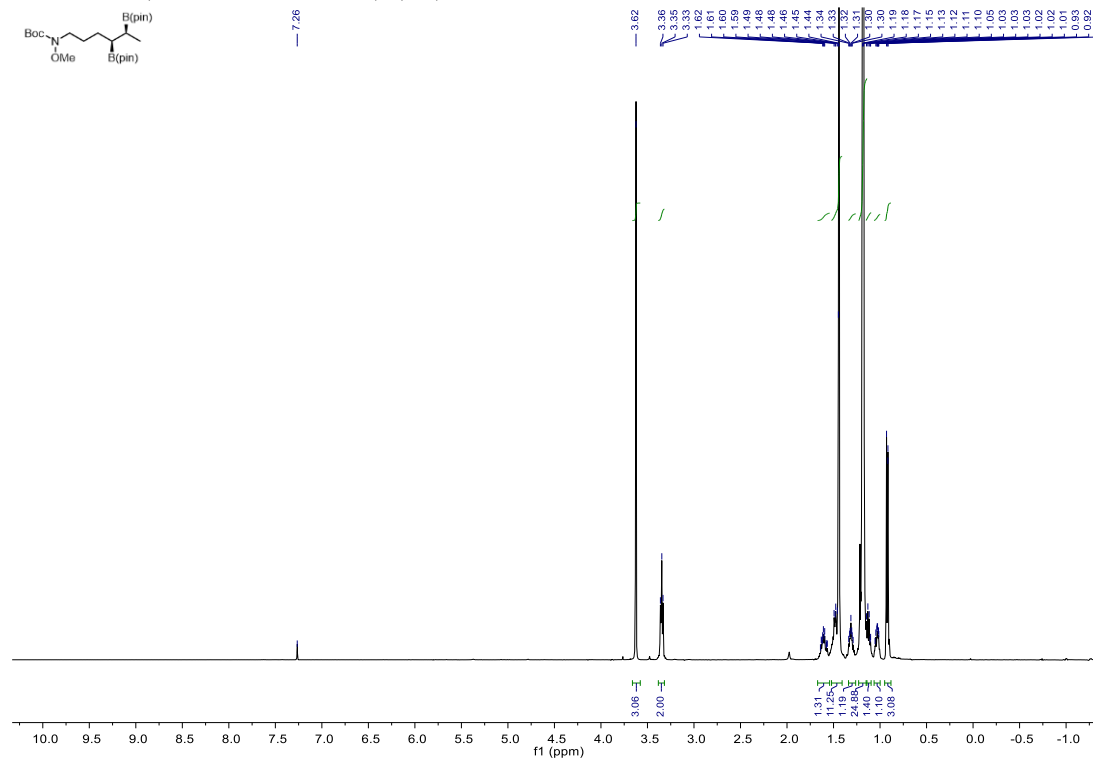
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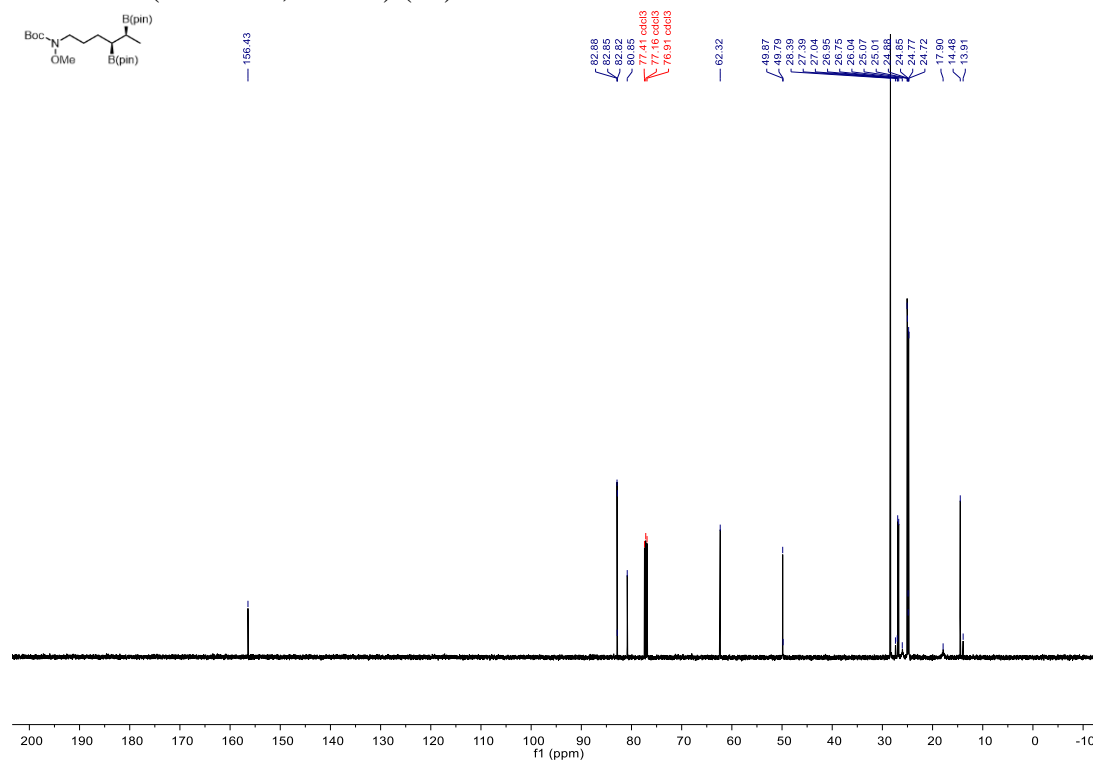
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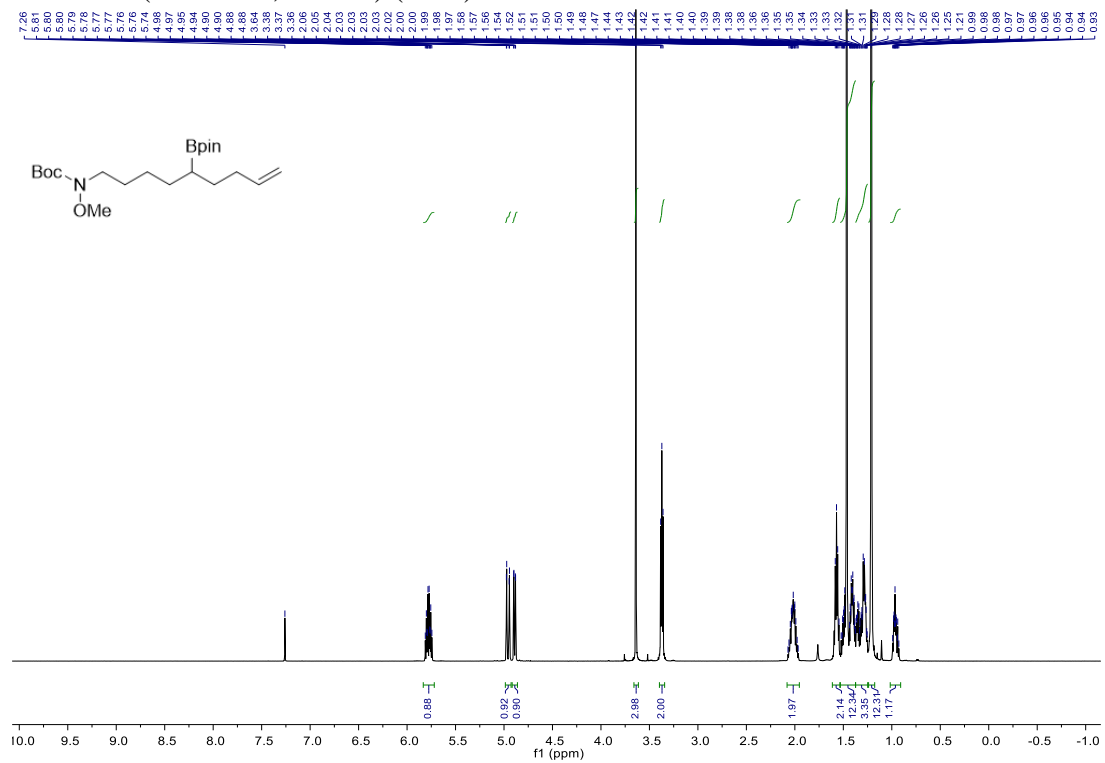
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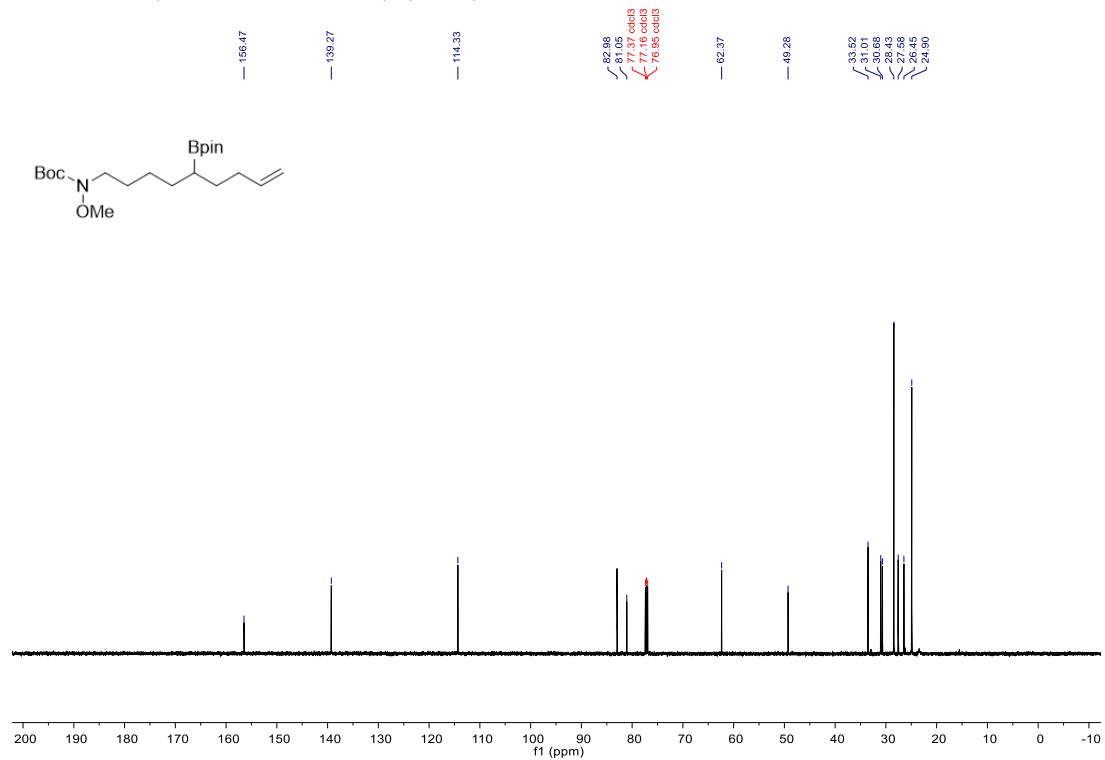
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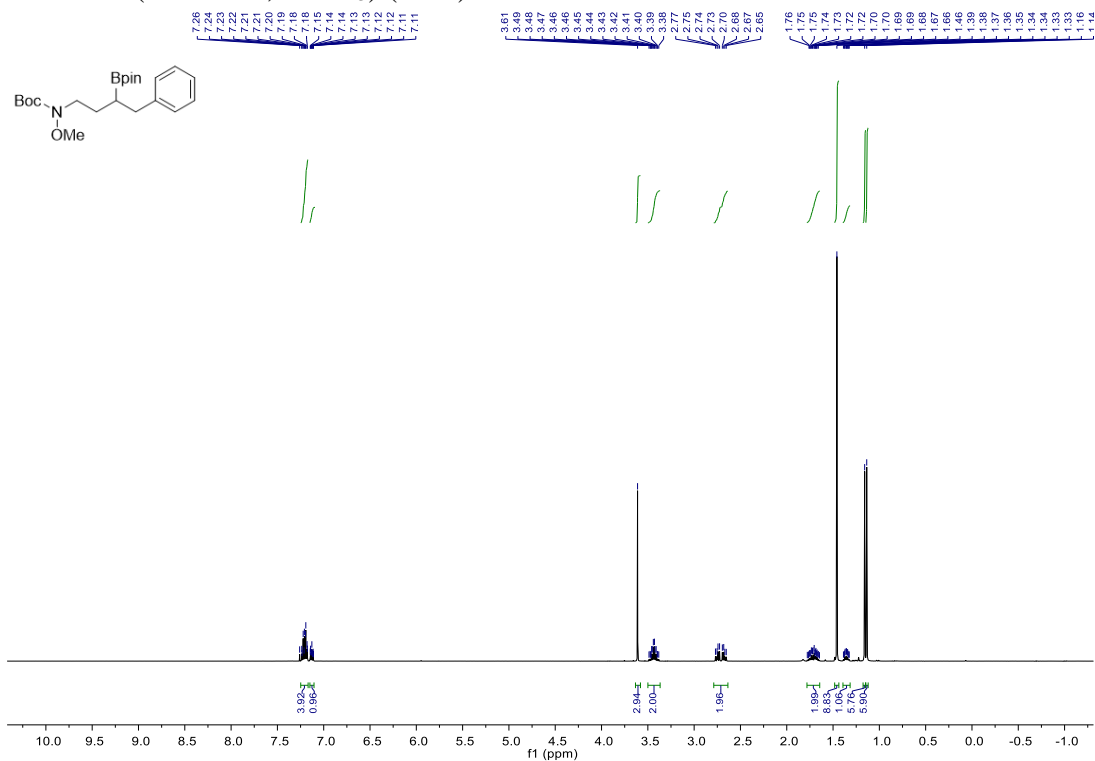
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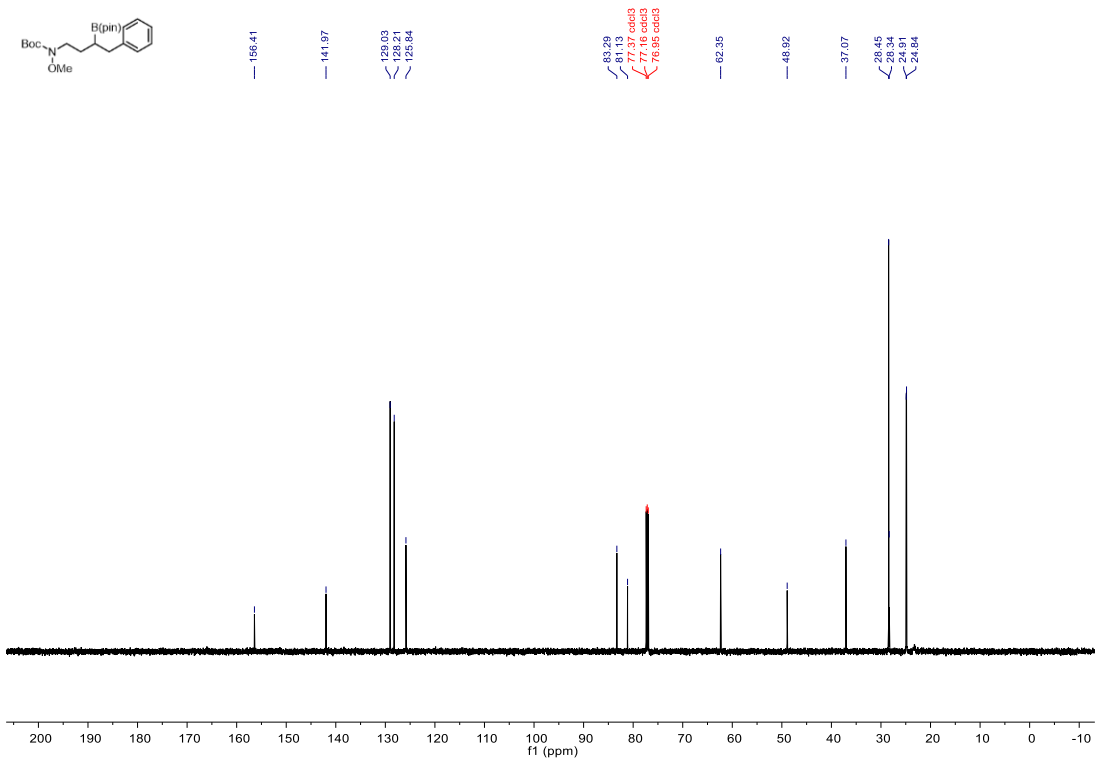
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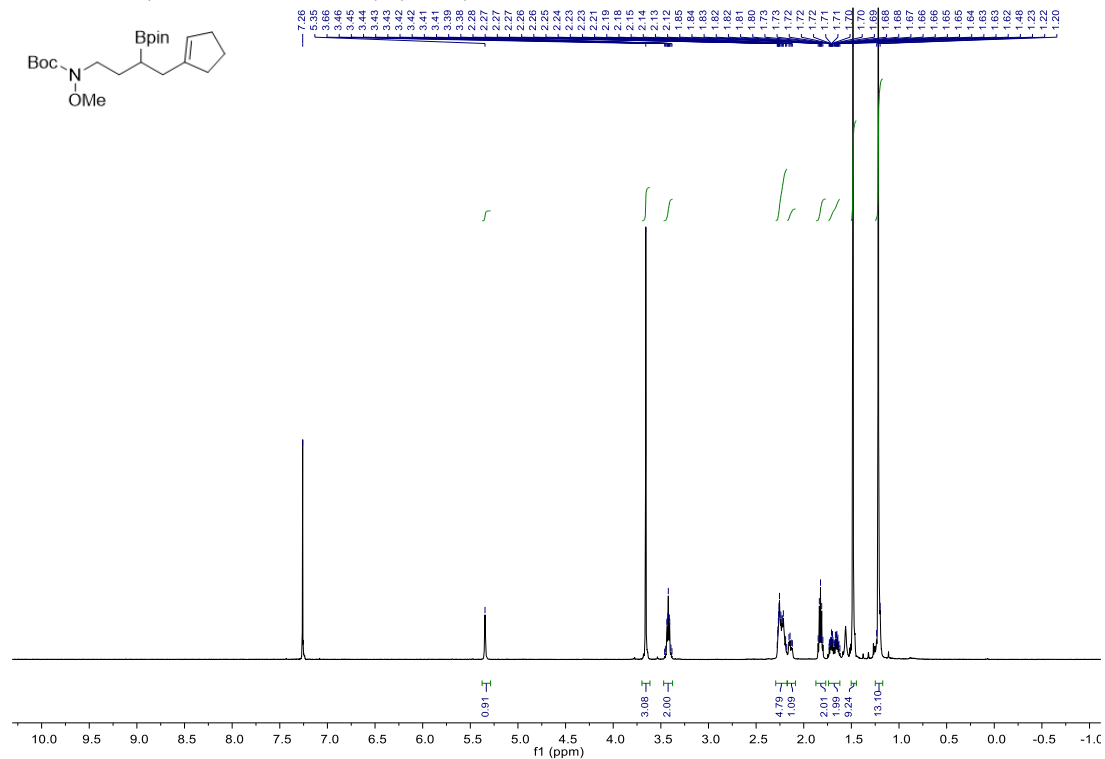
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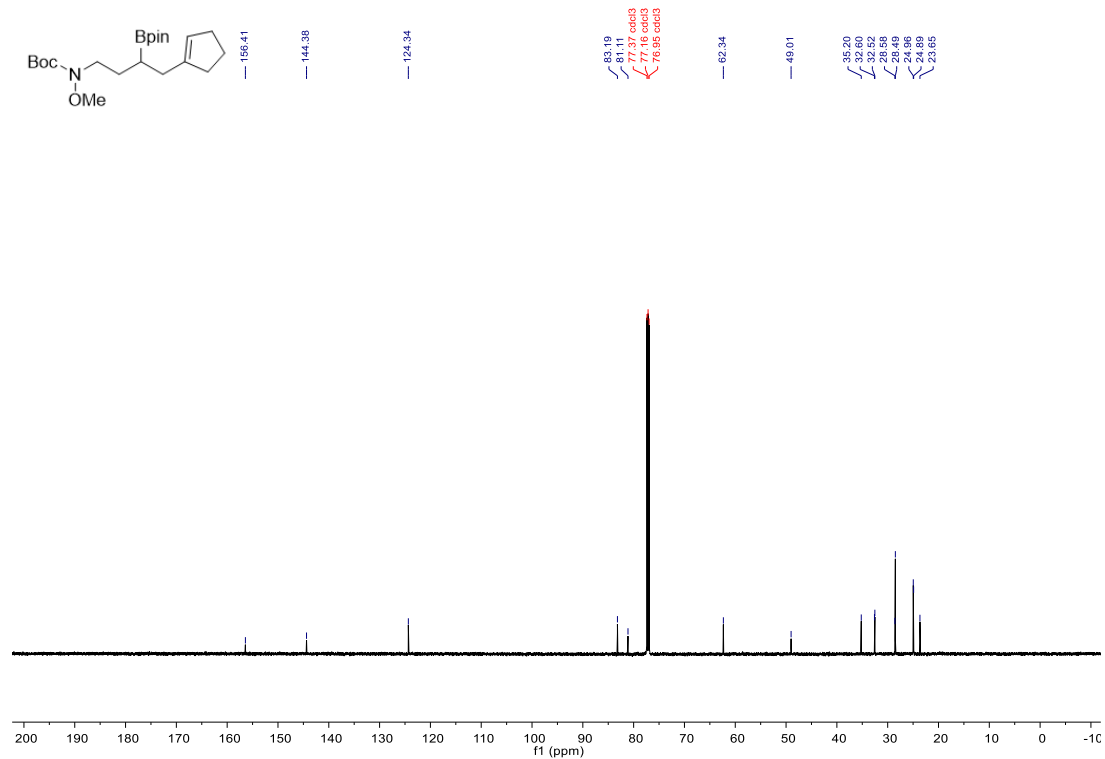
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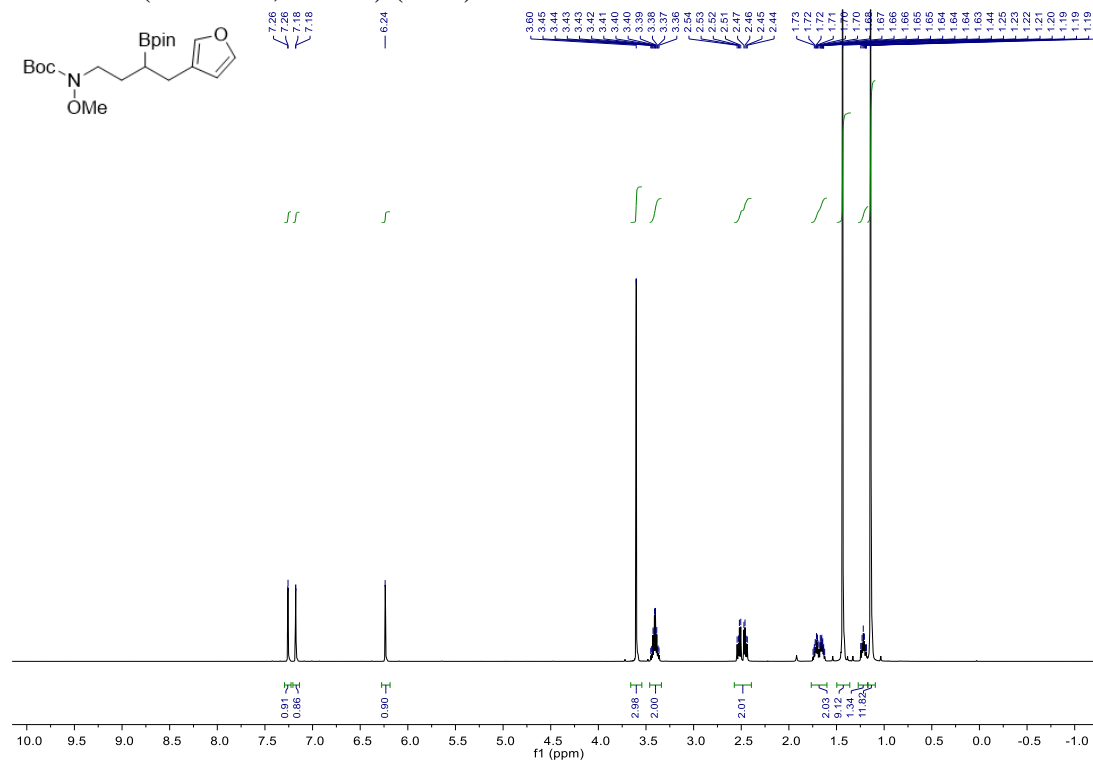
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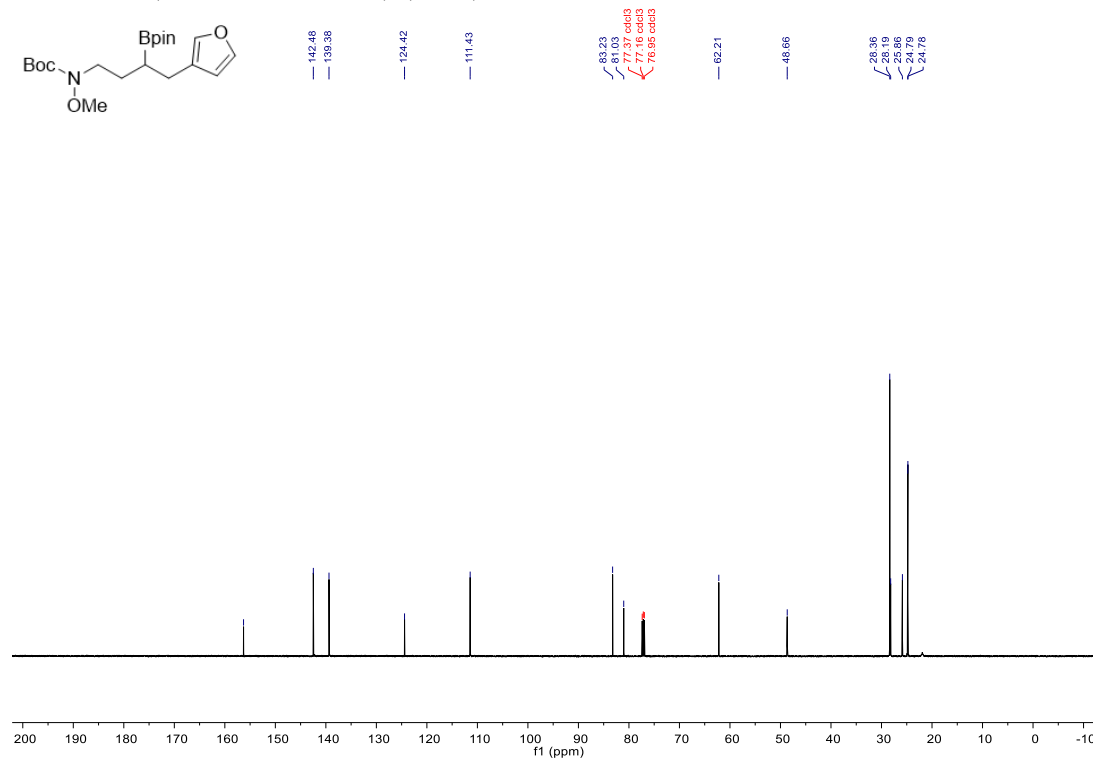
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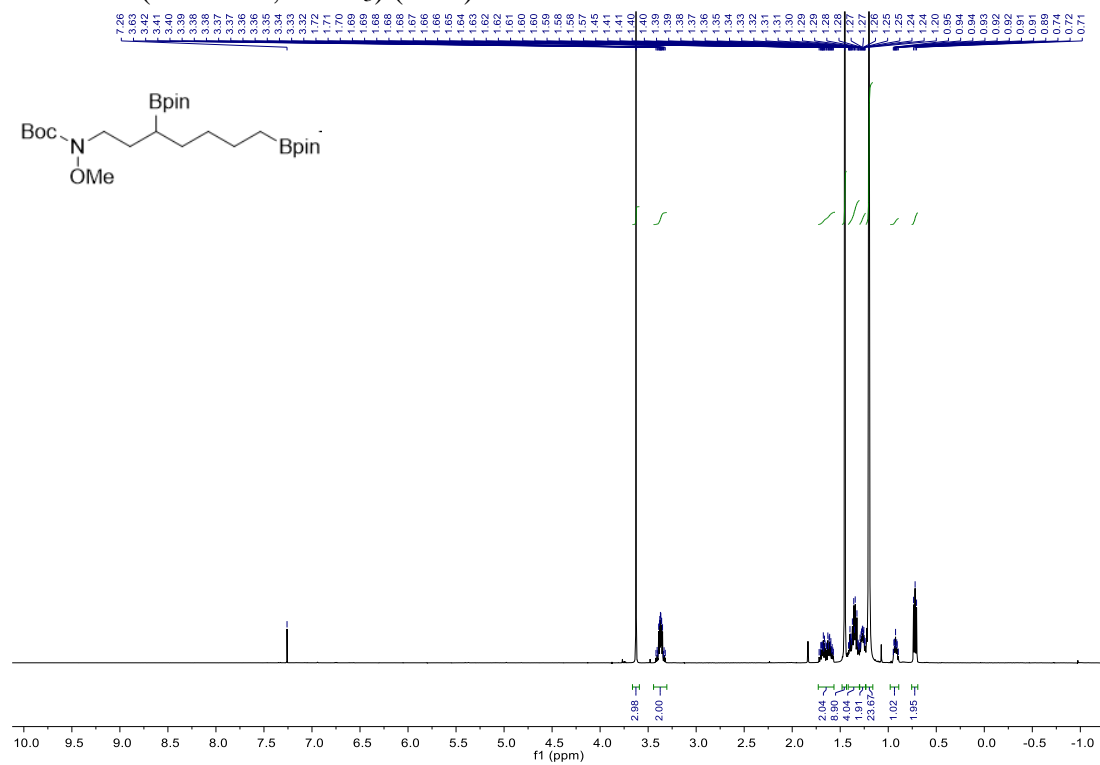
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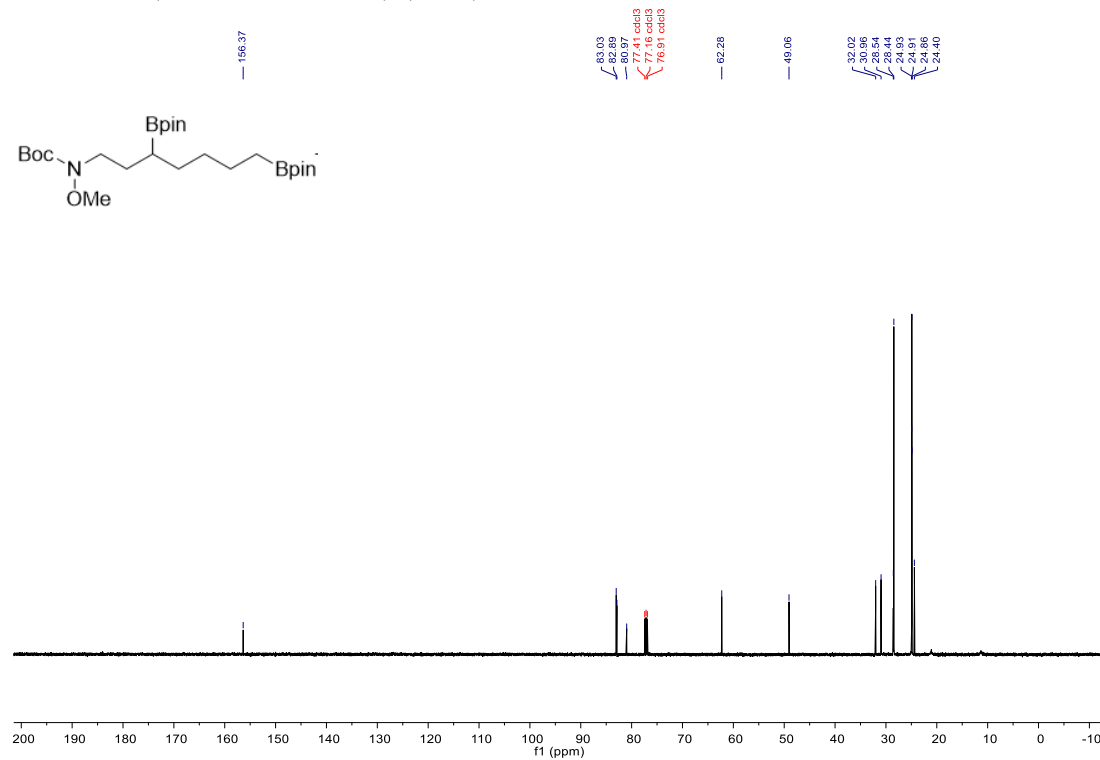
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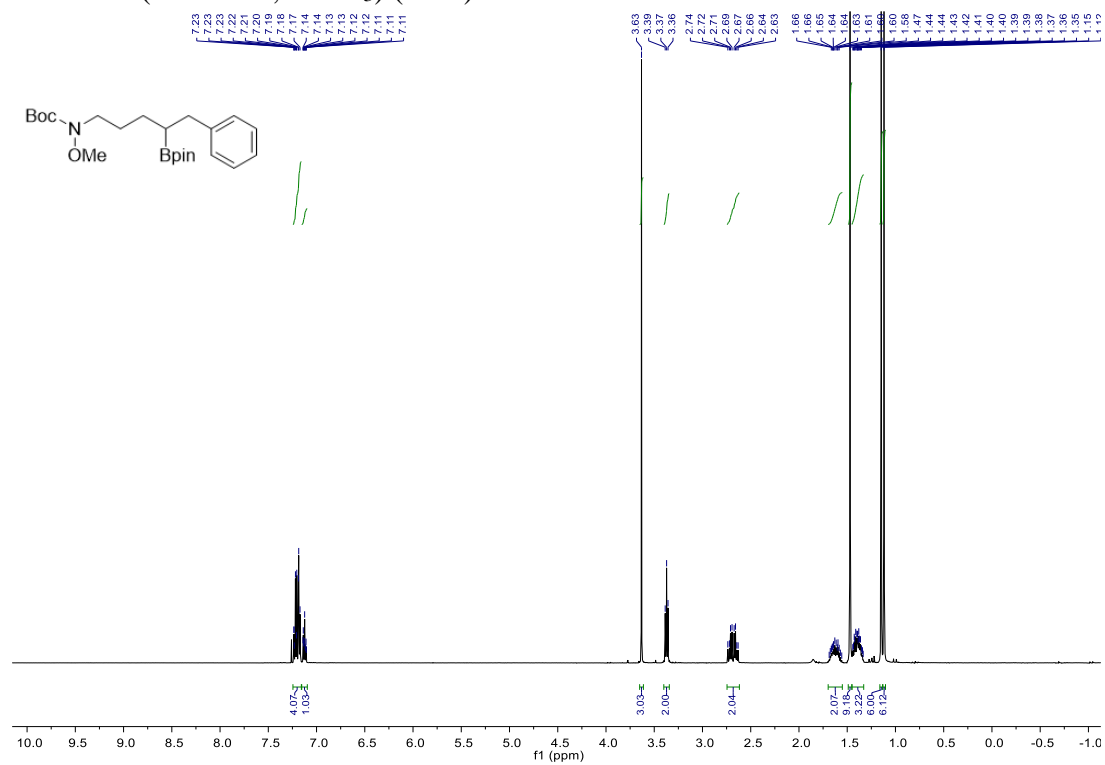
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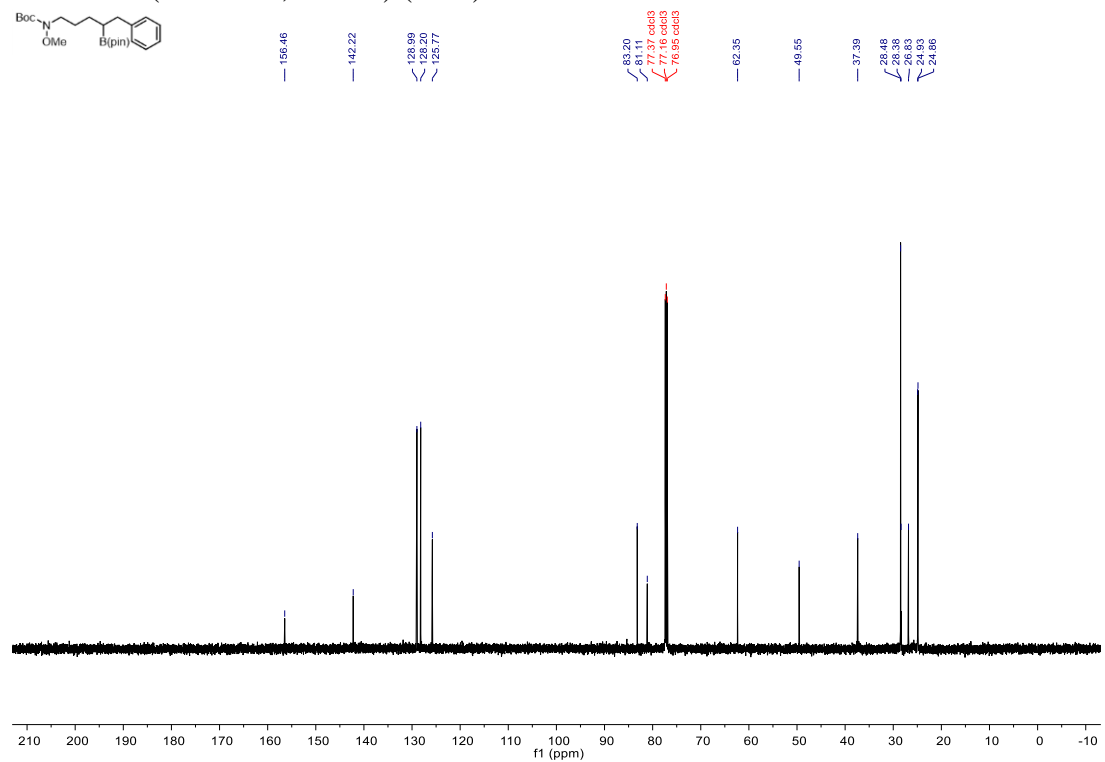
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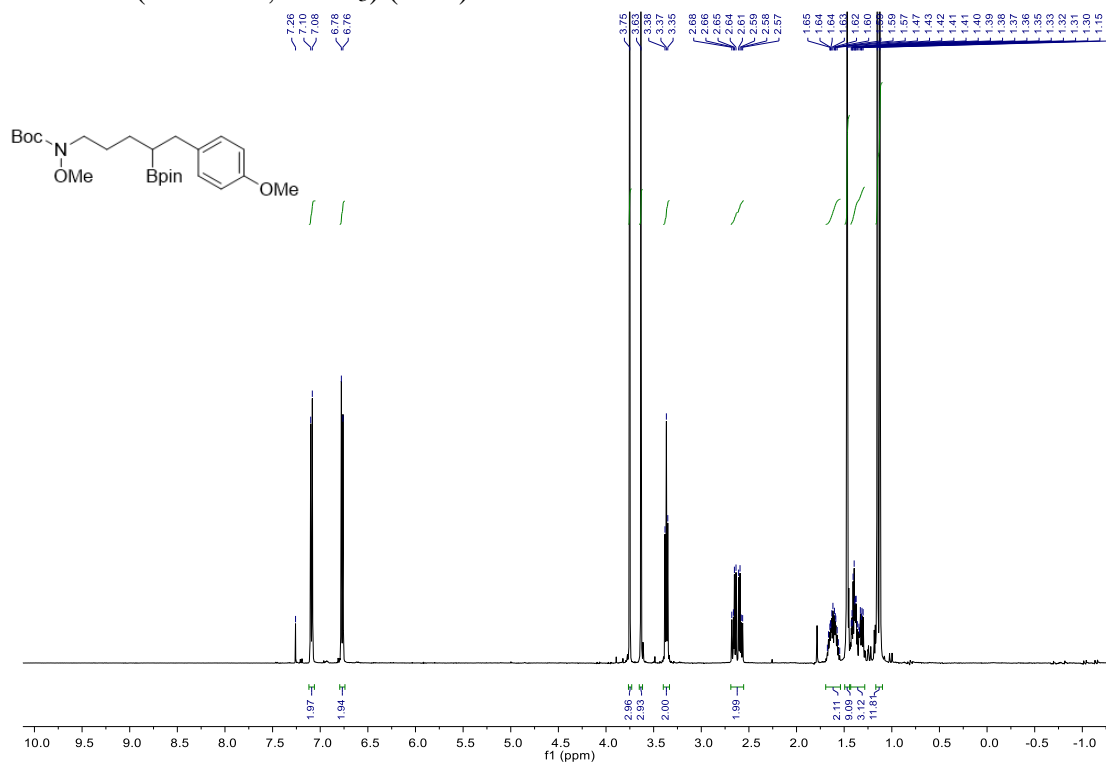
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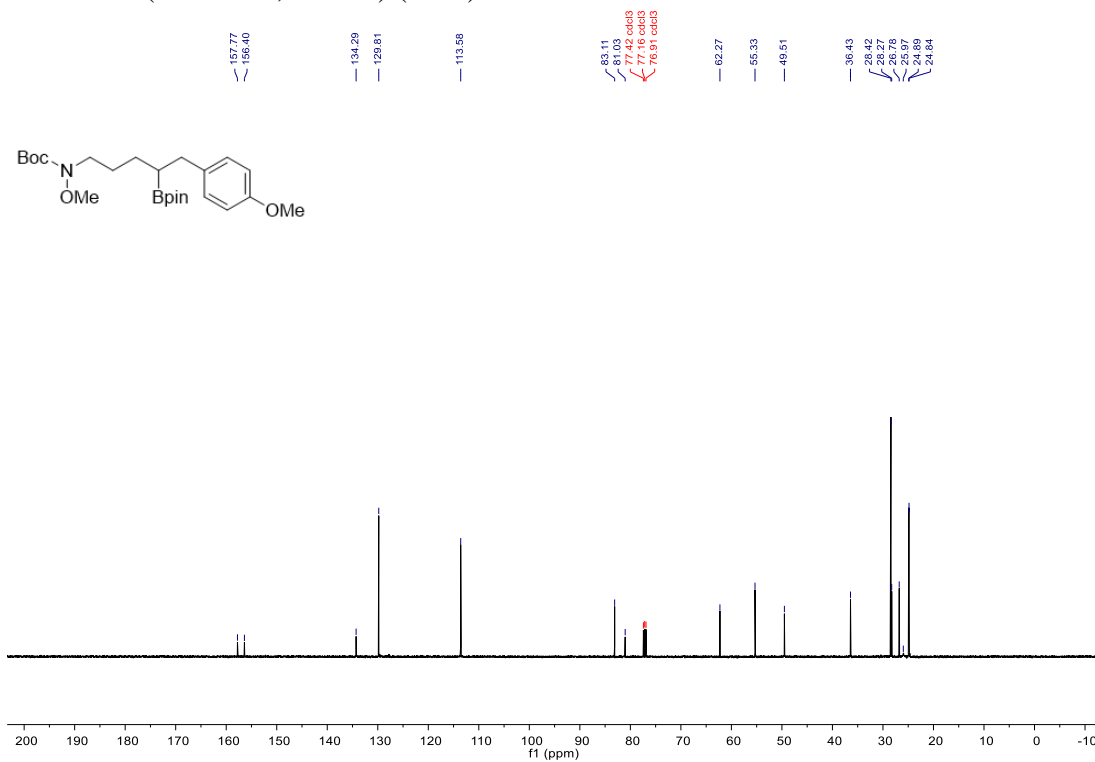
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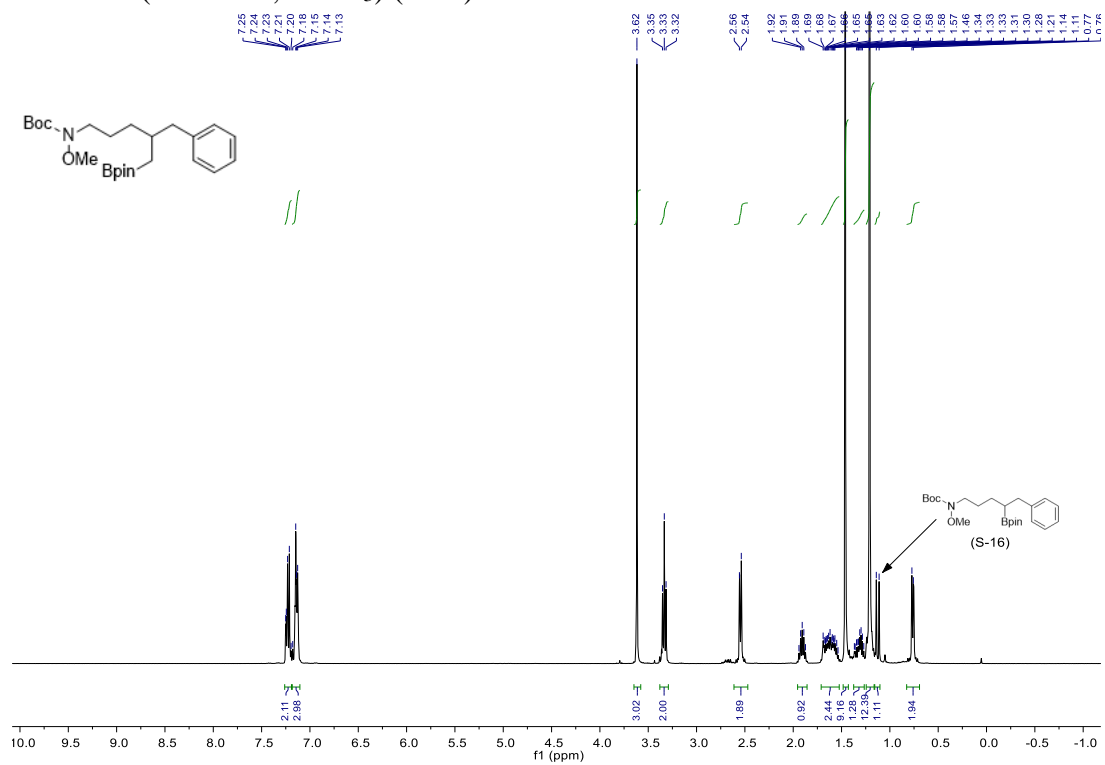
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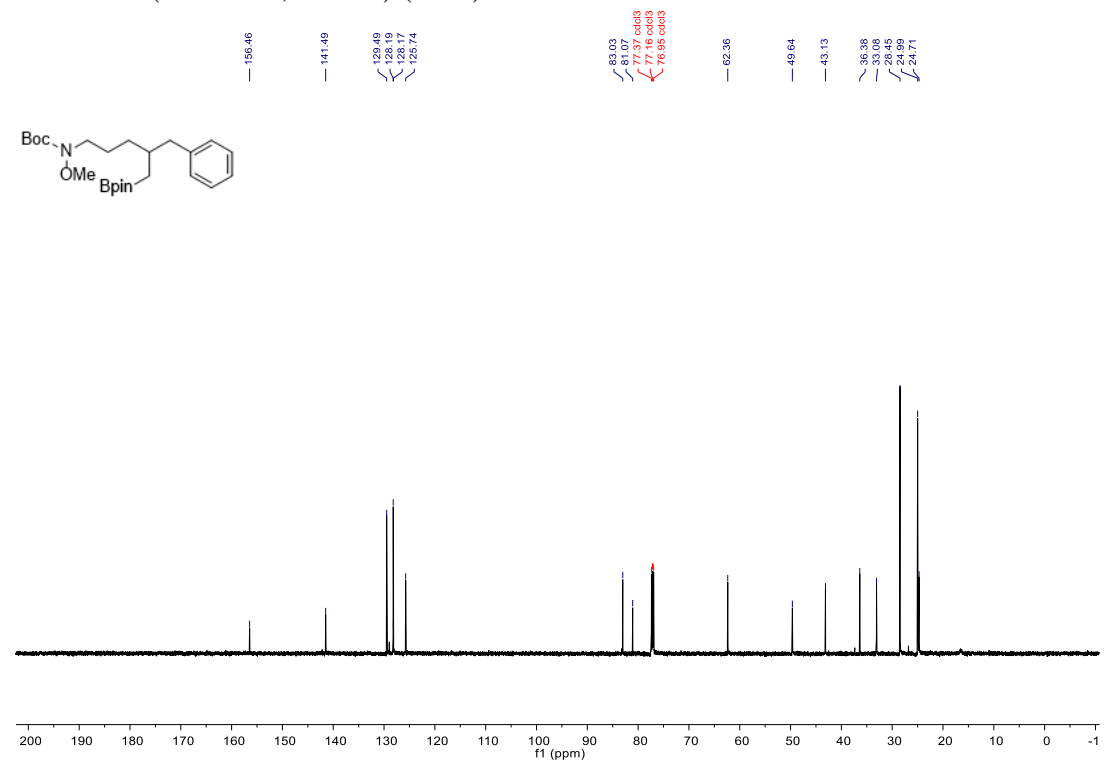
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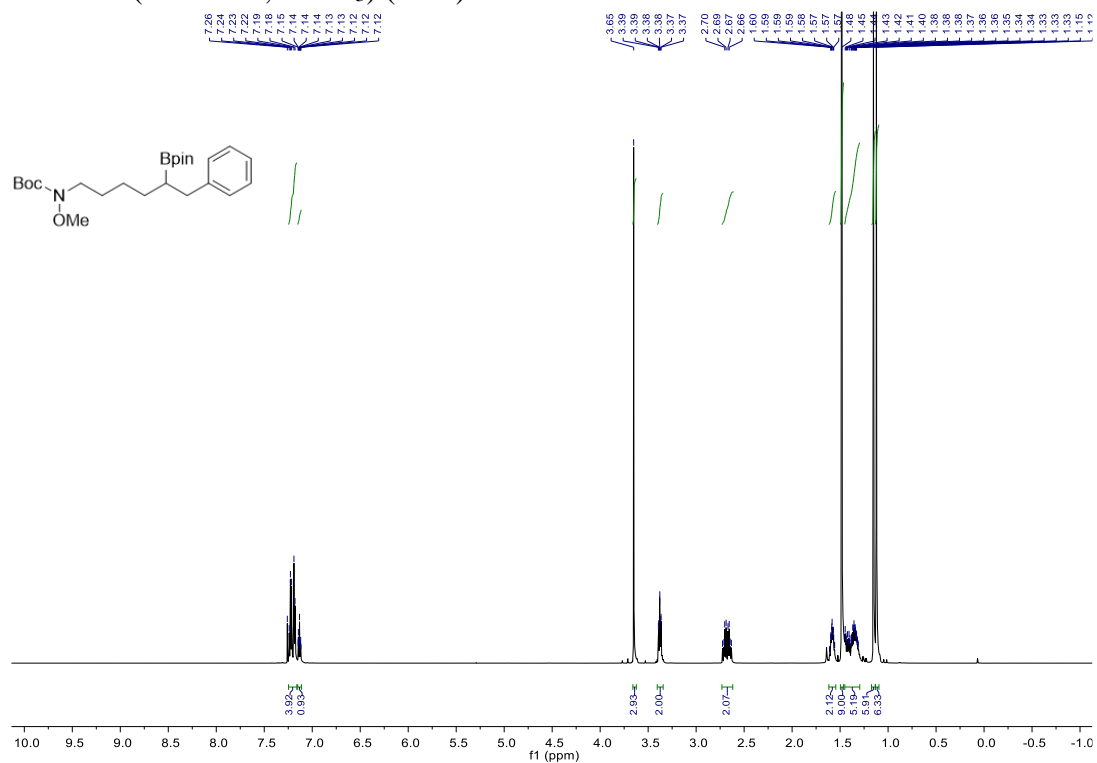
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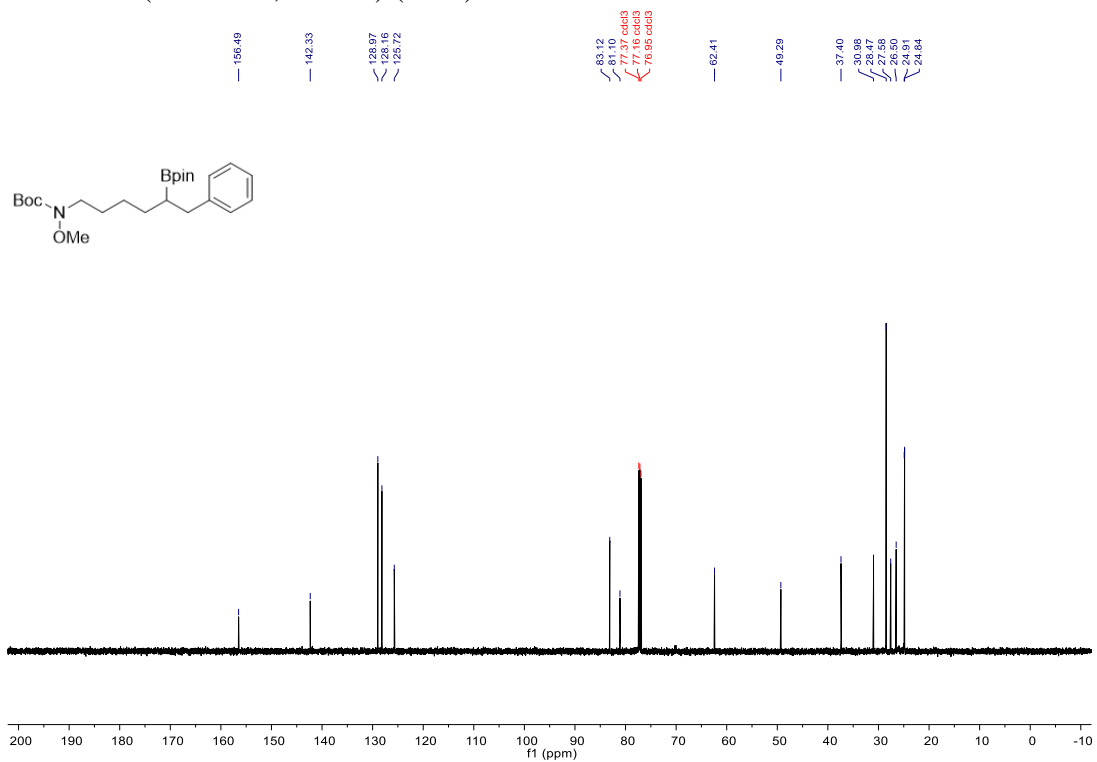
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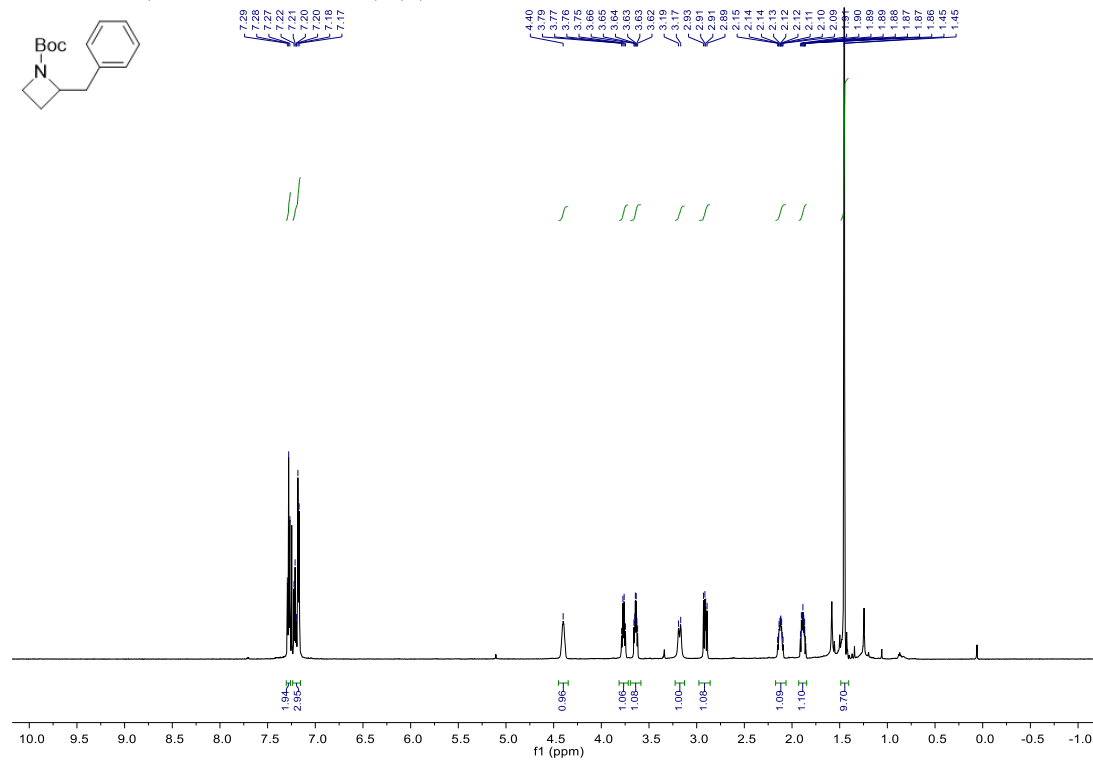
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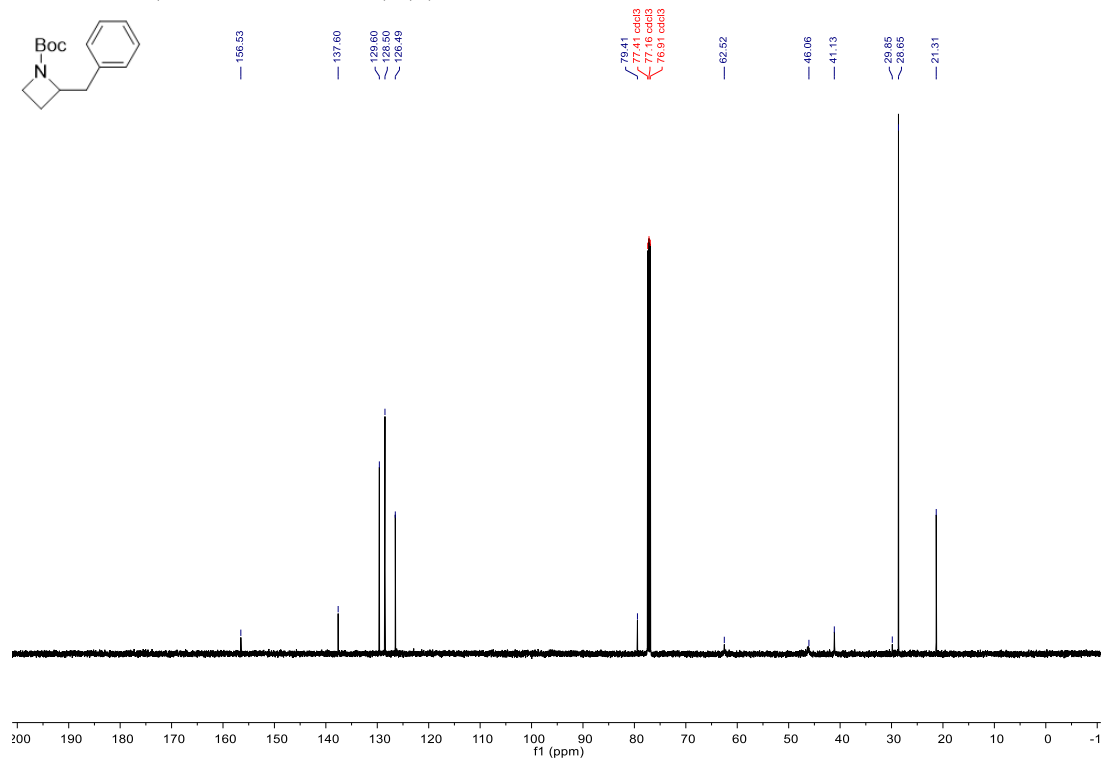
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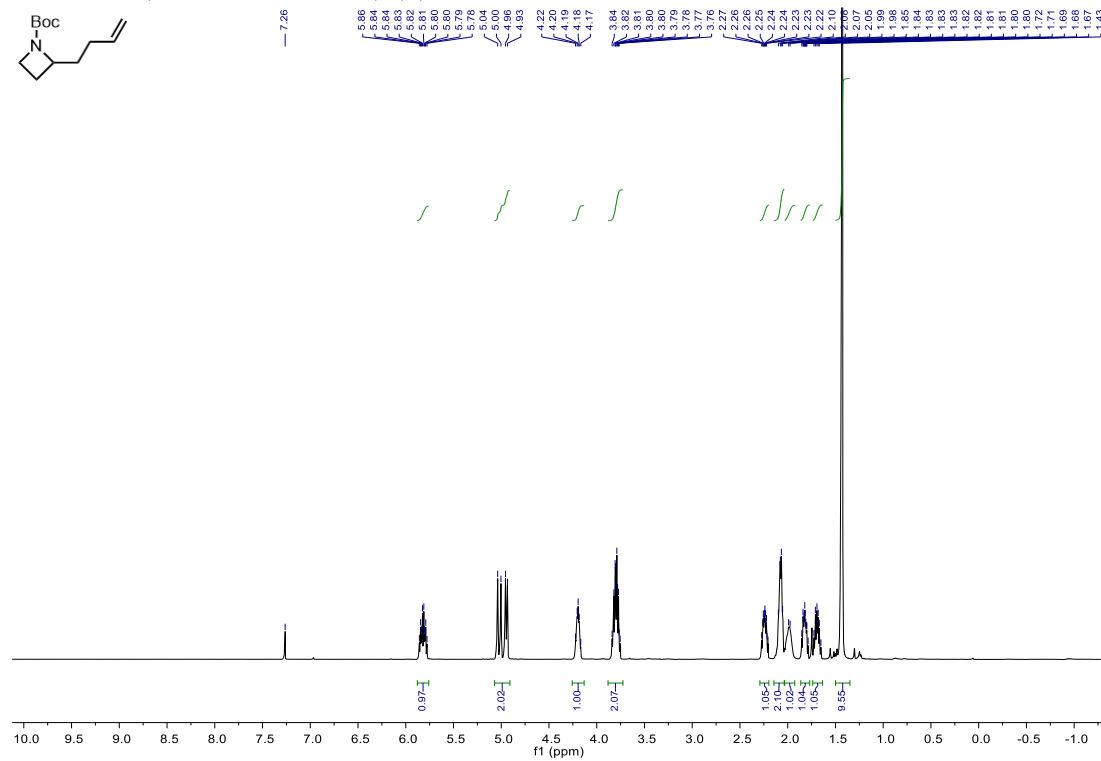
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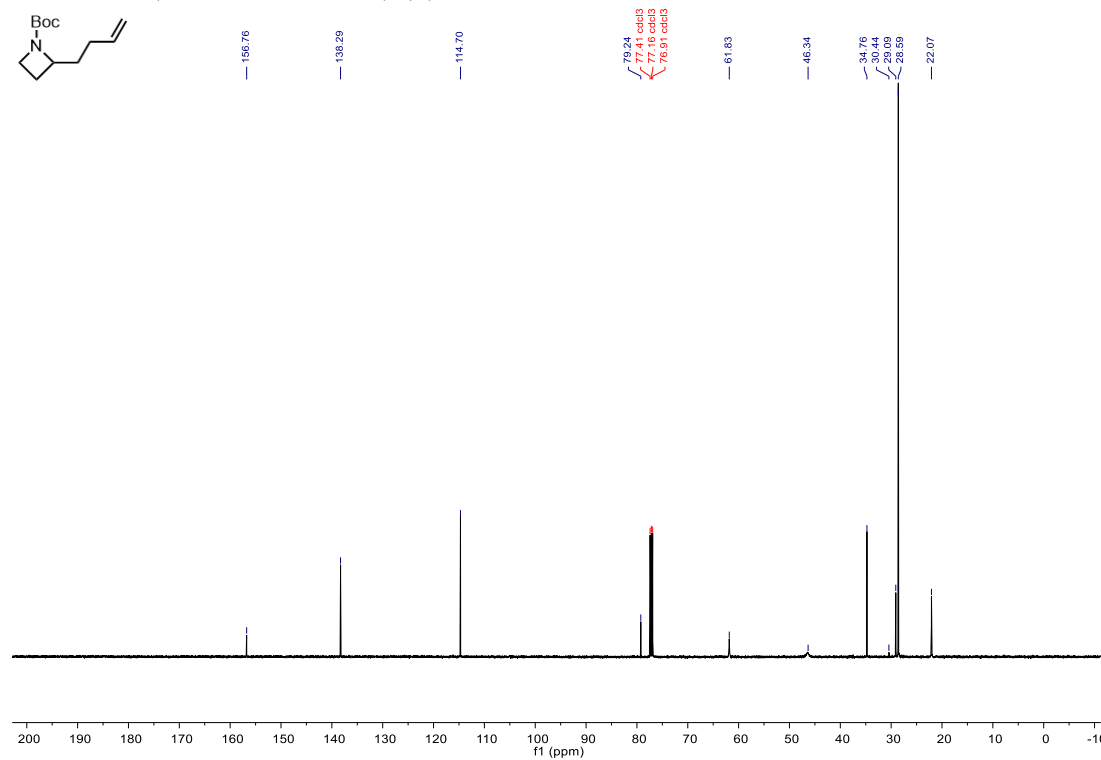
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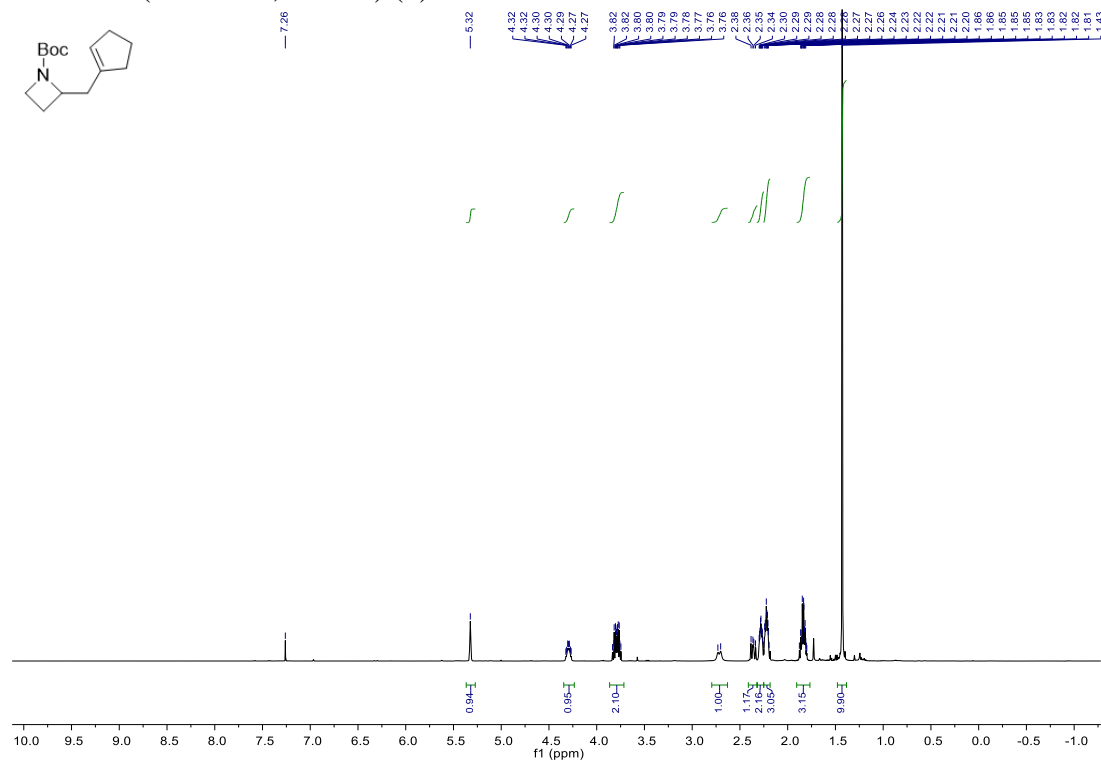
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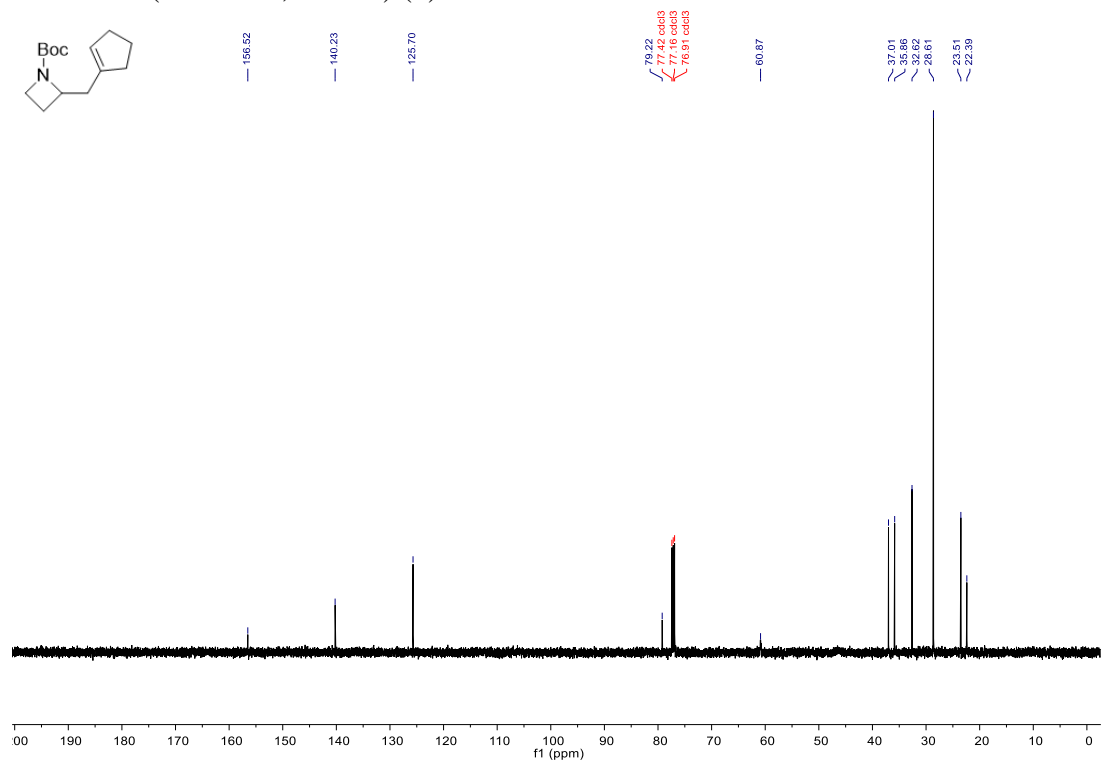
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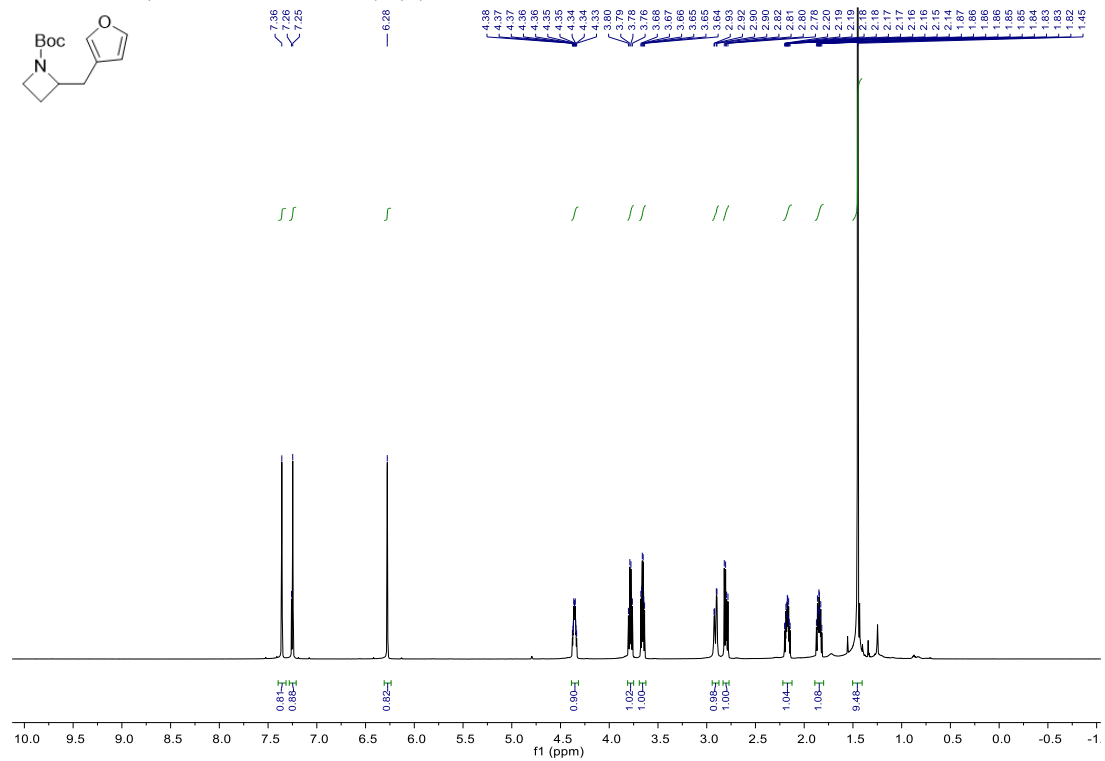
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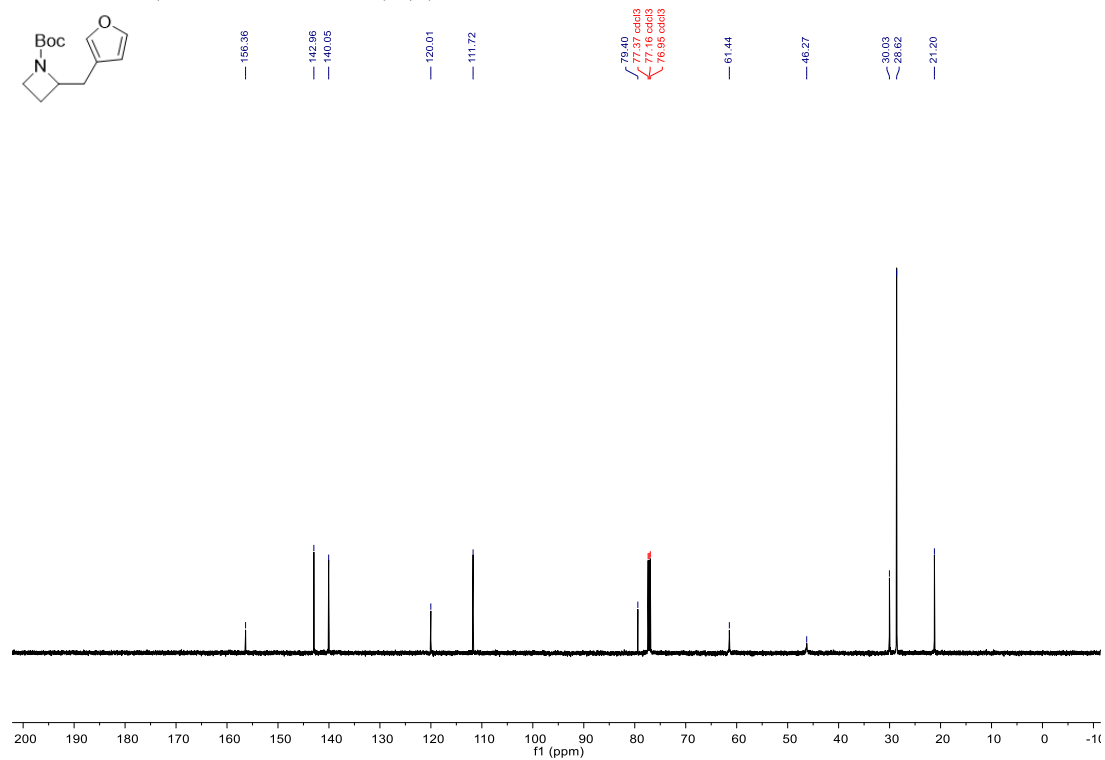
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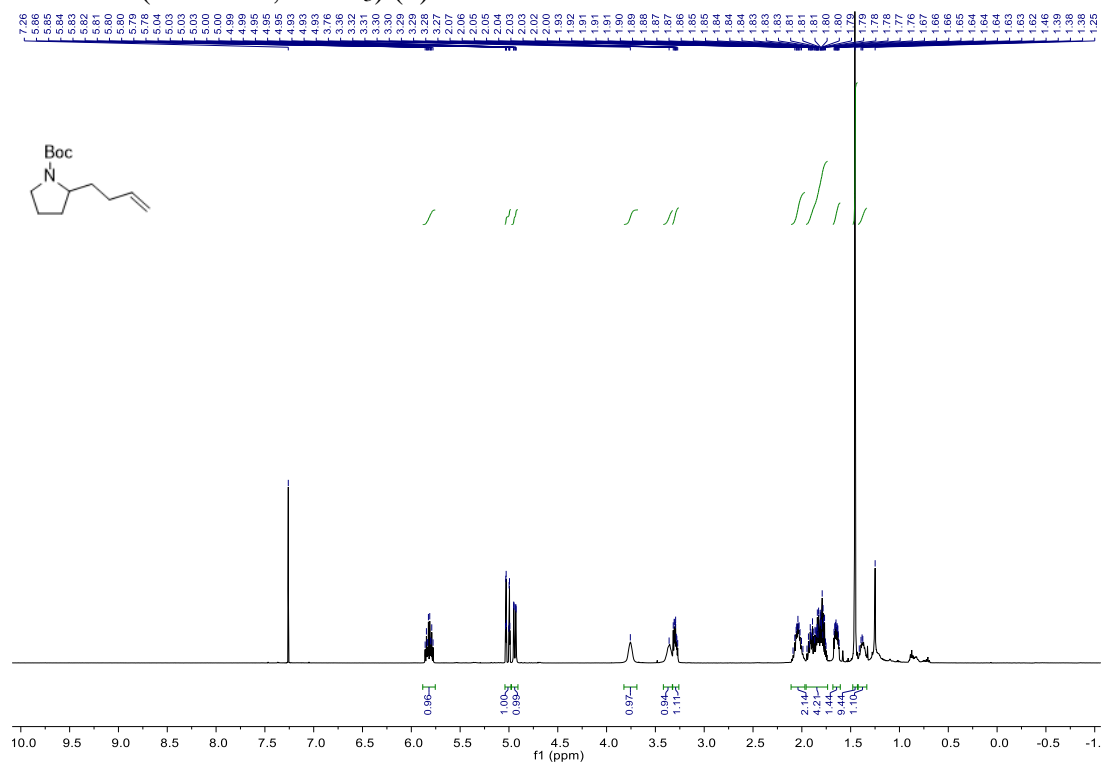
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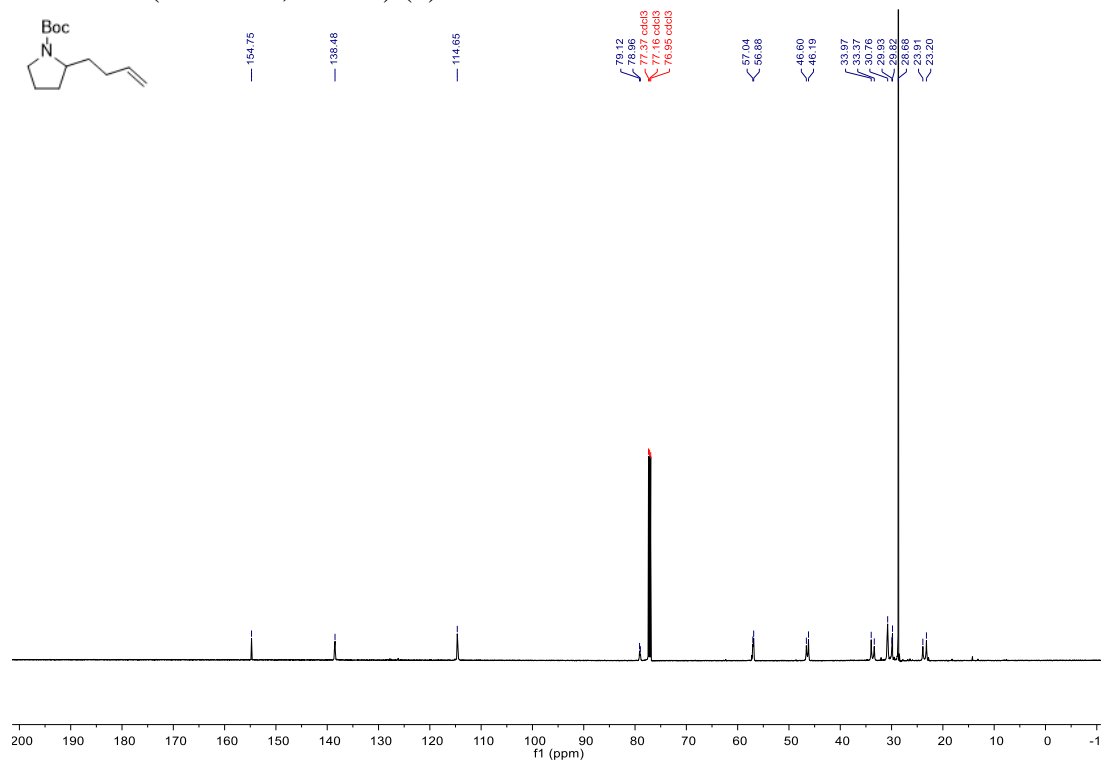
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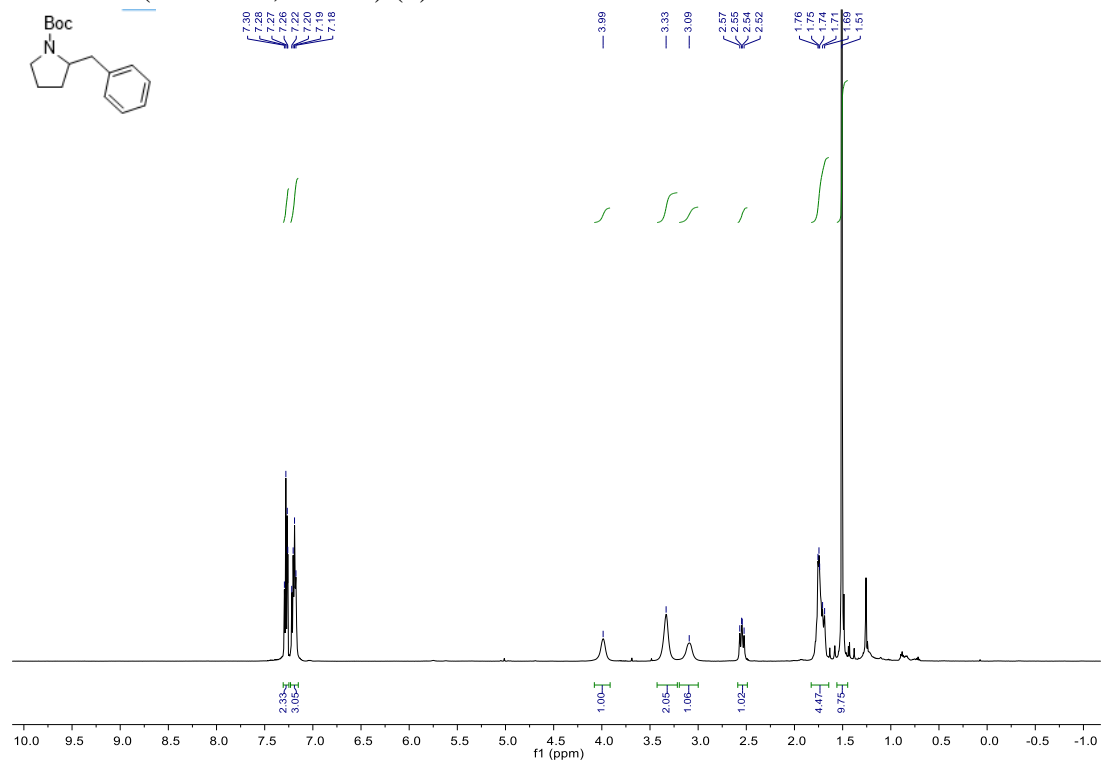
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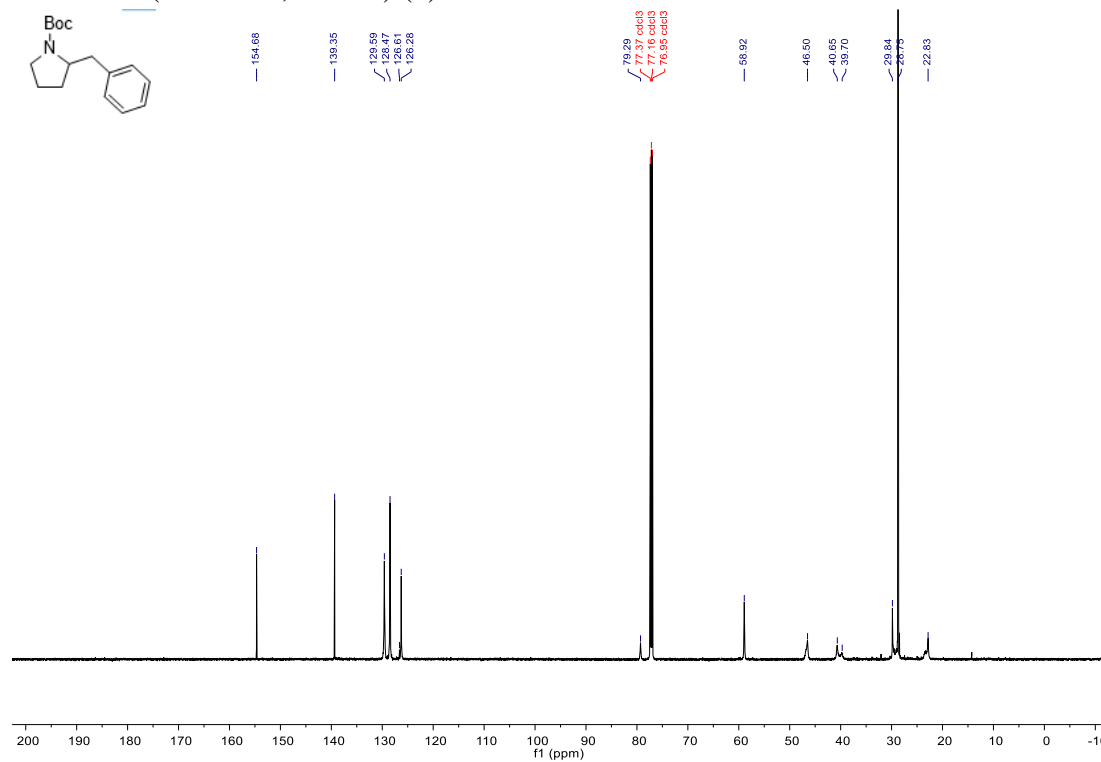
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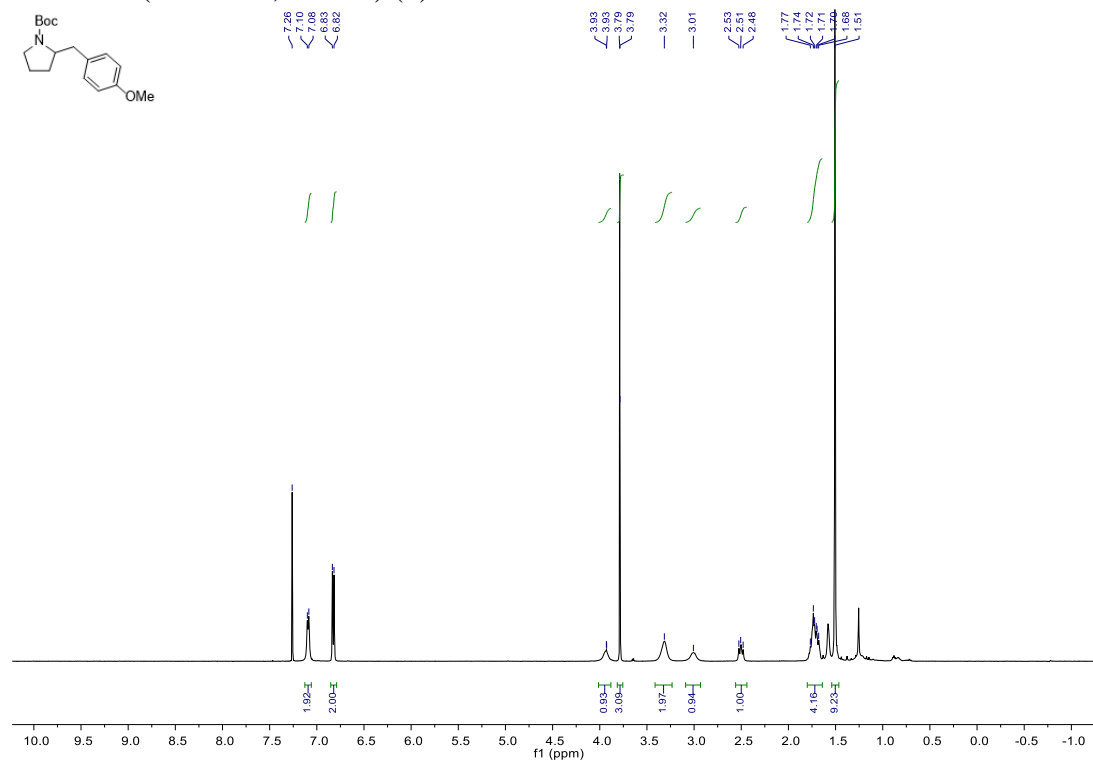
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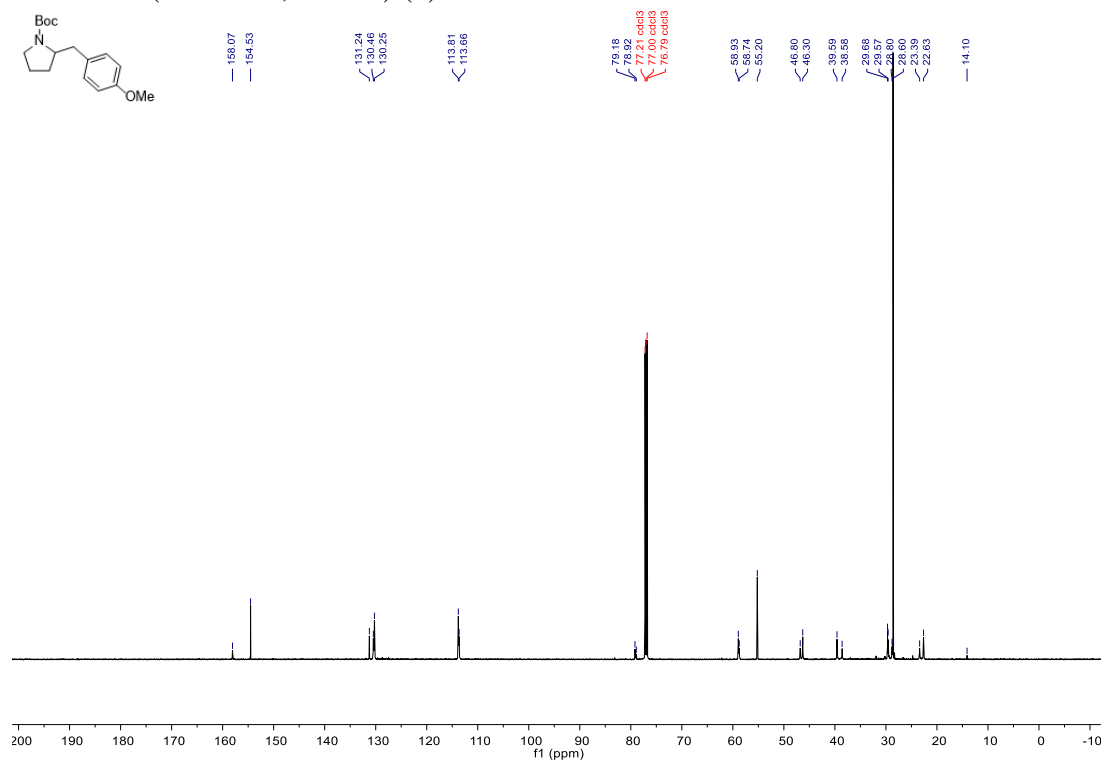
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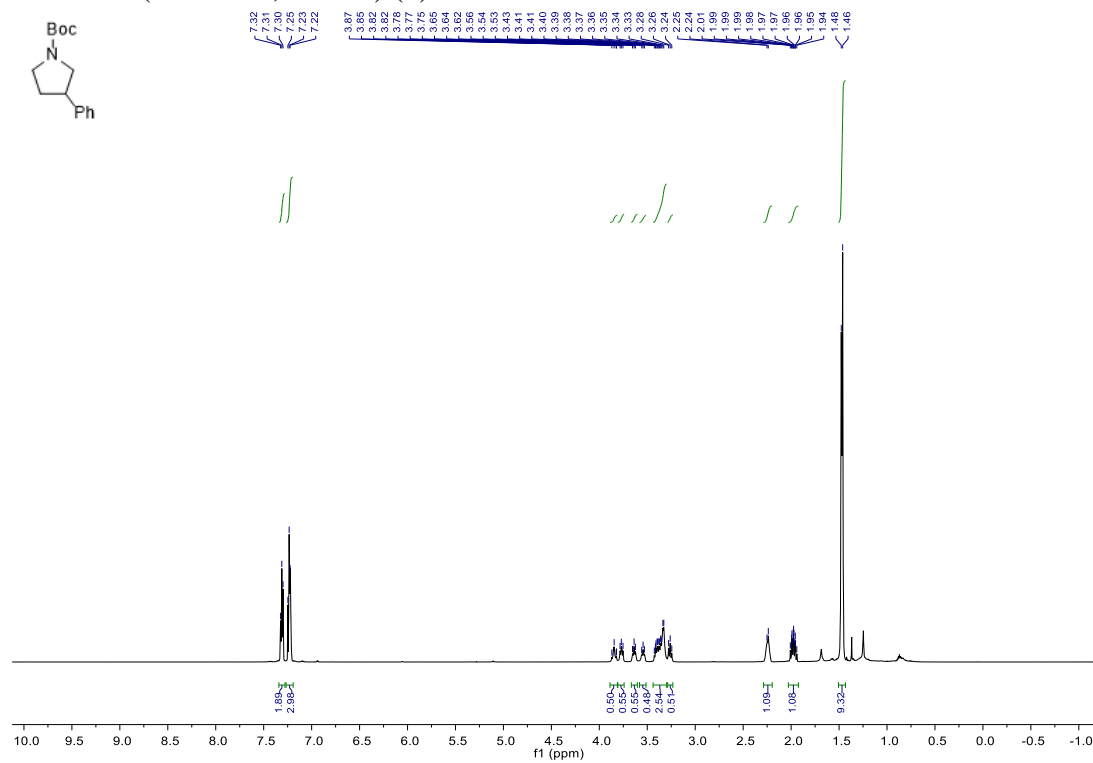
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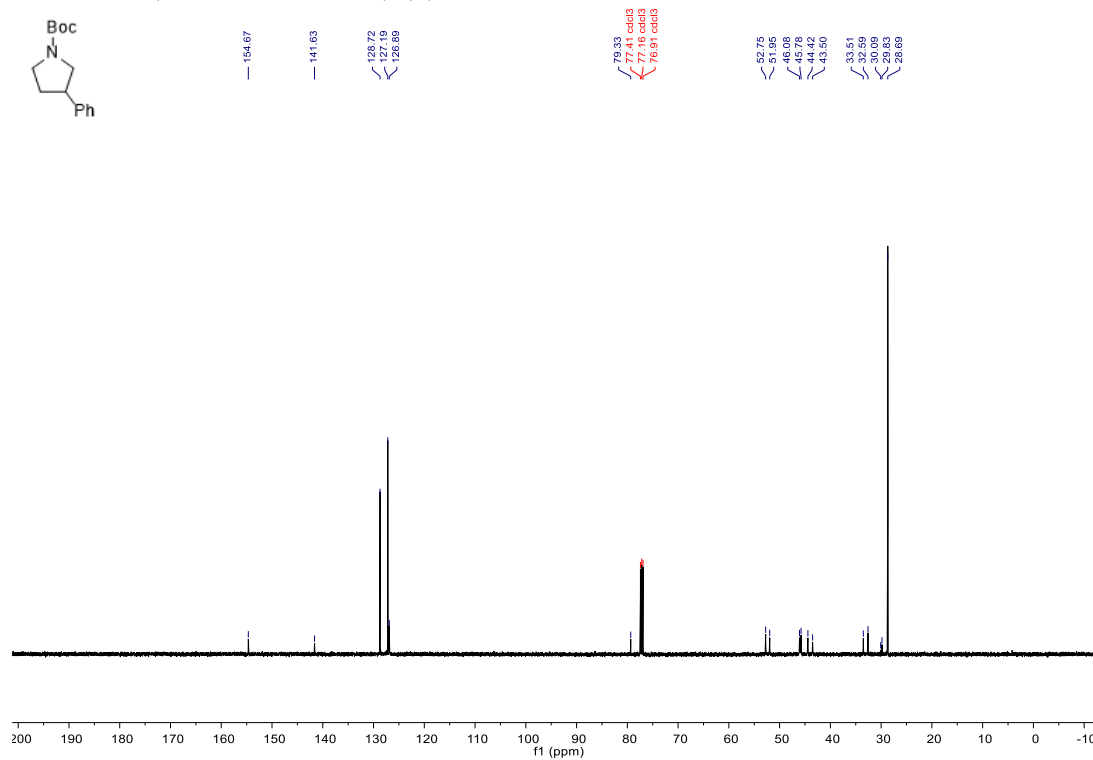
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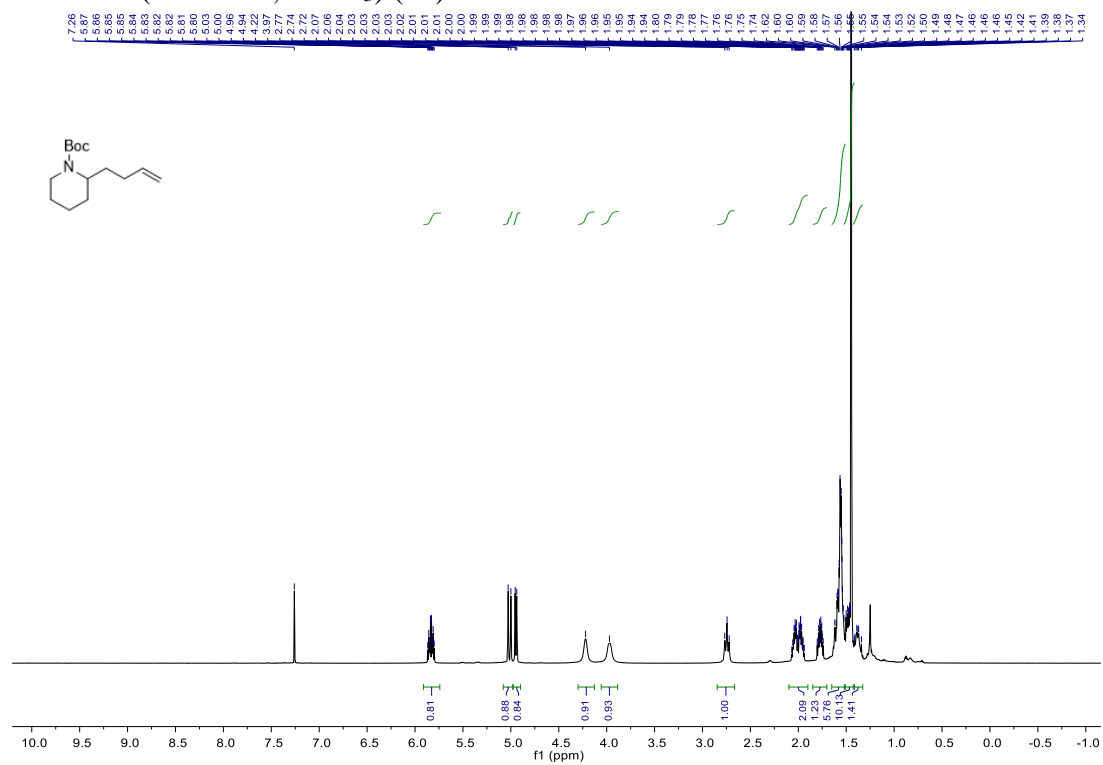
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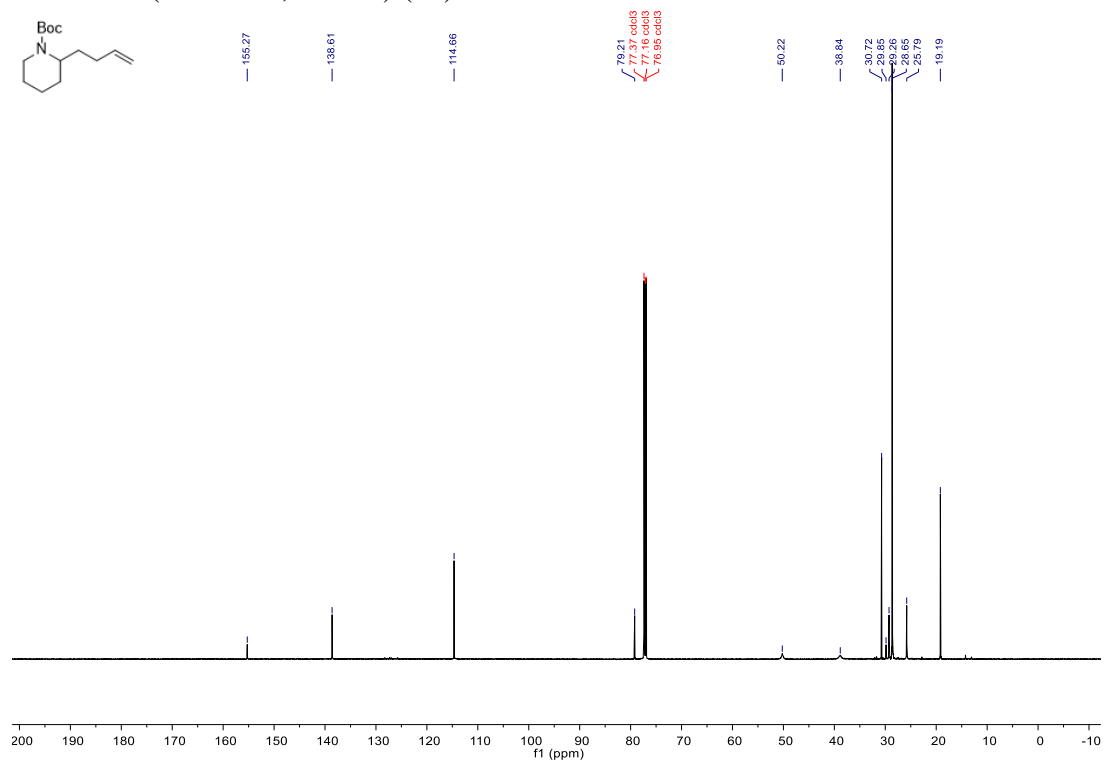
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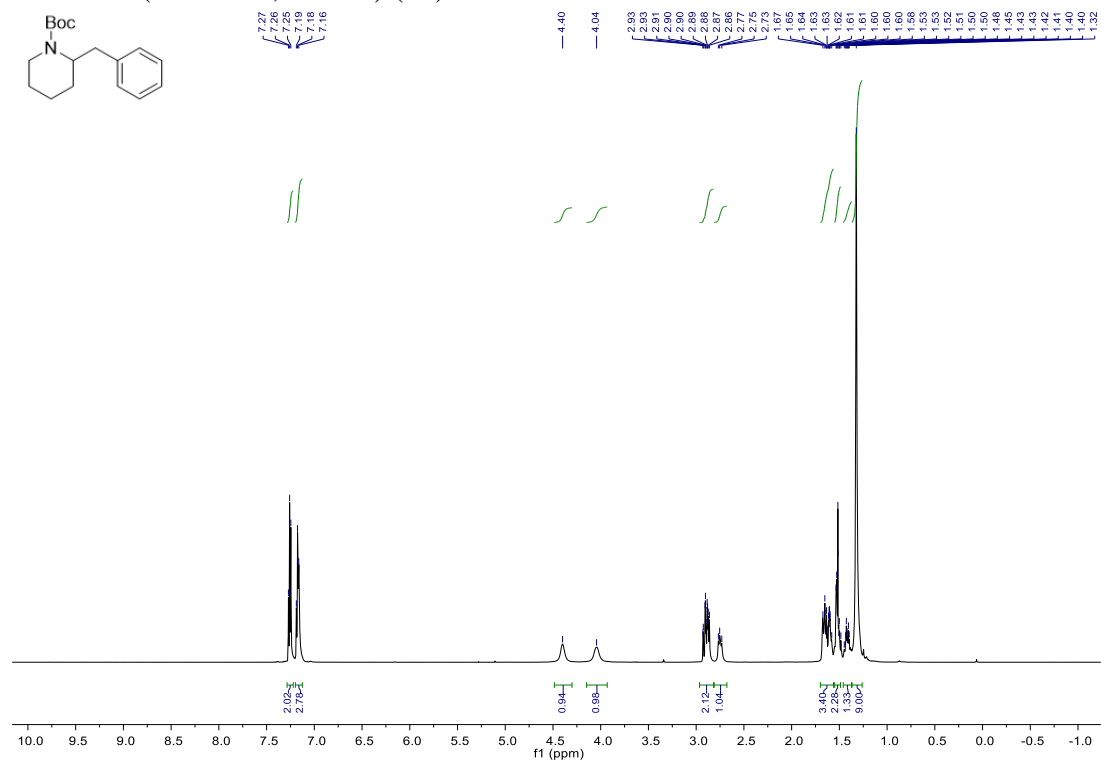
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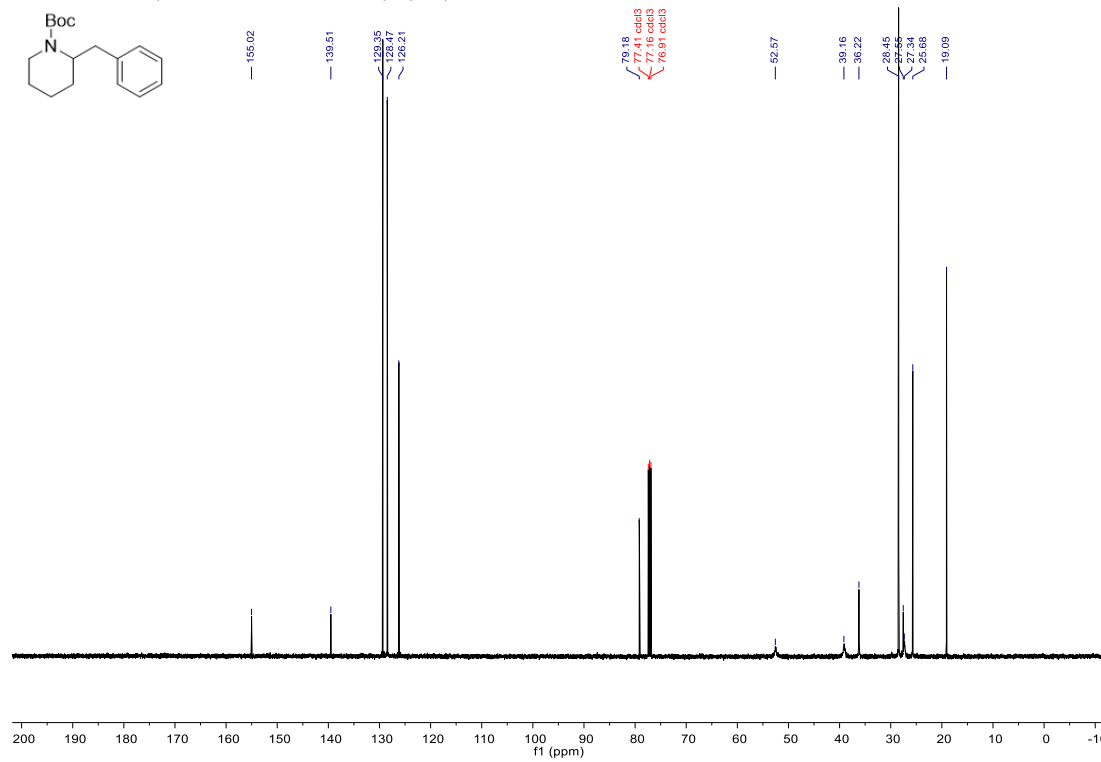
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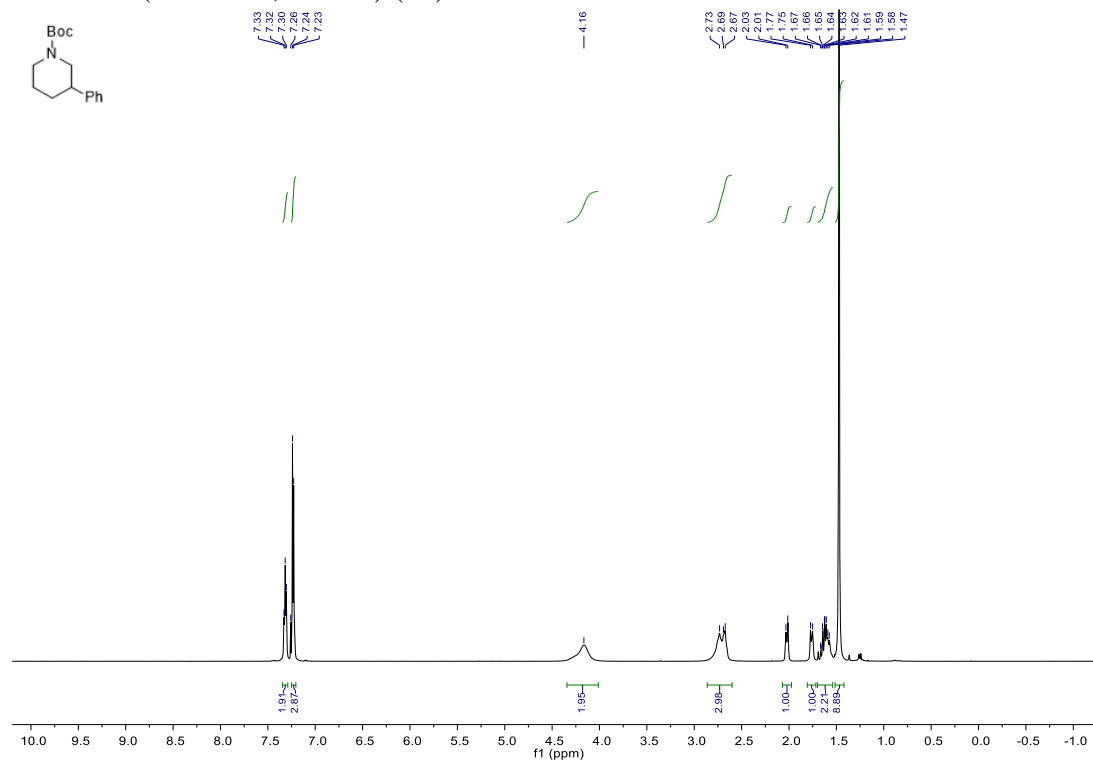
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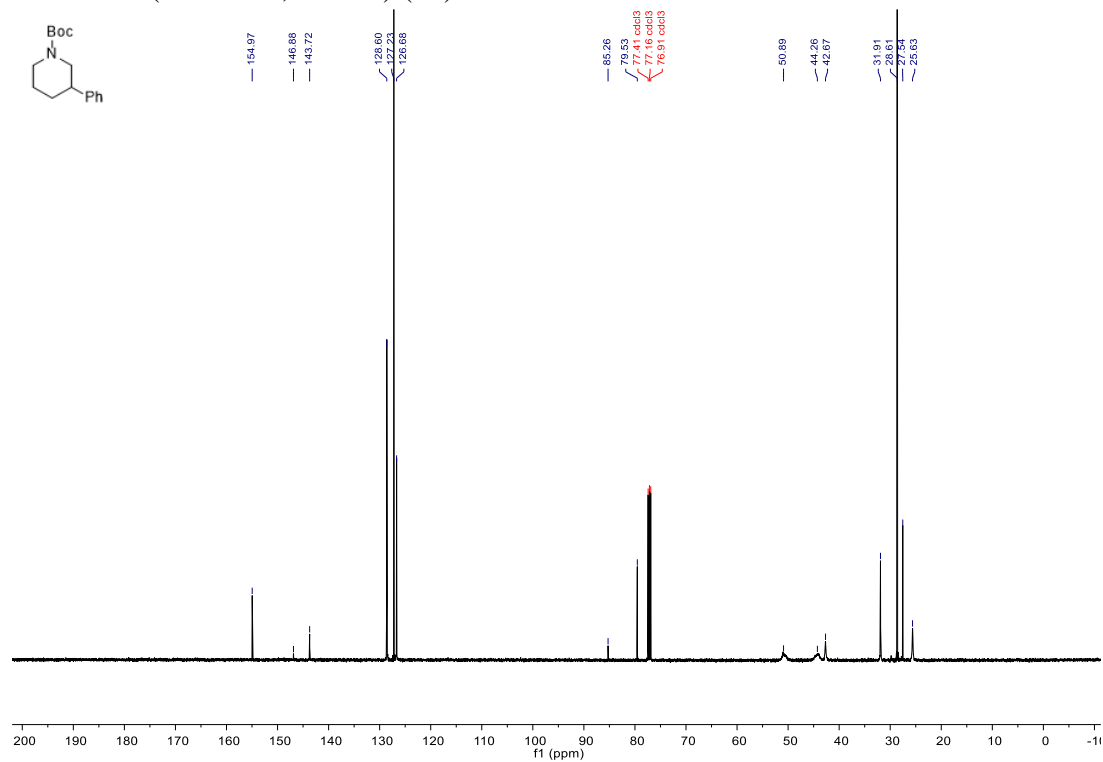
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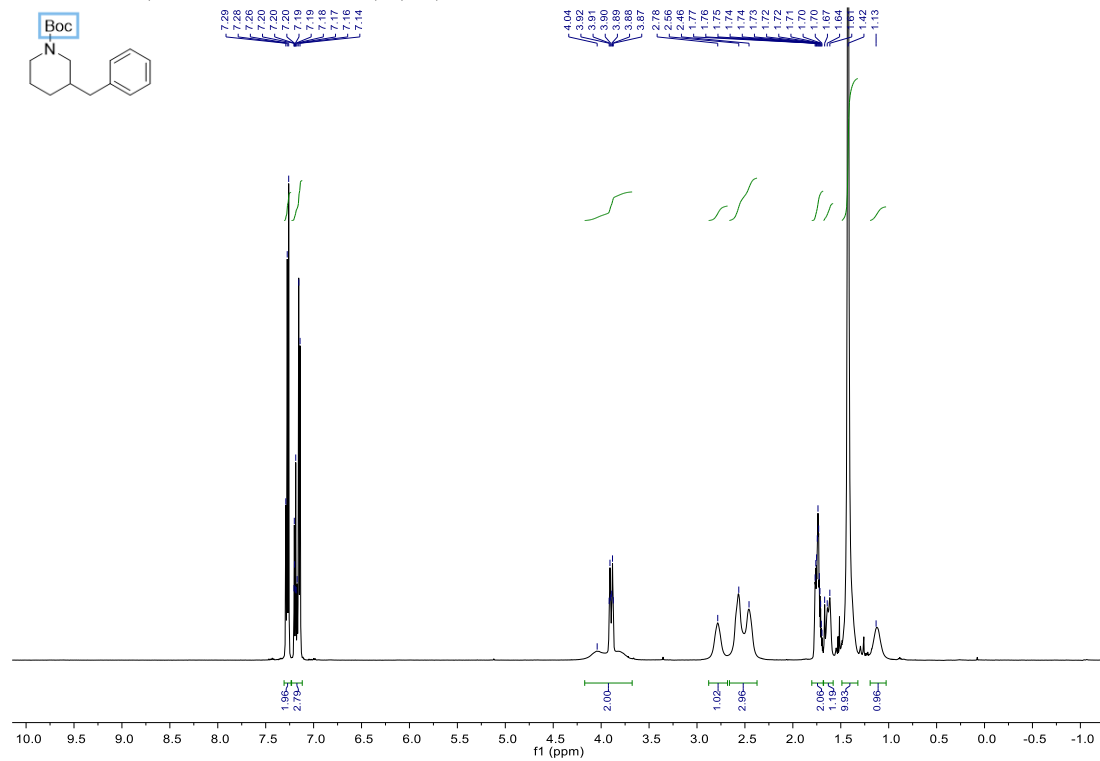
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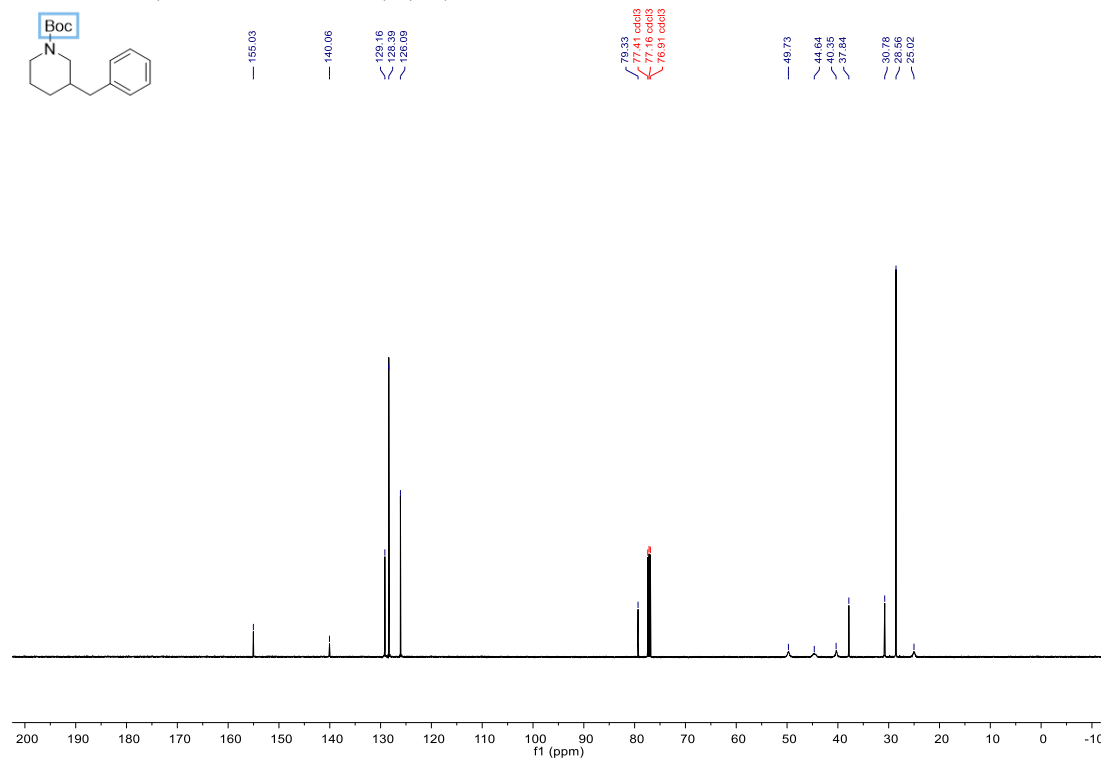
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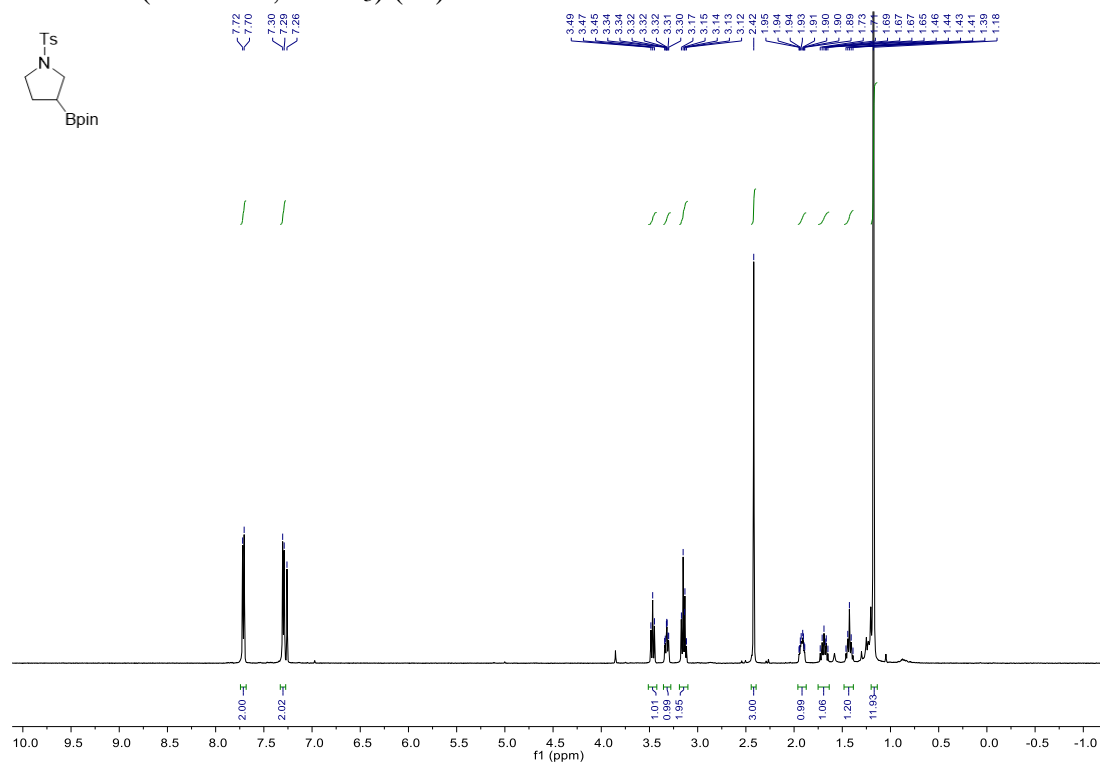
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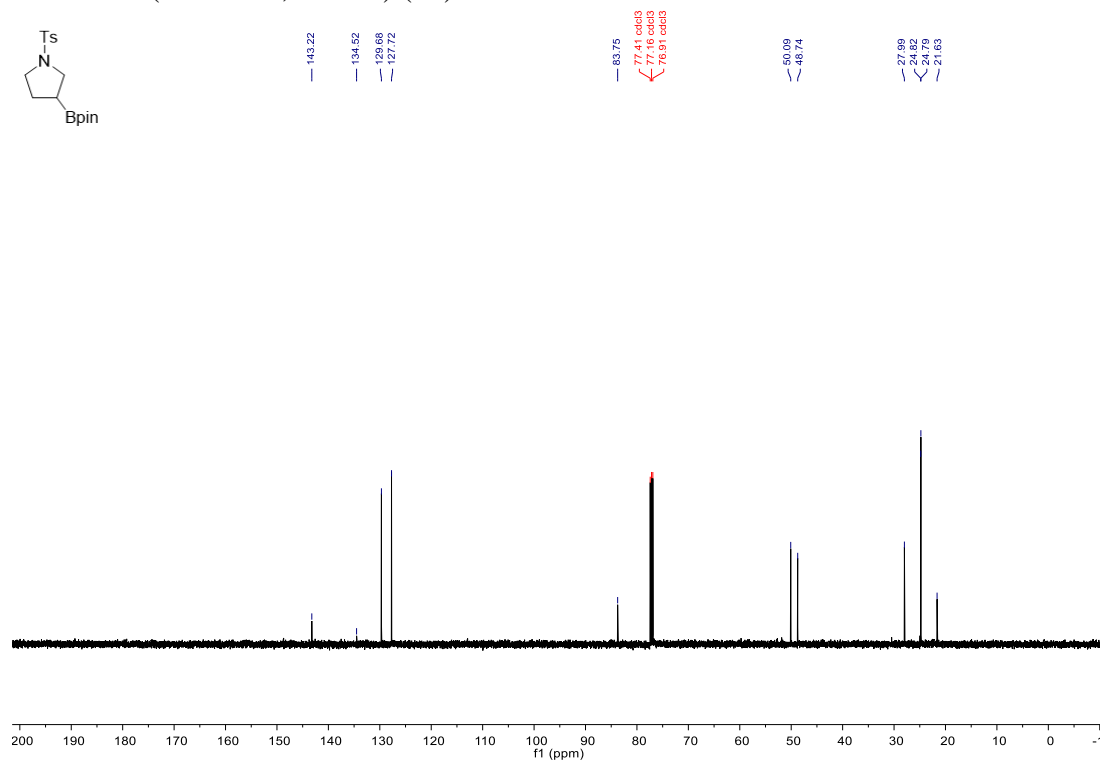
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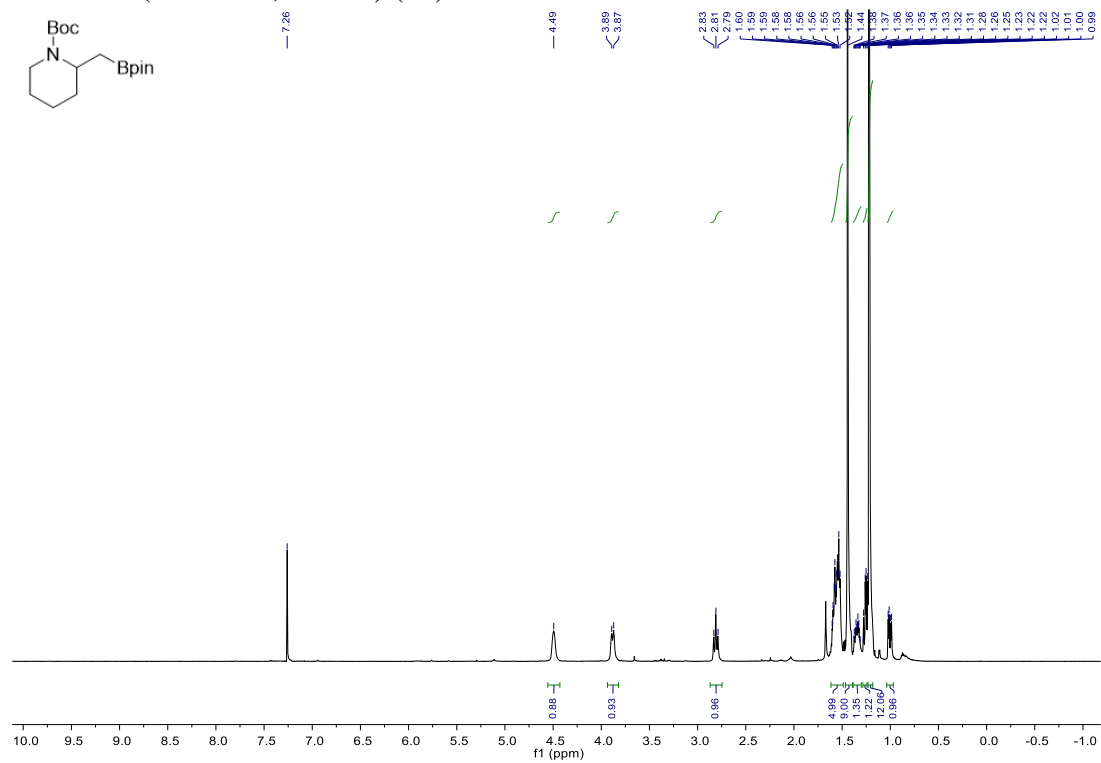
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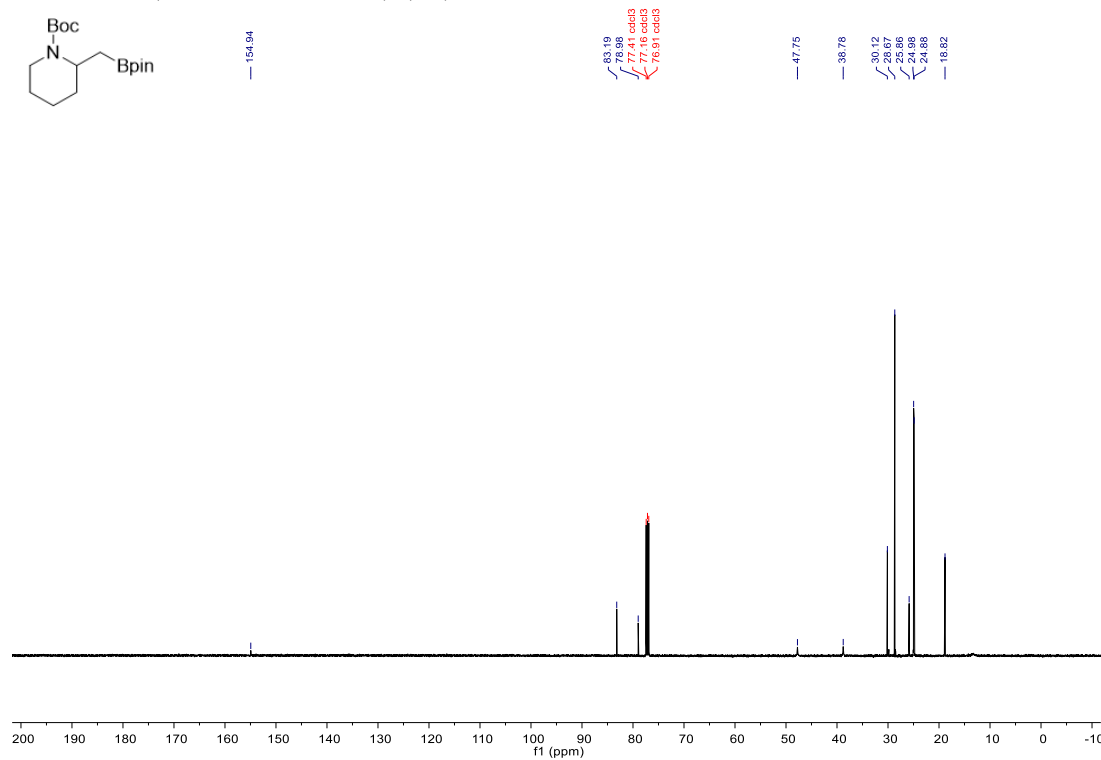
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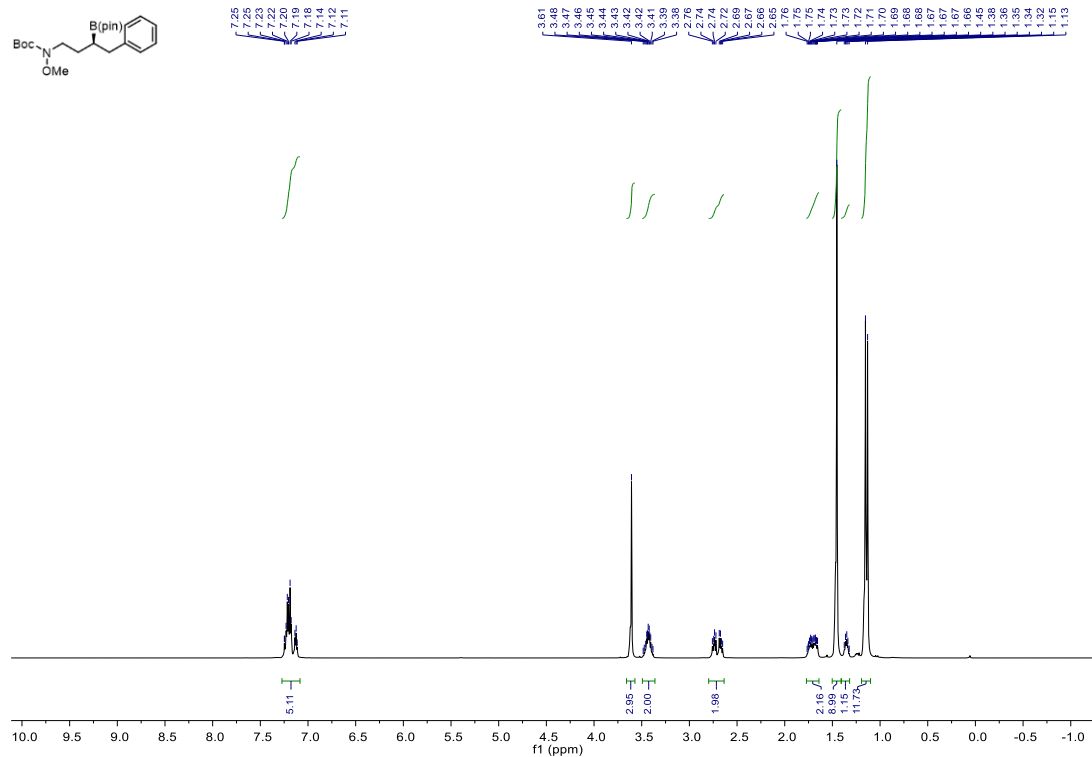
¹H NMR (600 MHz, CDCl₃) (19)



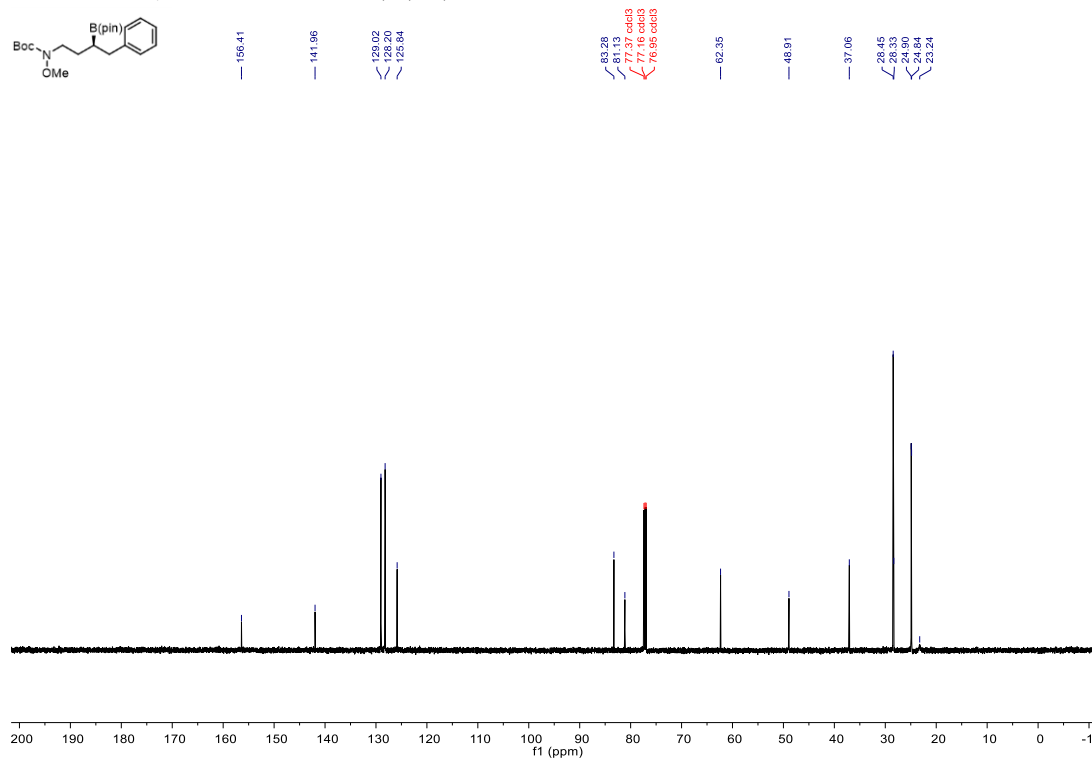
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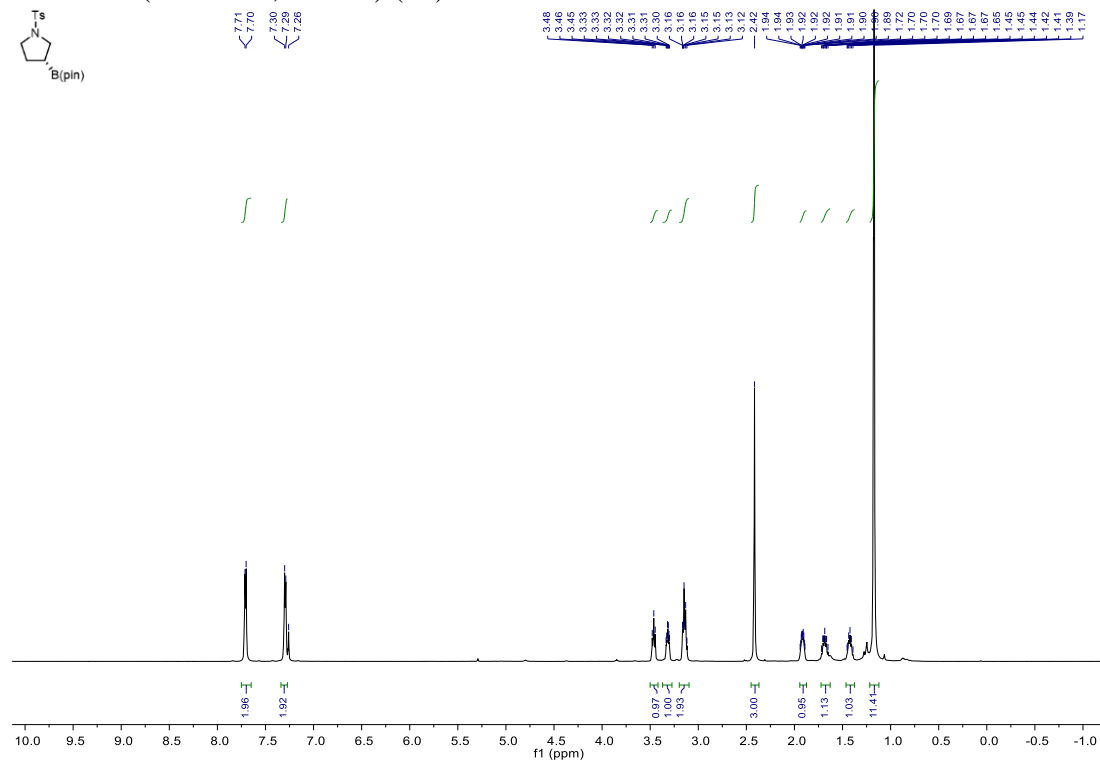
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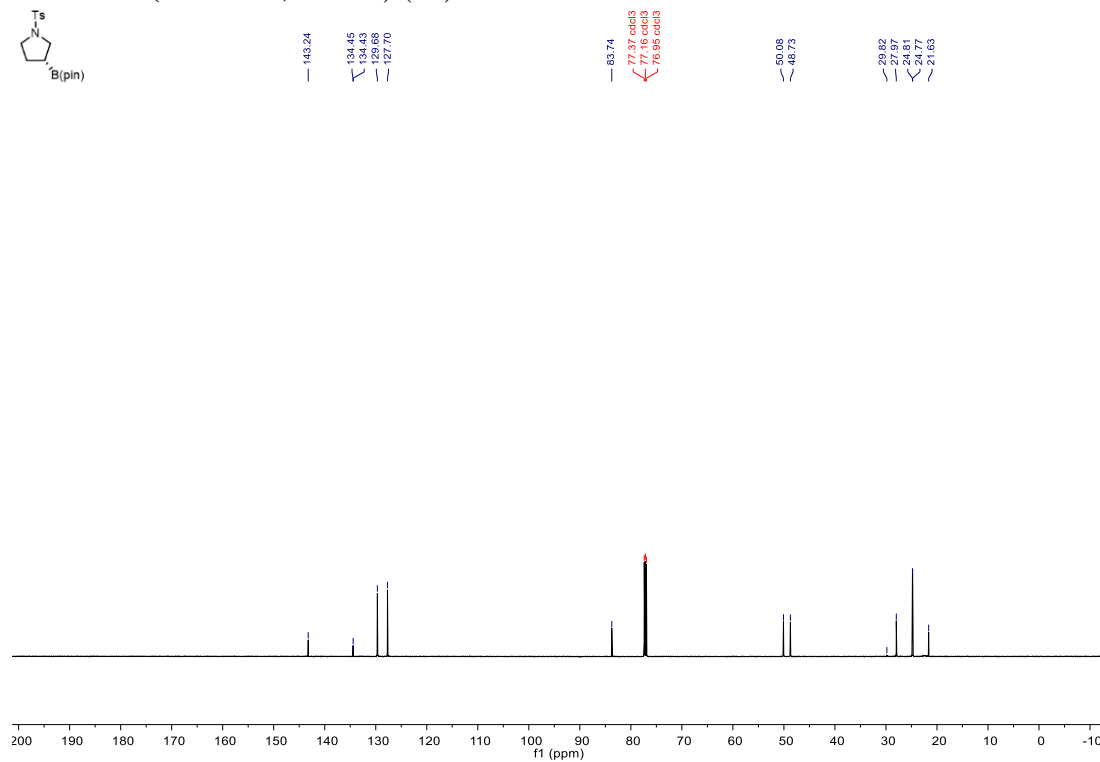
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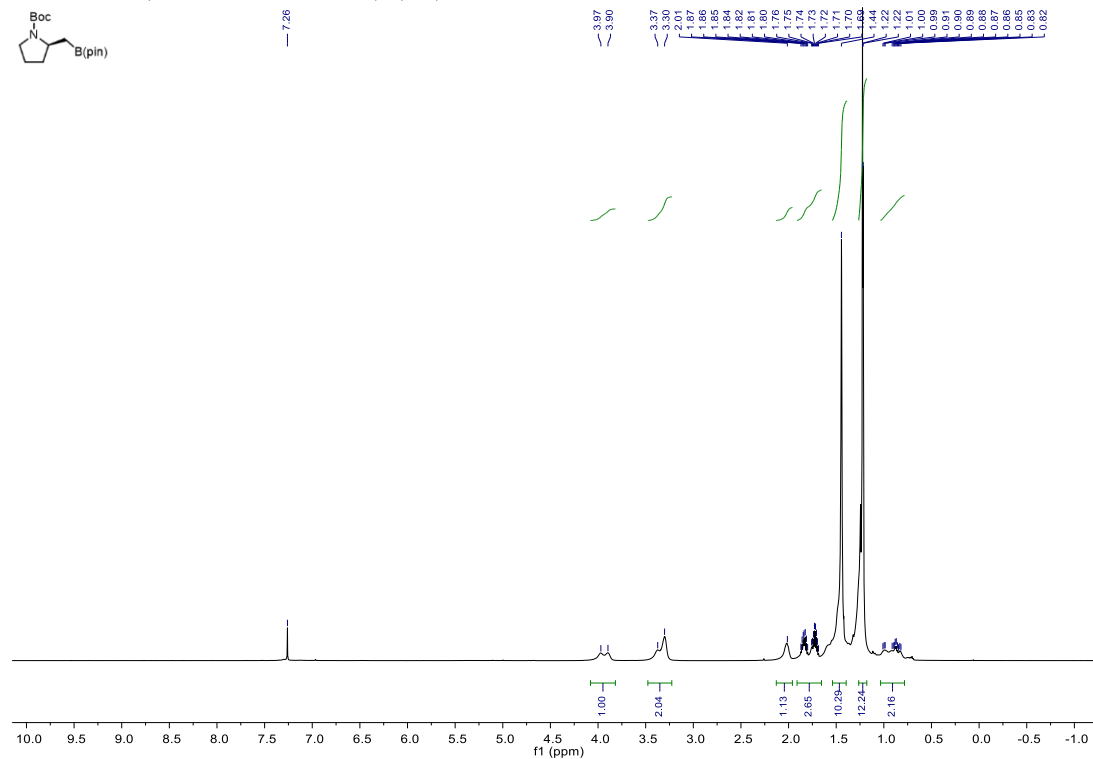
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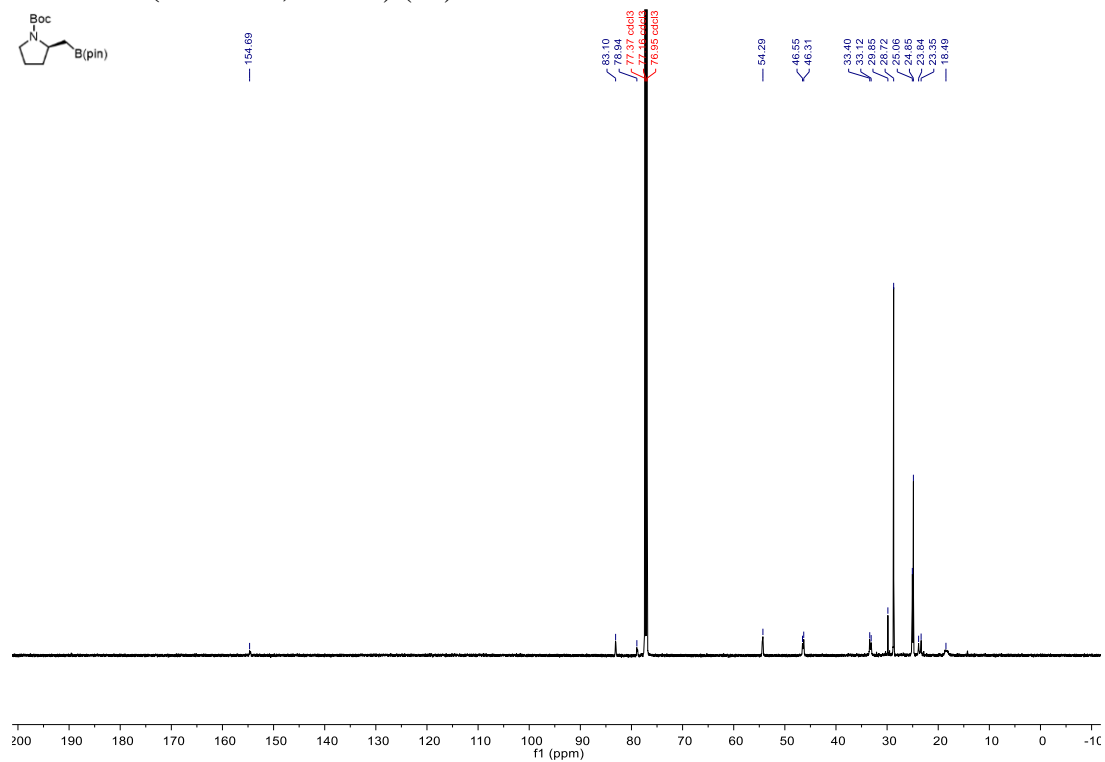
¹³C NMR (151 MHz, CDCl₃) (22)



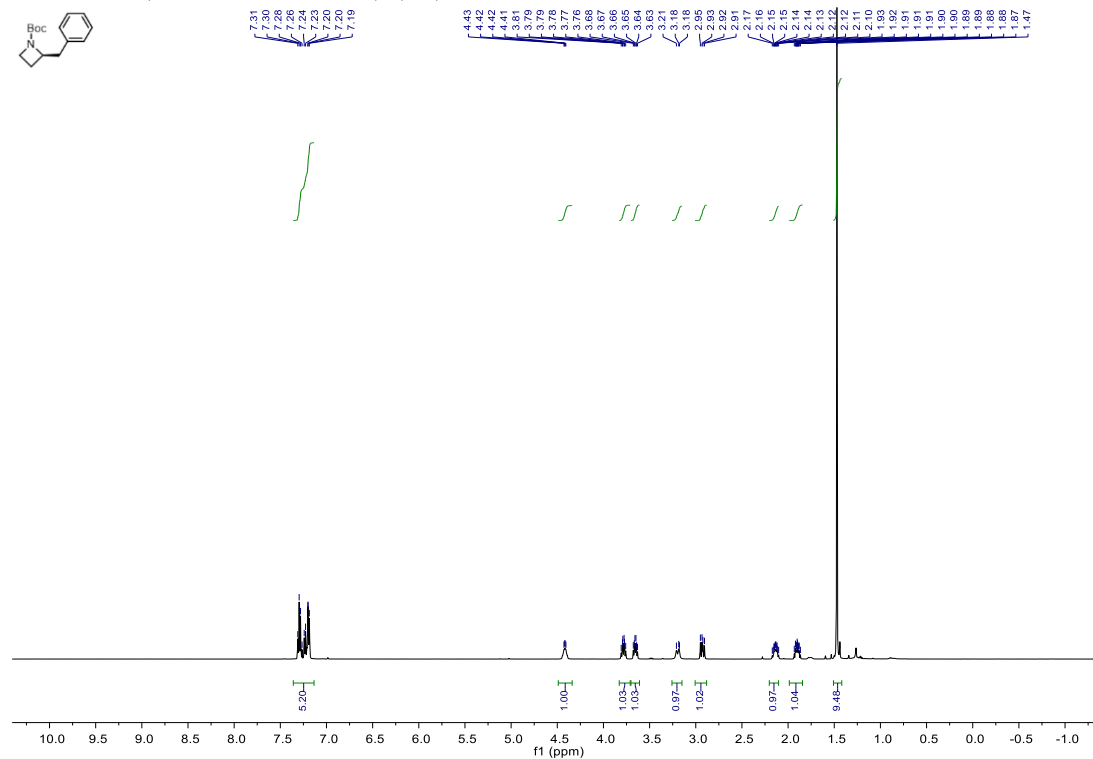
¹H NMR (600 MHz, CDCl₃) (27)



¹³C NMR (151 MHz, CDCl₃) (27)



¹H NMR (600 MHz, CDCl₃) (24)



¹³C NMR (151 MHz, CDCl₃) (24)

