Electronic Supplementary Information

Cooperation between an Alcoholic Proton and Boryl species in the Catalytic *gem*-Hydrodiborylation of Carboxylic Esters to Access 1,1-Diborylalkanes

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I. General Information

All reactions were performed isolating from moisture and oxygen by using standard Schlenk techniques under the nitrogen atmosphere with dry solvents. All glassware was oven dried by flame and cooled down under vacuum. Toluene (HPLC grade) was purified by using Pure Solv 7-SDS solvent drying system. EtOH was treated with magnesium powered. Commercially available chemicals were obtained from Acros Organics, Aldrich Chemical Co., Alfa Aesar, Strem, and TCI. $Fe(OAc)_2$ was purchased from Aldrich with 99.99% purity. $FeBr_2$ was purchased from Strem. Without otherwise noted, materials were used without further purification. Thin layer chromatography (TLC) employed using commercially available silica gel GF254 plates. Purification of products were performed by flash chromatography columns packing by 100-200 mesh silica gel in petroleum (60-90 b.p.). Chromatographic analyses were performed on a Shimadzu GC-2010 Plus instrument equipped with an FID detector and biphenyl was added as an internal standard. GC-MS spectra were recorded on a GCMS-QP2010 SE using He as the carrier gas. The High-Resolution MS analyses were recorded on Agilent 6530 Accurate Mass Q-TOF LC/MS with ESI mode. NMR spectra were recorded on a 400 MHz for ^1H and 101 MHz for ^{13}C NMR, using tetramethylsilane (TMS) as an internal reference and $CDCl_3$ as a solvent. Chemical shift values for protons were quoted in parts per million (ppm, δ scale) and are calibrated against the referenced to residual proton in tetramethylsilane of (TMS, 0 ppm). ^{13}C NMR were recorded at 101 MHz and were calibrated against the peaks of $CDCl_3$ (77.0 ppm). The boron-bound carbon was not detected due to quadrupolar relaxation.

The starting materials isopropyl octanoate (**1bc**),[1] *tert*-butyl octanoate (**1bd**),[1] benzyl octanoate (**1be**),[1] phenyl octanoate (**1bf**),[1] *p*-tolyl octanoate (**1bg**),[1] methyl 4-(octanoyloxy)benzoate (**1bh**),[1] methyl 2-cyclohexylacetate (**1fa**),[2] phenyl 2-cyclohexylacetate (**1fb**),[1] methyl 2-(1-methyl-1H-indol-3-yl)acetate (**1h**),[2] methyl 3-(benzo[d][1,3]dioxol-5-yl)propanoate (**1j**),[2] methyl 2-(4-isobutylphenyl)propanoate (**1o**),[2] methyl (R)-4-((3R,5R,8R,9S,10S,13R,14S,17R)-3-methoxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate (**1q**)[3] were prepared according to the literatures.

II. Procedures for the Fe-catalyzed gem-hydrodiborylation of Carboxylic Esters

Method A:

In a glove box, a flame dried 25 mL sealed tube equipped with a magnetic stirrer bar was placed with B_2pin_2 (304.8 mg, 1.2 mmol), NaO^tBu (86.5 mg, 0.9 mmol), $FeBr_2$ (6.5 mg, 0.03 mmol) and toluene (2 mL). The tube was sealed and taken out of the glove box. Then, the corresponding ester (0.3 mmol) and fresh EtOH (0.3 mmol) were added by syringe under N_2 atmosphere. The tube was sealed and stirred at 100 ºC for 24 h. Upon completion, the reaction was quenched by ethyl acetate and water, extracted with

ethyl acetate (3×15 mL), dried over anhydrous Na_2SO_4 and filtered. The solvent was then removed using rotary evaporator. The pure product was obtained by flash column chromatography on silica gel.

Method B:

In the glove box, a flame dried 25 mL Schlenk tube equipped with a magnetic stirrer bar was placed with B_2pin_2 (304.8 mg, 1.2 mmol), NaO^{t}Bu (86.5 mg, 0.9 mmol), $Fe(OAc)_2$ (5.2 mg, 0.03 mmol) and toluene (2 mL). The reaction flask was sealed with a rubber septum and taken out of the glove box. The mixture was reacted at 100 ^{o}C for 1h. After that, the corresponding ester (0.3 mmol) and fresh EtOH (0.3 mmol) were added sequentially by syringe and the temperature was maintained at 100 ^{o}C with stirring for 12 h. Upon completion, the reaction was quenched by ethyl acetate and water. Aqueous layer was extracted by ethyl acetate (3×15 mL), dried over anhydrous Na_2SO_4 and filtered. The combined organic solvent was removed by using rotary evaporator under reduced pressure. The pure product was obtained by flash column chromatography on silica gel.

Method C:

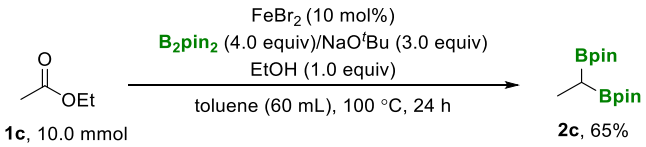
The procedure is identical to that of ***Method B*** except that $PCy_3{\cdot}HBF_4$ (22.1 mg, 0.06 mmol) was added and 3 mL toluene was used.

Method D:

The procedure is identical to that of ***Method A*** except that $Fe(OAc)_2$ (5.2 mg, 0.03 mmol) was used to replace $FeBr_2$.

III. Procedures for Gram scale experiment

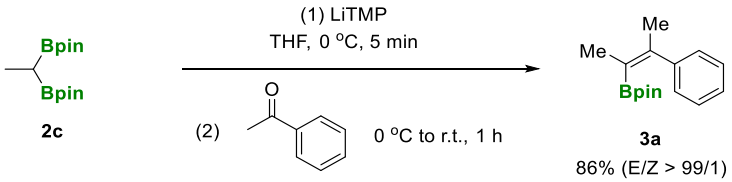
2,2'-(ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2c)



In a glove box, a flame dried 250 mL sealed tube equipped with a magnetic stirrer bar was charged with B_2pin_2 (10.16 g, 40.0 mmol), NaO^{t}Bu (2.88 g, 30.0 mmol), $FeBr_2$ (215.7 mg, 1.0 mmol) and toluene (60 mL). The tube was sealed and taken out of the glove box. Ethyl acetate (881.0 mg, 10.0 mmol, HPLC grade) and EtOH (460.0 mg, 10.0 mmol) were added by syringe under nitrogen atmosphere. The mixture was heated at 100 ^{o}C with stirring for 24 h. Then, the reaction was quenched by ethyl acetate, diluted with water, and extracted by ethyl acetate (3×100 mL). The combined organic layer was washed by brine (100 mL), dried over anhydrous Na_2SO_4 and filtered. The pure product was obtained by flash column chromatography on silica gel.

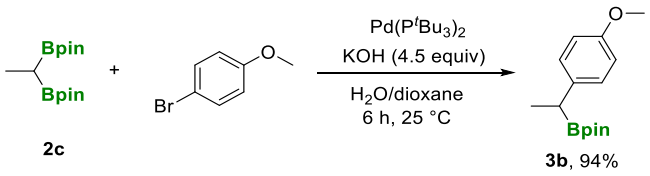
IV. Examples of introducing ester carbon chain into valuable molecules

(*E*)-4,4,5,5-tetramethyl-2-(3-phenylbut-2-en-2-yl)-1,3,2-dioxaborolane (3a)



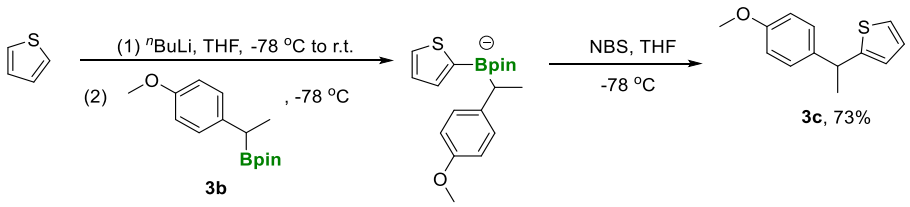
Compound **3a** was prepared according to the literature procedure.[4] In a glove box, a flame-dried Schlenk tube was charged with LiTMP (44.2 mg, 0.3 mmol) and 1.5 mL dry THF. The tube was sealed with a rubber septum and moved out of the glove box. Then, the solution of **2c** (84.6 mg, 0.3 mmol) in THF (0.5 mL) was added at 0 °C. After 5 min, acetophenone (24.0 mg, 0.2 mmol) was added at 0 °C. Upon completion, the reaction mixture was stirred at room temperature for 1 h. The pure product was obtained by flash column chromatography on silica gel.

2-(1-(4-methoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b)



Compound **3b** was prepared according to the literature procedure.[5] In a glove box, a flame-dried sealed tube was charged with **2c** (84.6 mg, 0.3 mmol), and Pd(P^{t}Bu$_3$)$_2$ (5.1 mg, 5 mol%) in 1 mL dioxane. The tube was sealed and taken out of the glove box. Then 4-bromoanisole (37.4 mg, 0.2 mmol) and KOH (0.9 mmol, 112 µL, 8M aq.) were added by syringe under nitrogen atmosphere. The tube was sealed and the mixture was stirred at 25 °C for 6 h. Upon completion, the mixture was filtered through a pad of silica gel with ethyl acetate. The pure product was obtained by silica gel column chromatography.

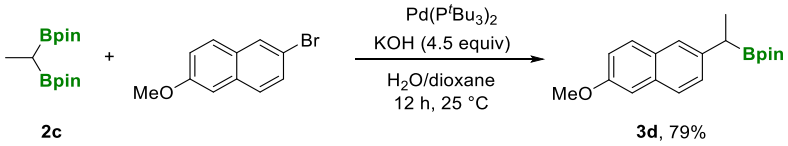
2-(1-(4-methoxyphenyl)ethyl)thiophene (3c)



Compound **3c** was prepared according to the literature procedure.[6] A flame-dried sealed tube was charged with thiophene (50.5 mg, 0.6 mmol) and THF (2 mL) and cooled down to -78 °C. The mixture was treated with ^{n}BuLi (0.375 mL, 0.6 mmol, 1.6 M in hexanes). Upon completion, the reaction mixture was stirred at room temperature for 0.5 h. After that the reaction system was cooled to -78 °C again, and

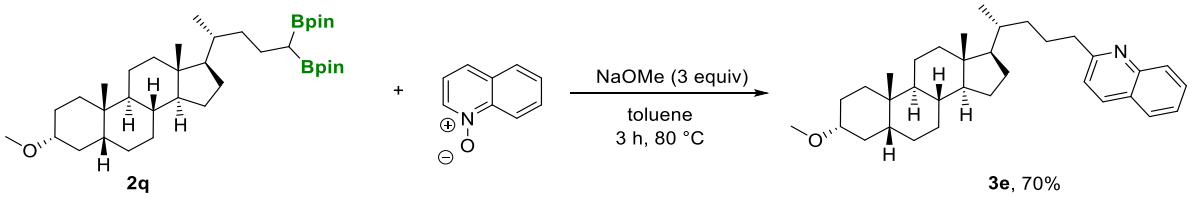
3b was added dropwise as a solution of THF (1.0 mL) and was stirred for 1 h. Then a solution of NBS (106.8 mg, 0.6 mmol) in THF (2 mL) was added dropwise at -78 °C. After 1 h, saturated solution of $Na_2S_2O_3$ (2 mL) was added and the mixture was allowed to warm to room temperature. The residual mixture was diluted by ethyl acetate (10 mL), then water (5 mL) was added. The aqueous layer was extracted by ethyl acetate (3×10 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated using rotary evaporator under reduced pressure. The crude product was purified by silica gel column chromatography.

2-(1-(6-methoxynaphthalen-2-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3d)



Compound **3d** was prepared according to the literature procedure.[5] In a glove box, a flame-dried sealed tube was charged with **2c** (84.6 mg, 0.3 mmol,), and Pd(P^{t}Bu$_3$)$_2$ (5.1 mg, 5 mol %) in 1 mL dioxane. The tube was sealed and taken out of the glove box. Then the 2-bromo-6-methoxynaphthalene (47.4 mg, 0.2 mmol) and KOH (0.9 mmol, 112 µL, 8M aq.) were added by syringe at room temperature under nitrogen atmosphere. The tube was sealed and the mixture was stirred at 25 °C for 12 h. Upon completion, the mixture was filtered through a pad of silica gel with ethyl acetate. The pure product was obtained by silica gel column chromatography.

2-((*R*)-4-((3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-methoxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentyl)quinoline (3e)



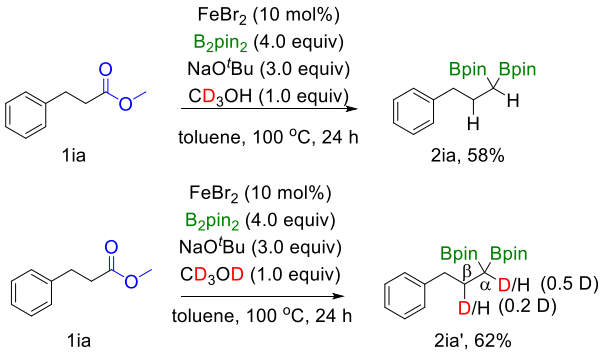
Compound **3e** was prepared according to the literature procedure.[7] In a glove box, a flame-dried sealed tube was charged with **2q** (245.0 mg, 0.4 mmol,), NaOMe (32.4 mg, 0.6 mmol) and quinoline *N*-oxide (29.0 mg, 0.2 mmol) in 2 mL toluene. The tube was sealed and taken out of the glove box. The mixture was stirred at 80 °C for 3 h. The crude mixture was filtered through celite and washed with ethyl acetate (20 mL). The filtrate was concentrated using rotary evaporator under reduced pressure. After that $NaBO_3 \cdot 4H_2O$ (93.0 mg, 0.6 mmol) and THF/H_2O (3.0 mL, 1:1) were added, followed by stirring at room temperature for 3 h. Upon completion, brine (5.0 mL) was added to reaction mixture and extracted with ethyl acetate (3×10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and filtered.

The solvent was removed under reduced pressure. The crude mixture was purified by silica gel column chromatography.

V. Mechanistic Studies

1. Deuterium-labelling experiments

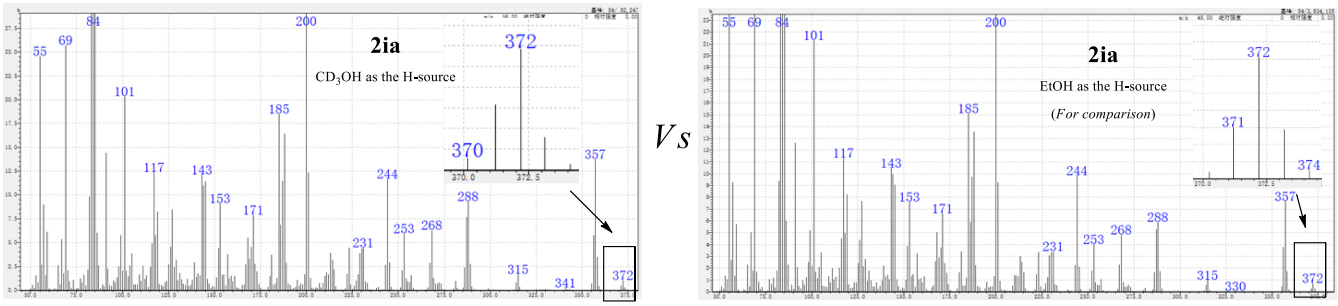
The procedure is identical to that of ***Method A*** except that different proton source was used.

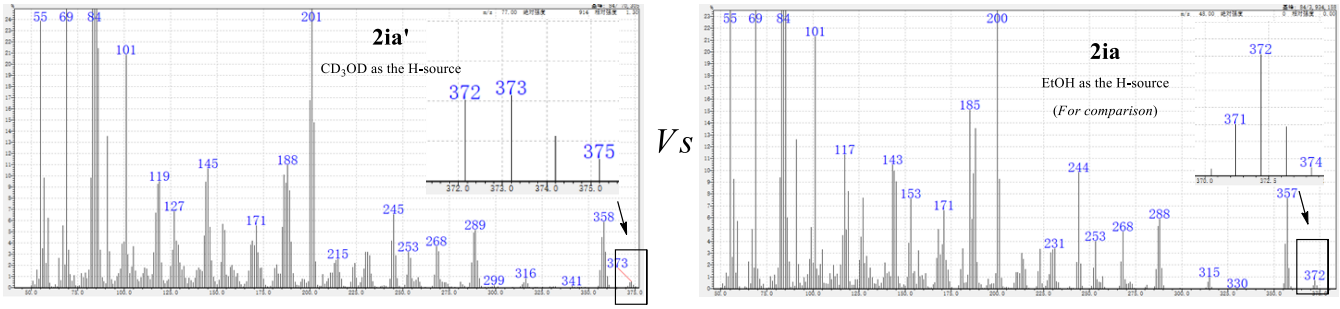


To verify the proton source of this reaction, deuterium-labelling experiments were carried out. Since it has the possibilities that the H comes from the β-hydride elimination of alcohol or from the protonation with alcohol, the d_3-methanol CD_3OH was first applied to confirm the H-source in the final product. As a result, no D-labeled **2ia** was observed from both MS spectra and ^1H NMR characterization. When fully deuterated CD_3OD was used, the D-labeled **2ia'** was observed. As shown in the MS spectra of **2ia'**, the peak of 372, 373 and 374 were observed (the MW of **2ia** is 372), indicating that both of one D-labeled, two D-labeled and none D-labeled products were obtained. Further ^1H NMR spectra exhibited that both the α-CH and the β-CH are partially D-labeled (The MS and 1H NMR spectra of the standard reaction with EtOH as the H-source are utilized for comparison). ***Therefore, we can conclude that the H-source of the formed C-H in the final product is originated from the alcoholic proton (O-H). Furthermore, the proton-exchange of the ester α-CH with alcohol occurs under the reaction condition.***

MS spectra of deuterium-labelling experiments

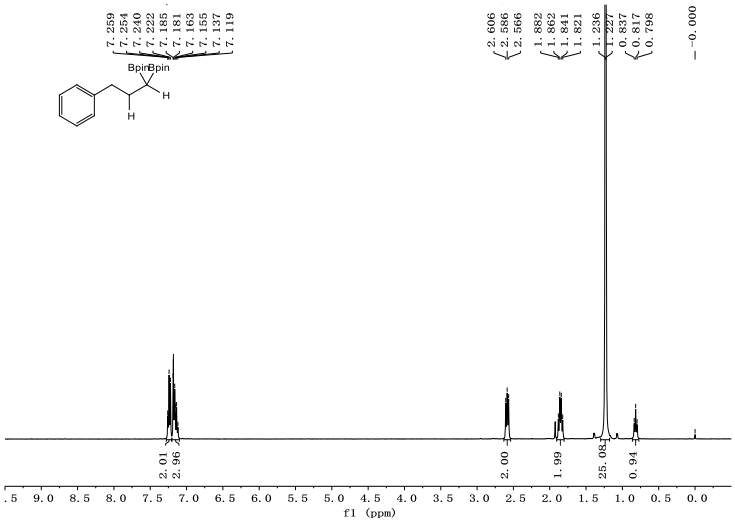
MS spectra of the standard **2ia** with EtOH as the hydrogen source.



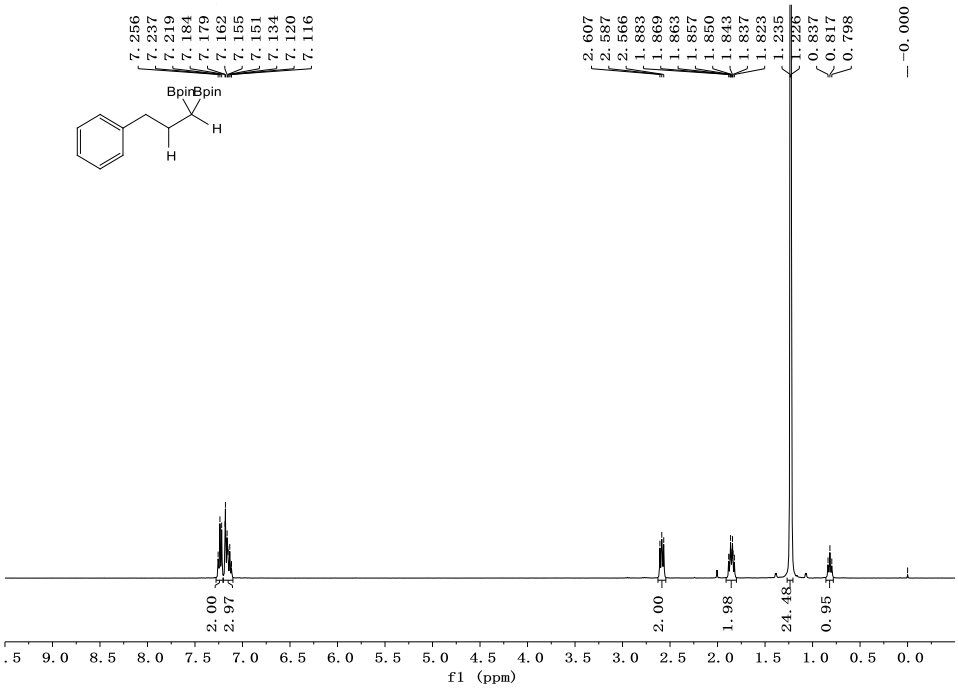


^{1}H NMR spectra of the deuterium-labelling experiments

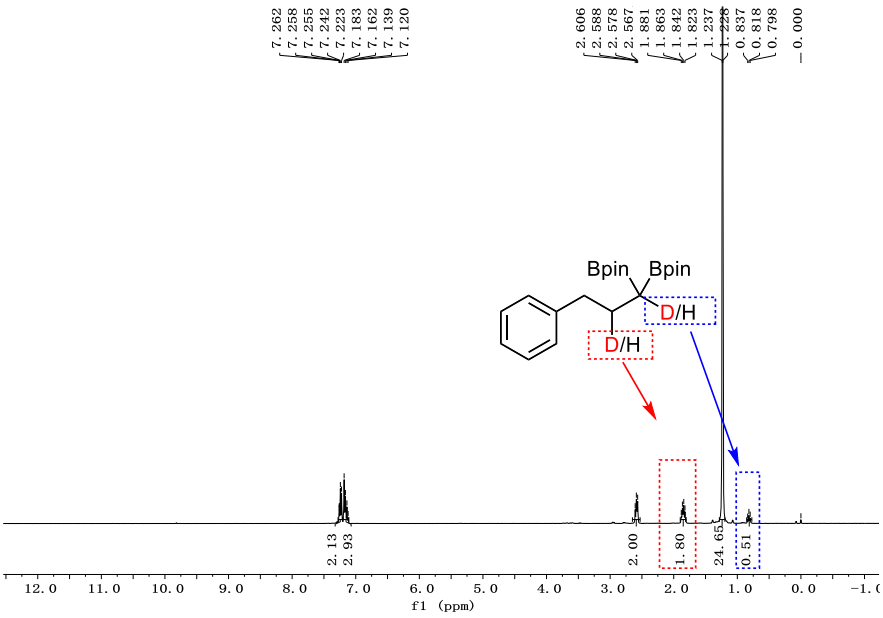
^{1}H NMR spectra of the standard reaction with EtOH as the H-source (for comparison).



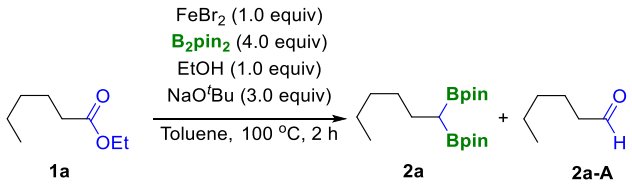
^{1}H NMR spectra of **2ia** with CD_3OH as the H-source



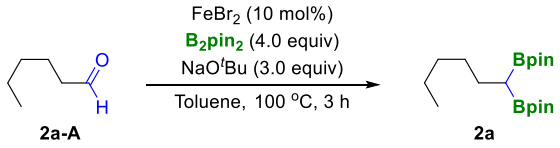
^{1}H NMR spectra of **2ia'** with CD_3OD as the H-source



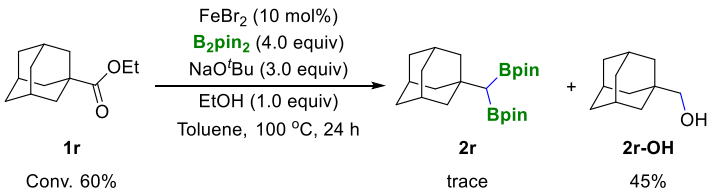
2. Procedure for Control Experiments



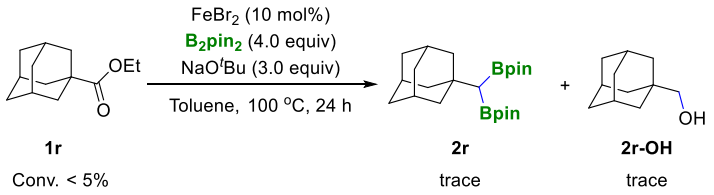
In a glove box, a flame-dried sealed tube was charged with $FeBr_2$ (64.7 mg, 0.3 mmol), B_2pin_2 (304.8 mg, 1.2 mmol) and NaO^{t}Bu (86.5 mg, 0.9 mmol) in toluene (4 mL). The tube was sealed and taken out of the glove box, then **1a** (43.3 mg, 0.3 mmol) and EtOH (13.8 mg, 0.3 mmol) were added by syringe under N_2 atmosphere. The tube was sealed and the mixture was heated at 100 ºC for 2 h. The reaction was quenched by ethyl acetate. The reaction mixture was analyzed by GC with biphenyl as the internal standard.



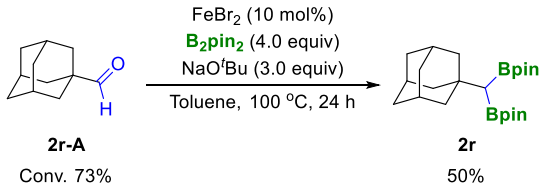
In a glove box, a flame-dried Schlenk tube was charged with $FeBr_2$ (6.5 mg, 0.03 mmol), B_2pin_2 (304.8 mg, 1.2 mmol) and NaO^{t}Bu (86.5 mg, 0.9 mmol) in toluene 2 mL. The tube was sealed and taken out of the glove box. The mixture was heated at 100 ºC. After that, compound **2a-A** (30.0 mg, 0.3 mmol) which was dissolved in 0.5 mL toluene was added by a peristaltic pump for 1 h. The reaction mixture was then stirred at 100 ºC for another 2 h. Upon completion, the reaction was quenched by ethyl acetate. The yield was determined by GC analysis with biphenyl as the internal standard.



The procedure is identical to that of ***Method A*** using ethyl (3r,5r,7r)-adamantane-1-carboxylate (62.5 mg, 0.3 mmol). The yield was determined by GC analysis with biphenyl as the internal standard.

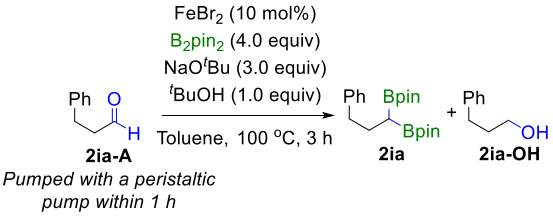


The procedure is identical to that of ***Method A*** except that no EtOH was added. The yield was determined by GC analysis with biphenyl as the internal standard.



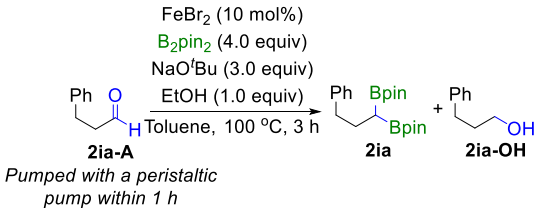
The procedure is identical to that of ***Method A*** except that (3*r*,5*r*,7*r*)-adamantane-1-carbaldehyde （49.3 mg, 0.3 mmol）was used without the addition of EtOH. The crude mixture was purified by silica gel column chromatography.

Alcohol and base effects

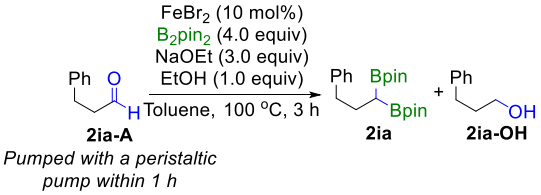


In a glove box, a flame-dried Schlenk tube was charged with $FeBr_2$ (6.5 mg, 0.03 mmol), B_2pin_2 (304.8 mg, 1.2 mmol), ^{t}BuOH (22.2 mg, 0.3 mmol) and NaO^{t}Bu (86.5 mg, 0.9 mmol) in toluene 2 mL. The tube was sealed and taken out of the glove box. The mixture was heated at 100 °C. After that, compound **2ia-A** (40.3 mg, 0.3 mmol), which was dissolved in 0.5 mL toluene, was added by a peristaltic pump for 1 h.

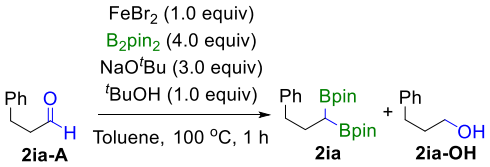
The reaction mixture was stirred at 100 ºC for another 2 h. Upon completion, the reaction was quenched by ethyl acetate. The yield was determined by GC analysis with biphenyl as the internal standard.



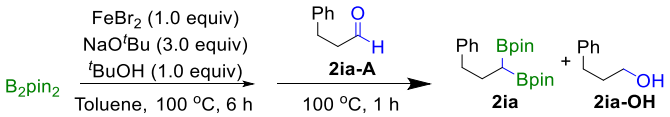
In a glove box, a flame-dried Schlenk tube was charged with $FeBr_2$ (6.5 mg, 0.03 mmol), B_2pin_2 (304.8 mg, 1.2 mmol), EtOH (13.8 mg, 0.3 mmol) and NaO^tBu (86.5 mg, 0.9 mmol) in toluene 2 mL. The tube was sealed and taken out of the glove box. The mixture was heated at 100 ºC. After that, compound **2ia-A** (40.3 mg, 0.3 mmol), which was dissolved in 0.5 mL toluene, was added by a peristaltic pump for 1 h. The reaction mixture was stirred at 100 ºC for another 2 h. Upon completion, the reaction was quenched by ethyl acetate. The yield was determined by GC analysis with biphenyl as the internal standard.



In a glove box, a flame-dried Schlenk tube was charged with $FeBr_2$ (6.5 mg, 0.03 mmol), B_2pin_2 (304.8 mg, 1.2 mmol), EtOH (13.8 mg, 0.3 mmol) and NaOEt (61.2 mg, 0.9 mmol) in toluene 2 mL. The tube was sealed and taken out of the glove box. The mixture was heated at 100 ºC. After that, compound **2ia-A** (40.3 mg, 0.3 mmol), which was dissolved in 0.5 mL toluene, was added by a peristaltic pump for 1 h. The reaction mixture was stirred at 100 ºC for another 2 h. Upon completion, the reaction was quenched by ethyl acetate. The yield was determined by GC analysis with biphenyl as the internal standard.



In a glove box, a flame-dried Schlenk tube was charged with $FeBr_2$ (64.7 mg, 0.3 mmol), B_2pin_2 (304.8 mg, 1.2 mmol), ^tBuOH (22.2 mg, 0.3 mmol), Compound **2ia-A** (40.3 mg, 0.3 mmol) and NaO^tBu (86.5 mg, 0.9 mmol) in toluene 4 mL. The tube was sealed and taken out of the glove box. The mixture was then stirred at 100 ºC for 1 h. Upon completion, the reaction was quenched by ethyl acetate. The yield was determined by GC analysis with biphenyl as the internal standard.

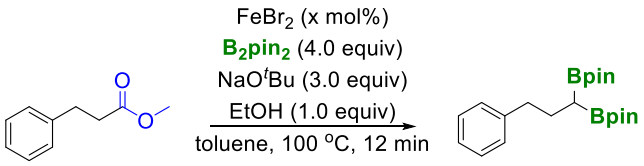


In a glove box, a flame-dried Schlenk tube was charged with $FeBr_2$ (64.7 mg, 0.3 mmol), B_2pin_2 (304.8 mg, 1.2 mmol), ^{t}BuOH (22.2 mg, 0.3 mmol), and NaO^{t}Bu (86.5 mg, 0.9 mmol) in toluene 4 mL. The tube was sealed and taken out of the glove box. The mixture was heated to 100 ºC for 6 h. After that Compound **2ia-A** (40.3 mg, 0.3 mmol) was added, then the mixture was stirred at 100 ºC for another 1 h. Upon completion, the reaction was quenched by ethyl acetate. The yield was determined by GC analysis with biphenyl as the internal standard.

Effect of initial concentration of $FeBr_2$ on reaction rate

In a glove box, flame-dried Schlenk tubes were parallelly charged with various amount of $FeBr_2$ (2.5, 5, 7.5, 10, 12.5 mol%), B_2pin_2 (304.8 mg, 1.2 mmol), and NaO^{t}Bu (86.5 mg, 0.9 mmol) in toluene (2 mL). The tube was sealed and taken out of the glove box. The mixtures were stirred at room temperature for 30 min. Then, EtOH (13.8 mg, 0.3 mmol) and compound **1ia** (49.3 mg, 0.3 mmol) were added by syringe and heated at 100 ºC for 12 min. Upon completion, the reactions were quenched by ethyl acetate. The yields were determined by GC analysis with biphenyl as the internal standard.

Table S1 Effect of initial concentration of $FeBr_2$ on reaction rate



1ia **2ia**

Entry	Concentration of $FeBr_2$(10^{-3} M)	Generating rate of **2ia** (M/h)
1	3.75	0.008
2	7.50	0.036
3	11.25	0.102
4	15.00	0.122
5	18.75	0.175

[a] Conditions: $FeBr_2$ (2.5-12.5 mol%) **1ia** (0.3 mmol), B_2pin_2 (1.2 mmol), EtOH (0.3 mmol), NaO^{t}Bu (0.9 mmol), toluene (2.0 mL), 100 °C, 12 min. [b] Yield determined by GC with biphenyl as internal standard.

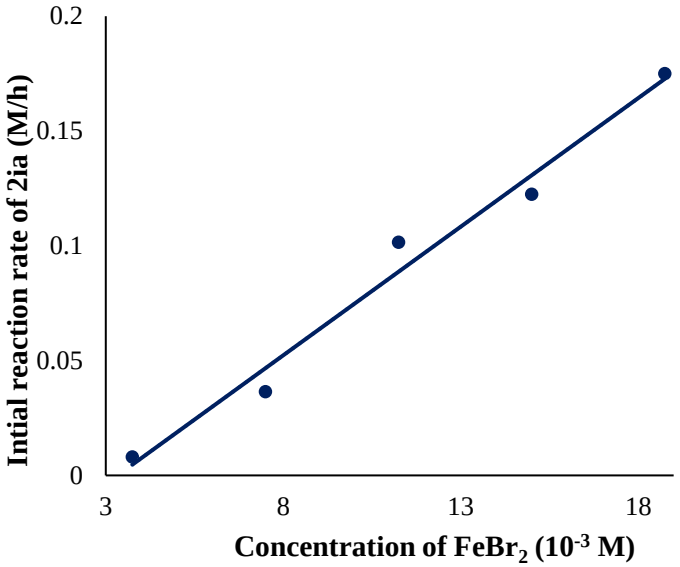
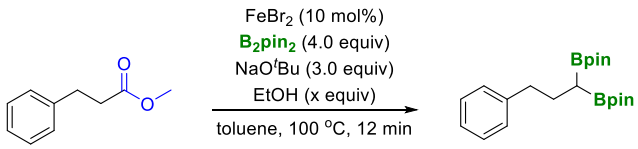


Figure S1 Effect of initial concentration of $FeBr_2$ on reaction rate

Effect of initial concentration of EtOH *on reaction rate*

In a glove box, flame-dried Schlenk tubes were charged with $FeBr_2$ (6.5 mg, 10 mol%), B_2pin_2 (304.8 mg, 1.2 mmol), and NaO^tBu (86.5 mg, 0.9 mmol) in toluene (2 mL). The tubes were sealed and taken out of the glove box. After that various amount of EtOH (0.18, 0.24, 0.3, 0.36, 0.42 mmol) and compound **1ia** (49.3 mg, 0.3 mmol) were added by syringe, respectively. Then the reaction mixtures were heated at 100 ºC for 12 min. Upon completion, the reactions were quenched by ethyl acetate. The yields were determined by GC analysis with biphenyl as the internal standard.

Table S2 Effect of initial concentration of EtOH on reaction rate



1ia **2ia**

Entry	Concentration of EtOH(M)	Generating rate of **2ia** (M/h)
1	0.09	0.114
2	0.12	0.138
3	0.15	0.167
4	0.18	0.192
5	0.21	0.226

[a] Conditions: $FeBr_2$ (10 mol%), 1ia (0.3 mmol), B_2pin_2 (1.2 mmol), EtOH (0.18-0.42 mmol), NaO^tBu (0.9 mmol), toluene (2.0 mL), 100 °C, 12 min. [b] Yield determined by GC with biphenyl as internal standard.

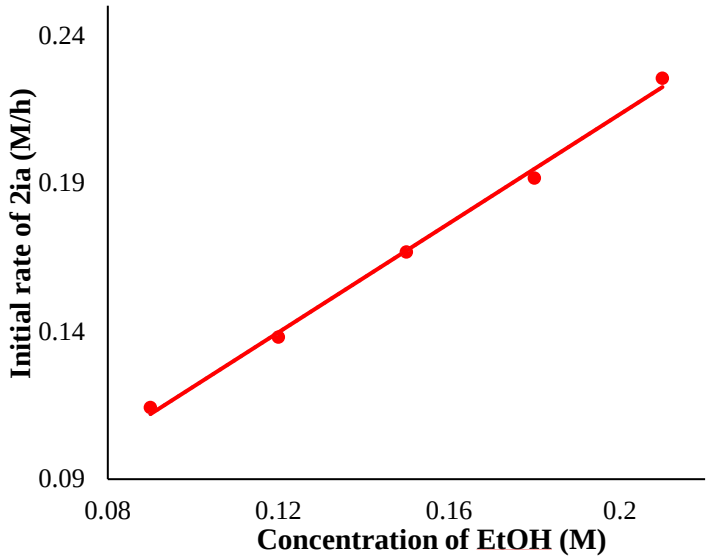
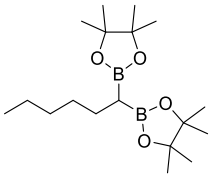
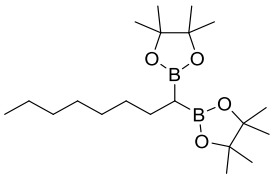


Figure S2 Effect of initial concentration of EtOH on reaction rate

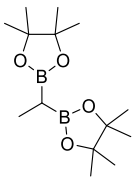
VI. Detailed Descriptions for Reaction Products



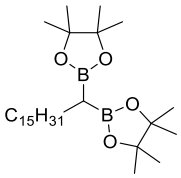
2,2'-(hexane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2a**).[8] The reaction was performed according to ***Method A*** with **1a** (0.3 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.58 - 1.48 (m, 2H), 1.33 - 1.16 (m, 30H), 0.86 (t, *J* = 6.8 Hz, 3H), 0.71 (t, *J* = 7.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 82.8, 32.2, 31.8, 25.6, 24.8, 24.5, 22.5, 14.0 ppm.



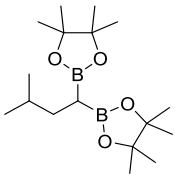
2,2'-(octane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2b**).[9] The reactions were treated with **1ba - 1bf** (0.3 mmol), **1bg** (0.3 mmol), were performed according to ***Method A***, ***Method B***, respectively. For **1bh** (0.3 mmol), ***Method B*** was used except that methyl 4-(octanoyloxy)benzoate (**1bh**, 83.5 mg, 0.3 mmol) which was dissolved in 0.4 mL toluene and added by syringe. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.60 - 1.48 (m, 2H), 1.34 - 1.18 (m, 34H), 0.86 (t, *J* = 6.8 Hz, 3H), 0.71 (t, *J* = 7.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 82.8, 32.5, 31.8, 29.5, 29.2, 25.6, 24.8, 24.4, 22.6, 14.1 ppm.



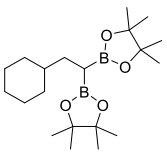
2,2'-(ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2c**).[4] The reaction was performed according to ***Method A*** with **1c** (0.3 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.23(5) (s, 12H), 1.22(7) (s, 12H), 1.04 (d, *J* = 7.2 Hz, 3H), 0.73 (q, *J* = 7.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 82.9, 24.8, 24.5, 9.0 ppm.



2,2'-(hexadecane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2d**). The reaction was performed according to ***Method A*** with **1d** (0.3 mmol), except that B_2pin_2 (342.9 mg, 1.35 mmol), NaO^{t}Bu (100.9 mg, 1.05 mmol), EtOH (20.7 mg, 0.45 mmol) and 3 mL toluene were used. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.59 - 1.48 (m, 2H), 1.33 - 1.16 (m, 50H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.71 (t, *J* = 7.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 82.8, 32.6, 31.9, 29.6(8), 29.6(5), 29.6(3), 29.5(9), 29.5(2), 29.3, 25.7, 24.8, 24.5, 22.7, 14.1 ppm. HRMS (ESI) calcd for $C_{28}H_{56}B_2O_4$ $[M+Na]^+$: 501.4262; found: 501.4267.

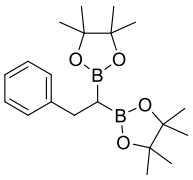


2,2'-(3-methylbutane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2e**).[8] The reaction was performed according to ***Method A*** with **1ea** or **1eb** (0.3 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.49 - 1.42 (m, 3H), 1.23 (s, 12H), 1.22 (s, 12H), 0.88 - 0.78 (m, 7H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 82.9, 34.5, 30.1, 24.8, 24.5, 22.4 ppm.

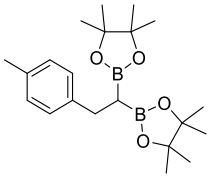


2,2'-(2-cyclohexylethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2f**).[10] Prepared according to ***Method B*** with compound **1fa** or **1fb** (0.3 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.76 - 1.58

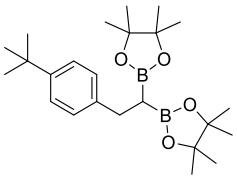
(m, 5H), 1.49 - 1.41 (m, 2H), 1.29 - 1.04 (m, 28H), 0.88 - 0.72 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 82.8, 39.8, 33.1, 32.9, 26.7, 26.4, 24.8, 24.5 ppm.



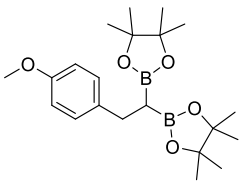
2,2'-(2-phenylethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2ga**).[8] Prepared according to ***Method B*** with compound **1ga** (0.3 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 - 7.18 (m, 4H), 7.15 - 7.07 (m, 1H), 2.88 (d, *J* = 8.4 Hz, 2H), 1.20 - 1.15 (m, 25H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.4, 128.2, 127.9, 125.2, 83.0, 31.2, 24.7, 24.4 ppm.



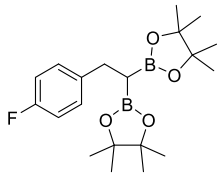
2,2'-(2-(*p*-tolyl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2gb**).[11] Prepared according to ***Method D*** with compound **1gb** (0.3 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 - 7.09 (m, 2H), 7.06 - 6.99 (m, 2H), 2.84 (d, *J* = 8.4 Hz, 2H), 2.28 (s, 3H), 1.20 - 1.09 (m, 25H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.3, 134.6, 128.6, 128.1, 83.0, 30.8, 24.8, 24.5, 21.0 ppm.



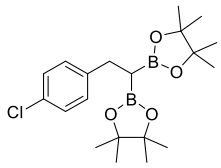
2,2'-(2-(4-(*tert*-butyl)phenyl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2gc**). Prepared according to ***Method B*** with compound **1gc** (0.3 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.11 (m, 4H), 2.85 (d, *J* = 8.0 Hz, 2H), 1.28 (s, 9H), 1.16 (s, 25H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.0, 141.3, 128.0, 124.8, 83.0, 34.2, 31.4, 30.7, 24.7, 24.5 ppm. HRMS (ESI) calcd for $C_{24}H_{40}B_2O_4$ $[M+Na]^+$: 437.3010; found: 437.3018.



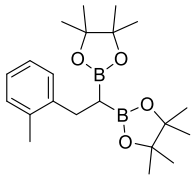
2,2'-(2-(4-methoxyphenyl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2gd**).[10] Prepared according to ***Method D*** with compound **1gd** (0.3 mmol).. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (d, *J* = 8.8 Hz, 2H), 6.77 (d, *J* = 8.8 Hz, 2H), 3.76 (s, 3H), 2.82 (d, *J* = 8.4 Hz, 2H), 1.20 - 1.10 (m, 25H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.4, 136.6, 129.2, 113.3, 83.0, 55.2, 30.4, 24.8, 24.5 ppm.



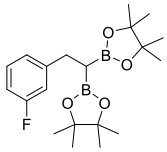
2,2'-(2-(4-fluorophenyl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2ge**).[10] Prepared according to ***Method D*** with compound **1ge** (0.3 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 - 7.11 (m, 2H), 6.98 - 6.83 (m, 2H), 2.84 (d, *J* = 8.4 Hz, 2H), 1.22 - 1.09 (m, 25H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.0 (d, *J* = 243.3 Hz), 140.0 (d, *J* = 3.2 Hz), 129.6 (d, *J* = 7.8 Hz), 114.5 (d, *J* = 21.0 Hz), 83.1, 30.5, 24.8, 24.4 ppm.



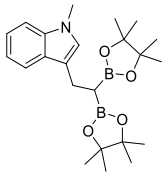
2,2'-(2-(4-chlorophenyl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2gf**). Prepared according to ***Method C*** with compound **1gf** (0.3 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 - 7.11 (m, 4H), 2.84 (d, *J* = 8.4 Hz, 2H), 1.19 (s, 12H), 1.17 (s, 12H), 1.12 (t, *J* = 8.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.9, 130.9, 129.7, 128.0, 83.2, 30.6, 24.8, 24.4 ppm. HRMS (ESI) calcd for $C_{20}H_{31}B_2ClO_4$ $[M+H]^+$: 393.2175; found: 393.2176.



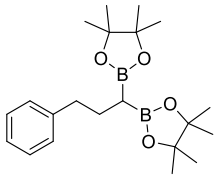
2,2'-(2-(*o*-tolyl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2gg**).[11] Prepared according to ***Method D*** with compound **1gg** (0.3 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 - 7.20 (m, 1H), 7.11 - 6.98 (m, 3H), 2.85 (d, *J* = 8.4 Hz, 2H), 2.31 (s, 3H), 1.20 - 1.12 (m, 25H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.4, 136.0, 129.8, 128.4, 125.5, 125.4, 83.0, 28.3, 24.8, 24.5, 19.4 ppm.



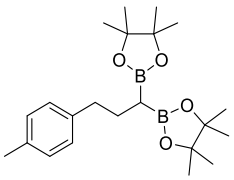
2,2'-(2-(3-fluorophenyl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2gh**). Prepared according to ***Method D*** with compound **1gh** (0.3 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 - 7.14 (m, 1H), 7.03 - 6.91 (m, 2H), 6.85 - 6.76 (m, 1H), 2.87 (d, *J* = 8.4 Hz, 2H), 1.20 - 1.10 (m, 25H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.6 (d, *J* = 245.4 Hz), 147.1 (d, *J* = 8.1 Hz) 129.3 (d, *J* = 8.1 Hz), 123.9 (d, *J* = 2.0 Hz), 115.2 (d, *J* = 20.2 Hz), 112.1 (d, *J* = 21.2 Hz), 83.2, 31.1, 24.7, 24.4 ppm. HRMS (ESI) calcd for $C_{20}H_{31}B_2FO_4$ $[M+Na]^+$: 399.2290; found: 399.2287.



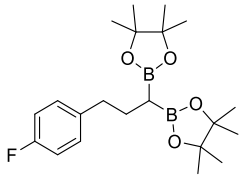
3-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-1-methyl-1*H*-indole (**2h**). The reaction was performed according to ***Method A*** with **1h** (0.3 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 - 7.62 (m, 1H), 7.28 - 7.13 (m, 2H), 7.09 - 7.02 (m, 1H), 6.86 (s, 1H), 3.70 (s, 3H), 3.00 (d, *J* = 8.0 Hz, 2H), 1.26 (t, *J* = 8.4 Hz, 1H), 1.19 (s, 12H), 1.18 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.9, 128.0, 126.0, 121.1, 119.5, 118.1, 117.8, 108.6, 83.0, 32.4, 24.7, 24.5, 20.5 ppm. HRMS (ESI) calcd for $C_{23}H_{35}B_2NO_4$ $[M+Na]^+$: 434.2650; found: 434.2654.



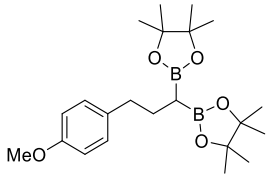
2,2'-(3-phenylpropane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)(2ia).[8] The reaction was performed according to ***Method A*** with **1ia** (0.3 mmol).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 - 7.21 (m, 2H), 7.20 - 7.11 (m, 3H), 2.59 (t, *J* = 8.0 Hz, 2H), 1.89 - 1.80 (m, 2H), 1.24 (s, 12H), 1.23 (s, 12H), 0.82 (t, *J* = 7.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.9, 128.6, 128.1, 125.4, 83.0, 38.7, 28.0, 24.9, 24.5 ppm.



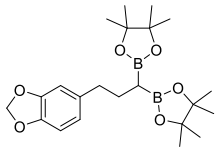
2,2'-(3-(*p*-tolyl)propane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)(2ib). The reaction was performed according to ***Method A*** with **1ib** (0.3 mmol).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10 - 7.02 (m, 4H), 2.60 - 2.48 (m, 2H), 2.30 (s, 3H), 1.88 - 1.76 (m, 2H), 1.24 (s, 12H), 1.23 (s, 12H), 0.81 (t, *J* = 7.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 139.8, 134.8, 128.8, 128.4, 82.9, 38.2, 28.1, 24.9, 24.4, 21.0 ppm. HRMS (ESI) calcd for $C_{22}H_{36}B_2O_4$ $[M+H]^+$: 387.2878; found: 387.2884.



2,2'-(3-(4-fluorophenyl)propane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2ic**).[12] The reaction was performed according to ***Method A*** with **1ic** (0.3 mmol).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 - 7.04 (m, 2H), 7.01 - 6.84 (m, 2H), 2.55 (t, *J* = 8.0 Hz, 2H), 1.92 - 1.75 (m, 2H), 1.28 - 1.15 (m, 24H), 0.78 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.1 (d, *J* = 244.4 Hz), 138.5 (d, *J* = 4.0 Hz), 129.8 (d, *J* = 8.1 Hz), 114.7 (d, *J* = 21.2 Hz), 83.0, 37.8, 28.0, 24.9, 24.5 ppm.

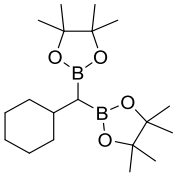


2,2'-(3-(4-methoxyphenyl)propane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2id**). The reaction was performed according to ***Method A*** with **1id** (0.3 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (d, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 3.77 (s, 3H), 2.57 - 2.46 (m, 2H), 1.88 - 1.76 (m, 2H), 1.24 (s, 12H), 1.23 (s, 12H), 0.80 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.5, 135.0, 129.4, 113.5, 82.9, 55.2, 37.8, 28.2, 24.9, 24.5 ppm. HRMS (ESI) calcd for $C_{22}H_{36}B_2O_5$ $[M+H]^+$: 403.2827; found: 403.2831.

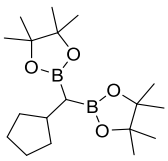


2,2'-(3-(benzo[*d*][1,3]dioxol-5-yl)propane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2j**). The reaction was performed according to ***Method A*** with slight modification, using **1j** (0.3 mmol) and toluene was 3 mL. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.72 - 6.66 (m, 2H), 6.64 - 6.57 (m, 1 H), 5.88 (s, 2H), 2.56 - 2.43 (m, 2H), 1.85 - 1.76 (m, 2H), 1.23 (s, 12H), 1.22 (s, 12H), 0.78 (t, *J* = 7.8 Hz, 1H); ^{13}C NMR

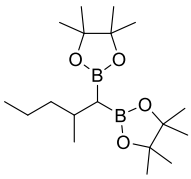
(101 MHz, $CDCl_3$): δ 147.3, 145.3, 136.8, 121.2, 109.1, 107.9, 100.5, 82.9, 38.3, 28.1, 24.8, 24.5 ppm. HRMS (ESI) calcd for $C_{22}H_{34}{}^{10}B_2O_6$ $[M]^+$: 414.2614; found: 414.2615.



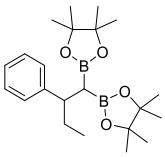
2,2'-(cyclohexylmethylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2k).[8] Prepared according to ***Method B*** with compound **1k** (0.3 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.82 - 1.55 (m, 6H), 1.34 - 1.01 (m, 27 H), 0.99 - 0.83 (m, 2H), 0.64 (d, *J* = 10.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 82.8, 36.0, 35.9, 26.7, 26.3, 24.8, 24.5 ppm.



2,2'-(cyclopentylmethylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2l**).[8] Prepared according to ***Method D***. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.16 - 2.03 (m, 1H), 1.93 - 1.83 (m, 2H), 1.61-1.44 (m, 4H), 1.23 (s, 12H), 1.22 (s, 12H), 1.05 - 0.93 (m, 2H), 0.66 (d, *J* = 10.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 82.8, 37.9, 35.1, 24.9, 24.8, 24.4 ppm.

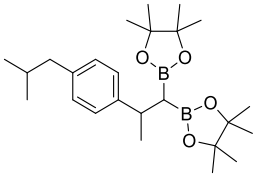


2,2'-(2-methylpentane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2m**).[8] The reaction was performed according to ***Method A*** with **1m** (0.3 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.98 - 1.84 (m, 1H), 1.42 - 1.04 (m, 28H), 0.93 (d, *J* = 6.4 Hz, 3H), 0.86 (t, *J* = 7.0 Hz, 3H), 0.70 (d, *J* = 10.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 82.8, 42.0, 30.8, 24.8(8), 24.8(7), 24.5(0), 24.4(7), 21.6, 20.1, 14.3 ppm.

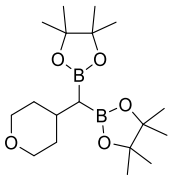


2,2'-(2-phenylbutane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2n**).[13] Prepared according to ***Method A*** with compound **1n** (0.3 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 - 7.16 (m, 4H), 7.13 - 7.07 (m, 1H), 2.95 - 2.84 (m, 1H), 1.79 - 1.68 (m, 1H), 1.52 - 1.42 (m, 1H), 1.30 - 1.22 (m,

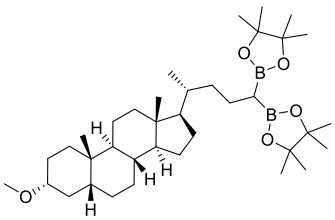
13H), 0.92 (s, 6H), 0.88 (s, 6H), 0.67 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.0, 128.0, 127.7, 125.5, 83.0, 82.7, 44.9, 32.7, 24.9, 24.4, 24.3, 24.1, 12.2 ppm.



2,2'-(2-(4-isobutylphenyl)propane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2o**). Prepared according to ***Method A*** with slight modification, using compound **1o** (0.3 mmol) and 3 mL toluene. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (d, J = 8.0 Hz, 2H), 6.99 (d, J = 8.4 Hz, 2H), 3.20 - 3.08 (m, 1H), 2.40 (d, J = 6.8 Hz, 2H), 1.83 - 1.75 (m, 1H), 1.28 - 1.22 (m, 16H), 0.95 (s, 6H), 0.90 (s, 6H), 0.86 (d, J = 2.4 Hz, 3H), 0.85 (d, J = 2.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.7, 138.7, 128.7, 126.7, 83.0, 82.7, 45.0, 37.5, 30.2, 26.2, 24.9, 24.4(2), 24.3(8), 24.2, 22.3, 22.2 ppm. HRMS (ESI) calcd for $C_{25}H_{42}B_2O_4$ $[M+Na]^+$: 451.3167; found: 451.3167.

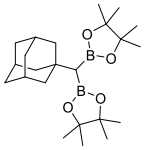


2,2'-((tetrahydro-2*H*-pyran-4-yl)methylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2p**). Prepared according to ***Method B*** with compound **1p** (0.3 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.95 - 3.86 (m, 2H), 3.45 - 3.33 (m, 2H), 1.96 - 1.85 (m, 1H), 1.73 - 1.66 (m, 2H), 1.40 - 1.11 (m, 26H), 0.69 (d, J = 10.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 83.0, 68.4, 35.4, 32.9, 24.9, 24.5 ppm. HRMS (ESI) calcd for $C_{18}H_{34}B_2O_5$ $[M+H]^+$: 353.2671; found: 353.2674.

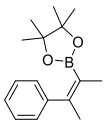


2,2'-((*R*)-4-((3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-methoxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2q**). The reaction was performed according to ***Method A*** with slight modification, using **1q** (0.3 mmol) and toluene was 3 mL.^{1}H NMR (400 MHz, $CDCl_3$): δ 3.35 (s, 3H), 3.23 - 3.10 (m, 1H), 1.97 - 1.53 (m, 8H), 1.40 - 0.87 (m, 50H), 0.68 - 0.55(m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 82.8, 80.4, 56.4, 55.9,

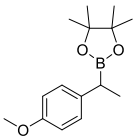
55.4, 42.6, 42.0, 40.2, 40.0, 39.1, 35.8(4), 35.7(8), 35.2, 34.8, 32.7, 28.2, 27.3, 26.7, 26.3, 24.8, 24.4, 24.2, 23.4, 22.1, 20.7, 18.8, 11.9 ppm. HRMS (ESI) calcd for $C_{37}H_{66}{}^{10}B_2O_5$ $[M]^+$: 610.5169; found: 610.5173.



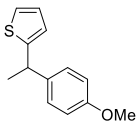
2,2'-(((*3r*,*5r*,*7r*)-adamantan-1-yl)methylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) （**2r**）. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.96 - 1.83 (m, 3H), 1.75 - 1.56 (m, 12H), 1.23 (s, 12H), 1.22 (s, 12H), 0.62 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 82.5, 44.2, 37.0, 33.6, 29.2, 24.9, 24.5 ppm. HRMS (ESI) calcd for $C_{23}H_{40}B_2O_4$ $[M]^+$: 402.3187; found: 402.3185.



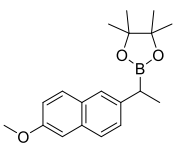
(*E*)-4,4,5,5-tetrametyl-2-(3-phenylbut-2-en-2-yl)-1,3,2-dioxaborolane (**3a**).[4] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 - 7.16 (m, 5H), 2.05 (d, *J* = 1.2 Hz, 3H), 1.84 (d, *J* = 1.2 Hz, 3H), 1.08 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.5, 146.3, 127.6(8), 127.6(6), 126.5, 82.9, 24.5, 20.2, 17.2 ppm.



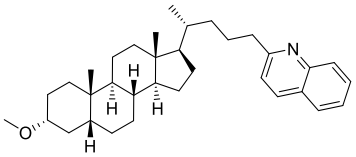
2-(1-(4-methoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3b**).[5] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (d, *J* = 6.4 Hz, 2H), 6.81 (d, *J* = 6.4 Hz, 2H), 3.77 (s, 3H), 2.37 (q, *J* = 7.8 Hz, 1H), 1.34 - 1.27 (m, 3H), 1.25 - 1.16(m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.2, 137.0, 128.6, 113.7, 83.2, 55.2, 24.6(0), 24.5(7), 17.4 ppm.



2-(1-(4-methoxyphenyl)ethyl)thiophene (**3c**).[14] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 - 7.05 (m, 3H), 6.93 - 6.75 (m, 4H), 4.29 (q, *J* = 7.2 Hz, 1H), 3.77 (s, 3H), 1.70 - 1.64 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.1, 151.2, 138.2, 128.2, 126.4, 123.4, 113.8, 55.2, 39.8, 23.4 ppm.



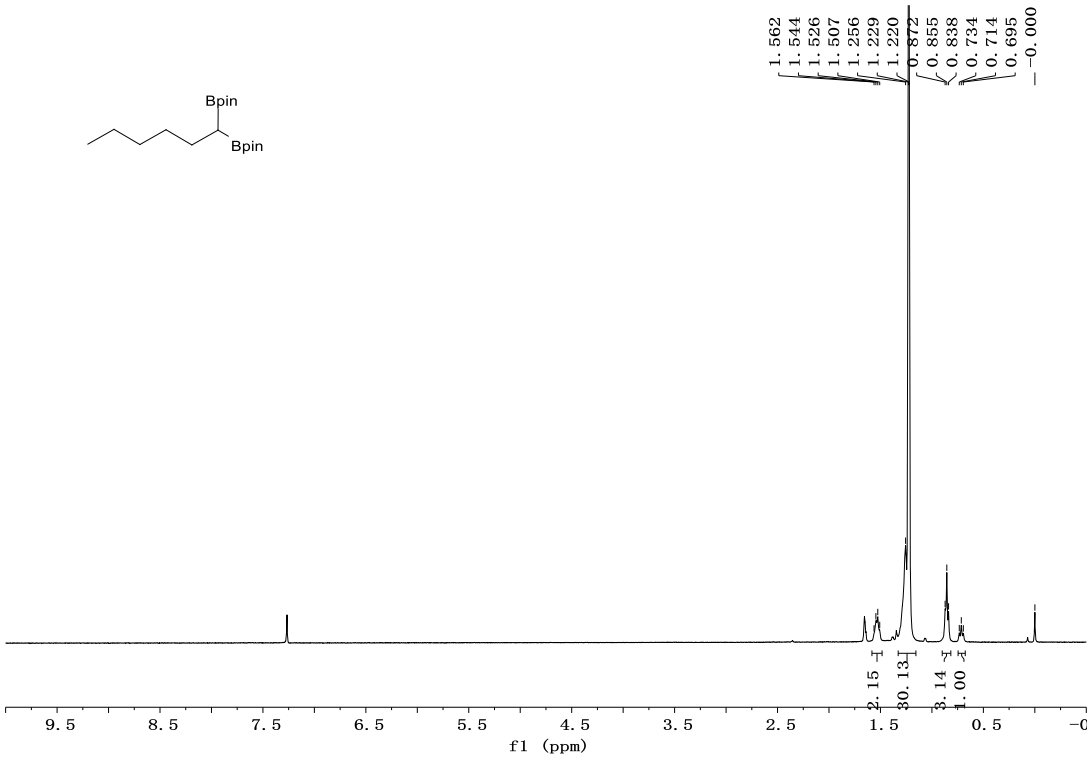
2-(1-(6-methoxynaphthalen-2-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3d**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 - 7.61 (m, 2H), 7.60 - 7.55 (m, 1H), 7.38 - 7.31 (m, 1H), 7.13 - 7.06 (m, 2H), 3.89 (s, 3H), 2.57 (q, *J* = 7.6 Hz, 1H), 1.41 (d, *J* = 7.6 Hz, 3H), 1.21 (s, 6H), 1.19 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.9, 140.1, 132.6, 129.3, 128.9, 127.6, 126.6, 125.1, 118.3, 105.5, 83.3, 55.2, 24.6(0), 24.5(6), 16.9 ppm. HRMS (ESI) calcd for $C_{19}H_{25}{}^{10}BO_3$ $[M]^+$: 311.1933; found: 311.1932.

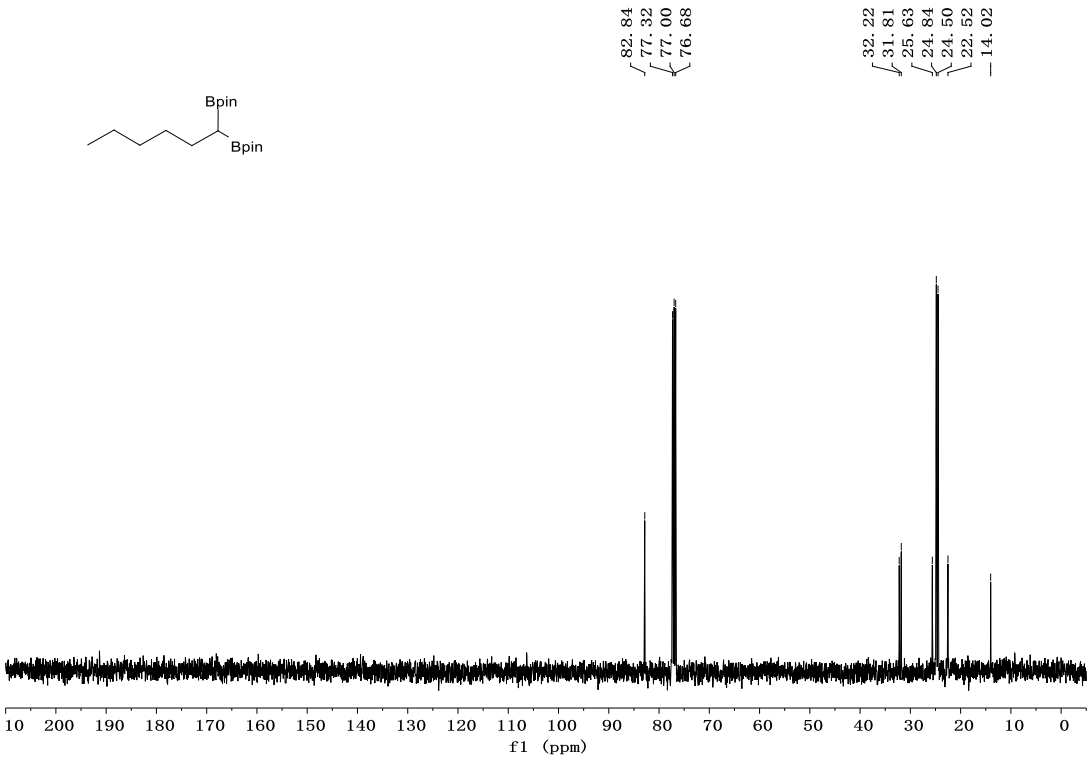


2-((*R*)-4-((3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-methoxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentyl)quinoline (**3e**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 - 8.00 (m, 2H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.72 - 7.62 (m, 1H), 7.54 - 7.43 (m, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 3.35 (s, 3H), 3.22-3.08 (m, 1H), 3.03 - 2.82 (m, 2 H), 1.96 - 1.51 (m, 11H), 1.45 - 0.98 (m, 17H), 0.93 - 0.88 (m, 6H), 0.62 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.1, 147.8, 136.1, 129.3, 128.7, 127.4, 126.6, 125.6, 121.3, 80.4, 56.4, 56.0, 55.5, 42.6, 42.0, 40.2, 40.1, 39.8, 35.7(9), 35.7(7), 35.7, 35.2, 34.8, 32.7, 28.2, 27.3, 26.7, 26.4, 24.2, 23.4, 20.7, 18.6, 12.0 ppm. HRMS (ESI) calcd for $C_{34}H_{49}NO$ $[M]^+$: 487.3814; found: 487.3813.

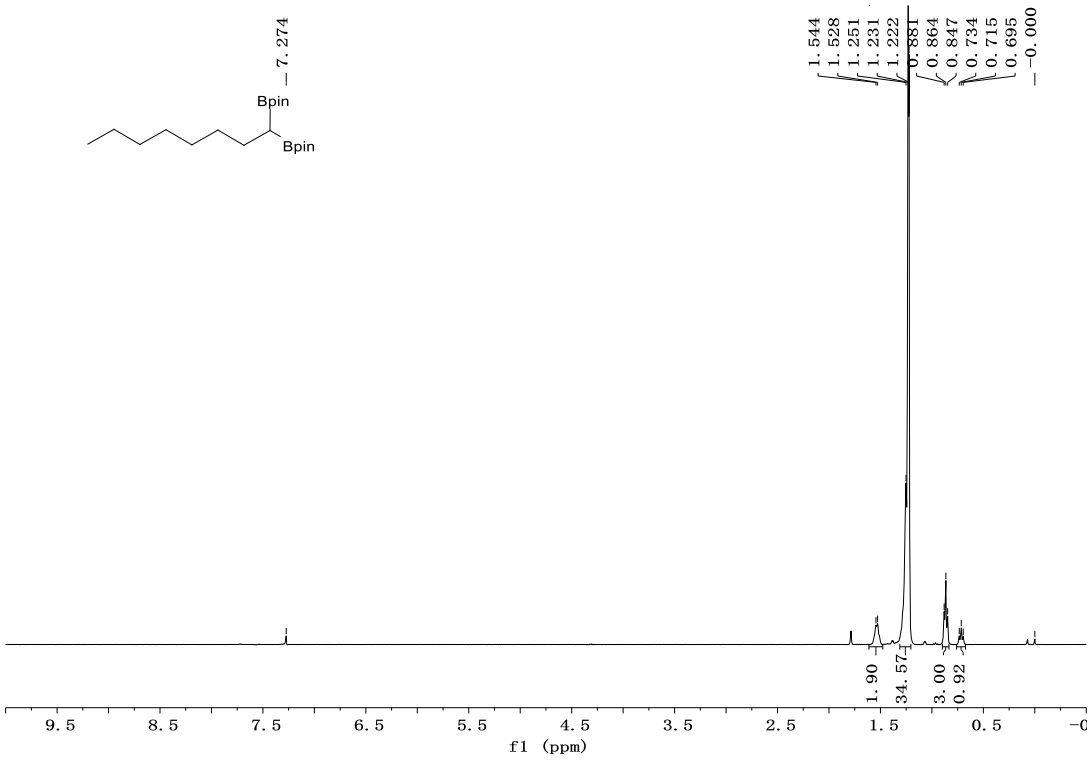
VII. Copies of Products ^{1}H NMR and ^{13}C NMR

2a





2b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0.695
-0.000
1.90
34.57
3.00
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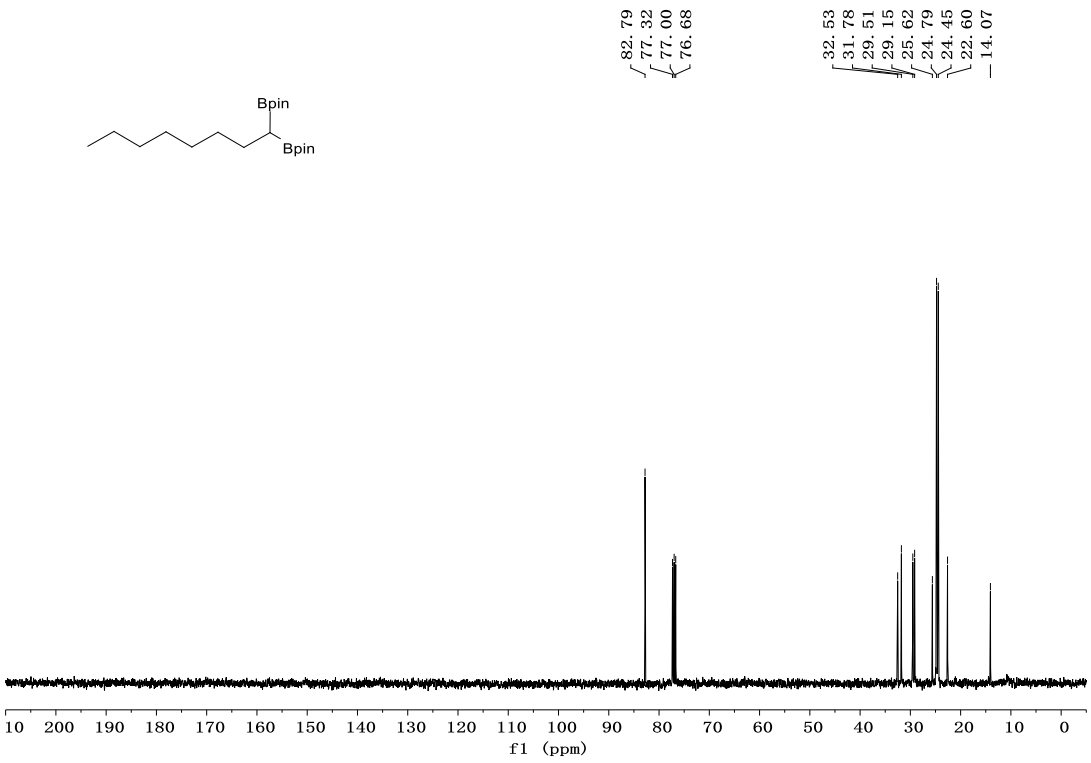
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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Bpin
Bpin
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200
190
180
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70
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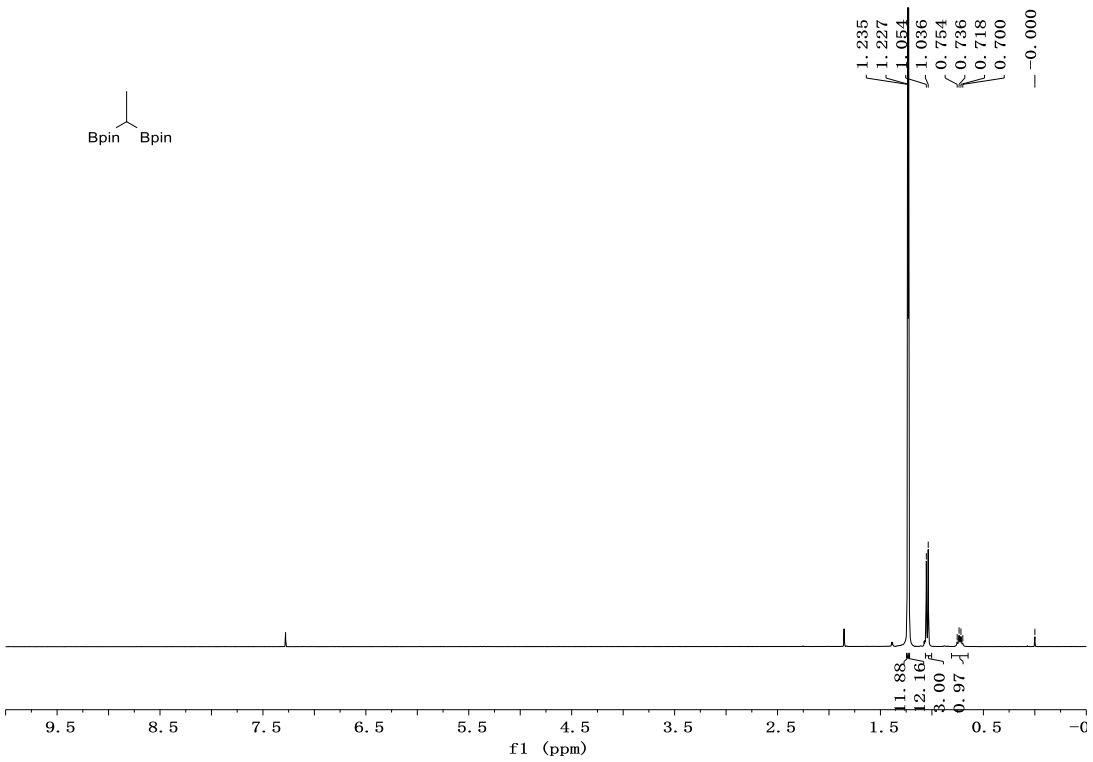
50
40
30
20
10
0
f1 (ppm)

2c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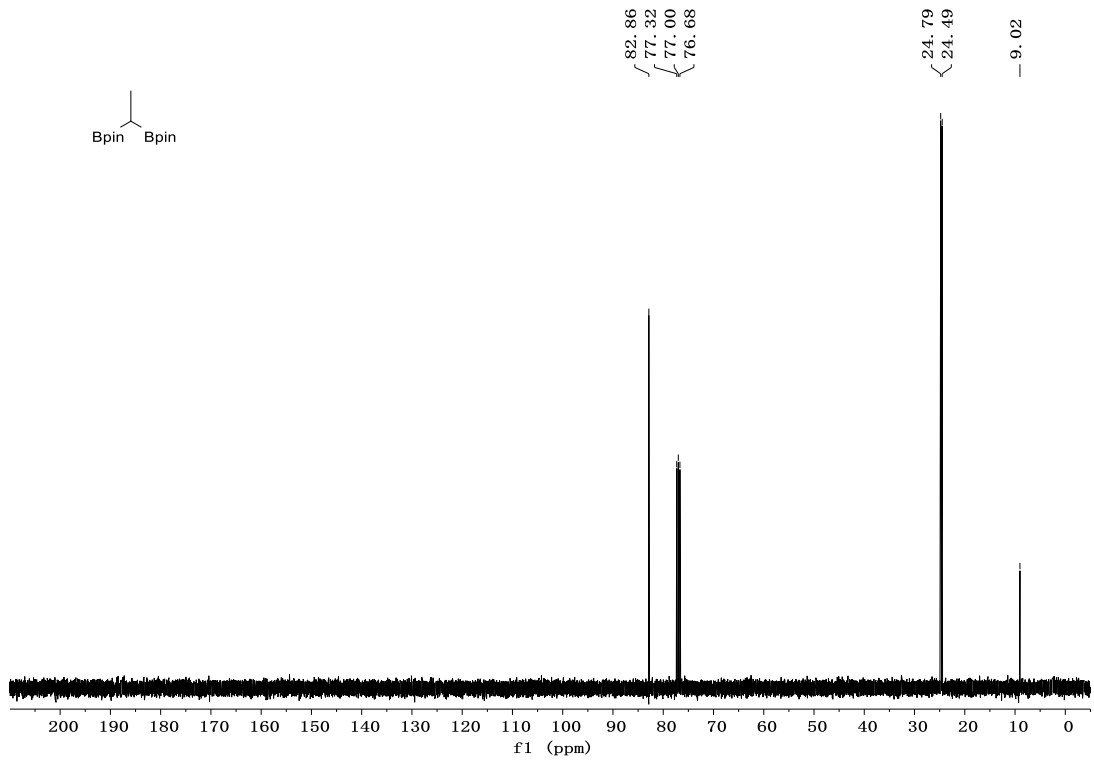
3.00
0.97
9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5
f1 (ppm)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24.79
24.49
9.02
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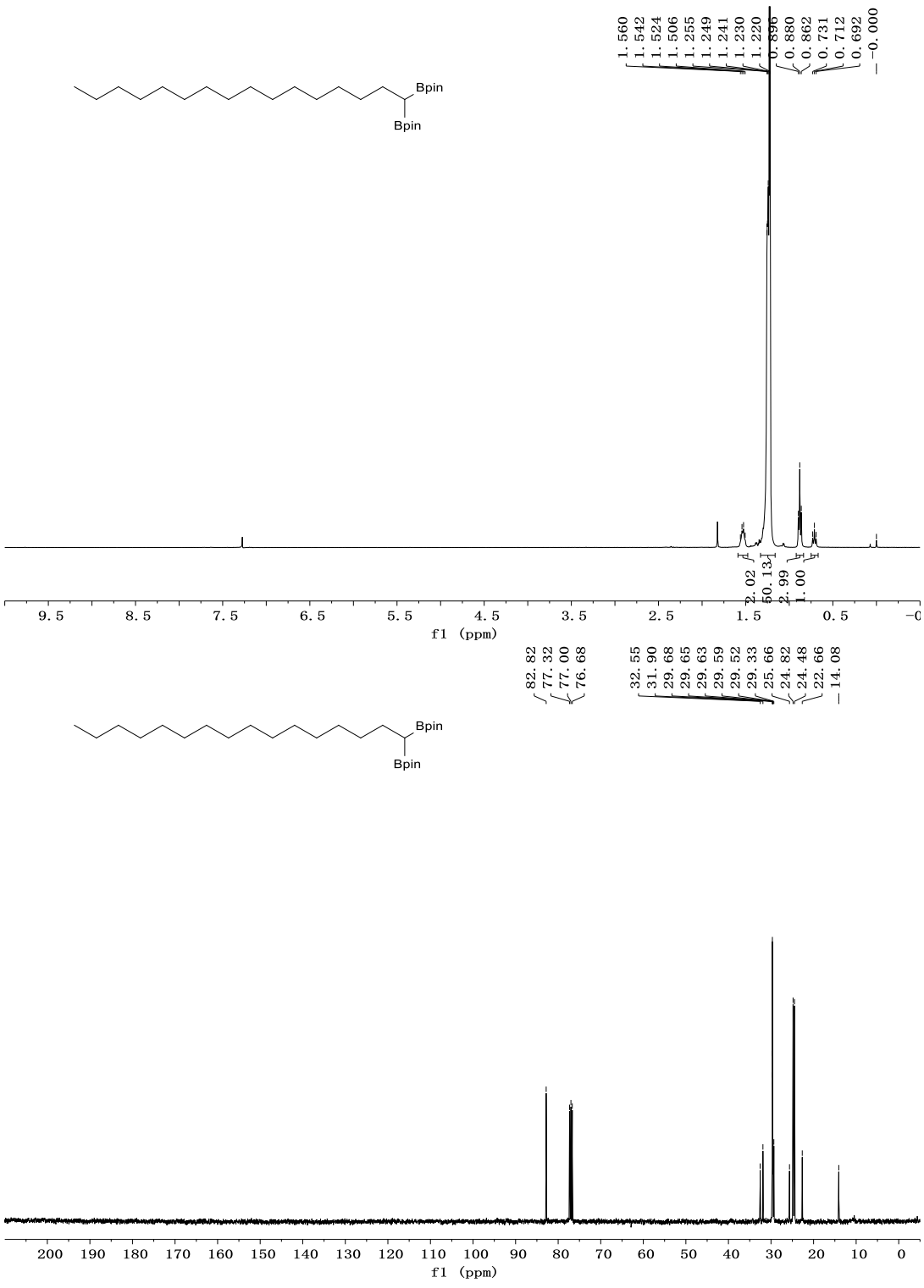
f1 (ppm)

2d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0.712
0.692
-0.000
2.02
50.13
2.99
1.00
9.5
8.5
7.5
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5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)
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77.00
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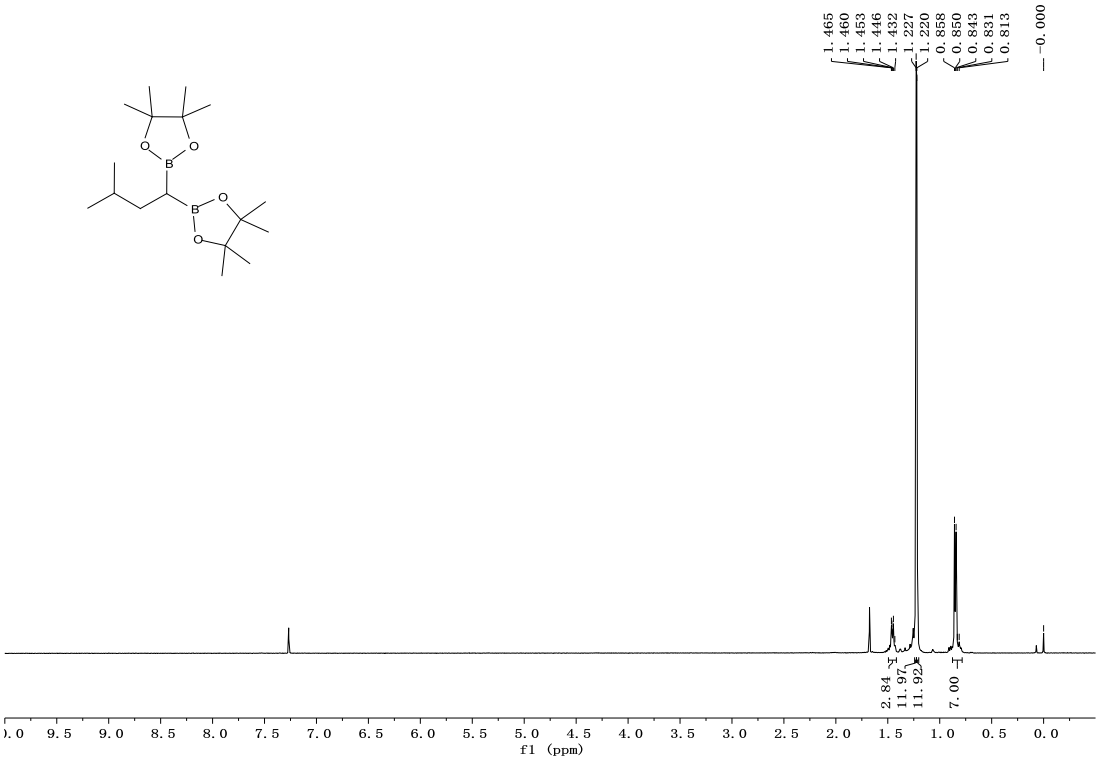
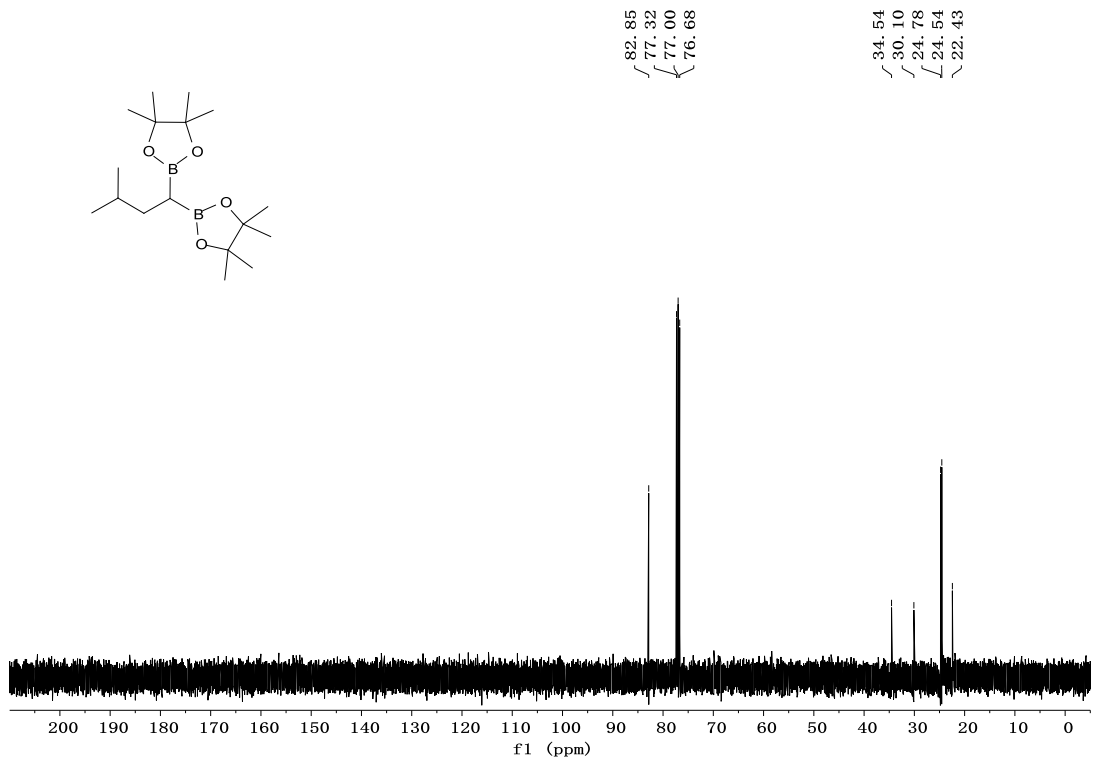
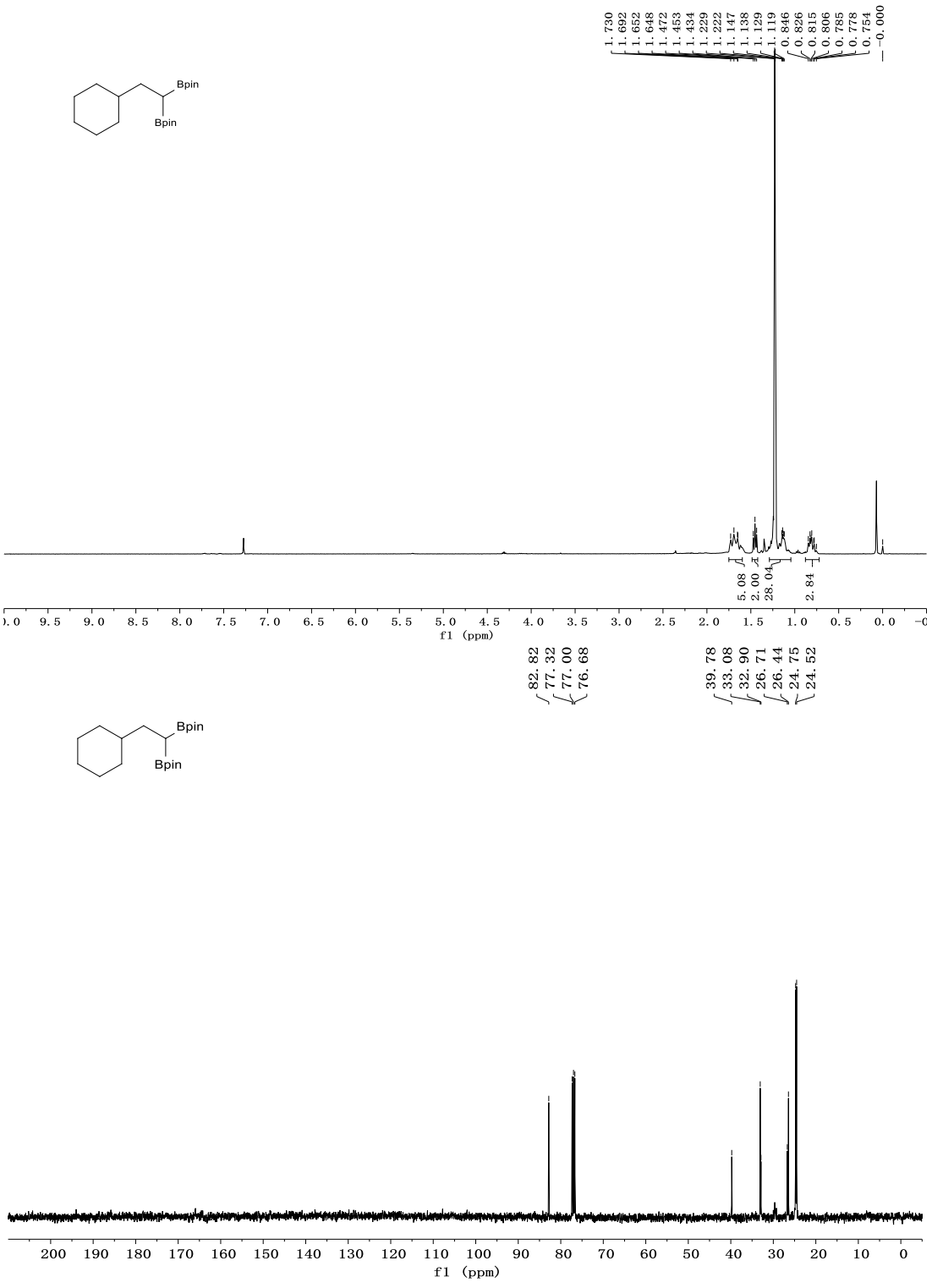
32.55
31.90
29.68
29.65
29.63
29.59
29.52
29.33
25.66
24.82
24.48
22.66
14.08
Bpin
Bpin
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2e

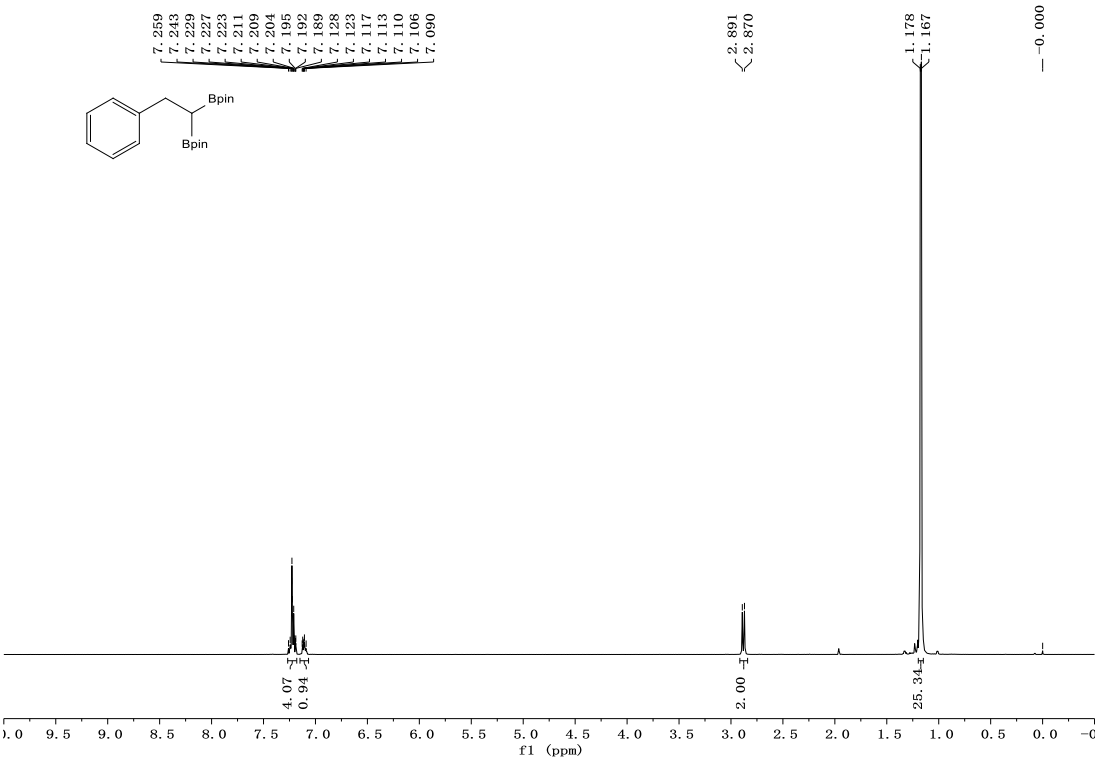

1.465
1.460
1.453
1.446
1.432
1.227
1.220
0.858
0.850
0.843
0.831
0.813
-0.000
2.84
11.97
11.92
7.00
f1 (ppm)

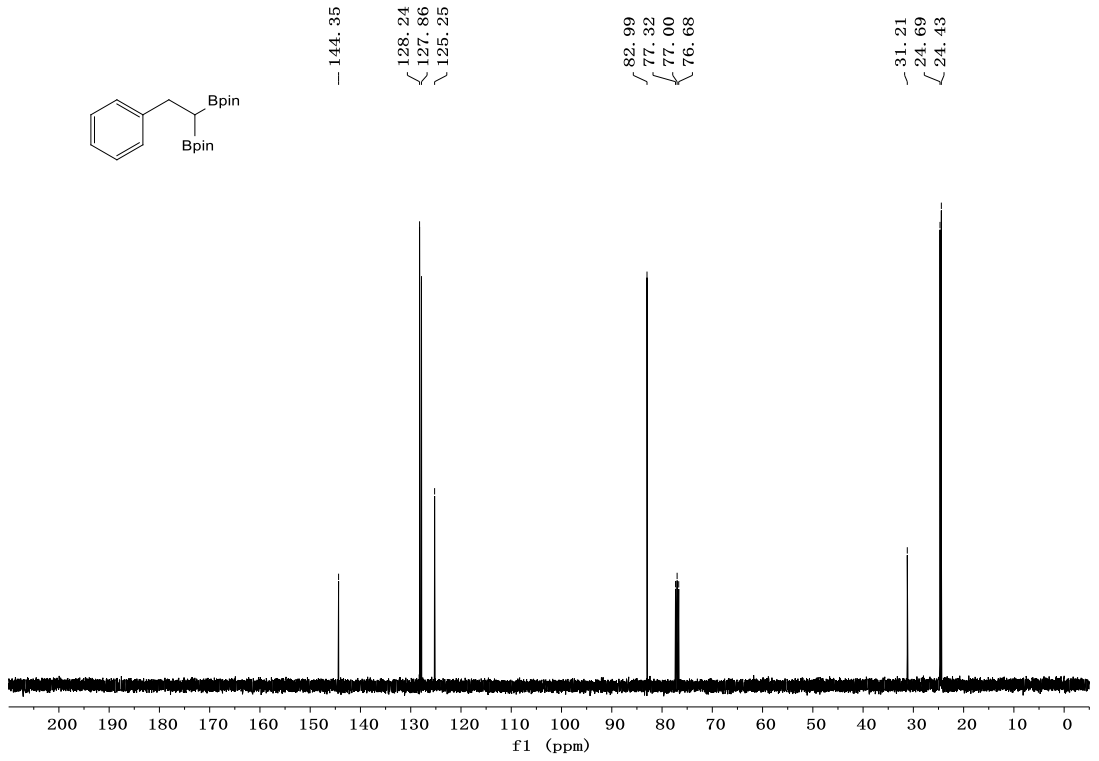

82.85
77.32
77.00
76.68
34.54
30.10
24.78
24.54
22.43
f1 (ppm)

2f

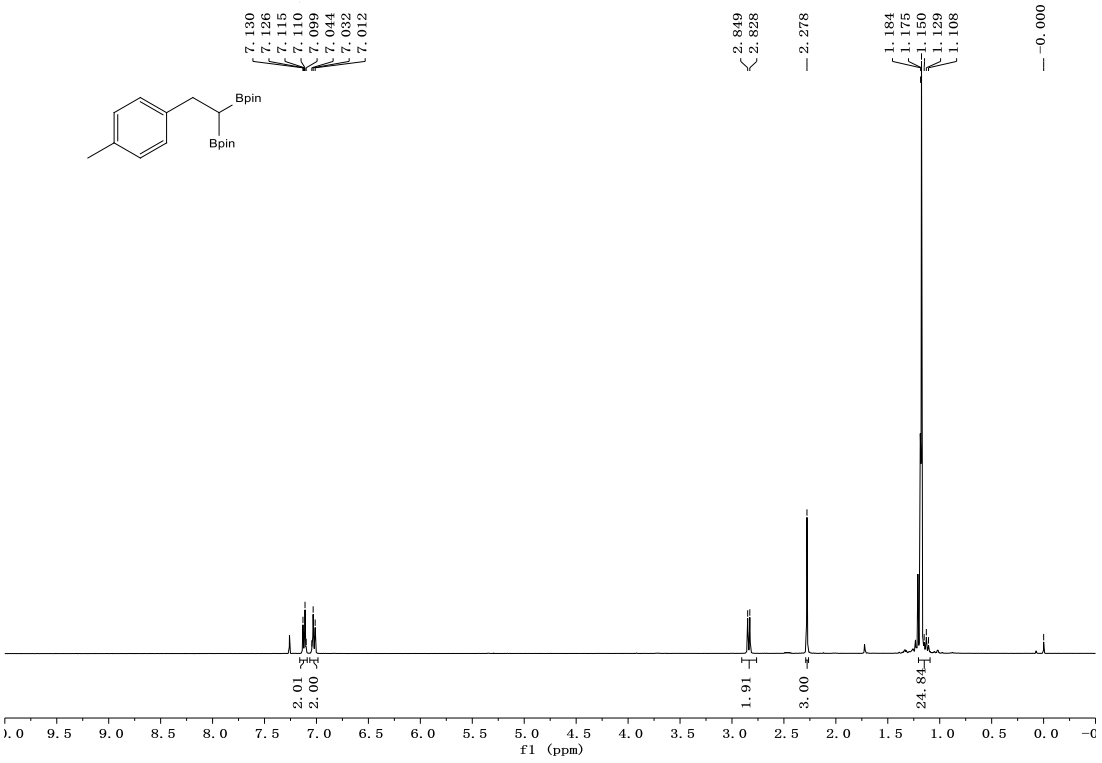

Bpin
Bpin
1.730
1.692
1.652
1.648
1.472
1.453
1.434
1.229
1.222
1.147
1.138
1.129
1.119
0.846
0.826
0.815
0.806
0.785
0.778
0.754
-0.000
5.08
2.00
28.04
2.84
f1 (ppm)
82.82
77.32
77.00
76.68
39.78
33.08
32.90
26.71
26.44
24.75
24.52
Bpin
Bpin
f1 (ppm)

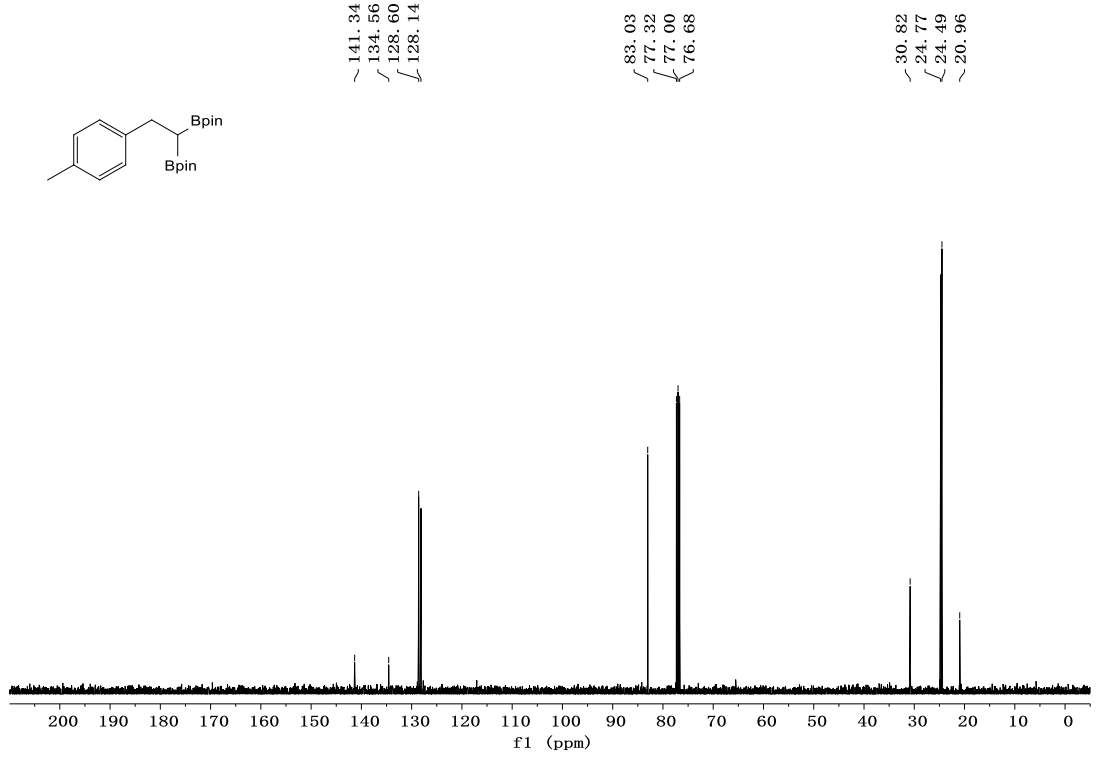
2ga


7.259
7.243
7.229
7.227
7.223
7.211
7.209
7.204
7.195
7.192
7.189
7.128
7.123
7.117
7.113
7.110
7.106
7.090
2.891
2.870
1.178
1.167
0.000
Bpin
Bpin
4.07
0.94
2.00
25.34
f1 (ppm)

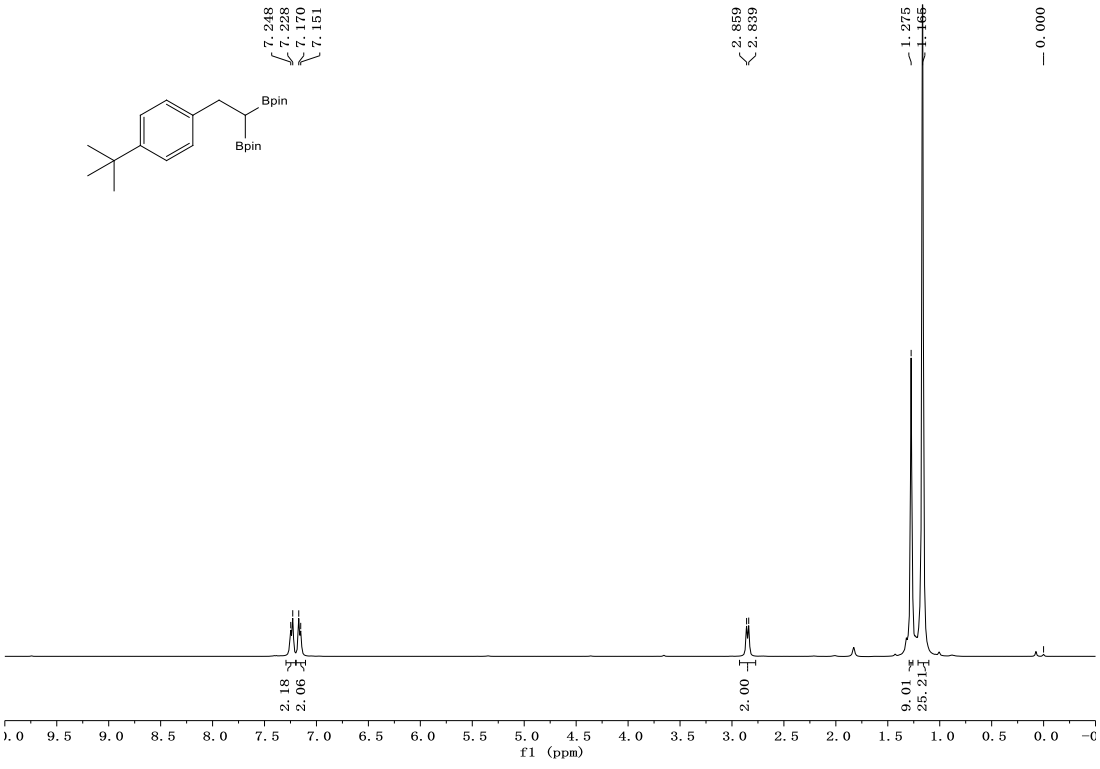

144.35
128.24
127.86
125.25
82.99
77.32
77.00
76.68
31.21
24.69
24.43
Bpin
Bpin
f1 (ppm)

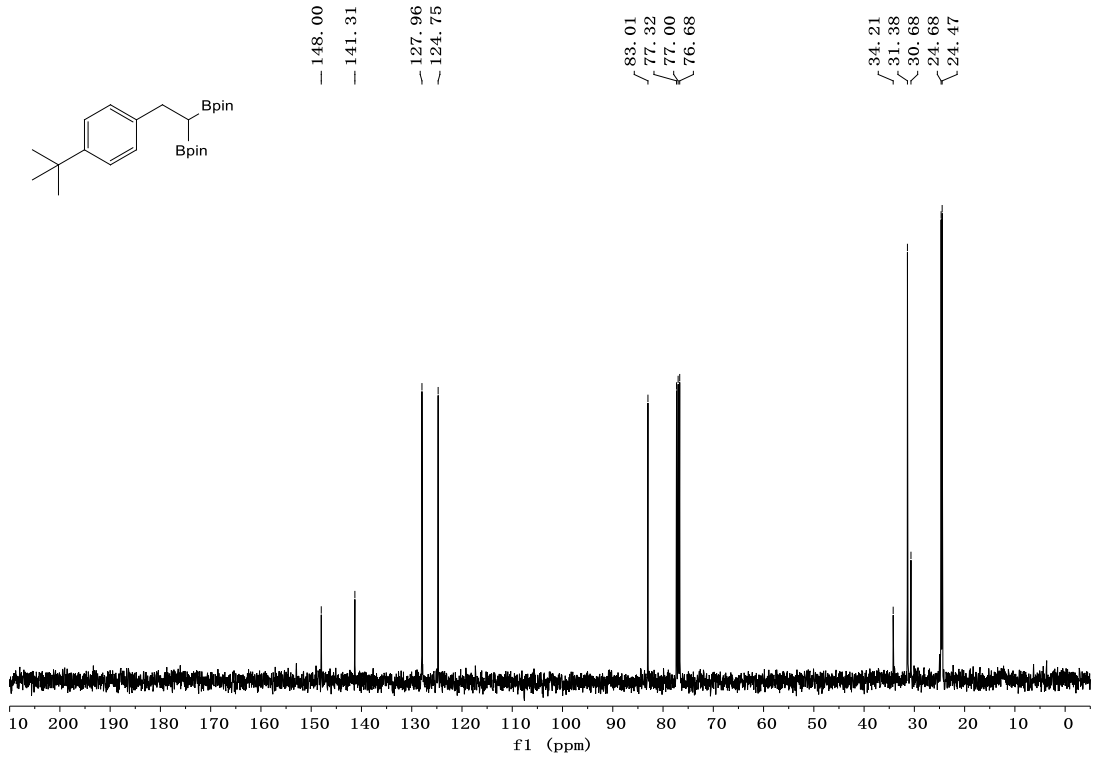
2gb


7.130
7.126
7.115
7.110
7.099
7.044
7.032
7.012
2.849
2.828
2.278
1.184
1.175
1.150
1.129
1.108
-0.000
Bpin
Bpin
2.01
2.00
1.91
3.00
24.84
f1 (ppm)

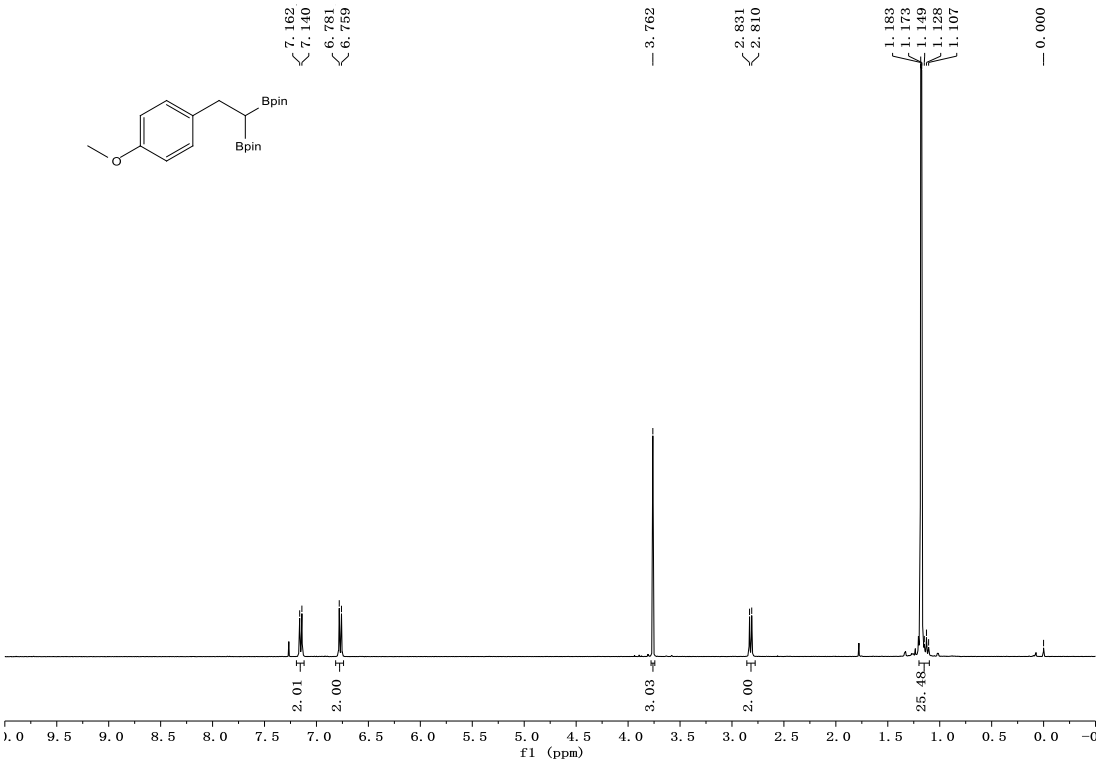

141.34
134.56
128.60
128.14
83.03
77.32
77.00
76.68
30.82
24.77
24.49
20.96
Bpin
Bpin
f1 (ppm)

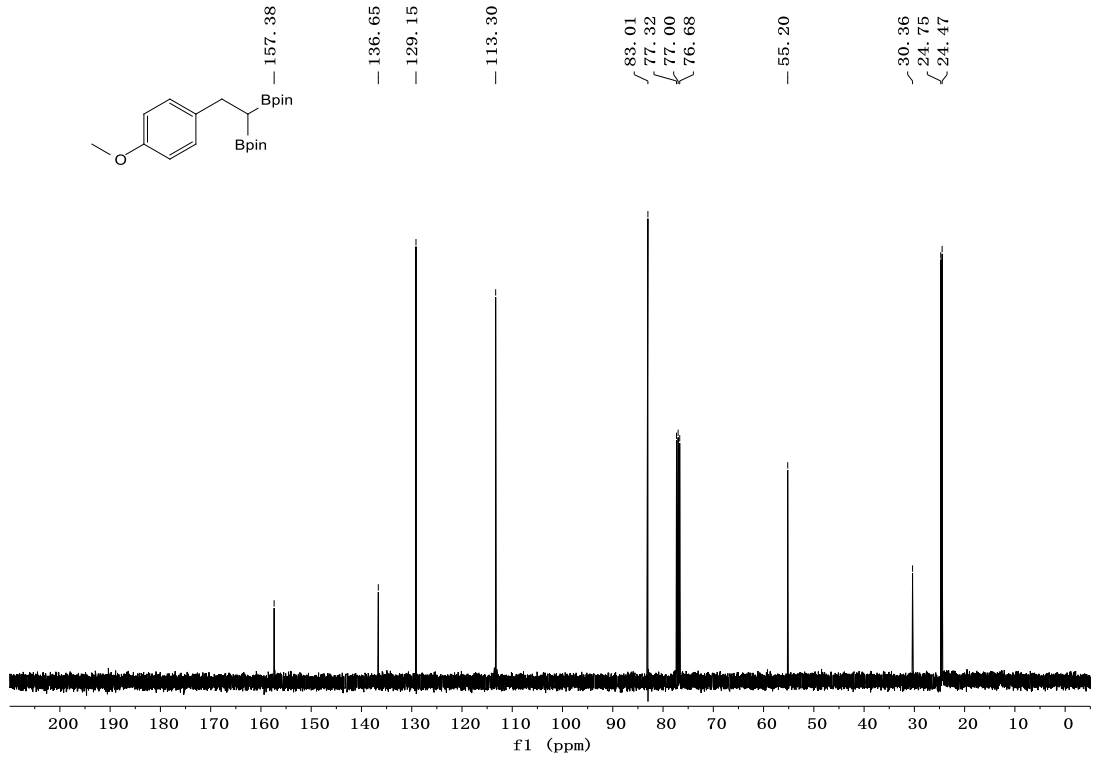
2gc


7.248
7.228
7.170
7.151
2.859
2.839
1.275
1.165
0.000
Bpin
Bpin
2.18
2.06
2.00
9.01
25.21
f1 (ppm)

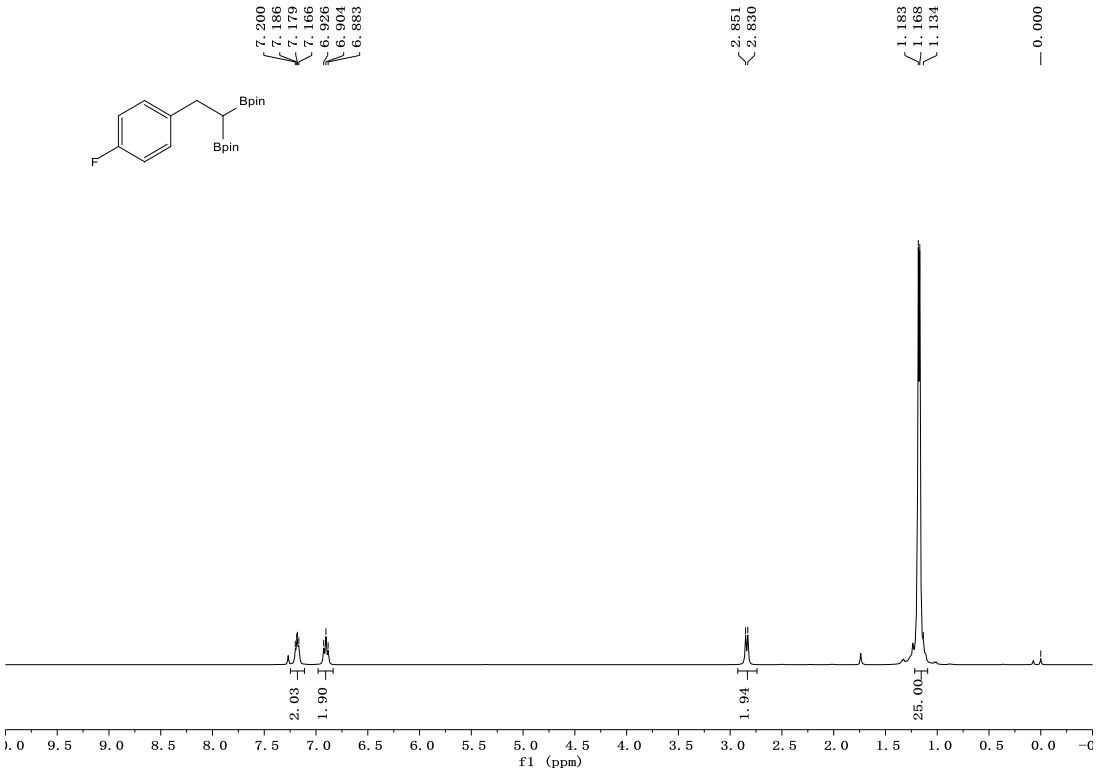

148.00
141.31
127.96
124.75
83.01
77.32
77.00
76.68
34.21
31.38
30.68
24.68
24.47
Bpin
Bpin
f1 (ppm)

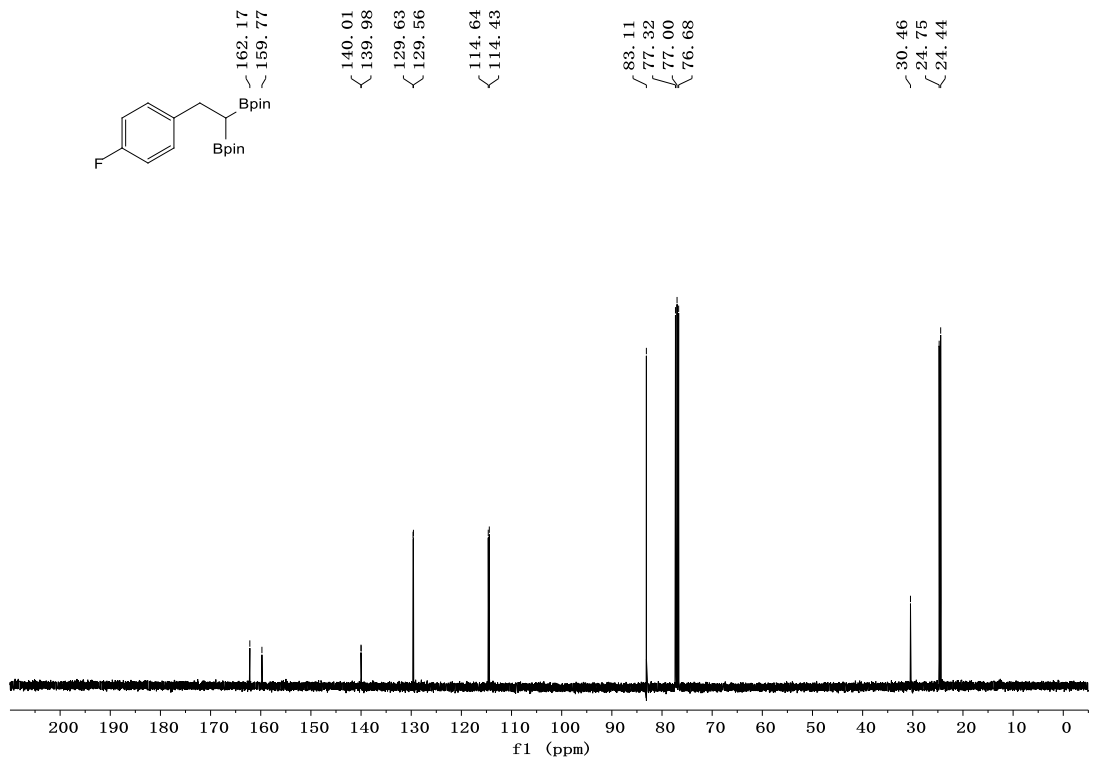
2gd


7.162
7.140
6.781
6.759
3.762
2.831
2.810
1.183
1.173
1.149
1.128
1.107
0.000
Bpin
Bpin
O
2.01
2.00
3.03
2.00
25.48
f1 (ppm)

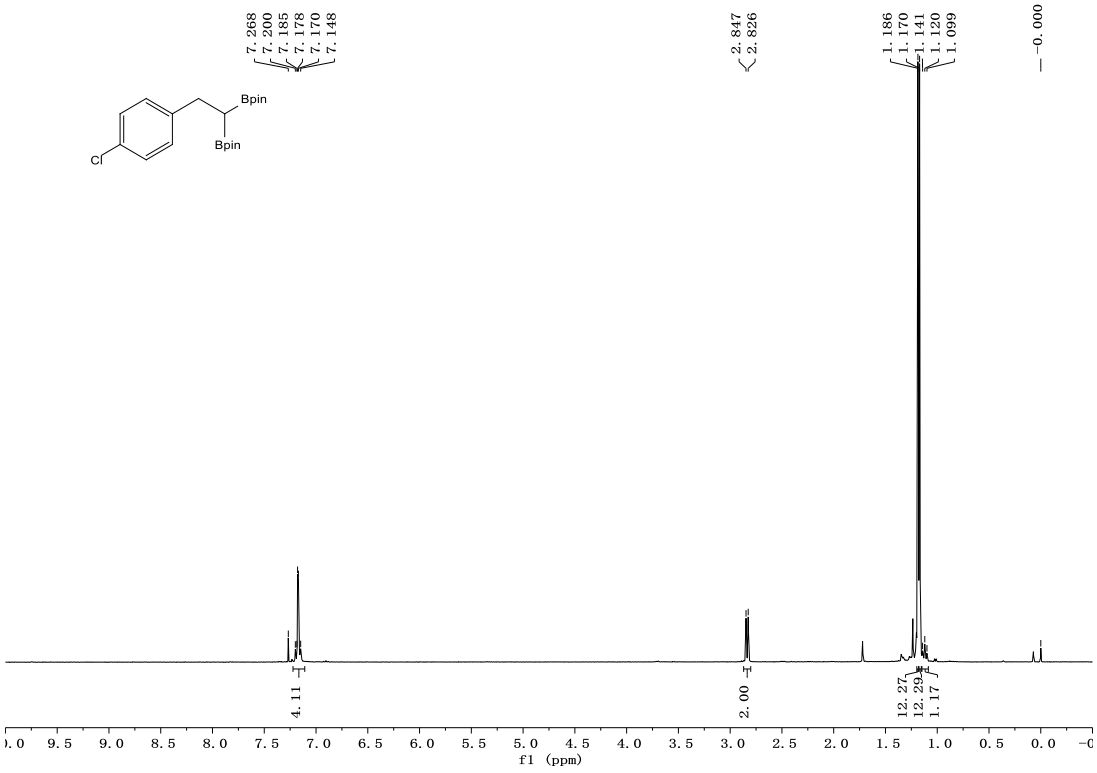

157.38
136.65
129.15
113.30
83.01
77.32
77.00
76.68
55.20
30.36
24.75
24.47
Bpin
Bpin
O
f1 (ppm)

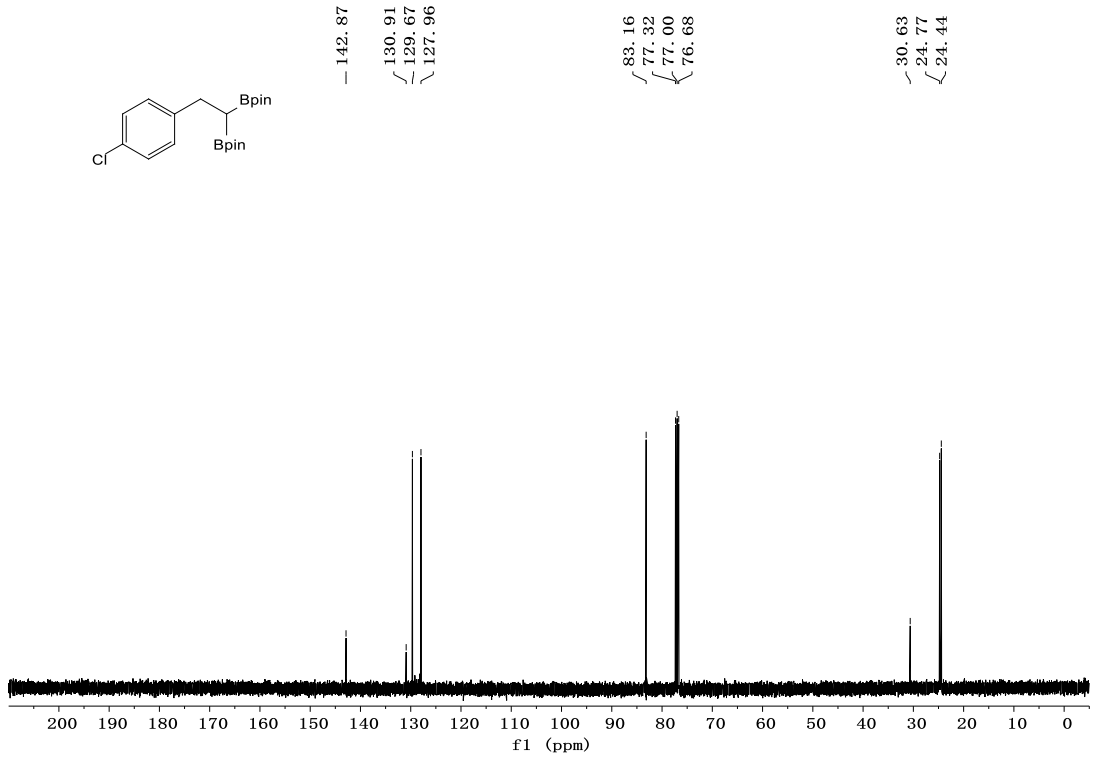
2ge


7.200
7.186
7.179
7.166
6.926
6.904
6.883
2.851
2.830
1.183
1.168
1.134
0.000
Bpin
Bpin
F
2.03
1.90
1.94
25.00
f1 (ppm)

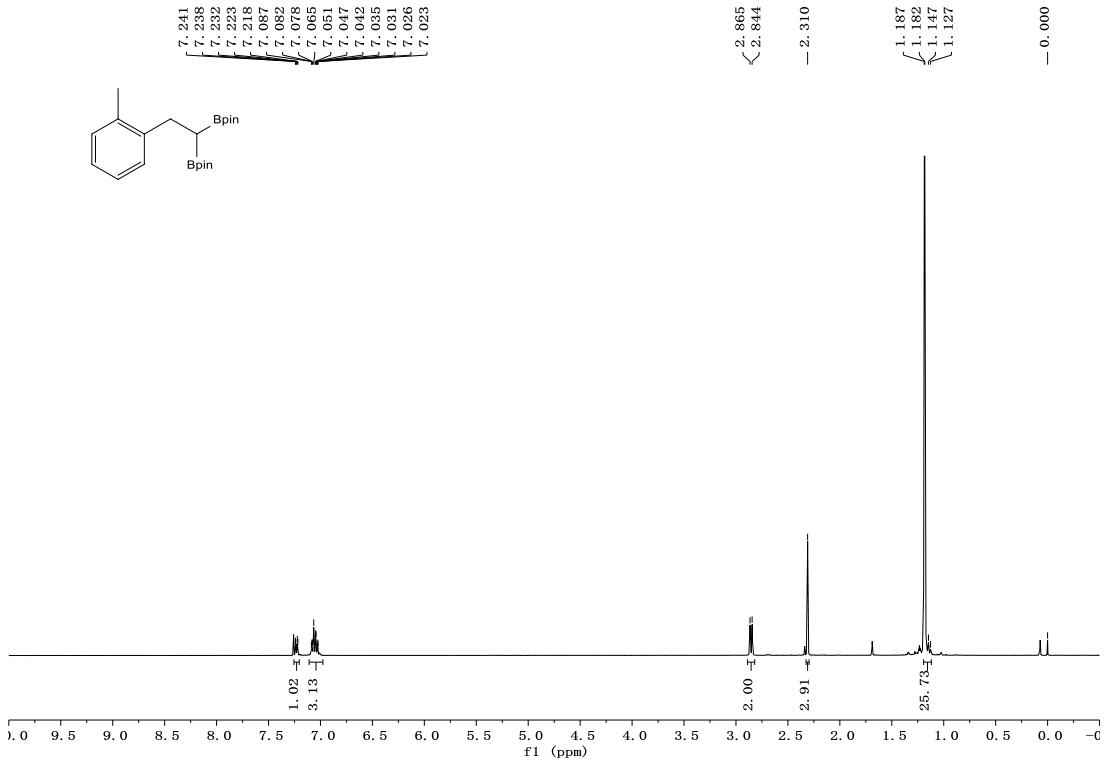

162.17
159.77
140.01
139.98
129.63
129.56
114.64
114.43
83.11
77.32
77.00
76.68
30.46
24.75
24.44
Bpin
Bpin
F
f1 (ppm)

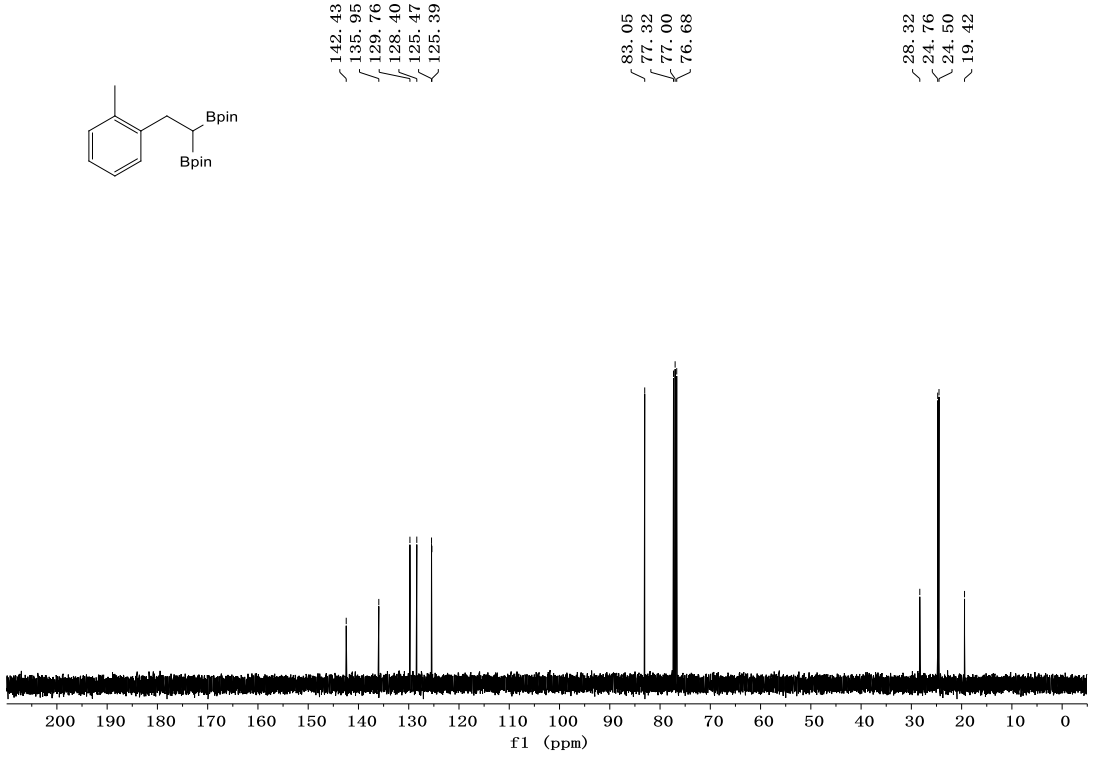
2gf


7.268
7.200
7.185
7.178
7.170
7.148
2.847
2.826
1.186
1.170
1.141
1.120
1.099
0.000
Bpin
Bpin
Cl
4.11
2.00
12.27
12.29
1.17
f1 (ppm)

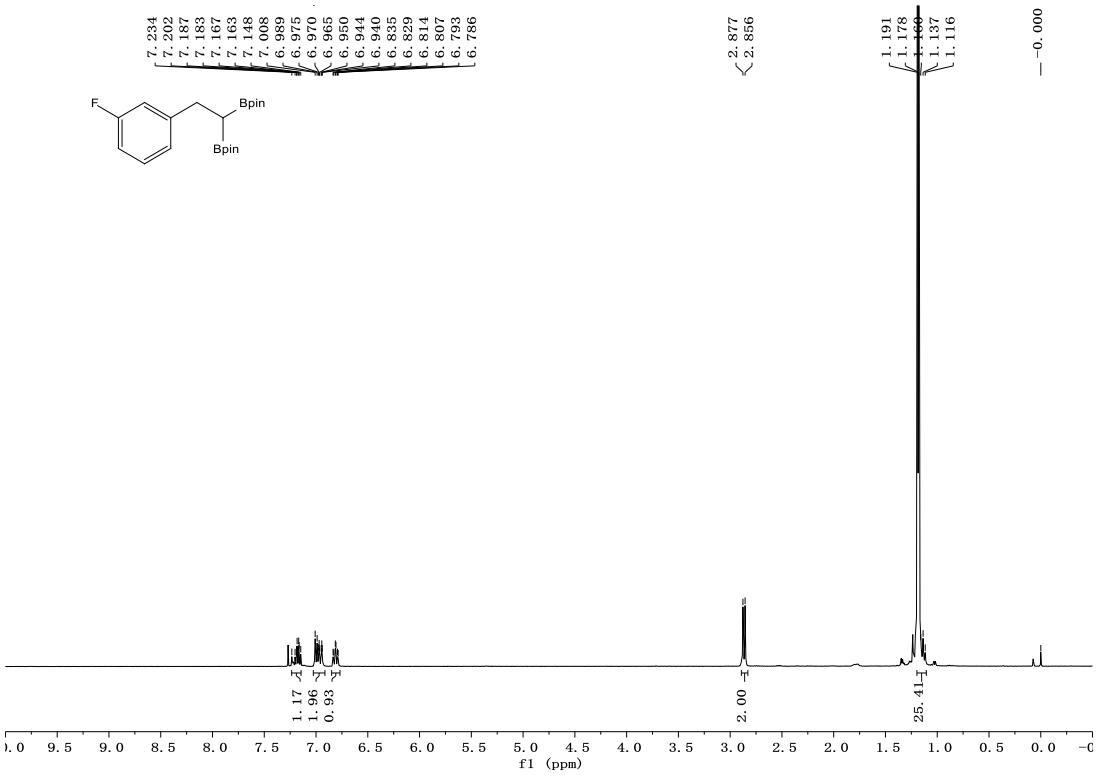

142.87
130.91
129.67
127.96
83.16
77.32
77.00
76.68
30.63
24.77
24.44
Bpin
Bpin
Cl
f1 (ppm)

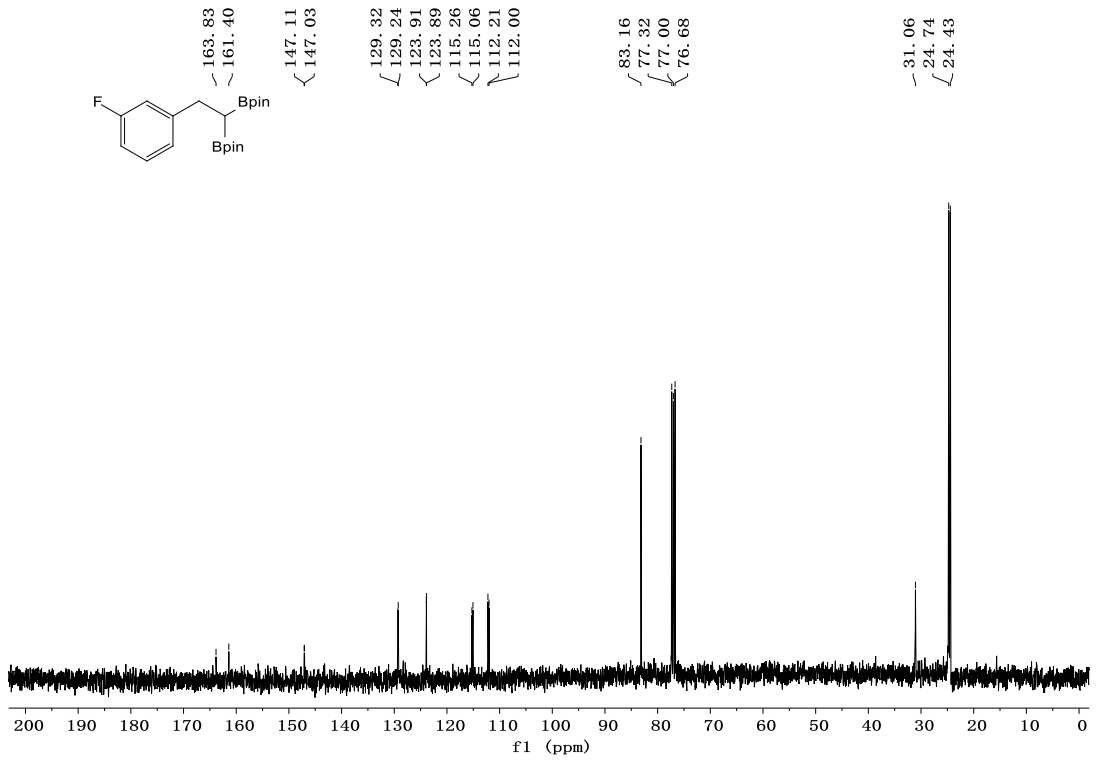
2gg


7.241
7.238
7.232
7.223
7.218
7.087
7.082
7.078
7.065
7.051
7.047
7.042
7.035
7.031
7.026
7.023
2.865
2.844
2.310
1.187
1.182
1.147
1.127
0.000
Bpin
Bpin
1.02
3.13
2.00
2.91
25.73
f1 (ppm)

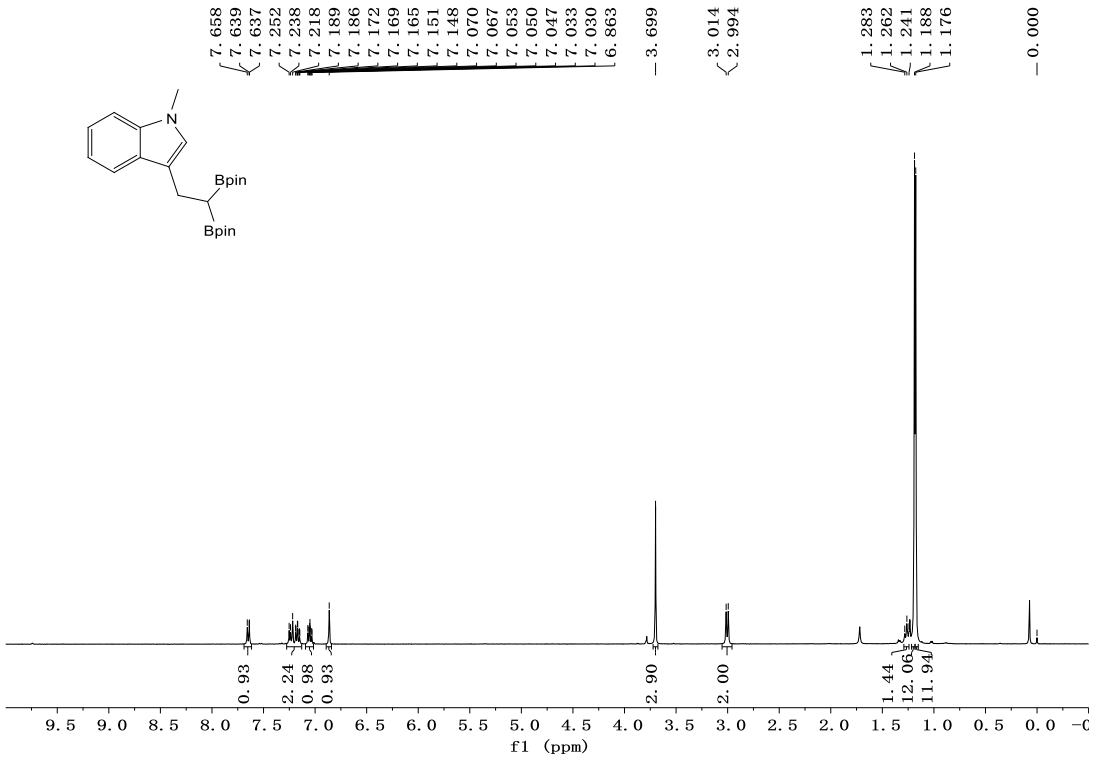

142.43
135.95
129.76
128.40
125.47
125.39
83.05
77.32
77.00
76.68
28.32
24.76
24.50
19.42
Bpin
Bpin
f1 (ppm)

2gh


7.234
7.202
7.187
7.183
7.167
7.163
7.148
7.008
6.989
6.975
6.970
6.965
6.950
6.944
6.940
6.835
6.829
6.814
6.807
6.793
6.786
2.877
2.856
1.191
1.178
1.160
1.137
1.116
0.000
F
Bpin
Bpin
1.17
1.96
0.93
2.00
25.41
f1 (ppm)


163.83
161.40
147.11
147.03
129.32
129.24
123.91
123.89
115.26
115.06
112.21
112.00
83.16
77.32
77.00
76.68
31.06
24.74
24.43
F
Bpin
Bpin
f1 (ppm)

2h


7.658
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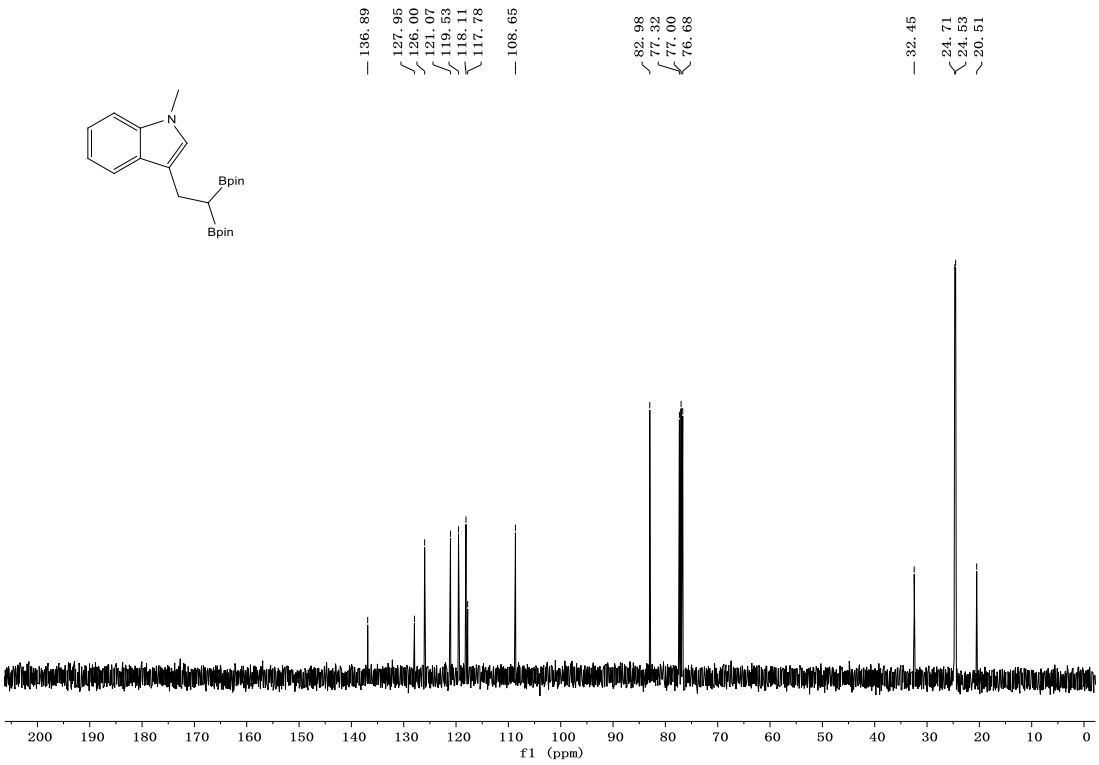
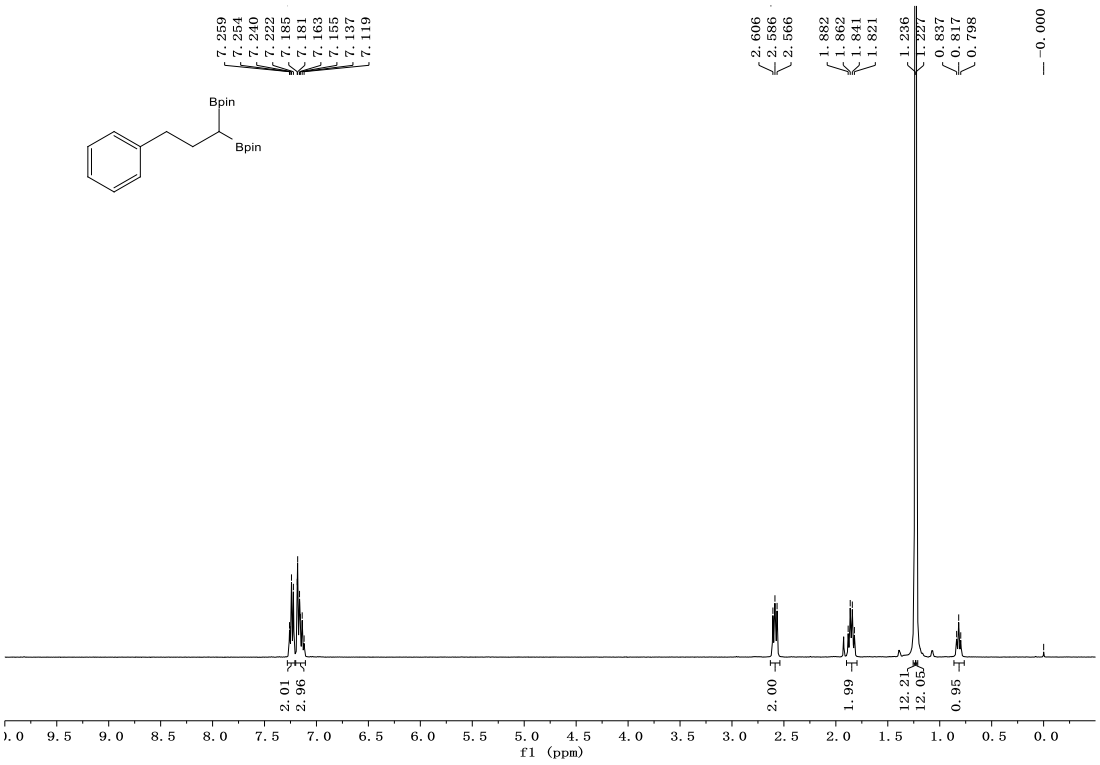
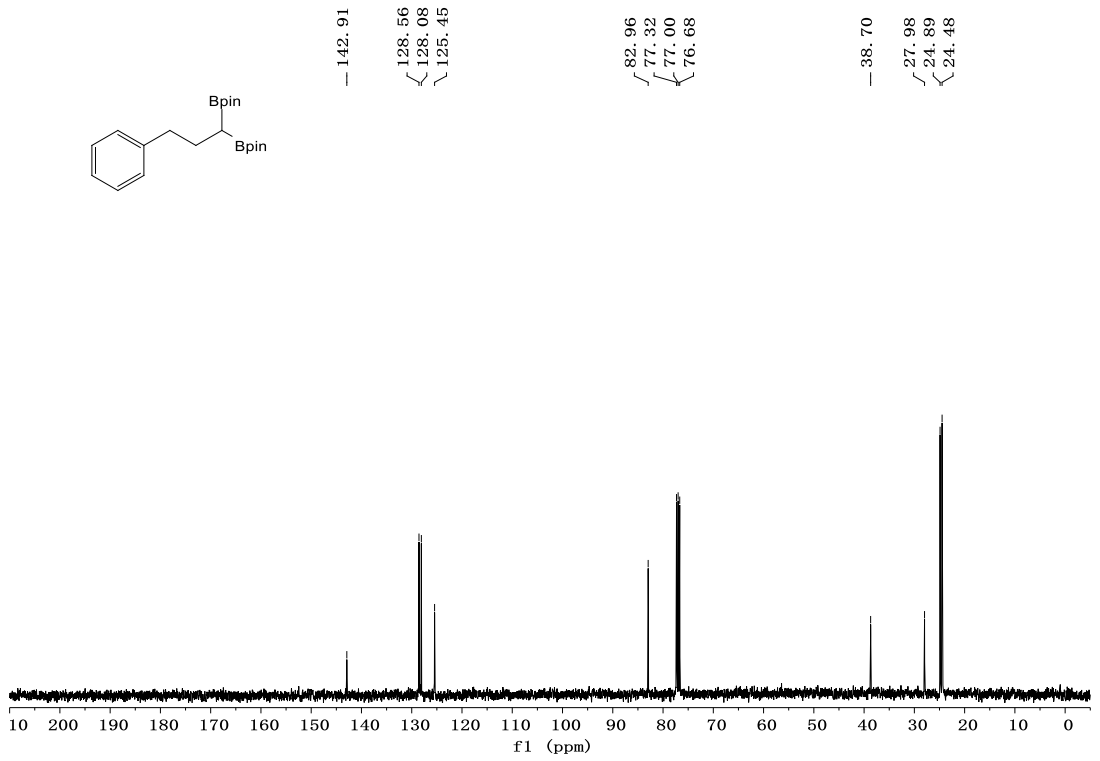
7.637
7.252
7.238
7.218
7.189
7.186
7.172
7.169
7.165
7.151
7.148
7.070
7.067
7.053
7.050
7.047
7.033
7.030
6.863
3.699
3.014
2.994
1.283
1.262
1.241
1.188
1.176
0.000
N
Bpin
Bpin
0.93
2.24
0.98
0.93
2.90
2.00
1.44
12.06
11.94
f1 (ppm)

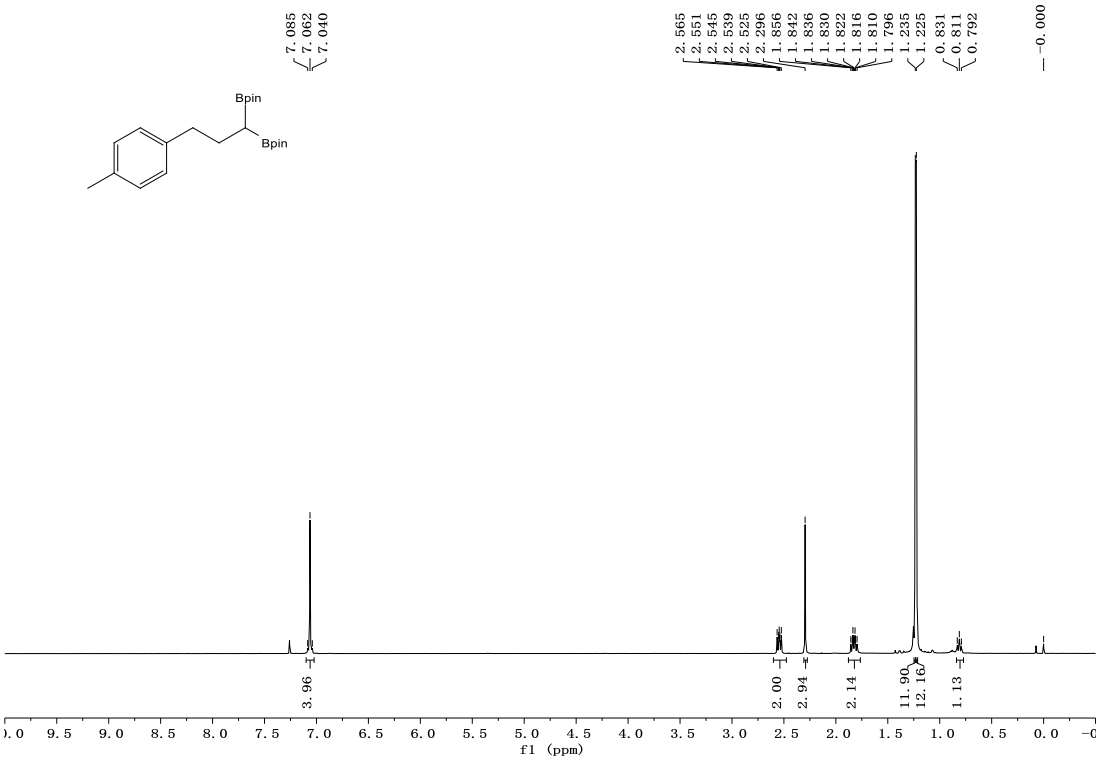

136.89
127.95
126.00
121.07
119.53
118.11
117.78
108.65
82.98
77.32
77.00
76.68
32.45
24.71
24.53
20.51
N
Bpin
Bpin
f1 (ppm)

2ia


7.259
7.254
7.240
7.222
7.185
7.181
7.163
7.155
7.137
7.119
2.606
2.586
2.566
1.882
1.862
1.841
1.821
1.236
1.227
0.837
0.817
0.798
-0.000
Bpin
Bpin
2.01
2.96
2.00
1.99
12.21
12.05
0.95
f1 (ppm)


142.91
128.56
128.08
125.45
82.96
77.32
77.00
76.68
38.70
27.98
24.89
24.48
Bpin
Bpin
f1 (ppm)

2ib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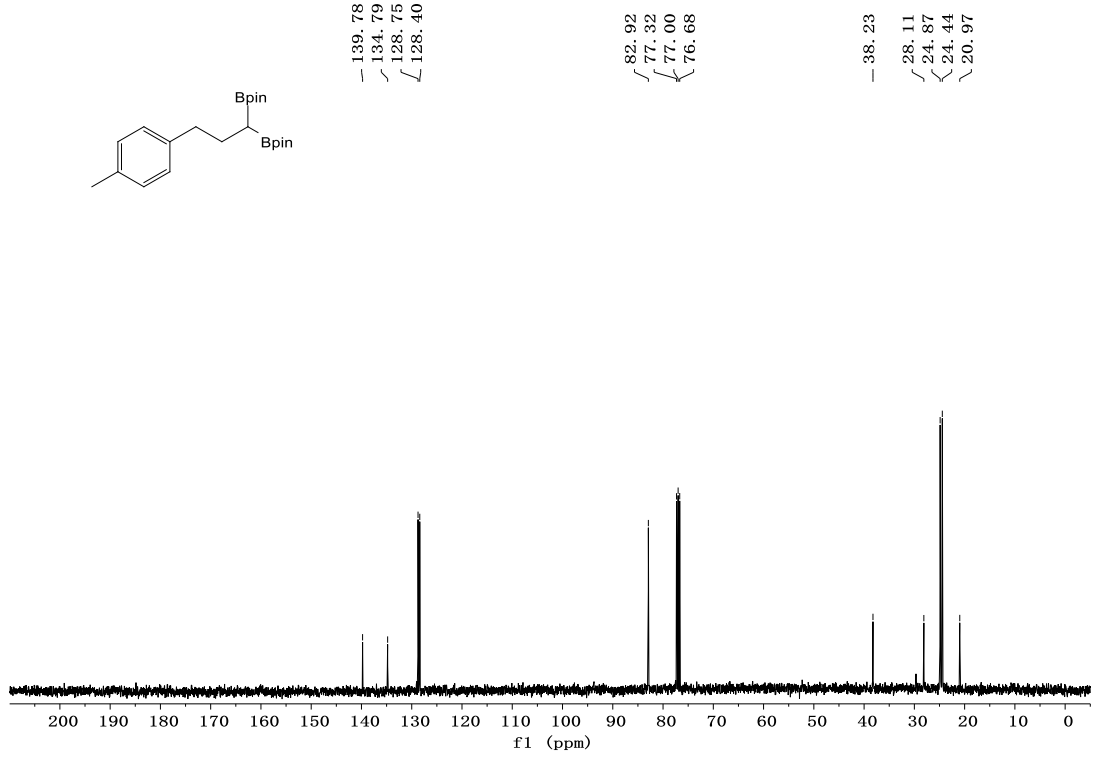
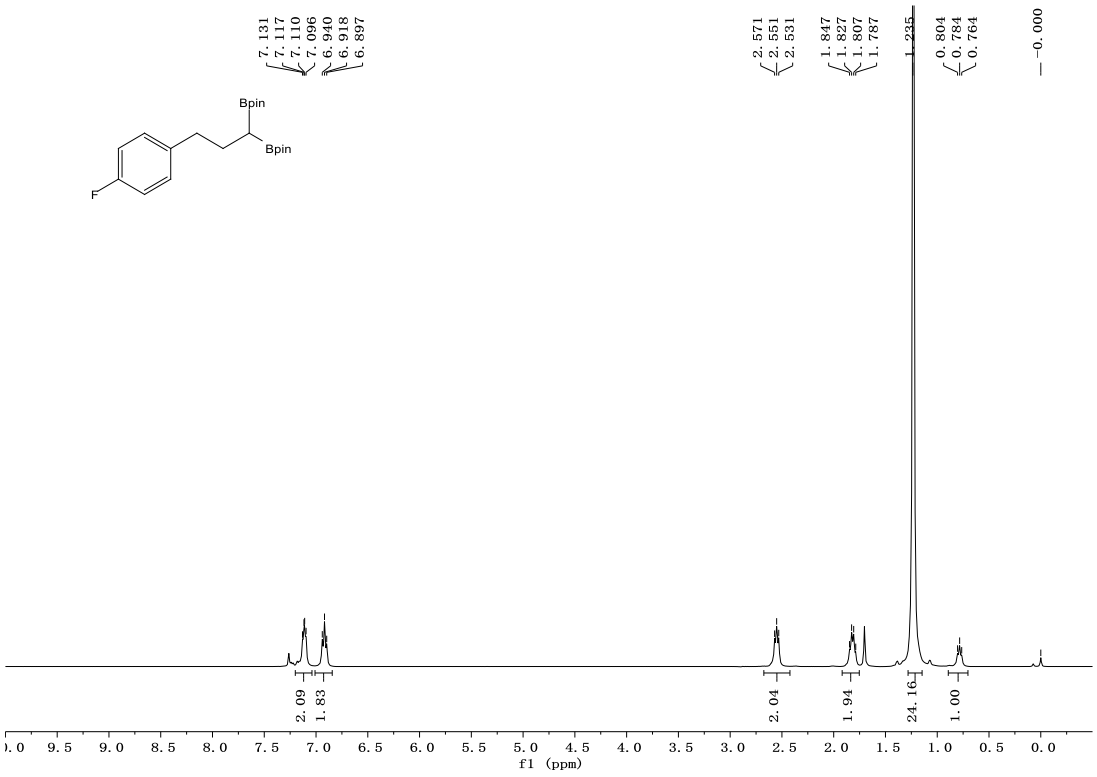
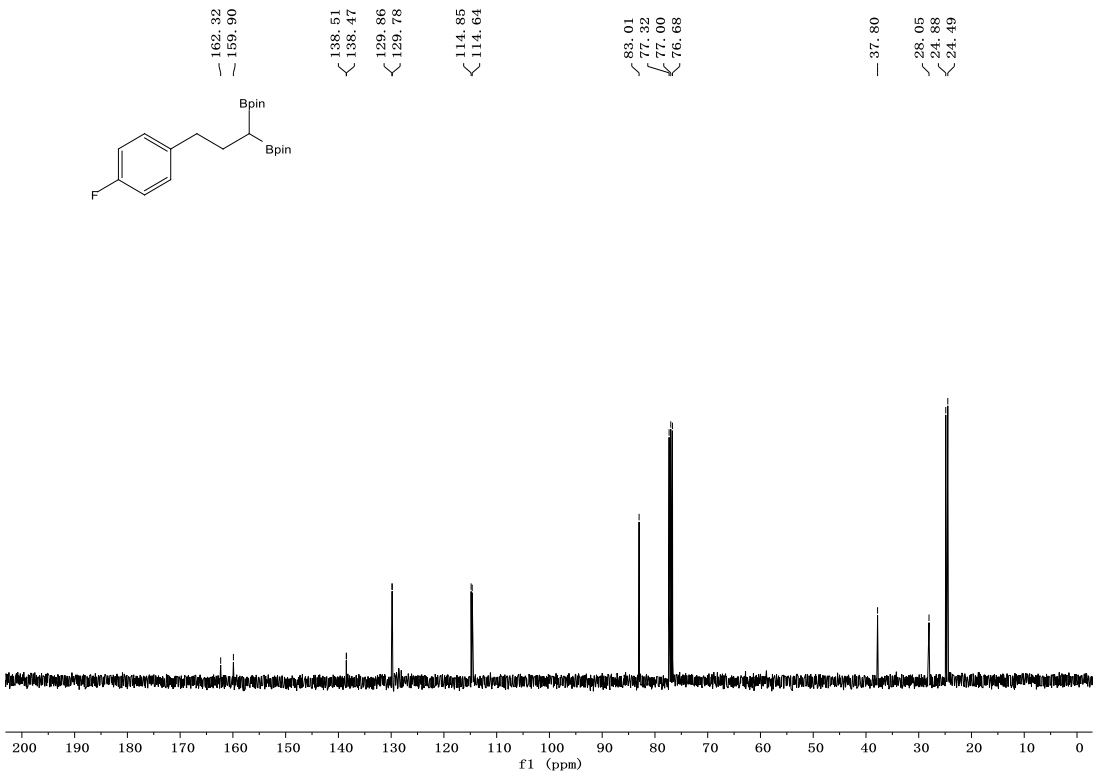
7.062
7.040
2.565
2.551
2.545
2.539
2.525
2.296
1.856
1.842
1.836
1.830
1.822
1.816
1.810
1.796
1.235
1.225
0.831
0.811
0.792
0.000
Bpin
Bpin
3.96
2.00
2.94
2.14
11.90
12.16
1.13
f1 (ppm)

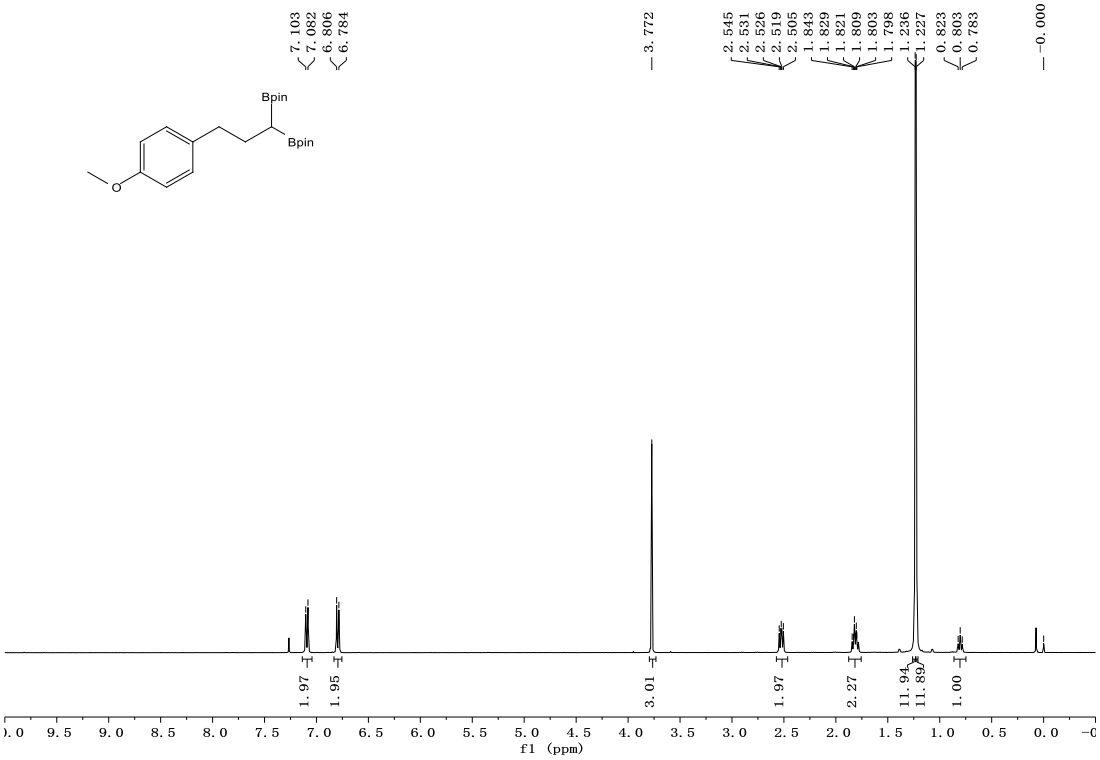

139.78
134.79
128.75
128.40
82.92
77.32
77.00
76.68
38.23
28.11
24.87
24.44
20.97
Bpin
Bpin
f1 (ppm)

2ic


7.131
7.117
7.110
7.096
6.940
6.918
6.897
2.571
2.551
2.531
1.847
1.827
1.807
1.787
1.235
0.804
0.784
0.764
-0.000
Bpin
Bpin
F
2.09
1.83
2.04
1.94
24.16
1.00
f1 (ppm)


162.32
159.90
138.51
138.47
129.86
129.78
114.85
114.64
83.01
77.32
77.00
76.68
37.80
28.05
24.88
24.49
Bpin
Bpin
F
f1 (ppm)

2id


7.103
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6.806
6.784
3.772
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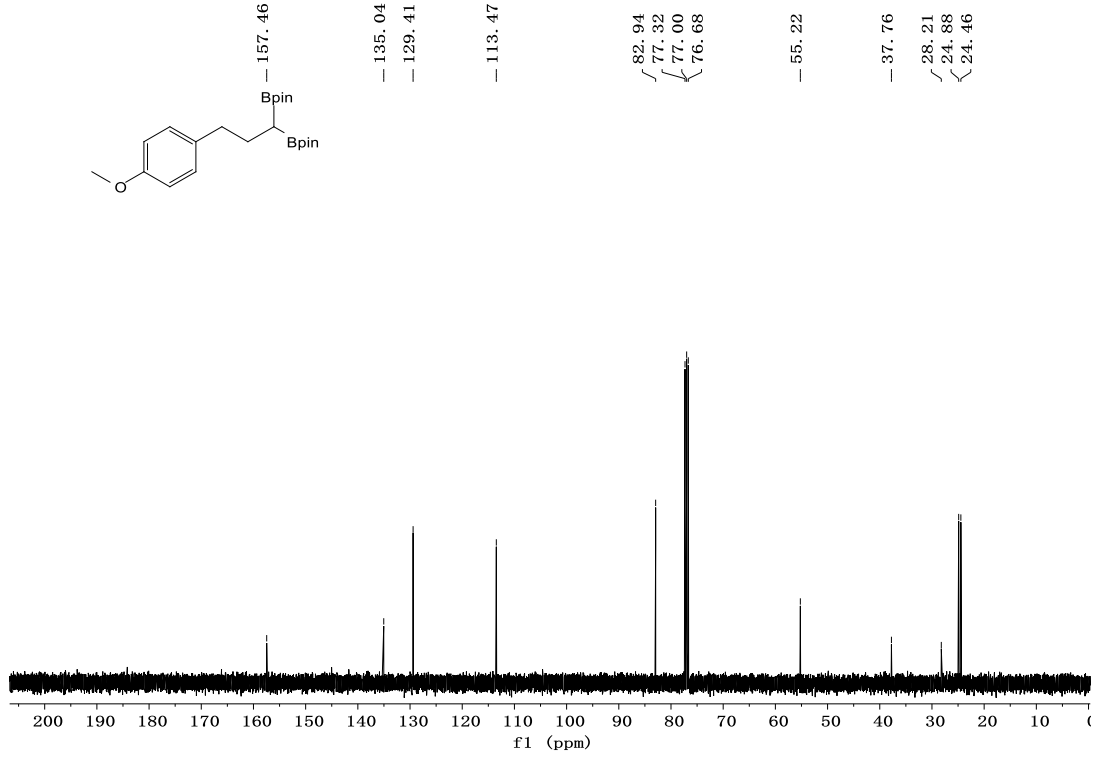
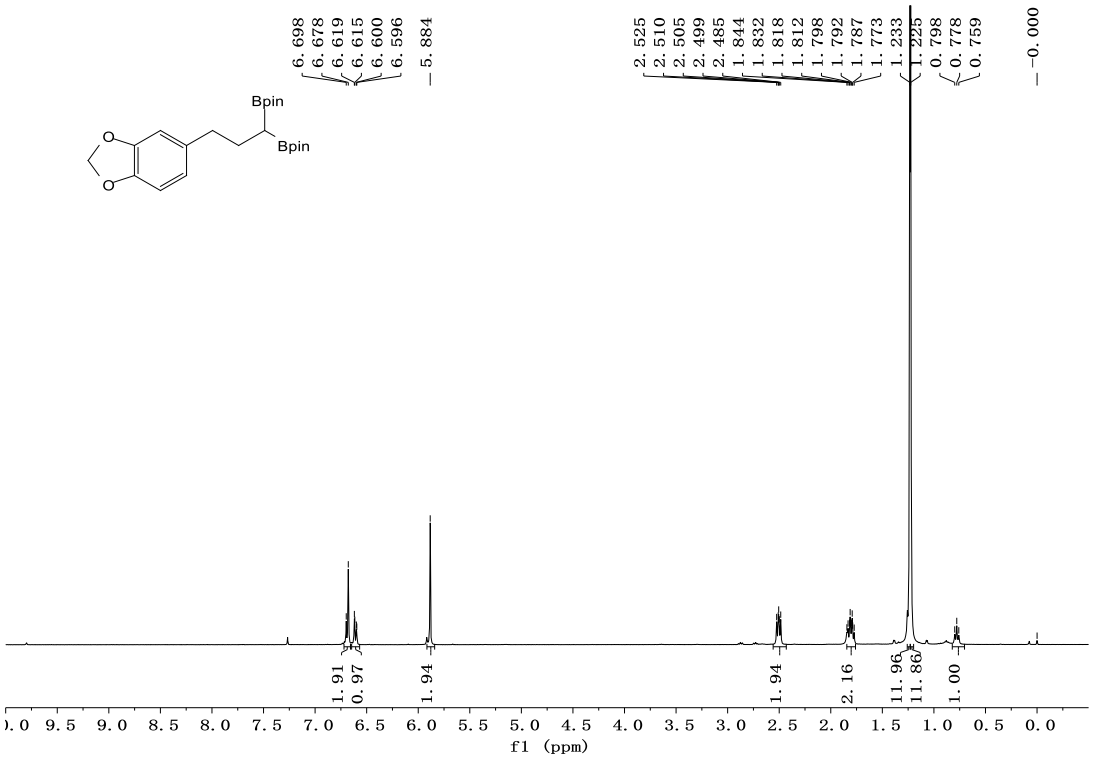
2.531
2.526
2.519
2.505
1.843
1.829
1.821
1.809
1.803
1.798
1.236
1.227
0.823
0.803
0.783
-0.000
Bpin
Bpin
O
1.97
1.95
3.01
1.97
2.27
11.94
11.89
1.00
f1 (ppm)


157.46
135.04
129.41
113.47
82.94
77.32
77.00
76.68
55.22
37.76
28.21
24.88
24.46
Bpin
Bpin
O
f1 (ppm)

2j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6.596
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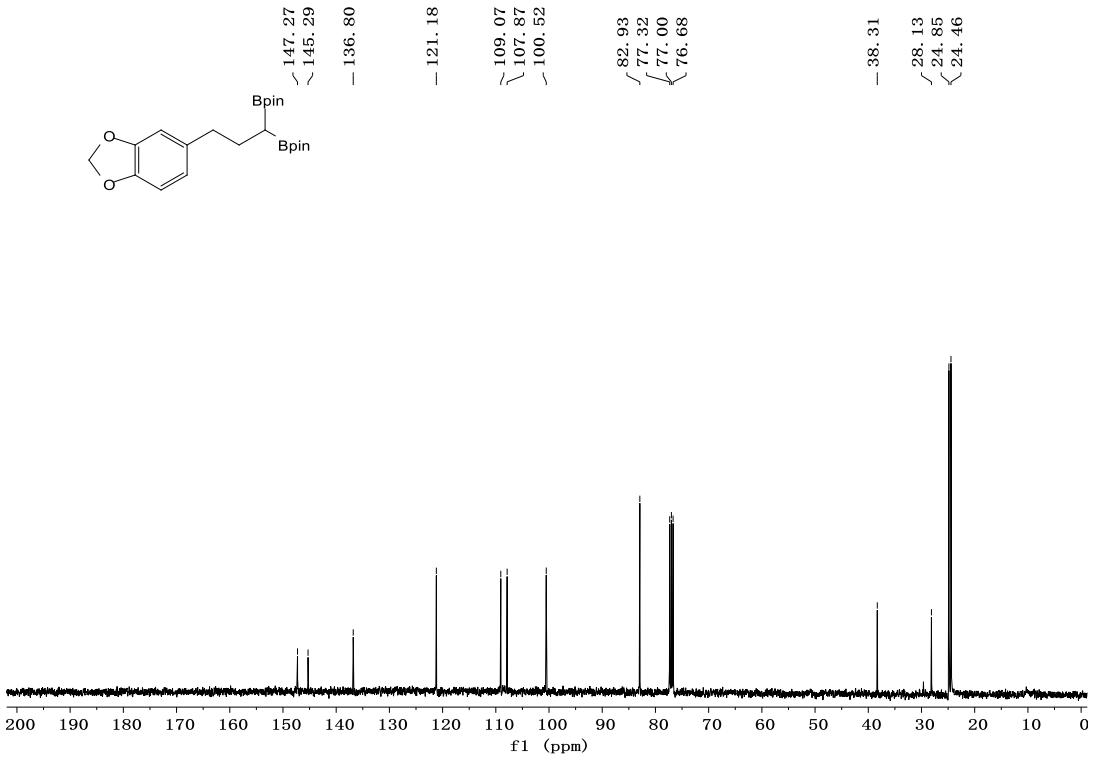
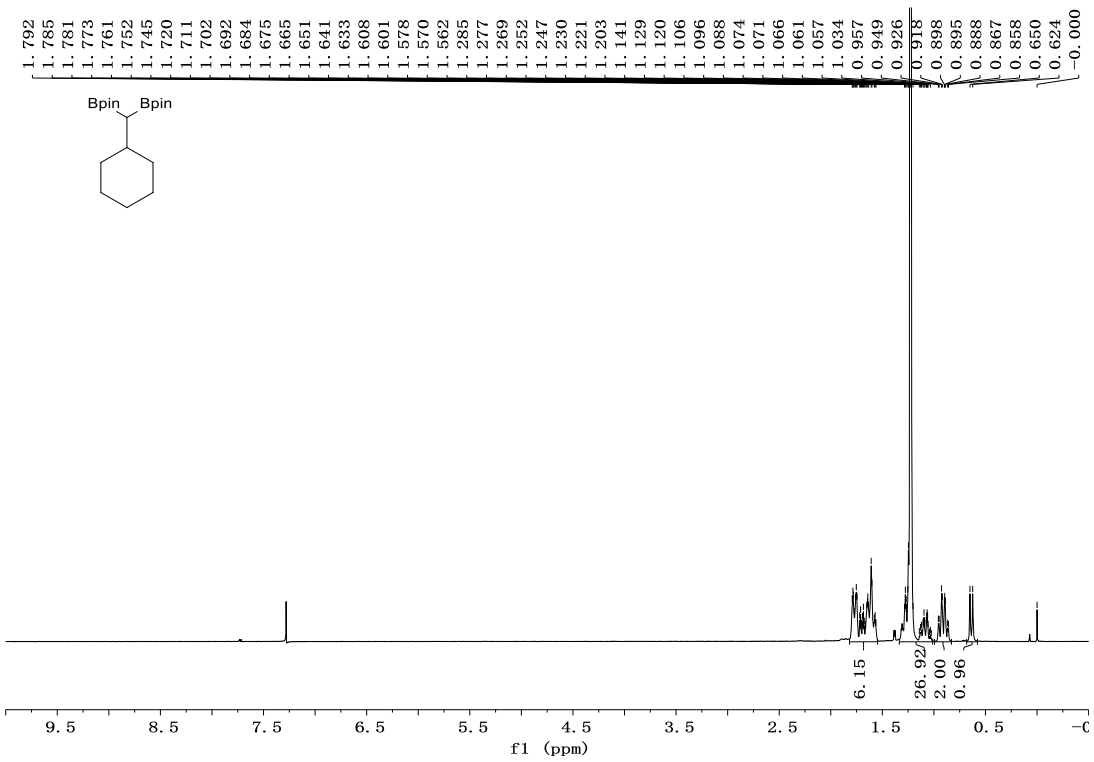
2.525
2.510
2.505
2.499
2.485
1.844
1.832
1.818
1.812
1.798
1.792
1.787
1.773
1.233
1.225
0.798
0.778
0.759
0.000
Bpin
Bpin
1.91
0.97
1.94
1.94
2.16
11.96
11.86
1.00
f1 (ppm)


147.27
145.29
136.80
121.18
109.07
107.87
100.52
82.93
77.32
77.00
76.68
38.31
28.13
24.85
24.46
Bpin
Bpin
f1 (ppm)

2k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1.781
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1.720
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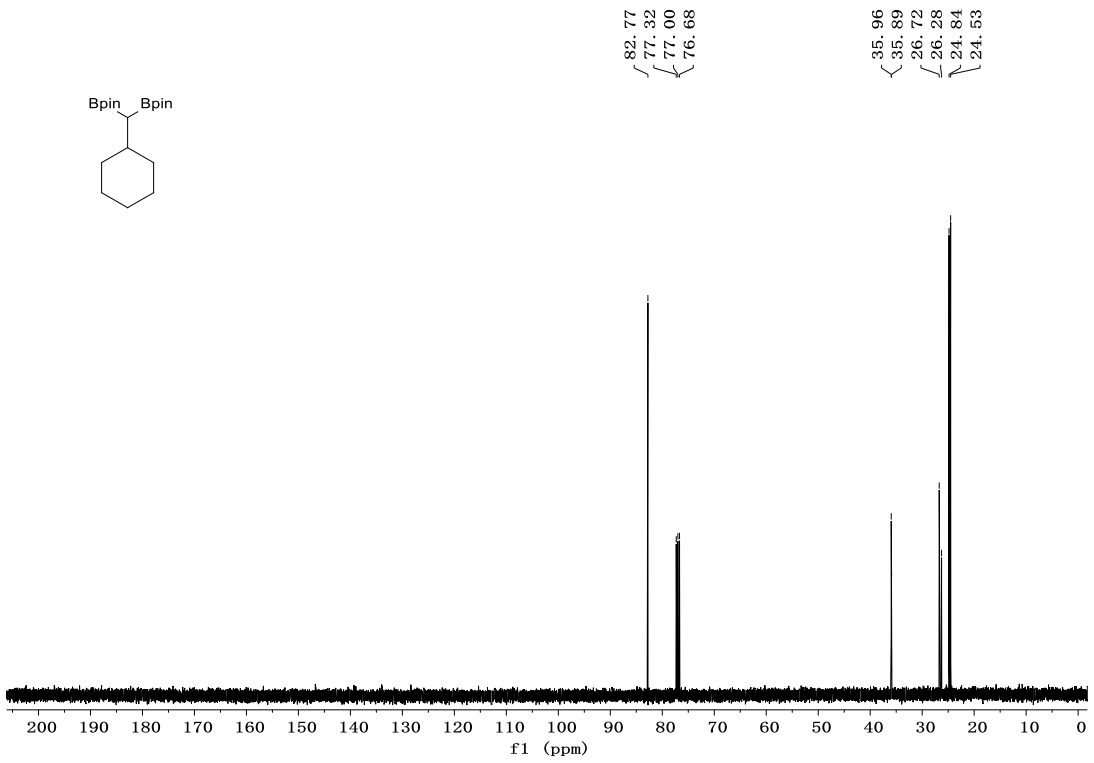
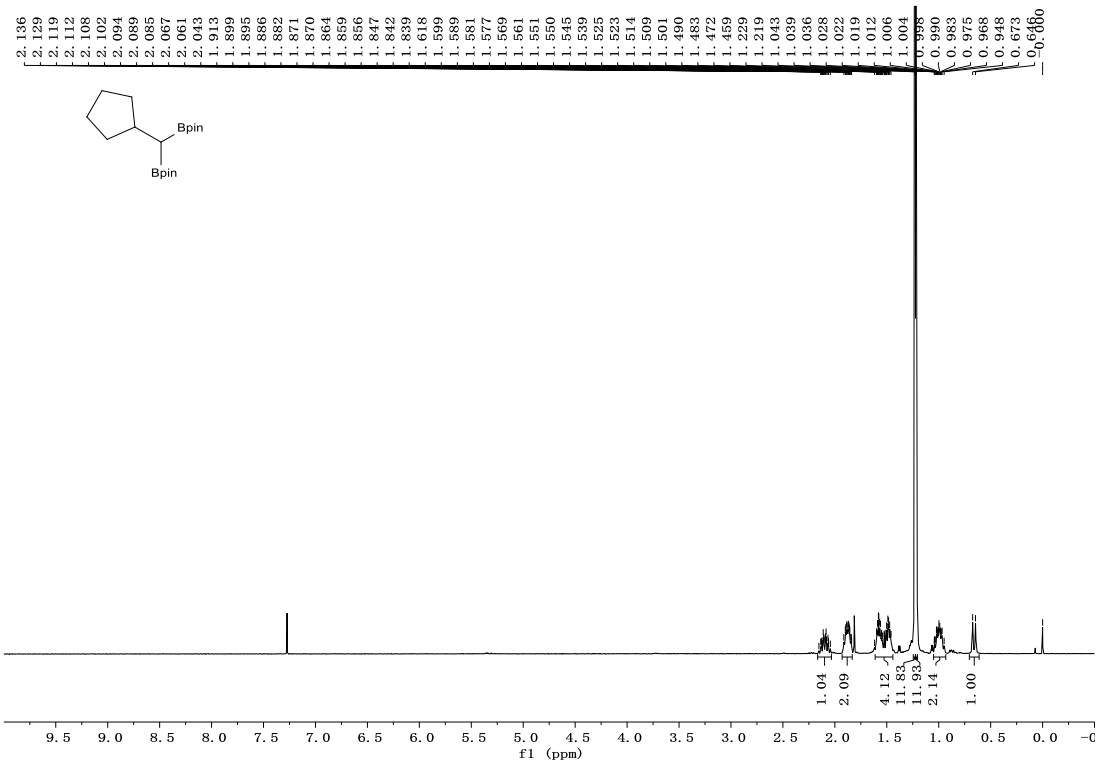
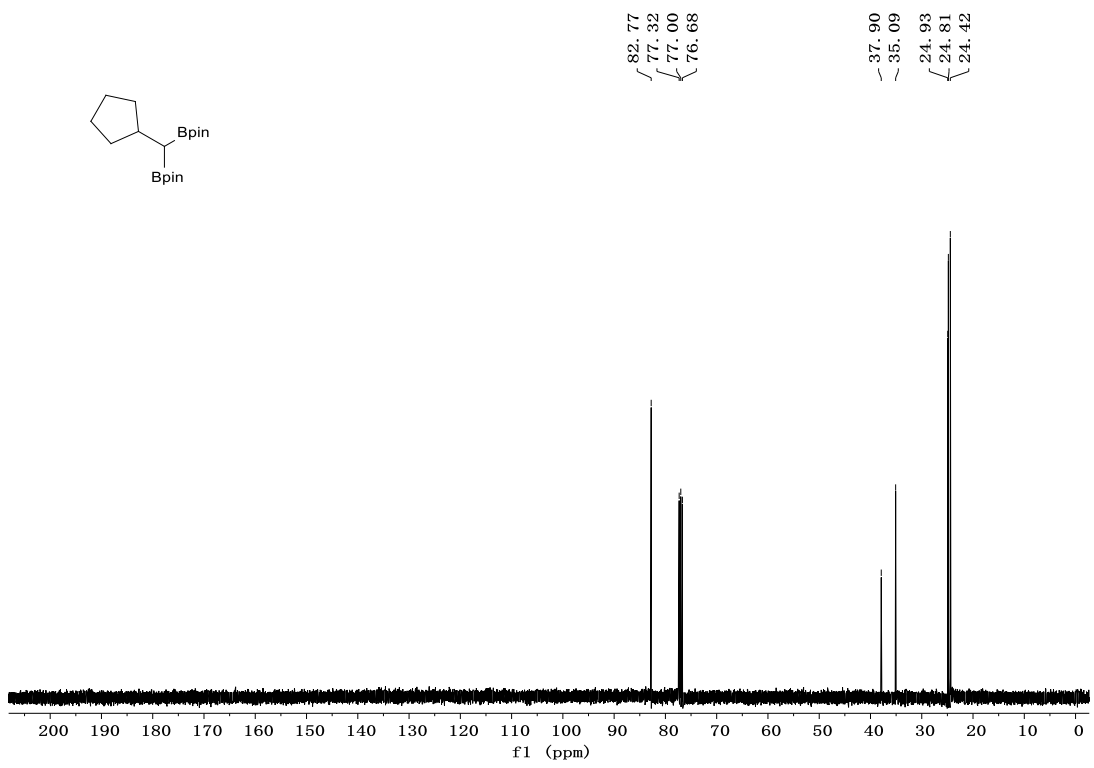
1.702
1.692
1.684
1.675
1.665
1.651
1.641
1.633
1.608
1.601
1.578
1.570
1.562
1.285
1.277
1.269
1.252
1.247
1.230
1.221
1.203
1.141
1.129
1.120
1.106
1.096
1.088
1.074
1.071
1.066
1.061
1.057
1.034
0.957
0.949
0.926
0.918
0.898
0.895
0.888
0.867
0.858
0.650
0.624
-0.000
Bpin
Bpin
6.15
26.92
2.00
0.96
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

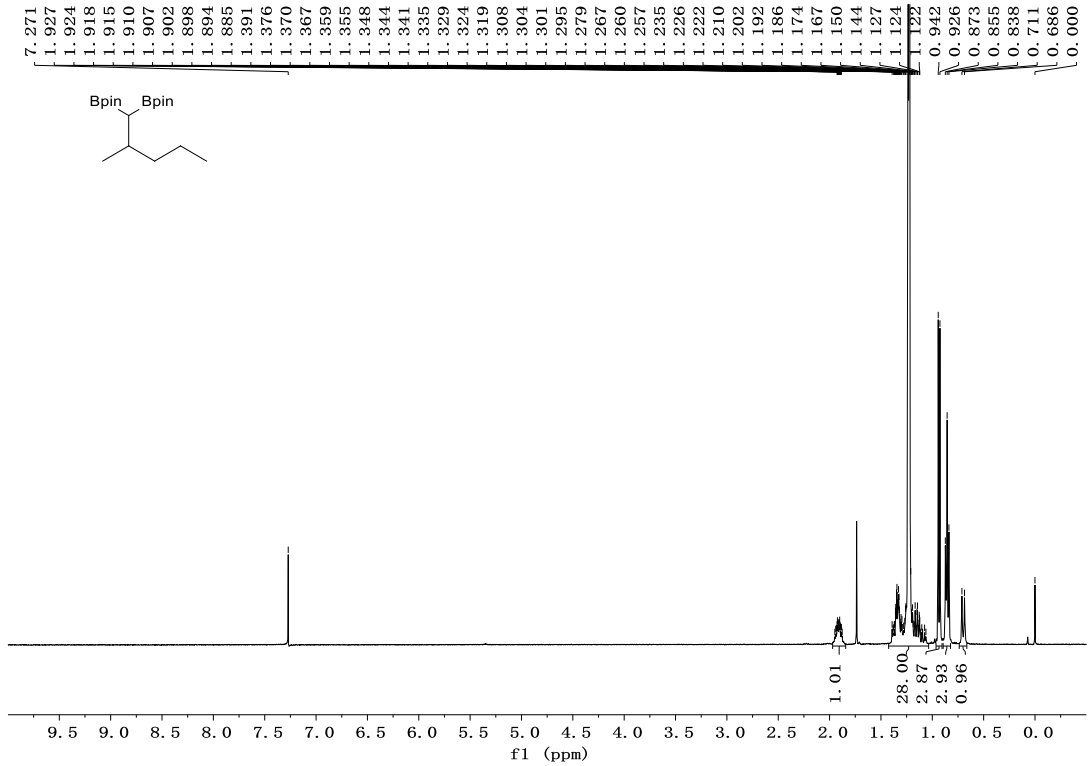

82.77
77.32
77.00
76.68
35.96
35.89
26.72
26.28
24.84
24.53
Bpin
Bpin
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2l


Bpin
Bpin
1.04
2.09
4.12
11.83
11.93
2.14
1.00
f1 (ppm)


82.77
77.32
77.00
76.68
37.90
35.09
24.93
24.81
24.42
Bpin
Bpin
f1 (ppm)

2m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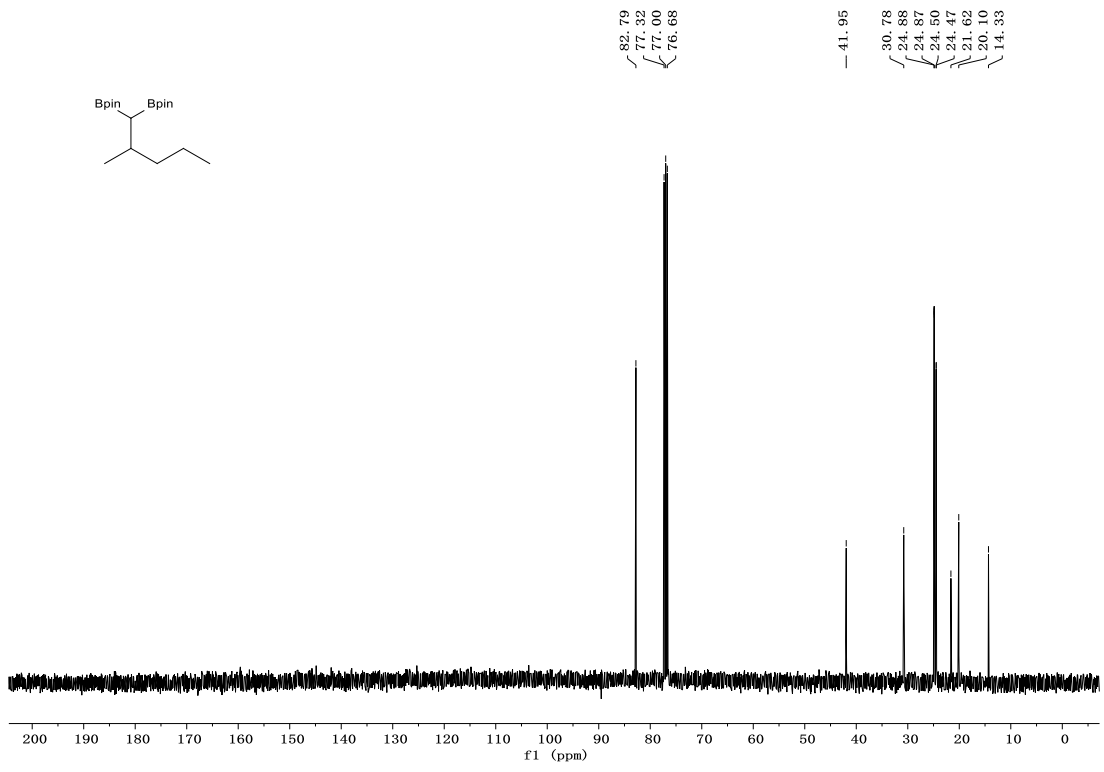
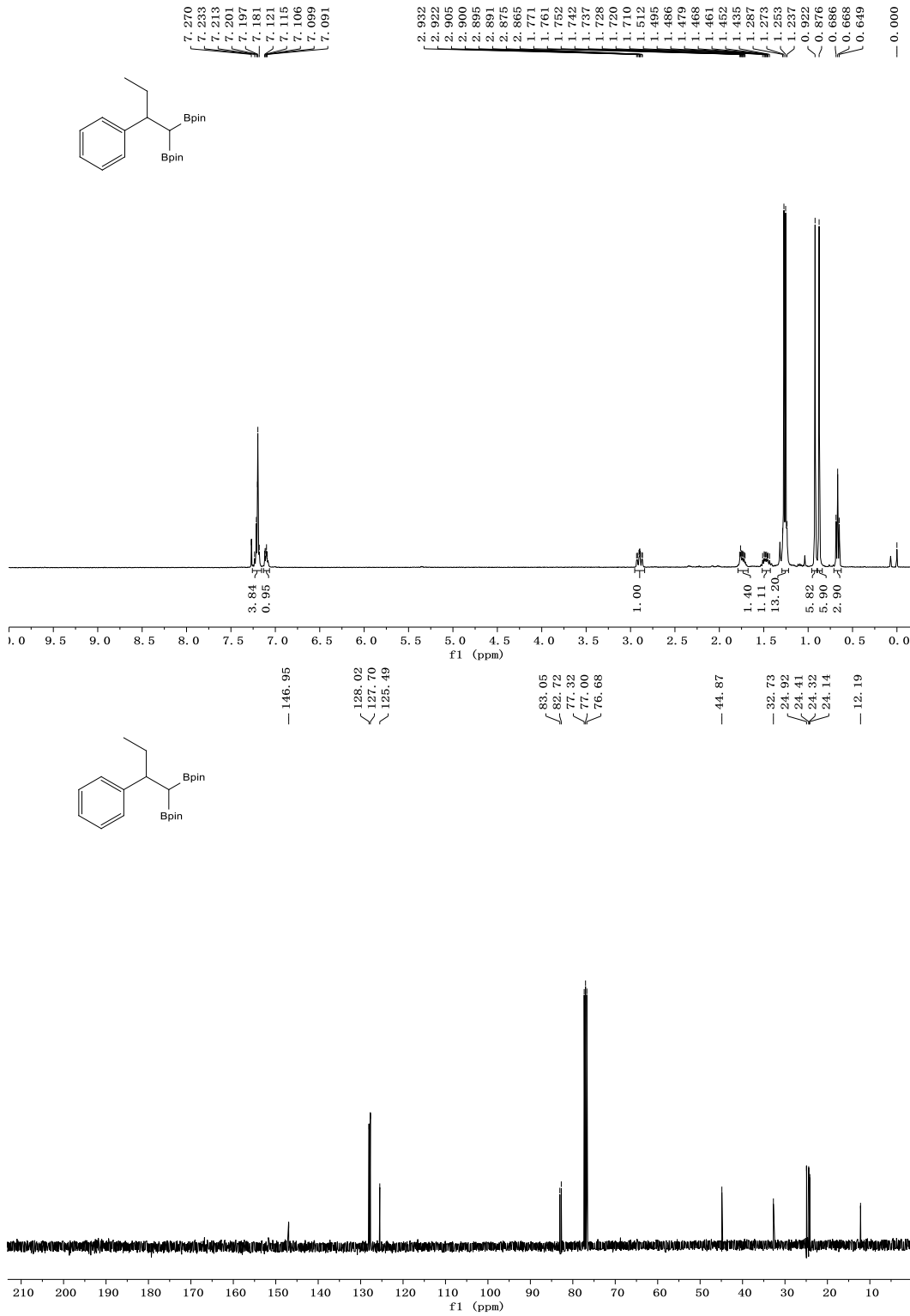
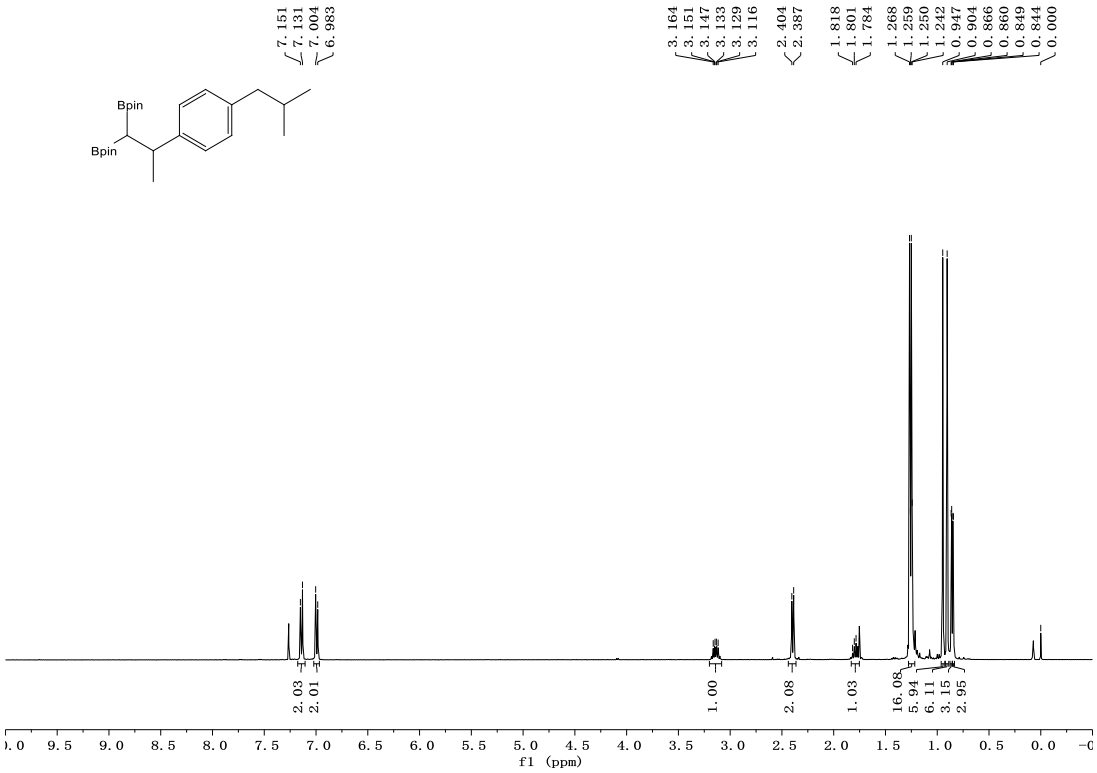
1.915
1.910
1.907
1.902
1.898
1.894
1.885
1.391
1.376
1.370
1.367
1.359
1.355
1.348
1.344
1.341
1.335
1.329
1.324
1.319
1.308
1.304
1.301
1.295
1.279
1.267
1.260
1.257
1.235
1.226
1.222
1.210
1.202
1.192
1.186
1.174
1.167
1.150
1.144
1.127
1.124
1.122
0.942
0.926
0.873
0.855
0.838
0.711
0.686
0.000
Bpin
Bpin
1.01
28.00
2.87
2.93
0.96
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)

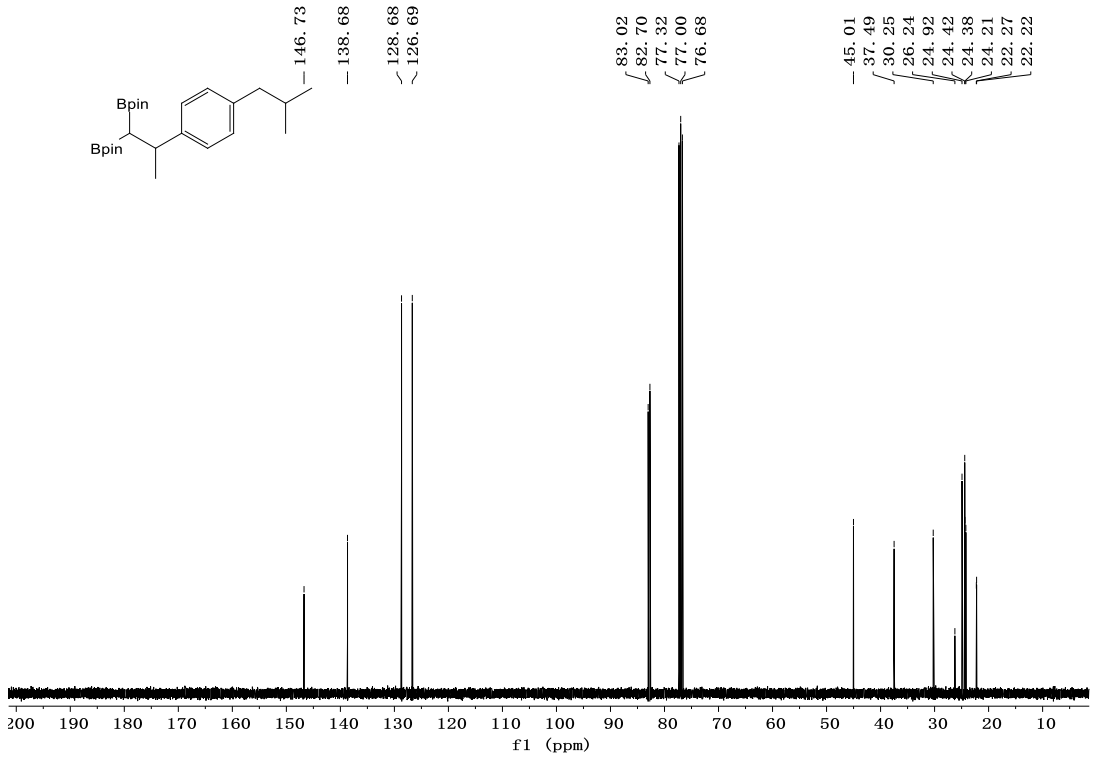

82.79
77.32
77.00
76.68
41.95
30.78
24.88
24.87
24.50
24.47
21.62
20.10
14.33
Bpin
Bpin
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

2n

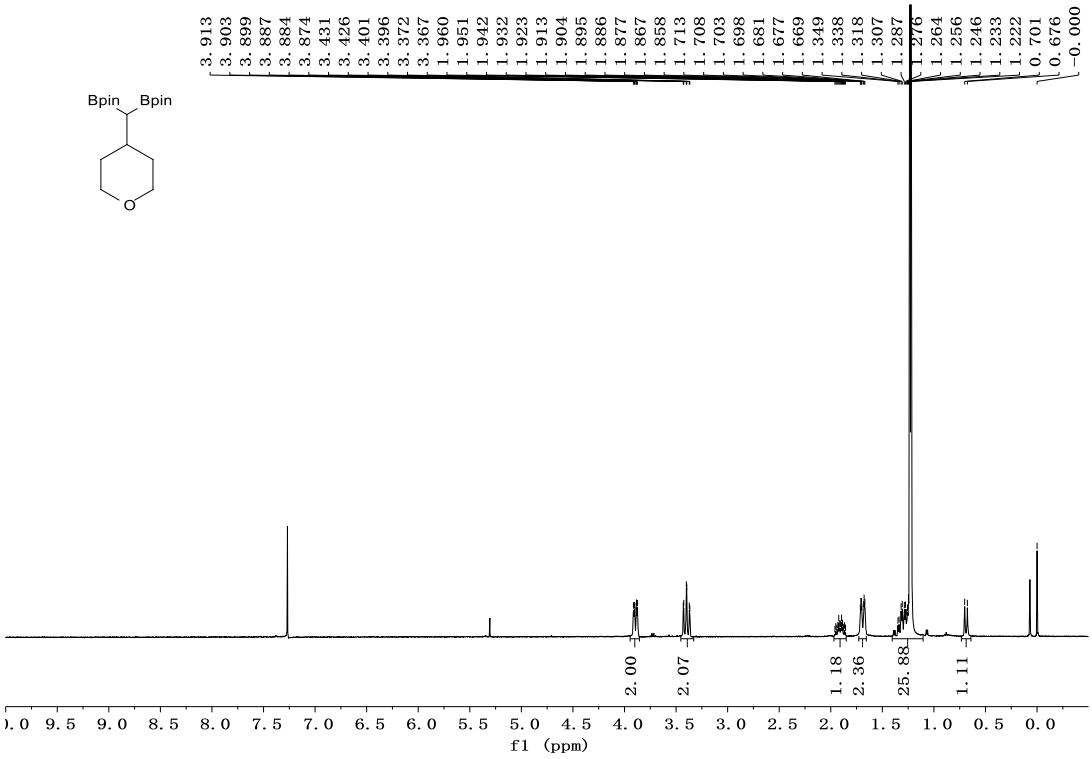

7.270
7.233
7.213
7.201
7.197
7.181
7.121
7.115
7.106
7.099
7.091
2.932
2.922
2.905
2.900
2.895
2.891
2.875
2.865
1.771
1.761
1.752
1.742
1.737
1.728
1.720
1.710
1.512
1.495
1.486
1.479
1.468
1.461
1.452
1.435
1.287
1.273
1.253
1.237
0.922
0.876
0.686
0.668
0.649
0.000
Bpin
Bpin
3.84
0.95
1.00
1.40
1.11
13.20
5.82
5.90
2.90
f1 (ppm)
146.95
128.02
127.70
125.49
83.05
82.72
77.32
77.00
76.68
44.87
32.73
24.92
24.41
24.32
24.14
12.19
Bpin
Bpin
f1 (ppm)

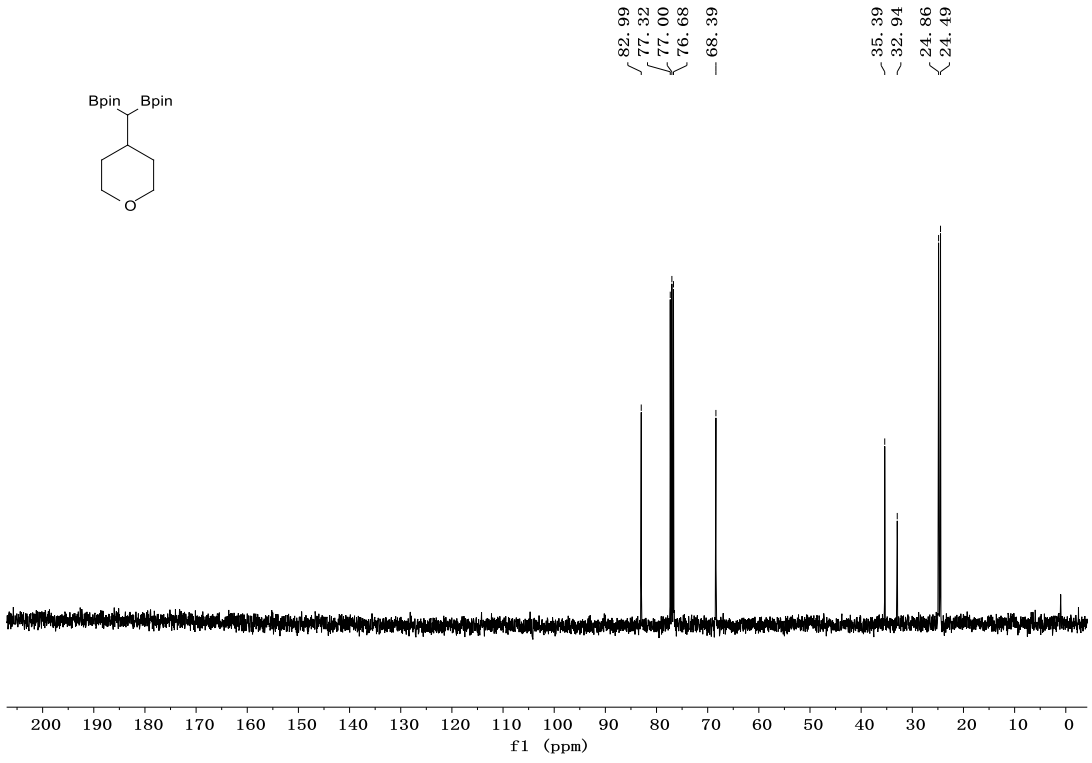
2o


7.151
7.131
7.004
6.983
3.164
3.151
3.147
3.133
3.129
3.116
2.404
2.387
1.818
1.801
1.784
1.268
1.259
1.250
1.242
0.947
0.904
0.866
0.860
0.849
0.844
0.000
Bpin
Bpin
2.03
2.01
1.00
2.08
1.03
16.08
5.94
6.11
3.15
2.95
f1 (ppm)

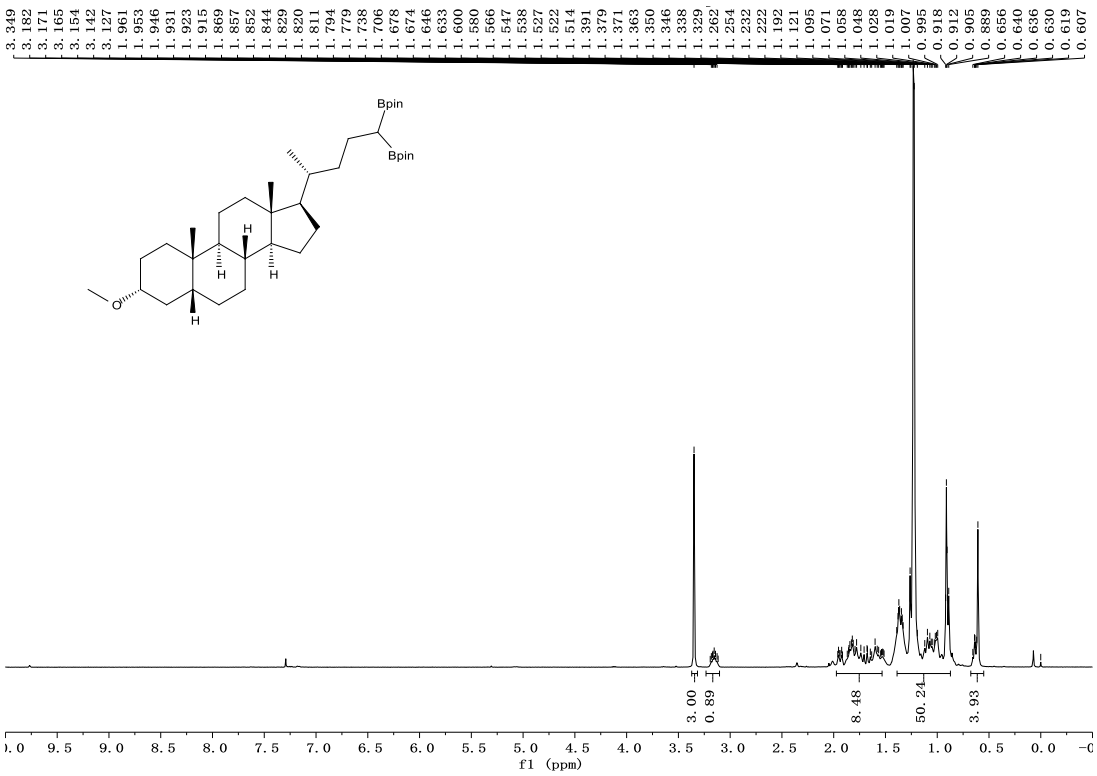

146.73
138.68
128.68
126.69
83.02
82.70
77.32
77.00
76.68
45.01
37.49
30.25
26.24
24.92
24.42
24.38
24.21
22.27
22.22
Bpin
Bpin
f1 (ppm)

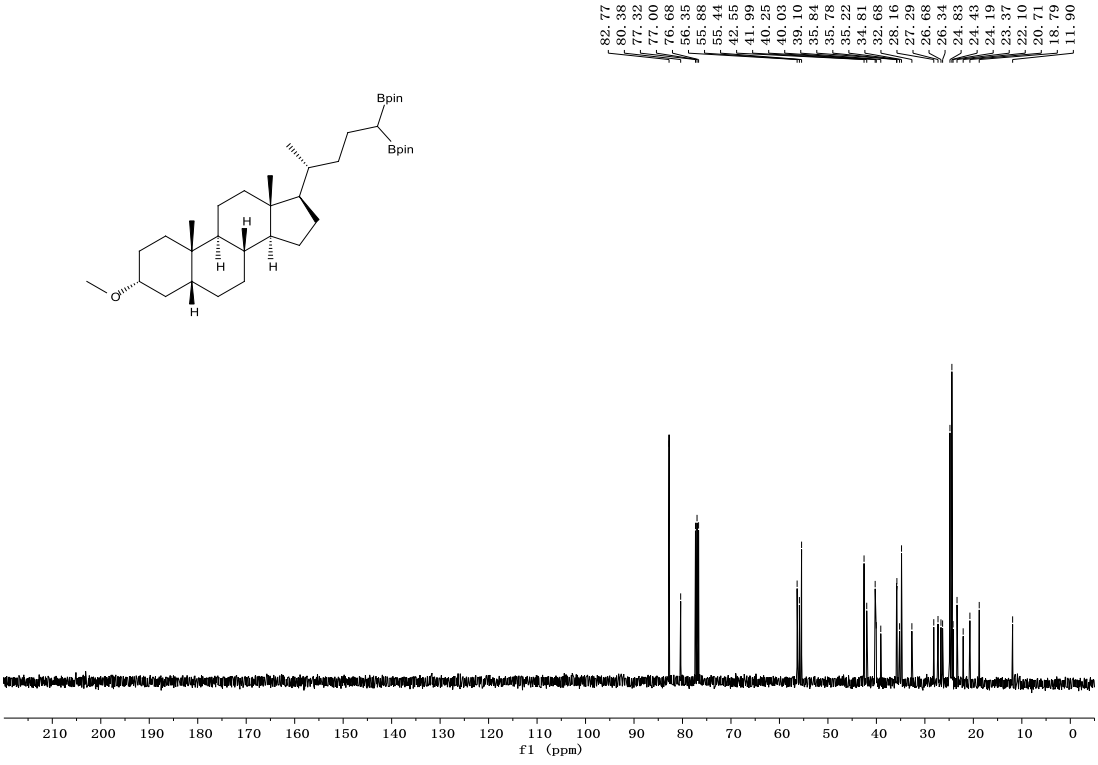
2p


3.913
3.903
3.899
3.887
3.884
3.874
3.431
3.426
3.401
3.396
3.372
3.367
1.960
1.951
1.942
1.932
1.923
1.913
1.904
1.895
1.886
1.877
1.867
1.858
1.713
1.708
1.703
1.698
1.681
1.677
1.669
1.349
1.338
1.318
1.307
1.287
1.276
1.264
1.256
1.246
1.233
1.222
0.701
0.676
0.000
Bpin
Bpin
O
2.00
2.07
1.18
2.36
25.88
1.11
f1 (ppm)

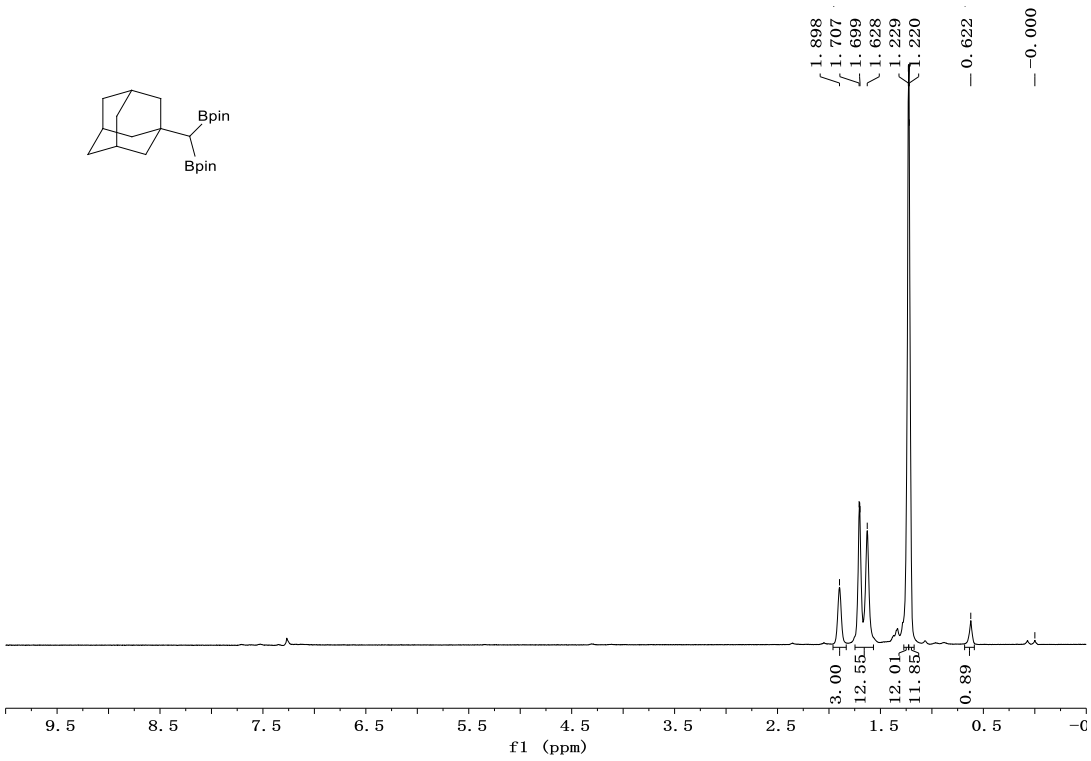

82.99
77.32
77.00
76.68
68.39
35.39
32.94
24.86
24.49
Bpin
Bpin
O
f1 (ppm)

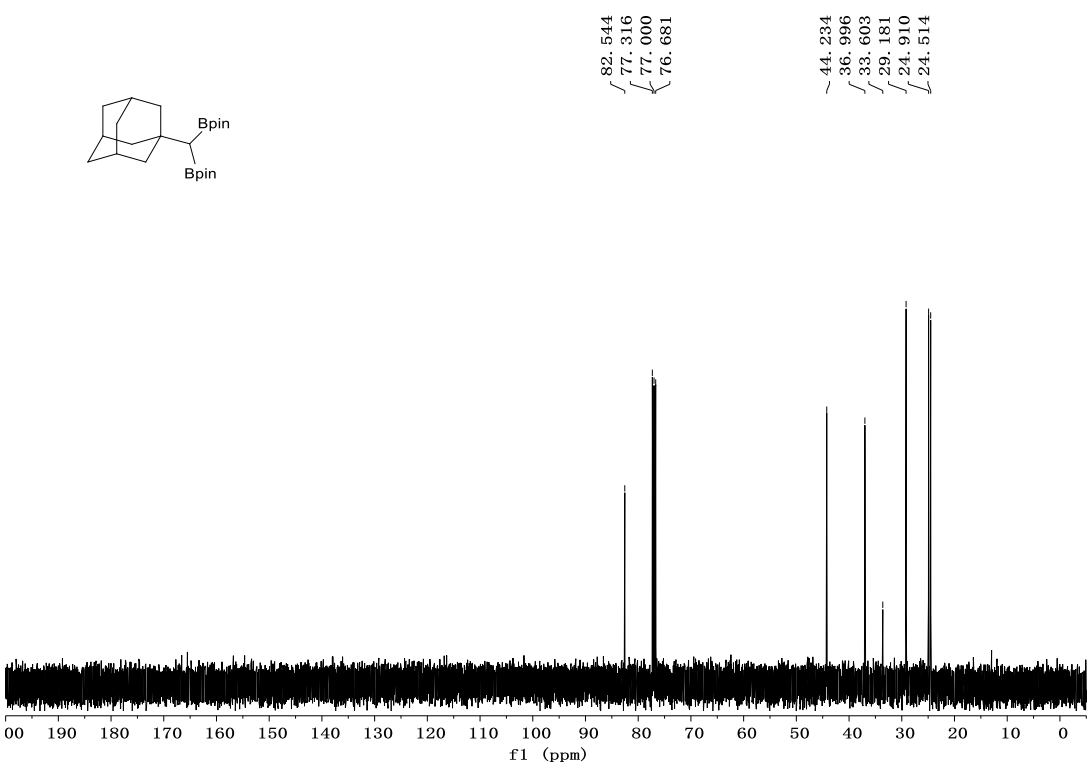
2q


Bpin
Bpin
H
H
H
O
H
3.00
0.89
8.48
50.24
3.93
f1 (ppm)

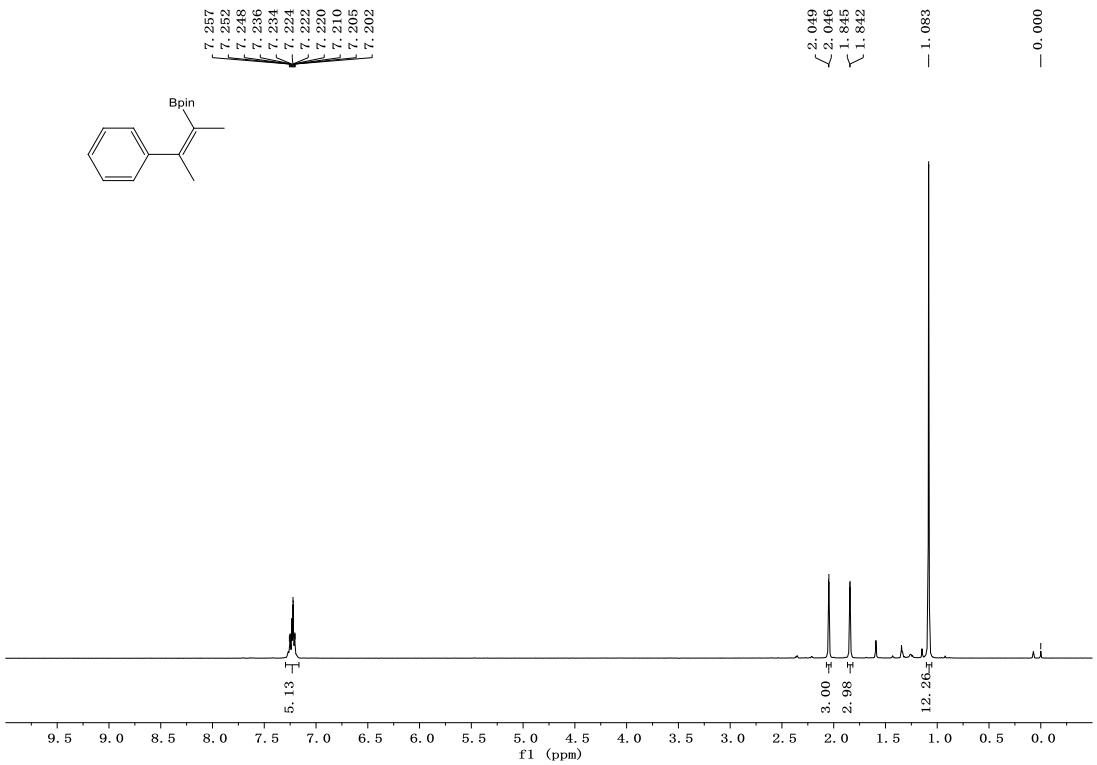

Bpin
Bpin
H
H
H
O
H
f1 (ppm)

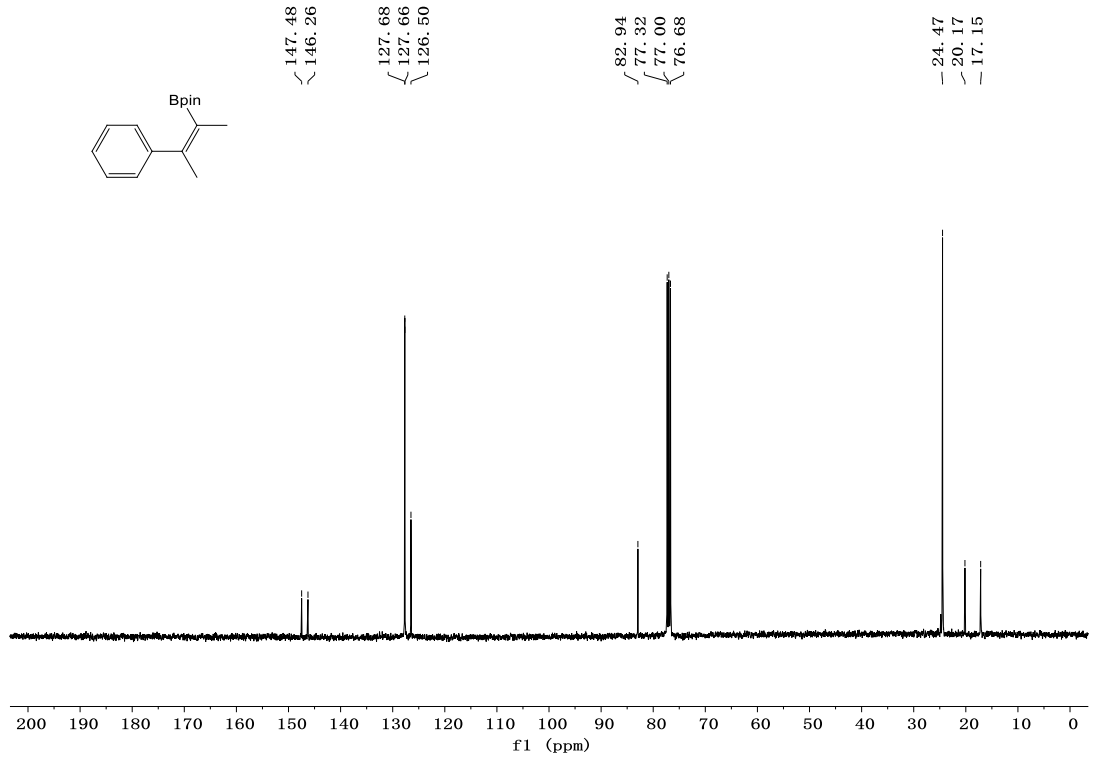
2r


Bpin
Bpin
1.898
1.707
1.699
1.628
1.229
1.220
0.622
-0.000
3.00
12.55
12.01
11.85
0.89
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

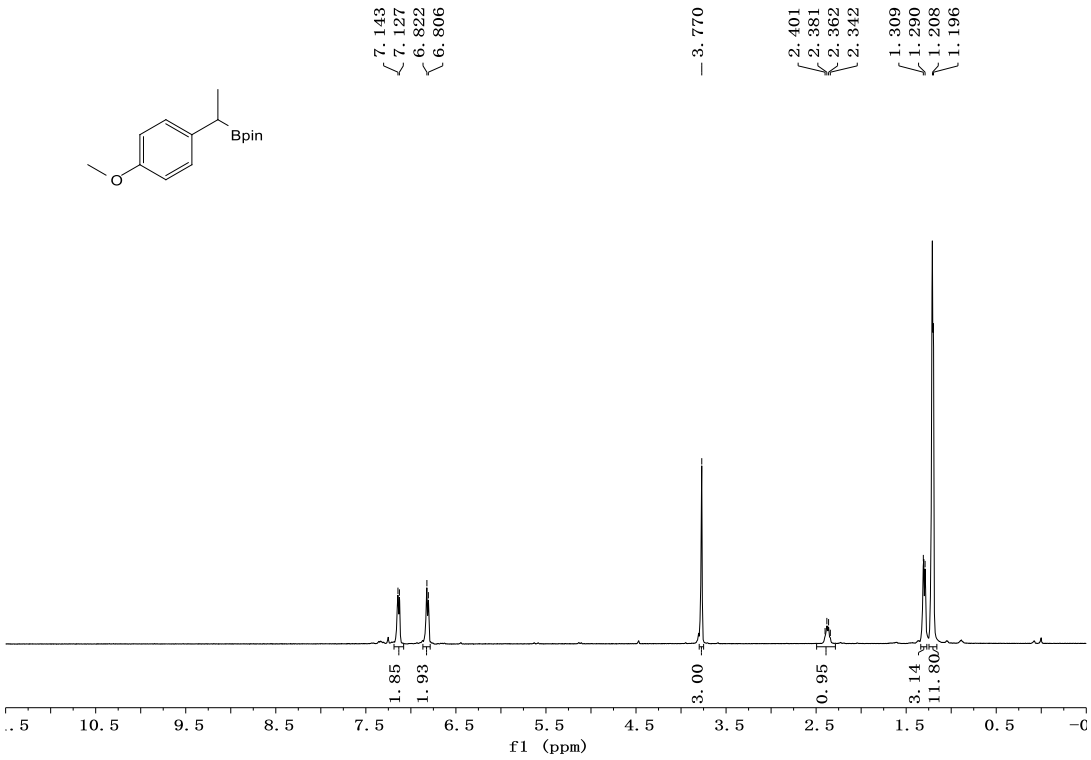

Bpin
Bpin
82.544
77.316
77.000
76.681
44.234
36.996
33.603
29.181
24.910
24.514
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

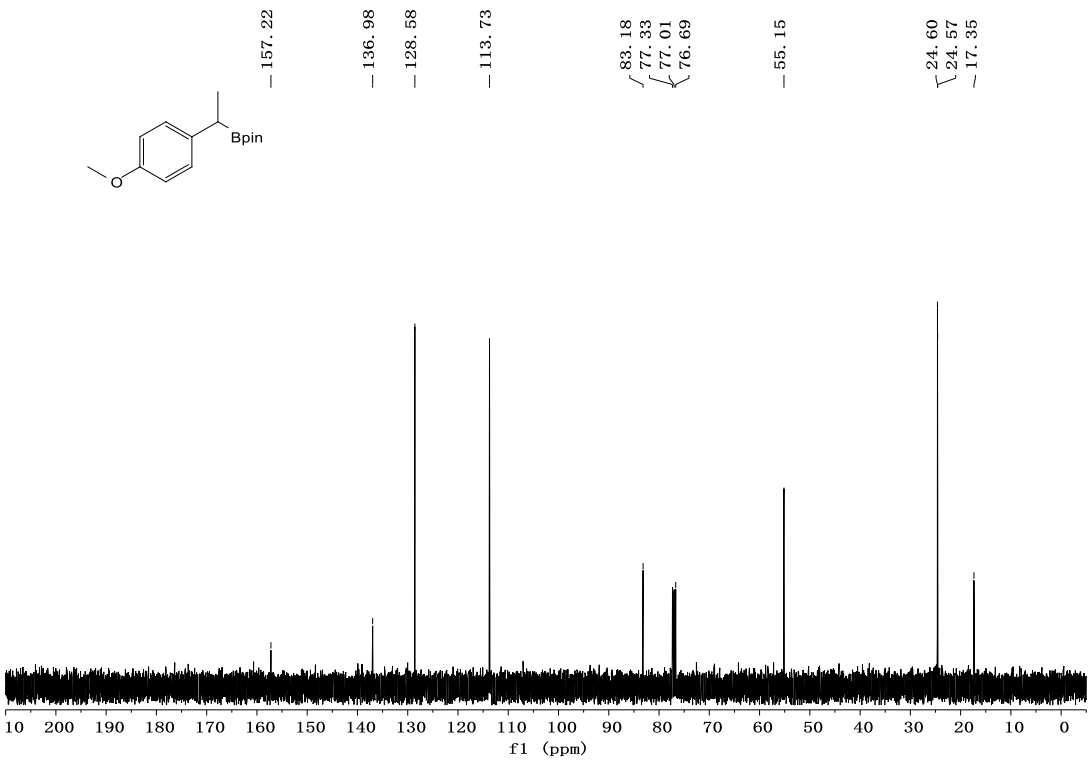
3a


7.257
7.252
7.248
7.236
7.234
7.224
7.222
7.220
7.210
7.205
7.202
2.049
2.046
1.845
1.842
1.083
0.000
Bpin
5.13
3.00
2.98
12.26
f1 (ppm)

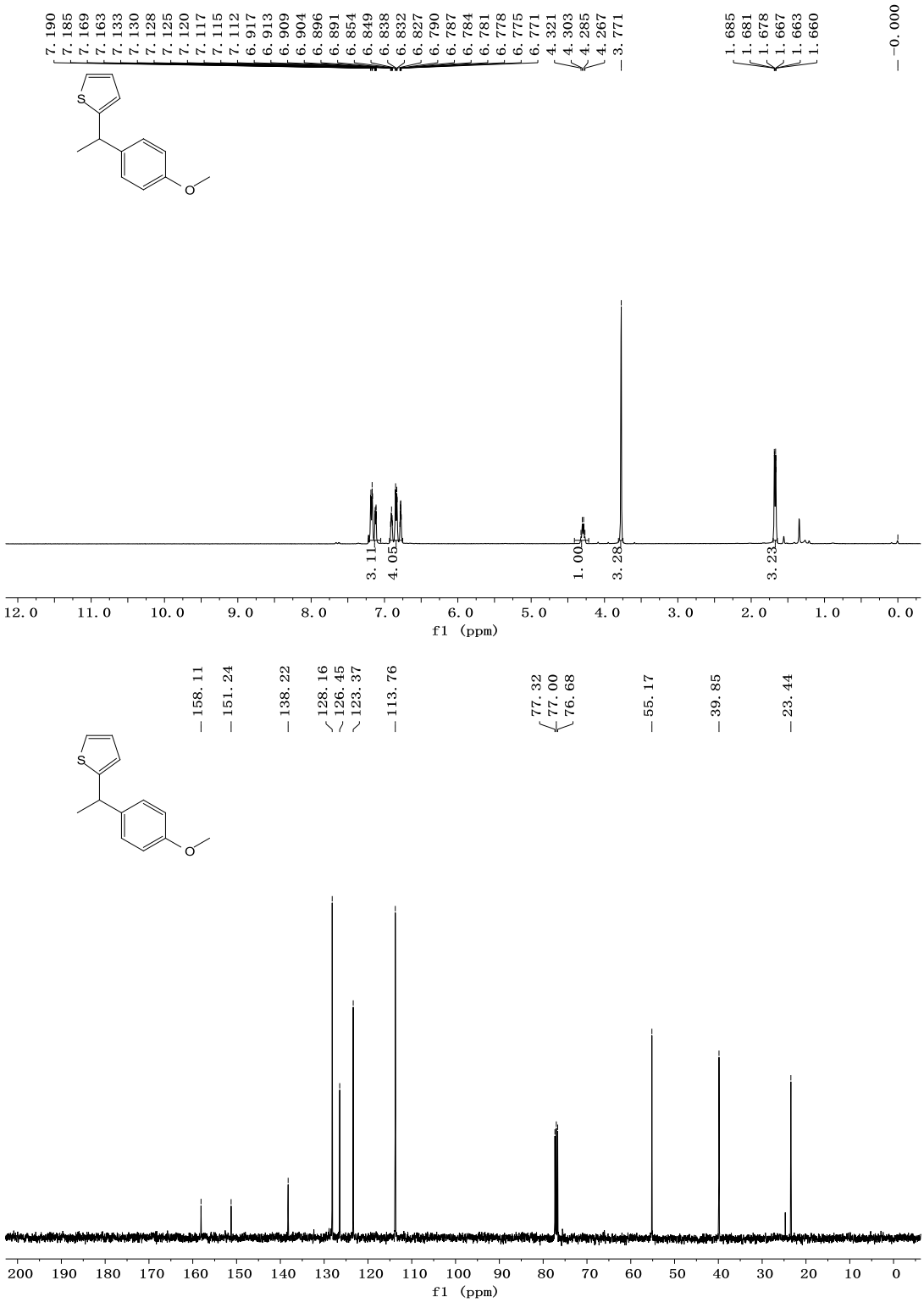

147.48
146.26
127.68
127.66
126.50
82.94
77.32
77.00
76.68
24.47
20.17
17.15
Bpin
f1 (ppm)

3b

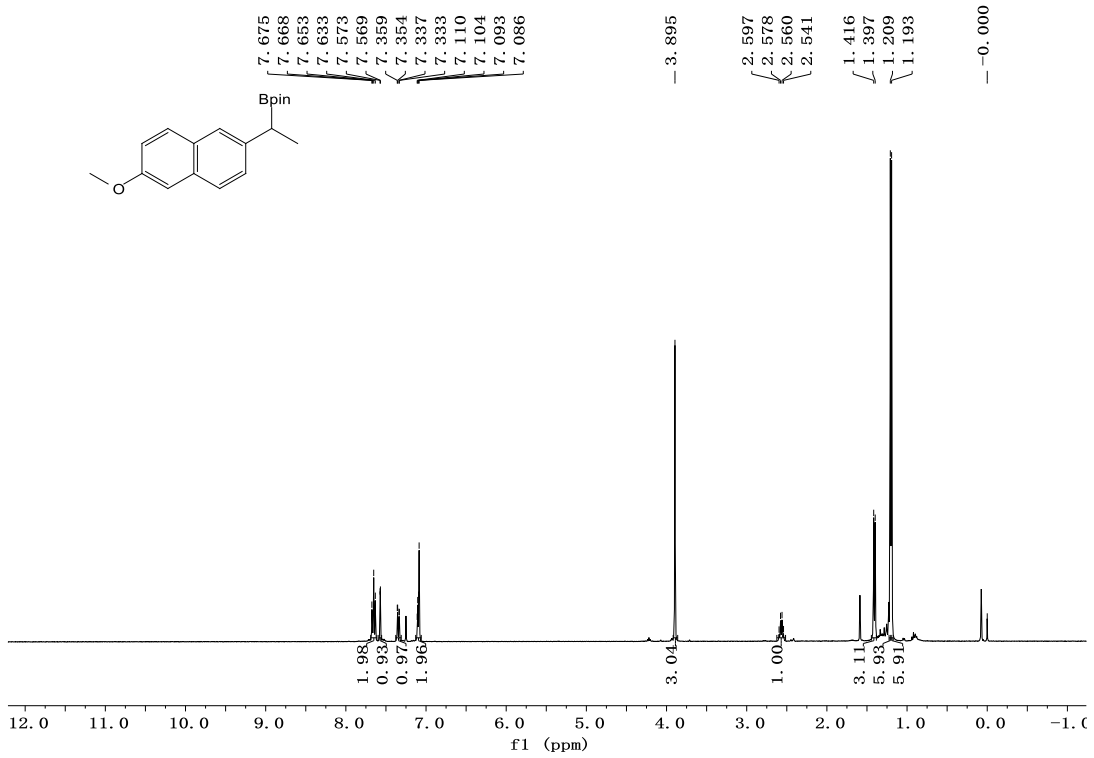

7.143
7.127
6.822
6.806
3.770
2.401
2.381
2.362
2.342
1.309
1.290
1.208
1.196
Bpin
O
1.85
1.93
3.00
0.95
3.14
11.80
f1 (ppm)

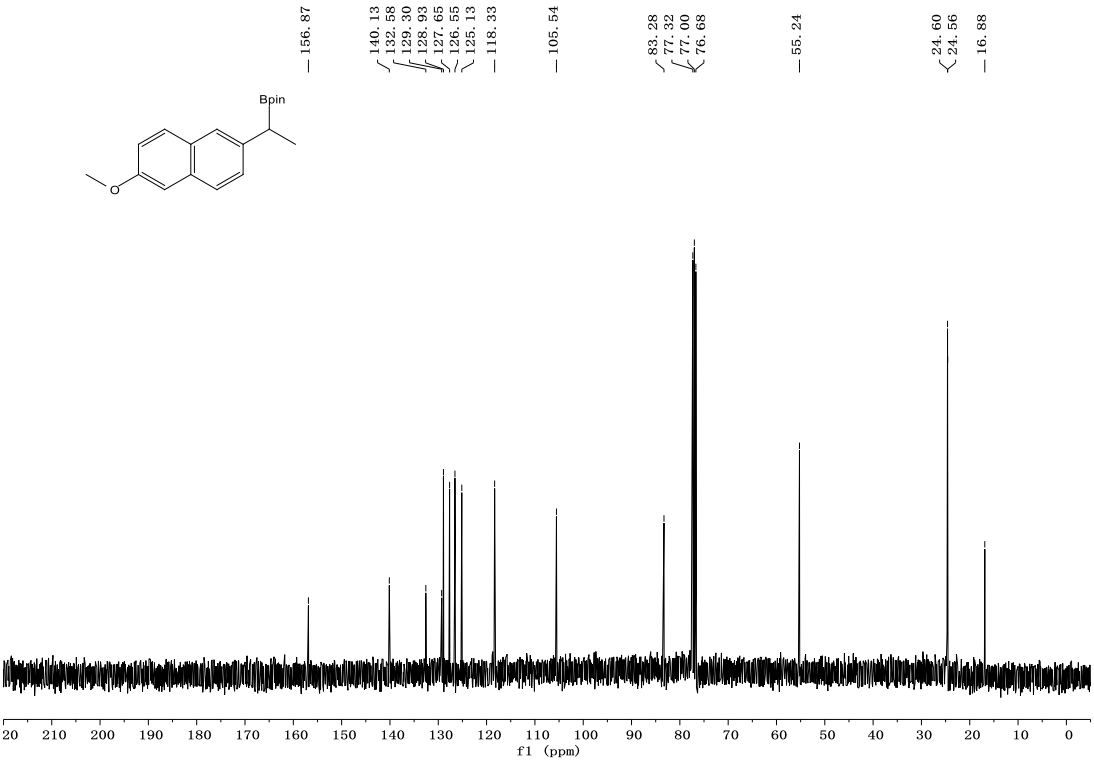

157.22
136.98
128.58
113.73
83.18
77.33
77.01
76.69
55.15
24.60
24.57
17.35
Bpin
O
f1 (ppm)

3c

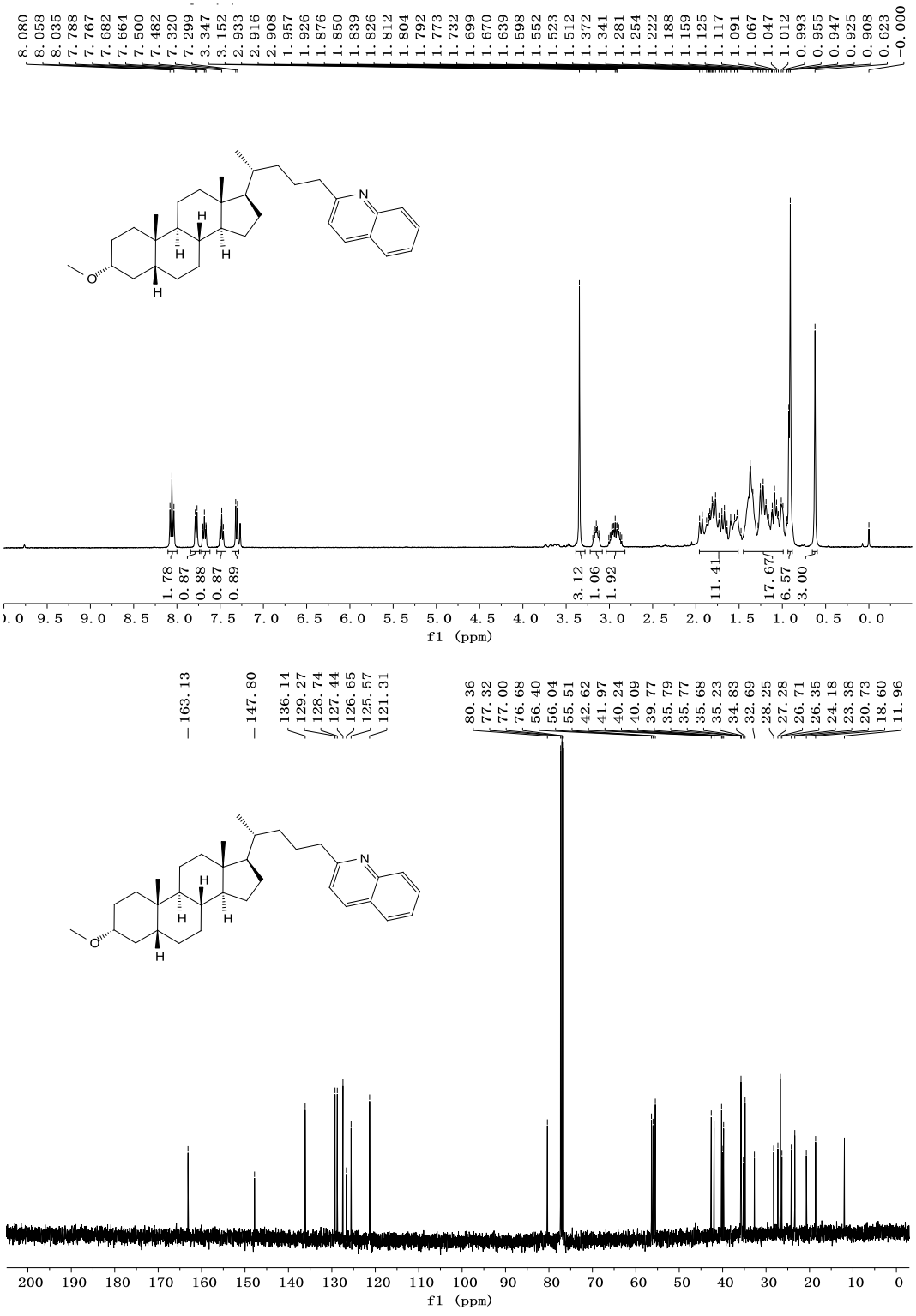

7.190
7.185
7.169
7.163
7.133
7.130
7.128
7.125
7.120
7.117
7.115
7.112
6.917
6.913
6.909
6.904
6.896
6.891
6.854
6.849
6.838
6.832
6.827
6.790
6.787
6.784
6.781
6.778
6.775
6.771
4.321
4.303
4.285
4.267
3.771
1.685
1.681
1.678
1.667
1.663
1.660
-0.000
S
O
3.11
4.05
1.00
3.28
3.23
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
158.11
151.24
138.22
128.16
126.45
123.37
113.76
77.32
77.00
76.68
55.17
39.85
23.44
S
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3d


7.675
7.668
7.653
7.633
7.573
7.569
7.359
7.354
7.337
7.333
7.110
7.104
7.093
7.086
3.895
2.597
2.578
2.560
2.541
1.416
1.397
1.209
1.193
0.000
Bpin
O
1.98
0.93
0.97
1.96
3.04
1.00
3.11
5.93
5.91
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


156.87
140.13
132.58
129.30
128.93
127.65
126.55
125.13
118.33
105.54
83.28
77.32
77.00
76.68
55.24
24.60
24.56
16.88
Bpin
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3e


8.080
8.058
8.035
7.788
7.767
7.682
7.664
7.500
7.482
7.320
7.299
3.347
3.152
2.933
2.916
2.908
1.957
1.926
1.876
1.850
1.839
1.826
1.812
1.804
1.792
1.773
1.732
1.699
1.670
1.639
1.598
1.552
1.523
1.512
1.372
1.341
1.281
1.254
1.222
1.188
1.159
1.125
1.117
1.091
1.067
1.047
1.012
0.993
0.955
0.947
0.925
0.908
0.623
-0.000
N
H
H
H
O
H
1.78
0.87
0.88
0.87
0.89
3.12
1.06
1.92
11.41
17.67
6.57
3.00
f1 (ppm)
163.13
147.80
136.14
129.27
128.74
127.44
126.65
125.57
121.31
80.36
77.32
77.00
76.68
56.40
56.04
55.51
42.62
41.97
40.24
40.09
39.77
35.79
35.77
35.68
35.23
34.83
32.69
28.25
27.28
26.71
26.35
24.18
23.38
20.73
18.60
11.96
f1 (ppm)

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