Three-Component 1,2-Carboamination of Vinyl Boronic Esters via Amidyl Radical Induced 1,2-Migration

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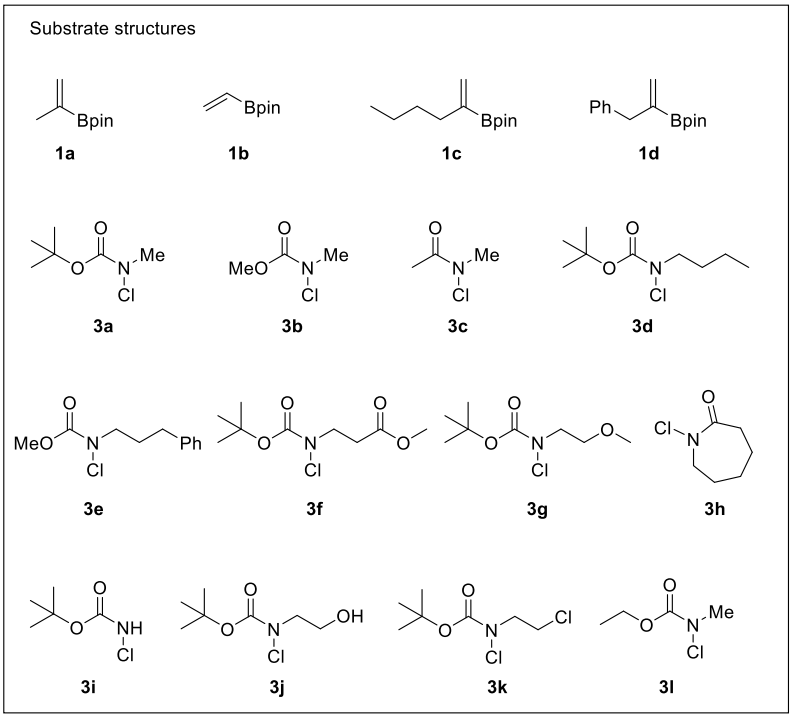
Contents

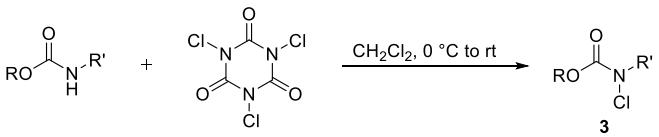
1. General information

All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in flame-dried glassware under an argon atmosphere using standard Schlenk techniques. Solvents used in reactions were either freshly distilled or obtained in extra-dry grade from commercial sources. Diethyl ether (Et_2O) was refluxed over K and freshly distilled from K-Na-alloy (4:1) afterwards. Tetrahydrofuran (THF) was refluxed over Na and distilled from K afterwards. All commercially available reagents were purchased from TCI, Sigma-Aldrich, Alfa Aesar, Acros or ABCR in the highest purity grade and used directly without further purification. Thin layer chromatography (TLC) was performed on Merck silica gel 60 F-254 plates and visualized by fluorescence quenching under UV light or staining with the standard solution of $KMnO_4$. Column chromatography was performed on Merck or Fluka silica gel 60 (40-63 μm). ^{1}H NMR, ^{13}C NMR, ^{11}B NMR and ^{19}F NMR spectra were recorded on Bruker Avance-II spectrometer (300 MHz) or Bruker AV 400 (400 MHz). Coupling constants were reported as Hertz (Hz), signal shapes and splitting patterns were indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Infrared spectra (IR) were measured on a Digilab 3100 FT-IR Excalibur Series spectrometer and the position of the absorption bands is given in wave numbers ν (cm^{-1}). Gas Chromatography (GC) was performed on an Hewlett Packard HP 6890 series GC system using an Agilent HP-1 column (30 m x 0.32 mm x 0.25 μm film thickness). The method used for GC was: start at 50 °C and 1.5 ml/min, 3.81 psi, increase to 300 °C at 10 °C/min, hold for 15 min. Mass spectra were recorded on a Finnigan MAT 4200S, a Bruker Daltonics Micro Tof, a Waters-Micromass Quatro LCZ (ESI); peaks are given in m/z (% of basis peak).

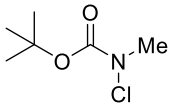
2. Synthetic procedures

1a and **1b** were purchased from commercial source and used without further purification. **1c**,[1] **1d**,[1] **3a-3h**,[2] **3i**,[3] and **3g-3l**[2] were prepared following literature procedures.





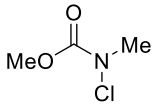
Procedure for the preparation of **3**:[2] Trichloroisocyanuric acid (1.1 equiv.) was added at 0 °C to a well stirred solution of the amide (1.0 equiv.) in CH_2Cl_2 (6 mL for 1 mmol amide) and the mixture was kept at room temperature overnight. Then the mixture was filtered on Celite and the solution evaporated under reduced pressure. Flash column chromatography afforded **3**.



***tert*-Butyl chloro(methyl)carbamate (3a):**

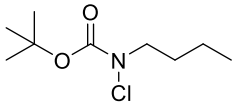
3a (48.0 mmol, 7.95 g, 86%) was prepared as a colorless. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.16 (s, 3H), 1.38 (s, 9H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 155.4, 82.7, 42.6, 28.1 ppm. **HRMS** (ESI):

Exact mass calculated for $C_6H_{12}ClNNaO_2^+$ ([M+Na]$^+$): 188.0449, mass found: 188.0443. **FTIR** (neat): υ (cm^{-1}) 2979, 2935, 1726, 1702, 1470, 1411, 1393, 1368, 1333, 1254, 1145, 1038, 974, 952, 853, 755, 609.



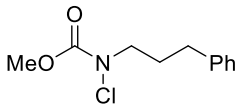
Methyl chloro(methyl)carbamate (3b):

3b (13.3 mmol, 1.64 g, 57%) was prepared as a colorless. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.76 (s, 3H), 3.29 (s, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 157.2, 54.6, 42.8 ppm. **HRMS** (ESI): Exact mass calculated for $C_3H_7ClNO_2^+$ ([M+H]$^+$): 124.0160, mass found: 124.0157. **FTIR** (neat): υ (cm^{-1}) 3382, 2957, 1710, 1532, 1443, 1409, 1327, 1260, 1195, 1159, 1004, 922, 779, 753, 683, 592.



***tert*-Butyl butylchlorocarbamate (3d):**

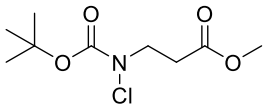
3d (9.3 mmol, 1.94 g, 93%) was prepared as a colorless. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.60 – 3.49 (m, 2H), 1.61 (dt, *J* = 12.6, 7.4 Hz, 2H), 1.46 (s, 9H), 1.36 – 1.25 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1, 82.7, 54.0, 29.6, 28.3, 19.5, 14.0 ppm. **HRMS** (ESI): Exact mass calculated for $C_9H_{18}ClNNaO_4^+$ ([M+Na]$^+$): 230.0918, mass found: 230.0917. **FTIR** (neat): υ (cm^{-1}) 2961, 2933, 2874, 1726, 1699, 1457, 1367, 1341, 1292, 1252, 1229, 1145, 1049, 1010, 935, 849, 751, 654, 603.



Methyl chloro(3-phenylpropyl)carbamate (3e):

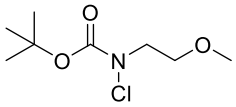
3e (15.4 mmol, 3.51 g, 85%) was prepared as a colorless. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 – 7.17 (m, 2H), 7.15 – 7.06 (m, 3H), 3.70 (s, 3H), 3.57 (t, *J* = 7.0 Hz, 2H), 2.62 – 2.50 (m, 2H), 1.92 (dt, *J* = 14.6, 7.2 Hz, 2H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 156.5, 141.1, 128.5, 128.4, 126.1,

54.4, 53.8, 32.3, 28.9 ppm. **HRMS** (ESI): Exact mass calculated for $C_{11}H_{15}ClNO_2^+$ ([M+H]$^+$): 228.0786, mass found: 228.0785. **FTIR** (neat): υ (cm^{-1}) 3026, 2951, 2860, 1703, 1602, 1496, 1444, 1344, 1292, 1272, 1233, 1193, 1135, 1090, 1026, 937, 847, 807, 747, 698, 600.



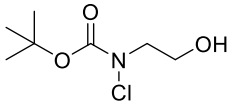
Methyl 3-((*tert*-butoxycarbonyl)chloroamino)propanoate (3f):

3f (11.8 mmol, 2.80 g, 91%) was prepared as a colorless. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.90 – 3.80 (m, 2H), 3.67 (s, 3H), 2.70 – 2.61 (m, 2H), 1.46 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 154.6, 83.4, 52.1, 50.3, 32.5, 28.2 ppm. **HRMS** (ESI): Exact mass calculated for $C_9H_{16}ClNNaO_4^+$ ([M+Na]$^+$): 260.0660, mass found: 260.0657. **FTIR** (neat): υ (cm^{-1}) 2979, 1731, 1699, 1438, 1368, 1342, 1282, 1250, 1196, 1148, 1071, 1030, 984, 895, 849, 810, 752, 624, 561.



***tert*-Butyl chloro(2-methoxyethyl)carbamate (3g):**

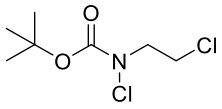
3g (17.2 mmol, 3.60 g, 87%) was prepared as a colorless. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.68 (t, *J* = 5.6 Hz, 2H), 3.53 (t, *J* = 5.6 Hz, 2H), 3.30 (s, 3H), 1.42 (s, 9H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 154.9, 82.8, 68.8, 58.8, 53.2, 28.0 ppm. **HRMS** (ESI): Exact mass calculated for $C_8H_{16}ClNNaO_3^+$ ([M+Na]$^+$): 232.0711, mass found: 232.0710. **FTIR** (neat): υ (cm^{-1}) 2979, 2931, 1699, 1455, 1426, 1392, 1366, 1341, 1276, 1240, 1198, 1146, 1118, 1023, 965, 927, 850, 752, 660, 608.



***tert*-Butyl chloro(2-hydroxyethyl)carbamate (3j):**

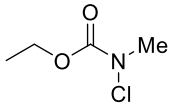
3j (8.2 mmol, 1.60 g, 82%) was prepared as a colorless. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (dd, *J* = 10.8, 5.4 Hz, 2H), 3.72 - 3.69 (m, 2H), 2.61 (t, *J* = 5.4 Hz, 1H), 1.46 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 83.4, 59.8, 56.4, 28.2 ppm. **HRMS** (ESI): Exact mass calculated for

$C_7H_{14}ClNNaO_3^+$ ([M+Na]$^+$): 218.0554, mass found: 218.0554. **FTIR** (neat): υ (cm^{-1}) 3415, 2978, 2934, 1697, 1455, 1430, 1367, 1339, 1253, 1147, 1056, 996, 932, 846, 751, 605.



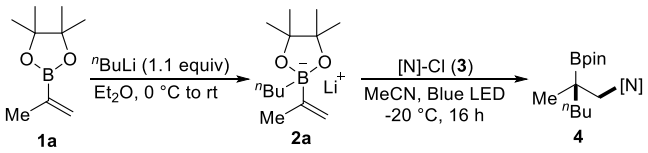
***tert*-Butyl chloro(2-chloroethyl)carbamate (3k):**

3k (15.0 mmol, 3.21 g, 90%) was prepared as a colorless. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.82 (t, *J* = 6.4 Hz, 2H), 3.64 (t, *J* = 6.4 Hz, 2H), 1.43 (s, 9H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 154.3, 83.5, 55.0, 40.1, 28.1 ppm. **HRMS** (ESI): Exact mass calculated for $C_7H_{13}Cl_2NNaO_2^+$ ([M+Na]$^+$): 236.0216, mass found: 236.0216. **FTIR** (neat): υ (cm^{-1}) 2978, 1697, 1366, 1241, 1143, 1063, 843, 749, 666.



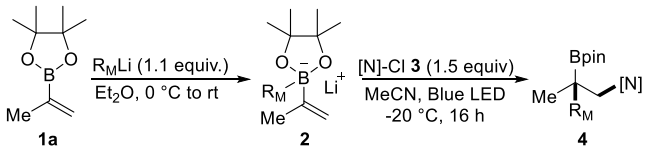
Ethyl chloro(methyl)carbamate (3l):

3l (10.5 mmol, 1.44 g, 73%) was prepared as a colorless. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.21 (q, *J* = 7.1 Hz, 2H), 3.30 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 156.8, 63.9, 42.8, 14.7 ppm. **HRMS** (ESI): Exact mass calculated for $C_4H_9ClNO_2^+$ ([M+Na]$^+$): 138.0316, mass found: 138.0314. **FTIR** (neat): υ (cm^{-1}) 2983, 1703, 1469, 1445, 1416, 1393, 1371, 1318, 1174, 1153, 1094, 1023, 969, 871, 754, 594.

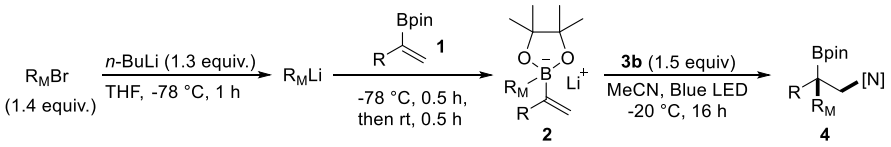


General Procedure A: Vinyl boronic ester **1a** (0.20 mmol, 1.0 equiv.) was dissolved in diethyl ether (2.0 mL) and *n*-butyllithium solution (0.22 mmol, 1.1 equiv.) was added dropwise over 5 minutes at 0 °C. The solution was then stirred for 0.5 h at 0 °C, warmed to room temperature and stirred for a further 0.5 h. Subsequently, the solvent was carefully removed *in vacuo* and the resulting residue was taken up in acetonitrile (4.0 mL). To this mixture, **3** (0.24 mmol, 1.2 equiv.) was added at -20 ºC. The reaction mixture was then irradiated with a 3 W blue LED

(465 nm) and stirred at -20 ºC for 16 h. The reaction mixture was filtered through a pad of silica and rinsed with 30 mL Et_2O. The organic solvent was removed under reduced pressure. Flash column chromatography eluting with pentane and Et_2O afforded the desired product. *Caution: In order to get a good yield, the chromatography should be finished within 10 min.*



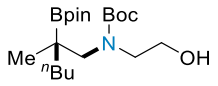
General Procedure B: Vinyl boronic ester **1a** (0.20 mmol, 1.0 equiv.) was dissolved in diethyl ether (2.0 mL) and the alkyl/aryllithium solution (0.22 mmol, 1.1 equiv.) was added dropwise over 5 minutes at 0 °C. The solution was then stirred for 0.5 h at 0 °C, warmed to room temperature and stirred for a further 0.5 h. Subsequently, the solvent was carefully removed *in vacuo* and the resulting residue was taken up in acetonitrile (4.0 mL). **3** (0.3 mmol, 1.5 equiv.) was dissolved in MeCN (1.0 mL) and then slowly added to the solution of the boronate-complex under irradiation with blue LED light (3W, 465 nm) at -20 °C. To ensure the solution of **3** was cooled down to -20°C before entering the reaction solution it was slowly added along the wall of the Schlenk tube. The reaction was then stirred under constant irradiation with blue LED light at -20°C for 16 h. The reaction mixture was filtered through a pad of silica and rinsed with 30 mL Et_2O. The organic solvent was removed under reduced pressure. Flash column chromatography eluting with pentane and Et_2O (or ethyl acetate) afforded the desired product. *Caution: In order to get a good yield, the chromatography should be finished within 10 min.*



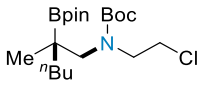
General Procedure C: To a solution of arylbromide (0.28 mmol, 1.4 equiv.) in THF (1.5 mL) at -78 °C was added a solution of *n*-butyllithium (1.6 M, 0.26 mmol, 1.3 equiv.) over a period of 5 minutes. The solution was then stirred for 1 h at -78 °C, at which point a solution of **1** (0.20 mmol, 1.0 equiv.) in THF (0.50 mL) was added dropwise. The solution was then stirred for 30

min at -78 °C, warmed to room temperature and stirred for a further 30 min. Subsequently, the solvent was carefully removed *in vacuo* and the resulting residue was taken up in acetonitrile (4.0 mL). **3b** (0.3 mmol, 1.5 equiv.) was dissolved in MeCN (1.0 mL) and then slowly added to the solution of the boronate-complex under irradiation with blue LED light (3W, 465 nm) at -20 °C. To ensure the solution of **3b** was cooled down to -20°C before entering the reaction solution it was slowly added along the wall of the Schlenk tube. The reaction was then stirred under constant irradiation with blue LED light at -20°C for 16 h. The reaction mixture was filtered through a pad of silica and rinsed with 30 mL Et_2O. The organic solvent was removed under reduced pressure. Flash column chromatography eluting with pentane and Et_2O (or ethyl acetate) afforded the desired product. *Caution: In order to get a good yield, the chromatography should be finished within 10 min.*

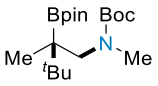
Unsuccessful examples:



<5% yield
with **1a**, ^{n}BuLi and **3j**

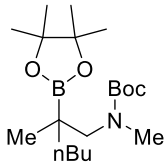


<5% yield
with **1a**, ^{n}BuLi and **3k**



traces
with **1a**, ^{t}BuLi and **3a**

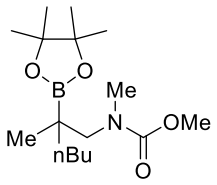
Reactions were carried out according to the general procedure B.



***tert*-Butyl methyl(2-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)carbamate (4a):**

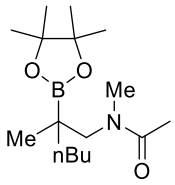
According to the General Procedure A, **4a** (60.6 mg, 85%) was prepared as a colorless oil after purification by flash chromatography (pentane/Et_2O = 5:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.21(minor) & 3.18 (major) (d, *J* = 13.8 Hz, 1H), 3.06 (major) & 3.03 (minor) (d, *J* = 13.8 Hz, 1H), 2.74 (s, 3H), 1.34 (s, 9H), 1.31 – 0.98 (m, 6H), 1.15 (major) & 1.14 (minor) (s, 12H), 0.86 – 0.74 (m, 6H). Multiple signals due to rotamers. ^{13}C NMR (101 MHz, CD_2Cl_2) δ 156.2, 83.2, 83.1, 78.7, 78.5, 56.1, 56.0, 37.6, 37.6, 36.4, 35.7, 35.7, 28.1, 27.9, 24.8, 24.6, 23.7, 19.2, 13.8 ppm, *the carbon attached to boron not observed*. Multiple signals due to rotamers. ^{11}B NMR

(128 MHz, CD_2Cl_2) δ 34.2 ppm. **HRMS** (ESI): Exact mass calculated for $C_{19}H_{38}BNNaO_4^+$ ($[M+Na]^+$): 378.2786, mass found: 378.2782. **FTIR** (neat): υ (cm^{-1}) 2975, 2930, 1694, 1389, 1371, 1310, 1161, 1139, 852.



Methyl methyl(2-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)carbamate (4b):

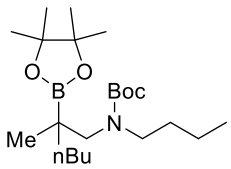
According to the General Procedure B, **4b** (52.1 mg, 83%) was prepared as a colorless oil after purification by flash chromatography (pentane/Et_2O = 3:1). ^1H NMR (400 MHz, CD_2Cl_2) δ 3.54 (s, 3H), 3.24 (minor) & 3.20 (major) (d, *J* = 13.8 Hz, 1H), 3.10 (major) & 3.07 (minor) (d, *J* = 13.8 Hz, 1H), 2.80 (s, 3H), 1.36 – 1.10 (m, 6H), 1.15 (major) & 1.15 (minor) (s, 12H), 0.84 – 0.77 (m, 6H). Multiple signals due to rotamers. ^{13}C NMR (101 MHz, CD_2Cl_2) δ 157.4, 83.2, 57.0, 55.8, 52.2, 52.0, 37.6, 36.5, 36.2, 27.9, 24.8, 24.6, 23.7, 19.4, 13.8, 0.8 ppm, *the carbon attached to boron not observed*. Multiple signals due to rotamers. ^{11}B NMR (128 MHz, CD_2Cl_2) δ 34.0 ppm. **HRMS** (ESI): Exact mass calculated for $C_{16}H_{32}BNNaO_4^+$ ($[M+Na]^+$): 336.2317, mass found: 336.2317. **FTIR** (neat): υ (cm^{-1}) 2977, 2957, 2933, 2871, 1705, 1485, 1388, 1371, 1312, 1216, 1191, 1169, 1140, 968, 852, 772, 668.



***N*-Methyl-*N*-(2-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)acetamide (4c):**

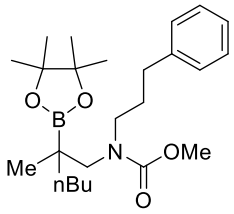
According to the General Procedure B, **4c** (38.0 mg, 64%) was prepared as a colorless oil after purification by flash chromatography (pentane/ethyl acetate = 1:2). ^1H NMR (400 MHz, CD_2Cl_2) δ 3.29 (major) & 3.27 (minor) (d, *J* = 13.9 Hz, 1H), 3.09 (minor) & 3.04 (major) (d, *J* = 13.9 Hz, 1H), 2.91 (major) & 2.78 (minor) (s, 3H), 1.99 (minor) & 1.94 (major) (s, 3H), 1.40

– 1.06 (m, 6H), 1.15 (minor) & 1.14 (major) (d, J = 4.6 Hz, 12H), 0.86 – 0.74 (m, 6H). Multiple signals due to rotamers. ^{13}C NMR (101 MHz, CD_2Cl_2) δ 170.8, 170.7, 83.5, 82.7, 58.6, 56.0, 38.4, 37.6, 34.3, 27.8, 27.7, 25.0, 24.9, 24.6, 23.7, 23.6, 21.8, 21.8, 19.5, 19.5, 13.9, 13.8, 0.8 ppm, *the carbon attached to boron not observed*. Multiple signals due to rotamers. ^{11}B NMR (128 MHz, CD_2Cl_2) δ 34.4, 31.9 ppm. Multiple signals due to rotamers. **HRMS** (ESI): Exact mass calculated for $C_{16}H_{32}BNNaO_3^+$ ([M+Na]$^+$): 320.2367, mass found: 320.2370. **FTIR** (neat): υ (cm^{-1}) 2959, 2930, 2872, 1650, 1468, 1389, 1372, 1314, 1214, 1141, 1111, 1020, 968, 852.



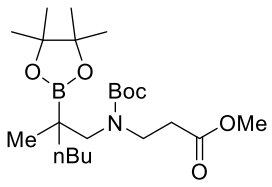
***tert*-Butyl butyl(2-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)carbamate (4d):**

According to the General Procedure A, **4d** (65.0 mg, 82%) was prepared as a colorless oil after purification by flash chromatography (pentane/Et_2O = 7:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.26 – 2.87 (m, 4H), 1.63 – 1.62 (m, 0.35H), 1.44 – 1.36 (m, 2.65H), 1.33 (s, 9H), 1.24 – 1.01 (m, 7H), 1.15 (minor) & 1.14 (major) (d, J = 2.5 Hz, 12H), 0.86 – 0.74 (m, 9H). Multiple signals due to rotamers. ^{13}C NMR (101 MHz, CD_2Cl_2) δ 156.0, 83.0, 78.4, 48.2, 46.9, 37.8, 31.9, 30.3, 29.7, 29.6, 29.4, 28.2, 28.0, 27.8, 27.8, 24.9, 24.7, 23.7, 20.0, 19.4, 13.8, 13.7, 0.8 ppm, *the carbon attached to boron not observed*. Multiple signals due to rotamers. ^{11}B NMR (128 MHz, CD_2Cl_2) δ 33.6 ppm. **HRMS** (ESI): Exact mass calculated for $C_{22}H_{44}BNNaO_4^+$ ([M+Na]$^+$): 420.3256, mass found: 420.3260. **FTIR** (neat): υ (cm^{-1}) 2978, 2929, 2859, 1468, 1371, 1305, 1272, 1145, 968, 855. 2960, 2930, 1692, 1368, 1310, 1139, 852.



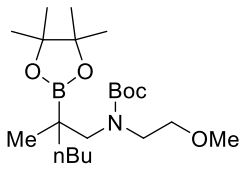
Methyl (2-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)(3-phenylpropyl) carbamate (4e):

According to the General Procedure B, **4e** (48.7 mg, 58%) was prepared as a colorless oil after purification by flash chromatography (pentane/Et_2O = 4:1). ^1H NMR (400 MHz, CD_2Cl_2) δ 7.23 – 7.16 (m, 2H), 7.13 – 7.08 (m, 3H), 3.54 (s, 3H), 3.18 – 3.07 (m, 3H), 2.55 – 2.44 (m, 2H), 1.83 – 1.74 (m, 2H), 1.37 – 1.28 (m, 1H), 1.24 – 1.05 (m, 6H), 1.15 (s, 6H), 1.14 (s, 6H) 0.84 – 0.78 (m, 6H). Multiple signals due to rotamers. ^{13}C NMR (101 MHz, CD_2Cl_2) δ 157.3, 142.0, 129.7, 129.3, 128.3, 128.2, 127.3, 126.8, 125.7, 83.2, 54.7, 52.0, 48.0, 37.7, 33.0, 30.8, 29.7, 28.0, 24.9, 24.7, 23.7, 19.6, 13.8, 0.8 ppm, *the carbon attached to boron not observed*. Multiple signals due to rotamers. ^{11}B NMR (128 MHz, CD_2Cl_2) δ 33.8 ppm. **HRMS** (ESI): Exact mass calculated for $C_{24}H_{40}BNNaO_4^+$ ($[M+Na]^+$): 440.2943, mass found: 440.2947. **FTIR** (neat): υ (cm^{-1}) 2956, 2931, 2862, 1702, 1468, 1438, 1389, 1371, 1313, 1140, 968, 852, 699.



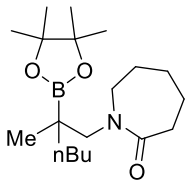
Methyl 3-((*tert*-butoxycarbonyl)(2-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)amino)propanoate (4f):

According to the General Procedure B, **4f** (49.4 mg, 58%) was prepared as a colorless oil after purification by flash chromatography (pentane/Et_2O = 5:1). ^1H NMR (400 MHz, CD_2Cl_2) δ 3.55 (s, 3H), 3.51 – 3.03 (m, 4H), 2.47 (t, J = 7.5 Hz, 2H), 1.34 (s, 9H), 1.32 – 1.06 (m, 6H), 1.14 & 1.14 (s, 12H), 0.82 – 0.78 (m, 6H). Multiple signals due to rotamers. ^{13}C NMR (101 MHz, CD_2Cl_2) δ 172.2, 155.7, 83.2, 79.1, 60.2, 54.4, 51.3, 44.5, 43.7, 37.7, 33.1, 32.1, 28.1, 27.9, 27.7, 27.7, 24.9, 24.6, 23.7, 19.4, 14.0, 13.8, 0.8 ppm, *the carbon attached to boron not observed*. Multiple signals due to rotamers. ^{11}B NMR (128 MHz, CD_2Cl_2) δ 33.9 ppm. **HRMS** (ESI): Exact mass calculated for $C_{22}H_{42}BNNaO_6^+$ ($[M+Na]^+$): 450.2997, mass found: 450.2998. **FTIR** (neat): υ (cm^{-1}) 2974, 2930, 1739, 1692, 1460, 1437, 1413, 1366, 1312, 1251, 1162, 1136, 1046, 969, 909, 851, 775, 703, 670, 580.



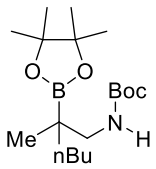
***tert*-Butyl (2-methoxyethyl)(2-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)carbamate (4g):**

According to the General Procedure B, **4g** (16.2 mg, 20%) was prepared as a colorless oil after purification by flash chromatography (pentane/Et_2O = 5:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.42 – 3.19 (m, 4H), 3.22 (s, 3H), 3.19 – 3.06 (m, 2H), 1.34 (s, 9H), 1.31 – 1.04 (m, 6H), 1.15 & 1.14 (s, 12H), 0.82 – 0.77 (m, 6H). Multiple signals due to rotamers. ^{13}C NMR (101 MHz, CD_2Cl_2) δ 155.8, 83.2, 83.1, 79.0, 78.8, 70.7, 70.0, 58.5, 55.0, 54.2, 47.9, 46.7, 37.8, 37.7, 28.1, 28.0, 27.8, 27.7, 24.9, 24.7, 23.7, 19.4, 13.8, 0.8 ppm, *the carbon attached to boron not observed*. Multiple signals due to rotamers. ^{11}B NMR (128 MHz, CD_2Cl_2) δ 33.8 ppm. **HRMS** (ESI): Exact mass calculated for $C_{21}H_{42}BNNaO_5^+$ ([M+Na]$^+$): 422.3048, mass found: 422.3047. **FTIR** (neat): υ (cm^{-1}) 2974, 2929, 1692, 1460, 1409, 1388, 1365, 1310, 1252, 1214, 1159, 1138, 1119, 1010, 969, 851, 774, 669, 580.



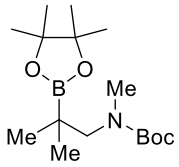
1-(2-Methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)azepan-2-one (4h):

According to the General Procedure B, **4h** (48.0 mg, 71%) was prepared as a colorless oil after purification by flash chromatography (pentane/ethyl acetate = 1:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.35 – 3.26 (m, 2H), 3.23 (d, *J* = 13.3 Hz, 1H), 3.07 (d, *J* = 13.3 Hz, 1H), 2.45 – 2.34 (m, 2H), 1.66 – 1.52 (m, 6H), 1.35 – 1.27 (m, 1H), 1.22 – 1.03 (m, 5H), 1.12 (s, 12H), 0.82 – 0.79 (m, 3H), 0.75 (s, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 178.0, 84.2, 59.4, 53.7, 39.1, 39.0, 31.8, 29.9, 29.3, 27.1, 27.0, 25.7, 25.2, 21.6, 15.8, 2.7 ppm, *the carbon attached to boron not observed*. ^{11}B NMR (128 MHz, CD_2Cl_2) δ 30.4 ppm. **HRMS** (ESI): Exact mass calculated for $C_{19}H_{36}BNNaO_3^+$ ([M+Na]$^+$): 360.2680, mass found: 360.2683. **FTIR** (neat): υ (cm^{-1}) 2957, 2927, 2859, 1646, 1617, 1459, 1371, 1354, 1313, 1195, 1141, 1110, 1078, 975, 854, 689.



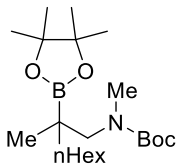
***tert*-Butyl (2-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)carbamate (4i):**

According to the General Procedure B, **4i** (37.4 mg, 55%) was prepared as a colorless oil after purification by flash chromatography (pentane/Et_2O = 5:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 4.73 (brs, 1H), 3.00 (dd, *J* = 13.2, 6.2 Hz, 1H), 2.87 (dd, *J* = 13.2, 6.2 Hz, 1H), 1.33 (s, 9H), 1.29 – 1.10 (m, 6H), 1.15 (s, 12H), 0.84 – 0.78 (m, 6H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 155.9, 83.3, 78.2, 47.8, 36.4, 28.1, 27.8, 24.5, 24.5, 23.6, 19.8, 13.8 ppm, *the carbon attached to boron not observed*. ^{11}B NMR (128 MHz, CD_2Cl_2) δ 34.0 ppm. **HRMS** (ESI): Exact mass calculated for $C_{18}H_{36}BNNaO_4^+$ ([M+Na]$^+$): 364.2630, mass found: 364.2631. **FTIR** (neat): υ (cm^{-1}) 2977, 2930, 1726, 1712, 1311, 1254, 1170, 1140, 852.



***tert*-Butyl methyl(2-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)carbamate (4j):**

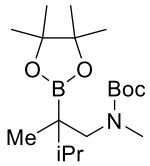
According to the General Procedure B, **4j** (47.2 mg, 75%) was prepared as a colorless oil after purification by flash chromatography (pentane/Et_2O = 5:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.09 (d, *J* = 19.9 Hz, 2H), 2.75 (s, 3H), 1.35 (s, 9H), 1.14 (s, 12H), 0.82 (s, 6H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 156.1, 83.2, 83.0, 78.8, 78.5, 57.3, 57.0, 36.2, 35.6, 28.1, 24.5, 22.7 ppm, *the carbon attached to boron not observed*. Multiple signals due to rotamers.^{11}B NMR (128 MHz, CD_2Cl_2) δ 34.0 ppm. **HRMS** (ESI): Exact mass calculated for $C_{16}H_{32}BNNaO_4^+$ ([M+Na]$^+$): 336.2317, mass found: 336.2318. **FTIR** (neat): υ (cm^{-1}) 2936, 2869, 1692, 1474, 1457, 1389, 1365, 1309, 1162, 1136, 969, 881, 849.



***tert*-Butyl methyl(2-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-**

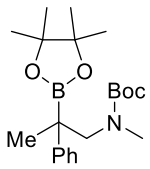
yl)octyl)carbamate (4k):

According to the General Procedure B, **4k** (52.4 mg, 68%) was prepared as a light-yellow oil after purification by flash chromatography (pentane/Et_2O = 7:1). ^1H NMR (400 MHz, CD_2Cl_2) δ 3.26 – 3.10 (m, 1H), 3.03 (d, *J* = 13.9 Hz, 1H), 2.74 (s, 3H), 1.34 (s, 9H), 1.25 – 1.03 (m, 10H), 1.14 (minor) & 1.14 (major) (s, 12H), 0.82 – 0.77 (m, 6H). Multiple signals due to rotamers. ^{13}C NMR (101 MHz, CD_2Cl_2) δ 156.3, 83.4, 83.3, 78.9, 78.6, 56.3, 56.2, 38.2, 38.1, 36.5, 35.9, 31.9, 30.5, 28.3, 25.8, 25.0, 24.8, 22.8, 19.4, 14.0 ppm, *the carbon attached to boron not observed*. Multiple signals due to rotamers.^{11}B NMR (128 MHz, CD_2Cl_2) δ 34.0 ppm. **HRMS** (ESI): Exact mass calculated for $C_{21}H_{42}BNNaO_4^+$ ($[M+Na]^+$): 406.3099, mass found: 406.3098. **FTIR** (neat): υ (cm^{-1}) 2976, 2928, 2858, 1695, 1457, 1388, 1365, 1309, 1159, 1139, 852.



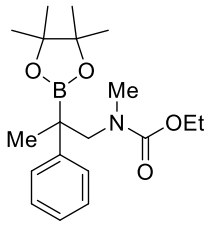
***tert*-butyl (2,3-dimethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)(methyl)carbamate (4l):**

According to the General Procedure B, **4l** (12.1 mg, 18%) was prepared as a colorless oil after purification by flash chromatography (pentane/Et_2O = 7:1). ^1H NMR (400 MHz, CD_2Cl_2) δ 3.45 & 3.31 (d, *J* = 12.6 Hz, 1H), 3.11 – 2.92 (m, 1H), 2.73 (major) & 2.70 (minor) (s, 3H), 1.54 – 1.49 (m, 1H), 1.34 (s, 9H), 1.15 & 1.15 (s, 12H), 0.82 (dd, *J* = 13.9, 6.9 Hz, 6H), 0.74 (s, 3H). Multiple signals due to rotamers. ^{13}C NMR (101 MHz, CD_2Cl_2) δ 156.2, 83.2, 78.8, 35.2, 34.2, 28.2, 28.1, 27.9, 25.1, 24.8, 24.6, 24.4, 21.6, 19.0, 18.1, 15.6, 15.6, 0.8 ppm, *the carbon attached to boron not observed*. Multiple signals due to rotamers. ^{11}B NMR (128 MHz, CD_2Cl_2) δ 34.0 ppm. **HRMS** (ESI): Exact mass calculated for $C_{18}H_{36}BNNaO_4^+$ ($[M+Na]^+$): 364.2630, mass found: 364.2631. **FTIR** (neat): υ (cm^{-1}) 2975, 1693, 1453, 1389, 1365, 1306, 1160, 1138, 1046, 968, 884, 855, 771, 669.



***tert*-butyl methyl(2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)carbamate (4m):**

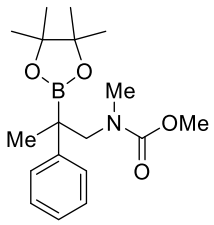
According to the General Procedure B, **4m** (51.6 mg, 69%) was prepared as a colorless oil after purification by flash chromatography (pentane/Et_2O = 10:1). ^1H NMR (400 MHz, CD_2Cl_2) δ 7.25 – 7.15 (m, 4H), 7.13 – 7.03 (m, 1H), 3.80 & 3.72 (d, *J* = 14.1 Hz, 1H), 3.43 – 3.21 (m, 1H), 2.40 (major) & 2.34 (minor) (s, 3H), 1.32 – 1.22 (m, 12H), 1.12 (minor) & 1.10 (major) (s, 12H). Multiple signals due to rotamers. ^{13}C NMR (101 MHz, CD_2Cl_2) δ 156.2, 156.0, 145.5, 145.1, 128.1, 128.0, 127.2, 125.5, 125.4, 83.6, 83.5, 78.8, 78.6, 57.0, 56.6, 36.0, 35.6, 28.1, 28.0, 27.8, 24.4, 24.2, 17.8, 17.6 ppm, *the carbon attached to boron not observed*. Multiple signals due to rotamers. ^{11}B NMR (128 MHz, CD_2Cl_2) δ 33.1 ppm. **HRMS** (ESI): Exact mass calculated for $C_{21}H_{34}BNNaO_4^+$ ($[M+Na]^+$): 398.2473, mass found: 398.2476. **FTIR** (neat): υ (cm^{-1}) 2975, 2931, 1691, 1599, 1481, 1453, 1380, 1364, 1312, 1271, 1212, 1136, 1103, 1048, 1028, 967, 921, 881, 853, 839, 770, 700, 680, 631.



Ethyl methyl(2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)carbamate (4n):

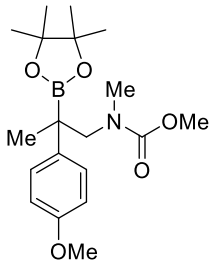
According to the General Procedure B, **4n** (50.1 mg, 72%) was prepared as a colorless oil after purification by flash chromatography (pentane/Et_2O = 3:1). ^1H NMR (400 MHz, CD_2Cl_2) δ 7.25 – 7.19 (m, 4H), 7.14 – 7.05 (m, 1H), 4.04 – 3.69 (m, 3H), 3.44 – 3.33 (m, 1H), 2.48 (major) & 2.40 (minor) (s, 3H), 1.27 (s, 3H), 1.15 (minor) & 1.13 (major) (s, 12H), 1.09 – 1.03 (m, 3H). Multiple signals due to rotamers. ^{13}C NMR (101 MHz, CD_2Cl_2) δ 157.1, 156.9, 145.3, 145.0, 128.1, 127.2, 125.5, 83.6, 60.9, 57.2, 56.8, 36.1, 35.6, 24.4, 24.2, 17.7, 14.4 ppm, *the carbon attached to boron not observed*. Multiple signals due to rotamers.^{11}B NMR (128 MHz, CD_2Cl_2)

δ 33.3 ppm. **HRMS** (ESI): Exact mass calculated for $C_{19}H_{30}BNNaO_4^+$ ([M+Na]$^+$): 370.2160, mass found: 370.2164. **FTIR** (neat): υ (cm^{-1}) 2977, 2934, 1700, 1457, 1381, 1372, 1319, 1142, 770, 701.



Methyl methyl(2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)carbamate (4o):

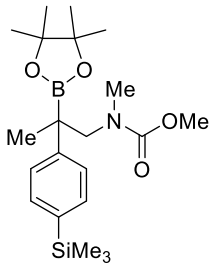
According to the General Procedure B, **4o** (48.8 mg, 73%) was prepared as a colorless oil after purification by flash chromatography (pentane/Et_2O = 3:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.26 – 7.18 (m, 4H), 7.13 – 7.07 (m, 1H), 3.89 (d, *J* = 13.8 Hz, 0.5H), 3.73 (d, *J* = 14.4 Hz, 0.5H), 3.53 – 3.30 (m, 4H), 2.48 (s, 1.5H), 2.38 (s, 1.5H), 1.26 (s, 3H), 1.15 (minor) & 1.13 (major) (s, 12H). Multiple signals due to rotamers. ^{13}C NMR (101 MHz, CD_2Cl_2) δ 157.6, 157.3, 145.2, 145.0, 128.1, 127.2, 125.5, 83.6, 57.3, 56.9, 52.2, 52.0, 36.3, 35.6, 24.4, 24.2, 17.6, 0.8 ppm, *the carbon attached to boron not observed*. Multiple signals due to rotamers.^{11}B NMR (128 MHz, CD_2Cl_2) δ 33.3 ppm. **HRMS** (ESI): Exact mass calculated for $C_{18}H_{28}BNNaO_4^+$ ([M+Na]$^+$): 356.2004, mass found: 356.2005. **FTIR** (neat): υ (cm^{-1}) 2978, 2940, 1701, 1458, 1381, 1372, 1317, 1203, 1141, 1104, 1068, 968, 771, 701.



Methyl (2-(4-methoxyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)(methyl) carbamate (4p):

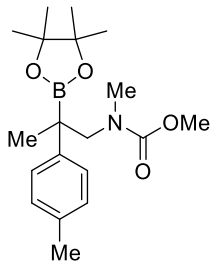
According to the General Procedure C, **4p** (22.1 mg, 30%) was prepared as a colorless oil after purification by flash chromatography (pentane/Et_2O = 3:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ

7.17 – 7.10 (m, 2H), 6.79 – 6.73 (m, 2H), 3.87 – 3.77 (m, 0.5H), 3.73 – 3.66 (m, 0.5H), 3.70 (s, 3H), 3.53 (s, 1.5H), 3.41 (s, 1.5H), 3.39 – 3.28 (m, 1H), 2.47 (s, 1.5H), 2.39 (s, 1.5H), 1.22 (s, 3H), 1.14 (minor) & 1.12 (major) (s, 12H). Multiple signals due to rotamers. ^{13}C NMR (101 MHz, CD_2Cl_2) δ 157.8, 137.1, 136.8, 128.2, 113.6, 83.7, 57.5, 57.0, 55.2, 52.4, 52.1, 36.4, 35.8, 24.6, 24.4, 18.0, 0.9 ppm, *the carbon attached to boron not observed*. Multiple signals due to rotamers.^{11}B NMR (128 MHz, CD_2Cl_2) δ 33.3, 22.5 ppm. Multiple signals due to rotamers. **HRMS** (ESI): Exact mass calculated for $C_{19}H_{30}BNNaO_5^+$ ([M+Na]$^+$): 386.2109, mass found: 386.2110. **FTIR** (neat): υ (cm^{-1}) 2978, 1702, 1512, 1457, 1308, 1250, 1142, 1034, 968, 848.



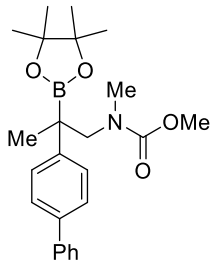
Methyl methyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(4-(trimethylsilyl)phenyl) propyl)carbamate (4q):

According to the General Procedure C, **4q** (44.3 mg, 55%) was prepared as a colorless oil after purification by flash chromatography (pentane/Et_2O = 3:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.38 (d, *J* = 8.2 Hz, 2H), 7.25 -7.15 (m, 2H), 3.87 (minor) & 3.67 (major) (d, *J* = 13.3 Hz, 1H), 3.58 – 3.28 (m, 4H), 2.52 (major) & 2.39 (minor) (s, 3H), 1.26 (s, 3H), 1.15 (minor) & 1.14 (major) (s, 12H), 0.18 (s, 9H). Multiple signals due to rotamers. ^{13}C NMR (101 MHz, CD_2Cl_2) δ 159.9, 159.6, 148.2, 147.9, 139.4, 135.5, 128.9, 86.0, 59.6, 59.3, 54.6, 54.2, 38.7, 38.0, 30.1, 26.8, 26.6, 20.0, 3.1, 1.2, 0.9, 0.6 ppm, *the carbon attached to boron not observed*. Multiple signals due to rotamers.^{11}B NMR (128 MHz, CD_2Cl_2) δ 33.3 ppm. **HRMS** (ESI): Exact mass calculated for $C_{21}H_{36}BNNaO_4Si^+$ ([M+Na]$^+$): 428.2399, mass found: 428.2403. **FTIR** (neat): υ (cm^{-1}) 2978, 2957, 1705, 1457, 1390, 1320, 1306, 1249, 1199, 1142, 1112, 968, 838.



Methyl methyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(p-tolyl)propyl)carbamate (4r):

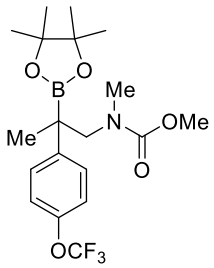
According to the General Procedure C, **4r** (29.1 mg, 42%) was prepared as a colorless oil after purification by flash chromatography (pentane/Et_2O = 3:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.14 – 7.07 (m, 2H), 7.05 – 7.02 (m, 2H), 3.85 (minor) & 3.70 (major) (d, *J* = 14.0 Hz, 1H), 3.53 (minor) & 3.40 (major) (s, 3H), 3.33 – 3.28 (m, 1H), 2.47 (major) & 2.39 (minor) (s, 3H), 2.23 (s, 3H), 1.23 (s, 3H), 1.14 (minor) & 1.12 (major) (s, 12H). Multiple signals due to rotamers. ^{13}C NMR (101 MHz, CD_2Cl_2) δ 157.6, 157.3, 142.0, 141.8, 135.1, 135.0, 128.8, 126.9, 83.6, 57.3, 56.9, 52.2, 51.9, 36.2, 35.7, 24.4, 24.2, 20.6, 17.7, 0.8 ppm, *the carbon attached to boron not observed*. Multiple signals due to rotamers.^{11}B NMR (128 MHz, CD_2Cl_2) δ 33.2 ppm. **HRMS** (ESI): Exact mass calculated for $C_{19}H_{30}BNNaO_4^+$ ([M+Na]$^+$): 370.2160, mass found: 370.2162. **FTIR** (neat): υ (cm^{-1}) 2977, 2932, 2883, 1702, 1461, 1321, 1309, 1140, 967, 847, 772, 670.



Methyl (2-([1,1'-biphenyl]-4-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl) (methyl)carbamate (4s):

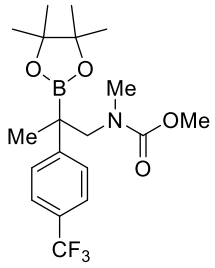
According to the General Procedure C, **4s** (32.8 mg, 40%) was prepared as a colorless sticky oil after purification by flash chromatography (pentane/Et_2O = 3:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.55 (d, *J* = 7.3 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.40 – 7.23 (m, 5H), 3.92 (minor) & 3.74 (major) (d, *J* = 13.9 Hz, 1H), 3.60 – 3.34 (m, 4H), 2.55 (major) & 2.44 (minor) (s, 3H),

1.31 (s, 3H), 1.17 (minor) & 1.15 (major) (s, 12H). Multiple signals due to rotamers. ^{13}C NMR (101 MHz, CD_2Cl_2) δ 157.7, 157.4, 144.6, 144.3, 140.9, 138.4, 131.9, 128.8, 127.7, 127.2, 126.9, 126.8, 83.8, 57.4, 57.0, 52.4, 52.1, 36.5, 35.9, 32.1, 30.2, 27.9, 24.6, 24.4, 17.9, 0.9 ppm, *the carbon attached to boron not observed*. Multiple signals due to rotamers.^{11}B NMR (128 MHz, CD_2Cl_2) δ 33.1 ppm. **HRMS** (ESI): Exact mass calculated for $C_{24}H_{32}BNNaO_4^+$ ($[M+Na]^+$): 432.2317, mass found: 432.2315. **FTIR** (neat): υ (cm^{-1}) 2978, 2936, 1700, 1486, 1457, 1380, 1322, 1197, 1166, 1140, 1095, 967, 848, 766, 738, 698, 667.



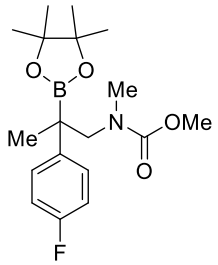
Methyl methyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(4-(trifluoromethoxy) phenyl)propyl)carbamate (4t):

According to the General Procedure C, **4t** (70.3 mg, 84%) was prepared as a colorless oil after purification by flash chromatography (pentane/Et_2O = 3:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.34 – 7.20 (m, 2H), 7.13 – 7.02 (m, 2H), 3.82 (minor) & 3.64 (major) (d, *J* = 13.8 Hz, 1H), 3.57 – 3.27 (m, 4H),2.57 (major) & 2.44 (minor) (s, 3H), 1.28 (s, 3H), 1.15 (minor) & 1.14 (major) (s, 12H). Multiple signals due to rotamers. ^{13}C NMR (101 MHz, CD_2Cl_2) δ 157.5, 157.2, 147.2, 147.2, 144.2, 143.9, 128.6, 120.6 (q, *J* = 256.1 Hz), 120.4, 83.8, 57.4, 57.0, 52.3, 51.8, 36.5, 35.74, 32.0, 24.4, 24.2, 18.1, 0.8 ppm, *the carbon attached to boron not observed*. Multiple signals due to rotamers.^{11}B NMR (128 MHz, CD_2Cl_2) δ 33.2 ppm. ^{19}F NMR (377 MHz, CD_2Cl_2) δ -58.3 ppm. **HRMS** (ESI): Exact mass calculated for $C_{19}H_{27}BF_3NNaO_5^+$ ($[M+Na]^+$): 440.1827, mass found: 440.1826. **FTIR** (neat): υ (cm^{-1}) 2981, 1703, 1508, 1462, 1382, 1326, 1258, 1209, 1161, 1141, 967, 852, 772, 668.



Methyl methyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(4-(trifluoromethyl)phenyl) propyl)carbamate (4u):

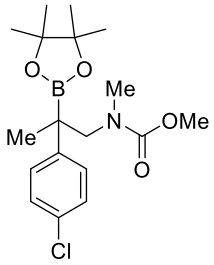
According to the General Procedure C, **4u** (68.5 mg, 85%) was prepared as a colorless oil after purification by flash chromatography (pentane/Et_2O = 3:1). ^1H NMR (400 MHz, CD_2Cl_2) δ 7.49 (d, *J* = 8.3 Hz, 2H), 7.43 – 7.32 (m, 2H), 3.88 & 3.70 (d, *J* = 13.5 Hz, 1H), 3.60 – 3.22 (m, 4H), 2.55 & 2.44 (s, 3H), 1.31 (s, 3H), 1.15 & 1.13 (s, 12H). Multiple signals due to rotamers. ^{13}C NMR (101 MHz, CD_2Cl_2) {^{19}F}: δ 157.5, 157.1, 149.9, 149.6, 128.0, 127.7, 127.4, 127.1, 124.8, 124.8, 124.5 (q, *J* = 271.6 Hz), 83.9, 57.3, 56.9, 52.3, 51.9, 36.5, 35.8, 30.1, 29.7, 24.4, 24.2, 17.8, 0.8 ppm, *the carbon attached to boron not observed*. Multiple signals due to rotamers.^{11}B NMR (128 MHz, CD_2Cl_2) δ 33.1 ppm. ^{19}F NMR (377 MHz, CD_2Cl_2) δ -62.6, -62.6 ppm. Multiple signals due to rotamers. **HRMS** (ESI): Exact mass calculated for $C_{19}H_{27}BF_3NNaO_4^+$ ([M+Na]$^+$): 424.1877, mass found: 424.1876. **FTIR** (neat): υ (cm^{-1}) 2981, 1701, 1457, 1373, 1323, 1206, 1163, 1140, 1119, 1074, 1016, 967, 849, 772, 692.



Methyl (2-(4-fluorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)(methyl) carbamate (4v):

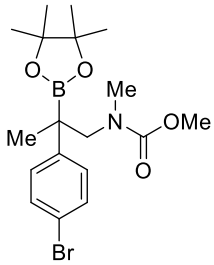
According to the General Procedure C, **4v** (57.7 mg, 82%) was prepared as a colorless oil after purification by flash chromatography (pentane/Et_2O = 3:1). ^1H NMR (400 MHz, CD_2Cl_2) δ 7.25 – 7.15 (m, 2H), 6.95 – 6.90 (m, 2H), 3.82 & 3.67 (d, *J* = 14.1 Hz, 1H), 3.56 – 3.31 (m, 4H), 2.51 & 2.42 (s, 3H), 1.25 (s, 3H), 1.14 & 1.12 (s, 12H). Multiple signals due to rotamers.

^{13}C NMR (101 MHz, CD_2Cl_2) {^{19}F}: δ 162.3, 159.9, 157.5, 157.2, 140.9, 140.6, 128.7, 128.6, 114.8, 114.6, 83.7, 65.7, 57.4, 57.0, 52.3, 52.0, 36.4, 35.8, 30.1, 29.7, 24.4, 24.2, 18.0, 15.1, 0.8 ppm, *the carbon attached to boron not observed*. Multiple signals due to rotamers.^{11}B NMR (128 MHz, CD_2Cl_2) δ 33.2 ppm. ^{19}F NMR (377 MHz, CD_2Cl_2) δ -118.8, -118.9 ppm. Multiple signals due to rotamers. **HRMS** (ESI): Exact mass calculated for $C_{18}H_{27}BFNNaO_4^+$ ([M+Na]$^+$): 374.1909, mass found: 374.1913. **FTIR** (neat): υ (cm^{-1}) 2977, 2939, 1701, 1508, 1460, 1381, 1320, 1303, 1224, 1202, 1164, 1140, 1109, 967, 850, 772.



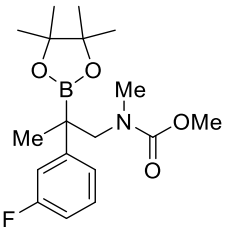
Methyl (2-(4-chlorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)(methyl) carbamate (4w):

According to the General Procedure C, **4w** (53.4 mg, 73%) was prepared as a colorless oil after purification by flash chromatography (pentane/Et_2O = 3:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.20 (s, 4H), 3.83 & 3.68 (d, *J* = 13.7 Hz, 1H), 3.59 – 3.29 (m, 4H), 2.52 & 2.43 (s, 3H), 1.25 (s, 3H), 1.14 & 1.12 (s, 12H). Multiple signals due to rotamers. ^{13}C NMR (101 MHz, CD_2Cl_2): δ 157.5, 157.2, 143.9, 143.6, 131.2, 128.7, 128.1, 83.8, 65.7, 57.3, 56.8, 52.3, 52.0, 36.4, 35.8, 24.4, 24.2, 17.8, 0.8 ppm, *the carbon attached to boron not observed*. Multiple signals due to rotamers.^{11}B NMR (128 MHz, CD_2Cl_2): δ 33.1 ppm. **HRMS** (ESI): Exact mass calculated for $C_{18}H_{27}BClNNaO_4^+$ ([M+Na]$^+$): 390.1614, mass found: 390.1618. **FTIR** (neat): υ (cm^{-1}) 2978, 1703, 1491, 1462, 1381, 1372, 1322, 1302, 1204, 1167, 1141, 1096, 1012, 967, 772.



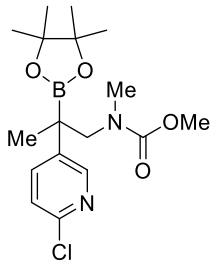
Methyl (2-(4-bromophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)(methyl) carbamate (4x):

According to the General Procedure C, **4x** (59.5 mg, 72%) was prepared as a colorless oil after purification by flash chromatography (pentane/Et_2O = 3:1). ^1H NMR (400 MHz, CD_2Cl_2) δ 7.38 – 7.30 (m, 2H), 7.17 – 7.08 (m, 2H), 3.83 & 3.67 (d, *J* = 14.0 Hz, 1H), 3.57 – 3.33 (m, 4H), 2.52 & 2.43 (s, 3H), 1.24 (s, 3H), 1.14 (minor) & 1.12 (major) (s, 12H). Multiple signals due to rotamers. ^{13}C NMR (101 MHz, CD_2Cl_2): δ 157.5, 157.2, 144.5, 144.2, 131.0, 129.1, 119.4, 83.8, 65.7, 57.2, 56.8, 52.3, 52.0, 36.4, 35.8, 31.9, 30.1, 27.8, 24.4, 24.2, 17.7, 15.1, 0.8 ppm, *the carbon attached to boron not observed*. Multiple signals due to rotamers.^{11}B NMR (128 MHz, CD_2Cl_2): δ 33.0 ppm. **HRMS** (ESI): Exact mass calculated for $C_{18}H_{27}BBrNNaO_4^+$ ($[M+Na]^+$): 434.1109, mass found: 434.1107. **FTIR** (neat): υ (cm^{-1}) 2976, 2935, 1701, 1487, 1460, 1381, 1372, 1321, 1140, 1008, 967, 861, 847, 771.



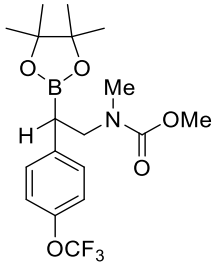
Methyl (2-(3-fluorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)(methyl) carbamate (4y):

According to the General Procedure C, **4y** (56.7 mg, 81%) was prepared as a colorless oil after purification by flash chromatography (pentane/Et_2O = 3:1). ^1H NMR (400 MHz, CD_2Cl_2) δ 7.20 (td, *J* = 8.0, 6.5 Hz, 1H), 7.09 – 6.92 (m, 2H), 6.84 – 6.79 (m, 1H), 3.86 & 3.71 (d, *J* = 13.7 Hz, 1H), 3.61 – 3.32 (m, 4H), 2.52 & 2.43 (s, 3H), 1.25 (s, 3H), 1.15 & 1.13 (s, 12H). Multiple signals due to rotamers. ^{13}C NMR (101 MHz, CD_2Cl_2) {^{19}F}: δ 164.1, 161.7, 157.5, 157.3, 148.3, 147.9, 129.4, 129.3, 123.1, 114.2, 113.9, 112.4, 112.2, 83.8, 57.2, 56.8, 52.3, 52.0, 36.3, 35.7, 24.4, 24.2, 17.7, 0.8 ppm, *the carbon attached to boron not observed*. Multiple signals due to rotamers.^{11}B NMR (128 MHz, CD_2Cl_2): δ 33.1 ppm. ^{19}F NMR (377 MHz, CD_2Cl_2) δ -114.3, -114.3 ppm. Multiple signals due to rotamers. **HRMS** (ESI): Exact mass calculated for $C_{18}H_{27}BFNNaO_4^+$ ($[M+Na]^+$): 374.1909, mass found: 374.1911. **FTIR** (neat): υ (cm^{-1}) 2979, 2936, 1701, 1612, 1585, 1484, 1462, 1381, 1322, 1269, 1139, 967, 922, 853, 772, 706, 668.



Methyl (2-(6-chloropyridin-3-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl) (methyl)carbamate (4z):

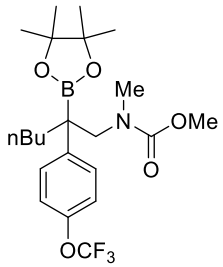
According to the General Procedure C, **4z** (60.5 mg, 82%) was prepared as a colorless sticky oil after purification by flash chromatography (pentane/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.23 (s, 1H), 7.60 – 7.49 (m, 1H), 7.23 (minor) & 7.17 (major) (d, *J* = 8.4 Hz, 1H), 3.72 & 3.60 (d, *J* = 15.9 Hz, 1H), 3.55 – 3.25 (m, 4H), 2.63 & 2.56 (s, 3H), 1.29 (s, 3H), 1.14 (s, 12H). Multiple signals due to rotamers. ^{13}C NMR (101 MHz, CD_2Cl_2): δ 157.5, 157.0, 149.0, 148.6, 139.6, 139.4, 137.9, 123.3, 84.0, 57.4, 56.8, 52.6, 52.4, 52.0, 51.9, 36.7, 36.2, 24.4, 24.4, 18.2, 17.9, 0.8 ppm, *the carbon attached to boron not observed*. Multiple signals due to rotamers.^{11}B NMR (128 MHz, CD_2Cl_2): δ 33.0 ppm. **HRMS** (ESI): Exact mass calculated for $C_{17}H_{26}BClN_2NaO_4^+$ ([M+Na]$^+$): 391.1566, mass found: 391.1570. **FTIR** (neat): υ (cm^{-1}) 2980, 1701, 1458, 1381, 1373, 1323, 1304, 1210, 1140, 1106, 1017, 967, 848, 772.



Methyl methyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(4-(trifluoromethoxy) phenyl)ethyl)carbamate (4aa):

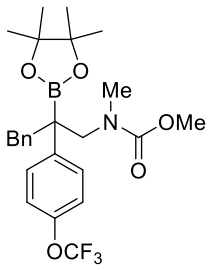
According to the General Procedure C, **4aa** (49.8 mg, 62%) was prepared as a colorless oil after purification by flash chromatography (pentane/Et_2O = 3:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.20 -7.14 (m, 2H), 7.06 (d, *J* = 8.5 Hz, 2H), 3.59 – 3.39 (m, 5H), 274 – 2.58 m, 4H), 1.15 (minor) & 1.14 (major) (s, 12H). Multiple signals due to rotamers. ^{13}C NMR (101 MHz,

CD_2Cl_2): δ 156.6, 147.3, 139.6, 130.4, 120.8, 120.6 (q, *J* = 256.1 Hz), 83.8, 52.1, 52.0, 51.6, 51.2, 34.6, 34.4, 24.4, 24.4, 0.8 ppm, *the carbon attached to boron not observed*. Multiple signals due to rotamers.[11]B NMR (128 MHz, CD_2Cl_2): δ 32.5 ppm. [19]F NMR (377 MHz, CD_2Cl_2) δ -58.3 ppm. **HRMS** (ESI): Exact mass calculated for $C_{18}H_{25}BF_3NNaO_5^+$ ([M+Na]$^+$): 426.1670, mass found: 426.1665. **FTIR** (neat): υ (cm^{-1}) 2981, 1704, 1507, 1484, 1382, 1373, 1328, 1258, 1211, 1163, 1141, 968, 855, 771.



Methyl methyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(4-(trifluoromethoxy)phenyl) hexyl)carbamate (4ab):

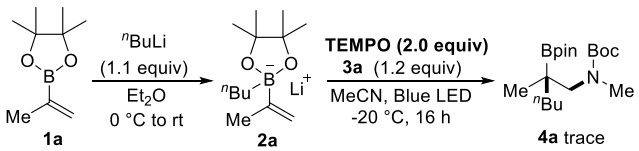
According to the General Procedure C, **4ab** (64.7 mg, 70%) was prepared as a colorless oil after purification by flash chromatography (pentane/Et_2O = 3:1). [1]H NMR (400 MHz, CD_2Cl_2) δ 7.32 – 7.20 (m, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 3.88 – 3.60 (m, 1H), 3.48 – 3.24 (m, 4H), 2.49 (major) & 2.34 (minor) (s, 3H), 1.80 – 1.68 (m, 2H), 1.33 – 1.14 (m, 4H), 1.20 (minor) & 1.18 (major) (s, 12H), 0.86 – 0.80 (m, 3H). Multiple signals due to rotamers. [13]C NMR (101 MHz, CD_2Cl_2): δ 157.3, 147.2, 147.2, 143.3, 129.7, 120.7 (q, *J* = 256.1 Hz), 120.4, 84.0, 56.1, 55.8, 52.3, 51.9, 36.8, 36.0, 33.0, 29.8, 28.2, 24.8, 24.7, 23.7, 13.8, 0.9 ppm, *the carbon attached to boron not observed*. Multiple signals due to rotamers.[11]B NMR (128 MHz, CD_2Cl_2): δ 33.1 ppm. [19]F NMR (377 MHz, CD_2Cl_2) δ -58.3 ppm. **HRMS** (ESI): Exact mass calculated for $C_{22}H_{33}BF_3NNaO_5^+$ ([M+Na]$^+$): 482.2296, mass found: 482.2295. **FTIR** (neat): υ (cm^{-1}) 2980, 2957, 2935, 1703, 1507, 1466, 1375, 1255, 1211, 1160, 1141, 852, 772, 668.



Methyl methyl(3-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(4-(trifluoromethoxy)phenyl)propyl)carbamate (4ac):

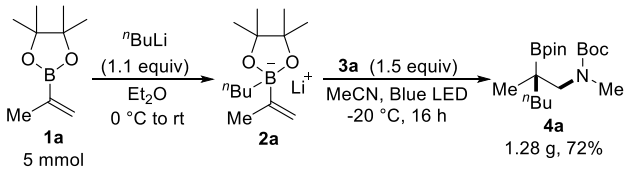
According to the General Procedure C, **4ac** (46.9 mg, 48%) was prepared as a colorless oil after purification by flash chromatography (pentane/Et_2O = 3:1). ^1H NMR (400 MHz, CD_2Cl_2) δ 7.36 – 7.31 (m, 2H), 7.11 – 7.01 (m, 5H), 6.98 – 6.90 (m, 2H), 3.78 & 3.75 (d, *J* = 13.6 Hz, 1H), 3.62 – 3.06 (m, 6H), 2.54 (s, 3H), 1.08 & 1.05 (s, 12H). Multiple signals due to rotamers. ^{13}C NMR (101 MHz, CD_2Cl_2): δ 157.4, 147.3, 142.9, 139.0, 130.2, 129.1, 128.5, 127.8, 126.1, 120.7 (q, *J* = 256.1 Hz), 120.2, 84.0, 63.7, 56.4, 52.5, 40.8, 39.4, 37.8, 36.2, 30.2, 29.8, 25.0, 24.9 15.2, 14.0, 0.9 ppm, *the carbon attached to boron not observed*. Multiple signals due to rotamers.^{11}B NMR (128 MHz, CD_2Cl_2): δ 31.1 ppm. ^{19}F NMR (377 MHz, CD_2Cl_2) δ -58.2 ppm. **HRMS** (ESI): Exact mass calculated for $C_{25}H_{31}BF_3NNaO_5^+$ ($[M+Na]^+$): 516.2140, mass found: 516.2142. **FTIR** (neat): υ (cm^{-1}) 2983, 2930, 1703, 1509, 1455, 1373, 1254, 1210, 1159, 1139, 1016, 966, 851, 770, 702.

3. Mechanistic studies

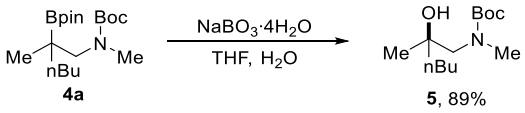


Control experiment: Vinyl boronic ester **1a** (0.20 mmol, 1.0 equiv.) was dissolved in diethyl ether (2.0 mL) and *n*-butyllithium solution (0.22 mmol, 1.1 equiv.) was added dropwise over 5 minutes at 0 °C. The solution was then stirred for 0.5 h at 0 °C, warmed to room temperature and stirred for a further 0.5 h. Subsequently, the solvent was carefully removed *in vacuo* and the resulting residue was taken up in acetonitrile (4.0 mL). After the addition of 2,2-6,6-tetramethyl piperidine-*N*-oxyl (TEMPO, 0.40 mmol, 2.0 equiv.), **3a** (0.24 mmol, 1.2 equiv.) was added at -20 ºC. The reaction mixture was irradiated with a 3 W blue LED (465 nm) and stirred at -20 ºC for 16 h. The yield of **4a** was determined by GC with n-$C_{14}H_{30}$ as an internal standard. Trace **4a** was obtained in the presence of TEMPO.

4. Gram-scale reaction and synthetic transformations



Vinyl boronic ester **1a** (5.0 mmol, 1.0 equiv.) was dissolved in diethyl ether (40 mL) and an *n*-butyllithium solution (5.5 mmol, 1.1 equiv.) was added dropwise over 10 minutes at 0 °C. The solution was then stirred for 0.5 h at 0 °C, warmed to room temperature and stirred for further 0.5 h. Subsequently, the solvent was carefully removed *in vacuo* and the resulting residue was taken up in acetonitrile (50 mL). A pre-cooled solution of **3a** (7.5 mmol, 1.5 equiv.) in MeCN (5.0 mL) was slowly added to the solution of the boronate-complex under irradiation with blue LED light (45W, 465 nm) at -20 °C. The reaction mixture was then stirred under constant irradiation with blue LED light at -20°C for 16 h. The reaction mixture was filtered through a pad of silica and rinsed with 150 mL Et_2O. The organic solvent was removed under reduced pressure. The product was purified by flash chromatography (pentane/Et_2O = 5:1) to afford **4a** (1.28 g, 72%) as a light-yellow oil.



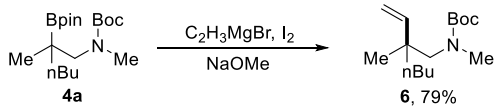
The title compound was prepared according to a literature procedure.[4]

A mixture of **4a** (71.1 mg, 0.20 mmol), $NaBO_3·4H_2O$ (123.1 mg, 0.80 mmol) and THF/H_2O (2.0 mL/2.0 mL) was stirred at room temperature for 4 h. After completion of the reaction, the reaction mixture was quenched with brine (5 mL) and extracted with ethyl acetate (5 mL × 3). The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated in *vacuo*. The residue was purified by column chromatography on silica gel with pentane/ethyl acetate (3:1) as eluent to afford the desired product **5** (43.6 mg, 89%) as a colorless oil.

***tert*-Butyl (2-hydroxy-2-methylhexyl)(methyl)carbamate (5):**

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.38 – 2.75 (m, 6H), 1.40 (s, 9H), 1.38 – 1.18 (m, 6H), 1.07 (s, 3H), 0.84 (t, *J* = 6.8 Hz, 3H). Multiple signals due to rotamers. ^{13}C NMR (101 MHz, $CDCl_3$): δ

158.5, 156.3, 80.4, 74.4, 59.8, 59.2, 40.7, 38.3, 37.7, 28.8, 28.6, 28.4, 26.1, 25.1, 23.6, 14.3, 1.3 ppm. Multiple signals due to rotamers. **HRMS** (ESI): Exact mass calculated for $C_{13}H_{27}NNaO_3^+$ ($[M+Na]^+$): 268.1883, mass found: 268.1881. **FTIR** (neat): υ (cm^{-1}) 3450, 2960, 2933, 2873, 1696, 1672, 1482, 1457, 1395, 1366, 1163, 906, 775.

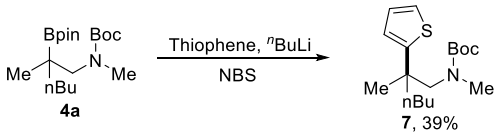


The title compound was prepared according to a literature procedure.[5]

To a solution of boronic ester **4a** (71.1 mg, 0.20 mmol) in THF (1.0 mL) at 0 °C, was added vinylmagnesium bromide (1.0 M in THF, 0.80 mL, 0.80 mmol). The resulting mixture was stirred at room temperature for 0.5 h, and recooled to -78 °C. A solution of iodine (0.5 M in THF, 1.6 mL, 0.80 mmol) was added dropwise and the resulting mixture was stirred at -78 °C for 20 min. A suspension of NaOMe (3 M in MeOH, 0.54 mL, 1.6 mmol) was added in a single portion, and the resulting mixture was stirred at 0 °C for 0.5 h. Saturated aqueous sodium thiosulfate and dichloromethane were added. The organic phase was separated and the aqueous phase was extracted twice with dichloromethane. The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel with pentane/Et_2O (25:1) as eluent to afford the desired product **6** (40.2 mg, 79%) as a colorless oil.

***tert*-Butyl methyl(2-methyl-2-vinylhexyl)carbamate (6):**

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.68 (dd, *J* = 16.7, 11.2 Hz, 1H), 4.95 (d, *J* = 10.7 Hz, 1H), 4.87 (dd, *J* = 17.5, 1.3 Hz, 1H), 3.22 & 3.14 (d, *J* = 14.0 Hz, 1H), 3.01 (major) & 2.97 (minor) (s, 1H), 2.79 & 2.76 (s, 3H), 1.38 (s, 9H), 1.25 – 1.07 (m, 6H), 0.92 (s, 3H), 0.81 (t, *J* = 7.1 Hz, 3H). Multiple signals due to rotamers. ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.8, 156.6, 146.4, 146.0, 113.1, 112.7, 79.7, 79.2, 60.0, 59.3, 42.9, 39.3, 39.1, 37.9, 28.7, 26.4, 23.8, 20.4, 14.3, 1.3 ppm. Multiple signals due to rotamers. **HRMS** (ESI): Exact mass calculated for $C_{15}H_{29}NNaO_2^+$ ($[M+Na]^+$): 278.2091, mass found: 278.2088. **FTIR** (neat): υ (cm^{-1}) 2962, 2932, 2874, 1697, 1457, 1391, 1365, 1292, 1167, 1135, 911, 877, 774.



The title compound was prepared according to a literature procedure.[6]

A solution of thiophene (19 µL, 20.2 mg, 0.24 mmol) in tetrahydrofuran (1.0 mL) was cooled to -78 °C and then n-butyllithium (0.15 mL, 0.24 mmol, 1.6 M in hexane) was added dropwise. Then, the mixture was allowed to warm to 0 °C and strring was continued for 30 minutes. After recooling to -78 °C, a solution of **4a** (71.1 mg, 0.20 mmol) in tetrahydrofuran (0.5 mL) added dropwise. The reaction mixture was allowed to stir at -78 °C for 1 hour. *N*-bromosuccinimide (42.7 mg, 0.24 mmol) in tetrahydrofuran (0.5 mL) was added dropwise and the mixture was stirred at -78 °C for 1 hour. Saturated aqueous sodium thiosulfate solution (2.0 mL) was added. The reaction mixture was allowed to warm to room temperature and was then diluted with water and ethyl acetate. The aqueous layer was extracted with ethyl acetate (3 x 15 mL). The combined organic layers were dried over magnesium sulfate, filtered and concentrated. The crude product was purified by flash column chromatography on silica gel (pentane/Et_2O = 10:1) to give the product **7** (24.5 mg, 39%) as colorless sticky oil.

***tert*-Butyl methyl(2-methyl-2-(thiophen-2-yl)hexyl)carbamate (7):**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 4.9 Hz, 1H), 6.89 – 6.83 (m, 1H), 6.73 (s, 1H), 3.64 (minor) & 3.52 (major) (d, *J* = 14.0 Hz, 1H), 3.07 (major) & 3.01 (minor) (d, *J* = 12.9 Hz, 1H), 2.46 (major) & 2.37 (minor) (s, 3H), 1.73 – 1.53 (m, 2H), 1.37 (s, 9H), 1.29 (s, 3H), 1.24 – 1.14 (m, 3H), 1.05 – 0.98 (m, 1H), 0.79 (t, *J* = 6.5 Hz, 3H). Multiple signals due to rotamers. ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.9, 156.6, 153.2, 152.6, 126.9, 124.0, 124.0, 123.7, 123.6, 79.8, 79.4, 62.9, 62.2, 43.5, 41.5, 37.0, 28.6, 26.4, 23.6, 23.3, 23.0, 14.3, 1.2 ppm. Multiple signals due to rotamers. **HRMS** (ESI): Exact mass calculated for $C_{17}H_{29}NNaO_2S^+$ ($[M+Na]^+$): 334.1811, mass found: 334.1810. **FTIR** (neat): υ (cm^{-1}) 2968, 2932, 2873, 1697, 1456, 1391, 1366, 1292, 1239, 1165, 1049, 878, 775, 694.

5. References

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3 D. Gwon, H. Hwang, H. K. Kim, S. R. Marder and S. Chang, *Chem. –Eur. J*., 2015, **21**, 17200.

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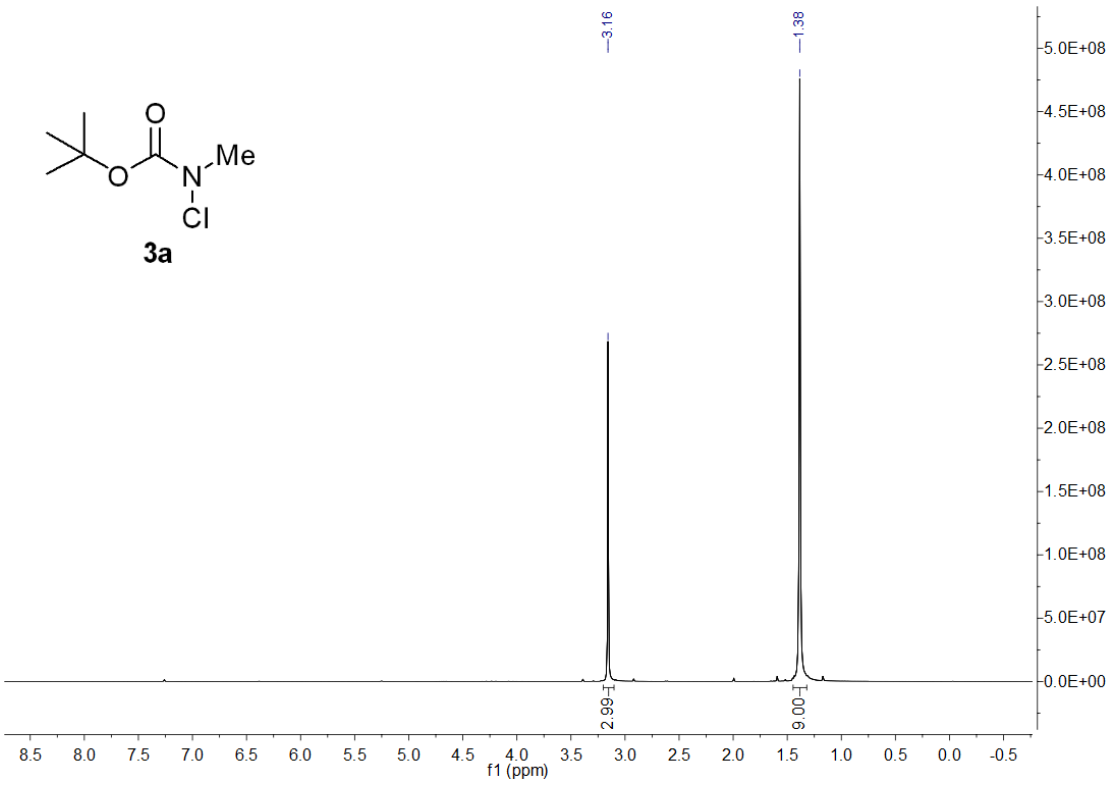
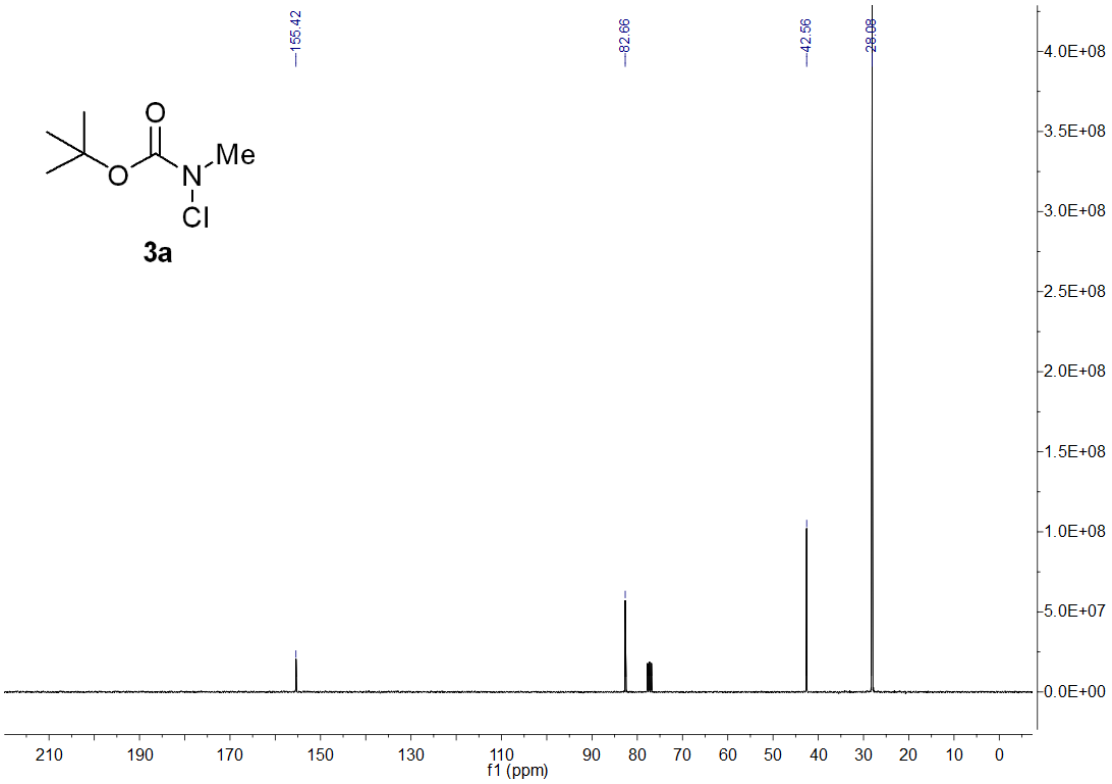
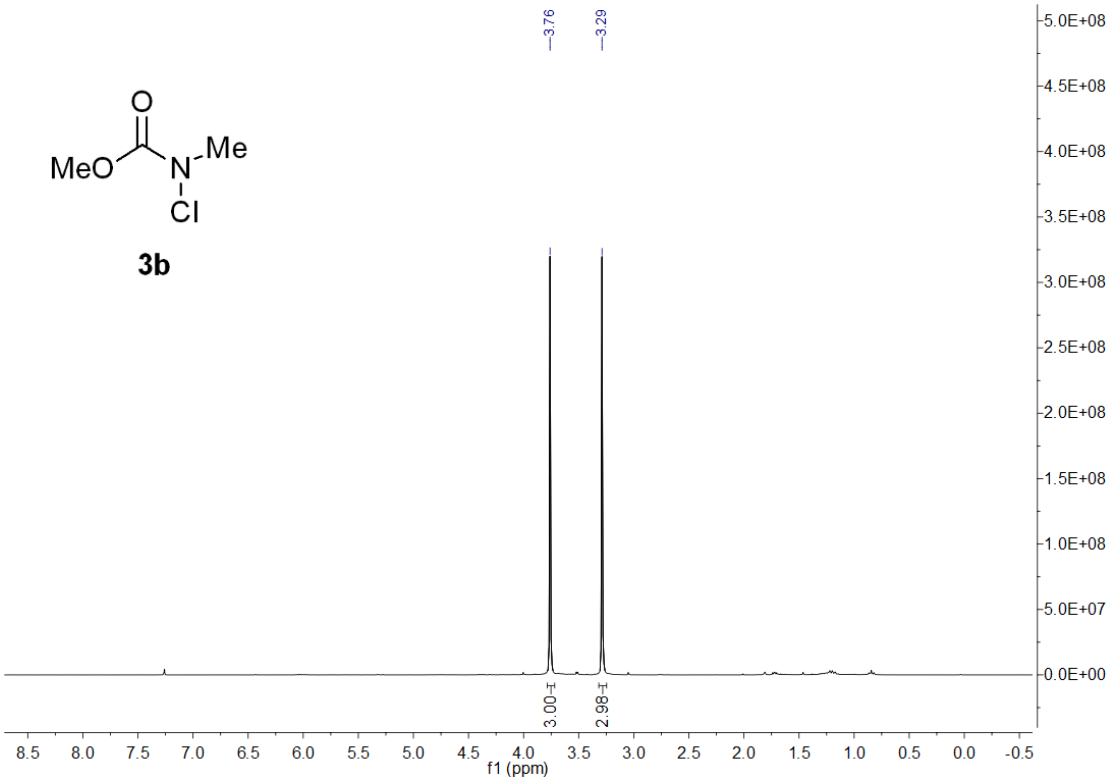
6. NMR spectra



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Cl
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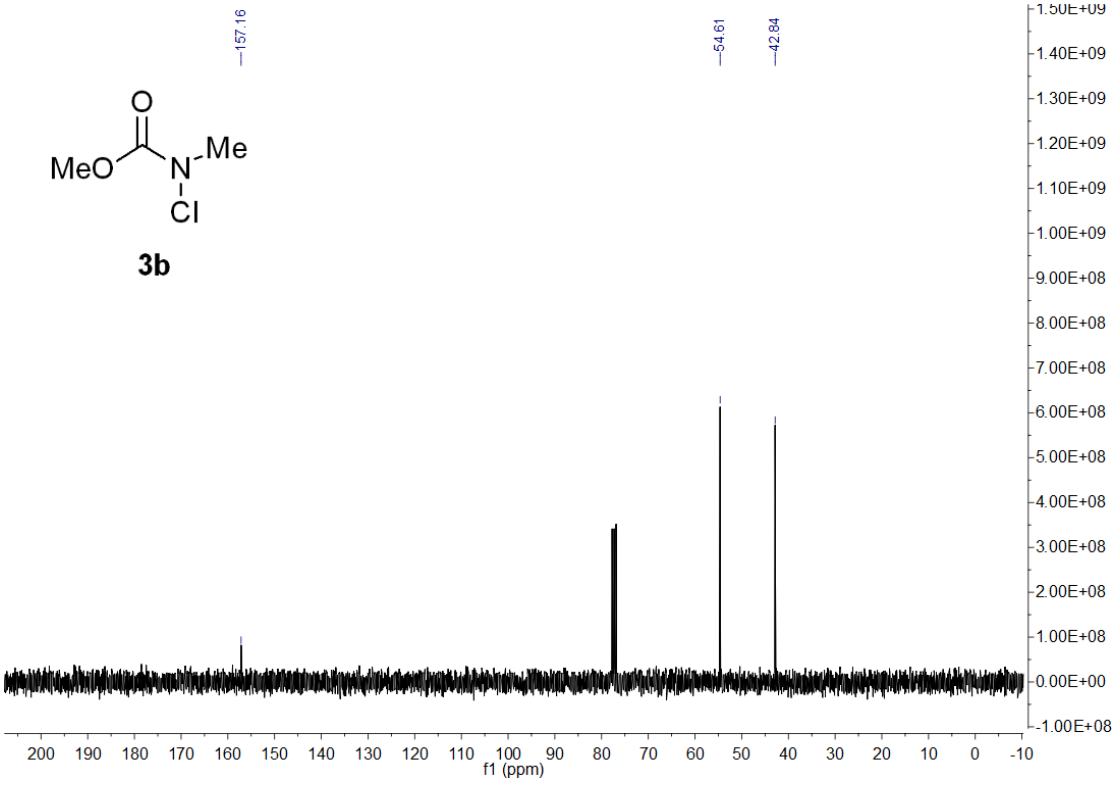
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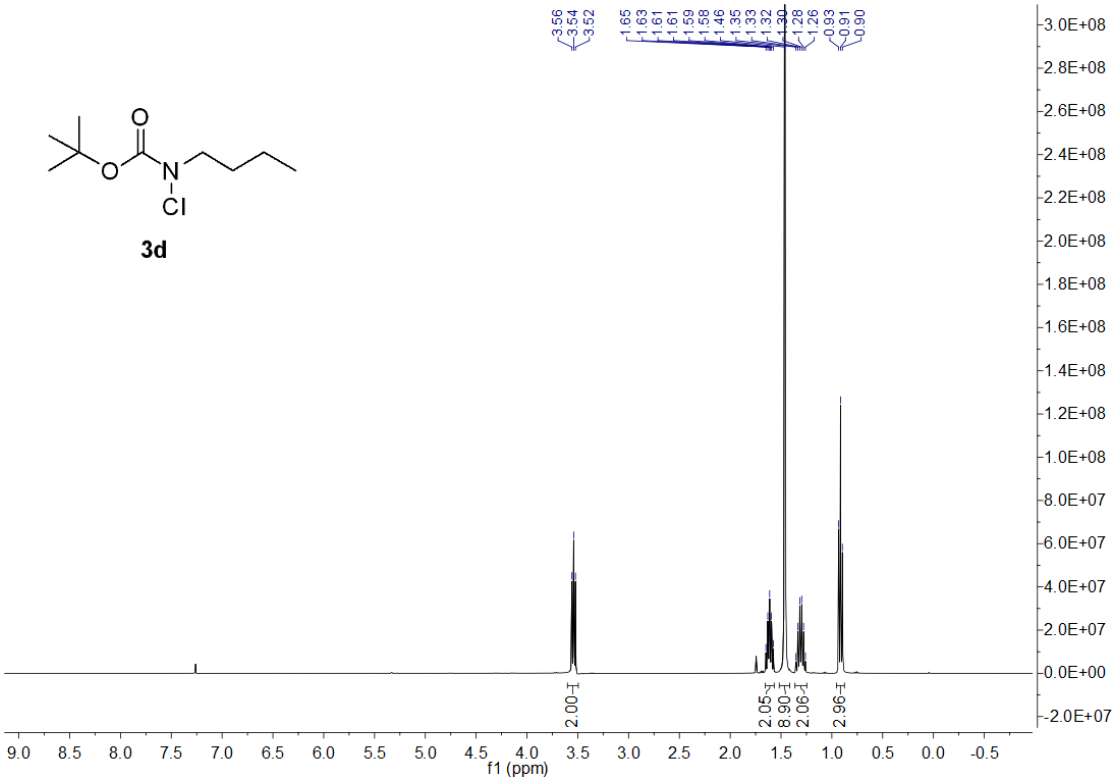
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1.61
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1.30
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1.26
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f1 (ppm)

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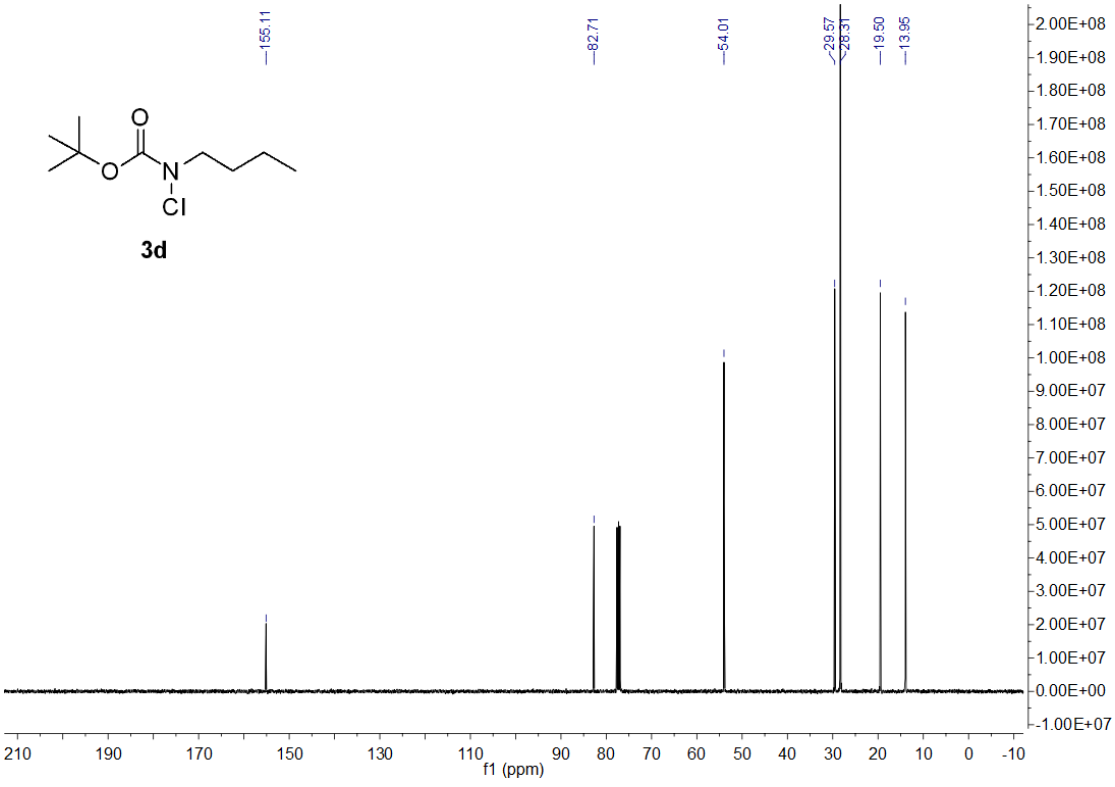
O
N
Cl

3d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f1 (ppm)

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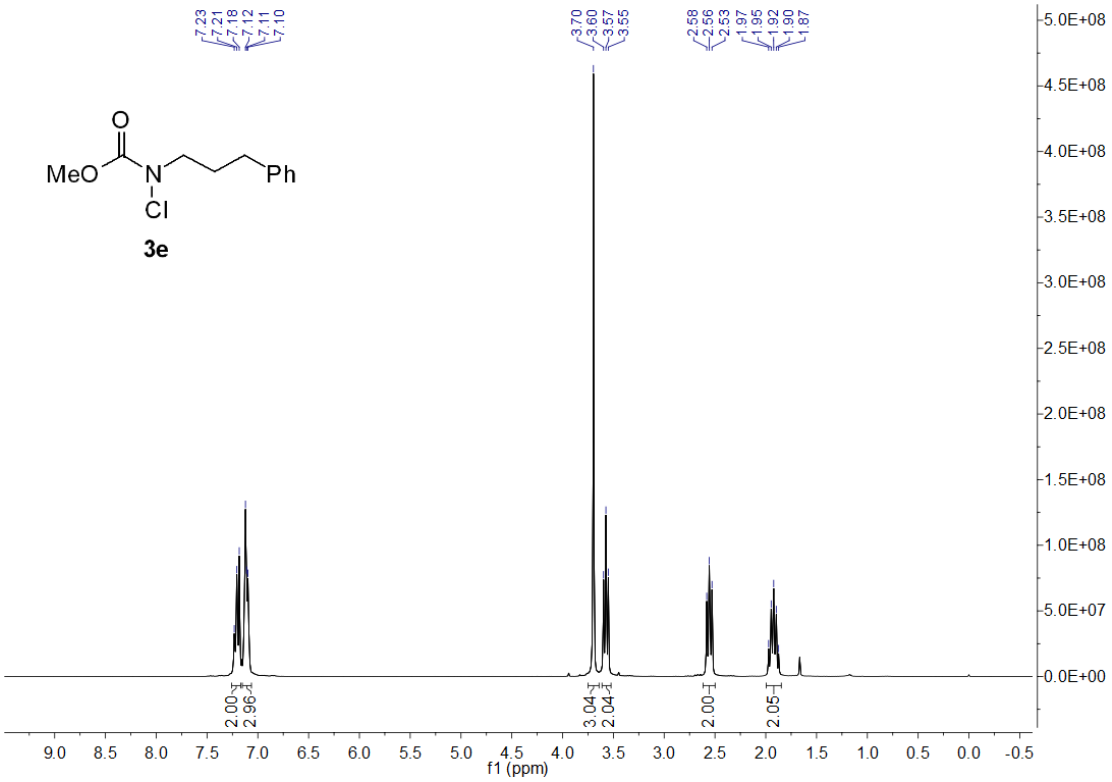
O
N
Cl

3d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1.95
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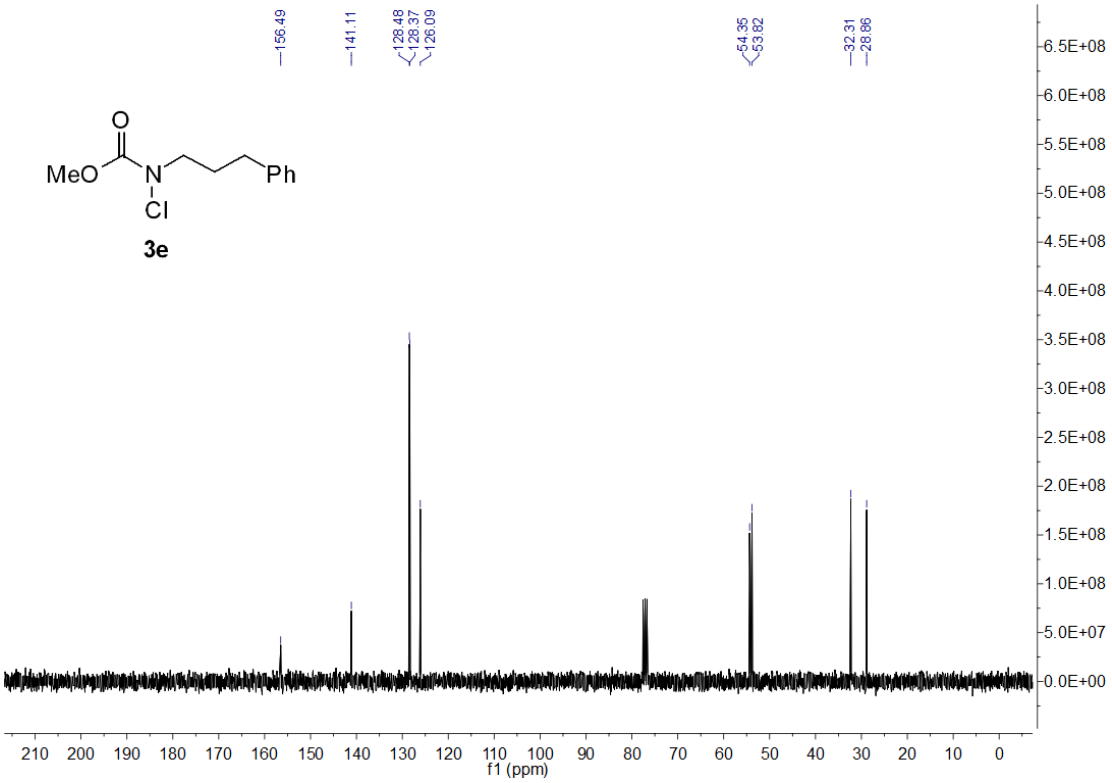
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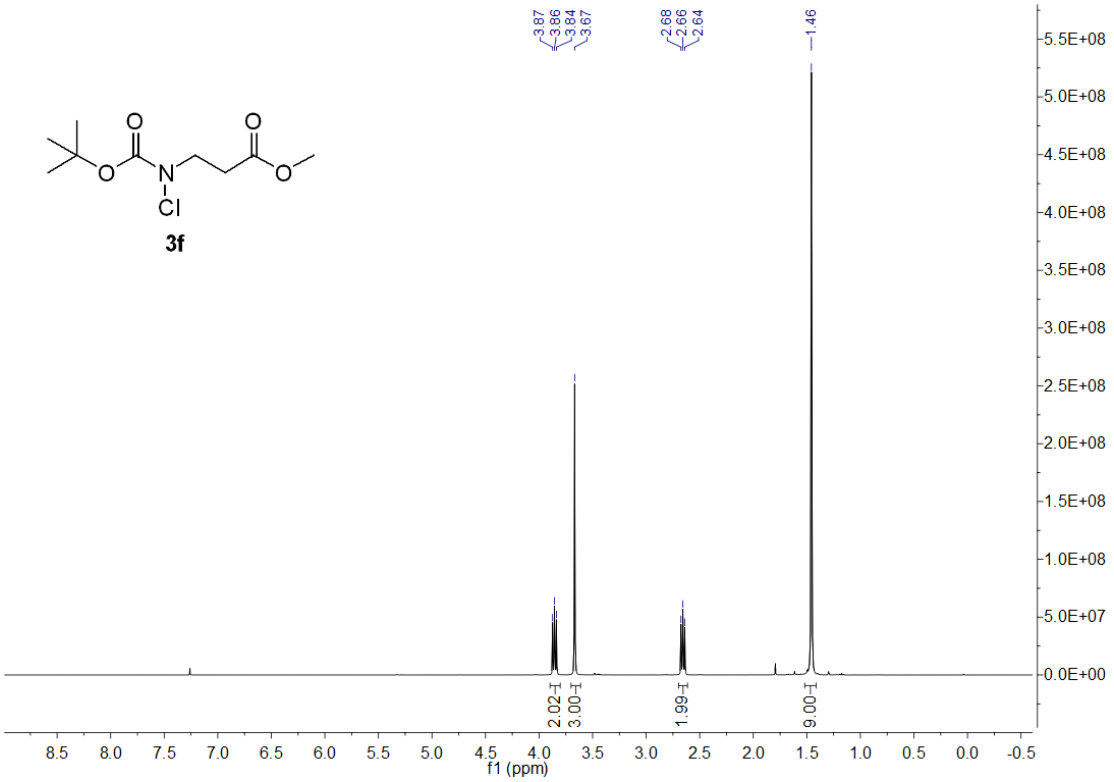
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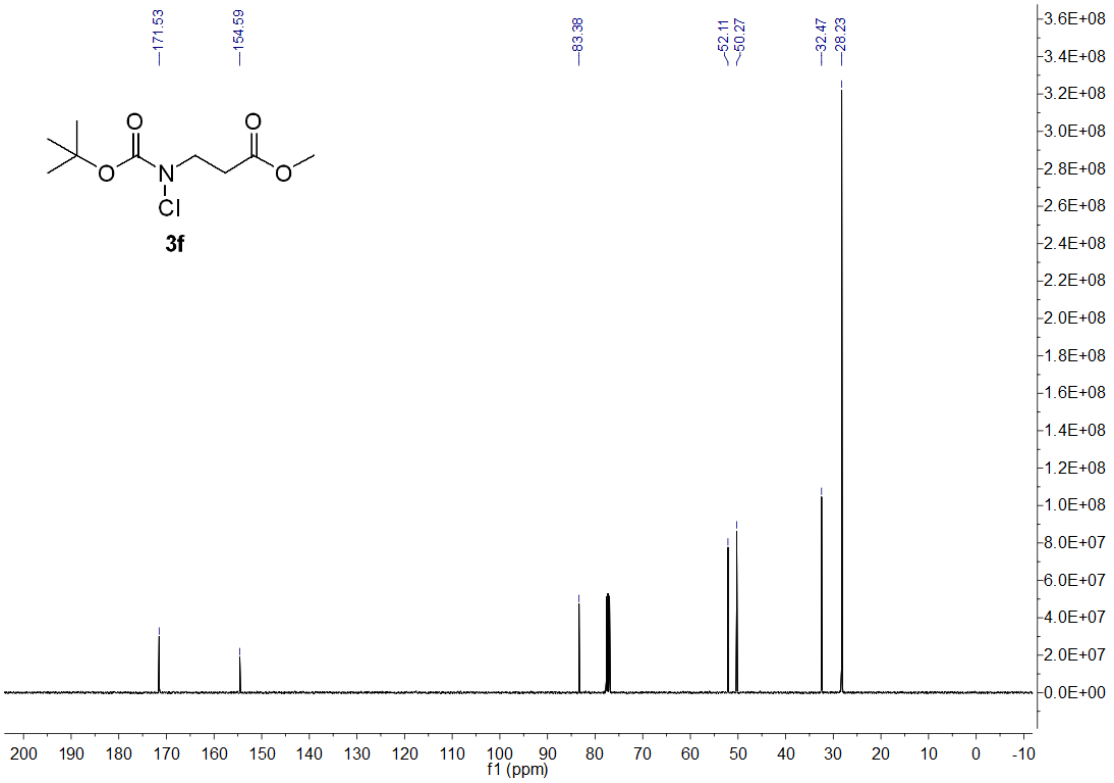
3f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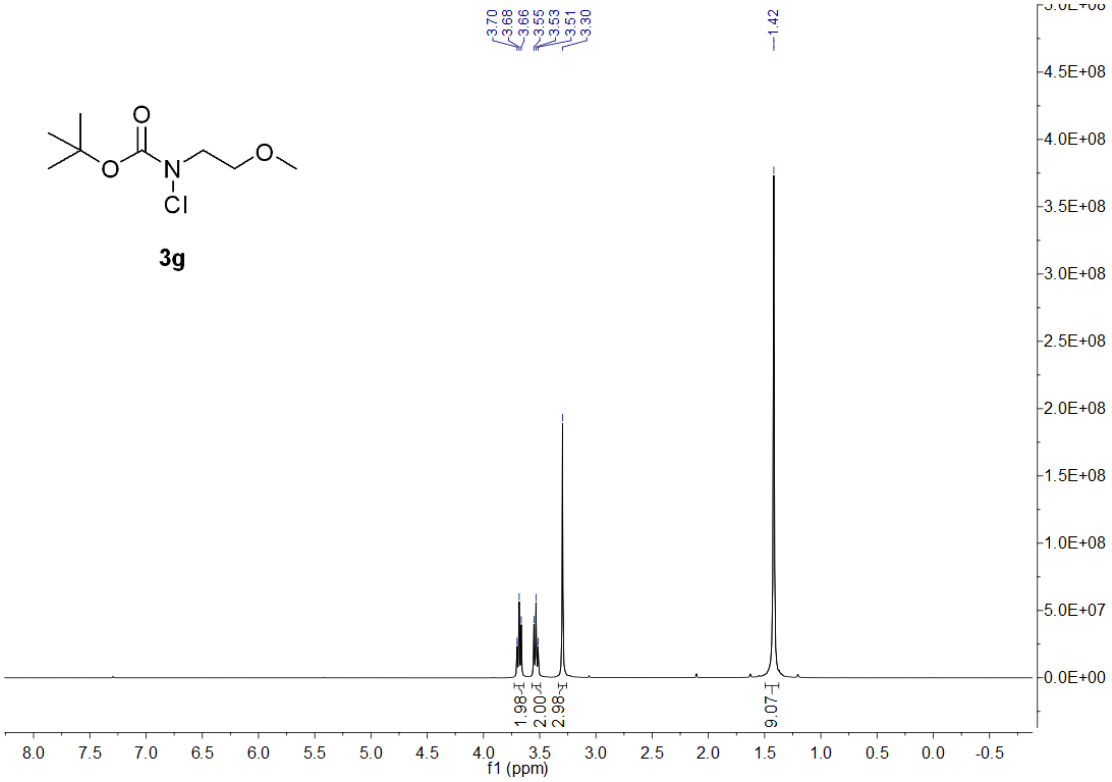
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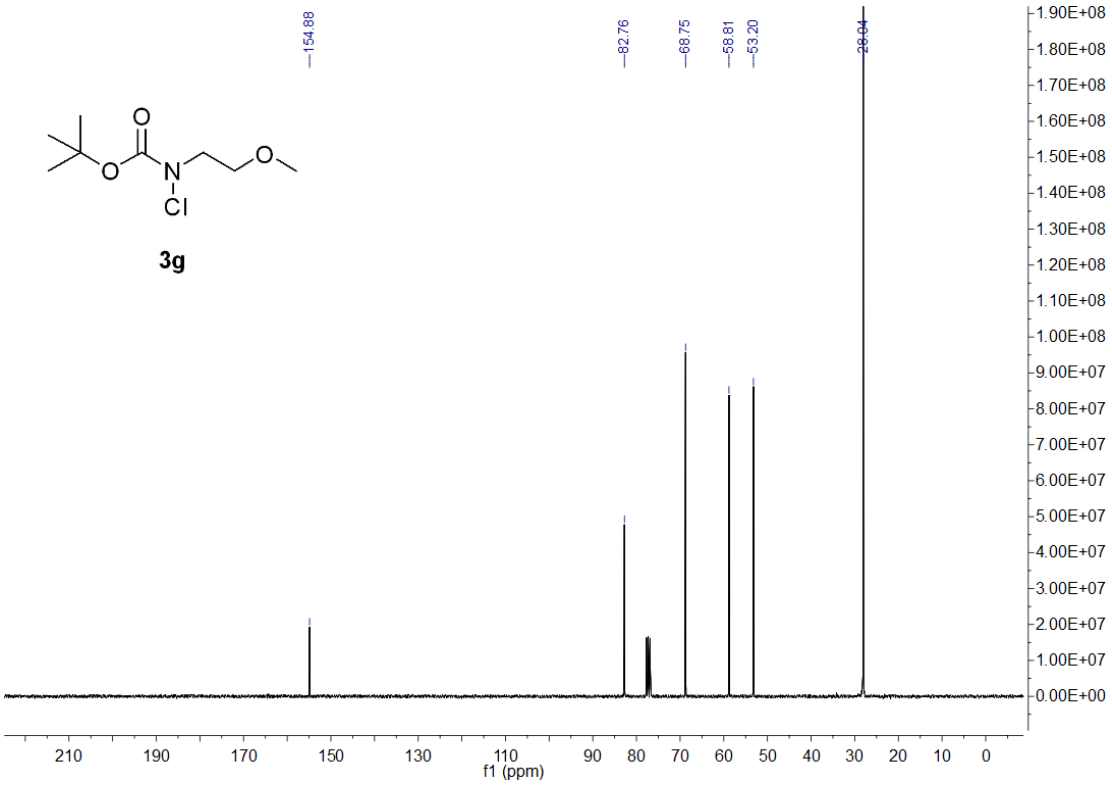
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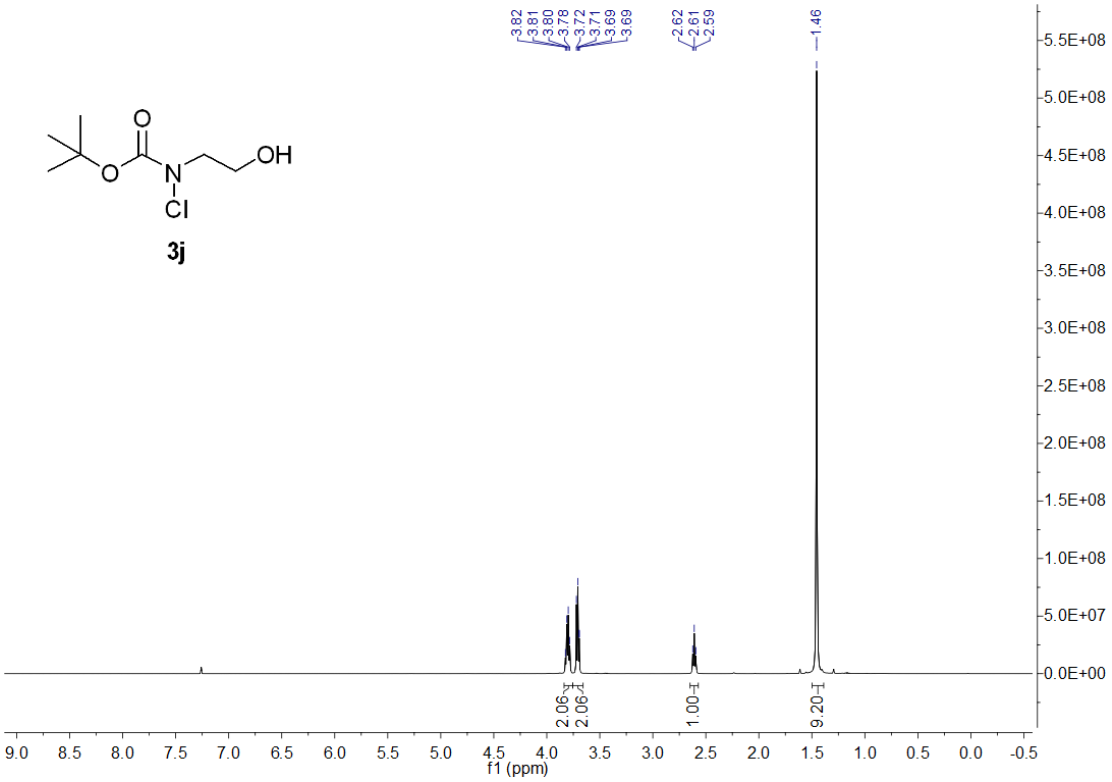
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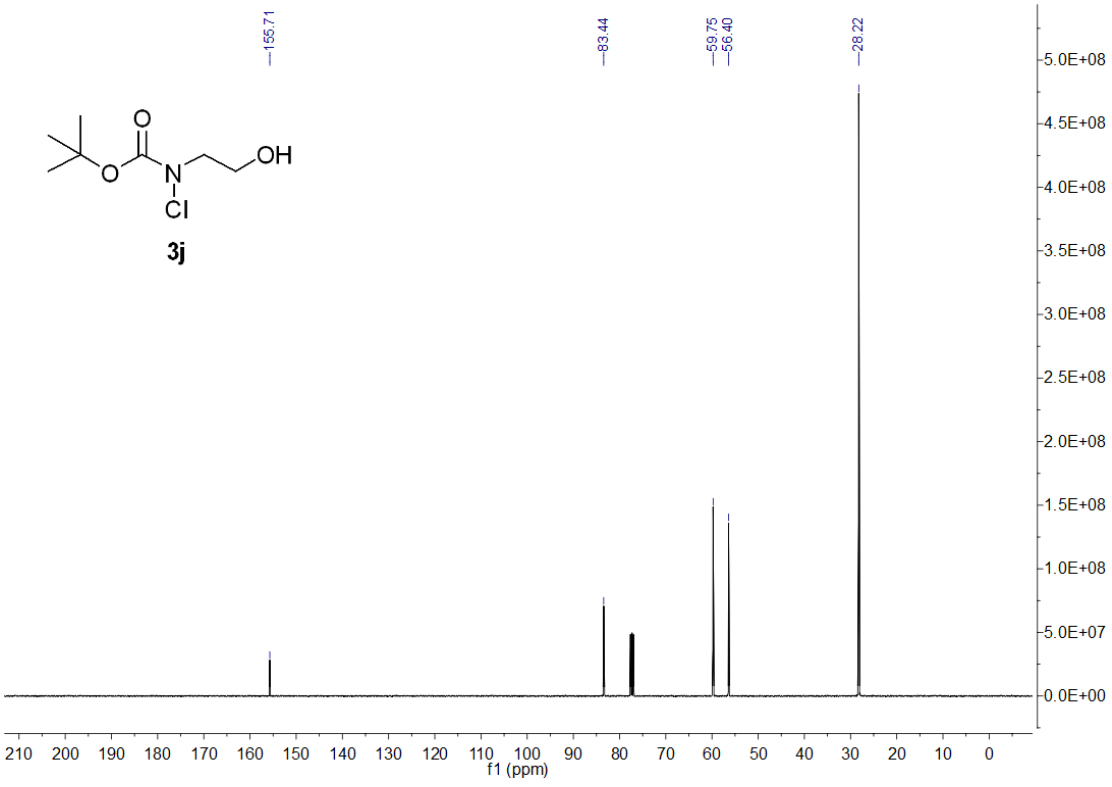
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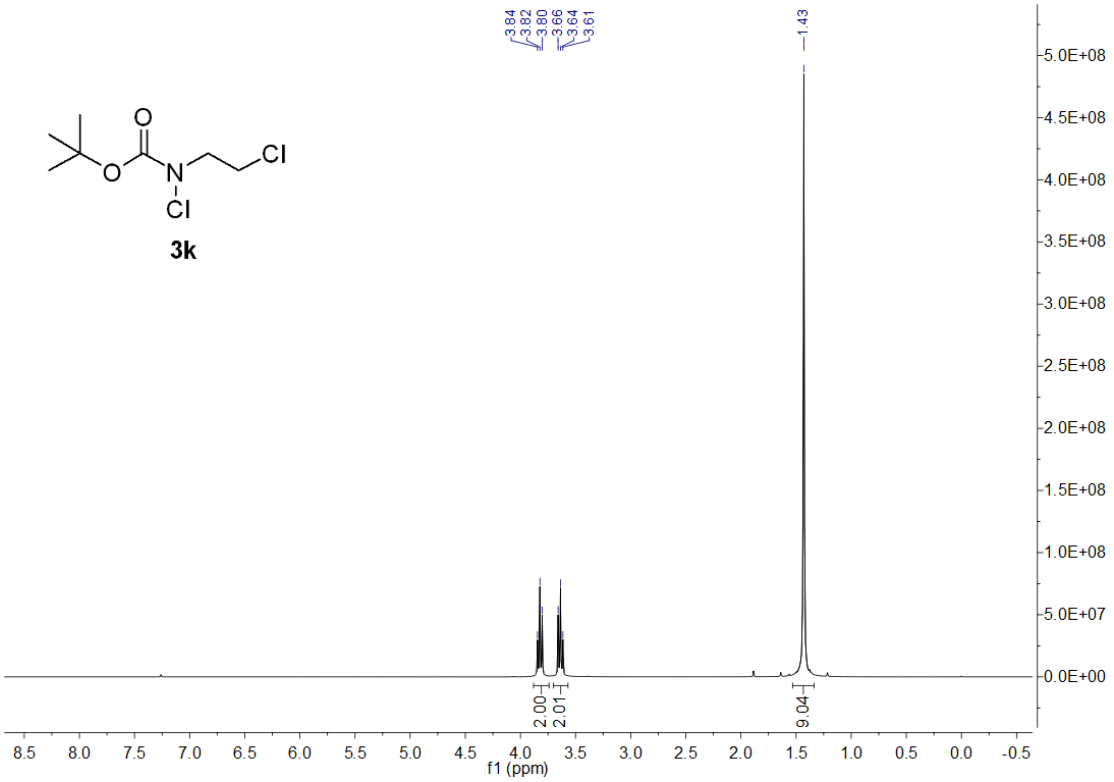
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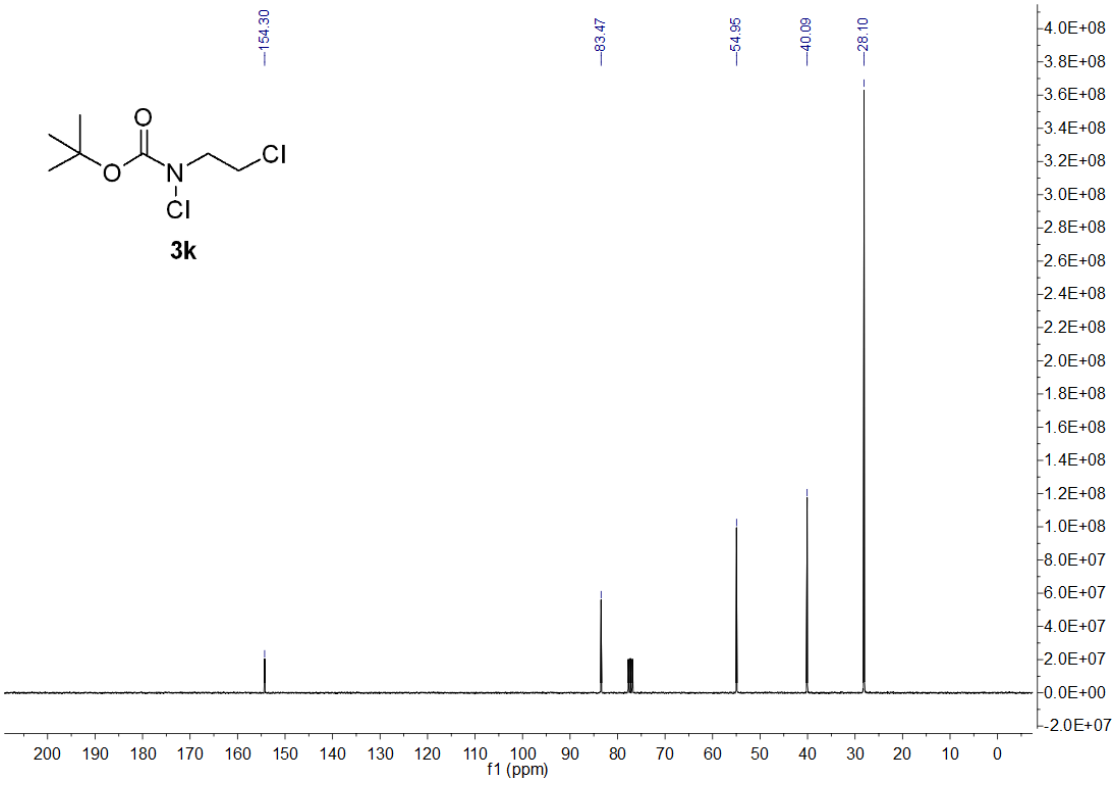
3k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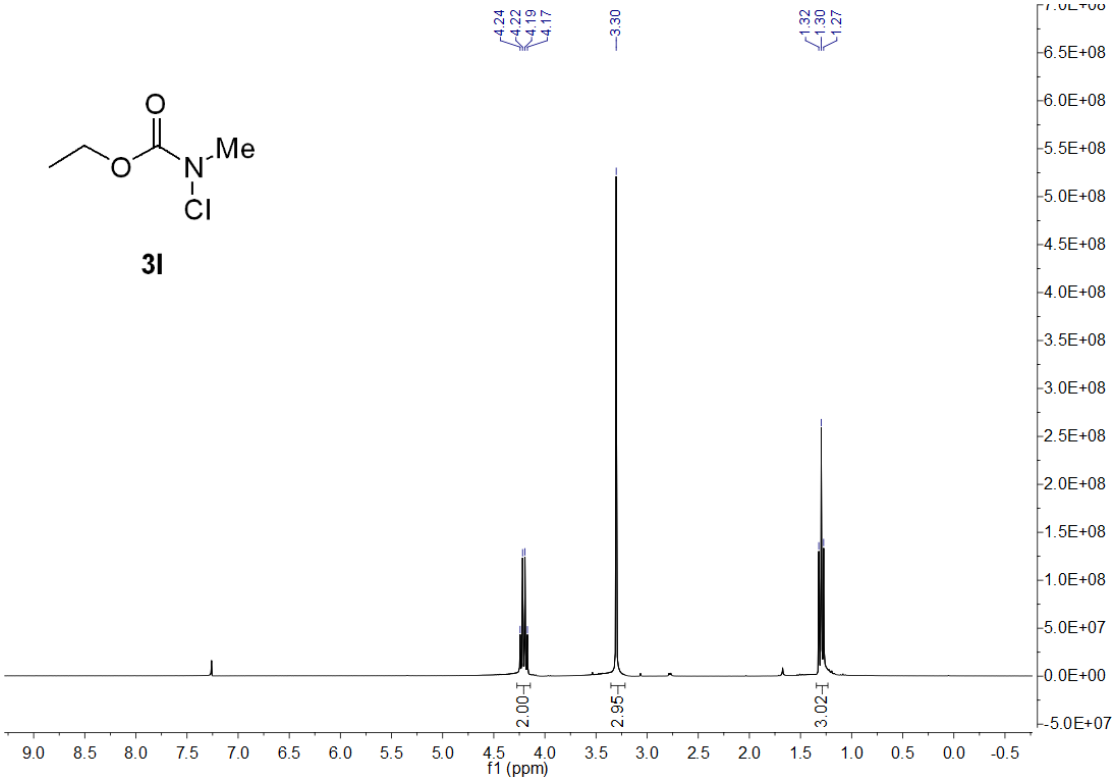
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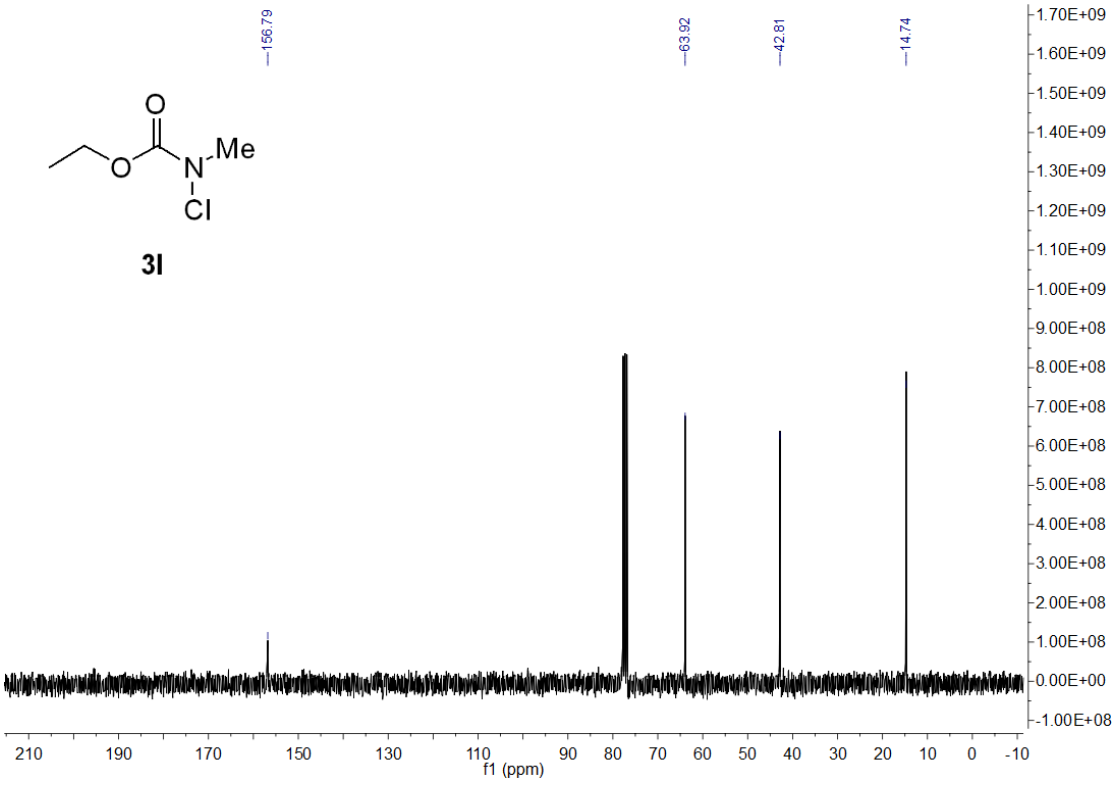
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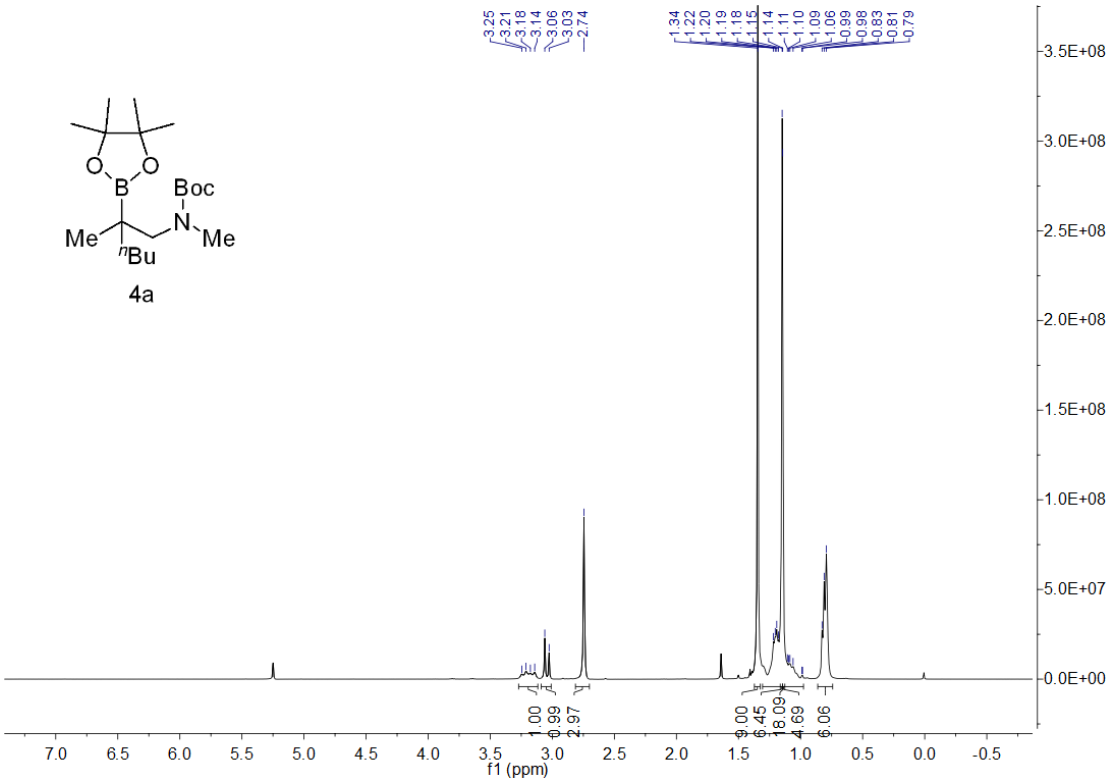
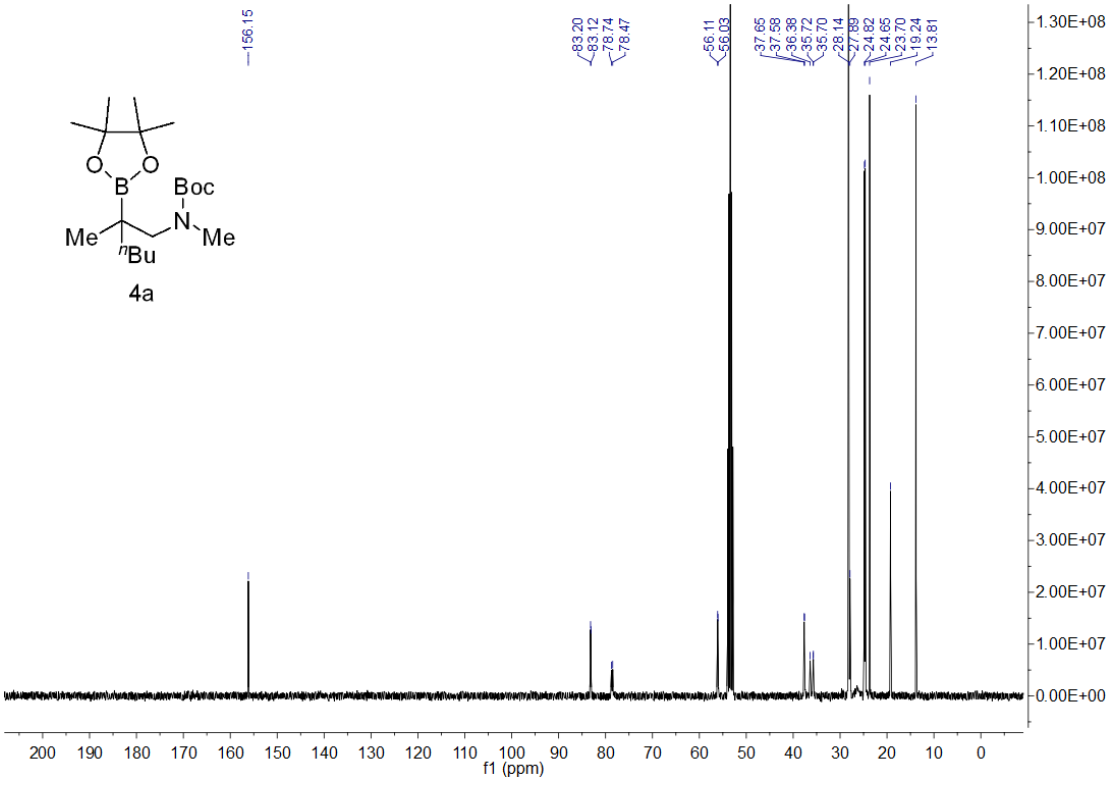
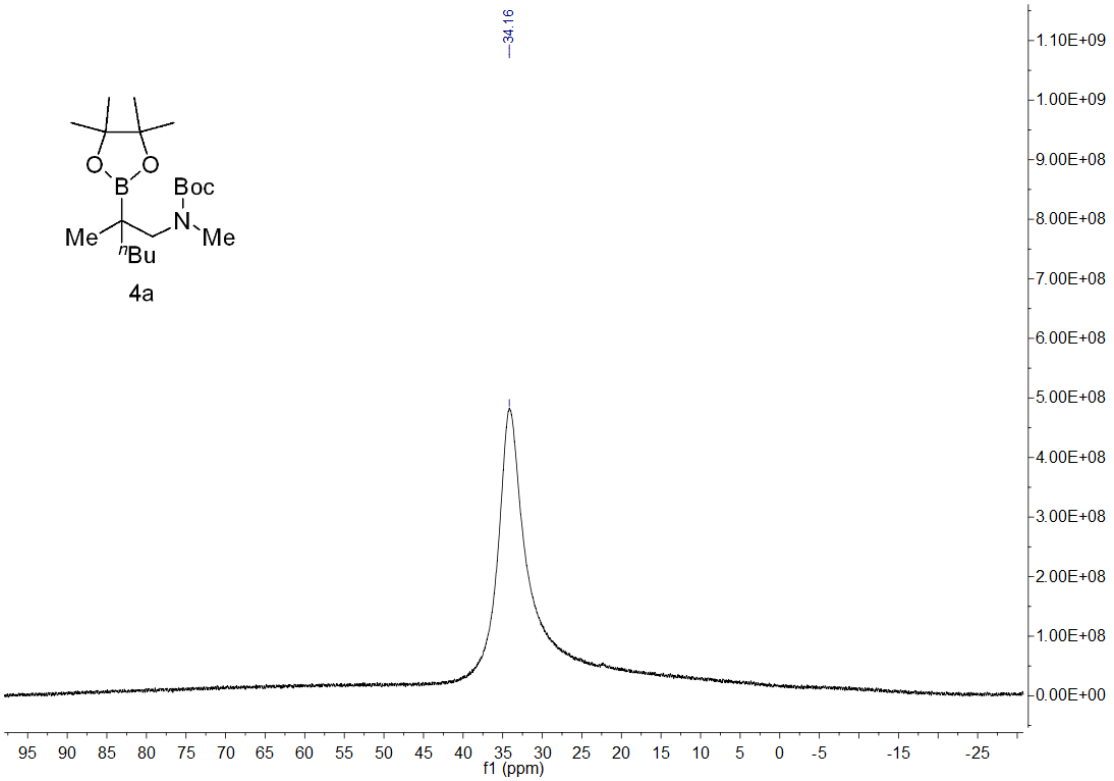
3l
f1 (ppm)

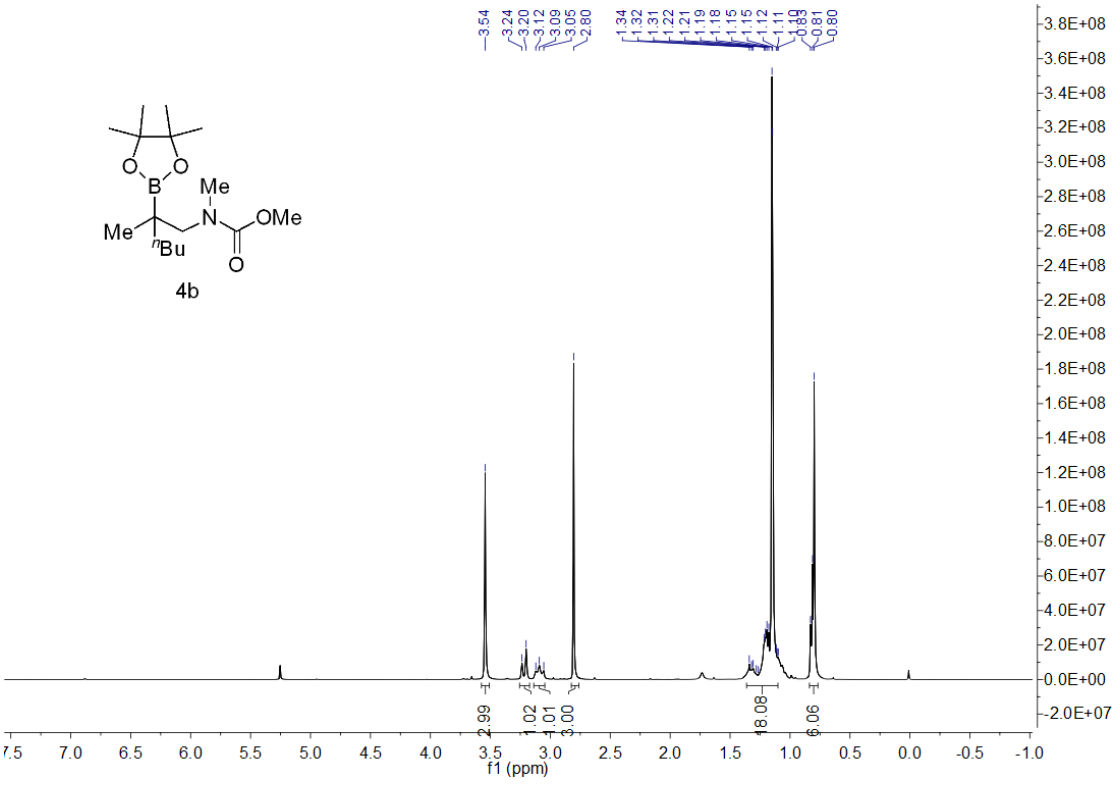

3.25
3.21
3.18
3.14
3.06
3.03
2.74
1.34
1.22
1.20
1.19
1.18
1.15
1.14
1.11
1.10
1.09
1.06
0.99
0.98
0.83
0.81
0.79
Boc
N
Me
Me
nBu
4a
1.00
0.99
2.97
9.00
6.45
18.09
4.69
6.06
f1 (ppm)


156.15
83.20
83.12
78.74
78.47
56.11
56.03
37.65
37.58
36.38
35.72
35.70
28.14
27.88
24.82
24.65
23.70
19.24
13.81
Boc
N
Me
Me
nBu
4a
f1 (ppm)



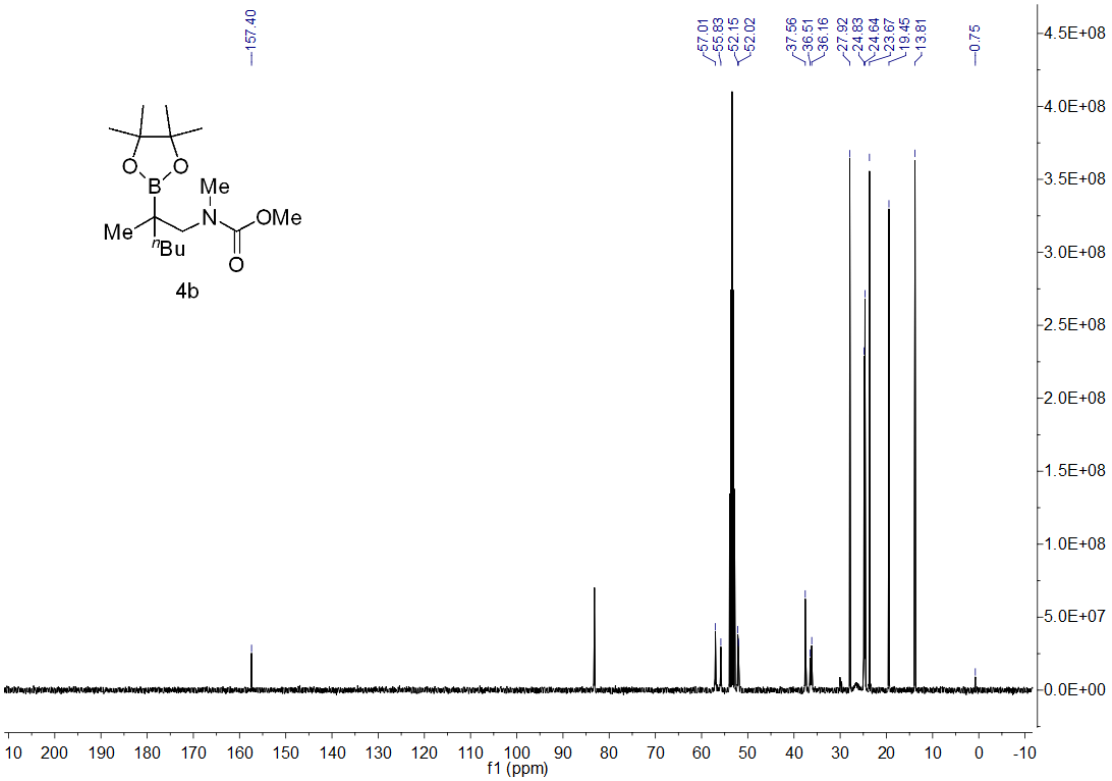
Me
Boc
N
Me
B
O
O
^{n}Bu

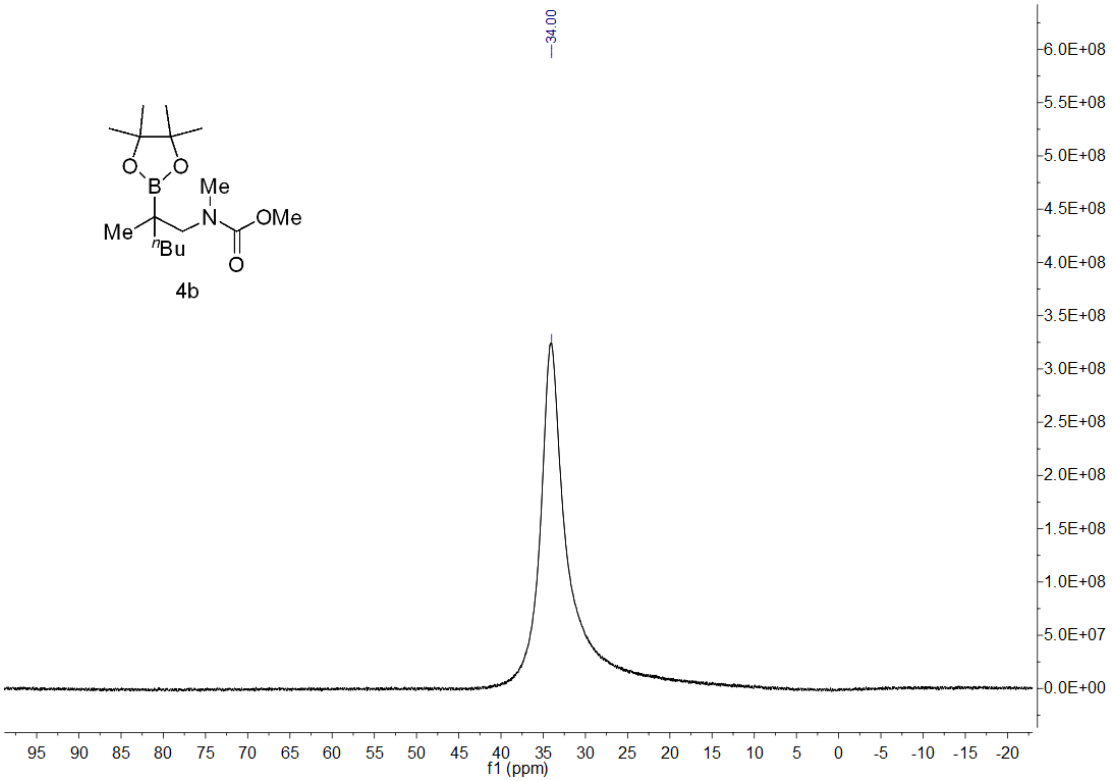
4a

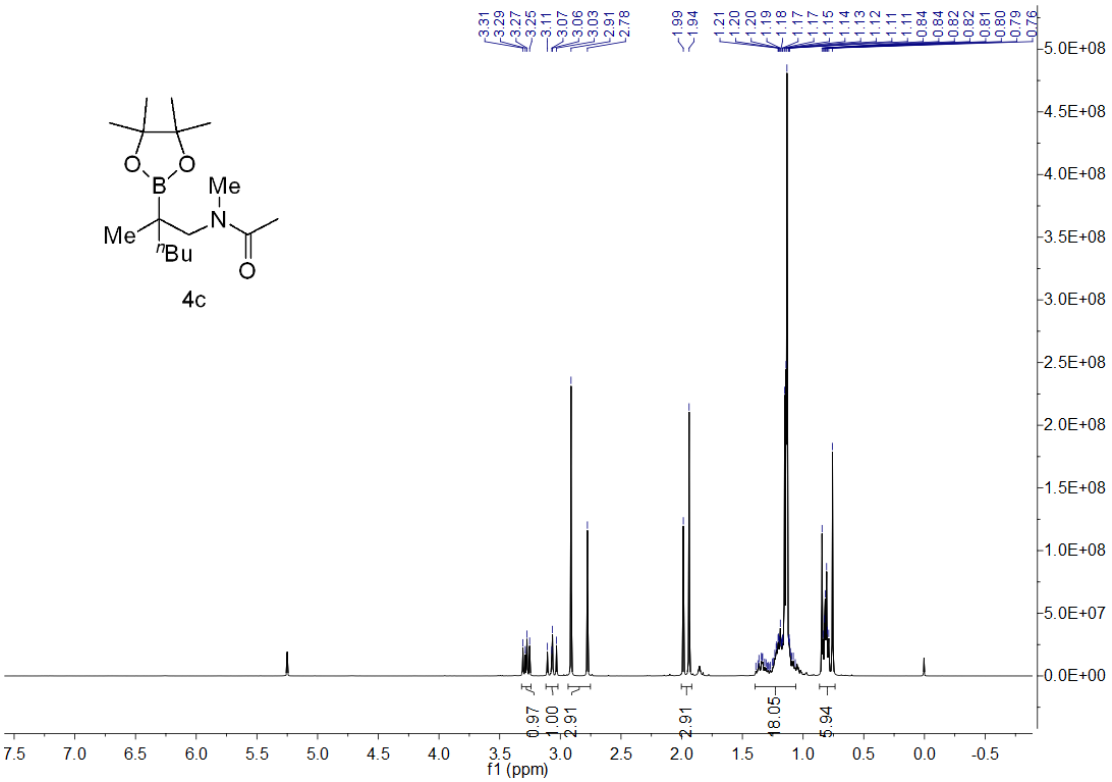


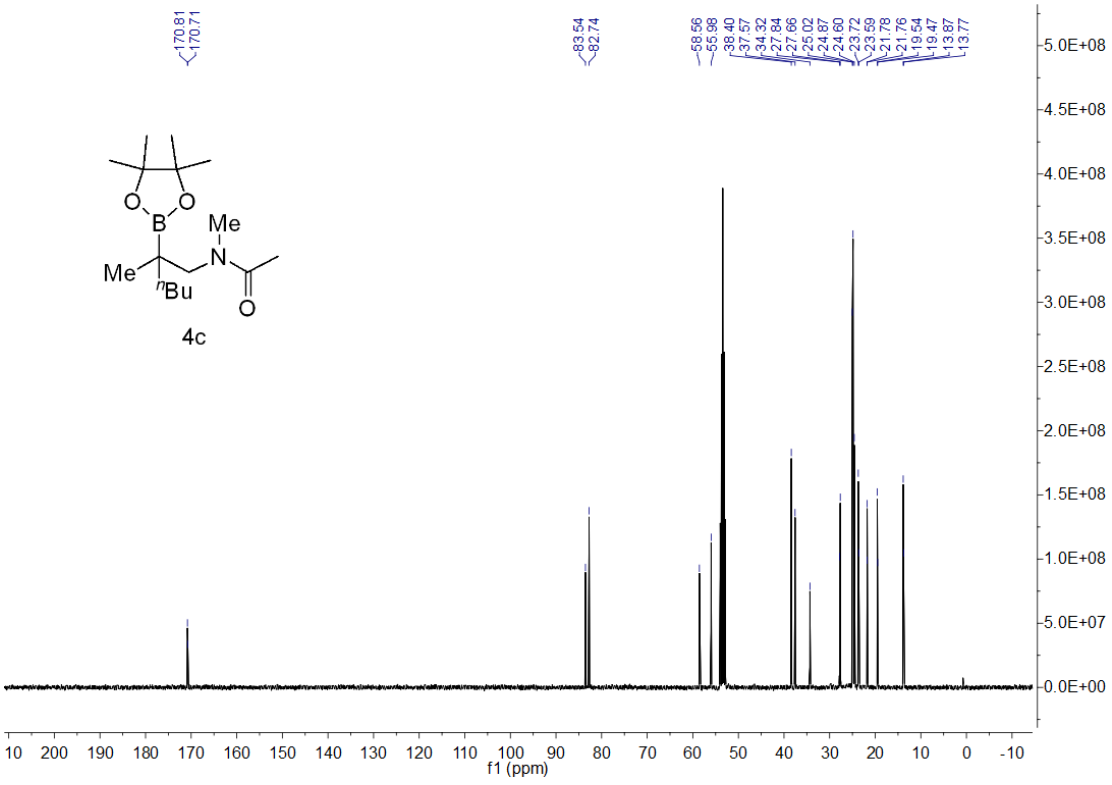
Me
Me
N
OMe
O
B
O
O
^{n}Bu

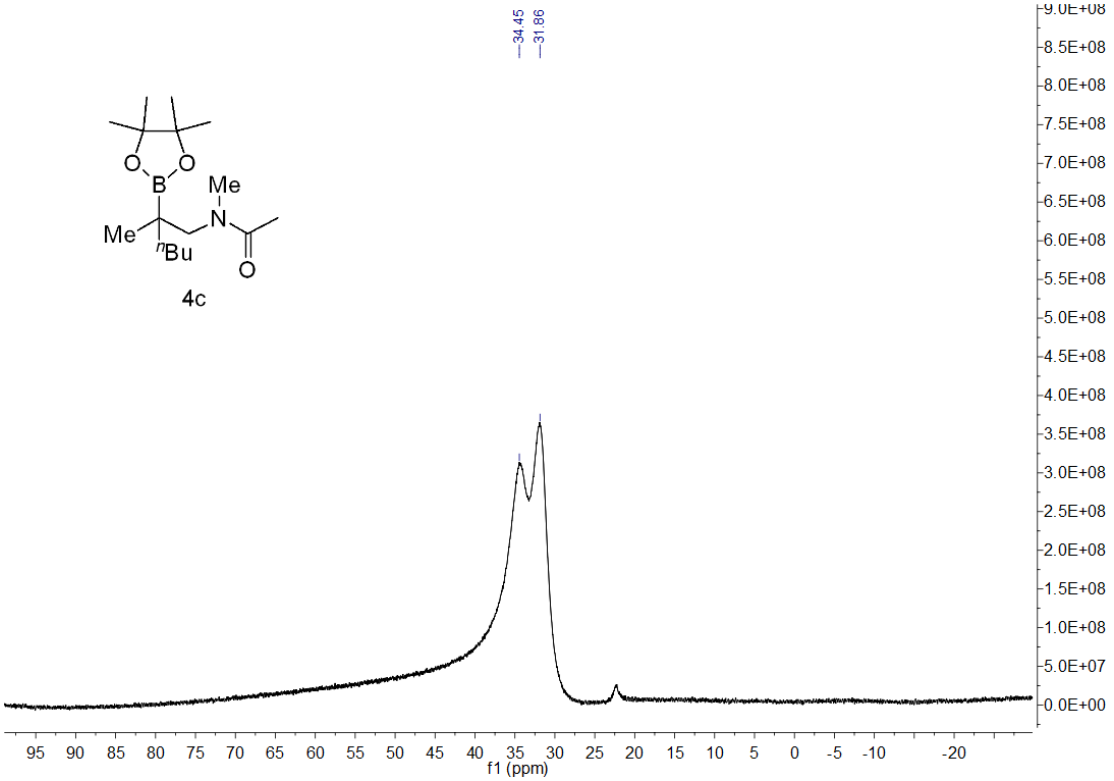
4b


157.40
57.01
55.83
52.15
52.02
37.56
36.51
36.16
27.92
24.83
24.64
23.67
19.45
13.81
0.75
Me
B
O
O
Me
N
OMe
Me
nBu
O
4b
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

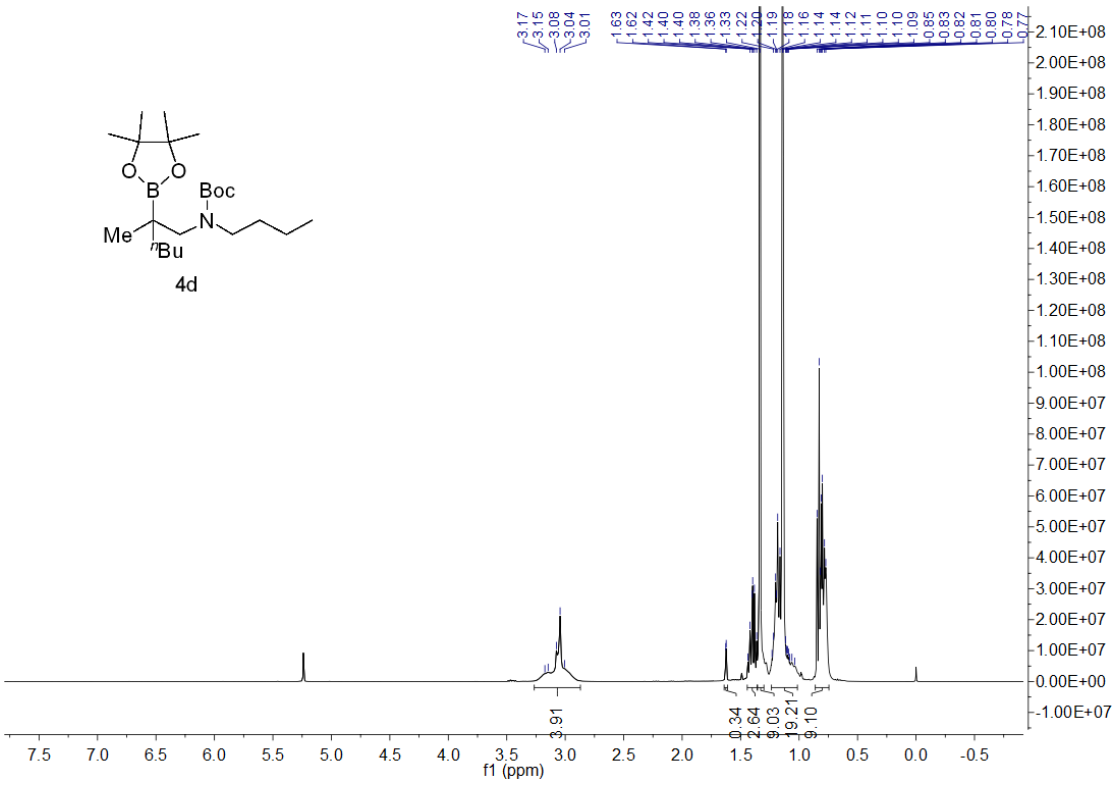

34.00
Me
B
O
O
Me
N
OMe
Me
nBu
O
4b
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20
f1 (ppm)


4c
3.31
3.29
3.27
3.25
3.11
3.07
3.06
3.03
2.91
2.78
1.99
1.94
1.21
1.20
1.20
1.19
1.18
1.17
1.17
1.15
1.14
1.13
1.12
1.11
1.11
0.84
0.84
0.82
0.82
0.81
0.80
0.79
0.76
0.97
1.00
2.91
2.91
18.05
5.94
f1 (ppm)

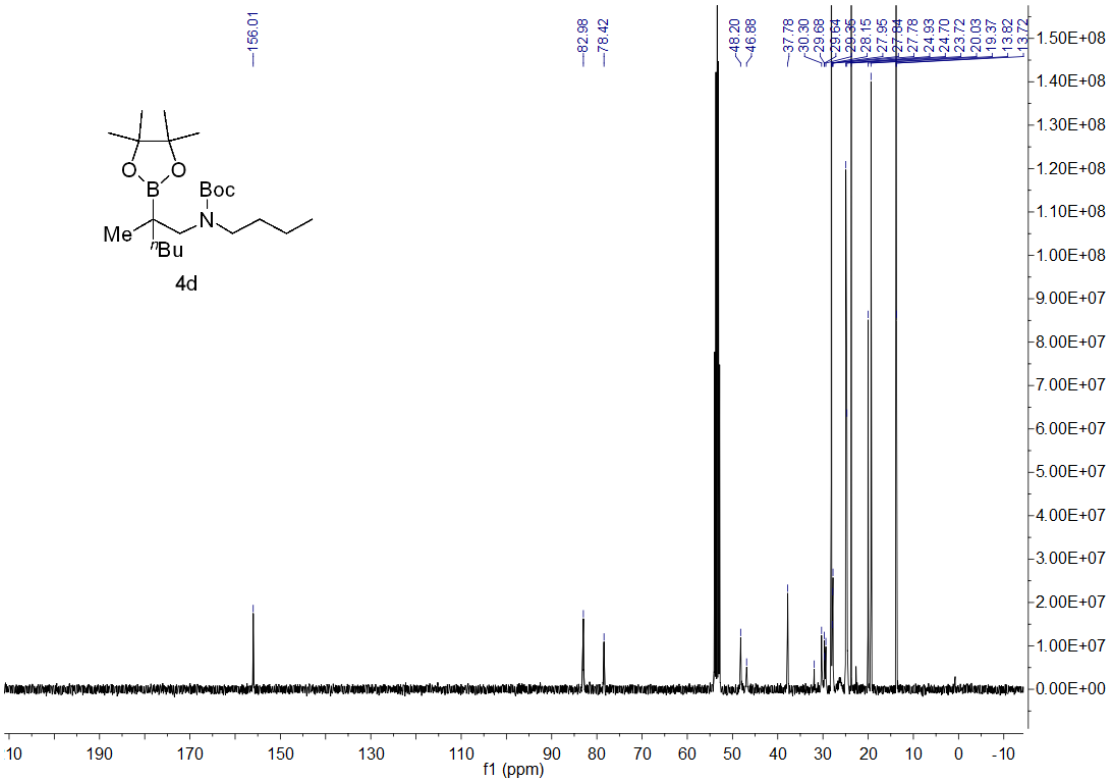

4c
170.81
170.71
83.54
82.74
58.56
55.98
38.40
37.57
34.32
27.84
27.66
25.02
24.87
24.60
23.72
23.59
21.78
21.76
19.54
19.47
13.87
13.77
f1 (ppm)

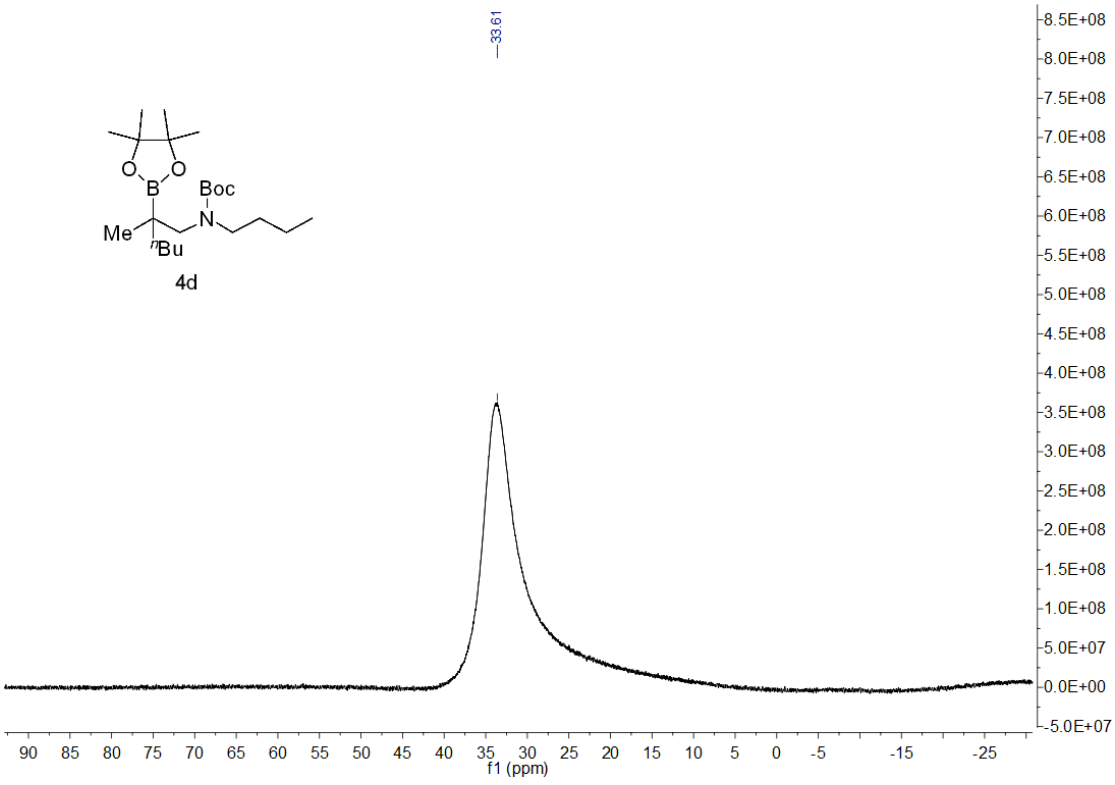

34.45
31.86
Me
N
Me
nBu
O
B
O
O
f1 (ppm)

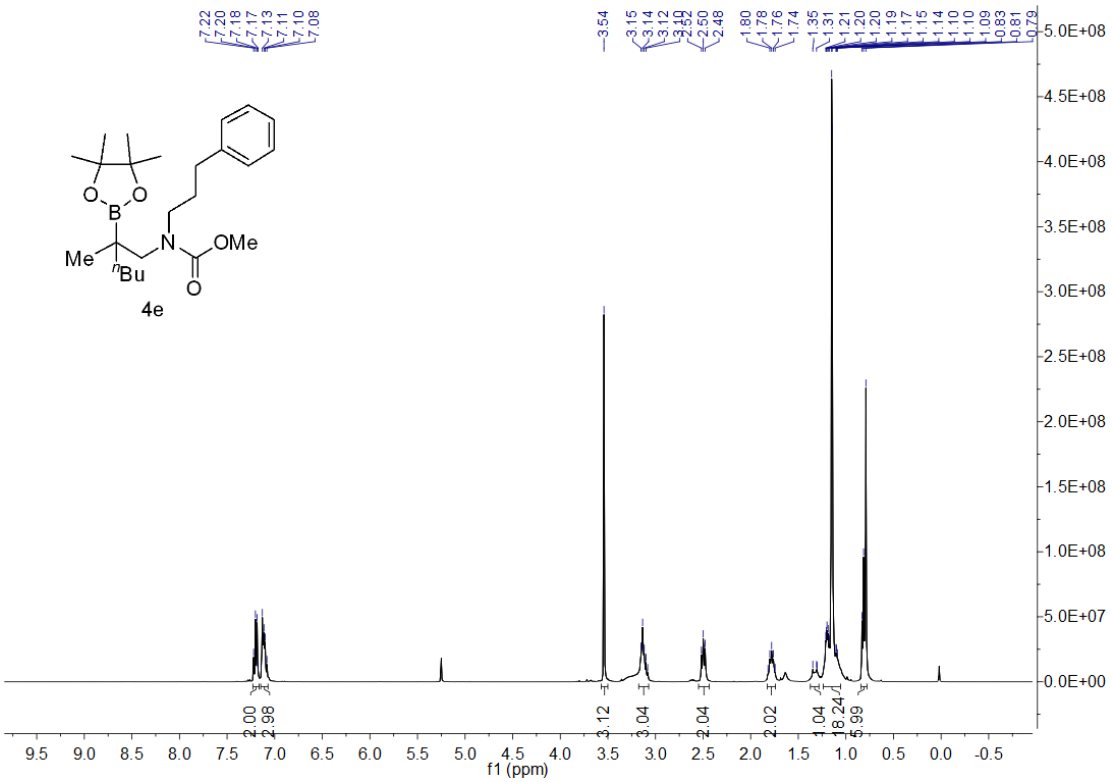
4c

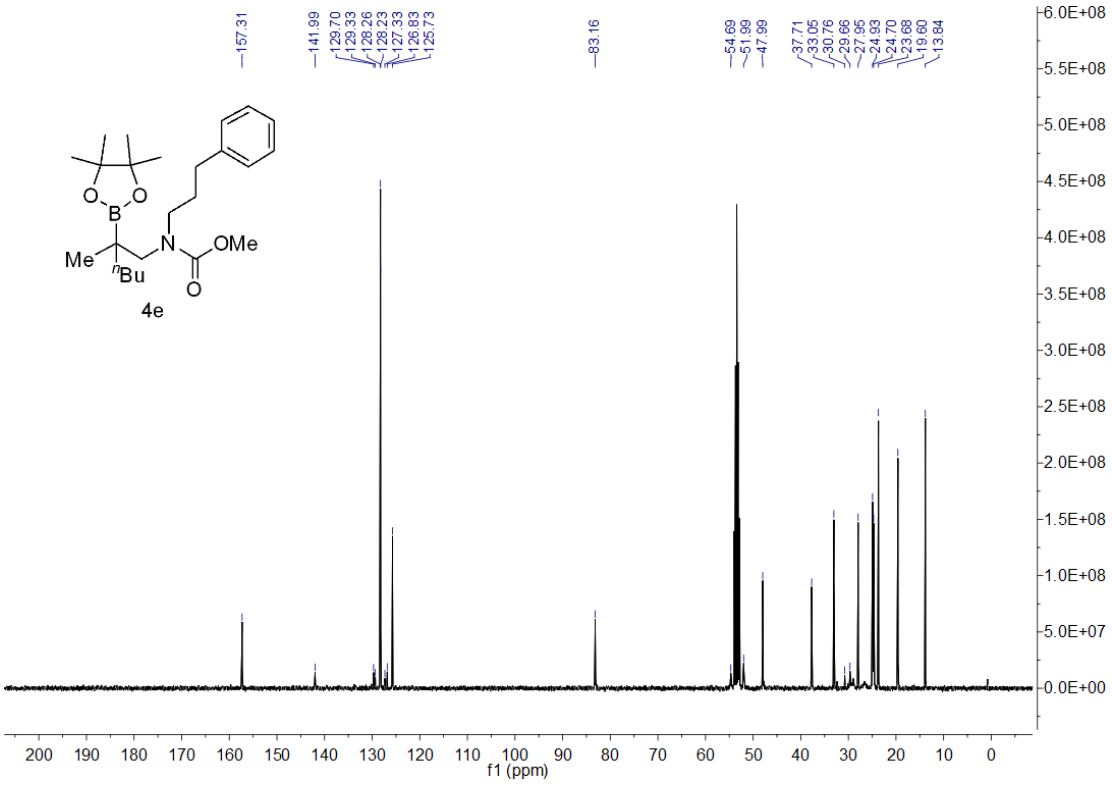

Boc
N
Me
nBu
B
O
O
3.91
0.34
2.64
9.03
19.21
9.10
f1 (ppm)

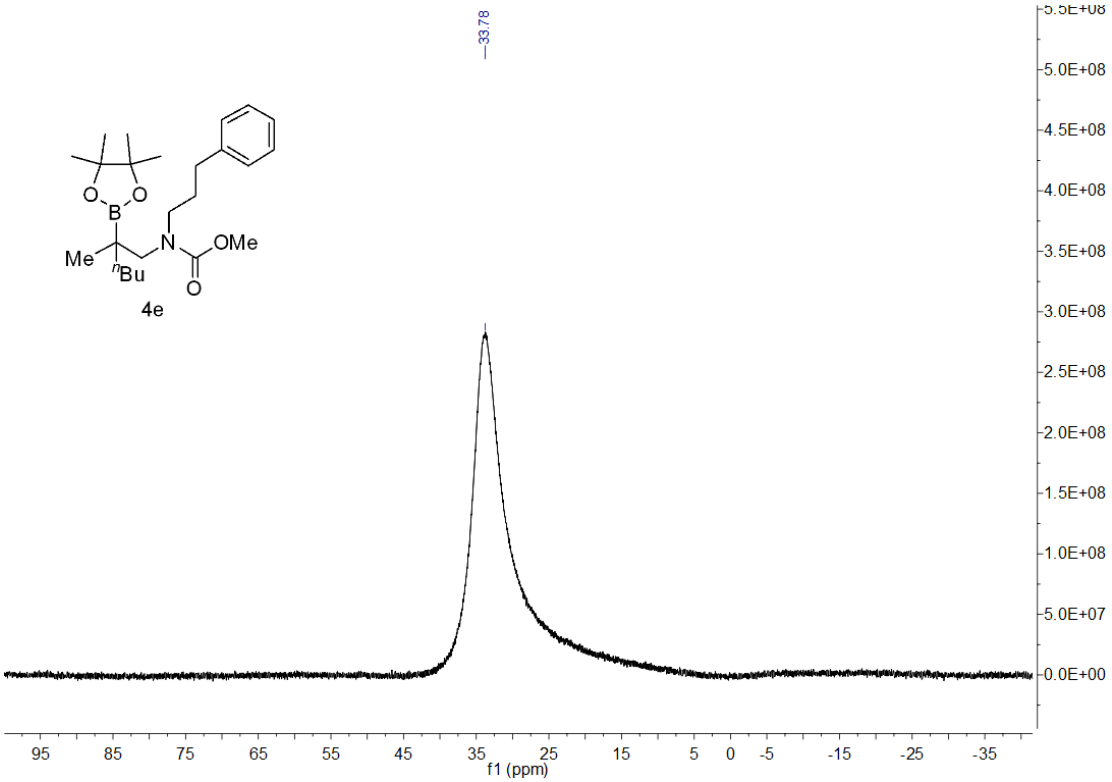
4d

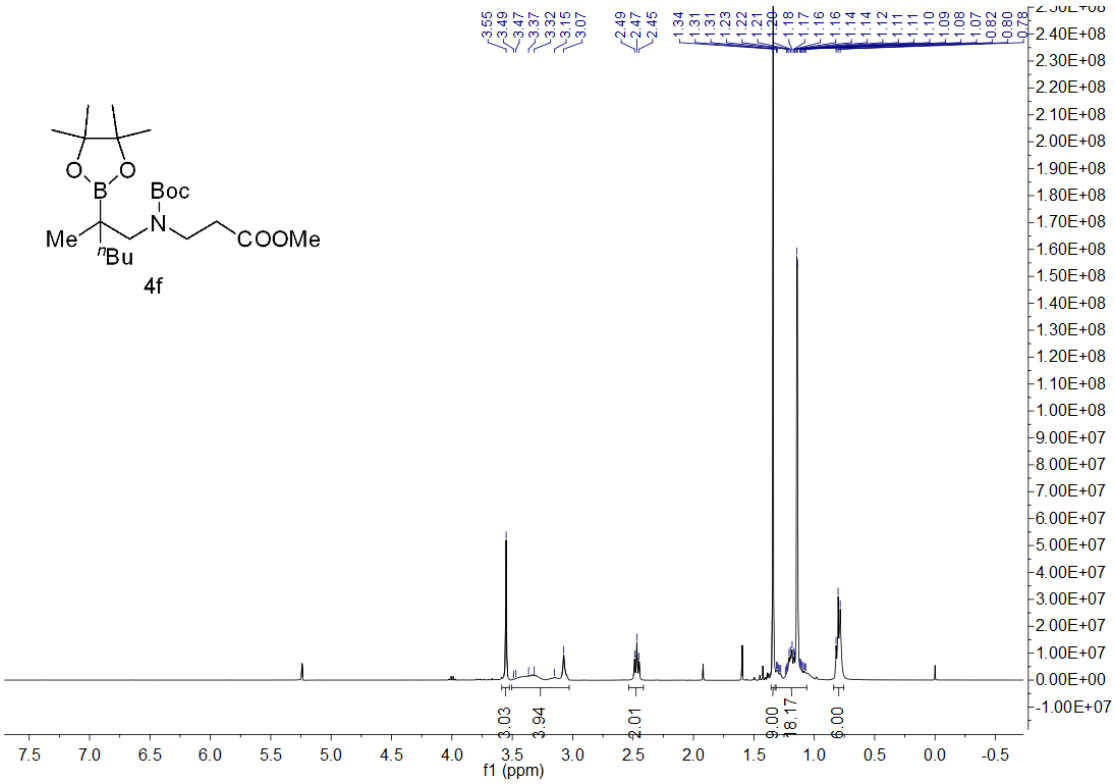

156.01
82.98
78.42
48.20
46.88
37.78
30.30
29.68
29.64
29.36
28.15
27.95
27.84
27.78
24.93
24.70
23.72
20.03
19.37
13.82
13.72
Boc
N
Me
nBu
4d
f1 (ppm)

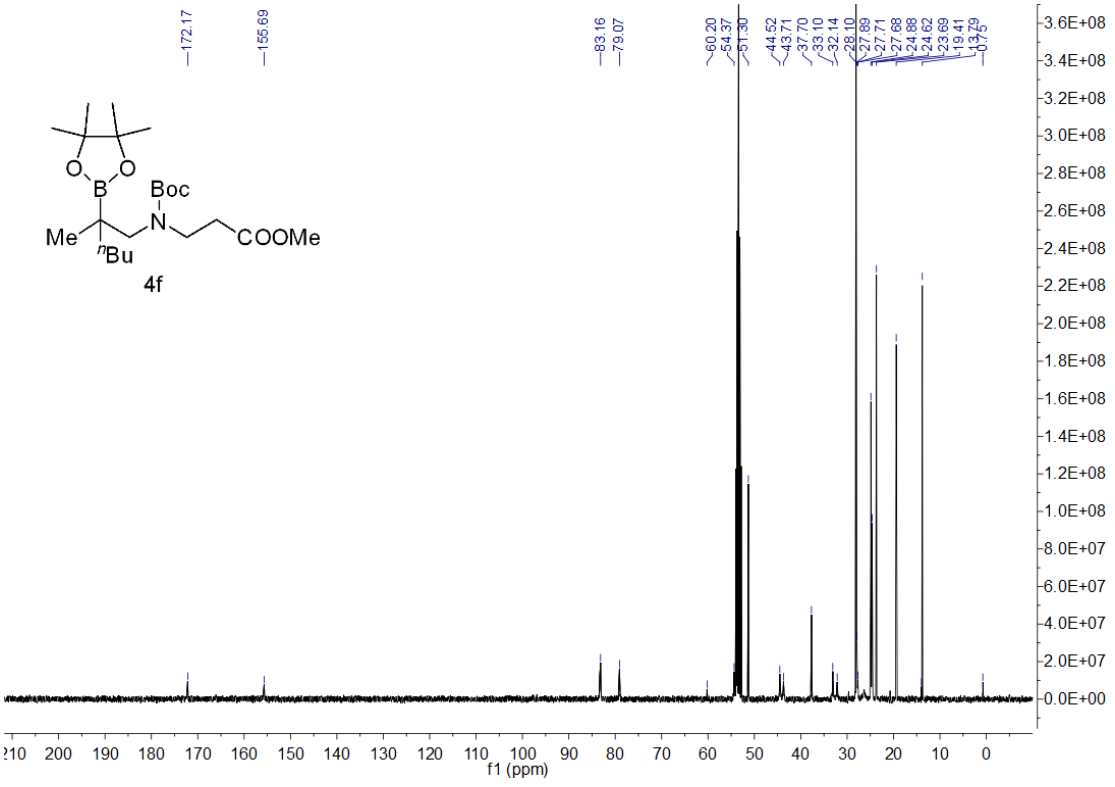

33.61
Boc
N
Me
nBu
4d
f1 (ppm)

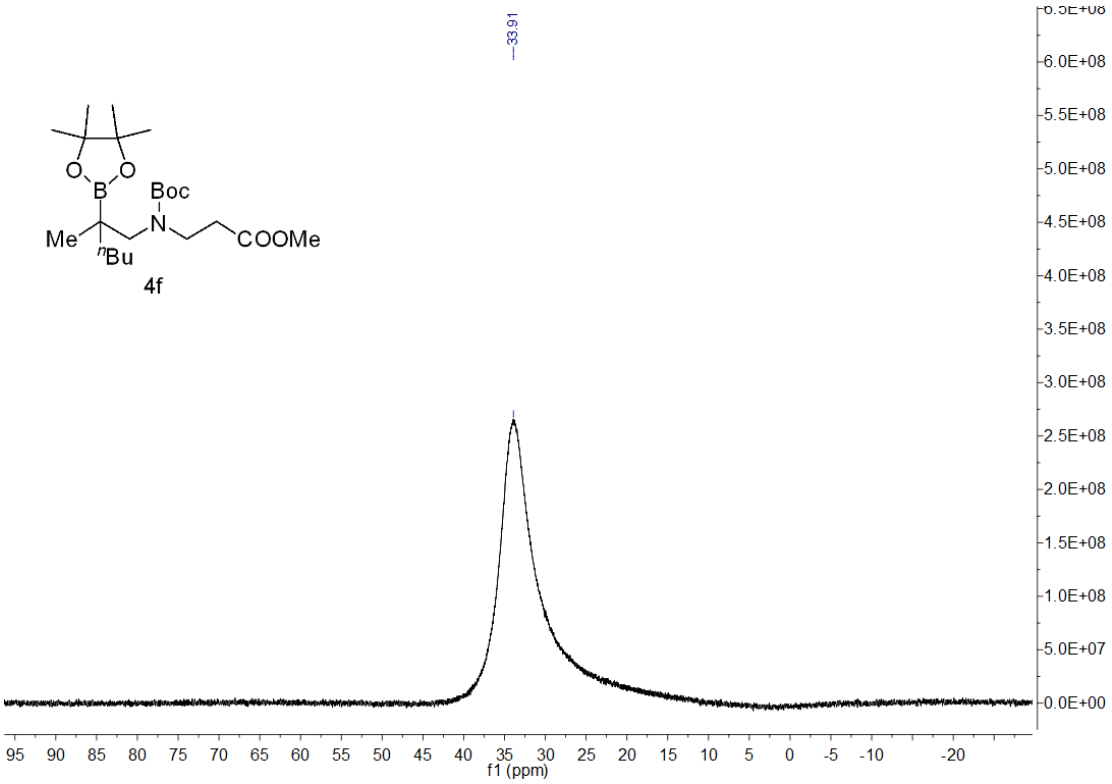

7.22
7.20
7.18
7.17
7.13
7.11
7.10
7.08
3.54
3.15
3.14
3.12
2.52
2.50
2.48
1.80
1.78
1.76
1.74
1.35
1.31
1.21
1.20
1.20
1.19
1.17
1.15
1.14
1.10
1.09
0.83
0.81
0.79
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
O
B
O
N
OMe
Me
nBu
O
4e
2.00
2.98
3.12
3.04
2.04
2.02
1.04
18.24
5.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

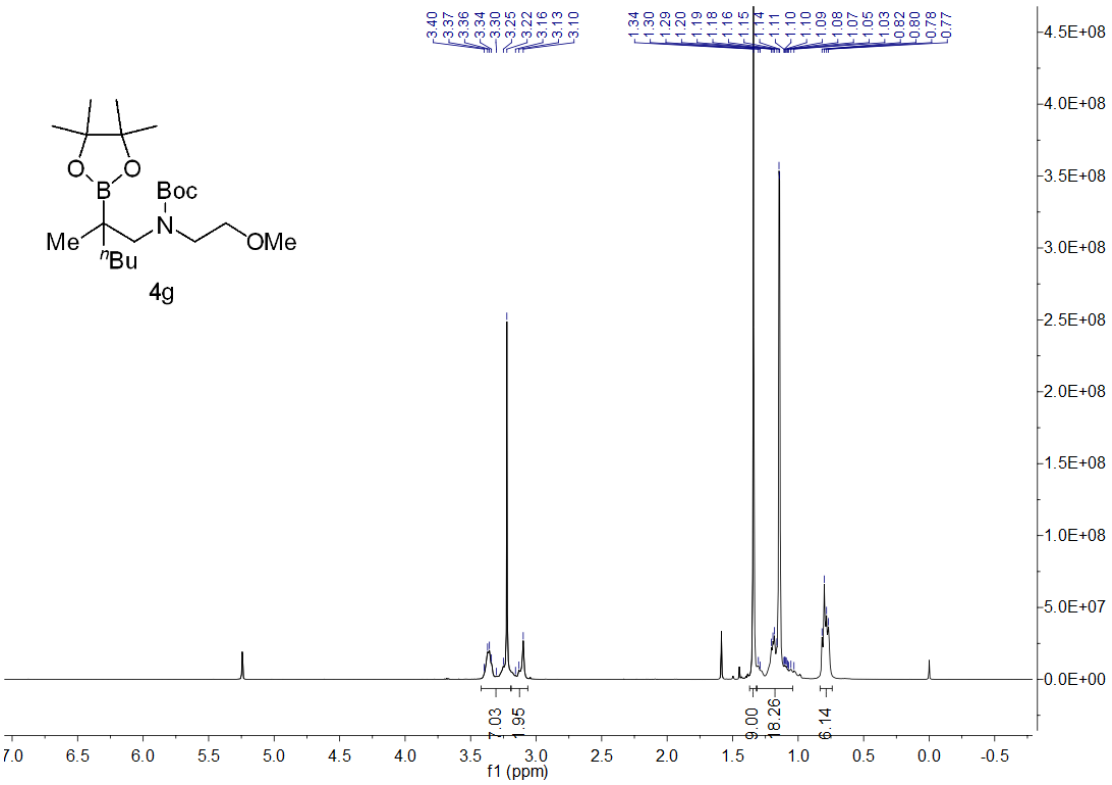

157.31
141.99
129.70
129.33
128.26
128.23
127.33
126.83
125.73
83.16
54.69
51.99
47.99
37.71
33.05
30.76
29.66
27.95
24.93
24.70
23.68
19.60
13.84
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
O
B
O
N
OMe
Me
nBu
O
4e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

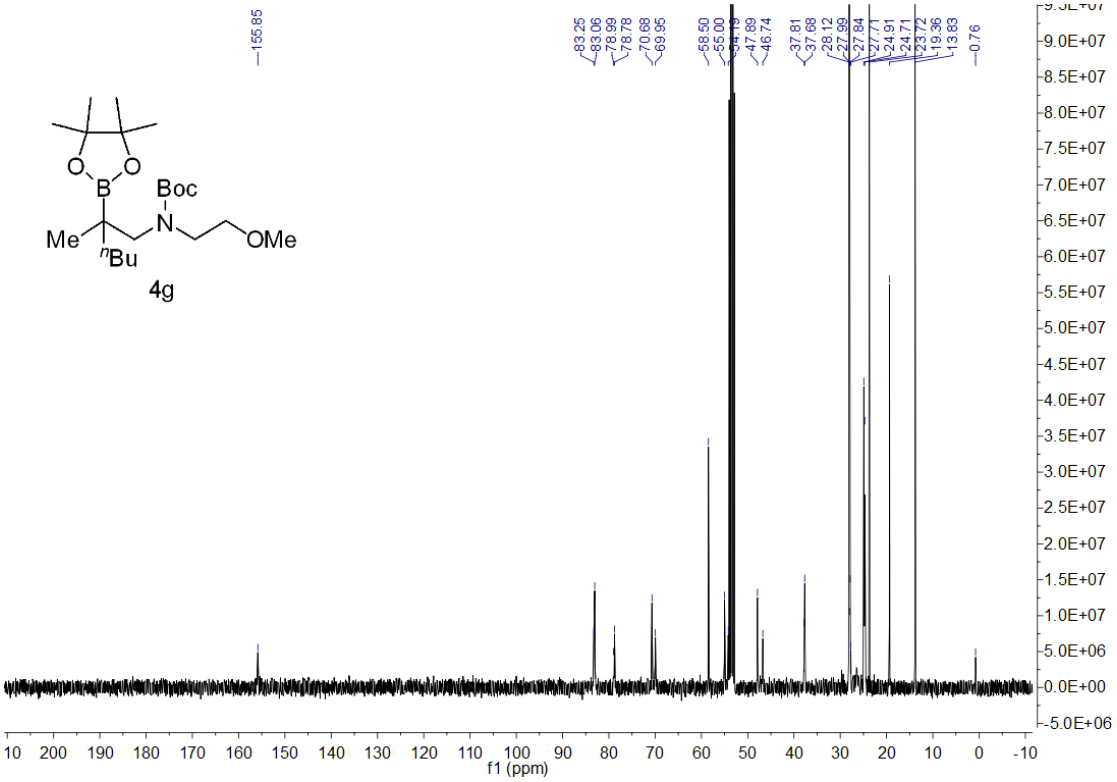

33.78
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
95
85
75
65
55
45
35
25
15
5
0
-5
-15
-25
-35
f1 (ppm)
Me
nBu
OMe
4e

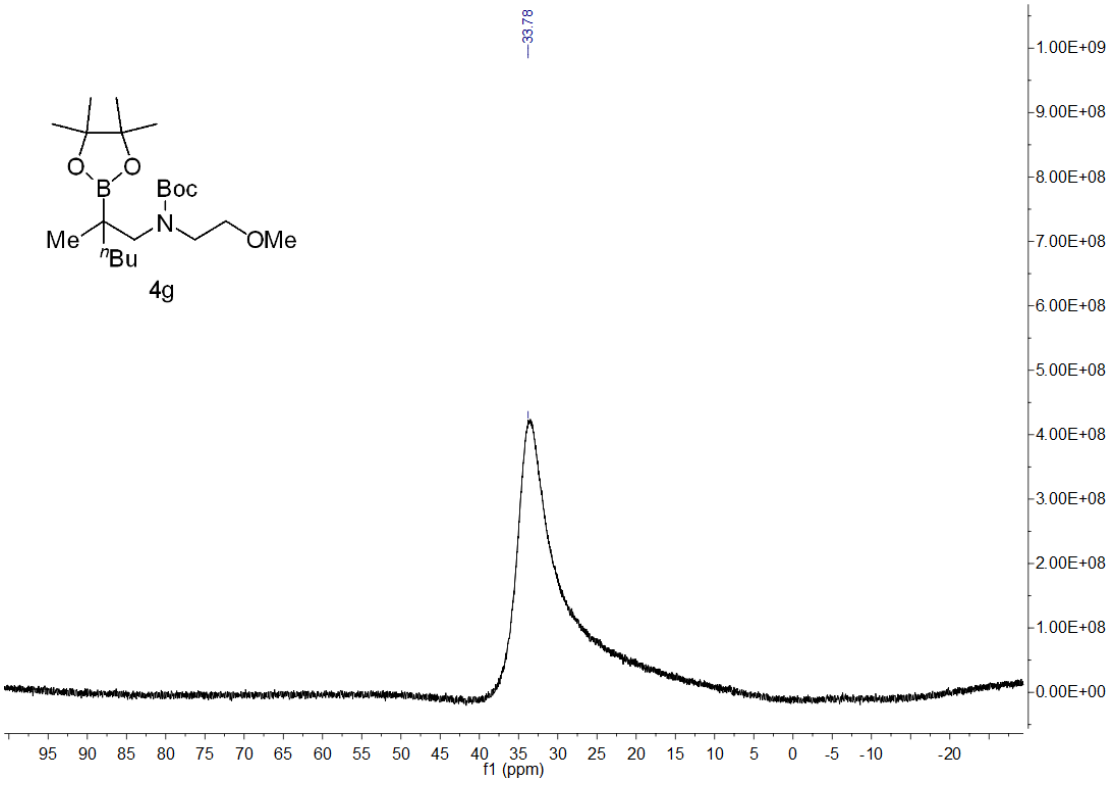

Boc
N
Me
nBu
COOMe
4f
f1 (ppm)

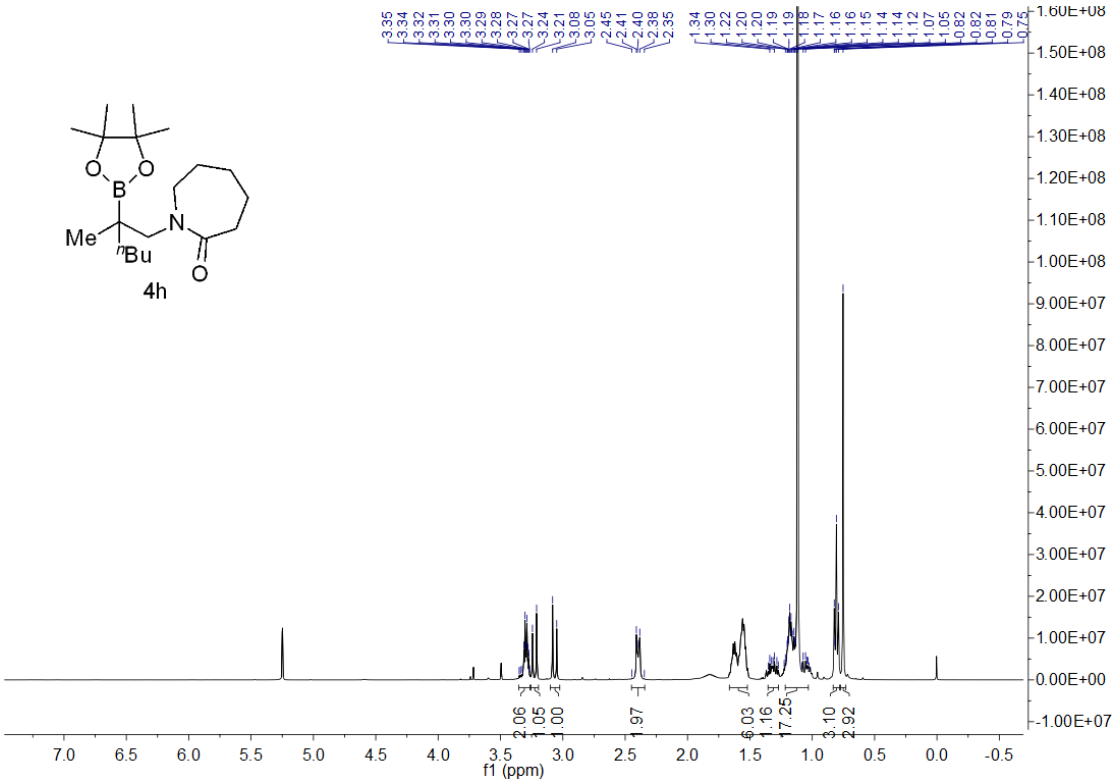

Boc
N
Me
nBu
COOMe
4f
f1 (ppm)

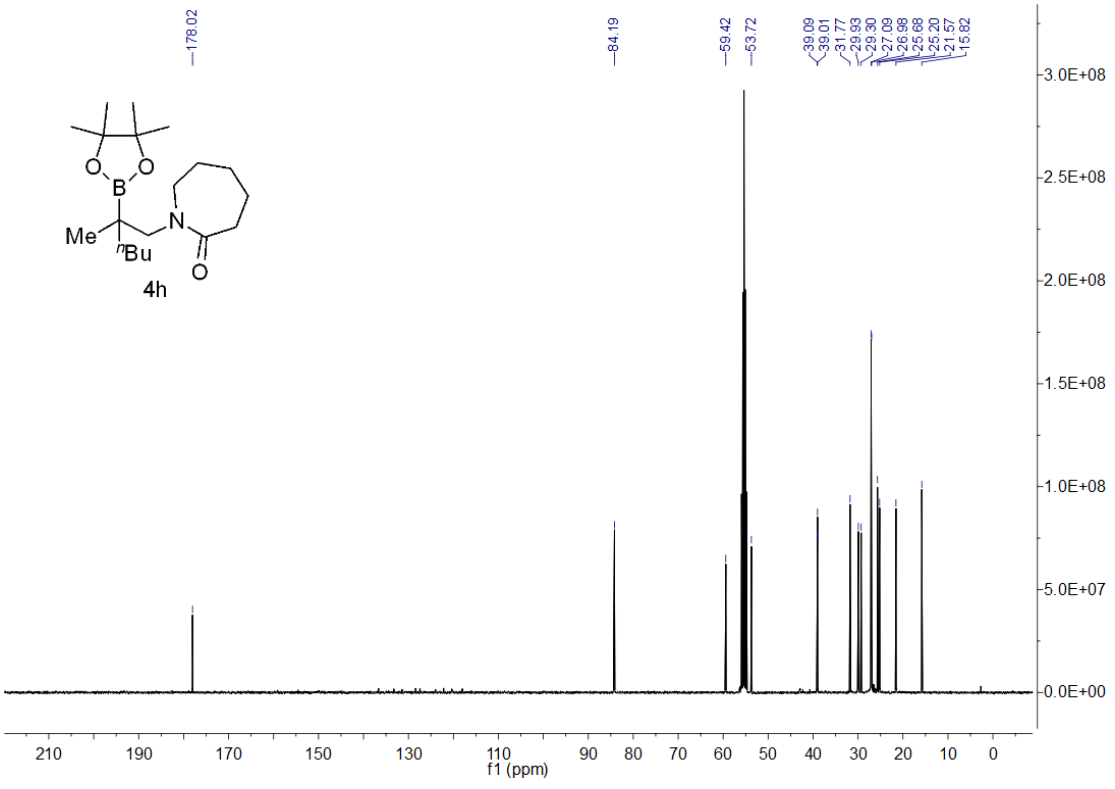

33.91
Boc
N
Me
nBu
COOMe
4f
f1 (ppm)

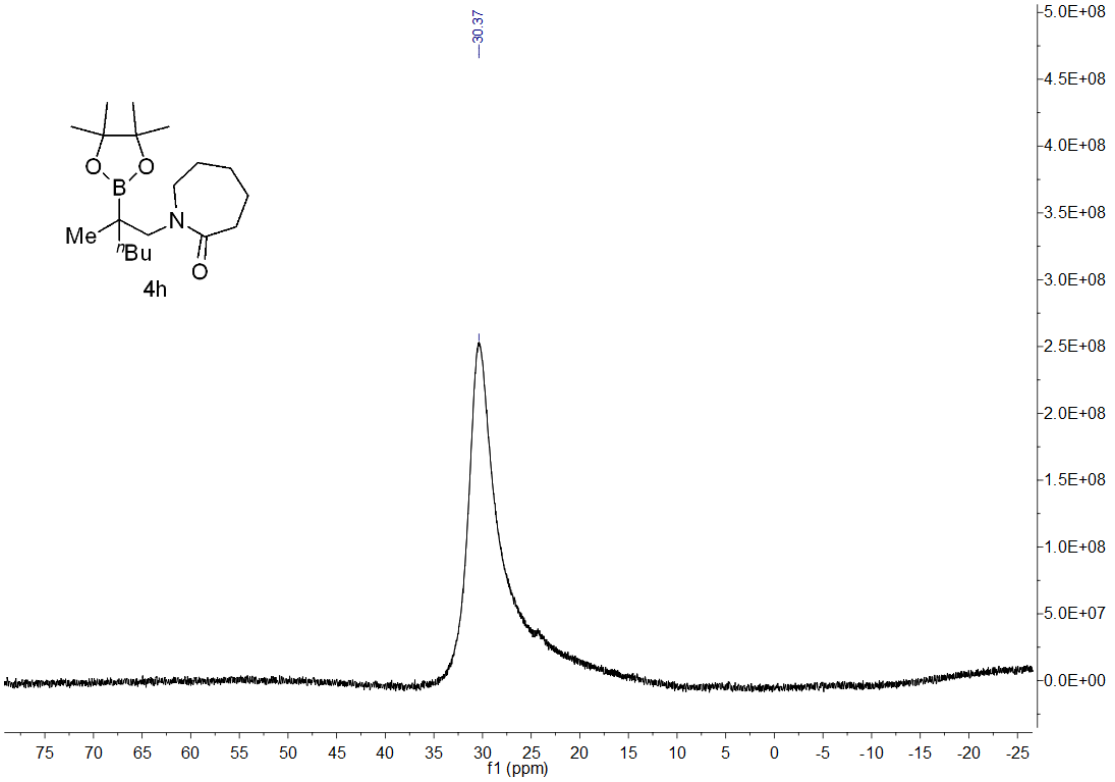

Boc
N
Me
nBu
OMe
4g
7.03
1.95
9.00
18.26
6.14
f1 (ppm)

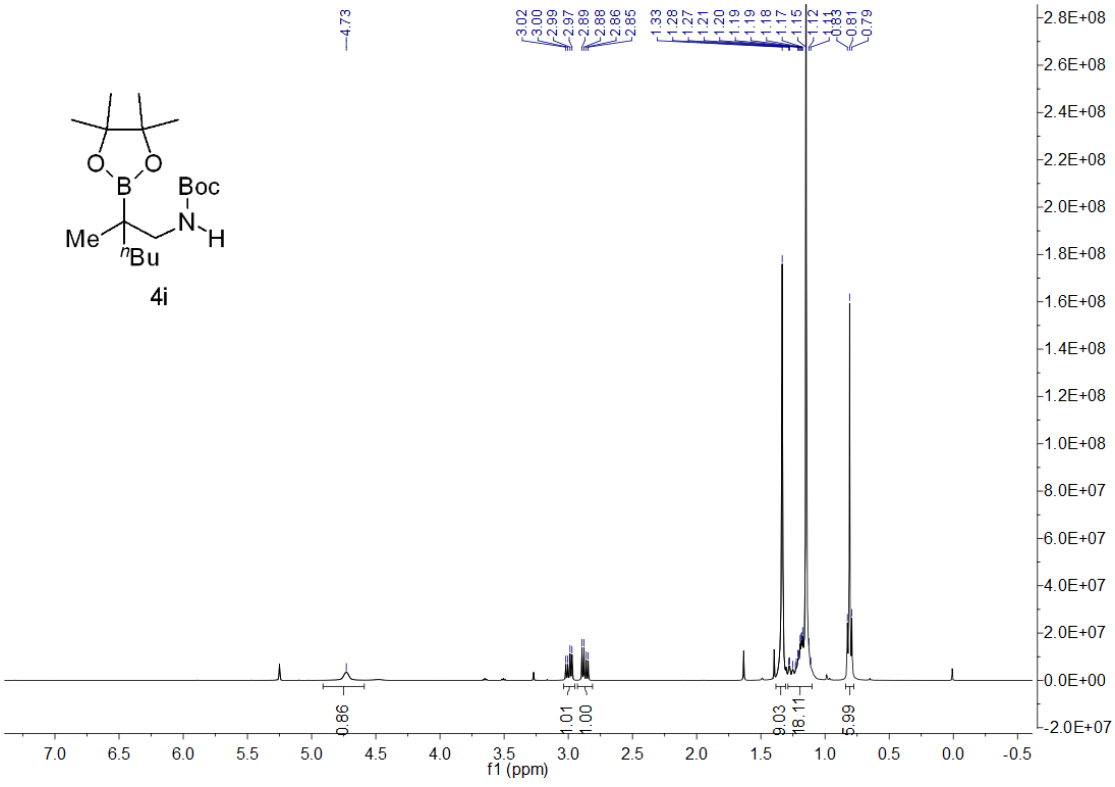

155.85
83.25
83.06
78.99
78.78
70.68
69.95
58.50
55.00
54.19
47.89
46.74
37.81
37.68
28.12
27.89
27.84
27.71
24.91
24.71
23.72
19.36
13.83
0.76
Boc
N
Me
nBu
OMe
4g
f1 (ppm)

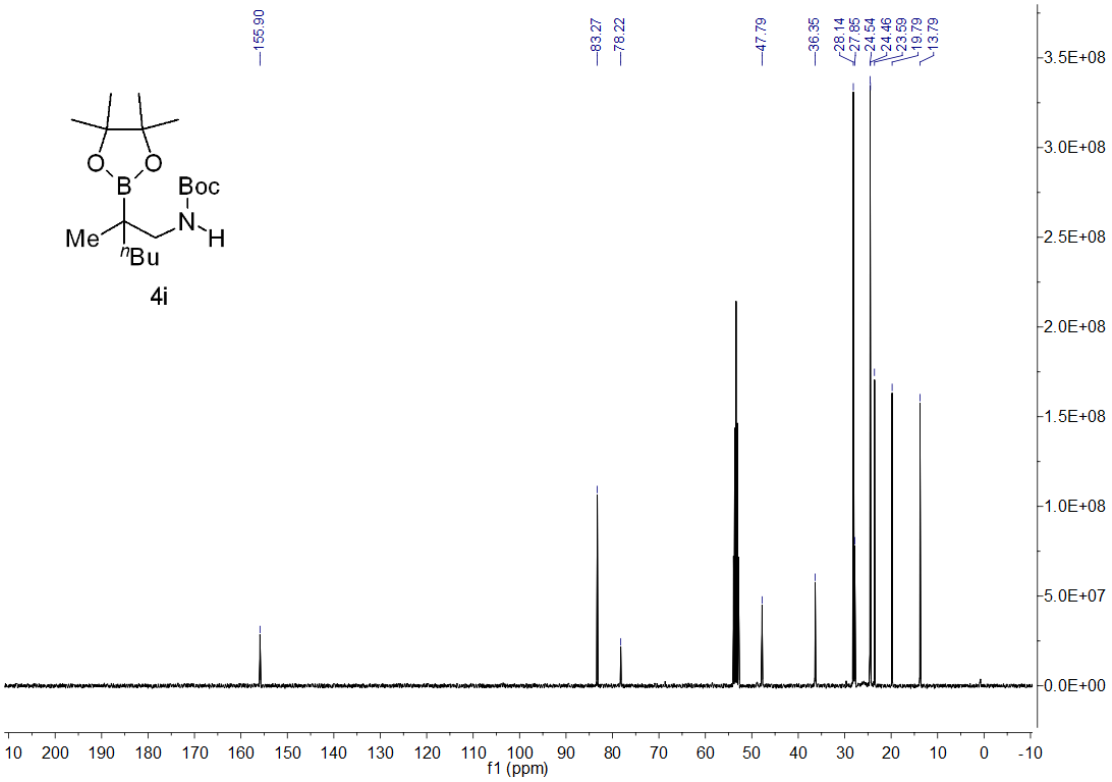

33.78
Boc
N
Me
nBu
OMe
4g
f1 (ppm)

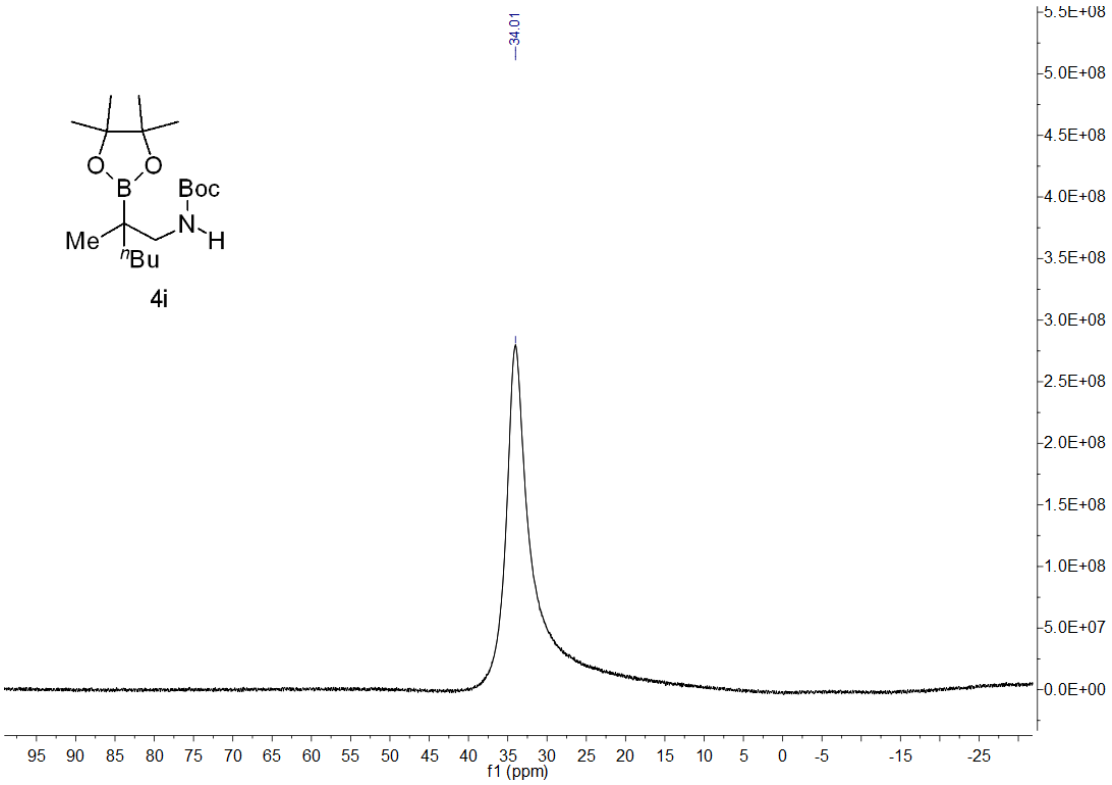

4h
f1 (ppm)

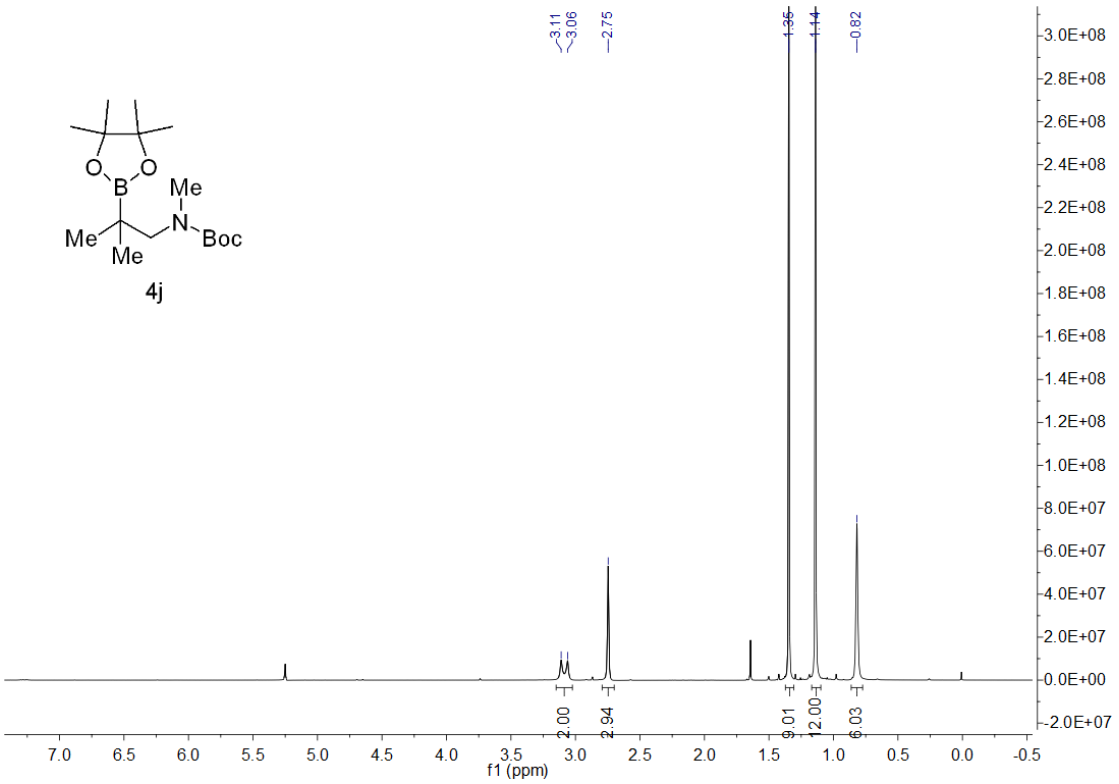

4h
f1 (ppm)

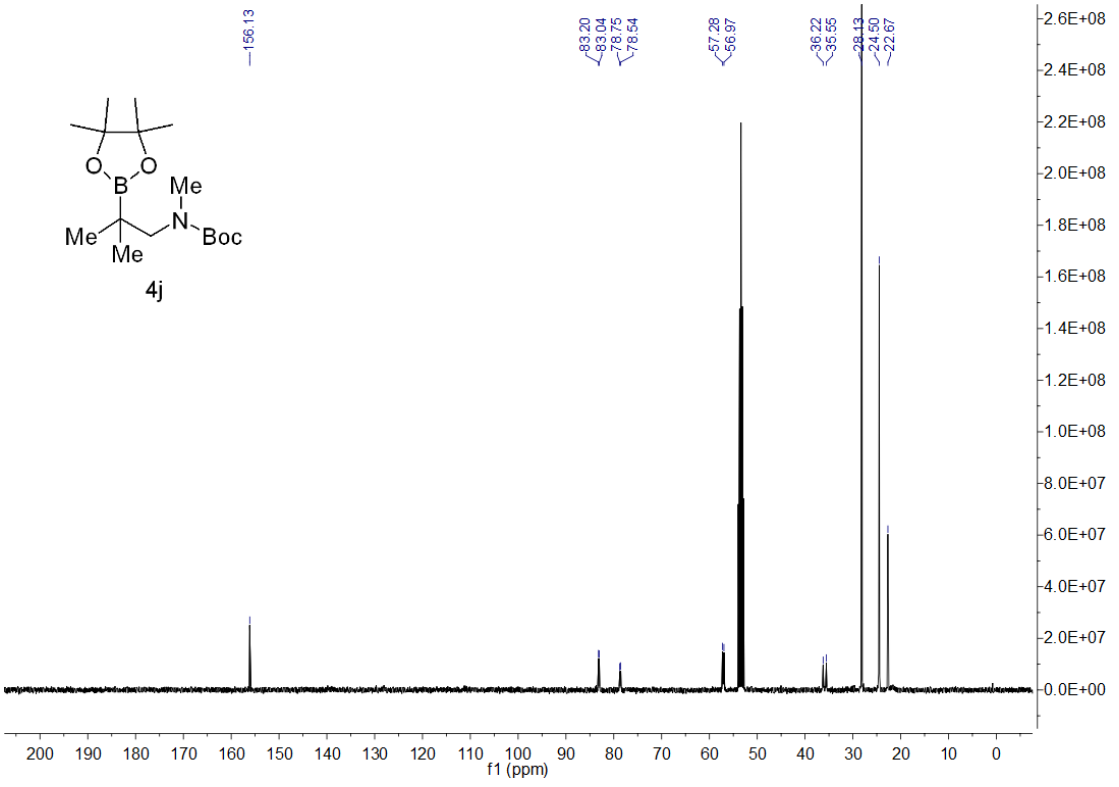

30.37
Me
nBu
B
O
O
N
O
4h
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25
f1 (ppm)

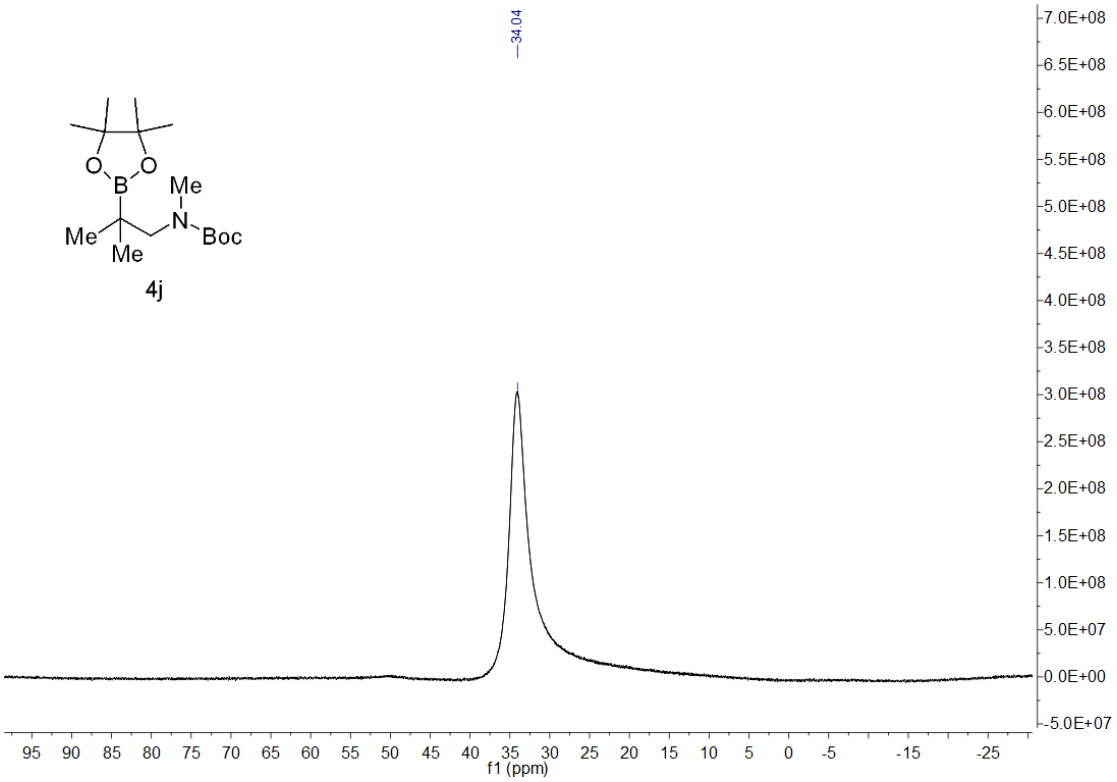

4.73
3.02
3.00
2.99
2.97
2.89
2.88
2.86
2.85
1.33
1.28
1.27
1.21
1.20
1.19
1.19
1.18
1.17
1.15
1.12
0.83
0.81
0.79
Boc
N
H
Me
nBu
B
O
O
4i
0.86
1.01
1.00
9.03
18.11
5.99
2.8E+08
2.6E+08
2.4E+08
2.2E+08
2.0E+08
1.8E+08
1.6E+08
1.4E+08
1.2E+08
1.0E+08
8.0E+07
6.0E+07
4.0E+07
2.0E+07
0.0E+00
-2.0E+07
7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

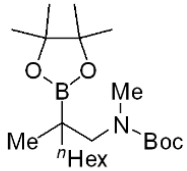

155.90
83.27
78.22
47.79
36.35
28.14
27.85
24.54
24.46
23.59
19.79
13.79
Boc
N
H
Me
nBu
4i
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
f1 (ppm)


34.01
Boc
N
H
Me
nBu
4i
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
f1 (ppm)


3.11
3.06
2.75
1.35
1.14
0.82
2.00
2.94
9.01
12.00
6.03
f1 (ppm)
Me
B
O
O
N
Boc
Me
Me
4j


156.13
83.20
83.04
78.75
78.54
57.28
56.97
36.22
35.55
28.13
24.50
22.67
f1 (ppm)
Me
B
O
O
N
Boc
Me
Me
4j


34.04
7.0E+08
6.5E+08
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -15 -25
f1 (ppm)

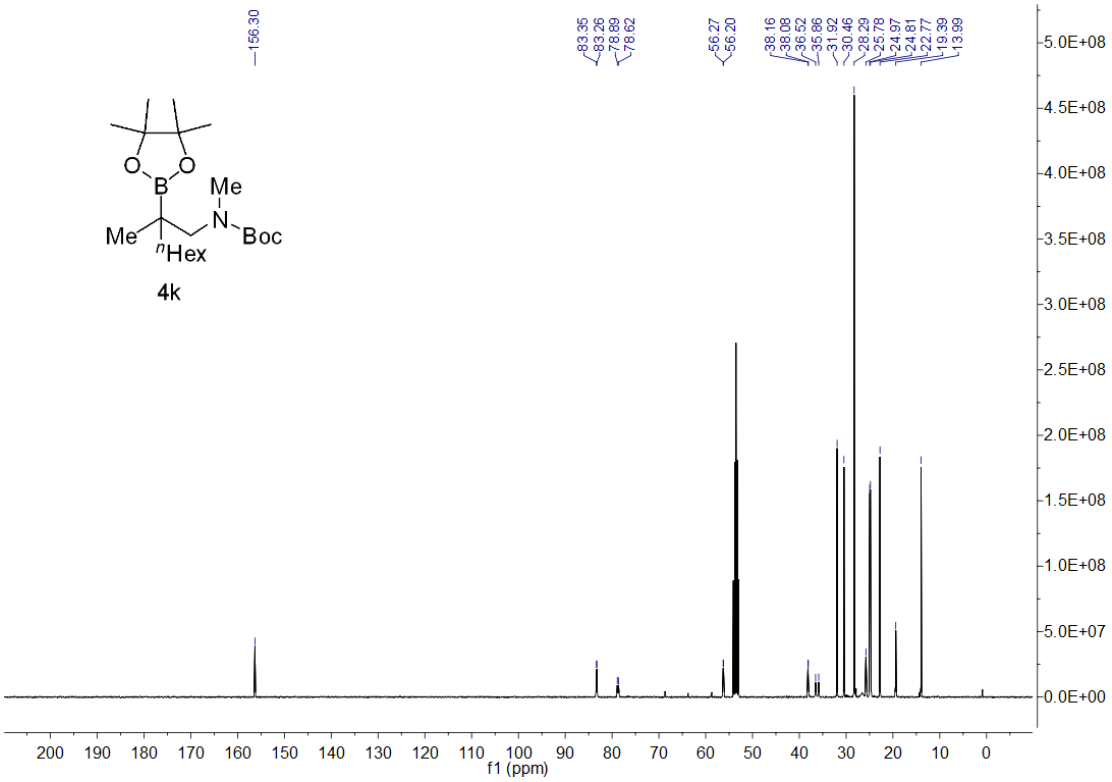

O
B
O
Me
N
Boc
Me
Me

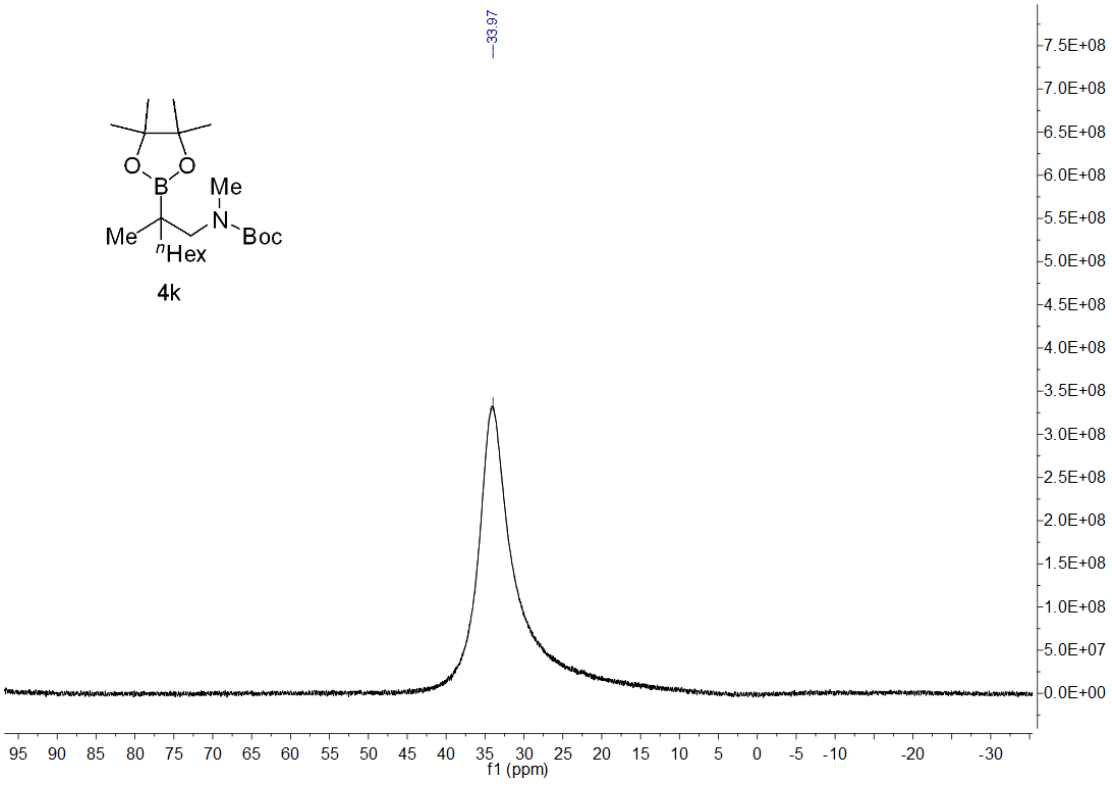
4j

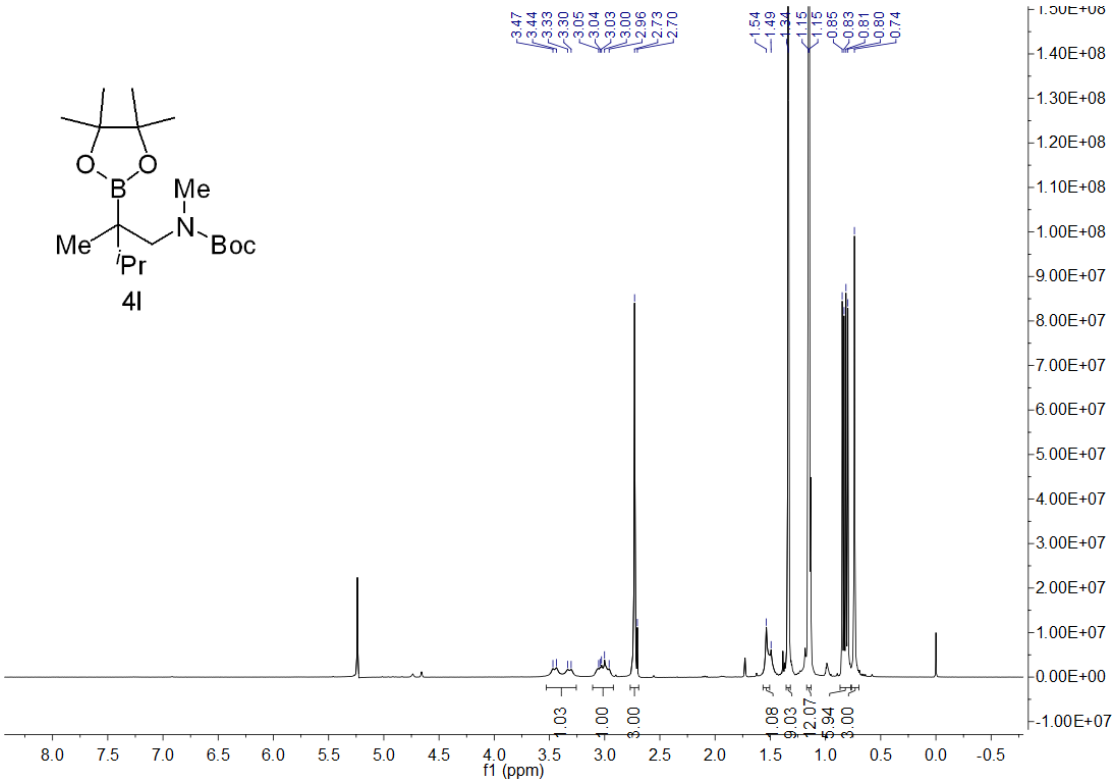
3.24
3.20
3.16
3.16
3.13
3.05
3.02
2.74
1.34
1.23
1.22
1.20
1.18
1.14
1.14
1.07
1.05
1.03
0.81
0.80
0.78
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
1.08
1.02
3.00
9.01
22.08
6.01
6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

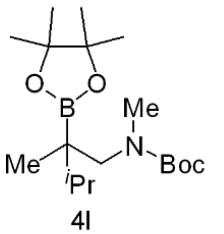
O
B
O
Me
N
Boc
Me
nHex

4k


156.30
83.35
83.26
78.89
78.62
56.27
56.20
38.16
38.08
36.52
35.86
31.92
30.46
28.29
25.78
24.97
24.81
22.77
19.39
13.99
Me
N
Boc
Me
nHex
4k
f1 (ppm)


33.97
Me
N
Boc
Me
nHex
4k
f1 (ppm)


3.47
3.44
3.33
3.30
3.05
3.04
3.03
3.00
2.96
2.73
2.70
1.54
1.49
1.34
1.15
0.85
0.83
0.81
0.80
0.74
1.03
1.00
3.00
1.08
9.03
12.07
5.94
3.00
f1 (ppm)

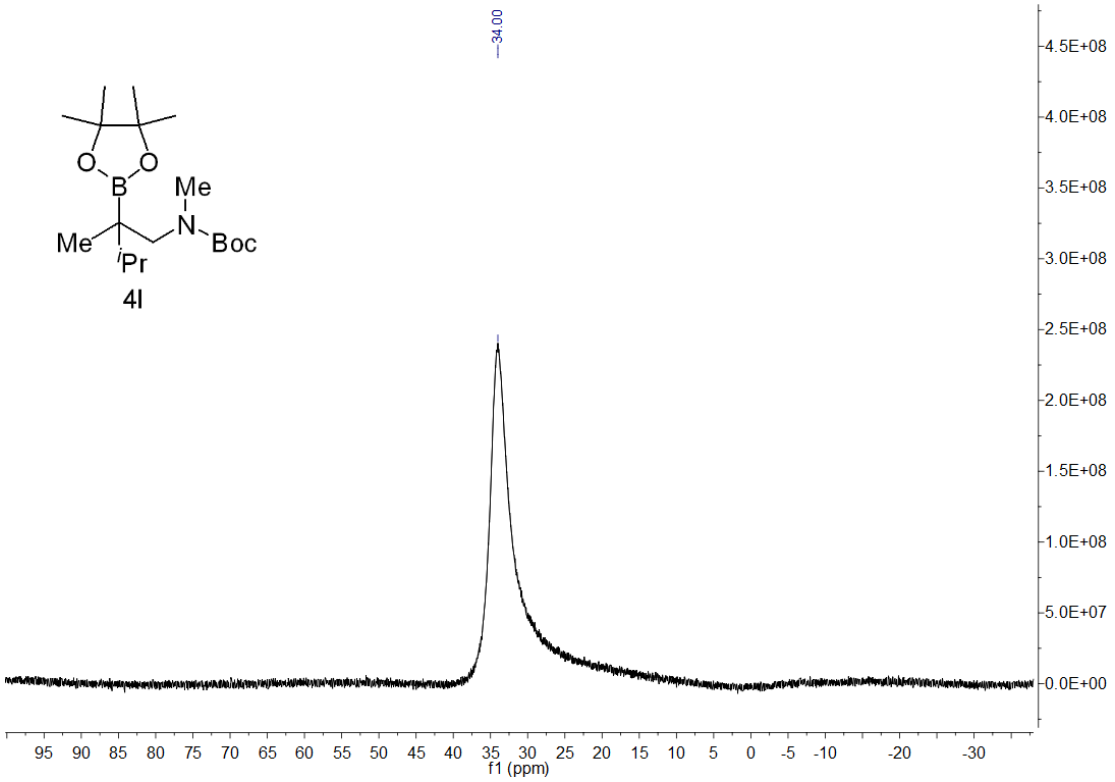

Me
B
O
O
Me
N
Boc
iPr

4l

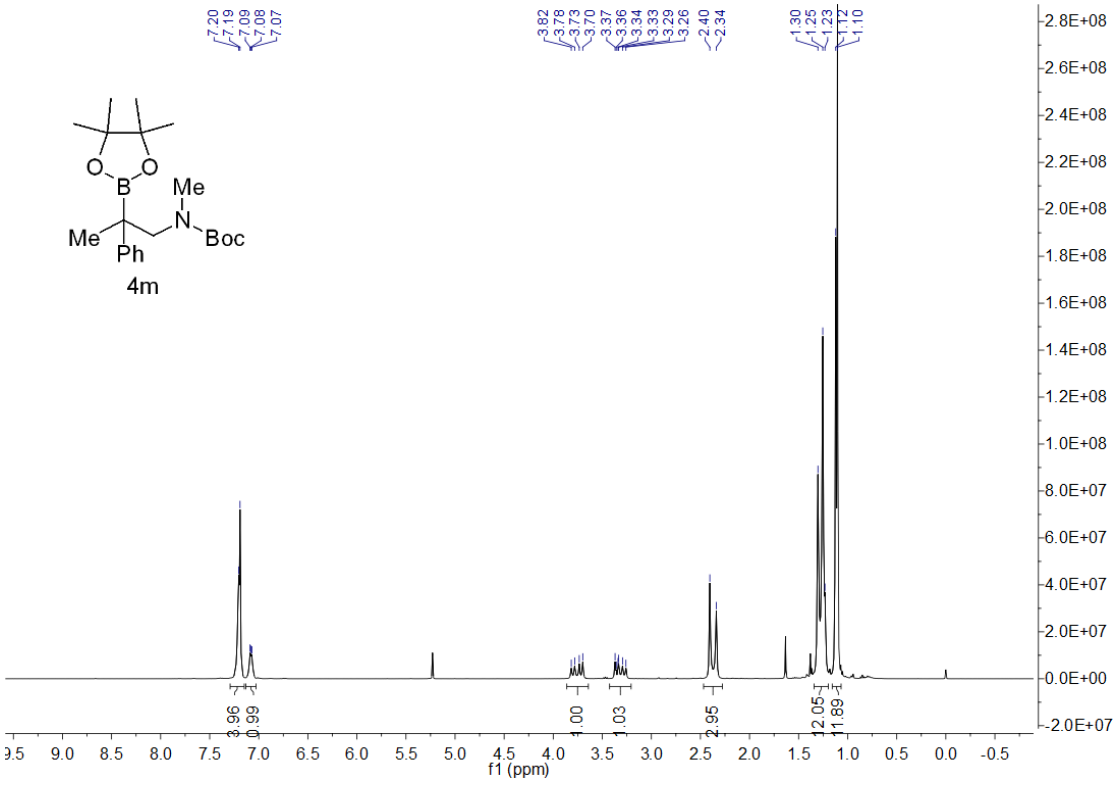
156.18
83.22
78.75
35.17
34.21
28.16
28.09
27.92
25.06
24.80
24.55
24.39
21.59
19.00
18.11
15.62
15.55
0.75
f1 (ppm)

Me
B
O
O
Me
N
Boc
iPr

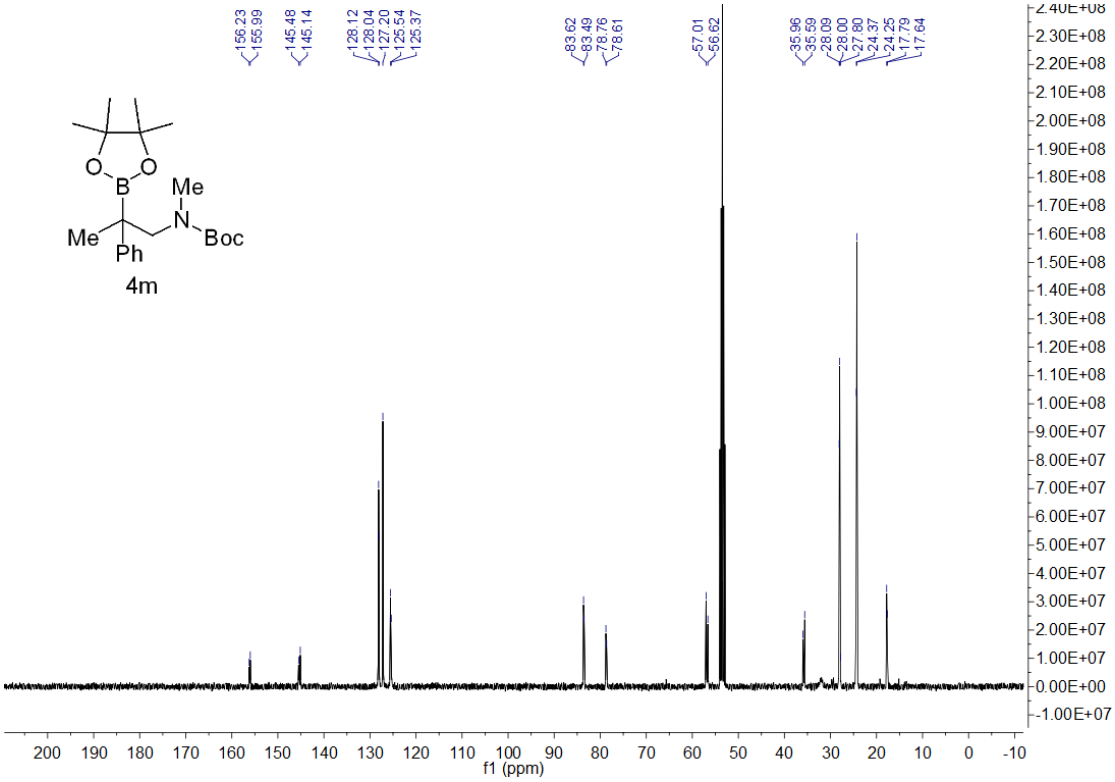
4l


34.00
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -20 -30
f1 (ppm)
O
O
B
Me
N
Boc
Me
iPr

4l


7.20
7.19
7.09
7.08
7.07
3.82
3.78
3.73
3.70
3.37
3.36
3.34
3.33
3.29
3.26
2.40
2.34
1.30
1.25
1.23
1.12
1.10
2.8E+08
2.6E+08
2.4E+08
2.2E+08
2.0E+08
1.8E+08
1.6E+08
1.4E+08
1.2E+08
1.0E+08
8.0E+07
6.0E+07
4.0E+07
2.0E+07
0.0E+00
-2.0E+07
3.96
0.99
1.00
1.03
2.95
12.05
11.89
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
O
O
B
Me
N
Boc
Me
Ph

4m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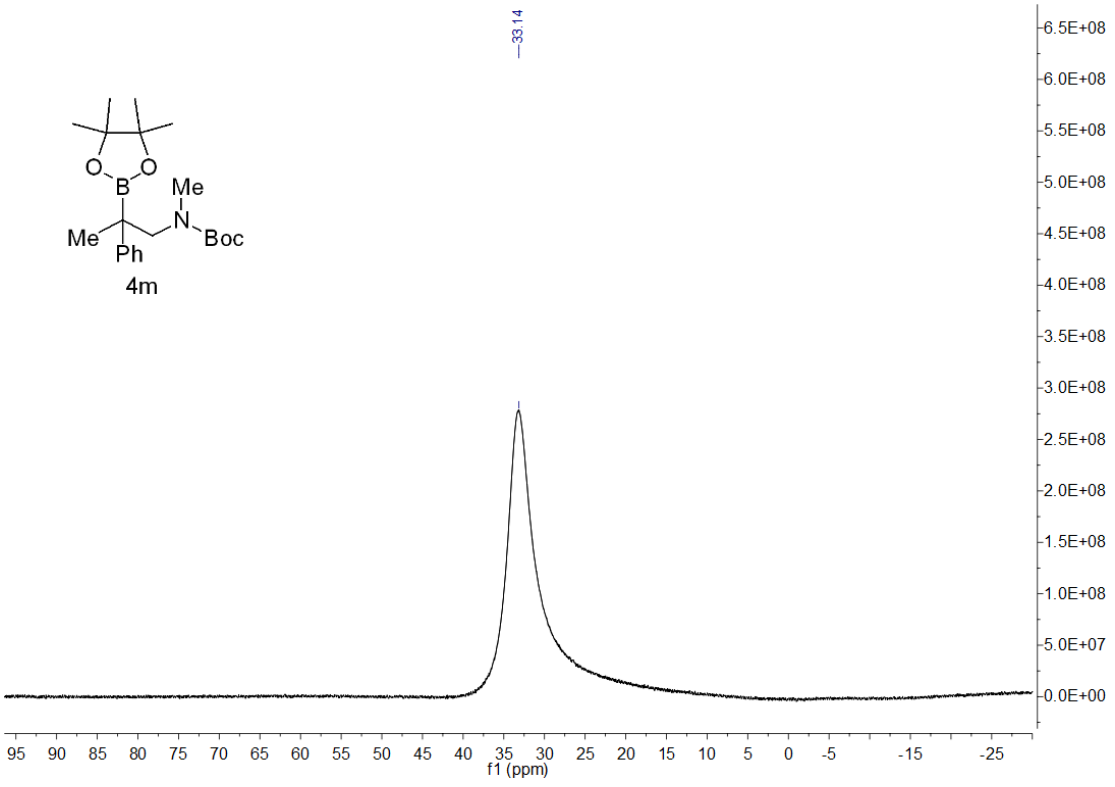
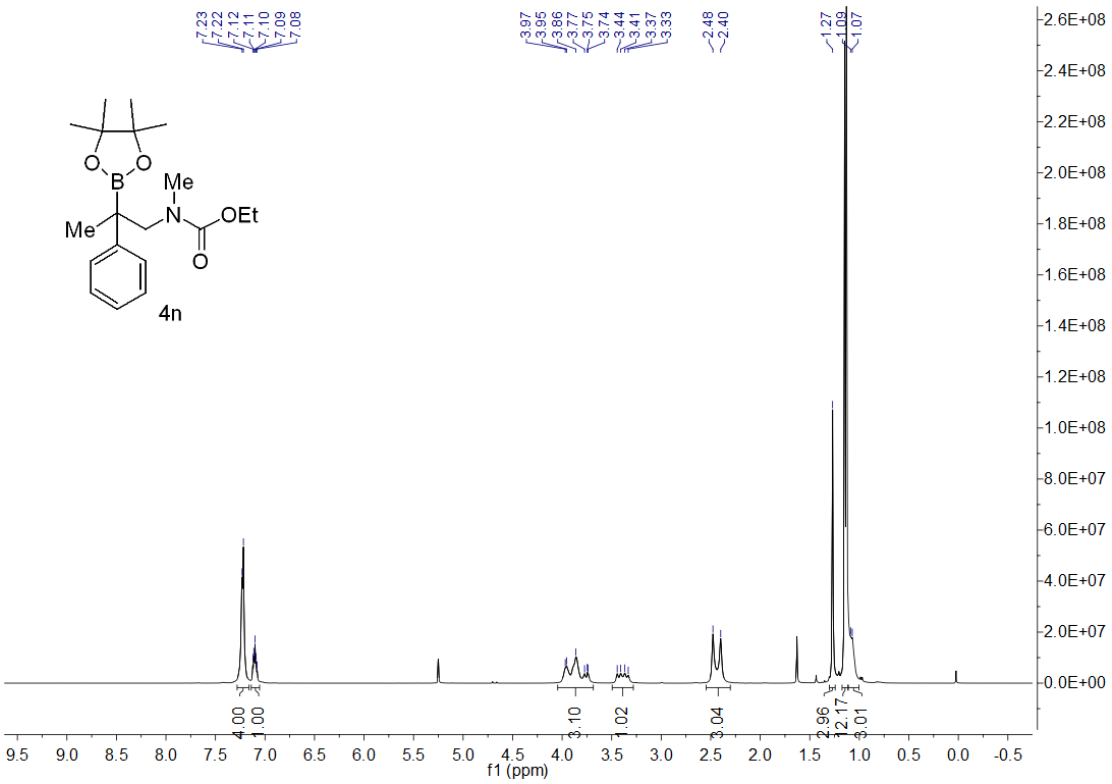
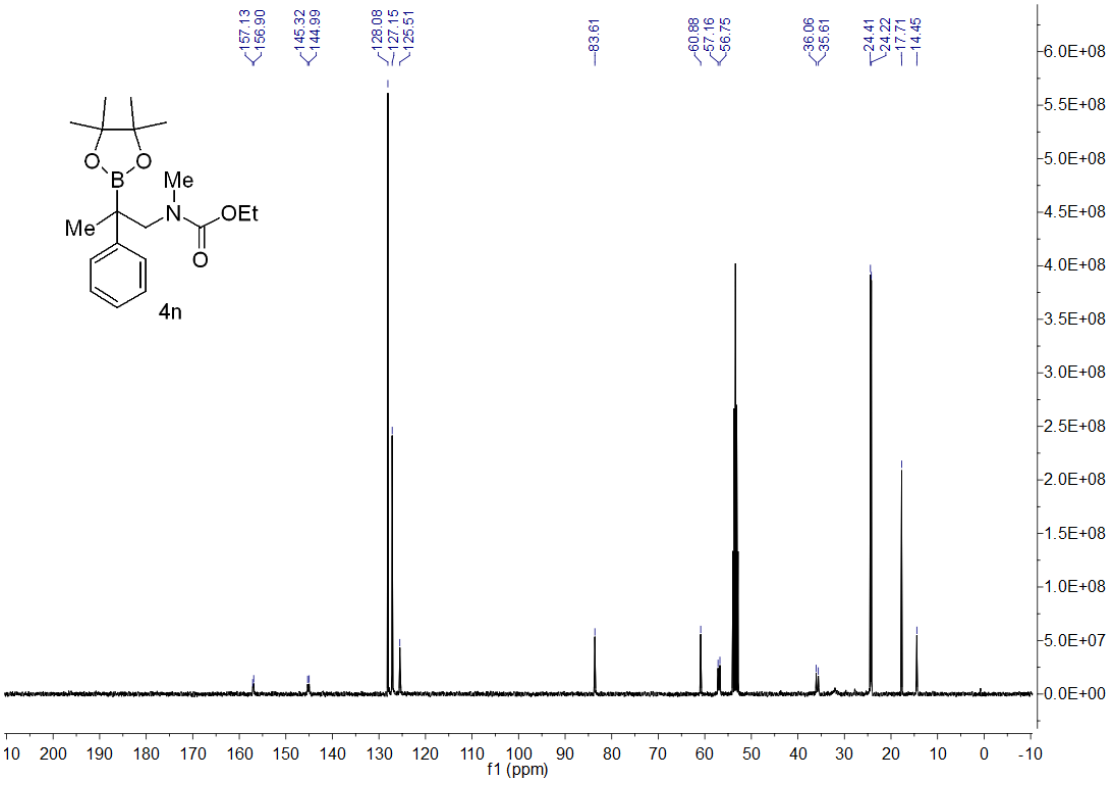
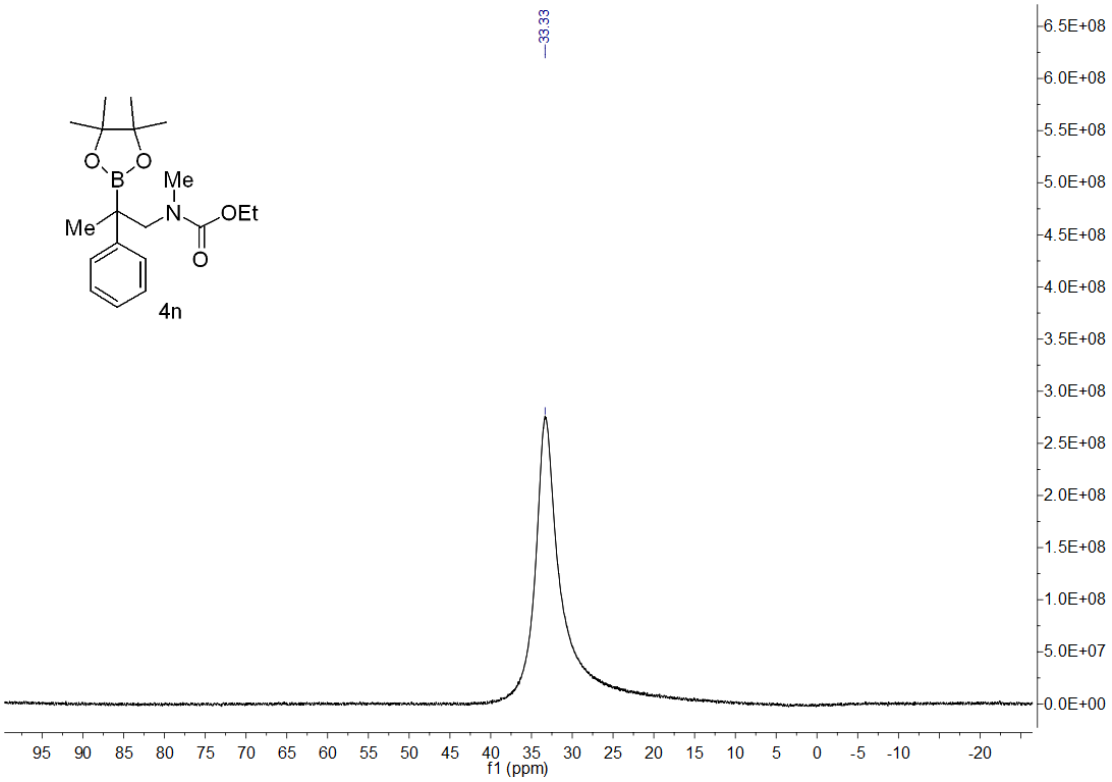
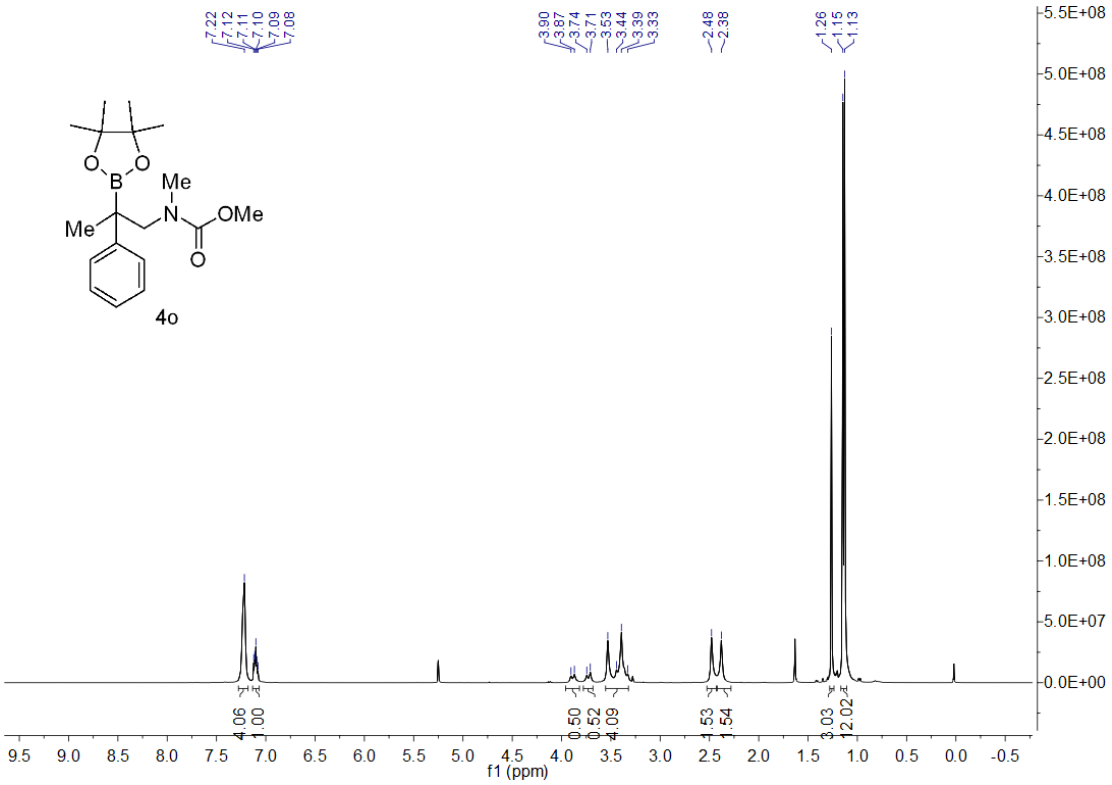
155.99
145.48
145.14
128.12
128.04
127.20
125.54
125.37
83.62
83.49
78.76
78.61
57.01
56.62
35.96
35.59
28.09
28.00
27.80
24.37
24.25
17.79
17.64
O
B
O
Me
N
Me
Boc
Ph
4m
f1 (ppm)

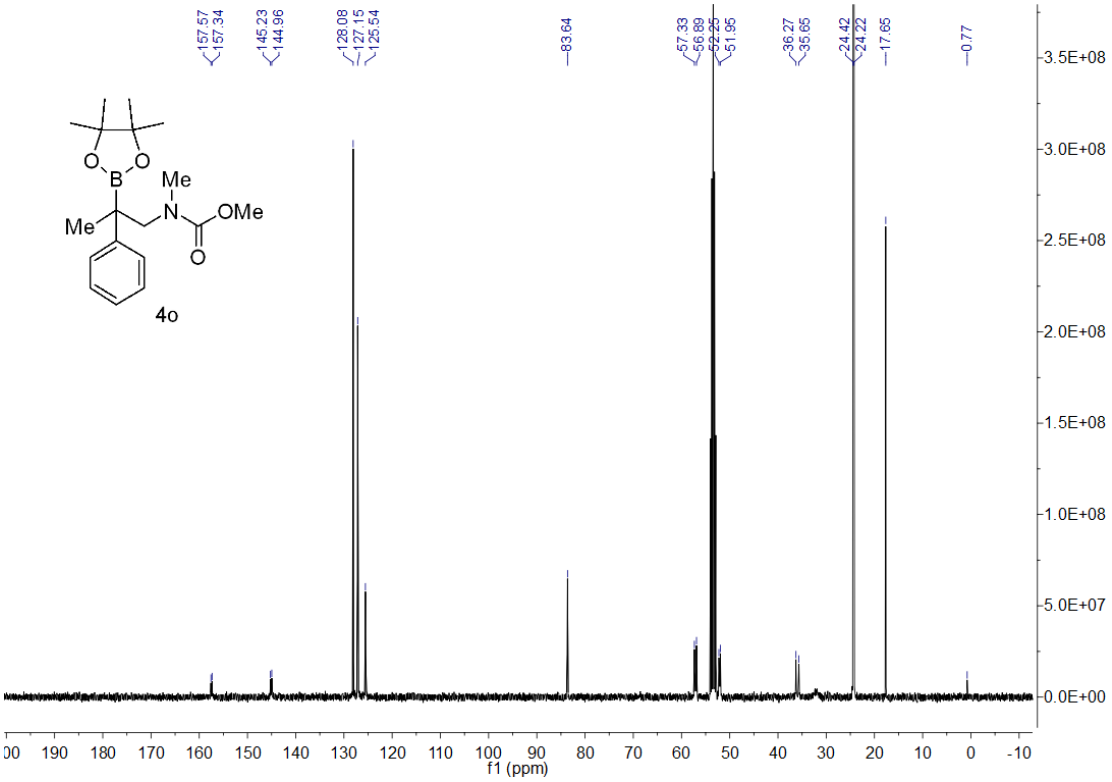

33.14
O
B
O
Me
N
Me
Boc
Ph
4m
f1 (ppm)

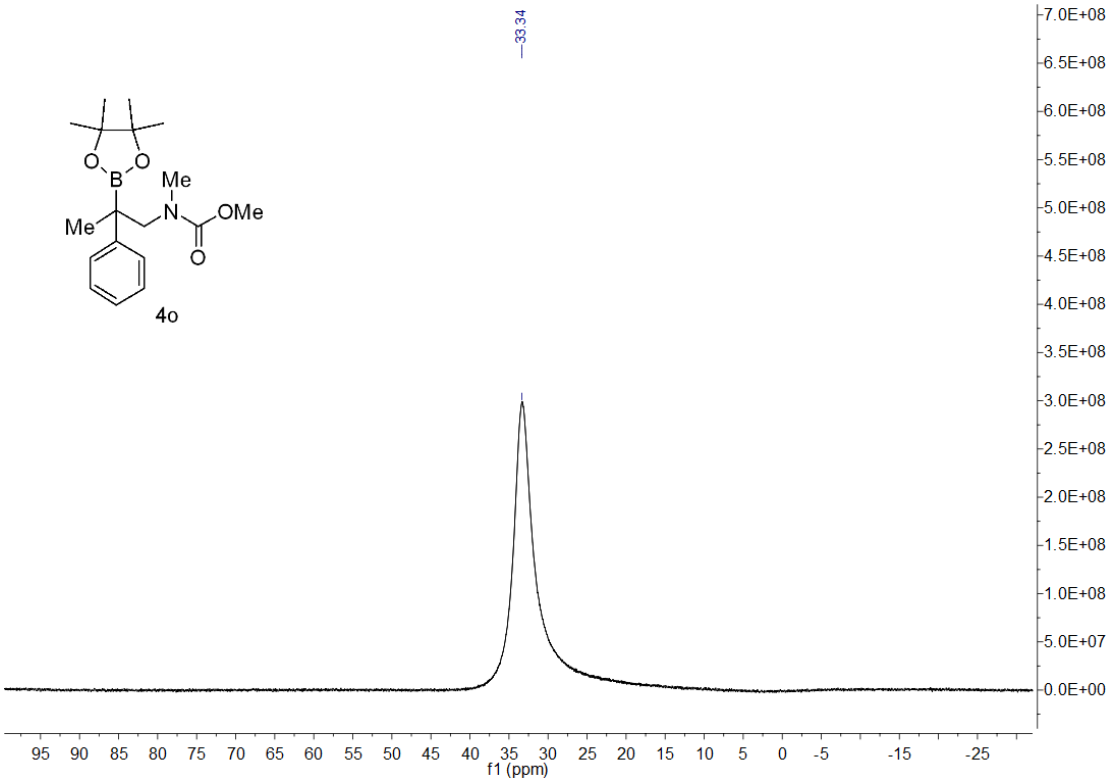

7.23
7.22
7.12
7.11
7.10
7.09
7.08
3.97
3.95
3.86
3.77
3.75
3.74
3.44
3.41
3.37
3.33
2.48
2.40
1.27
1.09
1.07
Me
N
OEt
O
Me
4n
4.00
1.00
3.10
1.02
3.04
2.96
12.17
3.01
f1 (ppm)

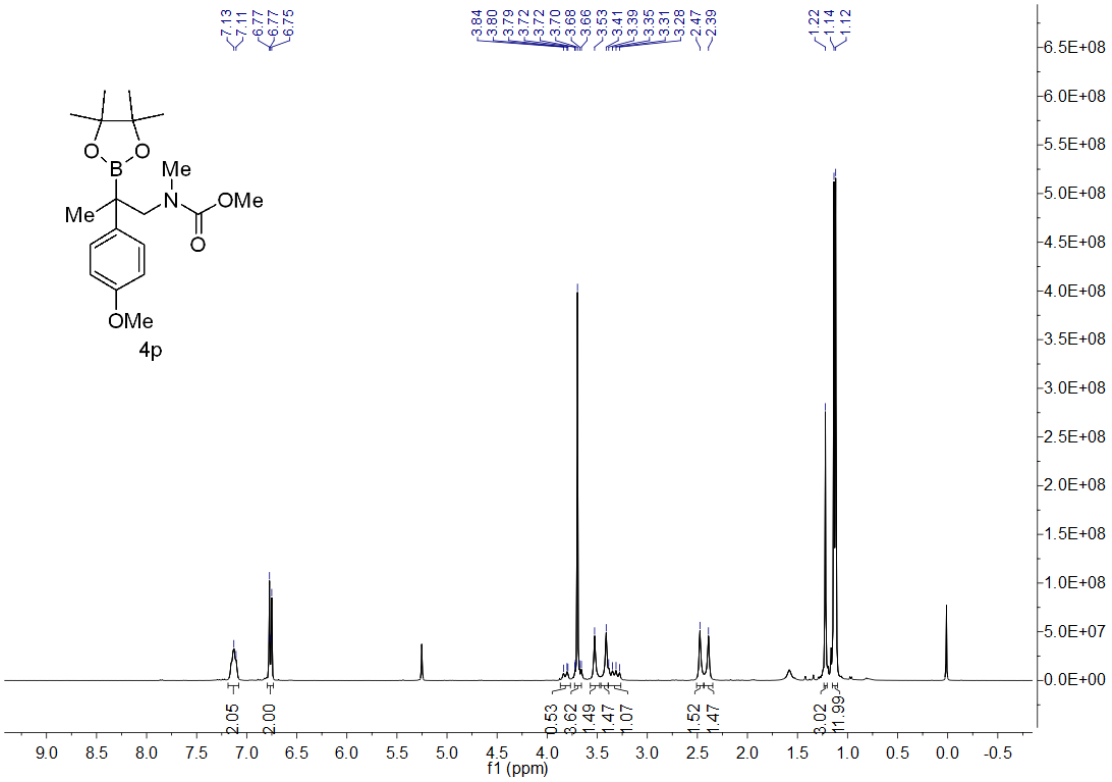

157.13
156.90
145.32
144.99
128.08
127.15
125.51
83.61
60.88
57.16
56.75
36.06
35.61
24.41
24.22
17.71
14.45
Me
N
OEt
O
Me
4n
f1 (ppm)

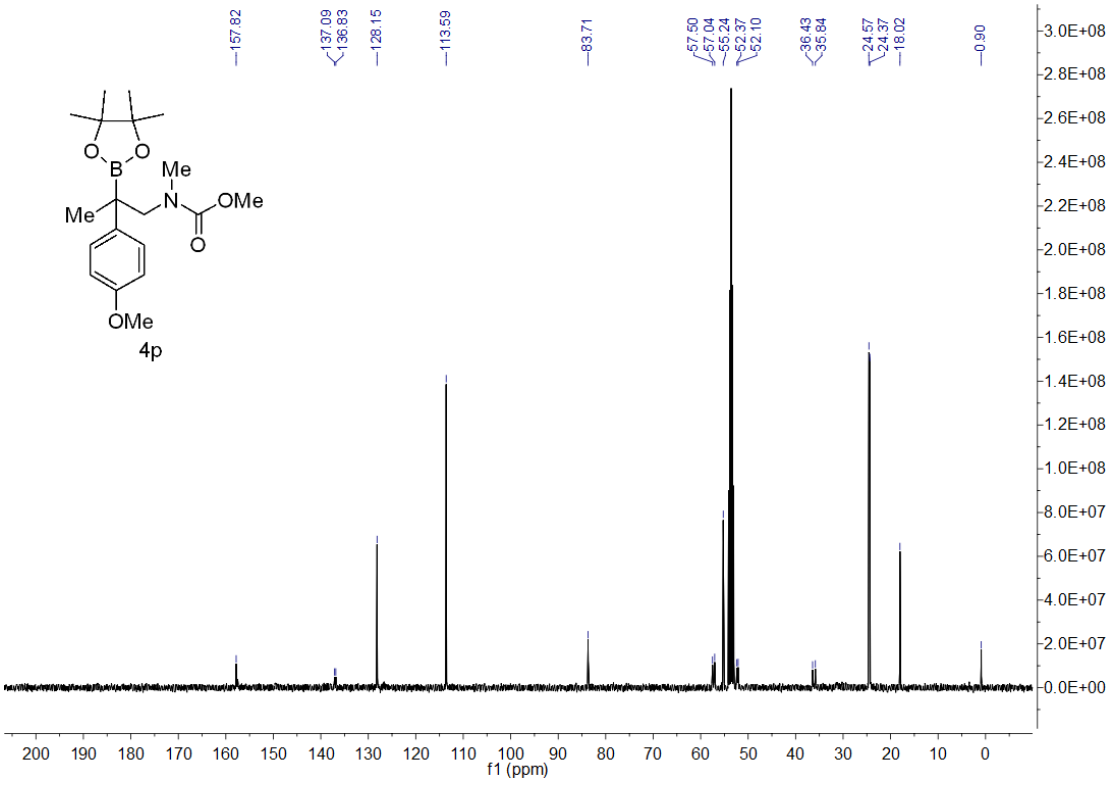

33.33
Me
N
OEt
Me
O
O
B
O
O
4n
6.5E+08
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -20
f1 (ppm)

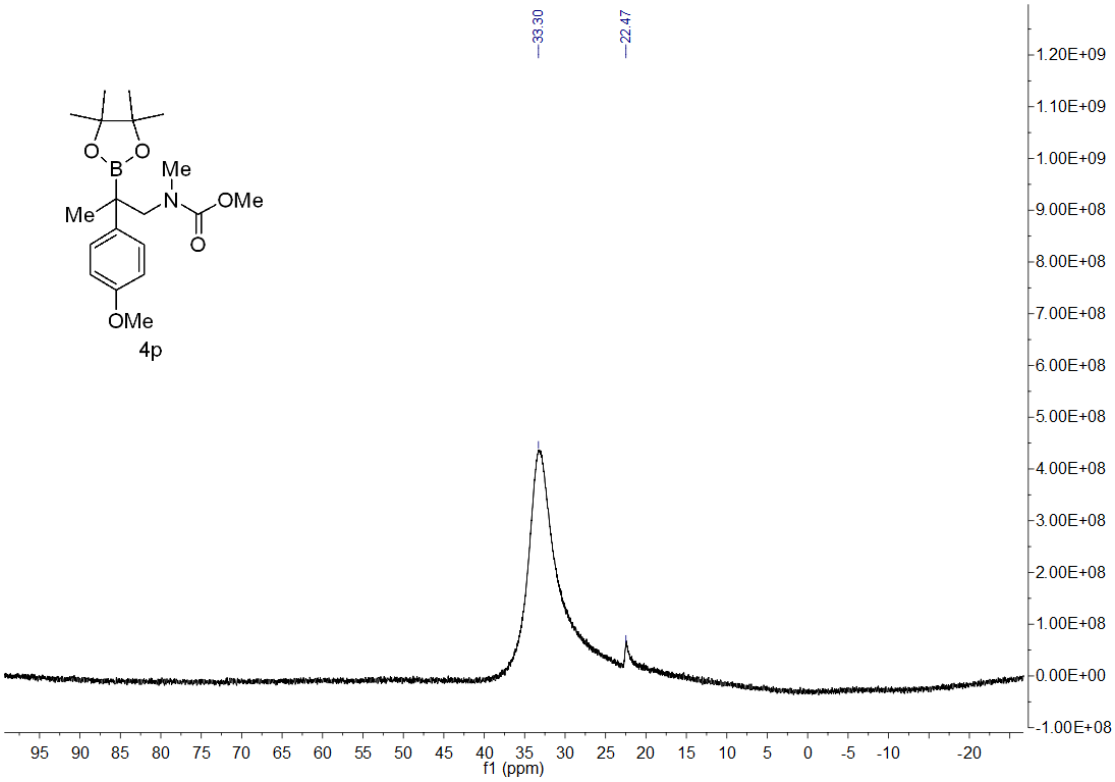

7.22
7.12
7.11
7.10
7.09
7.08
3.90
3.87
3.74
3.71
3.53
3.44
3.39
3.33
2.48
2.38
1.26
1.15
1.13
Me
N
OMe
Me
O
O
B
O
O
4o
4.06
1.00
0.50
0.52
4.09
1.53
1.54
3.03
12.02
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

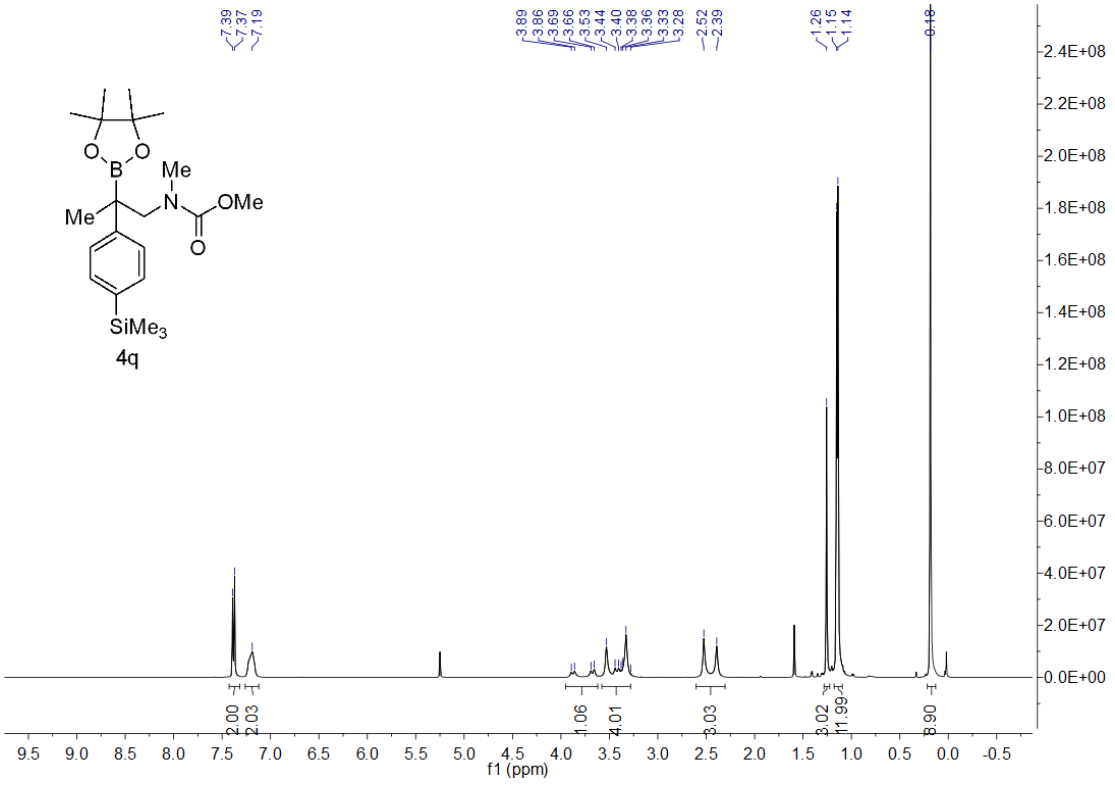

157.57
157.34
145.23
144.96
128.08
127.15
125.54
83.64
57.33
56.89
52.25
51.95
36.27
35.65
24.42
24.22
17.65
0.77
Me
N
OMe
O
Me
O
B
O
4o
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
f1 (ppm)

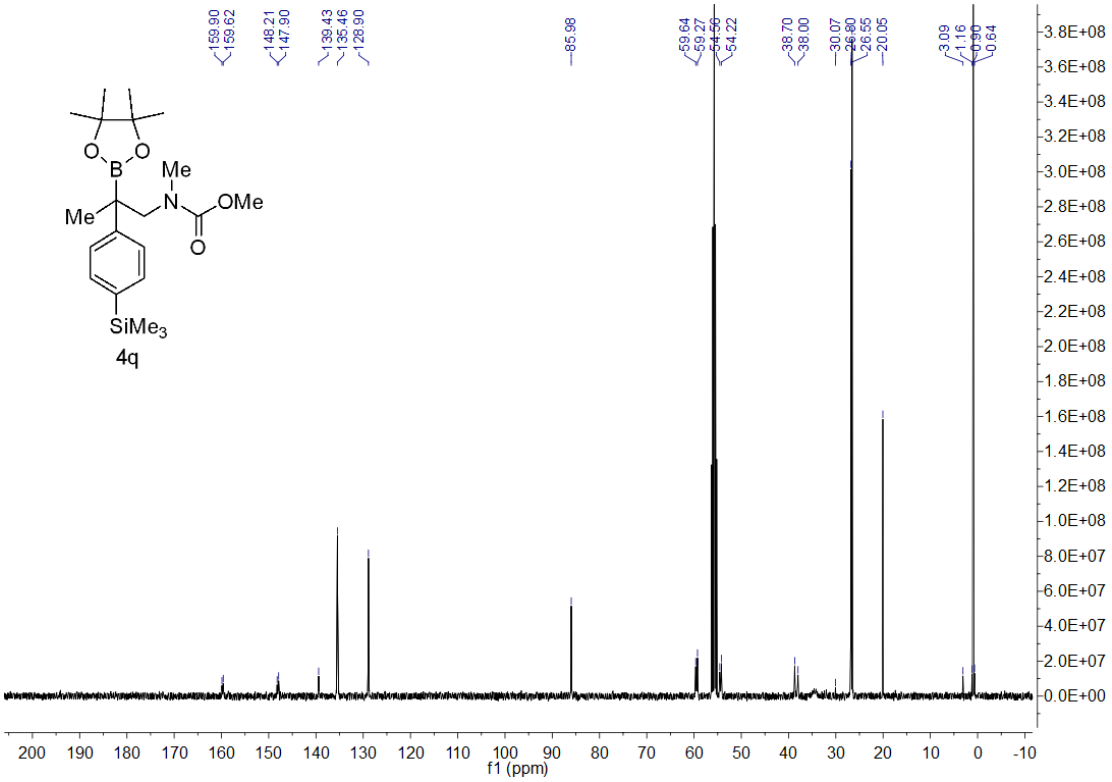

33.34
Me
N
OMe
O
Me
O
B
O
4o
7.0E+08
6.5E+08
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
f1 (ppm)

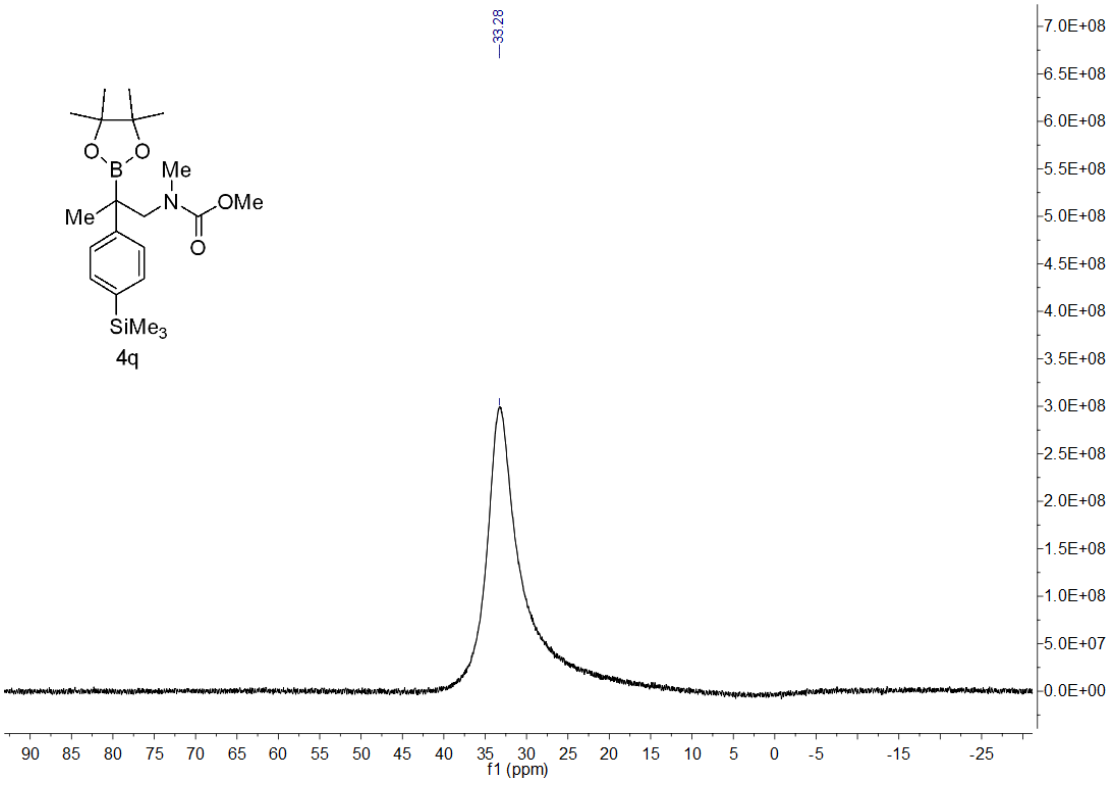

7.13
7.11
6.77
6.75
3.84
3.80
3.79
3.72
3.72
3.70
3.68
3.66
3.53
3.41
3.39
3.35
3.31
3.28
2.47
2.39
1.22
1.14
1.12
Me
N
OMe
O
Me
OMe
4p
2.05
2.00
0.53
3.62
1.49
1.47
1.07
1.52
1.47
3.02
11.99
f1 (ppm)

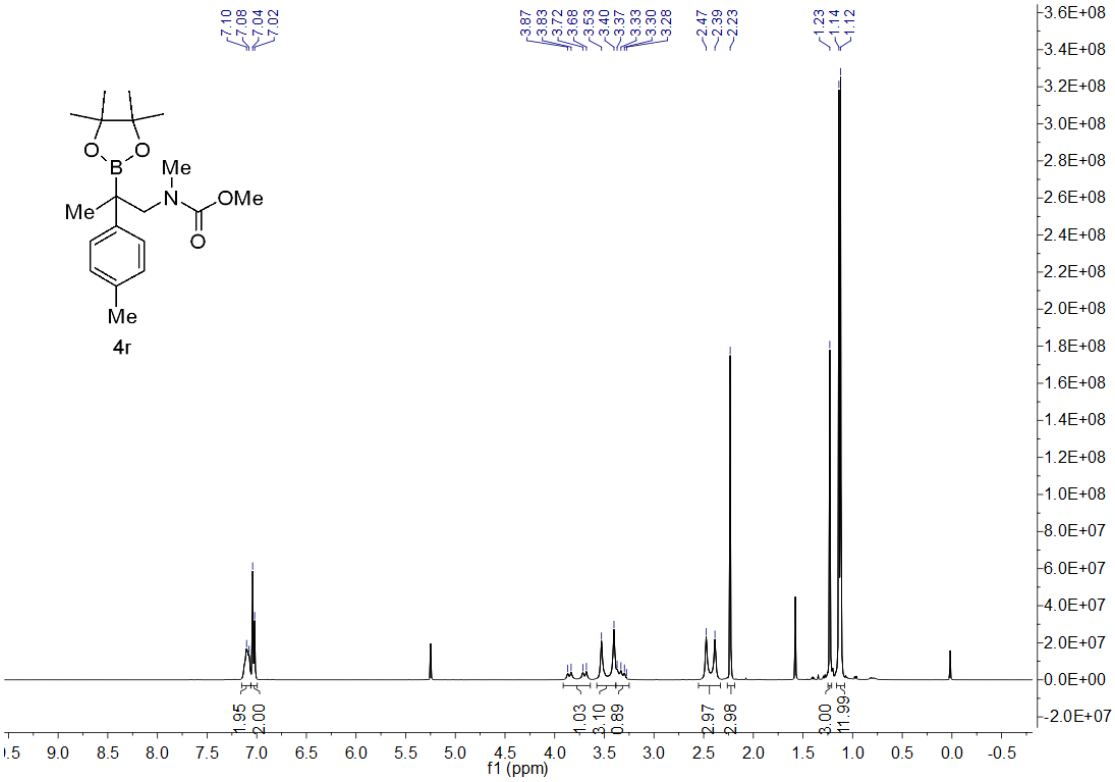

157.82
137.09
136.83
128.15
113.59
83.71
57.50
57.04
55.24
52.37
52.10
36.43
35.84
24.57
24.37
18.02
0.90
Me
N
OMe
O
Me
OMe
4p
f1 (ppm)

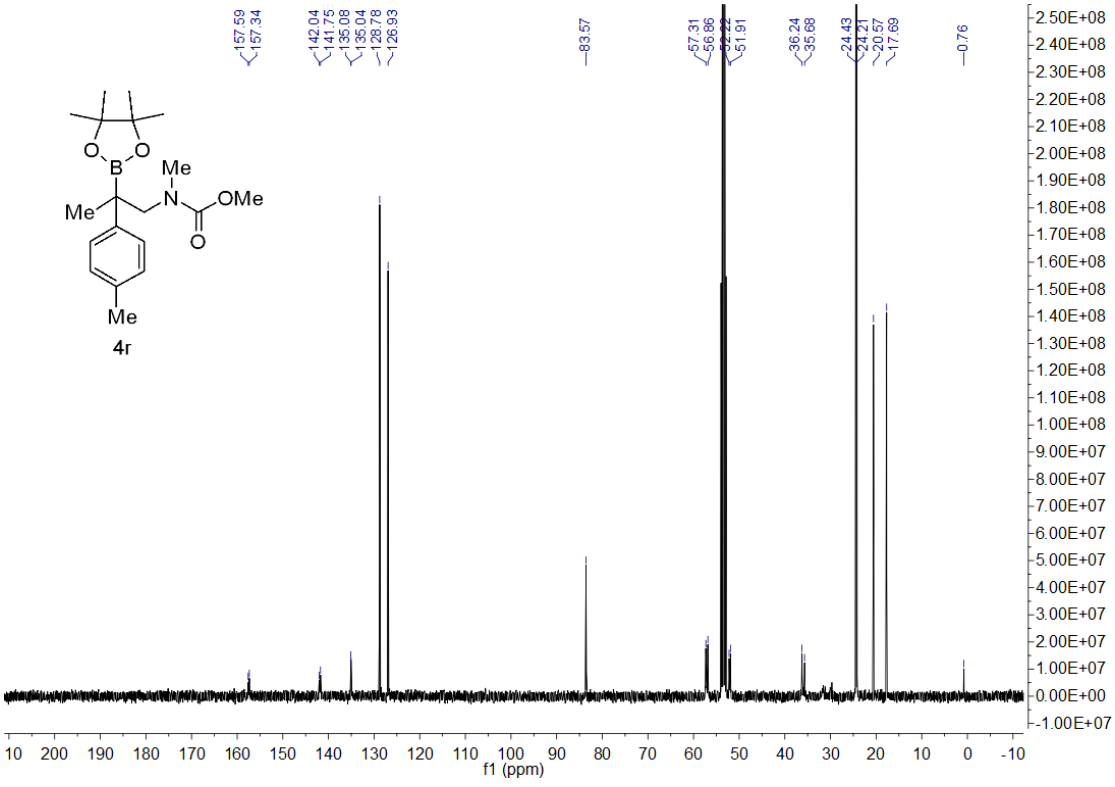

33.30
22.47
Me
N
OMe
O
Me
O
B
O
OMe
4p
f1 (ppm)


7.39
7.37
7.19
3.89
3.86
3.69
3.66
3.53
3.44
3.40
3.38
3.36
3.33
3.28
2.52
2.39
1.26
1.15
1.14
0.18
Me
N
OMe
O
Me
O
B
O
SiMe3
4q
2.00
2.03
1.06
4.01
3.03
3.02
11.99
8.90
f1 (ppm)


159.90
159.62
148.21
147.90
139.43
135.46
128.90
85.98
59.64
59.27
54.56
54.22
38.70
38.00
30.07
26.80
26.55
20.05
3.09
1.16
0.90
0.64
Me
N
OMe
O
Me
O
B
O
SiMe3
4q
f1 (ppm)


33.28
Me
N
OMe
O
Me
O
B
O
SiMe3
4q
f1 (ppm)


7.10
7.08
7.04
7.02
3.87
3.83
3.72
3.68
3.53
3.40
3.37
3.33
3.30
3.28
2.47
2.39
2.23
1.23
1.14
1.12
Me
N
OMe
O
Me
Me
4r
1.95
2.00
1.03
3.10
0.89
2.97
2.98
3.00
11.99
f1 (ppm)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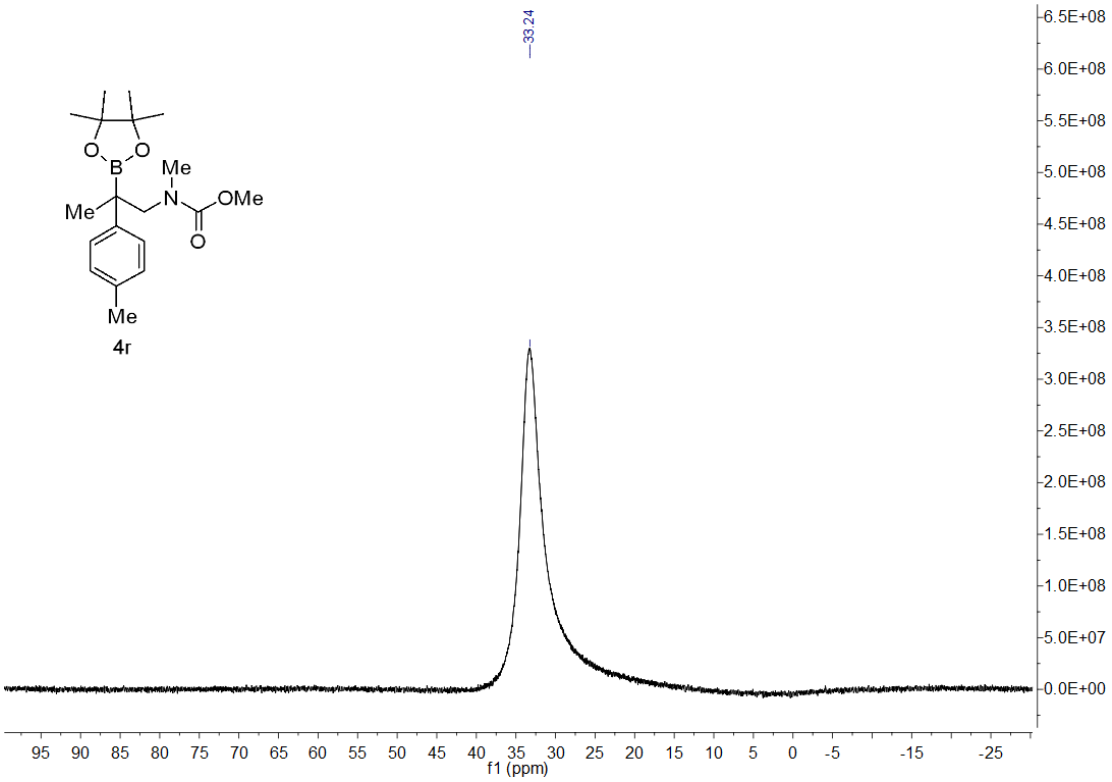
141.75
135.08
135.04
128.78
126.93
83.57
57.31
56.86
52.22
51.91
36.24
35.68
24.43
24.21
20.57
17.69
0.76
Me
N
OMe
O
Me
Me
4r
f1 (ppm)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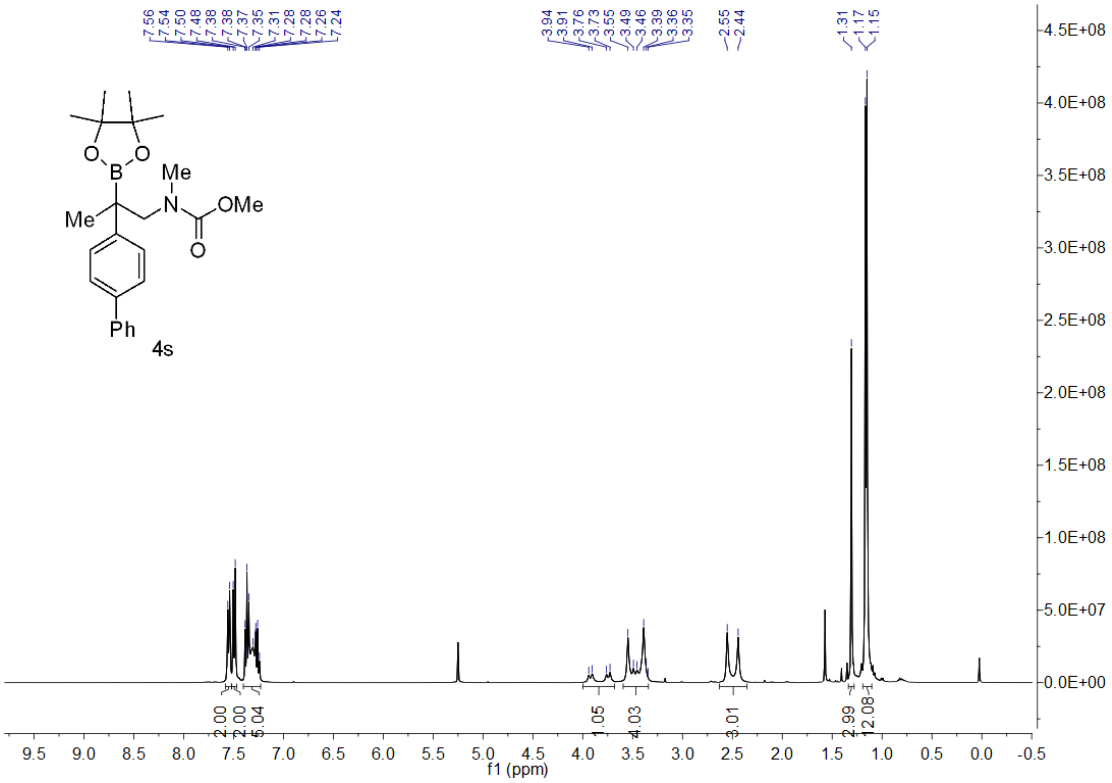
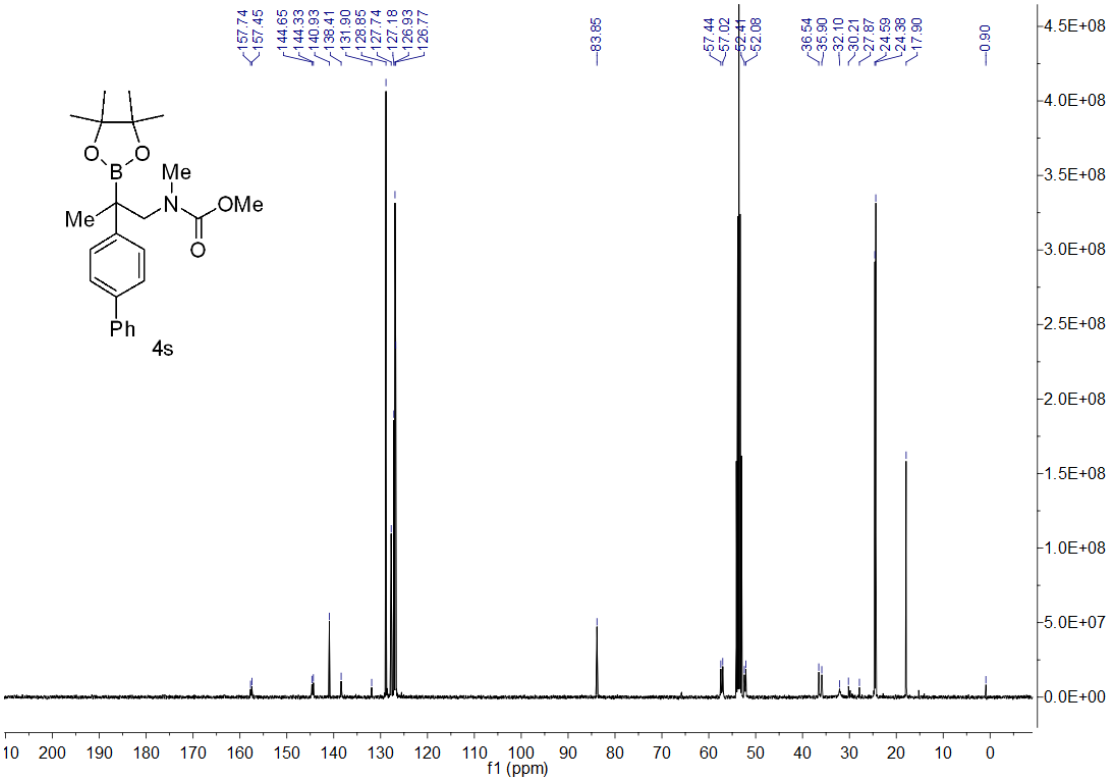
Me
N
OMe
O
Me
Me
4r
f1 (ppm)


7.56
7.54
7.50
7.48
7.38
7.38
7.37
7.35
7.31
7.28
7.28
7.26
7.24
3.94
3.91
3.76
3.73
3.55
3.49
3.46
3.39
3.36
3.35
2.55
2.44
1.31
1.17
1.15
Me
N
OMe
O
Me
Ph
4s
2.00
2.00
5.04
1.05
4.03
3.01
2.99
12.08
f1 (ppm)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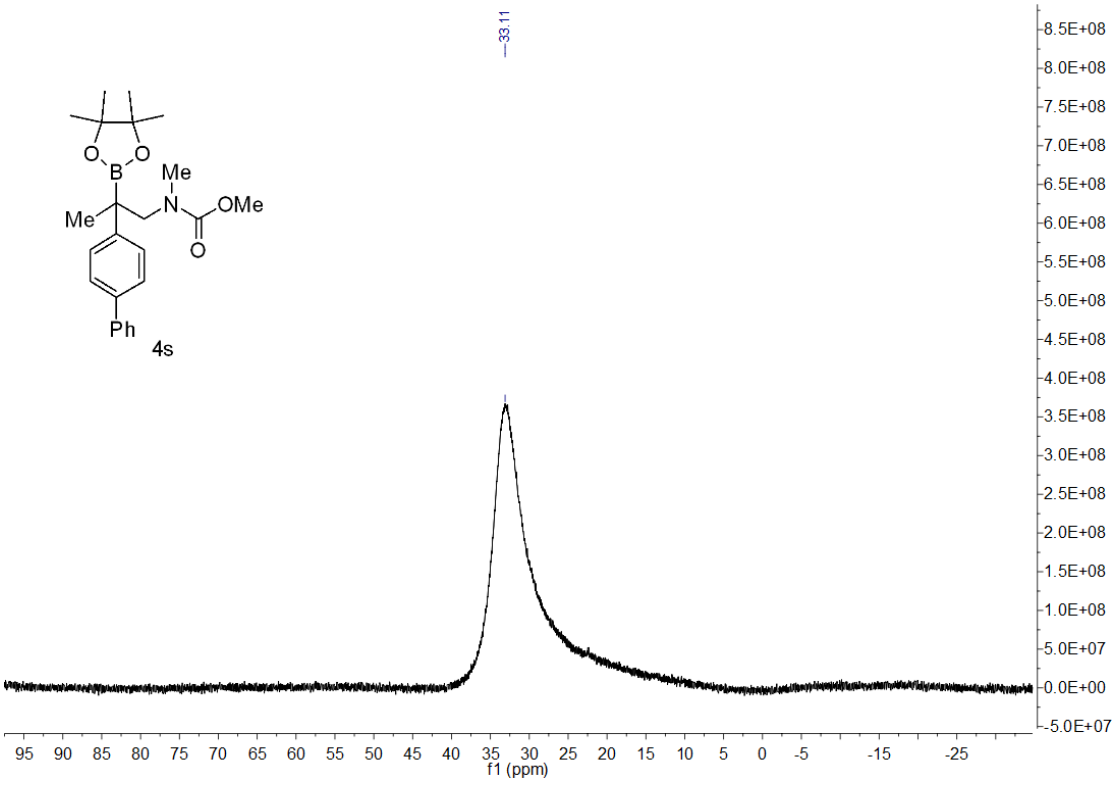
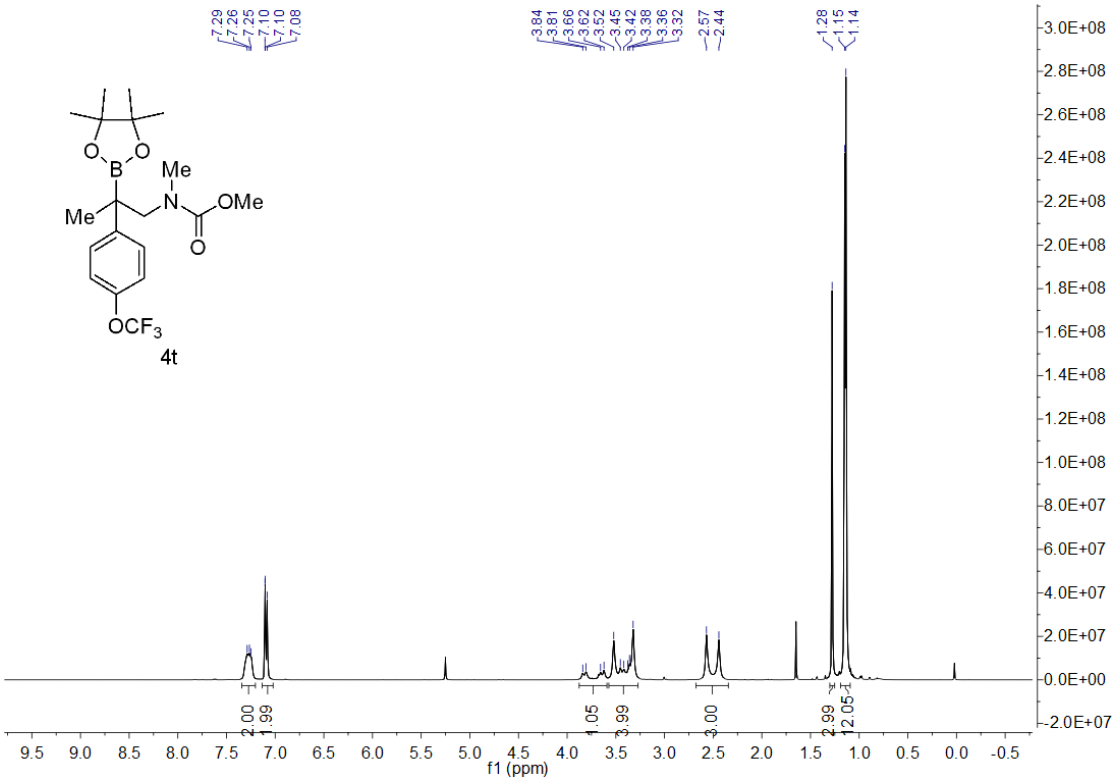
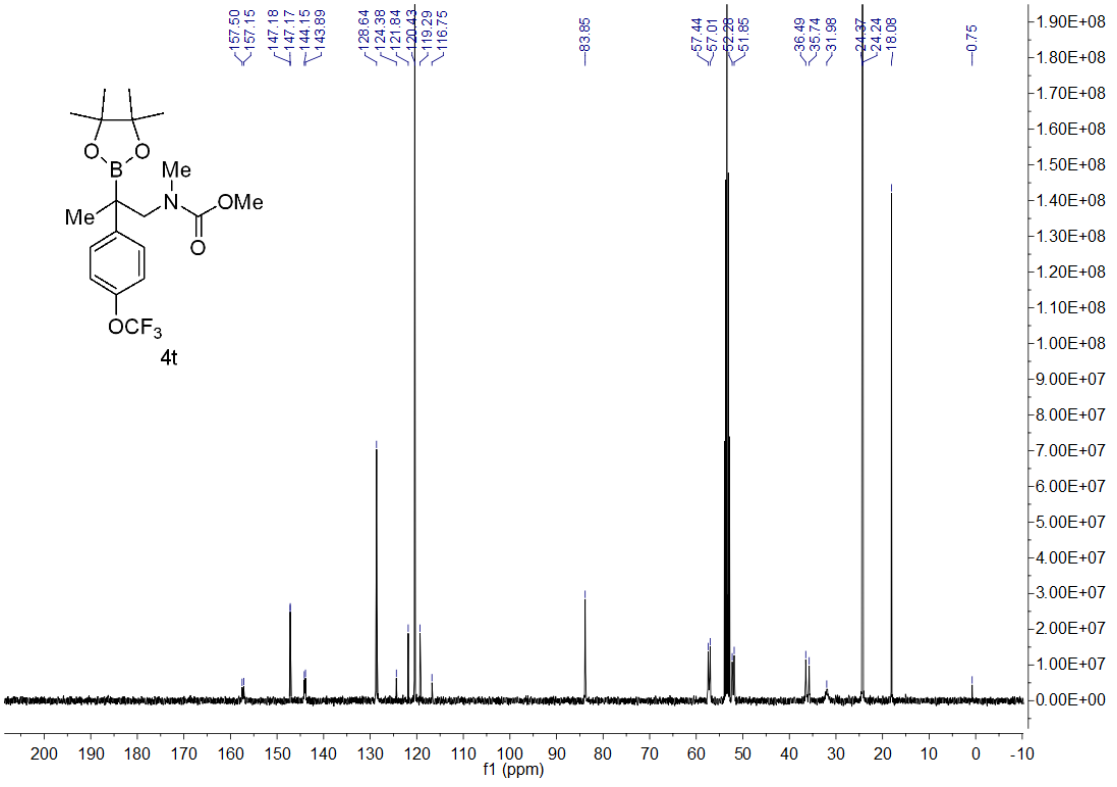
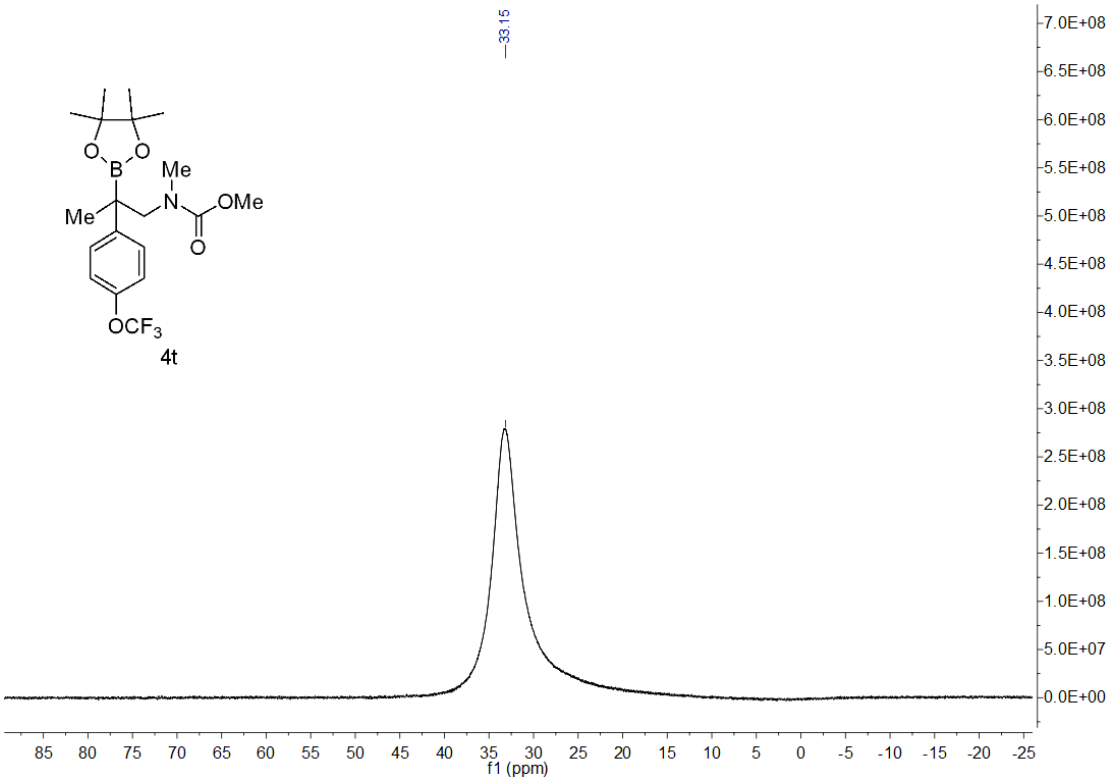
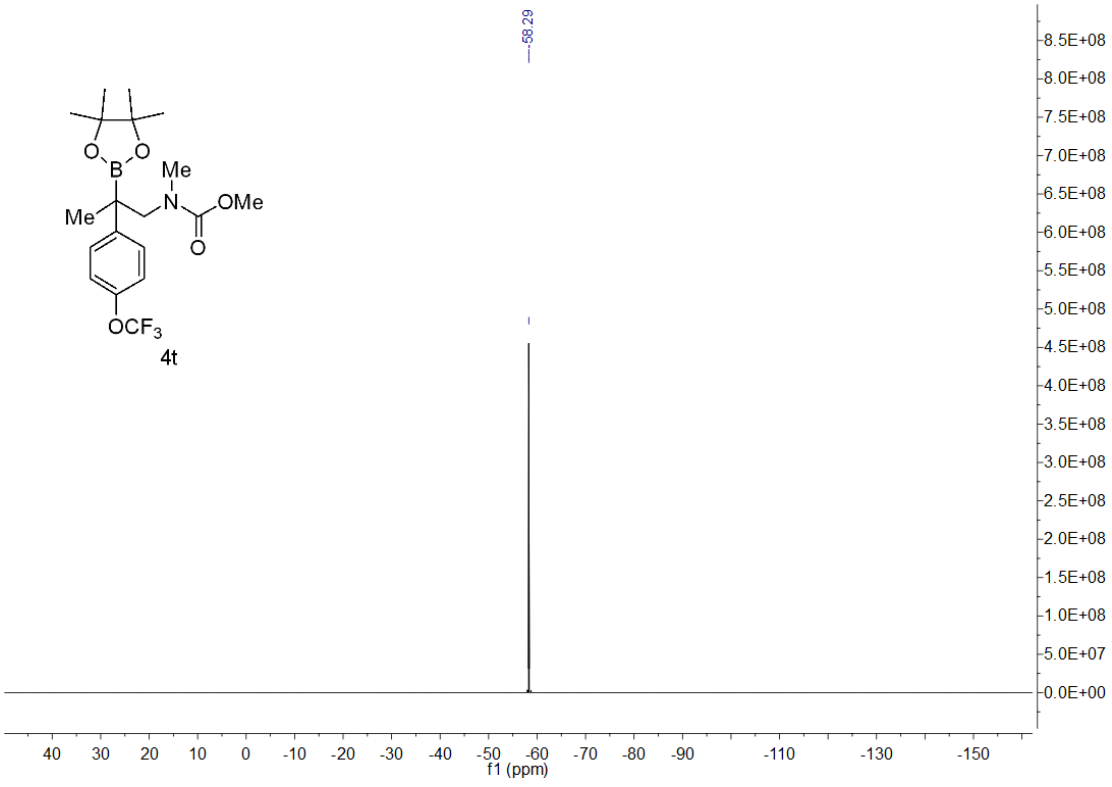
138.41
131.90
128.85
127.74
127.18
126.93
126.77
83.86
57.44
57.02
52.41
52.08
36.54
35.90
32.10
30.21
27.67
24.59
24.38
17.90
0.90
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
f1 (ppm)
Me
N
OMe
O
Me
Ph
4s

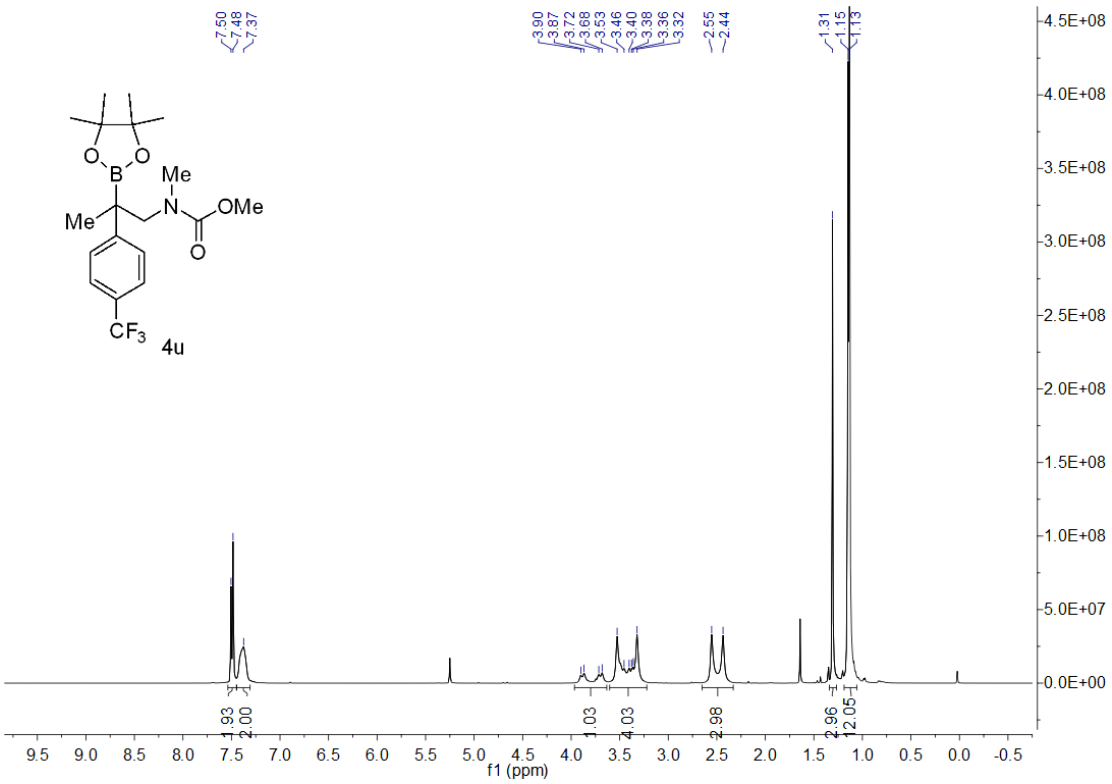

33.11
8.5E+08
8.0E+08
7.5E+08
7.0E+08
6.5E+08
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
f1 (ppm)
Me
N
OMe
O
Me
Ph
4s

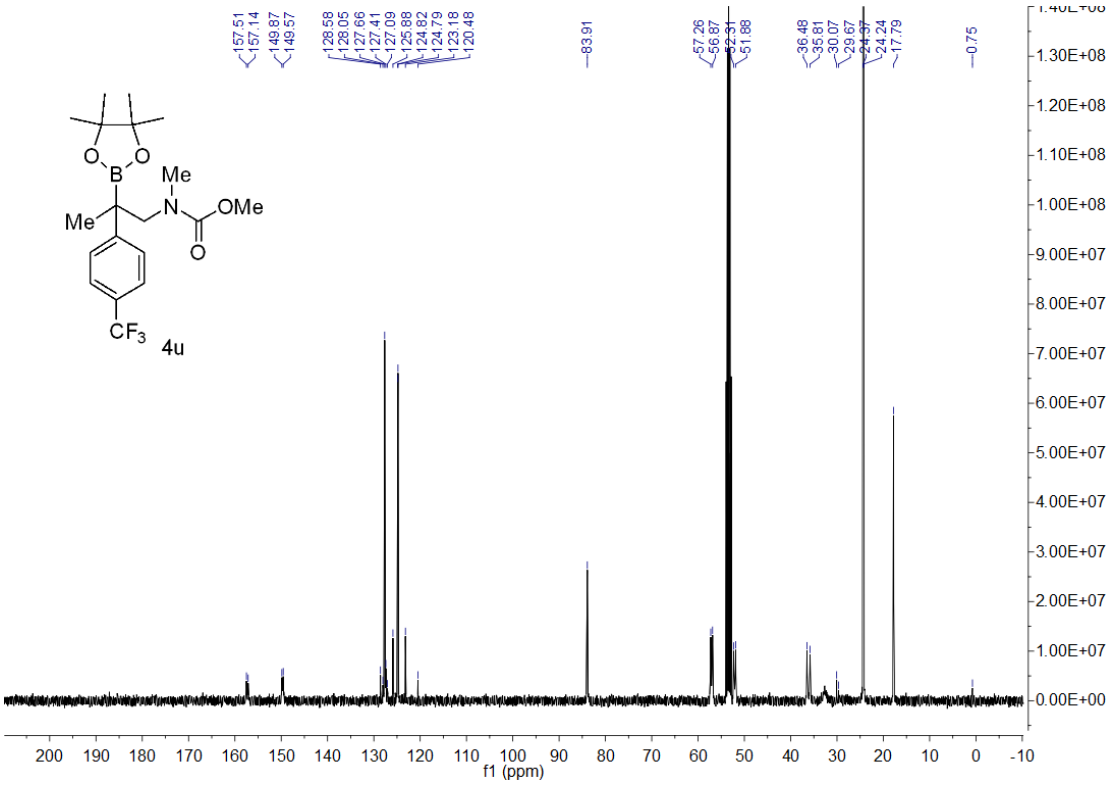

7.29
7.26
7.25
7.10
7.10
7.08
3.84
3.81
3.66
3.62
3.52
3.45
3.42
3.38
3.36
3.32
2.57
2.44
1.28
1.15
1.14
Me
N
OMe
Me
O
B
O
O
OCF3
4t
2.00
1.99
1.05
3.99
3.00
2.99
12.05
f1 (ppm)

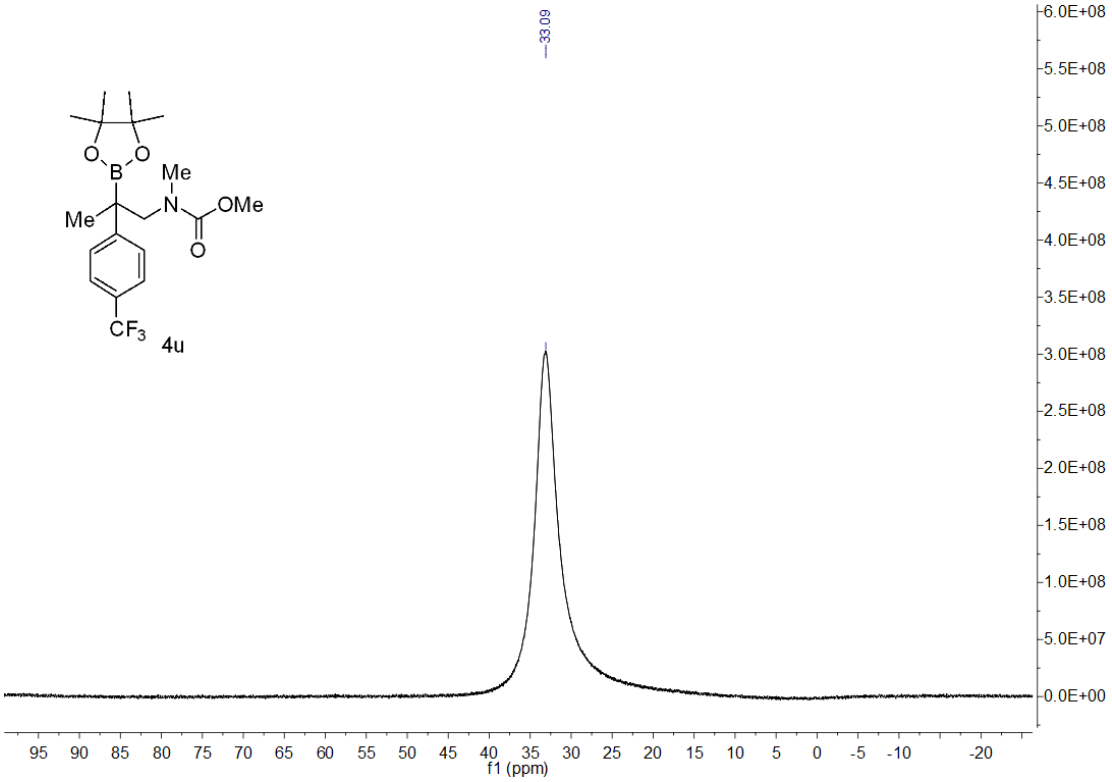

157.50
157.15
147.18
147.17
144.15
143.89
128.64
124.38
121.84
120.43
119.29
116.75
83.85
57.44
57.01
52.28
51.85
36.49
35.74
31.98
24.37
24.24
18.08
0.75
Me
N
OMe
Me
O
B
O
O
OCF3
4t
f1 (ppm)

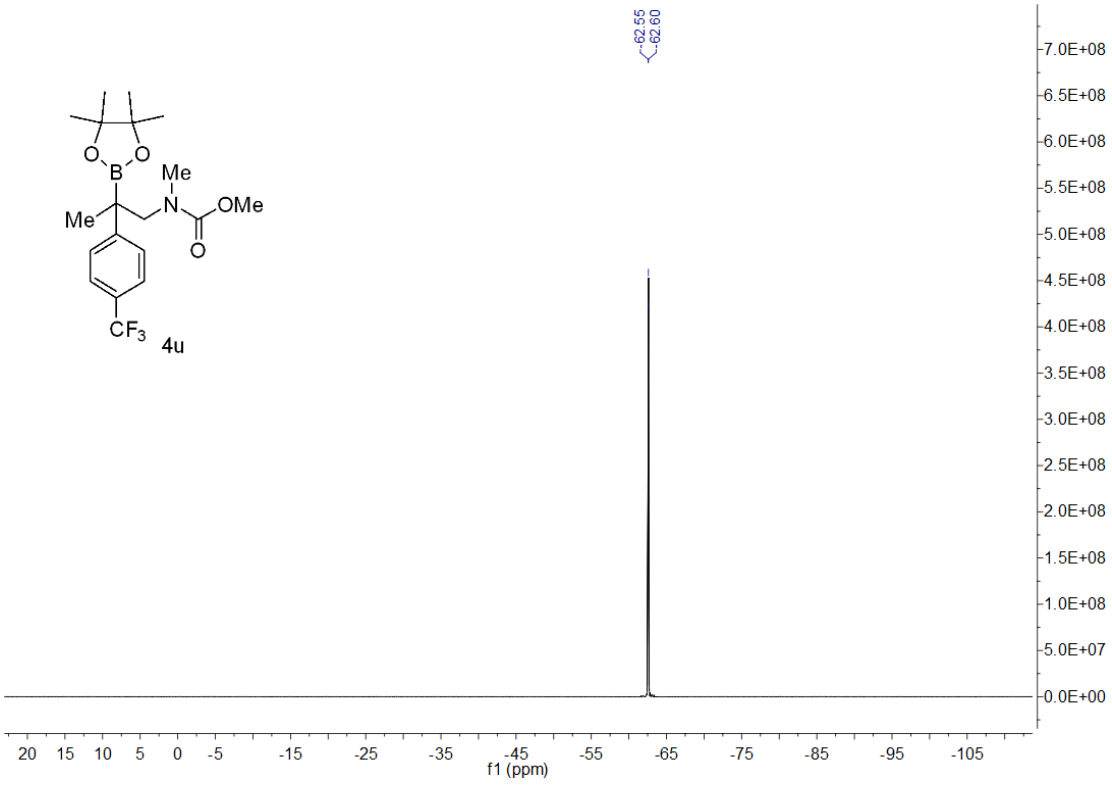

33.15
Me
N
OMe
O
Me
O
B
O
OCF3
4t
7.0E+08
6.5E+08
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25
f1 (ppm)

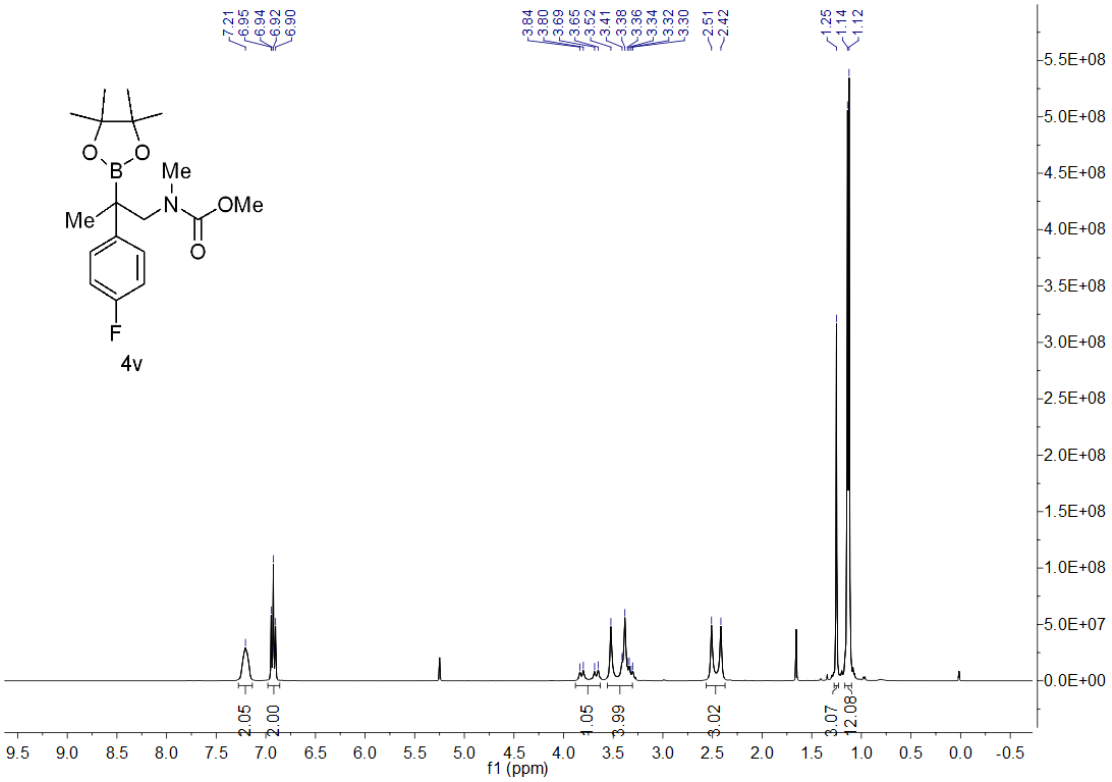

58.29
Me
N
OMe
O
Me
O
B
O
OCF3
4t
8.5E+08
8.0E+08
7.5E+08
7.0E+08
6.5E+08
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150
f1 (ppm)

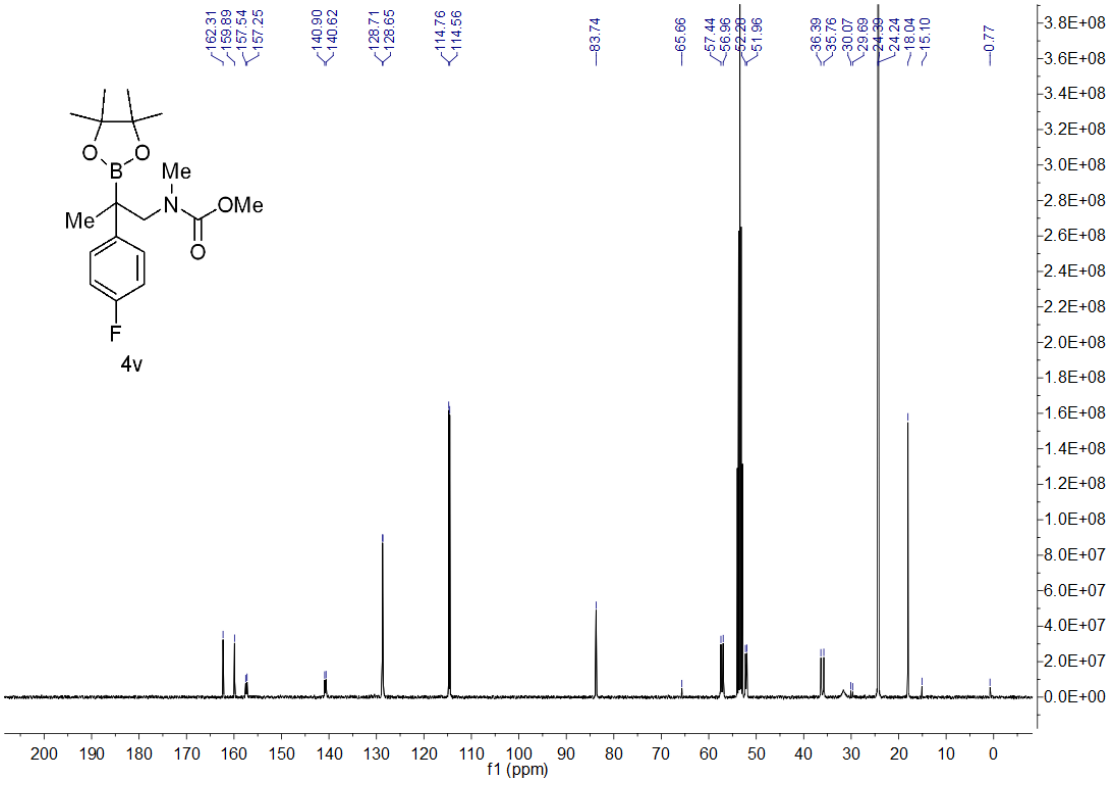

7.50
7.48
7.37
3.90
3.87
3.72
3.68
3.53
3.46
3.40
3.38
3.36
3.32
2.55
2.44
1.31
1.15
1.13
Me
N
OMe
O
Me
B
O
O
CF3
4u
1.93
2.00
1.03
4.03
2.98
2.96
12.05
f1 (ppm)

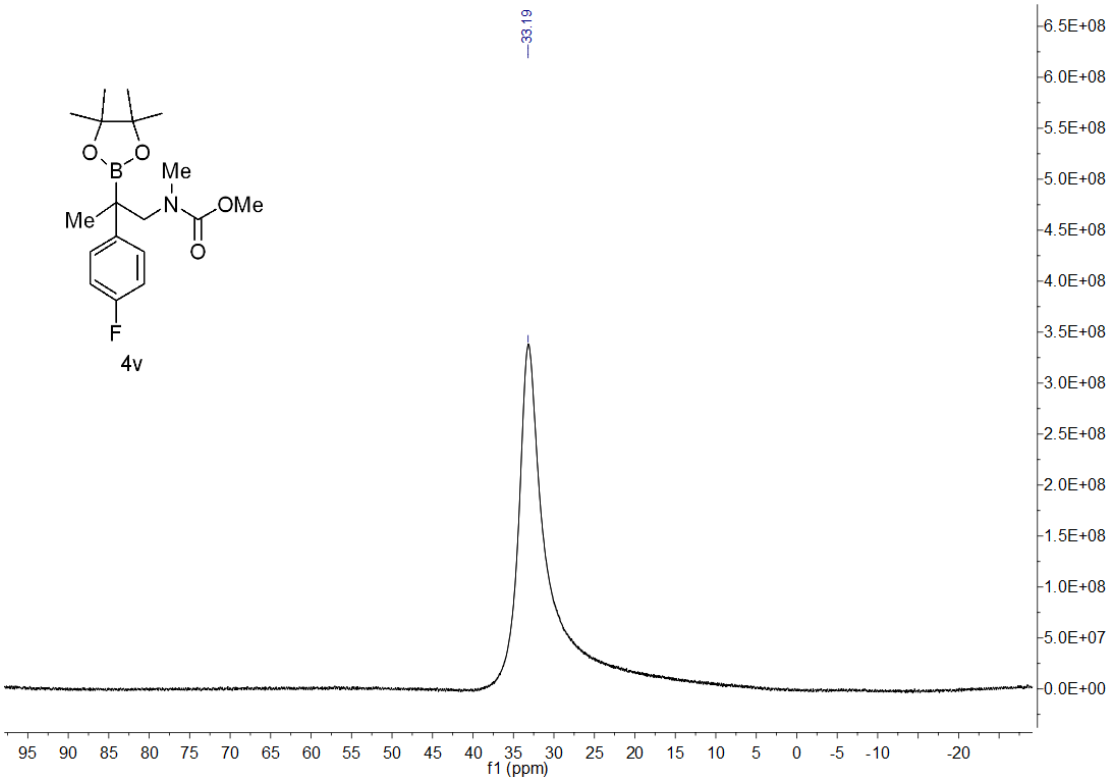

157.51
157.14
149.87
149.57
128.58
128.05
127.66
127.41
127.09
125.88
124.92
124.79
123.18
120.48
83.91
57.26
56.87
52.31
51.88
36.48
35.81
30.07
29.67
24.37
24.24
17.79
0.75
Me
N
OMe
O
Me
B
O
O
CF3
4u
f1 (ppm)

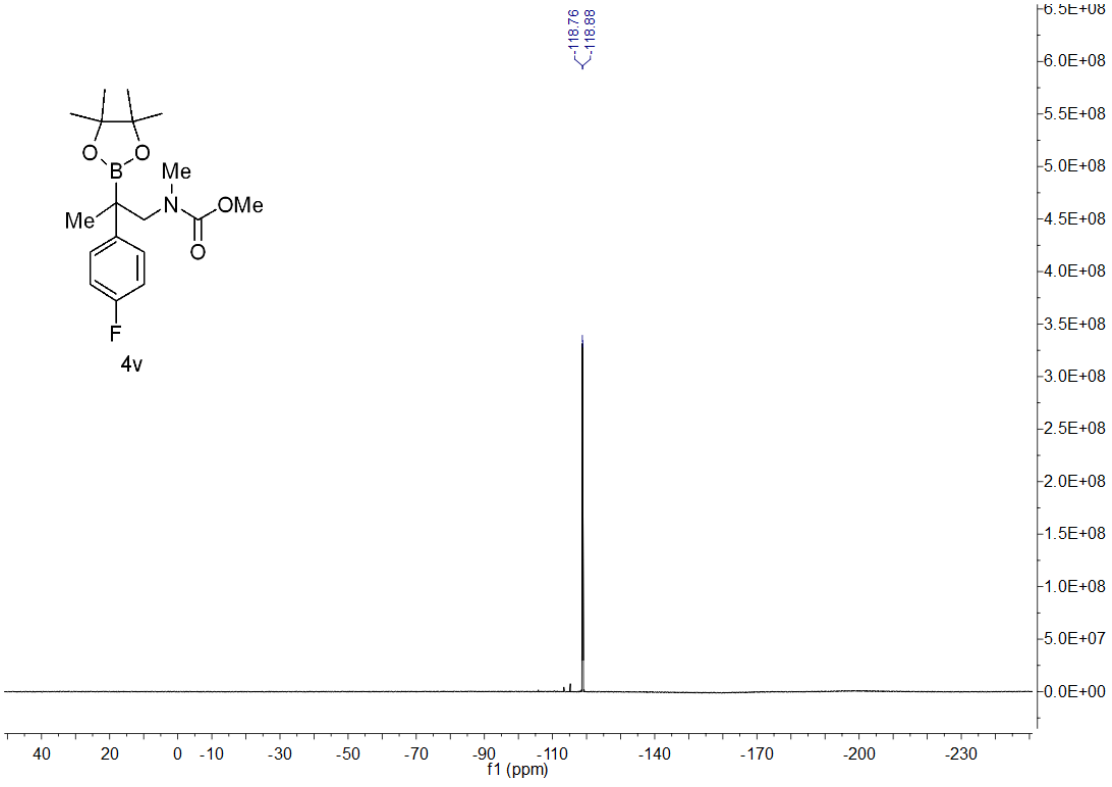

33.09
Me
N
OMe
O
Me
O
B
O
CF3
4u
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -20
f1 (ppm)

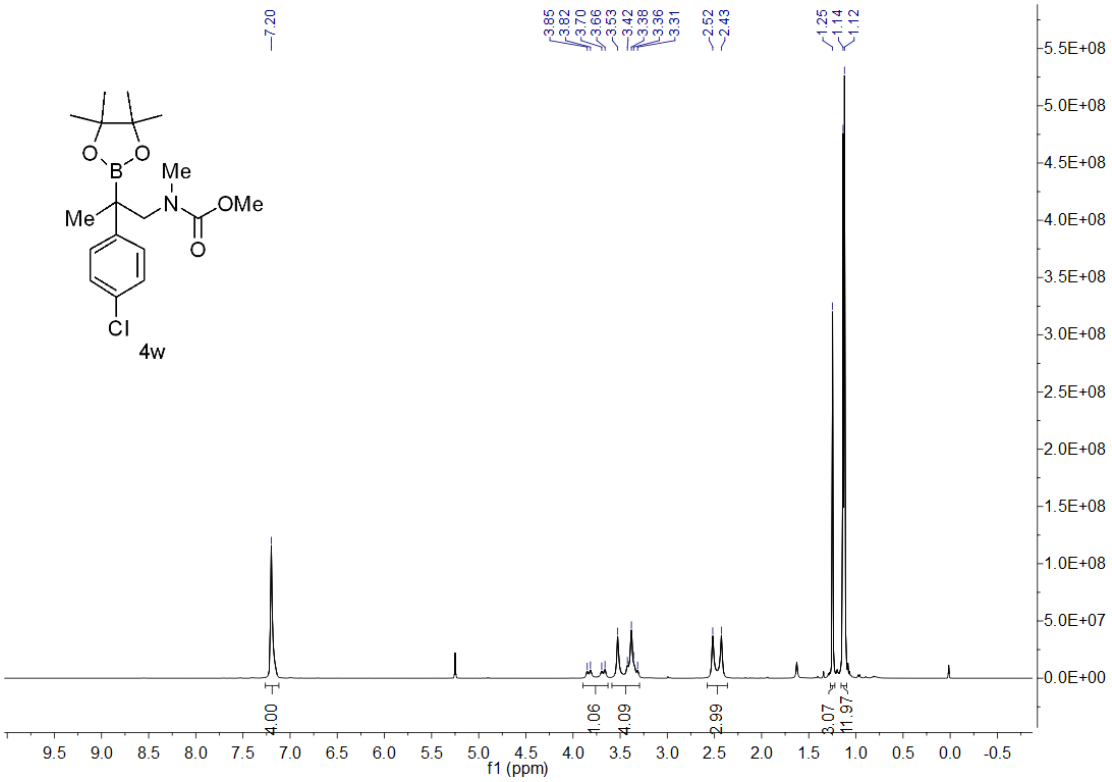

62.55
62.60
Me
N
OMe
O
Me
O
B
O
CF3
4u
7.0E+08
6.5E+08
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
20 15 10 5 0 -5 -15 -25 -35 -45 -55 -65 -75 -85 -95 -105
f1 (ppm)

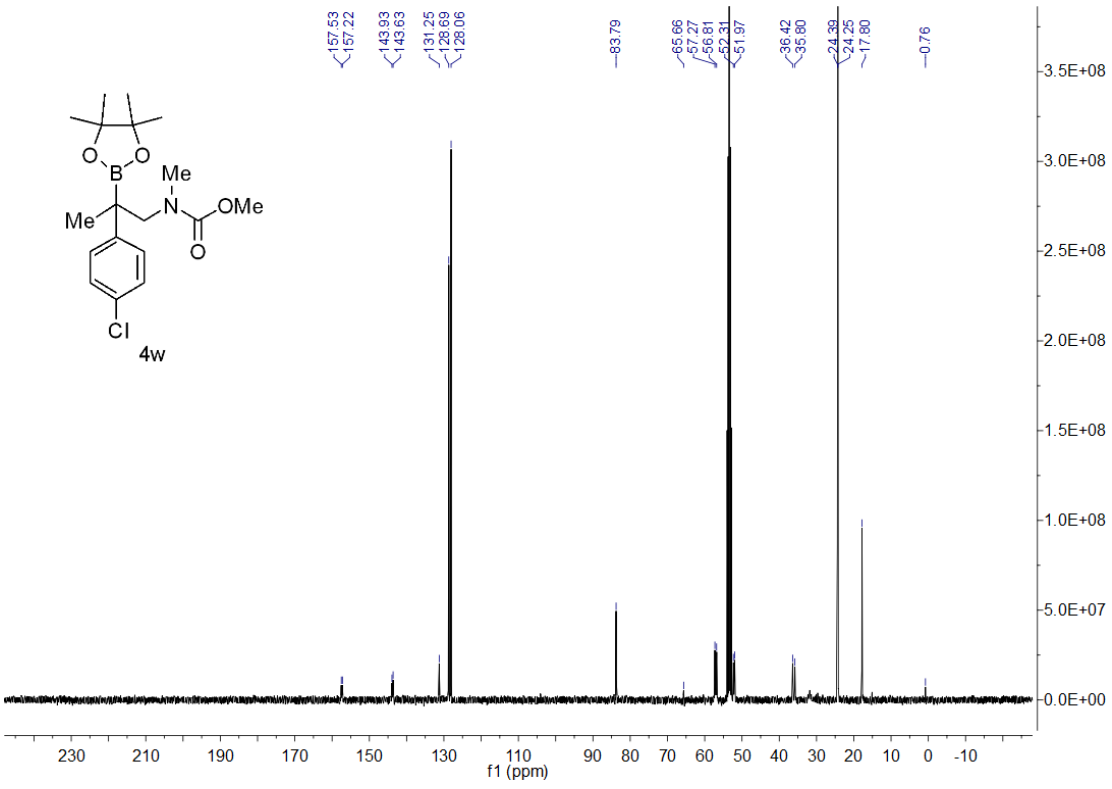

7.21
6.95
6.94
6.92
6.90
3.84
3.80
3.69
3.65
3.52
3.41
3.38
3.36
3.34
3.32
3.30
2.51
2.42
1.25
1.14
1.12
Me
N
OMe
O
Me
O
B
O
F
4v
2.05
2.00
1.05
3.99
3.02
3.07
12.08
f1 (ppm)

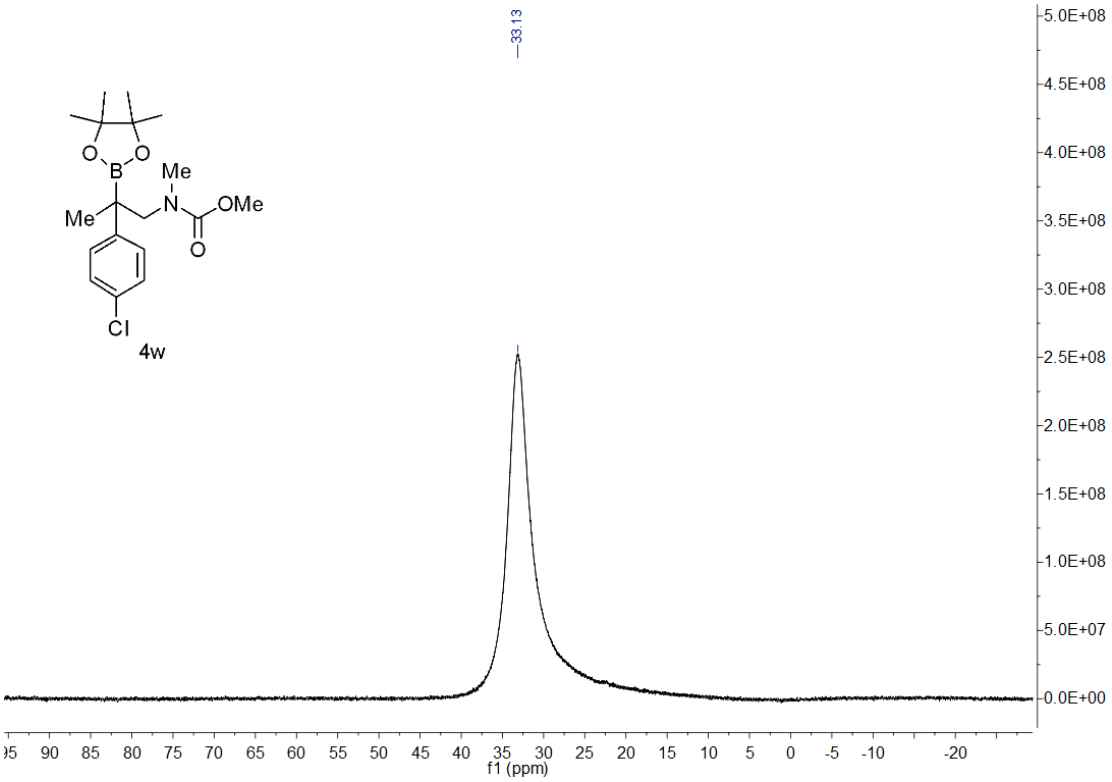

162.31
159.89
157.54
157.25
140.90
140.62
128.71
128.65
114.76
114.56
83.74
65.66
57.44
56.96
52.20
51.96
36.39
35.76
30.07
29.69
24.39
24.24
18.04
15.10
0.77
Me
N
OMe
O
Me
O
B
O
F
4v
f1 (ppm)

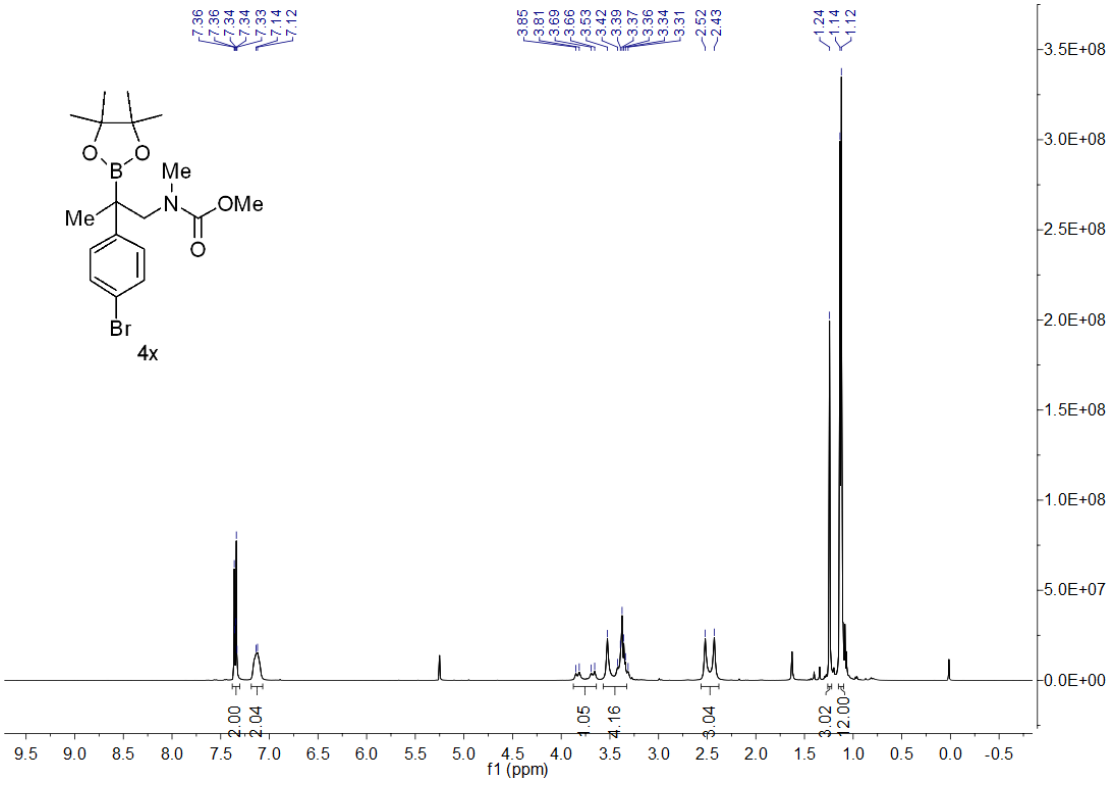

33.19
Me
N
OMe
O
Me
O
B
O
F
4v
6.5E+08
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -20
f1 (ppm)

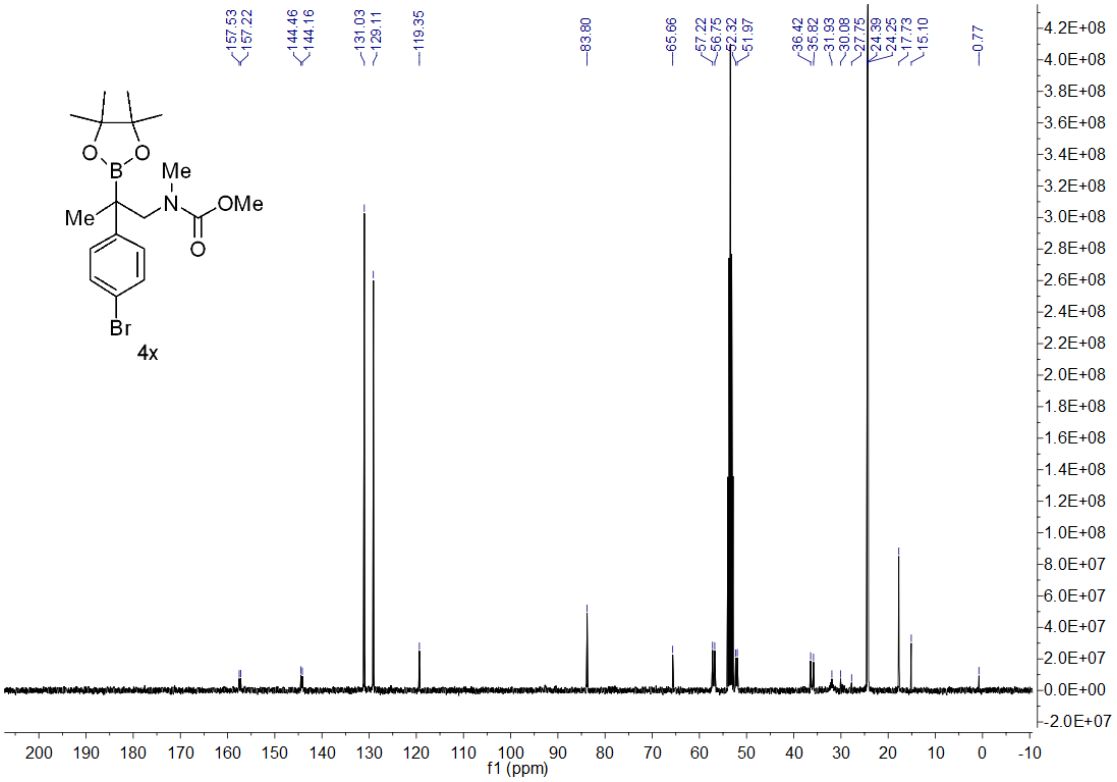

118.76
118.88
Me
N
OMe
O
Me
O
B
O
F
4v
6.5E+08
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
40 20 0 -10 -30 -50 -70 -90 -110 -140 -170 -200 -230
f1 (ppm)

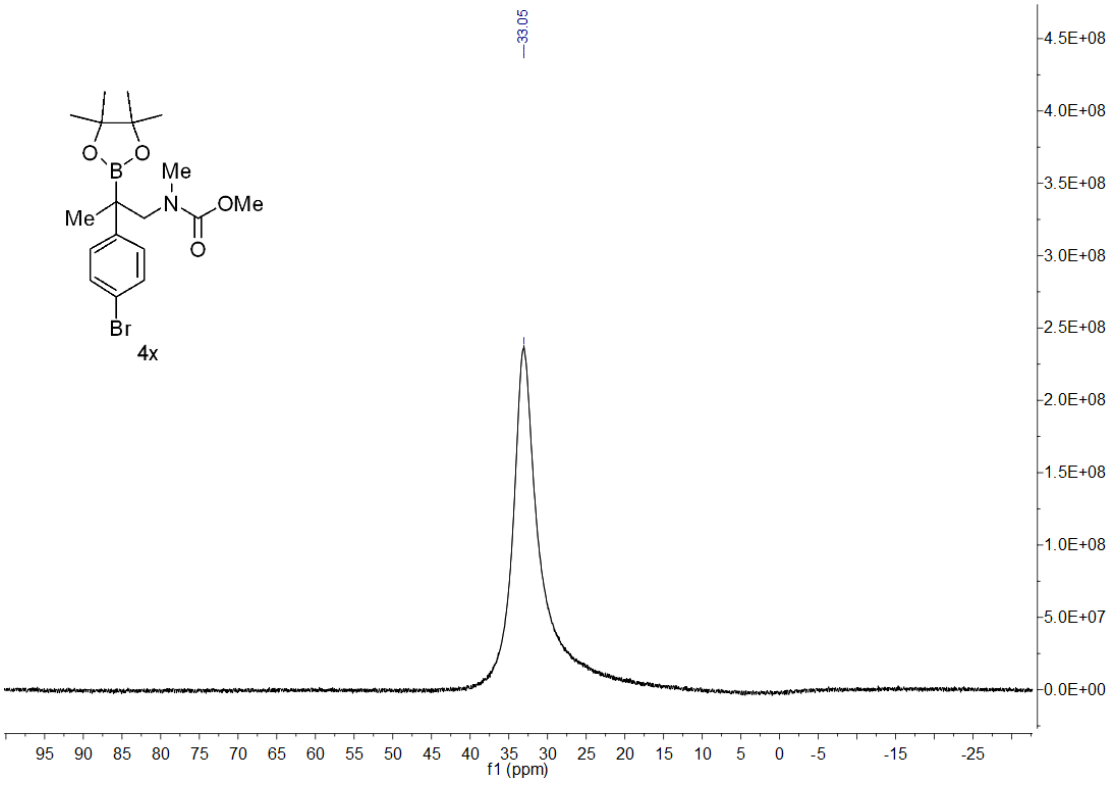

7.20
3.85
3.82
3.70
3.66
3.53
3.42
3.38
3.36
3.31
2.52
2.43
1.25
1.14
1.12
Me
N
OMe
O
Me
O
B
O
Cl
4w
4.00
1.06
4.09
2.99
3.07
11.97
f1 (ppm)

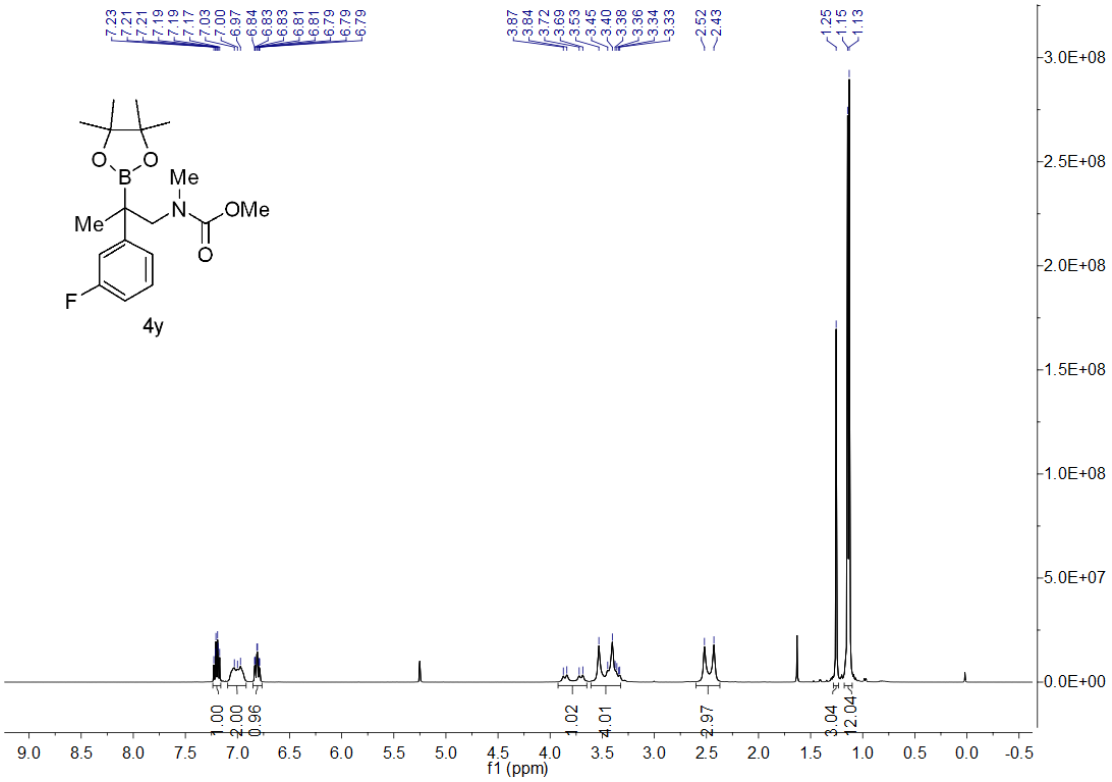

157.53
157.22
143.93
143.63
131.25
128.69
128.06
83.79
65.66
57.27
56.81
52.31
51.97
36.42
35.80
24.39
24.25
17.80
0.76
Me
N
OMe
O
Me
O
B
O
Cl
4w
f1 (ppm)

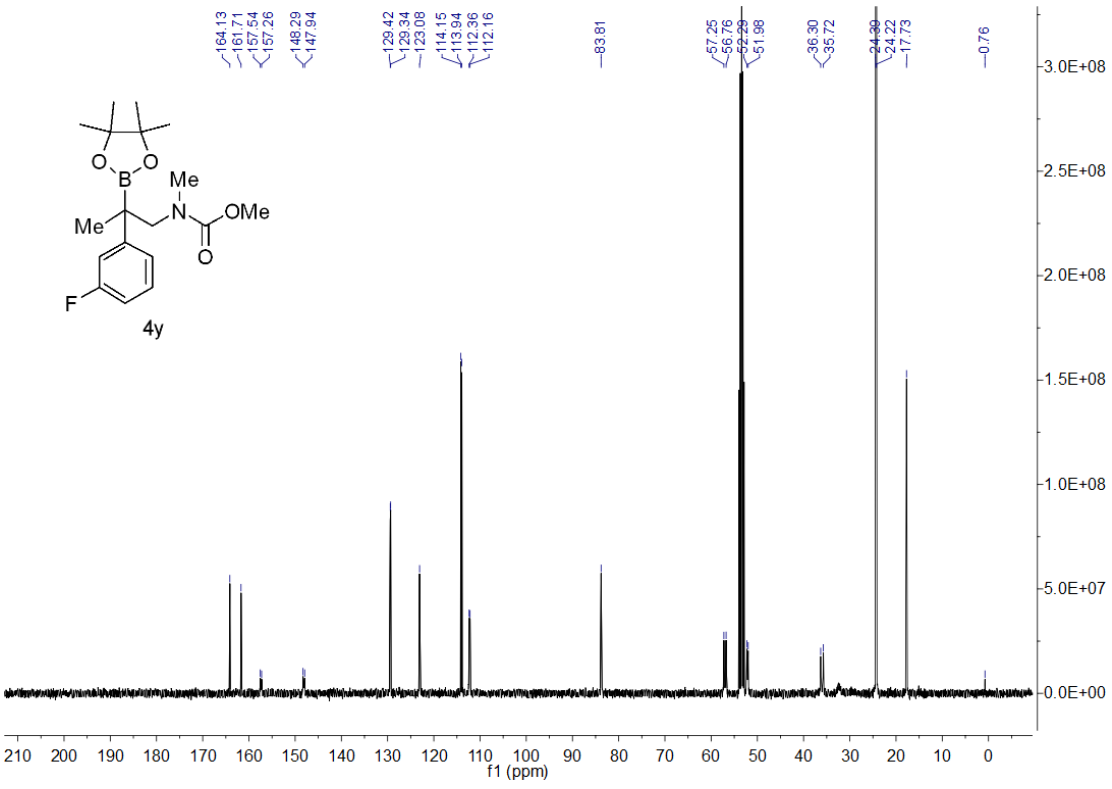

33.13
Me
N
OMe
O
Me
O
B
O
Cl
4w
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -20
f1 (ppm)

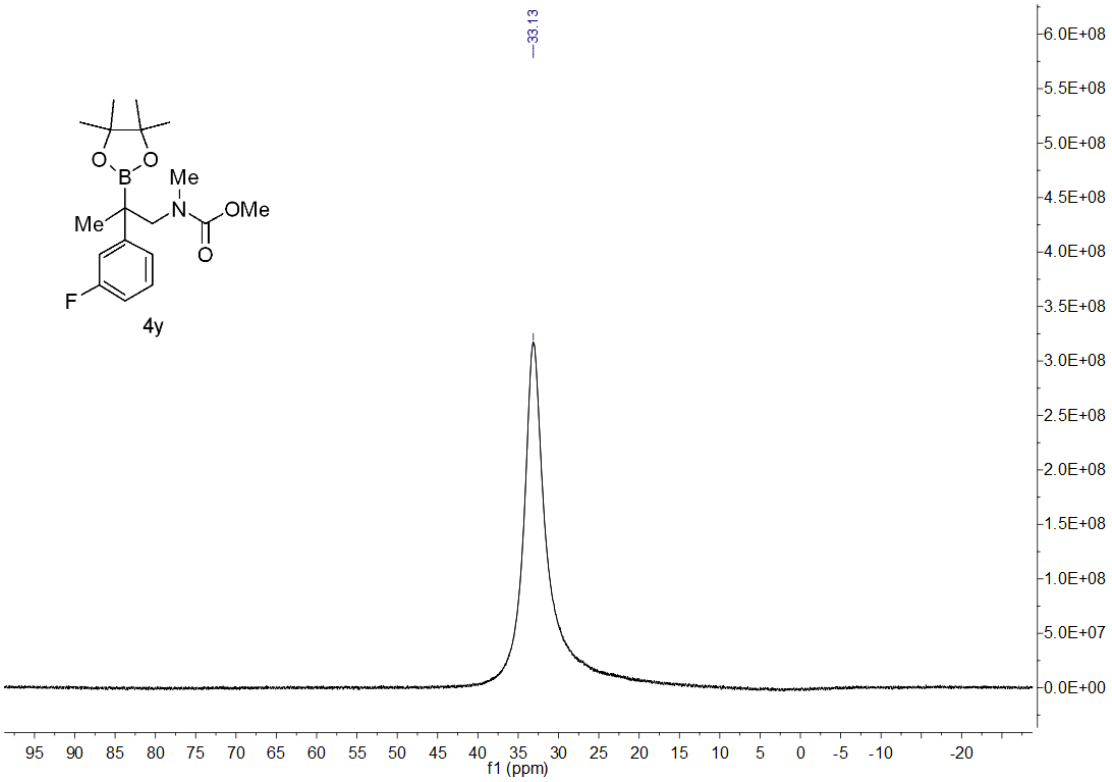

7.36
7.36
7.34
7.34
7.33
7.14
7.12
3.85
3.81
3.69
3.66
3.53
3.42
3.39
3.37
3.36
3.34
3.31
2.52
2.43
1.24
1.14
1.12
Me
N
OMe
O
Me
O
B
O
Br
4x
2.00
2.04
1.05
4.16
3.04
3.02
12.00
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


157.53
157.22
144.46
144.16
131.03
129.11
119.35
83.80
65.66
57.22
56.75
52.32
51.97
36.42
35.82
31.93
30.08
27.75
24.39
24.25
17.73
15.10
0.77
Me
N
OMe
O
Me
O
B
O
Br
4x
f1 (ppm)

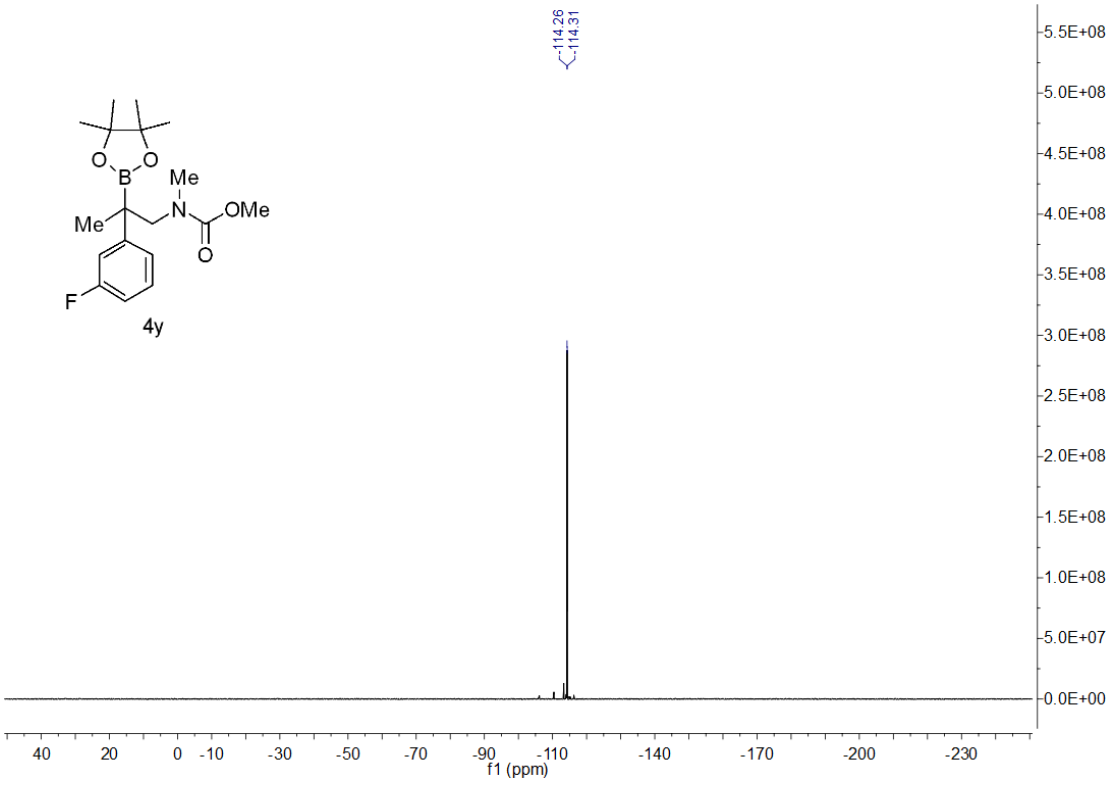

33.05
Me
N
OMe
O
Me
O
B
O
Br
4x
f1 (ppm)


7.23
7.21
7.21
7.19
7.19
7.17
7.03
7.00
6.97
6.84
6.83
6.83
6.81
6.81
6.79
6.79
6.79
3.87
3.84
3.72
3.69
3.53
3.45
3.40
3.38
3.36
3.34
3.33
2.52
2.43
1.25
1.15
1.13
O
B
O
Me
N
OMe
Me
O
F
4y
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
1.00
2.00
0.96
1.02
4.01
2.97
3.04
12.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

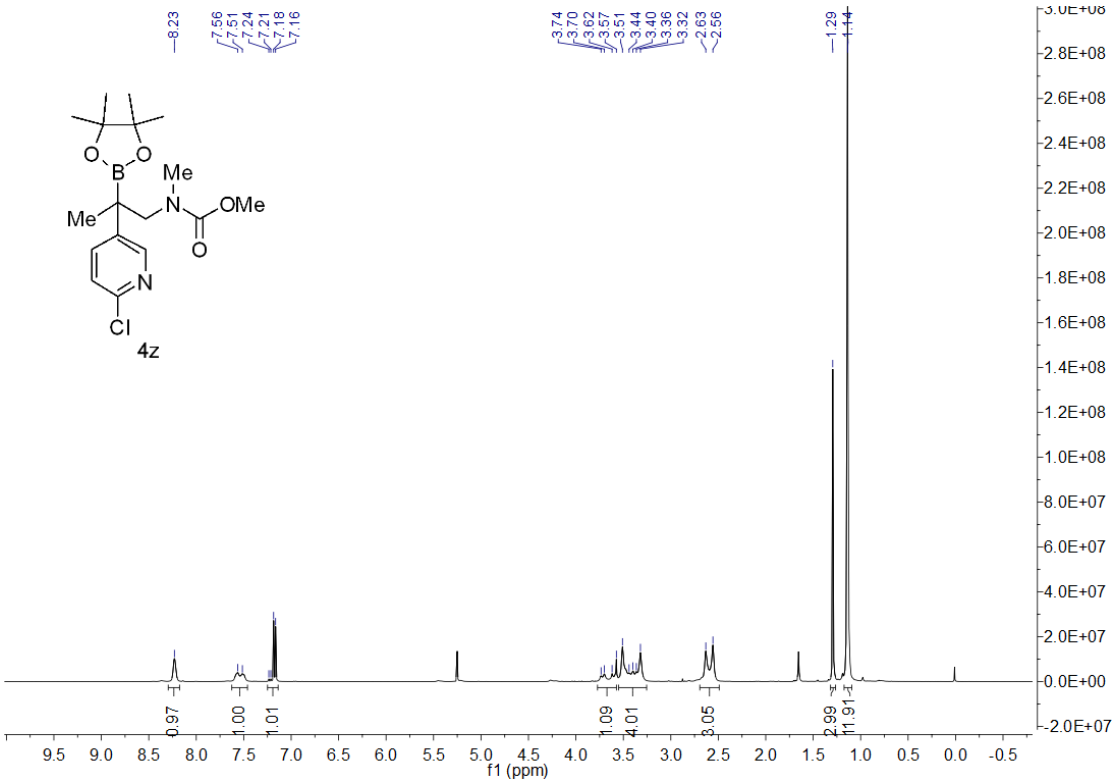

164.13
161.71
157.54
157.26
148.29
147.94
129.42
129.34
123.08
114.15
113.94
112.36
112.16
83.81
57.25
56.76
52.29
51.98
36.30
35.72
24.39
24.22
17.73
0.76
O
B
O
Me
N
OMe
Me
O
F
4y
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

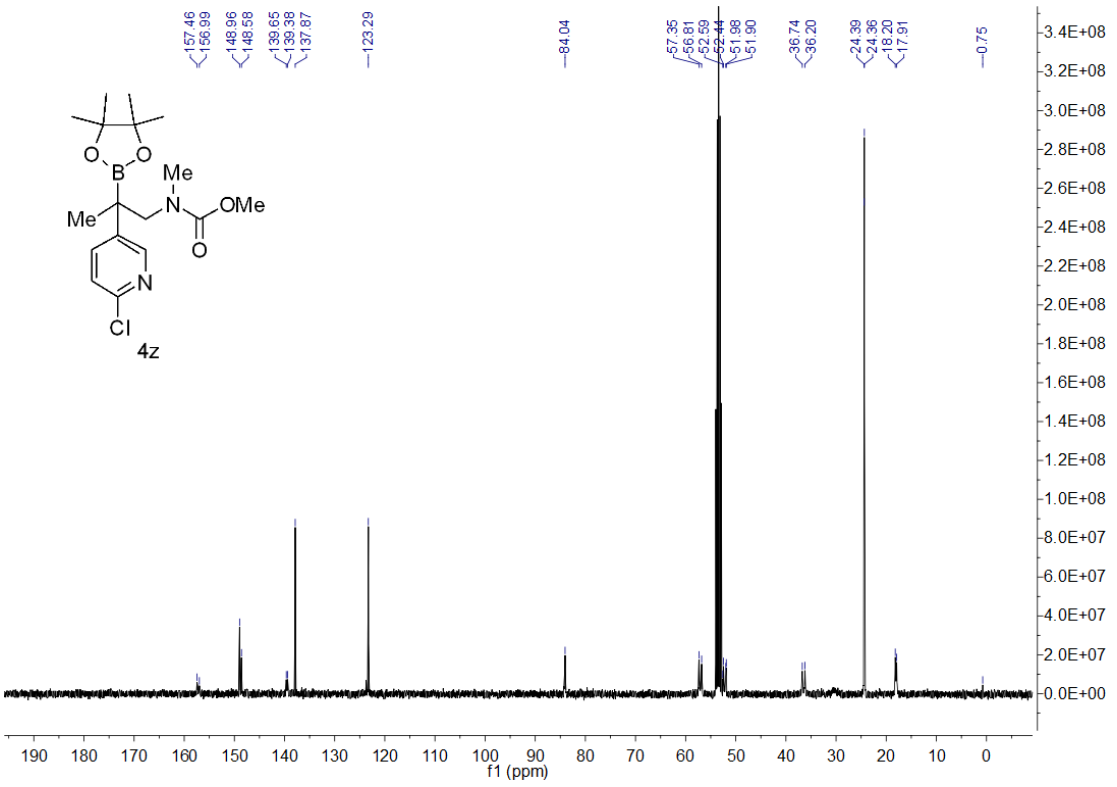

33.13
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -20
f1 (ppm)
O
B
O
Me
N
OMe
Me
O
F

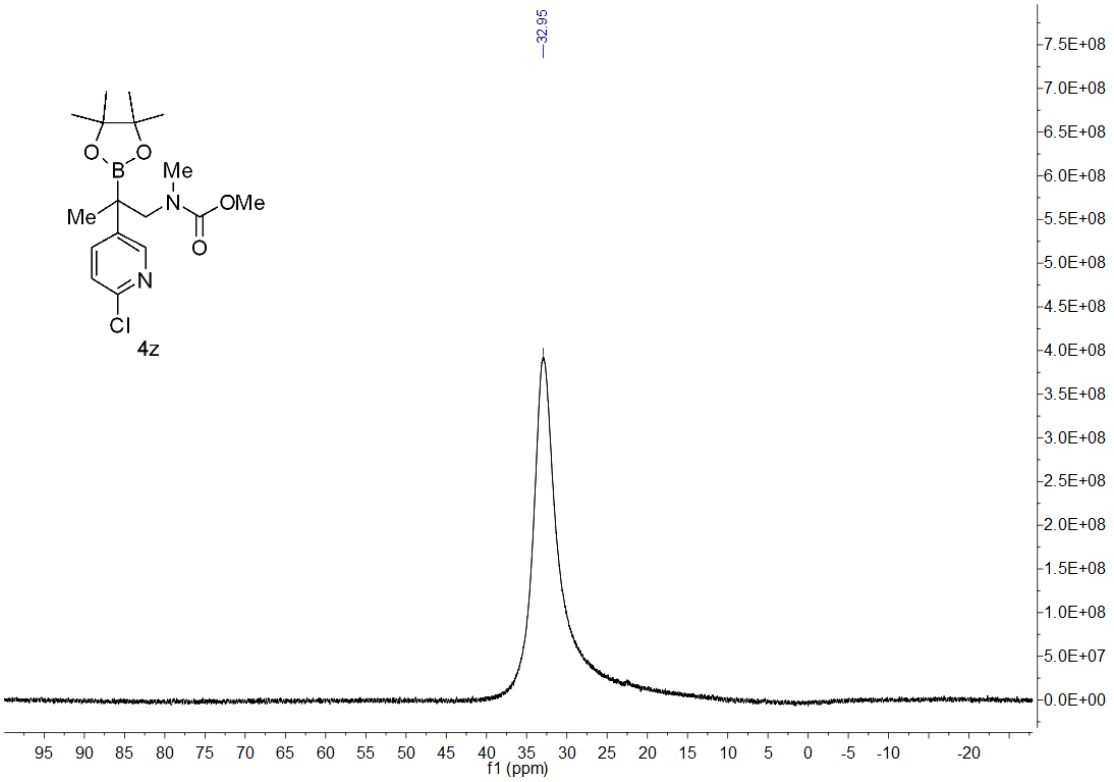
4y

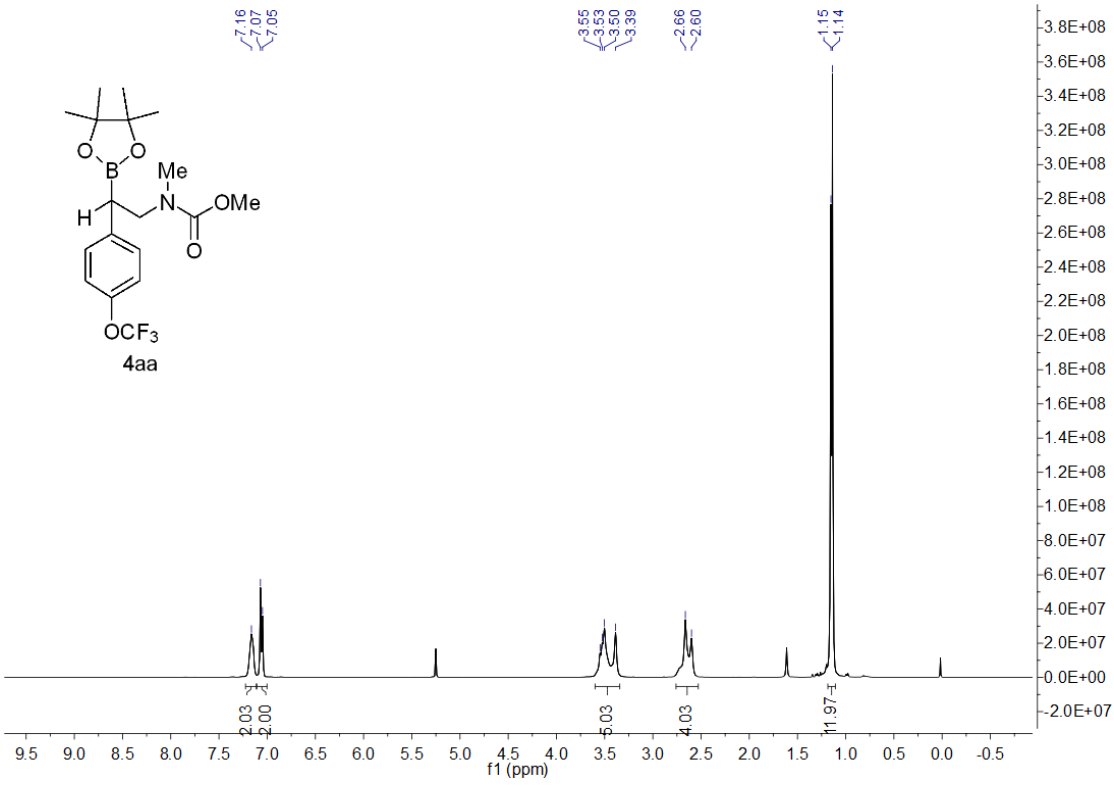

114.26
114.31
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
40 20 0 -10 -30 -50 -70 -90 -110 -140 -170 -200 -230
f1 (ppm)
O
B
O
Me
N
OMe
Me
O
F

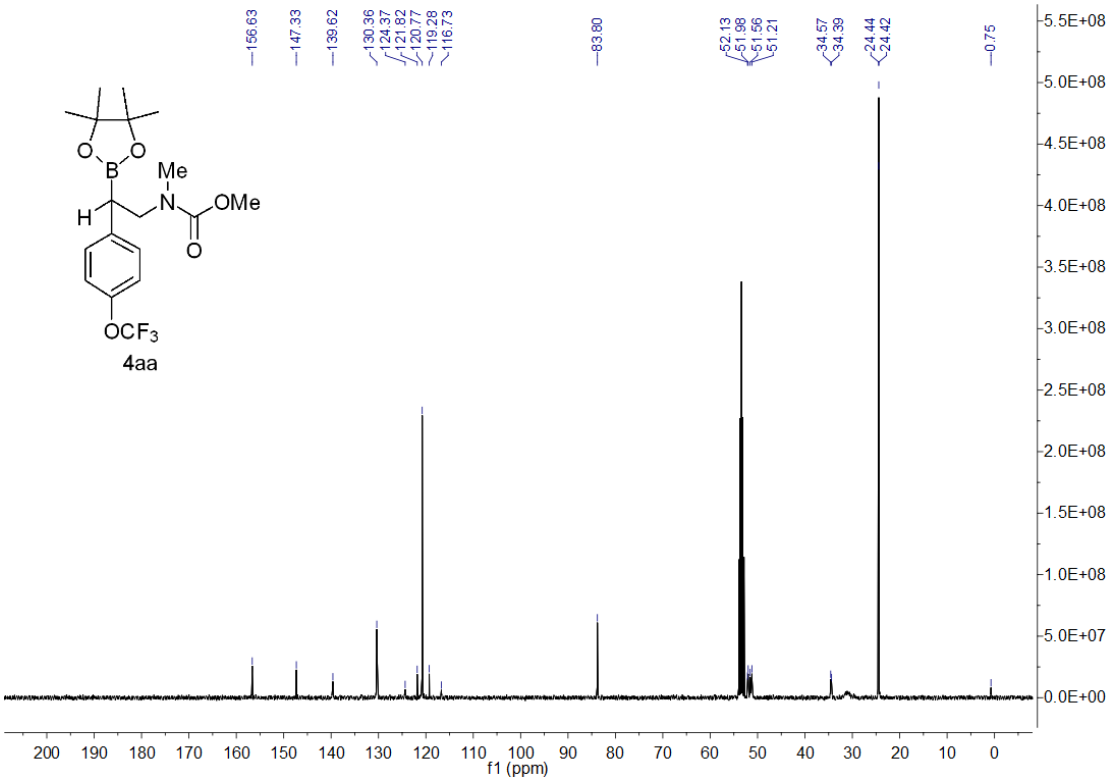
4y

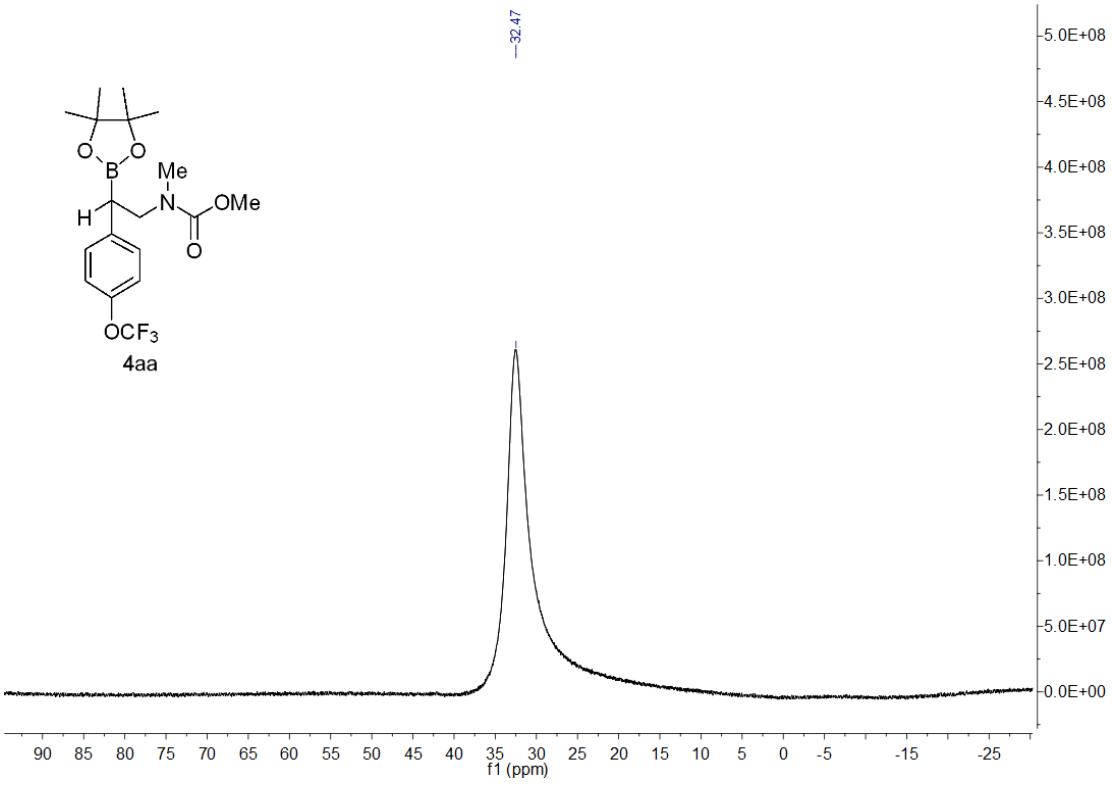

8.23
7.56
7.51
7.24
7.21
7.18
7.16
3.74
3.70
3.62
3.57
3.51
3.44
3.40
3.36
3.32
2.63
2.56
1.29
1.14
Me
N
OMe
O
Me
O
B
O
N
Cl
4z
0.97
1.00
1.01
1.09
4.01
3.05
2.99
11.91
f1 (ppm)

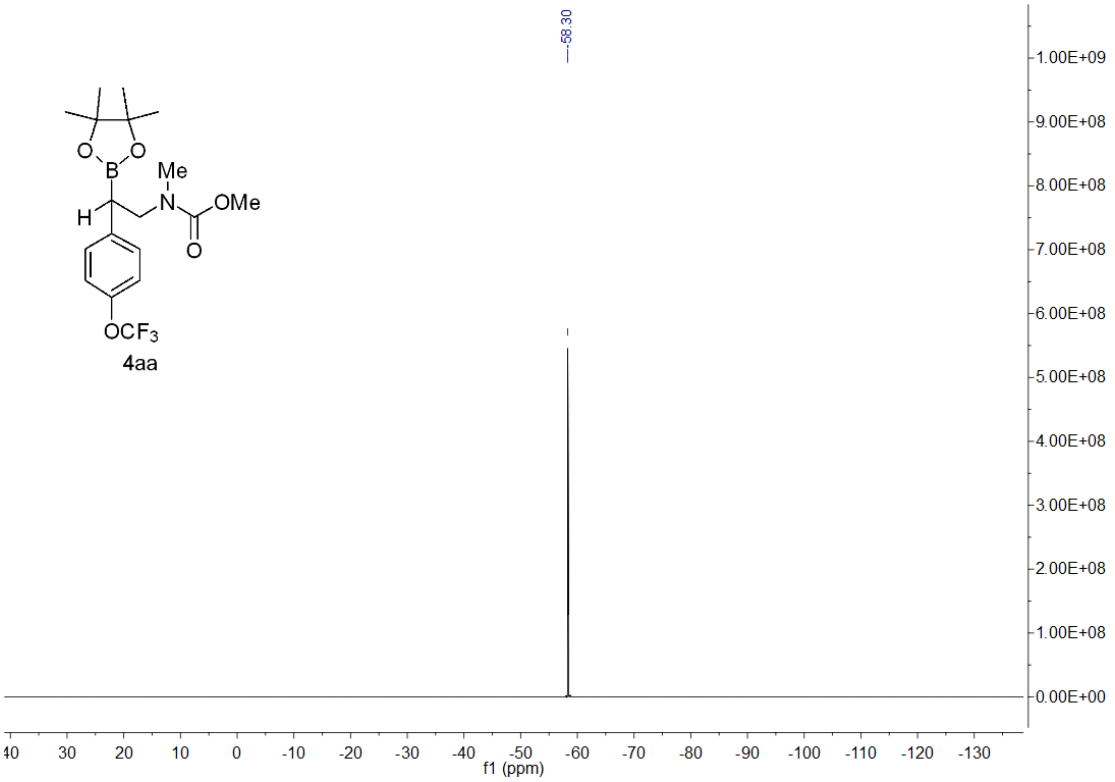

157.46
156.99
148.96
148.58
139.65
139.38
137.87
123.29
84.04
57.35
56.81
52.59
52.44
51.98
51.90
36.74
36.20
24.39
24.36
18.20
17.91
0.75
Me
N
OMe
O
Me
O
B
O
N
Cl
4z
f1 (ppm)


32.95
Me
N
OMe
O
Me
O
B
O
N
Cl
4z
f1 (ppm)

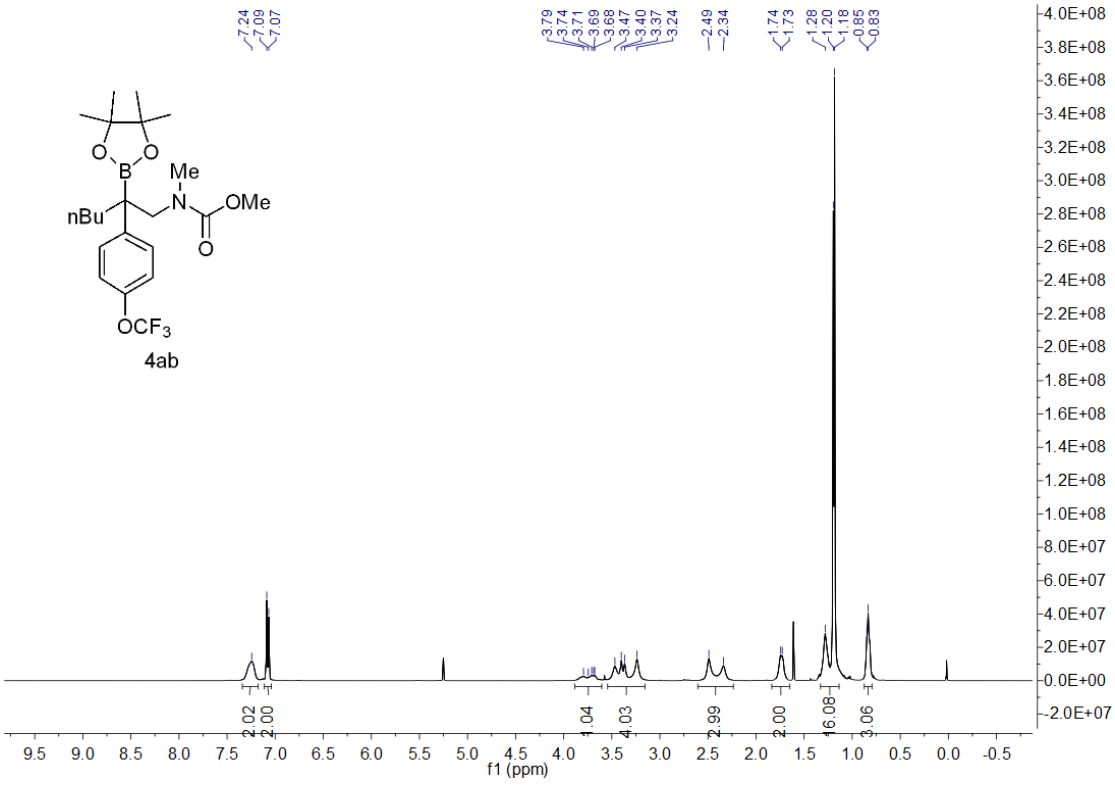

7.16
7.07
7.05
3.55
3.53
3.50
3.39
2.66
2.60
1.15
1.14
Me
N
OMe
O
H
O
B
O
OCF3
4aa
2.03
2.00
5.03
4.03
11.97
f1 (ppm)


156.63
147.33
139.62
130.36
124.37
121.82
120.77
119.28
116.73
83.80
52.13
51.98
51.56
51.21
34.57
34.39
24.44
24.42
0.75
Me
N
OMe
O
H
O
B
O
OCF3
4aa
f1 (ppm)

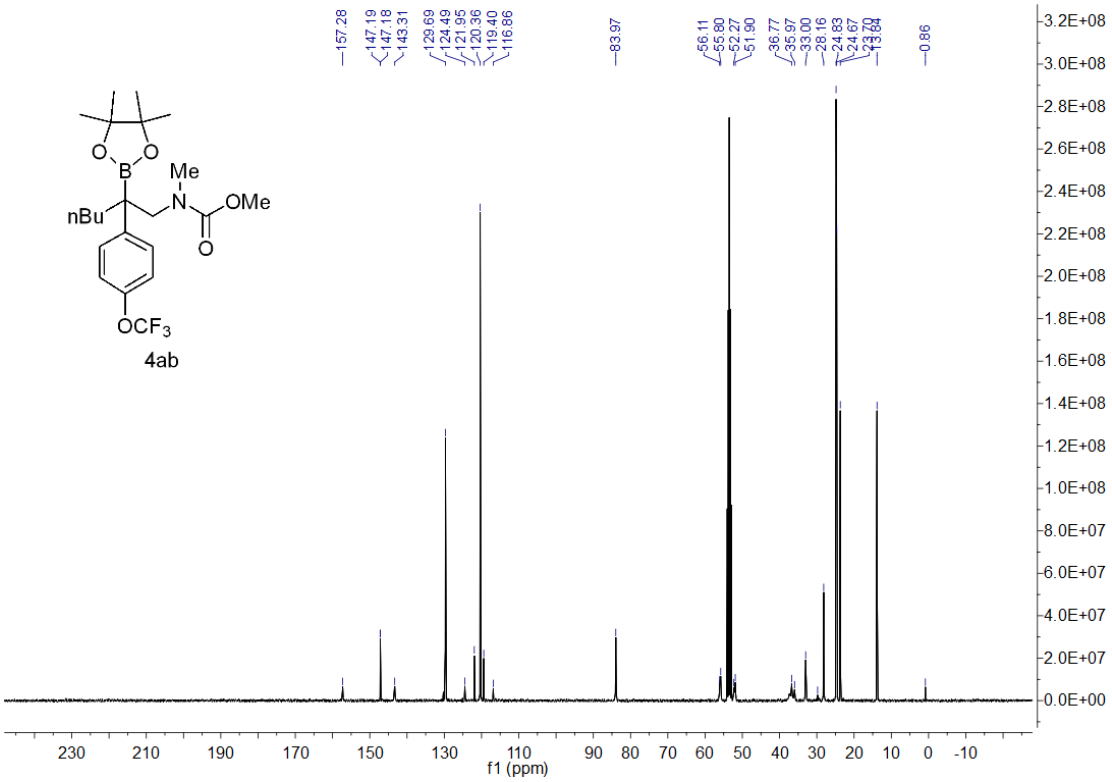

32.47
Me
N
OMe
O
H
O
B
O
OCF3
4aa
f1 (ppm)

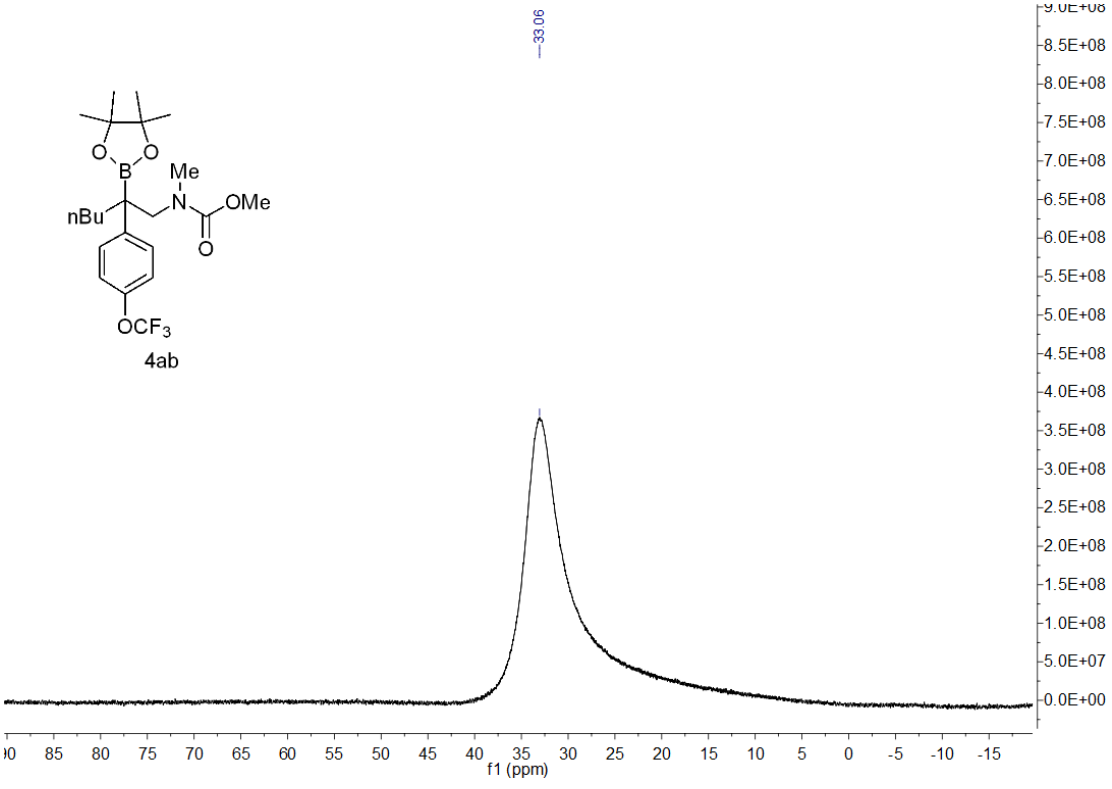

-58.30
1.00E+09
9.00E+08
8.00E+08
7.00E+08
6.00E+08
5.00E+08
4.00E+08
3.00E+08
2.00E+08
1.00E+08
0.00E+00
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130
f1 (ppm)
Me
N
OMe
O
H
B
O
O
OCF3

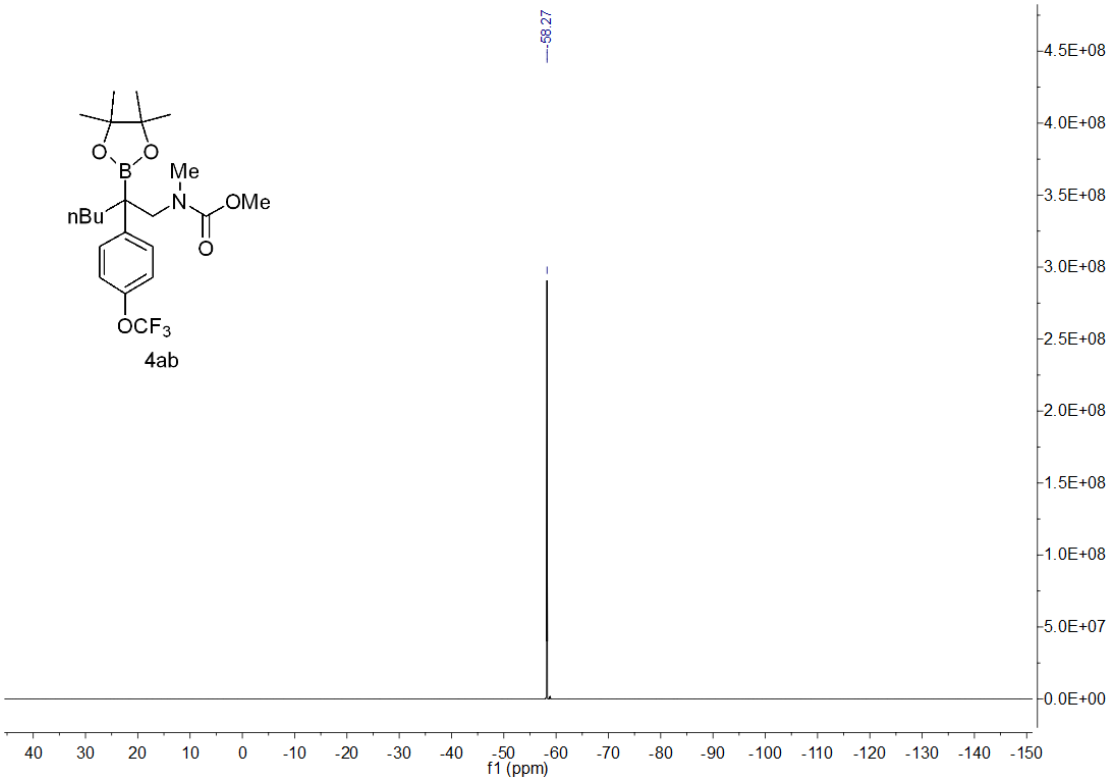
4aa


7.24
7.09
7.07
3.79
3.74
3.71
3.69
3.68
3.47
3.40
3.37
3.24
2.49
2.34
1.74
1.73
1.28
1.20
1.18
0.85
0.83
4.0E+08
3.8E+08
3.6E+08
3.4E+08
3.2E+08
3.0E+08
2.8E+08
2.6E+08
2.4E+08
2.2E+08
2.0E+08
1.8E+08
1.6E+08
1.4E+08
1.2E+08
1.0E+08
8.0E+07
6.0E+07
4.0E+07
2.0E+07
0.0E+00
-2.0E+07
2.02
2.00
1.04
4.03
2.99
2.00
16.08
3.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
Me
N
OMe
O
nBu
B
O
O
OCF3

4ab

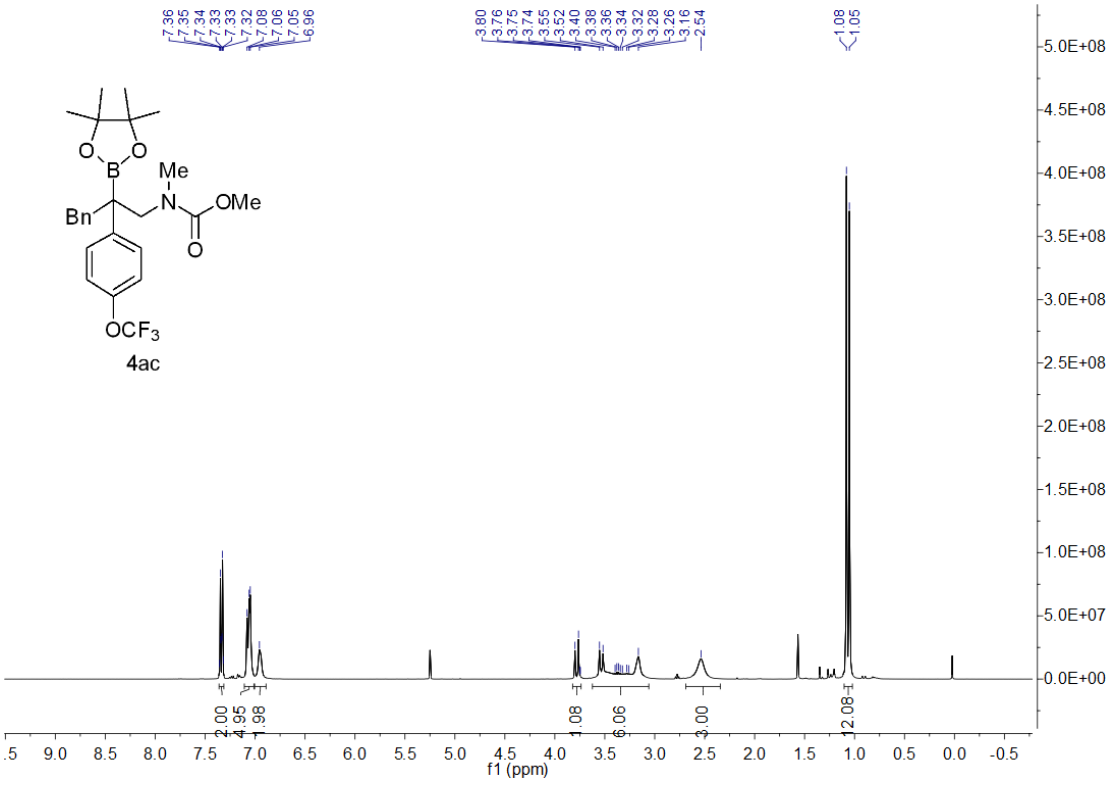

157.28
147.19
147.18
143.31
129.69
124.49
121.95
120.36
119.40
116.86
83.97
56.11
55.80
52.27
51.90
36.77
35.97
33.00
28.16
24.83
24.67
13.70
13.64
0.86
Me
N
OMe
O
nBu
O
B
O
OCF3
4ab
f1 (ppm)


33.06
Me
N
OMe
O
nBu
O
B
O
OCF3
4ab
f1 (ppm)


-58.27
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150
f1 (ppm)

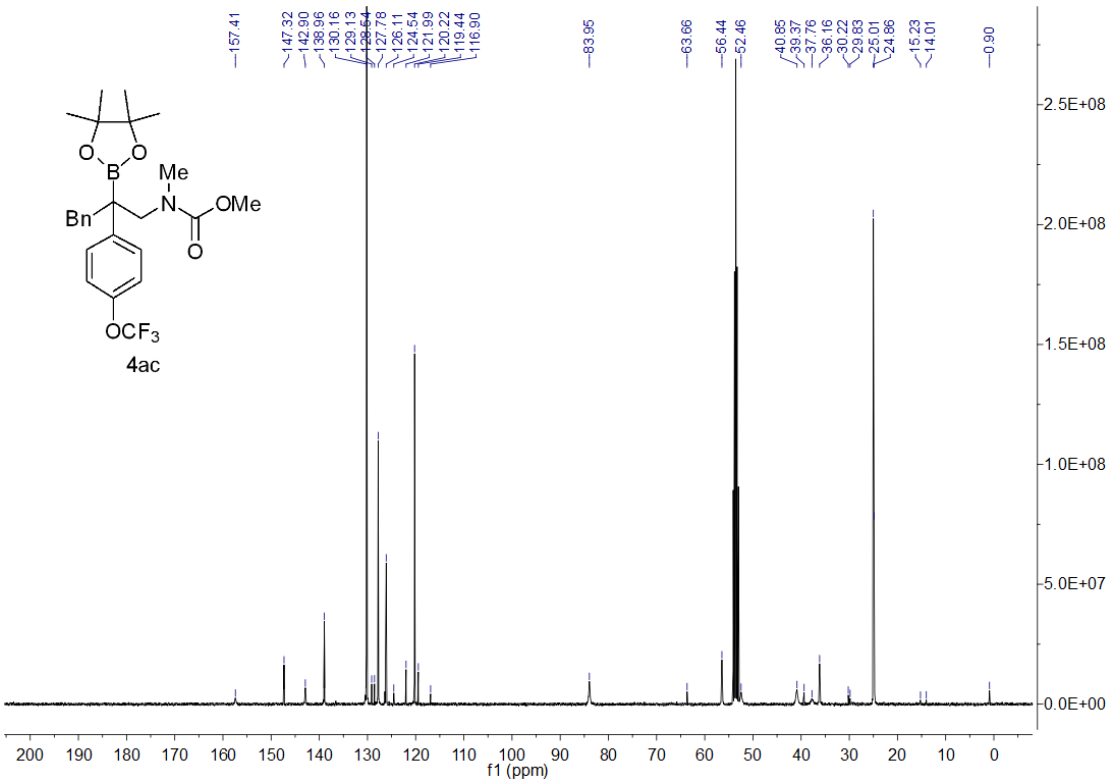
Me
nBu
N
OMe
O
O
B
O
O
OCF3

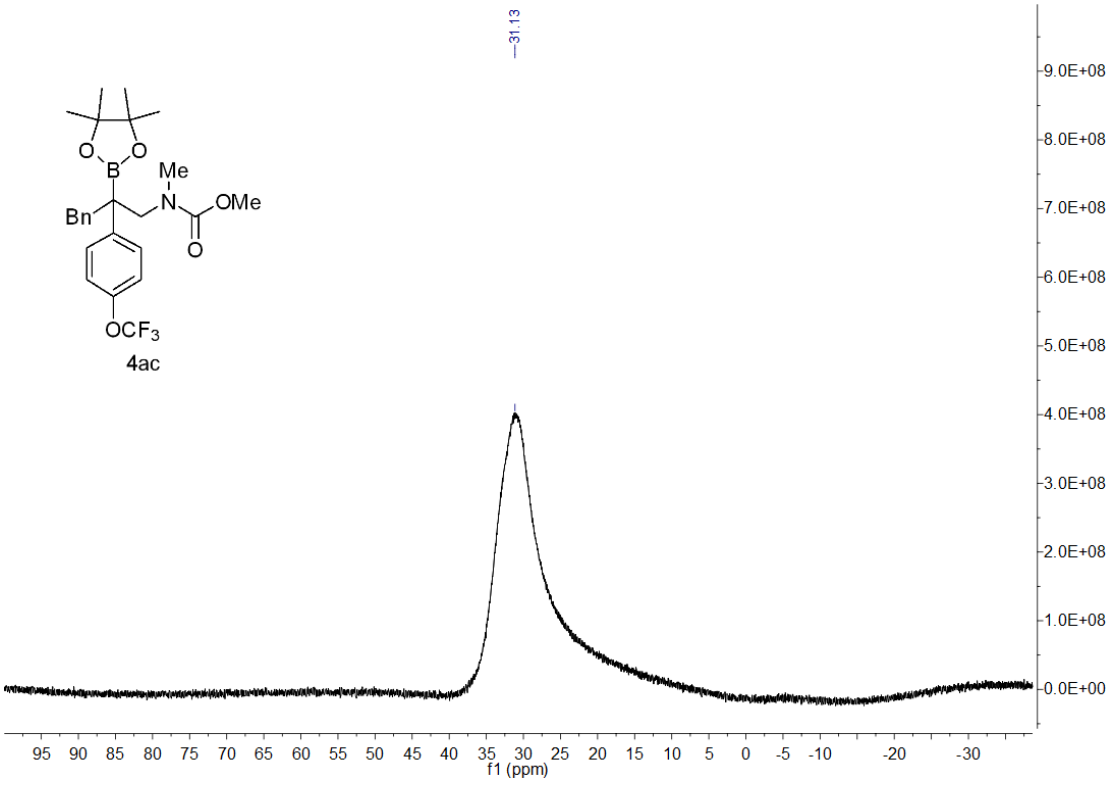
4ab

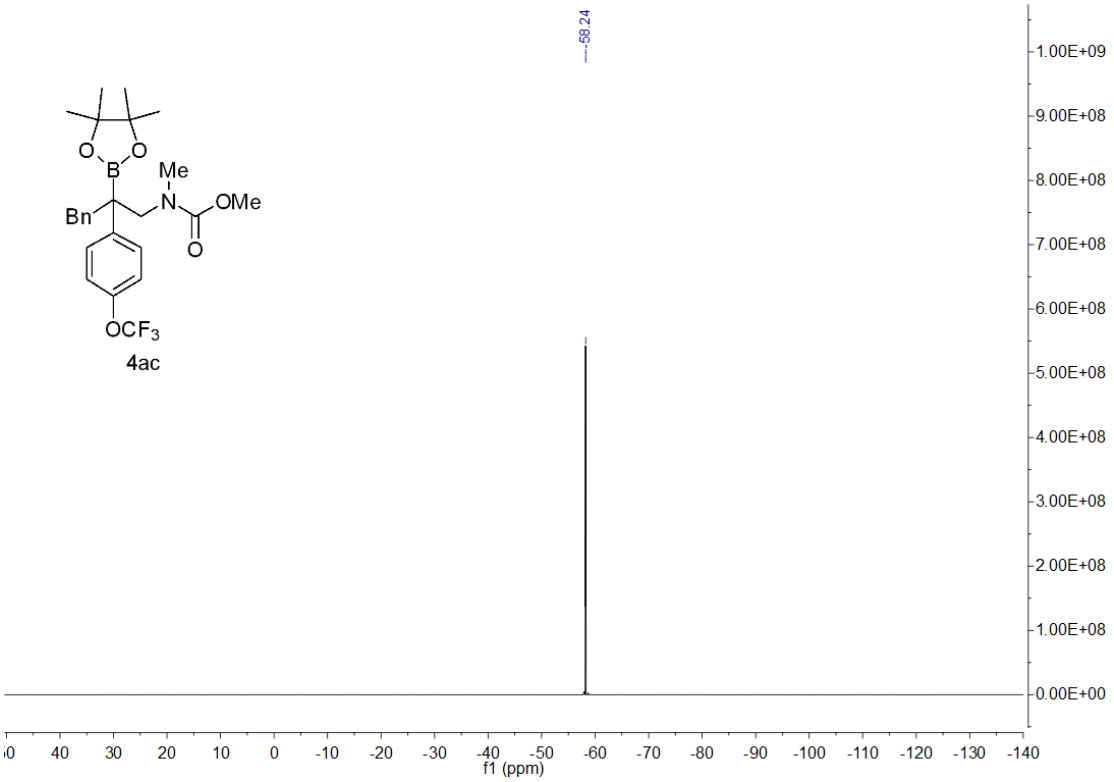

7.36
7.35
7.34
7.33
7.33
7.32
7.08
7.06
7.05
6.96
3.80
3.76
3.75
3.74
3.55
3.52
3.40
3.38
3.36
3.34
3.32
3.28
3.26
3.16
2.54
1.08
1.05
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
2.00
4.95
1.98
1.08
6.06
3.00
12.08
.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

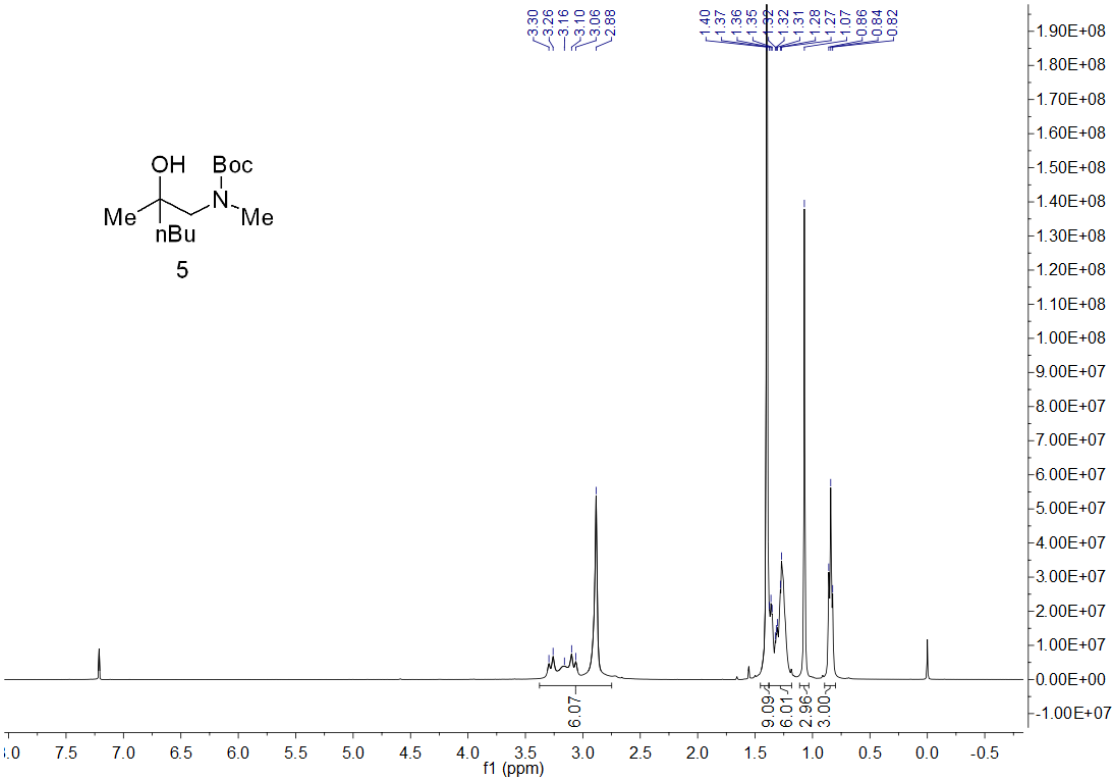
Me
Bn
N
OMe
O
O
B
O
O
OCF3

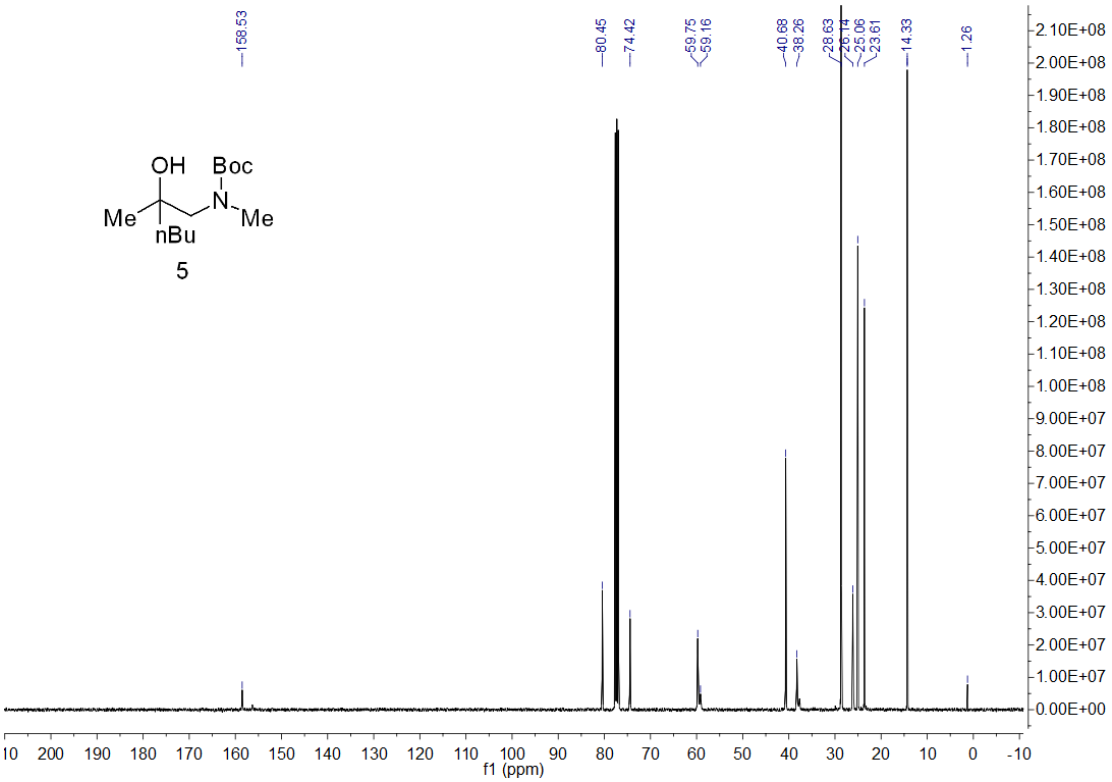
4ac

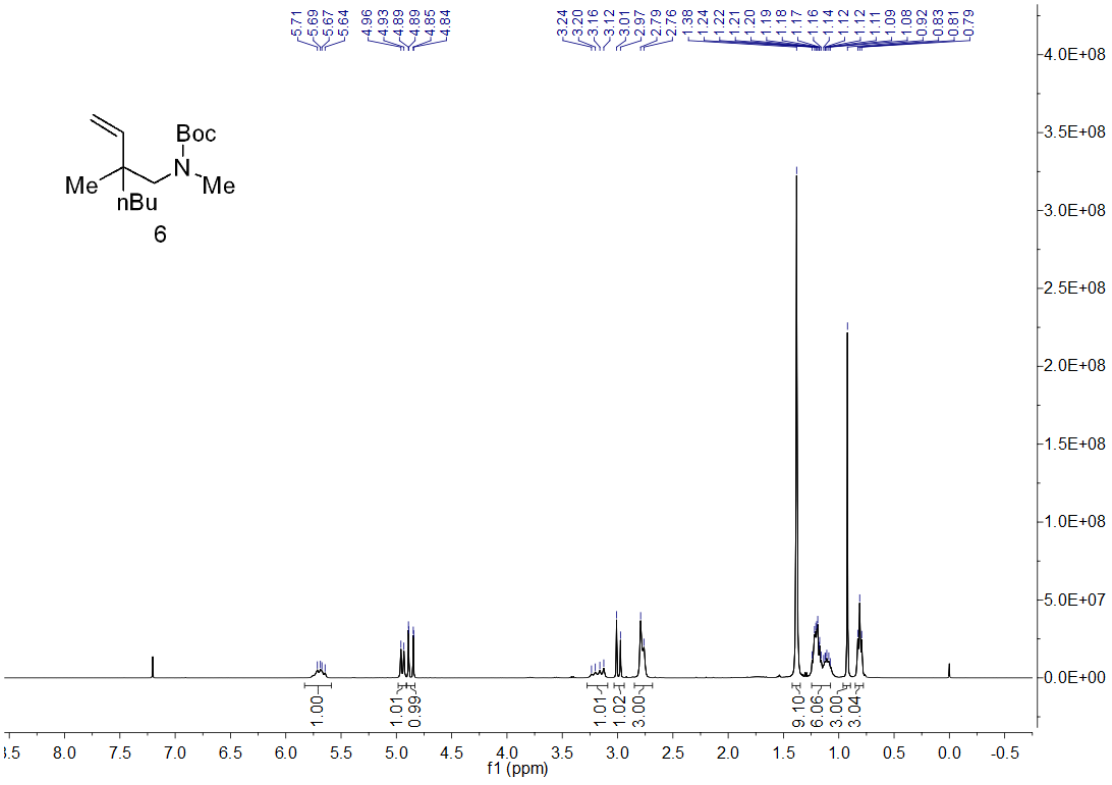

157.41
147.32
142.90
138.96
130.16
129.13
128.54
127.78
126.11
124.54
121.99
120.22
119.44
116.90
83.95
63.66
56.44
52.46
40.85
39.37
37.76
36.16
30.22
29.83
25.01
24.86
15.23
14.01
0.90
Me
N
OMe
O
Bn
O
B
O
OCF3
4ac
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

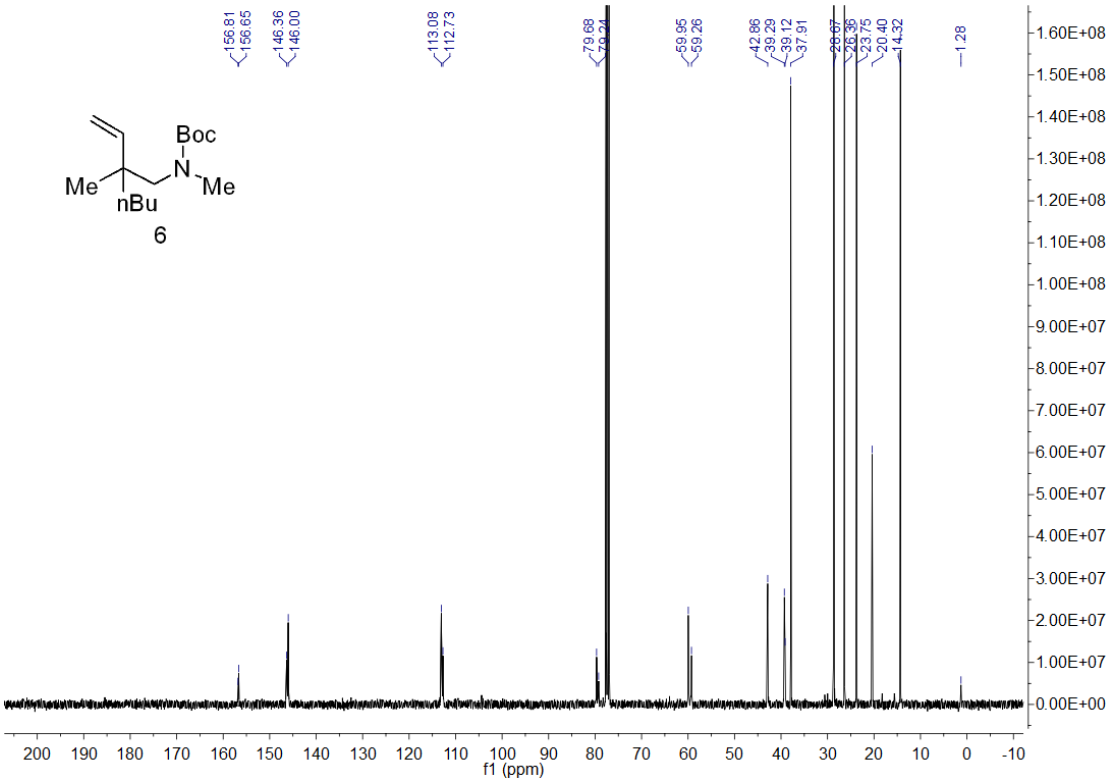

31.13
Me
N
OMe
O
Bn
O
B
O
OCF3
4ac
9.0E+08
8.0E+08
7.0E+08
6.0E+08
5.0E+08
4.0E+08
3.0E+08
2.0E+08
1.0E+08
0.0E+00
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -20 -30
f1 (ppm)

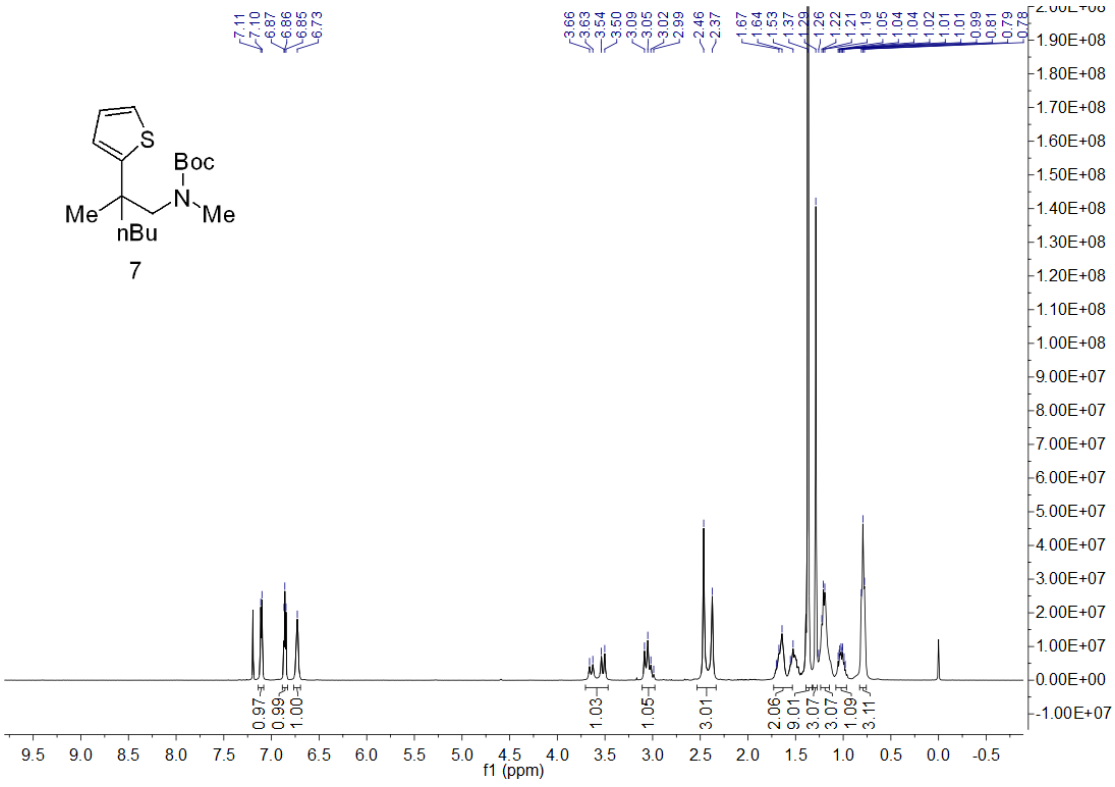

-58.24
1.00E+09
9.00E+08
8.00E+08
7.00E+08
6.00E+08
5.00E+08
4.00E+08
3.00E+08
2.00E+08
1.00E+08
0.00E+00
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140
f1 (ppm)

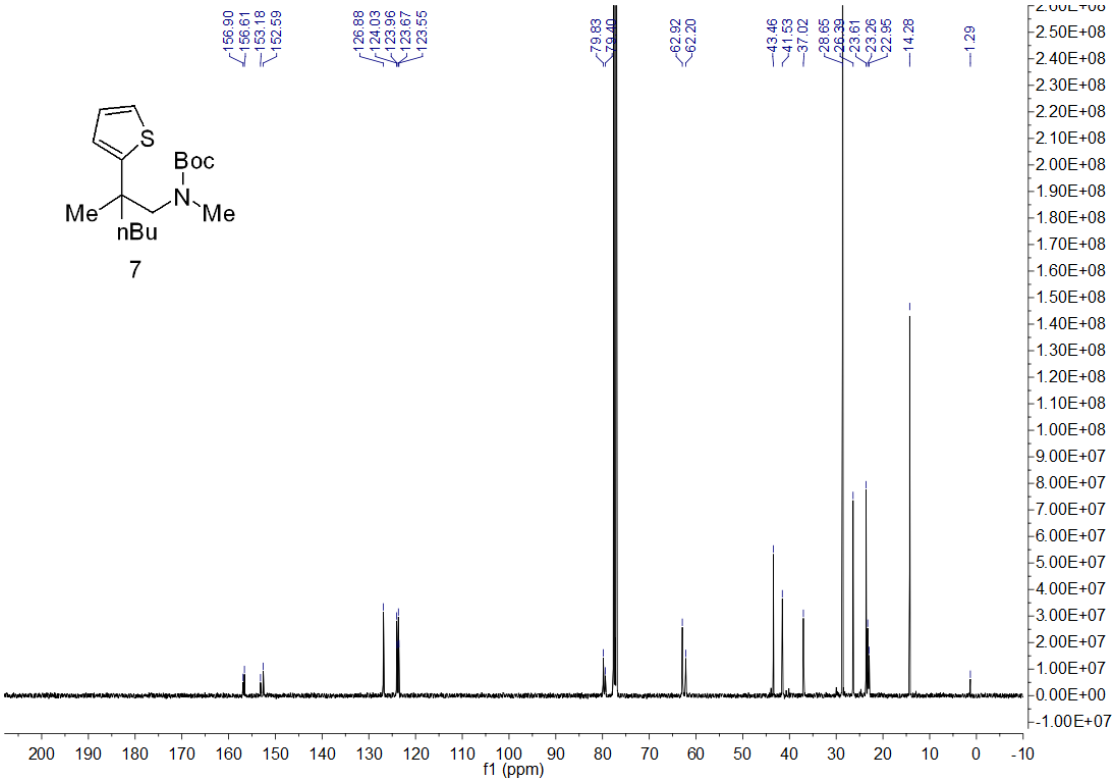

3.30
3.26
3.16
3.10
3.06
2.88
1.40
1.37
1.36
1.35
1.32
1.31
1.28
1.27
1.07
0.86
0.84
0.82
1.90E+08
1.80E+08
1.70E+08
1.60E+08
1.50E+08
1.40E+08
1.30E+08
1.20E+08
1.10E+08
1.00E+08
9.00E+07
8.00E+07
7.00E+07
6.00E+07
5.00E+07
4.00E+07
3.00E+07
2.00E+07
1.00E+07
0.00E+00
-1.00E+07
6.07
9.09
6.01
2.96
3.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


158.53
80.45
74.42
59.75
59.16
40.68
38.26
28.63
26.14
25.06
23.61
14.33
1.26
OH
Boc
Me
N
Me
nBu
5
f1 (ppm)


5.71
5.69
5.67
5.64
4.96
4.93
4.89
4.89
4.85
4.84
3.24
3.20
3.16
3.12
3.01
2.97
2.79
2.76
1.38
1.24
1.22
1.21
1.20
1.19
1.18
1.17
1.16
1.14
1.12
1.12
1.11
1.09
1.08
0.92
0.83
0.81
0.79
Boc
Me
N
Me
nBu
6
1.00
1.01
0.99
1.01
1.02
3.00
9.10
6.06
3.00
3.04
f1 (ppm)


156.81
156.65
146.36
146.00
113.08
112.73
79.68
79.24
59.95
59.26
42.86
39.29
39.12
37.91
28.67
28.36
23.75
20.40
14.32
1.28
Boc
N
Me
Me
nBu
6
f1 (ppm)


7.11
7.10
6.87
6.86
6.85
6.73
3.66
3.63
3.54
3.50
3.09
3.05
3.02
2.99
2.46
2.37
1.67
1.64
1.53
1.37
1.29
1.26
1.22
1.21
1.19
1.05
1.04
1.02
1.01
0.99
0.81
0.79
0.78
S
Boc
N
Me
Me
nBu
7
0.97
0.99
1.00
1.03
1.05
3.01
2.06
9.01
3.07
3.07
1.09
3.11
f1 (ppm)


156.90
156.61
153.18
152.59
126.88
124.03
123.96
123.67
123.55
79.83
79.40
62.92
62.20
43.46
41.53
37.02
28.65
26.39
23.61
23.26
22.95
14.28
1.29
S
Boc
N
Me
Me
nBu
7
f1 (ppm)