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Supporting Information

α-C-H Borylation of Secondary Alcohols via Ru/Fe Relay Catalysis: Building a Platform for Alcoholic C-H/C-O Functionalizations

*Qing Zhu[a,b], Zeyu He[a,b], Lu Wang[a], Yue Hu[a], Chungu Xia[a], and Chao Liu[a,c]**

[a] *State Key Laboratory for Oxo Synthesis and Selective Oxidation, Suzhou Research Institute of LICP, Lanzhou Institute of Chemical Physics (LICP), Chinese Academy of Sciences, Lanzhou 730000, P. R. China*

[b] *University of Chinese Academy of Sciences, Beijing 100049, P. R. China*

[c] *Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, Hangzhou Normal University, Hangzhou 311121, P.R. China*

E-mail: chaoliu@licp.cas.cn

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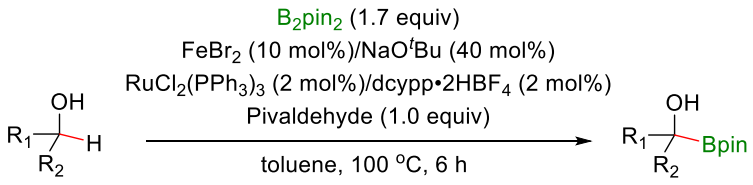
1. General Information

All synthetic manipulations were carried out using standard Schlenk techniques under a nitrogen atmosphere. All reactions were isolated from moisture and oxygen by a nitrogen atmosphere with a sealed tube. All glassware was oven dried at 110 °C for hours and cooled down under vacuum. Toluene, THF, ^{n}hexane and DCM were purified using Pure Solv 7-SDS solvent drying system. Unless otherwise noted, chemicals were obtained from Adamas-beta®, Aldrich, Acros Organics, Alfa Aesar, J&K without further purification. The aliphatic alcohols **1b, 1d-1i,** and **1r** were prepared by the reduction of ketone with $NaBH_4$ following the literature procedure.[1] The aliphatic alcohols **1j, 1q, 1t,** and **1u** were prepared by the reaction of aldehyde with organometallic reagents.[2] MeLi (1.6 M in Et_2O) was used for the syntheses of **1j, 1q**. ^{n}BuLi (2.5M in THF) was used for the synthesis of **1t**. ^{t}BuMgCl (2.0 M in Et_2O) was used for the synthesis of **1u**. Alcohols (**1b-1f**, **1h-1m, 1p, 1t**) were purified by re-distillation, others were used directly without purification. $RuCl_2(PPh_3)_3$ was prepared according to the literature.[3]

Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 100-200 mesh silica gel or through SepaBeam™ Machine SPB-3006012. Gas chromatographic analysis were performed on GC-2010 Plus gas chromatography instrument with a FID detector. GC-MS spectra were recorded on a GCMS-QP2010 SE. The High Resolution MS analyses were performed on Agilent 6530 Accurate – Mass Q-TOF LC/MS with ESI mode.

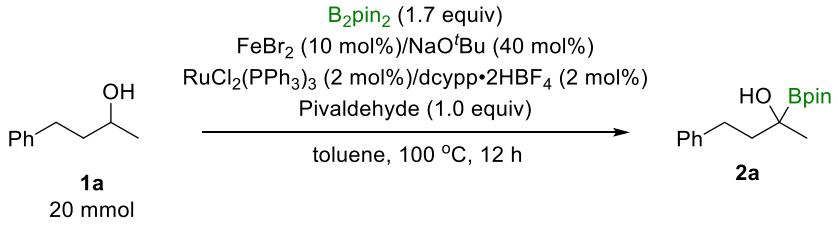
^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz instrument, using tetramethylsilane as the internal reference and $CDCl_3$ as the solvent. Chemical shifts (δ) are given in parts per million (ppm), and coupling constants (*J*) are given in Hertz (Hz) and tetramethylsilane (δ 0.00) is used the internal reference. Chemical shifts for carbons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of $CDCl_3$ (δ 77.0). The boron-bound carbon was not detected due to quadrupolar relaxation.

2. General Procedure for the α-C-H Borylation of Secondary Aliphatic Alcohols



In glove box, a 25 mL sealed tube equipped with a stirrer bar was charged with $RuCl_2(PPh_3)_3$ (9.6 mg, 0.01 mmol), dcypp·$2HBF_4$ (6.1 mg, 0.01 mmol), $FeBr_2$ (11.0 mg, 0.05 mmol), NaO^{t}Bu (19.2 mg, 0.20 mmol), B_2pin_2 (215.9 mg, 0.85 mmol), pivaldehyde (43.0 mg, 0.5 mmol) and 3 mL toluene. The tube was sealed with a Teflon screw cap and taken out of the glove box. Subsequently, the tube was unsealed and alcohol (0.5 mmol) was added under nitrogen atmosphere. Then, the tube was sealed and the mixture was heated at 100 °C with stirring for 6 h. Upon completion, the reaction was passed through a short silica gel column chromatography with MTBE as the eluent and then concentrated in vacuo. To remove excess amount of B_2pin_2 in the mixture, the crude product was dissolved in 8 mL MeCN with the addition of excess amount of trimethylamine *N*-oxide. The mixture was allowed to stir at room temperature for 5 minutes. The pure product was obtained by flash column chromatography on silica gel with DCM: MTBE = 20:1 as the eluent.

2.1 Procedure for gram scale for 2a

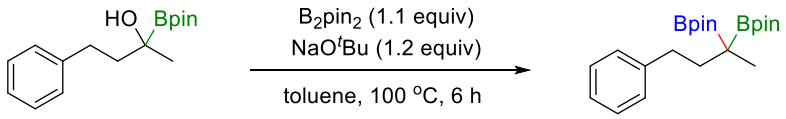


In glove box, a 350 mL sealed tube equipped with a stirrer bar was charged with $RuCl_2(PPh_3)_3$ (384.0 mg, 0.40 mmol), dcypp·$2HBF_4$ (244.0 mg, 0.40 mmol), $FeBr_2$ (440.0 mg, 2.0 mmol), NaO^{t}Bu (768.0 mg, 8.0 mmol), B_2pin_2 (8.64 g, 34.0 mmol), pivaldehyde (1.72 g, 20.0 mmol) and 100 mL toluene. The tube was sealed with a Teflon screw cap and taken out of the glove box. Then, the tube was unsealed and alcohol **1a** (3.00 g, 20.0 mmol) was added under nitrogen atmosphere. Then, the tube was sealed

and the mixture was heated at 100 °C with stirring for 12 h. Upon completion, the reaction was treated by a short silica gel column chromatography with MTBE and was concentrated in vacuo. To remove excess amount of B_2pin_2 in the mixture, the crude product was dissolved in MeCN with the addition of excess amount of trimethylamine *N*-oxide. The mixture was allowed to stir at room temperature for 5 minutes. The pure product was obtained by flash column chromatography on silica gel with DCM: MTBE = 20:1 as the eluent. Yield = 90%, this α-borylated alcohol **2a** was stored at -30 °C in glove box.

3. Procedure for the C-O/C-H Functionalization of α-borylated Alcohol

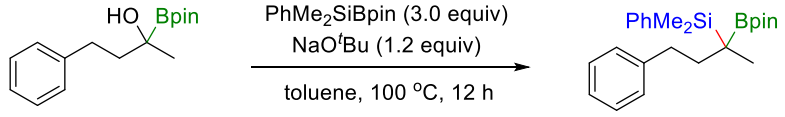
3.1.1 Procedure for the C-O borylation of α-borylated alcohol 2a



2a **2aa**

The procedure for the C-O borylation of α-borylated alcohol was performed according to the literature procedure.[4] In glove box, a 25 mL sealed tube equipped with a stirrer bar was charged with B_2pin_2 (139.7 mg, 0.66 mmol), NaO^tBu (57.6 mg, 0.60 mmol) and 3 mL toluene, then the α-borylated alcohol **2a** (138.0 mg, 0.50 mmol) was added. The tube was sealed with a Teflon screw cap and taken out of the glove box. Then, the mixture was heated at 100 °C with stirring for 6 h. Upon completion, the pure product was obtained by flash column chromatography on silica gel with hexane: EtOAc = 20:1 as the eluent, the yield = 66%.

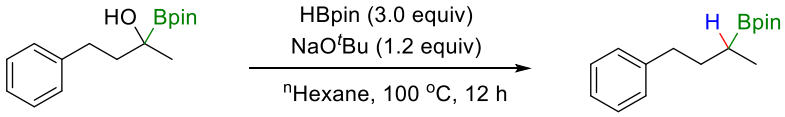
3.1.2 Procedure for the C-O silylation of α-borylated alcohol



2a **2ab**

The procedure for the C-O silylation of α-borylated alcohol was performed according to the literature procedure with some modification.[4] In glove box, a 25 mL sealed tube equipped with a stirrer bar was charged with $PhMe_2Si$-Bpin (393.0 mg, 1.5 mmol), NaO^tBu (57.6 mg, 0.60 mmol) and 3 mL toluene, then the α-borylated alcohol **2a** (138.0 mg, 0.50 mmol) was added. The tube was sealed with a Teflon screw cap and taken out of the glove box. Then, the mixture was heated at 100 °C with stirring for 12 h. Upon completion, the pure product was obtained by flash column chromatography on silica gel with hexane: EtOAc = 50:1 as the eluent, the yield = 62%.

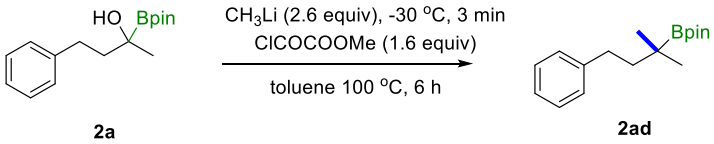
3.1.3 Procedure for the C-O hydrogenation of α-borylated alcohol



2a **2ac**

The procedure for the C-O hydrogenation of α-borylated alcohol was performed according to the literature procedure.[5] In glove box, a 25 mL sealed tube equipped with a stirrer bar was charged with NaO^tBu (57.6 mg, 0.60 mmol) and 3 mL ^{n}hexane, then the α-borylated alcohol **2a** (138.0 mg, 0.50 mmol) was added. The tube was sealed with a Teflon screw cap and taken out of the glove box. Then, the tube was unsealed and HBpin (192.0 mg, 1.5 mmol) was added under nitrogen atmosphere protection. Then, the tube was sealed and the mixture was heated at 100 °C for stirring 12h. Upon completion, the pure product was obtained by flash column chromatography on silica gel with hexane: EtOAc = 50:1 as the eluent, the yield = 40%.

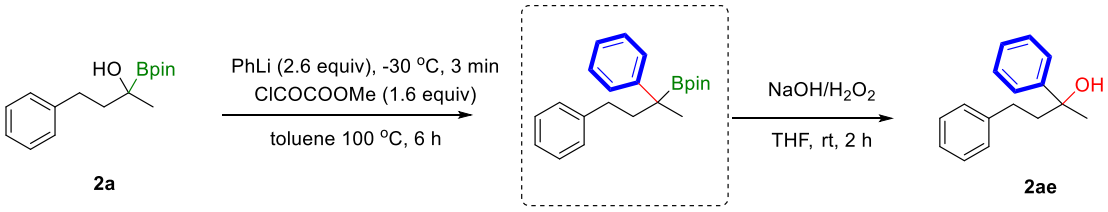
3.1.4 Procedure for the C-O alkylation of α-borylated alcohol



2a **2ad**

The procedure for the C-O arylation of α-borylated alcohol was performed according to the literature procedure with some modification.[6] In glove box, a 25 mL sealed tube equipped with a stirrer bar was charged with 3 mL toluene, then the α-borylated alcohol **2a** (138.0 mg, 0.50 mmol) was added. The tube was sealed with a Teflon screw cap and taken out of the glove box. Then, the tube was unsealed and CH_3Li (0.8 mL, 1.3 mmol, 1.6 M in Et_2O,) was added at -30 °C under nitrogen atmosphere. After 3 minutes, ClCOCOOMe (97.6 mg, 0.80 mmol) was added at -30 °C. Then, the tube was sealed and the mixture was heated at 100 °C for stirring 6 h. After the reaction was completed, the reaction mixture was passed through a short silica gel column eluting with EtOAc and concentrated in vacuo. The pure product was obtained by flash column chromatography on silica gel with hexane: EtOAc = 50:1 as the eluent.

3.1.5 Procedure for the C-O arylation of α-borylated alcohol

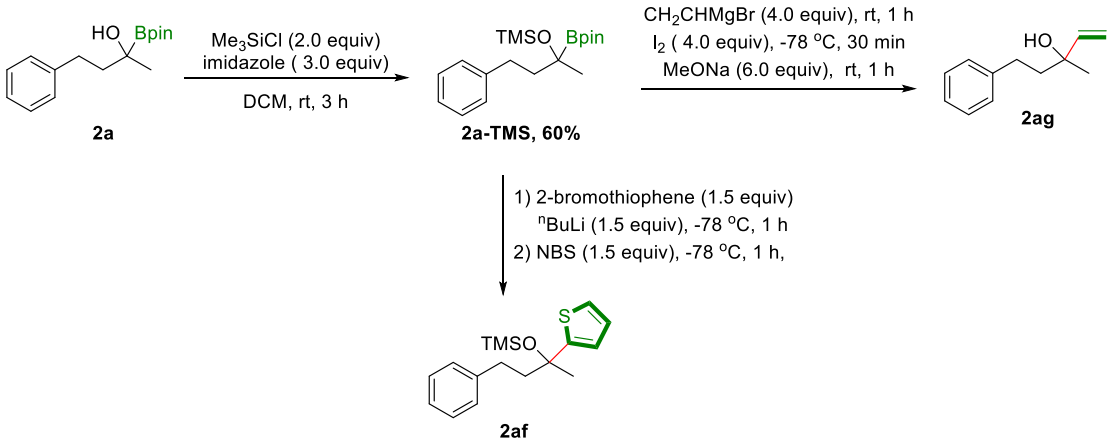


2a **2ae**

The procedure for the C-O arylation of α-borylated alcohol was performed according to the literature procedure.[6] In glove box, a 25 mL sealed tube equipped with a stirrer bar was charged with 3 mL toluene, then the α-borylated alcohol **2a** (138.0 mg, 0.50 mmol) was added. The tube was sealed with a Teflon screw cap and taken out of the glove box. Then, the tube was unsealed and PhLi (1.3 mL, 1.3 mmol, 1.0 M in Et_2O) was added at -30 °C under nitrogen atmosphere. After 3 minutes,

ClCOCOOMe (97.6 mg, 0.80 mmol) was added at -30 °C. Then, the tube was sealed and the mixture was heated at 100 °C for stirring 6 h. After the reaction was completed, the reaction mixture was passed through a short silica gel column eluting with EtOAc and concentrated in vacuo. The crude mixture was dissolved in 2 mL THF, then NaOH (aq) (0.5 ml, 3 M), H_2O_2 (aq) (0.5 mL, 30%) was added and stirred for 2 h at room temperature. Upon completion, the reaction was quenched by the addition saturated NH_4Cl solution, subsequently the reaction was extracted three times with EtOAc, dried over $MgSO_4$, the pure product was obtained by flash column chromatography on silica gel with hexane: EtOAc = 10:1 as the eluent, the yield = 40%.

3.2 Procedure for the C-H functionalization of α-borylated alcohol



3.2.1 Procedure for the silicon protected α-borylated alcohol (2a-TMS)

In glove box, a 50 mL sealed tube equipped with a stirrer bar was charged with imidazole (1.02 g, 15.0 mmol) and 20 mL DCM, then the α-borylated alcohol **2a** (1.38 g, 5.0 mmol) was added. The tube was sealed with a Teflon screw cap and taken out of the glove box. The tube was unsealed and the Me_3SiCl (1.09 g, 10.0 mmol) was added dropwise under nitrogen atmosphere. Then the reaction mixture was stirred for 3 h at room temperature. Upon completion, the pure product was obtained by flash column chromatography on silica gel with hexane: EtOAc = 20:1 as the eluent. Yield = 60%.

3.2.2 Procedure for the synthesis of 2af through the cross-coupling of 2a with 2-bromothiophene

The cross-coupling was performed according to the literature procedure.[7] A solution of bromothiophene (48.6 mg, 0.30 mmol) in THF (1.0 mL) was cooled to -78 °C and the ^{n}BuLi solution (120 μL, 0.30 mmol, 2.5 M in hexane) was added by drops. The reaction mixture was warmed to room temperature with stirring for 1 h. Then, the mixture was cooled to –78 °C and the silicon-protected α-borylated alcohol (**2a-TMS**) (69.6 mg, 0.20 mmol) in 0.5 mL THF was added and the reaction was stirred at -78 °C for 1 h. A solution of NBS (53.4 mg, 0.30 mmol) in THF (1.0 mL) was then added to the mixture. After 1 h at -78 °C, $Na_2S_2O_3$ saturated solution was added and the reaction mixture was warmed to room temperature. The mixture was extracted three times with EtOAc, dried over $MgSO_4$. The pure product was obtained by flash column chromatography on silica gel with hexane as the eluent. Yield = 40%.

3.2.3 Procedure for the synthesis of Zweifel olefination 2ag

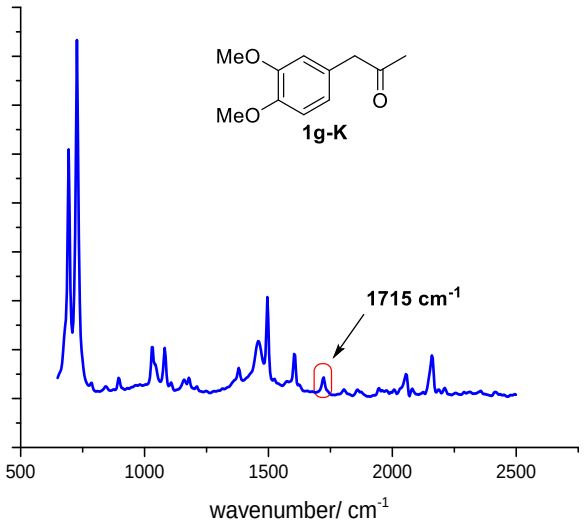
The synthesis of Zweifei olefination **2ag** was performed according to the literature.[8] In glove box, a 25 mL sealed tube equipped with a stirrer bar was charged with 2 mL THF, then the silicon-protected α-borylated alcohol **2a-TMS** (69.6 mg, 0.20 mmol) was added. The tube was sealed with a Teflon screw cap and taken out of the glove box. Then, the tube was unsealed and vinylmagnesium bromide (800 μL, 0.80 mmol, 1.0 M in THF,) was added at room temperature and stirring for 1h. Then the tube was treated at -78 ºC, I_2 (0.80 mmol in 1.6 mL MeOH) was added and stirring at -78 °C. After 30 minutes, MeONa (1.2 mmol in 1.2 mL MeOH) was added and the reaction was allowed to warm to room temperature. Then 10 mL NaS_2O_3 saturated solution and 40 mL hexane was added, the organ layer was collected and concentrated in vacuo, the pure product was obtained by flash column chromatography on silica gel with hexane: EtOAc = 10:1 as the eluent. Yield = 50%.

4. React IR Experiments

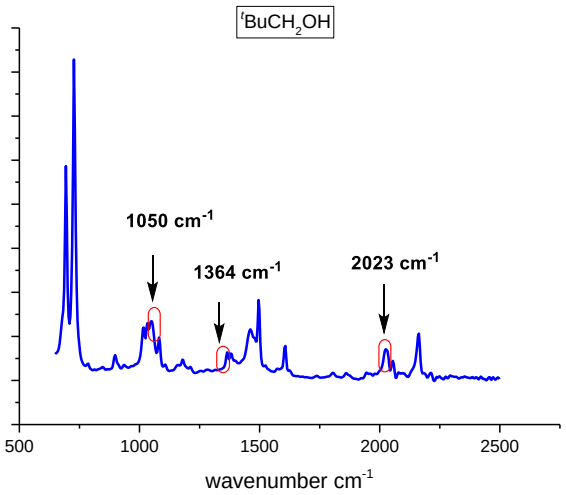
4.1 General React IR Experimental Details

For the React IR kinetic experiments, the reaction spectra were recorded using an IC 15 from Mettler-Toledo AutoChem fitted with a diamond-tipped probe. Data manipulation was carried out using the iC IR software, version 7.0.

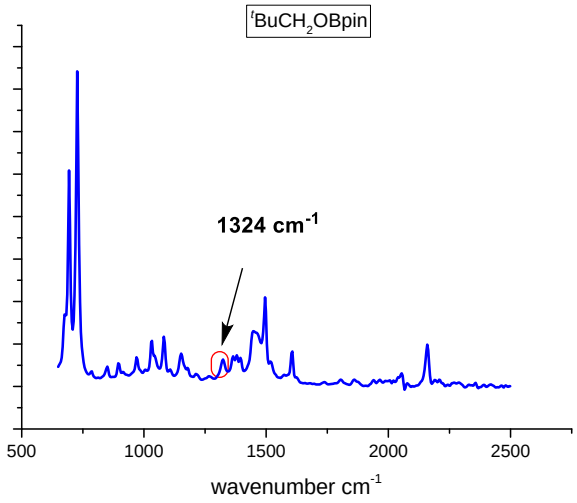
Characteristic IR band of **1g-K**

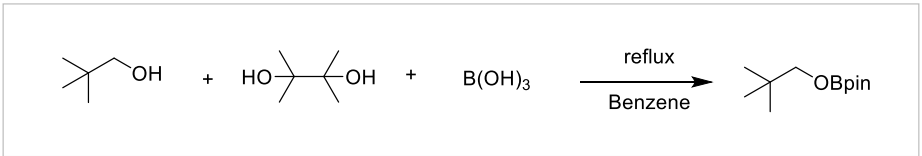


Characteristic IR band of $^{t}BuCH_2OH$



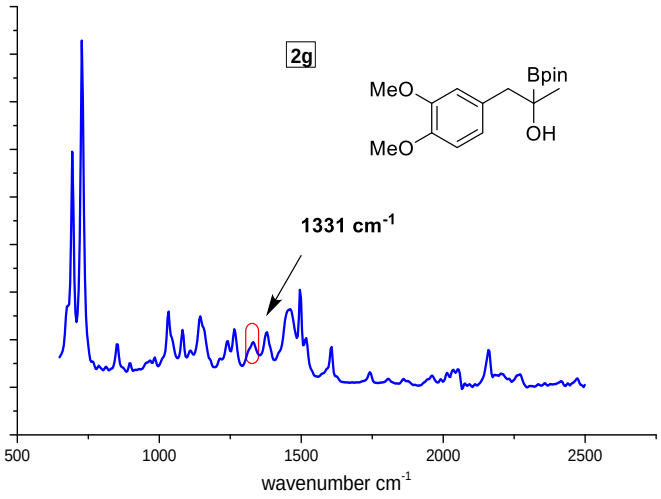
Characteristic IR band of ^{t}BuCH$_2$OBpin

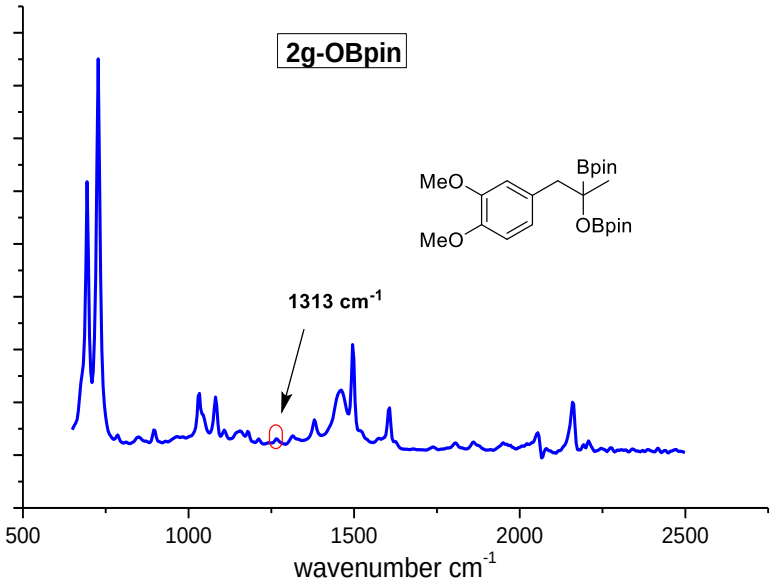




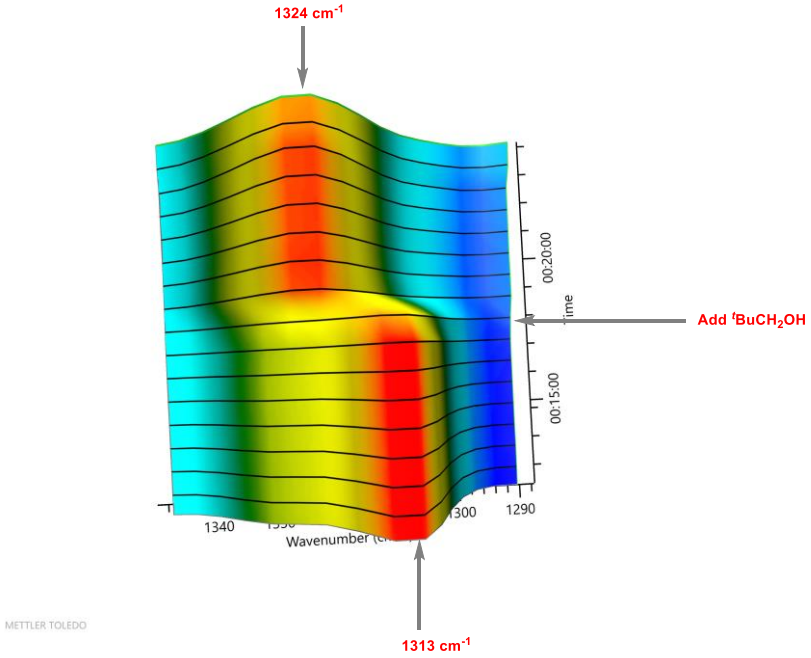
^{t}BuCH$_2$OBpin was prepared according to the literature with some modifications.[9] An oven dried 100 mL flask equipped with a stirrer bar was charged with 2,2-dimethylpropan-1-ol (0.88 g, 10 mmol), pinacol (0.59 g, 5 mmol), boric acid (0.31 g, 5 mmol) and 40 mL benzene. The mixture was allowed to stir at room temperature for 10 h, then mixture was heated at 100 ºC and removed the H_2O with oil-water separator. After the H_2O was removed absolutely, the mixture was concentrated in vacuo, and the product was used for IR experiment without other purification.

Characteristic IR band of **2g** and **2g-OBpin** (**2g-OBpin** was prepared by the addition of B_2pin_2 to **1g-K** using ICyCuCl catalyst according to the literature.[10])





It was deserved to be mentioned that when ^{t}BuCH$_2$OH (1.0 equiv. to 2**g-OBpin**) was added into **2g-OBpin**, the characteristic IR band of **2g-OBpin** in 1313 cm^{-1} disappeared rapidly within 30 seconds, in the meanwhile, a new broad band shown in 1324 cm^{-1} was raised, which was the characteristic IR band of ^{t}BuCH$_2$OBpin, and the characteristic IR band of **2g** in 1331 cm^{-1} could not distinguished from the broad band in 1324 cm^{-1}. In addition, a **2g** characteristic IR band in 1331 cm^{-1} was observed when the solution above was passed through a column chromatography on silica gel.



4.2 Procedure for Reaction course of alcohol 1g monitored by React IR

In glove box, a 15 mL sealed tube equipped with a stirrer bar was charged with $RuCl_2(PPh_3)_3$ (19.2 mg, 0.02 mmol), dcypp·2HBF$_4$ (12.2 mg, 0.02 mmol), $FeBr_2$ (22.0 mg, 0.10 mmol), NaO^{t}Bu (38.4 mg, 0.40 mmol), B_2pin_2 (432.0 mg, 1.70 mmol), naphthaline (32.0 mg, 0.25 mmol) as the internal standard. The tube was sealed with a Teflon screw cap and taken out of the glove box. Then, the tube was unsealed and linked to the IR probe through an adapter under nitrogen atmosphere. Subsequently, 3.5 mL toluene was added via syringe and the data collection was started, then the reaction was heated at 100 °C, after the curve was stable, pivaldehyde (86.0 mg, 1.0 mmol) was added. Within two minutes, the alcohol **1g** (1.0 mmol in 0.5 mL toluene) was added under nitrogen atmosphere. Then, the tube was sealed and the mixture was heated at 100 °C with stirring, 25 minutes later, the tube was unsealed and 50μl reaction mixture was extracted via syringe under nitrogen atmosphere and used for GC analysis

4.3 Procedure for standard dehydrogenation condition of 1g under Ru catalysis monitored by React IR

In glove box, an oven dried 15 mL sealed tube equipped with a stirrer bar was charged with $RuCl_2(PPh_3)_3$ (19.2 mg, 0.02 mmol), dcypp·2HBF_4 (12.2 mg, 0.02 mmol) NaO^tBu (38.4 mg, 0.40 mmol). The tube was sealed with a Teflon screw cap and taken out of the glove box. Then, the tube was unsealed and linked to the IR probe through an adapter under nitrogen atmosphere protection. 3.5 mL toluene was added via syringe and the data collection was started, then the reaction was heated at 100 °C, after the curve was stable, pivaldehyde (86.0 mg, 1.00 mmol) was added. Within two minutes, the alcohol **1g** (1.0 mmol in 0.5 mL toluene) was added under nitrogen atmosphere protection. Then, the tube was sealed and the mixture was heated at 100 °C for stirring. Upon completion the tube was unsealed and naphthaline was added as the internal standard for GC analysis.

4.3.1 Procedure for dehydrogenation of 1g under Ru catalysis with different amount of NaO^tBu monitored by React IR

The procedure for dehydrogenation of **1g** under Ru catalysis with different amount of NaO^tBu monitored by IC-IR was the same as the standard condition except for the amount of NaO^tBu (19.2 mg, 0.40 mmol or 9.6 mg, 0.20 mmol).

4.3.2 Procedure for dehydrogenation of 1g under Ru catalysis with B_2pin_2 monitored by React IR

The procedure for dehydrogenation of **1g** under Ru catalysis with $FeBr_2$ monitored by React-IR was the same as the standard condition except for the extra addition of B_2pin_2 (432.0 mg, 1.70 mmol) in glove box

4.3.3 Procedure for dehydrogenation of 1g under Ru catalysis with $FeBr_2$ monitored by React IR

The procedure for dehydrogenation of **1g** under Ru catalysis with $FeBr_2$ monitored by React-IR was the same as the standard condition except for the extra addition of $FeBr_2$ (22.0 mg, 0.10 mmol) in glove box

4.4 Procedure for standard borylation of 1g-K under Fe catalysis. monitored by React IR

In glove box, an oven dried 15 mL sealed tube equipped with a stirrer bar was charged with B_2pin_2 (432.0 mg, 1.70 mmol), NaO^tBu (38.4 mg, 0.40 mmol), $FeBr_2$ (22.0 mg, 0.10 mmol). The tube was sealed with a Teflon screw cap and taken out of the glove box. Then, the tube was unsealed and linked to the IR probe through an adapter under nitrogen atmosphere. Subsequently, 4.0 mL toluene was added via syringe and the data collection was started, then the reaction was heated at 100 °C, after the curve was stable, the ketone **1g-K** (194.0 mg, 1.0 mmol) was added under nitrogen atmosphere. Then, the tube was sealed and the mixture was heated at 100 °C with stirring. Upon completion the tube was unsealed and naphthaline was added as the internal standard for GC analysis.

4.4.1 Procedure for Borylation of 1g-K under Fe catalysis with ^{t}BuCH$_2$OH monitored by React IR

The procedure for dehydrogenation of **1g** under Ru catalysis with ^{t}BuCH$_2$OH monitored by React-IR was the same as the standard condition except for the extra addition of ^{t}BuCH$_2$OH (22.0 mg, 0.10 mmol) before the ketone **1g-K.**

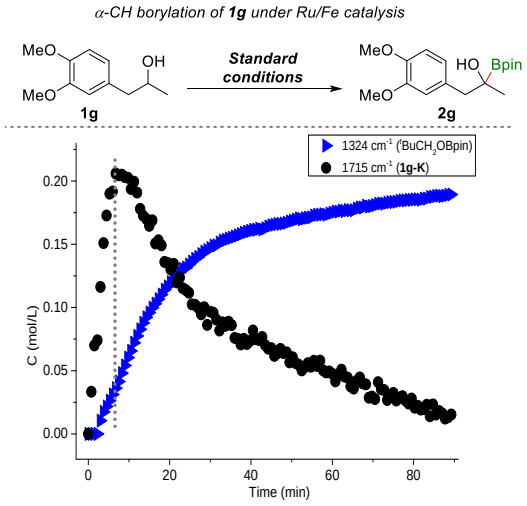
4.4.2 Procedure for Borylation of 1g-K under Fe catalysis with $RuCl_2(PPh_3)_3$ and dcypp·2HBF$_4$ monitored by React IR

The procedure for dehydrogenation of **1g** under Ru catalysis with with $RuCl_2(PPh_3)_3$ and dcypp·2HBF$_4$ monitored by React-IR was the same as the standard condition except for the extra addition of with $RuCl_2(PPh_3)_3$ (19.2 mg, 0.02 mmol), dcypp·2HBF$_4$ (12.2 mg, 0.02 mmol) in glove box.

4.4.3 Procedure for Borylation of 1g-K under Fe catalysis with $RuCl_2(PPh_3)_3$, dcypp·2HBF$_4$ and ^{t}BuCH$_2$OH monitored by React IR

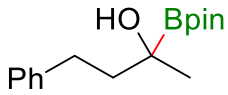
The procedure for dehydrogenation of **1g** under Ru catalysis with $RuCl_2(PPh_3)_3$ and dcypp·2HBF$_4$ monitored by React-IR was the same as the standard condition except for the extra addition of with $RuCl_2(PPh_3)_3$ (19.2 mg, 0.02 mmol), dcypp·2HBF$_4$ (12.2 mg, 0.02 mmol) in glove box and extra addition of ^{t}BuCH$_2$OH (22.0 mg, 0.10 mmol) before the ketone **1g-K.**

4.4.4 Reaction course of alcohol 1g monitored by IC-IR

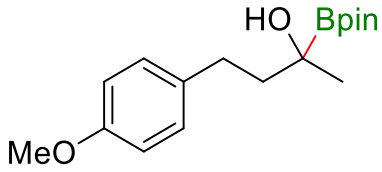


The reaction of 1g under the standard conditions was monitored by in situ IR spectroscopy. The kinetic profiles exhibited that the specific absorbance at 1715 cm-1 increased quickly within 10 min. Then, it was gradually consumed along with the increase of a broad absorbance at 1324 cm^{-1}. The peak 1715 cm^{-1} is a typical carbonyl absorption. By comparing to the standard samples, 1715 cm^{-1} was assigned to the specific absorbance of intermediary ketone **1g-K**, and 1324 cm^{-1} was assigned to the specific absorbance of ^{t}BuCH$_2$OBpin. These observations indicated that the alcohol dehydrogenation proceeded fast. As the specific absorbances of product **2g** were all covered by other species in the reaction mixture, and moreover the proton exchange of ^{t}BuCH$_2$OH with **2g-OBpin** to generate ^{t}BuCH$_2$OBpin is very fast (See details in SI 4.1). The kinetic profile of ^{t}BuCH$_2$OBpin (1324 cm-1) was recorded.

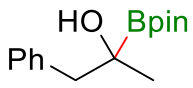
5. Detailed Descriptions for Products



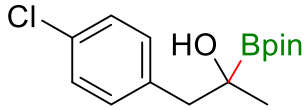
4-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-ol (2a).[10] Yield=85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.26 (m, 2H), 7.21-7.17 (m, 3H), 2.89-2.81 (m, 1H), 2.60-2.52 (m, 1H), 1.95-1.88 (m, 1H), 1.79-1.74 (m, 2H), 1.29 (m, 15H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7, 128.3(4), 128.3(0), 125.6, 84.4, 43.4, 31.8, 26.0, 24.8, 24.7 ppm.



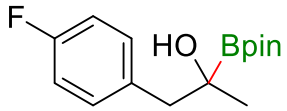
4-(4-methoxyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-ol (2b). Yield=62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-7.11 (m, 2H), 6.83-6.81 (m, 2H), 3.78 (s, 3H), 2.82-2.74 (m, 1H), 2.54-2.47 (m, 1H), 1.92-1.84 (m, 1H), 1.76-1.71 (m, 2H), 1.29-1.28 (m, 15H) ppm;^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 134.7, 129.2, 113.7, 84.3, 55.2, 43.7, 30.9, 26.0, 24.8, 24.7 ppm. HRMS (ESI) calcd for $C_{17}H_{27}BO_4$ $[M+Na]^+$: 329.1900; found: 329.1888.



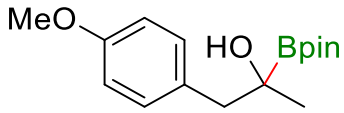
1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-ol (2c). Yield=78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.22 (m, 5H), 2.94-2.91 (m, 1H), 2.74-2.71 (m, 1H), 1.76 (s, 1H), 1.30 (s, 3H), 1.22 (s, 6H), 1.15 (s, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2, 130.3, 128.1, 126.4, 84.4, 46.7, 25.9, 24.9, 24.6 ppm. HRMS (ESI) calcd for $C_{15}H_{23}BO_3$ $[M+Na]^+$: 285.1638; found: 285.1637.



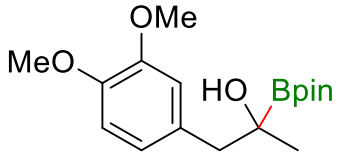
1-(4-chlorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-ol. (2d).[11] Yield=78%.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (m, 4H), 2.88-2.85 (m, 1H), 2.71-2.67 (m, 1H), 1.80 (s, 1H), 1.28 (s, 3H), 1.21 (s, 6H), 1.15 (s, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) 136.9, 132.0, 131.5, 127.9, 84.4, 45.8, 25.9, 24.7, 24.4 ppm.



1-(4-fluorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-ol (2e). Yield=84%**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.24 (m, 2H), 6.98-6.93 (m, 2H), 2.88-2.86 (m, 1H), 2.71-2.68 (m, 1H), 1.76 (s, 1H), 1.29 (s, 3H), 1.21 (s, 6H), 1.14 (s, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 160.5, 134.2(0), 134.1(7), 131.6(4), 131.5(6), 114.8, 114.6, 88.4, 45.8, 25.9, 24.8, 24.5 ppm. ^{19}F NMR (377 MHz, $CDCl_3$) δ -117.2 ppm. HRMS (ESI) calcd for $C_{15}H_{22}BF_5O_3$ $[M+Na]^+$: 303.1544; found: 303.1543.

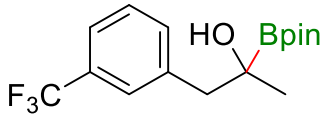


1-(4-methoxyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-ol (2f). Yield=85%**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.20 (m, 2H), 6.84-6.81 (m, 2H), 3.78 (s, 3H), 2.89-2.86 (m, 1H), 2.68-2.64 (m, 1H), 1.72 (s, 1H), 1.28 (s, 3H), 1.23 (s, 6H), 1.16 (s, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 131.1, 130.3, 113.4, 84.3, 55.2, 45.7, 25.6, 24.9, 24.5 ppm. HRMS (ESI) calcd for $C_{16}H_{25}BO_4$ $[M+Na]^+$: 315.1744; found: 315.1743.

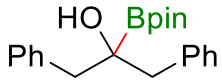


1-(3,4-dimethoxyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-ol (2g). Yield=80%**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86-6.75 (m, 3H), 3.87(s, 3H), 3.86 (s, 3H), 2.90-2.86 (m, 1H), 2.69-2.66 (m, 1H), 1.78 (s, 1H), 1.29 (s, 3H), 1.23 (s,

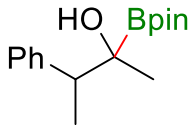
6H), 1.16 (s, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.4, 147.5, 130.7, 122.1, 113.5, 110.8, 84.3, 55.9, 55.8, 46.0, 25.7, 24.9, 24.5 ppm. HRMS (ESI) calcd for $C_{17}H_{27}BO_5$ $[M+Na]^+$: 345.1849; found:.345.1855.



2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(3-(trifluoromethyl)phenyl)propan-2-ol (2h). Yield=80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.36 (m, 4H), 2.96-2.92 (m, 1H), 2.80-2.77 (m, 1H), 1.83 (s, 1H), 1.32 (s, 3H), 1.19 (s, 6H), 1.11 (s, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) 139.7, 133.7(8), 133.7(7), 130.3, 130.0, 129.7, 128.3, 126.8(3), 126.8(0), 126.7(6), 126.7, 123.2, 123.1(1), 123.0(8), 123.0, 84.6, 46.5, 26.3, 24.8, 24.4 ppm. ^{19}F NMR (377 MHz, $CDCl_3$) -62.5 ppm. HRMS (ESI) calcd for $C_{16}H_{22}BF_3O_3$ $[M+Na]^+$: 353.1512; found: 353.1510.

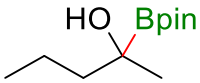


1,3-diphenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-ol (2i). Yield=85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.34 (m, 4H), 7.26-7.18 (m, 6H), 2.97-2.93 (m, 2H), 2.87-2.84 (m, 2H), 2.04 (s, 1H), 0.96 (s, 12H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 130.3, 127.9, 126.3, 84.5, 46.1, 24.8 ppm. HRMS (ESI) calcd for $C_{21}H_{27}BO_3$ $[M+Na]^+$: 361.1951; found: 361.1948.

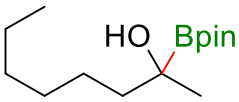


3-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-ol (2j). Yield=73%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.20 (m, 5H), 2.86-2.81 (m, 1H), 1.49 (s, 1H), 1.37 (d, J = 6.8 Hz, 3H), 1.28 (m, 12H), 1.01 (s, 3H) ppm; ^{13}C NMR (101 MHz,

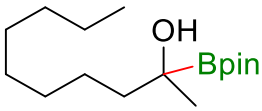
$CDCl_3$) δ 142.6, 129.0, 127.9, 126.3, 84.2, 47.4, 24.8, 24.7, 24.6, 17.6 ppm. HRMS (ESI) calcd for $C_{16}H_{25}BO_3$ $[M+Na]^+$: 299.1794; found: 299.1792.



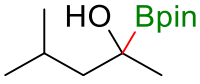
2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentan-2-ol (2k). Yield=72%. ^1H NMR (400 MHz, $CDCl_3$) δ 1.66-1.40 (m, 4H), 1.27 (s, 12H), 1.23 (s, 3H), 0.96-0.91 (m, 4H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 84.2, 43.8, 26.7, 24.7, 24.6, 18.6, 14.7 ppm. HRMS (ESI) calcd for $C_{11}H_{23}BO_3$ $[M+Na]^+$: 237.1638; found: 237.1637.



2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octan-2-ol (2l). Yield=78%. ^1H NMR (400 MHz, $CDCl_3$) δ 1.68-1.40 (m, 4H), 1.28-1.26 (m, 18 H), 1.23 (s, 3H), 0.97 (s, 1H), 0.89-0.86 (m, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 84.1, 41.5, 31.7, 29.8, 26.1, 25.3, 24.6(9), 24.6(6), 22.5, 14.1ppm. HRMS (ESI) calcd for $C_{14}H_{29}BO_3$ $[M+Na]^+$: 279.2107; found: 279.2107.

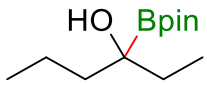


2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)decan-2-ol (2m). Yield=62%. ^1H NMR (400 MHz, $CDCl_3$) δ 1.68-1.66 (m, 1H), 1.59 -1.40 (m, 3H), 1.29-1.23 (m, 25H), 0.97 (s, 1H), 0.89-0.86 (m, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 84.2, 41.5, 31.8, 30.1, 29.5, 29.2, 26.1, 25.3, 24.7, 24.6, 22.6, 14.1 ppm. HRMS (ESI) calcd for $C_{16}H_{33}BO_3$ $[M+Na]^+$: 307.2420; found: 307.2421.

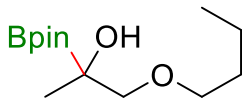


4-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentan-2-ol (2n).[11] Yield=70%. ^1H NMR (400 MHz, $CDCl_3$) δ 1.83-1.77 (m, 1H), 1.54-1.49 (m, 1H), 1.45-

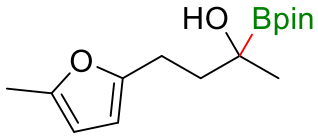
1.40 (m, 1H), 1.28 (s, 12H), 1.23 (s, 3H), 0.95 (d, J = 6.8 Hz, 3H), 0.92 (d, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 84.2, 50.0, 27.5, 25.4, 24.8, 24.6, 24.0, 23.6 ppm.



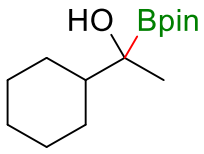
3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-3-ol (2o). Yield=62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.70 (s, 1H), 1.62-1.53 (m, 2H), 1.48-1.37 (m, 2H), 1.28 (m, 14H), 0.95-0.90 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 84.3, 42.4, 32.8, 26.7, 24.8, 18.5, 14.8, 9.4 ppm. HRMS (ESI) calcd for $C_{12}H_{25}BO_3$ $[M+Na]^+$: 251.1794; found: 251.1792.



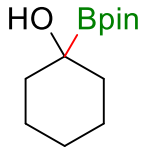
Butoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-ol (2p). Yield=30%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.53-3.51 (m, 1H), 3.48-3.42 (m, 2H), 3.28-3.25 (m, 1H), 1.56-1.50 (m, 2H), 1.39-1.33 (m, 2H), 1.28 (s, 12H), 1.18 (s, 3H), 0.97 (s, 1H), 0.93-0.89 (t, J = 7.2 Hz 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 84.2, 78.5, 71.1, 31.6, 24.6, 20.6, 19.2, 13.8 ppm. HRMS (ESI) calcd for $C_{13}H_{27}BO_4$ $[M+Na]^+$: 281.1900; found: 281.1899.



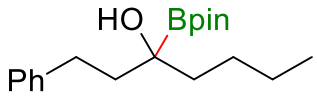
4-(5-methylfuran-2-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-ol (2q). Yield=67% ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84-5.83 (m, 2H), 2.83-2.76 (m, 1H), 2.60-2.51 (m, 1H), 2.24 (s, 3H), 1.98-1.90 (m, 1H), 1.81-1.72 (m, 2H), 1.28-1.27 (m, 15H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4, 150.1, 105.7, 105.0, 84.36, 39.5, 26.0, 24.7, 23.9, 13.5 ppm. HRMS (ESI) calcd for $C_{15}H_{25}BO_4$ $[M+Na]^+$: 303.1744; found: 303.1745.



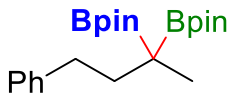
1-cyclohexyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethan-1-ol (2r).[11] Yield=85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.92-1.89 (m, 1H), 1.78-1.75 (m, 2H), 1.67-1.60 (m, 3H), 1.35-1.08 (m, 20H), 0.90 (s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 84.1, 47.0, 28.9, 26.9, 26.7, 26.6, 26.4, 24.8, 24.7, 23.0 ppm.



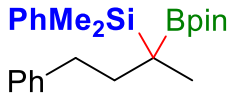
1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexan-1-ol (2s).[10] Yield=50%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.82-1.58 (m, 6H), 1.44-1.41 (m, 5H), 1.28-1.27 (s, 12H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 83.9, 35.6, 25.6, 24.6, 22.0 ppm.



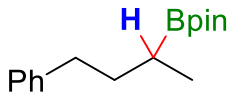
1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptan-3-ol (2t). Yield=72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.24 (m, 2H), 7.21-7.19 (m, 3H), 2.90-2.81 (m, 1H), 2.58-2.50 (m, 1H), 1.92-1.45 (m, 9H), 1.30 (s, 12H), 0.90 (t, J = 4.0 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 128.3(3), 128.2(8), 125.6, 84.5. 42.3, 39.8, 31.7, 27.4, 24.9, 24.8, 23.3, 14.0 ppm. HRMS (ESI) calcd for $C_{19}H_{31}BO_3$ $[M+Na]^+$: 341.2264; found: 341.2265.



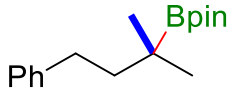
2,2'-(4-phenylbutane-2,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2aa).[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.20 (m, 4H), 7.15-7.12 (m, 1H), 2.60-2.56 (m, 2H), 1.84-1.81 (m, 2H), 1.23 (s, 24H), 1.16 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7, 128.5, 128.1, 125.4, 83.0, 36.7, 34.2, 24.7, 24.6, 16.0 ppm.



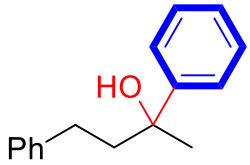
Dimethyl(phenyl)(4-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl)silane (2ab).[13] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.51 (m, 2H), 7.32-7.30 (m, 3H), 7.27-7.23 (m, 2H), 7.17-7.14 (m, 3H), 2.70-2.62 (m, 1H), 2.44-2.37 (m, 1H), 2.07-2.00 (m, 1H), 1.45-1.40 (m, 1H), 1.24 (s, 6H), 1.22 (s, 6H), 1.11 (s, 3H), 0.34 (s, 3H), 0.32 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 137.5, 134.8, 128.7, 128.5, 128.2, 127.3, 125.5, 82.9, 36.2, 34.2, 29.7, 25.3, 24.9, 15.6, -4.5, -4.7 ppm.



4,4,5,5-tetramethyl-2-(4-phenylbutan-2-yl)-1,3,2-dioxaborolane (2ac).[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.23 (m, 2H), 7.19-7.14 (m, 3H), 2.62 (t, J = 7.2 Hz, 2H), 1.82-1.75 (m, 1H), 1.63-1.56 (m, 1H), 1.24 (s, 12H), 1.13-1.06 (m, 1H), 1.03-1.01 (m, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 128.4, 128.1, 125.5, 82.8, 35.3, 35.2, 24.8, 24.7, 15.4 ppm.

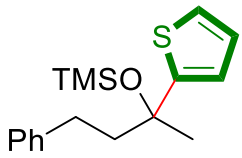


4,4,5,5-tetramethyl-2-(2-methyl-4-phenylbutan-2-yl)-1,3,2-dioxaborolane.[6] **(P1a).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.24 (m, 2H), 7.20-7.13 (m, 3H), 2.58-2.53 (m, 2H), 1.61-1.56 (m, 2H), 1.25 (s, 12H), 1.00 (s, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 128.3, 128.2, 125.4, 83.0, 43.5, 33.1, 24.7 ppm.

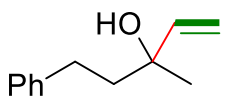


2,4-diphenylbutan-2-ol (2ae).[14] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.47 (m, 2H), 7.39-7.35 (m, 2H), 7.28-7.23 (m, 3H), 7.17-7.11 (m, 3H), 2.66-2.59 (m, 1H), 2.48-2.41 (m, 1H), 2.20-2.07 (m, 2H), 1.75 (s, 1H), 1.62 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5, 142.2, 128.4, 128.2(9), 128.2(6), 126.7, 125.7, 124.8, 74.7, 45.9, 30.6, 30.4 ppm.

trimethyl((4-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl)oxy)silane (2a-TMS). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.24 (m, 2H), 7.20-7.14 (m, 3H), 2.78-2.71 (m, 1H), 2.63-2.55 (m, 1H), 1.89-1.68 (m, 2H), 1.30 (s, 3H), 1.27 (s, 12H), 0.15 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 128.4, 128.2, 125.4, 88.7, 44.1, 31.1, 25.9, 25.0, 24.8, 2.5 ppm. HRMS (ESI) calcd for $C_{19}H_{33}BO_3Si$ $[M+Na]^+$: 371.2190; found:.371.2195.



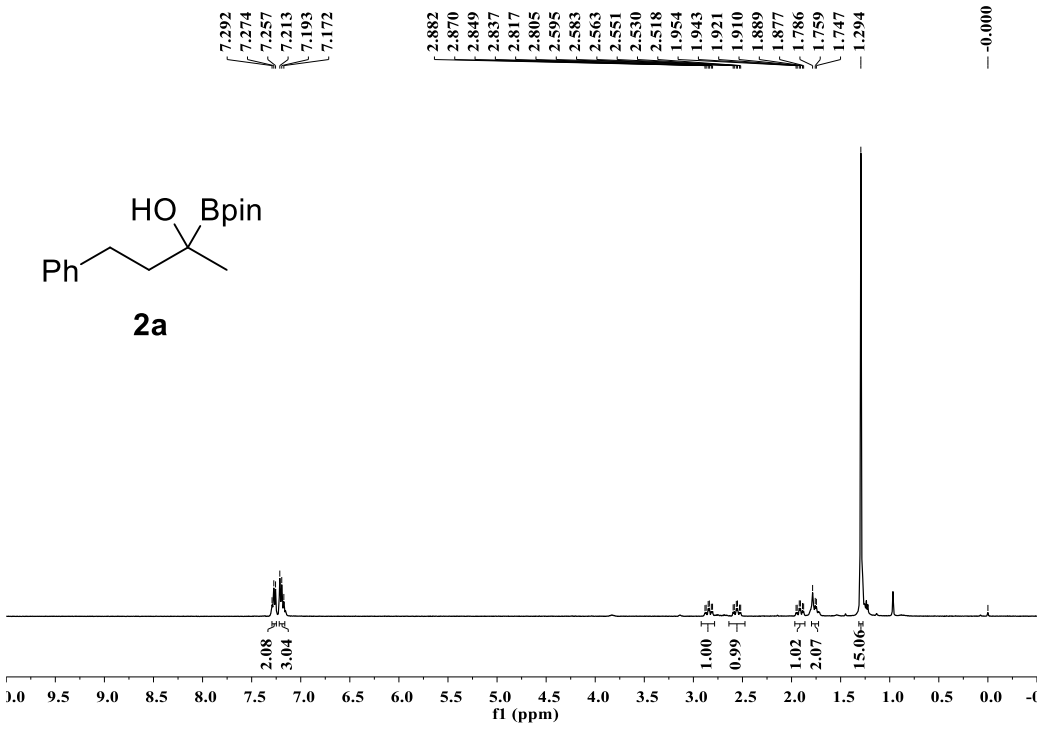
trimethyl((4-phenyl-2-(thiophen-2-yl)butan-2-yl)oxy)silane (2af). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.23 (m, 2H), 7.18-7.12 (m, 4H), 6.96-6.93 (m, 1H), 6.88-6.87 (m, 1H), 2.67-2.59 (m, 1H), 2.55-2.47 (m, 1H), 2.15-2.09 (m, 2H), 1.72 (s, 3H), 0.12 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 142.5, 128.3(2), 128.2(8), 126.5, 125.6, 123.5, 122.0, 76.7, 48.5, 30.7, 30.3, 2.2 ppm. HRMS (ESI) calcd for $C_{17}H_{24}OSSi$ $[M+Na]^+$: 327.1215; found:.327.1216.

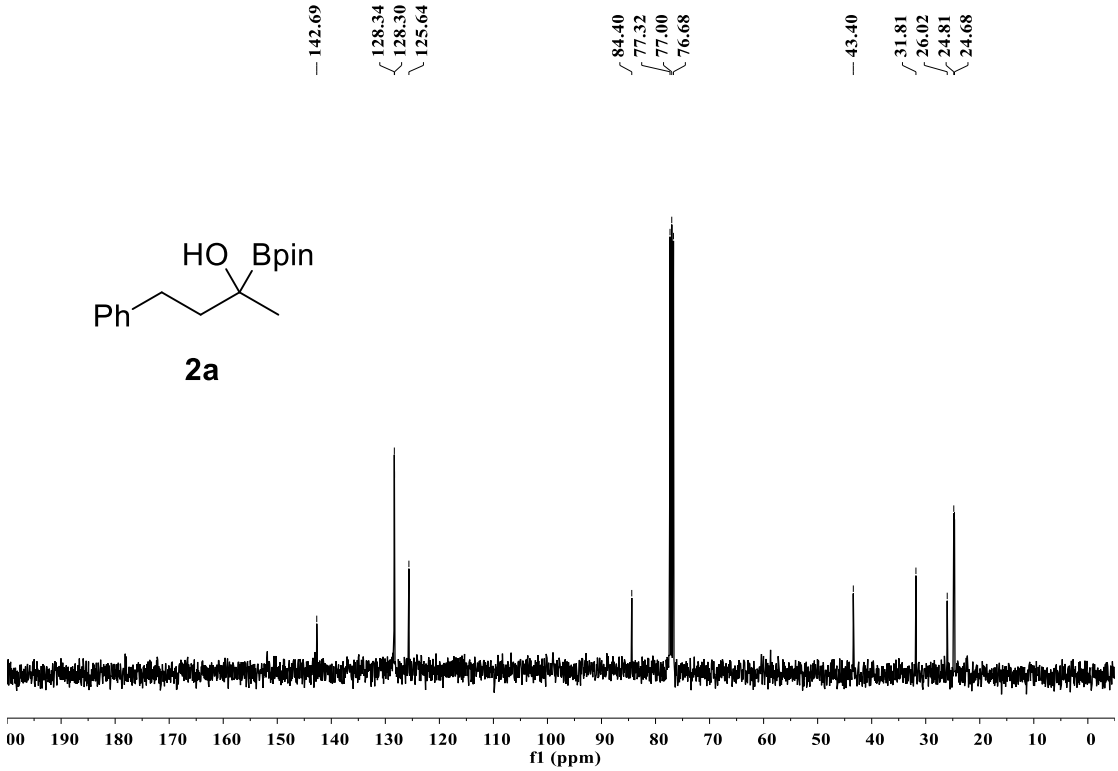


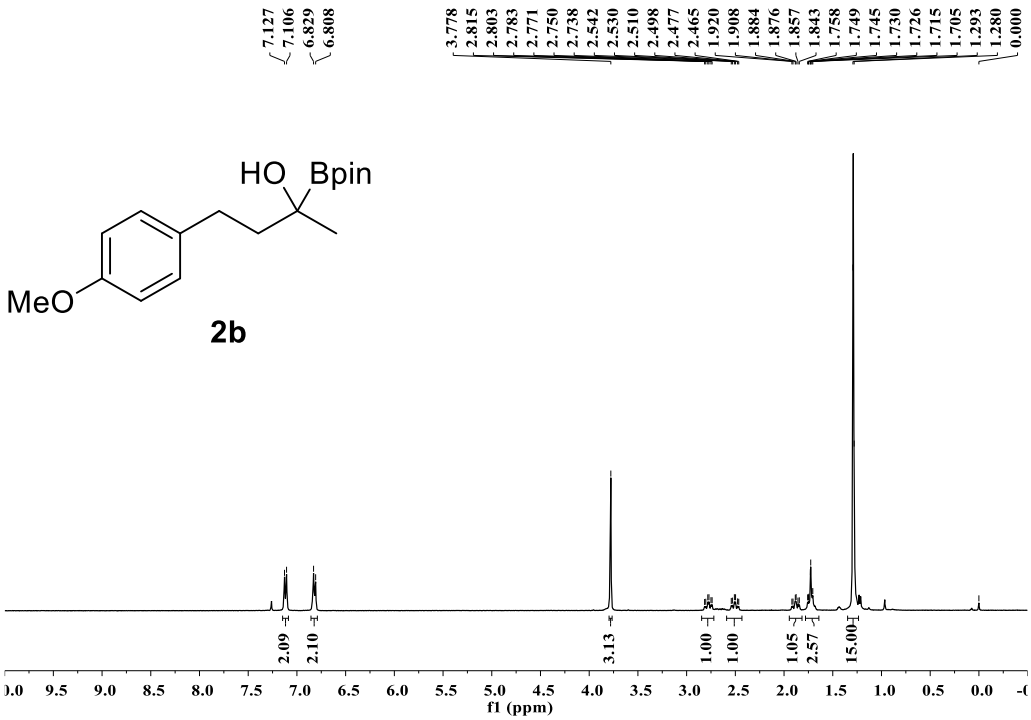
3-methyl-5-phenylpent-1-en-3-ol (2ag). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.25 (m, 2H), 7.19-7.17 (m, 3H), 5.97 (dd, J_1= 17.2 Hz, J_2= 10.4 Hz, 1H), 5.26 (d, J = 17.6 Hz, 1H), 5.11 (d, J = 10.8 Hz, 1H), 2.68-2.63 (m, 2H), 1.88-1.81 (m, 2H), 1.54 (s, 1H), 1.34

(s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 142.4, 128.4, 128.3, 125.7, 112.0, 73.2, 44.0, 30.3, 28.0 ppm. HRMS (ESI) calcd for $C_{12}H_{16}O$ $[M+Na]^+$: 199.1099; found: 199.1095.

6. Copies of Products ^{1}H NMR and ^{13}C NMR



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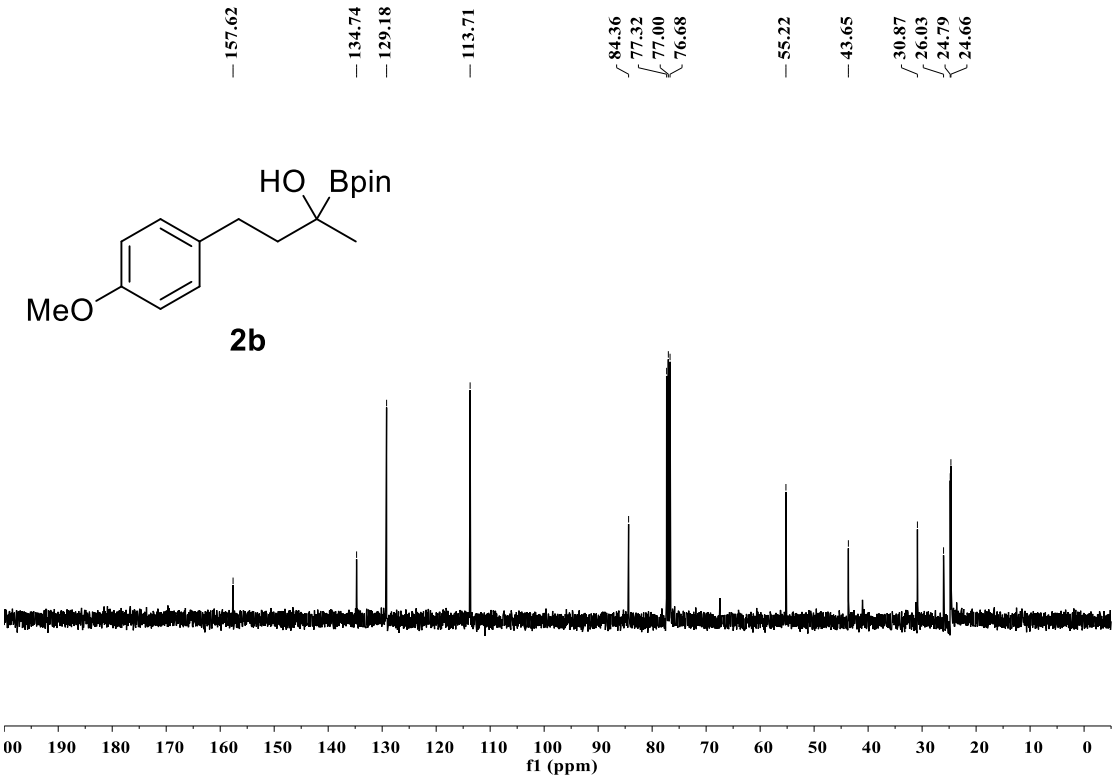
6.829
6.808
3.778
2.815
2.803
2.783
2.771
2.750
2.738
2.542
2.530
2.510
2.498
2.477
2.465
1.920
1.908
1.884
1.876
1.857
1.843
1.758
1.749
1.745
1.730
1.726
1.715
1.705
1.293
1.280
0.000
HO Bpin
MeO
2b
2.09
2.10
3.13
1.00
1.00
1.05
2.57
15.00
f1 (ppm)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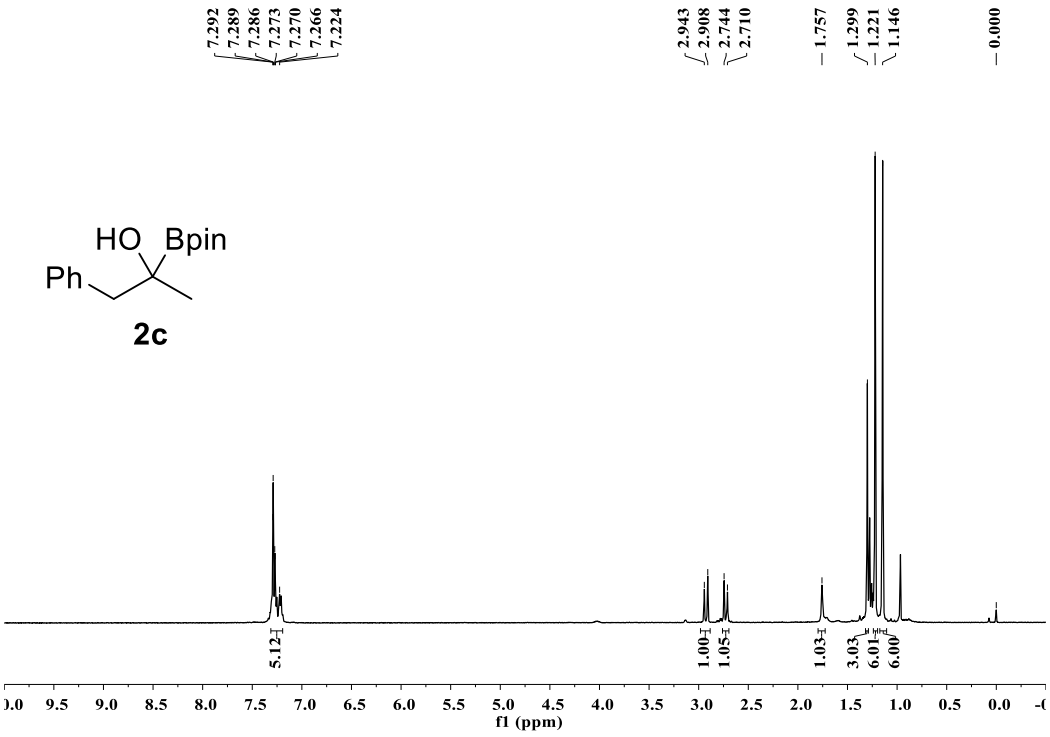
134.74
129.18
113.71
84.36
77.32
77.00
76.68
55.22
43.65
30.87
26.03
24.79
24.66
HO Bpin
MeO
2b
f1 (ppm)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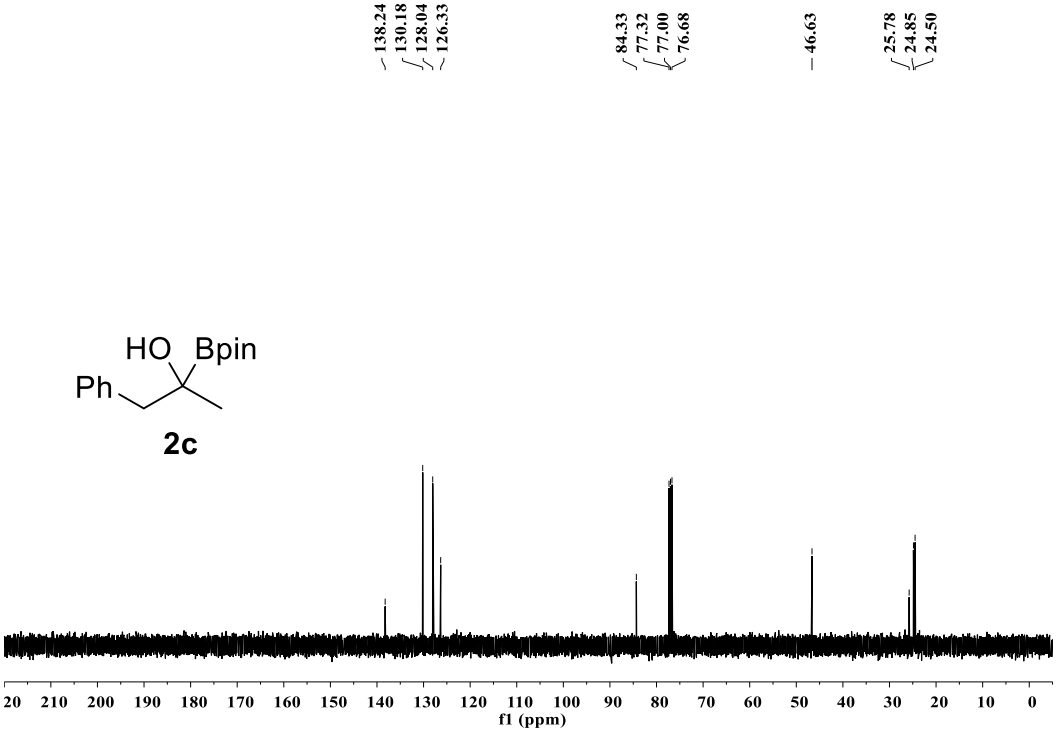
7.289
7.286
7.273
7.270
7.266
7.224
2.943
2.908
2.744
2.710
1.757
1.299
1.221
1.146
0.000
HO Bpin
Ph
2c
5.12
1.00
1.05
1.03
3.03
6.01
6.00
f1 (ppm)


138.24
130.18
128.04
126.33
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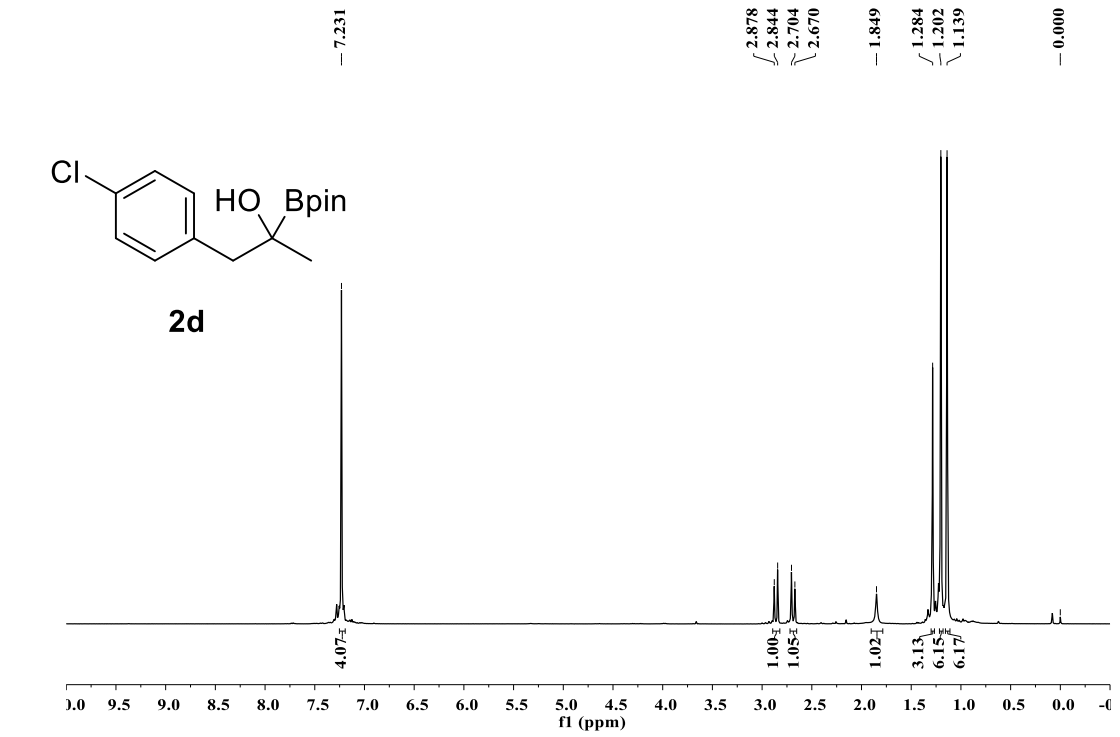
77.00
76.68
46.63
25.78
24.85
24.50
HO Bpin
Ph
2c
f1 (ppm)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2.704
2.670
1.849
1.284
1.202
1.139
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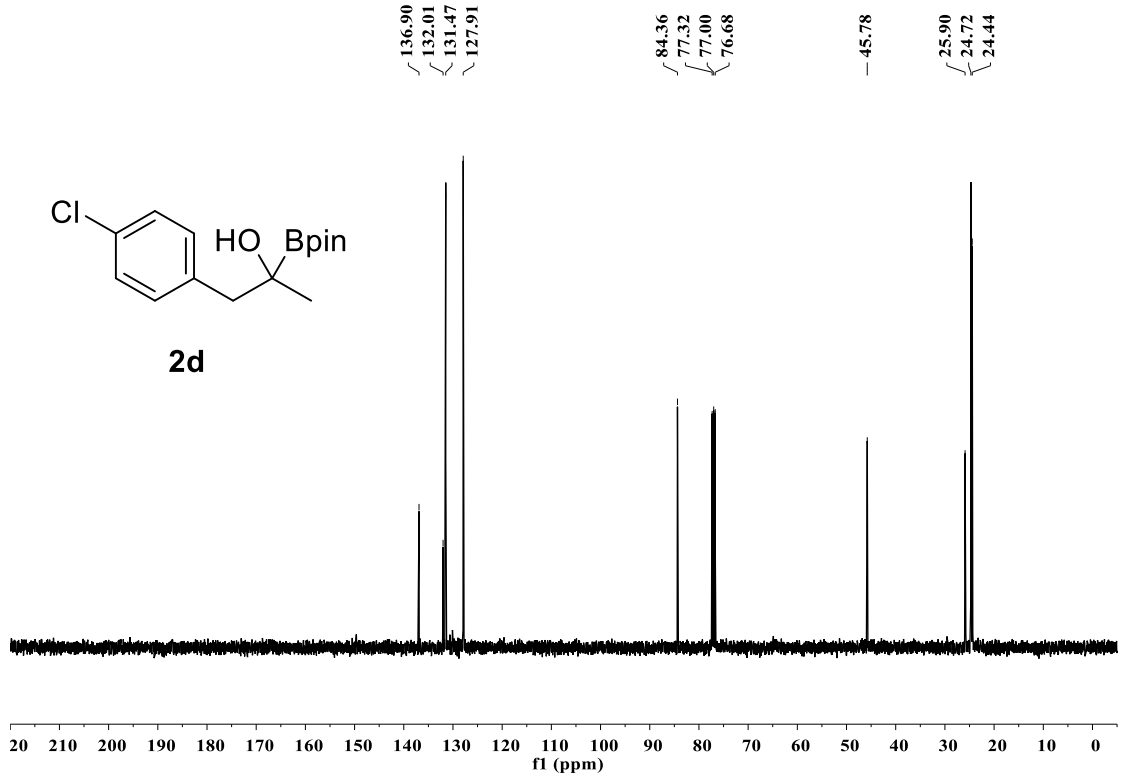
Cl
HO
Bpin
2d
4.07
1.00
1.05
1.02
3.13
6.15
6.17
f1 (ppm)


136.90
132.01
131.47
127.91
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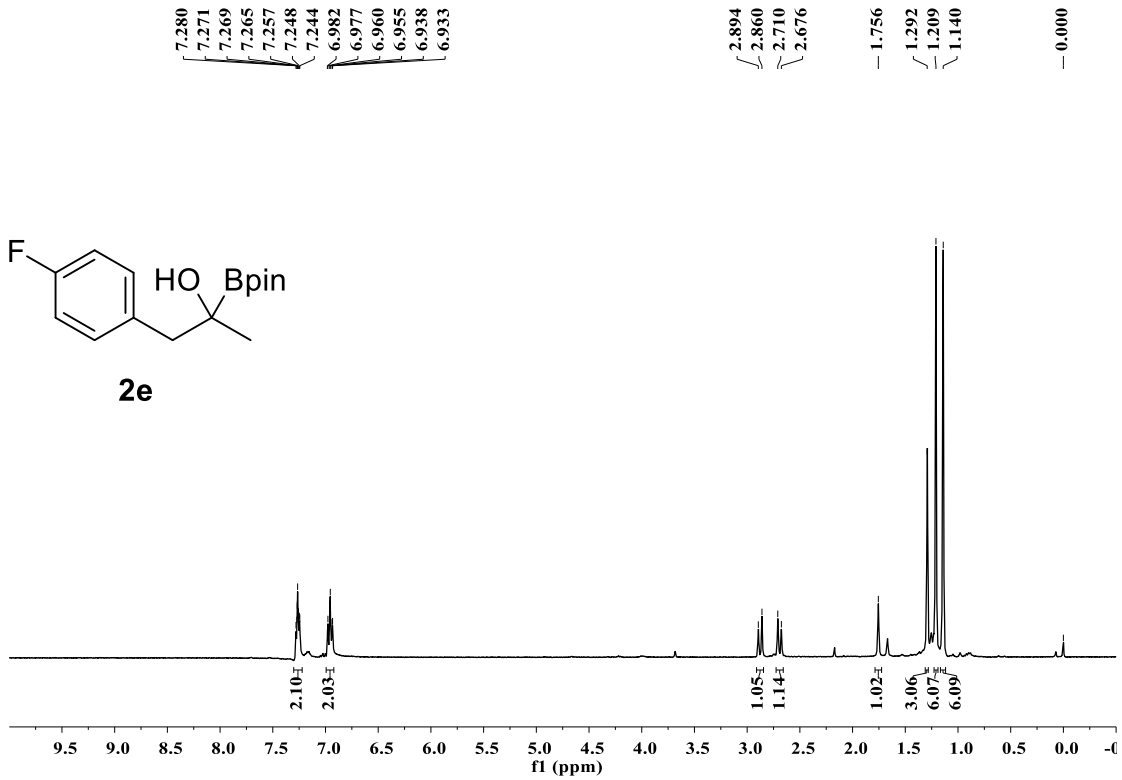
77.00
76.68
45.78
25.90
24.72
24.44
Cl
HO
Bpin
2d
f1 (ppm)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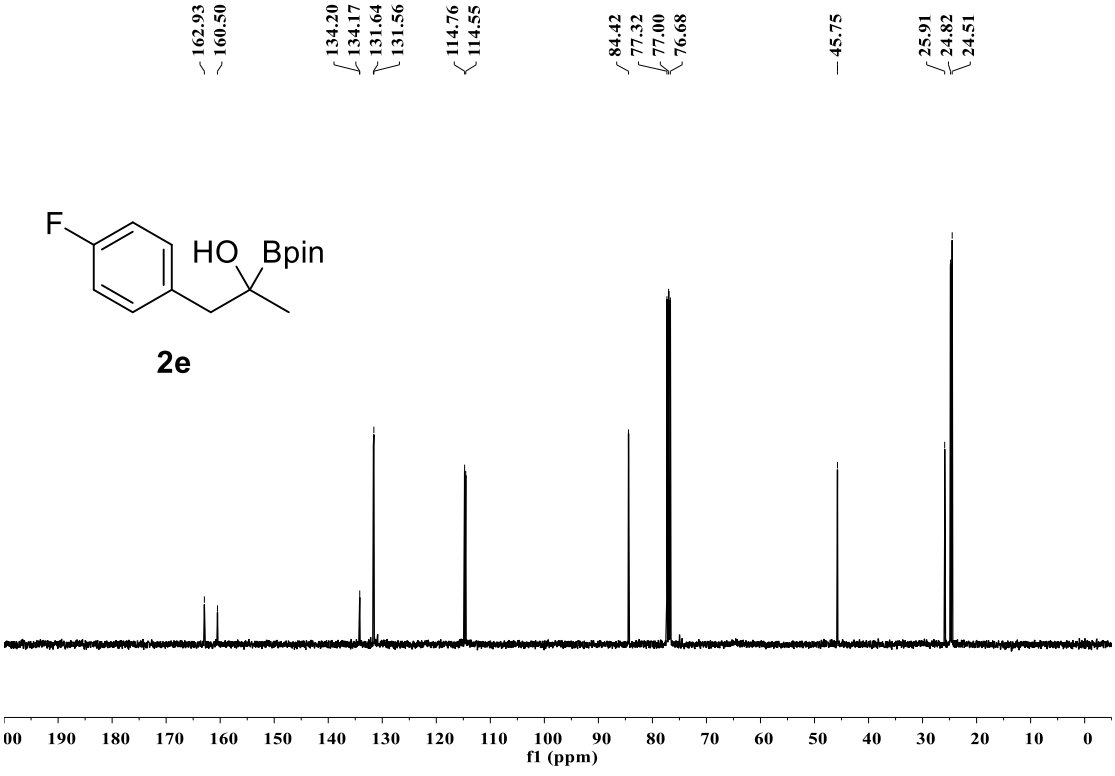
7.271
7.269
7.265
7.257
7.248
7.244
6.982
6.977
6.960
6.955
6.938
6.933
2.894
2.860
2.710
2.676
1.756
1.292
1.209
1.140
0.000
F
HO Bpin
2e
2.10
2.03
1.05
1.14
1.02
3.06
6.07
6.09
f1 (ppm)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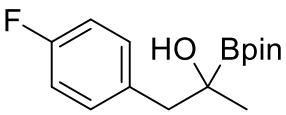
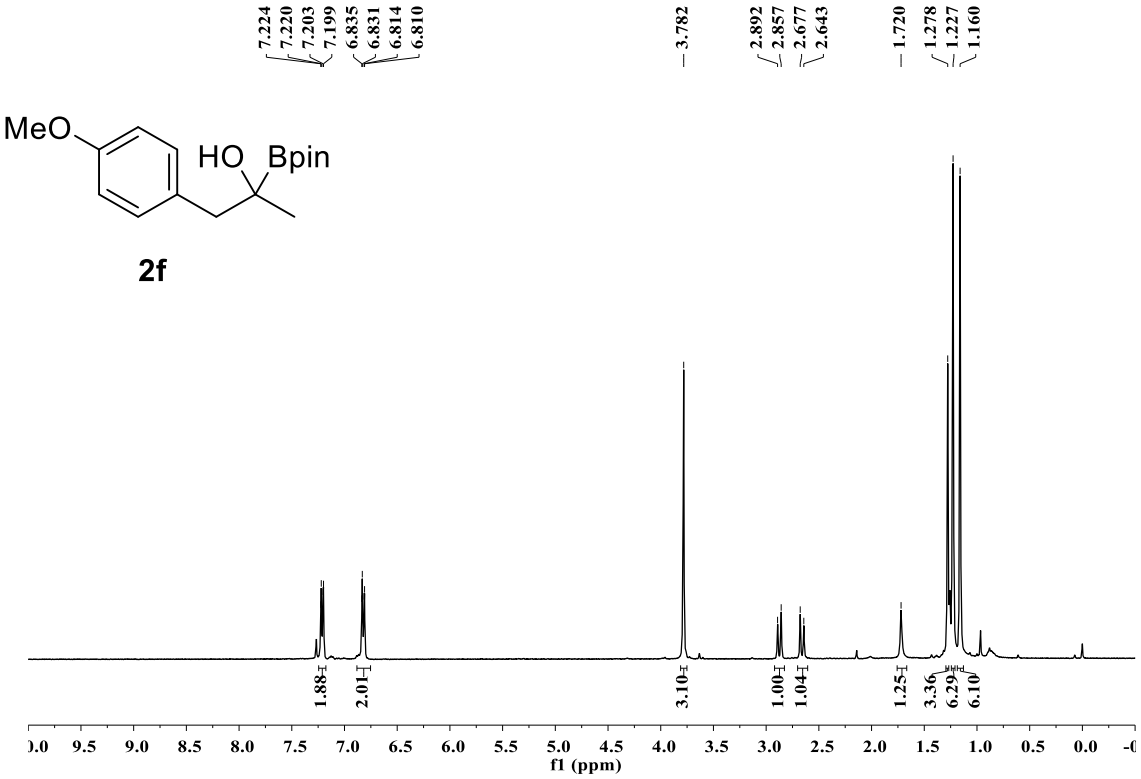
160.50
134.20
134.17
131.64
131.56
114.76
114.55
84.42
77.32
77.00
76.68
45.75
25.91
24.82
24.51
F
HO Bpin
2e
f1 (ppm)


F
HO
Bpin

2e

-117.218
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)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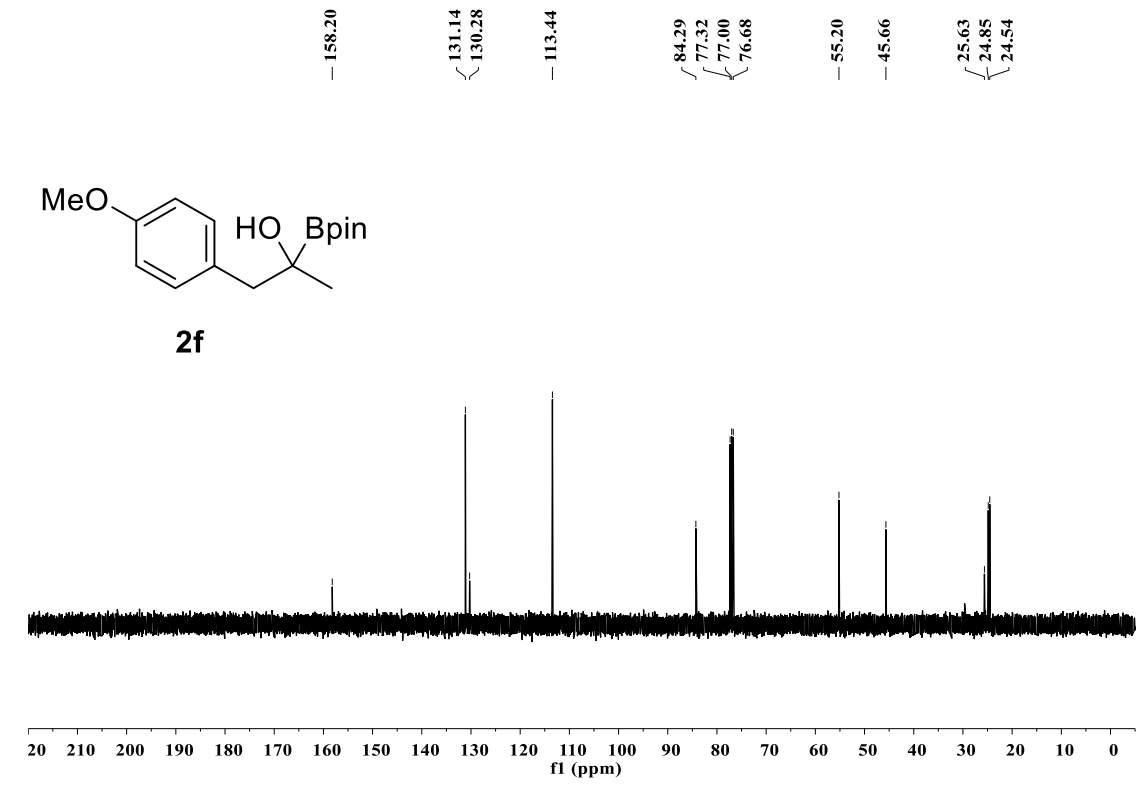
7.220
7.203
7.199
6.835
6.831
6.814
6.810
3.782
2.892
2.857
2.677
2.643
1.720
1.278
1.227
1.160
MeO
HO
Bpin
1.88
2.01
3.10
1.00
1.04
1.25
3.36
6.29
6.10
f1 (ppm)

2f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113.44
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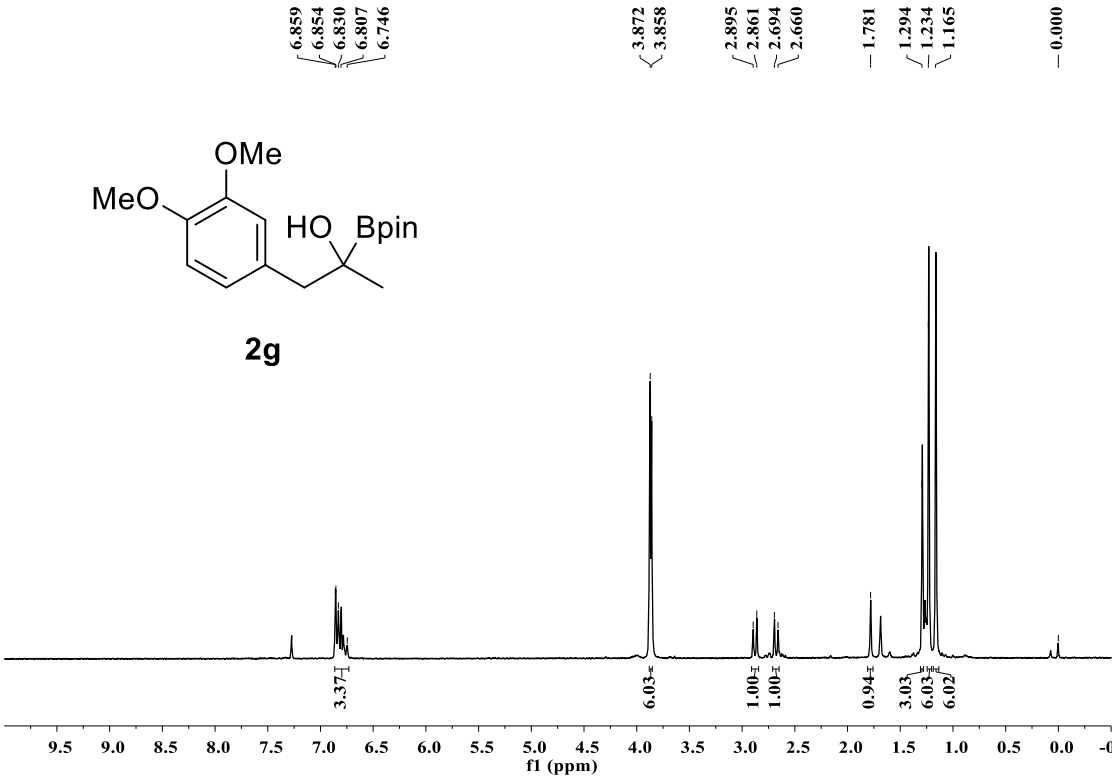
77.00
76.68
55.20
45.66
25.63
24.85
24.54
MeO
HO
Bpin
f1 (ppm)

2f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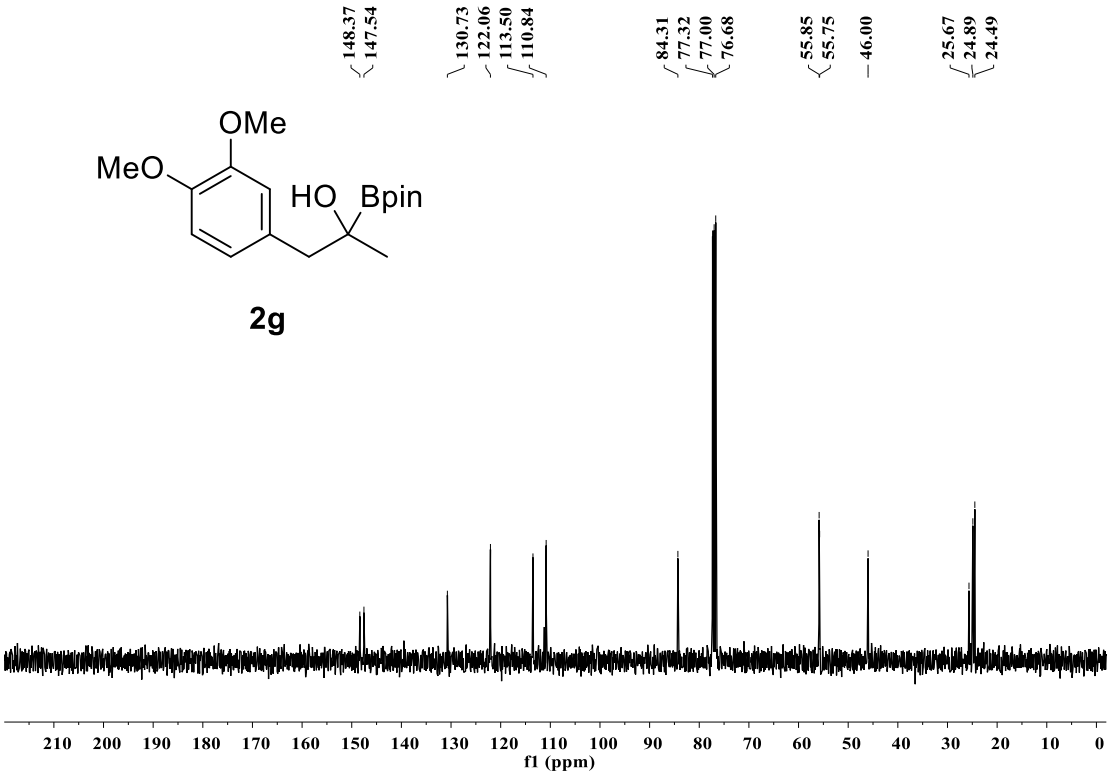
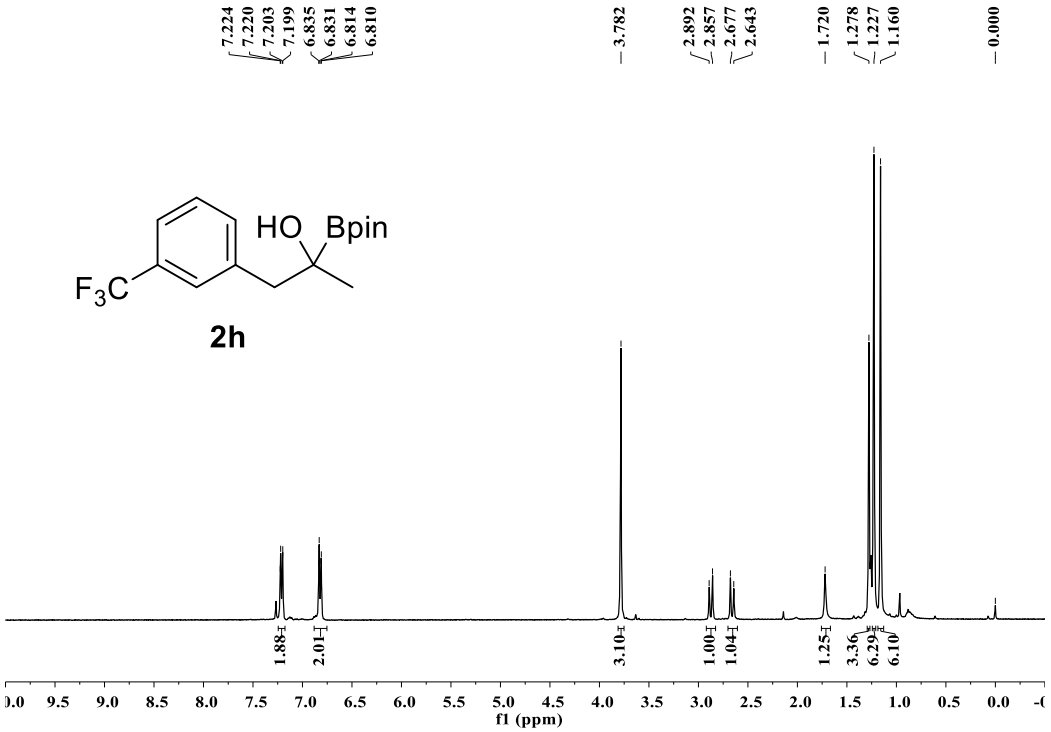
6.807
6.746
3.872
3.858
2.895
2.861
2.694
2.660
1.781
1.294
1.234
1.165
0.000
OMe
MeO
HO
Bpin
2g
3.37
6.03
1.00
1.00
0.94
3.03
6.03
6.02
f1 (ppm)


148.37
147.54
130.73
122.06
113.50
110.84
84.31
77.32
77.00
76.68
55.85
55.75
46.00
25.67
24.89
24.49
OMe
MeO
HO
Bpin
2g
f1 (ppm)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7.220
7.203
7.199
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6.831
6.814
6.810
3.782
2.892
2.857
2.677
2.643
1.720
1.278
1.227
1.160
0.000
HO Bpin
F3C
2h
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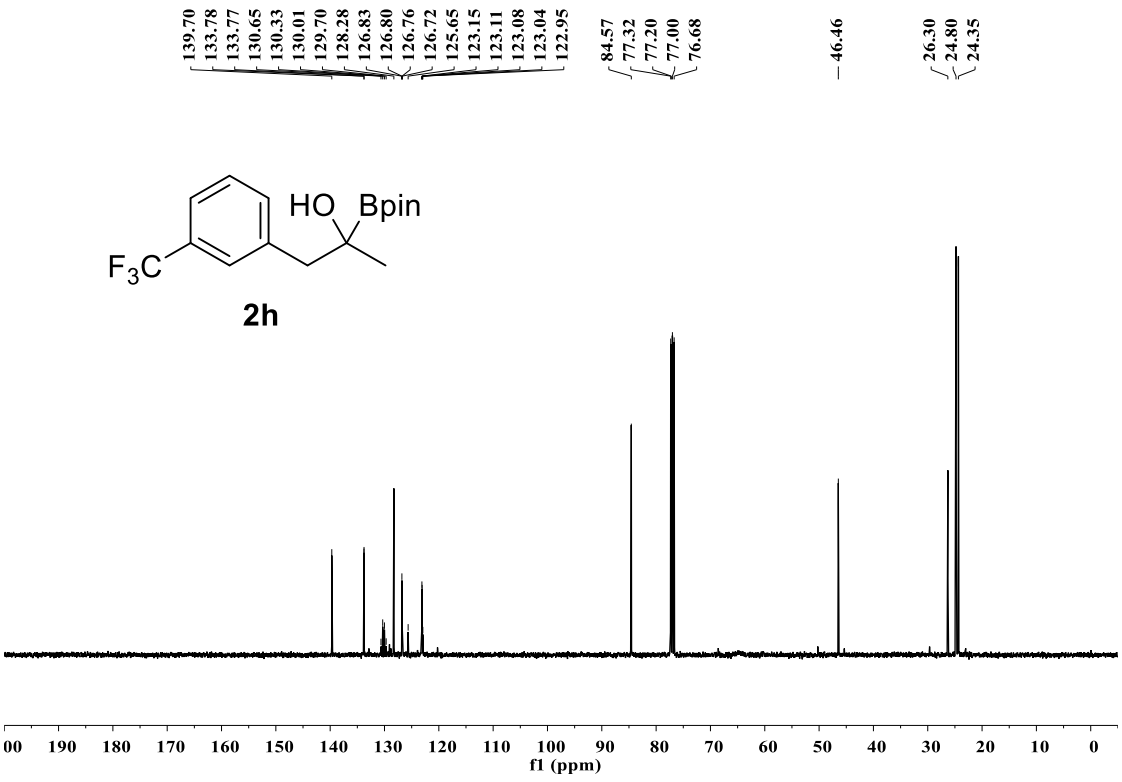
2.01
3.10
1.00
1.04
1.25
3.36
6.29
6.10
f1 (ppm)


139.70
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128.28
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126.80
126.76
126.72
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123.15
123.11
123.08
123.04
122.95
84.57
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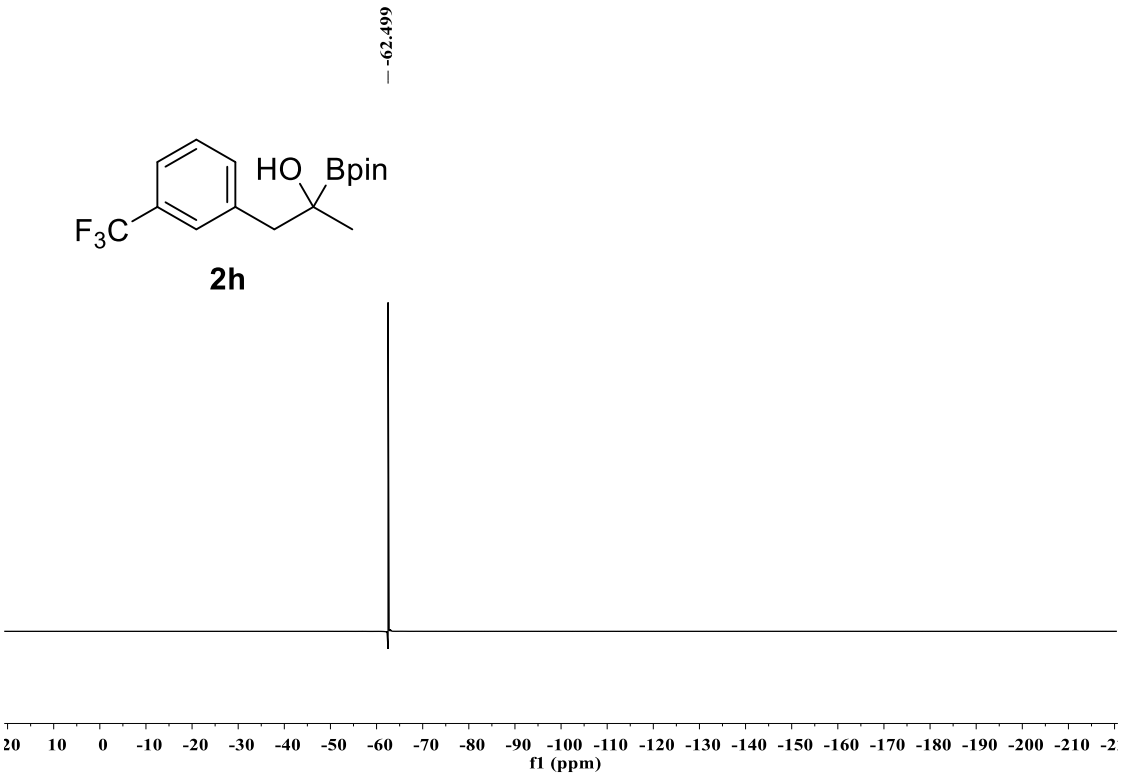
24.35
HO Bpin
F3C
2h
f1 (ppm)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Bpin
F3C
2h
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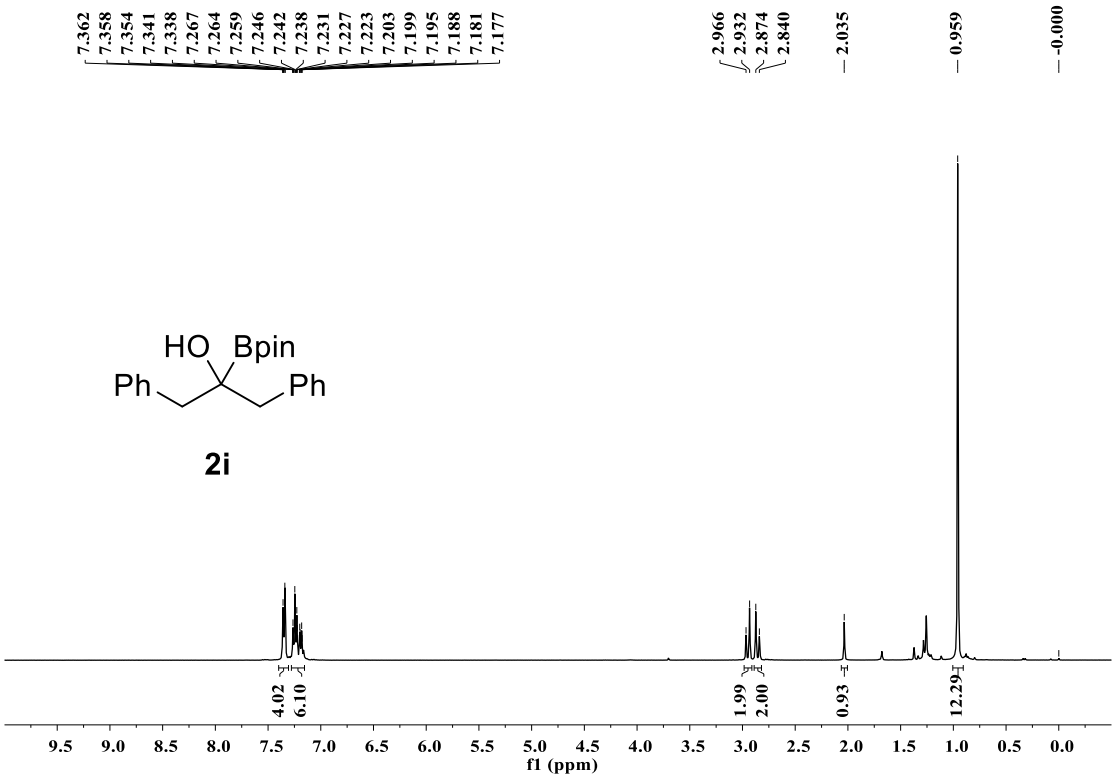
f1 (ppm)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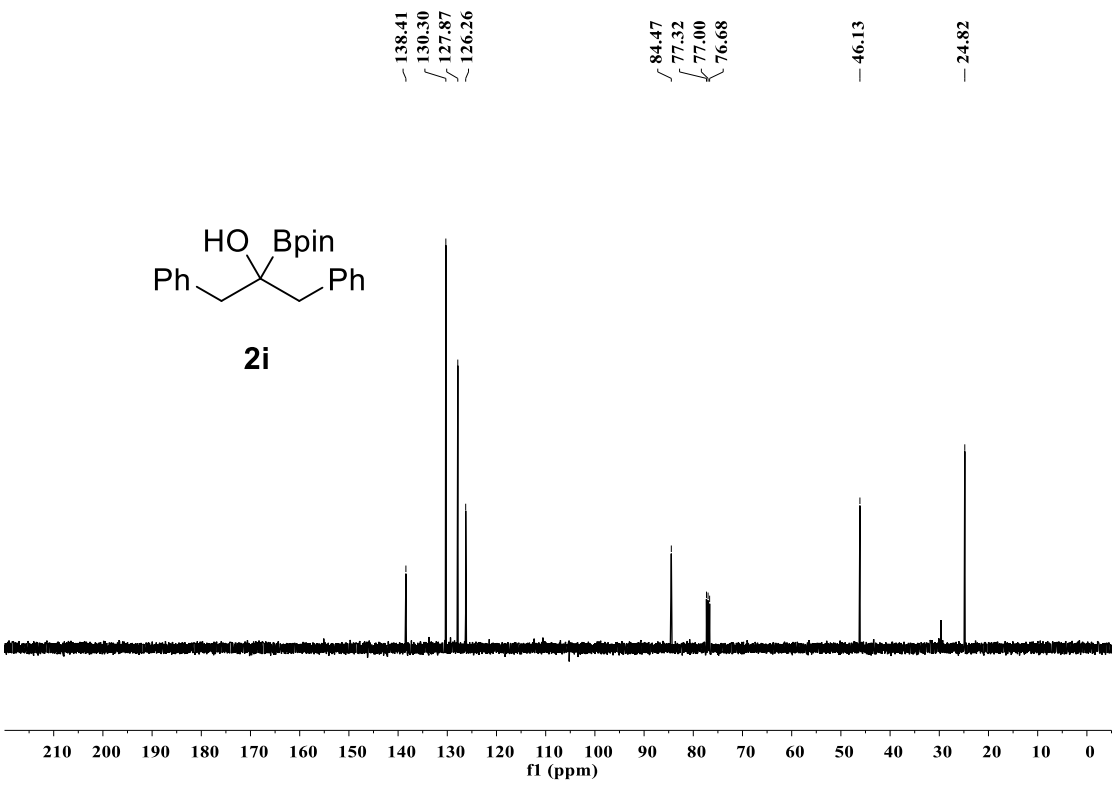
7.246
7.242
7.238
7.231
7.227
7.223
7.203
7.199
7.195
7.188
7.181
7.177
2.966
2.932
2.874
2.840
2.035
0.959
-0.000
HO Bpin
Ph Ph
2i
4.02
6.10
1.99
2.00
0.93
12.29
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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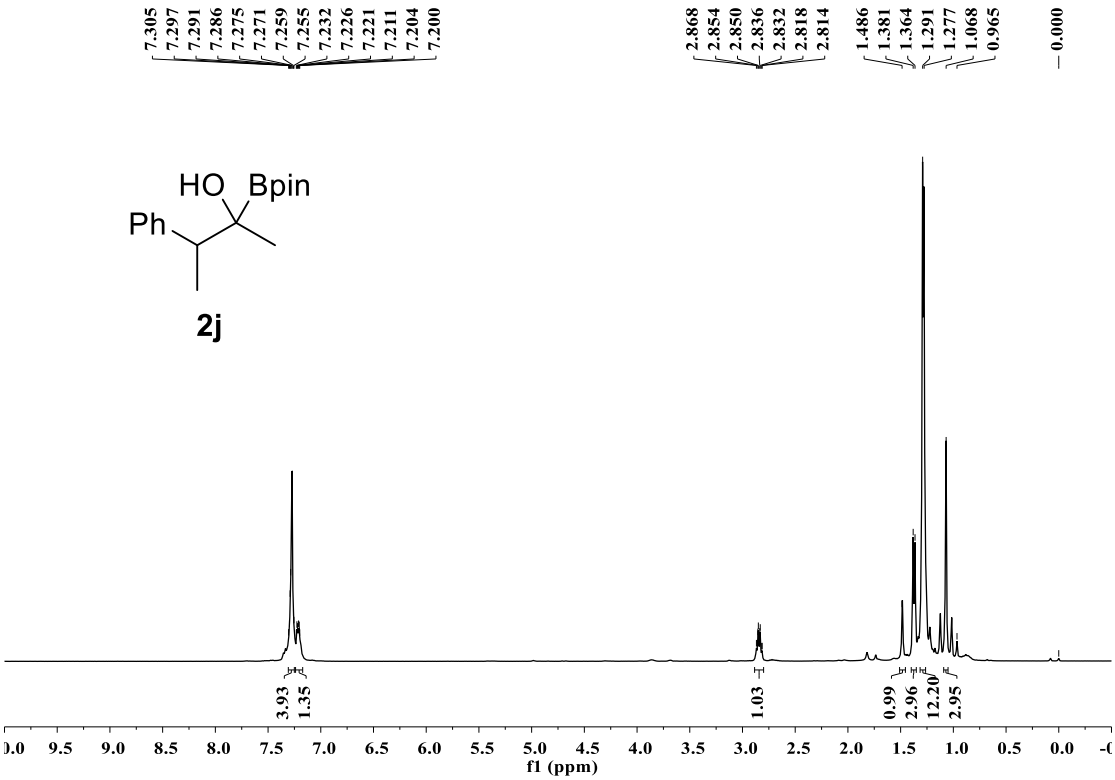
77.32
77.00
76.68
46.13
24.82
HO Bpin
Ph Ph
2i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.226
7.221
7.211
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7.200
2.868
2.854
2.850
2.836
2.832
2.818
2.814
1.486
1.381
1.364
1.291
1.277
1.068
0.965
0.000
HO Bpin
Ph
2j
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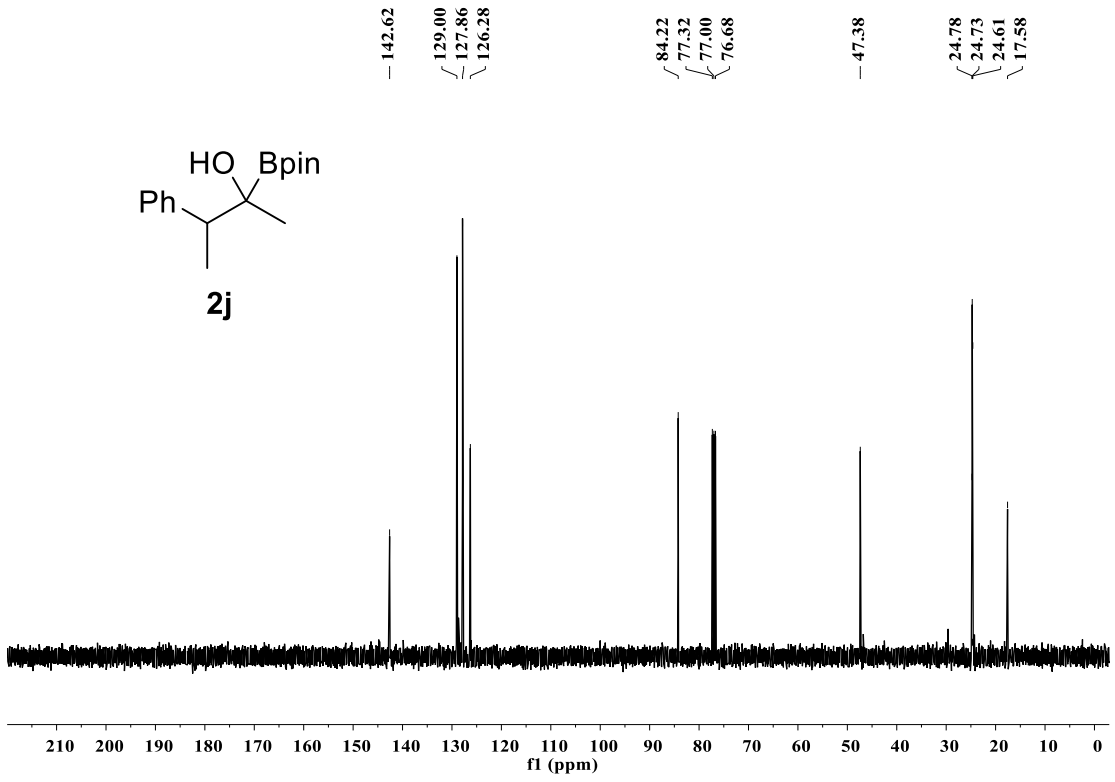
1.35
1.03
0.99
2.96
12.20
2.95
f1 (ppm)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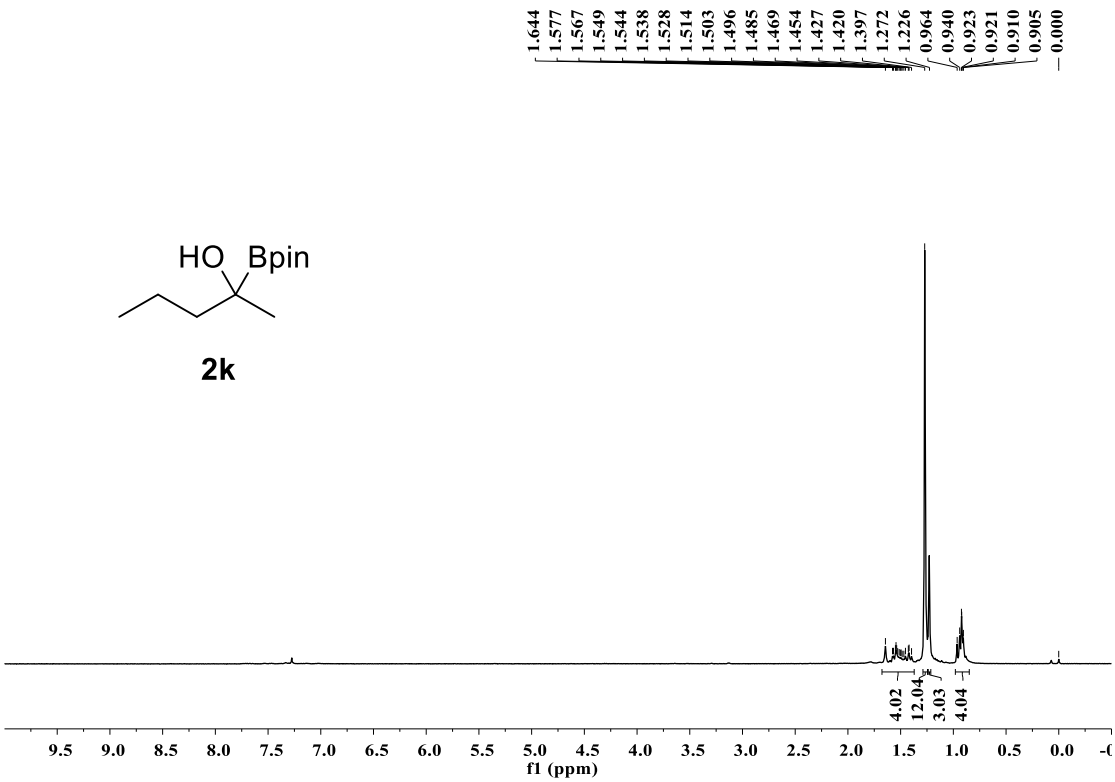
47.38
24.78
24.73
24.61
17.58
HO Bpin
Ph
2j
f1 (ppm)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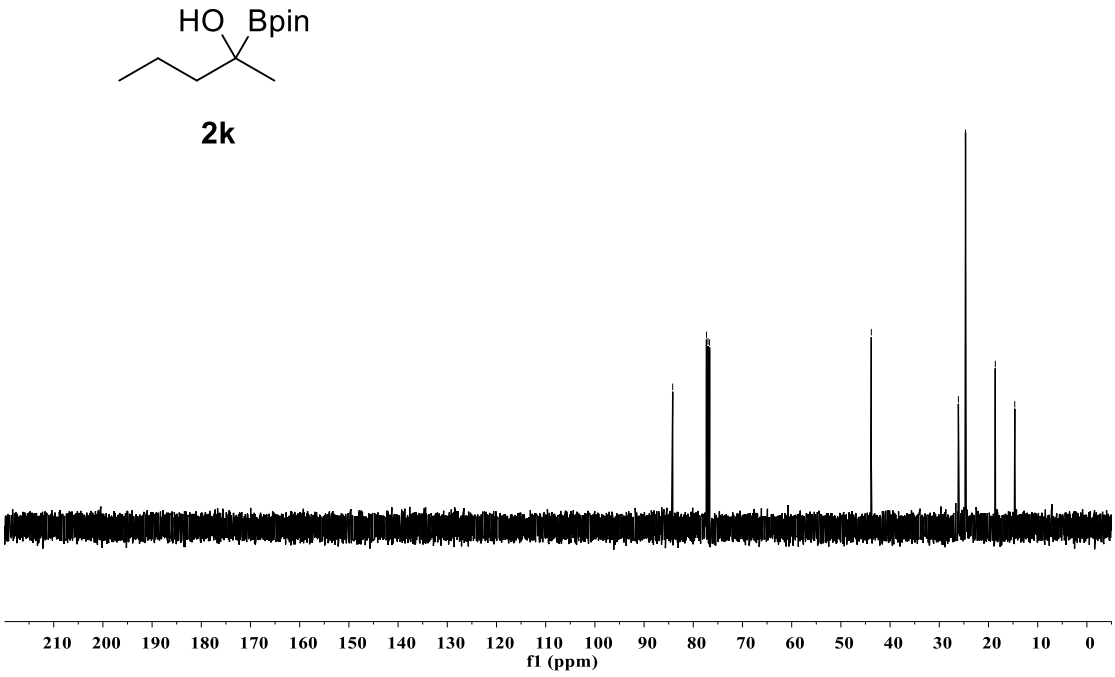
1.567
1.549
1.544
1.538
1.528
1.514
1.503
1.496
1.485
1.469
1.454
1.427
1.420
1.397
1.272
1.226
0.964
0.940
0.923
0.921
0.910
0.905
0.000
HO Bpin
2k
4.02
12.04
3.03
4.04
f1 (ppm)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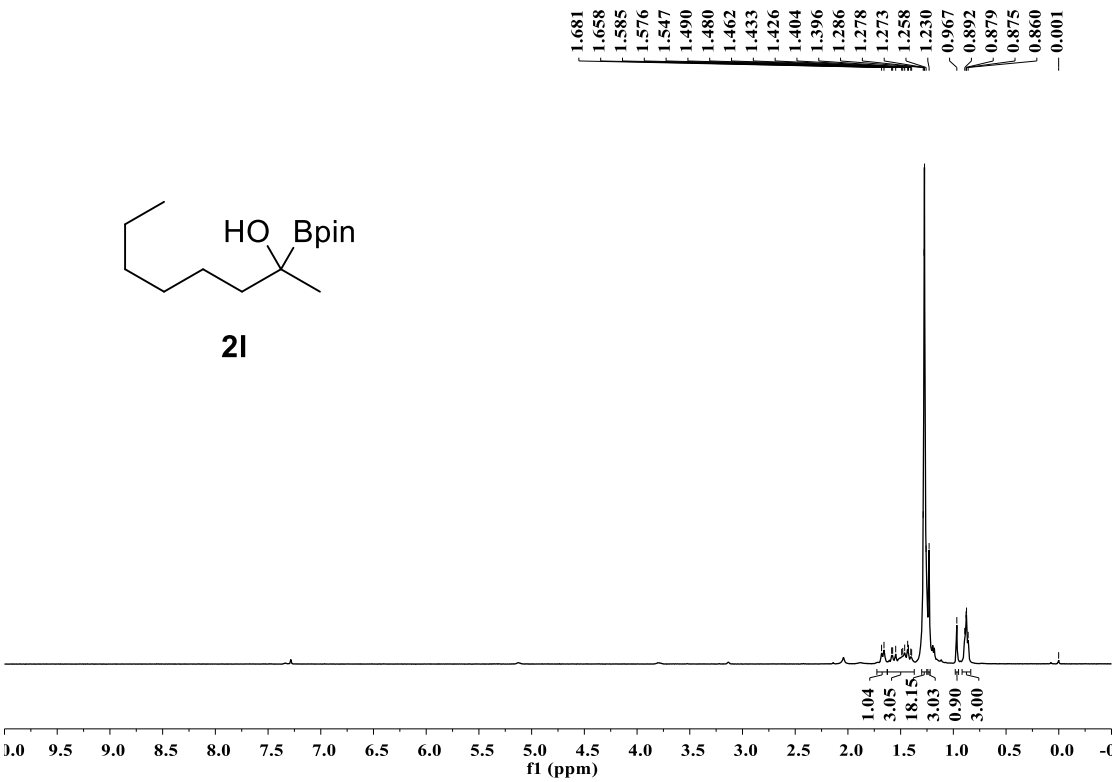
77.00
76.68
43.82
26.12
24.67
18.62
14.66
HO Bpin
2k
f1 (ppm)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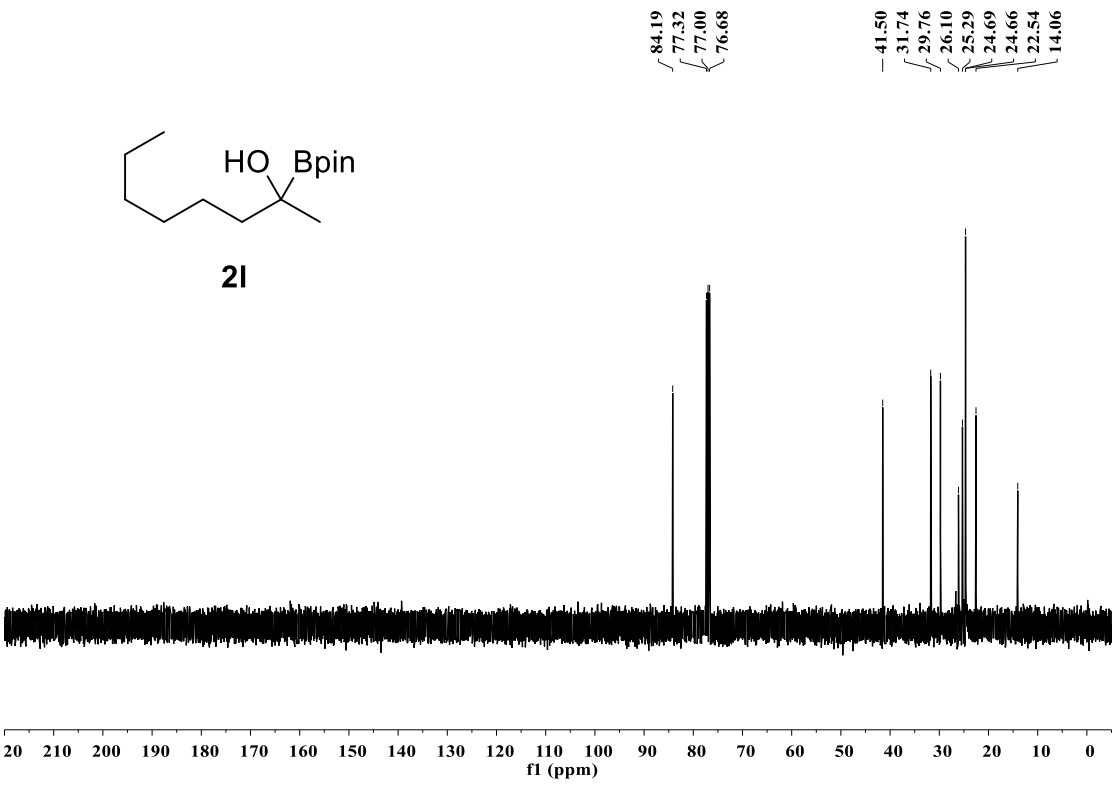
1.585
1.576
1.547
1.490
1.480
1.462
1.433
1.426
1.404
1.396
1.286
1.278
1.273
1.258
1.230
0.967
0.892
0.879
0.875
0.860
0.001
HO Bpin
2l
1.04
3.05
18.15
3.03
0.90
3.00
f1 (ppm)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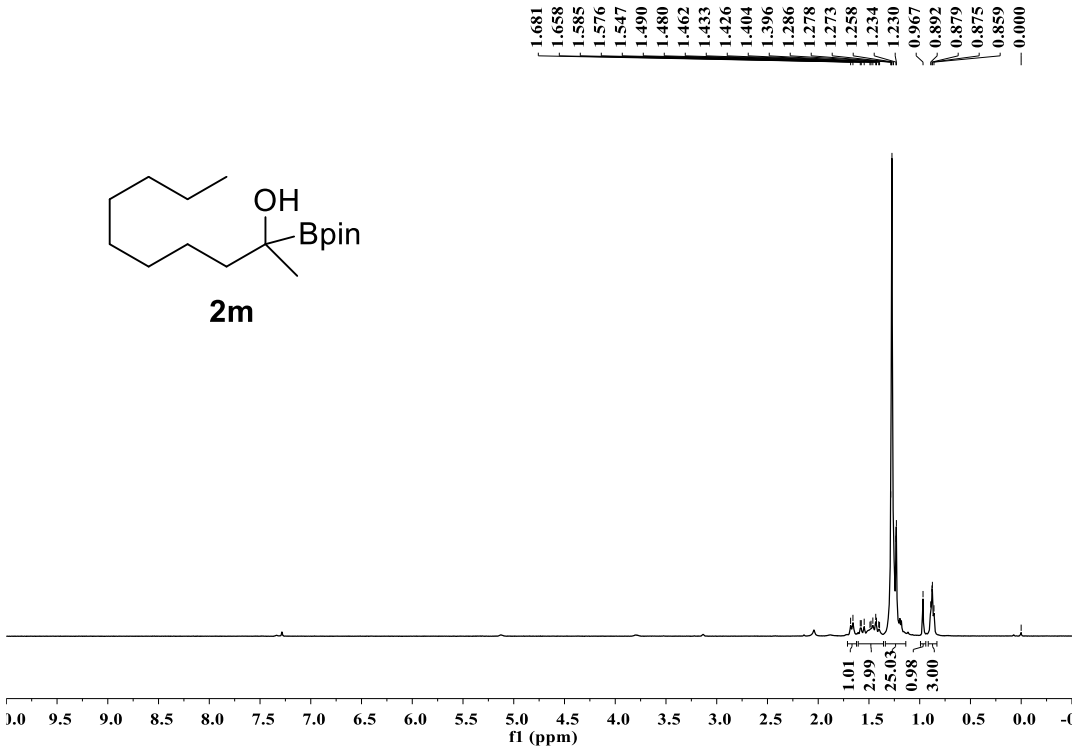
77.32
77.00
76.68
41.50
31.74
29.76
26.10
25.29
24.69
24.66
22.54
14.06
HO Bpin
2l
f1 (ppm)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1.404
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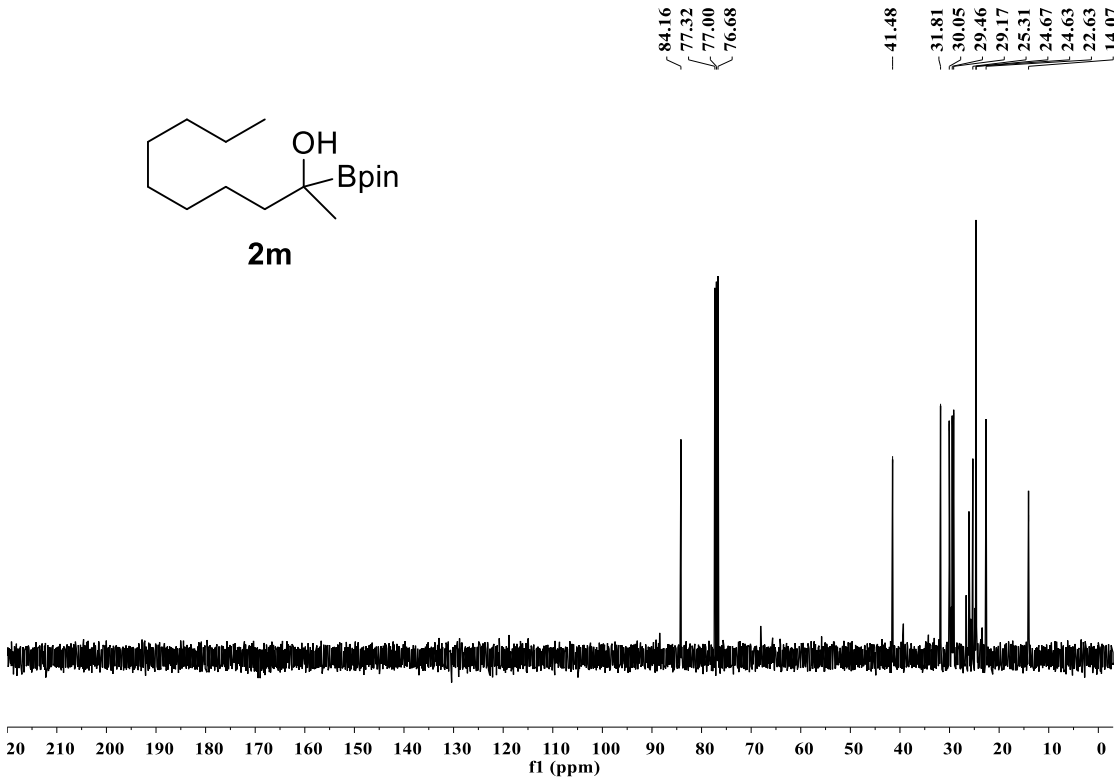
1.286
1.278
1.273
1.258
1.234
1.230
0.967
0.892
0.879
0.875
0.859
0.000
OH
Bpin
2m
1.01
2.99
25.03
0.98
3.00
f1 (ppm)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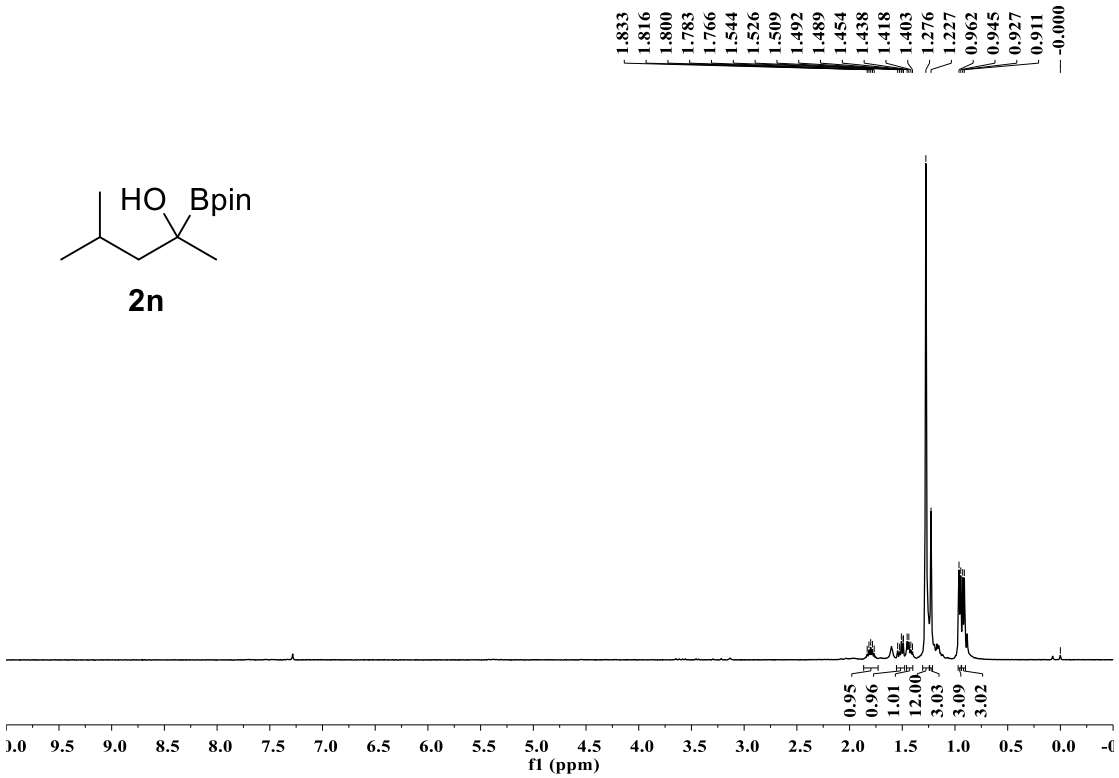
77.32
77.00
76.68
41.48
31.81
30.05
29.46
29.17
25.31
24.67
24.63
22.63
OH
Bpin
2m
f1 (ppm)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1.800
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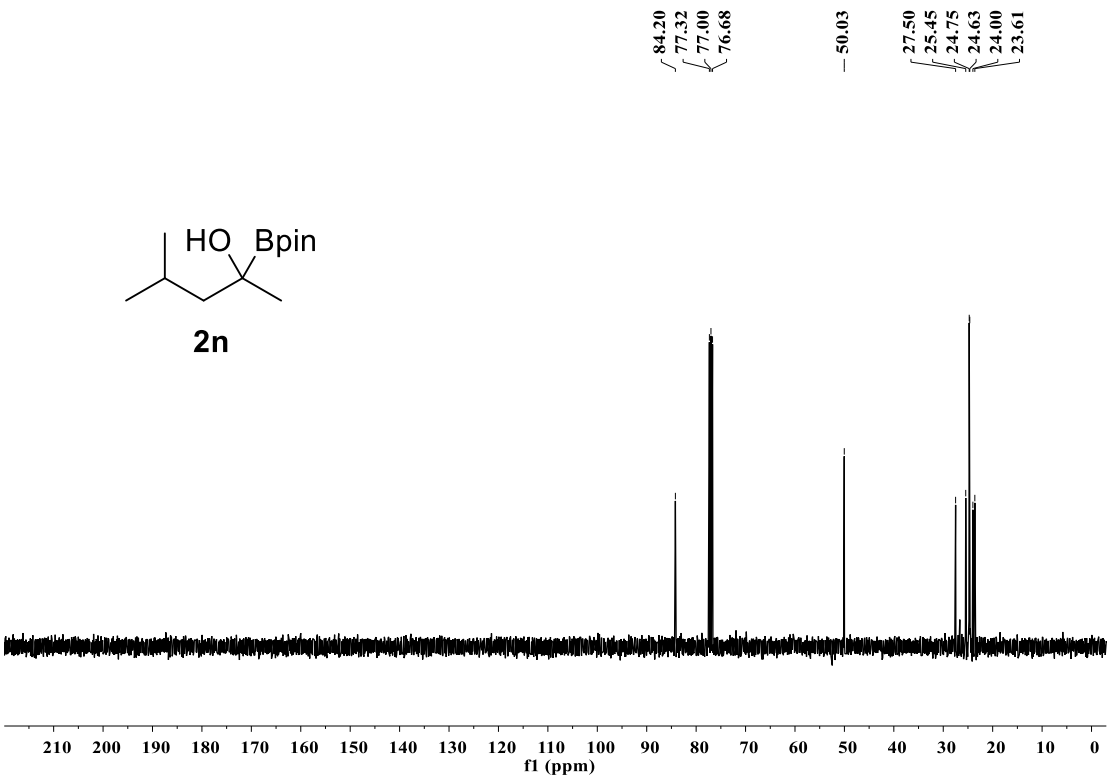
1.766
1.544
1.526
1.509
1.492
1.489
1.454
1.438
1.418
1.403
1.276
1.227
0.962
0.945
0.927
0.911
-0.000
HO Bpin
2n
0.95
0.96
1.01
12.00
3.03
3.09
3.02
f1 (ppm)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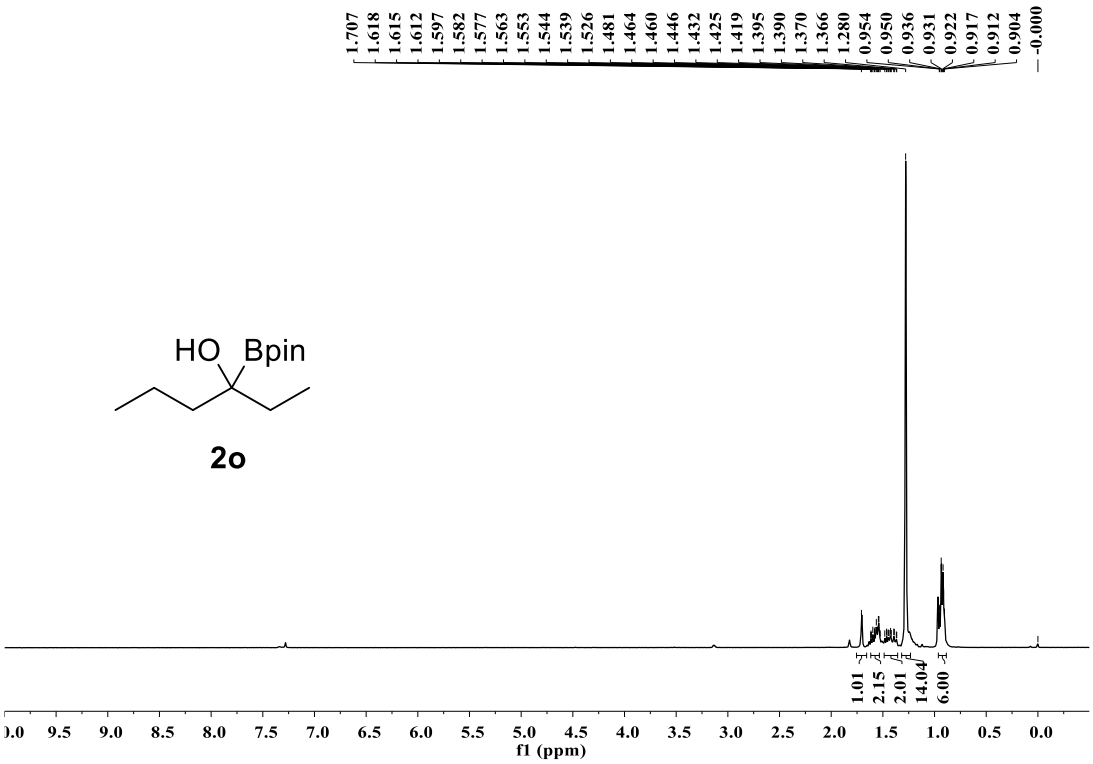
77.32
77.00
76.68
50.03
27.50
25.45
24.75
24.63
24.00
23.61
HO Bpin
2n
f1 (ppm)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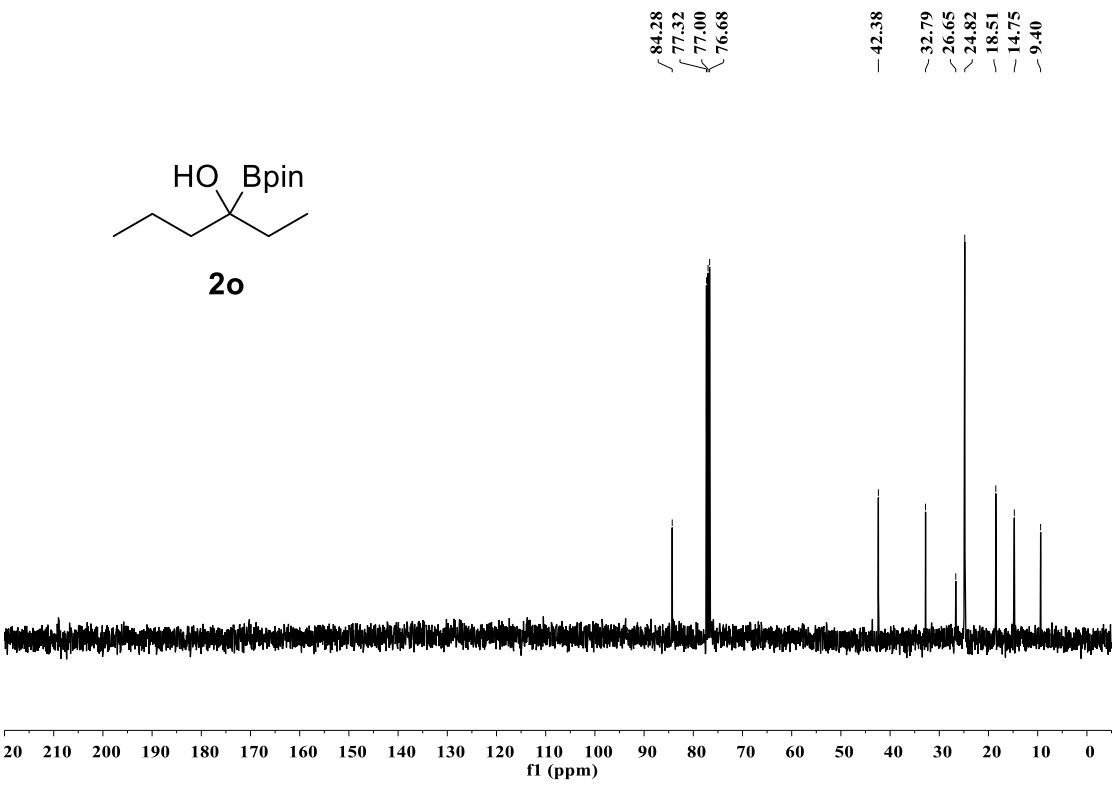
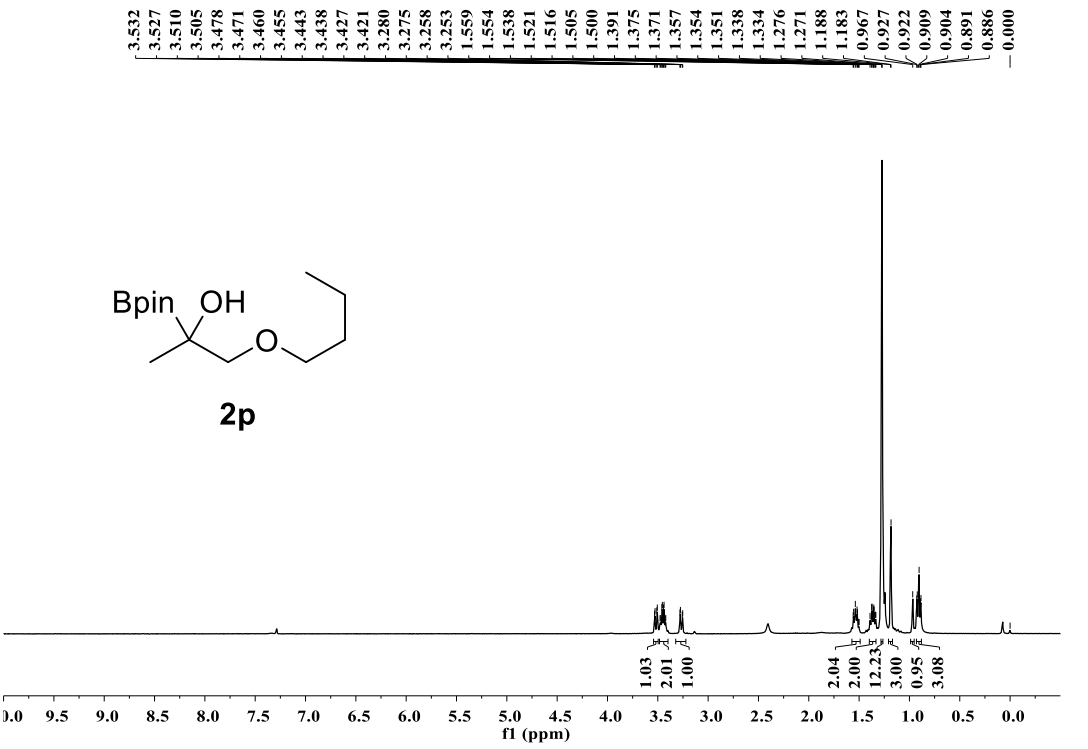
1.618
1.615
1.612
1.597
1.582
1.577
1.563
1.553
1.544
1.539
1.526
1.481
1.464
1.460
1.446
1.432
1.425
1.419
1.395
1.390
1.370
1.366
1.280
0.954
0.950
0.936
0.931
0.922
0.917
0.912
0.904
-0.000
HO Bpin
2o
1.01
2.15
2.01
14.04
6.00
f1 (ppm)


84.28
77.32
77.00
76.68
42.38
32.79
26.65
24.82
18.51
14.75
9.40
HO Bpin
2o
f1 (ppm)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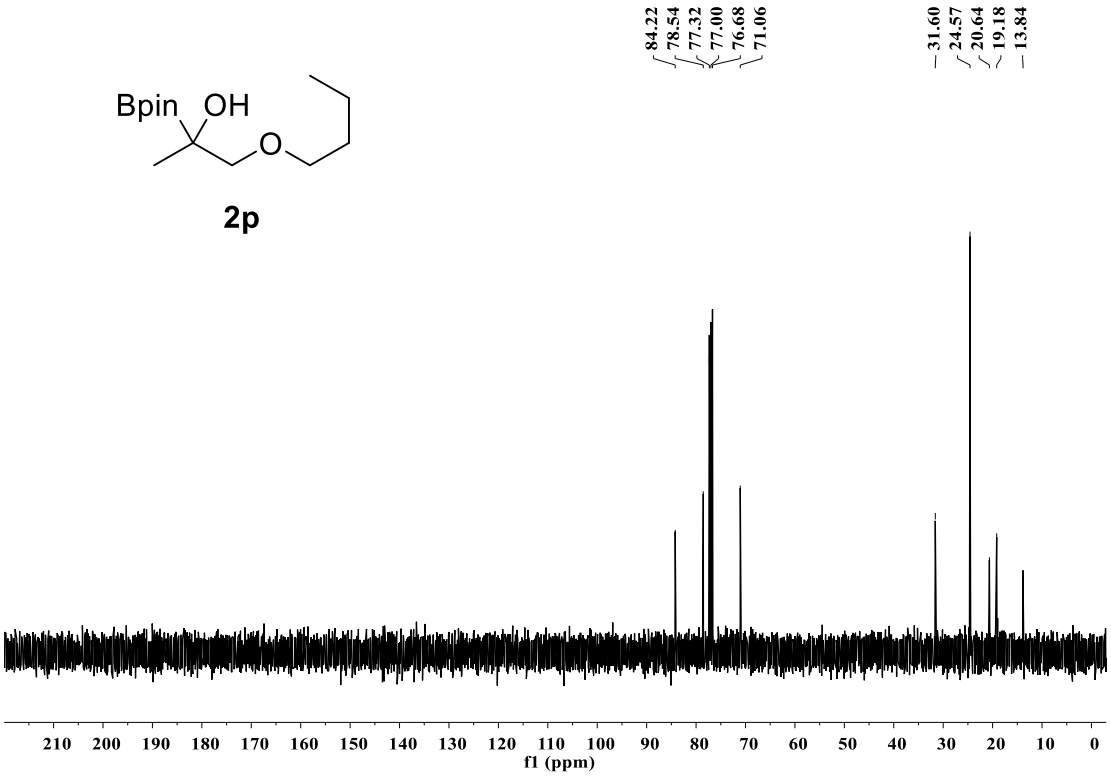
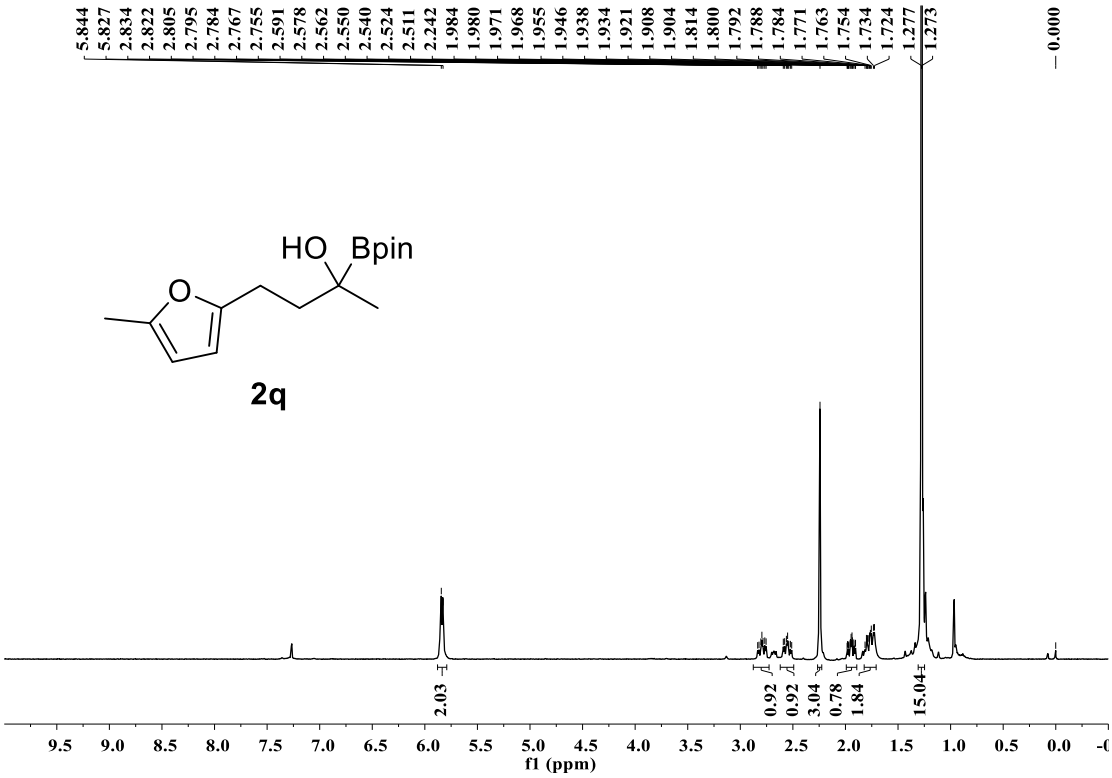
3.527
3.510
3.505
3.478
3.471
3.460
3.455
3.443
3.438
3.427
3.421
3.280
3.275
3.258
3.253
1.559
1.554
1.538
1.521
1.516
1.505
1.500
1.391
1.375
1.371
1.357
1.354
1.351
1.338
1.334
1.276
1.271
1.188
1.183
0.967
0.927
0.922
0.909
0.904
0.891
0.886
0.000
Bpin OH
O
2p
1.03
2.01
1.00
2.04
2.00
12.23
3.00
0.95
3.08
f1 (ppm)


84.22
78.54
77.32
77.00
76.68
71.06
31.60
24.57
20.64
19.18
13.84
Bpin OH
O
2p
f1 (ppm)


5.844
5.827
2.834
2.822
2.805
2.795
2.784
2.767
2.755
2.591
2.578
2.562
2.550
2.540
2.524
2.511
2.242
1.984
1.980
1.971
1.968
1.955
1.946
1.938
1.934
1.921
1.908
1.904
1.814
1.800
1.792
1.788
1.784
1.771
1.763
1.754
1.734
1.724
1.277
1.273
0.000
HO Bpin
O
2q
2.03
0.92
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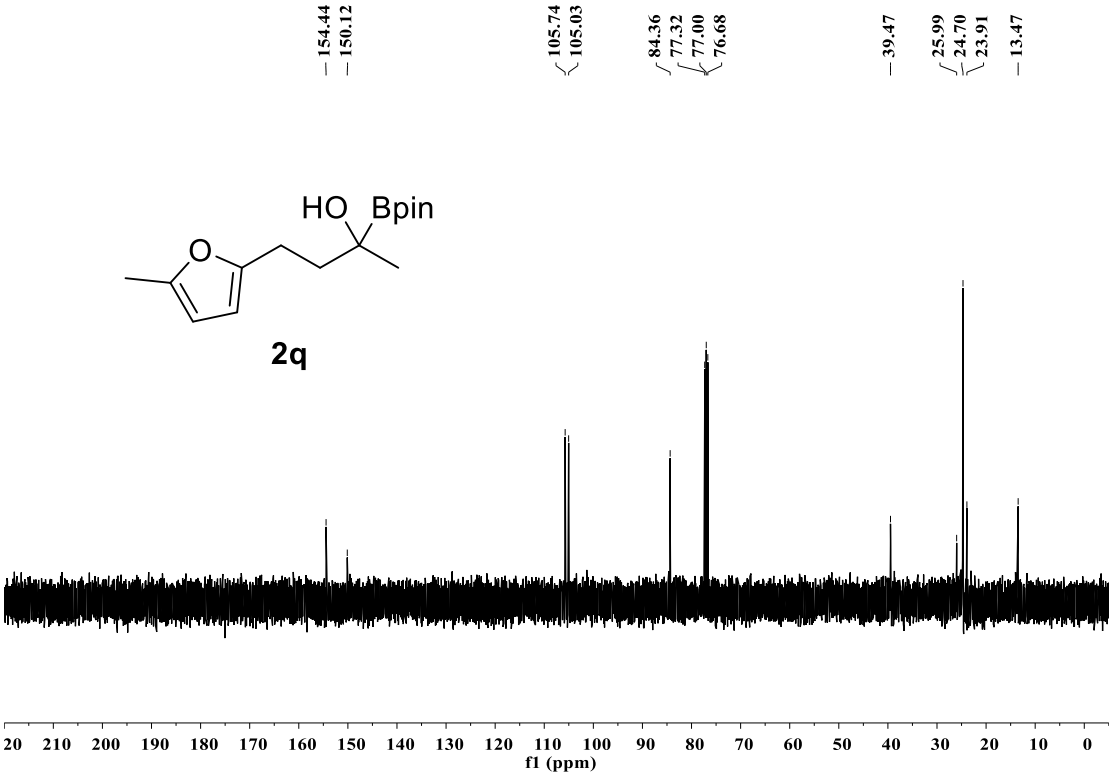
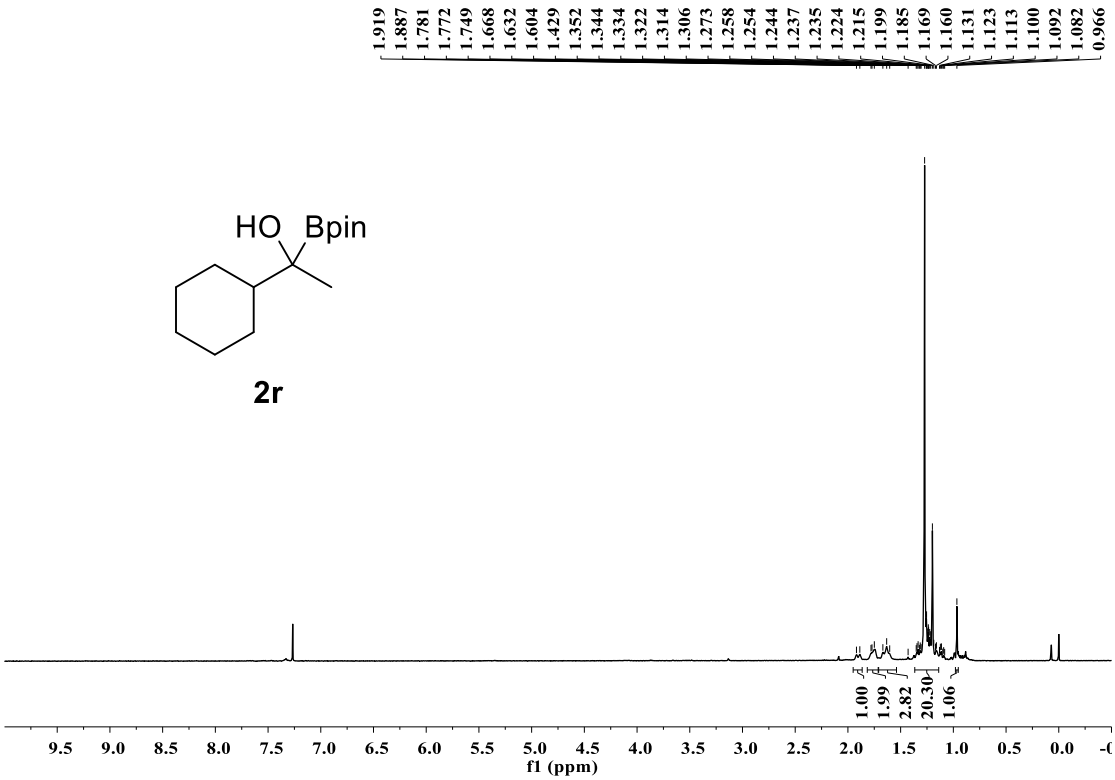
3.04
0.78
1.84
15.04
f1 (ppm)


154.44
150.12
105.74
105.03
84.36
77.32
77.00
76.68
39.47
25.99
24.70
23.91
13.47
HO Bpin
O
2q
f1 (ppm)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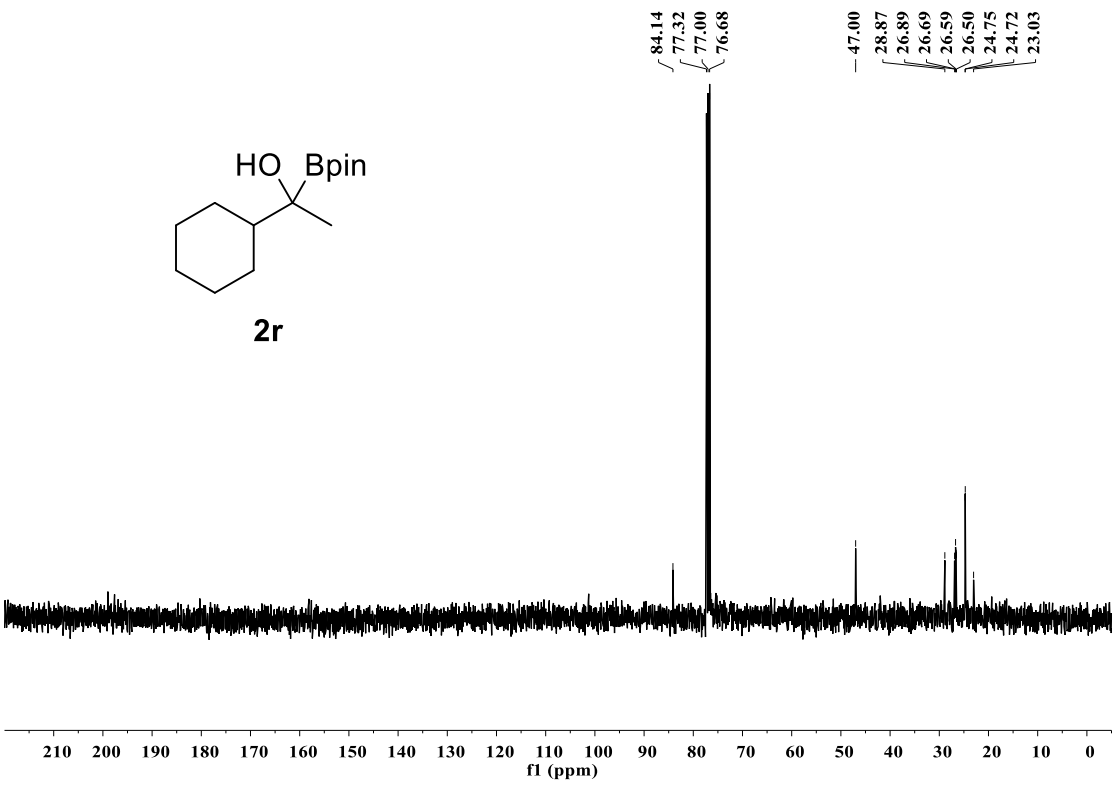
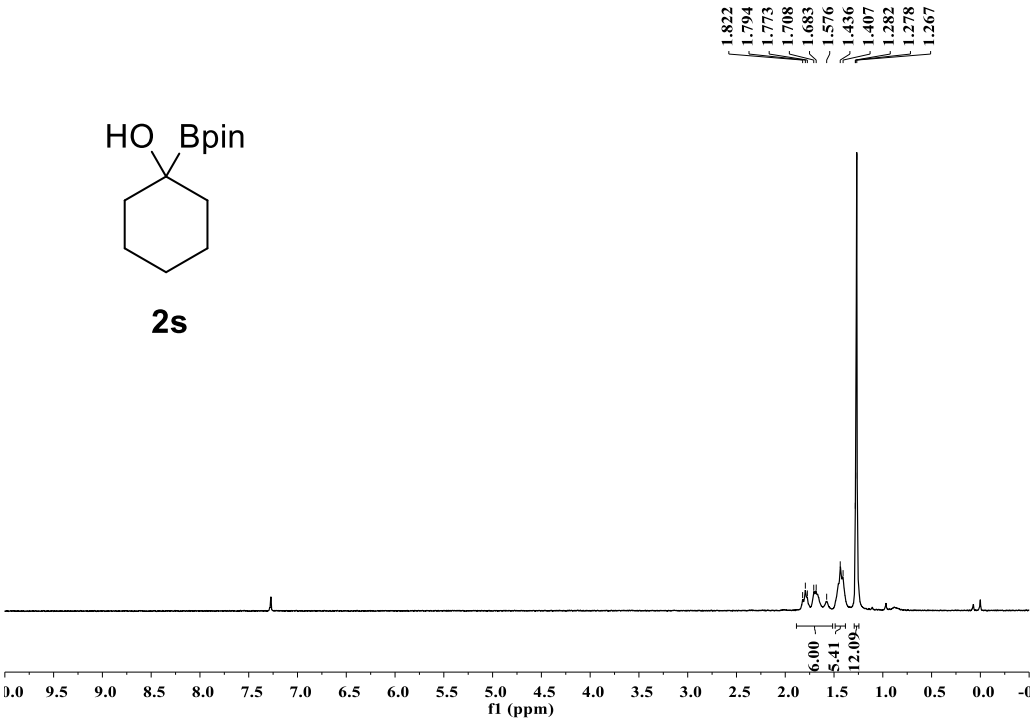
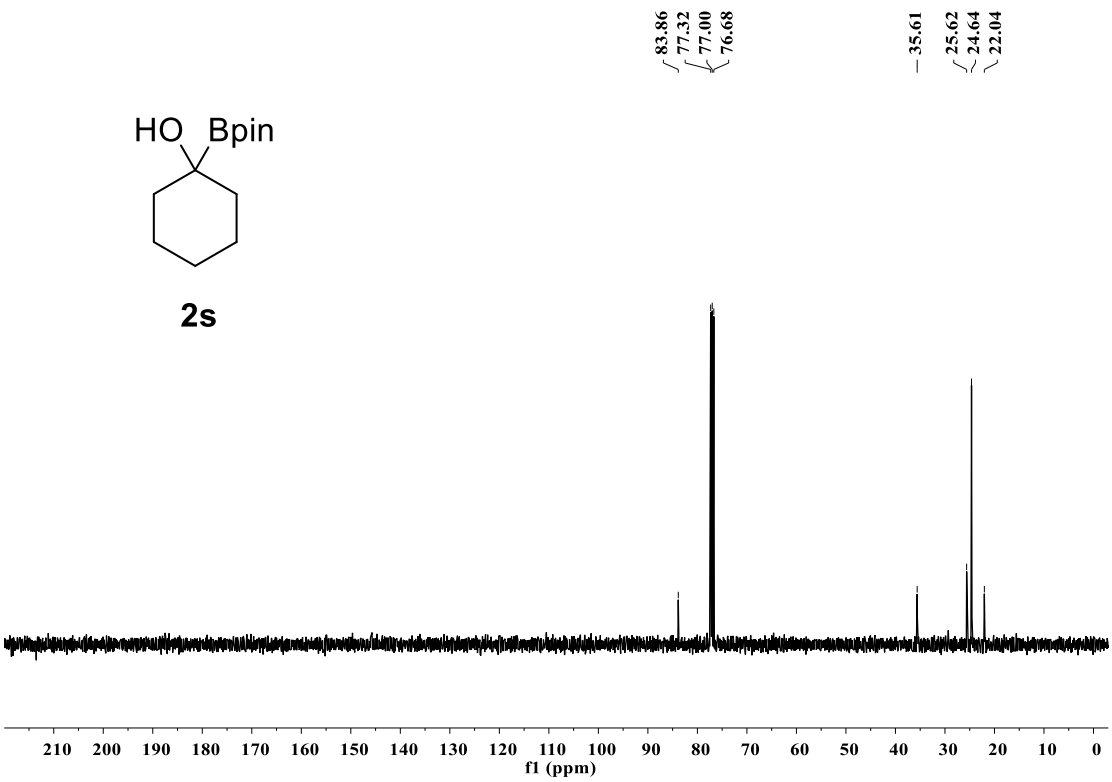
1.781
1.772
1.749
1.668
1.632
1.604
1.429
1.352
1.344
1.334
1.322
1.314
1.306
1.273
1.258
1.254
1.244
1.237
1.235
1.224
1.215
1.199
1.185
1.169
1.160
1.131
1.123
1.113
1.100
1.092
1.082
0.966
HO Bpin
2r
1.00
1.99
2.82
20.30
1.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


84.14
77.32
77.00
76.68
47.00
28.87
26.89
26.69
26.59
26.50
24.75
24.72
23.03
HO Bpin
2r
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


1.822
1.794
1.773
1.708
1.683
1.576
1.436
1.407
1.282
1.278
1.267
HO Bpin
2s
6.00
5.41
12.09
f1 (ppm)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77.00
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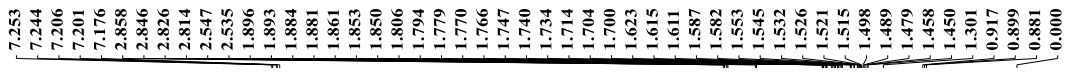
35.61
25.62
24.64
22.04
HO Bpin
2s
f1 (ppm)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7.206
7.201
7.176
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2.846
2.826
2.814
2.547
2.535
1.896
1.893
1.884
1.881
1.861
1.853
1.850
1.806
1.794
1.779
1.770
1.766
1.747
1.740
1.734
1.714
1.704
1.700
1.623
1.615
1.611
1.587
1.582
1.553
1.545
1.532
1.526
1.521
1.515
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1.489
1.479
1.458
1.450
1.301
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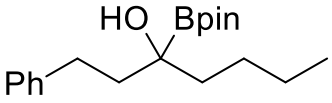
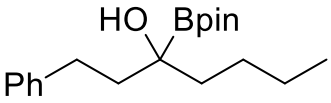
0.899
0.881
0.000


HO
Bpin
Ph

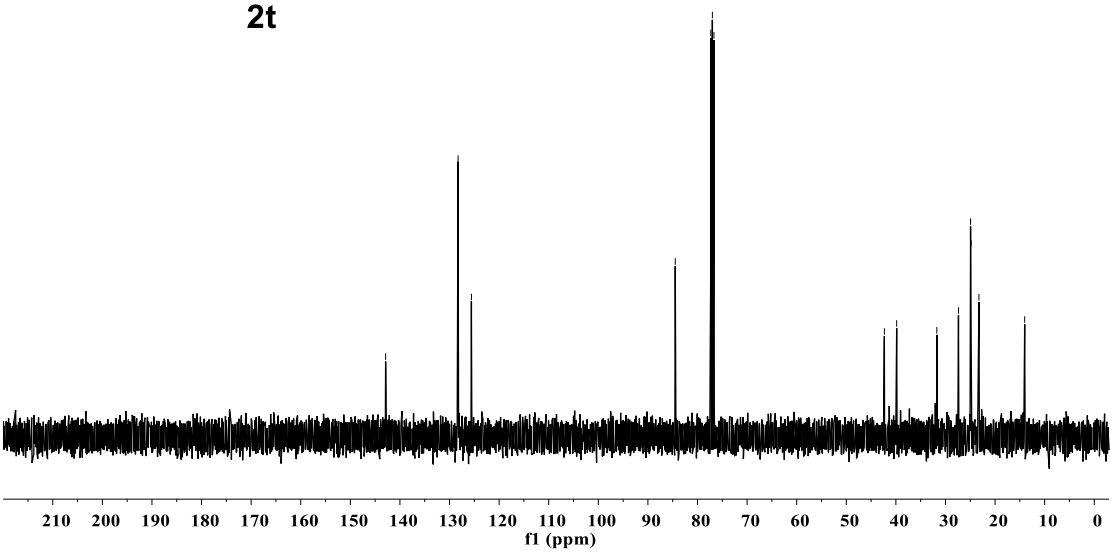
2t

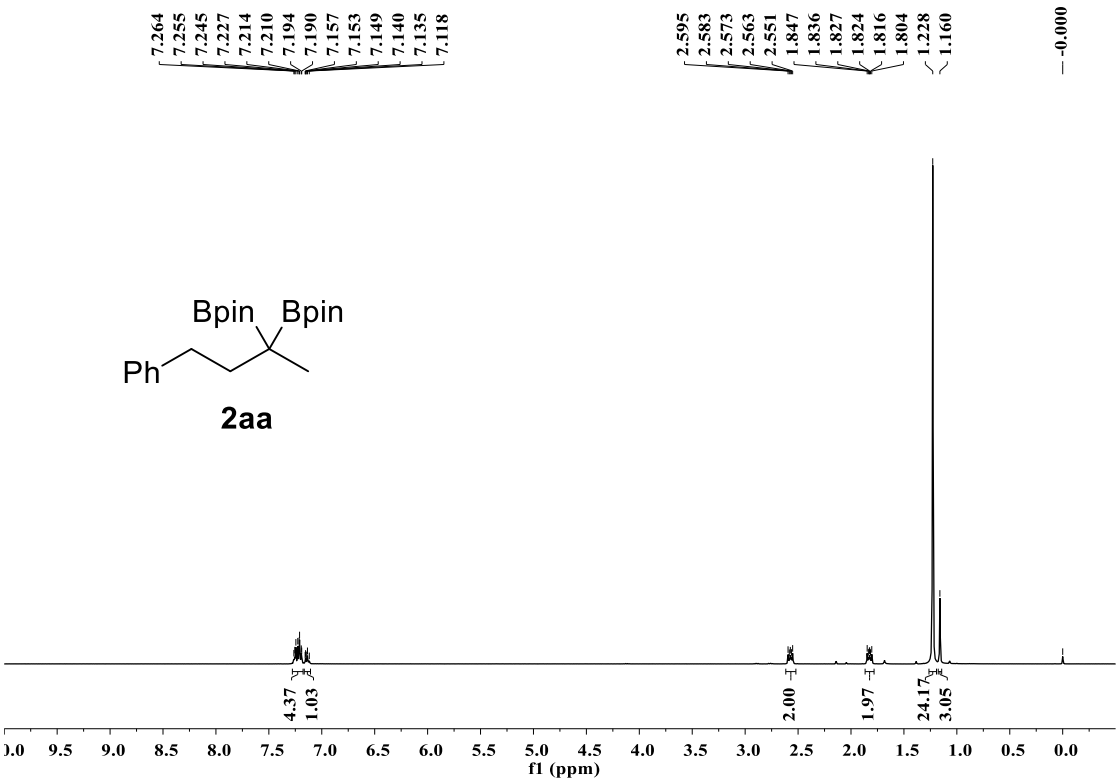
2.27
3.38
1.12
1.00
8.95
12.46
3.31
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


142.89
128.33
128.28
125.59
84.48
77.32
77.00
76.68
42.32
39.84
31.74
27.38
24.94
24.83
23.25
14.03


HO
Bpin
Ph

2t


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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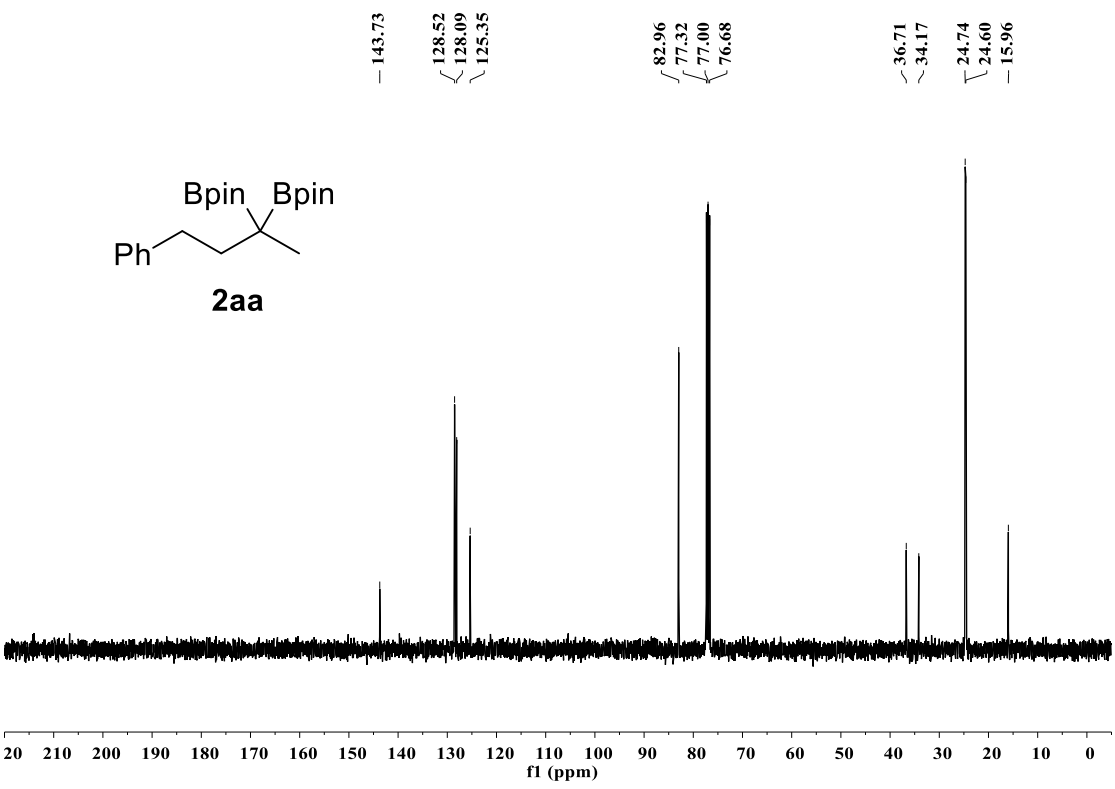
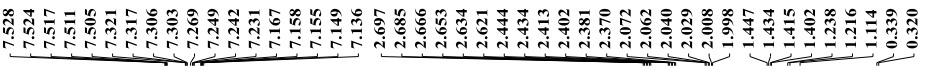
7.245
7.227
7.214
7.210
7.194
7.190
7.157
7.153
7.149
7.140
7.135
7.118
2.595
2.583
2.573
2.563
2.551
1.847
1.836
1.827
1.824
1.816
1.804
1.228
1.160
-0.000
Bpin
Bpin
Ph
2aa
4.37
1.03
2.00
1.97
24.17
3.05
f1 (ppm)


143.73
128.52
128.09
125.35
82.96
77.32
77.00
76.68
36.71
34.17
24.74
24.60
15.96
Bpin
Bpin
Ph
2aa
f1 (ppm)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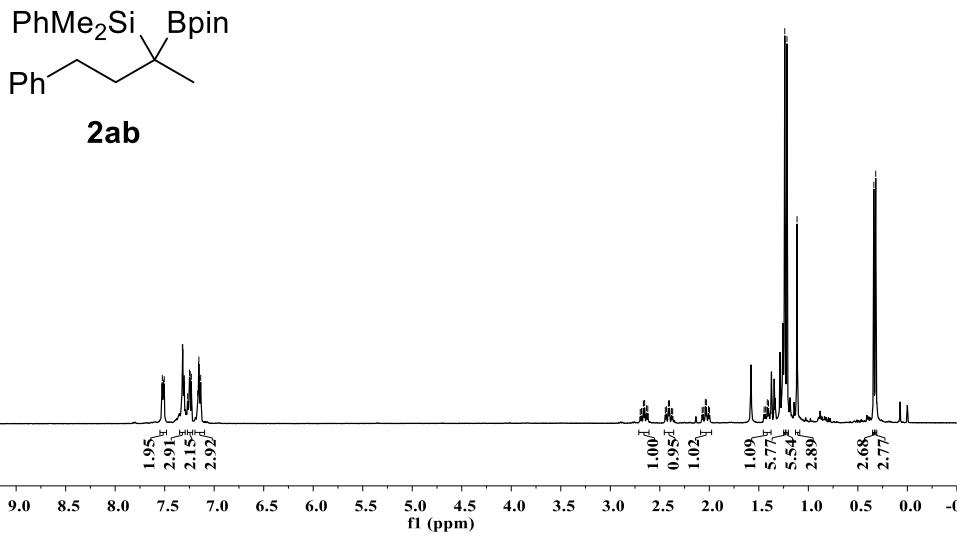
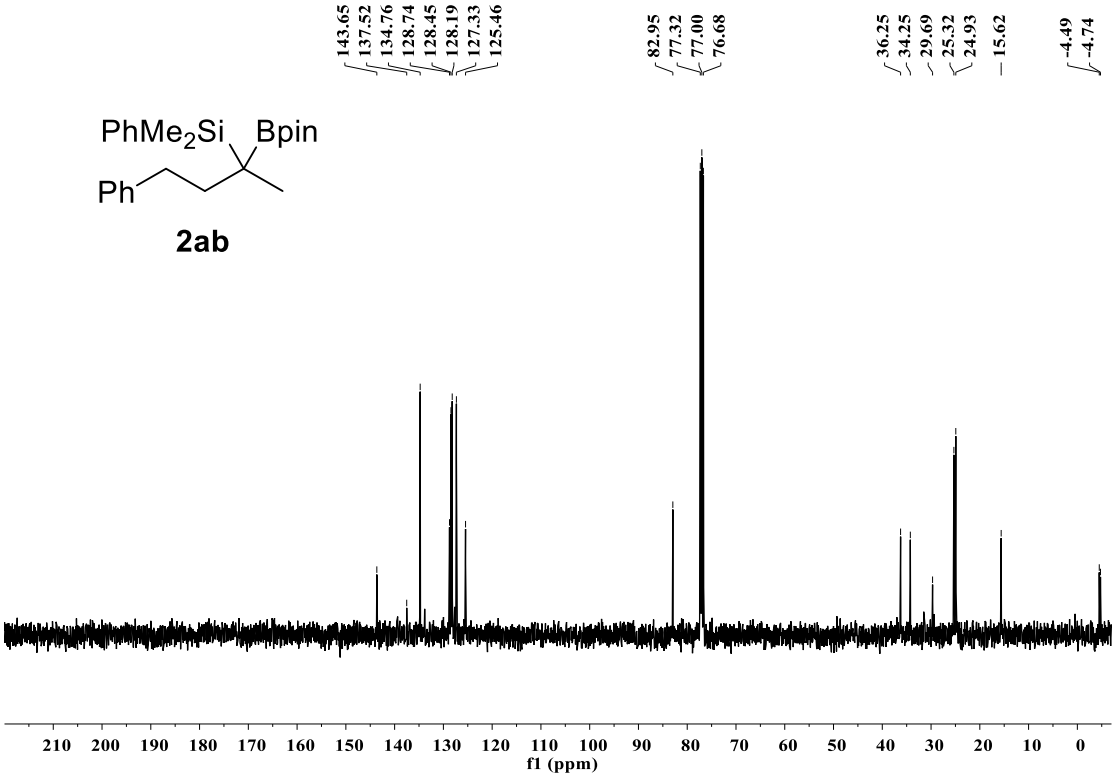
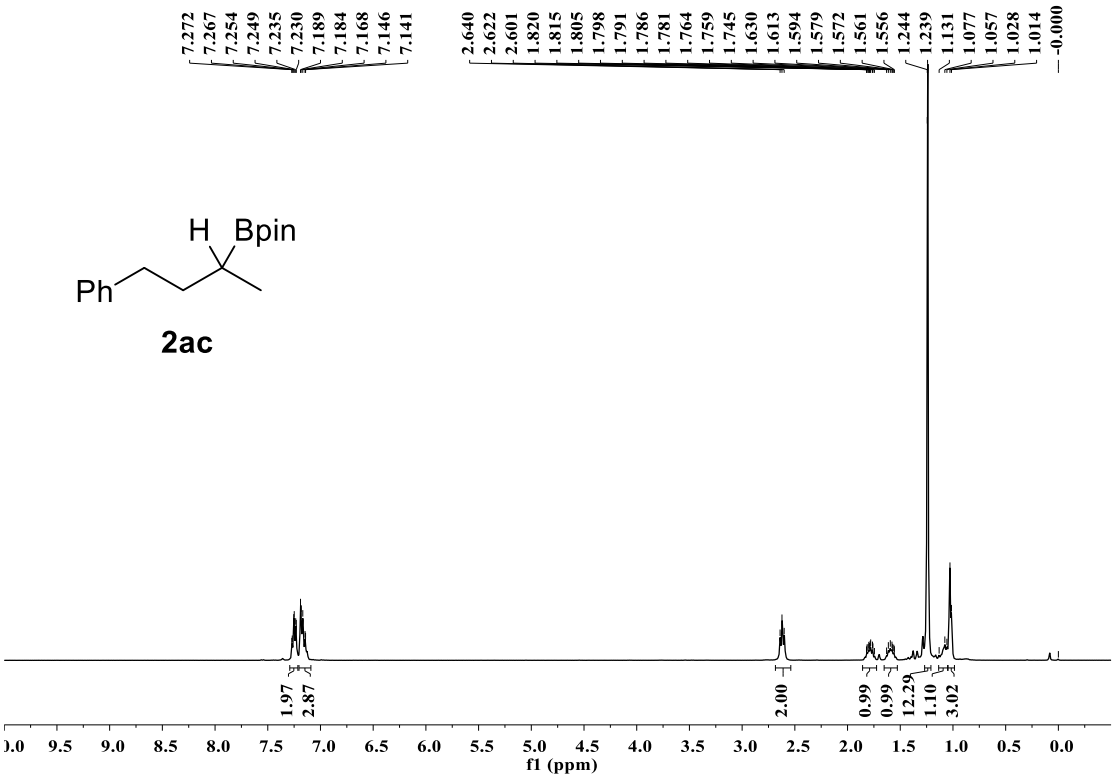
7.524
7.517
7.511
7.505
7.321
7.317
7.306
7.303
7.269
7.249
7.242
7.231
7.167
7.158
7.155
7.149
7.136
2.697
2.685
2.666
2.653
2.634
2.621
2.444
2.434
2.413
2.402
2.381
2.370
2.072
2.062
2.040
2.029
2.008
1.998
1.447
1.434
1.415
1.402
1.238
1.216
1.114
0.339
0.320


PhMe2Si
Bpin
Ph
2ab
1.95
2.91
2.15
2.92
1.00
0.95
1.02
1.09
5.77
5.54
2.89
2.68
2.77
f1 (ppm)


143.65
137.52
134.76
128.74
128.45
128.19
127.33
125.46
82.95
77.32
77.00
76.68
36.25
34.25
29.69
25.32
24.93
15.62
-4.49
-4.74
PhMe2Si
Bpin
Ph
2ab
f1 (ppm)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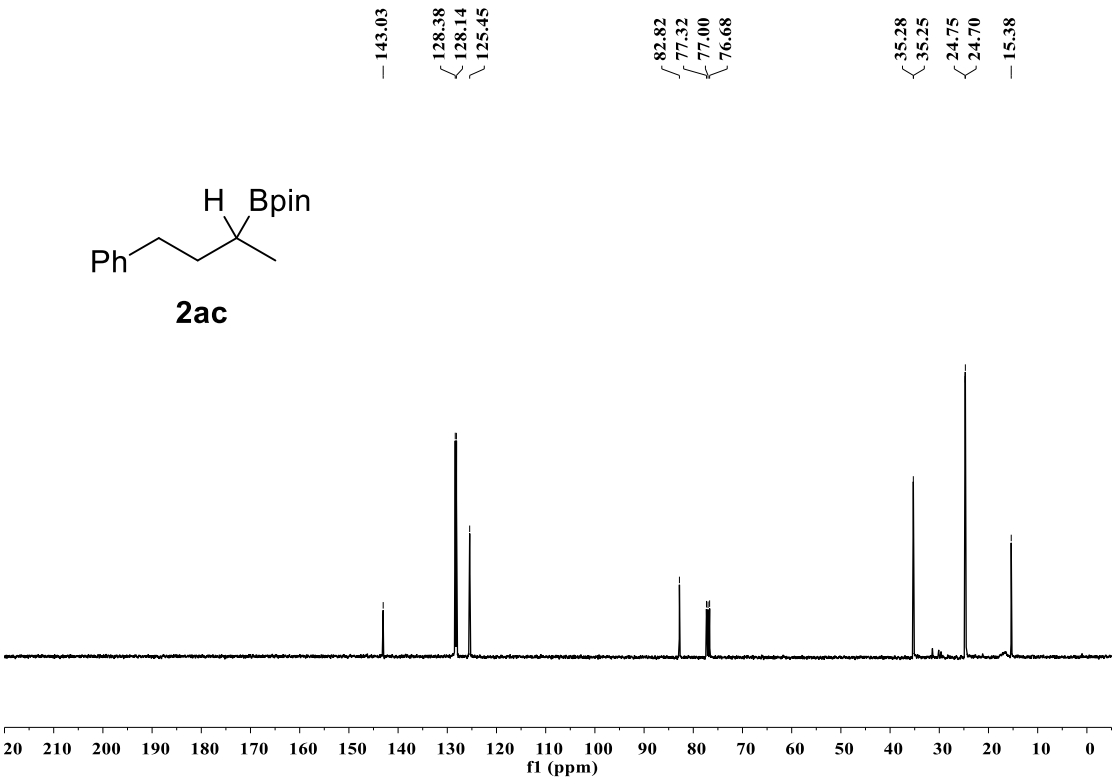
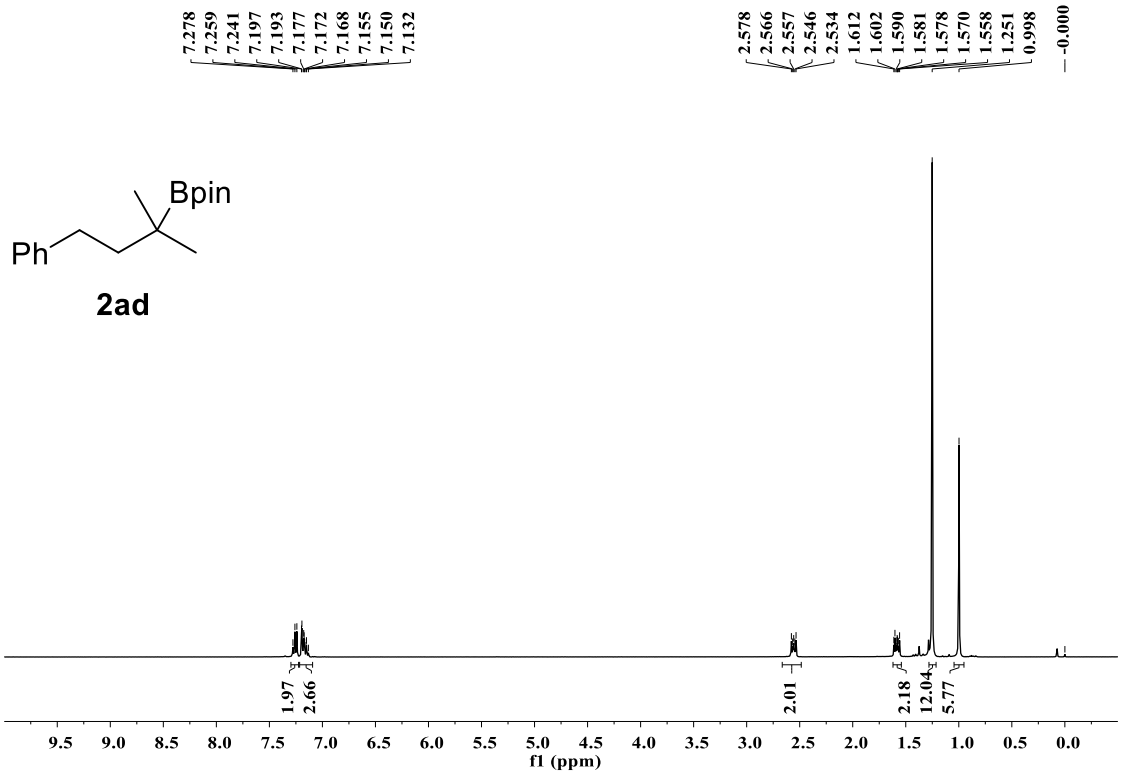
7.254
7.249
7.235
7.230
7.189
7.184
7.168
7.146
7.141
2.640
2.622
2.601
1.820
1.815
1.805
1.798
1.791
1.786
1.781
1.764
1.759
1.745
1.630
1.613
1.594
1.579
1.572
1.561
1.556
1.244
1.239
1.131
1.077
1.057
1.028
1.014
-0.000
H Bpin
Ph
2ac
1.97
2.87
2.00
0.99
0.99
12.29
1.10
3.02
f1 (ppm)


143.03
128.38
128.14
125.45
82.82
77.32
77.00
76.68
35.28
35.25
24.75
24.70
15.38
H Bpin
Ph
2ac
f1 (ppm)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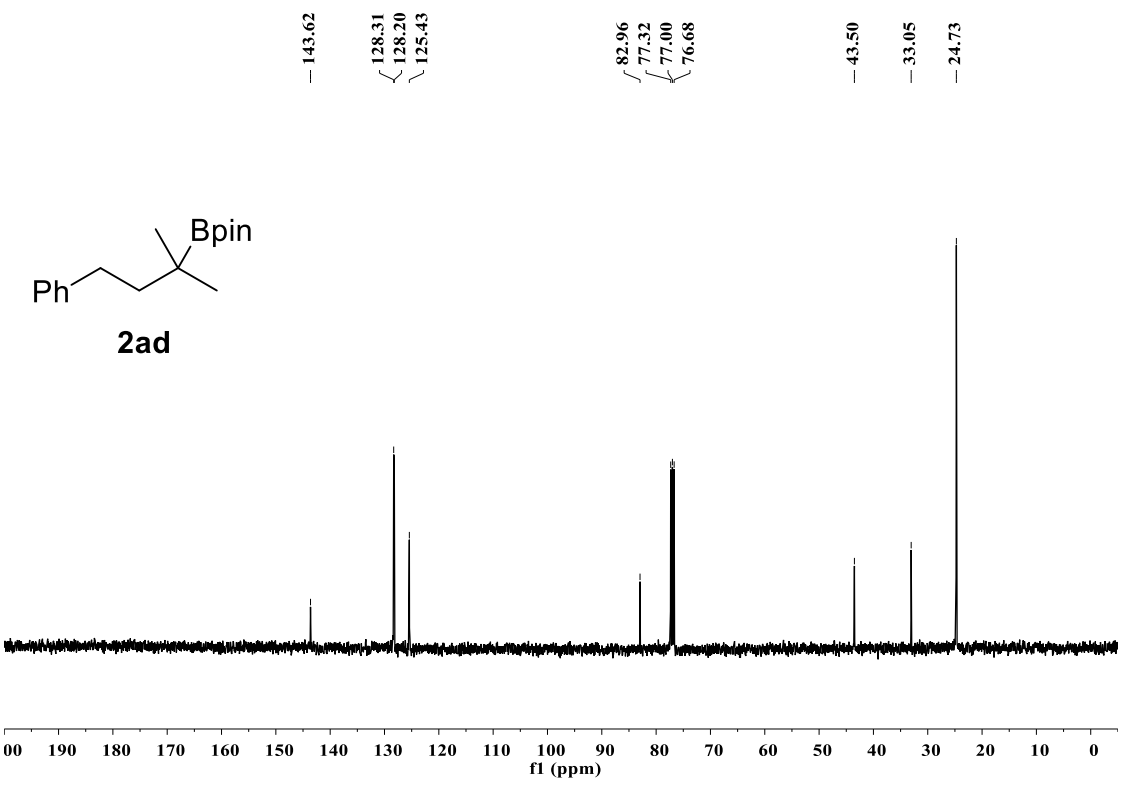
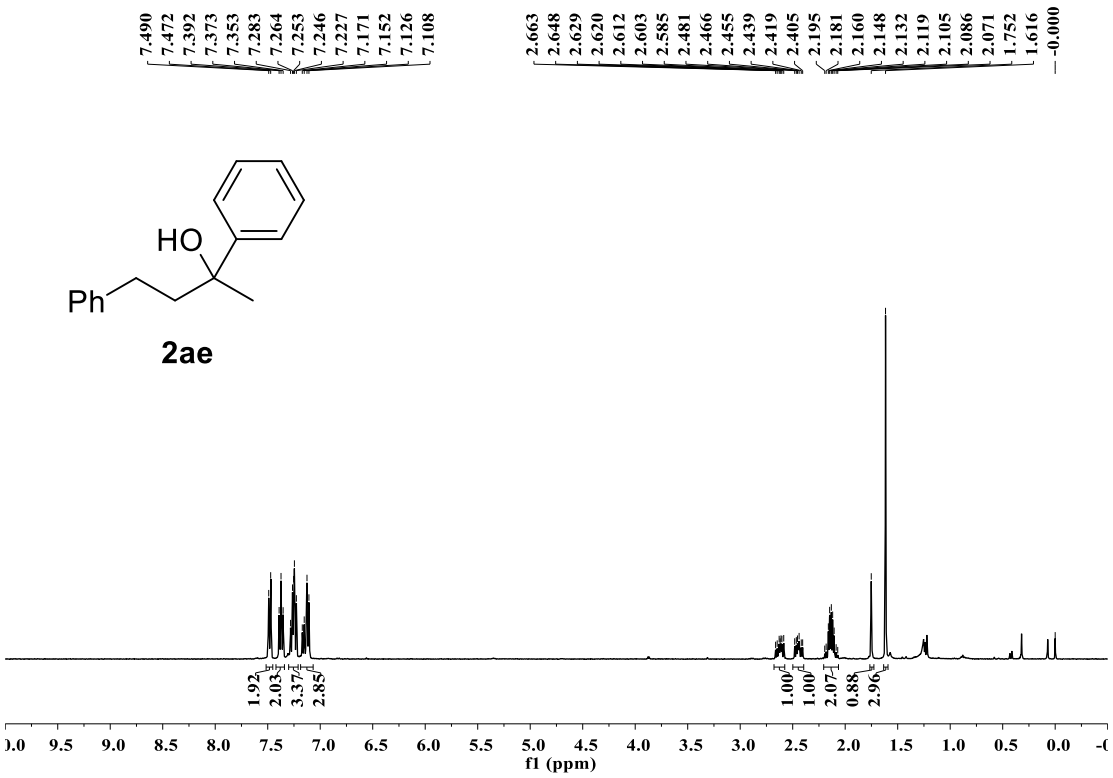
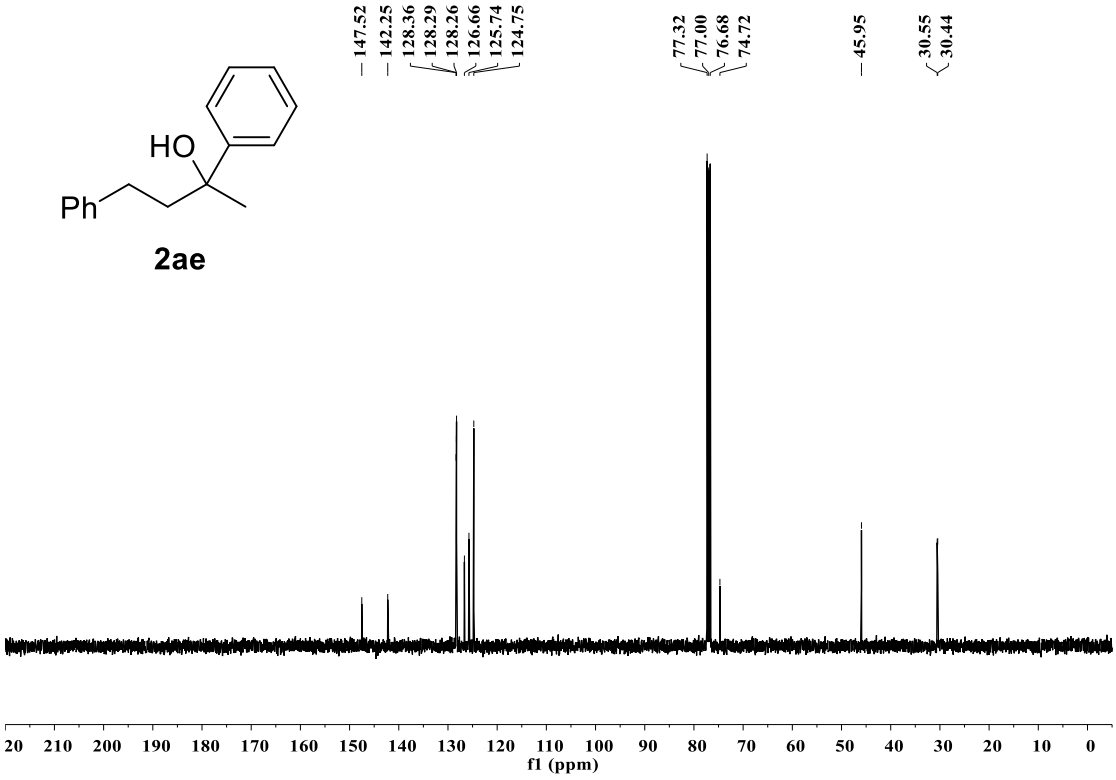
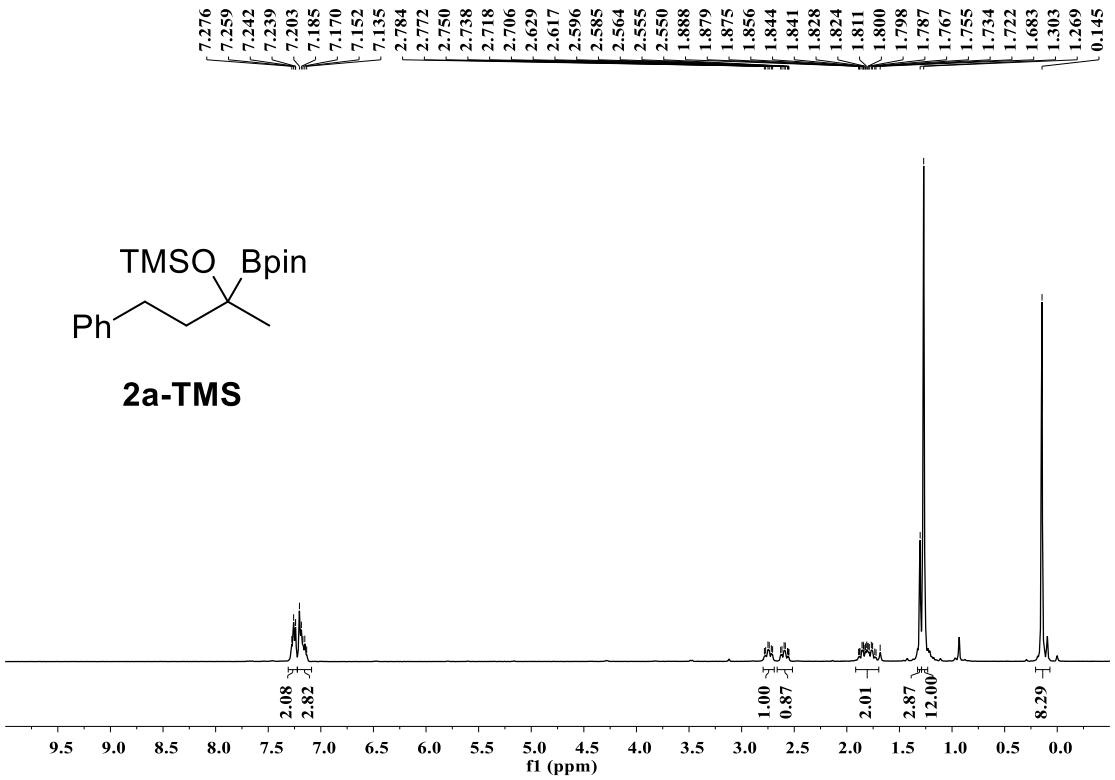
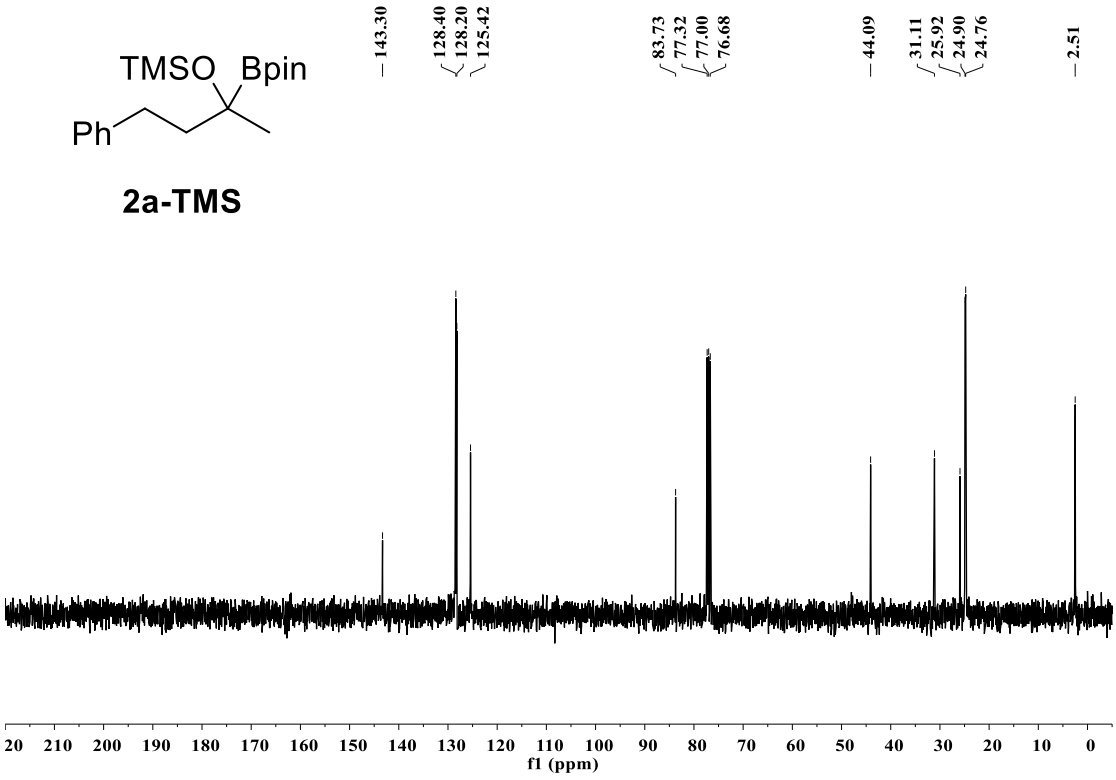
7.193
7.177
7.172
7.168
7.155
7.150
7.132
2.578
2.566
2.557
2.546
2.534
1.612
1.602
1.590
1.581
1.578
1.570
1.558
1.251
0.998
-0.000
Bpin
Ph
2ad
1.97
2.66
2.01
2.18
12.04
5.77
f1 (ppm)

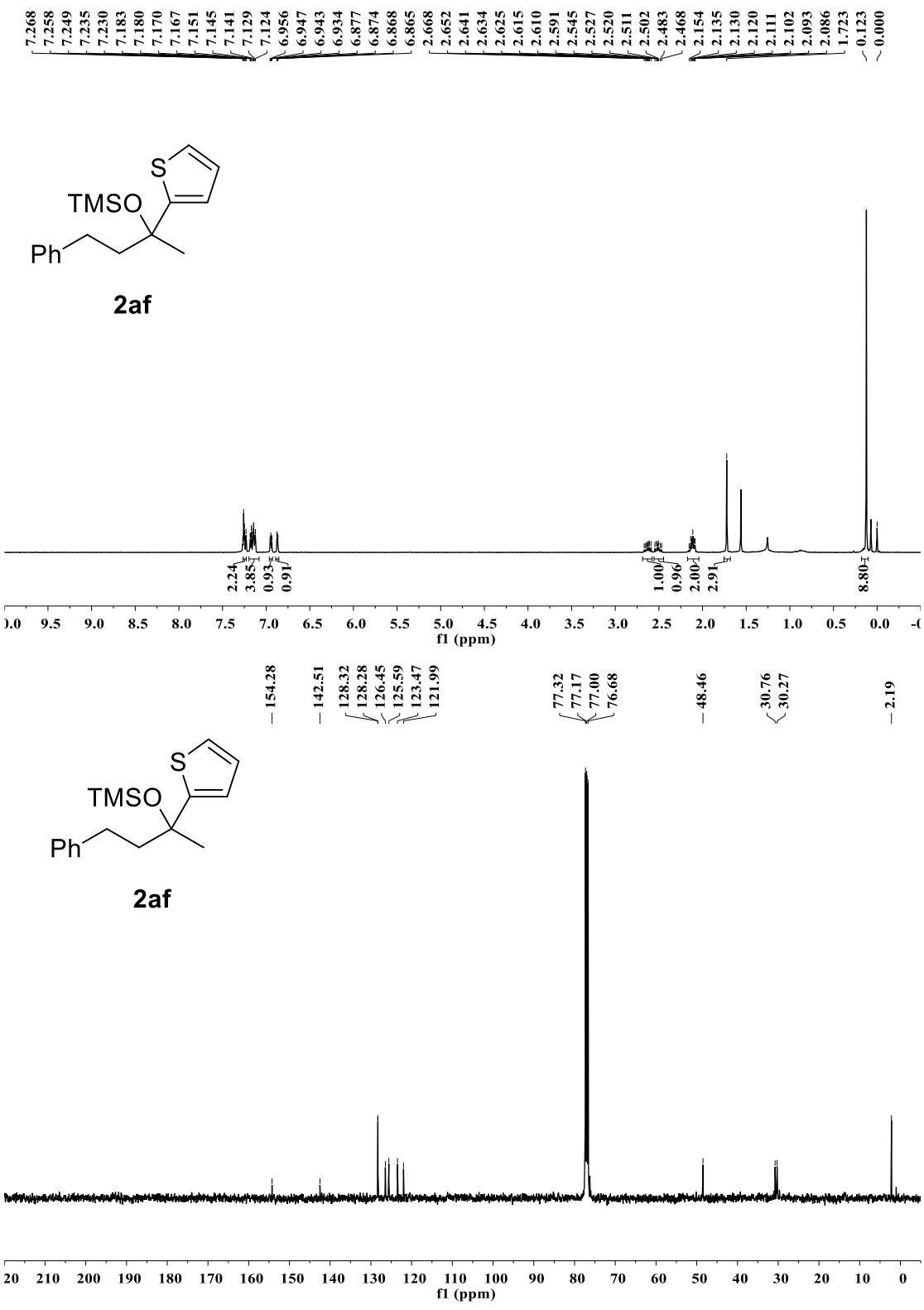

143.62
128.31
128.20
125.43
82.96
77.32
77.00
76.68
43.50
33.05
24.73
Bpin
Ph
2ad
f1 (ppm)


7.490
7.472
7.392
7.373
7.353
7.283
7.264
7.253
7.246
7.227
7.171
7.152
7.126
7.108
2.663
2.648
2.629
2.620
2.612
2.603
2.585
2.481
2.466
2.455
2.439
2.419
2.405
2.195
2.181
2.160
2.148
2.132
2.119
2.105
2.086
2.071
1.752
1.616
-0.000
HO
Ph
2ae
1.92
2.03
3.37
2.85
1.00
1.00
2.07
0.88
2.96
f1 (ppm)


147.52
142.25
128.36
128.29
128.26
126.66
125.74
124.75
77.32
77.00
76.68
74.72
45.95
30.55
30.44
HO
Ph
2ae
f1 (ppm)


7.276
7.259
7.242
7.239
7.203
7.185
7.170
7.152
7.135
2.784
2.772
2.750
2.738
2.718
2.706
2.629
2.617
2.596
2.585
2.564
2.555
2.550
1.888
1.879
1.875
1.856
1.844
1.841
1.828
1.824
1.811
1.800
1.798
1.787
1.767
1.755
1.734
1.722
1.683
1.303
1.269
0.145
TMSO Bpin
Ph
2a-TMS
2.08
2.82
1.00
0.87
2.01
2.87
12.00
8.29
f1 (ppm)


143.30
128.40
128.20
125.42
83.73
77.32
77.00
76.68
44.09
31.11
25.92
24.90
24.76
2.51
TMSO Bpin
Ph
2a-TMS
f1 (ppm)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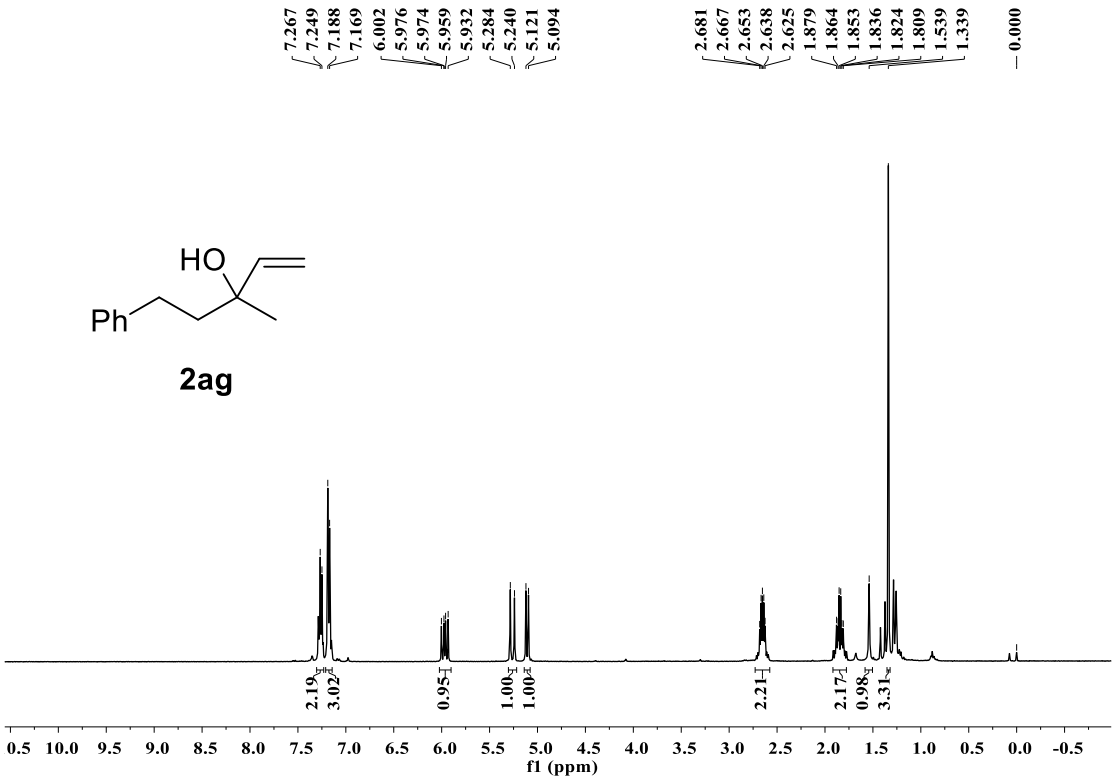
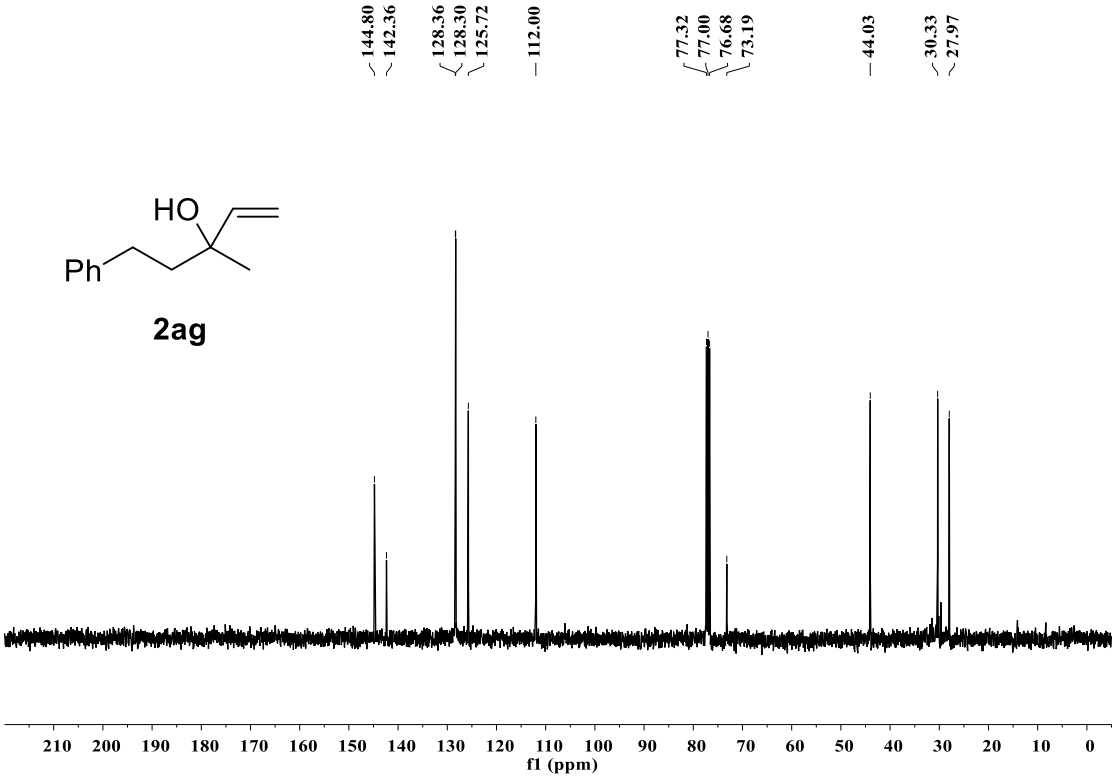
7.258
7.249
7.235
7.230
7.183
7.180
7.170
7.167
7.151
7.145
7.141
7.129
7.124
6.956
6.947
6.943
6.934
6.877
6.874
6.868
6.865
2.668
2.652
2.641
2.634
2.625
2.615
2.610
2.591
2.545
2.527
2.520
2.511
2.502
2.483
2.468
2.154
2.135
2.130
2.120
2.111
2.102
2.093
2.086
1.723
0.123
0.000
S
TMSO
Ph
2af
2.24
3.85
0.93
0.91
1.00
0.96
2.00
2.91
8.80
f1 (ppm)
154.28
142.51
128.32
128.28
126.45
125.59
123.47
121.99
77.32
77.17
77.00
76.68
48.46
30.76
30.27
2.19
S
TMSO
Ph
2af
f1 (ppm)


7.267
7.249
7.188
7.169
6.002
5.976
5.974
5.959
5.932
5.284
5.240
5.121
5.094
2.681
2.667
2.653
2.638
2.625
1.879
1.864
1.853
1.836
1.824
1.809
1.539
1.339
0.000
HO
Ph
2ag
2.19
3.02
0.95
1.00
1.00
2.21
2.17
0.98
3.31
f1 (ppm)


144.80
142.36
128.36
128.30
125.72
112.00
77.32
77.00
76.68
73.19
44.03
30.33
27.97
HO
Ph
2ag
f1 (ppm)

7. Reference

1. O. Tetsuo, I. Masanori and W. S. S., *Bull. Chem. Soc. Jpn.*, 1996, **69**, 3601-3605.
2. W. Francke and W. Reith, *Tetrahedron Lett.*, 1981, **22**, 2029-2032.
3. T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1966, **28**, 945-956.
4. L. Wang, T. Zhang, W. Sun, Z. He, C. Xia, Y. Lan and C. Liu, *J Am Chem Soc*, 2017, **139**, 5257-5264.
5. L. Wang, W. Sun and C. Liu, *Chin. J. Catal.*, 2018, **39**, 1725-1729.
6. D. Shi, L. Wang, C. Xia and C. Liu, *Angew Chem Int Ed.*, 2018, **57**, 10318-10322.
7. A. Bonet, M. Odachowski, D. Leonori, S. Essafi and V. K. Aggarwal, *Nat. Chem.*, 2014, **6**, 584.
8. R. J. Armstrong and V. K. Aggarwal, *Synthesis*, 2017, **49**, 3323-3336.
9. M. W. Andersen, B. Hildebrandt, G. Köster and R. W. Hoffmann, *Chem. Ber.*, 1989, **122**, 1777-1782.
10. M. L. McIntosh, C. M. Moore and T. B. Clark, *Org. Lett.*, 2010, **12**, 1996-1999.
11. K. Kubota, S. Osaki, M. Jin and H. Ito, *Angew Chem Int Ed.*, 2017, **56**, 6646-6650.
12. A. J. Wommack and J. S. Kingsbury, *Tetrahedron Lett.*, 2014, **55**, 3163-3166.
13. V. K. Aggarwal, M. Binanzer, M. C. de Ceglie, M. Gallanti, B. W. Glasspoole, S. J. F. Kendrick, R. P. Sonawane, A. Vázquez-Romero and M. P. Webster, *Org. Lett.*, 2011, **13**, 1490-1493.
14. H. Wang, X.-J. Dai and C.-J. Li, *Nat. Chem.*, 2016, **9**, 374.