

Supporting Information (SI)

Nickel(II)-Catalyzed Highly Selective 1,2-Diborylation of Non-Activated Monosubstituted Alkenes

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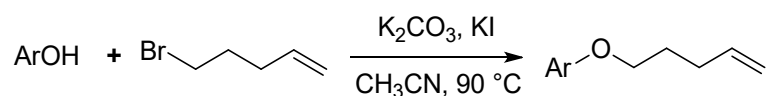
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1. General Information

Unless otherwise specified, all reagents are commercially obtained. NiCl₂·DME was purchased from Energy Chemical. B₂pin₂ and (1*S*,2*S*)-(+)-1,2-Diaminocyclohexane were purchased from Adamas. MeOLi and 1,4-Dioxane were purchased from J&K Scientific, Some other reagents were purchased from Adamas-beta. All reactions were carried out in Ar atmosphere. Thin layer chromatography (TLC) was carried out on 0.2-0.3 mm (Shanxi nuotai Biotechnology Co., Ltd.) neutral silica gel plate. Silica gel (300-400 mesh) (Shanxi nuotai Biotechnology Co., Ltd.) was used for column chromatography separation. Fourier transform infrared spectrometer (vertex 70) for infrared characterization; Reaction monitoring was performed by GC-MS-QP2010 SE; High resolution mass spectrometry was performed on waters synapt G2 Si Q-TOF mass spectrometer.; ¹H, ¹³C and ¹⁹F were recorded by nuclear magnetic resonance spectrometer (bruker avance III 300MHz), (bruker avance III 400MHz) and (bruker avance III 500MHz). ¹H chemical shifts were given in parts per million (ppm), CDCl₃ (¹H NMR is 7.26 ppm, ¹³C NMR is 77.0 ppm) was used as reference, and ¹H data were reported as follows: chemical shifts (ppm) Multiplicity (s = single line state, d = double line state, t = three line state, q = four line state, dd = double line state of double line state, m = double line state, bs = wide single line state), coupling constant (Hz) and integral.

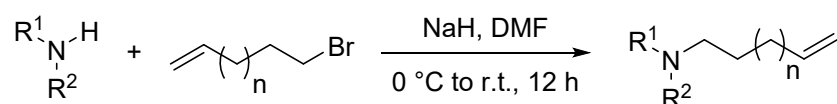
2. Preparation of Substrates

2.1. General procedure A for preparation of 1c, 1d, 1e, 1f, 1g



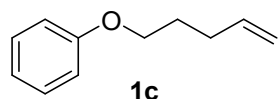
To a solution of aromatic alcohol (5.3 mmol, 1.0 equiv.), K₂CO₃ (7.95 mmol, 1.5 equiv.) and KI (10.6 mmol, 2.0 equiv.) in CH₃CN (10.0 mL) was added 5-bromopent-1-ene (10.6 mmol, 2.0 equiv.), and the mixture was refluxed for 12 h. After the filtration, the combined organic phase was dried over anhydrous MgSO₄ and concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography to provide the corresponding alkenes.

2.2. General procedure B for preparation of 1l, 1n, 1o, 1r



To a solution of amine (indole or 9*H*-carbazole) (5 mmol) in DMF (25 mL), sodium hydride powder (12 mmol, 60% dispersion in mineral oil) was added at 0 °C. The solution was kept at this temperature for 1 h and then bromides (7.5 mmol) were added slowly. Stirring overnight at r.t., the reaction was quenched by glacial water and then extracted with CH₂Cl₂. The organic phase was dried over Na₂SO₄, followed by usual work-up and purified on silica gel column chromatography to afford the desired compounds.

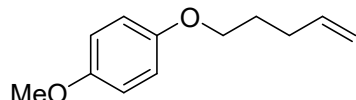
(Pent-4-en-1-yloxy)benzene (1c)¹



1c

According to General procedure A, **1c** was obtained as a colorless oil in 88% yield (0.758 g); ¹H NMR (300 MHz, CDCl₃) δ 7.30–7.28 (m, 2H), 6.96–6.88 (m, 3H), 5.93–5.79 (m, 1H), 5.10–4.98 (m, 2H), 3.97 (t, *J* = 6.3 Hz, 2H), 2.28–2.21 (m, 2H), 1.93–1.84 (m, 2H).

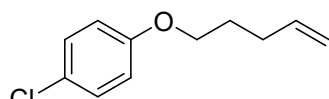
Methoxy-4-(pent-4-en-1-yloxy)benzene (1d)¹



1d

According to General procedure A, **1d** was obtained as yellow liquid in 82% yield (0.838 g); ¹H NMR (300 MHz, CDCl₃) δ 6.83 (s, 4H), 5.92–5.78 (m, 1H), 5.09–4.98 (m, 2H), 3.92 (t, *J* = 6.6 Hz, 2H), 3.77 (s, 3H), 2.27–2.19 (m, 2H), 1.91–1.81 (m, 2H).

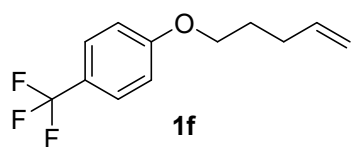
1-Chloro-4-(pent-4-en-1-yloxy)benzene (1e)¹



1e

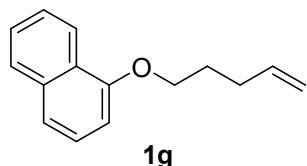
According to General procedure A, **1e** was obtained as colorless liquid. (0.968 g, 93%); ¹H NMR (400 MHz, CDCl₃) δ 7.22 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 9.2 Hz, 2H), 5.88–5.79 (m, 1H), 5.08–4.99 (m, 2H), 3.93 (t, *J* = 6.4 Hz, 2H), 2.26–2.20 (m, 2H), 1.91–1.84 (m, 2H).

1-(Pent-4-en-1-yloxy)-4-(trifluoromethyl)benzene (**1f**)¹



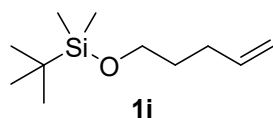
According to General procedure **A**, **1f** was obtained as a colorless oil in 72% yield (0.882 g); ¹H NMR (300 MHz, CDCl₃) δ 7.53 (d, *J* = 8.7 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 5.91–5.78 (m, 1H), 5.10–5.00 (m, 2H), 4.00 (t, *J* = 6.6 Hz, 2H), 2.25 (q, *J* = 6.9 Hz, 2H), 1.95–1.86 (m, 2H).

1-(Pent-4-en-1-yloxy)naphthalene (**1g**)¹



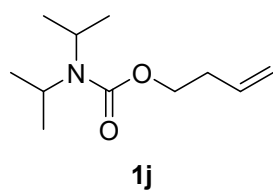
According to General procedure **A**, **1g** was obtained as a colorless oil in 95% yield (1.07 g); ¹H NMR (300 MHz, CDCl₃) δ 8.29 (d, *J* = 9.6 Hz, 1H), 7.81–7.78 (m, 1H), 7.51–7.44 (m, 2H), 7.43–7.34 (m, 2H), 6.81 (d, *J* = 7.2 Hz, 1H), 5.98–5.85 (m, 1H), 5.13–5.01 (m, 2H), 4.16 (t, *J* = 6.3 Hz, 2H), 2.36 (q, *J* = 6.9 Hz, 2H), 2.08–1.99 (m, 2H).

Tert-butyldimethyl((pent-4-en-1-yloxy)methyl)silane (**1i**)²



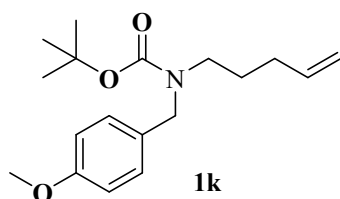
Synthesized according to a slightly modified literature procedure. To a solution of 4-penten-1-ol (0.43 g, 5.0 mmol, 1.0 eq.) in CH₂Cl₂ (5 mL) was added imidazole (0.41 g, 6.0 mmol, 1.2 eq.) followed by TBSCl (0.90 g, 6.0 mmol, 1.2 eq.) and the reaction mixture was stirred at 25 °C for 3 hours. After the reaction had completed, water (10 mL) was added and the mixture was extracted with EtOAc (3 × 10 mL). The organic layer was dried over Na₂SO₄ and concentrated in vacuo. The crude product was purified by silica gel column chromatography petroleum ether/ethyl acetate (100/1, v/v) to afford the protected alcohol as a colorless oil (0.5 g, 47%). The spectroscopic data of this compound matched with those in the literature. ¹H NMR (300 MHz, CDCl₃) δ 5.89–5.75 (m, 1H), 5.05–4.94 (m, 2H), 3.62 (t, *J* = 6.6 Hz, 2H), 2.14–2.07 (m, 2H), 1.6–1.59 (m, 2H), 0.89 (s, 9H), 0.05 (s, 6H).

But-3-en-1-yl diisopropylcarbamate (**1j**)³



A solution of but-3-en-1-ol (262 μL, 3.0 mmol), diisopropylcarbamoyl chloride (0.54 g, 3.3 mmol) and NEt₃ (460 μL, 3.3 mmol) in CH₂Cl₂ was heated under reflux for 48 h. The solution was diluted with H₂O (25 mL) and extracted with DCM (3 × 10 mL). The combined phases were dried over MgSO₄ and concentrated in vacuo. The crude product was purified by flash chromatography petroleum ether/ethyl acetate (15/1, v/v) to give the product as colourless oil (0.52 g, 87% yield). ¹H NMR (300 MHz, CDCl₃) δ 5.89–5.76 (m, 1H), 5.14–5.05 (m, 2H), 4.13 (t, *J* = 6.6 Hz, 2H), 4.06–3.54 (br, 2H), 2.40 (dd, *J* = 13.2, 6.6 Hz, 2H), 1.20 (s, 6H), 1.18 (s, 6H).

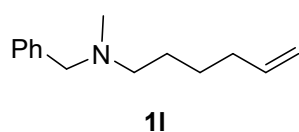
Tert-butyl (4-methoxybenzyl)(pent-4-en-1-yl)carbamate (**1k**)⁴



This substrate was prepared as follows, to a round-bottom flask with a magnetic stir bar were added 5-bromopent-1-ene (1.18 mL, 10 mmol), *p*-methoxybenzylamine (6.85 g, 50.0 equiv.) and ethanol (100 mL). The mixture was stirred at 80 °C for 6 h and then concentrated in vacuo to remove most of the solvent. The

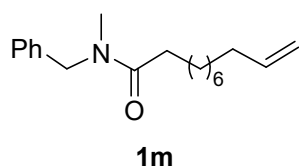
concentrate was washed with water, extracted with ethyl acetate (50 mL \times 3), dried over Na₂SO₄, filtrated, concentrated in vacuo and purified by silica gel (ethyl acetate /petroleum ether/triethylamine,10/100/1) to afford *N*-(4-methoxybenzyl)pent-4-en-1-amine as a colorless oil (1.7 g, 83% yield). To around-bottom flask with a magnetic stir bar charged with the obtained secondary amine (1.44 g, 7.0 mmol), Boc₂O (2.3 g, 10.5 mmol) and THF (50 mL), the reaction mixture was stirred overnight at 50 °C. Followed by the normal work-up, the crude product was purified by silica gel flash chromatography petroleum ether/ethyl acetate (10/1, v/v) to give the desired product as colorless thick oil (2.02 g, 94% yield). ¹H NMR (300 MHz, CDCl₃) δ 7.15 (s, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 5.84–5.71 (m, 1H), 4.96 (t, *J* = 8.7 Hz, 2H), 4.35 (s, 2H), 3.80 (s, 3H), 3.18–3.09 (m, 2H), 2.01–1.99 (m, 2H), 1.59 (s, 2H), 1.46 (s, 9H).

N-benzyl-*N*-methylhex-5-en-1-amine (1l)⁴



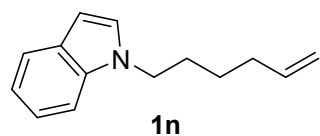
Prepared according to the general procedure **B** using benzyl methylamine (1.21 g, 10.0 mmol), NaH (480 mg, 12 mmol, 60% dispersion in mineral oil) and 6-bromo-1-hexene (2.0 mL, 15.0 mmol) in DMF (50 mL). The reaction was quenched by glacial water and then extracted with CH₂Cl₂ (50 mL \times 2). The organic phase was combined and dried over Na₂SO₄, filtrated, concentrated in vacuo and purified by silica gel flash chromatography petroleum ether/ethyl acetate (10/1, v/v) to afford the product as a colorless oil (1.03 g, 51% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.30 (d, *J* = 4.4, 4H), 7.25–7.22 (m, 1H), 5.85–5.75 (m, 1H), 5.01–4.92 (m, 2H), 3.47 (s, 2H), 2.36 (t, *J* = 7.6 Hz, 2H), 2.18 (s, 3H), 2.05 (dd, *J* = 14.0, 7.2 Hz, 2H), 1.55–1.49 (m, 2H), 1.44–1.37 (m, 2H).

N-benzyl-*N*-methylundec-10-enamide (1m)⁴



This substrate was prepared from undecenoic acid (1.2 mL, 8.9 mmol) and pivaloyl chloride (1.0 mL, 8.1 mmol) in the presence of triethylamine (2.9 mL, 24 mmol) in THF (20 mL) followed by the reaction with benzylmethylamine (1.2 mL, 9.0 mmol). The crude product was purified by silica gel (15/100/1, ethyl acetate /petroleum ether/triethylamine) to afford the desired enamide as a colorless oil (1.68 g, 66% yield). ¹H NMR (300 MHz, CDCl₃) δ 7.39–7.22 (m, 4H), 7.16 (d, *J* = 7.2 Hz, 1H), 5.88–5.73 (m, 1H), 5.01–4.91 (m, 2H), 4.56 (d, *J* = 17.7 Hz, 2H), 2.93 (d, *J* = 8.1 Hz, 3H), 2.39–2.34 (m, 2H), 2.07–1.99 (m, 2H), 1.73–1.63 (m, 2H), 1.40–1.24 (m, 10H).

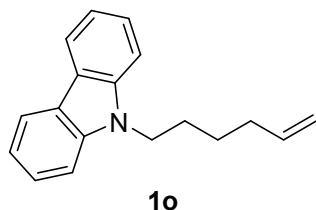
1-(Hex-5-en-1-yl)-1H-indole (1n)⁴



Prepared according to the general procedure **B** using indole (0.58 g, 5.0 mmol), NaH (240 mg, 6 mmol, 60% dispersion in mineral oil) and 6-bromo-1-hexene (1.0 mL, 7.5 mmol) in DMF (25 mL). The reaction was quenched by glacial water and then extracted with CH₂Cl₂ (25 mL \times 3). The organic phase was combined and dried over Na₂SO₄, followed by the usual work-up and purified by silica gel flash chromatography petroleum ether/ethyl acetate (20/1, v/v) to afford the product as a clear oil (0.73 g, 73% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.63 (d, *J* = 8.0, 1H), 7.34 (d, *J* = 8.4, 1H), 7.20 (t, *J* = 7.2, 8.4 Hz, 1H), 7.11–7.07 (m, 2H), 6.48 (d, *J* = 3.2

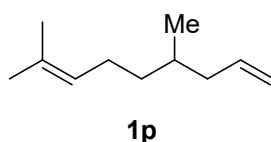
Hz, 1H), 5.81–5.71 (m, 1H), 5.01–4.97 (m, 2H), 4.13 (t, $J = 7.2$ Hz, 2H), 2.07 (q, $J = 7.2$ Hz, 2H), 1.89–1.82 (m, 2H), 1.46–1.39 (m, 2H).

9-(Hex-5-en-1-yl)-9H-carbazole (**1o**)⁴



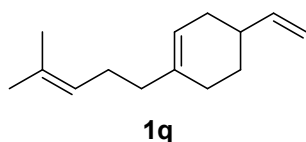
Prepared according to the general procedure **B** using carbazole (0.83 g, 5.0 mmol), NaH (240 mg, 6 mmol, 60% dispersion in mineral oil) and 6-bromo-1-hexene (1.0 mL, 7.5 mmol) in DMF (50 mL). The reaction was quenched by glacial water and then extracted with CH_2Cl_2 (25 mL \times 2). The organic phase was combined and dried over Na_2SO_4 , followed by the usual work-up and purified by silica gel flash chromatography petroleum ether/ethyl acetate (20/1, v/v) to afford the product as a white solid (0.171 g, 94% yield). ^1H NMR (400 MHz, CDCl_3) δ 8.10 (d, $J = 8.0$ Hz, 2H), 7.46 (t, $J = 7.2$ Hz, 2H), 7.41 (d, $J = 8.0$ Hz, 2H), 7.23 (t, $J = 6.8$ Hz, 2H), 5.81–5.70 (m, 1H), 5.01–4.93 (m, 2H), 4.32 (t, $J = 7.2$ Hz, 2H), 2.09 (dd, $J = 14.4, 7.2$ Hz, 2H), 1.94–1.86 (m, 2H), 1.52–1.46 (m, 2H).

4,8-Dimethylnona-1,7-diene (**1p**)⁵



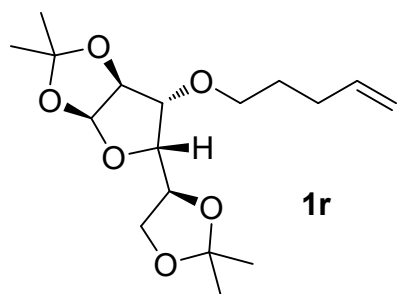
This substrate was prepared as follows, to a round-bottom flask with a magnetic stir bar was added *t*-BuOK (0.92 g, 7.5 mmol) and THF (20 mL) Under argon atmosphere, and methyltriphenylphosphonium Bromide (2.68 g, 7.5 mmol) was added dropwise at 0 °C (ice bath). After 30 min the Citronellal (906 μL 5.0 mmol) was added to the round-bottom flask, Then the reaction was allowed to warm to room temperature and stirred for additional 12 h. After the filtration, the combined organic phase was dried over anhydrous MgSO_4 and concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography petroleum ether/ethyl acetate (100/1, v/v) to give the product as colorless oil (0.48 g, 63% yield). ^1H NMR (400 MHz, CDCl_3) δ 5.83–5.73 (m, 1H), 5.10 (t, $J = 6.8$ Hz, 1H), 5.01–4.97 (m, 2H), 2.11–1.93 (m, 3H), 1.91–1.86 (m, 1H), 1.68 (s, 3H), 1.60 (s, 3H), 1.55–1.47 (m, 1H), 1.39–1.31 (m, 1H), 1.19–1.10 (m, 1H), 0.88 (d, $J = 6.4$ Hz, 3H).

1-(4-Methylpent-3-en-1-yl)-4-vinylcyclohex-1-ene (**1q**)⁵



This substrate was prepared as follows, to a round-bottom flask with a magnetic stir bar was added *t*-BuOK (0.92 g, 7.5 mmol) and THF (20 mL) Under argon, and methyltriphenylphosphonium Bromide (2.68 g, 7.5 mmol) was added dropwise at 0 °C (ice bath). After 30 min the Myrac aldehyde (1.01 mL, 5.0 mmol) was added to the round-bottom flask. Then the reaction was allowed to warm to room temperature and stirred for additional 12 h. After the filtration, the combined organic phase was dried over anhydrous MgSO_4 and concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography petroleum ether/ethyl acetate (100/1, v/v) to give the product as colourless oil (0.77 g, 81% yield). ^1H NMR (300 MHz, CDCl_3) δ 5.90–5.78 (m, 1H), 5.39 (s, 1H), 5.12–4.92 (m, 3H), 2.29–2.15 (m, 1H), 2.08–2.04 (m, 3H), 1.97–1.92 (m, 3H), 1.87–1.76 (m, 2H), 1.68 (s, 2H), 1.60 (s, 2H), 1.54 (s, 2H), 1.45–1.24 (m, 2H).

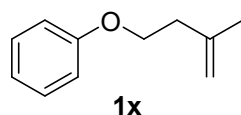
(3a*S*,5*S*,6*R*,6a*S*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl-6-(pent-4-en-1-yloxy)tetrahydrofuro[2,3-*d*][1,3]dioxole (1r**)⁴**



Prepared according to the general procedure **B** using diacetone-D-glucose (2.6 g, 10.0 mmol), NaH (480 mg, 12.0 mmol, 60% dispersion in mineral oil) and 5-bromopent-1-ene (1.78 mL, 15.0 mmol) in DMF (50 mL). The reaction was quenched by glacial water and then extracted with CH₂Cl₂ (20 mL ×3). The organic phase was combined and dried over Na₂SO₄, followed by the usual work-up and purified by silica gel flash chromatography petroleum

ether/ethyl acetate (10/1, v/v) to afford the product as a thick oil (2.2 g, 67% yield). ¹H NMR (300 MHz, CDCl₃) δ 5.87 (d, *J* = 3.6 Hz, 1H), 5.85–5.73 (m, 1H), 5.06–4.96 (m, 2H), 4.52 (d, *J* = 3.9 Hz, 1H), 4.31 (dd, *J* = 13.5, 6.0 Hz, 1H), 4.15–4.06 (m, 2H), 4.01–3.96 (m, 1H), 3.85 (d, *J* = 3.0 Hz, 1H), 3.66–3.58 (m, 1H), 3.56–3.48 (m, 1H), 2.13 (dd, *J* = 14.4, 6.9 Hz, 2H), 1.71–1.61 (m, 2H), 1.50 (s, 3H), 1.42 (s, 3H), 1.35 (s, 3H), 1.31 (s, 3H).

((3-Methylbut-3-en-1-yl)oxy)benzene (1x**)⁶**



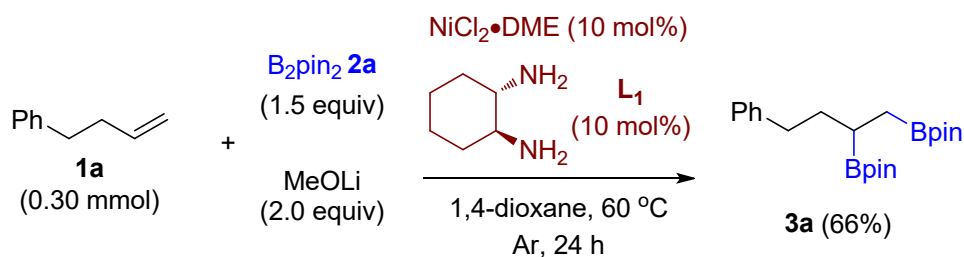
To a stirred solution of 3-methyl-3-buten-1-ol (840 μL, 8.19 mmol) in THF (25 mL) were added sequentially phenol (2.31g, 24.5 mmol), triphenylphosphine (2.78 g, 10.6 mmol) and Diethyl azodicarboxylate (1.81 mL, 10.6 mmol). The mixture was heated at 70 °C, overnight and

then was concentrated in vacuum. The residue was purified by silica gel flash chromatography petroleum ether/ethyl acetate (100/1, v/v) to afford **1x** was obtained as a yellow oil in 75% yield (0.99 g); ¹H NMR (400 MHz, CDCl₃) δ 7.30–7.28 (m, 2H), 6.96–6.90 (m, 3H), 4.82 (d, *J* = 16.0 Hz, 2H), 4.08 (t, *J* = 6.8 Hz, 2H), 2.51 (t, *J* = 6.9 Hz, 2H), 1.81 (s, 3H).

3. Optimal Conditions

During this process, it's noticed that four points should be highlighted. (1) Base plays a very essential role for promoting the transformation. As shown in Table S1, entries 2-5, replacing MeOLi with other bases such as sodium or potassium salts, or decrease its amount to 1.5 equiv only led to inferior yields (entry 6). (2) The screen of different nickel source indicates the use of NiCl₂•DME could deliver the best result (entry 7). (3) For the commercially ligand screened, it turns out that the employment of 1,2-cyclohexdiamine L1 enables to give the best yield in our hand (entry 8). (3) Temperature is very important for accelerating the rate, as its change to 40 °C gives rise to almost no reaction (entry 9). (4) Control experiments identify that both nickel salt and ligand L₁ is inevitable for the transformation (entries 10, 12, 13), and at least 10 mol% catalyst loading is necessary (entry 14). Noteworthy, the utilization of L₁ alone can also promote the diborylation, albeit with lower yields even in the presence of 40 mol% of L₁ (entry 11).

Table S1 Optimal conditions.^a

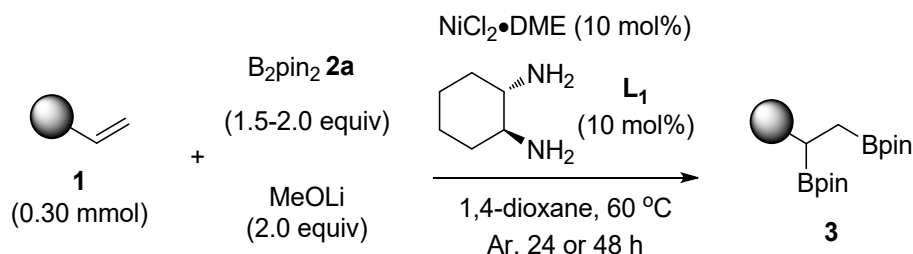


Entry	Deviation from standard conditions	Yield 3a (%) ^b
1	none	69 (66) ^c
2	MeONa or ^t BuONa instead of MeOLi	28/5
3	^t BuOK or K ₂ CO ₃ instead of MeOLi	Trace/NR
4	KHCO ₃ or K ₃ PO ₄ instead of MeOLi	NR/40
5	CsF instead of MeOLi	NR
6	with 1.5 equiv MeOLi	60
7	NiBr ₂ ·DME, NiI ₂ or Ni(acac) ₂ , instead of NiCl ₂ ·DME	38/65/14
8	 L₂ : 46% L₃ : 14% L₄ : 37% L₅ : 31%	
9	40 °C instead of 60 °C	4
10	No NiCl ₂ ·DME	40
11	With only 20 or 40 mol% L₁	51/60
12	No L₁	7
13	No NiCl ₂ ·DME or L₁	16
14	20 mol% or 5 mol% catalyst instead of 10 mol%	73/46

^a Conditions: **1a** (0.30 mmol), **2a** (1.5 equiv), NiCl₂·DME (0.030 mmol, 10 mol%), **L₁** (0.030 mmol, 10 mol%), MeOLi (2.0 equiv), 1,4-dioxane (1.0 mL) at 60 °C for 24 hours. ^b GC yield using *n*-dodecane as the internal standard. ^c Isolated yield. NR = no reaction.

4. General Procedure for the Synthesis of 1,2-Diboronation compounds

4.1. General Procedure C for the Synthesis of 3

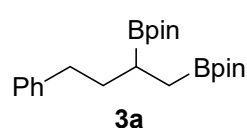


Under an argon atmosphere, 1,2-cyclohexdiamine was dissolved in 1,4-dioxane to obtain 1,2-cyclohexanediamine solution, and then $NiCl_2 \cdot DME$, 1,2-cyclohexdiamine solution, mono-substituted Aliphatic Alkenes, B_2pin_2 , MeOLi, 1,4-dioxane were added to the Schlenk tube in order, The mixture was stirred at T °C for 24 or 48 hours and then filtrated, concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography to provide the corresponding 1,2-Diboronation compounds.

4.2. General Procedure D for the Synthesis of 3u, 3v, 3w, 3x

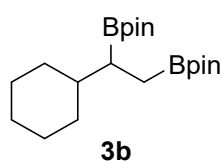
The Cs_2CO_3 (14.7 mg, 0.45 mmol) and the B_2pin_2 (83.8 mg, 0.33 mmol) were transferred into an oven-dried Schlenk tube, provided with stir bar, under argon. THF (1.2 mL) was added to dissolve the mixture. After that, the substrate (0.3 mmol) and MeOH (240 μ l, 6.0 mmol) were added, and the reaction mixture was stirred at a pre-determined temperature in an oil bath for 6 hours. The reaction mixture was cooled to room temperature. After the filtration, the combined organic phase was dried over anhydrous $MgSO_4$ and concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography to provide the corresponding 1,2-Diboronation compounds.

2,2'-(4-Phenylbutane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**3a**)⁷



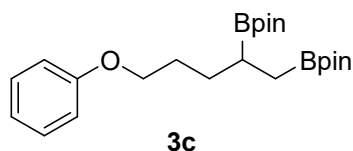
Under an argon atmosphere, 1,2-cyclohexdiamine (99.5 mg, 0.87 mmol) was dissolved in 1,4-dioxane (10 mL) to obtain 1,2-cyclohexanediamine solution (0.087 mol/L), and then $NiCl_2 \cdot DME$ (6.6 mg, 0.03 mmol, 10 mol%), 1,2-cyclohexanediamine solution (345 μ L, 0.03 mmol, 10 mol%), but-3-en-1-ylbenzene (46 μ L, 0.3 mmol), B_2pin_2 (114.3 mg, 0.45 mmol, 1.5 eq), MeOLi (22.8 mg, 0.6 mmol, 2 eq), 1,4-dioxane (0.65 mL) were added to the Schlenk tube in order, The mixture was stirred at 60 °C for 24 h and then filtrated, concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography petroleum ether/ethyl acetate (20/1, v/v) to afford the corresponding product **3a** (76.4 mg, 66% yield) as a colorless oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.24 (t, J = 7.6 Hz, 2H), 7.18–7.12 (m, 3H), 2.61 (t, J = 8.0 Hz, 2H), 1.83–1.74 (m, 1H), 1.68–1.59 (m, 1H), 1.24 (s, 12H), 1.23 (s, 12H), 1.19–1.17 (m, 1H), 0.98–0.84 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 128.4, 128.2, 125.4, 82.9, 77.4, 77.0, 76.7, 36.0, 35.4, 24.9, 24.9, 24.8, 24.8, 18.5, 12.4.

2,2'-(1-Cyclohexylethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**3b**)⁸



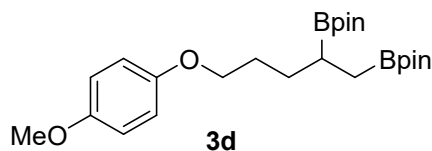
Under an argon atmosphere, 1,2-cyclohexdiamine (99.5 mg, 0.87 mmol) was dissolved in 1,4-dioxane (10 mL) to obtain 1,2-cyclohexanediamine solution (0.087 mol/L), and then NiCl₂·DME (6.6 mg, 0.03 mmol, 10 mol%), 1,2-cyclohexanediamine solution (345 μL, 0.03 mmol, 10 mol%), vinylcyclohexane (42 μL, 0.3 mmol), B₂pin₂ (152.4 mg, 0.6 mmol, 2.0 eq), MeOLi (22.8 mg, 0.6 mmol, 2 eq), 1,4-dioxane (0.65 mL) were added to the Schlenk tube in order. The mixture was stirred at 70 °C for 36 h and then filtrated, concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography petroleum ether/ethyl acetate (20/1, v/v) to afford the corresponding product **3b** (46.8 mg, 43% yield) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 1.66 (d, *J* = 10.4 Hz, 4H), 1.38–1.25 (m, 2H), 1.22 (s, 12H), 1.20 (s, 12H), 1.17–0.73 (m, 8H); ¹³C NMR (126 MHz, CDCl₃) δ 82.8, 82.7, 77.3, 77.0, 76.7, 41.5, 32.1, 32.0, 26.9, 26.8, 26.7, 25.0, 24.9, 24.9, 24.7, 9.6.

2,2'-(5-Phenoxy-pentane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**3c**)⁹



Under an argon atmosphere, 1,2-cyclohexdiamine (99.5 mg, 0.87 mmol) was dissolved in 1,4-dioxane (10 mL) to obtain 1,2-cyclohexanediamine solution (0.087 mol/L), and then NiCl₂·DME (6.6 mg, 0.03 mmol, 10 mol%), 1,2-cyclohexanediamine solution (345 μL, 0.03 mmol, 10 mol%), (pent-4-en-1-yloxy)benzene (55 μL, 0.3 mmol), B₂pin₂ (152.4 mg, 0.6 mmol, 2.0 eq), MeOLi (22.8 mg, 0.6 mmol, 2 eq), 1,4-dioxane (0.65 mL) were added to the Schlenk tube in order. The mixture was stirred at 60 °C for 24 h and then filtrated, concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography petroleum ether/ethyl acetate (20/1, v/v) to afford the corresponding product **3c** (77.0 mg, 62% yield) as a white solid. ¹H NMR (300 MHz, CDCl₃) δ 7.28–7.23 (m, 2H), 6.93–6.86 (m, 3H), 3.93 (t, *J* = 6.6 Hz, 2H), 1.85–1.75 (m, 2H), 1.64–1.57 (m, 1H), 1.54–1.42 (m, 1H), 1.23 (s, 12H), 1.23 (s, 12H), 1.18–1.13 (m, 1H), 0.93–0.80 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 159.1, 129.3, 120.2, 114.5, 82.8, 77.3, 77.0, 76.7, 68.1, 29.9, 28.5, 24.9, 24.8, 24.8, 24.7, 18.2, 12.6.

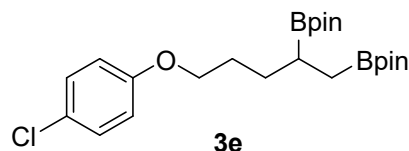
2,2'-(5-(4-Methoxyphenoxy)pentane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**3d**)



Under an argon atmosphere, 1,2-cyclohexdiamine (99.5 mg, 0.87 mmol) was dissolved in 1,4-dioxane (10 mL) to obtain 1,2-cyclohexanediamine solution (0.087 mol/L), and then NiCl₂·DME (6.6 mg, 0.03 mmol, 10 mol%), 1,2-cyclohexanediamine solution (345 μL, 0.03 mmol, 10 mol%), 1-methoxy-4-(pent-4-en-1-yloxy)benzene (61 μL, 0.3 mmol), B₂pin₂ (152.4 mg, 0.6 mmol, 2.0 eq), MeOLi (22.8 mg, 0.6 mmol, 2 eq), 1,4-dioxane (0.65 mL) were added to the Schlenk tube in order. The mixture was stirred at 60 °C for 24 h and then filtrated, concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography petroleum ether/ethyl acetate (15/1, v/v) to afford the corresponding product **3d** (89.0 mg, 66% yield) as a white solid. ¹H NMR (300 MHz, CDCl₃) δ 6.80 (s, 4H), 3.87 (t, *J* = 6.6 Hz, 2H), 3.74 (s, 3H), 1.83–1.72 (m, 2H), 1.64–1.55 (m, 1H), 1.52–1.43 (m, 1H), 1.22 (s, 12H), 1.22 (s, 12H), 1.16–1.11 (m, 1H), 0.95–0.78 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 153.5, 153.3, 115.4, 114.5, 82.8, 77.3, 77.0, 76.7, 68.8, 55.7,

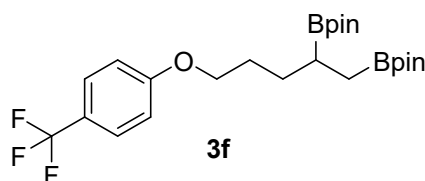
29.9, 28.5, 24.8, 24.8, 24.7, 24.7, 18.2, 12.4; IR (neat, cm^{-1}) 2978, 2924, 2373, 1511, 1469, 1356, 1317, 1228, 1136, 1041, 969, 884, 836, 740, 672; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{41}\text{B}_2\text{O}_6$ 447.3089; Found 447.3801

2,2'-(5-(4-Chlorophenoxy)pentane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3e)



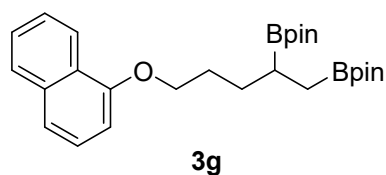
Under an argon atmosphere, 1,2-cyclohexdiamine (99.5 mg, 0.87 mmol) was dissolved in 1,4-dioxane (10 mL) to obtain 1,2-cyclohexanediamine solution (0.087 mol/L), and then $\text{NiCl}_2 \cdot \text{DME}$ (6.6 mg, 0.03 mmol, 10 mol%), 1,2-cyclohexanediamine solution (345 μL , 0.03 mmol, 10 mol%), 1-chloro-4-(pent-4-en-1-yloxy)benzene (61 μL , 0.3 mmol), B_2pin_2 (152.4 mg, 0.6 mmol, 2.0 eq), MeOLi (22.8 mg, 0.6 mmol, 2 eq), 1,4-dioxane (0.65 mL) were added to the Schlenk tube in order. The mixture was stirred at 60 $^\circ\text{C}$ for 24 h and then filtrated, concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography petroleum ether/ethyl acetate (20/1, v/v) to afford the corresponding product 3e (91 mg, 67% yield) as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.19 (d, $J = 8.9$ Hz, 2H), 6.79 (d, $J = 8.9$ Hz, 2H), 3.90 (t, $J = 6.7$ Hz, 2H), 1.82–1.74 (m, 2H), 1.63–1.54 (m, 1H), 1.51–1.42 (m, 1H), 1.23 (s, 12H), 1.22 (s, 12H), 1.17–1.13 (m, 1H), 0.94–0.80 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 157.8, 129.2, 125.1, 115.8, 82.9, 77.4, 77.0, 76.7, 68.6, 29.9, 28.4, 24.9, 24.9, 24.8, 24.8, 18.2, 12.7; IR (neat, cm^{-1}) 2971, 2925, 2861, 2369, 1632, 1451, 1379, 1313, 1261, 1086, 1043, 878, 807, 669; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{23}\text{H}_{38}\text{B}_2\text{ClO}_5$ 451.2594; Found 451.2585.

2,2'-(5-(4-(Trifluoromethyl)phenoxy)pentane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3f)



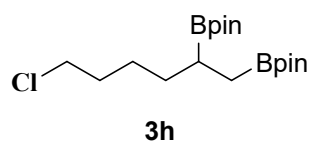
Under an argon atmosphere, 1,2-cyclohexdiamine (99.5 mg, 0.87 mmol) was dissolved in 1,4-dioxane (10 mL) to obtain 1,2-cyclohexanediamine solution (0.087 mol/L), and then $\text{NiCl}_2 \cdot \text{DME}$ (6.6 mg, 0.03 mmol, 10 mol%), 1,2-cyclohexanediamine solution (345 μL , 0.03 mmol, 10 mol%), 1-(pent-4-en-1-yloxy)-4-(trifluoromethyl)benzene (64 μL , 0.3 mmol), B_2pin_2 (152.4 mg, 0.6 mmol, 2.0 eq), MeOLi (22.8 mg, 0.6 mmol, 2 eq), 1,4-dioxane (0.65 mL) were added to the Schlenk tube in order. The mixture was stirred at 70 $^\circ\text{C}$ for 24 h and then filtrated, concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography petroleum ether/ethyl acetate (20/1, v/v) to afford the corresponding product 3f (93.5 mg, 64% yield) as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.50 (d, $J = 8.9$ Hz, 2H), 6.92 (d, $J = 8.8$ Hz, 2H), 3.97 (t, $J = 6.6$ Hz, 2H), 1.85–1.77 (m, 2H), 1.63–1.56 (m, 1H), 1.53–1.44 (m, 1H), 1.23 (s, 12H), 1.23 (s, 12H), 1.17–1.14 (m, 1H), 0.95–0.80 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 161.6, 128.6, 126.7, 126.7, 125.9, 123.2, 122.9, 122.5, 122.2, 121.9, 120.5, 114.5, 82.9, 82.9, 77.4, 77.0, 76.7, 68.5, 29.9, 28.3, 25.0, 24.9, 24.8, 24.8, 24.7, 18.1, 12.7; ^{19}F NMR (376 MHz, CDCl_3 , ppm) δ -61.39 (s, 1F); IR (neat, cm^{-1}) 2981, 2928, 1618, 1462, 1363, 1317, 1264, 1151, 1114, 1066, 1099, 963, 888, 839, 757, 704, 672, 629, 573; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{38}\text{B}_2\text{F}_3\text{O}_5$ 485.2857; Found 485.2736

2,2'-(5-(Naphthalen-1-yloxy)pentane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)
(3g)



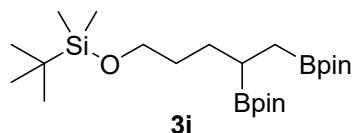
Under an argon atmosphere, 1,2-cyclohexdiamine (99.5 mg, 0.87 mmol) was dissolved in 1,4-dioxane (10 mL) to obtain 1,2-cyclohexanediamine solution (0.087 mol/L), and then NiCl₂·DME (6.6 mg, 0.03 mmol, 10 mol%), 1,2-cyclohexanediamine solution (345 μL, 0.03 mmol, 10 mol%), 1-(pent-4-en-1-yloxy)naphthalene (65 μL, 0.3 mmol), B₂pin₂ (114.3 mg, 0.45 mmol, 1.5 eq), MeOLi (22.8 mg, 0.6 mmol, 2 eq), 1,4-dioxane (0.65 mL) were added to the Schlenk tube in order. The mixture was stirred at 60 °C for 48 h and then filtrated, concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography petroleum ether/ethyl acetate (20/1, v/v) to afford the corresponding product **3g** (89.0 mg, 64% yield) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 8.33–8.30 (m, 1H), 7.79–7.77 (m, 1H), 7.49–7.43 (m, 2H), 7.41–7.33 (m, 2H), 6.79 (d, *J* = 8.8 Hz, 1H), 4.13 (t, *J* = 6.48 Hz, 2H), 2.00–1.93 (m, 2H), 1.79–1.69 (m, 1H), 1.67–1.58 (m, 1H), 1.26 (s, 12H), 1.24 (s, 12H), 1.01–0.85 (m, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 154.9, 134.4, 127.3, 126.2, 125.9, 125.7, 124.9, 122.2, 119.7, 104.4, 82.9, 82.8, 77.3, 77.0, 76.7, 68.3, 30.3, 28.6, 24.9, 24.8, 24.8, 24.7, 18.2, 12.6; IR (neat, cm⁻¹) 2978, 2928, 2868, 2376, 1586, 1504, 1462, 1356, 1313, 1267, 1139, 1097, 1066, 963, 842, 774, 669; HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₂₇H₄₁B₂O₅ 467.3140; Found 467.3105.

2,2'-(6-Chlorohexane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**3h**)⁷



Under an argon atmosphere, 1,2-cyclohexdiamine (99.5 mg, 0.87 mmol) was dissolved in 1,4-dioxane (10 mL) to obtain 1,2-cyclohexanediamine solution (0.087 mol/L), and then NiCl₂·DME (6.6 mg, 0.03 mmol, 10 mol%), 1,2-cyclohexanediamine solution (345 μL, 0.03 mmol, 10 mol%), 6-chlorohex-1-ene (41 μL, 0.3 mmol), B₂pin₂ (152.4 mg, 0.6 mmol, 2.0 eq), MeOLi (22.8 mg, 0.6 mmol, 2 eq), 1,4-dioxane (0.65 mL) were added to the Schlenk tube in order. The mixture was stirred at 70 °C for 24 h and then filtrated, concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography petroleum ether/ethyl acetate (20/1, v/v) to afford the corresponding product **3h** (58.1 mg, 52% yield) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 3.50 (t, *J* = 6.8 Hz, 2H), 1.77–1.70 (m, 2H), 1.48–1.30 (m, 4H), 1.22 (s, 12H), 1.21 (s, 12H), 1.14–1.05 (m, 1H), 0.90–0.75 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 82.9, 77.3, 77.0, 76.7, 45.1, 32.9, 32.8, 26.1, 24.9, 24.8, 24.8, 24.7, 18.8, 12.2.

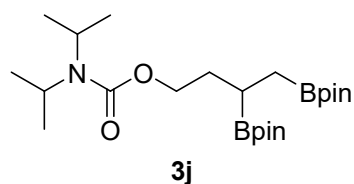
((4,5-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)oxy)(tert-butyl)dimethylsilane
(3i)¹⁰



Under an argon atmosphere, 1,2-cyclohexdiamine (99.5 mg, 0.87 mmol) was dissolved in 1,4-dioxane (10 mL) to obtain 1,2-cyclohexanediamine solution (0.087 mol/L), and then NiCl₂·DME (6.6 mg, 0.03 mmol, 10 mol%), 1,2-cyclohexanediamine solution (345 μL, 0.03 mmol, 10 mol%), tert-butyl dimethyl(pent-4-en-1-yloxy)silane (80 μL, 0.3 mmol), B₂pin₂ (114.3 mg, 0.45 mmol, 1.5 eq), MeOLi (22.8 mg, 0.6 mmol, 2 eq), 1,4-dioxane (0.65 mL) were added to the Schlenk tube in order. The mixture was

stirred at 60 °C for 36 h and then filtrated, concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography petroleum ether/ethyl acetate (20/1, v/v) to afford the corresponding product **3i** (73.1 mg, 54% yield) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 3.56 (t, *J* = 6.8 Hz, 2H), 1.53–1.48 (m, 2H), 1.46–1.41 (m, 1H), 1.34–1.29 (m, 1H), 1.21 (s, 12H), 1.21 (s, 12H), 1.11–1.05 (m, 1H), 0.86 (s, 9H), 0.85–0.79 (m, 2H), 0.01 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 82.8, 82.8, 77.3, 77.0, 76.7, 63.7, 32.3, 29.9, 26.0, 24.9, 24.8, 24.8, 24.7, 18.4, 18.2, 12.7, -5.2.

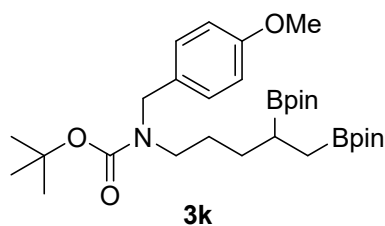
3,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl diisopropylcarbamate (**3j**)³



Under an argon atmosphere, 1,2-cyclohexdiamine (99.5 mg, 0.87 mmol) was dissolved in 1,4-dioxane (10 mL) to obtain 1,2-cyclohexanediamine solution (0.087 mol/L), and then NiCl₂·DME (6.6 mg, 0.03 mmol, 10 mol%), cyclohexanediamine solution (230 μL, 0.02 mmol, 10 mol%),

but-3-en-1-yl diisopropylcarbamate (46 μL, 0.2 mmol), B₂pin₂ (101.6 mg, 0.4 mmol, 2.0 eq), MeOLi (15.2 mg, 0.4 mmol, 2 eq), 1,4-dioxane (0.8 mL) were added to the Schlenk tube in order. The mixture was stirred at 70 °C for 48 h and then filtrated, concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography petroleum ether/ethyl acetate (10/1, v/v) to afford the corresponding product **3J** (42.1 mg, 46% yield) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 4.13–4.04 (m, 2H), 4.03–3.53 (br, 2H), 1.87–1.78 (m, 1H), 1.67–1.60 (m, 1H), 1.25 (s, 1H), 1.22 (s, 12H), 1.21 (s, 12H), 1.19 (s, 6H), 1.18 (s, 6H), 0.94–0.83 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 155.9, 83.5, 83.0, 82.9, 77.4, 77.0, 76.7, 64.3, 45.6, 32.3, 25.0, 24.8, 24.8, 24.8, 24.7, 21.1, 12.4.

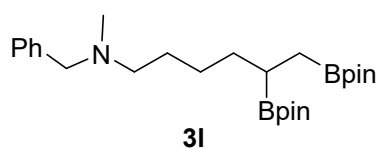
Tert-butyl(4,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)(4-methoxybenzyl)carbamate (**3k**)



Under an argon atmosphere, 1,2-cyclohexdiamine (99.5 mg, 0.87 mmol) was dissolved in 1,4-dioxane (10 mL) to obtain 1,2-cyclohexanediamine solution (0.087 mol/L), and then NiCl₂·DME (6.6 mg, 0.03 mmol, 10 mol%), 1,2-cyclohexanediamine solution (345 μL, 0.03 mmol, 10 mol%), tert-butyl(4-methoxybenzyl)(pent-4-en-1-yl)carbamate (93

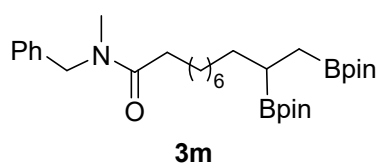
μL, 0.3 mmol), B₂pin₂ (152.4 mg, 0.6 mmol, 2.0 eq), MeOLi (22.8 mg, 0.6 mmol, 2 eq), 1,4-dioxane (0.65 mL) were added to the Schlenk tube in order. The mixture was stirred at 70 °C for 24 h and then filtrated, concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography petroleum ether/ethyl acetate (20/1, v/v) to afford the corresponding product **3k** (90.1 mg, 54% yield) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.14 (s, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 4.34 (s, 2H), 3.78 (s, 3H), 3.05 (s, 2H), 1.46 (s, 10H), 1.26 (s, 3H), 1.22 (s, 12H), 1.21 (s, 12H), 1.12–1.05 (m, 1H), 0.88–0.74 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 158.6, 130.6, 128.9, 128.3, 113.7, 83.4, 82.7, 79.1, 77.3, 77.0, 76.7, 55.1, 48.8, 46.2, 30.8, 28.4, 24.9, 24.8, 24.7, 24.7, 24.6, 18.1, 12.5; IR (neat, cm⁻¹) 2975, 2920, 2786, 2726, 1693, 1611, 1508, 1466, 1416, 1369, 1313, 1249, 1147, 1034, 966, 846; HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₃₀H₅₂B₂NO₇ 560.3930; Found 560.3931.

N-Benzyl-*N*-methyl-5,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-1-amine (**3l**)



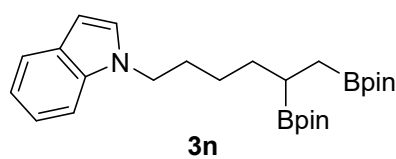
Under an argon atmosphere, 1,2-cyclohexdiamine (99.5 mg, 0.87 mmol) was dissolved in 1,4-dioxane (10 mL) to obtain 1,2-cyclohexanediamine solution (0.087 mol/L), and then NiCl₂·DME (6.6 mg, 0.03 mmol, 10 mol%), 1,2-cyclohexanediamine solution (345 μL, 0.03 mmol, 10 mol%), *N*-benzyl-*N*-methylhex-5-en-1-amine (70 μL, 0.3 mmol), B₂pin₂ (114.3 mg, 0.45 mmol, 1.5 eq), MeOLi (22.8 mg, 0.6 mmol, 2 eq), 1,4-dioxane (0.65 mL) were added to the Schlenk tube in order, The mixture was stirred at 60 °C for 48 h and then filtrated, concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography petroleum ether/ethyl acetate (4/1, v/v) to afford the corresponding product **3l** (102.3 mg, 74% yield) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.30–7.20 (m, 5H), 3.46 (s, 2H), 2.35 (t, *J* = 7.5 Hz, 2H), 2.15 (s, 3H), 1.54–1.46 (m, 3H), 1.35–1.29 (m, 3H), 1.22 (s, 12H), 1.22 (s, 12H), 1.15–1.08 (m, 1H), 0.90–0.74 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 138.8, 129.1, 128.1, 126.8, 82.8, 82.7, 77.3, 77.0, 76.7, 62.0, 57.5, 42.0, 33.7, 27.4, 26.7, 24.8, 24.8, 24.7, 24.7, 18.4, 12.6; IR (neat, cm⁻¹) 3088, 3046, 2858, 2811, 2744, 1646, 1459, 1369, 1317, 1267, 1218, 1143, 969, 853, 739, 694; HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₂₆H₄₆B₂NO₄ 458.3613; Found 458.3623.

N-Benzyl-*N*-methyl-10,11-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)undecanamide (**3m**)



Under an argon atmosphere, 1,2-cyclohexdiamine (99.5 mg, 0.87 mmol) was dissolved in 1,4-dioxane (10 mL) to obtain 1,2-cyclohexanediamine solution (0.087 mol/L), and then NiCl₂·DME (6.6 mg, 0.03 mmol, 10 mol%), 1,2-cyclohexanediamine solution (345 μL, 0.03 mmol, 10 mol%), *N*-benzyl-*N*-methylundec-10-enamide (91 μL, 0.3 mmol), B₂pin₂ (152.4 mg, 0.6 mmol, 2.0 eq), MeOLi (22.8 mg, 0.6 mmol, 2 eq), 1,4-dioxane (0.65 mL) were added to the Schlenk tube in order, The mixture was stirred at 70 °C for 24 h and then filtrated, concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography petroleum ether/ethyl acetate (4/1, v/v) to afford the corresponding product **3m** (100.2 mg, 62% yield) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.37–7.14 (m, 5H), 4.55 (d, *J* = 23.9 Hz, 2H), 2.91 (d, *J* = 10.3 Hz, 3H), 2.37–2.32 (m, 2H), 1.70–1.60 (m, 2H), 1.46–1.25 (m, 12H), 1.22 (d, *J* = 2.2 Hz, 24H), 1.10–1.06 (m, 1H), 0.89–0.74 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 173.5, 173.1, 137.4, 136.7, 128.7, 128.4, 127.8, 127.4, 127.1, 126.1, 82.6, 82.6, 77.3, 77.0, 76.7, 53.2, 50.6, 34.7, 33.7, 33.4, 33.0, 29.7, 29.5, 29.3, 29.3, 29.2, 28.7, 25.3, 25.1, 24.9, 24.8, 24.7, 24.6, 24.6, 18.2, 12.5; IR (neat, cm⁻¹) 3056, 2593, 2823, 1646, 1454, 1370, 1313, 1256, 1143, 967, 840, 722, 694; HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₃₁H₅₄B₂NO₅ 542.4118; Found 542.4221.

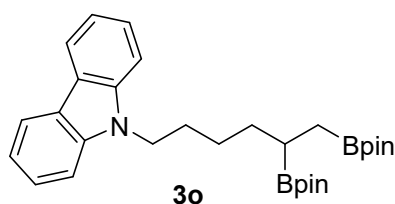
1-(5,6-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)-1H-indole (**3n**)



Under an argon atmosphere, 1,2-cyclohexdiamine (99.5 mg, 0.87 mmol) was dissolved in 1,4-dioxane (10 mL) to obtain 1,2-cyclohexanediamine solution (0.087 mol/L), and then NiCl₂·DME (6.6 mg, 0.03 mmol, 10 mol%), 1,2-cyclohexanediamine solution (345 μL, 0.03 mmol, 10 mol%), 1-(hex-5-en-1-yl)-1H-indole (64 μL,

0.3 mmol), B₂pin₂ (152.4 mg, 0.6 mmol, 2.0 eq), MeOLi (22.8 mg, 0.6 mmol, 2 eq), 1,4-dioxane (0.65 mL) were added to the Schlenk tube in order, The mixture was stirred at 70 °C for 24 h and then filtrated, concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography petroleum ether/ethyl acetate (20/1, v/v) to afford the corresponding product **3n** (80.3 mg, 59% yield) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.61 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.19 (t, *J* = 7.0 Hz, 1H), 7.10–7.06 (m, 2H), 6.46 (d, *J* = 3.0 Hz, 1H), 4.10 (t, *J* = 7.2 Hz, 2H), 1.86–1.79 (m, 2H), 1.55–1.44 (m, 1H), 1.39–1.30 (m, 3H), 1.23 (s, 12H), 1.19 (s, 12H), 1.14–1.07 (m, 1H), 0.91–0.76 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 135.9, 128.5, 127.8, 121.1, 120.8, 119.0, 109.4, 100.6, 82.8, 77.3, 77.0, 76.7, 46.2, 33.3, 30.3, 26.2, 24.9, 24.7, 24.6, 18.3, 12.8; IR (neat, cm⁻¹) 3081, 3024, 2823, 1466, 1369, 1313, 1264, 1143, 969, 849, 743; HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₂₆H₄₂B₂NO₄ 454.3300; Found 454.3355

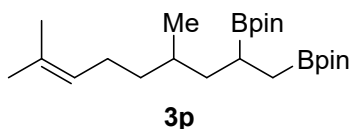
9-(5,6-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)-9H-carbazole (**3o**)



Under an argon atmosphere, 1,2-cyclohexdiamine (99.5 mg, 0.87 mmol) was dissolved in 1,4-dioxane (10 mL) to obtain 1,2-cyclohexanediamine solution (0.087 mol/L), and then NiCl₂·DME (6.6 mg, 0.03 mmol, 10 mol%), 1,2-cyclohexanediamine solution (345 μL, 0.03 mmol, 10 mol%), 9-(hex-5-en-1-yl)-9H-carbazole (75.0 mg, 0.3 mmol),

B₂pin₂ (152.4 mg, 0.6 mmol, 2.0 eq), MeOLi (22.8 mg, 0.6 mmol, 2 eq), 1,4-dioxane (0.65 mL) were added to the Schlenk tube in order, The mixture was stirred at 70 °C for 24 h and then filtrated, concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography petroleum ether/ethyl acetate (20/1, v/v) to afford the corresponding product **3o** (84.3 mg, 56% yield) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, *J* = 7.7 Hz, 2H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 7.9 Hz, 2H), 7.23 (t, *J* = 8.0 Hz, 2H), 4.30 (t, *J* = 7.3 Hz, 2H), 1.92–1.85 (m, 2H), 1.54–1.40 (m, 4H), 1.24 (s, 12H), 1.16 (s, 12H), 1.13–1.11 (m, 1H), 0.93–0.78 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 140.3, 125.5, 122.7, 120.2, 118.5, 108.6, 82.8, 82.7, 77.3, 77.0, 76.7, 42.9, 33.5, 29.1, 26.5, 24.8, 24.7, 24.7, 24.6, 18.3, 12.8; IR (neat, cm⁻¹) 2978, 2928, 2865, 1596, 1469, 1340, 1309, 1224, 1143, 963, 846, 754, 735; HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₃₀H₄₄B₂NO₄ 504.3456; Found 504.3448

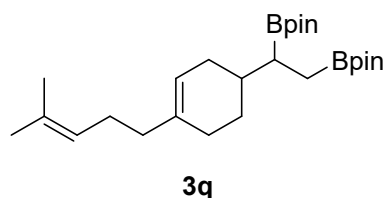
2,2'-(4,8-Dimethylnon-7-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**3p**)¹¹



Under an argon atmosphere, 1,2-cyclohexdiamine (99.5 mg, 0.87 mmol) was dissolved in 1,4-dioxane (10 mL) to obtain 1,2-cyclohexanediamine solution (0.087 mol/L), and then NiCl₂·DME (6.6 mg, 0.03 mmol, 10 mol%), 1,2-cyclohexanediamine solution (345 μL, 0.03 mmol, 10 mol%), 4,8-dimethylnona-1,7-diene (60 μL, 0.3 mmol), B₂pin₂ (152.4 mg, 0.6 mmol, 2.0 eq), MeOLi (22.8 mg, 0.6 mmol, 2 eq), 1,4-dioxane (0.65 mL) were added to the Schlenk tube in order, The mixture was stirred at 60 °C for 24 h and then filtrated, concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography petroleum ether/ethyl acetate (15/1, v/v) to afford the corresponding product **3P** (73.4 mg, 60% yield) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 5.09 (t, *J* = 7.1 Hz, 1H), 2.03–1.89 (m, 2H), 1.66 (s, 3H), 1.59 (s, 3H), 1.35–1.25 (m, 4H), 1.22 (s, 24H), 1.13–1.04 (m, 2H), 0.88–0.77 (m, 5H); ¹³C NMR (101 MHz, CDCl₃) δ 130.7, 130.6, 125.2, 82.8, 82.7, 82.7, 77.3,

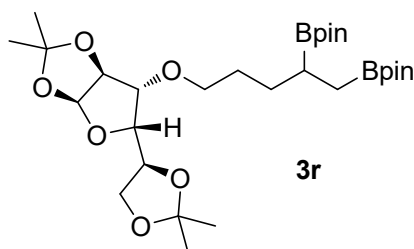
77.0, 76.7, 41.8, 40.8, 37.5, 37.2, 31.6, 31.0, 25.7, 25.5, 24.9, 24.9, 24.8, 24.8, 24.7, 24.7, 19.7, 19.4, 17.6.

2,2'-(1-(4-(4-Methylpent-3-en-1-yl)cyclohex-3-en-1-yl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3q)¹¹



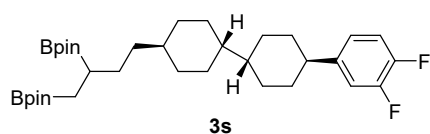
Under an argon atmosphere, 1,2-cyclohexdiamine (99.5 mg, 0.87 mmol) was dissolved in 1,4-dioxane (10 mL) to obtain 1,2-cyclohexanediamine solution (0.087 mol/L), and then NiCl₂·DME (6.6 mg, 0.03 mmol, 10 mol%), 1,2-cyclohexanediamine solution (345 μL, 0.03 mmol, 10 mol%), 1-(4-methylpent-3-en-1-yl)-4-vinylcyclohex-1-ene (68 μL, 0.3 mmol), B₂pin₂ (152.4 mg, 0.6 mmol, 2.0 eq), MeOLi (22.8 mg, 0.6 mmol, 2 eq), 1,4-dioxane (0.65 mL) were added to the Schlenk tube in order, The mixture was stirred at 70 °C for 24 h and then filtrated, concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography petroleum ether/ethyl acetate (35/1, v/v) to afford the corresponding product **3q** (40.6 mg, 30% yield) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 5.35 (s, 1H), 5.09 (t, *J* = 6.9 Hz, 1H), 2.19–1.96 (m, 4H), 1.93–1.89 (m, 3H), 1.82–1.69 (m, 2H), 1.67 (s, 3H), 1.58 (s, 3H), 1.54–1.32 (m, 2H), 1.23 (m, 12H), 1.22 (s, 12H), 1.14–1.06 (m, 1H), 0.90–0.76 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 137.8, 137.7, 137.3, 137.3, 131.1, 124.6, 120.8, 120.7, 120.4, 120.3, 82.8, 82.8, 77.4, 77.0, 76.7, 38.0, 37.9, 37.7, 37.5, 37.4, 33.9, 33.8, 30.8, 30.7, 29.3, 29.2, 28.4, 27.9, 26.5, 26.0, 25.7, 25.0, 24.8, 24.8, 24.7, 17.6, 9.7.

2,2'-(5-(((3aS,5S,6R,6aS)-5-((S)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl)oxy)pentane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3r)



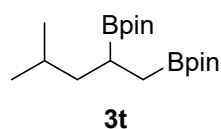
Under an argon atmosphere, 1,2-cyclohexdiamine (99.5 mg, 0.87 mmol) was dissolved in 1,4-dioxane (10 mL) to obtain 1,2-cyclohexanediamine solution (0.087 mol/L), and then NiCl₂·DME (6.6 mg, 0.03 mmol, 10 mol%), 1,2-cyclohexanediamine solution (345 μL, 0.03 mmol, 10 mol%), **1r** (118 μL, 0.3 mmol), B₂pin₂ (152.4 mg, 0.6 mmol, 2.0 eq), MeOLi (22.8 mg, 0.6 mmol, 2 eq), 1,4-dioxane (0.65 mL) were added to the Schlenk tube in order, The mixture was stirred at 60 °C for 24 h and then filtrated, concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography petroleum ether/ethyl acetate (7/1, v/v) to afford the corresponding product **3r** (132.5 mg, 76% yield) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 5.83 (d, *J* = 3.8 Hz, 1H), 4.49 (d, *J* = 2.3 Hz, 1H), 4.30–4.26 (m, 1H), 4.10 (dd, *J* = 7.2, 3.2 Hz, 1H), 4.03 (dd, *J* = 8.5, 6.2 Hz, 1H), 3.96 (dd, *J* = 8.6, 6.0 Hz, 1H), 3.80 (d, *J* = 3.0 Hz, 1H), 3.57–3.52 (m, 1H), 3.49–3.43 (m, 1H), 1.59–1.51 (m, 2H), 1.46 (s, 3H), 1.39 (s, 3H), 1.32 (s, 3H), 1.28 (s, 5H), 1.20 (s, 24H), 1.12–1.04 (m, 1H), 0.88–0.74 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 111.6, 108.7, 105.3, 82.8, 82.5, 82.0, 81.2, 77.4, 77.0, 76.7, 72.6, 71.0, 67.0, 30.1, 30.0, 29.0, 29.0, 26.9, 26.7, 26.3, 25.4, 24.9, 24.8, 24.8, 24.7, 18.1, 12.6; IR (neat, cm⁻¹) 2964, 2918, 2808, 1462, 1366, 1313, 1256, 1214, 1145, 1079, 1016, 966, 850, 679; HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₂₉H₅₃B₂O₁₀ 583.3825; Found 583.3818.

2,2'-(4-((1S,1'r,4R,4'R)-4'-(3,4-difluorophenyl)-[1,1'-bi(cyclohexan)]-4-yl)butane-1,2-diy)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3s)



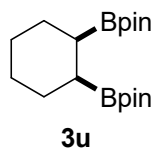
Under an argon atmosphere, 1,2-cyclohexdiamine (99.5 mg, 0.87 mmol) was dissolved in 1,4-dioxane (10 mL) to obtain 1,2-cyclohexanediamine solution (0.087 mol/L), and then NiCl₂·DME (6.6 mg, 0.03 mmol, 10 mol%), 1,2-cyclohexanediamine solution (345 μL, 0.03 mmol, 10 mol%), **1s** (99.7 mg, 0.3 mmol), B₂pin₂ (152.4 mg, 0.6 mmol, 2.0 eq), MeOLi (22.8 mg, 0.6 mmol, 2 eq), 1,4-dioxane (0.65 mL) were added to the Schlenk tube in order, The mixture was stirred at 70 °C for 24 h and then filtrated, concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography petroleum ether/ethyl acetate (20/1, v/v) to afford the corresponding product **3s** (104.6 mg, 59% yield) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.05–6.85 (m, 3H), 2.38 (t, *J* = 12.2 Hz, 1H), 1.88–1.67 (m, 8H), 1.40–1.28 (m, 4H), 1.22 (s, 12H), 1.21 (s, 12H), 1.18–1.03 (m, 7H), 1.03–0.92 (m, 3H), 0.89–0.80 (m, 3H), 0.78–0.75 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 151.4, 151.2, 149.7, 149.6, 148.9, 148.8, 147.3, 147.1, 144.9, 144.9, 144.8, 122.5, 122.4, 122.4, 122.4, 116.7, 116.6, 115.4, 115.2, 82.7, 82.7, 77.3, 77.0, 76.7, 43.8, 43.3, 42.8, 38.0, 36.7, 34.5, 33.6, 33.5, 31.1, 30.1, 30.0, 24.9, 24.8, 24.7, 24.7, 18.6, 12.7; ¹⁹F NMR (376 MHz, CDCl₃, ppm) δ -138.68 (d, *J* = 22.8 Hz), -142.60 (d, *J* = 22.8 Hz); IR (neat, cm⁻¹) 2981, 2921, 2851, 1516, 1441, 1369, 1309, 1214, 1143, 969, 821, 768; HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₃₄H₅₅B₂F₂O₄ 587.4255; Found 587.4315.

2,2'-(4-Methylpentane-1,2-diy)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3t)¹²



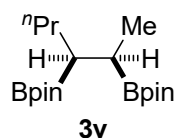
Under an argon atmosphere, 1,2-cyclohexdiamine (99.5 mg, 0.87 mmol) was dissolved in 1,4-dioxane (10 mL) to obtain 1,2-cyclohexanediamine solution (0.087 mol/L), and then NiCl₂·DME (6.6 mg, 0.03 mmol, 10 mol%), 1,2-cyclohexanediamine solution (345 μL, 0.03 mmol, 10 mol%), 4-methylpentane-1-ene (41 μL, 0.3 mmol), B₂pin₂ (152.4 mg, 0.6 mmol, 2.0 eq), MeOLi (22.8 mg, 0.6 mmol, 2 eq), 1,4-dioxane (0.65 mL) were added to the Schlenk tube in order, The mixture was stirred at 70 °C for 24 h and then filtrated, concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography petroleum ether/ethyl acetate (20/1, v/v) to afford the corresponding product **3t** (51.0 mg, 50% yield) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 1.63–1.53 (m, 1H), 1.38–1.32 (m, 1H), 1.22 (s, 12H), 1.21 (s, 12H), 1.17–1.11 (m, 2H), 0.85 (d, *J* = 6.6 Hz, 3H), 0.83 (d, *J* = 6.6 Hz, 3H), 0.81–0.74 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 82.8, 82.7, 77.3, 77.0, 76.7, 43.0, 26.7, 24.9, 24.8, 24.8, 24.7, 22.9, 22.6.

cis-1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexane (3u)⁸



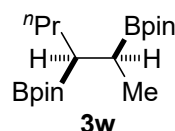
According to General procedure **D**, **3u** was obtained as a colorless oil in 56% yield (51.2 mg); ¹H NMR (400 MHz, CDCl₃) δ 1.61–1.57 (m, 2H), 1.57–1.53 (m, 2H), 1.46–1.34 (m, 4H), 1.23 (s, 24H), 1.21–1.12 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 82.6, 77.3, 77.0, 76.7, 27.9, 26.7, 24.8, 24.7, 23.1.

Cis-2,2'-(Hexane-2,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**3v**)⁸



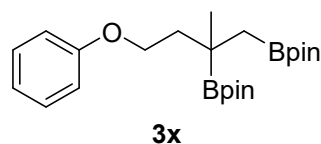
According to General procedure **D**, **3v** was obtained as a colorless oil in 50% yield (56.3 mg); ¹H NMR (400 MHz, CDCl₃) δ 1.51–1.41 (m, 1H), 1.34–1.25 (m, 3H), 1.21 (s, 12H), 1.20 (s, 12H), 1.15–1.09 (m, 2H), 0.93 (d, *J* = 7.2 Hz, 3H), 0.85 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 82.7, 82.7, 77.3, 77.0, 76.7, 32.7, 26.1, 25.0, 24.8, 22.5, 18.4, 14.4, 14.0.

Trans-2,2'-(Hexane-2,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**3w**)⁸



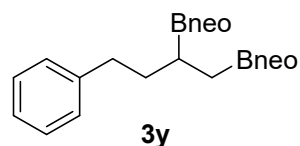
According to General procedure **D**, **3w** was obtained as a colorless oil in 55% yield (55.8 mg); ¹H NMR (400 MHz, CDCl₃) δ 1.50–1.41 (m, 2H), 1.33–1.27 (m, 2H), 1.21 (s, 12H), 1.21 (s, 12H), 1.17–1.12 (m, 1H), 1.08–1.03 (m, 1H) 0.94 (d, *J* = 7.2 Hz, 3H), 0.86 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 82.7, 77.3, 77.0, 76.7, 31.7, 25.0, 25.0, 24.7, 24.6, 22.4, 14.5, 14.3.

2,2'-(2-Methyl-4-phenoxybutane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**3x**)



According to General procedure **D**, **3x** was obtained as a white solid in 45% yield (56.2 mg) ¹H NMR (400 MHz, CDCl₃) δ 7.23 (t, *J* = 8.4 Hz, 2H), 6.88 (t, *J* = 8.0 Hz, 3H), 4.01 (t, *J* = 7.2 Hz, 2H), 1.93–1.77 (m, 2H), 1.23 (s, 12H), 1.21 (s, 12H), 1.06 (s, 3H), 0.91 (dd, *J* = 82.0, 15.6 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 159.1, 129.2, 120.2, 114.6, 83.0, 82.8, 77.3, 77.0, 76.7, 65.9, 39.9, 24.9, 24.8, 24.7, 24.7, 24.4; IR (neat, cm⁻¹) 2981, 2921, 2865, 1601, 1487, 1466, 1369, 1317, 1239, 1147, 1073, 1024, 963, 846, 757, 689; HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₂₃H₃₉B₂O₅ 417.2984; Found 417.2994.

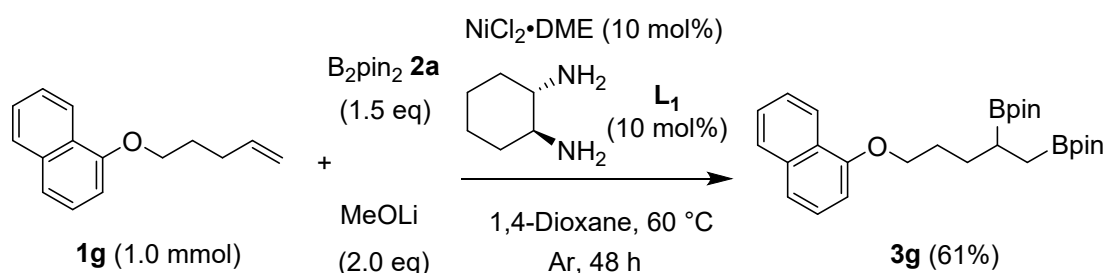
2,2'-(4-Phenylbutane-1,2-diyl)bis(5,5-dimethyl-1,3,2-dioxaborinane) (**3y**)



Under an argon atmosphere, 1,2-cyclohexdiamine (99.5 mg, 0.87 mmol) was dissolved in 1,4-dioxane (10 mL) to obtain 1,2-cyclohexanediamine solution (0.087 mol/L), and then NiCl₂·DME (6.6 mg, 0.03 mmol, 10 mol%), 1,2-cyclohexanediamine solution (345 μL, 0.03 mmol, 10 mol%), but-3-en-1-ylbenzene (46 μL, 0.3 mmol), **2b** (101.7 mg, 0.45 mmol, 1.5 eq), MeOLi (22.8 mg, 0.6 mmol, 2 eq), 1,4-dioxane (0.65 mL) were added to the Schlenk tube in order, The mixture was stirred at 60 °C for 24 h and then filtrated, concentrated in vacuo. Add *n*-dodecane (68 μl, 0.3 mmol) to the organic phase, yield of **3y** was 30% from GC-MS. ¹H NMR (400 MHz, CDCl₃) δ 7.27–7.23 (m, 2H), 7.19 (d, *J* = 7.2 Hz, 2H), 7.13 (d, *J* = 7.2 Hz, 1H), 3.56 (d, *J* = 11.6 Hz, 8H), 2.69–2.55 (m, 2H), 1.82–1.73 (m, 1H), 1.62–1.55 (m, 1H), 1.11–1.02 (m, 1H), 0.95 (s, 6H), 0.95 (s, 6H), 0.82 (d, *J* = 7.6 Hz, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 143.5, 128.4, 128.0, 125.2, 77.3, 77.0, 76.7, 71.9, 71.8, 36.0, 35.4, 31.6, 31.5, 21.8, 21.8, 21.7, 16.3; IR (neat, cm⁻¹) 3024, 2985, 2829, 1596, 1473, 1413, 1328, 1239, 1179, 1073, 1006, 913, 811, 736, 701; HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₂₀H₃₃B₂O₄ 359.2565; Found 359.2107.

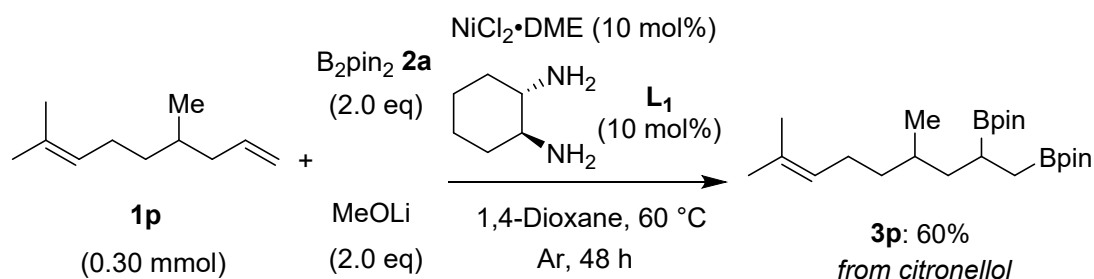
5. Synthetic Applications

5.1. Scale experiment

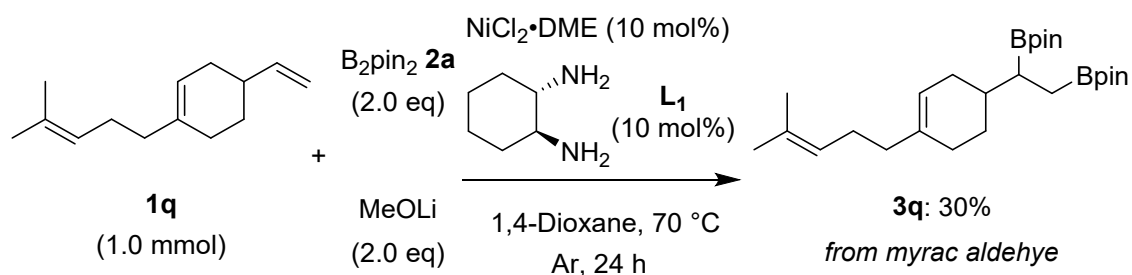


Under an argon atmosphere, 1,2-cyclohexdiamine (99.5 mg, 0.87 mmol) was dissolved in 1,4-dioxane (10 mL) to obtain 1,2-cyclohexanediamine solution (0.087 mol/L), and then $NiCl_2 \cdot DME$ (22.0 mg, 0.1 mmol, 10 mol%), 1,2-cyclohexanediamine solution (1.1 mL, 0.1 mmol, 10 mol%), 1-(pent-4-en-1-yloxy)naphthalene (210 μL , 1.0 mmol), B_2pin_2 (380.9 mg, 1.5 mmol, 1.5 eq), MeOLi (76.0 mg, 2.0 mmol, 2 eq), 1,4-dioxane (1.0 mL) were added to the Schlenk tube in order, The mixture was stirred at 60 °C for 48 h and then filtrated, concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography petroleum ether/ethyl acetate (20/1, v/v) to afford the corresponding product **3g** (282.0 mg, 61% yield) as a white solid.

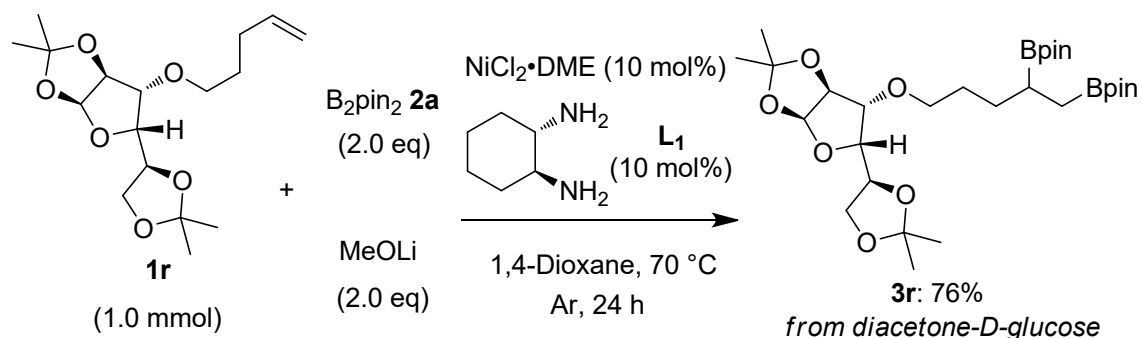
5.2. Modification of nature-related or functional molecules



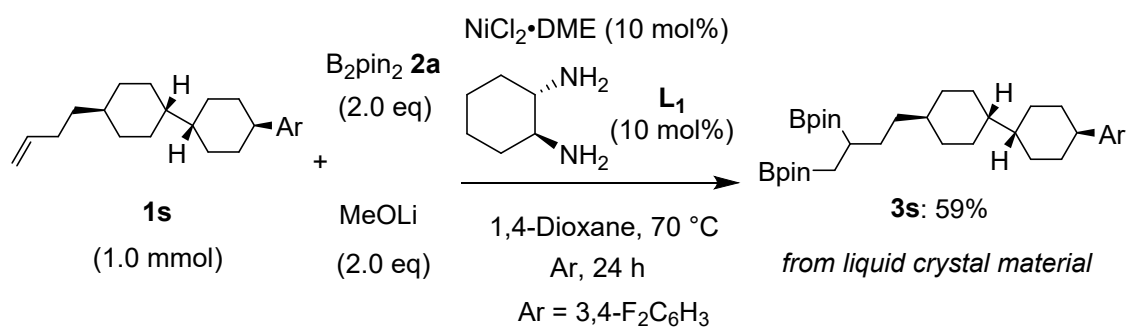
Under an argon atmosphere, 1,2-cyclohexdiamine (99.5 mg, 0.87 mmol) was dissolved in 1,4-dioxane (10 mL) to obtain 1,2-cyclohexanediamine solution (0.087 mol/L), and then $NiCl_2 \cdot DME$ (6.6 mg, 0.03 mmol, 10 mol%), 1,2-cyclohexanediamine solution (345 μL , 0.03 mmol, 10 mol%), 4,8-dimethylnona-1,7-diene (60 μL , 0.3 mmol), B_2pin_2 (152.4 mg, 0.6 mmol, 2.0 eq), MeOLi (22.8 mg, 0.6 mmol, 2 eq), 1,4-dioxane (0.65 mL) were added to the Schlenk tube in order, The mixture was stirred at 60 °C for 48 h and then filtrated, concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography petroleum ether/ethyl acetate (15/1, v/v) to afford the corresponding product **3p** (73.4 mg, 60% yield) as a colorless oil.



Under an argon atmosphere, 1,2-cyclohexdiamine (99.5 mg, 0.87 mmol) was dissolved in 1,4-dioxane (10 mL) to obtain 1,2-cyclohexanediamine solution (0.087 mol/L), and then $\text{NiCl}_2\cdot\text{DME}$ (6.6 mg, 0.03 mmol, 10 mol%), 1,2-cyclohexanediamine solution (345 μL , 0.03 mmol, 10 mol%), 1-(4-methylpent-3-en-1-yl)-4-vinylcyclohex-1-ene (68 μL , 0.3 mmol), B_2pin_2 (152.4 mg, 0.6 mmol, 2.0 eq), MeOLi (22.8 mg, 0.6 mmol, 2 eq), 1,4-dioxane (0.65 mL) were added to the Schlenk tube in order, The mixture was stirred at 70 $^\circ\text{C}$ for 24 h and then filtrated, concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography petroleum ether/ethyl acetate (35/1, v/v) to afford the corresponding product **3q** (40.6 mg, 30% yield) as a colorless oil.

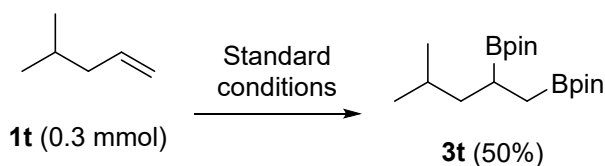


Under an argon atmosphere, 1,2-cyclohexdiamine (99.5 mg, 0.87 mmol) was dissolved in 1,4-dioxane (10 mL) to obtain 1,2-cyclohexanediamine solution (0.087 mol/L), and then $\text{NiCl}_2\cdot\text{DME}$ (6.6 mg, 0.03 mmol, 10 mol%), 1,2-cyclohexanediamine solution (345 μL , 0.03 mmol, 10 mol%), **1r** (118 μL , 0.3 mmol), B_2pin_2 (152.4 mg, 0.6 mmol, 2.0 eq), MeOLi (22.8 mg, 0.6 mmol, 2 eq), 1,4-dioxane (0.65 mL) were added to the Schlenk tube in order, The mixture was stirred at 70 $^\circ\text{C}$ for 24 h and then filtrated, concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography petroleum ether/ethyl acetate (7/1, v/v) to afford the corresponding product **3r** (132.5 mg, 76% yield) as a colorless oil.



Under an argon atmosphere, 1,2-cyclohexdiamine (99.5 mg, 0.87 mmol) was dissolved in 1,4-dioxane (10 mL) to obtain 1,2-cyclohexanediamine solution (0.087 mol/L), and then $\text{NiCl}_2 \cdot \text{DME}$ (6.6 mg, 0.03 mmol, 10 mol%), 1,2-cyclohexanediamine solution (345 μL , 0.03 mmol, 10 mol%), **1s** (99.7 mg, 0.3 mmol), B_2pin_2 (152.4 mg, 0.6 mmol, 2.0 eq), MeOLi (22.8 mg, 0.6 mmol, 2 eq), 1,4-dioxane (0.65 mL) were added to the Schlenk tube in order, The mixture was stirred at 70 °C for 24 h and then filtrated, concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography petroleum ether/ethyl acetate (20/1, v/v) to afford the corresponding product **3s** (104.6 mg, 59% yield) as a colorless oil.

5.3. Formal synthesis of drug intermediate



Under an argon atmosphere, 1,2-cyclohexdiamine (99.5 mg, 0.87 mmol) was dissolved in 1,4-dioxane (10 mL) to obtain 1,2-cyclohexanediamine solution (0.087 mol/L), and then $\text{NiCl}_2 \cdot \text{DME}$ (6.6 mg, 0.03 mmol, 10 mol%), 1,2-cyclohexanediamine solution (345 μL , 0.03 mmol, 10 mol%), 4-methylpent-1-ene (41 μL , 0.3 mmol), B_2pin_2 (152.4 mg, 0.6 mmol, 2.0 eq), MeOLi (22.8 mg, 0.6 mmol, 2 eq), 1,4-dioxane (0.65 mL) were added to the Schlenk tube in order, The mixture was stirred at 70 °C for 48 h and then filtrated, concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography petroleum ether/ethyl acetate (20/1, v/v) to afford the corresponding product **3t** (51.0 mg, 50% yield) as a colorless oil.

6. Selective 1,2-Diborylation of Aliphatic Alkenes

6.1. General Procedure E for 1,2-diborylation of aliphatic alkenes

The Cs₂CO₃ (29.4 mg, 0.09 mmol) and the B₂pin₂ (167.6 mg, 0.66 mmol) were transferred into an oven-dried Schlenk tube, provided with stir bar, under argon. THF (2.4 mL) was added to dissolve the mixture. After that, the but-3-en-1-ylbenzene (0.3 mmol), disubstituted alkene (0.3 mmol) and MeOH (480 μl, 12 mmol) were added, and the reaction mixture was stirred at 70 °C for 24 h. The reaction mixture was cooled to room temperature. After the filtration, concentrated in vacuo. Add n-dodecane (68 μl, 0.3 mmol) to the organic phase, yield of the reaction were calculated from GC-MS.

6.2. General Procedure F for 1,2-diborylation of aliphatic alkenes

Under an argon atmosphere, 1,2-cyclohexdiamine (99.5 mg, 0.87 mmol) was dissolved in 1,4-dioxane (10 mL) to obtain 1,2-cyclohexanediamine solution (0.087 mol/L), and then NiCl₂·DME (13.2 mg, 0.06 mmol), 1,2-cyclohexanediamine solution (690 μL, 0.06 mmol), but-3-en-1-ylbenzene (0.3 mmol), disubstituted alkene (0.3 mmol), B₂pin₂ (228.6 mg, 0.9 mmol), MeOLi (45.6 mg, 1.2 mmol), 1,4-dioxane (0.3 mL) were added to the Schlenk tube in order, The mixture was stirred at 60 °C for 24 h and then filtrated, concentrated in vacuo. Add n-dodecane (68 μl, 0.3 mmol) to the organic phase, yield of the reaction were calculated from GC-MS.

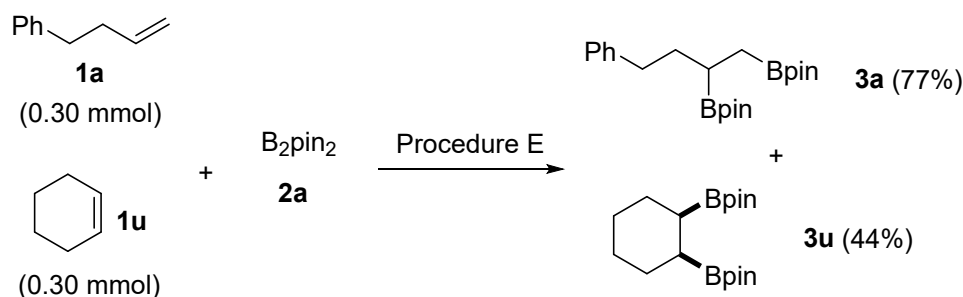
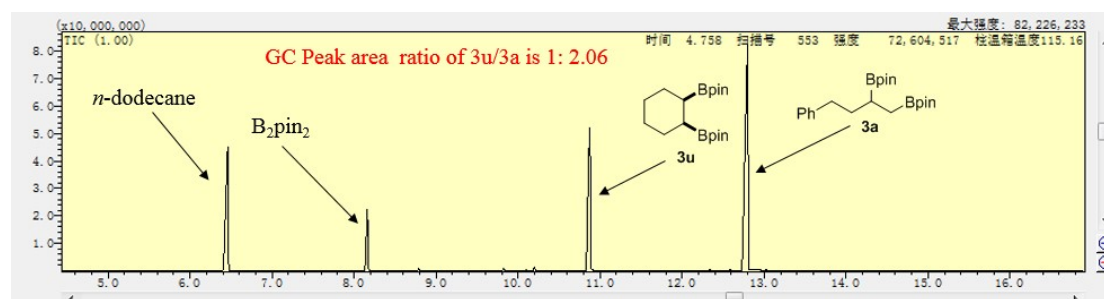


Figure S1. GC-MS spectrum of reaction by mixing **1a** and **1u** by Procedure E. According to Procedure E, yield of **3u** was 44%, yield of **3a** was 77%.



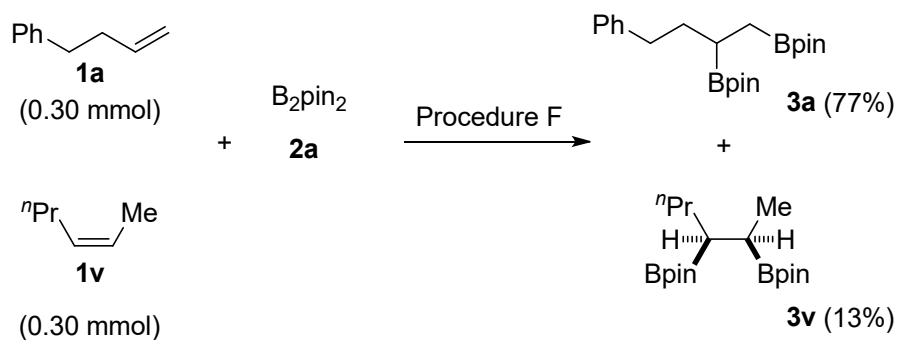


Figure S4. GC-MS spectrum. **1v** was used as a disubstituted alkene. According to Procedure F, yield of **3v** was 13%, yield of **3a** was 77%.

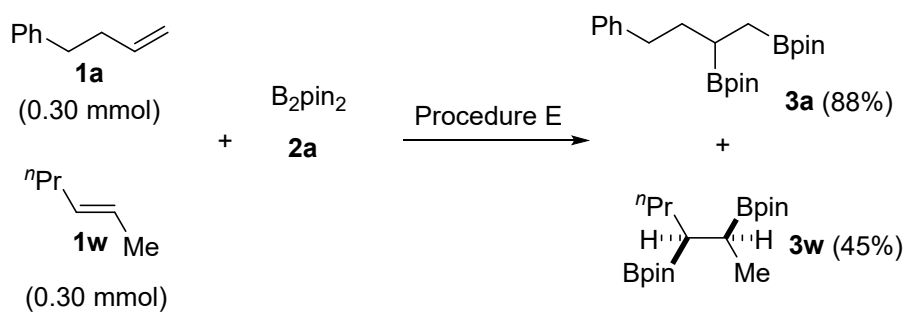
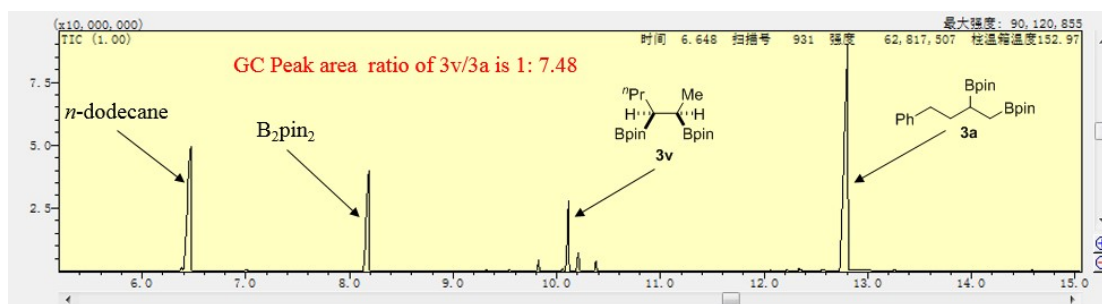
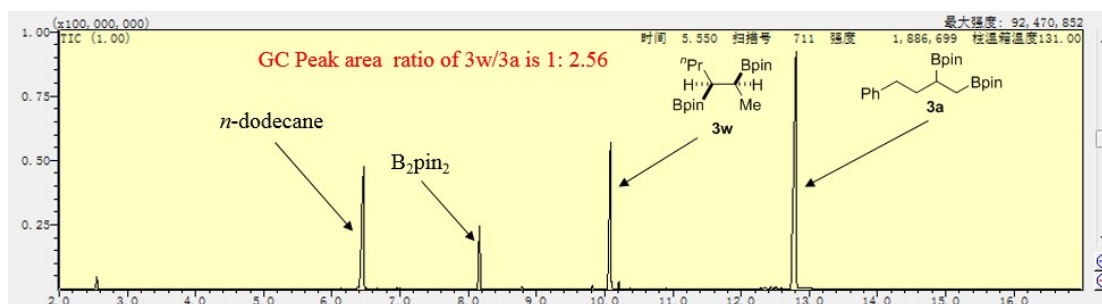


Figure S5. GC-MS spectrum. **1w** was used as a disubstituted alkene. According to Procedure E, yield of **3w** was 45%, yield of **3a** was 88%.



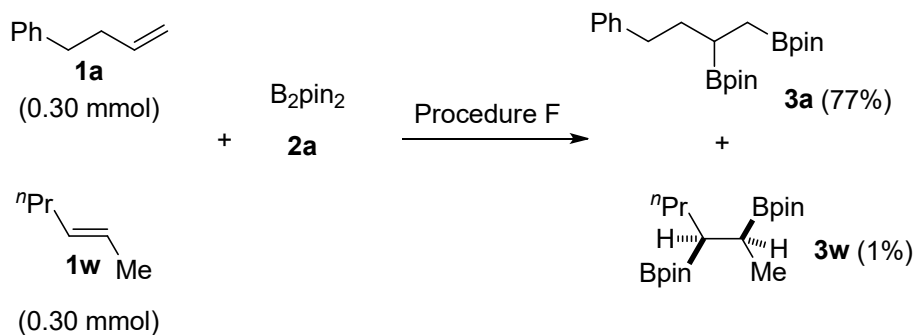


Figure S6. GC-MS spectrum. **1w** was used as a disubstituted alkene. According to Procedure F, yield of **3w** was 1%, yield of **3a** was 77%.

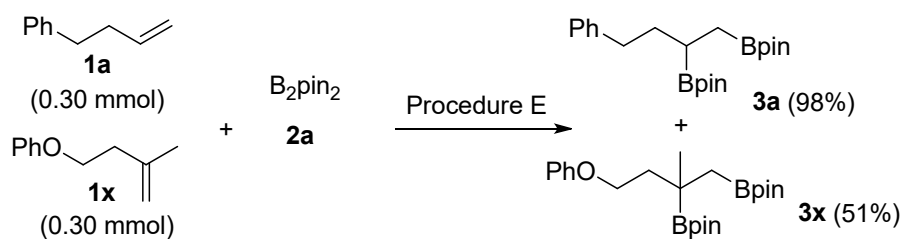
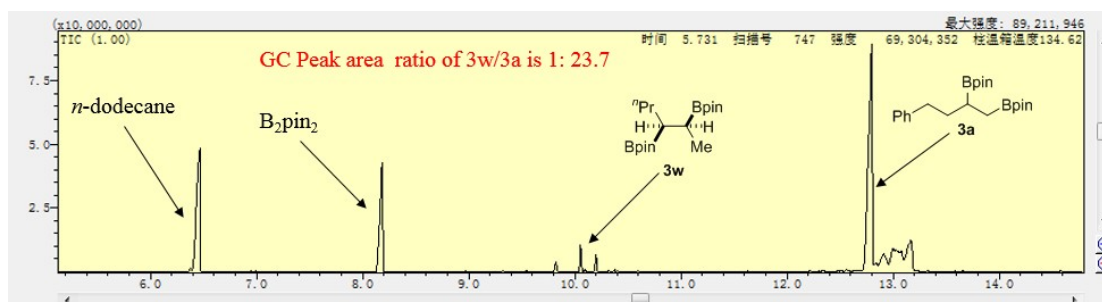
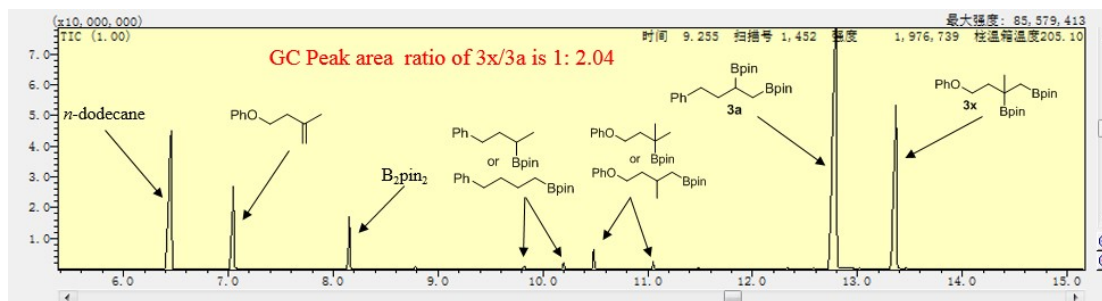


Figure S7. GC-MS spectrum. **1x** was used as a disubstituted alkene. According to Procedure E, yield of **1x** was 51%, yield of **3a** was 84%.



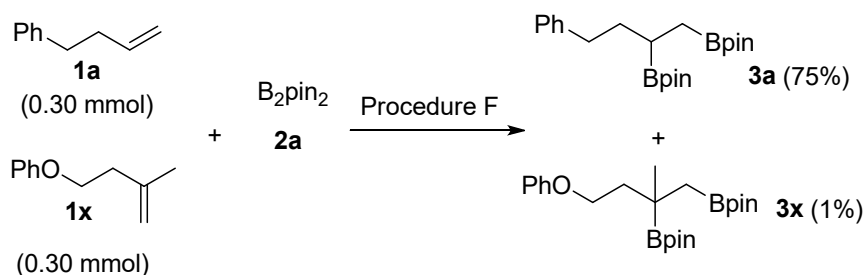
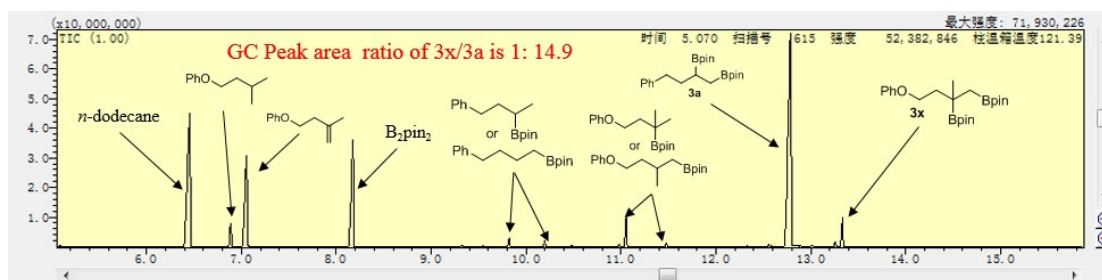


Figure S8. GC-MS spectrum. **1x** was used as a disubstituted alkene according to Procedure E, yield of **1x** was 1%, yield of **3a** was 75%.



7. Mechanistic Studies

7.1. Reaction using Ni(0) or Ni(I) catalysis

General Procedure G for 1,2-diborylation of aliphatic alkenes

Under an argon atmosphere, 1,2-cyclohexdiamine (99.5 mg, 0.87 mmol) was dissolved in 1,4-dioxane (10 mL) to obtain 1,2-cyclohexanediamine solution (0.087 mol/L), and then Ni catalysis (10 mol%), 1,2-cyclohexanediamine solution (345 μL , 0.03 mmol, 10 mol%), but-3-en-1-ylbenzene (46 μL , 0.3 mmol), B_2pin_2 (114.3 mg, 0.45 mmol, 1.5 eq), MeOLi (22.8 mg, 0.6 mmol, 2 eq), 1,4-dioxane (0.65 mL) were added to the Schlenk tube in order, The mixture was stirred at 60 $^\circ\text{C}$ for 24 h and then filtrated, concentrated in vacuo. Add *n*-dodecane (68 μl , 0.3 mmol) to the organic phase, yield of the reaction were calculated from GC-MS.

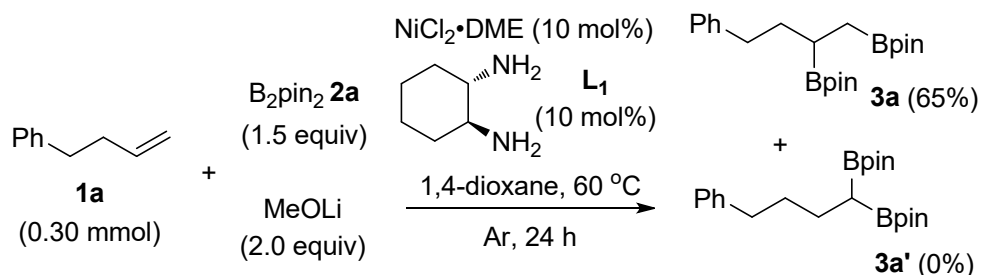


Figure S9. GC-MS spectrum of Ni(II)-catalyzed reaction according to Procedure G

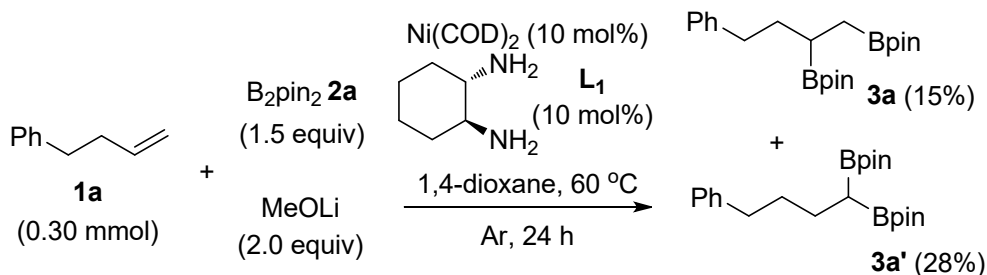
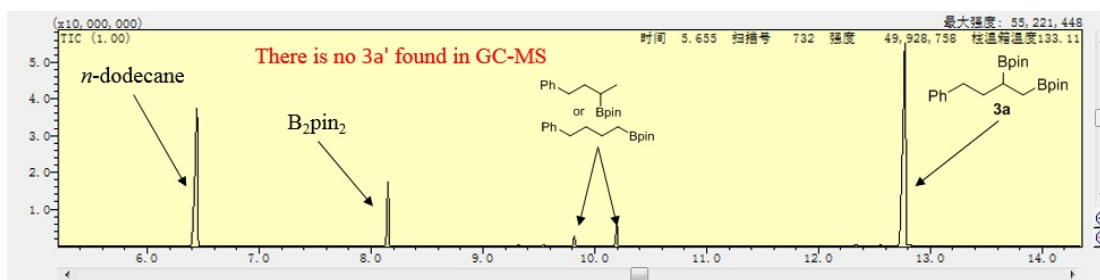


Figure S10. GC-MS spectrum of Ni(0)-catalyzed reaction according to Procedure G

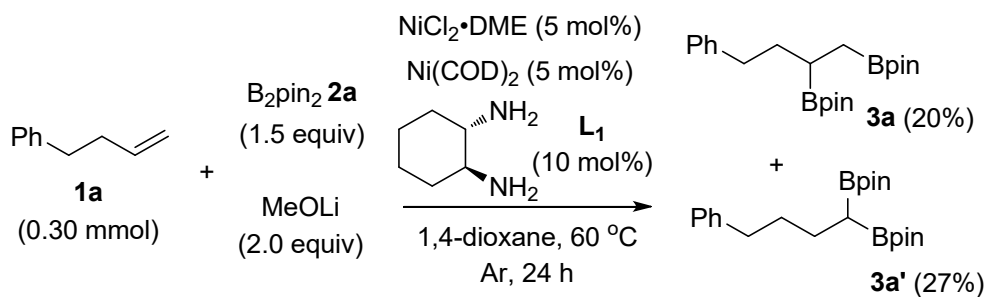
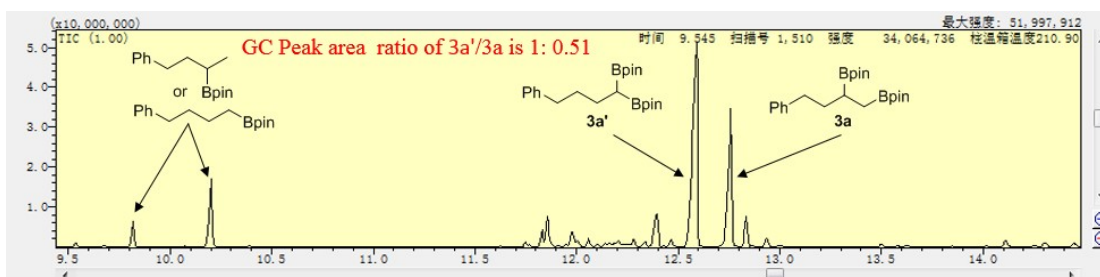
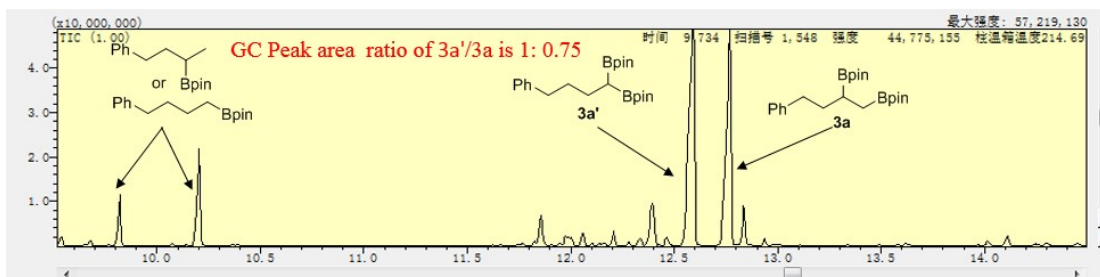
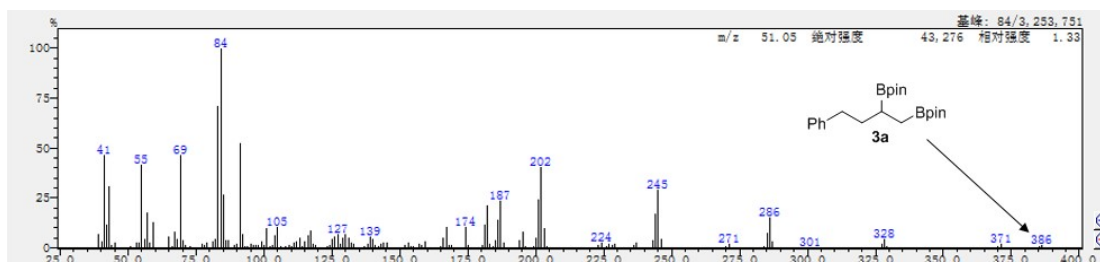
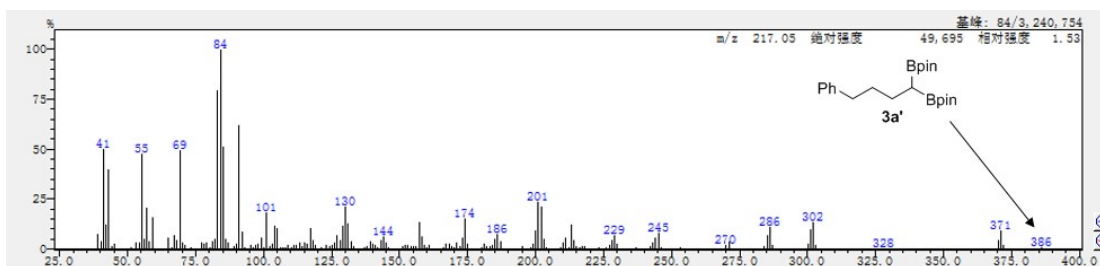


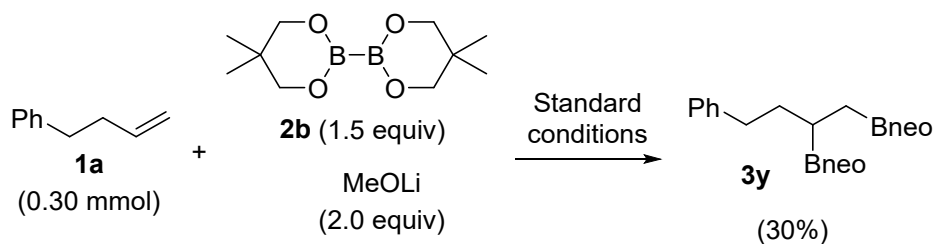
Figure S11. GC-MS spectrum of Ni(I)-catalyzed reaction according to Procedure G





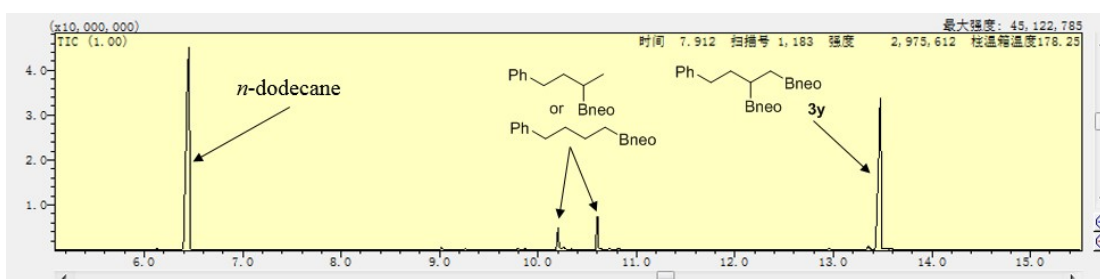
7.2. Cross-over experiment

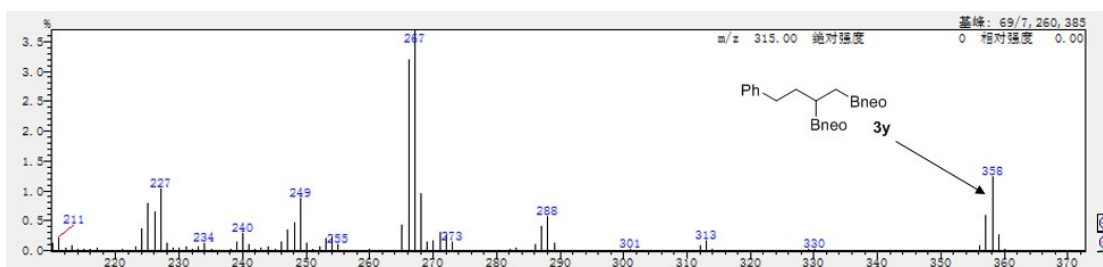
7.2.1 Synthesis of **3y**



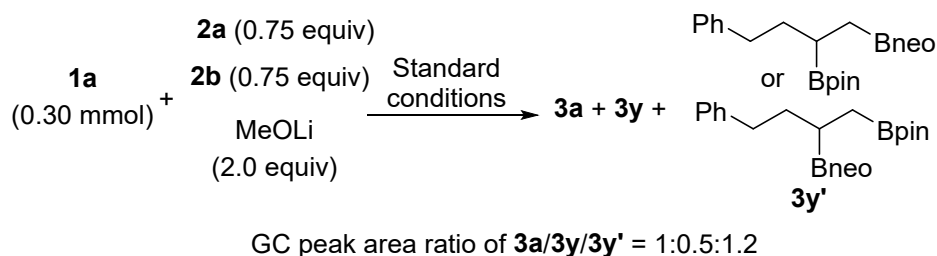
Under an argon atmosphere, 1,2-cyclohexanediamine (99.5 mg, 0.87 mmol) was dissolved in 1,4-dioxane (10 mL) to obtain 1,2-cyclohexanediamine solution (0.087 mol/L), and then NiCl₂·DME (6.6 mg, 0.03 mmol, 10 mol%), 1,2-cyclohexanediamine solution (345 μL, 0.03 mmol, 10 mol%), but-3-en-1-ylbenzene (46 μL, 0.3 mmol), **2b** (101.7 mg, 0.45 mmol, 1.5 eq), MeOLi (22.8 mg, 0.6 mmol, 2 eq), 1,4-dioxane (0.65 mL) were added to the Schlenk tube in order, The mixture was stirred at 60 °C for 24 h and then filtrated, concentrated in vacuo. Add *n*-dodecane(68 μL, 0.3 mmol) to the organic phase, yield of **3y** was 30% from GC-MS.

Figure S12. GC-MS spectrum of **3y**



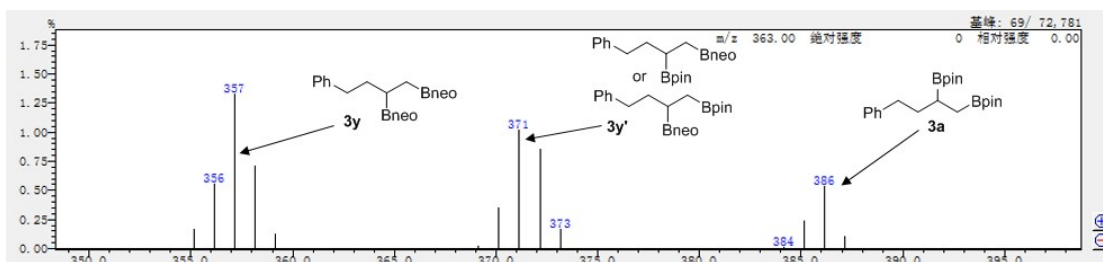
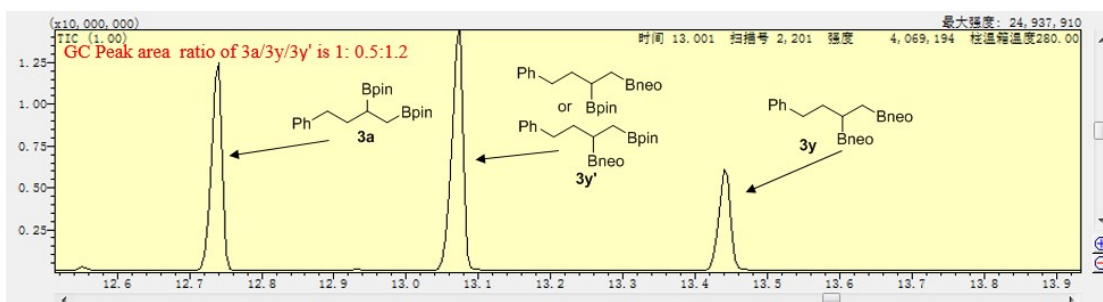


7.2.2 Cross-over experiment



Under an argon atmosphere, 1,2-cyclohexdiamine (99.5 mg, 0.87 mmol) was dissolved in 1,4-dioxane (10 mL) to obtain 1,2-cyclohexanediamine solution (0.087 mol/L), and then $\text{NiCl}_2 \cdot \text{DME}$ (6.6 mg, 0.03 mmol, 10 mol%), 1,2-cyclohexanediamine solution (345 μL , 0.03 mmol, 10 mol%), but-3-en-1-ylbenzene (46 μL , 0.3 mmol), B_2pin_2 (57.2 mg, 0.225 mmol, 0.75 eq), 2b (50.9 mg, 0.225 mmol, 0.75 eq), MeOLi (22.8 mg, 0.6 mmol, 2 eq), 1,4-dioxane (0.65 mL) were added to the Schlenk tube in order, The mixture was stirred at 60 $^\circ\text{C}$ for 24 h and then filtrated, concentrated in vacuo. Add n-dodecane(68 μL , 0.3 mmol) to the organic phase, GC Peak area ratio of $\text{3a}/\text{3y}/\text{3y}'$ is 1: 0.5: 1.2 from GC-MS.

Figure S13. GC-MS spectrum of 3a , 3y , $\text{3y}'$

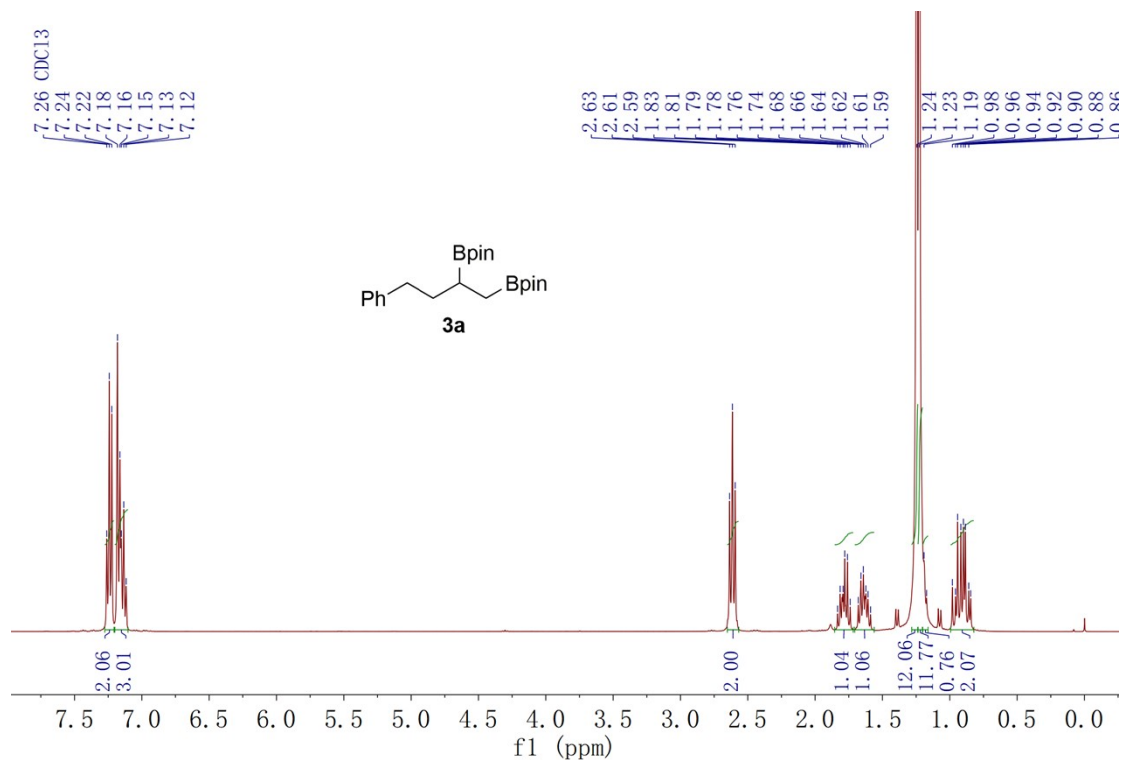


8. References

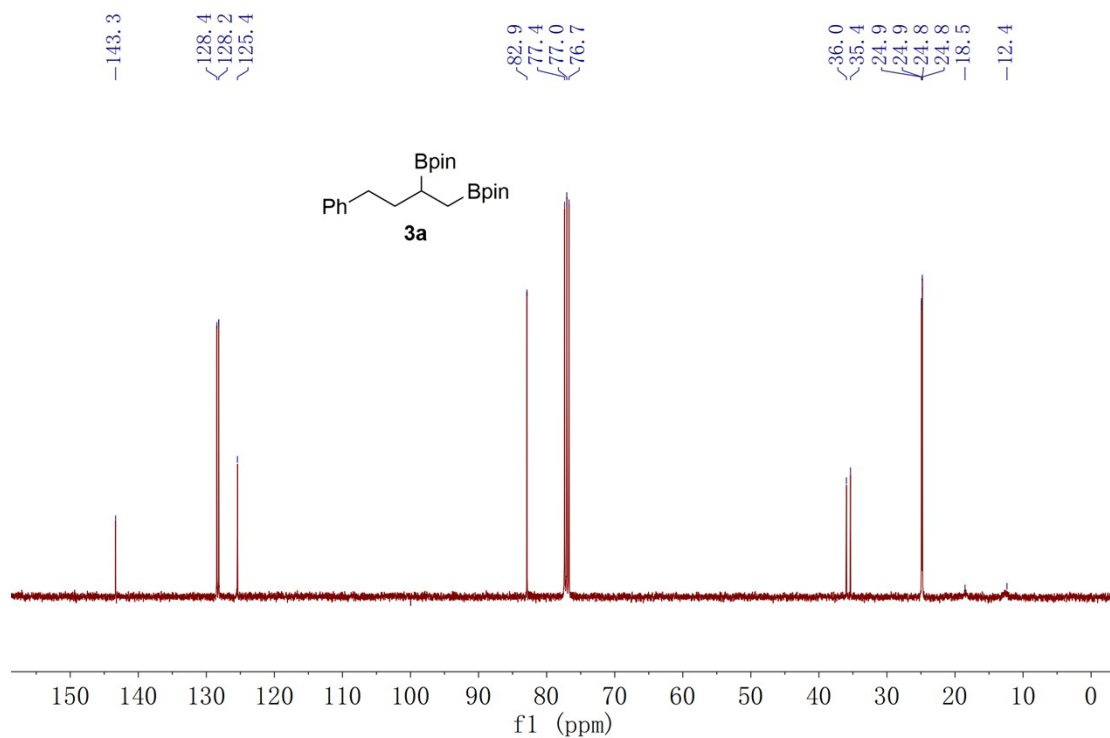
1. Wang, X.; Wu, Y. Direct oxidative isoperfluoropropylation of terminal alkenes via hexafluoropropylene (HFP) and silver fluoride. *Chem. Commun.* **2018**, *54*, 1877–1880.
2. Jones, G. R.; Basbug Alhan, H. E.; Karas, L. J.; Wu, J. I.; Harth, E. Switching the reactivity of palladium diimines with “ancillary” ligand to select between olefin polymerization, branching regulation, or olefin isomerization. *Angew. Chem., Int. Ed.* **2021**, *60*, 1635–1640.
3. Bonet, A.; Pubill-Ulldemolins, C.; Farre, A.; Briggs, R. Developing a bench-scale green diboration reaction toward industrial application. *Synthesis* **2017**, *49*, 4775–4782.
4. Li, L.; Gong, T.; Lu, X.; Xiao, B.; Fu, Y. Nickel-catalyzed synthesis of 1,1-diborylalkanes from terminal alkenes. *Nat Commun* **2017**, *8*, 345.
5. Ahmed Fouad, M.; Ferretti, F.; Formenti, D.; Milani, F.; Ragaini, F. Synthesis of indoles by reductive cyclization of nitro compounds using formate esters as CO surrogates. *Eur. J. Org. Chem* **2021**, *34*, 4876–4894.
6. Okoromoba, O. E.; Li, Z.; Robertson, N.; Mashuta, M. S.; Couto, U. R.; Tormena, C. F.; Xu, B.; Hammond, G. B. Achieving regio- and stereo-control in the fluorination of aziridines under acidic conditions. *Chem. Commun* **2016**, *52*, 13353–13356.
7. Wang, X. X.; Li, L.; Gong, T. J.; Xiao, B.; Lu, X.; Fu, Y. Vicinal diboration of alkyl bromides via tandem catalysis. *Org Lett* **2019**, *21*, 4298–4302.
8. Bonet, A.; Pubill-Ulldemolins, C.; Bo, C.; Gulyas, H.; Fernandez, E. Transition-metal-free diboration reaction by activation of diboron compounds with simple Lewis bases. *Angew. Chem., Int. Ed.* **2011**, *123*, 7296–7299.
9. Hu, J.; Zhao, Y.; Shi, Z. Highly tunable multi-borylation of gem-difluoroalkenes via copper catalysis. *Nat. Catal.* **2018**, *1*, 860–869.
10. Blaisdell, T. P.; Morken, J. P. Hydroxyl-directed cross-coupling: A scalable synthesis of debromohamigeran E and other targets of interest. *J. Am. Chem. Soc.* **2015**, *137*, 8712–8715.
11. Zhou, S.; Pu, Y.; Liu, Z.; Zhang, X.; Zhu, J.; Feng, Z. Iron-catalyzed diborylation of unactivated aliphatic gem-dihalogenoalkenes: Synthesis of 1,2-bis(boryl)alkanes. *Org Lett* **2021**, *23*, 5565–5570.
12. Willems, S.; Toupalas, G.; Reisenbauer, J. C.; Morandi, B. A site-selective and stereospecific cascade Suzuki-Miyaura annulation of alkyl 1,2-bisboronic esters and 2,2'-dihalo 1,1'-biaryls. *Chem. Commun.* **2021**, *57*, 3909–3912.

9. ^1H , ^{13}C and ^{19}F NMR Spectra

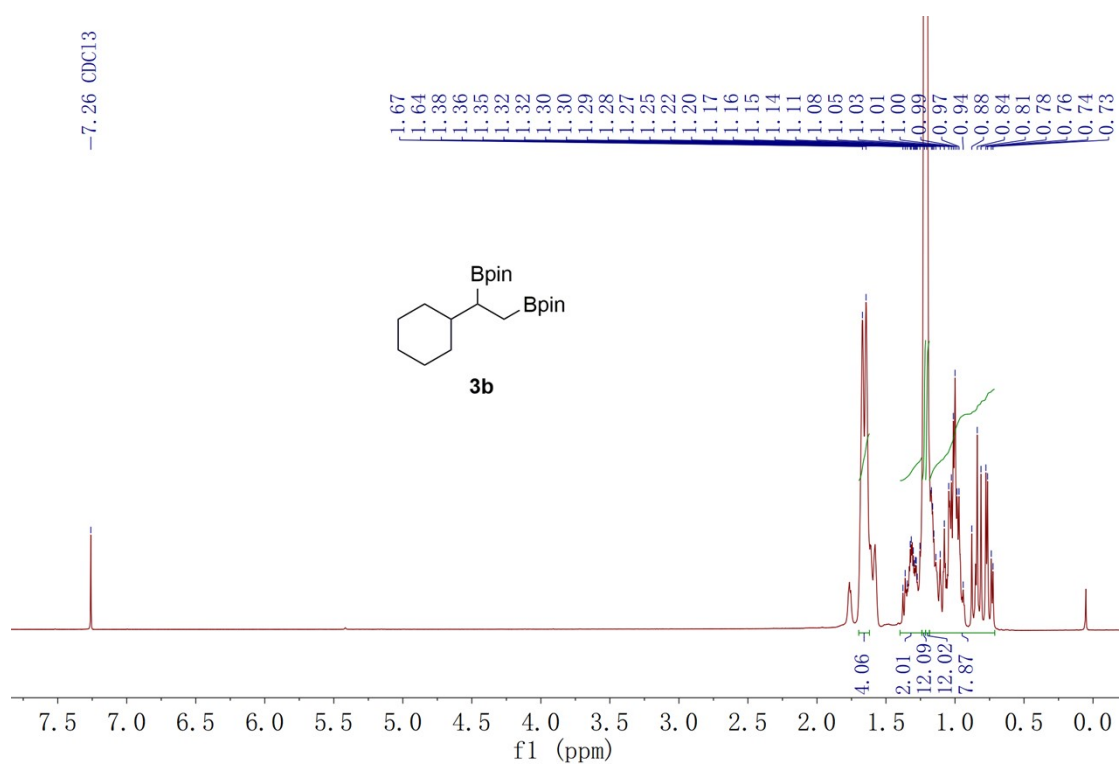
^1H NMR (CDCl_3 , 400 MHz) spectrum of compound **3a**.



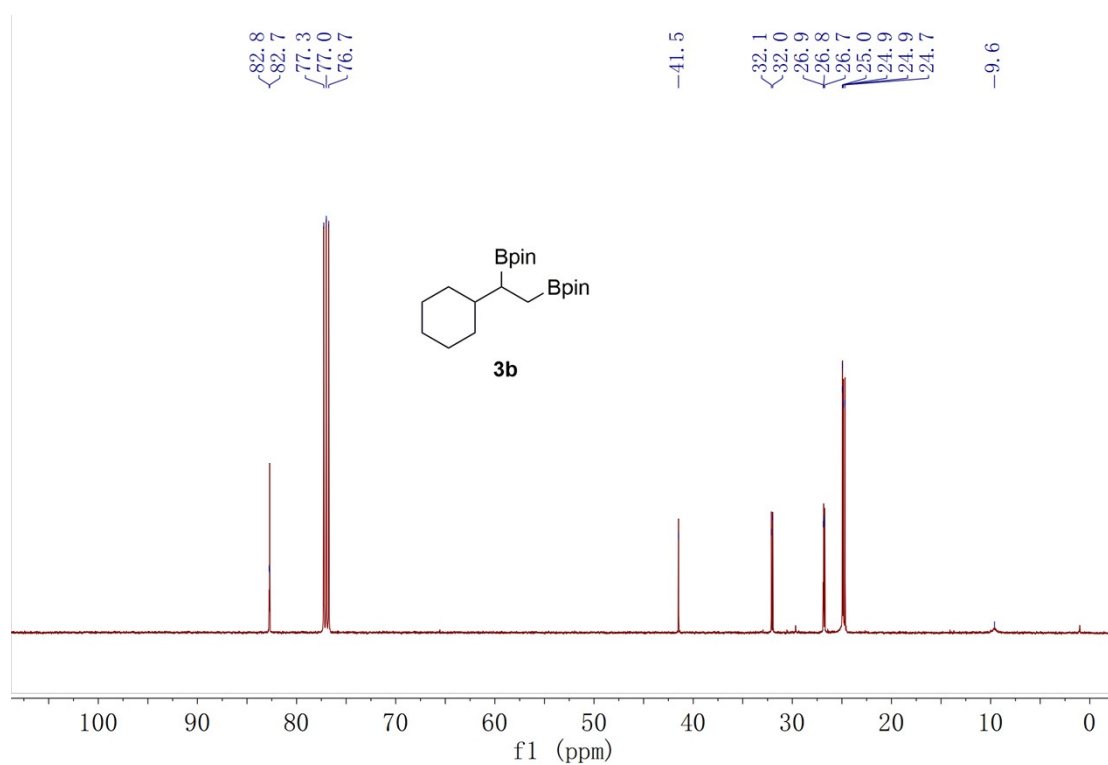
^{13}C NMR (CDCl_3 , 101 MHz) spectrum of compound **3a**.



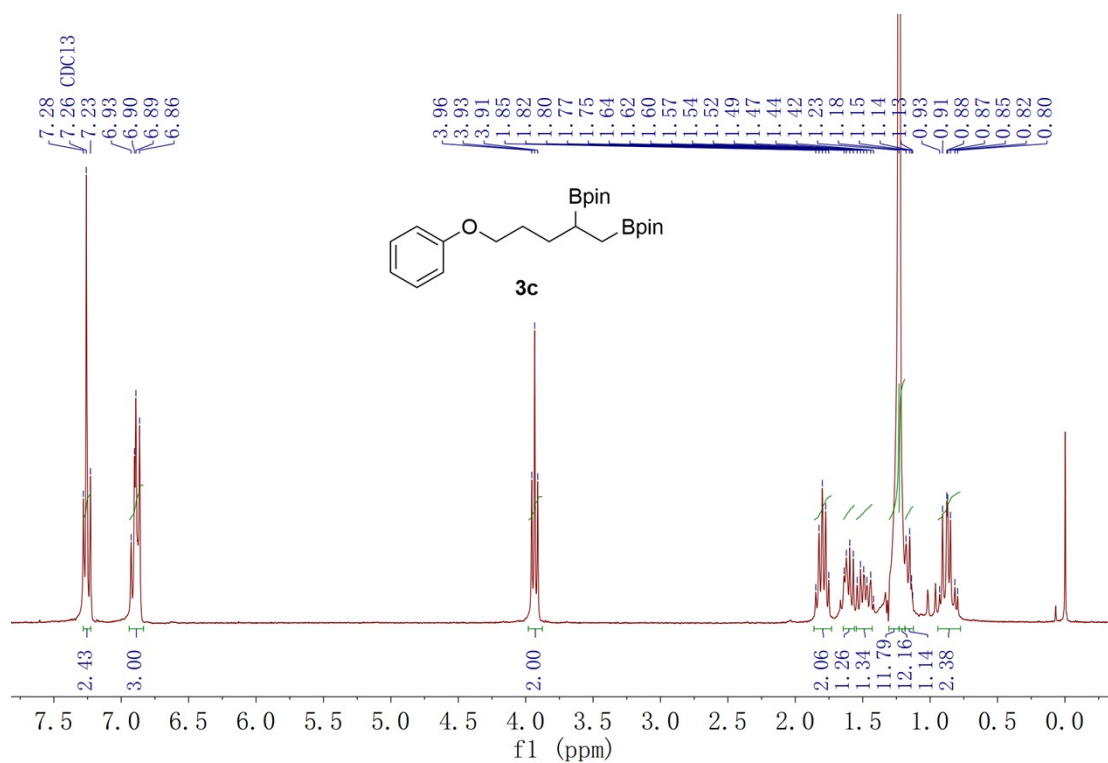
^1H NMR (CDCl_3 , 400 MHz) spectrum of compound **3b**.



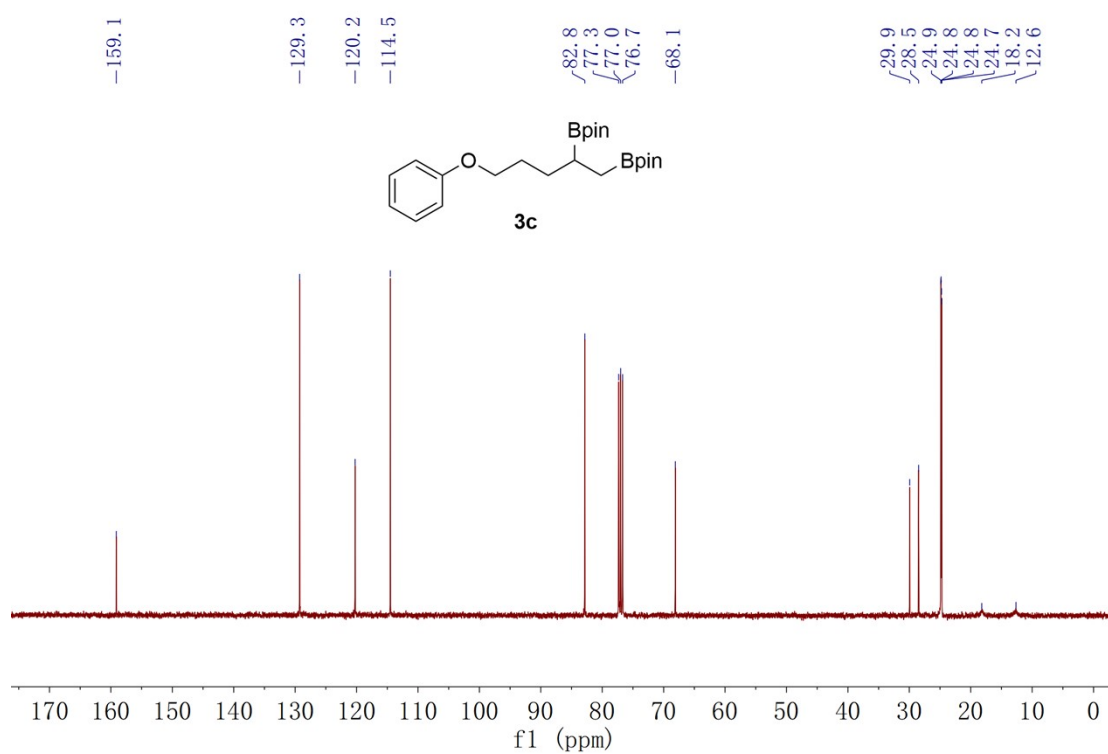
^{13}C NMR (CDCl_3 , 126 MHz) spectrum of compound **3b**.



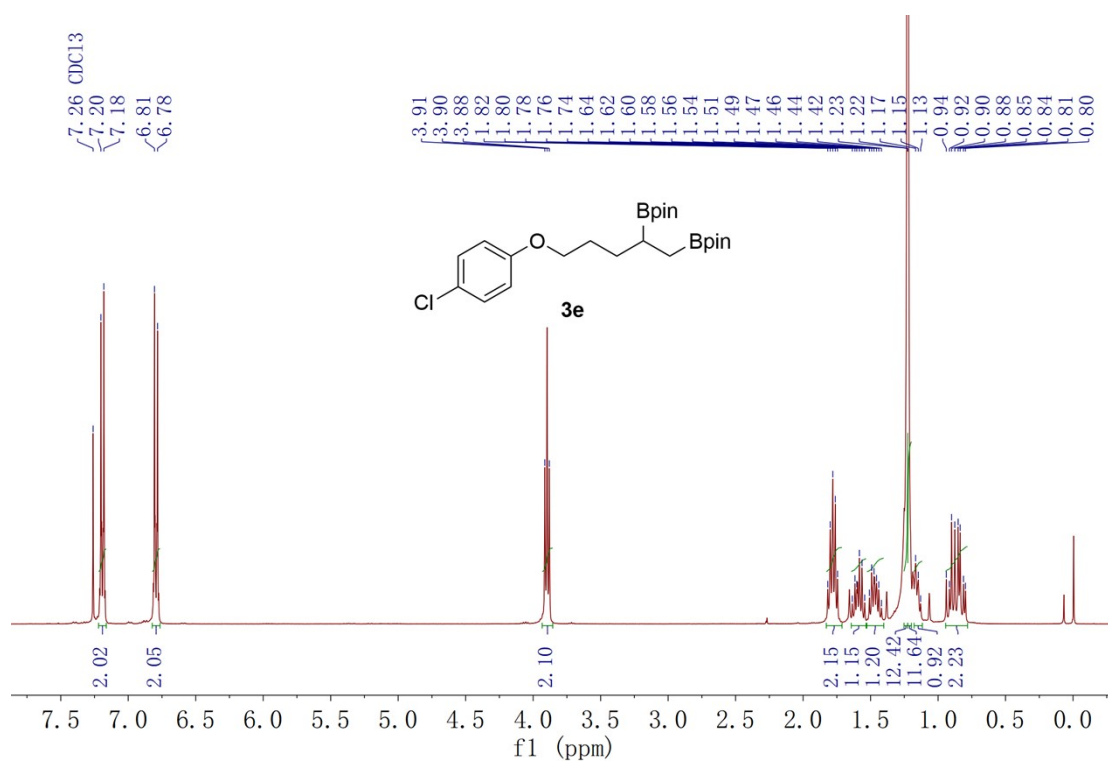
^1H NMR (CDCl_3 , 300 MHz) spectrum of compound **3c**.



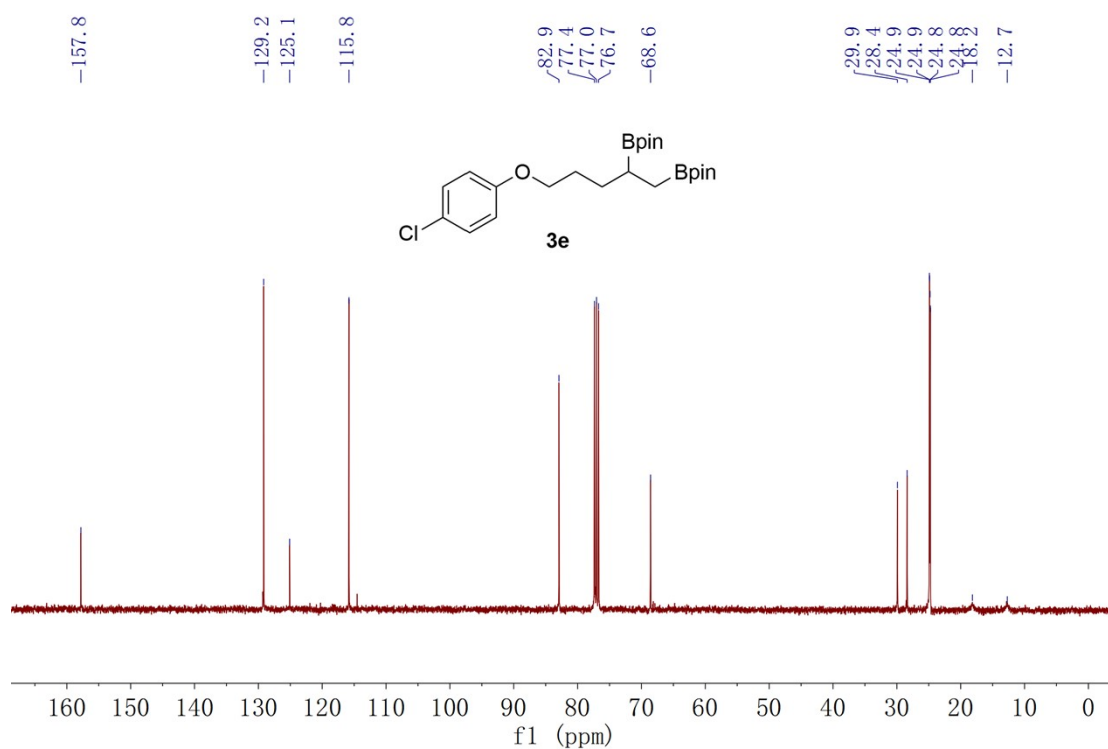
^{13}C NMR (CDCl_3 , 101 MHz) spectrum of compound **3c**.



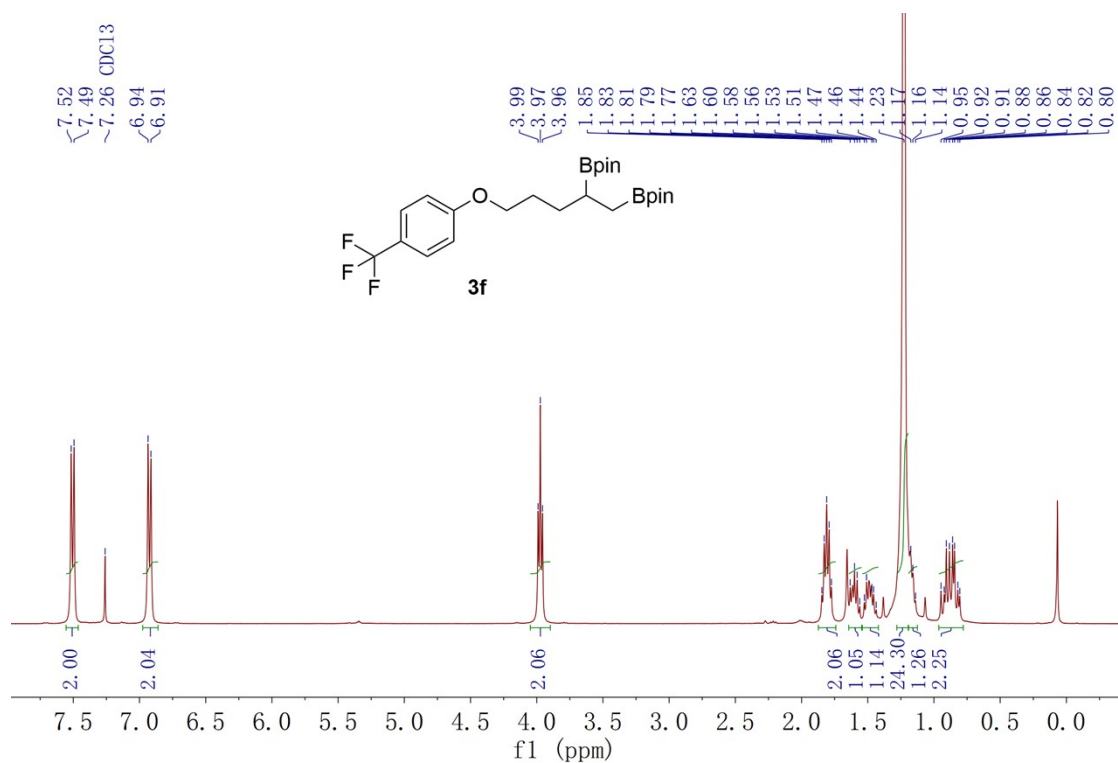
^1H NMR (CDCl_3 , 400 MHz) spectrum of compound **3e**.



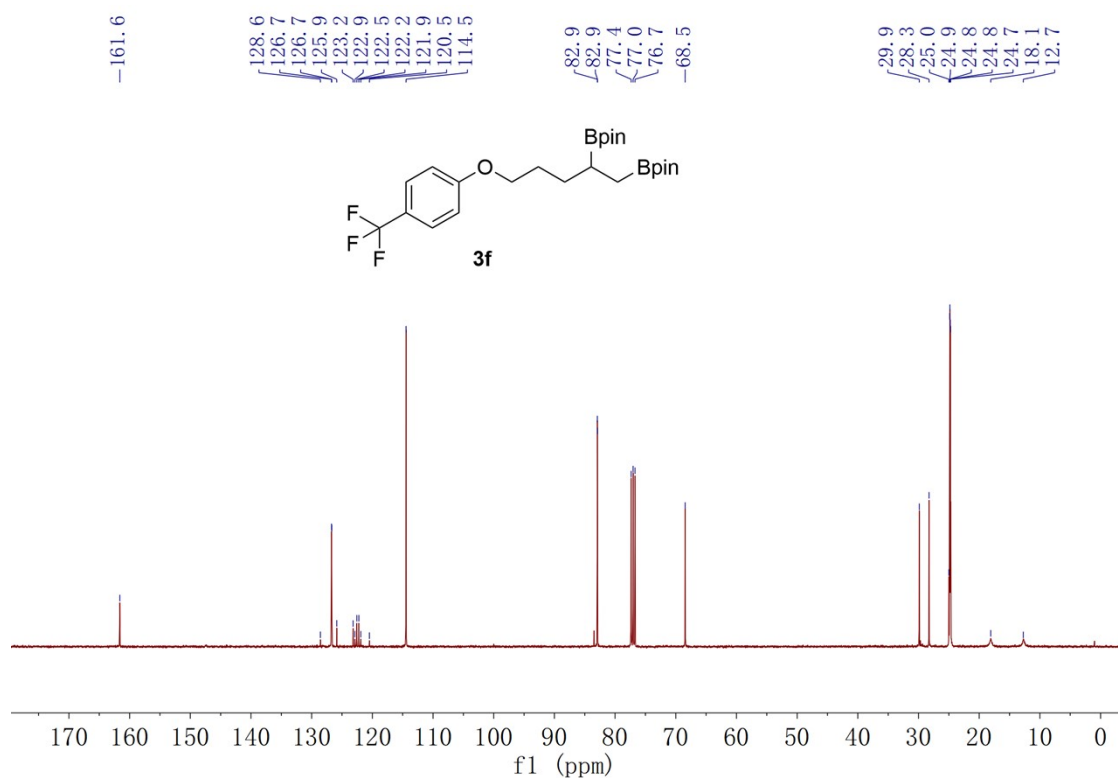
^{13}C NMR (CDCl_3 , 101 MHz) spectrum of compound **3e**.



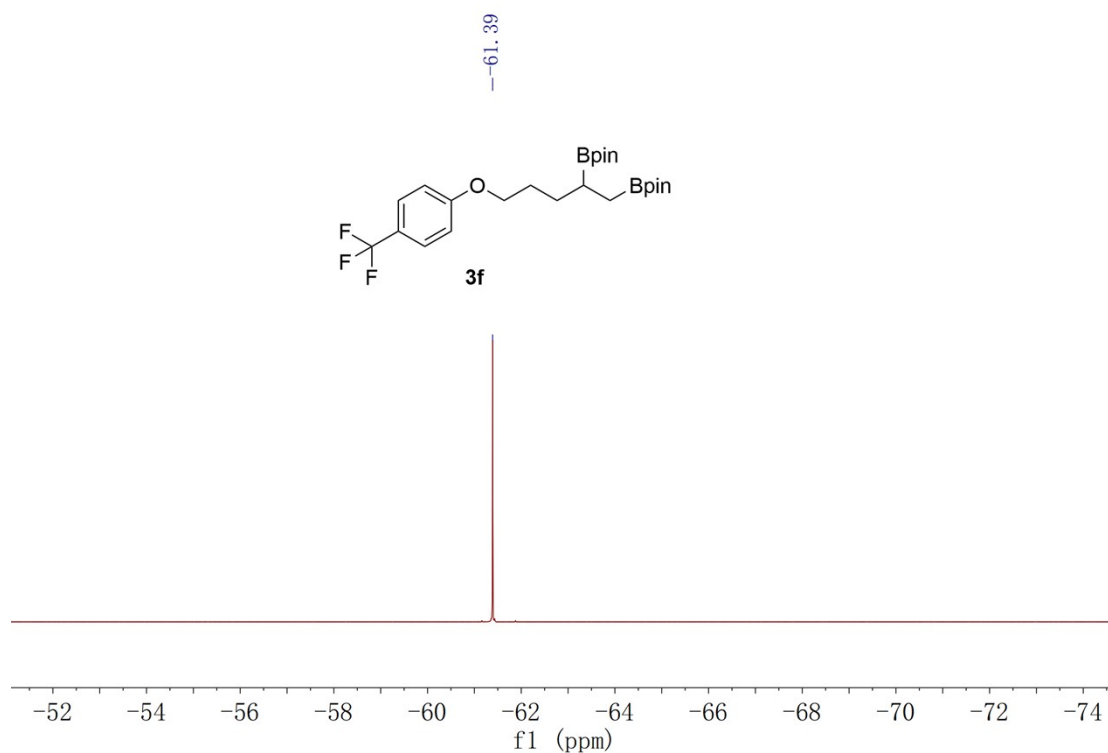
^1H NMR (CDCl_3 , 400 MHz) spectrum of compound **3f**.



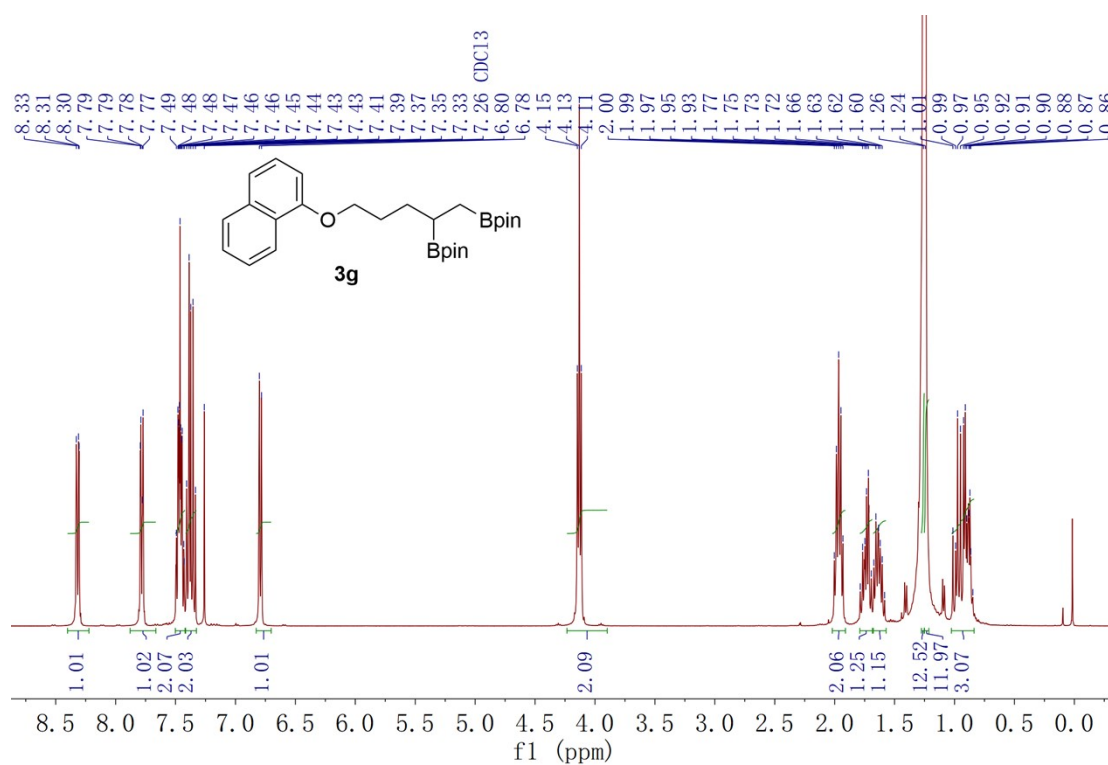
^{13}C NMR (CDCl_3 , 101 MHz) spectrum of compound **3f**.



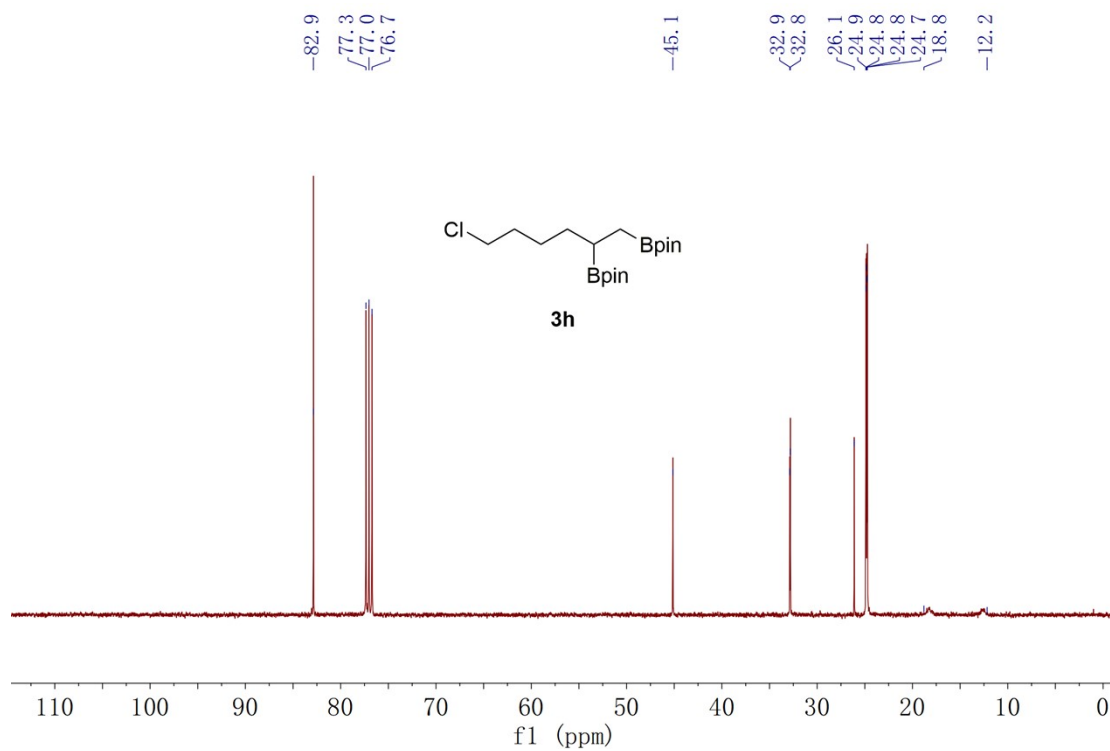
^{19}F NMR (CDCl_3 , 376 MHz) spectrum of compound **3f**.



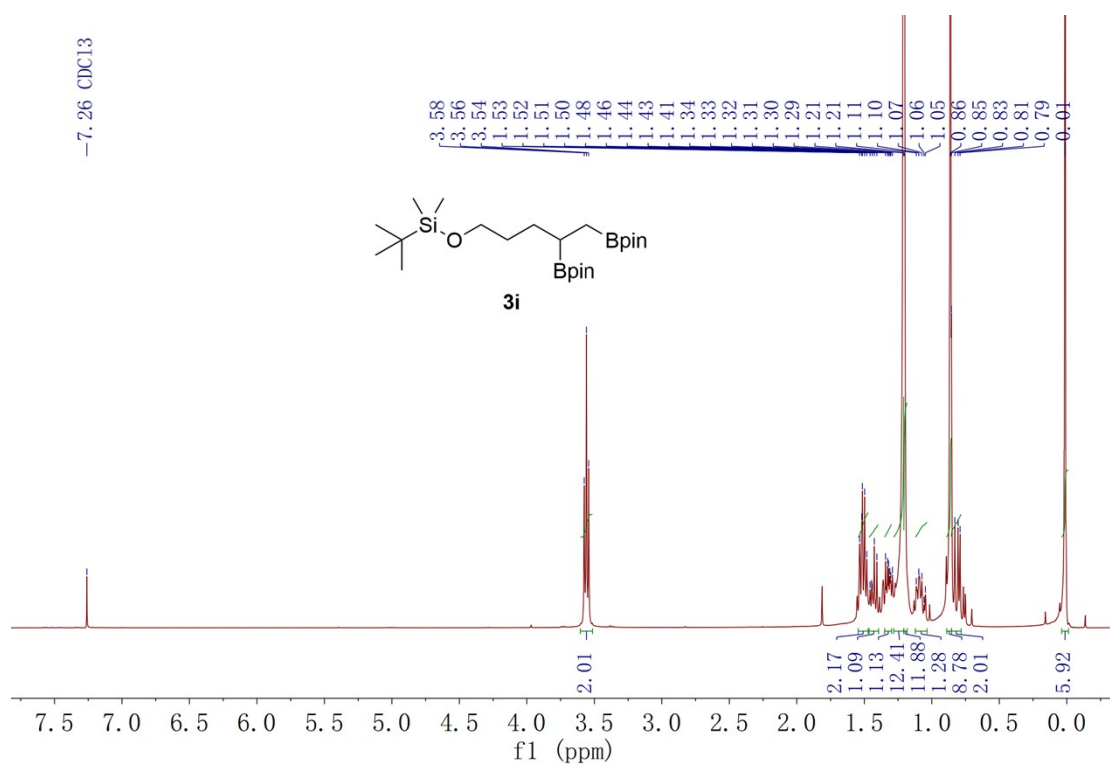
^1H NMR (CDCl_3 , 400 MHz) spectrum of compound **3g**.



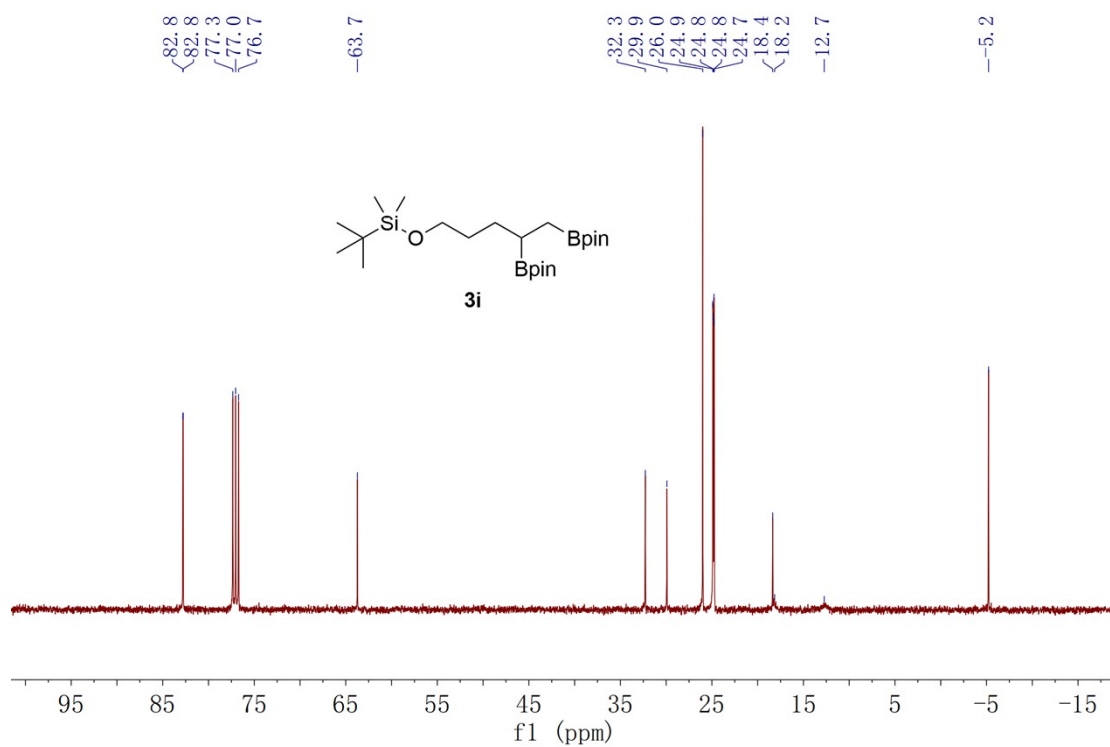
^{13}C NMR (CDCl_3 , 101 MHz) spectrum of compound **3h**



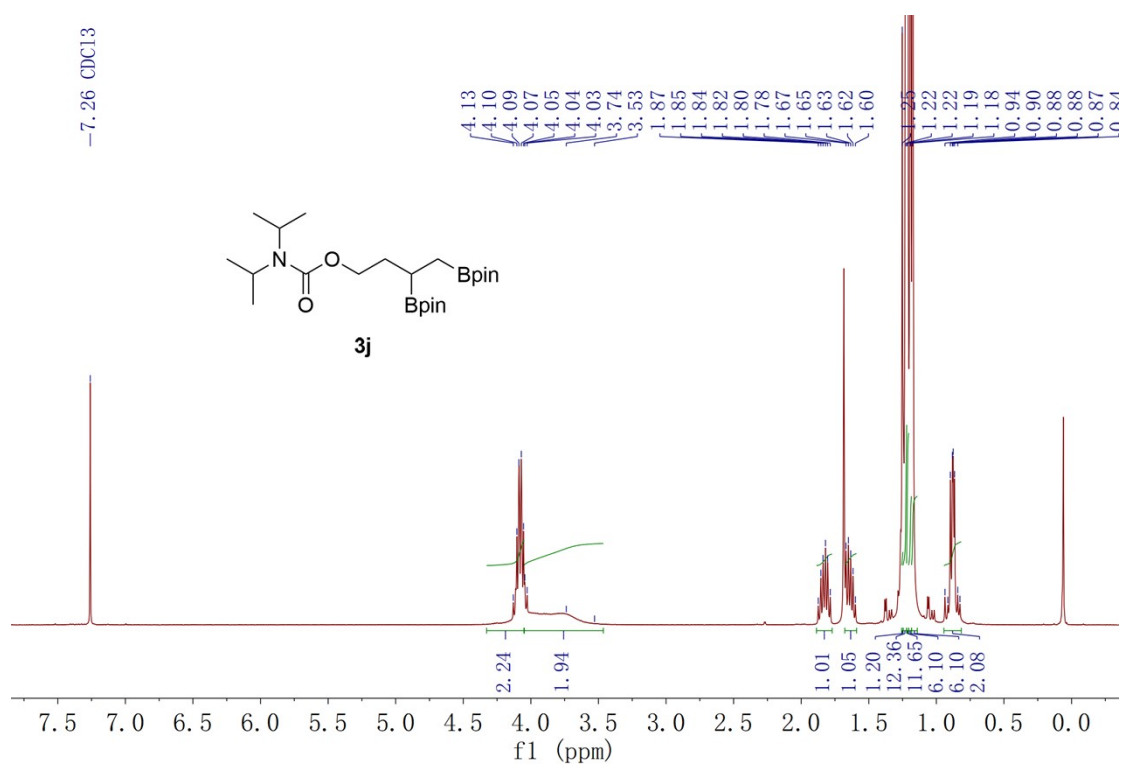
^1H NMR (CDCl_3 , 400 MHz) spectrum of compound **3i**.



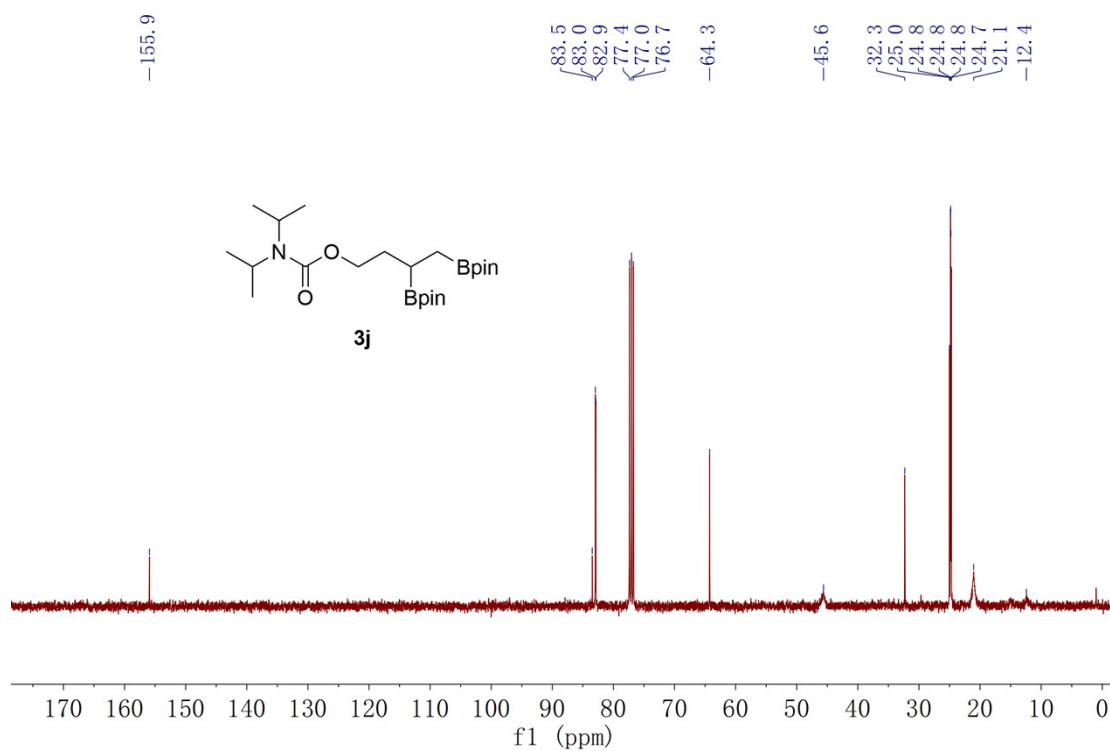
^{13}C NMR (CDCl_3 , 101 MHz) spectrum of compound **3i**.



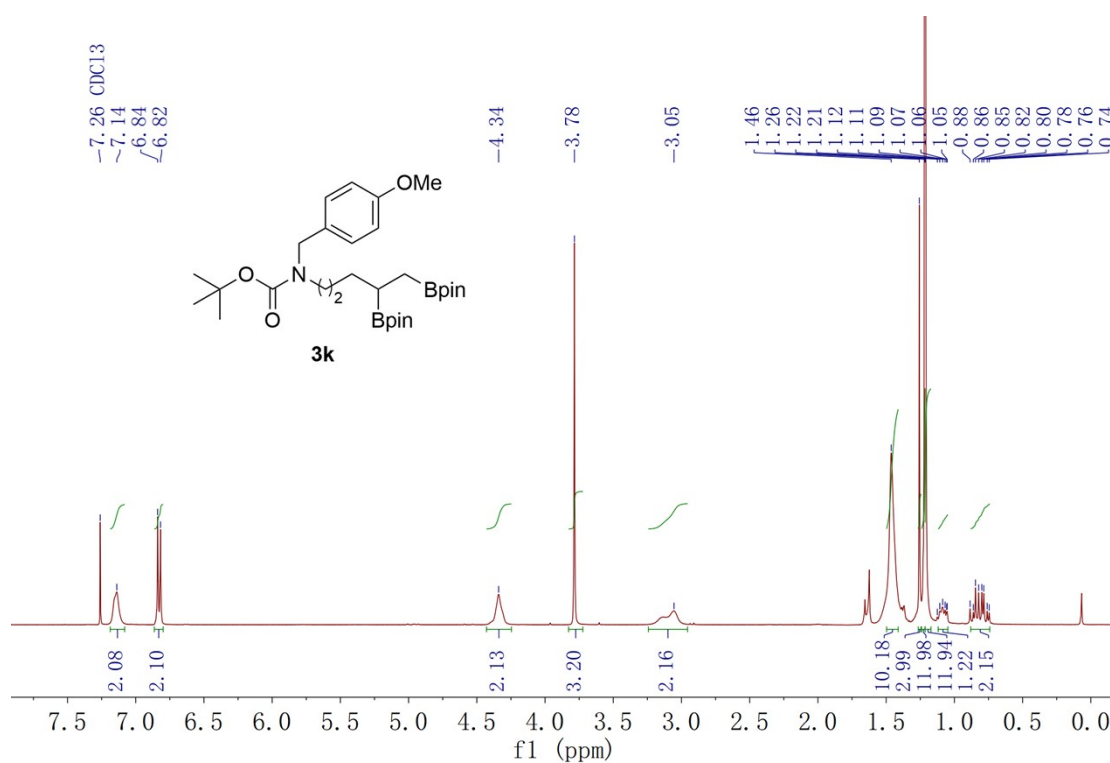
^1H NMR (CDCl_3 , 400 MHz) spectrum of compound **3j**.



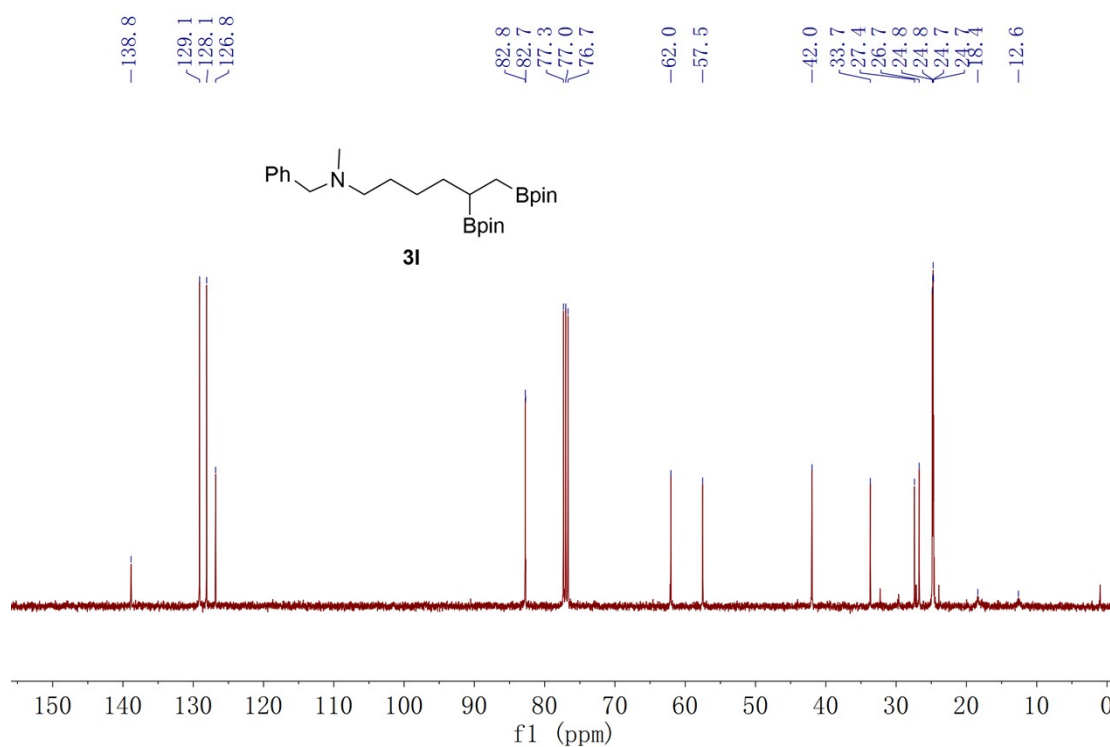
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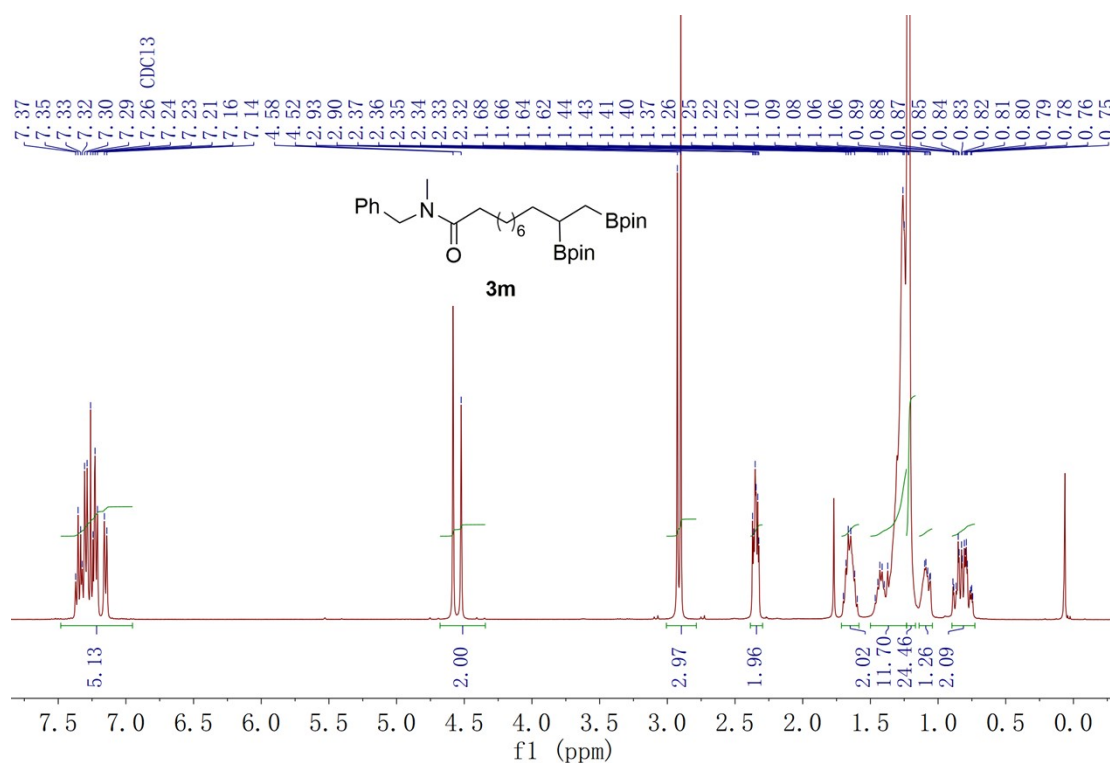
^1H NMR (CDCl_3 , 400 MHz) spectrum of compound **3k**.



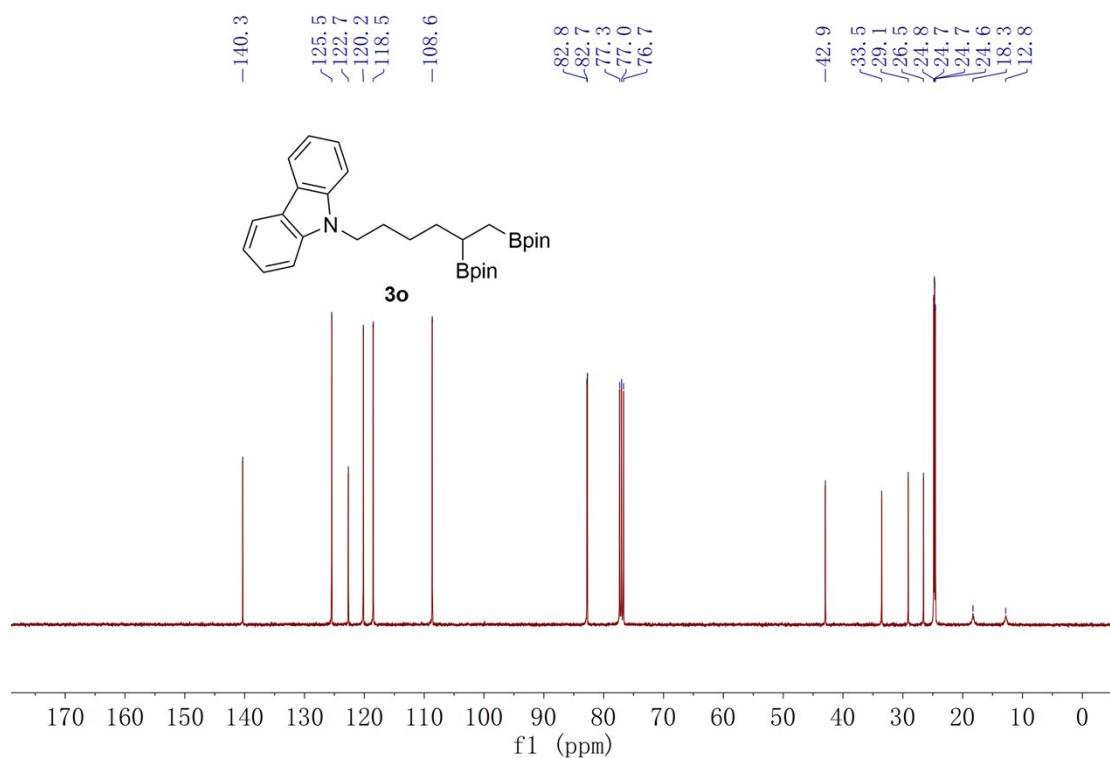
^{13}C NMR (CDCl_3 , 101 MHz) spectrum of compound **3l**.



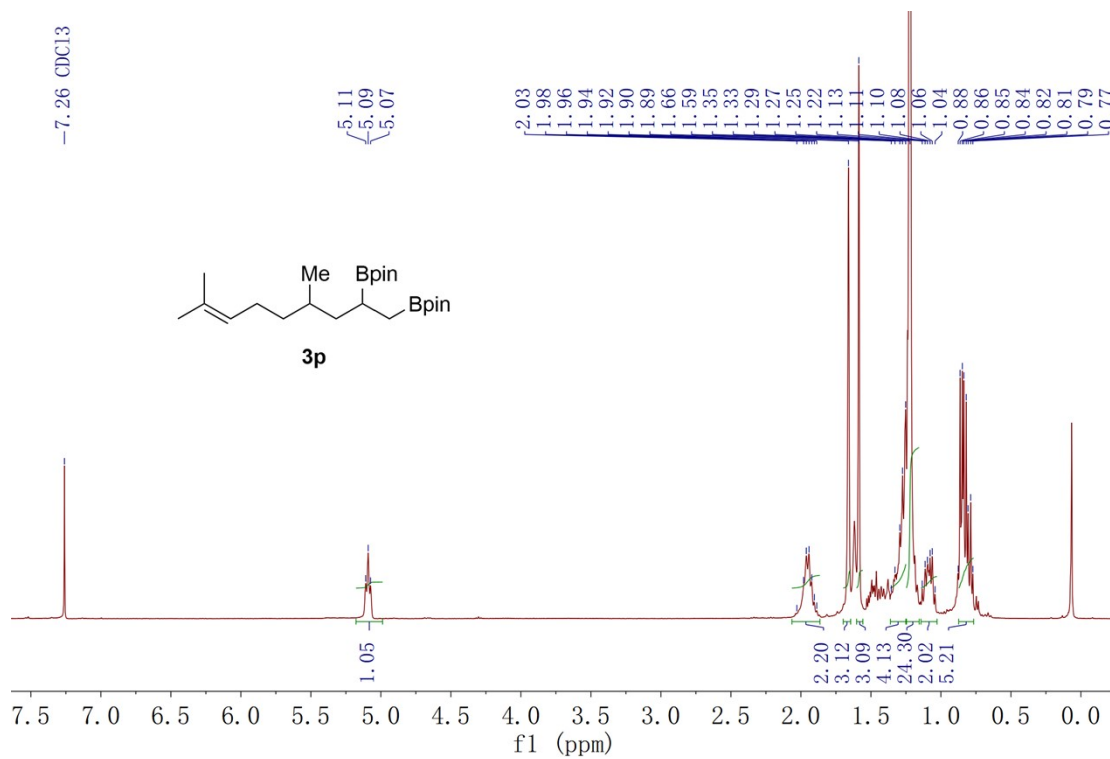
^1H NMR (CDCl_3 , 400 MHz) spectrum of compound **3m**.



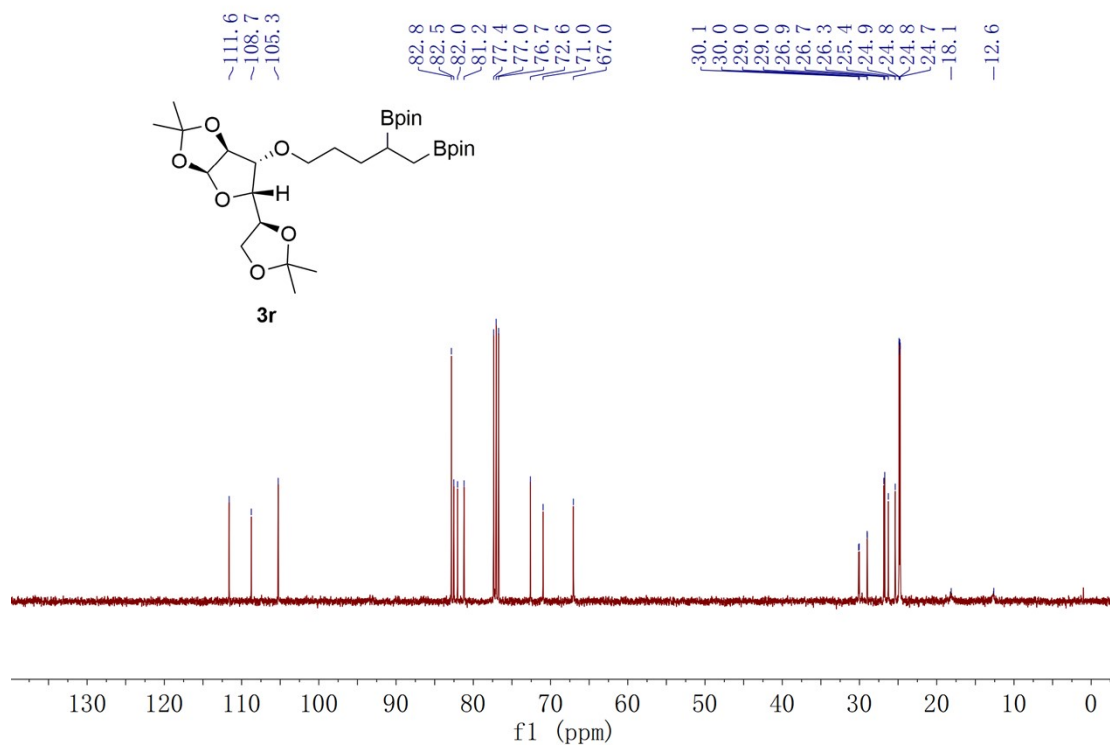
^{13}C NMR (CDCl_3 , 101 MHz) spectrum of compound **3o**.



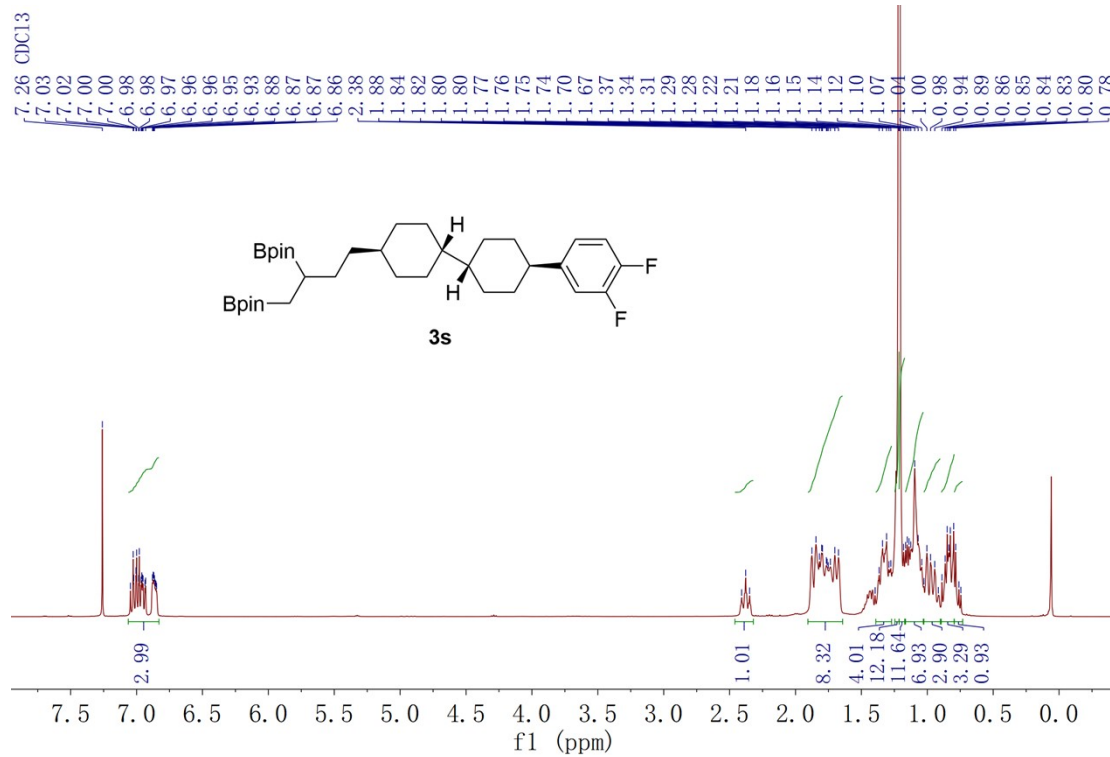
^1H NMR (CDCl_3 , 400 MHz) spectrum of compound **3p**.



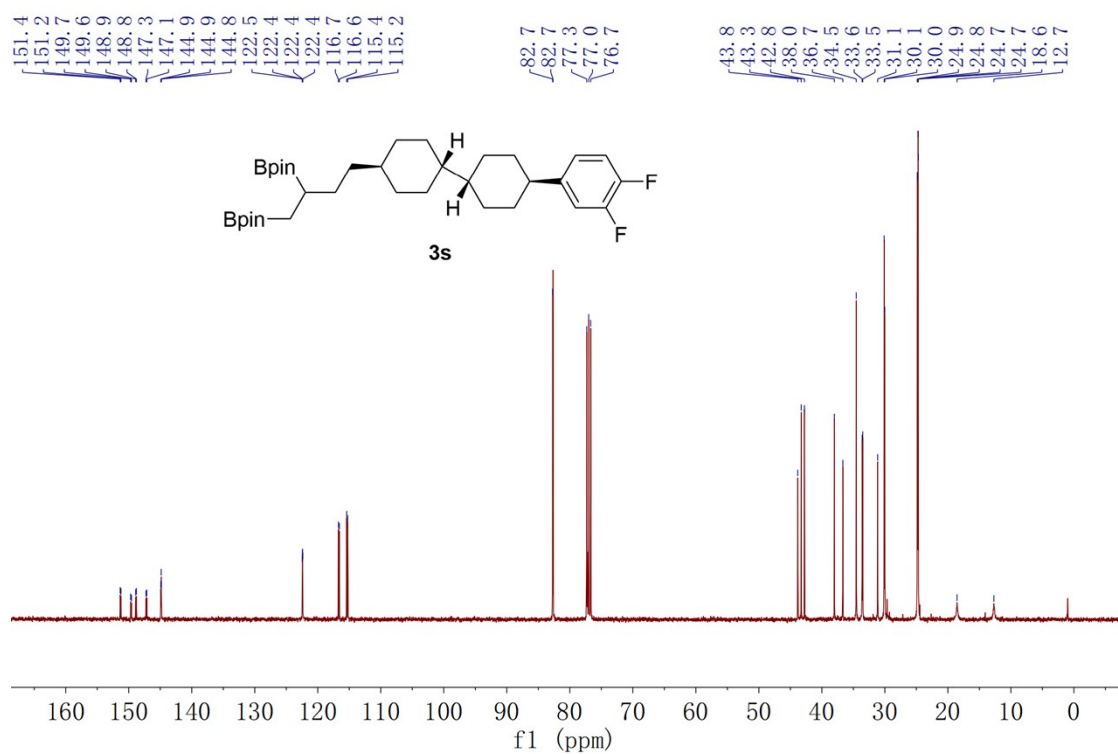
^{13}C NMR (CDCl_3 , 101 MHz) spectrum of compound **3r**.



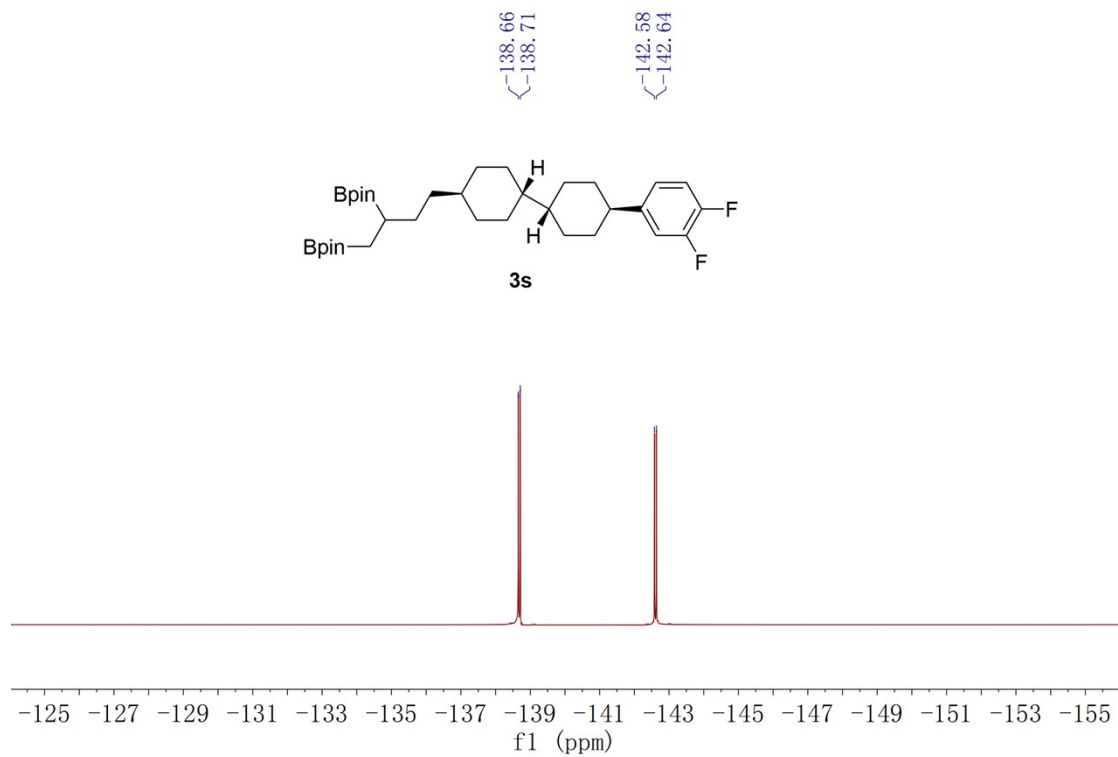
^1H NMR (CDCl_3 , 400 MHz) spectrum of compound **3s**.



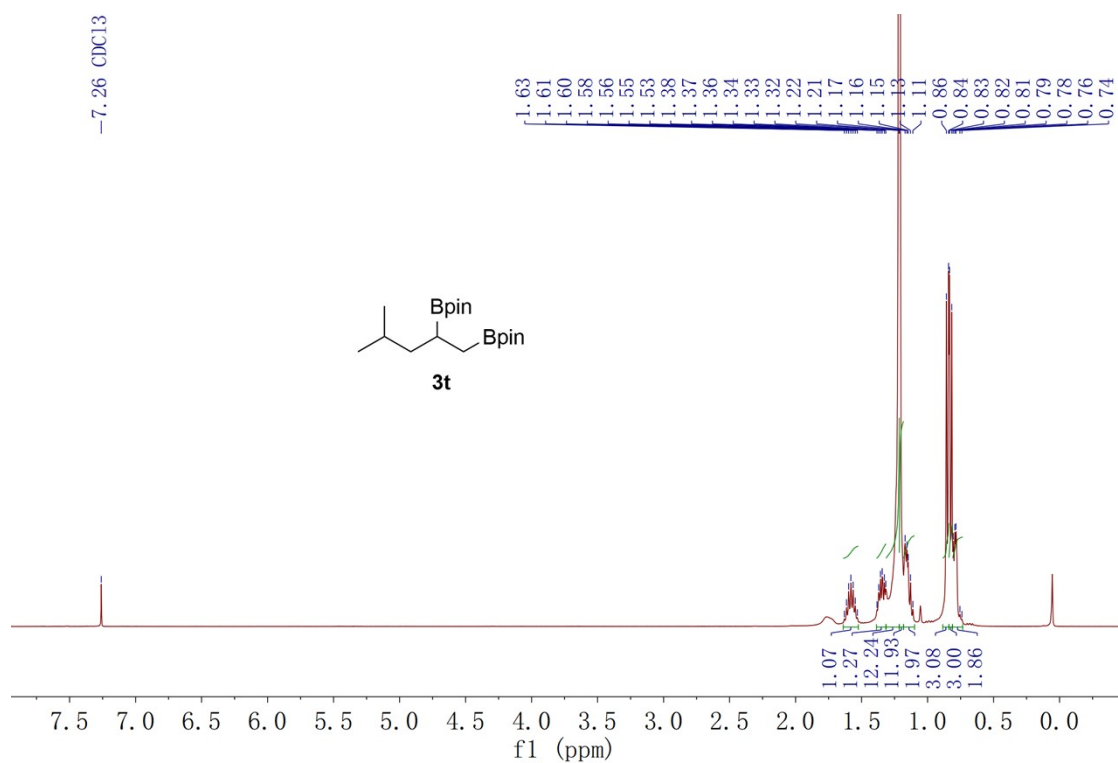
^{13}C NMR (CDCl_3 , 101 MHz) spectrum of compound **3s**.



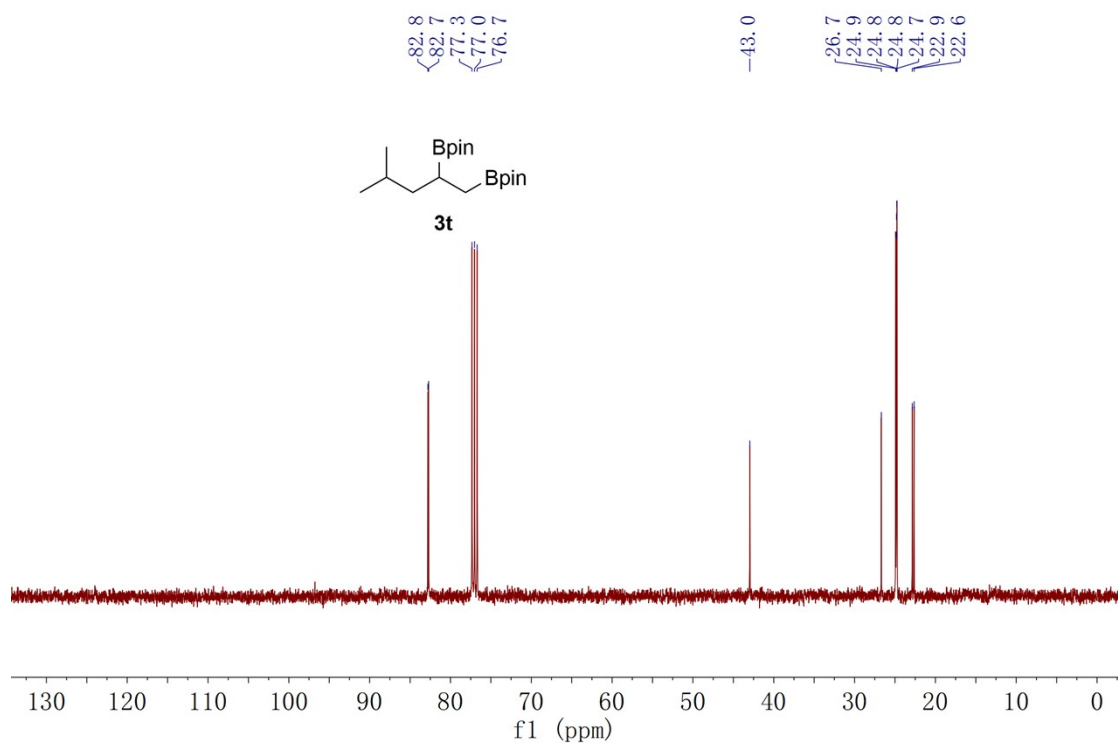
^{19}F NMR (CDCl_3 , 376 MHz) spectrum of compound **3s**.



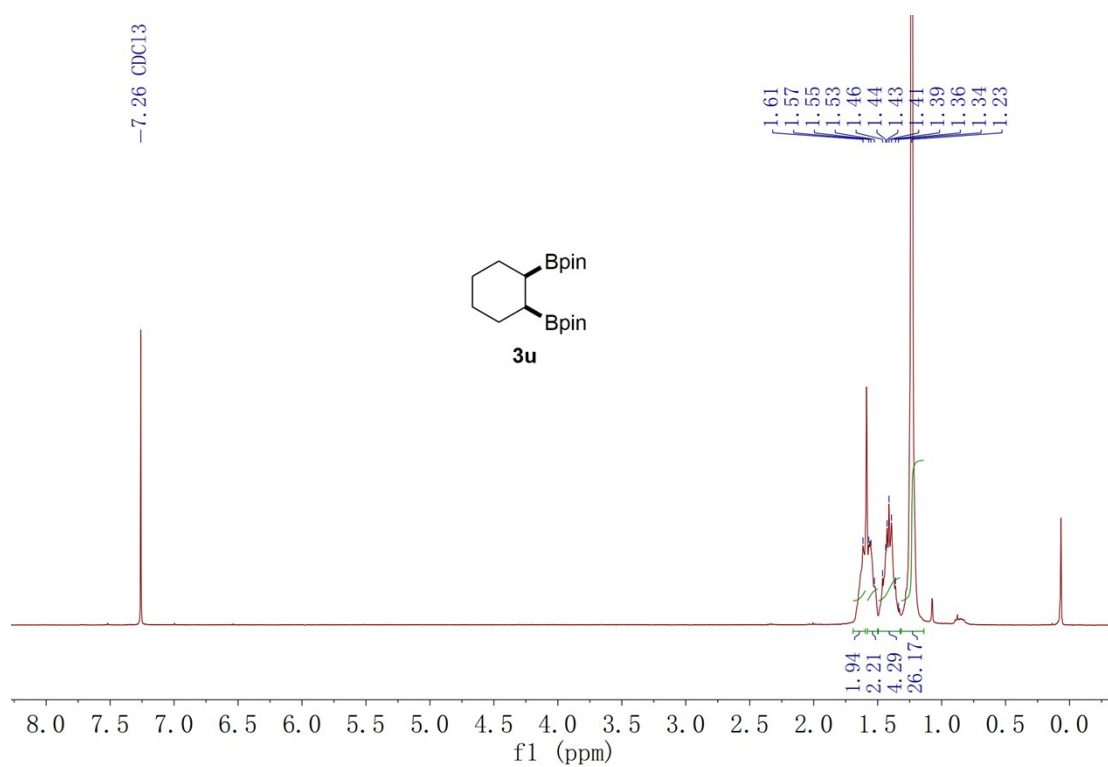
^1H NMR (CDCl_3 , 400 MHz) spectrum of compound **3t**.



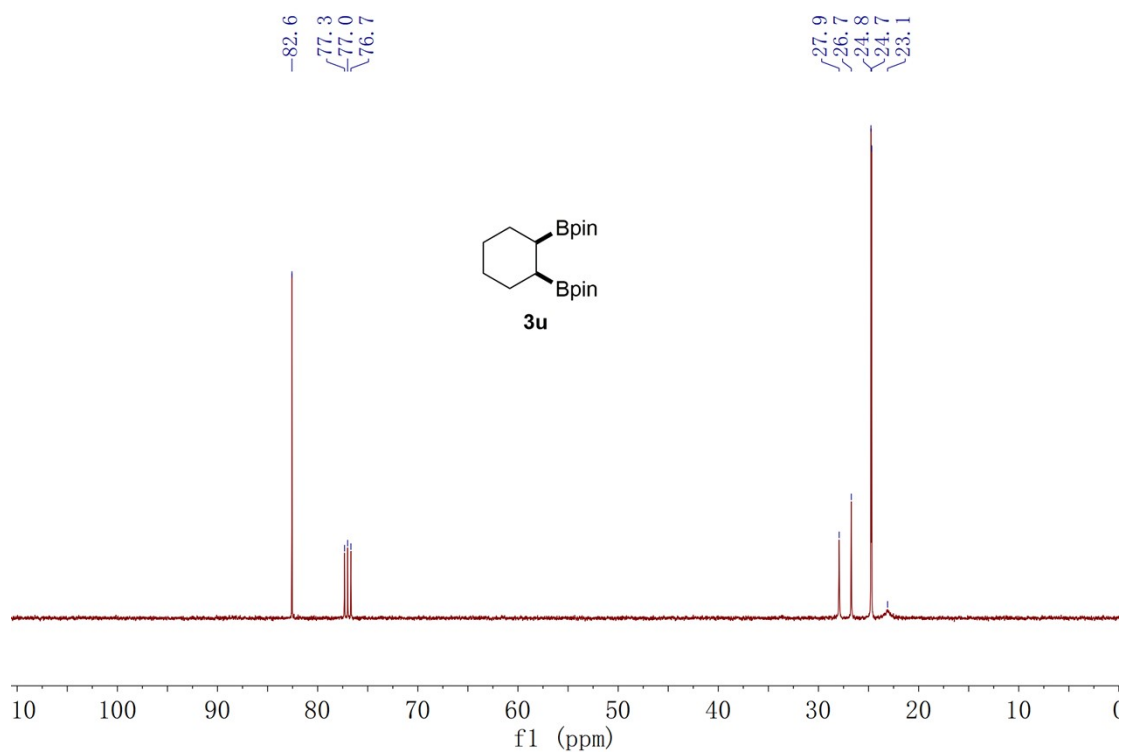
^{13}C NMR (CDCl_3 , 101 MHz) spectrum of compound **3t**.



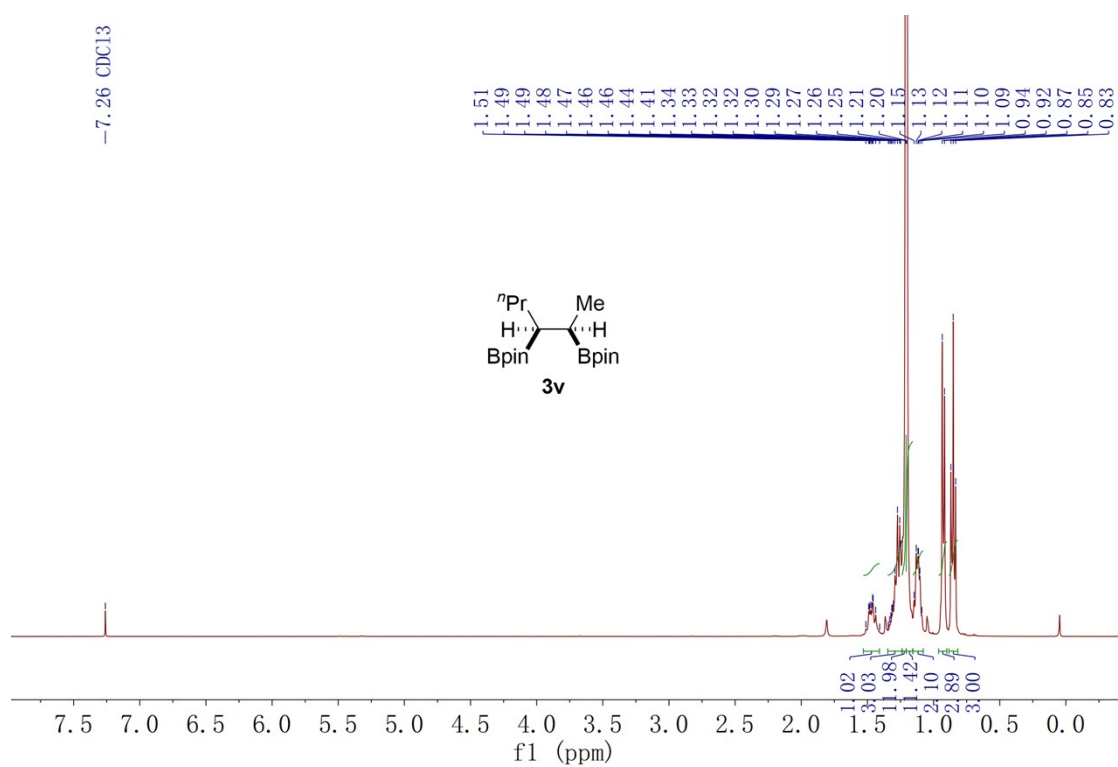
^1H NMR (CDCl_3 , 400 MHz) spectrum of compound **3u**.



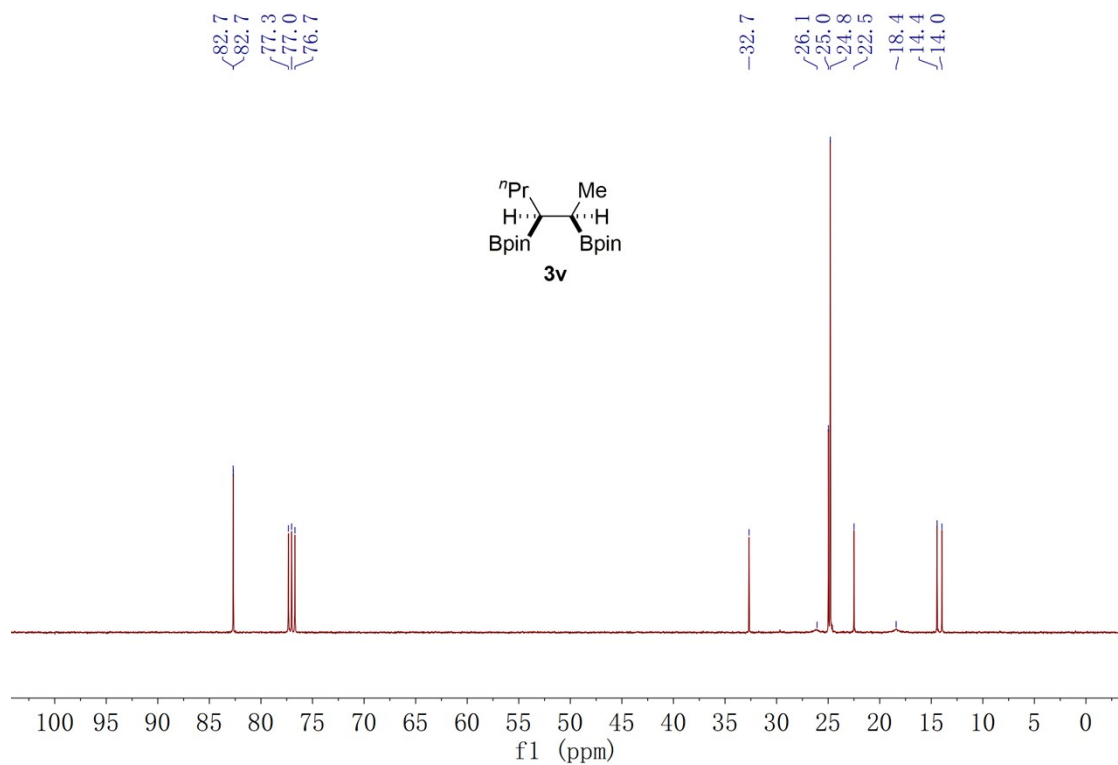
^{13}C NMR (CDCl_3 , 101 MHz) spectrum of compound **3u**.



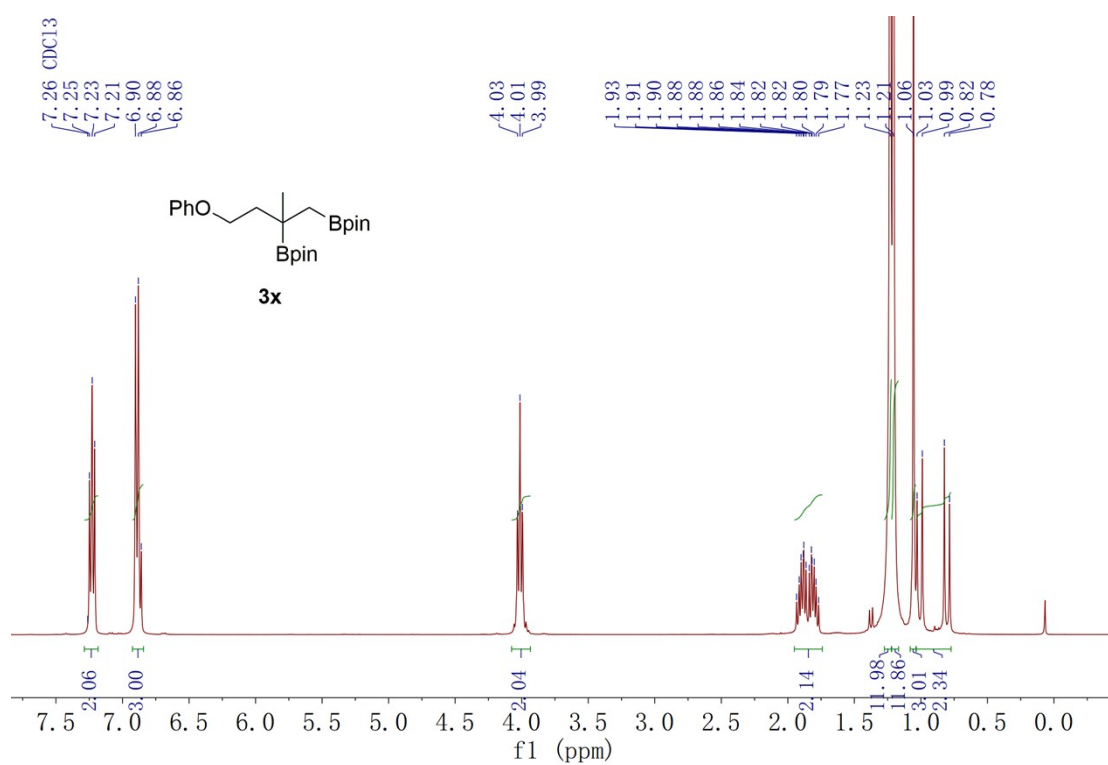
^1H NMR (CDCl_3 , 400 MHz) spectrum of compound **3v**.



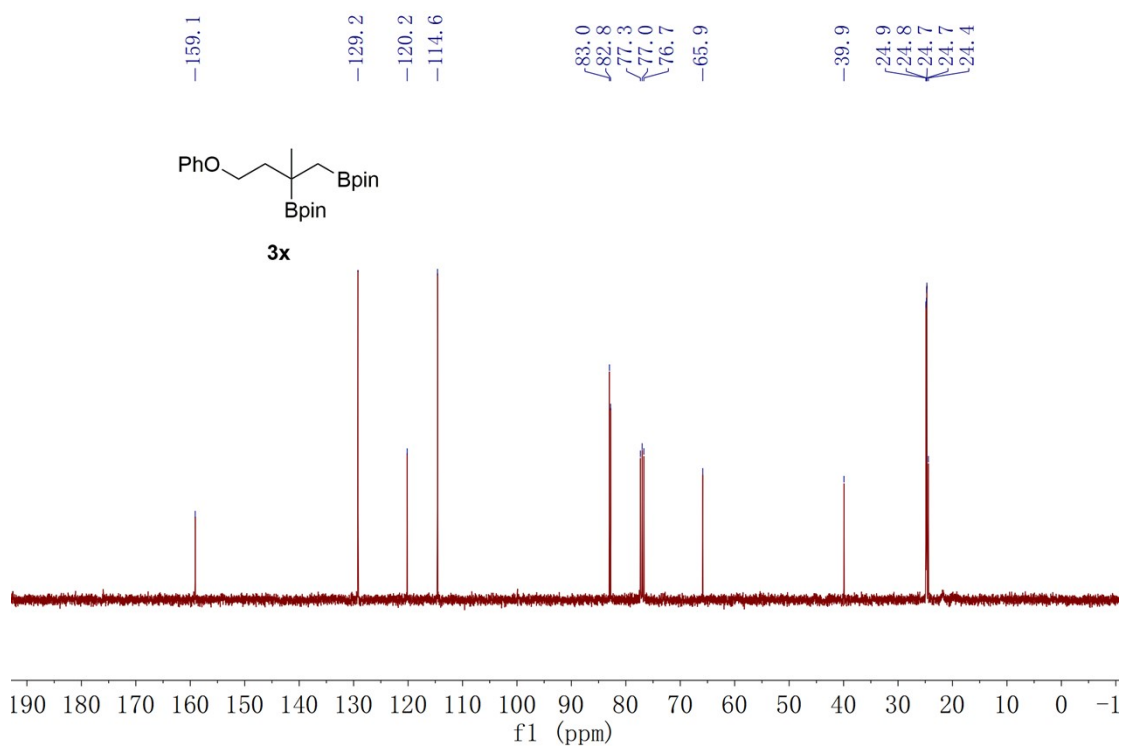
^{13}C NMR (CDCl_3 , 101 MHz) spectrum of compound **3v**.



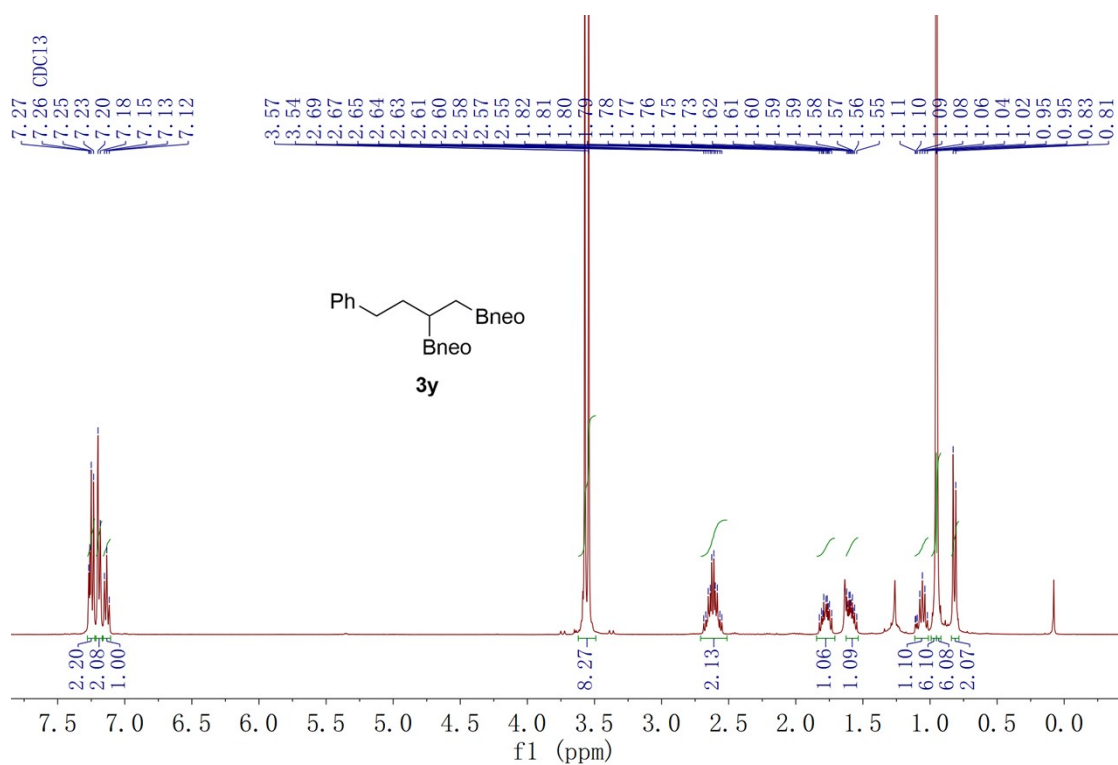
^1H NMR (CDCl_3 , 400 MHz) spectrum of compound **3x**.



^{13}C NMR (CDCl_3 , 101 MHz) spectrum of compound **3x**.



^1H NMR (CDCl_3 , 400 MHz) spectrum of compound **3y**.



^{13}C NMR (CDCl_3 , 126 MHz) spectrum of compound **3y**.

