Cover Page for Supporting Information

Manuscript Title:

Alkaline-Earth Metallacyclic Complexes Bearing Diborane-Bridged Tetraamide Ligand: Synthesis, Structure and Fluorescence Property

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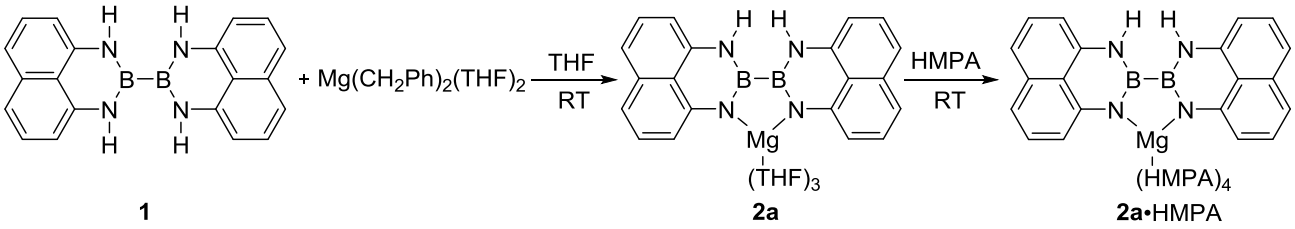
Contents

1) Experimental Details

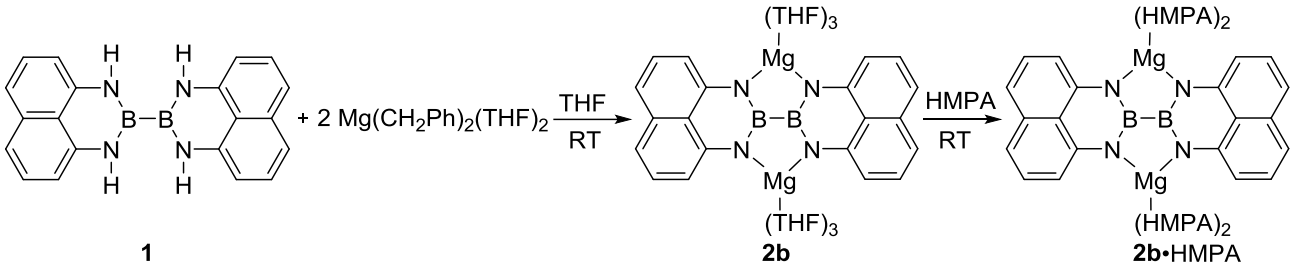
All reactions were carried out under an atmosphere of dry argon by using glove box (< 0.1 ppm O_2 and H_2O) with dry solvents under anhydrous conditions, unless otherwise noted. Reagents were purchased at the highest commercial quality and used without further purification. Tetrahydrofuran (THF), hexane, ether and toluene were distilled from sodium/benzophenone ketyl immediately before use. Hexamethylphosphoramide (HMPA) was distilled from calcium hydride and stored under an argon atmosphere. NMR spectra were recorded with a Bruker AV 400/500 spectrometer at 400 MHz (^{1}H NMR), 126 MHz (^{13}C NMR), 202 MHz (^{31}P NMR) and 160 MHz (^{11}B NMR). The following abbreviations are used to designate multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Elemental analysis was performed on a Vario EL elemental analyzer at the Analytical Center of Peking University. UV-Vis absorption spectra were recorded using a Shimadzu UV3600Plus UV-VIS-NIR spectrophotometer. The emission spectra and lifetime were obtained using a spectrometer (FLS920) from Edinburgh Instruments Ltd. The absolute quantum yields were measured using a Hamamatsu C9920-02 absolute PL quantum yield measurement system.



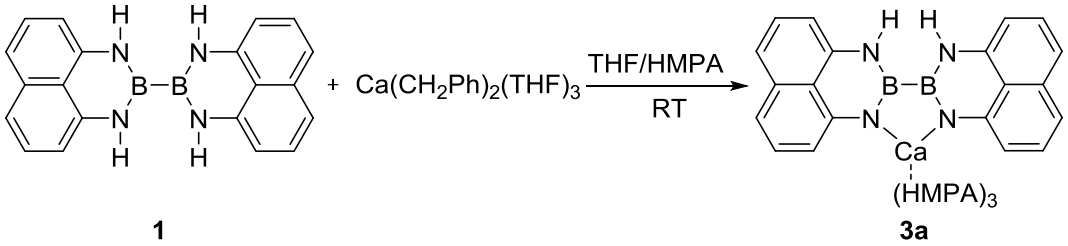
1 **2a** **2a**•HMPA

Complex 2a: To a solution of **1** (60 mg, 0.18 mmol) in THF (1.0 mL) was carefully added a THF (1.0 mL) solution of dibenzylmagnesium (63 mg, 0.18 mmol). The mixture was stood at RT for 8 h until all precipitate was formed. After vacuum filtration, **2a**·2THF was obtained as a THF-insoluble yellow crystal (72 mg, 70%), which was suitable for X-ray crystallography. Addition of drops of HMPA to a suspension of **2a**·2THF in THF gave a clear solution. The solution was evaporated under vacuum, leaving the product as a yellow solid, which was identified as **2a**·HMPA. Data for **2a**·HMPA : ^{1}H NMR (400 MHz, THF-d_8) δ 2.60 (d, J = 12.0 Hz, 72 H), 5.83 (d, J = 4.0 Hz, 2 H), 6.09 (d, J = 8.0 Hz, 2 H), 6.32 (d, J = 8.0 Hz, 2 H), 6.48 (d, J = 8.0 Hz, 2 H), 6.77–6.65 (m, 6 H); ^{13}C NMR (126 MHz, THF-d_8) δ 36.8 (d, J = 3.8 Hz), 102.0, 110.1, 111.2, 114.3, 125.7, 126.9, 128.1, 139.2, 146.6, 155.0; ^{31}P NMR (202 MHz, THF-d_8) δ 24.1; ^{11}B NMR (160 MHz, THF-d_8) δ 32.5. Anal. Calcd (%). for

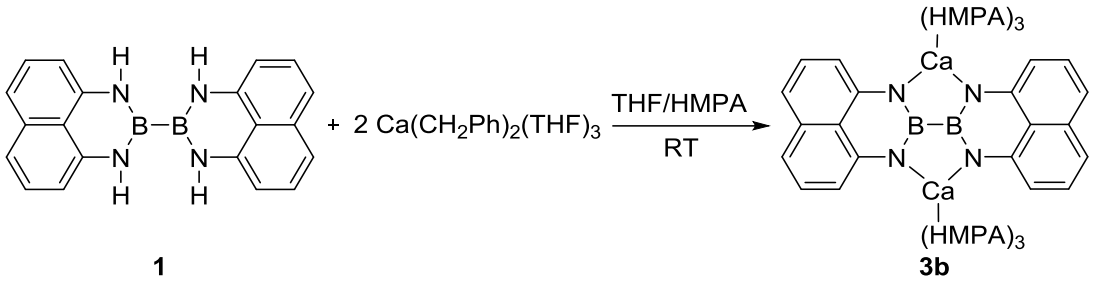
$C_{44}H_{86}B_2MgN_{16}O_4P_4$: C, 49.25; H, 8.08; N, 20.88; Found: C, 49.32; H, 8.04; N, 20.88.



Complex 2b: To a solution of dibenzylmagnesium (126 mg, 0.36 mmol) in THF (2.0 mL) was carefully added a THF (1.0 mL) solution of **1** (60 mg, 0.18 mmol). The mixture was stood at RT for 8 h until all precipitate was formed. After vacuum filtration, **2b** was obtained as a THF-insoluble yellow crystal (97 mg, 67%), which was suitable for X-ray crystallography. Addition of drops of HMPA to a suspension of **2b** in THF gave a light yellow precipitate, which were identified as **2b**·HMPA. No NMR spectrum of **2b**·HMPA was recorded due to the low solubility in various NMR solvents (0.5 mL). Data for **2b**·HMPA: Anal. Calcd (%). for $C_{44}H_{84}B_2Mg_2N_{16}O_4P_4$: C, 48.25; H, 7.73; N, 20.46; Found: C, 48.19; H, 7.69; N, 20.20.

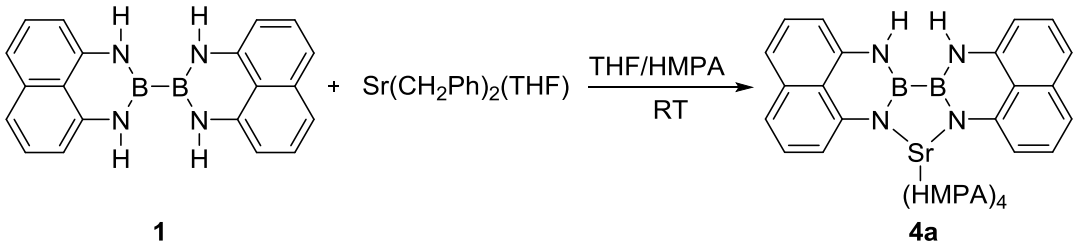


Complex 3a: To a stirred solution of **1** (60 mg, 0.18 mmol) in THF/HMPA (3.0/0.15 mL) was added dibenzylcalcium (79 mg, 0.18 mmol). After stirring at RT for 30 mins, the solvent was removed under reduced pressure and the residue was washed with ether (2 × 3 mL) and dried under vacuum to obtain **3a** as a yellow solid (107 mg, 65%). Single crystals of **3a**·HMPA could be grown from a concentrated solution in THF/ether at room temperature. Data for **3a**·HMPA: ^{1}H NMR (400 MHz, THF-d_8) δ 2.56 (d, J = 9.6 Hz, 72 H), 5.77 (d, J = 7.2 Hz, 2 H), 6.17 (d, J = 7.6 Hz, 2 H), 6.23 (d, J = 7.6 Hz, 2 H), 6.36 (d, J = 8.0 Hz, 2 H), 6.60 (t, J = 7.6 Hz, 2 H), 6.67 (t, J = 7.6 Hz, 2 H), 6.73 (s, 2 H); ^{13}C NMR (126 MHz, THF-d_8) δ 37.0 (d, J = 4.1 Hz), 100.8, 109.5, 110.7, 113.4, 125.8, 126.6, 128.1, 139.4, 147.2, 157.2; ^{31}P NMR (202 MHz, THF-d_8) δ 24.2; ^{11}B NMR (160 MHz, THF- d_8) δ 32.5. Anal. Calcd (%). for $C_{44}H_{86}B_2CaN_{16}O_4P_4$: C, 48.53; H, 7.96; N, 20.58; Found: C, 47.89; H, 8.10; N, 20.65.



1 **3b**

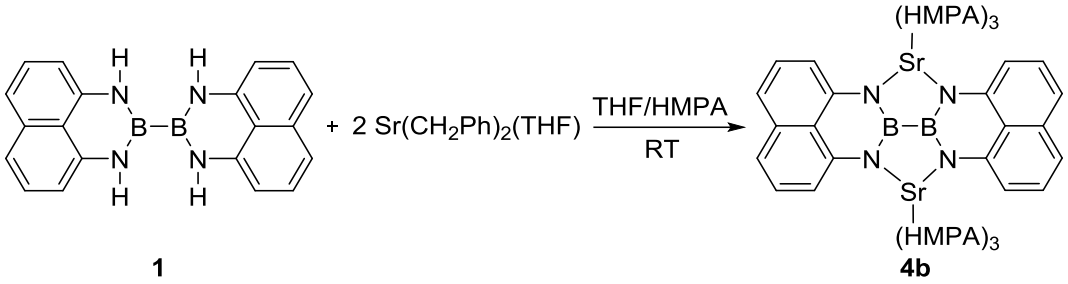
Complex 3b: To a stirred solution of **1** (40 mg, 0.12 mmol) in THF/HMPA (5.0/0.23 mL) was added dibenzylcalcium (104 mg, 0.24 mmol). After stirring at RT for 30 mins, the solvent was removed under reduced pressure and the residue was washed with ether (2 × 4 mL) and dried under vacuum to obtain **3b** as a yellow solid (107 mg, 60%). Single crystals of **3b** could be grown from a concentrated solution in THF/ether at room temperature. Data for **3b**: ^{1}H NMR (400 MHz, THF-d_8) δ 2.58 (d, J = 9.2 Hz, 108 H), 5.67 (d, J = 78.0 Hz, 2 H), 5.78 (d, J = 8.0 Hz, 2 H), 5.90 (d, J = 8.0 Hz, 2 H), 6.04 (d, J = 8.0 Hz, 2 H), 6.37 (t, J = 7.6 Hz, 2 H), 6.58 (t, J = 7.6 Hz, 2 H); ^{13}C NMR (126 MHz, THF-d_8) δ 36.9 (d, J = 3.9 Hz), 105.5, 107.0, 127.2, 128.2, 141.7, 159.9; ^{31}P NMR (202 MHz, THF-d_8) δ 23.9; ^{11}B NMR (160 MHz, THF-d_8) δ 33.9. Anal. Calcd (%). for $C_{56}H_{120}B_2Ca_2N_{22}O_6P_6$: C, 45.28; H, 8.14; N, 20.75; Found: C, 45.73; H, 8.17; N, 20.77.



1 **4a**

Complex 4a: Starting from dibenzylstrontium (51 mg, 0.15 mmol) and **1** (50 mg, 0.15 mmol), complex **4a** was obtained as a yellow solid (105 mg, 62% yield) in a manner analogous to that described for the synthesis of **3a**. Single crystals of **4a**·THF could be grown from a concentrated solution in THF/toluene at room temperature. Data for **4a**·THF: ^{1}H NMR (400 MHz, THF-d_8) δ 1.77 (s, 4 H; β-CH_2, THF), 2.58 (d, J = 9.6 Hz, 72 H), 3.62 (s, 4 H; α-CH_2, THF), 5.75 (d, J = 7.2 Hz, 2 H), 6.15 (d, J = 7.6 Hz, 2 H), 6.21 (d, J = 7.6 Hz, 2 H), 6.34 (d, J = 8.0 Hz, 2 H), 6.58 (t, J = 7.6 Hz, 2 H), 6.67–6.63 (m, 4 H); ^{13}C NMR (126 MHz, THF-d_8) δ 36.9 (d, J = 3.8 Hz), 100.5, 108.8, 110.6, 113.1, 125.9, 126.6, 128.2, 139.5, 147.6, 158.0; ^{31}P NMR (202 MHz, THF-d_8) δ 24.1; ^{11}B NMR (160 MHz,

THF-d_8) δ 33.6. Anal. Calcd (%). for $C_{48}H_{94}B_2SrN_{16}O_5P_4$: C, 47.71; H, 7.84; N, 18.54; Found: C, 47.99; H, 7.86; N, 18.29.



1 4b

Complex 4b: Starting from dibenzylstrontium (82 mg, 0.24 mmol) and **1** (40 mg, 0.12 mmol), complex **4b** was obtained as a yellow solid (104 mg, 55% yield) in a manner analogous to that described for the synthesis of **3b**. Single crystals of **4b** could be grown from a concentrated solution in THF/toluene at room temperature. No NMR spectrum of crystal **4b** was recorded due to the low solubility in various NMR solvents (0.5 mL). Data for **4b**: Anal. Calcd (%). for $C_{56}H_{120}B_2Sr_2N_{22}O_6P_6$: C, 42.56; H, 7.65; N, 19.50; Found: C, 43.28; H, 7.19; N, 18.69.

2) NMR Spectra of All New Complexes

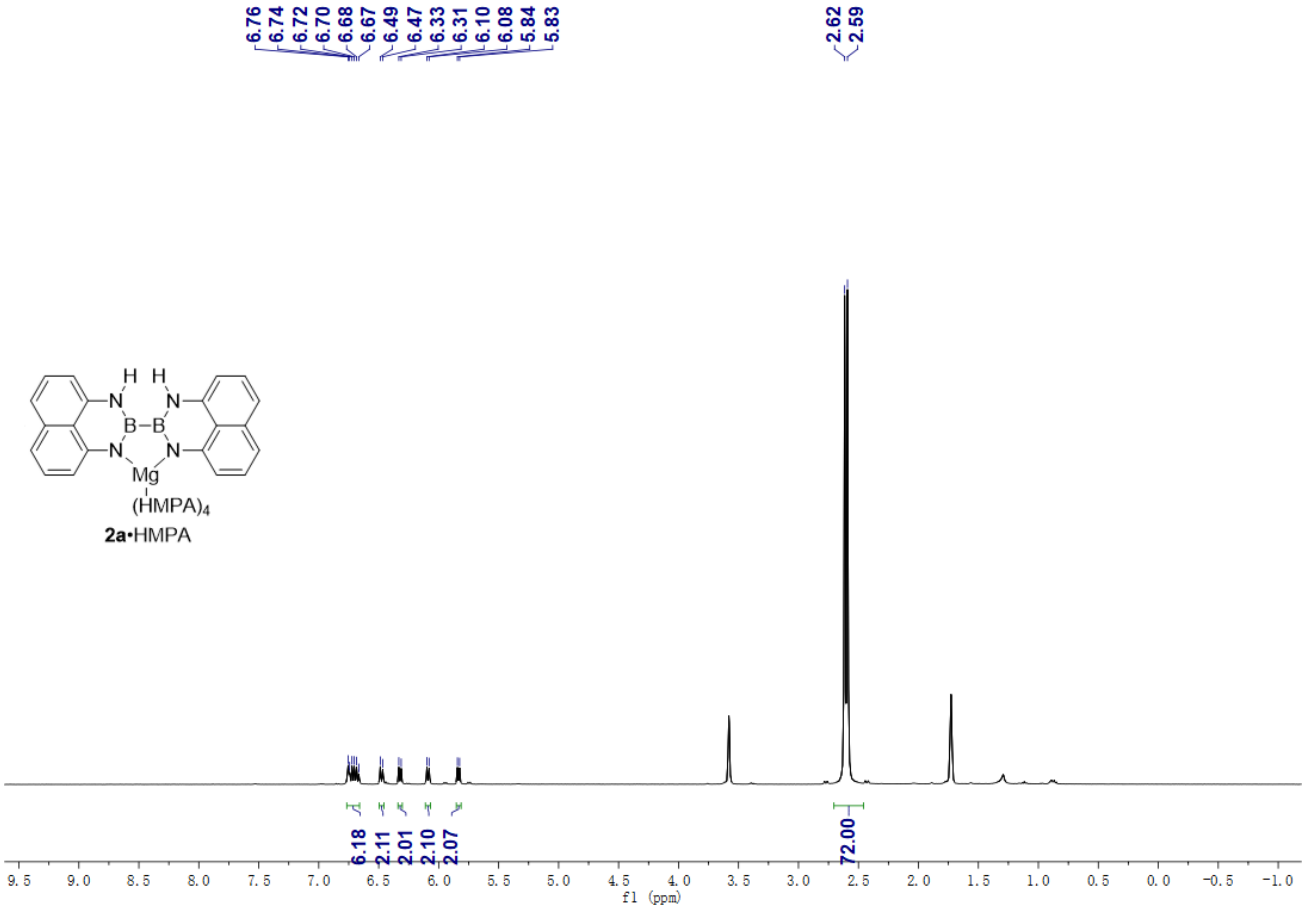


Figure S1. ^{1}H NMR Spectrum of **2a**·HMPA (25^{o}C, 400 MHz, THF-d_8).

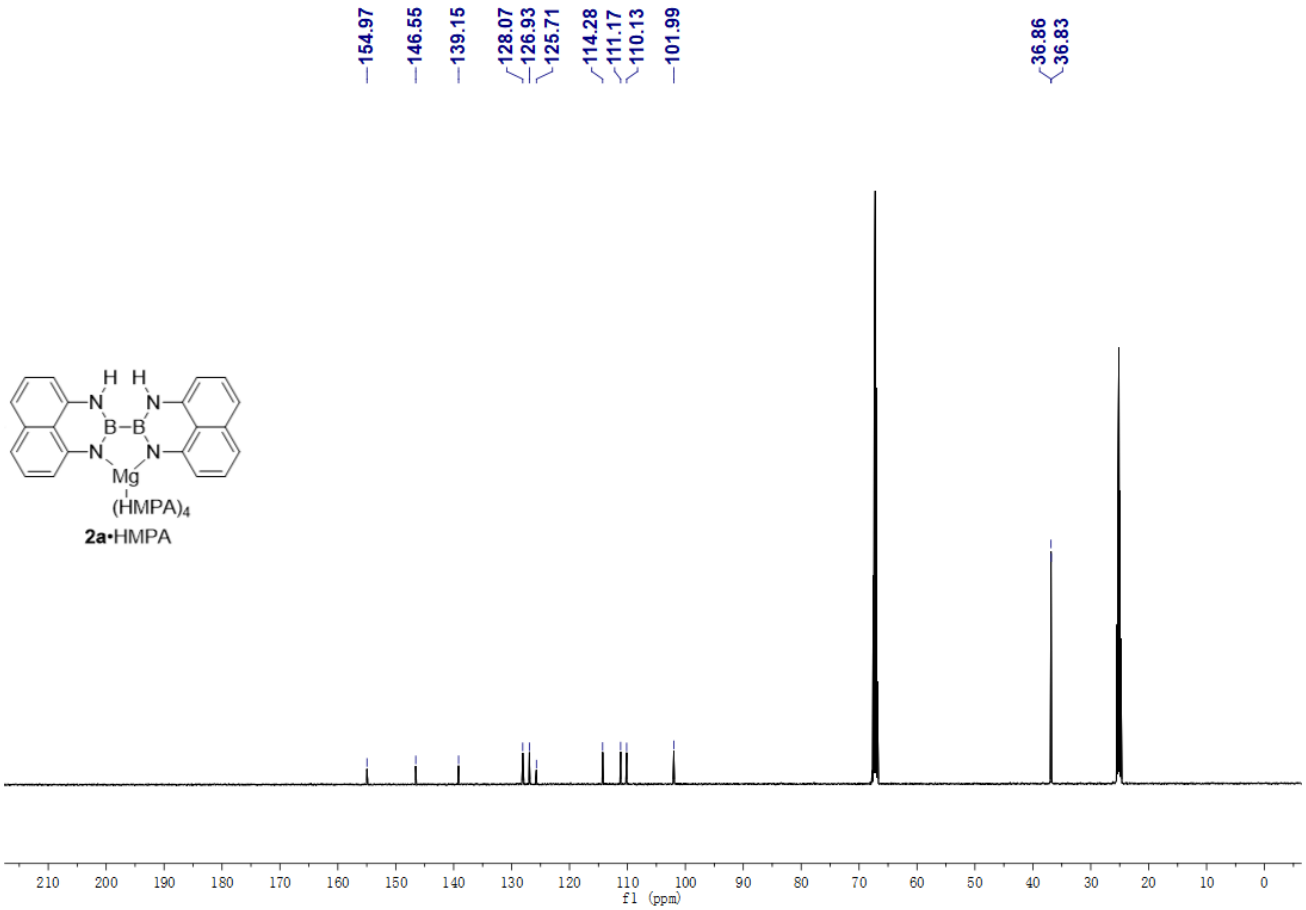


Figure S2. ^{13}C NMR Spectrum of **2a**·HMPA (25°C, 126 MHz, THF-d_8).

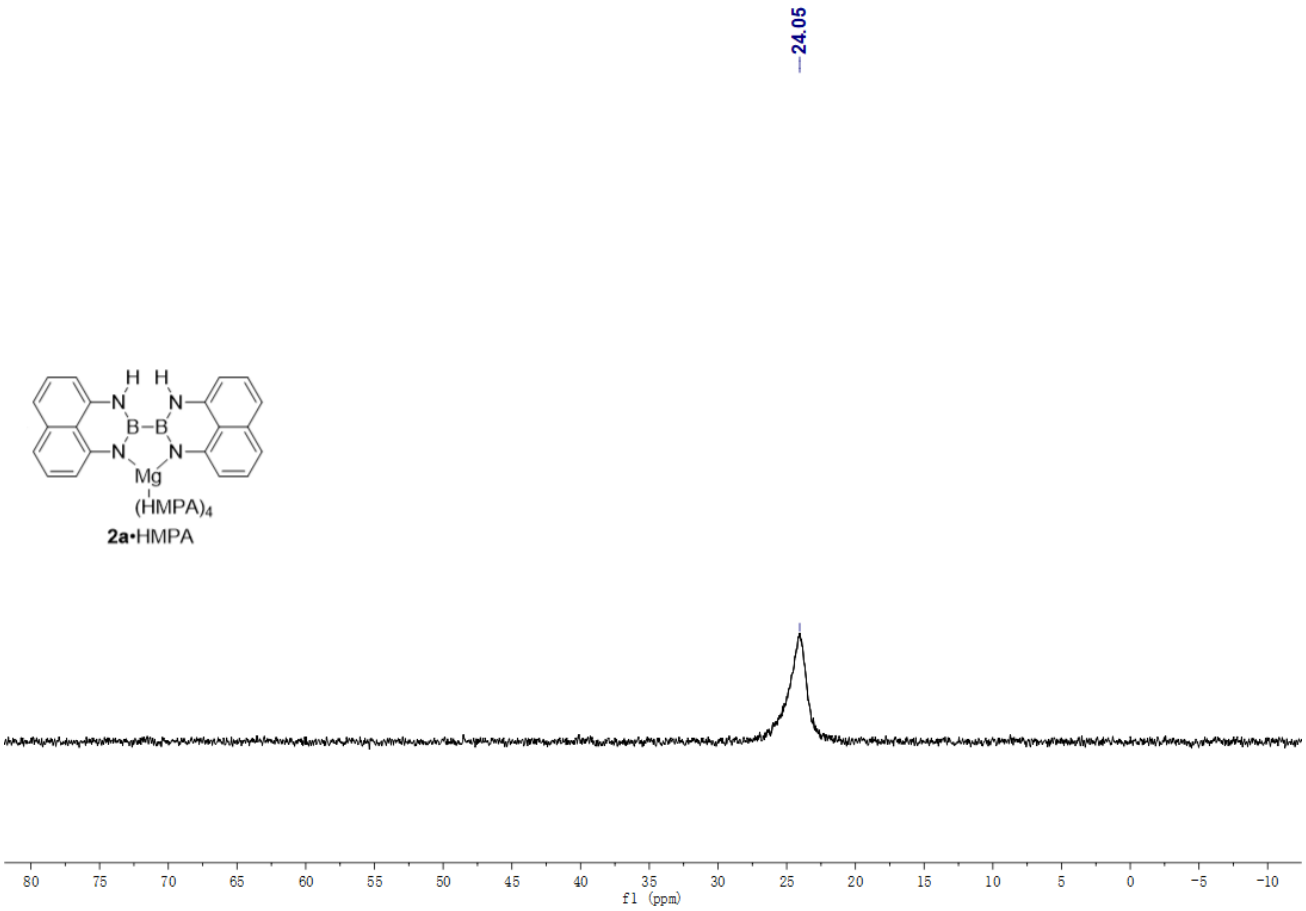


Figure S3. ^{31}P NMR Spectrum of **2a**·HMPA (25°C, 202 MHz, THF-d_8).

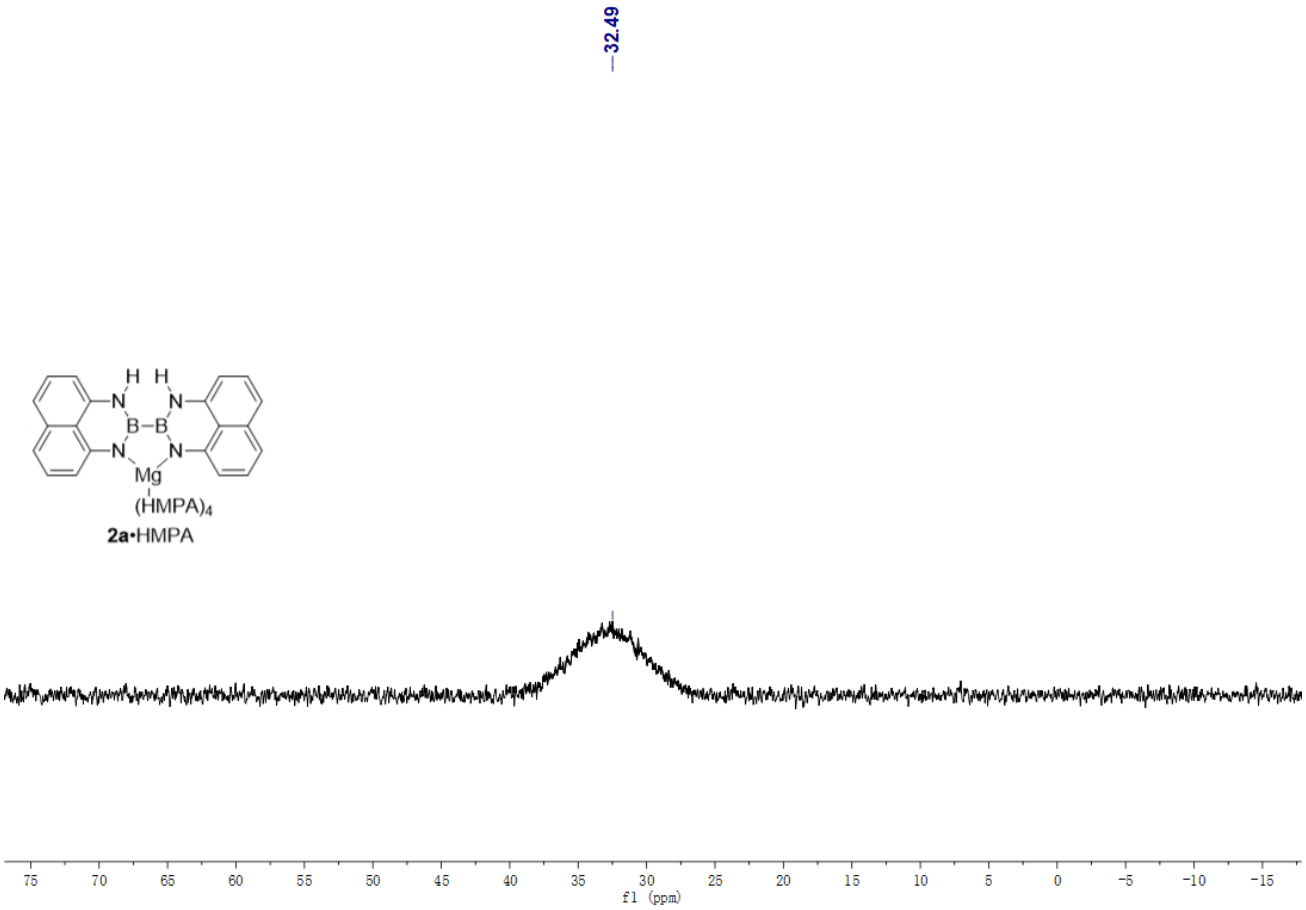


Figure S4. ^{11}B NMR Spectrum of **2a**·HMPA (25ºC, 160 MHz, THF-d_8).

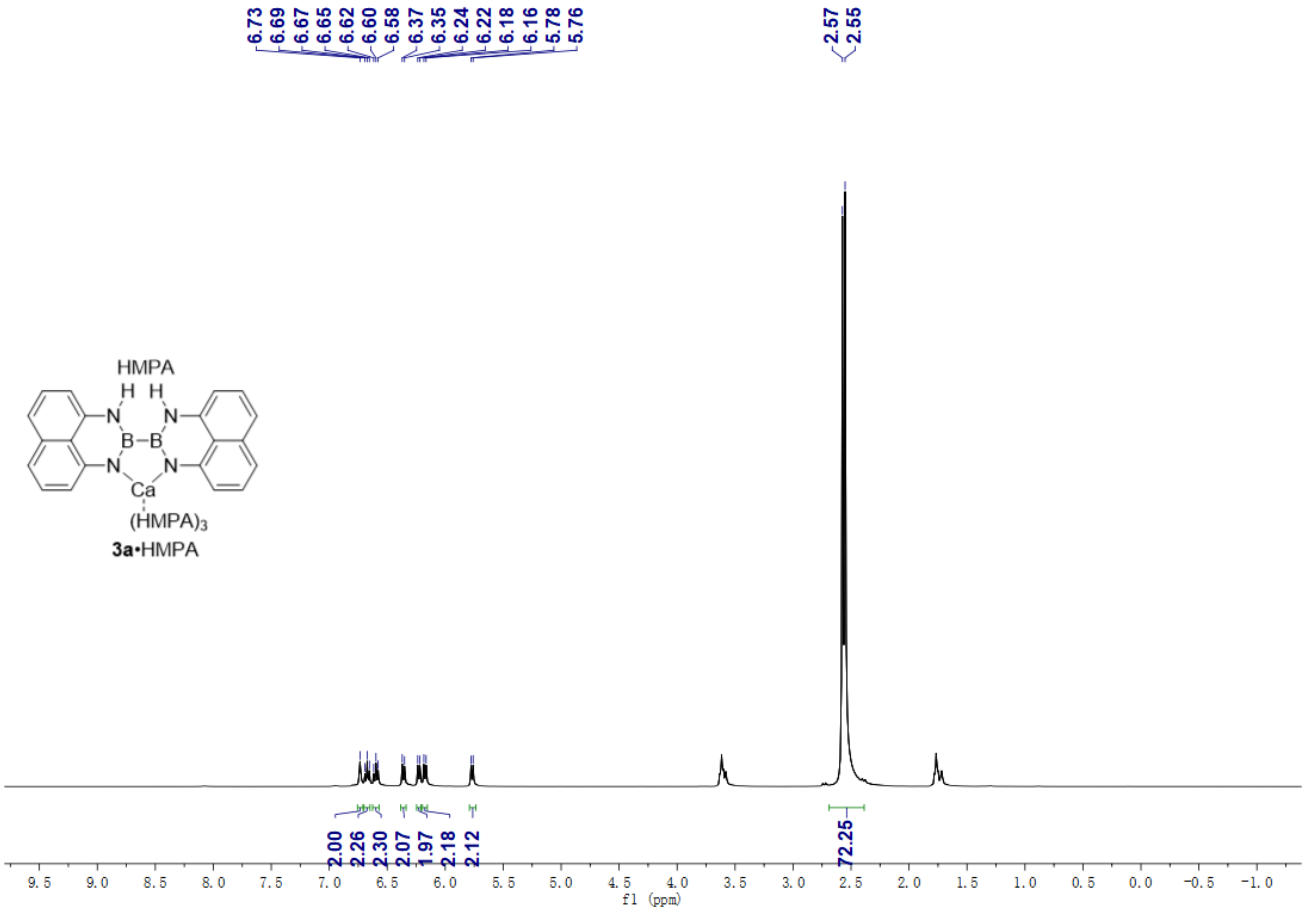


Figure S5. ^{1}H NMR Spectrum of **3a**·HMPA (25ºC, 400 MHz, THF-d_8).

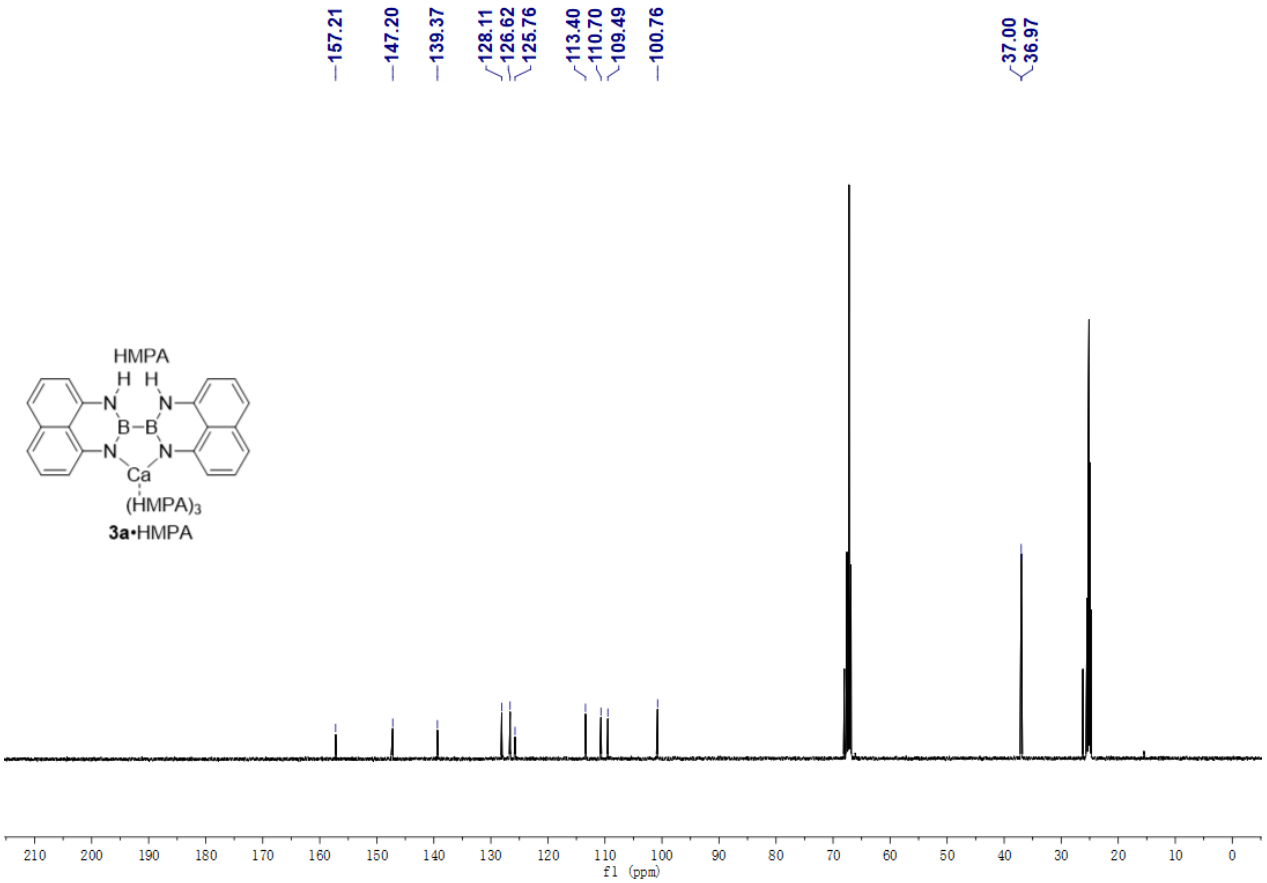


Figure S6. ^{13}C NMR Spectrum of **3a**·HMPA (25°C, 126 MHz, THF-d_8).

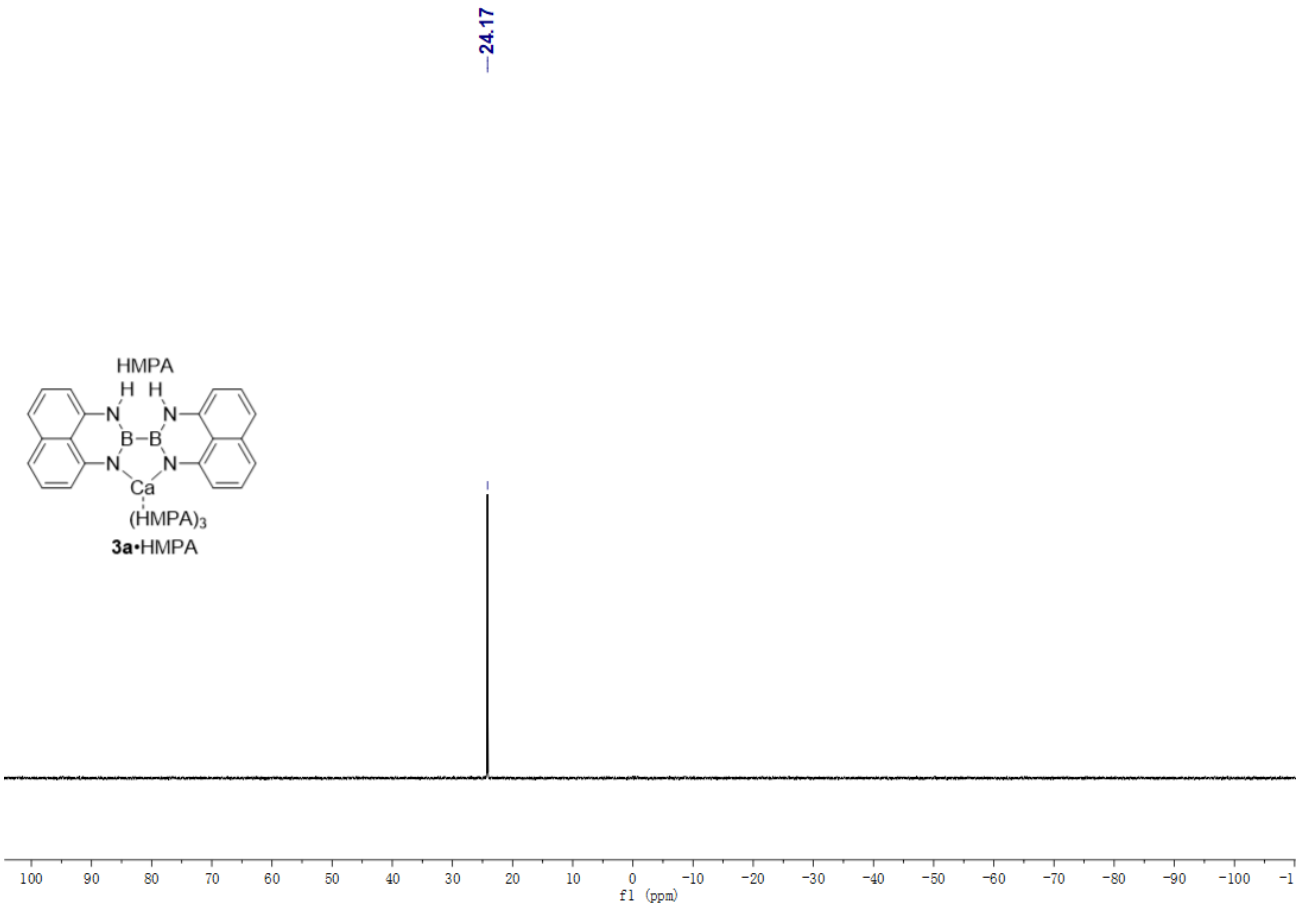


Figure S7. ^{31}P NMR Spectrum of **3a**·HMPA (25°C, 202 MHz, THF-d_8).

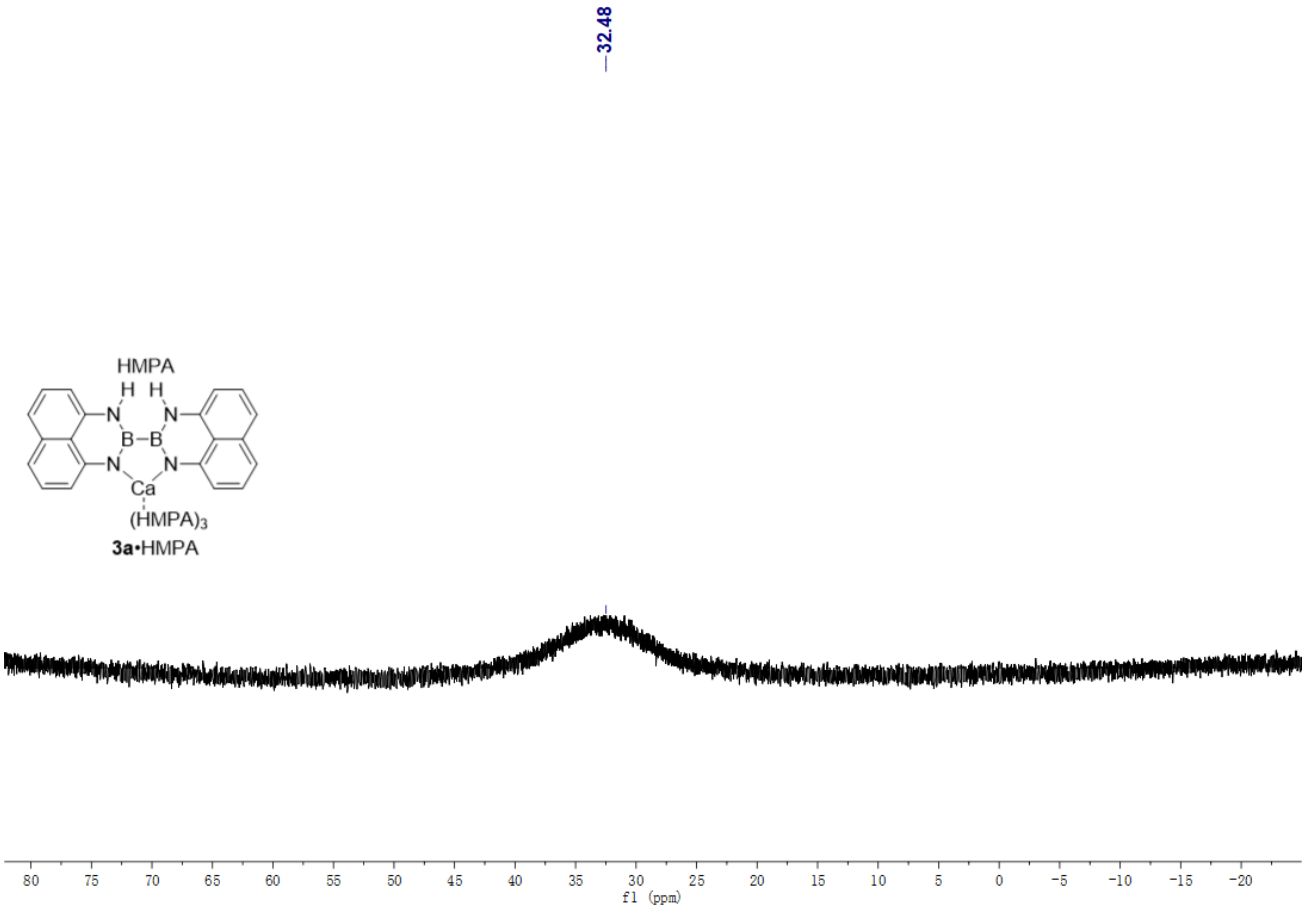


Figure S8. ^{11}B NMR Spectrum of **3a**·HMPA (25°C, 160 MHz, THF-d_8).

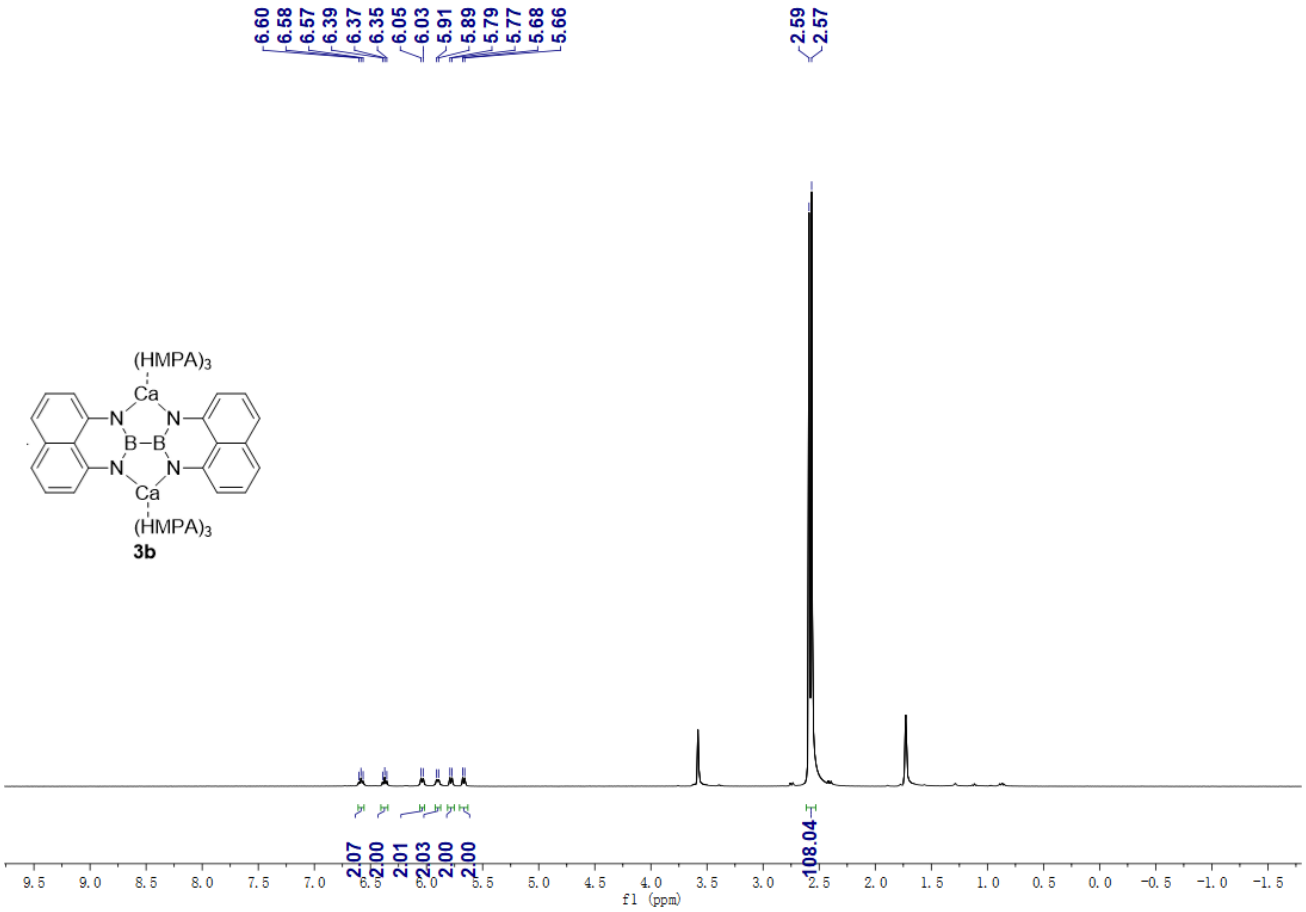


Figure S9. ^{1}H NMR Spectrum of **3b** (25°C, 400 MHz, THF-d_8).

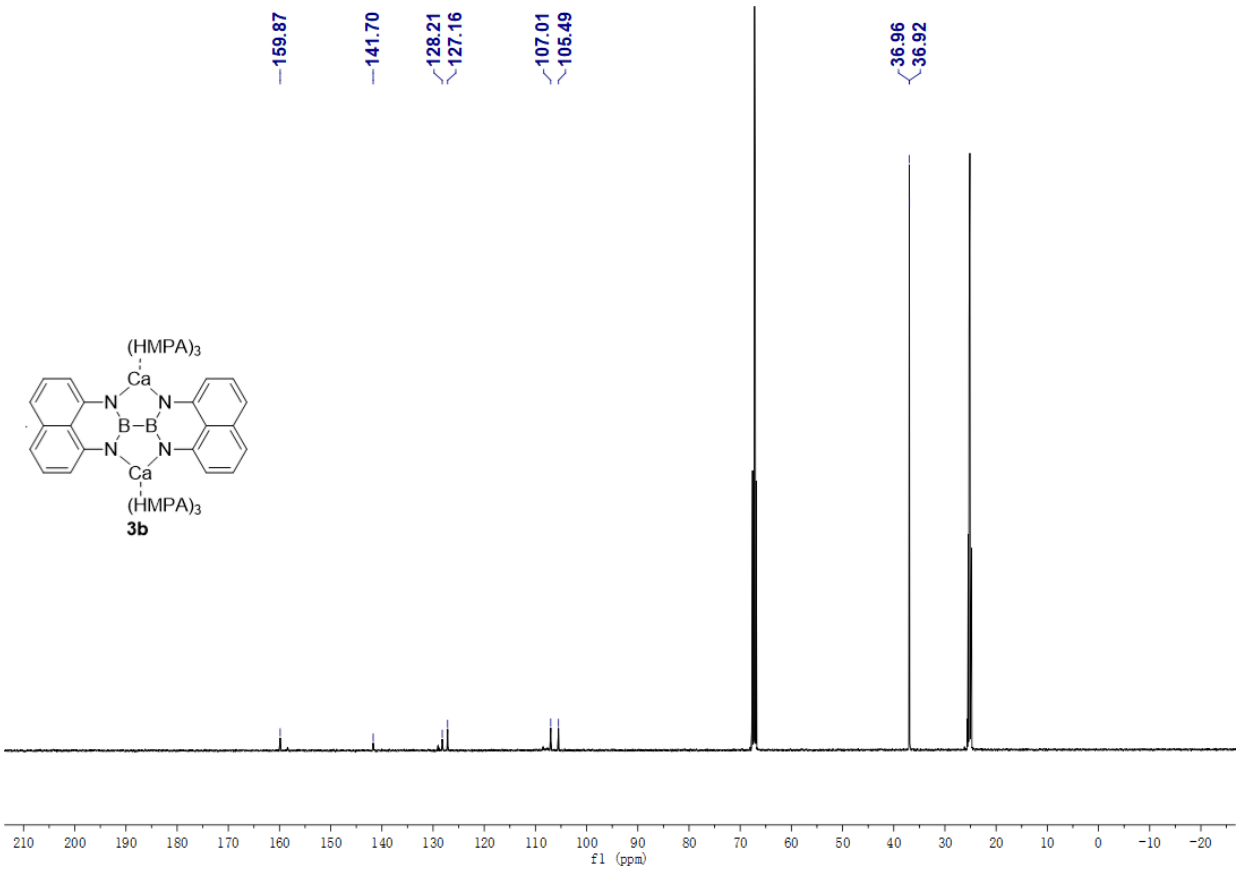


Figure S10. ^{13}C NMR Spectrum of **3b** (25°C, 126 MHz, THF-d_8).

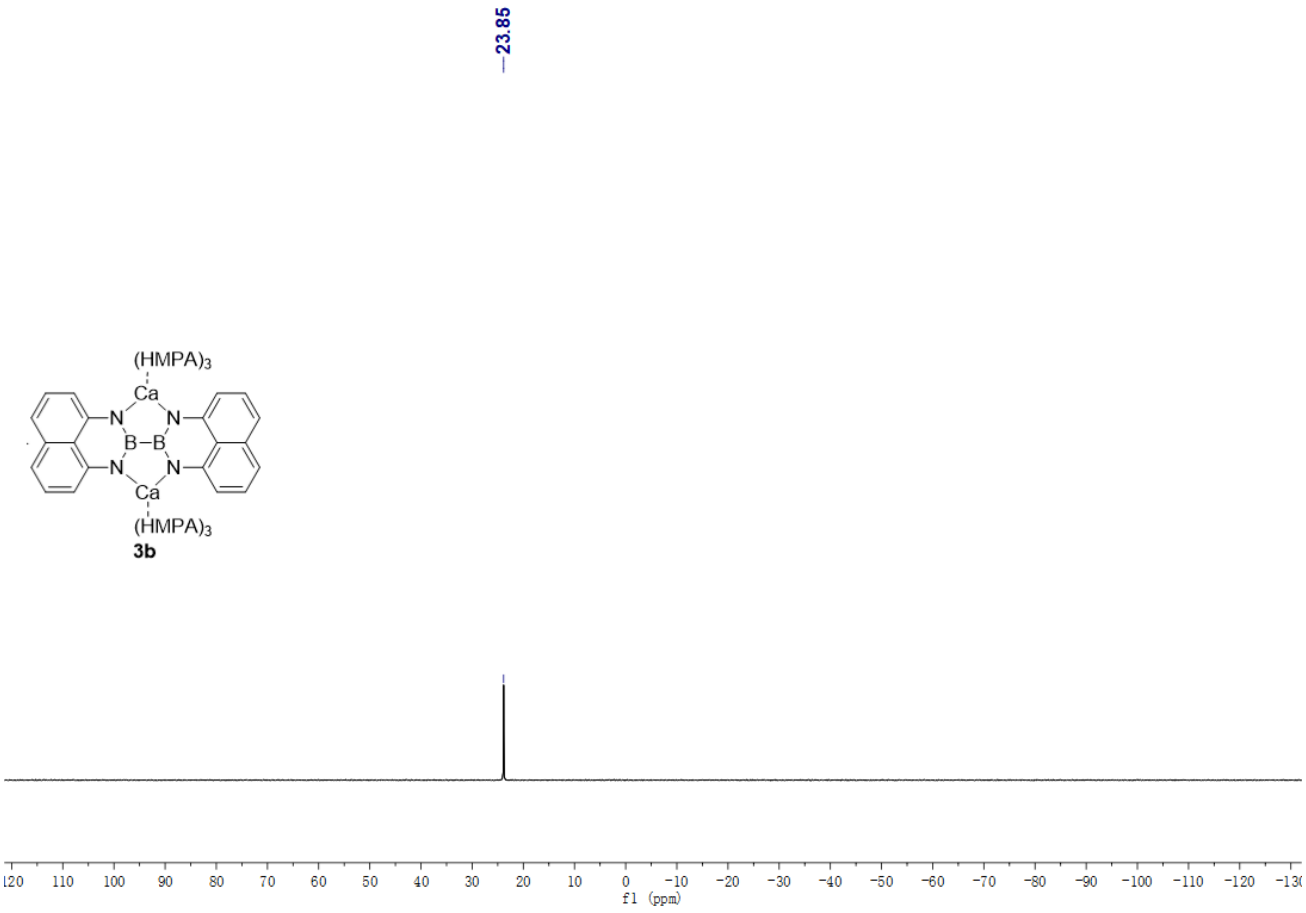


Figure S11. ^{31}P NMR Spectrum of **3b** (25°C, 202 MHz, THF-d_8).

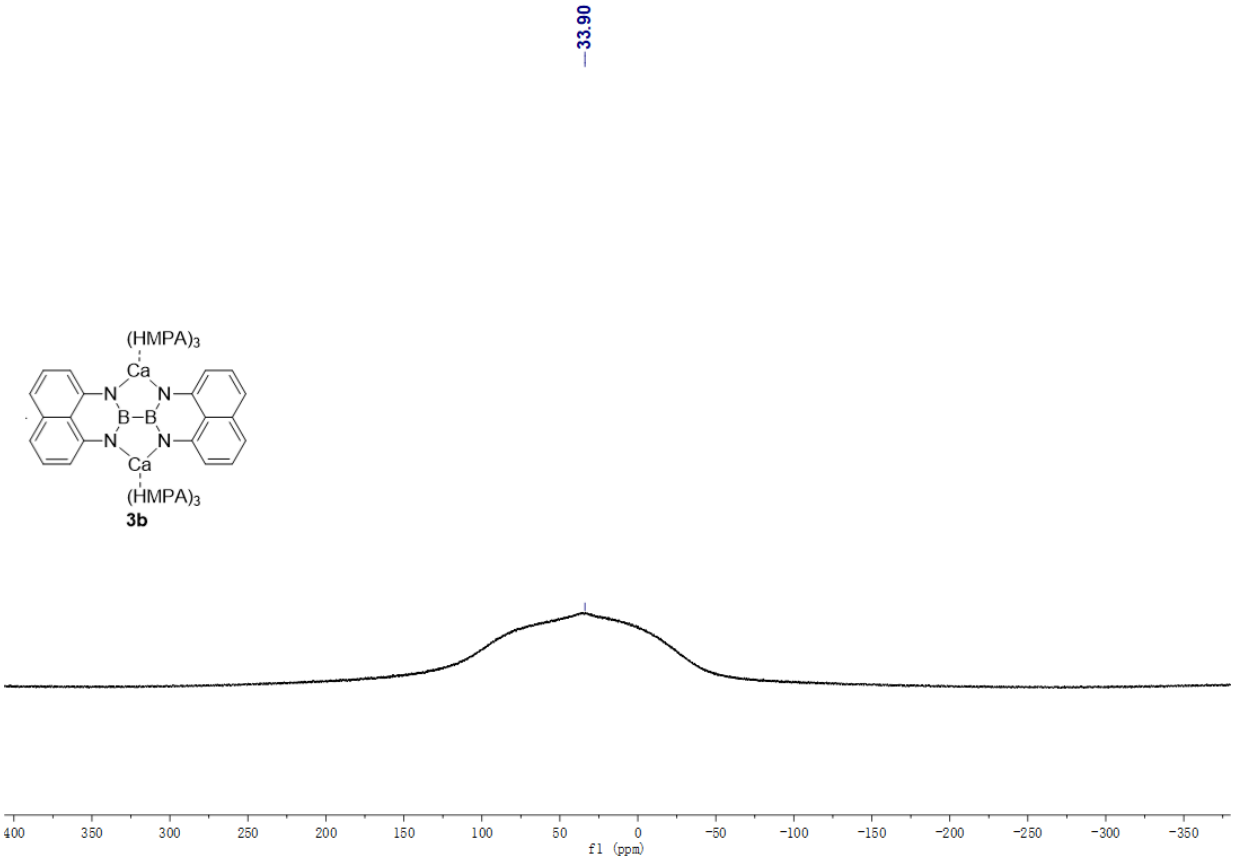


Figure S12. ^{11}B NMR Spectrum of **3b** (25°C, 160 MHz, THF-d_8).

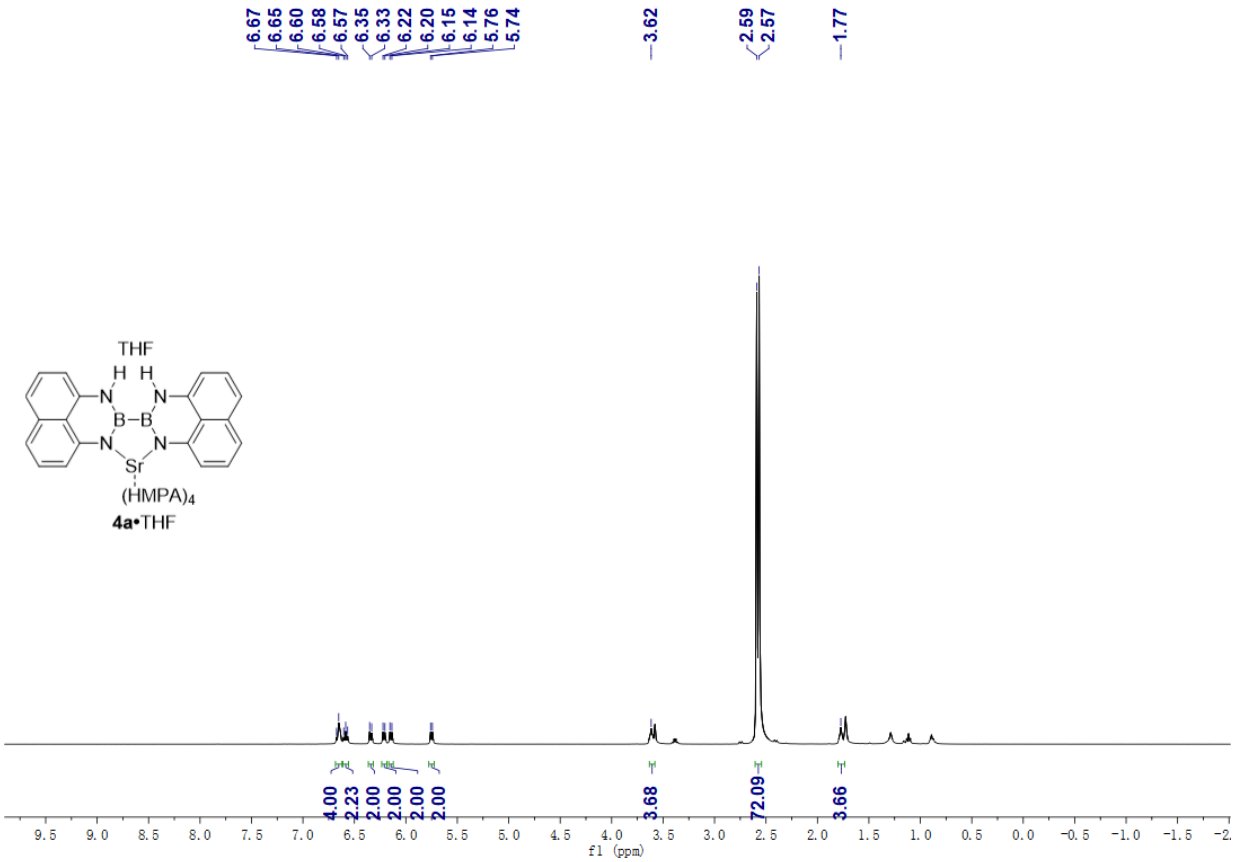


Figure S13. ^{1}H NMR Spectrum of **4a**·THF (25°C, 400 MHz, THF-d_8).

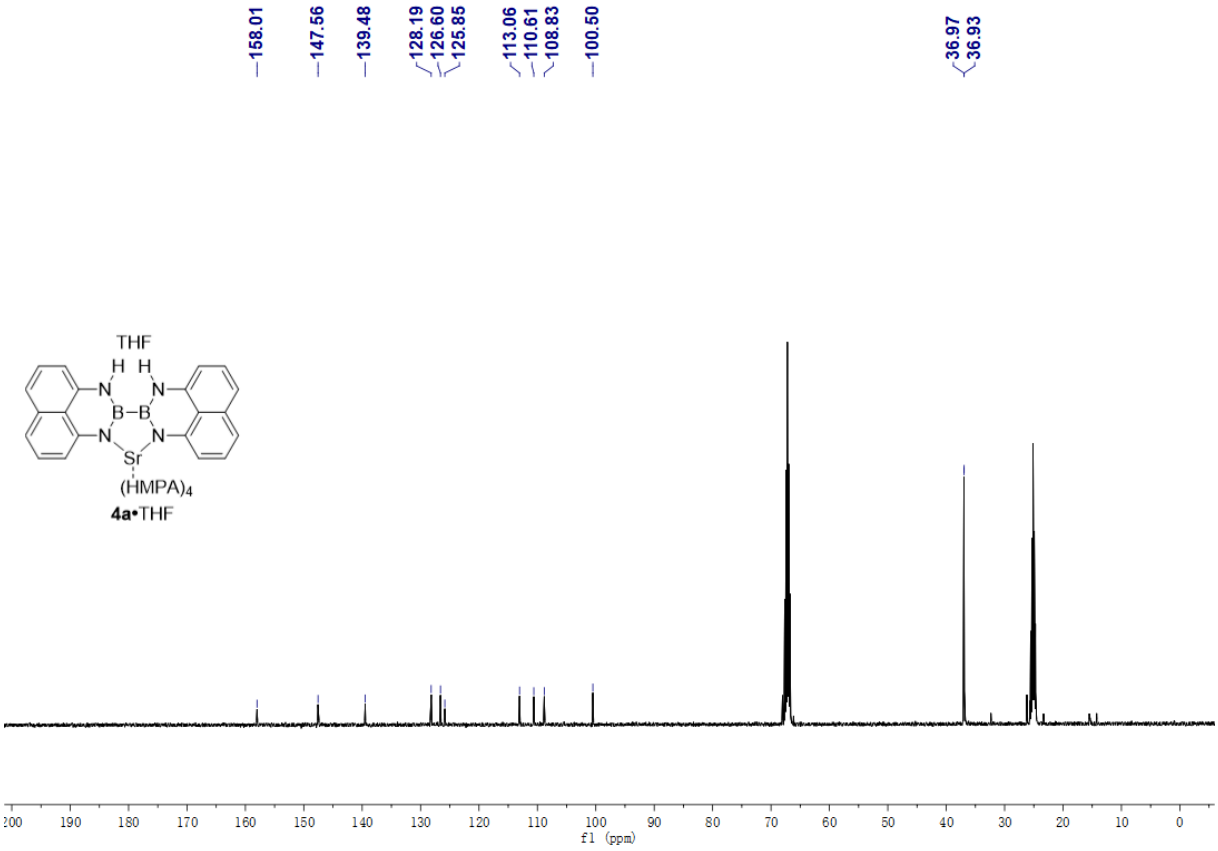


Figure S14. ^{13}C NMR Spectrum of **4a**·THF (25°C, 126 MHz, THF-d_8).

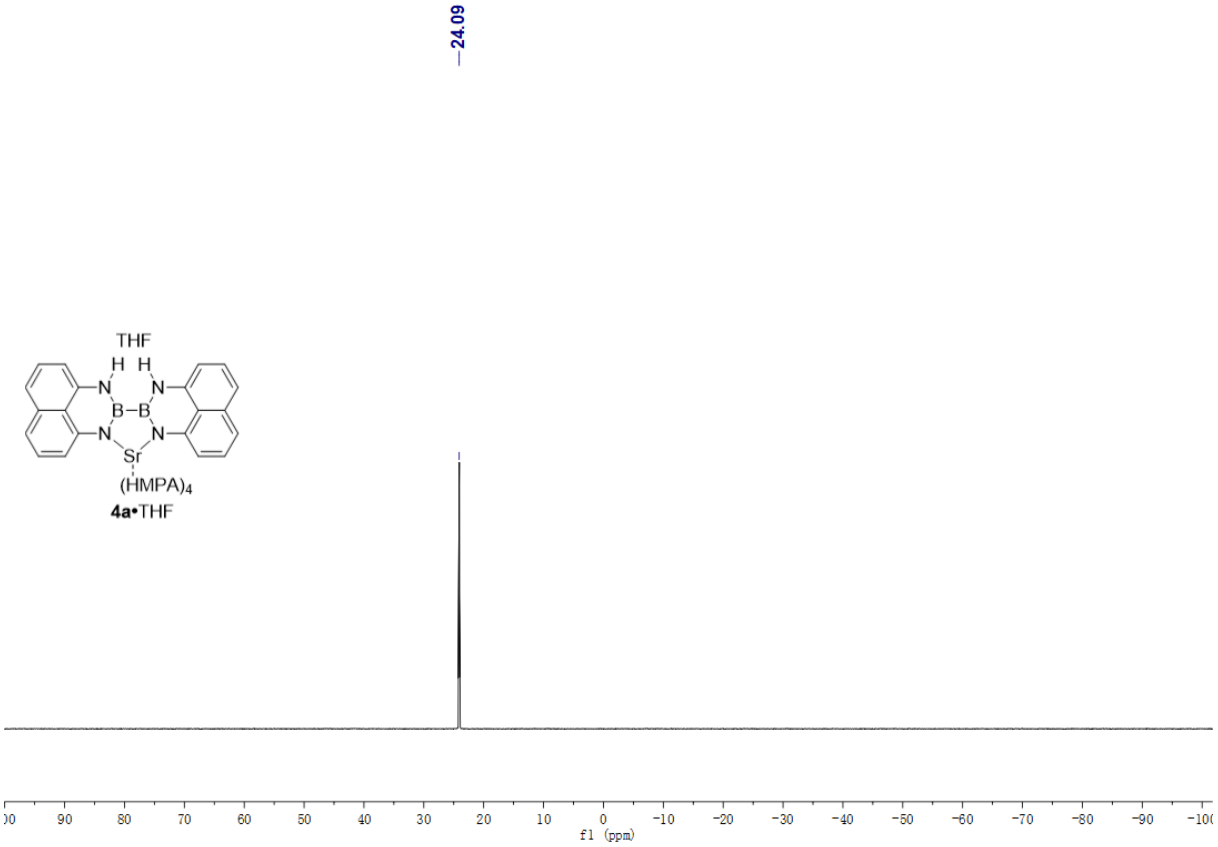


Figure S15. ^{31}P NMR Spectrum of **4a**·THF (25°C, 202 MHz, THF-d_8).

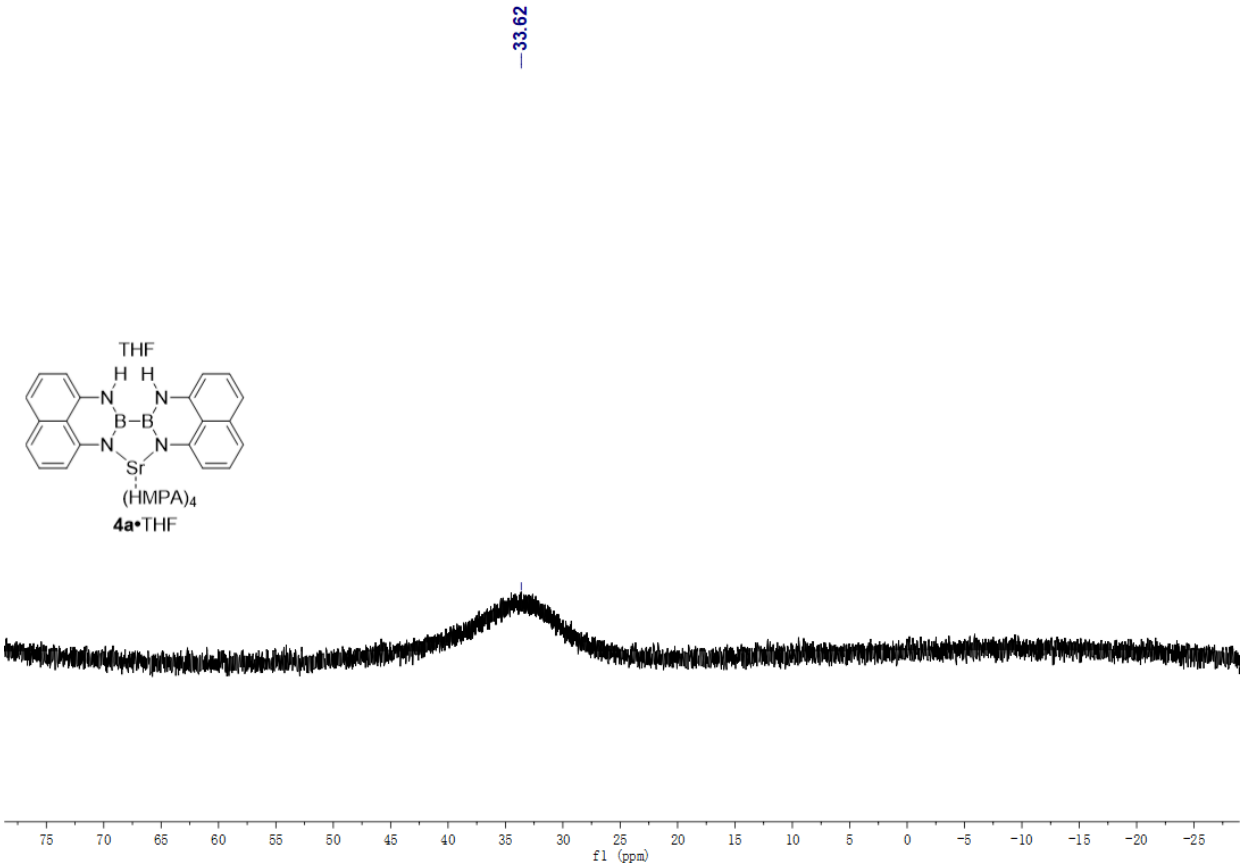


Figure S16. ^{11}B NMR Spectrum of **4a**·THF (25°C, 160 MHz, THF-d_8).

3) X-ray Crystallographic Studies

Data collections for all complexes were performed at 180 K or 100 K on a SuperNova diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved with the Olex2[1] and refined with the ShelXL[2] refinement package using Least Squares minimization. Refinement was performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystal data, data collection and processing parameters for all complexes were summarized. Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1910590 (**2a**·2THF), CCDC 1910583 (**2b**), CCDC 1910586 (**3a**·HMPA), CCDC 1910587 (**3b**), CCDC 1910588 (**4a**·THF), CCDC 1910589 (**4b**). Copies of these data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The slightly higher R factors of the crystal structures of 3a and 3b may be attributed to solvent (HMPA) disorder.

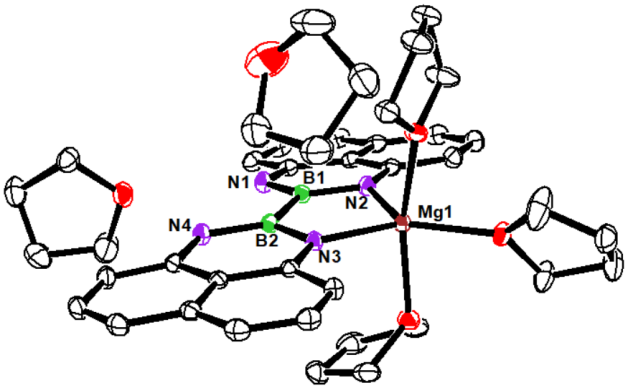


Figure S17. ORTEP Drawing and Crystallographic Data of Compound **2a**·2THF. Thermal ellipsoids are shown at 30% probability. H atoms are omitted for clarity.

Table S1. Crystallographic Data and Structure Refinement Details of **2a**·2THF.

Identification code	**2a**·2THF
Empirical formula	$C_{40}H_{54}B_2MgN_4O_5$
Formula weight	716.80
Temperature/K	180.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.2144(11)
b/Å	29.474(3)
c/Å	11.6873(11)
α/°	90
β/°	101.772(9)
γ/°	90
Volume/Å^3	3781.8(7)
Z	4
ρ_{calc}g/cm^3	1.259
μ/mm^{-1}	0.097
F(000)	1536.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.818 to 54.966
Index ranges	$-13 \le h \le 14$, $-38 \le k \le 30$, $-15 \le l \le 15$
Reflections collected	53589
Independent reflections	8653 [R_{int} = 0.0365, R_{sigma} = 0.0249]
Data/restraints/parameters	8653/0/469
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0590, wR_2 = 0.1522
Final R indexes [all data]	R_1 = 0.0713, wR_2 = 0.1598
Largest diff. peak/hole / e Å^{-3}	0.81/-0.38

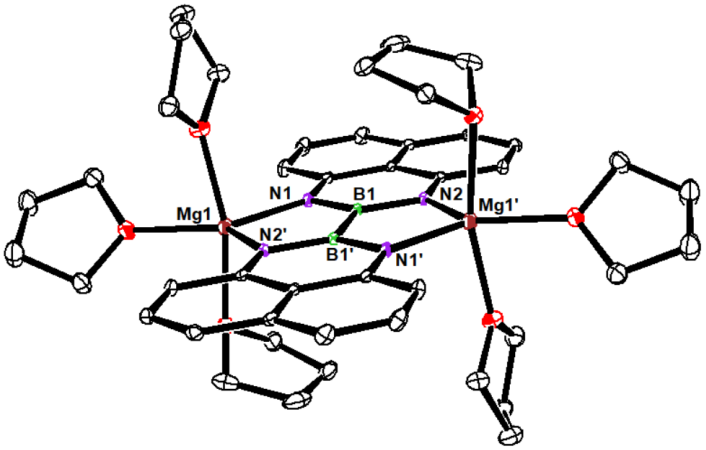


Figure S18. ORTEP Drawing and Crystallographic Data of Compound **2b**. Thermal ellipsoids are shown at 30% probability. H atoms are omitted for clarity.

Table S2. Crystallographic Data and Structure Refinement Details of **2b**.

Identification code	**2b**
Empirical formula	$C_{44}H_{60}B_2Mg_2N_4O_6$
Formula weight	811.20
Temperature/K	119.99(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.0637(3)
b/Å	14.0668(6)
c/Å	16.2694(6)
α/°	90
β/°	93.484(3)
γ/°	90
Volume/Å^3	2070.47(14)
Z	2
ρcalcg/cm^3	1.301
μ/mm^{-1}	0.112
F(000)	868.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.15 to 54.97
Index ranges	$-11 \le h \le 11$, $-18 \le k \le 17$, $-21 \le l \le 20$
Reflections collected	17412
Independent reflections	4662 [R_{int} = 0.0401, R_{sigma} = 0.0370]
Data/restraints/parameters	4662/0/262
Goodness-of-fit on F^2	1.056
Final R indexes [I>=2σ (I)]	R_1 = 0.0646, wR_2 = 0.1752
Final R indexes [all data]	R_1 = 0.0849, wR_2 = 0.1885
Largest diff. peak/hole / e Å^{-3}	0.77/-0.46

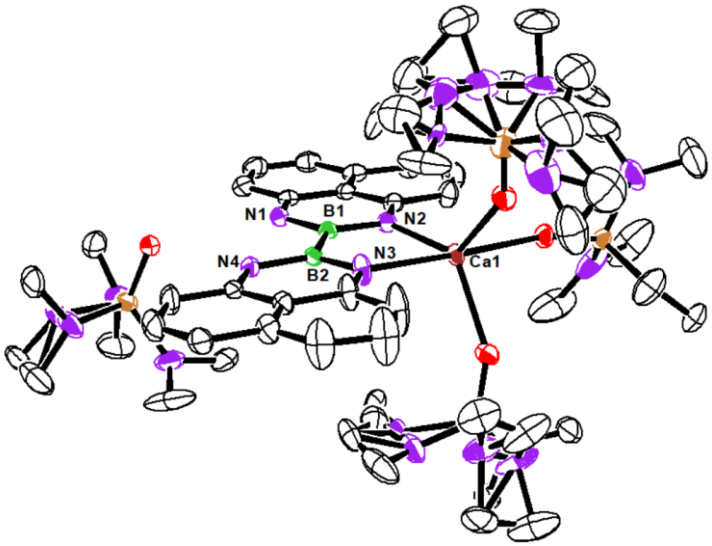


Figure S19. ORTEP Drawing and Crystallographic Data of Compound **3a**·HMPA. Thermal ellipsoids are shown at 30% probability. H atoms are omitted for clarity.

Table S3. Crystallographic Data and Structure Refinement Details of **3a**·HMPA.

Identification code	**3a**·HMPA
Empirical formula	$C_{44}H_{86}B_2CaN_{16}O_4P_4$
Formula weight	1088.86
Temperature/K	180.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	22.1723(9)
b/Å	14.0207(5)
c/Å	20.0498(8)
α/°	90
β/°	106.430(4)
γ/°	90
Volume/Å^3	5978.4(4)
Z	4
ρcalcg/cm^3	1.210
μ/mm^{-1}	0.264
F(000)	2336.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.954 to 52.042
Index ranges	-28 ≤ h ≤ 28, -18 ≤ k ≤ 18, -23 ≤ l ≤ 26
Reflections collected	66463
Independent reflections	13570 [R_{int} = 0.0348, R_{sigma} = 0.0285]
Data/restraints/parameters	13570/606/829
Goodness-of-fit on F^2	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0826, wR_2 = 0.2082
Final R indexes [all data]	R_1 = 0.1004, wR_2 = 0.2216
Largest diff. peak/hole / e Å^{-3}	1.26/-0.92

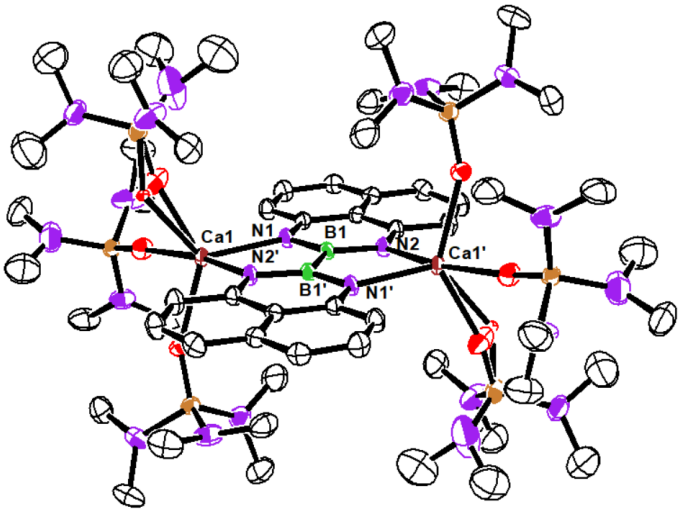


Figure S20. ORTEP Drawing and Crystallographic Data of Compound **3b**. Thermal ellipsoids are shown at 30% probability. H atoms are omitted for clarity.

Table S4. Crystallographic Data and Structure Refinement Details of **3b**.

Identification code	**3b**
Empirical formula	$C_{56}H_{120}B_2Ca_2N_{22}O_6P_6$
Formula weight	1485.33
Temperature/K	180.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.5167(7)
b/Å	23.8825(10)
c/Å	14.1982(8)
α/°	90
β/°	112.347(6)
γ/°	90
Volume/Å^3	3925.5(4)
Z	2
ρcalcg/cm^3	1.257
μ/mm^{-1}	0.326
F(000)	1596.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.824 to 52.044
Index ranges	-14 ≤ h ≤ 14, -27 ≤ k ≤ 28, -16 ≤ l ≤ 16
Reflections collected	38547
Independent reflections	6810 [Rint = 0.0668, Rsigma = 0.0483]
Data/restraints/parameters	6810/658/452
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0871, wR_2 = 0.2293
Final R indexes [all data]	R_1 = 0.0986, wR_2 = 0.2398
Largest diff. peak/hole / e Å^{-3}	1.06/-0.64

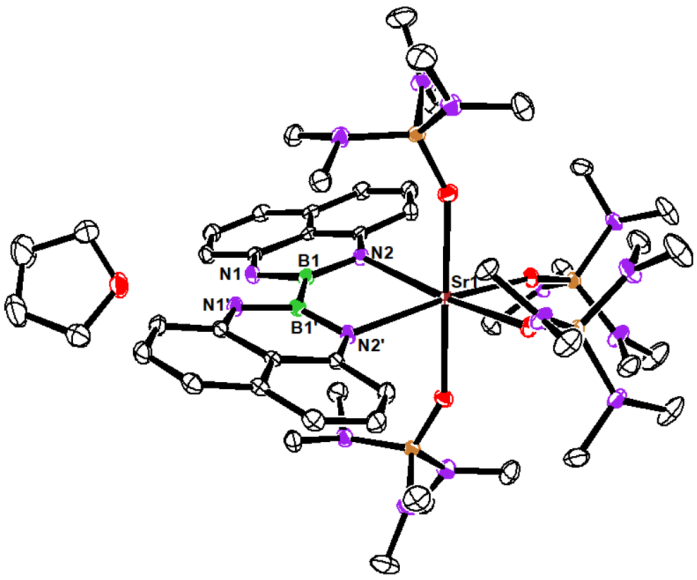


Figure S21. ORTEP Drawing and Crystallographic Data of Compound **4a**·THF. Thermal ellipsoids are shown at 30% probability. H atoms are omitted for clarity.

Table S5. Crystallographic Data and Structure Refinement Details of **4a**·THF.

Identification code	**4a**·THF
Empirical formula	$C_{48}H_{94}B_2N_{16}O_5P_4Sr$
Formula weight	1208.51
Temperature/K	180.00(10)
Crystal system	monoclinic
Space group	C2/c
a/Å	17.0218(5)
b/Å	17.4203(6)
c/Å	21.4191(7)
α/°	90
β/°	100.718(3)
γ/°	90
Volume/Å^3	6240.5(4)
Z	4
ρcalcg/cm^3	1.286
μ/mm^{-1}	1.022
F(000)	2568.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.754 to 54.97
Index ranges	-19 ≤ h ≤ 22, -22 ≤ k ≤ 22, -27 ≤ l ≤ 27
Reflections collected	31930
Independent reflections	7136 [R_{int} = 0.0375, R_{sigma} = 0.0277]
Data/restraints/parameters	7136/0/356
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0314, wR_2 = 0.0829
Final R indexes [all data]	R_1 = 0.0363, wR_2 = 0.0860
Largest diff. peak/hole / e Å^{-3}	0.74/-0.40

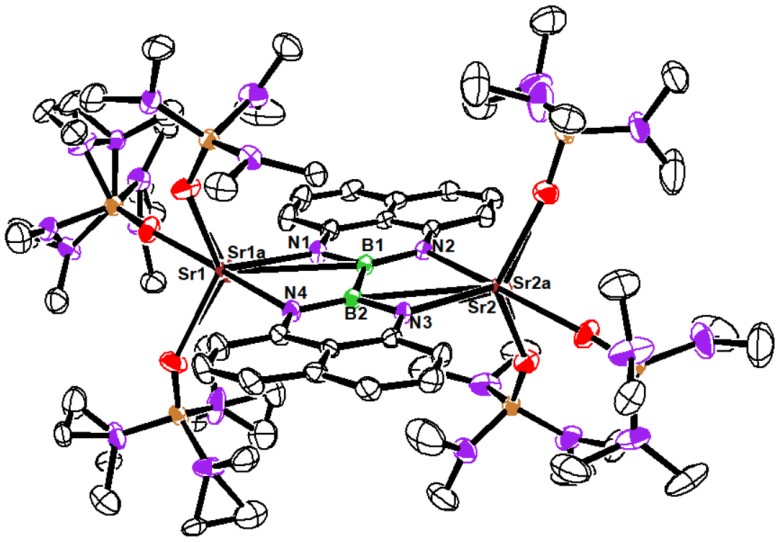


Figure S22. ORTEP Drawing and Crystallographic Data of Compound **4b**. Thermal ellipsoids are shown at 30% probability. H atoms are omitted for clarity.

Table S6. Crystallographic Data and Structure Refinement Details of **4b**.

Identification code	**4b**
Empirical formula	$C_{56}H_{120}B_2N_{22}O_6P_6Sr_2$
Formula weight	1580.41
Temperature/K	99.8(5)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.3034(2)
b/Å	23.7498(4)
c/Å	23.2747(4)
α/°	90
β/°	99.702(2)
γ/°	90
Volume/Å^3	7793.4(2)
Z	4
ρcalcg/cm^3	1.347
μ/mm^{-1}	1.551
F(000)	3336.0
Crystal size/mm^3	0.2 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.944 to 50.054
Index ranges	$-17 \le h \le 17$, $-28 \le k \le 28$, $-27 \le l \le 27$
Reflections collected	92785
Independent reflections	13532 [R_{int} = 0.0392, R_{sigma} = 0.0299]
Data/restraints/parameters	13532/2118/1029
Goodness-of-fit on F^2	1.022
Final R indexes [I>=2σ (I)]	R_1 = 0.0636, wR_2 = 0.1605
Final R indexes [all data]	R_1 = 0.0827, wR_2 = 0.1742
Largest diff. peak/hole / e Å^{-3}	1.46/-0.78

4) References

[1] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339-341
[2] G. M. Sheldrick, *Acta Cryst*. **2015**, *C71*, 3-8.