Supporting Information

Copper-Catalyzed Cross-Coupling Reactions of Epoxides with *gem*-Diborylmethane: Access to γ-Hydroxyl Boronic Esters

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I. General Information

a). Materials

All the reactions were carried out in oven-dried schlenk tubes under argon atmosphere (purity≥99.999%). Copper(I) iodide was purchased from Sinopharm Chemical Reagent Co., Ltd as an off-white powder (which refluxed in THF for 8 hrs in soxhlet extractor, the resulting mixture was filtered through Buchner funnel and dried under vacuum).[1] The following chemicals were purchased and used as received: LiO-*t*Bu (Acros, 99.9%), KO-*t*Bu (Acros), NaO-*t*Bu (Acros), 2-(phenoxymethyl)oxirane (adamas, 98%), (S)-2-((benzyloxy)methyl)oxirane (adamas, 98%), 2-((benzyloxy)methyl)oxirane (adamas, 98%), 2-phenyloxirane (adamas, 98%).

Anhydrous solvents (CH_3CN, DMF, 1, 4-dioxane, THF) were purchased from Acros and used without further purification. Anhydrous THF (Acros) was stored over 4 Å molecular sieves under an argon atmosphere in a septum-capped bottle.

All the other reagents and solvents mentioned in this text were purchased from commercial sources and used without purification.

b). Analytical Methods

^{1}H-NMR, ^{13}C-NMR and ^{19}F-NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature in $CDCl_3$ unless otherwise noted; Data for ^{1}H-NMR arereported as follows: chemical shift (δ ppm), multiplicity, integration, and coupling constant (Hz). Data for ^{13}C-NMR are reported in terms of chemical shift (δ ppm), multiplicity, and coupling constant (Hz). Gas chromatographic (GC) analysis was acquired on a Shimadzu GC-2014 Series GC System equipped with a flame-ionization detector. GC-MS analysis was performed on Thermo Scientific AS 3000 Series GC-MS System. HRMS analysis was performed on FinniganLCQ advantage Max Series MS System. HPLC analysis was performed on Waters-Breeze (2487 Dual Absorbance Detector and 1525 Binary HPLC Pump). Chiralpak IC, OD, AS, KM columns were purchased from Daicel Chemical Industries, LTD. Organic solutions were concentrated under reduced pressure on a Buchi rotary evaporator. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh).

II. Preparation of Substrates

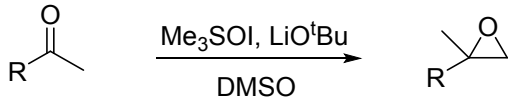
a). Synthesis of bis(boronates)

1,1-diborylmethane was prepared according to literature procedure,[2] and NMR data have reported there.

b). Synthesis and characterization of epoxides

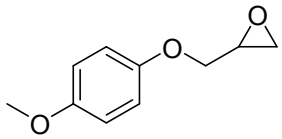
(A) Epoxide substrates were prepared starting from aromatic alcohols and alkenes as according to previously literatures procedure.[3-8]

(B) 2, 2-disubstituted epoxides were prepared according to literatures,[9-10] the method has modified as followed:



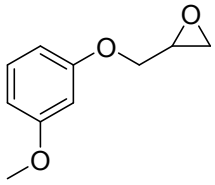
In dried and cleaned round bottom flask, charged with trimethylsulfoxonium iodide (15 mmol, 1.5 equiv.) and potassium tertbutoxyde (1.5 equiv.). 15 mL of DMSO was added, thenat room temperature the reaction mixture was stirred for 30 min. A solution of ketone (10 mmol, 1 equiv.) in DMSO (5 mL) was added. The reaction was left to react for more than 8 h at 50 - 60ºC. After reaction complete, extracted from water by EtOAc, washed, dried, concentrated and purified by column chromatography.

Characterization of epoxides



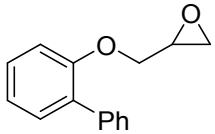
2-((4-methoxyphenoxy)methyl)oxirane (CAS: 2211-94-1)

This compound was perviuosly reported and our spectra data match those described.[7] following general procedure A. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 – 6.80 (m, 4H), 4.16 (dd, *J* = 11.0, 3.2 Hz, 1H), 3.89 (dd, *J* = 11.1, 5.7 Hz, 1H), 3.76 (s, 3H), 3.33 (ddt, *J* = 5.8, 3.9, 3.0 Hz, 1H), 2.88 (t, *J* = 4.5 Hz, 1H), 2.73 (dd, *J* = 4.9, 2.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.18, 152.65, 115.71, 114.64, 69.52, 55.69, 50.26, 44.71.



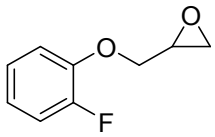
2-((3-methoxyphenoxy)methyl)oxirane (CAS: 2210-75-5)

Following general procedure A. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.14 (m, 1H), 6.56 – 6.46 (m, 3H), 4.20 (dd, *J* = 11.0, 3.2 Hz, 1H), 3.97 – 3.88 (m, 1H), 3.78 (s, 3H), 3.34 (ddt, *J* = 5.8, 4.1, 3.0 Hz, 1H), 2.92 – 2.87 (m, 1H), 2.74 (dd, *J* = 4.9, 2.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.84, 159.70, 129.94, 106.84, 106.62, 101.15, 68.74, 55.26, 50.10, 44.71.



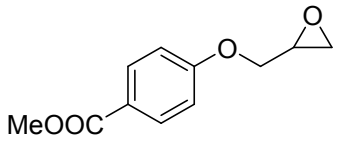
2-(([1,1'-biphenyl]-2-yloxy)methyl)oxirane (CAS: 7144-65-2)

Following general procedure A. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dt, *J* = 4.2, 2.3 Hz, 2H), 7.44 – 7.37 (m, 2H), 7.37 – 7.26 (m, 3H), 7.06 (tt, *J* = 7.5, 1.1 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 4.20 (dd, *J* = 11.2, 2.6 Hz, 1H), 3.97 (dd, *J* = 11.2, 5.1 Hz, 1H), 3.30 – 3.20 (m, 1H), 2.82 – 2.76 (m, 1H), 2.66 (dd, *J* = 5.0, 2.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.39, 138.29, 131.27, 131.02, 129.53, 128.60, 127.95, 126.93, 121.67, 113.18, 68.99, 50.21, 44.59.



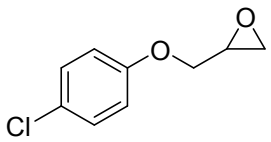
2-((2-fluorophenoxy)methyl)oxirane (CAS: 15620-80-1)

Following general procedure A. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 – 7.04 (m, 2H), 7.04 – 6.96 (m, 1H), 6.96 – 6.88 (m, 1H), 4.28 (dd, *J* = 11.2, 3.2 Hz, 1H), 4.08 – 3.98 (m, 1H), 3.41 – 3.33 (m, 1H), 2.90 (td, *J* = 4.5, 2.3 Hz, 1H), 2.76 (dt, *J* = 4.8, 2.2 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -133.96 – -134.08 (m). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.86 (d, *J* = 245.9 Hz), 146.56 (d, *J* = 10.6 Hz), 124.36 (d, *J* = 3.9 Hz), 121.93 (d, *J* = 6.9 Hz), 116.38 (d, *J* = 18.3 Hz), 115.75, 70.40, 50.08, 44.64.



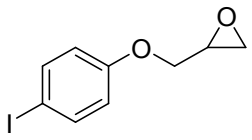
4-(oxiran-2-ylmethoxy)phenyl acetate (CAS: 172210-35-4)

Following general procedure A. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.95 (m, 2H), 6.99 – 6.89 (m, 2H), 4.34 – 4.26 (m, 1H), 3.97 (dd, *J* = 11.0, 5.8 Hz, 1H), 3.93 – 3.85 (m, 3H), 3.36 (ddt, *J* = 5.8, 4.1, 2.8 Hz, 1H), 2.97 – 2.88 (m, 1H), 2.76 (dd, *J* = 4.9, 2.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.73, 162.14, 131.62, 123.11, 114.19, 68.82, 51.90, 49.90, 44.58.



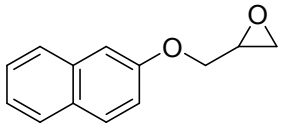
2-((4-chlorophenoxy)methyl)oxirane (CAS: 2212-05-7)

This compound was perviuosly reported and our spectra data match those described.[11-12] Following general procedure A. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.19 (m, 2H), 6.88 – 6.81 (m, 2H), 4.21 (dd, *J* = 11.0, 3.0 Hz, 1H), 3.93 – 3.85 (m, 1H), 3.33 (ddt, *J* = 5.8, 4.0, 2.8 Hz, 1H), 2.90 (t, *J* = 4.5 Hz, 1H), 2.74 (dd, *J* = 4.9, 2.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.09, 129.37, 126.09, 115.94, 69.06, 50.02, 44.56.



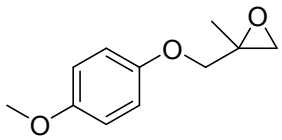
2-((4-iodophenoxy)methyl)oxirane (CAS: 828-25-1)

Following general procedure A. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.49 (m, 2H), 6.74 – 6.64 (m, 2H), 4.20 (ddd, *J* = 11.0, 2.9, 1.9 Hz, 1H), 3.94 – 3.84 (m, 1H), 3.37 – 3.28 (m, 1H), 2.93 – 2.85 (m, 1H), 2.74 (dt, *J* = 5.0, 2.6 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 158.38, 138.29, 117.05, 83.43, 68.86, 49.99, 44.61.



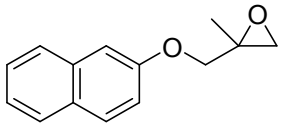
2-((naphthalen-2-yloxy)methyl)oxirane (CAS: 5234-06-0)

This compound was perviuosly reported and our spectra data match those described.[13] Following general procedure A. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.69 (m, 3H), 7.44 (t, *J* = 7.1 Hz, 1H), 7.37 – 7.31 (m, 1H), 7.18 (dt, *J* = 8.7, 4.4 Hz, 1H), 7.13 (d, *J* = 2.5 Hz, 1H), 4.34 (dd, *J* = 11.0, 3.1 Hz, 1H), 4.07 (dd, *J* = 11.0, 5.7 Hz, 1H), 3.48 – 3.37 (m, 1H), 2.99 – 2.89 (m, 1H), 2.81 (dd, *J* = 4.9, 2.7 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 156.42, 134.40, 129.54, 129.16, 127.66, 126.79, 126.45, 123.85, 118.78, 106.84, 68.73, 50.11, 44.78.



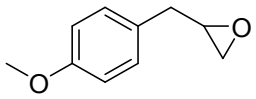
2-((4-methoxyphenoxy)methyl)-2-methyloxirane (CAS: 892390-16-8)

Following general procedure A. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 – 6.79 (m, 4H), 3.98 (d, *J* = 10.5 Hz, 1H), 3.90 (d, *J* = 10.5 Hz, 1H), 3.76 (s, 3H), 2.86 (d, *J* = 4.8 Hz, 1H), 2.72 (d, *J* = 4.8 Hz, 1H), 1.48 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 154.10, 152.82, 115.67, 114.61, 72.25, 55.70, 55.64, 52.03, 18.50.



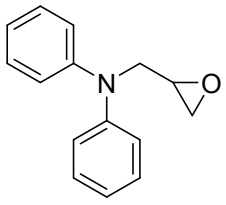
2-methyl-2-((naphthalen-2-yloxy)methyl)oxirane (CAS: 85686-31-3)

Following general procedure A. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 18.0, 8.7 Hz, 3H), 7.47 – 7.39 (m, 1H), 7.34 (ddd, *J* = 11.0, 6.0, 2.6 Hz, 1H), 7.21 – 7.16 (m, 1H), 7.13 (d, *J* = 2.4 Hz, 1H), 4.15 (d, *J* = 10.4 Hz, 1H), 4.06 (d, *J* = 10.4 Hz, 1H), 2.93 (d, *J* = 4.7 Hz, 1H), 2.77 (d, *J* = 4.7 Hz, 1H), 1.53 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 156.56, 134.44, 129.50, 129.15, 127.67, 126.81, 126.45, 123.83, 118.82, 106.92, 71.48, 55.57, 52.12, 18.60.



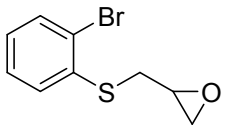
2-(4-methoxybenzyl)oxirane (CAS: 51410-45-8)

This compound was perviuosly reported and our spectra data match those described.[14] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.13 (m, 2H), 6.88 – 6.82 (m, 2H), 3.79 (s, 3H), 3.15 – 3.06 (m, 1H), 2.86 (dd, *J* = 14.6, 5.6 Hz, 1H), 2.80 – 2.70 (m, 2H), 2.52 (dd, *J* = 5.0, 2.7 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 158.43, 129.99, 129.14, 113.95, 55.26, 52.61, 46.80, 37.82.



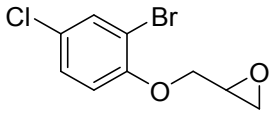
N-(oxiran-2-ylmethyl)-N-phenylaniline (CAS: 4510-27-4)

This compound was perviuosly reported and our spectra data match those described.[15] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 4H), 7.04 (d, *J* = 7.7 Hz, 4H), 6.97 (t, *J* = 7.3 Hz, 2H), 3.96 (dd, *J* = 15.8, 3.8 Hz, 1H), 3.86 (dd, *J* = 15.8, 4.8 Hz, 1H), 3.23 (td, *J* = 7.1, 4.0 Hz, 1H), 2.80 – 2.75 (m, 1H), 2.56 (dd, *J* = 4.9, 2.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.95, 129.37, 121.72, 121.02, 53.87, 50.37, 46.01.



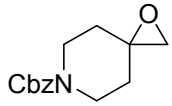
2-(((2-bromophenyl)thio)methyl)oxirane (CAS: 1094686-08-4)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.41 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.08 (td, *J* = 7.9, 1.6 Hz, 1H), 3.24 – 3.16 (m, 2H), 3.06 – 2.97 (m, 1H), 2.80 (t, *J* = 4.3 Hz, 1H), 2.58 (dd, *J* = 4.9, 2.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.64, 133.19, 129.78, 127.88, 127.56, 124.70, 50.59, 47.27, 35.70.



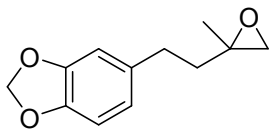
2-((2-bromo-4-chlorophenoxy)methyl)oxirane (CAS: 68224-01-1)

This compound was perviuosly reported and our spectra data match those described.[10] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 2.5 Hz, 1H), 7.22 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.86 (d, *J* = 8.8 Hz, 1H), 4.30 (dd, *J* = 11.3, 2.8 Hz, 1H), 4.02 (dd, *J* = 11.2, 5.3 Hz, 1H), 3.41 – 3.32 (m, 1H), 2.92 (t, *J* = 4.5 Hz, 1H), 2.84 (dd, *J* = 4.9, 2.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.84, 132.97, 128.32, 126.80, 114.51, 112.97, 69.96, 49.97, 44.55.



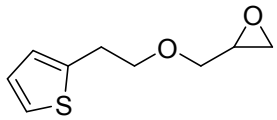
Benzyl 1-oxa-6-azaspiro[2.5]octane-6-carboxylate (CAS: 77211-75-7)

This compound was perviuosly reported and our spectra data match those described.[10] Following general procedure B.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 5H), 5.15 (s, 2H), 3.82 (s, 2H), 3.49 (ddd, *J* = 13.3, 9.7, 3.6 Hz, 2H), 2.70 (s, 2H), 1.83 (s, 2H), 1.45 (d, *J* = 12.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.26, 136.72, 128.52, 128.05, 127.92, 67.24, 56.93, 53.74, 42.66, 32.89.



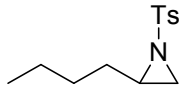
5-(2-(2-methyloxiran-2-yl)ethyl)benzo[d][1,3]dioxole (CAS: 1644661-06-2)

This compound was perviuosly reported and our spectra data match those described.[10] Following general procedure B.^{1}H NMR (300 MHz, $CDCl_3$) δ 6.76 – 6.59 (m, 3H), 5.92 (s, 2H), 2.70 – 2.54 (m, 4H), 1.94 – 1.71 (m, 2H), 1.36 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.61, 145.70, 135.43, 120.96, 108.73, 108.20, 100.80, 56.62, 53.92, 38.81, 31.18, 21.04.



2-((2-(thiophen-2-yl)ethoxy)methyl)oxirane (CAS: 1250057-30-7)

This compound was perviuosly reported and our spectra data match those described.[10] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.92 (dt, *J* = 8.2, 4.1 Hz, 1H), 6.87 – 6.83 (m, 1H), 3.82 – 3.66 (m, 3H), 3.42 (dt, *J* = 11.2, 5.6 Hz, 1H), 3.19 – 3.14 (m, 1H), 3.11 (t, *J* = 6.8 Hz, 2H), 2.82 – 2.77 (m, 1H), 2.62 (dd, *J* = 5.0, 2.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.06, 126.70, 125.18, 123.69, 72.01, 71.56, 50.81, 44.27, 30.45.



2-butyl-1-tosylaziridine (CAS: 116905-61-4)

This compound was perviuosly reported and our spectra data match those described.[10] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 2.78 – 2.67 (m, 1H), 2.63 (d, *J* = 7.0 Hz, 1H), 2.45 (s, 3H), 2.07 (t, *J* = 6.7 Hz, 1H), 1.61 – 1.48 (m, 1H), 1.35 (dt, *J* = 13.5, 6.9 Hz, 1H), 1.29 – 1.13 (m, 4H), 0.81 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.41, 135.23, 129.62, 128.00, 40.43, 33.82, 31.00, 28.88, 22.12, 21.63, 13.84.

III. General Experimental Procedures, Spectral Data and HPLC Analysis

Experimental Procedures for Examples Described in Table 1.

In air, clean and dried schlenk tube was charged with Cu catalyst (0.04 mmol), base (0.6 mmol, 3 equiv.), and diborylmethane (0.4 mmol, 2 equiv.) which equipped with a stirring bar. The vessel was evacuated and filled with argon (three times). Under inert gas 0.5 mL of solvent was added.The reaction mixture was stirred for 10 – 20 min at 60 °C. Then benzyl glycidyl ether substrate (0.2 mmol, 1 equiv.) was added under inert gas. The resulting suspension was stirred for 24 h at 60 °C. After completing of reaction, 4 mL of H_2O was added for reaction mixture, and extracted by EtOAc (3 x 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, concentrated under reduced pressure and purified by flash column chromatography over silic gel using petroleum ether/EtOAc (10/1 to 5/1, v/v) as eluent. The column fractions were collected together and evaporated under reduced pressure to obtain the desired product.

Experimental Procedures for Examples Described in Table 2.

In air, schlenk tube was charged with CuI (0.04 mmol), LiO^tBu (0.6 mmol, 3 equiv.), and diborylmethane (0.4 mmol, 2 equiv.) which equipped with a stirring bar. The vessel was evacuated and filled with argon (three times). Under inert gas 0.5 mL of THF was added.The reaction mixture was stirred for 20 min at 60 °C. Then oxirane substrate (0.2 mmol, 1 equiv.) was added under inert gas. The resulting suspension was stirred for 24 h at 60 °C. After completing of reaction, 4 mL of H_2O was added for reaction mixture, and extracted by EtOAc (3 x 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, concentrated under reduced pressure and purified by flash column chromatography using petroleum ether/EtOAc (10/1 to 2/1,

v/v) as eluent to afford the desired product.

Experimental Procedures for Examples Described in Table 3.

In air, schlenk tube was charged with CuI (0.04 mmol), LiO^{t}Bu (0.6 mmol, 3 equiv.), and diborylmethane (0.4 mmol, 2 equiv.) which equipped with a stirring bar. The vessel was evacuated and filled with argon (three times). Under inert gas 0.5 mL of THF was added.The reaction mixture was stirred for 20 min at 60 ^{o}C. Then 1,1-disubstituted epoxide substrate (0.2 mmol, 1 equiv.) was added under inert gas. The resulting suspension was stirred for 24 h at 60 or 80 ^{o}C (ketal group substrate, the reaction was performed at 80 ^{o}C). After completing of reaction, 4 mL of H_2O was added for reaction mixture, and extracted by EtOAc (3 x 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, concentrated under reduced pressure followed by flash column chromatography using petroleum ether/EtOAc (10/1 to 3/1, v/v) as eluent to afford the desired product.

Experimental Procedures for Examples Described in Scheme 2.

In air, schlenk tube was charged with CuI (0.04 mmol), LiO^{t}Bu (0.6 mmol, 3 equiv.), and diborylmethane (0.4 mmol, 2 equiv.) which equipped with a stirring bar. The vessel was evacuated and filled with argon (three times). Under inert gas 0.5 mL of THF was added.The reaction mixture was stirred for 15 min at 60 ^{o}C. Then N-sulfonyl aziridine (0.2 mmol, 1 equiv.) was added under inert gas. The resulting suspension was stirred for 24 h at 60 ^{o}C up to end of reaction. The resulting reaction mixture was filtered, concentrated under reduced pressure and purified by flash column chromatography using petroleum ether/EtOAc (5/1, v/v) as eluent to afford the desired product.

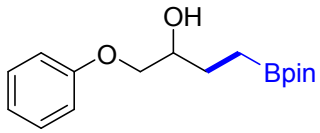
Experimental Procedures for Examples Described in Scheme 3.

A) In air, schlenk tube was charged with CuI (0.04 mmol), LiO^{t}Bu (0.6 mmol, 3 equiv.), and diborylmethane (0.4 mmol, 2 equiv.) which equipped with a stirring bar. The vessel was evacuated and filled with argon (three times). Under inert gas 0.5 mL of THF was added. The reaction mixture was stirred for 20 min at 60 ^{o}C. Then benzyl (S)-glycidyl ether (0.2 mmol, 1 equiv.) was added under inert gas. The resulting suspension was stirred for 24 h at 60 ^{o}C. After completing of reaction, 4 mL of H_2O was added for reaction mixture, extracted by EtOAc (3 x 5 mL), dried over anhydrous Na_2SO_4, filtered, concentrated and purified by flash column chromatography using petroleum ether/EtOAc (5/1, v/v) as eluent to afford γ-pinacolboronate alcohol product.

B) The oxidation step of pinacolboronate alcohol was conducted according to the previous literatures procedure.[16-18] In around-bottom flask, γ-pinacolboronate alcohol (0.13 mmol) in 4 mL THF was cooled to 0 ^{o}C (ice-water bath), and 0.65 mL of 3 N NaOH and 0.65 mL of 30% H_2O_2 were added dropwise. The mixture was then stirred at ambient temperature for 8 h. 2 mL of water was added to the resulting solution, and then extracted by EtOAc (3 x 5 mL), dried over anhydrous Na_2SO_4, filtered, concentrated and purified by column chromatography using petroleum ether/EtOAc (2/1, v/v) to afford 1,3-diol product. The enantiomeric purity of (S)-4-(benzyloxy)butane-1,3-diol was determined by HPLC analysis in comparison with racemic product (Chiralcel OD-H column, 90:10 hexanes/*i*-PrOH, 1.5

mL/min, 210 nm).

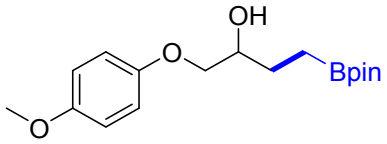
Substrate scope



Phenoxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-ol (3a)

Following general procedure, (49.5 mg, 85% yield) as a colorless oil ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.21 (m, 2H), 6.98 – 6.83 (m, 3H), 3.99 – 3.89 (m, 2H), 3.88 – 3.73 (m, 1H), 2.75 (br, 1H), 1.87 – 1.59 (m, 2H), 1.24 (s, 12H), 0.99 – 0.85 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.70, 129.42, 120.87, 114.54, 83.19, 71.83, 71.52, 27.61, 24.79, 7.06.

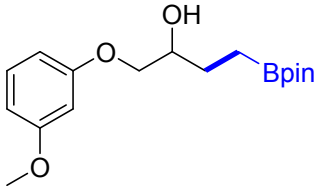
HRMS calcd for $C_{16}H_{25}BO_4[H]^+$: 293.1919; found: 293.1913.



1-(4-methoxyphenoxy)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-ol (3b)

Following general procedure, (52 mg, 81% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 – 6.68 (m, 4H), 3.88 – 3.80 (m, 2H), 3.76 – 3.70 (m, 1H), 3.68 (s, 3H), 2.40 (br, 1H), 1.75 – 1.50 (m, 2H), 1.25 (s, 12H), 0.94 – 0.75 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.07, 152.99, 115.64, 114.73, 83.34, 72.78, 71.79, 55.81, 27.66, 24.91, 7.17.

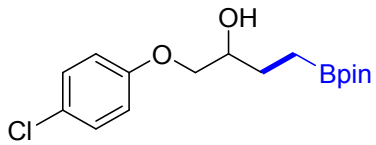
HRMS calcd for $C_{17}H_{27}BO_5[H]^+$: 323.2024; found: 323.2027.



1-(3-methoxyphenoxy)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-ol (3c)

Following general procedure, (35.8 mg, 56% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.07 (m, 1H), 6.61 – 6.35 (m, 3H), 4.00 – 3.89 (m, 2H), 3.89 – 3.80 (m, 1H), 3.78 (s, 3H), 2.57 (br, 1H), 1.86 – 1.56 (m, 2H), 1.25 (s, 12H), 1.03 – 0.84 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.92, 160.07, 130.00, 106.78, 106.73, 101.16, 83.39, 72.05, 71.73, 55.38, 27.68, 24.92, 7.28.

HRMS calcd for $C_{17}H_{27}BO_5[H]^+$: 323.2024; found: 323.2029.

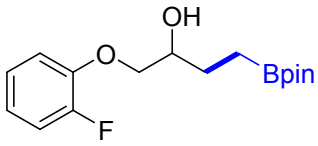


1-(4-chlorophenoxy)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-ol (3d)

Following general procedure, (53 mg, 81% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.19 (m, 2H), 6.86 – 6.79 (m, 2H), 3.98 – 3.88 (m, 2H), 3.86 – 3.77 (m, 1H), 2.45 (br, 1H), 1.83 –

1.57 (m, 2H), 1.25 (s, 12H), 1.01 – 0.86 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.46, 129.43, 125.91, 115.95, 83.44, 72.36, 71.68, 27.68, 24.92, 7.20.

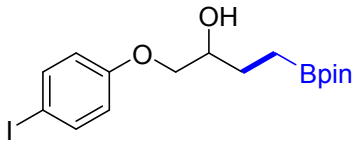
HRMS calcd for $C_{16}H_{24}BClO_4[H]^+$: 327.1529; found: 327.1531.



1-(2-fluorophenoxy)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-ol (3e)

Following general procedure, (48.5 mg, 78% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 – 7.00 (m, 2H), 6.99 – 6.84 (m, 2H), 4.20 – 3.68 (m, 3H), 2.61 (br, 1H), 1.85 – 1.57 (m, 2H), 1.25 (s, 12H), 1.03 – 0.84 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -134.26 – -134.55 (m). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.90 (d, J = 245.6 Hz), 146.94 (d, J = 10.6 Hz), 124.41 (d, J = 3.9 Hz), 121.56 (d, J = 6.9 Hz), 116.35 (d, J = 18.2 Hz), 115.41 (d, J = 1.6 Hz), 83.38, 73.58, 71.62, 27.50, 24.91, 7.12.

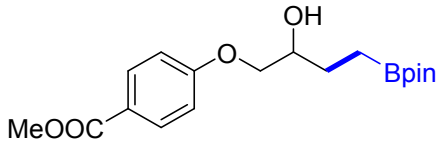
HRMS calcd for $C_{16}H_{24}BFO_4[H]^+$: 311.1824; found: 311.1827.



1-(4-iodophenoxy)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-ol (3f)

Following general procedure, (55.8 mg, 67% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.49 (m, 2H), 6.74 – 6.62 (m, 2H), 3.99 – 3.86 (m, 2H), 3.86 – 3.76 (m, 1H), 2.58 (br, 1H), 1.80 – 1.58 (m, 2H), 1.25 (s, 12H), 1.01 – 0.81 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.72, 138.31, 117.07, 83.42, 83.12, 72.14, 71.61, 27.67, 24.92, 7.15.

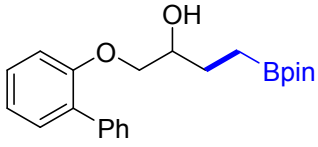
HRMS calcd for $C_{16}H_{24}BIO_4[H]^+$: 419.0885; found: 419.0889.



Methyl 4-(2-hydroxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butoxy)benzoate (3g)

Following general procedure, (51.2 mg, 73% yield) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 4.08 – 3.91 (m, 3H), 3.89 (s, 3H), 1.79 – 1.63 (m, 2H), 1.26 (s, 12H), 0.95 (t, J = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.96, 162.61, 131.72, 122.94, 114.28, 83.48, 72.19, 71.64, 52.01, 27.70, 24.94, 7.20.

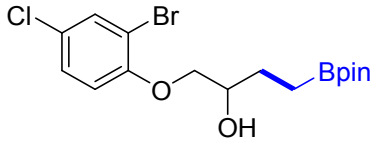
HRMS calcd for $C_{18}H_{27}BO_6[H]^+$: 351.1973; found: 351.1978.



1-([1,1'-biphenyl]-2-yloxy)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-ol (3h)

Following general procedure, (49.8 mg, 68% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.47 (m, 2H), 7.43 – 7.36 (m, 2H), 7.35 – 7.26 (m, 3H), 7.07 – 7.02 (m, 1H), 6.99 – 6.93 (m, 1H), 4.01 – 3.90 (m, 1H), 3.89 – 3.75 (m, 2H), 2.24 (br, 1H), 1.70 – 1.51 (m, 2H), 1.23 (s, 12H), 0.94 – 0.69 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.60, 138.54, 131.44, 130.98, 129.56, 128.77, 128.16, 127.08, 121.55, 113.24, 83.29, 72.80, 71.65, 27.47, 24.92, 7.23.

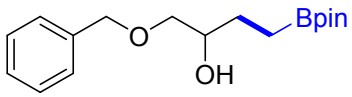
HRMS calcd for $C_{22}H_{29}BO_4[H]^+$: 369.2232; found: 369.2242.



1-(2-bromo-4-chlorophenoxy)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-ol (3i)

Following general procedure, (58 mg, 72% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.45 (m, 1H), 7.25 – 7.17 (m, 1H), 6.81 (d, *J* = 8.8 Hz, 1H), 4.03 – 3.94 (m, 2H), 3.93 – 3.81 (m, 1H), 2.68 (br, 1H), 1.88 – 1.63 (m, 2H), 1.26 (s, 12H), 1.06 – 0.85 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.04, 132.87, 128.42, 126.50, 114.29, 112.97, 83.40, 73.64, 71.50, 27.50, 24.92, 7.26.

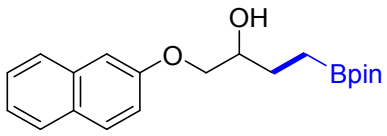
HRMS calcd for $C_{16}H_{23}BBrClO_4[H]^+$: 405.0634; found: 405.0637.



1-(benzyloxy)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-ol (3j)

Following general procedure, (41 mg, 67% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 5H), 4.61 – 4.50 (m, 2H), 3.86 – 3.63 (m, 1H), 3.53 – 3.45 (m, 1H), 3.43 – 3.28 (m, 1H), 2.42 (br, 1H), 1.66 – 1.51 (m, 2H), 1.24 (s, 12H), 0.93 – 0.80 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.20, 128.51, 127.82, 127.79, 83.23, 74.46, 73.38, 72.05, 27.64, 24.89, 7.25.

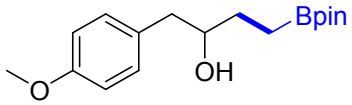
HRMS calcd for $C_{17}H_{27}BO_4[H]^+$: 307.2075; found: 307.2073.



1-(naphthalen-2-yloxy)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-ol (3k)

Following general procedure, (53.9 mg, 79% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.67 (m, 3H), 7.45 – 7.39 (m, 1H), 7.35 – 7.30 (m, 1H), 7.16 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.12 (d, *J* = 2.5 Hz, 1H), 4.11 – 3.94 (m, 3H), 2.46 (br, 1H), 1.87 – 1.65 (m, 2H), 1.25 (s, 12H), 1.03 – 0.90 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.77, 134.60, 129.51, 129.16, 127.74, 126.87, 126.48, 123.79, 118.94, 106.93, 83.39, 72.08, 71.74, 27.78, 24.93, 7.11.

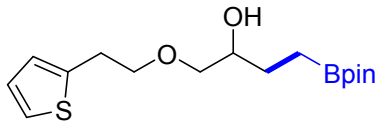
HRMS calcd for $C_{20}H_{27}BO_4[H]^+$: 343.2075; found: 343.2077.



1-(4-methoxyphenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-ol (3l)

Following general procedure, (48.5 mg, 79% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.08 (m, 2H), 6.88 – 6.79 (m, 2H), 3.78 (s, 3H), 3.76 – 3.66 (m, 1H), 2.80 – 2.68 (m, 1H), 2.68 – 2.56 (m, 1H), 1.74 – 1.63 (m, 1H), 1.60 – 1.53 (m, 1H), 1.24 (s, 12H), 0.95 – 0.85 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.27, 131.03, 130.45, 114.02, 83.33, 74.62, 55.40, 42.94, 31.00, 24.95.

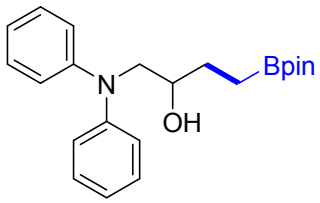
HRMS calcd for $C_{17}H_{27}BO_4[H]^+$: 307.2075 found: 307.2079.



4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(2-(thiophen-2-yl)ethoxy)butan-2-ol (3m)

Following general procedure, (50 mg, 77% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.05 (m, 1H), 6.99 – 6.87 (m, 1H), 6.86 – 6.77 (m, 1H), 3.78 – 3.62 (m, 3H), 3.56 – 3.43 (m, 1H), 3.32 (dd, *J* = 9.5, 7.6 Hz, 1H), 3.20 – 3.01 (m, 2H), 2.35 (br, 1H), 1.69 – 1.47 (m, 2H), 1.24 (s, 12H), 0.96 – 0.77 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.30, 126.77, 125.25, 123.83, 83.24, 75.11, 71.95, 71.83, 30.52, 27.55, 24.90, 7.06.

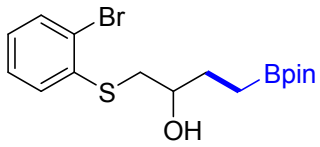
HRMS calcd for $C_{16}H_{27}BO_4S[H]^+$: 327.1796; found: 327.1796.



1-(diphenylamino)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-ol (3n)

Following general procedure, (51.1 mg, 70% yield) as light brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.22 (m, 4H), 7.07 (d, *J* = 7.7 Hz, 4H), 6.97 (t, *J* = 7.3 Hz, 2H), 3.92 – 3.78 (m, 2H), 3.69 – 3.60 (m, 1H), 1.76 – 1.52 (m, 2H), 1.24 (s, 12H), 0.90 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.64, 129.43, 121.83, 121.54, 83.34, 70.57, 58.98, 28.87, 24.94.

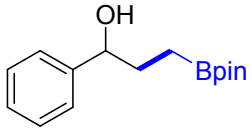
HRMS calcd for $C_{22}H_{30}BNO_3[H]^+$: 368.2392; found: 368.2388.



1-((2-bromophenyl)thio)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-ol (3o)

Following general procedure, (62.2 mg, 81% yield) as pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.54 (m, 1H), 7.35 – 7.33 (m, 1H), 7.28 – 7.24 (m, 1H), 7.06 – 7.02 (m, 1H), 3.70 (tt, *J* = 8.1, 4.0 Hz, 1H), 3.12 (dd, *J* = 13.4, 4.0 Hz, 1H), 2.93 (dd, *J* = 13.4, 8.2 Hz, 1H), 1.83 – 1.60 (m, 2H), 1.23 (s, 12H), 0.91 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.33, 133.17, 129.14, 127.88, 127.10, 124.37, 83.37, 71.10, 40.87, 30.65, 24.90, 7.54.

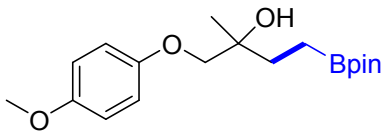
HRMS calcd for $C_{16}H_{24}BBrO_3S[H]^+$: 387.0795; found: 387.0801.



1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-ol (3p)

Following general procedure, (30 mg, 57% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 3H), 7.30 – 7.23 (m, 2H), 4.64 (t, *J* = 6.4 Hz, 1H), 2.28 (br, 1H), 1.90 –1.84 (m, 2H), 1.24 (s, 12H), 0.91 – 0.75 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.84, 128.42, 127.39, 126.01, 83.36, 76.09, 33.63, 24.94.

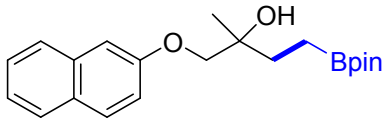
HRMS calcd for $C_{15}H_{23}BO_3[H]^+$: 263.1813; found: 263.1807.



1-(4-methoxyphenoxy)-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-ol (3ba)

Following general procedure, (49.5 mg, 74% yield) as pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 – 6.78 (m, 4H), 3.78 – 3.71 (m, 5H), 1.86 – 1.77 (m, 1H), 1.74 – 1.64 (m, 1H), 1.25 (s, 12H), 1.24 (s, 3H), 0.93 – 0.81 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.06, 153.23, 115.67, 114.74, 83.34, 75.56, 72.40, 55.89, 32.97, 24.96, 23.56.

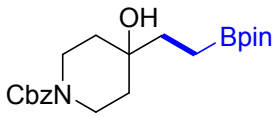
HRMS calcd for $C_{18}H_{29}BO_5[H]^+$: 337.2181; found: 337.2183.



2-methyl-1-(naphthalen-2-yloxy)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-ol (3bb)

Following general procedure, (42 mg, 59% yield) as pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.69 (m, 3H), 7.46 – 7.41 (m, 1H), 7.36 – 7.31 (m, 1H), 7.18 (dd, J = 8.8, 2.5 Hz, 1H), 7.15 – 7.12 (m, 1H), 3.93 (q, J = 8.9 Hz, 2H), 1.93 – 1.83 (m, 1H), 1.80 – 1.71 (m, 1H), 1.32 (s, 3H), 1.26 (s, 12H), 0.99 – 0.86 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.95, 134.65, 129.49, 129.19, 127.77, 126.90, 126.51, 123.81, 119.05, 106.98, 83.39, 74.87, 72.39, 33.07, 24.97, 23.70.

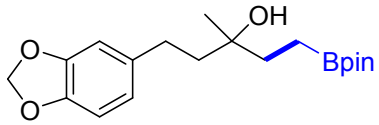
HRMS calcd for $C_{21}H_{29}BO_4[H]^+$: 357.2232; found: 357.2235.



Benzyl 4-hydroxy-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)piperidine-1-carboxylate (3bc)

Following general procedure, (52.7 mg, 68% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 5H), 5.12 (s, 2H), 3.90 (br, 2H), 3.23 (br, 2H), 1.67 – 1.42 (m, 6H), 1.25 (s, 12H), 0.83 (t, J = 7.8 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.41, 137.08, 128.58, 128.02, 127.92, 83.52, 69.77, 67.07, 40.25, 36.83, 36.58, 24.92, 4.05.

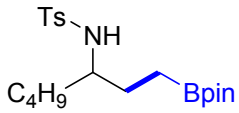
HRMS calcd for $C_{21}H_{32}BNO_5[H]^+$: 390.2446; found: 390.2448.



1-(benzo[d][1,3]dioxol-5-yl)-3-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentan-3-ol (3bd)

Following general procedure, (41.5 mg, 60% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 – 6.66 (m, 2H), 6.65 – 6.51 (m, 1H), 6.06 – 5.70 (m, 2H), 2.77 – 2.43 (m, 2H), 1.75 – 1.58 (m, 4H), 1.26 (s, 12H), 1.19 (s, 3H), 0.92 – 0.78 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.65, 145.59, 136.78, 121.06, 108.99, 108.28, 100.86, 83.38, 72.89, 44.09, 35.92, 30.29, 26.31, 24.95.

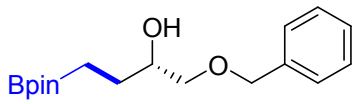
HRMS calcd for $C_{19}H_{29}BO_5[H]^+$: 349.2181; found: 349.2178.



4-methyl-N-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptan-3-yl)benzenesulfonamide (3ca)

Following general procedure, (62.5 mg, 79% yield) as off-white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.72 (m, 2H), 7.34 – 7.21 (m, 2H), 4.81 – 4.49 (m, 1H), 3.31 – 3.01 (m, 1H), 2.42 (s, 3H), 1.54 – 1.05 (m, 20H), 0.82 – 0.72 (m, 3H), 0.71 – 0.55 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.00, 138.62, 129.58, 127.17, 83.36, 55.56, 34.37, 28.70, 27.46, 24.86, 22.53, 13.99, 6.57.

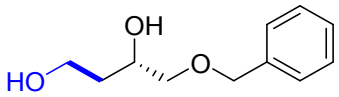
HRMS calcd for $C_{20}H_{34}BNO_4S[H]^+$: 396.2374; found: 396.2372.



(S)-1-(benzyloxy)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-ol (3aa)

Following general procedure, (48.2 mg, 79% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 5H), 4.55 (s, 2H), 3.84 – 3.67 (m, 1H), 3.53 – 3.43 (m, 1H), 3.35 (dd, *J* = 9.4, 7.6 Hz, 1H), 2.35 (br, 1H), 1.69 – 1.49 (m, 2H), 1.24 (s, 12H), 0.93 – 0.77 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.22, 128.5, 127.82, 127.79, 83.24, 74.48, 73.40, 72.07, 27.65, 24.89, 7.27.

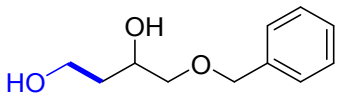
HRMS calcd for $C_{17}H_{27}BO_4[H]^+$: 307.2075; found: 307.2078.



(S)-4-(benzyloxy)butane-1,3-diol (3ab)

Following general procedure, (23.7 mg, 93% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 5H), 4.55 (s, 2H), 4.13 – 3.98 (m, 1H), 3.88 – 3.72 (m, 2H), 3.49 (dd, *J* = 9.5, 3.6 Hz, 1H), 3.44 – 3.37 (m, 1H), 2.64 (br, 2H), 1.78 – 1.60 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.93, 128.61, 127.99, 127.91, 74.51, 73.52, 70.27, 61.00, 34.98.

HRMS calcd for $C_{11}H_{16}O_3$ $[H]^+$: 197.1172; found: 197.1166.

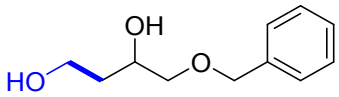


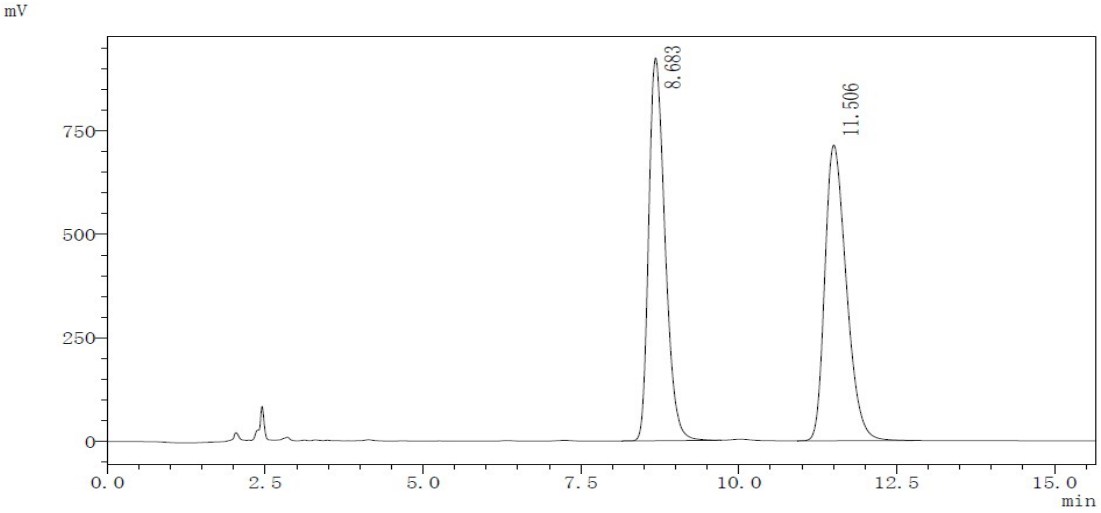
4-(benzyloxy)butane-1,3-diol (3ac)

Following general procedure, (21.9 mg, 86% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 5H), 4.55 (s, 2H), 4.12 – 3.98 (m, 1H), 3.89 – 3.73 (m, 2H), 3.49 (dd, *J* = 9.5, 3.6 Hz, 1H), 3.44 – 3.37 (m, 1H), 2.61 (br, 2H), 1.78 – 1.57 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.93, 128.61, 127.98, 127.90, 74.52, 73.52, 70.24, 60.97, 34.99.

HRMS calcd for $C_{11}H_{16}O_3[H]^+$: 197.1172; found: 197.1165.

HPLC Analysis





Peak	Ret. Time (min)	Area ((mAu*s)	Height (mAU)	Area %
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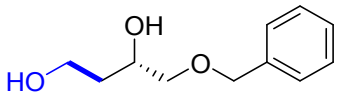
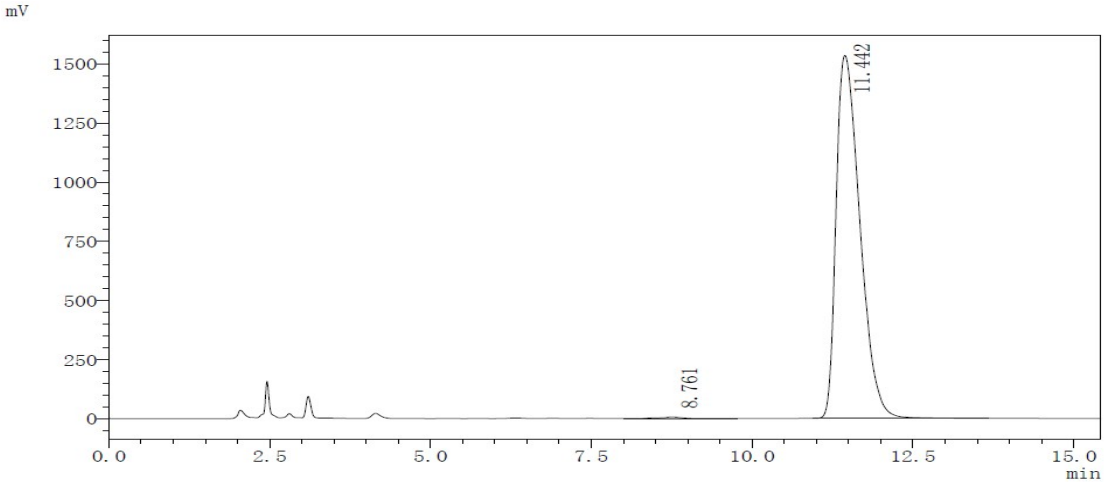
2	11.506	16888831	713493	50.402





Peak	Ret. Time (min)	Area ((mAu*s)	Height (mAU)	Area %
1	8.761	167134	6637	0.422
2	11.442	39450314	1534364	99.578

IV. References

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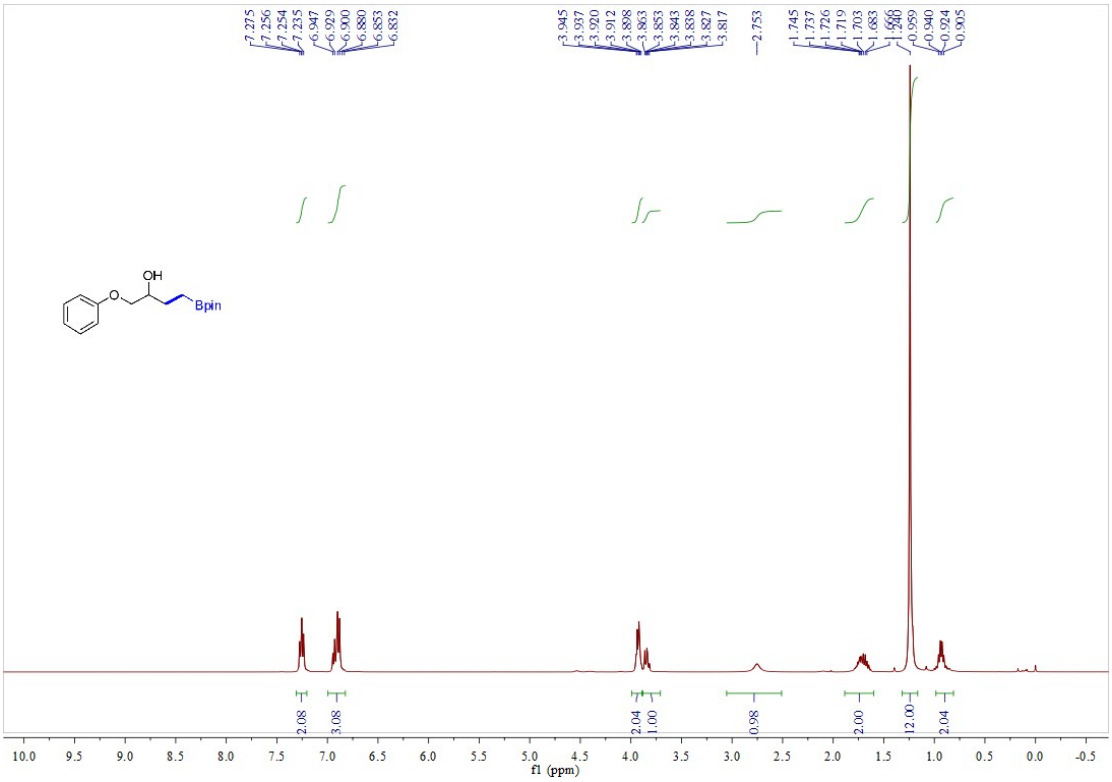
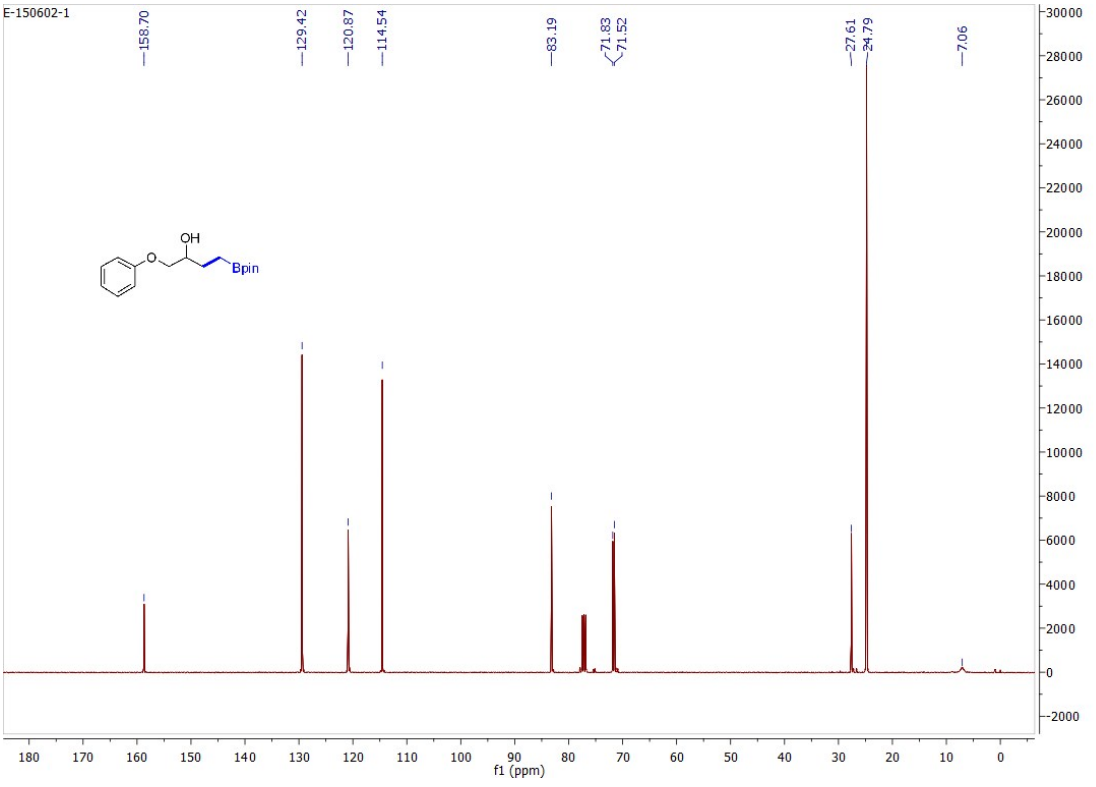
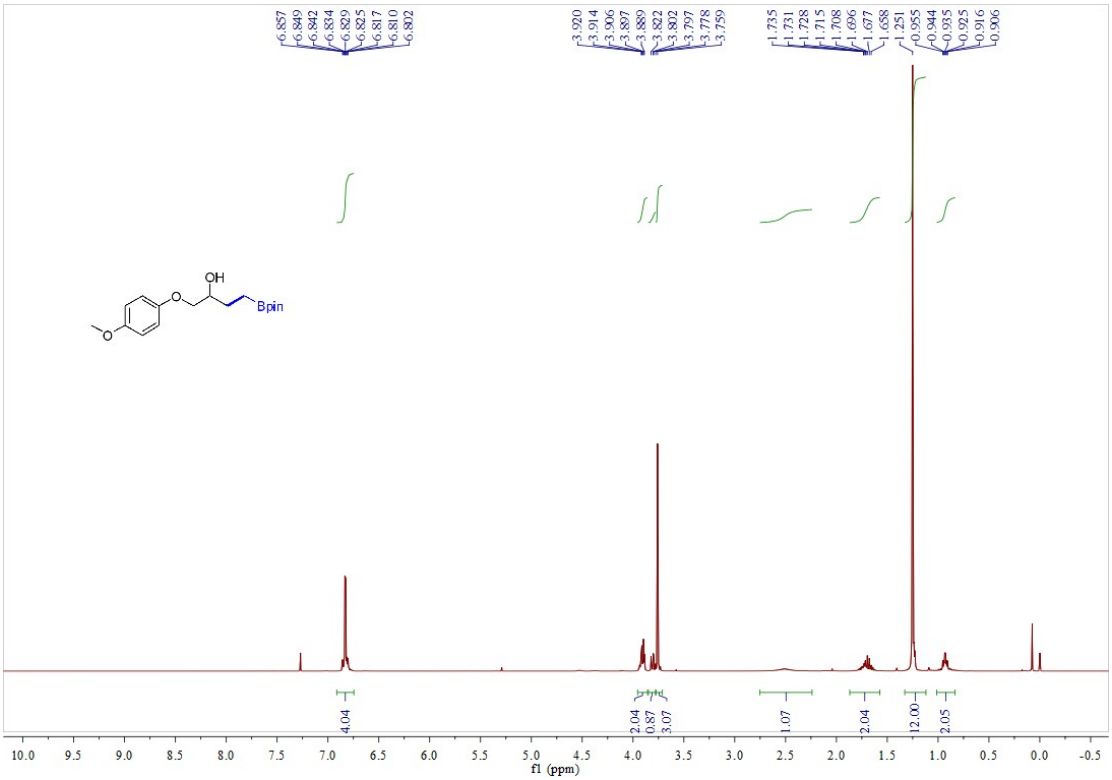
V. NMR Spectra



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3.802
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12.00
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9.0
8.5
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7.5
7.0
6.5
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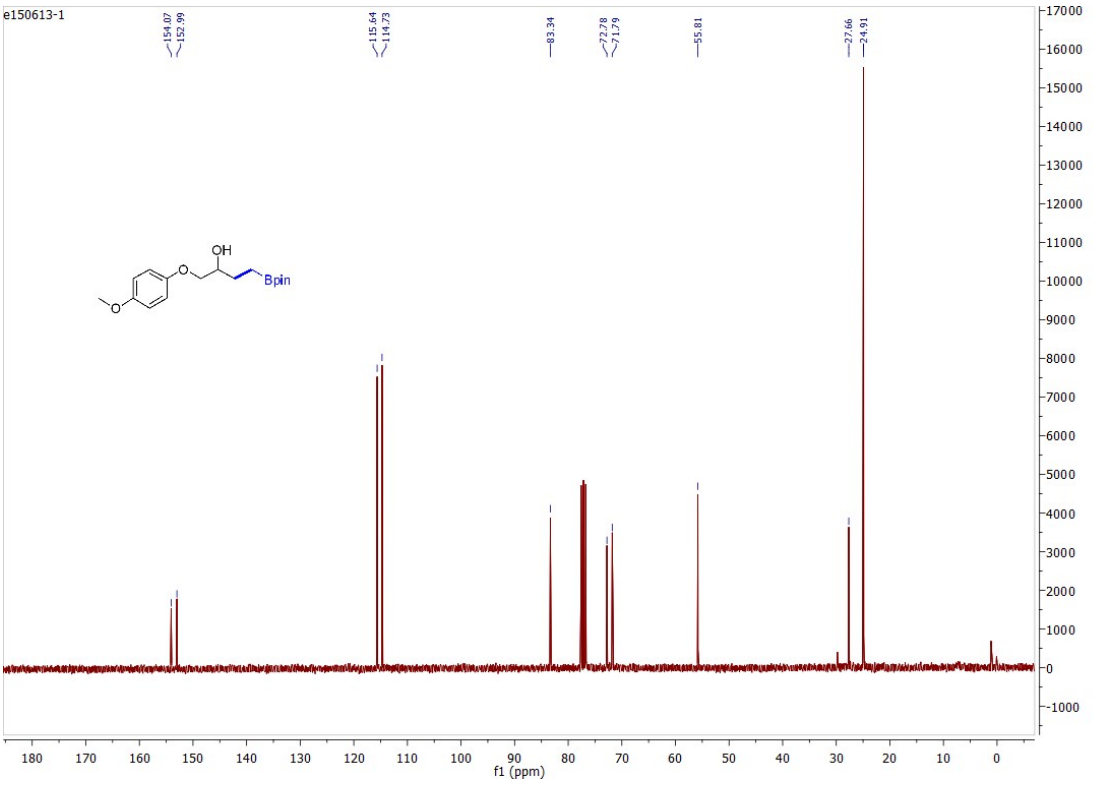
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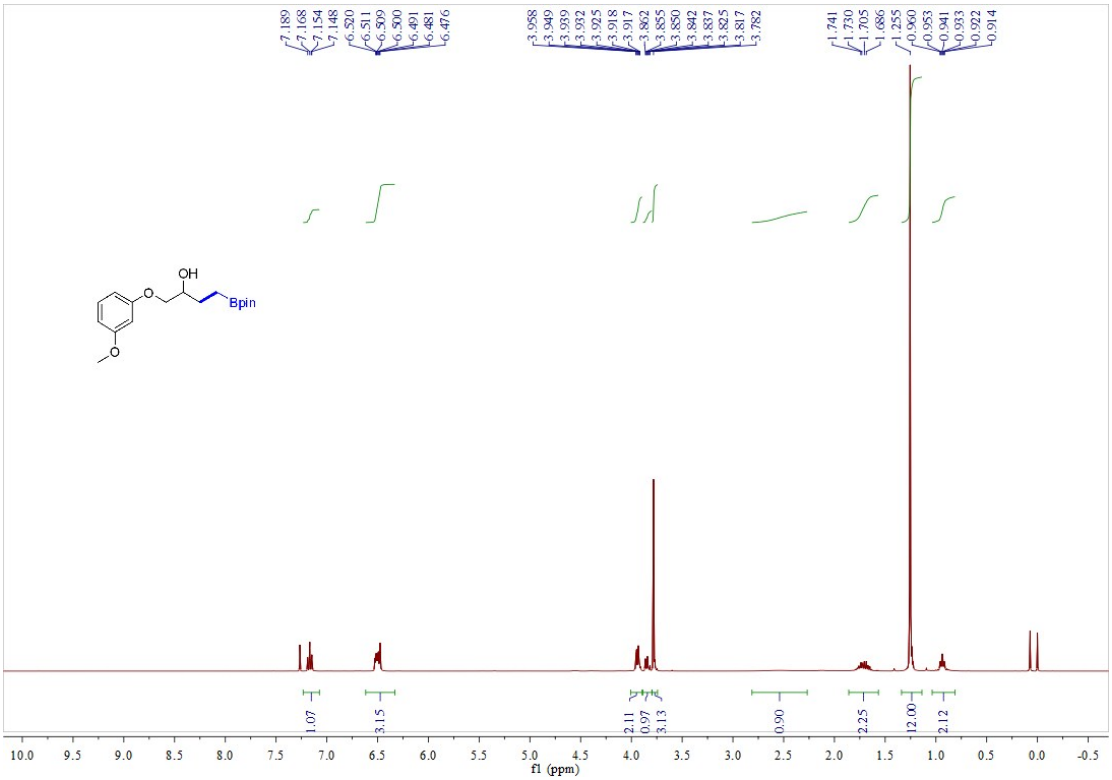
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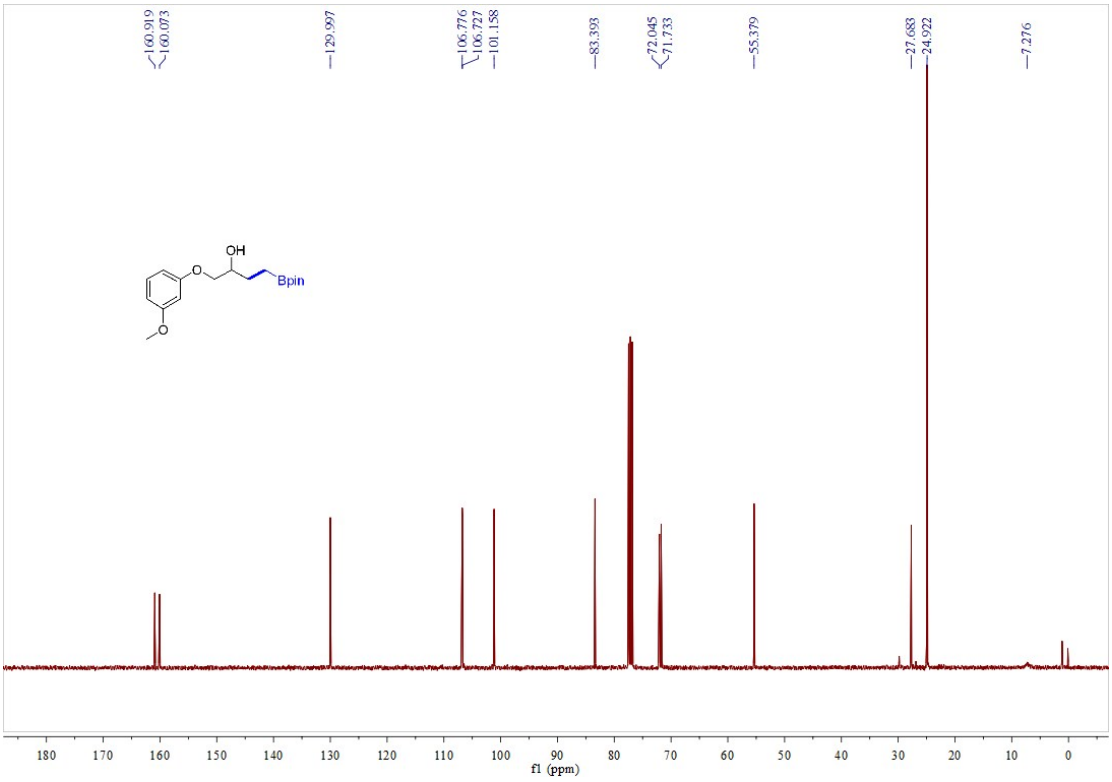
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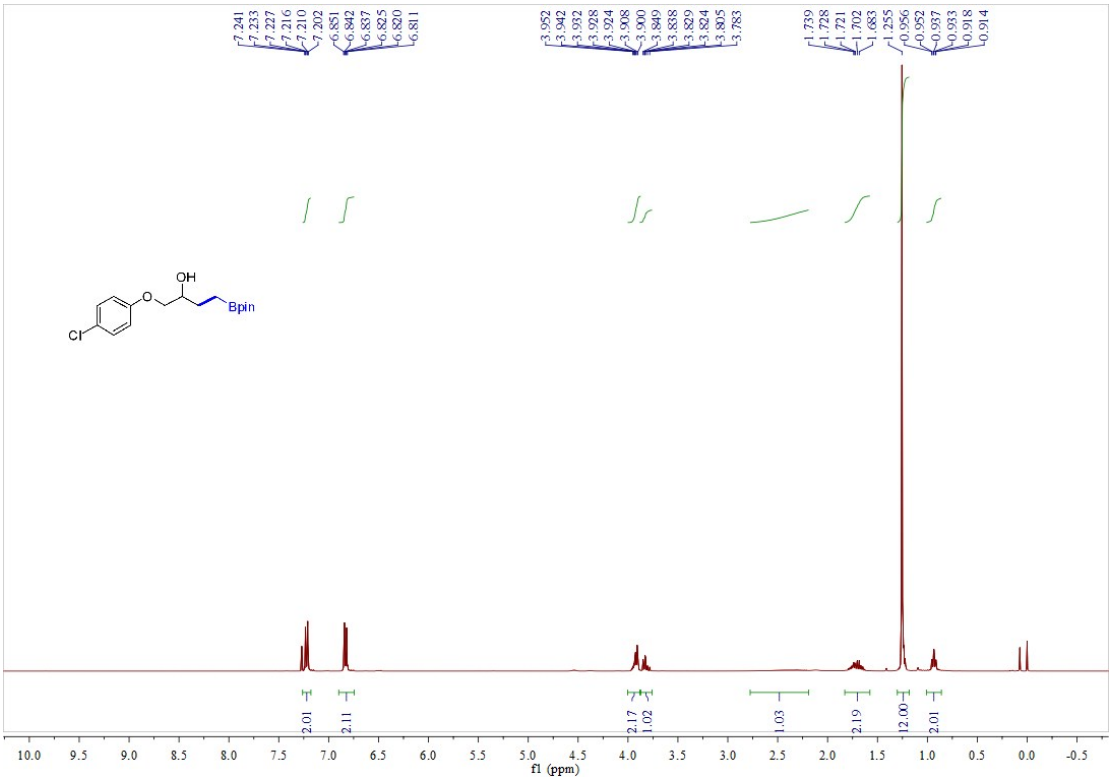
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2.11
2.17
1.02
1.03
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2.01
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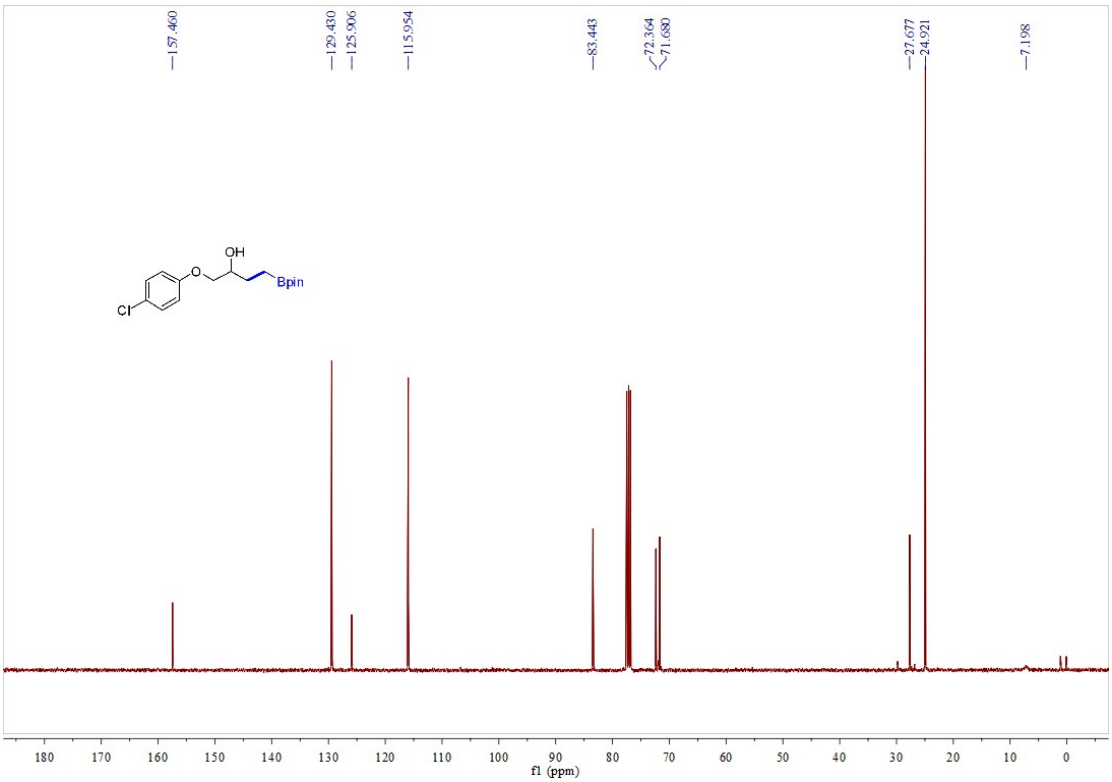
f1 (ppm)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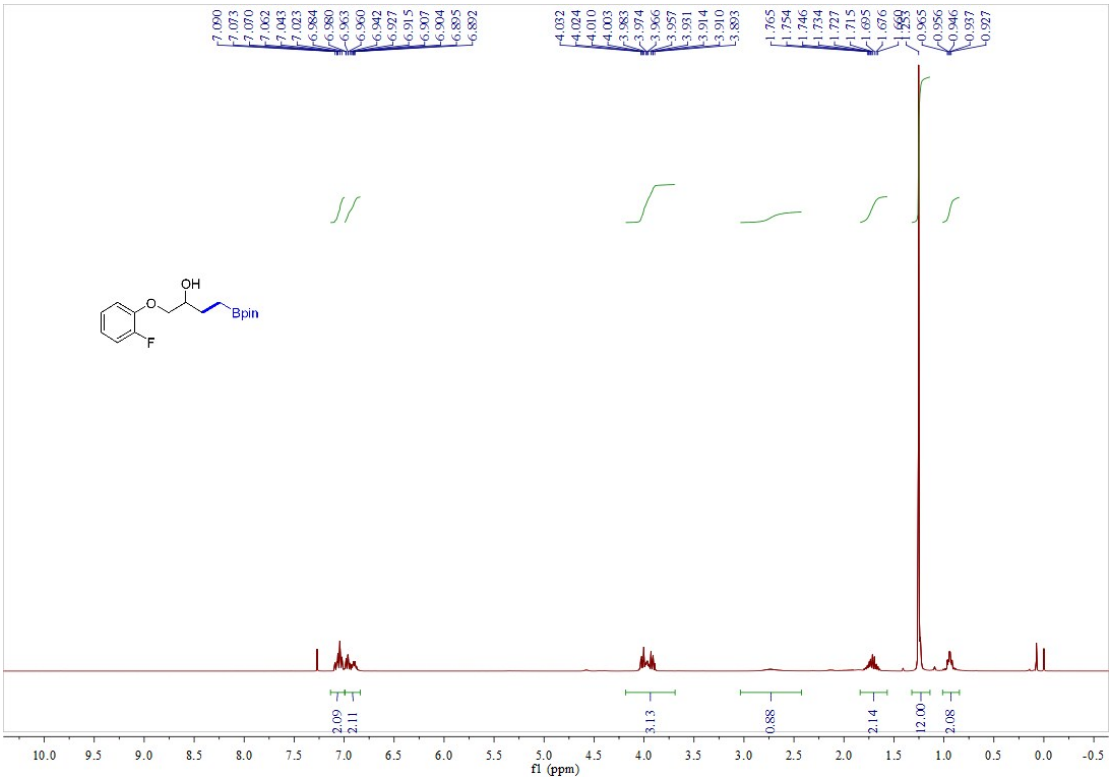
f1 (ppm)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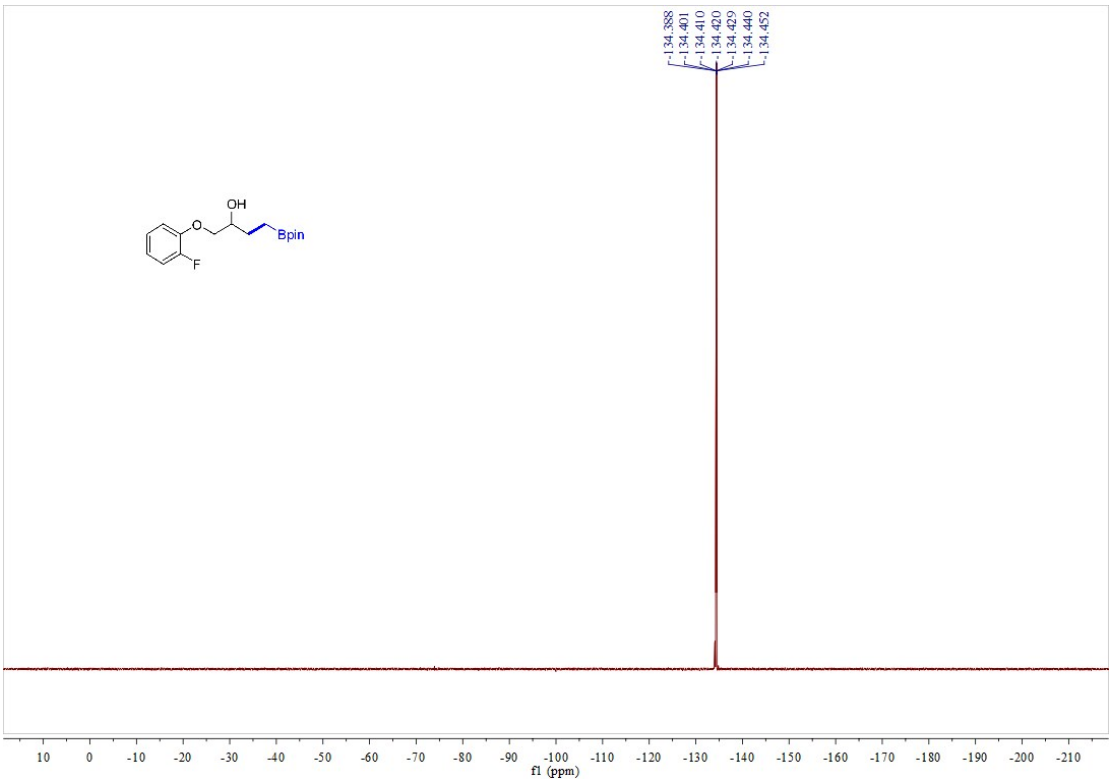
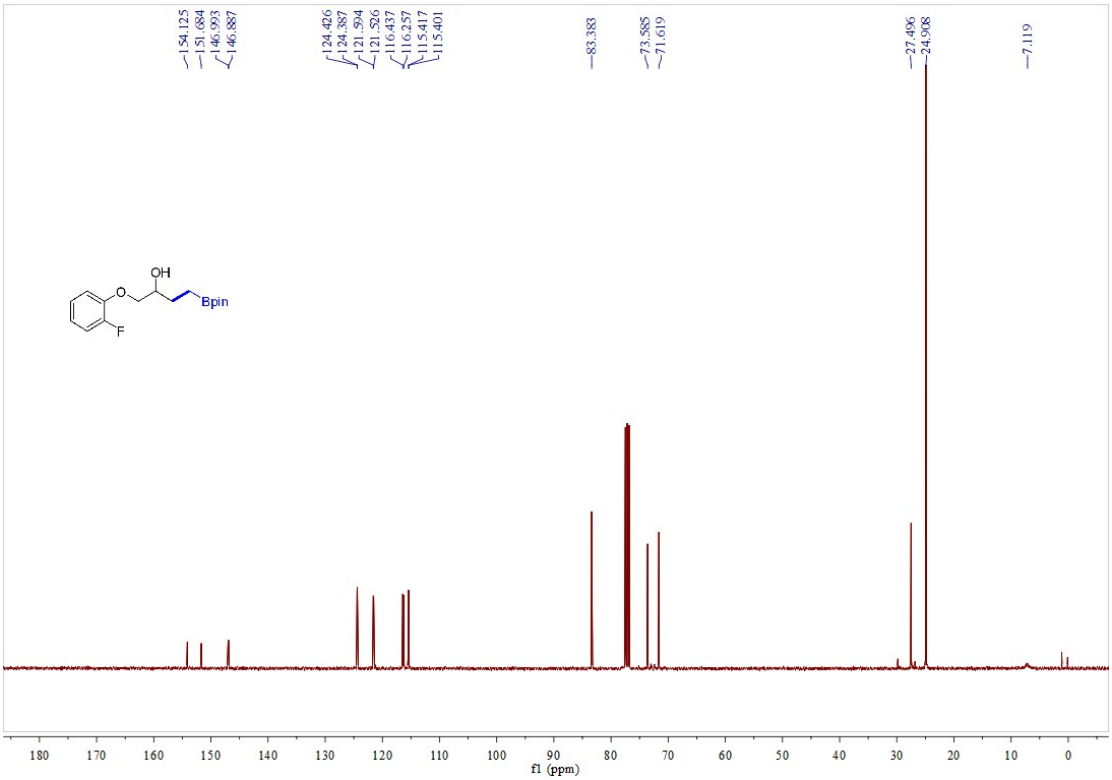
0.946
0.937
0.927
OH
O
Bpin
F
2.09
2.11
3.13
0.88
2.14
12.00
2.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


-134.388
-134.401
-134.410
-134.420
-134.429
-134.440
-134.452
OH
O
Bpin
F
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)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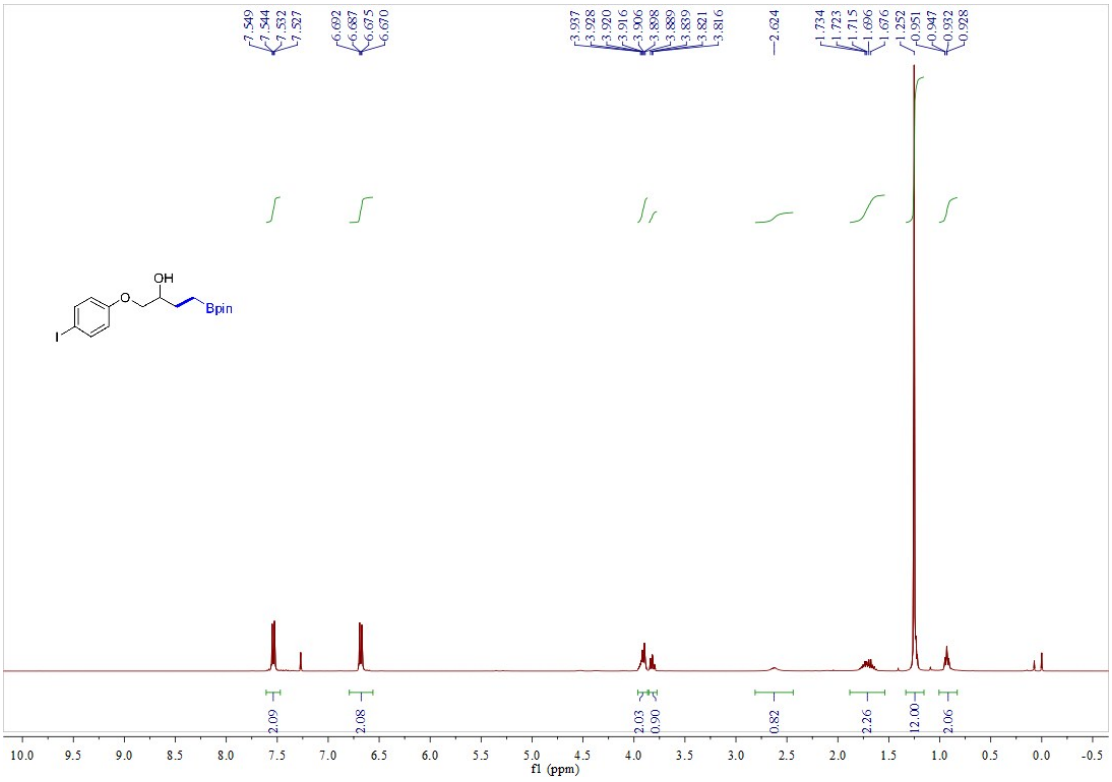
146.993
146.887
124.426
124.387
121.594
121.526
116.437
116.257
115.417
115.401
83.383
73.585
71.619
27.406
24.908
7.119
OH
Bpin
F
f1 (ppm)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7.532
7.527
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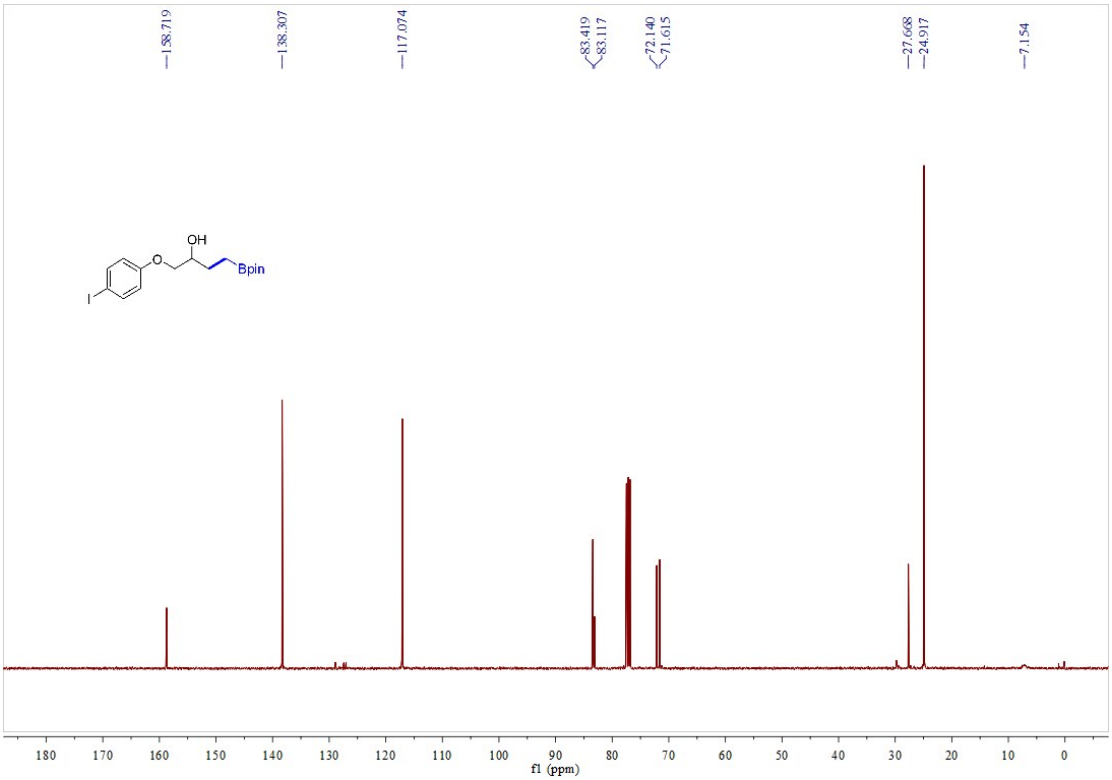
6.687
6.675
6.670
3.937
3.928
3.920
3.916
3.906
3.898
3.889
3.889
3.821
3.816
2.624
1.734
1.723
1.715
1.696
1.676
1.252
0.951
0.947
0.932
0.928
OH
Bpin
I
2.09
2.08
2.03
0.90
0.82
2.26
12.00
2.06
f1 (ppm)


158.719
138.307
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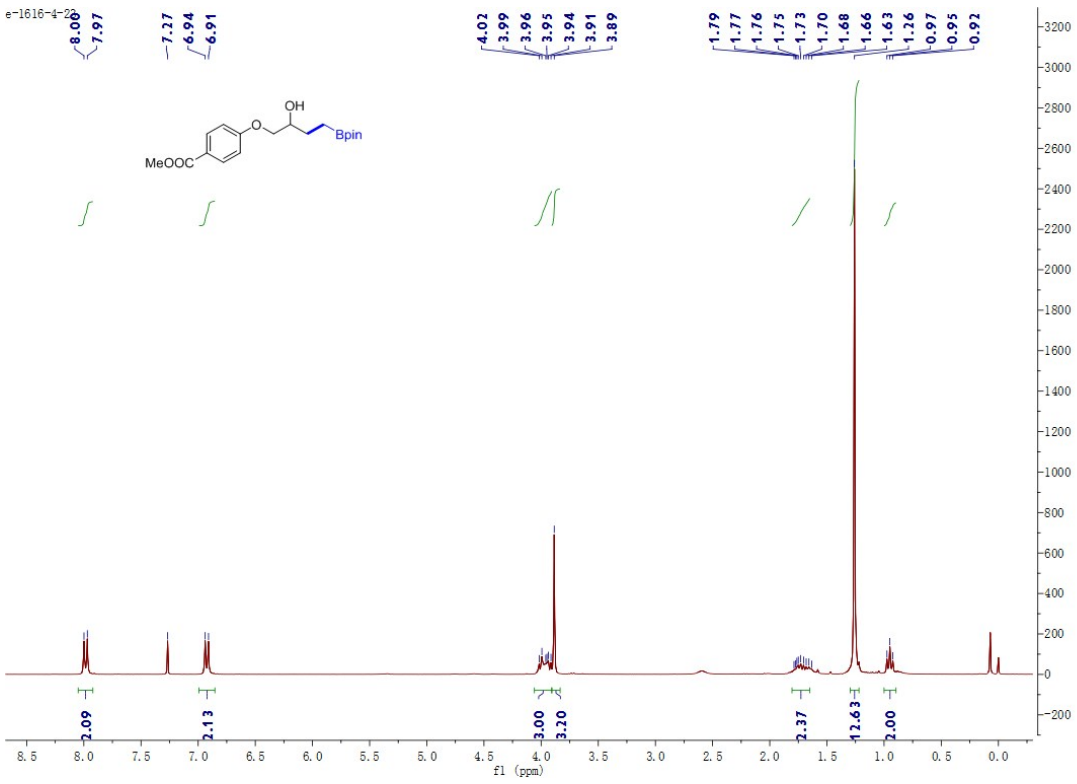
83.117
72.140
71.615
27.668
24.917
7.154
OH
O
Bpin
I
f1 (ppm)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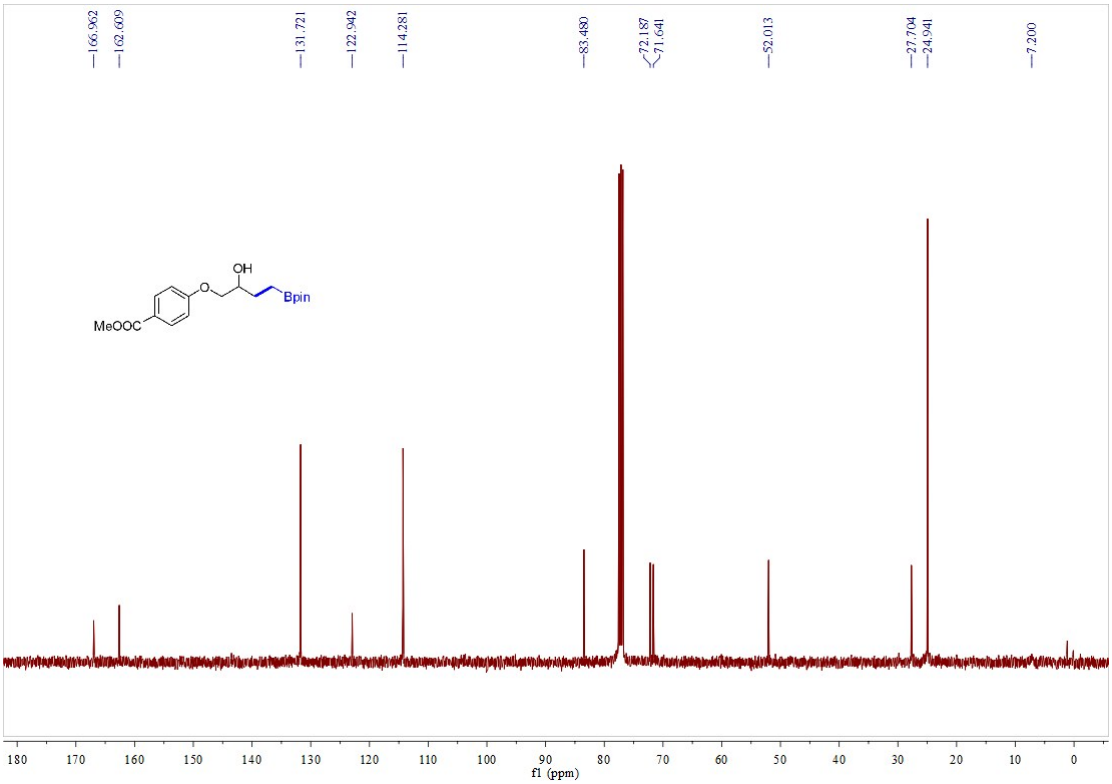
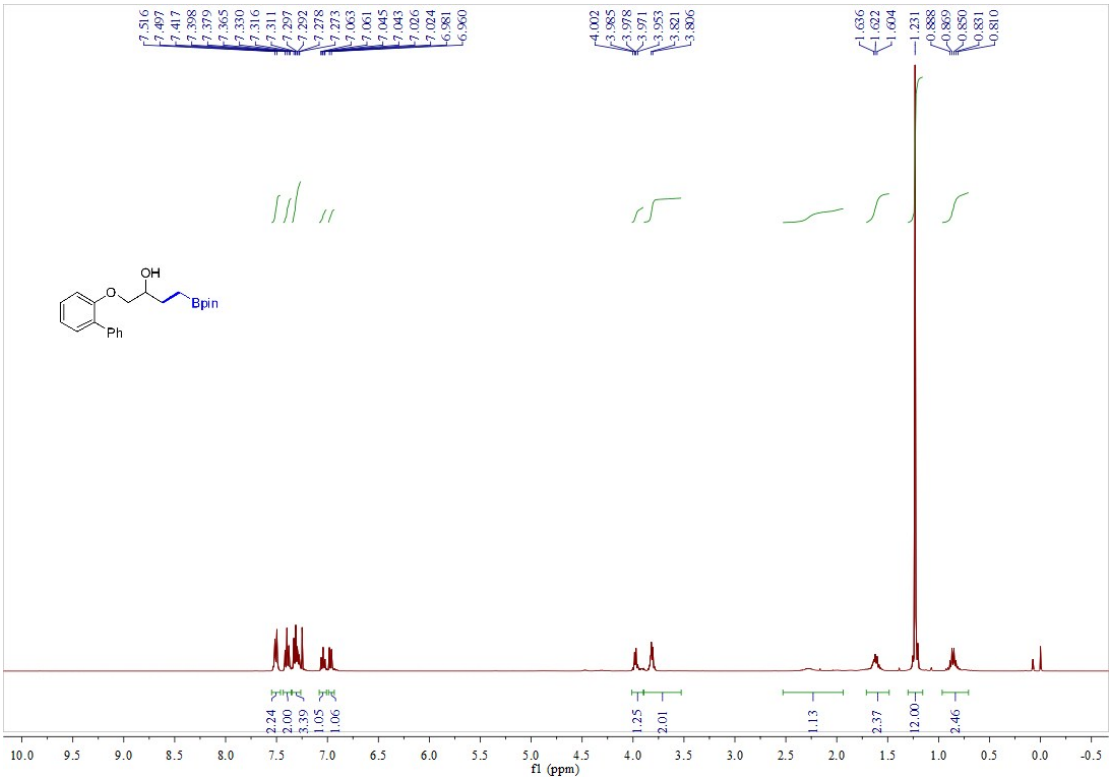
7.97
7.27
6.94
6.91
4.02
3.99
3.96
3.95
3.94
3.91
3.89
1.79
1.77
1.76
1.75
1.73
1.70
1.68
1.66
1.63
1.26
0.97
0.95
0.92
OH
O
Bpin
MeOOC
2.09
2.13
3.00
3.20
2.37
12.63
2.00
f1 (ppm)


166.962
162.609
131.721
122.942
114.281
83.480
72.187
71.641
52.013
27.704
24.941
7.200
OH
Bpin
MeOOC
f1 (ppm)


7.516
7.497
7.417
7.398
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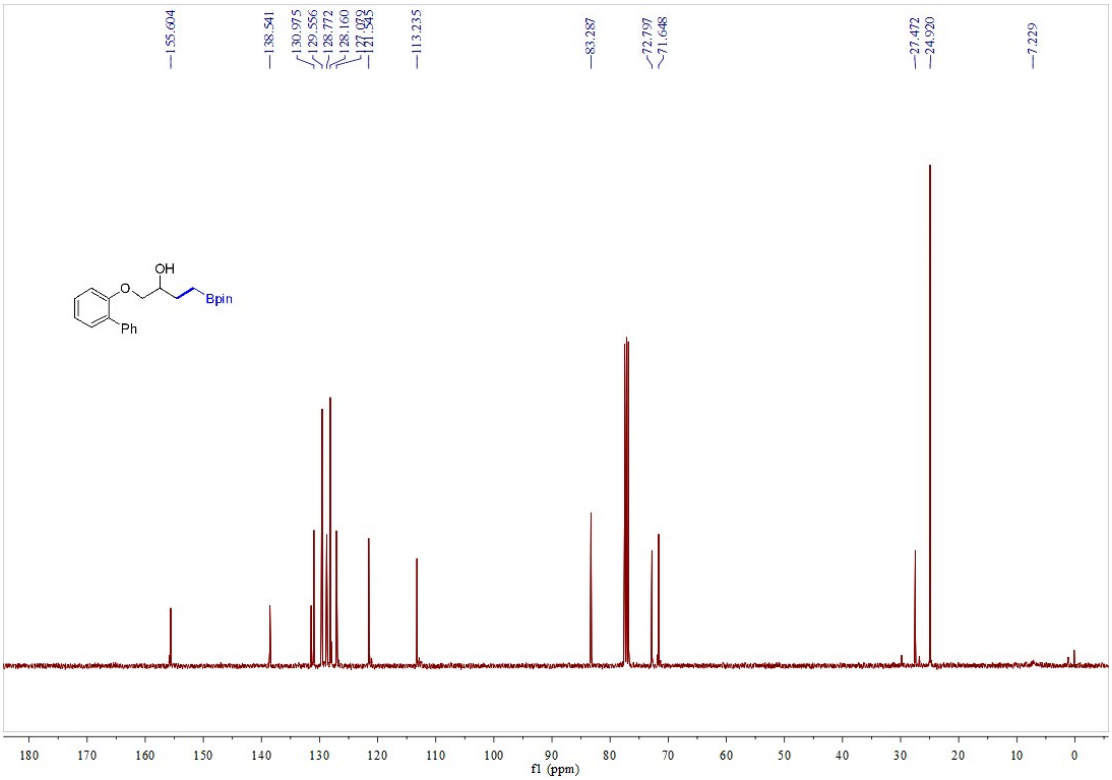
7.365
7.330
7.316
7.311
7.297
7.292
7.278
7.273
7.063
7.061
7.045
7.043
7.026
7.024
6.981
6.960
4.002
3.985
3.978
3.971
3.953
3.821
3.806
1.636
1.622
1.604
1.231
0.888
0.869
0.850
0.831
0.810
OH
Bpin
Ph
2.24
2.00
3.39
1.05
1.06
1.25
2.01
1.13
2.37
12.00
2.46
f1 (ppm)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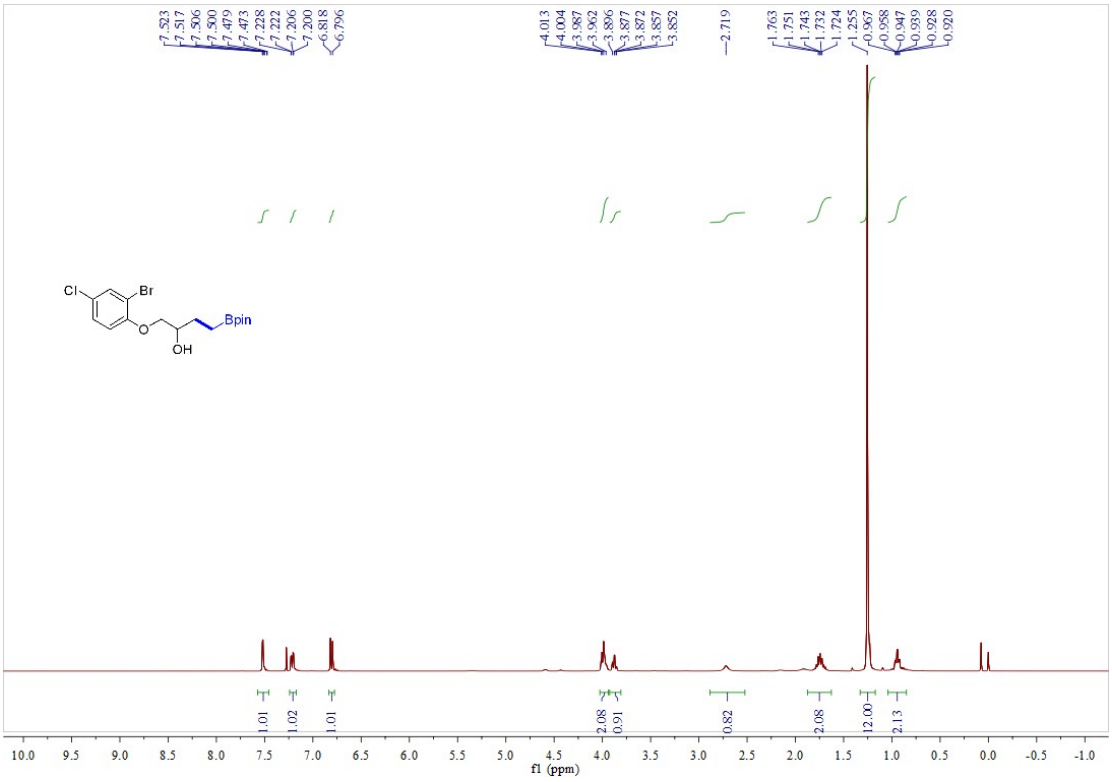
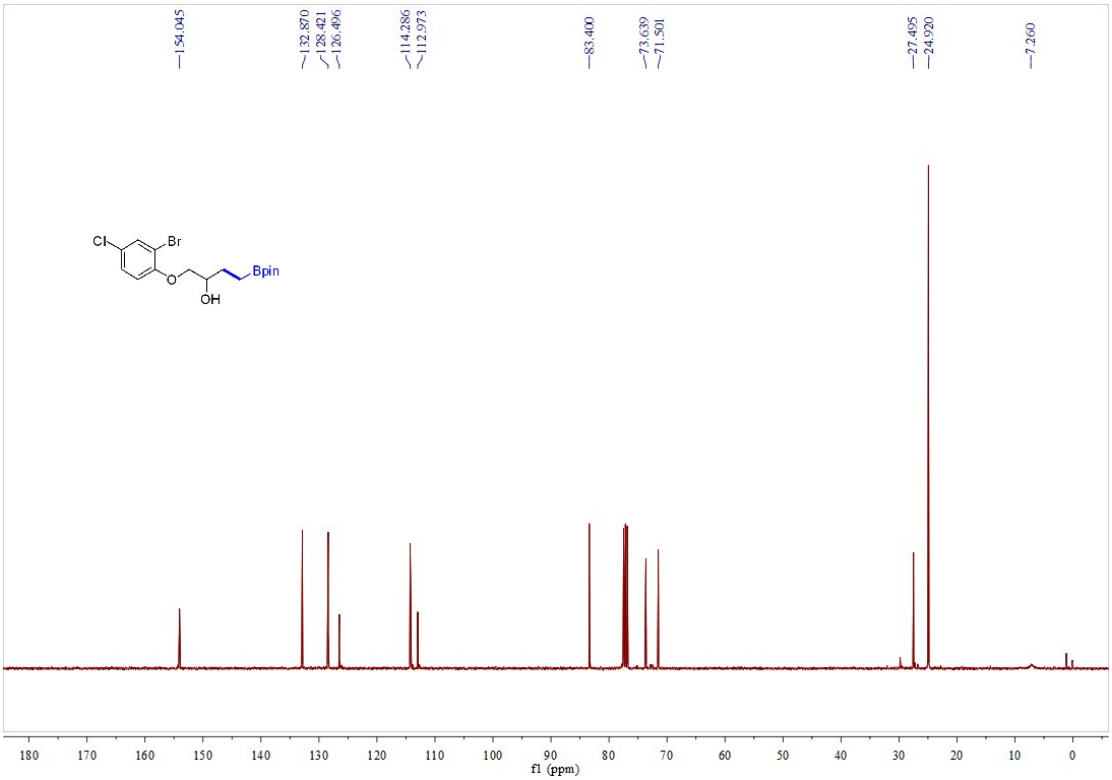
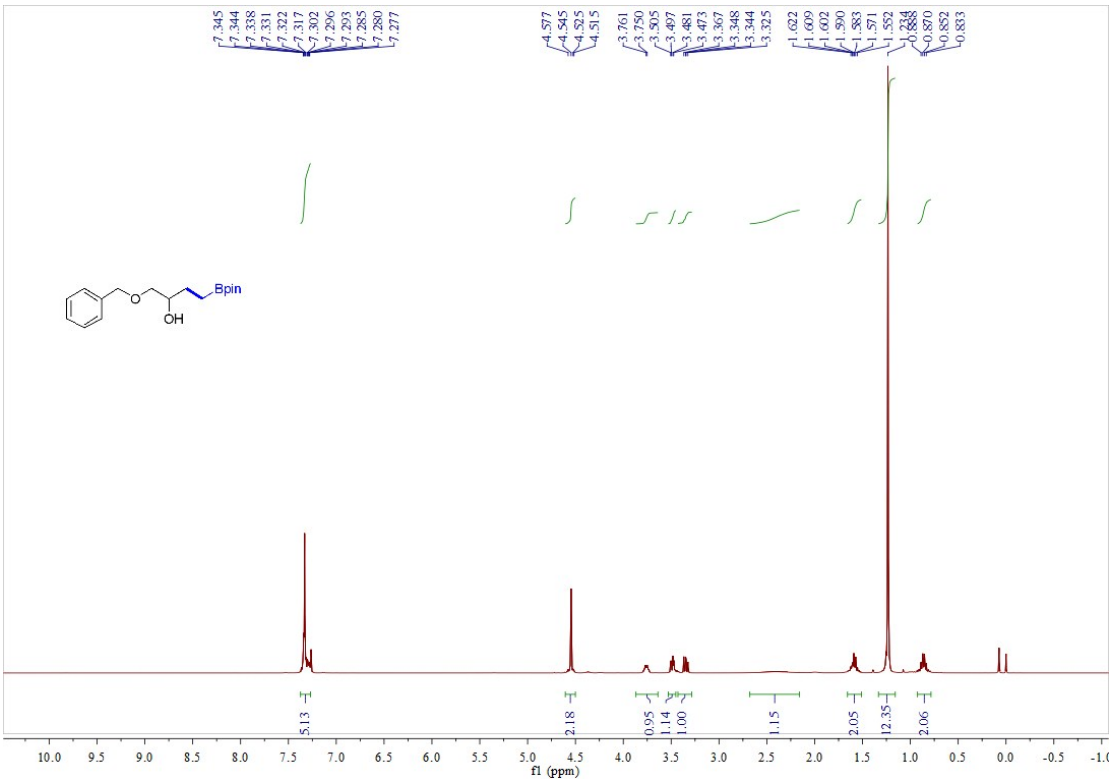
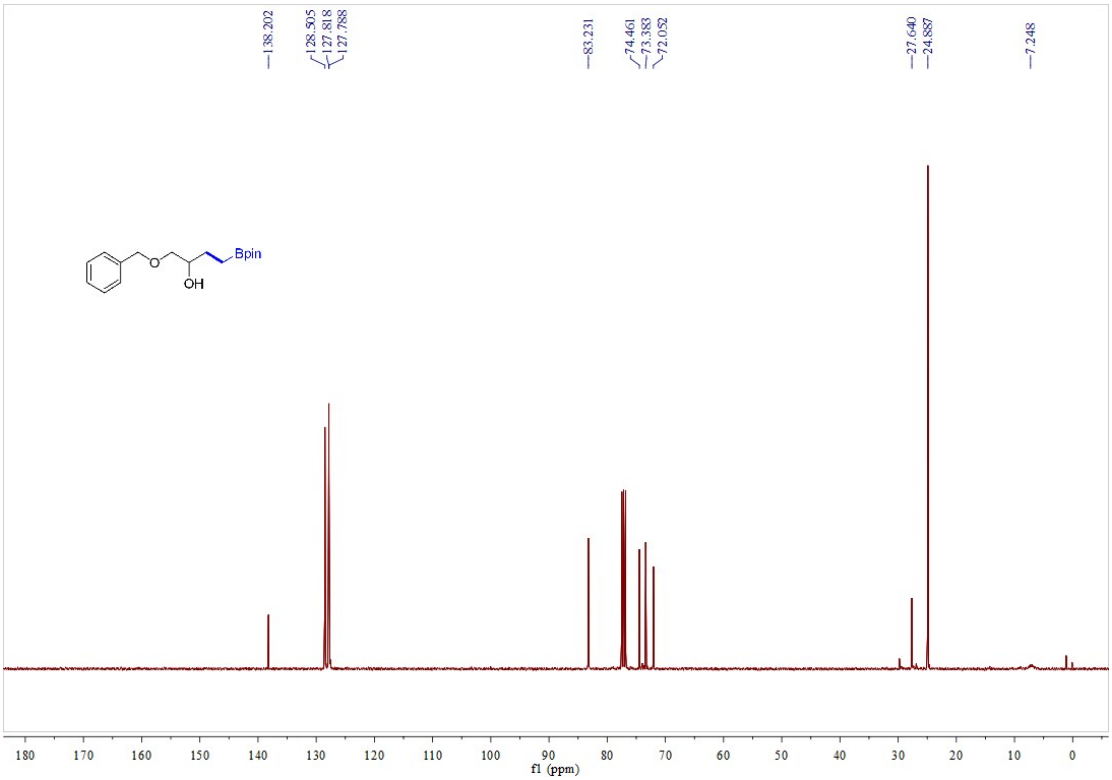
138.541
130.975
129.556
128.772
128.160
127.079
121.545
113.235
83.287
72.797
71.648
27.472
24.920
7.229
OH
Bpin
Ph
f1 (ppm)


7.523
7.517
7.506
7.500
7.479
7.473
7.228
7.222
7.206
7.200
6.818
6.796
4.013
4.004
3.987
3.962
3.896
3.877
3.872
3.857
3.852
2.719
1.763
1.751
1.743
1.732
1.724
1.255
0.967
0.958
0.947
0.939
0.928
0.920
Cl
Br
Bpin
OH
1.01
1.02
1.01
2.08
0.91
0.82
2.08
12.00
2.13
f1 (ppm)


154.045
132.870
128.421
126.496
114.286
112.973
83.400
73.639
71.501
27.495
24.920
7.260
Cl
Br
O
OH
Bpin
f1 (ppm)


7.345
7.344
7.338
7.331
7.322
7.317
7.302
7.296
7.293
7.285
7.280
7.277
4.577
4.545
4.525
4.515
3.761
3.750
3.505
3.497
3.481
3.473
3.367
3.348
3.344
3.325
1.622
1.609
1.602
1.590
1.583
1.571
1.552
1.234
0.888
0.870
0.852
0.833
O
OH
Bpin
5.13
2.18
0.95
1.14
1.00
1.15
2.05
12.35
2.06
f1 (ppm)


138.202
128.505
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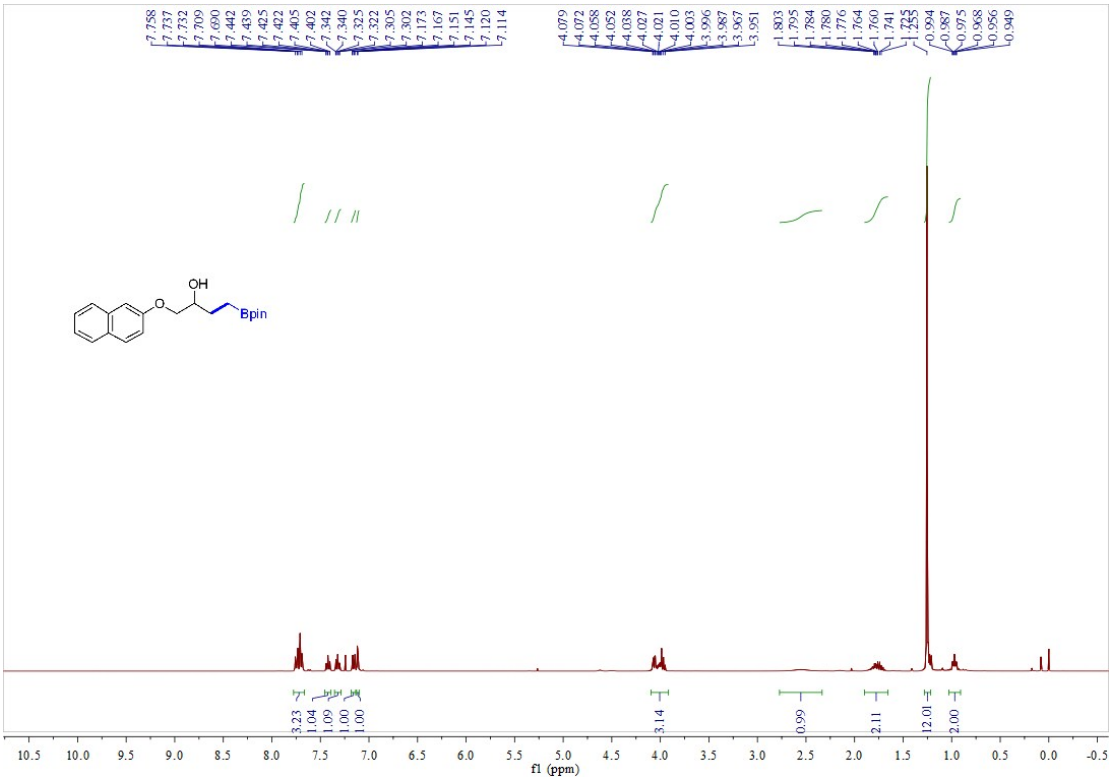
83.231
74.461
73.383
72.052
27.640
24.887
7.248
Bpin
OH
f1 (ppm)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7.737
7.732
7.709
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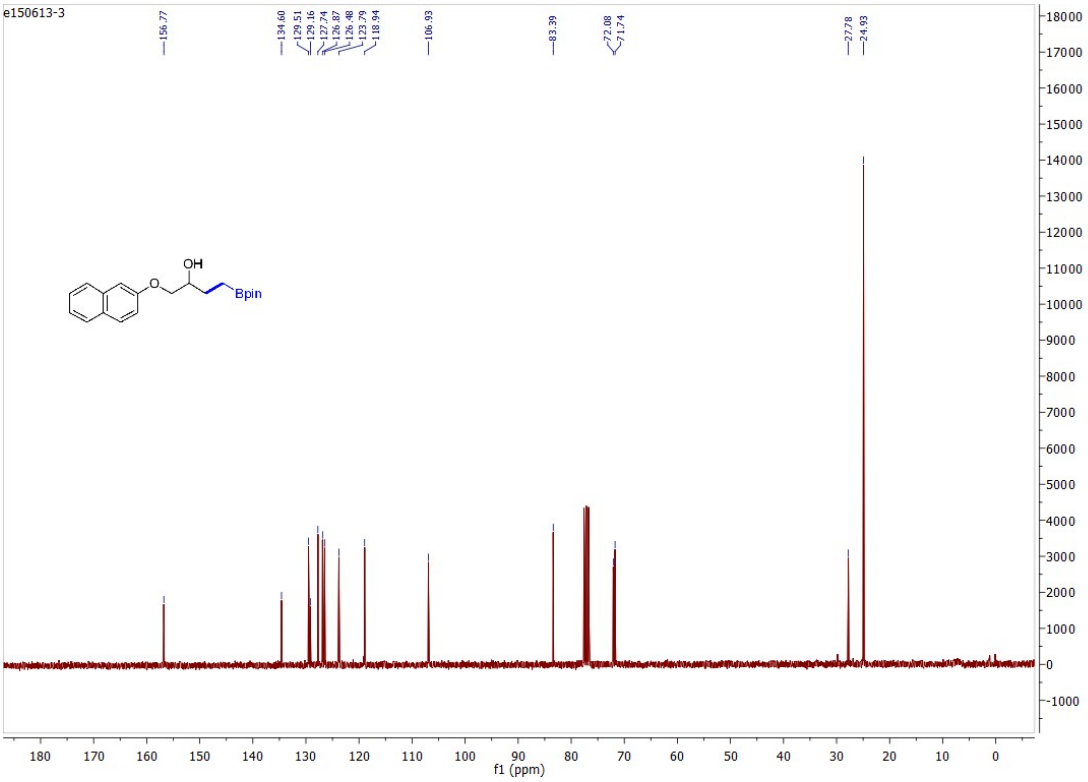
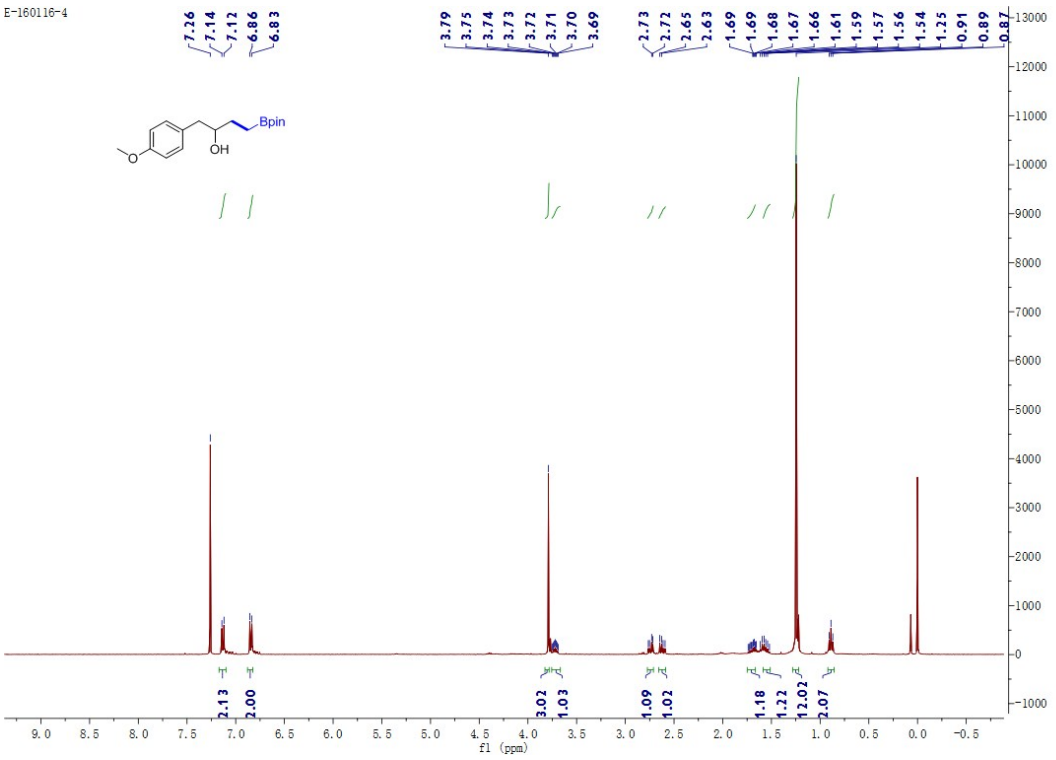
7.442
7.439
7.425
7.422
7.405
7.402
7.342
7.340
7.325
7.322
7.305
7.302
7.173
7.167
7.151
7.145
7.120
7.114
4.079
4.072
4.058
4.052
4.038
4.027
4.021
4.010
4.003
3.996
3.987
3.967
3.951
1.803
1.795
1.784
1.780
1.776
1.764
1.760
1.741
1.255
0.994
0.987
0.975
0.968
0.956
0.949
OH
Bpin
3.23
1.04
1.09
1.00
1.00
3.14
0.99
2.11
12.01
2.00
f1 (ppm)


e150613-3
156.77
134.60
129.51
129.16
127.74
126.87
126.48
123.79
118.94
106.93
83.39
72.08
71.74
27.78
24.93
OH
O
Bpin
f1 (ppm)


E-160116-4
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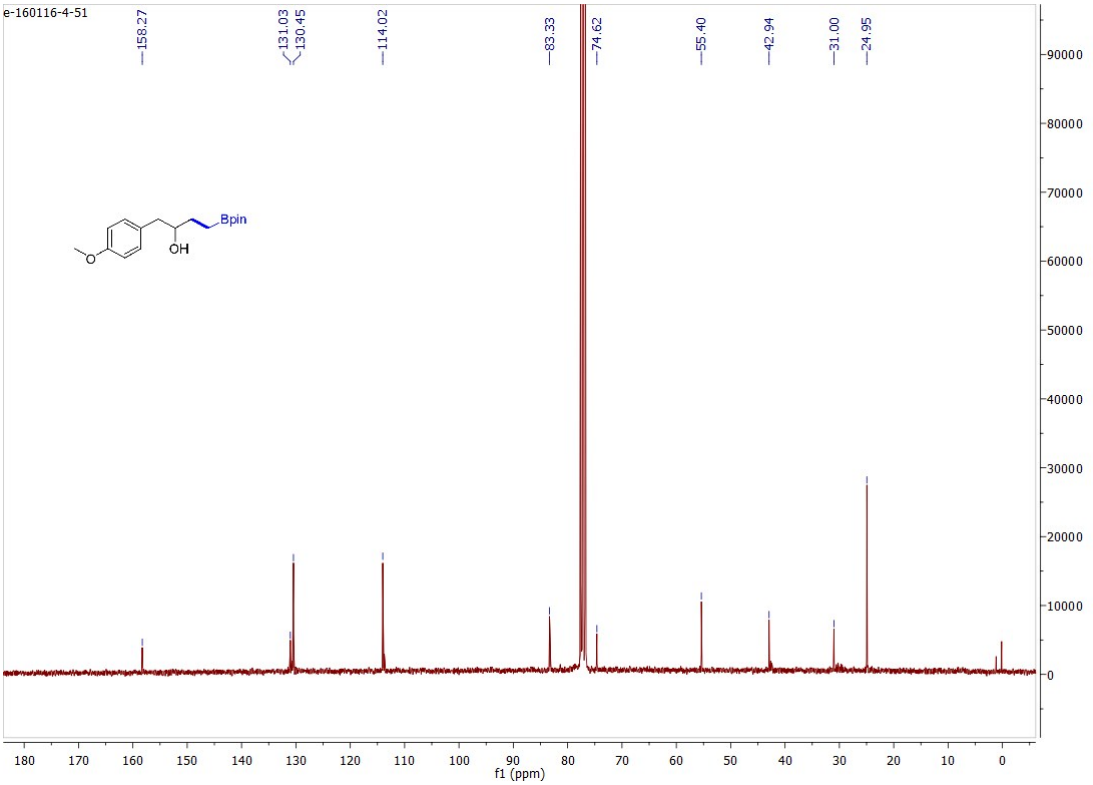
7.14
7.12
6.86
6.83
3.79
3.75
3.74
3.73
3.72
3.71
3.70
3.69
2.73
2.72
2.65
2.63
1.69
1.69
1.68
1.67
1.66
1.61
1.59
1.57
1.56
1.54
1.25
0.91
0.89
0.87
Bpin
OH
O
2.13
2.00
3.02
1.03
1.09
1.02
1.18
1.22
12.02
2.07
f1 (ppm)


e-160116-4-51
158.27
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83.33
74.62
55.40
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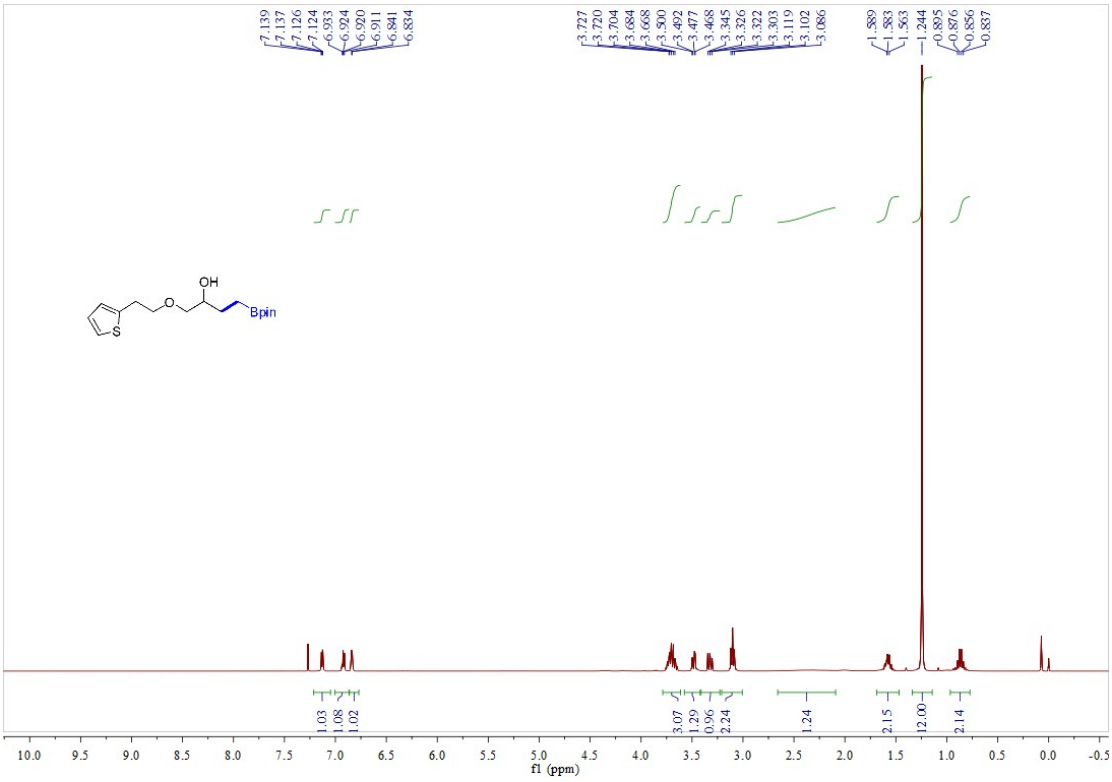
24.95
Bpin
OH
O
f1 (ppm)


7.139
7.137
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7.124
6.933
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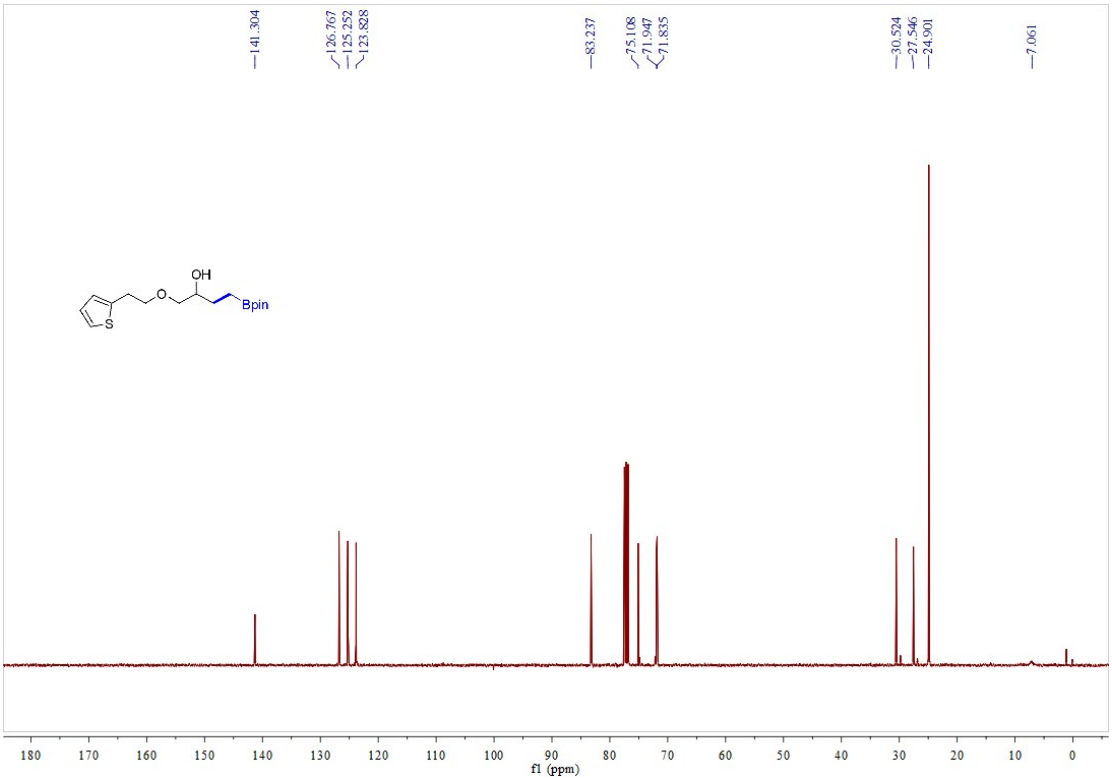
6.920
6.911
6.841
6.834
3.727
3.720
3.704
3.684
3.668
3.500
3.492
3.477
3.468
3.345
3.326
3.322
3.303
3.119
3.102
3.086
1.589
1.583
1.563
1.244
0.895
0.876
0.856
0.837
OH
Bpin
S
1.03
1.08
1.02
3.07
1.29
0.96
2.24
1.24
2.15
12.00
2.14
f1 (ppm)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126.767
125.252
123.828
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75.108
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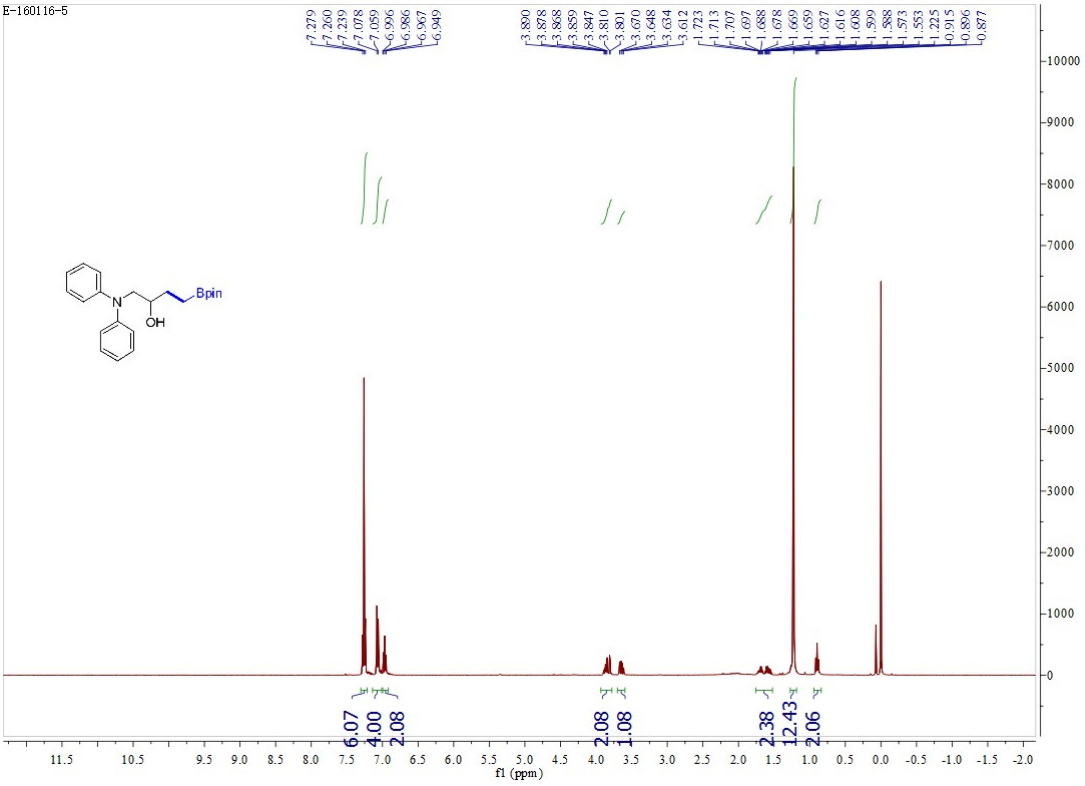
30.524
27.546
24.901
7.061
OH
O
S
Bpin
f1 (ppm)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6.967
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3.868
3.859
3.847
3.810
3.801
3.670
3.648
3.634
3.612
1.723
1.713
1.707
1.697
1.688
1.678
1.669
1.659
1.627
1.616
1.608
1.599
1.588
1.573
1.553
1.225
0.915
0.896
0.877
N
OH
Bpin
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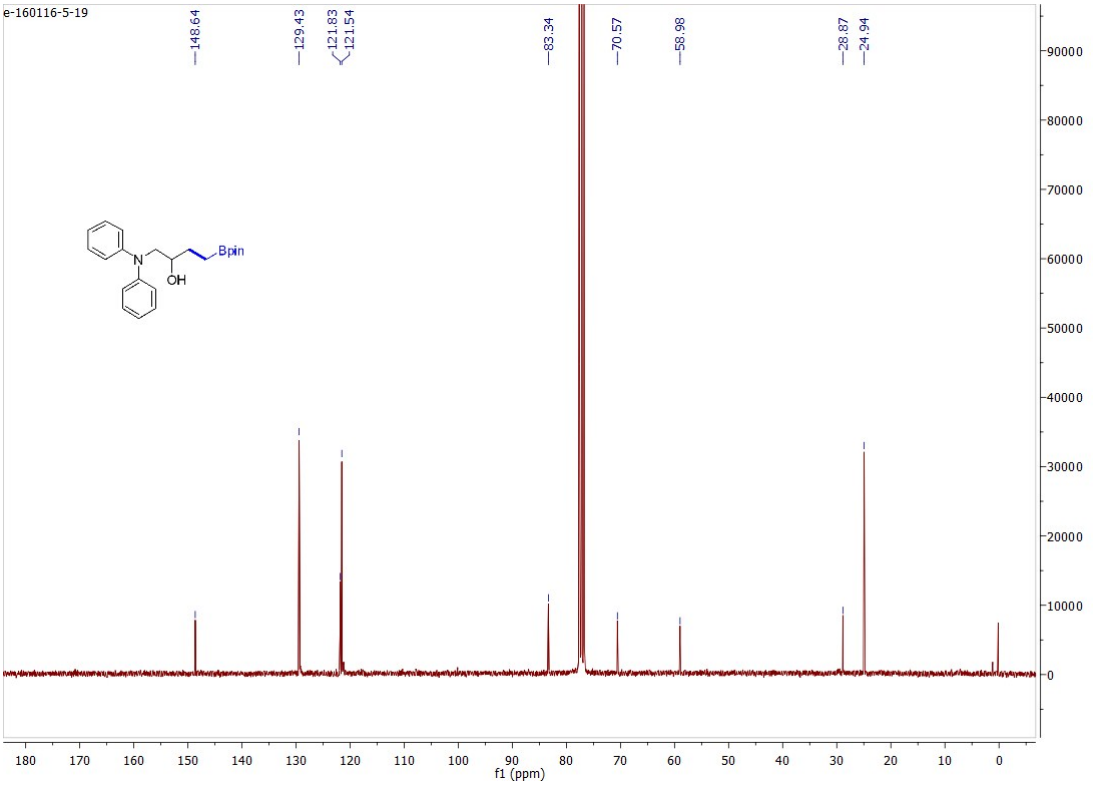
4.00
2.08
2.08
1.08
2.38
12.43
2.06
f1 (ppm)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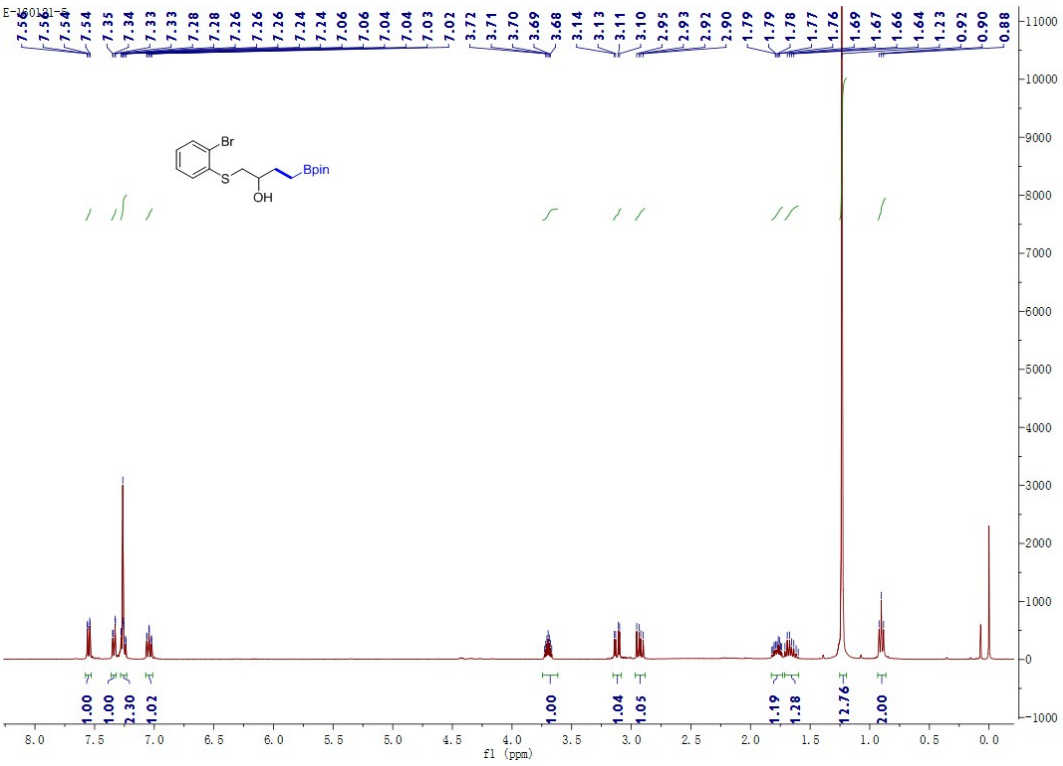
121.54
83.34
70.57
58.98
28.87
24.94
Bpin
OH
f1 (ppm)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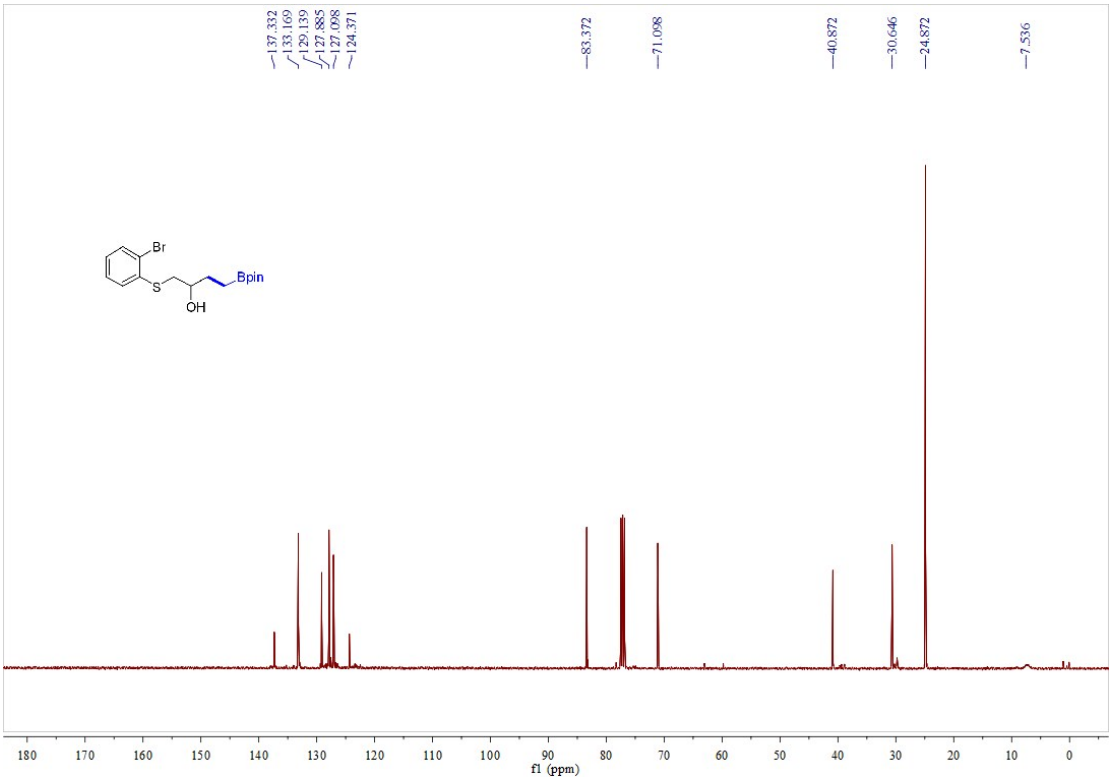
Br
S
Bpin
OH
f1 (ppm)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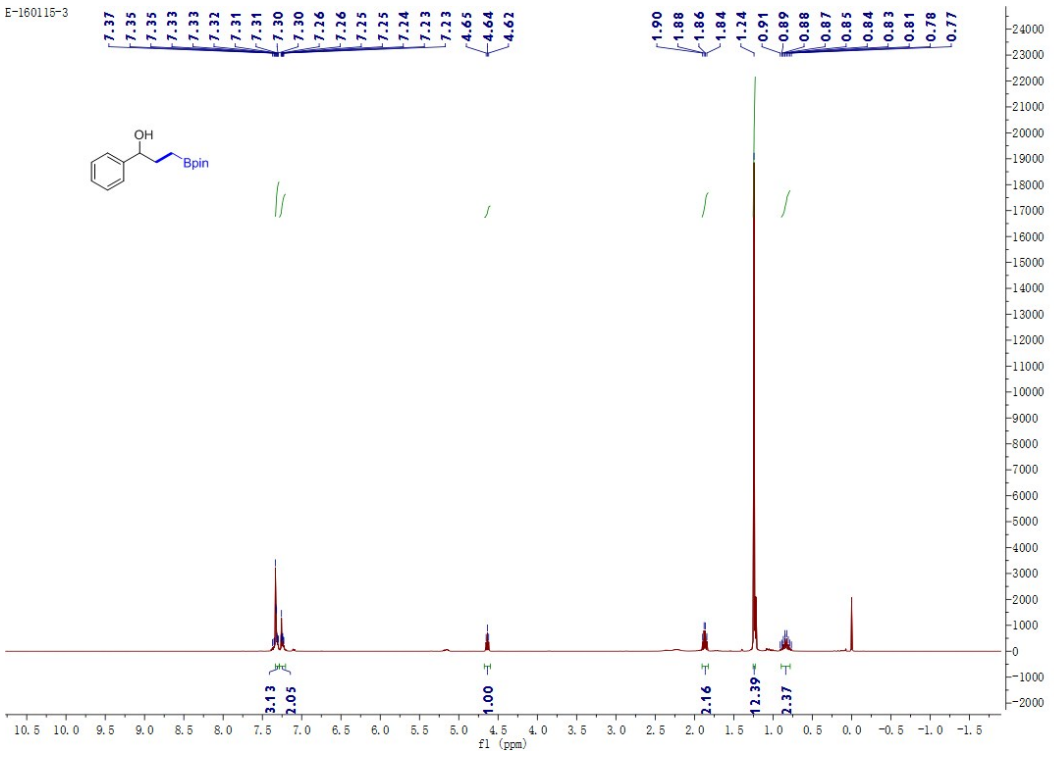
S
OH
Bpin
f1 (ppm)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7.32
7.31
7.31
7.30
7.30
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7.26
7.25
7.25
7.24
7.23
7.23
4.65
4.64
4.62
1.90
1.88
1.86
1.84
1.24
0.91
0.89
0.88
0.87
0.85
0.84
0.83
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0.77
OH
Bpin
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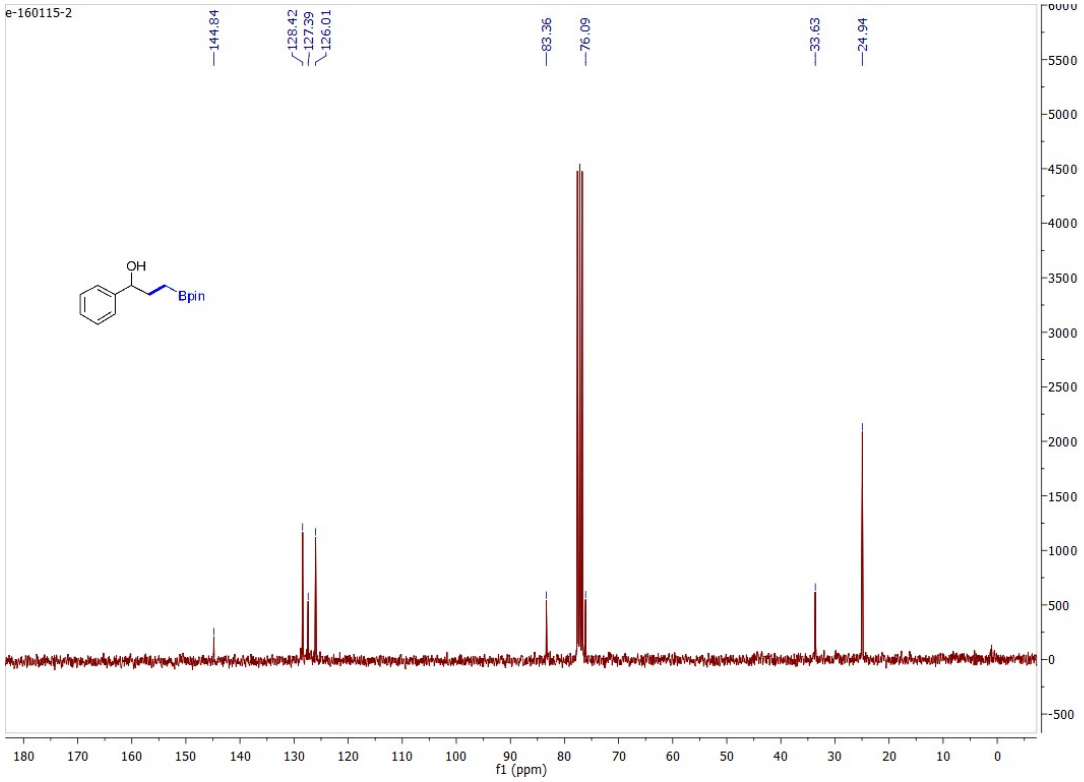
1.00
2.16
12.39
2.37
f1 (ppm)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33.63
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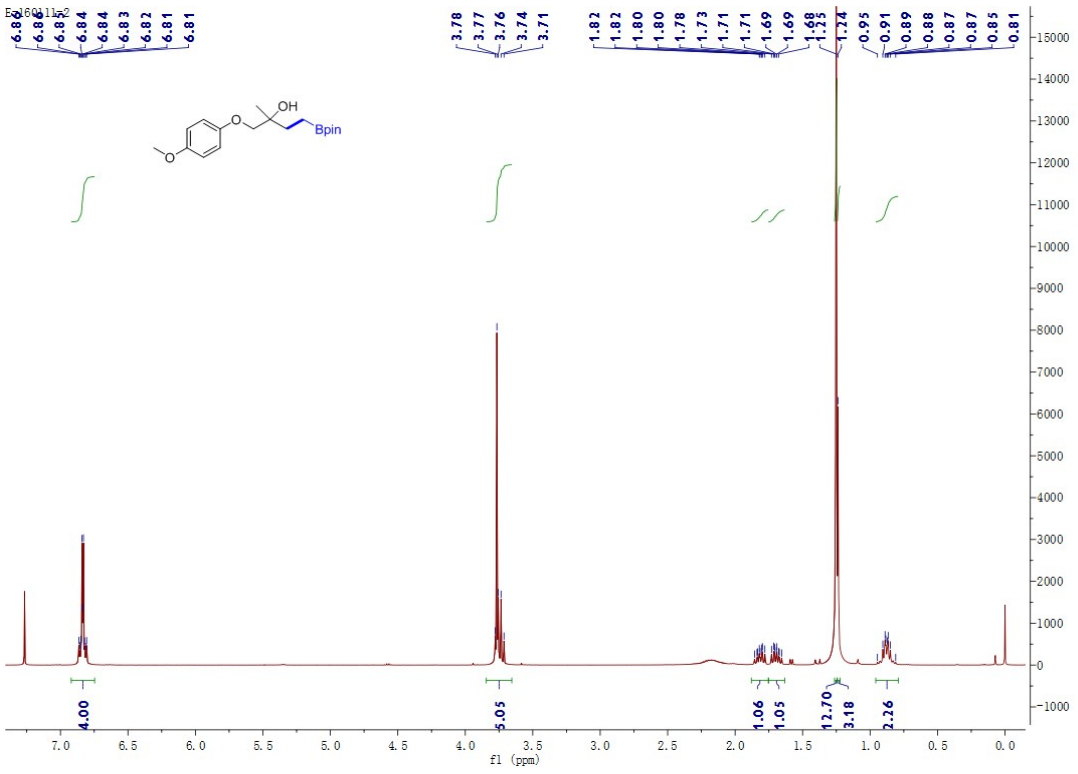
OH
Bpin
f1 (ppm)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6.85
6.85
6.84
6.84
6.83
6.82
6.81
6.81
3.78
3.77
3.76
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3.71
1.82
1.82
1.80
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1.78
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1.71
1.69
1.69
1.68
1.25
1.24
0.95
0.91
0.89
0.88
0.87
0.87
0.85
0.81
OH
Bpin
4.00
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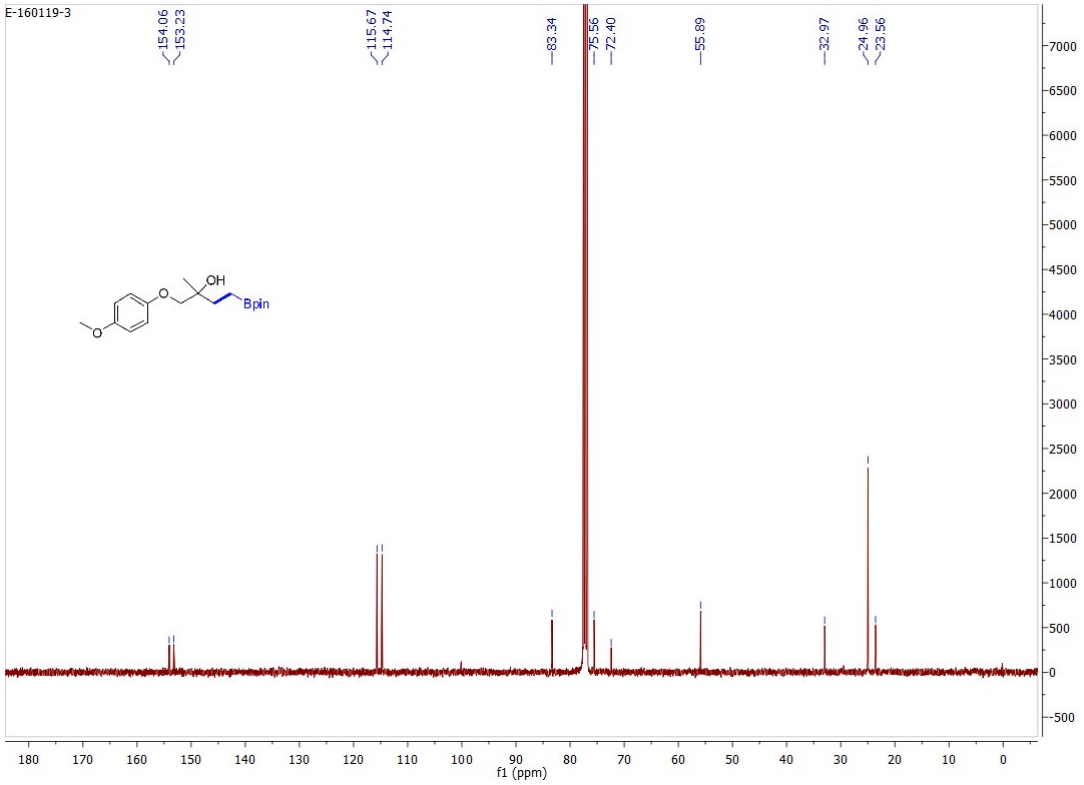
1.06
1.05
12.70
3.18
2.26
f1 (ppm)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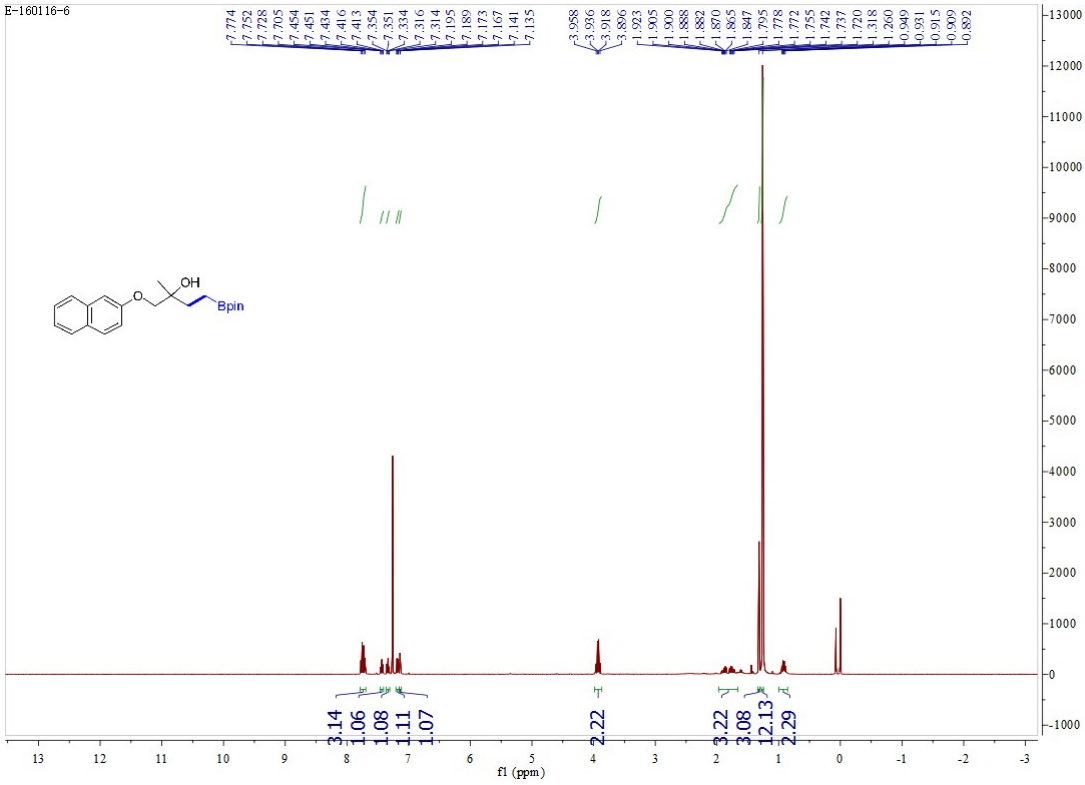
75.56
72.40
55.89
32.97
24.96
23.56
OH
Bpin
O
f1 (ppm)


E-160116-6
OH
Bpin
O
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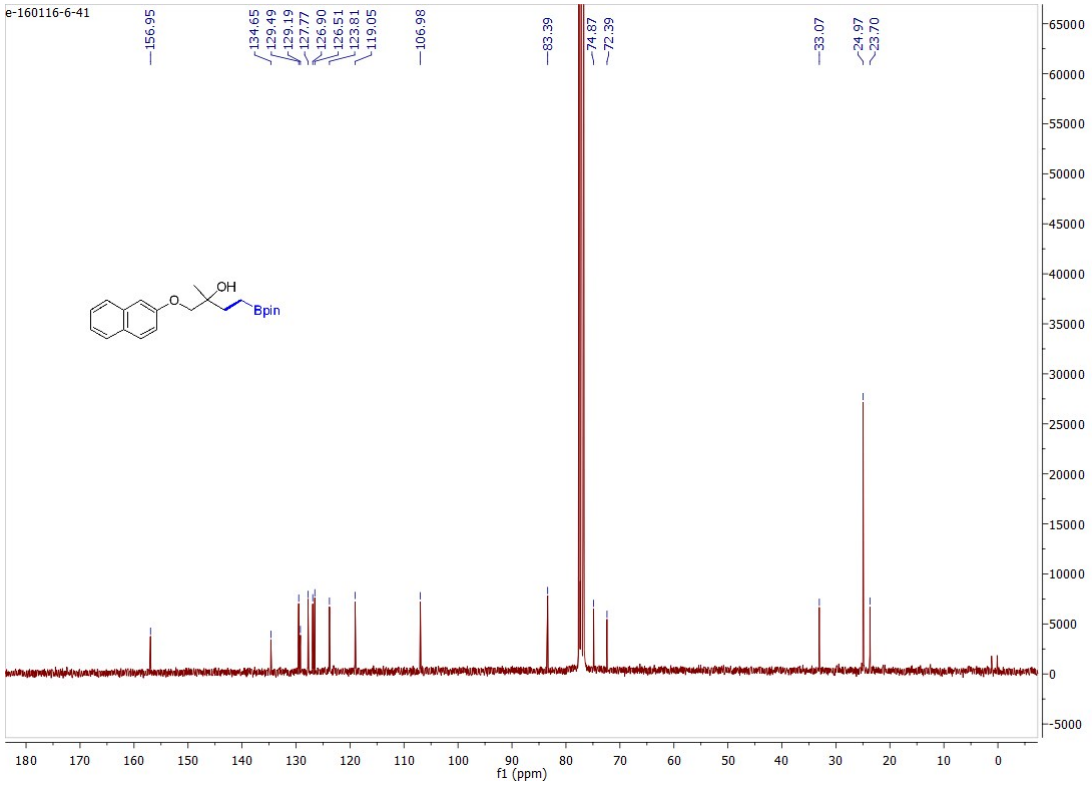
1.06
1.08
1.11
1.07
2.22
3.22
3.08
12.13
2.29
f1 (ppm)


e-160116-6-41
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126.90
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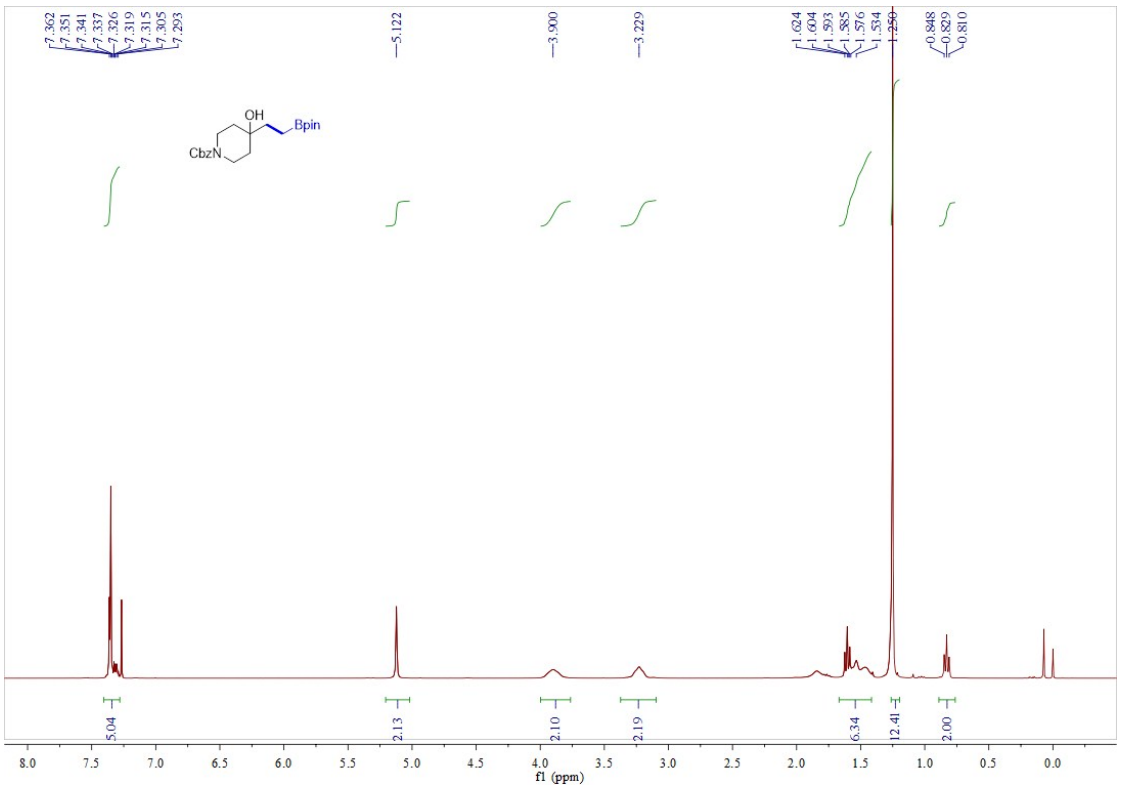
72.39
33.07
24.97
23.70
OH
O
Bpin
f1 (ppm)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7.319
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7.305
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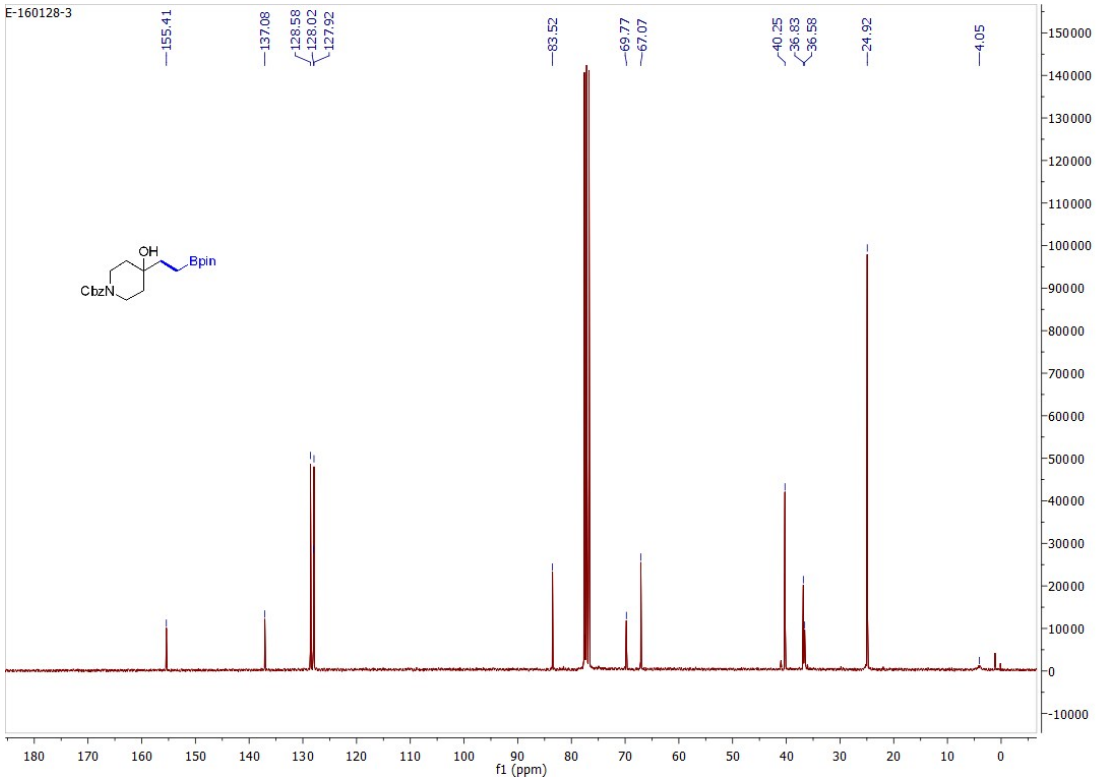
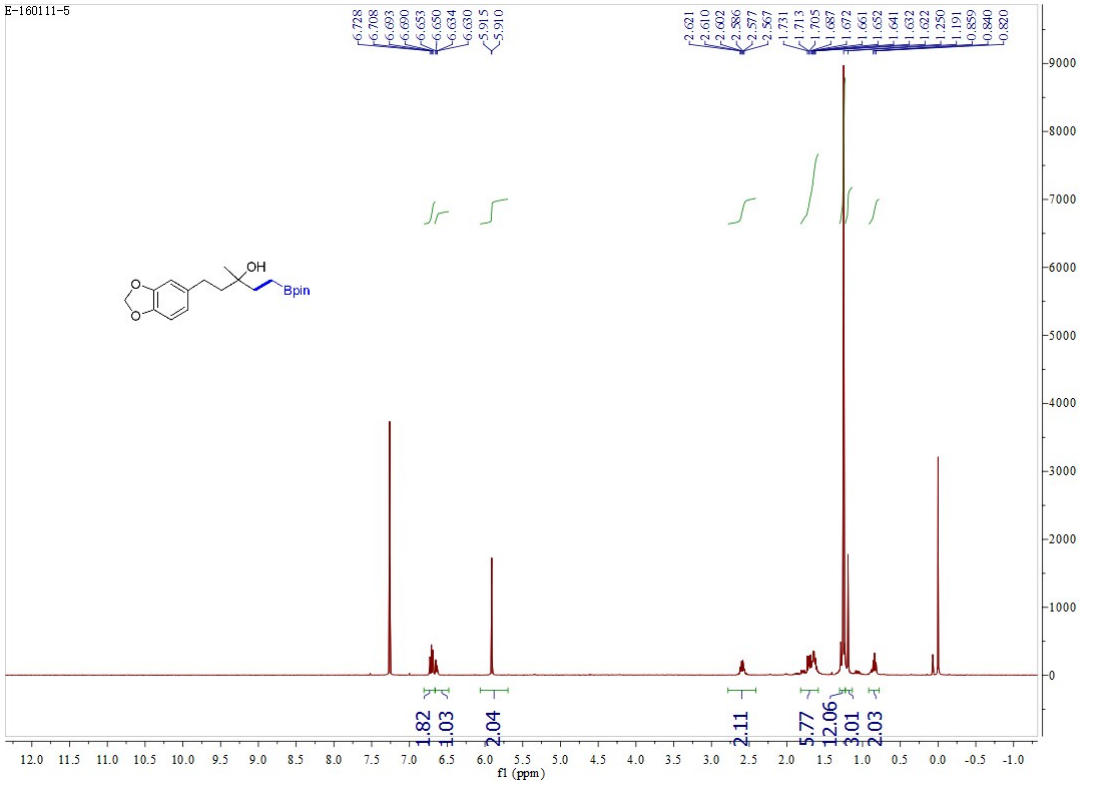
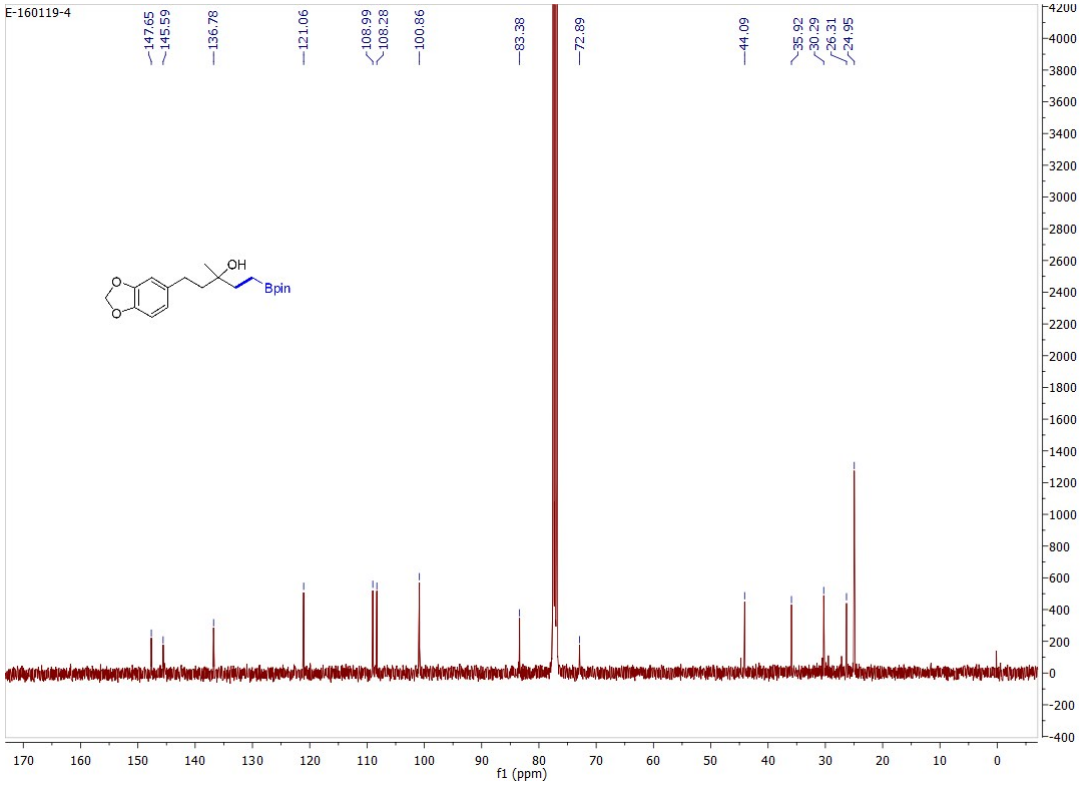
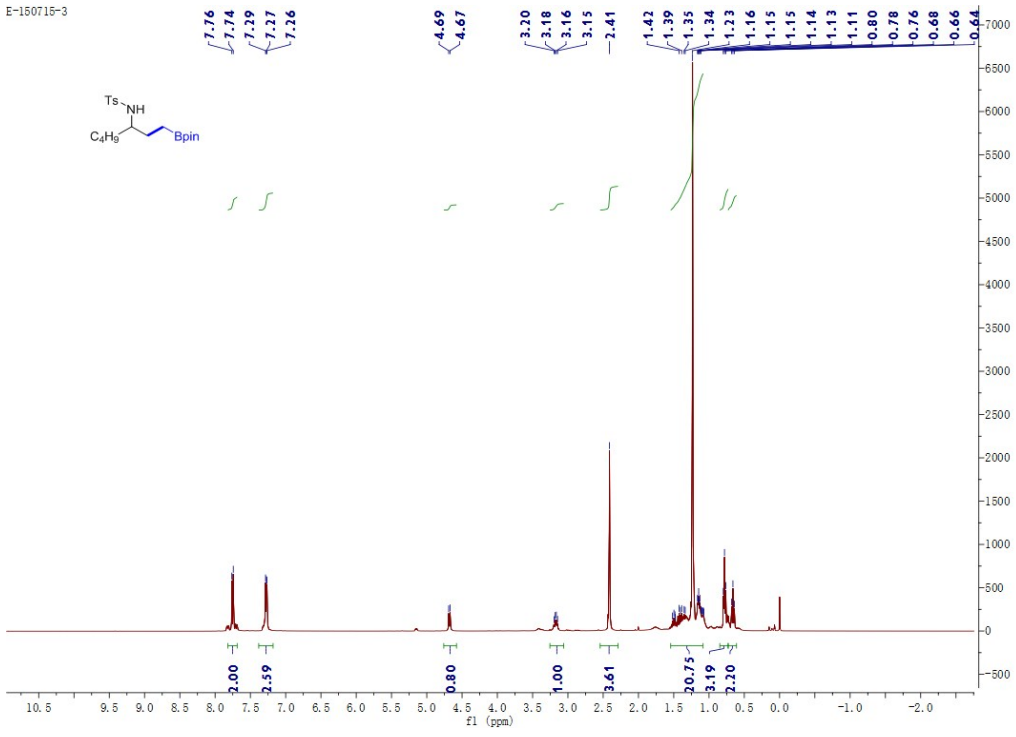
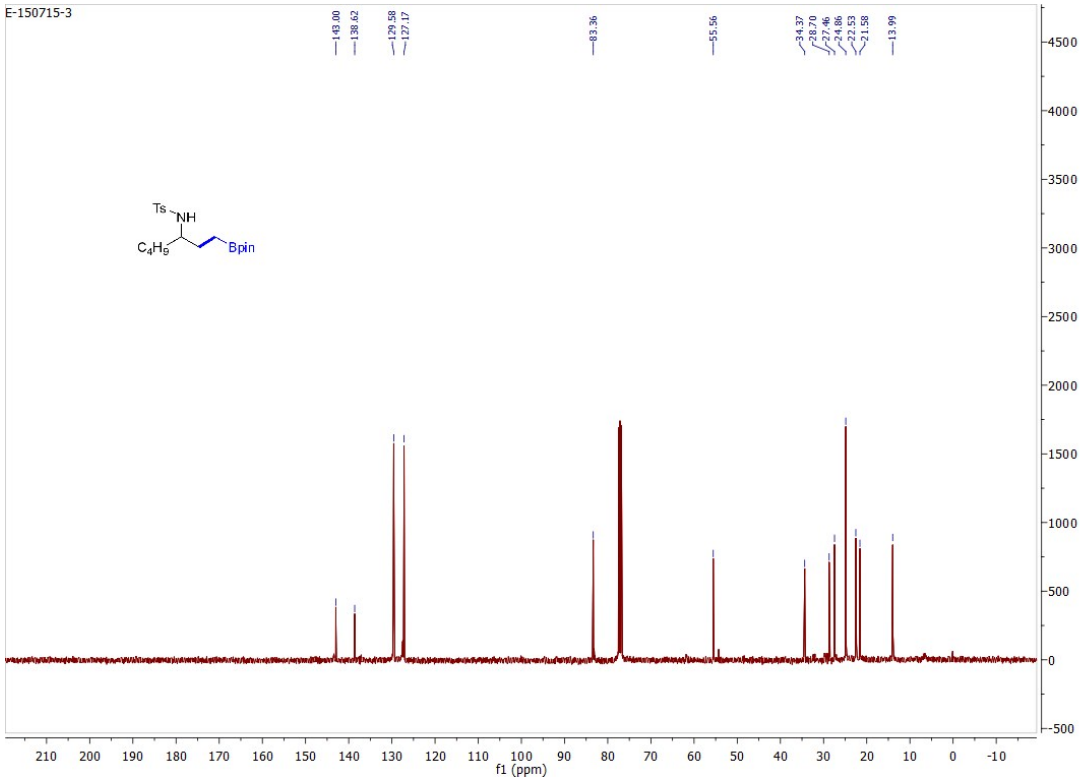
5.122
3.900
3.229
1.624
1.604
1.593
1.385
1.576
1.534
1.256
0.848
0.829
0.810
OH
Bpin
CbzN
5.04
2.13
2.10
2.19
6.34
12.41
2.00
f1 (ppm)

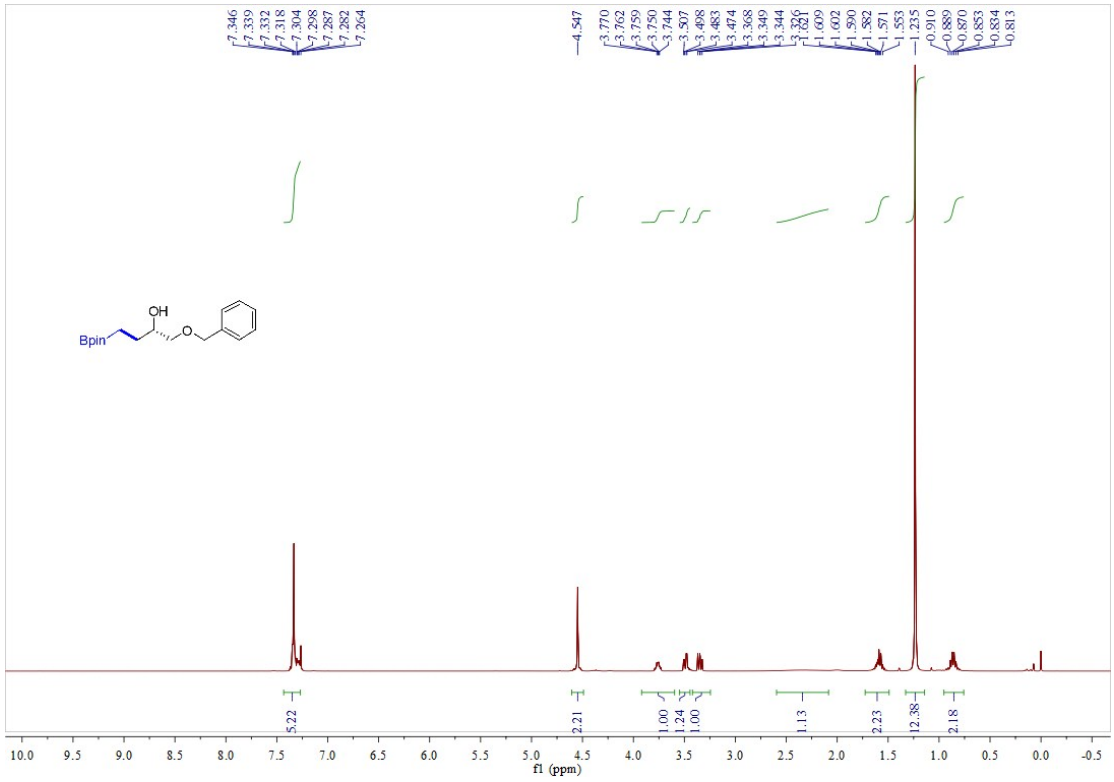

E-160128-3
155.41
137.08
128.58
128.02
127.92
83.52
69.77
67.07
40.25
36.83
36.58
24.92
4.05
OH
Bpin
CbzN
f1 (ppm)

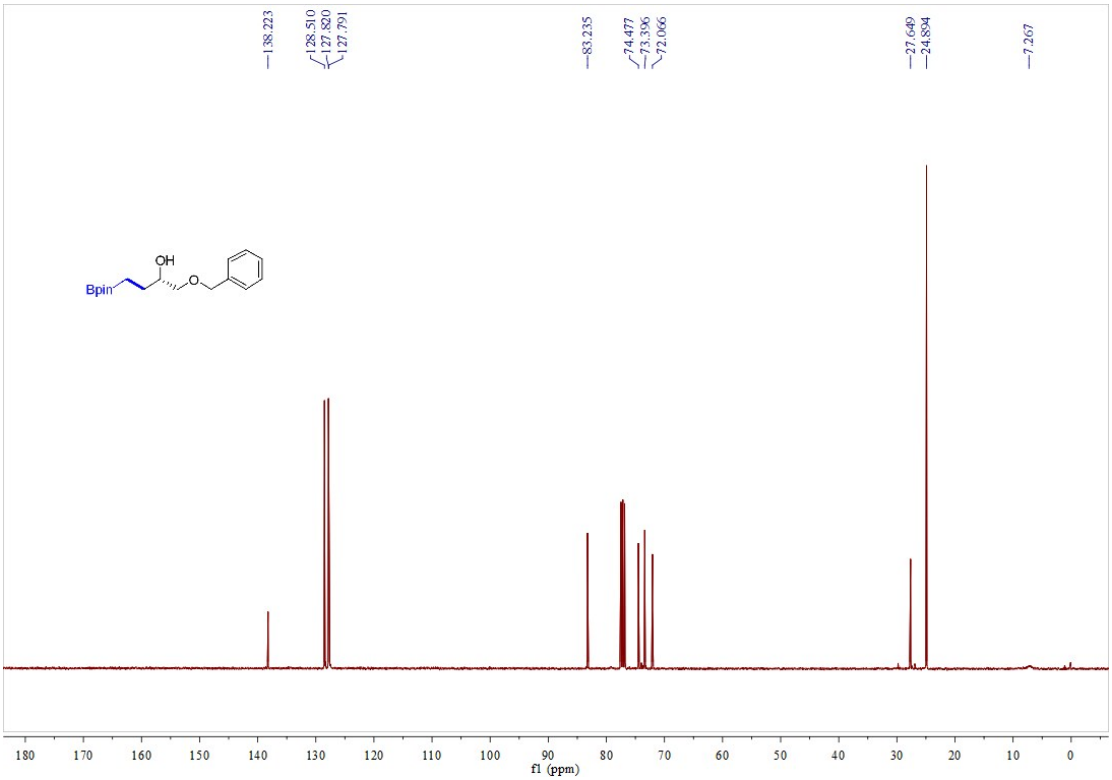

E-160111-5
6.728
6.708
6.693
6.690
6.653
6.650
6.634
6.630
5.915
5.910
2.621
2.610
2.602
2.586
2.577
2.567
1.731
1.713
1.705
1.687
1.672
1.661
1.652
1.641
1.632
1.622
1.250
1.191
0.859
0.840
0.820
OH
Bpin
1.82
1.03
2.04
2.11
5.77
12.06
3.01
2.03
f1 (ppm)

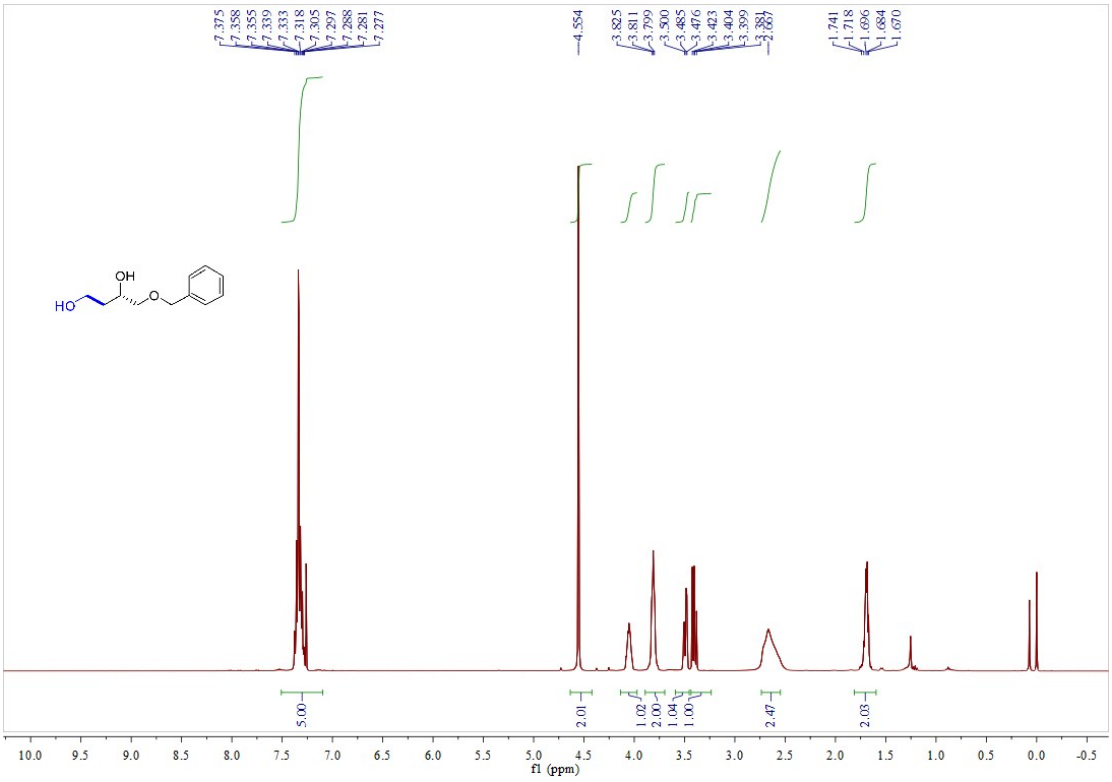

E-160119-4
147.65
145.59
136.78
121.06
108.99
108.28
100.86
83.38
72.89
44.09
35.92
30.29
26.31
24.95
OH
Bpin
f1 (ppm)

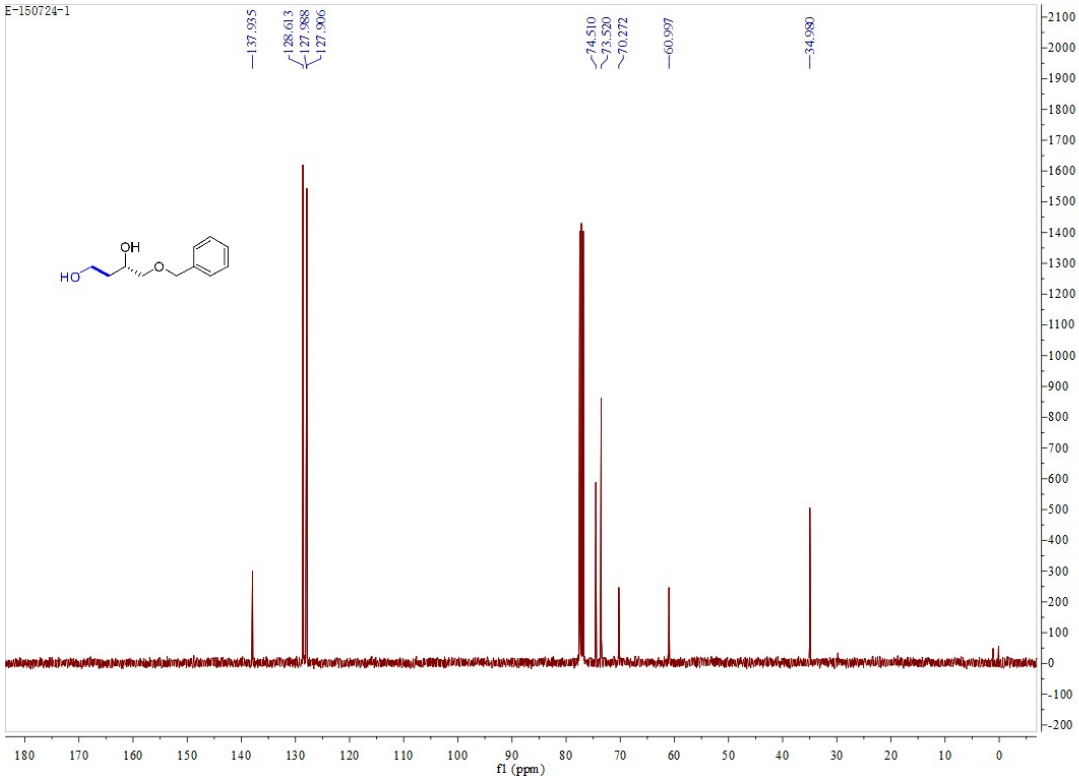

E-150715-3
7.76
7.74
7.29
7.27
7.26
4.69
4.67
3.20
3.18
3.16
3.15
2.41
1.42
1.39
1.35
1.34
1.23
1.16
1.15
1.15
1.14
1.13
1.11
0.80
0.78
0.76
0.68
0.66
0.64
Ts
NH
C4H9
Bpin
2.00
2.59
0.80
1.00
3.61
20.75
3.19
2.20
f1 (ppm)

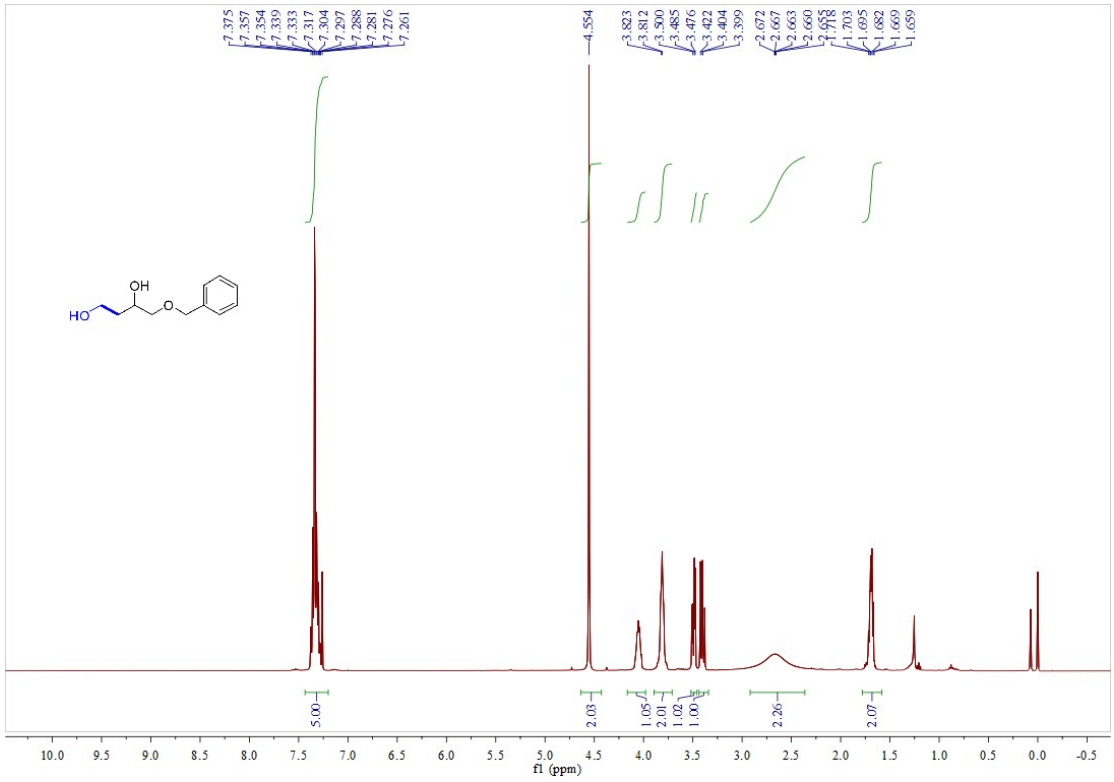

E-150715-3
143.00
138.62
129.58
127.17
83.36
55.56
34.37
28.70
27.46
24.86
22.53
21.58
13.99
Ts
NH
C4H9
Bpin
f1 (ppm)

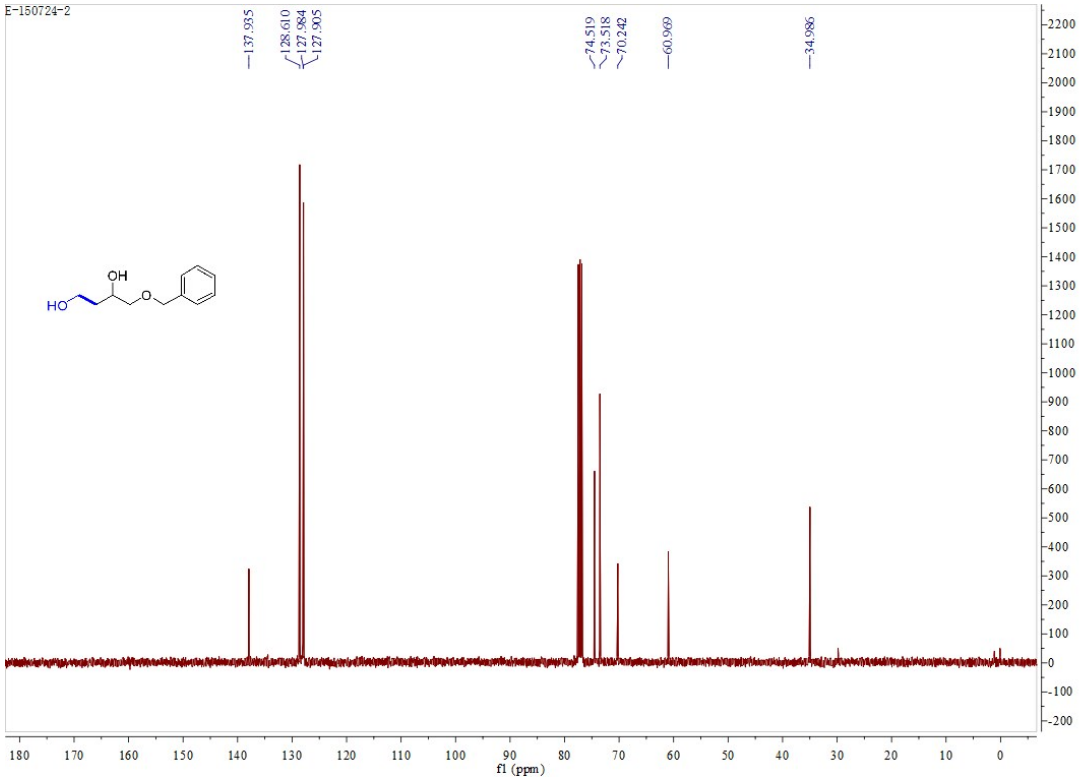

7.346
7.339
7.332
7.318
7.304
7.298
7.287
7.282
7.264
4.547
3.770
3.762
3.759
3.750
3.744
3.507
3.498
3.483
3.474
3.368
3.349
3.344
3.326
1.621
1.609
1.602
1.590
1.582
1.571
1.553
1.235
0.910
0.889
0.870
0.853
0.834
0.813
OH
Bpin
O
5.22
2.21
1.00
1.24
1.00
1.13
2.23
12.38
2.18
f1 (ppm)


138.223
128.510
127.820
127.791
83.235
74.477
73.396
72.066
27.649
24.894
7.267
OH
Bpin
O
f1 (ppm)


7.375
7.358
7.355
7.339
7.333
7.318
7.305
7.297
7.288
7.281
7.277
4.554
3.825
3.811
3.799
3.500
3.485
3.476
3.423
3.404
3.399
3.384
2.669
1.741
1.718
1.696
1.684
1.670
OH
HO
O
5.00
2.01
1.02
2.00
1.04
1.00
2.47
2.03
f1 (ppm)


E-150724-1
137.935
128.613
127.988
127.906
74.510
73.520
70.272
60.997
34.980
OH
HO
f1 (ppm)


7.375
7.357
7.354
7.339
7.333
7.317
7.304
7.297
7.288
7.281
7.276
7.261
4.554
3.823
3.812
3.500
3.485
3.476
3.422
3.404
3.399
2.672
2.667
2.663
2.660
2.655
1.718
1.703
1.695
1.682
1.669
1.659
OH
HO
5.00
2.03
1.05
2.01
1.02
1.00
2.26
2.07
f1 (ppm)


E-150724-2
137.935
128.610
127.984
127.905
74.519
73.518
70.242
60.969
34.986
OH
HO
O
f1 (ppm)