Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Complexation of Asymmetric Diborenes with Magnesium Bromide

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Contents:

1. Synthesis, physical and spectroscopic data for all new compounds

General considerations: All reactions were performed under an atmosphere of dry nitrogen or argon by using standard Schlenk or dry box techniques; solvents were dried over Na metal, K metal or CaH_2. ^{1}H, ^{11}B, ^{13}C, and ^{31}P NMR spectra were obtained with Bruker Avance 400, AVIII 400MHz BBFO1, BBFO2 and JEOL ECA400 spectrometer at 298 K unless otherwise stated. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, sep = septet, m = multiplet, br = broad signal. Coupling constants *J* are given in Hz. HRMS spectra were obtained at the Mass Spectrometry Laboratory at the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured with an OpticMelt Stanford Research System. UV-Vis spectra were measured with Cary 100 Bio UV-Visible spectrophotometer. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker ALPHA-Transmittance FT-IR Spectrometer

Compounds **1a**[1] and **1b**[2] were synthesized according to literature methods.

Synthesis of compound 2:

In a J-Young NMR tube, C_6D_6 (1 ml) was added to a mixture of **1a** (50 mg, 0.087 mmol) and $MgBr_2 \cdot Et_2O$ (23 mg, 0.087 mmol), the mixture was sonicated at ambient temperature to afforded a red solution. The reaction was monitored by NMR. After completion of the reaction, all volatiles were removed under reduced pressure. The residue was washed with a small amount of hexane and dried under vacuum to afford **2** as an orange powder (61%). Orange single crystals of **2** were obtained by recrystallization from a saturated toluene solution at ambient temperature.

M.p.: 210 °C (Dec.). **^{1}H NMR** (400 MHz, C_6D_6) δ 7.07 – 7.01 (m, 3H, Ar*H*), 4.00 – 3.87 (m, 2H, C*H₂*), 3.81 (sep, *J* = 6.8 Hz, 2H, C*H*(CH_3)$_2$), 3.26 (s, 3H, OC*H₃*), 1.40 (d, *J* = 6.8 Hz, 6H, CH(C*H₃*)$_2$), 1.27 (d, *J* = 6.8 Hz, 6H, CH(C*H₃*)$_2$), 1.13 – 1.02 (m, 18H, P(C*H₃*)$_3$), 0.60 (s, 18H, Si(C*H₃*)$_3$). **^{11}B NMR** (128 MHz, C_6D_6) δ 102.91 (br), 35.97 (s), –24.20 (s). **^{13}C NMR** (101 MHz, C_6D_6) δ 146.2 (*C*-Ar), 143.9 (*C*-Ar), 125.9 (*C*H-Ar), 122.9 (*C*H-Ar), 53.3 (O*C*H₃), 33.6 (*C*H₂), 27.7 (*C*H), 25.9 (CH(*C*H₃)₂), 24.5 (CH(*C*H₃)₂), 16.4 (d, *J* = 23.4 Hz, P(*C*H₃)₃), 16.2 (d, *J* = 23.4 Hz, P(*C*H₃)₃), 1.2

(Si(CH_3)$_3$). **^{31}P NMR** (162 MHz, C_6D_6) δ −20.59 (br). **FT-IR** (solid, cm^{-1}): 2954, 2909, 2853, 1467, 1444, 1382, 1354, 1326, 1286, 1241, 1202, 1163, 1118, 1056, 960, 926, 830, 808, 751, 734, 684. **HRMS** (ESI): *m/z* calcd for $C_{28}H_{59}B_3NOSi_2P_2Mg^{79}Br^{81}Br$: 760.2086 [($M + H$)]$^+$; found: 760.2114.

Synthesis of compound 3:

In a J-Young NMR tube, C_6D_6 (1 ml) was added to a mixture of **1b** (50 mg, 0.087 mmol) and $MgBr_2{\cdot}Et_2O$ (23 mg, 0.087 mmol), the mixture was sonicated at ambient temperature to afforded a brown solution. The reaction was monitored by NMR. After completion of the reaction, all volatiles were removed under reduced pressure. The residue was washed with a small amount of hexane and dried under vacuum to afford **3** as a pale yellow powder (38%). Colorless single crystals of **3** were obtained by recrystallization from a saturated toluene solution at ambient temperature.

M.p.: 176 °C (Dec.). **^{1}H NMR** (400 MHz, C_6D_6) δ 7.23 – 7.19 (m, 1H, Ar*H*), 7.14 – 7.05 (m, 2H, Ar*H*), 6.01 (broad triplet, *J* = 36.8 Hz, 1H, C(TMS)$_2$C*H*=C), 6.20 – 5.85 (br, 1H, B*H*), 3.59 – 3.39 (m, 2H, C*H*(CH_3)$_2$), 3.21 (s, 3H, OC*H$_3$*), 1.38 – 1.26 (m, 12H, CH(C*H$_3$*)$_2$), 1.23 – 1.05 (m, 18H, P(C*H$_3$*)$_3$), 0.54 (s, 18H, Si(C*H$_3$*)$_3$). **^{11}B NMR** (128 MHz, C_6D_6) δ 62.93 (br), 34.99 (s), −22.66 (s). **^{13}C NMR** (101 MHz, C_6D_6) δ 146.9 (*C*-Ar), 141.5 (*C*-Ar), 126.3 (*C*H-Ar), 125.9 (*C*H-Ar), 122.6 (C(TMS)$_2$*C*H=C), 52.8 (O*C*H$_3$), 27.8 (*C*H), 25.38 (CH(*C*H$_3$)$_2$), 24.3 (CH(*C*H$_3$)$_2$), 17.0 (P(*C*H$_3$)$_3$), 16.5 (P(*C*H$_3$)$_3$), 1.4 (Si(*C*H$_3$)$_3$). **^{31}P NMR** (162 MHz, C_6D_6) δ −8.82 (br), −13.73 (br). **FT-IR** (solid, cm^{-1}): 2959, 2909, 2869, 2436, 1591, 1472, 1422, 1377, 1360, 1337, 1286, 1247, 1135, 1101, 1056, 1027, 938, 836, 757, 678, 628. **HRMS** (ESI): *m/z* calcd for $C_{28}H_{59}B_3NOSi_2P_2Mg^{79}Br^{81}Br$: 760.2086 [($M + H$)]$^+$; found: 760.2106.

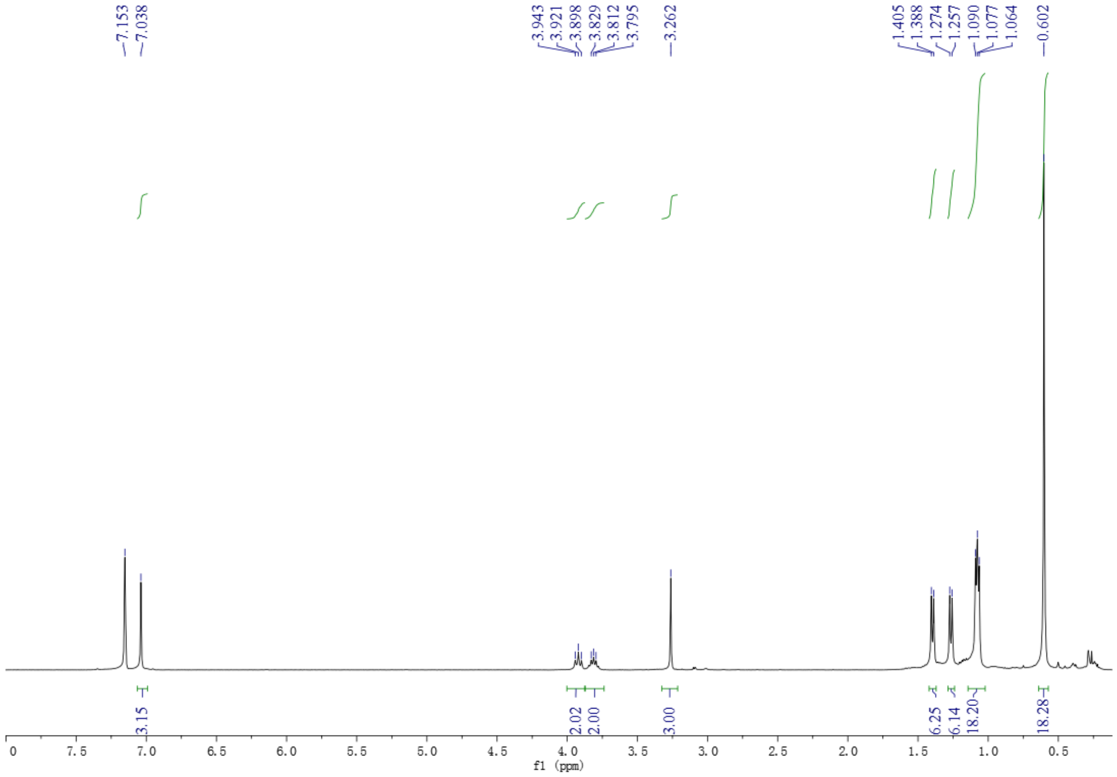


Figure S1. ^{1}H NMR spectrum of **2**

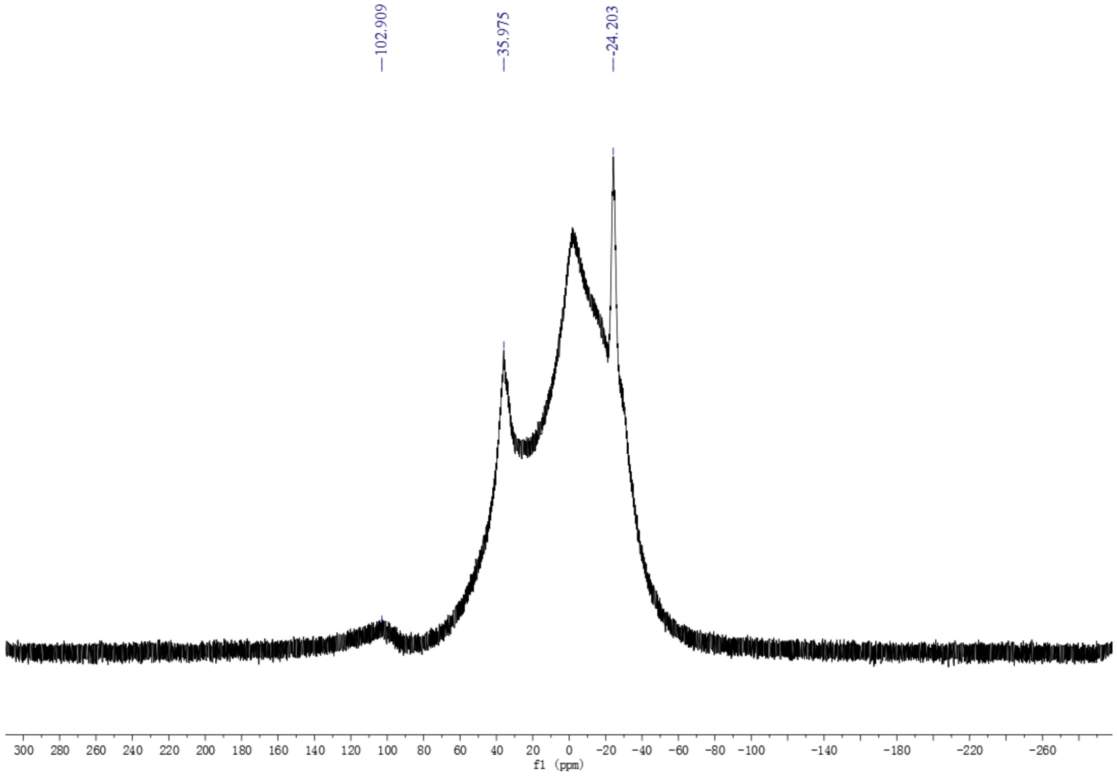


Figure S2. ^{11}B NMR spectrum of **2**

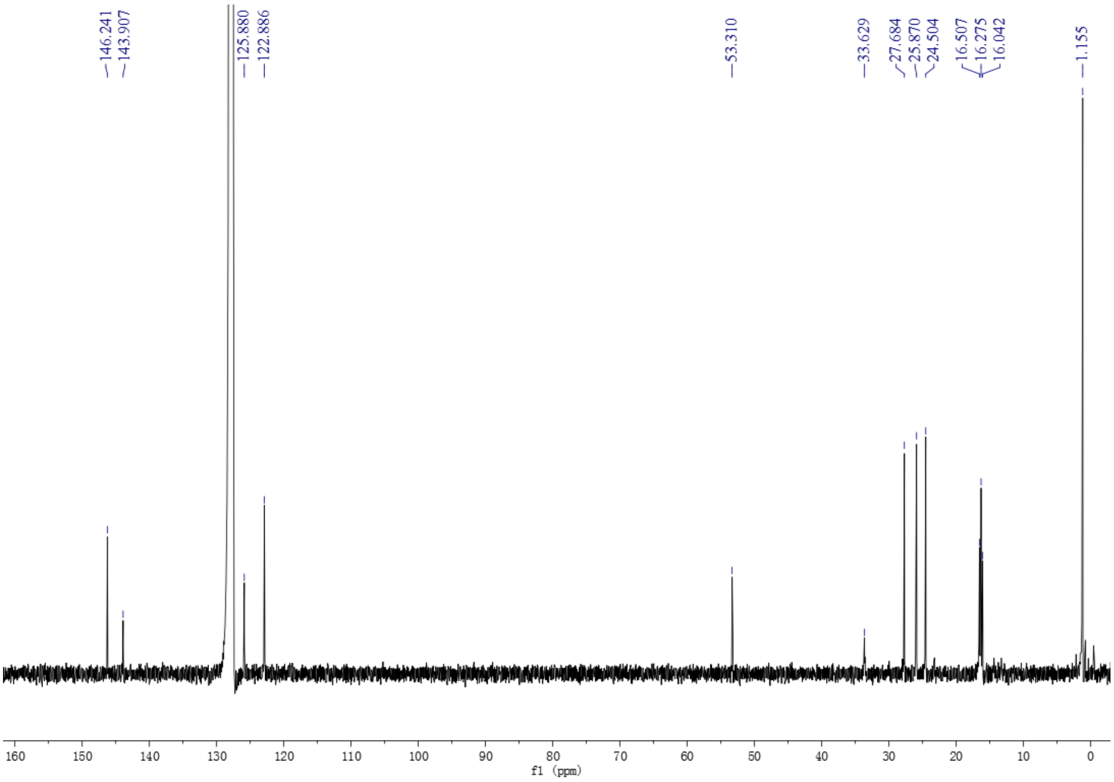


Figure S3. ^{13}C NMR spectrum of **2**

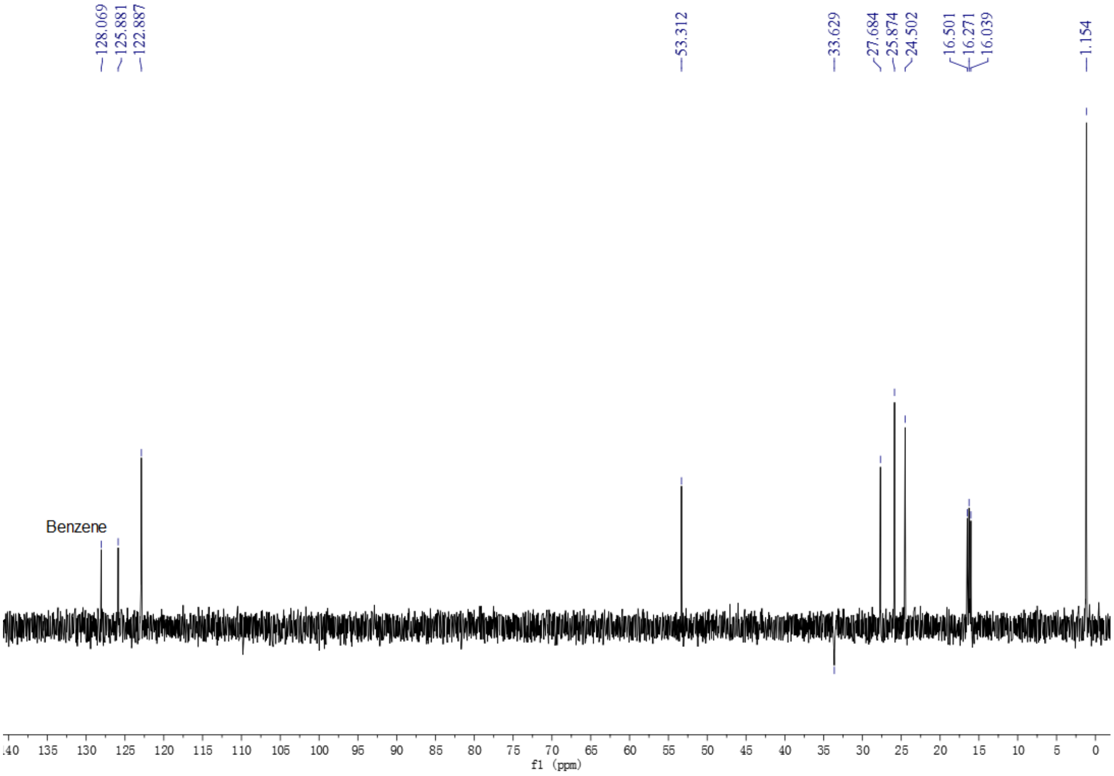


Figure S4. ^{13}C NMR (DEPT 135) spectrum of **2**

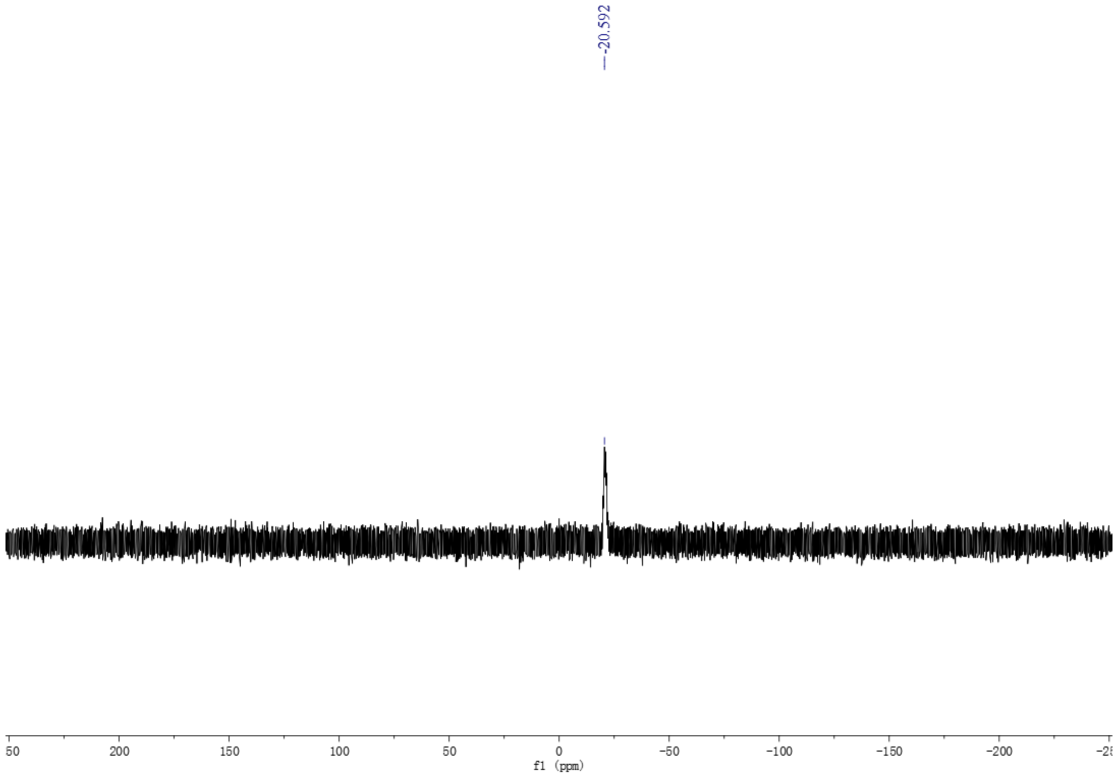


Figure S5. ^{31}P NMR spectrum of **2**

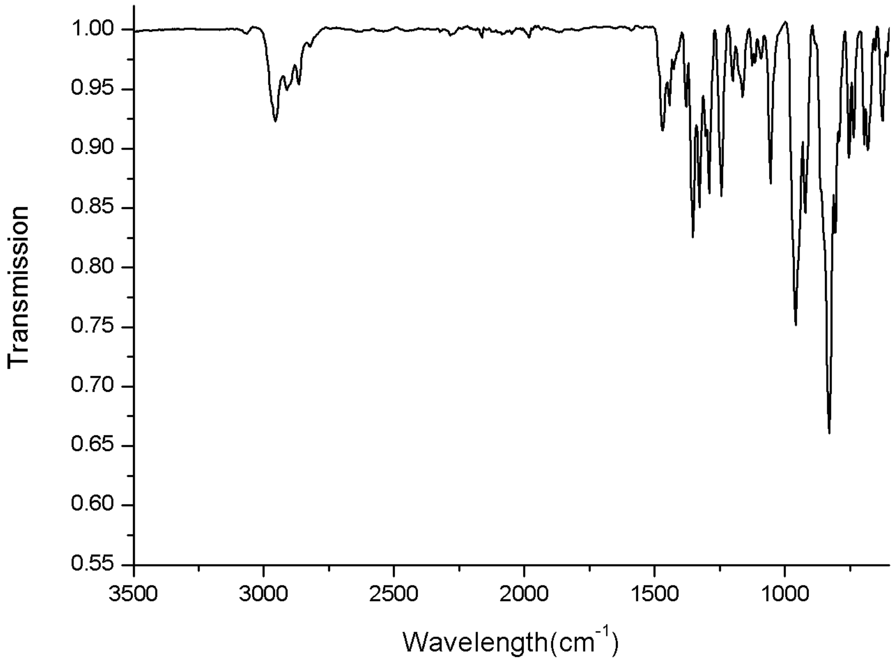


Figure S6. FT-IR spectrum of **2**

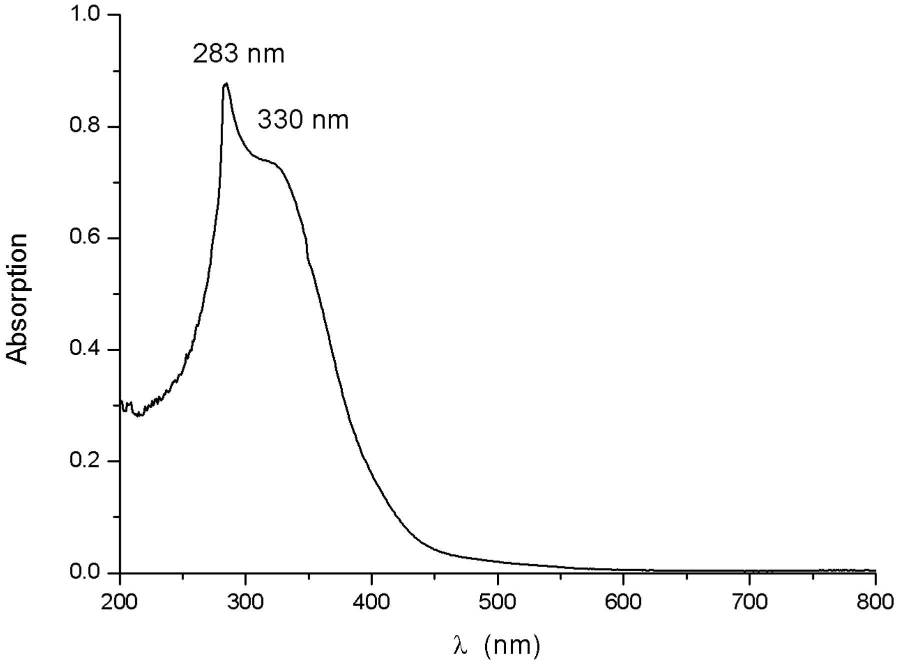


Figure S7. UV-Vis absorption spectra of **2** in toluene (*no emissive behavior was observed in this condition at room temperature).

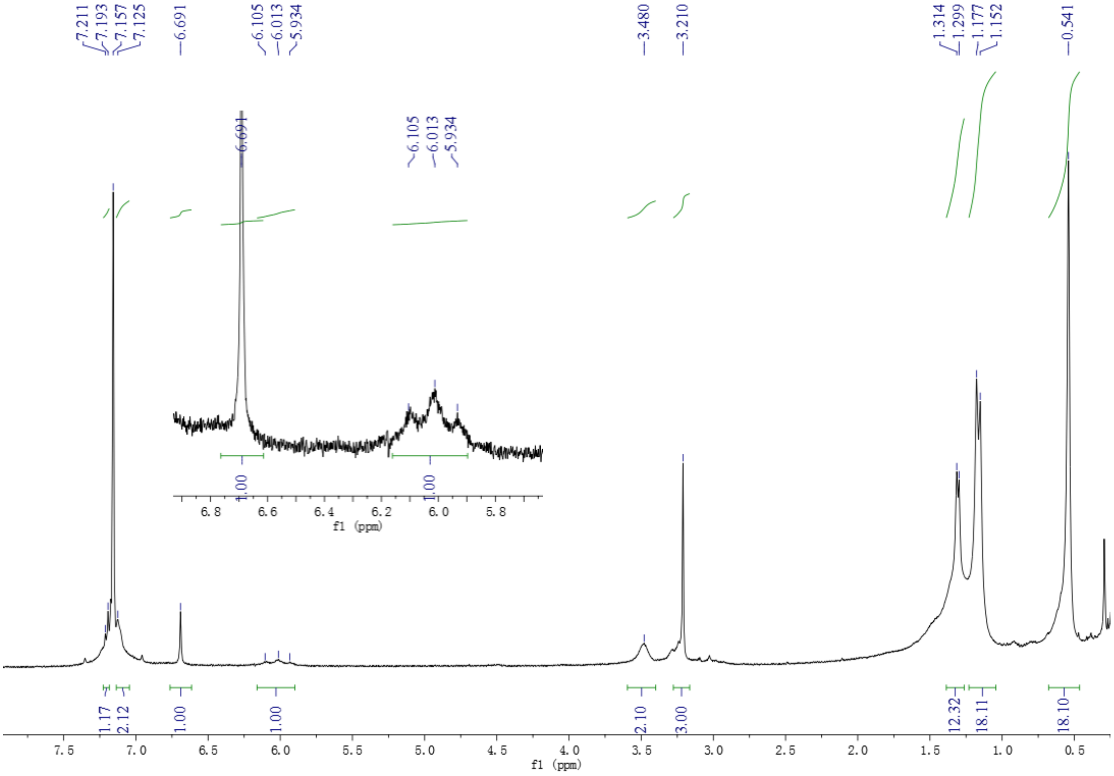


Figure S8. ^{1}H NMR spectrum of **3**

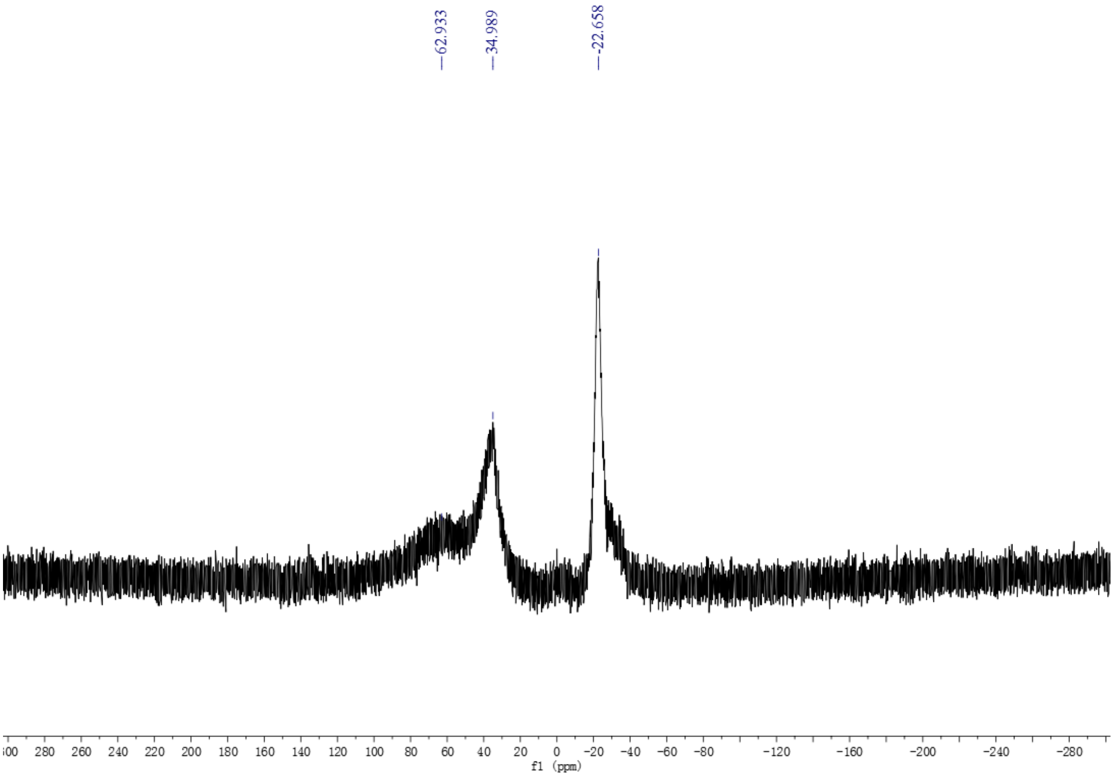


Figure S9. ^{11}B NMR spectrum of **3**

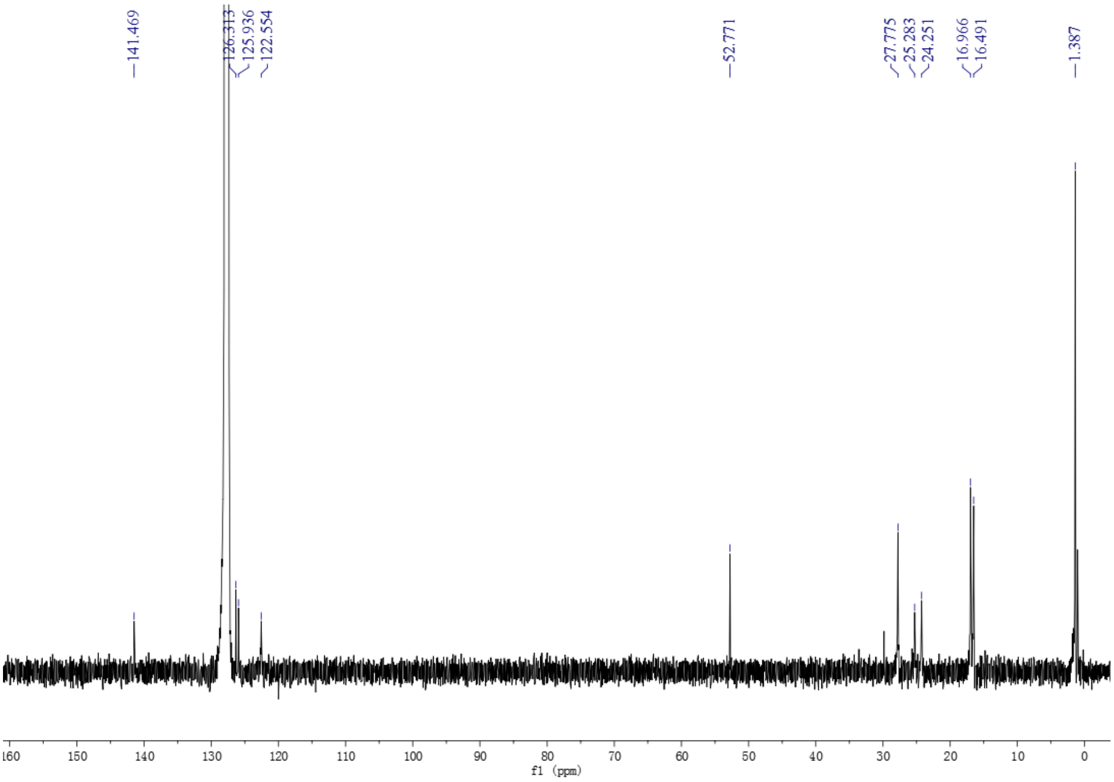


Figure S10. ^{13}C NMR spectrum of **3**

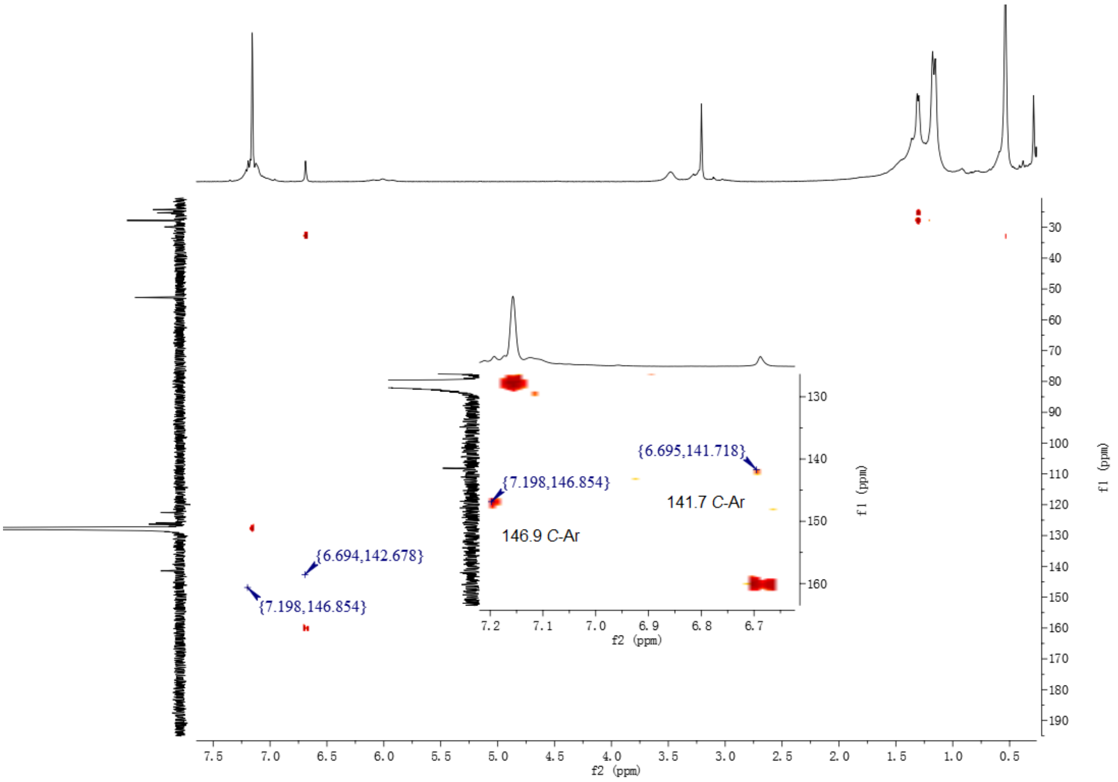


Figure S11. HMBC spectrum of **3**

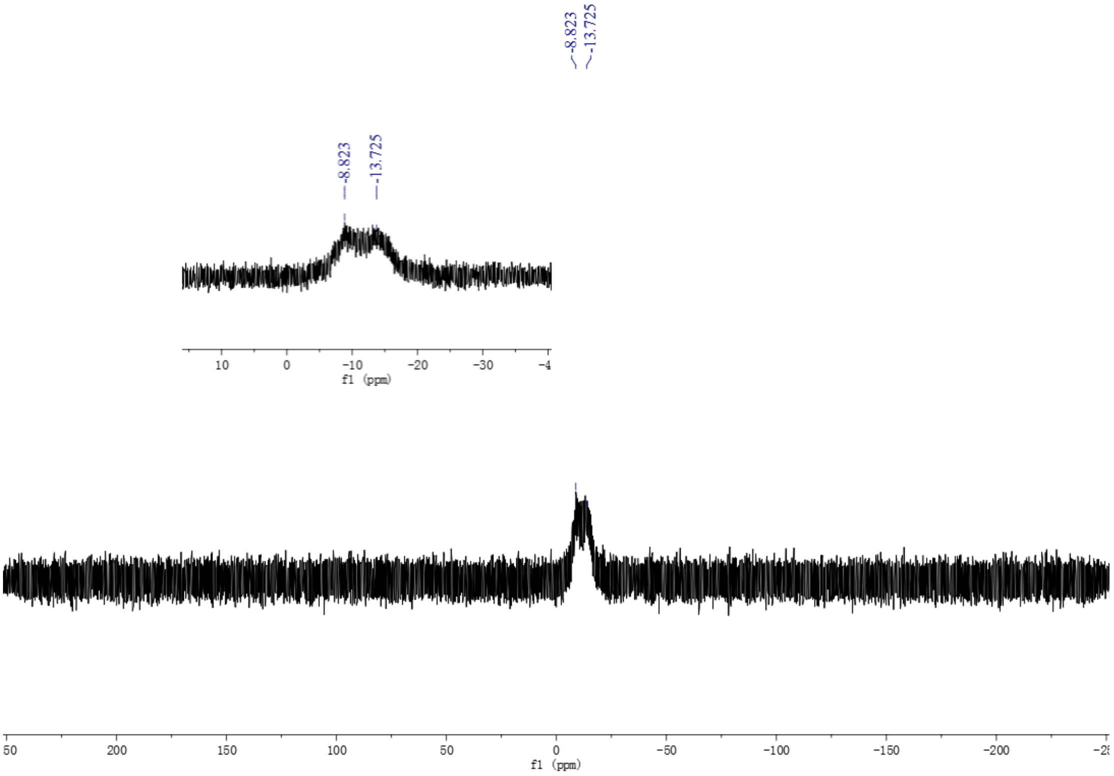


Figure S12. ^{31}P NMR spectrum of **3**

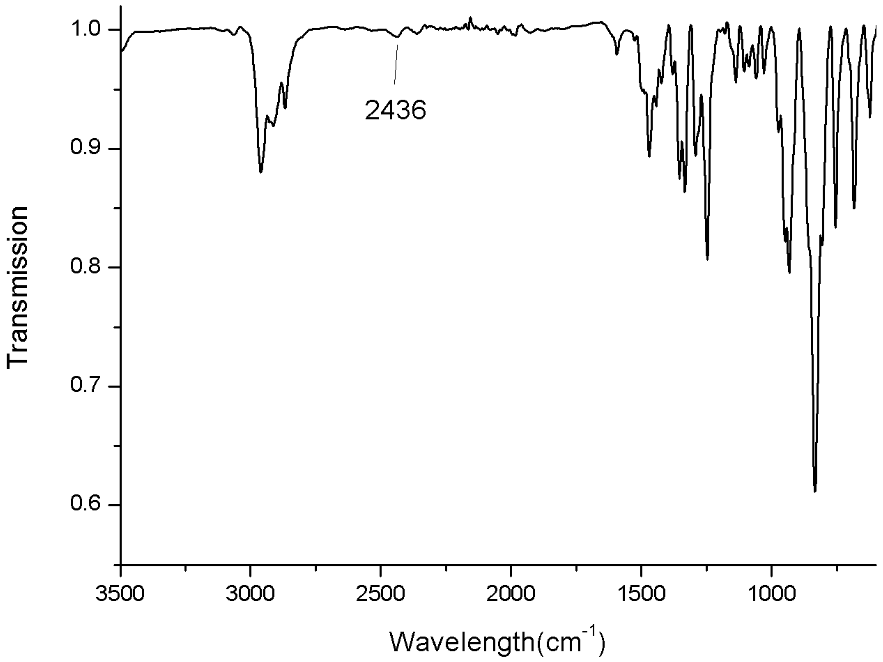


Figure S13. FT-IR spectrum of **3**

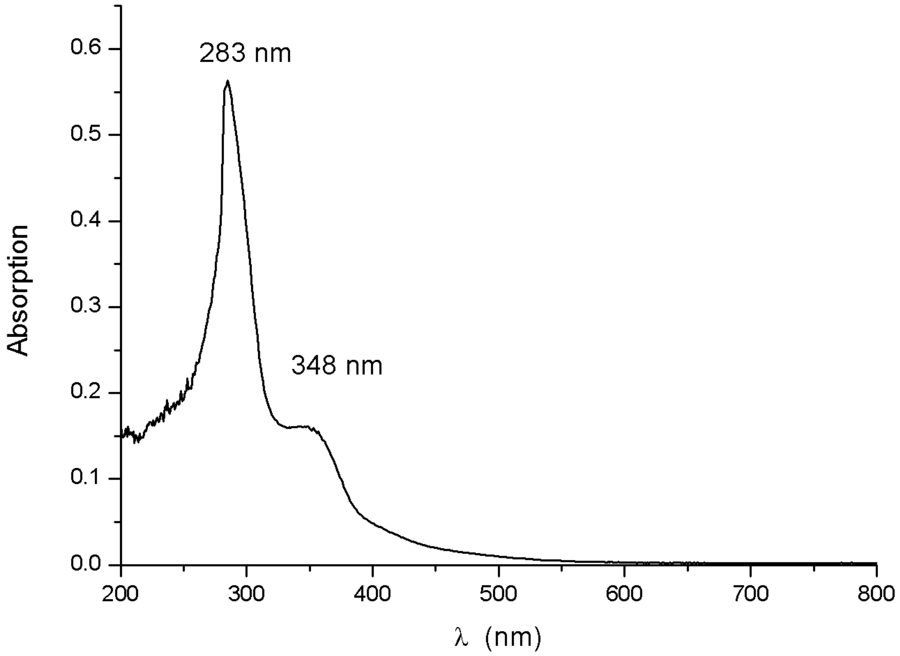


Figure S14. UV-Vis absorption spectra of **3** in toluene (*no emissive behavior was observed in this condition at room temperature).

2. Crystallographic details

X-ray data collection and structural refinement. Intensity data for compounds **2** and **3** were collected using a Bruker APEX II diffractometer. The structure was solved by direct phase determination (SHELXS-97) and refined for all data by full-matrix least squares methods on F^2.[3] All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride in their respective parent atoms; they were assigned appropriate isotropic thermal parameters and included in the structure-factor calculations. CCDC: 1833377 and 1833381 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallography Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. X-ray data for compounds **2** and **3**.

Compounds	**2**·(Toluene)$_{0.679}$·(Benzene)$_{0.3}$	**3**·(Benzene)$_4$
Formula	$C_{62.68}H_{123.36}B_6Br_4Mg_2N_2O_2P_4Si_4$	$C_{80}H_{140}B_6Br_4Mg_2N_2O_2P_4Si_4SSi_4$
Fw	1606.51	1831.29
Cryst syst	triclinic	monoclinic
Space group	P -1	P 1 21/c 1
Size (mm^3)	0.100 x 0.140 x 0.320	0.120 x 0.240 x 0.320
T/K	103(2)	100(2)
a, Å	16.6079(4)	10.1567(7)
b, Å	16.8383(4)	25.514(2)
c, Å	17.8970(5)	19.2566(14)
α, deg	107.0110(10)	90
β, deg	97.9820(10)	91.717(2)
γ, deg	109.3270(10)	90
V, A^3	4359.43(19)	4987.9(6)
Z	2	2
d_{calcd} g·cm^{-3}	1.224	1.219
μ, mm^{-1}	3.888	1.779
Refl collected	55372	57753
$T_{\text{max}}/T_{\text{min}}$	0.6970/0.3690	0.8150/0.6000
N_{measd}	15689	10207
[R int]	0.0719	0.1423
R [I>2σ(I)]	0.0448	0.0558
wR2[I>2σ(I)]	0.1187	0.1135
GOF	1.031	1.012
Largest diff. peak/ hole[e. Å^{-3}]	1.227/−0.828	0.846/−1.244

3. Computational details

Gaussian 09E was used for the density functional theory (DFT) calculations.[4] Geometry optimization, frequency calculations and Natural bond order (NBO) analysis of simplified model compounds **2’** and **3’** were performed at the B3LYP/6-311G* level of theory. For simplification, the TMS (trimethylsilyl) and 2,6-diisopropylphenyl groups of compounds **2** and **3** were replaced with methyl and phenyl groups, respectively.

To investigate the bonding property of compounds **2** and **3**, Amsterdam Density Functional (ADF)[5–7] program was used for the calculation of the optimized structures **opt-2’** and **opt-3’** at the PW91/TZP[8,9] level. ADF calculations were conducted within the zeroth-order regular approximation (ZORA) formalism.[10–13] Spin-restricted calculations were performed by constraining the projection of the total electronic spin along a reference axis to zero. The nature of bonding in **opt-2’** and **opt-3’** is described using the energy decomposition analysis (EDA)[5,14] (also known as “fragment approach”) according to the methods of Morokuma,[15] Ziegler and Rauk.[16] Using the EDA scheme, the energy E_{int} associated to the interaction between the two fragments **opt-2’**: ($RC{=}B{=}B(PMe_3)_2$ and $Mg_2Br_4{\cdot}RC{=}B{=}B(PMe_3)_2$) and **opt-3’**: ($R(H)B{=}B(PMe_3)_2$ and $Mg_2Br_4{\cdot}R(H)B{=}B(PMe_3)_2$), can be divided into three components: $E_{\text{int}} = E_{\text{elstat}} + E_{\text{Pauli}} + E_{\text{orb}}$; the first term, E_{elstat}, corresponds to the classical electrostatic interaction between the unperturbed charge distributions of the fragments (the overall density being the superposition of the fragment densities). The second term, E_{Pauli}, expresses the energy change that arises upon going from the simple superposition of the fragment densities to the wavefunction that obeys the Pauli principle through antisymmetrization and normalization of the product of the fragment wavefunctions. In the last term, E_{orb}, the energy that originates from the contributions from stabilizing orbital interactions (electron pair bonding, charge transfer, polarization) is given. To quantify the contributions of the σ and π interactions between the metal and the B–B moiety, the techniques based on the ETS-NOCV formalism were employed. To describe the charge transfer, the Natural

Orbitals for Chemical Valence (NOCV) description was used.[17,18] It is based on the NOCV wavefunction as an eigenvector of the deformation density matrix in the basis of fragment orbitals, the deformation density (Δρ) is then decomposed in the NOCV representation, as a sum of pairs of complimentary eigenfunctions. A useful qualitative data is the sign of Δρ, negative for an outflow of charge and positive for an inflow of charge in going from the constituent fragments to the whole system. The Graphical User Interface (ADF-GUI – a part of the ADF package) was used for visualization purposes.

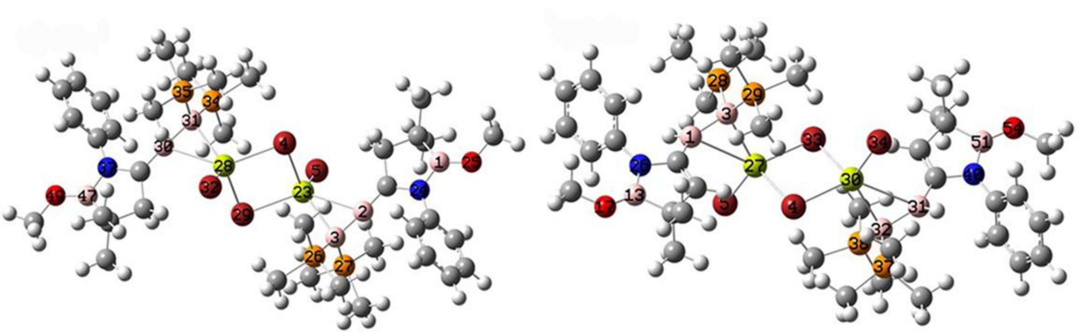
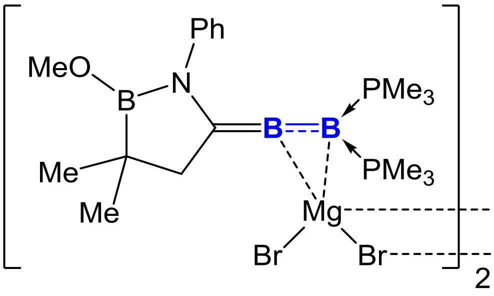


Figure S15. The optimized structures of **opt-2’** (left) and **opt-3’** (right).

Table S2: Optimized structures of a) **opt-2’** and b) **opt-3’**. (atom, x-, y-, z- positions in Å).

a) **opt-2’**



B	7.015704	2.133424	0.491839
B	4.333344	-0.378050	-0.140736
B	3.391952	-1.534742	-0.657234
Br	0.673741	1.303478	1.197453
Br	1.634230	1.597657	-2.868751
C	7.248935	-0.371429	0.859537
C	8.331875	-0.746662	0.058726
C	9.087244	-1.875801	0.374251
C	8.769271	-2.647521	1.488567
C	7.689759	-2.276844	2.292772
C	6.934095	-1.151202	1.979662
C	5.098156	0.747598	0.259656
C	4.601691	2.182659	0.379125
H	4.278422	2.369209	1.412567
H	3.745808	2.396288	-0.267675
C	5.819314	3.106515	0.065033
C	2.436174	-2.078654	2.233075
C	4.342147	-3.943997	1.121706
C	1.602188	-4.054391	0.266690
C	4.861575	-3.599648	-2.563179
C	2.331234	-2.583632	-3.495831
C	4.642479	-0.841009	-3.397342
Mg	1.589803	0.081813	-0.907521
N	6.502342	0.800428	0.571149
O	8.345976	2.355191	0.717221
P	2.935152	-2.851607	0.656938
P	3.764241	-2.122334	-2.439742
Mg	-1.590228	-0.080550	0.909085
Br	-0.675134	-1.300375	-1.196928
B	-4.333573	0.378575	0.141679
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Br	-1.631826	-1.598716	2.868802

C	-5.096686	-0.746805	-0.262723
P	-2.937137	2.855865	-0.647518
P	-3.768481	2.117001	2.446153
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C	-1.607315	4.060207	-0.251387
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C	-4.644899	0.831720	3.400093
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H	-3.743474	-2.395595	0.262254
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C	-9.087375	1.873741	-0.376800
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H	7.449095	-2.856706	3.179079
H	2.449358	-2.821503	3.033205
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H	3.128076	-1.269309	2.466495
H	5.192978	-3.330549	1.419007
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H	4.364041	-4.483668	-2.159420
H	5.773842	-3.419850	-1.992739
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H	-4.372930	4.477812	2.170924
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H	-1.725335	1.692977	3.686909
H	-1.713883	3.319923	3.002090
H	-2.671506	2.981891	4.462636
H	-4.836566	1.190551	4.414193
H	-5.584933	0.590162	2.905615
H	-4.033389	-0.070299	3.443245
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C	-5.896088	-3.369379	1.446524
C	-5.682644	-4.442038	-0.823583
C	8.953744	3.634678	0.698817

H	10.033672	3.483180	0.736740
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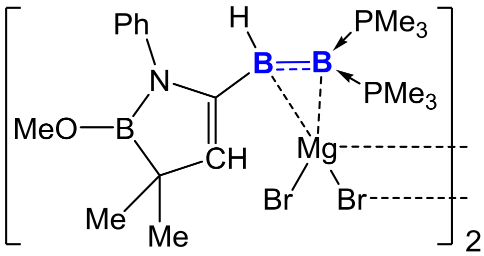
H	8.655532	4.230494	1.566674

b) **opt-3’**



B	4.569302	0.584125	0.058264
H	5.100298	0.885790	1.098500
B	3.343090	1.555686	-0.424656
Br	0.526196	-1.703829	-0.562607
Br	2.145942	-0.593976	3.093907
C	7.508081	-0.032197	0.161942
C	7.852438	1.056658	-0.647750
C	8.742029	2.026365	-0.191185
C	9.304054	1.920233	1.080799
C	8.963034	0.840459	1.893337
C	8.066172	-0.124656	1.440652
C	5.199327	-0.725369	-0.519605
B	6.866585	-2.383780	-0.711748
C	4.574960	-1.814239	-1.023759
C	5.478435	-3.017179	-1.178418
C	9.338647	-2.600491	-0.497291
O	8.032509	-3.083022	-0.778922
C	5.031412	-4.170006	-0.250137
C	5.525105	-3.521225	-2.636762
C	3.341313	2.957230	2.377366
C	5.066657	4.082795	0.367406
C	2.229642	4.516110	0.232366
C	4.165494	2.712128	-3.224217
C	1.340206	2.623971	-2.696789
C	2.786303	0.190094	-3.191253
N	6.609324	-1.028811	-0.308907

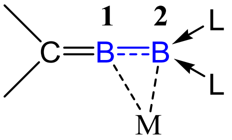
Mg	1.743360	0.186077	0.787808
P	3.464051	3.193480	0.566569
P	2.901475	1.761719	-2.270156
Mg	-1.707352	-0.218197	-0.547783
B	-4.566733	-0.633316	-0.055651
B	-3.378471	-1.492169	0.669357
Br	-0.516016	1.649866	0.866930
Br	-2.001211	0.504211	-2.888510
H	-4.989865	-1.090246	-1.088889
C	-5.258872	0.731373	0.264832
P	-3.337315	-3.242471	-0.111093
P	-3.104951	-1.450500	2.556006
C	-4.691193	1.890585	0.668397
N	-6.637222	0.979572	-0.137043
C	-3.020003	-3.214645	-1.914223
C	-4.925136	-4.170073	0.020592
C	-2.108192	-4.451263	0.528769
C	-4.361440	-2.421154	3.500660
C	-1.518536	-2.092320	3.213898
C	-3.238991	0.213206	3.296216
C	-5.049231	4.091237	-0.503300
C	-5.601635	3.091445	0.539087
C	-5.805380	3.814156	1.887504
C	-7.483557	-0.096305	-0.524536
B	-6.932600	2.376120	0.024743
C	-7.915024	-1.034833	0.420228

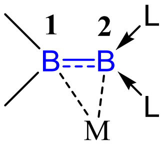
C	-7.897550	-0.236741	-1.852553
O	-8.095983	3.062144	-0.145824
C	-8.750502	-2.084900	0.046491
C	-8.740477	-1.281913	-2.224128
C	-9.358344	2.523614	-0.512387
C	-9.169855	-2.210508	-1.277615
H	3.507172	-1.863858	-1.203261
H	9.529051	-1.637309	-0.976746
H	10.043749	-3.337016	-0.885533
H	9.498184	-2.492507	0.578781
H	9.008106	2.859104	-0.835316
H	10.002153	2.672114	1.434499
H	9.387981	0.753492	2.888462
H	-3.656107	-2.471523	-2.393190
H	-1.980902	-2.948497	-2.109728
H	-3.221460	-4.199227	-2.342739
H	-4.863214	-5.141515	-0.476787
H	-5.182010	-4.325867	1.069813
H	-5.719634	-3.579475	-0.436889
H	-2.113915	-5.352149	-0.088733
H	-1.109811	-4.013491	0.506415
H	-2.347516	-4.742595	1.553179
H	-4.221985	-2.303547	4.578041
H	-5.360045	-2.077533	3.227440
H	-4.285185	-3.483250	3.259361
H	-1.518307	-2.041043	4.305322
H	-1.358227	-3.127700	2.915181
H	-0.677899	-1.502169	2.847120
H	-2.423447	0.841467	2.939192
H	-4.184902	0.674097	3.015044
H	-3.172326	0.129743	4.383313
H	-3.649017	1.980670	0.953890
H	-9.623871	1.657773	0.099037
H	-10.099668	3.309056	-0.358185
H	-9.372301	2.225856	-1.564002
H	-9.085713	-2.798645	0.793035
H	-9.825852	-3.024629	-1.568597
H	-9.054088	-1.376237	-3.259113
H	3.996880	2.149219	2.697274
H	2.321702	2.689466	2.655076
H	3.620673	3.881104	2.889560
H	5.100531	4.988346	0.978818
H	5.215076	4.358212	-0.678228
H	5.880725	3.418573	0.659952
H	2.343872	5.322291	0.960431
H	1.219448	4.112291	0.306421
H	2.370792	4.938407	-0.763975
H	3.916795	2.741359	-4.287847
H	5.141361	2.241908	-3.095978
H	4.227504	3.738375	-2.856655
H	1.255491	2.717425	-3.781881
H	1.303843	3.619660	-2.256404
H	0.479933	2.056644	-2.340327
H	1.955930	-0.402987	-2.807932
H	3.707739	-0.379150	-3.075608
H	2.608681	0.403151	-4.247639
H	-7.602473	-0.919960	1.453228
H	-7.536154	0.470793	-2.590902
H	7.429525	1.122933	-1.645067
H	7.774267	-0.950734	2.080051
H	-5.758150	4.908520	-0.668959
H	-4.857637	3.607069	-1.464541
H	-4.103729	4.529302	-0.163307
H	-6.522250	4.634087	1.782496
H	-4.863130	4.236857	2.255486
H	-6.187601	3.137980	2.658833
H	4.544342	-3.889736	-2.959436
H	4.046975	-4.551074	-0.544850
H	6.242130	-4.341376	-2.739263
H	5.741724	-5.001408	-0.296393
H	5.825863	-2.730695	-3.331666
H	4.957902	-3.844988	0.791228

Table S3. Energy decomposition (in kcal·mol−1) for **opt-2’** and **opt-3’**.

	ΔE_{Pauli}	ΔE_{OrbInt}	ΔE_{Elsta}	ΔE_{Int}
opt-2'	51.47	−37.25	−66.13	−51.91
opt-3'	50.48	−38.84	−64.45	−52.81

Table S4. Experimental and calculated ^{11}B NMR chemical shifts of **2** and **3**.





δ(^{11}B)[ppm]	exp.			cal.	
	B1	**B2**		**B1**	**B2**
2	102.9	–24.2	**opt-2'**	104.2	–29.3
3	62.9	–22.7	**opt-3'**	64.3	–24.7

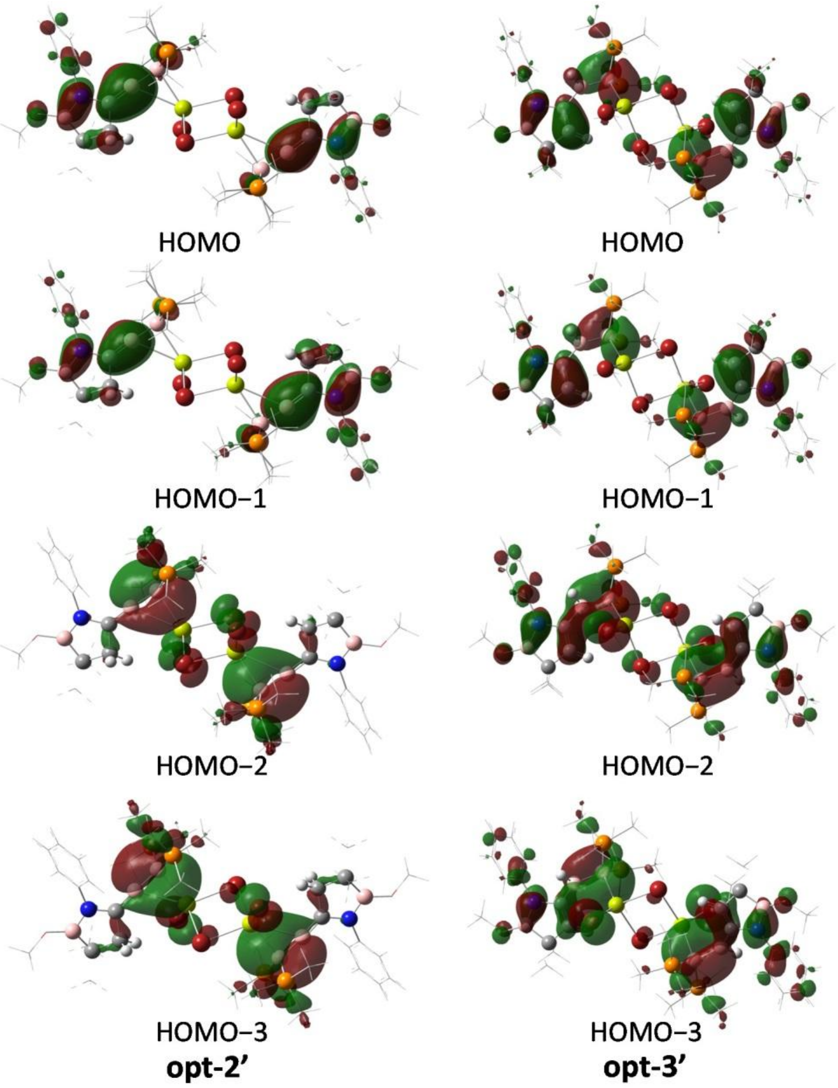
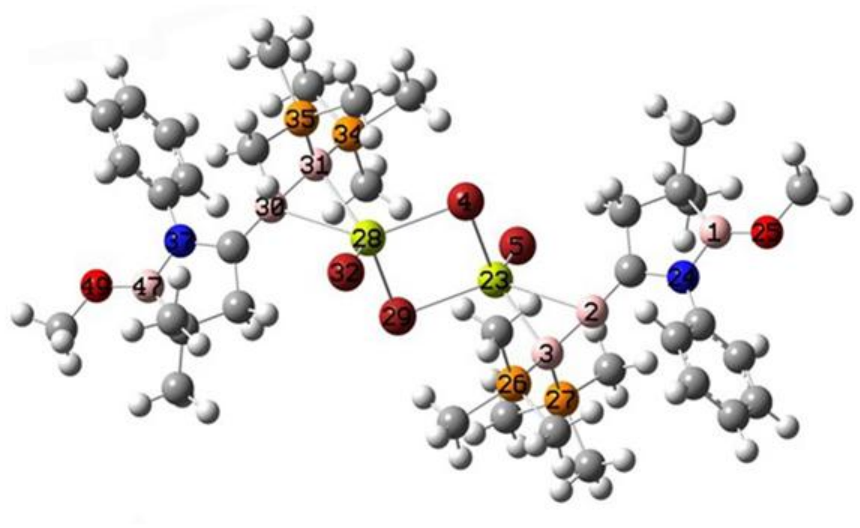


Figure S16. Plots of the selected molecular orbitals of **opt-2’** and **opt-3’**.

Table S5. Selected data of Natural Bond Orbital Analysis for **opt-2'**.



```
(Occupancy)     Bond orbital/ Coefficients/ Hybrids

-------------------------------------------------------------------------------

4. (1.74860) BD ( 2) B     2 - B     3

                  ( 18.78%)   0.4334* B     2 s(0.26%)p99.99(99.67%)d 0.26(0.07%)

                                              -0.0028 -0.0453 -0.0240 -0.0035 -0.7869

                                               0.0352 0.0061 0.6035 0.0569 -0.0098

                                               -0.0892 0.0257 -0.0020 -0.0018 0.0103

                                                 -0.0026    0.0219 -0.0094

                  ( 81.22%)   0.9012* B     3 s(4.18%)p22.90(95.81%)d 0.00(0.00%)

                                                 -0.0001 0.1967 -0.0561 0.0005 -0.8469

                                                  0.0359 0.0006 0.4706 -0.0427 0.0018

                                                 -0.1274 0.0059 -0.0001 -0.0004 0.0003

                                                  0.0001 -0.0062 0.0004

57. (1.74861) BD ( 2) B   30 - B   31

                  ( 18.78%)     0.4334* B   30 s(0.27%)p99.99( 99.67%)d 0.26(0.07%)
```

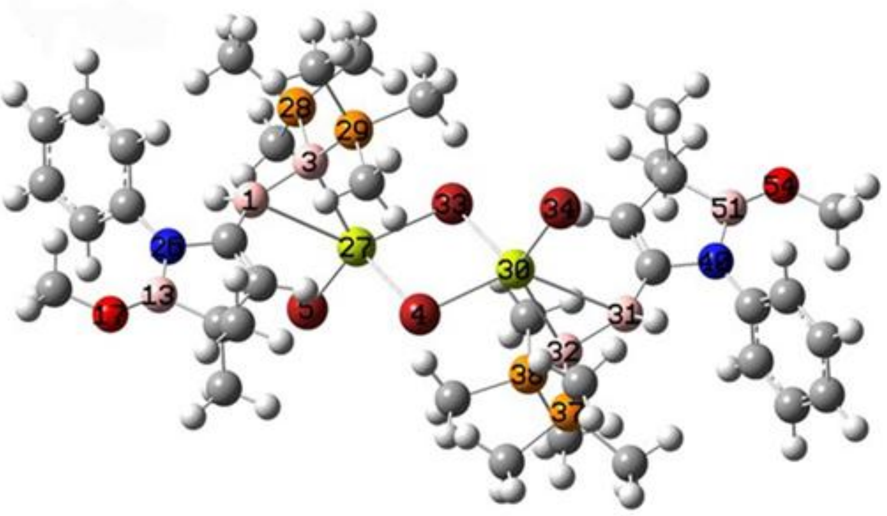
```
                                          -0.0028 -0.0453 -0.0240 -0.0035 0.7874
                                          -0.0350 -0.0061 -0.6030 -0.0568 0.0098
                                           0.0885 -0.0259 0.0021 -0.0018 0.0104
                                          -0.0026 0.0219 -0.0094
                ( 81.22%)     0.9012* B    31 s(4.18%)p22.90( 95.81%)d 0.00(0.00%)
                                          -0.0001 0.1967 -0.0561 0.0005 0.8473
                                          -0.0359 -0.0006 -0.4700 0.0426 -0.0018
                                           0.1270 -0.0058 0.0001 -0.0005 0.0003
                                           0.0001 -0.0062 0.0004
271. (0.35362) LP*( 1)Mg    23              s( 99.85%)p 0.00(0.11%)d 0.00(0.04%)
                                           0.0000 0.0000 0.9992 0.0001 0.0000
                                          -0.0000 0.0000 -0.0066 0.0117 -0.0084
                                          -0.0016 0.0000 0.0161 0.0031 0.0171
                                           0.0038 0.0000 -0.0089 -0.0084 -0.0125
                                          -0.0023 0.0037 -0.0081 -0.0120 0.0030
                                           0.0128
276. (0.35361) LP*( 1)Mg    28              s( 99.85%)p 0.00(0.11%)d 0.00(0.04%)
                                           0.0000 0.0000 0.9992 0.0001 0.0000
                                          -0.0000 0.0000 0.0067 -0.0116 0.0084
                                           0.0016 0.0000 -0.0161 -0.0031 -0.0170
                                          -0.0038 0.0000 0.0088 0.0084 0.0125
                                           0.0023 0.0037 -0.0081 -0.0120 0.0029
```

```
                                   0.0128

583. (0.00916) RY*( 3)Mg   23                   s(4.44%)p21.27(94.48%)d 0.24(1.08%)

                                  -0.0000 -0.0000 -0.0151 0.1972 0.0729

                                  -0.0006 -0.0000 -0.8236 0.1155 0.0989

                                   0.0212 -0.0000 0.4887 -0.0297 0.0390

                                  -0.0168 -0.0000 -0.0326 0.0013 -0.0192

                                  -0.0055 0.0297 -0.0088 0.0396 -0.0761

                                   0.0500

663. (0.00916) RY*( 3)Mg   28                   s(    4.42%)p21.38( 94.50%)d 0.24( 1.08%)

                                   0.0000 0.0000 -0.0150 0.1966 0.0728

                                  -0.0006 0.0000 0.8241 -0.1155 -0.0987

                                  -0.0212 0.0000 -0.4881 0.0291 -0.0388

                                   0.0168 0.0000 0.0322 -0.0019 0.0189

                                   0.0055 0.0298 -0.0090 0.0394 -0.0762

                                   0.0499
```

Table S6. Selected data of Second Order Perturbation Theory Analysis of **opt-2’**.

```
Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis

    Threshold for printing:    0.50 kcal/mol

   (Intermolecular threshold: 0.05 kcal/mol)

         E(2)   E(j)-E(i) F(i,j)

         Donor NBO (i)              Acceptor NBO (j)             kcal/mol      a.u.      a.u.

============================================================================

4. BD (2) B     2 - B     3            /271. LP*(1)Mg    23            42.56      0.20      0.085

4. BD (2) B     2 - B     3            /583. RY*(3)Mg    23             3.59      0.71      0.048

57. BD (2) B    30 - B    31            /276. LP*(1)Mg    28            42.56      0.20      0.085

57. BD (2) B    30 - B    31            /663. RY*(3)Mg    28             3.59      0.71      0.048
```

Table S7. Selected data of Natural Bond Orbital Analysis for **opt-3'**.



```
(Occupancy)     Bond orbital/ Coefficients/ Hybrids
--------------------------------------------------------------------------------
3. (1.72922) BD ( 2) B     1 - B     3
                    (17.30%)     0.4159* B     1 s(0.59%)p99.99(99.38%)d 0.05(0.03%)
                                                  -0.0032 -0.0584 -0.0496 -0.0014 -0.6223
                                                   0.0362 0.0119 -0.5996 -0.0205 0.0054
                                                    0.4941 0.0315 -0.0027 -0.0015 -0.0044
                                                   -0.0013 0.0158 -0.0066
                    (82.70%)     0.9094* B     3 s( 3.51%)p27.50(96.49%)d 0.00(0.00%)
                                                   -0.0002 0.1802 -0.0512 -0.0006 -0.8209
                                                    0.0309 0.0004 -0.3928 0.0335 -0.0001
                                                    0.3649 -0.0380 0.0004 -0.0032 -0.0003
66. (1.73056) BD (2) B    31 - B    32
                    (17.38%)     0.4169* B    31 s( 0.59%)p99.99( 99.38%)d 0.05( 0.03%)
                                                   -0.0032 -0.0573 -0.0506 -0.0015 0.6618
```

```
                                  -0.0335 -0.0116 0.5416 0.0173 -0.0062
                                  -0.5094 -0.0375 0.0025 -0.0005 -0.0013
                                  -0.0008 0.0163 -0.0068
               ( 82.62%)    0.9090* B   32 s( 3.43%)p28.16( 96.57%)d 0.00(   0.00%)
                                 -0.0003 0.1774 -0.0531 -0.0006 0.8416
                                 -0.0329 -0.0005 0.3763 -0.0294 0.0001
                                  -0.3352 0.0384 -0.0004 -0.0031 -0.0002
                                   0.0005 0.0009 0.0026
275. (0.35095) LP*( 1)Mg   27                s(99.78%)p 0.00( 0.16%)d 0.00(   0.06%)
                                   0.0000 0.0000 0.9989 0.0003 0.0000
                                  -0.0000 0.0000 -0.0082 0.0134 0.0023
                                  -0.0009 0.0000 -0.0094 0.0096 -0.0120
                                  -0.0030 0.0000 0.0238 0.0064 0.0204
                                   0.0043 0.0033 0.0142 -0.0068 0.0049
                                   0.0170 0.0002 0.0005 0.0030
276. (0.34934) LP*( 1)Mg   30                s( 99.80%)p 0.00(   0.15%)d 0.00(   0.05%)
                                   0.0000 0.0000 0.9990 0.0003 0.0000
                                  -0.0000 0.0000 0.0097 -0.0119 -0.0003
                                   0.0012 0.0000 0.0095 -0.0048 0.0103
                                   0.0027 0.0000 -0.0241 -0.0077 -0.0195
                                  -0.0043 0.0031 0.0129 -0.0055 0.0047
                                   0.0177
```

Table S8. Selected data of Second Order Perturbation Theory Analysis of **opt-3’**.

```
Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis

     Threshold for printing:    0.50 kcal/mol

    (Intermolecular threshold: 0.05 kcal/mol)

        E(2)   E(j)-E(i) F(i,j)

        Donor NBO (i)            Acceptor NBO (j)           kcal/mol      a.u.      a.u.

==============================================================

3. BD (2) B     1 - B     3          /275. LP*(1)Mg   27          42.52      0.19      0.083

66. BD (2) B   31 - B   32          /276. LP*(1)Mg   30          42.06      0.19      0.082
```

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