Supplementary Information

for

Synthesis of Cyclic Phosphonium-Borate Compounds through Reaction of Benzynes and Frustrated Lewis Pairs

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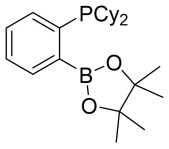
1 General Information

Unless otherwise indicated, all reactions were conducted under nitrogen atmosphere in oven-dried glassware with magnetic stirring bar. Et_2O, THF and toluene were distilled from Na/benzophenone. Trimethyl borate and ^{i}PrOBpin used after distillation, the other chemicals were obtained from commercial supplies and used as received without any further purification. Benzyne precursor **2a** was purchased from shanghai bidepharm company. (*o*-borylaryl)phosphine **1** and other arynes were prepared according to the literature methods. [S1-S3] Column chromatograph was performed with silica gel (200~300 mesh) and analytical TLC on silica gel 60-F_{254}. ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR were recorded on a Bruker AVANCE III spectrometer (400 MHz, 100 MHz, 376 MHz and 162 MHz, respectively), Chemical shifts are reported parts per million (ppm) referenced to $CDCl_3$ (δ 7.26 ppm), tetramethylsilane (TMS, δ 0.00 ppm) for ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR. High-resolution mass spectra (HRMS) were obtained on an LTQ Orbitrap XL mass spectrometry equipped with an ESI source from Thermo Scientific at Keeclound Biotech in Shanghai. X-Ray diffraction study for product **3aa** was carried out on Bruker D8 VENTURE photon II diffractometer with Iμs 3.0 microfocus X-ray source using APEX III program.

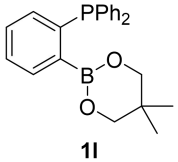
2 Experimental Section

2.1 Synthesis and characterization of 1k, 1l and 1m



1k

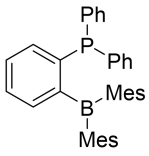
1k was synthesized according to reference [S3a]: A solution of (o-dicyclohexylphosphino)bromobenzene (0.53 g, 1.5 mmol) in THF (6.0 mL)was placed in a 25 mL Schlenk tube under N_2. ^{n}BuLi (1.6 M hexane solution, 1.04 mL, 1.65 mmol)was added to the solution at -78 ℃, and then the mixture was stirred at-78 ℃. After 2 h, ^{i}PrOBpin was added to the solution at -78 ℃, and the reaction mixture was allowed to stand at room temperature gradually. After 20 h, the reaction was quenched with $NH_4CI_{(aq)}$. The resulting mixture was extracted with Et_2O three times, and the combined organic layers were washed with water, brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica gel chromatography (PE: EA =9: 1, R_f=0.4) to give **1k** as colorless viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.44 (m, 2H), 7.37 – 7.26 (m, 2H), 1.93 – 1.84 (m, 4H), 1.80 – 1.73 (m, 2H), 1.69 – 1.56 (m, 6H), 1.39 (s, 12H), 1.30 – 1.27 (m, 1H), 1.23 – 1.05 (m, 9H). **^{31}P NMR** (162 MHz, $CDCl_3$) δ -0.6. Analytical data was in agreement with the literature.



1l

1l was synthesized according to reference [S3b]: ^{n}BuLi (1.35 mL, 2.5 M in hexanes, 3.40 mmol) was added to an Et_2O (25 mL) solution of 2-bromo-(diphenylphosphino)benzene (1.05 g, 3.07 mmol) at room temperature. The resulting dark yellow solution was stirred for ten minutes at room temperature leading to precipitation of the corresponding lithium salt as a white crystalline solid. Remove the ether solution with a syringe and add THF (10 mL). Trimethyl borate (1. 95 mL, 17.5 mmol)was added to a solution at -78 ℃. The mixture was stirred from -78 ℃ to room temperature overnight, then the solution was filtered off via cannula and the lithium salts washed twice with Et_2O (2 x 4 mL). After removing Et_2O under vacuum the residue obtained was dissolved in toluene (5 mL) and added to a solution of 2, 2-dimethyl-1, 3-propanediol in toluene (5

mL). The mixture was stirred at 100 °C for 3 h, thereafter was cooled to rt and filtered via cannula. Finally toluene was removed under vacuum; the desired product was further purified by crystallization in DCM/Et_2O (1: 1). Compound **1l** was obtained as colorless crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 – 7.73 (m, 1H), 7.37 – 7.25 (m, 11H), 7.25 – 7.21 (m, 1H), 6.88 – 6.80 (m, 1H), 3.52 (s, 4H), 0.78 (s, 6H). **^{31}P NMR** (162 MHz, $CDCl_3$) δ -2.7. Analytical data was in agreement with the literature.

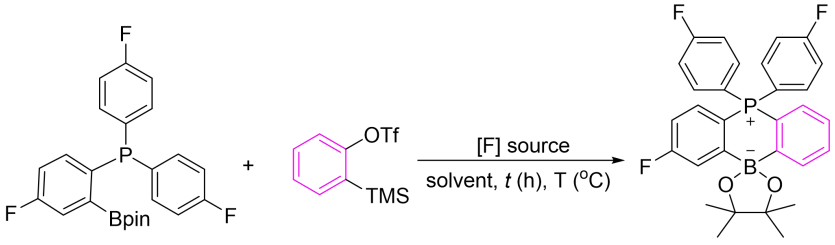


1m

1m was synthesized according to reference [S3c]: To a solution of 2-bromo-(diphenylphosphino)benzene (1.024 g, 3.00 mmol) in Et_2O (30 mL) was added *n*-BuLi (1.6 M in *n*-hexane, 2.08 mL, 3.30 mmol) at 0 ºC. After 30 min, $FB(Mes)_2$ (885 mg, 3.30 mmol) in Et_2O (10 mL) was added to the solution at –78 ºC, and the mixture was allowed to warm to room temperature overnight. The solvent was removed in vacuo, then CH_2Cl_2 was added, and the solution was filtered through a short pad of Celite®. After removal of the solvent in vacuo, the resulting solid was recrystallized from THF/MeOH to give **1m** (1.246 g, 2.44 mmol, 81%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 – 7.16 (m, 4H), 7.14 – 7.03 (m, 9H), 6.92 – 6.86 (m, 5H), 2.30 – 1.88 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2 (d, *J* = 42 Hz), 144.1, 141.6 (d, J = 11 Hz), 141.0, 139.6, 135.8, 135.8, 133.7, 133.5, 130.1, 129.1, 128.6, 128.3, 23.8, 21.7. **^{31}P NMR** (162 MHz, $CDCl_3$) δ -4.2. Analytical data was in agreement with the literature.

2.2 Screening of the reaction conditions for substrates 1f-1j

Table S1. Screening of the reaction conditions for substrates **1f-1j**[a,b]



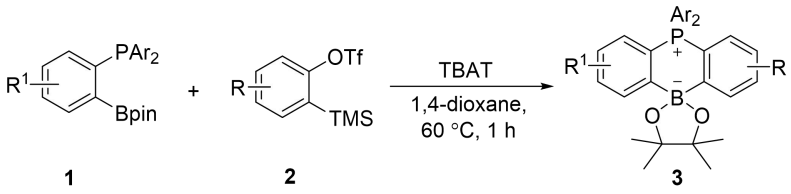
1f **2a** **3fa**

entry	[F] source	solvent	*t* (h)	T (°C)	yield (%)[b]
1	TBAT	1,4-dioxane	1	60	29
2	CsF	1,4-dioxane	1	60	26
3	CsF+18-C-6	1,4-dioxane	1	60	22
4	KF+18-C-6	1,4-dioxane	1	60	34
5	TMAF	1,4-dioxane	1	60	12
6	KF+18-C-6	THF	1	60	33
7	KF+18-C-6	CH_3CN	1	60	10
8	KF+18-C-6	DCM	1	60	26
9	KF+18-C-6	2-MeTHF	1	60	36
10	KF+18-C-6	DMF	1	60	20
11	KF+18-C-6	2-MeTHF	1	80	43
12	KF+18-C-6	2-MeTHF	1	100	46
13	KF+18-C-6	2-MeTHF	1	120	40
14	KF+18-C-6	2-MeTHF	9	100	50
15	KF+18-C-6	2-MeTHF	24	100	42

[a]Reaction conditions: **1f** (0.2 mmol), **2a** (0.24 mmol), [F] sources (0.4 mmol), solvent (2 mL). [b]Isolated yields.

2.3 General Procedure for Synthesis of Products

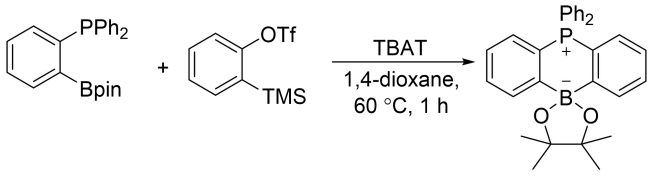
2.3.1 General Procedure for Synthesis of 3



1 **2** **3**

To an oven-dried 50 mL Schlenk sealed tube (with a Teflon cap) equipped with a magnetic stir bar was added the (*o*-borylaryl)phosphorus **1** (0.20 mmol) and TBAT (163 mg, 0.3 mmol, 1.5 equiv.). Then the Schlenk sealed tube was evacuated and backfilled with N_2 (1 atm, 3 times). The mixture was dissolved in 1,4-dioxane (2.0 mL) under N_2 atmosphere and aryne precursor **2** (0.24 mmol, 1.2 equiv.) was added into the stirring solution. Then, the reaction mixture was stirred at 60 °C for 1 h. When TLC showed the completion of the reaction, the reaction was stopped and evaporated with solvent to obtain the crude product. the crude residue was purified by column chromatography on silica gel (200-300 mesh, silica gel was basified with TEA) (PE/EA/TEA = 2/1/0.01) to afford the corresponding product **3** in moderate to good yields.

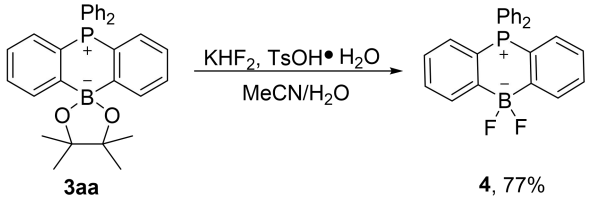
2.3.2 Gram-Scale Preparation of 3aa



1a (3.0 mmol) **2a** (3.6 mmol) **3aa**, 80%, 1.12 g

To an oven-dried 150 mL Schlenk sealed tube (with a Teflon cap) equipped with a magnetic stir bar was added the (*o*-borylaryl)phosphorus **1a** (1.164 g, 3.0 mmol) and TBAT (2.420 g, 0.3 mmol, 1.5 equiv). Then the Schlenk sealed tube was evacuated and backfilled with N_2 (1 atm, 3 times). The mixture was dissolved in 1,4-dioxane (30 mL) under N_2 atmosphere and aryne precursor **2a** (3.6 mmol, 1.2 equiv) was added into the stirring solution. Then, the reanction mixture was stirred at 60 °C for a total of 1 h. The reaction was stopped and evaporated with solvent to obtain the crude product, the crude residue was purified by column chromatography on silica gel (200-300 mesh, silica gel was basified with TEA) (PE/EA/TEA = 2/1/0.01) to afford the corresponding product **3aa** in 1.12 g and 80% isolated yields.

2.3.3 General Procedure for Synthesis of 4



3aa **4**, 77%

To an oven-dried 50 mL Schlenk tube equipped with a magnetic stir bar was added TsOH•H_2O (1.0 g, 5.27 mmol) and a solution of KHF_2 (392 mg, 5.02 mmol) in water (1.5 mL), and the mixture was stirred for 5 min at room temperature. Then a solution of **3aa** in MeCN (4 mL) was added and the mixture was stirred at room temperature for 24 h. After the reaction is completed, to the reaction mixture was added saturated aqueous solution of K_2CO_3 (15 mL) and MeCN (10 mL)

successively. The mixture was separated, the aqueous phase was extracted with DCM (2 × 5 mL). The combined organic layer were dried with anhydrous Na_2SO_4. The solvent was evaporated under vacuum to obtain the crude product, which was subjected to column chromatography on silica gel (200-300 mesh) (PE/EA = 2/1) to afford the pure product **4**.

2.4 Preparing Single-Crystal of 3aa and Relating Crystal Data:

Suitable single crystal for product **3aa** was obtained by slow volatilization of the solution (EtOAc : *n*-hexane (v/v = 2:1) as solvent) in a vial for three days.

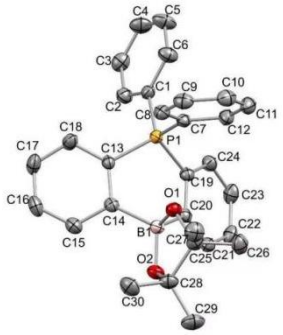


Figure S1 Crystal structure of **3aa** at 30% probability level.

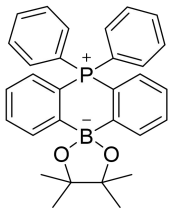
Table S2 Crystal data and structure refinement for **3aa**.

Empirical formula	$C_{30}H_{30}BO_2P$	
Formula weight	464.32	
Temperature	173.0 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 12.4726(5)Å	α= 90°.
	b = 10.8930(4) Å	β= 104.916(2)°.
	c = 18.9942(7) Å	γ = 90°.
Volume	2493.67(17) $Å^3$	
Z	4	
Density (calculated)	1.237 Mg/m^3	
Absorption coefficient	0.136 mm^{-1}	
F(000)	984.0	
Crystal size	0.16 x 0.14 x 0.13 mm^3	
Theta range for data collection	2.902 to 27.120°.	
Index ranges	-15<=h<=15, 0<=k<=13, 0<=l<=24	
Reflections collected	5596	
Independent reflections	5596 [R(int) = 0.0623]	
Completeness to theta = 67.679°	99.7 %	
Absorption correction	Semi-empirical from equivalents	

Max. and min. transmission	0.7455 and 0.6533
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5596/0/312
Goodness-of-fit on F^2	1.233
Final R indices [I>2sigma(I)]	$R_1 = 0.0618$, $wR_2 = 0.1282$
R indices (all data)	$R_1 = 0.0832$, $wR_2 = 0.1415$
Largest diff. peak and hole	0.342 and -0.322 e.Å^{-3}

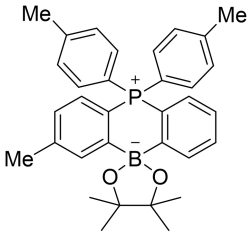
The CCDC number of product 3aa is 2244157.

2.5 Characterization of Products:



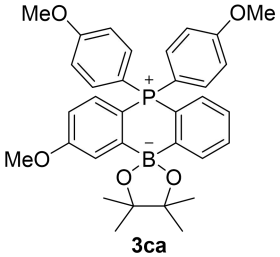
3aa

4',4',5',5'-tetramethyl-5,5-diphenyl-5*H*-spiro[dibenzo[*b*,*e*][1,4] phosphaborinine-10,2'-[1,3,2]dioxaborolan]-5-ium-10-uide 3aa: he crude mixture was purified by column chromatography (PE/EA/TEA = 2/1/0.01) to afford product **3aa** (78.6 mg, 88%) as a white solid; m.p.: 244-245 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (dd, J = 7.4, 4.4 Hz, 2H), 7.64-7.56 (m, 2H), 7.52-7.40 (m, 10H), 7.11-7.03 (m, 4H), 0.91 (s, 12H); **^{13}C NMR** (100 Hz, $CDCl_3$) δ 134.6 (d, J = 10.1Hz), 133.0 (d, J = 3.0 Hz), 132.0 (d, J = 15.0 Hz), 131.6 (d, J = 3.0 Hz), 128.8 (d, J = 12.4 Hz), 124.6 (d, J = 13.7 Hz), 123.8 (d, J = 86.1 Hz), 124 (d, J = 88.3 Hz), 79.1, 26.4; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 4.46; **HRMS** (ESI) m/z: $(M+H)^+$ calcd for $C_{30}H_{31}BO_2P$ 465.2149; Found 465.2148; **IR** (KBr, thin film): 3047, 2959, 2922, 1596, 1439, 1261, 1163, 1145, 1076, 1012, 833, 761, 723, 688, 3053 cm^{-1}.



3ba

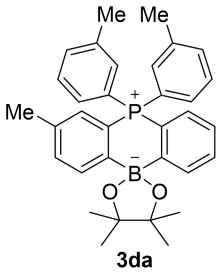
2,4',4',5',5'-pentamethyl-5,5-di-*p*-tolyl-5*H*-spiro[dibenzo[*b*,*e*][1,4]phosphaborin-ine-10,2'-[1,3,2]dioxaborolan]-5-ium-10-uide 3ba: he crude mixture was purified by column chromatography (PE/EA/TEA = 2/1/0.01) to afford product **3ba** (87.1 mg, 86%) as a white solid; m.p.: 115-116 ℃; **^{1}H NMR** (400 Hz, $CDCl_3$) δ 8.18 (s, 1H), 8.02 (s, 1H), 7.46-7.33 (m, 5H), 7.31-7.21 (m, 4H), 7.12-6.95 (m, 3H), 6.91 (s, 1H), 2.42 (s, 6H), 2.36 (s, 3H), 0.95 (s, 12H); **^{13}C NMR** (100 Hz, $CDCl_3$) δ 143.7 (d, J = 3.0 Hz), 141.5 (d, J = 3.3 Hz), 134.6 (d, J = 10.5 Hz), 133.0 (d, J = 15.0 Hz), 132.1 (d, J = 14.6 Hz), 131.6 (d, J = 13.2 Hz), 131.3 (d, J = 12.8 Hz), 131.1 (d, J = 3.2 Hz), 129.5 (d, J = 13.0 Hz), 125.4 (d, J = 14.6 Hz), 124.5 (d, J = 13.8 Hz), 123.2 (d, J = 88.8 Hz), 120.6 (d, J = 88.4 Hz), 119.4 (d, J = 90.7 Hz), 79.0, 26.6, 26.5, 22.0, 21.7; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 4.08; **HRMS** (ESI) m/z: $(M+H)^+$ calcd for $C_{33}H_{37}BO_2P$ 507.2619; Found 507.2622; **IR** (KBr, thin film): 2956, 2923, 1598, 1438, 1375, 1163, 1111, 1072, 1012, 800, 758, 737, 661 cm^{-1}.



3ca

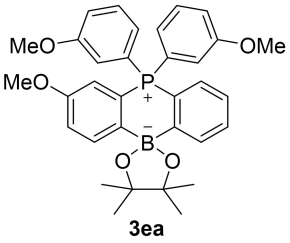
2-**methoxy-5,5-bis(4-methoxyphenyl)-4',4',5',5'-tetramethyl-5*H*-5λ^4,10λ^4-spiro[di-benzo[*b*,*e*][1,4]phosphaborinine-10,2'-[1,3,2]dioxaborolane] 3ca**: The crude mixture was purified by column chromatography (PE/EA/TEA = 1/1/0.01) to afford product **3ca** (93.1 mg, 84%) as a white solid; m.p.: 257-258 ℃; **^{1}H NMR** (400 Hz, $CDCl_3$) δ 8.18 (dd, J = 6.8, 4.4 Hz, 1H), 7.79 (s, 1H), 7.49-7.39 (m, 5H), 7.12-

7.05 (m, 2H), 7.05-7.01 (m, 1H), 7.00–6.94 (m, 4H), 6.65 (dt, *J* = 8.4, 2.8 Hz, 1H), 3.88 (s, 3H), 3.85 (s, 6H), 0.97 (d, *J* = 5.6 Hz, 12H); **^{13}C NMR** (100 Hz, $CDCl_3$) δ 163.3 (d, *J* = 2.9 Hz), 162.2 (d, *J* = 3.4 Hz), 136.4 (d, *J* = 11.5 Hz), 133.2 (d, *J* = 14.5 Hz), 132.1 (d, *J* = 14.7 Hz), 131.1 (d, *J* = 8.7 Hz), 131.0 (d, *J* = 3.7 Hz), 124.5 (d, *J* = 13.7 Hz), 124.2 (d, *J* = 89.9 Hz), 115.2 (d, *J* = 15.9 Hz), 114.8 (d, *J* = 94.1 Hz), 114.4 (d, *J* = 13.3 Hz), 113.6 (d, *J* = 96.2 Hz), 112.8 (d, *J* = 14.8 Hz), 79.0, 55.5, 55.1, 26.7, 26.6; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 3.35; **HRMS** (ESI) m/z: $(M+H)^+$ calcd for $C_{33}H_{37}BO_5P$ 555.2466; Found 555.2469; **IR** (KBr, thin film): 33045, 2960, 1595, 1504, 1460, 1296, 1261, 1182, 1114, 1074, 1008, 829, 802, 736 cm^{-1}.



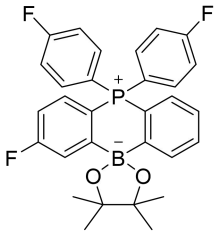
3da

3,4',4',5',5'-pentamethyl-5,5-di-m-tolyl-5*H*-spiro[dibenzo[*b*,*e*][1,4]hosphaborin-ine-10,2'-[1,3,2]dioxaborolan]-5-ium-10-uide 3da: The crude mixture was purified by column chromatography (PE/EA/TEA = 2/1/0.01) to afford product **3da** (82.0 mg, 81%) as a white solid; m.p.: 215-216 ℃; **^{1}H NMR** (400 Hz, $CDCl_3$) δ (dd, *J* = 6.8, 4.4 Hz, 1H), 8.10 (dd, *J* = 7.6, 4.4 Hz, 1H), 7.45-7.39 (m, 3H), 7.38-7.32 (m, 4H), 7.32-7.25 (m, 3H), 7.10-7.04 (m, 2H), 6.91 (d, *J* = 13.2 Hz, 1H), 2.34 (s, 6H), 2.22 (s, 3H), 0.94 (s, 12H); **^{13}C NMR** (100Hz, $CDCl_3$) δ 138.7 (d, *J* = 12.4 Hz), 134.9 (d, *J* = 10.1 Hz), 133.9 (d, *J* = 13.0 Hz), 133.8 (d, *J* = 2.9 Hz), 132.5 (d, *J* = 3.4 Hz), 132.1 (d, *J* = 15.4 Hz), 132.0 (d, *J* = 14.8 Hz), 131.9 (d, *J* = 9.9 Hz), 131.7 (d, *J* = 13.0 Hz), 131.5 (d, *J* = 13.2 Hz), 131.2 (d, *J* = 3.2 Hz), 128.6 (d, *J* = 13.2 Hz), 124.5 (d, *J* = 13.7 Hz), 123.7 (d, *J* = 85.3 Hz), 122.8 (d, *J* = 88.0 Hz), 122.5 (d, *J* = 87.4 Hz), 79.0, 26.6, 26.5, 21.5, 21.2; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 4.38; **HRMS** (ESI) m/z: $(M+H)^+$ calcd for $C_{33}H_{37}BO_2P$ 507.2619; Found 507.2620; **IR** (KBr, thin film): 3043, 2958, 2921, 1595, 1437, 1375, 1226, 1163, 1112, 1072, 1012, 819, 758, 736, 703 cm^{-1}.



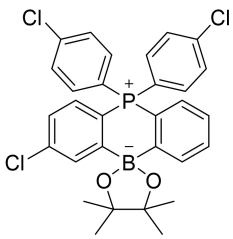
3ea

3-**methoxy-5,5-bis(3-methoxyphenyl)-4',4',5',5'-tetramethyl-5*H*-spiro[dibenzo[*b*,*e*][1,4]hosaborinine-10,2'-[1,3,2]dioxaborolan]5-ium-10-uide 3ea**: The crude mixture was purified by column chromatography (PE/EA/TEA = 1/1/0.01) to afford product **3ea** (62.1 mg, 56%) as a white solid; m.p.: 201-202 ℃; **^{1}H NMR** (400 Hz, $CDCl_3$) δ 8.19 (dd, *J* = 7.2, 4.4 Hz, 1H), 8.12 (dd, *J* = 8.0, 5.2 Hz, 1H), 7.48-7.38 (m, 3H), 7.17-7.09 (m, 6H), 7.08-6.99 (m, 3H), 6.68 (dd, *J* = 14.4, 2.4 Hz, 1H), 3.75 (s, 6H), 3.70 (s, 3H), 0.94 (s, 12H); **^{13}C NMR** (100 Hz, $CDCl_3$) δ 159.6 (d, *J* = 15.7 Hz), 156.9 (d, *J* = 17.6 Hz), 133.6 (d, *J* = 17.2 Hz), 132.0 (d, *J* = 14.9 Hz), 131.5 (d, *J* = 9.1 Hz), 131.5 (d, *J* = 3.5 Hz), 130.1 (d, *J* = 14.6 Hz), 126.8 (d, *J* = 9.7 Hz), 124.8 (d, *J* = 85.5 Hz), 124.6 (d, *J* = 13.9 Hz), 122.8 (d, *J* = 84.3 Hz), 122.0 (d, *J* = 84.7 Hz), 120.2 (d, *J* = 11.5 Hz), 118.5 (d, *J* = 2.9 Hz), 117.5 (d, *J* = 14.3 Hz), 116.9 (d, *J* = 3.3 Hz), 79.0, 55.5, 55.2, 26.5; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 5.14; **HRMS** (ESI) m/z: $(M+H)^+$ calcd for $C_{33}H_{37}BO_5P$ 555.2466; Found 555.2463; **IR** (KBr, thin film): 3045, 2960, 2927, 1591, 1438, 1425, 1290, 1251, 1161, 1113, 1039, 1010, 821, 736, 700 cm^{-1}.



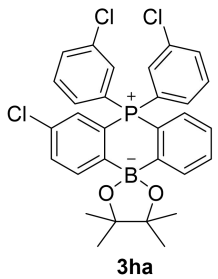
3fa

2-fluoro-5,5-bis(4-fluorophenyl)-4',4',5',5'-tetramethyl-5*H*-5λ^4,10λ^4-spiro[dibenzo[*b*,*e*][1,4]phosphaborinine-10,2'-[1,3,2]dioxaborolane] 3fa: The crude mixture was purified by column chromatography (PE/EA/TEA = 10/1/0.01) to afford product **3fa** (51.8 mg, 50%) as a white solid; m.p.: 289-290 ℃; **^{1}H NMR** (400 Hz, $CDCl_3$) δ 8.17 (dd, J = 7.2, 4.4 Hz, 1H), 7.88 (dt, J = 9.2, 3.2 Hz, 1H), 7.55-7.43 (m, 5H), 7.22 (td, J = 8.4, 2.4 Hz, 4H), 7.16-7.04 (m, 3H), 6.85-6.77 (m, 1H), 0.91 (d, J = 4.8 Hz, 12H); **^{13}C NMR** (100 z, $CDCl_3$) δ 165.9 (dd, J = 255.6, 3.2 Hz), 165.7 (dd, J = 255.9, 3.7 Hz), 137.1 (dd, J = 11.8, 9.2 Hz), 133.9 (dd, J = 14.8, 8.2 Hz), 132.2 (d, J = 15.0 Hz), 131.8 (d, J = 3.0 Hz), 131.2 (d, J = 13.2 Hz), 125.0 (d, J = 14.0 Hz), 122.04 (d, J = 89.5 Hz), 119.7 (d, J = 3.2 Hz), 119.8-118.7 (m), 119.0-118.6 (m), 117.44 (dd, J = 94.0, 2.0 Hz), 116.7 (dd, J = 21.7, 13.9 Hz), 112.5 (dd, J = 23.2, 15.2 Hz), 79.3, 26.4; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 3.85; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.44, -106.55; **HRMS** (ESI) m/z: $(M+H)^+$ calcd for $C_{30}H_{28}BF_3O_2P$ 519.1867; Found 519.1870; **IR** (KBr, thin film): 3049, 2962, 2923, 1591, 1500, 1438, 1379, 1242, 1163, 1110, 1072, 1012, 829, 802, 736 cm^{-1}.



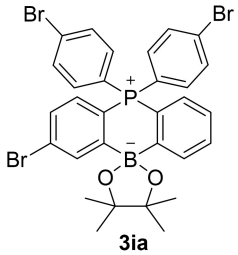
3ga

2-chloro-5,5-bis(4-chlorophenyl)-4',4',5',5'-tetramethyl-5*H*-spiro[dibenzo[*b*,*e*][1,4]phosp haborinine-10,2'-[1,3,2]dioxaborolan]-5-ium-10-uide 3ga: The crude mixture was purified by column chromatography (PE/EA/TEA = 10/1/0.01) to afford product **3ga** (44.3 mg, 39%) as a white solid; m.p.: 291-292 ℃; **^{1}H NMR** (400 Hz, $CDCl_3$) δ 8.21-8.11 (m, 2H), 7.54-7.40 (m, 9H), 7.18-7.09 (m, 2H), 7.09-7.97 (m, 2H), 0.90 (d, J = 6.4 Hz, 12H); **^{13}C NMR** (100 Hz, $CDCl_3$) δ 140.6 (d, J = 3.6 Hz), 139.8 (d, J = 4.1 Hz), 135.7 (d, J = 11.1 Hz), 132.7 (d, J = 14.1 Hz), 132.3 (d, J = 6.3 Hz), 132.2 (d, J = 5.8 Hz), 132.0 (d, J = 3.4 Hz), 131.3 (d, J = 13.1 Hz), 129.5 (d, J = 13.4 Hz), 125.2 (d, J = 11.4 Hz), 125.1 (d, J = 10.7 Hz), 121.6 (d, J = 88.7 Hz), 121.20 (d, J = 88.9 Hz), 120.0 (d, J = 92.2 Hz), 79.4, 26.3; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 4.41; **HRMS** (ESI) m/z: $(M+Na)^+$ calcd for $C_{30}H_{28}BCl_3O_2P$ 567.0980; Found 567.0989; **IR** (KBr, thin film): 3049, 2960, 2923, 1577, 1438, 1390, 1161, 1112, 1087, 1014, 819, 752, 734 cm^{-1}.



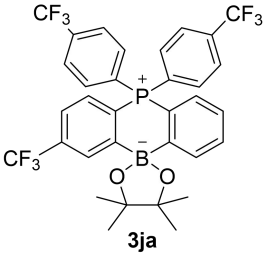
3ha

3-chloro-5,5-bis(3-chlorophenyl)-4',4',5',5'-tetramethyl-5*H*-spiro[dibenzo[*b*,*e*][1,4]phosphaborinine-10,2'-[1,3,2]dioxaborolan]-5-ium-10-uide 3ha: The crude mixture was purified by column chromatography (PE/EA/TEA = 10/1/0.01) to afford product **13ha** (51.5 mg, 45%) as a white solid; m.p.: 206-207 ℃; **^{1}H NMR** (400 Hz, $CDCl_3$) δ 8.22-8.11 (m, 2H), 7.67 (d, J = 8.0 Hz, 2H), 7.54-7.35 (m, 8H), 7.20-7.13 (m, 1H), 7.13-7.00 (m, 2H), 0.90 (s, 12H); **^{13}C NMR** (100 Hz, $CDCl_3$) δ 135.7 (d, J = 16.5 Hz), 134.3 (d, J = 11.4 Hz), 134.0 (d, J = 18.5 Hz), 133.9 (d, J = 2.6 Hz), 132.5 (d, J = 9.7 Hz), 132.2 (d, J = 2.9 Hz), 132.2 (d, J = 11.8 Hz), 131.5 (d, J = 13.4 Hz), 131.0 (d, J = 17.8 Hz), 130.5 (d, J = 13.7 Hz), 130.3 (d, J = 14.3 Hz), 125.2 (d, J = 14.3 Hz), 125.0 (d, J = 85.3 Hz), 123.4 (d, J = 88.5 Hz), 120.4 (d, J = 88.5 Hz), 79.3, 26.3; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 4.04; **HRMS** (ESI) m/z: $(M+H)^+$ calcd for $C_{30}H_{28}BCl_3O_2P$ 567.0980; Found 567.0988; **IR** (KBr, thin film): 33055, 2960, 2923, 1564, 1467, 1436, 1400, 1197, 1132, 1072, 1014, 831, 783, 734, 682 cm^{-1}.



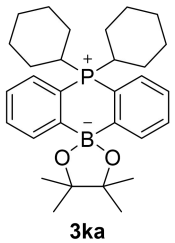
3ia

2-bromo-5,5-bis(4-bromophenyl)-4',4',5',5'-tetramethyl-5*H*-spiro[dibenzo[*b*,*e*][1,4]hosphaborinine-0,2'-[1,3,2]dioxaborolan]-5-ium-10-uide 3ia: The crude mixture was purified by column chromatography (PE/EA/TEA = 10/1/0.01) to afford product **3ia** (63.1 mg, 45%) as a white solid; m.p.: 292-293 ℃; **^{1}H NMR** (400 Hz, $CDCl_3$) δ 8.33 (s, 1H), 8.15 (dd, J = 7.2, 4.4 Hz, 1H), 7.67 (d, J = 7.2 Hz, 4H), 7.47 (t, J = 7.2 Hz, 1H), 7.36 (dd, J = 12.8, 8.8 Hz, 4H), 7.31-7.25 (m, 1H), 7.18-7.03 (m, 2H), 6.94 (dd, J = 12.4, 8.0 Hz, 1H), 0.90 (d, J = 6.8 Hz, 12H); **^{13}C NMR** (100 Hz, $CDCl_3$) δ 135.8 (d, J = 11.0 Hz), 135.3 (d, J = 15.4 Hz), 132.8 (d, J = 14.0 Hz), 132.5 (d, J = 13.2 Hz), 132.2 (d, J = 15.1 Hz), 132.1 (d, J = 3.3 Hz), 131.3 (d, J = 13.3 Hz), 129.4 (d, J = 4.1 Hz), 129.24 (d, J = 3.6 Hz), 128.1 (d, J = 14.4 Hz), 125.2 (d, J = 14.0 Hz), 122.0 (d, J = 88.3 Hz), 121.0 (d, J = 88.7 Hz), 120.4 (d, J = 91.5 Hz), 79.4, 26.3. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 5.05; **HRMS** (ESI) m/z: $(M+H)^+$ calcd for $C_{30}H_{28}BBr_3O_2P$ 700.9444; Found 700.9448; **IR** (KBr, thin film): 3047, 2958, 2923, 1575, 1479, 1427, 1384, 1159, 1115, 1069, 1010, 813, 742, 707 cm^{-1}.



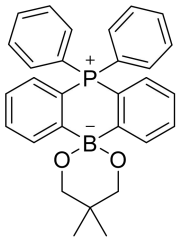
3ja

4',4',5',5'-tetramethyl-2-(trifluoromethyl)-5,5-bis(4-(trifluoromethyl)phenyl)-5*H*-spiro[dibenzo[*b*,*e*][1,4] phosphaborinine-10,2'-[1,3,2]dioxaborolan]-5-ium-10-uide 3ja: The crude mixture was purified by column chromatography (CH_2Cl_2/MeOH = 25/1) to afford product **3ja** (98.3 mg, 98%) as a white solid; m.p.: 179-180 ℃; **^{1}H NMR** (400 Hz, $CDCl_3$) δ 8.49 (s, 1H), 8.21 (dd, J = 7.6, 4.4 Hz, 1H), 7.86-7.79 (m, 4H), 7.69 (dd, J = 12.8, 8.0 Hz, 4H), 7.56 (t, J = 7.6 Hz, 1H), 7.42 (d, J = 6.8 Hz, 1H), 7.21 (dd, J = 12.8, 7.6 Hz, 2H), 7.10 (dd, J = 12.8, 8.0 Hz, 1H), 0.85 (d, J = 9.2 Hz, 12H); **^{13}C NMR** (100 Hz, $CDCl_3$) δ 135.8-135.4 (m), 135.1(d, J = 10.6 Hz), 132.6 (d, J = 3.2 Hz), 132.4 (d, J = 15.2 Hz), 131.6-131.3 (m), 128.9-128.5 (m), 127.2 (d, J = 84.8 Hz), 126.1 (d, J = 3.8 Hz), 125.5(d, J = 14.2 Hz), 125.4(d, J = 88.2 Hz), 124.5, 122.8, 121.8-121.2 (m), 119.6 (d, J = 88.1 Hz), 79.5, 26.1, 26.0; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.61; **HRMS** (ESI) m/z: $(M+H)^+$ calcd for $C_{33}H_{28}BF_9O_2P$ 669.1771; Found 669.1775; **IR** (KBr, thin film): 3051, 2962, 2925, 1400, 1323, 1172, 1128, 1064, 1016, 833, 759, 742, 713 cm^{-1}.



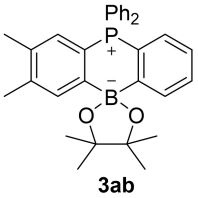
3ka

5,5-dicyclohexyl-4',4',5',5'-tetramethyl-5*H*-spiro[dibenzo[*b*,*e*][1,4]phosphaborinine-10,2'-[1,3,2]dioxaborolan]-5-ium-10-uide The crude mixture was purified by column chromatography (PE/EA/TEA = 2/1/0.01) to afford product **3ka** (52.3 mg, 55%) as a white solid; m.p.: 198-199 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (dd, J = 6.4, 3.2 Hz, 2H), 7.53 (t, J = 10.0 Hz, 2H), 7.42 (t, J = 7.2 Hz, 2H), 7.21 – 7.14 (m, 2H), 3.64 – 3.47 (m, 2H), 2.04 – 1.95 (m, 4H), 1.90 – 1.77 (m, 6H), 1.74 – 1.63 (m, 4H), 1.36 – 1.26 (m, 6H), 1.12 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 133.1 (d, J = 13.4 Hz), 130.8 (d, J = 3.1 Hz), 129.0 (d, J = 10.7 Hz), 124.3 (d, J = 12.1 Hz), 121.0, 120.2, 79.2, 34.6, 34.2, 27.2, 27.1, 26.9, 26.9, 26.0. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 7.10. **HRMS** (ESI) m/z: $(M+H)^+$ calcd for $C_{30}H_{43}BO_2P$ 477.3088; Found 477.3092; **IR** (KBr, thin film): 2958, 2926, 1596, 1163, 1145, 1090, 1028, 842, 763, 726, 680, cm^{-1}.



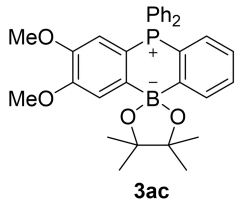
3la

5',5'-dimethyl-5,5-diphenyl-5*H*-spiro[dibenzo[*b*,*e*][1,4]phosphaborinine-10,2'-[1,3,2]dioxaborinan]-5-ium-10-uide The crude mixture was purified by column chromatography (PE/EA/TEA = 2/1/0.01) to afford product **3la** (78.3 mg, 87%) as a white solid; m.p.: 312-313 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 – 8.16 (m, 2H), 7.63 – 7.58 (m, 2H), 7.53 – 7.42 (m, 10H), 7.19 – 7.10 (m, 4H), 3.27 (s, 4H), 0.79 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 133.9 (d, *J* = 10.0 Hz), 132.9 (d, *J* = 2.9 Hz), 132.5 (d, *J* = 13.2 Hz), 132.3 (d, *J* = 14.7 Hz), 131.4 (d, *J* = 3.3 Hz), 129.0 (d, *J* = 13.9 Hz), 125.1 (d, *J* = 12.4 Hz), 124.6 (d, *J* = 86.8 Hz), 121.9 (d, *J* = 89.9 Hz), 72.7, 33.1, 23.7. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 7.33. **HRMS** (ESI) m/z: $(M+H)^+$ calcd for $C_{29}H_{29}BO_2P$ 451.1993; Found 451.1998; **IR** (KBr, thin film): 3050, 2962, 2924, 1602, 1442, 1260, 1147, 1062, 1010, 837, 761, 725, 670 cm^{-1}.



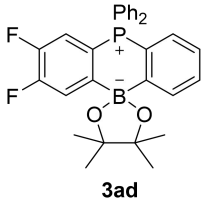
3ab

2,3,4',4',5',5'-hexamethyl-5,5-diphenyl-5*H*-spiro[dibenzo[*b*,*e*][1,4]phosphaborin-ine-10,2' -[1,3,2]dioxaborolan]-5-ium-10-uide 3ab: The crude mixture was purified by column chromatography (PE/EA:TEA = 2/1/0.01) to afford product **3ab** (65.3mg, 76%) as a white solid; m.p.: 290-291 ℃; **^{1}H NMR** (400 Hz, $CDCl_3$) *δ* 8.18 (dd, *J* = 6.8, 4.4 Hz, 1H), 7.96 (d, *J* = 4.0 Hz, 1H), 7.62 (t, *J* = 6.8 Hz, 2H), 7.55-7.51 (m, 2H), 7.51-7.45 (m, 6H), 7.44-7.39 (m, 1H), 7.11-7.01 (m, 2H), 6.85 (d, *J* = 12.8 Hz, 1H), 2.30 (s, 3H), 2.12 (s, 3H), 0.92 (s, 12H); **^{13}C NMR** (100 Hz, $CDCl_3$) *δ* 140.7 (d, *J* = 3.3 Hz), 134.6 (d, *J* = 10.0 Hz), 133.7 (d, *J* = 15.6 Hz), 132.9 (d, *J* = 14.0 Hz), 132.8 (d, *J* = 2.8 Hz), 132.3 (d, *J* = 13.3 Hz), 132.0 (d, *J* = 14.8 Hz), 131.3 (d, *J* = 12.8 Hz), 131.2 (d, *J* = 3.0 Hz), 128.8 (d, *J* = 12.5 Hz), 124.4 (d, *J* = 13.7 Hz), 124.2 (d, *J* = 85.9 Hz), 122.8 (d, *J* = 88.5 Hz), 119.10 (d, *J* = 89.5 Hz), 79.0, 26.6, 26.4, 20.1, 19.5; **^{31}P NMR** (162 MHz, $CDCl_3$) *δ* 4.00; **HRMS** (ESI) m/z: $(M+H)^+$ calcd for $C_{32}H_{35}BO_2P$ 493.2462; Found 493.2469; **IR** (KBr, thin film): 3053, 2956, 2921, 1593, 1438, 1261, 1163, 1112, 1070, 1026, 827, 725, 692 cm^{-1}.



3ac

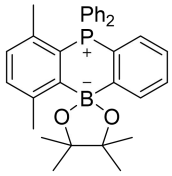
2,3-dimethoxy-4',4',5',5'-tetramethyl-5,5-diphenyl-5*H*-spiro[dibenzo[*b*,*e*][1,4]phosphabo rinine-10,2'-[1,3,2]dioxaborolan]-5-ium-10-uide 3ac: The crude mixture was purified by column chromatography (PE/EA:TEA = 2/1/0.01) to afford product **3ac** (82.5 mg, 73%) as a white solid; m.p.: 244-245 ℃; **^{1}H NMR** (400 Hz, $CDCl_3$) *δ* 8.18 (dd, *J* = 7.2, 4.0 Hz, 1H), 7.80 (d, *J* = 3.6 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 2H), 7.59-7.43 (m, 9H), 7.17-7.04 (m, 2H), 6.56 (d, *J* = 12.8 Hz, 1H), 3.99 (s, 3H), 3.61 (s, 3H), 0.96 (d, *J* = 3.6 Hz, 12H); **^{13}C NMR** (100Hz, $CDCl_3$) *δ* 152.3 (d, *J* = 3.3 Hz), 146.6 (d, *J* = 17.4 Hz), 134.5 (d, *J* = 10.0 Hz), 133.0 (d, *J* = 2.9 Hz), 132.0 (d, *J* = 14.9 Hz), 131.3 (d, *J* = 2.7 Hz), 131.2 (d, *J* = 14.9 Hz), 128.8 (d, *J* = 12.5 Hz), 124.5 (d, *J* = 13.7 Hz), 124.2 (d, *J* = 86.2 Hz), 123.2 (d, *J* = 89.4 Hz), 114.8 (d, *J* = 18.1 Hz), 114.5 (d, *J* = 16.0 Hz), 111.2(d, *J* = 95.7 Hz), 79.0, 56.1, 55.8, 26.7, 26.5; **^{31}P NMR** (162 MHz, $CDCl_3$) *δ* 3.84; **HRMS** (ESI) m/z: $(M+H)^+$ calcd for $C_{32}H_{35}BO_4P$ 525.2360; Found 525.2358; **IR** (KBr, thin film): 3058, 2958, 1585, 1544, 1485, 1438, 1263, 1163, 1110, 1070, 1053, 1614, 729, 690 cm^{-1}.



3ad

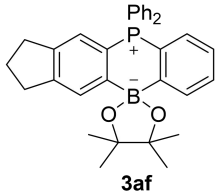
2,3-difluoro-4',4',5',5'-tetramethyl-5,5-diphenyl-5*H*-spiro[dibenzo[*b*,*e*][1,4]phos-phabor inine-10,2'-[1,3,2]dioxaborolan]-5-ium-10-uide 3ad: The crude mixture was purified by column chromatography

(PE/EA:TEA = 2/1/0.01) to afford product **3ad** (72.0 mg, 72%) as a white solid; m.p.: 284-285 ℃; **^{1}H NMR** (400 Hz, $CDCl_3$) δ 8.16 (dd, J = 7.6, 4.4 Hz, 1H), 7.97 (ddd, J = 10.8, 8.4, 4.0 Hz, 1H), 7.73-7.65 (m, 2H), 7.59-7.44 (m, 9H), 7.18-7.08 (m, 2H), 6.91 (ddd, J = 12.8, 10.0, 6.8 Hz, 1H), 0.90 (s, 12H); **^{13}C NMR** (100Hz, $CDCl_3$) δ 154.6- 151.9 (m), 149.7-146.8 (m), 134.50, 134.6 (d, J = 10.3 Hz), 133.4 (d, J = 12.8 Hz), 132.0 (d, J = 14.9 Hz), 131.7 (d, J = 3.2 Hz), 131.6 (d, J = 13.6 Hz), 129.1 (d, J = 12.6 Hz), 124.9 (d, J = 14.0 Hz), 123.0 (d, J = 87.0 Hz), 121.9 (d, J = 89.0 Hz), 120.8 (dd, J = 17.6, 13.6 Hz), 120.6 – 120.2 (m), 118.7-117.6 (m), 79.3, 26.4; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 4.22; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -133.07 (d, J = 19.6 Hz), -143.2 (d, J = 16.2 Hz); **HRMS** (ESI) m/z: $(M+H)^+$ calcd for $C_{30}H_{29}BF_2O_2P$ 501.1961; Found 501.1966; **IR** (KBr, thin film): 2958, 2921, 1579, 1467, 1441, 1273, 1153, 1107, 1026, 904, 756, 730, 690 cm^{-1}.



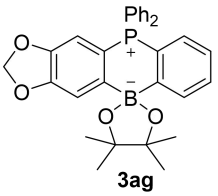
3ae

1,4,4',4',5',5'-hexamethyl-5,5-diphenyl-5*H*-spiro[dibenzo[*b*,*e*][1,4]phosphaborin-ine-10,2' -[1,3,2]dioxaborolan]-5-ium-10-uide 3ae: The crude mixture was purified by column chromatography (PE/EA:TEA = 2/1/0.01) to afford product **3ae** (69.9 mg, 71%) as a white solid; m.p.: 248-249 ℃; **^{1}H NMR** (400 Hz, $CDCl_3$) δ 8.02 (dd, J = 7.0, 4.0 Hz, 1H), 7.77 (dd, J = 13.6, 8.0 Hz, 2H), 7.62-7.53 (m, 2H), 7.52-7.46 (m, 2H), 7.43-7.35 (m, 3H), 7.32-7.19 (m, 2H), 7.09 (d, J = 7.6 Hz, 1H), 7.03 (dd, J = 12.0, 7.2 Hz, 1H), 6.85 (dd, J = 12.0, 7.6 Hz, 1H), 6.79 (t, J = 6.8 Hz, 1H), 2.81 (s, 3H), 1.73 (s, 3H), 1.11 (s, 3H), 1.03 (s, 3H), 0.37 (s, 3H), 0.16 (s, 3H); **^{13}C NMR** (100 Hz, $CDCl_3$) δ 138.8 (d, J = 15.2 Hz), 138.4 (d, J = 12.0 Hz), 134.0 (d, J = 3.5 Hz), 133.9 (d, J = 9.3 Hz), 133.3 (d, J = 10.2 Hz), 132.4 (d, J = 2.3 Hz), 132.3 (d, J = 12.0 Hz), 131.7 (d, J = 3.2 Hz), 130.8 (d, J = 3.3 Hz), 129.9 (d, J = 14.2 Hz), 129.1 (d, J = 11.5 Hz), 128.4 (d, J = 13.2 Hz), 128.4 (d, J = 80.5 Hz), 127.6 (d, J = 13.9 Hz), 126.1 (d, J = 3.8 Hz), 125.2 (d, J = 1.0 Hz), 124.2 (d, J = 14.0 Hz), 122.1 (d, J = 87.4 Hz), 79.9, 78.0, 26.4, 25.3, 24.9, 24.5, 23.6 (d, J = 5.1 Hz), 22.7; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 3.27; **HRMS** (ESI) m/z: $(M+H)^+$ calcd for $C_{32}H_{35}BO_2P$ 493.2462; Found 493.2469; **IR** (KBr, thin film): 33040, 2960, 2921, 1485, 1375, 1265, 1161, 1115, 1072, 1026, 827, 736, 715, 702 cm^{-1}.

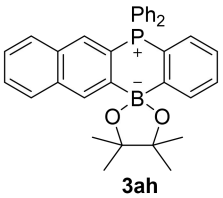


3af

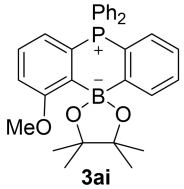
4',4',5',5'-tetramethyl-5,5-diphenyl-1,2,3,5-tetrahydrospiro[benzo[*b*]indeno[5,6-*e*][1,4] phosphaborinine-10,2'-[1,3,2] dioxaborolan]-5-ium-10-uide 3af: The crude mixture was purified by column chromatography (PE/EA:TEA = 2/1/0.01) to afford product **3af** (77.7 mg, 77%) as a white solid; m.p.: 297-298 ℃; **^{1}H NMR** (400 Hz, $CDCl_3$) δ 8.19 (dd, J = 7.2, 4.4 Hz, 1H), 8.06 (d, J = 3.6 Hz, 1H), 7.63 (t, J = 6.4 Hz, 2H), 7.56-7.51 (m, 2H), 7.51-7.44 (m, 6H), 7.44-7.40 (m, 1H), 7.11-7.01 (m, 2H), 6.96 (d, J = 12.8 Hz, 1H), 2.93 (t, J = 7.2 Hz, 2H), 2.77 (t, J = 7.2 Hz, 2H), 2.07-1.97 (m, 2H), 0.91 (s, 12H); **^{13}C NMR** (100Hz, $CDCl_3$) δ 148.8 (d, J = 3.2 Hz), 140.4(d, J = 14.7 Hz), 134.6 (d, J = 10.0 Hz), 132.8 (d, J = 2.8 Hz), 132.0 (d, J = 14.9 Hz), 131.3 (d, J = 12.9 Hz), 131.2 (d, J = 3.1 Hz), 128.7 (d, J = 12.4 Hz), 128.2 (d, J = 16.4 Hz), 127.4 (d, J = 13.5 Hz), 124.4 (d, J = 85.9 Hz), 124.4 (d, J = 13.6 Hz), 122.8 (d, J = 88.5 Hz), 119.2 (d, J = 89.6 Hz), 79.0, 33.1, 32.5, 26.6, 26.4, 25.1; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 5.68; **HRMS** (ESI) m/z: $(M+H)^+$ calcd for $C_{33}H_{35}BO_2P$ 505.2462; Found 505.2481; **IR** (KBr, thin film): 3058, 2958, 1438, 1375, 1353, 1161, 1109, 1068, 1022, 823, 756, 725, 690 cm^{-1}.



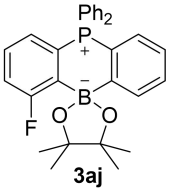
4',4',5',5'-tetramethyl-5,5-diphenyl-5*H*-spiro[benzo[5',6'][1,4]phosphaborinino[2',3':4,5]benzo[1,2-*d*][1,3]dioxole-10,2'-[1,3,2]dioxaborolan]-5-ium-10-uide 3ag: The crude mixture was purified by column chromatography (PE/EA:TEA = 2/1/0.01) to afford product **3ag** (86.4 mg, 85%) as a white solid; m.p.: 286-287 ℃; **^{1}H NMR** (400 Hz, $CDCl_3$) δ 8.16 (dd, J = 7.2, 4.4 Hz, 1H), 7.72 (d, J = 3.2 Hz, 1H), 7.66-7.60 (m, 2H), 7.55-7.43 (m, 9H), 7.14-7.02 (m, 2H), 6.54 (d, J = 12.0 Hz, 1H), 5.91 (s, 2H), 0.91 (d, J = 7.7 Hz, 12H); **^{13}C NMR** (100Hz, $CDCl_3$) δ 151.1 (d, J = 3.3 Hz), 145.3 (d, J = 21.2 Hz), 134.5 (d, J = 10.1 Hz), 133.0 (d, J = 3.2 Hz), 131.9 (d, J = 14.8 Hz), 131.3 (d, J = 6.3 Hz), 131.3 (d, J = 3.6 Hz), 128.8 (d, J = 12.6 Hz), 124.5 (d, J = 13.8 Hz), 124.2 (d, J = 86.7 Hz), 122.9 (d, J = 89.4 Hz), 112.6 (d, J = 18.2 Hz), 112.5 (d, J = 96.6 Hz), 111.1 (d, J = 16.6 Hz), 100.6, 79.1, 26.5, 26.4; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 5.30; **HRMS** (ESI) m/z: $(M+H)^+$ calcd for $C_{31}H_{31}BO_4P$ 509.2048; Found 509.2044; **IR** (KBr, thin film): 3055, 2960, 2923, 1591, 1463, 1438, 1377, 1238, 1161, 1110, 1016, 810, 736, 721 cm^{-1}.



4',4',5',5'-tetramethyl-5,5-diphenyl-5*H*-spiro[benzo[b]naphtho[2,3-*e*][1,4]phosph-aborinine-12,2'-[1,3,2]dioxaborolan]-5-ium-12-uide 3ah: The crude mixture was purified by column chromatography (PE/EA:TEA = 2/1/0.01) to afford product **3ah** (59.7 mg, 58%) as a white solid; m.p.: 257-258 ℃; **^{1}H NMR** (400 Hz, $CDCl_3$) δ 8.55 (d, J = 4.0 Hz, 1H), 8.23 (dd, J = 6.8, 4.4 Hz, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.71-7.63 (m, 3H), 7.71-7.46 (m, 11H), 7.34 (t, J = 7.6 Hz, 1H), 7.15-7.07 (m, 2H), 0.92 (d, J = 3.6 Hz, 12H); **^{13}C NMR** (100Hz, $CDCl_3$) δ 135.3 (d, J = 2.8 Hz), 134.7 (d, J = 10.1 Hz), 133.6 (d, J = 12.2 Hz), 133.1 (d, J = 2.8 Hz), 132.1 (d, J = 15.1 Hz), 131.7 (d, J = 3.0 Hz), 131.6 (d, J = 13.0 Hz), 130.7 (d, J = 15.4 Hz), 130.3 (d, J = 14.2 Hz), 128.9 (d, J = 12.6 Hz), 128.4, 128.0 (d, J = 3.4 Hz), 125.0, 124.7 (d, J = 13.7 Hz), 123.8 (d, J = 86.2 Hz), 122.7 (d, J = 87.2 Hz), 122.1 (d, J = 88.5 Hz), 79.2, 26.4; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 6.74; **HRMS** (ESI) m/z: $(M+H)^+$ calcd for $C_{34}H_{33}BO_2P$ 514.2342; Found 514.2340; **IR** (KBr, thin film): 3051, 2958, 2922, 1589, 1438, 1375, 1163, 1109, 1068, 1029, 987, 823, 748, 731, 689 cm^{-1}.

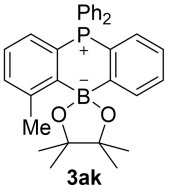


1-methoxy-4',4',5',5'-tetramethyl-5,5-diphenyl-5*H*-spiro[dibenzo[*b*,*e*][1,4]phosp-haborin ine-10,2'-[1,3,2]dioxaborolan]-5-ium-10-uide 3ai: The crude mixture was purified by column chromatography (PE/EA = 2/1) to afford product **3ai** (71.2 mg, 72%); m.p.: 209-210 ℃; **^{1}H NMR** (400 Hz, $CDCl_3$) δ 8.28 (dd, J = 6.8, 4.0 Hz, 1H), 7.64-7.57 (m, 2H), 7.52-7.40 (m, 9H), 7.13-6.99 (m, 3H), 6.93 (d, J = 8.4 Hz, 1H), 6.69 (dd, J = 12.8, 7.6 Hz, 1H), 3.83 (s, 3H), 0.80 (s, 6H), 0.72 (s, 6H); **^{13}C NMR** (100Hz, $CDCl_3$) δ 162.2 (d, J = 20.4 Hz), 134.1 (d, J = 9.9 Hz), 132.6 (d, J = 2.3 Hz), 131.9 (d, J = 14.8 Hz), 131.4 (d, J = 12.5 Hz), 131.2 (d, J = 2.9 Hz), 129.8 (d, J = 12.9 Hz), 128.6 (d, J = 12.4 Hz), 125.5 (d, J = 16.4 Hz), 125.4 (d, J = 86.3 Hz), 124.7 (d, J = 89.1 Hz), 124.4 (d, J = 11.6 Hz), 122.0 (d, J = 88.6 Hz), 113.8 (d, J = 3.0 Hz), 78.8, 55.1, 25.7, 25.4; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 5.59; **HRMS** (ESI) m/z: $(M+H)^+$ calcd for $C_{31}H_{33}BO_3P$ 495.2255; Found 495.2234; **IR** (KBr, thin film): 3053, 2960, 2927, 1556, 1438, 1350, 1247, 1110, 1074, 1014, 865, 721, 703 cm^{-1}.



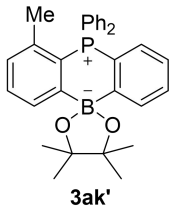
3aj

1-fluoro-4',4',5',5'-tetramethyl-5,5-diphenyl-5H-spiro[dibenzo[*b*,*e*][1,4] phosphaborinine-10,2'-[1,3,2]dioxaborolan]-5-ium-10-uide 3aj: The crude mixture was purified by column chromatography (PE/EA:TEA = 2/1/0.01 to afford product **3aj** (71.2 mg, 72%) as a white solid; m.p.: 255-256 ℃; **^{1}H NMR** (400 Hz, $CDCl_3$) δ 8.23 (dd, J = 7.2, 4.02 Hz, 1H), 7.65 (dd, J = 8.0, 4.8 Hz, 2H), 7.52-7.44 (m, 9H), 7.17-7.02 (m, 4H), 6.94-6.85 (m, 1H), 0.86 (s, 6H), 0.76 (s, 6H); **^{13}C NMR** (100Hz, CD_3OD) δ 164.5 (dd, J = 245.0, 21.5 Hz), 134.3 (d, J = 10.0 Hz), 133.0 (d, J = 2.8 Hz), 131.8 (d, J = 22.1 Hz), 131.7 (d, J = 11.3 Hz), 128.8 (d, J = 12.6 Hz), 127.0-125.9 (m), 126.0 (dd, J = 16.8, 7.8 Hz), 124.7 (d, J = 13.5 Hz), 124.2 (d, J = 86.7 Hz) , 121.7 (d, J = 88.0 Hz), 119.9 (dd, J = 28.1, 2.9 Hz), 79.1, 25.9, 25.2; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 5.59; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.28 (d, J = 9.0 Hz); **HRMS** (ESI) m/z: $(M+H)^+$ calcd for $C_{30}H_{30}BFO_2P$ 483.2055; Found 483.2044; **IR** (KBr, thin film): 3055, 2960, 2923, 1436, 1377, 1353, 1226, 1161, 1113, 1074, 1020, 821, 762, 727, 703 cm^{-1}.



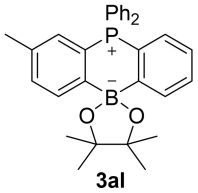
3ak

1,4',4',5',5'-pentamethyl-5,5-diphenyl-5*H*-spiro[dibenzo[*b*,*e*][1,4]phosphaborin-ine-10,2'-[1,3,2]dioxaborolan]-5-ium-10-uide 3ak: The crude mixture was purified by column chromatography (PE/EA:TEA = 5/1:0.01) to afford product **3ak** (42.6 mg, 45%) as a white solid; m.p.: 257-258 ℃; **^{1}H NMR** (400 Hz, $CDCl_3$) δ 8.09 (dd, J = 7.6, 4.0 Hz, 1H), 7.69-7.48 (m, 4H), 7.49-7.41 (m, 5H), 7.26 (t, J = 9.6 Hz, 2H), 7.17 (d, J = 6.8 Hz, 1H), 7.13-7.05 (m, 2H),6.99-6.86 (m, 2H), 2.87 (s, 3H), 1.18 (s, 3H), 1.06 (s, 3H), 0.40 (s, 3H), 0.21 (s, 3H); **^{13}C NMR** (100Hz, $CDCl_3$) δ 141.7 (d, J = 14.9 Hz), 135.3 (d, J = 8.9 Hz), 133.9 (d, J = 3.3 Hz), 133.1 (d, J = 2.2 Hz), 132.7 (d, J = 10.2 Hz), 131.9 (d, J = 12.5 Hz), 131.7 (d, J = 2.8 Hz), 131.1 (d, J = 3.2 Hz), 130.9 (d, J = 8.7 Hz), 130.73 (d, J = 10.4 Hz), 129.0 (d, J = 11.3 Hz), 128.3 (d, J = 13.4 Hz), 126.9 (d, J = 91.1 Hz), 125.7 (d, J = 82.5 Hz), 124.2 (d, J = 13.6 Hz), 123.8 (d, J = 88.3 Hz), 123.7 (d, J = 15.5 Hz), 122.79 (d, J = 89.2 Hz), 80.1, 77.9, 26.8, 25.4, 24.9, 24.6, 22.6 (d, J = 1.6 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 7.68; **HRMS** (ESI) m/z: $(M+H)^+$ calcd for $C_{31}H_{33}BO_2P$ 479.2306; Found 479.2301; **IR** (KBr, thin film): 3049, 2958, 2921, 1587, 1438, 1353, 1164, 1112, 1080, 1014, 873, 738, 721, 702 cm^{-1}.



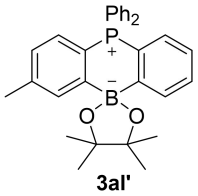
3ak'

4,4',4',5',5'-pentamethyl-5,5-diphenyl-5*H*-spiro[dibenzo[*b*,*e*][1,4]phosphaborin-ine-10,2'-[1,3,2]dioxaborolan]-5-ium-10-uide 3ak': The crude mixture was purified by column chromatography (PE/EA:TEA = 2/1/0.01) to afford product **3ak'** (42.1 mg, 44%) as a white solid; m.p.: 304-305 ℃; **^{1}H NMR** (400 Hz, $CDCl_3$) δ 8.16-8.07 (m, 2H), 7.62 (td, J = 7.2, 2.0 Hz, 2H), 7.56 (dd, J = 12.8, 7.2 Hz, 4H), 7.51-7.44 (m, 4H), 7.44-7.35 (m, 2H), 7.09-7.02 (m, 1H), 6.98-6.88 (m, 2H), 1.77 (s, 3H), 0.85 (s, 12H); **^{13}C NMR** (100Hz, $CDCl_3$) δ 140.6 (d, J = 12.1 Hz), 134.1 (d, J = 10.2 Hz), 132.7 (d, J = 3.2 Hz), 132.1 (d, J = 13.7 Hz), 131.5 (d, J = 3.3 Hz), 131.2 (d, J = 3.2 Hz), 131.1 (d, J = 7.6 Hz), 129.7 (d, J = 14.9 Hz), 129.0 (d, J = 12.4 Hz), 128.3 (d, J = 12.3 Hz), 125.2 (d, J = 83.8 Hz), 124.6 (d, J = 90.0 Hz), 124.55 (d, J = 13.9 Hz), 120.1 (d, J = 86.1 Hz), 79.0, 26.4, 26.2, 23.3 (d, J = 4.6 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 0.51; **HRMS** (ESI) m/z: $(M+H)^+$ calcd for $C_{31}H_{33}BO_2P$ 479.2306; Found 479.2301; **IR** (KBr, thin film): 3045, 2958, 2923, 1438, 1375, 1353, 1161, 1110, 1070, 1024, 811, 756, 725, 702 cm^{-1}.



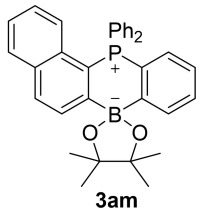
3al

3,4',4',5',5'-pentamethyl-5,5-diphenyl-5*H*-spiro[dibenzo[*b*,*e*][1,4]phosphaborinine-10,2'-[1,3,2]dioxaborolan]-5-ium-10-uide 3al: The crude mixture was purified by column chromatography (PE/EA:TEA = 2/1/0.01) to afford product **3al** (41.1 mg, 43%) as a white solid; m.p.: 110-111 ℃; **^{1}H NMR** (400 Hz, $CDCl_3$) δ8.19 (dd, J = 7.6, 4.4 Hz, 1H), 8.02 (s, 1H), 7.63 (t, J = 6.8 Hz, 2H), 7.56-7.41 (m, 9H), 7.12-6.91 (m, 4H), 2.37 (s, 3H), 0.91 (d, J = 4.0 Hz, 12H); **^{13}C NMR** (100Hz, $CDCl_3$) δ 141.8 (d, J = 3.2 Hz), 134.6 (d, J = 10.1 Hz), 132.9 (d, J = 12.4 Hz), 132.9 (d, J = 2.8 Hz), 132.1 (d, J = 14.8 Hz), 131.7 (d, J = 13.4 Hz), 131.4 (d, J = 12.9 Hz), 131.3 (d, J = 3.1 Hz), 128.8 (d, J = 12.5 Hz), 125.5 (d, J = 14.2 Hz), 124.5 (d, J = 12.9 Hz), 124.1 (d, J = 86.4 Hz), 122.7 (d, J = 88.6 Hz), 118.9 (d, J = 90.5 Hz), 79.0, 26.5, 26.4, 22.0 (d, J = 1.3 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 4.90; **HRMS** (ESI) m/z: $(M+H)^+$ calcd for $C_{31}H_{33}BO_2P$ 479.2306; Found 479.2316; **IR** (KBr, thin film): 3055, 2960, 2923, 1587, 1438, 1377, 1163, 1112, 1072, 1010, 908, 800, 727, 703 cm^{-1}.



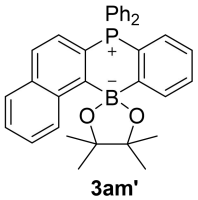
3al'

2,4',4',5',5'-pentamethyl-5,5-diphenyl-5*H*-spiro[dibenzo[*b*,*e*][1,4]phosphaborin-ine-10,2'-[1,3,2]dioxaborolan]-5-ium-10-uide 13al': The crude mixture was purified by column chromatography (PE/EA:TEA = 2/1/0.01) to afford product **13al'** (41.1 mg, 43%) as a white solid; m.p.: 279-280 ℃; **^{1}H NMR** (400 Hz, $CDCl_3$) δ 8.18 (dd, J = 7.6, 4.4 Hz, 1H), 8.08 (dd, J = 7.6, 4.4 Hz, 1H), 7.65 (t, J = 6.8 Hz, 2H), 7.58-7.42 (m, 9H), 7.30 (d, J = 7.6 Hz, 1H), 7.15-7.03 (m, 2H), 6.90 (d, J = 13.2 Hz, 1H), 2.23 (s, 3H), 0.91 (s, 12H); **^{13}C NMR** (100Hz, $CDCl_3$) δ134.6 (d, J = 10.1 Hz), 133.9 (d, J = 14.0 Hz), 132.9 (d, J = 2.9 Hz), 132.6 (d, J = 3.5 Hz), 132.2 (d, J = 16.4 Hz), 132.0 (d, J = 15.7 Hz), 131.6 (d, J = 13.8 Hz), 131.4 (d, J = 13.5 Hz), 132.3 (d, J = 4.1 Hz), 128.8 (d, J = 12.4 Hz), 124.5 (d, J = 12.7 Hz), 124.0 (d, J = 85.5 Hz), 122.6, 122.4 (d, J = 88.2 Hz), 79.0, 26.4, 26.4,21.2; **HRMS** (ESI) m/z: $(M+H)^+$ calcd for $C_{31}H_{33}BO_2P$ 479.2306; Found 478.2288; **IR** (KBr, thin film): 3055, 2958, 2921, 1586, 1440, 1376, 1166, 1112, 1074, 1012, 820, 757, 725, 690 cm^{-1}.



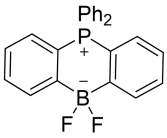
3am

4',4',5',5'-tetramethyl-12,12-diphenyl-12*H*-spiro[benzo[b]naphtho[2,1-*e*][1,4]phosphaborinine-7,2'-[1,3,2]dioxaborolan]-12-ium-7-uide 3am: The crude mixture was purified by column chromatography (PE/EA:TEA = 2/1/0.01) to afford product **3am** (25.7 mg, 25%) as a white solid; m.p.: 271-272 ℃; **^{1}H NMR** (400 Hz, $CDCl_3$) δ 8.51 (dd, J = 8.0, 3.6 Hz, 1H), 8.18 (dd, J = 6.8, 4.0 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.63-7.52 (m, 6H), 7.48-7.40 (m, 5H), 7.29-7.21 (m, 2H), 7.11-6.98 (m, 2H), 6.90 (dd, J = 12.8, 7.6 Hz, 1H), 0.90 (s, 6H), 0.84 (s, 6H); **^{13}C NMR** (100Hz, CD_3OD) δ 134.0 (d, J = 10.2 Hz), 133.6 (d, J = 12.4 Hz), 132.8 (d, J = 8.5 Hz), 132.7 (d, J = 2.8 Hz), 132.0 (d, J = 14.4 Hz), 131.6 (d, J = 3.4 Hz), 131.3 (d, J = 14.2 Hz), 131.1 (d, J = 2.8 Hz), 130.5 (d, J = 16.7 Hz), 129.7 (d, J = 2.1 Hz), 129.1 (d, J = 12.5 Hz), 125.6 (d, J = 83.9 Hz), 125.5 (d, J = 14.2 Hz), 125.1 (d, J = 89.1 Hz), 124.6, 124.5 (d, J = 2.7 Hz), 124.0, 115.0 (d, J = 88.9 Hz), 79.1, 26.3; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 1.14; **HRMS** (ESI) m/z: $(M+H)^+$ calcd for $C_{34}H_{33}BO_2P$ 515.2306; Found 515.2307; **IR** (KBr, thin film): 3051, 2956, 1585, 1438, 1375, 1353, 1159, 1109, 1072, 1022, 829, 744, 727, 690 cm^{-1}.



3am'

4',4',5',5'-tetramethyl-7,7-diphenyl-7*H*-spiro[benzo[b]naphtho[1,2-*e*][1,4]phosp-haborin ine-12,2'-[1,3,2]dioxaborolan]-7-ium-12-uide 3am': The crude mixture was purified by column chromatography (PE/EA:TEA = 5/1/0.01) to afford product **3am'** (72.0 mg, 70%) as a white solid; m.p.: 114-115 ℃; **^{1}H NMR** (400 Hz, $CDCl_3$) δ10.2 (d, J = 7.2 Hz, 1H), 8.25-8.16 (m, 1H), 7.75-7.66 (m, 3H), 7.64-7.54 (m, 3H), 7.53-7.48 (m, 3H), 7.48-7.41 (m, 5H), 7.31-7.22 (m, 1H), 7.15-7.10 (m, 2H), 7.09-7.02 (m, 1H), 1.17 (d, J = 7.6 Hz, 6H), 0.29 (s, 6H); **^{13}C NMR** (100Hz, CD_3OD) δ 136.5 (d, J = 16.7 Hz), 135.1 (d, J = 9.5 Hz), 134.2 (d, J = 2.8 Hz), 133.1 (d, J = 11.4 Hz), 133.0 (d, J = 6.2 Hz), 131.9, 131.8 (d, J = 12.6 Hz), 131.2 (d, J = 2.1 Hz), 131.1 (d, J = 14.6 Hz), 129.1 (d, J = 11.2 Hz), 128.4 (d, J = 13.5 Hz), 128.0, 127.4 (d, J = 14.3 Hz), 127.2, 125.0, 124.8 (d, J = 14.2 Hz), 124.4 (d, J = 13.8 Hz), 123.2 (d, J = 89.3 Hz), 118.7 (d, J = 91.7 Hz), 80.4, 78.1, 26.8, 26.2, 25.2, 24.8; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 6.35; **HRMS** (ESI) m/z: $(M+H)^+$ calcd for $C_{34}H_{33}BO_2P$ 515.2306; Found 515.2303; **IR** (KBr, thin film): 3051, 2983, 2960, 1587, 1438, 1377, 1163, 1151, 1110, 1068, 1028, 987, 812, 729, 702, 690 cm^{-1}.



4

10,10-difluoro-5,5-diphenyl-5,10-dihydrodibenzo[*b*,*e*][1,4]phosphaborinin-5-ium-10-uide 4: The crude mixture was purified by column chromatography (DCM) to afford product **4** (147.4 mg, 77%) as a white solid; m.p.: 318-319 ℃; **^{1}H NMR** (400 Hz, $CDCl_3$) δ 8.24 (dd, J = 7.2, 4.4 Hz, 2H), 7.71-7.62 (m, 4H), 7.58-7.47 (m, 8H), 7.32 (td, J = 7.6, 4.0 Hz, 2H), 7.22 (dd, J = 12.8, 7.6 Hz, 2H); **^{13}C NMR** (1 00Hz, $CDCl_3$) δ 134.0 (d, J = 10.2 Hz), 133.8 (d, J = 3.0 Hz), 133.1 (d, J = 3.3 Hz), 132.5 (d, J = 14.4 Hz), 131.2 (d, J = 12.4 Hz), 129.6 (d, J = 12.4 Hz), 126.7 (d, J = 13.4 Hz), 122.5 (d, J = 85.9 Hz), 120.9 (dt, J = 88.6, 4.5 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 4.03; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -158.86; **HRMS** (ESI) m/z: $(M+H)^+$ calcd for $C_{24}H_{19}BF_2P$ 387.1280; Found 387.1286; **IR** (KBr, thin film): 3055, 2921, 1485, 1438, 1253, 1182, 1157, 1126, 1107, 987, 865, 773, 740, 692 cm^{-1}.

3 Computational details

All theoretical calculations were performed with Gaussian 16[S4]. All structures were completely optimized by using the M06-2X-D3[S5] method and the 6-31G(d) basis set in solvent of 1,4-dioxane, which employs the integral equation formalism polarizable continuum model (IEFPCM)[S6]. Frequency calculations were carried out at the same level to confirm all the optimized structures as minima (no imaginary frequency) or transition states (only one imaginary frequency), and provided the thermal relative Gibbs free energy correction. For all transition states (TSs), intrinsic reaction coordinate (IRC)[S7] calculations were employed to verify the TS led to its relevant intermediates. The single-point energies (SPE) by using a higher computational level of the M06-2X-D3 method and the def2-TZVP basis set in solvent of 1,4-dioxane, which employs the integral equation formalism polarizable continuum model (SMD)[S8]. All thermodynamic data were corrected by Shermo[S9] software at 333.15 K, 1.0 atm. Images of the 3D structures of molecules were generated using CYLview[S10]. For all the steps, besides the M06-2X functional,

B3LYP-D3[S11] and ωB97X-D[S12] with 6-31G(d) and 6-311+G(d,p) using IEFPCM and SMD solvation modes were also employed (**Table S2**).

3.1. Test calculations.

Table S3. Different computational levels.

Level	Functional	Basis set (opt, freq)	Basis set (sp)	solvent	T (K)
L1	M06-2X-D3	6-31G(d)	6-311+G(d, p)	-	298.15
L2	M06-2X-D3	6-31G(d)	6-311+G(d, p)	1,4-dioxane	298.15
L3	ωB97X-D	6-31G(d)	6-311+G(d, p)	1,4-dioxane	298.15
L4	B3LYP-D3	6-31G(d)	6-311+G(d, p)	1,4-dioxane	298.15
L5	M06-2X-D3	6-31G(d)	def2-TZVP	1,4-dioxane	298.15
L6	M06-2X-D3	6-31G(d)	def2-TZVP	1,4-dioxane	333.15

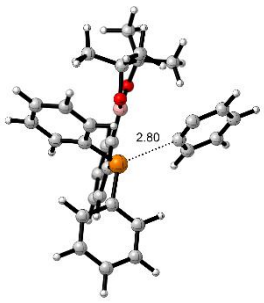
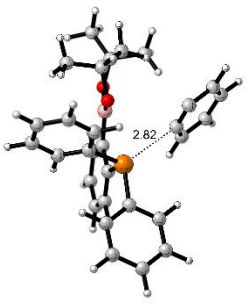
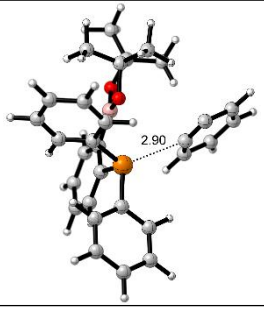
Table S4. Comparison of relative energies at different levels. Energies are given in kcal/mol.

Species	L1	L2	L3	L4	L5	L6
aryne	-230.8177	-230.8193	-230.8286	-230.9296	-230.8489	-230.8489
1a	-1446.4122	-1446.4169	-1446.5202	-1446.9719	-1446.5481	-1446.5481
Int-1	-1677.2251	-1677.2300	-1677.3422	-1677.8966	-1677.3880	-1677.3880
Ts-1	-1677.2210	-1677.2261	-1677.3385	-1677.8918	-1677.3839	-1677.3839
Int-2	-1677.2516	-1677.2597	-1677.3771	-1677.9215	-1677.4227	-1677.4227
Ts-2	-1677.2486	-1677.2567	-1677.3735	-1677.9190	-1677.4198	-1677.4198
3aa	-1677.3100	-1677.3168	-1677.4253	-1677.9766	-1677.4788	-1677.4788

Table S5. Comparison of corrective relative energies at different levels by Schermo. Energies are given in kcal/mol.

Species	L1	L2	L3	L4	L5	L6
aryne	-230.8193	-230.8209	-230.8299	-230.9298	-230.8506	-230.8544
1a	-1446.4210	-1446.4256	-1446.5266	-1446.9718	-1446.5568	-1446.5657
Int-1	-1677.2328	-1677.2376	-1677.3471	-1677.8903	-1677.3956	-1677.4058
Ts-1	-1677.2301	-1677.2350	-1677.3449	-1677.8898	-1677.3928	-1677.4029
Int-2	-1677.2618	-1677.2700	-1677.3848	-1677.9217	-1677.4331	-1677.4430
Ts-2	-1677.2589	-1677.2669	-1677.3810	-1677.9189	-1677.4300	-1677.4398
3aa	-1677.3201	-1677.3271	-1677.4348	-1677.9764	-1677.4891	-1677.4988

Table S5. The 3D structure diagram of **Ts-1** and **Ts-2** at different levels.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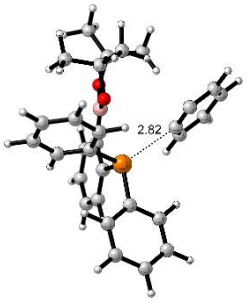	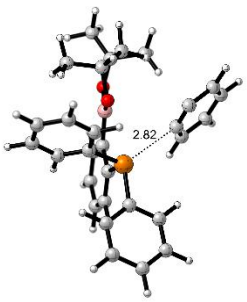	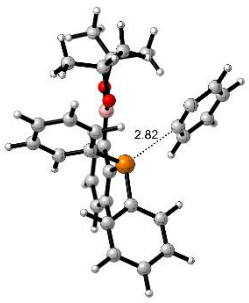
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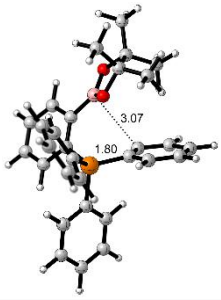	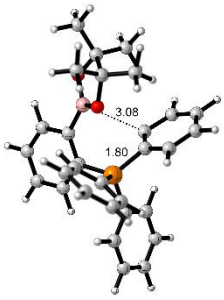	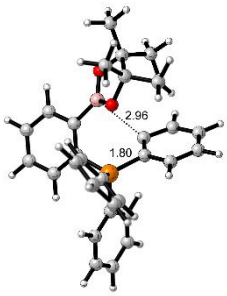
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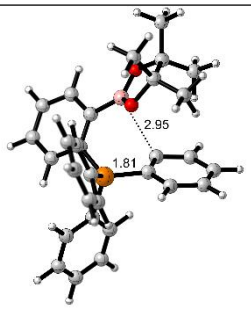	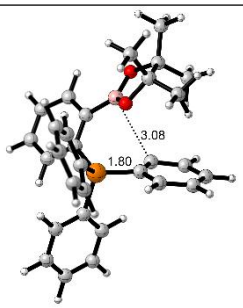	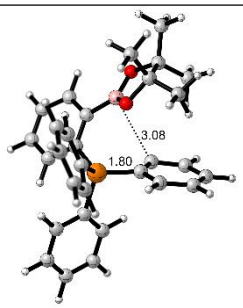
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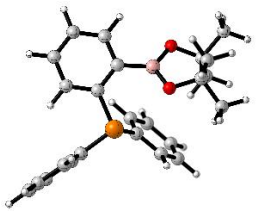

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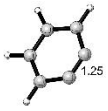

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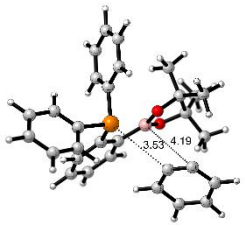

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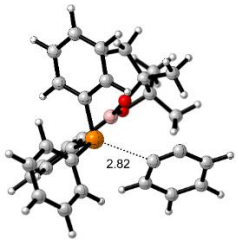
C	4.89067	-2.19593	-1.44096
H	5.15294	-3.09288	-1.99379
C	1.66618	4.4089	-0.20821
H	1.72582	5.49128	-0.14802
C	1.46404	-2.18692	3.05042
H	2.15819	-2.83617	3.57616
C	0.22551	-1.88762	3.60706
H	-0.05987	-2.29926	4.57024
O	-1.33009	0.8099	-0.3266
C	-2.44723	1.70669	-0.51321
C	-3.47279	1.16023	0.53036
O	-2.60417	0.63213	1.56101
C	-4.38296	2.21243	1.1406
H	-5.06318	1.74011	1.85495
H	-3.80949	2.97861	1.66612
H	-4.98424	2.69349	0.36178
C	-4.28242	-0.0178	-0.00566
H	-4.82125	-0.48406	0.82409
H	-5.00908	0.30559	-0.75744
H	-3.62305	-0.7681	-0.45409
C	-1.94556	3.10948	-0.17816
H	-2.71598	3.86358	-0.36731
H	-1.63737	3.17407	0.87052
H	-1.07189	3.32947	-0.79892
C	-2.89772	1.62352	-1.96172
H	-3.80904	2.21125	-2.11605
H	-2.1126	2.02736	-2.60763
H	-3.0828	0.58795	-2.25575
C	-2.16542	-2.11883	-2.37942
C	-3.4018	-2.74009	-2.48247
C	-1.39289	-2.21536	-1.40495
C	-3.6861	-3.4968	-1.3305
H	-4.09035	-2.6785	-3.31834
C	-1.54762	-2.93038	-0.23319
C	-2.79301	-3.58927	-0.24892
H	-4.63009	-4.03229	-1.27538
H	-0.84933	-3.00581	0.59271
H	-3.06866	-4.19581	0.60943



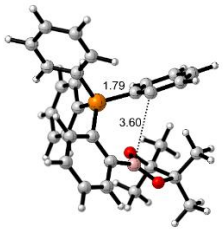
TS-1

Imaginary frequency = -45.8478 cm^{-1}

Charge = 0 Multiplicity = 1

P	1.27511	-0.11682	-0.33859
B	-1.56231	0.13709	1.16559
C	1.10648	1.69136	-0.59869
C	4.04663	0.62227	-0.40529
H	3.73703	1.64672	-0.21818
C	1.01162	-0.32107	1.48092
C	0.79071	2.12013	-1.89219
H	0.66291	1.38507	-2.68379
C	-0.30314	-0.25708	2.00356
C	3.0843	-0.38781	-0.50888
C	3.50137	-1.70048	-0.76201
H	2.75679	-2.48733	-0.8656
C	5.39956	0.32078	-0.54259
H	6.13846	1.11248	-0.4631
C	1.22627	2.63575	0.42418

H	1.45587	2.31019	1.43573
C	2.06917	-0.65807	2.33171
H	3.08117	-0.71719	1.94377
C	0.61187	3.47405	-2.16256
H	0.36669	3.79676	-3.17002
C	1.04106	3.99061	0.15453
H	1.13447	4.71745	0.95594
C	-0.50216	-0.52926	3.36196
H	-1.51336	-0.48142	3.75735
C	5.80541	-0.9911	-0.77917
H	6.86075	-1.22285	-0.88541
C	4.85418	-2.00348	-0.88716
H	5.16433	-3.02586	-1.07994
C	0.73545	4.41189	-1.13791
H	0.58934	5.46751	-1.3457
C	1.84459	-0.92101	3.68289
H	2.68301	-1.17486	4.32489
C	0.55695	-0.85945	4.20342
H	0.37804	-1.06888	5.25351
O	-1.51064	0.67075	-0.09048
C	-2.82398	1.19023	-0.38928
C	-3.72653	0.31529	0.53705
O	-2.84161	0.03503	1.65139
C	-4.9702	1.01328	1.05948
H	-5.53651	0.32792	1.69637
H	-4.71328	1.89689	1.64735
H	-5.6134	1.3179	0.22707
C	-4.0758	-1.02873	-0.097
H	-4.51298	-1.67841	0.66654
H	-4.7986	-0.90833	-0.90982
H	-3.17951	-1.5161	-0.4956
C	-2.80174	2.66584	0.00494
H	-3.73742	3.16633	-0.26284
H	-2.63555	2.78203	1.08105
H	-1.9746	3.15166	-0.52273
C	-3.08465	1.03729	-1.87819
H	-4.11358	1.32587	-2.11917
H	-2.40367	1.69259	-2.42993
H	-2.90855	0.01079	-2.20632
C	-1.12211	-1.99179	-2.46502
C	-2.0755	-2.96854	-2.76361
C	-0.52099	-2.0306	-1.35735
C	-2.2732	-3.92392	-1.75293
H	-2.63973	-3.01761	-3.69168
C	-0.59647	-2.8907	-0.2853
C	-1.55287	-3.88897	-0.54844
H	-3.0031	-4.71522	-1.90362
H	-0.02579	-2.84315	0.63638
H	-1.73401	-4.65064	0.20478

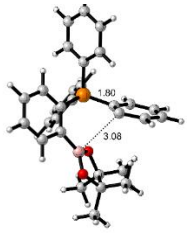


Int-2

Charge = 0 Multiplicity = 1

P	1.19257	-0.02945	-0.07013
B	-1.85354	-0.62038	0.96957
C	1.02291	1.77003	0.12079
C	3.91392	0.62057	0.18399
H	3.58271	1.54035	0.65688
C	0.72678	-0.83388	1.49603
C	1.5291	2.60122	-0.88693
H	2.04494	2.1692	-1.74141
C	-0.62196	-1.0933	1.81033
C	2.98084	-0.31084	-0.28645
C	3.41623	-1.4987	-0.88454
H	2.66972	-2.21746	-1.21804
C	5.27614	0.36903	0.04472
H	5.99673	1.09465	0.40833
C	0.37675	2.33211	1.22336
H	-0.02291	1.6915	2.00323
C	1.74455	-1.2227	2.36853
H	2.7837	-1.0389	2.11619
C	1.37962	3.98088	-0.79355
H	1.77153	4.61994	-1.57815
C	0.23417	3.7143	1.31519
H	-0.26684	4.14671	2.17545
C	-0.90031	-1.76617	3.00379
H	-1.93565	-1.98895	3.24611
C	5.70947	-0.80798	-0.56123
H	6.77229	-1.00086	-0.671
C	4.78025	-1.73826	-1.02238
H	5.11679	-2.65781	-1.49059
C	0.73119	4.53746	0.30792
H	0.61693	5.61443	0.3817

C	1.437	-1.87258	3.56284
H	2.23737	-2.17069	4.23247
C	0.11358	-2.15231	3.87835
H	-0.13124	-2.67323	4.79875
O	-1.89848	0.56806	0.29163
C	-3.29001	0.81507	-0.02561
C	-3.88954	-0.62657	0.00363
O	-3.0472	-1.28605	0.98269
C	-5.33514	-0.70624	0.46288
H	-5.66392	-1.749	0.45528
H	-5.45585	-0.31449	1.47506
H	-5.98118	-0.13839	-0.21507
C	-3.68478	-1.37145	-1.31172
H	-3.93312	-2.42563	-1.16166
H	-4.3258	-0.96888	-2.10222
H	-2.64021	-1.30882	-1.6357
C	-3.83218	1.71178	1.08604
H	-4.86792	2.00607	0.89272
H	-3.7867	1.20529	2.05564
H	-3.21607	2.61404	1.13907
C	-3.37797	1.51852	-1.36876
H	-4.42589	1.67081	-1.649
H	-2.89463	2.49788	-1.29659
H	-2.87797	0.94302	-2.14952
C	0.29595	-0.68924	-1.47747
C	-0.26906	0.15932	-2.44573
C	0.33717	-2.09525	-1.47774
C	-0.84615	-0.43605	-3.55631
H	-0.27836	1.24134	-2.32943
C	-0.28298	-2.61855	-2.64478
C	-0.84529	-1.83643	-3.65039
H	-1.29798	0.17172	-4.3357
H	-0.32829	-3.70168	-2.7805
H	-1.29907	-2.30729	-4.52139



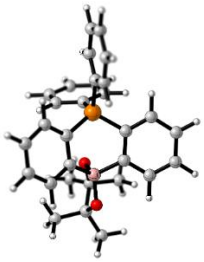
TS-2

Imaginary frequency = -46.5504 cm^{-1}

Charge = 0 Multiplicity = 1

P	-1.17816	-0.00539	0.02239
B	1.89883	-0.64588	-0.93832
C	-1.16104	1.78865	-0.26995
C	-3.97712	0.27173	-0.27676
H	-3.77517	1.16299	-0.86446
C	-0.66577	-0.84874	-1.51116
C	-1.92567	2.63714	0.54129
H	-2.58201	2.22155	1.30159
C	0.68649	-1.10767	-1.81141
C	-2.9226	-0.45723	0.28444
C	-3.18806	-1.60915	1.03272
H	-2.36074	-2.17396	1.45477
C	-5.29038	-0.14614	-0.08132
H	-6.10672	0.42348	-0.51372
C	-0.33649	2.33408	-1.25814
H	0.26263	1.68259	-1.8858
C	-1.673	-1.2507	-2.3909
H	-2.71641	-1.07394	-2.1529
C	-1.85876	4.01592	0.36726
H	-2.45397	4.66737	0.99888
C	-0.27644	3.71398	-1.42995
H	0.36348	4.13096	-2.20104
C	0.97791	-1.77716	-3.00276
H	2.01717	-1.99352	-3.23318
C	-5.55338	-1.29124	0.66808
H	-6.57855	-1.61407	0.82073
C	-4.50393	-2.02221	1.2202
H	-4.70796	-2.91533	1.80177
C	-1.03373	4.55476	-0.61787
H	-0.98438	5.63047	-0.75454
C	-1.35275	-1.90331	-3.58082
H	-2.1467	-2.20817	-4.255
C	-0.02541	-2.17349	-3.88515
H	0.23081	-2.69472	-4.8024
O	1.88179	0.49041	-0.18079
C	3.23566	0.77909	0.225
C	3.99003	-0.57087	-0.07064
O	3.13943	-1.20913	-1.05172
C	5.37788	-0.39909	-0.67028
H	5.81283	-1.38381	-0.86209
H	5.3468	0.15162	-1.61259
H	6.03189	0.13352	0.02826
C	4.04673	-1.50944	1.13058
H	4.45324	-2.47024	0.80237

H	4.68974	-1.10921	1.92035
H	3.0452	-1.68093	1.53422
C	3.69963	1.94208	-0.64964
H	4.71028	2.26778	-0.38637
H	3.68375	1.66502	-1.70855
H	3.01239	2.781	-0.50575
C	3.21637	1.18228	1.69124
H	4.23466	1.34908	2.05905
H	2.65153	2.11288	1.80192
H	2.72993	0.41686	2.30126
C	-0.26892	-0.51757	1.49327
C	-0.27971	0.3443	2.60372
C	0.27488	-1.80898	1.40938
C	0.29151	-0.11474	3.78057
H	-0.7048	1.34535	2.55771
C	0.82021	-2.20335	2.66086
C	0.8381	-1.40481	3.80369
H	0.31619	0.51594	4.66463
H	1.27684	-3.19303	2.74786
H	1.28319	-1.77642	4.72557



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Charge = 0 Multiplicity = 1

P	1.26317	0.00323	0.01141
B	-1.61302	-0.90557	-0.10014
C	0.88881	1.75081	0.2732
C	3.90976	0.92168	0.20526
H	3.49291	1.90596	0.39592
C	0.60493	-1.04815	1.31589
C	0.90351	2.62197	-0.81808
H	1.10489	2.24386	-1.8173
C	-0.71651	-1.49619	1.13877
C	3.0654	-0.16686	-0.02165
C	3.60485	-1.43767	-0.26518
H	2.94576	-2.28447	-0.44021
C	5.29172	0.73999	0.18598
H	5.94735	1.58641	0.36208
C	0.59788	2.21838	1.55512
H	0.55729	1.52542	2.39067
C	1.40347	-1.42736	2.4016
H	2.42378	-1.0639	2.4989
C	0.63025	3.97187	-0.6205
H	0.63155	4.65198	-1.46604
C	0.32717	3.56979	1.74464
H	0.0907	3.93771	2.73768
C	-1.20144	-2.38518	2.10292
H	-2.21314	-2.76565	1.98541
C	5.82599	-0.52126	-0.05792
H	6.90246	-0.65952	-0.07282
C	4.98296	-1.6106	-0.28323
H	5.40051	-2.59395	-0.47269
C	0.34261	4.4439	0.65924
H	0.1223	5.4961	0.80966
C	0.87471	-2.29499	3.35046
H	1.47613	-2.60301	4.19978
C	-0.42529	-2.77866	3.19098
H	-0.83153	-3.47028	3.92422
O	-1.79722	0.53623	0.20388
C	-3.1258	0.87399	-0.14079
C	-3.89322	-0.45993	0.14412
O	-2.95755	-1.46007	-0.23504
C	-4.2099	-0.61809	1.63529
H	-4.55099	-1.64292	1.81482
H	-3.31207	-0.44216	2.23642
H	-4.99614	0.07028	1.96424
C	-5.16774	-0.63907	-0.67267
H	-5.65047	-1.58348	-0.40176
H	-5.87687	0.17466	-0.48075
H	-4.94514	-0.66629	-1.74219
C	-3.55987	2.05795	0.71781
H	-4.61909	2.29557	0.5648
H	-3.39148	1.85364	1.77762
H	-2.96655	2.93731	0.44466
C	-3.18818	1.27473	-1.62048
H	-4.17446	1.66311	-1.8979
H	-2.44241	2.05692	-1.79724
H	-2.95097	0.42671	-2.26855
C	0.58789	-0.61014	-1.53999
C	1.36852	-0.65187	-2.70168
C	-0.73783	-1.07462	-1.48467
C	0.81539	-1.18443	-3.86053

H	2.39338	-0.28798	-2.70041
C	-1.24731	-1.62244	-2.66672
C	-0.49103	-1.67698	-3.83513
H	1.40202	-1.22664	-4.77272
H	-2.26647	-2.00223	-2.65247
H	-0.91766	-2.1066	-4.73761

4 References

[S1] Bernard, J.; Malacea-Kabbara, R.; Clemente, G. S.; Burke, B. P.; Eymin, M.-J.; Archibald, S. J.; Jugé, S. *o*-Boronato- and *o*-Trifluoroborato-Phosphonium Salts Supported by L-*α*-Amino Acid Side Chain, *J. Org. Chem*., **2015**, *80*, 4289-4298.

[S2] (a) Velder, J.; Robert, T.; Weidner, I.; Neudörfl, J.-M.; Lex, J.; Schmalz, H.-G. *Adv. Synth. Catal*. **2008**, *350*, 1309-1315. (b) Wan, C.; Guo, Y.; Chen, X.; Gu, R.; Shi, J.; Li, Y. *Org. Lett*. **2022**, *24*, 7276-7281.

[S3] (a) Porcel, S.; Bouhadir, G.; Saffon, N.; Maron, L.; Bourissou, D. *Angew. Chem., Int. Ed.* **2010**, *49*, 6186-6189; (b) Fukuda, K.; Harada, T.; Iwasawa, N.; Takaya, J. *Dalton Trans.* **2022**, *51*, 7035-7039. (c) Ito, T.; Iwasawa, N.; Takaya, J. *Angew. Chem. Int. Ed*. 2020, *59*, 11913-11917.

[S4] Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

[S5] (a) Zhao, Y. and Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215-241; (b) Zhao, Y. and Truhlar, D. G. *Acc. Chem. Res.* **2008**, *41*, 157-167.

[S6] (a) Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *106* , 5151-5158; (b) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102* (*11*), 1995-2001.

[S7] (a) Fukui, K. *J. Phys. Chem.* **2002**, *74*, 4161-4163.; (b) Fukui, K. *Acc. Chem. Res.* **2002**, *14*, 363-368.

[S8] (a) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2009**, *113*, 6378-6396; (b) Engelage, E.; Schulz, N.; Heinen, F.; Huber, S. M.; Truhlar, D. G.; Cramer, C. J. *Chem. Eur. J.* **2018**, *24*, 15983-15987.

[S9] Lu, T.; Chen, Q. *Comput. Theor. Chem*. **2021**, *1200*, 113249.

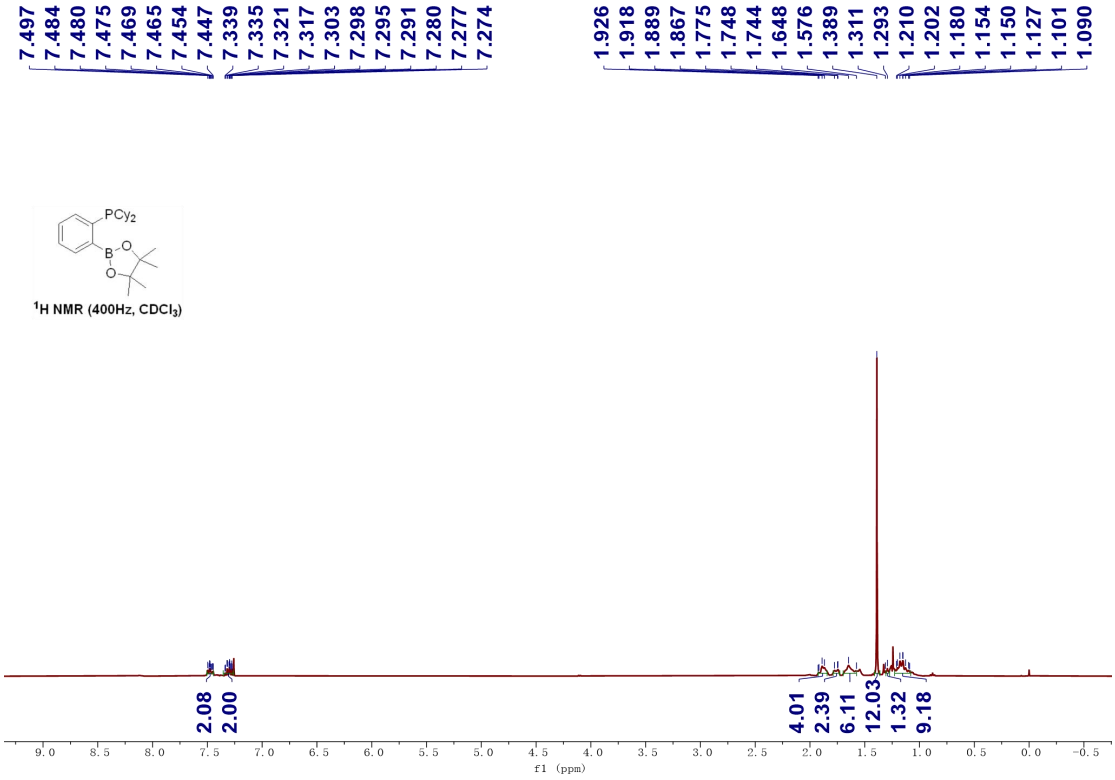
[S10] CYLview, 1.0b; Legault, C. Y., Université de Sherbrooke, 2009; (http://www.cylview.org).

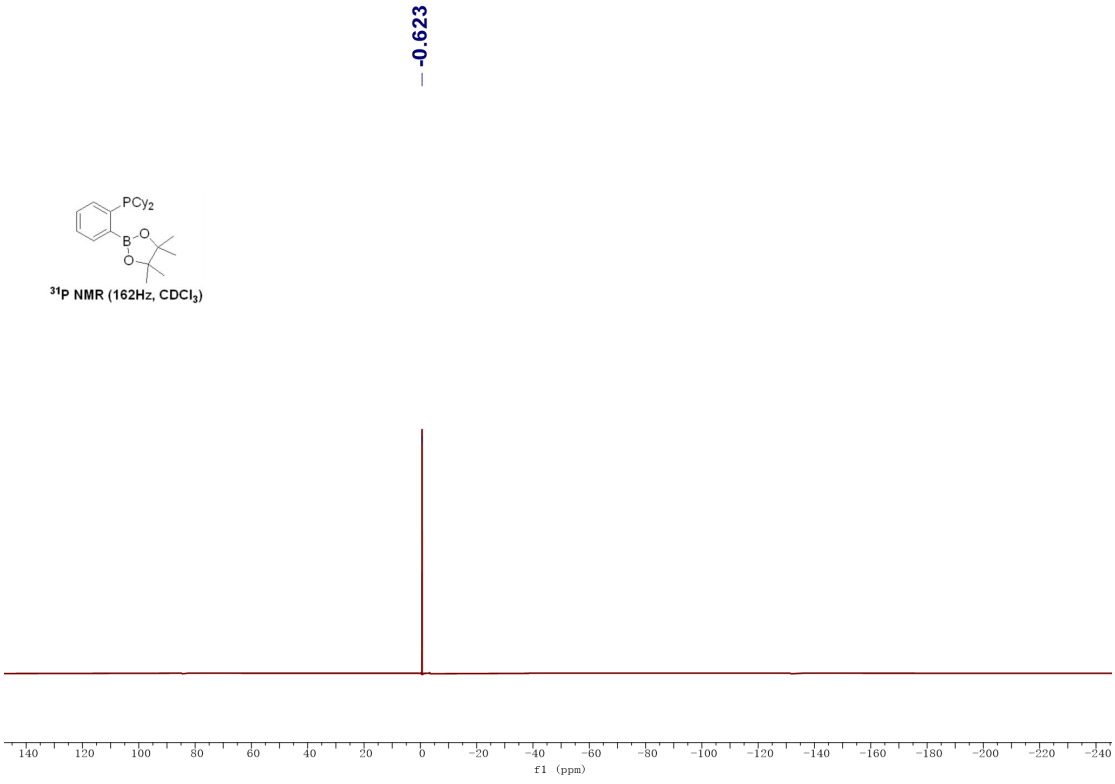
[S11] (a) Lee, C.; Yang, W.; Parr, R.G. *Phys. Rev. B* **1988**, *37*, 785–789; (b) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623–11627.

[S12] Chai, J.D.; Head-Gordon, M. Phys. *Chem. Chem. Phys.* **2008**, *10*, 6615–6620.

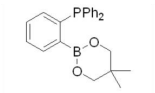
5 NMR Spectra of Compounds

1k

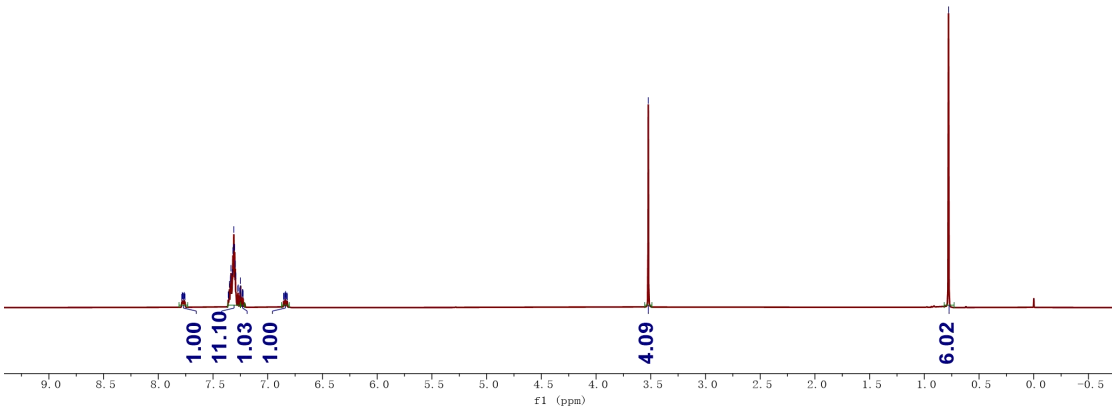


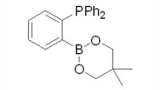


1l

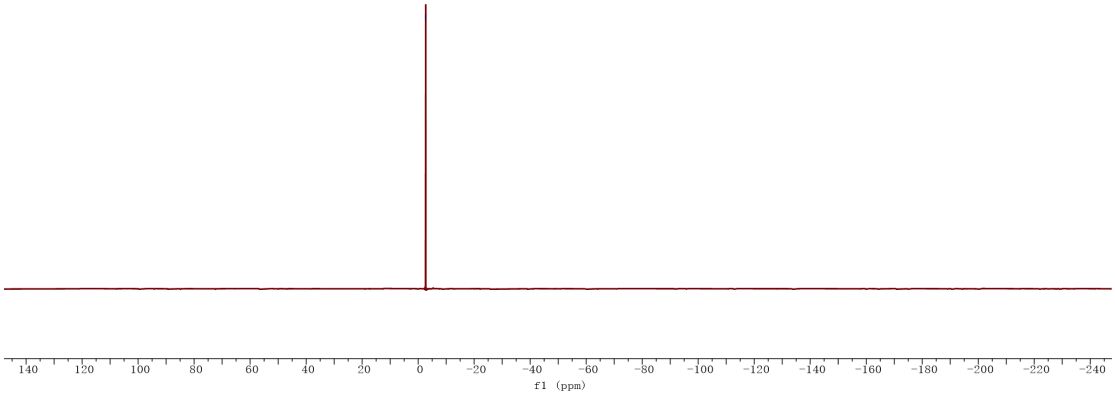


^{1}H NMR (400Hz, $CDCl_3$)

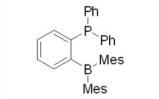




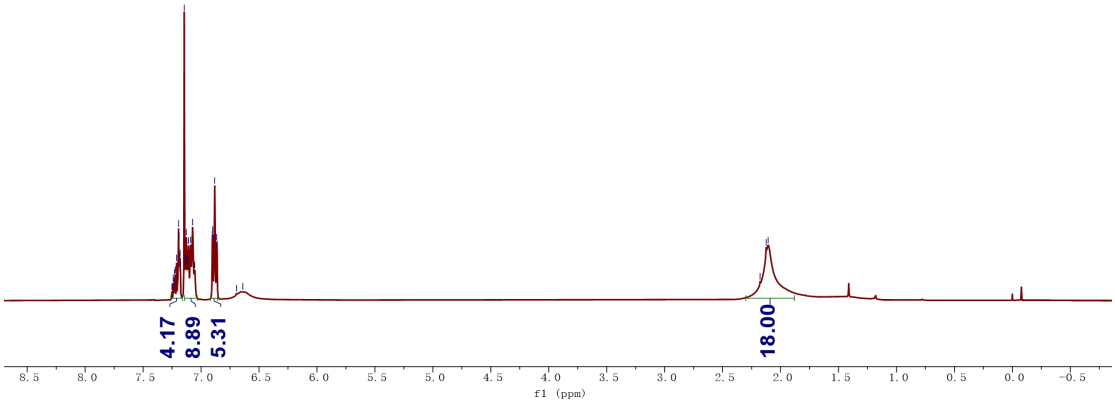
^{31}P NMR (162Hz, $CDCl_3$)

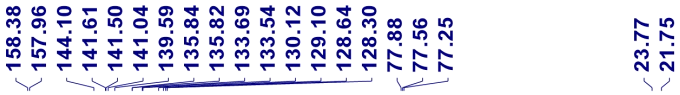


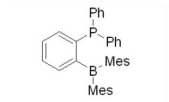
1m



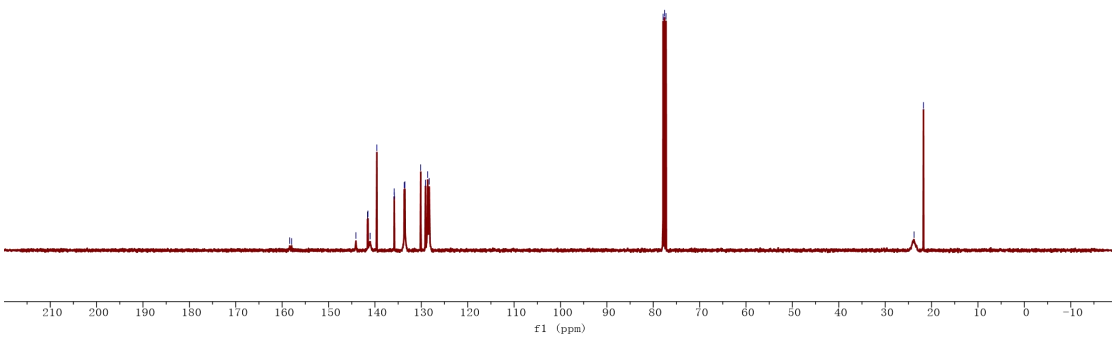
^{1}H NMR (400 Hz, $CDCl_3$)

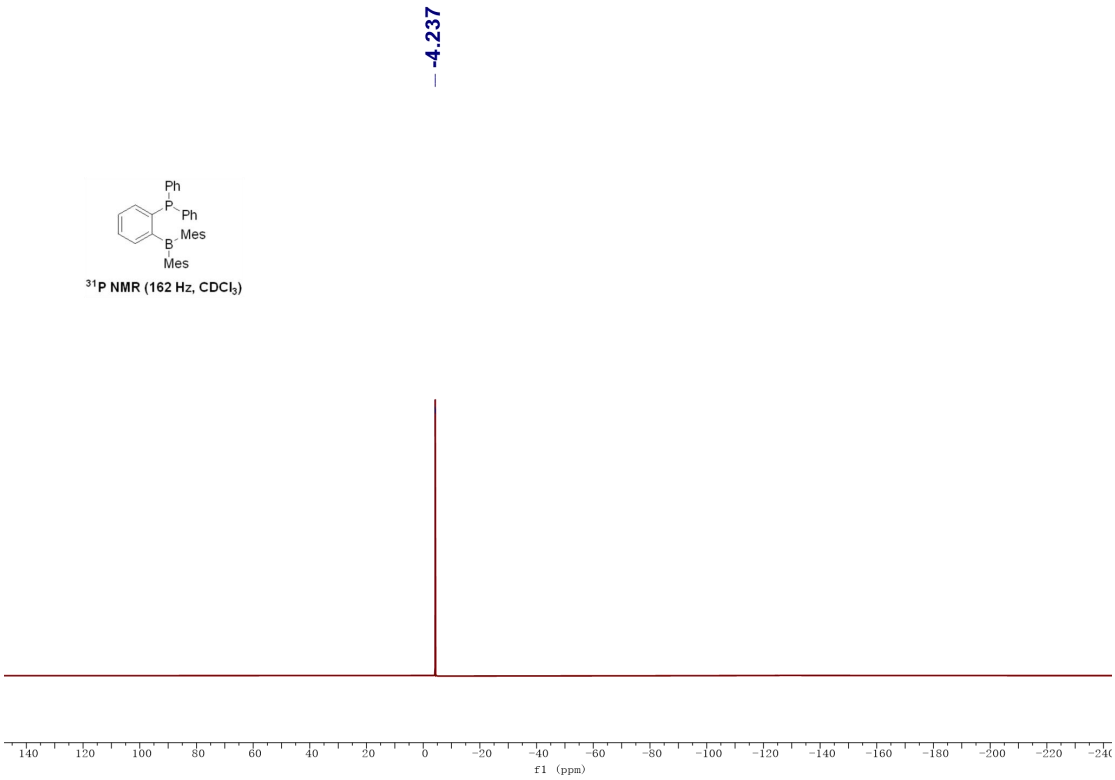




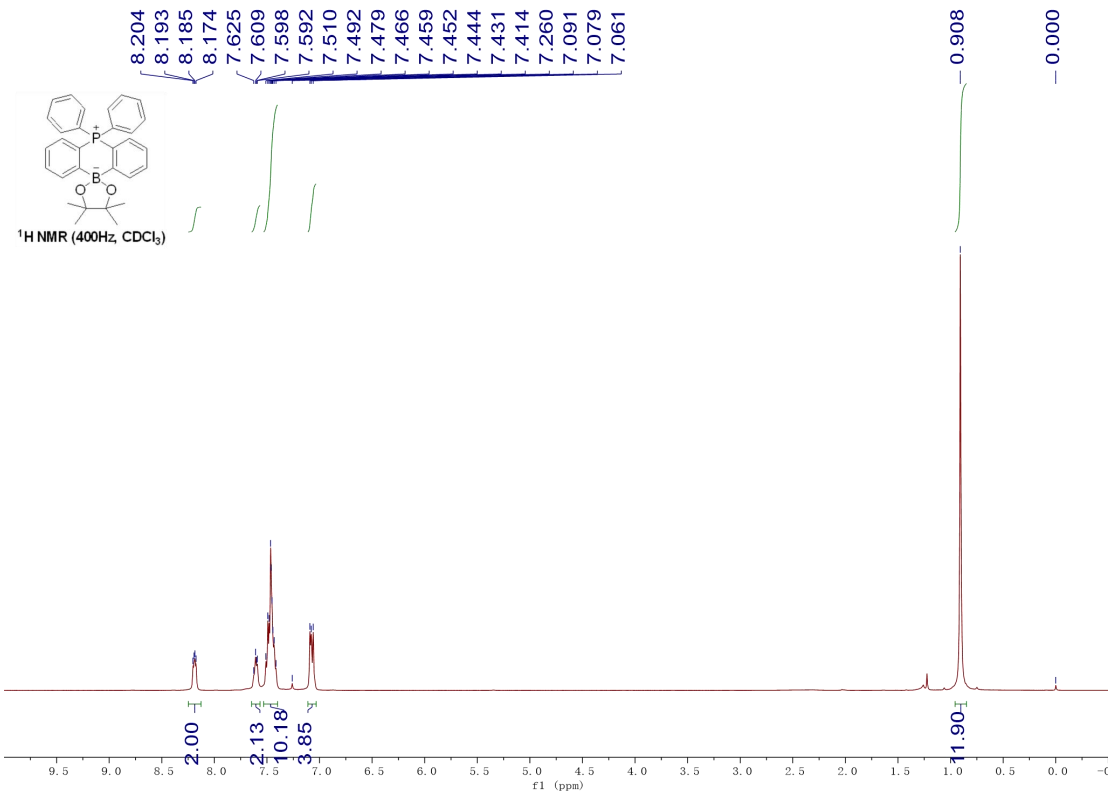


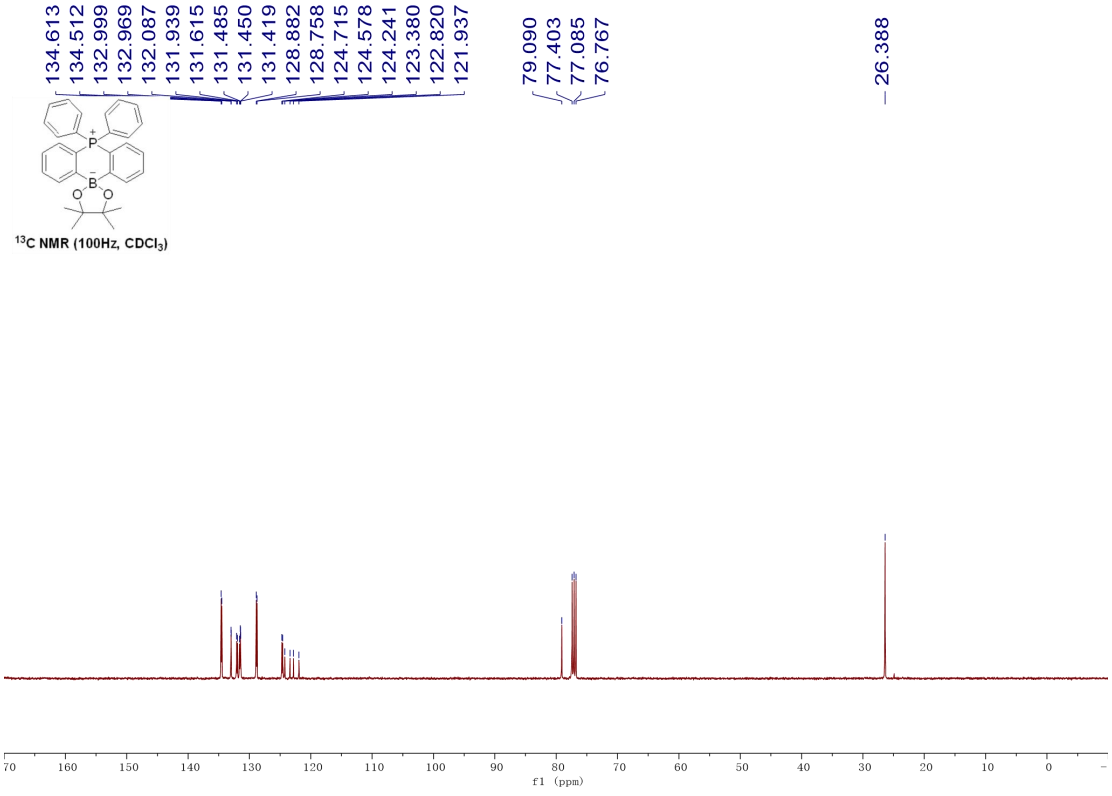
^{13}C NMR (100 Hz, $CDCl_3$)



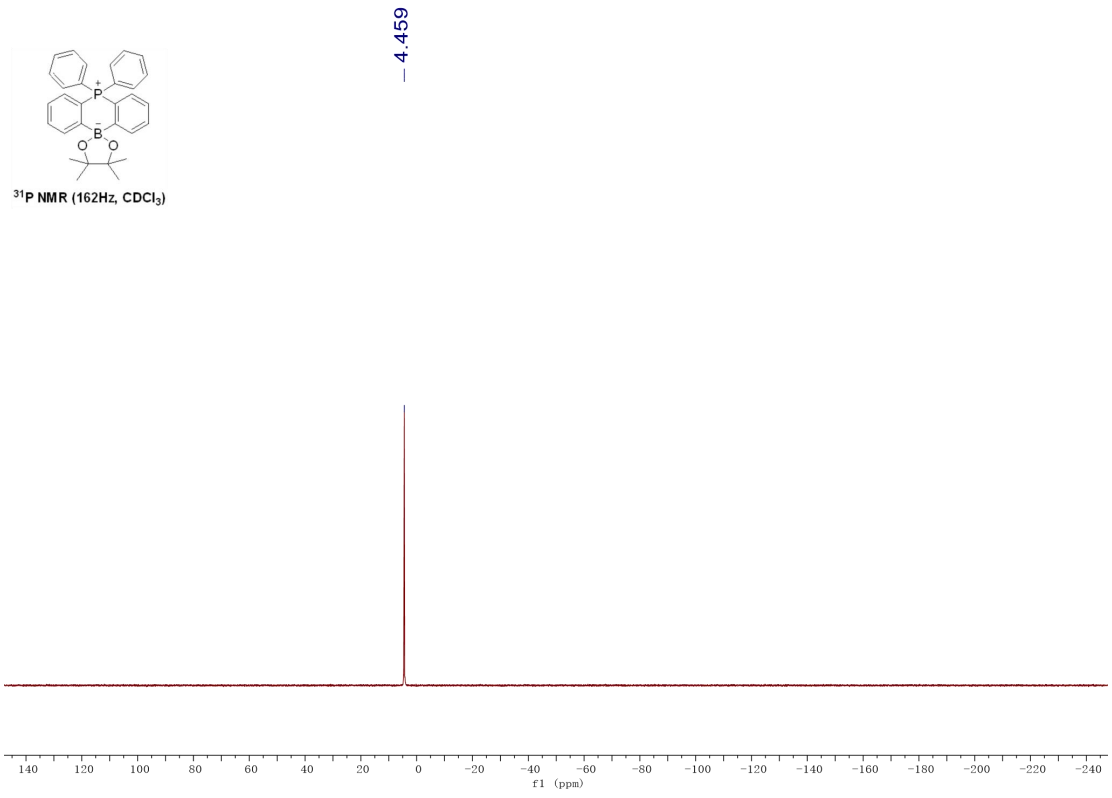

-4.237
Ph
P
Ph
Mes
B
Mes
31P NMR (162 Hz, CDCl3)
f1 (ppm)

3aa


8.204
8.193
8.185
8.174
7.625
7.609
7.598
7.592
7.510
7.492
7.479
7.466
7.459
7.452
7.444
7.431
7.414
7.260
7.091
7.079
7.061
0.908
0.000
1H NMR (400Hz, CDCl3)
2.00
2.13
10.18
3.85
11.90
f1 (ppm)

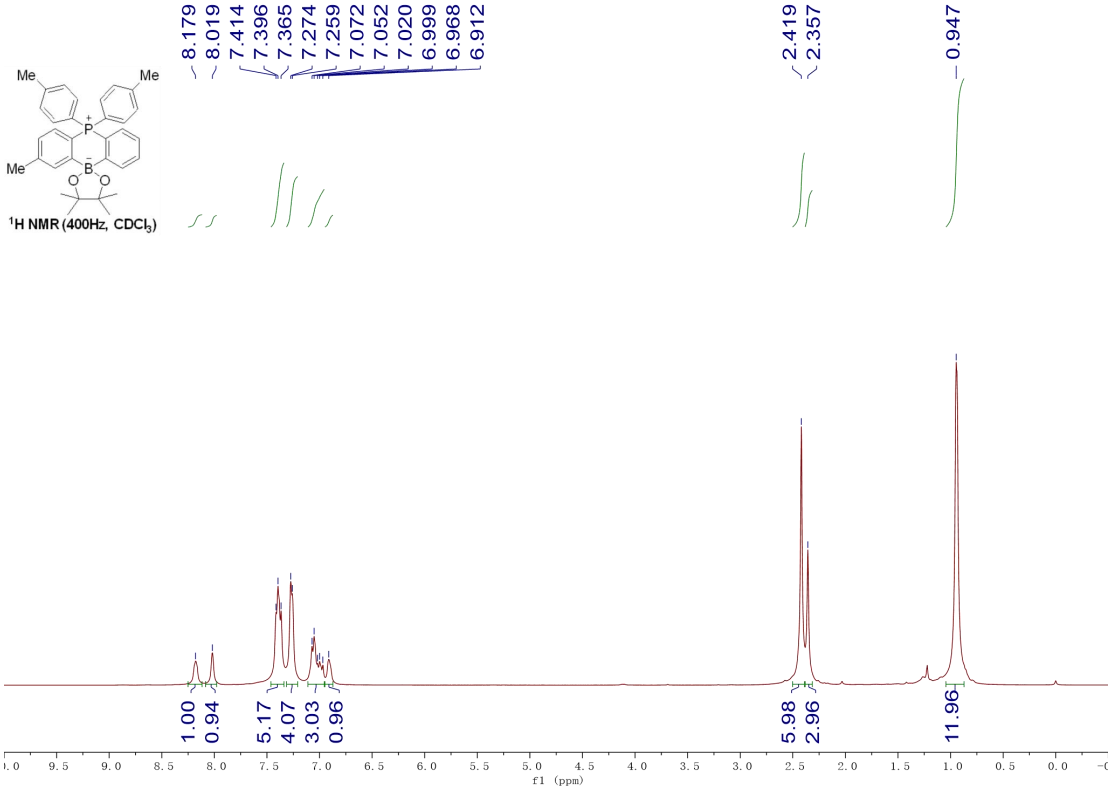


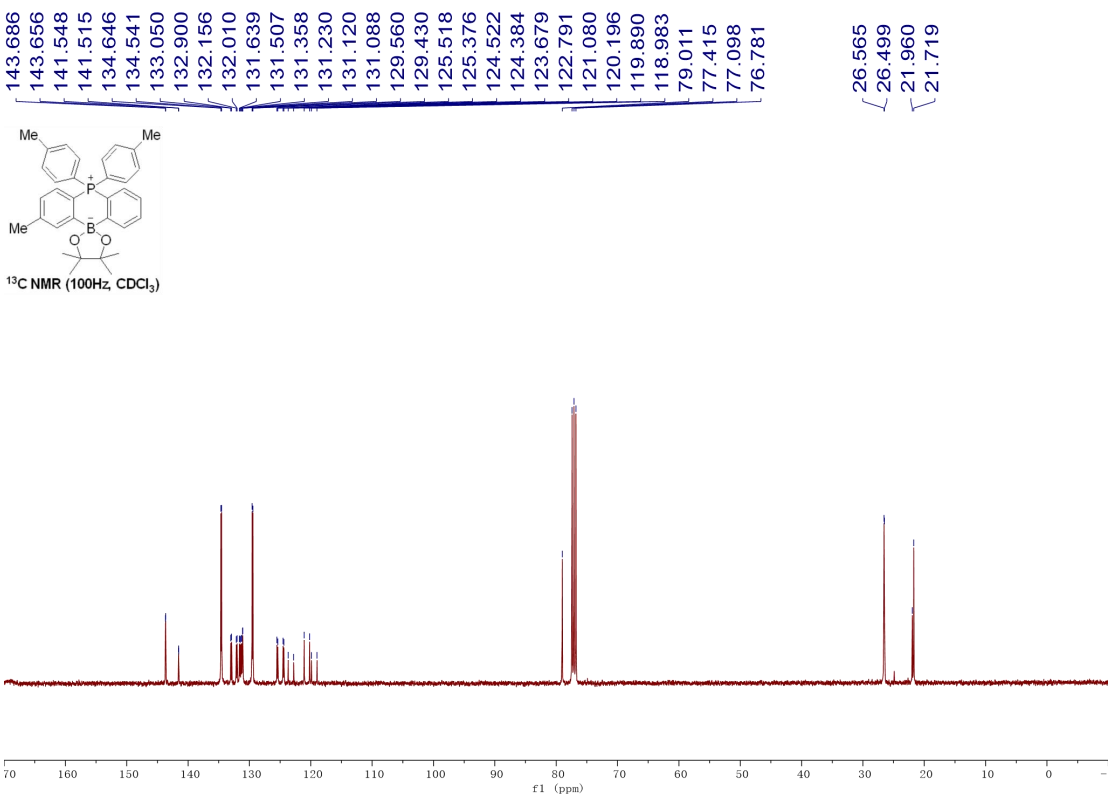
^{13}C NMR (100Hz, $CDCl_3$)

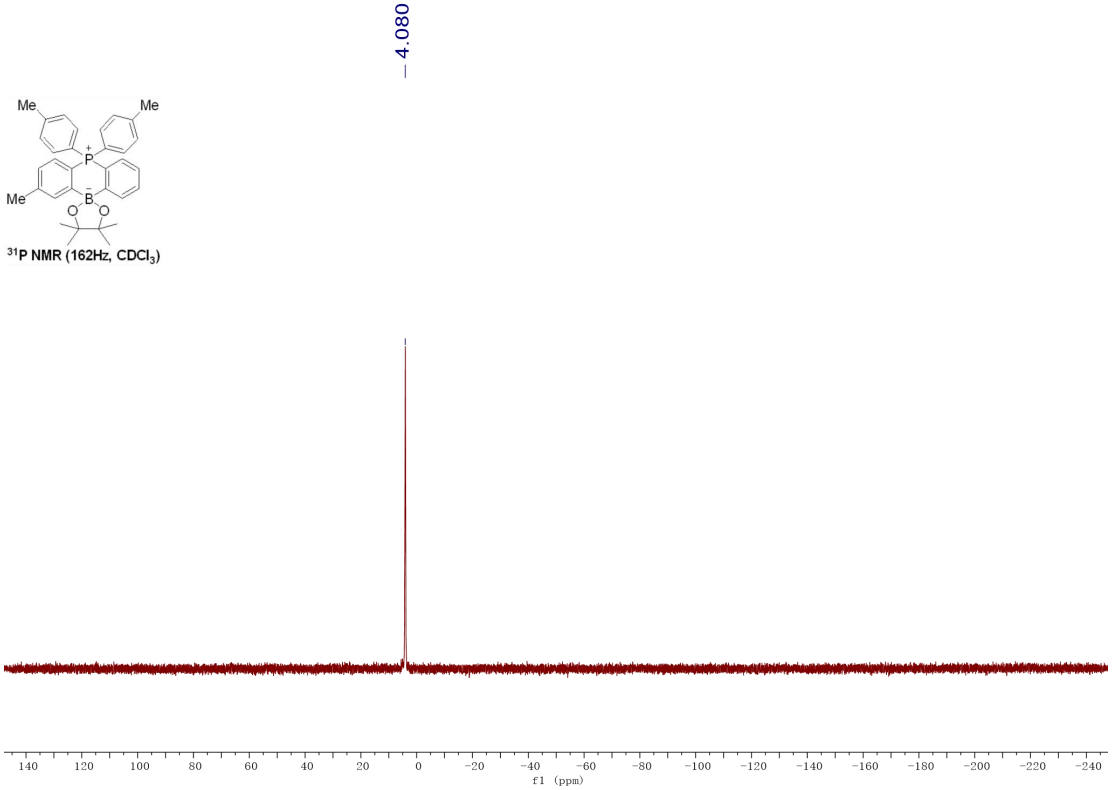


^{31}P NMR (162Hz, $CDCl_3$)

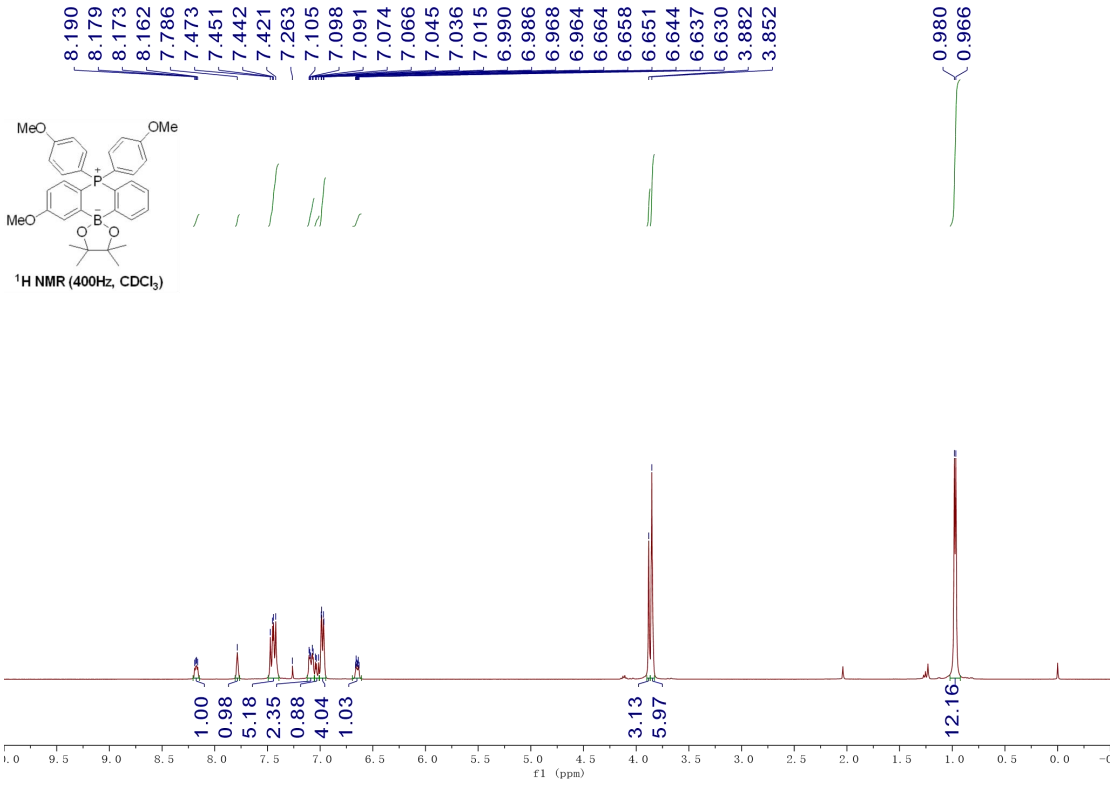
3ba

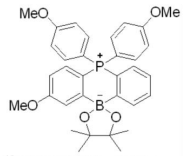

8.179
8.019
7.414
7.396
7.365
7.274
7.259
7.072
7.052
7.020
6.999
6.968
6.912
2.419
2.357
0.947
Me
Me
Me
P
B
O
O
1H NMR (400Hz, CDCl3)
1.00
0.94
5.17
4.07
3.03
0.96
5.98
2.96
11.96
f1 (ppm)


143.686
143.656
141.548
141.515
134.646
134.541
133.050
132.900
132.156
132.010
131.639
131.507
131.358
131.230
131.120
131.088
129.560
129.430
125.518
125.376
124.522
124.384
123.679
122.791
121.080
120.196
119.890
118.983
79.011
77.415
77.098
76.781
26.565
26.499
21.960
21.719
Me
Me
Me
P
B
O
O
13C NMR (100Hz, CDCl3)
f1 (ppm)

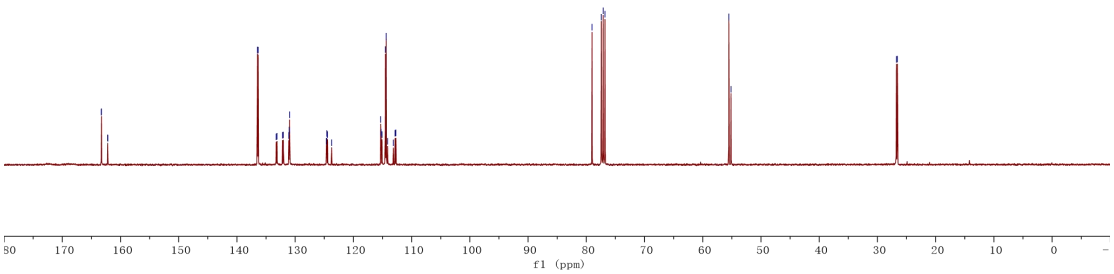

4.080
Me
Me
Me
P
B
O
O
31P NMR (162Hz, CDCl3)
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

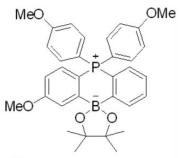
3ca


8.190
8.179
8.173
8.162
7.786
7.473
7.451
7.442
7.421
7.263
7.105
7.098
7.091
7.074
7.066
7.045
7.036
7.015
6.990
6.986
6.968
6.964
6.664
6.658
6.651
6.644
6.637
6.630
3.882
3.852
0.980
0.966
MeO
OMe
MeO
P
B
O
O
1H NMR (400Hz, CDCl3)
1.00
0.98
5.18
2.35
0.88
4.04
1.03
3.13
5.97
12.16
f1 (ppm)

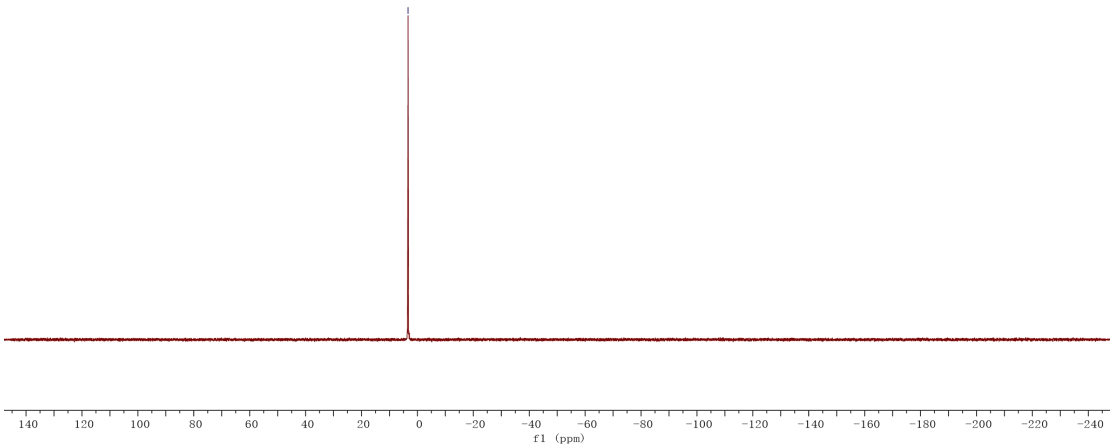


^{13}C NMR (100Hz, $CDCl_3$)

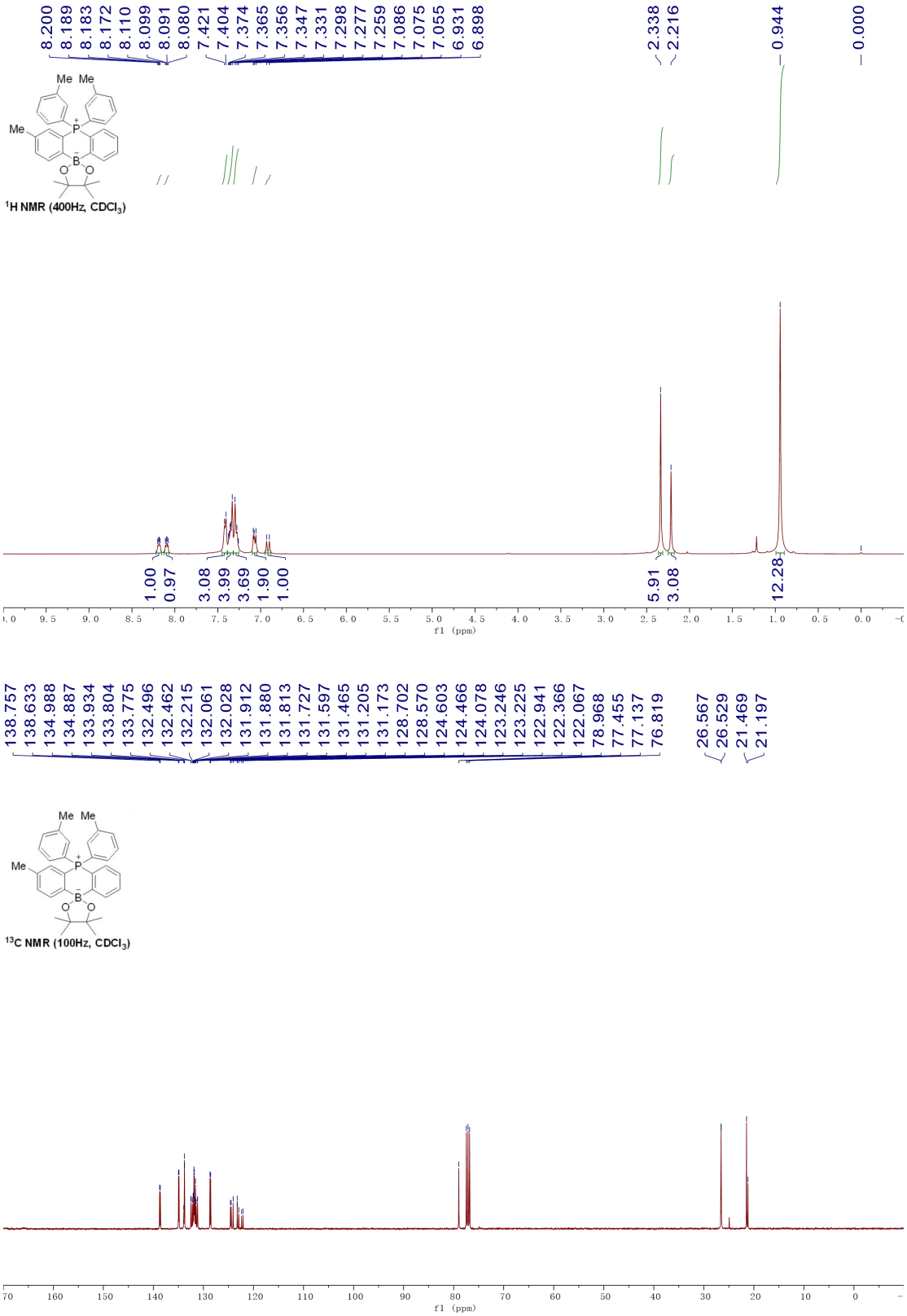


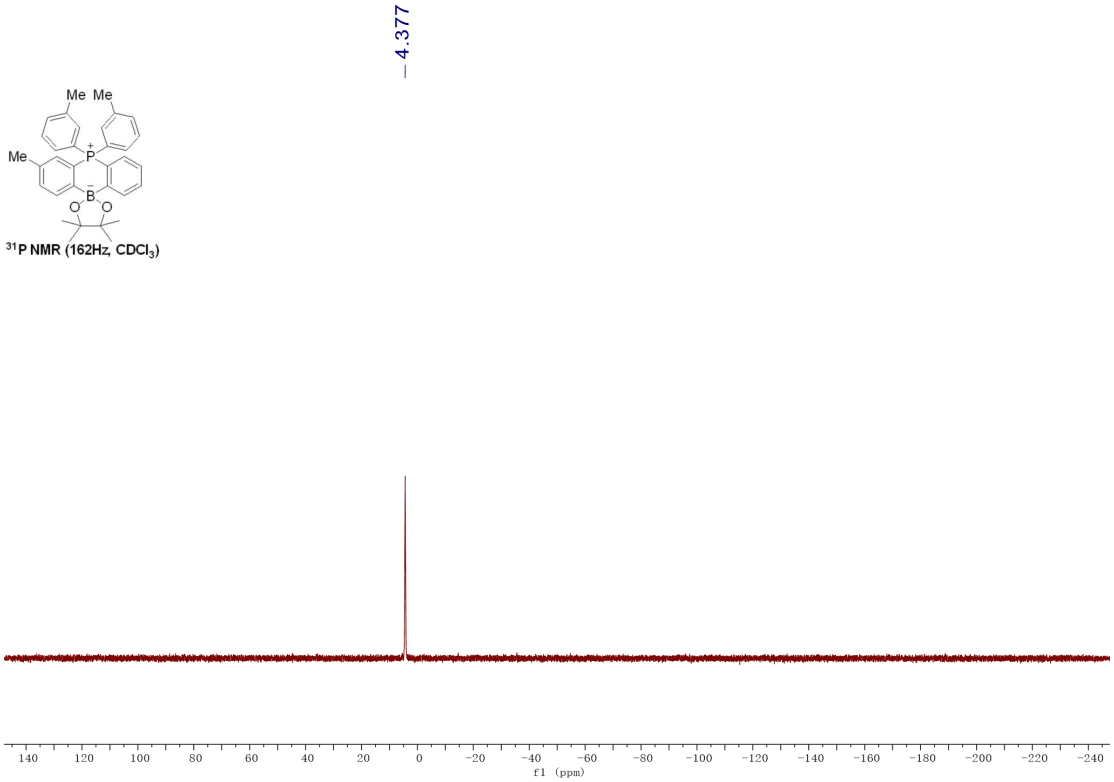


^{31}P NMR (162Hz, $CDCl_3$)

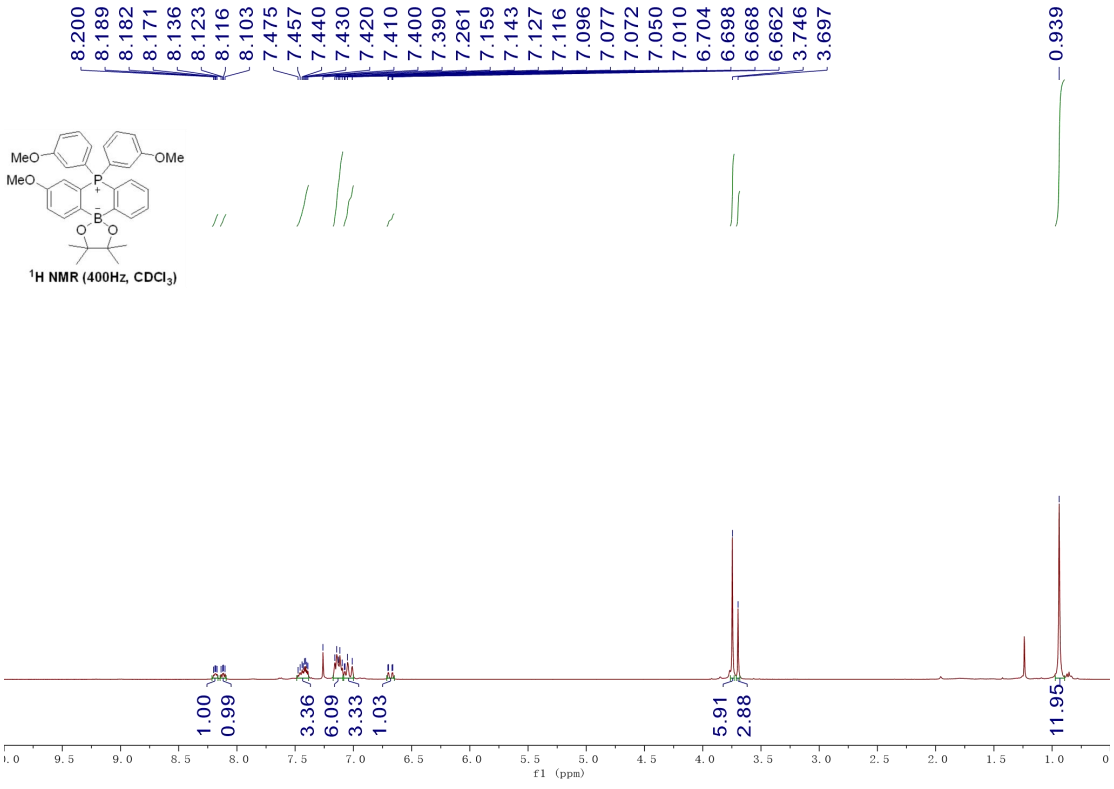


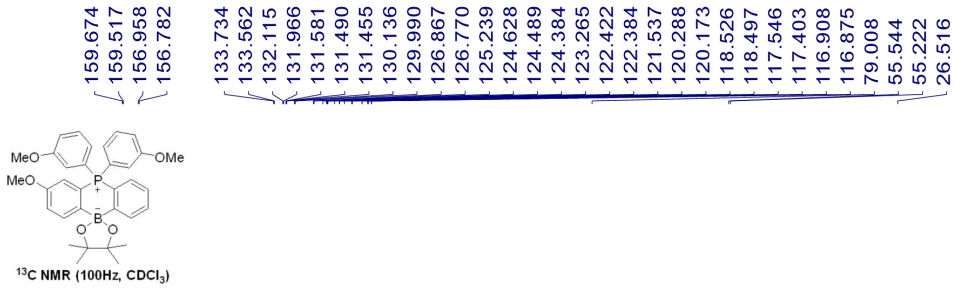
3da


8.200
8.189
8.183
8.172
8.110
8.099
8.091
8.080
7.421
7.404
7.374
7.365
7.356
7.347
7.331
7.298
7.277
7.259
7.086
7.075
7.055
6.931
6.898
2.338
2.216
0.944
0.000
Me Me
Me
P
B
O O
1H NMR (400Hz, CDCl3)
1.00
0.97
3.08
3.99
3.69
1.90
1.00
5.91
3.08
12.28
f1 (ppm)
138.757
138.633
134.988
134.887
133.934
133.804
133.775
132.496
132.462
132.215
132.061
132.028
131.912
131.880
131.813
131.727
131.597
131.465
131.205
131.173
128.702
128.570
124.603
124.466
124.078
123.246
123.225
122.941
122.366
122.067
78.968
77.455
77.137
76.819
26.567
26.529
21.469
21.197
Me Me
Me
P
B
O O
13C NMR (100Hz, CDCl3)
f1 (ppm)

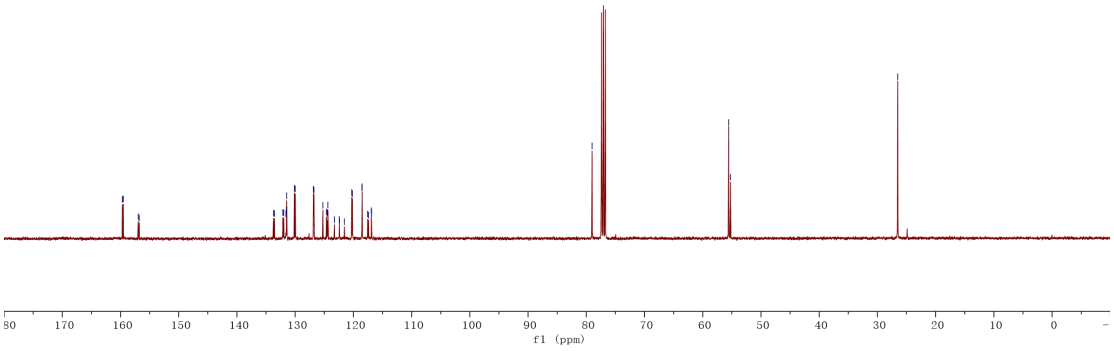

4.377
Me Me
Me
P
B
O
O
31P NMR (162Hz, CDCl3)
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

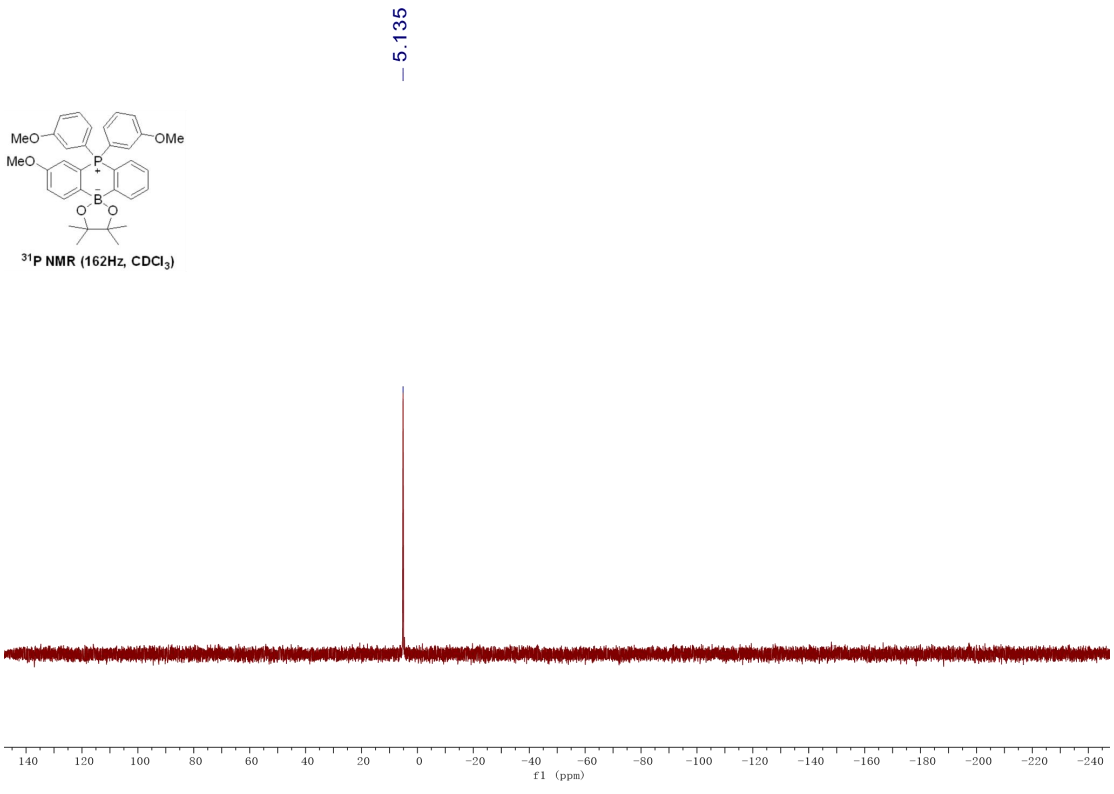
3ea


8.200
8.189
8.182
8.171
8.136
8.123
8.116
8.103
7.475
7.457
7.440
7.430
7.420
7.410
7.400
7.390
7.261
7.159
7.143
7.127
7.116
7.096
7.077
7.072
7.050
7.010
6.704
6.698
6.668
6.662
3.746
3.697
0.939
MeO
MeO
OMe
P
B
O
O
1H NMR (400Hz, CDCl3)
1.00
0.99
3.36
6.09
3.33
1.03
5.91
2.88
11.95
f1 (ppm)



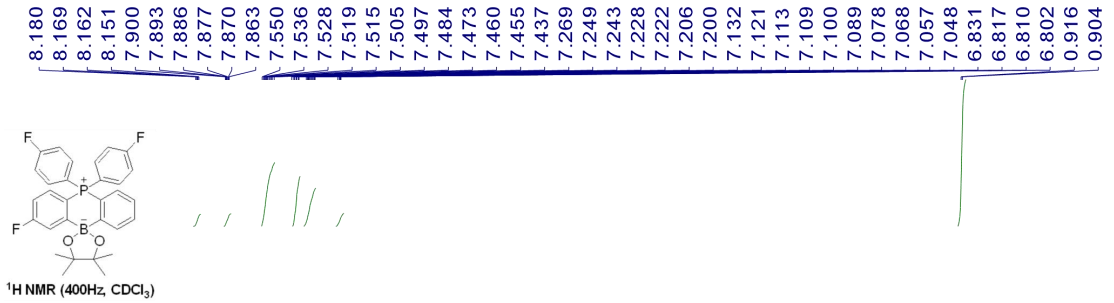
^{13}C NMR (100Hz, $CDCl_3$)



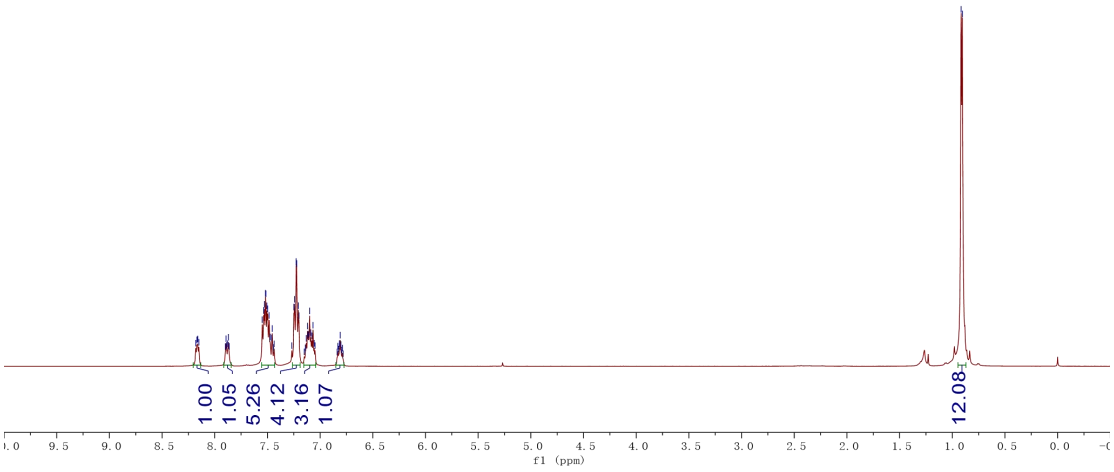


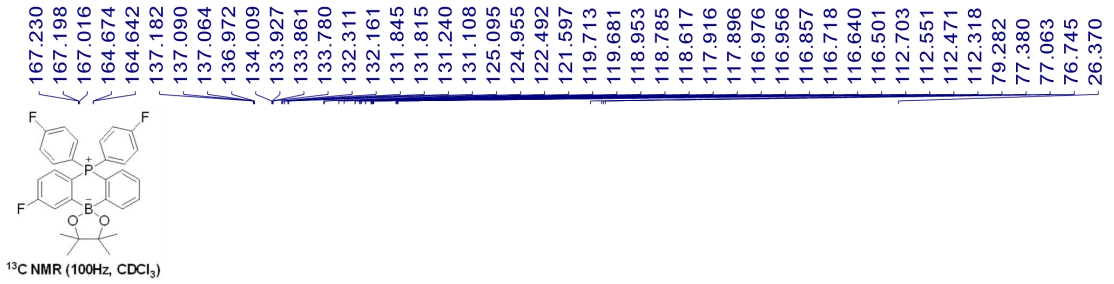
^{31}P NMR (162Hz, $CDCl_3$)

3fa

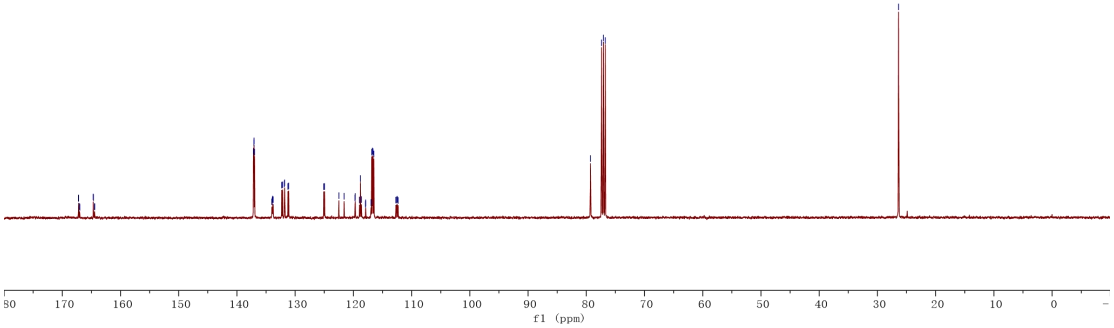


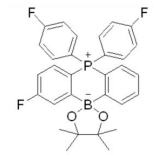
^{1}H NMR (400Hz, $CDCl_3$)



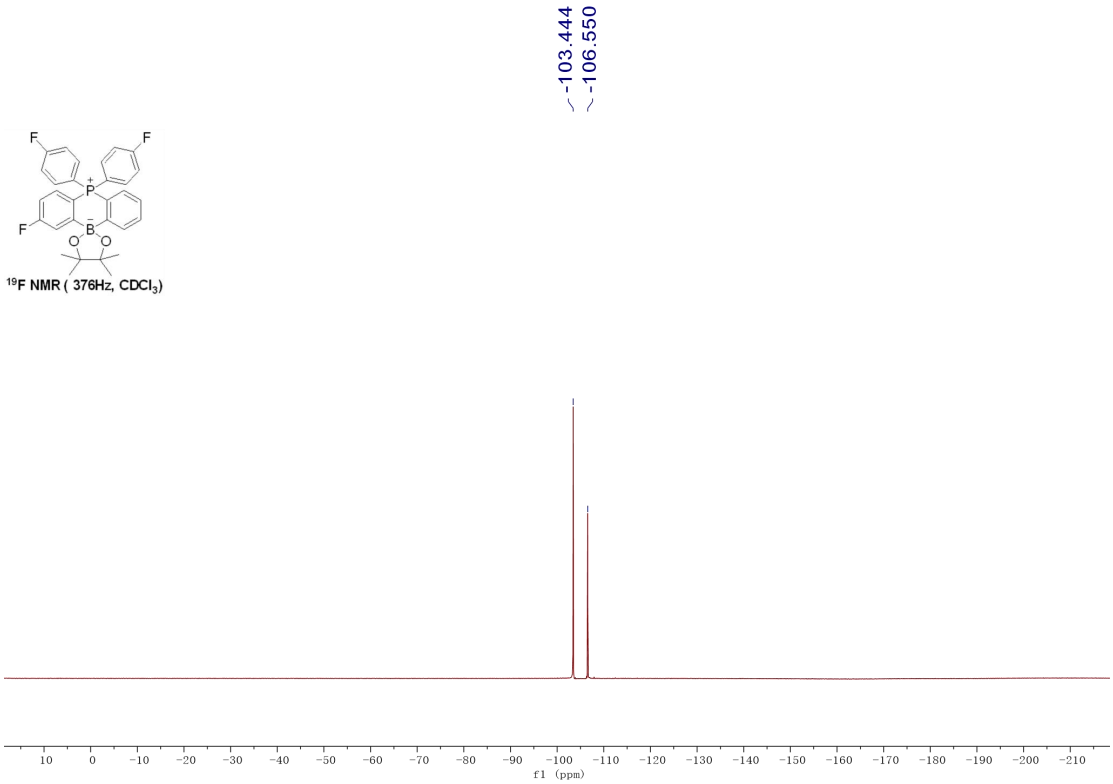


^{13}C NMR (100Hz, $CDCl_3$)

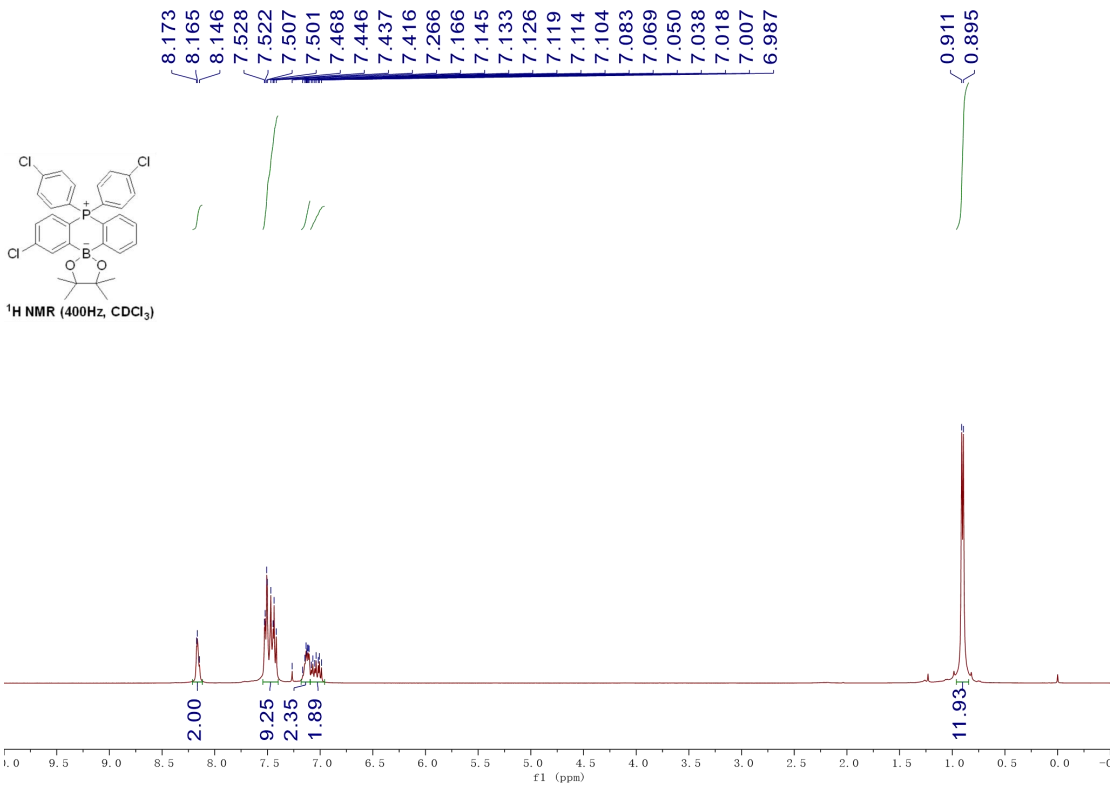


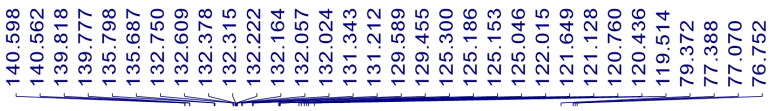


^{31}P NMR (162Hz, $CDCl_3$)

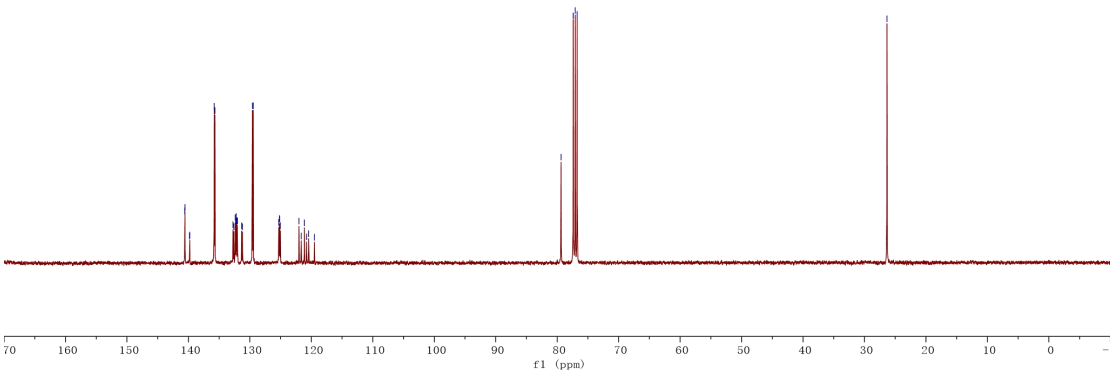

-103.444
-106.550
F
F
F
P
B
O
O
19F NMR (376Hz, CDCl3)
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

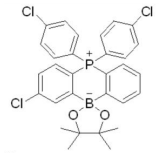
3ga


8.173
8.165
8.146
7.528
7.522
7.507
7.501
7.468
7.446
7.437
7.416
7.266
7.166
7.145
7.133
7.126
7.119
7.114
7.104
7.083
7.069
7.050
7.038
7.018
7.007
6.987
0.911
0.895
Cl
Cl
Cl
P
B
O
O
1H NMR (400Hz, CDCl3)
2.00
9.25
2.35
1.89
11.93
f1 (ppm)

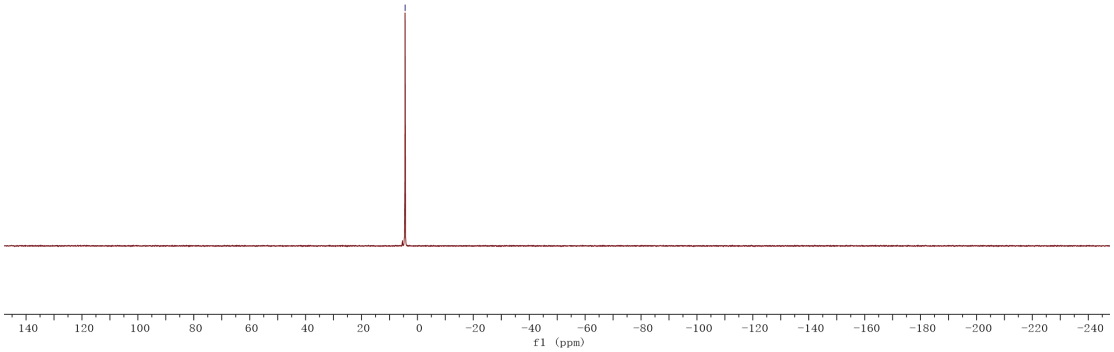


^{13}C NMR (100Hz, $CDCl_3$)

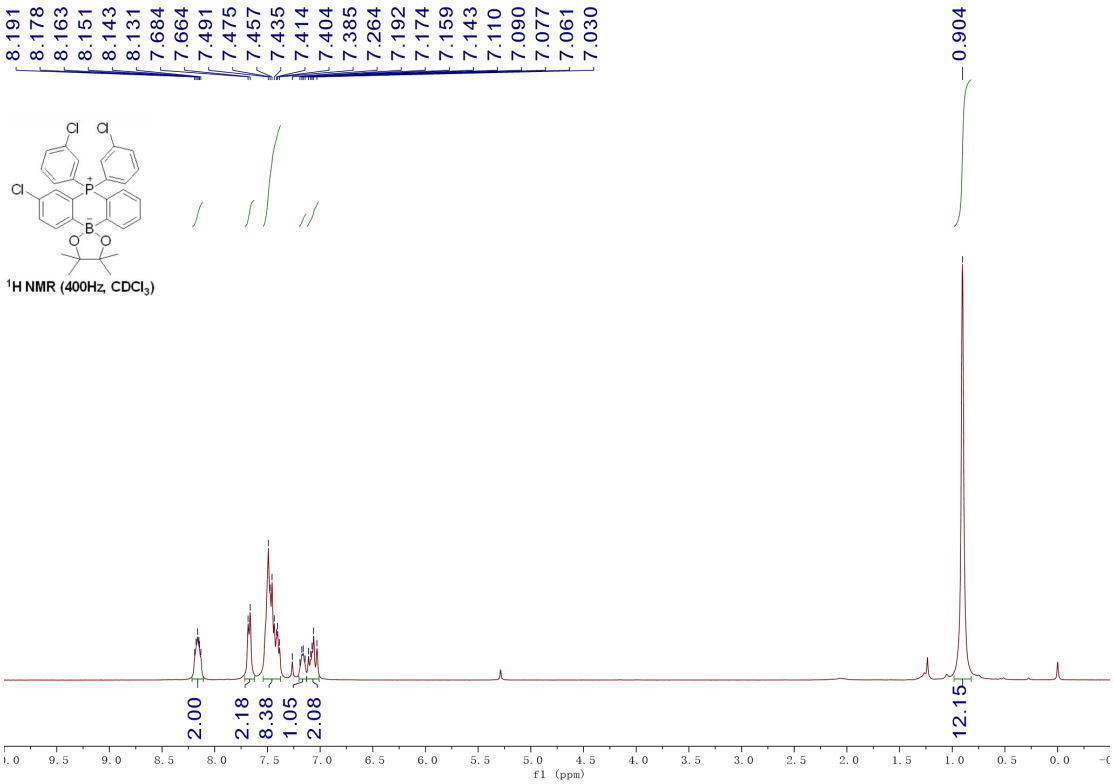


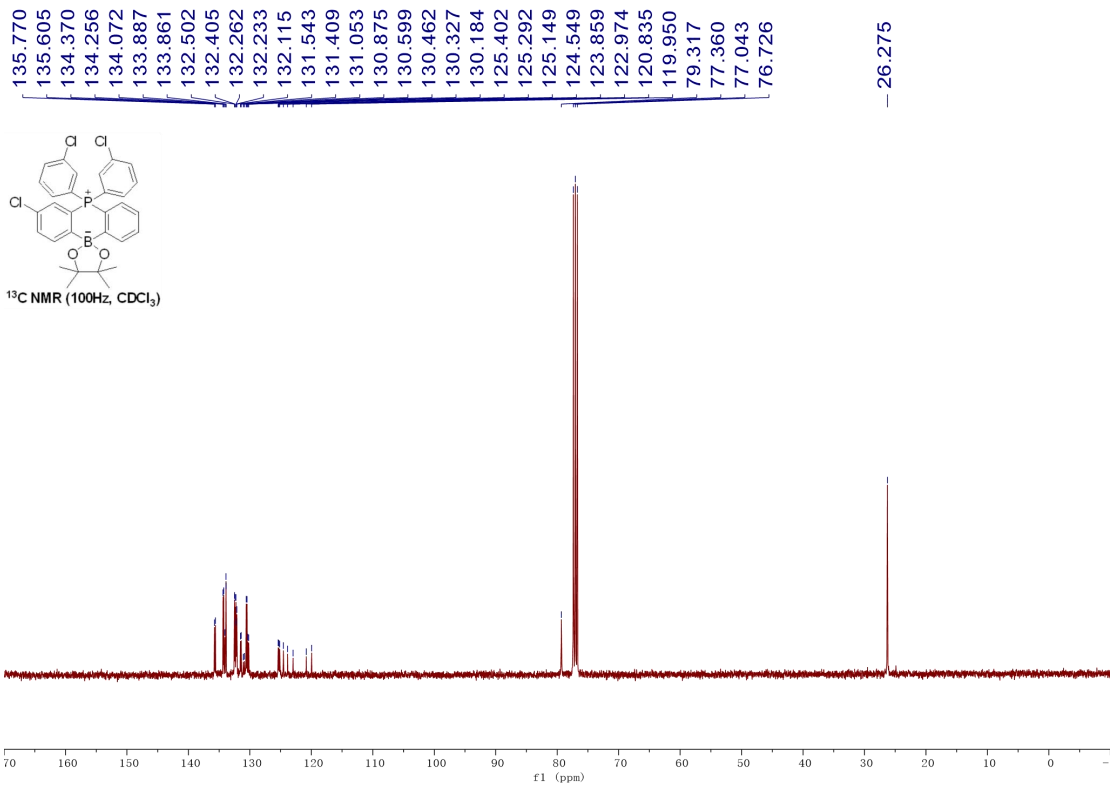


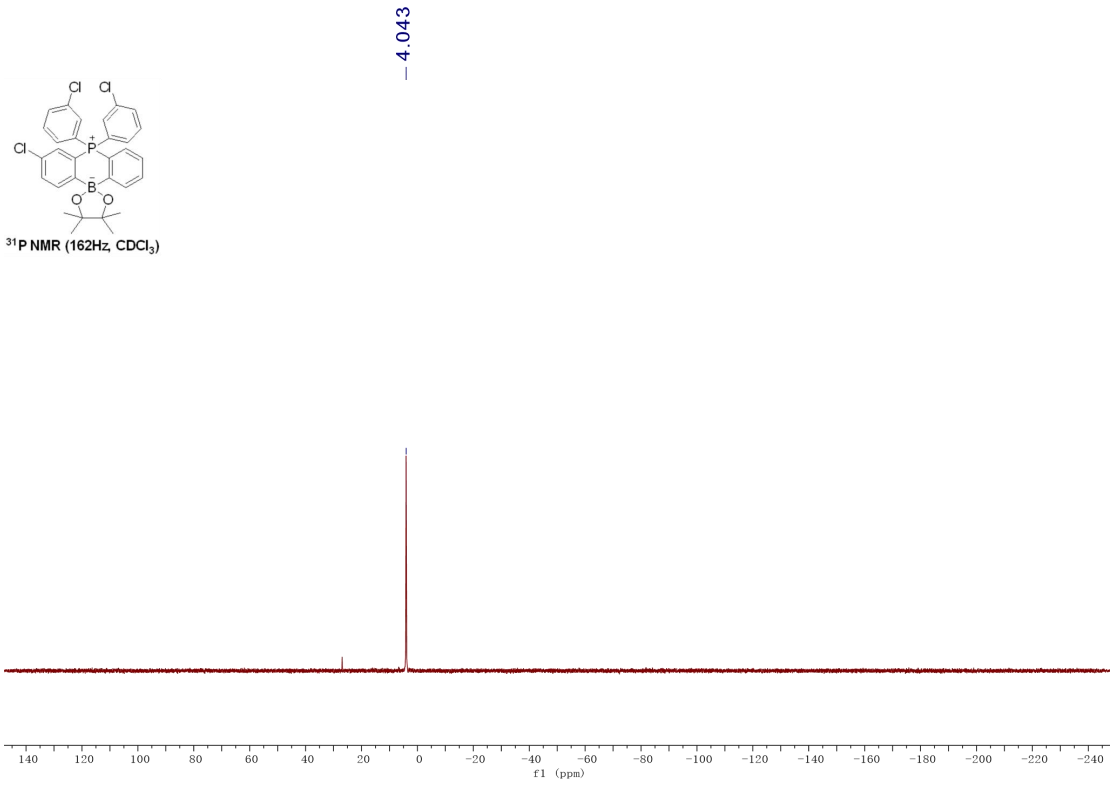
^{31}P NMR (162Hz, $CDCl_3$)



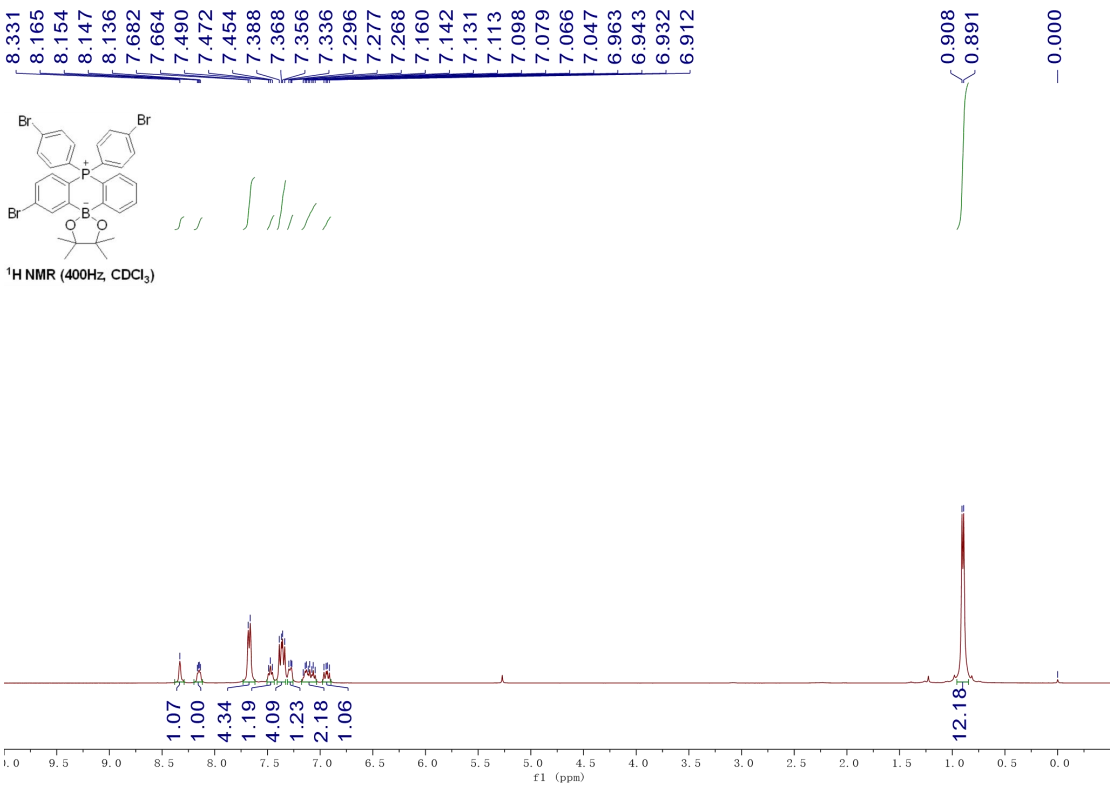
3ha

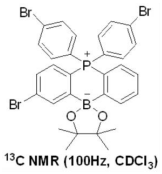

8.191
8.178
8.163
8.151
8.143
8.131
7.684
7.664
7.491
7.475
7.457
7.435
7.414
7.404
7.385
7.264
7.192
7.174
7.159
7.143
7.110
7.090
7.077
7.061
7.030
0.904
^{1}H NMR (400Hz, CDCl$_3$)
2.00
2.18
8.38
1.05
2.08
12.15
f1 (ppm)


135.770
135.605
134.370
134.256
134.072
133.887
133.861
132.502
132.405
132.262
132.233
132.115
131.543
131.409
131.053
130.875
130.599
130.462
130.327
130.184
125.402
125.292
125.149
124.549
123.859
122.974
120.835
119.950
79.317
77.360
77.043
76.726
26.275
^{13}C NMR (100Hz, CDCl$_3$)
f1 (ppm)

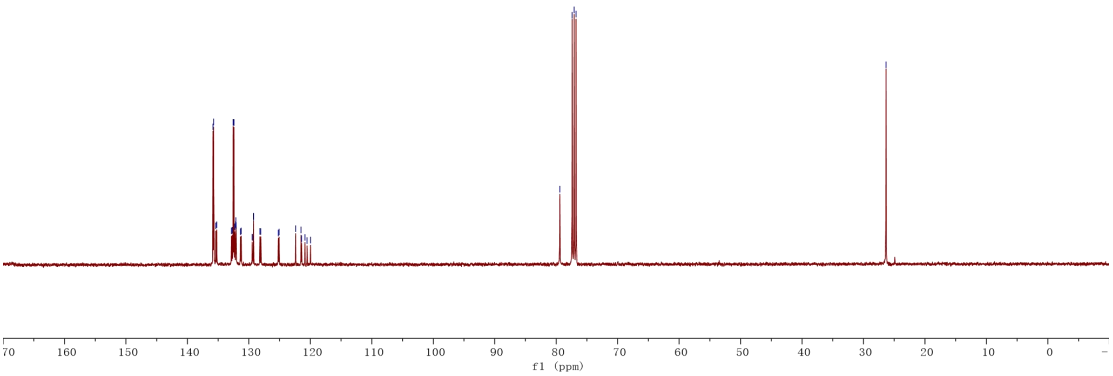

4.043
Cl
Cl
Cl
P
B
O
O
31P NMR (162Hz, CDCl3)
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

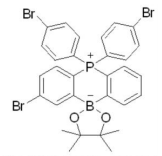
3ia


8.331
8.165
8.154
8.147
8.136
7.682
7.664
7.490
7.472
7.454
7.388
7.368
7.356
7.336
7.296
7.277
7.268
7.160
7.142
7.131
7.113
7.098
7.079
7.066
7.047
6.963
6.943
6.932
6.912
0.908
0.891
0.000
Br
Br
Br
P
B
O
O
1H NMR (400Hz, CDCl3)
1.07
1.00
4.34
1.19
4.09
1.23
2.18
1.06
12.18
f1 (ppm)



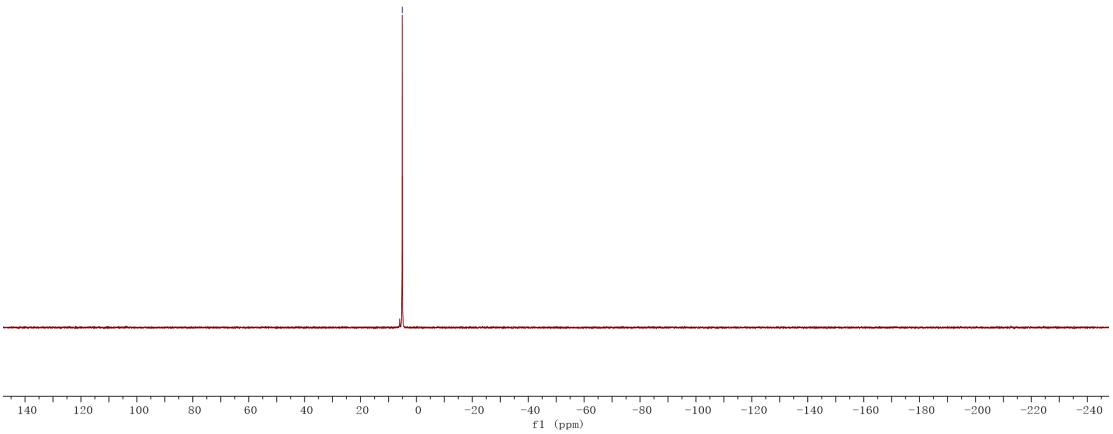
^{13}C NMR (100Hz, $CDCl_3$)



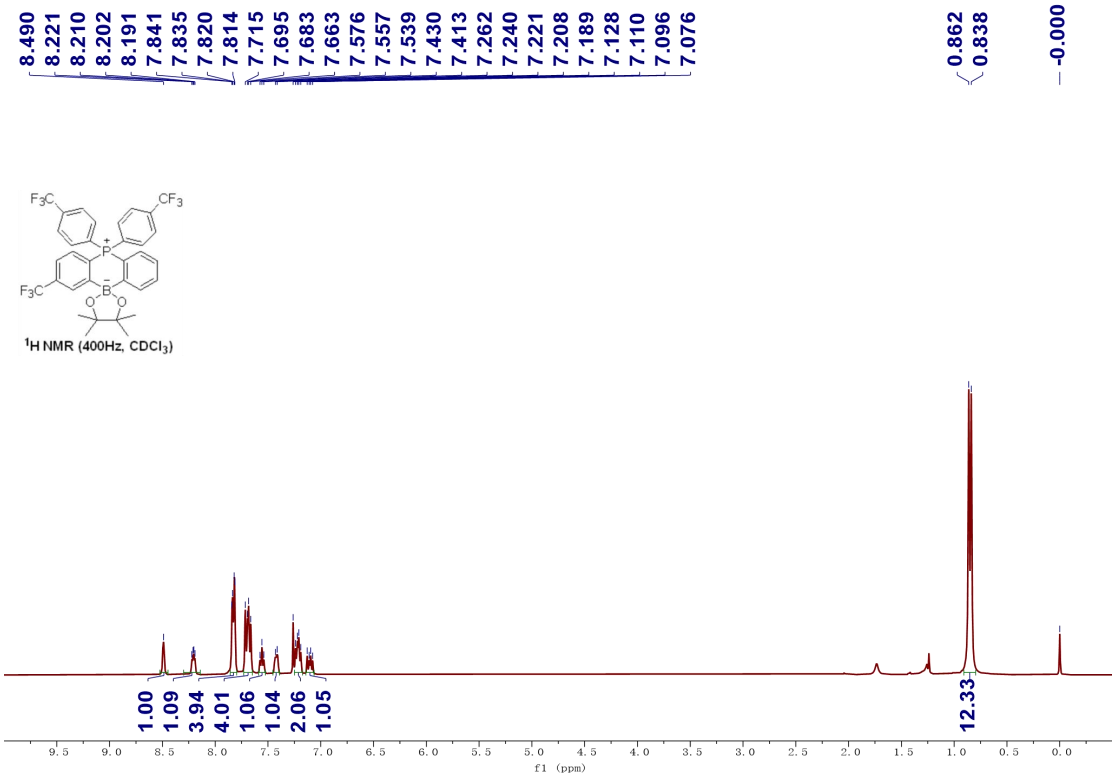


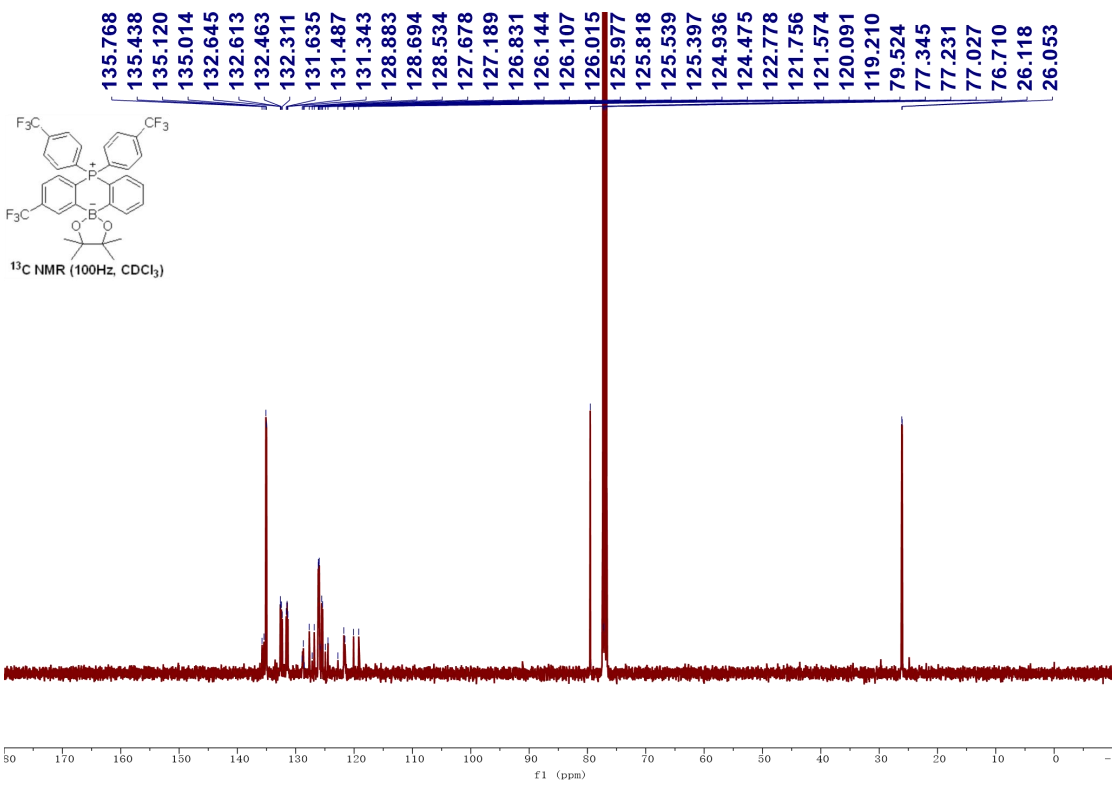
5.055

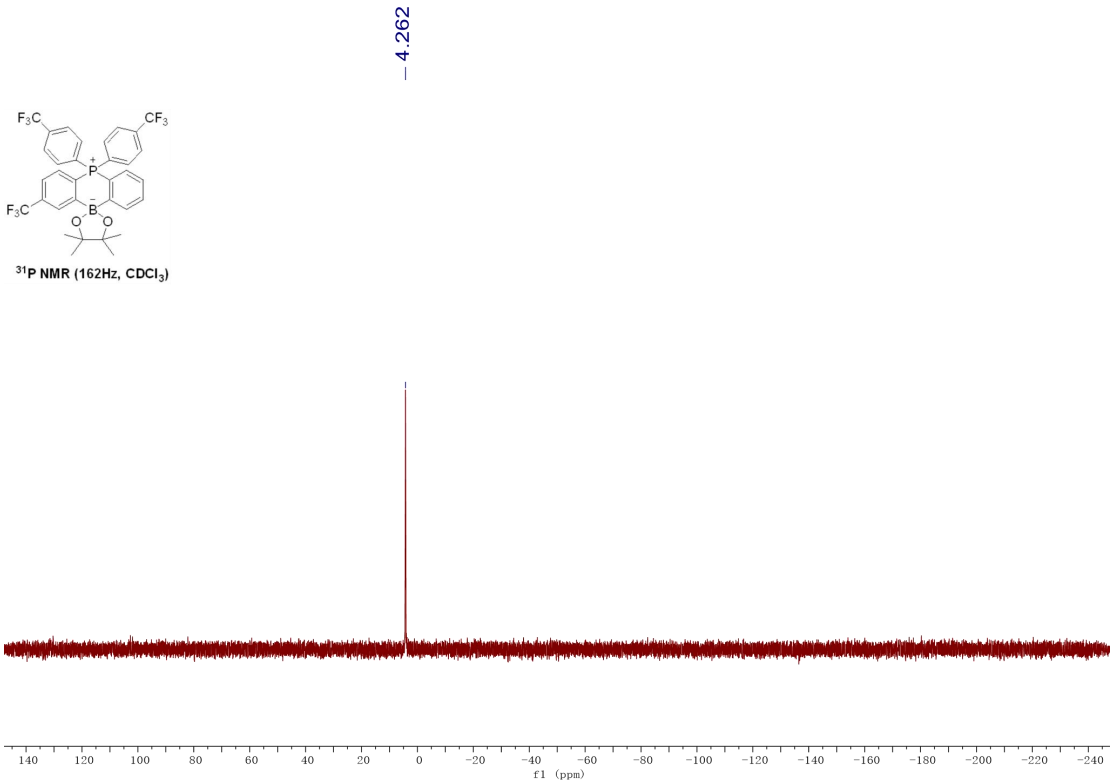
^{31}P NMR (162Hz, $CDCl_3$)



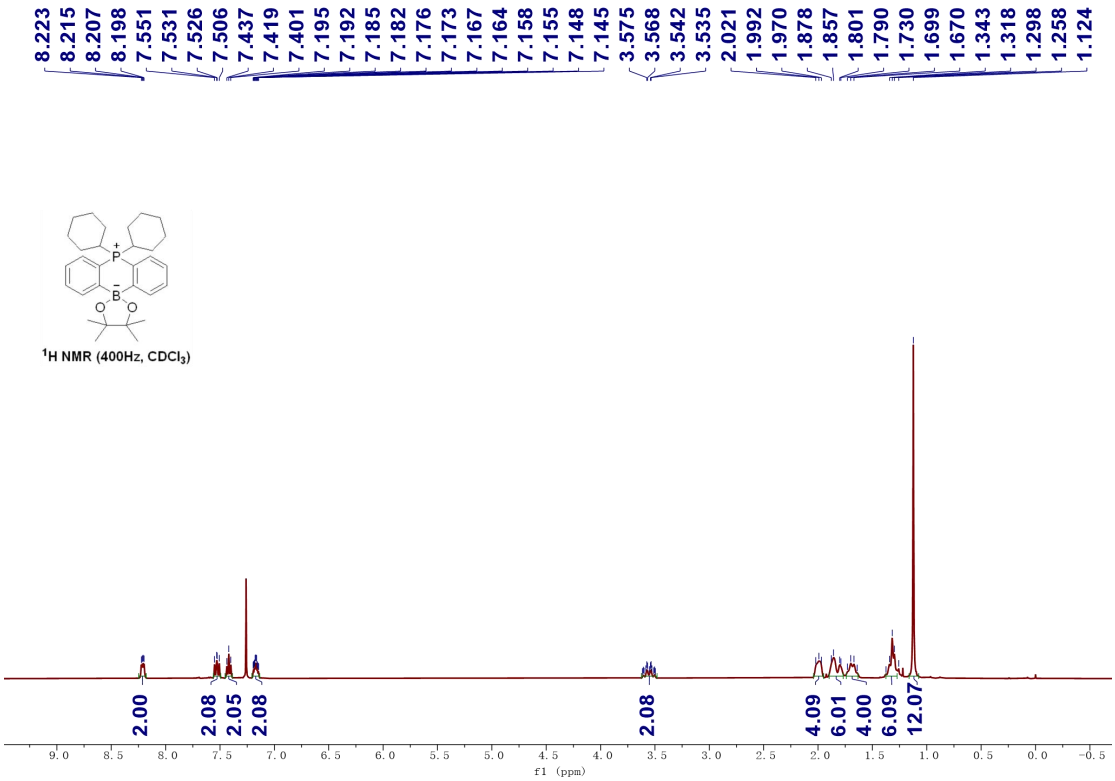
3ja

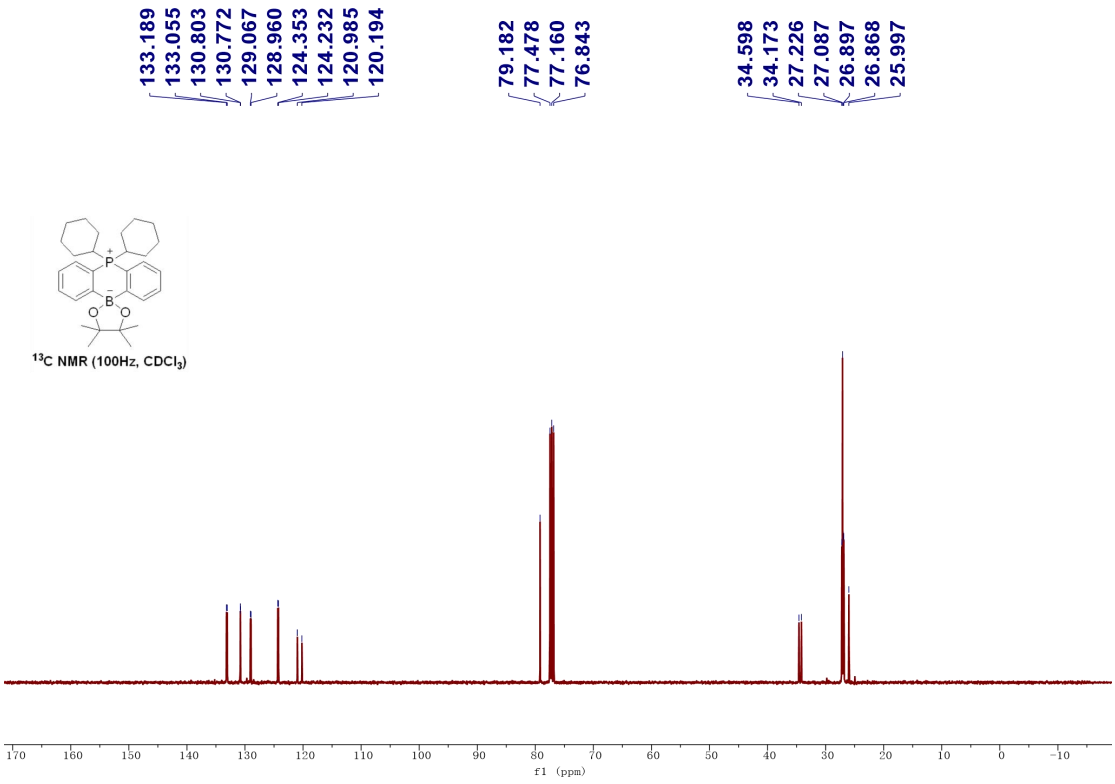

8.490
8.221
8.210
8.202
8.191
7.841
7.835
7.820
7.814
7.715
7.695
7.683
7.663
7.576
7.557
7.539
7.430
7.413
7.262
7.240
7.221
7.208
7.189
7.128
7.110
7.096
7.076
0.862
0.838
-0.000
1H NMR (400Hz, CDCl3)
1.00
1.09
3.94
4.01
1.06
1.04
2.06
1.05
12.33
f1 (ppm)

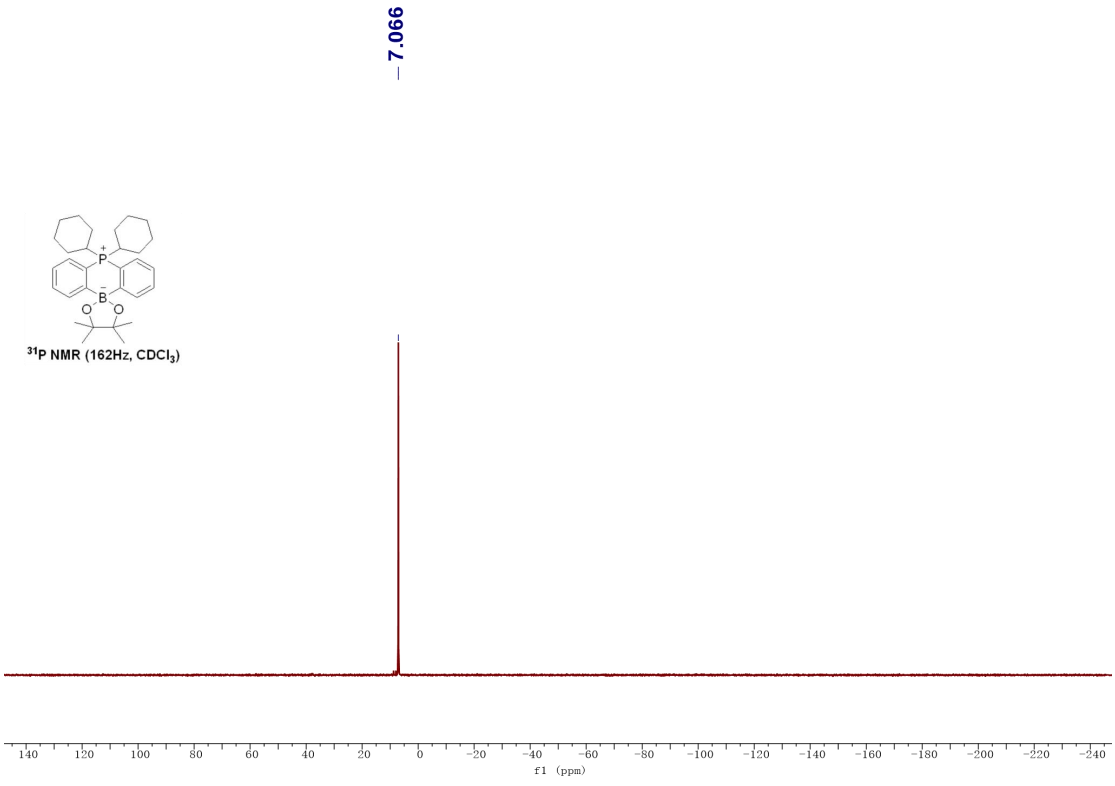

135.768
135.438
135.120
135.014
132.645
132.613
132.463
132.311
131.635
131.487
131.343
128.883
128.694
128.534
127.678
127.189
126.831
126.144
126.107
126.015
125.977
125.818
125.539
125.397
124.936
124.475
122.778
121.756
121.574
120.091
119.210
79.524
77.345
77.231
77.027
76.710
26.118
26.053
13C NMR (100Hz, CDCl3)
f1 (ppm)


4.262
31P NMR (162Hz, CDCl3)
f1 (ppm)

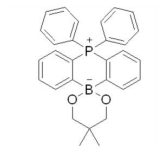
3ka


8.223
8.215
8.207
8.198
7.551
7.531
7.526
7.506
7.437
7.419
7.401
7.195
7.192
7.185
7.182
7.176
7.173
7.167
7.164
7.158
7.155
7.148
7.145
3.575
3.568
3.542
3.535
2.021
1.992
1.970
1.878
1.857
1.801
1.790
1.730
1.699
1.670
1.343
1.318
1.298
1.258
1.124
1H NMR (400Hz, CDCl3)
2.00
2.08
2.05
2.08
2.08
4.09
6.01
4.00
6.09
12.07
f1 (ppm)

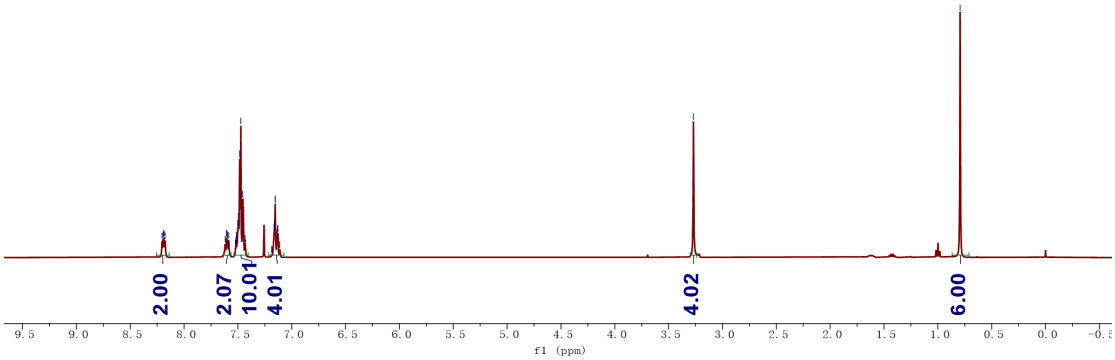

133.189
133.055
130.803
130.772
129.067
128.960
124.353
124.232
120.985
120.194
79.182
77.478
77.160
76.843
34.598
34.173
27.226
27.087
26.897
26.868
25.997
13C NMR (100Hz, CDCl3)
f1 (ppm)

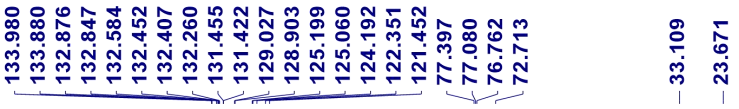

7.066
31P NMR (162Hz, CDCl3)
f1 (ppm)

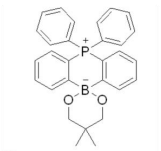
3la



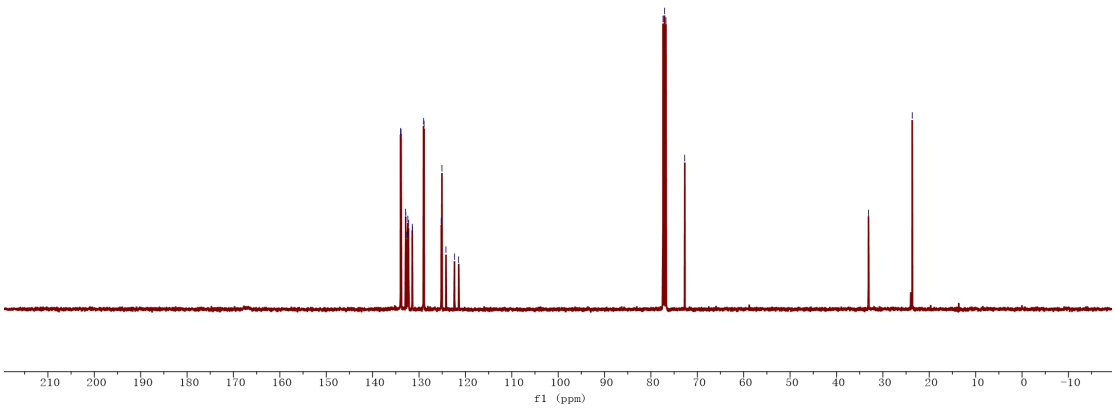
^{1}H NMR (400Hz, $CDCl_3$)

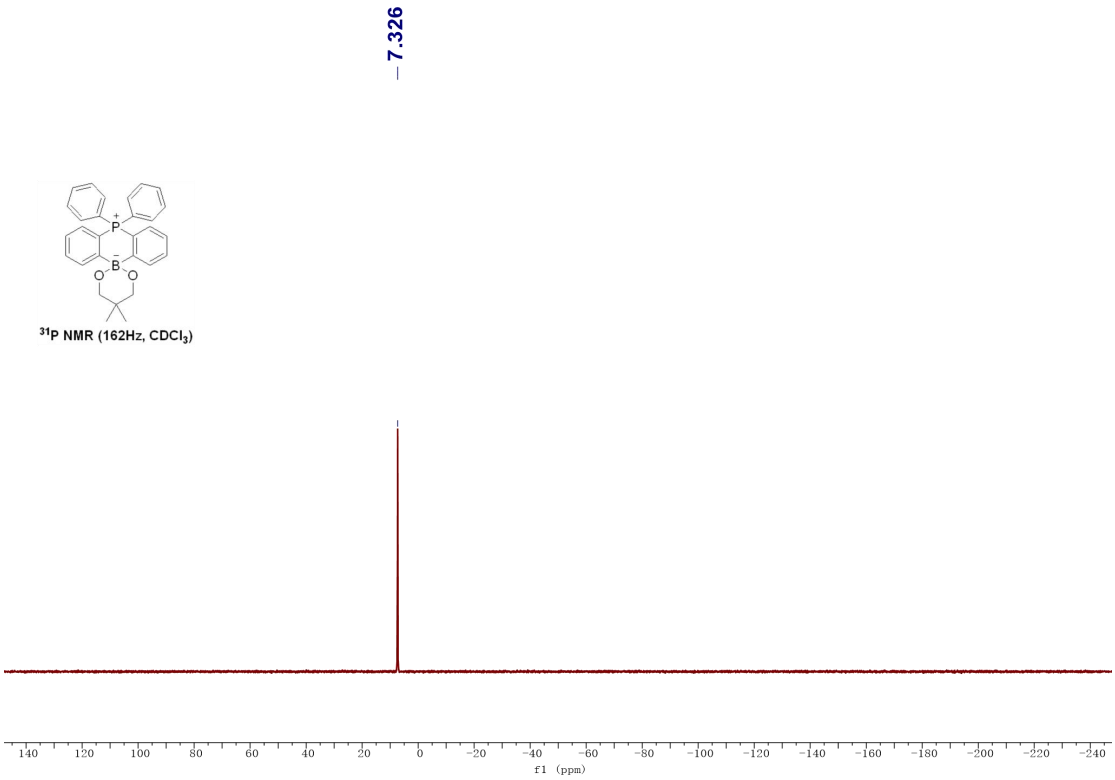




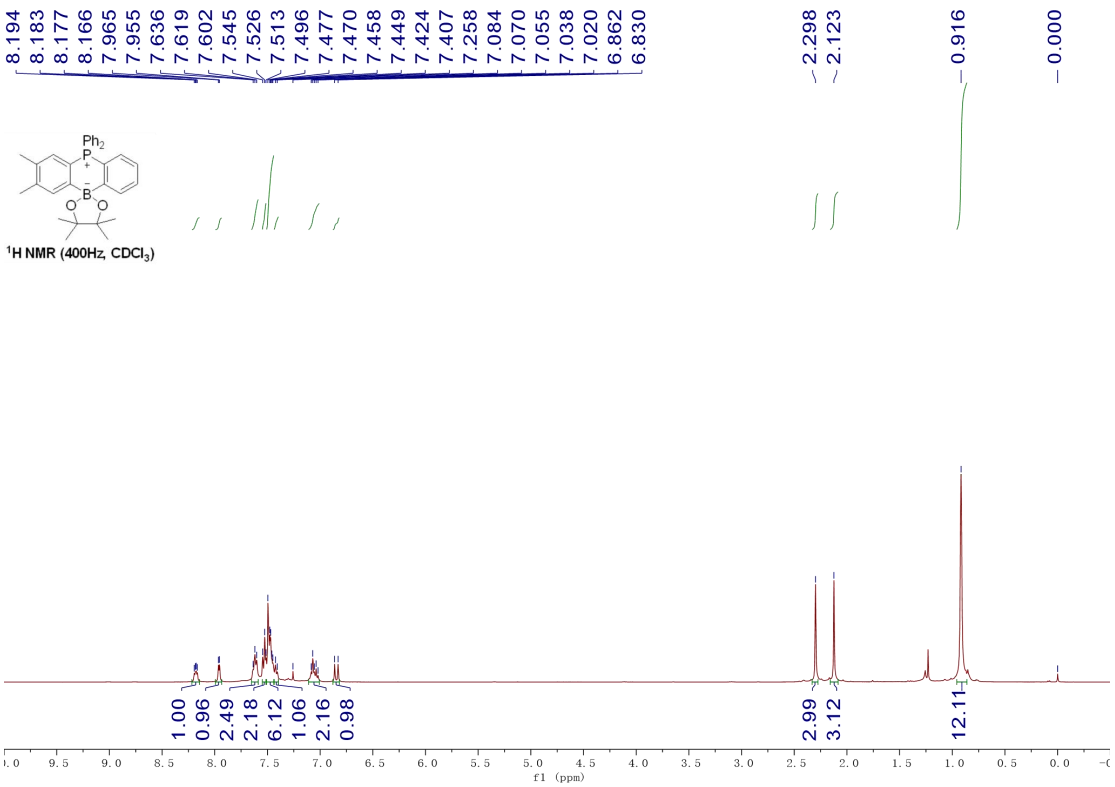


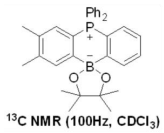
^{13}C NMR (100Hz, $CDCl_3$)



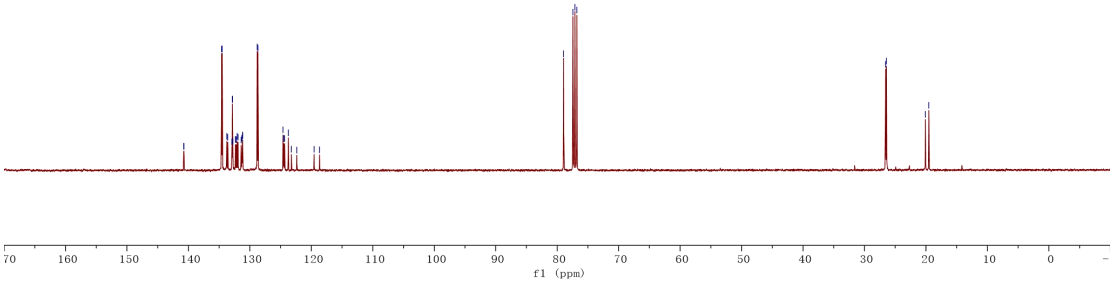

7.326
31P NMR (162Hz, CDCl3)
f1 (ppm)

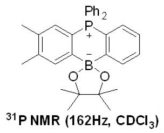
3ab


8.194
8.183
8.177
8.166
7.965
7.955
7.636
7.619
7.602
7.545
7.526
7.513
7.496
7.477
7.470
7.458
7.449
7.424
7.407
7.258
7.084
7.070
7.055
7.038
7.020
6.862
6.830
2.298
2.123
0.916
0.000
1H NMR (400Hz, CDCl3)
1.00
0.96
2.49
2.18
6.12
1.06
2.16
0.98
2.99
3.12
12.11
f1 (ppm)

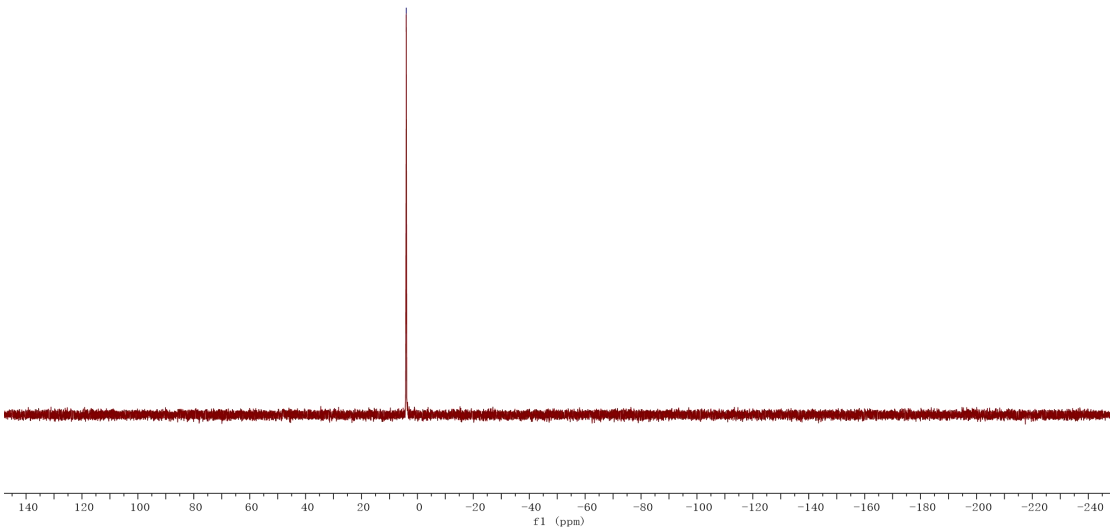


^{13}C NMR (100Hz, $CDCl_3$)

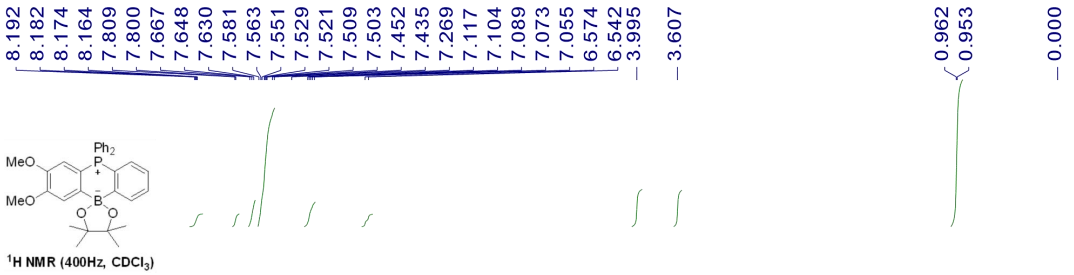




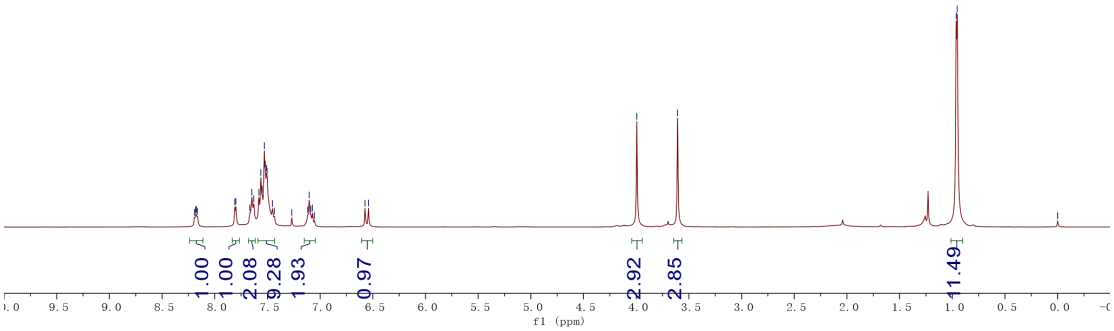
^{31}P NMR (162Hz, $CDCl_3$)

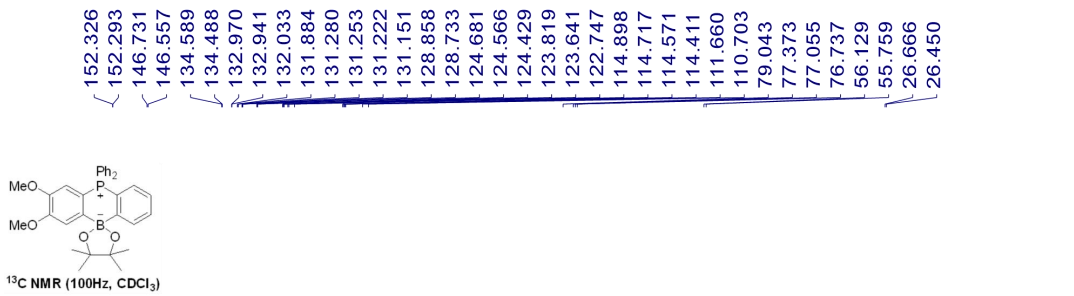


3ac

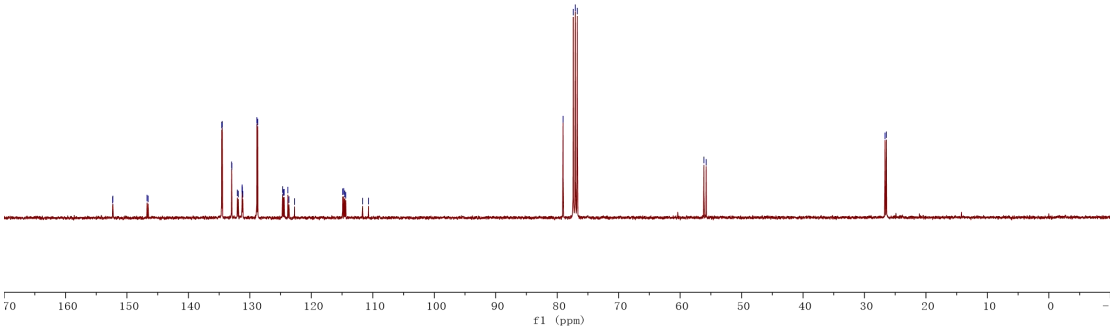


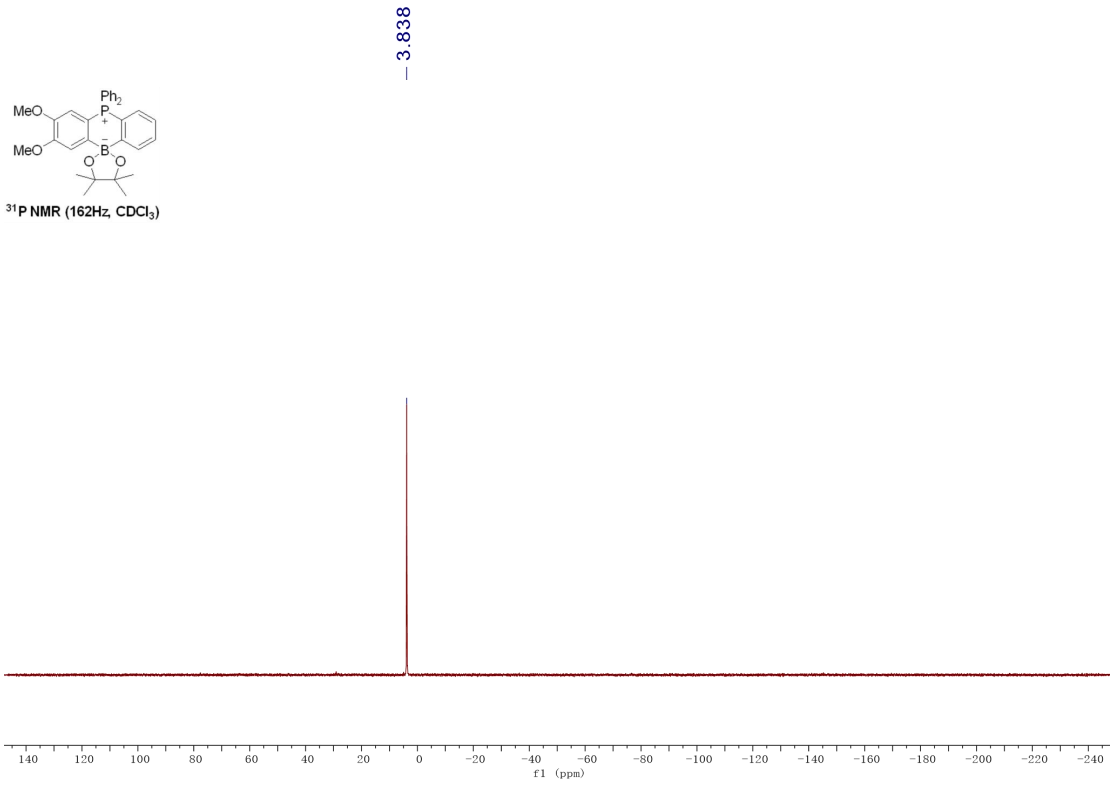
^{1}H NMR (400Hz, $CDCl_3$)



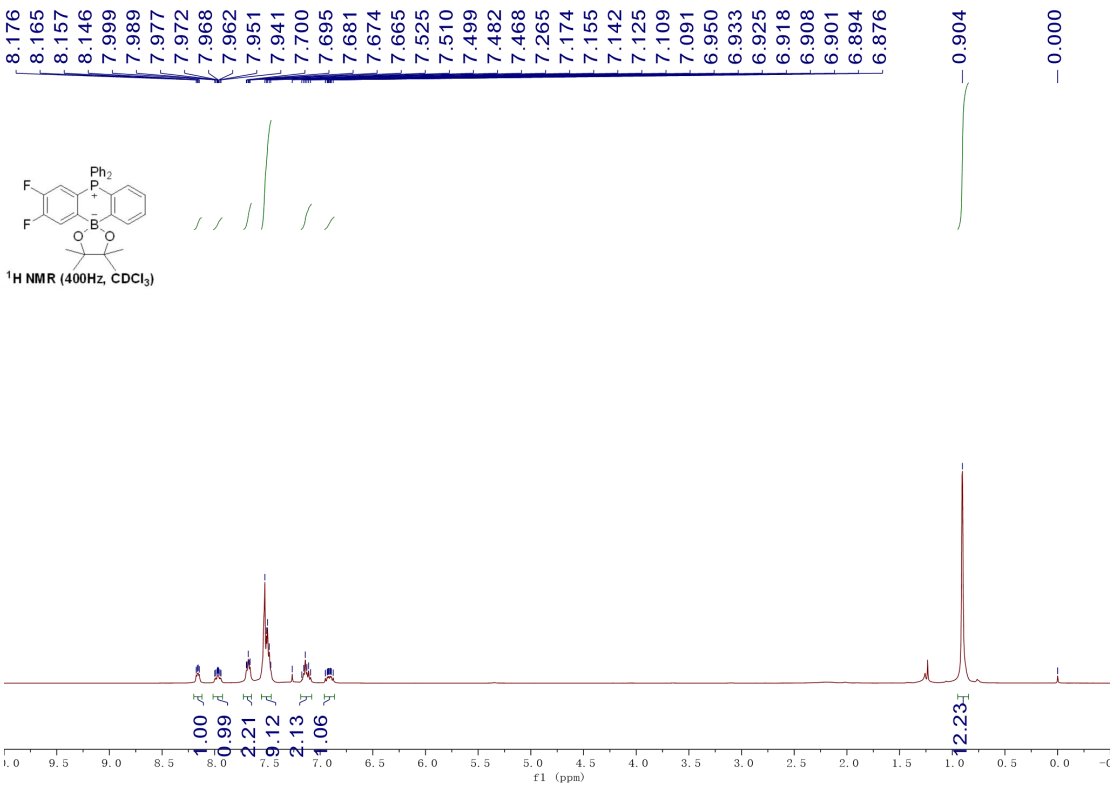


^{13}C NMR (100Hz, $CDCl_3$)

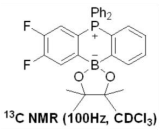



3.838
MeO
MeO
Ph2
P
B
O
O
31P NMR (162Hz, CDCl3)
f1 (ppm)

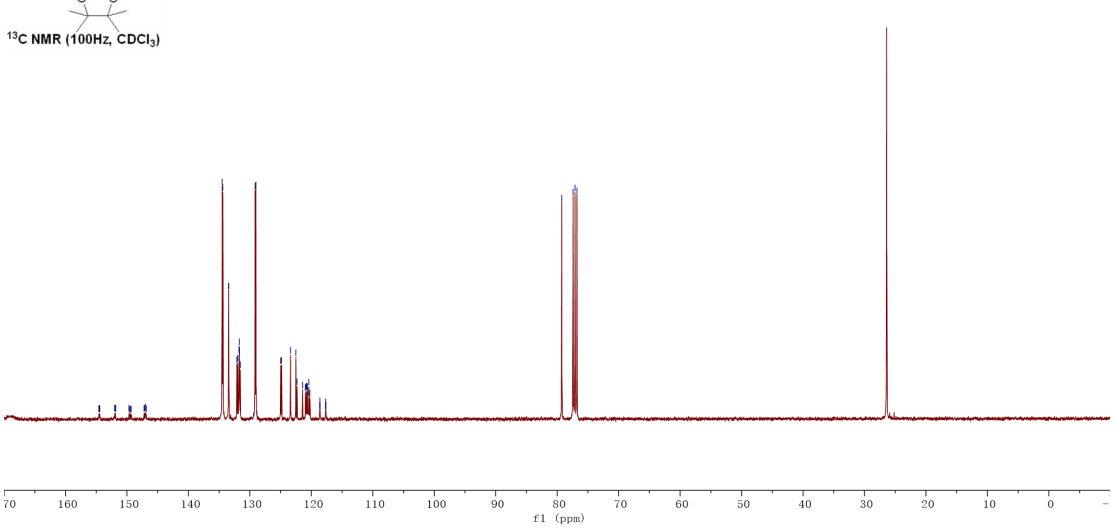
3ad


8.176
8.165
8.157
8.146
7.999
7.989
7.977
7.972
7.968
7.962
7.951
7.941
7.700
7.695
7.681
7.674
7.665
7.525
7.510
7.499
7.482
7.468
7.265
7.174
7.155
7.142
7.125
7.109
7.091
6.950
6.933
6.925
6.918
6.908
6.901
6.894
6.876
0.904
0.000
F
F
Ph2
P
B
O
O
1H NMR (400Hz, CDCl3)
1.00
0.99
2.21
9.12
2.13
1.06
12.23
f1 (ppm)

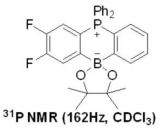
154.568
154.452
151.992
151.963
151.876
149.672
147.217
147.076
147.008
134.504
134.401
133.460
133.432
132.111
131.962
131.765
131.733
131.705
131.569
129.147
129.021
124.981
124.841
123.387
122.517
122.329
121.439
120.959
120.824
120.784
120.648
120.567
120.399
120.237
118.645
118.604
118.569
117.703
117.665
117.630
79.259
77.417
77.099
76.781
26.389



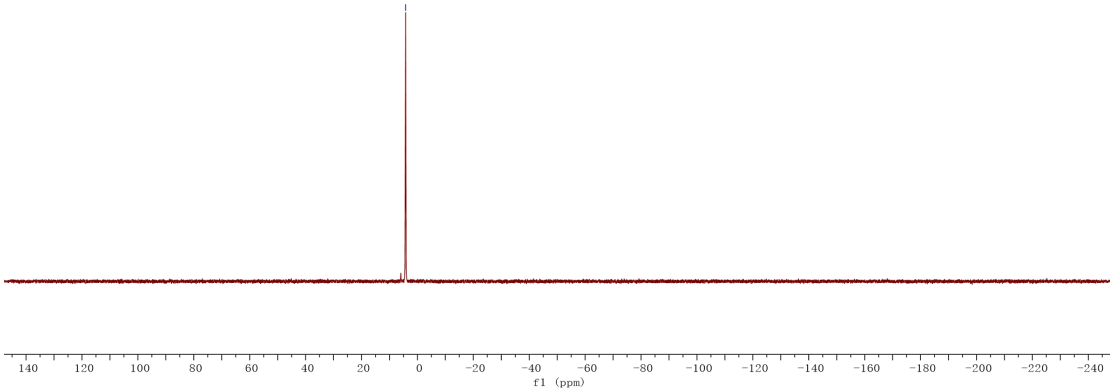
^{13}C NMR (100Hz, $CDCl_3$)

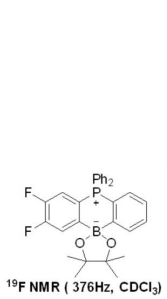


4.223

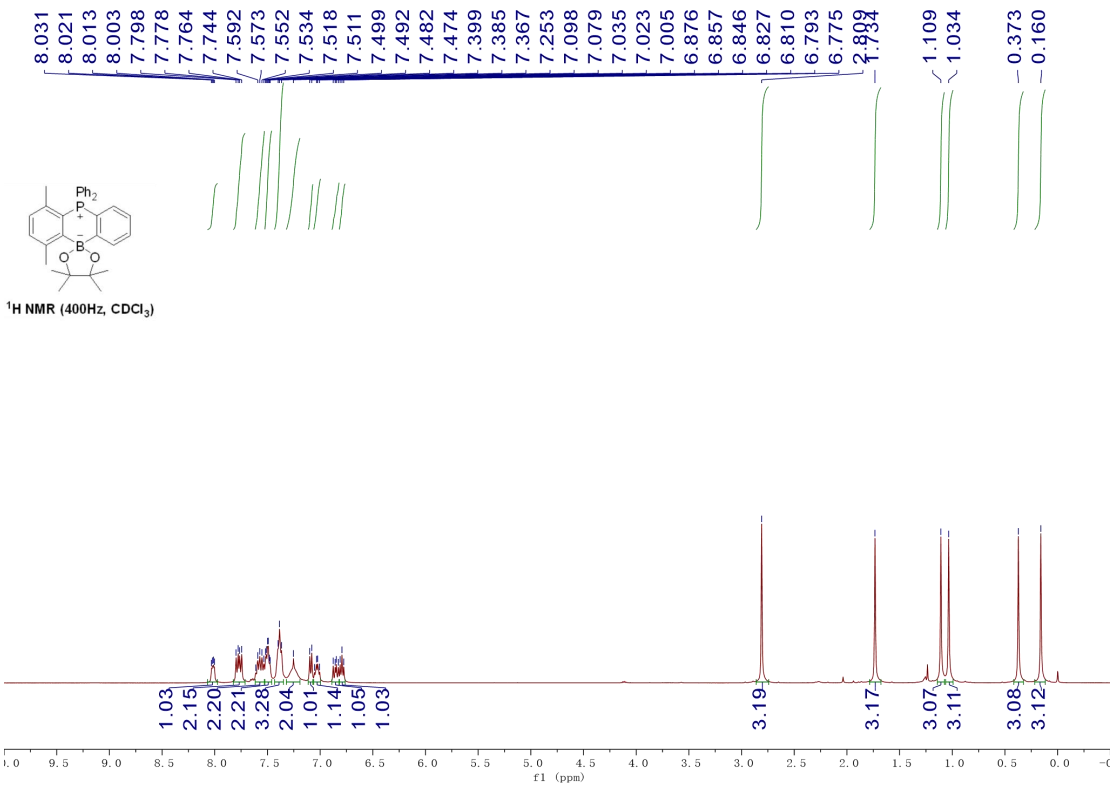


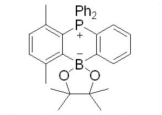
^{31}P NMR (162Hz, $CDCl_3$)



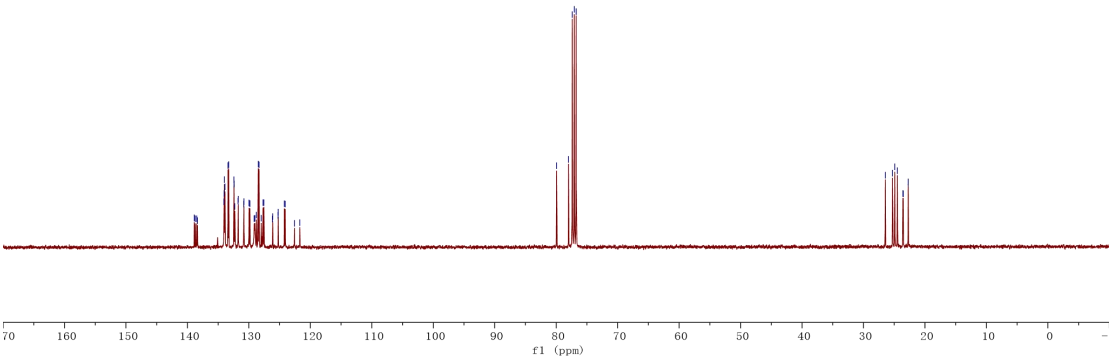

-133.042
-133.094
-143.130
-143.173
Ph2
F
F
P
B
O
O
19F NMR (376Hz, CDCl3)
f1 (ppm)

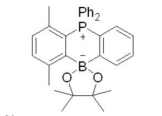
3ae


8.031
8.021
8.013
8.003
7.798
7.778
7.764
7.744
7.592
7.573
7.552
7.534
7.518
7.511
7.499
7.492
7.482
7.474
7.399
7.385
7.367
7.253
7.098
7.079
7.035
7.023
7.005
6.876
6.857
6.846
6.827
6.810
6.793
6.775
2.809
1.734
1.109
1.034
0.373
0.160
Ph2
P
B
O
O
1H NMR (400Hz, CDCl3)
1.03
2.15
2.20
2.21
3.28
2.04
1.01
1.14
1.05
1.03
3.19
3.17
3.07
3.11
3.08
3.12
f1 (ppm)

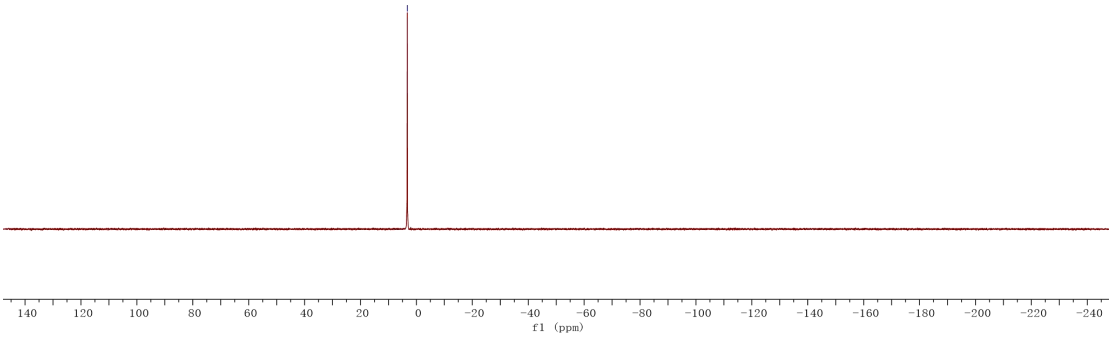


^{13}C NMR (100Hz, $CDCl_3$)

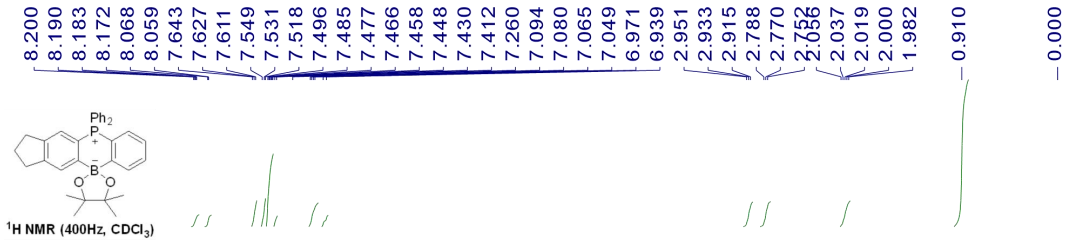




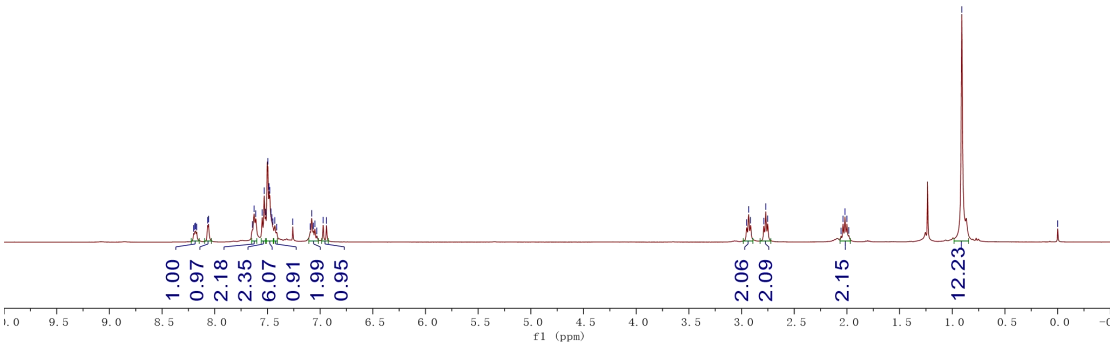
^{31}P NMR (162Hz, $CDCl_3$)



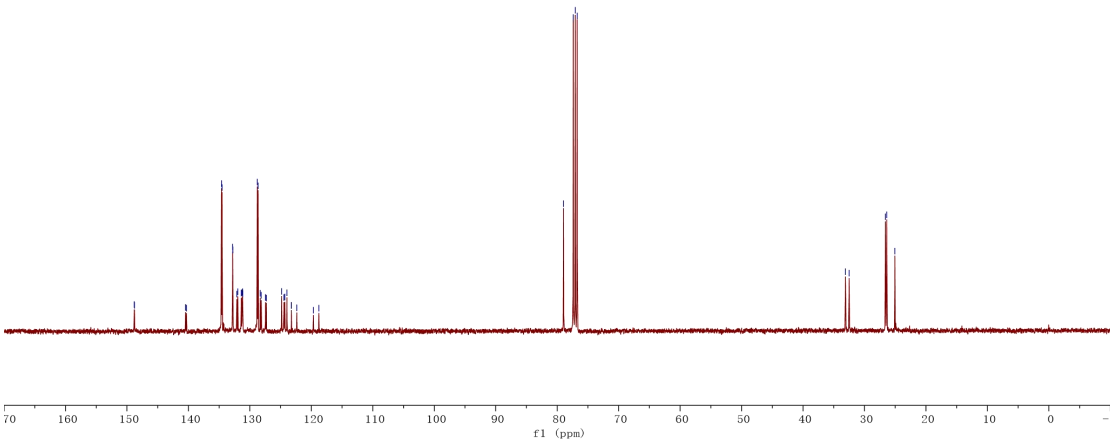
3af

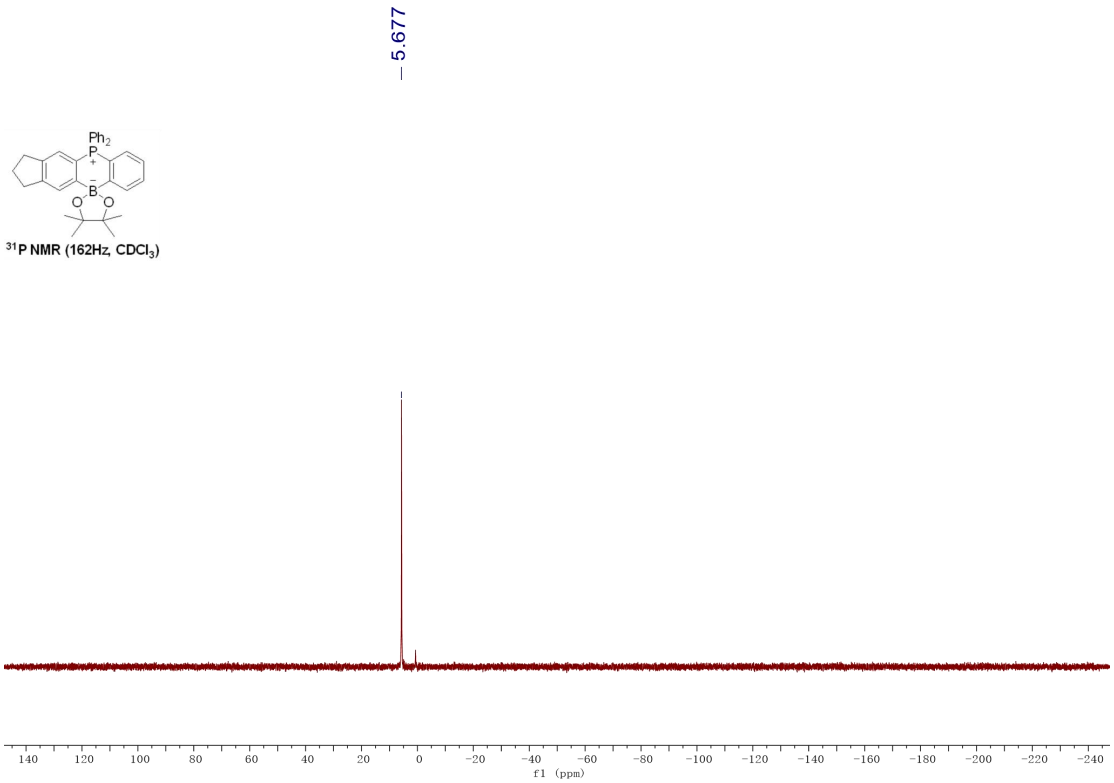


^{1}H NMR (400Hz, $CDCl_3$)

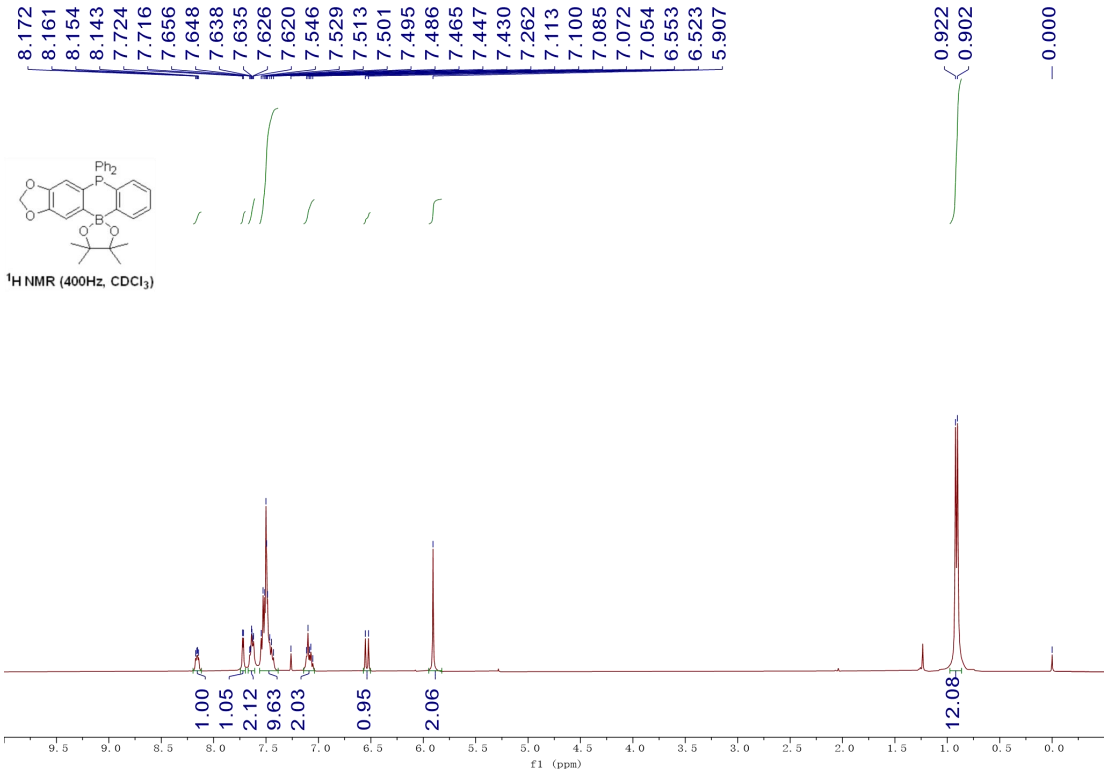


^{13}C NMR (100Hz, $CDCl_3$)

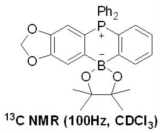



5.677
Ph2
P
B
O
O
31P NMR (162Hz, CDCl3)
f1 (ppm)

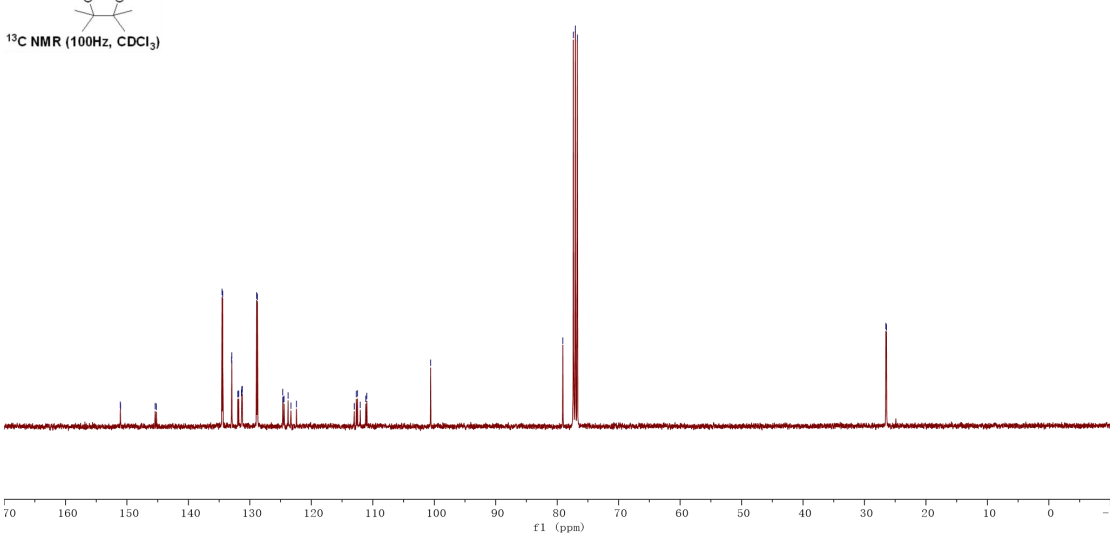
3ag


8.172
8.161
8.154
8.143
7.724
7.716
7.656
7.648
7.638
7.635
7.626
7.620
7.546
7.529
7.513
7.501
7.495
7.486
7.465
7.447
7.430
7.262
7.113
7.100
7.085
7.072
7.054
6.553
6.523
5.907
0.922
0.902
0.000
Ph2
P
B
O
O
O
O
1H NMR (400Hz, CDCl3)
1.00
1.05
2.12
9.63
2.03
0.95
2.06
12.08
f1 (ppm)

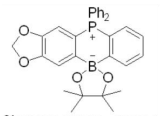
151.081
151.048
145.414
145.202
134.525
134.424
132.975
132.943
131.969
131.821
131.370
131.307
131.274
131.238
128.901
128.776
124.646
124.585
124.447
123.779
123.320
122.426
113.018
112.683
112.501
112.052
111.144
110.978
100.587
79.081
77.364
77.046
76.729
26.527
26.425



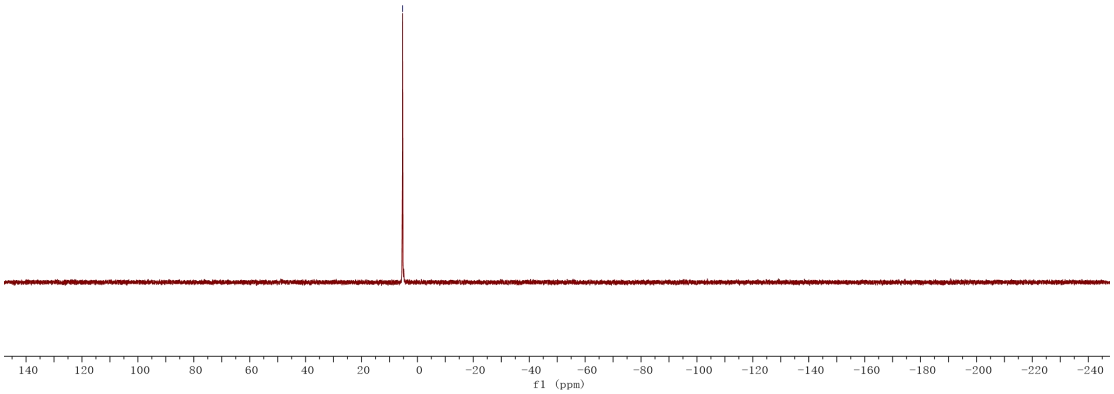
^{13}C NMR (100Hz, $CDCl_3$)



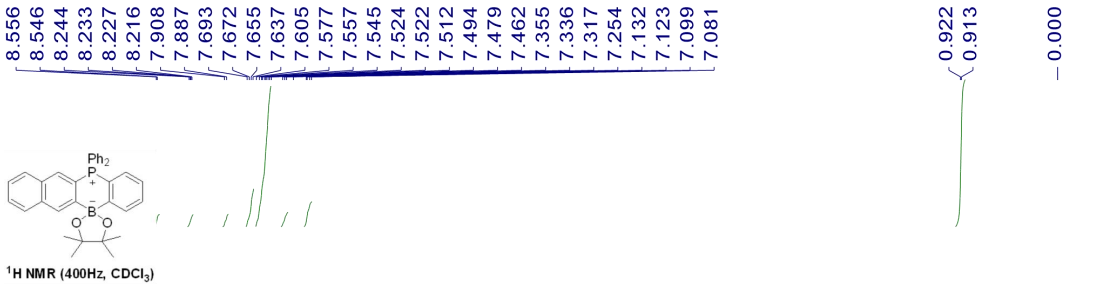
5.298



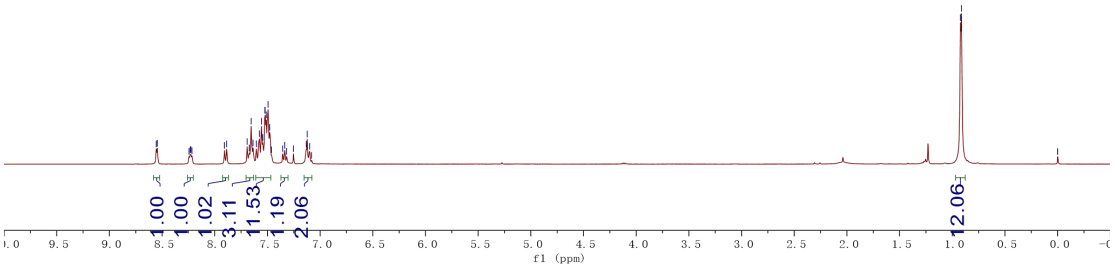
^{31}P NMR (162Hz, $CDCl_3$)

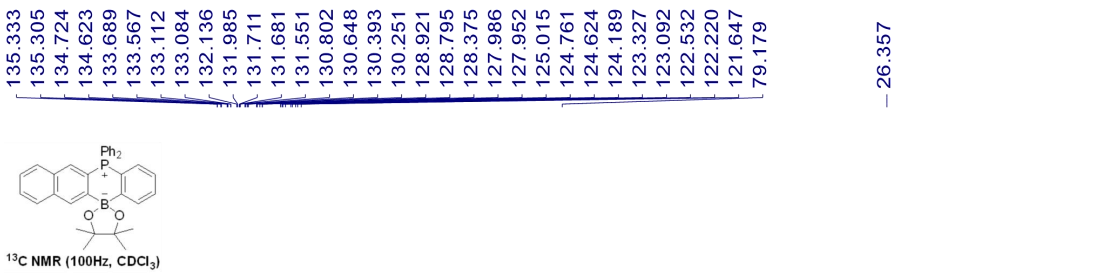


3ah

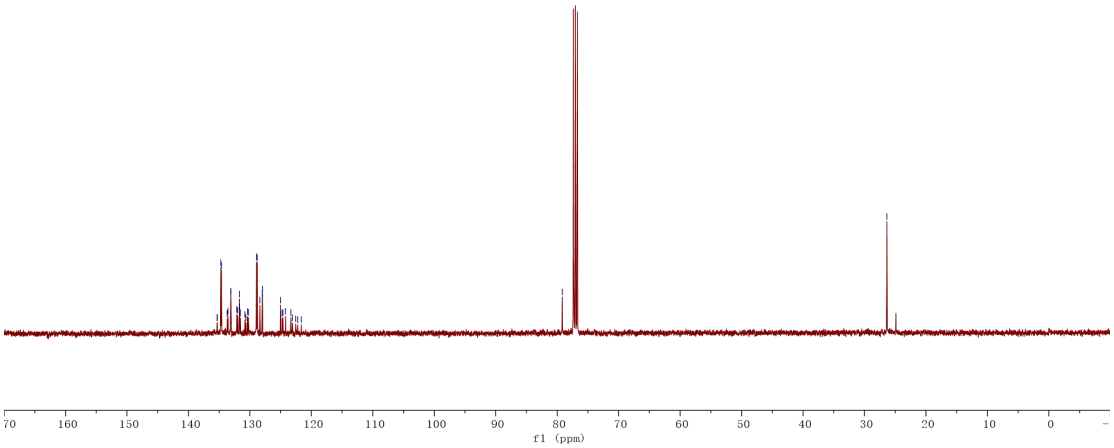


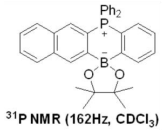
^{1}H NMR (400Hz, $CDCl_3$)





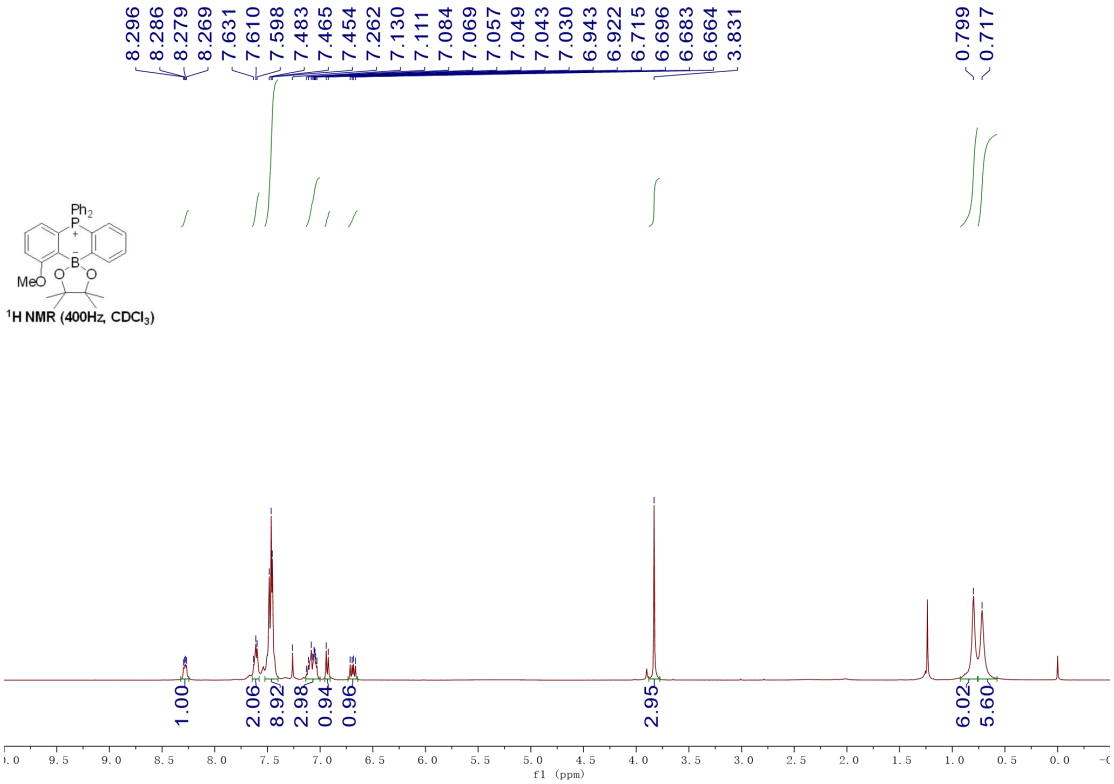
^{13}C NMR (100Hz, $CDCl_3$)



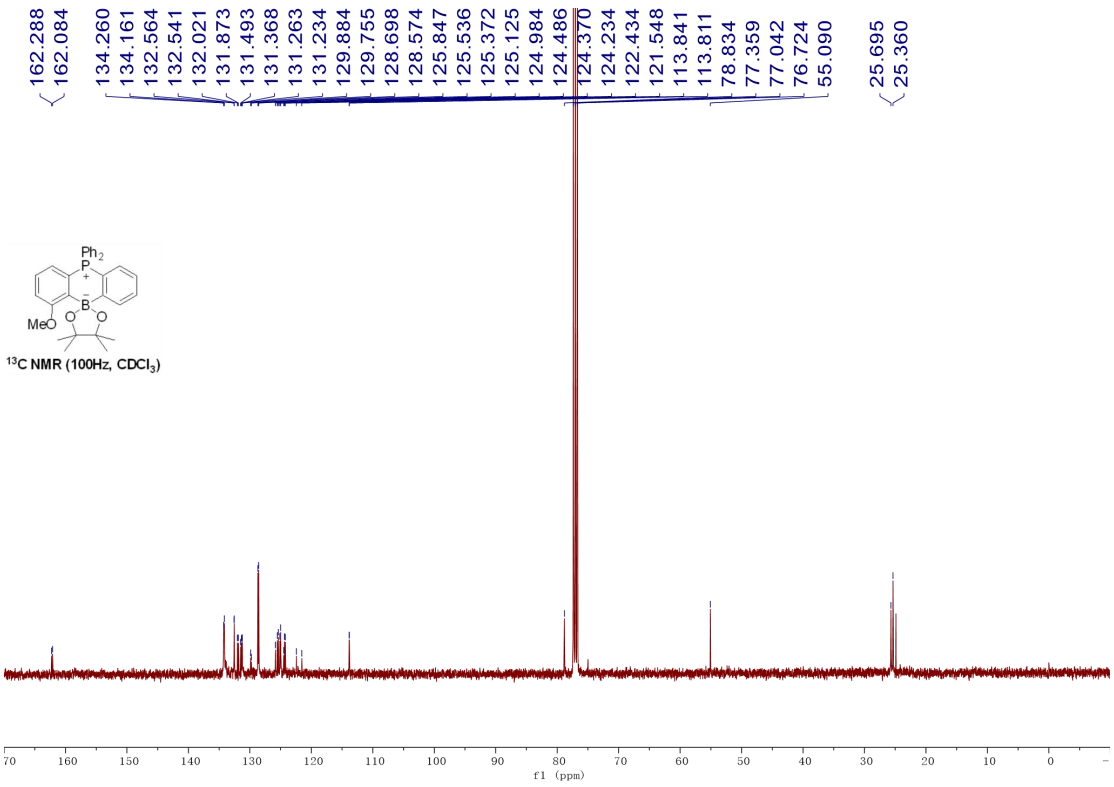


^{31}P NMR (162Hz, $CDCl_3$)

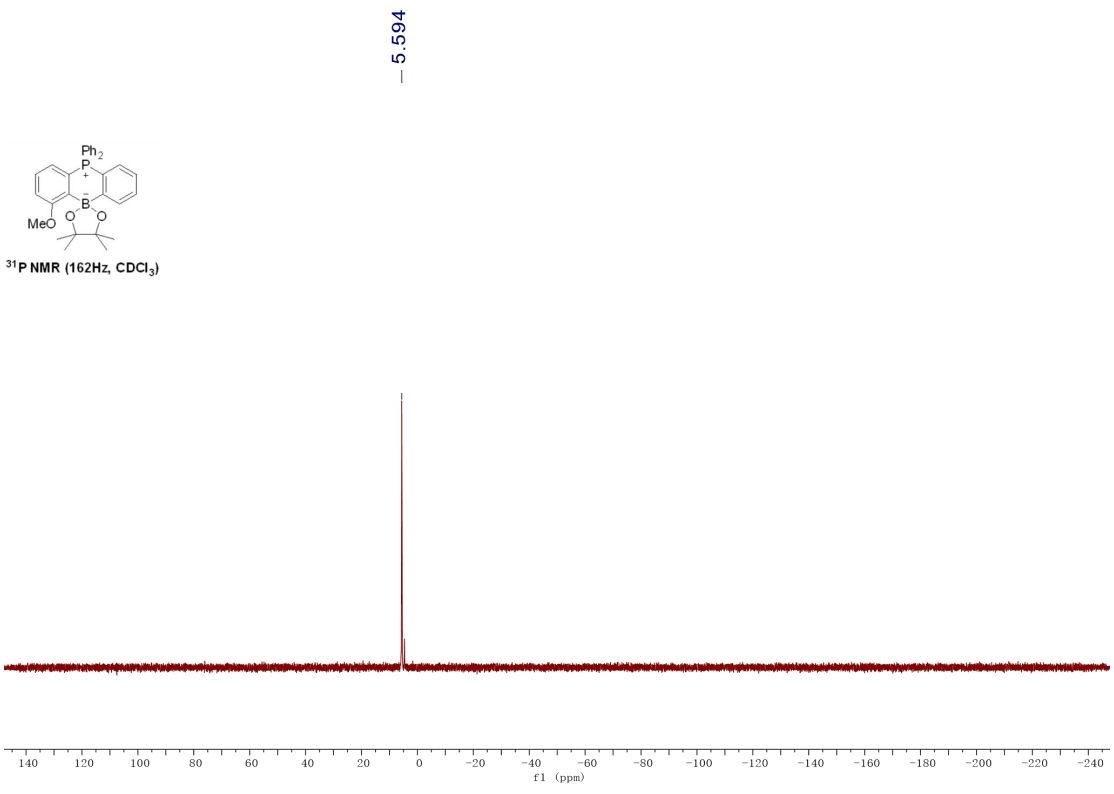
3ai



^{1}H NMR (400Hz, $CDCl_3$)

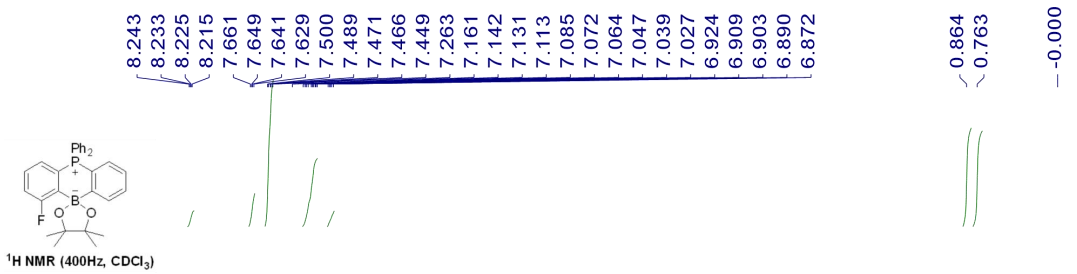


^{13}C NMR (100Hz, $CDCl_3$)

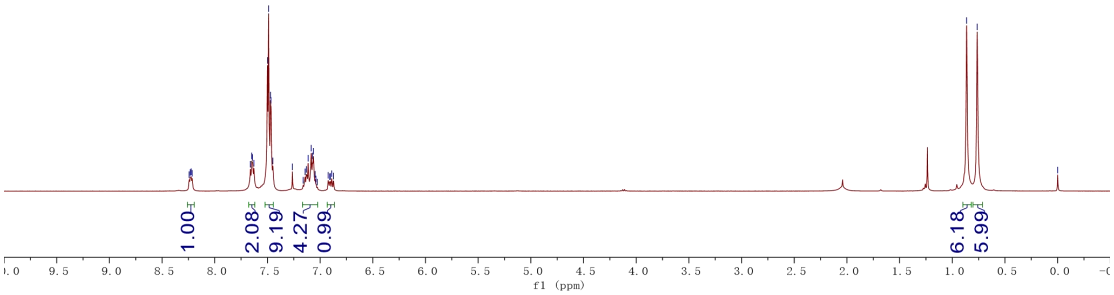


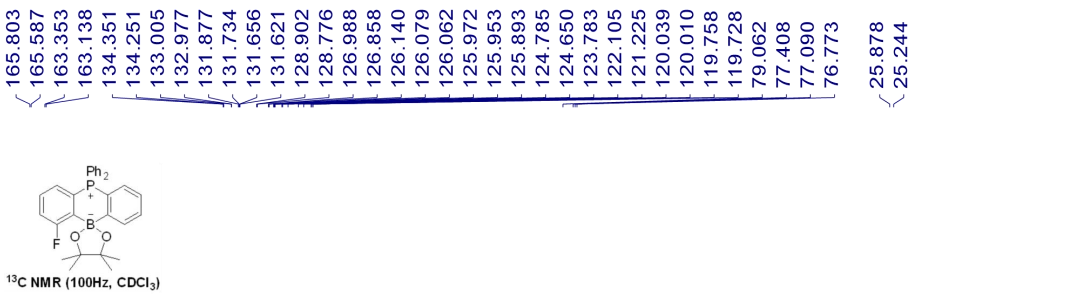
^{31}P NMR (162Hz, $CDCl_3$)

3aj

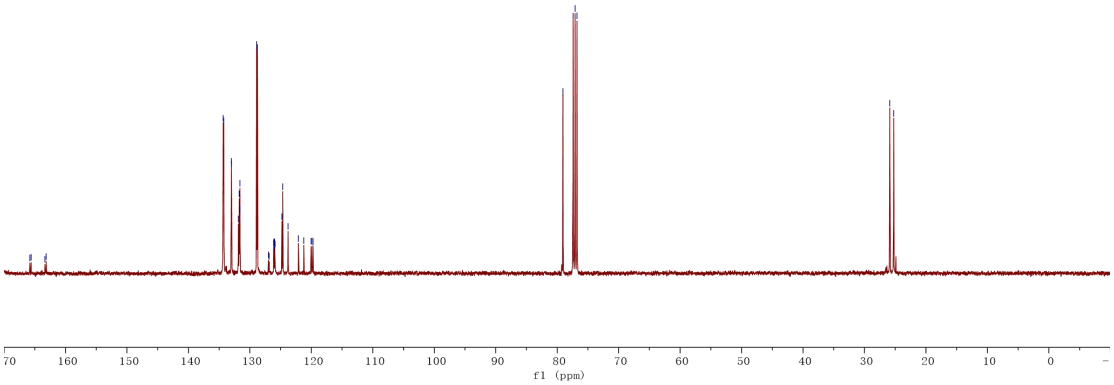


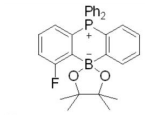
^{1}H NMR (400Hz, $CDCl_3$)



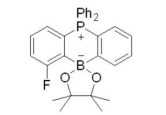


^{13}C NMR (100Hz, $CDCl_3$)



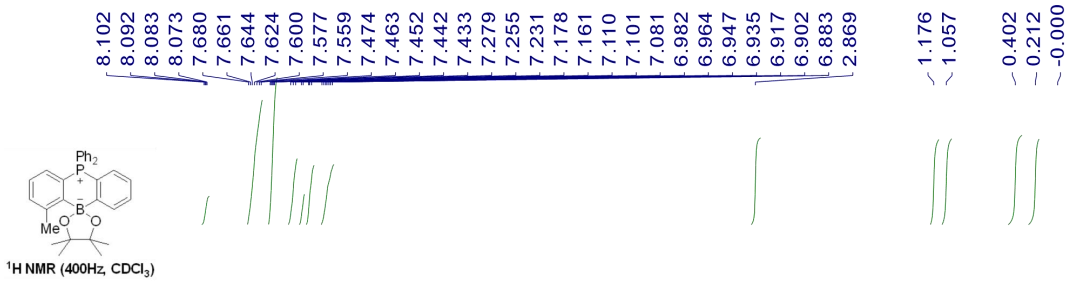


^{31}P NMR (162Hz, $CDCl_3$)

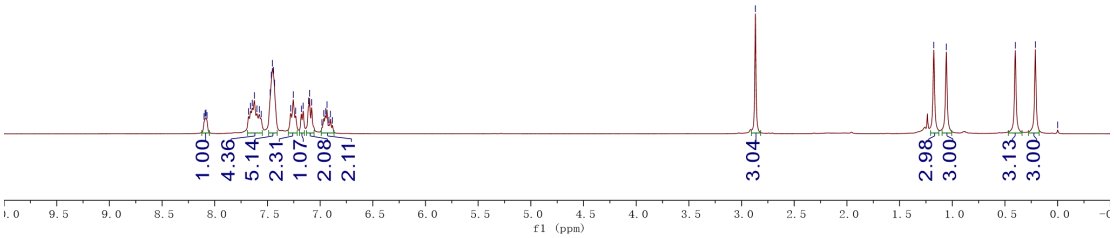


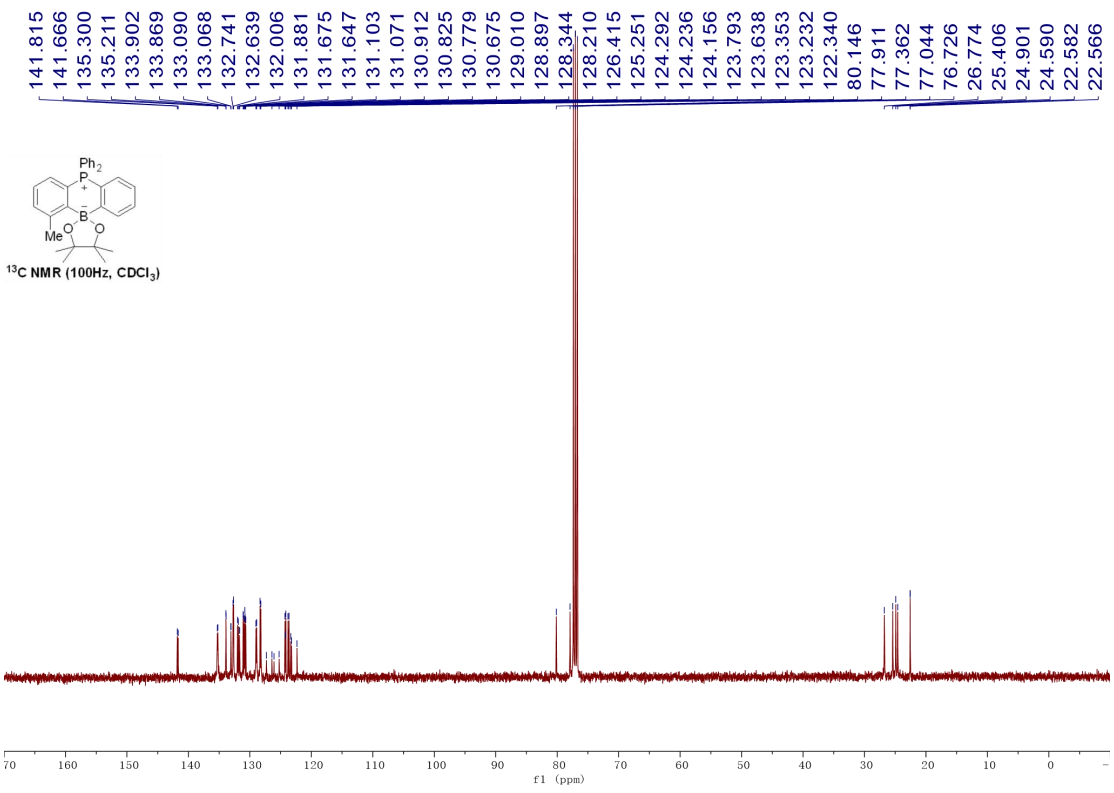
^{19}F NMR (376Hz, $CDCl_3$)

3ak

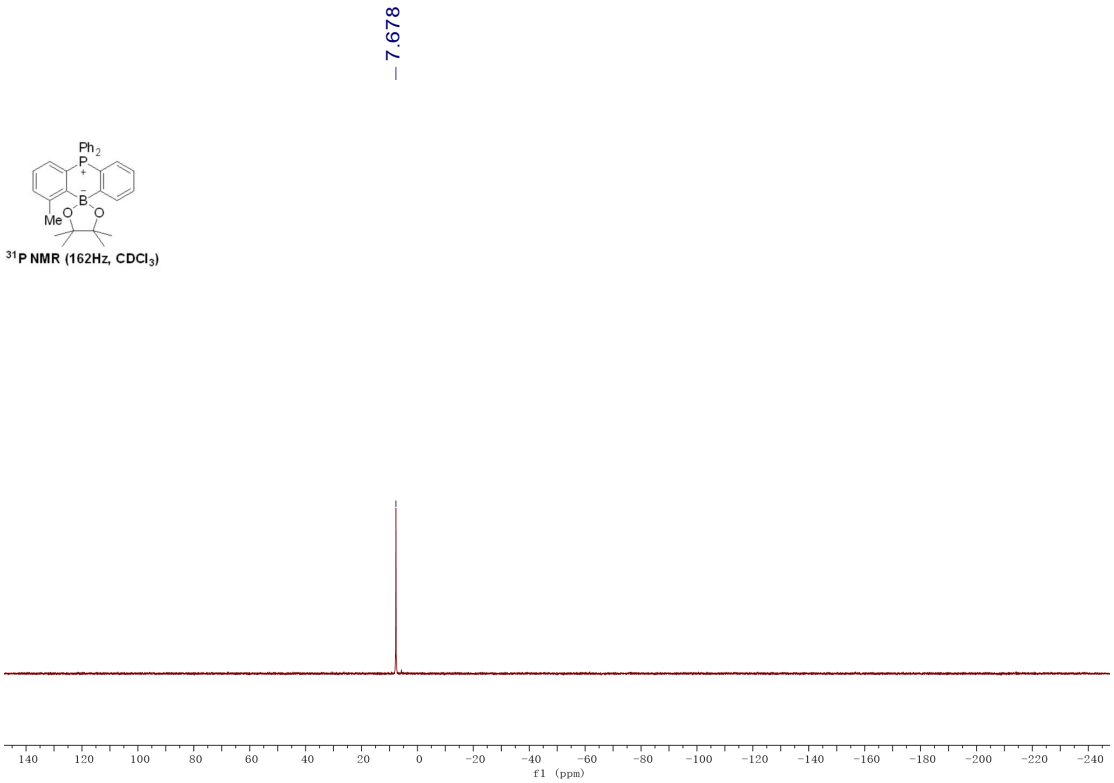


^{1}H NMR (400Hz, $CDCl_3$)

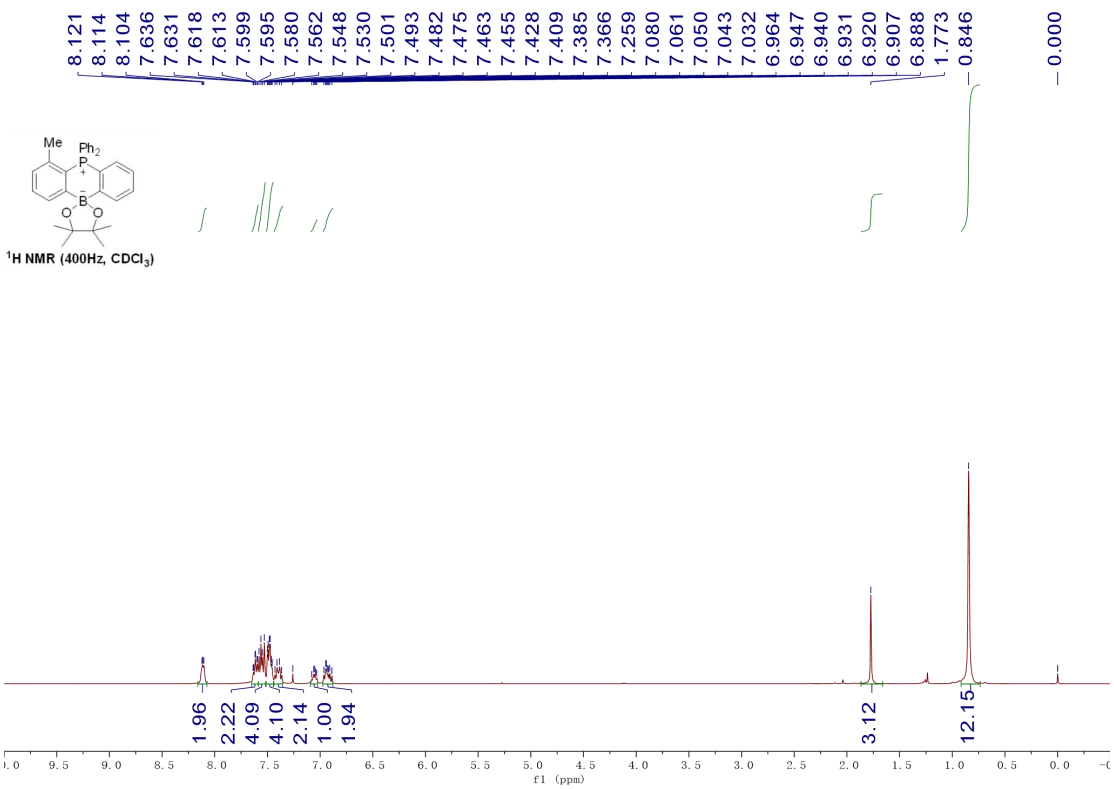


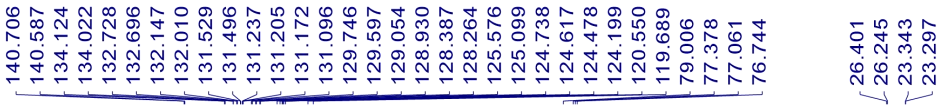


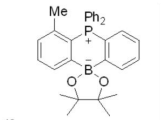
^{13}C NMR (100Hz, $CDCl_3$)


7.678
Ph2
P
B
O
O
Me
31P NMR (162Hz, CDCl3)
f1 (ppm)

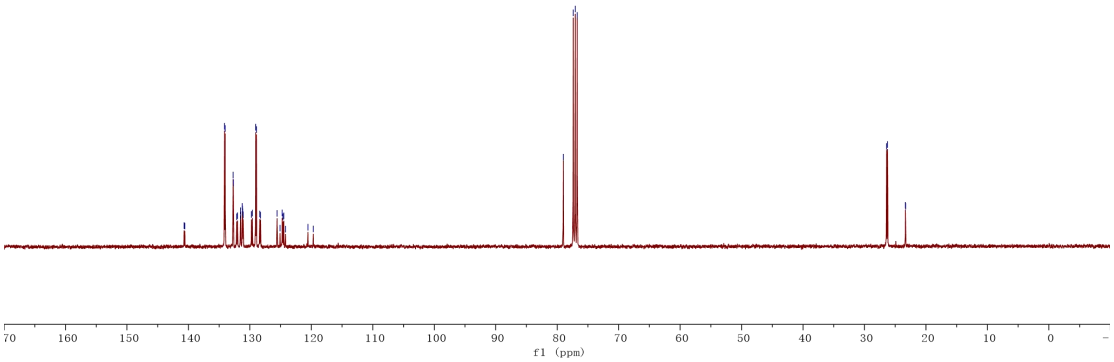
3ak'

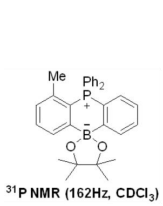

8.121
8.114
8.104
7.636
7.631
7.618
7.613
7.599
7.595
7.580
7.562
7.548
7.530
7.501
7.493
7.482
7.475
7.463
7.455
7.428
7.409
7.385
7.366
7.259
7.080
7.061
7.050
7.043
7.032
6.964
6.947
6.940
6.931
6.920
6.907
6.888
1.773
0.846
0.000
Me
Ph2
P
B
O
O
1H NMR (400Hz, CDCl3)
1.96
2.22
4.09
4.10
2.14
1.00
1.94
3.12
12.15
f1 (ppm)



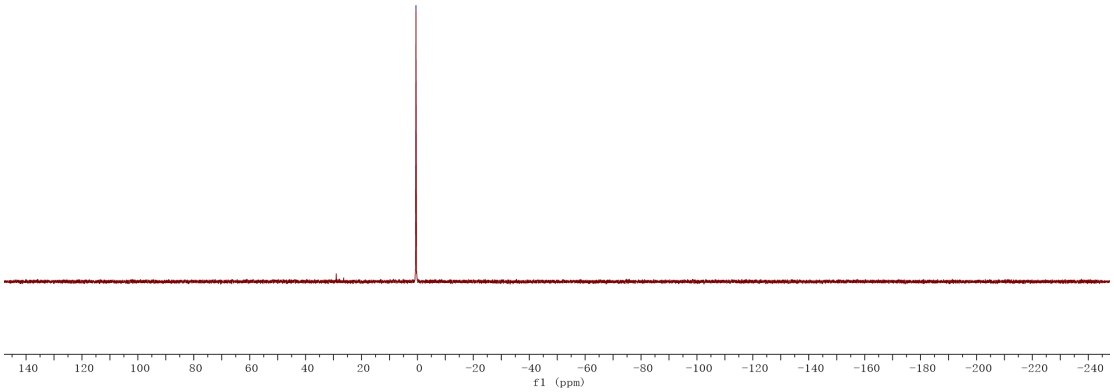


^{13}C NMR (100Hz, $CDCl_3$)

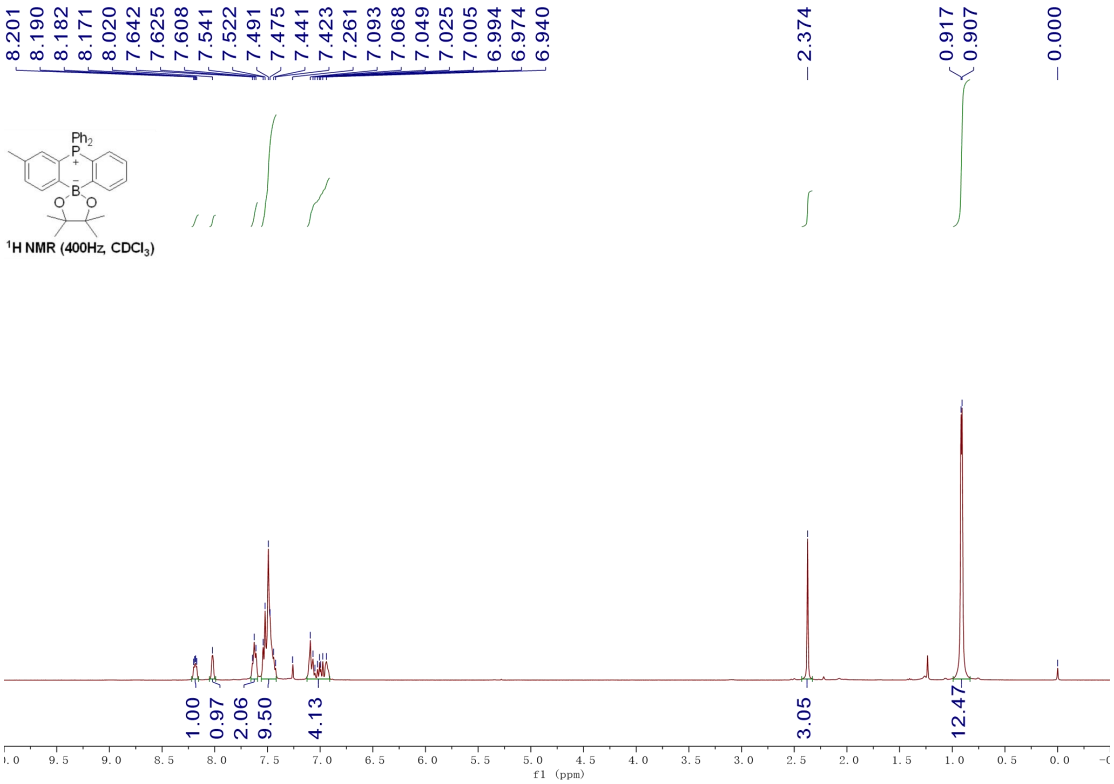


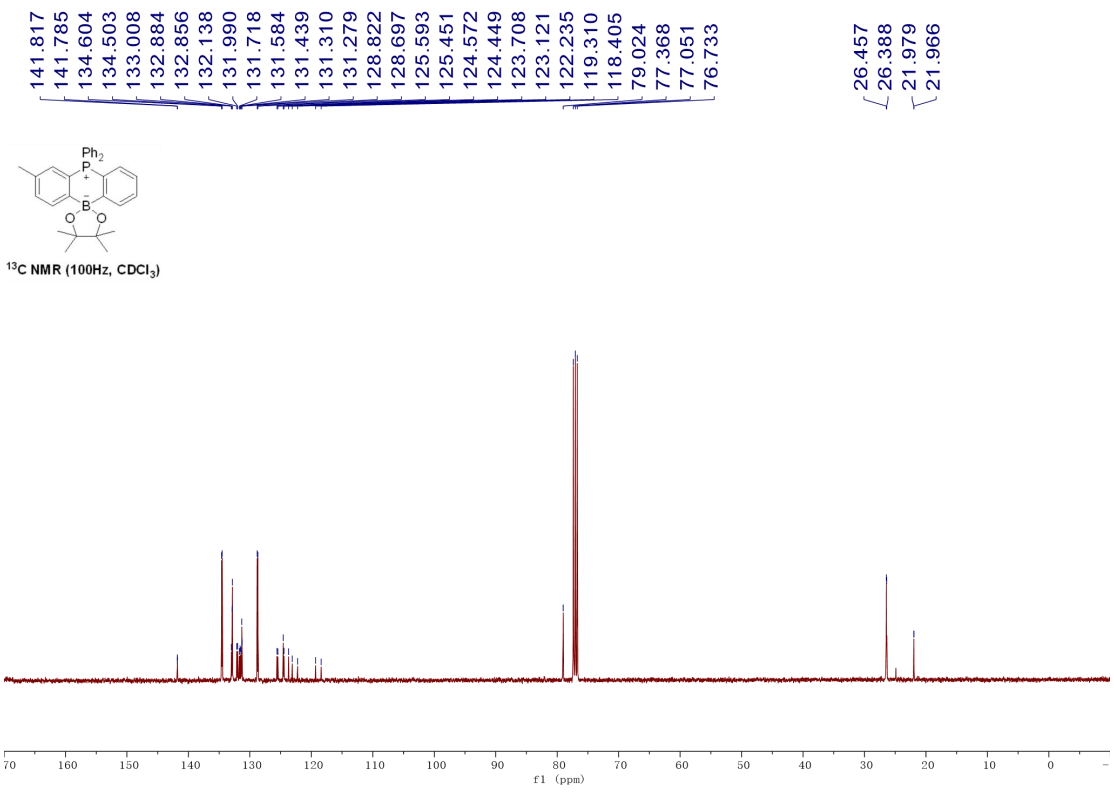


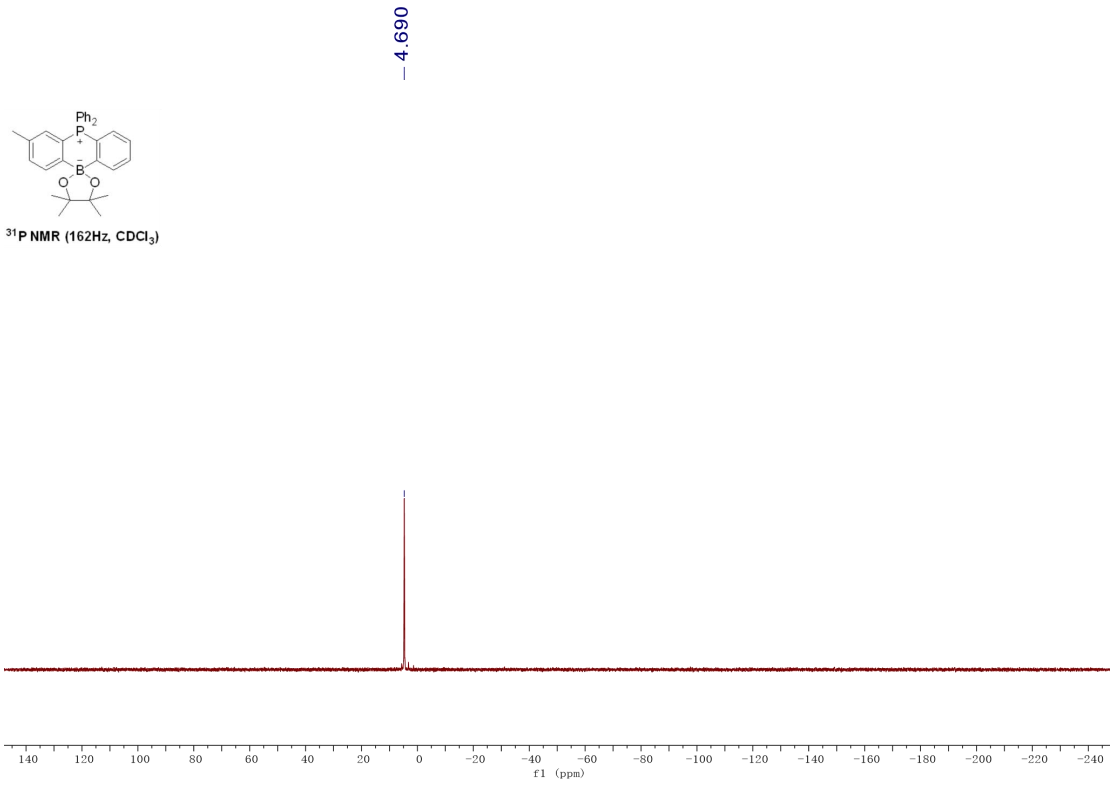
^{31}P NMR (162Hz, $CDCl_3$)



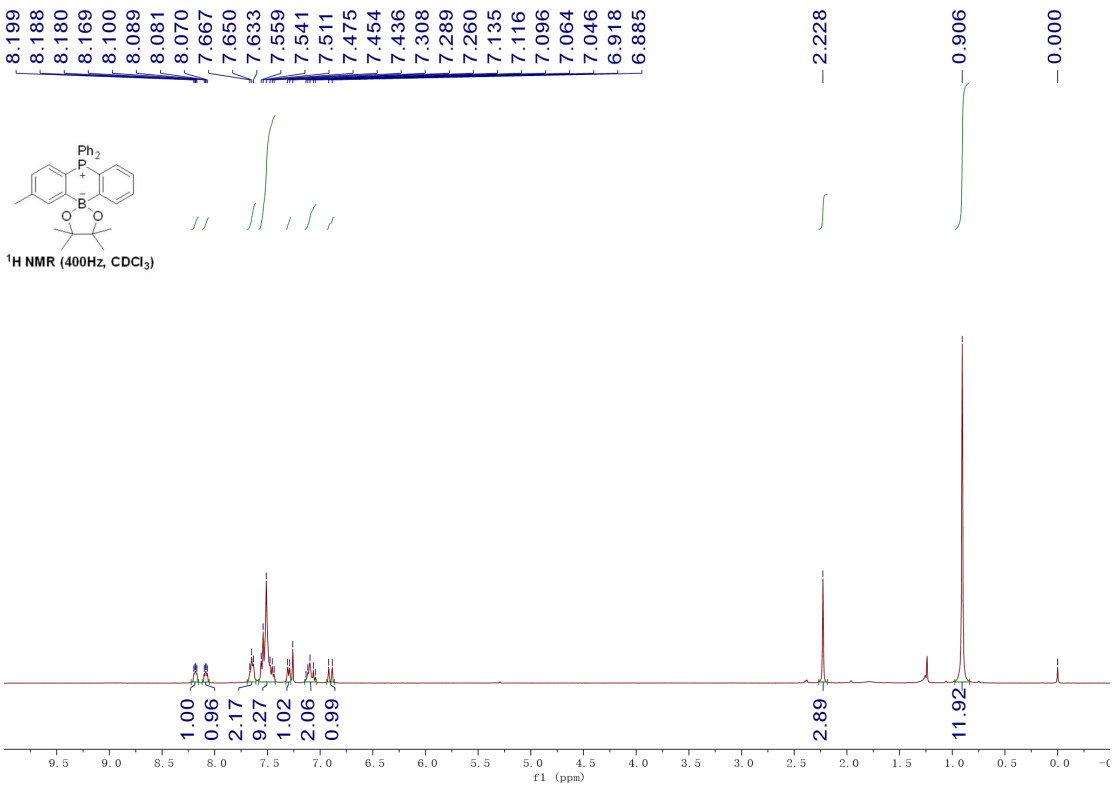
3al

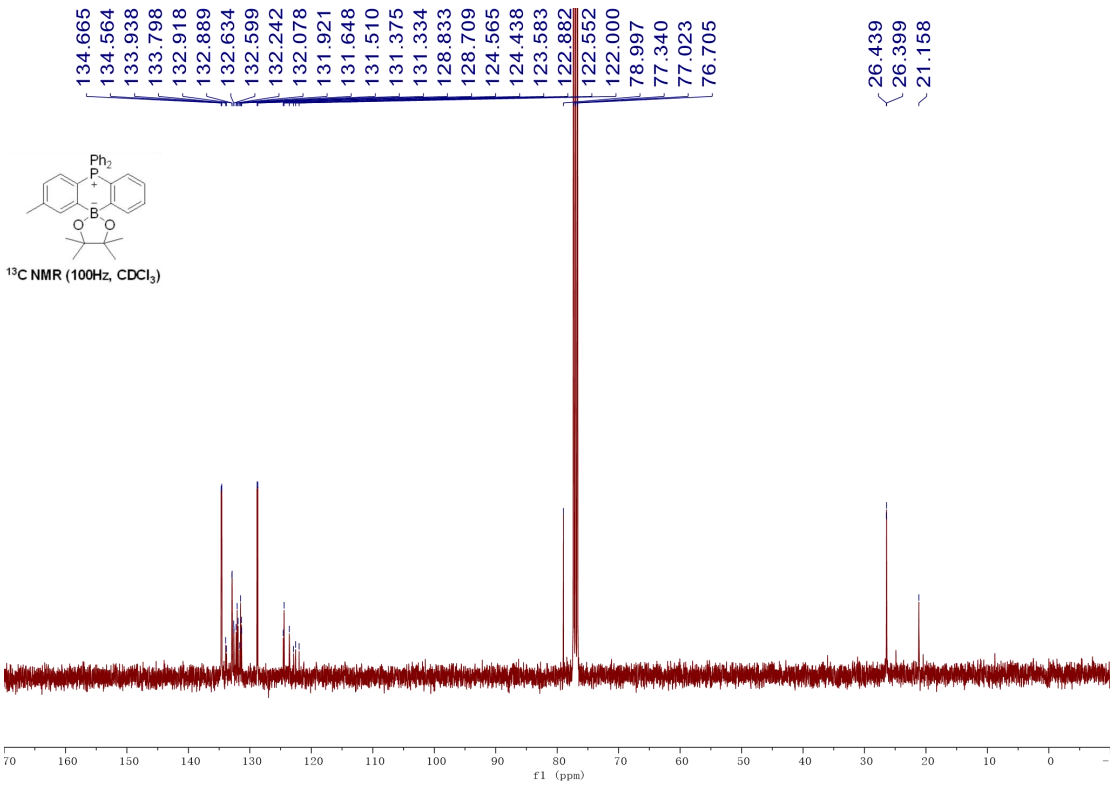

8.201
8.190
8.182
8.171
8.020
7.642
7.625
7.608
7.541
7.522
7.491
7.475
7.441
7.423
7.261
7.093
7.068
7.049
7.025
7.005
6.994
6.974
6.940
2.374
0.917
0.907
0.000
Ph2
P
B
O
O
1H NMR (400Hz, CDCl3)
1.00
0.97
2.06
9.50
4.13
3.05
12.47
f1 (ppm)


141.817
141.785
134.604
134.503
133.008
132.884
132.856
132.138
131.990
131.718
131.584
131.439
131.310
131.279
128.822
128.697
125.593
125.451
124.572
124.449
123.708
123.121
122.235
119.310
118.405
79.024
77.368
77.051
76.733
26.457
26.388
21.979
21.966
Ph2
P
B
O
O
13C NMR (100Hz, CDCl3)
f1 (ppm)

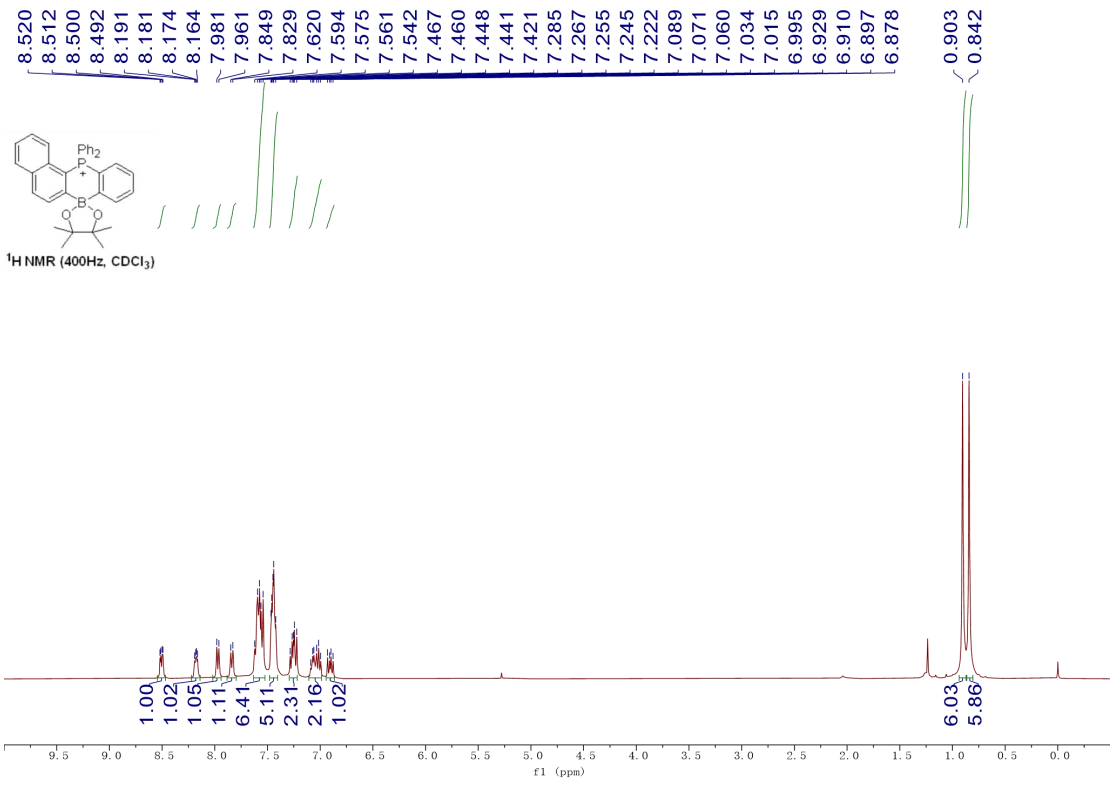

4.690
Ph2
P
B
O
O
31P NMR (162Hz, CDCl3)
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

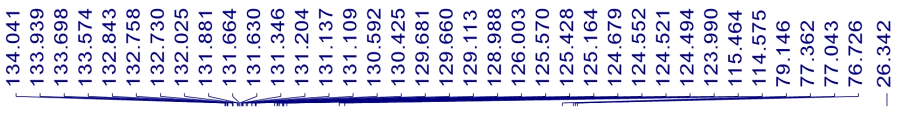
3al'

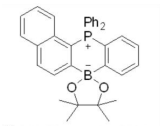

8.199
8.188
8.180
8.169
8.100
8.089
8.081
8.070
7.667
7.650
7.633
7.559
7.541
7.511
7.475
7.454
7.436
7.308
7.289
7.260
7.135
7.116
7.096
7.064
7.046
6.918
6.885
2.228
0.906
0.000
Ph2
P
B
O
O
1H NMR (400Hz, CDCl3)
1.00
0.96
2.17
9.27
1.02
2.06
0.99
2.89
11.92
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


134.665
134.564
133.938
133.798
132.918
132.889
132.634
132.599
132.242
132.078
131.921
131.648
131.510
131.375
131.334
128.833
128.709
124.565
124.438
123.583
122.882
122.552
122.000
78.997
77.340
77.023
76.705
26.439
26.399
21.158
Ph2
P
B
O
O
13C NMR (100Hz, CDCl3)
f1 (ppm)

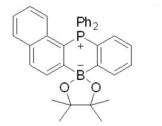
3am


8.520
8.512
8.500
8.492
8.191
8.181
8.174
8.164
7.981
7.961
7.849
7.829
7.620
7.594
7.575
7.561
7.542
7.467
7.460
7.448
7.441
7.421
7.285
7.267
7.255
7.245
7.222
7.089
7.071
7.060
7.034
7.015
6.995
6.929
6.910
6.897
6.878
0.903
0.842
Ph2
P
B
O
O
1H NMR (400Hz, CDCl3)
1.00
1.02
1.05
1.11
6.41
5.11
2.31
2.16
1.02
6.03
5.86
f1 (ppm)

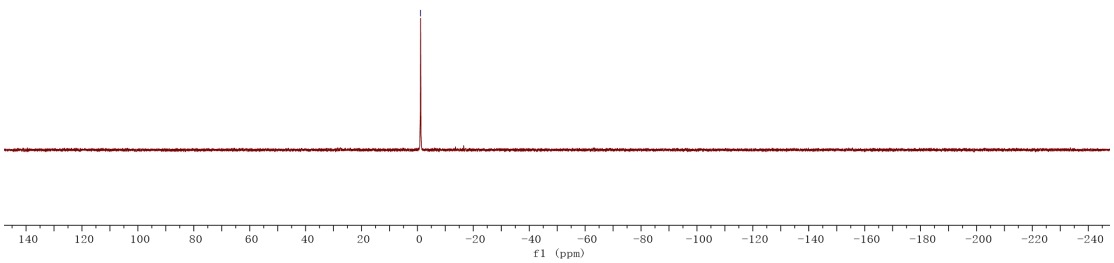




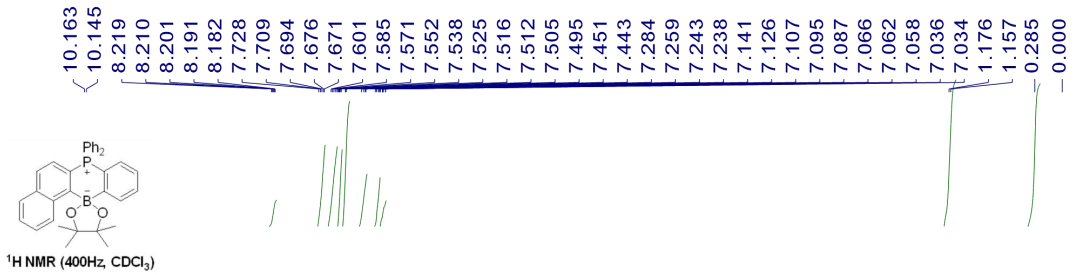
^{13}C NMR (100Hz, $CDCl_3$)



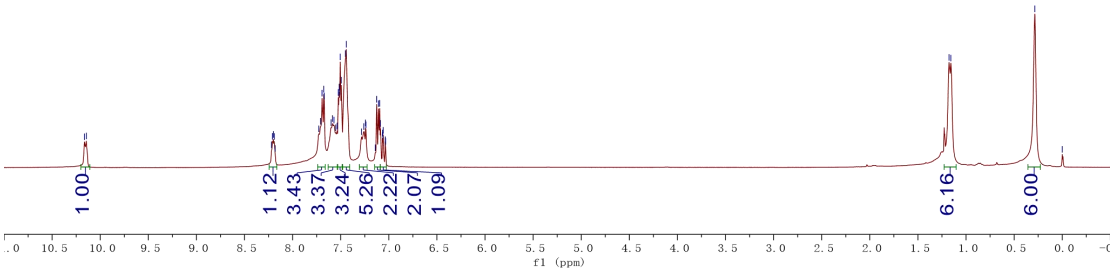
^{31}P NMR (162Hz, $CDCl_3$)

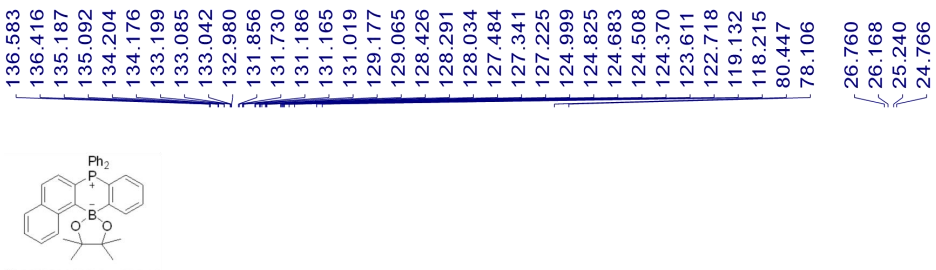


3am'

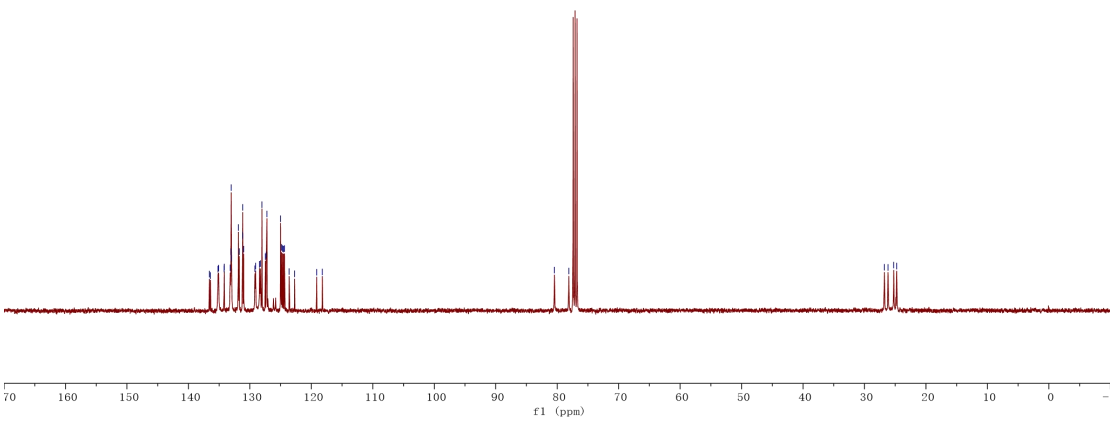


^{1}H NMR (400Hz, $CDCl_3$)



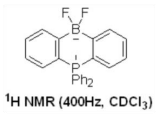


^{13}C NMR (100Hz, $CDCl_3$)

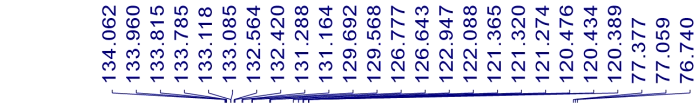


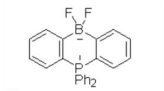
^{31}P NMR (162Hz, $CDCl_3$)

4

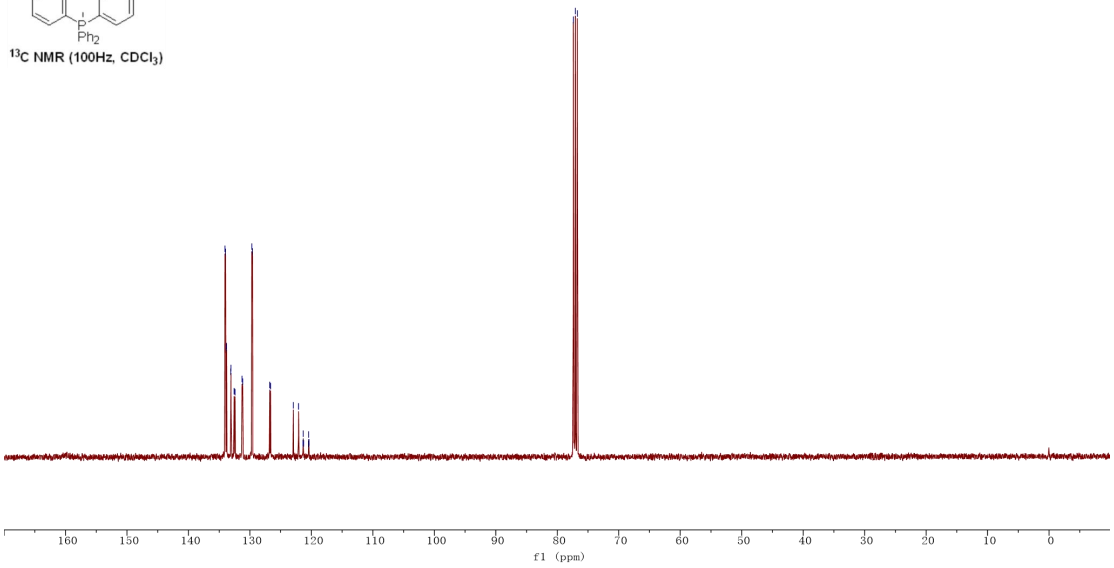


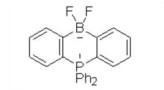
^{1}H NMR (400Hz, $CDCl_3$)



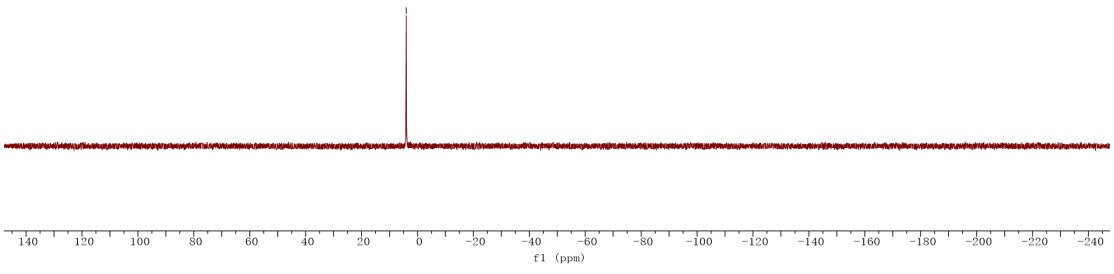


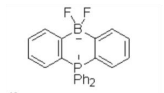
^{13}C NMR (100Hz, $CDCl_3$)





^{31}P NMR (162Hz, $CDCl_3$)





^{19}F NMR (376Hz, $CDCl_3$)

-158.864