Photocatalytic [3+2]-Annulation via Sodium Tetraarylborate : A Fundamental Approach for Synthesizing 1,4,2-Diazaborole Analogs

Hao-Ni Qin[a], Hao-Wen Jiang[a], Yi Zhao[b], Saira Qurban[a], Ke-Chun Wang[a], and Peng-Fei Xu[a, *]

[a]State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, Gansu, China

[b]Tecon Pharmaceutical Co., Ltd, No. 109, Jintun Road, Urumqi City 830023, Xinjiang, China

Corresponding Author: Email: xupf@lzu.edu.cn

SUPPORTING INFORMATION

Contents

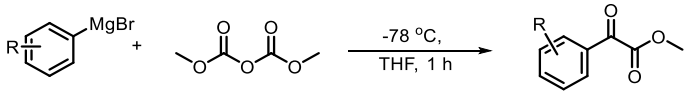
1. General Information

All glassware was thoroughly oven-dried. Chemicals and solvents were purchased from commercial suppliers and used as received. Thin-layer chromatography plates were visualized by exposure to ultraviolet light and/or staining with phosphomolybdic acid followed by heating on a hot plate. Flash chromatography was carried out using silica gel (200-300 mesh). ^{1}H NMR、^{13}C NMR and ^{11}B NMR spectra were recorded on a 400 MHz spectrometer. The spectra were recorded in deuterochloroform ($CDCl_3$) as solvent at room temperature, and ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to the residual solvent peak. The residual solvent signals were used as references, and the chemical shifts were converted to the TMS scale ($CDCl_3$: δH = 7.26 ppm, δC = 77.0 ppm). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet doublet), integration, coupling constant (Hz), and assignment. Data for ^{13}C NMR are reported as chemical shift. HRMS analysis was performed on a Bruker Apex II mass instrument (ESI).

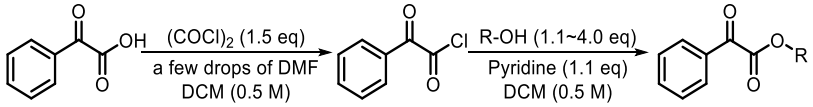
Note: 1: The resonances of carbon atoms connected to the boron atom were not observed in ^{13}C NMR spectra of all boron-nitrogen heterocycles because of quadrupole broadening. 2: All ^{11}B NMR spectra were recorded using natural quartz NMR tubes (S-5-500-QTZ-7), selected specifically to minimize background interference from glass.

2. Preparation of Reagents and Substrates

2.1 General procedure for the synthesis of α-ketoester[1][2]

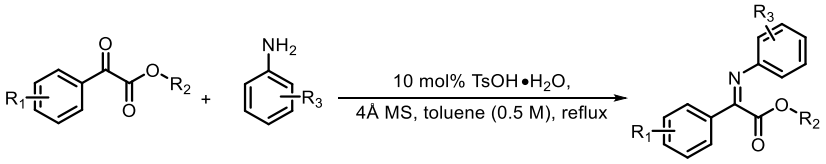


A solution of dimethyl oxalate (1.5 equiv.) was added to Aryl magnesium bromide (1.0 M solution in THF, 1.0 equiv.) at - 78 °C, and then stirred at -78 °C for 1 h. After completion, sat. aq. NH_4Cl solution was added and the reaction mixture was separated, the aqueous layer was then extracted with EtOAc for three times. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by chromatography on silica gel to give the desired α-ketoester product.



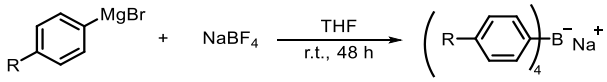
To a solution of 2-oxo-2-phenylacetic acid (1 equiv) in dry DCM (0.5 M) were added oxalyl dichloride (1.5 equiv) and a few drops of DMF at 0 °C, the reaction mixture was warmed up to room temperature and stirred for at least 0.5 h until no gas is generated. Then DCM and oxalyl dichloride were removed in vacuo. DCM (0.5 M), pyridine (1.1 equiv), and alcohol (1.1 – 4.0 equiv) were added to the residue and the reaction mixture was stirred for at least 2 hours at room temperature. The reaction mixture was purified by silica gel flash column chromatography to give corresponding α-ketoester.

2.2 General procedure for the synthesis of imine[3]



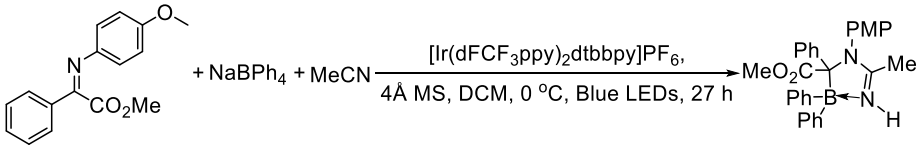
To a solution of α-ketoesters (1.0 equiv.) and aniline (1.1 equiv.) in anhydrous toluene (30-50 mL) was added $TsOH·H_2O$ (10 mol%) and 4Å molecular sieve at room temperature. The mixture was heated to reflux and monitored by thin layer chromatography (TLC). When the reaction was finished (1–3 days), the reaction mixture was cooled to room temperature, then filtered through a pad of celite and the filter cake was washed with DCM. Volatiles was then removed under reduced pressure to obtain the crude product, which was purified by flash column chromatography (silica gel, PE/EA = 10/1 to 1/1) to afford products.

2.3 General procedure for the synthesis of sodium tetraarylborates[4]



$NaBF_4$ (1.0 equiv) was added to a dark gray solution of the aryl Grignard reagent (5.0 eq), the reaction mixture was stirred for additional 48-72 h at room temperature. The reaction mixture was then poured into a solution of Na_2CO_3 in water and stirred for 20 min. After filtering, the filtrate was extracted with ethyl acetate, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was recrystallized from petroleum ether to afford sodium tetraarylborates.

3. General Procedure for the Synthesis of 1,4,2-Diazaborole Analogs

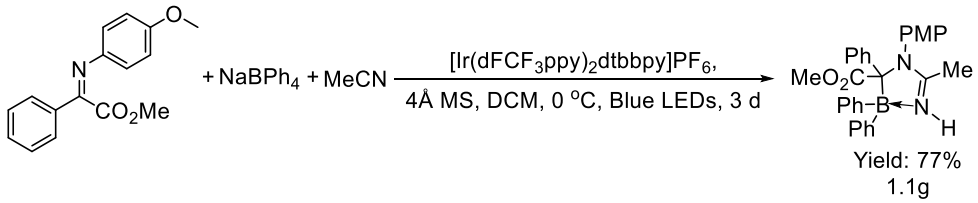


To a 10 mL Schlenk tube equipped with a magnetic stir bar was added 4Å molecular sieve (20 mg), $NaBPh_4$ (0.05 mmol), imine (0.175 mmol), $Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (4 mol%), then dry MeCN (0.5 mL) and dry DCM (0.5 mL) was added. The mixture was degassed by three cycles of freeze-pump-thaw and then placed in the irradiation apparatus equipped with two 30 W blue light-emitting diode (LED) downlights. The resulting mixture was stirred at 0 °C. Upon completion of the reaction, the reaction mixture was concentrated under reduced pressure, and the resulting crude mixture was purified by flash column chromatography on silica gel (PE/EA = 5/1~3/2). The products were further purified by recrystallization in DCM/n-Hexane.

Standard reaction setup

During the photoinduced reaction, heat generated from the LED downlights resulted in warming of the reaction. Therefore, we lowered the temperature to - 6°C, and the precise temperature of the reaction vessel can be displayed by the thermometer. The 30W Blue Leds were bought from https://www.taobao.com/

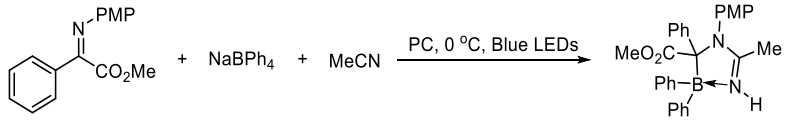
The scale-up reaction



To a 250 mL Schlenk tube equipped with a magnetic stir bar was added 4Å molecular sieve (1.2 g), $NaBPh_4$ (3.0 mmol), imine (10.5 mmol), $Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (4 mol%), then dry MeCN (30 mL) and dry DCM (30 mL) was added. The mixture was degassed by three cycles of freeze-pump-thaw and then placed in the irradiation apparatus equipped with two 30 W blue light-emitting diode (LED) downlights. The resulting mixture was stirred at 0 °C for 3 days. Upon completion of the reaction, the reaction mixture was concentrated under reduced pressure, and the resulting crude mixture was purified by flash column chromatography on silica gel (PE/EA = 5/1). The product were further purified by recrystallization in DCM/n-hexane to afford the desired product.

4. Initial Studies and the Reaction Optimization

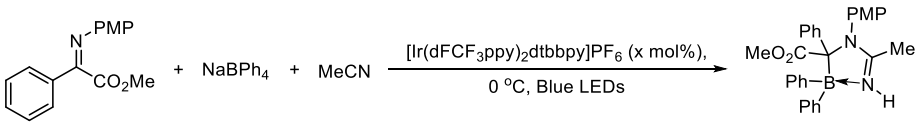
Table S1. Screen of the Photocatalysts



Entry	Photocatalyst	Yield (%)[a,b]
1	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	47
2	3DPAFIPN	26
3	4CzIPN	33
4	$[Ir(dF(Me)ppy)_2dtbbpy]PF6$	27
5	$[Ir(ppy)_2dtbbpy]PF_6$	22
6	$Acr\text{-}Mes(ClO_4)$	0
7	$Ru(bpy)_3(PF_6)_2$	0

[a]Unless otherwise noted, reaction conditions are as follows: imine (0.05 mmol), $NaBPh_4$ (0.10 mmol), PC (0.0015 mmol), MeCN (0.5 mL), 30 W Blue LEDs, 0 °C, 12 h, under an argon atmosphere. [b]Isolated yield.

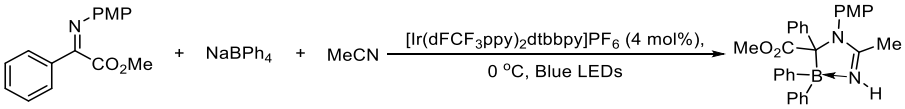
Table S2. Screen of the ratio of substrates and the dosage of photocatalyst.



Entry	1a:2a	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	Yield (%)[c]
1	1:1	3 mol%	34[a]
2	1:2	3 mol%	47[a]
3	1:3	3 mol%	49[a]
4	1:4	3 mol%	44[a]
5	1:3	1 mol%	44[b]
6	1:3	2 mol%	46[b]
7	1:3	3 mol%	49[b]
8	1:3	4 mol%	51[b]
9	1:3	5 mol%	52[b]

[a]Unless otherwise noted, reaction conditions are as follows: imine (0.05 mmol), $NaBPh_4$ (x mmol), $[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$ (0.0015 mmol), MeCN (0.5 mL), 30 W Blue LEDs, 0 °C, 12 h, under an argon atmosphere. [b]Unless otherwise noted, reaction conditions are as follows: imine (0.05 mmol), $NaBPh_4$ (0.15 mmol), $[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$ (x mol%), MeCN (0.5 mL), 30 W Blue LEDs, 0 °C, 12 h, under an argon atmosphere. [c]Isolated yield.

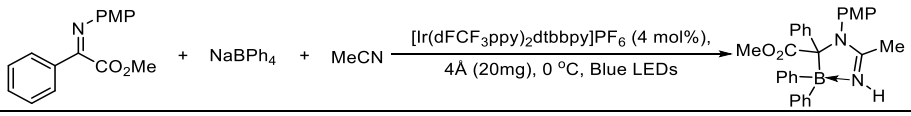
Table S3. Screen of the molecular sieve.



Entry	Molecular Sieve	Yield (%)[a,b]
1	3Å (20 mg)	46
2	4Å (20 mg)	55
3	4Å (40 mg)	37
4	4Å (60 mg)	47
5	4Å (80 mg)	45
6	4Å (100 mg)	42

[a]Unless otherwise noted, reaction conditions are as follows: imine (0.05 mmol), $NaBPh_4$ (0.15 mmol), $[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$ (0.002 mmol), MeCN (0.5 mL), 30 W Blue LEDs, 0 °C, 12 h, under an argon atmosphere. [b]Isolated yield.

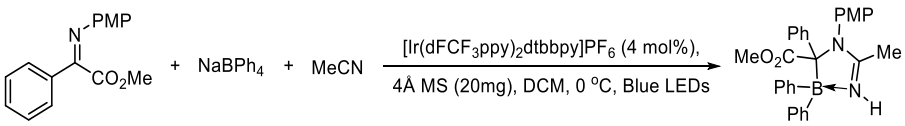
Table S4. Screen of the solvent and reaction time.



Entry	Solvent	Reaction time	Yield (%)[a,b]
1	MeCN (0.5 mL)	12 h	55
2	MeCN + toluene (0.5 mL + 0.5 mL)	12 h	0
3	MeCN + DCM (0.5 mL + 0.5 mL)	12 h	60
4	MeCN + DCM (0.5 mL + 0.5 mL)	18 h	65
5	MeCN + DCM (0.5 mL + 0.5 mL)	24 h	73
6	MeCN + DCM (0.5 mL + 0.5 mL)	27 h	78
7	MeCN + DCM (0.5 mL + 0.5 mL)	30 h	58

[a]Unless otherwise noted, reaction conditions are as follows: imine (0.05 mmol), $NaBPh_4$ (0.15 mmol), $[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$ (0.002 mmol), 4Å molecular sieve (20 mg), 30 W Blue LEDs, 0 °C, 12 h, under an argon atmosphere. [b]Isolated yield.

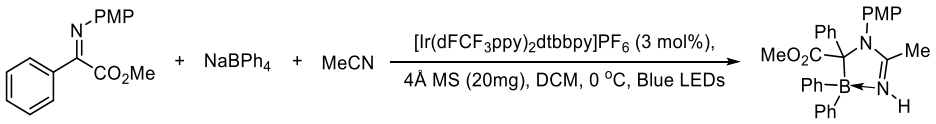
Table S5. Screen of the ratio of substrates again



Entry	1a:2a	Yield (%)[a,b]
1	1:1	42
2	1.5:1	50
3	2:1	71
4	2.5:1	65
5	3:1	82
6	3.5:1	91
7	4:1	81

[a]Unless otherwise noted, reaction conditions are as follows: imine (x mmol), $NaBPh_4$ (0.05 mmol), $[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$ (0.002 mmol), 4Å molecular sieve (20 mg), MeCN (0.5 mL), DCM (0.5 mL), 30 W Blue LEDs, 0 °C, 27 h, under an argon atmosphere. [b]Isolated yield.

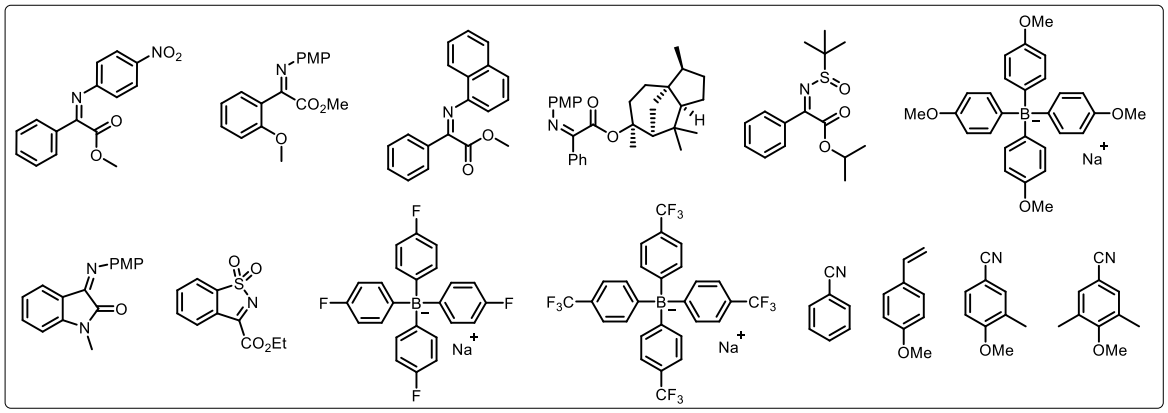
Table S7. Control Experiments



Entry	PC	Light	Yield (%)[a,b]
1	√	√	47
2	-	√	0
3	√	-	0
4	-	-	0

[a]Unless otherwise noted, reaction conditions are as follows: imine (0.05 mmol), $NaBPh_4$ (0.10 mmol), $[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$ (0.0015 mmol), MeCN (0.5 mL), 30 W Blue LEDs, 0 °C, 12 h, under an argon atmosphere. [b]Isolated yield.

Table S8. Unsuccessful substrates



5. Mechanistic Investigations

5.1 Radical inhibition experiment

When TEMPO (2.0 equiv) was introduced into the model reactions, no corresponding products were observed according to both TLC and HR-MS analysis. These results indicated that a free radical process was involved.

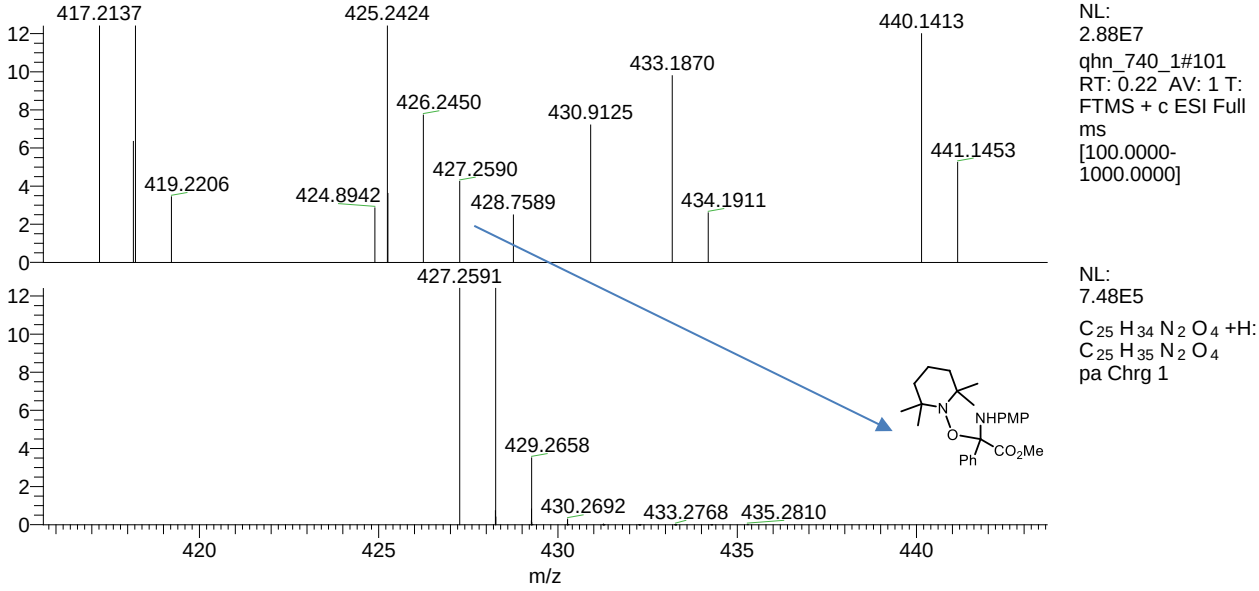
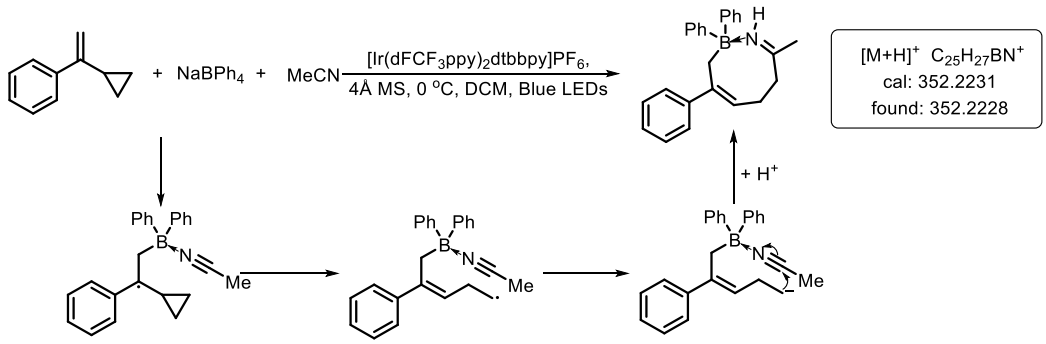


Figure S1. HR-MS for the corresponding radical trapping product

5.2 Radical clock experiment



To a 10 mL Schlenk tube equipped with a magnetic stir bar was added 4Å molecular sieve (20 mg), $NaBPh_4$ (0.05 mmol), (1-cyclopropylvinyl)benzene (0.175 mmol), $Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (4 mol%), then dry MeCN (0.5 mL) and dry DCM (0.5 mL)

was added. The mixture was degassed by three cycles of freeze-pump-thaw and then placed in the irradiation apparatus equipped with two 30 W blue light-emitting diode (LED) downlights. The resulting mixture was stirred at 0 °C for 27 h. Due to the yield was not good, we did not try to isolate product. The reaction mixture was sent for HR-MS analysis.

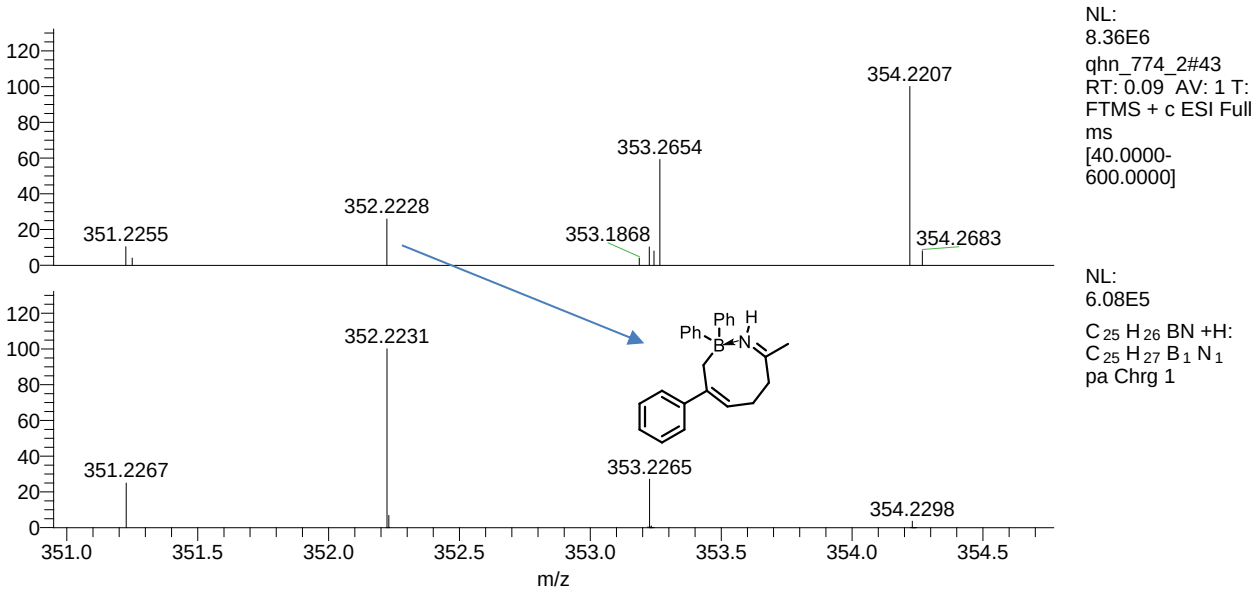
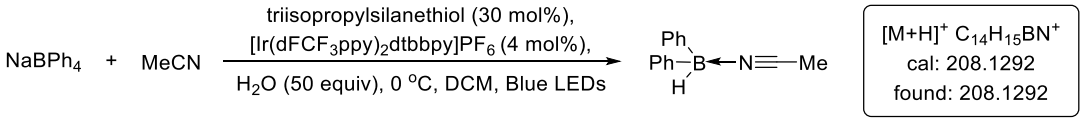


Figure S2. HR-MS for the corresponding product

5.3 Hydrogen abstraction reaction



To verify the presence of intermediate **II**, we performed hydrogen extraction experiment. To a 10 mL Schlenk tube equipped with a magnetic stir bar was added $NaBPh_4$ (0.05 mmol), triisopropylsilanethiol (30 mol%), H_2O (50 equiv), $Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (4 mol%), then dry MeCN (0.5 mL) and dry DCM (0.5 mL) was added. The mixture was degassed by three cycles of freeze-pump-thaw and then placed in the irradiation apparatus equipped with two 30 W blue light-emitting diode (LED) downlights. The resulting mixture was stirred at 0 °C for 27 h. The reaction mixture was sent for HR-MS analysis directly, then we tried to isolate, but failed.

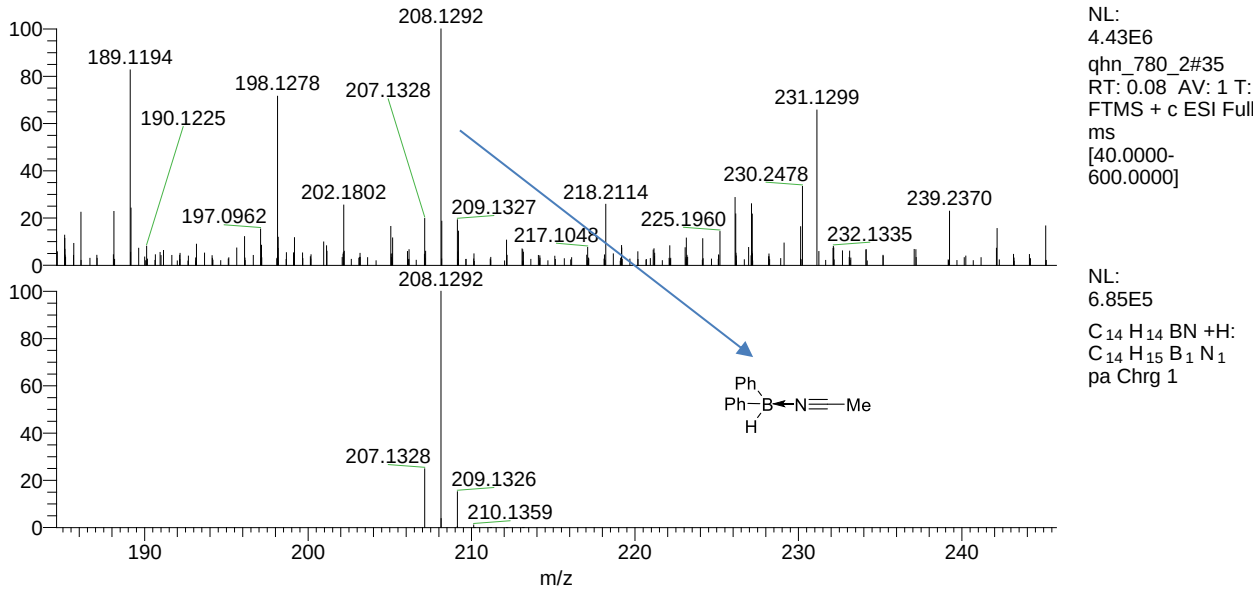
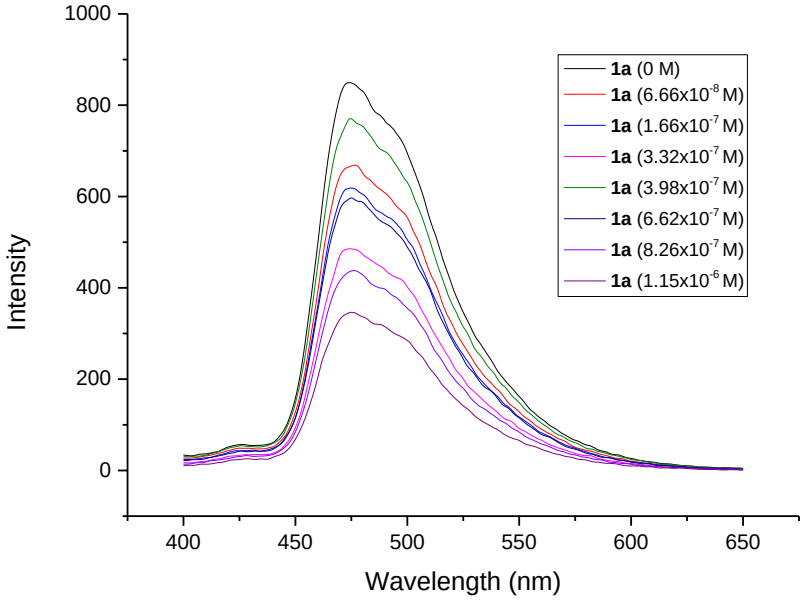


Figure S3. HR-MS for the corresponding hydrogenated product

5.4 Stern-Volmer fluorescence quenching experiments

Stern-Volmer fluorescence quenching experiments were run with freshly prepared solutions of 1.33×10^{-5} M $[Ir(dFCF_3ppy)_2(dtbbpy)]PF_6$ and varying concentrations of quencher in MeCN in a screw-top quartz cuvette at room temperature. The solutions were irradiated at 420 nm and fluorescence was measured from 400 nm to 650 nm. Control experiments showed that the excited state photocatalyst was mainly quenched by imine **1a**.



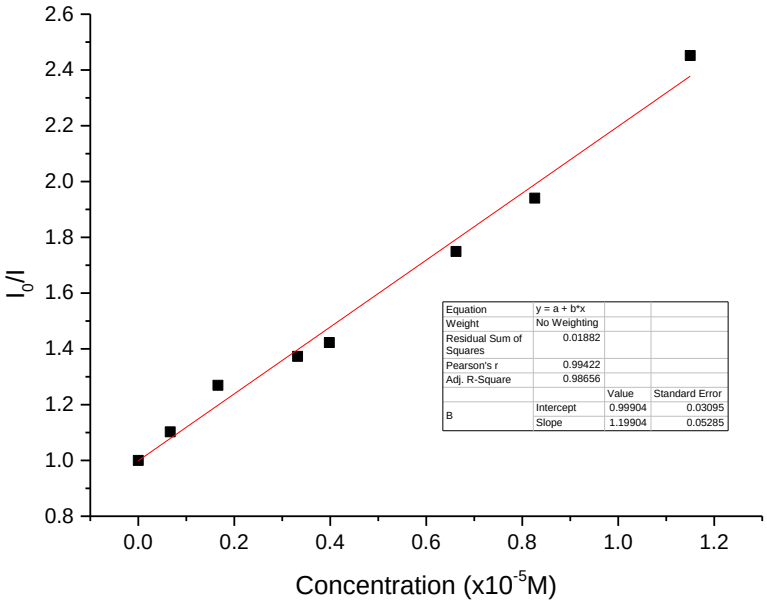
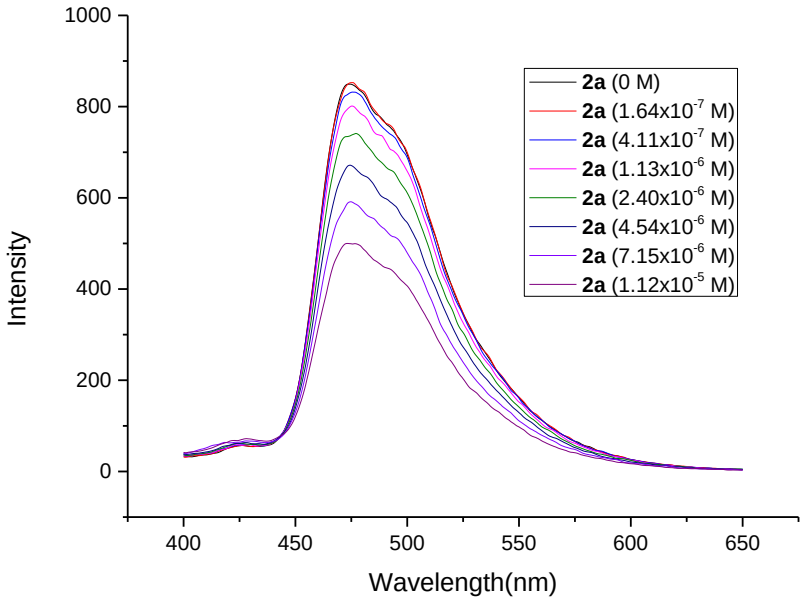


Figure S4. Fluorescence quenching experiments date with [Ir(dFCF$_3$ppy)$_2$(dtbbpy)]PF$_6$ and variable imine **1a**.



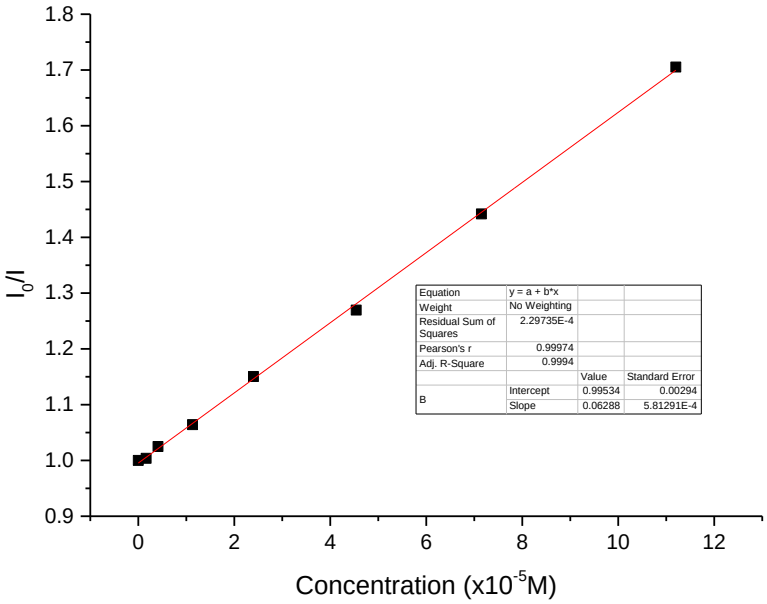


Figure S5. Fluorescence quenching experiments date with $[Ir(dFCF_3ppy)_2(dtbbpy)]PF_6$ and variable $NaBPh_4$ **2a**.

5.5 Light on-off experiment

To a 25 mL Schlenk tube equipped with a magnetic stir bar was added 4Å molecular sieve (120 mg), $NaBPh_4$ (0.3 mmol), imine (1.05 mmol), $Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (4 mol%), 1,3,5-trimethoxybenzene (0.3 mmol), then dry MeCN (3.0 mL) and dry DCM (3.0 mL) was added. The mixture was degassed by three cycles of freeze-pump-thaw, then stirred rapidly and irradiated with Blue LEDs at 0 °C. After 1 hours, the Blue LEDs was turned off, and a 100 μL sample of the reaction mixture was taken with a syringe and measured by ^1H NMR. After being stirred for 1 hours in dark, a 100 μL sample of the reaction mixture was also taken with a syringe and measured by ^1H NMR. The reaction mixture was then irradiated with Blue LEDs and stirred for 1 hours. Repeating this process three times. These resulted in a total interruption of the reaction progress in the absence of light and recuperation of reactivity on further illumination. The results demonstrated that light was a necessary component of the reaction. Even though we could not definitively rule out a radical-chain process, the data shown that any chain-propagation process must be short-lived.

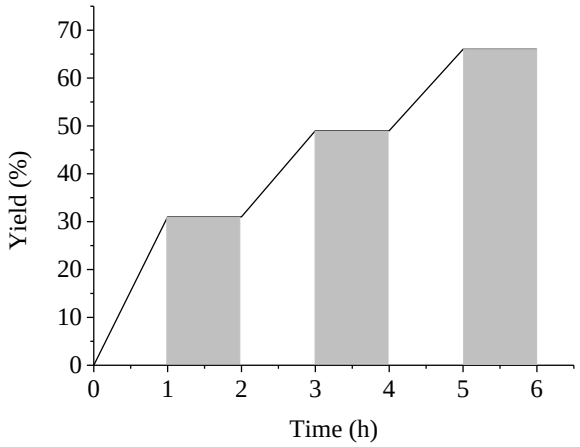


Figure S6. Time profile of the transformation with the light on-off over time. Yields were determined by crude ^{1}H NMR spectra using 1,3,5-trimethoxybenzene as an internal standard.

5.6 Investigate whether the H on N in the product comes from the solvent

The Methyl 4-ethenylbenzoate was selected as the substrate for the study. Experiments were conducted by substituting the solvent with CD_3CN or a mixture of CD_2Cl_2 and CD_3CN under template reaction conditions. A comparison of the resulting products with product **6a** revealed that the hydrogen on nitrogen remains unaffected by both two solvents. This observation allows for the exclusion of acetonitrile and dichloromethane as potential hydrogen donors. Based on the analysis of the reaction system, we speculate that the trace amount of water in the system may is the source.

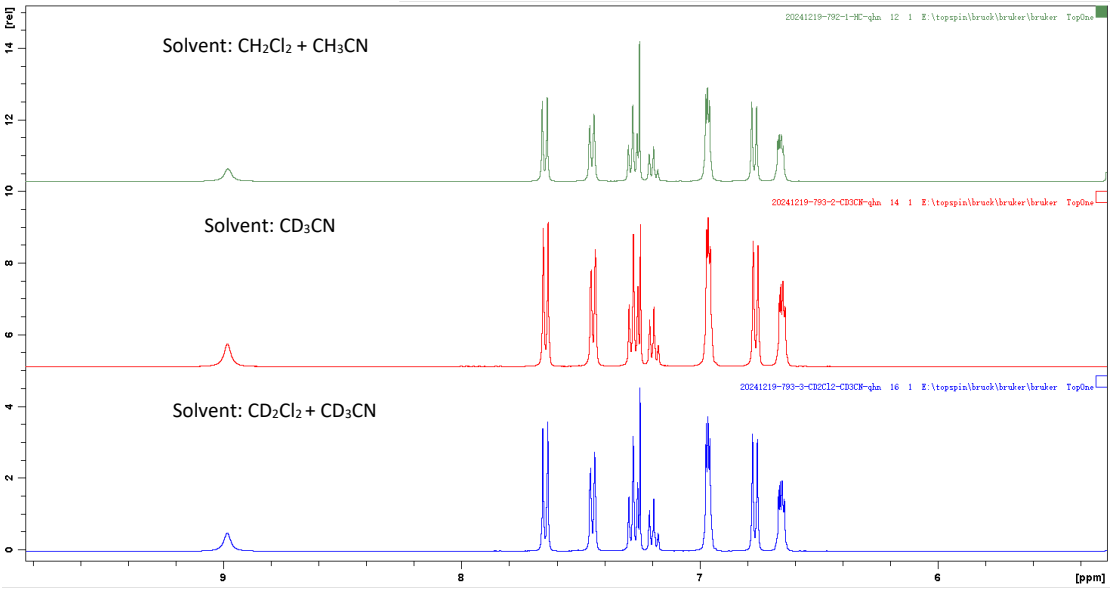


Figure S7. Comparing the ^{1}H NMR spectra of products from three reactions.

5.7 Plausible mechanism

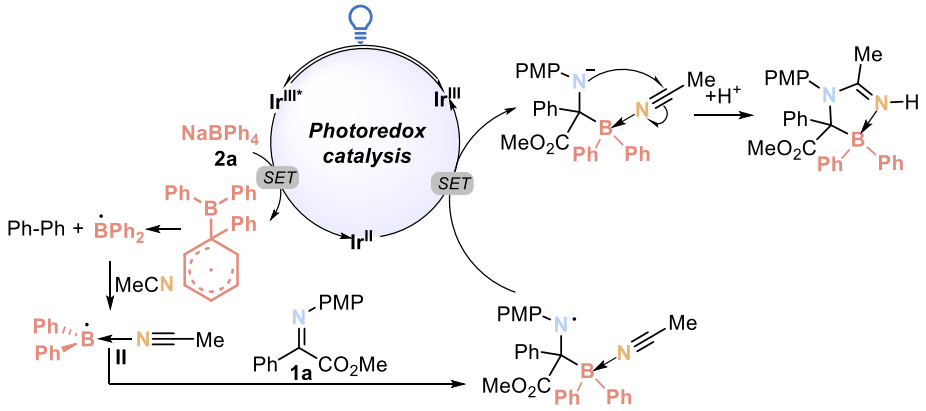
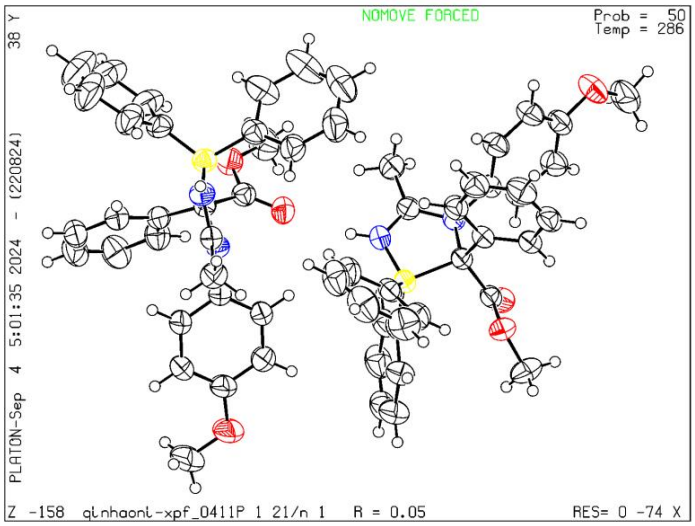
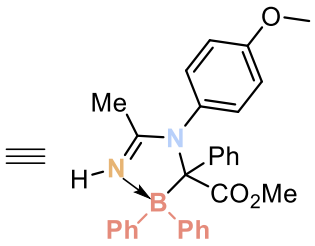


Figure S8. Mechanism of direct attack by the boryl radical on the imine

6. X-Ray Crystallographic Data





CCDC: 2381718

Bond precision:	C-C = 0.0028 A	Wavelength=1.54184	
Cell:	a = 11.04999(19)	b = 23.4910(6)	c = 22.4123(4)
	alpha = 90	beta = 100.7718 (17)	gamma = 90
Temperature:	286 K		
	Calculated	Reported	
Volume	5715.2 (2)	5715.2 (2)	
Space group	P 21/n	P 1 21/n 1	
Hall group	-P 2yn	-P 2yn	
Moiety formula	$C_{30}H_{29}BN_2O_3$	$2(C_{30}H_{29}BN_2O_3)$	
Sum formula	$C_{30}H_{29}BN_2O_3$	$C_{60}H_{57}B_2N_4O_6$	
Mr	476.36	951.71	
Dx,g cm^{-3}	1.107	1.106	
Z	8	4	
Mu (mm^{-1})	0.562	0.562	
F000	2016.0	2012.0	
F000’	2021.78		
h, k, lmax	13, 29, 28	13, 29, 28	
Nref	11862	11257	
Tmin,Tmax	0.947, 0.967	0.694, 1.000	
Tmin’	0.940		
Correction method = # Reported T Limits: Tmin = 0.694 Tmax = 1.000			
AbsCorr = MULTI-SCAN			
Data completeness = 0.949		Theta(max) = 75.555	
R(reflections) = 0.0467 (8288)		wR2(reflections) = 0.1283(11257)	
S = 1.032		Npar = 663	
Displacement ellipsoids are drawn at 50% probability level			

7. Reference

[1] Liang, Y.; Kleinmans, R.; Daniliuc, C. G.; Glorius, F. Synthesis of Polysubstituted 2-Oxabicyclo[2.1.1]Hexanes via Visible-Light-Induced Energy Transfer. *J. Am. Chem. Soc.* **2022**, *144* (44), 20207–20213.

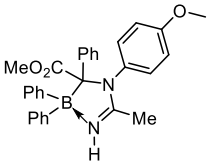
[2] Liu, Y.; Luo, G.; Yang, X.; Jiang, S.; Xue, W.; Chi, Y. R.; Jin, Z. Carbene-Catalyzed Enantioselective Aromatic N-Nucleophilic Addition of Heteroarenes to Ketones. *Angew. Chem. Int. Ed.* **2020**, *59* (1), 442–448.

[3] Curto, J. M.; Dickstein, J. S.; Berritt, S.; Kozlowski, M. C. Asymmetric Synthesis of α-Allyl-α-Aryl α-Amino Acids by Tandem Alkylation/π-Allylation of α-Iminoesters. *Org. Lett.* **2014**, *16* (7), 1948–1951.

[4] Yue, F.; Ma, H.; Ding, P.; Song, H.; Liu, Y.; Wang, Q. Formation of C–B, C–C, and C–X Bonds from Nonstabilized Aryl Radicals Generated from Diaryl Boryl Radicals. *ACS Cent. Sci.* **2023**, *9* (12), 2268–2276.

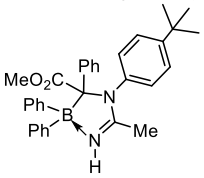
8. Characterization of Products

methyl 4-(4-methoxyphenyl)-5-methyl-2,2,3-triphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4aa)



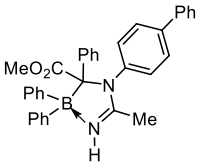
White solid; 91% yield;**^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.28 – 7.22 (m, 4H), 7.18 (t, *J* = 7.3 Hz, 2H), 7.11 – 7.04 (m, 3H), 7.00 (m, 2H), 6.93 (d, *J* = 4.3 Hz, 4H), 6.68 – 6.60 (m, 3H), 6.57 (d, *J* = 9.1 Hz, 2H), 3.65 (s, 3H), 2.99 (s, 3H), 1.94 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)**δ 173.3, 167.5, 159.1, 141.8, 133.1, 132.8, 130.9, 130.7, 130.3, 126.9, 126.5, 126.4, 126.2, 125.4, 124.2, 113.4, 55.2, 50.5, 17.0. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 0.17. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $[C_{30}H_{29}BN_2O_3Na]$: 499.2163; Found 499.2163.

methyl 4-(4-(tert-butyl)phenyl)-5-methyl-2,2,3-triphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4ab)



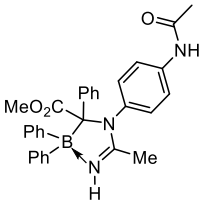
White solid; 83% yield;**^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.29 – 7.28 (m, 1H), 7.25 – 7.23 (m, 2H), 7.21 – 7.16 (m, 3H), 7.13 – 7.06 (m, 6H), 7.03 (m, 2H), 6.98 (m, 3H), 6.66 (d, *J* = 8.1 Hz, 2H), 6.60 (s, 1H), 3.02 (s, 3H), 2.14 (s, 3H), 1.22 (s, 9H).**^{13}C NMR (101 MHz, Chloroform-*d*)**δ 173.2, 167.3, 151.1, 141.9, 135.5, 133.1, 132.7, 130.1, 129.0, 126.8, 126.5, 126.4, 126.1, 125.4, 125.2, 124.1, 50.5, 34.5, 31.2, 17.2.**^{11}B NMR (128 MHz, Chloroform-*d*)** δ 0.26. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $[C_{33}H_{35}BN_2O_2Na]$: 525.2684; Found 525.2684.

methyl 4-([1,1'-biphenyl]-4-yl)-5-methyl-2,2,3-triphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4ac)



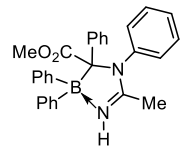
White solid; 91% yield; **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.29 – 7.23 (m, 4H), 7.21 – 7.16 (m, 3H), 7.16 – 7.12 (m, 2H), 7.12 – 7.06 (m, 5H), 7.04 – 6.99 (m, 2H), 6.95 (d, *J* = 4.2 Hz, 4H), 6.79 – 6.72 (m, 3H), 6.69 – 6.64 (m, 2H), 3.02 (s, 3H), 2.08 (s, 3H).**^{13}C NMR (101 MHz, Chloroform-*d*)**δ 173.1, 167.2, 146.3, 141.7, 138.2, 133.1, 132.7, 130.2, 129.6, 129.2, 128.3, 128.2, 126.9, 126.5, 126.4, 126.2, 125.5, 124.2, 118.5, 115.1, 50.5, 17.0.**^{11}B NMR (128 MHz, Chloroform-*d*)** δ 0.14. HRMS (ESI) m/z: $[M+H]^+$ calcd for $[C_{35}H_{32}BN_2O_2]$: 523.2551; Found 523.2552.

methyl 4-(4-acetamidophenyl)-5-methyl-2,2,3-triphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4ad)



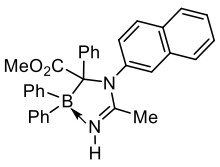
White solid; 56% yield; **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.27 – 7.20 (m, 7H), 7.17 (t, J = 7.4 Hz, 2H), 7.10 – 7.05 (m, 3H), 7.03 – 6.99 (m, 2H), 6.97 – 6.91 (m, 4H), 6.76 (s, 1H), 6.67 (d, J = 8.4 Hz, 2H), 3.03 (s, 3H), 2.08 (s, 3H), 2.05 (s, 3H).**^{13}C NMR (101 MHz, Chloroform-*d*)** δ 173.3, 168.4, 167.3, 141.6, 137.7, 133.7, 133.1, 132.7, 130.3, 130.2, 126.9, 126.5, 126.4, 126.3, 125.5, 124.2, 119.2, 50.5, 24.5, 17.0.**^{11}B NMR (128 MHz, Chloroform-*d*)** δ 0.22. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $[C_{31}H_{30}BN_3O_3Na]$: 526.2272; Found 526.2272.

methyl 5-methyl-2,2,3,4-tetraphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4ae)



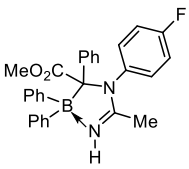
White solid; 89% yield; **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.29 – 7.26 (m, 2H), 7.25 – 7.22 (m, 2H), 7.21 – 7.18 (m, 2H), 7.16 (d, *J* = 4.9 Hz, 1H), 7.14 – 7.06 (m, 5H), 7.02 (m, 2H), 6.96 (d, *J* = 4.3 Hz, 4H), 6.80 – 6.75 (d, *J* = 7.3 Hz, 2H), 6.65 (s, 1H), 3.02 (s, 3H), 2.15 (s, 3H).**^{13}C NMR (101 MHz, Chloroform-*d*)**δ 173.1, 167.1, 141.7, 133.1, 132.8, 130.2, 129.7, 128.3, 128.3, 126.9, 126.6, 126.4, 126.3, 125.5, 124.2, 76.7, 50.5, 17.1.**^{11}B NMR (128 MHz, Chloroform-*d*)**δ 0.19. HRMS (ESI) m/z: $[M+H]^+$ calcd for $[C_{29}H_{28}BN_2O_2]$: 447.2238; Found 447.2231.

methyl 5-methyl-4-(naphthalen-2-yl)-2,2,3-triphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4af)



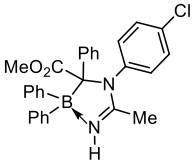
White solid; 72% yield; **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.75 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.48 – 7.39 (m, 2H), 7.33 – 7.27 (m, 4H), 7.21 (t, *J* = 7.4 Hz, 2H), 7.12 (m, 4H), 7.08 – 7.04 (m, 2H), 6.98 (d, *J* = 4.3 Hz, 4H), 6.95 (d, *J* = 8.6 Hz, 1H), 6.71 (s, 1H), 3.03 (s, 3H), 2.18 (s, 3H).**^{13}C NMR (101 MHz, Chloroform-*d*)** δ 173.2, 167.2, 141.9, 135.5, 133.1, 132.8, 132.7, 132.5, 130.4, 128.6, 128.3, 127.9, 127.6, 127.4, 127.0, 126.8, 126.6, 126.5, 126.4, 126.3, 125.6, 124.2, 50.6, 17.2.**^{11}B NMR (128 MHz, Chloroform-*d*)** δ 0.16. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $[C_{33}H_{29}BN_2O_2Na]$: 519.2214, found 519.2213.

methyl 4-(4-fluorophenyl)-5-methyl-2,2,3-triphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4ag)



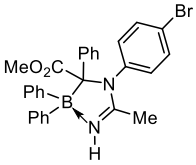
White solid; 67% yield; **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.24 (m, 4H), 7.18 (t, *J* = 7.3 Hz, 2H), 7.12 – 7.07 (m, 3H), 7.05 – 7.00 (m, 2H), 6.98 – 6.90 (m, 4H), 6.80 (m, 2H), 6.74 (m, 2H), 6.68 (s, 1H), 3.03 (s, 3H), 2.09 (s, 3H).**^{13}C NMR (101 MHz, Chloroform-*d*)**δ 173.2, 167.2, 163.3, 160.8, 141.5, 133.9, 133.1, 132.7, 131.7, 131.6, 130.2, 127.0, 126.6, 126.5, 126.4, 125.6, 124.3, 115.3, 115.1, 50.6, 17.0. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 0.15. HRMS (ESI) m/z: $[M+H]^+$ calcd for $[C_{29}H_{27}BFN_2O_2]$: 465.2144; Found 465.2141.

methyl 4-(4-chlorophenyl)-5-methyl-2,2,3-triphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4ah)



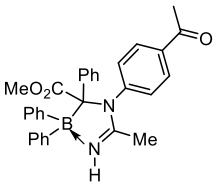
White solid; 66% yield; **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.26 – 7.21 (m, 4H), 7.18 (t, *J* = 7.4 Hz, 2H), 7.12 – 7.06 (m, 5H), 7.06 – 7.00 (m, 2H), 6.99 – 6.90 (m, 4H), 6.71 (d, *J* = 7.6 Hz, 3H), 3.04 (s, 3H), 2.14 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)**δ 173.2, 167.0, 141.4, 136.5, 134.4, 133.1, 132.7, 131.1, 130.2, 128.6, 127.1, 126.6, 126.5, 125.6, 124.3, 50.6, 17.1.**^{11}B NMR (128 MHz, Chloroform-*d*)** δ -0.83. HRMS (ESI) m/z: $[M+H]^+$ calcd for $[C_{29}H_{27}BClN_2O_2]$: 481.1849; Found 481.1848.

methyl 4-(4-bromophenyl)-5-methyl-2,2,3-triphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4ai)



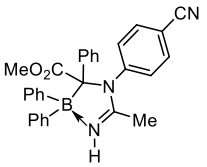
White solid; 75% yield; **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.27 (s, 1H), 7.26 – 7.21 (m, 5H), 7.20 – 7.15 (m, 2H), 7.12 – 7.06 (m, 3H), 7.03 (m, 2H), 6.99 – 6.91 (m, 4H), 6.72 (s, 1H), 6.65 (d, *J* = 8.6 Hz, 2H), 3.04 (s, 3H), 2.15 (s, 3H).**^{13}C NMR (101 MHz, Chloroform-*d*)**δ 173.2, 166.9, 141.4, 137.1, 133.1, 132.7, 131.6, 131.5, 130.2, 127.1, 126.6, 126.5, 126.5, 125.6, 124.3, 122.6, 50.6, 17.1.**^{11}B NMR (128 MHz, Chloroform-*d*)** δ 0.23. HRMS (ESI) m/z: $[M+H]^+$ calcd for $[C_{29}H_{27}BBrN_2O_2]$: 525.1343; Found 525.1343.

methyl 4-(4-acetylphenyl)-5-methyl-2,2,3-triphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4aj)



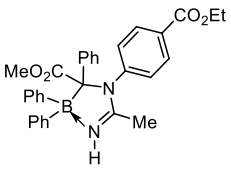
White solid; 71% yield;**^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.75 – 7.71 (m, 2H), 7.28 (m, 1H), 7.24 – 7.20 (m, 3H), 7.20 – 7.17 (m, 2H), 7.13 – 7.06 (m, 4H), 7.06 – 7.04 (m, 1H), 7.02 (m, 1H), 6.97 (m, 3H), 6.89 – 6.86 (m, 2H), 6.81 (s, 1H), 3.03 (s, 3H), 2.52 (s, 3H), 2.20 (s, 3H).**^{13}C NMR (101 MHz, Chloroform-*d*)**δ 197.2, 173.1, 166.7, 142.5, 141.4, 136.4, 133.0, 132.7, 129.9, 129.7, 128.4, 127.1, 126.6, 126.5, 126.5, 125.7, 124.3, 50.7, 26.6, 17.2.**^{11}B NMR (128 MHz, Chloroform-*d*)** δ 0.39. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $[C_{31}H_{29}BN_2O_3Na]$: 511.2163; Found 511.2160.

methyl 4-(4-cyanophenyl)-5-methyl-2,2,3-triphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4ak)



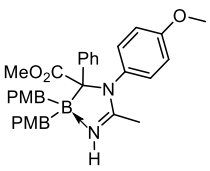
White solid; 75% yield;**^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.41 (d, *J* = 8.3 Hz, 2H), 7.26 – 7.23 (m, 2H), 7.22 – 7.16 (m, 4H), 7.13 – 7.01 (m, 5H), 6.97 (t, *J* = 7.6 Hz, 2H), 6.94 – 6.86 (m, 5H), 3.04 (s, 3H), 2.15 (s, 3H).**^{13}C NMR (101 MHz, Chloroform-*d*)**δ 173.1, 166.6, 142.4, 141.2, 133.0, 132.7, 132.3, 130.4, 129.8, 127.2, 126.7, 126.7, 126.5, 125.7, 124.4, 117.9, 112.2, 50.7, 17.1. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 0.47. HRMS (ESI) m/z: $[M+K]^+$ calcd for $[C_{30}H_{26}BN_3O_2K]$: 510.1750; Found 510.1744.

methyl 4-(4-(ethoxycarbonyl)phenyl)-5-methyl-2,2,3-triphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4al)



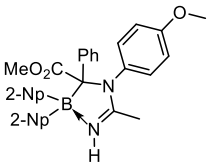
White solid; 80% yield;**^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.84 – 7.80 (m, 2H), 7.27 (m, 1H), 7.25 (m, 1H), 7.24 – 7.16 (m, 4H), 7.12 – 7.06 (m, 3H), 7.03 (m, 2H), 6.99 – 6.93 (m, 4H), 6.87 – 6.83 (m, 2H), 6.77 (s, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 3.03 (s, 3H), 2.19 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H).**^{13}C NMR (101 MHz, Chloroform-*d*)**δ 173.1, 166.8, 165.7, 142.3, 141.4, 133.0, 132.7, 130.2, 130.0, 129.7, 129.5, 127.1, 126.6, 126.5, 125.6, 124.3, 121.0 61.2, 50.6, 17.2, 14.3. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 0.37. HRMS (ESI) m/z: $[M+H]^+$ calcd for $[C_{32}H_{32}BN_2O_4]$: 519.2450; Found 519.2449.

methyl 4-(4-methoxyphenyl)-5-methyl-3-phenyl-2,2-di-p-tolyl-3,4-dihydro-2H-1,4,2l4-diazaborole-3-carboxylate (4ba)



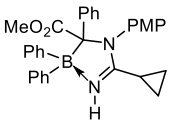
White solid; 41% yield;**^{1}H NMR (400 MHz, Chloroform-*d*)**δ 7.11 (m, 4H), 7.05 – 7.01 (m, 1H), 7.00 – 6.95 (m, 6H), 6.90 (d, *J* = 7.6 Hz, 2H), 6.67 (d, *J* = 8.6 Hz, 2H), 6.62 (m, 2H), 6.55 (s, 1H), 3.71 (s, 3H), 3.06 (s, 3H), 2.24 (s, 6H), 2.10 (s, 3H).**^{13}C NMR (101 MHz, Chloroform-*d*)**δ 173.4, 167.2, 159.1, 141.9, 134.5, 133.1, 132.7, 130.9, 130.8, 130.4, 127.4, 127.2, 126.9, 126.2, 113.3, 55.3, 50.5, 21.2, 21.1, 17.0. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ -0.43. HRMS (ESI) m/z: $[M+H]^+$ calcd for $[C_{32}H_{34}BN_2O_3]$: 505.2657; Found 505.2655.

methyl 4-(4-methoxyphenyl)-5-methyl-2,2-di(naphthalen-2-yl)-3-phenyl-3,4-dihydro-2H-1,4,2l4-diazaborole-3-carboxylate (4bb)



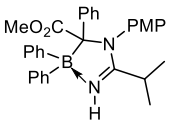
White solid; 45% yield;**^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.74 – 7.69 (m, 3H), 7.68 – 7.62 (m, 4H), 7.56 – 7.51 (m, 2H), 7.50 – 7.47 (m, 1H), 7.36 – 7.29 (m, 4H), 7.01 (dd, *J* = 7.0, 1.6 Hz, 2H), 6.98 – 6.95 (m, 1H), 6.92 – 6.87 (m, 2H), 6.82 (s, 1H), 6.72 (d, *J* = 8.5 Hz, 2H), 6.65 – 6.61 (m, 2H), 3.70 (s, 3H), 2.92 (s, 3H), 2.18 (s, 3H).**^{13}C NMR (101 MHz, Chloroform-*d*)**δ 173.3, 167.7, 159.2, 141.5, 133.4, 133.0, 132.6, 132.2, 132.2, 131.7, 131.7, 130.9, 130.7, 130.4, 130.3, 128.0, 127.5, 127.2, 127.0, 126.4, 125.3, 125.0, 124.6, 124.5, 124.0, 113.5, 55.3, 50.6, 17.1.**^{11}B NMR (128 MHz, Chloroform-*d*)**δ 0.52. HRMS (ESI) m/z: $[M+H]^+$ calcd for $[C_{38}H_{34}BN_2O_3]$: 577.2657; Found 577.2657.

methyl 5-cyclopropyl-4-(4-methoxyphenyl)-2,2,3-triphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4ca)



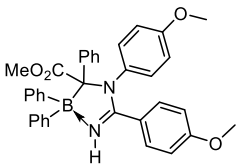
White solid; 60% yield;**^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.24 – 7.14 (m, 6H), 7.08 (m, 3H), 7.04 – 6.99 (m, 2H), 6.98 – 6.91 (m, 4H), 6.80 (d, *J* = 8.3 Hz, 2H), 6.66 – 6.61 (m, 2H), 5.95 (s, 1H), 3.72 (s, 3H), 3.02 (s, 3H), 1.47 (m, 1H), 1.31 – 1.24 (m, 1H), 1.21 – 1.14 (m, 1H), 1.08 (m, 2H).**^{13}C NMR (101 MHz, Chloroform-*d*)**δ 173.3, 171.9, 159.0, 141.9, 133.1, 132.7, 131.2, 130.7, 130.2, 126.9, 126.6, 126.4, 126.1, 125.4, 124.1, 113.3, 55.2, 50.4, 10.0, 9.6, 9.4. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 0.00. HRMS (ESI) m/z: $[M+H]^+$ calcd for $[C_{32}H_{32}BN_2O_3]$: 503.2500; Found 503.2501.

methyl 5-isopropyl-4-(4-methoxyphenyl)-2,2,3-triphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4cb)



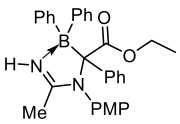
White solid; 56% yield;**^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.24 (m, 5H), 7.17 (t, *J* = 7.4 Hz, 2H), 7.12 – 7.05 (m, 3H), 7.05 – 6.99 (m, 2H), 6.98 – 6.89 (m, 4H), 6.70 (s, 1H), 6.62 (d, *J* = 7.4 Hz, 2H), 6.53 (s, 1H), 3.71 (s, 3H), 3.01 (s, 3H), 2.65 – 2.55 (m, 1H), 1.45 (d, *J* = 6.9 Hz, 3H), 1.21 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)**δ 175.6, 173.3, 159.1, 142.0, 133.1, 132.8, 131.2, 130.3, 130.1, 126.9, 126.5, 126.4, 126.2, 125.4, 124.1, 113.3, 55.2, 50.4, 27.7, 20.4, 20.1. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ -0.24. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $[C_{32}H_{33}BN_2O_3Na]$: 527.2476, found 527.2475.

methyl 4,5-bis(4-methoxyphenyl)-2,2,3-triphenyl-3,4-dihydro-2H-1,4,2l4-diazaborole-3-carboxylate (4cc)



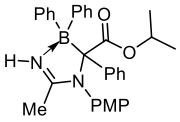
White solid; 61% yield;**^{1}H NMR (400 MHz, Chloroform-*d*)**δ 7.43 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 7.4 Hz, 2H), 7.27 – 7.24 (m, 2H), 7.18 (t, J = 7.4 Hz, 2H), 7.08 (q, J = 7.5 Hz, 5H), 7.01 (d, J = 7.1 Hz, 1H), 6.93 (s, 3H), 6.85 (d, J = 8.5 Hz, 2H), 6.77 (s, 1H), 6.67 (d, J = 8.5 Hz, 2H), 6.45 (d, J = 8.6 Hz, 2H), 3.81 (s, 3H), 3.63 (s, 3H), 3.04 (s, 3H).**^{13}C NMR (101 MHz, Chloroform-*d*)**δ 173.3, 167.9, 162.0, 158.0, 141.7, 133.2, 132.8, 132.5, 130.2, 130.2, 129.8, 126.9, 126.6, 126.3, 125.8, 125.4, 124.2, 121.1, 114.3, 113.1, 55.4, 55.1, 50.6.**^{11}B NMR (128 MHz, Chloroform-*d*)**δ 0.17. HRMS (ESI) m/z: $[M+H]^+$ calcd for $[C_{36}H_{34}BN_2O_4]$: 569.2606; Found 569.2606.

ethyl 4-(4-methoxyphenyl)-5-methyl-2,2,3-triphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4am)



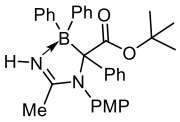
White solid; 85% yield;**^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.28 – 7.26 (m, 2H), 7.25 (s, 2H), 7.18 – 7.14 (m, 2H), 7.09 (td, *J* = 7.5, 6.8, 1.8 Hz, 3H), 7.05 – 6.99 (m, 2H), 6.99 – 6.93 (m, 4H), 6.69 (d, *J* = 8.6 Hz, 2H), 6.65 – 6.61 (m, 2H), 6.59 (s, 1H), 3.72 (s, 3H), 3.58 – 3.47 (m, 1H), 3.31 – 3.21 (m, 1H), 2.12 (s, 3H), 0.95 (t, *J* = 7.2 Hz, 3H).**^{13}C NMR (101 MHz, Chloroform-*d*)** δ 172.9,167.4, 159.1, 142.1, 133.2, 132.8, 130.9, 130.2, 126.9, 126.5, 126.4, 126.1, 125.5, 124.1, 113.3, 59.8, 55.3, 17.1, 13.7.**^{11}B NMR (128 MHz, Chloroform-*d*)** δ 0.19. HRMS (ESI) m/z: $[M+H]^+$ calcd for $[C_{31}H_{32}BN_2O_3]$: 491.2500; Found 491.2496.

isopropyl 4-(4-methoxyphenyl)-5-methyl-2,2,3-triphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4an)



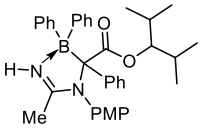
White solid; 70% yield;**^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.31 – 7.23 (m, 4H), 7.17 – 7.12 (m, 2H), 7.12 – 7.06 (m, 3H), 7.06 – 6.99 (m, 2H), 6.99 – 6.93 (m, 4H), 6.69 – 6.57 (m, 5H), 4.31 (hept, *J* = 6.3 Hz, 1H), 3.71 (s, 3H), 2.05 (s, 3H), 1.02 (d, *J* = 6.3 Hz, 3H), 0.68 (d, *J* = 6.3 Hz, 3H).**^{13}C NMR (101 MHz, Chloroform-*d*)**δ 172.5, 167.3, 159.0, 142.6, 133.5, 132.9, 131.0, 131.0, 130.2, 126.8, 126.6, 126.4, 126.0, 125.5, 124.1, 113.3, 68.0, 55.2, 21.7, 21.0, 17.1.**^{11}B NMR (128 MHz, Chloroform-*d*)** δ 0.10. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $[C_{32}H_{33}BN_2O_3Na]$: calcd 527.2476; Found 527.2476.

tert-butyl 4-(4-methoxyphenyl)-5-methyl-2,2,3-triphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4ao)



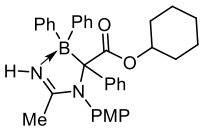
White solid; 59% yield;**^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.29 (d, *J* = 6.9 Hz, 2H), 7.24 (s, 1H), 7.15 (m, 3H), 7.11 – 7.07 (m, 3H), 7.06 – 7.03 (m, 1H), 7.00 – 6.94 (m, 5H), 6.69 – 6.64 (m, 4H), 6.56 (s, 1H), 3.73 (s, 3H), 2.06 (s, 3H), 0.98 (s, 9H).**^{13}C NMR (101 MHz, Chloroform-*d*)**δ 172.1, 167.2, 158.9, 144.2, 143.3, 133.9, 132.9, 131.0, 130.3, 126.8, 126.3, 125.9, 125.5, 124.0, 113.2, 80.6, 55.2, 27.4, 17.2. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 0.14. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $[C_{33}H_{35}BN_2O_3Na]$: 541.2633; Found 541.2633.

2,4-dimethylpentan-3-yl 4-(4-methoxyphenyl)-5-methyl-2,2,3-triphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4ap)



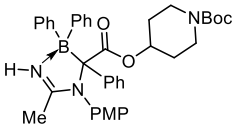
White solid; 42% yield;**^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.34 – 7.31 (m, 2H), 7.28 (t, *J* = 1.7 Hz, 1H), 7.12 (m, 4H), 7.08 – 7.03 (m, 3H), 7.03 – 6.99 (m, 2H), 6.97 (m, 3H), 6.64 (m, 5H), 4.33 (m, 1H), 3.73 (s, 3H), 2.12 (s, 3H), 1.37 (m, 1H), 1.15 (h, *J* = 6.7 Hz, 1H), 0.69 (d, *J* = 7.0 Hz, 3H), 0.55 (dd, *J* = 6.8, 3.6 Hz, 6H), 0.32 (d, *J* = 6.8 Hz, 3H).**^{13}C NMR (101 MHz, Chloroform-*d*)**δ 172.3, 167.3, 159.0, 143.0, 133.7, 132.8, 131.9, 130.5, 129.8, 126.9, 126.4, 126.0, 125.5, 124.0, 113.4, 83.8, 55.4, 29.6, 28.9, 19.5, 19.4, 19.0, 18.6, 17.4.**^{11}B NMR (128 MHz, Chloroform-*d*)** δ 0.31. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $[C_{36}H_{41}BN_2O_3Na]$: 583.3102; Found 583.3102.

cyclohexyl 4-(4-methoxyphenyl)-5-methyl-2,2,3-triphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4aq)



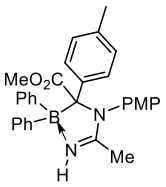
White solid; 62% yield;**^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.32 – 7.28 (m, 2H), 7.26 – 7.22 (m, 2H), 7.12 (m, 5H), 7.06 – 6.92 (m, 6H), 6.69 – 6.59 (m, 4H), 6.57 (s, 1H), 4.09 (m, 1H), 3.71 (s, 3H), 2.02 (s, 3H), 1.72 – 1.63 (m, 1H), 1.62 – 1.53 (m, 1H), 1.46 (m, 1H), 1.37 (m, 1H), 1.32 – 1.24 (m, 1H), 1.24 – 1.10 (m, 3H), 1.10 – 1.05 (m, 1H), 0.90 – 0.77 (m, 1H).**^{13}C NMR (101 MHz, Chloroform-*d*)** δ 172.5, 167.3, 159.0, 142.6, 133.6, 132.9, 131.0, 130.9, 130.3, 126.8, 126.6, 126.4, 126.1, 125.6, 124.1, 113.3, 73.1, 55.3, 31.6, 30.8, 25.4, 23.9, 23.8, 17.1.**^{11}B NMR (128 MHz, Chloroform-*d*)** δ 0.10. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $[C_{35}H_{37}BN_2O_3Na]$: 567.2789; Found 567.2787.

tert-butyl 4-((4-(4-methoxyphenyl)-5-methyl-2,2,3-triphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carbonyl)oxy)piperidine-1-carboxylate (4ar)



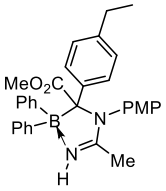
White solid; 68% yield;**^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.27 – 7.21 (m, 4H), 7.11 (m, 5H), 7.06 – 6.99 (m, 2H), 6.97 – 6.91 (m, 4H), 6.70 (s, 1H), 6.64 (m, 4H), 4.23 (m, 1H), 3.72 (s, 3H), 3.56 – 3.48 (m, 1H), 3.38 (m, 1H), 3.05 (m, 1H), 2.91 (m, 1H), 2.06 (s, 3H), 1.61 (s, 1H), 1.42 (s, 9H), 1.23 – 1.17 (m, 1H), 0.91 (m, 2H).**^{13}C NMR (101 MHz, Chloroform-*d*)**δ 172.5, 167.3, 159.1, 154.6, 142.3, 133.6, 132.8, 130.9, 130.8, 130.2, 126.9, 126.6, 126.5, 126.2, 125.7, 124.2, 121.9, 115.3, 114.1, 113.3, 79.4, 70.0, 55.2, 30.4, 29.7, 29.7, 28.4, 17.0. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 0.17. HRMS (ESI) m/z: $[M+K]^+$ calcd for $[C_{39}H_{44}BN_3O_5K]$: calcd 684.3006; Found 684.3006.

methyl 4-(4-methoxyphenyl)-5-methyl-2,2-diphenyl-3-(p-tolyl)-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4as)



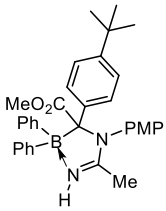
White solid; 72% yield; **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.28 – 7.26 (m, 1H), 7.24 (m, 3H), 7.17 (m, 2H), 7.13 – 7.07 (m, 3H), 7.07 – 7.02 (m, 1H), 6.79 (m, 4H), 6.71 – 6.56 (m, 5H), 3.72 (s, 3H), 3.03 (s, 3H), 2.20 (s, 3H), 2.10 (s, 3H).**^{13}C NMR (101 MHz, Chloroform-*d*)** δ 173.5, 167.2, 159.1, 138.6, 135.8, 133.1, 132.8, 131.0, 130.7, 130.3, 127.6, 126.5, 126.4, 125.4, 124.1, 113.3, 55.3, 50.5, 21.0, 17.1. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ -0.00. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $[C_{31}H_{31}BN_2O_3Na]$: 513.2320; Found 513.2319.

methyl 3-(4-ethylphenyl)-4-(4-methoxyphenyl)-5-methyl-2,2-diphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4at)



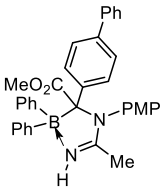
White solid; 75% yield; **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.27 (m, 1H), 7.26 – 7.22 (m, 3H), 7.20 – 7.14 (m, 2H), 7.10 (m, 3H), 7.06 – 7.01 (m, 1H), 6.83 – 6.77 (m, 4H), 6.69 – 6.56 (m, 5H), 3.72 (s, 3H), 3.03 (s, 3H), 2.50 (q, *J* = 7.6 Hz, 2H), 2.10 (s, 3H), 1.13 (dd, *J* = 7.9, 7.1 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)**δ 173.6, 167.2, 159.1, 142.4, 138.9, 133.1, 132.8, 131.0, 130.7, 130.4, 126.5, 126.4, 126.4, 125.4, 124.1, 113.3, 55.3, 50.5, 28.3, 17.1, 15.6.**^{11}B NMR (128 MHz, Chloroform-*d*)** δ -0.17. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $[C_{32}H_{33}BN_2O_3Na]$: 527.2476; Found 527.2476.

methyl 3-(4-(tert-butyl)phenyl)-4-(4-methoxyphenyl)-5-methyl-2,2-diphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4au)



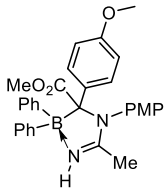
White solid; 68% yield;**^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.25 (d, *J* = 5.3 Hz, 4H), 7.17 (t, *J* = 4.9 Hz, 2H), 7.08 (q, *J* = 4.8 Hz, 3H), 7.04 – 7.01 (m, 1H), 6.96 (d, *J* = 5.6 Hz, 2H), 6.81 (d, *J* = 5.7 Hz, 2H), 6.64 (d, *J* = 5.1 Hz, 2H), 6.61 – 6.57 (m, 3H), 3.72 (s, 3H), 3.03 (s, 3H), 2.10 (s, 3H), 1.21 (s, 9H).**^{13}C NMR (101 MHz, Chloroform-*d*)**δ 173.6, 167.2, 159.1, 149.3, 138.5, 133.1, 132.8, 131.0, 130.7, 130.0, 126.5, 126.4, 125.4, 124.1, 123.7, 113.2, 55.3, 50.5, 34.2, 31.3, 17.0. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ -0.17. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $[C_{34}H_{37}BN_2O_3Na]$: 555.2789, found 555.2787.

methyl 3-([1,1'-biphenyl]-4-yl)-4-(4-methoxyphenyl)-5-methyl-2,2-diphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4av)



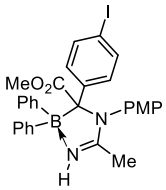
White solid; 72% yield;**^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.55 – 7.51 (m, 2H), 7.41 – 7.36 (m, 2H), 7.28 (m, 5H), 7.25 – 7.22 (m, 2H), 7.21 – 7.16 (m, 2H), 7.12 – 7.07 (m, 3H), 7.02 (m, 3H), 6.75 (d, *J* = 8.5 Hz, 2H), 6.65 – 6.60 (m, 3H), 3.71 (s, 3H), 3.06 (s, 3H), 2.14 (s, 3H).**^{13}C NMR (101 MHz, Chloroform-*d*)** δ 173.3, 167.5, 159.2, 140.9, 140.6, 138.5, 133.1, 132.8, 130.9, 130.8, 130.7, 128.6, 127.1, 126.8, 126.6, 126.5, 125.5, 125.4, 124.3, 113.4, 55.3, 50.6, 17.1.**^{11}B NMR (128 MHz, Chloroform-*d*)** δ 0.12. HRMS (ESI) m/z: $[M+H]^+$ calcd for $[C_{36}H_{34}BN_2O_3]$: 553.2657; Found 553.2654.

methyl 3,4-bis(4-methoxyphenyl)-5-methyl-2,2-diphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4aw)



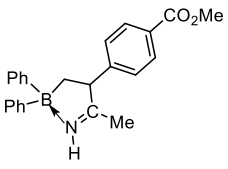
White solid; 59% yield;**^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.27 (d, *J* = 1.5 Hz, 1H), 7.24 (d, *J* = 6.7 Hz, 2H), 7.19 – 7.14 (m, 2H), 7.14 – 7.09 (m, 3H), 7.08 – 7.01 (m, 2H), 6.84 – 6.81 (m, 2H), 6.71 – 6.62 (m, 4H), 6.56 (s, 1H), 6.53 – 6.48 (m, 2H), 3.72 (s, 3H), 3.71 (s, 3H), 3.02 (s, 3H), 2.09 (s, 3H).**^{13}C NMR (101 MHz, Chloroform-*d*)**δ 173.5, 167.2, 159.1, 157.8, 134.0, 133.1, 132.8, 131.6, 131.0, 130.6, 126.5, 126.5, 125.4, 124.2, 113.4, 112.2, 55.3, 55.0, 50.5, 17.0.**^{11}B NMR (128 MHz, Chloroform-*d*)** δ -0.01. HRMS (ESI) m/z: $[M+K]^+$ calcd for $[C_{31}H_{31}BN_2O_4K]$: 545.2008; Found 545.2007.

methyl 3-(4-iodophenyl)-4-(4-methoxyphenyl)-5-methyl-2,2-diphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4ax)



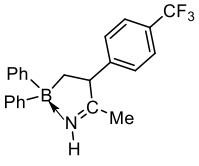
White solid; 89% yield;**^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.28 (d, *J* = 2.1 Hz, 1H), 7.26 – 7.15 (m, 7H), 7.13 – 7.04 (m, 4H), 6.75 – 6.70 (m, 3H), 6.70 – 6.65 (m, 3H), 6.62 (s, 1H), 3.74 (s, 3H), 3.01 (s, 3H), 2.14 (s, 3H).**^{13}C NMR (101 MHz, Chloroform-*d*)**δ 172.8, 167.7, 159.3, 141.5, 135.9, 133.0, 132.7, 132.3, 130.8, 130.5, 126.6, 126.6, 125.6, 124.4, 113.6, 91.8, 55.3, 50.6, 17.1. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 0.32. HRMS (ESI) m/z: $[M+H]^+$ calcd for $[C_{30}H_{29}BIN_2O_3]$: 603.1310; Found 603.1306.

methyl 4-(5-methyl-2,2-diphenyl-2,3-dihydro-4H-1l4,4,2l4-diazaborol-4-yl)benzoate (6a)



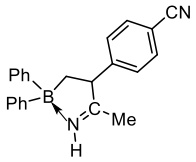
White solid; 85% yield;**^{1}H NMR (400 MHz, Chloroform-*d*)**δ 8.98 (s, 1H), 7.68 – 7.62 (m, 2H), 7.48 – 7.43 (m, 2H), 7.31 – 7.26 (m, 2H), 7.23 – 7.16 (m, 1H), 6.97 (m, 3H), 6.80 – 6.74 (m, 2H), 6.66 (m, 2H), 3.82 (s, 3H), 3.42 (t, *J* = 8.3 Hz, 1H), 3.16 (m, 1H), 3.00 (m, 1H), 2.46 (s, 3H).**^{13}C NMR (101 MHz, Chloroform-*d*)**δ 191.2, 167.6, 153.1, 132.8, 132.1, 128.8, 127.4, 127.0, 126.6, 125.6, 125.3, 124.8, 51.7, 45.1, 21.8.**^{11}B NMR (128 MHz, Chloroform-*d*)** δ 2.89. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $[C_{24}H_{24}BNO_2Na]$: 392.1792; Found: 392.1790.

5-methyl-2,2-diphenyl-4-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2H-1l4,2l4-azaborole(6b) White solid; 70% yield; **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.77 (s, 1H), 7.48 – 7.41 (m, 2H), 7.29 (m, 2H), 7.24 – 7.17 (m, 3H), 6.98 (m, 3H), 6.77 (d, *J* = 8.0 Hz, 2H), 6.62 (m, 2H), 3.37 (t, *J* = 8.4 Hz, 1H), 3.11 (dd, *J* = 19.3, 8.1 Hz, 1H), 2.91 (dd, *J* = 18.4, 7.9 Hz, 1H), 2.36 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)**δ 191.2, 151.1, 132.8, 132.2, 127.4, 127.2, 126.7, 126.0, 125.8, 125.7, 125.5, 124.9, 124.2, 124.2, 124.1, 124.1, 123.3,



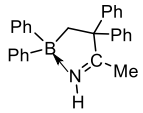
45.1, 21.7. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 2.82. HRMS (ESI) m/z: $[M+H]^+$ calcd for $[C_{23}H_{22}BF_3N]$: 380.1792; Found:380.1793.

4-(5-methyl-2,2-diphenyl-3,4-dihydro-2H-1l4,2l4-azaborol-4-yl)benzonitrile (6c)



White solid; 55% yield; **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 9.00 (s, 1H), 7.45 (m, 2H), 7.30 (m, 2H), 7.23 (m, 3H), 6.99 (m, 3H), 6.77 (m, 2H), 6.66 – 6.61 (m, 2H), 3.45 (t, *J* = 8.3 Hz, 1H), 3.20 (dd, *J* = 19.4, 8.1 Hz, 1H), 2.99 (dd, *J* = 20.2, 7.5 Hz, 1H), 2.51 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)**δ 191.0, 153.4, 132.8, 132.0, 131.1, 127.6, 127.4, 126.7, 125.8, 124.9, 119.9, 106.6, 44.8, 21.6. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 2.89. HRMS (ESI) m/z: $[M+H]^+$ calcd for $[C_{23}H_{22}BN_2]$: 337.1871; Found:337.1870.

5-methyl-2,2,4,4-tetraphenyl-3,4-dihydro-2H-1l4,2l4-azaborole (6d)

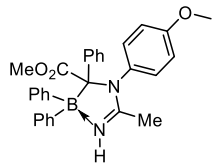


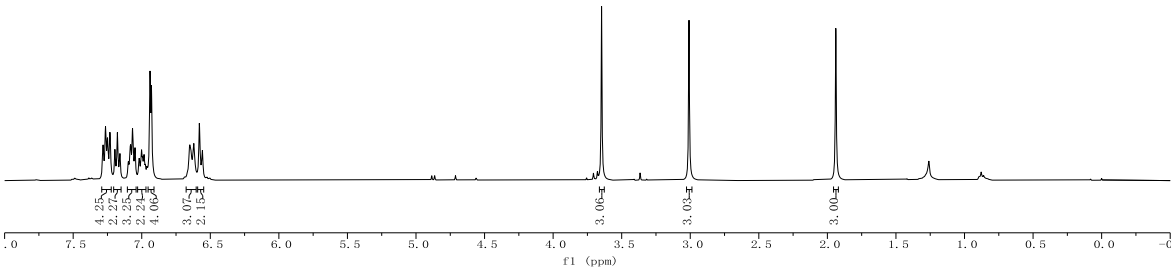
White solid; 62% yield; **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.84 (s, 1H), 7.04 – 6.94 (m, 16H), 6.90 (m, 4H), 3.76 (s, 2H), 2.49 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)**δ 188.5, 150.2, 134.1, 128.6, 127.2, 126.5, 124.8, 124.1, 52.4, 22.0.**^{11}B NMR (128 MHz, Chloroform-*d*)** δ 4.40. HRMS (ESI) m/z: $[M+H]^+$ calcd for $[C_{28}H_{27}BN]$: 388.2231; Found:388.2221.

9. NMR Spectra of Compounds

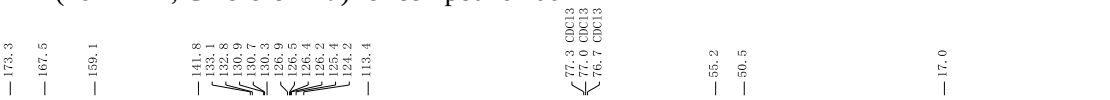
methyl 4-(4-methoxyphenyl)-5-methyl-2,2,3-triphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4aa)

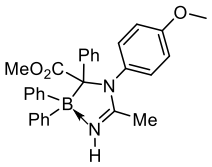
^{1}H NMR (400 MHz, Chloroform-*d*) for compound **4aa**

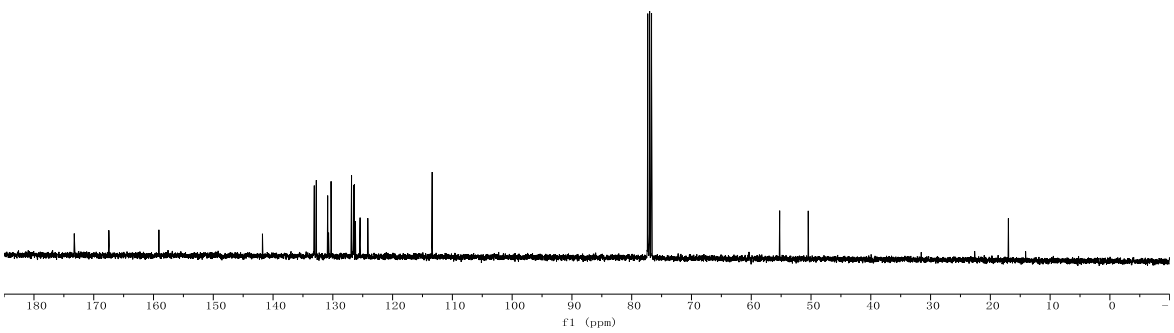




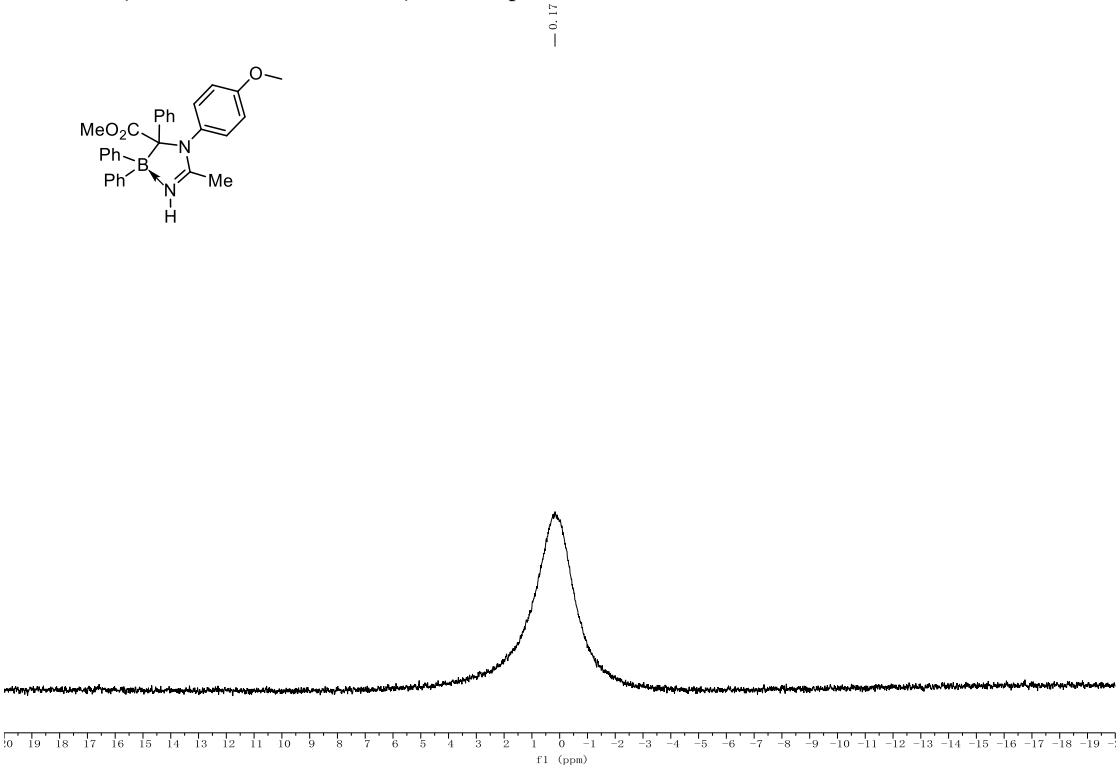
^{13}C NMR (101 MHz, Chloroform-*d*) for compound **4aa**





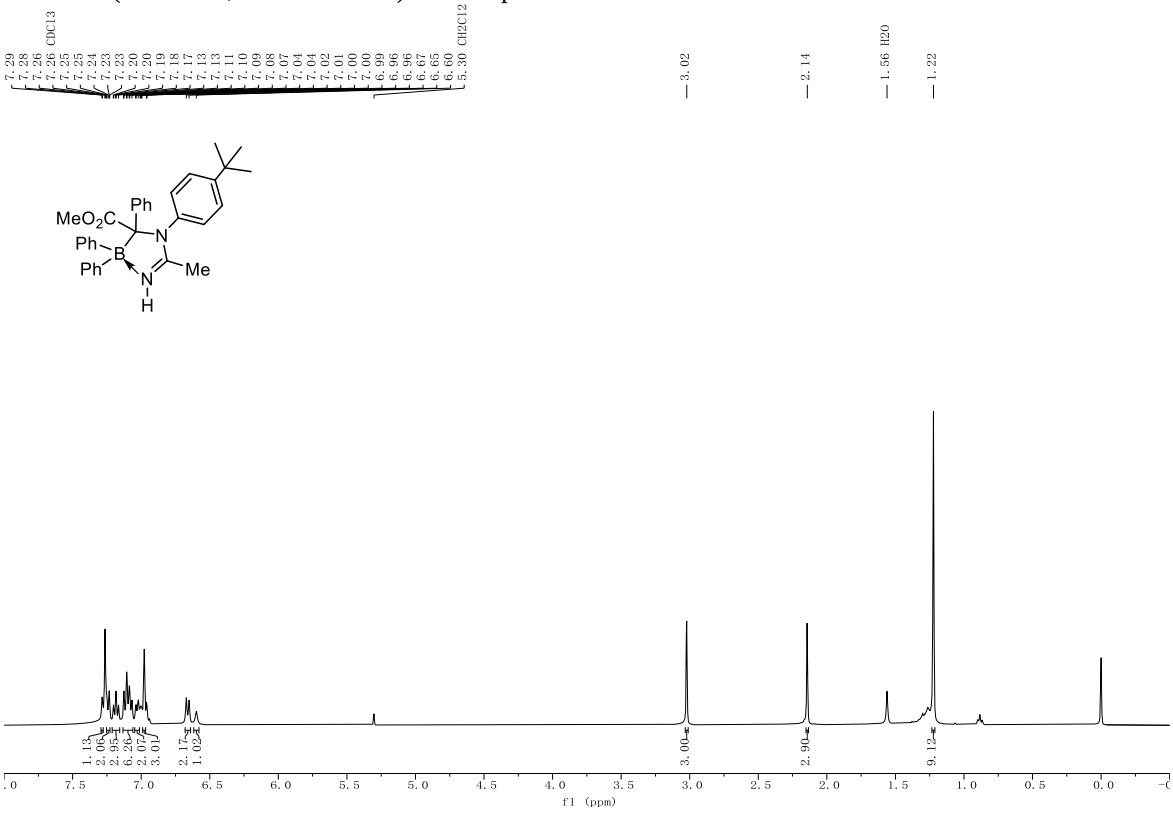


^{11}B NMR (128 MHz, Chloroform-*d*) for compound **4aa**

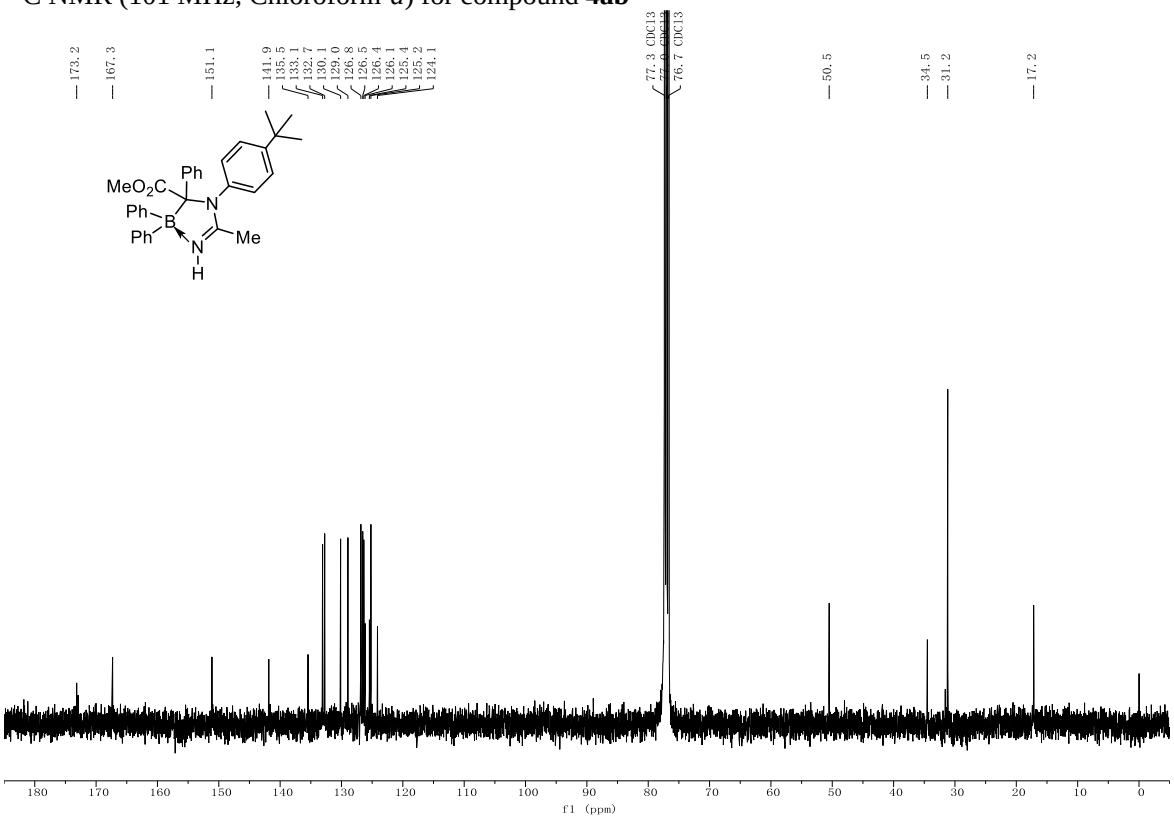


methyl 4-(4-(tert-butyl)phenyl)-5-methyl-2,2,3-triphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4ab)

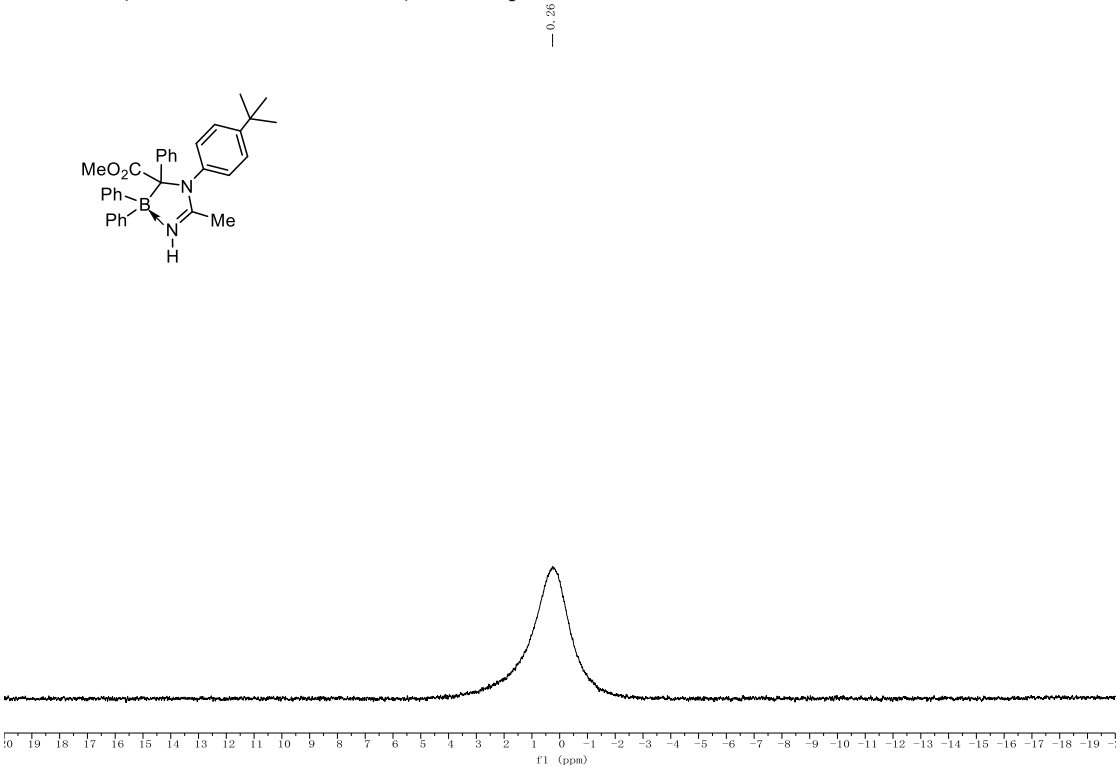
^{1}H NMR (400 MHz, Chloroform-*d*) for compound **4ab**



^{13}C NMR (101 MHz, Chloroform-*d*) for compound **4ab**

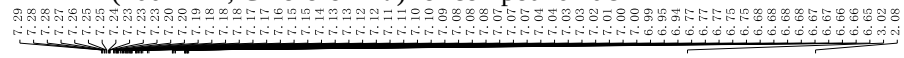


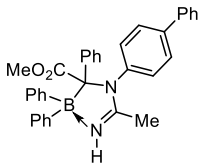
^{11}B NMR (128 MHz, Chloroform-*d*) for compound **4ab**

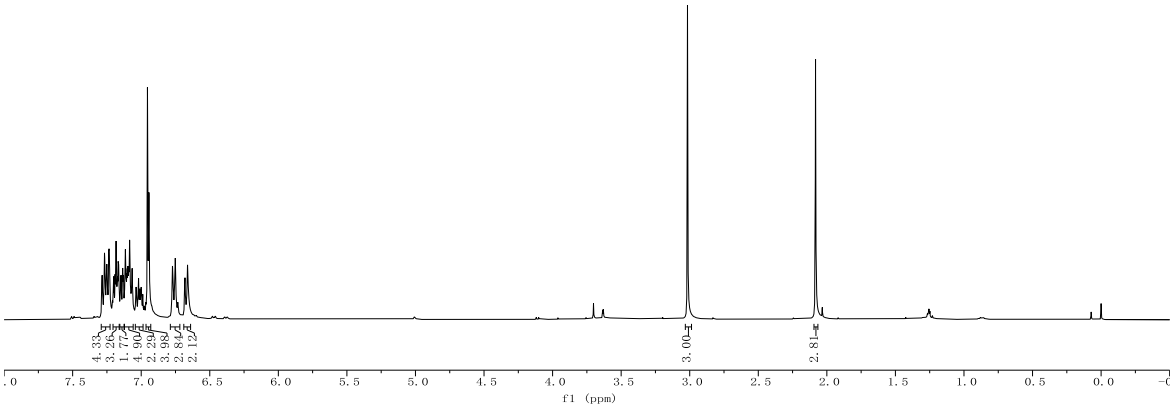


methyl 4-([1,1'-biphenyl]-4-yl)-5-methyl-2,2,3-triphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4ac)

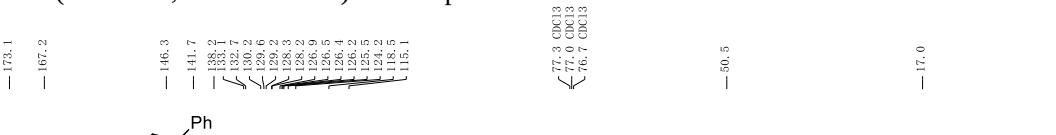
^{1}H NMR (400 MHz, Chloroform-*d*) for compound **4ac**

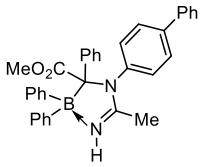




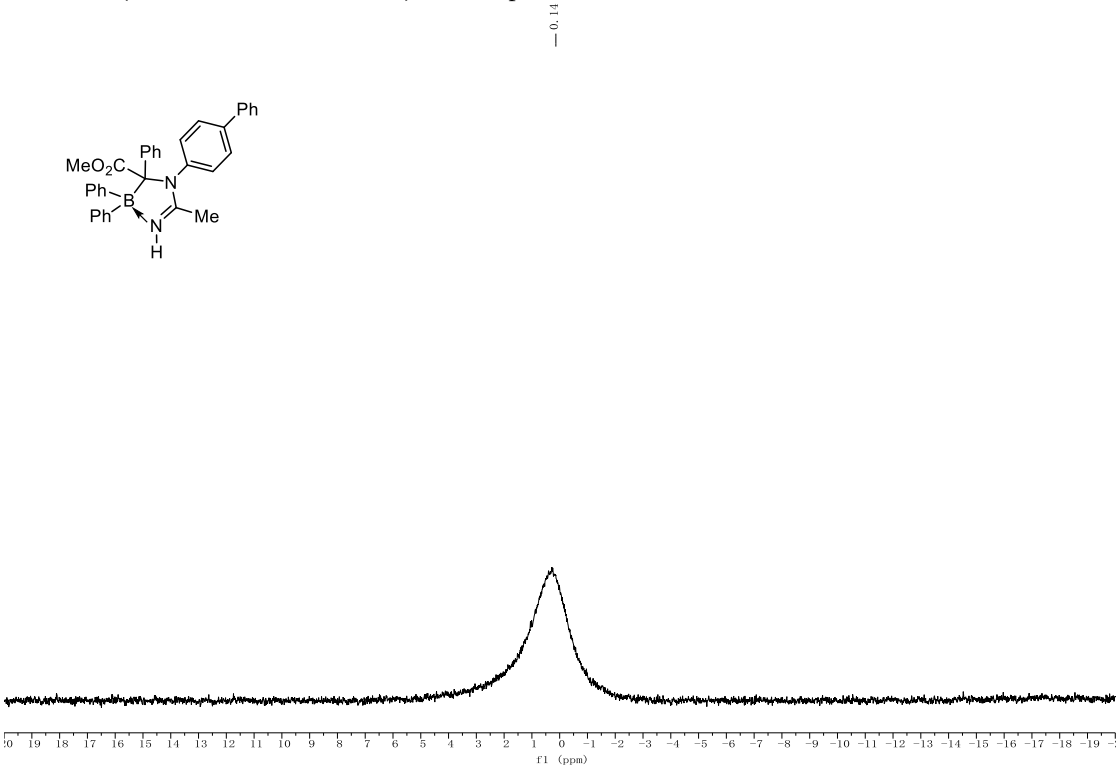


^{13}C NMR (101 MHz, Chloroform-*d*) for compound **4ac**



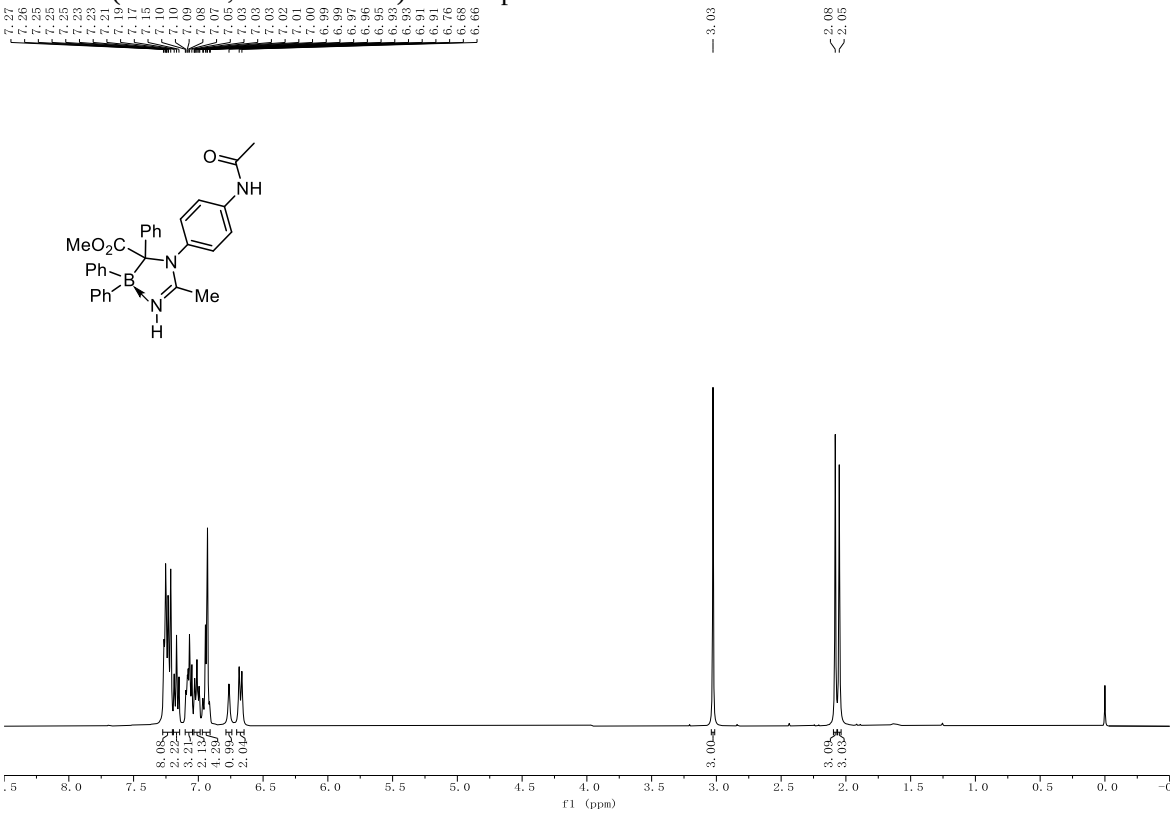


^{11}B NMR (128 MHz, Chloroform-*d*) for compound **4ac**

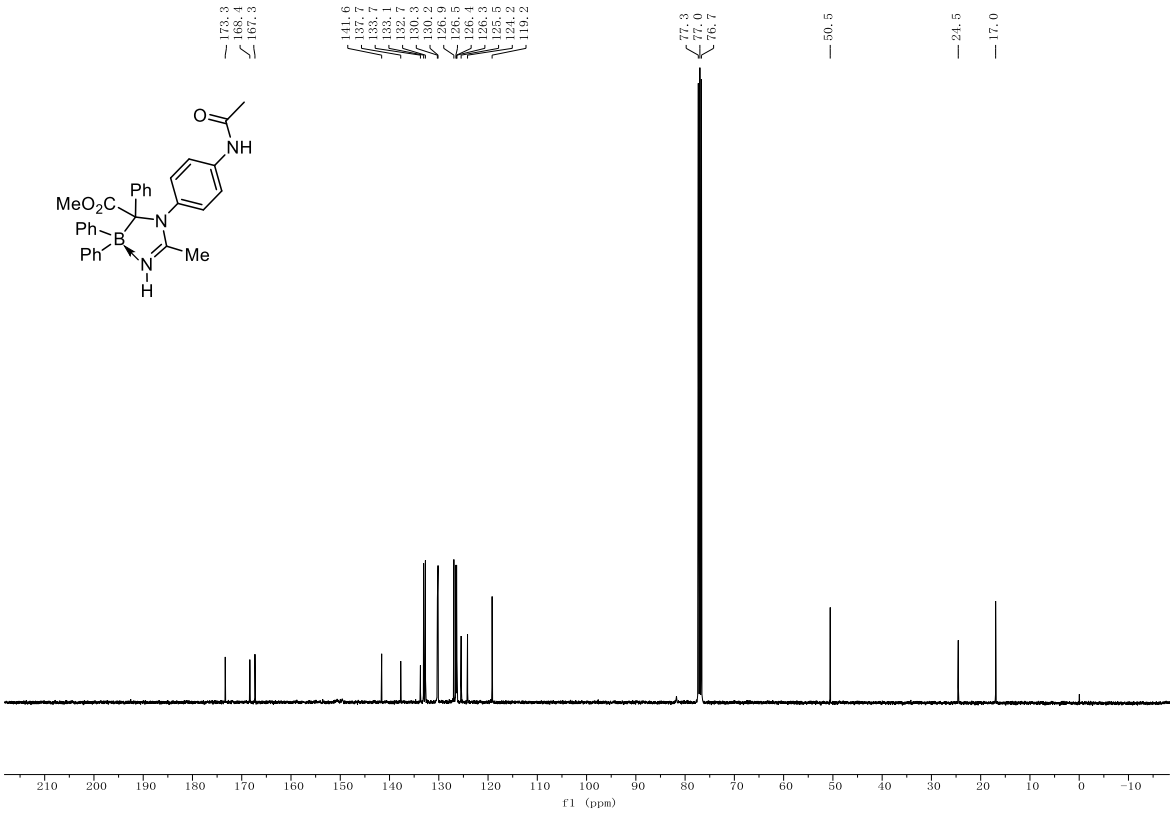


methyl 4-(4-acetamidophenyl)-5-methyl-2,2,3-triphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4ad)

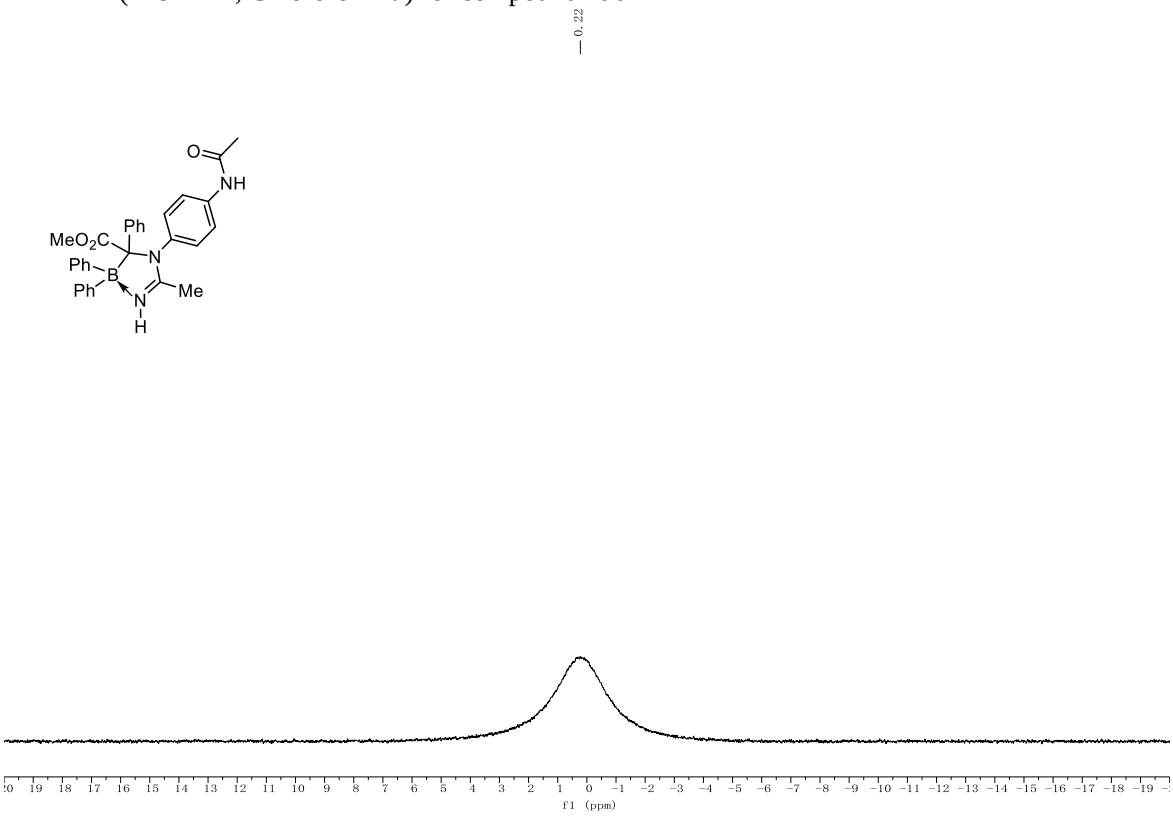
^{1}H NMR (400 MHz, Chloroform-*d*) for compound **4ad**



^{13}C NMR (101 MHz, Chloroform-*d*) for compound **4ad**

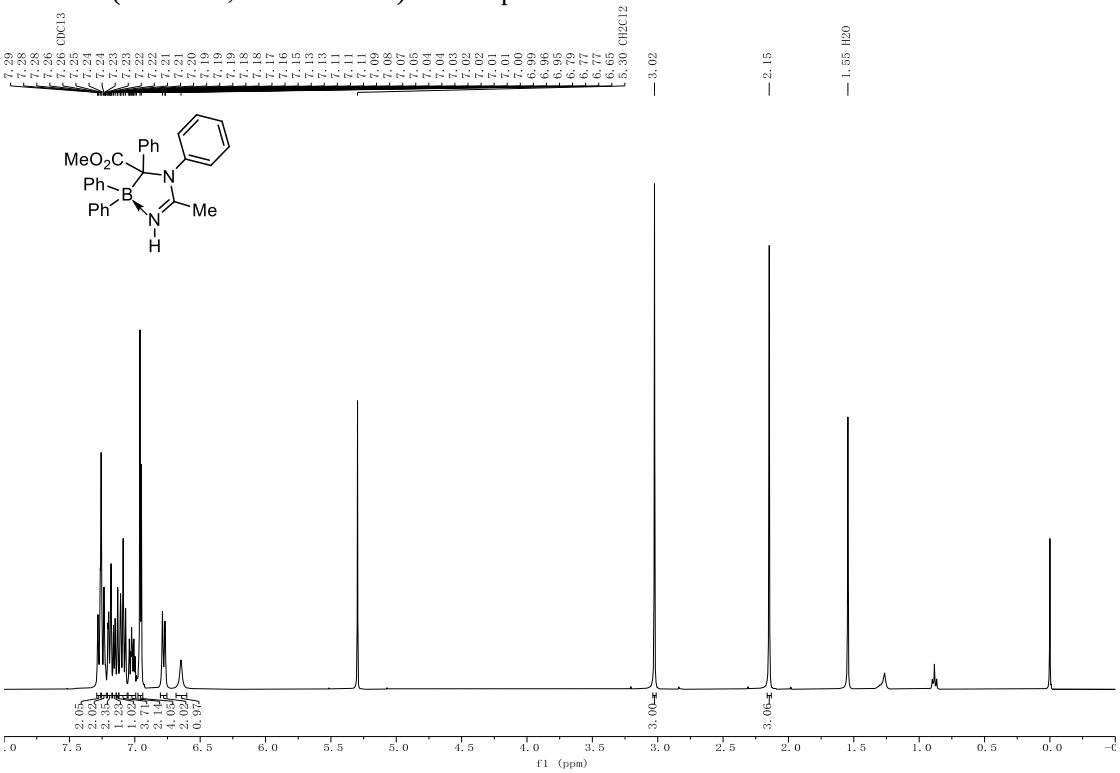


^{11}B NMR (128 MHz, Chloroform-*d*) for compound **4ad**

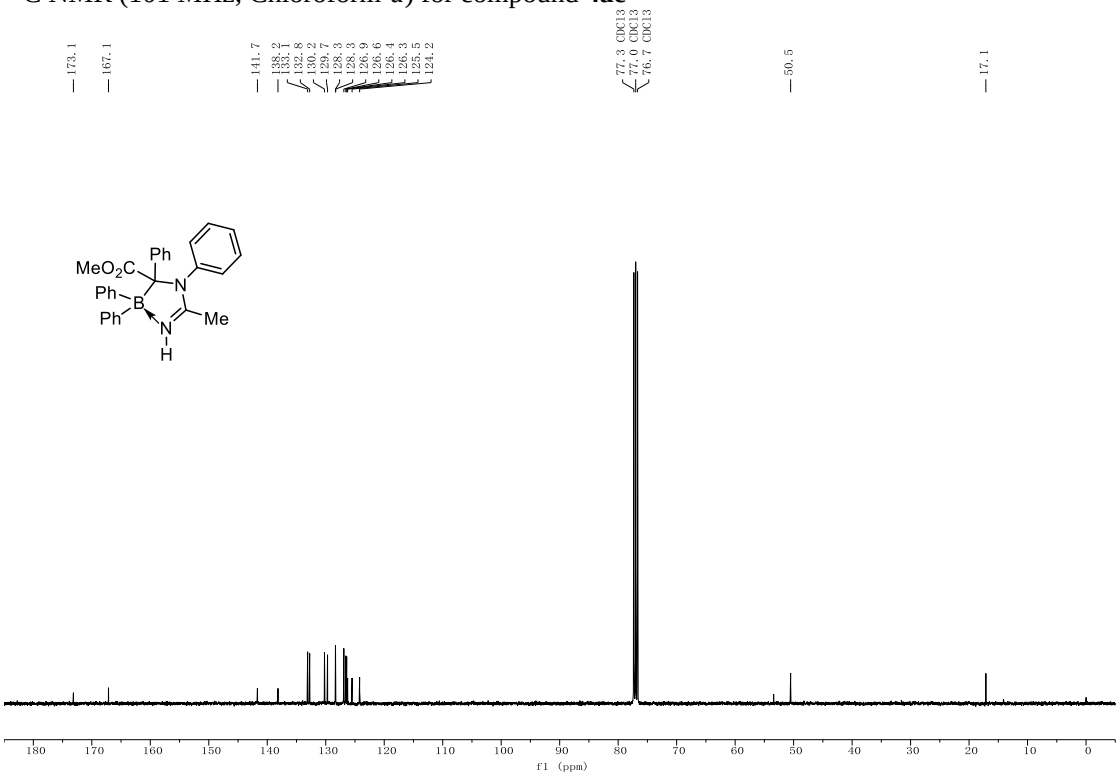


methyl 5-methyl-2,2,3,4-tetraphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4ae)

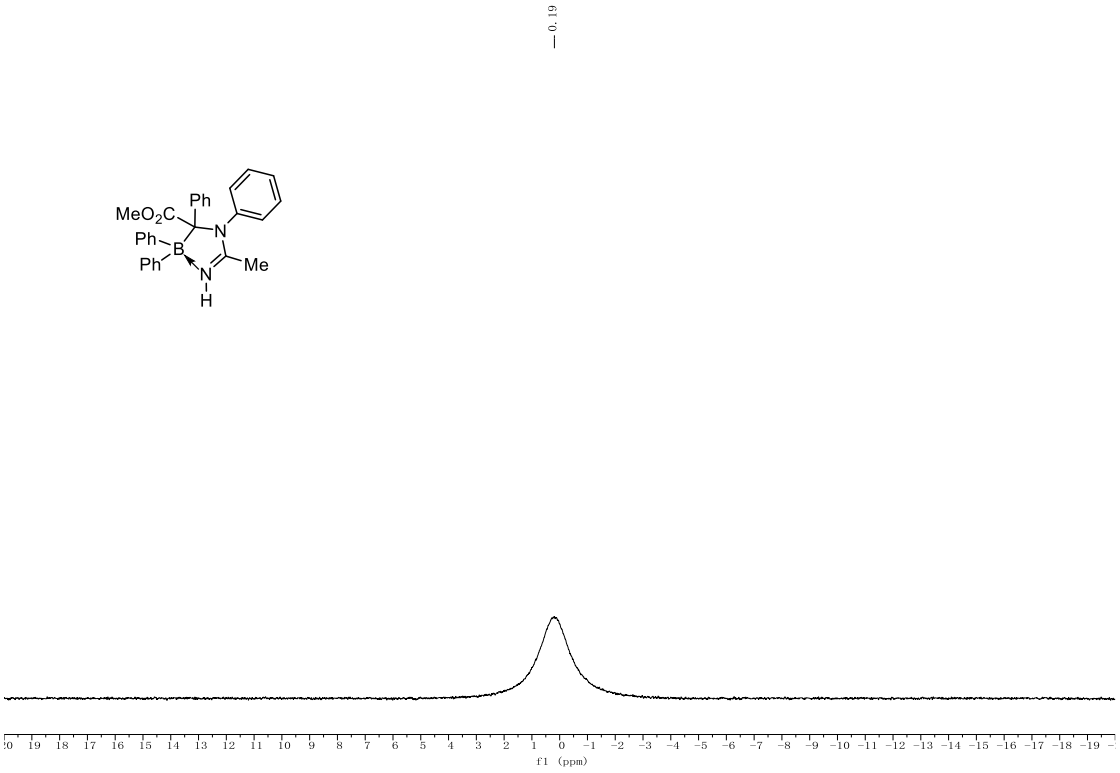
^{1}H NMR (400 MHz, Chloroform-*d*) for compound **4ae**



^{13}C NMR (101 MHz, Chloroform-*d*) for compound **4ae**

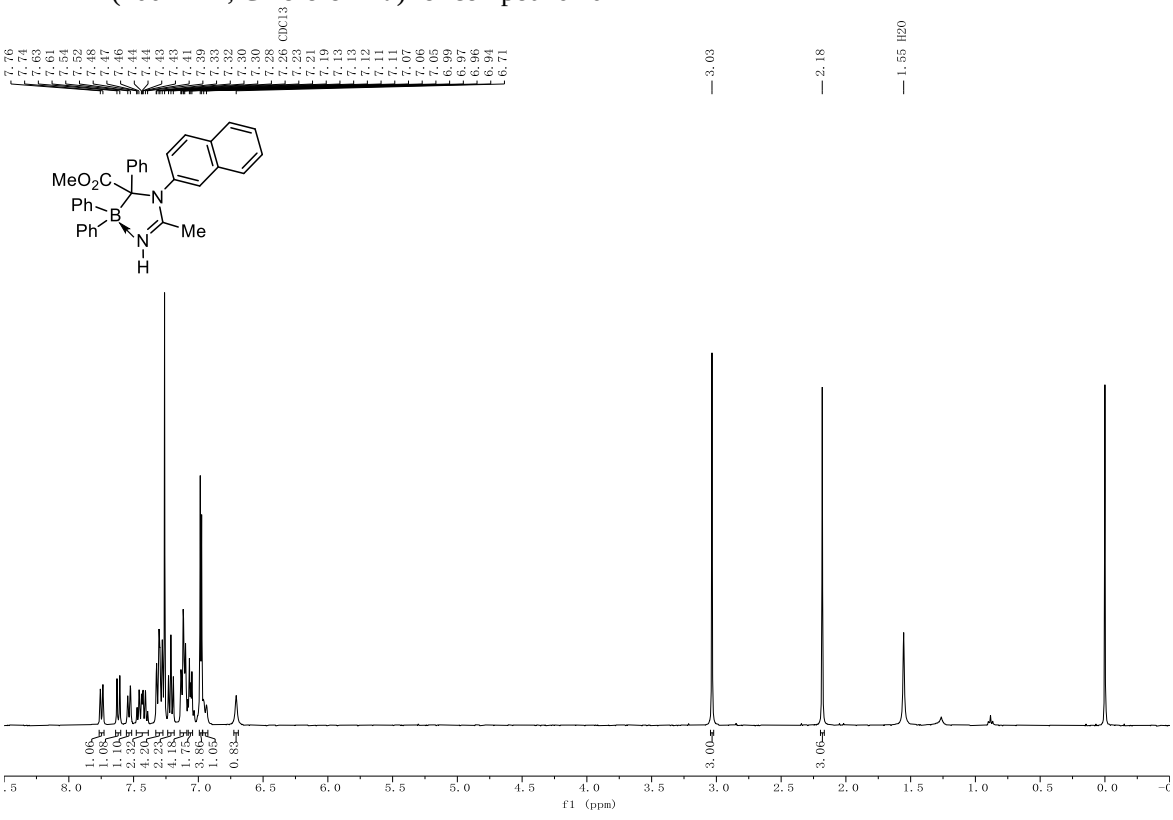


^{11}B NMR (128 MHz, Chloroform-*d*) for compound **4ae**

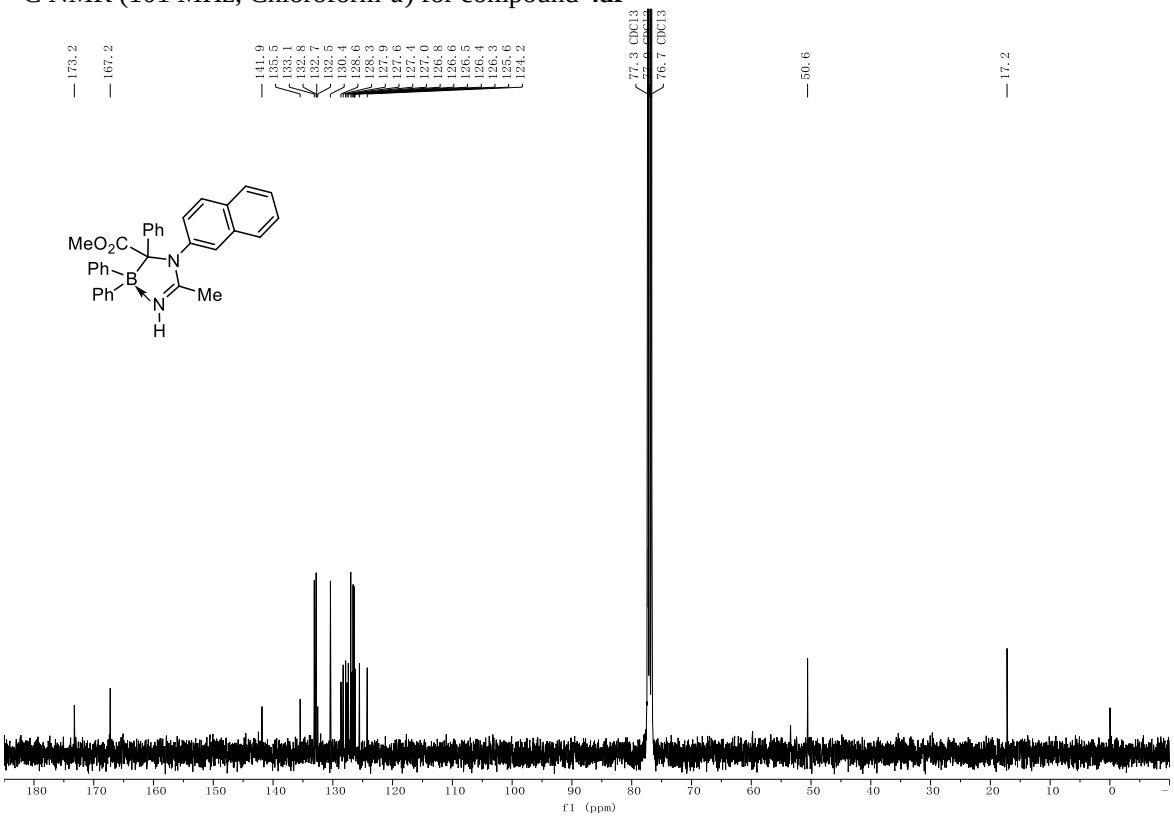


methyl 5-methyl-4-(naphthalen-2-yl)-2,2,3-triphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4af)

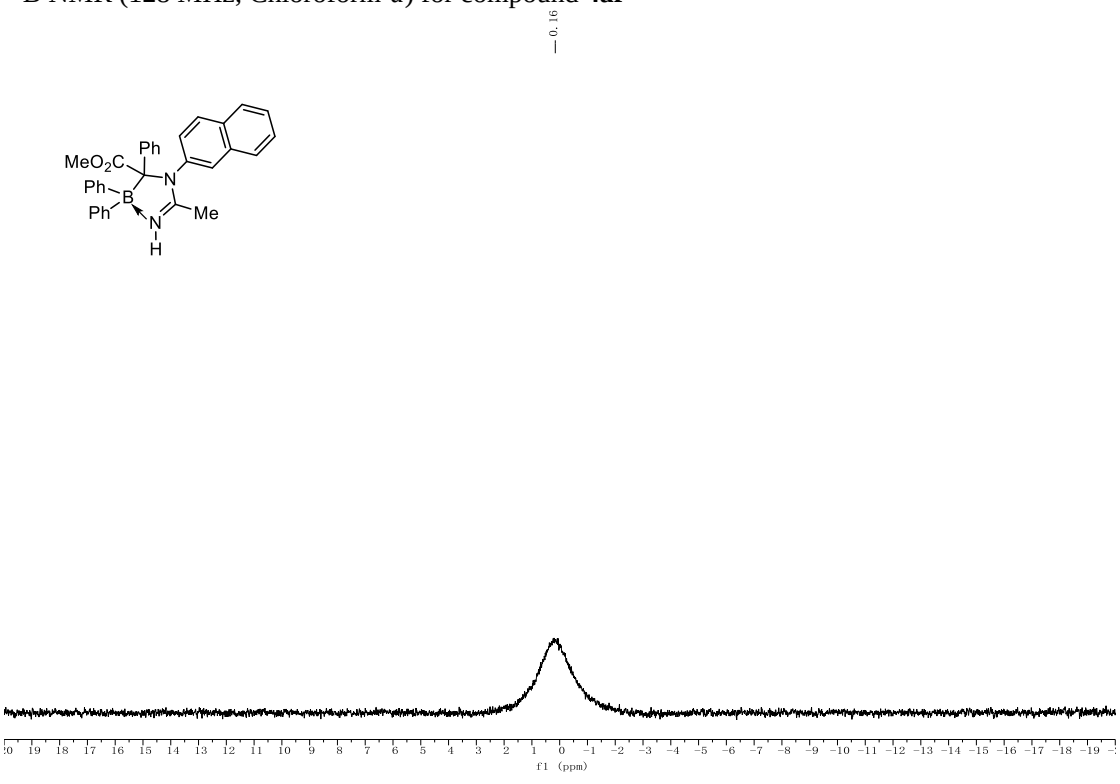
^{1}H NMR (400 MHz, Chloroform-*d*) for compound **4af**



^{13}C NMR (101 MHz, Chloroform-*d*) for compound **4af**

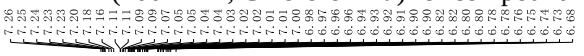


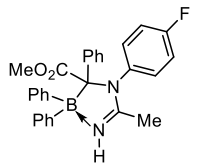
^{11}B NMR (128 MHz, Chloroform-*d*) for compound **4af**

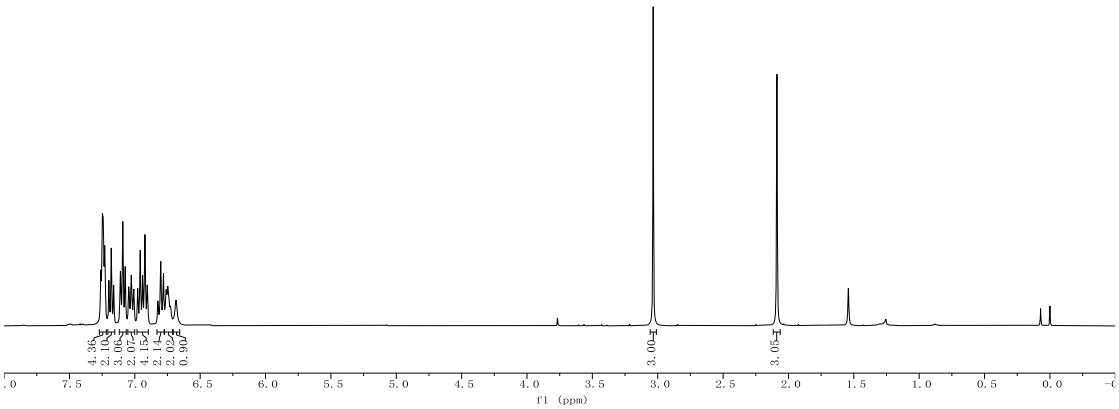


methyl 4-(4-fluorophenyl)-5-methyl-2,2,3-triphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4ag)

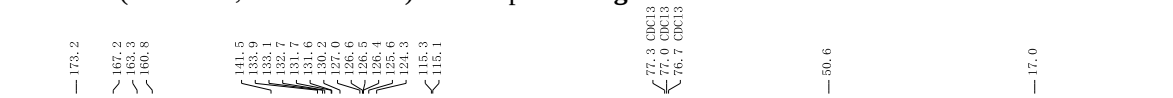
^{1}H NMR (400 MHz, Chloroform-*d*) for compound **4ag**

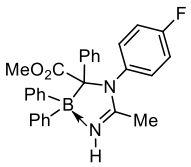




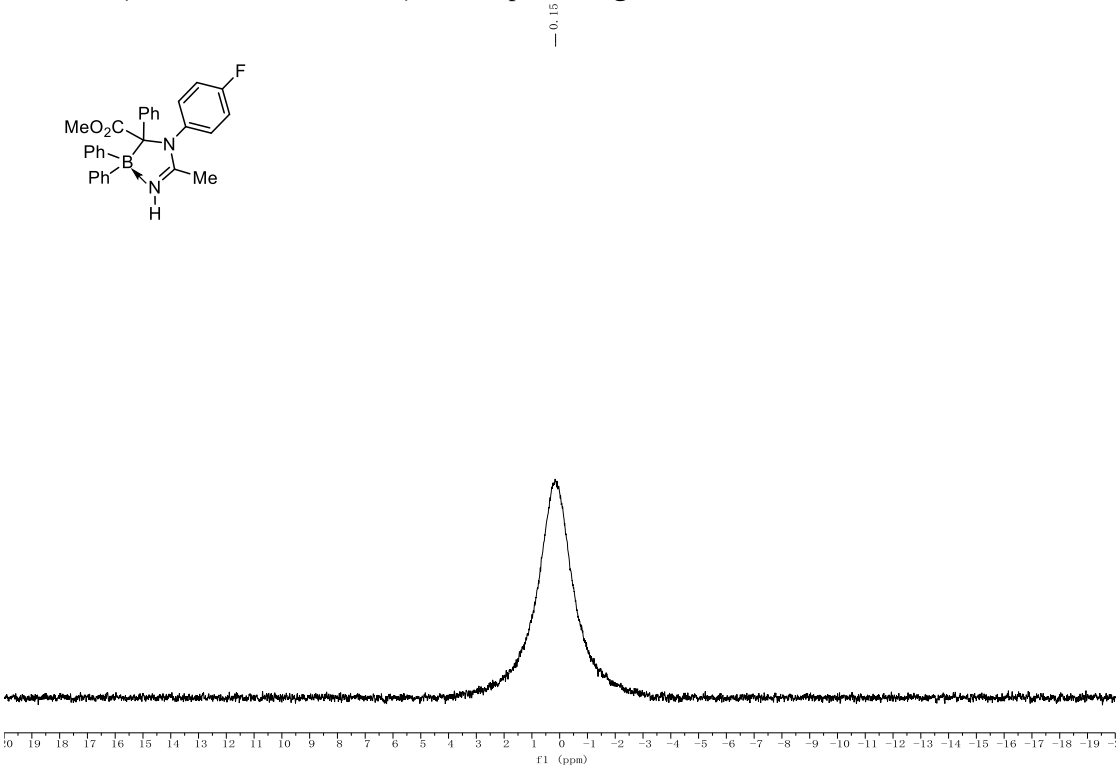


^{13}C NMR (101 MHz, Chloroform-*d*) for compound **4ag**



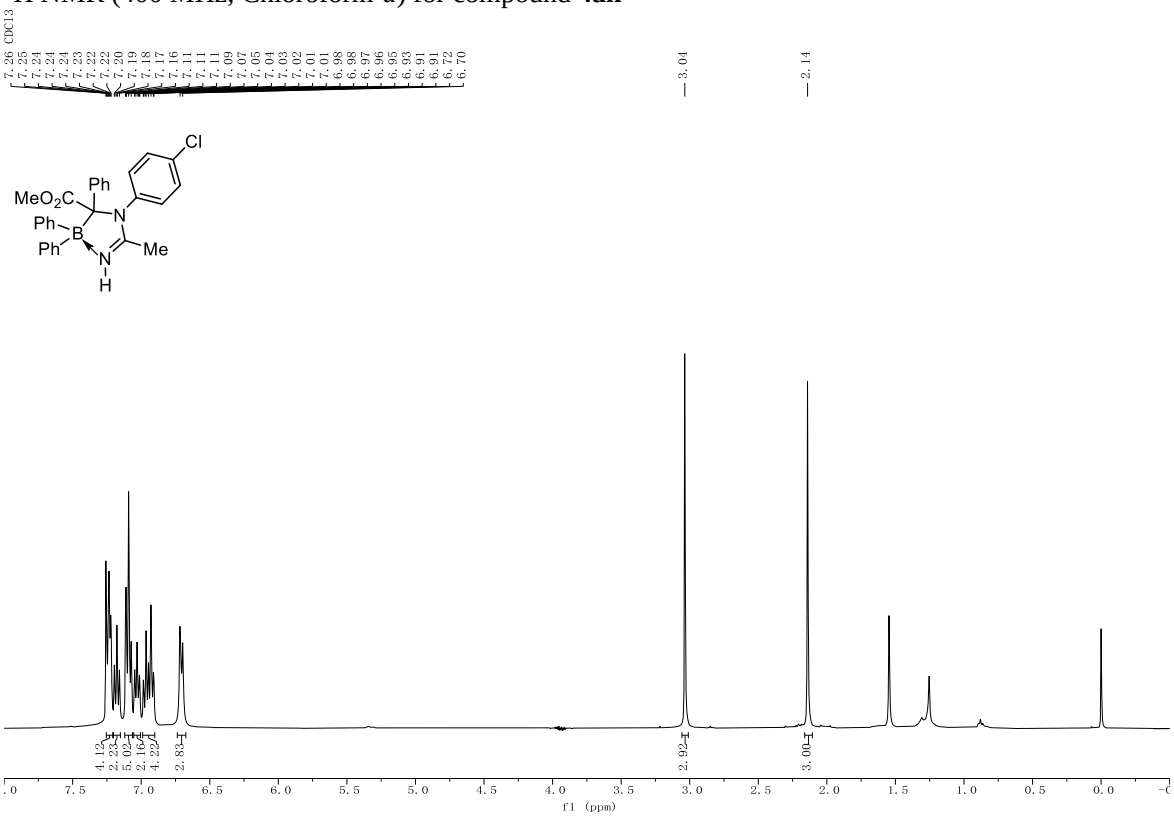


^{11}B NMR (128 MHz, Chloroform-*d*) for compound **4ag**

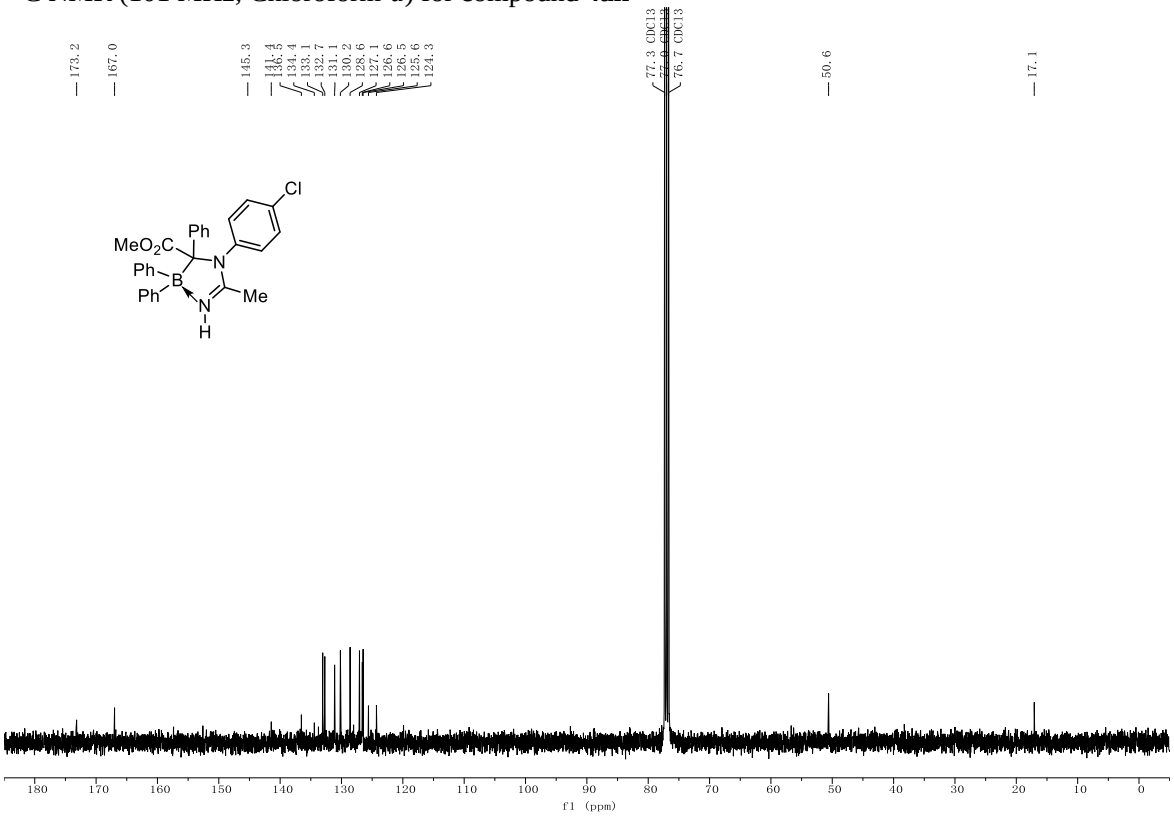


methyl 4-(4-chlorophenyl)-5-methyl-2,2,3-triphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4ah)

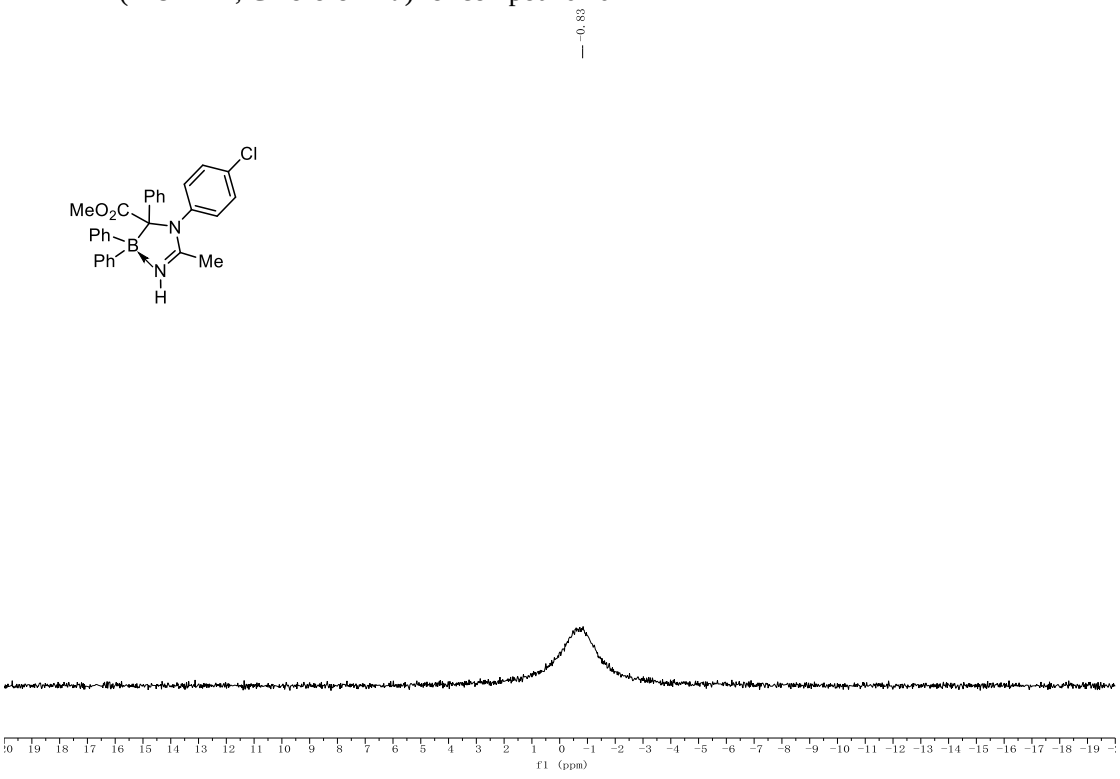
^{1}H NMR (400 MHz, Chloroform-*d*) for compound **4ah**



^{13}C NMR (101 MHz, Chloroform-*d*) for compound **4ah**

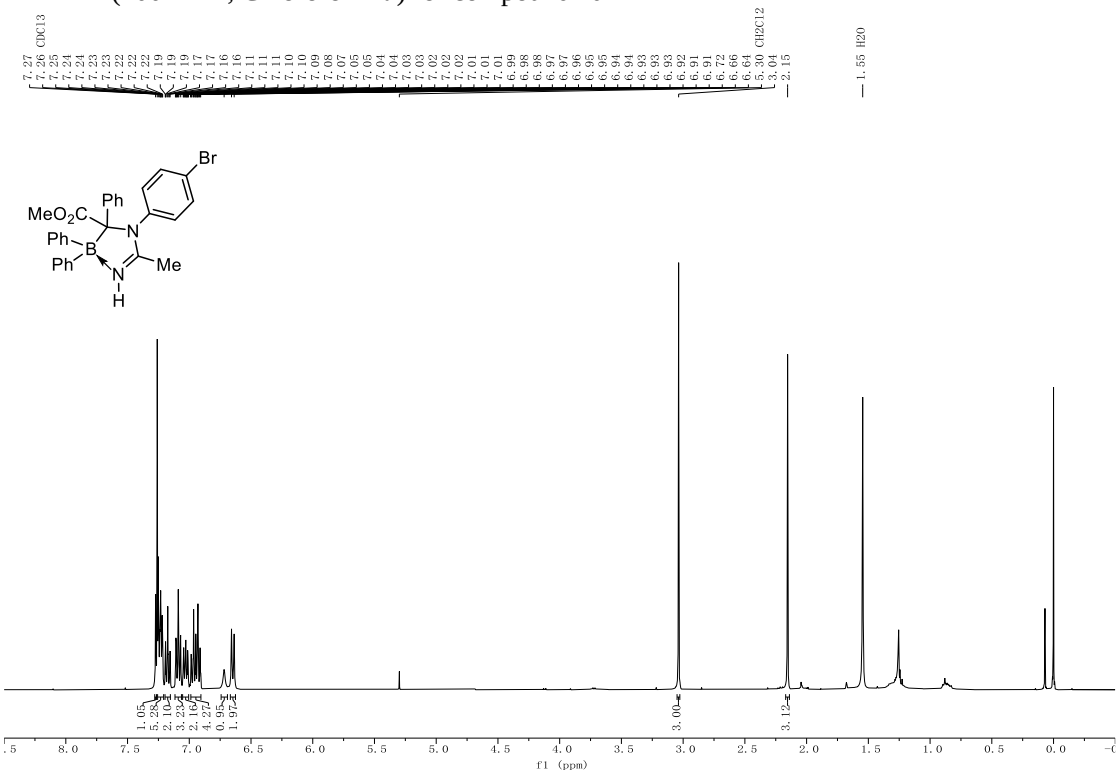


^{11}B NMR (128 MHz, Chloroform-*d*) for compound **4ah**

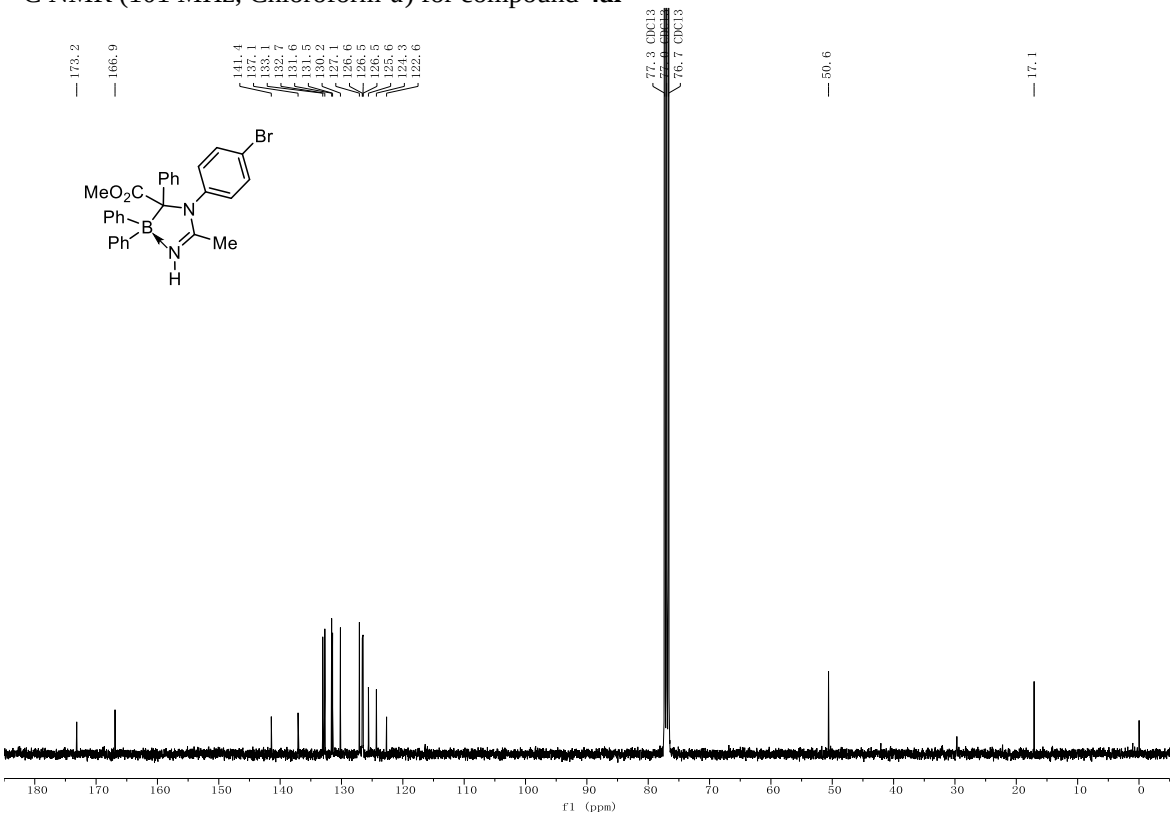


methyl 4-(4-bromophenyl)-5-methyl-2,2,3-triphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4ai)

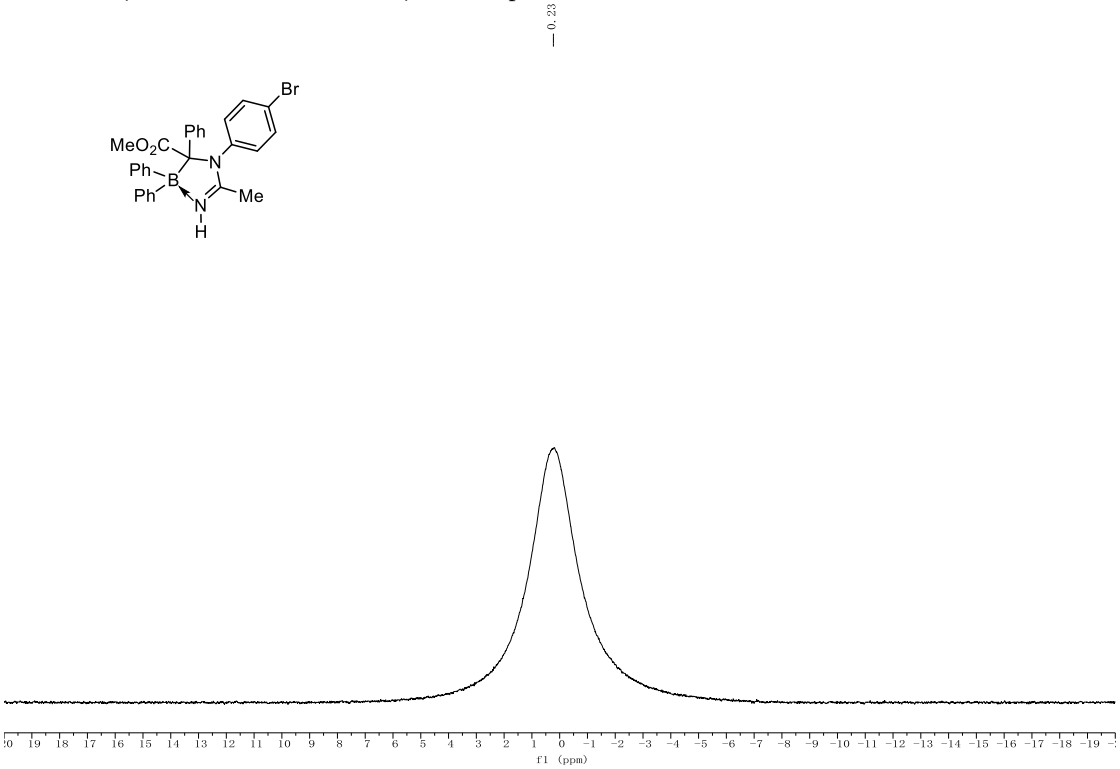
^{1}H NMR (400 MHz, Chloroform-*d*) for compound **4ai**



^{13}C NMR (101 MHz, Chloroform-*d*) for compound **4ai**

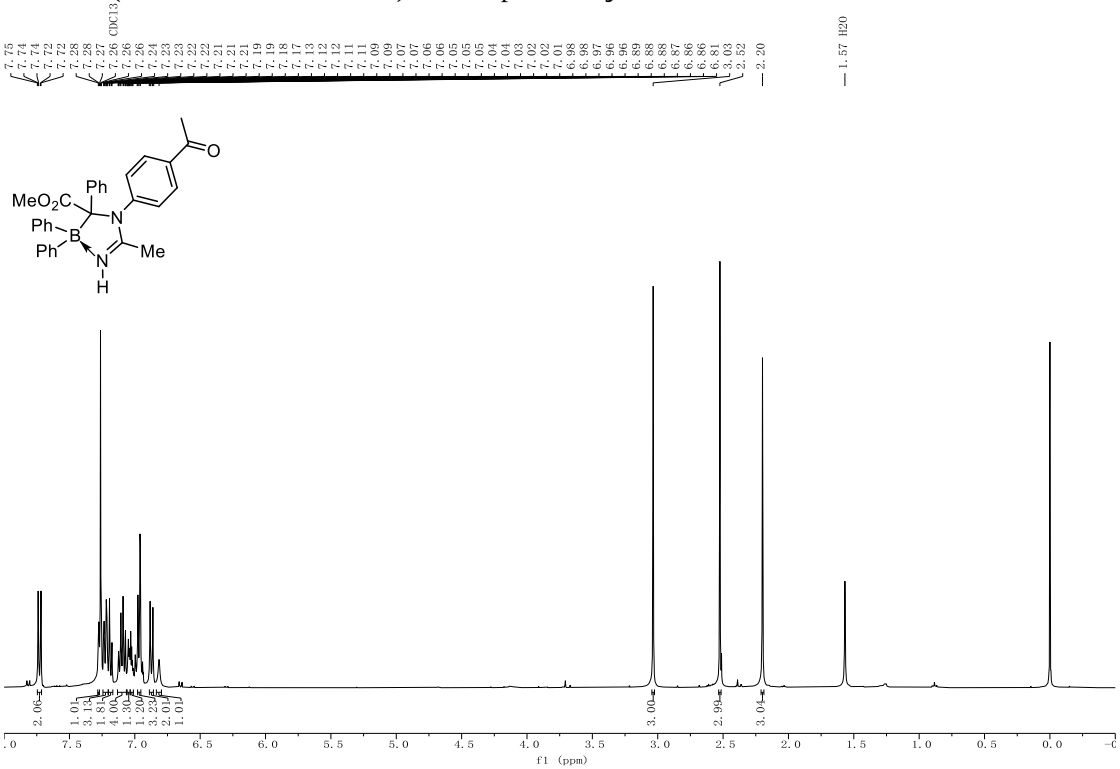


^{11}B NMR (128 MHz, Chloroform-*d*) for compound **4ai**

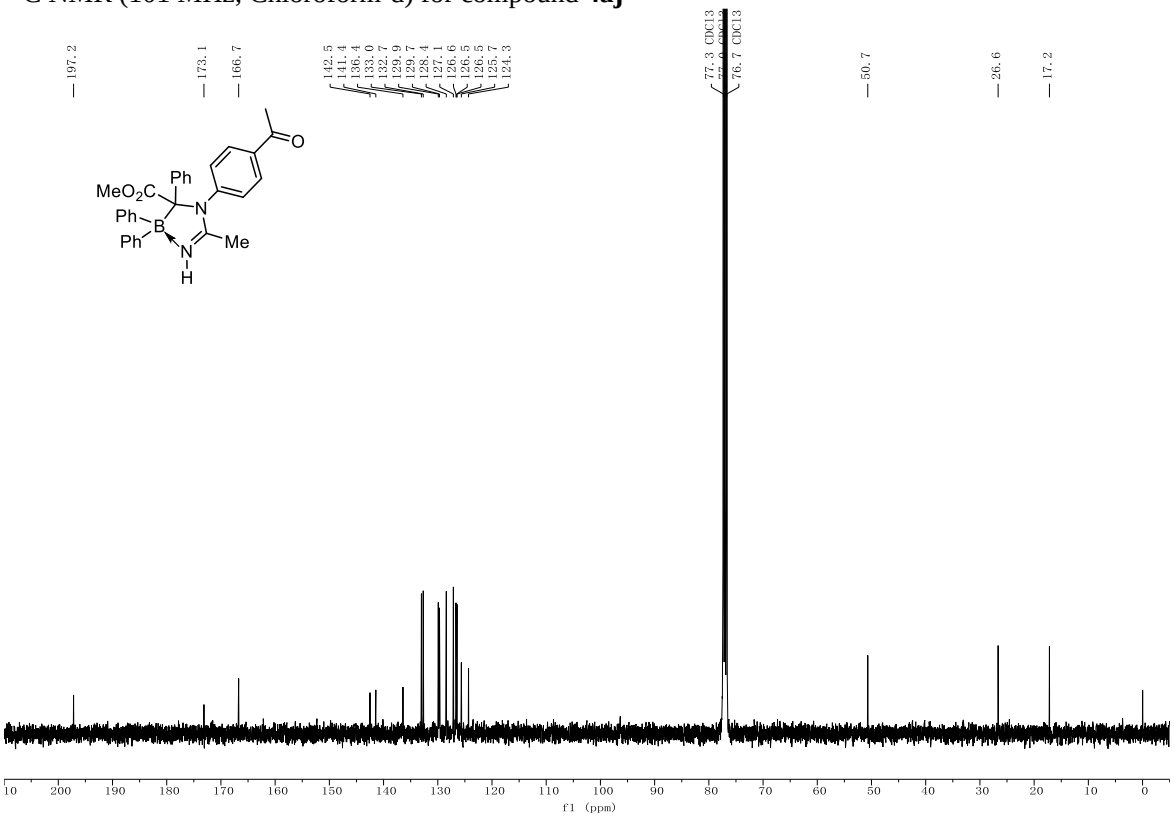


methyl 4-(4-acetylphenyl)-5-methyl-2,2,3-triphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4aj)

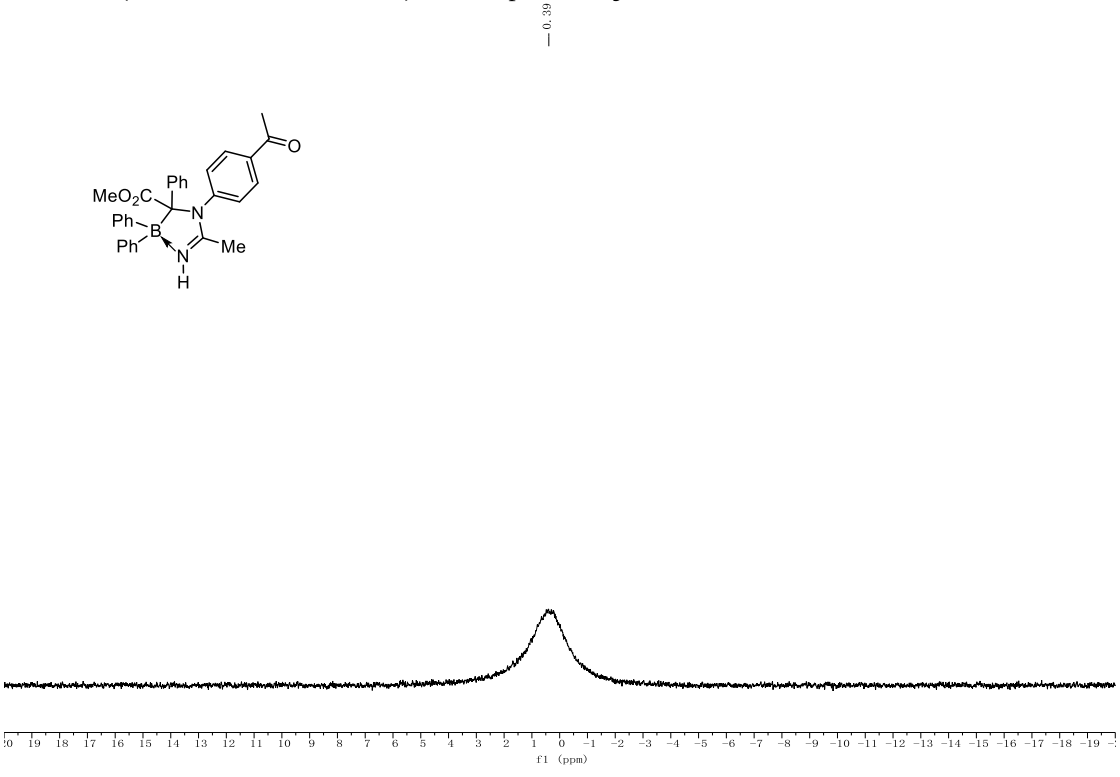
^{1}H NMR (400 MHz, Chloroform-*d*) for compound **4aj**



^{13}C NMR (101 MHz, Chloroform-d) for compound **4aj**

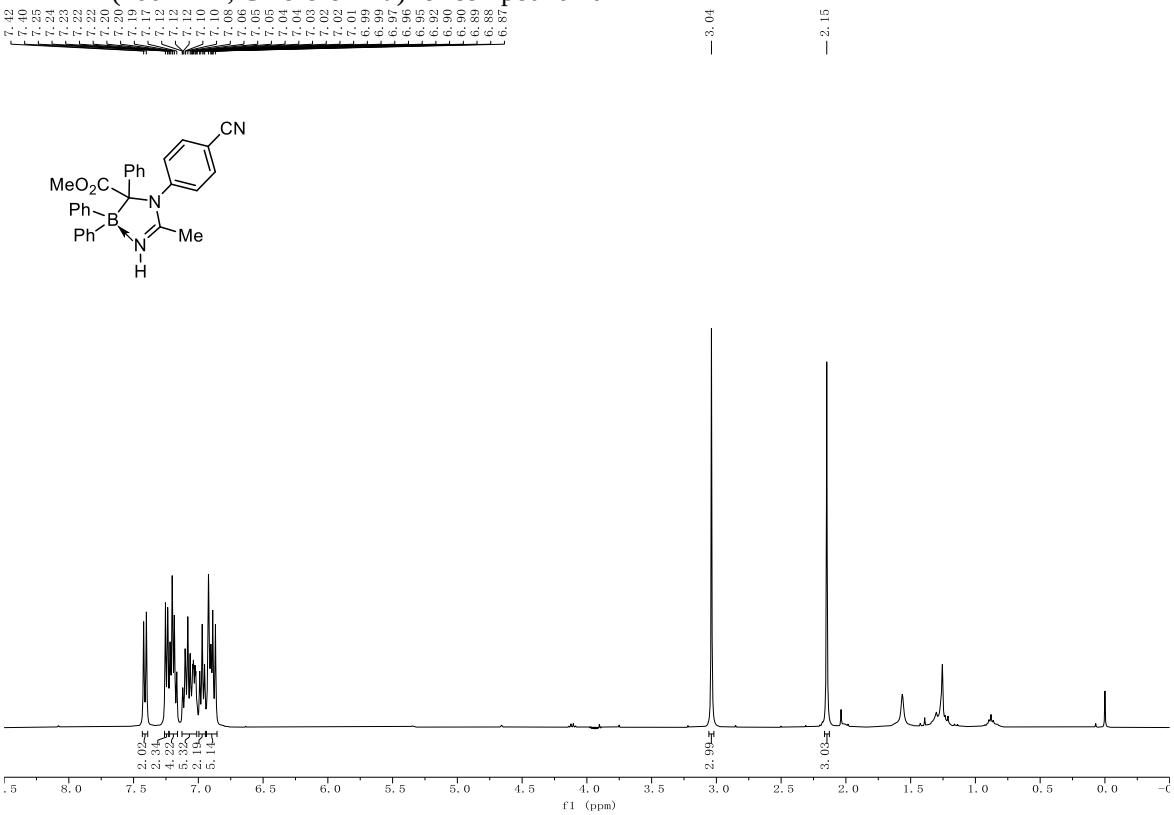


^{11}B NMR (128 MHz, Chloroform-*d*) for compound **4aj**

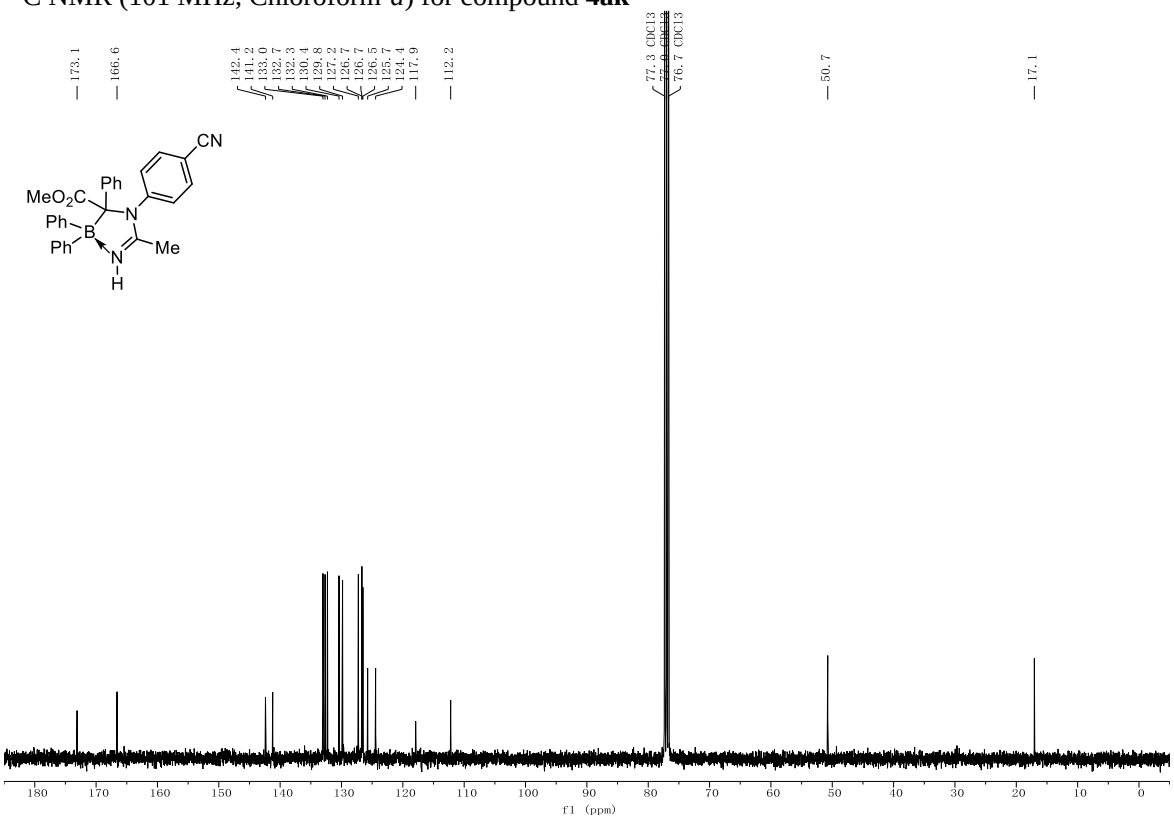


methyl 4-(4-cyanophenyl)-5-methyl-2,2,3-triphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4ak)

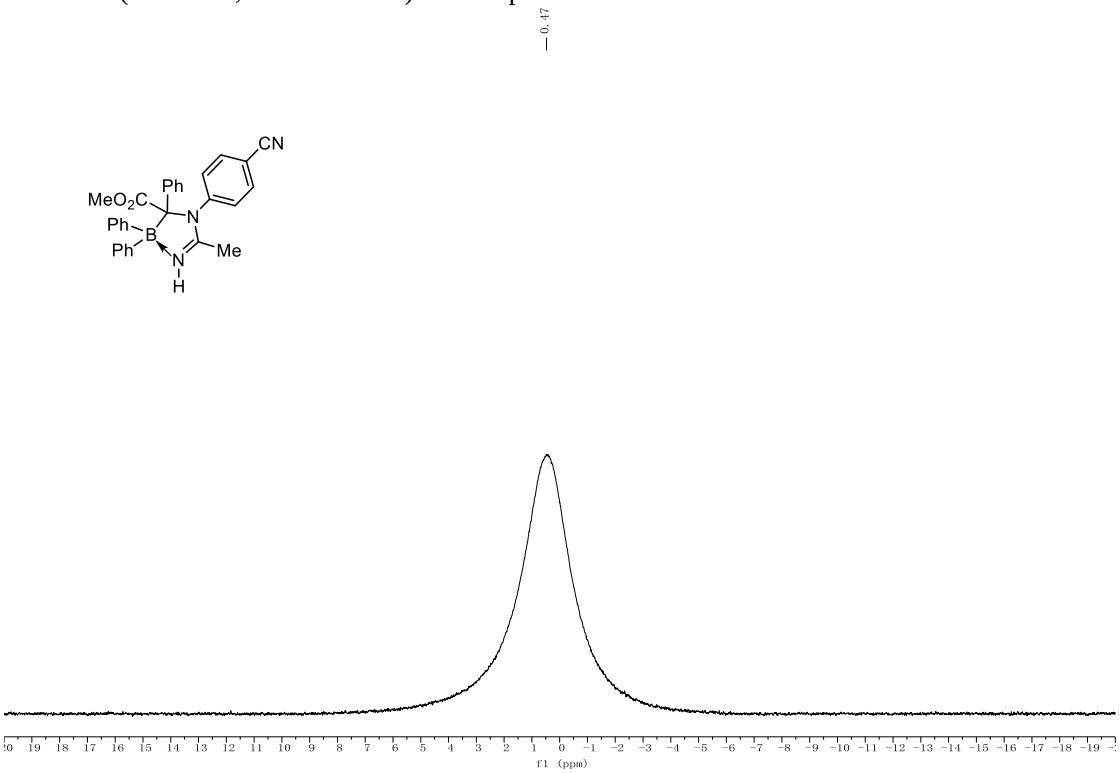
^{1}H NMR (400 MHz, Chloroform-*d*) for compound **4ak**



^{13}C NMR (101 MHz, Chloroform-*d*) for compound **4ak**

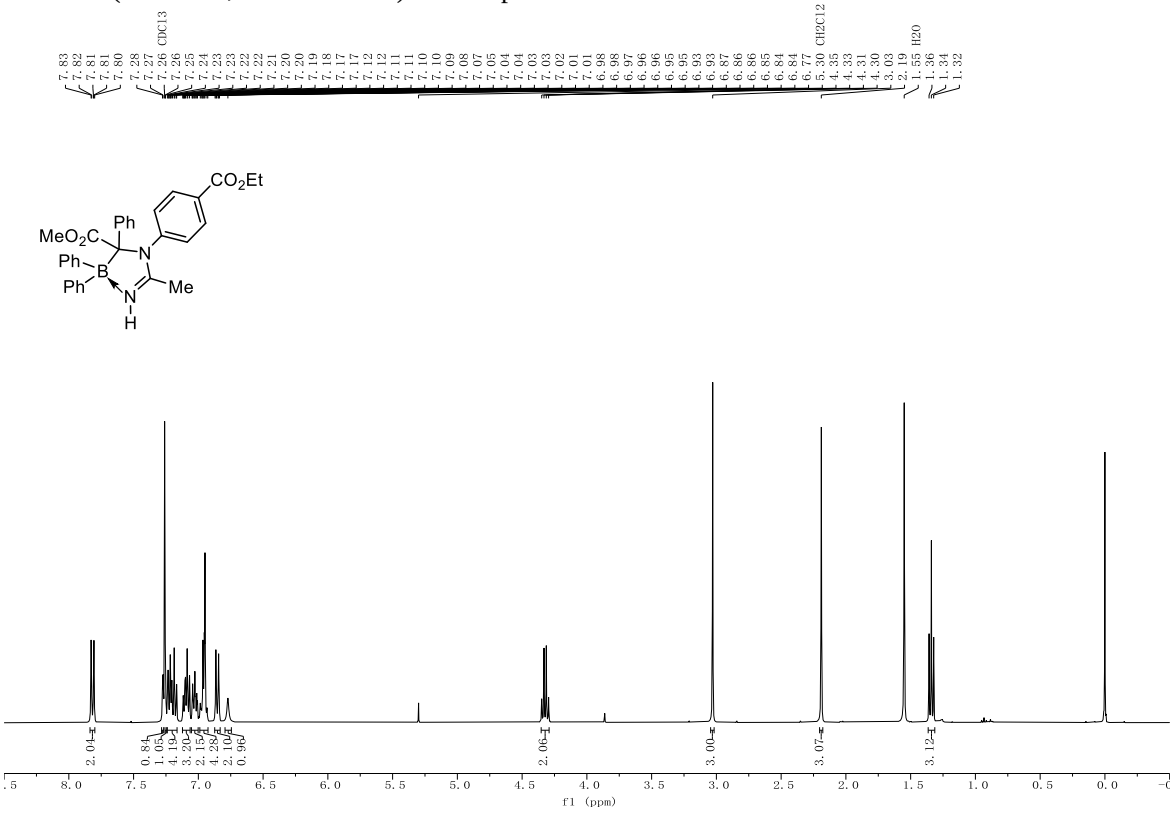


^{11}B NMR (128 MHz, Chloroform-*d*) for compound **4ak**

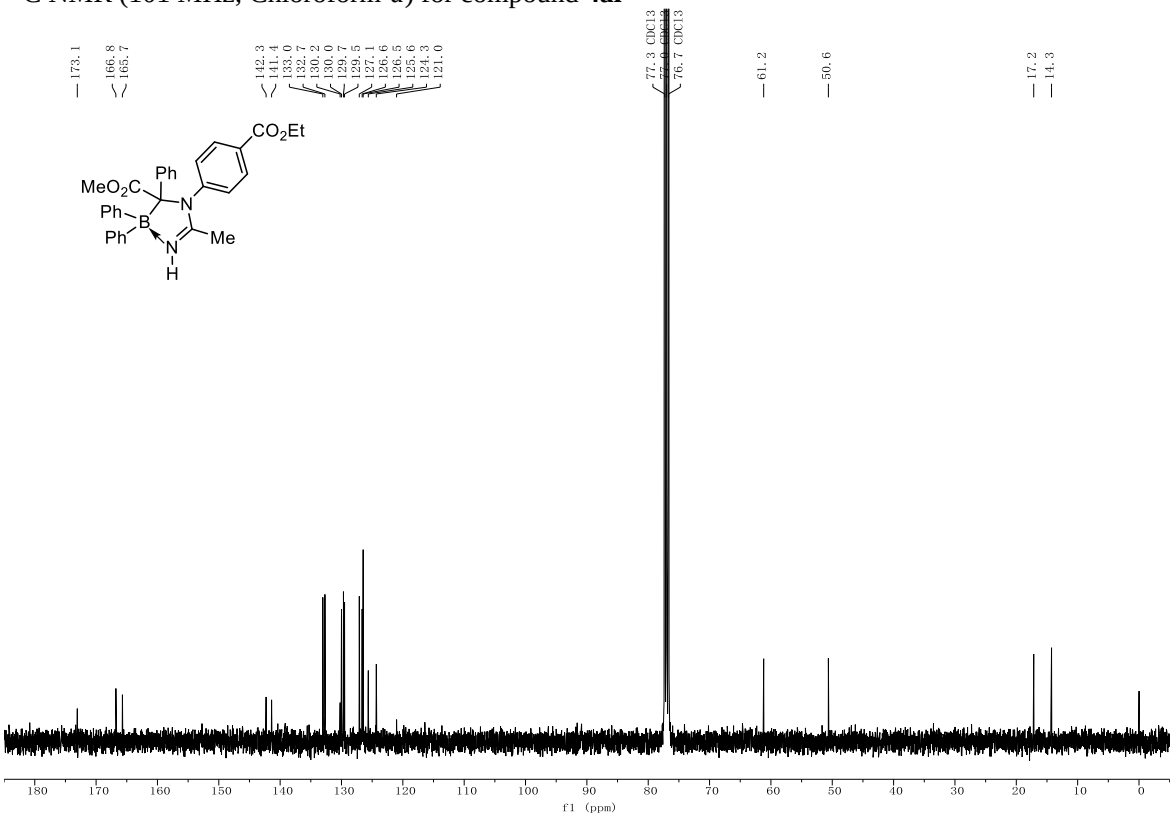


methyl 4-(4-(ethoxycarbonyl)phenyl)-5-methyl-2,2,3-triphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4al)

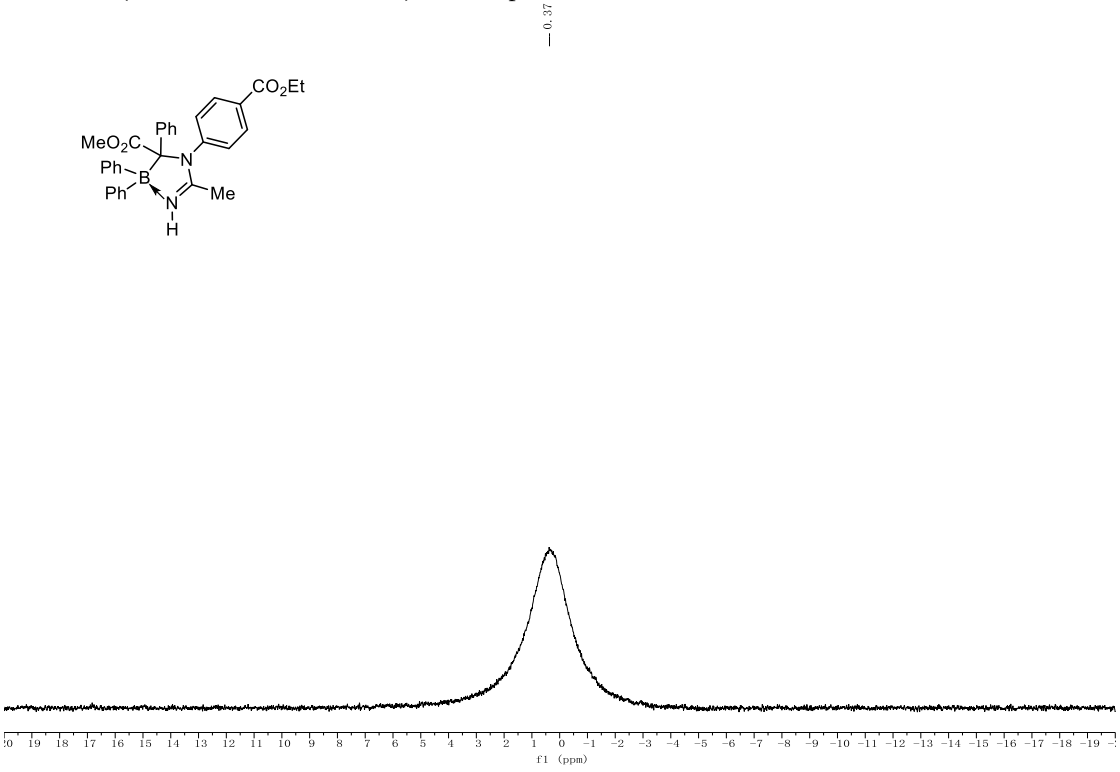
^{1}H NMR (400 MHz, Chloroform-*d*) for compound **4al**



^{13}C NMR (101 MHz, Chloroform-*d*) for compound **4al**

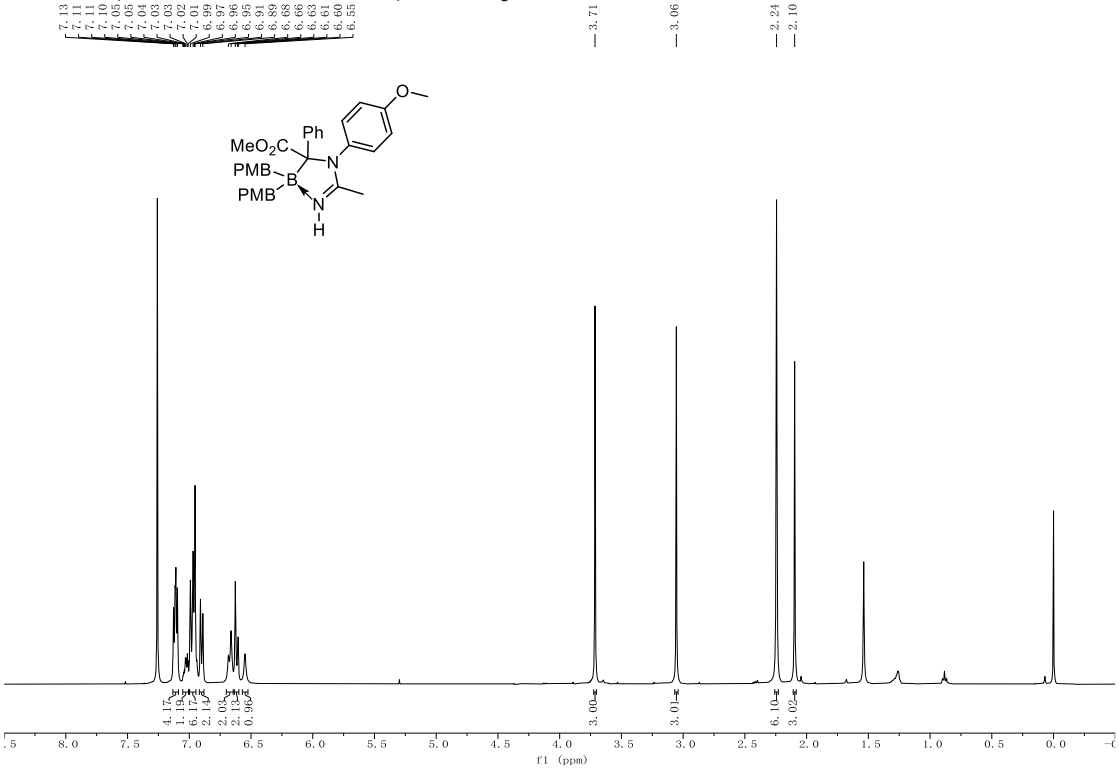


^{11}B NMR (128 MHz, Chloroform-*d*) for compound **4al**

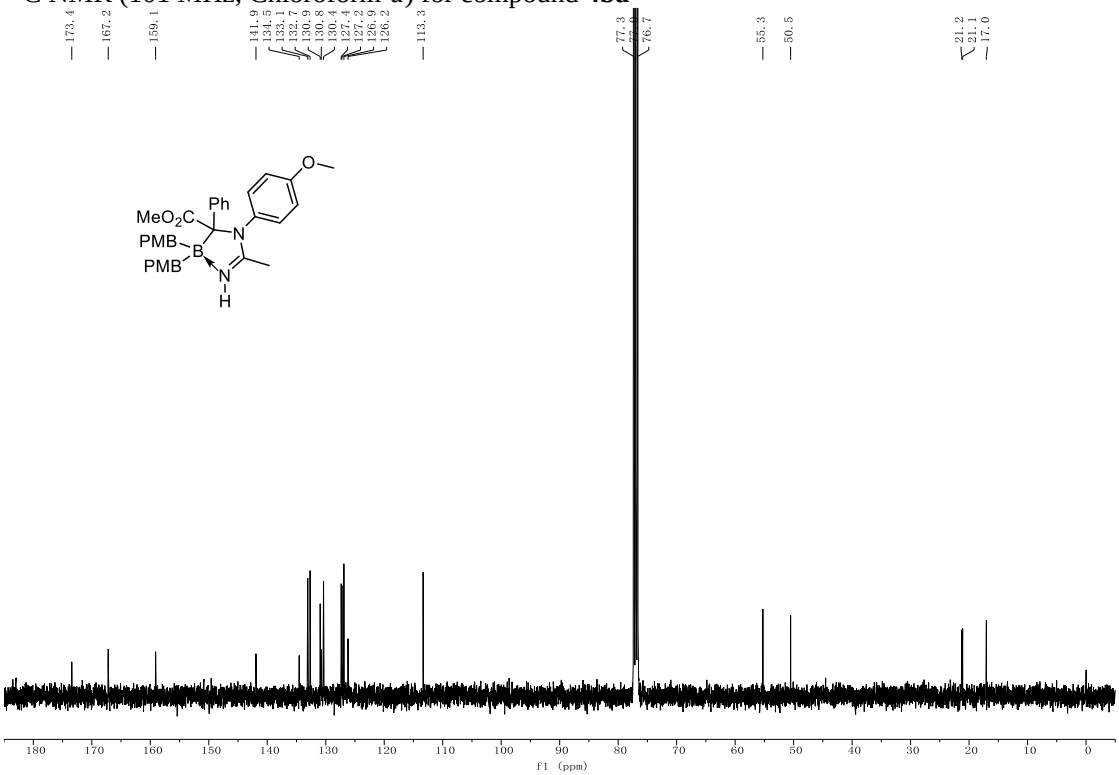


Methyl 4-(4-methoxyphenyl)-5-methyl-3-phenyl-2,2-di-p-tolyl-3,4-dihydro-2H-1,4,2l4-diazaborole-3-carboxylate (4ba)

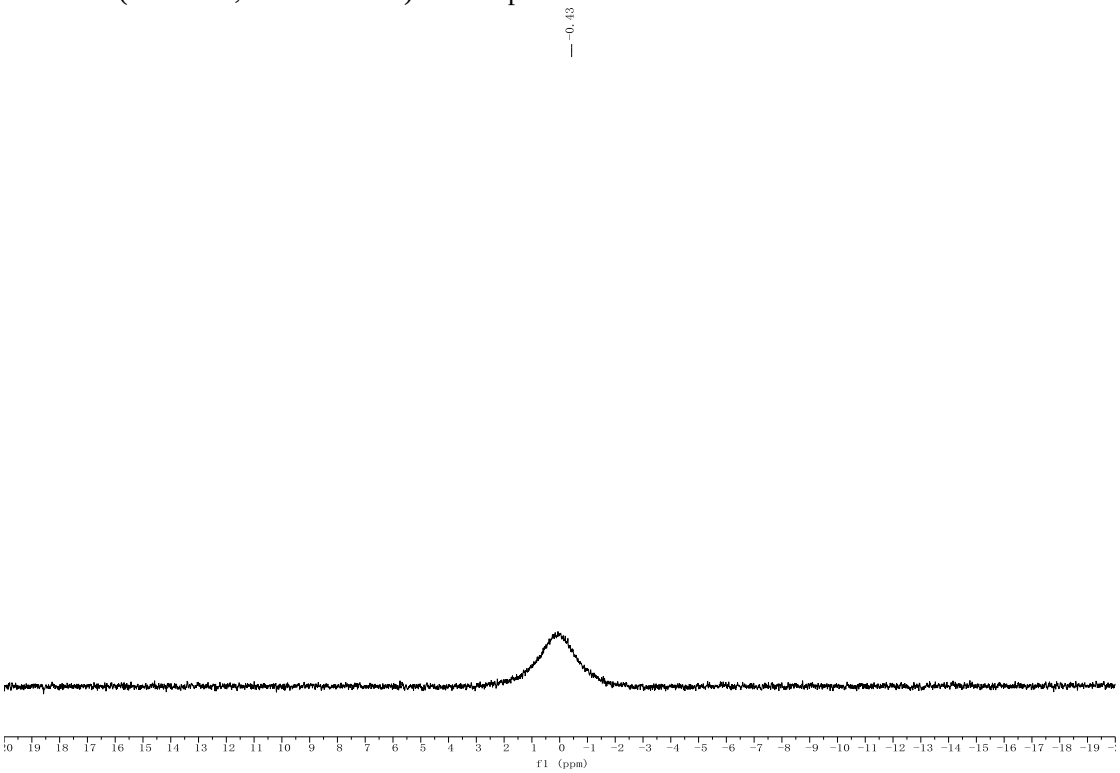
^{1}H NMR (400 MHz, Chloroform-*d*) for compound **4ba**



^{13}C NMR (101 MHz, Chloroform-*d*) for compound **4ba**

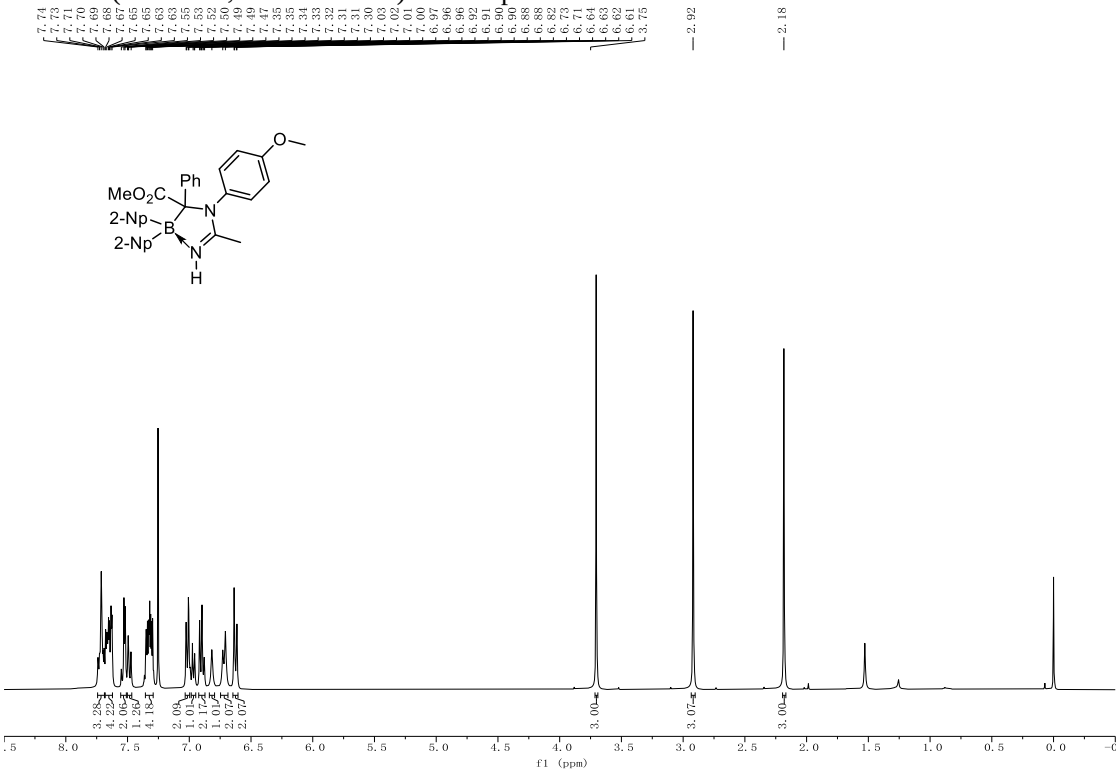


^{11}B NMR (128 MHz, Chloroform-*d*) for compound **4ba**

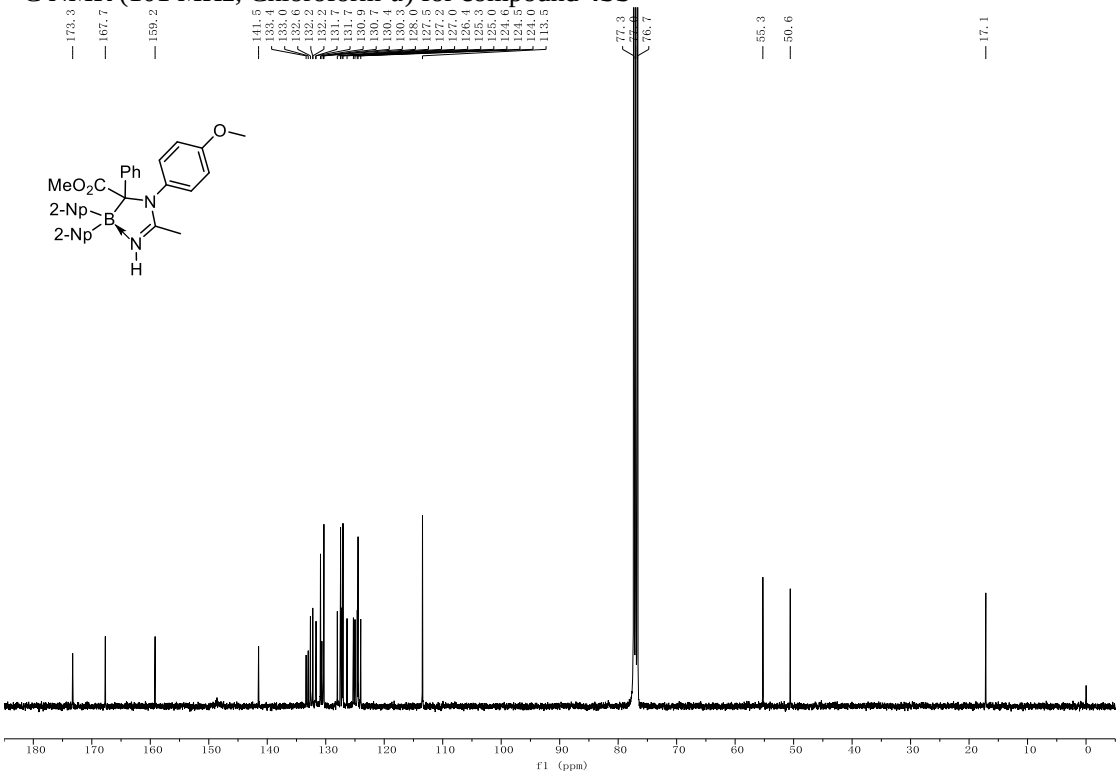


methyl 4-(4-methoxyphenyl)-5-methyl-2,2-di(naphthalen-2-yl)-3-phenyl-3,4-dihydro-2H-1,4,2l4-diazaborole-3-carboxylate (4bb)

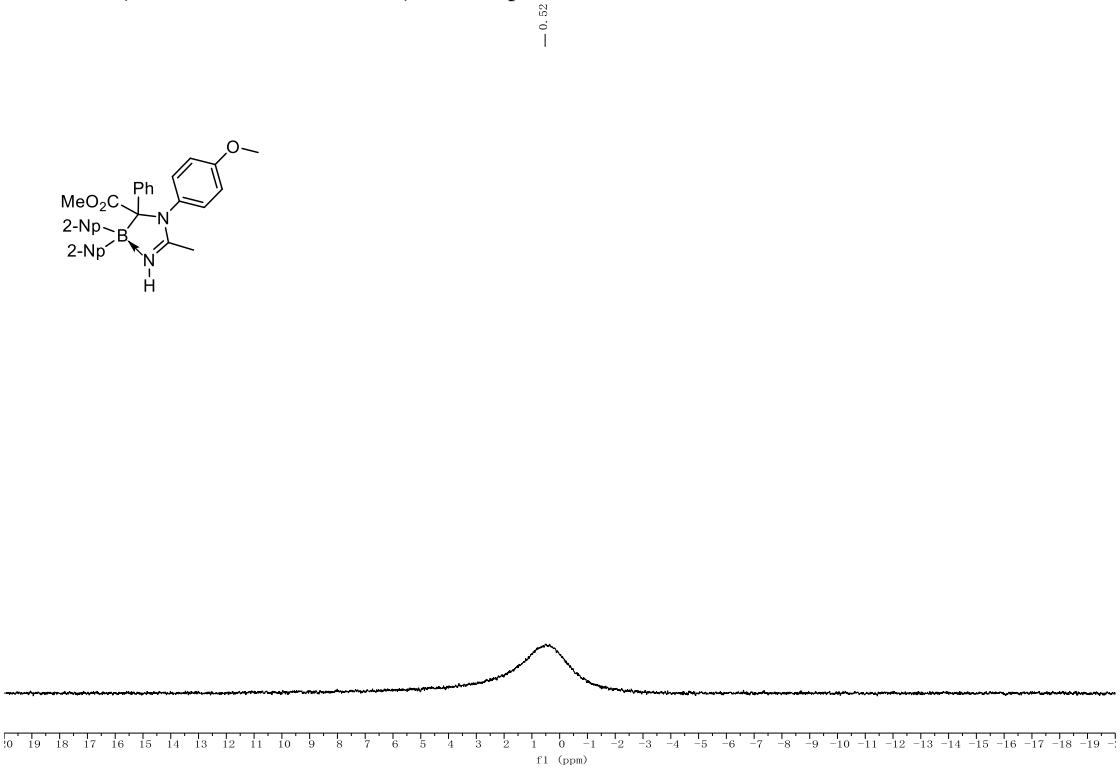
^{1}H NMR (400 MHz, Chloroform-*d*) for compound **4bb**



^{13}C NMR (101 MHz, Chloroform-*d*) for compound **4bb**

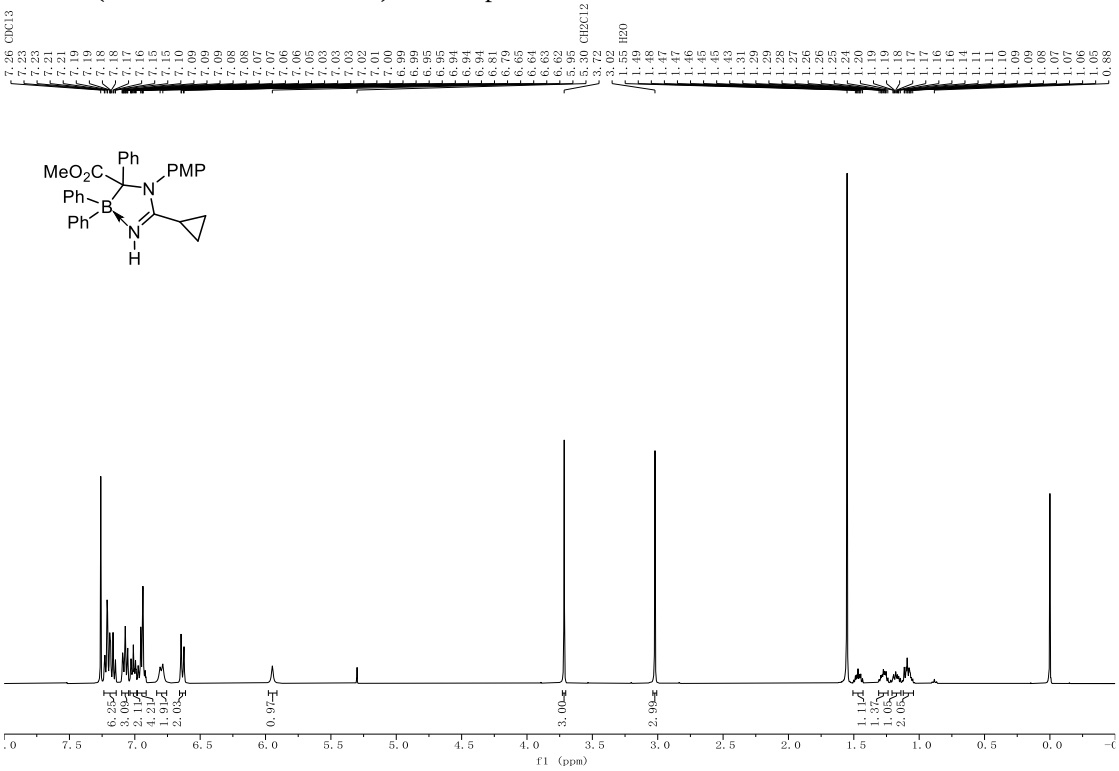


^{11}B NMR (128 MHz, Chloroform-*d*) for compound **4bb**

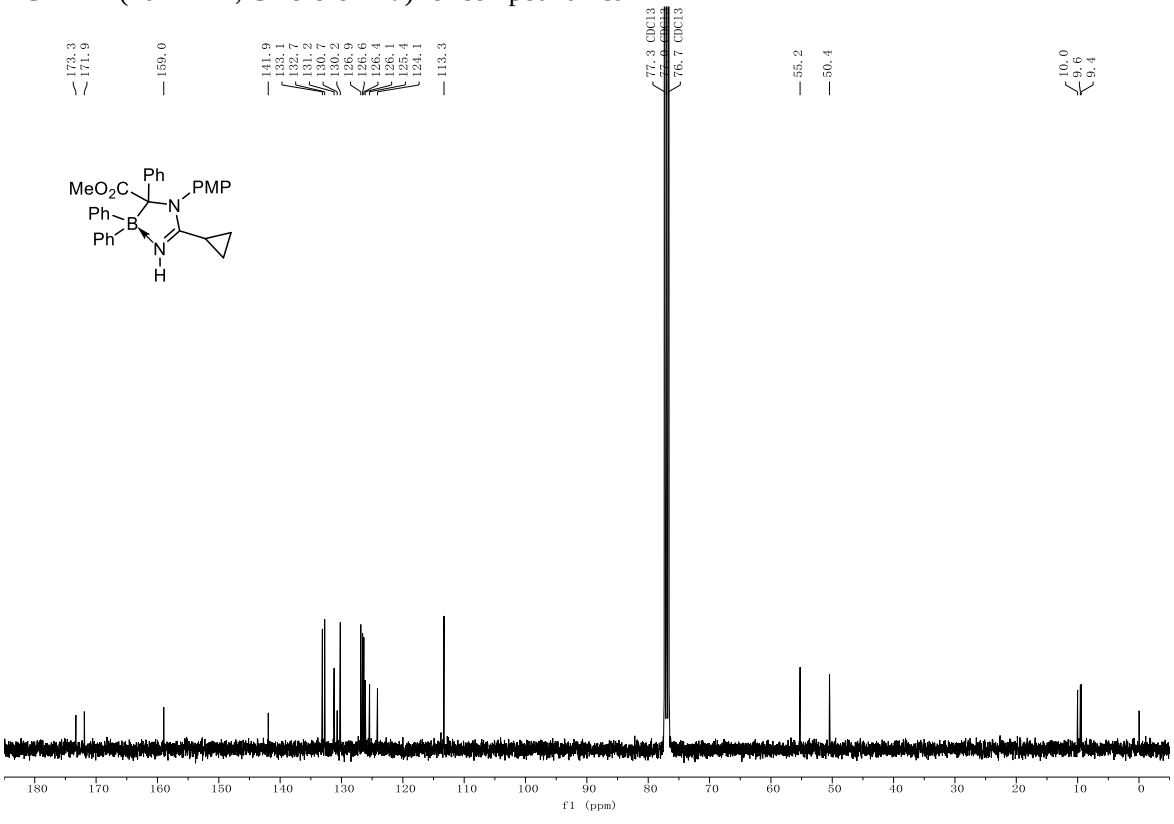


methyl 5-cyclopropyl-4-(4-methoxyphenyl)-2,2,3-triphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4ca)

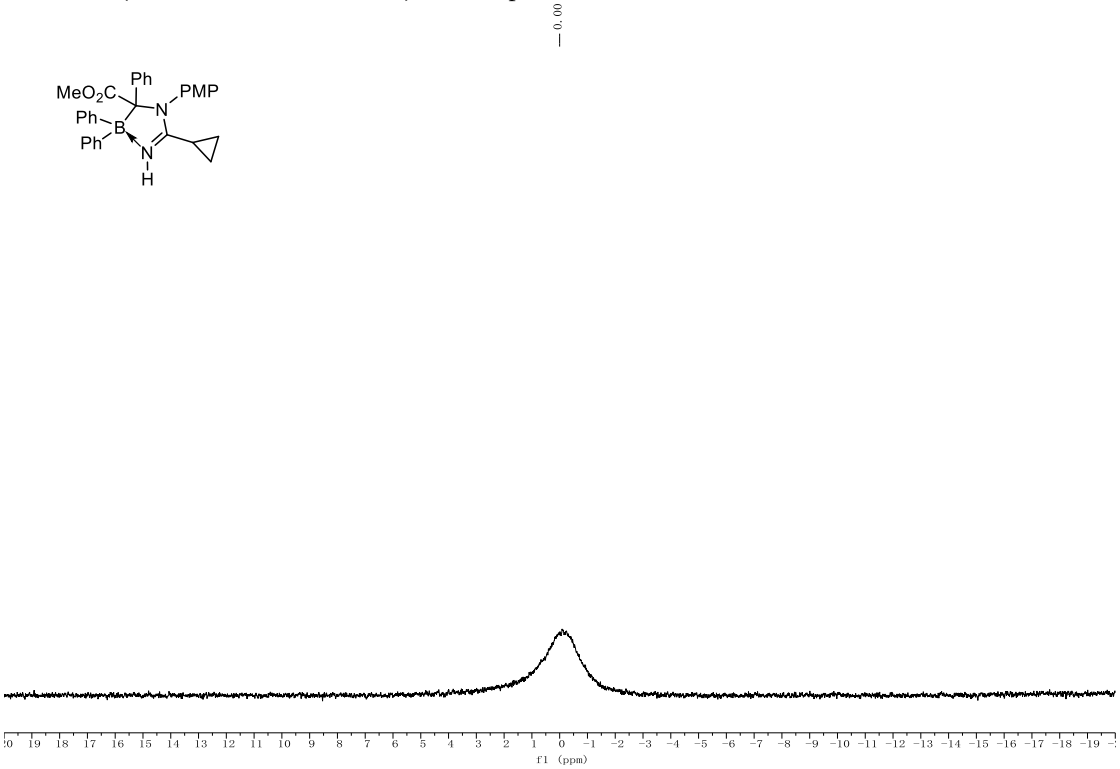
^{1}H NMR (400 MHz, Chloroform-*d*) for compound **4ca**



^{13}C NMR (101 MHz, Chloroform-*d*) for compound **4ca**

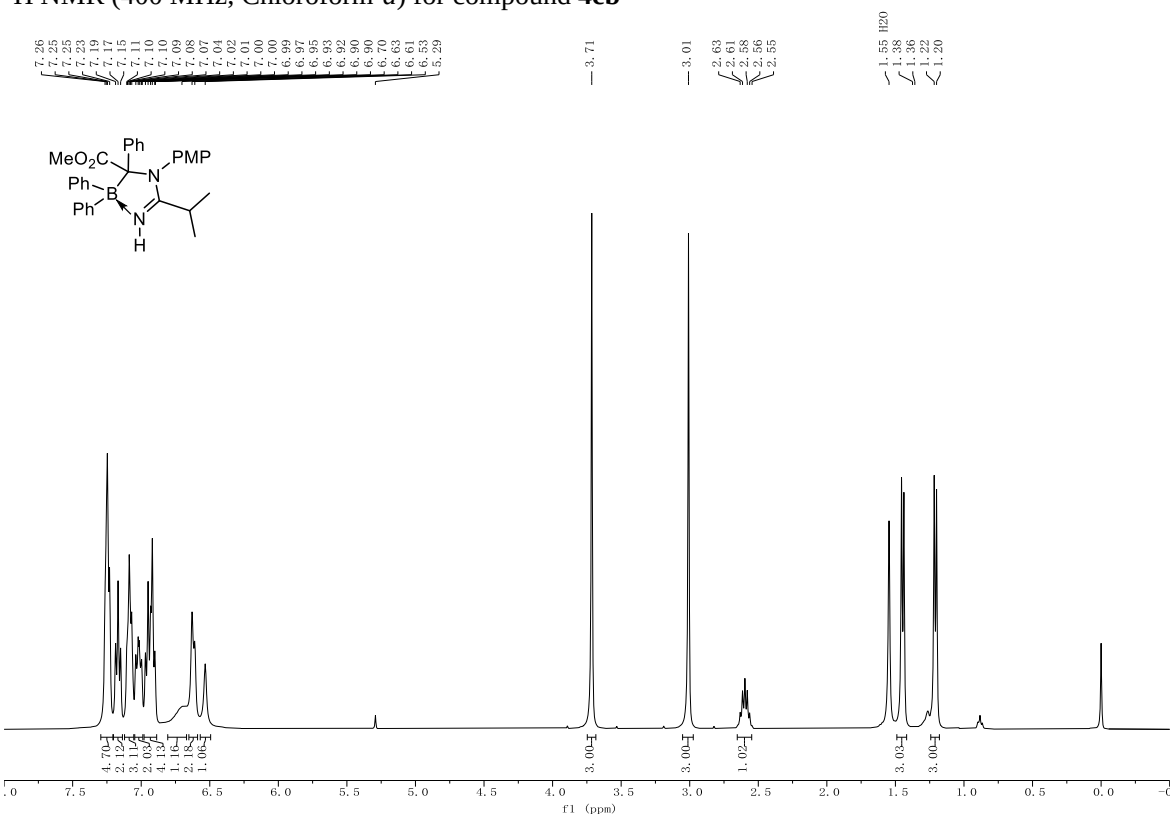


^{11}B NMR (128 MHz, Chloroform-*d*) for compound **4ca**

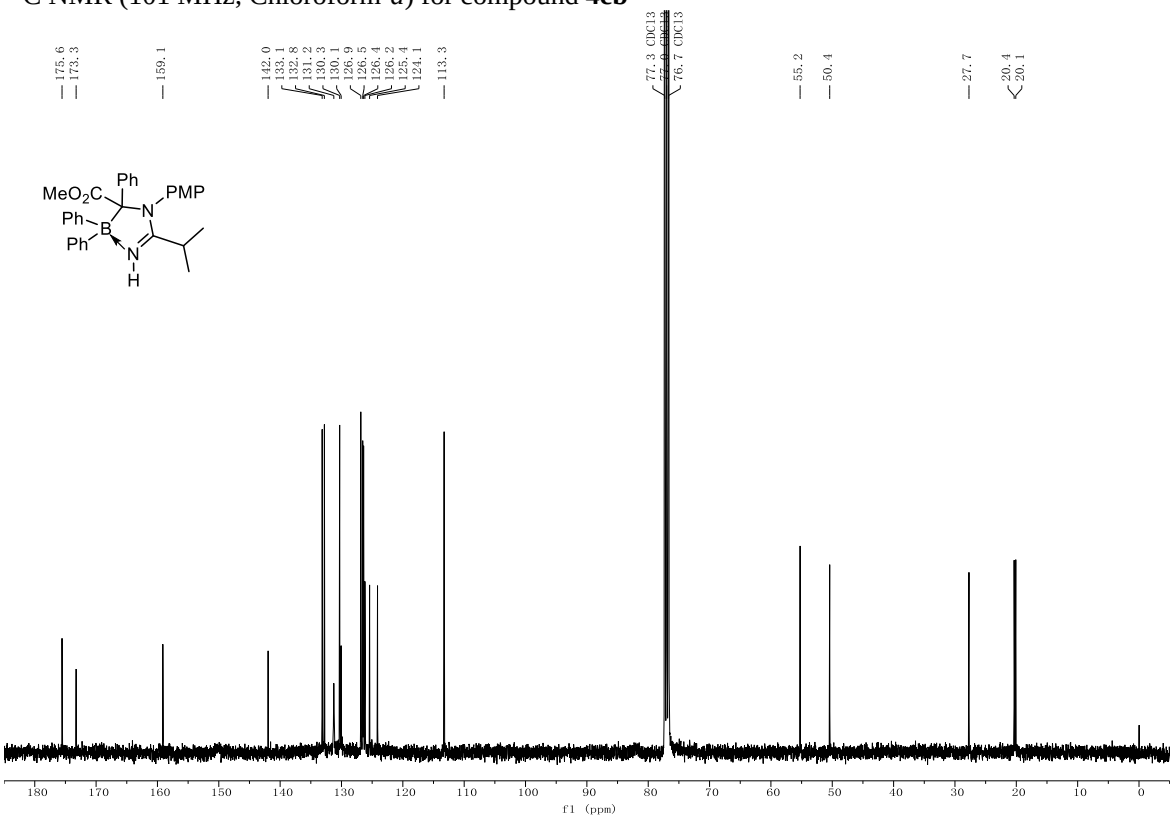


methyl 5-isopropyl-4-(4-methoxyphenyl)-2,2,3-triphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4cb)

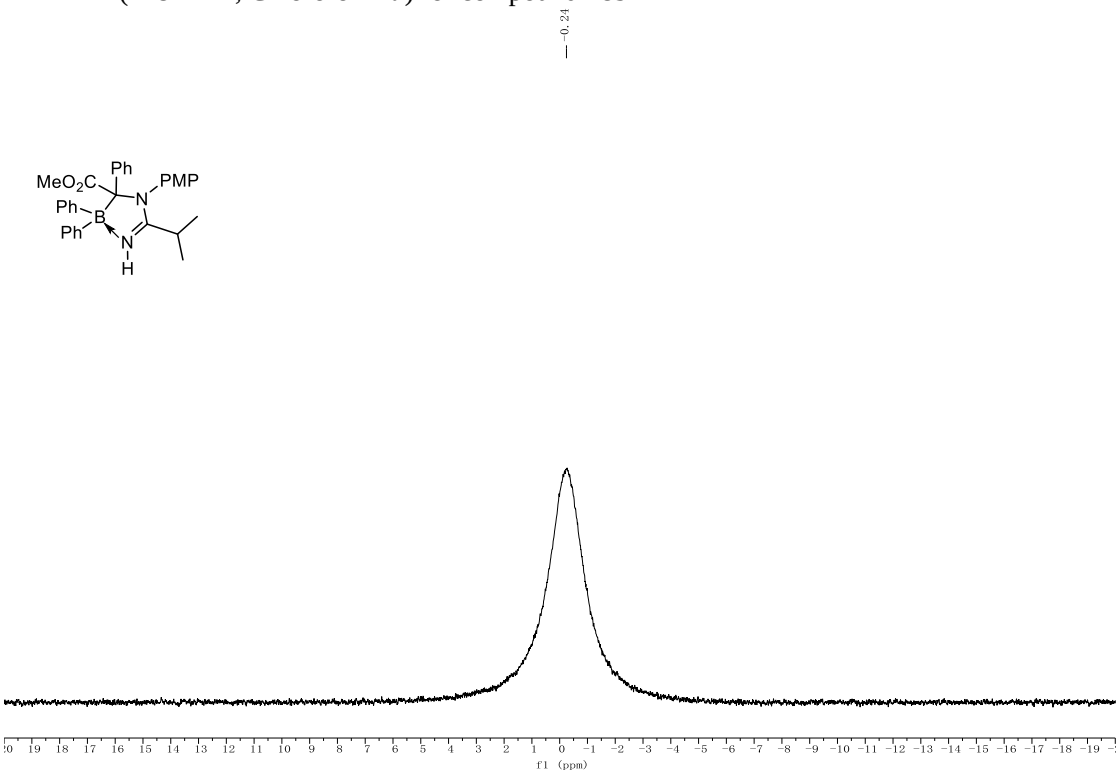
^{1}H NMR (400 MHz, Chloroform-*d*) for compound **4cb**



^{13}C NMR (101 MHz, Chloroform-*d*) for compound **4cb**

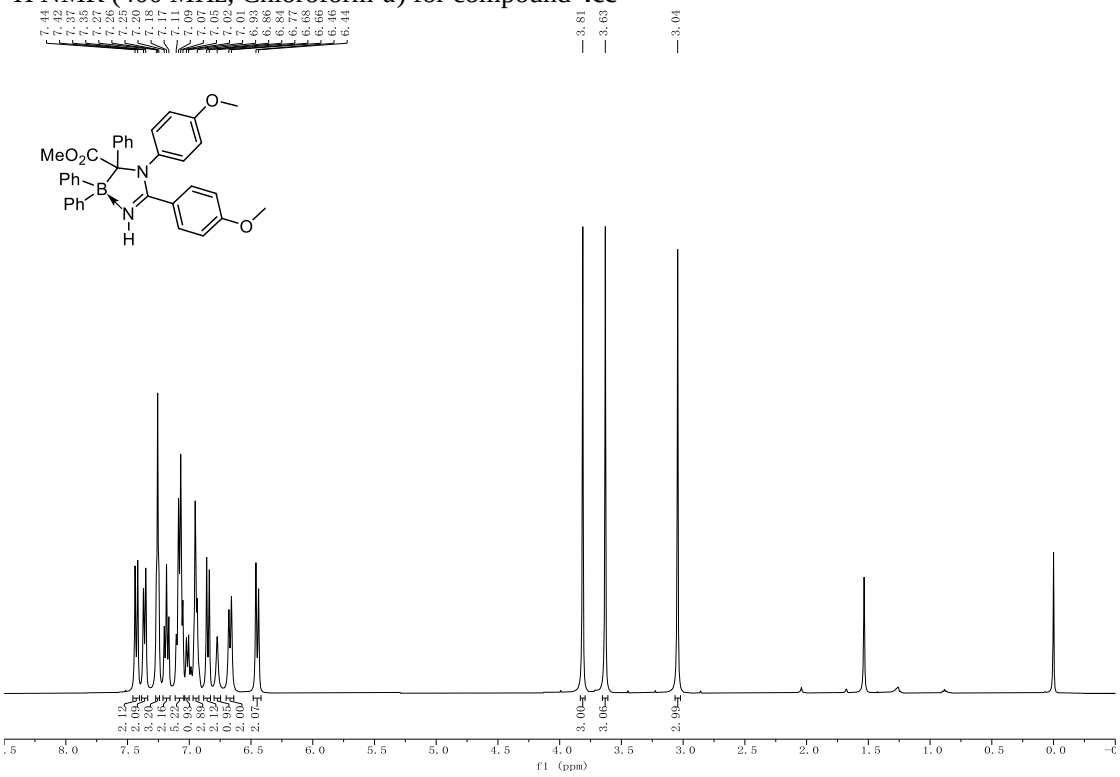


^{11}B NMR (128 MHz, Chloroform-*d*) for compound **4cb**

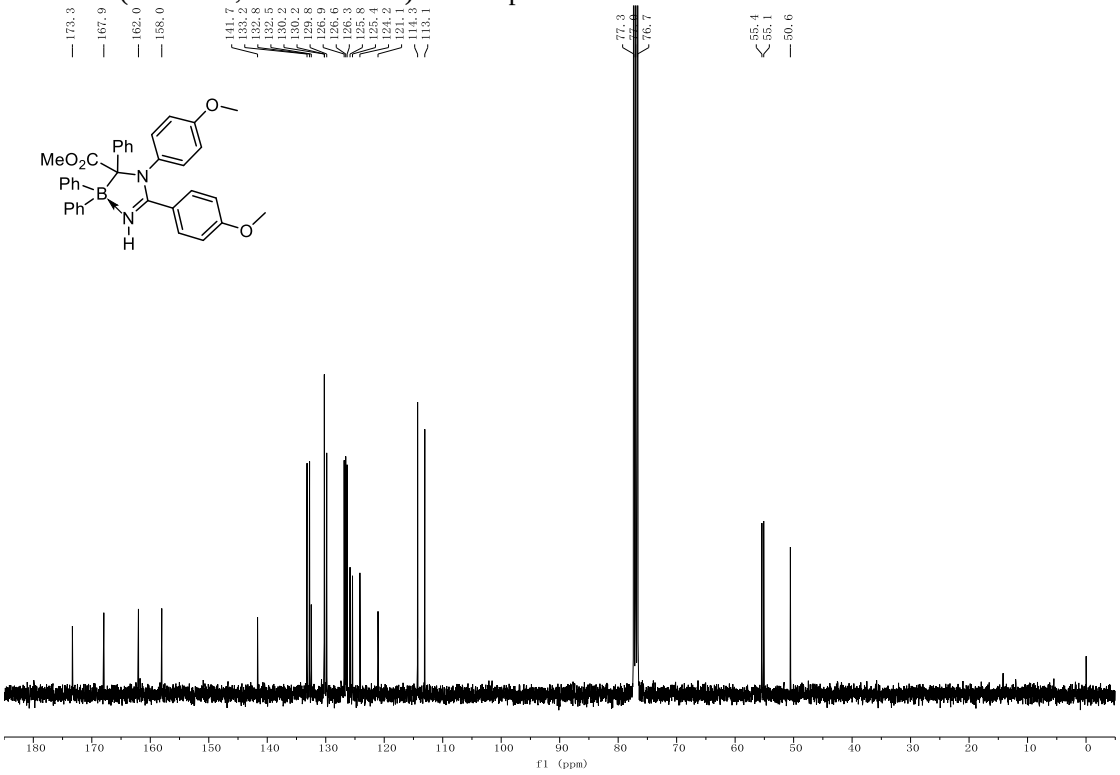


methyl 4,5-bis(4-methoxyphenyl)-2,2,3-triphenyl-3,4-dihydro-2H-1,4,2l4-diazaborole-3-carboxylate (4cc)

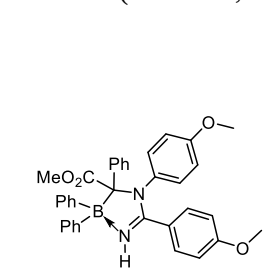
^{1}H NMR (400 MHz, Chloroform-*d*) for compound **4cc**



^{13}C NMR (101 MHz, Chloroform-*d*) for compound **4cc**

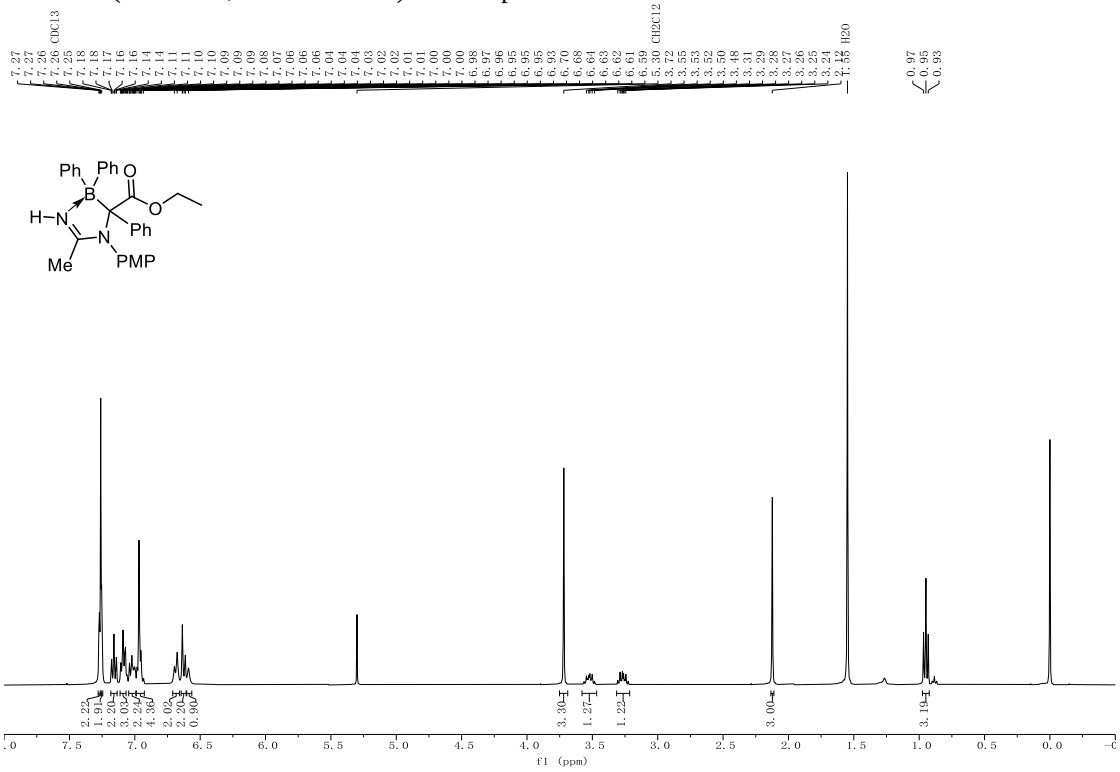


^{11}B NMR (128 MHz, Chloroform-*d*) for compound **4cc**

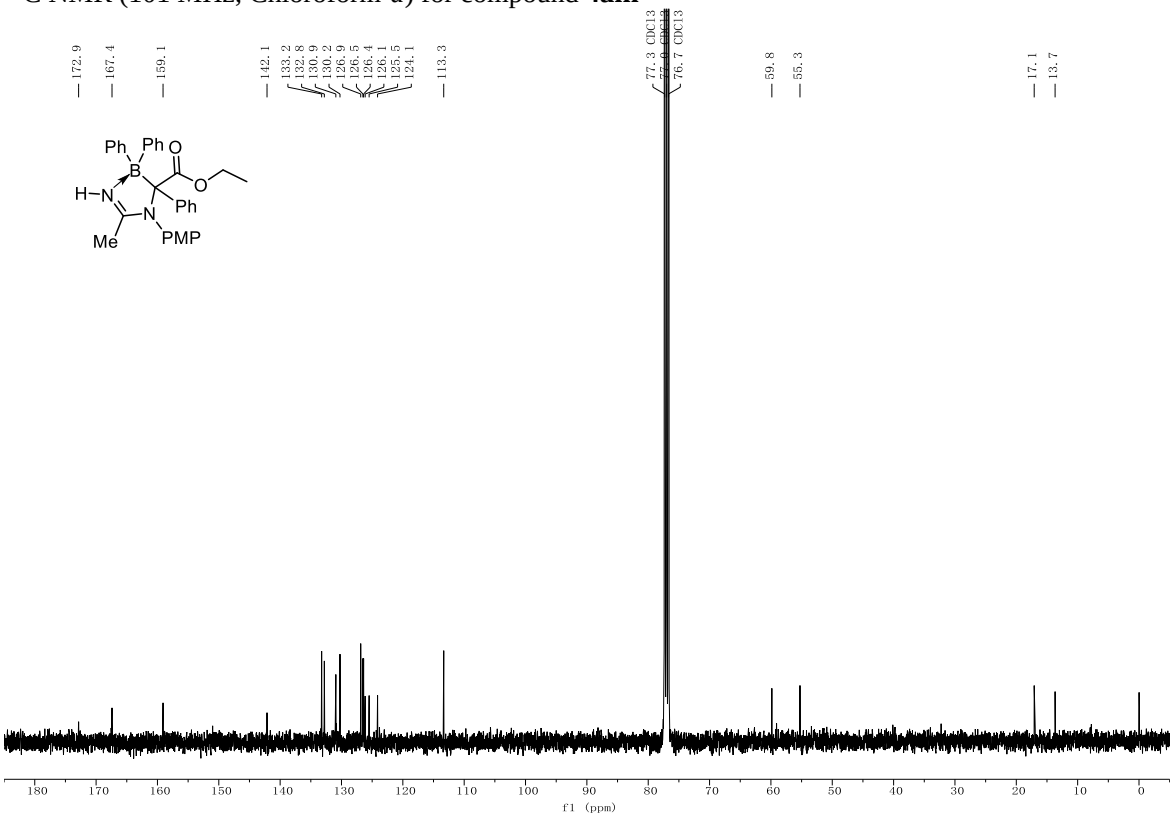


ethyl 4-(4-methoxyphenyl)-5-methyl-2,2,3-triphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4am)

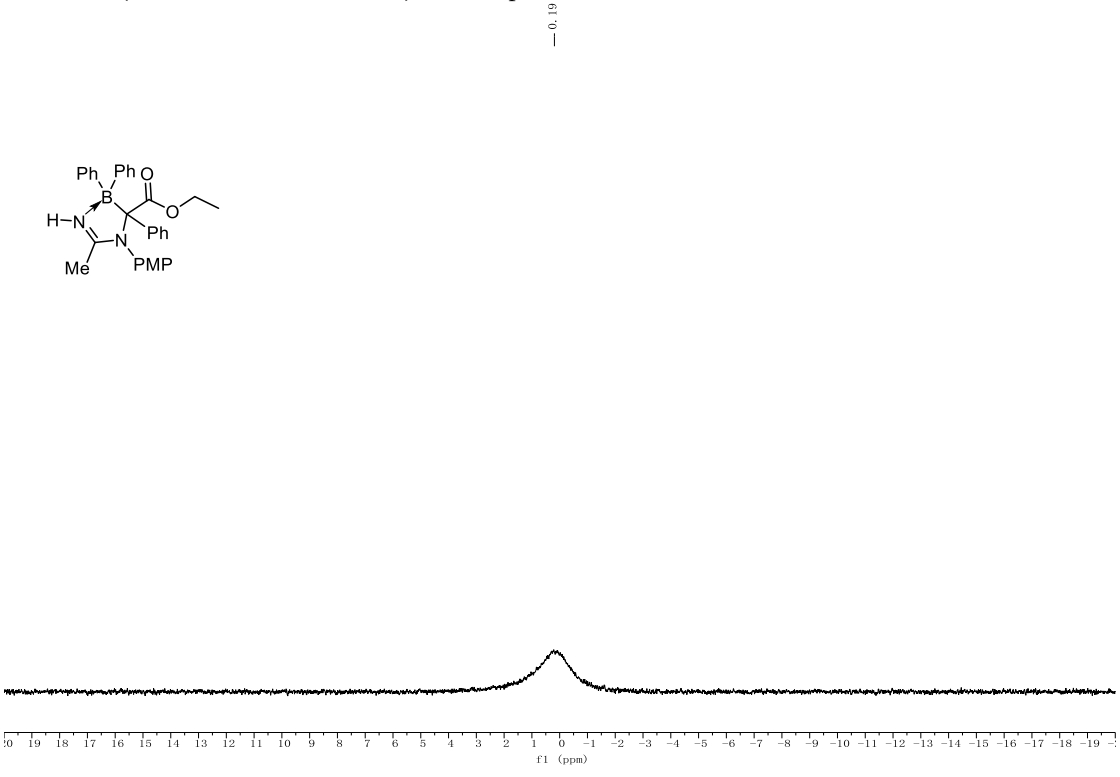
^{1}H NMR (400 MHz, Chloroform-*d*) for compound **4am**



^{13}C NMR (101 MHz, Chloroform-*d*) for compound **4am**

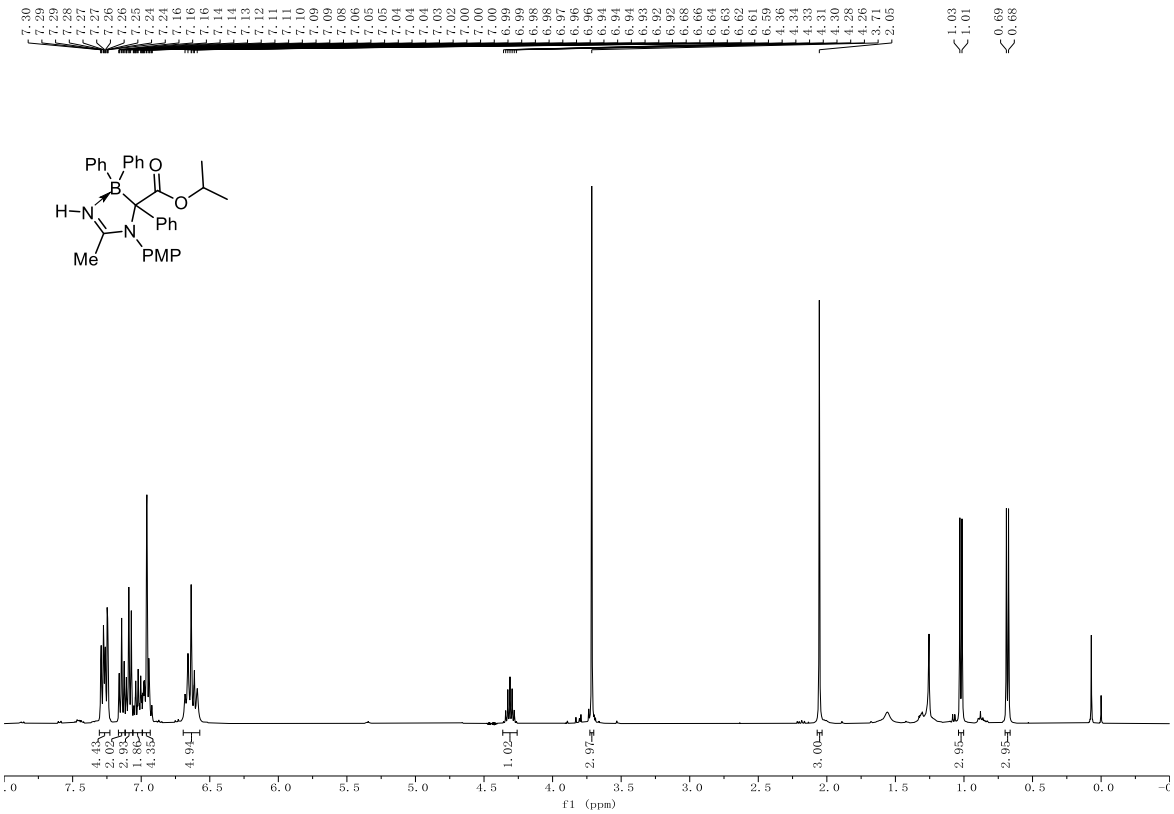


^{11}B NMR (128 MHz, Chloroform-*d*) for compound **4am**

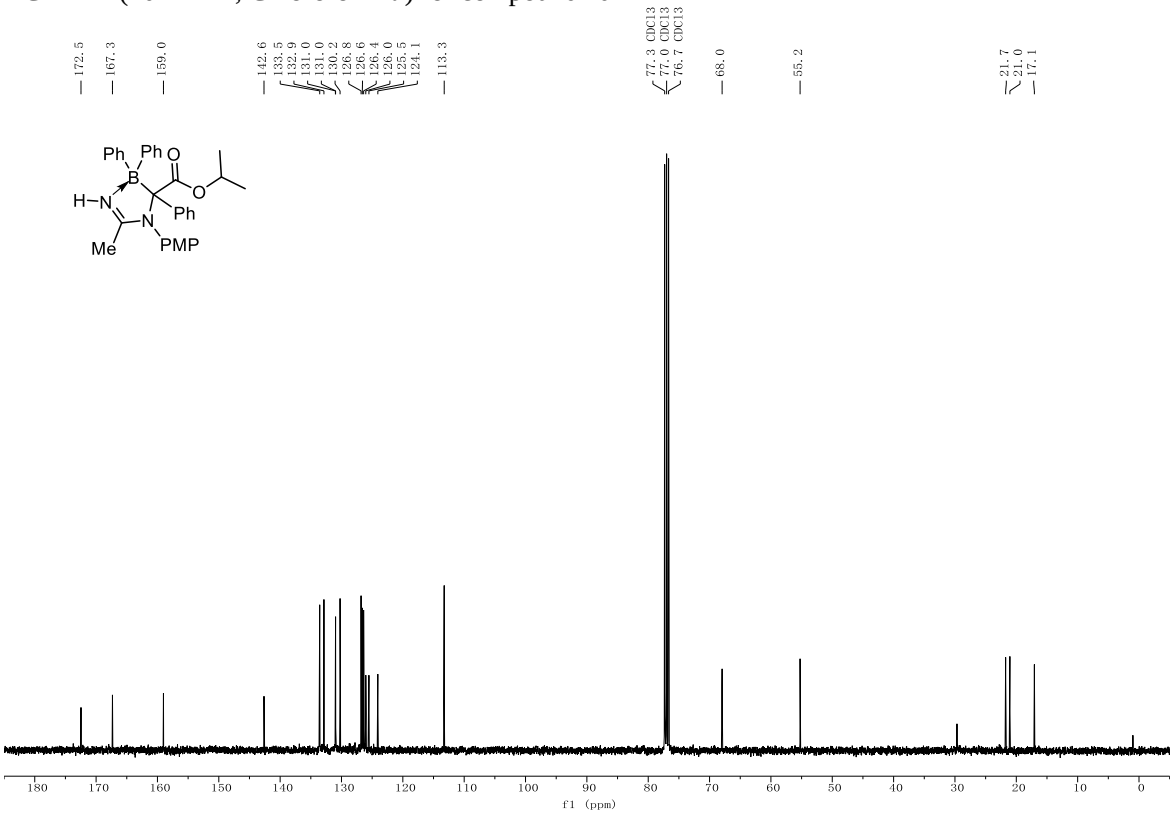


isopropyl 4-(4-methoxyphenyl)-5-methyl-2,2,3-triphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4an)

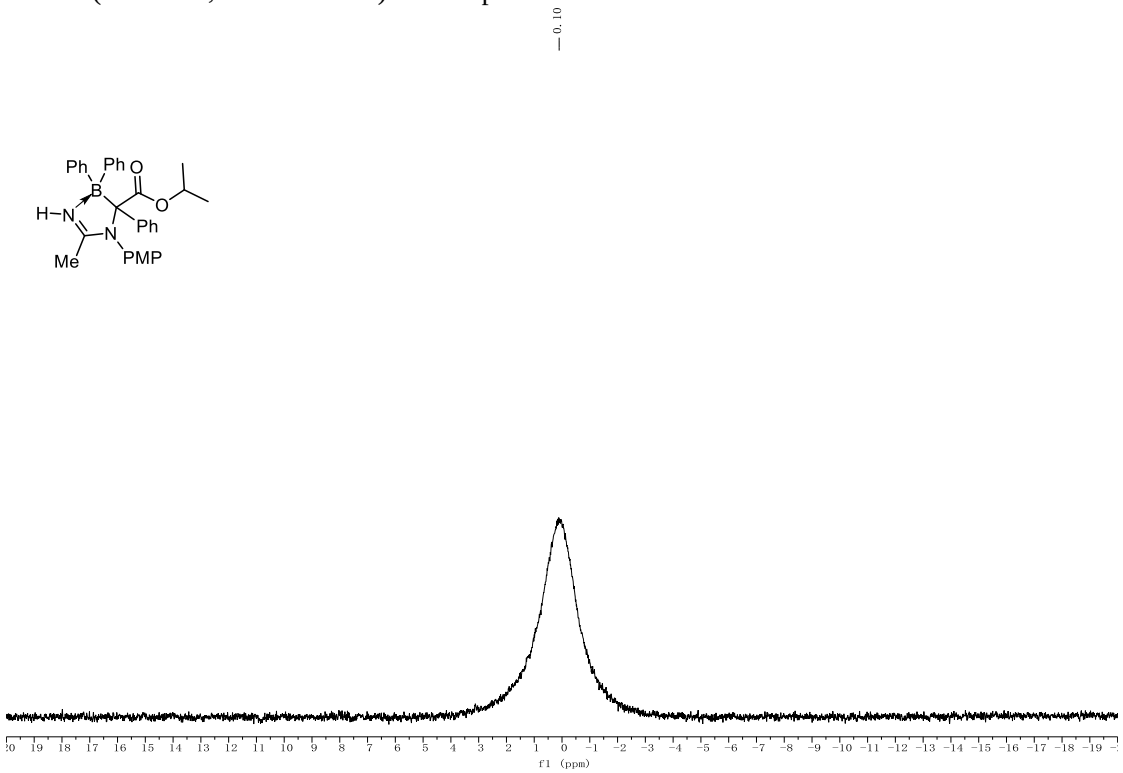
^{1}H NMR (400 MHz, Chloroform-*d*) for compound **4an**



^{13}C NMR (101 MHz, Chloroform-*d*) for compound **4an**

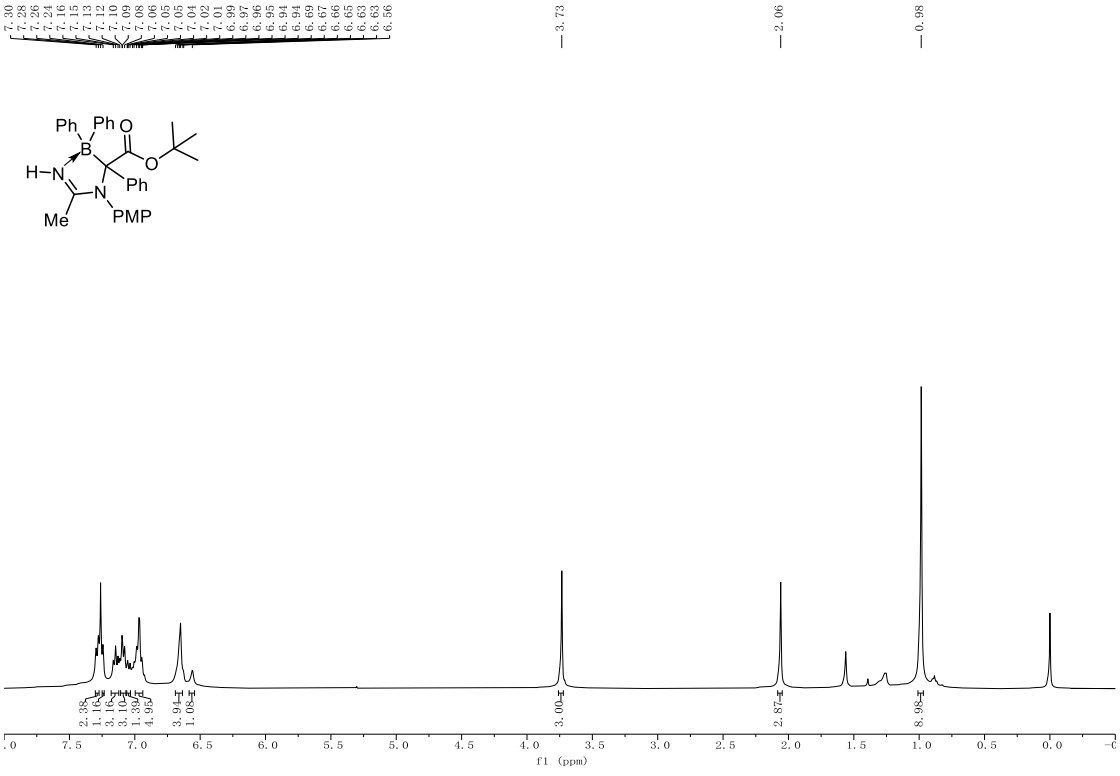


^{11}B NMR (128 MHz, Chloroform-*d*) for compound **4an**

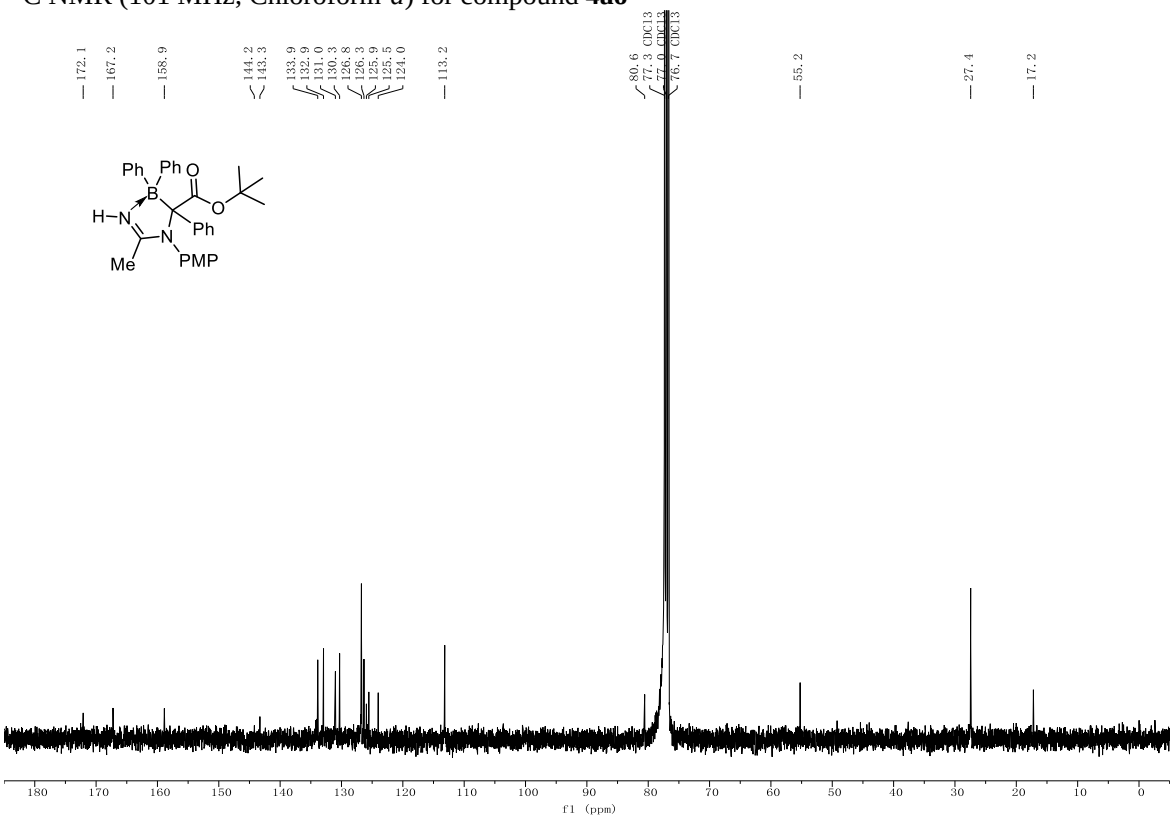


tert-butyl 4-(4-methoxyphenyl)-5-methyl-2,2,3-triphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4ao)

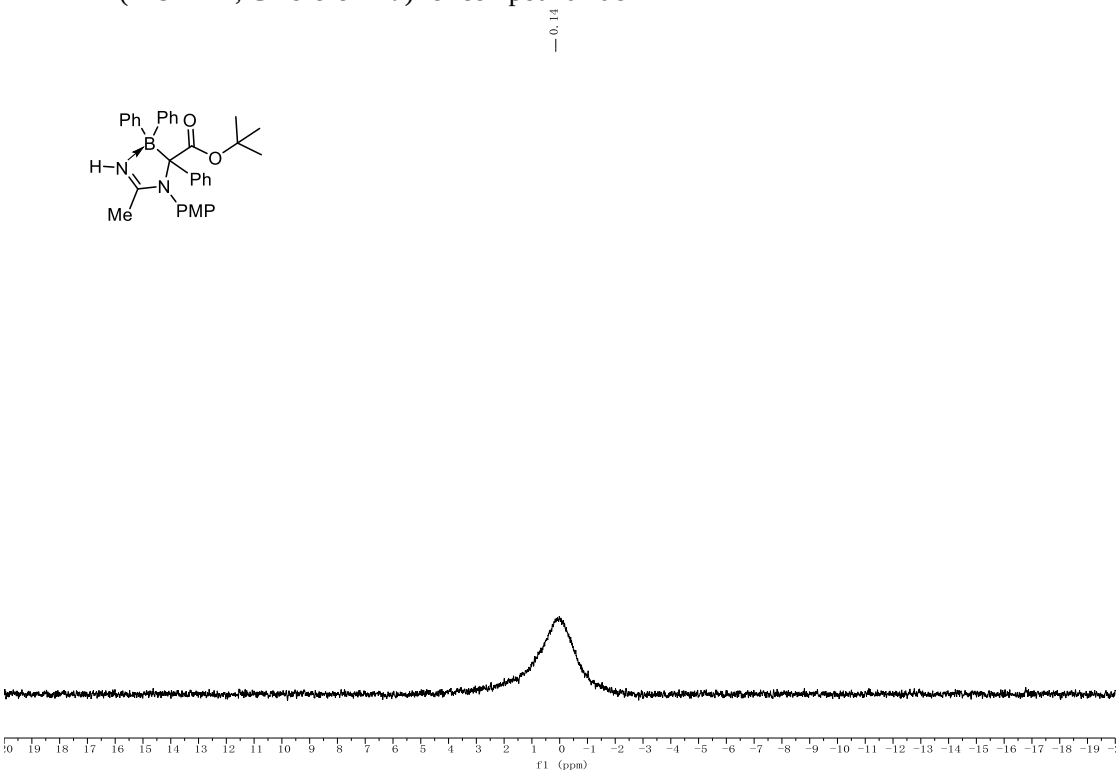
^{1}H NMR (400 MHz, Chloroform-*d*) for compound **4ao**



^{13}C NMR (101 MHz, Chloroform-*d*) for compound **4ao**

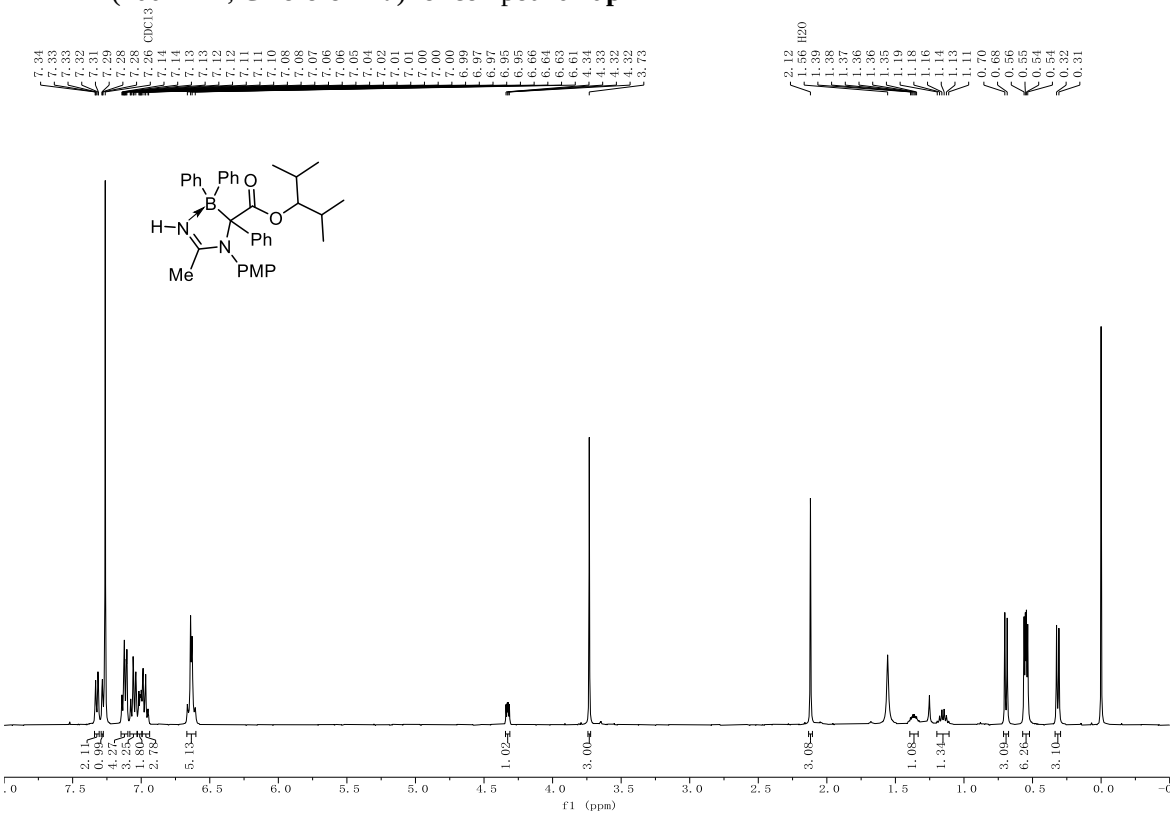


^{11}B NMR (128 MHz, Chloroform-*d*) for compound **4ao**

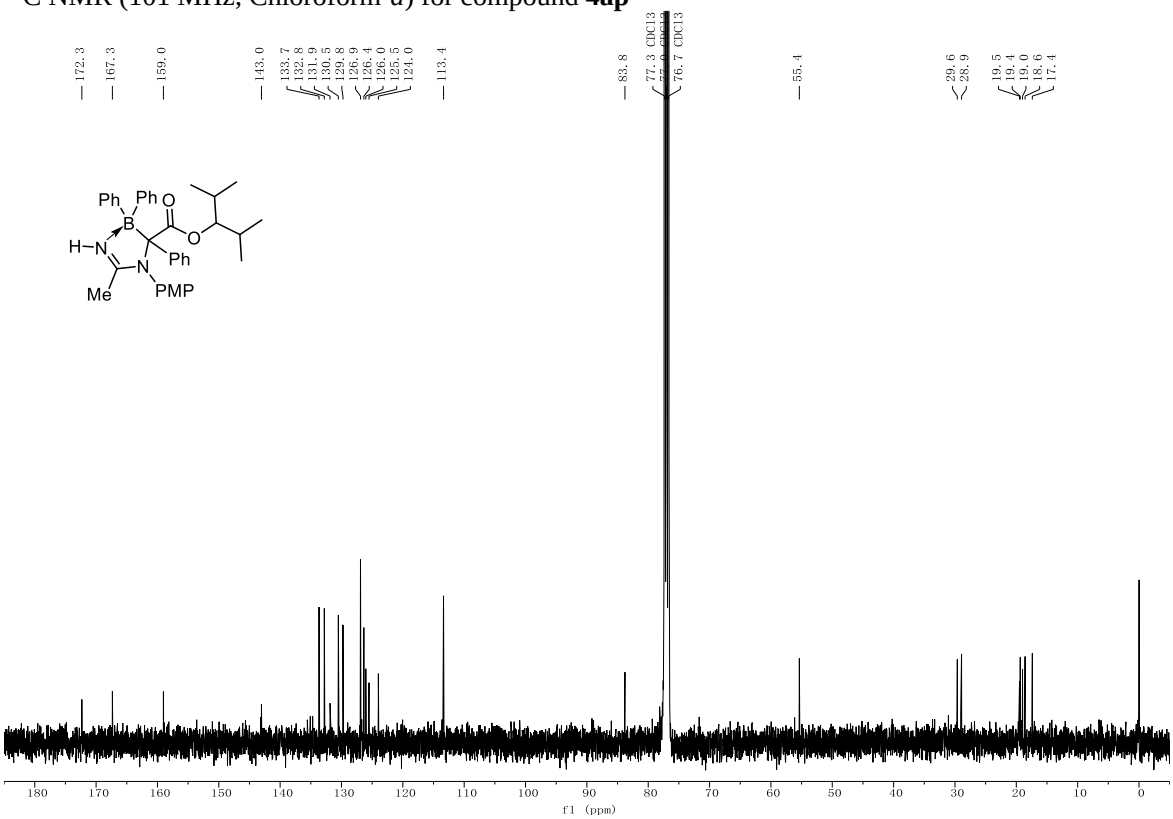


2,4-dimethylpentan-3-yl 4-(4-methoxyphenyl)-5-methyl-2,2,3-triphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4ap)

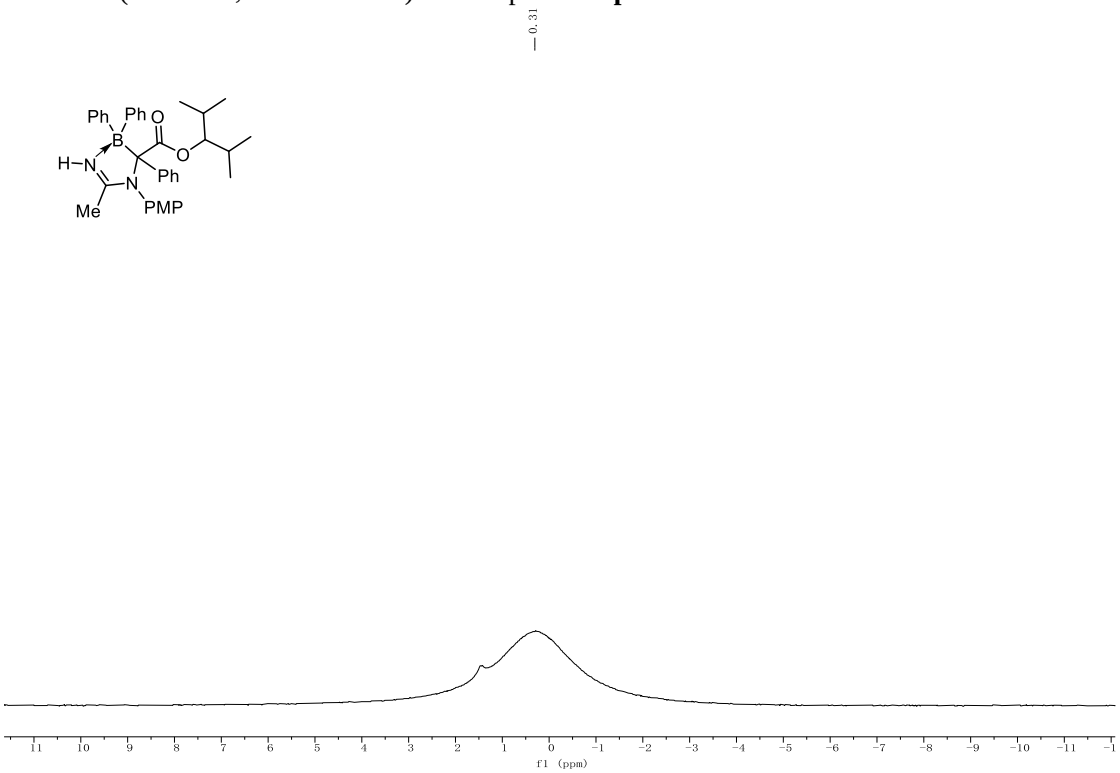
^{1}H NMR (400 MHz, Chloroform-*d*) for compound **4ap**



^{13}C NMR (101 MHz, Chloroform-*d*) for compound **4ap**

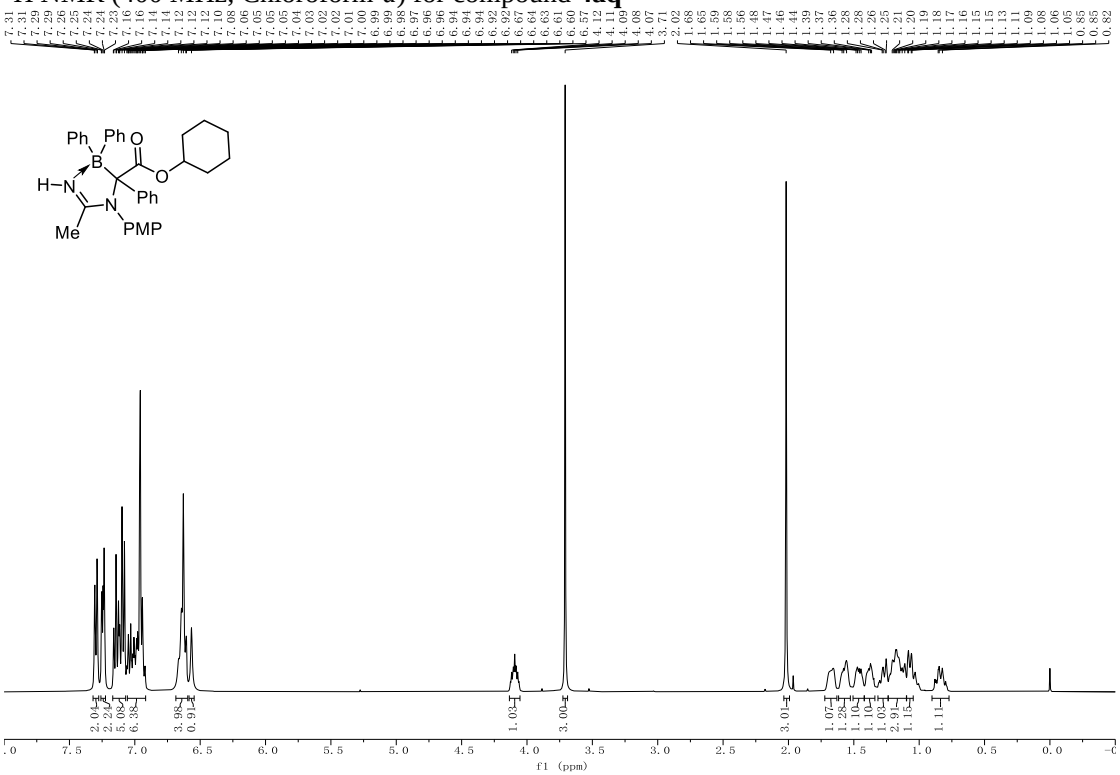


^{11}B NMR (128 MHz, Chloroform-*d*) for compound **4ap**

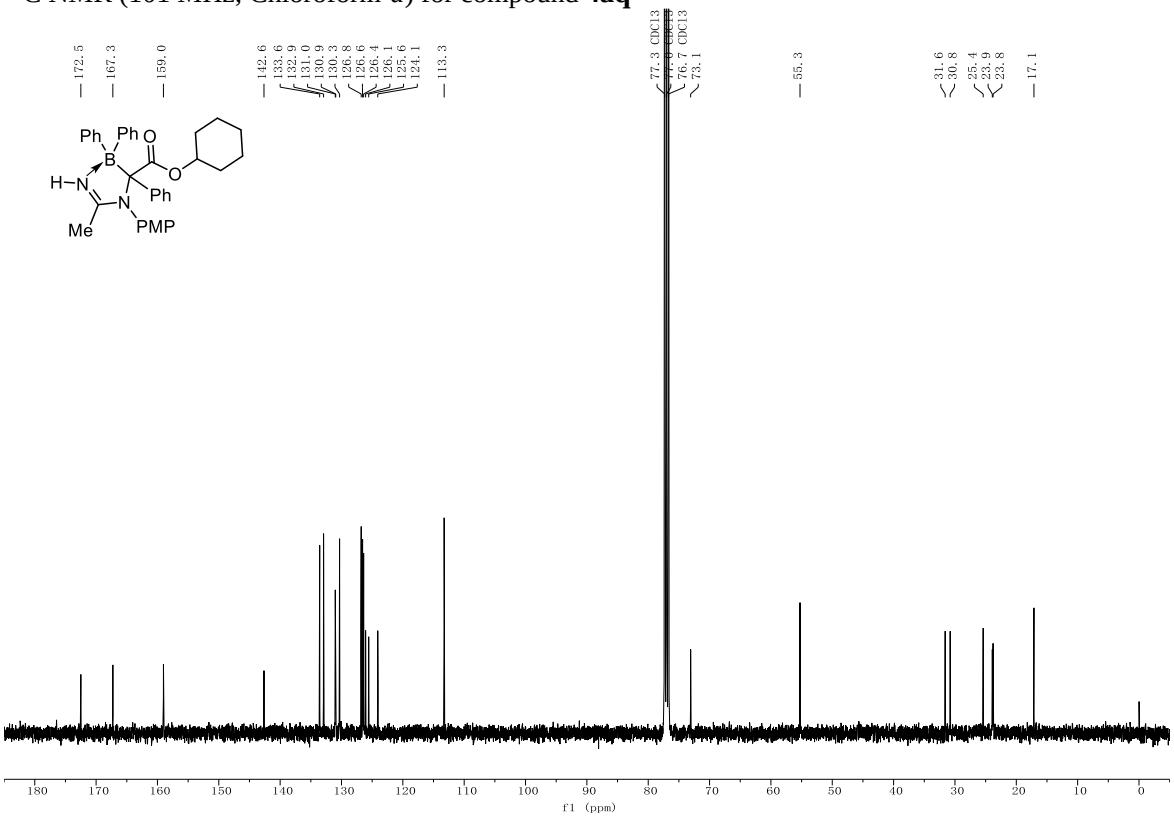


cyclohexyl 4-(4-methoxyphenyl)-5-methyl-2,2,3-triphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4aq)

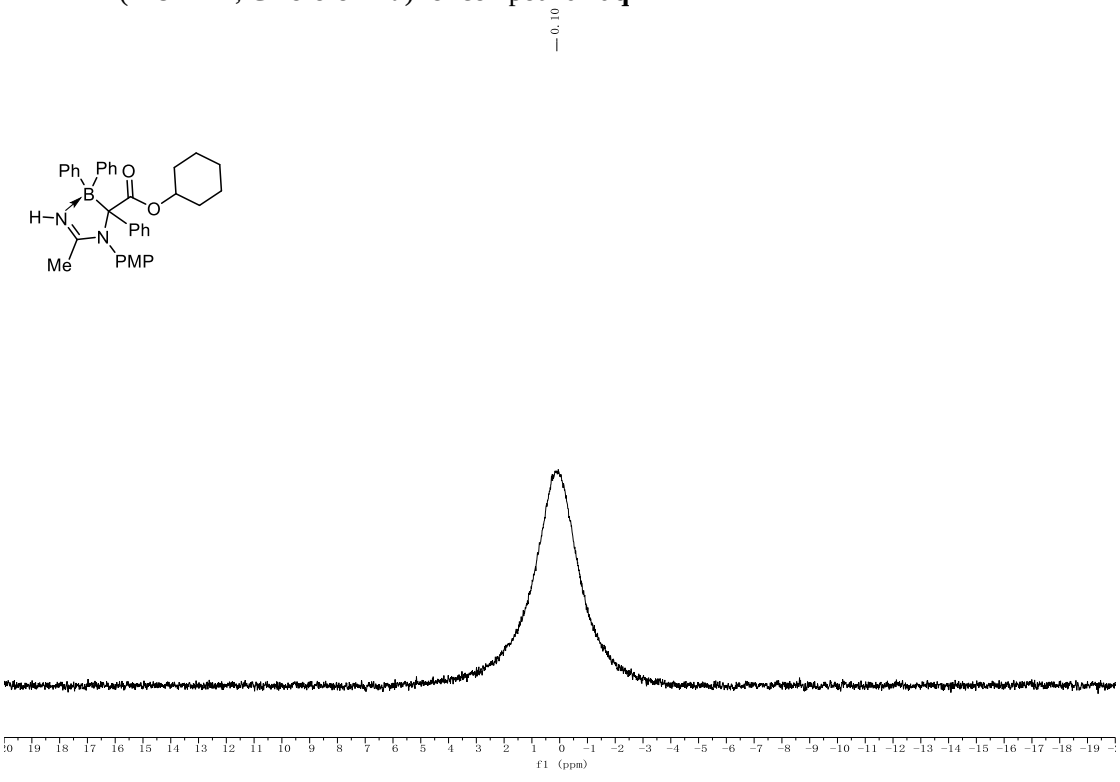
^{1}H NMR (400 MHz, Chloroform-*d*) for compound **4aq**



^{13}C NMR (101 MHz, Chloroform-*d*) for compound **4aq**

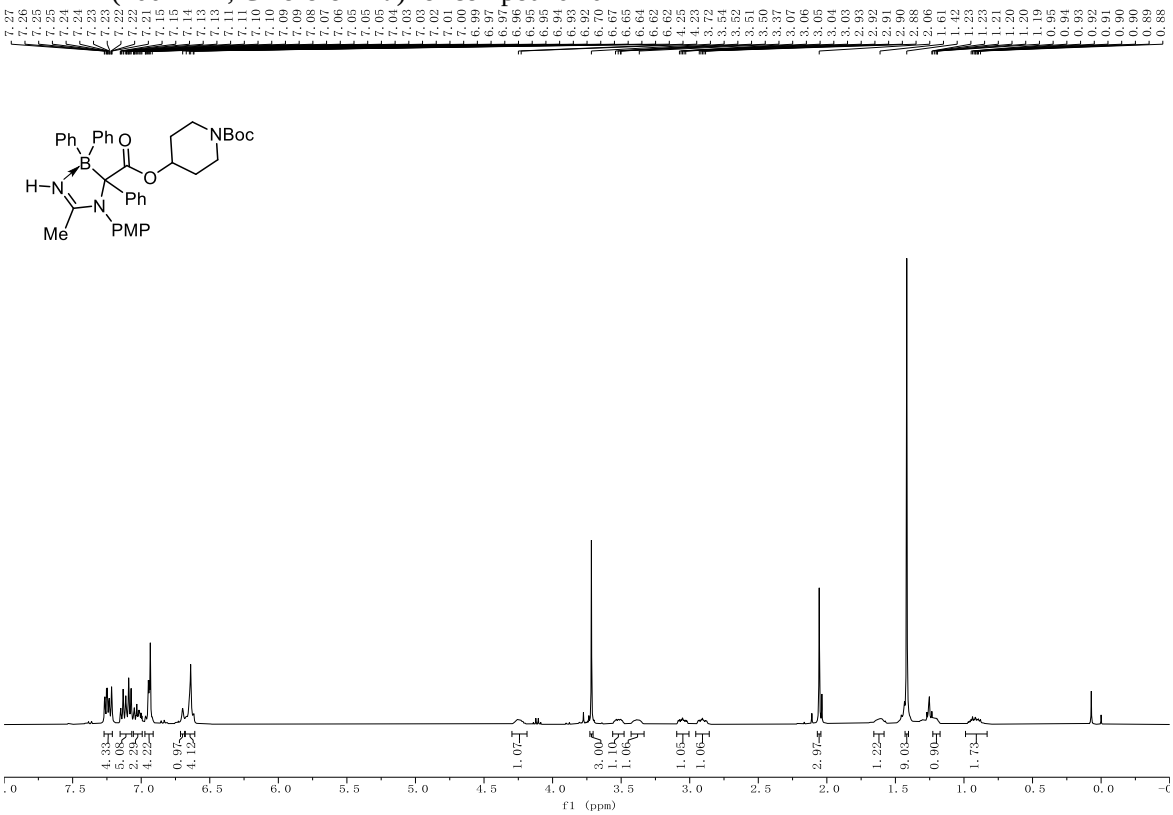


^{11}B NMR (128 MHz, Chloroform-*d*) for compound **4aq**

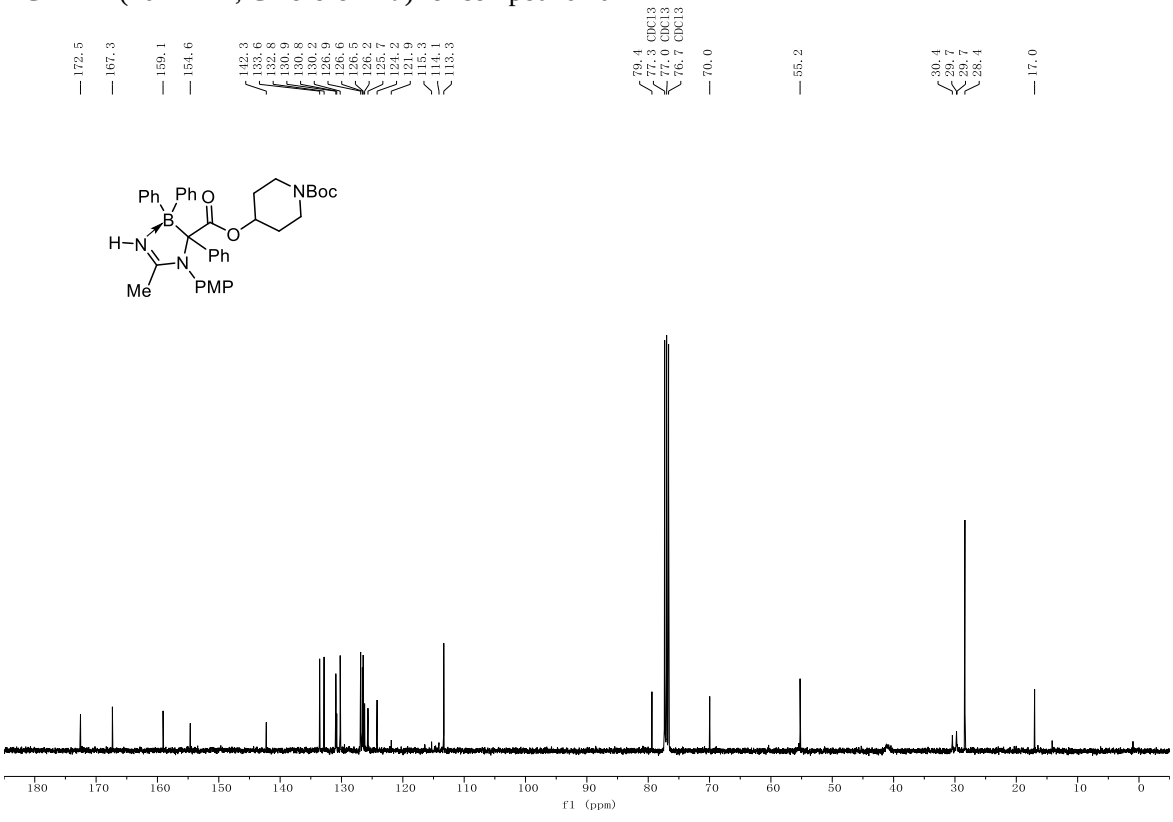


tert-butyl 4-((4-(4-methoxyphenyl)-5-methyl-2,2,3-triphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carbonyl)oxy)piperidine-1-carboxylate (4ar)

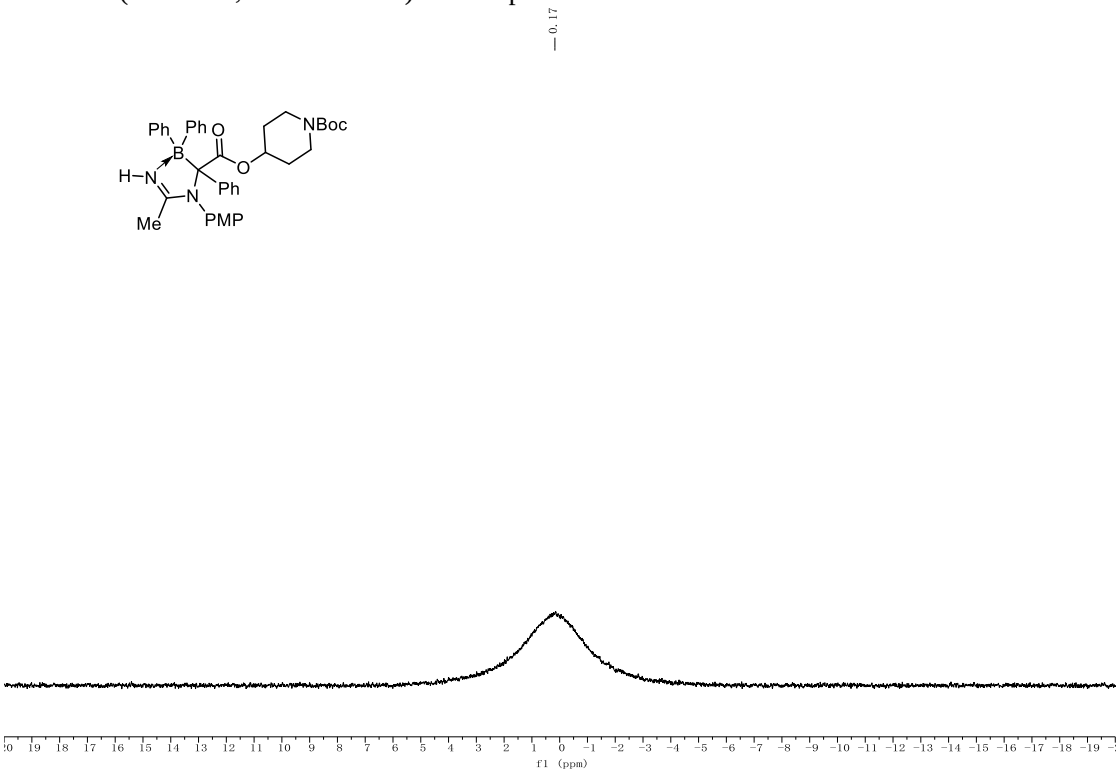
^{1}H NMR (400 MHz, Chloroform-*d*) for compound **4ar**



^{13}C NMR (101 MHz, Chloroform-*d*) for compound **4ar**

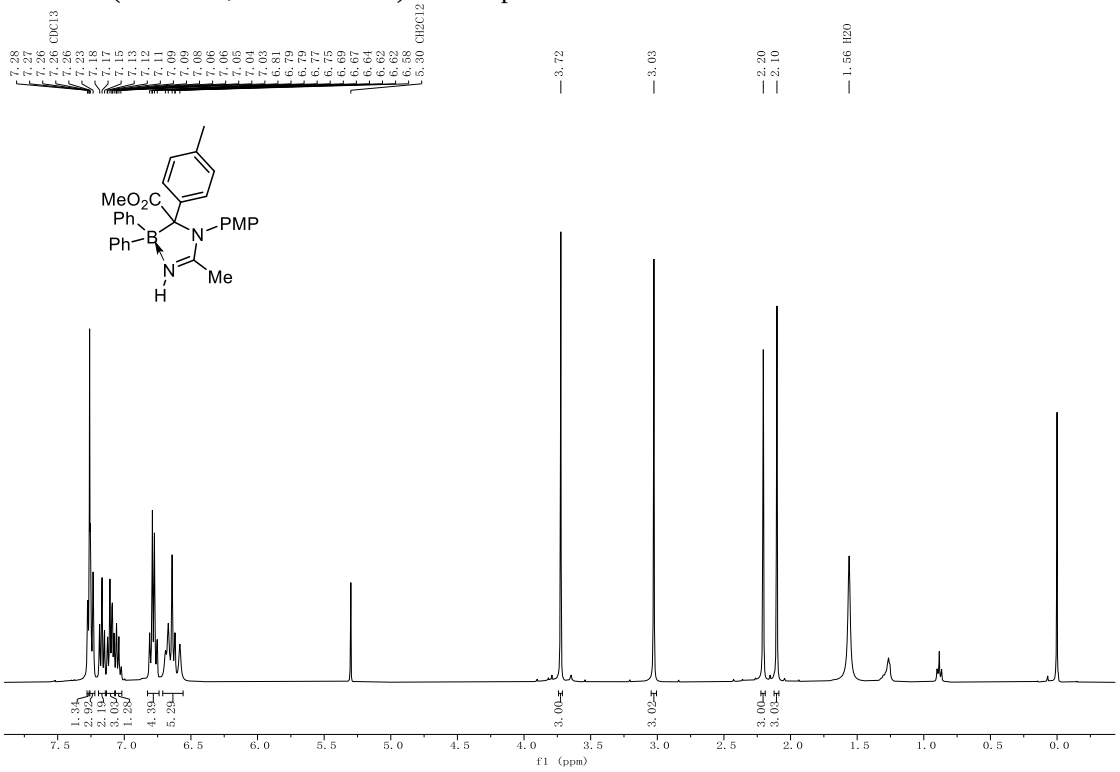


^{11}B NMR (128 MHz, Chloroform-*d*) for compound **4ar**

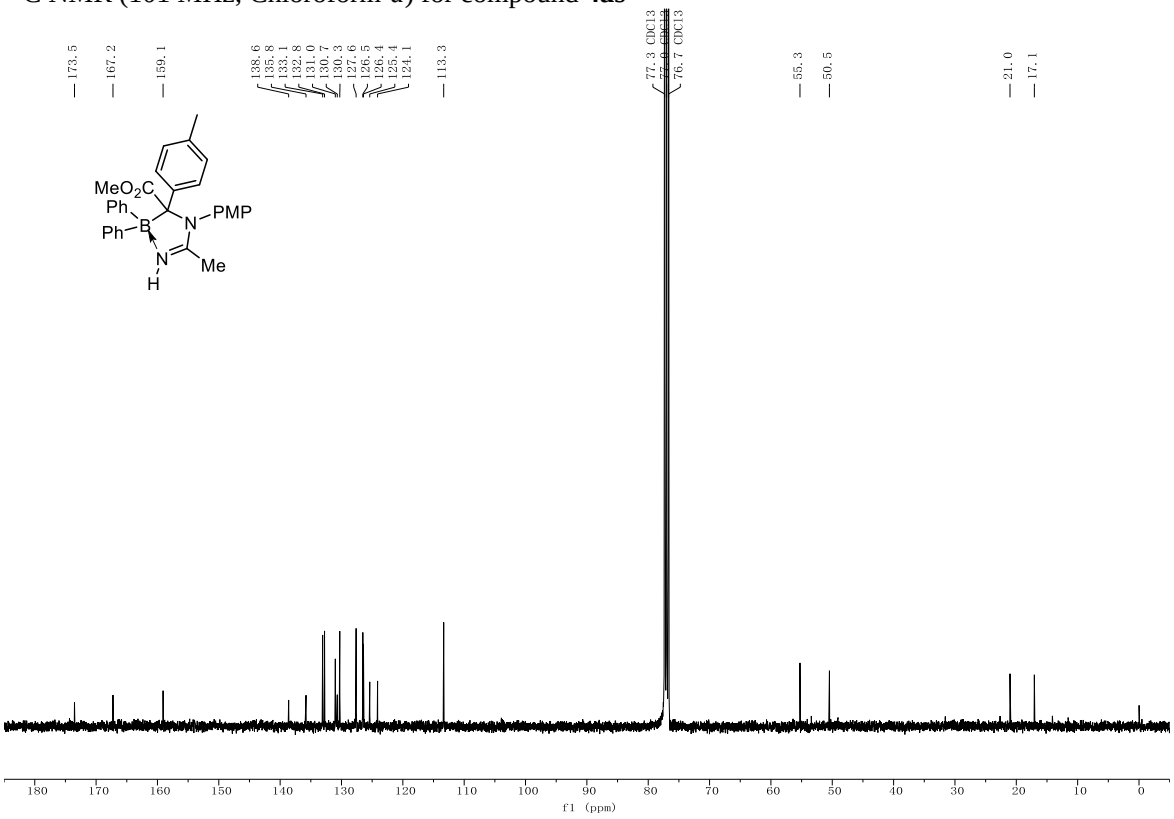


methyl 4-(4-methoxyphenyl)-5-methyl-2,2-diphenyl-3-(p-tolyl)-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4as)

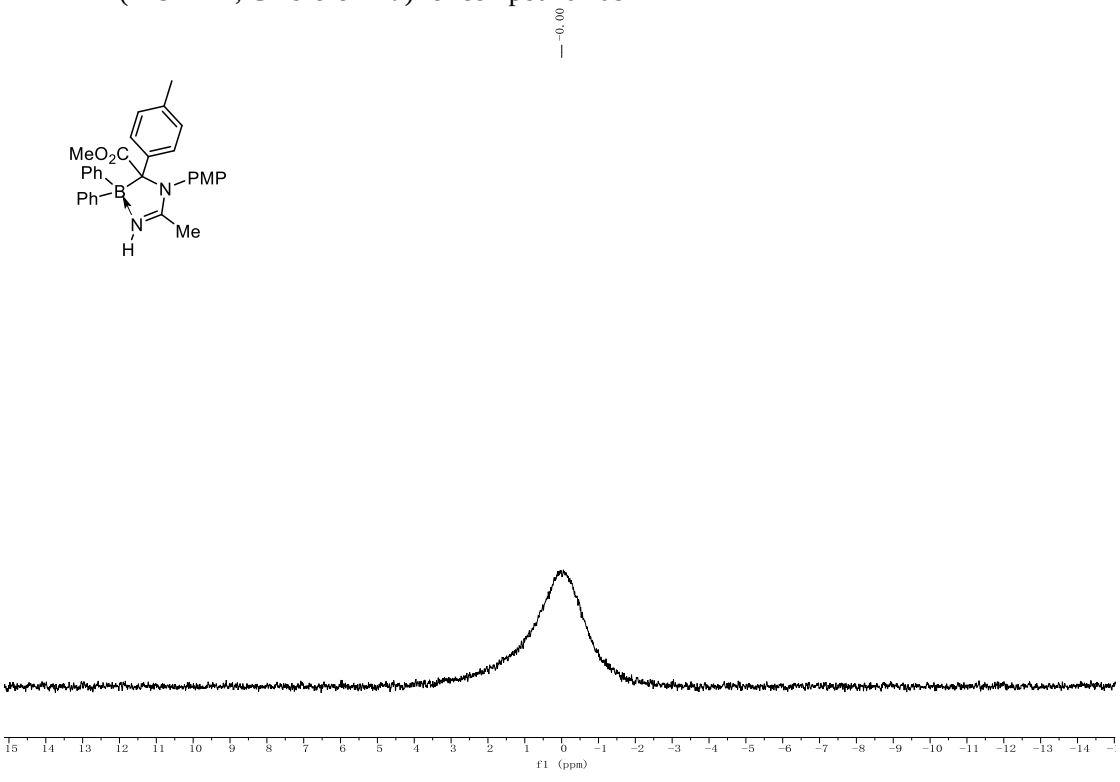
^{1}H NMR (400 MHz, Chloroform-*d*) for compound **4as**



^{13}C NMR (101 MHz, Chloroform-*d*) for compound **4as**

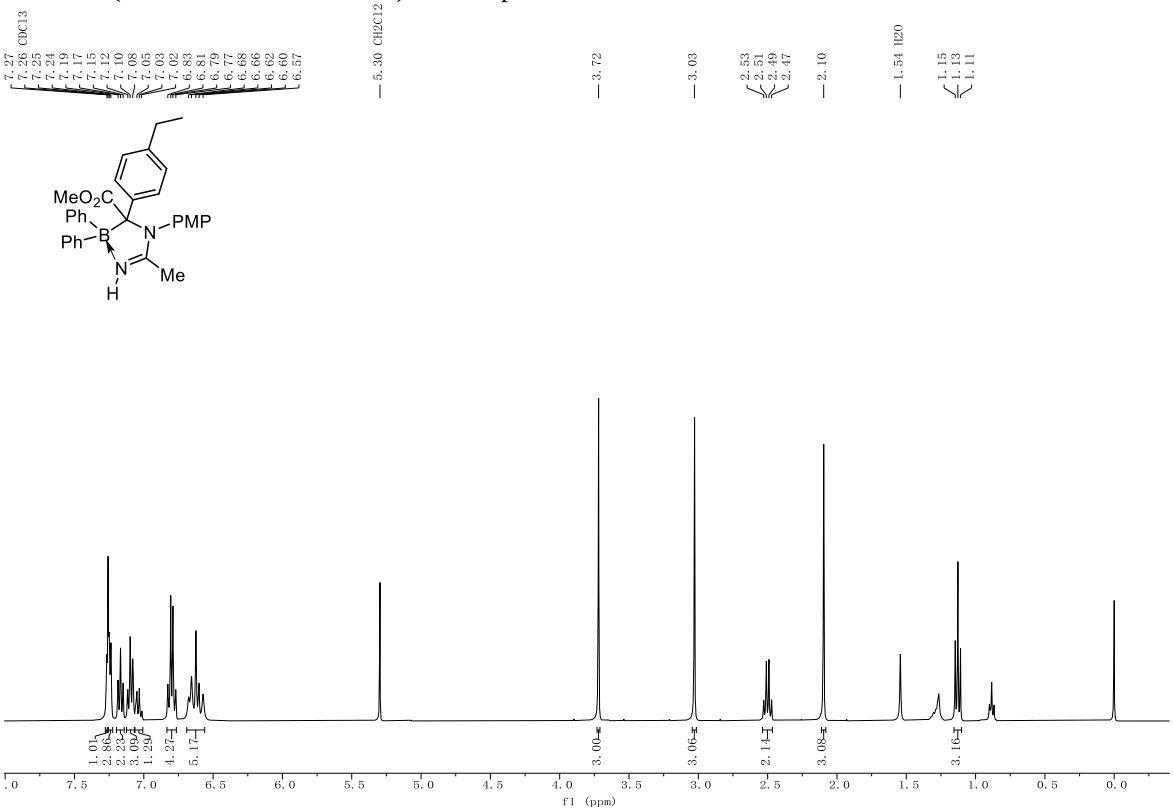


^{11}B NMR (128 MHz, Chloroform-*d*) for compound **4as**

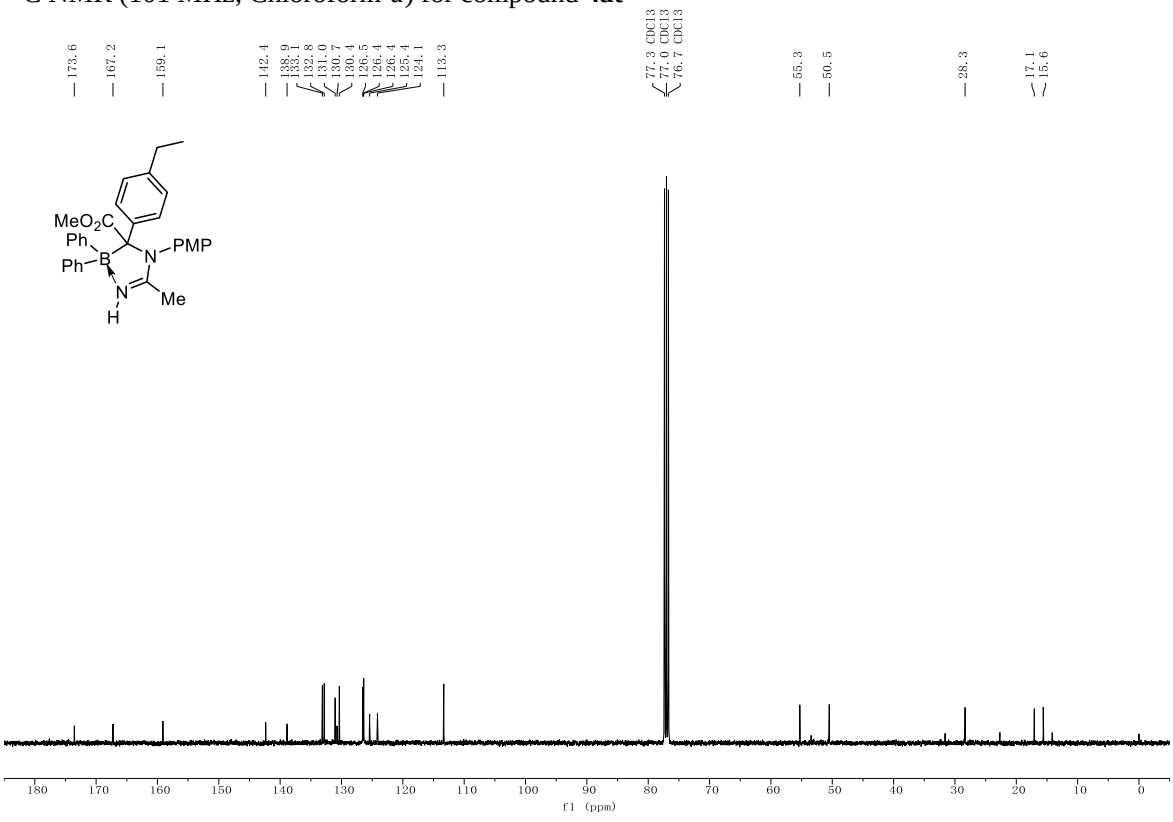


methyl 3-(4-ethylphenyl)-4-(4-methoxyphenyl)-5-methyl-2,2-diphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4at)

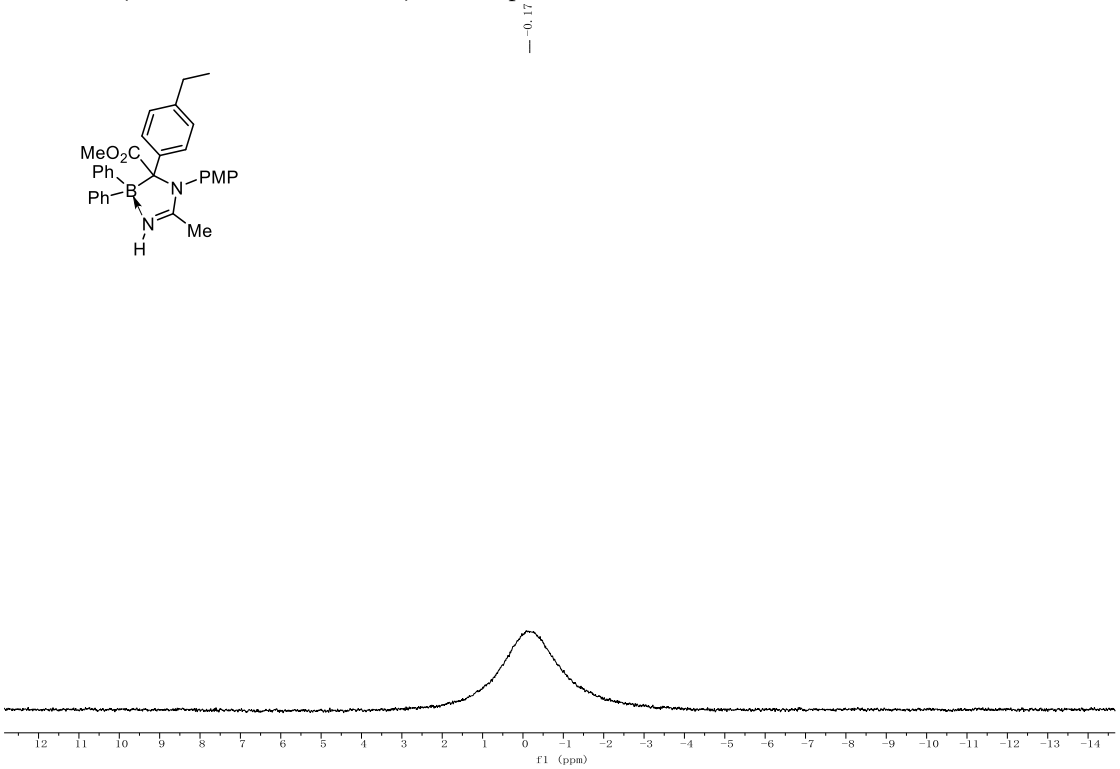
^{1}H NMR (400 MHz, Chloroform-*d*) for compound **4at**



^{13}C NMR (101 MHz, Chloroform-*d*) for compound **4at**

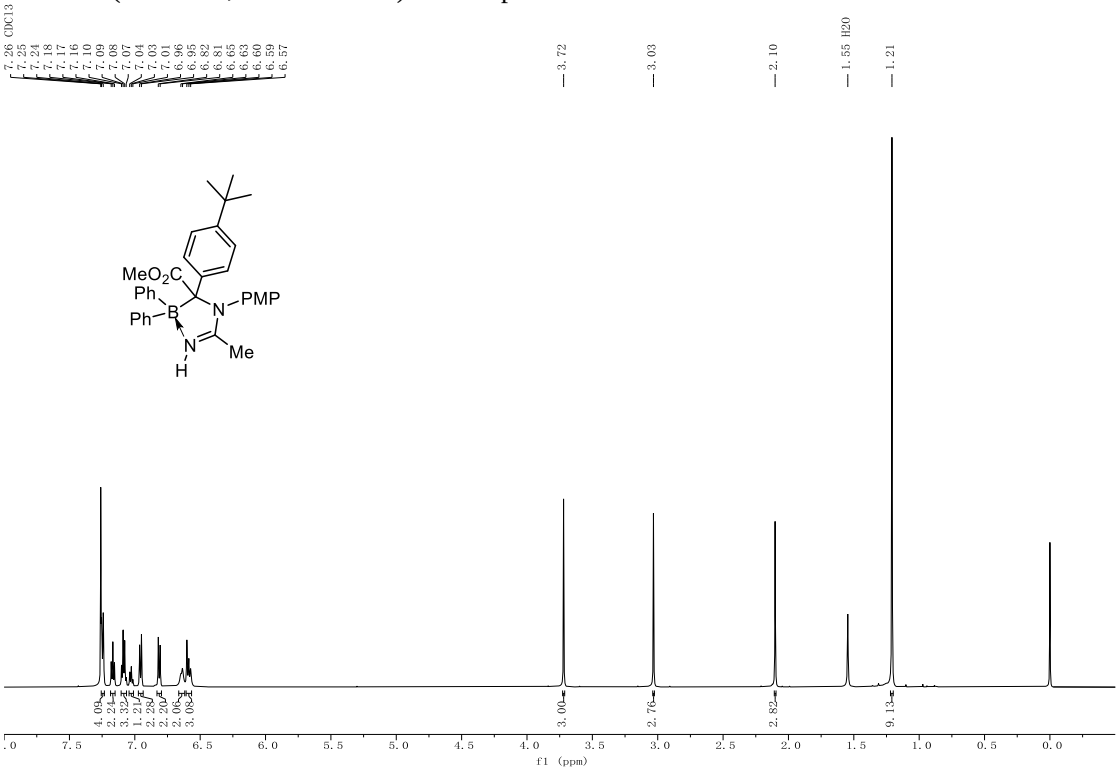


^{11}B NMR (128 MHz, Chloroform-*d*) for compound **4at**

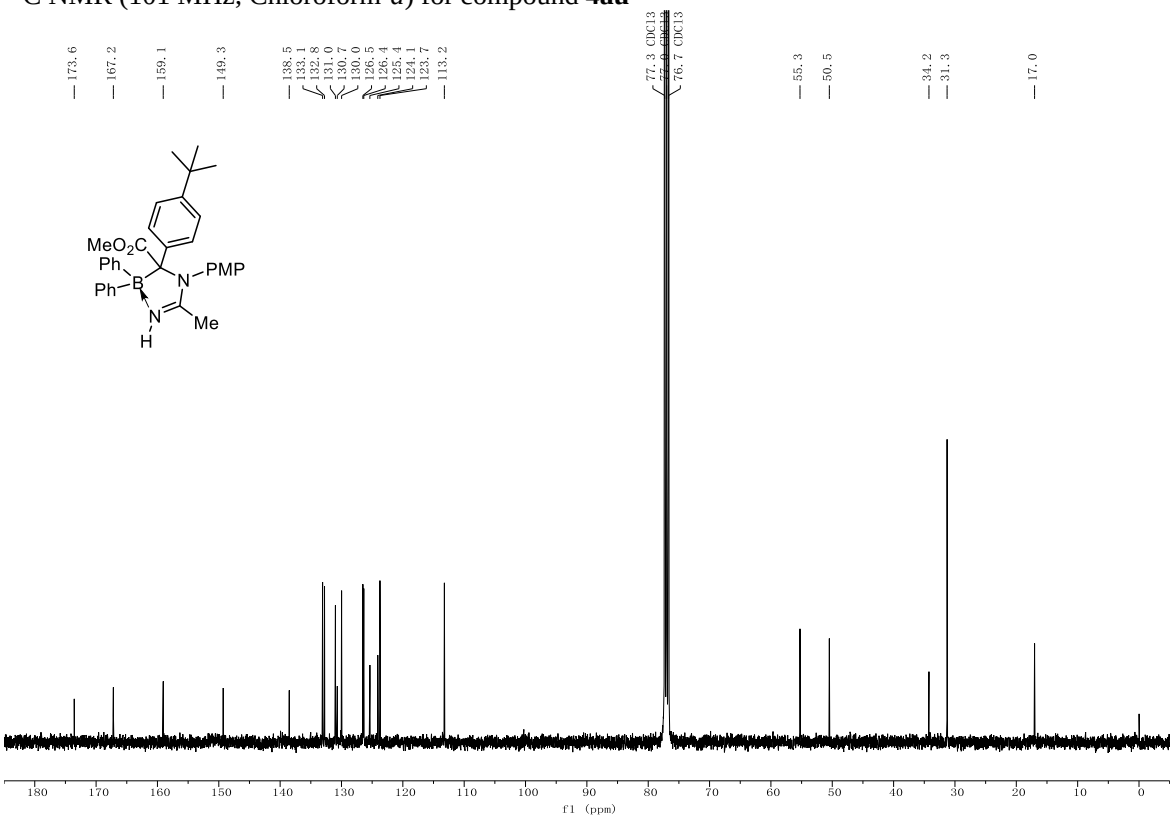


methyl 3-(4-(tert-butyl)phenyl)-4-(4-methoxyphenyl)-5-methyl-2,2-diphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4au)

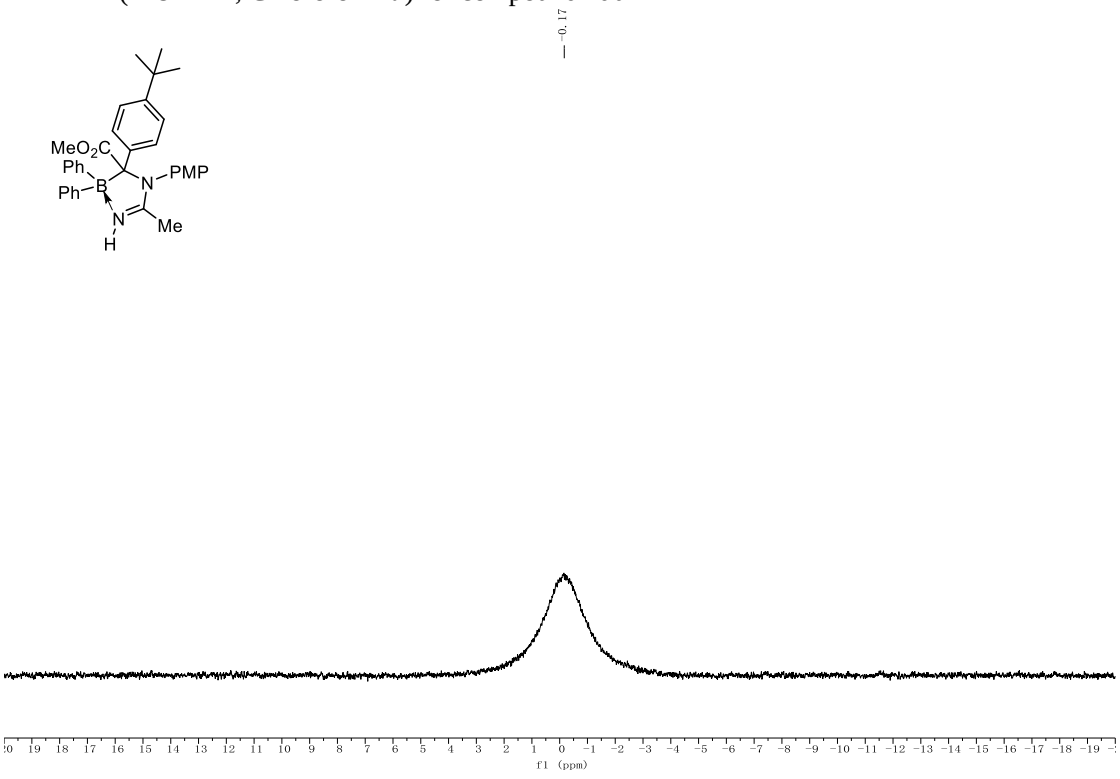
^{1}H NMR (400 MHz, Chloroform-*d*) for compound **4au**



^{13}C NMR (101 MHz, Chloroform-*d*) for compound **4au**

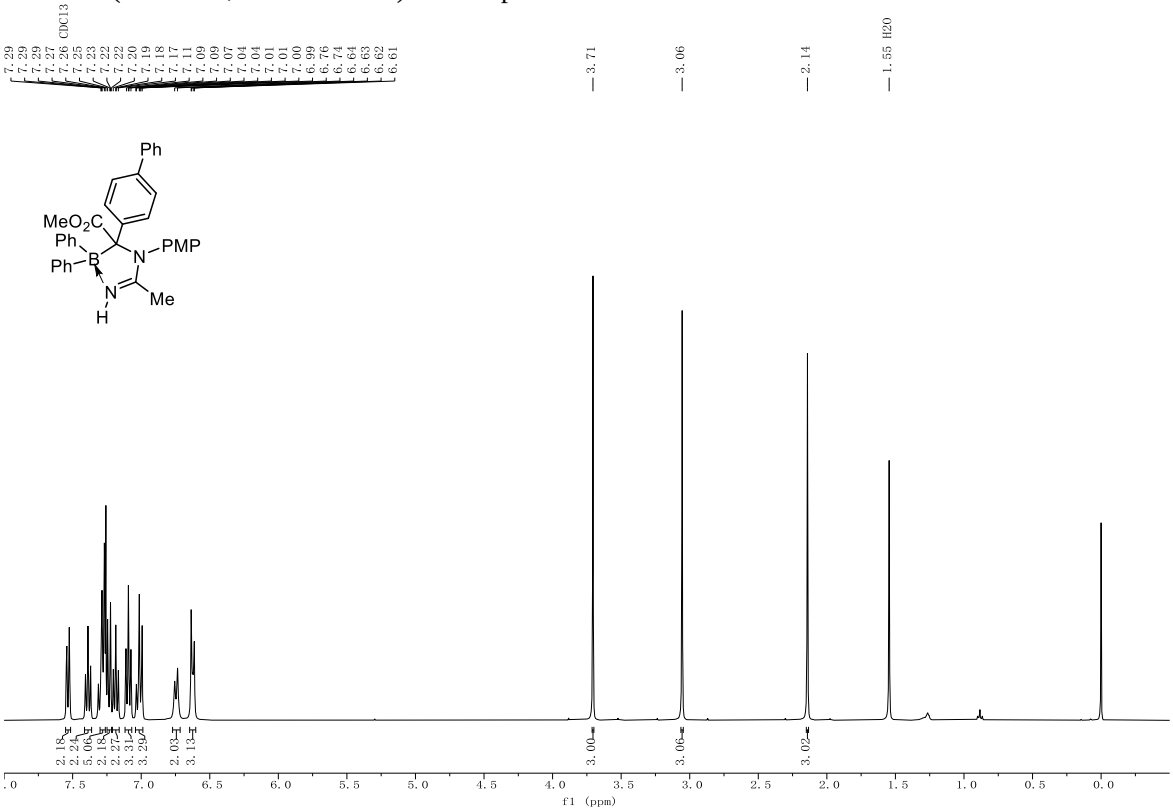


^{11}B NMR (128 MHz, Chloroform-*d*) for compound **4au**

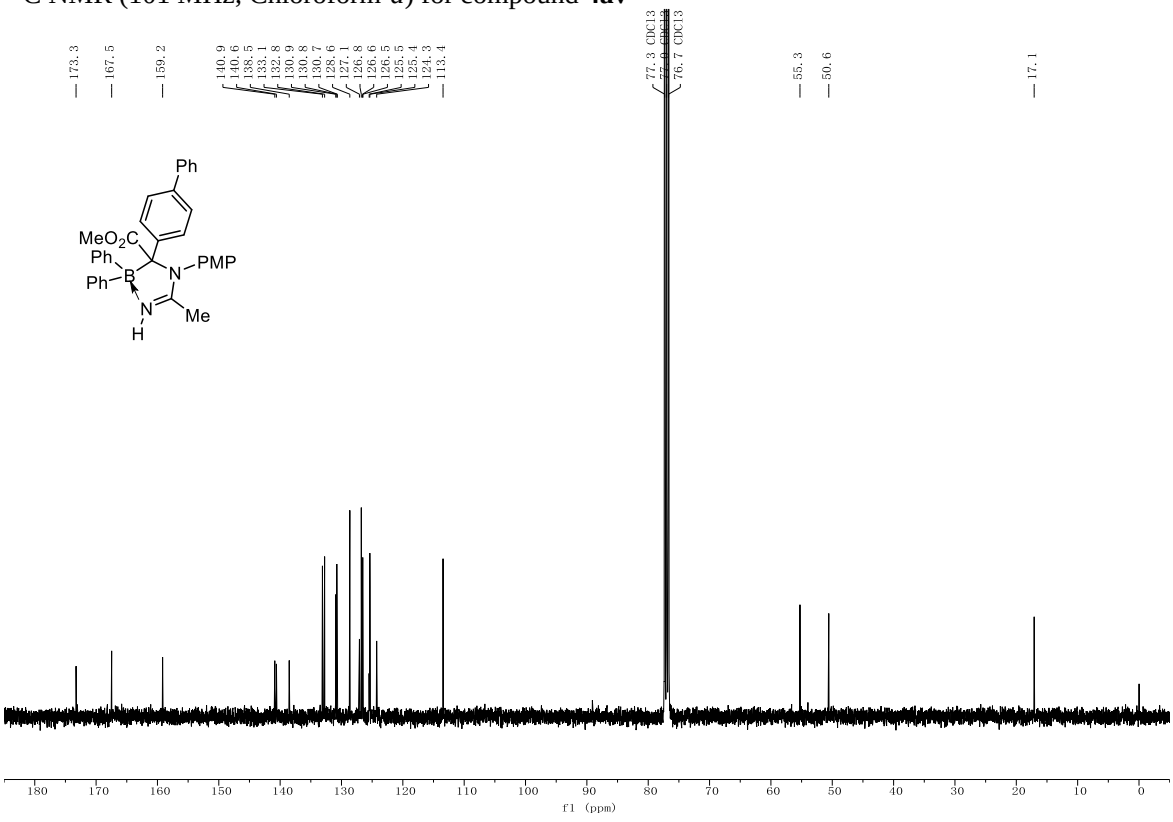


methyl 3-([1,1'-biphenyl]-4-yl)-4-(4-methoxyphenyl)-5-methyl-2,2-diphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4av)

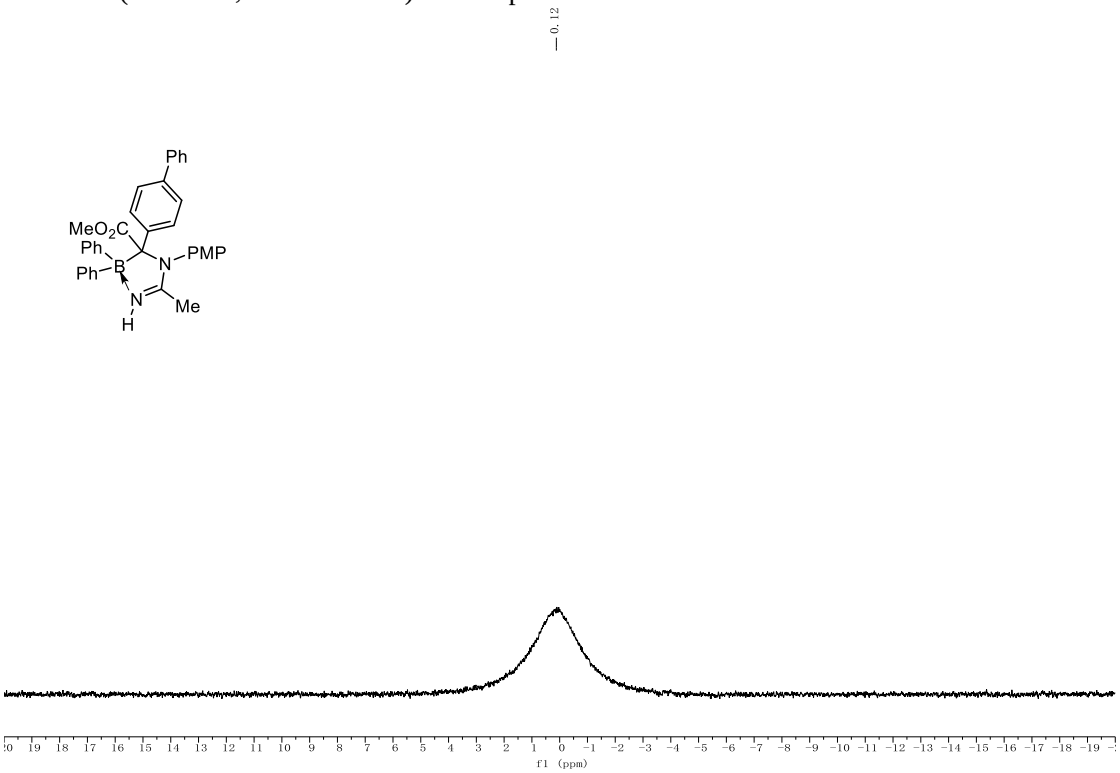
^{1}H NMR (400 MHz, Chloroform-*d*) for compound **4av**



^{13}C NMR (101 MHz, Chloroform-*d*) for compound **4av**

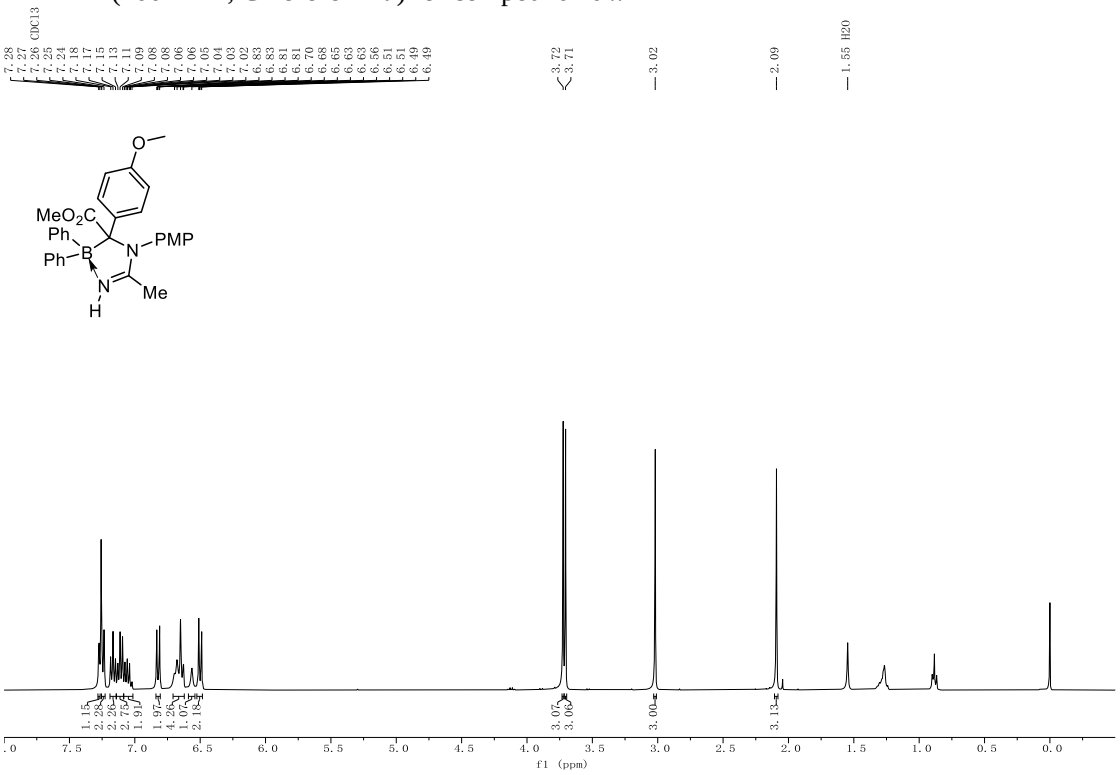


^{11}B NMR (128 MHz, Chloroform-*d*) for compound **4av**

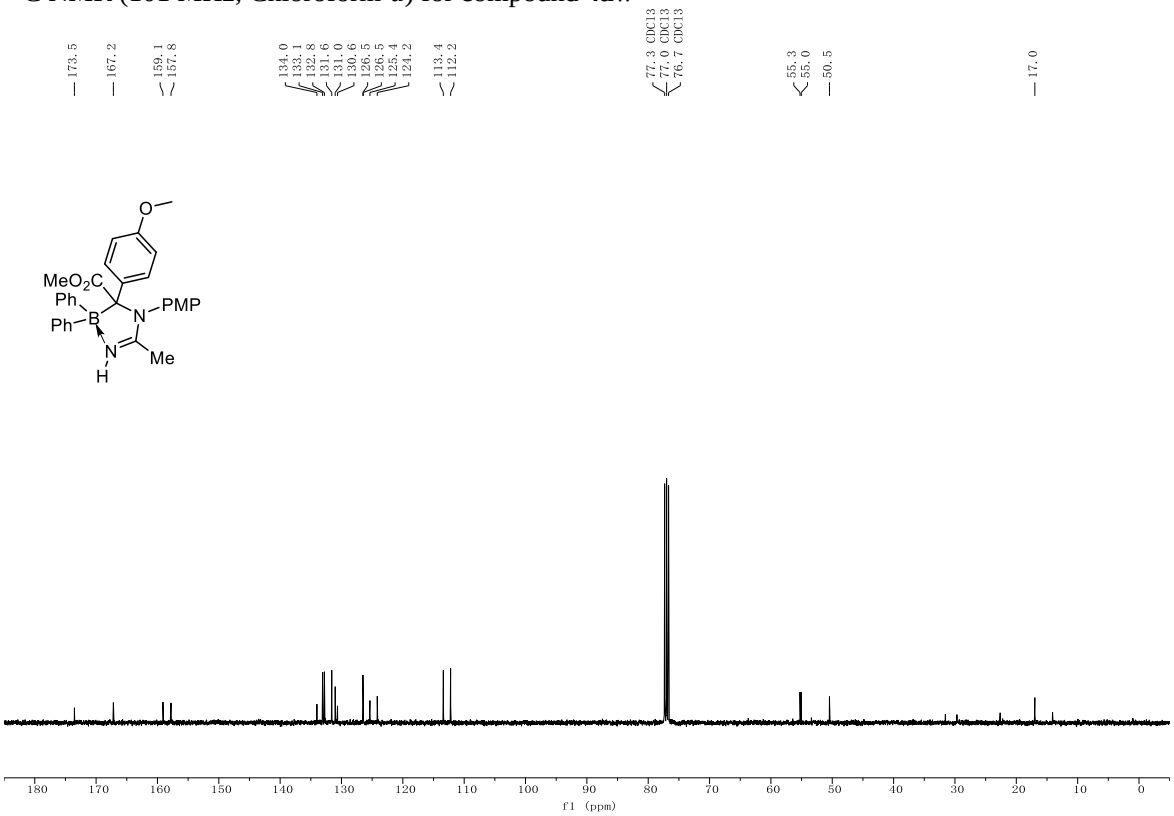


methyl 3,4-bis(4-methoxyphenyl)-5-methyl-2,2-diphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4aw)

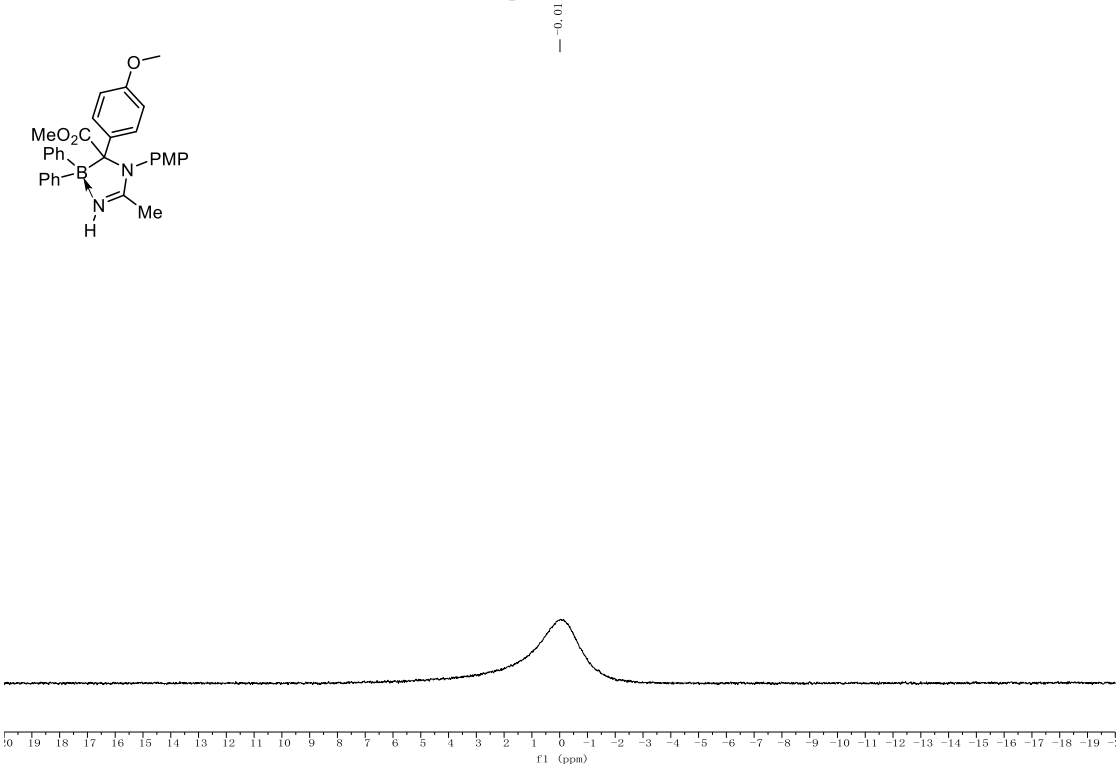
^{1}H NMR (400 MHz, Chloroform-*d*) for compound **4aw**



^{13}C NMR (101 MHz, Chloroform-*d*) for compound **4aw**

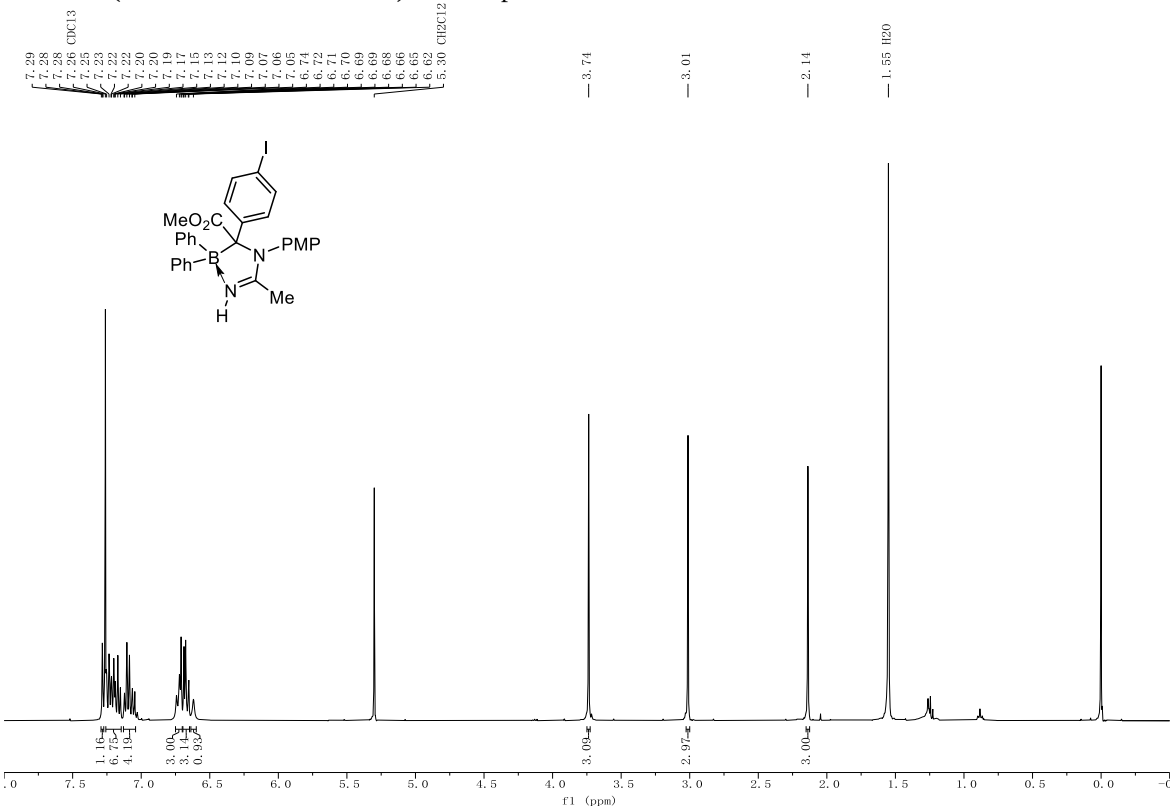


^{11}B NMR (128 MHz, Chloroform-*d*) for compound **4aw**

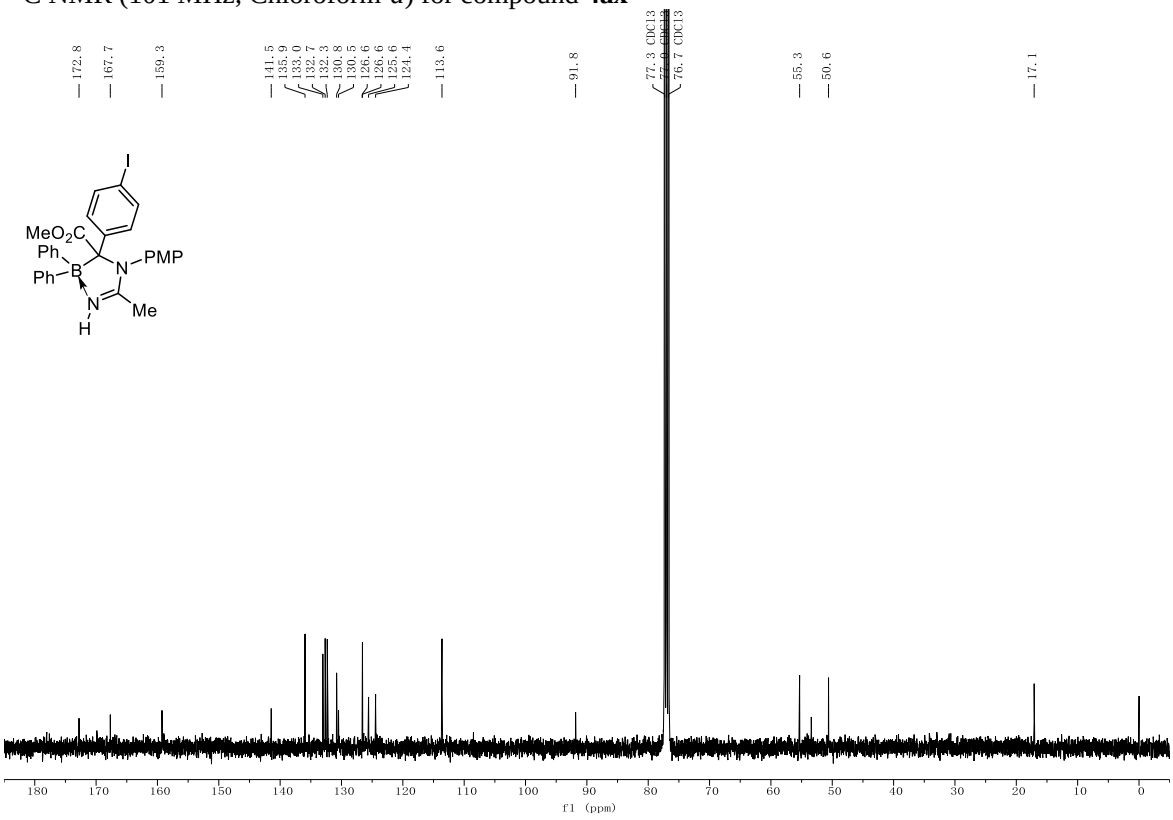


methyl 3-(4-iodophenyl)-4-(4-methoxyphenyl)-5-methyl-2,2-diphenyl-3,4-dihydro-2H-1l4,4,2l4-diazaborole-3-carboxylate (4ax)

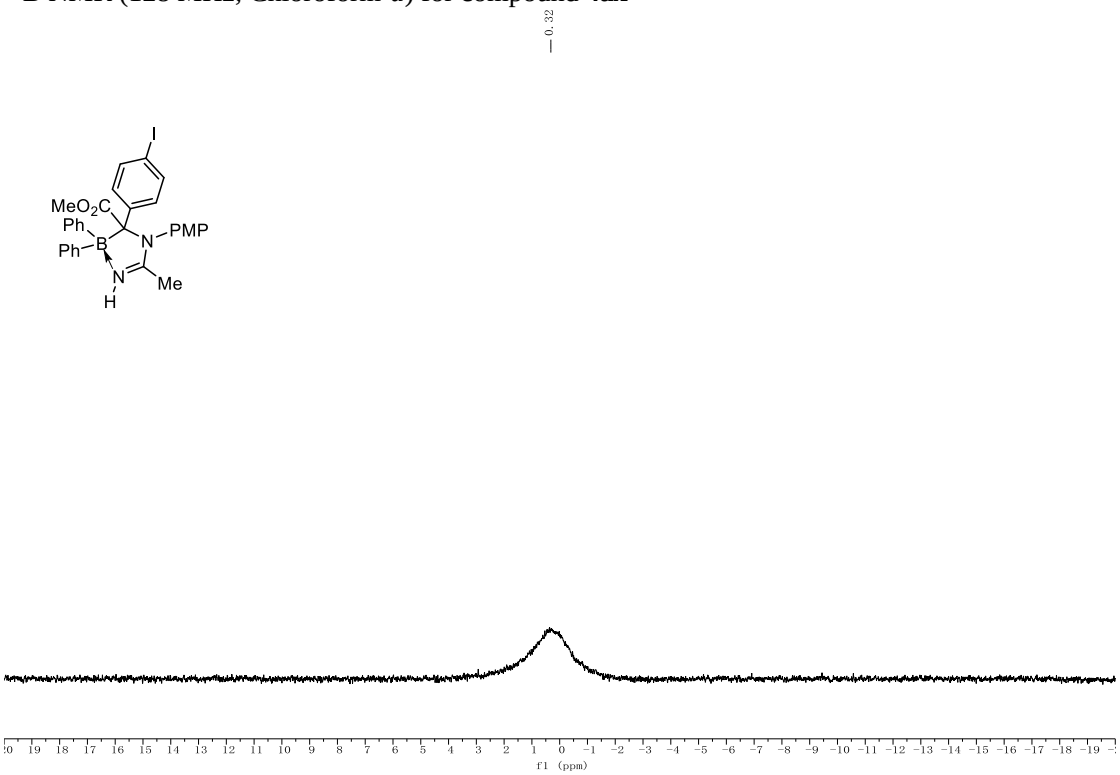
^{1}H NMR (400 MHz, Chloroform-*d*) for compound **4ax**



^{13}C NMR (101 MHz, Chloroform-*d*) for compound **4ax**

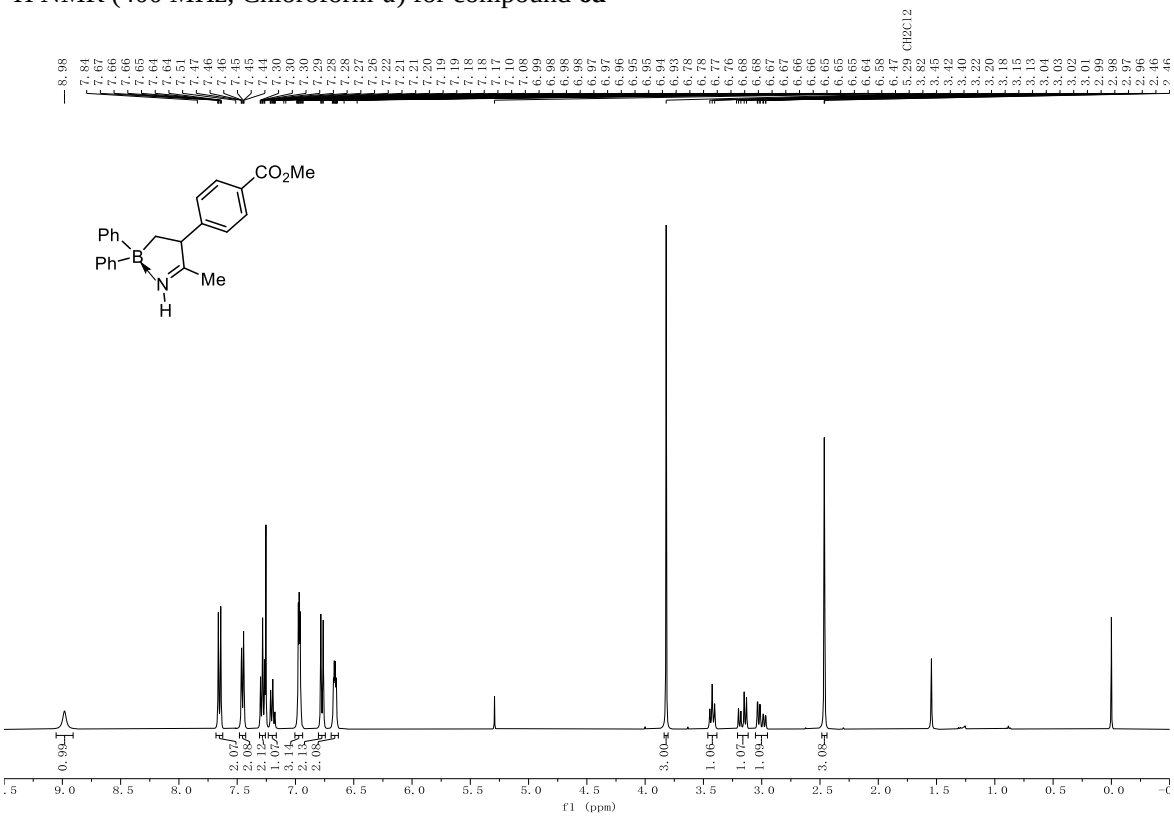


^{11}B NMR (128 MHz, Chloroform-*d*) for compound **4ax**

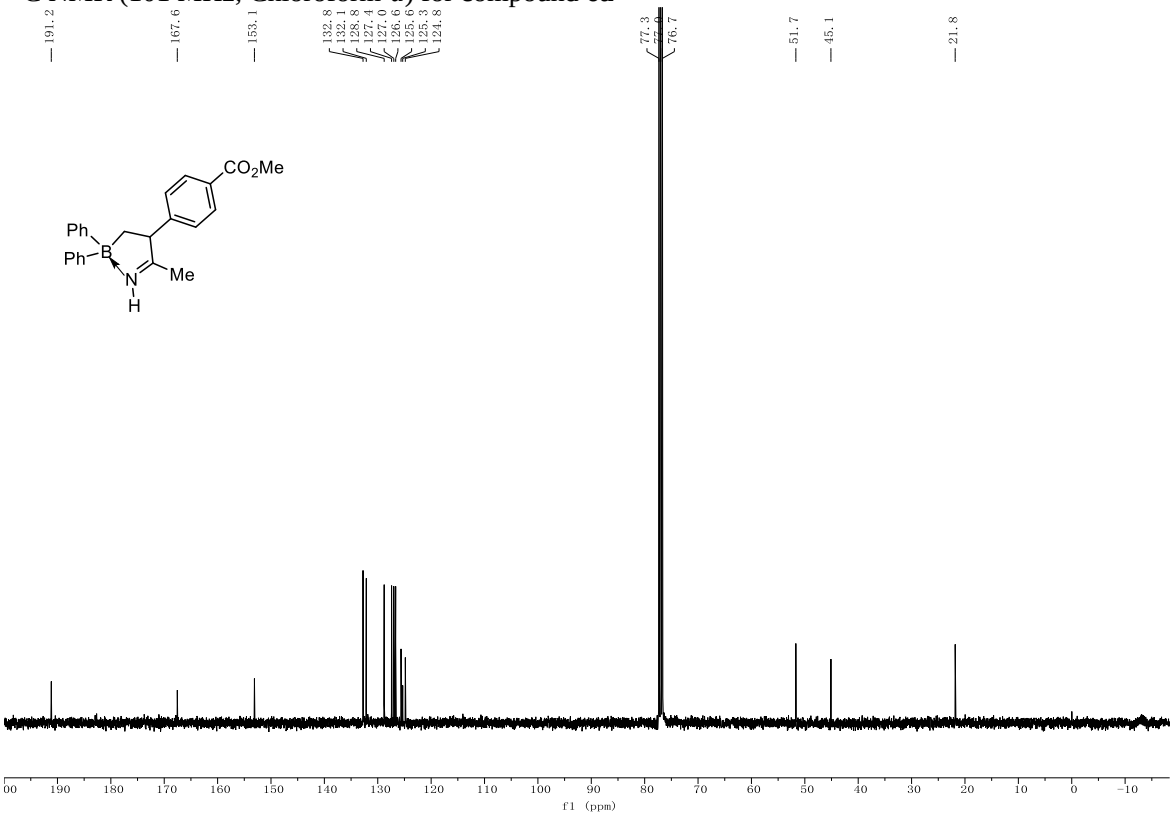


methyl 4-(5-methyl-2,2-diphenyl-2,3-dihydro-4H-1l4,4,2l4-diazaborol-4-yl)benzoate (6a)

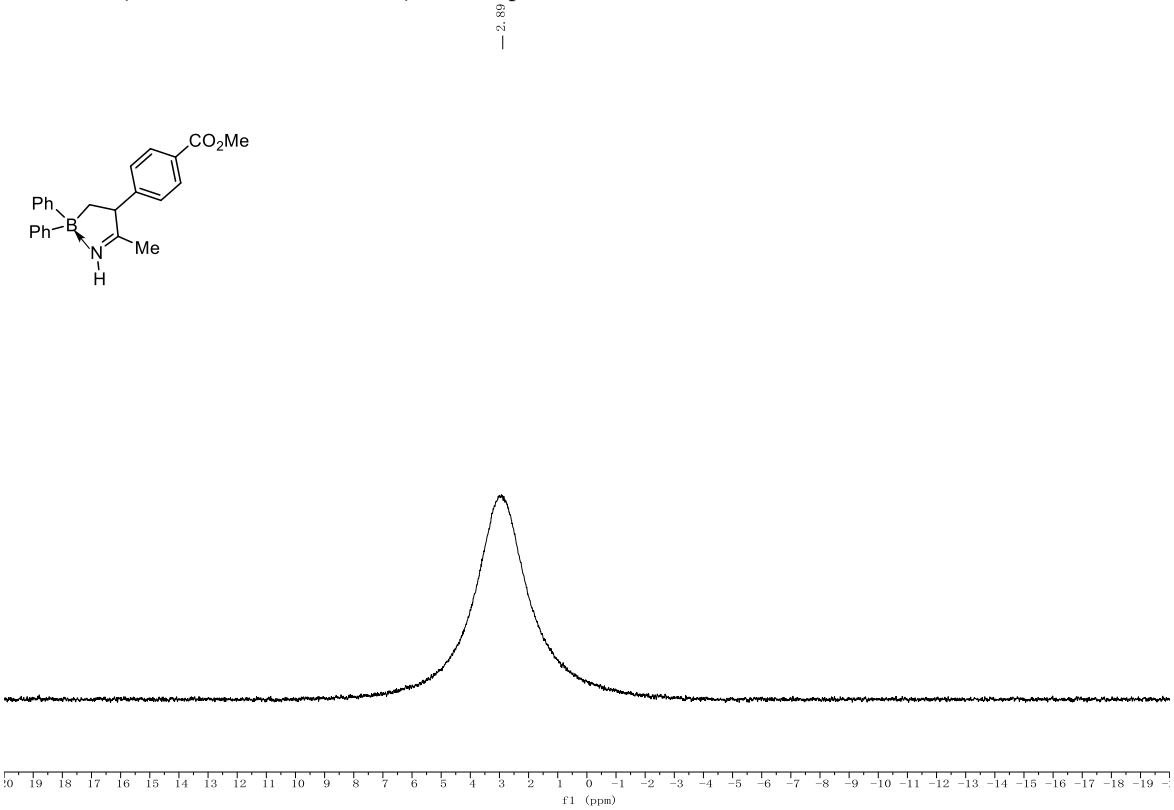
^{1}H NMR (400 MHz, Chloroform-*d*) for compound **6a**



^{13}C NMR (101 MHz, Chloroform-*d*) for compound **6a**

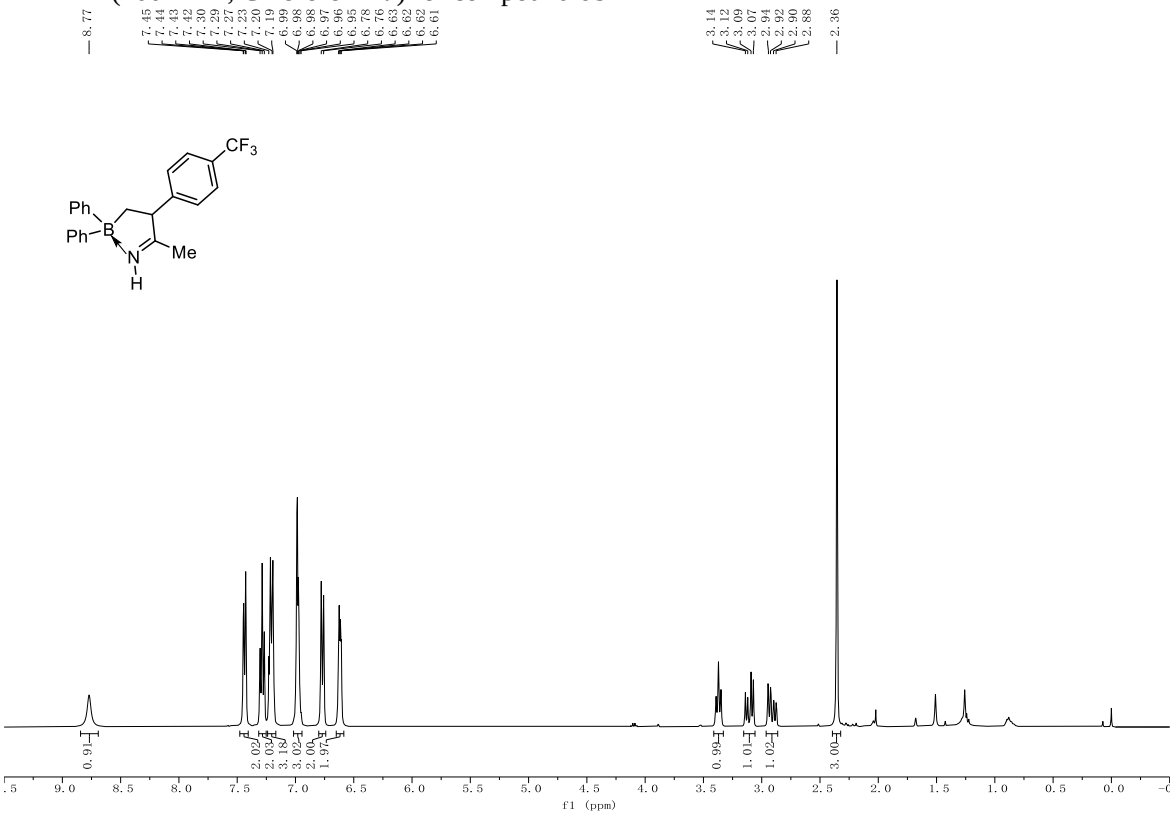


^{11}B NMR (128 MHz, Chloroform-*d*) for compound **6a**

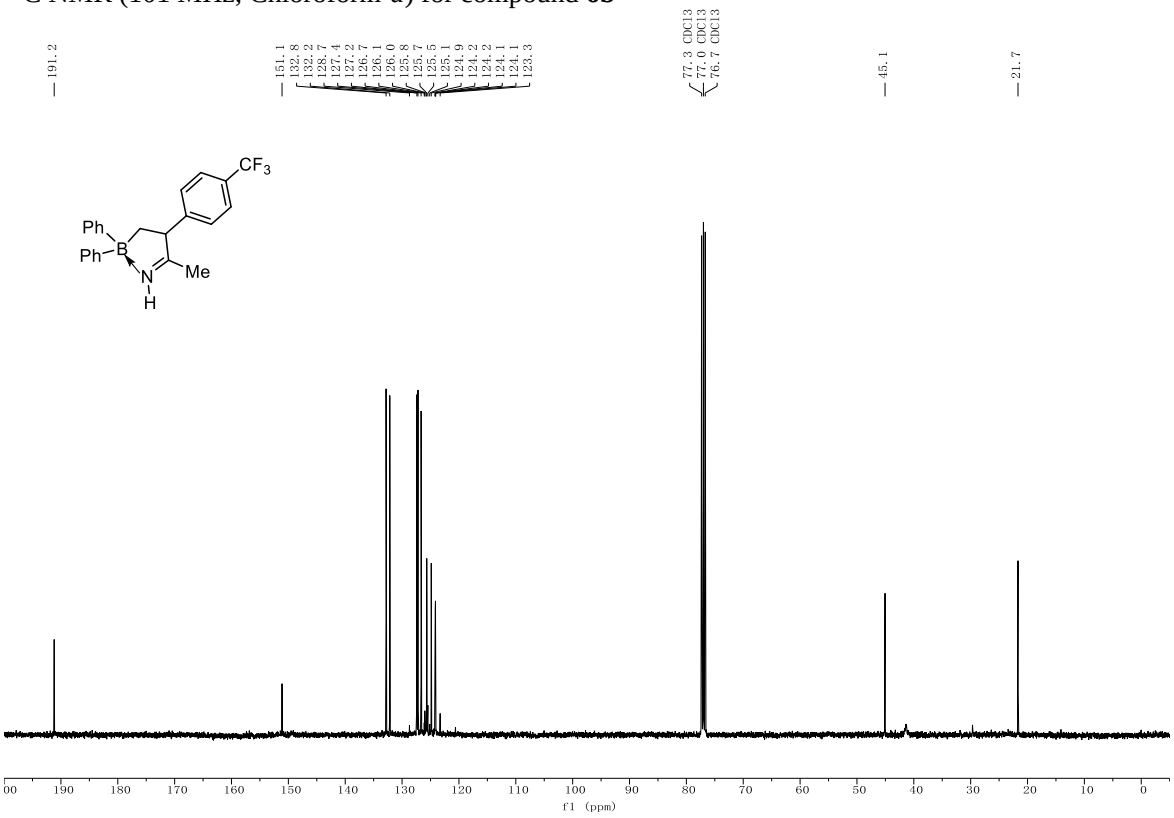


5-methyl-2,2-diphenyl-4-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2H-1l4,2l4-azaborole (6b)

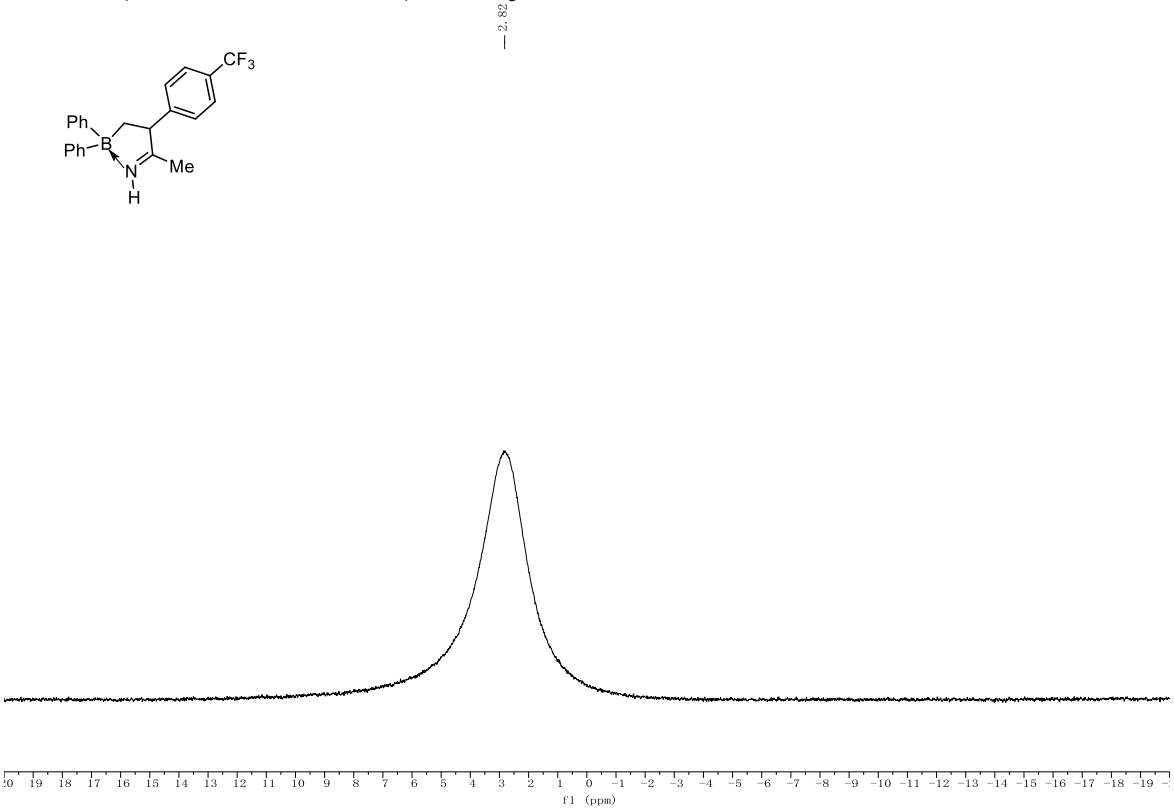
^{1}H NMR (400 MHz, Chloroform-*d*) for compound **6b**



^{13}C NMR (101 MHz, Chloroform-*d*) for compound **6b**

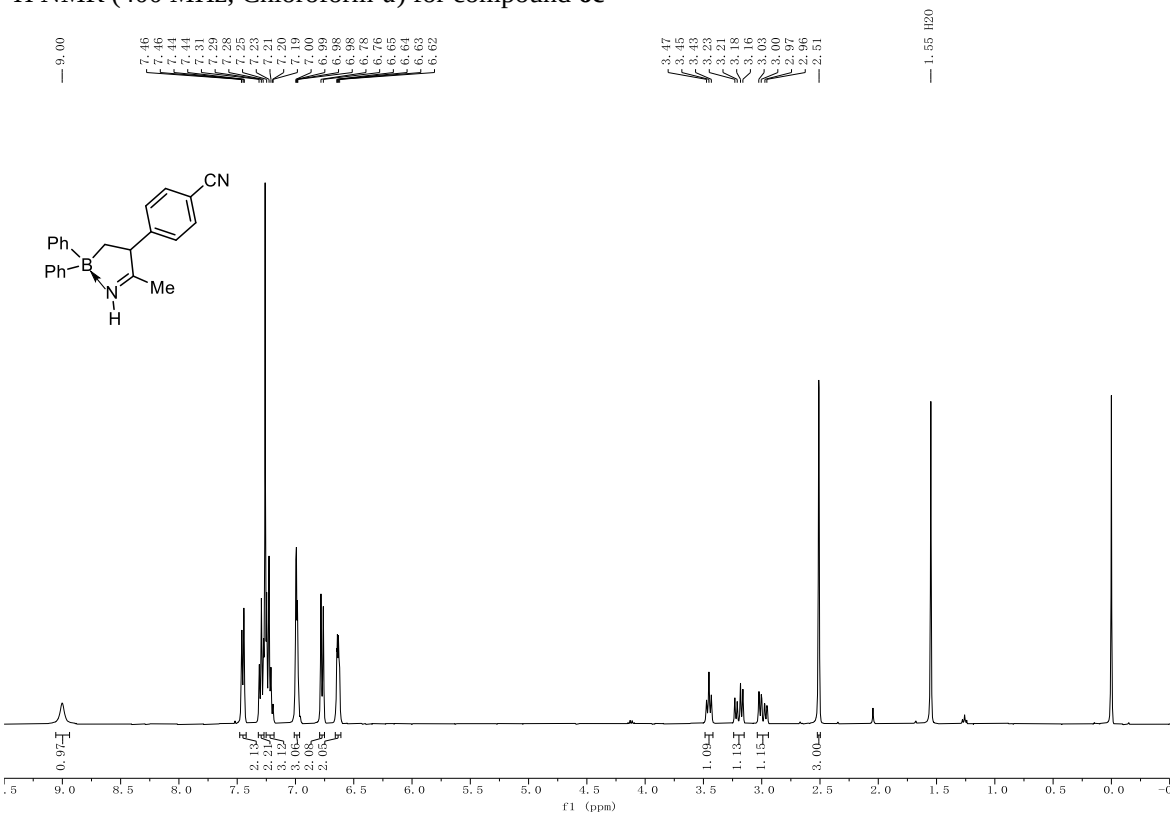


^{11}B NMR (128 MHz, Chloroform-*d*) for compound **6b**

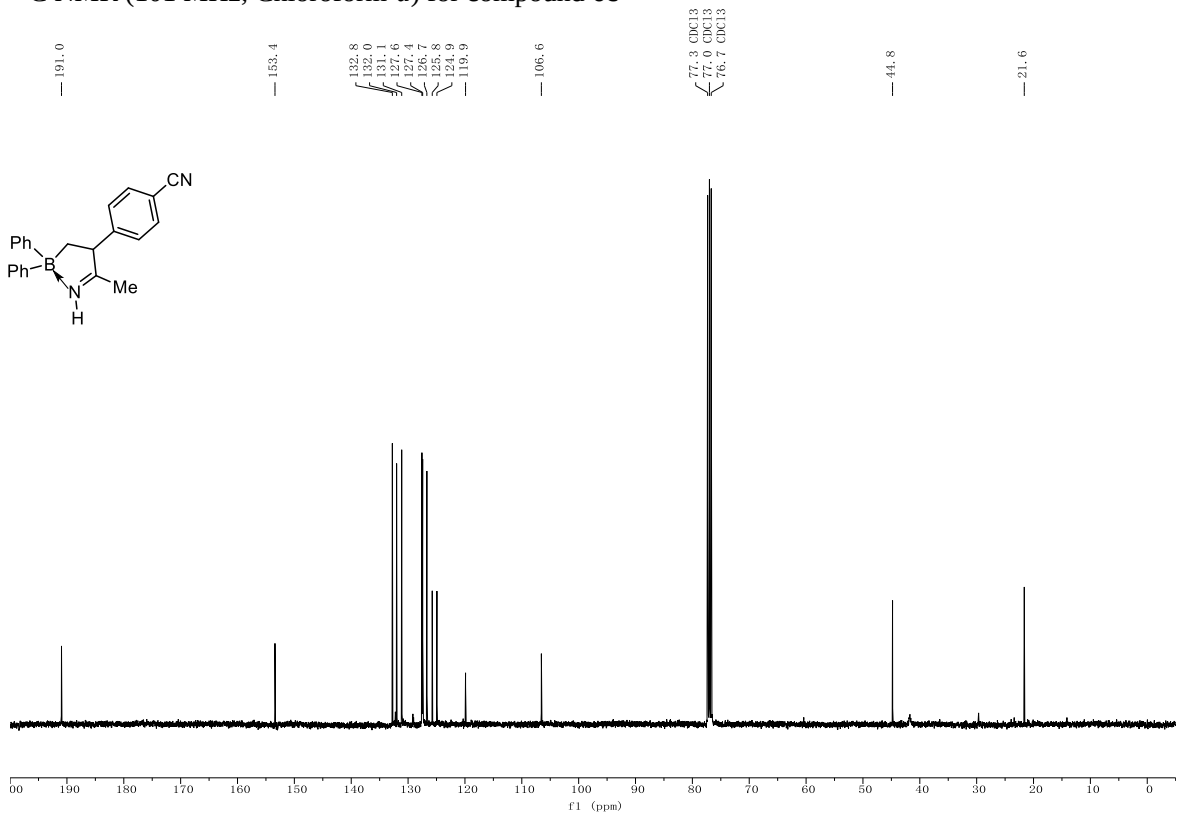


4-(5-methyl-2,2-diphenyl-3,4-dihydro-2H-1l4,2l4-azaborol-4-yl)benzonitrile (6c)

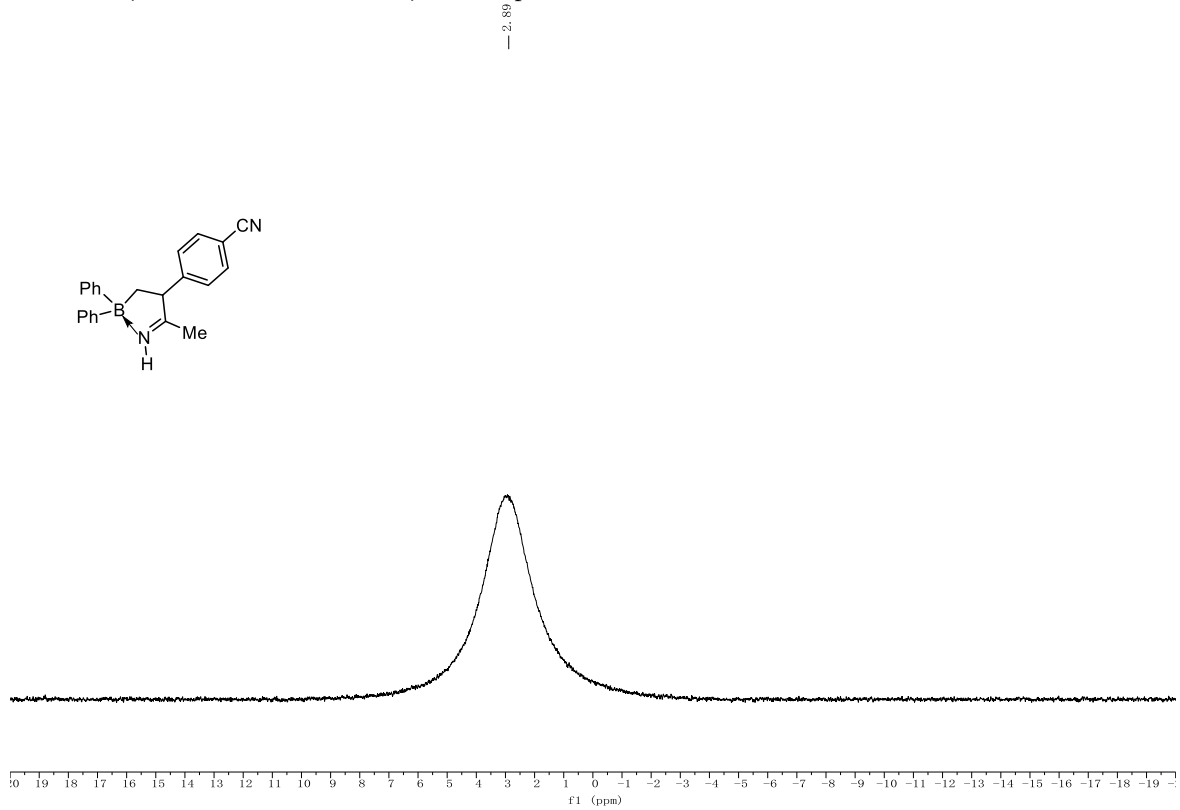
^{1}H NMR (400 MHz, Chloroform-*d*) for compound **6c**



^{13}C NMR (101 MHz, Chloroform-*d*) for compound **6c**

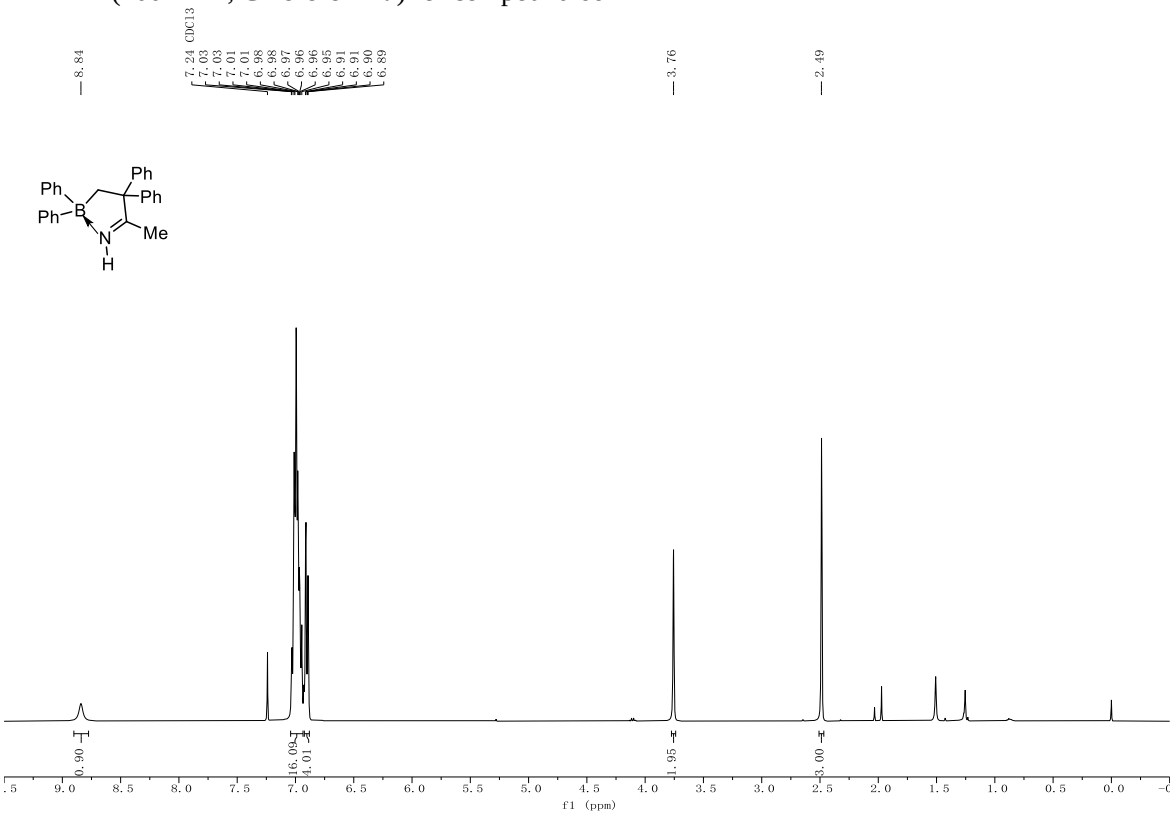


^{11}B NMR (128 MHz, Chloroform-*d*) for compound **6c**

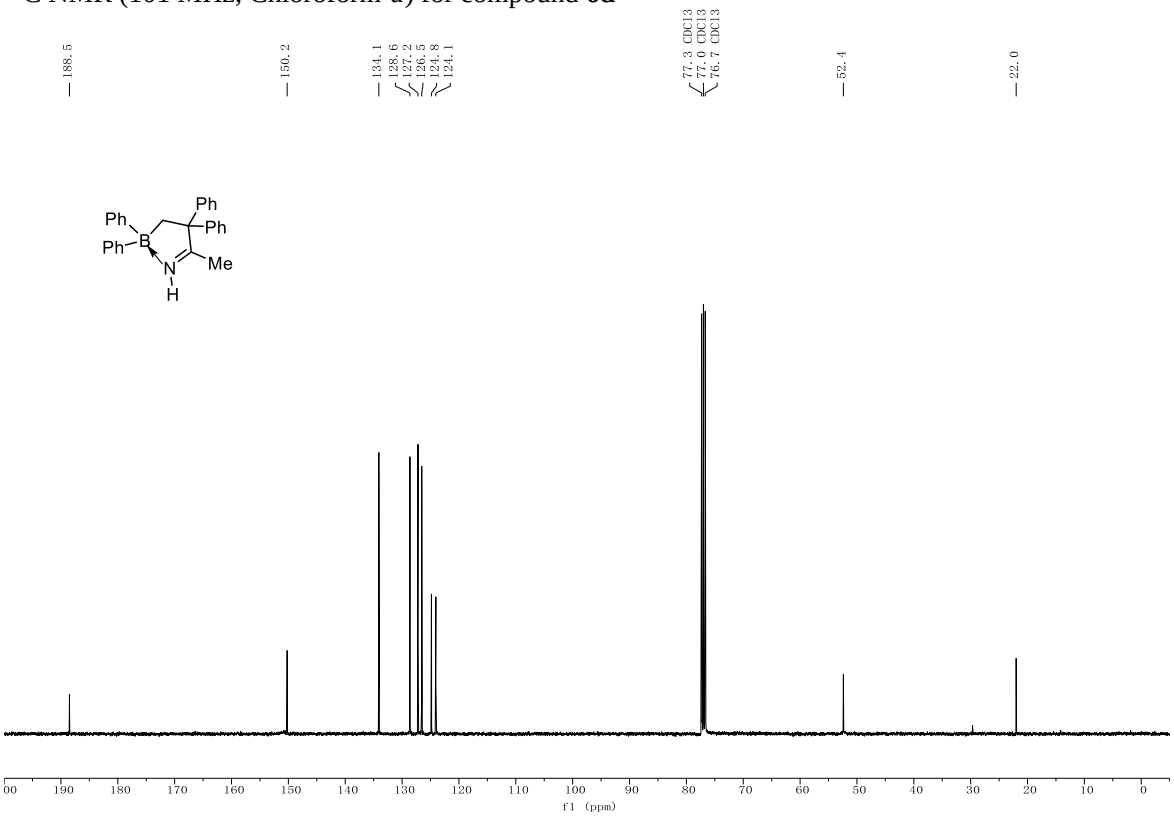


5-methyl-2,2,4,4-tetraphenyl-3,4-dihydro-2H-1l4,2l4-azaborole (6d)

^{1}H NMR (400 MHz, Chloroform-*d*) for compound **6d**



^{13}C NMR (101 MHz, Chloroform-*d*) for compound **6d**



^{11}B NMR (128 MHz, Chloroform-*d*) for compound **6d**