Iridium-Catalyzed B-H Insertion of Sulfoxonium Ylides and Borane Adducts: A Versatile Platform to α-Boryl Carbonyls.

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1. General information

Unless otherwise noted, all reactions were carried out at room temperature under an atmosphere of nitrogen with flame-dried glassware. If reaction was not conducted at room temperature, reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated. The dry solvents used were purified by distillation over the drying agents indicated in parentheses and were transferred under nitrogen: THF (Na-benzophenone), 1,2-dichloroethane (CaH_2), dichloromethane (CaH_2). Anhydrous CF_3CH_2OH, CH_3CN, DMF and MeOH were purchased from Acros Organics and stored under nitrogen atmosphere. Commercially available chemicals were obtained from commercial suppliers and used without further purification unless otherwise stated.

Proton NMR (^1H) were recorded at 400 MHz, and Carbon NMR (^{13}C) at 101 MHz NMR spectrometer unless otherwise stated. The following abbreviations are used for the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, br s: broad singlet for proton spectra. Coupling constants (*J*) are reported in Hertz (Hz).

High-resolution mass spectra (HRMS) were recorded on a BRUKER VPEXII spectrometer with EI and ESI mode unless otherwise stated.

Analytical thin layer chromatography was performed on Polygram SIL G/UV_{254} plates. Visualization was accomplished with short wave UV light, or $KMnO_4$ staining solutions followed by heating. Flash column chromatography was performed using silica gel (200-300 mesh) with solvents distilled prior to use.

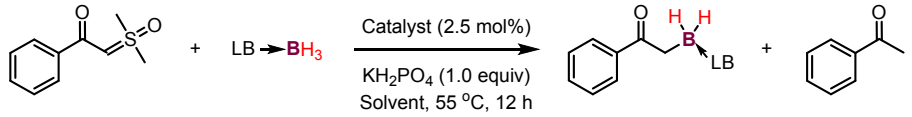
No attempts were made to optimize yields for substrate synthesis.

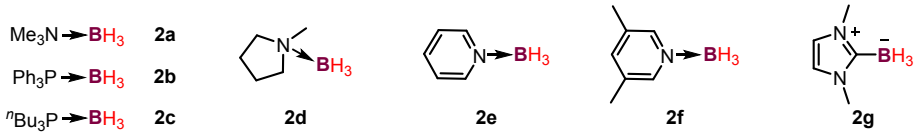
2. Synthesis of substrates 1, 2

The substrates of sulfoxonium ylides **1** were prepared accroding to the procedure reported by Burtoloso and Aïssa.[1] Borane adduct **2** were prepared following the procedure reported by Zhou.[2] All the characteristic data are consistent with the data reported before.[3]

3. Optimization of Reaction Conditions

Table 1. Catalytic B−H Bond Insertion Reactions: Optimization of Reaction Conditions[a]





Entry	Catalyst	Solvent	**2**	Product	Yield (**3**[b]/**19**[d])
1	$(Cp^*IrCl_2)_2$	DCM	**2a**	3**aa**	36%/17%
2	$[Ir(cod)Cl]_2$	DCM	**2a**	3**aa**	58%/15%
3	$(Cp^*RhCl_2)_2$	DCM	**2a**	3**aa**	15%/8%
4	$Rh_2(OAc)_4$	DCM	**2a**	3**aa**	Trace/ND[c]
5	CuI	DCM	**2a**	3**aa**	Trace/ND
6	$Cu(MeCN)_4PF_6$	DCM	**2a**	3**aa**	Trace/ND
7	$[Ir(cod)Cl]_2$	THF	**2a**	3**aa**	54%/21%
8	$[Ir(cod)Cl]_2$	Et_2O	**2a**	3**aa**	57%/18%
9	$[Ir(cod)Cl]_2$	PhMe	**2a**	3**aa**	46%/16%
10	$[Ir(cod)Cl]_2$	acetone	**2a**	3**aa**	36%/9%
11	**$[Ir(cod)Cl]_2$**	**PhCl**	**2a**	**3aa**	**75%/10%**
12	$[Ir(cod)Cl]_2$	EA	**2a**	3**aa**	47%/11%
13	$[Ir(cod)Cl]_2$	PhCl	**2b**	3**ab**	ND/ND
14	$[Ir(cod)Cl]_2$	PhCl	**2c**	3**ac**	Trace/ND
15	$[Ir(cod)Cl]_2$	PhCl	**2d**	3**ad**	61%/20%
16	$[Ir(cod)Cl]_2$	PhCl	**2e**	3**ae**	15%/5%
17	$[Ir(cod)Cl]_2$	PhCl	**2f**	3**af**	12%/4%
18	$[Ir(cod)Cl]_2$	PhCl	**2g**	3**ag**	Trace/ND
19	-	PhCl	**2a**	3**aa**	ND/ND

[a]Reaction Conditons: **1a** (0.2 mmol), **2** (1.5 equiv), catalyst (2.5 mol %), KH_2PO_4 (1.0 equiv), solvent (0.2 M), 55 °C, 12 h. [b]Isolated yield. [c]ND = not detected. [d]Yield was determined by ^1H NMR using 1-iodo4-methoxybenzene as internal standard

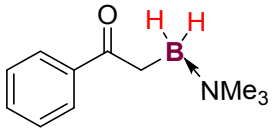
4. General procedure and characterization of products

General procedure A

In an oven-dried Schlenk tube under air, a mixture of the substrates **1** (0.2 mmol, 1.0 equiv), trimethylamine-borane **2a** (21.9 mg, 0.3 mmol, 1.5 equiv), $[Ir(Cod)Cl]_2$ (3.4 mg, 0.005 mmol, 2.5 mmol%), KH_2PO_4 (27.2 mg, 0.2 mmol, 1.0 equiv), and PhCl (2.0 mL) was stirred at 55 °C for 1 h - 12 h. The reaction mixture was then diluted with DCM (10.0 mL) and washed with H_2O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product **3**.

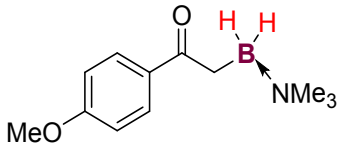
Characterization of products

2-(trimethylamine-boranyl)-1-phenylethan-1-one (3aa)



Following the general procedure A, the product **3aa** was obtained in 75% yield (28.6 mg, 0.20 mmol) as a yellow liquid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.23. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, J = 7.5 Hz, 2H), 7.45 (t, J = 7.2 Hz, 1H), 7.38 (t, J = 7.3 Hz, 2H), 2.59 (s, 9H), 2.45 (s, 2H), 2.35-1.50 (br, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.9, 138.1, 131.7, 128.7, 128.0, 52.2, 34.2. ^{11}B NMR (128 MHz, $CDCl_3$) δ -3.53 (t, J = 101.8 Hz).

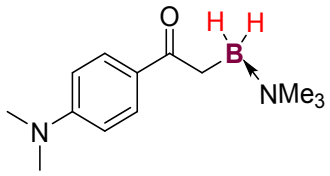
2-(trimethylamine-boranyl)-1-(4-methoxyphenyl)ethan-1-one (3ba)



Following the general procedure A, the product **3ba** was obtained in 66% yield (29.1mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.26. ^{1}H NMR (500 MHz, CDCl3) δ 7.98 (d, J = 7.5 Hz, 2H), 6.88

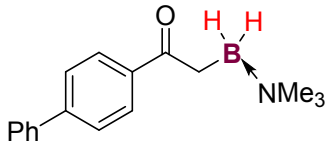
(d, J = 7.5 Hz, 2H), 3.83 (s, 3H), 2.59 (s, 9H), 2.40 (s, 2H), 2.34-1.50 (br, 2H). ^{13}C NMR (126 MHz, CDCl3) δ 206.95, 162.54, 131.16, 130.94, 113.21, 55.43, 52.23, 33.97. ^{11}B NMR (128 MHz, CDCl3) δ -3.42 (t, J = 97.8 Hz).

2-(trimethylamine-boranyl)-1-(4-(dimethylamino)phenyl)ethan-1-one (3ca)



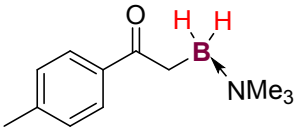
Following the general procedure A, the product **3ca** was obtained in 58% yield (27.2mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.24. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.9 Hz, 2H), 6.64 (d, *J* = 8.9 Hz, 2H), 3.01 (s, 3H), 2.60 (s, 9H), 2.38 (s, 2H), 2.23-1.45 (br, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.21, 152.85, 130.86, 126.36, 110.60, 52.27, 40.20, 34.09. ^{11}B NMR (128 MHz, $CDCl_3$) δ -3.42 (t, *J* = 97.8 Hz). ESI-MS: calculated $C_{13}H_{24}BN_2O$ $[M+H]^+$ 235.1976; Found 235.1975.

1-([1,1'-biphenyl]-4-yl)-2- trimethylamine-boranylethan-1-one (3da)



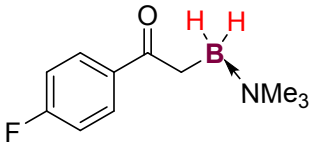
Following the general procedure A, the product **3da** was obtained in 52% yield (27.7mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.25. ^{1}H NMR (400 MHz, CDCl3) δ 8.08 (d, J = 8.4 Hz, 2H), 7.68 – 7.54 (m, 4H), 7.45 (t, J = 7.5 Hz, 2H), 7.36 (t, J = 7.3 Hz, 1H), 2.63 (s, 9H), 2.50 (s, 2H), 1.98-1.46 (br, 2H). ^{13}C NMR (101 MHz, CDCl3) δ 207.51, 144.33, 140.50, 136.79, 129.31, 128.85, 127.76, 127.25, 126.68, 52.19, 34.36. ^{11}B NMR (128 MHz, CDCl3) δ -3.53 (t, J = 100.9 Hz). ESI-MS: calculated $C_{17}H_{22}BNONa$ $[M+Na]^+$ 290.1687; Found 290.1685.

2-(trimethylamine-boranyl)-1-(p-tolyl)ethan-1-one (3ea)



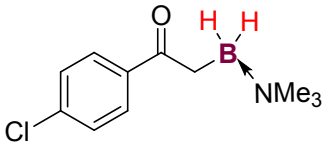
Following the general procedure A, the product **3ea** was obtained in 43% yield (17.6mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.25. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, J = 7.5 Hz, 1H), 7.19 (d, J = 14.4 Hz, 2H), 7.11 (t, J = 8.2 Hz, 2H), 2.53 (s, 9H), 2.39 (s, 3H), 2.33 (s, 2H), 2.23-1.39 (br, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.42, 140.85, 136.87, 131.34, 129.74, 128.54, 125.22, 52.29, 37.43, 21.12. ^{11}B NMR (128 MHz, $CDCl_3$) δ -4.02 (t, J = 99.8 Hz). ESI-MS: calculated $C_{12}H_{20}BNONa$ $[M+Na]^+$ 228.1530; Found 228.1527.

2-(trimethylamine-boranyl)-1-(4-fluorophenyl)ethan-1-one (3fa)



Following the general procedure A, the product **3fa** was obtained in 50% yield (20.8mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc 4:1): 0.24. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (m, J = 8.8, 5.6 Hz, 2H), 7.05 (t, J = 8.7 Hz, 2H), 2.60 (s, 9H), 2.42 (s, 2H), 2.33-1.46 (br, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.4, 165.1 (d, J = 252.1 Hz), 134.5 (d, J = 2.8 Hz), 131.3 (d, J = 9.0 Hz), 115.0 (d, J = 21.6 Hz), 52.2, 34.2. ^{11}B NMR (128 MHz, $CDCl_3$) δ -3.62 (t, J = 100.0 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -108.37 (s). ESI-MS: calculated $C_{11}H_{17}BFNONa$ $[M+Na]^+$ 232.1282; Found 232.1266.

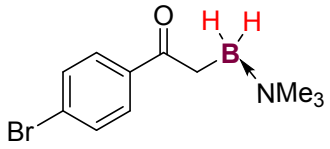
2-(trimethylamine-boranyl)-1-(4-chlorophenyl)ethan-1-one (3ga)



Following the general procedure A, the product **3ga** was obtained in 50% yield (18.2mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc 4:1): 0.26. 1H NMR (500 MHz, CDCl3) δ 7.93 (d, J = 7.1 Hz, 2H), 7.36 (d, J = 7.1 Hz, 2H), 2.60 (s, 9H), 2.42 (s, 2H), 2.30-1.49 (br, 2H). 13C NMR (126 MHz, CDCl3) δ

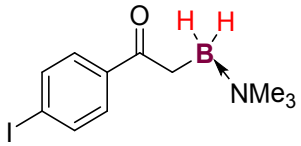
206.70, 138.06, 136.42, 130.31, 128.36, 52.29, 34.28. 11B NMR (128 MHz, CDCl3) δ -3.71 (t, J = 97.6 Hz).

2-(trimethylamine-boranyl)-1-(4-bromophenyl)ethan-1-one (3ha)



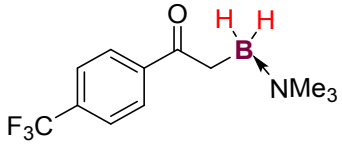
Following the general procedure A, the product **3ha** was obtained in 58% yield (31.2mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc 4:1): 0.23. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.3 Hz, 2H), 7.52 (d, *J* = 7.3 Hz, 2H), 2.59 (s, 9H), 2.41 (s, 2H), 2.32-1.50 (br, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.82, 136.82, 131.36, 130.48, 126.76, 52.27, 34.35. ^{11}B NMR (128 MHz, $CDCl_3$) δ -3.69 (t, *J* = 99.2 Hz).

2-(trimethylamine-boranyl)-1-(4-iodophenyl)ethan-1-one (3ia)



Following the general procedure A, the product **3ia** was obtained in 68% yield (43.2mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc 4:1): 0.22. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (m, *J* = 8.6 Hz, 4H), 2.59 (s, 9H), 2.40 (s, 2H), 2.31-1.47 (br, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.02, 137.39, 130.45, 99.44, 52.27, 34.25. ^{11}B NMR (128 MHz, $CDCl_3$) δ -3.71 (t, *J* = 97.7 Hz). ESI-MS: calculated $C_{11}H_{17}BINONa$ $[M+Na]^+$ 340.0340; Found 340.0329.

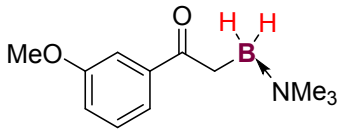
2-(trimethylamine-boranyl)-1-(4-(trifluoromethyl)phenyl)ethan-1-one (3ja)



Following the general procedure A, the product **3ja** was obtained in 45% yield (23.4mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v).

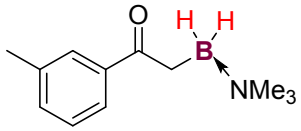
RF (Petroleum ether/EtOAc 3:1): 0.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.1 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 2H), 2.61 (s, 9H), 2.47 (s, 2H), 2.35-1.46 (br, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.61, 140.93 (s), 133.15 (q, J = 32.5 Hz), 129.07, 125.19 (q, J = 3.6 Hz), 124.09 (q, J = 272.5 Hz), 52.30, 34.52. ^{11}B NMR (128 MHz, $CDCl_3$) δ -3.83 (t, *J* = 99.5 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.88.

2-(trimethylamine-boranyl)-1-(3-methoxyphenyl)ethan-1-one (3ka)



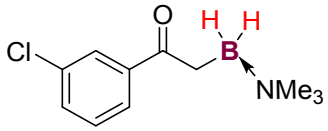
Following the general procedure A, the product **3ka** was obtained in 70% yield (30.8mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.7 Hz, 1H), 7.54 (s, 1H), 7.30 (t, *J* = 7.9 Hz, 1H), 7.01 (dd, *J* = 8.2, 2.0 Hz, 1H), 3.83 (s, 3H), 2.60 (s, 9H), 2.44 (s, 2H), 2.24-1.47 (br, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.69, 159.57, 139.67, 129.07, 121.63, 118.27, 112.96, 55.44, 52.25, 34.52. ^{11}B NMR (128 MHz, $CDCl_3$) δ -3.54 (t, *J* = 99.9 Hz). ESI-MS: calculated $C_{12}H_{20}BNO_2Na$ $[M+Na]^+$ 244.1479; Found 244.1469.

2-(trimethylamine-boranyl)-1-(m-tolyl)ethan-1-one (3la)



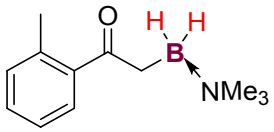
Following the general procedure A, the product **3la** was obtained in 62% yield (25.4mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.24. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.1 Hz, 1H), 7.21 (d, *J* = 5.0 Hz, 1H), 2.53 (s, 4H), 2.38 (s, 1H), 2.31 (s, 1H), 2.18-1.39 (br, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.42, 138.20, 137.73, 132.58, 129.19, 128.00, 126.10, 52.26, 34.50, 21.51. ^{11}B NMR (128 MHz, $CDCl_3$) δ -3.36 (t, *J* = 139.8 Hz). ESI-MS: calculated $C_{12}H_{20}BNONa$ $[M+Na]^+$ 228.1530; Found 228.1520.

2-(trimethylamine-boranyl)-1-(3-chlorophenyl)ethan-1-one (3ma)



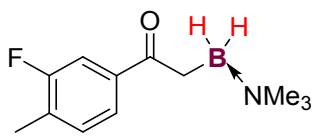
Following the general procedure A, the product **3ma** was obtained in 59% yield (26.6mg, 0.20 mmol) as a yellow liquid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.21. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (t, *J* = 1.8 Hz, 1H), 7.86 (d, *J* = 9.0 Hz, 1H), 7.43 (d, *J* = 7.9 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 1H), 2.61 (s, 9H), 2.43 (s, 2H), 2.28-1.45 (br, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.42, 139.85, 134.40, 131.71, 129.46, 128.86, 126.99, 52.31, 34.56. ^{11}B NMR (128 MHz, $CDCl_3$) δ -3.78 (t, *J* = 100.3 Hz). ESI-MS: calculated $C_{11}H_{17}BClNONa$ $[M+Na]^+$ 248.0984; Found 248.0979.

2-(trimethylamine-boranyl)-1-(o-tolyl)ethan-1-one (3na)



Following the general procedure A, the product **3na** was obtained in 54% yield (22.1mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.26. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.11 (t, *J* = 8.2 Hz, 2H), 2.53 (s, 9H), 2.39 (s, 3H), 2.33 (s, 2H), 2.21-1.41 (br, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.44, 140.83, 136.83, 131.32, 129.73, 128.50, 125.20, 52.25, 37.48, 21.09. ^{11}B NMR (128 MHz, $CDCl_3$) δ -4.02 (t, *J* = 99.5 Hz).

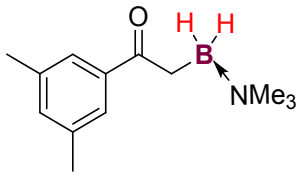
2-(trimethylamine-boranyl)-1-(3-fluoro-4-methylphenyl)ethan-1-one (3oa)



Following the general procedure A, the product **3oa** was obtained in 64% yield (28.4mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.28. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 18.7, 9.9 Hz, 2H), 7.19 (t, *J* = 7.7 Hz, 1H), 2.60 (s, 9H), 2.39 (s, 2H), 2.29 (s, 3H), 2.18-1.44 (br, 2H). ^{13}C NMR (101

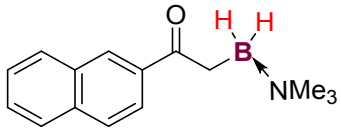
MHz, $CDCl_3$) δ 206.52, 161.19 (d, J = 244.9 Hz), 138.07 (d, J = 6.2 Hz), 131.04 (d, J = 4.7 Hz), 129.05 (d, J = 17.5 Hz), 124.38 (d, J = 3.1 Hz), 115.09 (d, J = 22.9 Hz), 52.26, 34.50, 14.79. ^{11}B NMR (128 MHz, $CDCl_3$) δ -3.62 (t, *J* = 100.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.75. ESI-MS: calculated $C_{12}H_{19}BFNONa$ $[M+Na]^+$ 246.1436; Found 246.1433.

2-(trimethylamine-boranyl)-1-(3,5-dimethylphenyl)ethan-1-one (3pa)



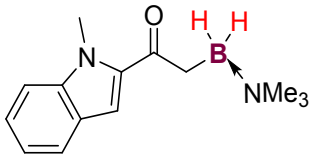
Following the general procedure A, the product **3pa** was obtained in 69% yield (30.2mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.25. ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 2H), 7.10 (s, 1H), 2.60 (s, 9H), 2.43 (s, 2H), 2.34 (s, 6H), 2.11-1.47 (br, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.69, 138.31, 137.57, 133.47, 126.56, 52.27, 34.36, 21.41. ^{11}B NMR (128 MHz, $CDCl_3$) δ -3.54 (t, *J* = 99.0 Hz). ESI-MS: calculated $C_{13}H_{22}BNONa$ $[M+Na]^+$ 242.1687; Found 242.1683.

2-(trimethylamine-boranyl)-1-(naphthalen-2-yl)ethan-1-one (3qa)



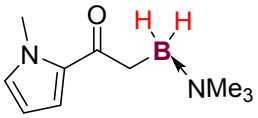
Following the general procedure A, the product **3qa** was obtained in 64% yield (30.9mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.28. ^1H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.07 (d, *J* = 1.6 Hz, 1H), 7.95 (d, *J* = 7.9 Hz, 1H), 7.84 (d, *J* = 8.5 Hz, 2H), 7.62 – 7.43 (m, 2H), 2.61 (s, 9H), 2.58 (s, 2H), 2.37-1.46 (br, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.10, 135.48, 135.23, 132.83, 130.03, 129.70, 127.72, 127.68, 126.24, 125.19, 52.28, 34.61. ^{11}B NMR (128 MHz, $CDCl_3$) δ -3.44 (t, *J* = 98.4 Hz).

2-(trimethylamine-boranyl)-1-(1-methyl-1H-indol-2-yl)ethan-1-one (3ra)



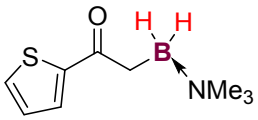
Following the general procedure A, the product **3ra** was obtained in 65% yield (32.0mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 1H), 7.39 – 7.27 (m, 3H), 7.11 (t, *J* = 7.9 Hz, 1H), 4.06 (s, 3H), 2.63 (s, 9H), 2.43 (s, 2H), 2.25-1.47 (br, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.33, 139.64, 136.40, 126.22, 124.67, 122.68, 120.12, 110.66, 110.22, 52.26, 35.93, 32.21. ^{11}B NMR (128 MHz, $CDCl_3$) δ -2.92 (t, *J* = 98.1 Hz). ESI-MS: calculated $C_{14}H_{21}BN_2ONa$ $[M+Na]^+$ 267.1639; Found 267.1633.

2-(trimethylamine-boranyl)-1-(1-methyl-1H-pyrrol-2-yl)ethan-1-one (3sa)



Following the general procedure A, the product **3sa** was obtained in 58% yield (22.0mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (dd, *J* = 4.0, 1.7 Hz, 1H), 6.74 – 6.57 (m, 1H), 6.06 (dd, *J* = 3.9, 2.5 Hz, 1H), 3.91 (s, 3H), 2.61 (s, 9H), 2.23 (s, 2H), 2.11-1.45 (br, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.61, 131.79, 129.17, 118.74, 107.12, 52.23, 37.71, 34.92. ^{11}B NMR (128 MHz, $CDCl_3$) δ -2.80 (t, *J* = 99.5 Hz). ESI-MS: calculated $C_{10}H_{19}BN_2ONa$ $[M+Na]^+$ 217.1483; Found 217.1479.

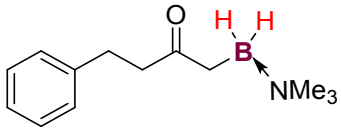
2-(trimethylamine-boranyl)-1-(thiophen-2-yl)ethan-1-one (3ta)



Following the general procedure A, the product **3ta** was obtained in 41% yield (16.1mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.22. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.49 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.06 (dd, *J* = 4.9, 3.7 Hz, 1H), 2.62 (s, 9H), 2.39 (s, 2H), 2.32-

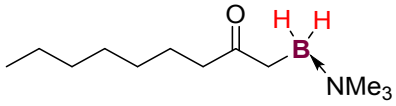
1.47 (br, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.17, 145.94, 131.69, 131.59, 127.77, 52.33, 35.58. ^{11}B NMR (128 MHz, $CDCl_3$) δ -3.27 (t, J = 101.3 Hz).

1-(trimethylamine-boranyl)-4-phenylbutan-2-one (5aa)



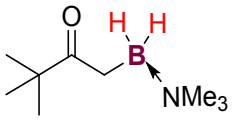
Following the general procedure A, the product **5aa** was obtained in 83% yield (36.4mg, 0.20 mmol) as a yellow liquid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc :1): 0.23. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.13 (m, 5H), 2.96 – 2.85 (m, 2H), 2.83 – 2.74 (m, 2H), 2.54 (s, 9H), 1.96 (s, 2H), 2.39-1.38 (br, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 217.65, 142.29, 128.59, 128.34, 125.76, 52.21, 43.48, 38.72, 30.57. ^{11}B NMR (128 MHz, $CDCl_3$) δ -4.12 (t, J = 98.9 Hz). ESI-MS: calculated $C_{13}H_{22}BNONa$ $[M+Na]^+$ 242.1687; Found 242.1680.

1-trimethylamine-boranylnonan-2-one (5ba)



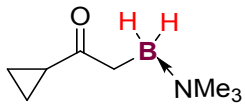
Following the general procedure A, the product **5ba** was obtained in 74% yield (31.5mg, 0.20 mmol) as a colorless liquid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.56 (s, 9H), 2.44 – 2.34 (m, 2H), 1.92 (s, 2H), 1.56 – 1.44 (m, 2H), 1.25 (s, 8H), 0.85 (t, J = 6.8 Hz, 3H), 2.24-1.55 (br, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 219.36, 52.16, 42.20, 38.62, 31.90, 29.60, 29.31, 24.75, 22.76, 14.21. ^{11}B NMR (128 MHz, $CDCl_3$) δ -4.04 (t, J = 98.0 Hz). ESI-MS: calculated $C_{12}H_{28}BNONa$ $[M+Na]^+$ 236.2152; Found 236.2152.

1-(trimethylamine-boranyl)-3,3-dimethylbutan-2-one (5ca)



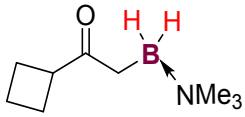
Following the general procedure A, the product **5ca** was obtained in 43% yield (14.8mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.25. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.59 (s, 9H), 1.98 (s, 2H), 1.13 (s, 9H), 2.23-1.39 (br, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 52.21, 44.16, 32.44, 27.56. ^{11}B NMR (128 MHz, $CDCl_3$) δ -4.12 (t, J = 99.5 Hz). ESI-MS: calculated $C_9H_{22}BNONa$ $[M+Na]^+$ 194.1687; Found 194.1685.

2-(trimethylamine-boranyl)-1-cyclopropylethan-1-one (5da)



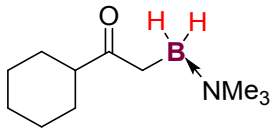
Following the general procedure A, the product **5da** was obtained in 83% yield (25.8mg, 0.20 mmol) as a yellow liquid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.22. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.57 (s, 9H), 2.05 (s,3H), 0.94 – 0.79 (m, 2H), 0.71 (m, *J* = 6.7, 3.4 Hz, 2H), 2.24-1.46 (br, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 218.51, 52.29, 39.45, 20.09, 9.80. ^{11}B NMR (128 MHz, $CDCl_3$) δ -4.18 (t, *J* = 100.7 Hz).

2-(trimethylamine-boranyl)-1-cyclobutylethan-1-one (5ea)



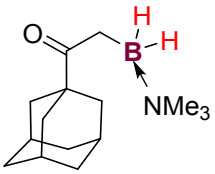
Following the general procedure A, the product **5ea** was obtained in 72% yield (24.4mg, 0.20 mmol) as a colorless liquid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.59 (s, 9H), 2.22 (m, *J* = 17.8, 9.0, 2.3 Hz, 2H), 2.12 – 2.02 (m, 2H), 1.98 – 1.85 (m, 3H), 1.82 – 1.69 (m, 2H), 2.35-1.37 (br, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 52.27, 44.91, 35.99, 25.20, 17.85. ^{11}B NMR (128 MHz, $CDCl_3$) δ -4.25 (t, *J* = 99.9 Hz). ESI-MS: calculated $C_9H_{20}BNONa$ $[M+Na]^+$ 192.1530; Found 192.1527.

2-(trimethylamine-boranyl)-1-cyclohexylethan-1-one (5fa)



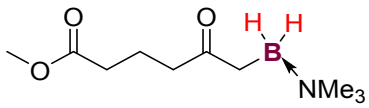
Following the general procedure A, the product **5fa** was obtained in 84% yield (33.1mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.28. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.55 (s, 9H), 1.93 (s, 2H), 1.75 (dd, *J* = 18.0, 10.9 Hz, 4H), 1.62 (d, *J* = 10.0 Hz, 1H), 1.36 – 1.12 (m, 6H), 2.32-1.38 (br, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 52.28, 49.83, 36.82, 29.30, 26.21, 26.11. ^{11}B NMR (128 MHz, $CDCl_3$) δ -4.35 (t, *J* = 99.3 Hz).

1-((3r,5r,7r)-adamantan-1-yl)-2-trimethylamine-boranylethan-1-one (5ga)



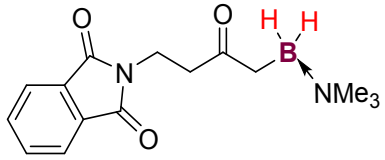
Following the general procedure A, the product **5ga** was obtained in 62% yield (31.0mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.24. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.58 (s, 9H), 1.97 (d, *J* = 14.0 Hz, 5H), 1.85 (s, 6H), 1.68 (s, 6H), 2.28-1.43 (br, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 52.24, 46.35, 39.19, 37.01, 32.27, 28.52. ^{11}B NMR (128 MHz, $CDCl_3$) δ -4.32 (t, *J* = 99.2 Hz). ESI-MS: calculated $C_{15}H_{28}BNONa$ $[M+Na]^+$ 272.2156; Found 272.2151.

methyl 6-(trimethylamine-boranyl)-5-oxohexanoate (5ha)



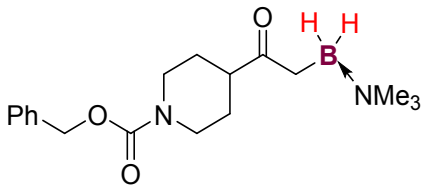
Following the general procedure A, the product **5ha** was obtained in 51% yield (21.9mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.28. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.65 (s, 3H), 2.56 (s, 9H), 2.48 (t, *J* = 7.3 Hz, 2H), 2.31 (t, *J* = 7.5 Hz, 2H), 1.92 (s, 2H), 1.85 (m, *J* = 14.7, 7.5 Hz, 2H), 2.49-1.35 (br, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 217.69, 174.15, 52.29, 51.55, 40.87, 38.74, 33.71, 19.80. ^{11}B NMR (128 MHz, $CDCl_3$) δ -4.10 (t, *J* = 99.0 Hz). ESI-MS: calculated $C_{10}H_{22}BNO_3Na$ $[M+Na]^+$ 238.1585; Found 238.1578.

2-(4-(trimethylamine-boranyl)-3-oxobutyl)isoindoline-1,3-dione (5ia)



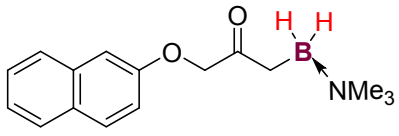
Following the general procedure A, the product **5ia** was obtained in 68% yield (39.9mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 1:1 v/v). RF (Petroleum ether/EtOAc 1:1): 0.28. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 – 7.75 (m, 2H), 7.73 – 7.64 (m, 2H), 3.89 (t, *J* = 7.5 Hz, 2H), 2.86 (s, 2H), 2.53 (s, 9H), 1.92 (s, 2H), 2.24-1.37 (br, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 215.37, 168.27, 133.87, 132.32, 123.17, 52.19, 39.79, 38.67, 33.89. ^{11}B NMR (128 MHz, $CDCl_3$) δ -4.21 (t, *J* = 97.5 Hz). ESI-MS: calculated $C_{15}H_{21}BN_2O_3Na$ $[M+Na]^+$ 311.1537; Found 311.1533.

benzyl 4-(2-(trimethylamine)-boranylacetyl)piperidine-1-carboxylate (5ja)



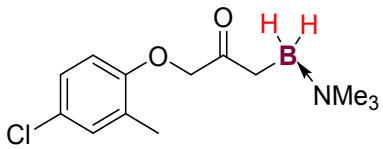
Following the general procedure A, the product **5ja** was obtained in 70% yield (46.5mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 5H), 5.10 (s, 2H), 4.16 (s, 2H), 2.81 (t, *J* = 11.1 Hz, 2H), 2.64 (m, *J* = 11.5, 9.4, 3.6 Hz, 1H), 2.56 (s, 9H), 1.95 (s, 2H), 1.77 (s, 2H), 1.54 (m, *J* = 16.3, 12.5, 4.2 Hz, 2H), 2.31-1.35 (br, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 219.36, 155.32, 137.04, 128.54, 127.97, 127.87, 67.04, 52.26, 47.36, 43.88, 36.62, 28.22. ^{11}B NMR (128 MHz, $CDCl_3$) δ -3.77, -4.47, -5.19. ESI-MS: calculated $C_{18}H_{29}BN_2O_3Na$ $[M+Na]^+$ 355.2163; Found 355.2159.

1-(trimethylamine-boranyl)-3-(naphthalen-2-yloxy)propan-2-one (5ka)



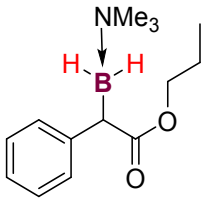
Following the general procedure A, the product **5ka** was obtained in 47% yield (25.5mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.26. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.66 (m, 1H), 7.45 – 7.38 (m, 1H), 7.35 – 7.28 (m, 1H), 7.25 – 7.20 (m, 1H), 7.12 (d, *J* = 2.4 Hz, 1H), 4.77 (s, 1H), 2.60 (s, 3H), 2.08 (s, 1H), 2.48-1.49 (br, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.56, 156.45, 134.58, 129.54, 129.26, 127.72, 126.91, 126.41, 123.79, 119.02, 107.32, 71.97, 52.31, 34.45. ^{11}B NMR (128 MHz, $CDCl_3$) δ -4.15 (t, *J* = 96.9 Hz). ESI-MS: calculated $C_{16}H_{22}BNO_2Na$ $[M+Na]^+$ 294.1636; Found 294.1631.

1-(trimethylamine-boranyl)-3-(4-chloro-2-methylphenoxy)propan-2-one (5la)



Following the general procedure A, the product **5la** was obtained in 55% yield (29.6mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 2.4 Hz, 1H), 7.04 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.63 (d, *J* = 8.7 Hz, 1H), 4.59 (s, 2H), 2.59 (s, 10H), 2.24 (d, *J* = 19.0 Hz, 4H), 2.04 (s, 3H), 2.31-1.39 (br, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.81, 155.42, 130.58, 129.01, 126.34, 125.42, 112.67, 72.48, 52.31, 34.29, 16.40. ^{11}B NMR (128 MHz, $CDCl_3$) δ -4.23 (t, *J* = 100.1 Hz). ESI-MS: calculated $C_{13}H_{21}BClNO_2Na$ $[M+Na]^+$ 292.1246; Found 292.1244.

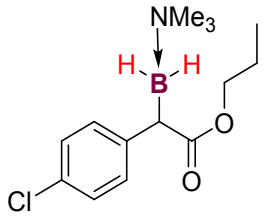
propyl 2-(trimethylamine-boranyl)-2-phenylacetate (7aa)



Following the general procedure A, the product **7aa** was obtained in 50% yield (24.8mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc :1): 0.26. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.4 Hz, 2H), 7.30 – 7.23 (m, 2H), 7.12 (t, *J* = 7.3 Hz, 1H), 4.00 (q, *J* = 5.4 Hz, 2H), 3.26 (s, 1H), 2.55 (s, 9H), 1.65 (dt, *J* = 14.0, 7.0 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H), 2.44-1.55 (br, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ

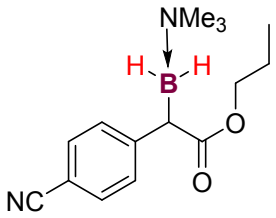
178.40, 143.80, 129.30, 127.90, 124.90, 65.48, 52.51, 46.61, 22.26, 10.67. ^{11}B NMR (128 MHz, $CDCl_3$) δ -0.70 (t, *J* = 102.2 Hz). ESI-MS: calculated $C_{14}H_{24}BNO_2Na$ $[M+Na]^+$ 272.1792; Found 272.1790.

propyl 2-(trimethylamine-boranyl)-2-(4-chlorophenyl)acetate (7ba)



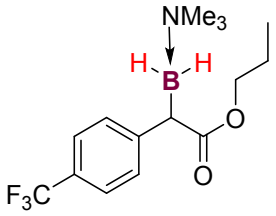
Following the general procedure A, the product **7ba** was obtained in 56% yield (31.9mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc 4:1): 0.24. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 3.96 (m, *J* = 10.7, 5.4 Hz, 2H), 3.19 (s, 1H), 2.52 (s, 9H), 1.72 – 1.51 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H), 2.41-1.36 (br, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.07, 142.45, 130.60, 130.54, 127.94, 65.62, 52.55, 46.08, 22.27, 10.67. ^{11}B NMR (128 MHz, $CDCl_3$) δ 2.32 – -6.55 (m). ESI-MS: calculated $C_{14}H_{23}BClNO_2Na$ $[M+Na]^+$ 306.1403; Found 306.1400.

propyl 2-(trimethylamine-boranyl)-2-(4-cyanophenyl)acetate (7ca)



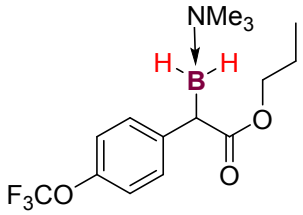
Following the general procedure A, the product **7ca** was obtained in 46% yield (25.2mg, 0.20 mmol) as a yellow liquid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.24. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.38 (m, 4H), 4.13 – 3.82 (m, 2H), 3.28 (s, 1H), 2.55 (s, 9H), 1.74 – 1.46 (m, 2H), 0.99 – 0.74 (m, 3H), 2.53-1.37 (br, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.37, 150.10, 131.67, 129.84, 119.74, 108.38, 65.84, 52.52, 47.39, 22.22, 10.67. ^{11}B NMR (128 MHz, $CDCl_3$) δ 4.12 – -7.51 (m). ESI-MS: calculated $C_{15}H_{23}BN_2O_2Na$ $[M+Na]^+$ 297.1745; Found 297.1745.

propyl 2-(trimethylamine-boranyl)-2-(4-(trifluoromethyl)phenyl)acetate (7da)



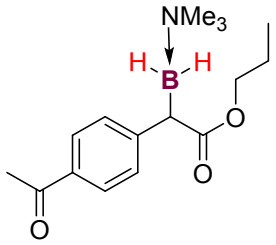
Following the general procedure A, the product **7da** was obtained in 43% yield (27.3mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc 4:1): 0.24. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 3.99 (m, *J* = 12.5, 6.5 Hz, 2H), 3.29 (s, 1H), 2.55 (s, 9H), 1.70 – 1.53 (m, 4H), 0.92 (t, *J* = 7.4 Hz, 3H), 2.39-1.40 (br, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.78, 148.30, 129.39, 127.09 (q, J = 32.0 Hz), 124.78 (q, J = 271.3 Hz), 124.75 (q, J = 3.7 Hz), 65.74, 52.54, 46.85, 22.26, 10.68. ^{11}B NMR (128 MHz, $CDCl_3$) δ 6.57 – -5.93 (m). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.10. ESI-MS: calculated $C_{15}H_{23}BF_3NO_2Na$ $[M+Na]^+$ 340.1666; Found 340.1662.

propyl 2-(trimethylamine-boranyl)-2-(4-(trifluoromethoxy)phenyl)acetate (7ea)



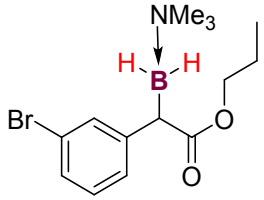
Following the general procedure A, the product **7ea** was obtained in 38% yield (25.3mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc 4:1): 0.26. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.5 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 3.97 (m, *J* = 11.6, 5.2 Hz, 2H), 3.23 (s, 1H), 2.54 (s, 9H), 1.69 – 1.53 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H), 2.42-1.44 (br, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.18, 146.82, 142.70, 130.30, 120.70 (q, J = 256.1 Hz), 120.42, 65.66, 52.52, 45.84, 22.25, 10.66. ^{11}B NMR (128 MHz, $CDCl_3$) δ 4.12 – -5.70 (m). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.86. ESI-MS: calculated $C_{15}H_{23}BF_3NO_3Na$ $[M+Na]^+$ 356.1615; Found 356.1611.

propyl 2-(4-acetylphenyl)-2- trimethylamine-boranylacetate (7fa)



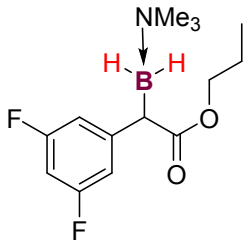
Following the general procedure A, the product **7fa** was obtained in 35% yield (20.4mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.22. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.3 Hz, 2H), 7.52 (d, J = 8.3 Hz, 2H), 4.11 – 3.75 (m, 2H), 3.31 (s, 1H), 2.55 (s, 3H), 2.53 (s, 9H), 1.63 (m, J = 14.2, 7.1 Hz, 2H), 0.92 (t, J = 7.4 Hz, 3H), 2.39-1.36 (br, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.26, 177.60, 150.30, 134.18, 129.28, 128.16, 65.72, 52.53, 47.15, 26.62, 22.25, 10.67. ^{11}B NMR (128 MHz, $CDCl_3$) δ 3.89 – -5.52 (m). ESI-MS: calculated $C_{16}H_{26}BNO_3Na$ $[M+Na]^+$ 314.1898; Found 314.1891.

propyl 2-(trimethylamine-boranyl)-2-(3-bromophenyl)acetate (7ga)



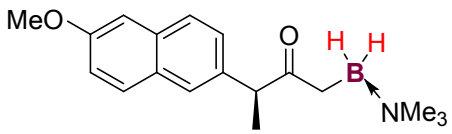
Following the general procedure A, the product **7ga** was obtained in 38% yield (25.0mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc 4:1): 0.26. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.36 (d, J = 7.7 Hz, 1H), 7.22 (d, J = 7.8 Hz, 1H), 7.10 (t, J = 7.8 Hz, 1H), 4.04 – 3.80 (m, 2H), 3.18 (s, 1H), 2.54 (s, 9H), 1.70 – 1.51 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H), 2.42-1.45 (br, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.86, 146.37, 132.19, 129.39, 127.97, 121.99, 65.68, 52.55, 46.46, 22.25, 10.68. ^{11}B NMR (128 MHz, $CDCl_3$) δ 2.08 – -3.94 (m). ESI-MS: calculated $C_{14}H_{23}BBrNO_2Na$ $[M+Na]^+$ 350.0897; Found 350.0896.

propyl 2-(trimethylamine-boranyl)-2-(3,5-difluorophenyl)acetate (7ha)



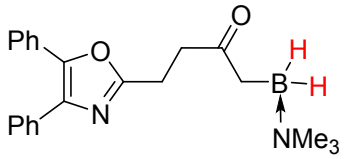
Following the general procedure A, the product **7ha** was obtained in 41% yield (23.4mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc 4:1): 0.24. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.97 (d, *J* = 8.6 Hz, 2H), 6.53 (m, *J* = 9.0, 1.8 Hz, 1H), 3.98 (q, *J* = 5.4 Hz, 2H), 3.20 (s, 1H), 2.55 (s, 9H), 1.63 (m, *J* = 7.1 Hz, 1H), 0.92 (t, *J* = 7.3 Hz, 3H), 2.42-1.45 (br, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.42, 162.69 (dd, J = 245.7, 13.3 Hz), 148.04 (t, J = 9.4 Hz), 111.85 (dd, J = 19.3, 5.6 Hz), 100.21 (t, J = 25.5 Hz), 65.78, 52.53, 46.30 (d, J = 103.0 Hz), 22.23, 10.66. ^{11}B NMR (128 MHz, $CDCl_3$) δ 4.12 – -3.94 (m). ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.06. ESI-MS: calculated $C_{14}H_{22}BF_2NO_2Na$ $[M+Na]^+$ 308.1604; Found 308.1603.

(S)-1-(trimethylamine-boranyl)-3-(6-methoxynaphthalen-2-yl)butan-2-one (8)



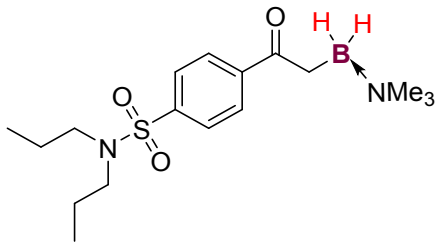
Following the general procedure A, the product **8** was obtained in 80% yield (47.9mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.63 (m, 3H), 7.40 (d, *J* = 9.4 Hz, 1H), 7.14 – 7.07 (m, 2H), 4.18 (q, *J* = 6.9 Hz, 1H), 3.89 (s, 3H), 2.52 (s, 9H), 2.05 (s, 2H), 1.42 (d, *J* = 7.0 Hz, 3H), 2.26-1.49 (br, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 218.07, 157.44, 138.18, 133.47, 129.29, 129.22, 127.19, 126.97, 126.46, 118.74, 105.74, 55.39, 52.23, 51.00, 37.44, 18.50. ^{11}B NMR (128 MHz, $CDCl_3$) δ -1.72 – -8.38 (m). ESI-MS: calculated $C_{18}H_{26}BNO_2Na$ $[M+Na]^+$ 322.1949; Found 322.1948.

1-(trimethylamine-boranyl)-4-(4,5-diphenyloxazol-2-yl)butan-2-one (9)



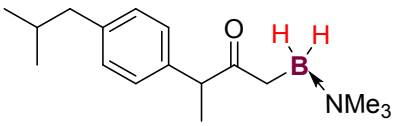
Following the general procedure A, the product **9** was obtained in 52% yield (37.7mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.26. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 2H), 7.59 – 7.54 (m, 2H), 7.33 (m, *J* = 10.7, 9.1, 4.4, 2.7 Hz, 6H), 3.17 – 3.02 (m, 4H), 2.55 (s, 9H), 2.02 (s, 2H), 2.44-1.42 (br, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.80, 163.52, 145.18, 135.16, 132.87, 129.36, 128.68, 128.60, 128.35, 128.08, 128.02, 126.58, 52.29, 38.58, 23.03, 19.29. ^{11}B NMR (128 MHz, $CDCl_3$) δ -0.38 – -7.74 (m). ESI-MS: calculated $C_{22}H_{27}BN_2O_2Na$ $[M+Na]^+$ 385.2058; Found 385.2054.

4-(2-trimethylamine-boranylacetyl)-N,N-dipropylbenzenesulfonamide (10)



Following the general procedure A, the product **10** was obtained in 48% yield (34.0mg, 0.20 mmol) as a yellow liquid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.24. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.1 Hz, 2H), 7.80 (d, *J* = 8.1 Hz, 2H), 3.16 – 2.98 (m, 4H), 2.60 (s, 9H), 2.45 (s, 2H), 1.53 (dd, *J* = 15.1, 7.5 Hz, 4H), 0.85 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.44, 142.62, 141.06, 129.26, 126.87, 52.25, 50.18, 34.68, 22.15, 11.27. ^{11}B NMR (128 MHz, $CDCl_3$) δ -1.29 – -6.60 (m). ESI-MS: calculated $C_{17}H_{31}BN_2O_3SNa$ $[M+Na]^+$ 377.2041; Found 377.2039.

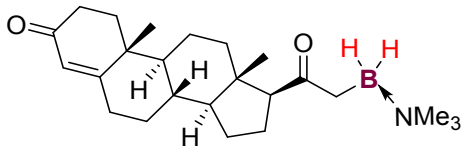
1-(trimethylamine-boranyl)-3-(4-isobutylphenyl)butan-2-one (11)



Following the general procedure A, the product **11** was obtained in 70% yield (40.0mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF

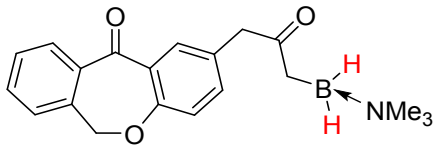
(Petroleum ether/EtOAc 4:1): 0.25. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, *J* = 7.4 Hz, 2H), 7.05 (d, *J* = 7.5 Hz, 2H), 4.01 (q, *J* = 6.9 Hz, 1H), 2.52 (s, 9H), 2.42 (d, *J* = 7.1 Hz, 2H), 2.03 (s, 1H), 1.87 – 1.79 (m, 1H), 1.77 (s, 1H), 1.33 (d, *J* = 6.9 Hz, 3H), 0.88 (d, *J* = 6.6 Hz, 6H), 2.32-1.47 (br, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 218.29, 140.02, 139.78, 129.23, 127.83, 52.21, 50.68, 45.16, 37.36, 30.28, 22.50, 18.38. ^{11}B NMR (128 MHz, $CDCl_3$) δ -4.23 (t, *J* = 96.6 Hz). ESI-MS: calculated $C_{17}H_{30}BNONa$ $[M+Na]^+$ 298.2313; Found 298.2311.

(8S,9S,10R,13S,14S,17S)-17-(2-trimethylamine-boranylacetyl)-10,13-dimethyl-1,2,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-3H-cyclopenta[a]phenanthren-3-one (12)



Following the general procedure A, the product **12** was obtained in 65% yield (50.1mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.24. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.04 (s, 1H), 5.38 (s, 1H), 2.80 (t, *J* = 9.0 Hz, 1H), 2.55 (s, 9H), 2.48 (d, *J* = 12.4 Hz, 1H), 2.30 (m, *J* = 18.1, 5.1 Hz, 1H), 2.21 – 2.10 (m, 2H), 2.02 (m, *J* = 16.4, 6.5 Hz, 2H), 1.92 – 1.80 (m, 2H), 1.73 – 1.54 (m, 5H), 1.41 (d, *J* = 9.0 Hz, 2H), 1.34 – 1.13 (m, 5H), 0.94 (s, 3H), 0.66 (s, 3H), 2.22-1.50 (br, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.64, 130.35, 127.14, 124.29, 61.05, 57.15, 52.31, 48.10, 44.06, 40.08, 38.89, 34.93, 34.64, 31.88, 31.79, 30.80, 29.82, 24.71, 23.87, 21.31, 19.00, 13.70. ^{11}B NMR (128 MHz, $CDCl_3$) δ 2.31 – -11.95 (m). ESI-MS: calculated $C_{24}H_{40}BNO_2Na$ $[M+Na]^+$ 408.3044; Found 408.3066.

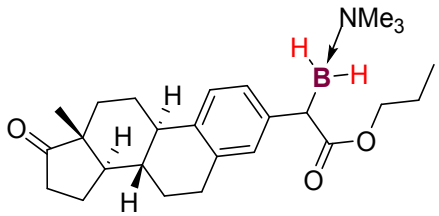
2-(3-trimethylamine-boranyl-2-oxopropyl)dibenzo[b,e]oxepin-11(6H)-one (13)



Following the general procedure A, the product **13** was obtained in 45% yield (30.4mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.24. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 2.1 Hz, 1H), 7.91 – 7.84 (m, 1H), 7.53 (td, *J* = 7.4, 1.2 Hz, 1H), 7.45 (td, *J* = 7.6, 1.0 Hz, 1H), 7.36 (dd, *J* = 12.9, 4.6

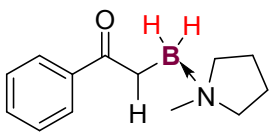
Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 1H), 5.16 (s, 2H), 3.76 (s, 2H), 2.58 (s, 9H), 2.00 (s, 2H), 2.43-1.47 (br, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.22, 191.16, 160.12, 140.69, 137.20, 135.87, 132.71, 132.62, 130.42, 129.58, 129.25, 127.84, 125.18, 120.72, 73.73, 52.33, 47.73, 38.05. ^{11}B NMR (128 MHz, $CDCl_3$) δ -4.22 (t, *J* = 97.5 Hz). ESI-MS: calculated $C_{20}H_{24}BNO_3Na$ $[M+Na]^+$ 360.1741; Found 360.1743.

Propyl 2-trimethylamine-boranyl-2-((8S,9R,13R,14R)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)acetate (14)



Following the general procedure A, the product **14** was obtained in 46% yield (39.2mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.26. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, J = 12.4 Hz, 1H), 7.14 (t, J = 7.3 Hz, 2H), 4.03 – 3.84 (m, 2H), 3.16 (s, 1H), 2.89 (d, J = 3.8 Hz, 2H), 2.60 (s, 1H), 2.55 (s, 9H), 2.48 (dd, J = 19.0, 8.7 Hz, 1H), 2.43 – 2.35 (m, 1H), 2.25 (t, J = 9.3 Hz, 1H), 2.17 – 2.05 (m, 1H), 1.95 (dd, J = 25.2, 11.3 Hz, 2H), 1.77 (s, 1H), 1.69 – 1.53 (m, 4H), 1.53 – 1.46 (m, 2H), 1.44 – 1.35 (m, 1H), 0.93 (t, J = 7.3 Hz, 3H), 0.88 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.77, 141.06, 141.00, 136.06, 136.04, 135.71, 135.63, 129.57, 129.53, 126.69, 126.59, 124.84, 124.71, 65.44, 52.45, 52.16, 50.66, 48.15, 45.97, 44.41, 38.36, 38.33, 36.00, 31.74, 29.61, 29.55, 26.83, 26.81, 25.77, 25.75, 22.23, 21.69, 13.97, 10.70. ^{11}B NMR (128 MHz, $CDCl_3$) δ 4.12– -2.36 (m). ESI-MS: calculated $C_{26}H_{40}BNO_3Na$ $[M+Na]^+$ 448.2993; Found 448.2989.

2-(1-methylpyrrolidine-boranyl)-1-phenylethan-1-one (3ad)

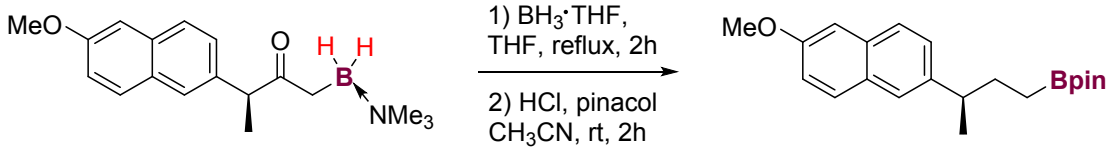


Following the general procedure A, the product **3ad** was obtained in 62% yield (26.9mg, 0.20 mmol) as a yellow liquid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v).

RF (Petroleum ether/EtOAc 4:1): 0.24. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 6.9 Hz, 1H), 7.39 (t, *J* = 7.2 Hz, 1H), 3.14 (s, 1H), 2.83 (s, 1H), 2.63 (s, 2H), 2.47 (s, 1H), 1.96 (dd, *J* = 21.8, 6.5 Hz, 2H), 2.37-1.53 (br, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.23, 138.18, 131.75, 128.75, 128.10, 61.55, 47.94, 34.62, 22.59. ^{11}B NMR (128 MHz, $CDCl_3$) δ -4.76 (t, *J* = 98.7 Hz). ESI-MS: calculated $C_{13}H_{20}BNONa$ $[M+Na]^+$ 240.1530; Found 240.1528.

5. Synthetic application of the product 3aa

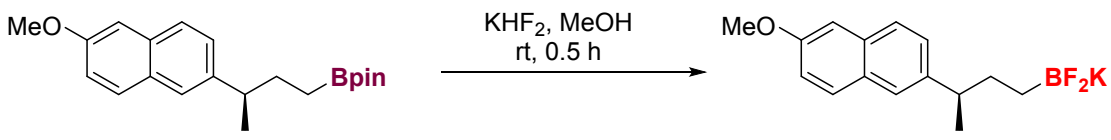
4.1 Synthesis of (R)-2-(3-(6-methoxynaphthalen-2-yl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



8 **15**

To a solution of **8** (149.7 mg, 0.5 mmol) in anhydrous THF (10.0 ml) was slowly added a solution of $BH_3 \cdot THF$ (1.5 mL, 1.0M) at 0 °C. The reaction mixture was warm to reflux and stirred under nitrogen atmosphere for 2 hours. The solvent was removed under vacuo, follow by adding 10.0 mL of MeOH, and the mixture was heated to refluxed for 1 hour. After evaporation under vacuo, the residue was dissolved in 10.0 mL MeCN, HCl (1.3 mL, 1.0 M in water) and pinacol (118.2 mg, 1.0 mmol) were then added. The reaction mixture was stirred under nitrogen atmosphere for 2 hours at room temperature and quenched with saturated $NaHCO_3$ aqueous. The reaction mixture was extracted three times with ethyl acetate. The combined extracts were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude material was purified by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 20:1) to give **15** (115.7 mg, 0.34 mmol) in 68% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, J = 8.4, 2.9 Hz, 2H), 7.55 (s, 1H), 7.33 (dd, J = 8.5, 1.7 Hz, 1H), 7.17 – 7.09 (m, 2H), 3.91 (s, 3H), 2.79 (dd, J = 14.0, 7.0 Hz, 1H), 1.83 – 1.72 (m, 2H), 1.34 (d, J = 6.9 Hz, 3H), 1.23 (s, 12H), 0.82 – 0.68 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.19, 142.80, 133.25, 129.22, 129.13, 126.76, 126.63, 125.30, 118.55, 105.74, 82.97, 55.37, 42.19, 32.78, 24.92, 21.80. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.77 (s). ESI-MS: calculated $C_{21}H_{29}BNO_3Na$ $[M+Na]^+$ 363.2102; Found 363.2115.

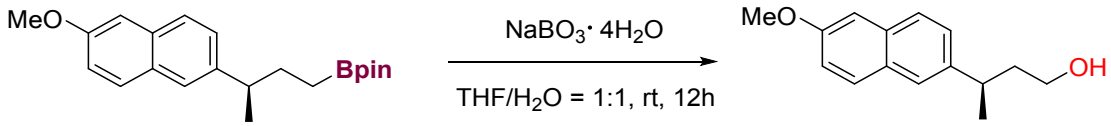
4.2 Synthesis of (R)-difluoro(3-(6-methoxynaphthalen-2-yl)butyl)borane, potassium salt



15 **16**

To a solution of pinacol ester **15** (68.1 mg, 0.2 mmol) in methanol (1.0 mL) was added 4.5 M KHF_2(aq) (35.9 mg, 0.46 mmol) The resulting mixture was stirred for 1h, and concentrated to dryness. The residue, a white solid, was extracted with hot acetone (2×10), and the combined filtered extracts were concentrated to a volume of ca. 2.0 mL. Ether (10 mL) was added and the resultant precipitate was collected and dried to afford the title compound **16** (57.2 mg, 95%) as a white solid. ^{1}H NMR (400 MHz, DMSO) δ 7.69 (dd, J = 15.9, 8.7 Hz, 2H), 7.50 (s, 1H), 7.27 (d, J = 8.4 Hz, 1H), 7.21 (d, J = 2.2 Hz, 1H), 7.07 (dd, J = 8.9, 2.5 Hz, 1H), 3.83 (s, 3H), 2.60 (dd, J = 13.8, 6.9 Hz, 1H), 1.52 – 1.31 (m, 2H), 1.18 (d, J = 6.9 Hz, 3H), 0.03 – -0.38 (m, 2H). ^{13}C NMR (101 MHz, DMSO) δ 156.90, 144.85, 133.02, 129.26, 129.08, 127.21, 126.64, 124.89, 118.50, 106.15, 55.55, 42.59, 35.44, 22.39. ^{11}B NMR (128 MHz, DMSO) δ 5.86. ^{19}F NMR (376 MHz, DMSO) δ -136.91.

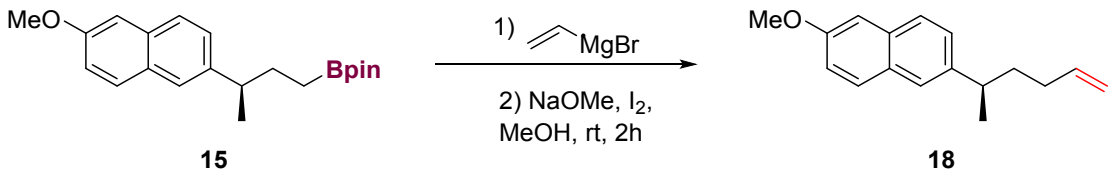
4.3 Synthesis of (R)-3-(6-methoxynaphthalen-2-yl)butan-1-ol



15 **17**

To a solution of pinacol ester **15** (68.1 mg, 0.2 mmol) in aqueous THF (1.0 ml 1:1(v/v)) was added Sodium perborate tetrahydrate (92.3 mg, 0.6 mmol) The resulting mixture was stirred for 12 h at room temperature. The reaction was quenched with water and extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The crude material was purified by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 8 : 1) to give **17** (40.1 mg, 87%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 8.5, 4.2 Hz, 2H), 7.57 (s, 1H), 7.34 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.17 – 7.11 (m, 2H), 3.92 (s, 3H), 3.58 (m, *J* = 10.6, 6.6 Hz, 2H), 3.03 (dd, *J* = 14.4, 7.2 Hz, 1H), 1.93 (q, *J* = 7.0 Hz, 2H), 1.46 (s, 1H), 1.35 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.38, 142.07, 133.37, 129.22, 129.14, 127.12, 126.18, 125.17, 118.83, 105.80, 61.36, 55.42, 41.03, 36.51, 22.61. ESI-MS: calculated $C_{15}H_{18}O_2Na$ $[M+Na]^+$ 253.1199; Found 253.1195.

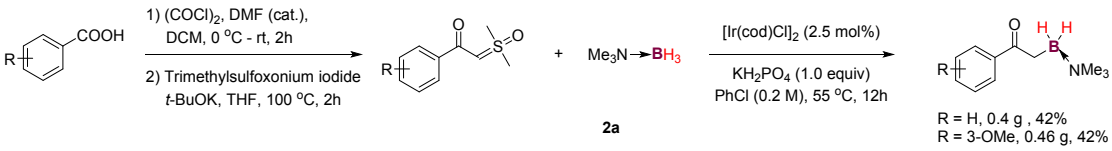
4.4 Synthesis of (R)-2-(hex-5-en-2-yl)-6-methoxynaphthalene



15 **18**

A stirred solution of boronic ester **15** (0.2 mmol) in THF (0.5 mL) and DMSO (0.5 mL) was cooled to 0 °C and a solution of Grignard reagent (0.3 mmol) was added dropwise [N.B. upon addition of the Grignard reagent a white precipitate was observed]. The resulting mixture was stirred at room temperature for 30 min and then cooled to 0 °C. A suspension of NaOMe (30 wt% in MeOH, 32.4 mg, 0.6 mmol) in was added in a single portion, followed by dropwise addition of a solution of I_2 (0.5 M in MeOH, 0.48 mL, 0.24 mmol). The resulting mixture was stirred at 0 °C for 30 min and then saturated aqueous sodium thiosulfate and dichloromethane were added. The organic phase was separated and the aqueous phase was extracted twice with dichloromethane. The combined organic extracts were washed with water twice, dried over anhydrous Na_2SO_4. The crude material was purified by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 100 : 1) to give **18** (38.4 mg, 80%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.4 Hz, 2H), 7.56 (s, 1H), 7.34 (dd, J = 8.4, 1.6 Hz, 1H), 7.19 – 7.09 (m, 2H), 5.83 (m J = 16.9, 10.2, 6.6 Hz, 1H), 5.10 – 4.85 (m, 2H), 3.93 (s, 3H), 2.99 – 2.74 (m, 1H), 2.22 – 1.88 (m, 2H), 1.89 – 1.63 (m, 2H), 1.35 (d, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.32, 142.68, 138.98, 133.31, 129.25, 129.16, 126.95, 126.41, 125.24, 118.73, 114.52, 105.81, 55.43, 39.40, 37.59, 32.03, 22.44.

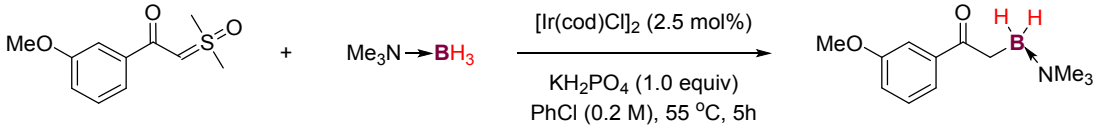
4.5 One-Pot Sequence



To a solution of the carboxylic acid (5.0 mmol, 1.0 equiv) in dry CH_2Cl_2 (30 mL) at 0 °C under N_2 was added dropwise of $(COCl)_2$ (0.85 mL, 10 mmol, 2 equiv) followed by a catalytic amount of dry DMF (2 drops). The reaction was allowed to stir at room temperature until completion (typically 3 h). The solvent was then removed under reduce pressure to afford the corresponding crude acid chloride.

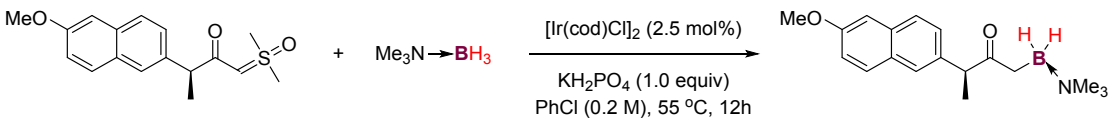
In a 100 mL flame-dried round bottom flask attached to a reflux condenser, under argon atmosphere, 1.68 g of potassium tert-butoxide (15.0 mmol, 3.0 equiv) and 15.0 mL of anhydrous THF were added. Then, 2.20 g of trimethylsulfoxonium iodide (10.0 mmol; 2.0 equiv) was added in one portion. The suspension was heated at reflux for 2 hours. After this time, the mixture was cooled at 0 °C, followed by slow addition of the crude acid chloride diluted with anhydrous THF. The reaction mixture temperature was naturally increased to room temperature and this mixture stirred for additional 3 hours. Then, the solvent was removed on a rotary evaporator. trimethylamine-borane **2a** (547.5 mg, 7.5 mmol, 1.5 equiv), $[Ir(cod)Cl]_2$ (83.9 mg, 0.125 mmol, 2.5 mmol%), KH_2PO_4 (680.5 mg, 5.0 mmol, 1.0 equiv), and PhCl (25 mL) was stirred at 55 °C for 1 h - 12 h. The reaction mixture was then diluted with DCM (10 mL) and washed with H_2O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The crude material was purified by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 4:1) to give **3aa** (0.4 g, 42%) and **3ka** (0.46 g, 42%).

4.6 Gram- Scale Synthesis



1k **2a** **3ka**, 0.67 g, 61%

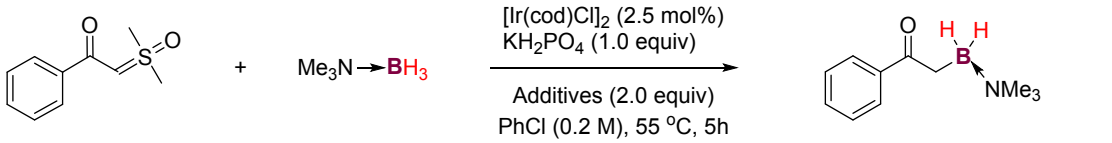
In an oven-dried Schlenk tube under air, a mixture of the substrates **1k** (5.0 mmol, 1.0 equiv), trimethylamine-borane **2a** (547.5 mg, 7.5 mmol, 1.5 equiv), $[Ir(cod)Cl]_2$ (83.9 mg, 0.125 mmol, 2.5 mmol%),KH_2PO_4 (680.5 mg, 5.0 mmol, 1.0 equiv), and PhCl (25.0 mL) was stirred at 55 °C for 12 h. The reaction mixture was then diluted with DCM (50 mL) and washed with H_2O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The crude material was purified by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 4:1) to give **3ka** (0.67 g, 61%).



1u **2a** **8**,1.0 g, 67%

In an oven-dried Schlenk tube under air, a mixture of the substrates **1u** (5.0 mmol, 1.0 equiv), trimethylamine-borane **2a** (547.5 mg, 7.5 mmol, 1.5 equiv), $[Ir(cod)Cl]_2$ (83.9 mg, 0.125 mmol, 2.5 mmol%), KH_2PO_4 (680.5 mg, 5.0 mmol, 1.0 equiv), and PhCl (25.0 mL) was stirred at 55 ^oC for 12 h. The reaction mixture was then diluted with DCM (10.0 mL) and washed with H_2O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The crude material was purified by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 2:1) to give **8** (1.0 g, 67%).

6. Mechanistic experiments

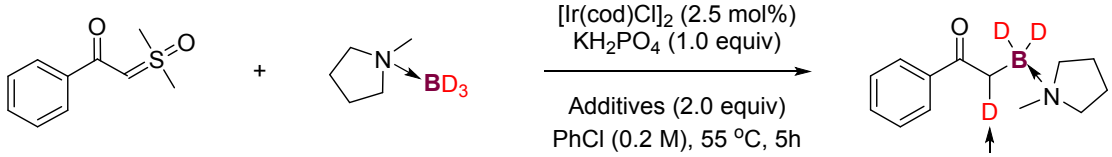


1a 2a

Additives: **TEMPO** (2.0 equiv), 74%
BHT (2.0 equiv), 70%

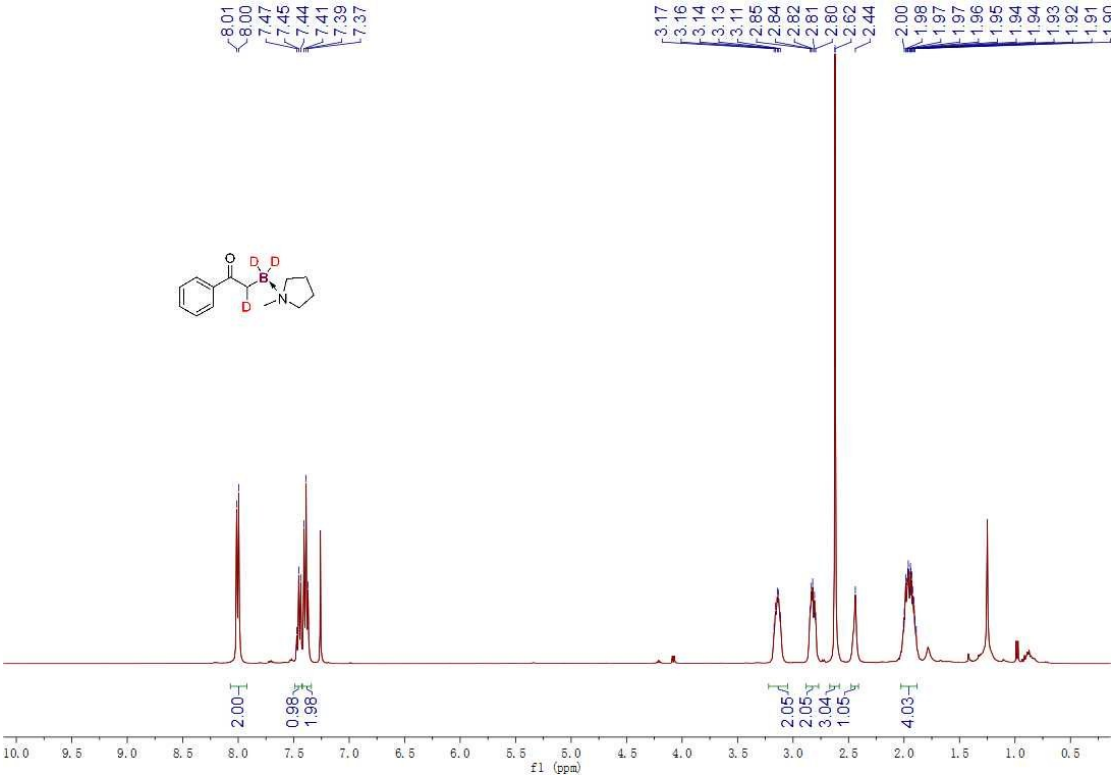
In an oven-dried Schlenk tube under air, a mixture of the substrates **1a** (0.2 mmol, 1.0 equiv), trimethylamine-borane **2a** (21.9 mg, 0.3 mmol, 1.5 equiv), [Ir(cod)Cl]2 (3.4 mg, 0.005 mmol, 2.5 mmol%),KH_2PO_4 (27.2 mg, 0.2 mmol, 1.0 equiv), TEMPO (156.3 mg, 0.4 mmol, 2.0 equiv) and PhCl(2.0 mL) was stirred at 55 °C for 1 h - 12 h. The reaction mixture was then diluted with DCM (10 mL) and washed with H_2O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product **3aa** as a yellow liquid (28.2 mg, 74%).

In an oven-dried Schlenk tube under air, a mixture of the substrates **1a** (0.2 mmol, 1.0 equiv), trimethylamine-borane **2a** (21.9 mg, 0.3 mmol, 1.5 equiv), [Ir(cod)Cl]2 (3.4 mg, 0.005 mmol, 2.5 mmol%),KH_2PO_4 (27.2 mg, 0.2 mmol, 1.0 equiv), BHT (220.4 mg, 0.4 mmol, 2.0 equiv) and PhCl(2.0 mL) was stirred at 55 °C for 1 h - 12 h. The reaction mixture was then diluted with DCM (10 mL) and washed with H_2O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product **3aa** as a yellow liquid (26.7 mg, 70%).

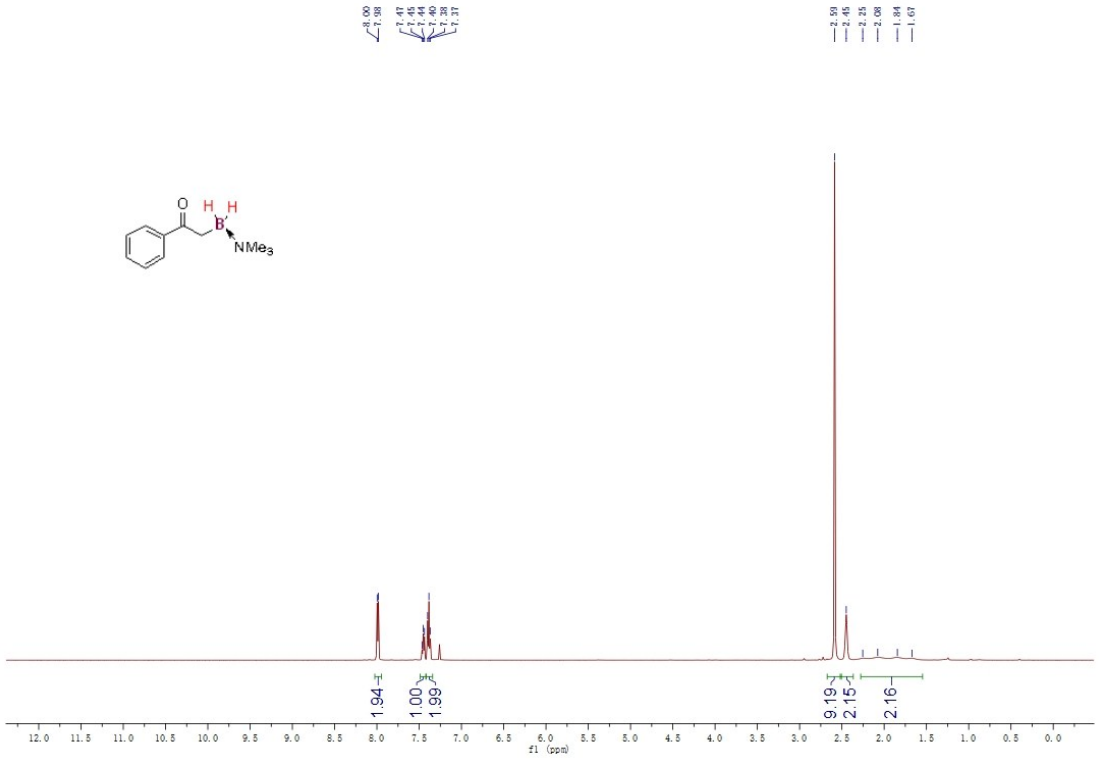


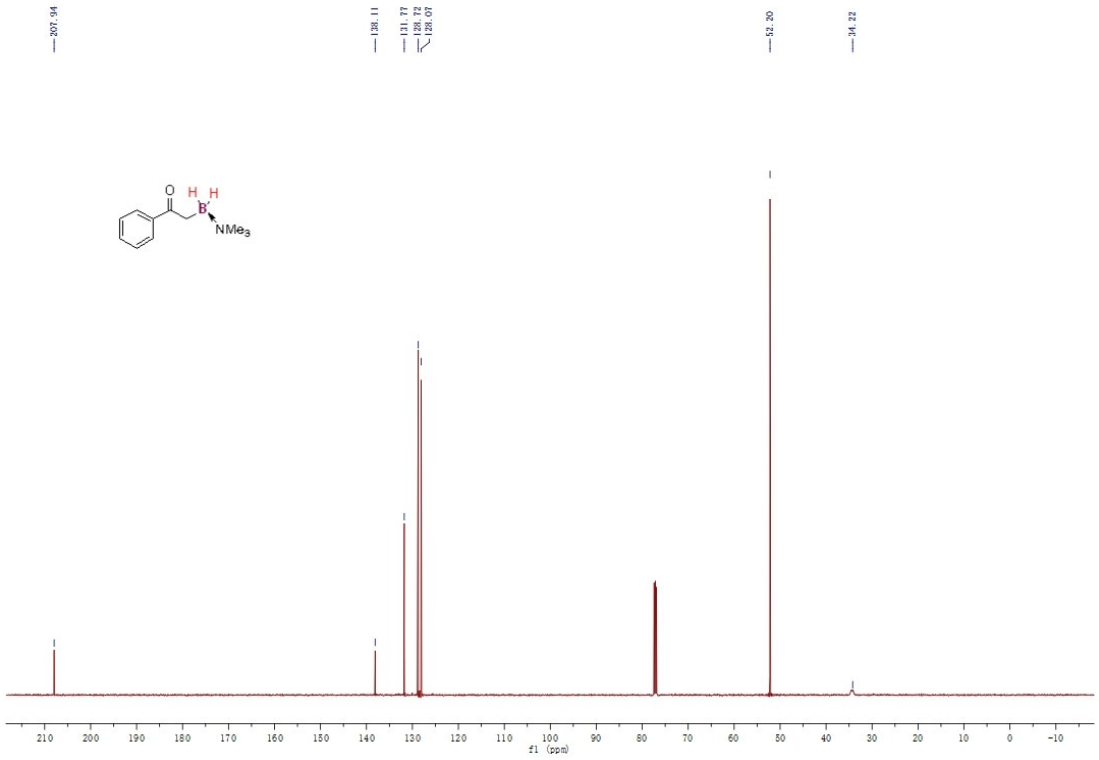
1a **2d-D_3**

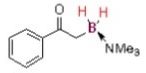
In an oven-dried Schlenk tube under air, a mixture of the substrates **1a** (0.2 mmol, 1.0 equiv), 1-methylpyrrolidine-boranyl **2d-D$_3$** (30.6 mg, 0.3 mmol, 1.5 equiv), [Ir(cod)Cl]$_2$ (3.4 mg, 0.005 mmol, 2.5 mmol%),KH_2PO_4 (27.2 mg, 0.2 mmol, 1.0 equiv) and PhCl (2.0 mL) was stirred at 55 ^oC for 1 h - 12 h. The reaction mixture was then diluted with DCM (10 mL) and washed with H_2O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product as a white solid (22.9 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.1 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 7.3 Hz, 2H), 3.19 – 3.07 (m, 2H), 2.89 – 2.74 (m, 2H), 2.62 (s, 3H), 2.44 (s, 1H), 2.05 – 1.86 (m, 4H), 2.37-1.52 (br, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.23, 138.18, 131.75, 128.75, 128.10, 61.55, 47.94, 34.62, 22.59. ^{11}B NMR (128 MHz, $CDCl_3$) δ -4.76 (t, *J* = 98.7 Hz)

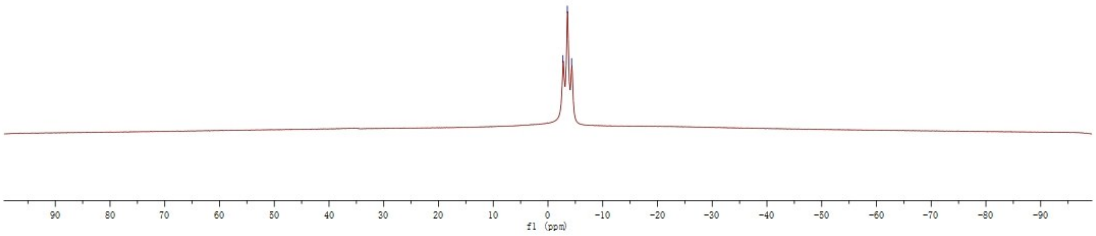


7. NMR Spectra for New Compounds

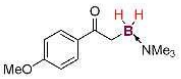


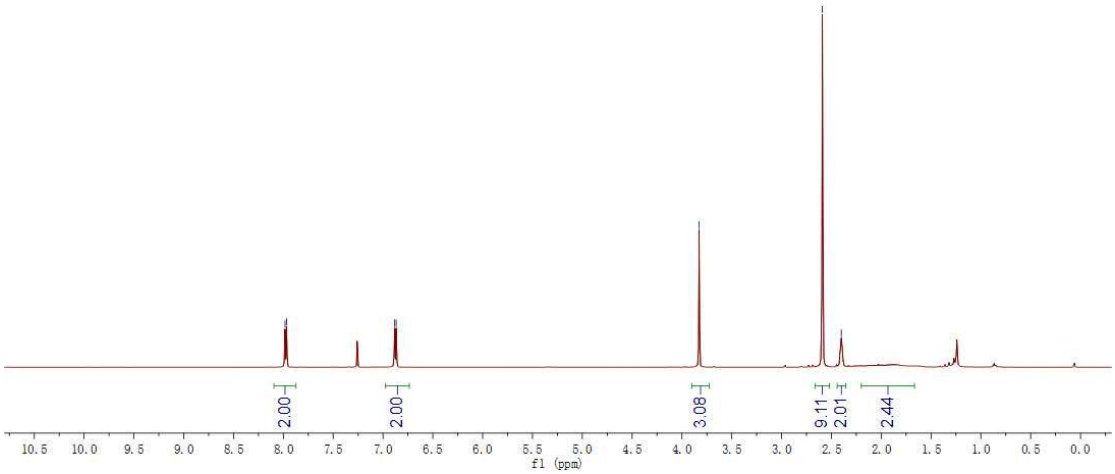


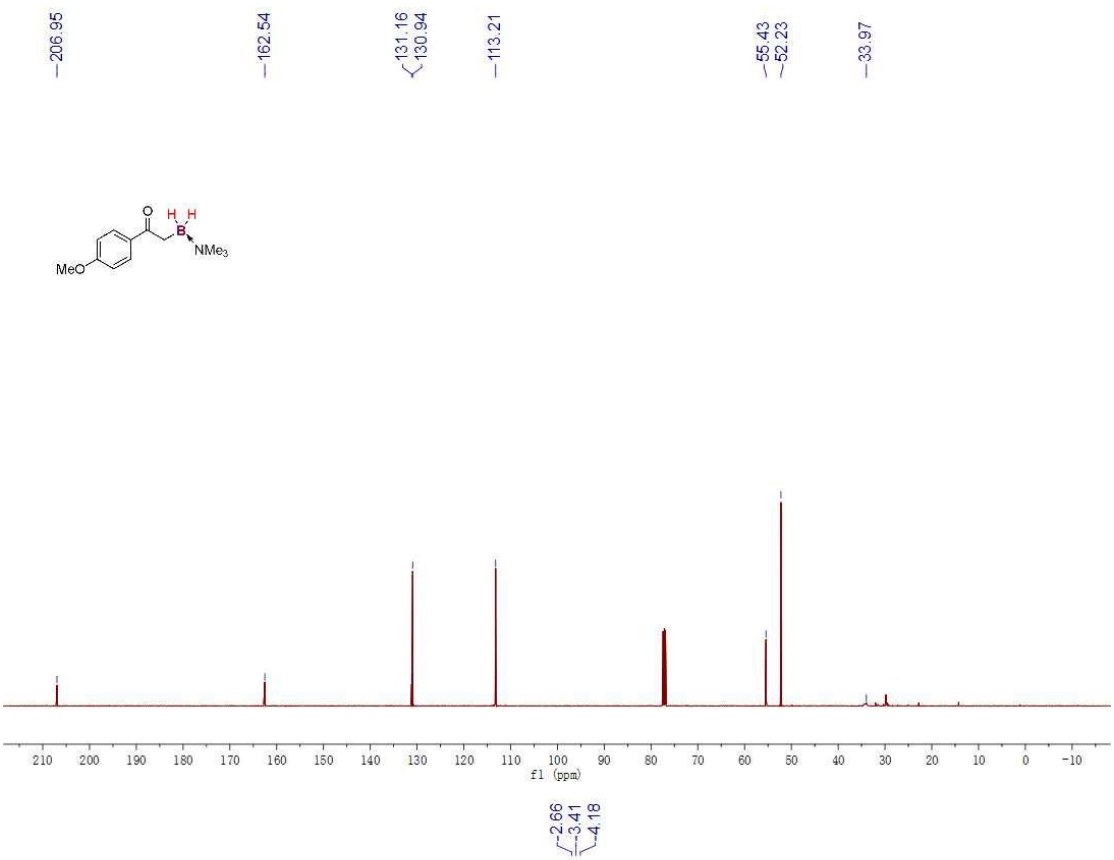


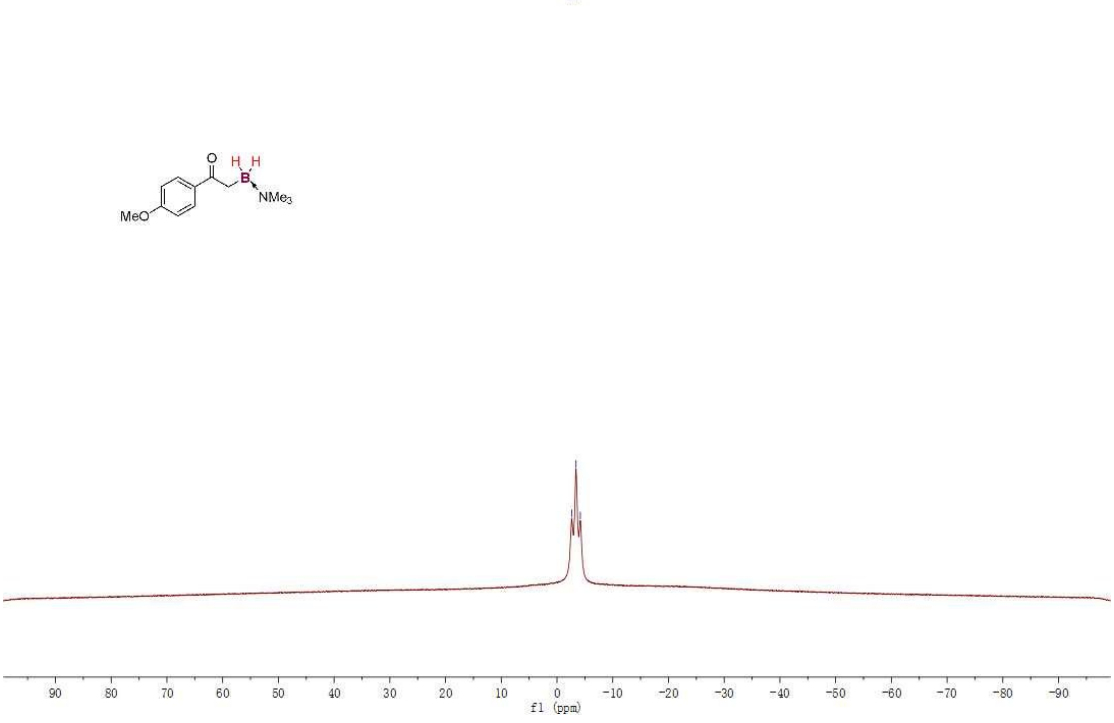


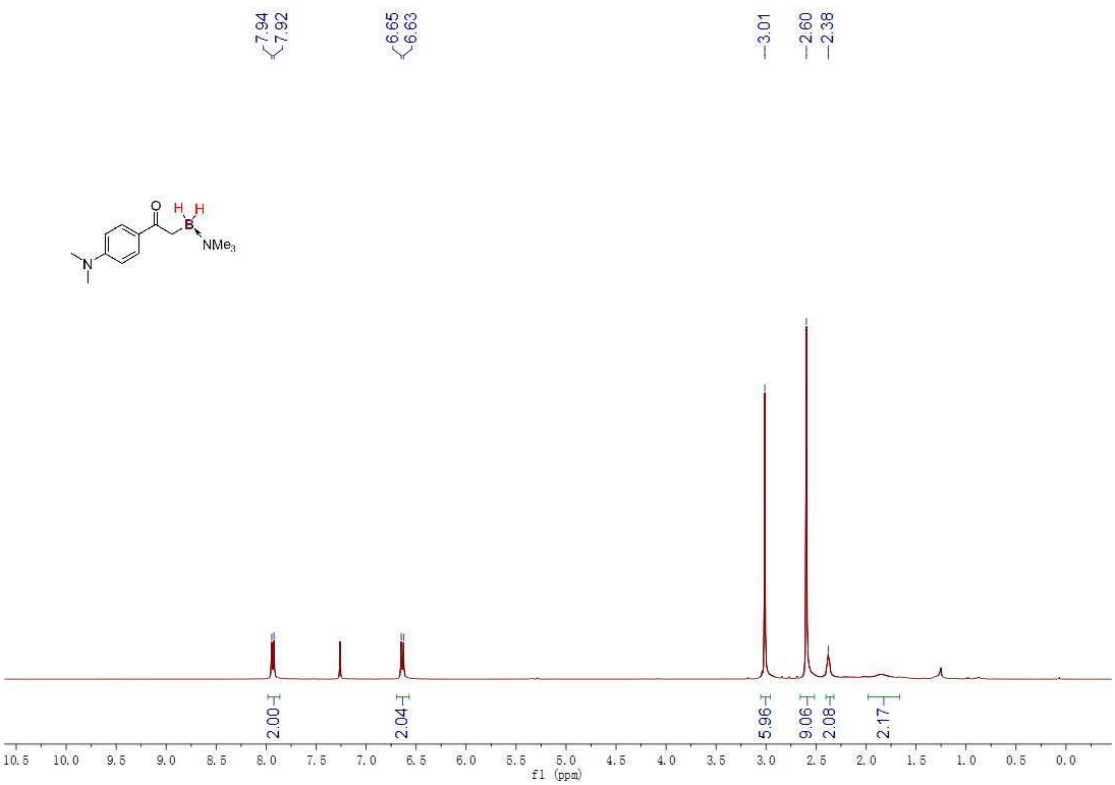
7.98
7.97
6.88
6.87
3.83
2.59
2.40

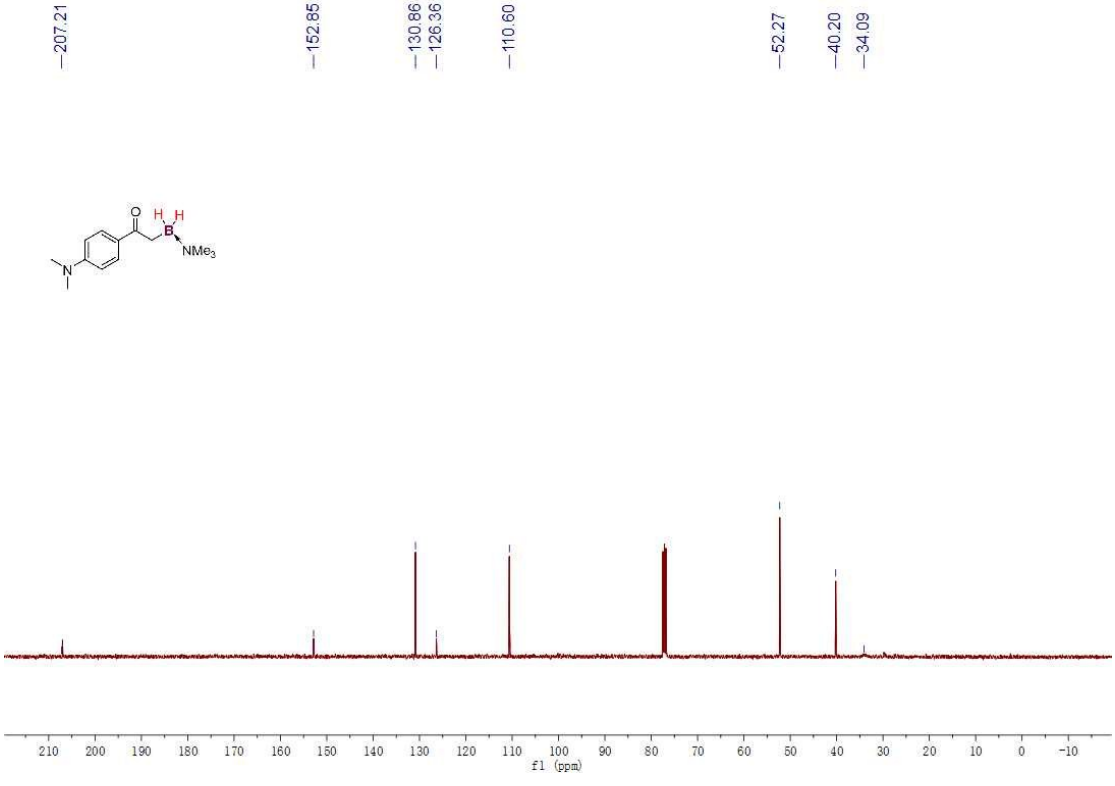


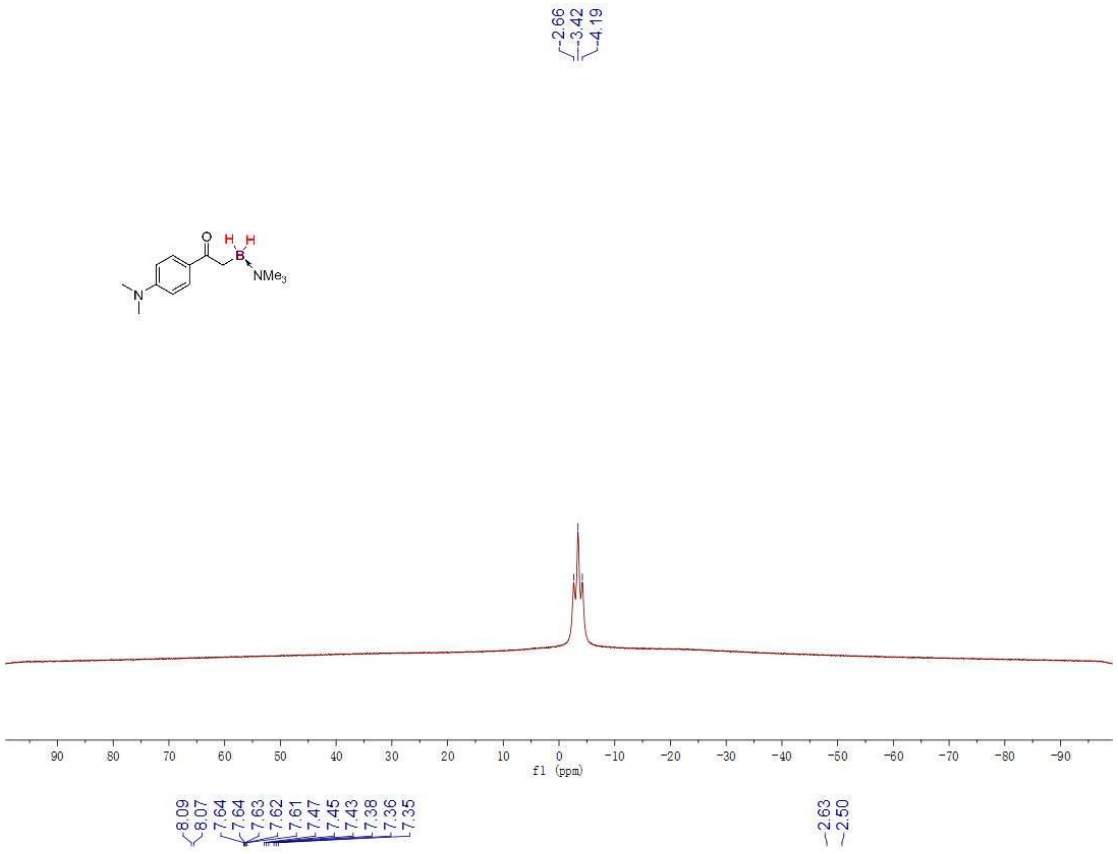


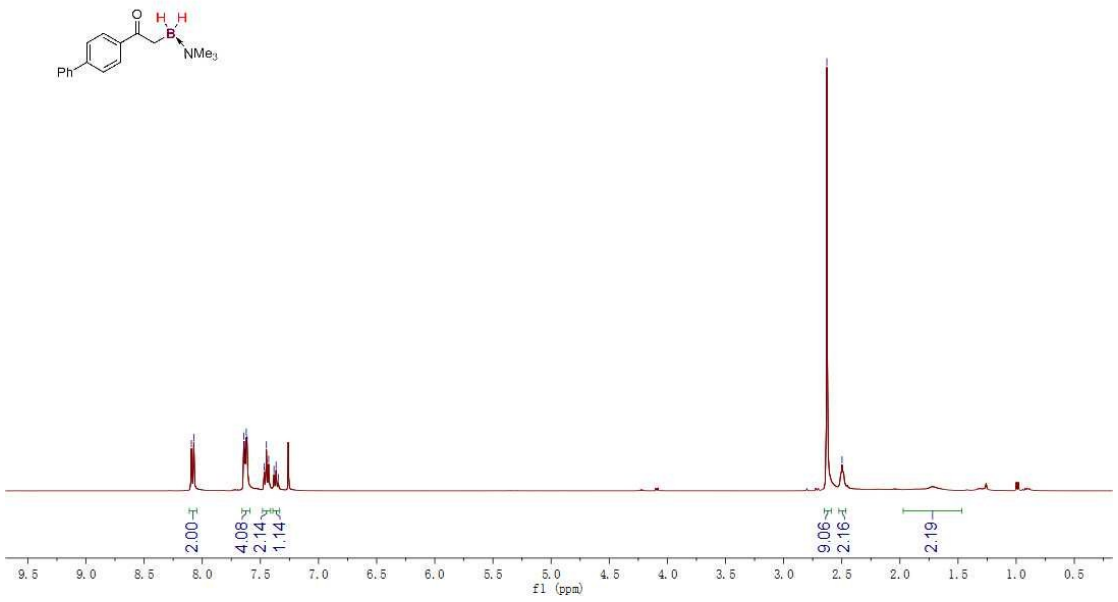

206.95
162.54
131.16
130.94
113.21
55.43
52.23
33.97
MeO
NMe3
f1 (ppm)

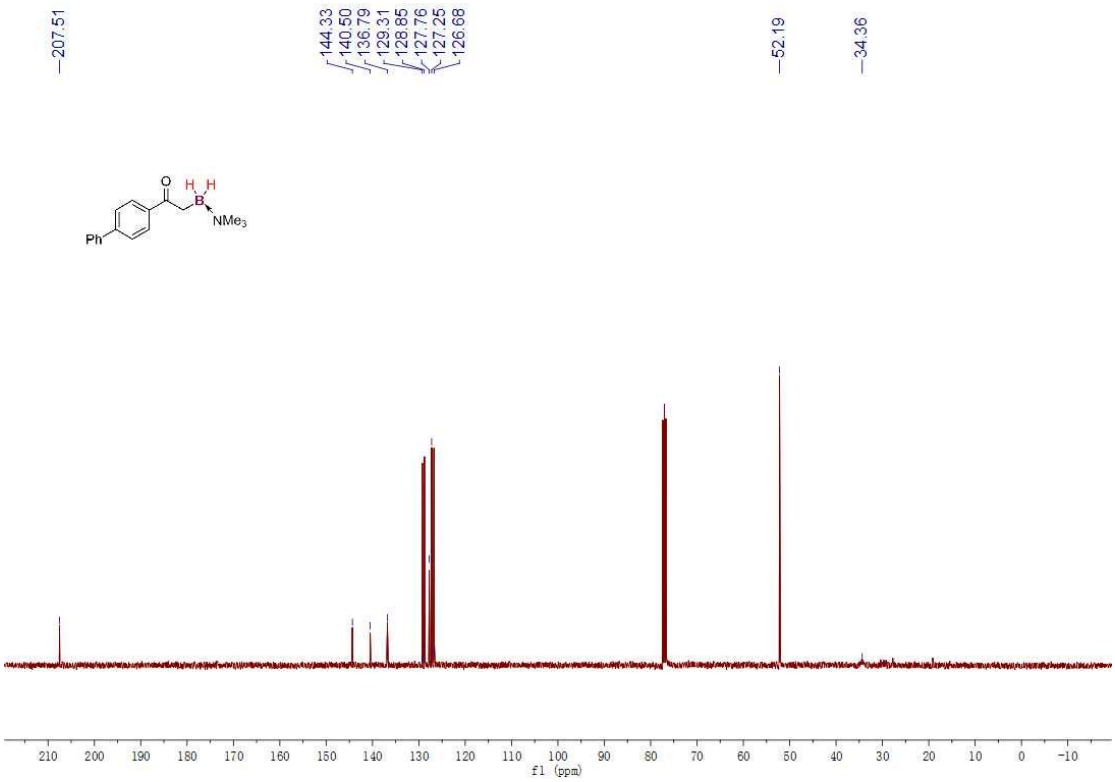

2.66
3.41
4.18
MeO
NMe3
f1 (ppm)

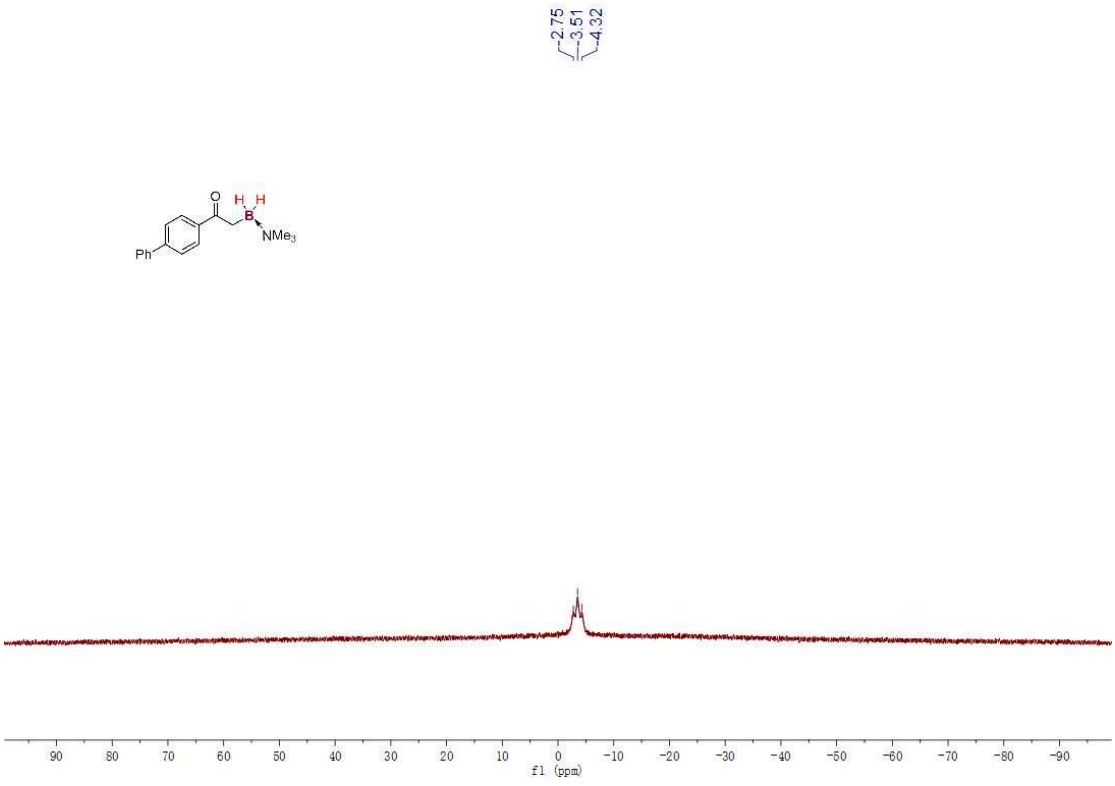

7.94
7.92
6.65
6.63
3.01
2.60
2.38
2.00
2.04
5.96
9.06
2.08
2.17
f1 (ppm)

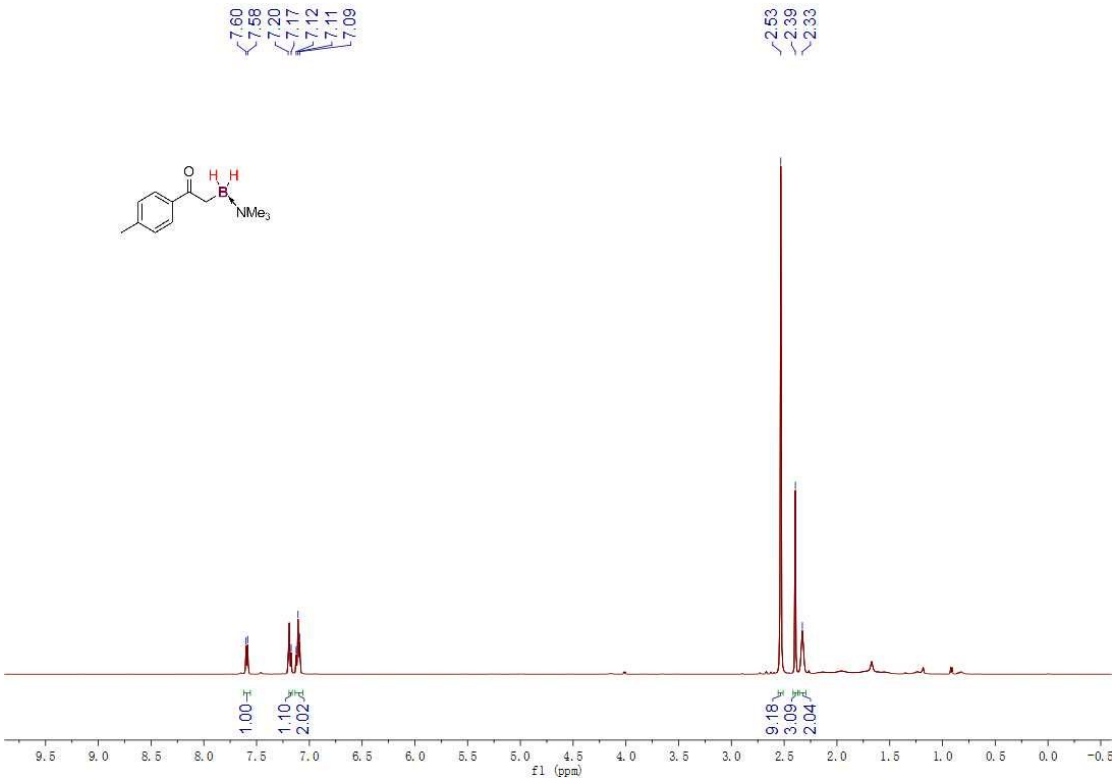

207.21
152.85
130.86
126.36
110.60
52.27
40.20
34.09
f1 (ppm)

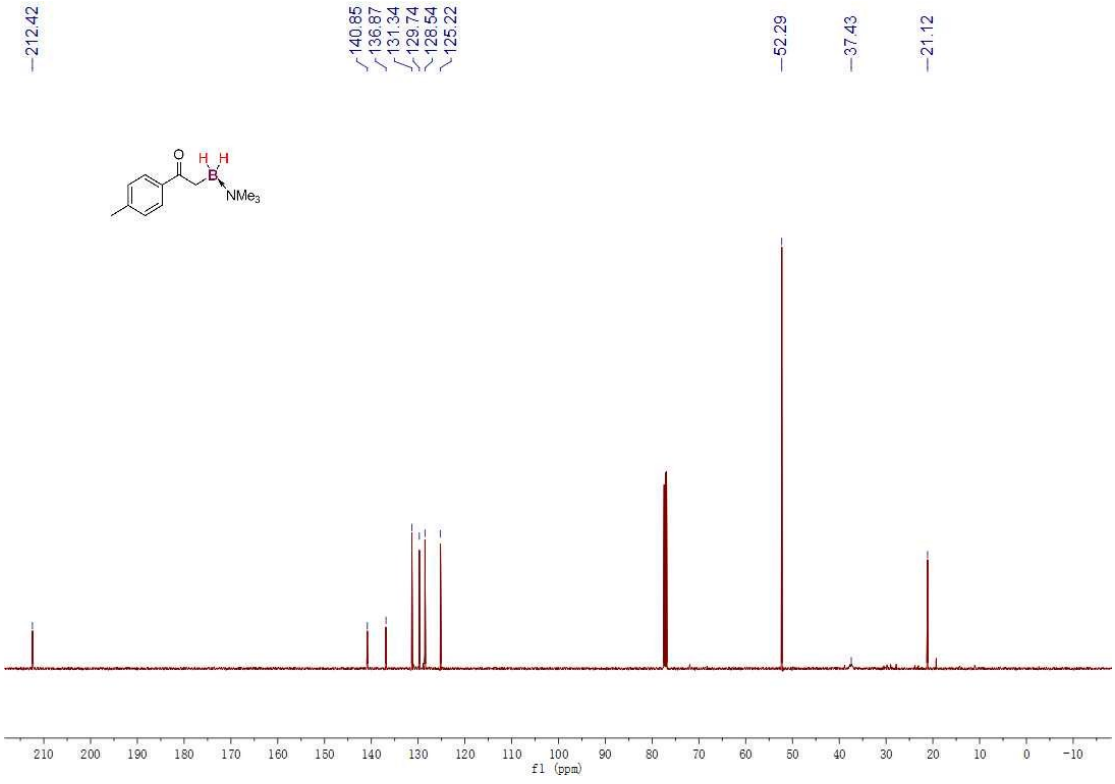

2.66
3.42
4.19
NMe3
f1 (ppm)
8.09
8.07
7.64
7.64
7.63
7.62
7.61
7.47
7.45
7.43
7.38
7.36
7.35
2.63
2.50

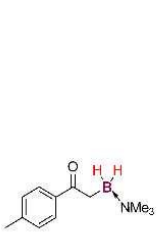

Ph
NMe3
2.00
4.08
2.14
1.14
9.06
2.16
2.19
f1 (ppm)


207.51
144.33
140.50
136.79
129.31
128.85
127.76
127.25
126.68
52.19
34.36
O
H
H
B
NMe3
Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

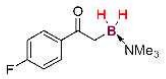

2.75
3.51
4.32
O
H
H
B
NMe3
Ph
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

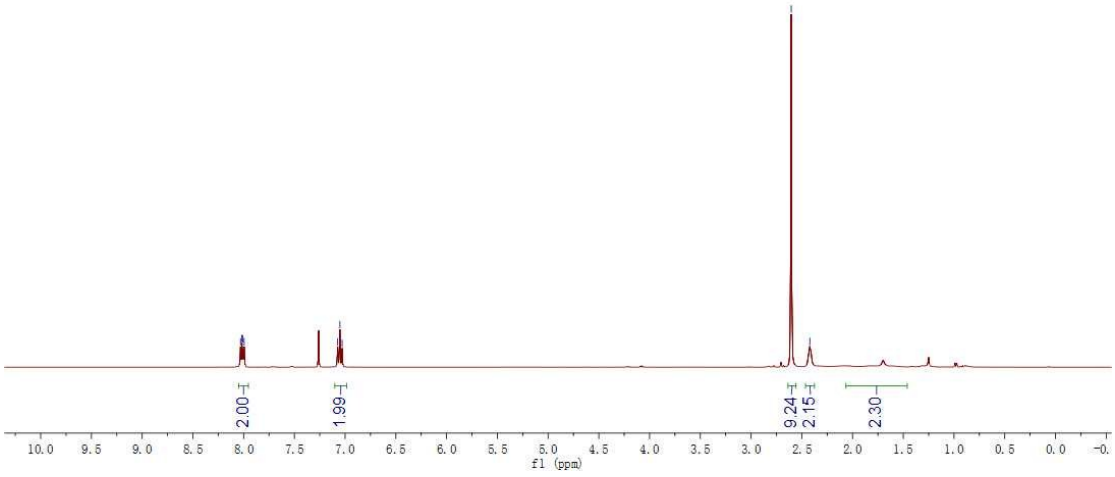

7.60
7.58
7.20
7.17
7.12
7.11
7.09
2.53
2.39
2.33
O
H
H
B
NMe3
1.00
1.10
2.02
9.18
3.09
2.04
f1 (ppm)

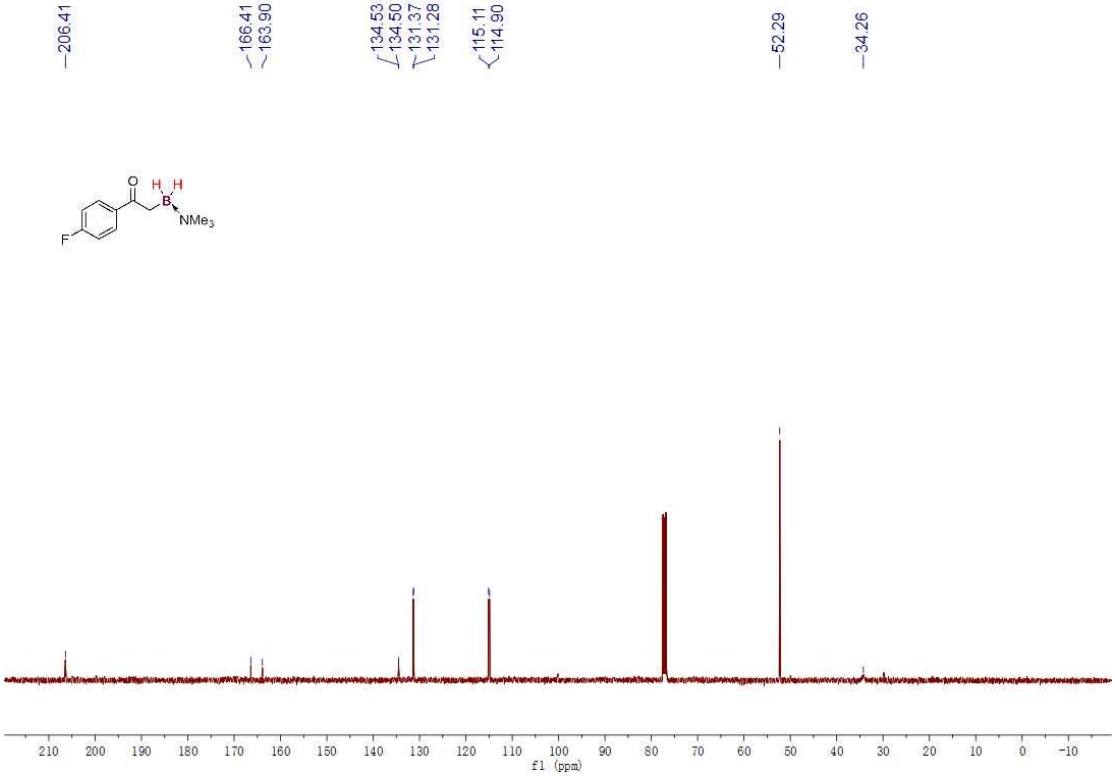

212.42
140.85
136.87
131.34
129.74
128.54
125.22
52.29
37.43
21.12
O
H
H
B
NMe3
f1 (ppm)

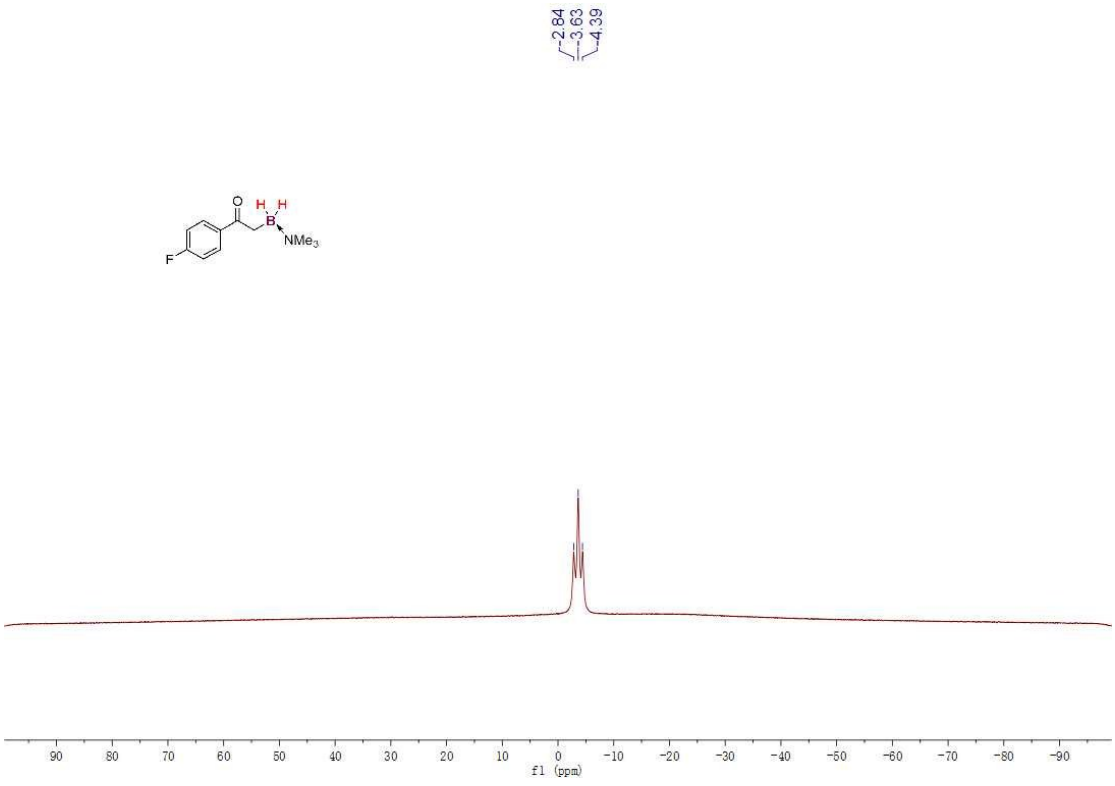

O
H H
B
NMe3

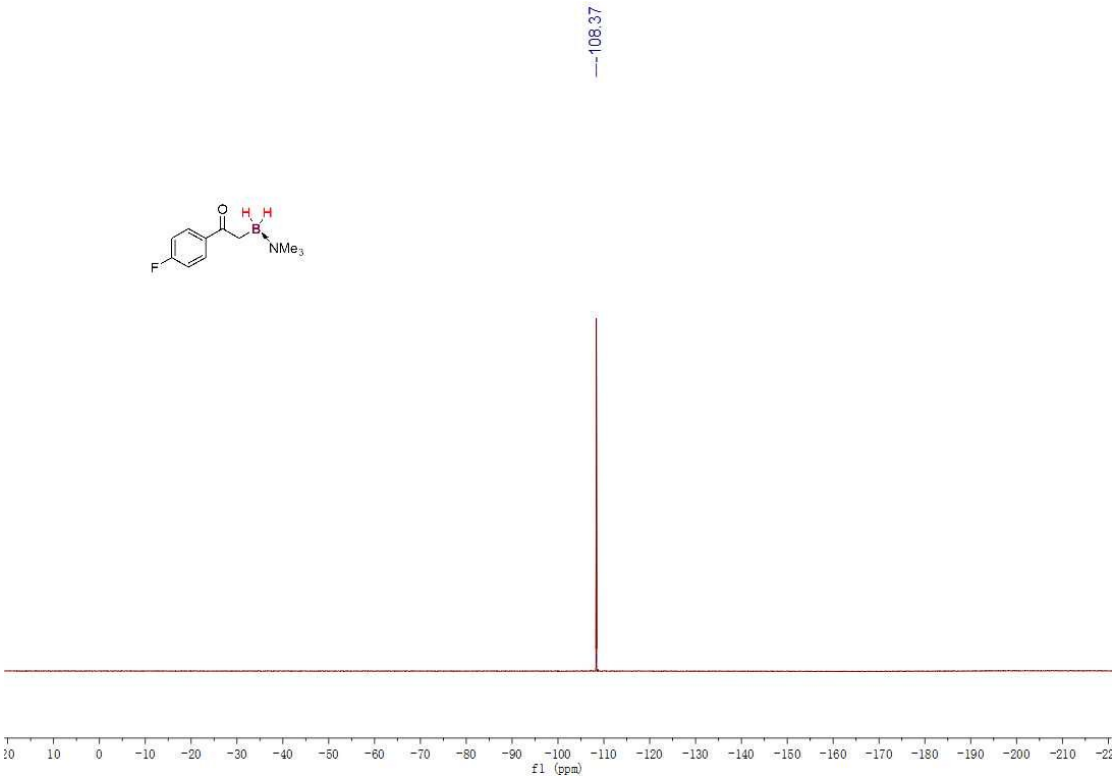
3.24
4.01
4.80
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)
8.03
8.02
8.01
7.99
7.07
7.05
7.03
2.60
2.42

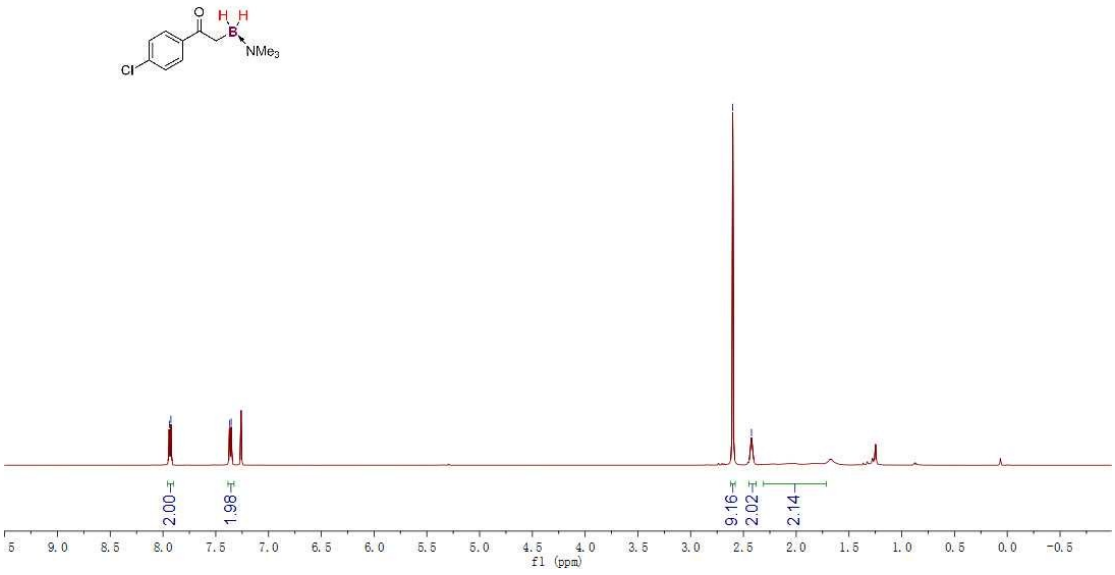

O
H H
B
NMe3
F

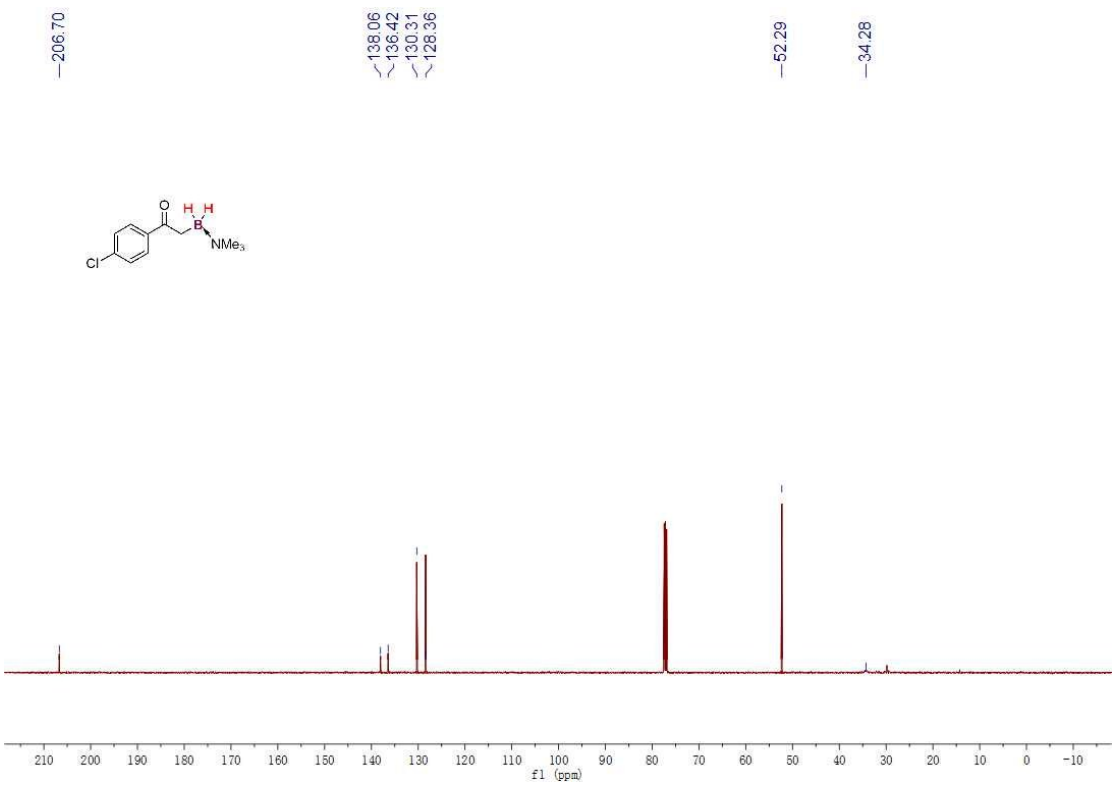

2.00
1.99
9.24
2.15
2.30
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

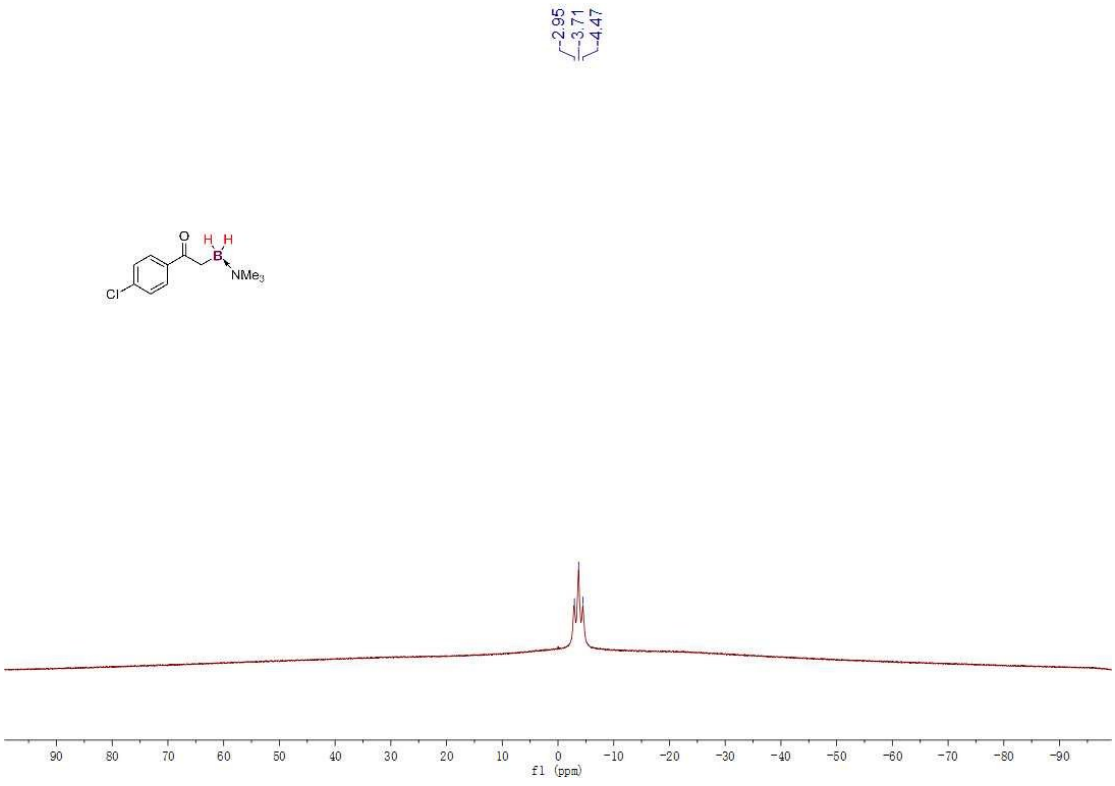

206.41
166.41
163.90
134.53
134.50
131.37
131.28
115.11
114.90
52.29
34.26
O
H
H
B
NMe3
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

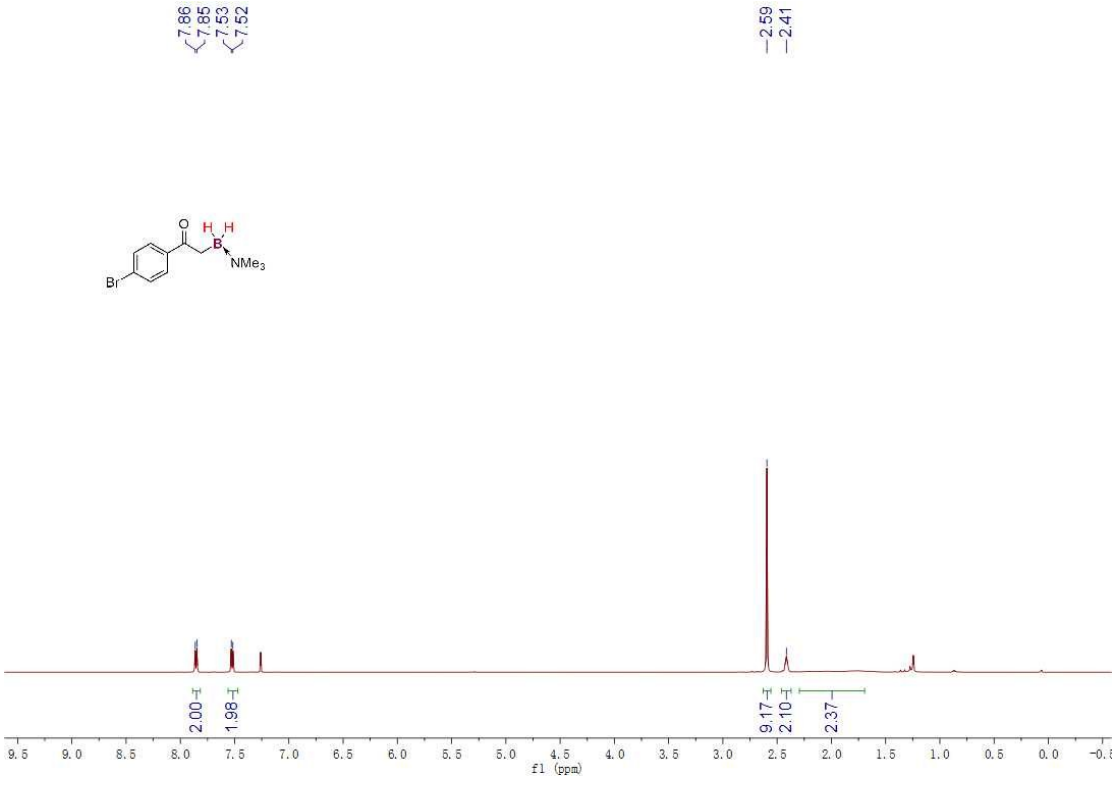

2.84
3.63
4.39
O
H
H
B
NMe3
F
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

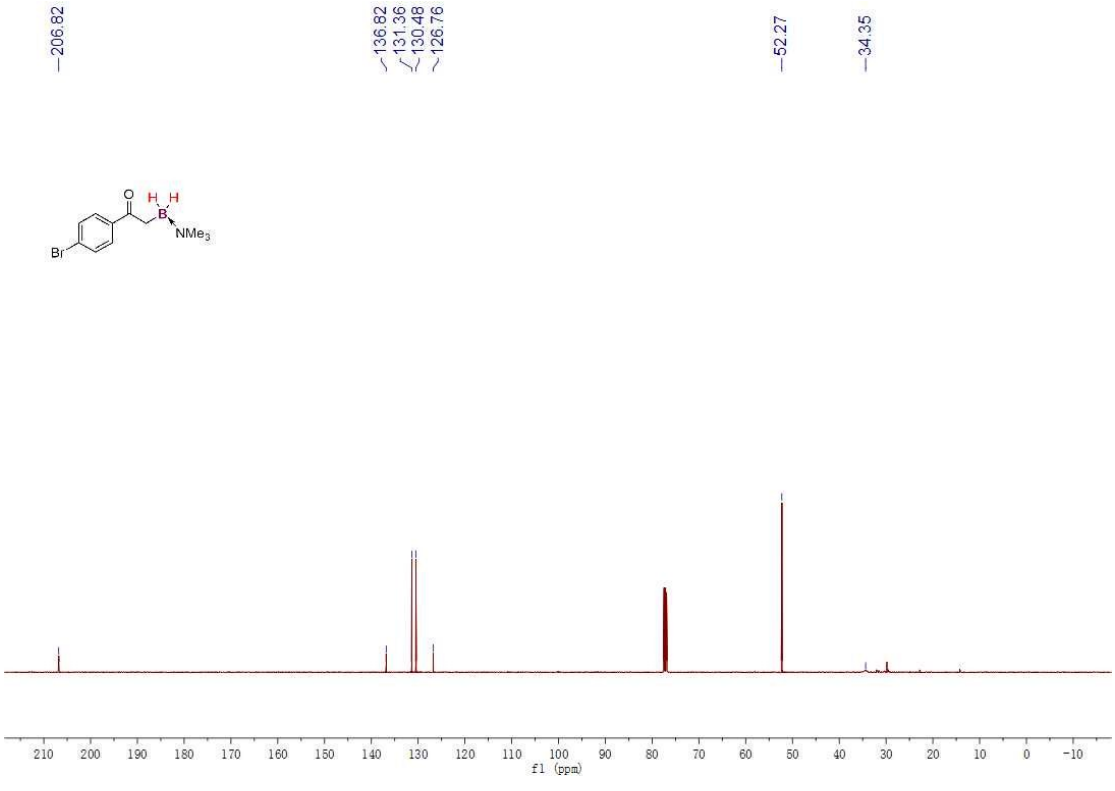

-108.37
F
O
H
H
B
NMe3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22
f1 (ppm)
7.94
7.93
7.37
7.35
2.60
2.42

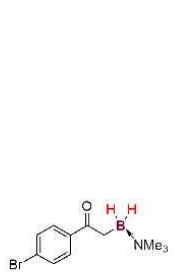

Cl
O
H
H
B
NMe3
2.00
1.98
9.16
2.02
2.14
5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

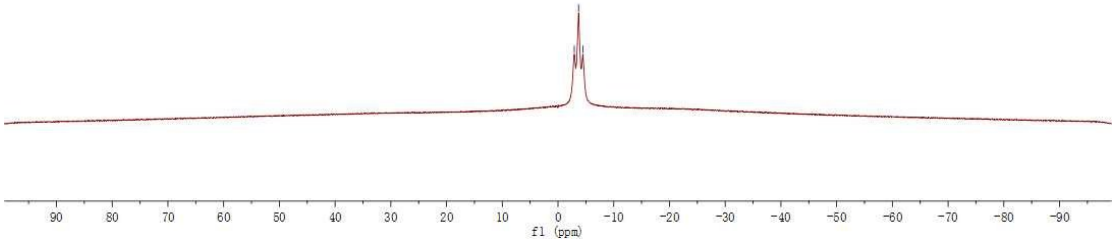

206.70
138.06
136.42
130.31
128.36
52.29
34.28
O
H
H
B
NMe3
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

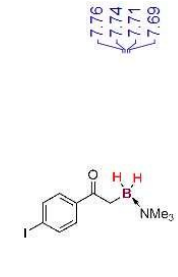

2.95
3.71
4.47
O
H
H
B
NMe3
Cl
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

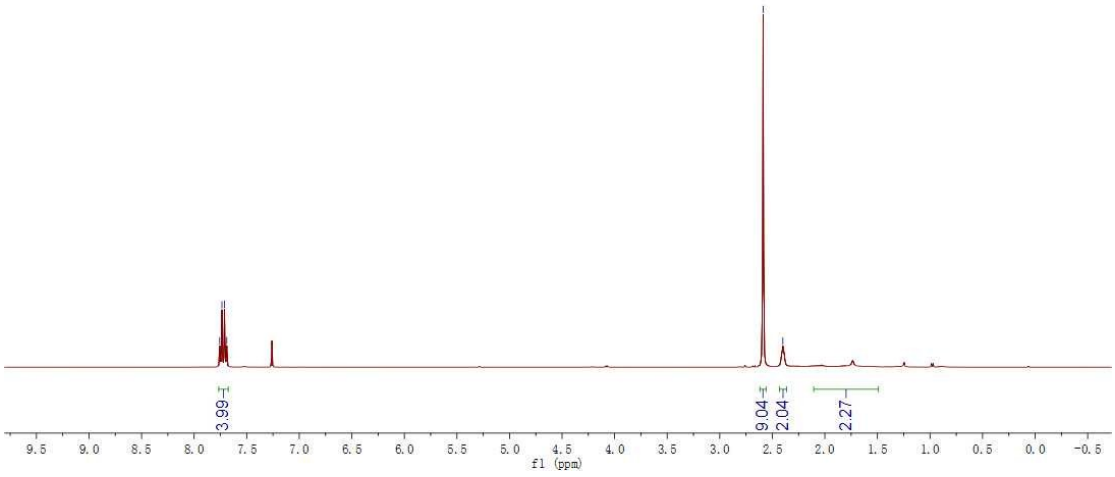

7.86
7.85
7.53
7.52
2.59
2.41
O
H
H
B
NMe3
Br
2.00
1.98
9.17
2.10
2.37
f1 (ppm)

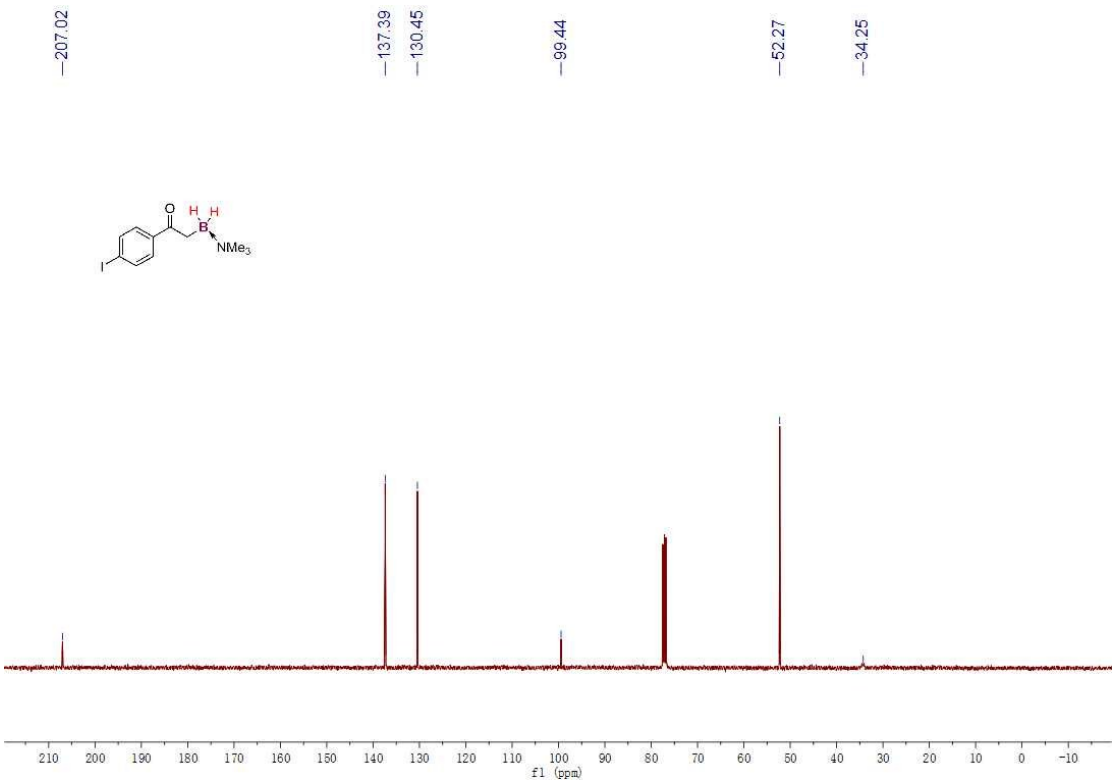

206.82
136.82
131.36
130.48
126.76
52.27
34.35
O
H
H
B
NMe3
Br
f1 (ppm)

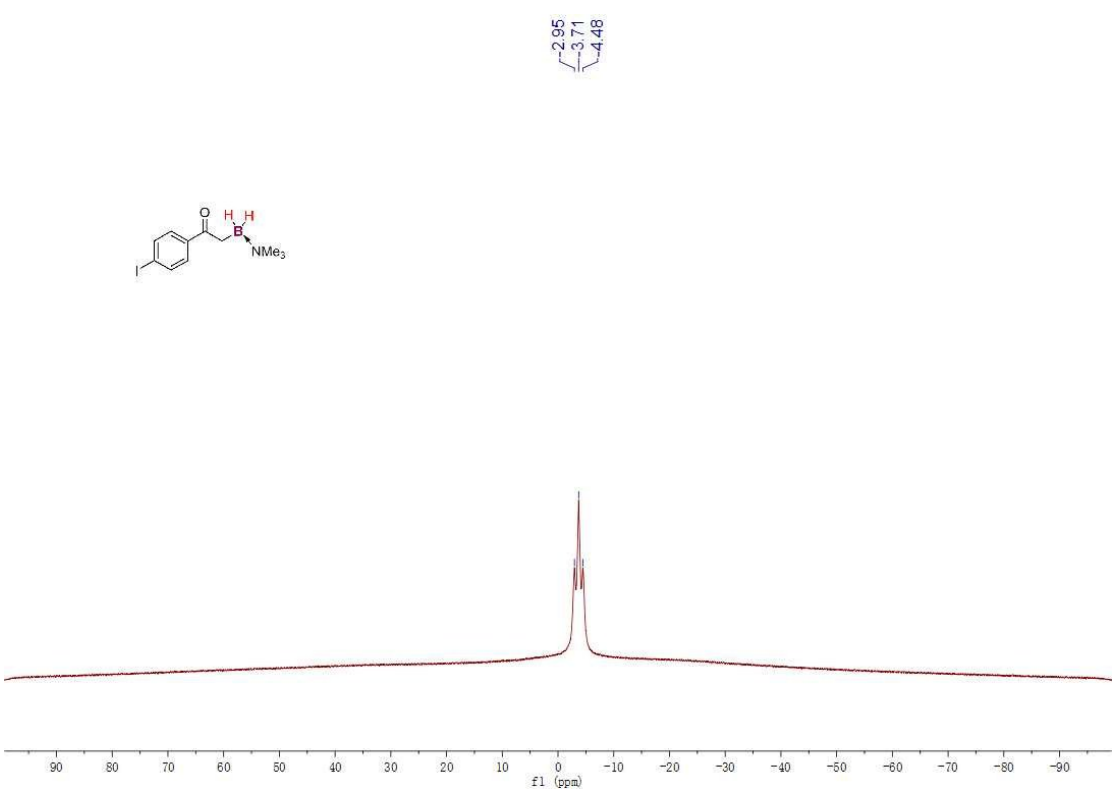

2.92
3.69
4.47
O
H
H
B
NMe3
Br

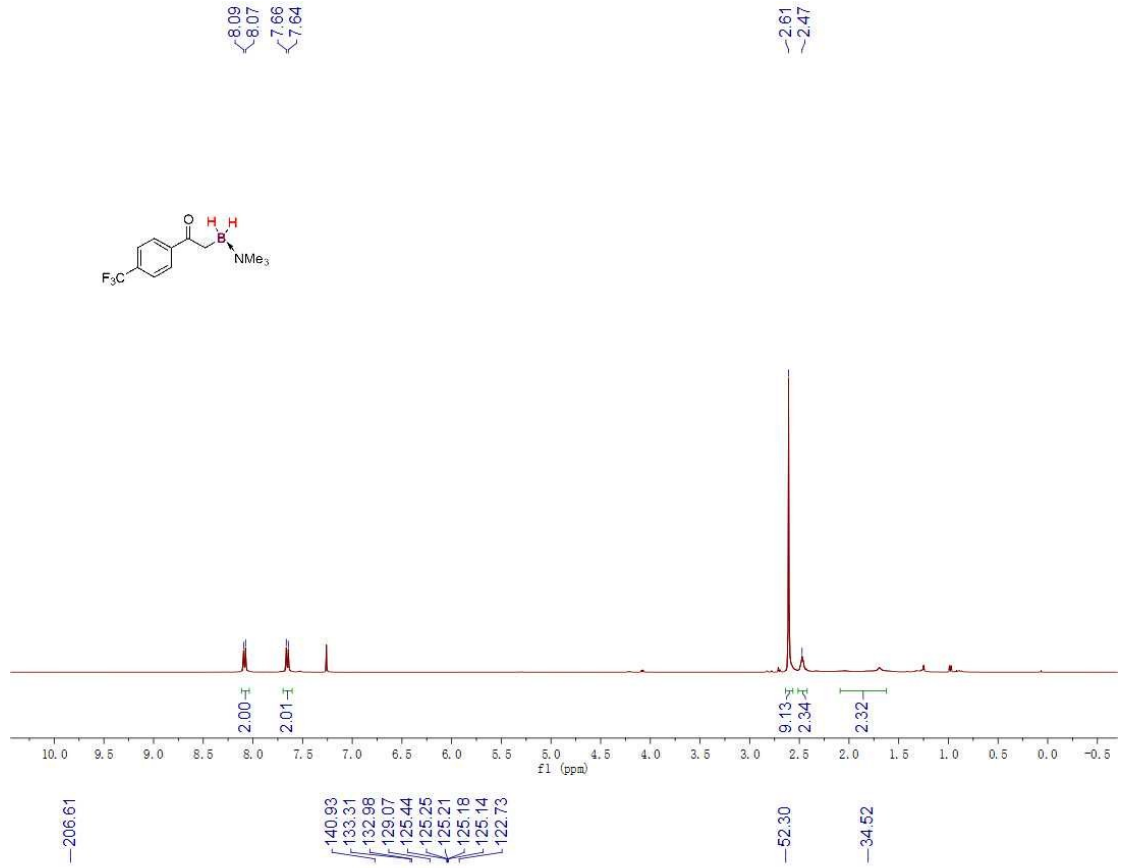

90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

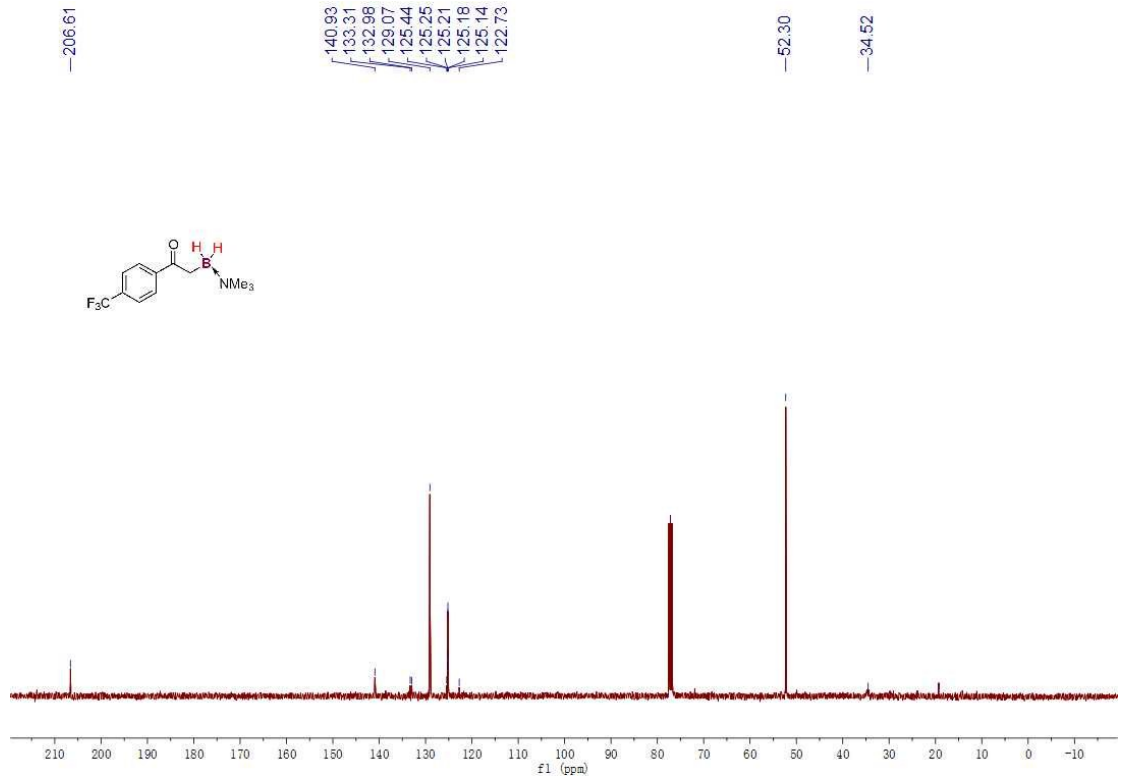

7.76
7.74
7.71
7.69
2.59
2.40
O
H
H
B
NMe3
I

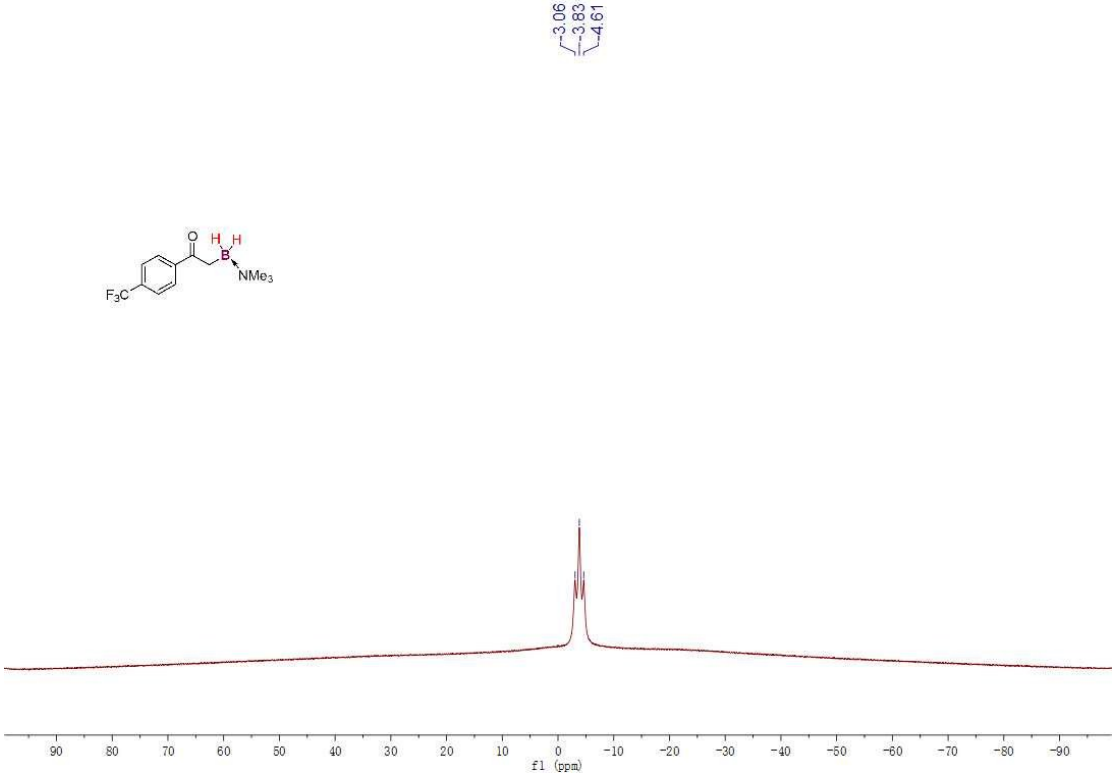

3.99
9.04
2.04
2.27
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

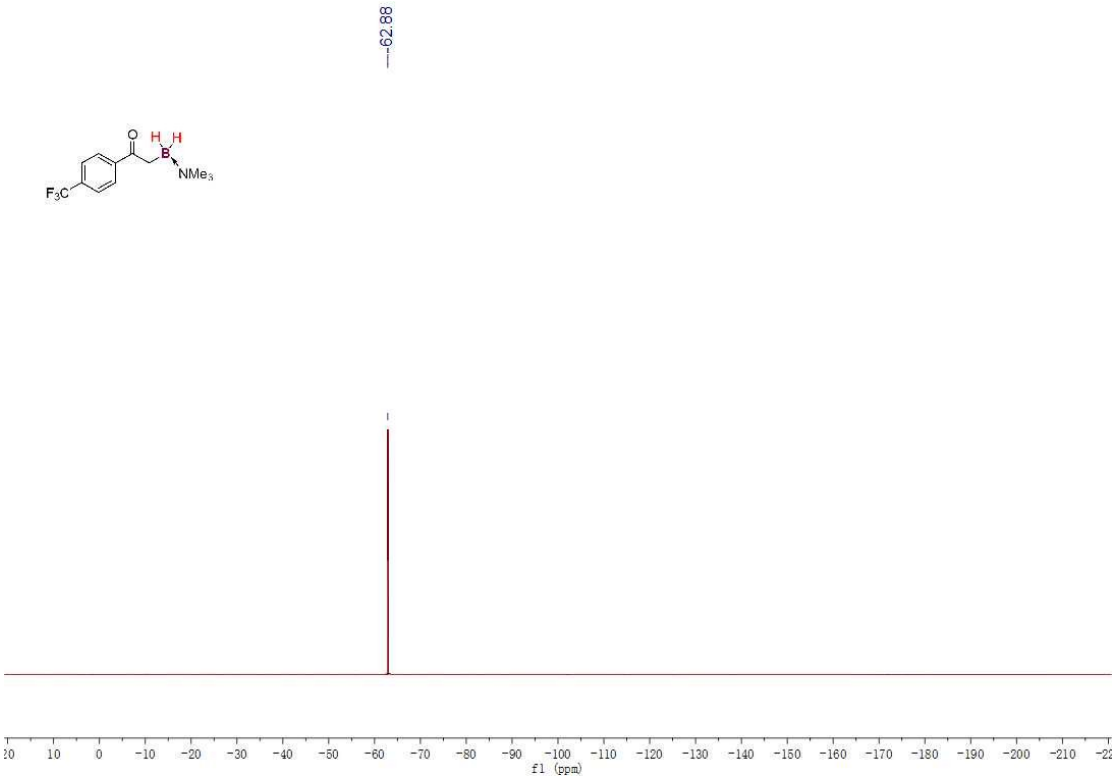

207.02
137.39
130.45
99.44
52.27
34.25
O
H
H
B
NMe3
I
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


2.95
3.71
4.48
O
H
H
B
NMe3
I
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)


8.09
8.07
7.66
7.64
2.61
2.47
O
H
H
B
NMe3
F3C
2.00
2.01
9.13
2.34
2.32
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


206.61
140.93
133.31
132.98
129.07
125.44
125.25
125.21
125.18
125.14
122.73
52.30
34.52
O
H
H
B
NMe3
F3C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


3.06
3.83
4.61
O
H
H
B
NMe3
F3C
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)


-62.88
O
H
H
B
NMe3
F3C
10
0
-10
-20
-30
-40
-50
-60
-70
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-90
-100
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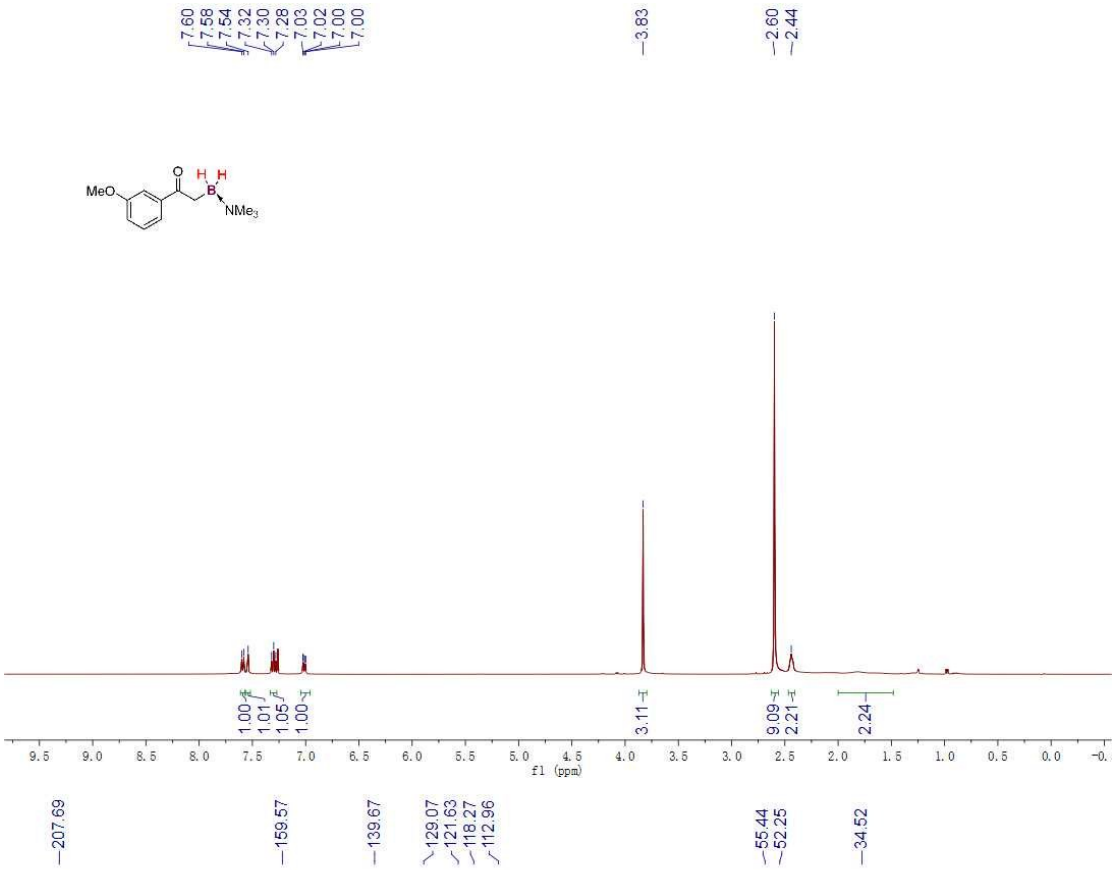
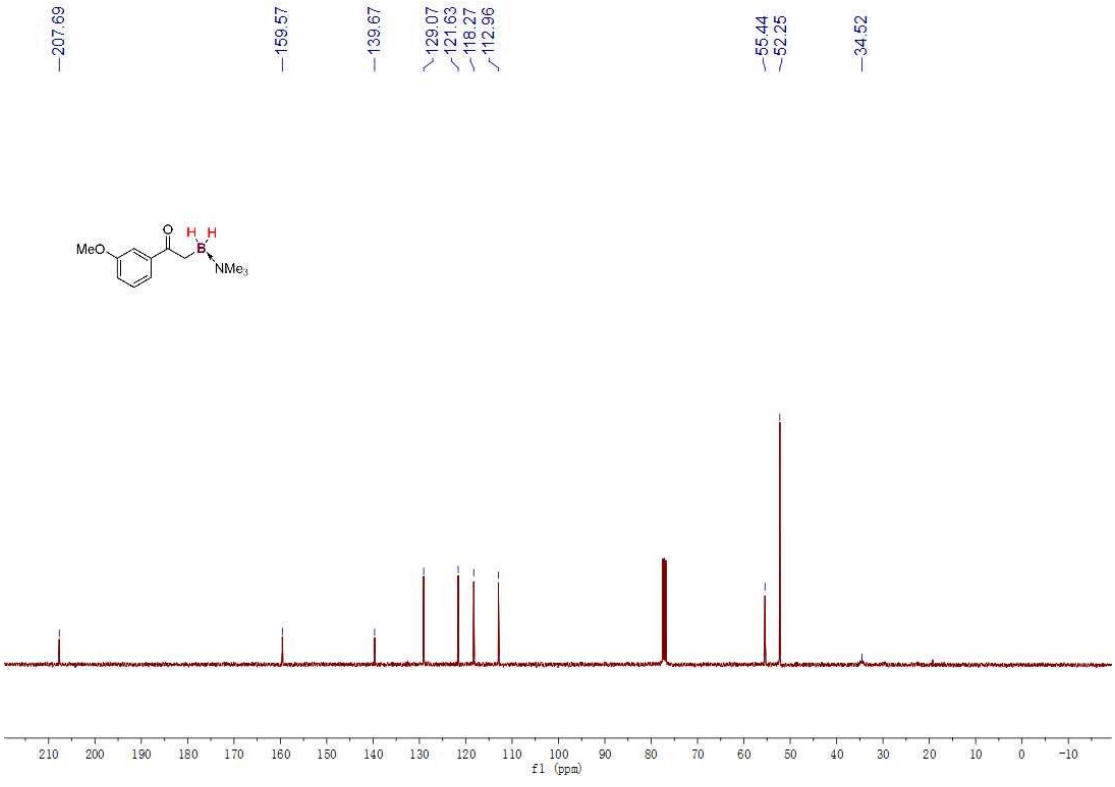
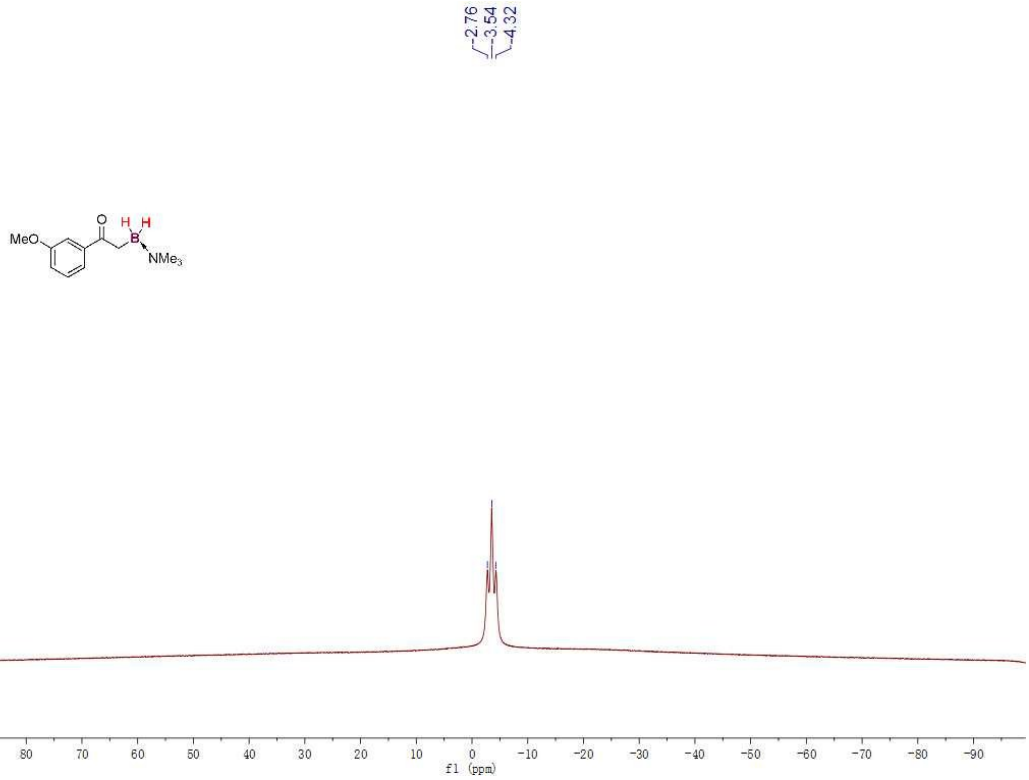
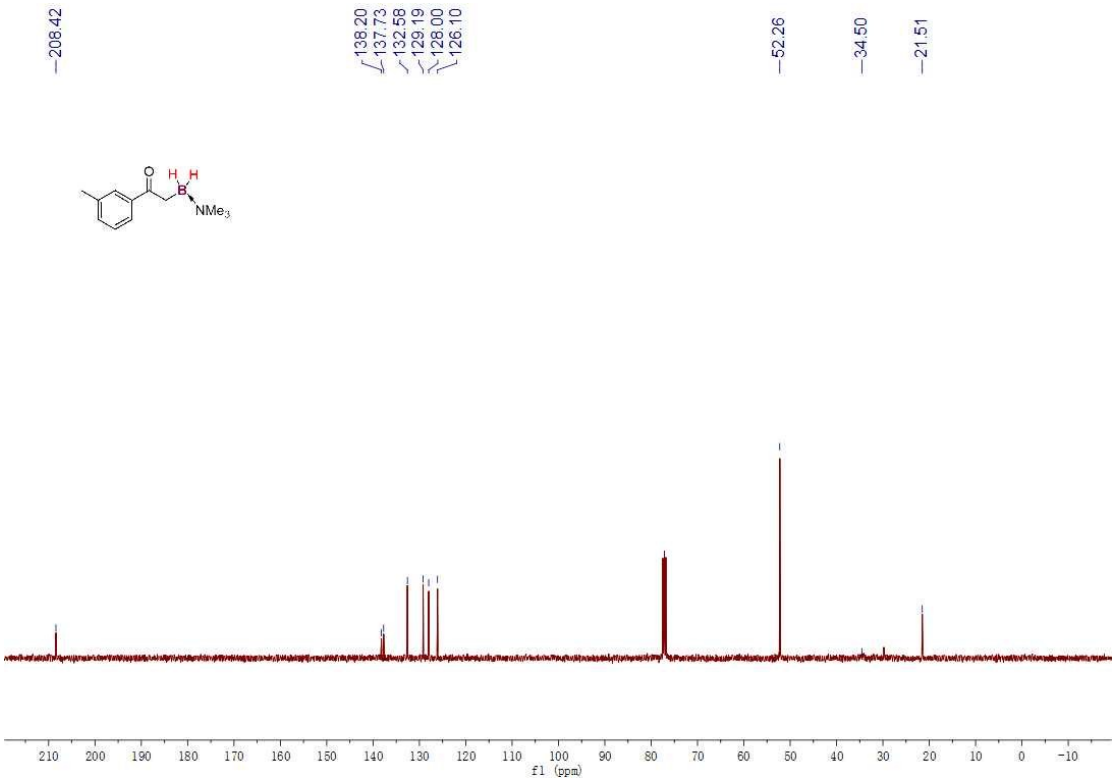
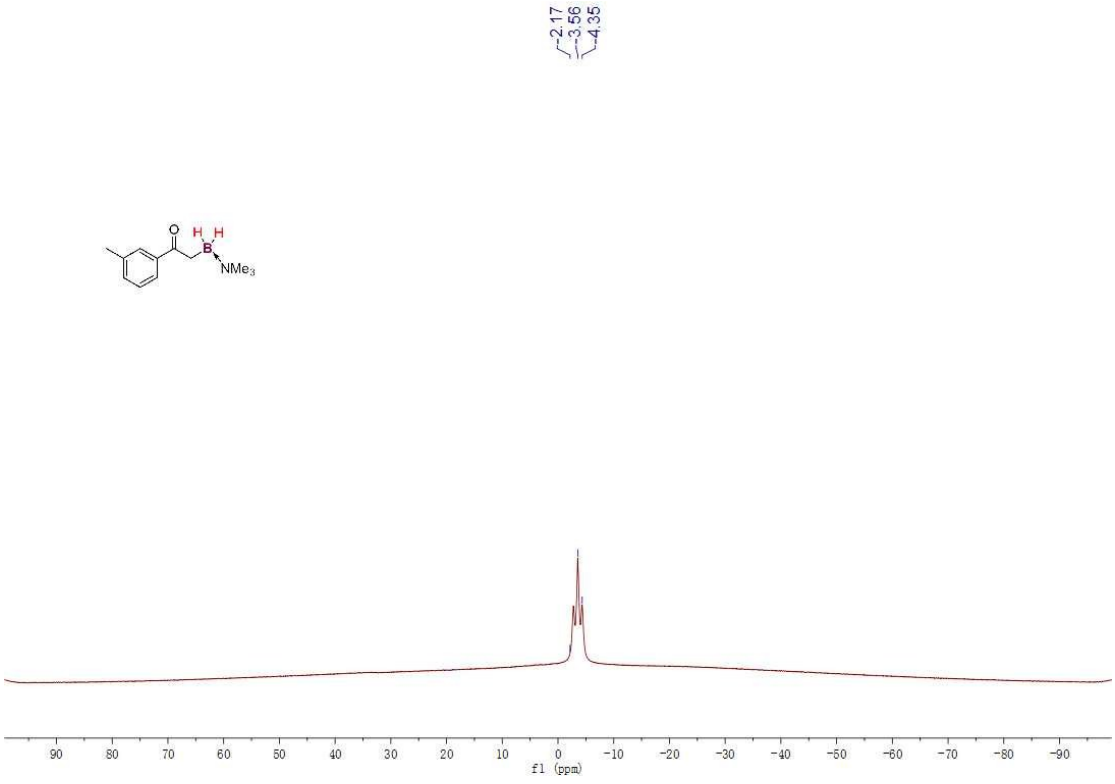
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

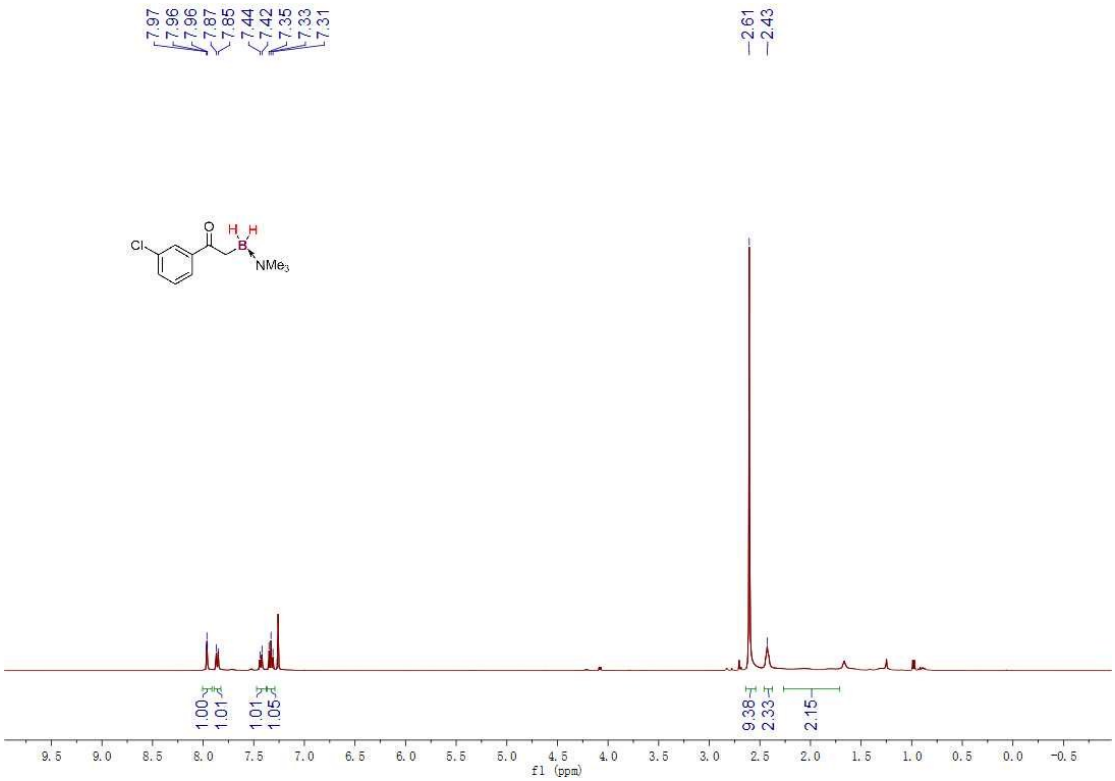

7.60
7.58
7.54
7.32
7.30
7.28
7.03
7.02
7.00
7.00
3.83
2.60
2.44
MeO
NMe3
1.00
1.01
1.05
1.00
3.11
9.09
2.21
2.24
f1 (ppm)

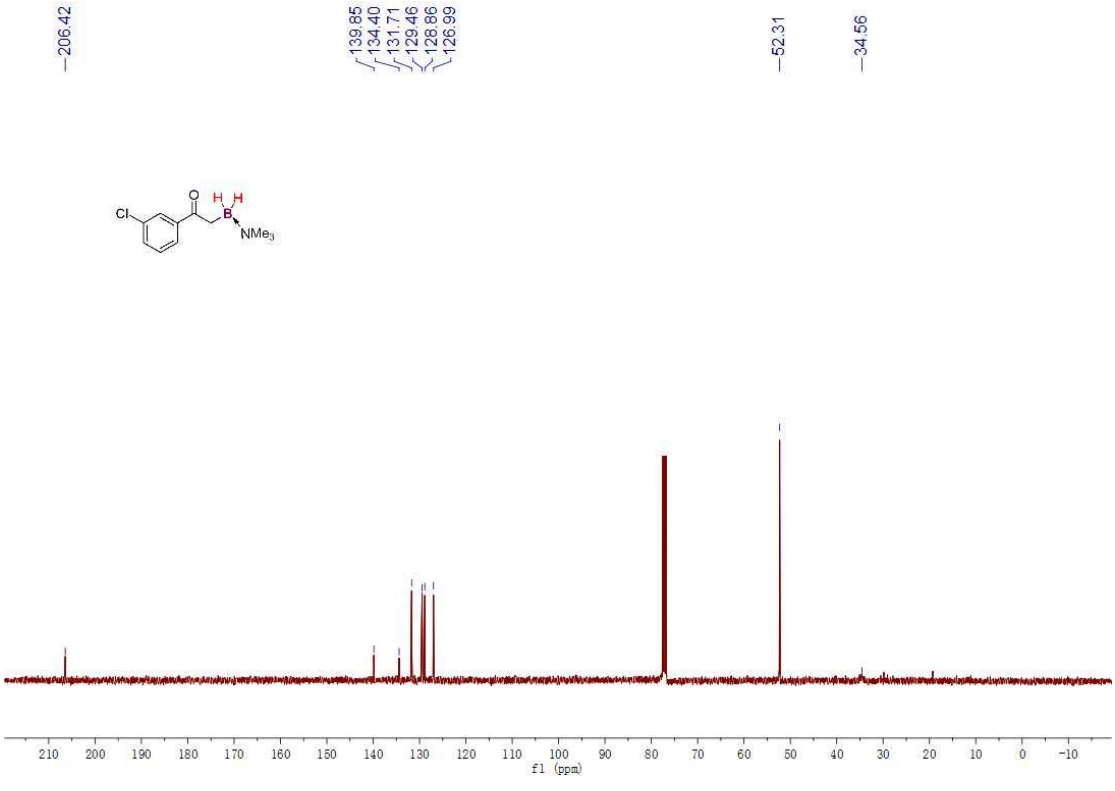

207.69
159.57
139.67
129.07
121.63
118.27
112.96
55.44
52.25
34.52
MeO
NMe3
f1 (ppm)

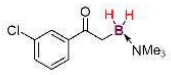

2.76
3.54
4.32
MeO
H
H
B
NMe3
f1 (ppm)
7.74
7.71
7.22
7.20
2.53
2.38
2.31
2.00
2.05
9.12
1.98
3.16
2.27

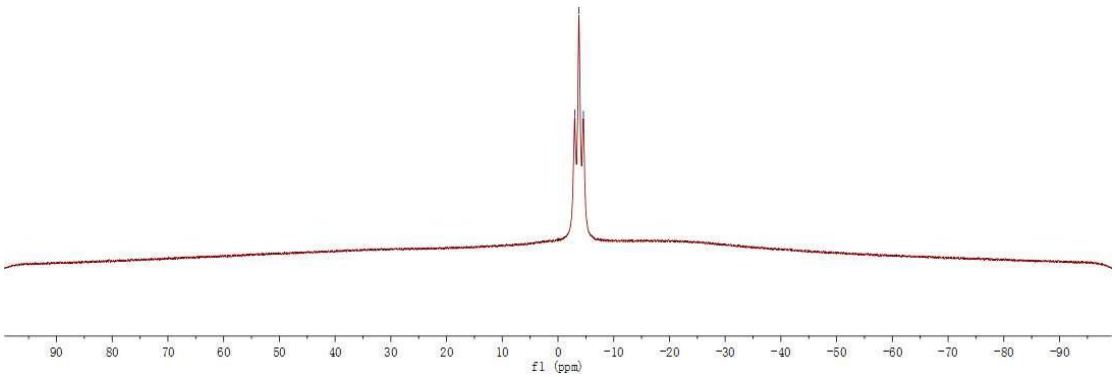

208.42
138.20
137.73
132.58
129.19
128.00
126.10
52.26
34.50
21.51
O
H
H
B
NMe3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


2.17
3.56
4.35
O
H
H
B
NMe3
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

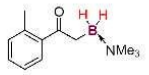

7.97
7.96
7.96
7.87
7.85
7.44
7.42
7.35
7.33
7.31
2.61
2.43
Cl
O
H
H
B
NMe3
1.00
1.01
1.01
1.05
9.38
2.33
2.15
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

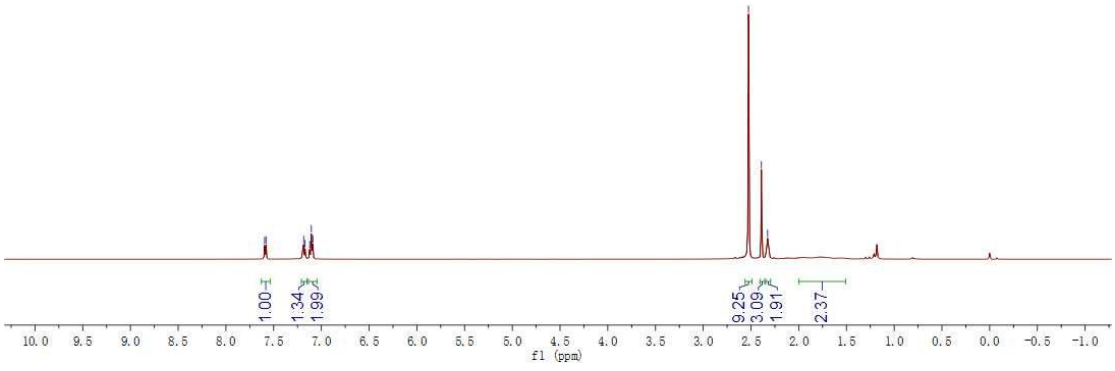

206.42
139.85
134.40
131.71
129.46
128.86
126.99
52.31
34.56
Cl
O
H
H
B
NMe3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

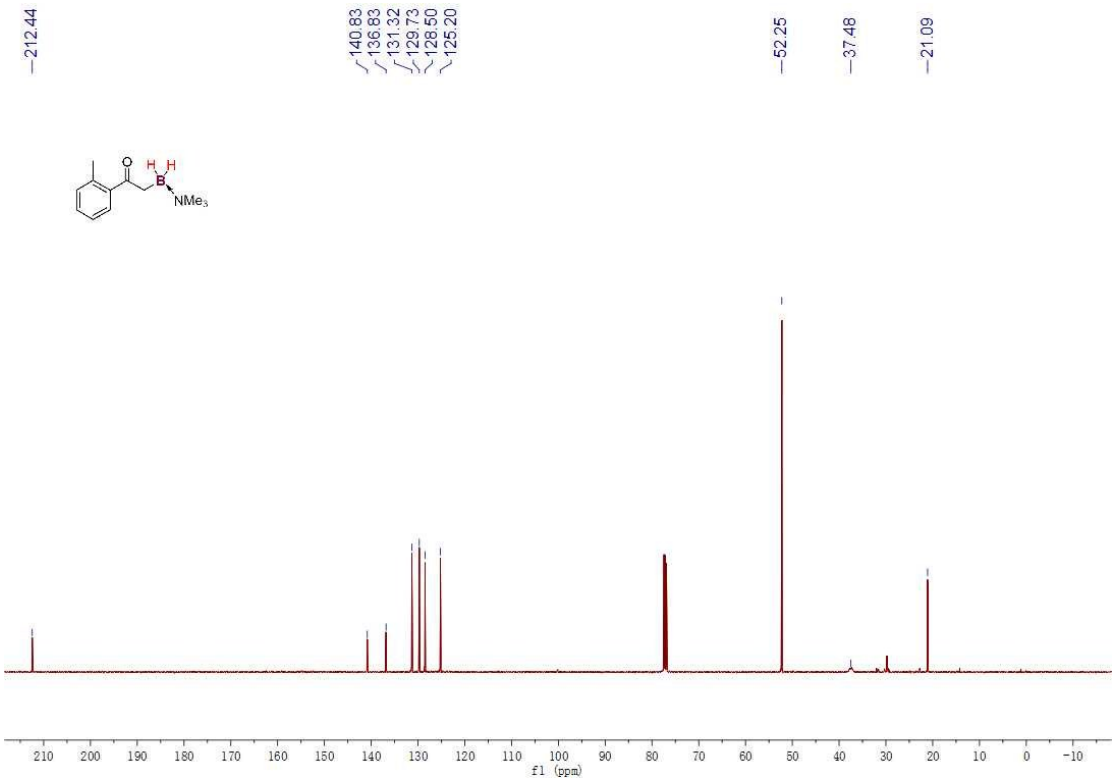

Cl
O
H H
B
NMe3

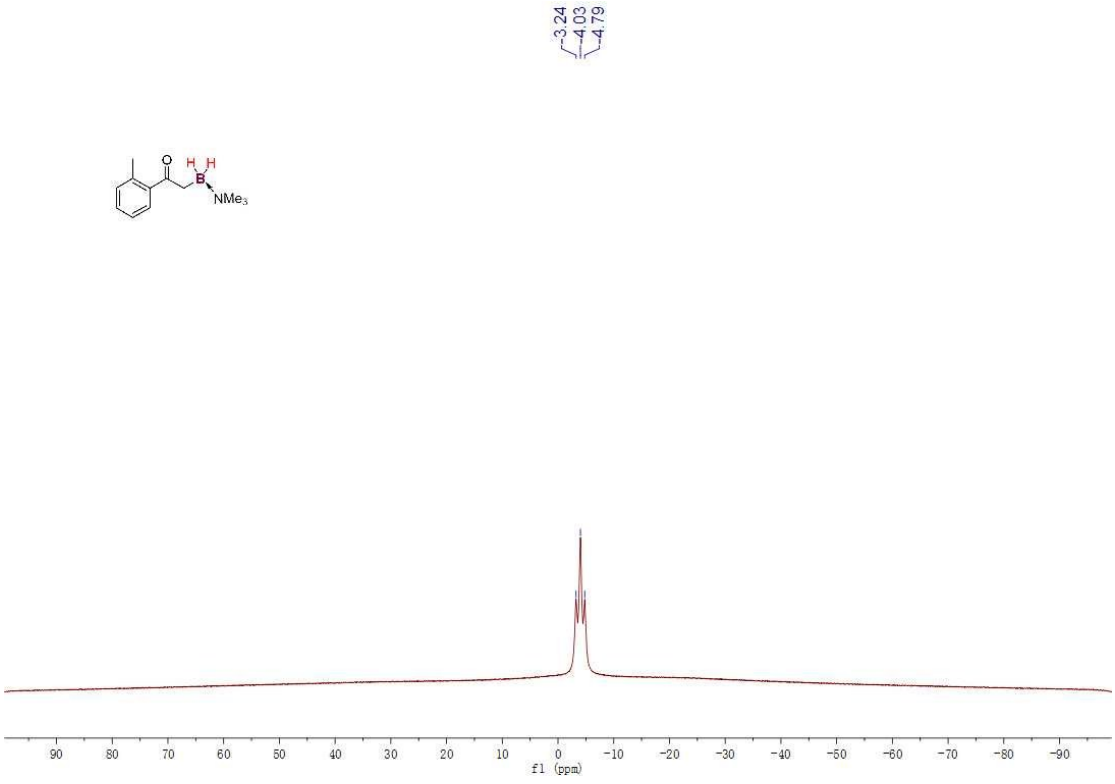

3.01
3.76
4.57
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

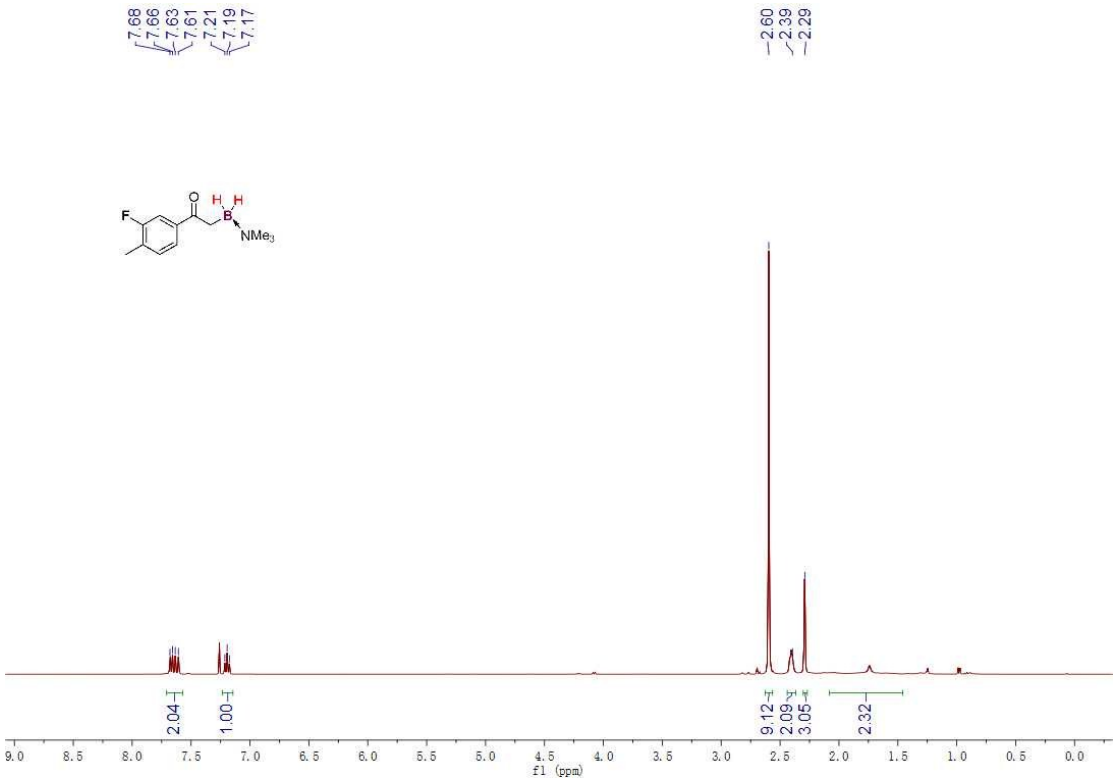
7.59
7.58
7.19
7.17
7.12
7.11
7.09
2.53
2.39
2.33

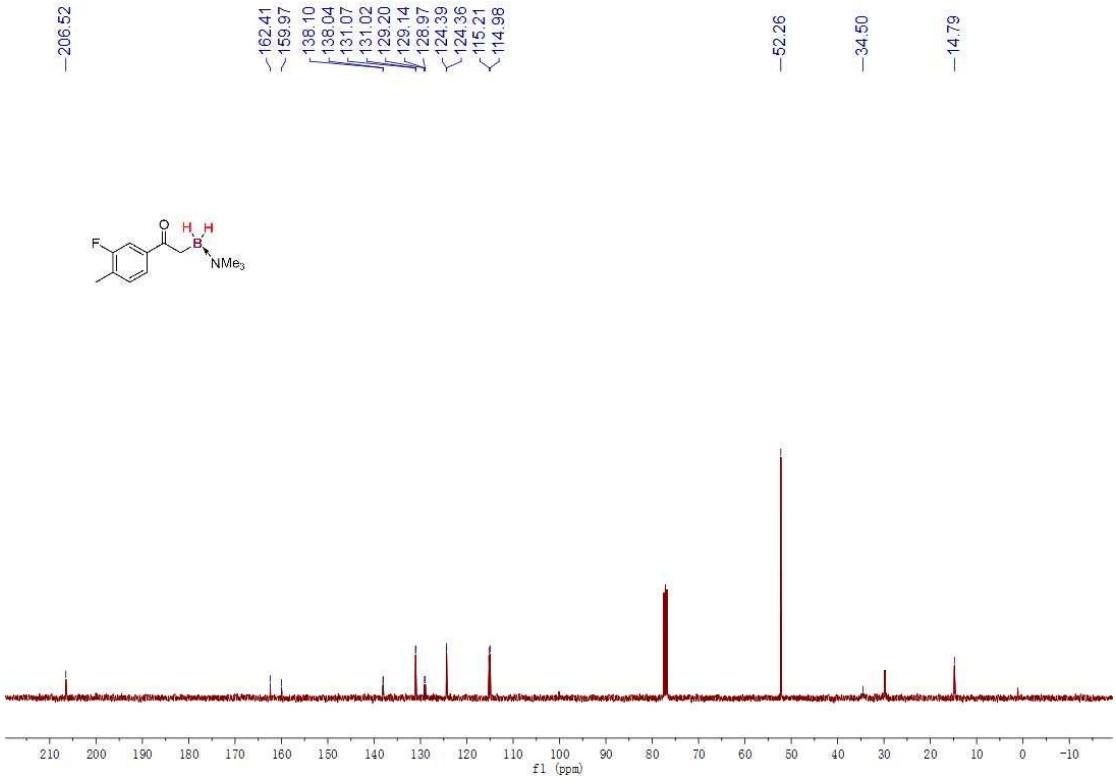

O
H H
B
NMe3

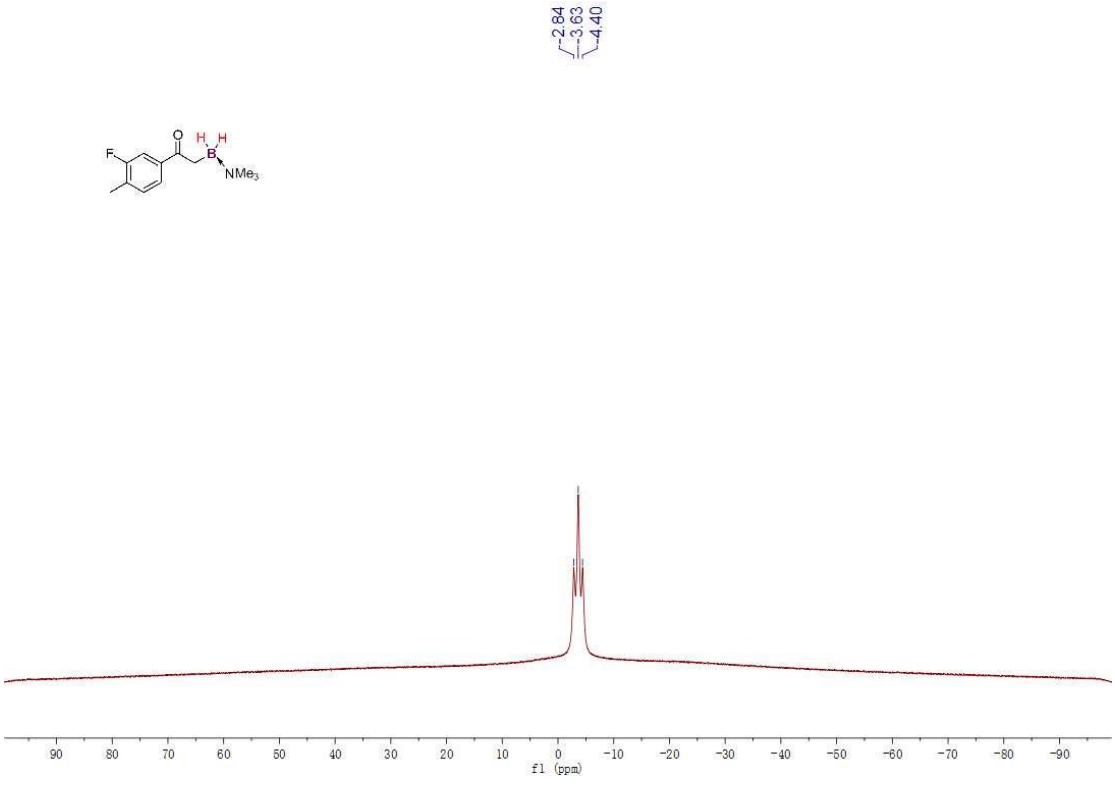

1.00
1.34
1.99
9.25
3.09
1.91
2.37
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

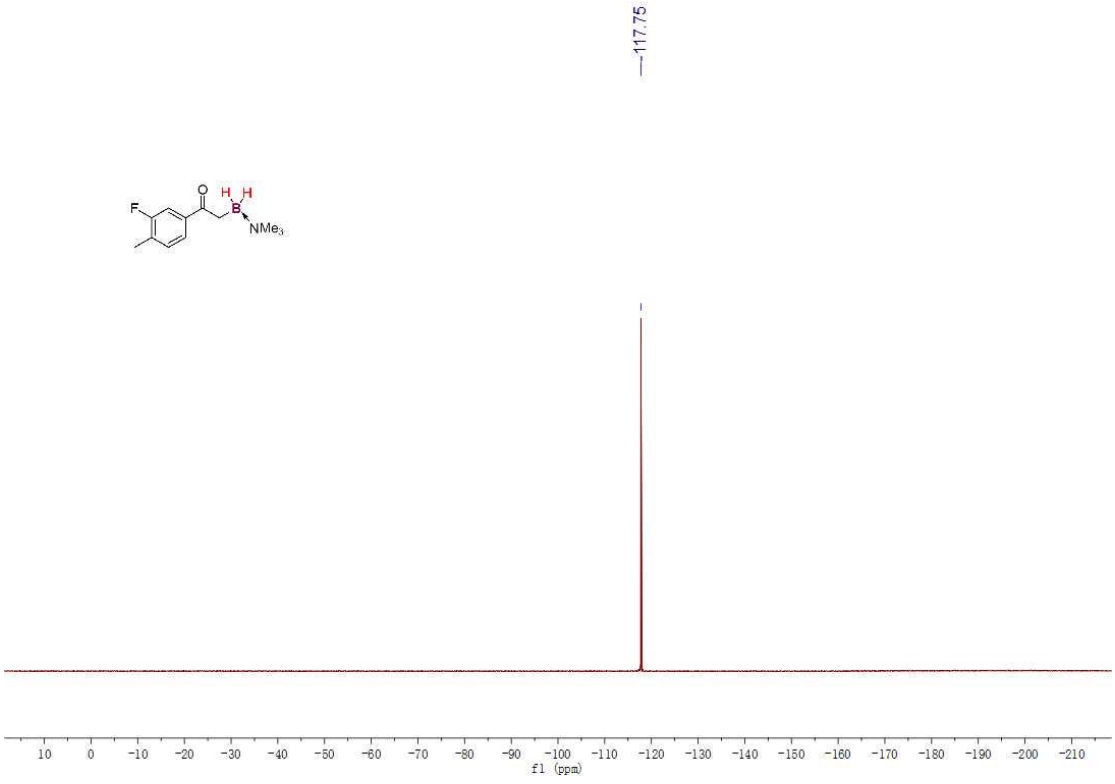

212.44
140.83
136.83
131.32
129.73
128.50
125.20
52.25
37.48
21.09
NMe3
f1 (ppm)

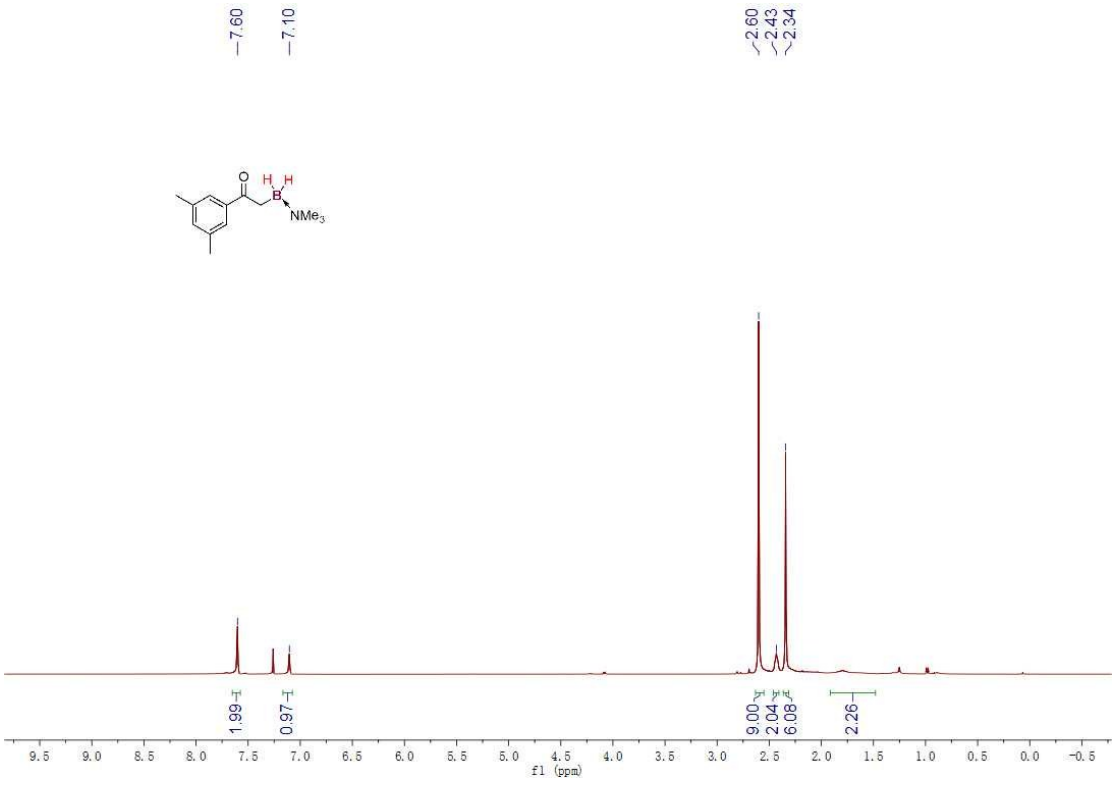

3.24
4.03
4.79
NMe3
f1 (ppm)

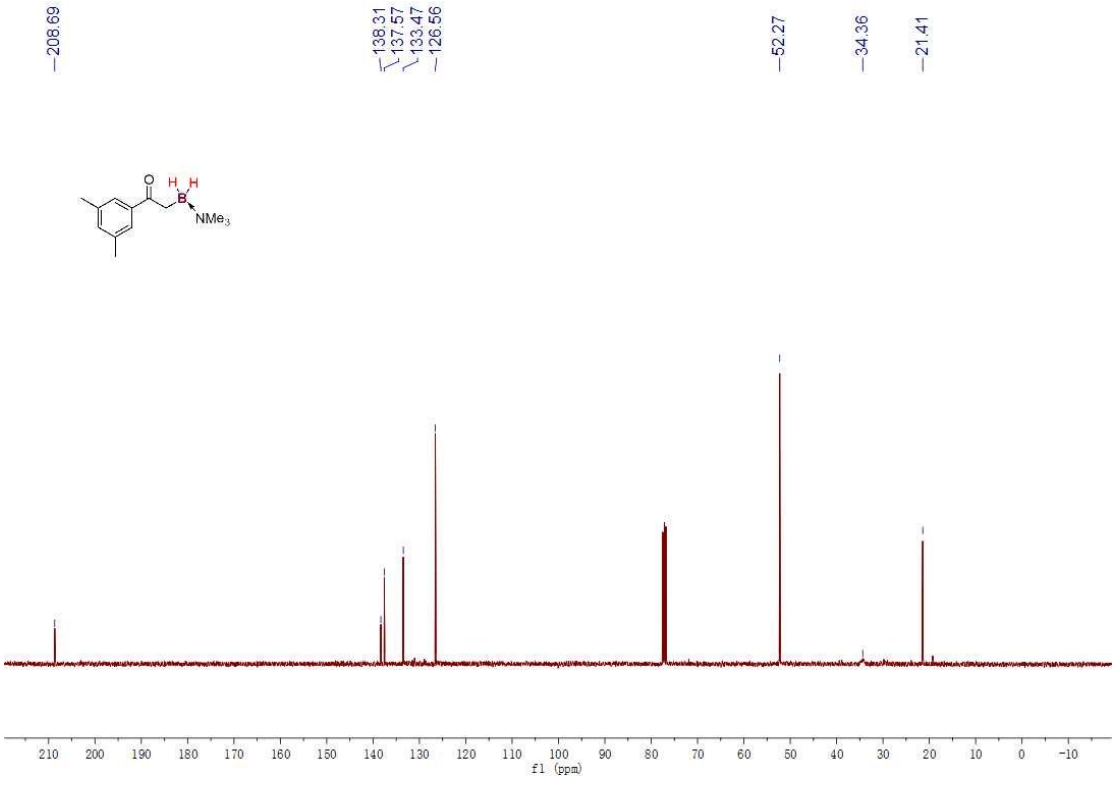

7.68
7.66
7.63
7.61
7.21
7.19
7.17
2.60
2.39
2.29
F
O
H
H
B
NMe3
2.04
1.00
9.12
2.09
3.05
2.32
f1 (ppm)

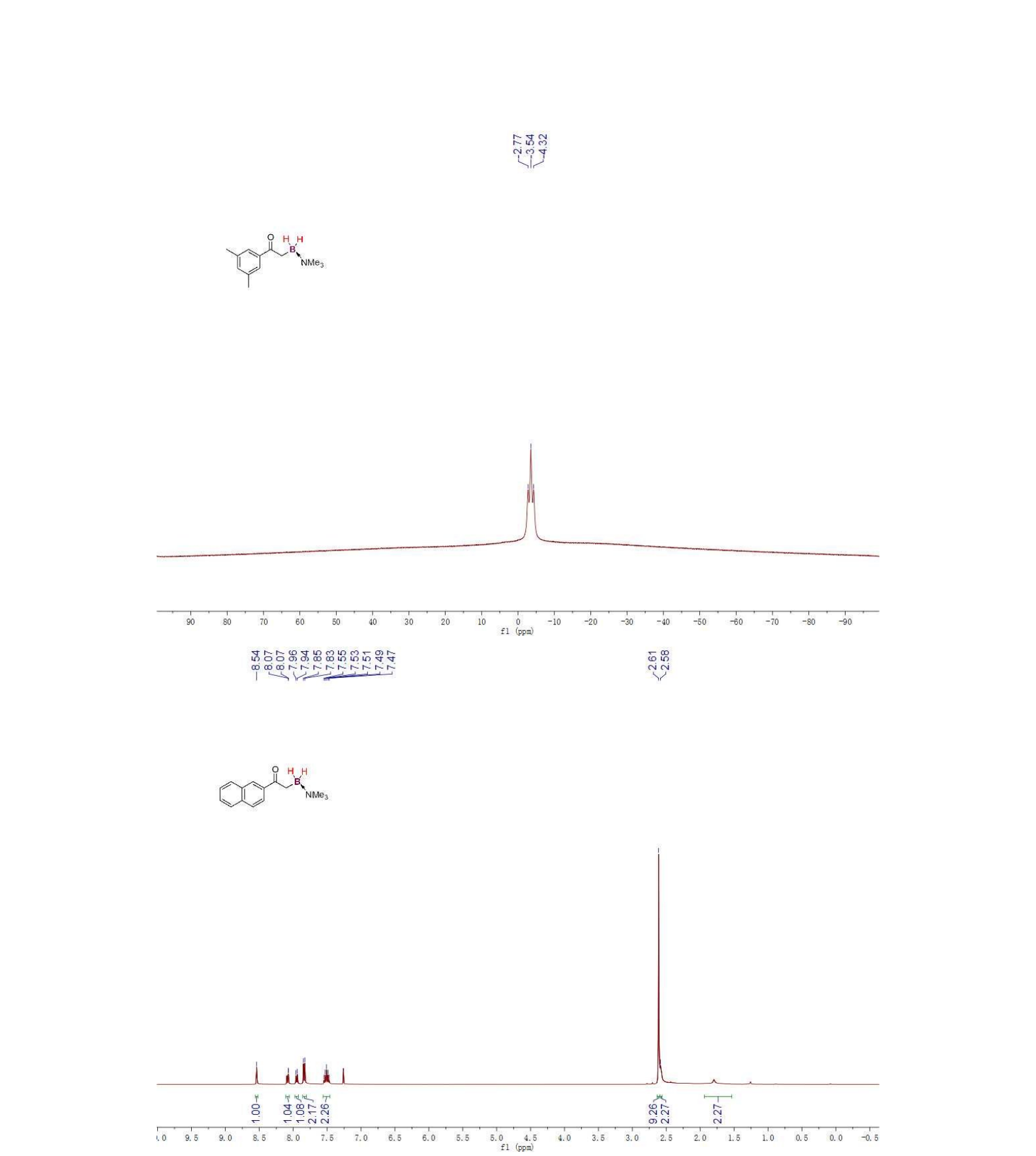

206.52
162.41
159.97
138.10
138.04
131.07
131.02
129.20
129.14
128.97
124.39
124.36
115.21
114.98
52.26
34.50
14.79
F
O
H
H
B
NMe3
f1 (ppm)

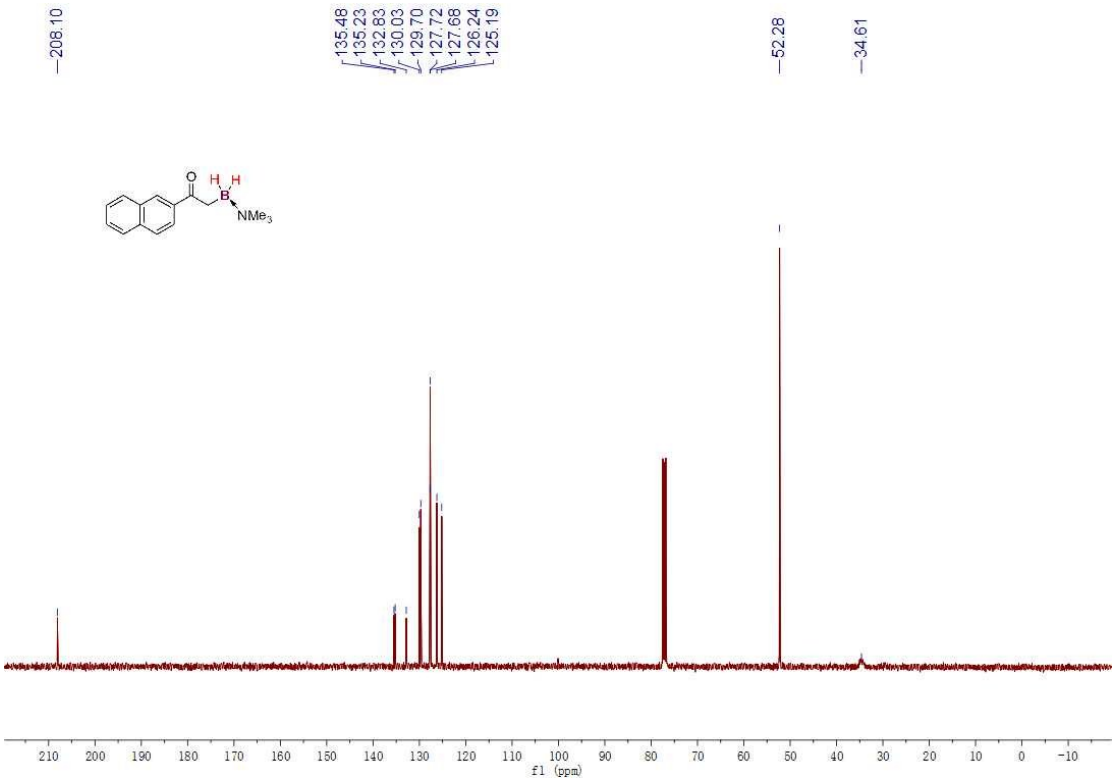

2.84
3.63
4.40
F
O
H
H
B
NMe3
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

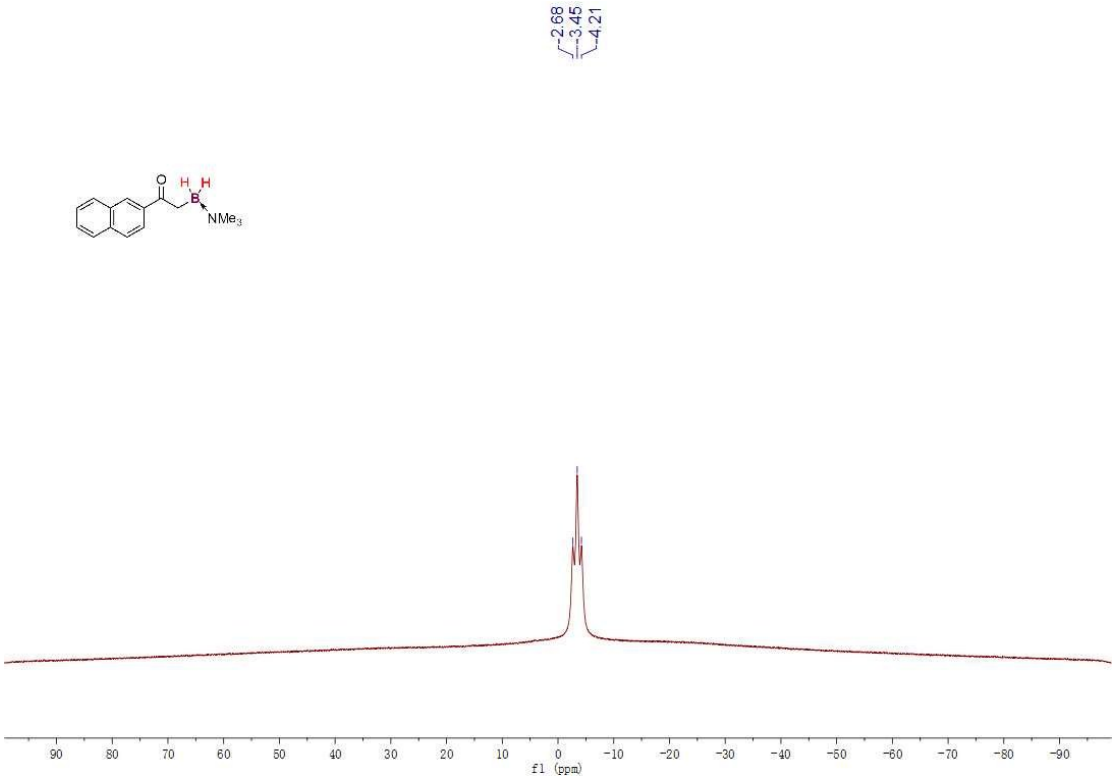

-117.75
F
O
H
H
B
NMe3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

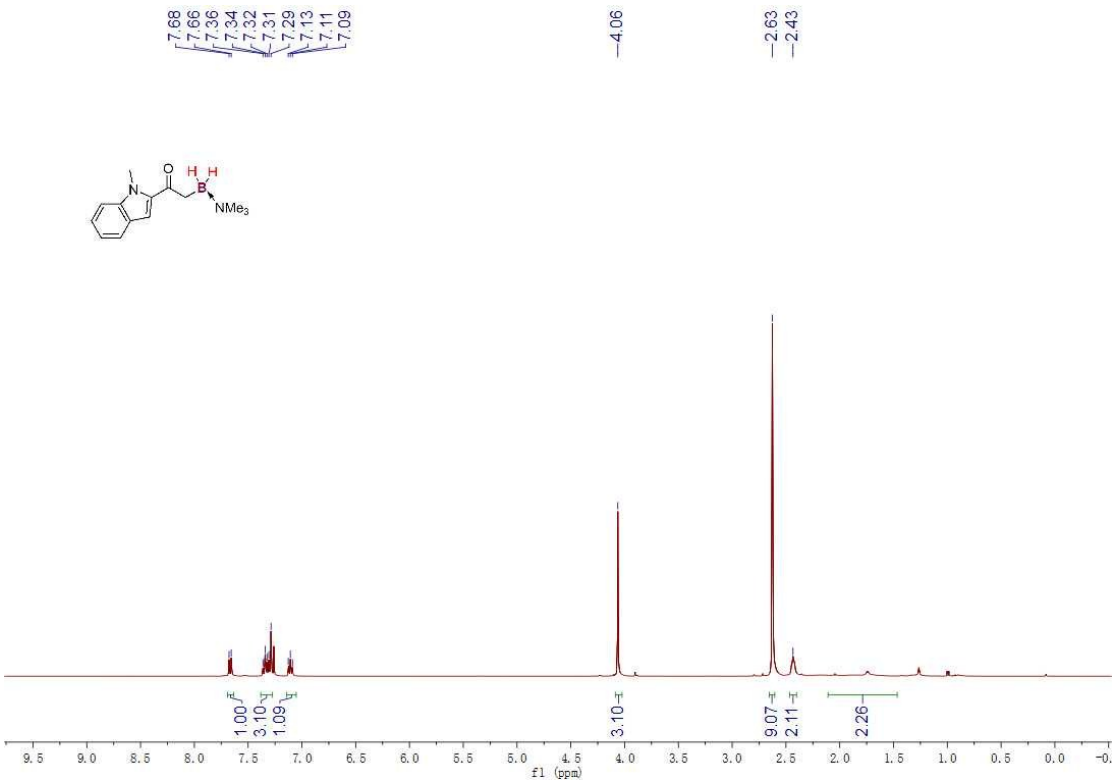

7.60
7.10
2.60
2.43
2.34
O
H
H
B
NMe3
1.99
0.97
9.00
2.04
6.08
2.26
f1 (ppm)

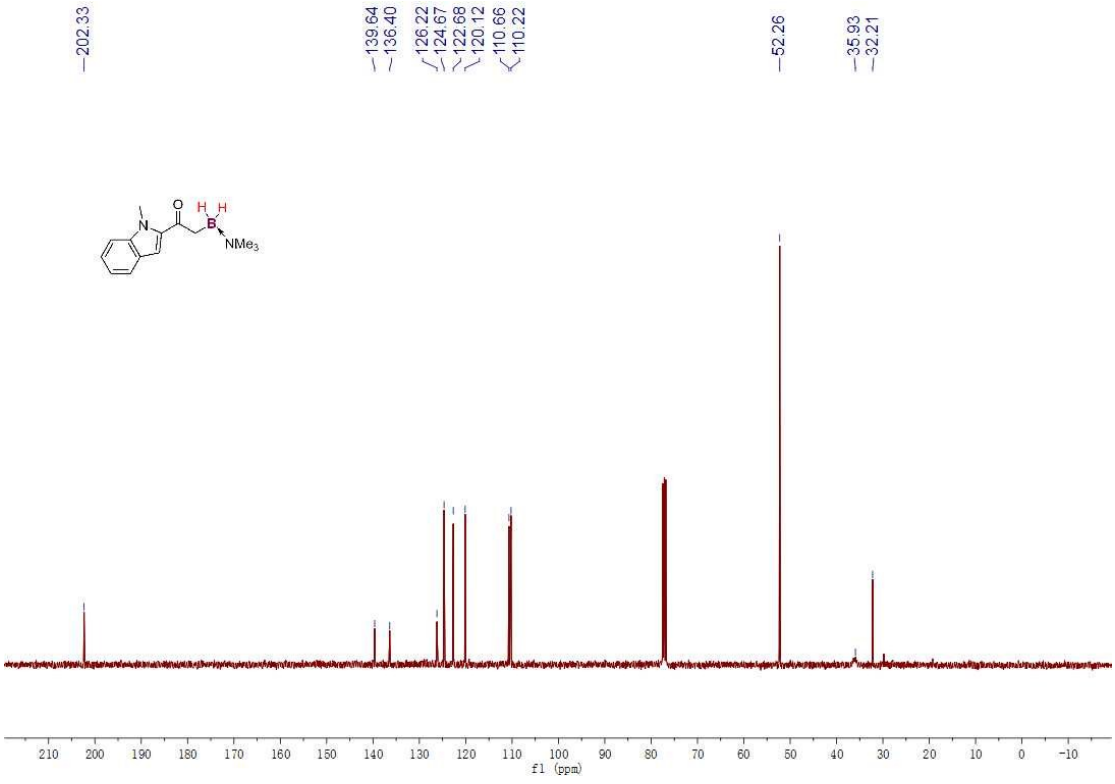

208.69
138.31
137.57
133.47
126.56
52.27
34.36
21.41
O
H
H
B
NMe3
f1 (ppm)

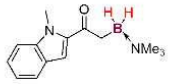

2.77
3.54
4.32
O
H
H
B
NMe3
f1 (ppm)
8.54
8.07
8.07
7.96
7.94
7.85
7.83
7.55
7.53
7.51
7.49
7.47
2.61
2.58
1.00
1.04
1.08
2.17
2.26
9.26
2.27
2.27

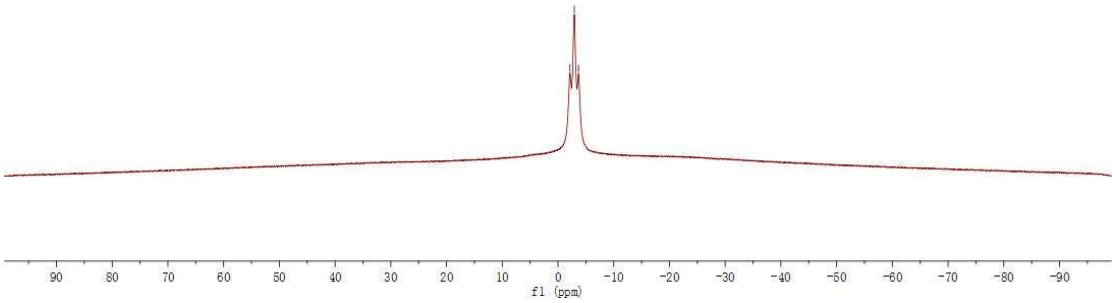

208.10
135.48
135.23
132.83
130.03
129.70
127.72
127.68
126.24
125.19
52.28
34.61
NMe3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

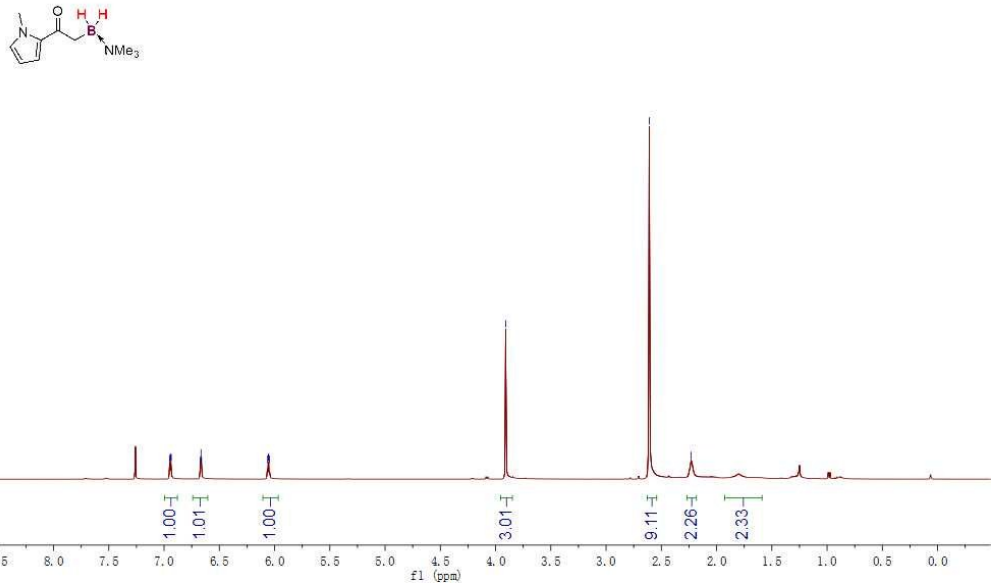

2.68
3.45
4.21
NMe3
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

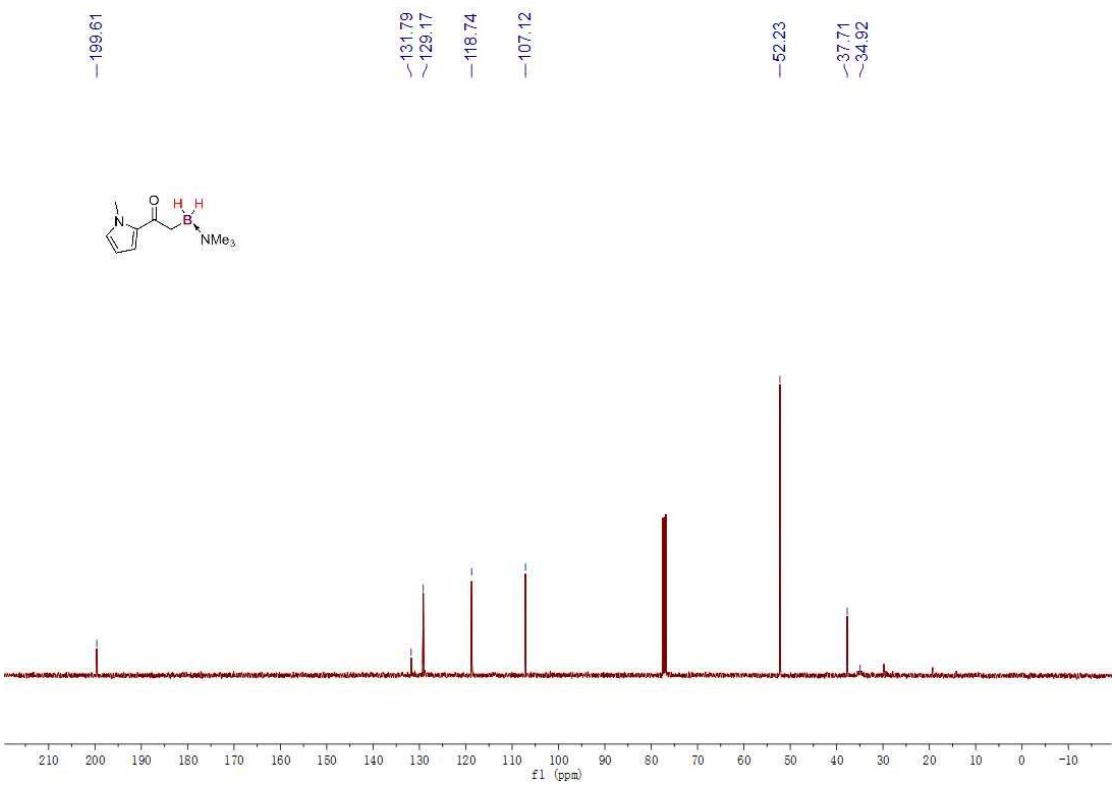

7.68
7.66
7.36
7.34
7.32
7.31
7.29
7.13
7.11
7.09
4.06
2.63
2.43
O
H H
B
NMe3
1.00
3.10
1.09
3.10
9.07
2.11
2.26
f1 (ppm)

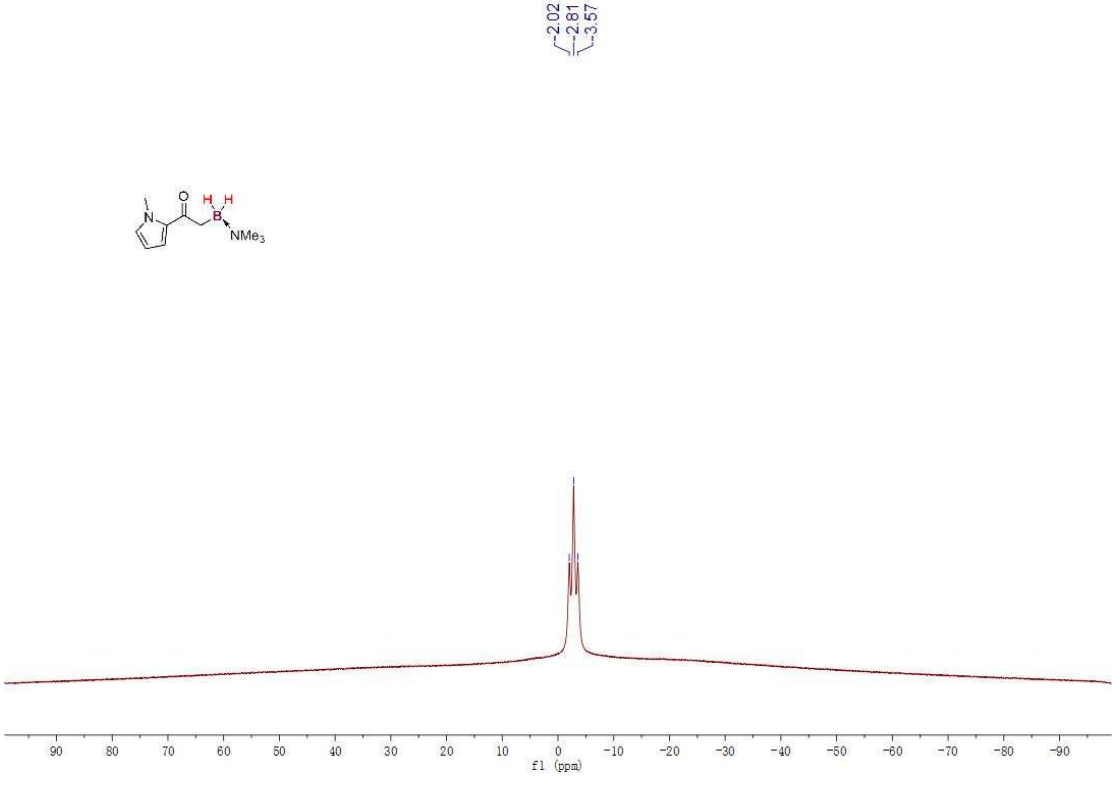

202.33
139.64
136.40
126.22
124.67
122.68
120.12
110.66
110.22
52.26
35.93
32.21
O
H H
B
NMe3
f1 (ppm)

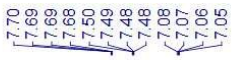




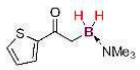


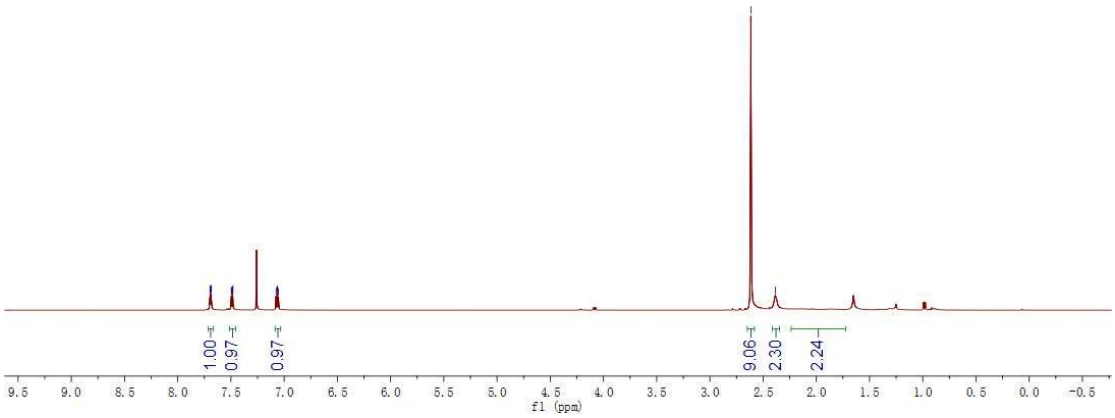

199.61
131.79
129.17
118.74
107.12
52.23
37.71
34.92
NMe3
f1 (ppm)


2.02
2.81
3.57
NMe3
f1 (ppm)

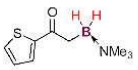

7.70
7.69
7.69
7.68
7.50
7.49
7.48
7.48
7.08
7.07
7.06
7.05

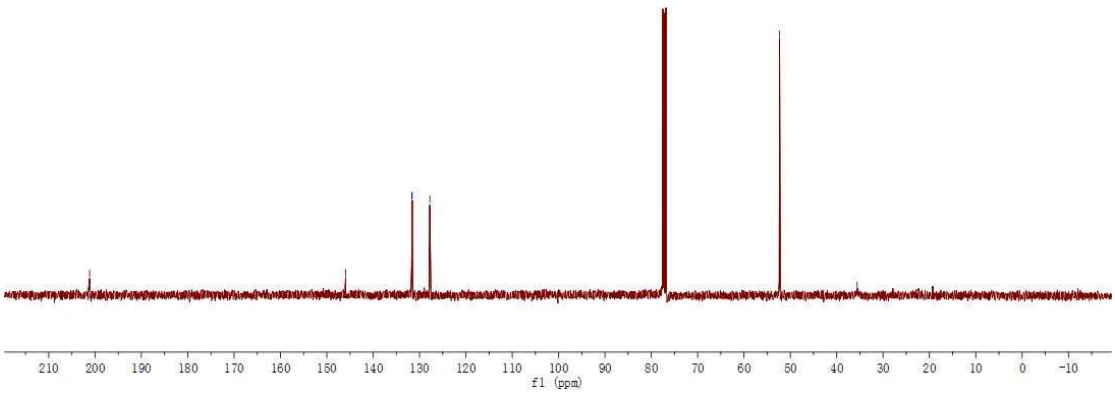

2.62
2.39

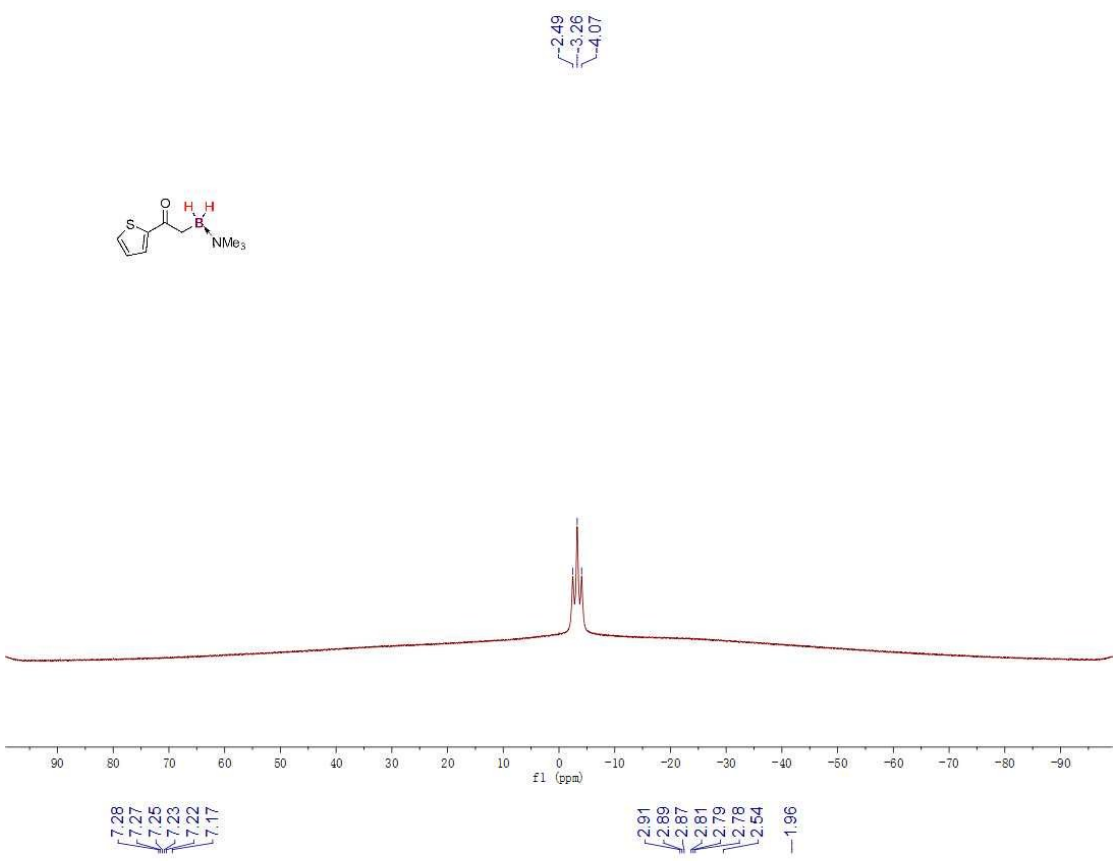

O
H
H
B
S
NMe3

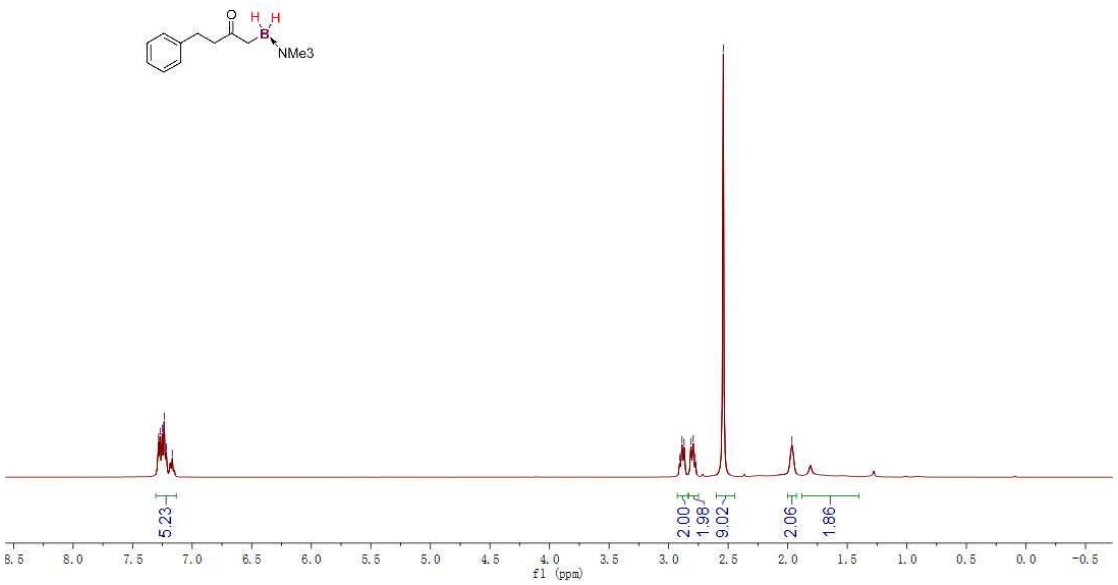

1.00
0.97
0.97
9.06
2.30
2.24
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

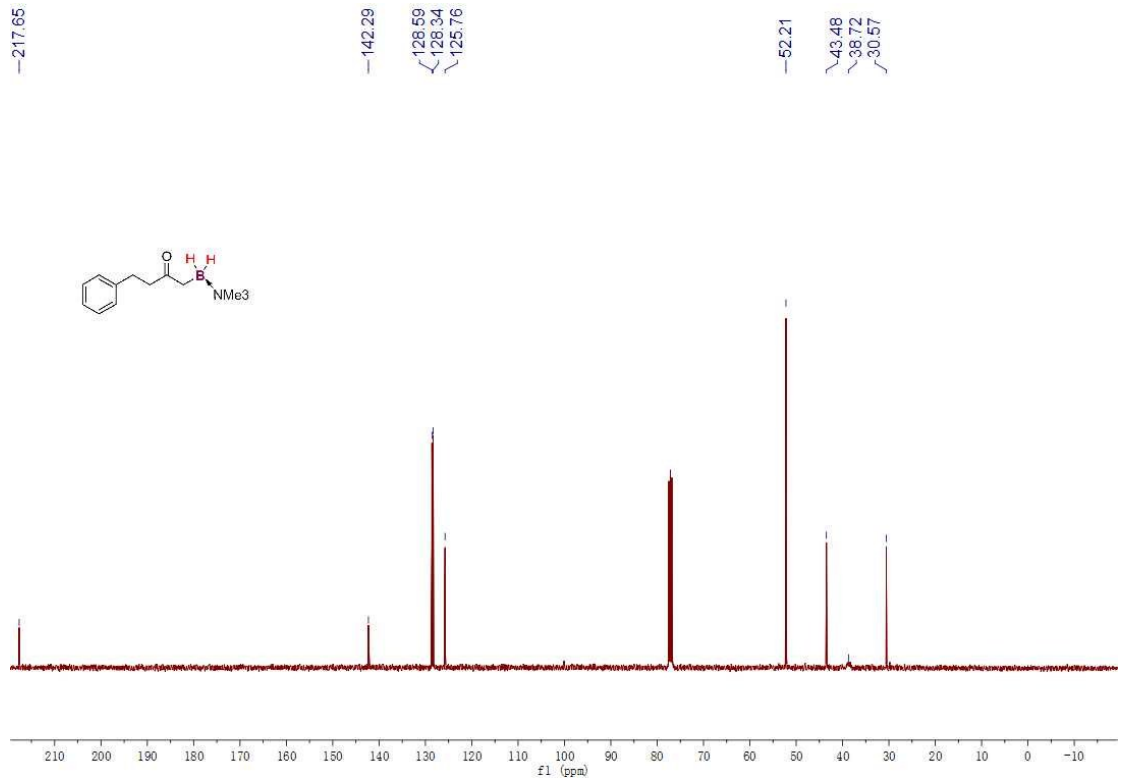

201.17
145.94
131.69
131.59
127.77
52.33
35.58

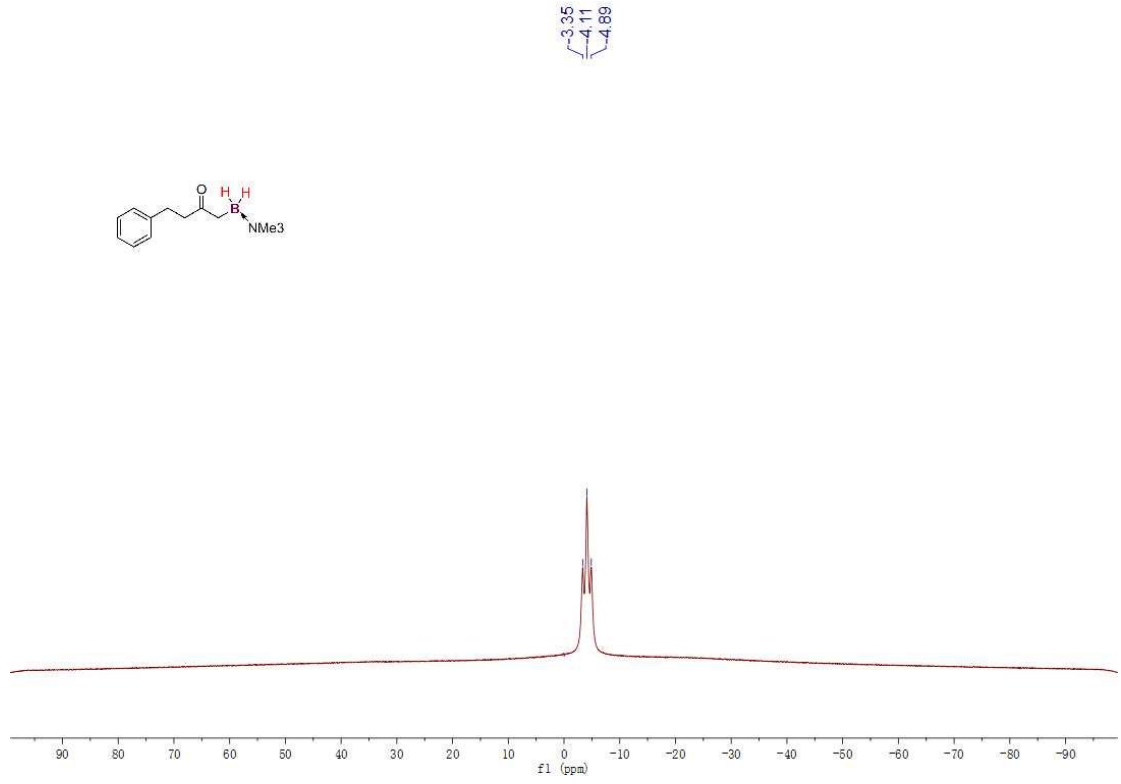

O
H
H
B
S
NMe3

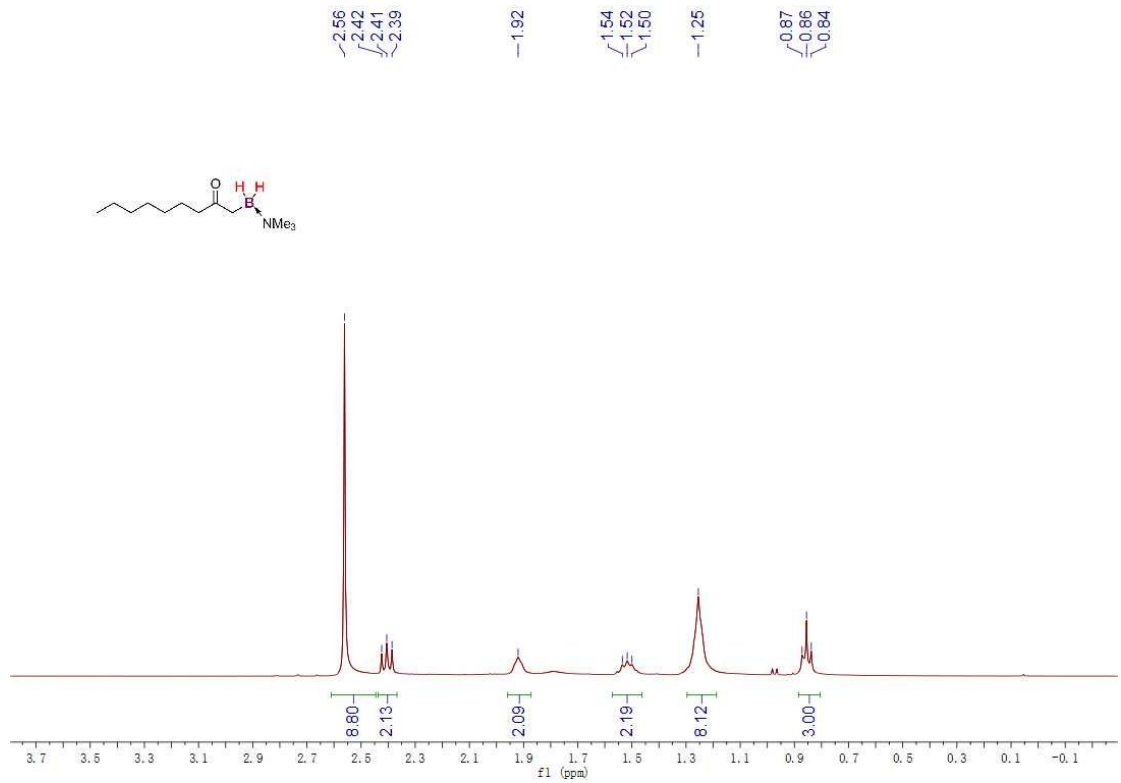

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

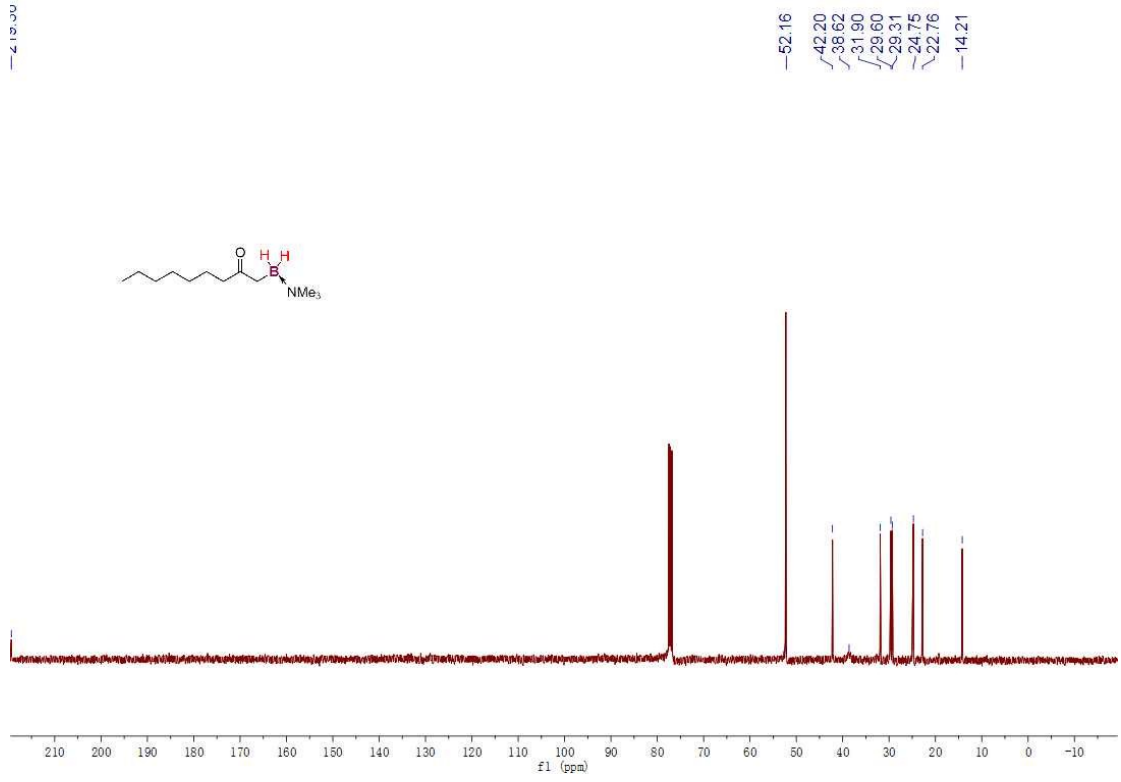

2.49
3.26
4.07
NMe3
f1 (ppm)
7.28
7.27
7.25
7.23
7.22
7.17
2.91
2.89
2.87
2.81
2.79
2.78
2.54
1.96

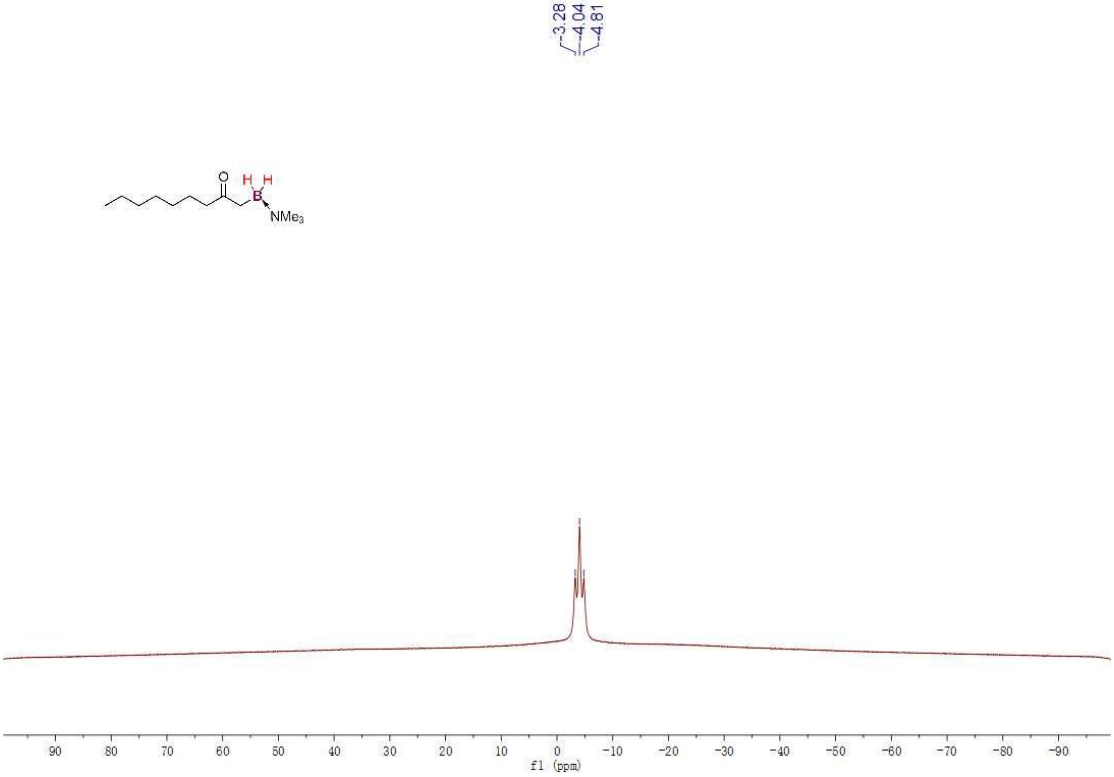

NMe3
5.23
2.00
1.98
9.02
2.06
1.86
f1 (ppm)

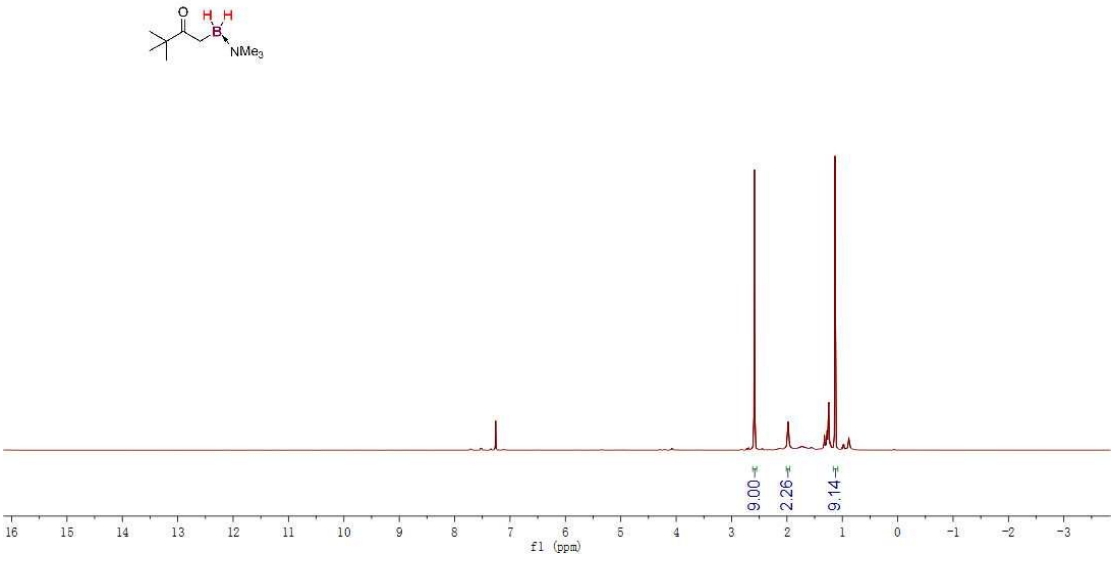

217.65
142.29
128.59
128.34
125.76
52.21
43.48
38.72
30.57
NMe3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

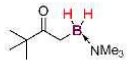

3.35
4.11
4.89
NMe3
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)


2.56
2.42
2.41
2.39
1.92
1.54
1.52
1.50
1.25
0.87
0.86
0.84
O
H
H
B
NMe3
8.80
2.13
2.09
2.19
8.12
3.00
f1 (ppm)

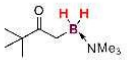

52.16
42.20
38.62
31.90
29.60
29.31
24.75
22.76
14.21
O
H
H
B
NMe3
f1 (ppm)


3.28
4.04
4.81
O
H H
B
NMe3
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

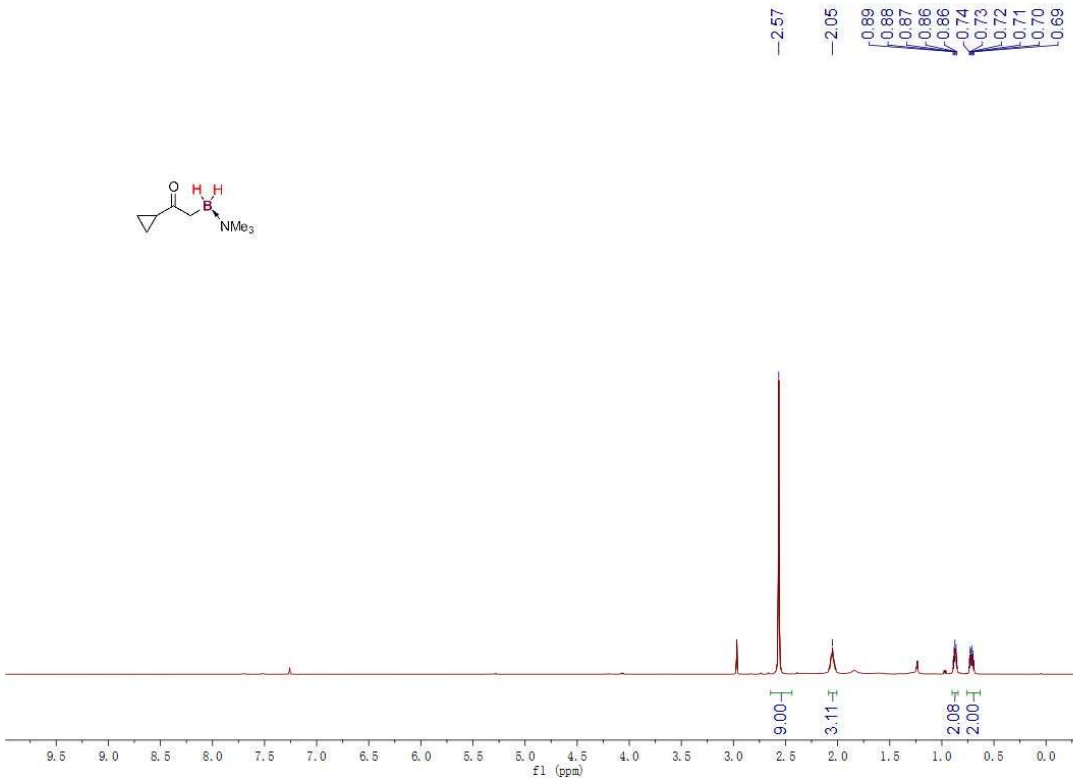

O
H H
B
NMe3
9.00
2.26
9.14
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

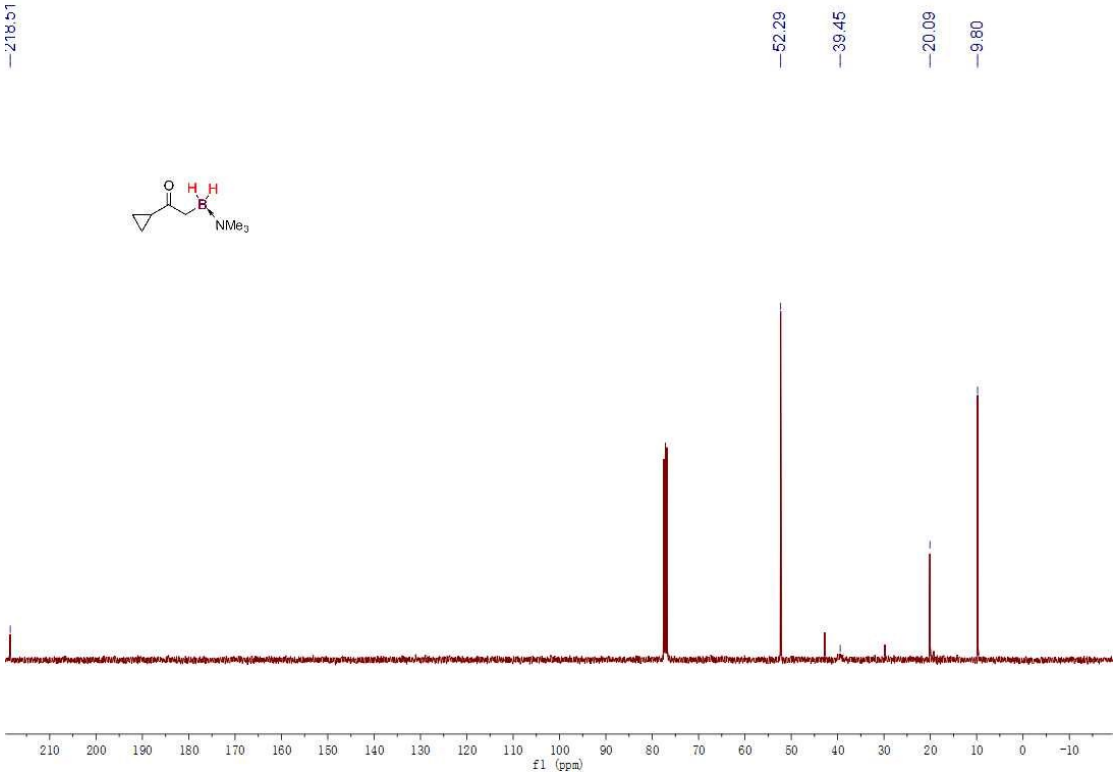

O
H
H
B
NMe3

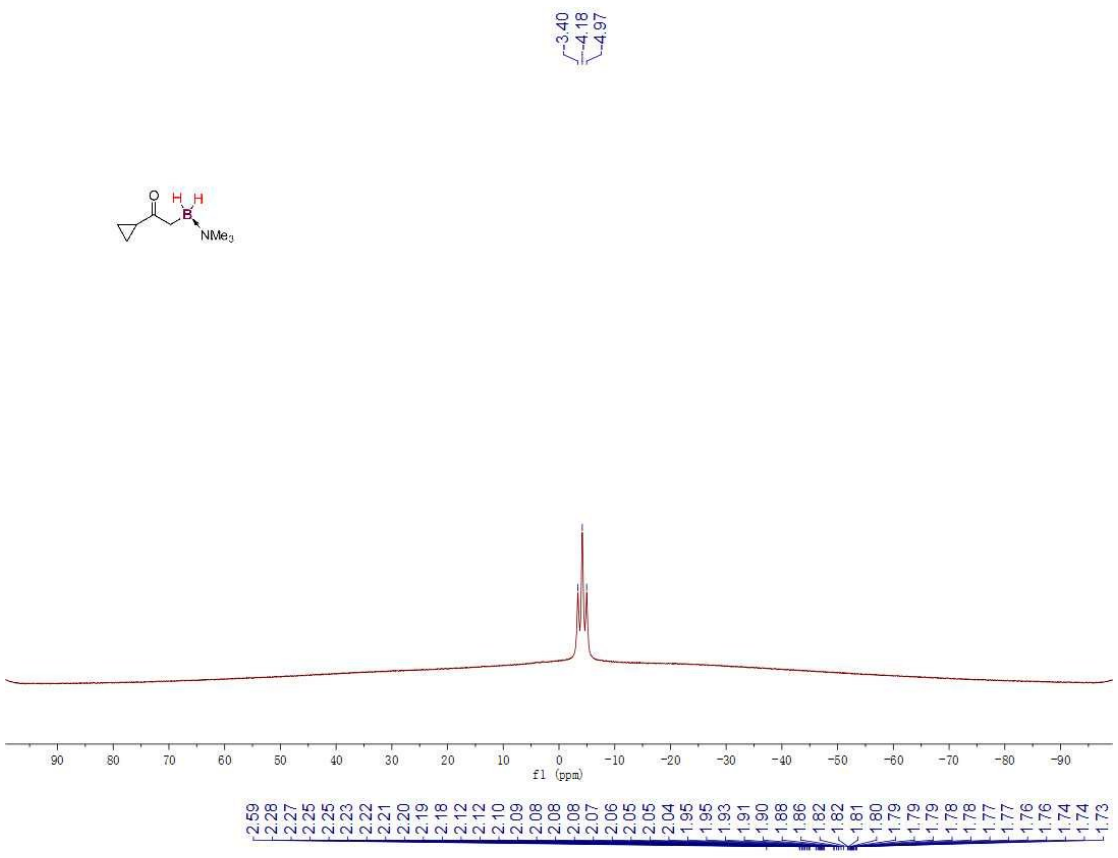
52.21
44.16
32.44
27.56
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

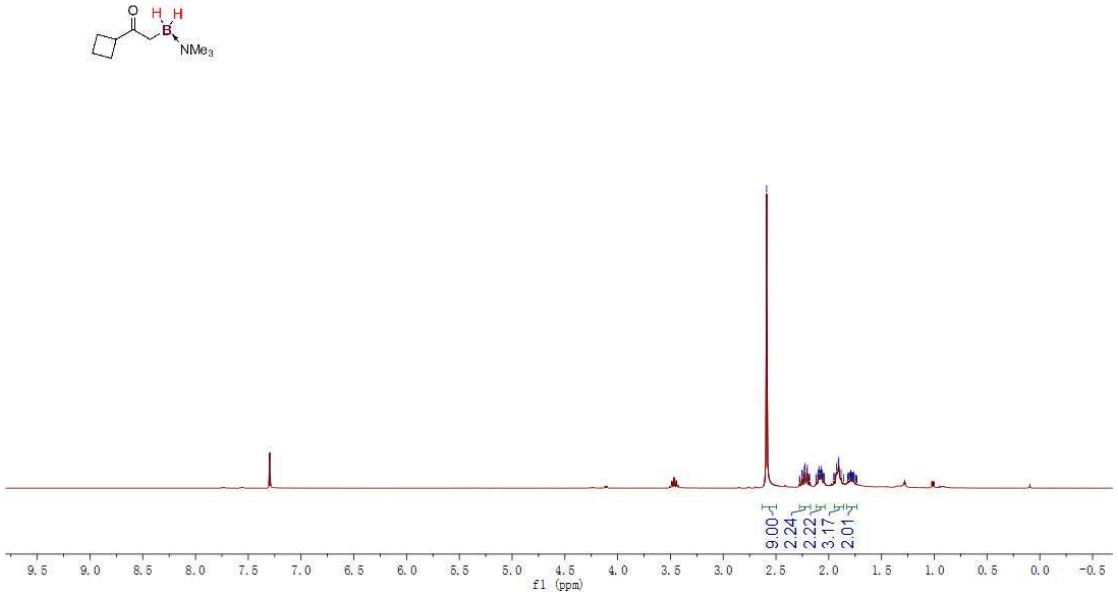

O
H
H
B
NMe3

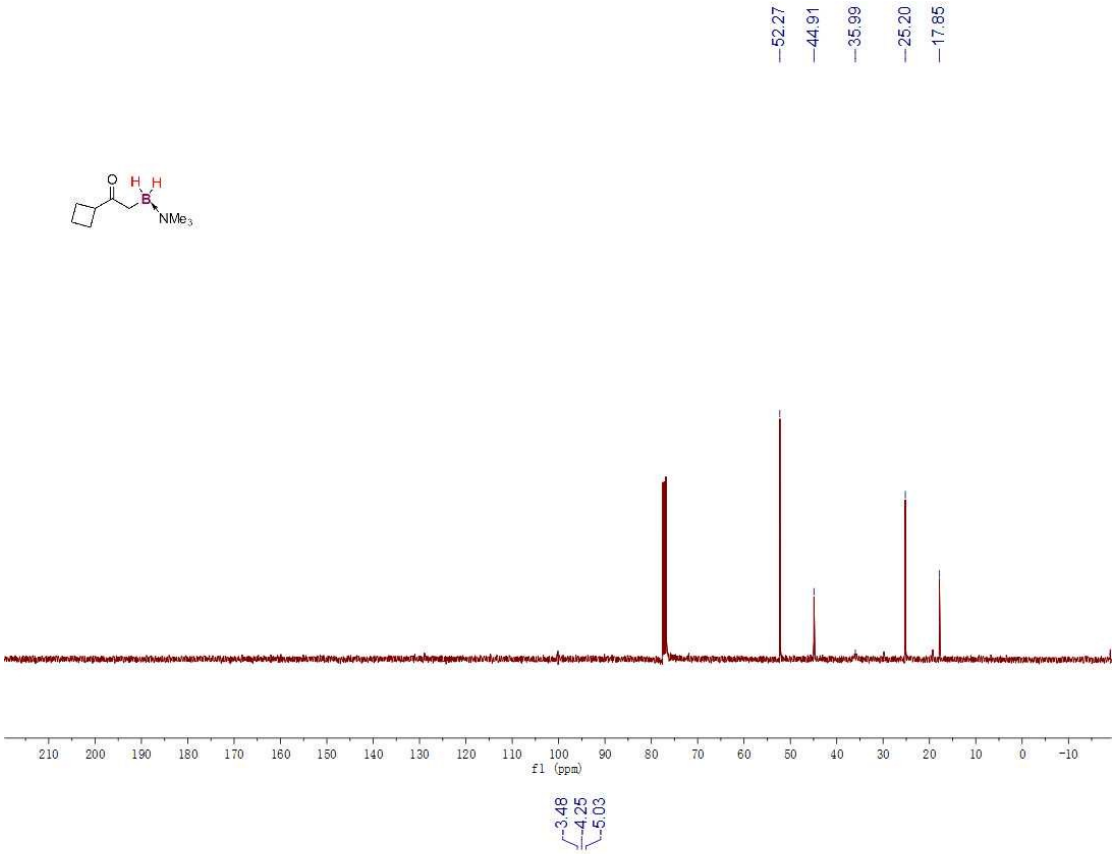
3.34
4.11
4.89
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

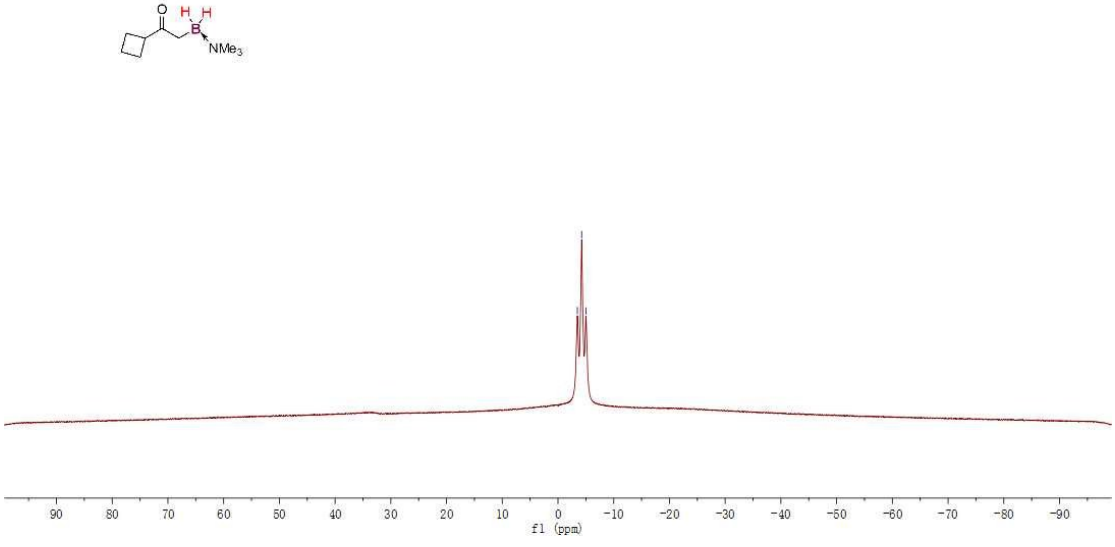

2.57
2.05
0.89
0.88
0.87
0.86
0.86
0.74
0.73
0.72
0.71
0.70
0.69
NMe3
9.00
3.11
2.08
2.00
f1 (ppm)

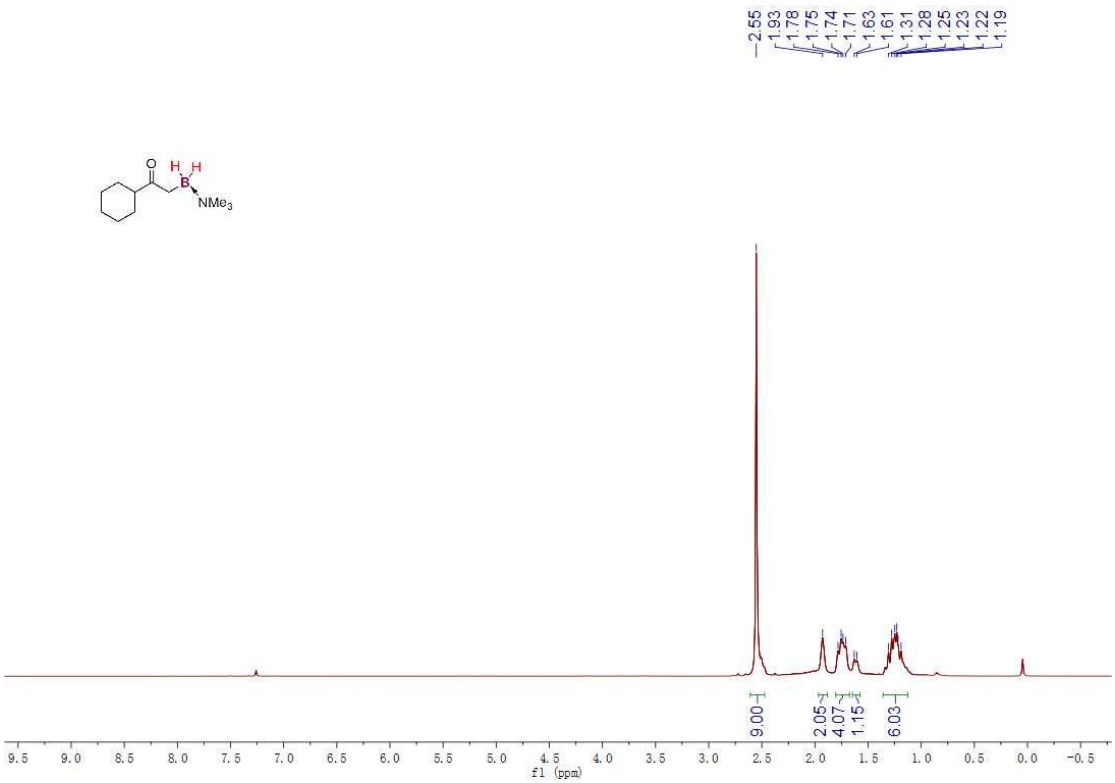

218.51
52.29
39.45
20.09
9.80
NMe3
f1 (ppm)

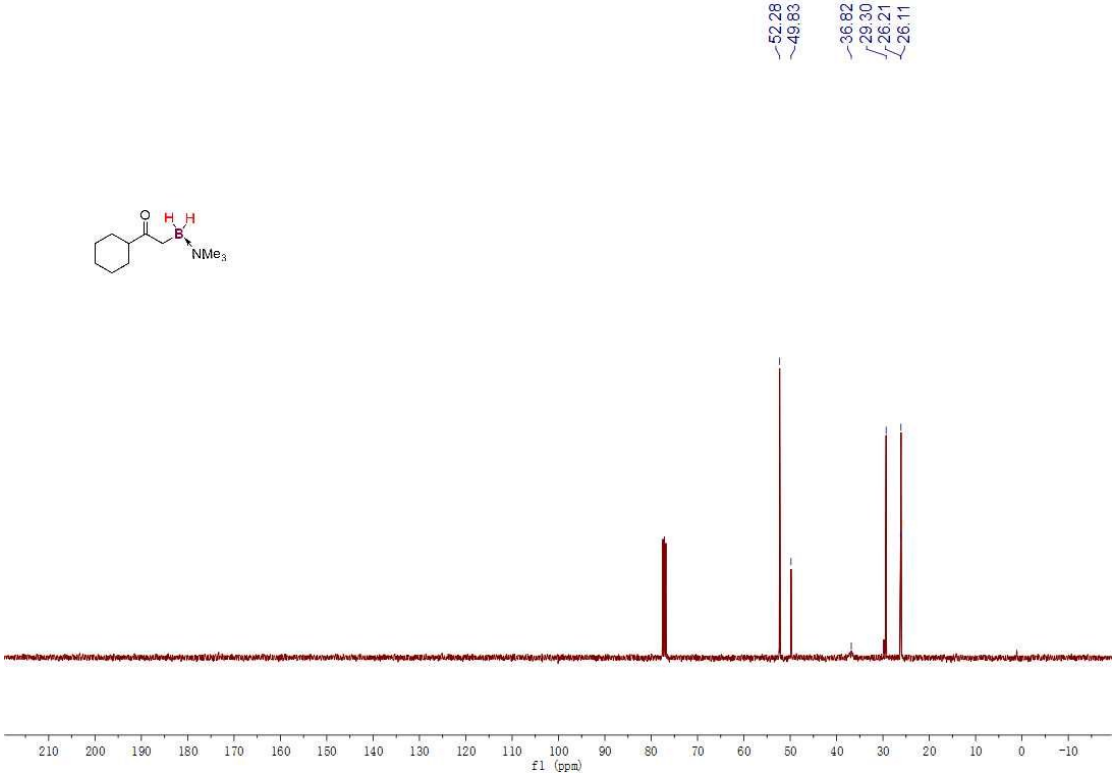

3.40
4.18
4.97
NMe3
f1 (ppm)
2.59
2.28
2.27
2.25
2.25
2.23
2.22
2.21
2.20
2.19
2.18
2.12
2.12
2.10
2.09
2.08
2.08
2.08
2.07
2.06
2.05
2.05
2.04
1.95
1.95
1.93
1.91
1.90
1.88
1.86
1.82
1.82
1.81
1.80
1.79
1.79
1.79
1.78
1.78
1.77
1.77
1.76
1.76
1.74
1.74
1.73

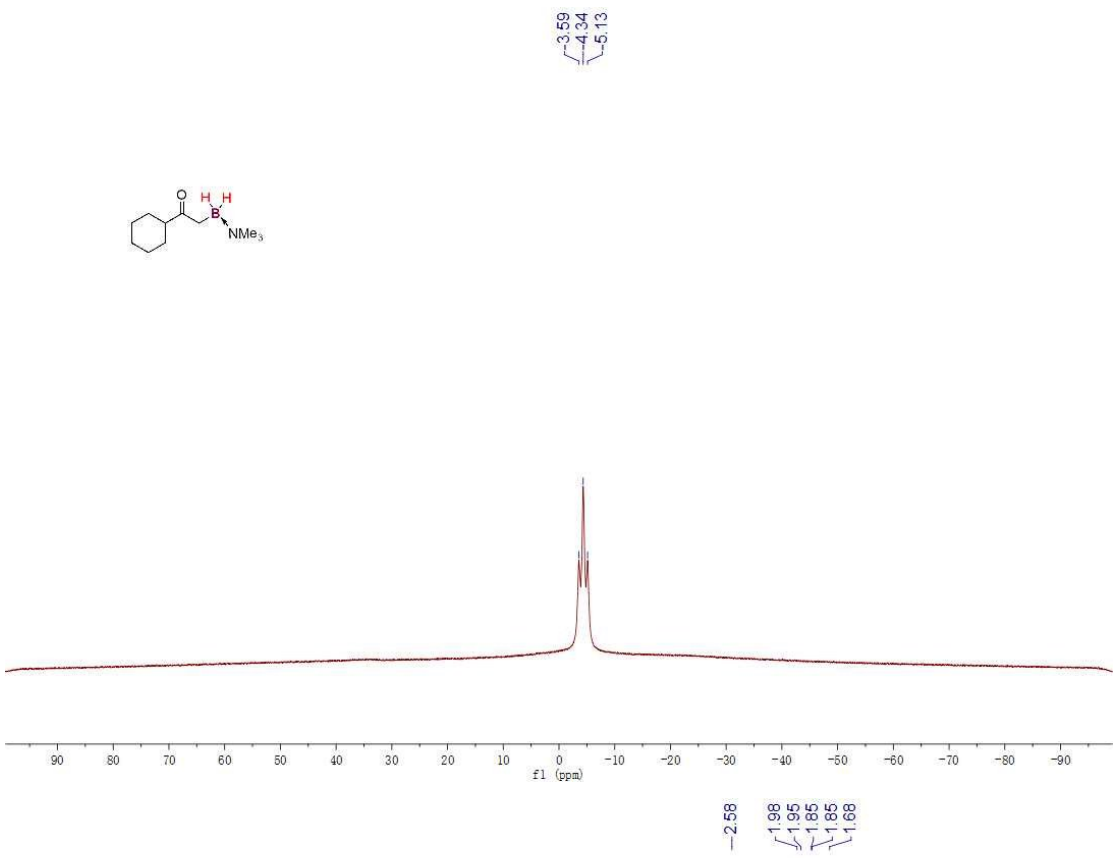

NMe3
9.00
2.24
2.22
3.17
2.01
f1 (ppm)

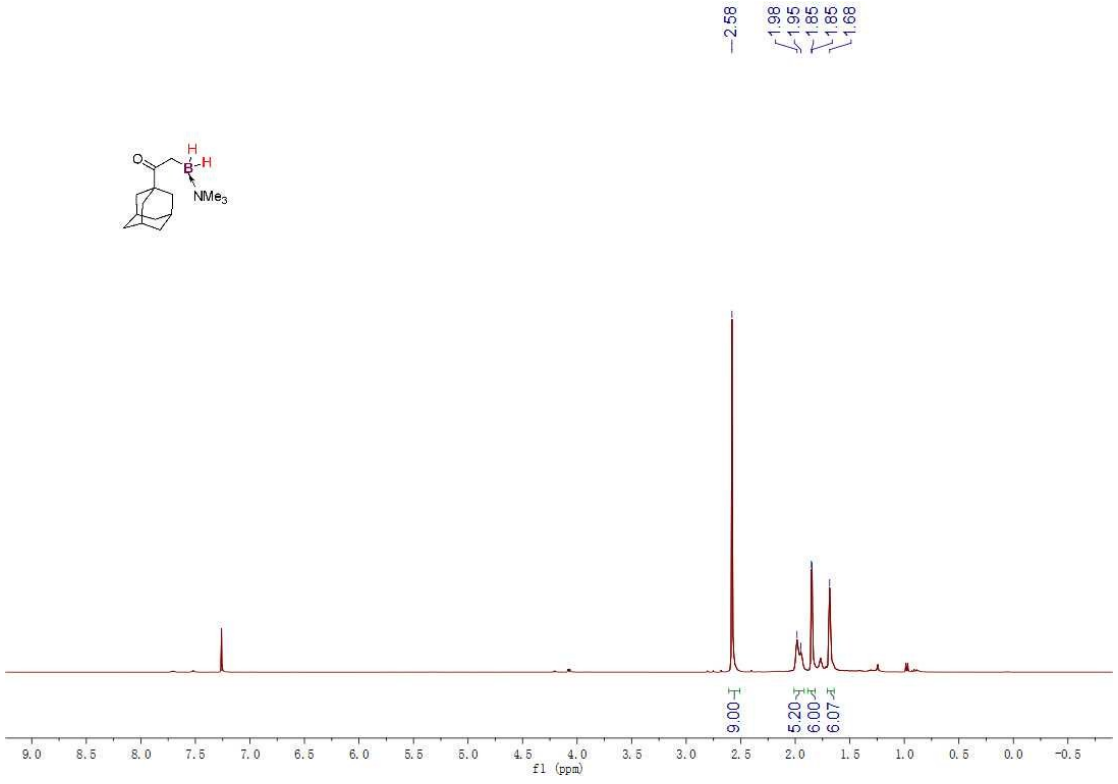

52.27
44.91
35.99
25.20
17.85
O
H
H
B
NMe3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

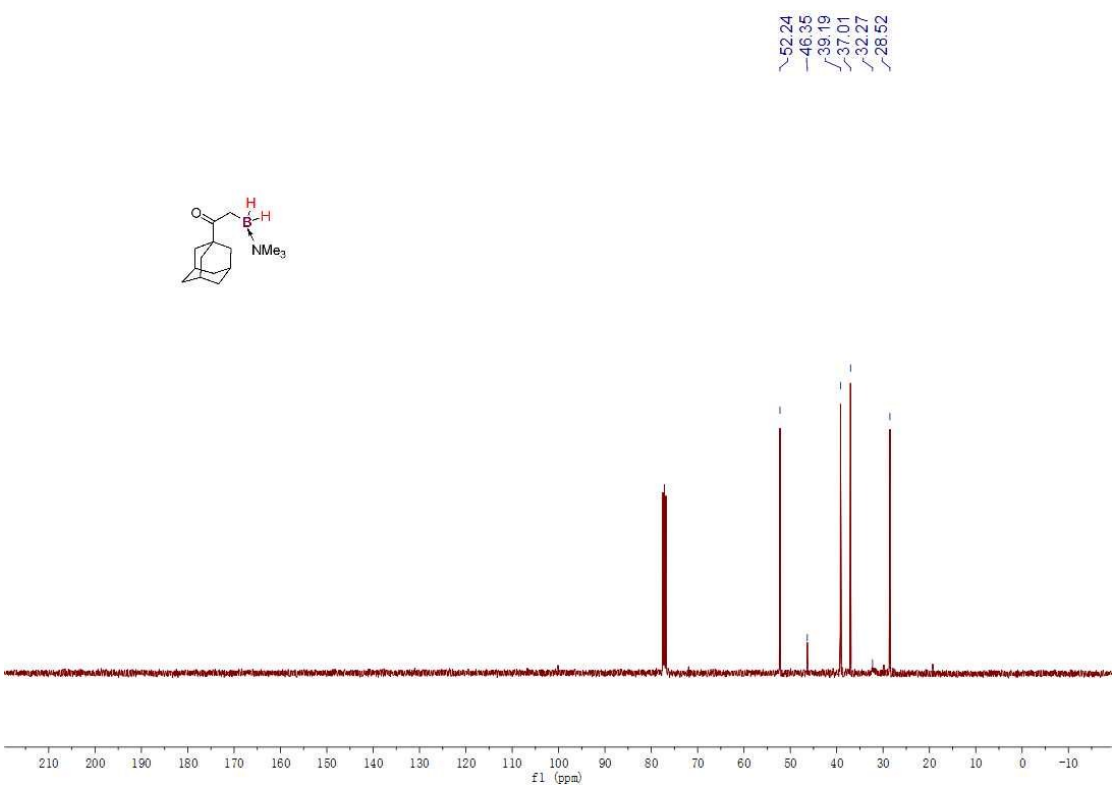

3.48
4.25
5.03
O
H
H
B
NMe3
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

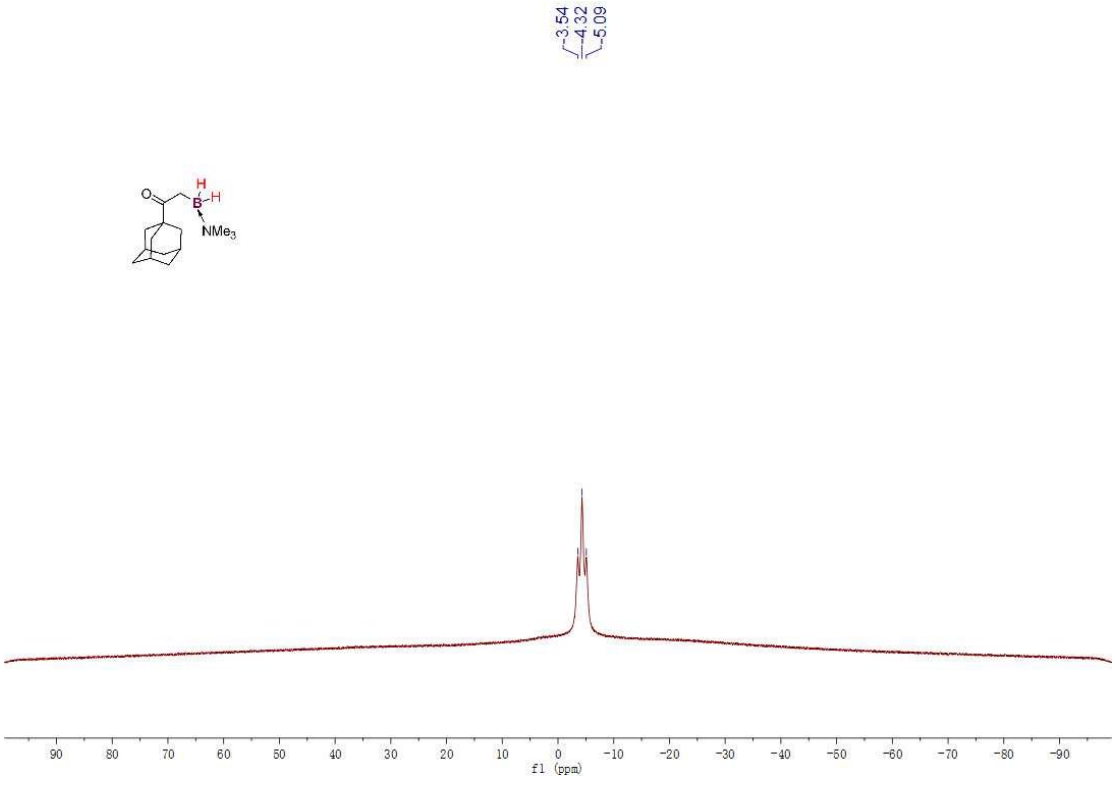

2.55
1.93
1.78
1.75
1.74
1.71
1.63
1.61
1.31
1.28
1.25
1.23
1.22
1.19
O
H
H
B
NMe3
9.00
2.05
4.07
1.15
6.03
f1 (ppm)


52.28
49.83
36.82
29.30
26.21
26.11
O
H
H
B
NMe3
f1 (ppm)

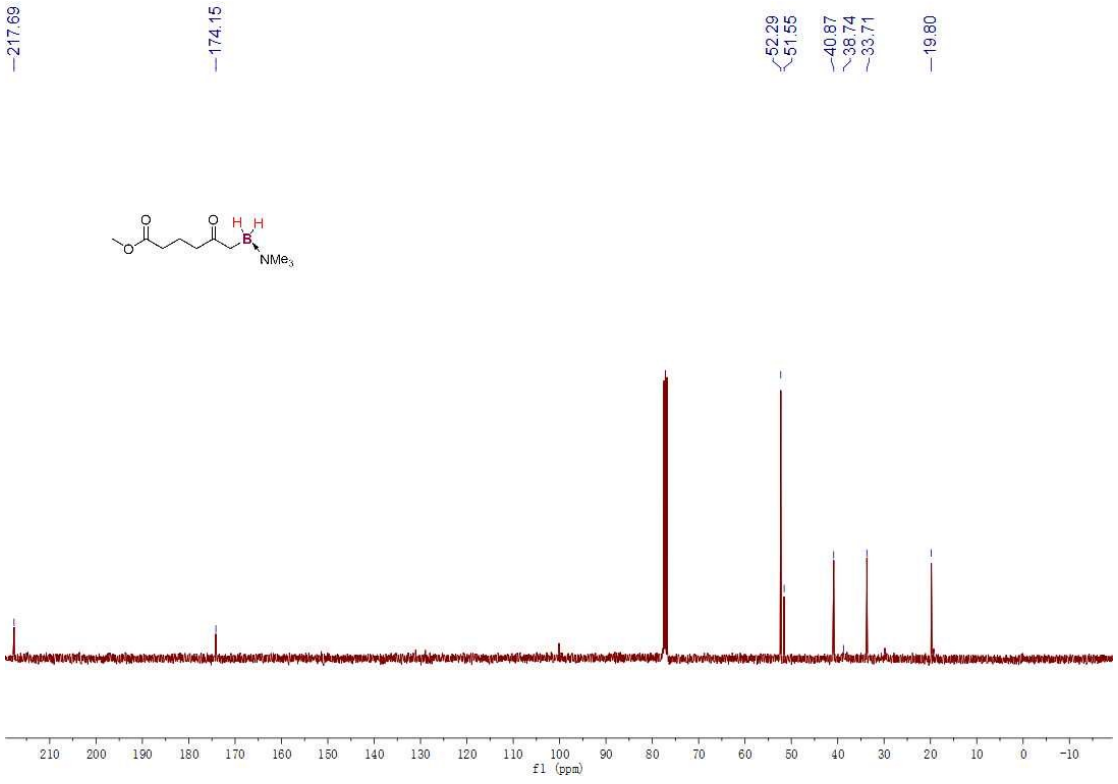

3.59
4.34
5.13
O
H
H
B
NMe3
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

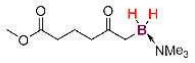

2.58
1.98
1.95
1.85
1.85
1.68
O
H
B
H
NMe3
9.00
5.20
6.00
6.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

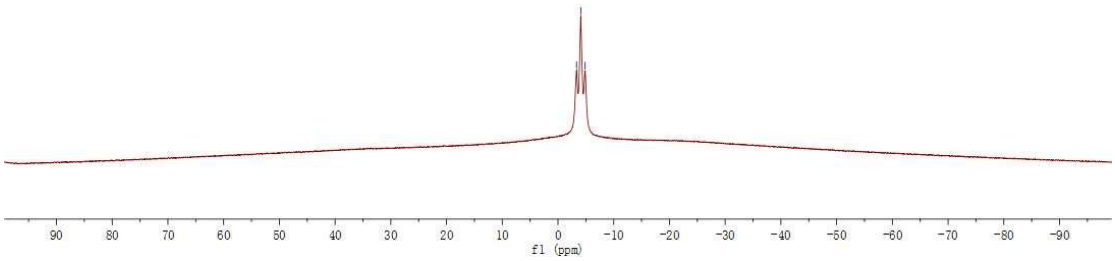

52.24
46.35
39.19
37.01
32.27
28.52
O
H
B
H
NMe3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

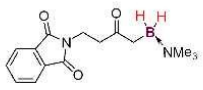

3.54
4.32
5.09
O
H
B
H
NMe3
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

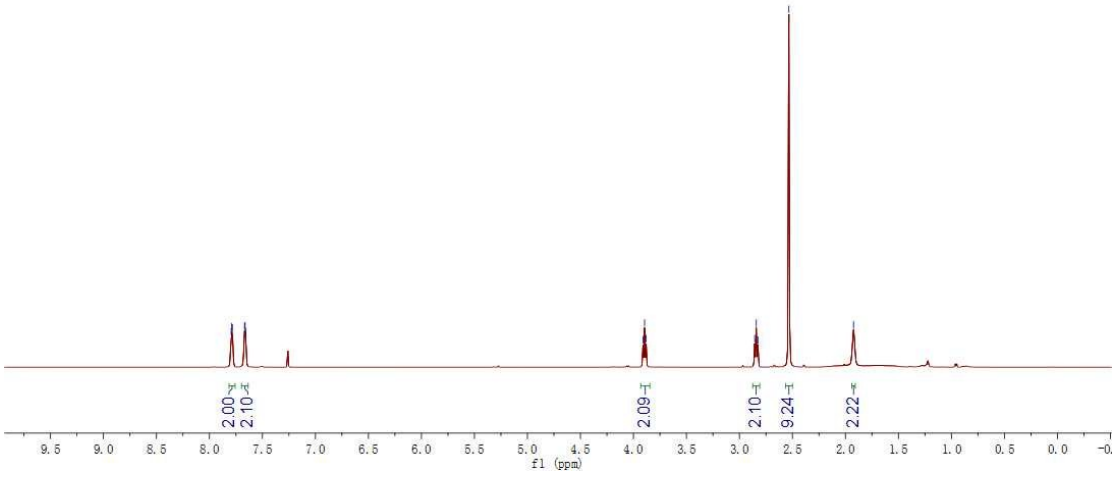

3.65
2.56
2.50
2.48
2.46
2.33
2.31
2.29
1.92
1.89
1.87
1.85
1.84
1.82
O
O
H
H
B
NMe3
3.00
8.92
2.28
2.09
2.18
2.26
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

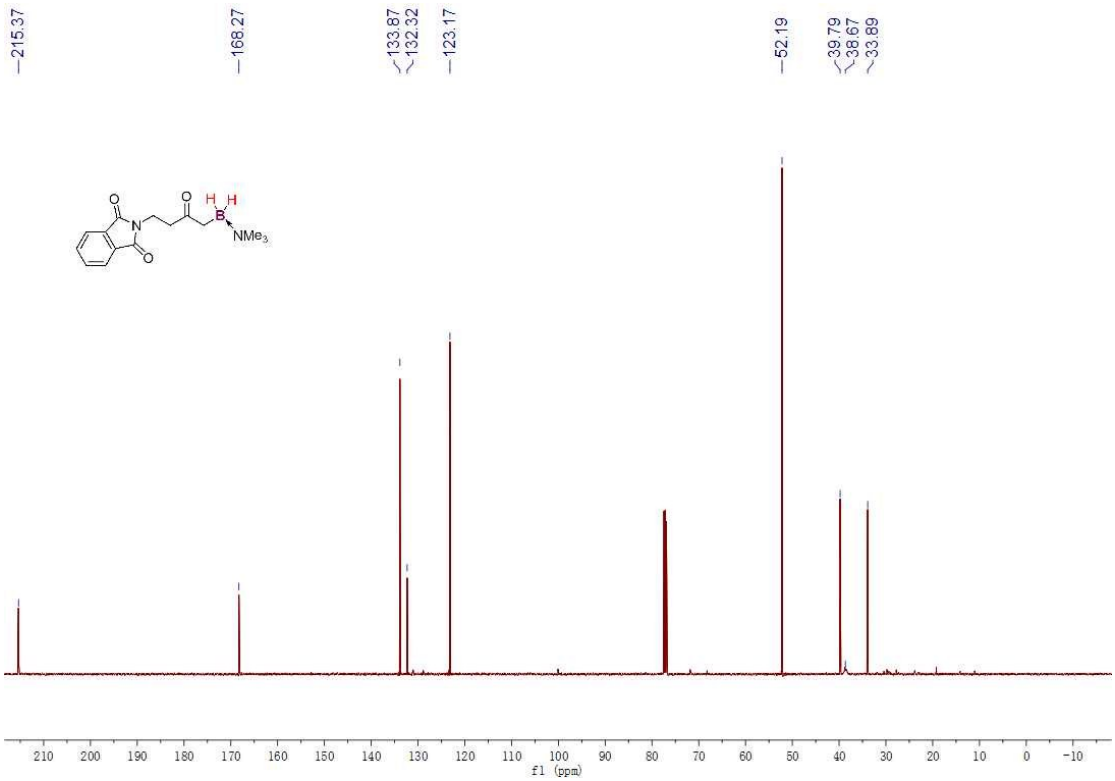

217.69
174.15
52.29
51.55
40.87
38.74
33.71
19.80
O
O
H
H
B
NMe3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

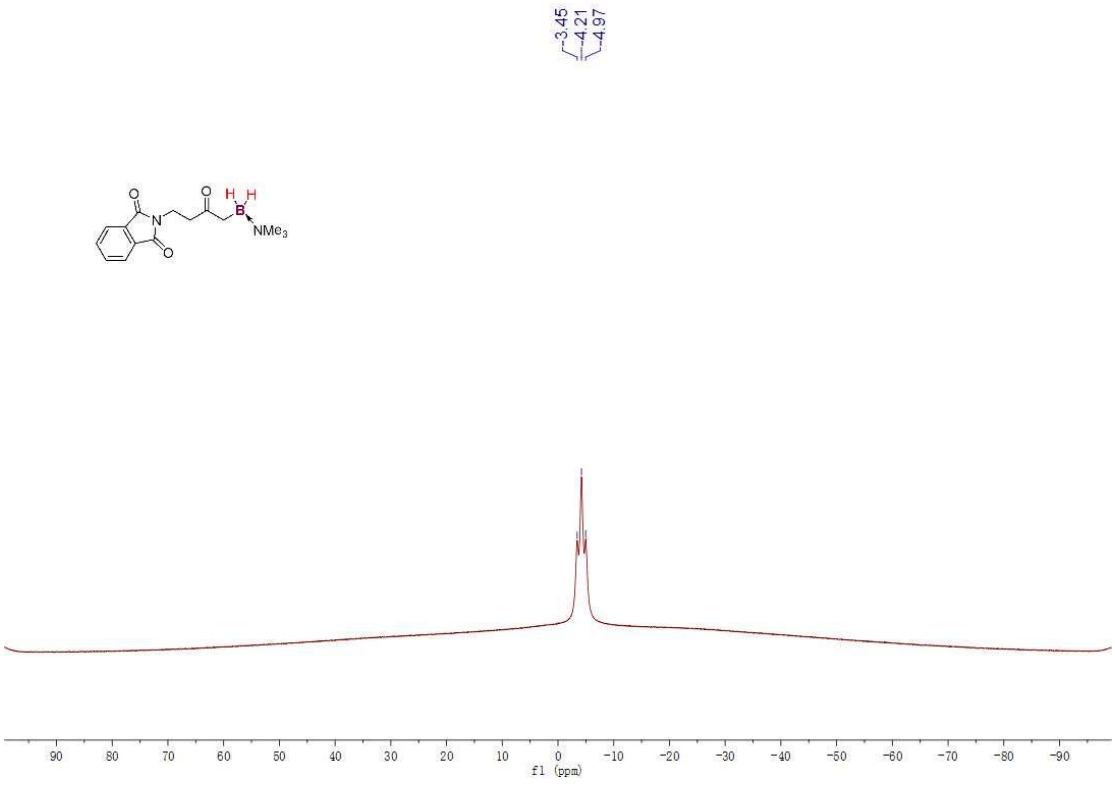


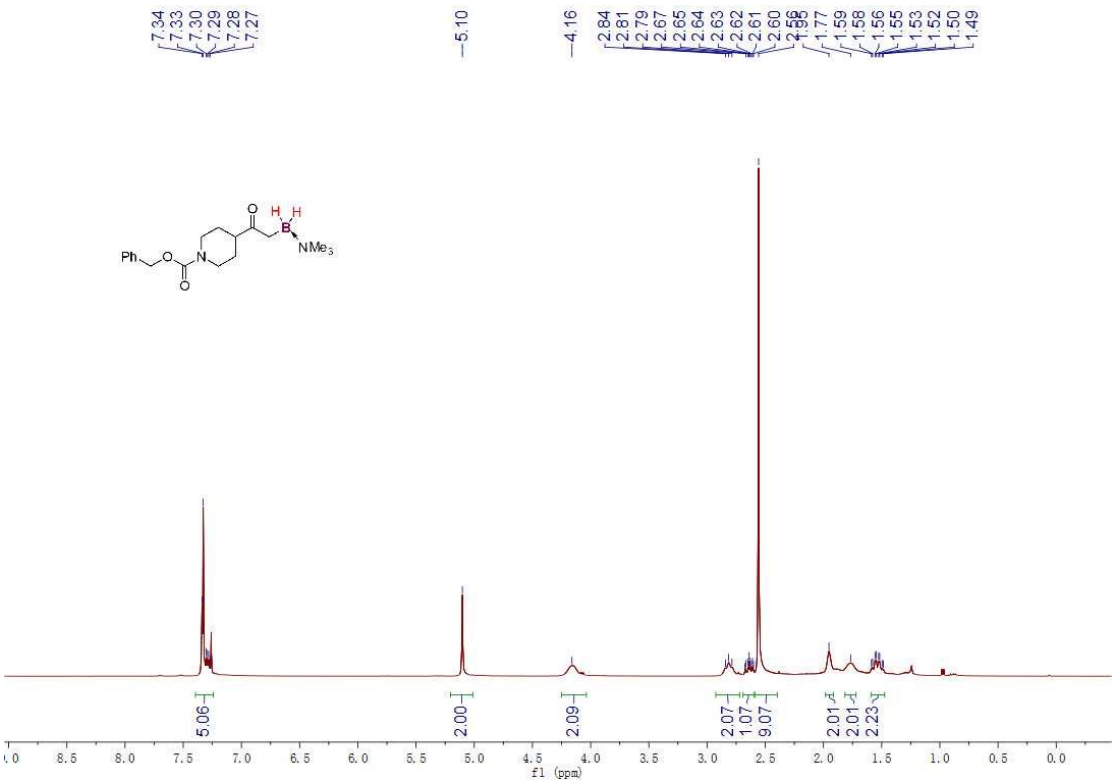


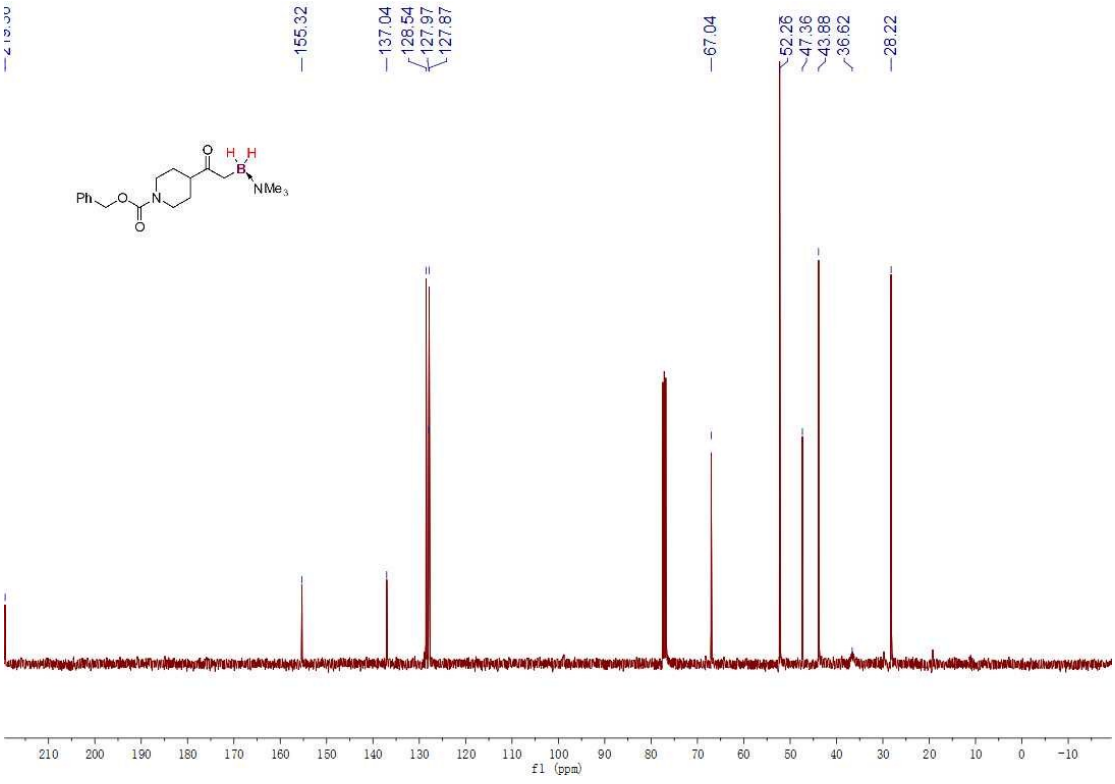


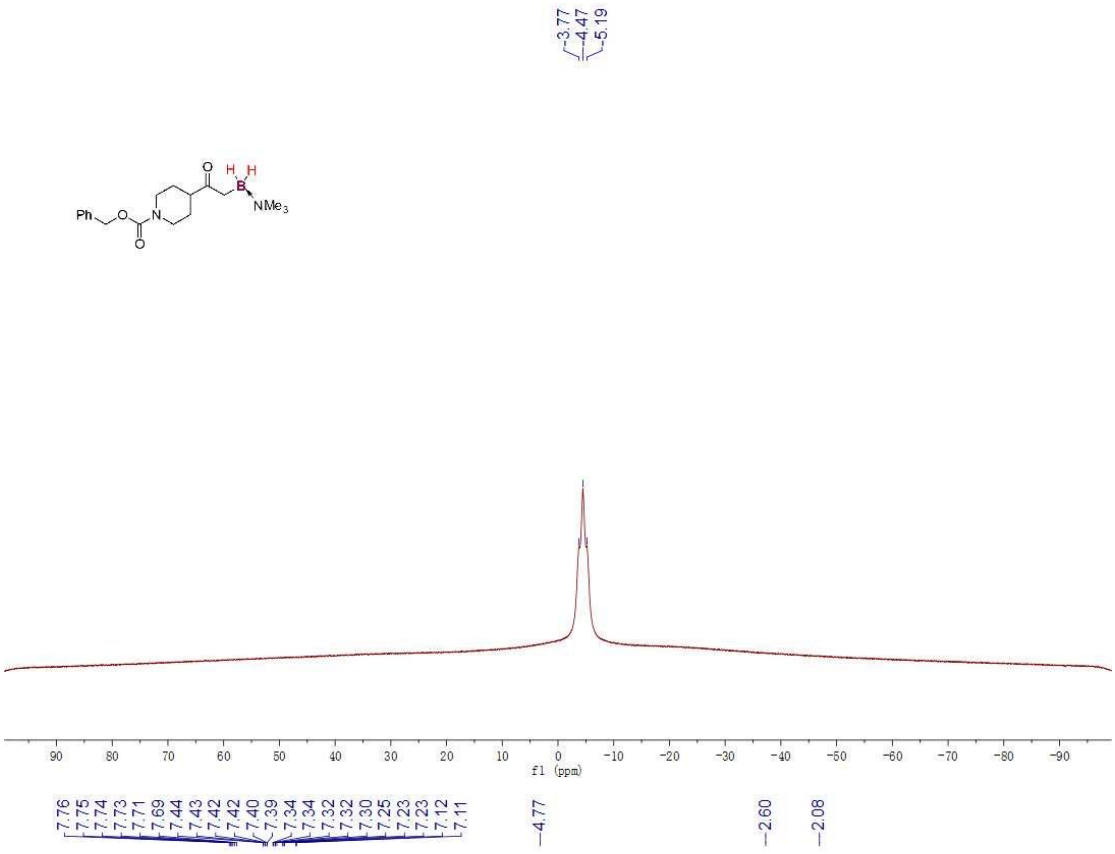


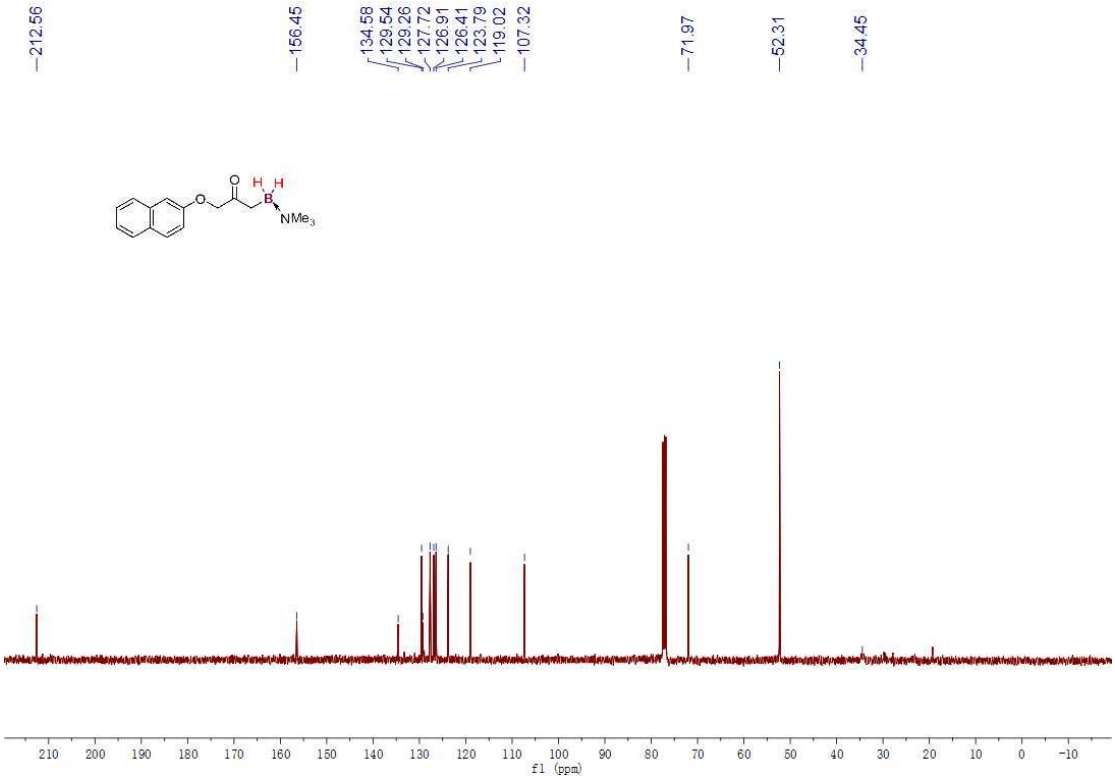

215.37
168.27
133.87
132.32
123.17
52.19
39.79
38.67
33.89
NMe3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

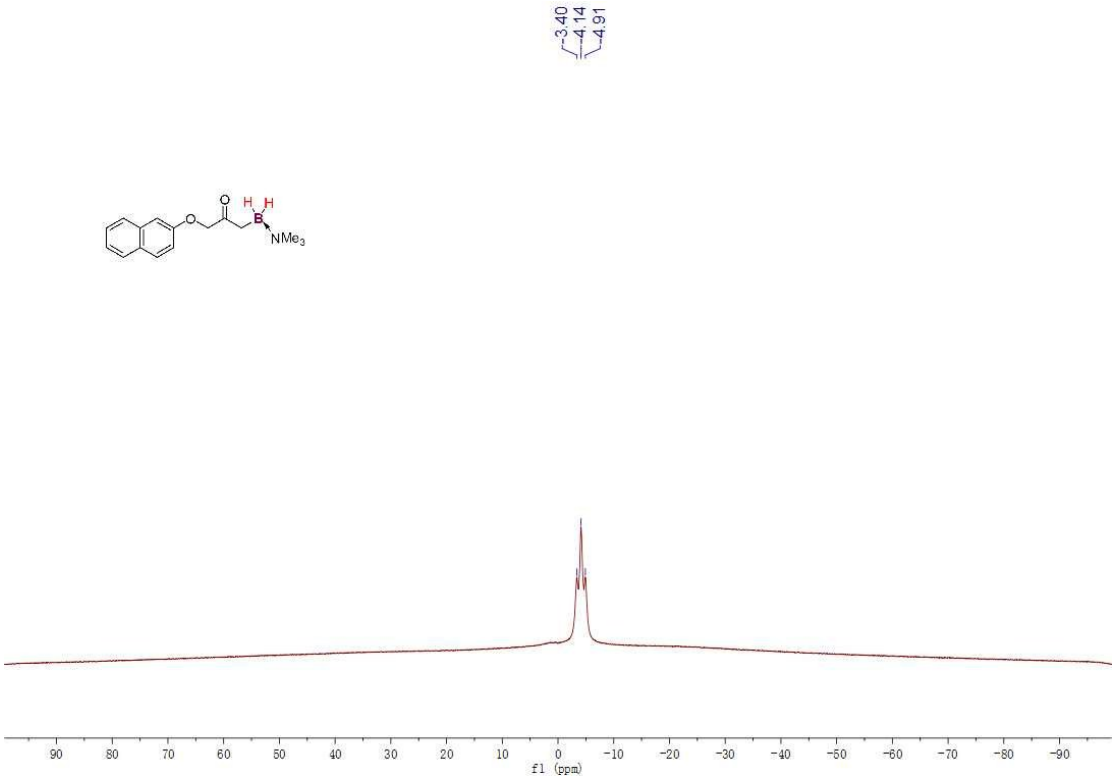

3.45
4.21
4.97
NMe3
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

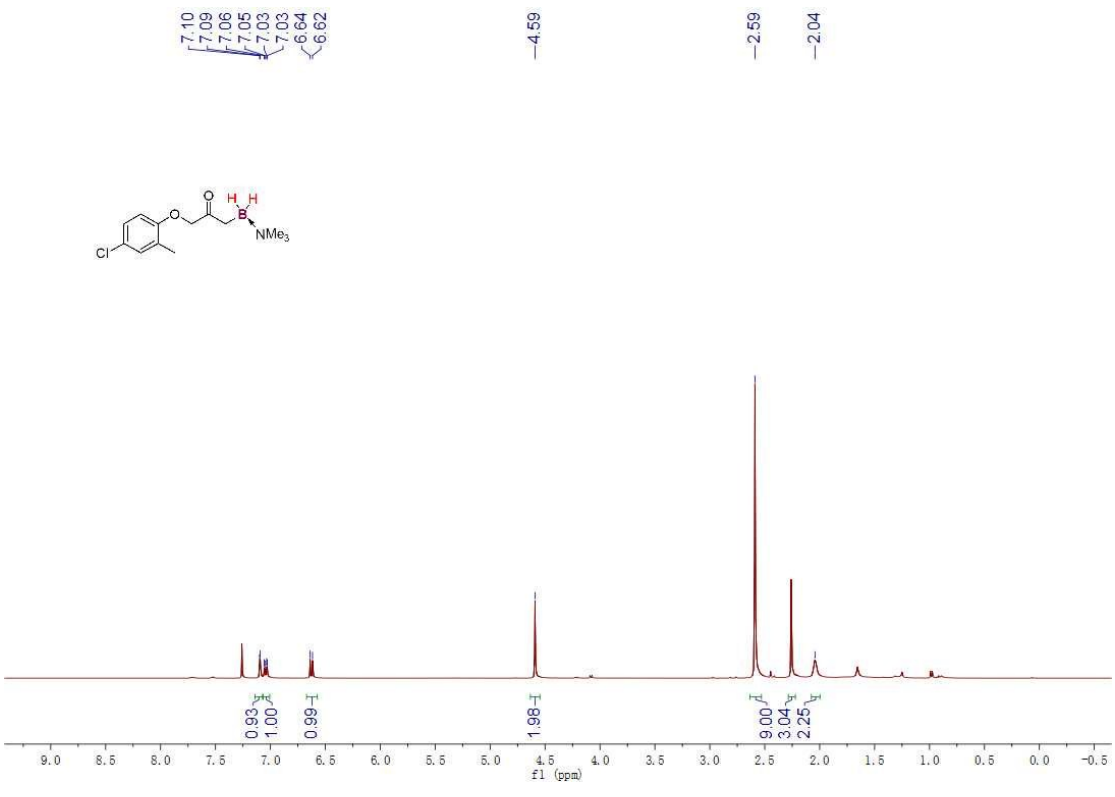

7.34
7.33
7.30
7.29
7.28
7.27
5.10
4.16
2.84
2.81
2.79
2.67
2.65
2.64
2.63
2.62
2.61
2.60
1.77
1.59
1.58
1.56
1.55
1.53
1.52
1.50
1.49
Ph
O
N
O
O
H
H
B
NMe3
5.06
2.00
2.09
2.07
1.07
9.07
2.01
2.01
2.23
f1 (ppm)

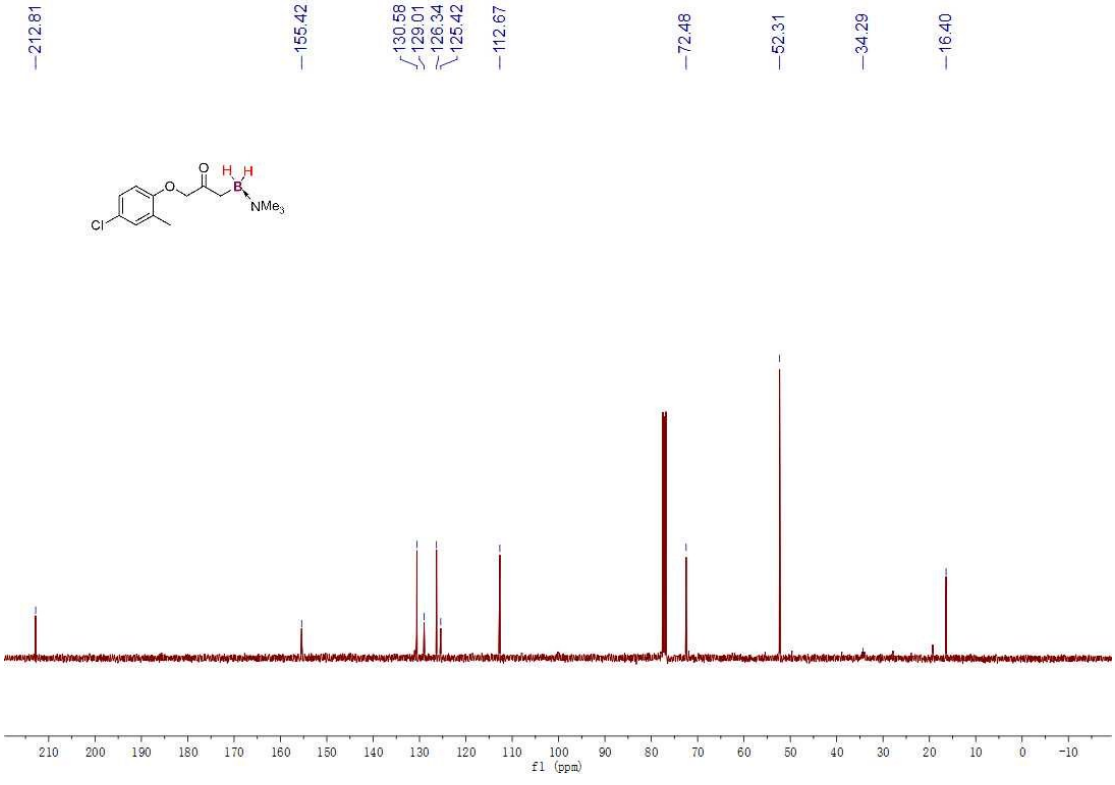

155.32
137.04
128.54
127.97
127.87
67.04
52.26
47.36
43.88
36.62
28.22
Ph
O
N
O
O
H
H
B
NMe3
f1 (ppm)

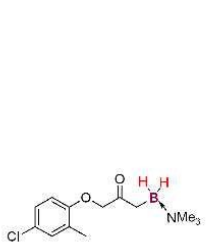

3.77
4.47
5.19
Ph
O
N
O
O
H
H
B
NMe3
f1 (ppm)
7.76
7.75
7.74
7.73
7.71
7.69
7.44
7.43
7.42
7.42
7.40
7.39
7.34
7.34
7.32
7.32
7.30
7.25
7.23
7.23
7.12
7.11
4.77
2.60
2.08
O
H
H
B
NMe3
3.07
1.00
1.00
0.95
0.99
2.09
9.09
2.13
f1 (ppm)


212.56
156.45
134.58
129.54
129.26
127.72
126.91
126.41
123.79
119.02
107.32
71.97
52.31
34.45
NMe3
f1 (ppm)

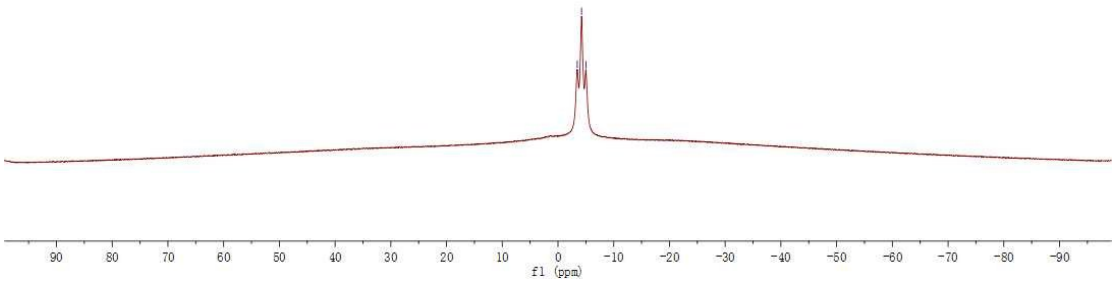

3.40
4.14
4.91
NMe3
f1 (ppm)


7.10
7.09
7.06
7.05
7.03
7.03
6.64
6.62
4.59
2.59
2.04
O
H
H
B
NMe3
Cl
0.93
1.00
0.99
1.98
9.00
3.04
2.25
f1 (ppm)


212.81
155.42
130.58
129.01
126.34
125.42
112.67
72.48
52.31
34.29
16.40
O
H
H
B
NMe3
Cl
f1 (ppm)



3.45
4.22
5.01



7.47
7.46
7.29
7.27
7.25
7.14
7.12
7.11

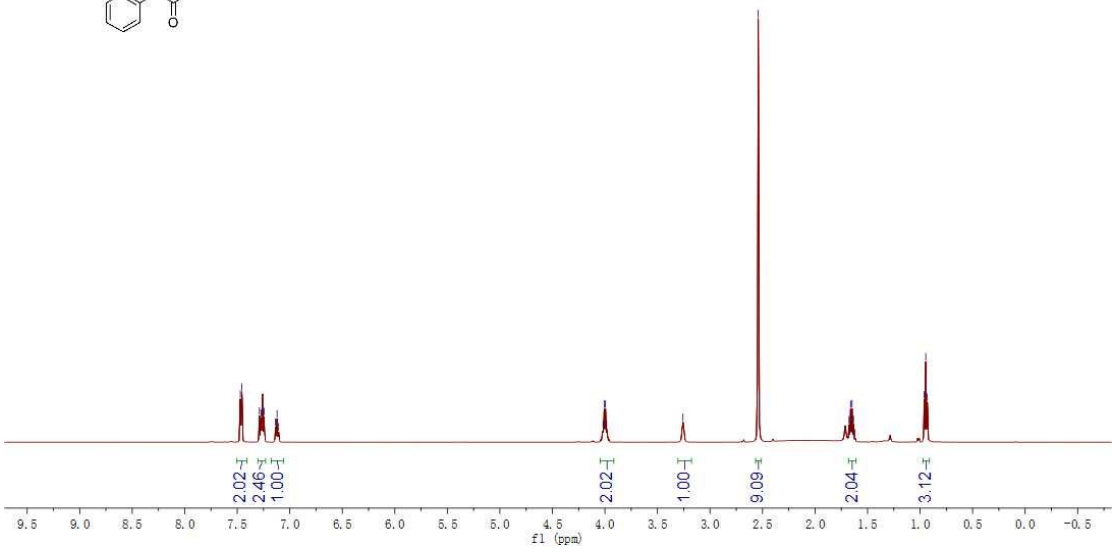
4.02
4.01
3.99
3.98

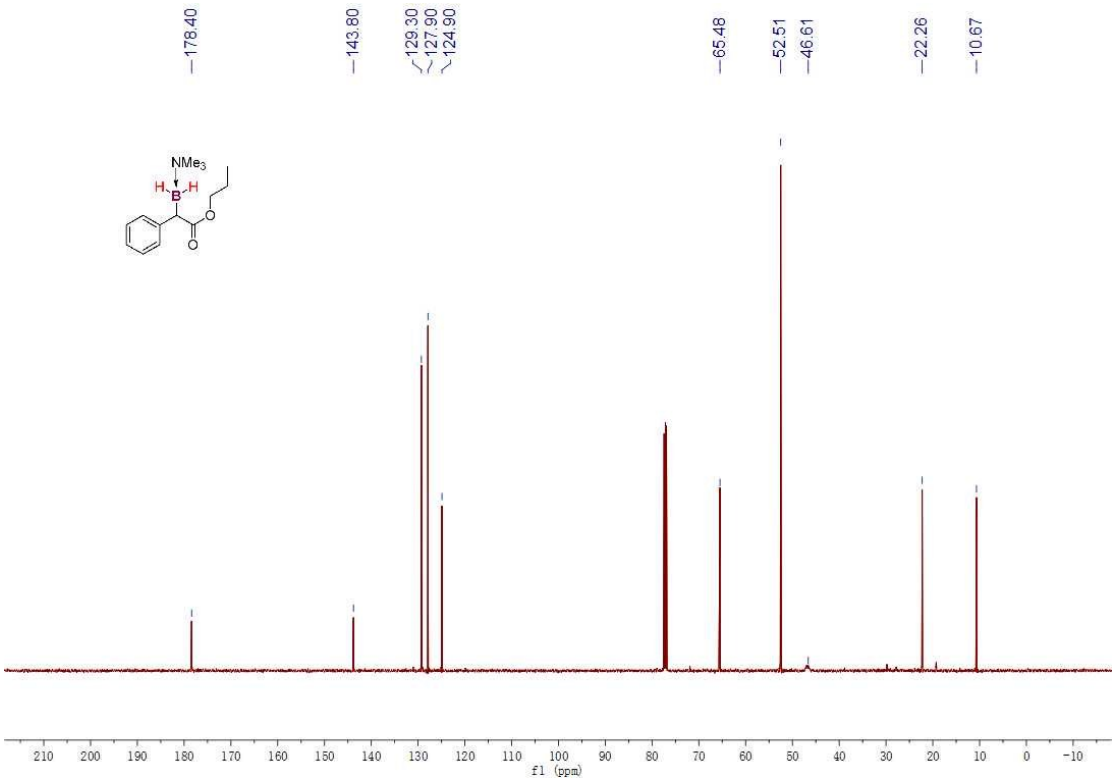
3.26

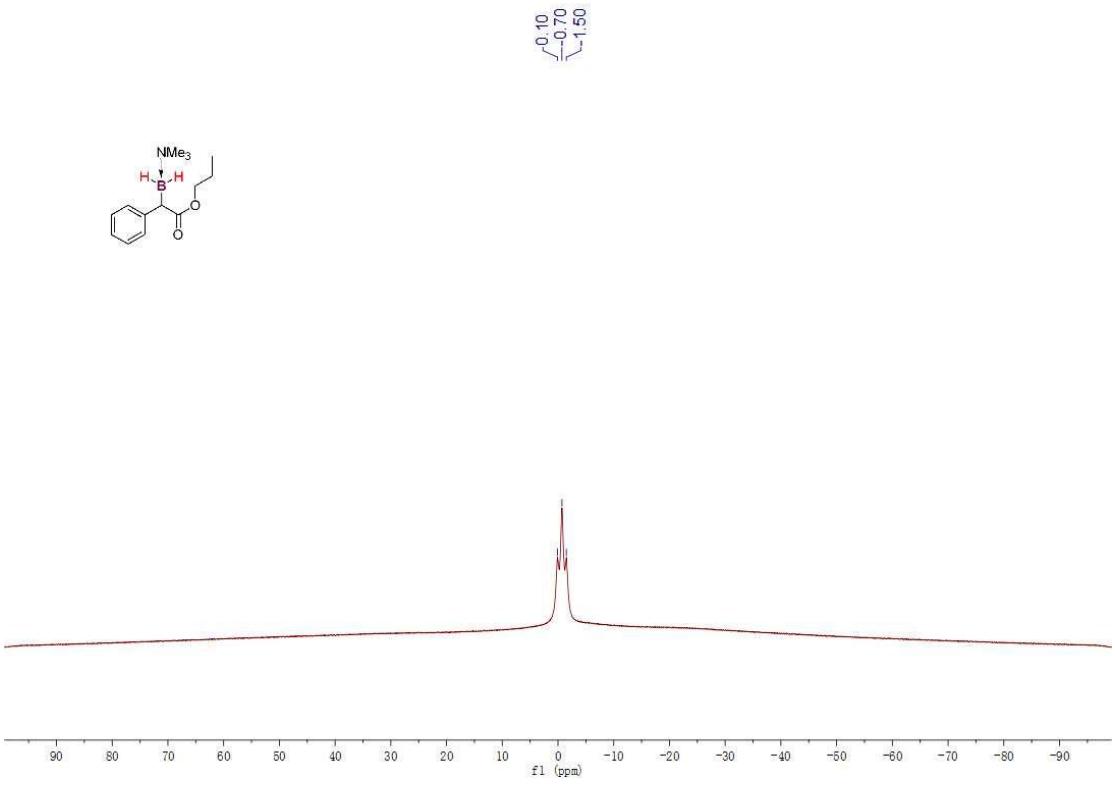
2.54

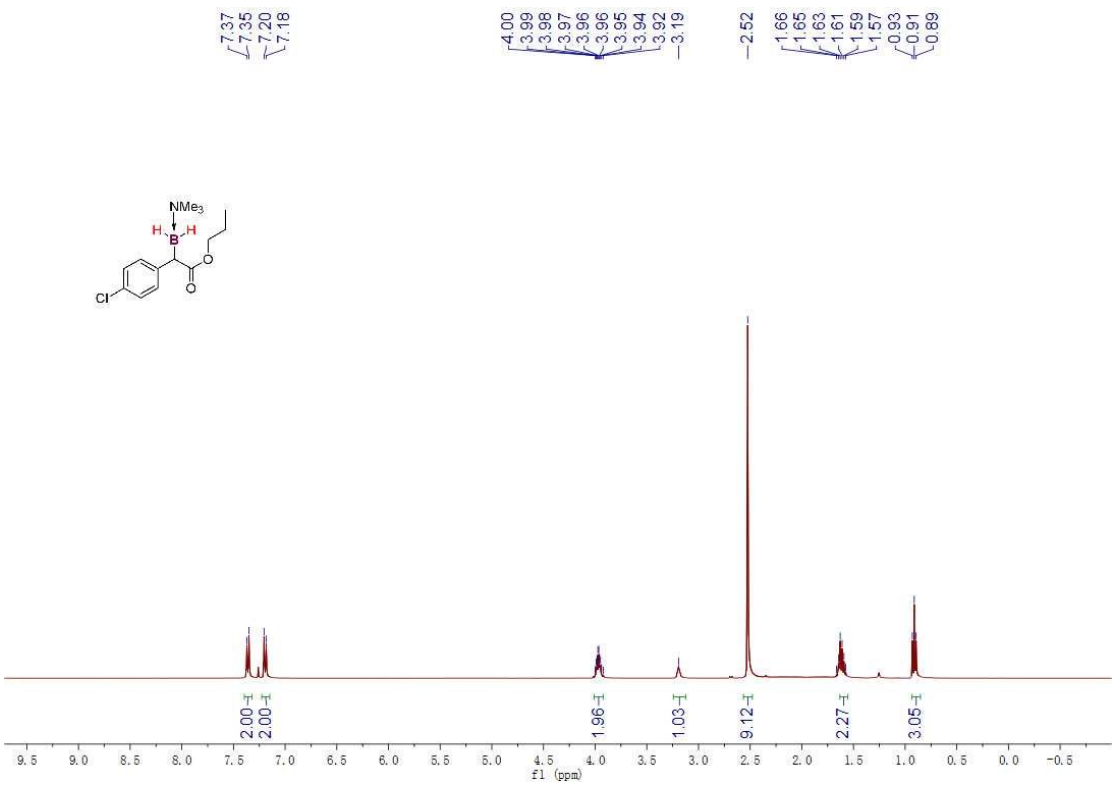
1.68
1.66
1.65
1.63
1.62

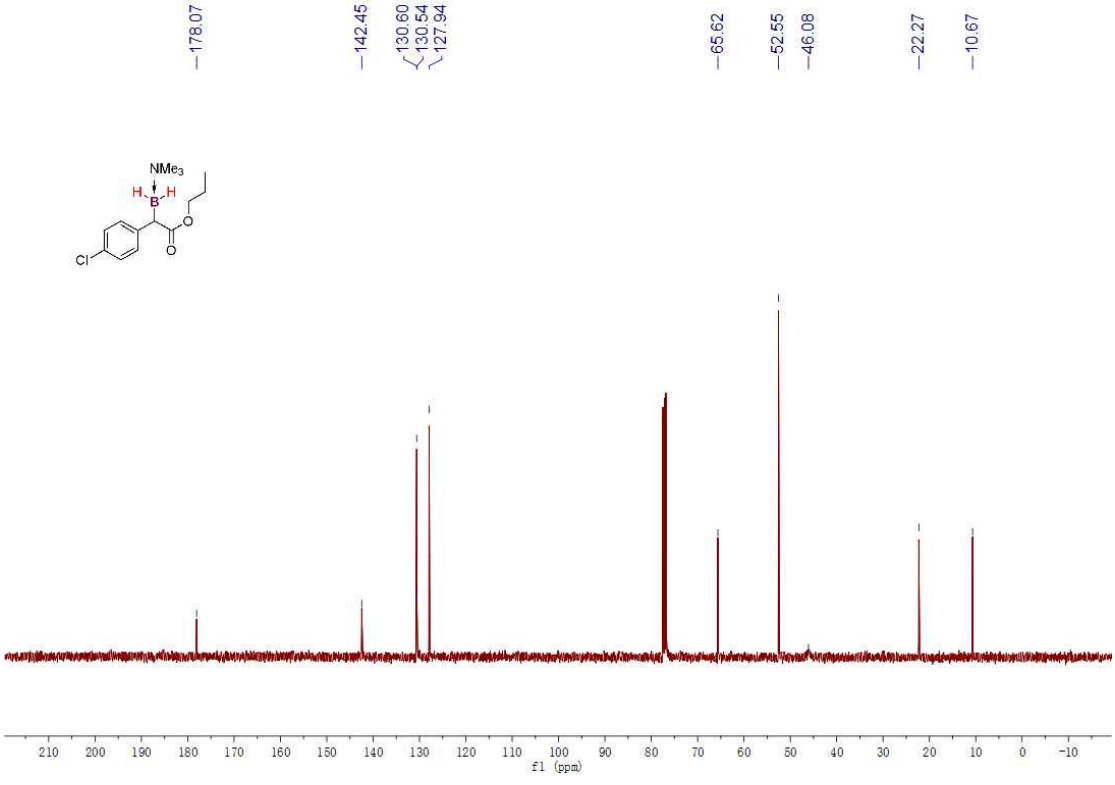
0.96
0.95
0.93

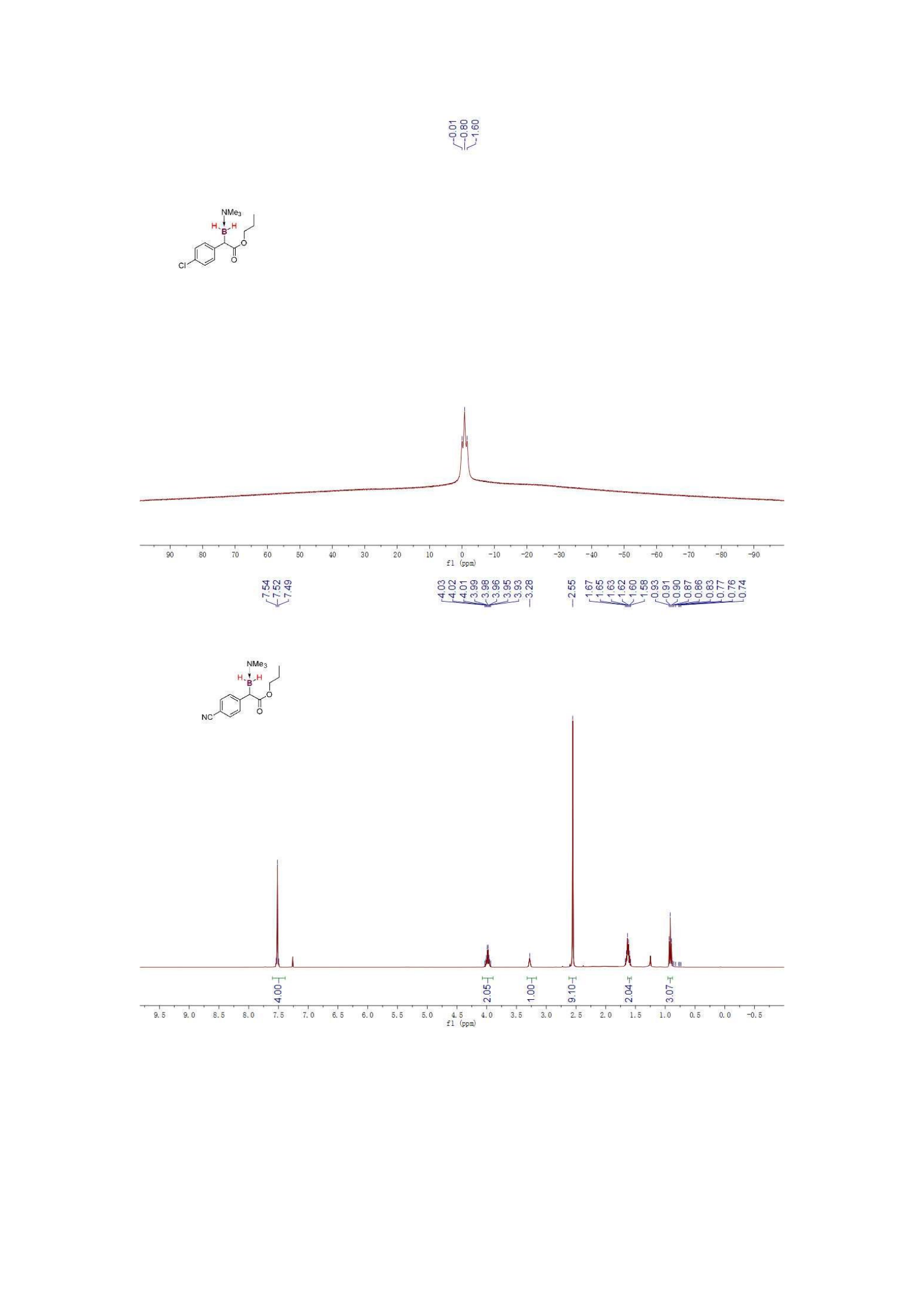


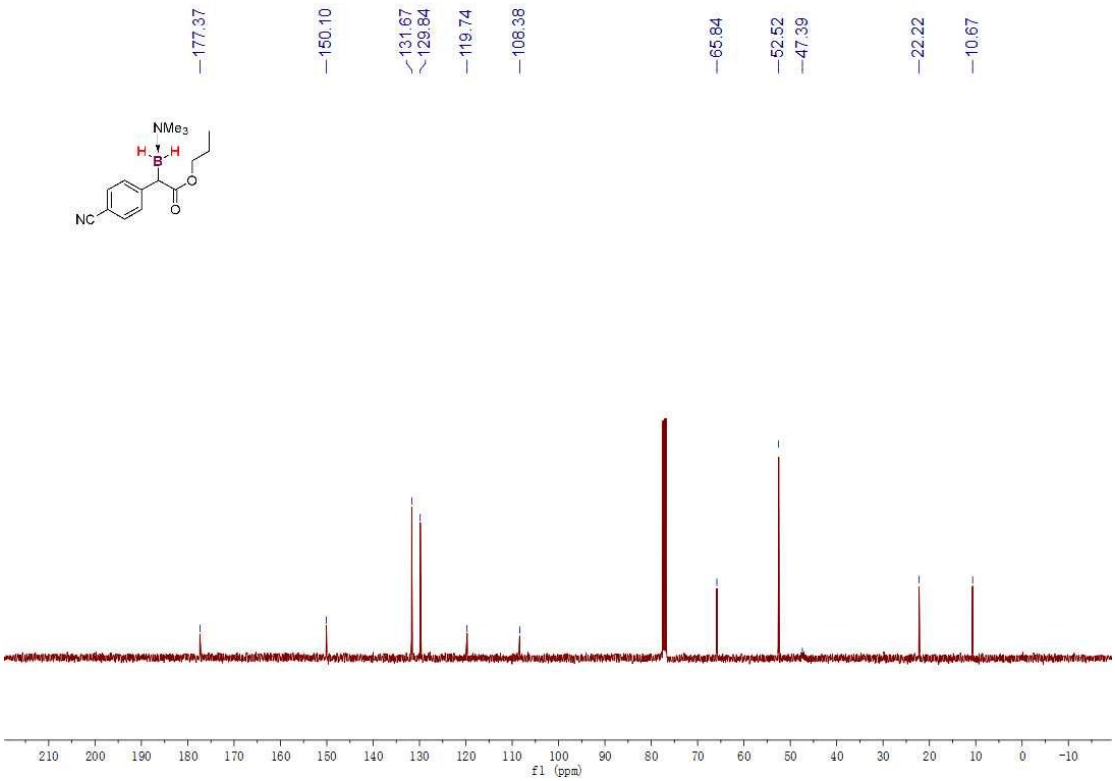

178.40
143.80
129.30
127.90
124.90
65.48
52.51
46.61
22.26
10.67
NMe3
H
B
H
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

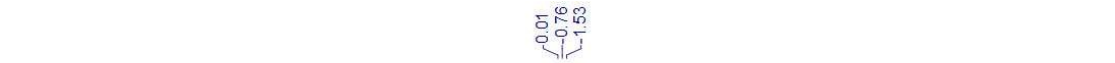

0.10
0.70
1.50
NMe3
H
B
H
O
O
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

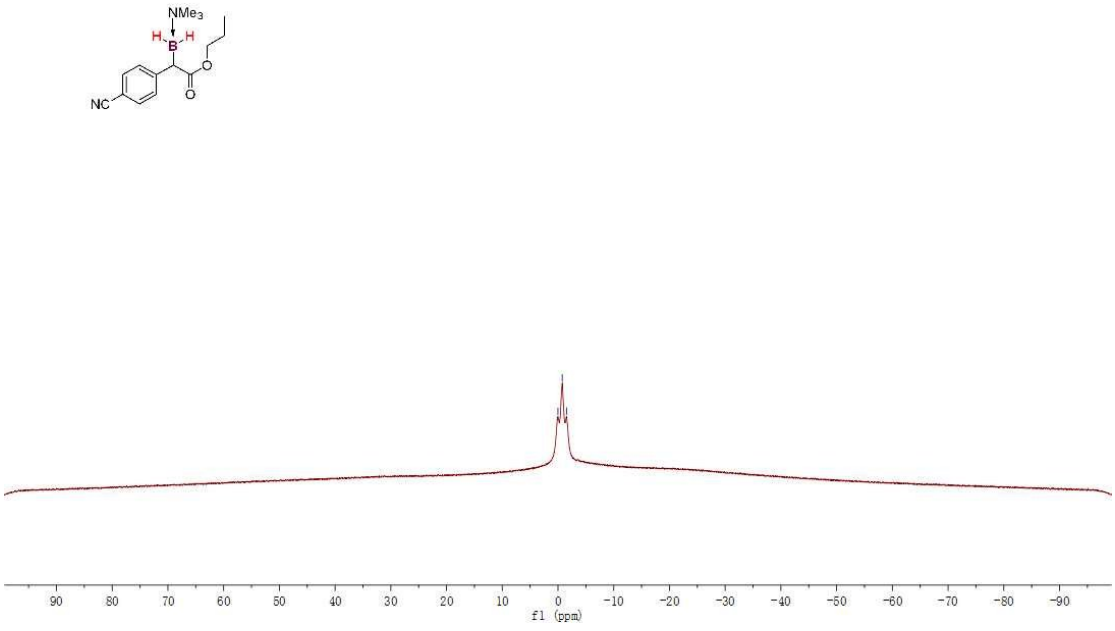

7.37
7.35
7.20
7.18
4.00
3.99
3.98
3.97
3.96
3.96
3.95
3.94
3.92
3.19
2.52
1.66
1.65
1.63
1.61
1.59
1.57
0.93
0.91
0.89
NMe3
H
B
H
O
O
Cl
2.00
2.00
1.96
1.03
9.12
2.27
3.05
f1 (ppm)

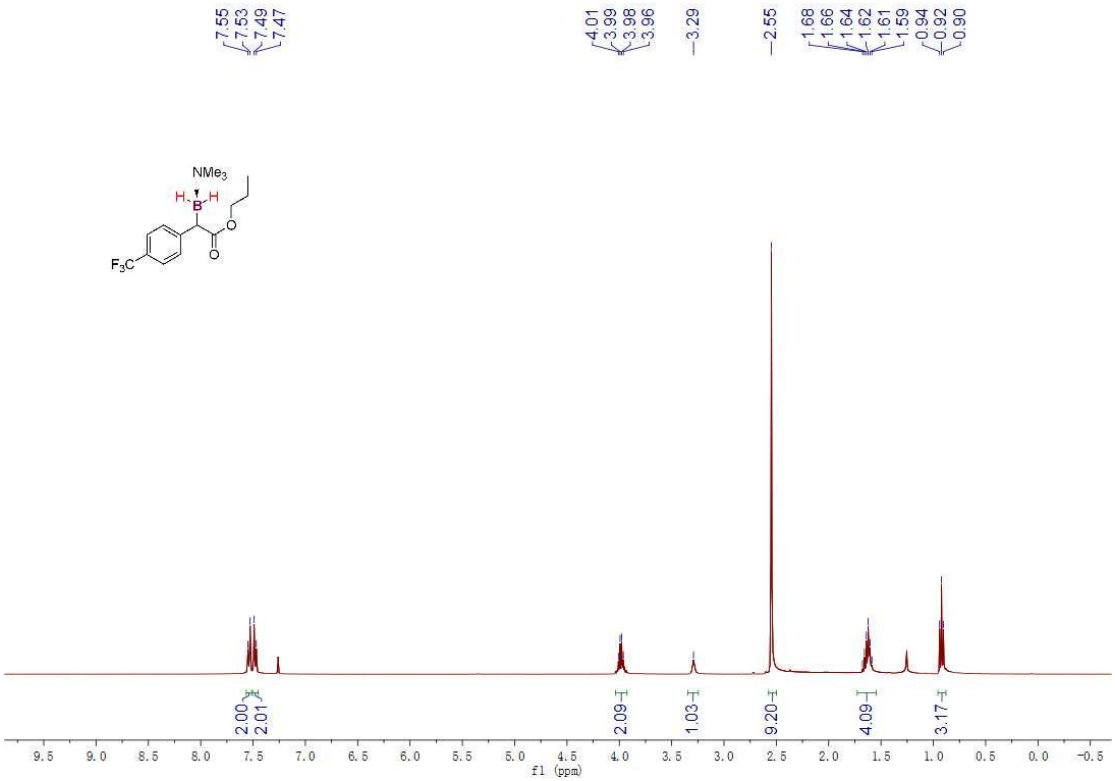

178.07
142.45
130.60
130.54
127.94
65.62
52.55
46.08
22.27
10.67
NMe3
H
B
H
O
O
Cl
f1 (ppm)


0.01
0.80
1.60
NMe3
H
B
H
O
O
Cl
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)
7.54
7.52
7.49
4.03
4.02
4.01
3.99
3.98
3.96
3.95
3.93
3.28
2.55
1.67
1.65
1.63
1.62
1.60
1.58
0.93
0.91
0.90
0.87
0.86
0.83
0.77
0.76
0.74
NMe3
H
B
H
O
O
NC
4.00
2.05
1.00
9.10
2.04
3.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


177.37
150.10
131.67
129.84
119.74
108.38
65.84
52.52
47.39
22.22
10.67
NMe3
H
B
H
O
O
NC
f1 (ppm)


0.01
0.76
1.53


NMe3
H
B
H
O
O
NC
f1 (ppm)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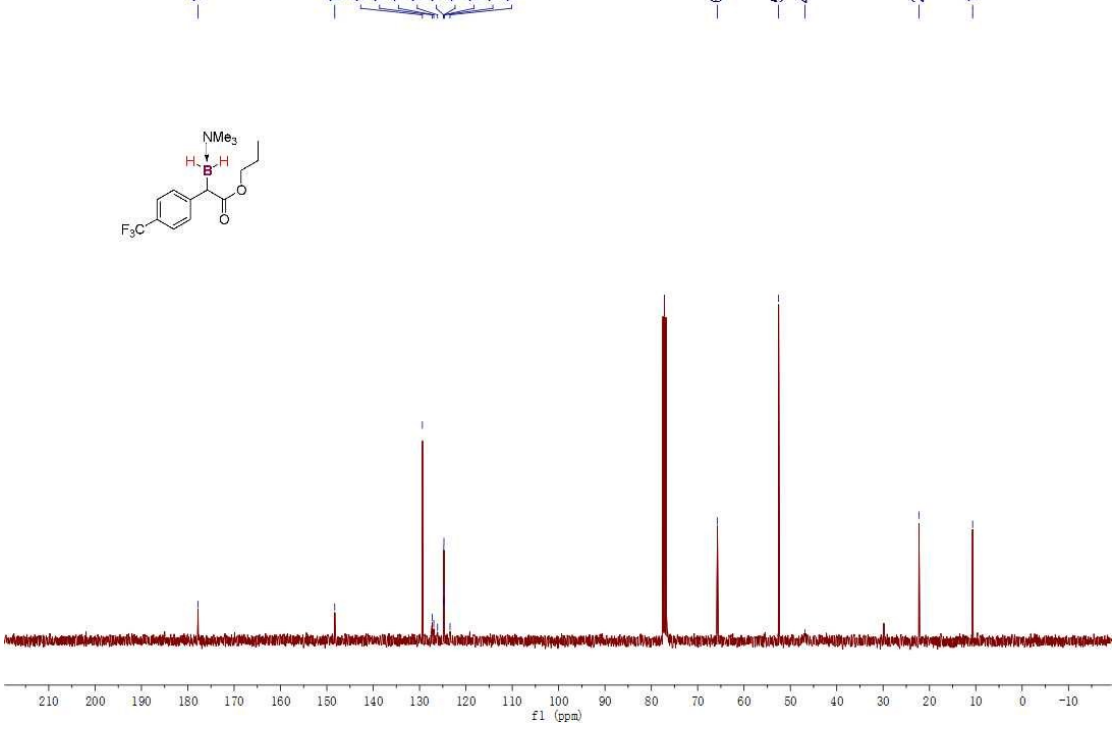
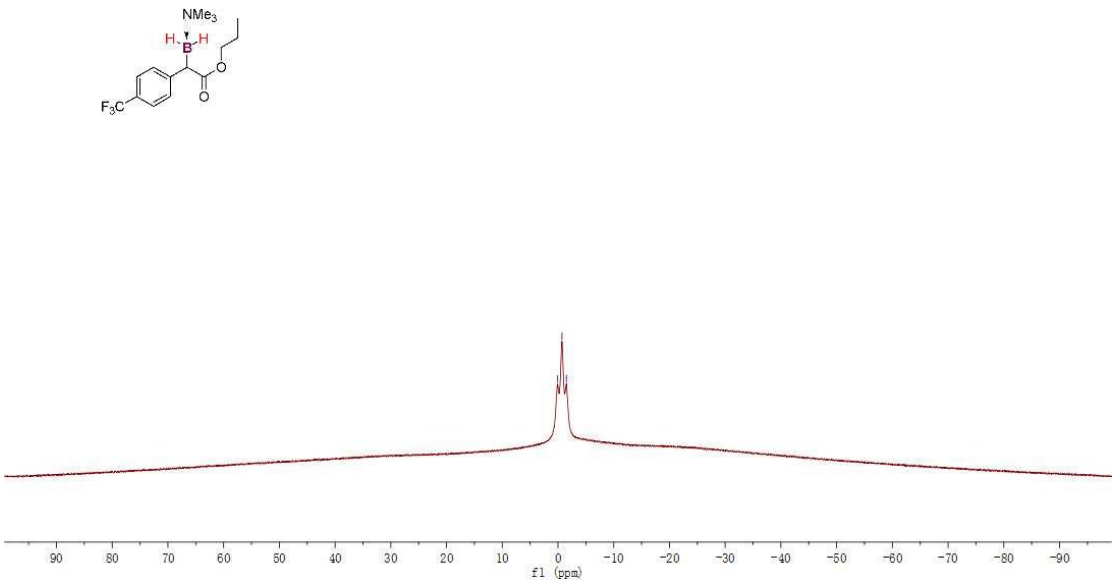
7.53
7.49
7.47
4.01
3.99
3.98
3.96
3.29
2.55
1.68
1.66
1.64
1.62
1.61
1.59
0.94
0.92
0.90
NMe3
H
B
H
O
O
F3C
2.00
2.01
2.09
1.03
9.20
4.09
3.17
f1 (ppm)


177.78
148.30
129.39
127.25
126.93
126.12
124.81
124.77
124.73
124.70
123.43
65.74
52.54
46.85
22.26
10.68
NMe3
H
B
H
O
O
F3C
f1 (ppm)


0.06
0.71
1.50
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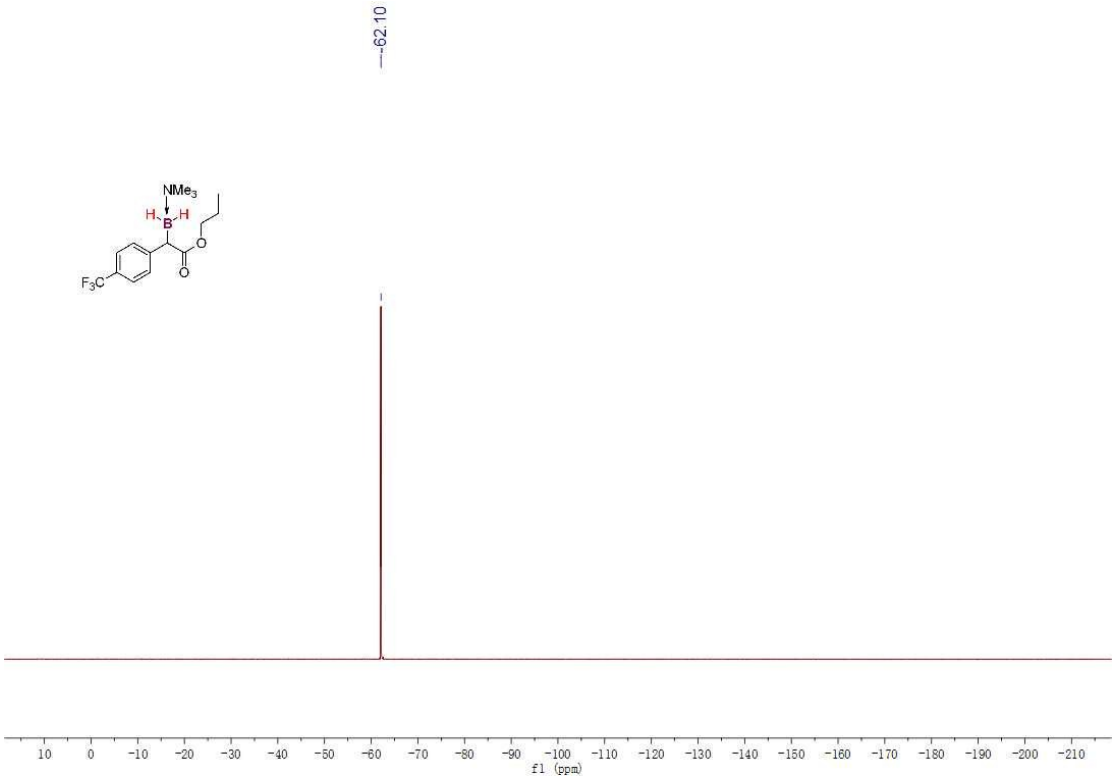
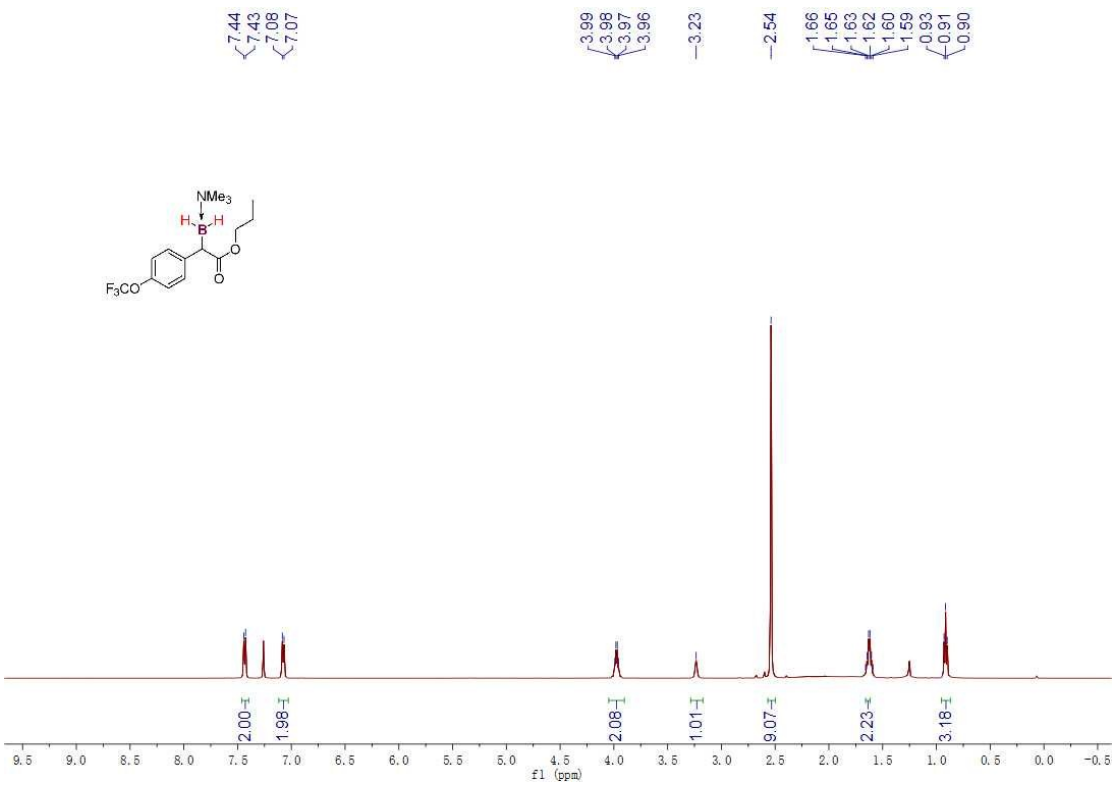
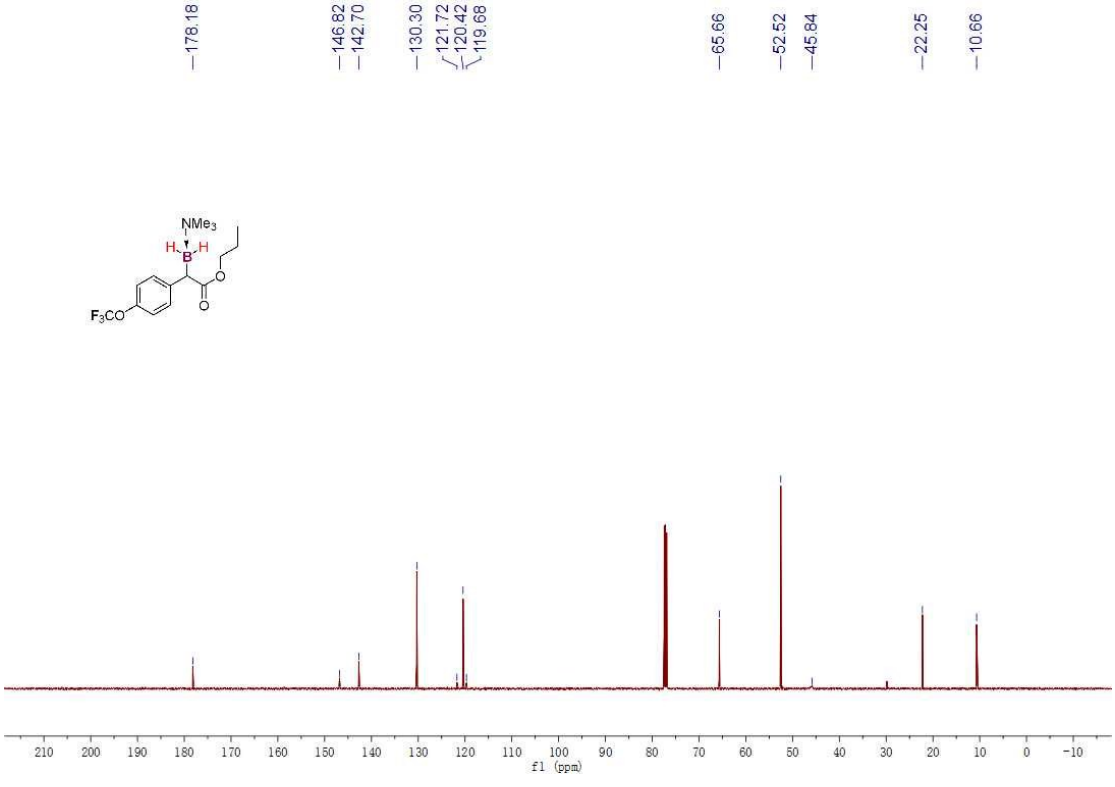
H
B
H
O
O
F3C
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)


-62.10
NMe3
H
B
H
O
O
F3C
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.44
7.43
7.08
7.07
3.99
3.98
3.97
3.96
3.23
2.54
1.66
1.65
1.63
1.62
1.60
1.59
0.93
0.91
0.90
NMe3
H
B
H
O
O
F3CO
2.00
1.98
2.08
1.01
9.07
2.23
3.18
f1 (ppm)


178.18
146.82
142.70
130.30
121.72
120.42
119.68
65.66
52.52
45.84
22.25
10.66
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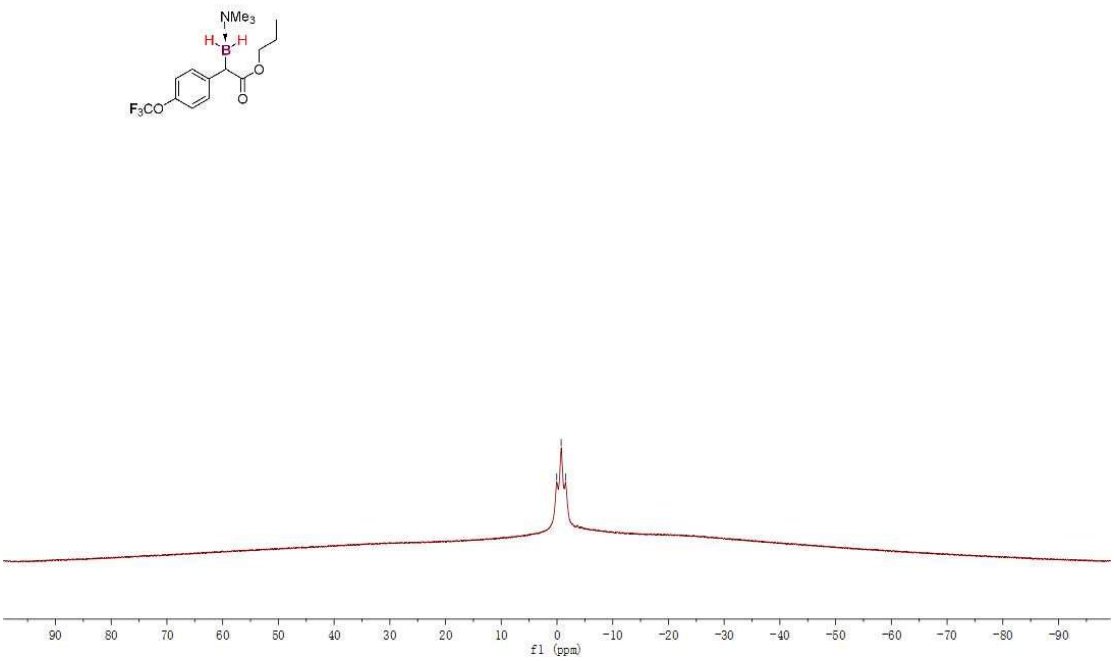
H
B
H
O
O
F3CO
f1 (ppm)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0.75
1.54
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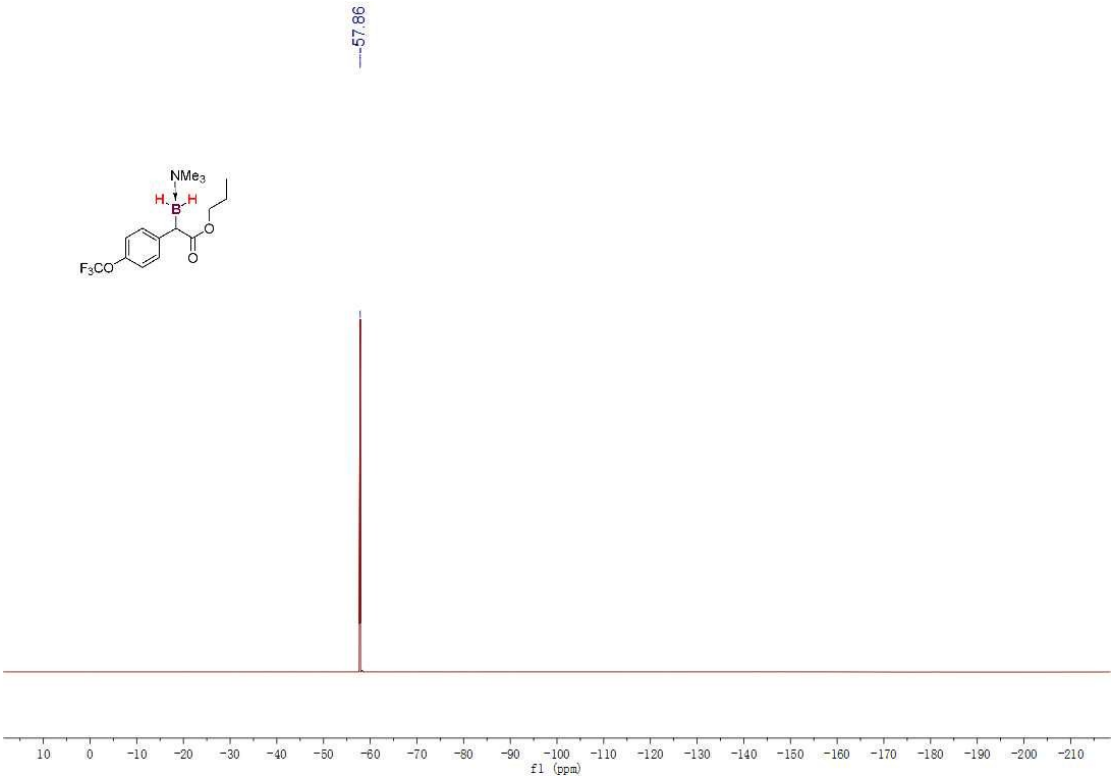
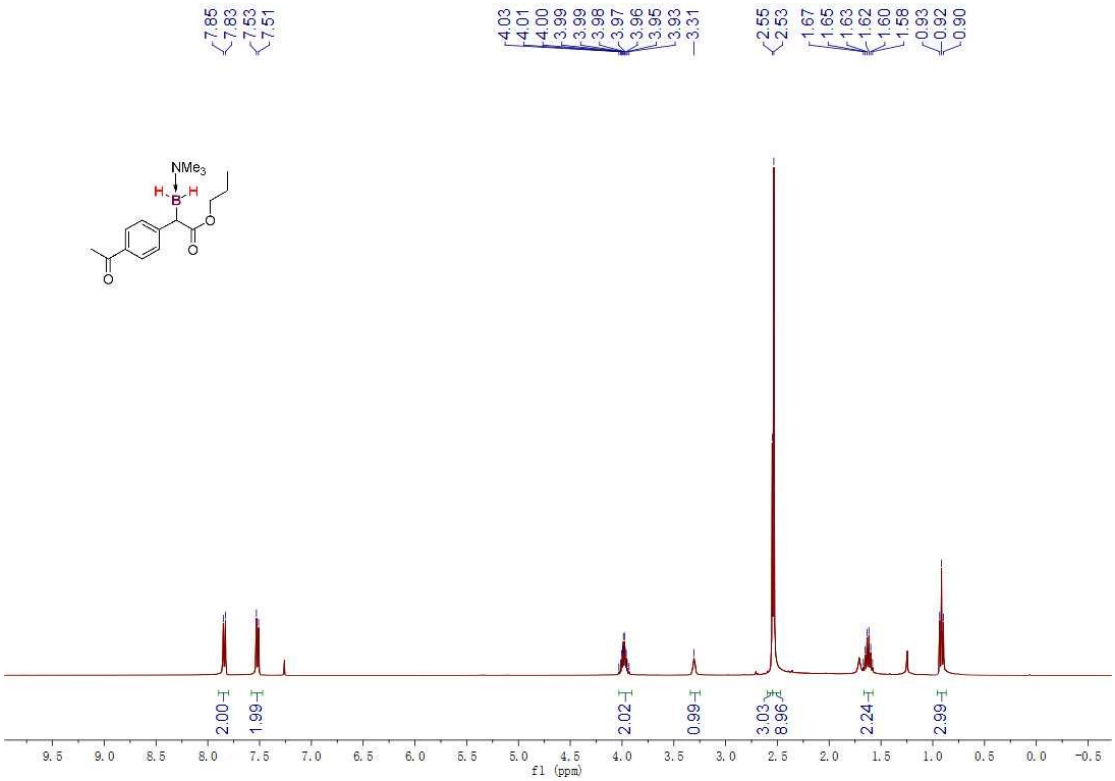
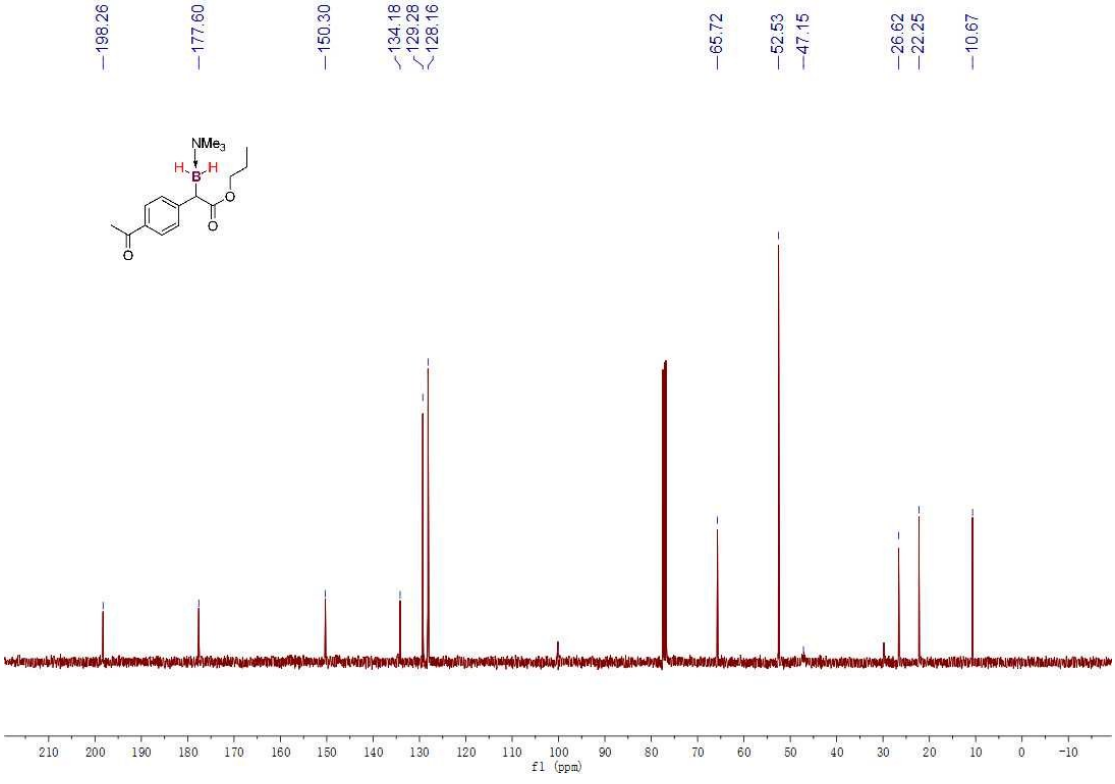
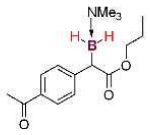
H
B
H
O
O
F3CO
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

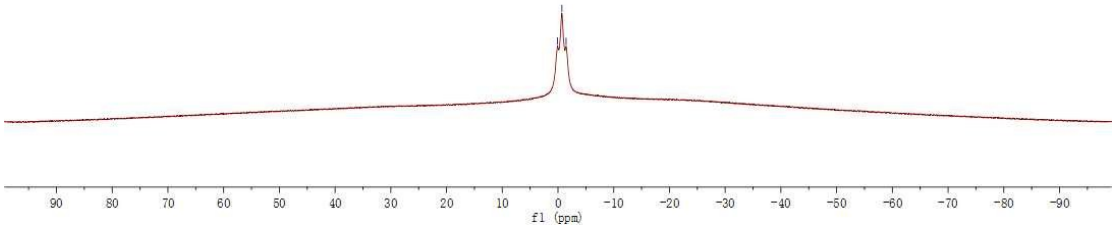

-57.86
NMe3
H
B
H
O
O
F3CO
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

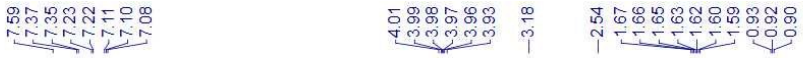

7.85
7.83
7.53
7.51
4.03
4.01
4.00
3.99
3.99
3.98
3.97
3.96
3.95
3.93
3.31
2.55
2.53
1.67
1.65
1.63
1.62
1.60
1.58
0.93
0.92
0.90
NMe3
H
B
H
O
O
O
2.00
1.99
2.02
0.99
3.03
8.96
2.24
2.99
f1 (ppm)


198.26
177.60
150.30
134.18
129.28
128.16
65.72
52.53
47.15
26.62
22.25
10.67
NMe3
H
B
H
O
O
O
f1 (ppm)


NMe3
H
B
H
O
O
O


0.09
0.70
1.46


f1 (ppm)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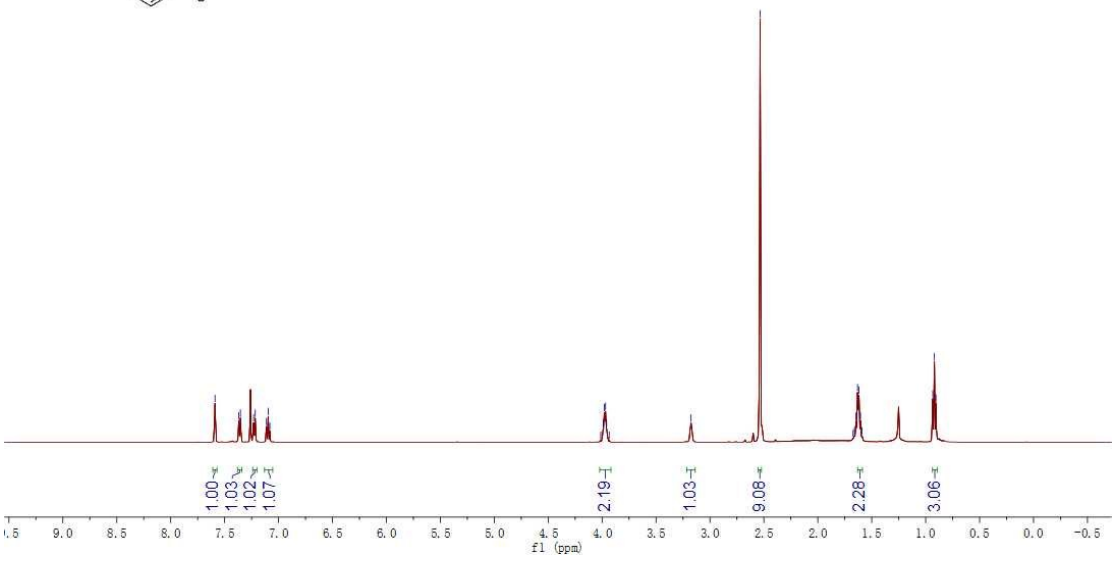
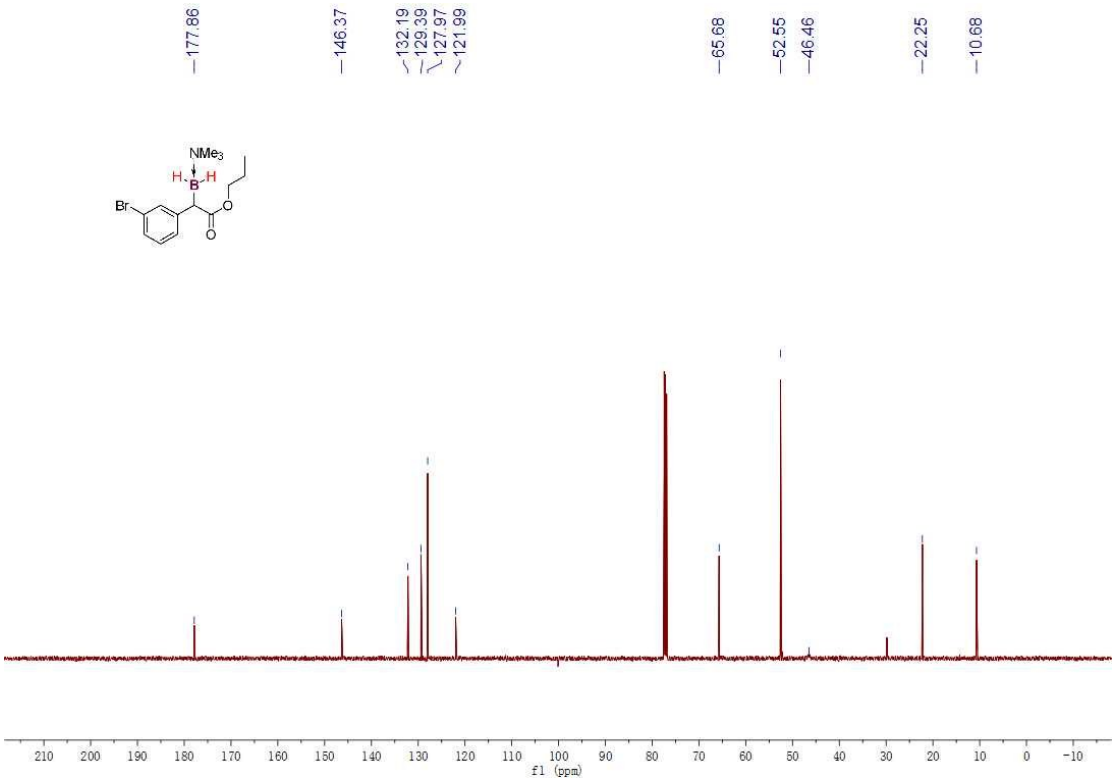
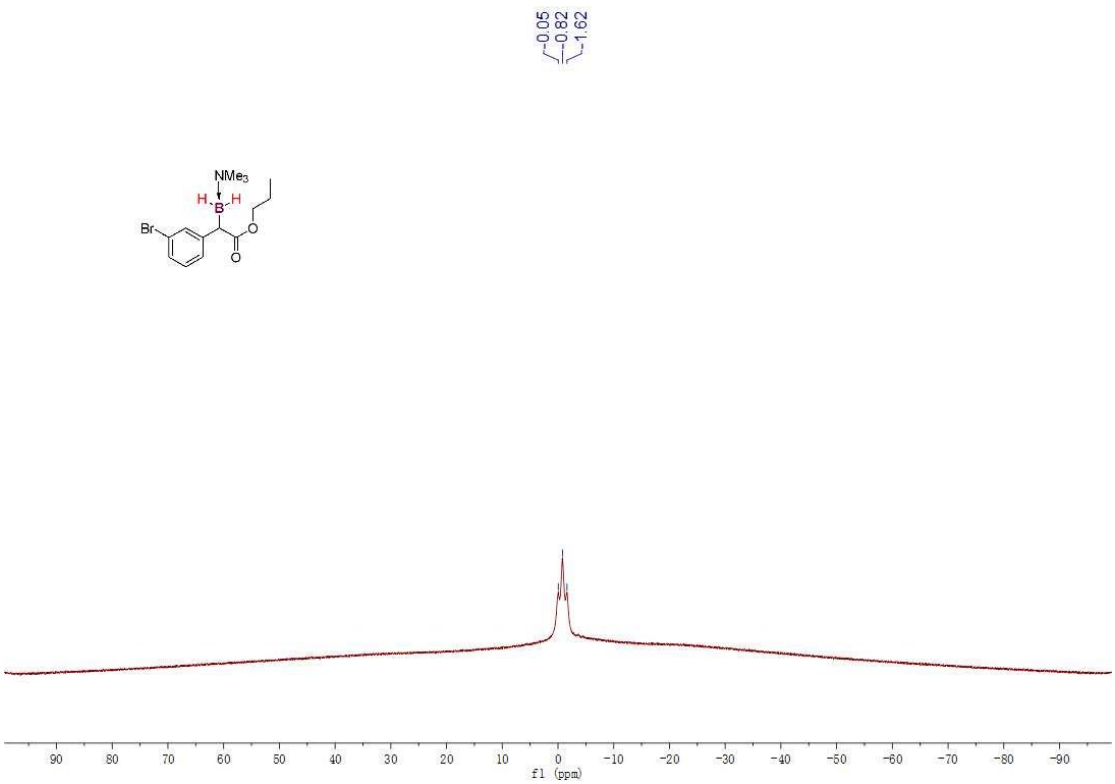
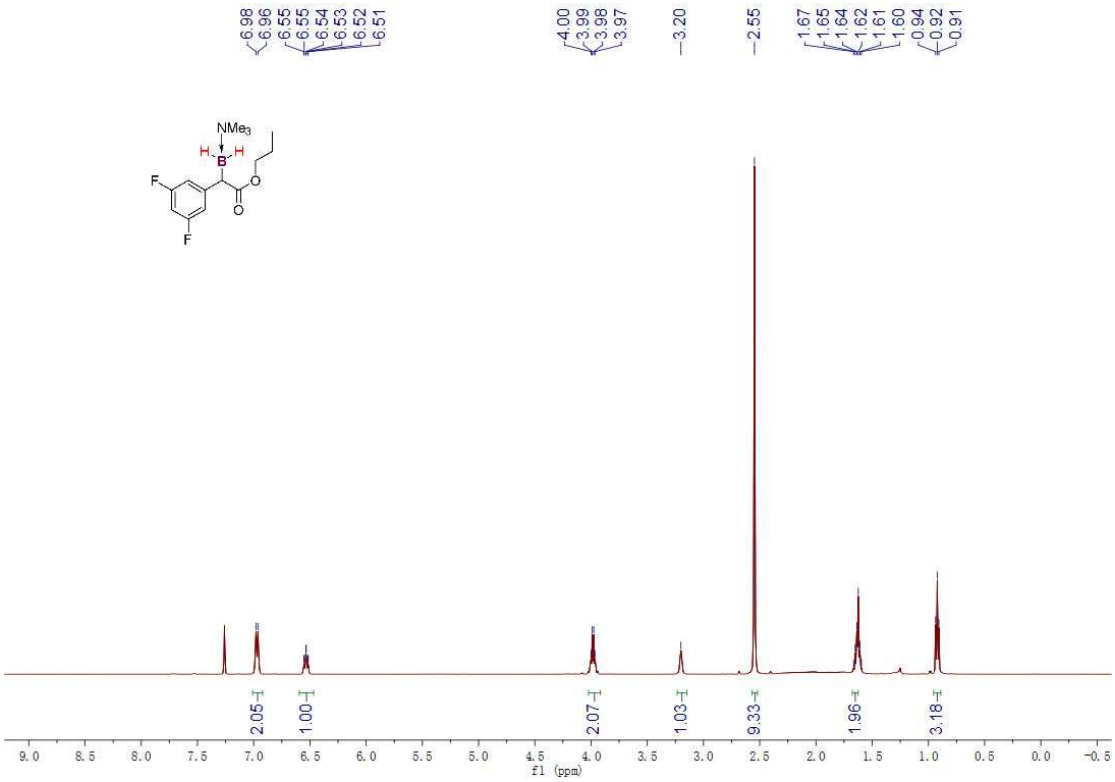
7.37
7.35
7.23
7.22
7.11
7.10
7.08
4.01
3.99
3.98
3.97
3.96
3.93
3.18
2.54
1.67
1.66
1.65
1.63
1.62
1.60
1.59
0.93
0.92
0.90

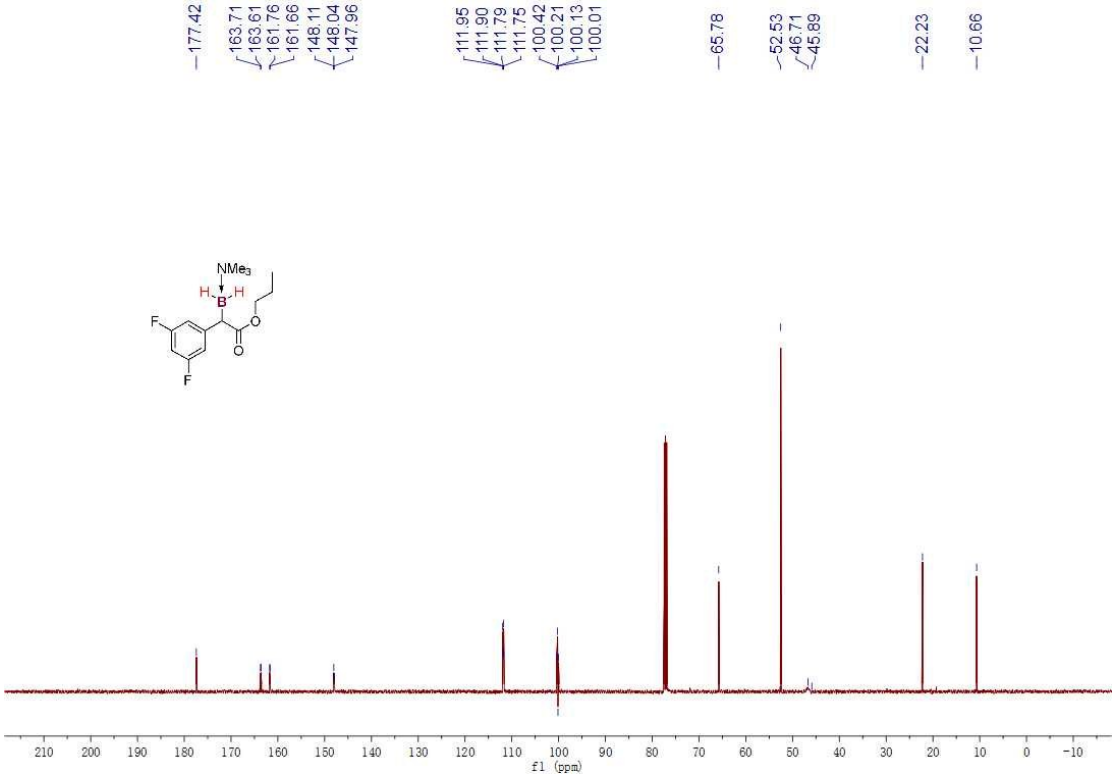

NMe3
H
B
H
Br
O
O

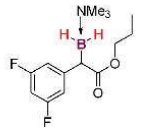

1.00
1.03
1.02
1.07
2.19
1.03
9.08
2.28
3.06
f1 (ppm)


177.86
146.37
132.19
129.39
127.97
121.99
65.68
52.55
46.46
22.25
10.68
NMe3
H
B
H
Br
O
O
f1 (ppm)


0.05
0.82
1.62
NMe3
H
B
H
Br
O
O
f1 (ppm)


6.98
6.96
6.55
6.55
6.54
6.53
6.52
6.51
4.00
3.99
3.98
3.97
3.20
2.55
1.67
1.65
1.64
1.62
1.61
1.60
0.94
0.92
0.91
NMe3
H
B
H
F
O
O
F
2.05
1.00
2.07
1.03
9.33
1.96
3.18
f1 (ppm)

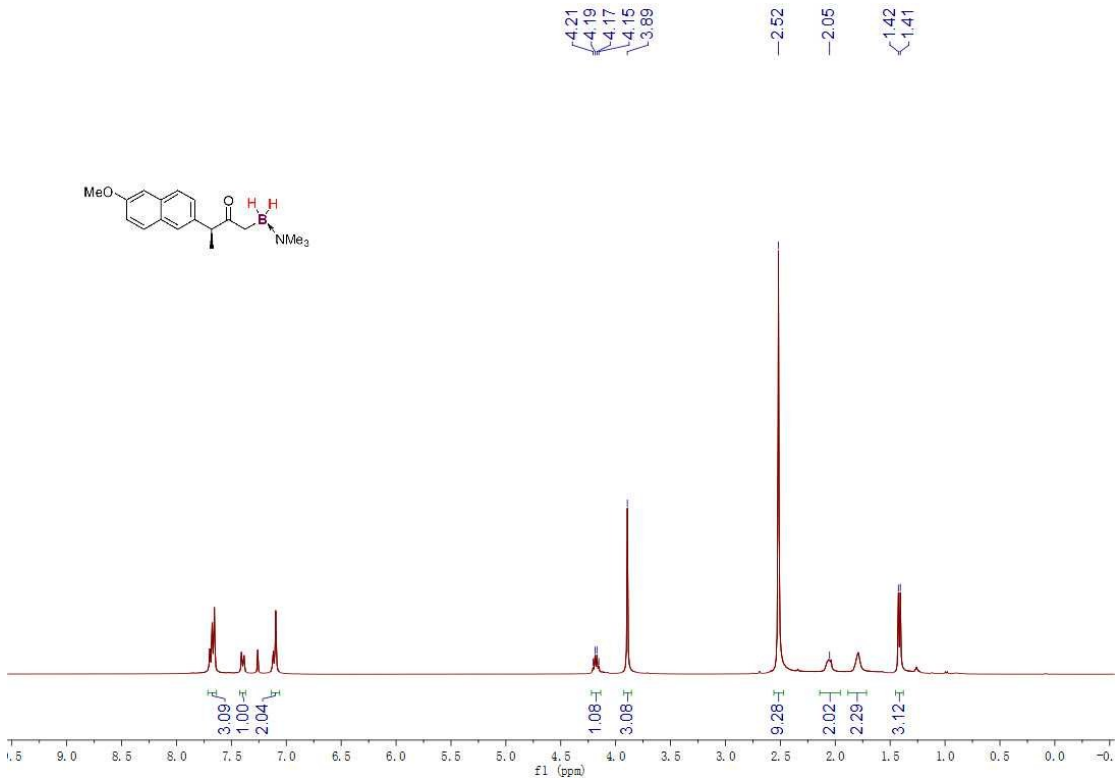

177.42
163.71
163.61
161.76
161.66
148.11
148.04
147.96
111.95
111.90
111.79
111.75
100.42
100.21
100.13
100.01
65.78
52.53
46.71
45.89
22.23
10.66
NMe3
H
B
H
F
O
O
F
f1 (ppm)

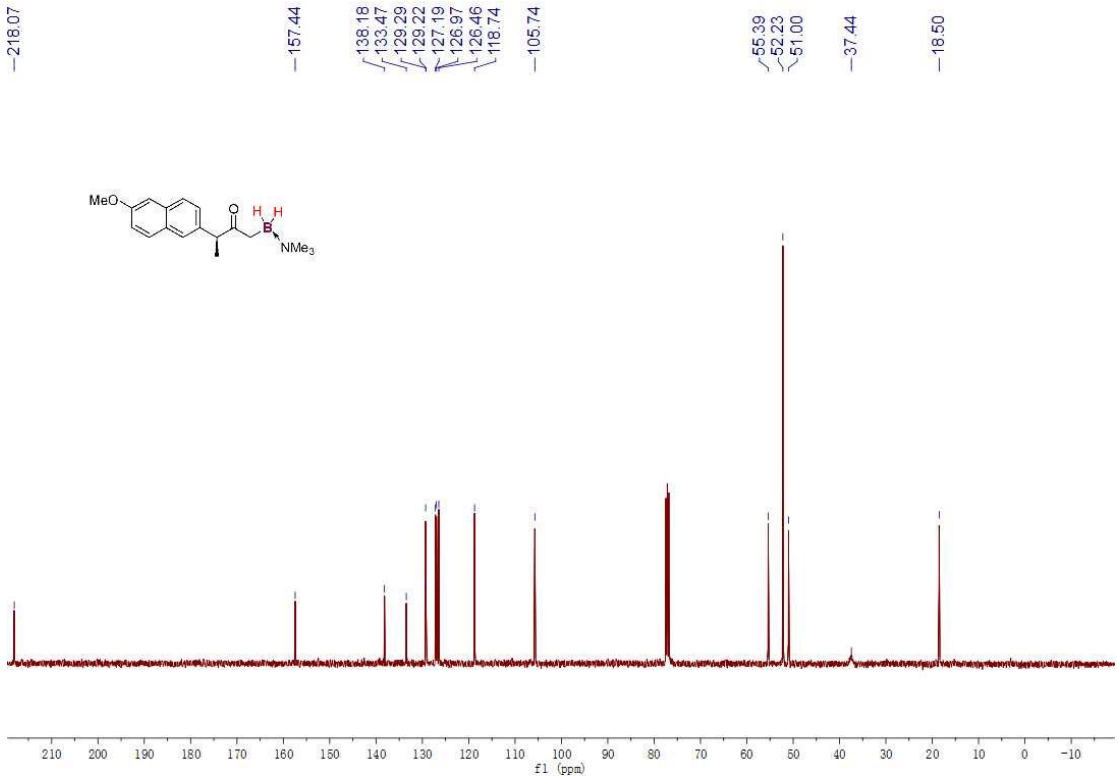

NMe3
H
B
H
F
O
O
F

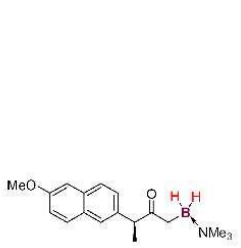
0.11
0.91
1.70
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)


NMe3
H
B
H
F
O
O
F

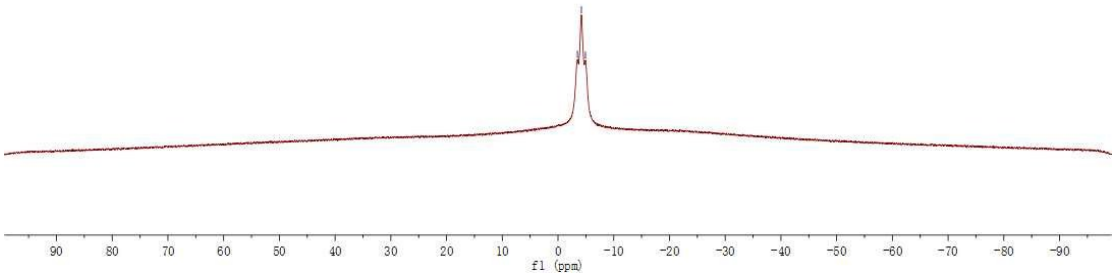
-112.06
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


4.21
4.19
4.17
4.15
3.89
2.52
2.05
1.42
1.41
MeO
H
H
B
NMe3
3.09
1.00
2.04
1.08
3.08
9.28
2.02
2.29
3.12
f1 (ppm)

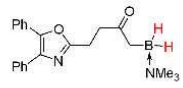

218.07
157.44
138.18
133.47
129.29
129.22
127.19
126.97
126.46
118.74
105.74
55.39
52.23
51.00
37.44
18.50
MeO
H
H
B
NMe3
f1 (ppm)

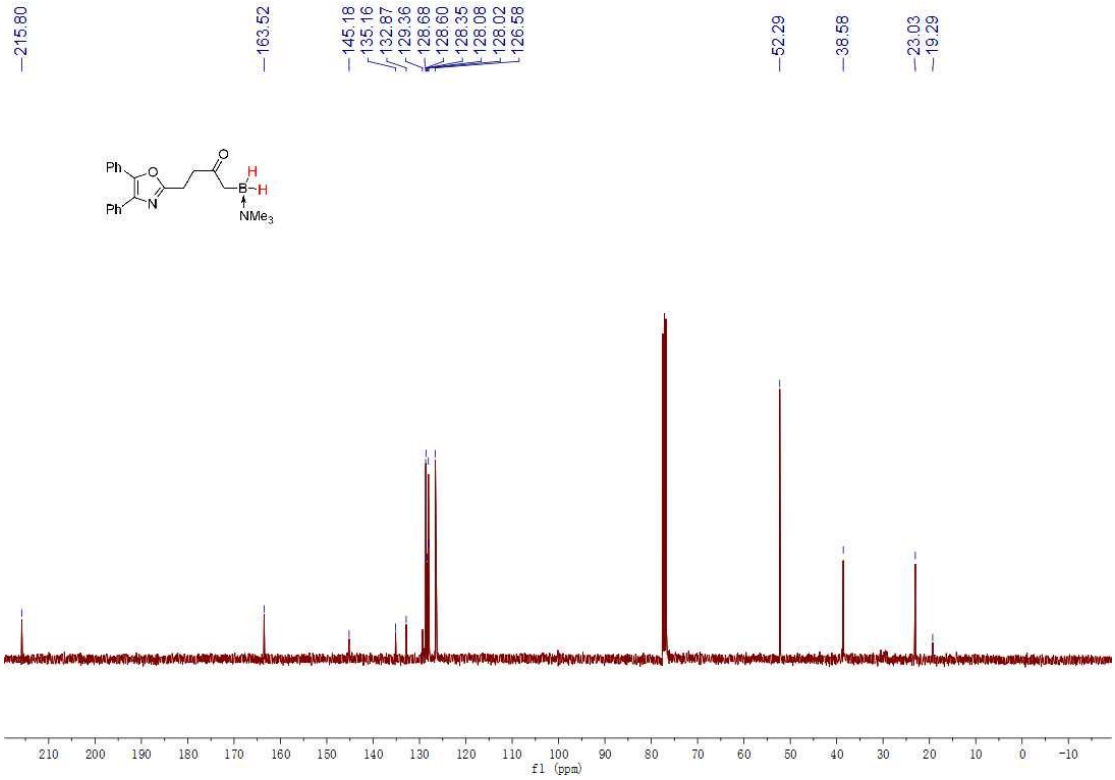


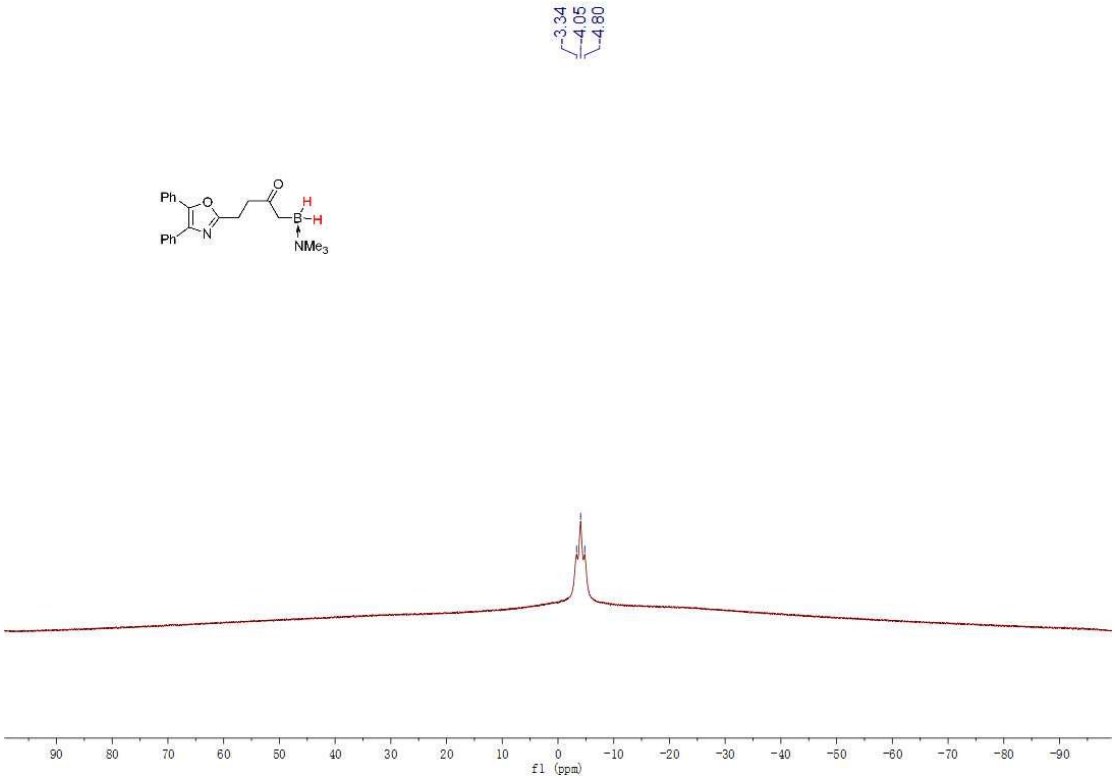
3.48
4.20
4.93

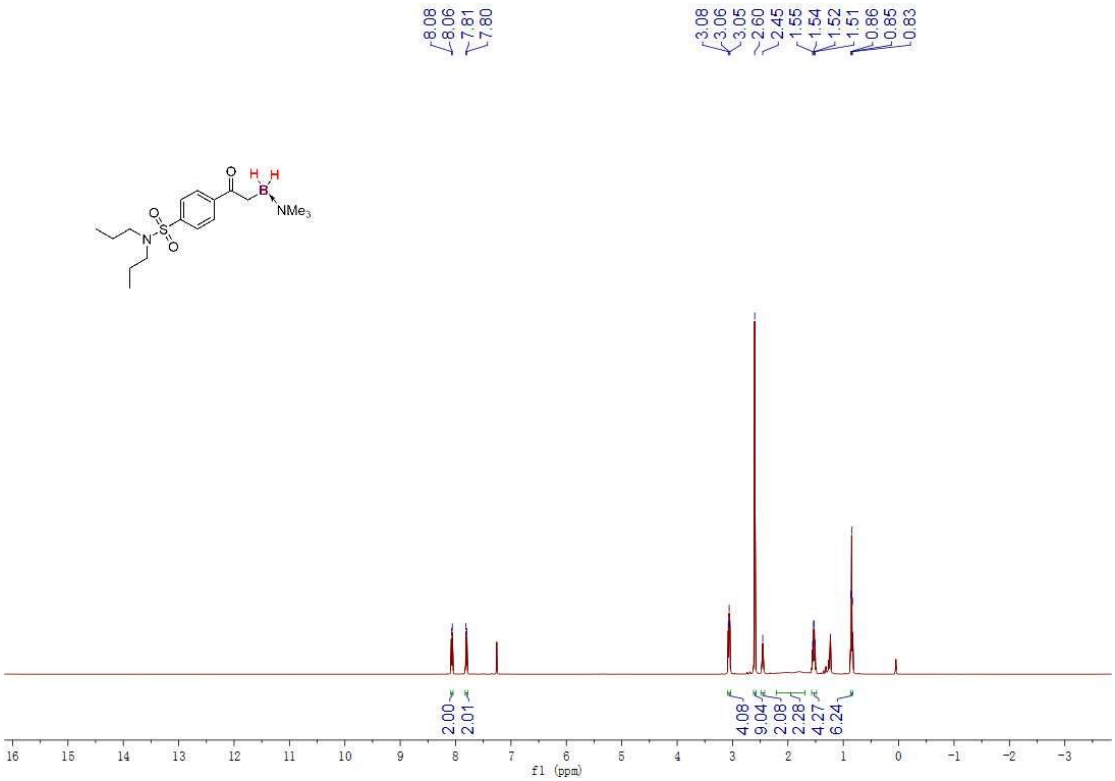


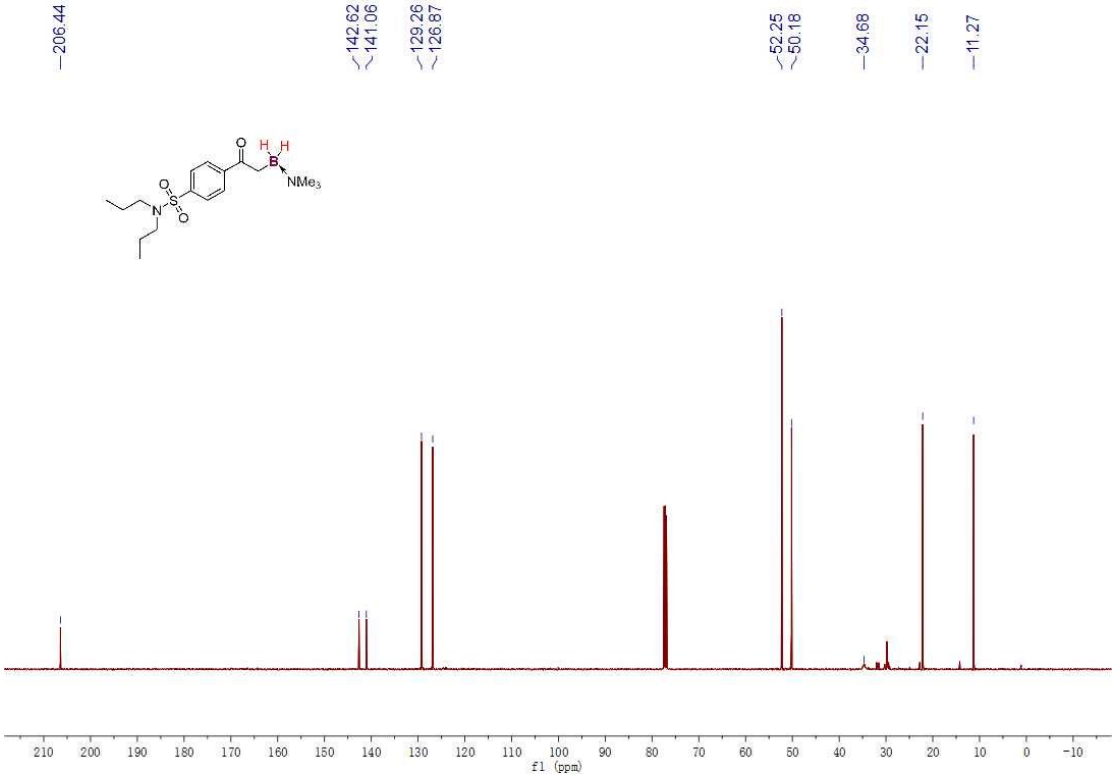
7.64 7.63 7.63 7.62 7.62 7.61 7.58 7.58 7.57 7.57 7.56 7.56 7.37 7.37 7.36 7.36 7.35 7.34 7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.30 7.29 7.28
3.12 3.11 3.09 3.09 3.08 3.08 3.07 3.06 3.06 3.04 3.03
2.55
2.02




215.80
163.52
145.18
135.16
132.87
129.36
128.68
128.60
128.35
128.08
128.02
126.58
52.29
38.58
23.03
19.29
Ph
O
N
Ph
H
B
H
NMe3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


3.34
4.05
4.80
Ph
O
N
Ph
H
B
H
NMe3
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)


8.08
8.06
7.81
7.80
3.08
3.06
3.05
2.60
2.45
1.55
1.54
1.52
1.51
0.86
0.85
0.83
NMe3
2.00
2.01
4.08
9.04
2.08
2.28
4.27
6.24
f1 (ppm)


206.44
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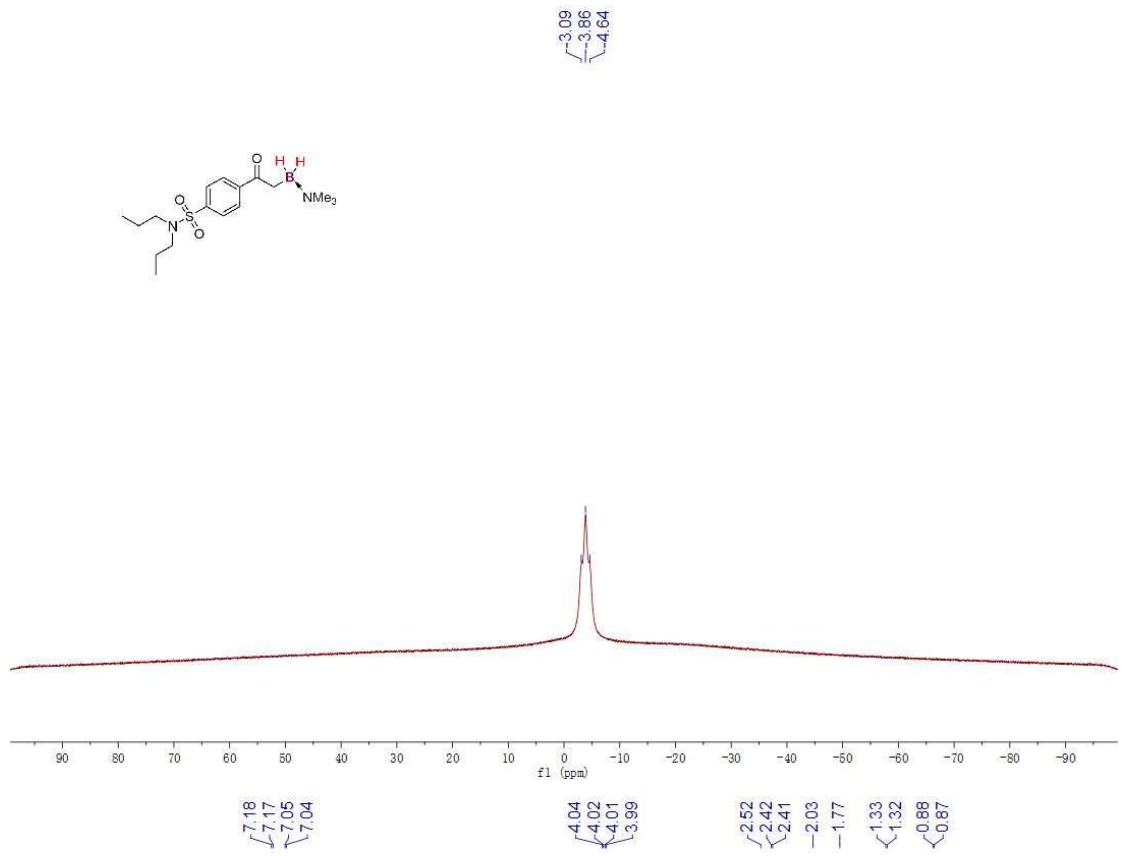
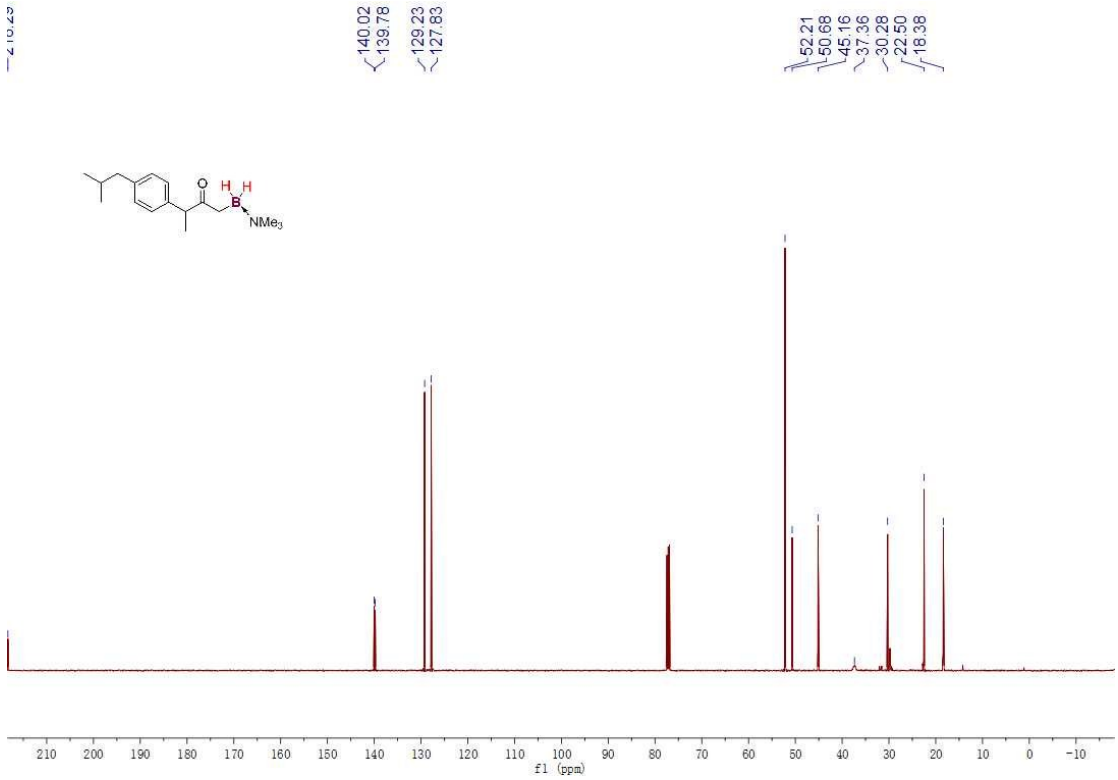
129.26
126.87
52.25
50.18
34.68
22.15
11.27
NMe3
f1 (ppm)


3.09
3.86
4.64
NMe3
f1 (ppm)
7.18
7.17
7.05
7.04
4.04
4.02
4.01
3.99
2.52
2.42
2.41
2.03
1.77
1.33
1.32
0.88
0.87
NMe3
2.00
2.02
1.00
9.07
2.09
1.24
1.12
1.32
3.14
6.07
f1 (ppm)


140.02
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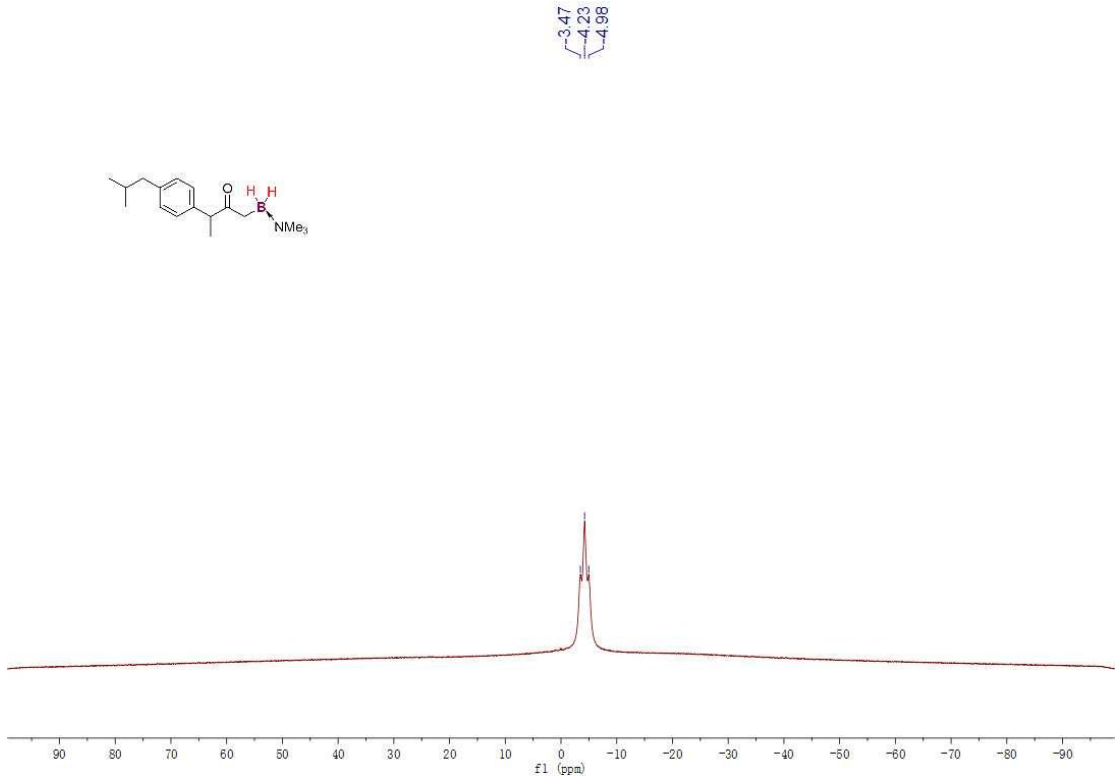
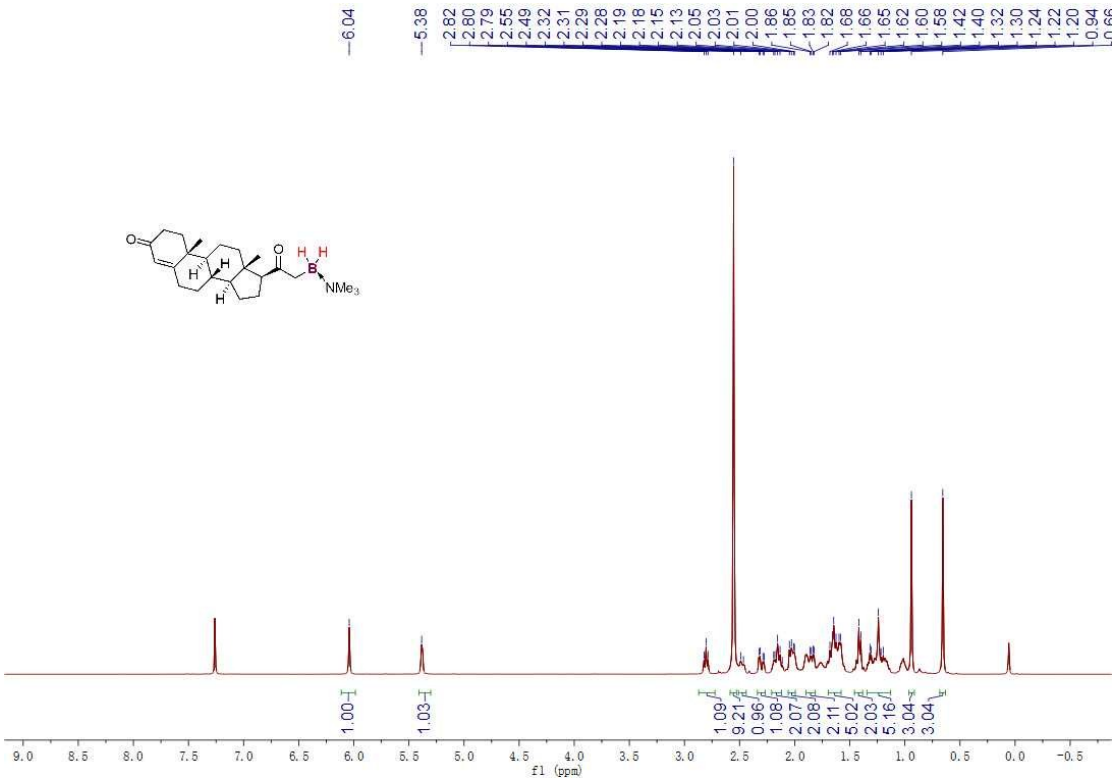
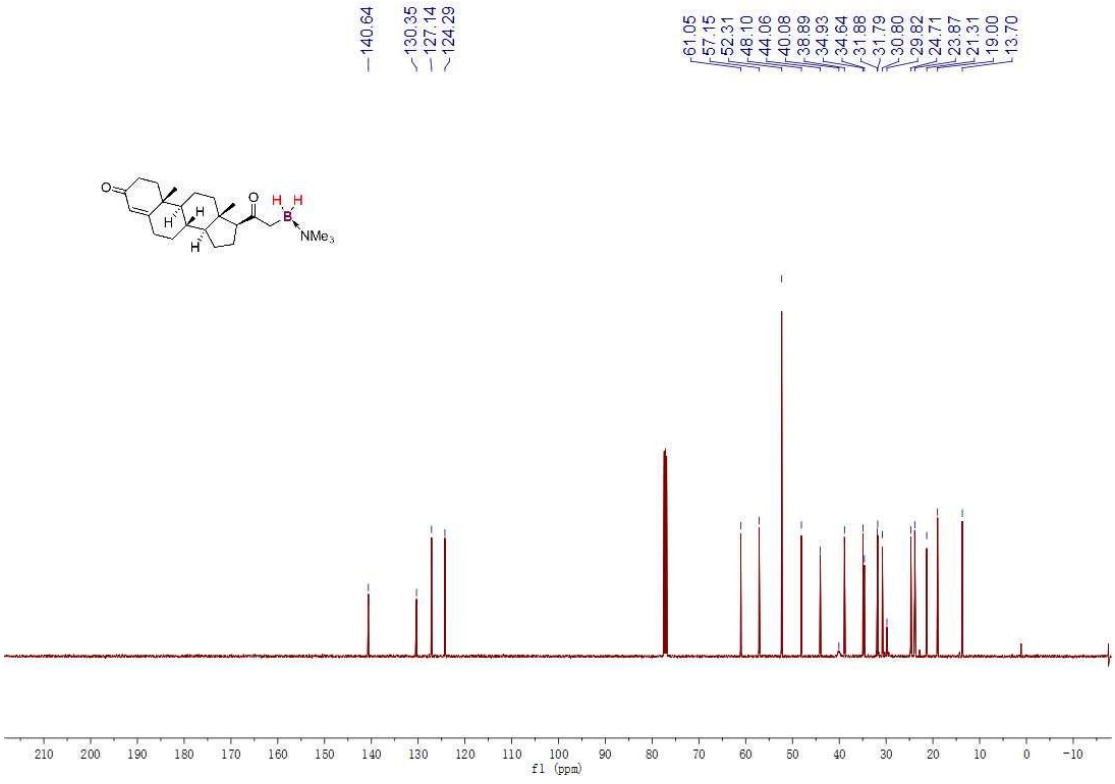
52.21
50.68
45.16
37.36
30.28
22.50
18.38
NMe3
f1 (ppm)


3.47
4.23
4.98
NMe3
f1 (ppm)


6.04
5.38
2.82
2.80
2.79
2.55
2.49
2.32
2.31
2.29
2.28
2.19
2.18
2.15
2.13
2.05
2.03
2.01
2.00
1.86
1.85
1.83
1.82
1.68
1.66
1.65
1.62
1.60
1.58
1.42
1.40
1.32
1.30
1.24
1.22
1.20
0.94
O
H
H
H
O
H
H
B
NMe3
1.00
1.03
1.09
9.21
0.96
1.08
2.07
2.08
2.11
5.02
2.03
5.16
3.04
3.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


140.64
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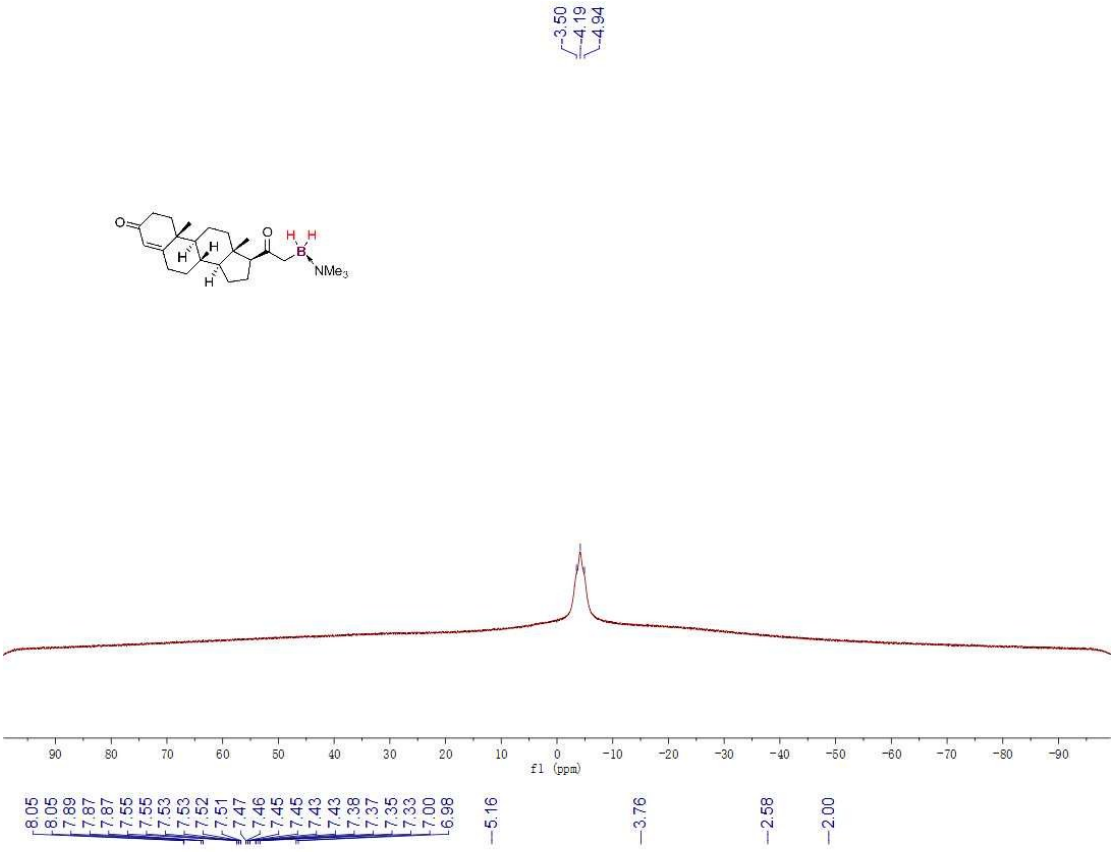
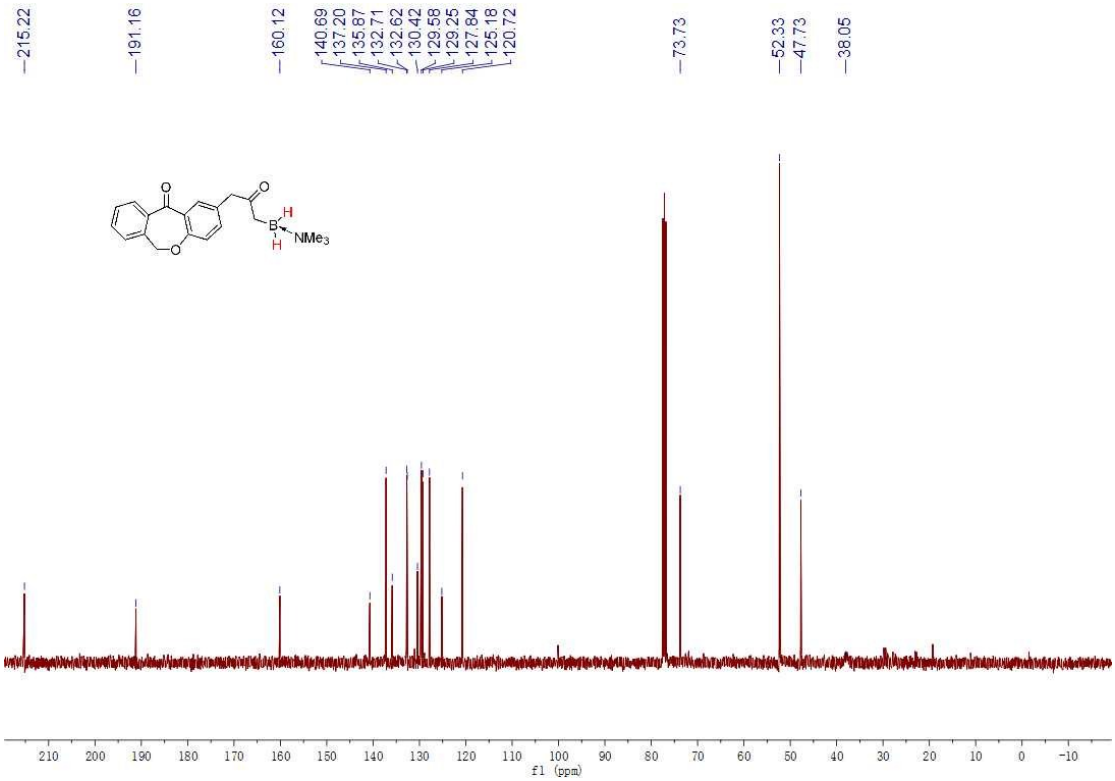
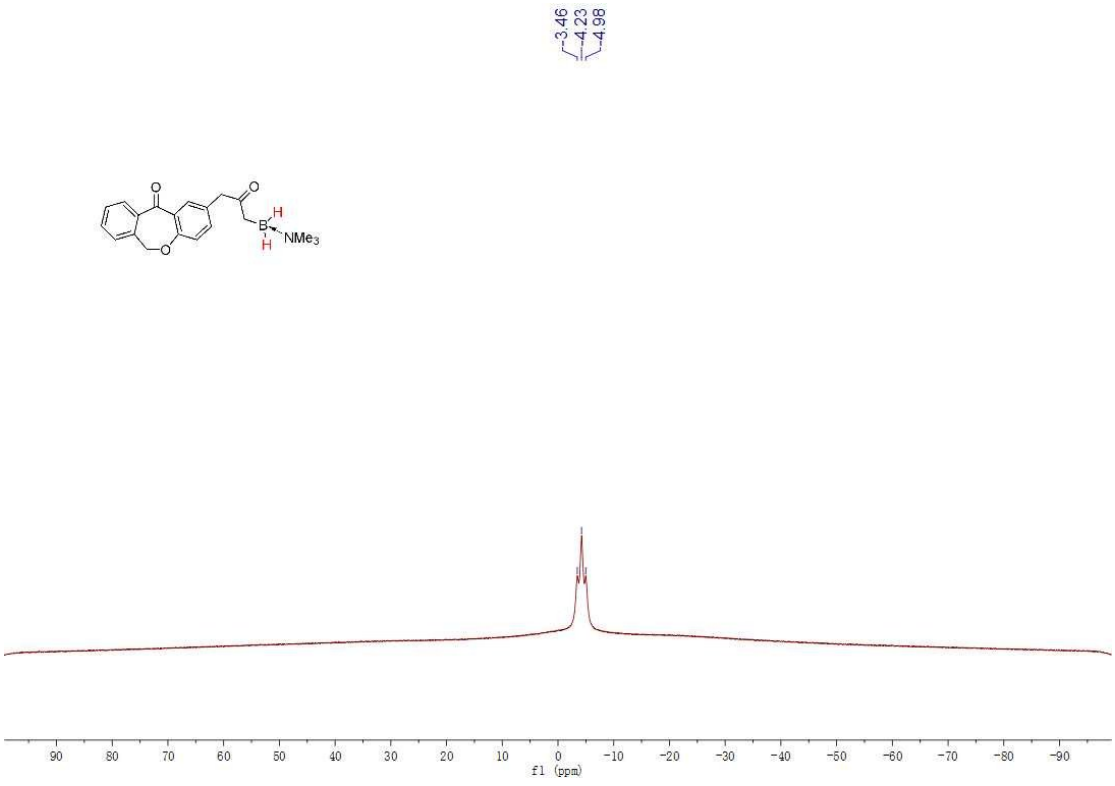
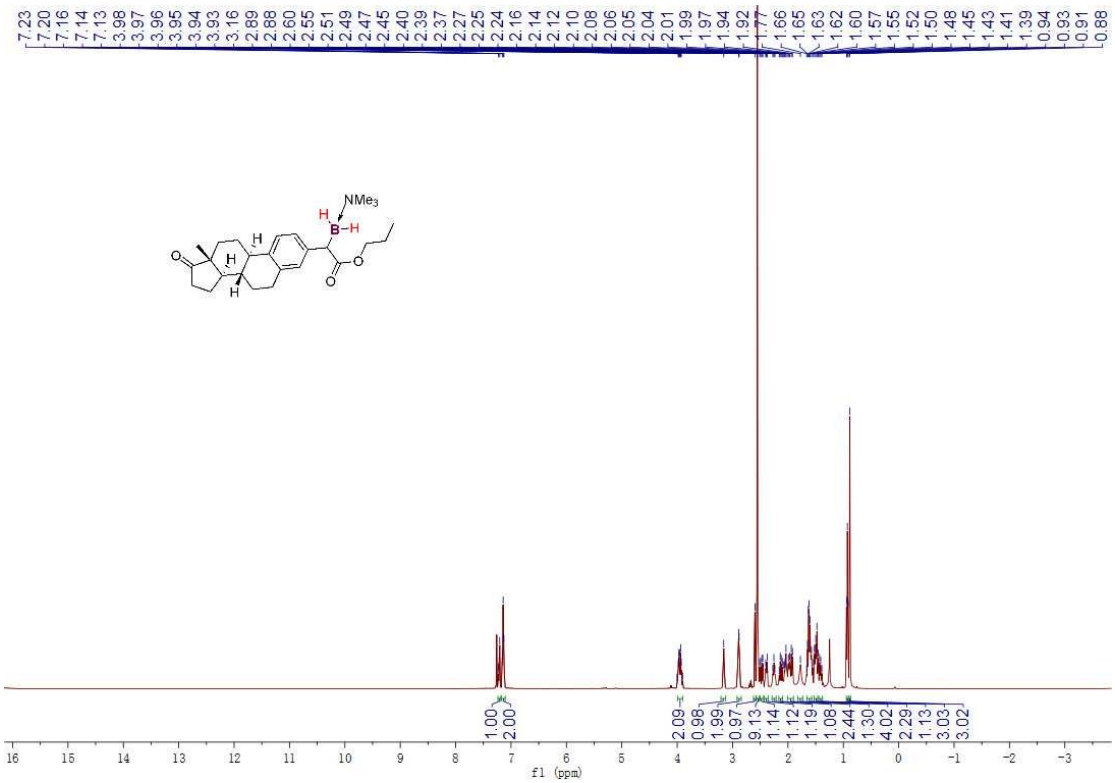
127.14
124.29
61.05
57.15
52.31
48.10
44.06
40.08
38.89
34.93
34.64
31.88
31.79
30.80
29.82
24.71
23.87
21.31
19.00
13.70
O
H
H
H
O
H
H
B
NMe3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

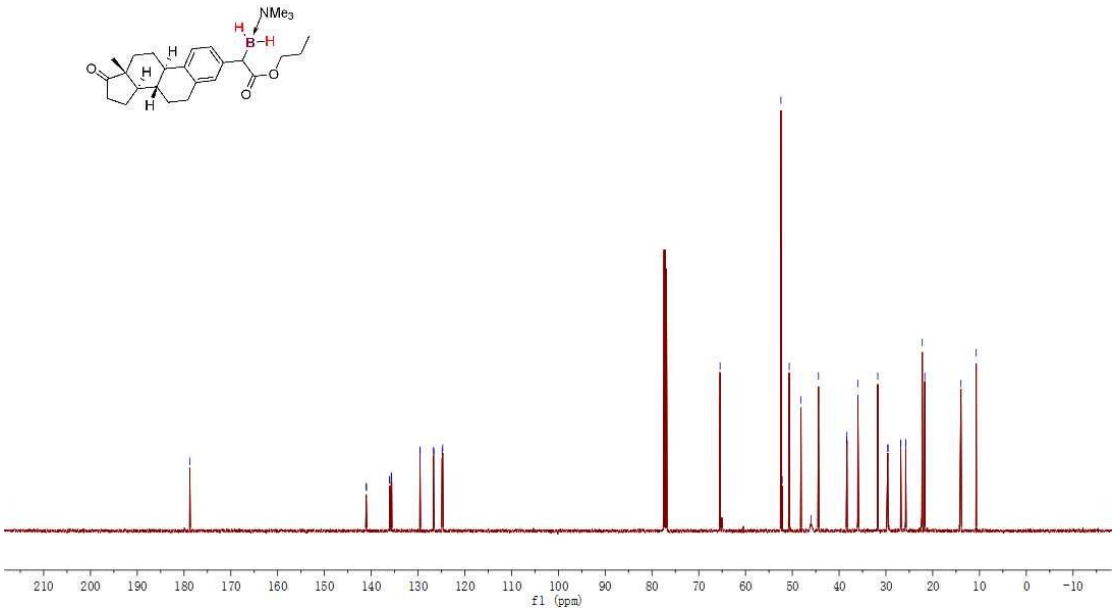

3.50
4.19
4.94
NMe3
f1 (ppm)
8.05
8.05
7.89
7.87
7.87
7.55
7.55
7.53
7.53
7.52
7.51
7.47
7.46
7.45
7.45
7.43
7.43
7.38
7.37
7.35
7.33
7.00
6.98
5.16
3.76
2.58
2.00
NMe3
1.00
1.04
1.19
1.10
2.12
1.02
2.11
2.04
9.21
2.12
f1 (ppm)

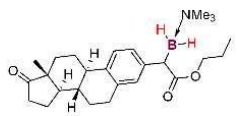

215.22
191.16
160.12
140.69
137.20
135.87
132.71
132.62
130.42
129.58
129.25
127.84
125.18
120.72
73.73
52.33
47.73
38.05
NMe3
f1 (ppm)

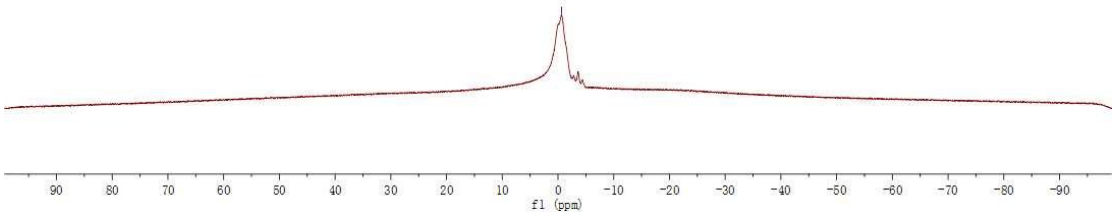

3.46
4.23
4.98
NMe3
f1 (ppm)

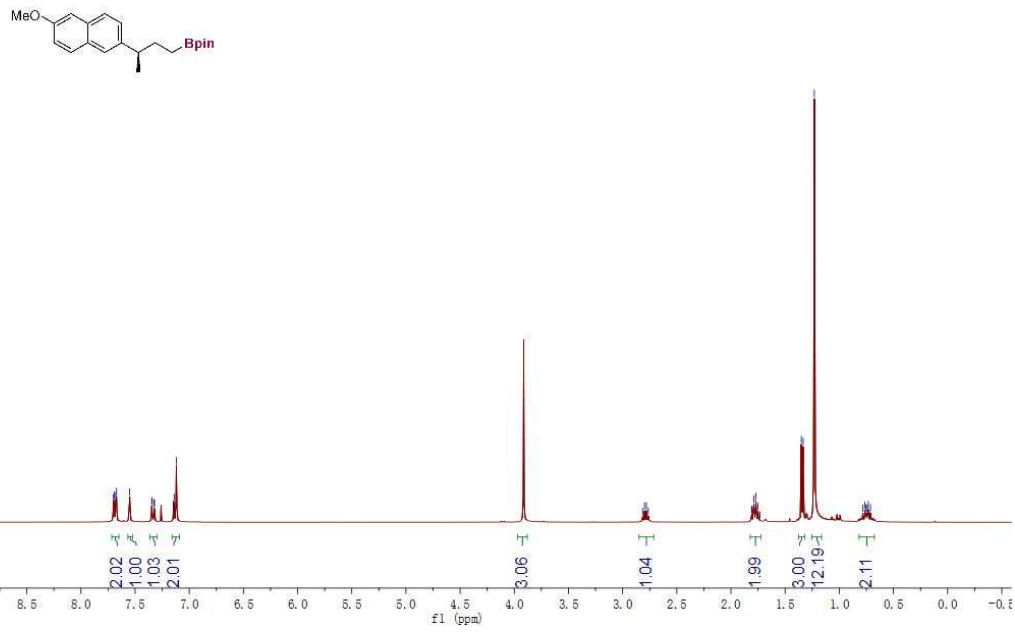

7.23 7.20 7.16 7.14 7.13 3.98 3.97 3.96 3.95 3.94 3.93 3.16 2.89 2.88 2.60 2.55 2.51 2.49 2.47 2.45 2.40 2.39 2.37 2.27 2.25 2.24 2.16 2.14 2.12 2.10 2.08 2.06 2.05 2.04 2.01 1.99 1.97 1.94 1.92 1.77 1.66 1.65 1.63 1.62 1.60 1.57 1.55 1.52 1.50 1.48 1.45 1.43 1.41 1.39 0.94 0.93 0.91 0.88
NMe3
H
B–H
1.00 2.00 2.09 0.98 1.99 0.97 9.13 1.14 1.12 1.19 1.08 2.44 1.30 4.02 2.29 1.13 3.03 3.02
f1 (ppm)

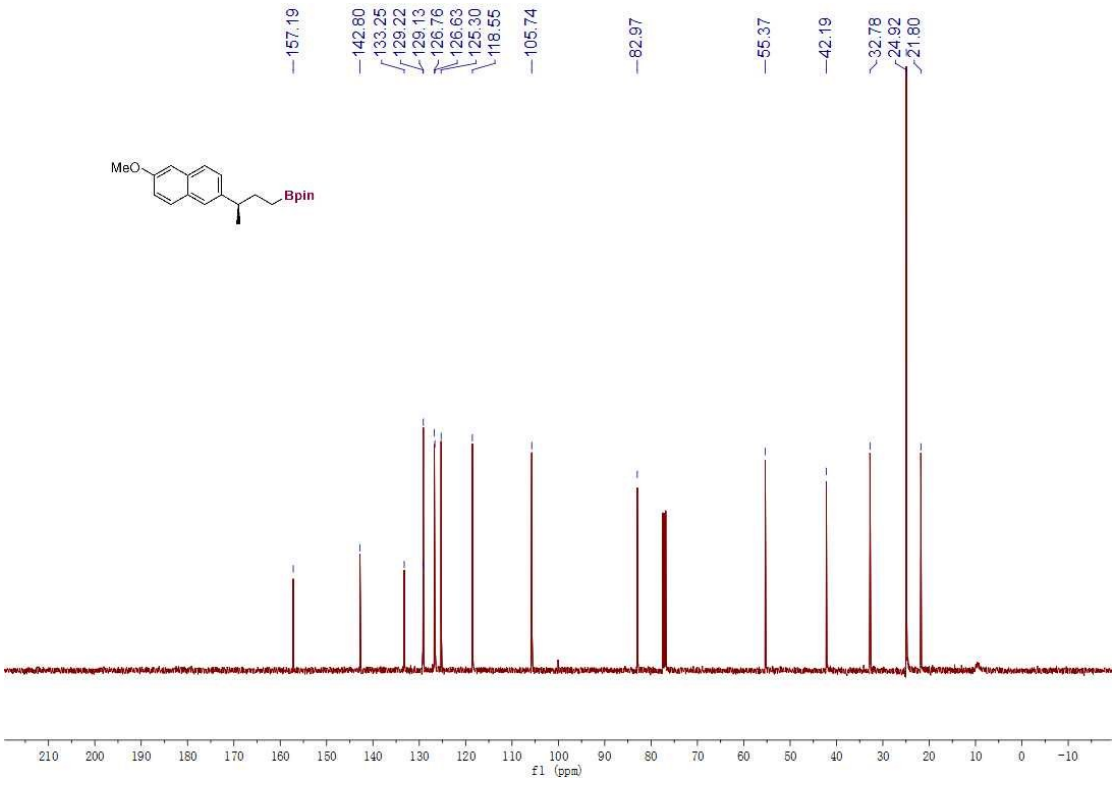

178.77
141.06 141.00 136.06 136.04 135.71 135.63 129.57 129.53 126.69 126.59 124.84 124.71
65.44 52.45 52.16 50.66 48.15 45.97 44.41 38.36 38.33 36.00 31.74 29.61 29.55 26.83 26.81 25.77 25.75 22.23 21.69 13.97 10.70

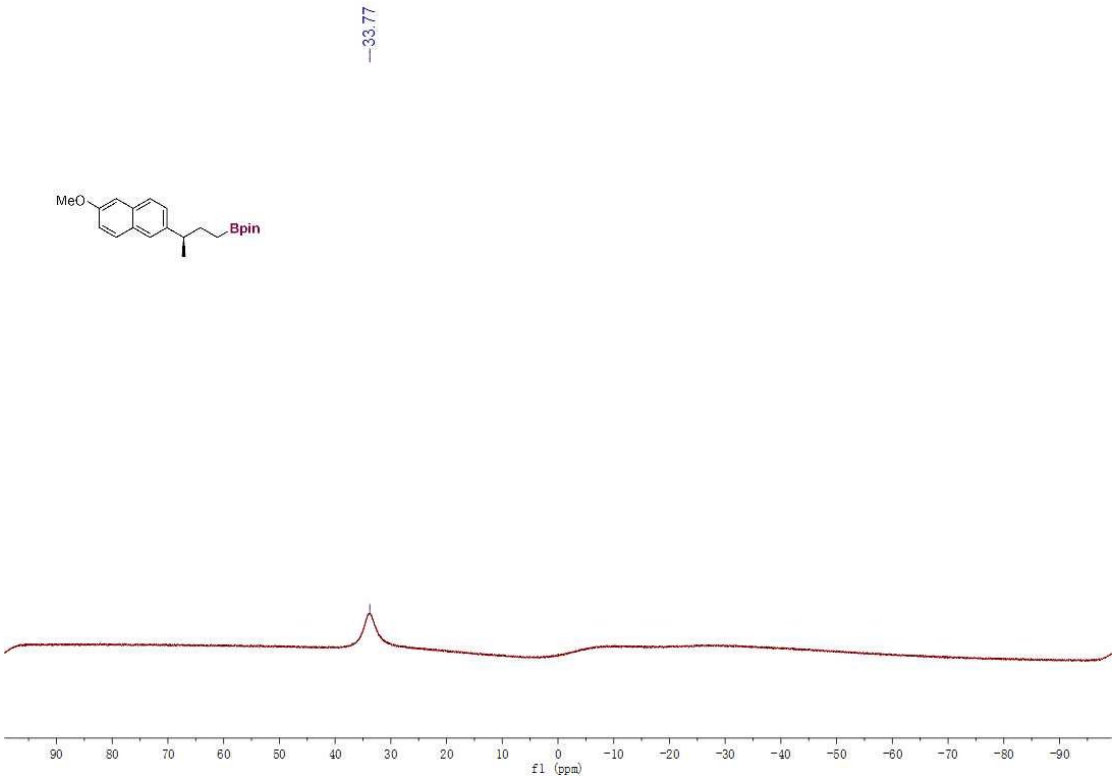

NMe3
H
B–H
f1 (ppm)

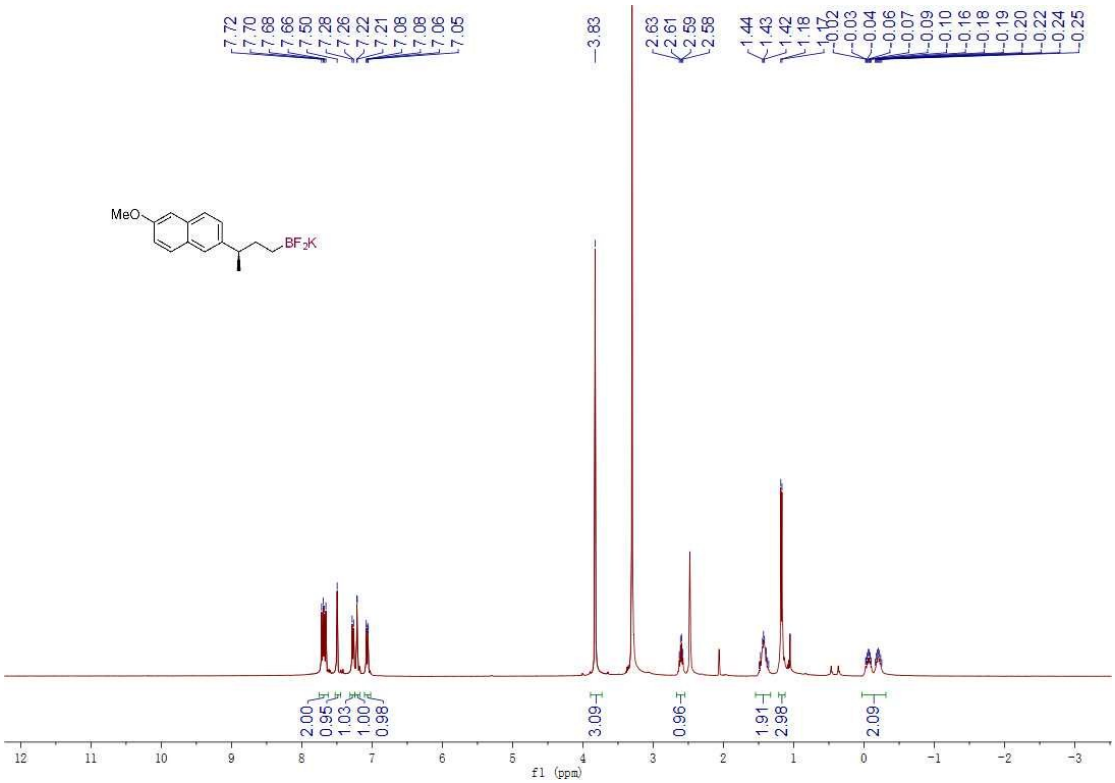

NMe3
H
B
H
O
O
O
H
H

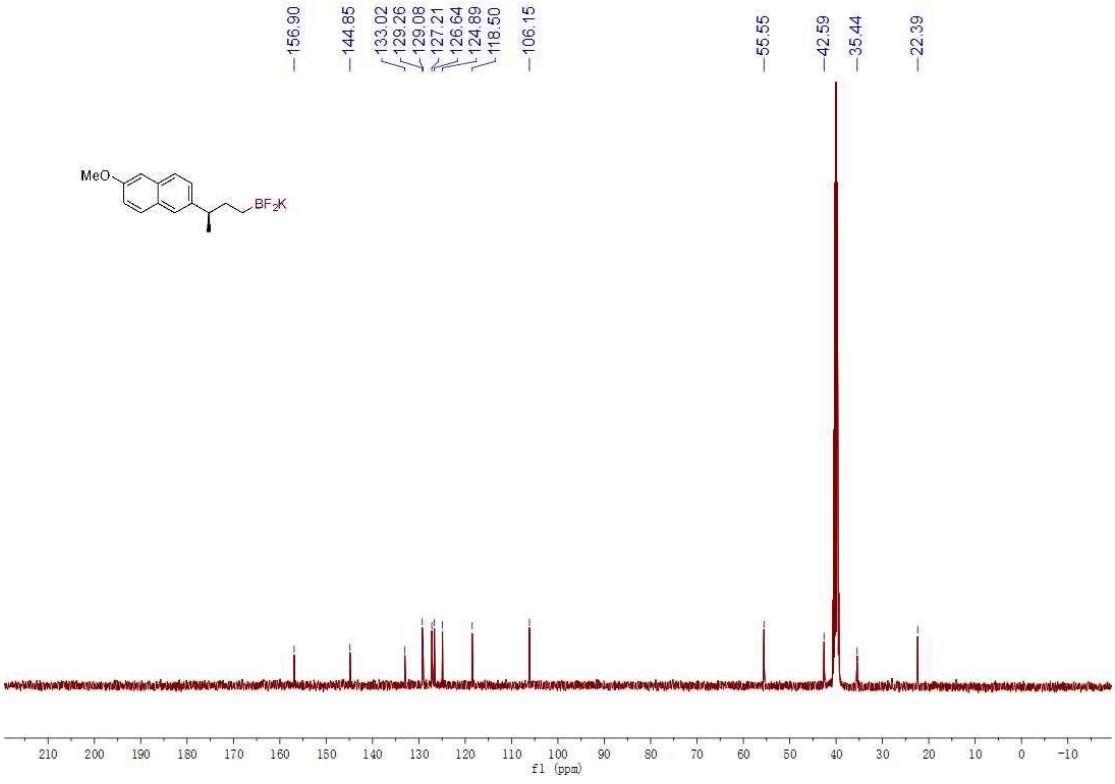

f1 (ppm)


MeO
Bpin
f1 (ppm)

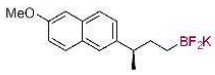

157.19
142.80
133.25
129.22
129.13
126.76
126.63
125.30
118.55
105.74
82.97
55.37
42.19
32.78
24.92
21.80
MeO
Bpin
f1 (ppm)

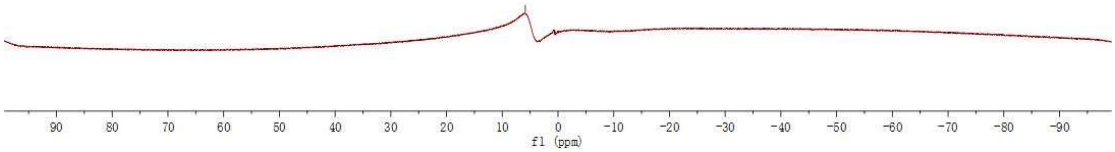

33.77
MeO
Bpin
f1 (ppm)


7.72
7.70
7.68
7.66
7.50
7.28
7.26
7.22
7.21
7.08
7.06
7.05
3.83
2.63
2.61
2.59
2.58
1.44
1.43
1.42
1.18
1.17
0.02
0.03
0.04
0.06
0.07
0.09
0.10
0.16
0.18
0.19
0.20
0.22
0.24
0.25
MeO
BF2K
2.00
0.95
1.03
1.00
0.98
3.09
0.96
1.91
2.98
2.09
f1 (ppm)

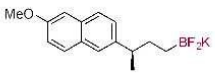

156.90
144.85
133.02
129.26
129.08
127.21
126.64
124.89
118.50
106.15
55.55
42.59
35.44
22.39
MeO
BF2K
f1 (ppm)

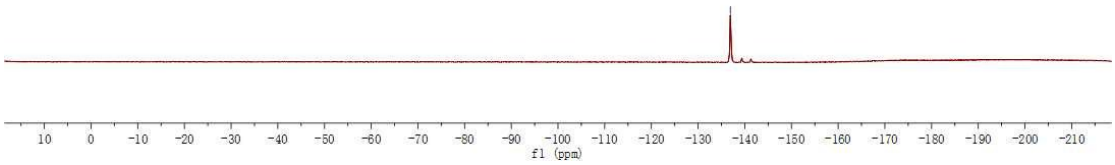
5.86

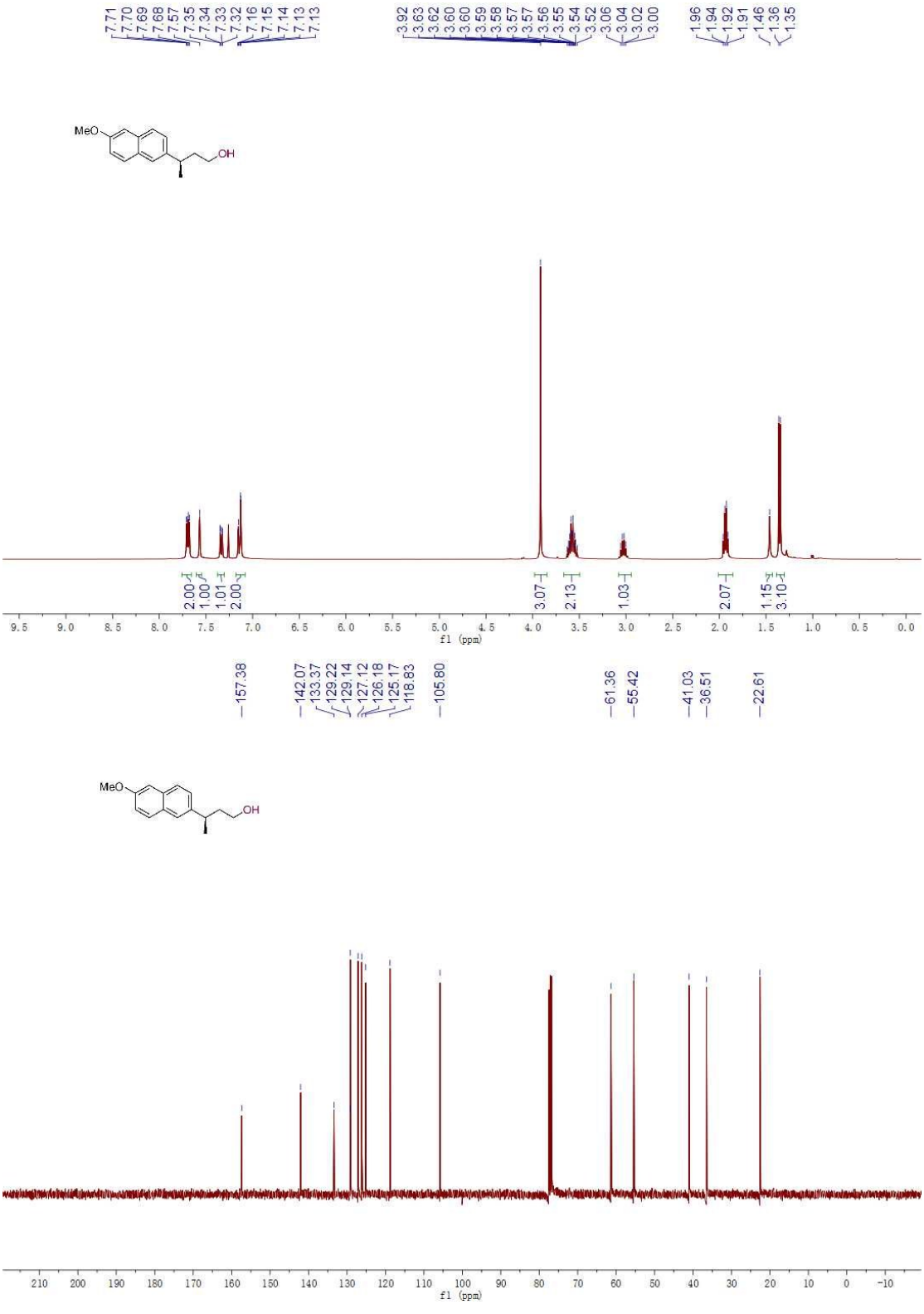

MeO
BF3K

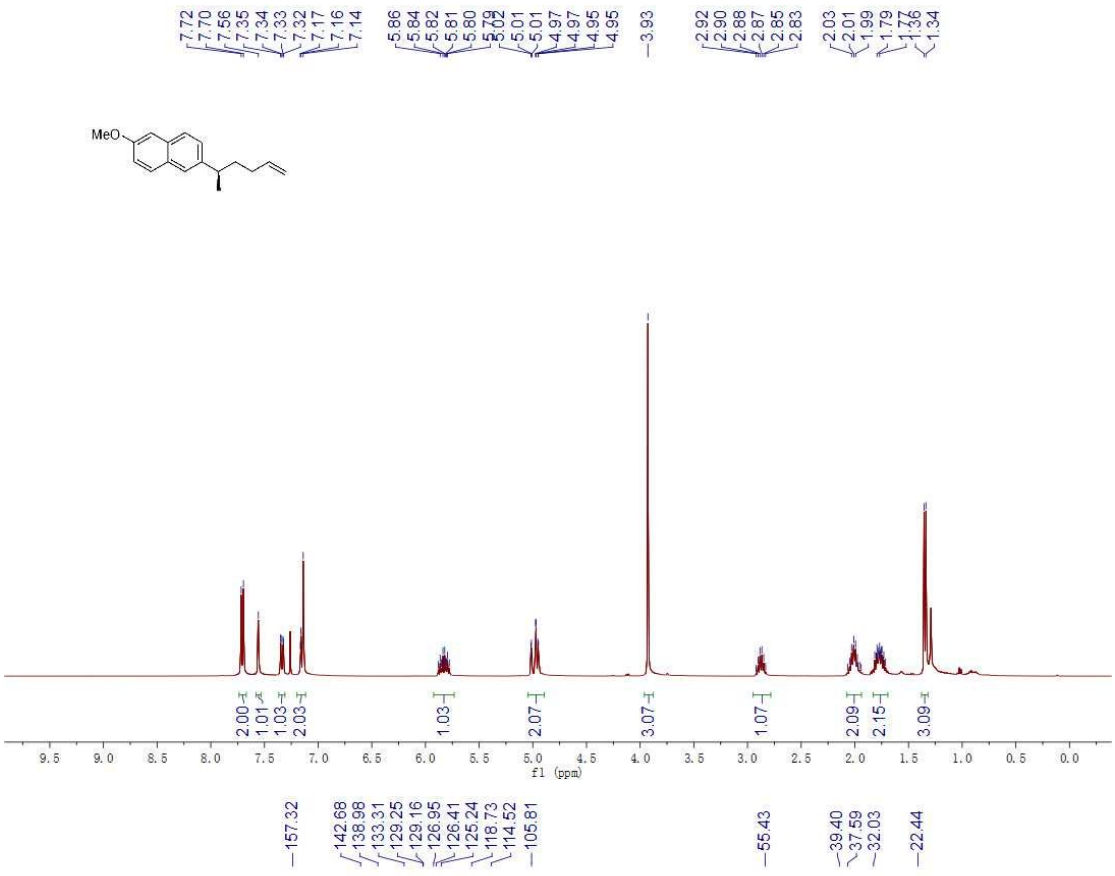

90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

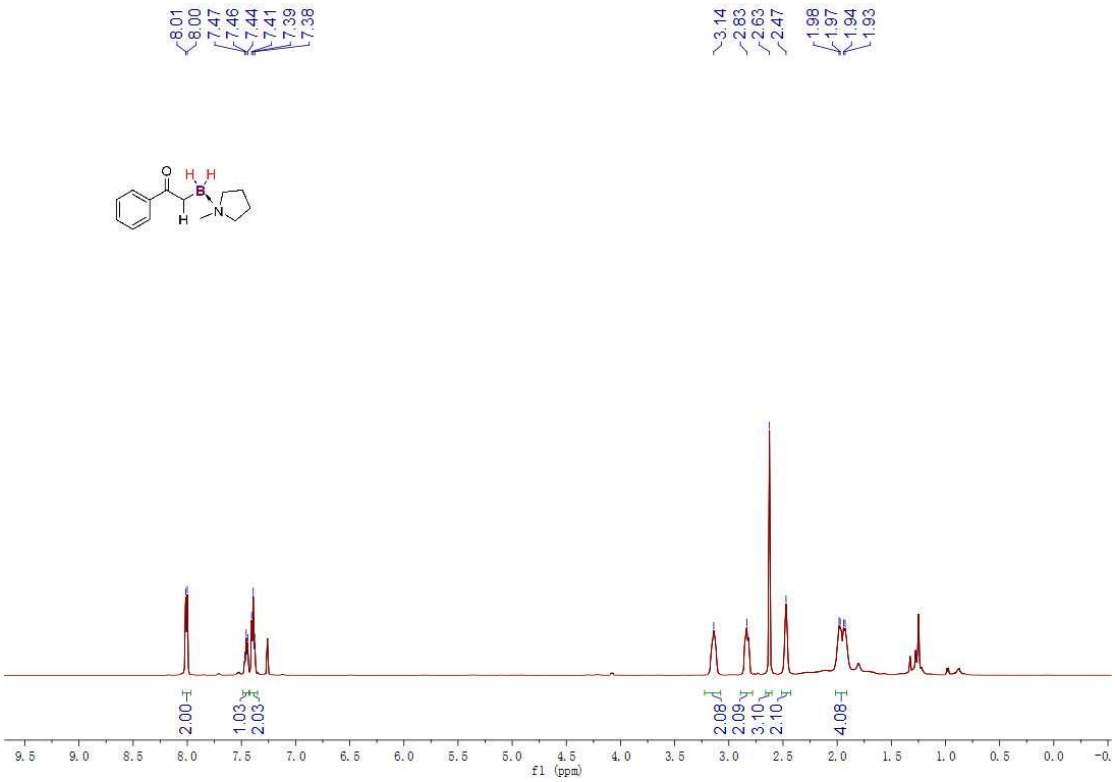
136.91

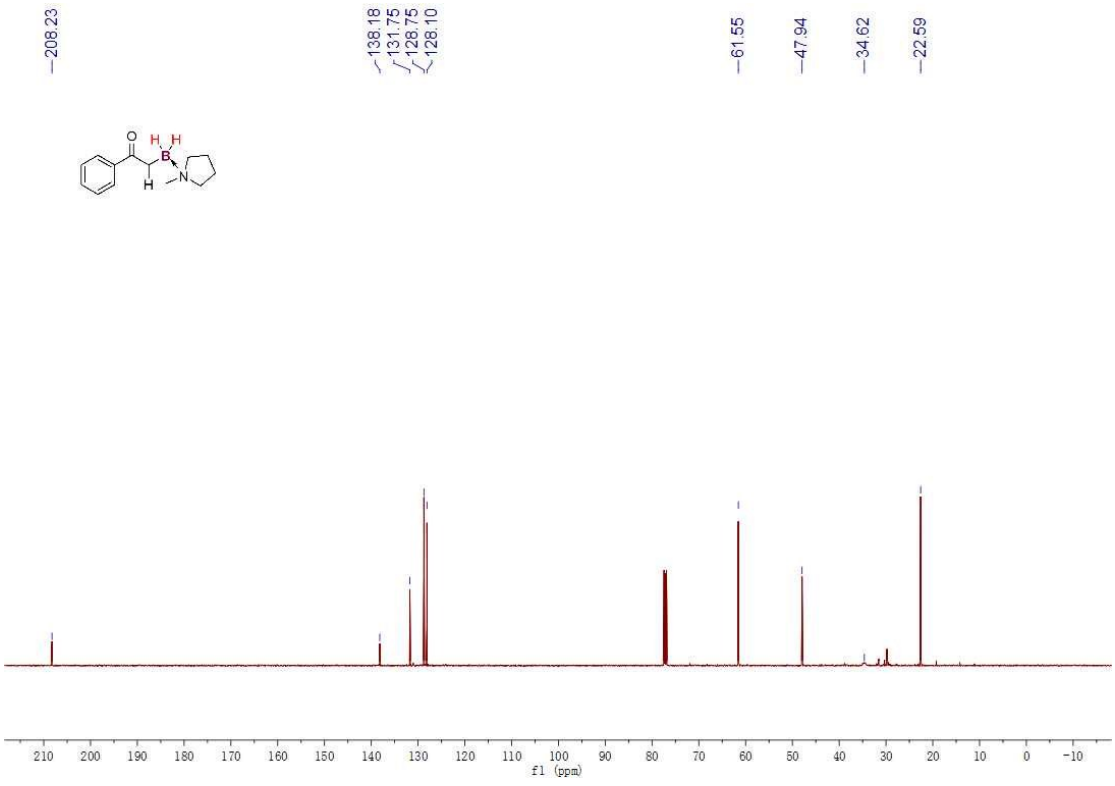

MeO
BF3K

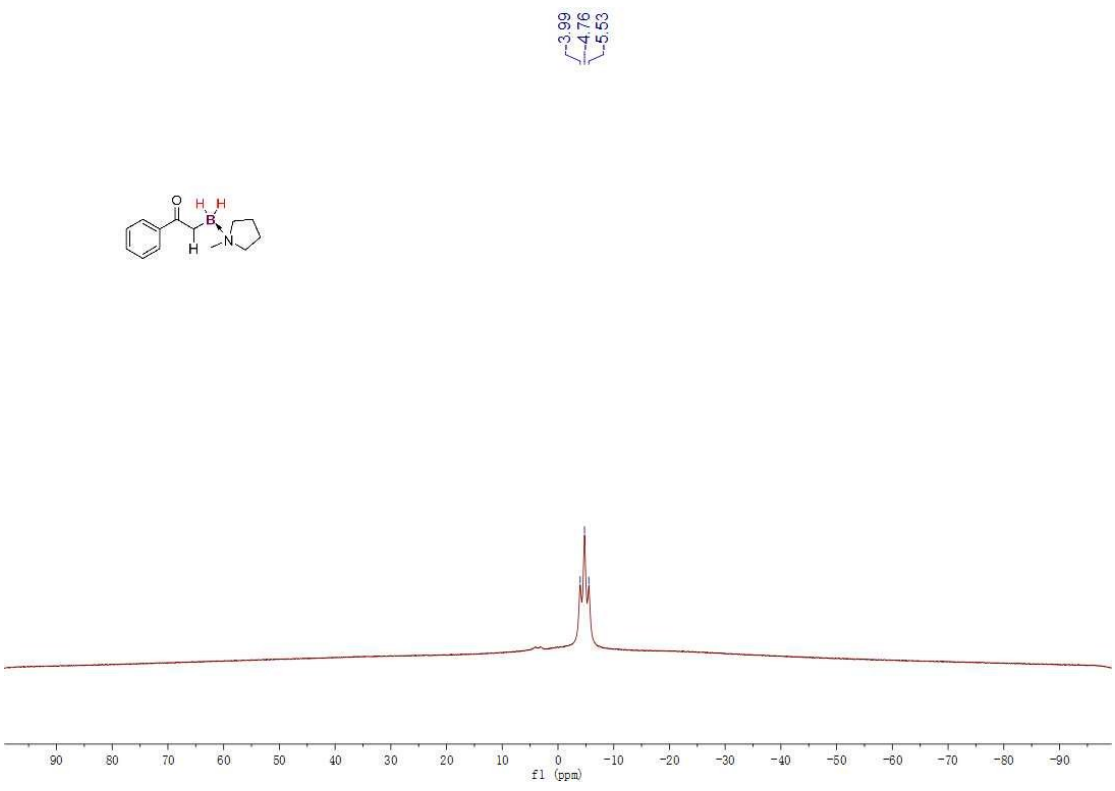

10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.71
7.70
7.69
7.68
7.57
7.35
7.34
7.33
7.32
7.16
7.15
7.14
7.13
7.13
3.92
3.63
3.62
3.60
3.60
3.59
3.58
3.57
3.57
3.56
3.55
3.54
3.52
3.06
3.04
3.02
3.00
1.96
1.94
1.92
1.91
1.46
1.36
1.35
MeO
OH
2.00
1.00
1.01
2.00
3.07
2.13
1.03
2.07
1.15
3.10
f1 (ppm)
157.38
142.07
133.37
129.22
129.14
127.12
126.18
125.17
118.83
105.80
61.36
55.42
41.03
36.51
22.61
MeO
OH
f1 (ppm)


7.72
7.70
7.56
7.35
7.34
7.33
7.32
7.17
7.16
7.14
5.86
5.84
5.82
5.81
5.80
5.79
5.02
5.01
5.01
4.97
4.97
4.95
4.95
3.93
2.92
2.90
2.88
2.87
2.85
2.83
2.03
2.01
1.99
1.79
1.77
1.36
1.34
MeO
2.00
1.01
1.03
2.03
1.03
2.07
3.07
1.07
2.09
2.15
3.09
f1 (ppm)
157.32
142.68
138.98
133.31
129.25
129.16
126.95
126.41
125.24
118.73
114.52
105.81
55.43
39.40
37.59
32.03
22.44
MeO
f1 (ppm)


8.01
8.00
7.47
7.46
7.44
7.41
7.39
7.38
3.14
2.83
2.63
2.47
1.98
1.97
1.94
1.93
2.00
1.03
2.03
2.08
2.09
3.10
2.10
4.08
f1 (ppm)


208.23
138.18
131.75
128.75
128.10
61.55
47.94
34.62
22.59
f1 (ppm)


3.99
4.76
5.53
O
H
H
B
H
N
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

8. Reference

(1) (a) Talero, A. G.; Martins, B. S.; Burtoloso, A. C. B. *Org. Lett*. **2018**, *20*, 7206-7211. (b) Janot, C.; Palamini, P.; Dobson, B. C.; Muir, J.; Aïssa, C. *Org. Lett*., **2019**, *21*, 296-299.

(2) Cheng, Q. Q.; Zhu, S.-F.; Zhang, Y.-Z.; Xie, X.-L.; Zhou, Q.-L. *J. Am. Chem. Soc*., **2013**, *135*, 14094-14097.

(3) (a) Yang, J.-M.; Zhao, Y.-T.; Li, Z.-Q.; Gu, X.-S.; Zhu, S.-F.; Zhou, Q.-L. *ACS Catal.*, **2018**, *8*, 7351−7355. (b) Li, J.; He, H.; Huang, M.; Chen, Y.; Luo, Y.; Yan, K.; Wang, Q.; Wu, Y. *Org. Lett*., **2019**, DOI: 10.1021/acs.orglett.9b03410.