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Supporting Information

Regioselective Multicomponent Synthesis of α-Boryl Ureas: Discovery of a Potent Main Protease Inhibitor

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1. General Information

Analytical thin layer chromatography (TLC) was carried out using silica gel 60 F254 pre-coated plates. Visualization was accomplished with UV lamp or I_2 stain. Silica gel 230-400 mesh size was used for flash column chromatography using the combination of ethyl acetate and petroleum ether as eluent. Unless noted, all reactions were carried out in oven-dried glassware under an atmosphere of nitrogen/argon using anhydrous solvents. All commercial reagents were used as received. ^{1}H NMR, ^{13}C NMR, ^{11}B NMR and ^{19}F NMR spectra were recorded on Varian-Inova-400, Bruker-ARX-400 or Bruker Avance-III-800 spectrometer at ambient temperature. Multiplicities are indicated as s (singlet), d (doublet), t (triplet), m (multiplet), and br (broad). Mass spectra (MS) were obtained using ESI mass spectrometers.

2. General synthetic and main protease assay protocols

General Procedure A for α-Boryl Ureas

To a 25 mL Round-bottom flask, a haloboronated compound (1.0 equiv), DMF (0.5 M), TMSNCO (1.5 equiv), and NaI (1.0 equiv) were added. The mixture was stirred at 23 °C under a nitrogen atmosphere. Amine (1.5 equiv) was added to the reaction. On completion according to TLC, the reaction mixture was quenched with chilled water and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography to obtain the desired product.

General Procedure B for α-Boryl Ureas

To a 25 mL round-bottom flask were added the haloboronated compound (1.0 equiv), DMF (0.5 M), TMSNCO (1.5 equiv), and NaI (1.0 equiv) under a nitrogen atmosphere. The resulting mixture was stirred at 23 °C. Subsequently, the amine-HCl salt (1.5 equiv) and triethylamine (3.0 equiv) were added, and the reaction was stirred until completion as monitored by TLC. The reaction mixture was then quenched with chilled water and extracted with ethyl acetate. The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by flash column chromatography to afford the desired product.

Main Protease (MPro) Assay Experiment

We conducted the assay using 20 nM MPro and 10 μM of Sub3 by previously reported method.[1] We dissolved all compounds (Nirmatrelvir and NS-D-154) in DMSO as 10 mM stock solutions. Sub3 was dissolved in DMSO as a 1 mM stock solution and diluted 100 times in the final assay buffer containing 10 mMNaxHyPO4, 10 mM NaCl, 0.5 mM EDTA, and 1.25% DMSO at pH 7.6. We incubated MPro and an inhibitor in the final assay buffer for 30 min before adding the substrate to initiate the reaction catalyzed by MPro. The production format was monitored in a fluorescence plate reader with excitation at 336 nm and emission at 490 nm. All data were analyzed and fitted to a four-parameter variable slope inhibition equation in GraphPad Prism 10 to obtain the IC_{50} values.

3. HRMS data for int-3

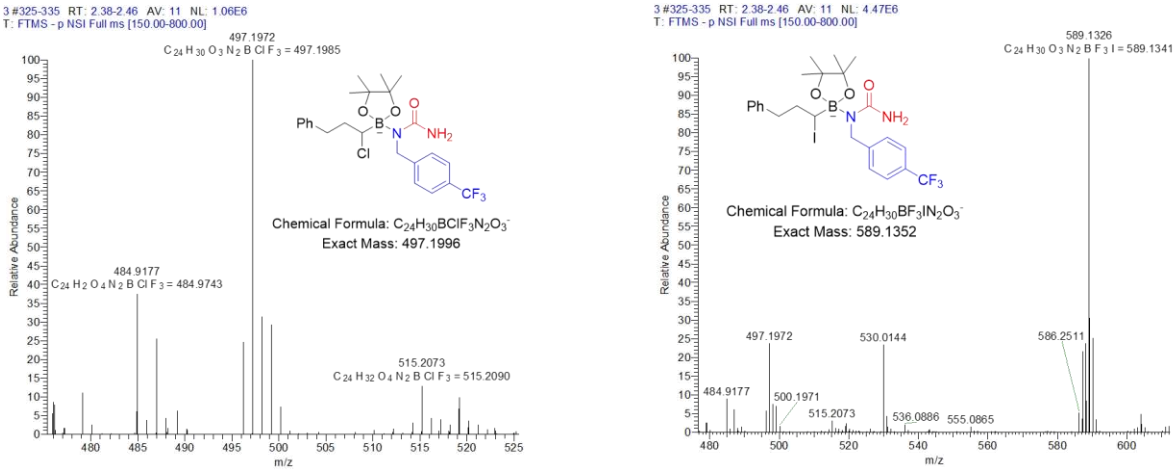


Figure S1 HRMS spectrum showing the formation of the **int-3**.

4. Unsuccessful amines

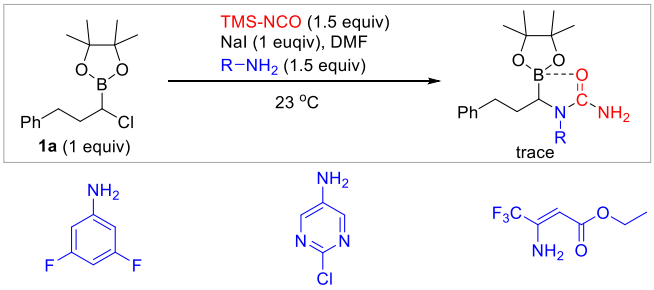


Figure S2 Unsuccessful amines under the standard conditions.

5. Reaction of chiral α-haloboronate

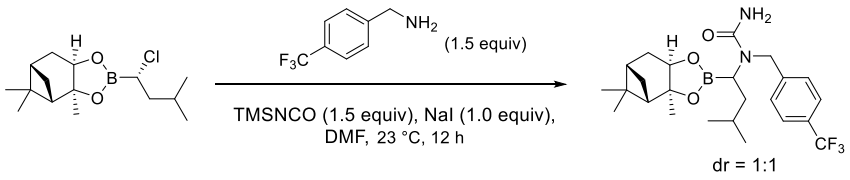
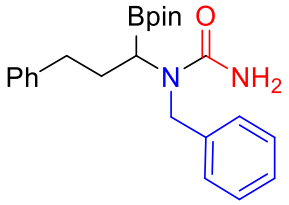


Figure S3 Reaction of chiral α-chloroboronate under the standard conditions led to a diastereomeric mixture of α-boryl ureas (dr = 1:1). This observation is consistent with the known racemization of chiral α-chloroboronates upon treatment with TMSI or NaBr.[2]

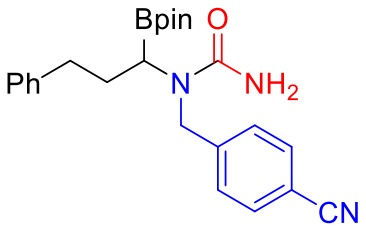
6. Experimental and characterization data

1-Benzyl-3-(3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)urea (4):



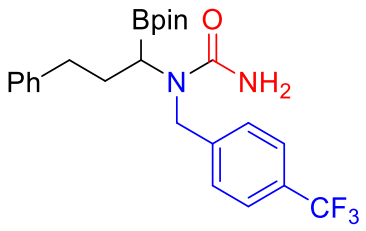
Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-6% methanol in dichloromethane, yielding a white solid (130 mg, 66%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.54 (s, 1H), 7.37 (dd, J = 8.0, 6.5 Hz, 2H), 7.32 – 7.18 (m, 6H), 7.14 (d, J = 7.4 Hz, 3H), 4.66 (d, J = 16.2 Hz, 1H), 4.22 (d, J = 16.3 Hz, 1H), 2.73 – 2.61 (m, 1H), 2.46 – 2.34 (m, 1H), 2.14 (dd, J = 7.5, 2.5 Hz, 1H), 1.83 – 1.68 (m, 1H), 1.66 – 1.56 (m, 1H), 1.04 (s, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.34, 143.46, 136.42, 128.55, 128.16, 128.12, 127.55, 127.33, 125.30, 78.21, 45.35, 31.63, 30.66, 25.65. ^{11}B NMR (128 MHz, DMSO-d_6) δ 11.20. HRMS (ESI) calcd for $C_{23}H_{30}BN_2O_3$ $[M–H]^+$, 393.2344; found, 393.2354.

1-(4-cyanobenzyl)-3-(3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)urea (5):



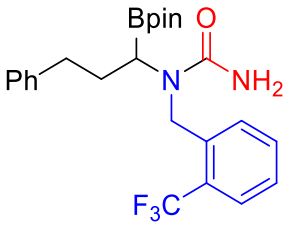
Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-6% methanol in dichloromethane, yielding a white solid (113 mg, 54%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.85 (d, J = 8.3 Hz, 2H), 7.59 (s, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.23 (t, J = 7.5 Hz, 2H), 7.17 – 7.06 (m, 3H), 4.72 (d, J = 17.0 Hz, 1H), 4.39 (d, J = 17.0 Hz, 1H), 2.70 – 2.60 (m, 1H), 2.47 – 2.36 (m, 1H), 2.13 (dd, J = 7.7, 2.6 Hz, 1H), 1.83 – 1.68 (m, 1H), 1.65 – 1.54 (m, 1H), 1.05 (s, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.52, 143.29, 142.41, 132.54, 128.20, 128.14, 128.11, 125.33, 118.72, 110.14, 78.32, 45.23, 31.63, 30.66, 25.64. ^{11}B NMR (128 MHz, DMSO-d_6) δ 10.98. HRMS (ESI) calcd for $C_{24}H_{31}BN_3O_3$ $[M+H]^+$, 420.2453; found, 420.2454.

1-(3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-3-(4-(trifluoromethyl)benzyl)urea (6):



Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-6% methanol in dichloromethane, yielding a white solid (157 mg, 68%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.75 (d, J = 8.1 Hz, 2H), 7.60 (s, 2H), 7.41 (d, J = 8.0 Hz, 2H), 7.26 – 7.18 (m, 2H), 7.16 – 7.07 (m, 3H), 4.73 (d, J = 16.8 Hz, 1H), 4.39 (d, J = 16.7 Hz, 1H), 2.74 – 2.60 (m, 1H), 2.47 – 2.35 (m, 1H), 2.14 (dd, J = 7.4, 2.6 Hz, 1H), 1.82 – 1.67 (m, 1H), 1.66 – 1.53 (m, 1H), 1.05 (s, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.50, 143.33, 141.42, 128.16, 128.13, 128.09, 127.85, 125.49 (q, J = 3.8 Hz), 125.31, 124.25 (q, J = 272.4 Hz), 78.28, 45.18, 31.61, 30.69, 25.64. ^{19}F NMR (376 MHz, DMSO-d_6) δ -60.88. ^{11}B NMR (128 MHz, DMSO-d_6) δ 10.91. HRMS (ESI) calcd for $C_{24}H_{31}BF_3N_2O_3$ $[M+H]^+$, 463.2374; found, 463.2378.

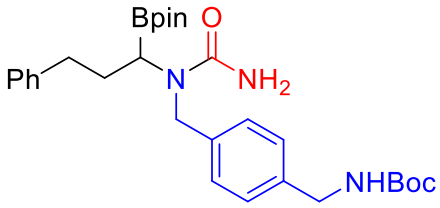
1-(3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-3-(2-(trifluoromethyl)benzyl)urea (7):



Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a white solid (136 mg, 59%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.80 – 7.71 (m, 2H), 7.66 (s, 2H), 7.52 (t, J = 7.6 Hz, 1H), 7.26 – 7.15 (m, 3H), 7.14 – 7.06 (m, 3H), 4.79 (d, J = 17.7 Hz, 1H), 4.47 (d, J = 17.6 Hz, 1H), 2.66 – 2.58 (m, 1H), 2.48 – 2.39 (m, 1H), 2.14 (dd, J = 7.3, 2.9 Hz, 1H), 1.67 – 1.50 (m, 2H), 1.07 – 0.97 (m, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 163.59, 162.84, 143.64, 135.09, 133.43, 128.65, 128.39, 128.29, 127.91, 127.25

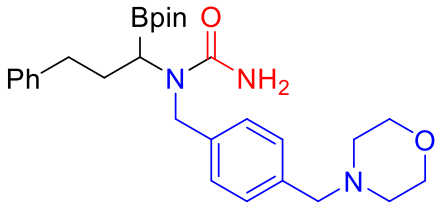
(q, *J* = 274 Hz), 126.91 (d, *J* = 29.9 Hz), 125.84, 81.85, 78.86, 74.02, 42.97, 36.26, 32.30, 31.24, 26.07, 25.39, 24.93. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -60.31. ^{11}B NMR (128 MHz, DMSO-d_6) δ 22.08. HRMS (ESI) calculated for $C_{24}H_{29}BF_3N_2O_3$ $[M+H]^+$ 461.2223, found: 461.2224.

***tert*-butyl (4-((3-(3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)ureido)methyl) benzyl)carbamate (8):**



Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a white solid (167 mg, 65%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.53 (s, 2H), 7.36 (t, *J* = 6.2 Hz, 1H), 7.27 – 7.18 (m, 4H), 7.17 – 7.10 (m, 5H), 4.64 (d, *J* = 16.1 Hz, 1H), 4.21 – 4.05 (m, 3H), 2.74 – 2.59 (m, 1H), 2.47 – 2.34 (m, 1H), 2.16 – 2.07 (m, 1H), 1.81 – 1.68 (m, 1H), 1.66 – 1.53 (m, 1H), 1.39 (s, 9H), 1.03 (s, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.27, 155.81, 143.47, 139.35, 134.72, 128.18, 128.12, 127.55, 127.15, 125.27, 78.20, 77.75, 45.12, 43.13, 31.64, 30.65, 28.25, 25.64. ^{11}B NMR (128 MHz, DMSO-d_6) δ 10.32. HRMS (ESI) calcd for $C_{29}H_{43}BN_3O_5$ $[M+H]^+$, 524.3290; found, 524.3298.

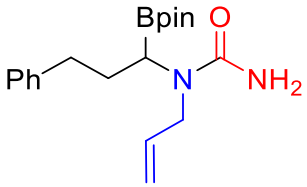
1-(4-(morpholinomethyl)benzyl)-3-(3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)urea (9):



Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a white solid (135 mg, 55%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.26 (dd, *J* = 9.7, 5.4 Hz, 7H), 7.14 (t, *J* = 6.9 Hz, 4H), 4.35 – 4.18 (m, 2H), 3.54 (t, *J* = 4.6 Hz, 4H), 3.43 (s, 2H), 2.70 – 2.61 (m, 1H), 2.46 (s, 1H), 2.37 – 2.27 (m, 4H), 2.24 (t, *J* = 6.7 Hz, 1H), 1.69 – 1.57 (m, 1H), 1.44 (s, 1H), 1.01 (s, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.30,

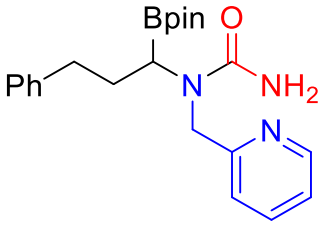
143.16, 136.64, 128.99, 128.17, 127.21, 125.34, 78.35, 66.14, 62.10, 53.11, 34.96, 33.50, 25.56, 25.36. ^{11}B NMR (128 MHz, DMSO-d_6) δ 12.61. HRMS (ESI) calcd for $C_{28}H_{41}BN_3O_4$ $[M+H]^+$, 494.3185; found, 494.3183.

1-allyl-3-(3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)urea (10):



Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a white solid (91mg, 53%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.32 (s, 2H), 7.27 – 7.21 (m, 2H), 7.20 – 7.09 (m, 3H), 5.78 – 5.65 (m, 1H), 5.21 – 5.10 (m, 2H), 4.06 – 3.92 (m, 1H), 3.71 – 3.59 (m, 1H), 2.74 – 2.61 (m, 1H), 2.48 – 2.40 (m, 1H), 2.24 (dd, J = 7.6, 2.7 Hz, 1H), 1.78 – 1.66 (m, 1H), 1.66 – 1.54 (m, 1H), 1.05 (s, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.07, 143.51, 132.37, 128.15, 128.13, 125.31, 117.08, 78.22, 44.62, 31.76, 31.04, 25.67, 24.96. ^{11}B NMR (128 MHz, DMSO-d_6) δ 14.76. HRMS (ESI) calcd for $C_{19}H_{29}BN_2O_3Na$ $[M + Na]^+$, 367.2163; found, 367.2149.

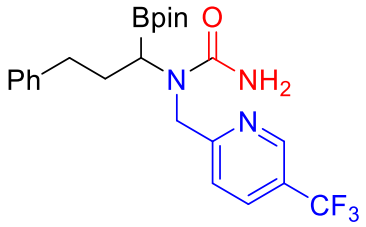
1-(3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-3-(pyridin-2-ylmethyl)urea (11):



Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a yellow solid (105 mg, 53%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.59 – 8.52 (m, 1H), 7.86 – 7.77 (m, 1H), 7.53 (s, 2H), 7.36 – 7.29 (m, 1H), 7.23 (dd, J = 11.8, 7.6 Hz, 3H), 7.15 – 7.06 (m, 3H), 4.70 (d, J = 16.7 Hz, 1H), 4.37 (d, J = 16.6 Hz, 1H), 2.73 – 2.60 (m, 1H), 2.43 – 2.32 (m, 1H), 2.20 (dd, J = 7.3, 2.7 Hz, 1H), 1.81 – 1.67 (m, 1H), 1.65 – 1.53 (m, 1H), 1.05 (s, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.80, 156.19, 149.36, 143.46, 137.05,

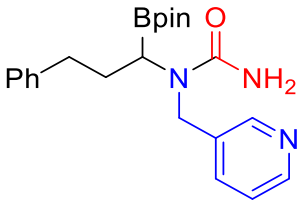
128.13, 128.09, 125.29, 122.63, 121.62, 78.23, 47.81, 31.68, 30.91, 25.63. ^{11}B NMR (128 MHz, DMSO-d_6) δ 10.92. HRMS (ESI) calcd for $C_{22}H_{31}BN_3O_3$ $[M+H]^+$, 396.2453; found, 396.2447.

1-(3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-3-((5-(trifluoromethyl)pyridin-2-yl)methyl)urea (12):



Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a light yellow solid (120 mg, 52%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.00 – 8.94 (m, 1H), 8.26 (dd, J = 8.3, 2.4 Hz, 1H), 7.64 – 7.51 (m, 2H), 7.46 (d, J = 8.2 Hz, 1H), 7.20 (t, J = 7.4 Hz, 2H), 7.15 – 7.03 (m, 3H), 4.80 (d, J = 17.3 Hz, 1H), 4.53 (d, J = 17.2 Hz, 1H), 2.71 – 2.60 (m, 1H), 2.46 – 2.34 (m, 1H), 2.23 – 2.17 (m, 1H), 1.79 – 1.68 (m, 1H), 1.65 – 1.53 (m, 1H), 1.14 – 0.88 (m, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.87, 161.02, 146.14, 143.32, 134.54, 128.18, 128.07, 125.29, 124.00 (q, J = 32.3 Hz), 123.75 (q, J = 272.2 Hz), 121.68, 78.28, 73.51, 47.64, 31.67, 30.83, 25.64. ^{19}F NMR (376 MHz, DMSO-d_6) δ -60.75. ^{11}B NMR (128 MHz, DMSO-d_6) δ 10.80. HRMS (ESI) calcd for $C_{23}H_{30}BF_3N_3O_3$ $[M+H]^+$, 464.2327; found, 464.2320.

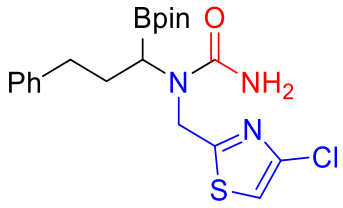
1-(3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-3-(pyridin-3-ylmethyl)urea (13):



Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a light yellow solid (99 mg, 50%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.60 – 8.38 (m, 2H), 7.73 – 7.49 (m, 3H), 7.41 (d, J = 5.8 Hz, 1H), 7.30 – 7.07 (m, 5H), 4.68 (d, J = 16.5 Hz, 1H), 4.31 (d, J = 16.5 Hz, 1H), 2.72 – 2.61 (m, 1H), 2.46 – 2.36 (m, 1H), 2.12 (d, J = 7.1 Hz, 1H), 1.84 – 1.70 (m, 1H), 1.70 – 1.54 (m, 1H), 1.04 (s, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.36, 148.81, 148.63, 143.34, 135.32, 132.14, 128.15, 128.13, 125.33, 123.70, 78.28,

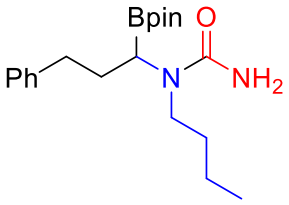
43.10, 31.57, 30.65, 25.63, 25.61. ^{11}B NMR (128 MHz, DMSO-d_6) δ 13.08. HRMS (ESI) calcd for $C_{22}H_{31}BN_3O_3$ $[M+H]^+$, 396.2453; found, 396.2449.

1-((4-chlorothiazol-2-yl)methyl)-3-(3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)urea (14):



Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a yellow solid (128 mg, 59%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.69 (s, 2H), 7.56 (s, 1H), 7.26 (t, J = 7.5 Hz, 2H), 7.21 – 7.10 (m, 3H), 4.78 (d, J = 16.7 Hz, 1H), 4.46 (d, J = 16.7 Hz, 1H), 2.73-2.64 (m, 1H), 2.48 – 2.33 (m, 1H), 2.21-2.14 (m,1H), 1.87 – 1.74 (m, 1H), 1.71-1.59 (m, H), 1.04 (m, 12H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.95, 158.65, 150.35, 149.55, 143.31, 141.95, 140.73, 138.58, 136.15, 128.22 (d, J = 6.5 Hz), 125.42, 78.41, 38.16, 35.93, 31.58, 30.47, 25.65 (d, J = 5.3 Hz). ^{11}B NMR (128 MHz, DMSO-d_6) δ 10.07. HRMS (ESI) calculated for $C_{20}H_{26}BClN_3O_3S$ $[M-H]^+$ 434.1476, found: 434.1486.

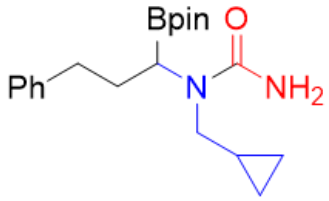
1-butyl-3-(3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)urea (15):



Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a white solid (99 mg, 55%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.20 (d, J = 0.9 Hz, 1H), 7.35 – 7.09 (m, 6H), 3.49 – 3.37 (m, 1H), 3.31 – 3.24 (m, 1H), 2.73 – 2.61 (m, 1H), 2.57 – 2.51 (m, 1H), 2.27 (dd, J = 8.1, 3.3 Hz, 1H), 1.82 – 1.63 (m, 2H), 1.50 – 1.36 (m, 2H), 1.24 – 1.17 (m, 2H), 1.10 (s, 12H), 0.87 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 165.50, 142.69, 128.21, 128.18, 125.54, 79.43, 44.48, 31.74, 29.41, 28.74, 25.53, 25.38, 18.99, 13.37.

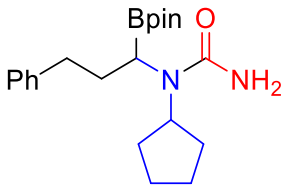
^{11}B NMR (128 MHz, DMSO-d_6) δ 15.83. HRMS (ESI) calcd for $C_{20}H_{32}BN_2O_3$ [M–H]$^+$, 359.2500; found, 359.2510.

1-(cyclopropylmethyl)-3-(3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)urea (16):



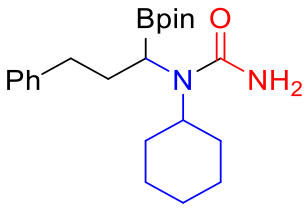
Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a white solid (98 mg, 55%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.29 – 7.21 (m, 4H), 7.20 – 7.10 (m, 3H), 3.29 (d, J = 6.4 Hz, 1H), 2.80 (dd, J = 15.0, 7.5 Hz, 1H), 2.75 – 2.64 (m, 1H), 2.45 (dd, J = 7.5, 2.3 Hz, 1H), 2.42 – 2.32 (m, 1H), 1.80 – 1.66 (m, 1H), 1.66 – 1.55 (m, 1H), 1.06 (s, 12H), 0.96 – 0.84 (m, 1H), 0.52 – 0.36 (m, 2H), 0.24 – 0.11 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.82, 143.56, 128.15, 128.12, 125.28, 78.12, 45.71, 31.53, 30.64, 25.68, 9.08, 3.87, 2.29.^{11}B NMR (128 MHz, DMSO-d_6) δ 10.83. HRMS (ESI) calcd for $C_{20}H_{32}BN_2O_3$ [M + H]$^+$, 359.2500; found, 359.2496.

1-cyclopentyl-3-(3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)urea (17):



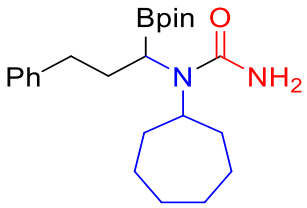
Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a white solid (121 mg, 65%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.33 – 7.19 (m, 4H), 7.19 – 7.08 (m, 3H), 3.85 – 3.72 (m, 1H), 2.74 – 2.61 (m, 1H), 2.56 – 2.51 (m, 1H), 2.34 (dd, J = 8.0, 2.1 Hz, 1H), 2.06 – 1.96 (m, 1H), 1.80 – 1.42 (m, 9H), 1.05 (s, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.32, 143.54, 128.15, 128.09, 125.29, 78.17, 55.85, 33.63, 31.57, 30.24, 27.87, 25.66, 24.94, 22.92, 22.57. ^{11}B NMR (128 MHz, DMSO-d_6) δ 13.66. HRMS (ESI) calcd for $C_{21}H_{34}BN_2O_3$ [M + H]$^+$, 373.2657; found, 373.2652.

1-cyclohexyl-3-(3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)urea(18):



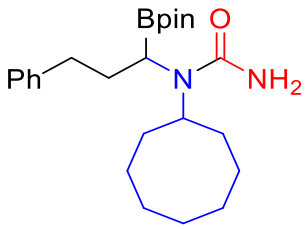
Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a white solid (135 mg, 70%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.34 – 7.21 (m, 4H), 7.19 – 7.09 (m, 3H), 3.41 – 3.34 (m, 1H), 2.80 – 2.66 (m, 1H), 2.49 – 2.43 (m, 1H), 2.39 (dd, J = 7.1, 2.3 Hz, 1H), 1.93 – 1.84 (m, 1H), 1.82 – 1.14 (m, 11H), 1.04 (s, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.84, 143.72, 128.16, 125.25, 78.09, 54.27, 33.92, 32.03, 31.28, 29.64, 25.63, 25.35, 25.14, 24.91. ^{11}B NMR (128 MHz, DMSO-d_6) δ 10.29. HRMS (ESI) calcd for $C_{22}H_{36}BN_2O_3$ [M + H]$^+$, 387.2813; found, 387.2815.

1-cycloheptyl-3-(3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)urea (19):



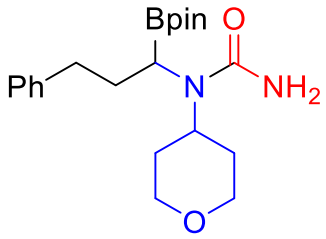
Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a white solid (140 mg, 70%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.28 – 7.23 (m, 2H), 7.22 – 7.07 (m, 5H), 3.51 – 3.41 (m, 1H), 2.75 – 2.65 (m, 1H), 2.60 – 2.52 (m, 1H), 2.36 (dd, J = 7.8, 2.5 Hz, 1H), 1.84 (s, 1H), 1.76 – 1.31 (m, 13H), 1.04 (s, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.40, 143.67, 128.17, 128.10, 125.27, 78.13, 56.54, 33.57, 31.77, 31.64, 26.83, 26.67, 25.68, 24.60, 24.39. ^{11}B NMR (128 MHz, DMSO-d_6) δ 10.59. HRMS (ESI) calcd for $C_{23}H_{38}BN_2O_3$ [M+H]$^+$, 401.2970 ; found, 401.2969.

1-cyclooctyl-3-(3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)urea (20):



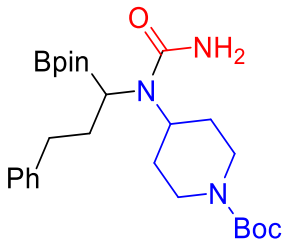
Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a white solid (141 mg, 68%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.29 – 7.21 (m, 2H), 7.20 – 7.03 (m, 5H), 3.52 – 3.40 (m, 1H), 2.78 – 2.62 (m, 1H), 2.59 – 2.52 (m, 1H), 2.33 (dd, J = 8.0, 2.4 Hz, 1H), 1.90 – 1.35 (m, 18H), 1.04 (s, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.15, 143.59, 128.19, 128.09, 125.30, 78.12, 55.50, 33.36, 32.18, 31.77, 30.58, 26.05, 25.66, 25.53, 25.08, 24.98, 24.05. ^{11}B NMR (128 MHz, DMSO-d_6) δ 10.97. HRMS (ESI) calcd for $C_{24}H_{40}BN_2O_3$ $[M + H]^+$, 415.3127; found, 415.3123.

1-(3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-3-((tetrahydro-2*H*-pyran-4-yl)methyl)urea (21):



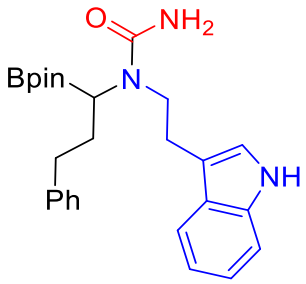
Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a white solid (137 mg, 68%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 (dd, J = 8.2, 6.7 Hz, 2H), 7.26 – 7.17 (m, 3H), 5.88 (s, 2H), 4.09 – 3.75 (m, 2H), 3.35-3.29 (m, 2H), 3.11 – 2.89 (m, 2H), 2.83 – 2.65 (m, 2H), 2.55 (dd, J = 8.1, 2.7 Hz, 1H), 2.43 (s, 2H), 2.05 – 1.90 (m, 1H), 1.85 – 1.72 (m, 2H), 1.69 – 1.49 (m, 2H), 1.62-1.25 (m, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.36, 143.26, 128.56, 128.44, 125.80, 79.75, 67.52, 48.50, 33.04, 32.61, 30.71, 30.48 (d, J = 5.9 Hz), 25.69, 25.45. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 10.39. HRMS (ESI) calculated for $C_{22}H_{36}BN_2O_4$ $[M+H]^+$ 403.2768, found: 403.2762.

***tert*-butyl4-((3-(3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)ureido)methyl) piperidine-1-carboxylate (22):**



Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a white solid (120 mg, 48%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.28 – 7.24 (m, 2H), 7.18 – 7.12 (m, 3H), 3.96 – 3.75 (m, 3H), 3.49 (d, J = 10.2 Hz, 1H), 2.89 – 2.66 (m, 3H), 2.23 (d, J = 7.0 Hz, 1H), 1.79 – 1.66 (m, 3H), 1.54 – 1.43 (m, 1H), 1.39 (s, 9H), 1.30 – 1.21 (m, 2H), 1.01 (s, 12H).^{13}C NMR (101 MHz, DMSO-d_6) δ 160.32, 153.94, 153.85, 143.27, 128.25, 125.42, 78.79, 78.72, 78.34, 73.59, 44.32, 34.93, 33.66, 31.58, 28.11, 25.60, 25.44, 24.98. ^{11}B NMR (128 MHz, DMSO-d_6) δ 12.09. HRMS (ESI) calculated for $C_{26}H_{42}BN_3O_5$ $[M+H]^+$ 488.3296, found: 488.3284.

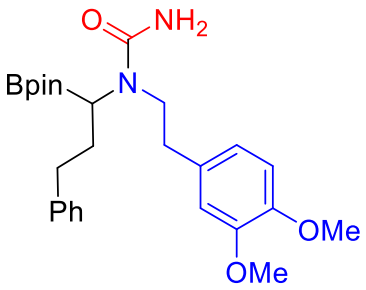
1-(2-(1*H*-indol-3-yl)ethyl)-3-(3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)urea (23):



Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a white solid (152 mg, 68%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.92 – 10.81 (m, 1H), 7.50 (d, J = 7.9 Hz, 1H), 7.40 – 7.28 (m, 3H), 7.25 (t, J = 7.4 Hz, 2H), 7.21 – 7.11 (m, 4H), 7.09 – 7.04 (m, 1H), 7.01 – 6.94 (m, 1H), 3.69 – 3.56 (m, 1H), 3.30 – 3.22 (m, 1H), 2.97 – 2.85 (m, 1H), 2.83 – 2.68 (m, 2H), 2.48 – 2.39 (m, 2H), 1.84 – 1.73 (m, 1H), 1.73 – 1.62 (m, 1H), 1.08 (s, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.94, 143.51, 136.08, 128.18,

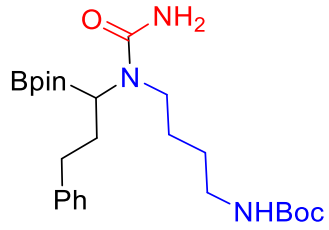
128.15, 127.06, 125.33, 122.97, 120.97, 118.30, 118.20, 111.37, 110.78, 78.22, 42.37, 31.76, 31.03, 25.73, 22.24. ^{11}B NMR (128 MHz, DMSO-d_6) δ 10.4. HRMS (ESI) calcd for $C_{26}H_{35}BN_3O_3$ $[M+H]^+$, 448.2766; found, 448.2770.

1-(3,4-dimethoxyphenethyl)-3-(3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)urea (24):



Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a white solid (122 mg, 52%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.33 – 7.21 (m, 4H), 7.21 – 7.10 (m, 3H), 6.88 – 6.81 (m, 2H), 6.78 – 6.71 (m, 1H), 3.77 (s, 3H), 3.71 (s, 3H), 3.61 – 3.49 (m, 1H), 3.20 – 3.09 (m, 1H), 2.77 – 2.57 (m, 3H), 2.47 – 2.33 (m, 2H), 1.84 – 1.69 (m, 1H), 1.69 – 1.56 (m, 1H), 1.05 (s, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.91, 148.61, 147.33, 143.52, 130.99, 128.17, 125.33, 120.72, 112.74, 111.81, 78.18, 55.50, 55.46, 43.24, 31.97, 31.67, 30.79, 25.67, 25.64. ^{11}B NMR (128 MHz, DMSO-d_6) δ 10.89. HRMS (ESI) calcd for $C_{26}H_{38}BN_2O_5$ $[M+H]^+$, 469.2868; found, 469.2871.

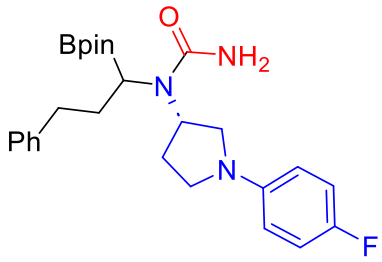
***tert*-butyl (4-(3-(3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)ureido)butyl) carbamate (25):**



Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a white solid (131 mg, 55%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.35 – 7.21 (m, 4H), 7.20 – 7.10 (m, 3H), 6.85 (t, J = 5.8 Hz, 1H),

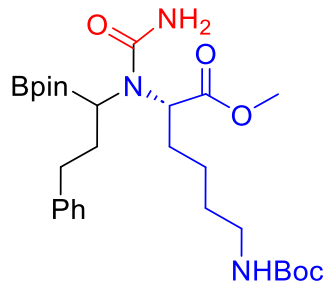
3.31 – 3.23 (m, 1H), 3.06 – 2.95 (m, 1H), 2.91 (q, *J* = 6.2 Hz, 2H), 2.77 – 2.63 (m, 1H), 2.46 – 2.33 (m, 1H), 2.27 (dd, *J* = 7.3, 2.5 Hz, 1H), 1.79 – 1.65 (m, 1H), 1.65 – 1.54 (m, 1H), 1.37 (s, 13H), 1.04 (s, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.88, 155.70, 143.54, 128.13, 125.30, 78.14, 77.41, 41.39, 31.66, 30.91, 28.28, 26.81, 25.63, 23.97. ^{11}B NMR (128 MHz, DMSO-d_6) δ 10.08. HRMS (ESI) calcd for $C_{25}H_{43}BN_3O_5$ $[M+H]^+$, 476.3290; found, 476.3296.

1-((*R*)-1-(4-fluorophenyl)pyrrolidin-3-yl)-3-(3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)urea (26):



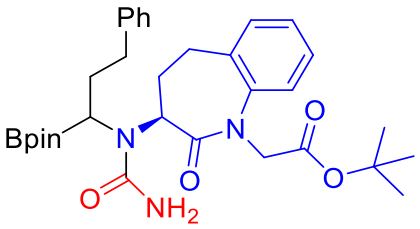
Prepared the following general Procedure **B** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a white solid (133 mg, 57%) as a mixture of diastereomers (dr = 1:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.48 (s, 1H), 7.32 – 7.06 (m, 5H), 7.06 – 6.94 (m, 2H), 6.62 – 6.45 (m, 2H), 4.39 – 4.16 (m, 1H), 3.57 (t, *J* = 8.5 Hz, 1H), 3.44 – 3.36 (m, 1H), 3.26 – 3.02 (m, 2H), 2.77 – 2.61 (m, 1H), 2.59 – 2.52 (m, 1H), 2.42 (d, *J* = 7.4 Hz, 1H), 2.30 – 1.87 (m, 2H), 1.85 – 1.41 (m, 2H), 1.33 – 0.85 (m, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.46, 162.37, 154.56 (d, *J* = 236.1 Hz), 144.40, 144.35, 143.44, 143.40, 128.21, 128.16, 128.15, 128.11, 125.32, 115.37 (d, *J* = 21.8 Hz), 112.86 (d, *J* = 7.2 Hz),112.72 (d, *J* = 7.2 Hz), 78.30, 53.65, 53.49, 51.64, 49.52, 46.72, 46.60, 33.44, 31.67, 31.59, 29.41, 27.77, 25.66, 24.96, 24.48. ^{19}F NMR (377 MHz, DMSO-d_6) δ -129.45, -129.58. ^{11}B NMR (128 MHz, DMSO-d_6) δ 10.89. HRMS (ESI) calcd for $C_{26}H_{36}BFN_3O_3$ $[M+H]^+$, 468.2828; found, 468.2828.

methyl *N*6-(*tert*-butoxycarbonyl)-*N*2-((3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)carbamoyl)-*L*-lysinate (27):



Prepared the following general Procedure **B** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a white solid (134 mg, 49%) as a mixture of diastereomers (dr = 1:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.39 – 7.06 (m, 7H), 6.79 (s, 1H), 4.16 (s, 1H), 3.66 (d, J = 5.7 Hz, 3H), 2.89 (t, J = 5.8 Hz, 2H), 2.65 (s, 1H), 2.25 (s, 1H), 1.67 – 1.56 (m, 2H), 1.41 – 1.17 (m, 16H), 1.01 (s, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.20, 161.83, 155.62, 142.99, 128.19, 125.39, 78.66, 78.29, 77.29, 53.41, 52.09, 52.03, 34.71, 33.50, 31.05, 28.82, 28.26, 25.47, 25.28, 22.52. ^{11}B NMR (128 MHz, DMSO-d_6) δ 16.16. HRMS (ESI) calcd for $C_{28}H_{47}BN_3O_7$ $[M+H]^+$, 548.3502; found, 548.3507.

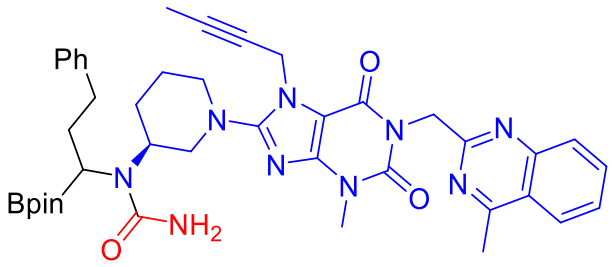
***tert*-butyl 2-((3*S*)-2-oxo-3-(3-(3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl) ureido)-2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepin-1-yl)acetate (28):**



Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a white solid (165 mg, 57%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.42 – 7.31 (m, 3H), 7.30 – 7.11 (m, 5H), 7.10 – 7.05 (m, 1H), 7.04 – 6.98 (m, 2H), 4.49 (s, 2H), 3.90 (dd, J = 11.9, 8.3 Hz, 1H), 3.19 – 3.02 (m, 1H), 2.83 – 2.62 (m, 2H), 2.57 – 2.51 (m, 1H), 2.46 – 2.36 (m, 1H), 2.19 – 2.08 (m, 1H), 2.05 (dd, J = 8.1, 3.0 Hz, 1H), 1.58 – 1.48 (m, 1H), 1.41 – 1.31 (m, 10H), 1.12 – 0.88 (m, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.88, 167.88, 162.93,

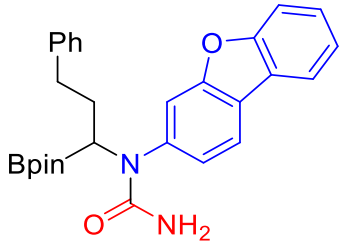
143.03, 140.85, 134.70, 129.37, 128.05, 127.97, 126.76, 125.19, 122.26, 81.30, 78.17, 56.75, 53.69, 50.83, 32.20, 31.60, 30.90, 27.62, 25.67. ^{11}B NMR (128 MHz, DMSO-d_6) δ 10.94. HRMS (ESI) calcd for C32H45BN3O6 $[M+H]^+$, 578.3396; found, 578.3380.

1-((*S*)-1-(7-(but-2-yn-1-yl)-3-methyl-1-((4-methylquinazolin-2-yl)methyl)-2,6-dioxo-2,3,6,7-tetrahydro-1*H*-purin-8-yl)piperidin-3-yl)-3-(3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)urea (29):



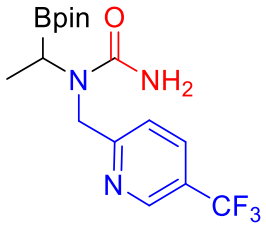
Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a white solid (159 mg, 42%), as a mixture of diastereomers (dr = 8 : 2). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.78 – 7.73 (m, 1H), 7.55 – 7.49 (m, 1H), 7.26 (s, 1H), 7.23 – 7.10 (m, 5H), 5.56 (s, 2H), 4.94 – 4.76 (m, 2H), 3.87 (d, *J* = 9.7 Hz, 1H), 3.60 (d, *J* = 12.7 Hz, 1H), 3.53 (s, 3H), 3.14 (s, 1H), 3.01 (s, 2H), 2.88 (s, 3H), 2.83 (t, *J* = 9.3 Hz, 2H), 2.72 – 2.58 (m, 2H), 2.17 (s, 1H), 2.00 (d, *J* = 25.9 Hz, 2H), 1.91 – 1.82 (m, 2H), 1.77 (s, 3H), 1.37-1.11 (m, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.52, 161.24, 161.10,156.27,155.76,154.54, 154.45, 151.96,154.84, 150.02, 148.09, 147.59, 141.85, 133.24, 128.94, 128.45, 128.38, 126.71, 125.95, 124.89, 123.18, 104.55, 81.28, 74.96, 73.40, 55.60, 53.82, 50.51, 46.65, 46.35, 35.81, 33.59, 31.87, 31.07, 29.77, 24.87, 23.65, 21.82, 3.76. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 3.16; HRMS (ESI) calculated for $C_{41}H_{49}BN_9O_5$ $[M-H]^+$ 758.3950, found: 758.3955.

1-(dibenzo[*b*,*d*]furan-3-yl)-3-(3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)urea (30):



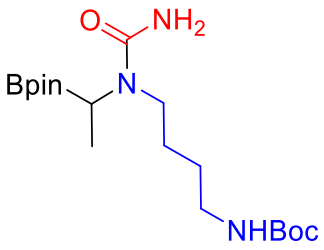
Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a yellow solid (134 mg, 57%). ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 8.29 – 7.92 (m, 2H), 7.64 – 7.58 (m, 1H), 7.58 – 7.49 (m, 2H), 7.46 – 7.40 (m, 1H), 7.30 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.18 – 7.10 (m, 2H), 7.09 – 7.01 (m, 1H), 7.01 – 6.95 (m, 2H), 2.90 (dd, *J* = 7.3, 4.1 Hz, 1H), 2.63 – 2.51 (m, 2H), 1.84 – 1.51 (m, 2H), 1.30 – 1.05 (m, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.48, 156.08, 155.76, 143.23, 136.97,128.12, 127.94, 127.83, 125.29, 123.42, 123.14, 122.79, 121.97 (d, *J* = 5.5 Hz), 121.31, 111.72, 110.80, 78.50, 54.92, 32.05, 25.76, 24.96. ^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 11.91; HRMS (ESI) calculated for $C_{28}H_{31}BN_2O_4$ $[M+H]^+$ 471.2455, found: 471.2451.

1-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-3-((5-(trifluoromethyl)pyridin-2-yl)methyl)urea (31):



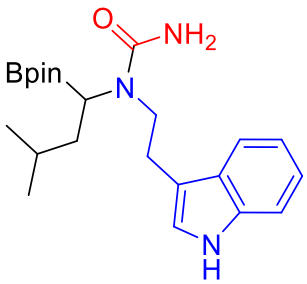
Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a yellow solid (93 mg, 50%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.00 – 8.94 (m, 1H), 8.26 (dd, *J* = 8.2, 2.4 Hz, 1H), 7.52 (s, 2H), 7.45 (d, *J* = 8.2 Hz, 1H), 4.76 (d, *J* = 17.4 Hz, 1H), 4.54 (d, *J* = 17.4 Hz, 1H), 2.18 (q, *J* = 6.9 Hz, 1H), 0.99 (d, *J* = 3.1 Hz, 12H), 0.86 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.59, 161.16, 146.07 (q, *J* = 4.2 Hz), 134.49, 123.95 (q, *J* = 32.4 Hz), 123.76 (q, *J* = 271.8 Hz),121.56, 78.16, 47.27, 25.44, 25.24, 14.65. ^{19}F NMR (377 MHz, DMSO-d_6) δ -60.73. ^{11}B NMR (128 MHz, DMSO-d_6) δ 10.90. HRMS (ESI) calcd for $C_{16}H_{24}BF_3N_3O_3$ $[M+H]^+$, 374.1857; found, 374.1851.

***tert*-butyl (4-(3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)ureido)butyl)carbamate (32):**



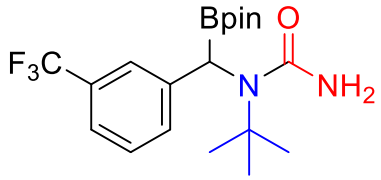
Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a yellow solid (106 mg, 55%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.23 (s, 2H), 6.85 (t, J = 5.7 Hz, 1H), 3.27 – 3.16 (m, 1H), 3.06 – 2.96 (m, 1H), 2.92 (q, J = 6.4 Hz, 2H), 2.22 (q, J = 6.9 Hz, 1H), 1.40 – 1.29 (m, 13H), 0.98 (s, 12H), 0.88 (d, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.52, 155.70, 78.03, 77.40, 41.16, 28.28, 26.79, 25.44, 25.25, 23.97, 14.70. ^{11}B NMR (128 MHz, DMSO-d_6) δ 9.77. HRMS (ESI) calcd for $C_{18}H_{37}BN_3O_5$ $[M+H]^+$, 386.2821; found, 386.2818.

1-(2-(1*H*-indol-3-yl)ethyl)-3-(3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)urea (33):



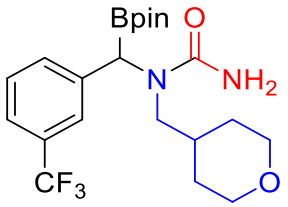
Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a brown solid (90 mg, 45%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.86 (s, 1H), 7.54 (d, J = 7.9 Hz, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.27 (s, 2H), 7.19 (d, J = 2.3 Hz, 1H), 7.07 (t, J = 7.5 Hz, 1H), 6.99 (t, J = 7.4 Hz, 1H), 3.63 – 3.52 (m, 1H), 3.31 – 3.23 (m, 1H), 2.98 – 2.86 (m, 1H), 2.85 – 2.73 (m, 1H), 2.33 (dd, J = 8.9, 4.0 Hz, 1H), 1.88 – 1.77 (m, 1H), 1.48 – 1.39 (m, 1H), 1.15 – 1.08 (m, 1H), 1.02 (s, 12H), 0.84 (d, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.68, 136.13, 127.07, 123.01, 121.02, 118.34, 118.11, 111.44, 110.79, 78.29, 42.74, 25.83, 25.67, 25.40, 24.98, 23.80, 22.46, 22.32.^{11}B NMR (128 MHz, DMSO-d6) δ 3.62; HRMS (ESI) calculated for $C_{22}H_{35}BN_3O_3$ $[M+H]^+$ 400.2771, found: 400.2766.

1-(*tert*-butyl)-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(3-(trifluoromethyl)phenyl) methyl)urea (34):



Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a yellow oil (106 mg, 53%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.31 (m, 2H), 7.28 (s, 1H), 7.24 (d, *J* = 7.1 Hz, 1H), 6.11 (s, 2H), 3.98 (s, 1H), 1.34 (s, 9H), 1.20 (s, 3H), 1.10 (s, 3H), 1.00 (s, 3H), 0.60 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.91,146.54, 129.98 (q, *J* = 31.9 Hz), 129.23, 128.30, 124.52 (q, *J* = 272.1 Hz), 122.64, 121.54 (q, *J* = 3.9 Hz), 79.98, 79.77, 56.00, 49.97, 29.42, 25.28, 25.17, 24.68, 24.02. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.53. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 9.41. HRMS (ESI) calculated for $C_{19}H_{29}BF_3N_2O_3$ $[M+H]^+$ 401.2223, found: 401.2221.

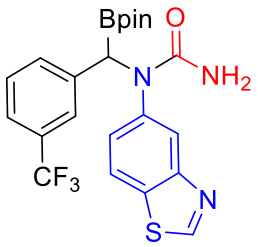
1-((tetrahydro-2*H*-pyran-4-yl)methyl)-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(3-(trifluoromethyl)phenyl)methyl)urea (35):



Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a white solid (126 mg, 57%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.71 (s, 2H), 7.50 – 7.37 (m, 2H), 7.26 – 7.17 (m, 2H), 3.91 – 3.72 (m, 2H), 3.5 (s, 1H), 3.2 – 3.33 (m, 3H), 2.57 (dd, *J* = 14.5, 6.3 Hz, 1H), 1.84 – 1.71 (m, 1H), 1.38 (t, *J* = 14.2 Hz, 2H), 1.21 – 1.09 (m, 2H), 1.03 (s, 3H), 0.96 – 0.83 (m, 6H), 0.49 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 163.55, 144.43, 131.03, 128.99, 128.77 (q, *J* = 31.2 Hz), 125.07 (q, *J* = 271.9 Hz), 123.50, 121.93, 79.02, 78.94, 67.01, 66.93, 48.31, 32.91, 30.40, 29.81, 25.62, 25.14. ^{11}B NMR (128 MHz, DMSO-

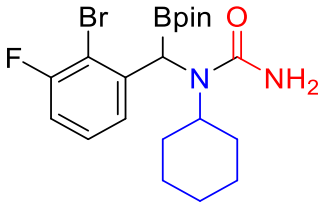
d_6) δ 10.07; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -56.19; HRMS (ESI) calculated for $C_{21}H_{31}BF_3N_2O_4$ $[M+H]^+$ 443.2329, found: 443.2323.

1-(benzo[*d*]thiazol-5-yl)-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(3-(trifluoromethyl) phenyl)methyl)urea (36):



Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a dark-brown solid (143 mg, 60%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.99 (s, 1H), 8.07 (d, *J* = 8.7 Hz, 1H), 7.77 (d, *J* = 2.0 Hz, 1H), 7.39 (s, 1H), 7.38 – 7.28 (m, 3H), 7.24 (d, *J* = 7.7 Hz, 1H), 4.29 (s, 1H), 1.09 (s, *J* = 74.4 Hz, 6H), 0.90 (s, *J* = 74.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.96, 155.98, 152.77, 141.76, 135.44, 134.89, 131.11, 129.98 (q, *J* = 31.9 Hz),128.30, 125.31, 124.55, 124.45 (q, *J* = 271.8 Hz), 124.44, 122.55, 119.89, 80.54, 25.13, 24.47. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.53. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 11.11. HRMS (ESI) calculated for $C_{22}H_{24}BF_3N_3O_3S$ $[M+H]^+$ 478.1584, found: 478.1587.

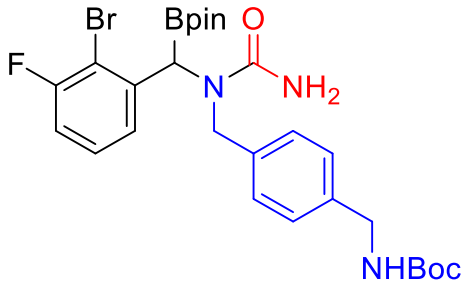
1-((2-bromo-3-fluorophenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3-cyclohexylurea (37):



Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a white solid (148 mg, 65%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.71 (s, 2H), 7.27 – 7.19 (m, 1H), 7.04 – 6.96 (m, 1H), 6.74 (dd, *J* = 7.9, 1.3 Hz, 1H), 3.95 (s, 1H), 3.52 (t, *J* = 11.5 Hz, 1H), 1.72 (d, *J* = 11.8 Hz, 2H), 1.46 (t, *J* = 12.0 Hz, 2H), 1.38 – 1.21 (m, 3H), 1.17 – 1.05 (m, 1H), 1.01 (s, 3H), 0.95 (s, 3H), 0.88 (s, 3H), 0.86 – 0.77 (m, 1H),

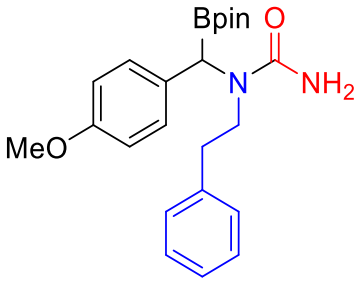
0.72 – 0.60 (m, 1H), 0.57 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.84, 157.71 (d, J = 241.9 Hz), 147.31, 127.27 (d, J = 8.3 Hz), 124.99 (d, J = 2.9 Hz), 111.91 (d, J = 22.5 Hz), 108.03 (d, J = 20.2 Hz), 78.63, 78.40, 54.77, 31.77, 30.16, 25.38, 25.26, 25.16, 24.93, 24.91, 24.83, 24.76. ^{19}F NMR (376 MHz, DMSO-d_6) δ -106.29. ^{11}B NMR (128 MHz, DMSO-d_6) δ 10.67. HRMS (ESI) calcd for $C_{20}H_{30}BBrFN_2O_3$ $[M+H]^+$, 455.1511; found, 455.1515.

***tert*-butyl (4-((3-((2-bromo-3-fluorophenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl) ureido)methyl)benzyl)carbamate (38):**



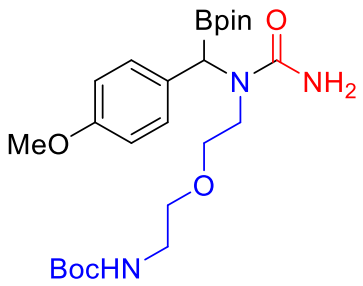
Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a white solid (180 mg, 61%). ^{1}H NMR (400 MHz, CD_3CN) δ 7.36 – 7.15 (m, 5H), 6.98 – 6.90 (m, 1H), 6.89 – 6.77 (m, 1H), 6.73 (s, 1H), 6.53 (s, 1H), 5.81 (s, 1H), 4.35 (t, J = 7.2 Hz, 2H), 4.19 (dd, J = 10.2, 6.3 Hz, 2H), 4.10 (s, 1H), 1.41 (s, 9H), 1.18 – 0.81 (m, 12H). ^{13}C NMR (101 MHz, CD_3CN) δ 164.52, 162.18, 159.54 (d, J = 242.3 Hz), 157.08, 147.52, 140.67, 138.59, 128.40 (d, J = 7.9 Hz),128.17, 124.05 (d, J = 3 Hz), 113.33 (d, J = 22.3 Hz), 109.40 (d, J = 20.5 Hz), 80.79, 80.50, 79.45, 75.23, 44.42, 41.84, 28.64, 25.82, 25.46, 25.17. ^{19}F NMR (377 MHz, CD_3CN) δ -107.66. ^{11}B NMR (128 MHz, CD_3CN) δ 12.06. HRMS (ESI) calcd for $C_{27}H_{35}BBrFN_3O_5$ $[M-H]^+$, 590.1832; found, 590.1842.

1-((4-methoxyphenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3-phenethylurea (39):



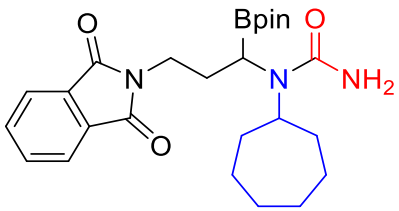
Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a yellow solid (105 mg, 51%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.12 (m, 3H), 7.02 (d, *J* = 8.6 Hz, 2H), 6.93 (dd, *J* = 7.7, 1.7 Hz, 2H), 6.76 (d, *J* = 8.6 Hz, 2H), 6.14 (s, 2H), 3.70 (s, 1H), 3.63 (s, 3H), 3.41 – 3.32 (m, 1H), 3.14 – 3.04 (m, 1H), 2.82 – 2.53 (m, 2H), 1.23 (s, 6H), 1.02 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.50, 157.83, 138.08, 133.08, 128.80, 128.77, 128.57, 126.77, 113.59, 79.92, 75.20, 55.17, 45.18, 32.93, 29.82, 25.12, 24.99, 24.47. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 9.41. HRMS (ESI) calculated for $C_{23}H_{32}BN_2O_4$ $[M+H]^+$ 411.2455, found: 411.2451.

***tert*-butyl(2-(2-(3-((4-methoxyphenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl) kkureido)ethoxy)ethyl)carbamate (40):**



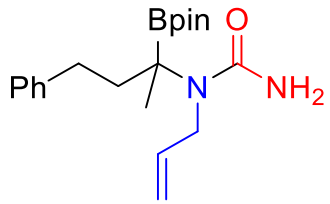
Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a yellow oil (143 mg, 58%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.06 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 5.87 (s, 2H), 4.80 (s, 1H), 3.77 (s, 3H), 3.60 (s, 1H), 3.53 – 3.34 (m, 3H), 3.32 – 3.22 (m, 5H), 1.43 (s, 9H), 1.31-0.73 (m, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.53, 157.82, 156.33, 133.08, 129.26, 113.35, 79.74, 75.08, 70.93, 69.86, 55.24, 45.58, 40.28, 29.75, 28.49, 25.09, 24.91, 29.70, 24.56. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 10.48. HRMS (ESI) calculated for $C_{24}H_{41}BN_3O_7$ $[M+H]^+$ 494.3038, found: 494.3041.

1-cycloheptyl-3-(3-(1,3-dioxoisoindolin-2-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)urea (41):



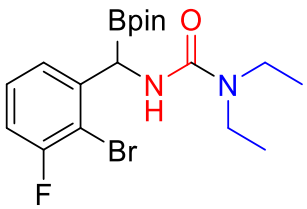
Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a White solid (127 mg, 54%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.68 (dd, *J* = 5.4, 3.0 Hz, 2H), 5.82 (s, 2H), 4.03 – 3.94 (m, 1H), 3.83 – 3.71 (m, 1H), 3.44 – 3.19 (m, 1H), 2.63 (dd, *J* = 7.5, 3.4 Hz, 1H), 2.20 (s, 2H), 2.09 – 1.99 (m, 2H), 1.81 – 1.67 (m, 4H), 1.64 – 1.35 (m, 6H), 1.22 – 1.09 (m, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.63, 161.60, 133.88, 132.48, 123.14, 79.75, 58.03, 35.66, 33.35, 32.79, 29.67, 27.28, 27.09, 25.72, 25.63, 25.49, 25.24; ^{11}B NMR (128 MHz, Chloroform-*d*) δ 10.29. HRMS (ESI) calculated for $C_{25}H_{37}BN_3O_5$ $[M+H]^+$ 470.2826, found: 470.2819.

1-allyl-3-(4-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl)urea (42):



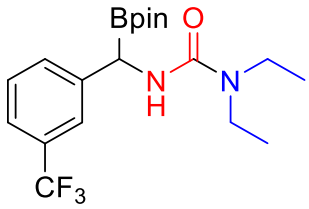
Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding **42** as a yellow oil (63 mg, 35%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 7.20 (m, 3H), 7.18 – 7.13 (m, 2H), 5.84 – 5.61 (m, 1H), 5.36 – 5.23 (m, 2H), 5.15 (s, 2H), 3.81 – 3.73 (m, 1H), 3.66 – 3.59 (m, 1H), 2.95 (td, *J* = 12.6, 4.6 Hz, 1H), 2.43 (td, *J* = 12.6, 4.8 Hz, 1H), 1.78 – 1.74 (m, 1H), 1.71 – 1.65 (m, 1H), 1.27 – 1.25 (m, 6H)1.17 – 1.13 (m, 6H), 1.12 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.52, 143.98, 133.67, 128.55, 128.45, 125.55, 118.98, 79.91, 79.39, 43.20, 40.29, 31.97, 25.39, 25.13, 22.27, 1.15. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 11.91. HRMS (ESI) calculated for $C_{20}H_{31}BN_2O_3$ $[M+H]^+$ 358.2500, found: 359.2497.

3-((2-bromo-3-fluorophenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1,1-diethylurea (43):



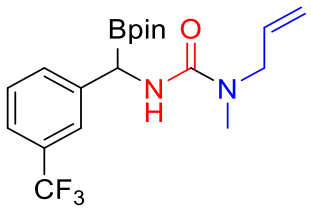
Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a light yellow solid **43** (118 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.15 (m, 1H) (m, 1H), 7.09 – 7.04 (m, 1H), 6.89 (td, *J* = 8.2, 1.5 Hz, 1H), 5.23 (s, 1H), 4.42 (s, 1H), 3.33 (s, 4H), 1.22 (t, *J* = 7.3 Hz, 6H), 1.10 (s, 6H), 0.96 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ162.10, 158.88 (d, *J* = 244.3 Hz), 145.83,127.72 (d, *J* = 8.3 Hz), 123.54 (d, *J* = 3.0 Hz), 112.67 (d, *J* = 23.0 Hz), 109.56 (d, *J* = 20.5 Hz), 79.99, 77.36, 25.35, 24.74, 13.38. ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.31. ^{11}B NMR (128 MHz, $CDCl_3$) δ 12.17. HRMS (ESI) calcd for $C_{18}H_{28}BBrFN_2O_3$ $[M+H]^+$, 429.1355; found, 429.1356.

1,1-diethyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(3-(trifluoromethyl)phenyl) methyl)urea (44):



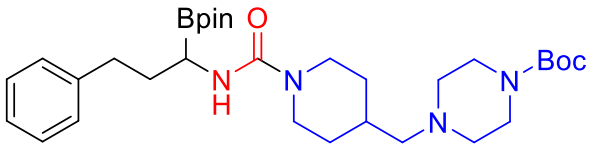
Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a white solid **44** (58 mg, 29%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 (s, 1H), 7.39 – 7.30 (m, 3H), 5.43 (s, 1H), 3.87 (d, *J* = 1.5 Hz, 1H), 3.46 – 3.15 (m, 4H), 1.23 (t, *J* = 7.2 Hz, 7H), 1.07 (s, 6H), 0.93 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.04, 144.90, 130.12 (q, *J* = 31.5 Hz), 129.69, 128.26, 124.61 (q, *J* = 272.4 Hz), 123.10 (q, *J* = 3.8 Hz), 122.07 (q, *J* = 3.7 Hz), 80.02, 77.37, 25.24, 24.67, 13.34. ^{19}F NMR (377 MHz, Chloroform-*d*) δ -62.42. ^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 12.35. HRMS (ESI) calculated for $C_{19}H_{28}BF_3N_2O_3Na$ $[M+Na]^+$ 423.2043, found: 423.2035.

1-allyl-1-methyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(3-(trifluoromethyl)phenyl) methyl)urea (45):



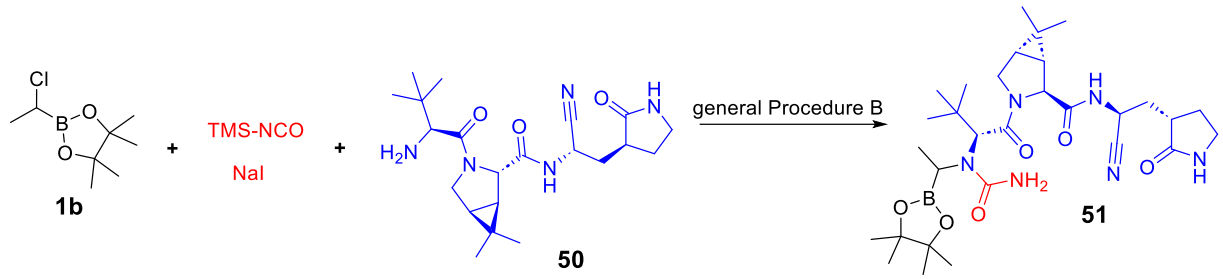
Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a white solid **45** (60 mg, 30%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (s, 1H), 7.39 – 7.25 (m, 3H), 5.86 – 5.69 (m, 2H), 5.39 – 5.26 (m, 1H), 3.90 (s, 2H), 3.88 – 3.83 (m, 1H), 2.98 (s, 3H), 1.05 (s, 6H), 0.91 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.86, 144.60, 130.08 (q, *J* = 31.9 Hz), 129.80, 128.20, 124.60 (q, *J* = 272.3 Hz), 123.19, 123.16, 122.10 (q, *J* = 3.9 Hz), 80.15, 77.36, 29.82, 25.18, 24.65. ^{19}F NMR (377 MHz, Chloroform-*d*) δ -62.42. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 12.09. HRMS (ESI) calculated for $C_{19}H_{25}BF_3N_2O_3$ $[M-H]^+$ 398.1910, found: 397.1912.

***tert*-butyl 4-((1-((3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)carbamoyl) piperidin-4-yl)methyl)piperazine-1-carboxylate (46):**



Prepared the following general Procedure **A** on a 0.5 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a white solid **46** (128 mg, 45%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.33 – 7.09 (m, 6H), 3.88 (d, *J* = 12.9 Hz, 2H), 3.60 (dd, *J* = 9.1, 5.0 Hz, 1H), 3.29 (s, 4H), 2.95 (s, 2H), 2.78 – 2.69 (m, 1H), 2.66 – 2.57 (m, 1H), 2.27 (s, 4H), 2.13 (d, *J* = 6.6 Hz, 2H), 1.84 – 1.65 (m, 5H), 1.39 (s, 9H), 1.05 (s, 14H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 160.43, 153.73, 142.05, 128.31, 128.25, 125.62, 79.68, 78.75, 52.90, 45.91, 44.12, 43.29, 33.20, 32.63, 29.50, 28.04, 25.14, 24.93, 21.04. ^{11}B NMR (128 MHz, DMSO-d_6) δ 8.14.

(1*R*,2*S*,5*S*)-*N*-((*S*)-1-cyano-2-((*S*)-2-oxopyrrolidin-3-yl)ethyl)-3-((2*S*)-3,3-dimethyl-2-(3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)ureido)butanoyl)-6,6-dimethyl-3-azabicyclo[3.1.0]hexane-2-carboxamide (51):



2-(1-Chloroethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(1b)** was synthesized according to the protocol reported in the literature.[2] (1*R*,2*S*,5*S*)-*N*-((*S*)-1-cyano-2-((*S*)-2-oxopyrrolidin-3-yl)ethyl)-3-((*S*)-3,3-dimethyl-2-ureidobutanoyl)-6,6-dimethyl-3-azabicyclo[3.1.0]hexane-2-carboxamide **(50)** was synthesized followed the literature.[3]

Prepared the following general Procedure **B** on a 0.15 mmol scale, and the product was isolated by flash chromatography on silica gel using 3-7 % methanol in dichloromethane, yielding a white solid compound **51** (36 mg, 40%) as a 1:1 mixture of diastereomers (dr = 1:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.26 – 8.84 (m, 1H), 7.82 – 7.61 (m, 1H), 7.39 – 7.08 (m, 1H), 6.78 – 6.41 (m, 1H), 5.77 – 5.38 (m, 1H), 5.06 – 4.81 (m, 1H), 4.42 – 4.02 (m, 2H), 3.98 – 3.71 (m, 2H), 3.21 – 2.95 (m, 2H), 2.47 – 1.98 (m, 4H), 1.92 – 0.45 (m, 33H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 177.55, 177.51, 177.49, 177.37, 171.06, 171.01, 170.85, 170.75, 170.71, 170.68, 168.87, 161.75, 161.70, 158.49, 158.44, 119.62, 119.52, 119.05, 119.01, 118.90, 78.75, 78.07, 73.52, 59.85, 58.36, 57.11, 47.44, 47.31, 37.92, 37.83, 37.43, 37.30, 36.82, 36.70, 34.34, 34.29, 34.10, 33.35, 31.30, 30.29, 29.03, 27.71, 27.57, 27.48, 27.25, 27.18, 26.87, 26.39, 26.34, 26.22, 26.15, 26.12, 26.09, 25.94, 25.84, 25.82, 25.56, 25.33, 25.27, 25.05, 24.96, 24.50, 22.10, 18.93, 18.86, 18.83, 18.75, 18.69, 17.83, 17.76, 13.96, 12.93, 12.77, 12.60, 12.50. ^{11}B NMR (128 MHz, DMSO-d_6) δ 11.34. HRMS (ESI) calcd for $C_{30}H_{50}BN_6O_6$ $[M+H]^+$, 601.3879; found, 601.3872.

7. X-Ray crystallography data

7.1. X-Ray crystallography data for α-boryl urea (4)

Experimental

α-Boryl urea (**4**) was crystallized from mixture of ethyl acetate and Hexane. The atoms are depicted with 50% probability ellipsoids. The crystallographic data are summarized in the following table.

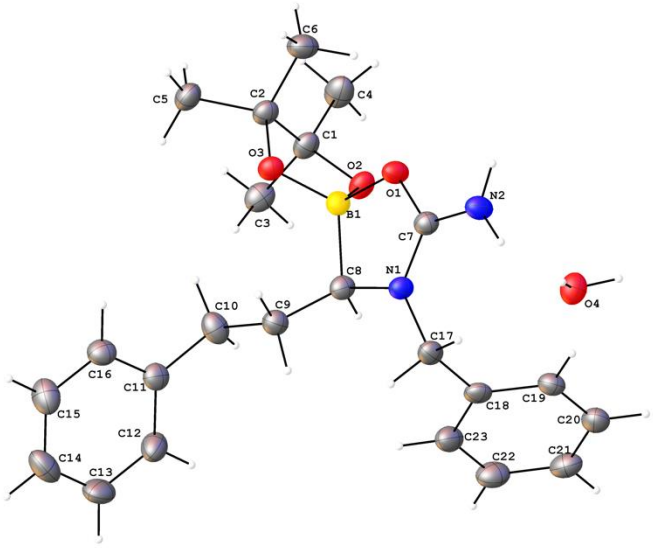


Figure S4 Thermal ellipsoids plot (50% probability) of compound **4**. Hydrogen atoms are shown at an arbitrarily chosen small radius, and not labeled, for clarity.

Crystal Data

Compound	**4**
Formula	$C_{23}H_{33}BN_2O_4$
$D_{calc.}$/ g cm^{-3}	1.211
μ/mm^{-1}	0.653
Formula Weight	412.32
Color	colorless
Shape	needle-shaped
Size/mm^3	0.48×0.02×0.01
T/K	99.9(4)
Crystal System	monoclinic
Space Group	$P2_1/c$
a/Å	7.2002(3)
b/Å	14.5736(8)

c/Å	21.7237(10)
α/°	90
β/°	97.027(4)
γ/°	90
V/Å^3	2262.41(19)
Z	4
Z'	1
Wavelength/Å	1.54184
Radiation type	Cu K$_\alpha$
Θ_{min}/°	3.661
Θ_{max}/°	74.479
Measured Refl's.	5286
Indep't Refl's	5286
Refl's I≥2 σ(I)	4694
R_{int}	.
Parameters	279
Restraints	0
Largest Peak	0.246
Deepest Hole	-0.254
GooF	1.065
wR_2 (all data)	0.1221
wR_2	0.1144
R_1 (all data)	0.0521
R_1	0.0456

Structure Quality Indicators

Reflections:	d min (CuKα) 2Θ=149.0° 0.80	I/σ(I) -1.0	Rint m=1.88 MERG 0	Full 135.4° 98% to 149.0° 99.5
Refinement:	Shift 0.000	Max Peak 0.2	Min Peak -0.2	GooF 1.065

Reflection Statistics

Total reflections (after filtering)	8516	Unique reflections	4522
Completeness	0.981	Mean I/σ	35.57
hkl$_{max}$ collected	(8, 18, 27)	hkl$_{min}$ collected	(-4, -18, -27)
hkl$_{max}$ used	(8, 18, 27)	hkl$_{min}$ used	(-8, 0, 0)
Lim d$_{max}$ collected	999.0	Lim d$_{min}$ collected	0.8
d$_{max}$ used	12.07	d$_{min}$ used	0.8
Friedel pairs	84	Friedel pairs merged	1
Inconsistent equivalents	307	R$_{int}$	-1.0

R_{sigma}	-1.0	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	6
Multiplicity	(4922, 258)	Maximum multiplicity	3
Removed systematic absences	0	Filtered off (Shel/OMIT)	228

Bond lengths [Å] and angles [°].

Table S1: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for compound **4**. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij}.

Atom	x	y	z	U_{eq}
O1	6973.8(18)	3785.3(8)	4575.0(5)	25.0(3)
O2	8394.9(18)	2267.7(9)	4684.1(6)	26.1(3)
O3	5160.3(17)	2340.2(8)	4536.4(5)	22.8(3)
N1	7103(2)	4046.0(10)	5587.9(6)	22.1(3)
N2	7482(2)	5249.3(10)	4888.1(7)	26.8(3)
C1	7720(3)	1468.9(13)	4334.4(9)	25.8(4)
C2	5741(3)	1775.8(13)	4046.3(8)	24.4(4)
C3	7645(3)	668.2(13)	4786.0(9)	30.6(4)
C4	9055(3)	1231.6(16)	3865.3(10)	35.2(5)
C5	4353(3)	1000.9(14)	3906.2(9)	30.1(4)
C6	5793(3)	2373.9(14)	3468.3(9)	33.5(4)
C7	7202(2)	4377.0(12)	5021.6(8)	22.3(3)
C8	6785(3)	3042.2(12)	5582.6(8)	22.9(4)
C9	5035(3)	2800.7(12)	5887.7(8)	25.5(4)
C10	4745(3)	1763.8(14)	5933.0(10)	31.7(4)
C11	3329(3)	1506.7(12)	6359.5(9)	26.0(4)
C12	3886(3)	1267.9(15)	6974.8(10)	35.6(5)
C13	2577(4)	1018.4(16)	7362.1(10)	40.9(5)
C14	702(3)	996.4(15)	7142.0(10)	39.7(5)
C15	136(3)	1235.1(15)	6530.9(11)	37.8(5)
C16	1445(3)	1494.2(13)	6146.3(9)	29.3(4)
C17	7381(3)	4598.9(12)	6156.6(8)	24.4(4)
C18	9308(3)	4478.2(12)	6508.7(8)	24.1(4)
C19	10725(3)	5103.7(13)	6434.0(8)	24.8(4)
C20	12507(3)	4991.5(14)	6748.8(8)	29.2(4)
C21	12884(3)	4250.6(15)	7143.4(9)	31.8(4)
C22	11481(3)	3625.6(15)	7223.3(9)	35.9(5)
C23	9705(3)	3739.7(14)	6910.6(9)	31.4(4)
B1	6800(3)	2785.4(13)	4843.3(9)	21.9(4)
O4	8330.1(19)	6815.0(9)	5598.3(6)	29.8(3)

Table S2: Anisotropic Displacement Parameters (×10^4) for compound **4**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	37.4(7)	18.0(6)	19.8(6)	-2.0(5)	4.3(5)	-2.0(5)
O2	26.7(6)	22.1(6)	29.2(6)	-8.2(5)	2.4(5)	-0.6(5)
O3	25.7(6)	20.9(6)	22.1(6)	-3.7(5)	3.5(5)	1.3(5)
N1	28.9(7)	17.9(7)	19.4(7)	-1.5(5)	2.5(6)	-1.1(6)
N2	40.0(9)	19.3(7)	21.5(7)	0.0(6)	5.1(6)	-1.8(7)
C1	27.5(9)	22.3(9)	27.5(9)	-7.4(7)	2.3(7)	-0.1(7)
C2	28.6(9)	21.2(8)	23.3(8)	-5.2(7)	2.9(7)	-0.3(7)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C3	34.1(10)	22.8(9)	33.8(10)	-2.5(8)	-0.8(8)	4.8(8)
C4	31.3(10)	36.3(11)	39.4(11)	-12.2(9)	10.2(8)	-0.4(9)
C5	29.7(10)	29.9(10)	29.6(9)	-6.1(8)	0.2(8)	-4.4(8)
C6	46.0(12)	31.3(10)	22.7(9)	0.0(8)	3.0(8)	-1.7(9)
C7	23.9(8)	21.2(8)	21.4(8)	-1.2(7)	1.9(6)	0.6(7)
C8	28.9(9)	16.5(8)	22.7(8)	0.5(6)	0.7(7)	0.7(7)
C9	30.2(9)	21.9(9)	24.7(9)	-0.9(7)	4.2(7)	-0.3(7)
C10	33.7(10)	23.2(9)	39.7(11)	4.1(8)	11.0(8)	1.2(8)
C11	31.8(10)	17.2(8)	28.7(9)	1.5(7)	3.2(7)	0.3(7)
C12	36.9(11)	32.8(10)	34.5(10)	9.1(8)	-6.0(8)	-8.9(9)
C13	59.2(14)	38.1(12)	24.2(9)	9.1(8)	0.2(9)	-8.6(11)
C14	50.0(13)	31.8(11)	41.3(11)	6.0(9)	21.6(10)	-1.5(10)
C15	29.4(10)	33.7(11)	50.2(13)	9.5(10)	4.5(9)	1.2(9)
C16	35.9(10)	24.8(9)	26.4(9)	3.6(7)	1.1(8)	1.7(8)
C17	31.9(9)	19.6(8)	22.3(8)	-4.0(7)	5.5(7)	-2.3(7)
C18	32.8(9)	23.4(9)	16.6(8)	-4.5(6)	4.7(7)	0.8(8)
C19	30.7(9)	24.6(9)	19.5(8)	1.0(7)	5.1(7)	1.3(8)
C20	31.8(10)	32.2(10)	24.3(9)	-2.3(7)	6.3(7)	-1.3(8)
C21	33.8(10)	36.6(11)	23.6(9)	-2.9(8)	-1.2(8)	4.4(9)
C22	48.9(12)	30.6(10)	26.6(10)	3.7(8)	-2.7(8)	2.5(9)
C23	43.5(11)	24.9(9)	25.0(9)	0.7(7)	1.7(8)	-5.4(9)
B1	25.1(10)	17.7(9)	22.5(9)	1.5(7)	1.4(7)	0.1(8)
O4	28.2(7)	21.4(6)	39.1(7)	-1.0(6)	1.6(6)	1.7(6)

Table S3: Bond Lengths in Å for compound **4**.

Atom	Atom	Length/Å
O1	C7	1.293(2)
O1	B1	1.580(2)
O2	C1	1.442(2)
O2	B1	1.451(2)
O3	C2	1.447(2)
O3	B1	1.437(2)
N1	C7	1.332(2)
N1	C8	1.481(2)
N1	C17	1.468(2)
N2	C7	1.325(2)
C1	C2	1.551(3)
C1	C3	1.530(3)
C1	C4	1.523(3)
C2	C5	1.514(3)
C2	C6	1.533(3)
C8	C9	1.535(3)
C8	B1	1.650(3)
C9	C10	1.530(3)
C10	C11	1.507(3)
C11	C12	1.392(3)
C11	C16	1.378(3)
C12	C13	1.387(3)
C13	C14	1.376(3)
C14	C15	1.385(3)
C15	C16	1.387(3)

Atom	Atom	Length/Å
C17	C18	1.510(3)
C18	C19	1.393(3)
C18	C23	1.393(3)
C19	C20	1.388(3)
C20	C21	1.385(3)
C21	C22	1.387(3)
C22	C23	1.383(3)

Table S4: Bond Angles in ° for compound **4**.

Atom	Atom	Atom	Angle/°
C7	O1	B1	110.29(13)
C1	O2	B1	108.67(14)
B1	O3	C2	107.65(13)
C7	N1	C8	112.12(14)
C7	N1	C17	124.16(15)
C17	N1	C8	123.63(14)
O2	C1	C2	102.33(14)
O2	C1	C3	108.32(15)
O2	C1	C4	109.66(15)
C3	C1	C2	112.09(16)
C4	C1	C2	114.78(16)
C4	C1	C3	109.30(16)
O3	C2	C1	101.59(13)
O3	C2	C5	109.20(15)
O3	C2	C6	108.52(15)
C5	C2	C1	114.66(16)
C5	C2	C6	109.95(15)
C6	C2	C1	112.42(16)
O1	C7	N1	115.79(16)
O1	C7	N2	118.98(16)
N2	C7	N1	125.22(16)
N1	C8	C9	110.96(14)
N1	C8	B1	102.25(13)
C9	C8	B1	118.14(15)
C10	C9	C8	112.34(15)
C11	C10	C9	113.15(16)
C12	C11	C10	121.03(18)
C16	C11	C10	120.57(17)
C16	C11	C12	118.39(19)
C13	C12	C11	120.7(2)
C14	C13	C12	120.41(19)
C13	C14	C15	119.3(2)
C14	C15	C16	120.3(2)
C11	C16	C15	120.98(18)
N1	C17	C18	112.60(15)
C19	C18	C17	120.38(16)
C19	C18	C23	118.78(18)
C23	C18	C17	120.84(17)
C20	C19	C18	120.80(17)
C21	C20	C19	119.75(19)
C20	C21	C22	119.96(19)
C23	C22	C21	120.23(19)

Atom	Atom	Atom	Angle/°
C22	C23	C18	120.48(19)
O1	B1	C8	99.22(13)
O2	B1	O1	106.90(14)
O2	B1	C8	116.71(15)
O3	B1	O1	110.05(14)
O3	B1	O2	106.48(14)
O3	B1	C8	116.82(15)

Table S5: Torsion Angles in ° for compound **4**.

Atom	Atom	Atom	Atom	Angle/°
O2	C1	C2	O3	-35.34(16)
O2	C1	C2	C5	-152.97(15)
O2	C1	C2	C6	80.47(17)
N1	C8	C9	C10	-175.81(15)
N1	C8	B1	O1	-4.60(16)
N1	C8	B1	O2	109.68(16)
N1	C8	B1	O3	-122.72(16)
N1	C17	C18	C19	96.73(19)
N1	C17	C18	C23	-83.0(2)
C1	O2	B1	O1	-123.04(14)
C1	O2	B1	O3	-5.42(18)
C1	O2	B1	C8	127.07(16)
C2	O3	B1	O1	96.78(16)
C2	O3	B1	O2	-18.73(18)
C2	O3	B1	C8	-151.16(15)
C3	C1	C2	O3	80.50(17)
C3	C1	C2	C5	-37.1(2)
C3	C1	C2	C6	-163.69(15)
C4	C1	C2	O3	-154.04(16)
C4	C1	C2	C5	88.3(2)
C4	C1	C2	C6	-38.2(2)
C7	O1	B1	O2	-115.97(15)
C7	O1	B1	O3	128.79(16)
C7	O1	B1	C8	5.71(18)
C7	N1	C8	C9	-124.27(16)
C7	N1	C8	B1	2.59(19)
C7	N1	C17	C18	-100.9(2)
C8	N1	C7	O1	1.3(2)
C8	N1	C7	N2	-179.83(17)
C8	N1	C17	C18	75.5(2)
C8	C9	C10	C11	166.34(16)
C9	C8	B1	O1	117.48(15)
C9	C8	B1	O2	-128.23(17)
C9	C8	B1	O3	-0.6(2)
C9	C10	C11	C12	-95.9(2)
C9	C10	C11	C16	84.8(2)
C10	C11	C12	C13	-179.0(2)
C10	C11	C16	C15	178.29(18)
C11	C12	C13	C14	0.5(4)
C12	C11	C16	C15	-1.1(3)
C12	C13	C14	C15	-0.6(4)
C13	C14	C15	C16	-0.1(3)

Atom	Atom	Atom	Atom	Angle/°
C14	C15	C16	C11	1.0(3)
C16	C11	C12	C13	0.4(3)
C17	N1	C7	O1	178.04(16)
C17	N1	C7	N2	-3.1(3)
C17	N1	C8	C9	58.9(2)
C17	N1	C8	B1	-174.19(15)
C17	C18	C19	C20	-179.08(16)
C17	C18	C23	C22	178.91(17)
C18	C19	C20	C21	-0.2(3)
C19	C18	C23	C22	-0.8(3)
C19	C20	C21	C22	-0.1(3)
C20	C21	C22	C23	-0.1(3)
C21	C22	C23	C18	0.5(3)
C23	C18	C19	C20	0.6(3)
B1	O1	C7	N1	-4.8(2)
B1	O1	C7	N2	176.23(16)
B1	O2	C1	C2	25.23(18)
B1	O2	C1	C3	-93.31(17)
B1	O2	C1	C4	147.48(16)
B1	O3	C2	C1	33.34(17)
B1	O3	C2	C5	154.84(15)
B1	O3	C2	C6	-85.30(17)
B1	C8	C9	C10	66.6(2)

Table S6: Hydrogen Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for compound **4**. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij}.

Atom	x	y	z	U_{eq}
H2A	7509.73	5418.35	4500.44	32
H2B	7639.5	5659.69	5187.06	32
H3A	8874.95	589.32	5028.29	46
H3B	7302.57	105.2	4552.61	46
H3C	6709.49	797.05	5066.34	46
H4A	9262	1776.43	3618.24	53
H4B	8509.64	742.16	3591.16	53
H4C	10250.77	1023.68	4084.81	53
H5A	4113.83	707.83	4294.81	45
H5B	4868.53	547.51	3640.22	45
H5C	3179.53	1245.57	3692.93	45
H6A	4583.1	2680.79	3366.99	50
H6B	6047.02	1987.6	3118.88	50
H6C	6781.97	2835.69	3549.35	50
H8	7890.65	2742.6	5825.46	27
H9A	5151.04	3069.38	6309.17	31
H9B	3923.48	3076.6	5643.21	31
H10A	4328.07	1519.26	5513.62	38
H10B	5956.36	1471.37	6083.74	38
H12	5177.27	1275.84	7131.15	43
H13	2976.03	861.63	7781.88	49
H14	-193.39	819.47	7406.31	48
H15	-1155.36	1221.36	6374.52	45
H16	1038.66	1665.55	5729.66	35
H17A	6430.94	4423.29	6428.25	29

Atom	x	y	z	U_{eq}
H17B	7188.44	5254.34	6047.12	29
H19	10469.2	5613.47	6164.39	30
H20	13464.92	5421.32	6693.75	35
H21	14102.34	4170.6	7359.15	38
H22	11741.73	3117.19	7493.85	43
H23	8748.15	3311.51	6970.32	38
H4D	9242.82	7164.1	5511.37	45
H4E	7345.92	7165.4	5542.39	45

Table S7: Hydrogen Bond information for compound **4**.

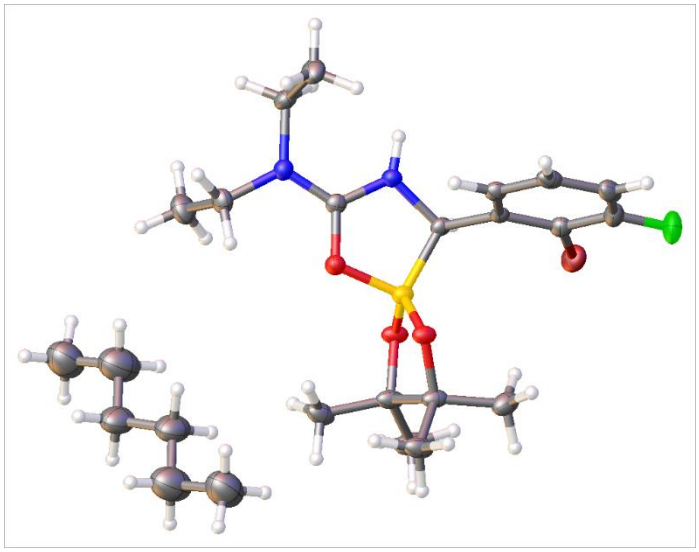
D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
N2	H2B	O4	0.88	1.94	2.780(2)	158.7
O4	H4D	O2[1]	0.87	1.98	2.8421(19)	168.8
O4	H4E	O3[2]	0.87	1.93	2.7817(18)	165.4

[1]2-x,1-y,1-z; [2]1-x,1-y,1-z

7.2. X-Ray crystallography data for α-boryl urea (43)

Experimental

α-Boryl urea (**43**) was crystallized from mixture of ethyl acetate and hexane. The crystallographic data are summarized in the following table



Crystal Data

Crystal Data. $C_{21}H_{34}BBrFN_2O_3$, M_r = 472.22, monoclinic, $P2_1/c$ (No. 14), a = 11.3295(2) Å, b =

22.0996(3) Å, c = 10.3207(2) Å, β = 114.717(2)°, α = γ = 90°, V = 2347.32(8) Å^3, T = 99.9(7) K, Z = 4, Z' = 1, μ(Cu K$_\alpha$) = 2.643, 22936 reflections measured, 4457 unique (R_{int} = 0.0480) which were used in all calculations. The final wR_2 was 0.1307 (all data) and R_1 was 0.0467 (I≥2 σ(I)).

Compound	**43**
Formula	$C_{21}H_{34}BBrFN_2O_3$
$D_{calc.}$/ g cm^{-3}	1.336
μ/mm^{-1}	2.643
Formula Weight	472.22
Color	colorless
Shape	plate-shaped
Size/mm^3	0.20×0.10×0.01
T/K	99.9(7)
Crystal System	monoclinic
Space Group	$P2_1/c$
a/Å	11.3295(2)
b/Å	22.0996(3)
c/Å	10.3207(2)
α/°	90
β/°	114.717(2)
γ/°	90
V/Å^3	2347.32(8)
Z	4
Z'	1
Wavelength/Å	1.54184
Radiation type	Cu K$_\alpha$
Θ_{min}/°	4.001
Θ_{max}/°	75.487
Measured Refl's.	22936
Indep't Refl's	4457
Refl's I≥2 σ(I)	4050
R_{int}	0.0480
Parameters	269
Restraints	0
Largest Peak	1.082
Deepest Hole	-0.571
GooF	1.089
wR_2 (all data)	0.1307
wR_2	0.1276
R_1 (all data)	0.0513
R_1	0.0467

Structure Quality Indicators

Reflections:	d min (CuKα) 2Θ=151.0° 0.80	I/σ(I) 31.7	Rint m=5.24 4.80%	Full 135.4° 92% to 151.0° 99.1
Refinement:	Shift 0.001	Max Peak 1.1	Min Peak -0.6	GooF 1.089

Reflection Statistics

Total reflections (after filtering)	23336	Unique reflections	4457
Completeness	0.917	Mean I/σ	22.66
hkl_{max} collected	(14, 25, 12)	hkl_{min} collected	(-14, -26, -9)
hkl_{max} used	(12, 26, 12)	hkl_{min} used	(-14, 0, 0)
Lim d_{max} collected	100.0	Lim d_{min} collected	0.77
d_{max} used	11.05	d_{min} used	0.8
Friedel pairs	1942	Friedel pairs merged	1
Inconsistent equivalents	14	R_{int}	0.048
R_{sigma}	0.0315	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	1
Multiplicity	(4155, 2635, 1548, 841, 459, 298, 161, 61, 15, 7)	Maximum multiplicity	18
Removed systematic absences	399	Filtered off (Shel/OMIT)	0

Bond lengths [Å] and angles [°].

Table S8: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for compound **43**. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij}.

Atom	x	y	z	U_{eq}
Br1	8693.1(3)	7673.3(2)	5663.9(3)	32.25(14)
F1	9161.7(19)	6657.0(9)	4066(2)	42.6(5)
O1	3583.5(19)	8328.7(8)	3429(2)	21.8(4)
O2	5671(2)	8895.2(8)	4281.9(19)	23.4(4)
O3	4981.6(19)	8367.8(8)	2142.2(19)	20.9(4)
N1	4456(2)	7516.6(10)	4759(2)	19.4(5)
N2	2337(2)	7813.9(10)	4304(3)	22.2(5)
C1	6104(3)	7242.4(11)	3903(3)	18.1(5)
C2	7434(3)	7168.5(13)	4280(3)	23.3(6)
C3	7869(3)	6712.6(14)	3678(3)	28.5(6)
C4	7037(3)	6319.5(13)	2689(3)	30.3(7)
C5	5715(3)	6386.6(12)	2293(3)	26.1(6)
C6	5265(3)	6844.1(12)	2889(3)	21.1(5)
C7	5597(3)	7729.4(11)	4558(3)	18.5(5)
C8	3446(3)	7886.5(12)	4172(3)	18.9(5)
C9	2132(3)	7277.6(13)	5036(3)	26.7(6)
C10	1829(3)	6718.1(14)	4110(4)	33.5(7)
C11	1283(3)	8258.1(14)	3711(3)	27.5(6)
C12	1326(3)	8713.3(15)	4825(4)	38.1(8)
C13	5588(3)	9323.4(12)	3196(3)	26.3(6)
C14	5676(3)	8903.5(12)	2027(3)	23.6(6)
C15	4285(4)	9656.2(13)	2682(3)	33.3(7)

Atom	x	y	z	U_{eq}
C16	6693(4)	9772.0(14)	3834(4)	37.4(8)
C17	5031(3)	9156.3(13)	530(3)	30.7(7)
C18	7068(3)	8714.3(14)	2354(4)	32.5(7)
B1	5046(3)	8349.5(14)	3571(3)	20.6(6)
C19	-245(5)	10164.5(18)	456(5)	57.5(11)
C20	61(7)	9902(2)	1878(6)	78.8(16)
C21	-344(6)	10265(2)	2838(6)	74.2(14)

Table S9: Anisotropic Displacement Parameters (×10^4) for compound **43**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	20.54(19)	39.4(2)	32.7(2)	0.17(12)	7.05(15)	-3.17(11)
F1	28.6(10)	48.4(11)	56.0(13)	2.8(9)	22.8(9)	12.8(8)
O1	23.4(10)	22.4(9)	21.7(9)	3.6(7)	11.5(8)	2.5(7)
O2	35.6(11)	19.6(9)	17.8(9)	-0.4(7)	13.8(9)	-4.6(8)
O3	29.9(10)	16.9(9)	18.7(9)	-1.2(7)	12.8(8)	-3.1(7)
N1	21.2(12)	18.7(10)	19.5(11)	3.0(9)	9.8(10)	0.5(9)
N2	21.6(12)	23.4(11)	23.7(12)	1.8(9)	11.4(10)	1.7(9)
C1	21.1(13)	18.4(12)	17.1(12)	5.8(10)	10.4(11)	1.7(10)
C2	25.3(14)	24.5(13)	20.8(14)	4.9(10)	10.5(12)	2.5(11)
C3	25.2(15)	35.0(16)	29.1(15)	8.4(12)	15.1(13)	8.5(12)
C4	45.1(18)	23.9(14)	31.0(16)	4.5(12)	24.9(15)	9.8(13)
C5	42.5(17)	20.6(13)	20.1(14)	2.3(10)	18.0(13)	1.3(12)
C6	25.8(14)	22.2(13)	17.1(13)	2.8(10)	10.6(11)	0.5(10)
C7	22.1(14)	19.7(12)	16.4(12)	-0.9(9)	10.8(11)	-1.8(10)
C8	22.2(13)	20.5(13)	14.3(12)	-1.3(9)	8.1(11)	-0.5(10)
C9	26.0(15)	28.6(15)	30.6(16)	4.1(11)	16.8(14)	-1.1(11)
C10	26.9(16)	28.0(15)	48(2)	-1.6(13)	18.2(15)	-4.1(12)
C11	23.3(14)	30.5(15)	26.7(15)	2.1(12)	8.5(12)	5.4(11)
C12	40.8(19)	29.7(16)	44.8(19)	-4.5(14)	18.9(16)	6.2(13)
C13	44.2(17)	19.2(13)	21.1(14)	-1.3(10)	19.2(13)	-4.2(12)
C14	36.8(16)	17.4(12)	21.4(14)	-3.0(10)	16.7(13)	-6.0(11)
C15	56(2)	21.9(14)	30.8(16)	2.2(12)	26.1(16)	6.5(13)
C16	59(2)	27.9(16)	33.1(17)	-9.3(13)	26.3(17)	-16.7(15)
C17	52(2)	21.7(14)	23.9(15)	0.3(11)	20.9(14)	-1.3(13)
C18	39.5(18)	29.0(15)	36.9(17)	-4.7(13)	23.8(15)	-7.2(13)
B1	25.2(15)	19.9(14)	19.2(15)	1.3(11)	11.8(13)	-0.4(11)
C19	79(3)	34.9(19)	74(3)	1.7(19)	48(3)	-2.6(19)
C20	115(5)	56(3)	82(4)	8(3)	58(4)	10(3)
C21	93(4)	66(3)	71(3)	14(3)	42(3)	18(3)

Table S10: Bond Lengths in Å for compound **43**.

Atom	tom	Length/Å
Br1	C2	1.901(3)
F1	C3	1.353(3)

Atom	tom	Length/Å
O1	C8	1.291(3)
O1	B1	1.602(4)
O2	C13	1.440(3)
O2	B1	1.435(4)
O3	C14	1.453(3)
O3	B1	1.446(3)
N1	C7	1.469(3)
N1	C8	1.329(4)
N2	C8	1.328(4)
N2	C9	1.476(4)
N2	C11	1.468(4)
C1	C2	1.399(4)
C1	C6	1.393(4)
C1	C7	1.507(3)
C2	C3	1.379(4)
C3	C4	1.371(5)
C4	C5	1.386(5)
C5	C6	1.387(4)
C7	B1	1.665(4)
C9	C10	1.512(4)
C11	C12	1.514(4)
C13	C14	1.558(4)
C13	C15	1.532(5)
C13	C16	1.515(4)
C14	C17	1.513(4)
C14	C18	1.527(4)
C19	C19[1]	1.470(8)
C19	C20	1.479(7)
C20	C21	1.489(8)

Table S11: Bond Angles in ˚ for compound **43**.

Atom	Atom	Atom	Angle/˚
C8	O1	B1	110.2(2)
B1	O2	C13	107.3(2)
B1	O3	C14	107.9(2)
C8	N1	C7	112.3(2)
C8	N2	C9	120.5(2)
C8	N2	C11	121.1(2)
C11	N2	C9	118.4(2)
C2	C1	C7	121.8(2)
C6	C1	C2	116.9(2)
C6	C1	C7	121.3(2)
C1	C2	Br1	121.5(2)
C3	C2	Br1	118.0(2)
C3	C2	C1	120.4(3)
F1	C3	C2	118.7(3)
F1	C3	C4	119.0(3)
C4	C3	C2	122.3(3)
C3	C4	C5	118.3(3)
C4	C5	C6	120.0(3)

Atom	Atom	Atom	Angle/°
C5	C6	C1	122.1(3)
N1	C7	C1	111.0(2)
N1	C7	B1	102.9(2)
C1	C7	B1	115.4(2)
O1	C8	N1	116.2(2)
O1	C8	N2	120.4(2)
N2	C8	N1	123.4(2)
N2	C9	C10	112.1(2)
N2	C11	C12	111.4(3)
O2	C13	C14	101.9(2)
O2	C13	C15	108.9(2)
O2	C13	C16	108.6(2)
C15	C13	C14	112.5(2)
C16	C13	C14	114.7(2)
C16	C13	C15	109.8(3)
O3	C14	C13	102.1(2)
O3	C14	C17	109.7(2)
O3	C14	C18	107.6(2)
C17	C14	C13	114.3(2)
C17	C14	C18	109.8(2)
C18	C14	C13	112.7(2)
O1	B1	C7	98.10(19)
O2	B1	O1	109.9(2)
O2	B1	O3	107.6(2)
O2	B1	C7	113.6(2)
O3	B1	O1	107.3(2)
O3	B1	C7	119.5(2)
C19[1]	C19	C20	116.5(5)
C19	C20	C21	116.0(4)

Table S12: Torsion Angles in ° for compound **43.**

Atom	Atom	Atom	Atom	Angle/°
Br1	C2	C3	F1	-1.9(4)
Br1	C2	C3	C4	178.9(2)
F1	C3	C4	C5	-179.4(3)
O2	C13	C14	O3	35.2(3)
O2	C13	C14	C17	153.7(2)
O2	C13	C14	C18	-80.0(3)
N1	C7	B1	O1	-0.6(2)
N1	C7	B1	O2	115.3(2)
N1	C7	B1	O3	-115.9(3)
C1	C2	C3	F1	179.8(2)
C1	C2	C3	C4	0.6(4)
C1	C7	B1	O1	120.4(2)
C1	C7	B1	O2	-123.7(3)
C1	C7	B1	O3	5.1(4)
C2	C1	C6	C5	1.1(4)
C2	C1	C7	N1	-144.1(2)
C2	C1	C7	B1	99.4(3)
C2	C3	C4	C5	-0.2(4)
C3	C4	C5	C6	0.3(4)
C4	C5	C6	C1	-0.8(4)

Atom	Atom	Atom	Atom	Angle/°
C6	C1	C2	Br1	-179.30(18)
C6	C1	C2	C3	-1.0(4)
C6	C1	C7	N1	35.9(3)
C6	C1	C7	B1	-80.6(3)
C7	N1	C8	O1	6.1(3)
C7	N1	C8	N2	-174.9(2)
C7	C1	C2	Br1	0.7(3)
C7	C1	C2	C3	179.0(2)
C7	C1	C6	C5	-178.9(2)
C8	O1	B1	O2	-114.9(2)
C8	O1	B1	O3	128.4(2)
C8	O1	B1	C7	3.9(2)
C8	N1	C7	C1	-126.7(2)
C8	N1	C7	B1	-2.8(3)
C8	N2	C9	C10	-76.8(3)
C8	N2	C11	C12	-95.5(3)
C9	N2	C8	O1	174.2(2)
C9	N2	C8	N1	-4.8(4)
C9	N2	C11	C12	85.3(3)
C11	N2	C8	O1	-5.0(4)
C11	N2	C8	N1	176.0(2)
C11	N2	C9	C10	102.4(3)
C13	O2	B1	O1	-97.6(2)
C13	O2	B1	O3	19.0(3)
C13	O2	B1	C7	153.6(2)
C14	O3	B1	O1	123.3(2)
C14	O3	B1	O2	5.0(3)
C14	O3	B1	C7	-126.4(3)
C15	C13	C14	O3	-81.3(3)
C15	C13	C14	C17	37.1(3)
C15	C13	C14	C18	163.5(2)
C16	C13	C14	O3	152.4(3)
C16	C13	C14	C17	-89.2(3)
C16	C13	C14	C18	37.1(3)
B1	O1	C8	N1	-6.4(3)
B1	O1	C8	N2	174.5(2)
B1	O2	C13	C14	-33.3(3)
B1	O2	C13	C15	85.7(3)
B1	O2	C13	C16	-154.8(2)
B1	O3	C14	C13	-24.7(3)
B1	O3	C14	C17	-146.3(2)
B1	O3	C14	C18	94.2(3)
C19[1]	C19	C20	C21	175.1(6)

Table S13: Hydrogen Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for compound **43**. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij}.

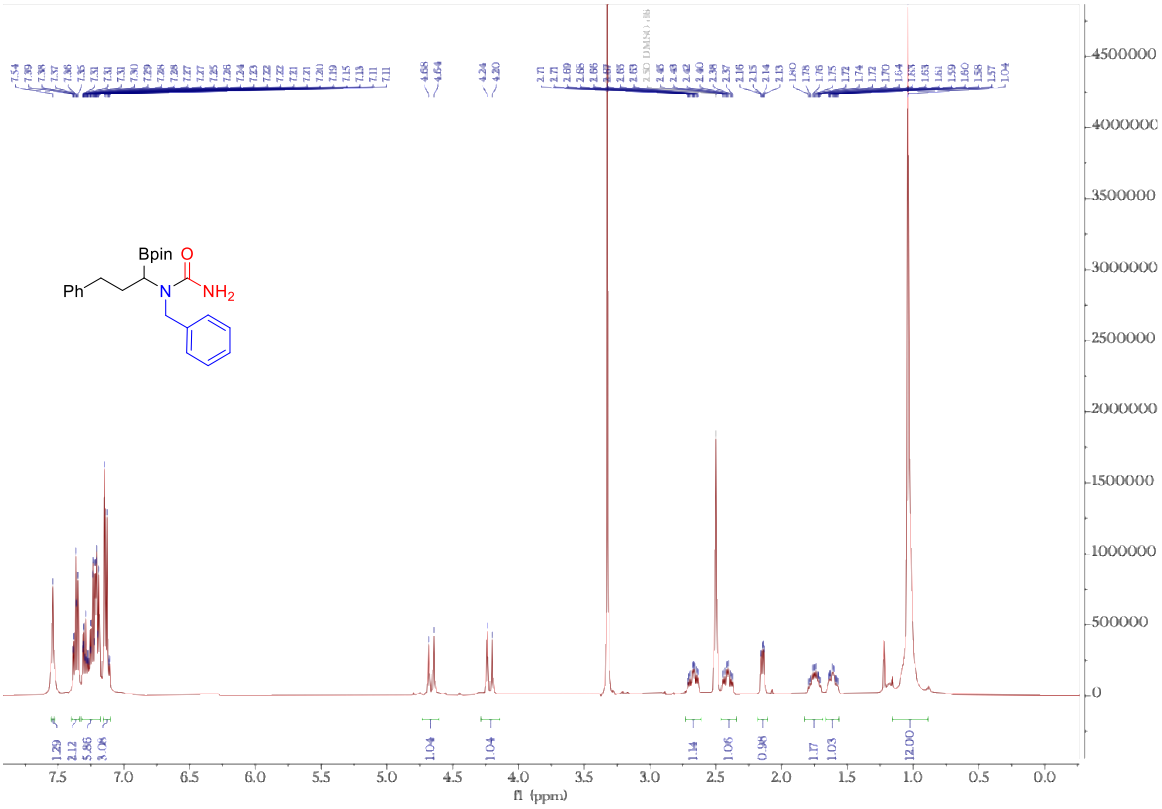
Atom	x	y	z	U_{eq}
H1	4443.49	7182.14	5215.4	23
H4	7358.68	6009.37	2285.36	36
H5	5117.15	6119.23	1612.94	31
H6	4355.13	6887.28	2597.3	25

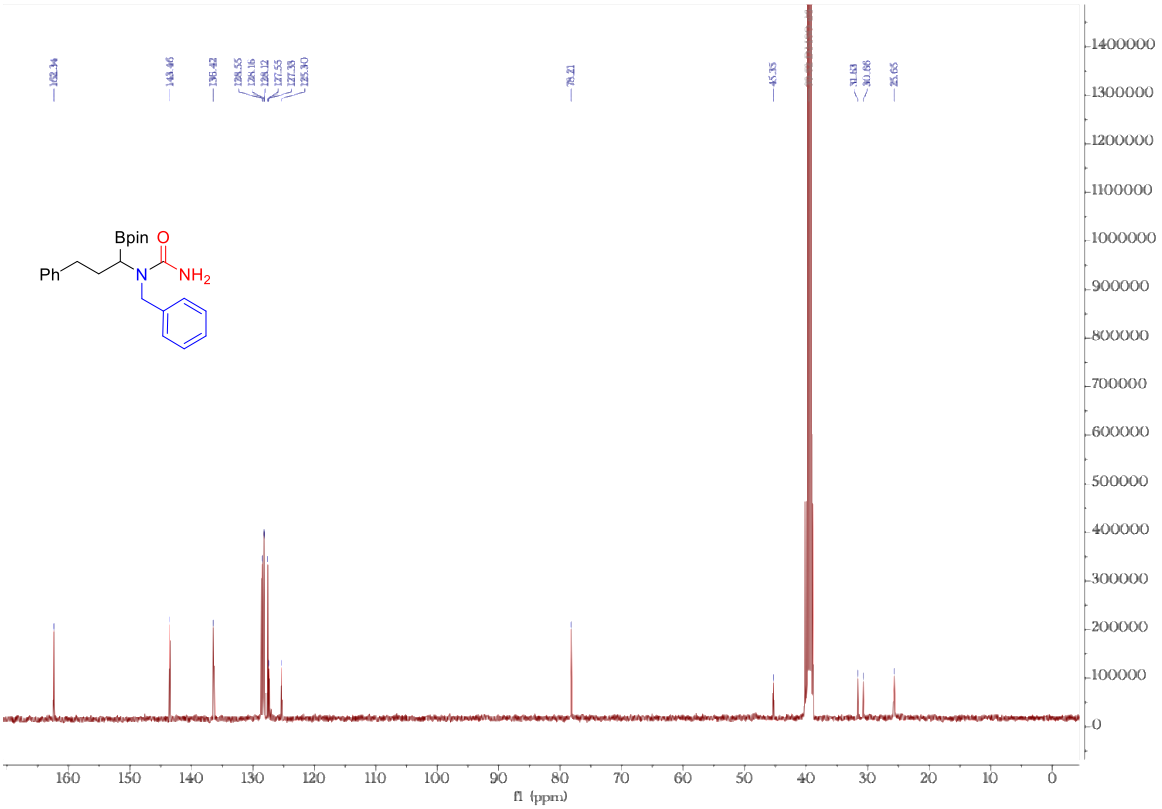
Atom	x	y	z	U_{eq}
H7	6295.47	7845.51	5504.81	22
H9A	1404.37	7357.78	5306.38	32
H9B	2922.43	7204.4	5922.66	32
H10A	1023.01	6781.42	3252.97	50
H10B	1724.8	6371.02	4643.93	50
H10C	2543.17	6639.28	3832.78	50
H11A	436.8	8045.01	3336.6	33
H11B	1356.77	8473.04	2906.43	33
H12A	576.45	8985.06	4416.69	57
H12B	2129.6	8949.83	5135.65	57
H12C	1300.61	8499.95	5645.67	57
H15A	3574.49	9369.31	2204.74	50
H15B	4255.72	9975.8	2011.12	50
H15C	4190.19	9836.22	3501.17	50
H16A	6563.75	10017.29	4555.04	56
H16B	6712.04	10036.13	3080.09	56
H16C	7518.06	9552.83	4279.15	56
H17A	5116.32	8865.69	-143.08	46
H17B	5451.06	9537.93	480.61	46
H17C	4108.58	9229.08	282.68	46
H18A	7505.13	8584.87	3351.1	49
H18B	7536.75	9057.98	2192.13	49
H18C	7056.15	8378.78	1727.55	49
H19A	-1201.78	10195.84	-60.07	69
H19B	107.89	10581.02	591.92	69
H20A	1011.73	9837.18	2364.35	95
H20B	-358.7	9499.53	1743.61	95
H21A	-88.37	10053.73	3750.89	111
H21B	-1289.81	10317.6	2393.31	111
H21C	78	10661.94	3002.21	111

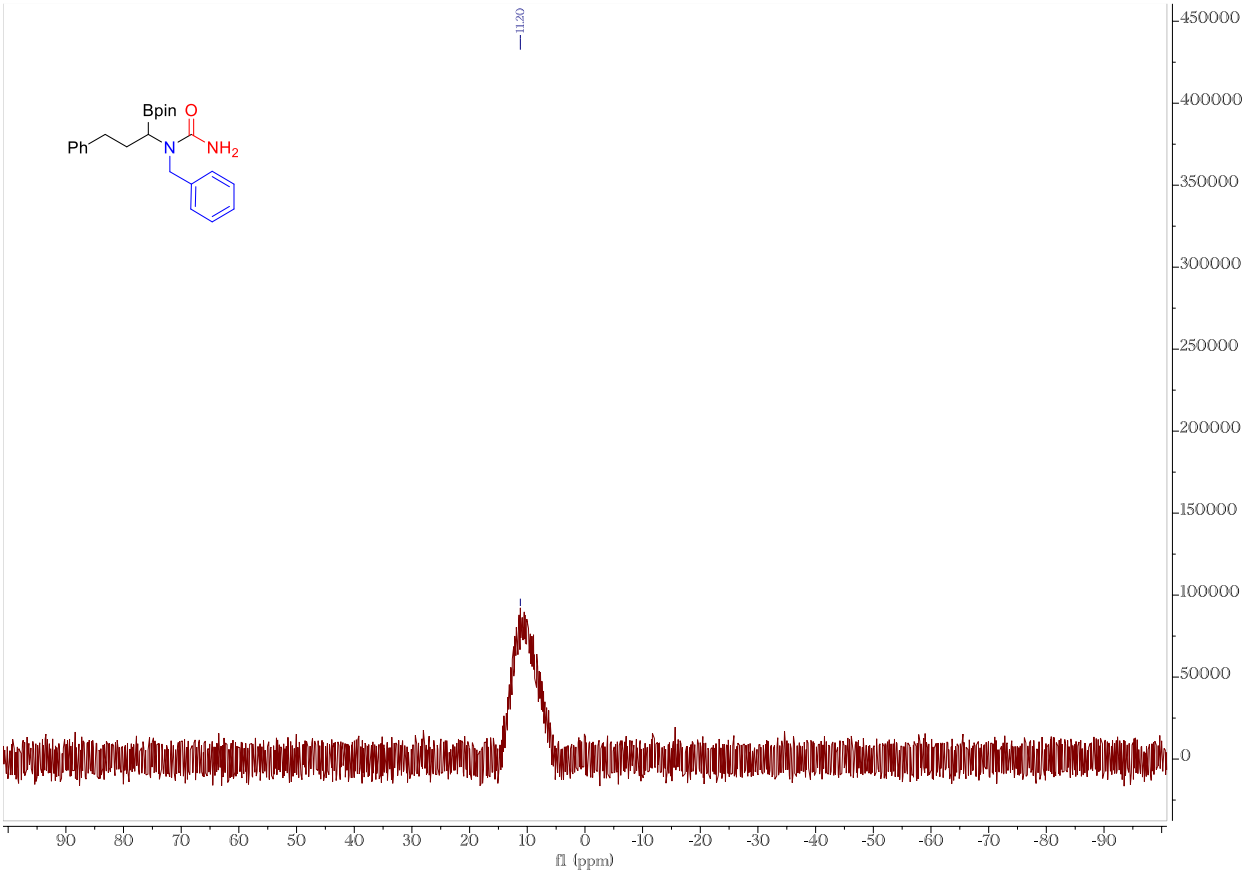
8. References:

1. Vatansever, E. C.; Yang, K. S.; Drelich, A. K.; Kratch, K. C.; Cho, C.-C.; Kempaiah, K. R.; Hsu, J. C.; Mellott, D. M.; Xu, S.; Tseng, C.-T. K.; Liu, W. R., Bepridil is potent against SARS-CoV-2 in vitro. *Proc Natl Acad Sci USA* **2021,** *118* (10), e2012201118.
2. Wang, D.; Zhou, J.; Hu, Z.; Xu, T., Deoxygenative Haloboration and Enantioselective Chloroboration of Carbonyls. *J Am Chem Soc* **2022,** *144* (50), 22870-22876.
3. Kincaid, J. R. A.; Caravez, J. C.; Iyer, K. S.; Kavthe, R. D.; Fleck, N.; Aue, D. H.; Lipshutz, B. H., A sustainable synthesis of the SARS-CoV-2 M(pro) inhibitor nirmatrelvir, the active ingredient in Paxlovid. *Commun Chem* **2022,** *5* (1), 156.

9. Copies of ^{1}H, ^{13}C, ^{11}B and ^{19}F NMR Spectra



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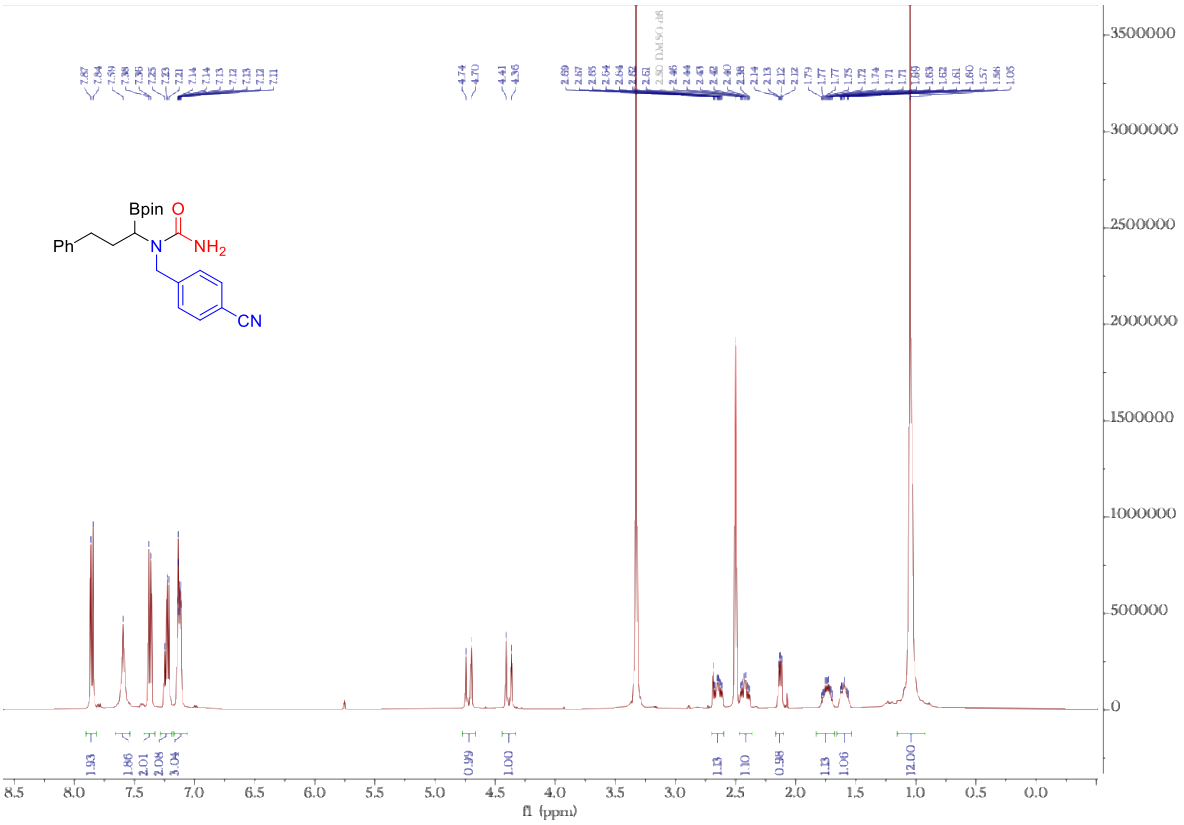
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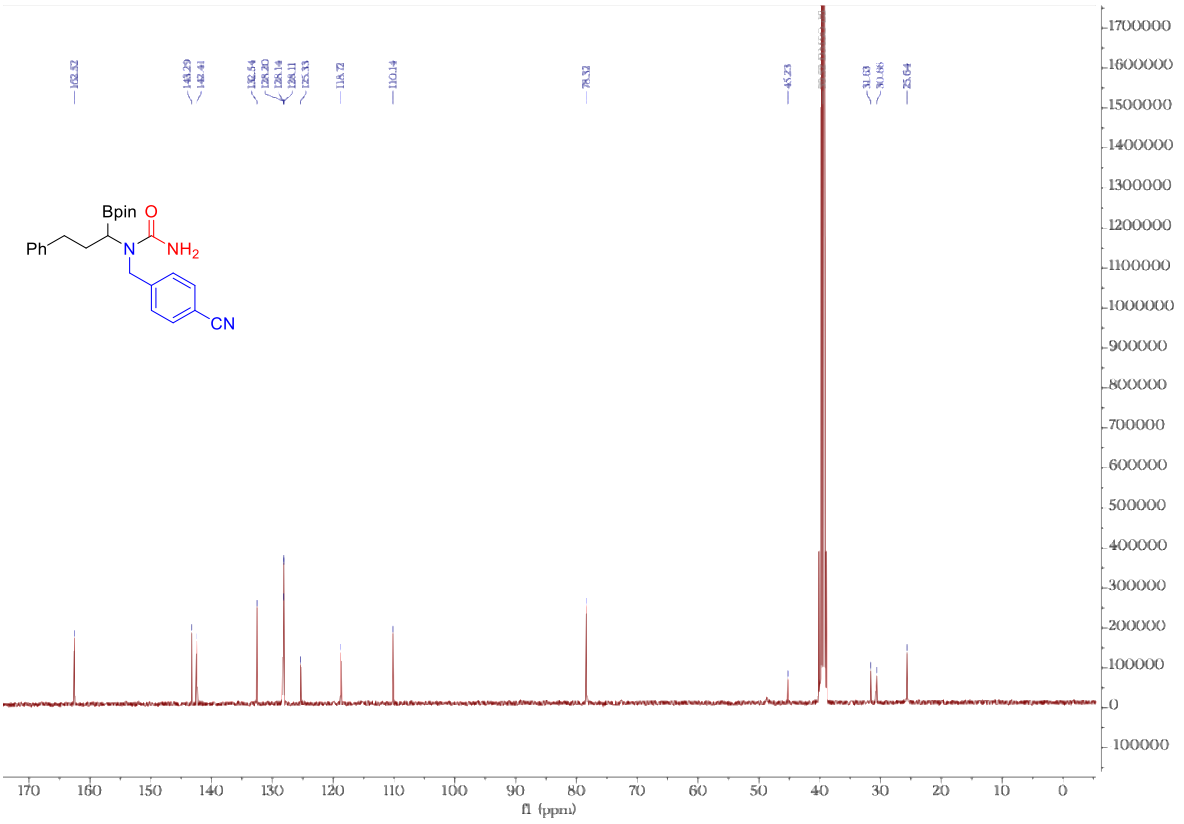
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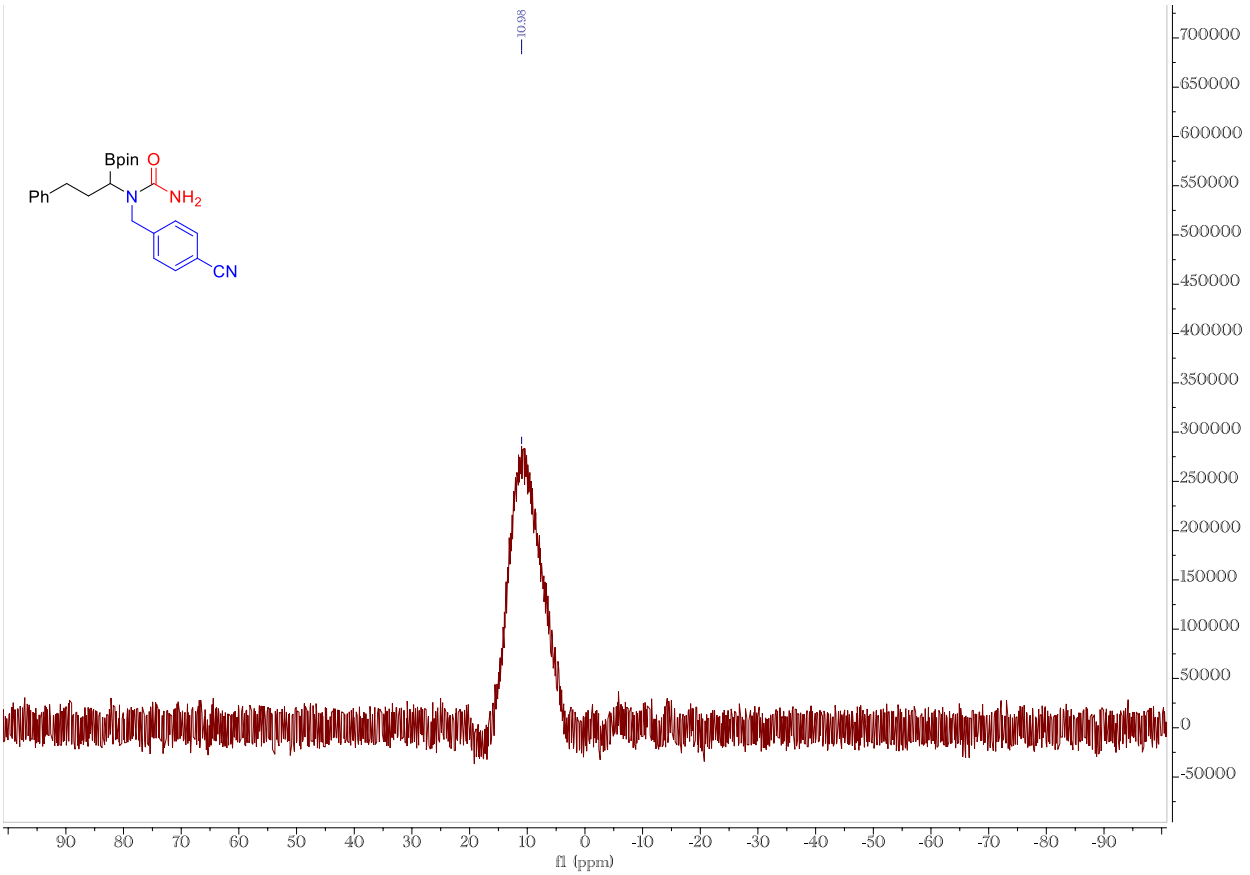
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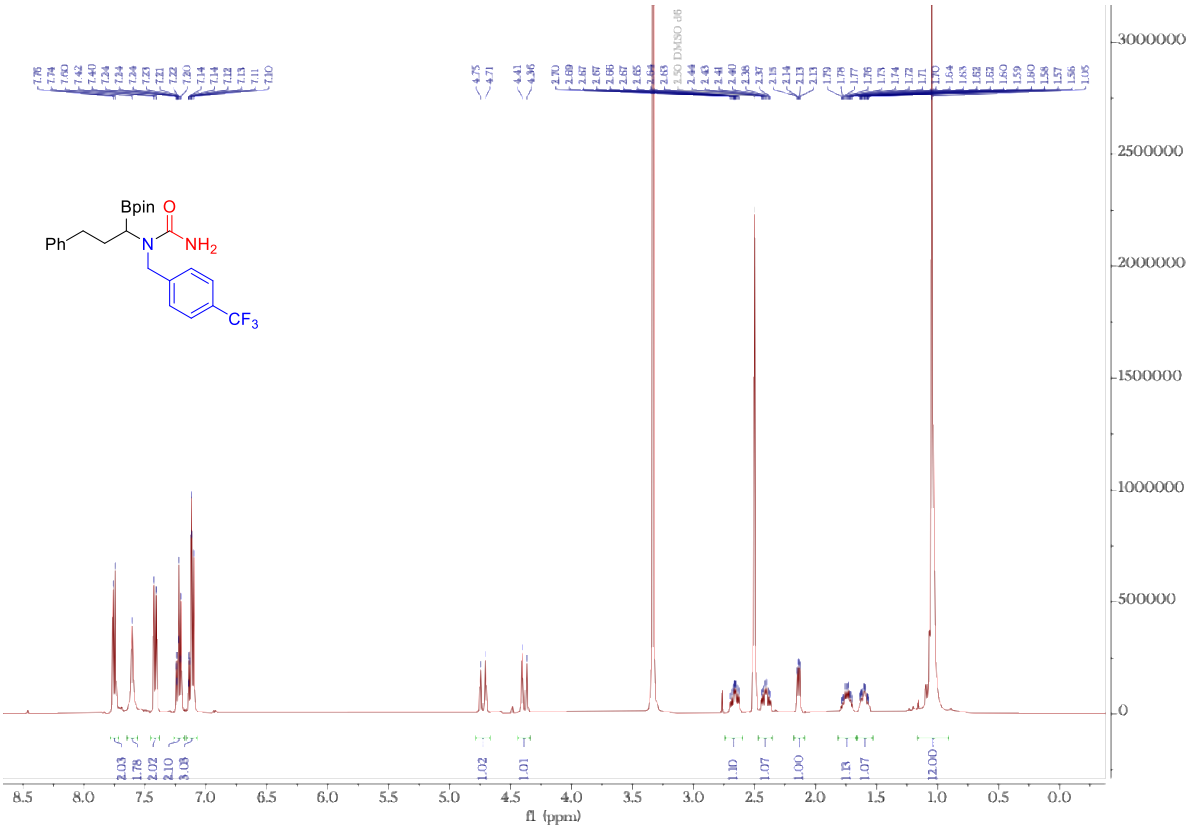
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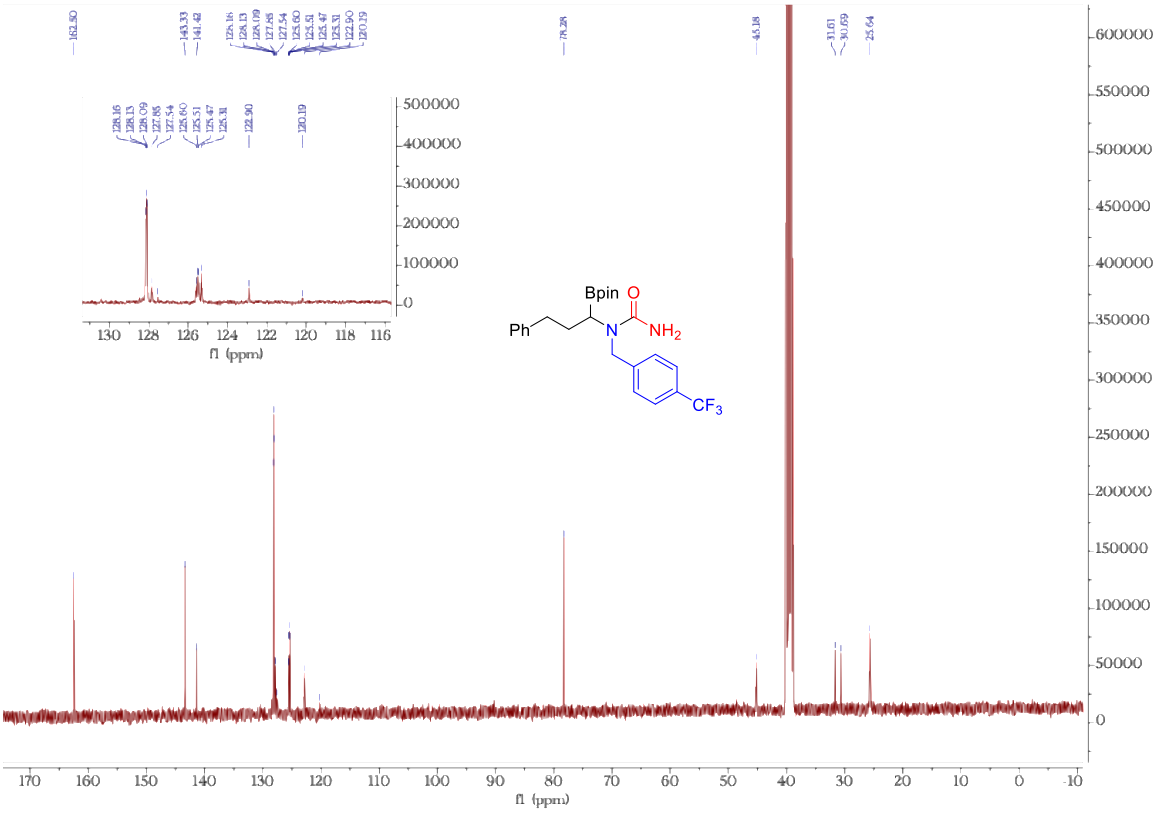
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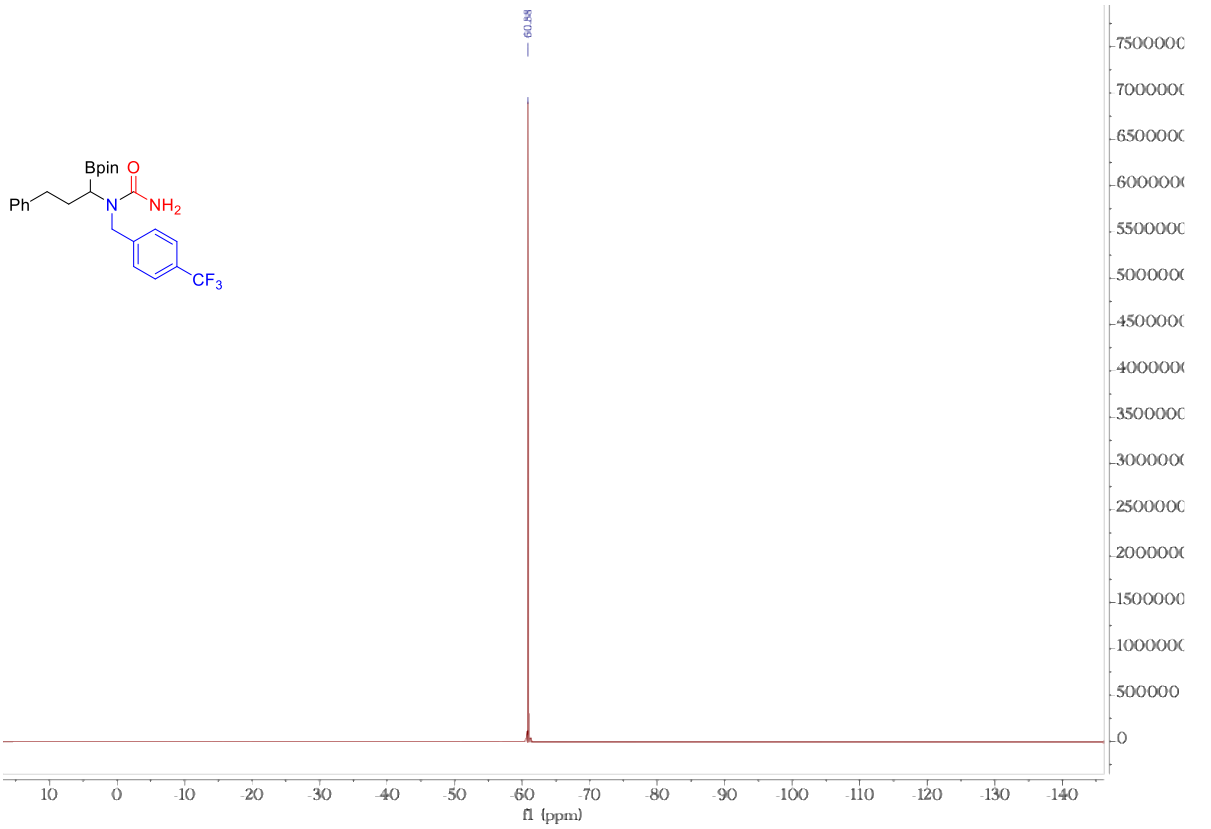
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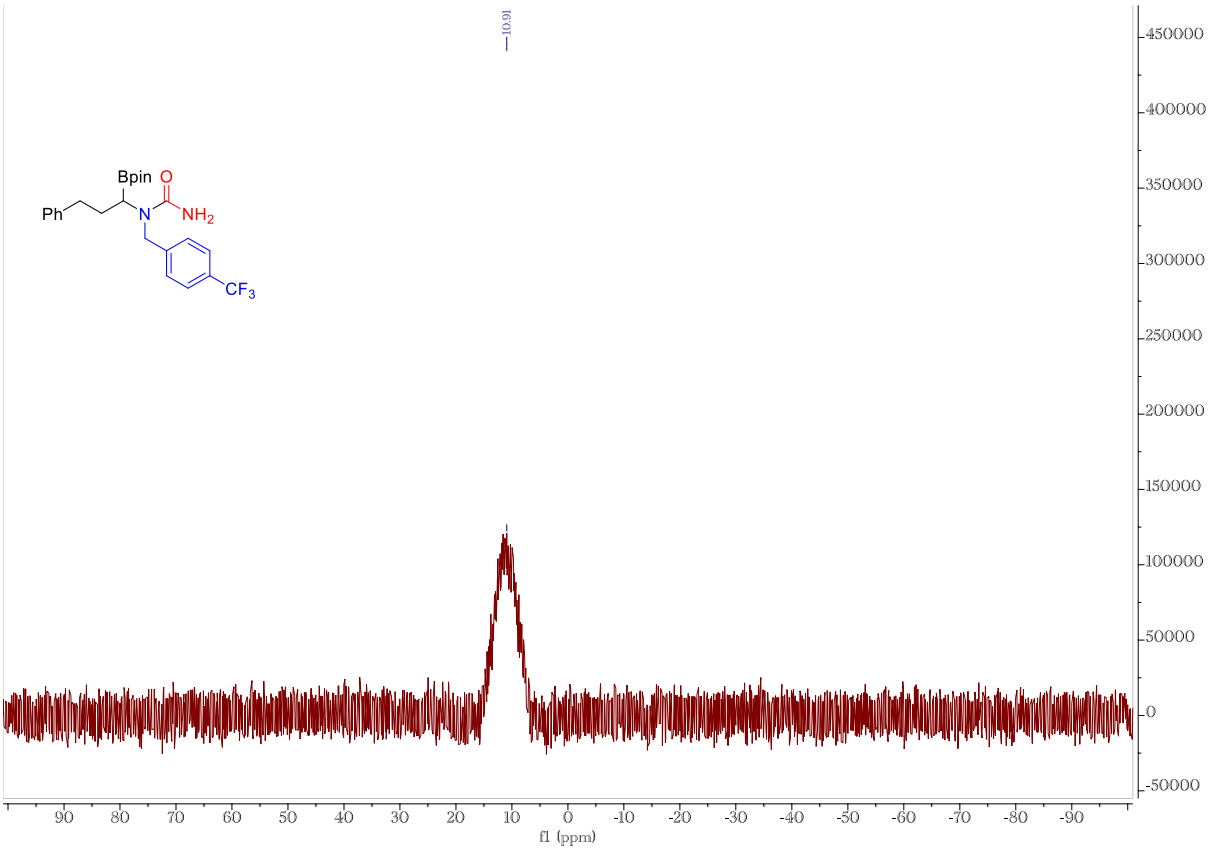
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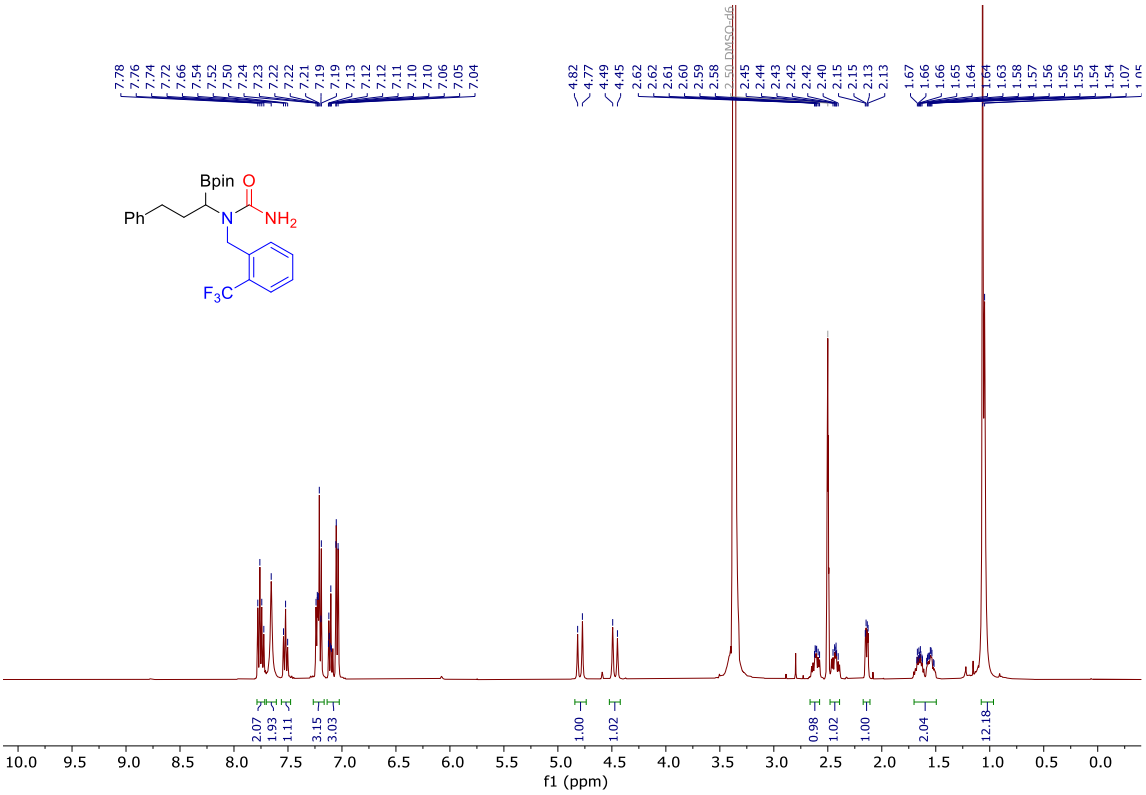
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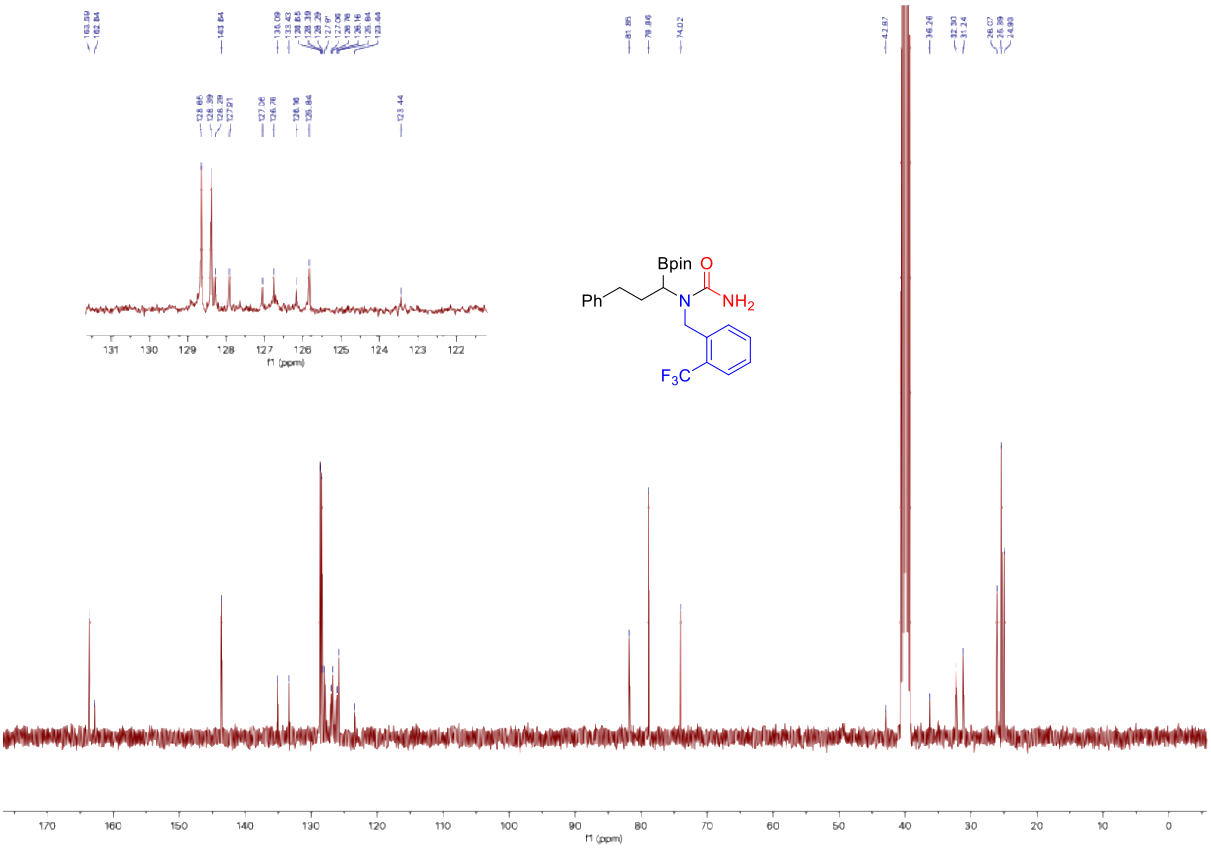
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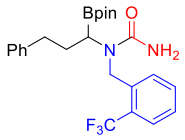
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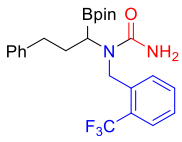
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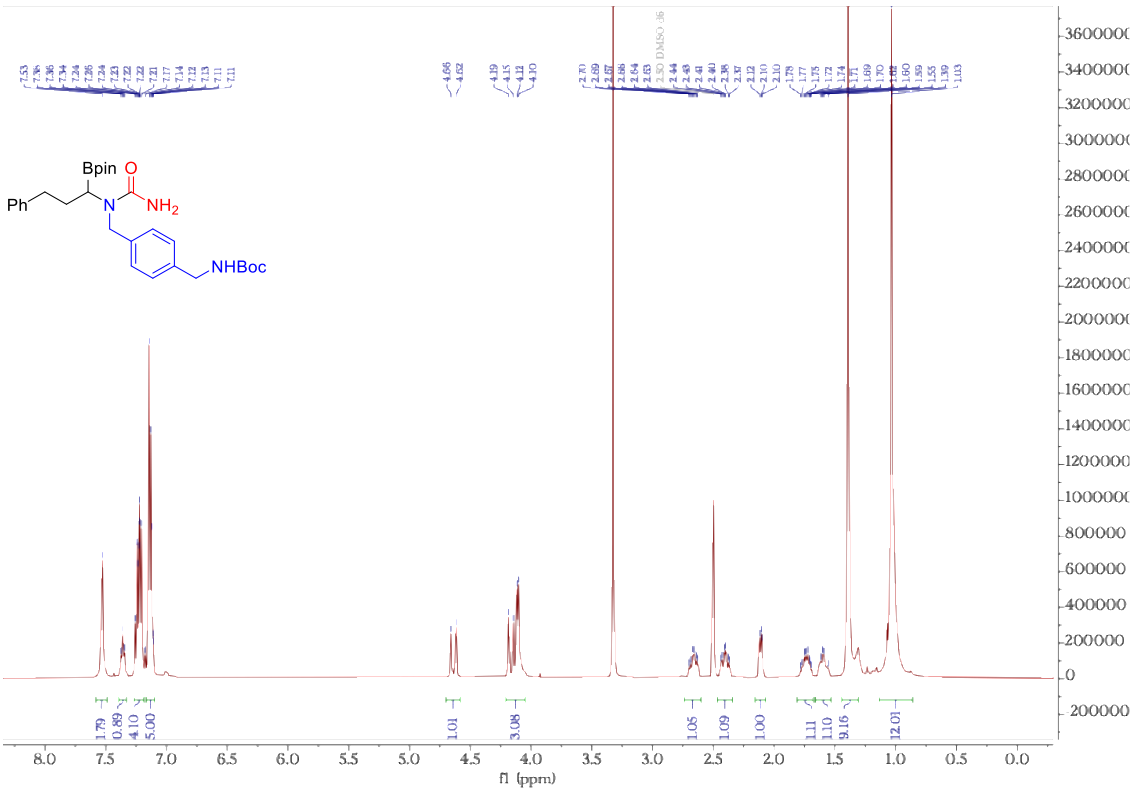
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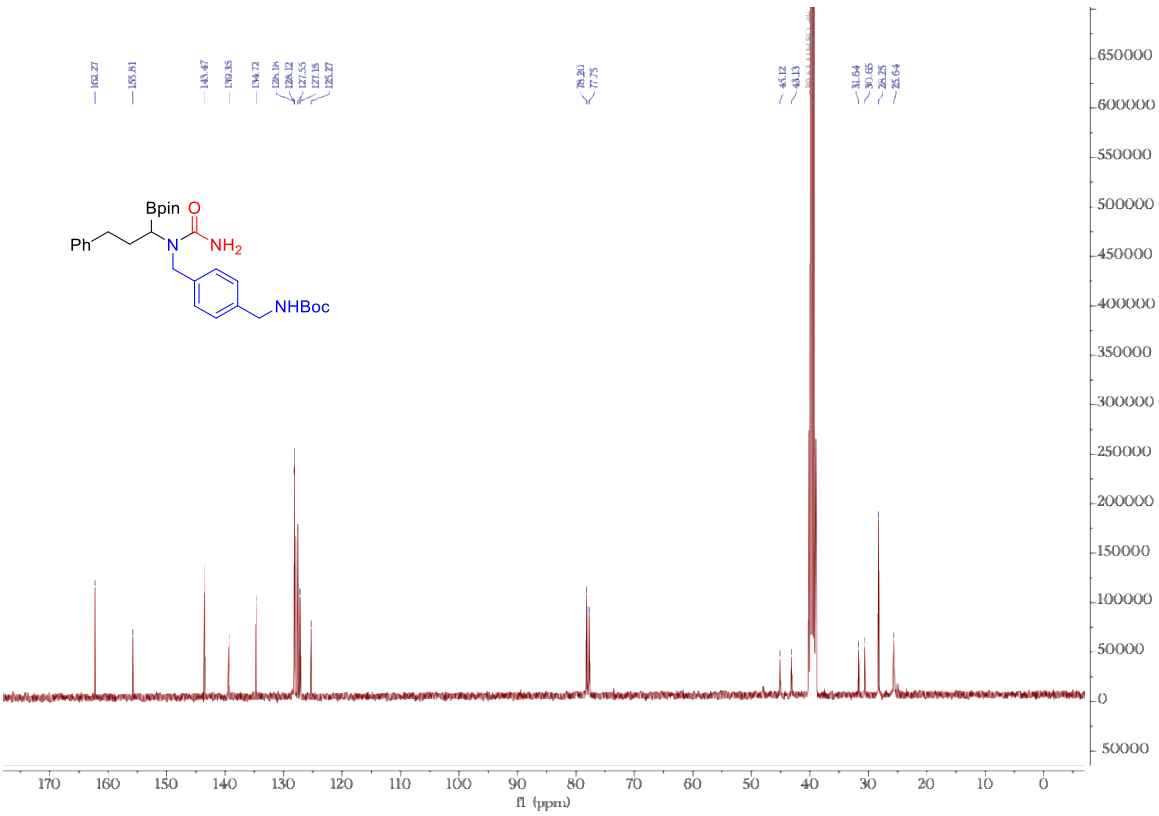
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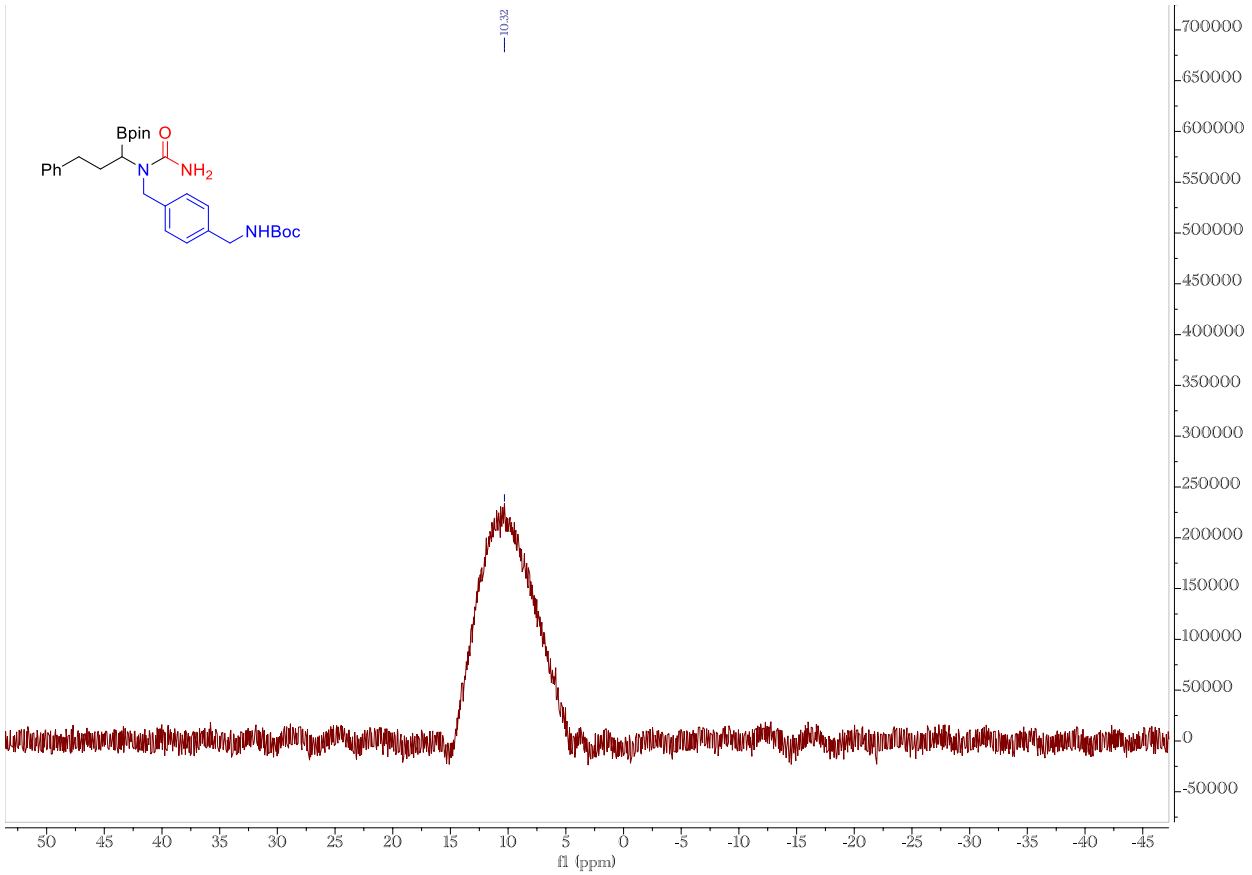
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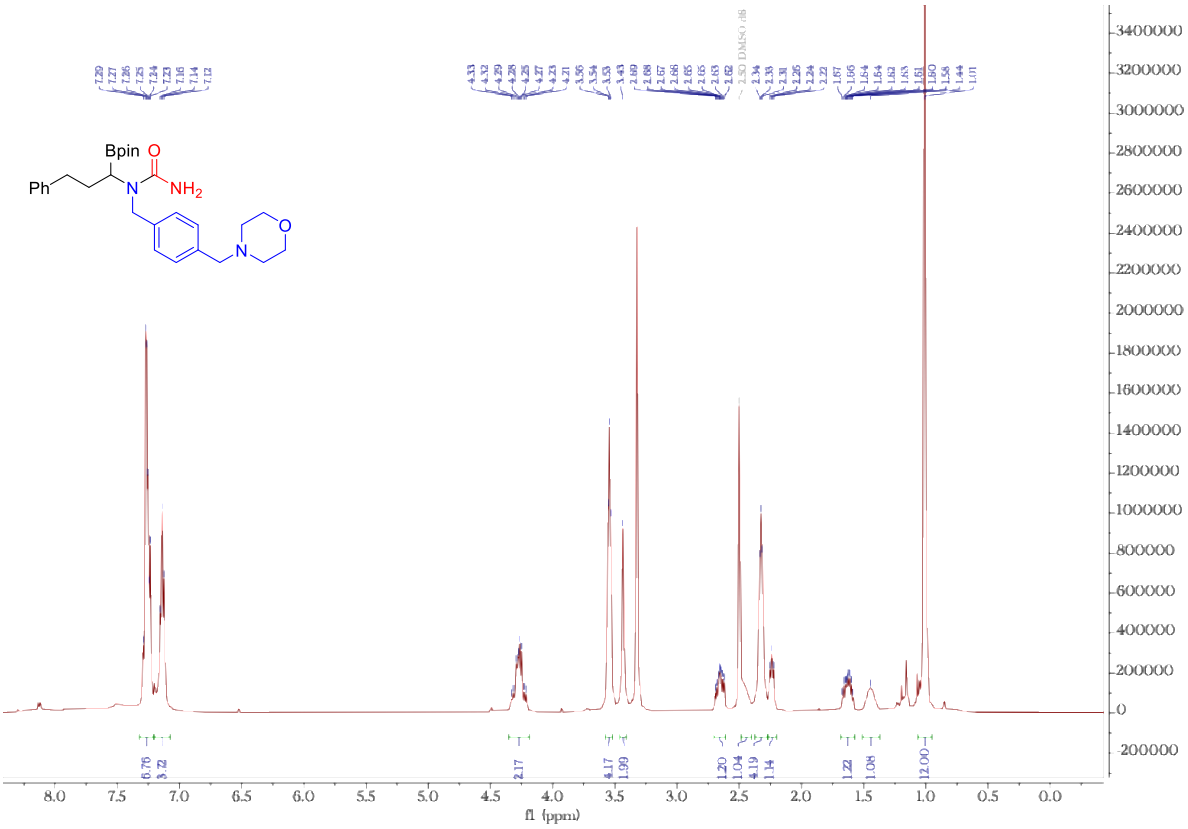
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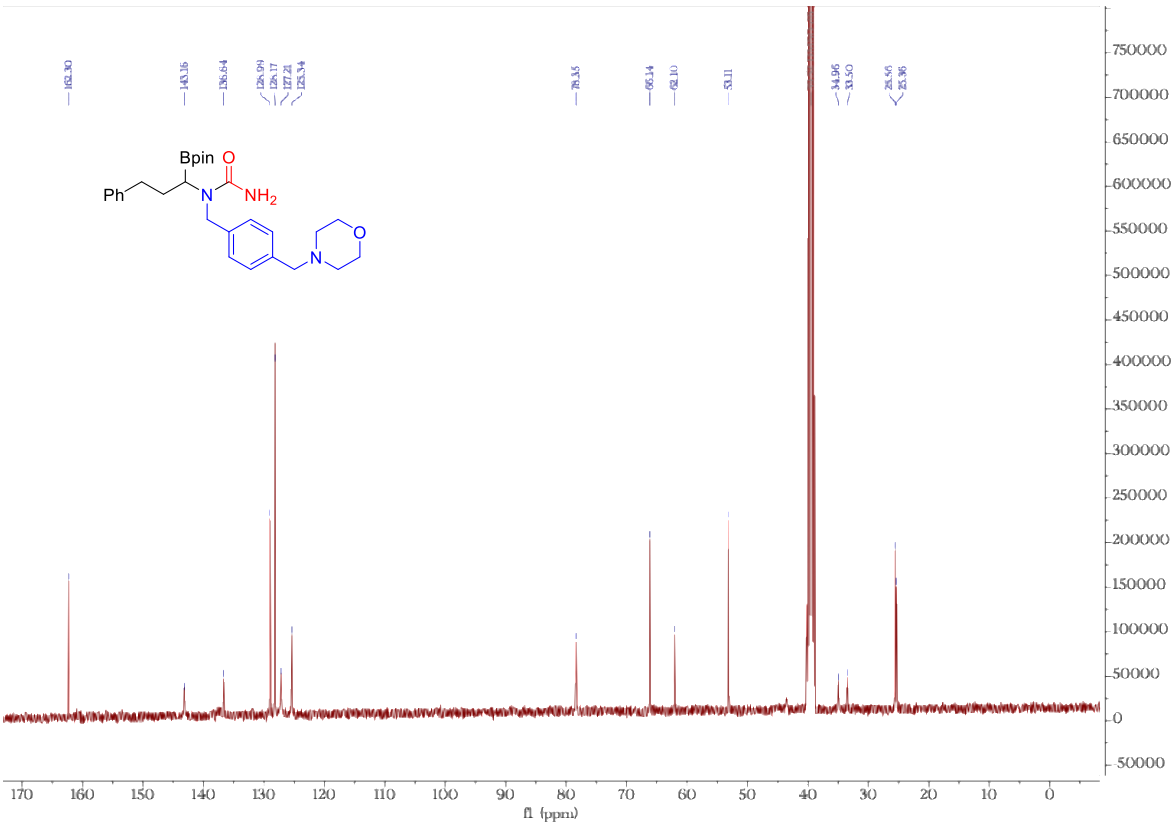
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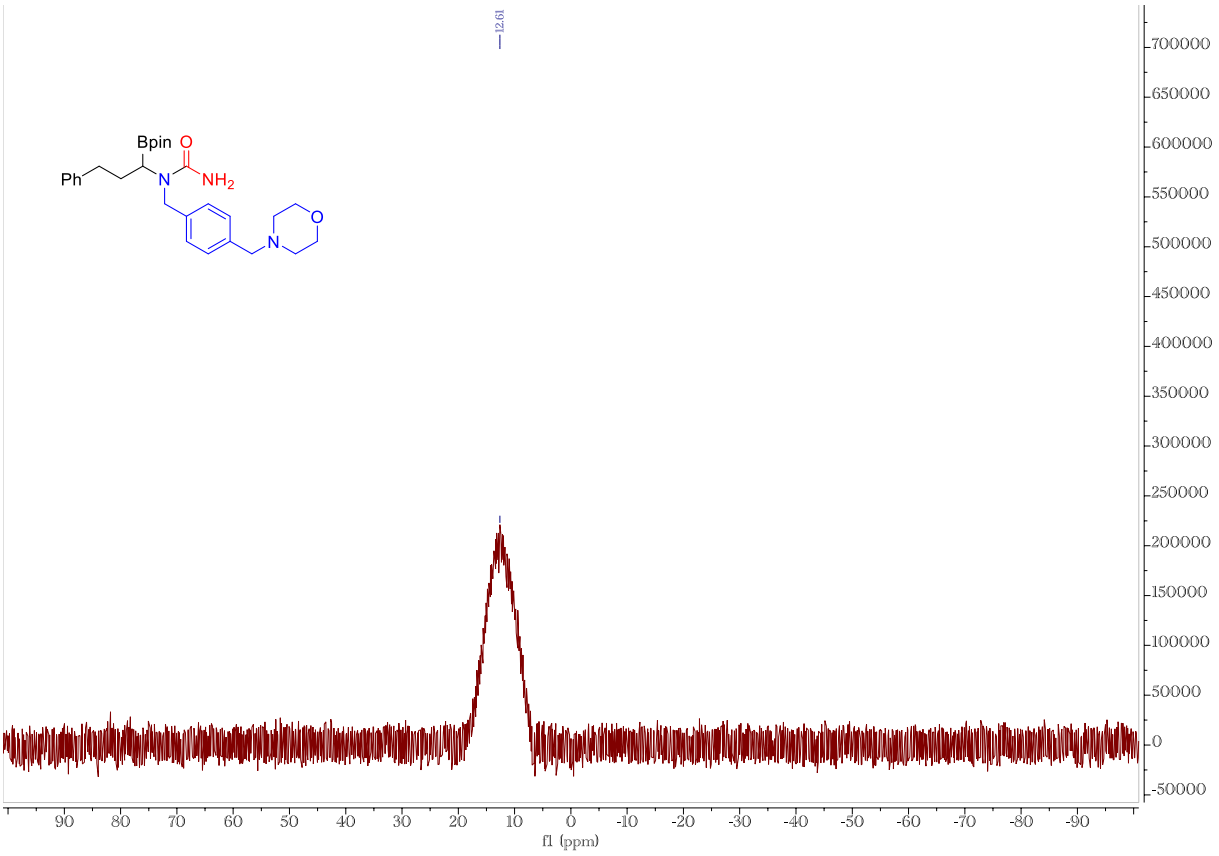
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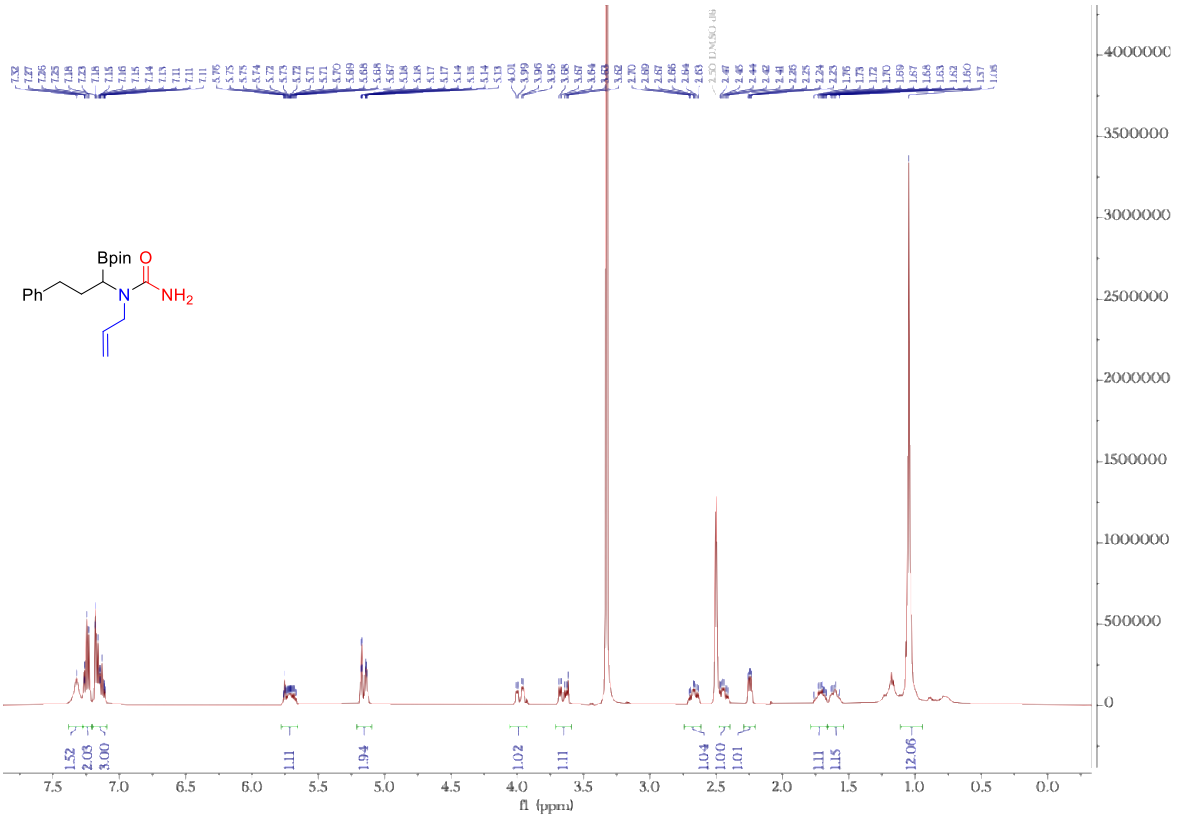
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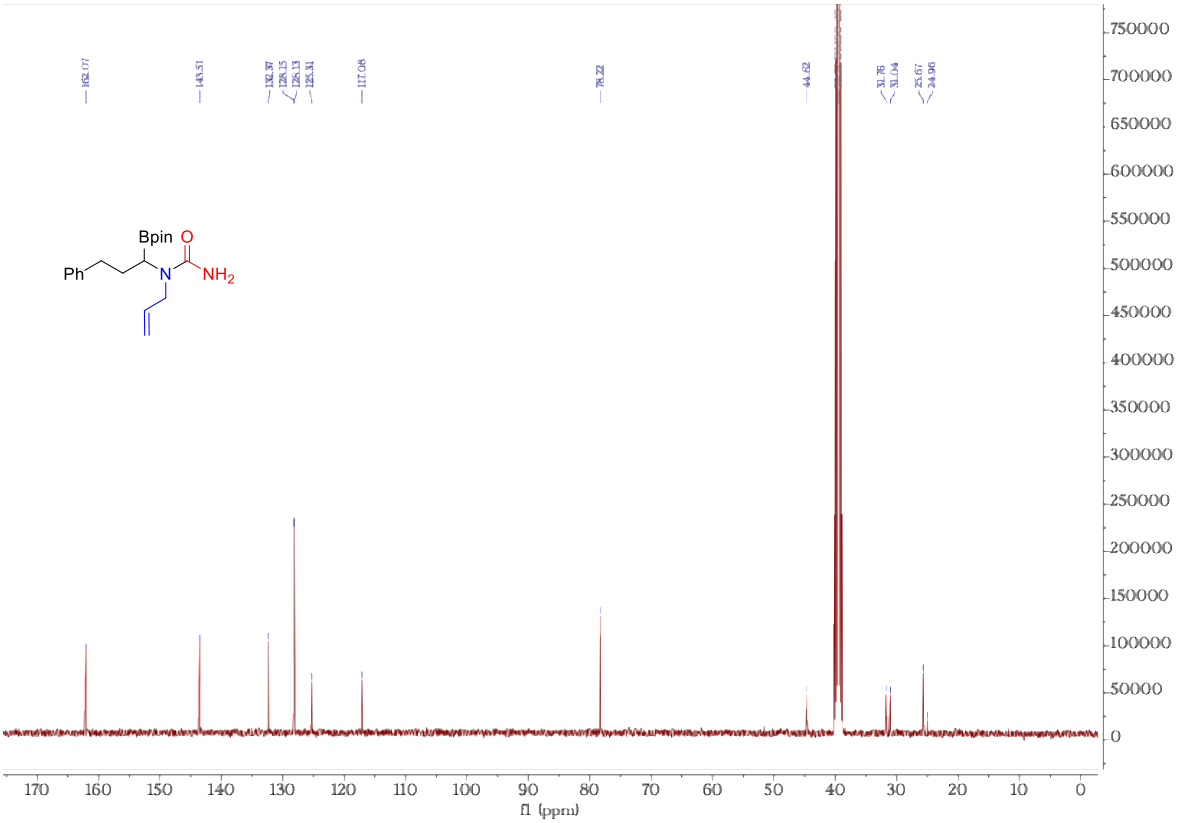
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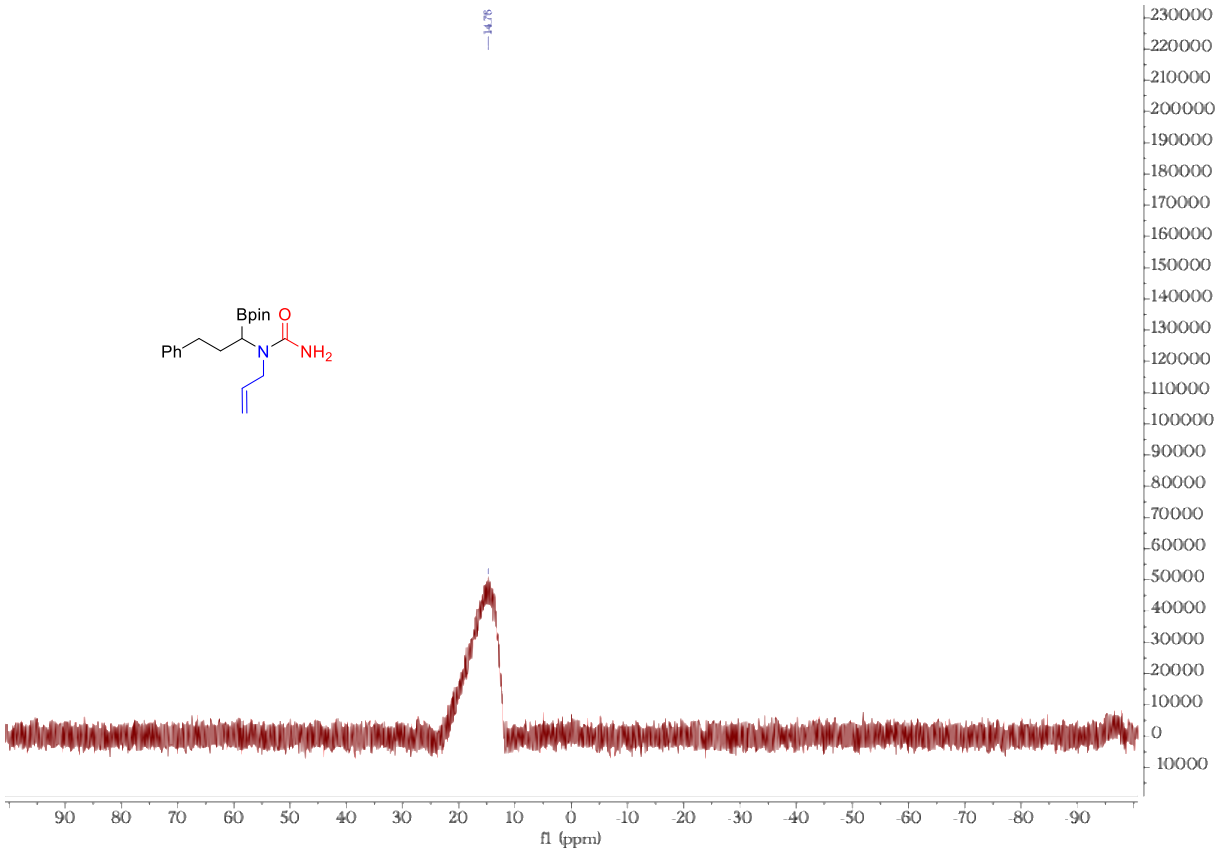
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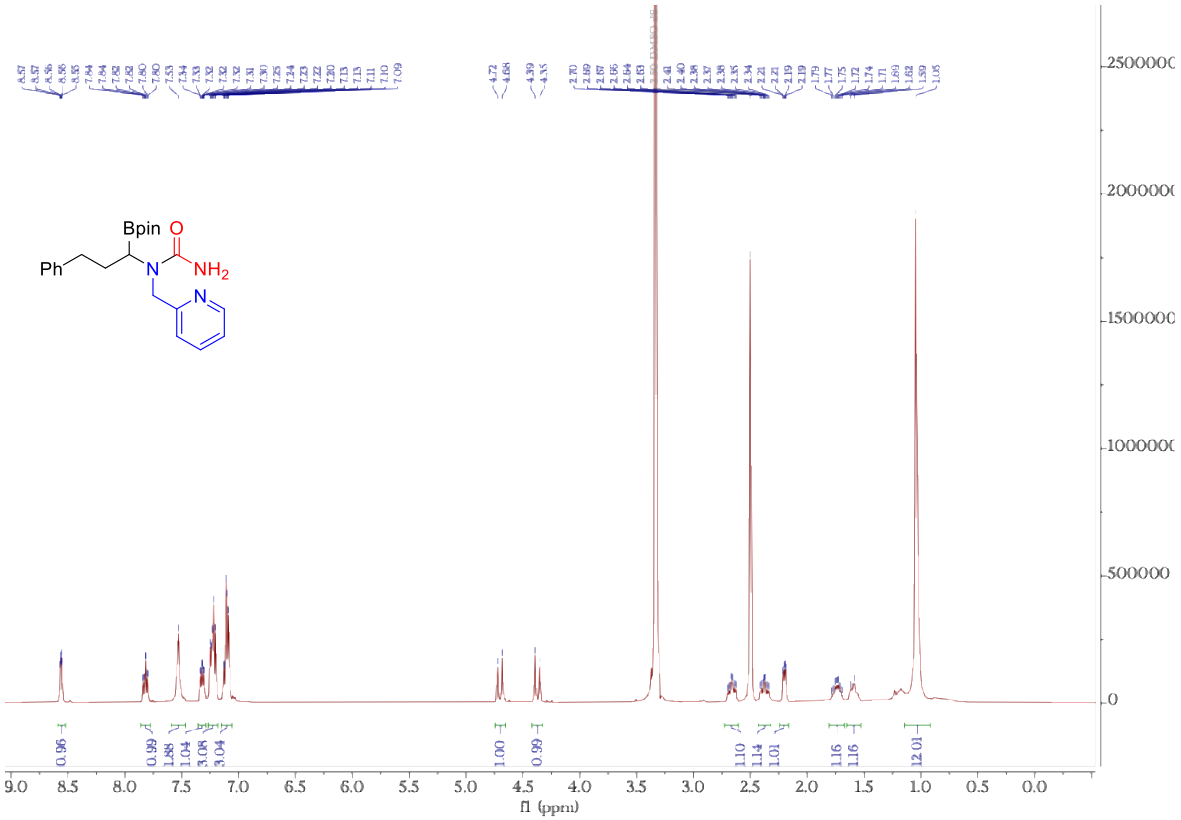
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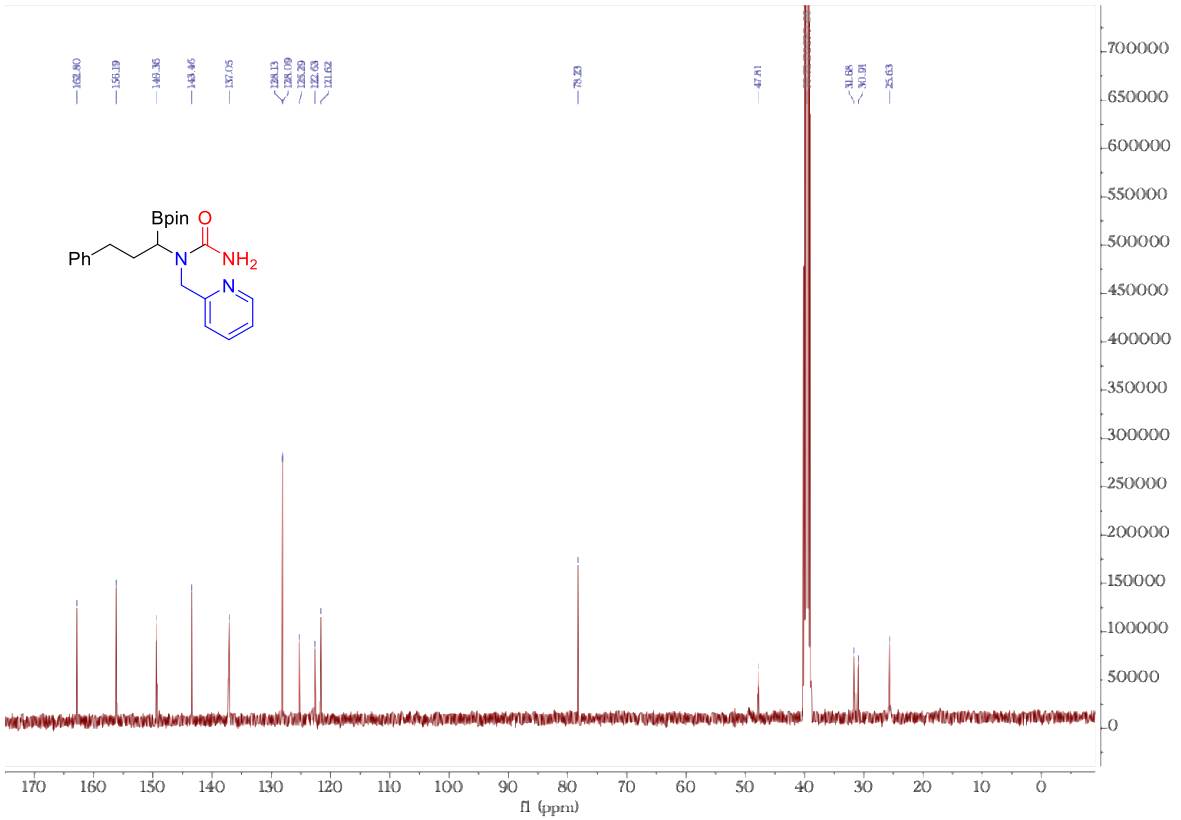
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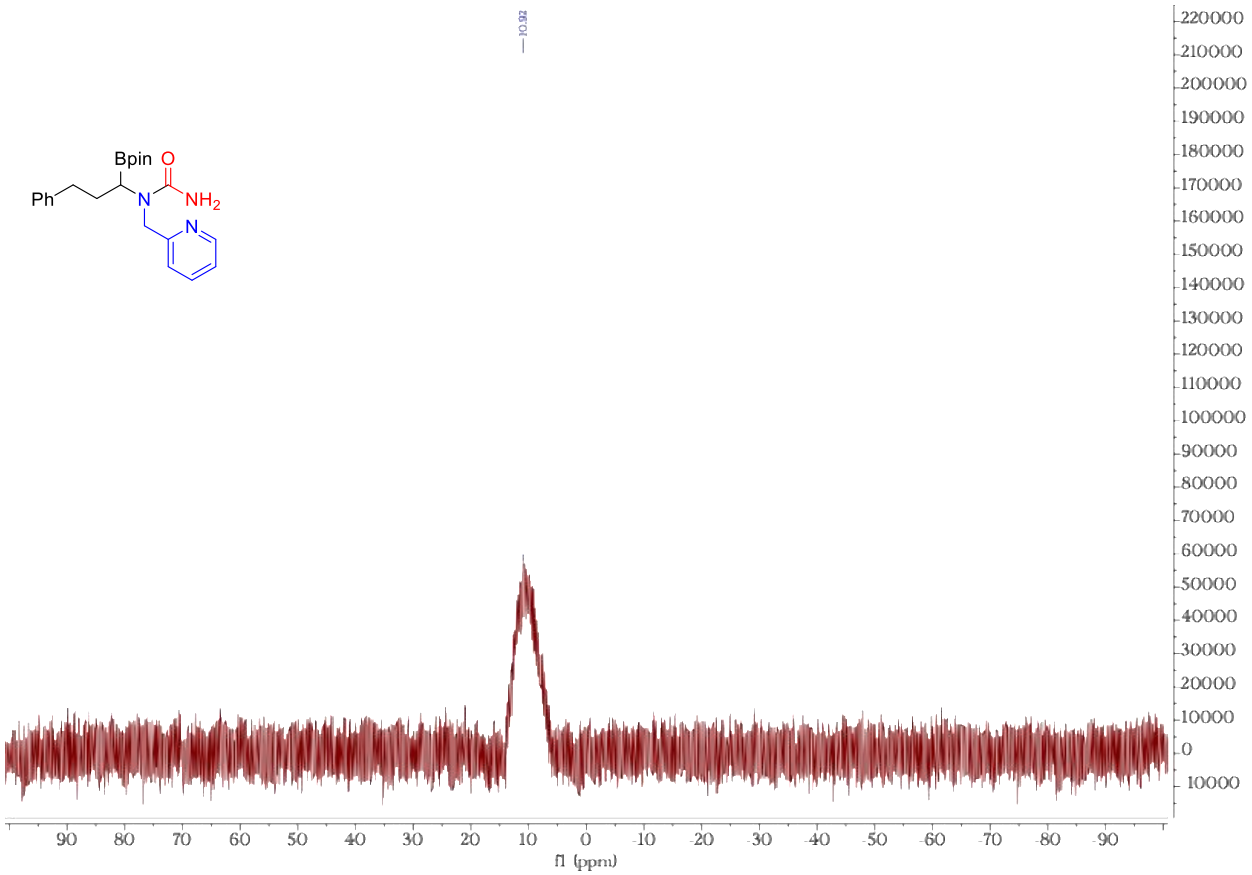
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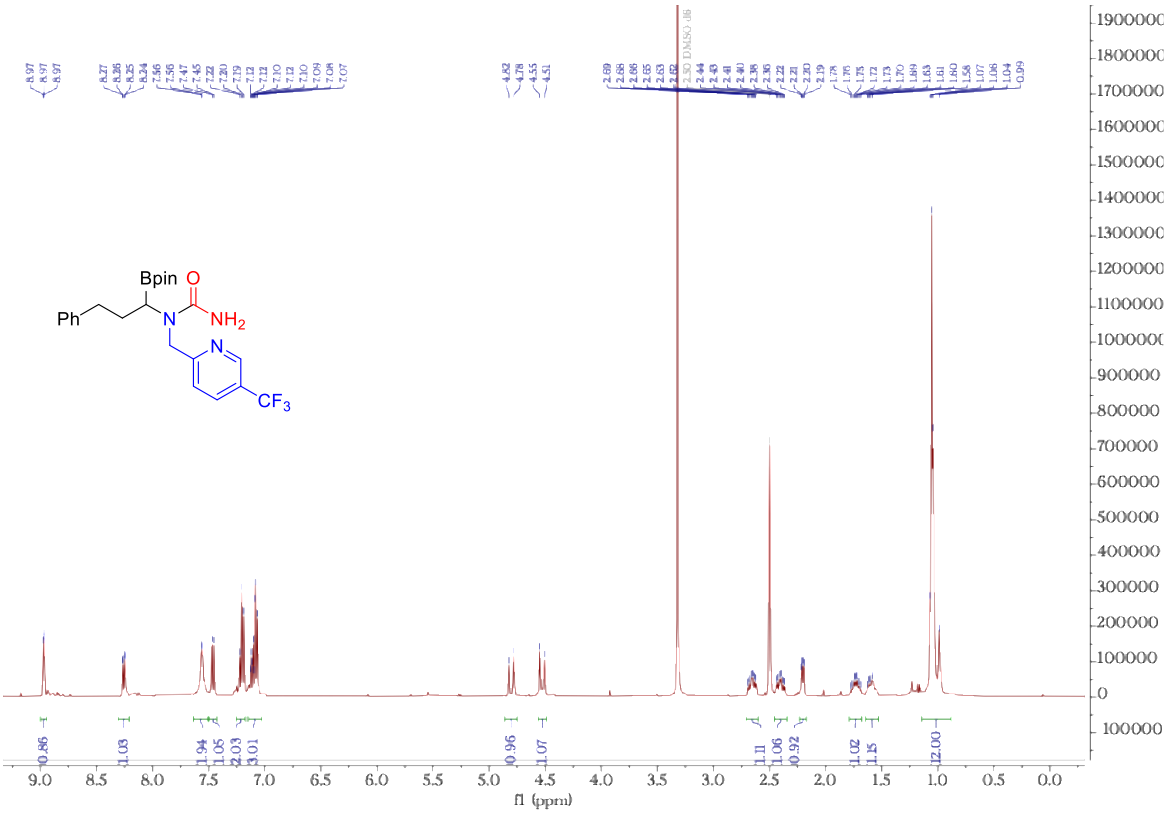
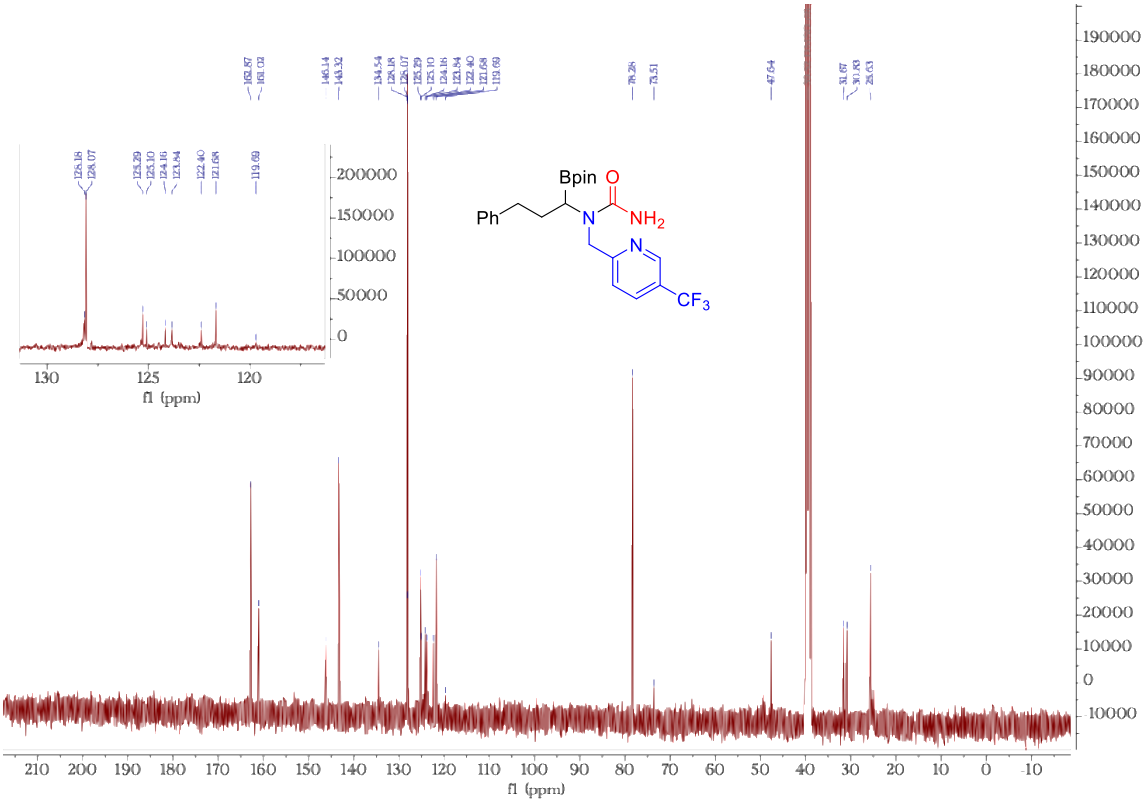
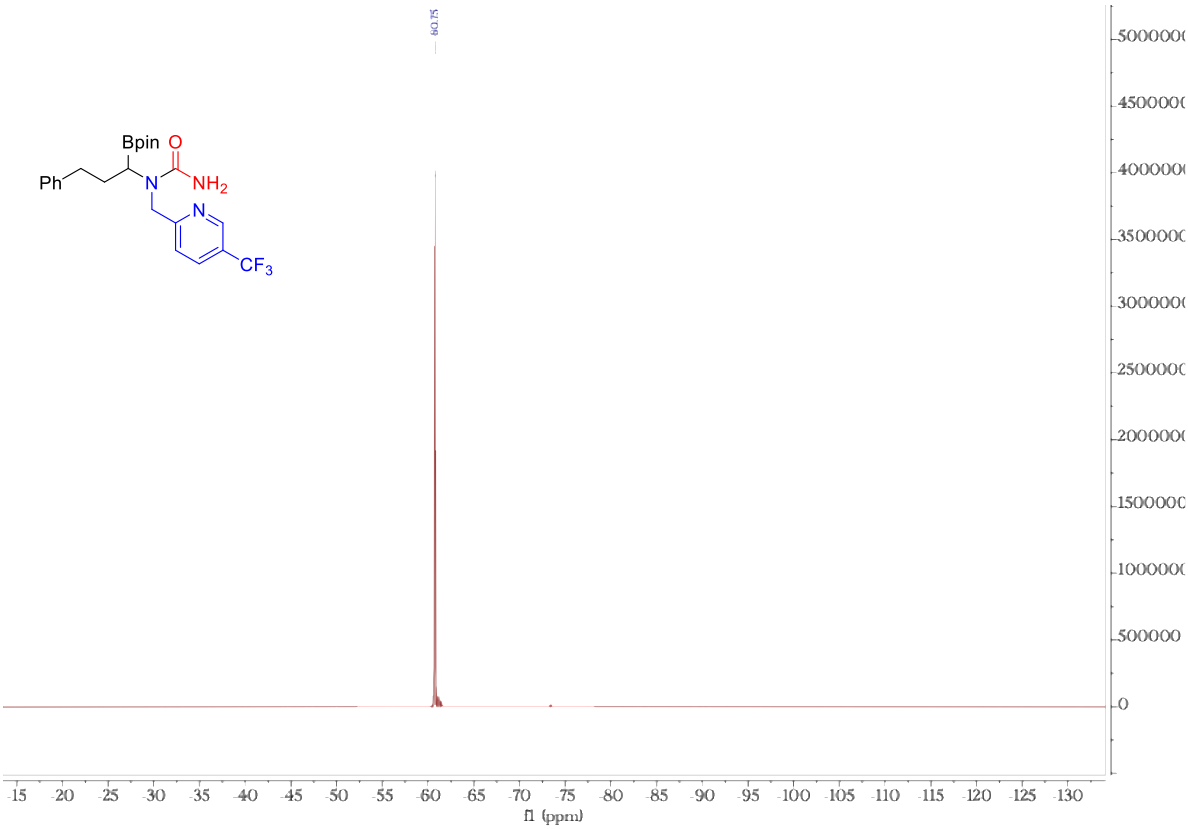
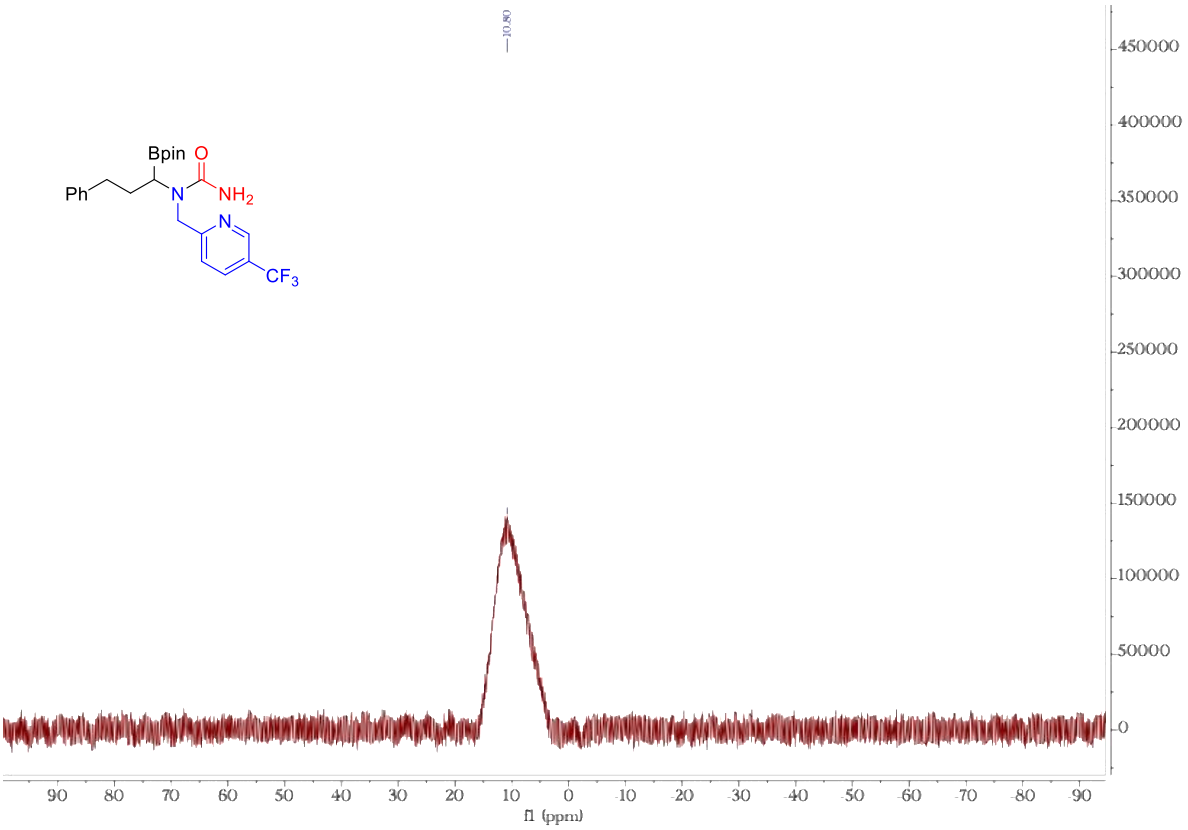
O
Ph
N
NH2
N
10.92
220000
210000
200000
190000
180000
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
10000
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)


Bpin
O
Ph
N
NH2
N
CF3
f1 (ppm)


Bpin
O
Ph
N
NH2
N
CF3
f1 (ppm)
f1 (ppm)


Bpin
O
Ph
N
NH2
N
CF3
60.75
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130
f1 (ppm)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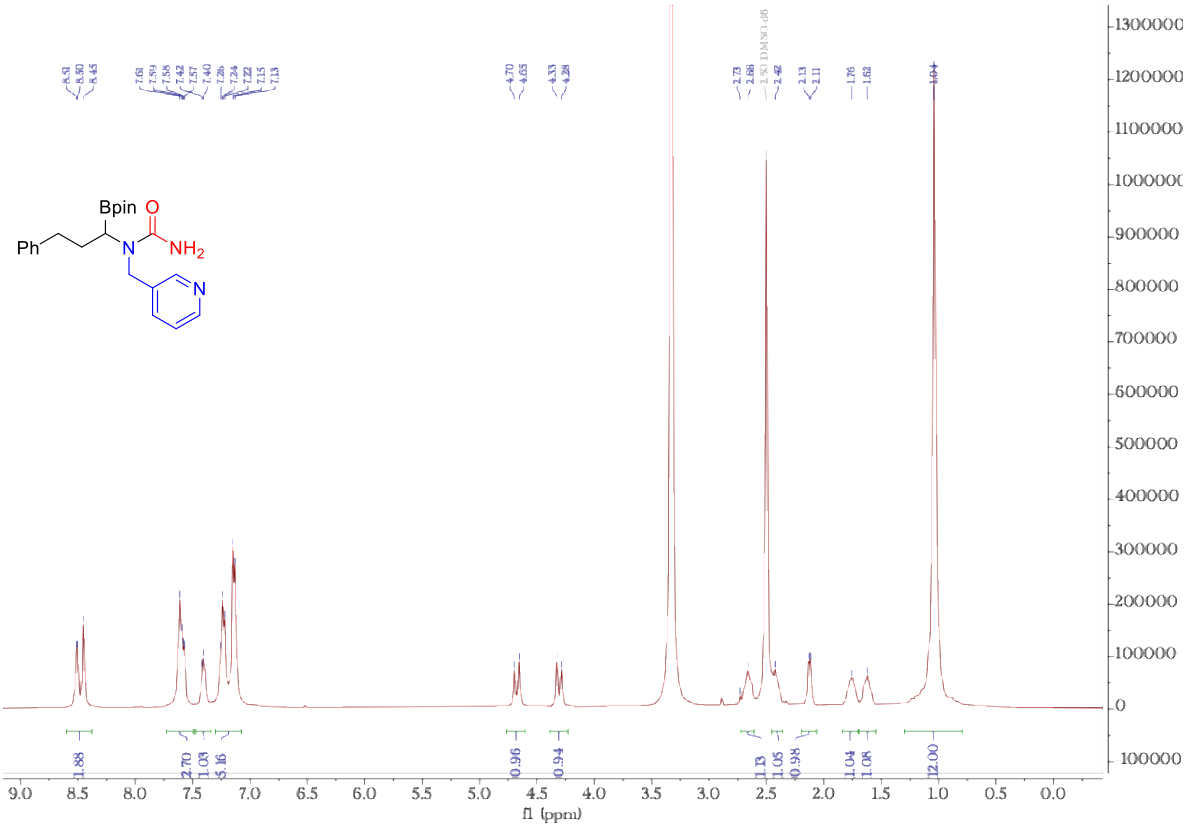
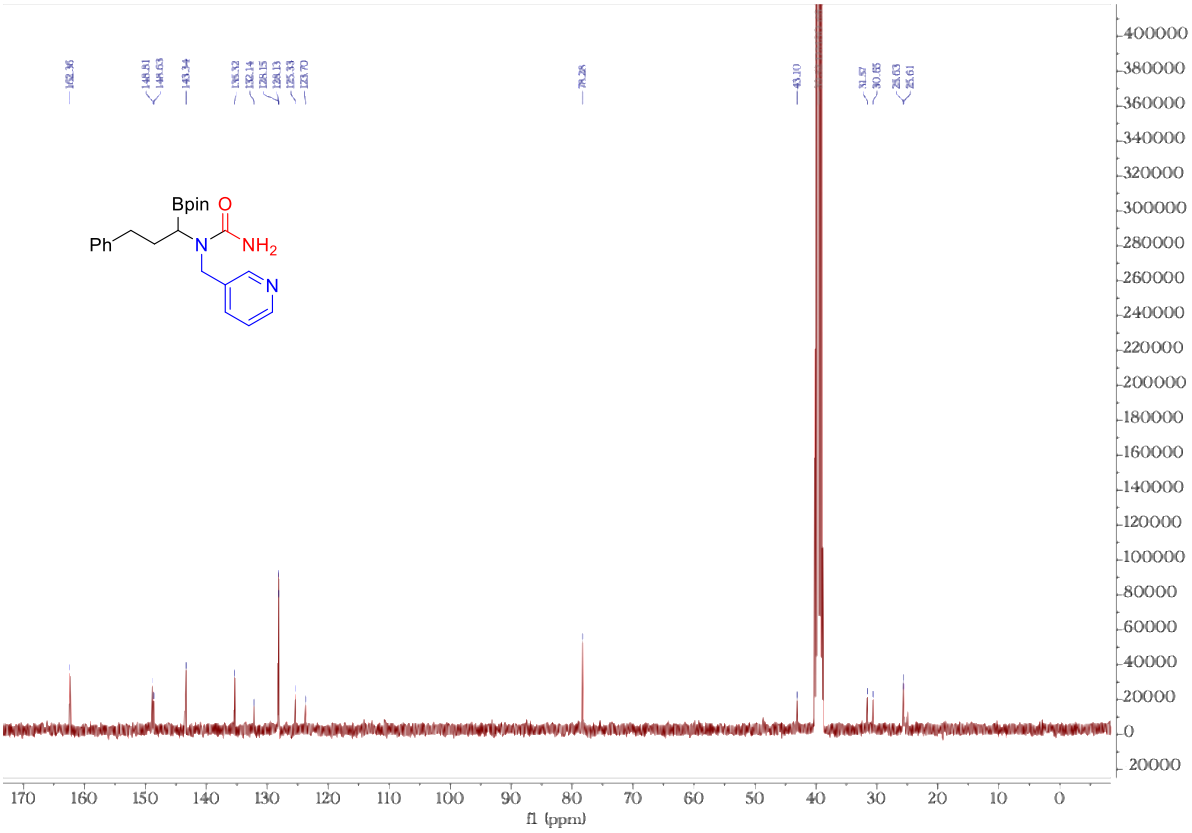
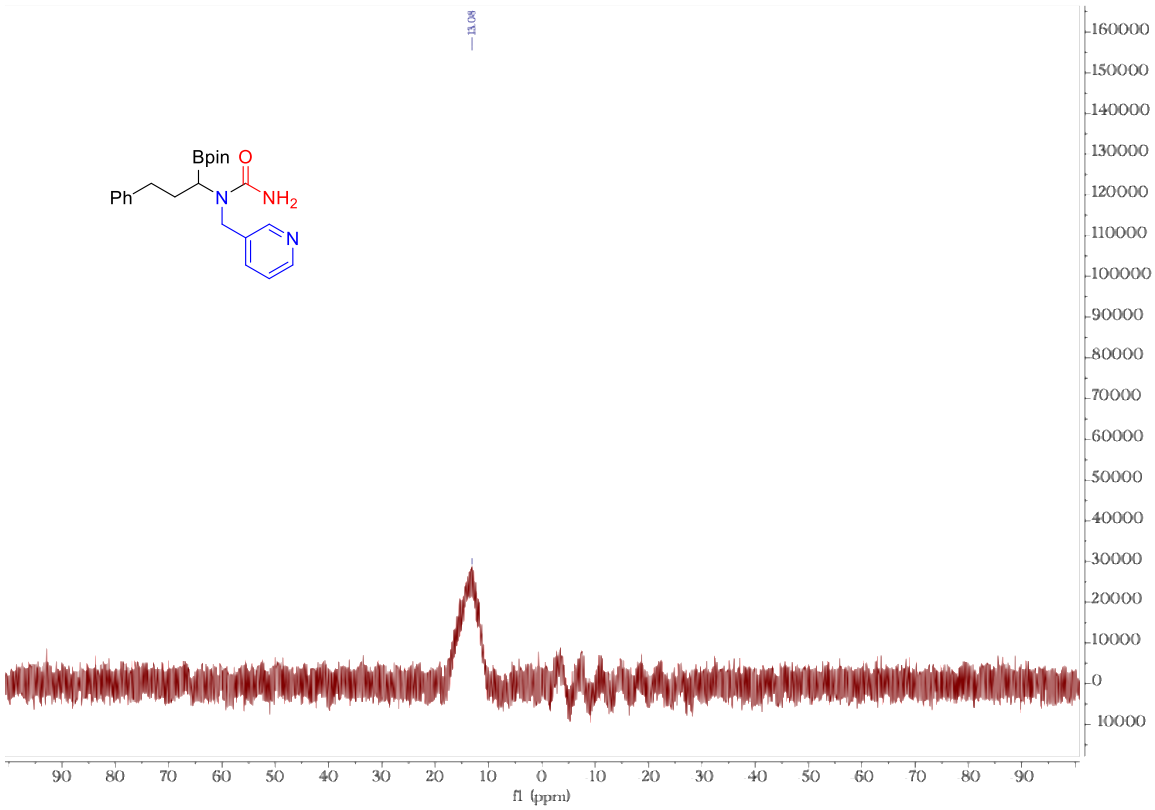
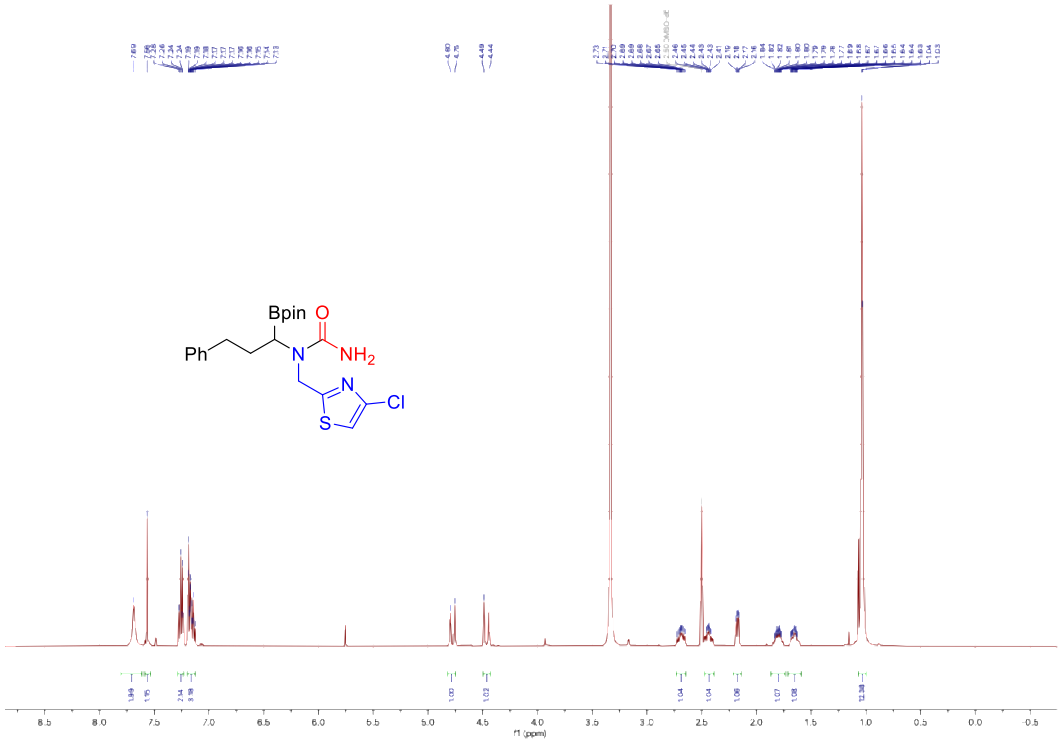
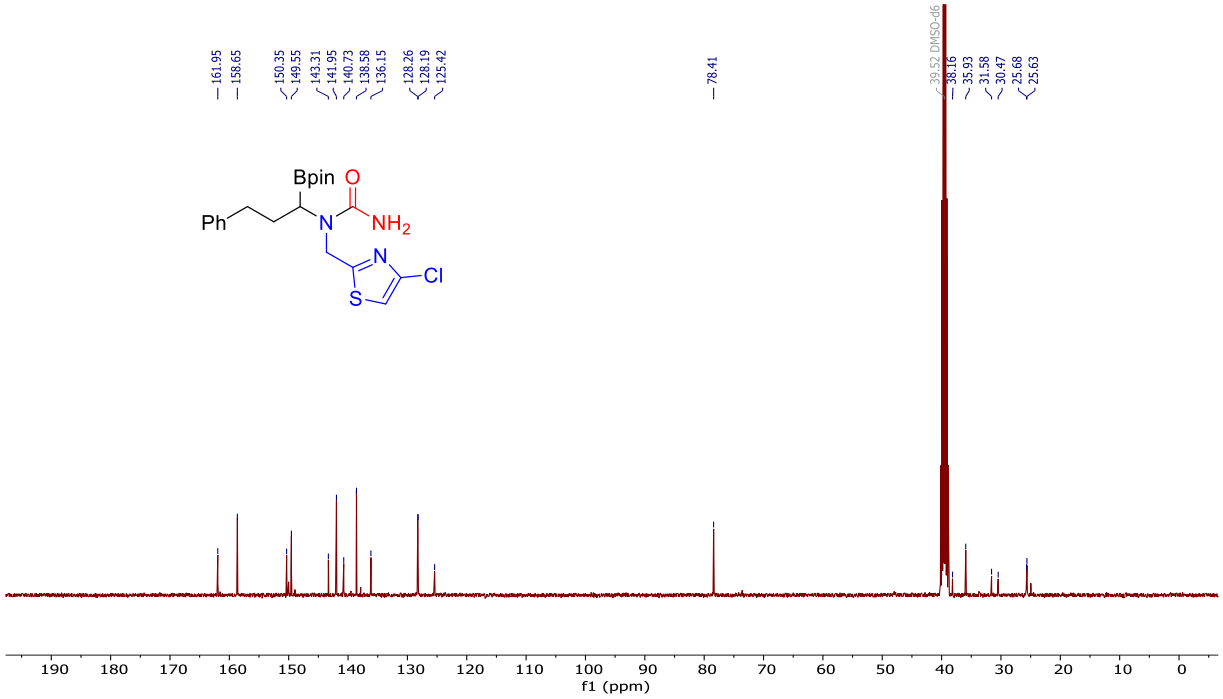
O
Ph
N
NH2
N
CF3
10.80
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

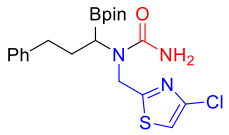

Bpin
O
Ph
N
NH2
N
f1 (ppm)


Bpin
O
Ph
N
NH2
N
f1 (ppm)

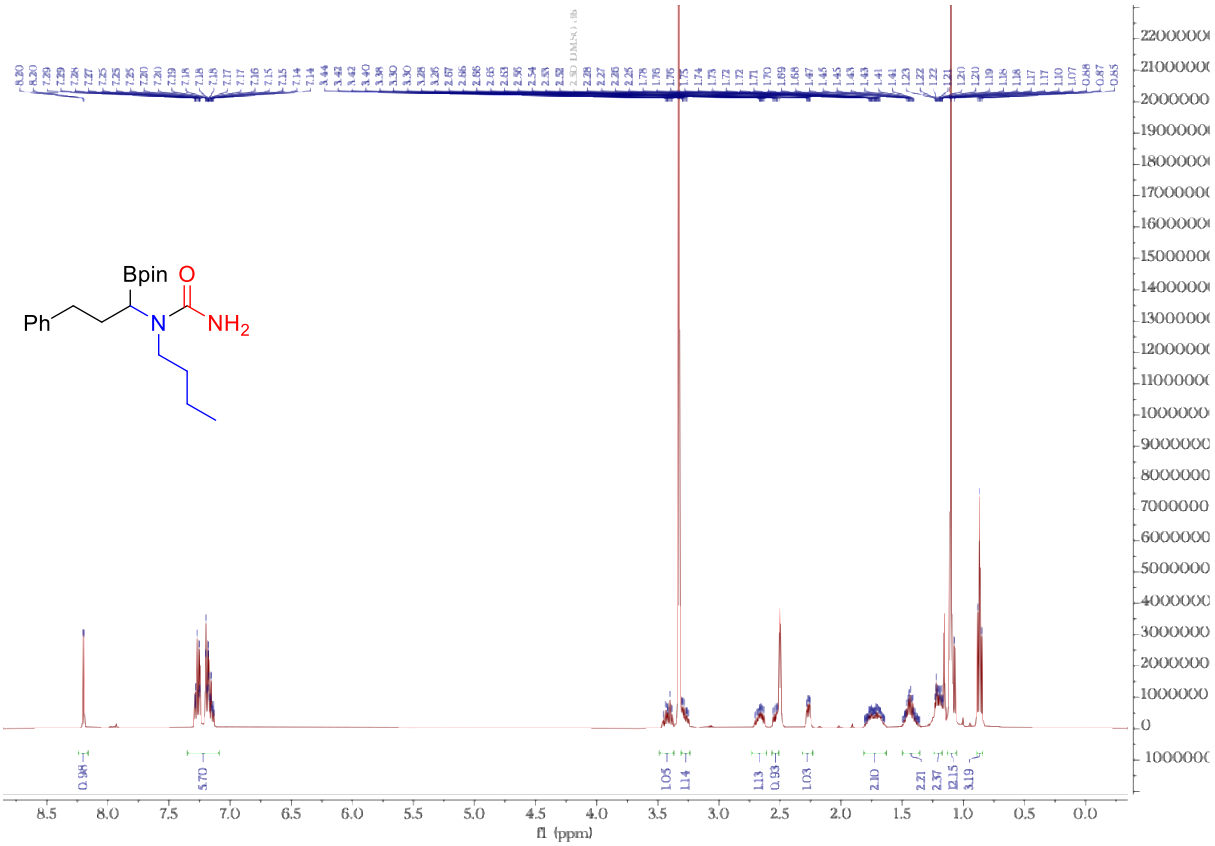

Bpin
O
Ph
N
NH2
N
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
10000
90 80 70 60 50 40 30 20 10 0 10 20 30 40 50 60 70 80 90
f1 (ppm)

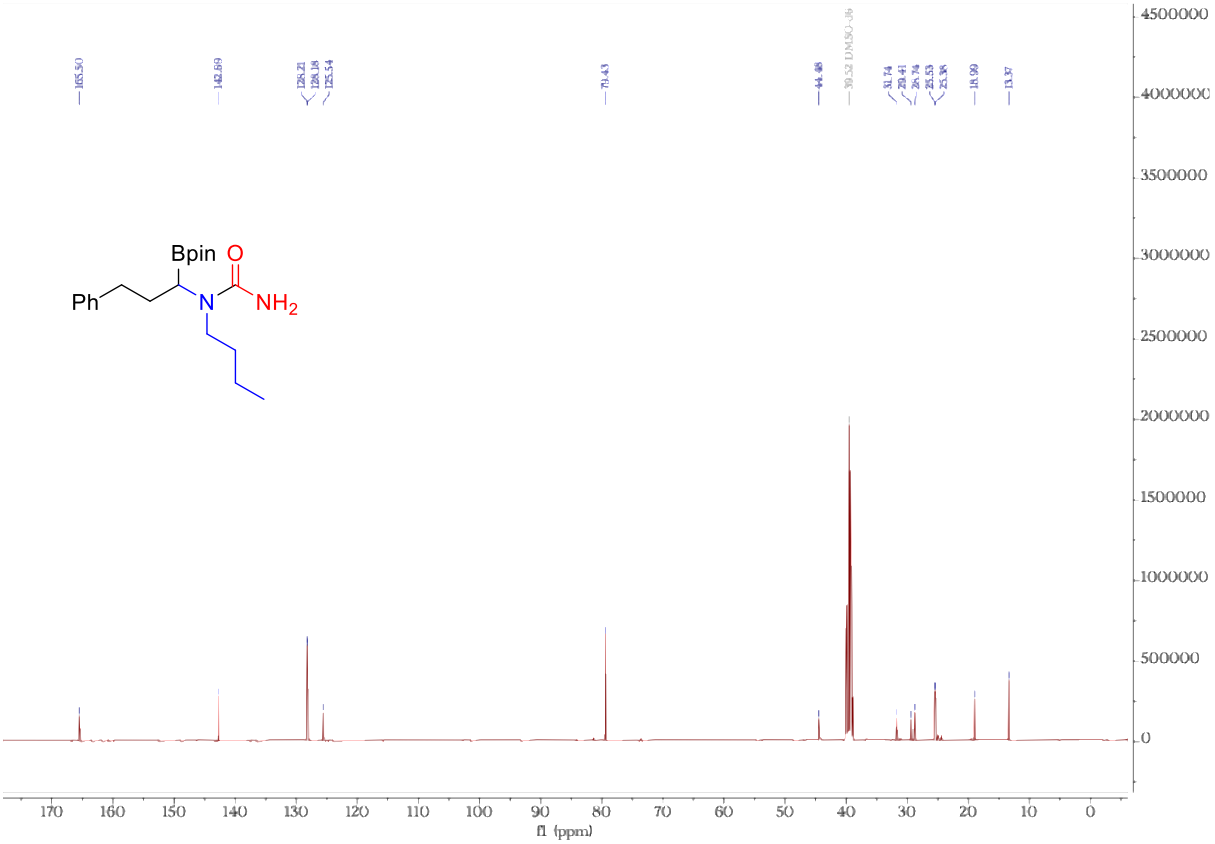

Bpin
O
Ph
N
NH2
N
S
Cl

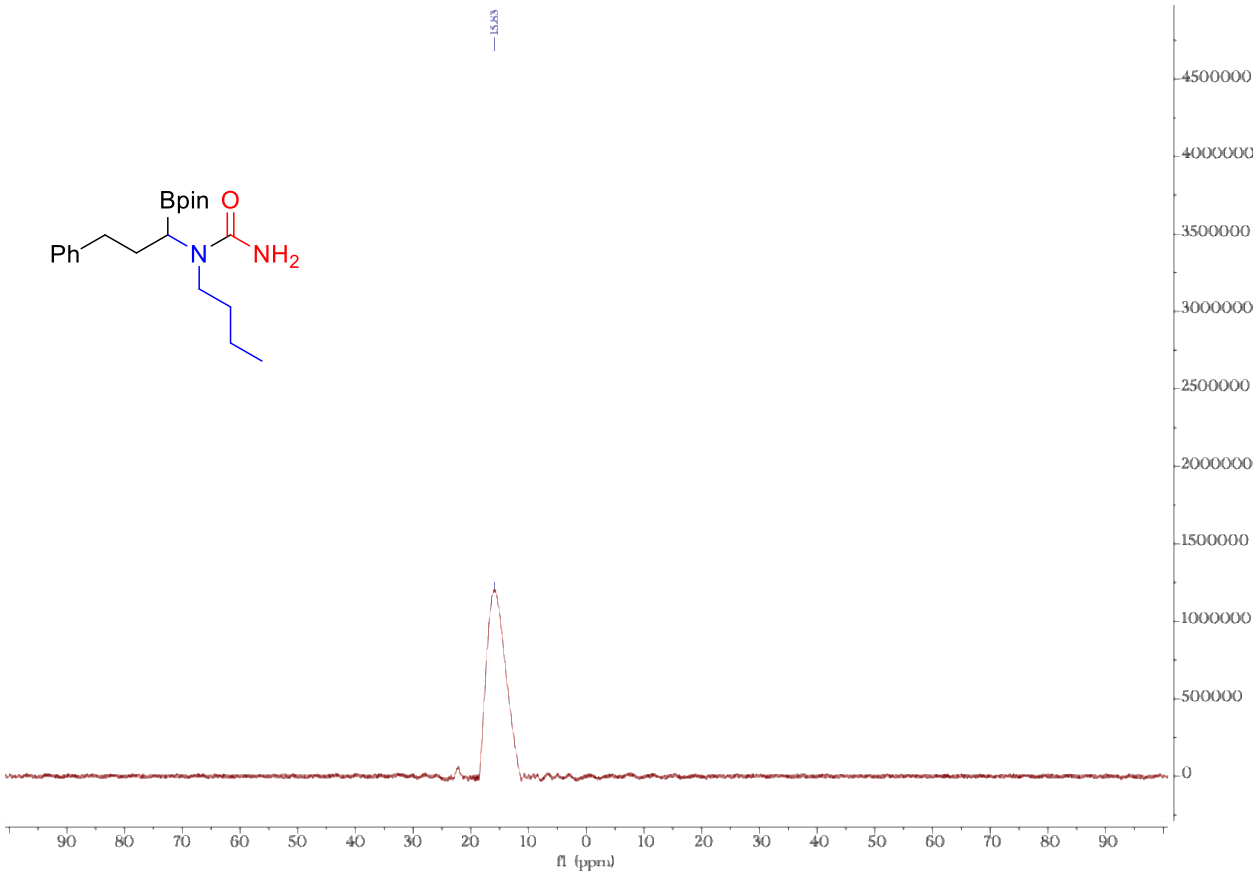

161.95
158.65
150.35
149.55
143.31
141.95
140.73
138.58
136.15
128.26
128.19
125.42
78.41
39.52 DMSO-d6
38.16
35.93
31.58
30.47
25.68
25.63
Bpin
O
Ph
N
NH2
N
S
Cl
f1 (ppm)

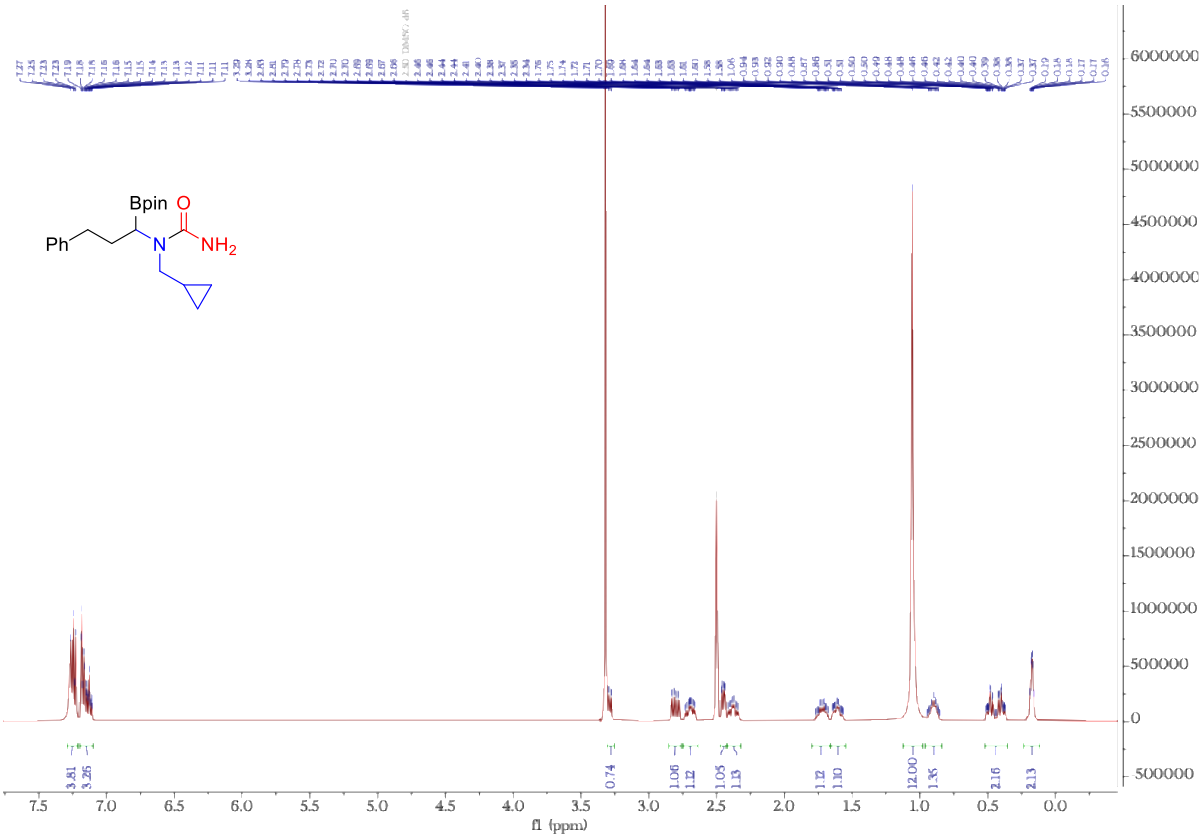

Bpin
O
Ph
N
NH2
N
Cl
S

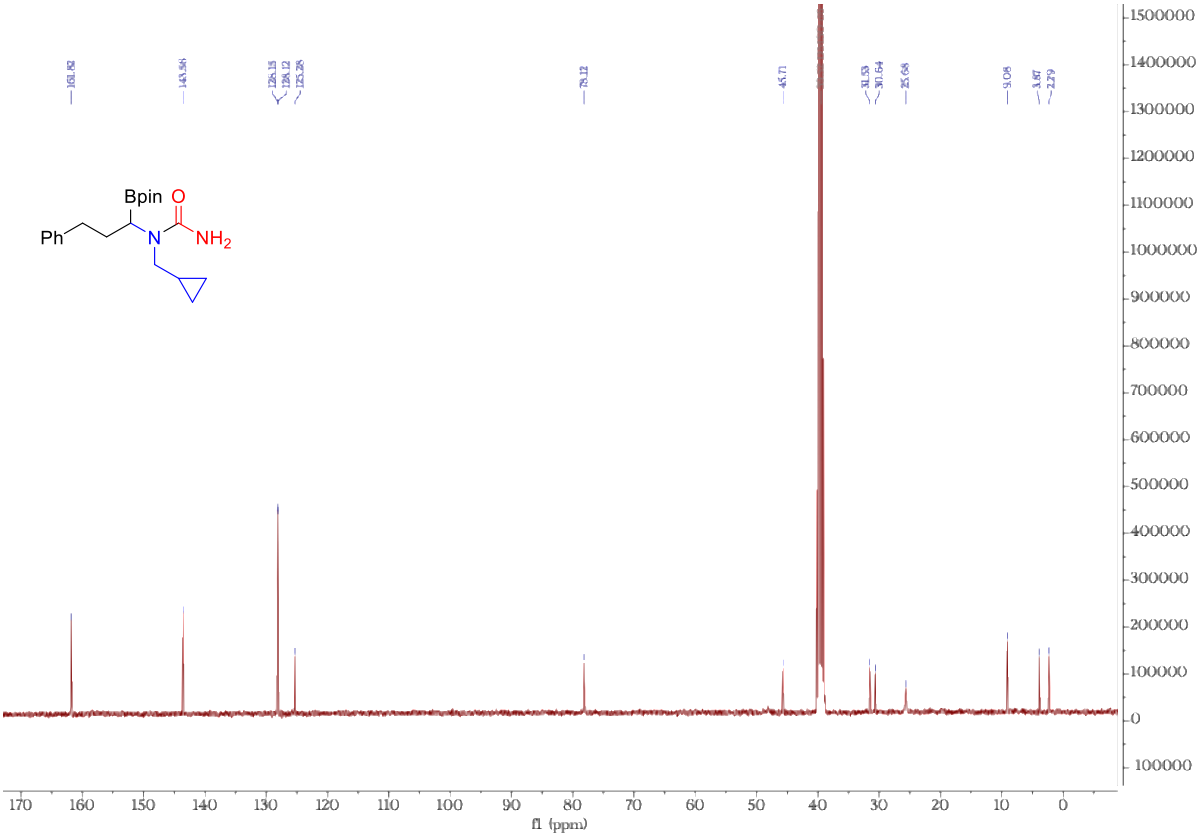
10.05
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70

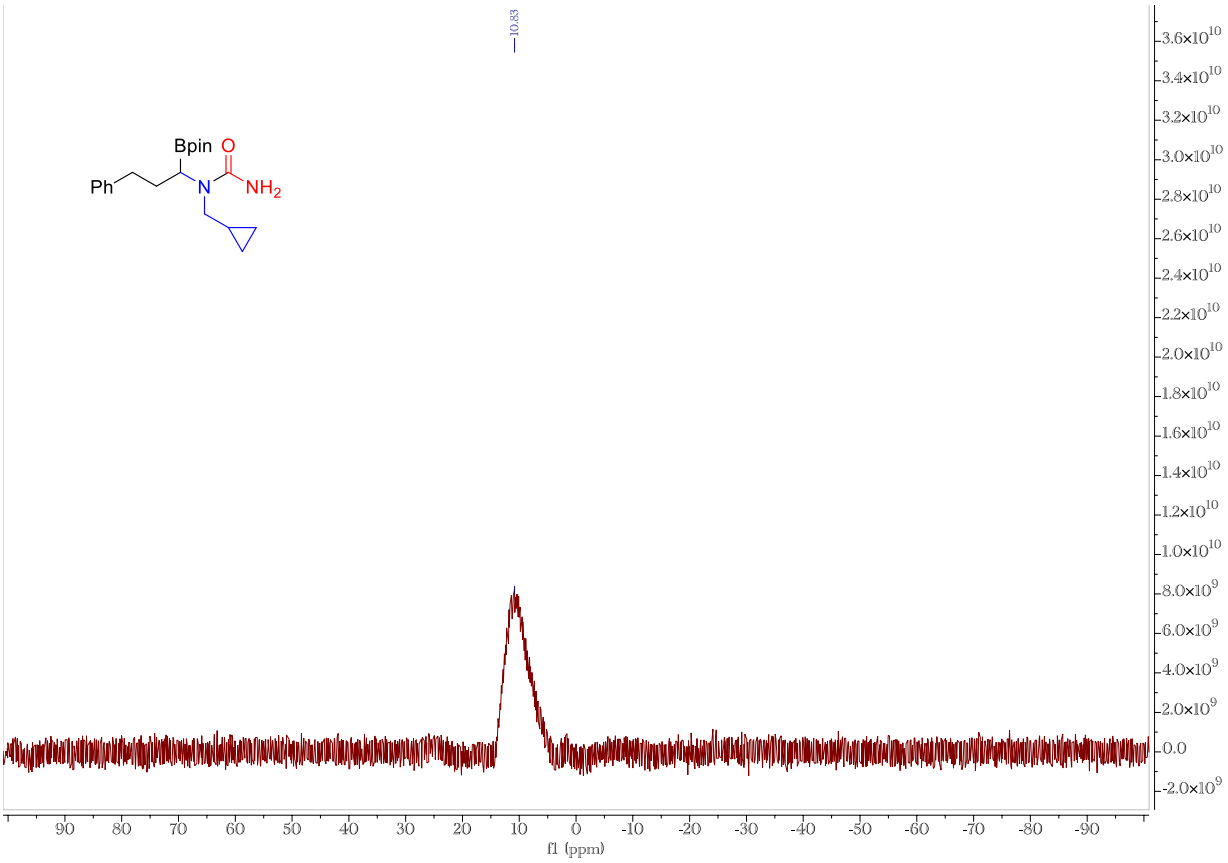

Bpin
O
Ph
N
NH2
f1 (ppm)

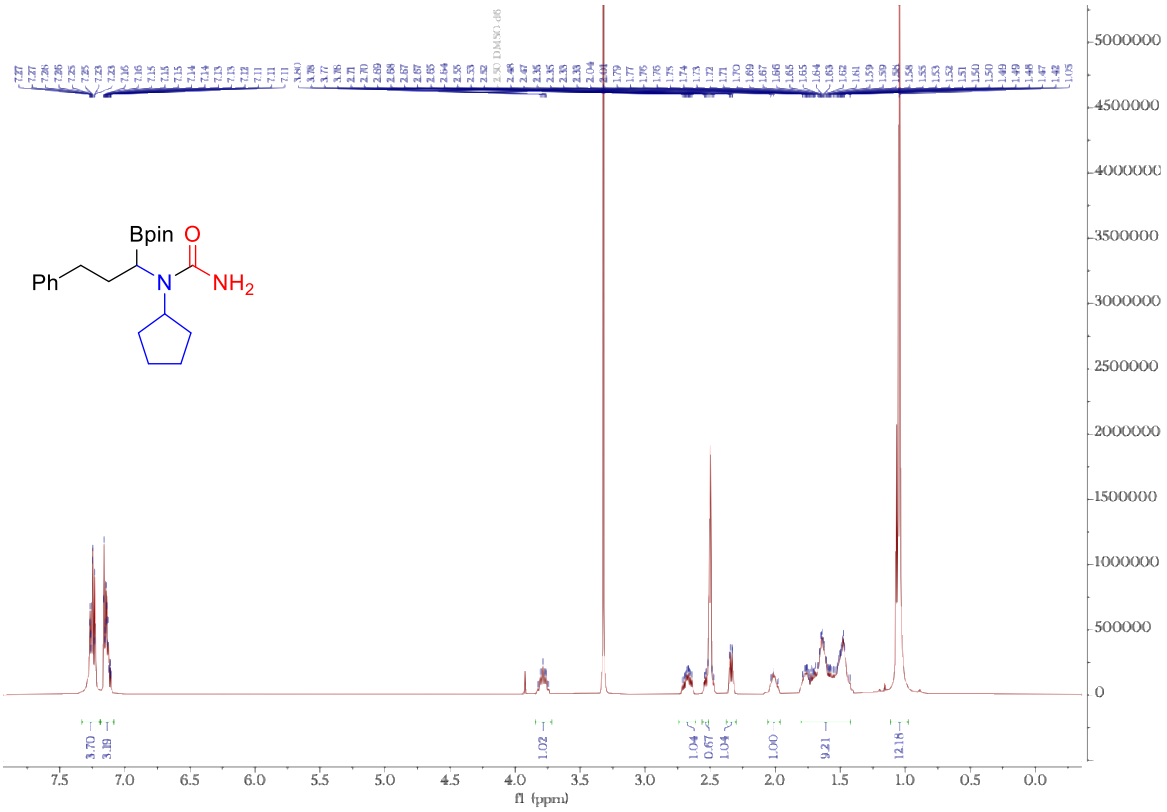

Bpin
O
Ph
N
NH2
f1 (ppm)

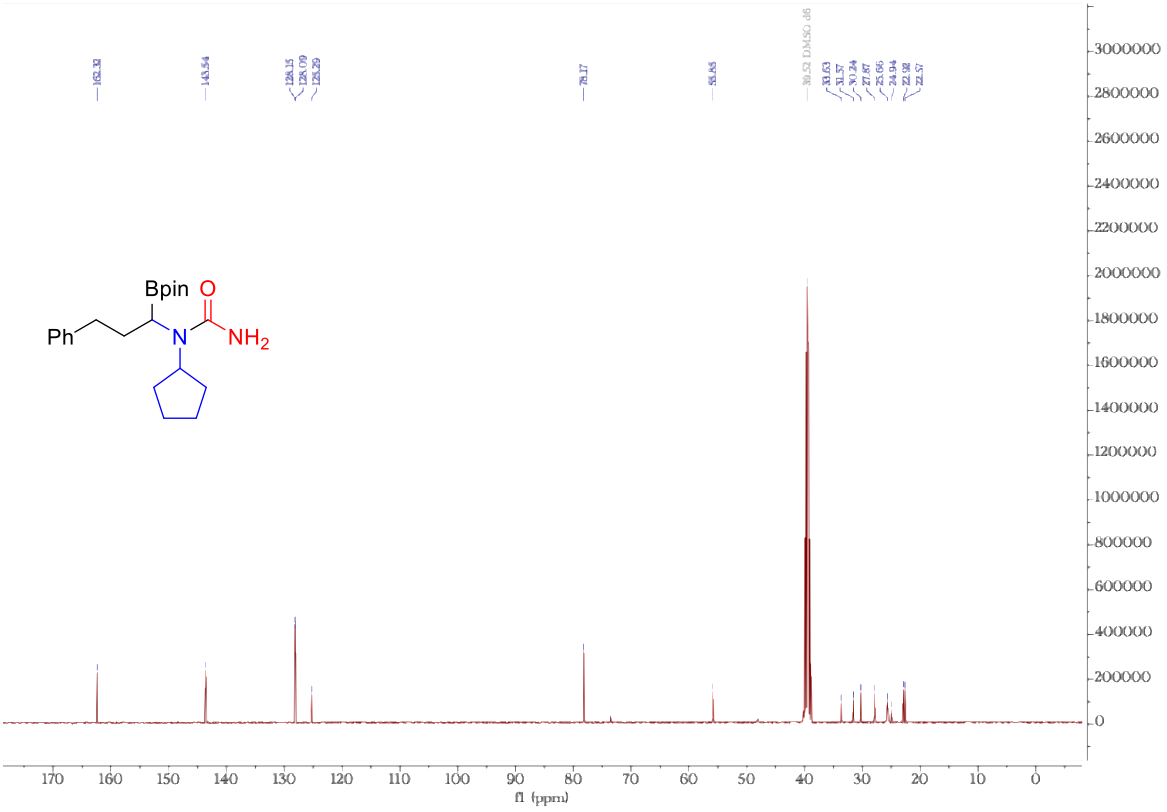

15.83
Bpin
O
Ph
N
NH2
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
90
80
70
60
50
40
30
20
10
0
10
20
30
40
50
60
70
80
90
f1 (ppm)

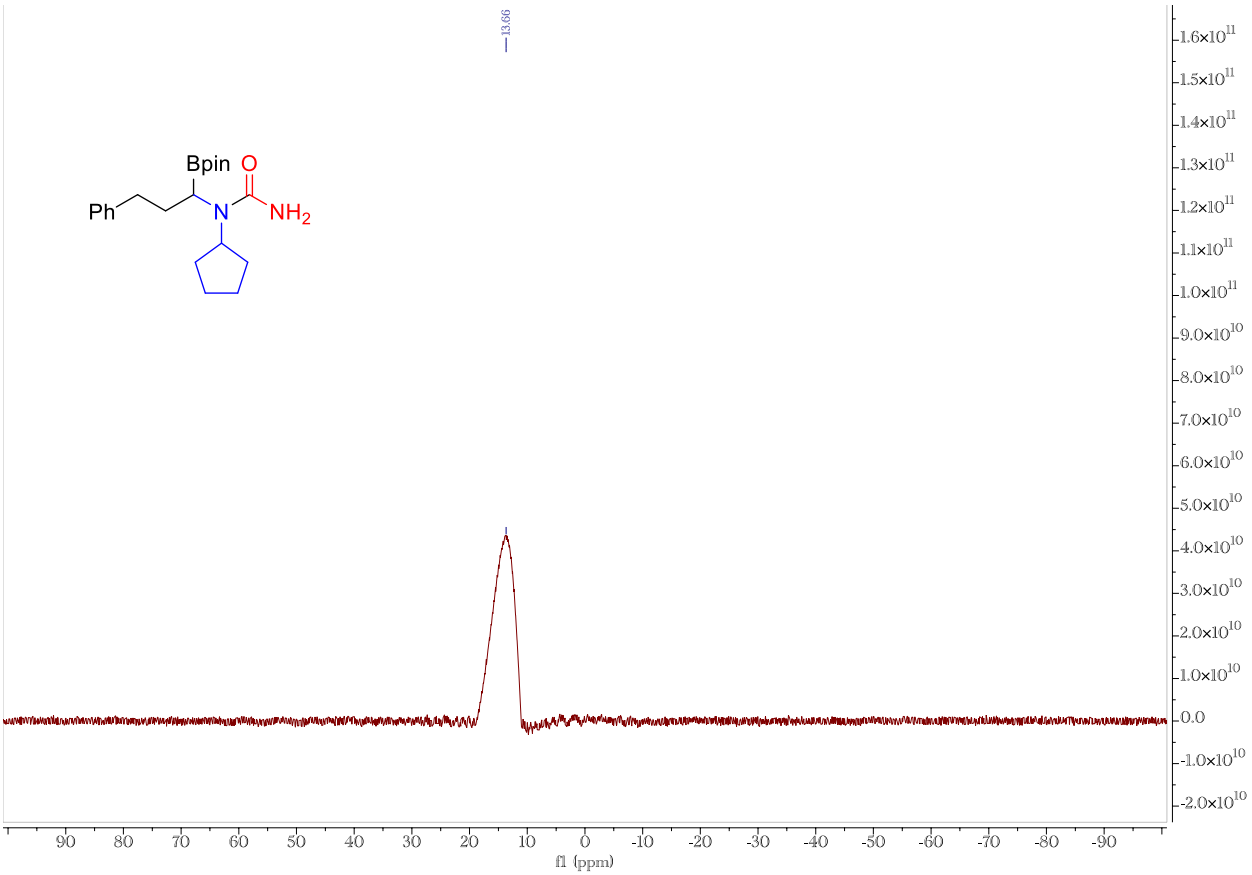

Bpin
O
Ph
N
NH2
f1 (ppm)

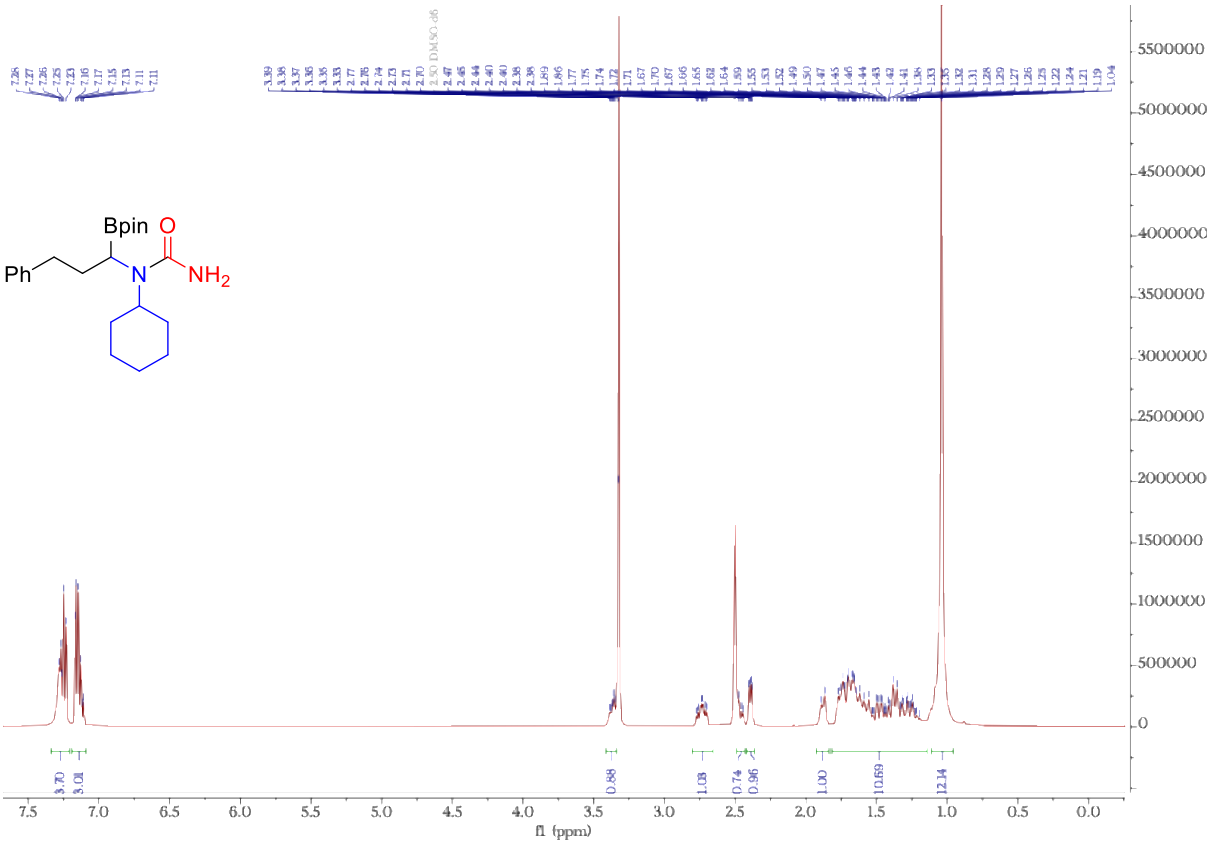

Bpin
O
Ph
N
NH2
f1 (ppm)

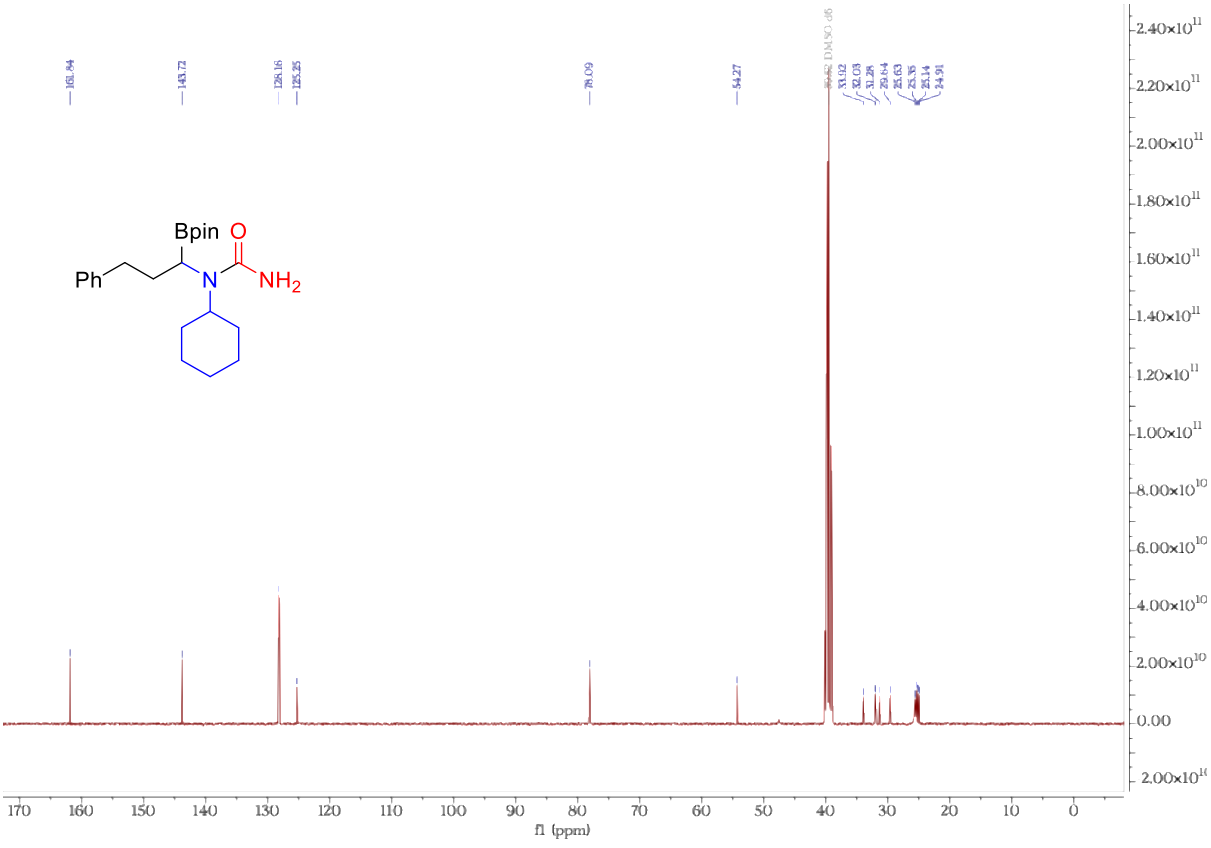

10.83
Bpin
O
Ph
N
NH2
3.6x10^10
3.4x10^10
3.2x10^10
3.0x10^10
2.8x10^10
2.6x10^10
2.4x10^10
2.2x10^10
2.0x10^10
1.8x10^10
1.6x10^10
1.4x10^10
1.2x10^10
1.0x10^10
8.0x10^9
6.0x10^9
4.0x10^9
2.0x10^9
0.0
-2.0x10^9
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

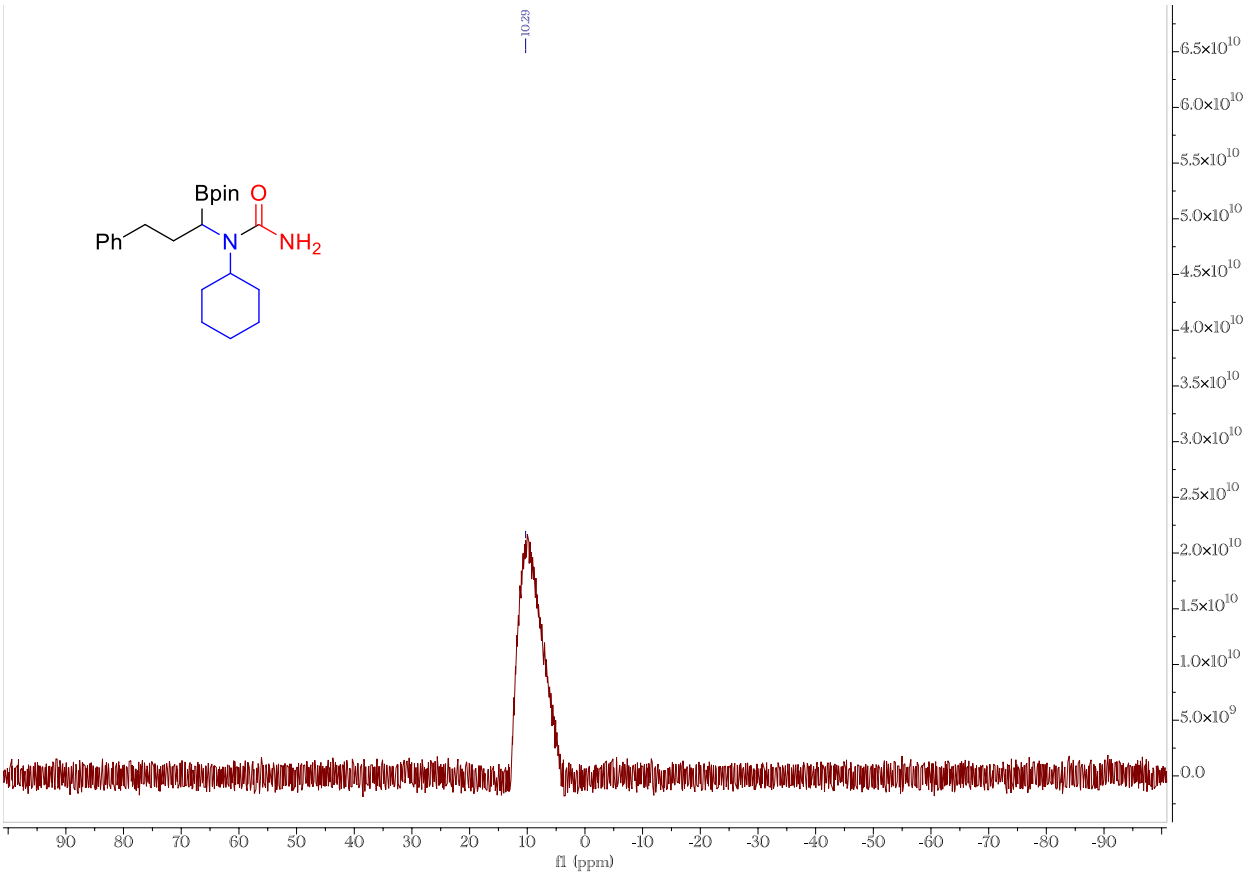

Bpin
O
Ph
N
NH2
f1 (ppm)

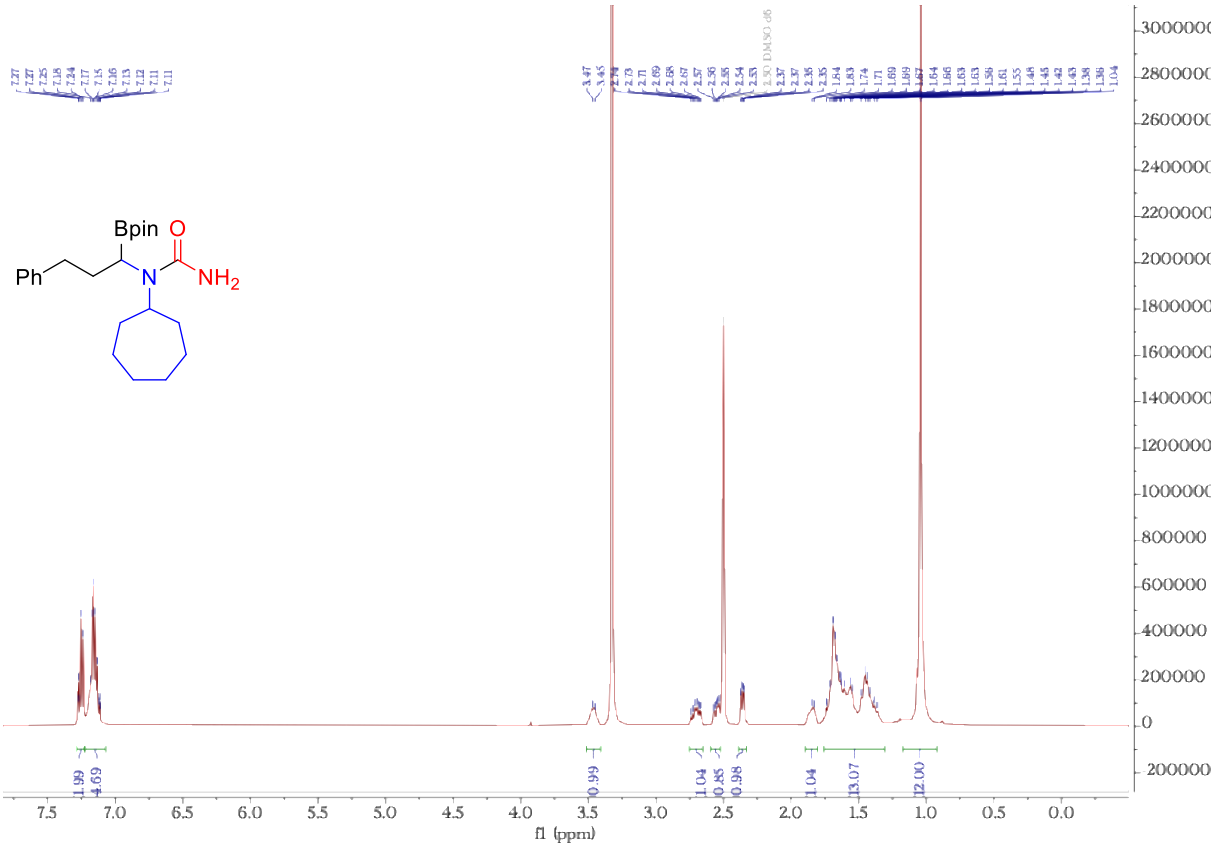

Bpin
O
Ph
N
NH2
f1 (ppm)

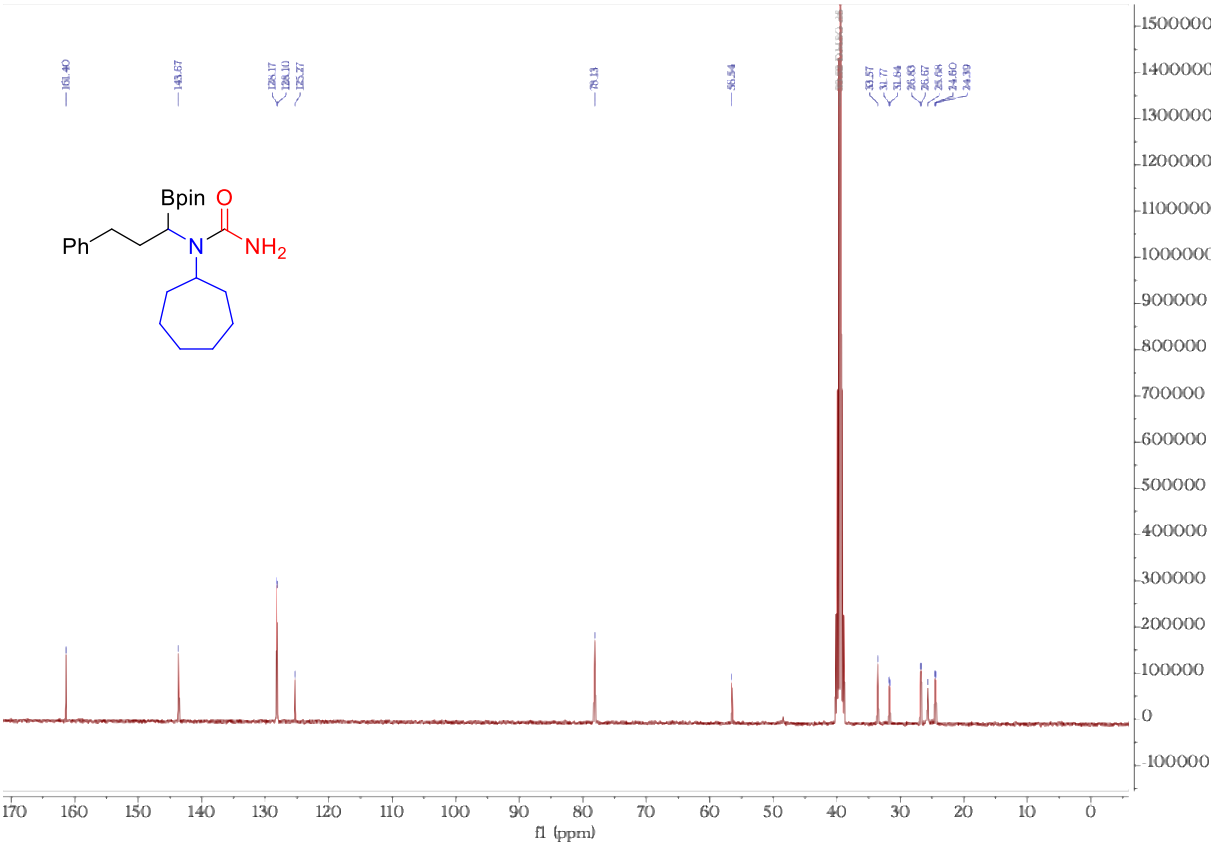

13.66
Bpin
O
Ph
N
NH2
1.6×10^11
1.5×10^11
1.4×10^11
1.3×10^11
1.2×10^11
1.1×10^11
1.0×10^11
9.0×10^10
8.0×10^10
7.0×10^10
6.0×10^10
5.0×10^10
4.0×10^10
3.0×10^10
2.0×10^10
1.0×10^10
0.0
-1.0×10^10
-2.0×10^10
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

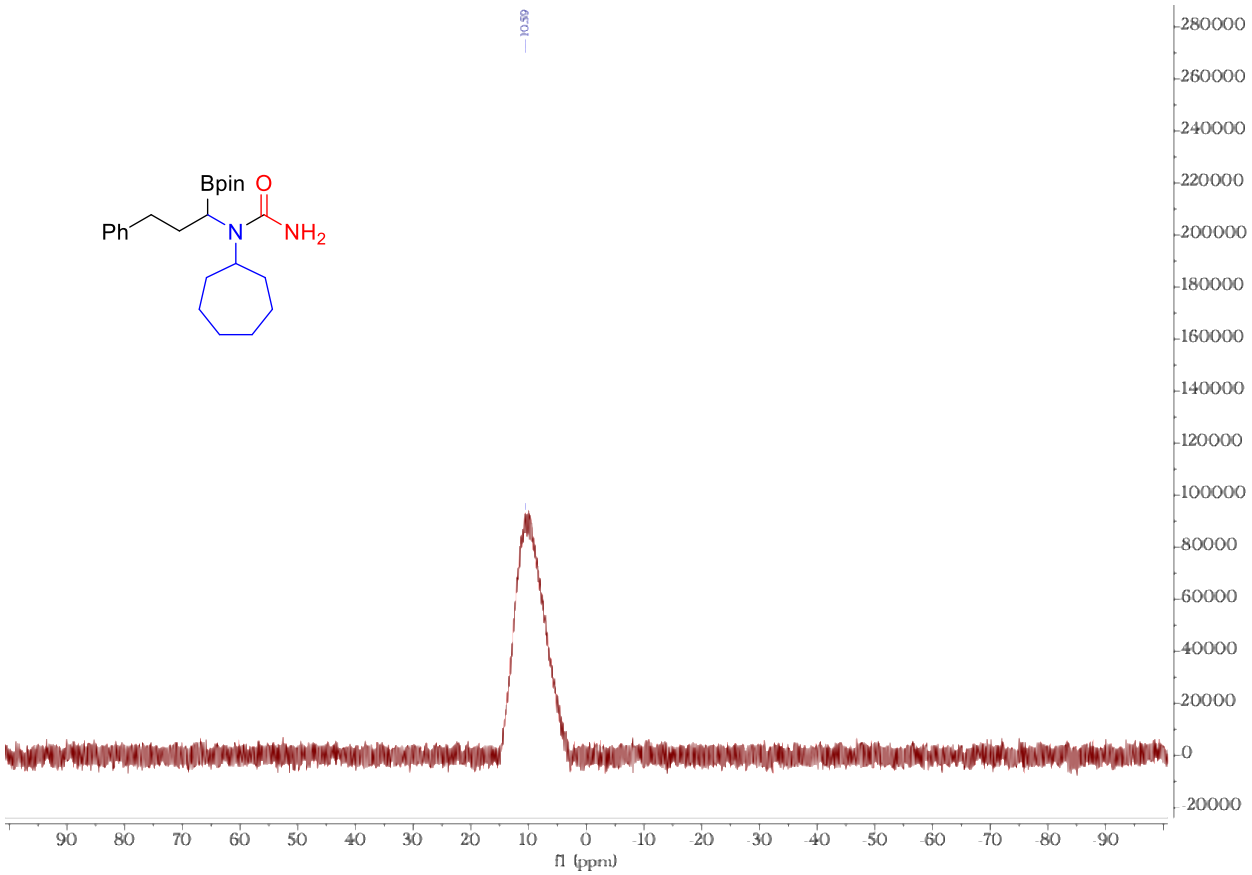

Bpin
O
Ph
N
NH2
f1 (ppm)

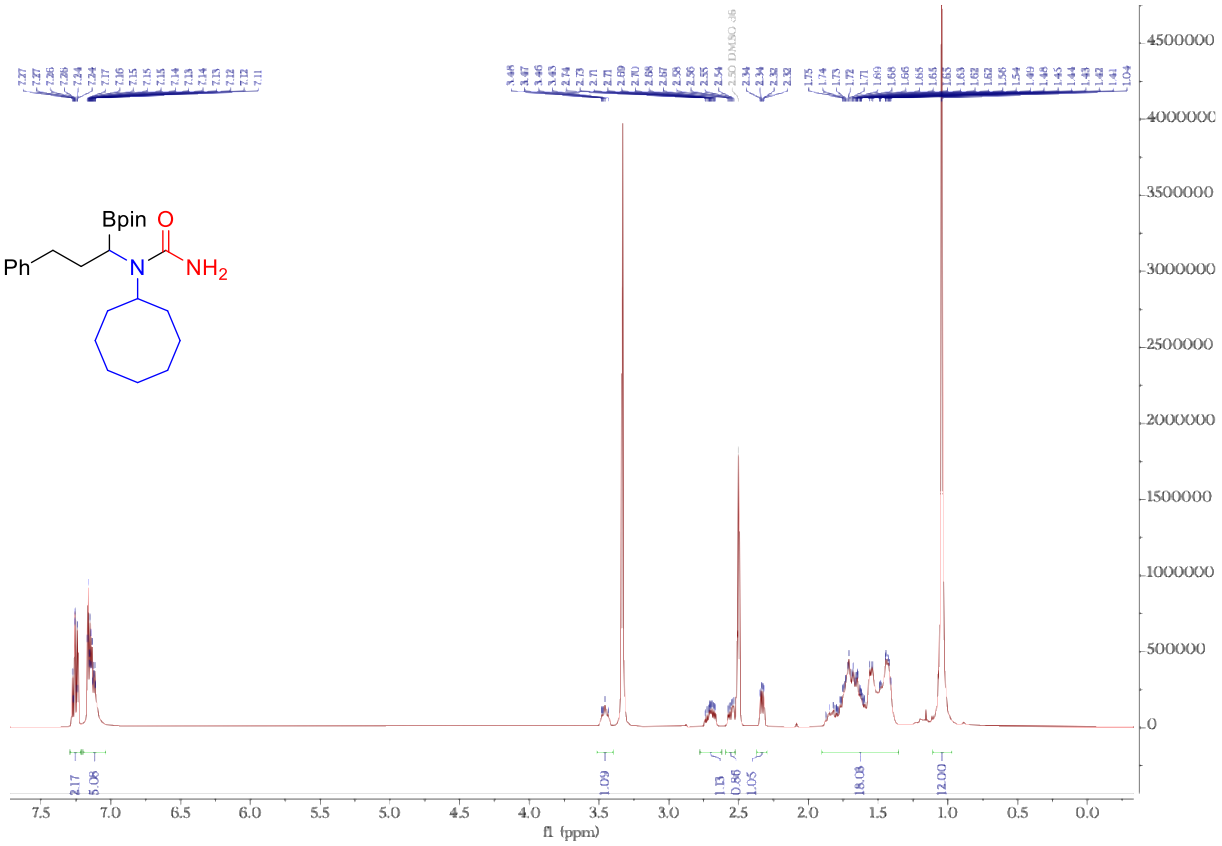

Bpin
O
Ph
N
NH2
f1 (ppm)

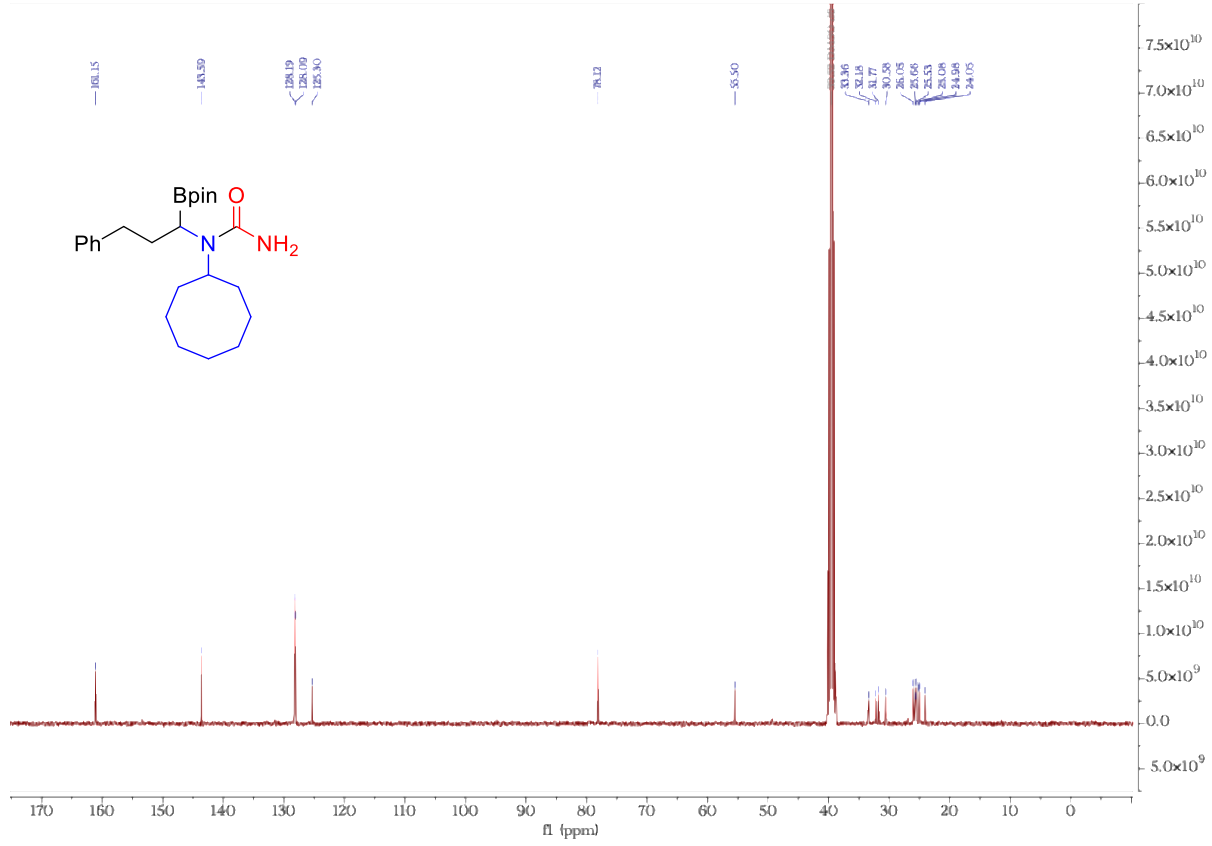

10.29
Bpin
O
Ph
N
NH2
6.5x10^10
6.0x10^10
5.5x10^10
5.0x10^10
4.5x10^10
4.0x10^10
3.5x10^10
3.0x10^10
2.5x10^10
2.0x10^10
1.5x10^10
1.0x10^10
5.0x10^9
0.0
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

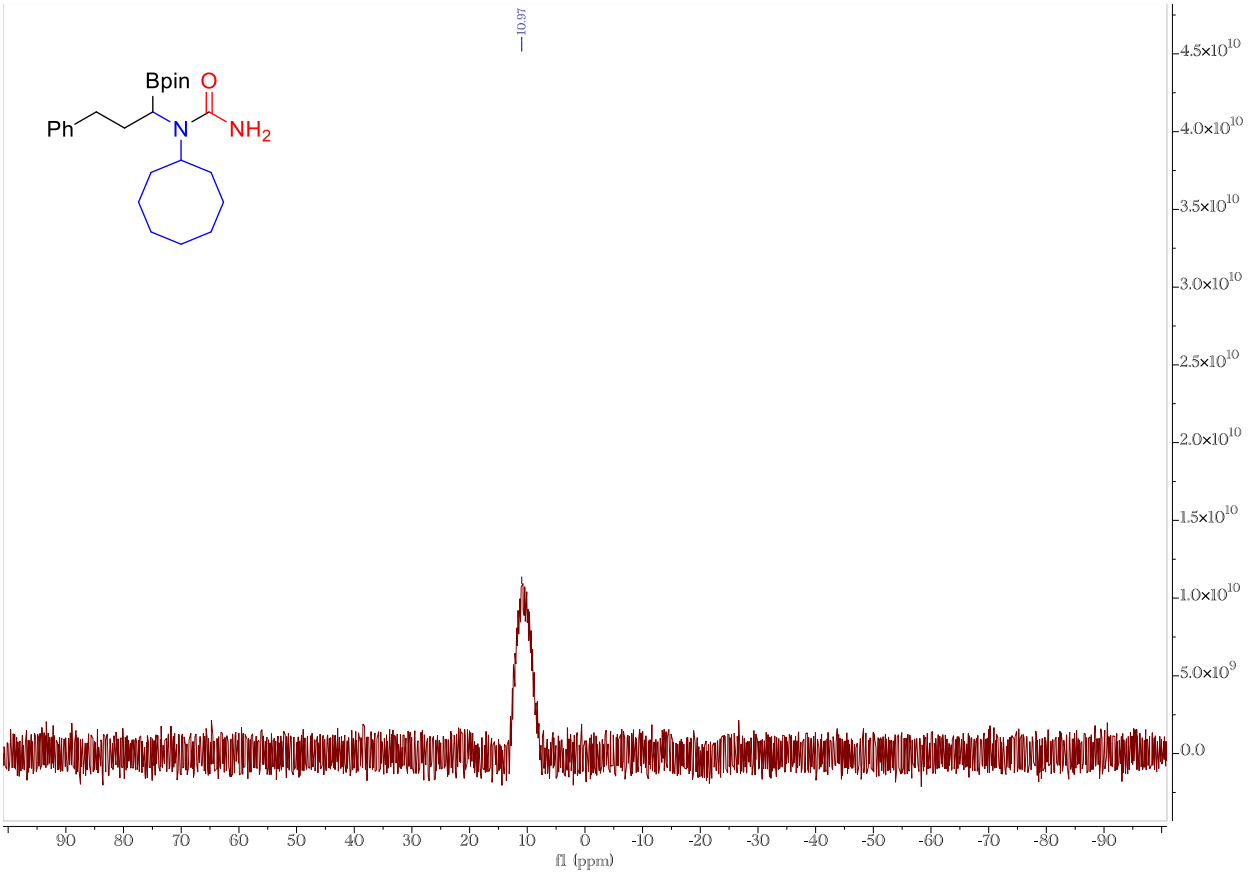

Bpin
O
Ph
N
NH2
f1 (ppm)

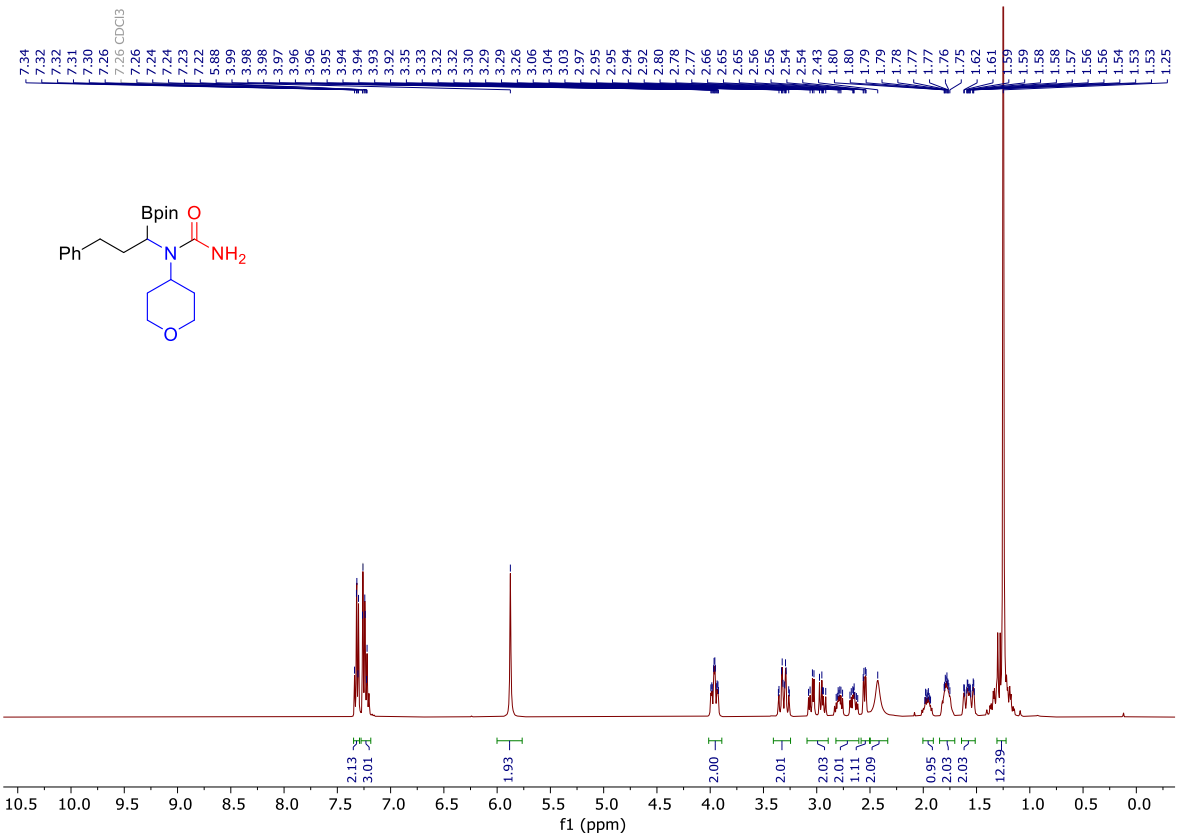

Bpin
O
Ph
N
NH2
f1 (ppm)

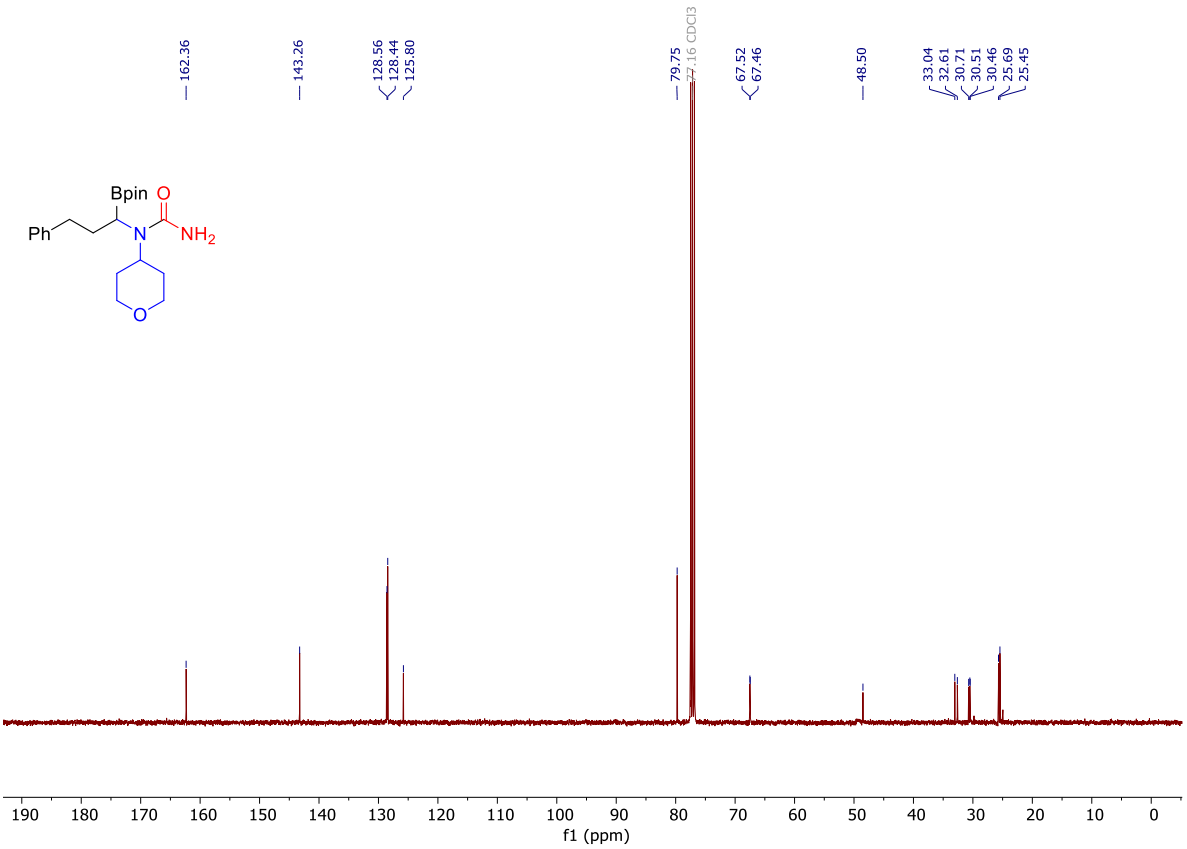

Bpin
O
Ph
N
NH2
10.59
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

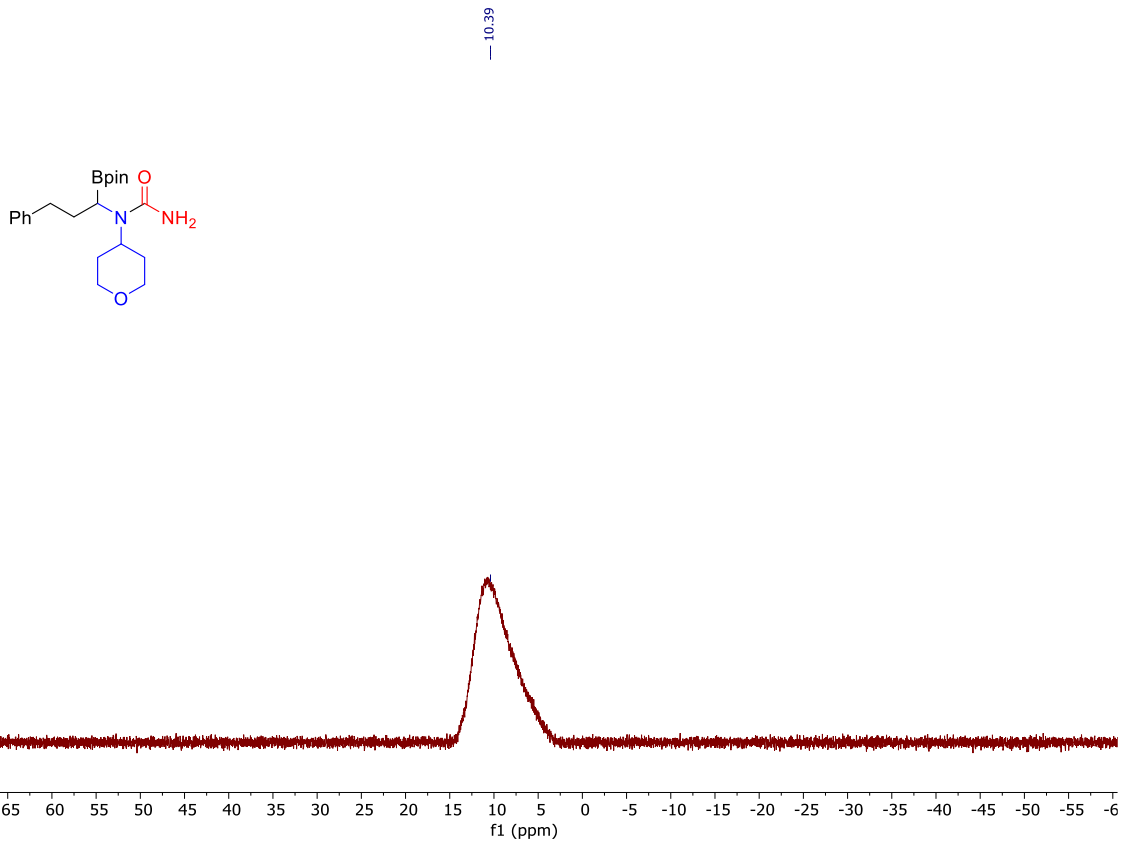

Bpin
O
Ph
N
NH2
f1 (ppm)

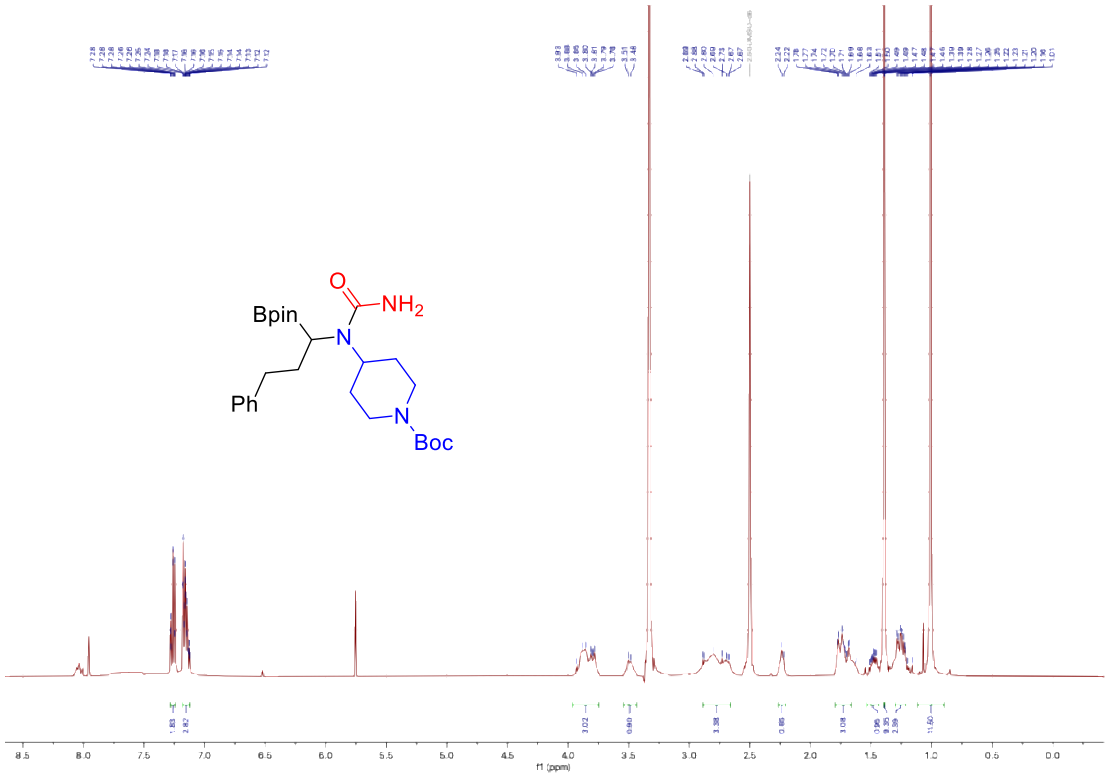

Bpin
O
Ph
N
NH2
f1 (ppm)

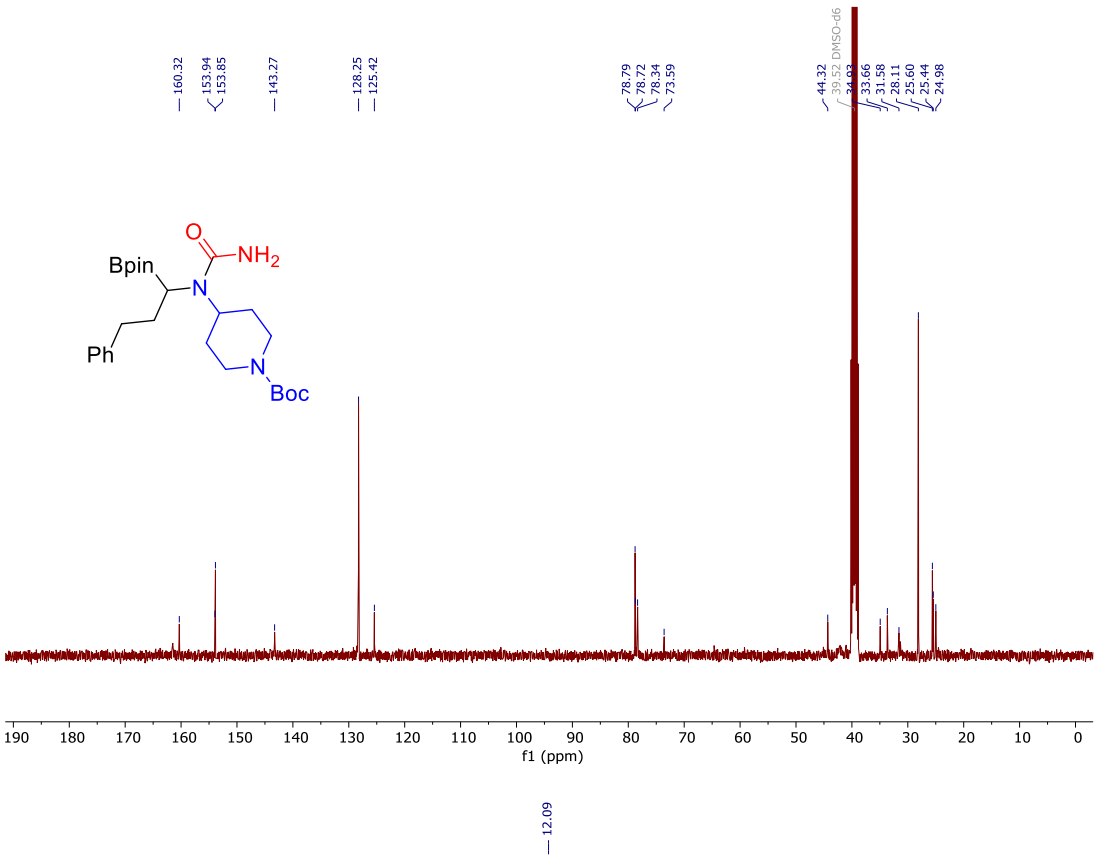

Bpin
O
Ph
N
NH2
10.97
4.5×10^10
4.0×10^10
3.5×10^10
3.0×10^10
2.5×10^10
2.0×10^10
1.5×10^10
1.0×10^10
5.0×10^9
0.0
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

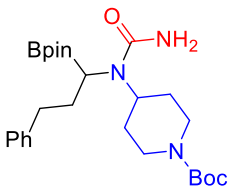

7.34 7.32 7.32 7.31 7.30 7.26 7.26 CDCl3 7.24 7.24 7.23 7.22 5.88 3.99 3.98 3.98 3.97 3.96 3.96 3.95 3.94 3.94 3.93 3.92 3.35 3.33 3.32 3.32 3.30 3.29 3.29 3.26 3.06 3.04 3.03 2.97 2.95 2.95 2.94 2.92 2.80 2.78 2.77 2.66 2.65 2.56 2.56 2.54 2.54 2.43 1.80 1.79 1.79 1.78 1.77 1.77 1.76 1.75 1.62 1.61 1.59 1.59 1.58 1.58 1.57 1.56 1.56 1.54 1.53 1.53 1.25
Bpin
O
Ph
N
NH2
O
2.13
3.01
1.93
2.00
2.01
2.03
2.01
1.11
2.09
0.95
2.03
2.03
12.39
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

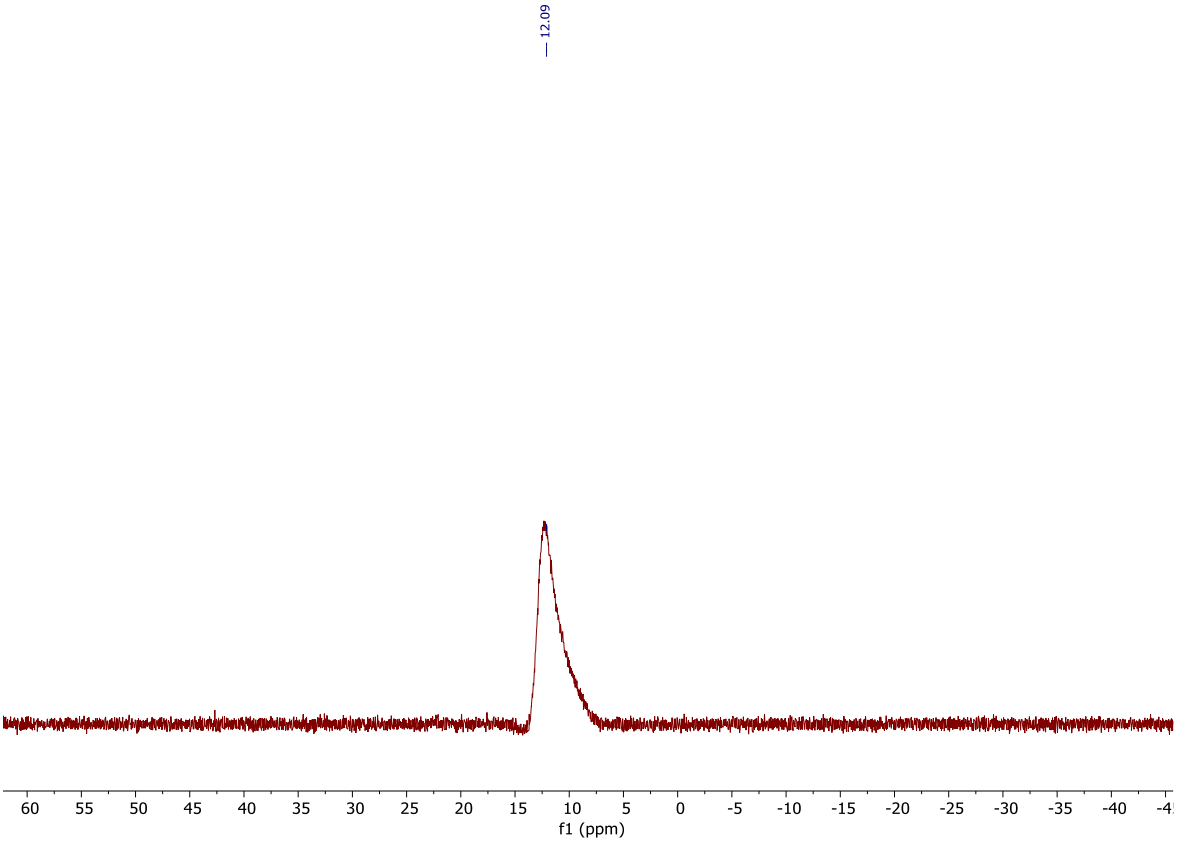

162.36
143.26
128.56
128.44
125.80
79.75
77.16 CDCl3
67.52
67.46
48.50
33.04
32.61
30.71
30.51
30.46
25.69
25.45
Bpin
O
Ph
N
NH2
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

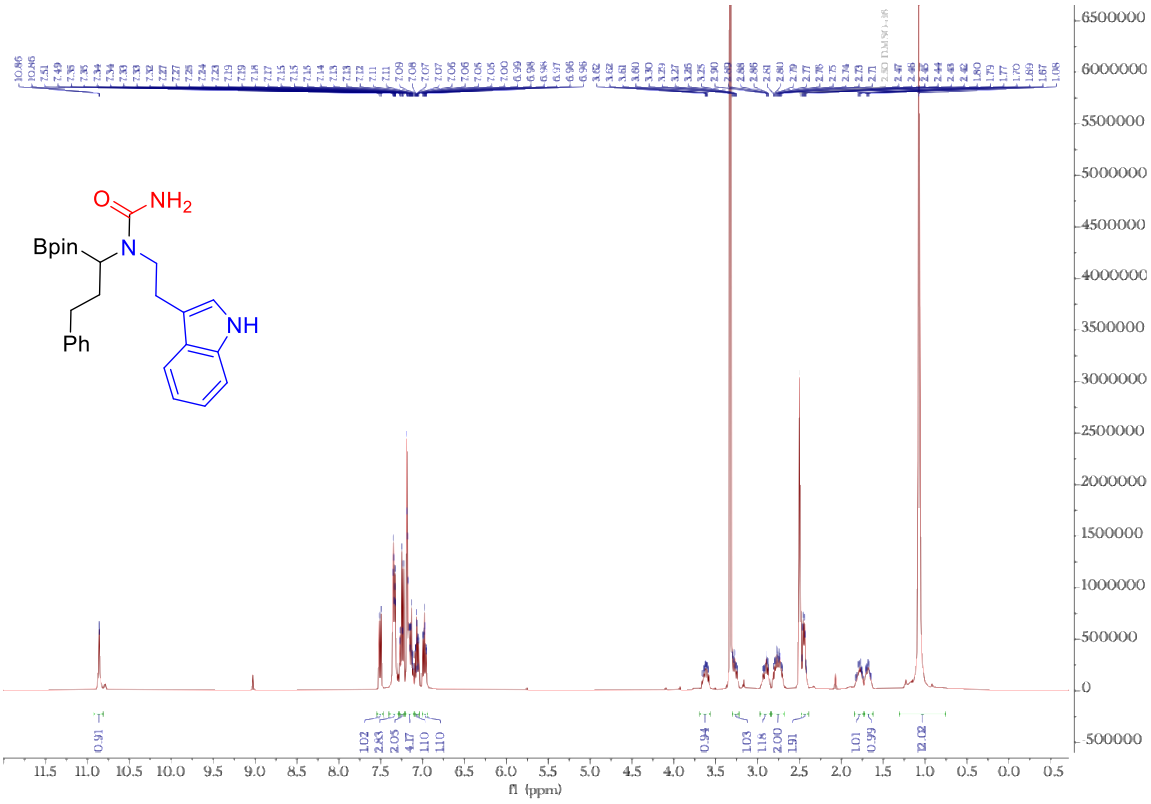

10.39
Bpin
O
Ph
N
NH2
O
70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -6
f1 (ppm)

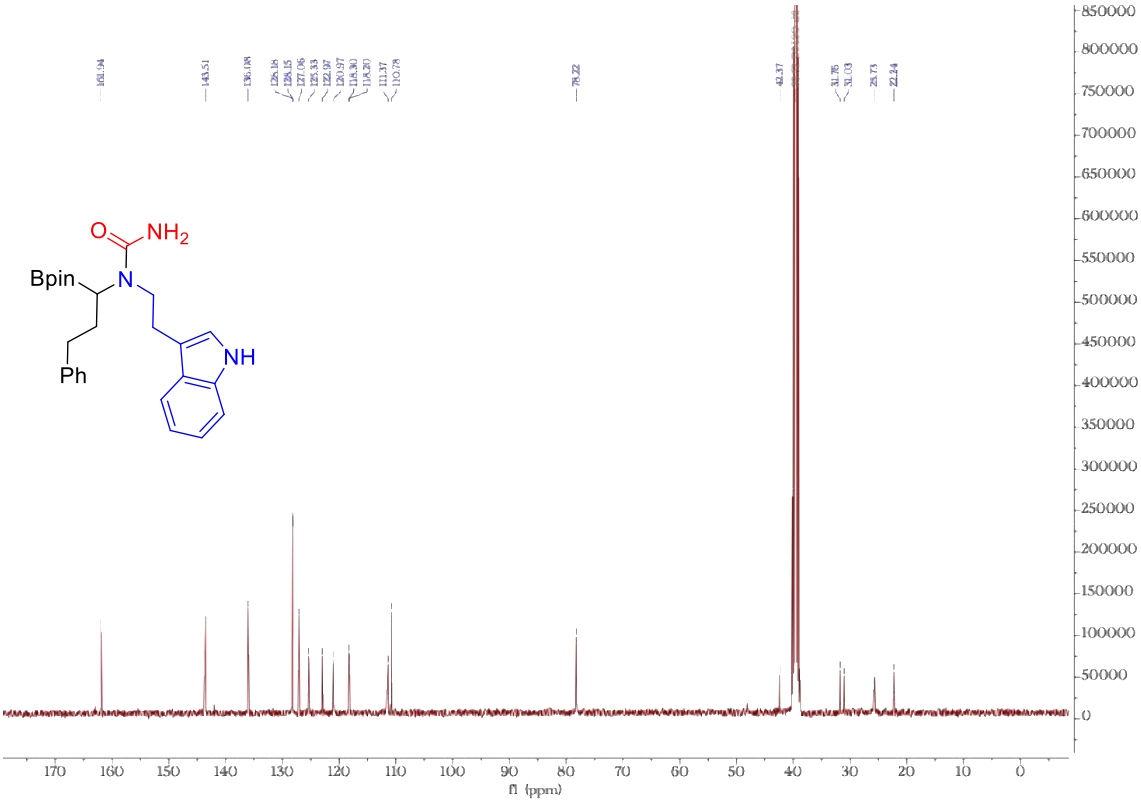

O
NH2
Bpin
N
Ph
N
Boc
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

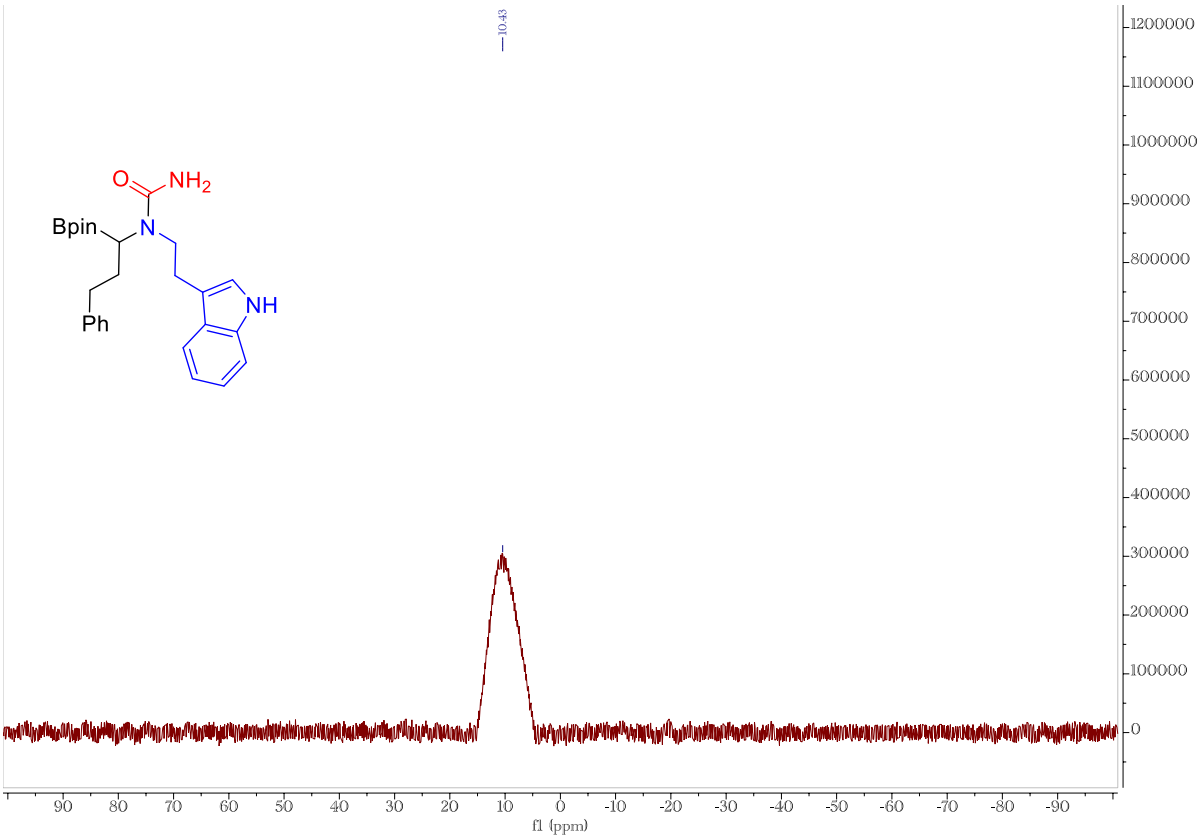

160.32
153.94
153.85
143.27
128.25
125.42
78.79
78.72
78.34
73.59
44.32
39.52 DMSO-d6
34.03
33.66
31.58
28.11
25.60
25.44
24.98
O
NH2
Bpin
N
Ph
N
Boc
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
12.09

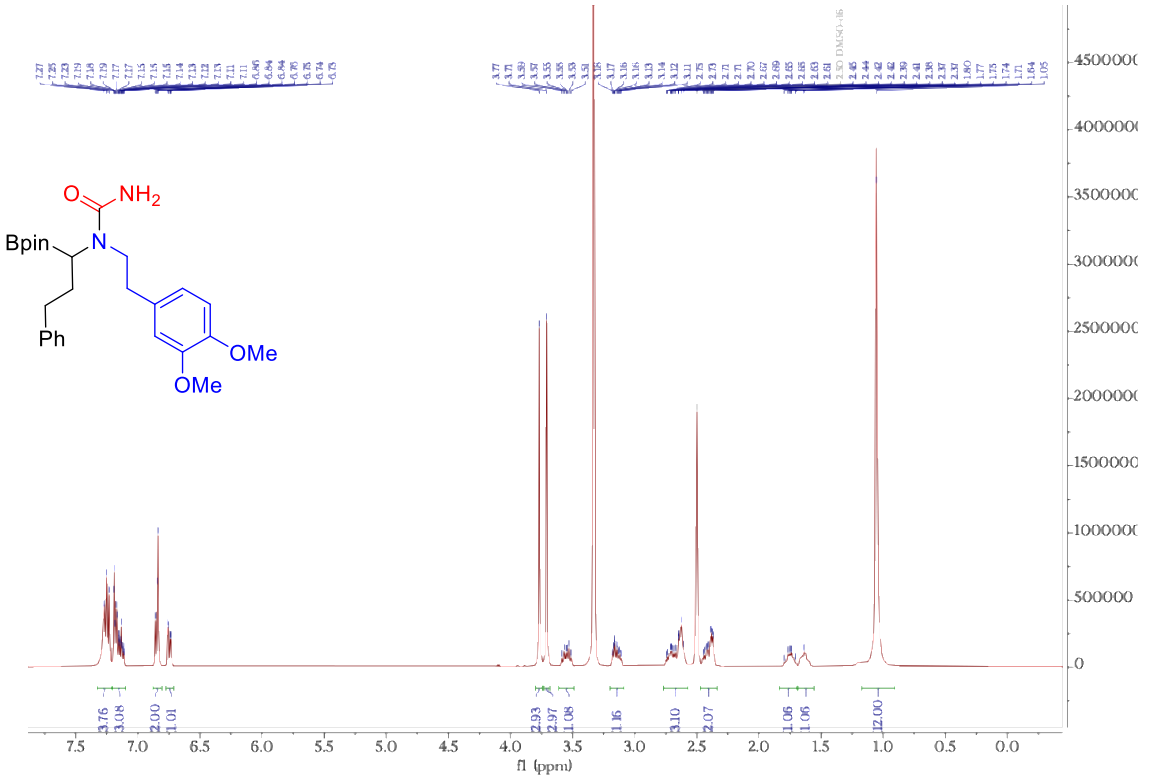

O
NH2
Bpin
N
Ph
N
Boc

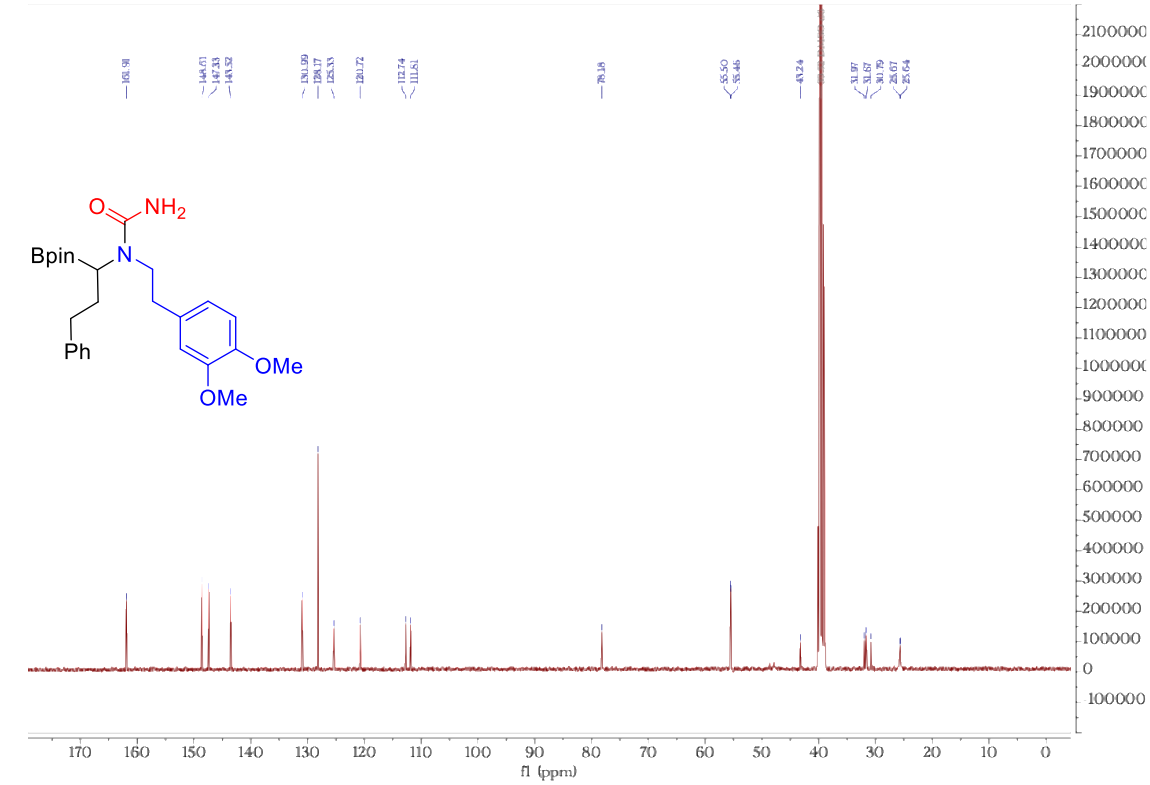

12.09
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-4
f1 (ppm)

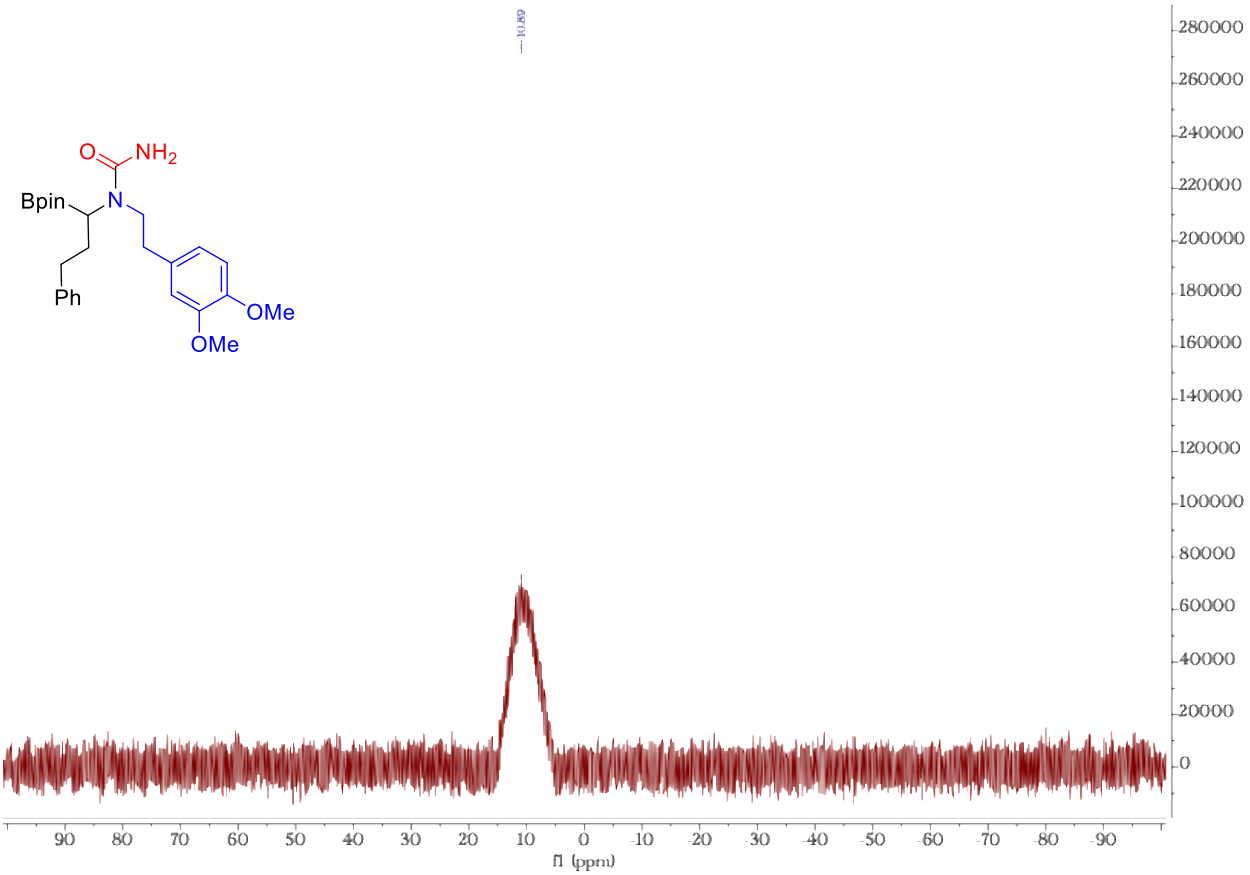

O
NH2
Bpin
N
NH
Ph
f1 (ppm)

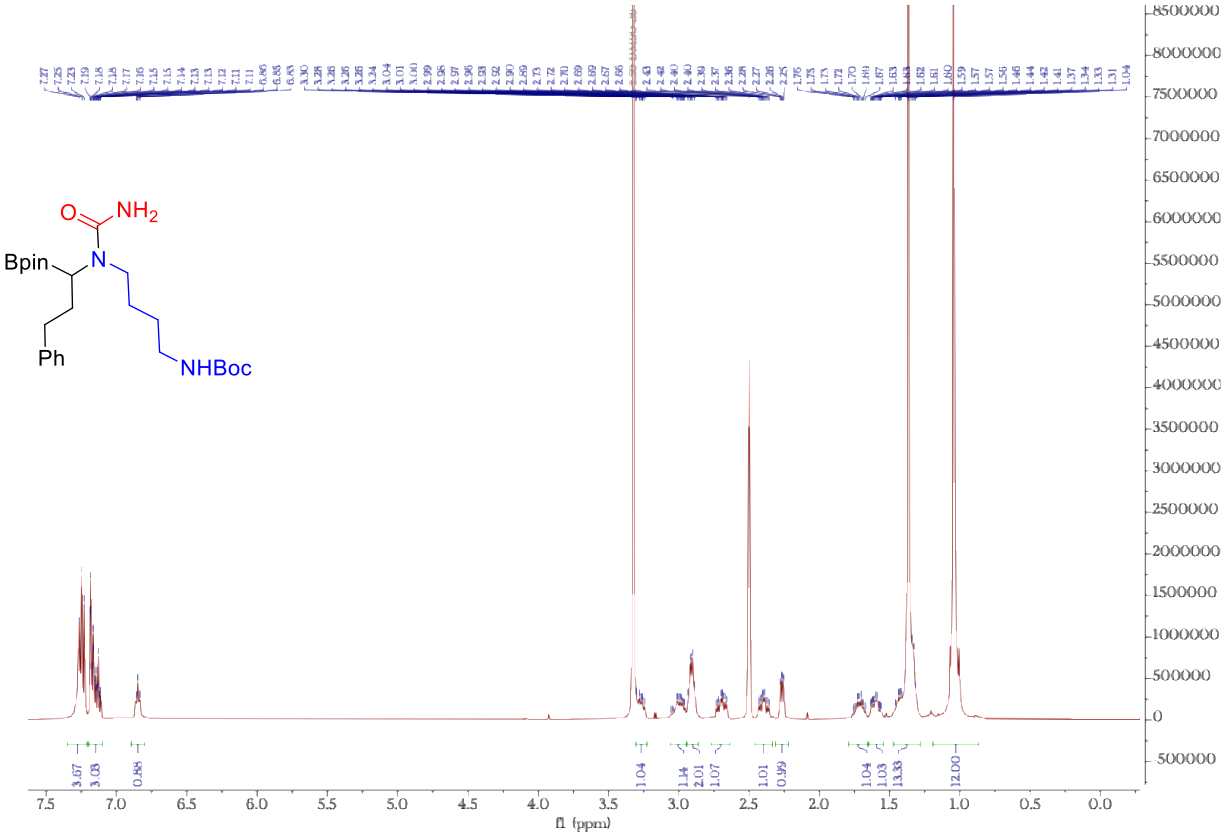

O
NH2
Bpin
N
NH
Ph
f1 (ppm)

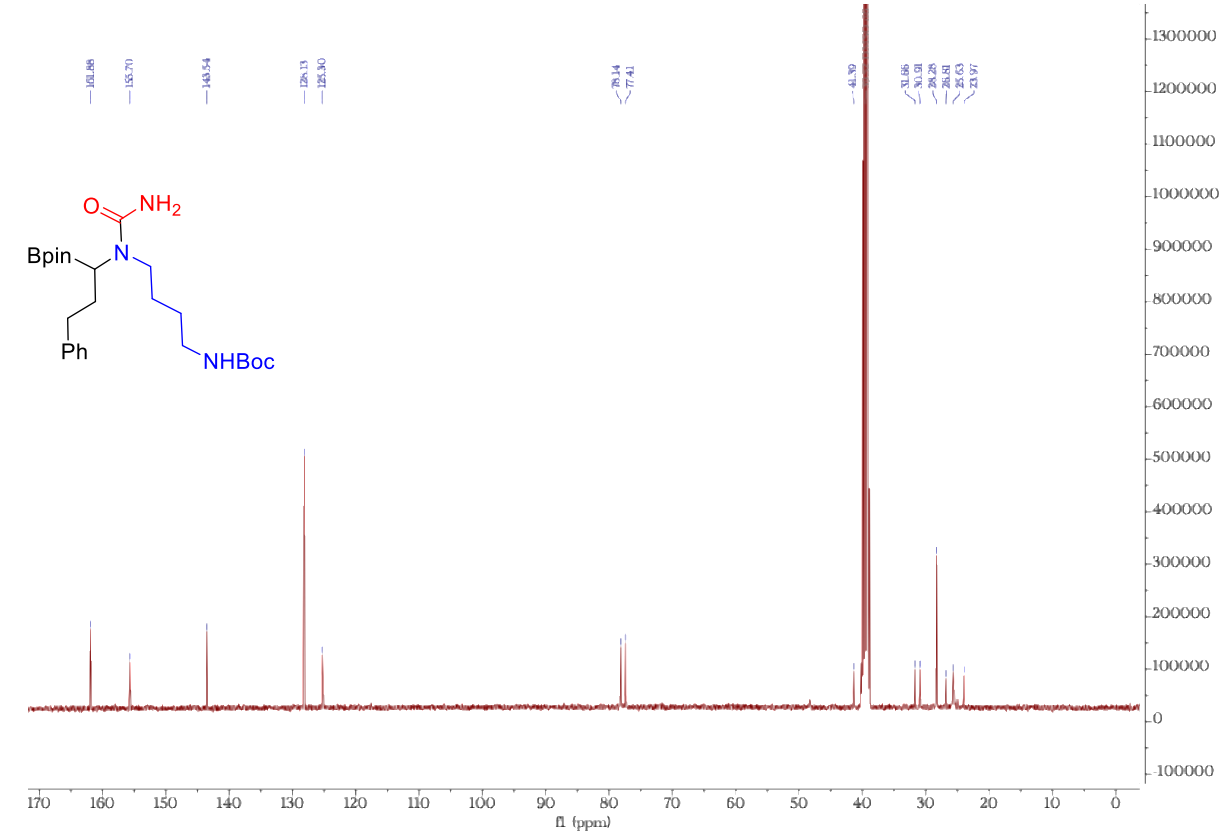

10.43
O
NH2
Bpin
N
NH
Ph
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

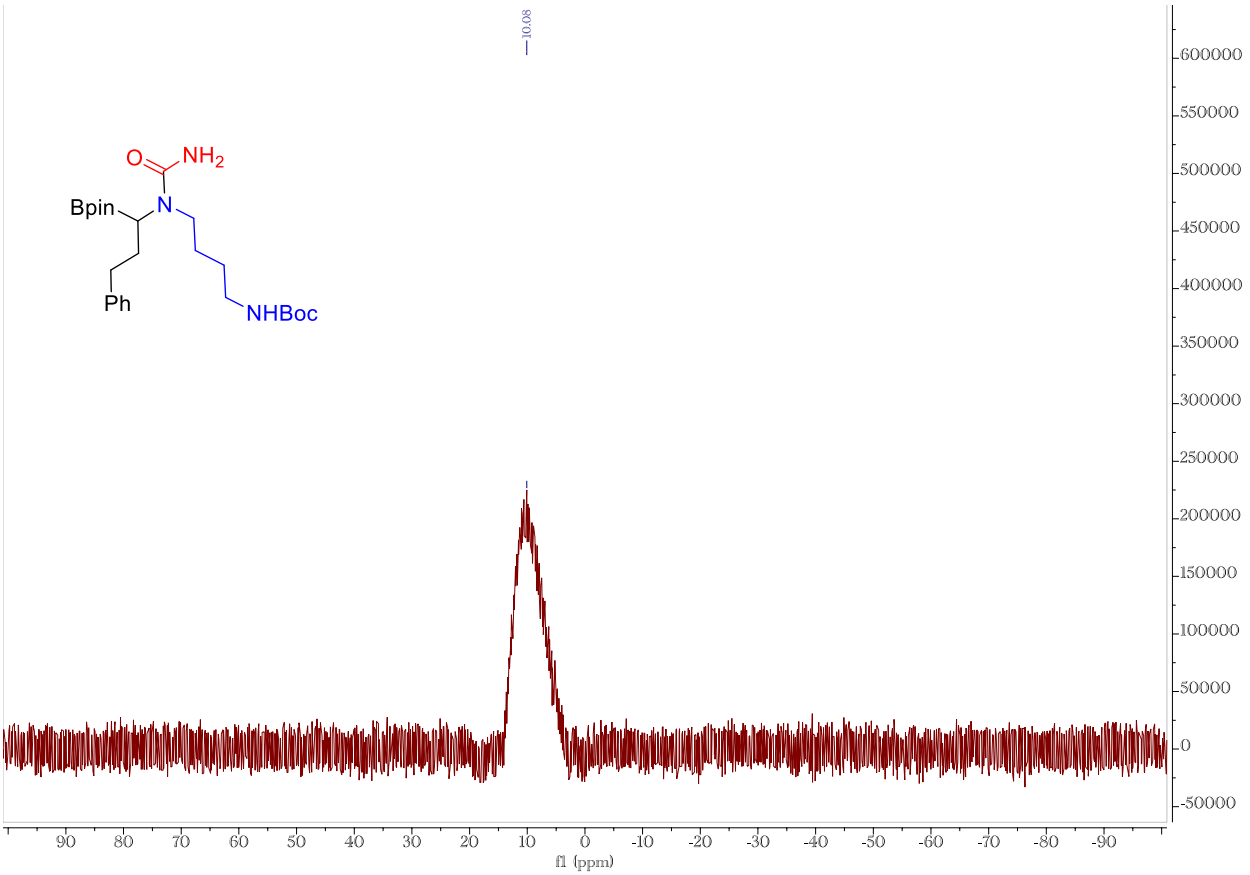

O
NH2
Bpin
N
Ph
OMe
OMe
fl (ppm)


O
NH2
Bpin
N
Ph
OMe
OMe
fl (ppm)


O
NH2
Bpin
N
Ph
OMe
OMe
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)


O
NH2
Bpin
N
Ph
NHBoc
f1 (ppm)


O
NH2
Bpin
N
Ph
NHBoc
f1 (ppm)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N
Ph
NHBoc
600000
550000
500000
450000
400000
350000
300000
250000
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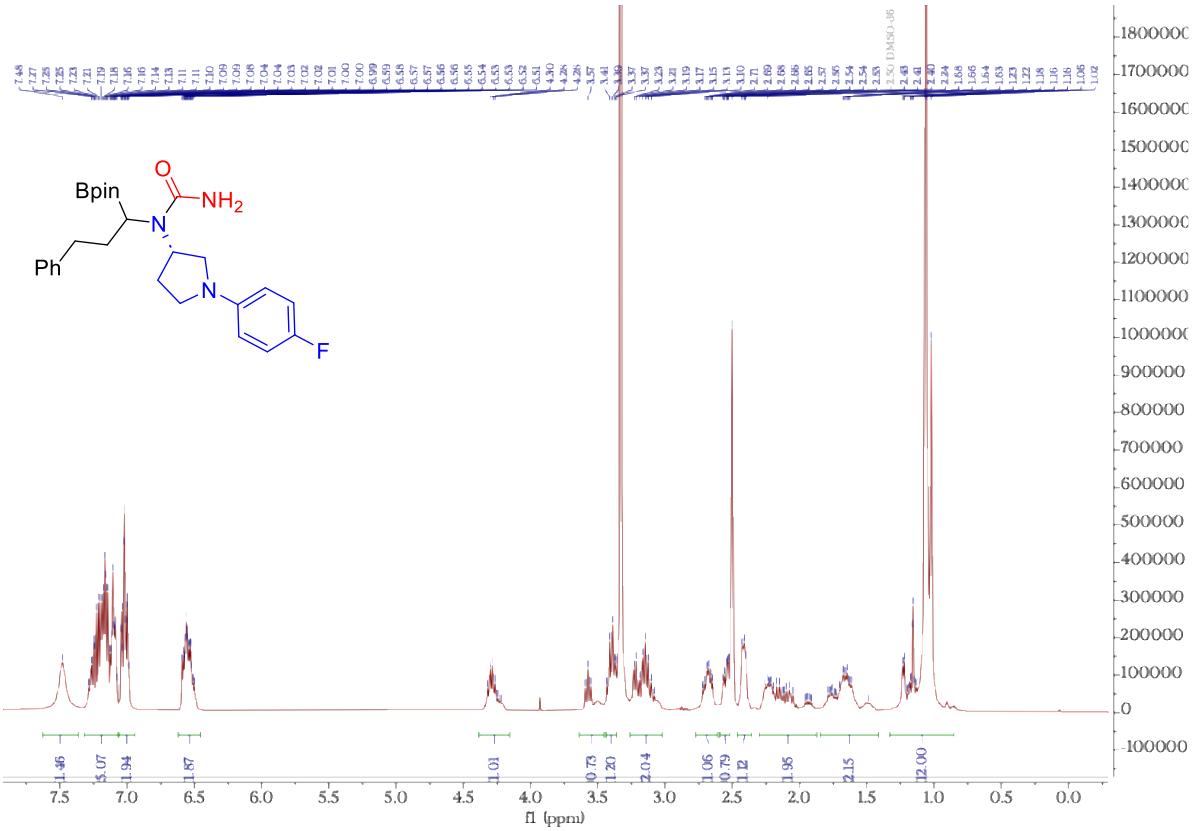
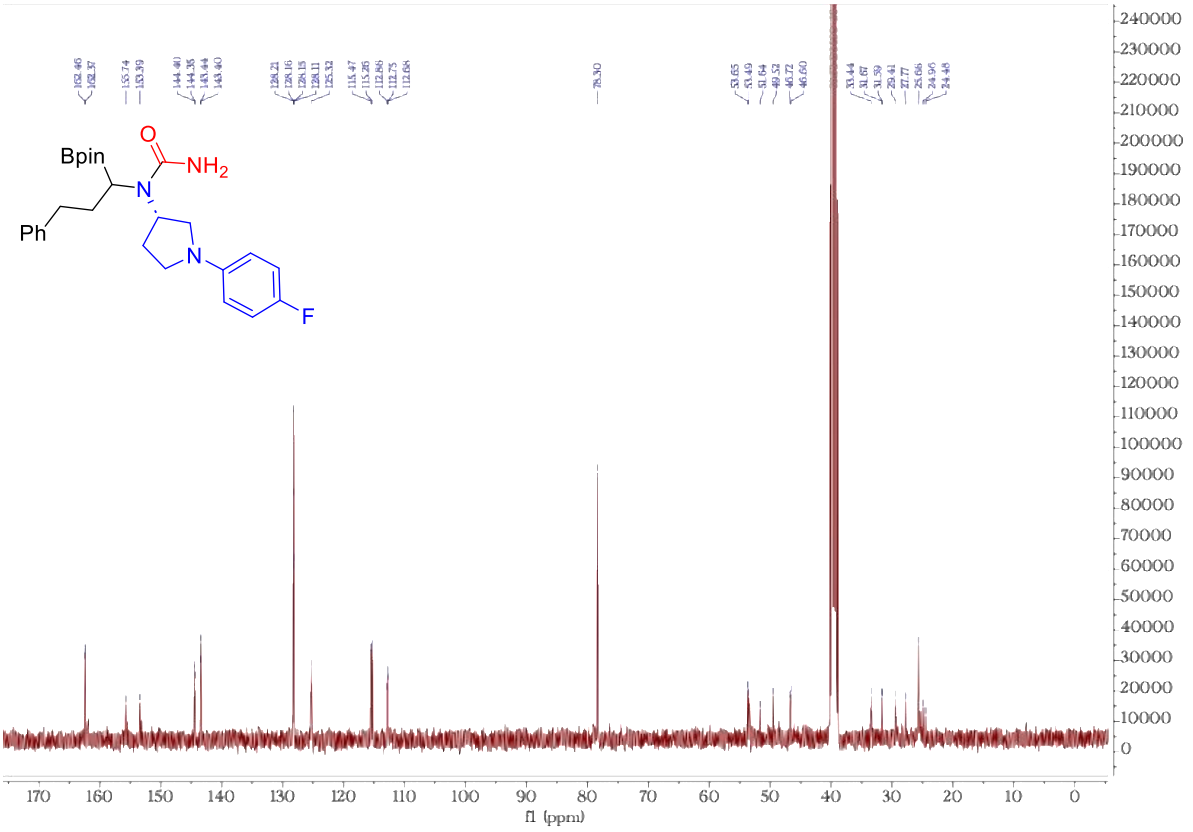
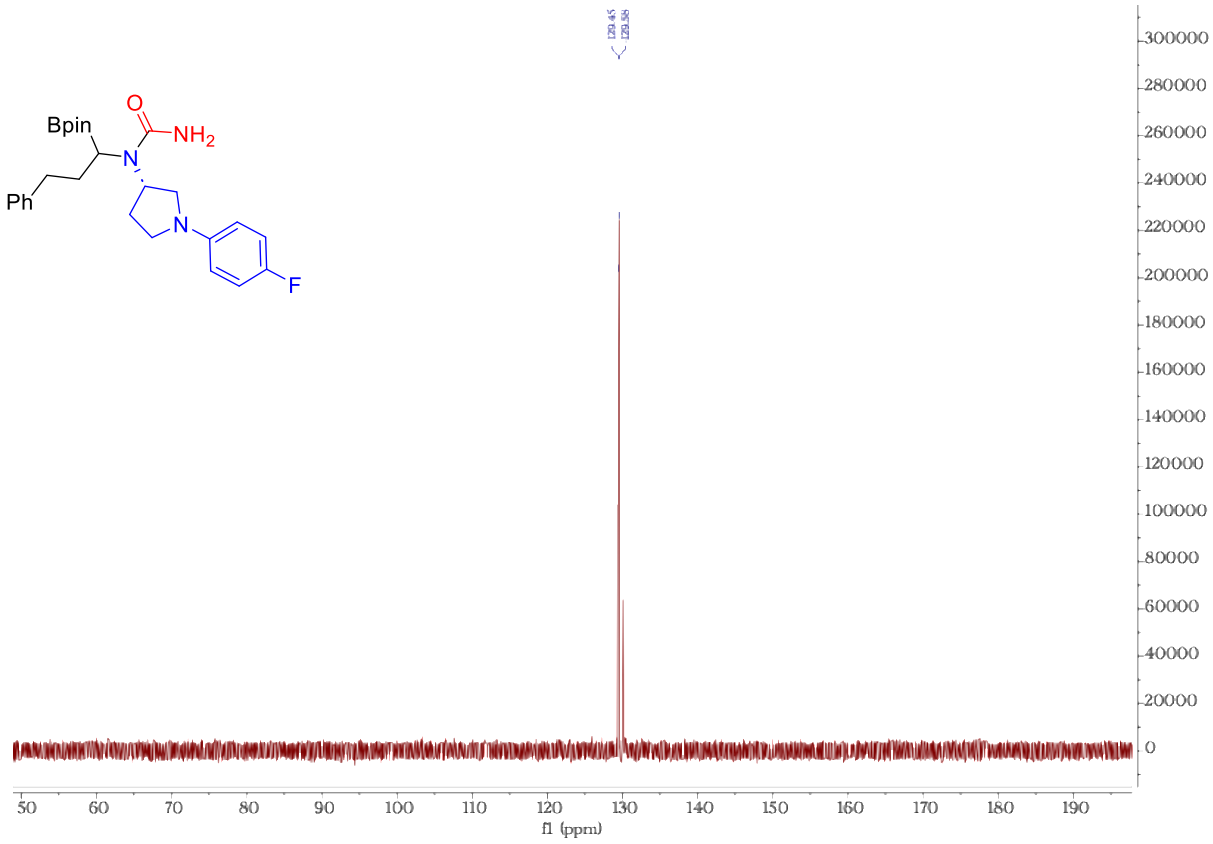
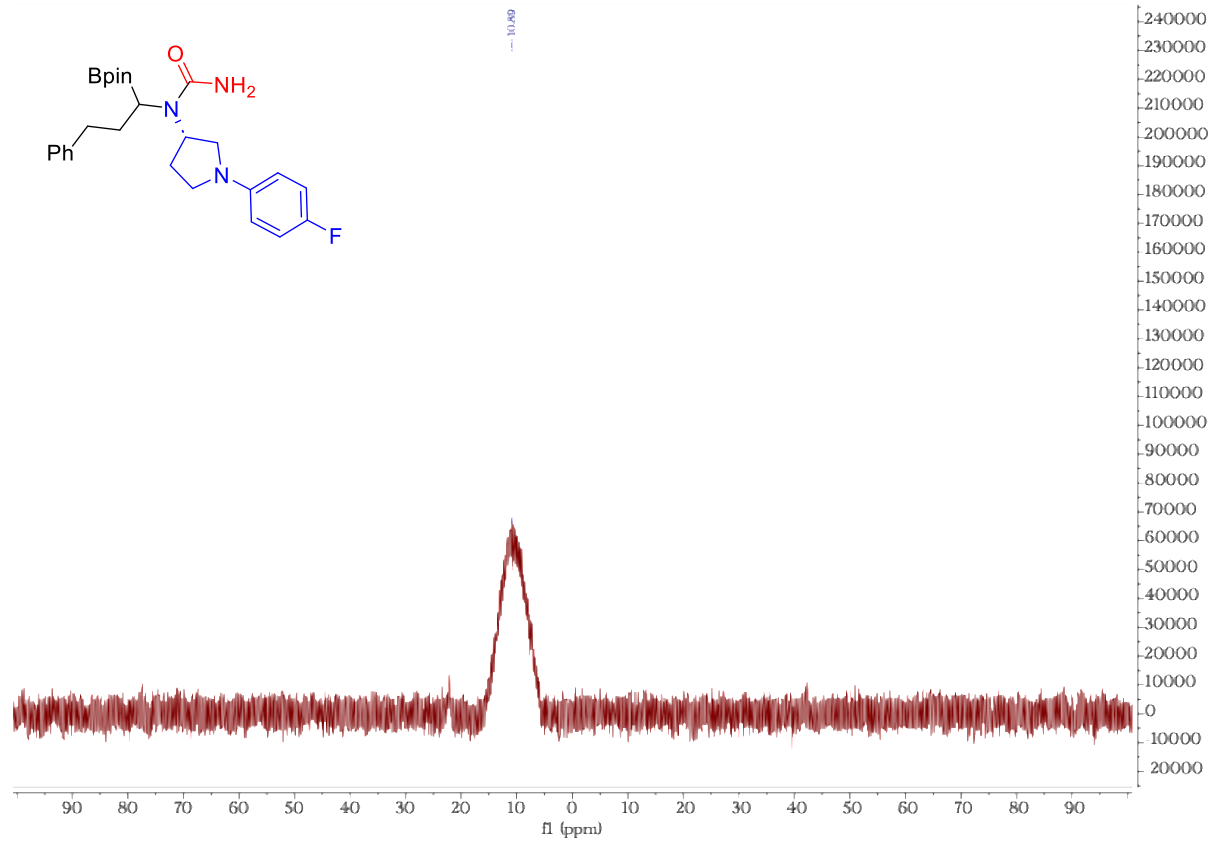
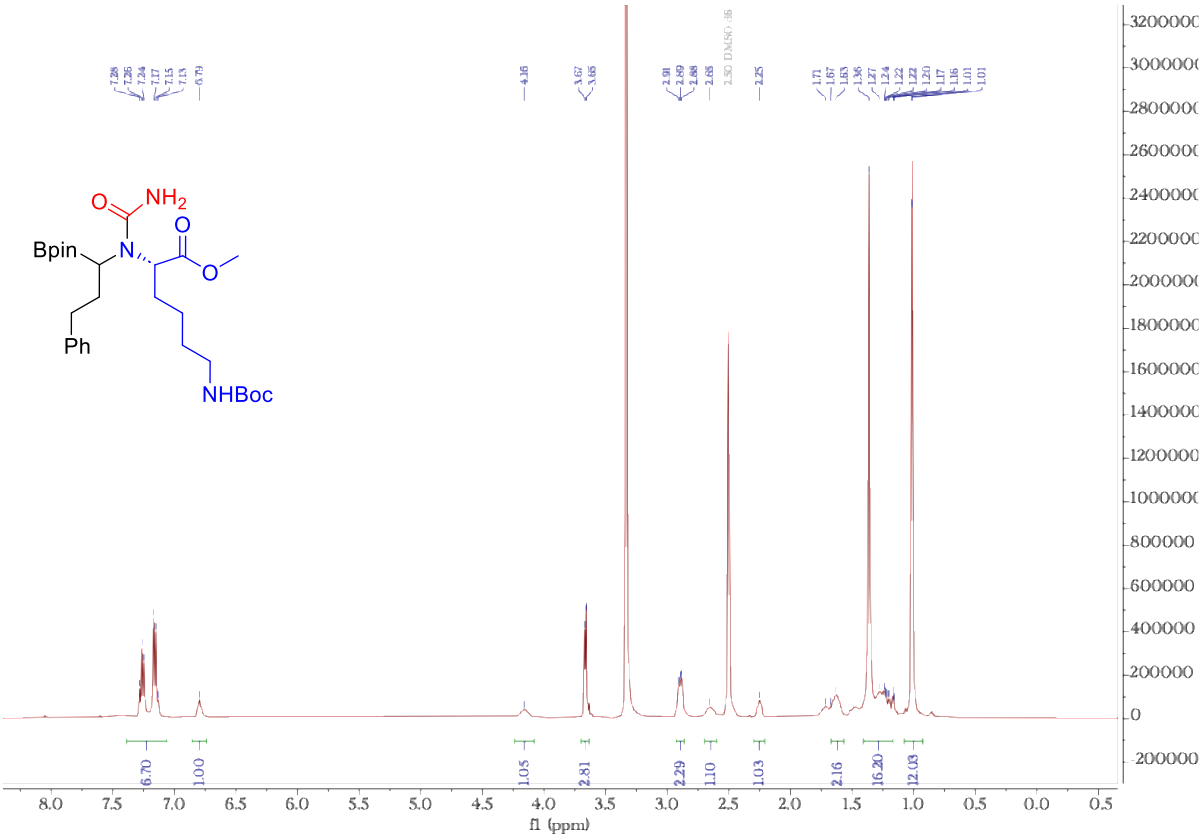
150000
100000
50000
0
-50000
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)


Bpin
O
NH2
N
Ph
N
F
f1 (ppm)


Bpin
O
NH2
N
Ph
N
F
f1 (ppm)


Bpin
O
NH2
N
Ph
N
F
129.45
129.56
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
f1 (ppm)


10.00
Bpin
O
NH2
N
Ph
N
F
240000
230000
220000
210000
200000
190000
180000
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
10000
20000
90
80
70
60
50
40
30
20
10
0
10
20
30
40
50
60
70
80
90
f1 (ppm)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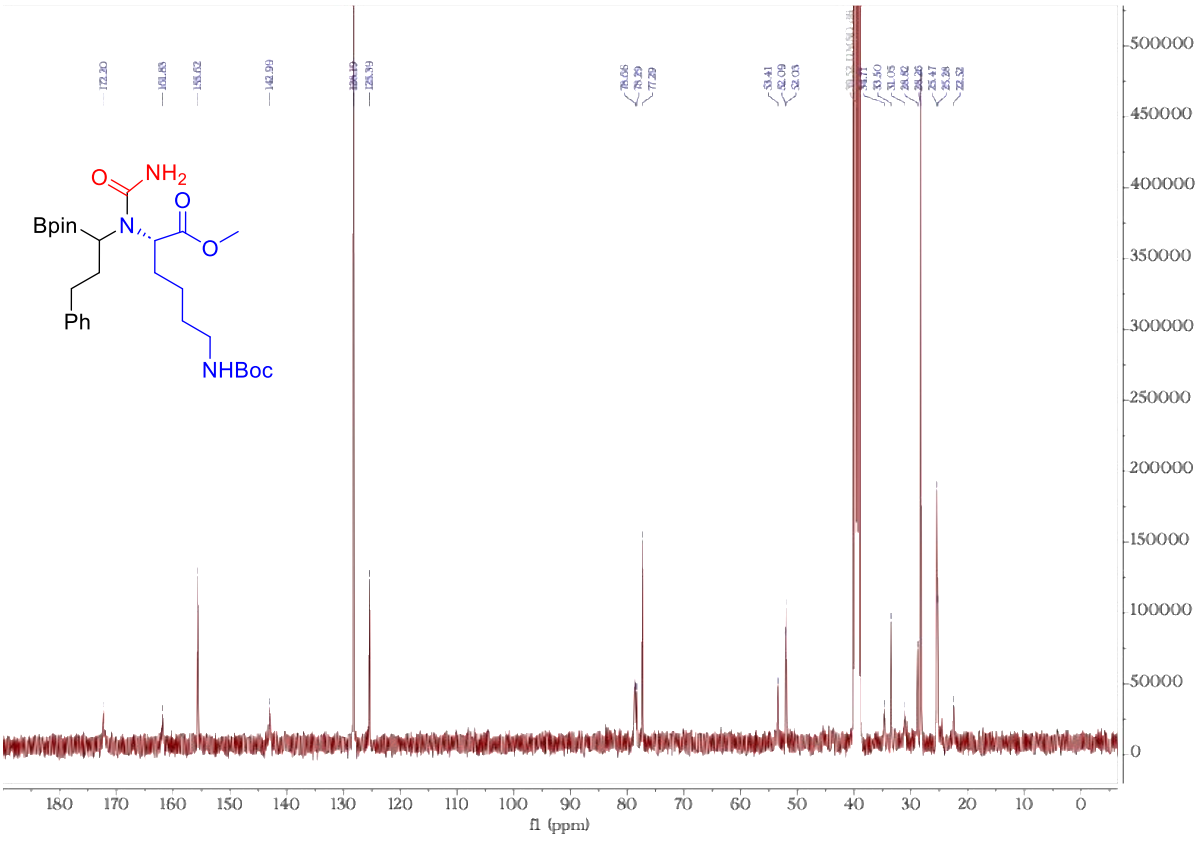
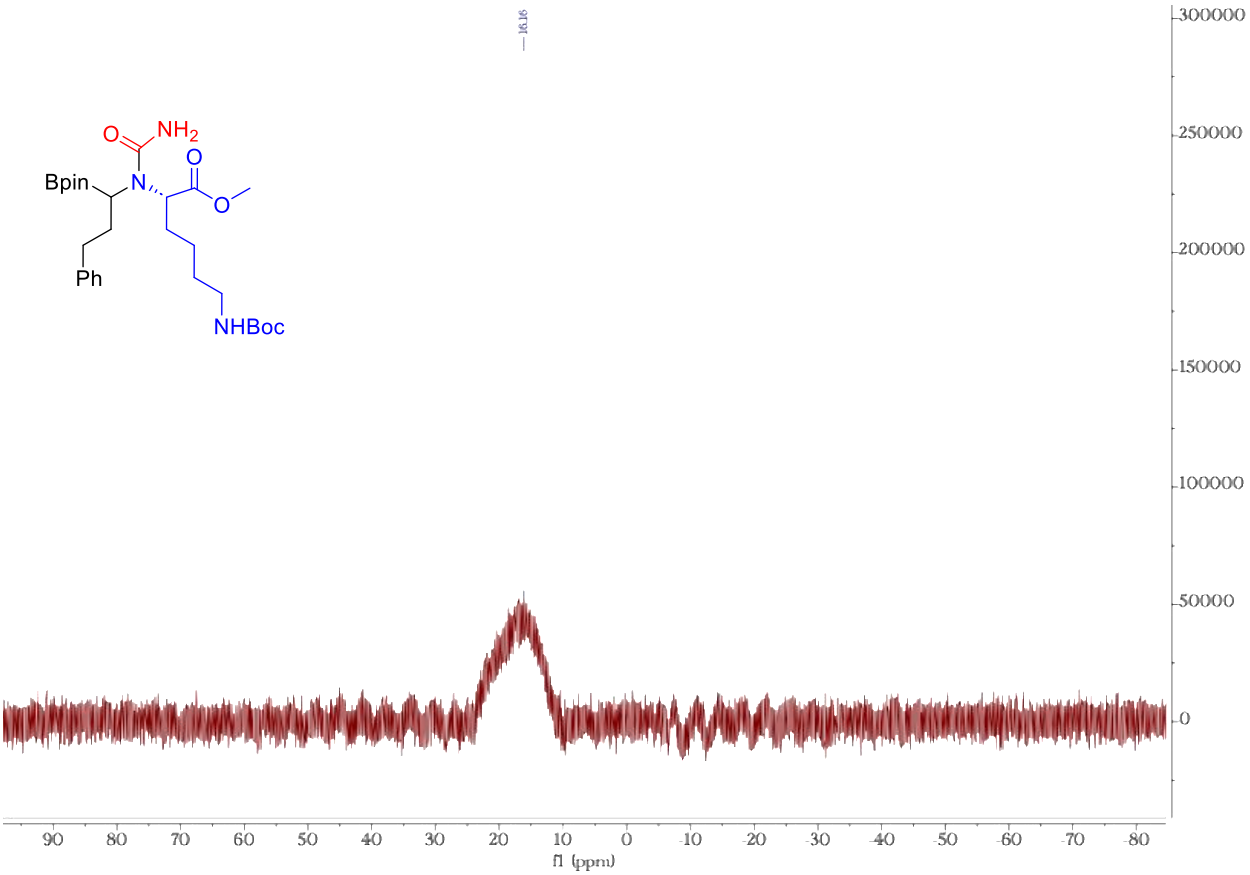
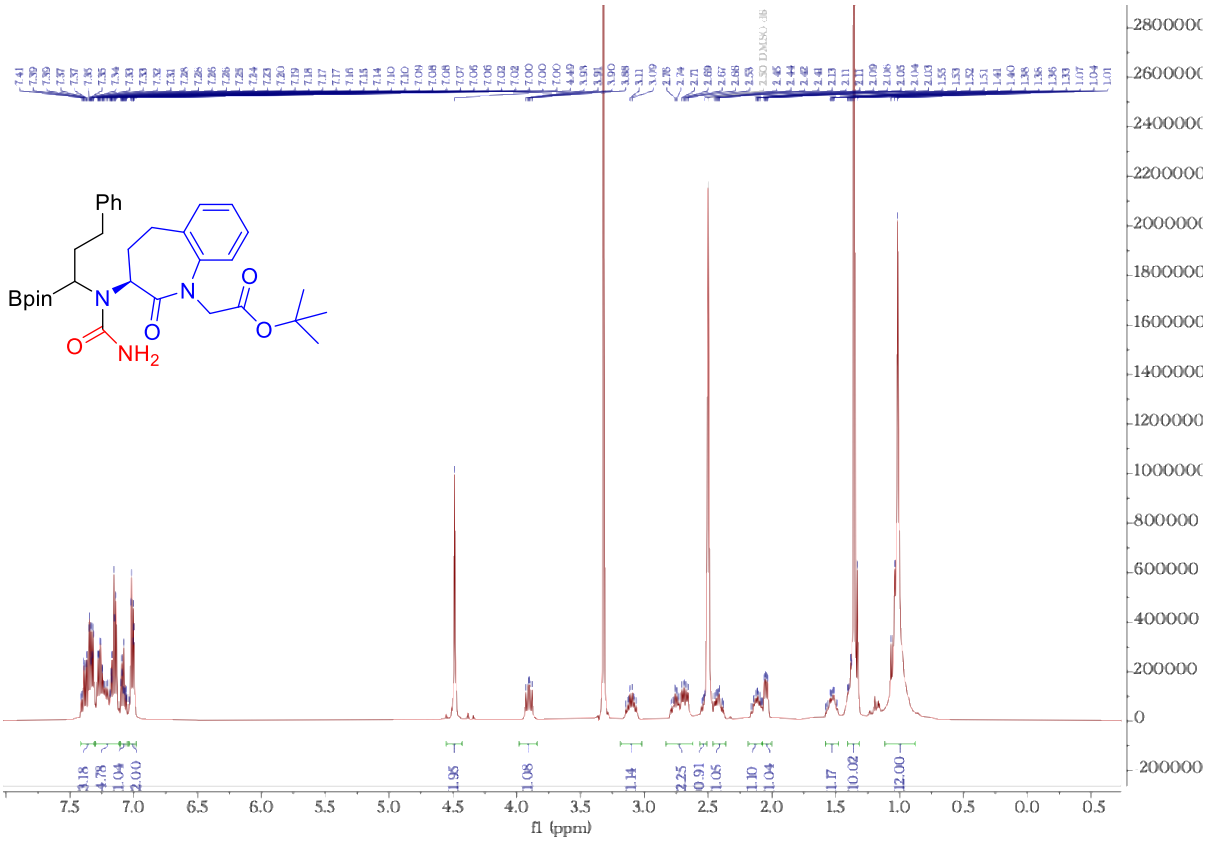
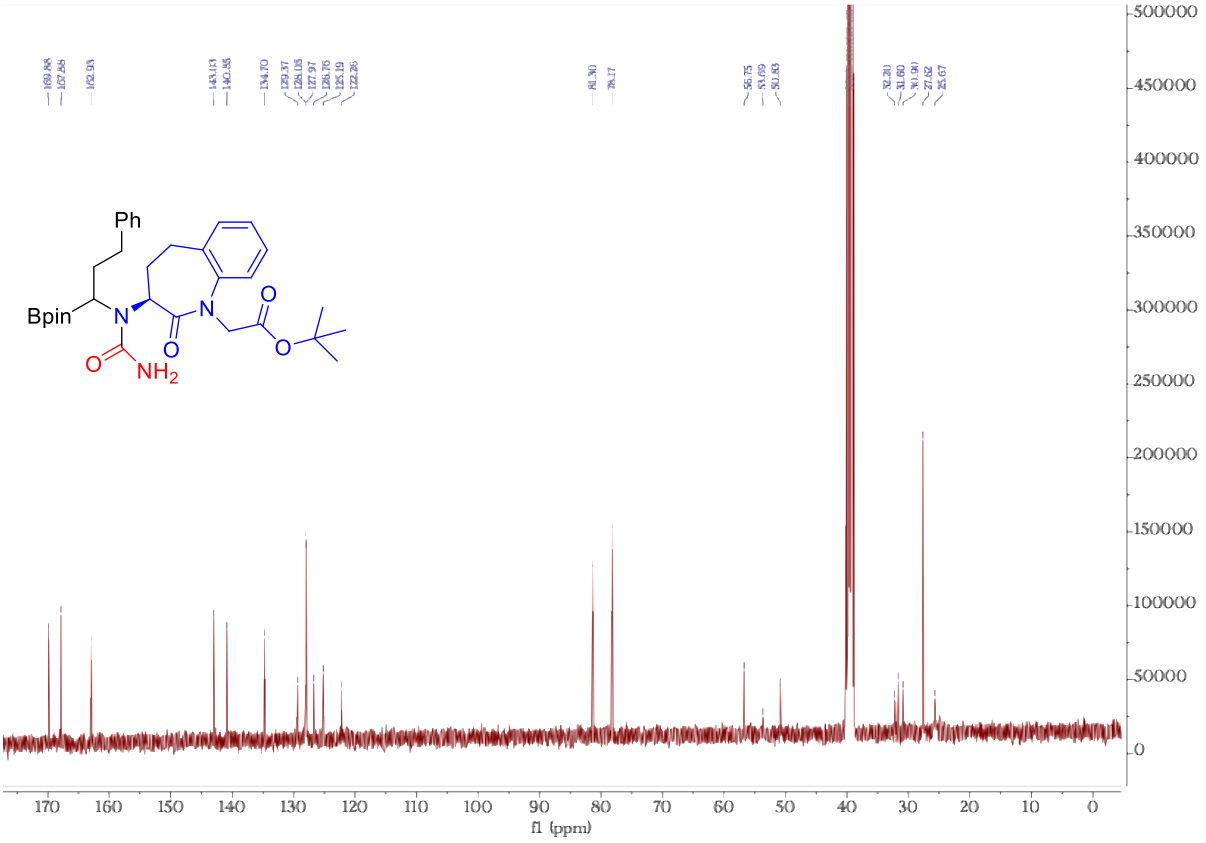
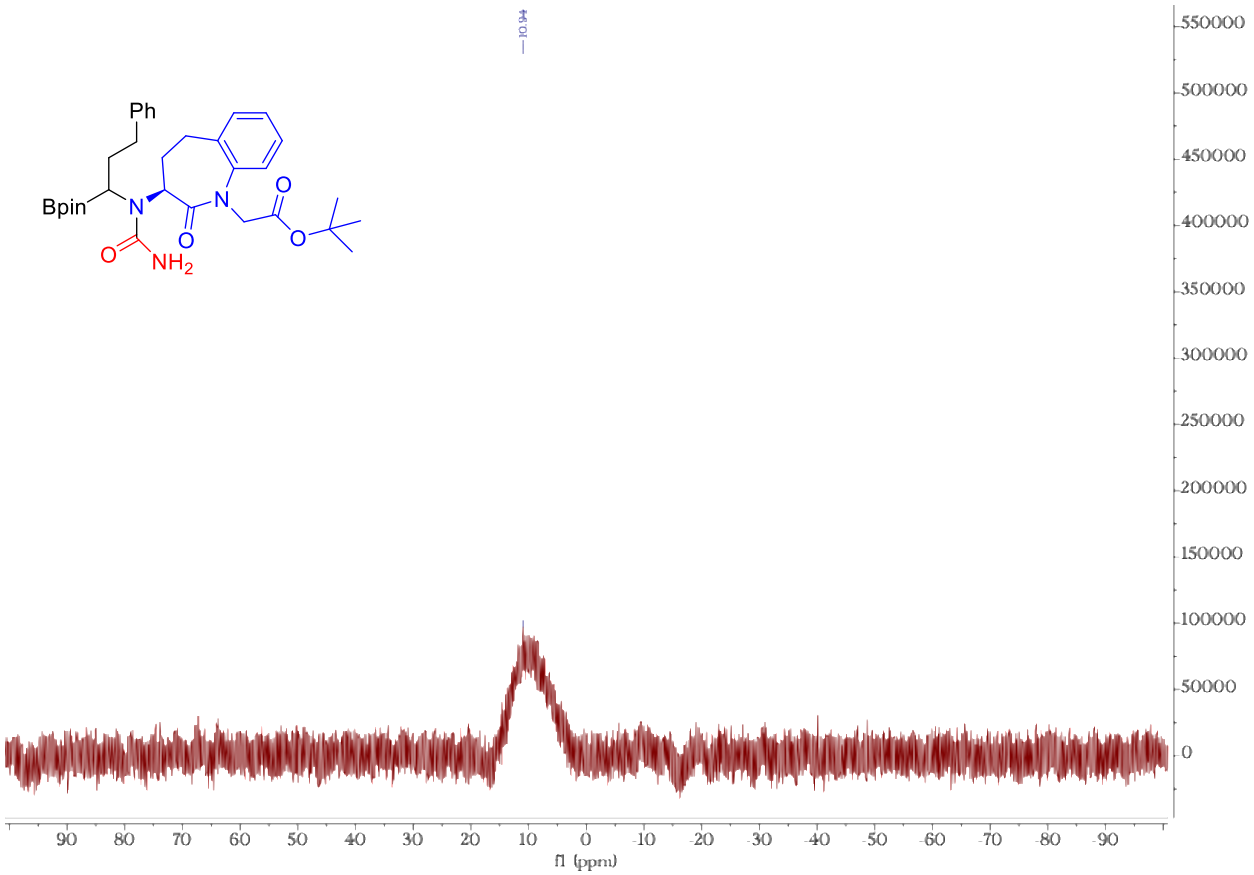
NH2
Bpin
N
O
O
Ph
NHBoc
f1 (ppm)

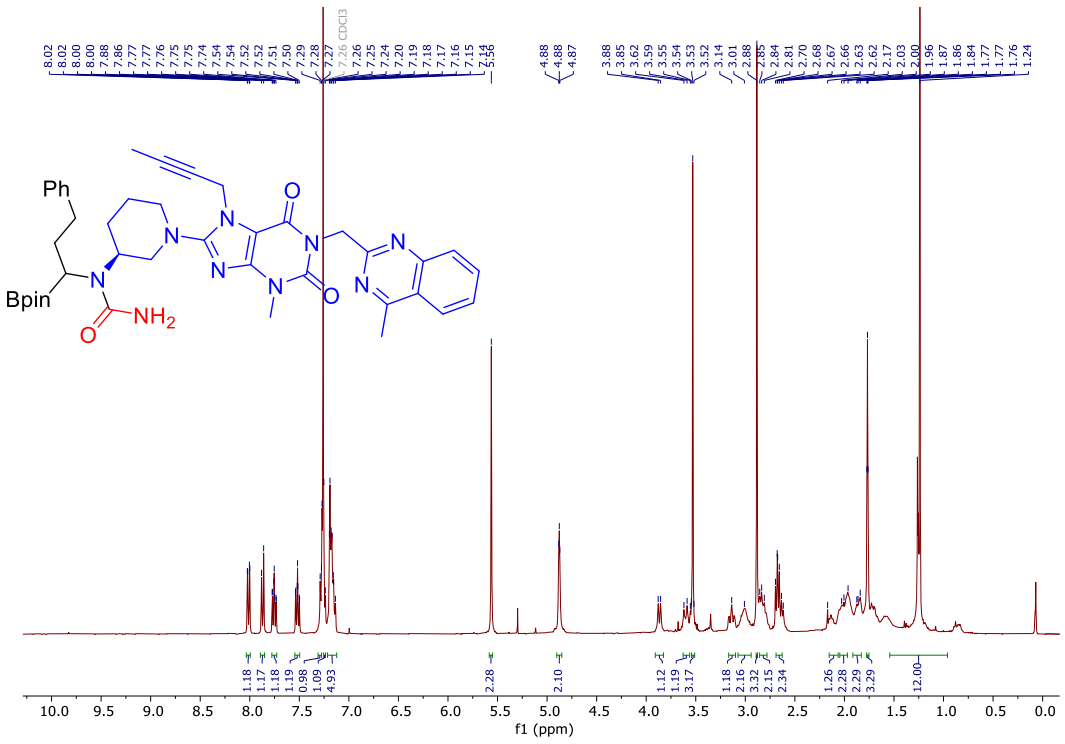

O
NH2
Bpin
N
O
O
Ph
NHBoc
f1 (ppm)

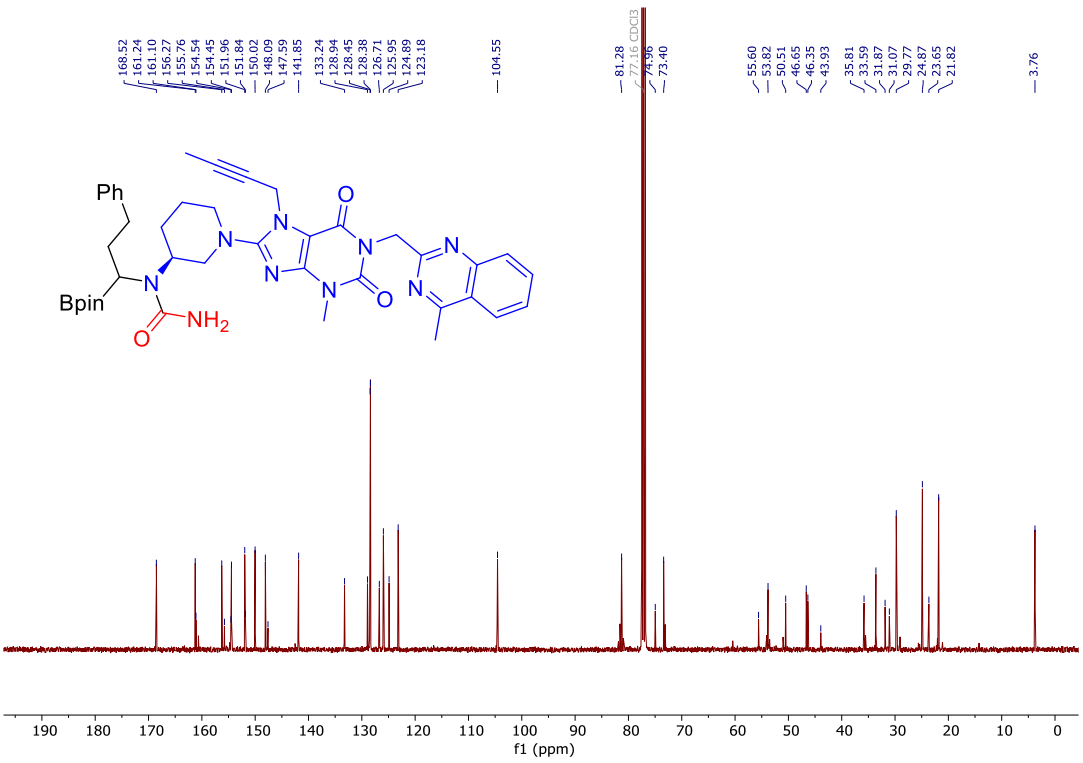

O
NH2
O
Bpin
N
O
Ph
NHBoc
300000
250000
200000
150000
100000
50000
0
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
f1 (ppm)

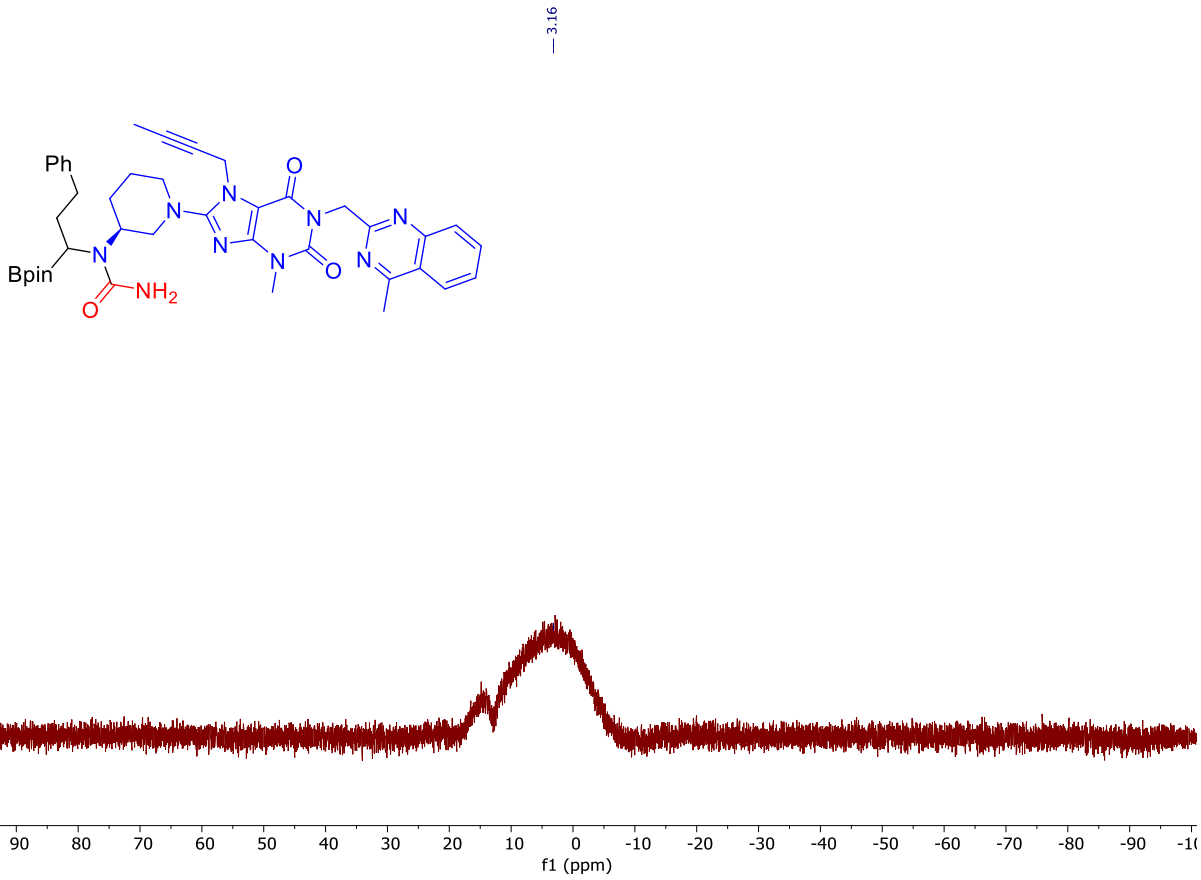

Ph
Bpin
N
O
NH2
f1 (ppm)

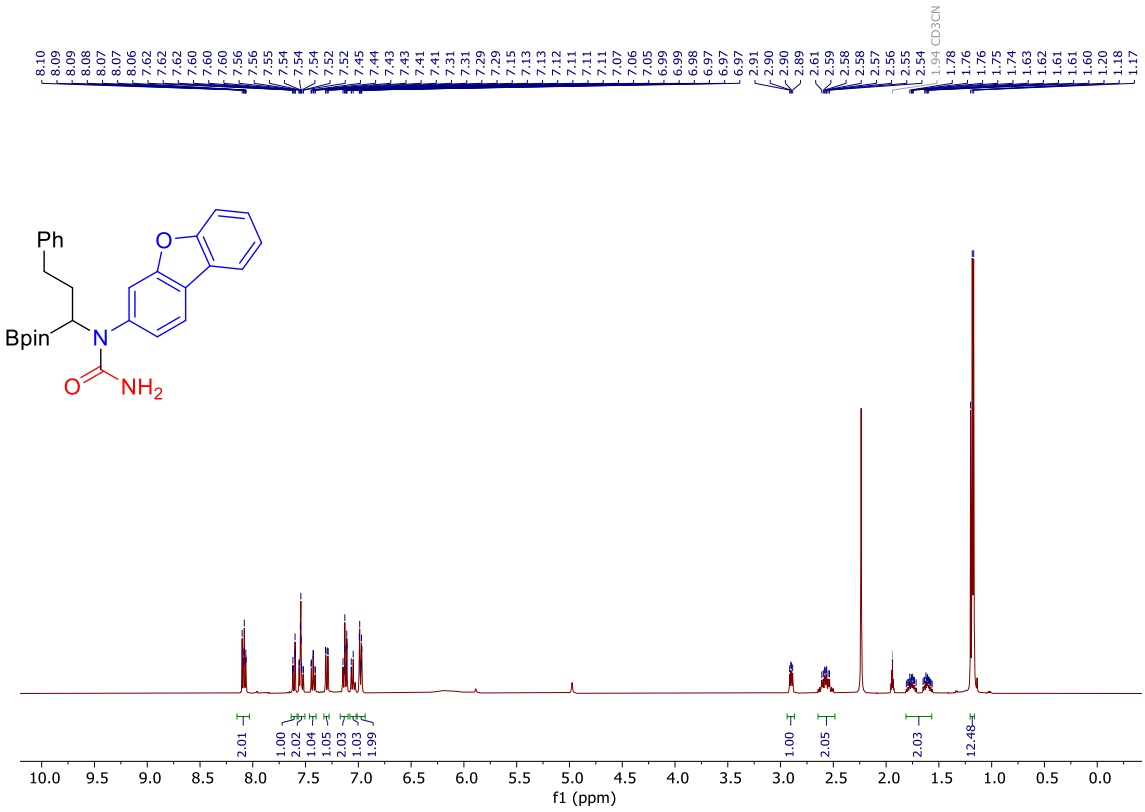

Ph
Bpin
N
O
NH2
f1 (ppm)

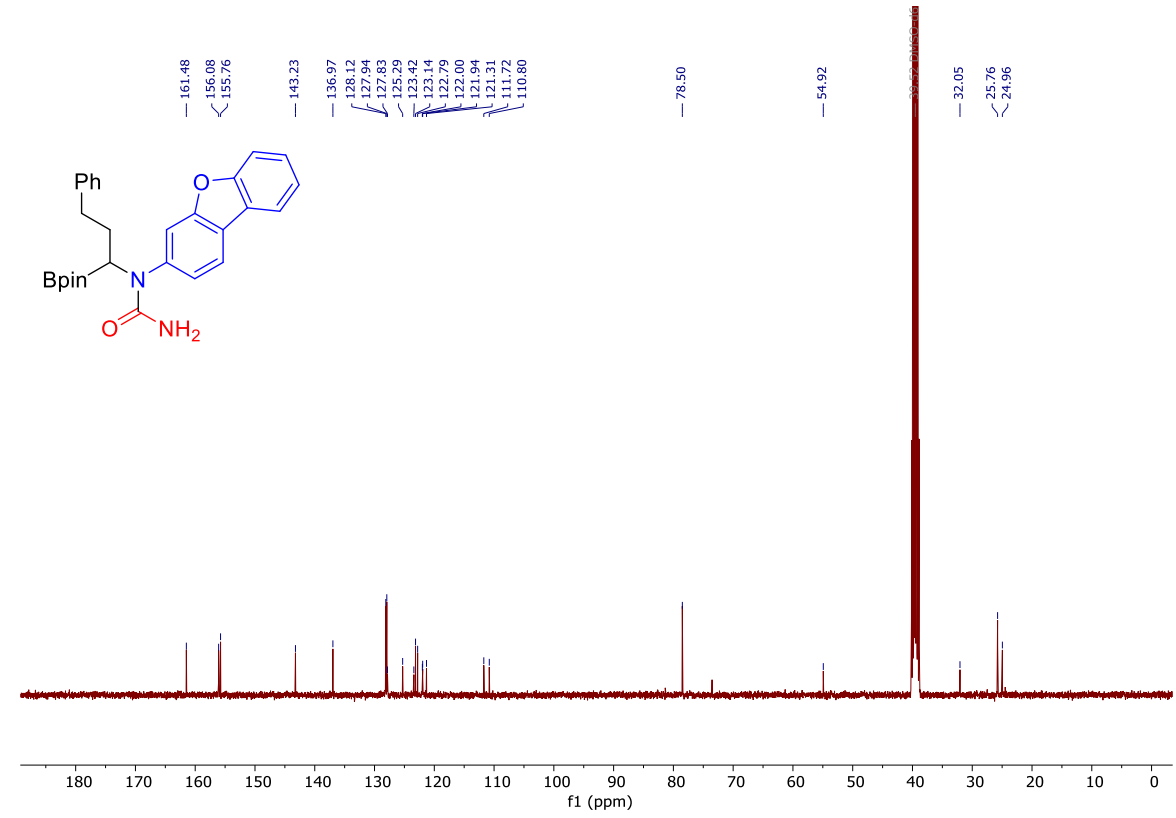

Ph
Bpin
N
O
NH2
N
O
O
O
10.94
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

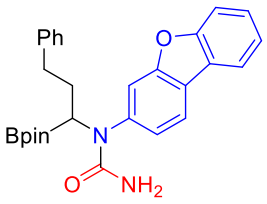

Ph
Bpin
NH2
O
f1 (ppm)


Ph
Bpin
NH2
O
f1 (ppm)

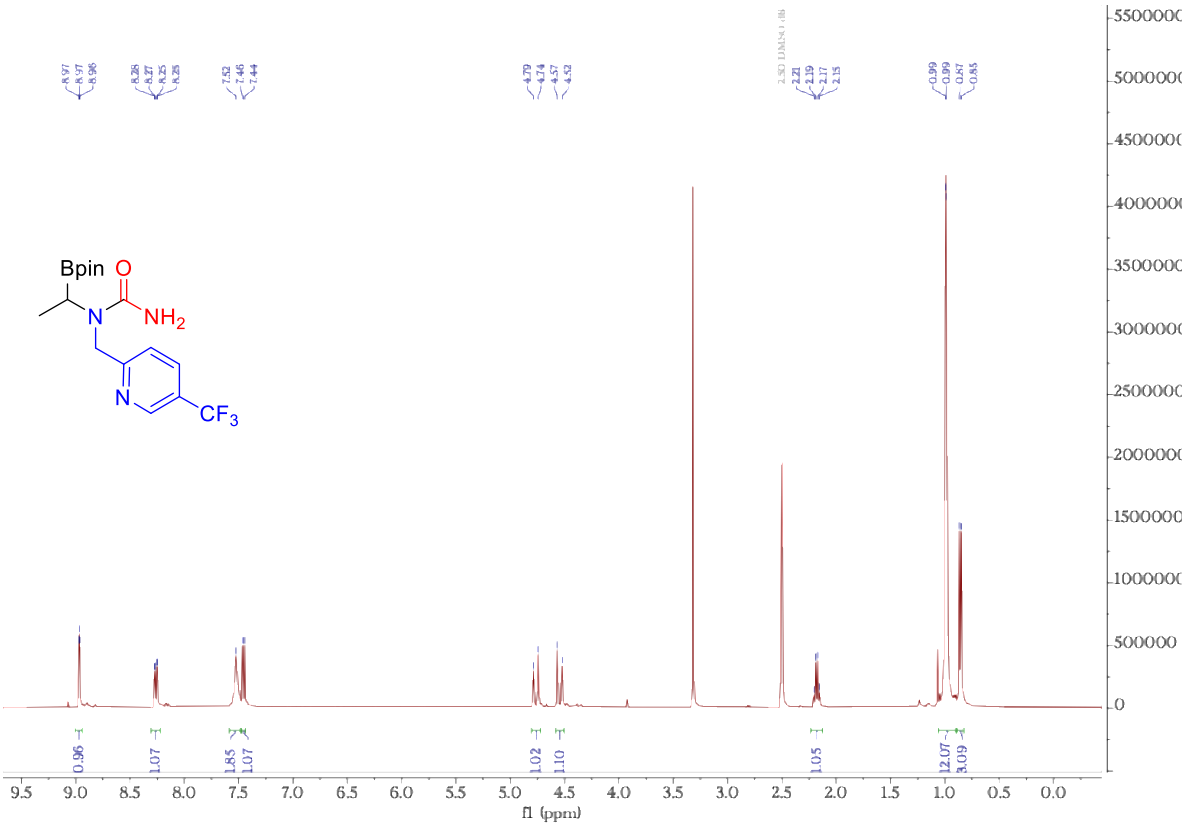

3.16
Ph
Bpin
N
O
NH2
f1 (ppm)

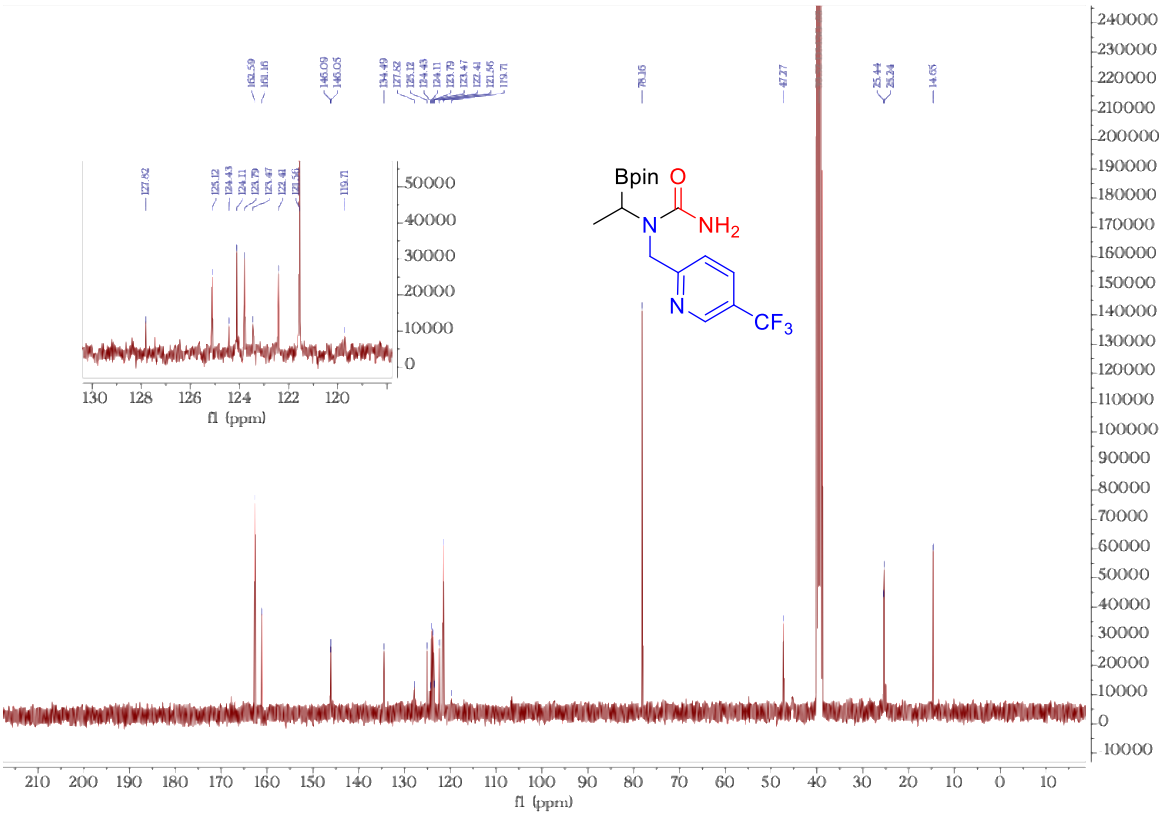

Ph
O
Bpin
N
O
NH2
f1 (ppm)

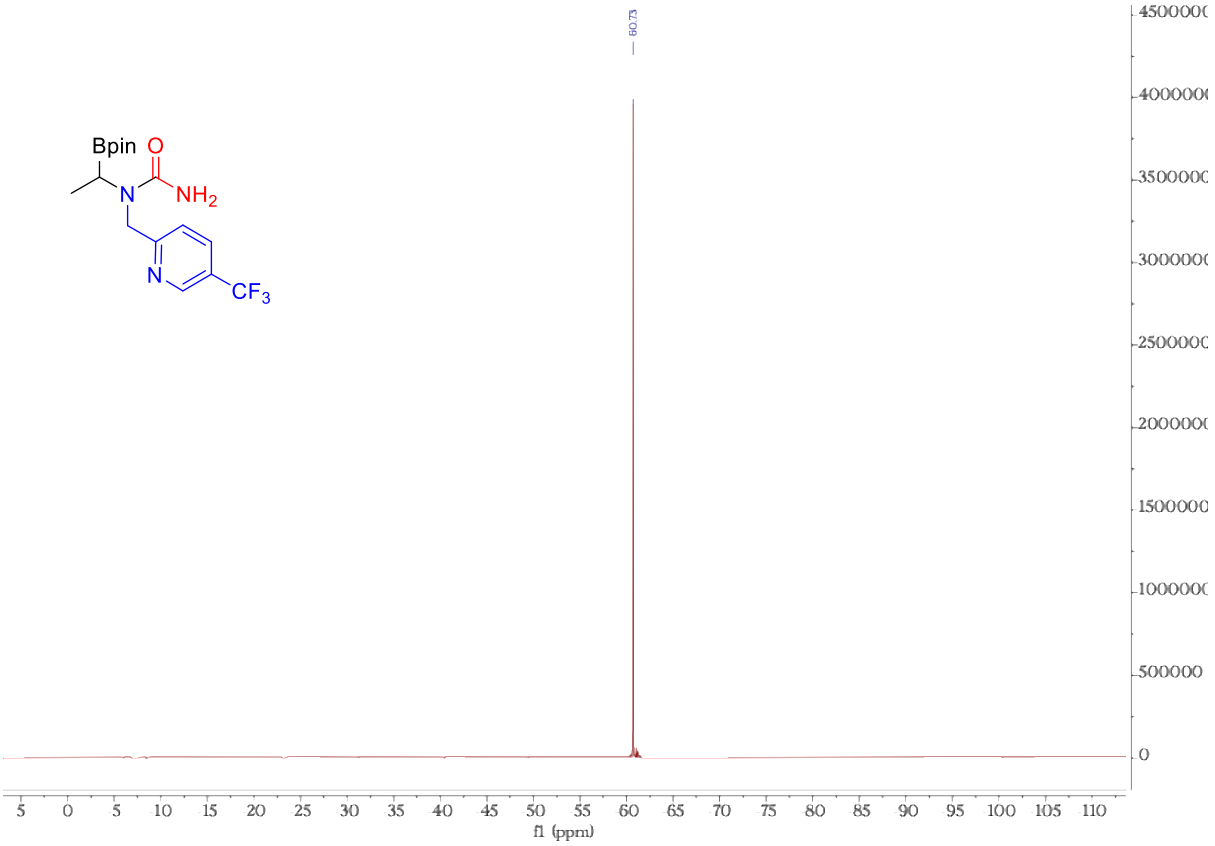

Ph
O
Bpin
N
O
NH2
f1 (ppm)

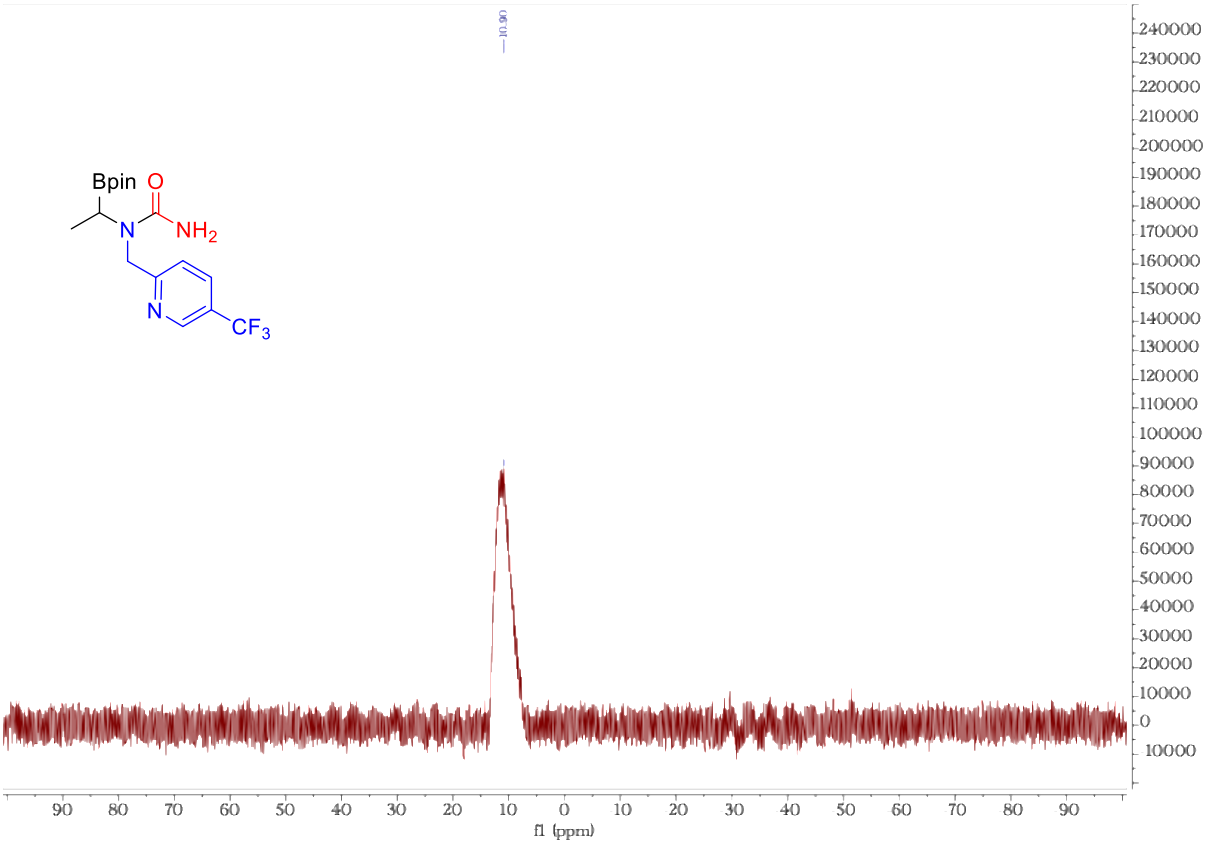

Ph
O
Bpin
N
O
NH2

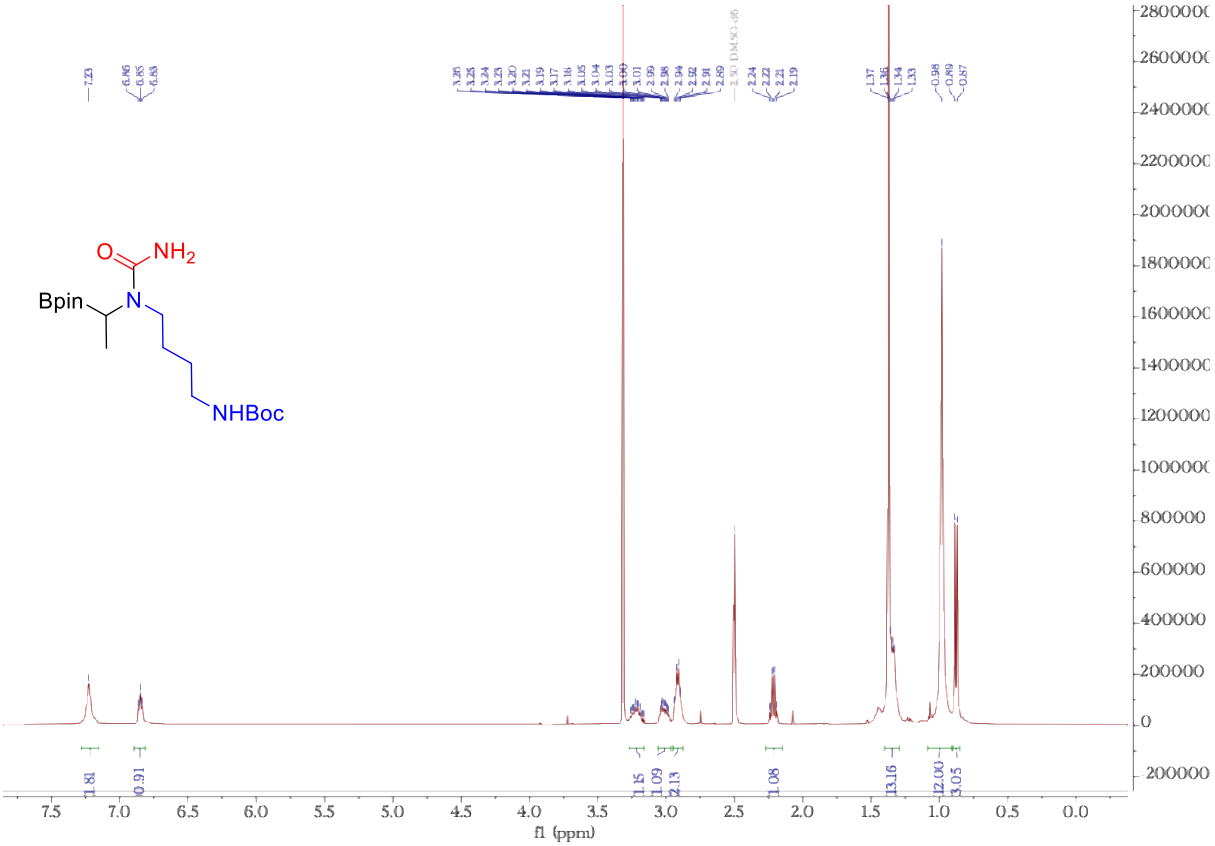
11.91
55
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
f1 (ppm)

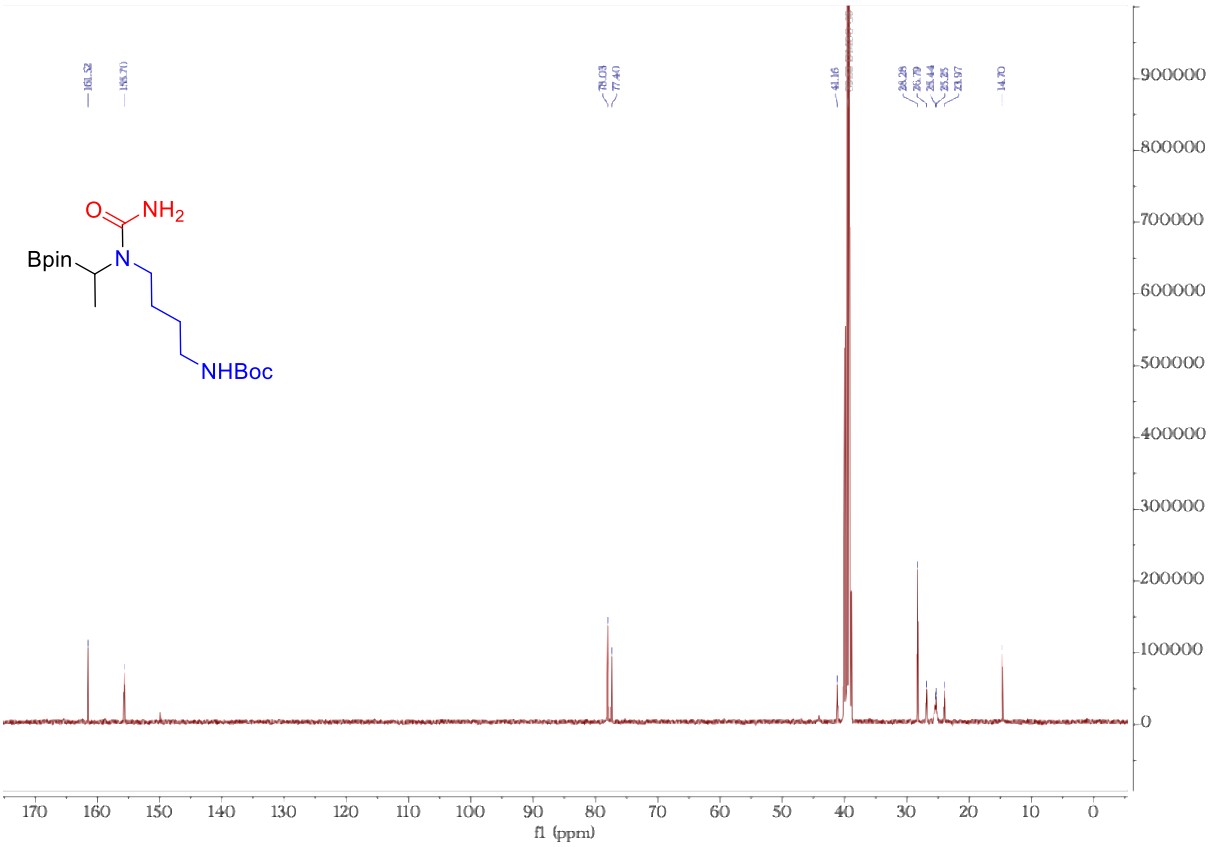

Bpin
O
NH2
N
N
CF3
f1 (ppm)

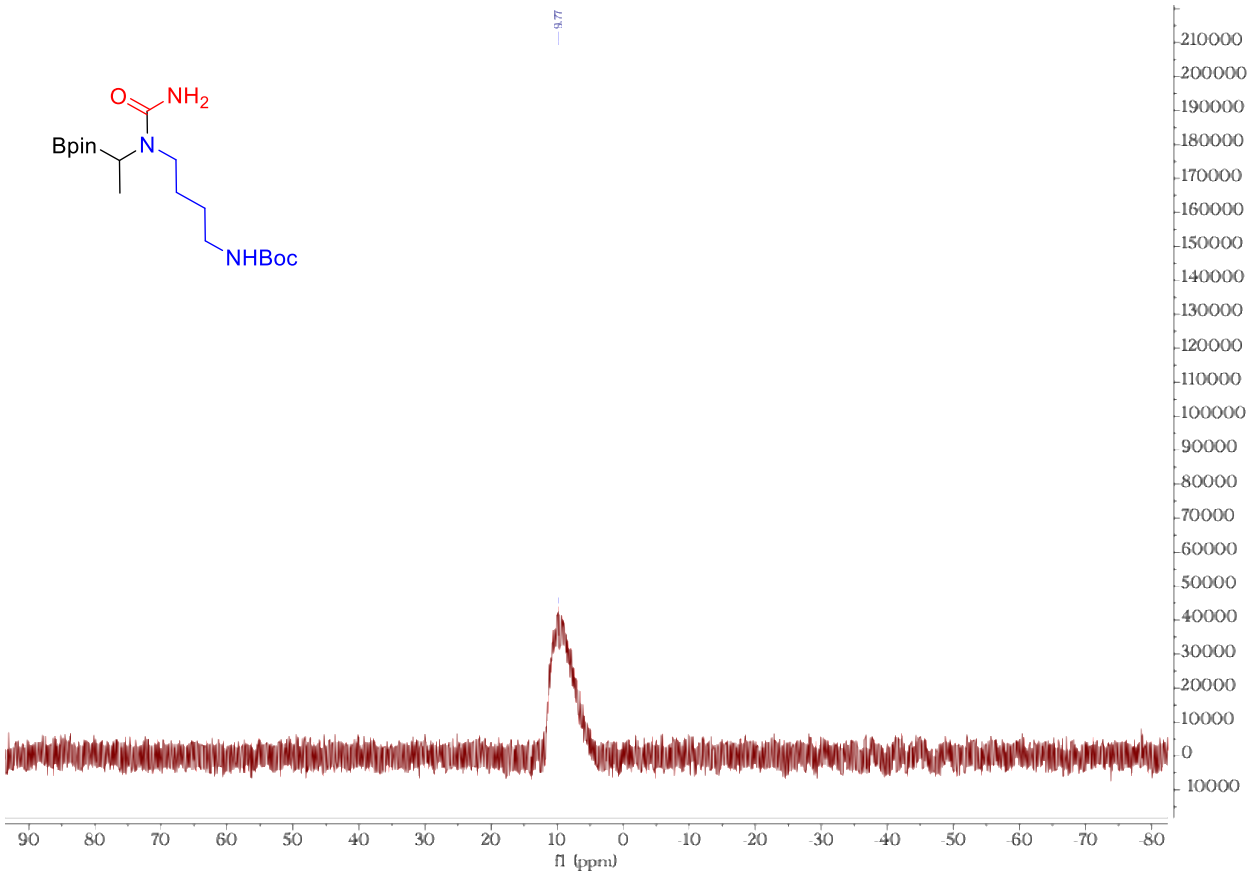

Bpin
O
NH2
N
N
CF3
f1 (ppm)

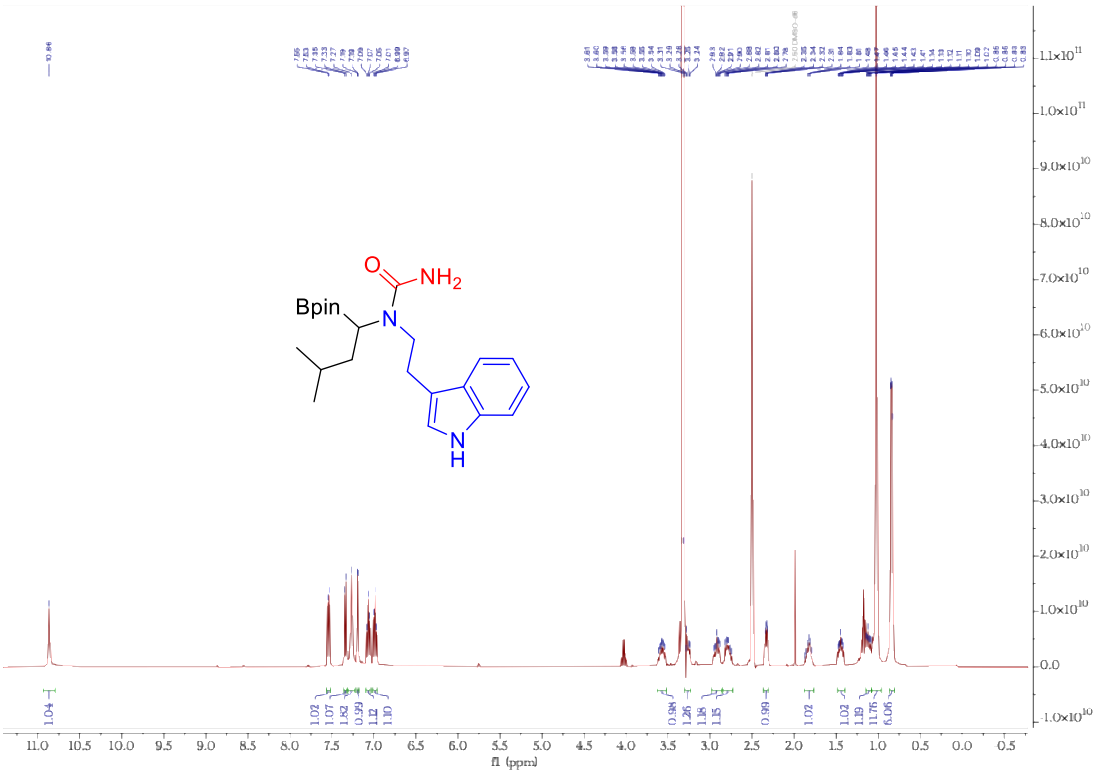

60.73
Bpin
O
NH2
N
N
CF3
f1 (ppm)

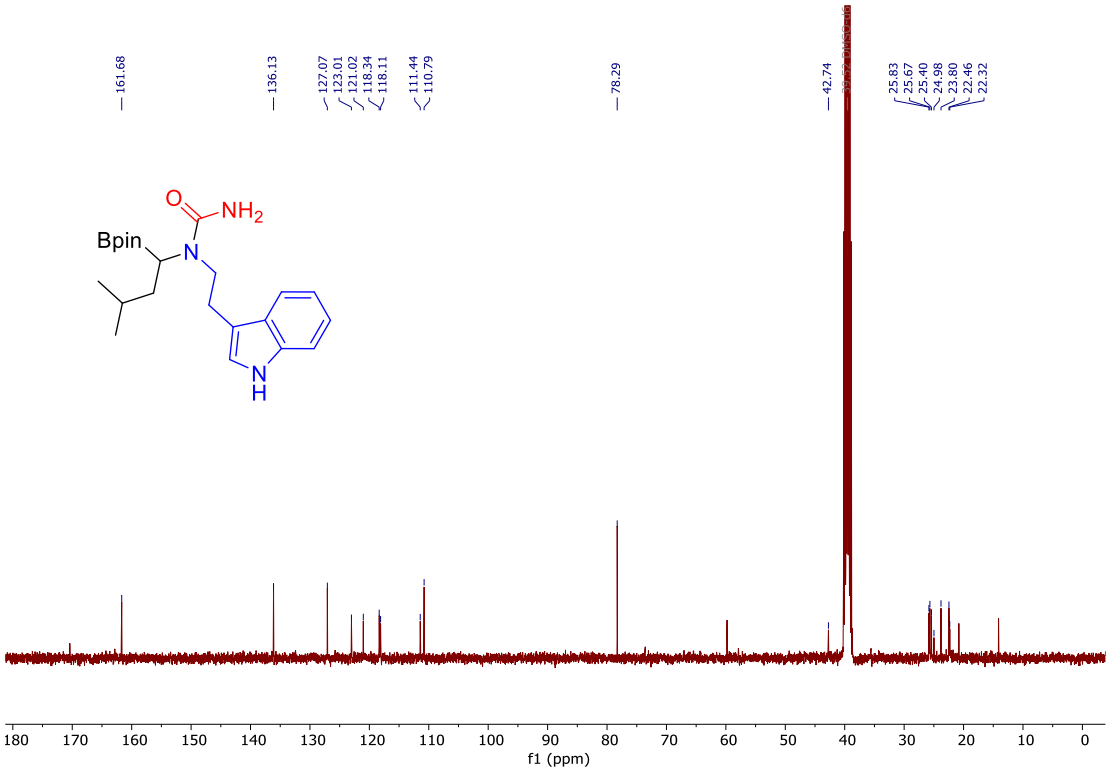

10.90
Bpin
O
NH2
N
N
CF3
f1 (ppm)

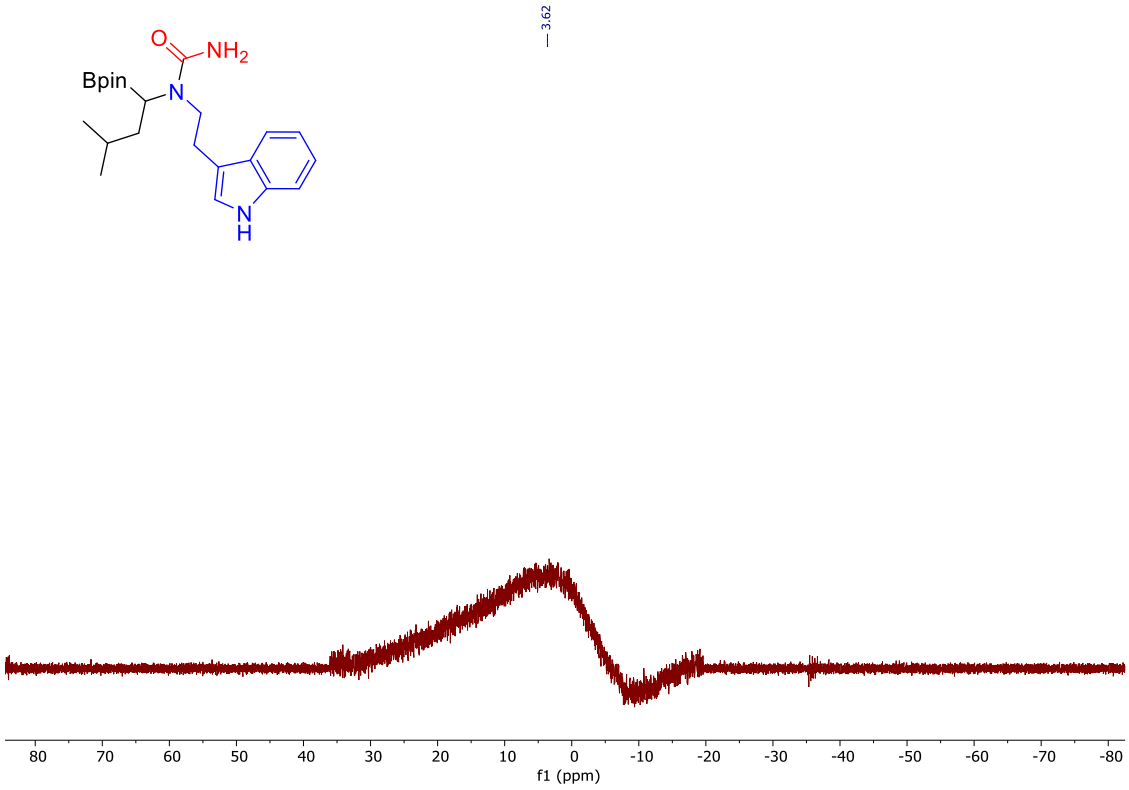

O
NH2
Bpin
N
NHBoc
f1 (ppm)


O
NH2
Bpin
N
NHBoc
f1 (ppm)


O
NH2
Bpin
N
NHBoc
9.77
210000
200000
190000
180000
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
f1 (ppm)


O
NH2
Bpin
N
N
H
f1 (ppm)


161.68
136.13
127.07
123.01
121.02
118.34
118.11
111.44
110.79
78.29
42.74
25.83
25.67
25.40
24.98
23.80
22.46
22.32
O
NH2
Bpin
N
N
H
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


3.62
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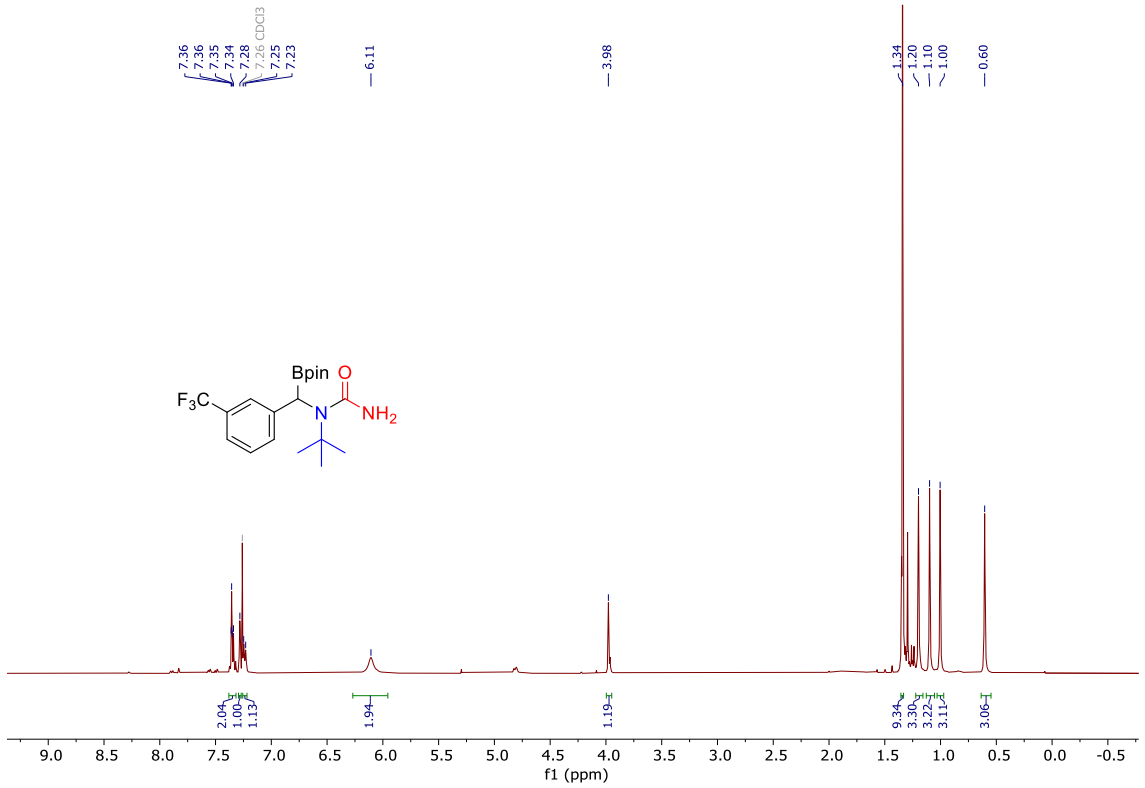
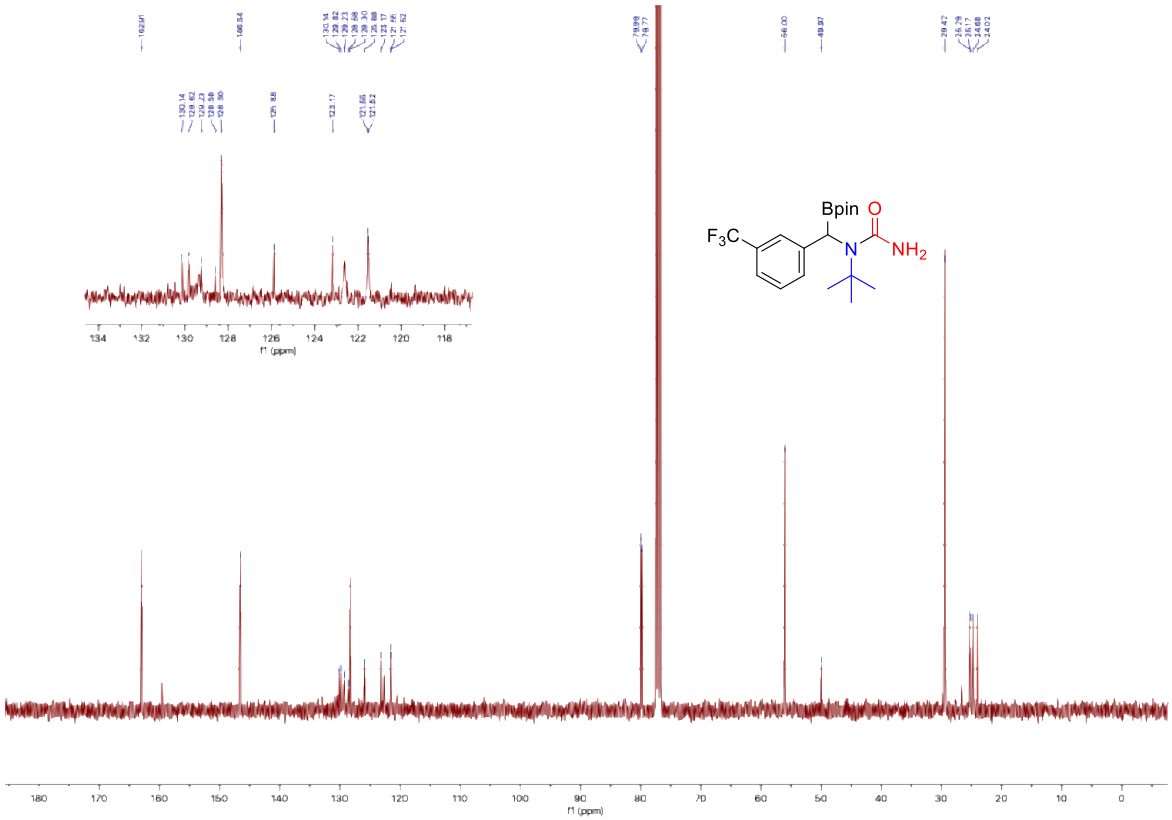
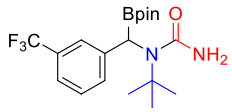
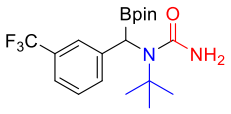
NH2
Bpin
N
N
H
80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80
f1 (ppm)

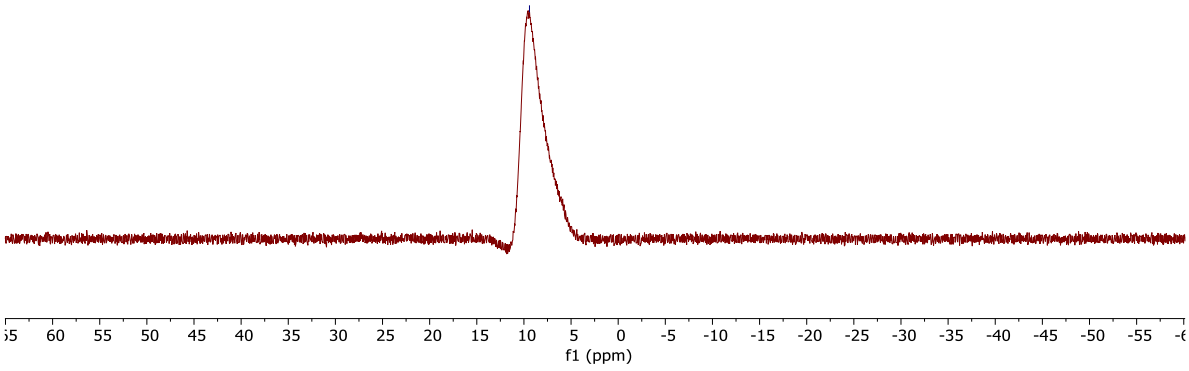

7.36
7.36
7.35
7.34
7.28
7.26 CDCl3
7.25
7.23
6.11
3.98
1.34
1.20
1.10
1.00
0.60
Bpin
O
F3C
N
NH2
2.04
1.00
1.13
1.94
1.19
9.34
3.30
3.22
3.11
3.06
f1 (ppm)


Bpin
O
F3C
N
NH2
f1 (ppm)


Bpin
O
F3C
N
NH2

-62.53
9.41
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
f1 (ppm)


Bpin
O
F3C
N
NH2


60
55
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
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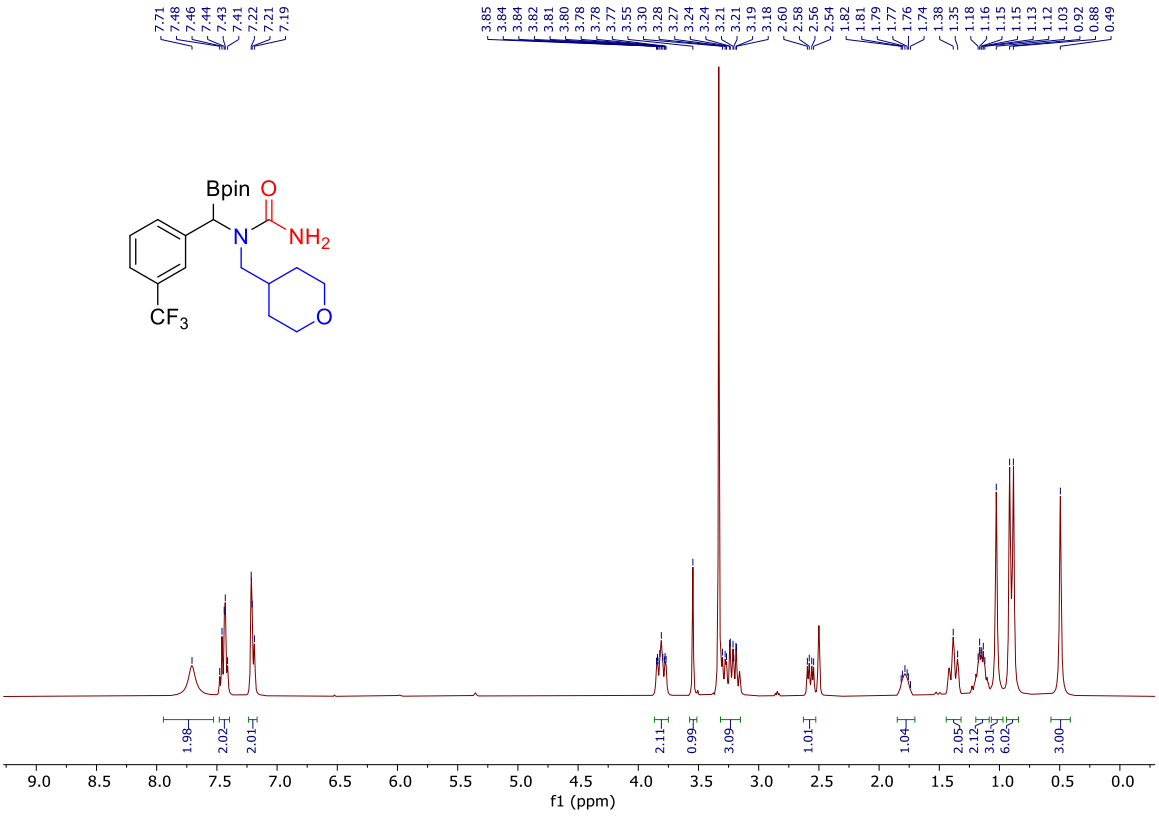
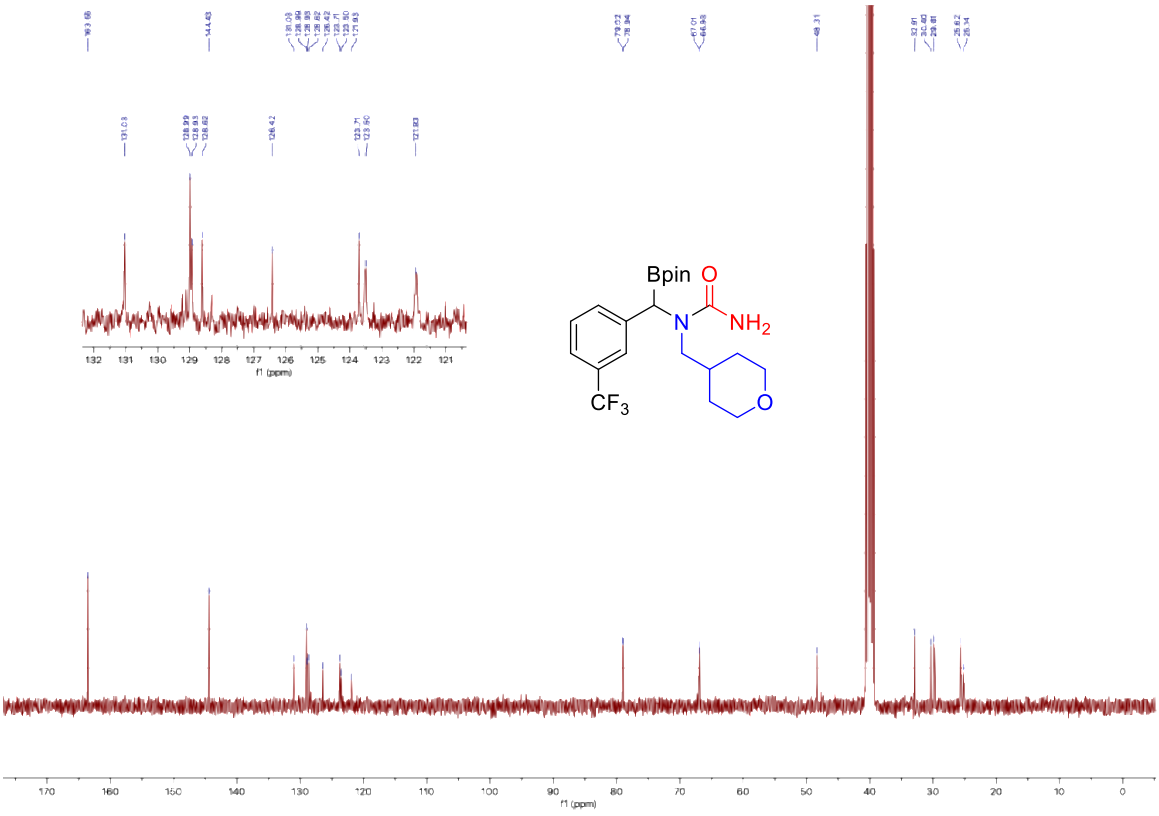
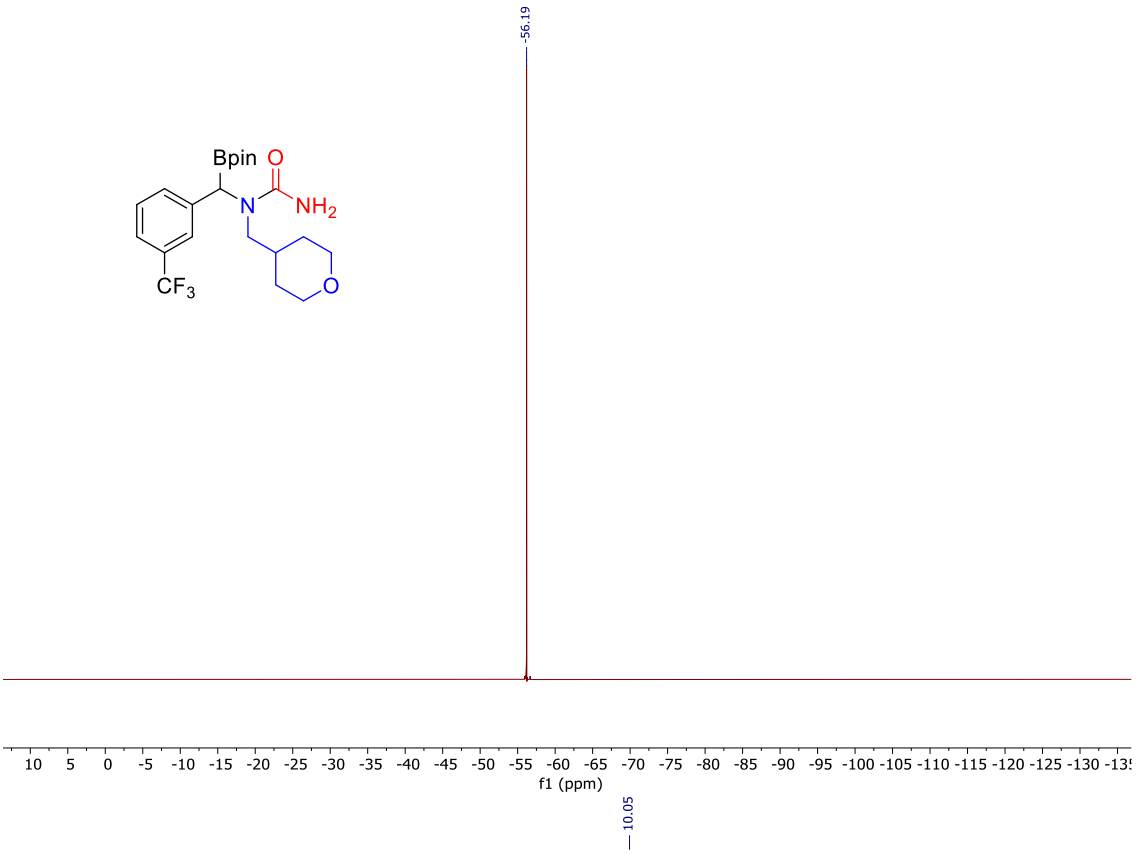
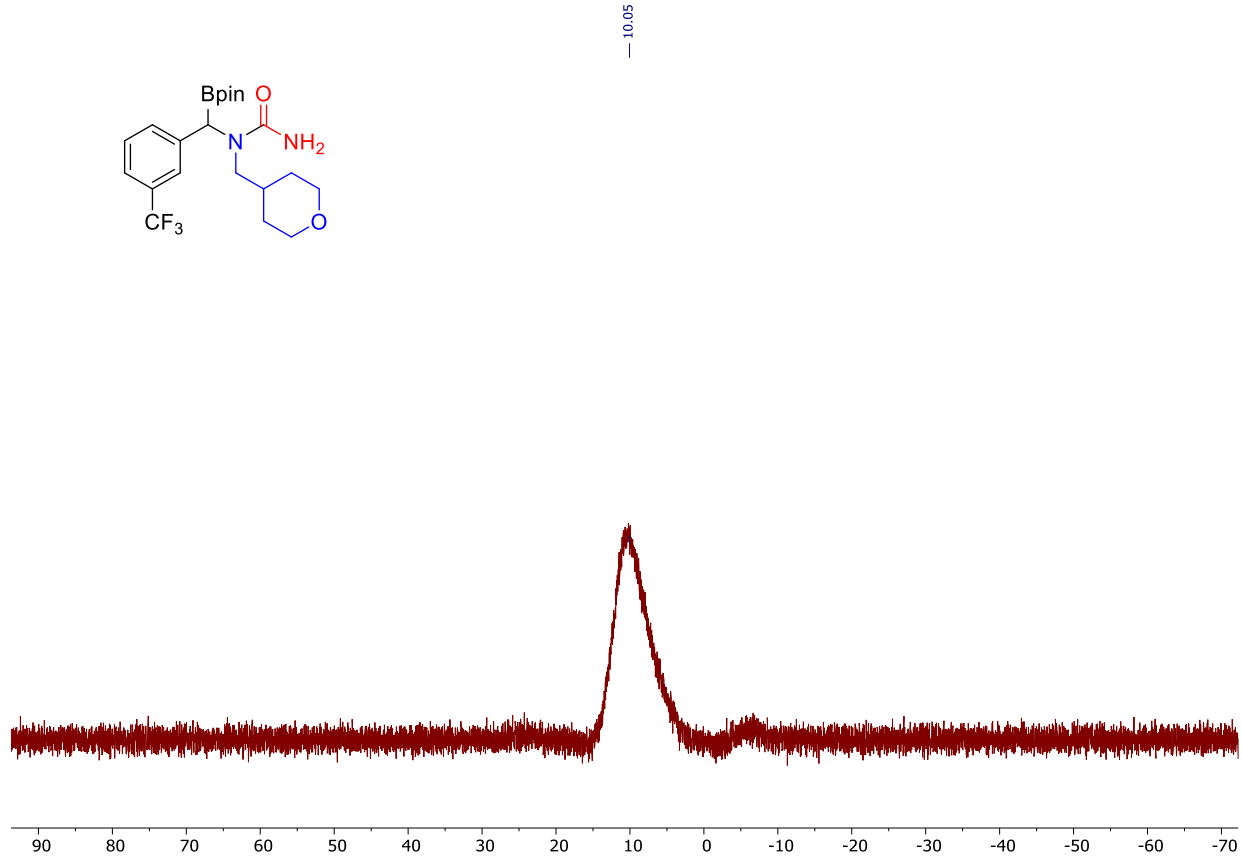
-35
-40
-45
-50
-55
f1 (ppm)


Bpin
O
N
NH2
CF3
O
f1 (ppm)


Bpin
O
N
NH2
CF3
O
f1 (ppm)


-56.19
Bpin
O
N
NH2
CF3
O
10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -13
f1 (ppm)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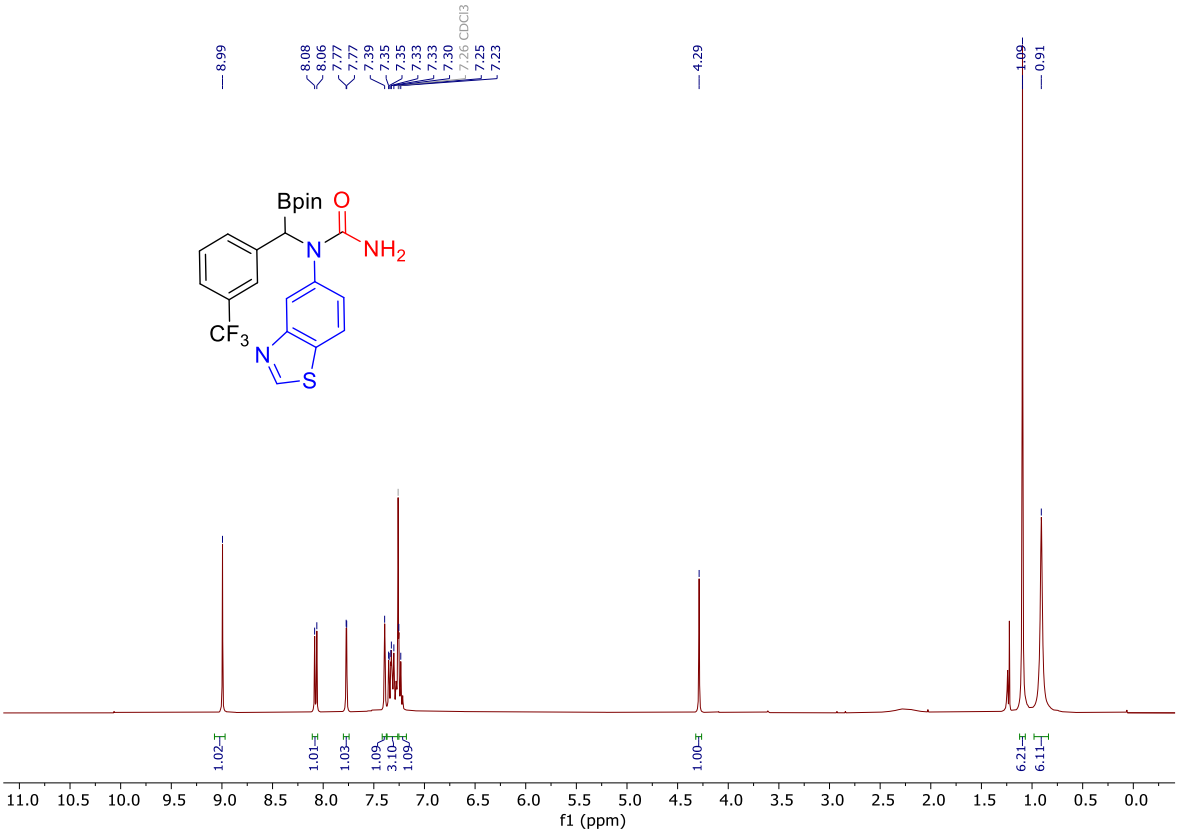
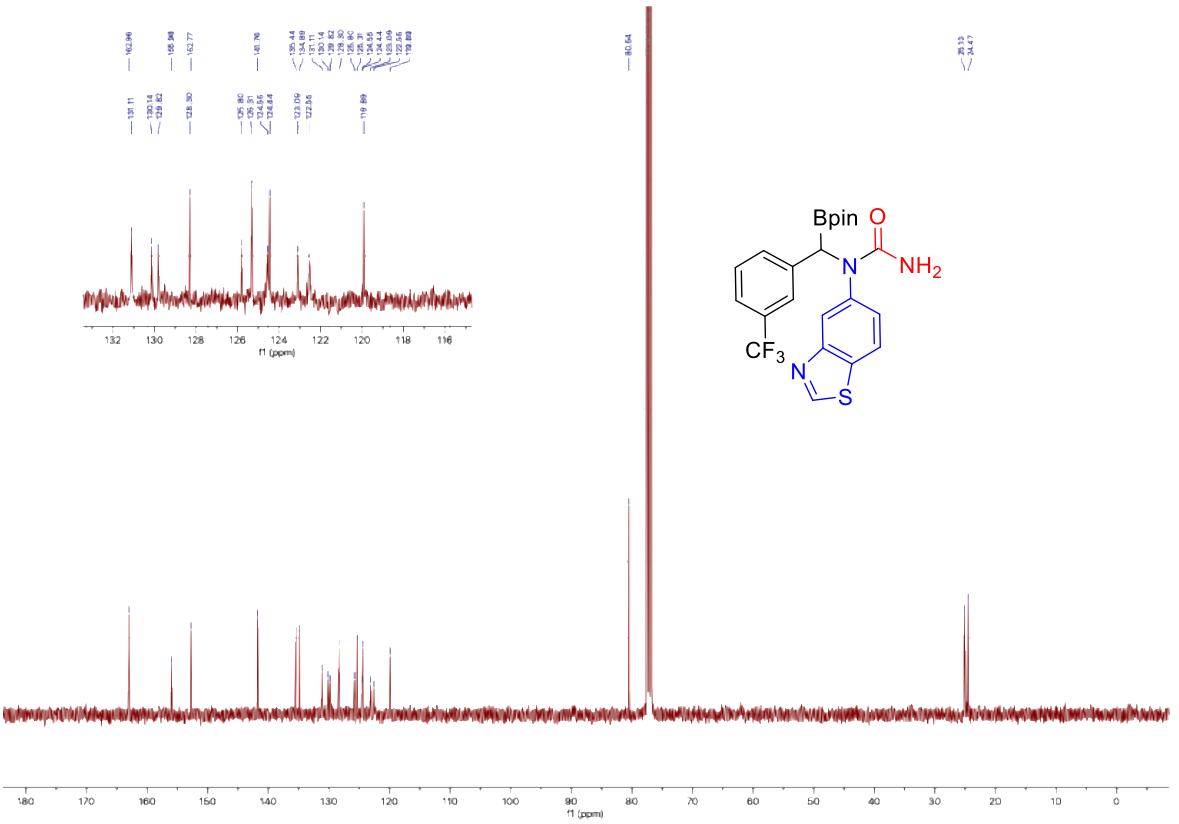
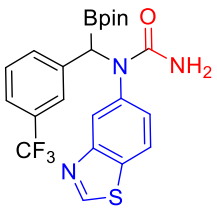
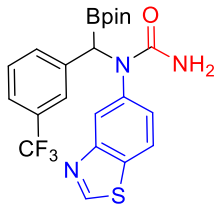
Bpin
O
N
NH2
CF3
O
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70


8.99
8.08
8.06
7.77
7.77
7.39
7.35
7.35
7.33
7.33
7.30
7.26 CDCl3
7.25
7.23
4.29
1.09
0.91
Bpin
O
N
NH2
CF3
N
S
1.02
1.01
1.03
1.09
3.10
1.09
1.00
6.21
6.11
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

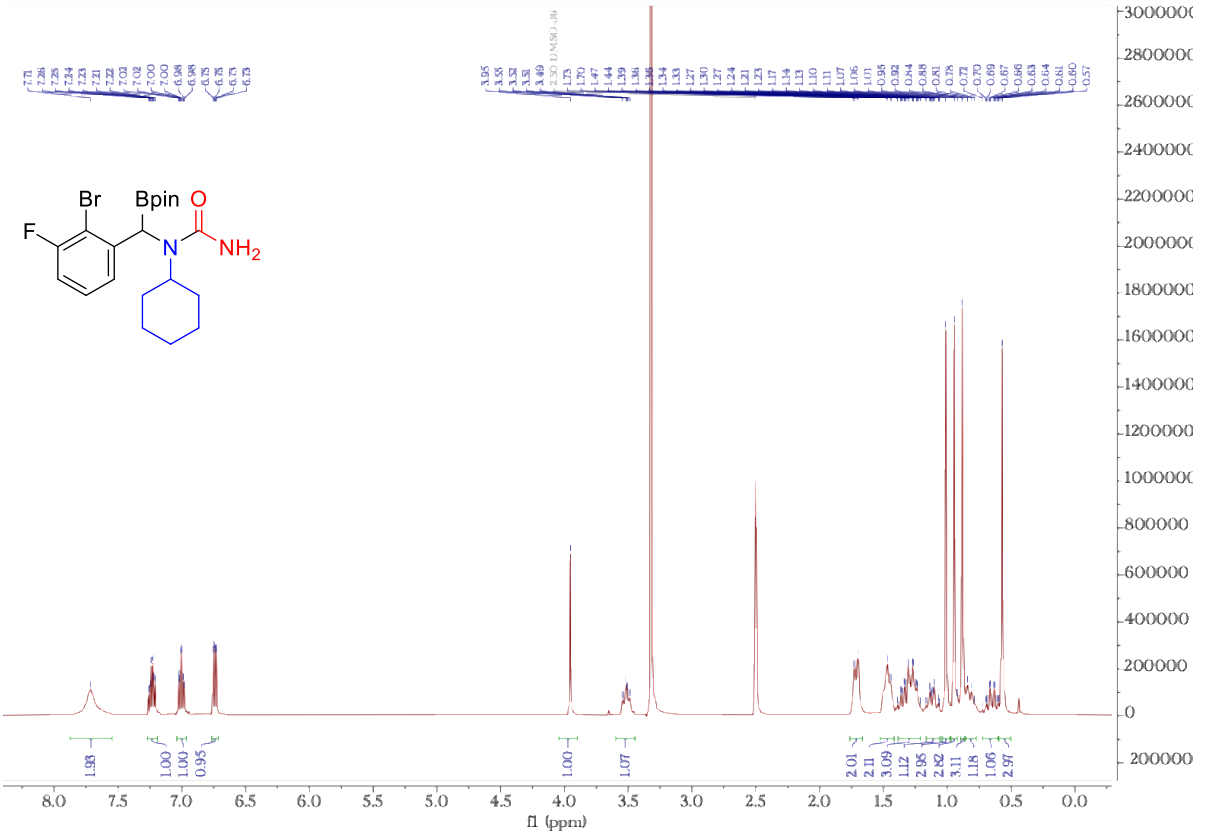

162.96
158.98
142.77
141.76
135.44
134.89
131.11
130.14
129.82
128.30
126.86
126.31
124.46
124.44
123.09
122.85
119.89
80.64
25.13
24.47
132 130 128 126 124 122 120 118 116
f1 (ppm)
Bpin
O
N
NH2
CF3
N
S
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

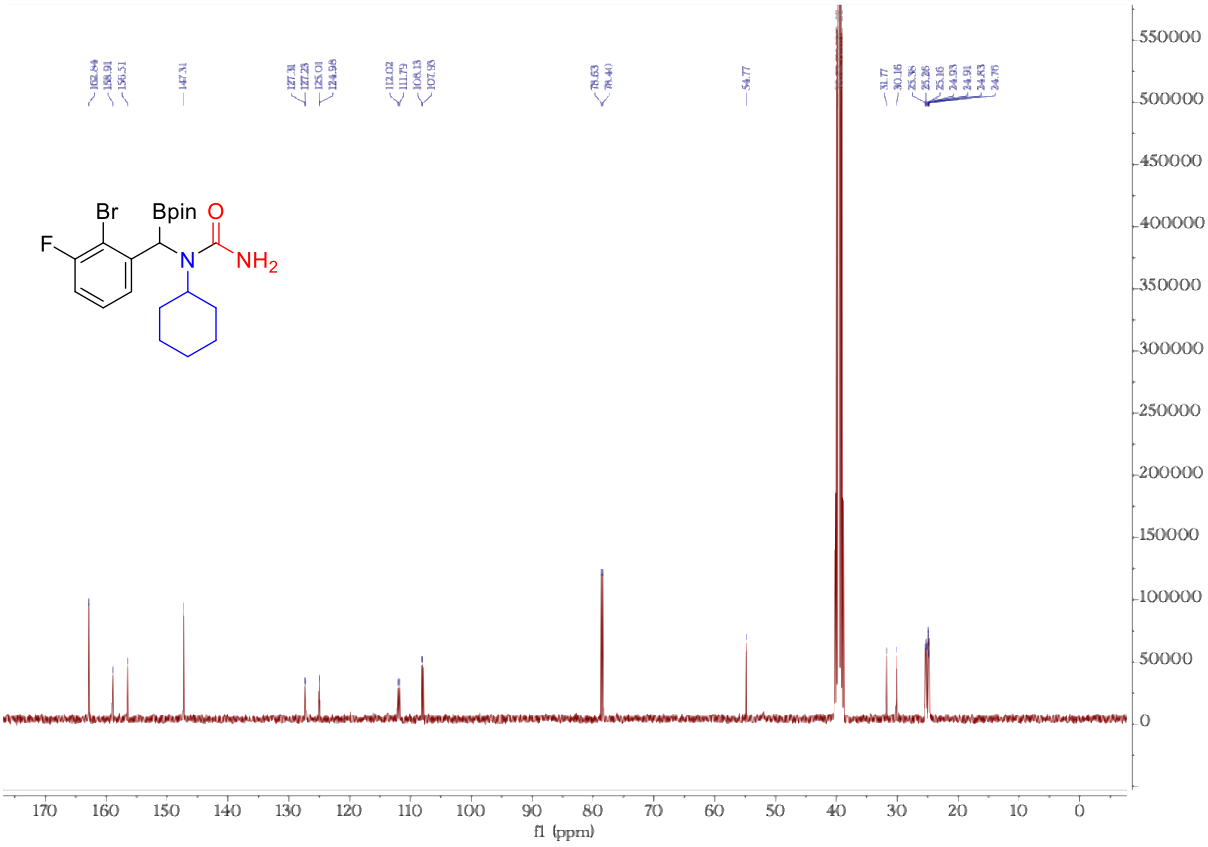

Bpin
O
NH2
N
CF3
N
S

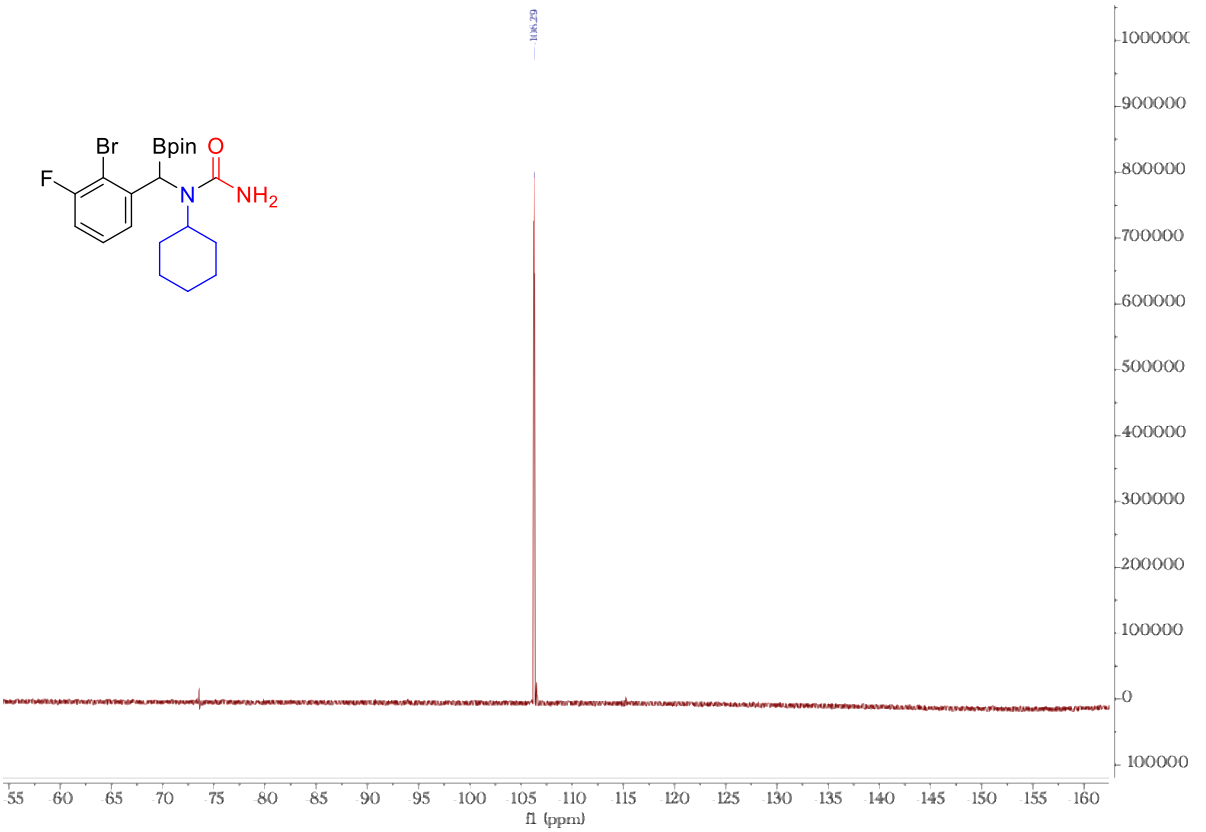
-62.53
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-1
f1 (ppm)

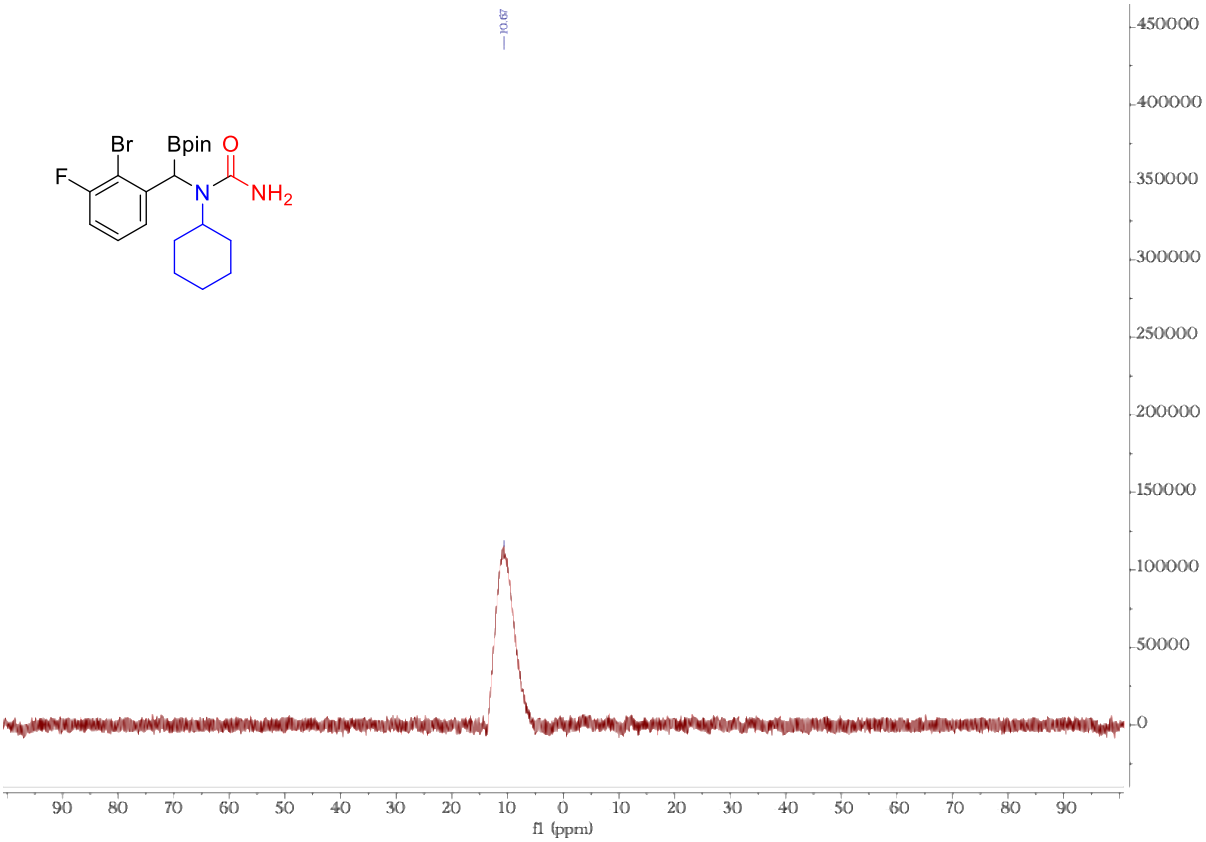

Bpin
O
NH2
N
CF3
N
S

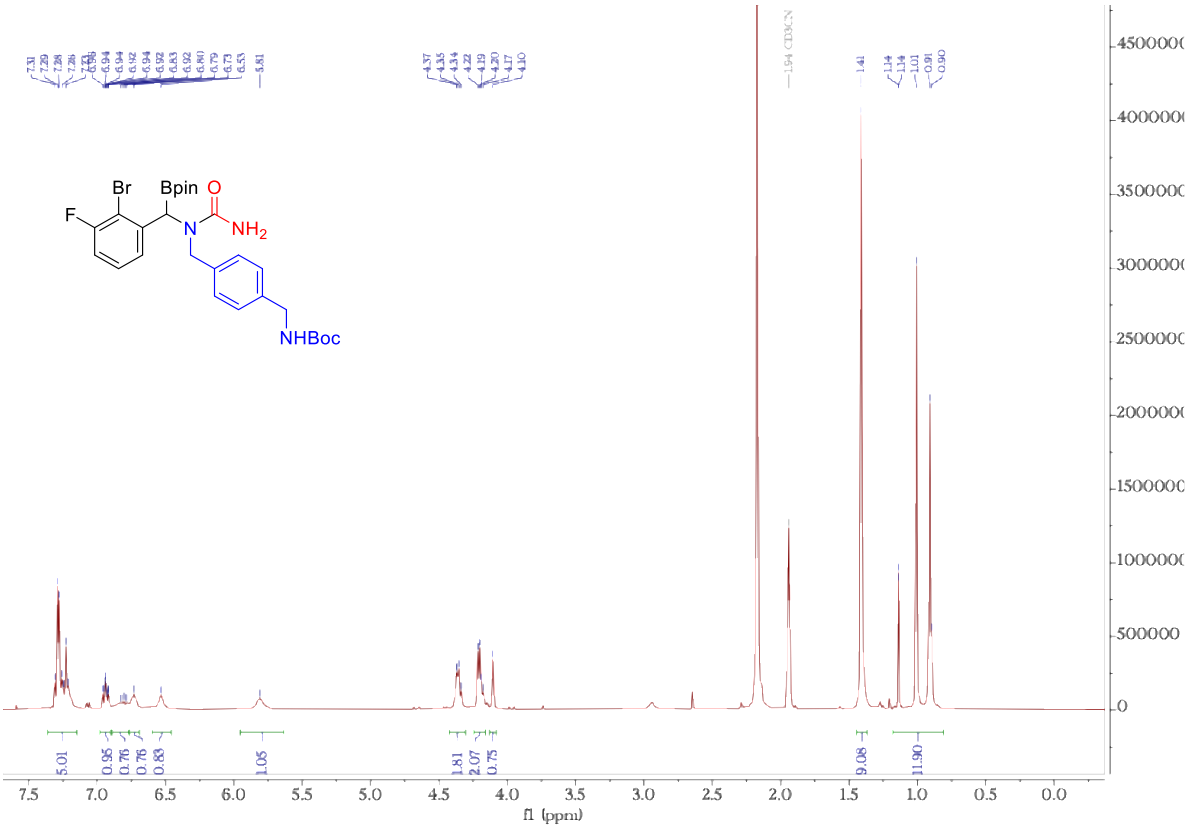
11.11
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)

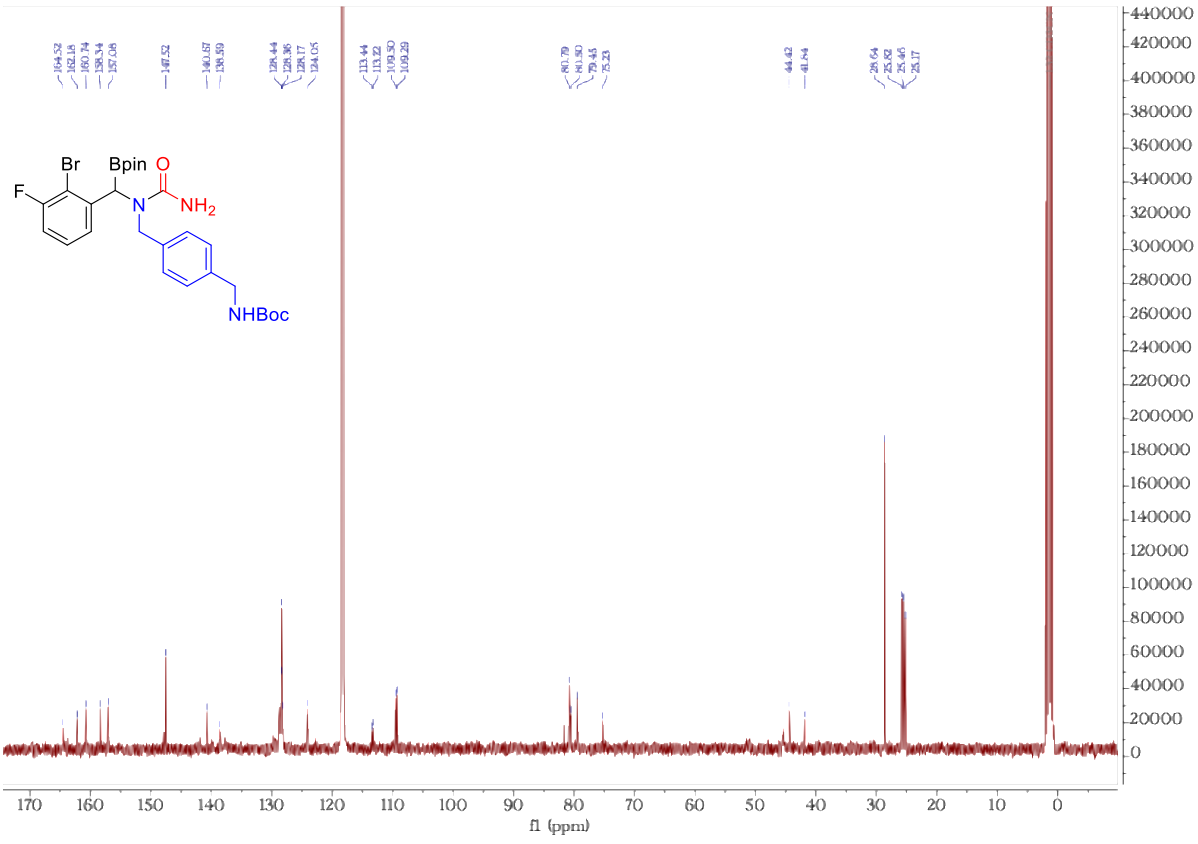

Br
Bpin
O
F
N
NH2
f1 (ppm)

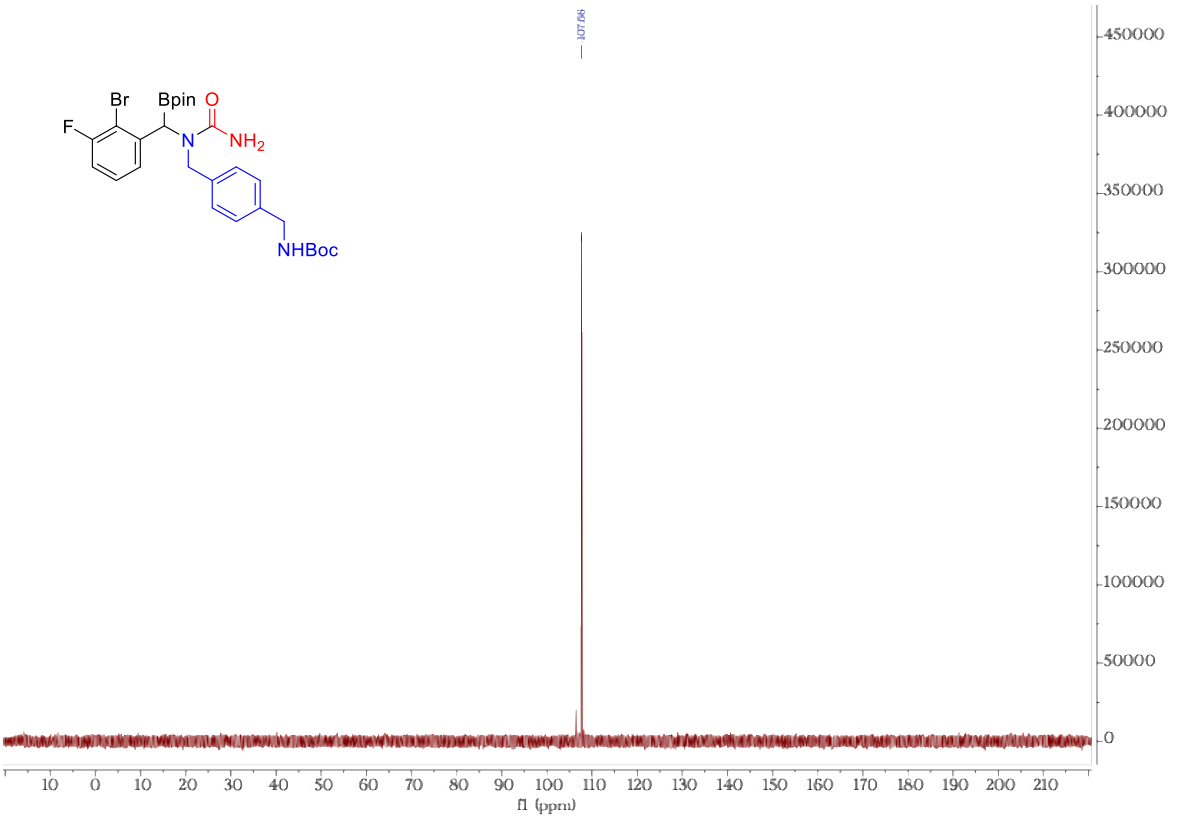

Br
Bpin
O
F
N
NH2
f1 (ppm)

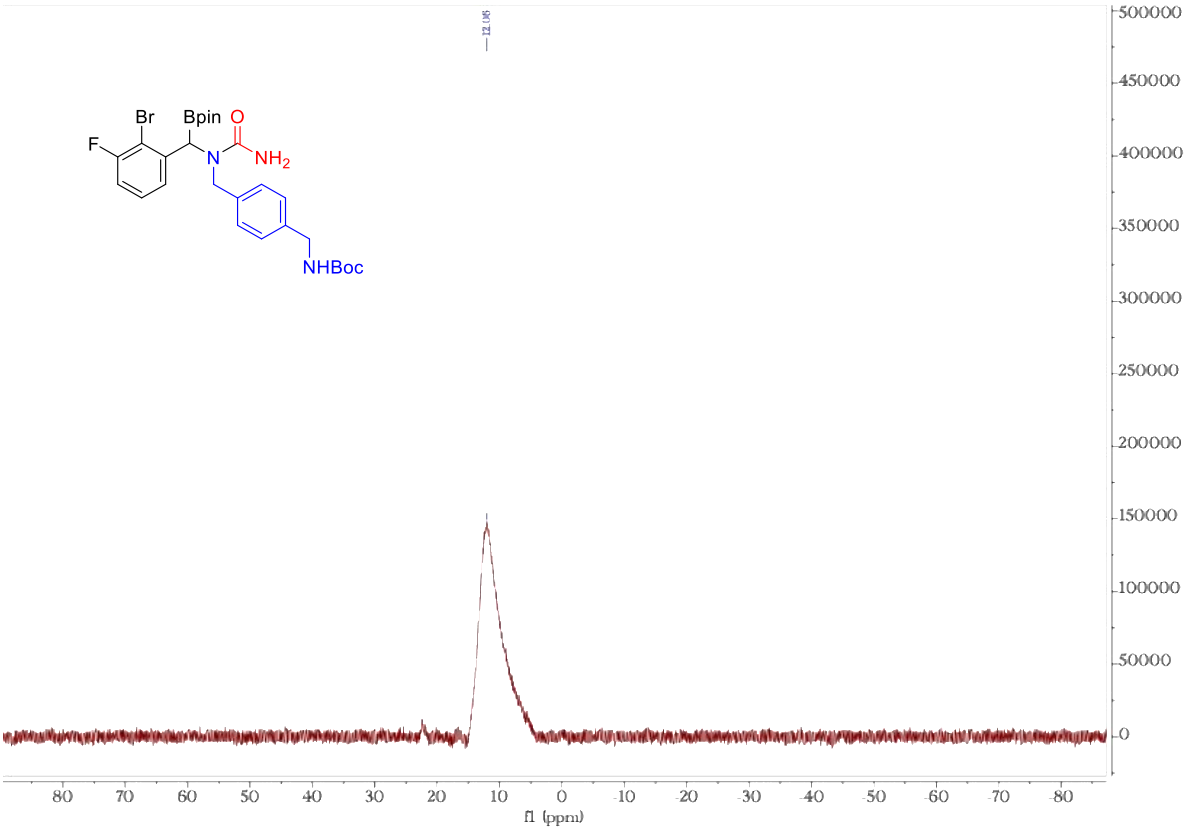

Br
Bpin
O
F
N
NH2
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
100000
55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160
f1 (ppm)

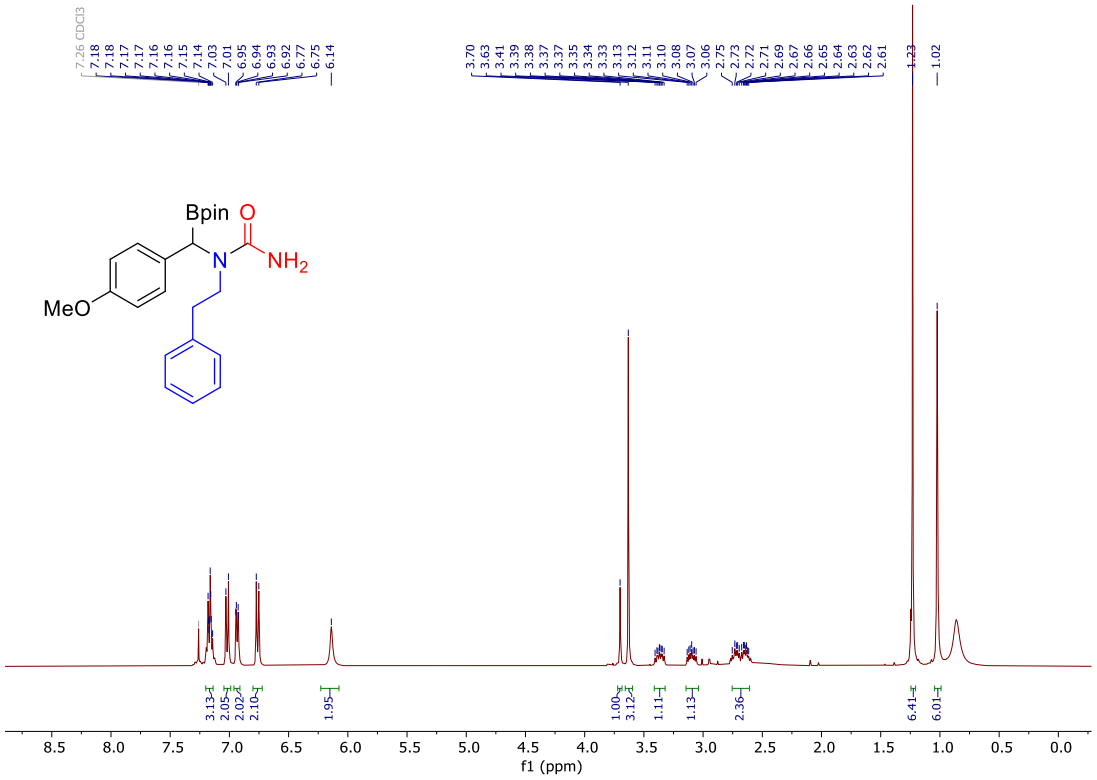

Br
Bpin
O
F
N
NH2
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
90 80 70 60 50 40 30 20 10 0 10 20 30 40 50 60 70 80 90
f1 (ppm)

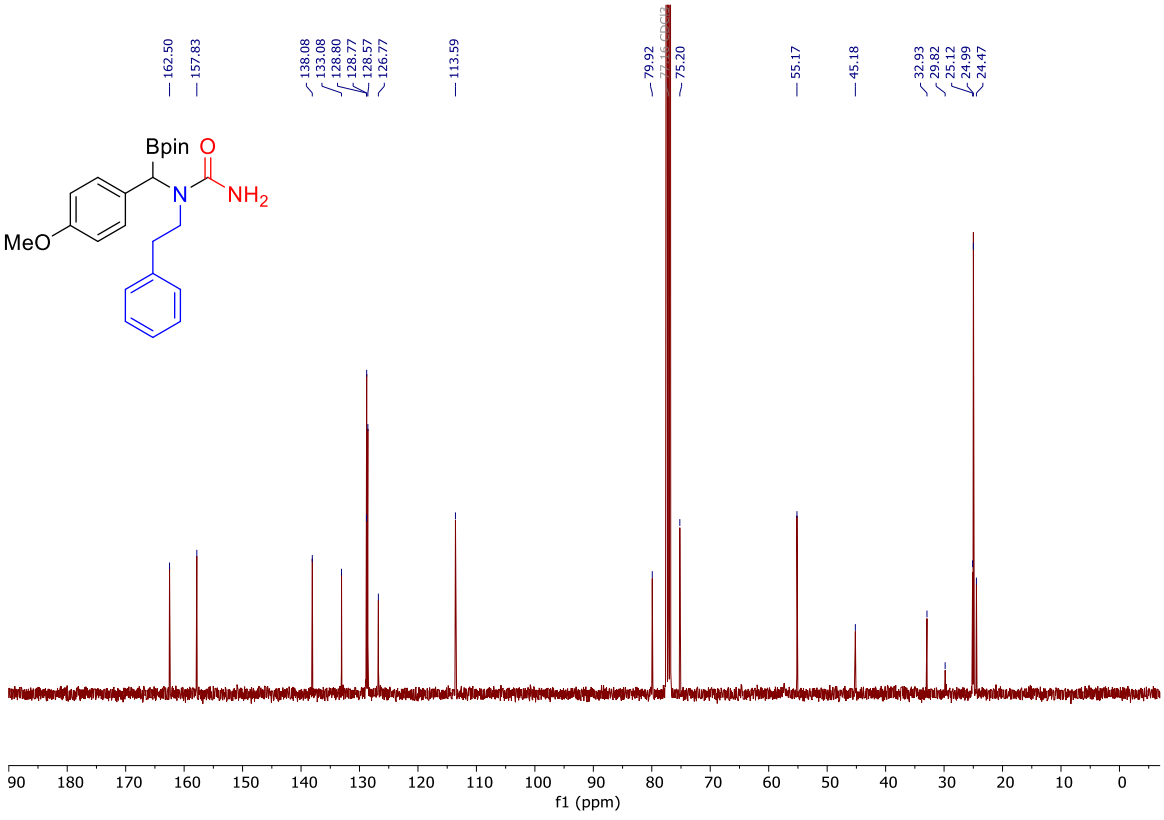

Br
Bpin
O
F
N
NH2
NHBoc
f1 (ppm)

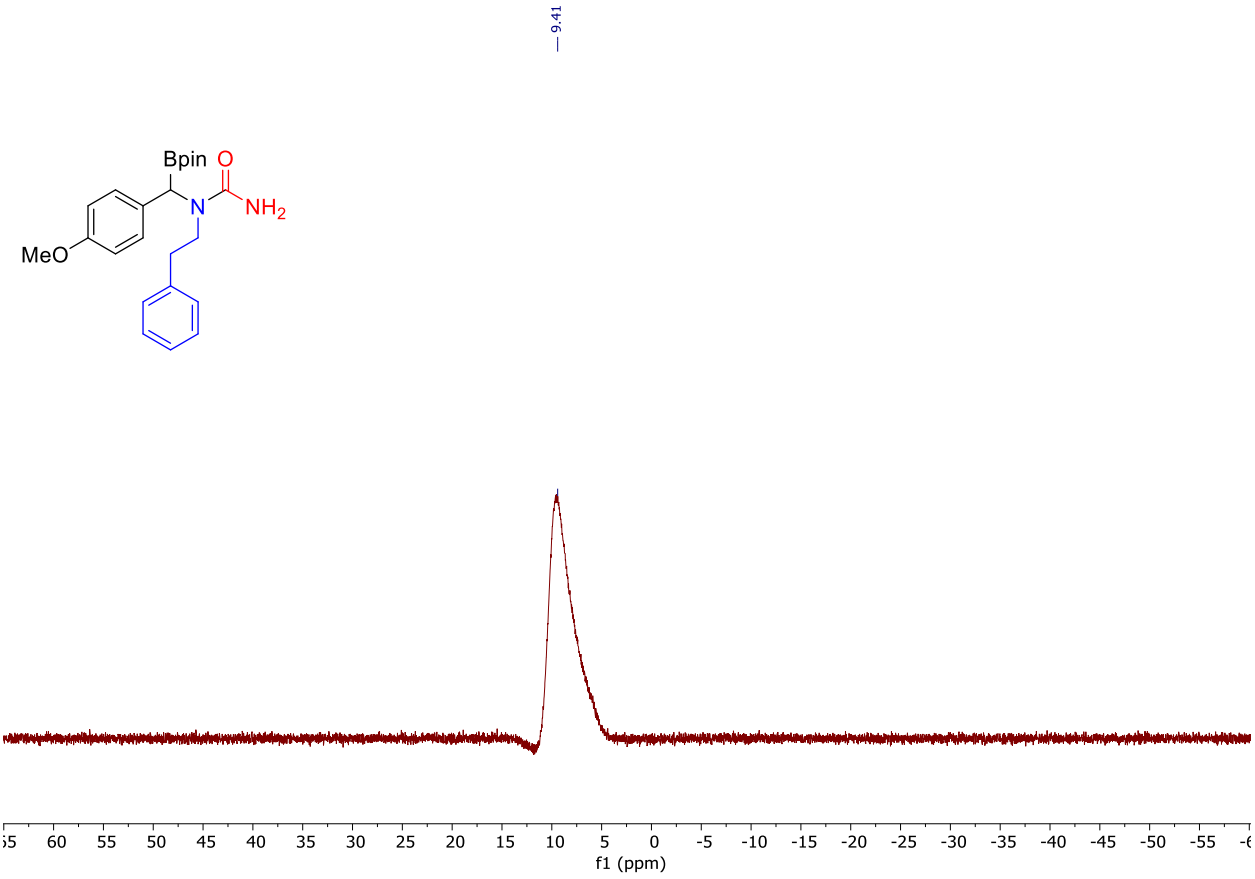

Br
Bpin
O
F
N
NH2
NHBoc
f1 (ppm)

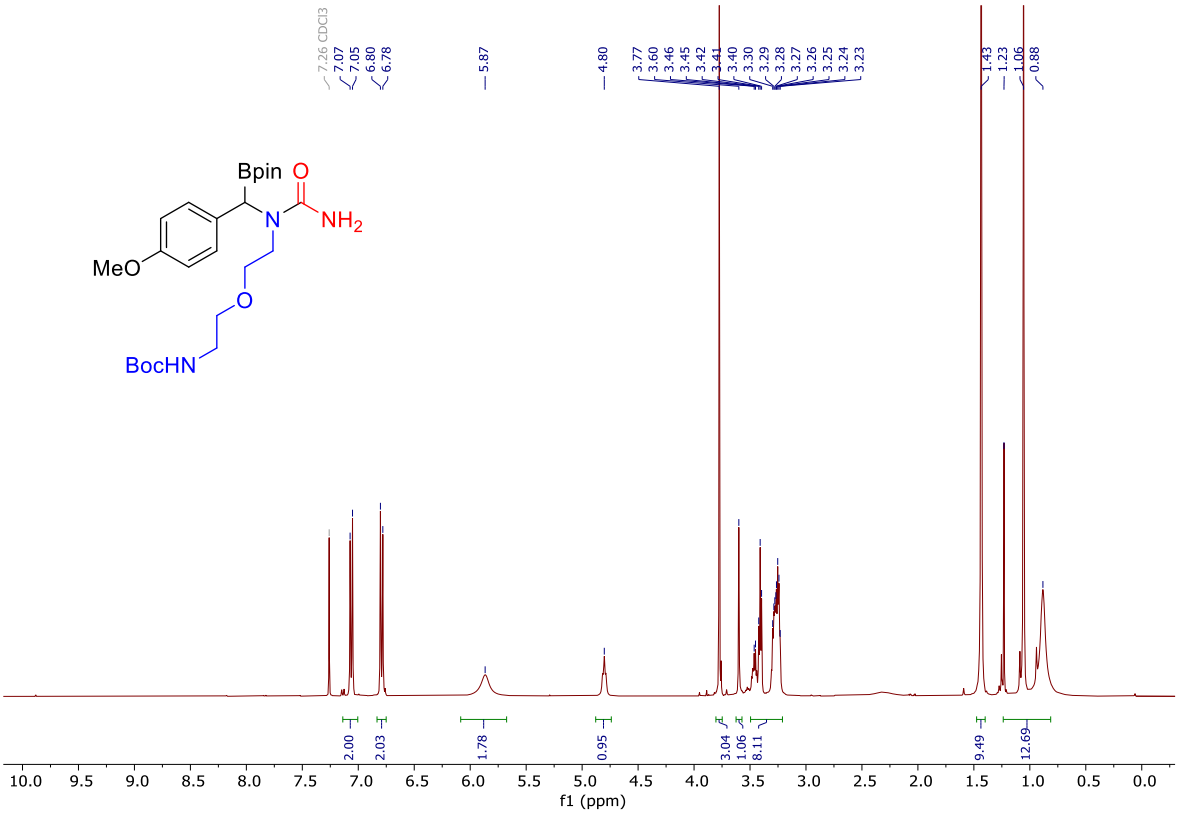

Br
Bpin
O
F
N
NH2
NHBoc
107.66
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
10 0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210
f1 (ppm)

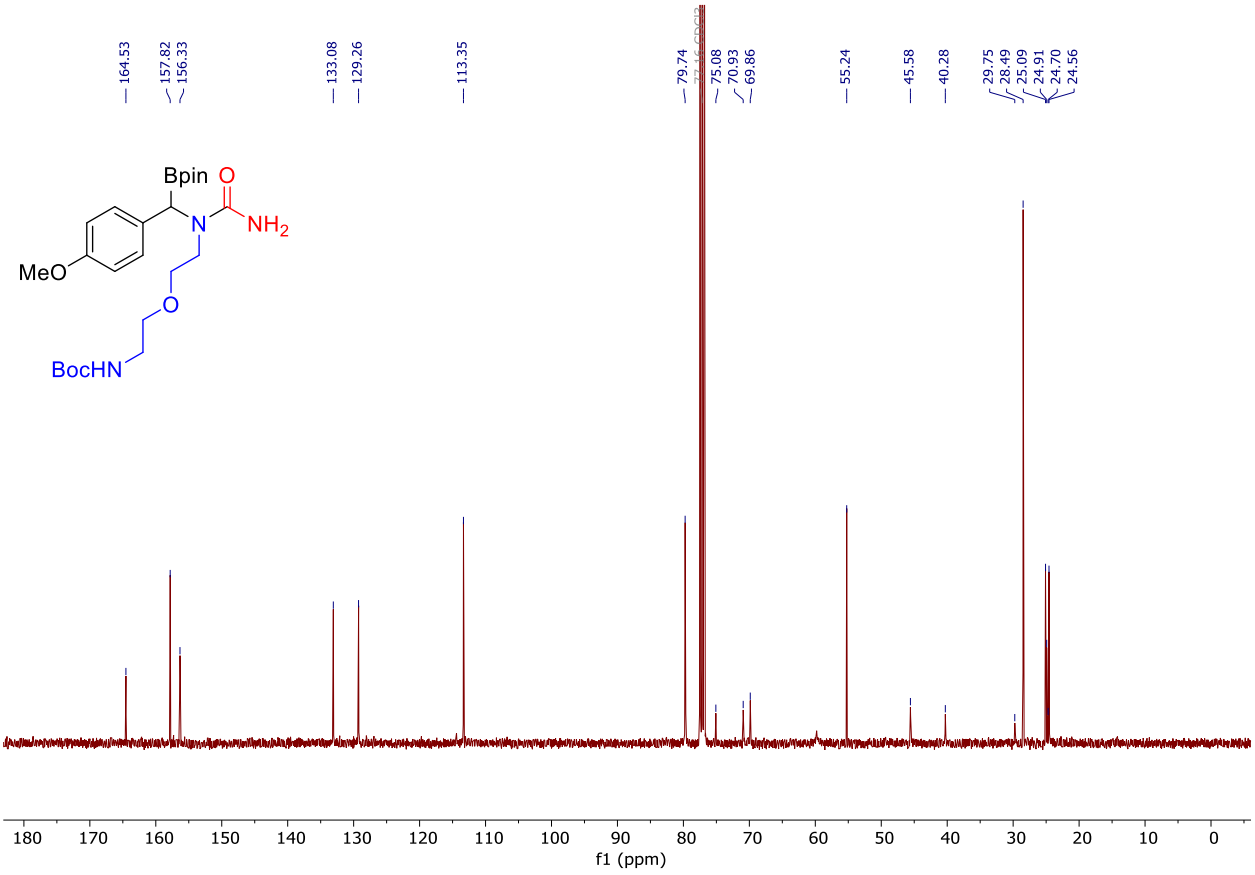

Br
Bpin
O
F
N
NH2
NHBoc
12.06
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80
f1 (ppm)

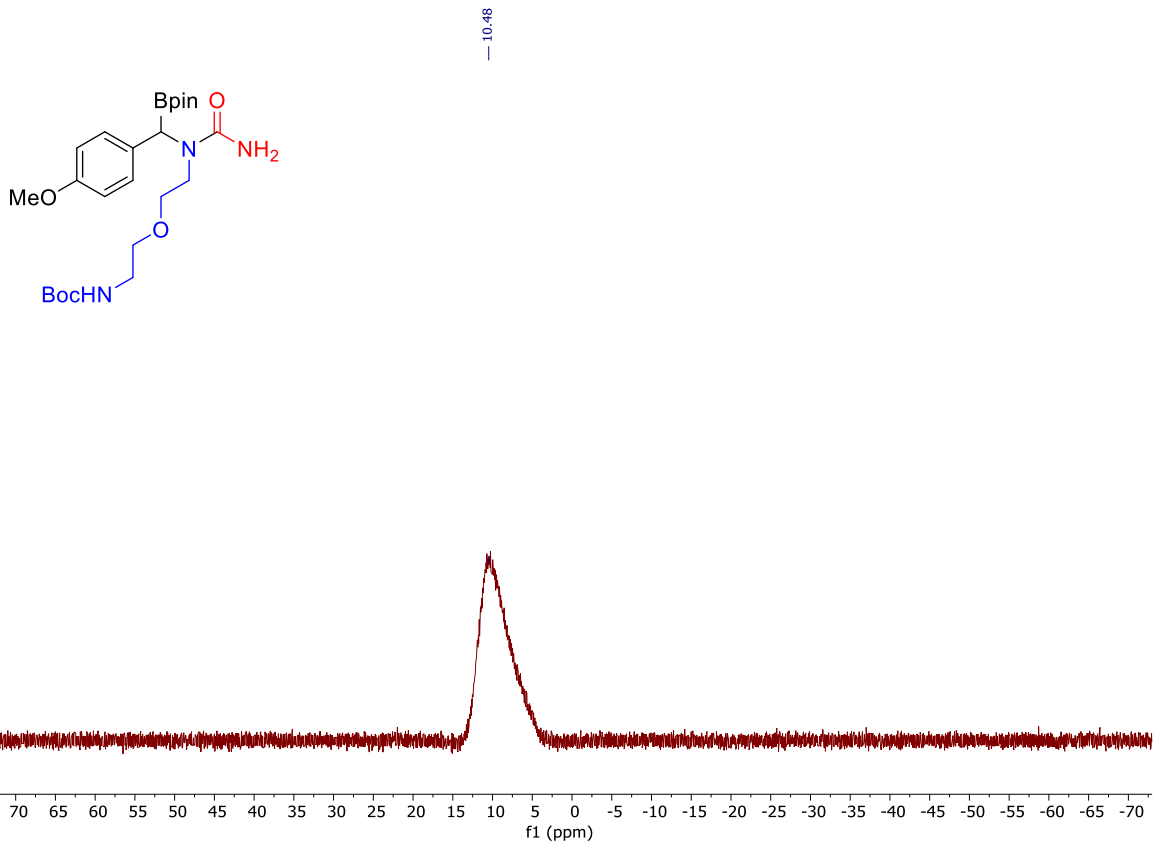

Bpin
O
N
NH2
MeO
f1 (ppm)

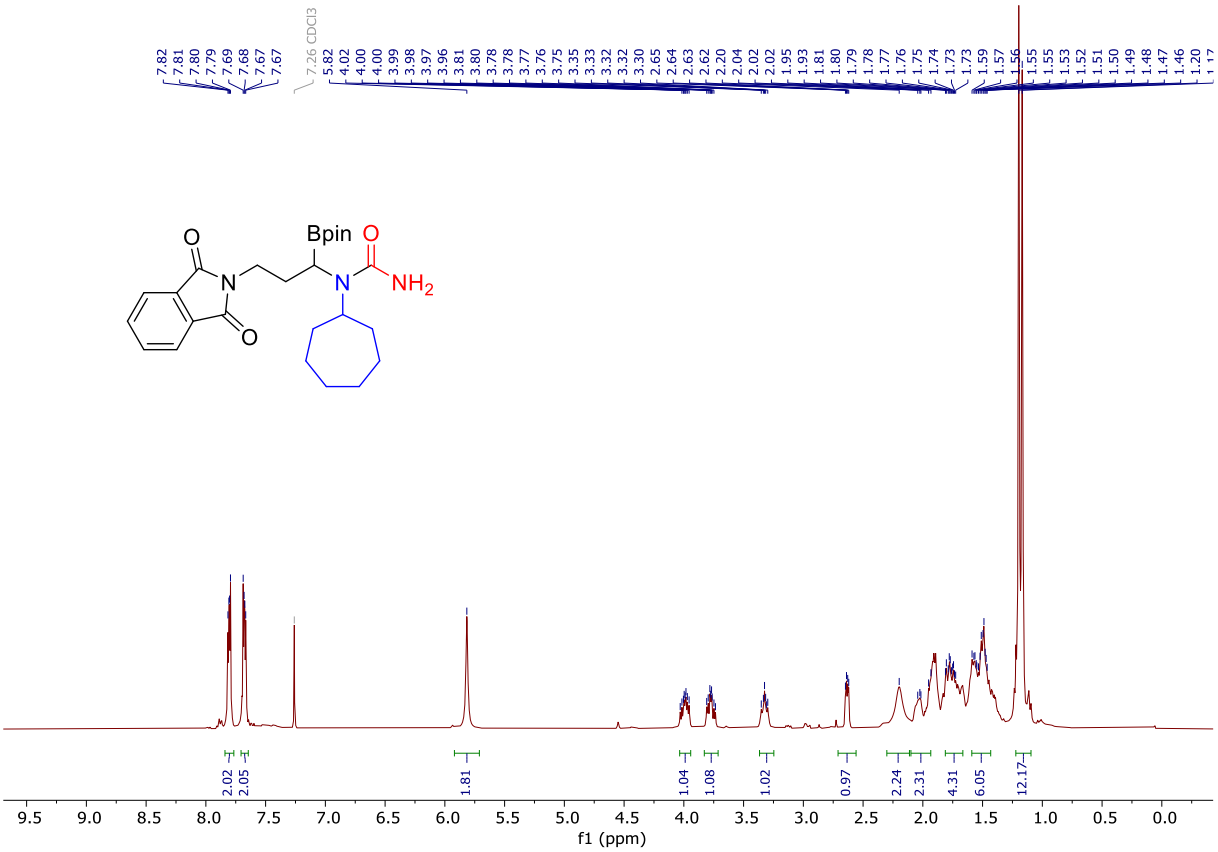

Bpin
O
N
NH2
MeO
f1 (ppm)

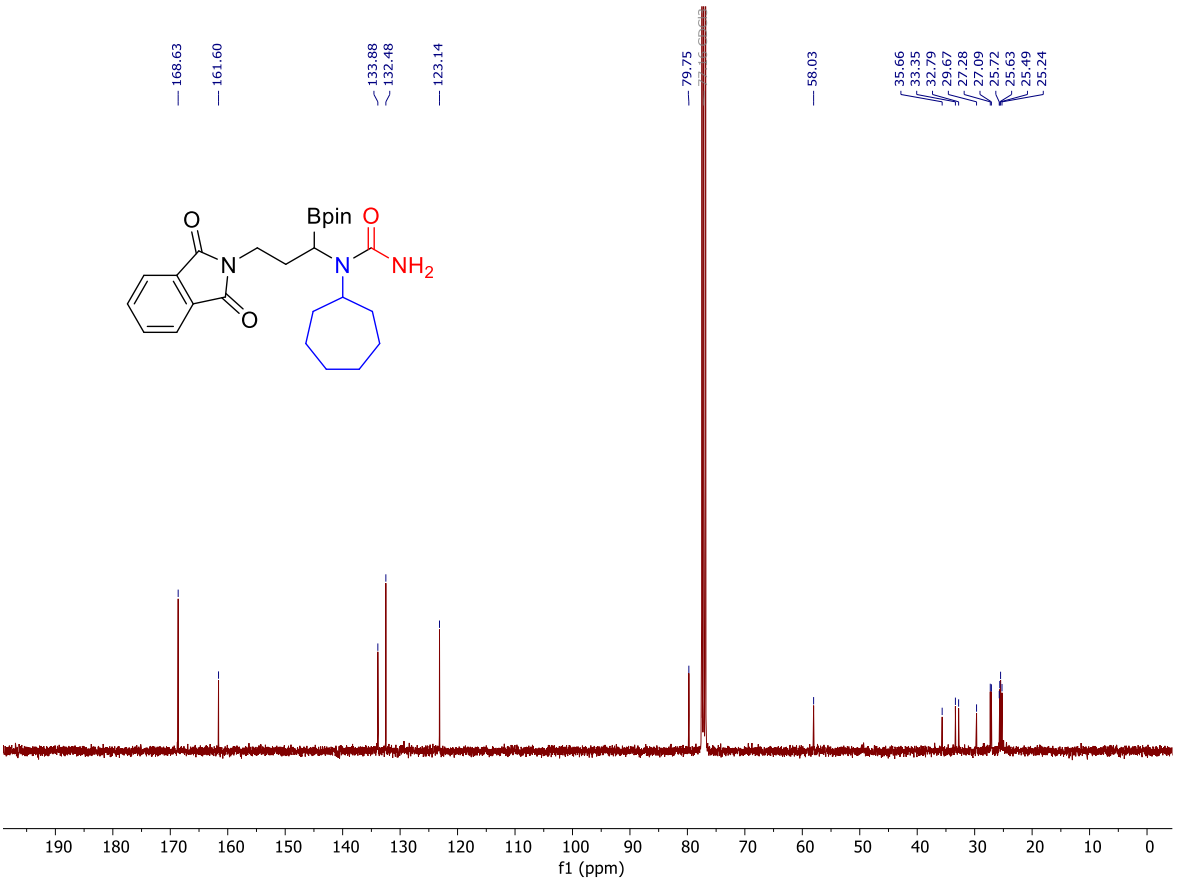

9.41
Bpin
O
N
NH2
MeO
65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55
f1 (ppm)

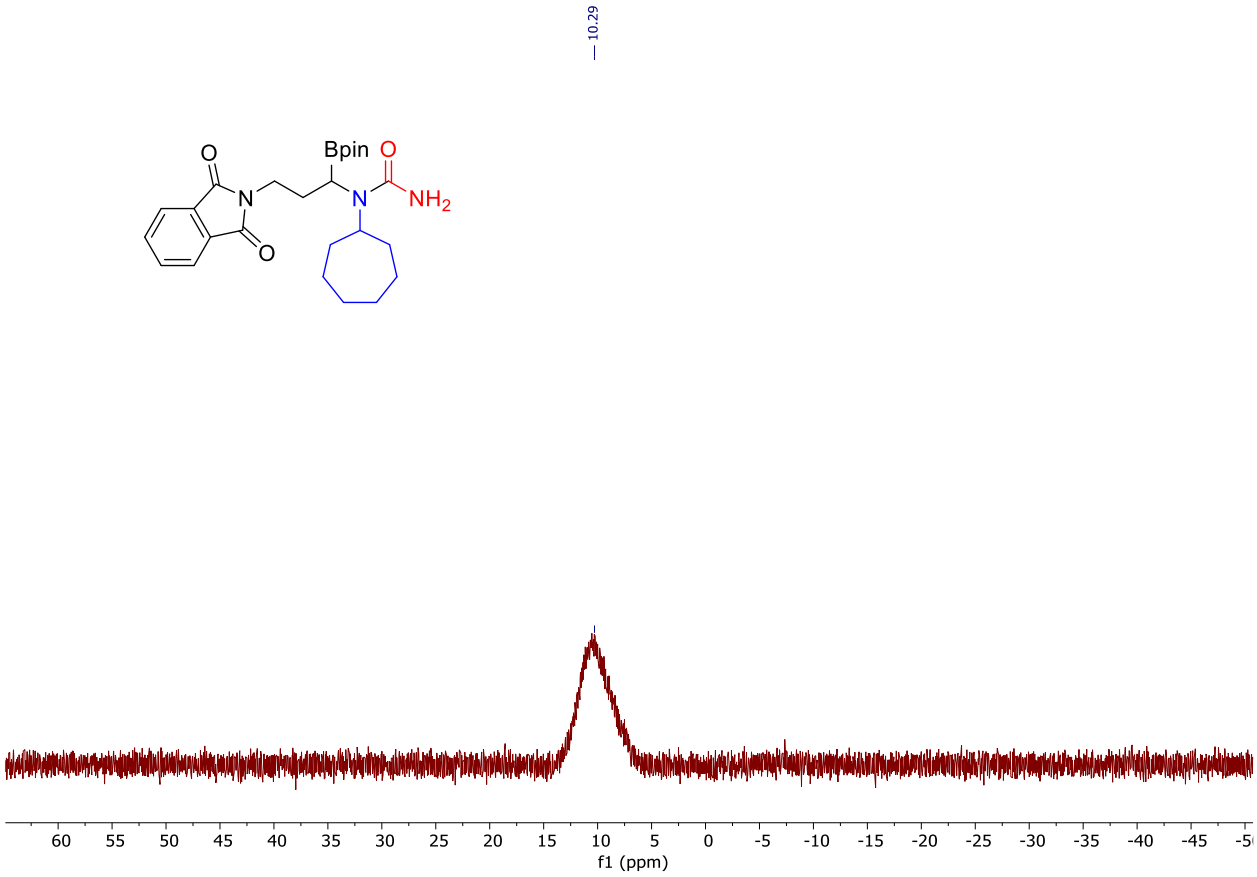

7.26 CDCl3
7.07
7.05
6.80
6.78
5.87
4.80
3.77
3.60
3.46
3.45
3.42
3.41
3.40
3.30
3.29
3.28
3.27
3.26
3.25
3.24
3.23
1.43
1.23
1.06
0.88
Bpin
O
N
NH2
MeO
O
BocHN
2.00
2.03
1.78
0.95
3.04
1.06
8.11
9.49
12.69
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

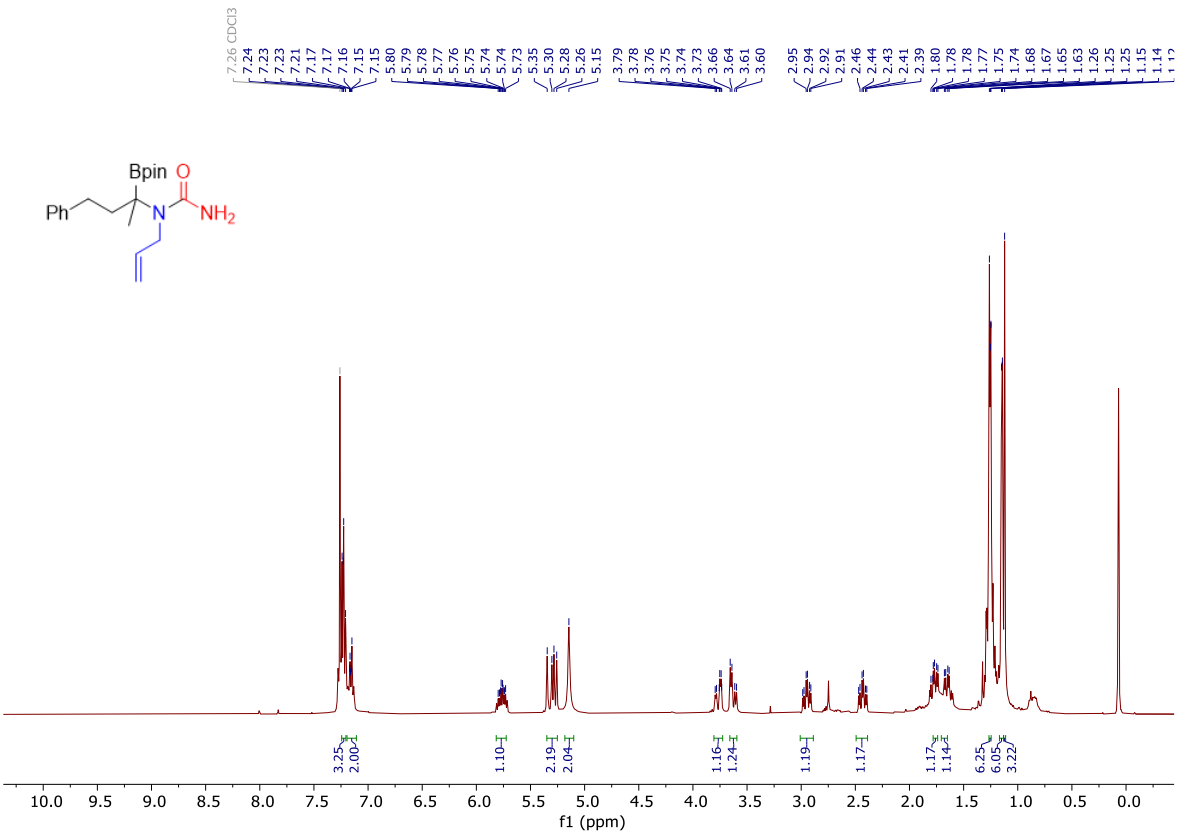

164.53
157.82
156.33
133.08
129.26
113.35
79.74
77.16 CDCl3
75.08
70.93
69.86
55.24
45.58
40.28
29.75
28.49
25.09
24.91
24.70
24.56
Bpin
O
N
NH2
MeO
O
BocHN
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

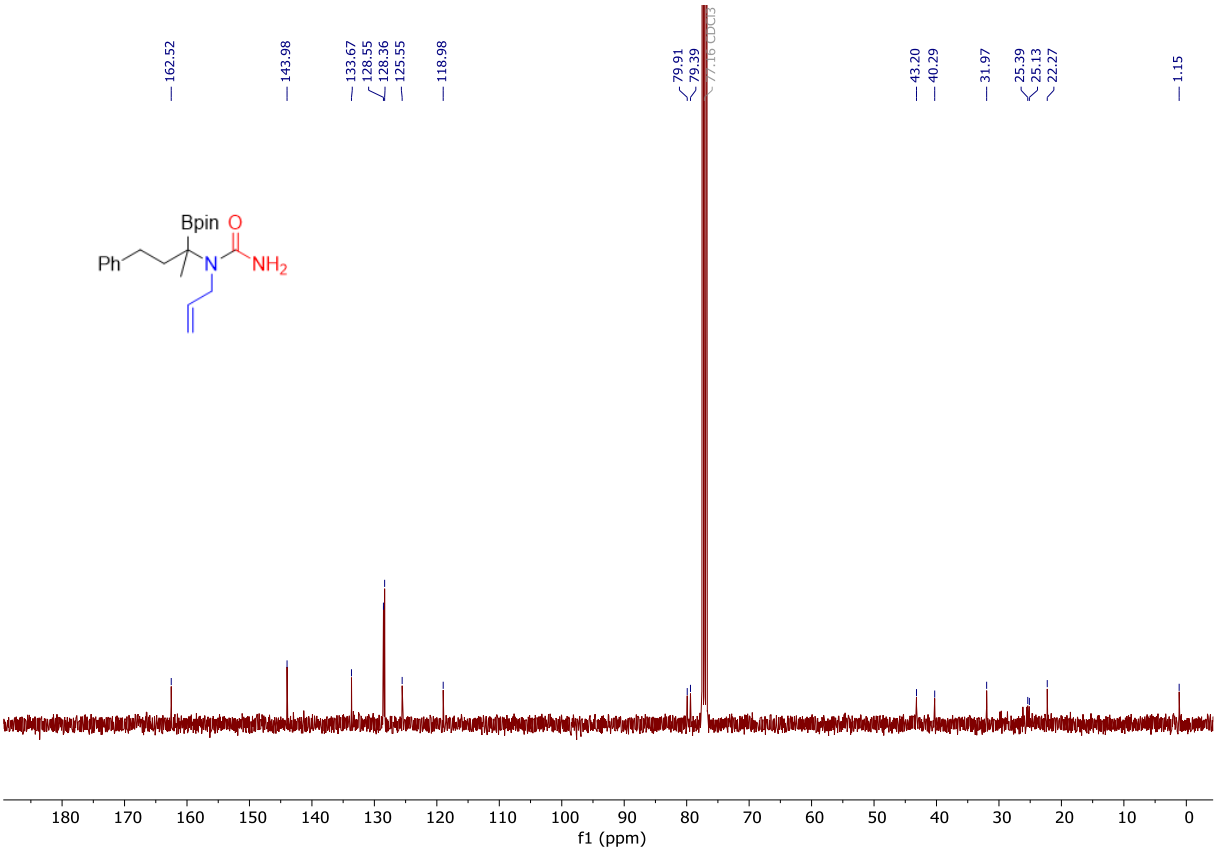

10.48
Bpin
O
N
NH2
MeO
O
BocHN
75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70
f1 (ppm)

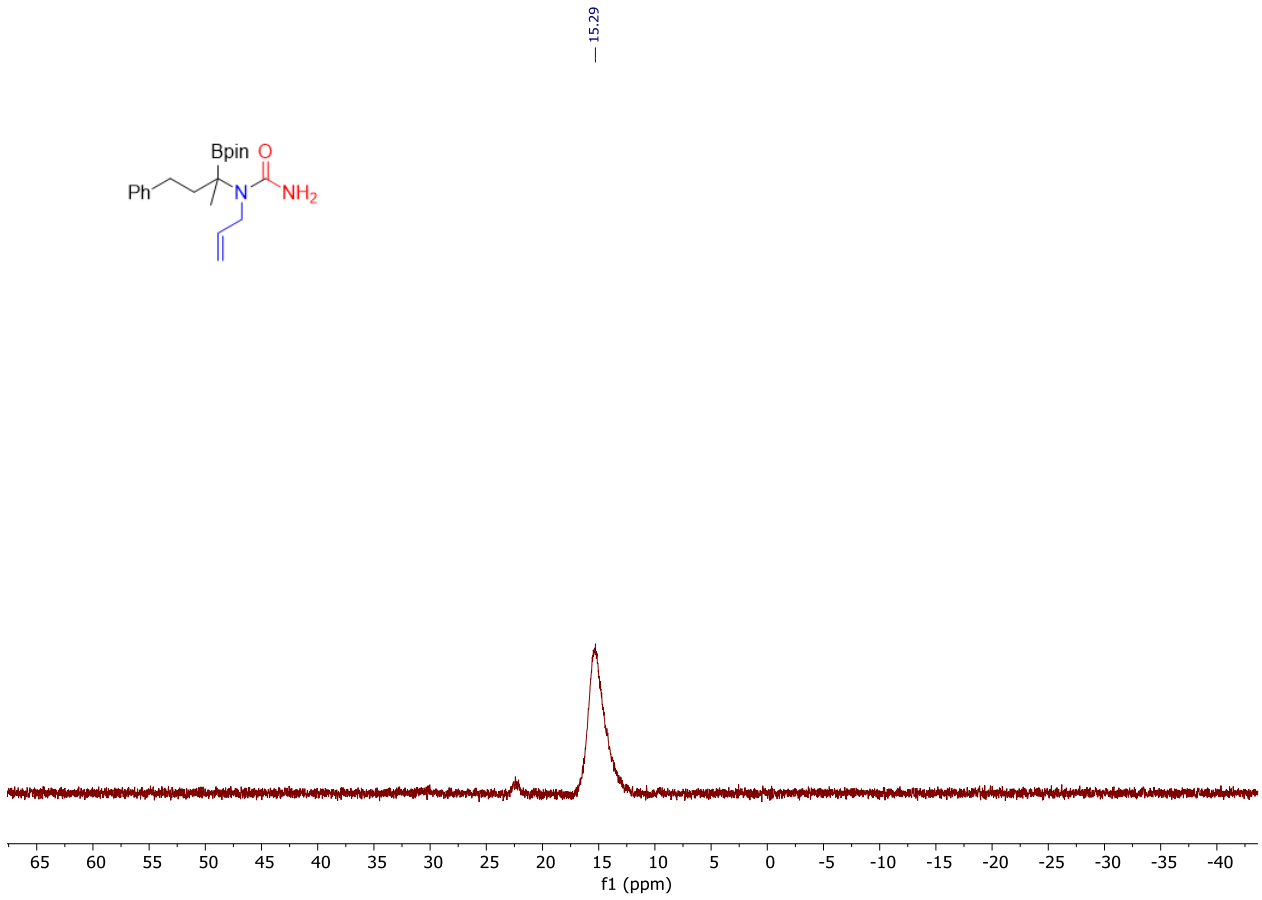

7.82
7.81
7.80
7.79
7.69
7.68
7.67
7.67
7.26 CDCl3
5.82
4.02
4.00
4.00
3.99
3.98
3.97
3.96
3.81
3.80
3.78
3.78
3.77
3.76
3.75
3.35
3.33
3.32
3.32
3.30
2.65
2.64
2.63
2.62
2.20
2.04
2.02
2.02
1.95
1.93
1.81
1.80
1.79
1.78
1.77
1.76
1.75
1.74
1.73
1.73
1.59
1.57
1.56
1.55
1.55
1.53
1.52
1.51
1.50
1.49
1.48
1.47
1.46
1.20
Bpin
O
N
N
NH2
O
O
2.02
2.05
1.81
1.04
1.08
1.02
0.97
2.24
2.31
4.31
6.05
12.17
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
f1 (ppm)

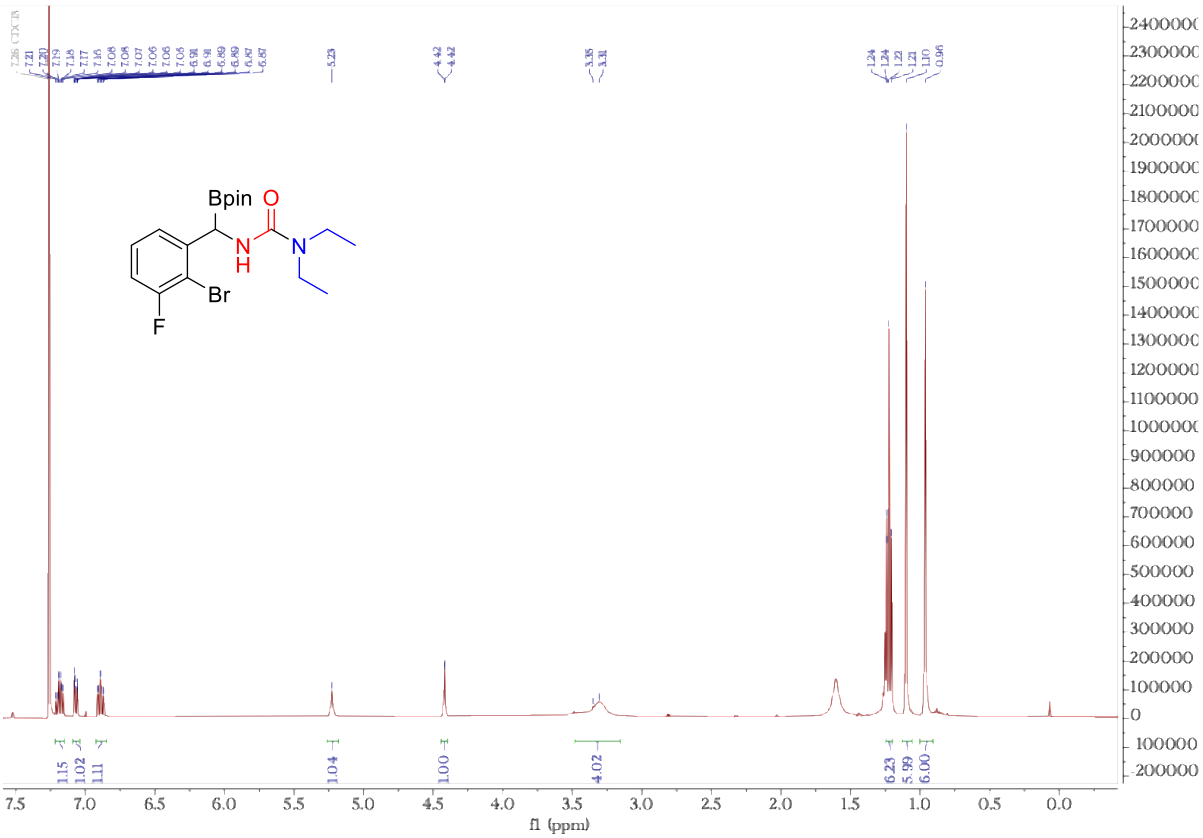

168.63
161.60
133.88
132.48
123.14
79.75
58.03
35.66
33.35
32.79
29.67
27.28
27.09
25.72
25.63
25.49
25.24
Bpin
O
N
N
NH2
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

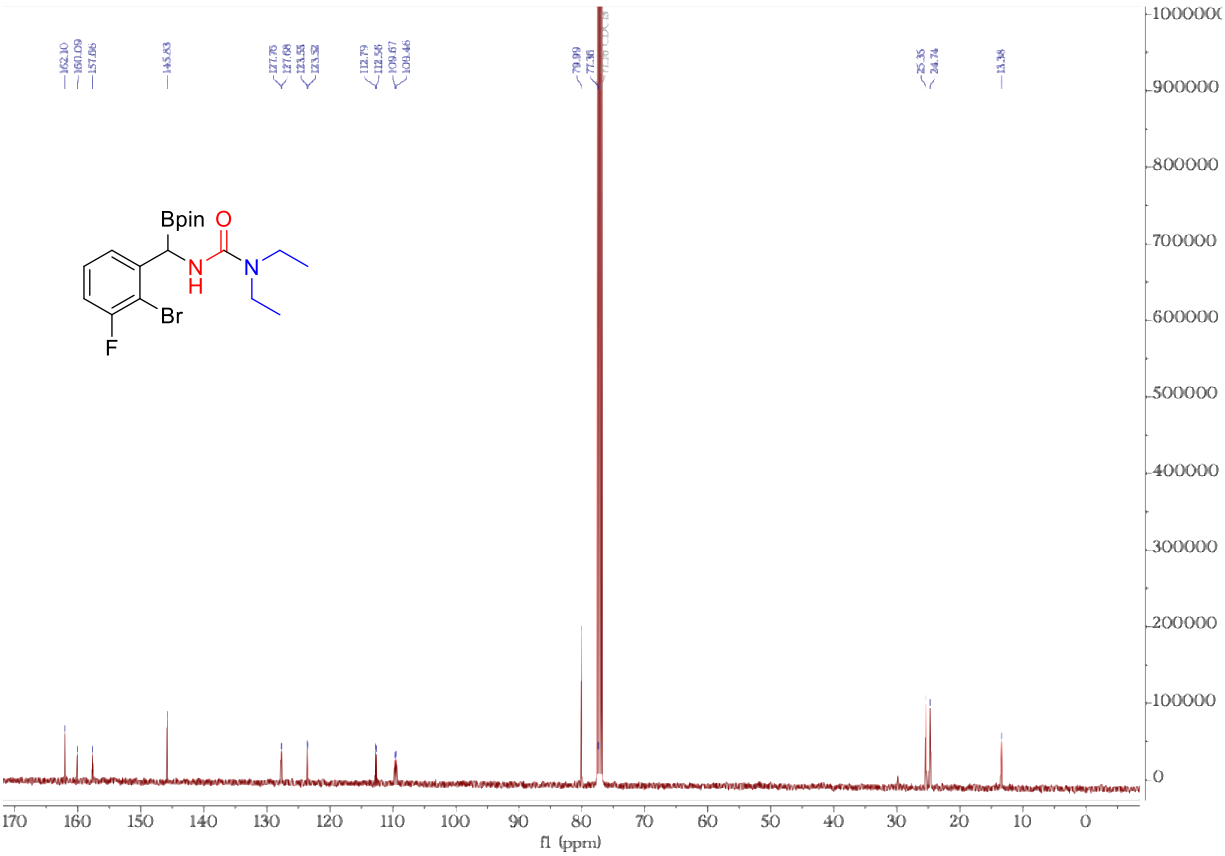

10.29
Bpin
O
N
O
O
N
NH2
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
f1 (ppm)

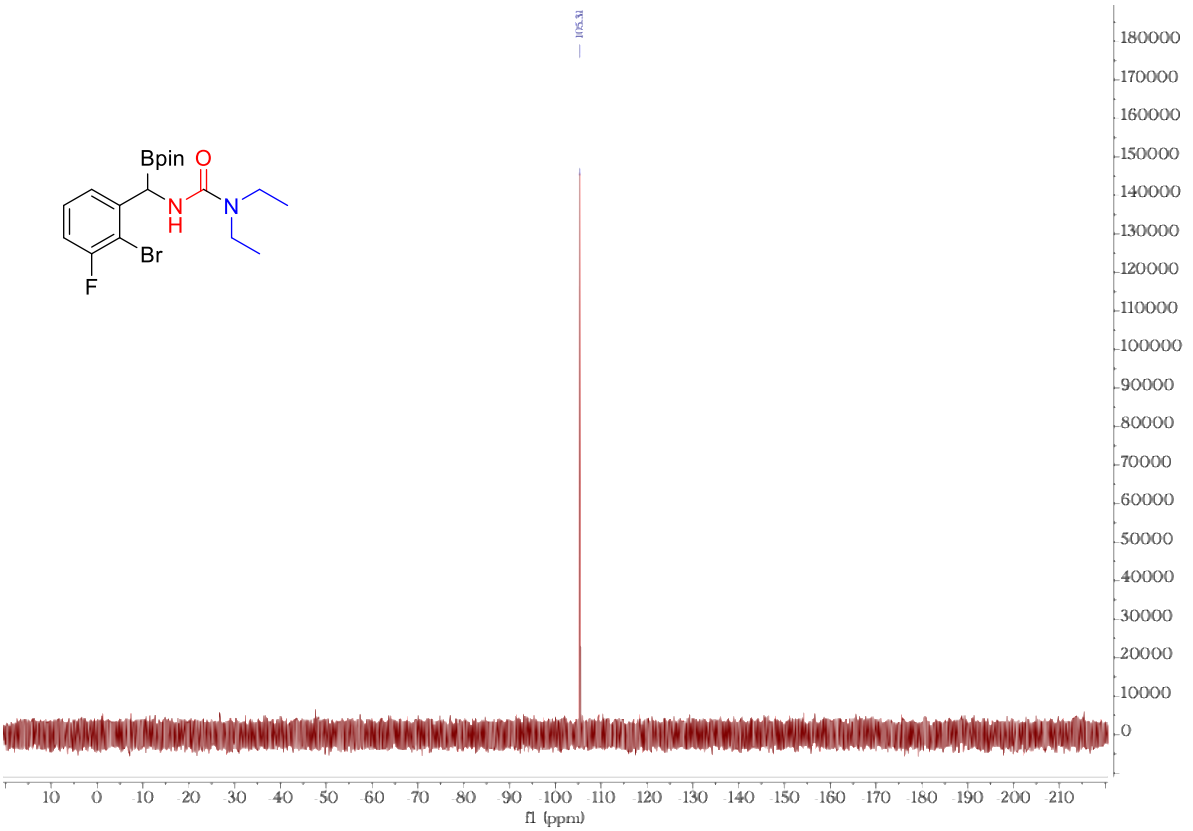

7.26 CDCl3
7.24
7.23
7.23
7.21
7.17
7.17
7.16
7.15
7.15
5.80
5.79
5.78
5.77
5.76
5.75
5.74
5.74
5.73
5.35
5.30
5.28
5.26
5.15
3.79
3.78
3.76
3.75
3.74
3.73
3.66
3.64
3.61
3.60
2.95
2.94
2.92
2.91
2.46
2.44
2.43
2.41
2.39
1.80
1.78
1.78
1.77
1.75
1.74
1.68
1.67
1.65
1.63
1.26
1.25
1.25
1.15
1.14
Bpin
O
Ph
N
NH2
3.25
2.00
1.10
2.19
2.04
1.16
1.24
1.19
1.17
1.17
1.14
6.25
6.05
3.22
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

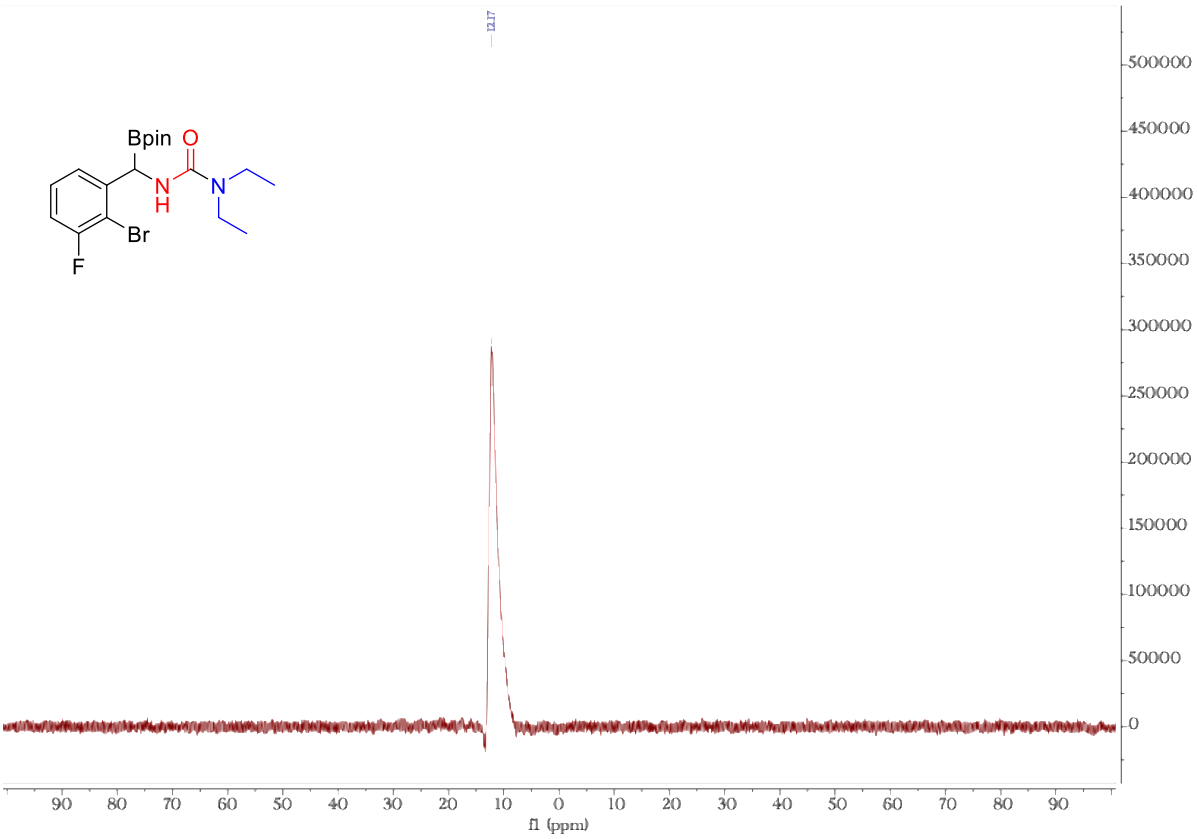

162.52
143.98
133.67
128.55
128.36
125.55
118.98
79.91
79.39
77.16 CDCl3
43.20
40.29
31.97
25.39
25.13
22.27
1.15
Bpin
O
Ph
N
NH2
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

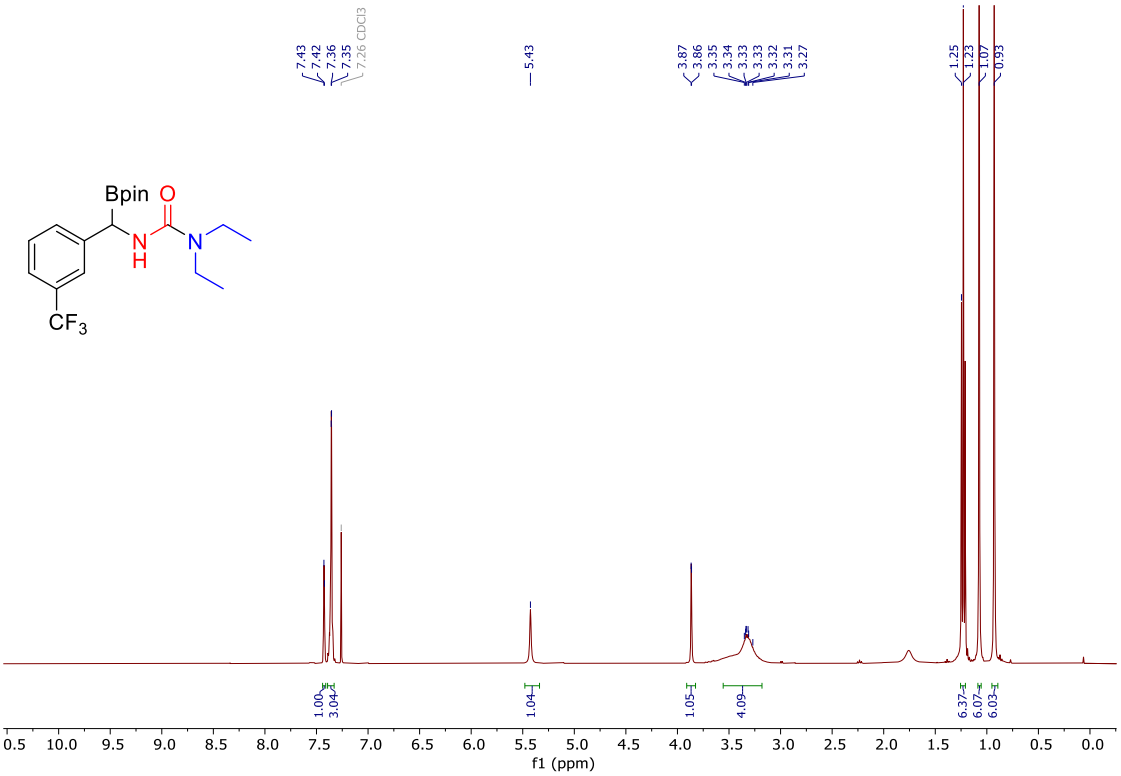

15.29
Bpin
O
Ph
N
NH2
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
f1 (ppm)

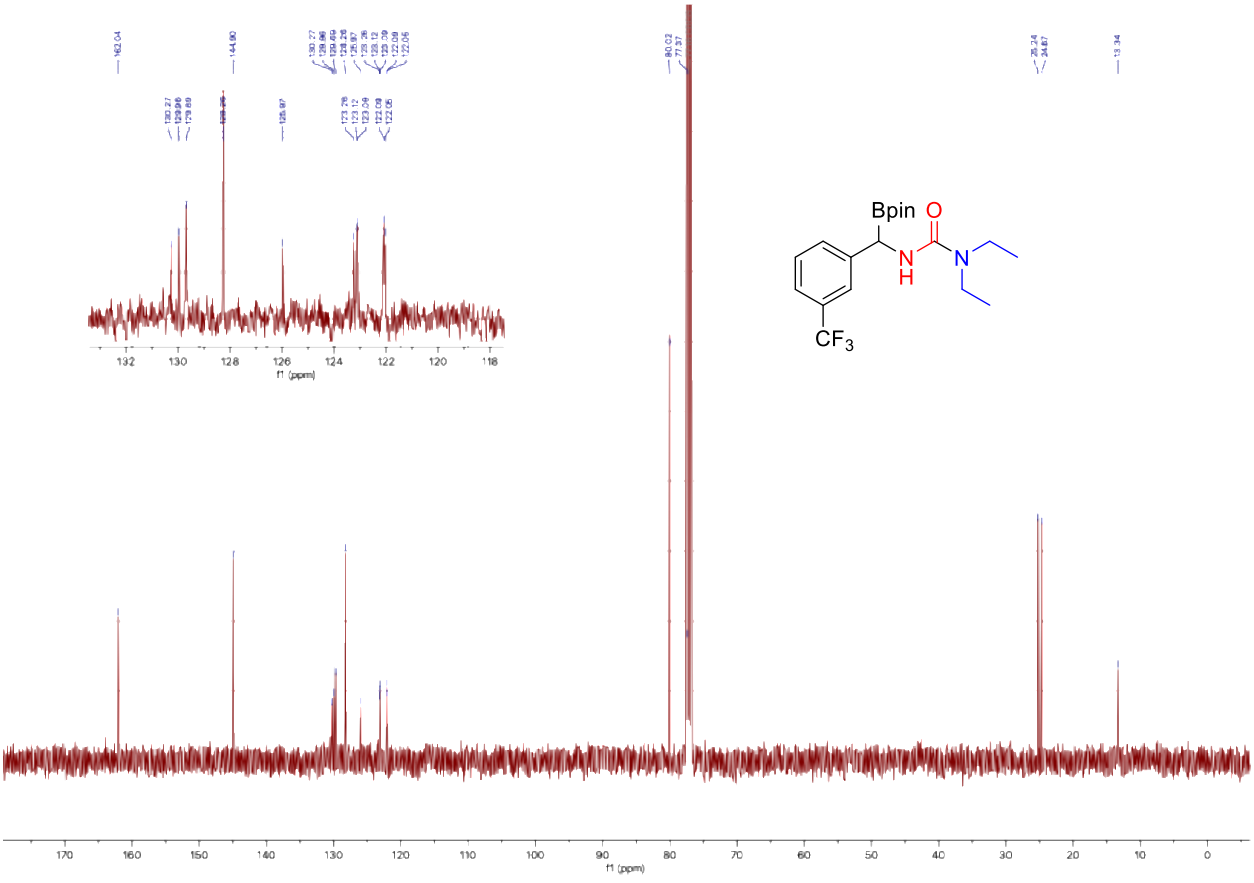

Bpin
O
N
H
N
Br
F
1.15
1.02
1.11
1.04
1.00
4.02
6.23
5.99
6.00
f1 (ppm)

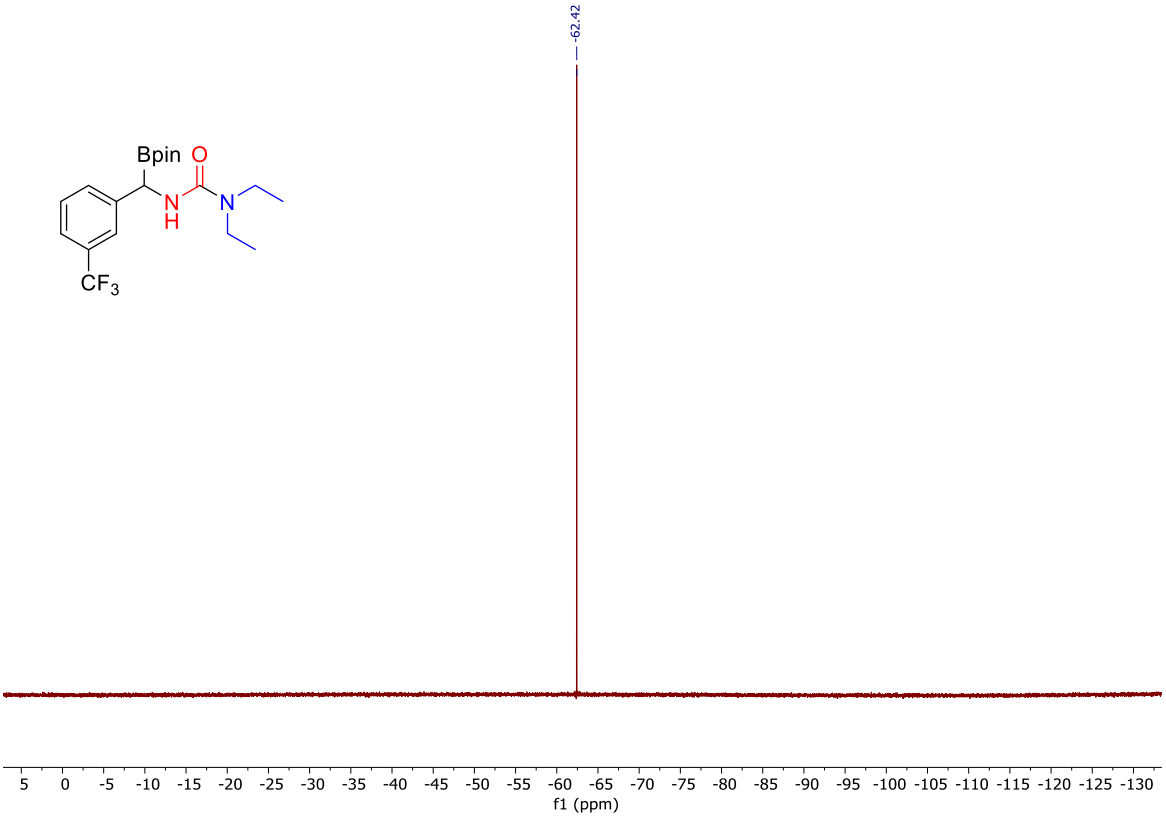

Bpin
O
N
H
N
Br
F
f1 (ppm)

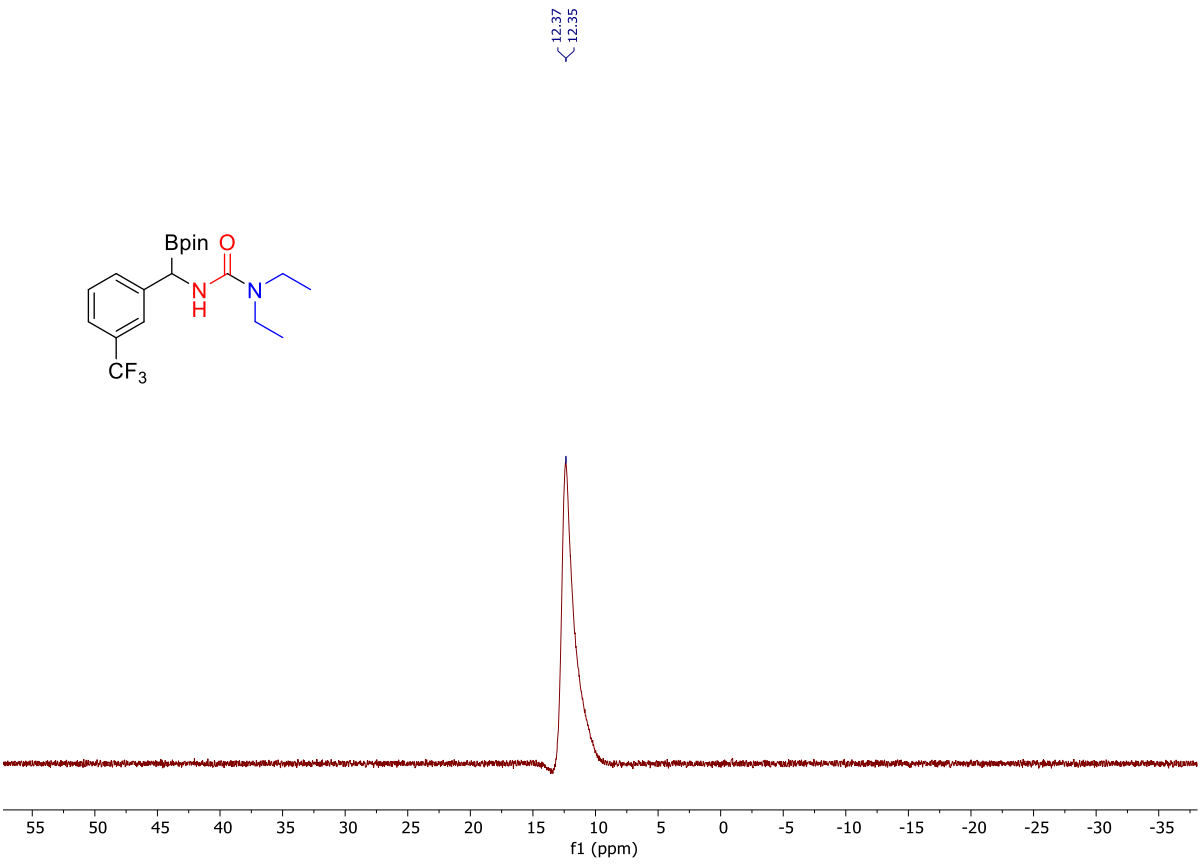

Bpin
O
N
H
N
Br
F
105.31
180000
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

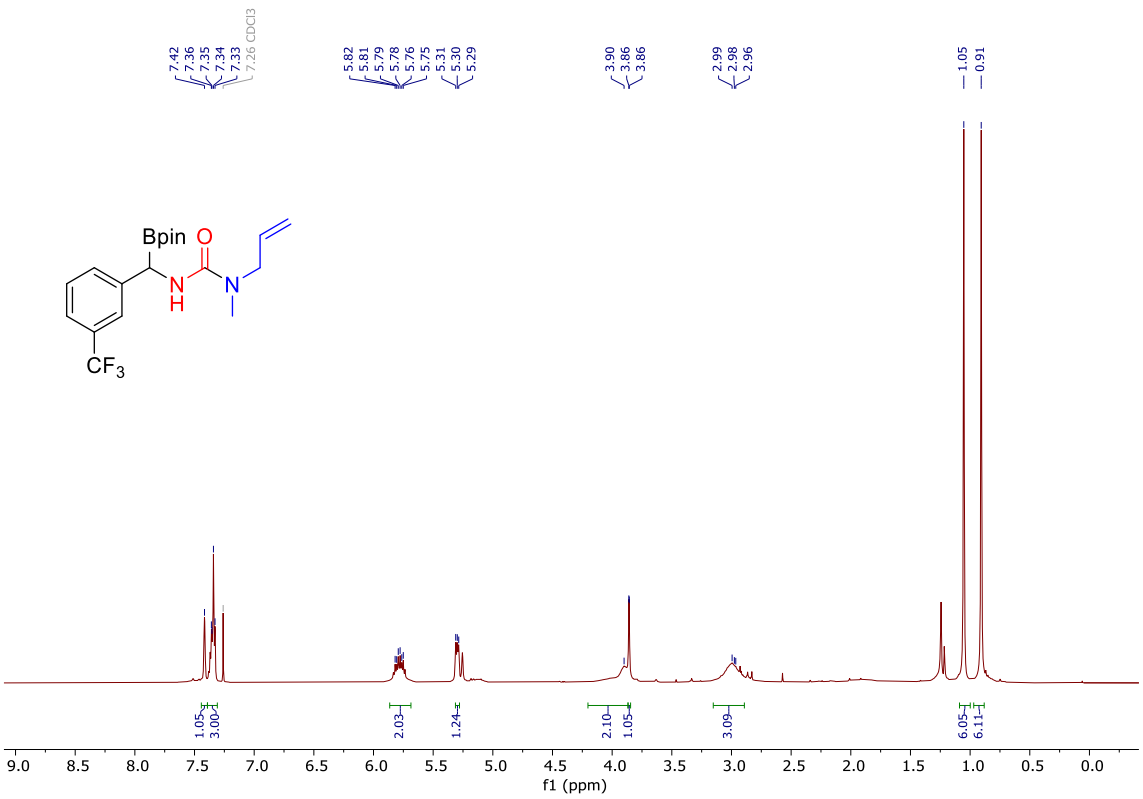

Bpin
O
N
H
N
Br
F
12.17
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

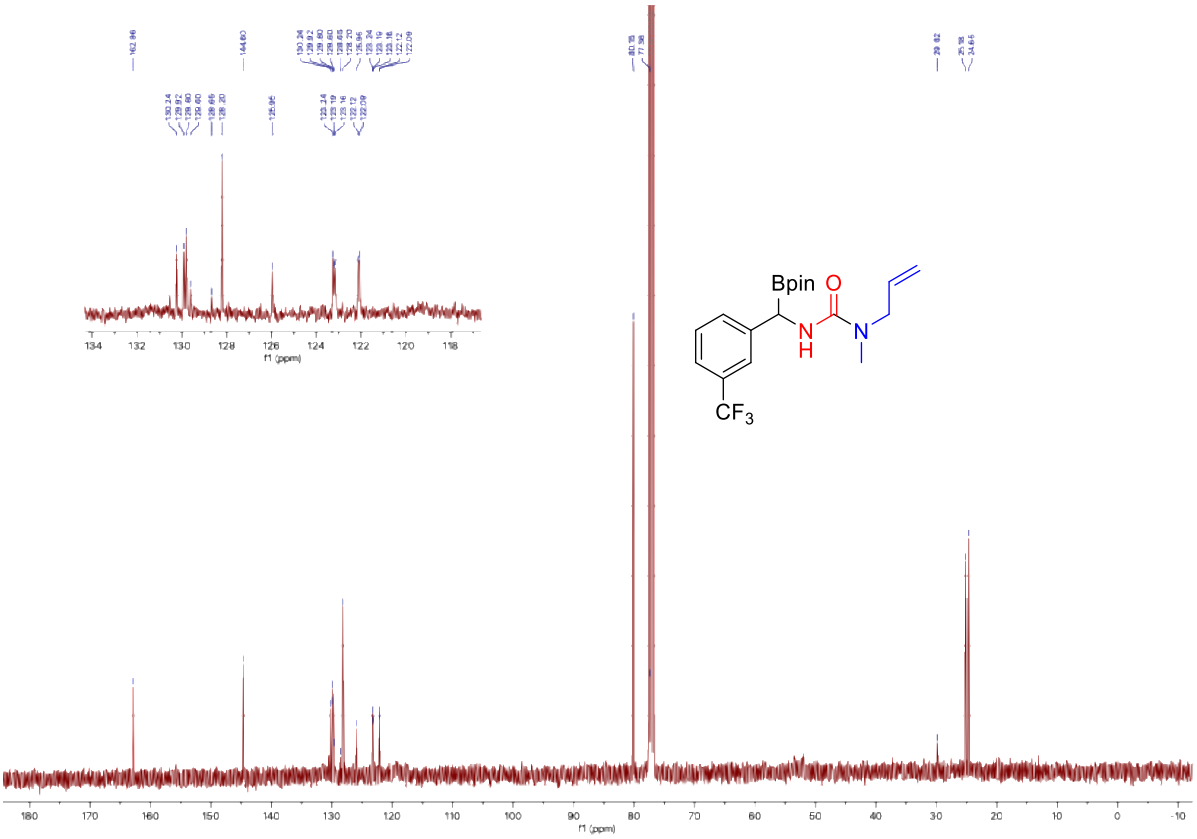

7.43
7.42
7.36
7.35
7.26 CDCl3
5.43
3.87
3.86
3.35
3.34
3.33
3.33
3.32
3.31
3.27
1.25
1.23
1.07
0.93
Bpin
O
N
H
N
CF3
1.00
3.04
1.04
1.05
4.09
6.37
6.07
6.03
f1 (ppm)

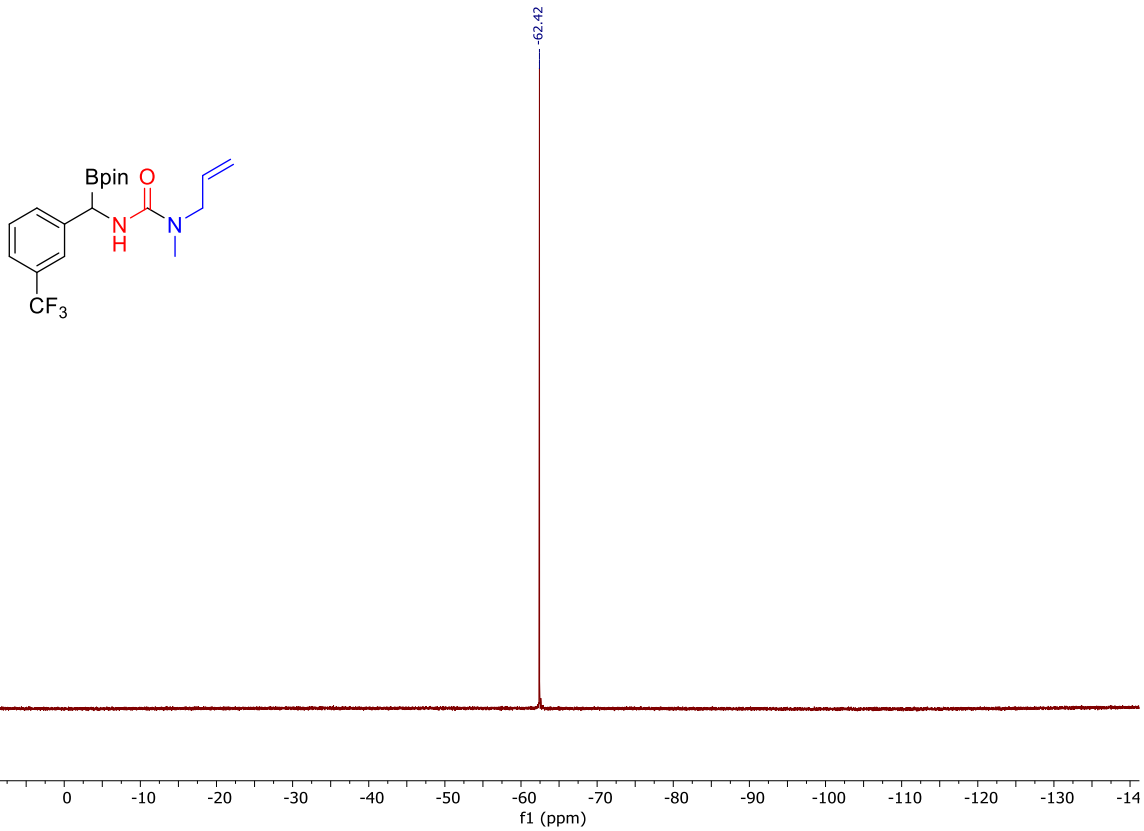

162.04
144.90
130.27
129.96
129.66
128.35
126.97
123.26
123.12
123.04
122.09
122.06
80.02
77.37
25.24
24.87
13.34
Bpin
O
N
H
N
CF3
f1 (ppm)

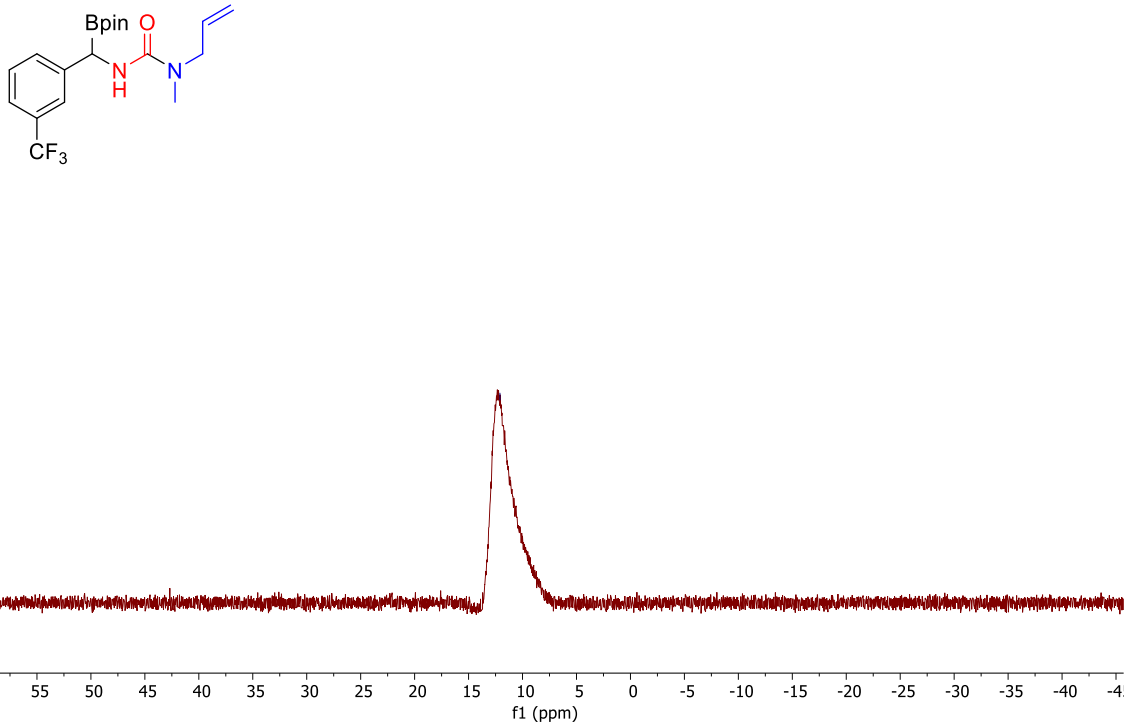

-62.42
Bpin
O
N
H
N
CF3
5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130
f1 (ppm)

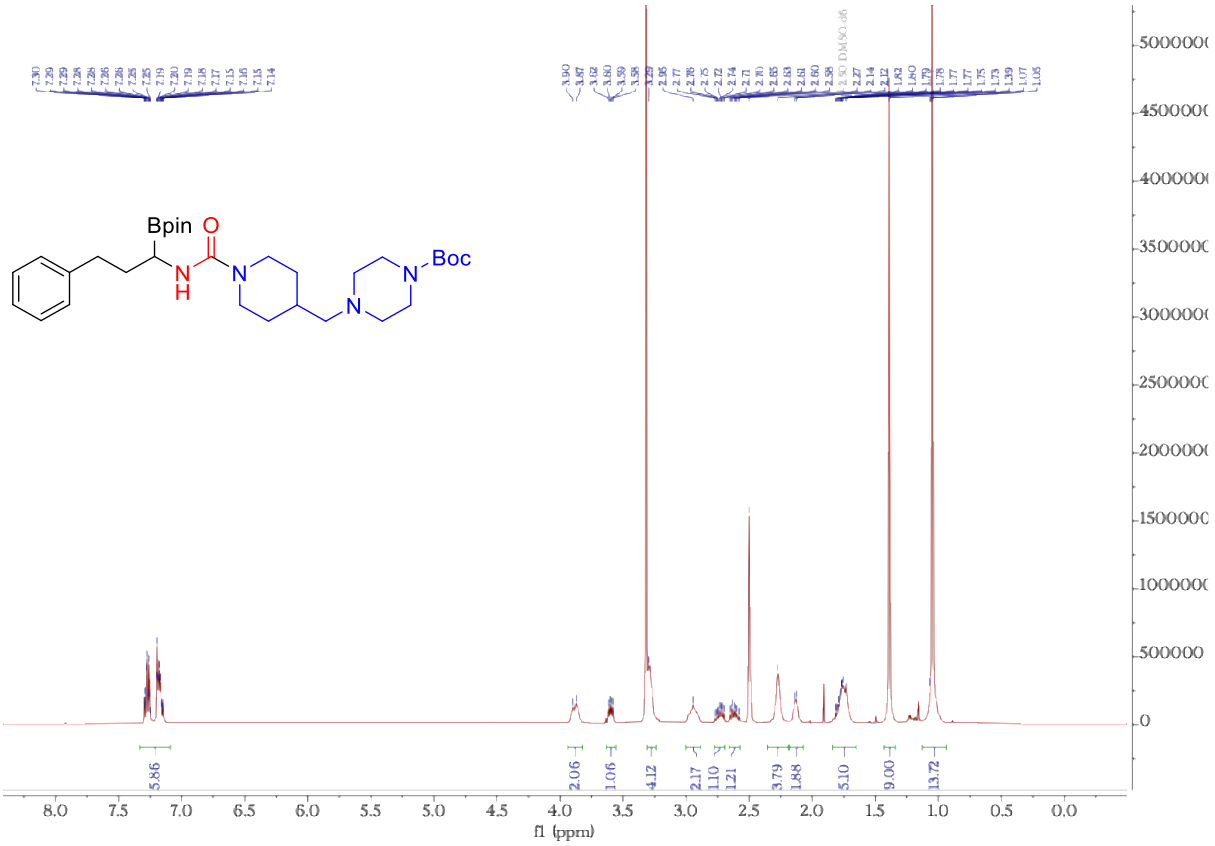

12.37
12.35
Bpin
O
N
H
N
CF3
55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35
f1 (ppm)

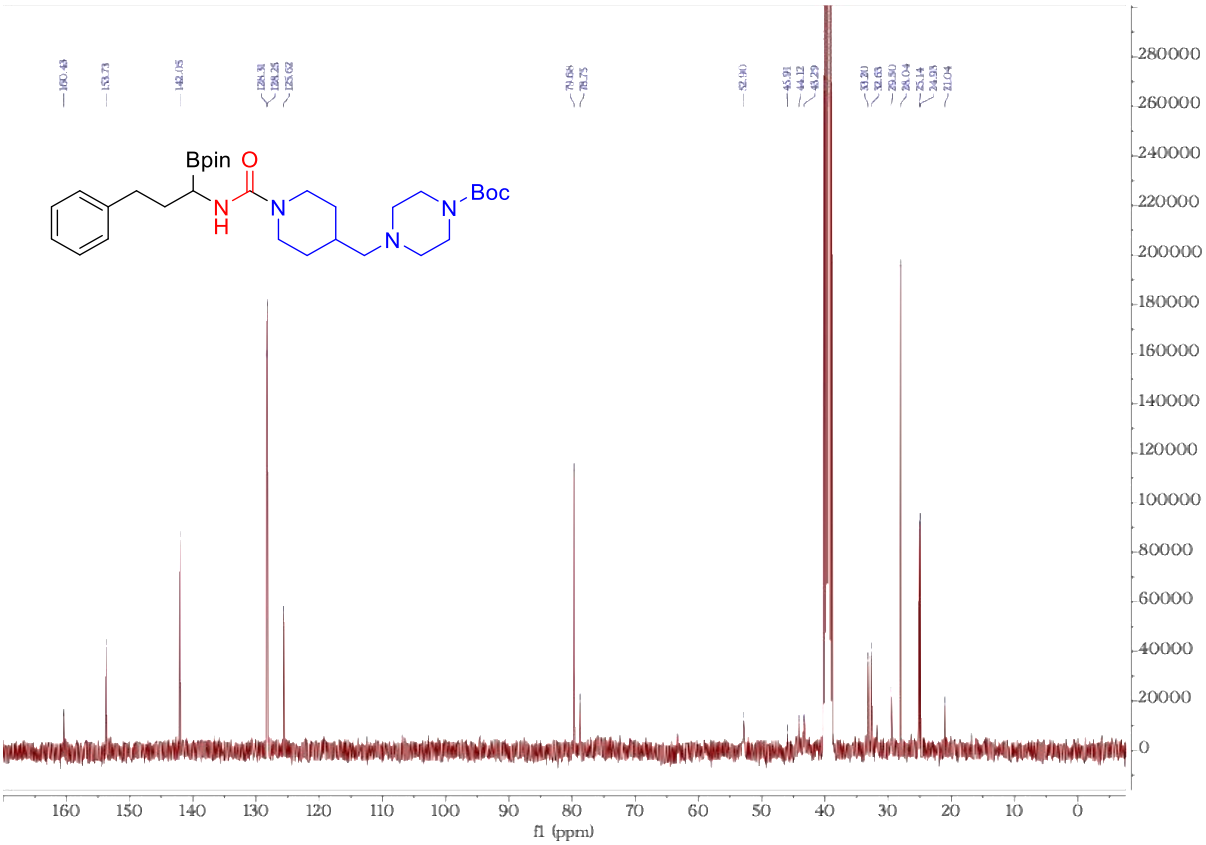

7.42
7.36
7.35
7.34
7.33
7.26 CDCl3
5.82
5.81
5.79
5.78
5.76
5.75
5.31
5.30
5.29
3.90
3.86
3.86
2.99
2.98
2.96
1.05
0.91
Bpin
O
N
H
N
CF3
1.05
3.00
2.03
1.24
2.10
1.05
3.09
6.05
6.11
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

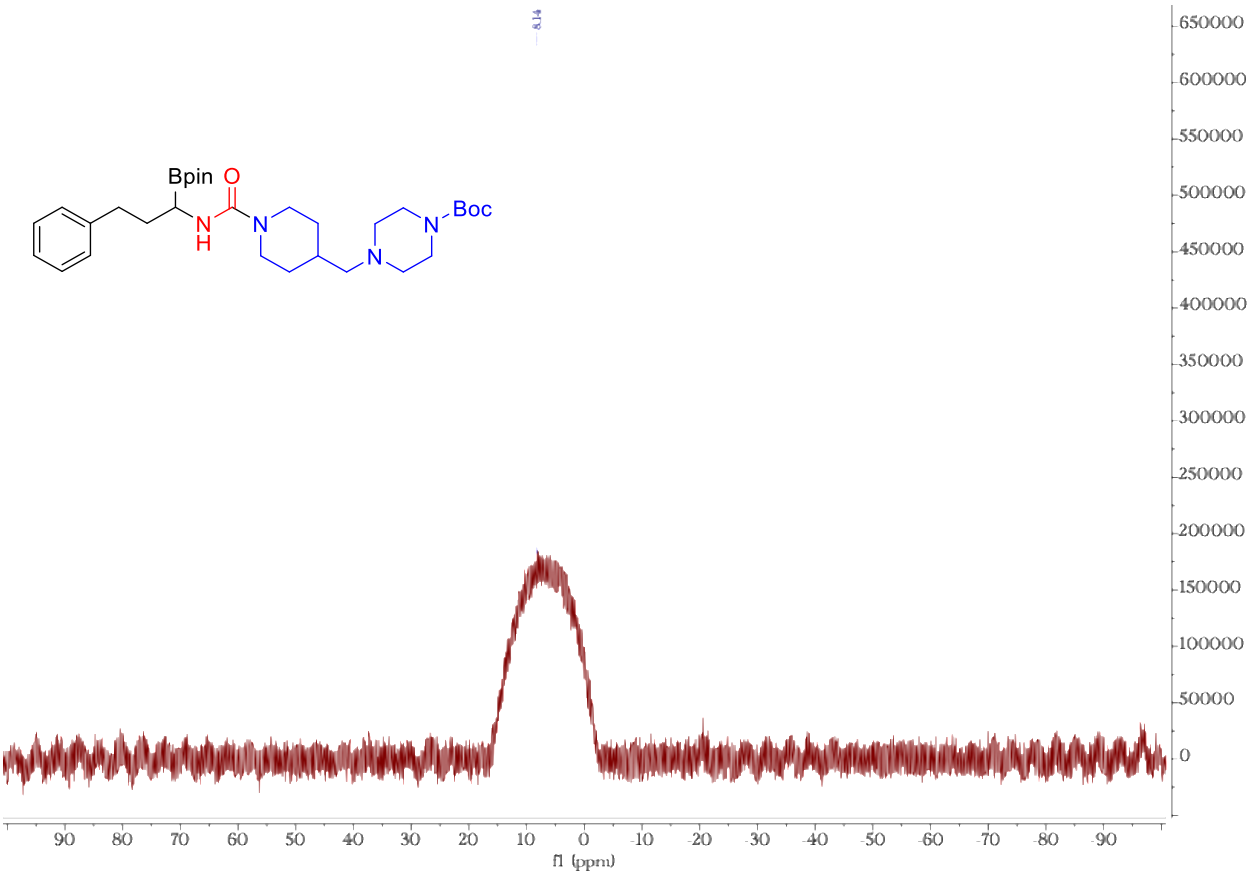

162.96
144.60
130.24
129.87
129.60
129.33
128.66
128.20
125.96
123.54
123.19
122.84
122.72
122.09
80.15
77.36
29.62
25.18
24.64
Bpin
O
N
H
N
CF3
134
132
130
128
126
124
122
120
118
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

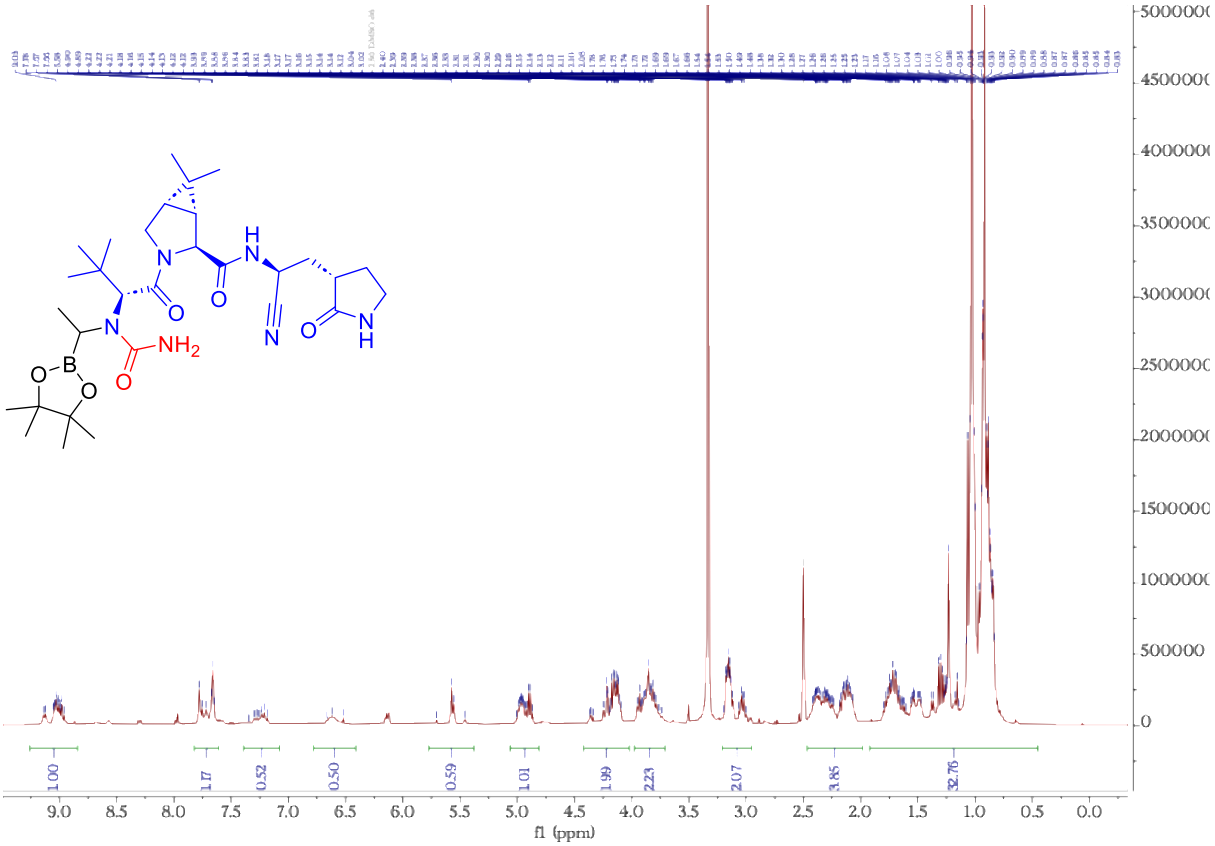

-62.42
Bpin
O
N
H
N
CF3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-14
f1 (ppm)

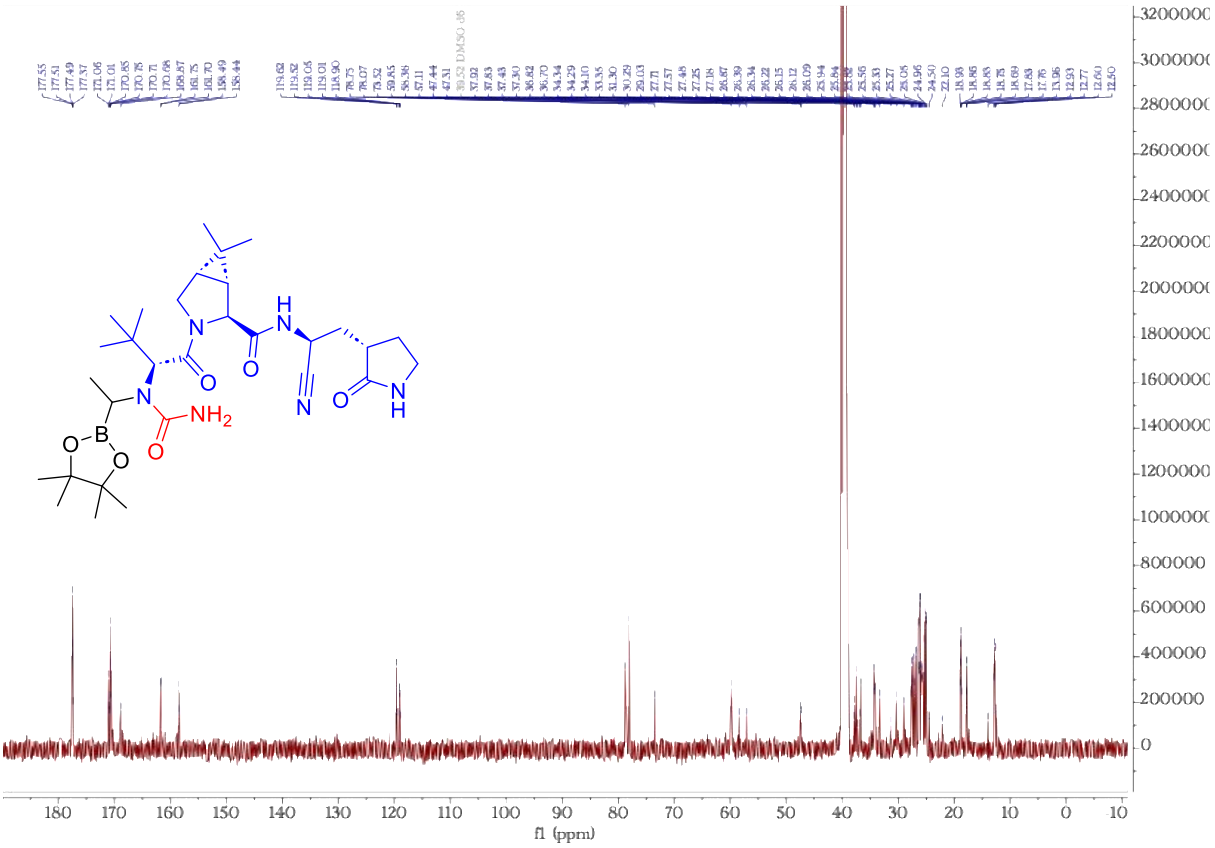

12.09
Bpin
O
N
H
N
CF3
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-4
f1 (ppm)

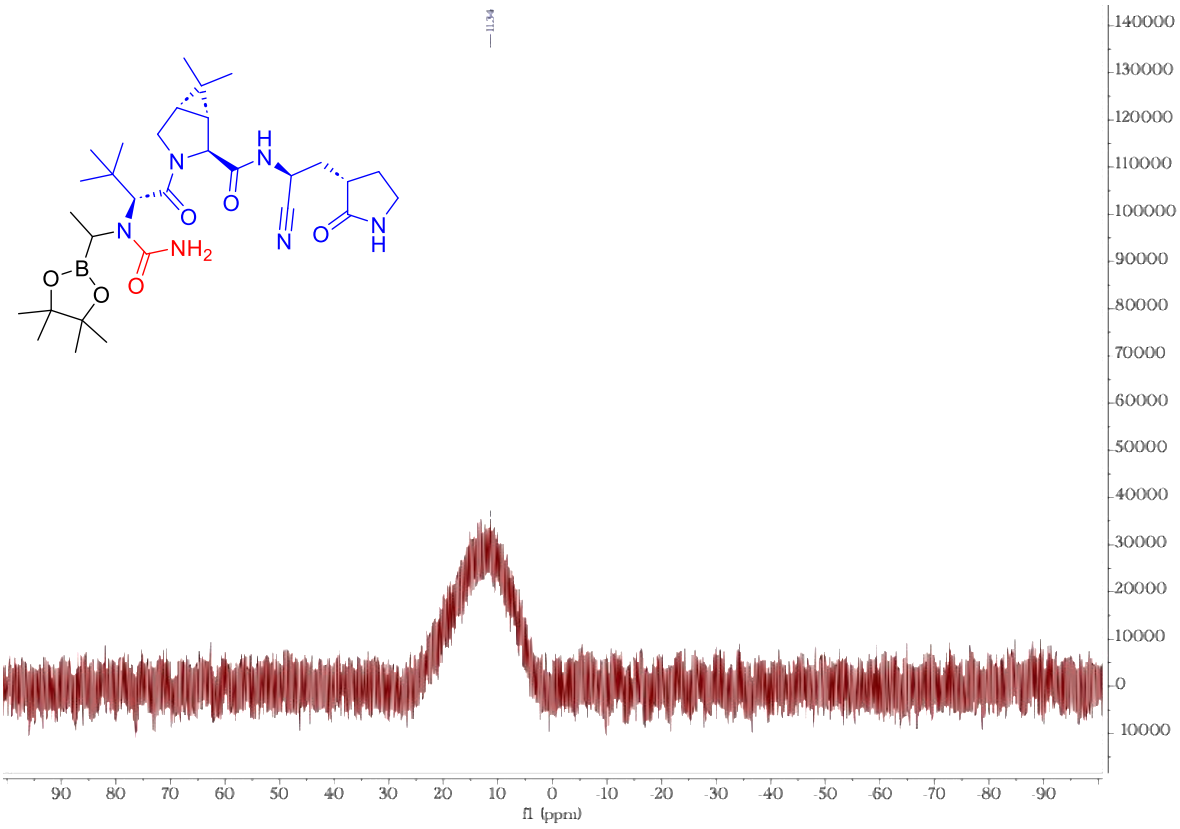

Bpin
O
N
H
N
N
N
Boc
f1 (ppm)


Bpin
O
N
H
N
N
N
Boc
f1 (ppm)


Bpin
O
N
H
N
N
N
Boc
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)


1.00
1.17
0.52
0.50
0.59
1.01
1.99
2.23
2.07
3.85
32.76
f1 (ppm)


f1 (ppm)


11.34
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
10000
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)