

# **Supplementary Information**

## **Bifurcated Hydrogen Bonds Stabilized Boron Analogues of Carboxylic Acids**

### **Contents**

1. Synthesis of compounds **2-4** and their spectral data
2. Crystallographic details
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## Method

**General.** All reactions were performed under an atmosphere of nitrogen by using standard Schlenk or dry box techniques; solvents were dried over Na metal, K metal or CaH<sub>2</sub>. <sup>1</sup>H, <sup>13</sup>C and <sup>11</sup>B spectra were obtained with BRUKER AVANCE III HD 500MHz spectrometer at 298 K. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad signal. Coupling constants *J* are given in Hz. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker ALPHA II FTIR spectrometer. Element analyses (C, H, and N) were determined with an elemental Vairo EL III analyzer (Bruker, Germany). Melting points were measured on a X4 Melting Point apparatus (Beijing Tech, CN) in sealed capillaries and are uncorrected. DmpB(OH)<sub>2</sub> (Dmp = 2,6-bis(2,4,6-trimethylphenyl)phenyl)<sup>S1</sup>, bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr)<sup>S2</sup> and 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (IPr<sub>2</sub>Me<sub>2</sub>)<sup>S3</sup> were synthesized according to literature procedures.

**Compound 2:** A toluene solution (10 mL) of **1** (358 mg, 1 mmol) was added into **IPr** (388 mg, 1 mmol) at room temperature. The resulting mixture was stirred for 10 min at room temperature. All volatiles were removed under vacuum and washed with cold n-hexane to afford a white powder of **2** in 88% yield (656 mg).

Mp: 137.2 °C; <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 7.24 – 7.20 (m, 3H, Ar-H), 7.10 (d, *J* = 7.6 Hz, 4H, Ar-H), 6.93 (d, *J* = 7.6 Hz, 2H, Ar-H), 6.83 (s, 4H, Ar-H), 6.39 (s, 2H, C<sub>2</sub>-H<sub>2</sub>), 5.74 (s, 2H, O-H), 2.60 (sept, *J* = 6.9 Hz, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.30 (s, 6H, CH<sub>3</sub>), 2.13 (s, 12H, CH<sub>3</sub>), 1.12 (d, *J* = 6.9 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.08 (d, *J* = 6.9 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C NMR (125 MHz,

$C_6D_6$ ):  $\delta = 208.8$  (NCN), 146.1 ( $C^q$ ), 144.8 ( $C^q$ ), 141.0 ( $C^q$ ), 137.0 ( $C^q$ ), 136.6 ( $C^q$ ), 135.3 ( $C^q$ ), 129.7 (CH), 128.5 (CH), 128.4 (CH), 128.1 (CH), 126.9 (CH), 123.7 (CH), 121.7 (CH), 28.7 (CH( $CH_3$ )<sub>2</sub>), 24.6 (CH( $CH_3$ )<sub>2</sub>), 23.8 (CH( $CH_3$ )<sub>2</sub>), 21.4 (CH<sub>3</sub>), 21.0 (CH<sub>3</sub>), B-C was not observed;  $^{11}B$  NMR (160 MHz,  $C_6D_6$ ):  $\delta = 29.8$  (br); IR (solid,  $cm^{-1}$ ): 2960 (H-bonded OH stretching); Anal. Calcd for  $C_{51}H_{63}BN_2O_2$ : C, 82.02; H, 8.50; N, 3.75. Found: C, 82.21; H, 8.13; N, 3.39.

**Compound 2-D:** Following the similar procedure, product **2-D** was obtained by using DmpB(OD)<sub>2</sub> as the precursor.  $^1H$  NMR (500 MHz,  $C_6D_6$ ):  $\delta = 7.18 - 7.15$  (m, 3H, Ar-H), 7.04 (d, 4H, Ar-H), 6.85 (d, 2H, Ar-H), 6.74 (s, 4H, Ar-H), 6.39 (s, 2H,  $C_2$ -H<sub>2</sub>), 2.64 (sept, 4H, CH( $CH_3$ )<sub>2</sub>), 2.20 (s, 6H, CH<sub>3</sub>), 2.04 (s, 12H, CH<sub>3</sub>), 1.07 (d, 12H, CH( $CH_3$ )<sub>2</sub>), 1.06 (d, 12H, CH( $CH_3$ )<sub>2</sub>). IR (solid,  $cm^{-1}$ ): 2360 (O–H stretching).

**Compound 3:** A toluene solution (10 mL) of **1** (358 mg, 1 mmol) was added into **IPr<sub>2</sub>Me<sub>2</sub>** (90 mg, 0.5 mmol) at room temperature. The resulting mixture was stirred for 10 min at room temperature. All volatiles were removed under vacuum and washed with cold n-hexane to afford a white powder of **3** in 92% yield (412 mg).

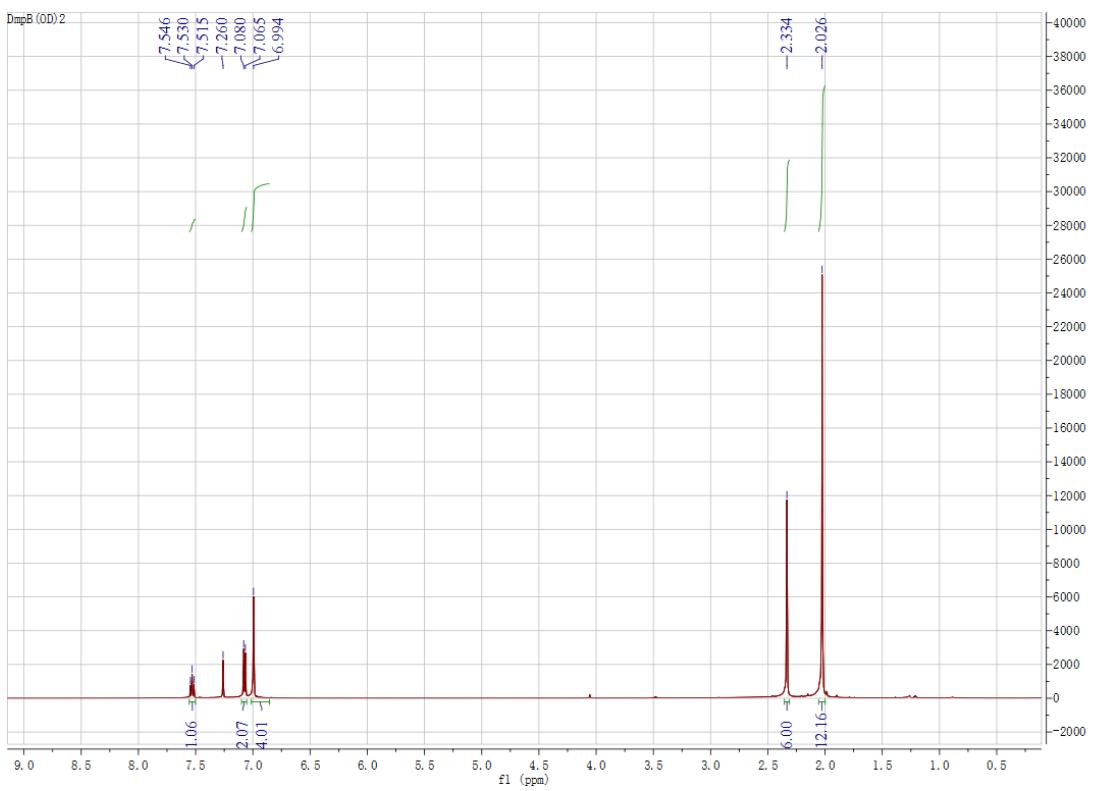
Mp: 209.5°C;  $^1H$  NMR (500 MHz,  $C_6D_6$ ):  $\delta = 7.32$  (t,  $J = 7.5$  Hz, 2H, Ar-H), 7.05 (d,  $J = 7.5$  Hz, 4H, Ar-H), 6.87 (s, 8H, Ar-H), 3.47 (sept,  $J = 6.8$  Hz, 2H, CH( $CH_3$ )<sub>2</sub>), 2.33 (s, 12H, CH<sub>3</sub>), 2.25 (s, 24H, CH<sub>3</sub>), 1.31 (s, 6H, CH<sub>3</sub>), 0.86 (d,  $J = 6.8$  Hz, 12H, CH<sub>3</sub>).  $^{13}C$  NMR (125 MHz,  $C_6D_6$ ):  $\delta = 144.3$  ( $C^q$ ), 142.2 ( $C^q$ ), 136.9 ( $C^q$ ), 134.7 ( $C^q$ ), 128.4 (NCHN), 127.9 (CH), 127.6 (CH), 126.8 (CH), 50.9 (NCH( $CH_3$ )<sub>2</sub>), 21.6 (CH<sub>3</sub>), 21.5 (CH<sub>3</sub>), 21.4 (CH<sub>3</sub>), 7.7 (CH<sub>3</sub>), B-C was not observed;  $^{11}B$  NMR (160 MHz,  $C_6D_6$ ):  $\delta = 29.0$  (br); IR (solid,  $cm^{-1}$ ): 3129

(H-bonded O–H stretching), 1558 (B=O stretching); Anal. Calcd for C<sub>58</sub>H<sub>72</sub>B<sub>2</sub>N<sub>2</sub>O<sub>4</sub>: C, 78.91; H, 8.22; N, 3.17. Found: C, 78.72; H, 8.54; N, 3.17.

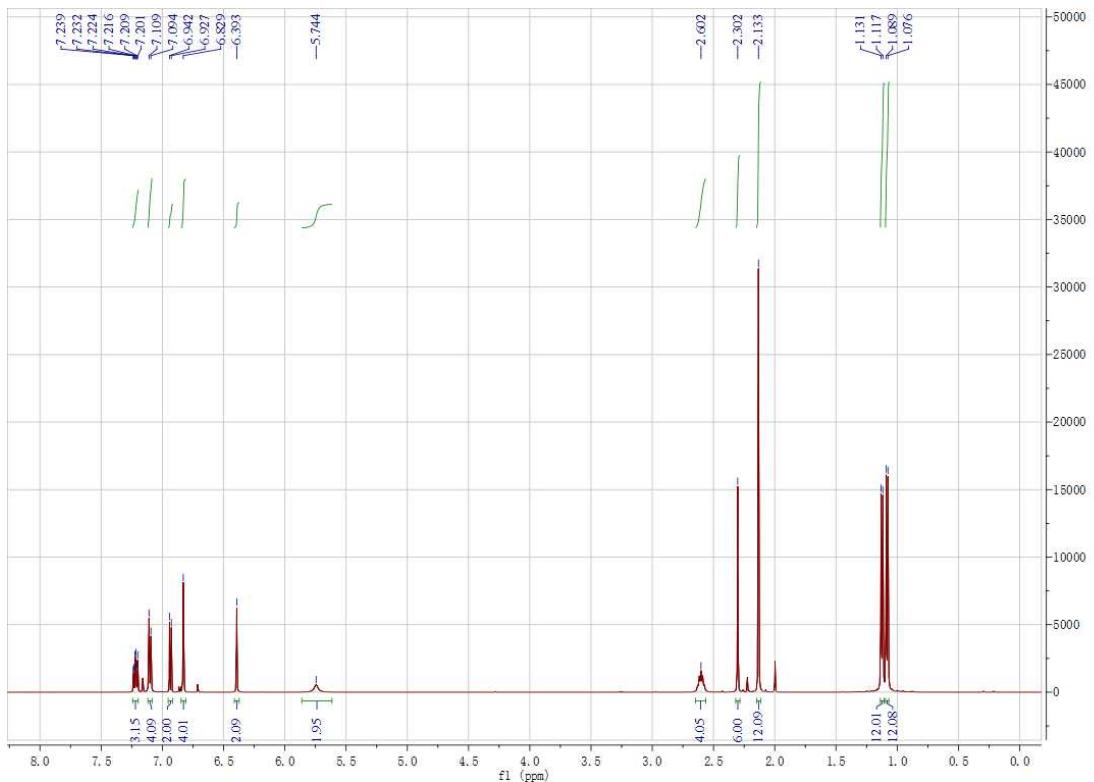
**Compound 3-D:** Following the similar procedure, product **3-D** was obtained by using DmpB(OD)<sub>2</sub> as the precursor. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 7.19 (t, 2H, Ar-H), 7.05 (d, 4H, Ar-H), 6.88 (s, 8H, Ar-H), 3.50 (sept, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.34 (s, 12H, CH<sub>3</sub>), 2.25 (s, 24H, CH<sub>3</sub>), 1.30 (s, 6H, CH<sub>3</sub>), 0.91 (d, J = 6.8 Hz, 12H, CH<sub>3</sub>). IR (solid, cm<sup>-1</sup>): 2310 (O–H stretching).

**Compound 4:** A toluene solution (10 mL) of **1** (358 mg, 1 mmol) was added into **I<sup>t</sup>Bu** (90 mg, 0.5 mmol) at room temperature. The resulting suspension was stirred for 10 min at room temperature. All volatiles were removed under vacuum and washed with cold n-hexane to afford a white powder of **4** in 98% yield (439 mg).

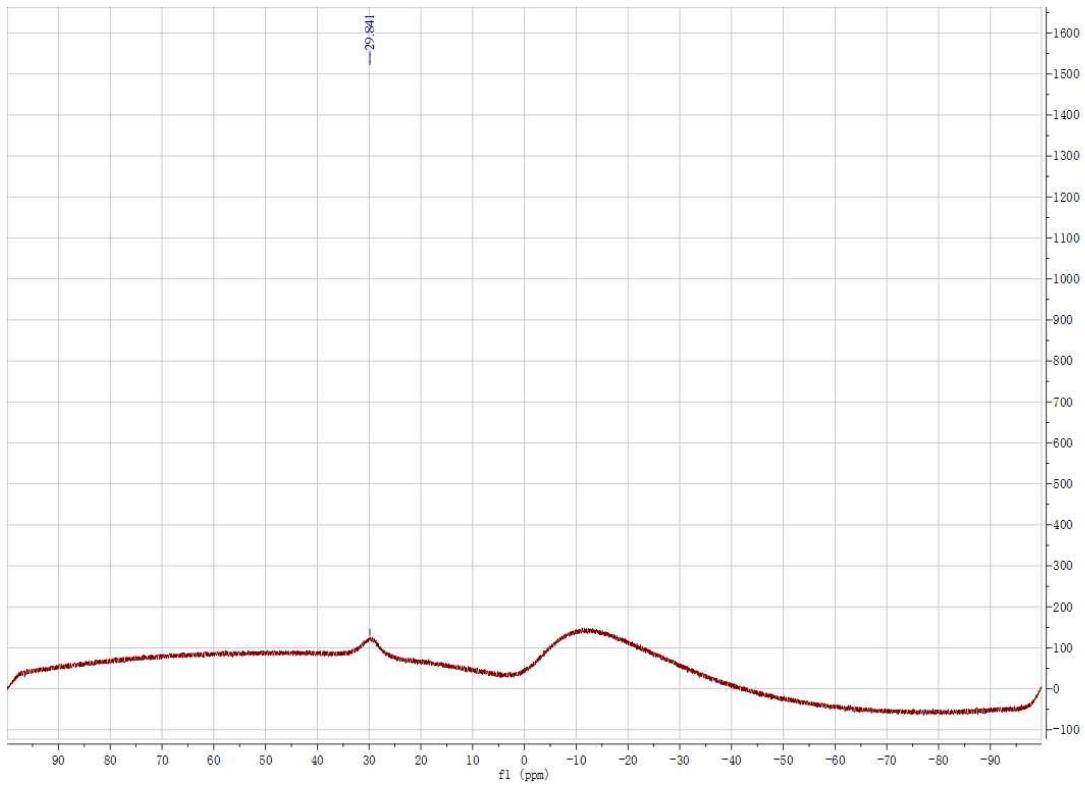
Mp: 189.3 °C; <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 7.32 (t, J = 7.5 Hz, 2H, Ar-H), 7.03 (d, J = 7.5 Hz, 4H, Ar-H), 6.86 (s, 8H, Ar-H), 6.00 (s, 2H, C<sub>2</sub>-H<sub>2</sub>), 2.30 (s, 12H, CH<sub>3</sub>), 2.23 (s, 24H, CH<sub>3</sub>), 0.95 (s, 18H, CH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 144.2 (C<sup>q</sup>), 142.2 (C<sup>q</sup>), 136.9 (C<sup>q</sup>), 134.8 (C<sup>q</sup>), 128.4 (NCHN), 128.0 (CH), 127.5 (CH), 126.8 (CH), 117.0 (C=C), 60.0 (C(CH<sub>3</sub>)<sub>3</sub>), 29.4 (C(CH<sub>3</sub>)<sub>3</sub>), 21.4 (CH<sub>3</sub>), 21.4 (CH<sub>3</sub>), B-C was not observed; <sup>11</sup>B NMR (160.4 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 28.4 (br); IR (solid, cm<sup>-1</sup>): 3150 (H-bonded OH stretching), 1575 (B=O stretching); Anal. Calcd for C<sub>58</sub>H<sub>72</sub>B<sub>2</sub>N<sub>2</sub>O<sub>4</sub>: C, 78.91; H, 8.22; N, 3.17. Found: C, 78.49; H, 8.44; N, 3.23.



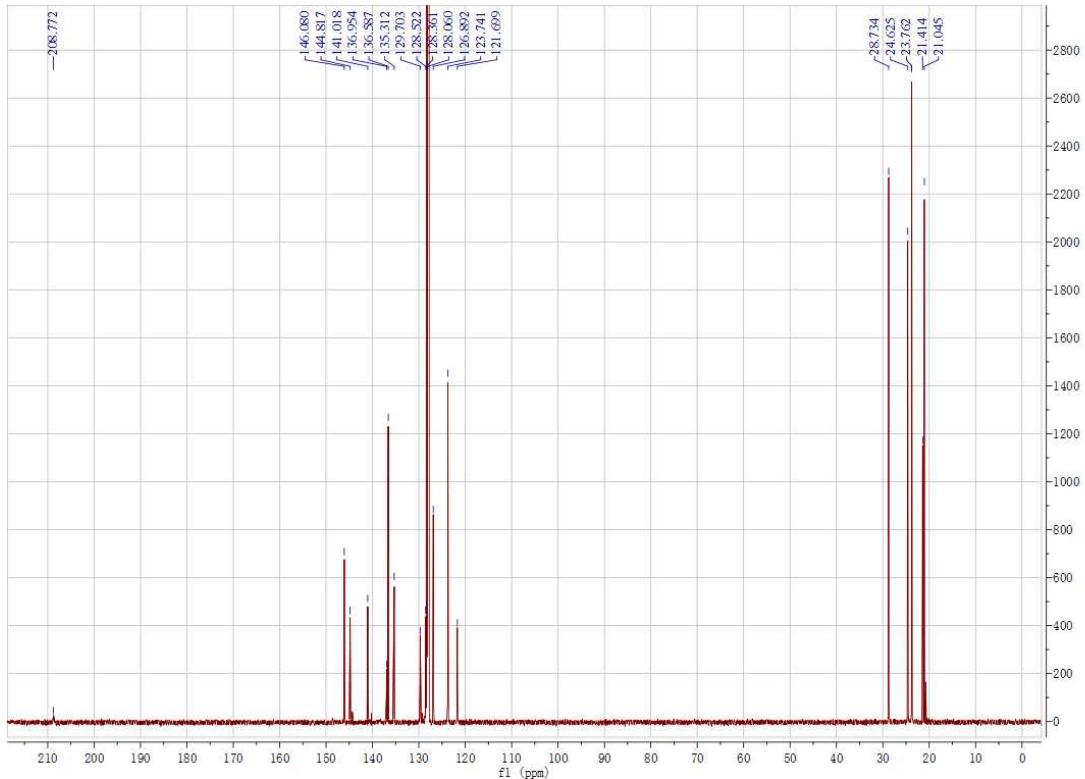
**Figure S1.** <sup>1</sup>H NMR spectrum of DmpB(OD)<sub>2</sub> in CDCl<sub>3</sub>.



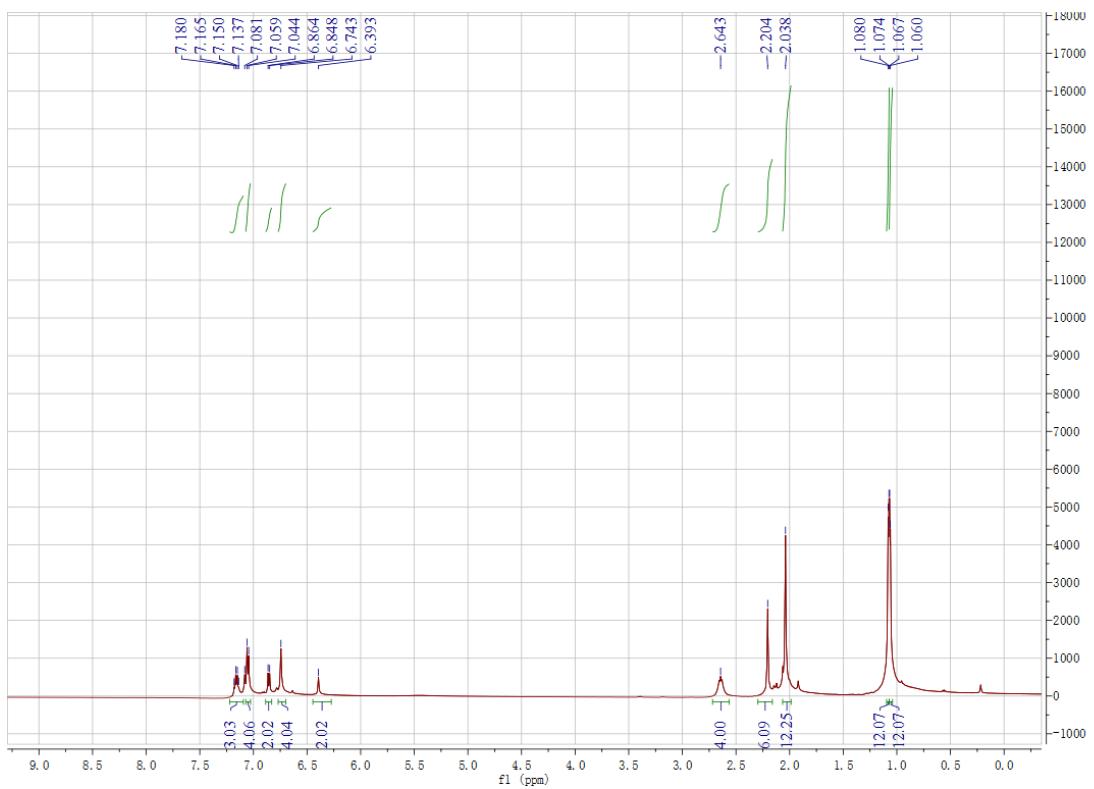
**Figure S2.** <sup>1</sup>H NMR spectrum of **2**.



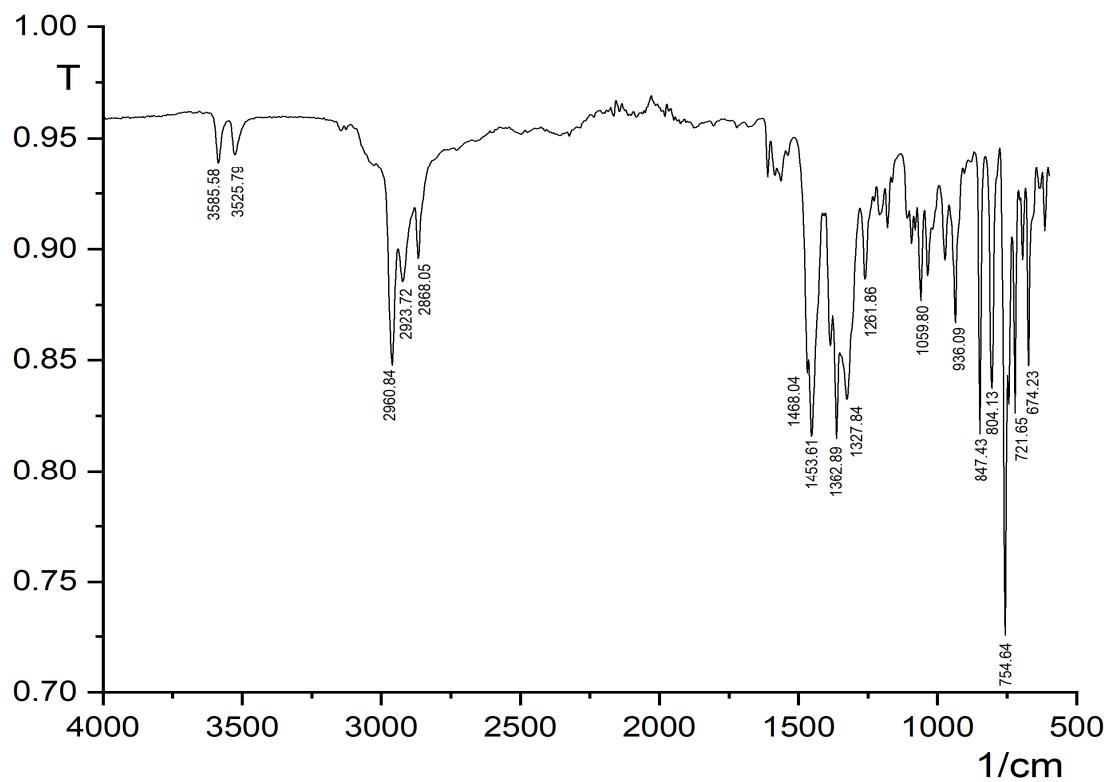
**Figure S3.** <sup>11</sup>B NMR spectrum of **2**.



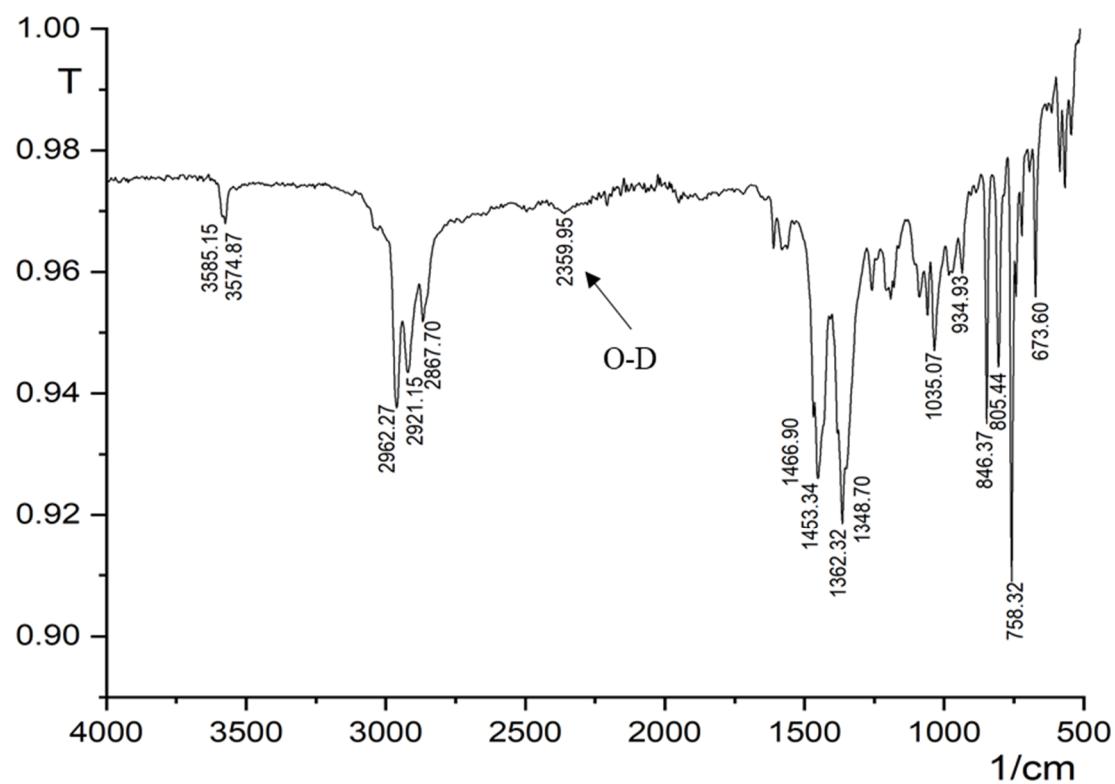
**Figure S4.** <sup>13</sup>C NMR spectrum of **2**.



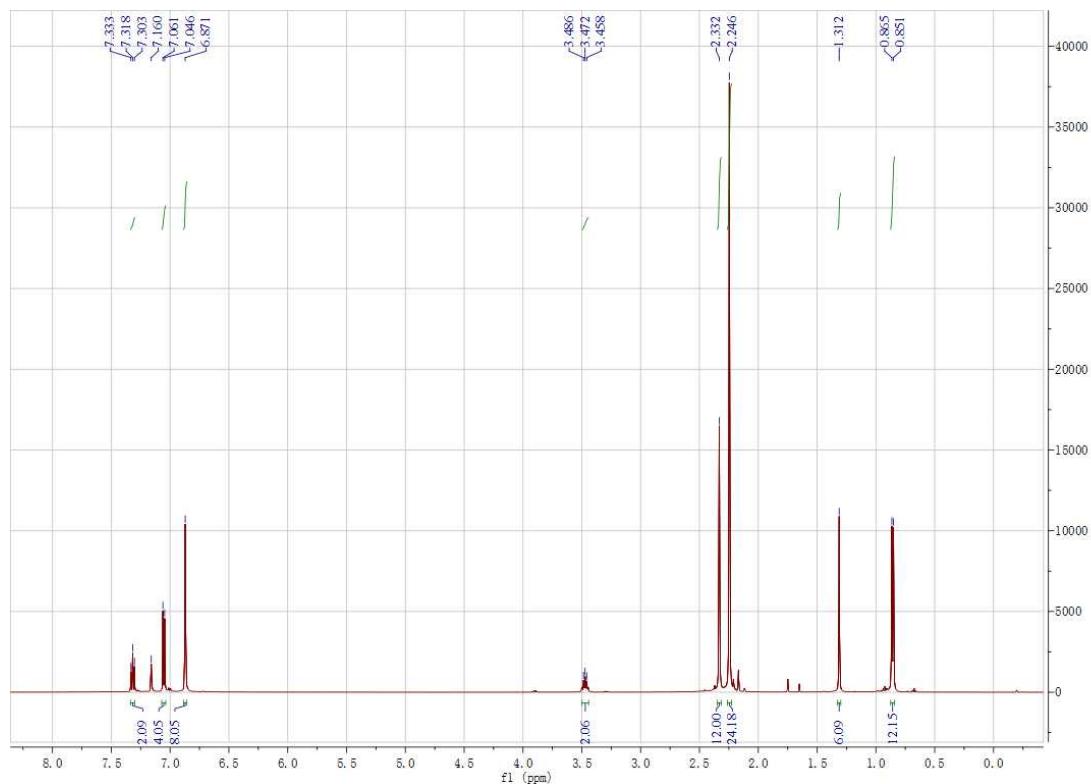
**Figure S5.** <sup>1</sup>H NMR spectrum of **2-D**.



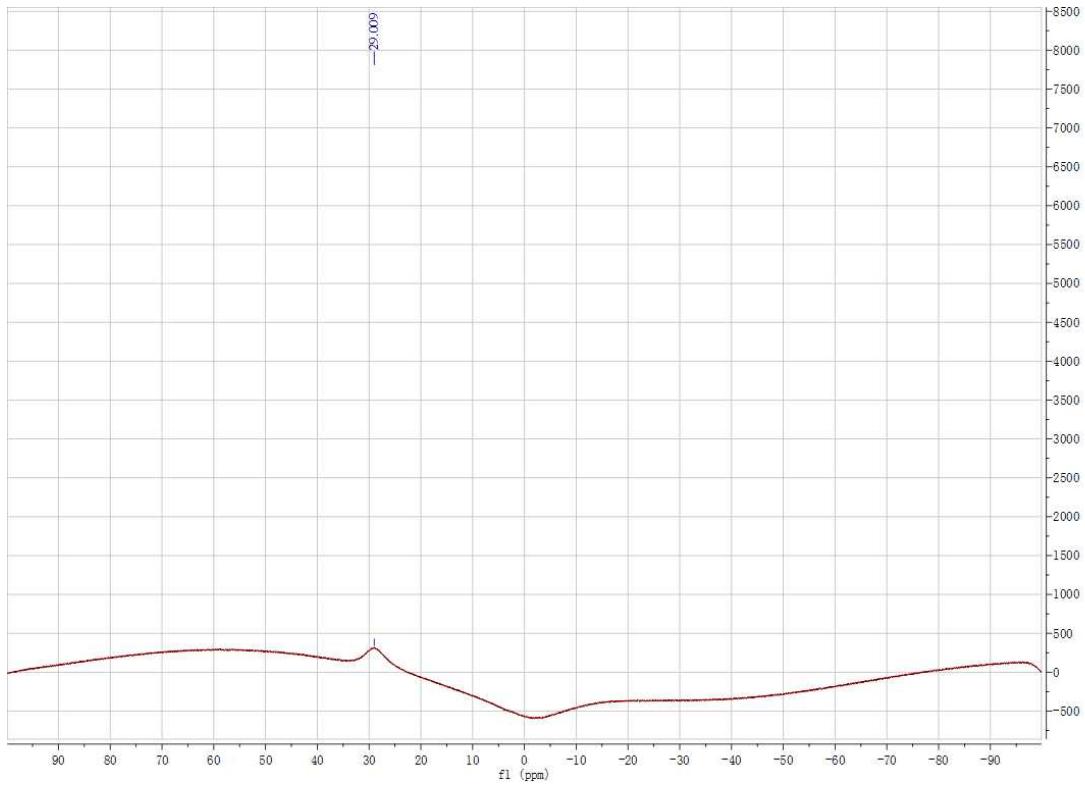
**Figure S6.** IR spectrum of **2**.



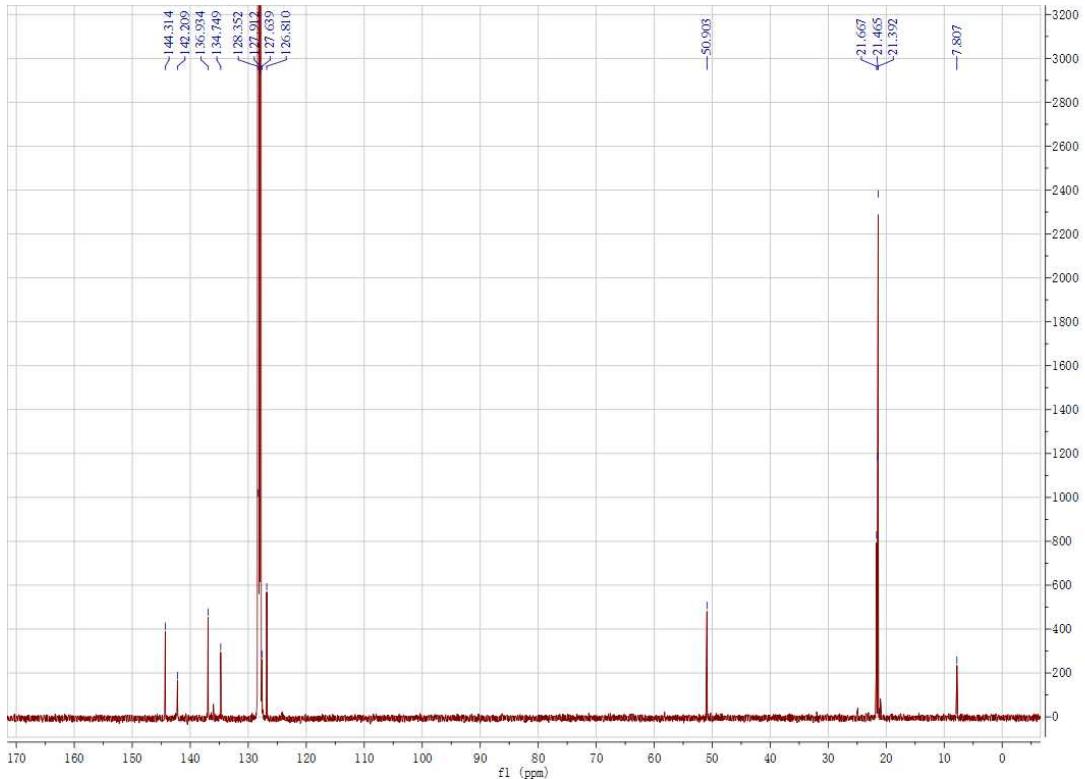
**Figure S7.** IR spectrum of **2-D**.



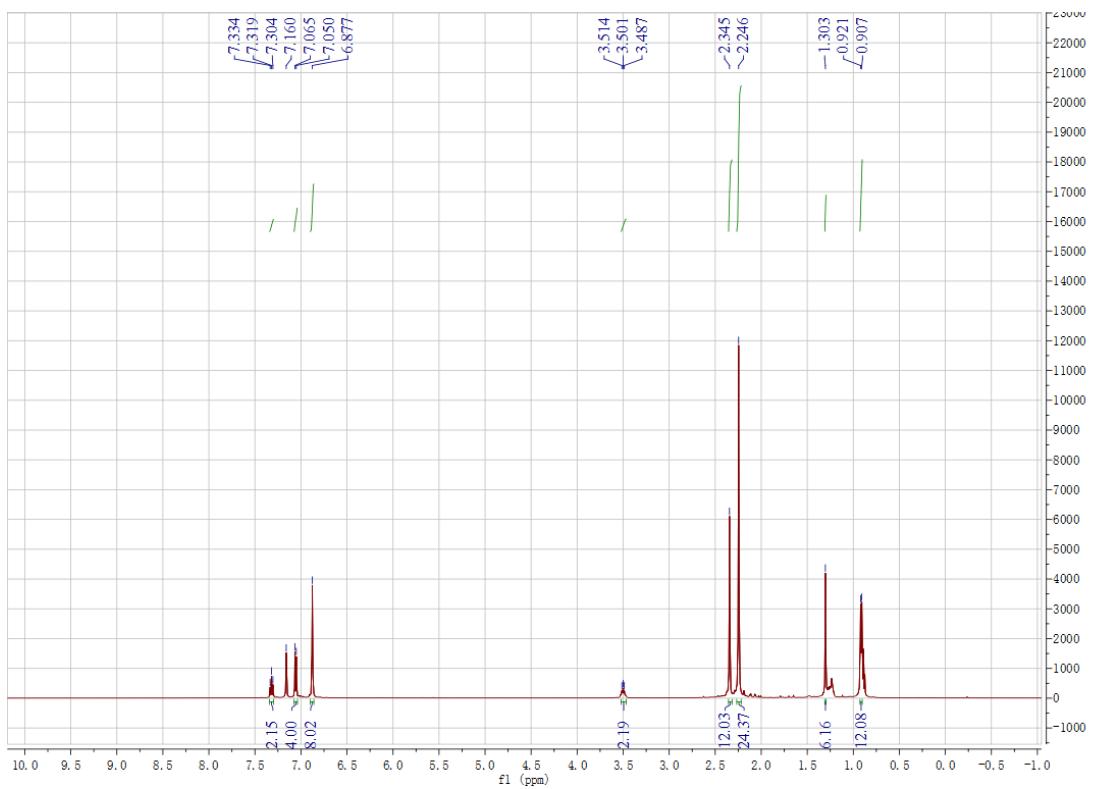
**Figure S8.**  $^1\text{H}$  NMR spectrum of **3**.



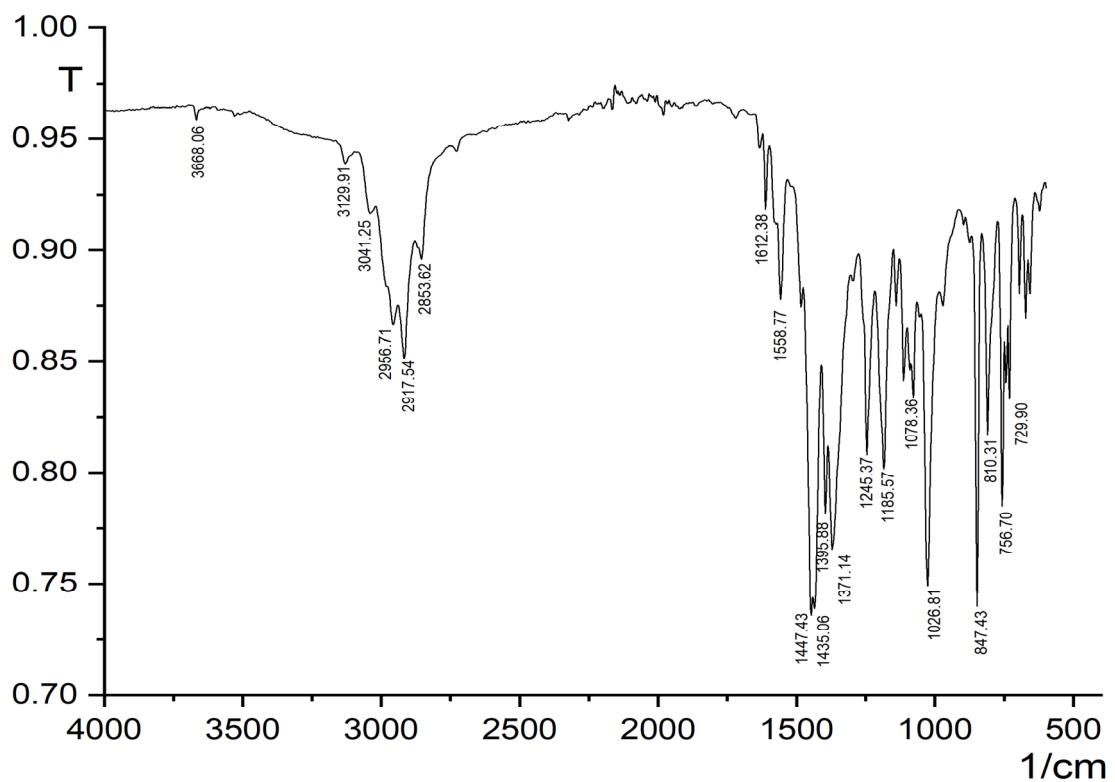
**Figure S9.** <sup>11</sup>B NMR spectrum of **3**.



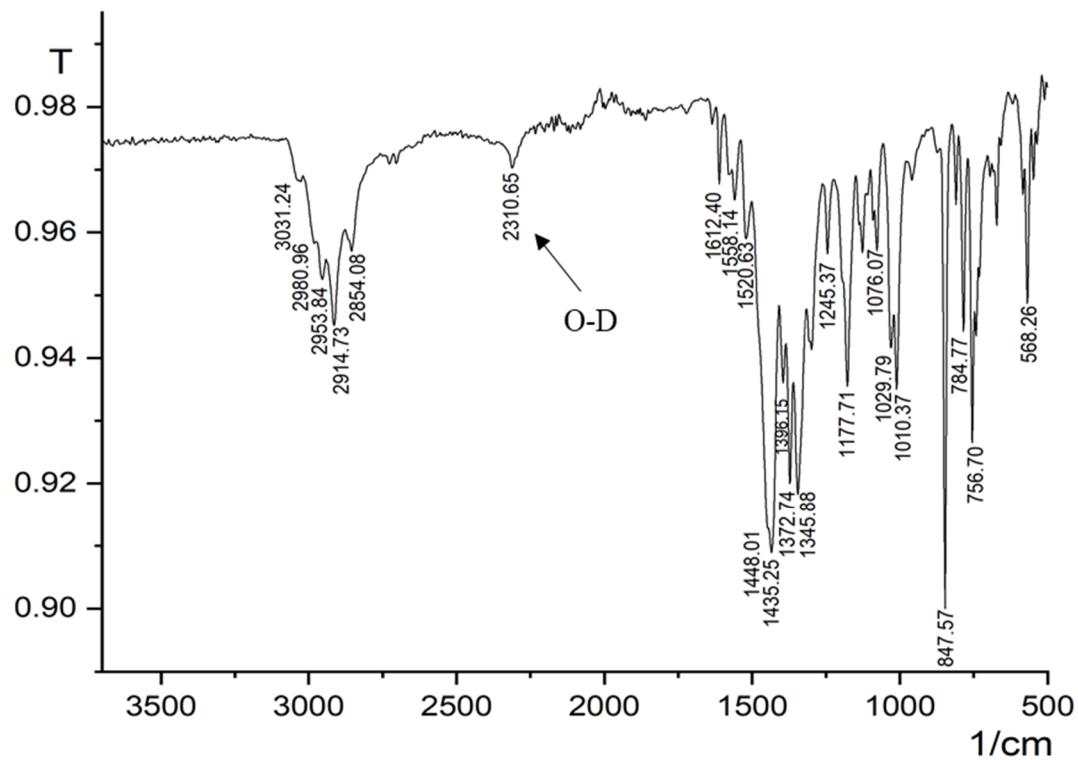
**Figure S10.** <sup>13</sup>C NMR spectrum of **3**.



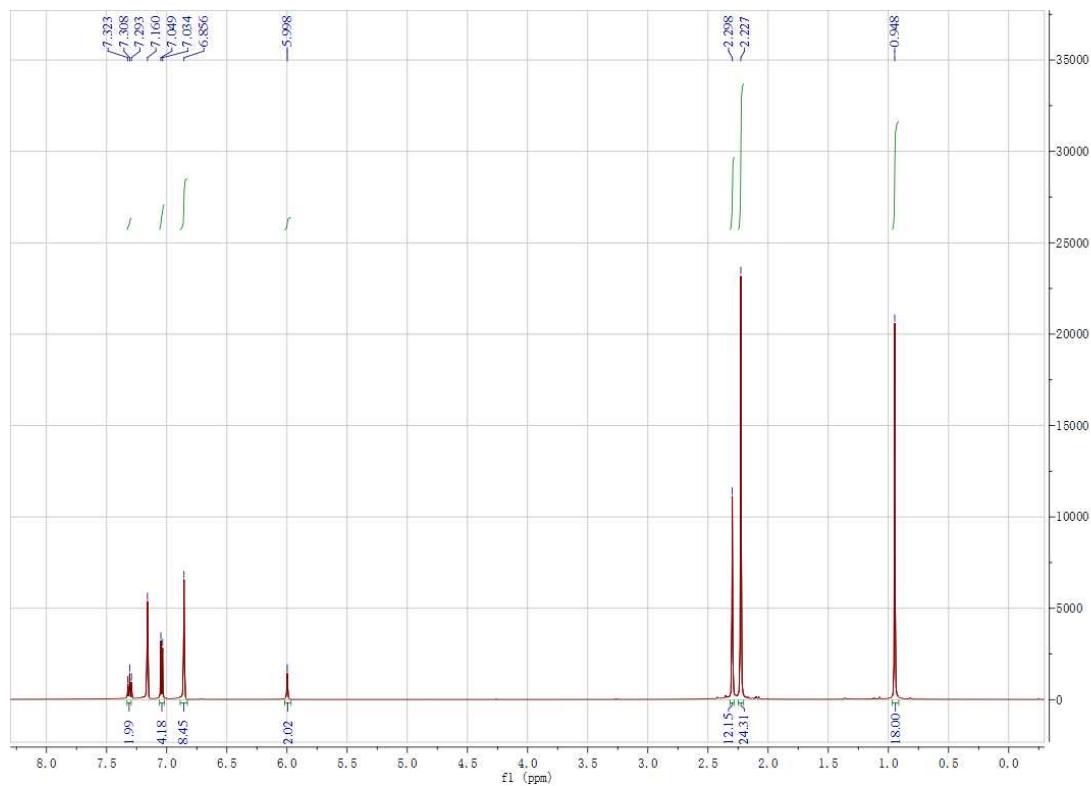
**Figure S11.**  $^1\text{H}$  NMR spectrum of **3-D**.



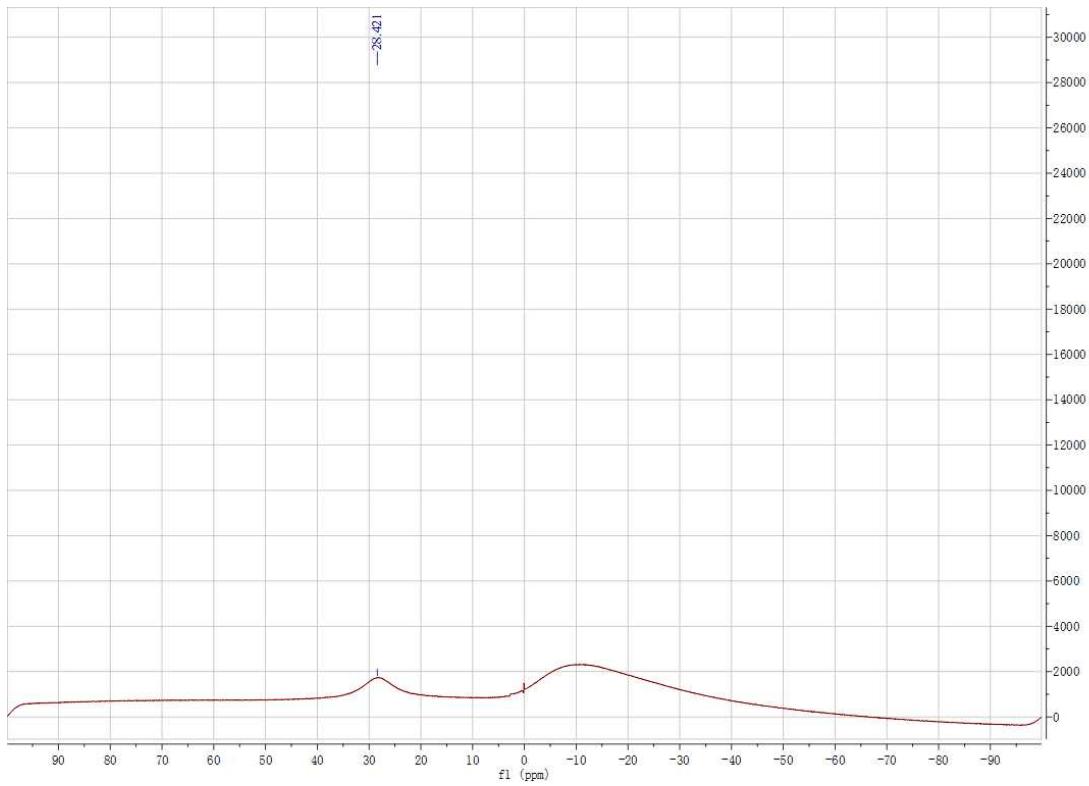
**Figure S12.** IR spectrum of **3**.



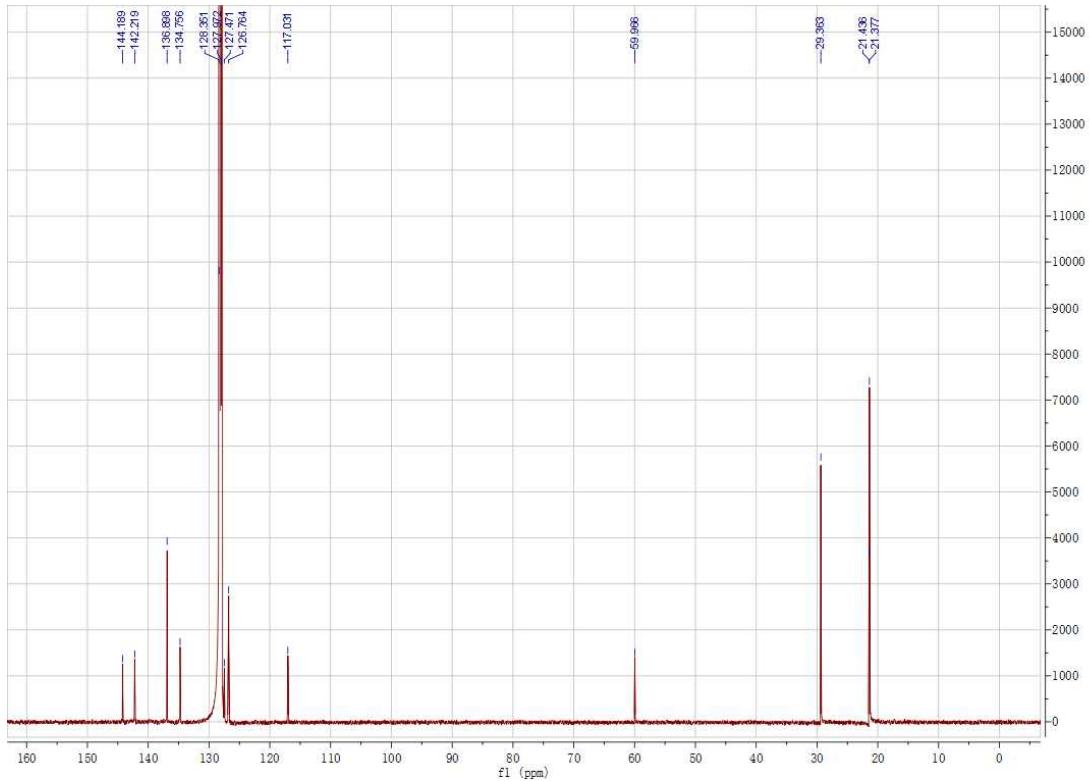
**Figure S13.** IR spectrum of **3-D**.



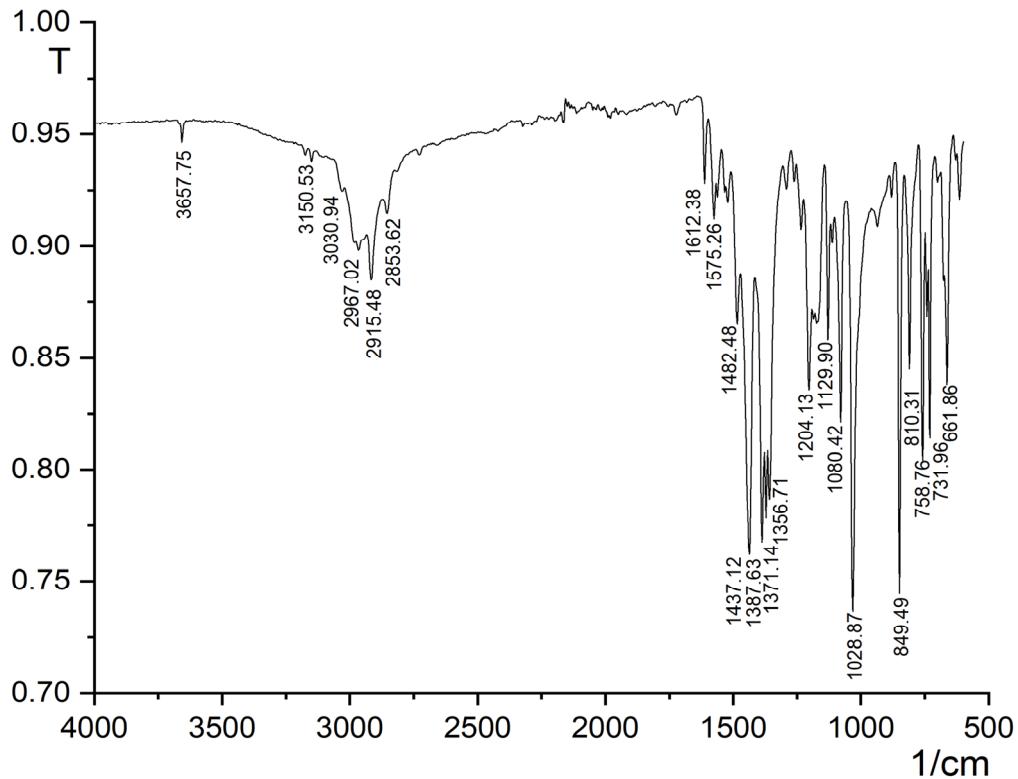
**Figure S14.**  $^1\text{H}$  NMR spectrum of **4**.



**Figure S15.** <sup>11</sup>B NMR spectrum of **4**.



**Figure S16.** <sup>13</sup>C NMR spectrum of **4**.



**Figure S17.** IR spectrum of **4**.

### Crystallographic details

X-ray data collection and structural refinement. Intensity data for compounds **2** and **3** was collected using a Rigaku XtaLABSynergy diffractometer. The crystals were measured at 173 K. The structure was solved by direct phase determination (SHELX-2013) and refined or all data by full-matrix least squares methods on  $F^2$ .<sup>S4</sup> 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. Appropriate restraints or constraints (DFIX, SADI, FLAT, SIMU, RIGU, ISOR) were applied to the geometry and the atomic displacement parameters of the atoms in compounds **2** and **3**. CCDC; 1916984 and 1916985 contain 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](http://www.ccdc.cam.ac.uk/data_request/cif).

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

Compounds	<b>2·(toluene)</b>	<b>3·(benzene)<sub>2</sub></b>
Formula	C <sub>58</sub> H <sub>71</sub> BN <sub>2</sub> O <sub>2</sub>	C <sub>71</sub> H <sub>86</sub> B <sub>2</sub> N <sub>2</sub> O <sub>4</sub>
Fw	838.97	1053.03
Crystalsyst	monoclinic	triclinic
Space group	P21/m	P-1
Size (mm <sup>3</sup> )	0.5 × 0.3 × 0.2	0.8 × 0.5 × 0.4
T/K	172.99(10)	172.99(10)
a, Å	12.4305(3)	11.2870(4)
b, Å	16.7827(6)	13.1664(4)
c, Å	13.0648(4)	21.7762(6)
α, deg	90	88.489(2)
β, deg	107.590(3)	85.848(2)
γ, deg	90	78.785(2)
V, Å <sup>3</sup>	2598.11(14)	3165.77(17)
Z	2	2
d <sub>calcd</sub> g·cm <sup>-3</sup>	1.072	1.105
μ, mm <sup>-1</sup>	0.482	0.511
Refl collected	15750	34055
T <sub>max</sub> / T <sub>min</sub>	0.910/0.795	0.822/0.685
N <sub>measd</sub>	4758	11219
[R int]	0.0625	0.0676
R <sub>1</sub> [I>2sigma(I)]	0.0590	0.0645
wR <sub>2</sub> [all data]	0.1575	0.1670
GOF	1.090	1.030
Largest diff. peak/ hole[e. Å <sup>-3</sup> ]	0.26/-0.31	0.40/-0.33

## Computational details

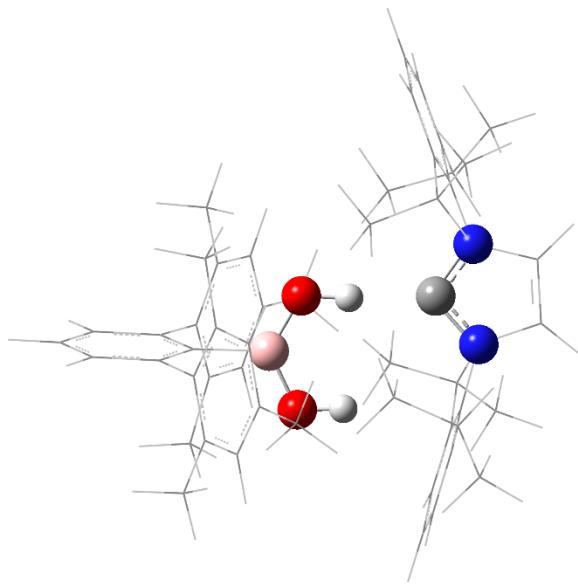
DFT calculations were carried out employing Gaussian 09 program package<sup>S5</sup>. The geometrical parameters were calculated at M06-2X<sup>S6</sup> functional level combined with the 6-311G(d,p) basis set. Full optimization was applied in the reactants, intermediates, transition states, and the corresponding products of the research system. At the same level, the harmonic vibrational frequency calculations were implemented for all optimized geometries to verify the character of stationary points, making sure the stationary points to be minima (no imaginary frequency) or transition states (only one imaginary frequency). Additionally, the solvent effects were taken into account in toluene using the SMD<sup>S7</sup> model. NBO analysis was carried out using NBO 3.1 in Gaussian 09 package. The second order perturbation theory analysis was performed based on Fock or Kohn-Sham Matrix in NBO basis to estimate donor-acceptor (bond-antibond) interactions, which is given by the formula,

$$\Delta E_{i \rightarrow j^*}^{(2)} = -2 \frac{\langle \sigma_i | \hat{F} | \sigma_j^* \rangle^2}{\varepsilon_{j^*} - \varepsilon_i}$$

where  $\hat{F}$  is the Fock or Kohn-Sham operator,  $\varepsilon_i = \langle \sigma_i | \hat{F} | \sigma_i \rangle$  and  $\varepsilon_{j^*} = \langle \sigma_j^* | \hat{F} | \sigma_j^* \rangle$  are the respective orbital energies of donor and acceptor NBOs. The program Multiwfn 3.3.9<sup>S8</sup> was used for AIM analysis. All values in the square brackets of figures are the optimized bond distances in solution unless indicated.

- O
- N
- C
- B

**Note S1.** Coordinates for optimized geometries of **2**.



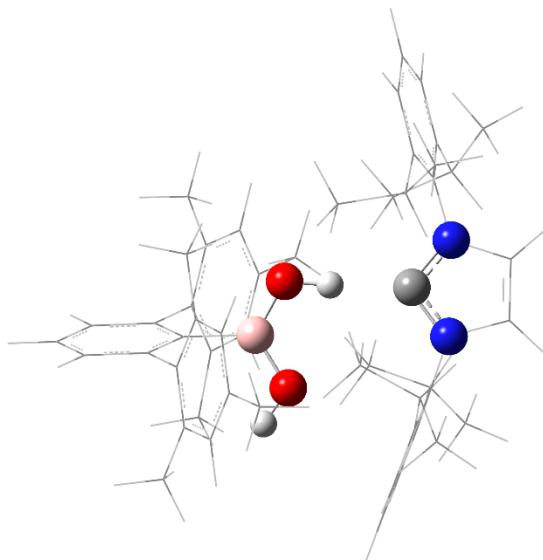
O	1.27532200	1.10830700	1.13397700
O	0.18949900	0.28059600	-0.85838600
C	1.95881100	2.06485100	-1.09840500
C	3.23564300	1.68195400	-1.53324900
C	3.99415300	2.54115200	-2.32943400
H	4.97996500	2.22945300	-2.65964700
C	3.49058400	3.78357900	-2.69663800
H	4.08204900	4.44693900	-3.31790500
C	3.78598000	0.34784100	-1.13849300
C	3.49650700	-0.78412600	-1.91151800
C	4.01380200	-2.02155800	-1.52080600
H	3.78639100	-2.89829000	-2.12106100
C	4.80971400	-2.15568700	-0.38859000
C	5.08359500	-1.01573900	0.36719600
H	5.69149100	-1.10604900	1.26396200
C	4.57727700	0.23256200	0.01693900
C	4.83988800	1.43623400	0.88386400
H	5.32228500	2.23938600	0.32098800
H	5.47874100	1.17461600	1.72897200
H	3.89637100	1.83222500	1.27099700
C	2.62987100	-0.67272900	-3.13918400
H	1.61974300	-0.35213700	-2.86786600
H	2.56352700	-1.63243100	-3.65398700
H	3.02925800	0.06736900	-3.83775900
C	5.33952900	-3.49805600	0.04379100
H	6.43273100	-3.51552900	0.02637400

H	4.97977300	-4.29534300	-0.60890100
H	5.02682000	-3.72872400	1.06670600
B	1.07724300	1.07952600	-0.22514600
H	0.72639700	0.48475600	1.62458700
H	-0.37457800	-0.32365700	-0.28982400
C	1.46339700	3.32371400	-1.46393500
C	2.22944200	4.17589500	-2.26156200
H	1.83287800	5.14810200	-2.53721900
C	0.12080900	3.76538500	-0.97015900
C	-1.03549800	3.48593600	-1.71078500
C	-2.27081800	3.92342400	-1.22755800
H	-3.16593800	3.70575300	-1.80348800
C	-2.38209100	4.62283000	-0.03027500
C	-1.22071300	4.87388600	0.69903100
H	-1.29279300	5.40209900	1.64649400
C	0.02815900	4.44910000	0.25412500
C	1.25585900	4.68091500	1.09631000
H	2.04633500	5.17923300	0.52997600
H	1.01737700	5.29148200	1.96895600
H	1.65823900	3.72362000	1.44252500
C	-0.95625300	2.69457200	-2.99008300
H	-0.63409500	1.67042000	-2.77801700
H	-1.92784200	2.65693400	-3.48545100
H	-0.23128600	3.12829600	-3.68350700
C	-3.71955900	5.09077700	0.48230300
H	-3.78764900	6.18219300	0.46111300
H	-4.53748600	4.69375000	-0.12173300
H	-3.87549000	4.77595300	1.51801000
N	-1.42457600	-1.80299200	1.95400800
N	-2.30534800	-2.37017500	0.10958100
C	-1.40696500	-1.49850200	0.63106000
C	-2.87436200	-3.18648500	1.07597100
H	-3.61115900	-3.93487300	0.83604600
C	-2.31550800	-2.82322600	2.25245200
H	-2.46106300	-3.18665400	3.25608700
C	-0.64140700	-1.09286200	2.92678700
C	-1.14108000	0.11567400	3.42995200
C	-0.34720100	0.80817500	4.34669000
H	-0.69418400	1.75554600	4.74265400
C	0.88325200	0.30791600	4.74348900
H	1.48704500	0.86310800	5.45179000
C	-2.45268800	0.71188900	2.95193700
H	-3.01015300	-0.06261300	2.41949200

C	-2.16827900	1.85785600	1.97242400
H	-1.57576000	2.63846500	2.45773000
H	-3.10232500	2.30898600	1.62666600
H	-1.61379000	1.51766000	1.09285300
C	-3.32463700	1.19782400	4.11332200
H	-3.49322900	0.40773300	4.84906200
H	-4.29682300	1.52515900	3.73635500
H	-2.87066600	2.04914600	4.62694400
C	-2.65544400	-2.42350500	-1.28408800
C	-1.94285200	-3.28755400	-2.12423600
C	-2.31891300	-3.33469500	-3.46667300
H	-1.78444900	-3.98466100	-4.14960800
C	-3.35821500	-2.54753600	-3.94351900
H	-3.63416200	-2.59599900	-4.99073000
C	-0.74313900	-4.07316100	-1.62702600
H	-0.79922400	-4.13326700	-0.53729800
C	-0.70193800	-5.50374600	-2.16887000
H	-1.63587200	-6.03537300	-1.97118800
H	0.11197500	-6.05718100	-1.69404700
H	-0.52120200	-5.52256200	-3.24648400
C	0.53984100	-3.31293100	-1.99225100
H	0.63778800	-3.24569000	-3.08040600
H	1.41802600	-3.83202100	-1.59906100
H	0.53041200	-2.29502200	-1.59311400
C	0.60435900	-1.61917700	3.30360100
C	1.35521400	-0.89349400	4.22745700
H	2.32497600	-1.26078700	4.54026600
C	1.14985100	-2.87669600	2.64986100
H	0.30248600	-3.51652400	2.38779300
C	1.88409200	-2.49991000	1.35407800
H	2.72256900	-1.83287100	1.57316400
H	2.27982100	-3.39635700	0.86699500
H	1.22947000	-1.98949200	0.64356500
C	2.07554400	-3.68068200	3.56403900
H	1.62028600	-3.87603300	4.53807600
H	2.30644700	-4.64145700	3.09799200
H	3.02578800	-3.16494800	3.72553500
C	-3.69524400	-1.60465300	-1.74051800
C	-4.03464000	-1.68649000	-3.09107300
H	-4.82701400	-1.05902000	-3.48264800
C	-4.37227700	-0.59285700	-0.83446400
H	-4.14413400	-0.85294200	0.20229100
C	-5.89491400	-0.58544500	-0.98656700

H	-6.31801200	-1.58180100	-0.83741400
H	-6.33877900	0.08710200	-0.24832200
H	-6.20125500	-0.23170800	-1.97409800
C	-3.78426900	0.79894000	-1.10829400
H	-4.00129300	1.10382400	-2.13709600
H	-4.21998600	1.54038800	-0.43248900
H	-2.69871000	0.80736200	-0.97528300

**Note S2.** Coordinates for optimized geometries of **2'**.



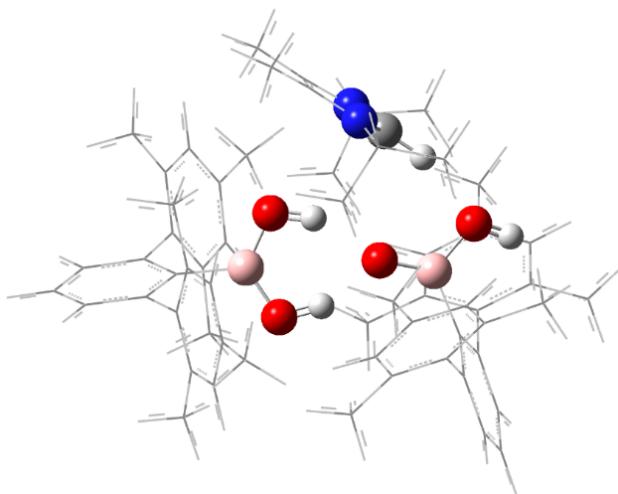
O	1.32811700	0.68430700	1.05700700
O	0.04415500	0.39159700	-0.88923300
C	1.96955100	2.04943300	-1.03123200
C	3.27166200	1.72743700	-1.44898600
C	4.05635500	2.67525300	-2.10681800
H	5.05667100	2.40577200	-2.43011900
C	3.55882300	3.94934900	-2.35259700
H	4.17093500	4.68277100	-2.86528200
C	3.82252700	0.35658500	-1.20856500
C	3.45667300	-0.69903700	-2.06126900
C	3.99948000	-1.96349700	-1.84060300
H	3.72193900	-2.77835900	-2.50368100
C	4.88891600	-2.20885100	-0.79645100
C	5.23392600	-1.15071600	0.03902400
H	5.92325800	-1.32417800	0.86093100
C	4.71456100	0.13044800	-0.15087200
C	5.13719800	1.25403900	0.76317100
H	5.88640500	1.89135400	0.28380200
H	5.57080900	0.86138400	1.68424200

H	4.29955300	1.90662900	1.02269300
C	2.51475000	-0.46317200	-3.21442000
H	1.53624700	-0.12666200	-2.86177400
H	2.37765500	-1.37792100	-3.79325900
H	2.90192800	0.31267300	-3.88112000
C	5.41017100	-3.59835400	-0.54265800
H	6.36086100	-3.57567400	-0.00681900
H	5.55571300	-4.14449400	-1.47683300
H	4.69980700	-4.16848500	0.06594800
B	1.07298100	0.98970300	-0.25916600
H	2.11954500	1.10583200	1.39973400
H	-0.48594000	-0.23996100	-0.30804100
C	1.47676200	3.33924400	-1.28455900
C	2.27287800	4.27951200	-1.94145000
H	1.87574400	5.27220300	-2.12830900
C	0.09751700	3.72624900	-0.84624300
C	-0.99306000	3.51565800	-1.70105300
C	-2.26685600	3.89702200	-1.27855500
H	-3.11128300	3.72800400	-1.94030100
C	-2.48245000	4.48217000	-0.03438400
C	-1.38549400	4.67576800	0.80233600
H	-1.53699300	5.11476400	1.78524800
C	-0.10024600	4.29754600	0.42091600
C	1.05094800	4.45511700	1.38190200
H	1.89215100	4.98189400	0.92526300
H	0.74249600	5.00280900	2.27388400
H	1.41870200	3.47313500	1.69808900
C	-0.80498600	2.84377400	-3.03514900
H	-0.48176500	1.81007500	-2.88277500
H	-1.73848300	2.83396500	-3.59976000
H	-0.04155300	3.34494000	-3.63549000
C	-3.86475600	4.88658900	0.40884300
H	-3.95916000	5.97517000	0.45917800
H	-4.62442300	4.51576000	-0.28151500
H	-4.08786300	4.49415300	1.40471900
N	-1.29582000	-1.81265100	1.94180000
N	-2.50941600	-2.17945100	0.24060100
C	-1.46485500	-1.41645200	0.65458700
C	-2.97362500	-3.02864000	1.23510500
H	-3.79267000	-3.70956800	1.07431800
C	-2.20532700	-2.78884600	2.32094300
H	-2.21546300	-3.21217100	3.31145700
C	-0.29686100	-1.26055400	2.81686300

C	-0.59221000	-0.08124900	3.50385000
C	0.40643500	0.45977600	4.31475900
H	0.21680500	1.38091600	4.85420500
C	1.64175400	-0.15981000	4.42951300
H	2.40533400	0.27296800	5.06647200
C	-1.91162400	0.64559700	3.32234000
H	-2.62009600	-0.04019500	2.84999100
C	-1.71196200	1.84101300	2.38278600
H	-0.98132300	2.53794800	2.80564600
H	-2.65237300	2.38124300	2.24110700
H	-1.34355300	1.52976100	1.40181400
C	-2.51918000	1.09723500	4.65334700
H	-2.61194300	0.26531300	5.35561100
H	-3.51508800	1.51552800	4.48625000
H	-1.91613400	1.87540100	5.12849100
C	-3.02936900	-2.17678300	-1.09927600
C	-2.37102500	-2.93708800	-2.07154500
C	-2.91890500	-2.95391800	-3.35614200
H	-2.42951400	-3.52476500	-4.13734700
C	-4.07327800	-2.24399400	-3.64767300
H	-4.48692800	-2.27461200	-4.64916700
C	-1.06779400	-3.66553200	-1.79141500
H	-0.89885100	-3.67378800	-0.71147200
C	-1.09627400	-5.11959100	-2.26976200
H	-1.93496400	-5.66795700	-1.83398100
H	-0.17212500	-5.62553300	-1.97875900
H	-1.17689200	-5.18501700	-3.35805800
C	0.08816500	-2.89246200	-2.44046300
H	-0.04978600	-2.84370200	-3.52527300
H	1.04390700	-3.38439400	-2.23903800
H	0.13862300	-1.87002300	-2.05866000
C	0.94106100	-1.90731700	2.90944600
C	1.90664400	-1.33370600	3.73401100
H	2.87976800	-1.80069000	3.82955100
C	1.25235500	-3.12719300	2.06137300
H	0.31807200	-3.66919300	1.88757600
C	1.80219300	-2.66881000	0.70296400
H	2.71974900	-2.09187600	0.84614900
H	2.03524400	-3.53373700	0.07310000
H	1.09343200	-2.03068900	0.17135700
C	2.23188200	-4.09353100	2.72947900
H	1.91392200	-4.36162300	3.74016200
H	2.30418300	-5.01204400	2.14153500

H	3.23733500	-3.66806400	2.78942300
C	-4.18078300	-1.42356500	-1.37304700
C	-4.69481700	-1.48001100	-2.66701100
H	-5.58482200	-0.91509100	-2.91665100
C	-4.77521600	-0.49723700	-0.32630100
H	-4.59304100	-0.93479200	0.65898200
C	-6.28442300	-0.30005000	-0.47227900
H	-6.81624700	-1.25377500	-0.51600300
H	-6.66578900	0.26256600	0.38316900
H	-6.53266300	0.27136500	-1.37037600
C	-4.04755500	0.85562600	-0.38935200
H	-4.20857100	1.31983900	-1.36738400
H	-4.42868700	1.53555900	0.37856900
H	-2.96977400	0.74343800	-0.24916500

**Note S3.** Coordinates for optimized geometries of **3**.



O	0.94403100	-0.24442700	-1.46496400
H	0.40164800	0.42563300	-0.96698600
O	0.84021200	-1.28345600	0.67464800
H	0.28426200	-0.48486100	0.81701000
C	2.15856500	-2.45289500	-1.18230000
C	3.52567300	-2.22567800	-1.41224000
C	4.33577000	-3.23254900	-1.94125200
H	5.38975500	-3.03255000	-2.10583800
C	3.80075900	-4.47414300	-2.25738600
H	4.43047200	-5.24954600	-2.67888400
C	2.45400900	-4.71564400	-2.02381300

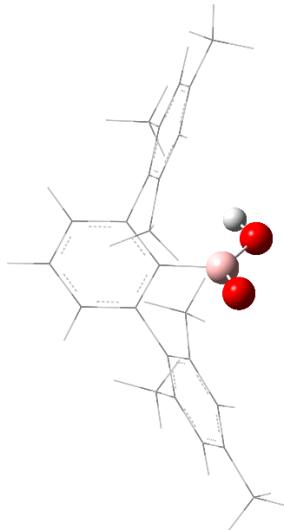
H	2.02392100	-5.68364400	-2.26100200
C	1.63499300	-3.72179400	-1.48136900
C	0.20027200	-4.06983900	-1.22890900
C	-0.12273100	-4.88987700	-0.13249500
C	-1.44701800	-5.27498400	0.06358500
H	-1.69524800	-5.90625500	0.91374200
C	-2.46103300	-4.87318000	-0.80572600
C	-2.11954800	-4.06974300	-1.88803200
H	-2.89391100	-3.76019100	-2.58491900
C	-0.80385800	-3.65584900	-2.11531000
C	0.94993200	-5.34232000	0.82650700
H	1.68630500	-5.97900100	0.33033900
H	0.51815000	-5.90817300	1.65401300
H	1.49342100	-4.48288200	1.23084300
C	-3.89247900	-5.26369700	-0.54492900
H	-4.28184500	-4.74061700	0.33515700
H	-3.98520600	-6.33530000	-0.35255900
H	-4.53240600	-5.01381000	-1.39306100
C	-0.47380100	-2.80803200	-3.31790200
H	-0.14514900	-1.80768700	-3.02158200
H	-1.34359700	-2.70682000	-3.96907500
H	0.33910300	-3.25624100	-3.89547900
C	4.17826200	-0.92028900	-1.07675500
C	4.40987000	0.02736000	-2.08833200
C	5.15092300	1.16661500	-1.78925900
H	5.34334500	1.89285200	-2.57540200
C	5.65091500	1.40198600	-0.50730200
C	5.35331500	0.48391800	0.49407100
H	5.71536900	0.65890300	1.50376400
C	4.62476300	-0.67938000	0.22769200
C	3.84321000	-0.18123700	-3.46814500
H	4.23123100	-1.09347800	-3.92890000
H	4.08333100	0.66076200	-4.11956200
H	2.75490800	-0.28266800	-3.41058500
C	6.49284700	2.62276200	-0.23788200
H	6.75298800	2.70476200	0.81882600
H	5.97253800	3.53861300	-0.53323800
H	7.42437100	2.58222700	-0.80942600
C	4.34579200	-1.67179100	1.32950000
H	3.26836800	-1.81781700	1.46138400
H	4.77455300	-1.32896600	2.27361500
H	4.77488600	-2.65066900	1.09630000
B	1.25880100	-1.26666200	-0.62790000

O	-0.52816900	1.02422100	0.30665700
O	-2.36874300	2.04217100	1.38724100
H	-3.11589500	2.61527500	1.19623300
C	-1.82990400	2.82867600	-0.99736200
C	-0.90525400	3.80003900	-1.41972800
C	-1.16015200	4.57984100	-2.54875600
H	-0.43483600	5.32730800	-2.85479500
C	-2.33199600	4.40346300	-3.27583900
H	-2.52253300	5.00377200	-4.15849500
C	-3.26311300	3.45926900	-2.86202600
H	-4.18426600	3.31933400	-3.41888100
C	-3.02253400	2.68310000	-1.72663500
C	-4.06739400	1.71200900	-1.27047400
C	-3.91920900	0.33810000	-1.50990000
C	-4.91163400	-0.53583600	-1.06081400
H	-4.80034100	-1.59913600	-1.25747900
C	-6.02978900	-0.08674500	-0.36588100
C	-6.15048900	1.28086100	-0.12593400
H	-7.01269300	1.64948900	0.42356800
C	-5.19260200	2.18754200	-0.57487700
C	-2.71655500	-0.20131700	-2.24252400
H	-2.64015000	0.22673100	-3.24644400
H	-2.77946400	-1.28740600	-2.33048500
H	-1.78630000	0.03835700	-1.71962600
C	-7.09036900	-1.04594200	0.10922100
H	-7.97462900	-1.00091000	-0.53338500
H	-7.41373400	-0.80571900	1.12484700
H	-6.72653100	-2.07534500	0.09953100
C	-5.37385600	3.66254000	-0.30648300
H	-4.45110900	4.13417600	0.04429400
H	-6.15289100	3.82581500	0.43989400
H	-5.66154400	4.19723000	-1.21627500
C	0.35598300	4.00975600	-0.64276400
C	0.32591900	4.70718600	0.57313400
C	1.50968900	4.86302100	1.29694700
H	1.48392400	5.41168400	2.23475900
C	2.71358800	4.32902300	0.85150800
C	2.72111900	3.63764200	-0.35819000
H	3.64319900	3.18431000	-0.70941300
C	1.56565200	3.47838300	-1.11814100
C	-0.95931000	5.27890400	1.11999600
H	-1.52673700	5.80101400	0.34585300
H	-0.75383700	5.98054700	1.93040300

H	-1.60164100	4.48687000	1.51614900
C	3.97828900	4.47453300	1.65779600
H	4.52800800	3.53006100	1.68888500
H	3.76016100	4.77975800	2.68378300
H	4.64416300	5.22577300	1.22202500
C	1.63006200	2.73927300	-2.43015900
H	0.76346900	2.09255700	-2.57411700
H	2.52540200	2.11725800	-2.46855800
H	1.65928100	3.44026000	-3.27085300
B	-1.50564200	1.88805500	0.26471700
N	-1.32980200	-1.32071000	2.99714000
N	0.29325500	0.00137900	3.52586900
C	-0.93604400	-0.05045100	3.02148700
C	0.70786300	-1.28530100	3.84152800
C	-0.31491000	-2.12023500	3.49949300
C	1.14699600	1.21027200	3.58713800
H	1.73502900	1.09531100	4.50159700
C	0.29216200	2.46440000	3.68745600
H	-0.24794900	2.64065000	2.75294500
H	0.95042900	3.31847400	3.85573600
H	-0.41896100	2.40663700	4.51498900
C	2.06601400	1.25901100	2.36744700
H	2.58730100	0.31260600	2.21318200
H	2.80865800	2.04706400	2.51005700
H	1.48416600	1.48496900	1.46905100
C	2.03000500	-1.57376000	4.46210000
H	2.84272400	-1.09577400	3.91281200
H	2.21154500	-2.64815200	4.45913200
H	2.06807300	-1.22637500	5.49848100
C	-0.43196800	-3.60147100	3.56432100
H	-1.20109500	-3.91780300	4.27400500
H	0.51716500	-4.03533200	3.87751700
H	-0.68214200	-4.00409900	2.57927600
C	-2.56590900	-1.80516700	2.34016800
H	-2.74764400	-2.79281400	2.76919100
C	-2.31321300	-1.91769400	0.84198200
H	-2.12625800	-0.92218400	0.42880700
H	-3.19191400	-2.34395300	0.35518300
H	-1.44704500	-2.54619500	0.62798900
C	-3.74086600	-0.89075000	2.65603700
H	-3.86617300	-0.75504600	3.73290600
H	-4.65212200	-1.33997600	2.25539000
H	-3.61430100	0.08356200	2.17704400

H	-1.50619100	0.78573200	2.64127900
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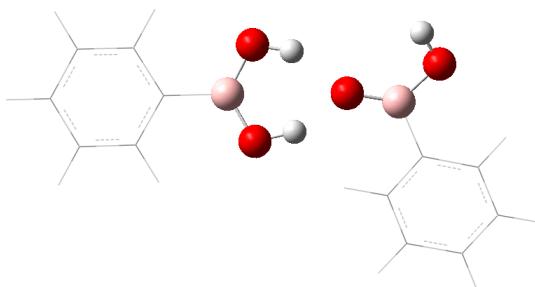
**Note S4.** Coordinates for optimized geometries of **3'**.



O	-0.19264700	-2.13040200	-0.70662500
O	0.19319400	-0.29620600	-2.21997600
H	0.39705300	0.63621200	-2.12882500
C	0.00126400	0.23615700	0.27095400
C	-1.20302500	0.72387100	0.81178000
C	-1.20569000	1.64222400	1.86528800
H	-2.15370000	1.99654600	2.25984300
C	-0.00979100	2.09687900	2.40899900
H	-0.01483500	2.80521800	3.23052200
C	1.19195900	1.62755900	1.89242700
H	2.13501600	1.96630500	2.31176100
C	1.20016300	0.71283300	0.83583600
C	2.52193000	0.23623500	0.31749900
C	2.99249500	-1.04365200	0.66265900
C	4.23501900	-1.45525100	0.18654000
H	4.59742400	-2.44501100	0.45198800
C	5.01955900	-0.64103700	-0.62897700
C	4.53451100	0.61834500	-0.96338600
H	5.12521800	1.26376900	-1.60783300
C	3.29719400	1.06963500	-0.49992600
C	2.15803200	-1.96468600	1.51271300
H	1.81043600	-1.46073100	2.41882600
H	2.73185400	-2.84725300	1.80271400
H	1.27361100	-2.27774800	0.94312200

C	6.34522600	-1.13492100	-1.15002400
H	6.97125300	-1.51750800	-0.33963500
H	6.89410300	-0.33833800	-1.65554300
H	6.20227900	-1.95022000	-1.86490500
C	2.80656500	2.44256300	-0.88921900
H	1.76383600	2.41350900	-1.21479400
H	3.41130300	2.85432400	-1.69914900
H	2.84890000	3.13892700	-0.04675000
C	-2.52512000	0.26279200	0.27777700
C	-3.19510900	1.02147000	-0.68937300
C	-4.45282900	0.60916500	-1.13441800
H	-4.96615100	1.19859600	-1.88923100
C	-5.05258100	-0.54571500	-0.64465400
C	-4.35578500	-1.30468600	0.29513100
H	-4.79761300	-2.22654900	0.66471900
C	-3.09840200	-0.92669900	0.75828900
C	-2.53992000	2.24105400	-1.28614500
H	-2.28177300	2.97985700	-0.52350600
H	-3.19012600	2.71401200	-2.02408800
H	-1.60961800	1.95100800	-1.78271000
C	-6.41407600	-0.98547100	-1.12012900
H	-6.38259300	-2.00721500	-1.50730500
H	-6.78496300	-0.33575200	-1.91485400
H	-7.14199500	-0.96779100	-0.30358100
C	-2.32372400	-1.81064000	1.69685400
H	-1.45982000	-2.20236300	1.14396700
H	-2.93861700	-2.64061300	2.05090300
H	-1.95103900	-1.25483600	2.56136300
B	-0.01220300	-0.88032300	-0.92863500

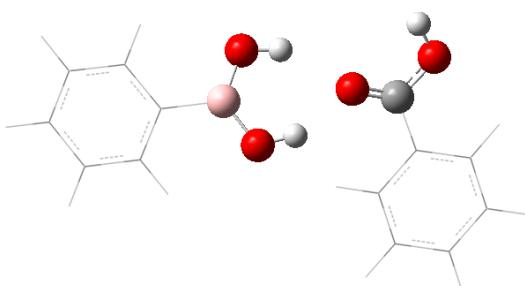
**Note S5.** Coordinates for optimized geometries of **3a**



O	-0.82073100	-0.33464800	0.61806200
H	0.05126900	0.16364600	0.60523400

O	-1.47709700	1.77039300	-0.29999700
H	-0.51056400	1.91546700	-0.16582800
C	-3.26173500	0.00473600	0.02219400
C	-3.61867500	-1.28174300	0.43810700
C	-4.93654900	-1.72275900	0.36826600
H	-5.19540500	-2.72425700	0.69498700
C	-5.92672600	-0.87483600	-0.12137500
H	-6.95550700	-1.21448400	-0.17618600
C	-5.59201600	0.41004300	-0.54058600
H	-6.36128000	1.07289700	-0.92232000
C	-4.27081500	0.84023200	-0.46701400
B	-1.76295400	0.50337100	0.11559300
O	1.06348400	1.38596900	0.30311700
O	3.06840300	2.68928800	0.16333200
H	2.42339400	3.39213000	0.28204000
C	3.32033500	0.19867900	0.00633900
C	4.71567400	0.30315400	0.01899400
C	5.53085800	-0.81616100	-0.12619000
H	6.61093500	-0.71086900	-0.10992300
C	4.95842700	-2.07433100	-0.29464800
H	5.58890500	-2.94976300	-0.40966100
C	3.57201200	-2.20208300	-0.31543100
H	3.11936600	-3.17932300	-0.44848500
C	2.76859400	-1.07582000	-0.16502700
B	2.36255700	1.47201200	0.17178000
H	1.68715700	-1.17467600	-0.18212900
H	5.16117000	1.28503100	0.14593700
H	-4.00342700	1.84109200	-0.79047800
H	-2.84280900	-1.93649800	0.82205200

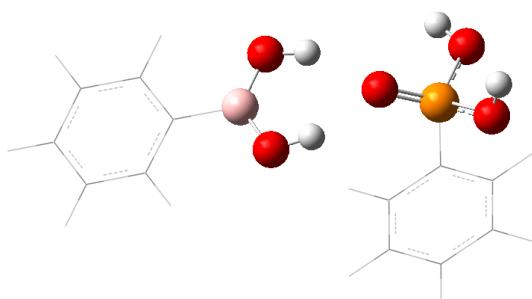
**Note S6.** Coordinates for optimized geometries of **3b**



O	-0.90728100	-0.33671300	0.71492800
H	-0.03253000	0.07069400	0.75981300

O	-1.51541700	1.75774800	-0.28984800
H	-0.57950700	1.96393400	-0.18459700
C	-3.31491800	0.02274800	0.04168200
C	-3.69111100	-1.25363200	0.47283900
C	-5.01021800	-1.68237500	0.37493600
H	-5.28784900	-2.67467200	0.71209700
C	-5.97731300	-0.83332700	-0.15599200
H	-7.00706100	-1.16457800	-0.23155300
C	-5.62178300	0.44092800	-0.58936900
H	-6.37439400	1.10321900	-1.00230400
C	-4.30020800	0.86131800	-0.49003500
B	-1.82927600	0.50684400	0.15974100
O	1.29415700	1.39998400	0.27083500
O	3.20048700	2.53658700	0.16598900
H	2.58176600	3.27092200	0.29339900
C	3.33274500	0.18968200	-0.00803000
C	4.72649200	0.25993500	0.01554900
C	5.47286900	-0.90045500	-0.13529200
H	6.55467100	-0.85248900	-0.11338700
C	4.83127200	-2.12235200	-0.31524400
H	5.41641400	-3.02682000	-0.43436400
C	3.44101300	-2.19008100	-0.34431200
H	2.94413100	-3.14155300	-0.48817400
C	2.68892900	-1.03511300	-0.18966300
H	1.60654400	-1.07717800	-0.21639800
H	5.21624400	1.21529800	0.15460300
H	-4.01948500	1.85394400	-0.82616800
H	-2.93620600	-1.91211100	0.88980300
C	2.50357600	1.40544400	0.15514600

**Note S7.** Coordinates for optimized geometries of **3c**



O	1.22145100	-0.47441400	1.38121100
H	0.35279400	-0.90290900	1.39247300
O	1.43796300	-1.67612400	-0.68084500
H	0.53402400	-1.94621200	-0.46209500
C	3.36932000	-0.23050400	0.07329300
C	3.91428900	0.64811000	1.01570900
C	5.18286500	1.19033400	0.84031800
H	5.59190500	1.87066700	1.57893000
C	5.92854200	0.85823300	-0.28743900
H	6.91788100	1.28012400	-0.42652300
C	5.40378900	-0.01595500	-1.23543700
H	5.98486300	-0.27573500	-2.11333300
C	4.13427300	-0.55341300	-1.05272000
B	1.93419100	-0.83117400	0.26807100
O	-1.11316500	-1.70546200	0.44149800
C	-2.73337100	0.46672900	-0.04425000
C	-3.96835500	0.98410200	-0.44476100
C	-4.12403600	2.35622400	-0.57498900
H	-5.07867500	2.76332900	-0.88526200
C	-3.05281100	3.20658900	-0.30899400
H	-3.17873800	4.27811600	-0.41244600
C	-1.82481900	2.68987800	0.08668600
H	-0.99355900	3.35281300	0.29287700
C	-1.65909300	1.31586000	0.22055100
H	-0.70314100	0.90961900	0.53253600
H	-4.79867500	0.31862200	-0.65368800
H	3.72257000	-1.23519500	-1.78961400
H	3.33139600	0.90516500	1.89414500
P	-2.50505300	-1.29358100	0.11742800
O	-3.61935500	-1.71680300	1.17197200
H	-3.66831400	-2.66630000	1.34581100
O	-3.06569600	-1.99536600	-1.21284800
H	-2.42263300	-2.04428600	-1.93128800

**Table S2.** The NPA charges of **3**.

Atom	No	Natural Charge	Natural Population			
			Core	Valence	Rydberg	Total
O	1	-0.95830	1.99973	6.95168	0.00689	8.95830
H	2	0.53301	0.00000	0.46013	0.00686	0.46699
O	3	-0.96707	1.99973	6.96016	0.00718	8.96707
H	4	0.53005	0.00000	0.46288	0.00707	0.46995
C	5	-0.33755	1.99881	4.32135	0.01740	6.33755
C	6	-0.02234	1.99899	4.00430	0.01905	6.02234
C	7	-0.21265	1.99903	4.19766	0.01596	6.21265
H	8	0.21556	0.00000	0.78196	0.00248	0.78444
C	9	-0.20301	1.99913	4.18790	0.01599	6.20301
H	10	0.21202	0.00000	0.78566	0.00232	0.78798
C	11	-0.21423	1.99904	4.19940	0.01580	6.21423
H	12	0.21457	0.00000	0.78295	0.00248	0.78543
C	13	-0.02793	1.99898	4.00983	0.01912	6.02793
C	14	-0.06494	1.99882	4.04848	0.01765	6.06494
C	15	0.00855	1.99895	3.97851	0.01399	5.99145
C	16	-0.24639	1.99895	4.23140	0.01604	6.24639
H	17	0.20612	0.00000	0.79076	0.00313	0.79388
C	18	-0.01028	1.99901	3.99679	0.01448	6.01028
C	19	-0.23744	1.99896	4.22262	0.01586	6.23744
H	20	0.20928	0.00000	0.78763	0.00308	0.79072
C	21	0.01692	1.99894	3.97032	0.01382	5.98308
C	22	-0.61136	1.99929	4.60251	0.00956	6.61136
H	23	0.22199	0.00000	0.77615	0.00186	0.77801
H	24	0.20309	0.00000	0.79527	0.00164	0.79691
H	25	0.22388	0.00000	0.77370	0.00242	0.77612
C	26	-0.60070	1.99928	4.59157	0.00985	6.60070
H	27	0.20937	0.00000	0.78872	0.00191	0.79063
H	28	0.21436	0.00000	0.78392	0.00172	0.78564
H	29	0.21008	0.00000	0.78836	0.00156	0.78992
C	30	-0.62019	1.99928	4.61137	0.00954	6.62019
H	31	0.24315	0.00000	0.75452	0.00233	0.75685
H	32	0.20639	0.00000	0.79208	0.00152	0.79361
H	33	0.22021	0.00000	0.77798	0.00181	0.77979
C	34	-0.06560	1.99882	4.04913	0.01765	6.06560
C	35	0.02066	1.99895	3.96600	0.01440	5.97934
C	36	-0.23872	1.99895	4.22381	0.01596	6.23872
H	37	0.20965	0.00000	0.78739	0.00296	0.79035
C	38	-0.01335	1.99902	3.99986	0.01448	6.01335

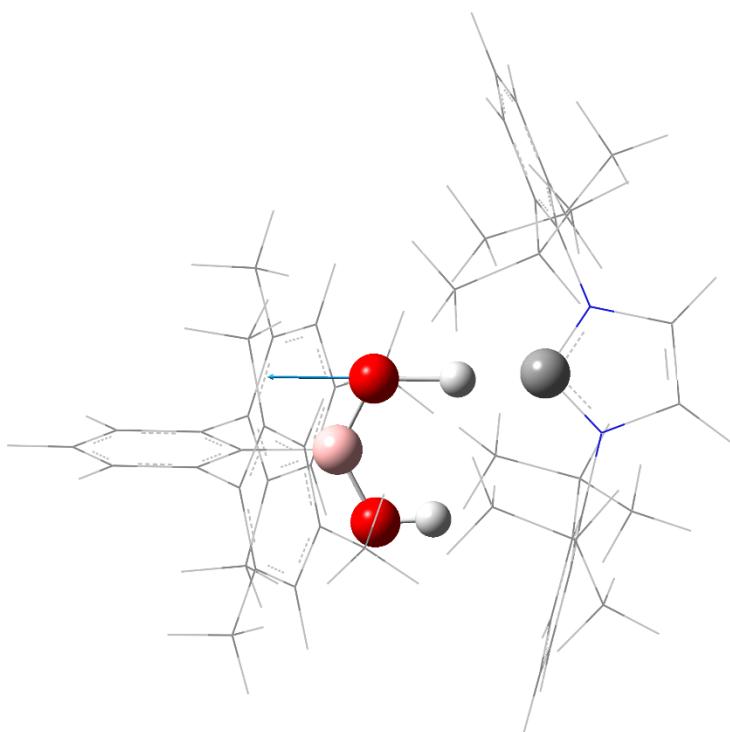
C	39	-0.23853	1.99896	4.22352	0.01606	6.23853
H	40	0.20472	0.00000	0.79195	0.00332	0.79528
C	41	0.00996	1.99894	3.97705	0.01405	5.99004
C	42	-0.61517	1.99929	4.60669	0.00919	6.61517
H	43	0.21753	0.00000	0.78071	0.00176	0.78247
H	44	0.20583	0.00000	0.79270	0.00147	0.79417
H	45	0.23797	0.00000	0.75984	0.00219	0.76203
C	46	-0.60335	1.99928	4.59444	0.00963	6.60335
H	47	0.20708	0.00000	0.79142	0.00150	0.79292
H	48	0.21377	0.00000	0.78440	0.00183	0.78623
H	49	0.21617	0.00000	0.78204	0.00179	0.78383
C	50	-0.62024	1.99929	4.61159	0.00936	6.62024
H	51	0.23113	0.00000	0.76601	0.00286	0.76887
H	52	0.20212	0.00000	0.79610	0.00178	0.79788
H	53	0.22135	0.00000	0.77670	0.00194	0.77865
B	54	1.16466	1.99930	1.80039	0.03565	3.83534
O	55	-1.09734	1.99968	7.09251	0.00516	9.09734
O	56	-0.96936	1.99975	6.96223	0.00737	8.96936
H	57	0.48506	0.00000	0.51009	0.00486	0.51494
C	58	-0.36273	1.99879	4.34627	0.01767	6.36273
C	59	-0.02414	1.99897	4.00574	0.01943	6.02414
C	60	-0.21207	1.99903	4.19731	0.01573	6.21207
H	61	0.21430	0.00000	0.78314	0.00256	0.78570
C	62	-0.20345	1.99914	4.18839	0.01593	6.20345
H	63	0.21087	0.00000	0.78684	0.00229	0.78913
C	64	-0.21490	1.99903	4.19989	0.01598	6.21490
H	65	0.21337	0.00000	0.78407	0.00257	0.78663
C	66	-0.03825	1.99898	4.02009	0.01919	6.03825
C	67	-0.06688	1.99883	4.05023	0.01783	6.06688
C	68	0.01506	1.99894	3.97209	0.01391	5.98494
C	69	-0.23313	1.99896	4.21843	0.01575	6.23313
H	70	0.20664	0.00000	0.78998	0.00338	0.79336
C	71	-0.01335	1.99901	4.00028	0.01407	6.01335
C	72	-0.23328	1.99896	4.21790	0.01642	6.23328
H	73	0.20645	0.00000	0.79019	0.00336	0.79355
C	74	-0.00571	1.99895	3.99234	0.01442	6.00571
C	75	-0.62712	1.99927	4.61789	0.00996	6.62712
H	76	0.22240	0.00000	0.77565	0.00195	0.77760
H	77	0.20882	0.00000	0.78831	0.00287	0.79118
H	78	0.24053	0.00000	0.75614	0.00333	0.75947
C	79	-0.60001	1.99929	4.59106	0.00966	6.60001
H	80	0.21659	0.00000	0.78158	0.00183	0.78341
H	81	0.21030	0.00000	0.78798	0.00171	0.78970
H	82	0.20571	0.00000	0.79252	0.00177	0.79429

C	83	-0.60676	1.99929	4.59794	0.00952	6.60676
H	84	0.21240	0.00000	0.78544	0.00216	0.78760
H	85	0.20804	0.00000	0.79037	0.00158	0.79196
H	86	0.22272	0.00000	0.77550	0.00178	0.77728
C	87	-0.06083	1.99882	4.04438	0.01763	6.06083
C	88	0.00206	1.99894	3.98501	0.01399	5.99794
C	89	-0.24118	1.99896	4.22584	0.01638	6.24118
H	90	0.20256	0.00000	0.79388	0.00356	0.79744
C	91	-0.01375	1.99900	4.00054	0.01421	6.01375
C	92	-0.23026	1.99893	4.21619	0.01514	6.23026
H	93	0.21328	0.00000	0.78150	0.00522	0.78672
C	94	0.02288	1.99893	3.96349	0.01470	5.97712
C	95	-0.60901	1.99929	4.60019	0.00953	6.60901
H	96	0.21858	0.00000	0.77953	0.00190	0.78142
H	97	0.20562	0.00000	0.79280	0.00157	0.79438
H	98	0.21677	0.00000	0.78019	0.00305	0.78323
C	99	-0.60659	1.99928	4.59755	0.00976	6.60659
H	100	0.21230	0.00000	0.78516	0.00255	0.78770
H	101	0.20442	0.00000	0.79383	0.00175	0.79558
H	102	0.21576	0.00000	0.78216	0.00208	0.78424
C	103	-0.60967	1.99927	4.60067	0.00972	6.60967
H	104	0.22690	0.00000	0.77053	0.00257	0.77310
H	105	0.21544	0.00000	0.78103	0.00353	0.78456
H	106	0.20955	0.00000	0.78848	0.00197	0.79045
B	107	1.14338	1.99921	1.81641	0.04100	3.85662
N	108	-0.37124	1.99919	5.35772	0.01433	7.37124
N	109	-0.36965	1.99919	5.35644	0.01402	7.36965
C	110	0.28207	1.99915	3.68978	0.02900	5.71793
C	111	0.17209	1.99893	3.81124	0.01774	5.82791
C	112	0.17891	1.99893	3.80442	0.01774	5.82109
C	113	0.01396	1.99921	3.96974	0.01709	5.98604
H	114	0.20434	0.00000	0.79241	0.00325	0.79566
C	115	-0.61180	1.99931	4.60196	0.01054	6.61180
H	116	0.23110	0.00000	0.76588	0.00302	0.76890
H	117	0.22221	0.00000	0.77614	0.00165	0.77779
H	118	0.20803	0.00000	0.79011	0.00186	0.79197
C	119	-0.62203	1.99928	4.61095	0.01181	6.62203
H	120	0.21252	0.00000	0.78435	0.00312	0.78748
H	121	0.21198	0.00000	0.78541	0.00261	0.78802
H	122	0.25314	0.00000	0.74331	0.00355	0.74686
C	123	-0.62632	1.99927	4.61877	0.00828	6.62632
H	124	0.22964	0.00000	0.76844	0.00192	0.77036
H	125	0.23142	0.00000	0.76698	0.00160	0.76858
H	126	0.22318	0.00000	0.77506	0.00176	0.77682

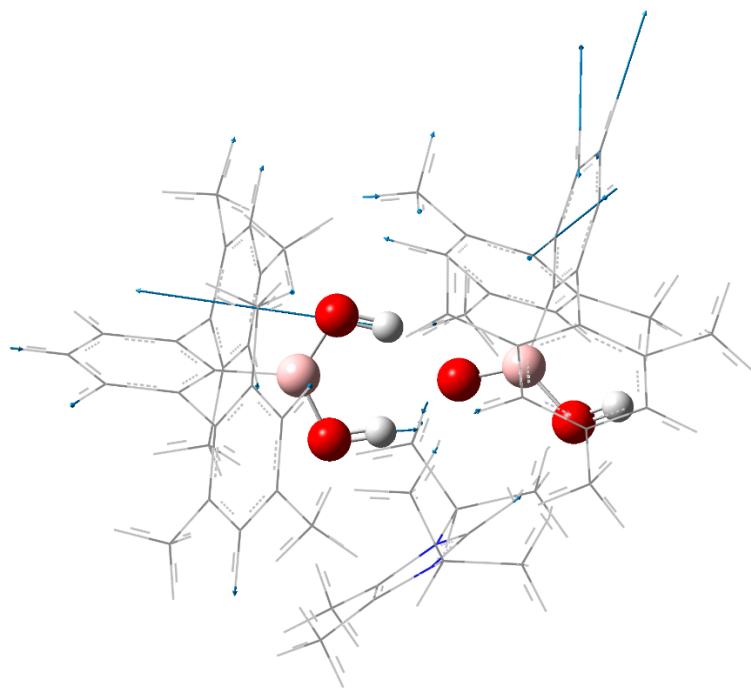
C	127	-0.63154	1.99927	4.62378	0.00849	6.63154
H	128	0.22263	0.00000	0.77553	0.00184	0.77737
H	129	0.23130	0.00000	0.76694	0.00176	0.76870
H	130	0.23453	0.00000	0.76250	0.00296	0.76547
C	131	0.01548	1.99920	3.96848	0.01683	5.98452
H	132	0.20616	0.00000	0.79045	0.00339	0.79384
C	133	-0.62724	1.99928	4.61534	0.01262	6.62724
H	134	0.23431	0.00000	0.76189	0.00380	0.76569
H	135	0.21247	0.00000	0.78440	0.00313	0.78753
H	136	0.23129	0.00000	0.76419	0.00453	0.76871
C	137	-0.61194	1.99930	4.60245	0.01018	6.61194
H	138	0.20641	0.00000	0.79162	0.00198	0.79359
H	139	0.21894	0.00000	0.77885	0.00221	0.78106
H	140	0.23175	0.00000	0.76551	0.00275	0.76825
H	141	0.29114	0.00000	0.70478	0.00407	0.70886

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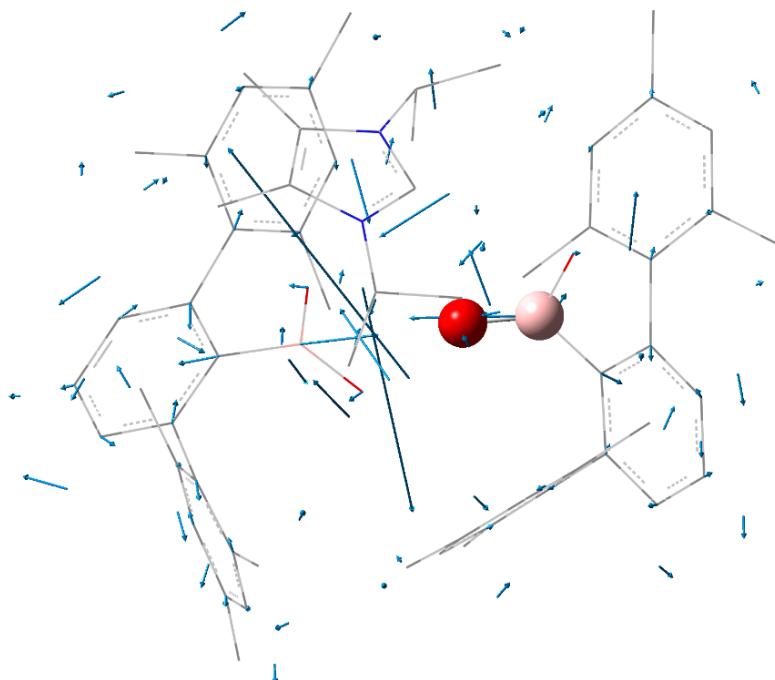
\* Total \*    0.00000    133.94071    348.88384    1.17545    484.00000



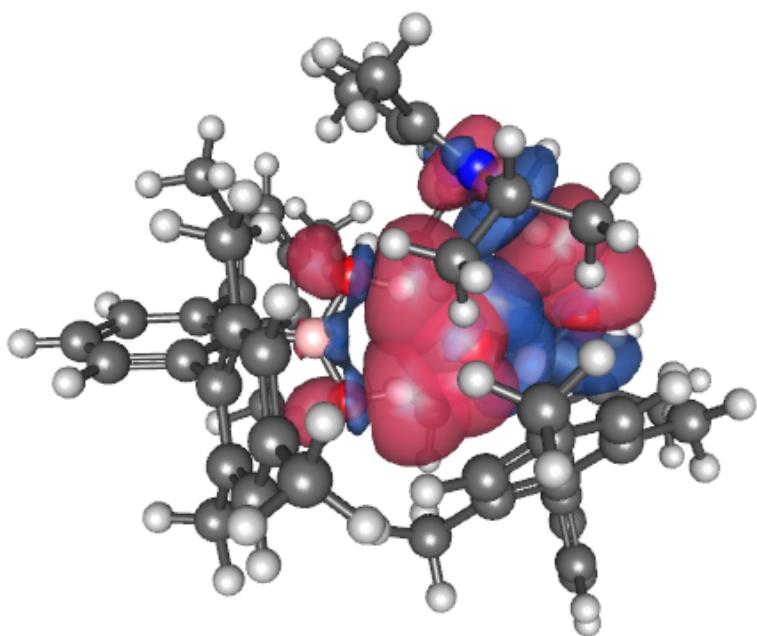
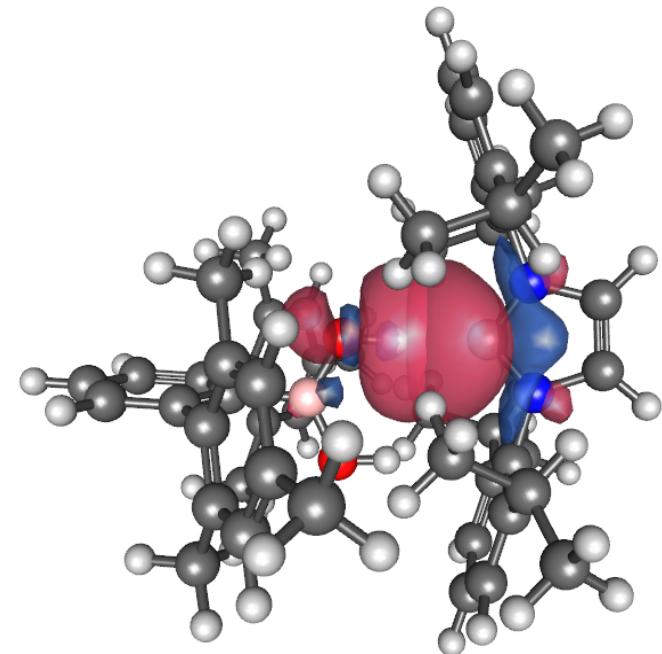
**Figure S18.** Frequency calculation result of **2**. The picture displays that the vibration mode # 289 ( $2935\text{ cm}^{-1}$ ) involves O–H stretching.



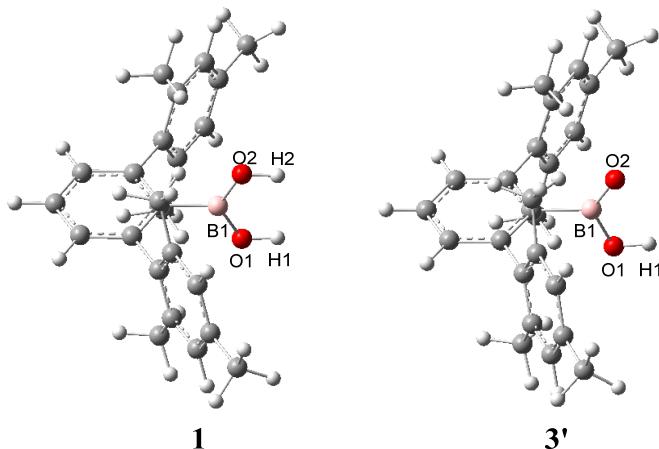
**Figure S19.** Frequency calculation result of **3**. The picture displays that the vibration mode # 410 ( $3171\text{ cm}^{-1}$ ) involves O–H stretching.



**Figure S20.** Frequency calculation result of **3**. The picture displays that the vibration mode # 329 ( $1559\text{ cm}^{-1}$ ) involves B=O stretching.



**Figure S21.** NBO plots showing the hydrogen bond interactions in **2** (top) and **3** (bottom).



**Figure S22.** The optimized structures of complexes **1** and **3'**.

**Table S3.** Selected topological parameters for complexes **1** and **3'**.

Complexes	Bond	Ellipticity of electron density	Bond distances (Å)
<b>1</b>	B1–O2	0.0739	1.366
	B1–O1	0.0741	1.366
	O2–H2	0.0067	0.962
	O1–H1	0.0067	0.962
	B1–O2	0.0131	1.288
<b>3'</b>	B1–O1	0.1020	1.430
	O1–H1	0.0100	0.963

We have compared the ellipticity at the bond critical point (BCP) for the boron oxygen bond before and after deprotonation, as shown in **Figure S22**. However, although the bond distance clearly demonstrates the  $\pi$  character of the B1–O2 bond after deprotonation (1.288 Å), the changes of the ellipticity for the B1–O2 bond and the B1–O1 bond did not show helpful information. This might be due to the ellipticity at the BCP is not a sensitive indicator of  $\pi$  contributions to the bonding, especially for heteroatomic bonds having large charge separation.<sup>S9</sup> Therefore, we did not further discuss the ellipticity in this case.



**Figure S23.** Control experiments on reaction of **1** with IPr.



**Figure S24.** Control experiments on reaction of **1** with  $\text{IPr}_2\text{Me}_2$ .

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