Supporting Information

The anionic oxoborane and thioxoborane molecules supported by a 1,2-bis(imino)acenaphthene ligand

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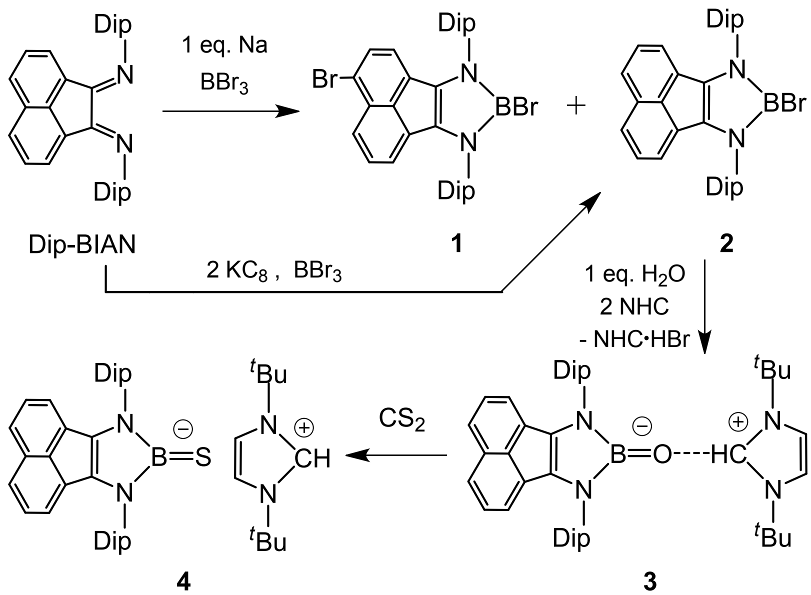
A. General remarks

All manipulations were carried out under inert atmosphere (N_2) using standard Schlenk techniques. Glass wares were heat-dried and cooled down under vacuum prior to use. Hexane was deoxygenated and then refluxed over NaH, another solvents were refluxed over sodium/benzophenone, distilled and deoxidized prior to use. CS_2 was dried by P_2O_5. The solid reactants were weighed in the glove box, and liquid reagents were added with syringe or drip funnel under inert atmosphere. BBr_3 and Na were purchased from Arcos. KC_8[1], Dip-BIAN[2] and NHC[3] were synthesized according to the literature procedures. The solution ^{1}H, $^{13}C\{^{1}H\}$ and $^{11}B\{^{1}H\}$ NMR spectra were recorded on Bruker AVANCE IIIIII 400 and ECZ 400R. Chemical shift of the deuterated solvents in ^{1}H NMR data: C_6D_6, 7.16 ppm; $CDCl_3$, 7.26 ppm. $^{13}C\{^{1}H\}$ NMR: C_6D_6, 128.06 ppm; $CDCl_3$, 77.16 ppm. Elemental analysis (C, H, N) was performed with 0.05 mL tin-capsules on a Perkin-Elmer 2400 CHN elemental analyze. The UV/visible spectrum was recorded on a SP-756P spectrometer. IR spectra were recorded in KBr pellets on a Bruker TENSOR27 spectrometer and the flaky sample was prepared in the glove box.

The single-crystal X-ray diffractions were performed on Agilent Technologies SuperNova Single Crystal Diffractometer (compound **1**) and Bruker D8 Quest detector (compound **3**) at 150 K with a Mo-Kα X-ray source (λ = 0.71073 Å). Compound **4** was measured on a Bruker D8 VENTURE PHOTON Ⅱ detector at 150 K with a Ga-target Liquid X-ray source (λ = 1.34139 Å). All structures were solved by direct methods and refined by full matrix least squares on F^2 with the SHELXL-2014 or Olex2 program. All thermal displacement parameters were refined anisotropically for non-hydrogen atoms and isotropically for H atoms. The graphical representation of the molecular structures was carried out using Ortep3. Crystal data, details of data collections and refinement can be showed in Table S1-S3.

B. **Chemical equations**



Scheme S1 Synthesis of compounds **1-4.** NHC = :C(^{t}Bu-NCH)$_2$.

C. Experimental Sections

Synthesis of compound 1

To the solution of Dip-BIAN (612 mg, 1.22 mmol) in toluene (20 mL) at -40 °C were added BBr_3 (306 mg, 1.22 mmol) and sodium metal (28.1 mg, 1.22 mmol) under vigorous stirring, then the mixture was stirred at room temperature overnight. Hereafter, the mixture was stirred at 80 °C till the sodium dissolved completely. The solvent was removed under reduced pressure and the residue was extracted with hexane (20 mL), the precipitated NaBr was filtered off. Compound **1** crystallized as red crystals (452 mg, 0.675 mmol, 54%) by cooling the solution at 0 °C for 3 days. The crystal was measured by the single-crystal X-ray diffraction analysis. Additionally, compound **2** has also been found as one of the side products in the observation of ^{1}H NMR of the hexane solution.

M.p. 288-290 °C. **^{1}H NMR** (400 MHz, C_6D_6, 298 K): δ (ppm) = 1.09 (d, 12H, $^{3}J_{HH}$ = 7 Hz, CH(C*H*$_3$)$_2$), 1.35 (m, 12H, $^{3}J_{HH}$ = 7 Hz, CH(C*H*$_3$)$_2$), 3.43 (m, 4H, $^{3}J_{HH}$ = 7 Hz, C*H*(CH$_3$)$_2$), 6.30 (d, 1H, $^{3}J_{HH}$ = 7 Hz, *o-H*-acenaphthene), 6.57 (d, 1H, $^{3}J_{HH}$ = 7 Hz, *o-H*-acenaphthene), 6.73 (d, 1H, $^{3}J_{HH}$ = 7 Hz, *m-H*-acenaphthene), 6.90 (t, 1H, $^{3}J_{HH}$ = 7 Hz, *m-H*-acenaphthene), 7.24 (m, 4H, $^{3}J_{HH}$ = 7 Hz, *m-H*-Ar), 7.31 (m, 2H, $^{3}J_{HH}$ = 7 Hz, *p-H*-Ar), 7.57 (d, 1H, $^{3}J_{HH}$ = 8 Hz, *p-H*-acenaphthene). **^{13}C{^{1}H} NMR** (100 MHz, C_6D_6, 298 K): δ (ppm) = 24.0 (s, CH(*C*H$_3$)$_2$), 24.2 (s, CH(*C*H$_3$)$_2$), 29.2 (s, *C*H(CH$_3$)$_2$), 119.0 (s, *p-C*H-acenaphthene), 124.2 (s, *m-C*H-Ar), 125.6 (s, *p-C*H-acenaphthene), 126.7 (s, *m-C*H-acenaphthene), 127.5 (s, *m-C*H-acenaphthene), 129.0 (s, *p-C*H-Ar), 130.2 (s, *o-C*-acenaphthene), 130.8 (s, *i-C*-acenaphthene), 134.4 (s, *C*$_2$N$_2$), 135.5 (s, *i-C*-Ar), 146.3 (s, *o-C*-Ar), 146.4 (s, *o-C*-Ar). **^{11}B{^{1}H} NMR** (128.3 MHz, C_6D_6, 298 K): δ (ppm) = 22 (s). Anal. Calcd for $C_{36}H_{39}BBr_2N_2$: C, 64.51; H, 5.86; N, 4.18. Found: C, 65.03; H, 5.90; N, 4.34%.

Synthesis of compound 2

To the solution of Dip-BIAN (1.01 g, 2.01 mmol) in toluene (40 mL) was added KC_8 (761 mg, 5.63 mmol) under vigorous stirring. After stirring for 12 h, a solution of BBr_3 (604 mg, 2.41 mmol) in hexane was added to the flask at -40 °C and stirred at room temperature overnight. Removal of the solvent under reduced pressure afforded red solid. Toluene (20 mL) was added to the residue, and the resulting suspension was filtered. This operation was repeated for three times. Subsequently, the clear filtrate was concentrated. Compound **2** crystallized as red crystals (999 mg, 1.69 mmol, 84%) by cooling the solution at -20 °C for 2 days. All spectroscopic data matches those of the reported compound.[4,5]

Synthesis of compound 3

To the solution of **2** (600 mg, 1.01 mmol) in toluene (25 mL) was dropped a solution of water (18.2 mg, 1.01 mmol) and NHC (457 mg, 2.54 mmol) in toluene (15 mL) under vigorous stirring. After stirring for 12 h, the color of the reaction mixture changed from red to blue. Volatiles were removed under reduced pressure and the green solid crude was washed with hexane (20 mL). Toluene (40 mL) was added to the residue, the resulting suspension was filtered, and the clear filtrate was concentrated. The product **3** crystallized as blue crystals (459 mg, 0.648 mmol, 64%) by cooling the solution at -20 °C for 24 h.

M.p. >188 °C decomp. **^{1}H NMR** (400 MHz, C_6D_6, 298 K): δ (ppm) = 1.04 (s, 18H, C(CH_3)$_3$), 1.37 (d, 12H, $^3J_{HH}$ = 7 Hz, CH(CH_3)$_2$), 1.51 (d, 12H, $^3J_{HH}$ = 7 Hz, CH(CH_3)$_2$), 4.16 (sept, 4H, $^3J_{HH}$ = 7 Hz, C*H*(CH$_3$)$_2$), 5.84 (s, 2H, NC*H*=C*H*N), 6.72 (d, 2H, $^3J_{HH}$ = 7 Hz, *o*-*H*-acenaphthene), 6.95 (t, 2H, $^3J_{HH}$ = 8 Hz, *m*-*H*-acenaphthene), 7.10 (d, 2H, $^3J_{HH}$ = 8 Hz, *p*-*H*-acenaphthene), 7.39 (m, 6H, *H*-Ar), 13.80 (s, 1H, N$_2$C*H*). **^{13}C{^{1}H} NMR** (100 MHz, C_6D_6, 298 K): δ (ppm) = 24.0 (s, CH(*C*H$_3$)$_2$), 24.6 (s, CH(*C*H$_3$)$_2$), 28.9 (s, C(*C*H$_3$)$_3$), 29.7 (s, *C*H(CH$_3$)$_2$), 59.5 (s, *C*(CH$_3$)$_3$), 115.7 (s, N*C*HN), 116.3 (s, *p*-*C*H-acenaphthene), 122.9 (s, imidazolium *C*H=*C*H), 123.5 (s, *m*-*C*H-Ar), 125.4 (s, *m*-*C*H-acenaphthene), 127.3 (s, *p*-*C*H-Ar), 129.6 (s, *o*-*C*-acenaphthene), 131.6 (s, i-*C*-acenaphthene), 134.7 (s, C_2N_2), 142.5 (s, *i*-*C*-Ar), 147.8 (s, *o*-*C*-Ar). **^{11}B{^{1}H} NMR** (128.3MHz, C_6D_6, 298K): δ = 21 (s). Anal. Calcd for $C_{47}H_{61}BON_4$: C, 79.64; H, 8.67; N, 7.90. Found: C, 81.04; H, 8.77; N, 7.16%. There was a slight inaccuracy in the EA data, possibly due to the small amount of toluene in the sample.

Synthesis of compound 4

To the solution of **3** (559 mg, 0.789 mmol) in toluene (25 mL) was added anhydrous CS_2 (900 mg, 11.8 mmol) under vigorous stirring. After stirring for 12 h, volatiles were removed under reduced pressure and the blue solid crude was washed with hexane (20 mL). Toluene (40 mL) was added to the residue, the resulting suspension was filtered, and the clear filtrate was concentrated. The compound **4** crystallized as blue crystals by cooling the solution at -20 °C for 1 day, and the crystals were suitable for X-ray diffraction measurement. The supernate was further concentrated and crystallized at -20 °C, 422 mg **4** (0.582 mmol, 74%) as the combined yield.

M.p. >236 °C decomp. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): *δ* (ppm) = 1.06 (d, 12H, $^3J_{HH}$ = 7 Hz, $CH(CH_3)_2$), 1.29 (d, 12H, $^3J_{HH}$ = 7 Hz, $CH(CH_3)_2$), 1.55 (s, 18H, $C(CH_3)_3$), 3.62 (sept, 4H, $^3J_{HH}$ = 7 Hz, $CH(CH_3)_2$), 6.17 (d, 2H, $^3J_{HH}$ = 7 Hz, NC*H*=C*H*N), 6.96 (t, 2H, $^3J_{HH}$ = 8 Hz, *m*-*H*-acenaphthene), 7.14 (d, 2H, $^3J_{HH}$ = 8 Hz, *p*-*H*-acenaphthene), 7.19 (d, 2H, $^3J_{HH}$ = 7 Hz, *o*-*H*-acenaphthene), 7.22 (m, 6H, *H*-Ar), 7.24 (s, 1H, N_2CH). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$, 298 K): *δ* (ppm) = 23.8 (s, $CH(CH_3)_2$), 24.5 (s, $CH(CH_3)_2$), 28.6 (s, $CH(CH_3)_2$), 30.2 (s, $CH(CH_3)_3$), 60.9 (s, $C(CH_3)_3$), 116.4 (s, N*C*HN), 118.9 (s, *p*-*C*H--acenaphthene), 122.7 (s, imidazolium *C*H=*C*H), 123.3 (s, *m*-*C*H-Ar), 125.8 (s, *m*-*C*H-acenaphthene), 127.1 (s, *p*-*C*H-Ar), 129.1 (s, *o*-*C*-acenaphthene), 123.6 (s, *i*-*C*-acenaphthene), 133.8 (s, C_2N_2), 141.0 (s, *i*-*C*-Ar), 147.2 (s, *o*-*C*-Ar). **^{11}B{^{1}H} NMR** (128.3 MHz, $CDCl_3$, 298 K): δ = 36 (s). Anal. Calcd for $C_{47}H_{61}BSN_4$: C, 77.88; H, 8.48; N, 7.73. Found: C, 78.22; H, 8.41; N, 7.52%.

D. Crystal and structure refinement data for compounds 1, 3 and 4

Crystallographic data for compound 1

Identification code	Compound 1
Empirical formula	$C_{36}H_{39}BBr_2N_2$
Formula weight	670.32
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	14.0533(6)
b/Å	13.0296(9)
c/Å	18.3019(12)
α/°	90
β/°	99.056(5)

γ/°	90
Volume/Å^3	3309.5(3)
Z	4
ρ_{calc}g/cm^3	1.345
μ/mm^{-1}	2.476
F(000)	1376.0
Crystal size/mm^3	0.14 × 0.13 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.872 to 50.052
Index ranges	-16 ≤ h ≤ 15, -15 ≤ k ≤ 10, -20 ≤ l ≤ 21
Reflections collected	14690
Independent reflections	5818 [R_{int} = 0.1113, R_{sigma} = 0.1900]
Data/restraints/parameters	5831/883/388
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0923, wR_2 = 0.2072
Final R indexes [all data]	R_1 = 0.1955, wR_2 = 0.2646
Largest diff. peak/hole / e Å^{-3}	0.54/-0.89

Table S1. Bond lengths [Å] and angles [°] for compound **1**

Br(1)-B(1)	1.904(11)	C(13)-N(2)-B(1)	129.6(7)
Br(2)-C(6)	1.908(10)	C(2)-N(2)-C(13)	124.0(7)
Br(2')-C(8)	1.787(15)	C(2)-N(2)-B(1)	106.2(7)
N(2)-C(13)	1.443(10)	C(1)-N(1)-C(25)	121.6(6)
N(2)-C(2)	1.403(10)	C(1)-N(1)-B(1)	107.7(7)
N(2)-B(1)	1.437(13)	B(1)-N(1)-C(25)	130.5(8)
N(1)-C(25)	1.467(11)	C(30)-C(25)-N(1)	120.1(8)
N(1)-C(1)	1.383(10)	C(30)-C(25)-C(26)	122.4(9)
N(1)-B(1)	1.410(11)	C(26)-C(25)-N(1)	117.5(8)
C(25)-C(30)	1.389(12)	C(12)-C(11)-C(1)	105.0(7)
C(25)-C(26)	1.428(11)	C(10)-C(11)-C(12)	118.6(8)
C(11)-C(12)	1.416(12)	C(10)-C(11)-C(1)	136.5(9)
C(11)-C(1)	1.462(11)	C(25)-C(30)-C(31)	121.1(9)
C(11)-C(10)	1.375(11)	C(29)-C(30)-C(25)	117.5(9)
C(30)-C(29)	1.374(13)	C(29)-C(30)-C(31)	121.3(9)
C(30)-C(31)	1.513(13)	C(11)-C(12)-C(3)	111.3(8)
C(12)-C(7)	1.364(12)	C(7)-C(12)-C(11)	125.0(9)
C(12)-C(3)	1.436(12)	C(7)-C(12)-C(3)	123.7(9)
C(1)-C(2)	1.359(11)	N(1)-C(1)-C(11)	141.2(8)
C(13)-C(14)	1.402(12)	C(2)-C(1)-N(1)	109.7(7)
C(13)-C(18)	1.383(17)	C(2)-C(1)-C(11)	109.1(8)

C(14)-C(22)	1.508(13)	C(14)-C(13)-N(2)	119.7(8)
C(14)-C(15)	1.362(13)	C(18)-C(13)-N(2)	118.3(8)
C(2)-C(3)	1.452(13)	C(18)-C(13)-C(14)	122.0(9)
C(29)-C(28)	1.402(13)	C(13)-C(14)-C(22)	121.6(8)
C(26)-C(34)	1.508(12)	C(15)-C(14)-C(13)	117.1(9)
C(26)-C(27)	1.402(12)	C(15)-C(14)-C(22)	121.3(9)
C(7)-C(6)	1.416(13)	N(2)-C(2)-C(3)	139.8(8)
C(7)-C(8)	1.408(12)	C(1)-C(2)-N(2)	109.3(8)
C(34)-C(35)	1.526(12)	C(1)-C(2)-C(3)	110.8(8)
C(34)-C(36)	1.541(12)	C(30)-C(29)-C(28)	122.6(10)
C(3)-C(4)	1.369(13)	C(25)-C(26)-C(34)	121.8(8)
C(28)-C(27)	1.373(13)	C(25)-C(26)-C(27)	116.8(9)
C(22)-C(23)	1.534(13)	C(27)-C(26)-C(34)	121.3(8)
C(22)-C(24)	1.545(14)	C(12)-C(7)-C(6)	116.5(9)
C(10)-C(9)	1.431(12)	C(12)-C(7)-C(8)	116.3(9)
C(6)-C(5)	1.380(13)	C(8)-C(7)-C(6)	127.1(9)
C(8)-C(9)	1.391(14)	C(26)-C(34)-C(35)	110.7(8)
C(4)-C(5)	1.398(13)	C(26)-C(34)-C(36)	113.7(8)
C(31)-C(33)	1.551(15)	C(35)-C(34)-C(36)	110.2(7)
C(31)-C(32)	1.519(13)	C(12)-C(3)-C(2)	103.9(8)
C(18)-C(19)	1.543(14)	C(4)-C(3)-C(12)	117.7(9)
C(18)-C(17)	1.404(13)	C(4)-C(3)-C(2)	138.4(9)
C(15)-C(16)	1.349(14)	C(27)-C(28)-C(29)	118.9(9)
C(19)-C(20)	1.472(17)	C(14)-C(22)-C(23)	111.2(9)
C(19)-C(21)	1.488(15)	C(14)-C(22)-C(24)	110.5(9)
C(16)-C(17)	1.364(14)	C(24)-C(22)-C(23)	112.4(9)
C(13)-C(18)-C(17)	117.7(10)	C(11)-C(10)-C(9)	117.9(9)
C(17)-C(18)-C(19)	120.2(10)	C(28)-C(27)-C(26)	121.8(9)
C(14)-C(15)-C(16)	120.2(10)	C(7)-C(6)-Br(2)	121.4(7)
C(6)-C(5)-C(4)	121.0(10)	C(5)-C(6)-Br(2)	117.6(8)
N(2)-B(1)-Br(1)	125.5(6)	C(5)-C(6)-C(7)	121.0(9)
N(1)-B(1)-Br(1)	127.4(8)	C(9)-C(8)-C(7)	120.6(9)
N(1)-B(1)-N(2)	107.1(8)	C(3)-C(4)-C(5)	120.1(9)
C(20)-C(19)-C(18)	114.4(11)	C(30)-C(31)-C(33)	111.9(9)
C(20)-C(19)-C(21)	114.4(11)	C(32)-C(31)-C(30)	111.3(8)
C(21)-C(19)-C(18)	111.0(11)	C(32)-C(31)-C(33)	110.9(9)
C(15)-C(16)-C(17)	121.7(10)	C(8)-C(9)-C(10)	121.6(9)
C(16)-C(17)-C(18)	119.3(10)	C(13)-C(18)-C(19)	122.0(9)
C(9)-C(8)-Br(2')	116.6(11)	C(7)-C(8)-Br(2')	122.5(11)

Crystallographic data for compound 3

Identification code	Compound 3
Empirical formula	$C_{155}H_{199}B_3N_{12}O_3$
Formula weight	2310.68
Temperature/K	153.15
Crystal system	triclinic
Space group	P-1
a/Å	19.0151(12)
b/Å	19.0592(13)
c/Å	24.0200(16)
α/°	82.716(3)
β/°	68.186(3)
γ/°	60.437(3)
Volume/Å^3	7012.4(8)
Z	2
ρ_{calc}g/cm^3	1.094
μ/mm^{-1}	0.490
F(000)	2504.0
Crystal size/mm^3	0.14 × 0.13 × 0.12
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	5.628 to 136.618
Index ranges	-20 ≤ h ≤ 22, -22 ≤ k ≤ 22, -28 ≤ l ≤ 28
Reflections collected	124361
Independent reflections	25511 [R_{int} = 0.0747, R_{sigma} = 0.0496]
Data/restraints/parameters	25511/48/1693
Goodness-of-fit on F^2	1.093
Final R indexes [I>=2σ (I)]	R_1 = 0.0689, wR_2 = 0.1942
Final R indexes [all data]	R_1 = 0.0831, wR_2 = 0.2073
Largest diff. peak/hole / e Å^{-3}	0.94/-0.62

Table S2. Bond lengths [Å] and angles [°] for compound **3**

N(1)-C(1)	1.378(3)	C(1)-N(1)-C(25)	124.44(16)
N(1)-C(25)	1.423(3)	C(1)-N(1)-B(1)	108.79(16)
N(1)-B(1)	1.505(3)	C(25)-N(1)-B(1)	126.76(17)
N(2)-C(2)	1.386(2)	C(2)-N(2)-C(13)	124.26(16)
N(2)-C(13)	1.429(2)	C(2)-N(2)-B(1)	108.73(15)
N(2)-B(1)	1.499(3)	C(13)-N(2)-B(1)	126.33(16)
N(3)-C(37)	1.332(3)	C(37)-N(3)-C(39)	108.2(2)

N(3)-C(39)	1.380(3)	C(37)-N(3)-C(40)	125.9(2)
N(3)-C(40)	1.492(4)	C(39)-N(3)-C(40)	125.9(2)
N(4)-C(37)	1.332(3)	C(37)-N(4)-C(38)	108.4(2)
N(4)-C(38)	1.385(3)	C(37)-N(4)-C(44)	124.27(18)
N(4)-C(44)	1.499(3)	C(38)-N(4)-C(44)	127.19(19)
N(5)-C(51)	1.380(2)	C(51)-N(5)-C(75)	123.14(15)
N(5)-C(75)	1.422(2)	C(51)-N(5)-B(2)	108.74(14)
N(5)-B(2)	1.503(3)	C(75)-N(5)-B(2)	128.06(15)
N(6)-C(52)	1.379(2)	C(52)-N(6)-C(63)	123.19(15)
N(6)-C(63)	1.426(2)	C(52)-N(6)-B(2)	108.75(14)
N(6)-B(2)	1.510(2)	C(63)-N(6)-B(2)	127.91(15)
N(7)-C(89)	1.337(3)	C(89)-N(7)-C(91)	107.8(2)
N(7)-C(91)	1.374(3)	C(89)-N(7)-C(96)	125.45(18)
N(7)-C(96)	1.490(3)	C(91)-N(7)-C(96)	126.7(2)
N(8)-C(89)	1.322(3)	C(89)-N(8)-C(90)	107.8(2)
N(8)-C(90)	1.378(4)	C(89)-N(8)-C(92)	124.6(2)
N(8)-C(92)	1.501(3)	C(90)-N(8)-C(92)	127.6(2)
N(9)-C(104)	1.377(3)	C(104)-N(9)-C(115)	123.86(15)
N(9)-C(115)	1.427(2)	C(104)-N(9)-B(3)	108.59(15)
N(9)-B(3)	1.498(3)	C(115)-N(9)-B(3)	127.37(16)
N(10)-C(103)	1.382(3)	C(103)-N(10)-C(127)	124.18(16)
N(10)-C(127)	1.427(2)	C(103)-N(10)-B(3)	108.72(15)
N(10)-B(3)	1.504(3)	C(127)-N(10)-B(3)	127.03(16)
N(11)-C(139)	1.332(3)	C(139)-N(11)-C(141)	107.8(2)
N(11)-C(141)	1.376(3)	C(139)-N(11)-C(142)	123.35(18)
N(11)-C(142)	1.500(3)	C(141)-N(11)-C(142)	128.8(2)
N(12)-C(139)	1.332(3)	C(139)-N(12)-C(140)	107.4(2)
N(12)-C(140)	1.380(4)	C(139)-N(12)-C(146)	125.1(2)
N(12)-C(146)	1.496(3)	C(140)-N(12)-C(146)	127.5(2)
O(1)-B(1)	1.293(3)	N(1)-C(1)-C(11)	139.79(18)
O(2)-B(2)	1.291(3)	C(2)-C(1)-N(1)	110.46(16)
O(3)-B(3)	1.288(3)	C(2)-C(1)-C(11)	109.74(18)
C(1)-C(2)	1.367(3)	N(2)-C(2)-C(3)	139.60(17)
C(1)-C(11)	1.453(3)	C(1)-C(2)-N(2)	110.30(17)
C(2)-C(3)	1.451(3)	C(1)-C(2)-C(3)	110.10(17)
C(3)-C(4)	1.366(3)	C(4)-C(3)-C(2)	137.93(19)
C(3)-C(12)	1.430(3)	C(4)-C(3)-C(12)	117.73(19)
C(4)-C(5)	1.427(3)	C(12)-C(3)-C(2)	104.33(17)
C(5)-C(6)	1.369(4)	C(3)-C(4)-C(5)	118.8(2)
C(6)-C(7)	1.419(4)	C(6)-C(5)-C(4)	122.8(2)
C(7)-C(8)	1.423(3)	C(5)-C(6)-C(7)	120.0(2)

C(7)-C(12)	1.389(3)	C(6)-C(7)-C(8)	127.1(2)
C(8)-C(9)	1.363(4)	C(12)-C(7)-C(6)	116.3(2)
C(9)-C(10)	1.426(4)	C(12)-C(7)-C(8)	116.6(2)
C(10)-C(11)	1.381(3)	C(9)-C(8)-C(7)	119.8(2)
C(11)-C(12)	1.425(3)	C(8)-C(9)-C(10)	123.1(2)
C(13)-C(14)	1.400(3)	C(11)-C(10)-C(9)	118.5(2)
C(13)-C(18)	1.403(3)	C(10)-C(11)-C(1)	137.8(2)
C(14)-C(15)	1.395(3)	C(10)-C(11)-C(12)	117.6(2)
C(14)-C(23)	1.517(3)	C(12)-C(11)-C(1)	104.58(17)
C(15)-C(16)	1.378(3)	C(7)-C(12)-C(3)	124.4(2)
C(16)-C(17)	1.379(3)	C(7)-C(12)-C(11)	124.4(2)
C(17)-C(18)	1.399(3)	C(11)-C(12)-C(3)	111.25(18)
C(18)-C(19)	1.518(3)	C(14)-C(13)-N(2)	118.83(17)
C(19)-C(20)	1.523(3)	C(14)-C(13)-C(18)	121.31(17)
C(19)-C(21)	1.529(3)	C(18)-C(13)-N(2)	119.84(17)
C(22)-C(23)	1.541(4)	C(13)-C(14)-C(23)	121.75(17)
C(23)-C(24)	1.515(4)	C(15)-C(14)-C(13)	118.22(18)
C(25)-C(26)	1.397(3)	C(15)-C(14)-C(23)	120.03(19)
C(25)-C(30)	1.396(3)	C(16)-C(15)-C(14)	121.1(2)
C(26)-C(27)	1.389(3)	C(15)-C(16)-C(17)	119.99(19)
C(26)-C(34)	1.522(3)	C(16)-C(17)-C(18)	121.14(19)
C(27)-C(28)	1.381(4)	C(13)-C(18)-C(19)	120.34(17)
C(28)-C(29)	1.376(4)	C(17)-C(18)-C(13)	118.01(19)
C(29)-C(30)	1.393(4)	C(17)-C(18)-C(19)	121.64(18)
C(30)-C(31)	1.525(5)	C(18)-C(19)-C(20)	110.71(18)
C(31)-C(32)	1.481(7)	C(18)-C(19)-C(21)	113.42(18)
C(31)-C(33)	1.429(8)	C(20)-C(19)-C(21)	110.3(2)
C(34)-C(35)	1.517(4)	C(14)-C(23)-C(22)	111.76(19)
C(34)-C(36)	1.528(4)	C(24)-C(23)-C(14)	111.5(2)
C(38)-C(39)	1.331(4)	C(24)-C(23)-C(22)	109.9(2)
C(40)-C(41)	1.503(4)	C(26)-C(25)-N(1)	120.46(18)
C(40)-C(42)	1.472(8)	C(30)-C(25)-N(1)	118.78(19)
C(40)-C(43)	1.530(8)	C(30)-C(25)-C(26)	120.7(2)
C(44)-C(45)	1.616(6)	C(25)-C(26)-C(34)	120.55(18)
C(44)-C(47)	1.481(6)	C(27)-C(26)-C(25)	119.0(2)
C(44)-C(49)	1.477(8)	C(27)-C(26)-C(34)	120.5(2)
C(44)-C(46)	1.285(12)	C(28)-C(27)-C(26)	120.8(2)
C(44)-C(48)	1.817(17)	C(29)-C(28)-C(27)	119.6(2)
C(44)-C(50)	1.49(3)	C(28)-C(29)-C(30)	121.4(2)
C(51)-C(52)	1.367(2)	C(25)-C(30)-C(31)	120.2(2)
C(51)-C(61)	1.455(3)	C(29)-C(30)-C(25)	118.4(2)

C(52)-C(53)	1.460(3)	C(29)-C(30)-C(31)	121.3(2)
C(53)-C(54)	1.375(3)	C(32)-C(31)-C(30)	112.8(3)
C(53)-C(62)	1.426(3)	C(33)-C(31)-C(30)	113.4(5)
C(54)-C(55)	1.428(3)	C(33)-C(31)-C(32)	112.2(4)
C(55)-C(56)	1.364(4)	C(26)-C(34)-C(36)	111.8(2)
C(56)-C(57)	1.432(3)	C(35)-C(34)-C(26)	111.1(2)
C(57)-C(58)	1.424(3)	C(35)-C(34)-C(36)	111.0(2)
C(57)-C(62)	1.386(3)	N(4)-C(37)-N(3)	108.42(19)
C(58)-C(59)	1.373(3)	C(39)-C(38)-N(4)	107.1(2)
C(59)-C(60)	1.425(3)	C(38)-C(39)-N(3)	107.8(2)
C(60)-C(61)	1.372(3)	N(3)-C(40)-C(41)	110.1(2)
C(61)-C(62)	1.431(3)	N(3)-C(40)-C(43)	106.1(3)
C(63)-C(64)	1.399(3)	C(41)-C(40)-C(43)	108.4(4)
C(63)-C(68)	1.404(3)	C(42)-C(40)-N(3)	108.0(4)
C(64)-C(65)	1.396(3)	C(42)-C(40)-C(41)	110.2(4)
C(64)-C(72)	1.519(3)	C(42)-C(40)-C(43)	113.9(6)
C(65)-C(66)	1.370(4)	N(4)-C(44)-C(45)	104.6(3)
C(66)-C(67)	1.377(3)	N(4)-C(44)-C(48)	93.5(5)
C(67)-C(68)	1.394(3)	C(47)-C(44)-N(4)	111.8(3)
C(68)-C(69)	1.518(3)	C(47)-C(44)-C(45)	109.0(4)
C(69)-C(70)	1.525(3)	C(49)-C(44)-N(4)	111.8(4)
C(69)-C(71)	1.521(3)	C(49)-C(44)-C(45)	105.8(6)
C(72)-C(73)	1.517(5)	C(49)-C(44)-C(47)	113.3(6)
C(72)-C(74)	1.535(4)	C(46)-C(44)-N(4)	113.9(5)
C(75)-C(76)	1.399(3)	C(46)-C(44)-C(48)	105.7(16)
C(75)-C(80)	1.402(3)	C(46)-C(44)-C(50)	134.0(13)
C(76)-C(77)	1.390(3)	C(50)-C(44)-N(4)	107.0(10)
C(76)-C(81)	1.524(4)	C(50)-C(44)-C(48)	92(2)
C(77)-C(78)	1.389(4)	N(5)-C(51)-C(61)	139.10(16)
C(78)-C(79)	1.368(4)	C(52)-C(51)-N(5)	110.61(16)
C(79)-C(80)	1.391(3)	C(52)-C(51)-C(61)	110.27(16)
C(80)-C(84)	1.506(3)	N(6)-C(52)-C(53)	139.92(16)
C(81)-C(82)	1.511(5)	C(51)-C(52)-N(6)	110.36(16)
C(81)-C(83)	1.530(4)	C(51)-C(52)-C(53)	109.71(16)
C(84)-C(86)	1.638(6)	C(54)-C(53)-C(52)	137.69(19)
C(84)-C(87)	1.386(7)	C(54)-C(53)-C(62)	118.01(18)
C(84)-C(85)	1.377(5)	C(62)-C(53)-C(52)	104.29(15)
C(84)-C(88)	1.601(6)	C(53)-C(54)-C(55)	118.4(2)
C(90)-C(91)	1.323(5)	C(56)-C(55)-C(54)	122.86(19)
C(92)-C(93)	1.526(7)	C(55)-C(56)-C(57)	120.18(19)
C(92)-C(94)	1.479(5)	C(58)-C(57)-C(56)	127.21(19)

C(92)-C(95)	1.485(5)	C(62)-C(57)-C(56)	115.9(2)
C(96)-C(97)	1.553(7)	C(62)-C(57)-C(58)	116.83(19)
C(96)-C(99)	1.484(6)	C(59)-C(58)-C(57)	119.63(19)
C(96)-C(101)	1.453(8)	C(58)-C(59)-C(60)	123.0(2)
C(96)-C(98)	1.473(8)	C(61)-C(60)-C(59)	118.42(19)
C(96)-C(100)	1.567(6)	C(60)-C(61)-C(51)	137.62(18)
C(96)-C(102)	1.545(13)	C(60)-C(61)-C(62)	118.30(17)
C(103)-C(104)	1.371(3)	C(62)-C(61)-C(51)	104.05(15)
C(103)-C(113)	1.453(3)	C(53)-C(62)-C(61)	111.64(16)
C(104)-C(105)	1.448(3)	C(57)-C(62)-C(53)	124.57(18)
C(105)-C(106)	1.372(3)	C(57)-C(62)-C(61)	123.79(18)
C(105)-C(114)	1.428(3)	C(64)-C(63)-N(6)	119.96(17)
C(106)-C(107)	1.422(3)	C(64)-C(63)-C(68)	121.24(17)
C(107)-C(108)	1.364(4)	C(68)-C(63)-N(6)	118.80(16)
C(108)-C(109)	1.424(3)	C(63)-C(64)-C(72)	121.79(18)
C(109)-C(110)	1.425(3)	C(65)-C(64)-C(63)	118.16(19)
C(109)-C(114)	1.387(3)	C(65)-C(64)-C(72)	120.04(19)
C(110)-C(111)	1.369(4)	C(66)-C(65)-C(64)	121.1(2)
C(111)-C(112)	1.420(3)	C(65)-C(66)-C(67)	120.19(19)
C(112)-C(113)	1.376(3)	C(66)-C(67)-C(68)	121.2(2)
C(113)-C(114)	1.426(3)	C(63)-C(68)-C(69)	120.72(17)
C(115)-C(116)	1.401(3)	C(67)-C(68)-C(63)	117.94(19)
C(115)-C(120)	1.399(3)	C(67)-C(68)-C(69)	121.32(18)
C(116)-C(117)	1.397(3)	C(68)-C(69)-C(70)	110.59(19)
C(116)-C(124)	1.523(4)	C(68)-C(69)-C(71)	113.25(18)
C(117)-C(118)	1.369(4)	C(71)-C(69)-C(70)	110.4(2)
C(118)-C(119)	1.386(3)	C(64)-C(72)-C(74)	111.2(2)
C(119)-C(120)	1.393(3)	C(73)-C(72)-C(64)	112.0(3)
C(120)-C(121)	1.525(3)	C(73)-C(72)-C(74)	110.7(3)
C(121)-C(122)	1.526(3)	C(76)-C(75)-N(5)	118.60(18)
C(121)-C(123)	1.519(4)	C(76)-C(75)-C(80)	121.68(18)
C(124)-C(125)	1.513(4)	C(80)-C(75)-N(5)	119.72(17)
C(124)-C(126)	1.480(6)	C(75)-C(76)-C(81)	119.94(18)
C(127)-C(128)	1.405(3)	C(77)-C(76)-C(75)	117.7(2)
C(127)-C(132)	1.408(3)	C(77)-C(76)-C(81)	122.4(2)
C(128)-C(129)	1.389(3)	C(78)-C(77)-C(76)	121.0(2)
C(128)-C(136)	1.523(3)	C(79)-C(78)-C(77)	120.6(2)
C(129)-C(130)	1.376(4)	C(78)-C(79)-C(80)	120.5(2)
C(130)-C(131)	1.379(4)	C(75)-C(80)-C(84)	120.94(17)
C(131)-C(132)	1.396(3)	C(79)-C(80)-C(75)	118.5(2)
C(132)-C(133)	1.516(3)	C(79)-C(80)-C(84)	120.5(2)

C(133)-C(134)	1.517(4)	C(76)-C(81)-C(83)	112.9(2)
C(133)-C(135)	1.526(4)	C(82)-C(81)-C(76)	110.1(3)
C(136)-C(137)	1.510(5)	C(82)-C(81)-C(83)	112.0(3)
C(136)-C(138)	1.524(4)	C(80)-C(84)-C(86)	105.6(3)
C(140)-C(141)	1.324(5)	C(80)-C(84)-C(88)	111.6(3)
C(142)-C(143)	1.533(4)	C(87)-C(84)-C(80)	120.1(4)
C(142)-C(144)	1.493(4)	C(87)-C(84)-C(86)	110.8(6)
C(142)-C(145)	1.505(4)	C(85)-C(84)-C(80)	122.4(4)
C(146)-C(147)	1.529(4)	C(85)-C(84)-C(88)	111.3(4)
C(146)-C(149)	1.487(5)	N(8)-C(89)-N(7)	108.87(19)
C(146)-C(151)	1.475(4)	C(91)-C(90)-N(8)	108.0(2)
C(146)-C(150)	1.705(12)	C(90)-C(91)-N(7)	107.5(2)
C(146)-C(148)	1.496(12)	N(8)-C(92)-C(93)	105.8(3)
C(146)-C(152)	1.569(12)	C(94)-C(92)-N(8)	110.8(3)
C(153)-C(154)	1.474(5)	C(94)-C(92)-C(93)	111.1(5)
C(154)-C(155)	1.379(4)	C(94)-C(92)-C(95)	113.2(4)
C(154)-C(159)	1.386(5)	C(95)-C(92)-N(8)	108.8(2)
C(155)-C(156)	1.372(5)	C(95)-C(92)-C(93)	106.7(4)
C(156)-C(157)	1.355(6)	N(7)-C(96)-C(97)	104.1(4)
C(157)-C(158)	1.357(6)	N(7)-C(96)-C(100)	109.6(3)
C(158)-C(159)	1.381(6)	N(7)-C(96)-C(102)	107.0(5)
C(160)-C(161)	1.421(8)	C(99)-C(96)-N(7)	105.4(3)
C(161)-C(162)	1.351(8)	C(99)-C(96)-C(97)	109.0(6)
C(161)-C(166)	1.476(10)	C(101)-C(96)-N(7)	109.5(3)
C(162)-C(163)	1.455(8)	C(101)-C(96)-C(97)	110.1(5)
C(163)-C(164)	1.263(9)	C(101)-C(96)-C(99)	117.7(6)
C(164)-C(165)	1.347(12)	C(98)-C(96)-N(7)	115.3(4)
C(165)-C(166)	1.288(10)	C(98)-C(96)-C(100)	108.3(6)
C(131)-C(132)-C(127)	117.7(2)	C(98)-C(96)-C(102)	111.5(9)
C(131)-C(132)-C(133)	119.9(2)	C(102)-C(96)-C(100)	104.6(7)
C(132)-C(133)-C(134)	110.9(2)	N(10)-C(103)-C(113)	139.47(17)
C(132)-C(133)-C(135)	112.9(2)	C(104)-C(103)-N(10)	109.92(17)
C(134)-C(133)-C(135)	110.2(2)	C(104)-C(103)-C(113)	110.17(17)
C(128)-C(136)-C(138)	114.0(2)	N(9)-C(104)-C(105)	139.33(16)
C(137)-C(136)-C(128)	110.8(2)	C(103)-C(104)-N(9)	110.81(17)
C(137)-C(136)-C(138)	109.6(3)	C(103)-C(104)-C(105)	109.53(17)
N(12)-C(139)-N(11)	109.06(19)	C(106)-C(105)-C(104)	137.17(19)
C(141)-C(140)-N(12)	108.1(2)	C(106)-C(105)-C(114)	117.95(19)
C(140)-C(141)-N(11)	107.6(3)	C(114)-C(105)-C(104)	104.79(16)
N(11)-C(142)-C(143)	106.9(2)	C(105)-C(106)-C(107)	118.4(2)
N(11)-C(142)-C(145)	110.0(2)	C(108)-C(107)-C(106)	123.4(2)

C(144)-C(142)-N(11)	108.16(19)	C(107)-C(108)-C(109)	119.7(2)
C(144)-C(142)-C(143)	108.9(2)	C(108)-C(109)-C(110)	127.2(2)
C(144)-C(142)-C(145)	112.2(2)	C(114)-C(109)-C(108)	116.4(2)
C(145)-C(142)-C(143)	110.5(3)	C(114)-C(109)-C(110)	116.4(2)
N(12)-C(146)-C(147)	106.4(3)	C(111)-C(110)-C(109)	119.7(2)
N(12)-C(146)-C(150)	114.5(4)	C(110)-C(111)-C(112)	123.0(2)
N(12)-C(146)-C(152)	111.8(6)	C(113)-C(112)-C(111)	118.8(2)
C(149)-C(146)-N(12)	105.0(2)	C(112)-C(113)-C(103)	138.10(19)
C(149)-C(146)-C(147)	110.2(3)	C(112)-C(113)-C(114)	117.65(19)
C(151)-C(146)-N(12)	106.9(2)	C(114)-C(113)-C(103)	104.24(16)
C(151)-C(146)-C(147)	111.6(3)	C(109)-C(114)-C(105)	124.23(19)
C(151)-C(146)-C(149)	116.0(4)	C(109)-C(114)-C(113)	124.44(19)
C(148)-C(146)-N(12)	120.3(6)	C(113)-C(114)-C(105)	111.26(17)
C(148)-C(146)-C(150)	99.7(8)	C(116)-C(115)-N(9)	119.37(18)
C(148)-C(146)-C(152)	109.4(9)	C(120)-C(115)-N(9)	119.10(17)
C(152)-C(146)-C(150)	98.4(9)	C(120)-C(115)-C(116)	121.52(17)
C(155)-C(154)-C(153)	122.3(4)	C(115)-C(116)-C(124)	120.33(19)
C(155)-C(154)-C(159)	117.2(3)	C(117)-C(116)-C(115)	118.1(2)
C(159)-C(154)-C(153)	120.5(3)	C(117)-C(116)-C(124)	121.5(2)
C(156)-C(155)-C(154)	121.3(3)	C(118)-C(117)-C(116)	121.1(2)
C(157)-C(156)-C(155)	121.8(3)	C(117)-C(118)-C(119)	120.19(18)
C(156)-C(157)-C(158)	117.1(4)	C(118)-C(119)-C(120)	120.9(2)
C(157)-C(158)-C(159)	123.0(4)	C(115)-C(120)-C(121)	120.86(16)
C(158)-C(159)-C(154)	119.5(3)	C(119)-C(120)-C(115)	118.07(18)
C(160)-C(161)-C(166)	107.5(8)	C(119)-C(120)-C(121)	121.07(19)
C(162)-C(161)-C(160)	131.1(8)	C(120)-C(121)-C(122)	112.95(18)
C(162)-C(161)-C(166)	120.5(6)	C(123)-C(121)-C(120)	110.79(19)
C(161)-C(162)-C(163)	118.9(5)	C(123)-C(121)-C(122)	110.6(2)
C(164)-C(163)-C(162)	120.6(8)	C(125)-C(124)-C(116)	113.1(2)
C(163)-C(164)-C(165)	116.2(9)	C(126)-C(124)-C(116)	110.9(3)
C(166)-C(165)-C(164)	133.8(7)	C(126)-C(124)-C(125)	112.9(3)
C(165)-C(166)-C(161)	109.9(6)	C(128)-C(127)-N(10)	119.13(18)
N(2)-B(1)-N(1)	101.72(16)	C(128)-C(127)-C(132)	121.47(17)
O(1)-B(1)-N(1)	129.22(19)	C(132)-C(127)-N(10)	119.37(18)
O(1)-B(1)-N(2)	129.07(18)	C(127)-C(128)-C(136)	120.97(19)
N(5)-B(2)-N(6)	101.49(15)	C(129)-C(128)-C(127)	118.2(2)
O(2)-B(2)-N(5)	128.59(17)	C(129)-C(128)-C(136)	120.9(2)
O(2)-B(2)-N(6)	129.92(17)	C(130)-C(129)-C(128)	121.1(2)
N(9)-B(3)-N(10)	101.90(16)	C(129)-C(130)-C(131)	120.5(2)
O(3)-B(3)-N(9)	128.96(18)	C(130)-C(131)-C(132)	121.0(2)
O(3)-B(3)-N(10)	129.12(18)	C(127)-C(132)-C(133)	122.30(17)

Crystallographic data for compound 4

Identification code	Compound 4
Empirical formula	$C_{47}H_{61}BN_4S$
Formula weight	724.86
Temperature/K	150(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.7222(8)
b/Å	19.6535(12)
c/Å	17.2812(10)
α/°	90
β/°	96.436(2)
γ/°	90
Volume/Å^3	4293.7(5)
Z	4
ρ_{calc}g/cm^3	1.121
μ/mm^{-1}	0.111
F(000)	1568.0
Crystal size/mm^3	0.200 × 0.200 × 0.100
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.15 to 51.396
Index ranges	$-14 \leq h \leq 15$, $-21 \leq k \leq 23$, $-20 \leq l \leq 21$
Reflections collected	40925
Independent reflections	8130 [R_{int} = 0.0465, R_{sigma} = 0.0318]
Data/restraints/parameters	8130/0/504
Goodness-of-fit on F^2	1.024
Final R indexes [I>=2σ (I)]	R_1 = 0.0425, wR_2 = 0.1077
Final R indexes [all data]	R_1 = 0.0545, wR_2 = 0.1163
Largest diff. peak/hole / e Å^{-3}	0.32/-0.21

Table S3. Bond lengths [Å] and angles [°] for compound **4**

S(1)-B(1)	1.7682(17)	C(37)-N(3)-C(38)	108.08(13)
N(3)-C(37)	1.3389(19)	C(37)-N(3)-C(44)	124.64(12)
N(3)-C(38)	1.376(2)	C(38)-N(3)-C(44)	127.26(13)
N(3)-C(44)	1.5073(18)	C(1)-N(1)-C(25)	121.58(12)
N(1)-C(1)	1.3860(19)	C(1)-N(1)-B(1)	108.42(12)
N(1)-C(25)	1.4265(19)	C(25)-N(1)-B(1)	129.30(12)
N(1)-B(1)	1.477(2)	C(37)-N(4)-C(39)	107.78(13)

N(4)-C(37)	1.327(2)	C(37)-N(4)-C(40)	126.20(14)
N(4)-C(39)	1.369(2)	C(39)-N(4)-C(40)	126.01(14)
N(4)-C(40)	1.507(2)	C(2)-N(2)-C(13)	121.87(12)
N(2)-C(2)	1.3965(18)	C(2)-N(2)-B(1)	108.44(12)
N(2)-C(13)	1.4305(19)	C(13)-N(2)-B(1)	129.68(12)
N(2)-B(1)	1.477(2)	C(11)-C(12)-C(3)	111.62(13)
C(12)-C(3)	1.432(2)	C(7)-C(12)-C(3)	124.43(15)
C(12)-C(11)	1.427(2)	C(7)-C(12)-C(11)	123.94(15)
C(12)-C(7)	1.385(2)	N(1)-C(1)-C(11)	139.17(14)
C(1)-C(2)	1.359(2)	C(2)-C(1)-N(1)	110.48(13)
C(1)-C(11)	1.460(2)	C(2)-C(1)-C(11)	110.34(14)
C(2)-C(3)	1.462(2)	N(2)-C(2)-C(3)	140.39(14)
C(3)-C(4)	1.375(2)	C(1)-C(2)-N(2)	109.61(13)
C(25)-C(26)	1.406(2)	C(1)-C(2)-C(3)	109.91(13)
C(25)-C(30)	1.404(2)	C(12)-C(3)-C(2)	104.06(13)
C(11)-C(10)	1.376(2)	C(4)-C(3)-C(12)	117.95(14)
C(26)-C(34)	1.520(3)	C(4)-C(3)-C(2)	137.99(15)
C(26)-C(27)	1.391(2)	C(26)-C(25)-N(1)	118.18(14)
C(7)-C(8)	1.421(2)	C(30)-C(25)-N(1)	119.10(14)
C(7)-C(6)	1.430(3)	C(30)-C(25)-C(26)	122.66(15)
C(30)-C(29)	1.394(2)	C(12)-C(11)-C(1)	104.07(13)
C(30)-C(32)	1.526(3)	C(10)-C(11)-C(12)	118.48(14)
C(39)-C(38)	1.355(2)	C(10)-C(11)-C(1)	137.45(16)
C(4)-C(5)	1.428(2)	C(25)-C(26)-C(34)	120.71(15)
C(8)-C(9)	1.369(3)	C(27)-C(26)-C(25)	117.32(16)
C(29)-(C28)	1.386(3)	C(27)-C(26)-C(34)	121.89(16)
C(10)-C(9)	1.425(2)	C(12)-C(7)-C(8)	116.37(16)
C(14)-C(13)	1.404(2)	C(12)-C(7)-C(6)	116.12(15)
C(14)-C(22)	1.522(3)	C(8)-C(7)-C(6)	127.51(15)
C(14)-C(15)	1.396(2)	N(4)-C(37)-N(3)	109.35(14)
C(5)-C(6)	1.366(3)	C(25)-C(30)-C(32)	120.16(14)
C(13)-C(18)	1.400(2)	C(29)-C(30)-C(25)	117.41(16)
C(22)-C(24)	1.533(3)	C(29)-C(30)-C(32)	122.43(16)
C(22)-C(23)	1.535(3)	C(38)-C(39)-N(4)	108.19(15)
C(44)-C(46)	1.520(2)	C(3)-C(4)-C(5)	118.39(16)
C(44)-C(45)	1.516(2)	C(9)-C(8)-C(7)	120.33(15)
C(44)-C(47)	1.521(2)	C(28)-C(29)-C(30)	120.70(18)
C(18)-C(19)	1.521(3)	C(39)-C(38)-N(3)	106.58(15)
C(18)-C(17)	1.401(3)	C(11)-C(10)-C(9)	118.13(16)
C(40)-C(43)	1.519(3)	C(13)-C(14)-C(22)	120.31(15)
C(40)-C(41)	1.530(3)	C(15)-C(14)-C(13)	117.60(17)

C(40)-C(42)	1.499(3)	C(15)-C(14)-C(22)	122.09(17)
C(31)-C(32)	1.528(2)	C(6)-C(5)-C(4)	122.97(16)
C(34)-C(35)	1.519(3)	C(14)-C(13)-N(2)	119.23(14)
C(34)-C(36)	1.528(3)	C(18)-C(13)-N(2)	118.71(15)
C(27)-C(28)	1.378(3)	C(18)-C(13)-C(14)	122.06(15)
C(32)-C(33)	1.530(3)	C(14)-C(22)-C(24)	111.12(15)
C(15)-C(16)	1.374(3)	C(14)-C(22)-C(23)	114.52(17)
C(16)-C(17)	1.374(3)	C(24)-C(22)-C(23)	109.03(15)
C(19)-C(21)	1.534(3)	N(3)-C(44)-C(46)	108.05(12)
C(19)-C(20)	1.521(3)	N(3)-C(44)-C(45)	108.48(13)
N(1)-B(1)-S(1)	128.55(12)	N(3)-C(44)-C(47)	107.87(13)
N(1)-B(1)-N(2)	103.03(12)	C(46)-C(44)-C(47)	110.86(14)
N(2)-B(1)-S(1)	128.42(12)	C(45)-C(44)-C(46)	110.53(14)
C(28)-C(27)-C(26)	121.08(18)	C(45)-C(44)-C(47)	110.92(14)
C(8)-C(9)-C(10)	122.73(16)	C(13)-C(18)-C(19)	120.25(15)
C(30)-C(32)-C(31)	110.72(14)	C(13)-C(18)-C(17)	117.56(18)
C(30)-C(32)-C(33)	113.98(16)	C(17)-C(18)-C(19)	122.11(17)
C(31)-C(32)-C(33)	109.98(16)	N(4)-C(40)-C(43)	109.22(13)
C(16)-C(15)-C(14)	121.08(19)	N(4)-C(40)-C(41)	106.81(15)
C(15)-C(16)-C(17)	120.64(18)	C(43)-C(40)-C(41)	109.42(16)
C(27)-C(28)-C(29)	120.77(17)	C(42)-C(40)-N(4)	107.73(14)
C(18)-C(19)-C(21)	110.07(15)	C(42)-C(40)-C(43)	110.27(19)
C(18)-C(19)-C(20)	114.15(19)	C(42)-C(40)-C(41)	113.3(2)
C(20-C(19)-C(21)	111.0(2)	C(5)-C(6)-C(7)	120.09(15)
C(16)-C(17)-C(18)	120.99(19)	C(26)-C(34)-C(36)	113.38(17)
C(35)-C(34)-C(36)	109.82(16)	C(35)-C(34)-C(26)	110.60(15)

E. NMR spectra of 1, 3 and 4.

Compound **1**

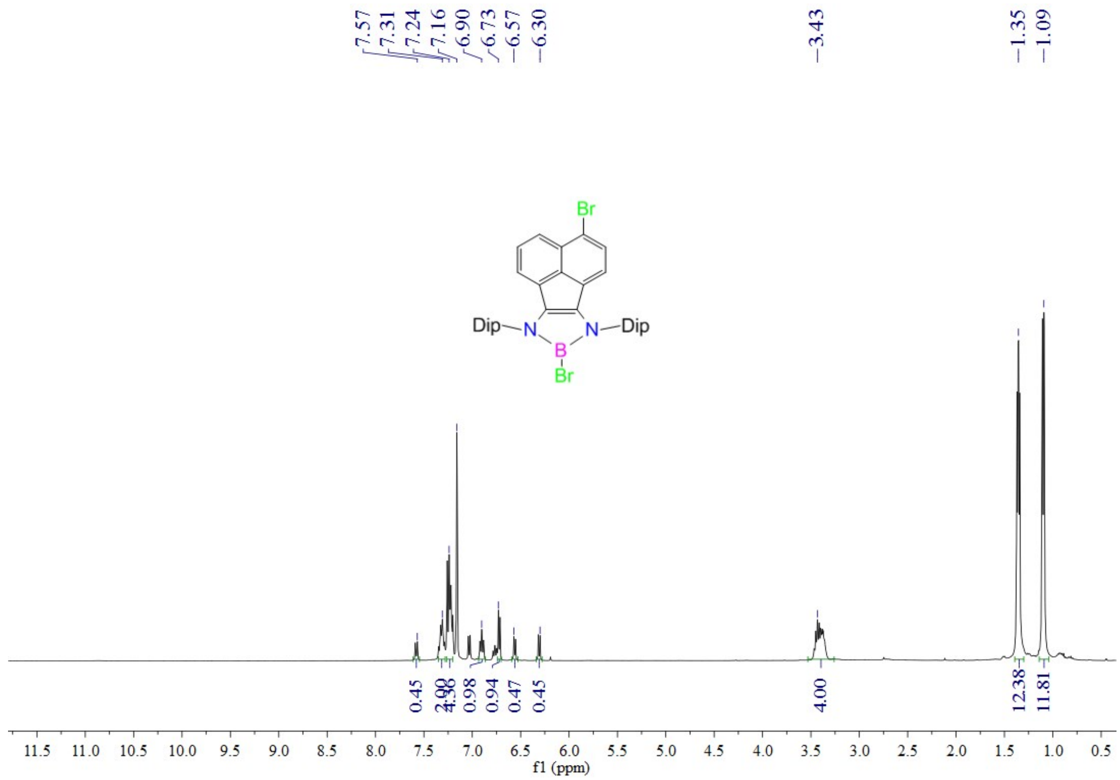


Figure S1 ^{1}H-NMR (400 MHz) spectrum of **1** in C_6D_6.

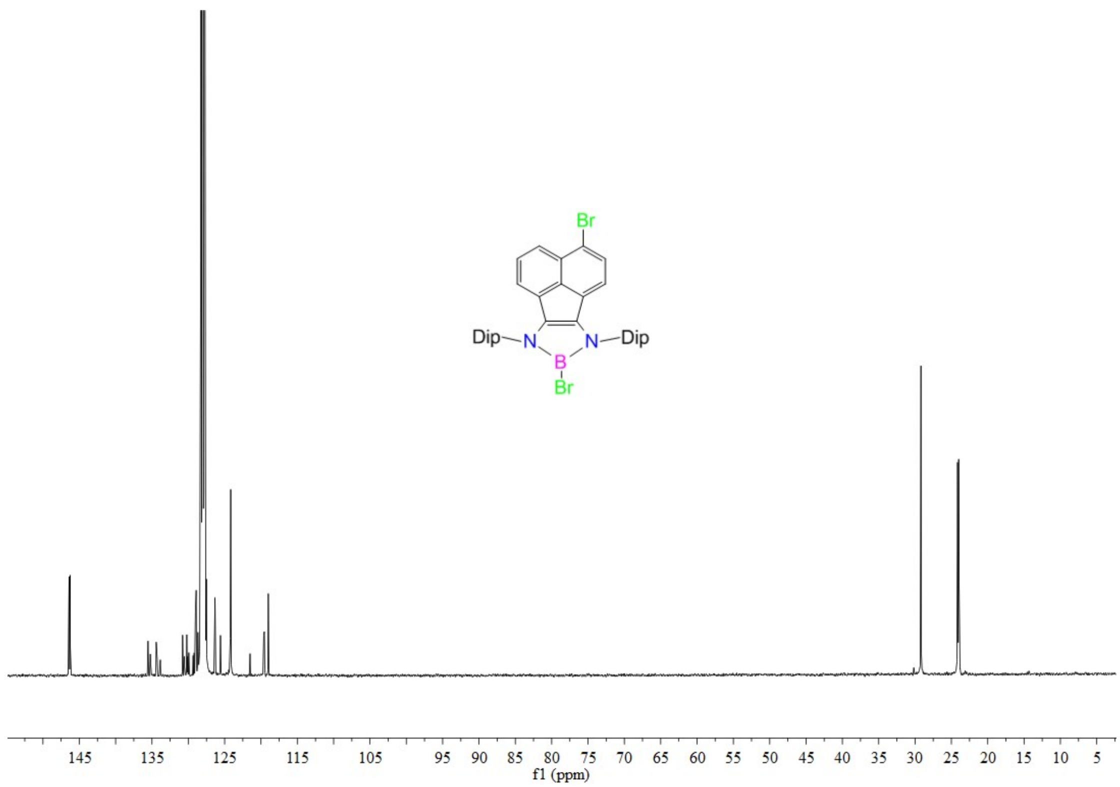


Figure S2 ^{13}C-NMR (100 MHz) spectrum of **1** in C_6D_6.

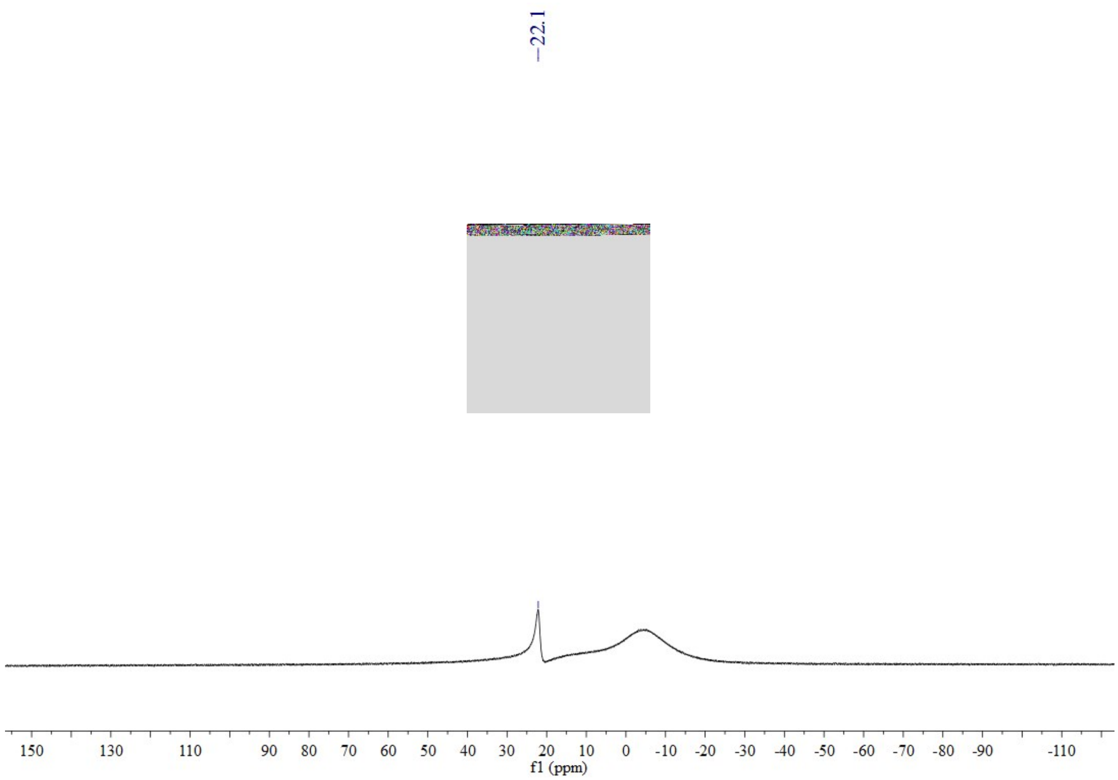


Figure S3 ^{11}B-NMR (128.3 MHz) spectrum of **1** in C_6D_6.

Compound **3**

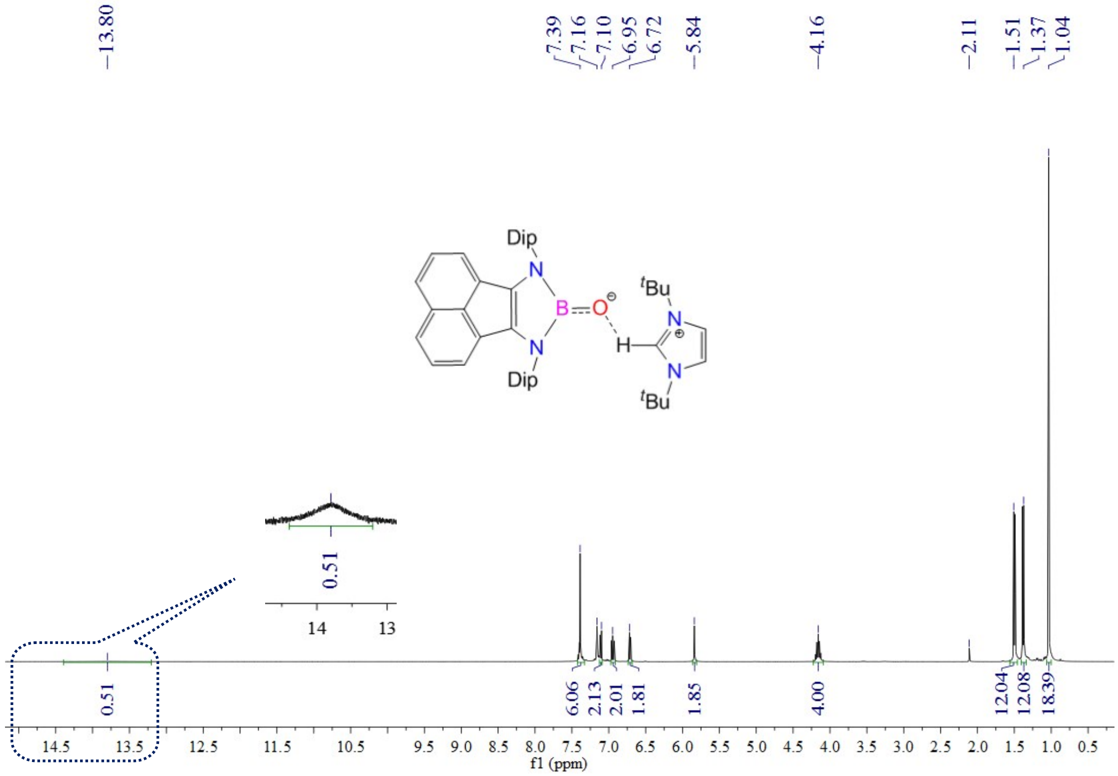


Figure S4 ^{1}H-NMR (400 MHz) spectrum of **3** in C_6D_6.

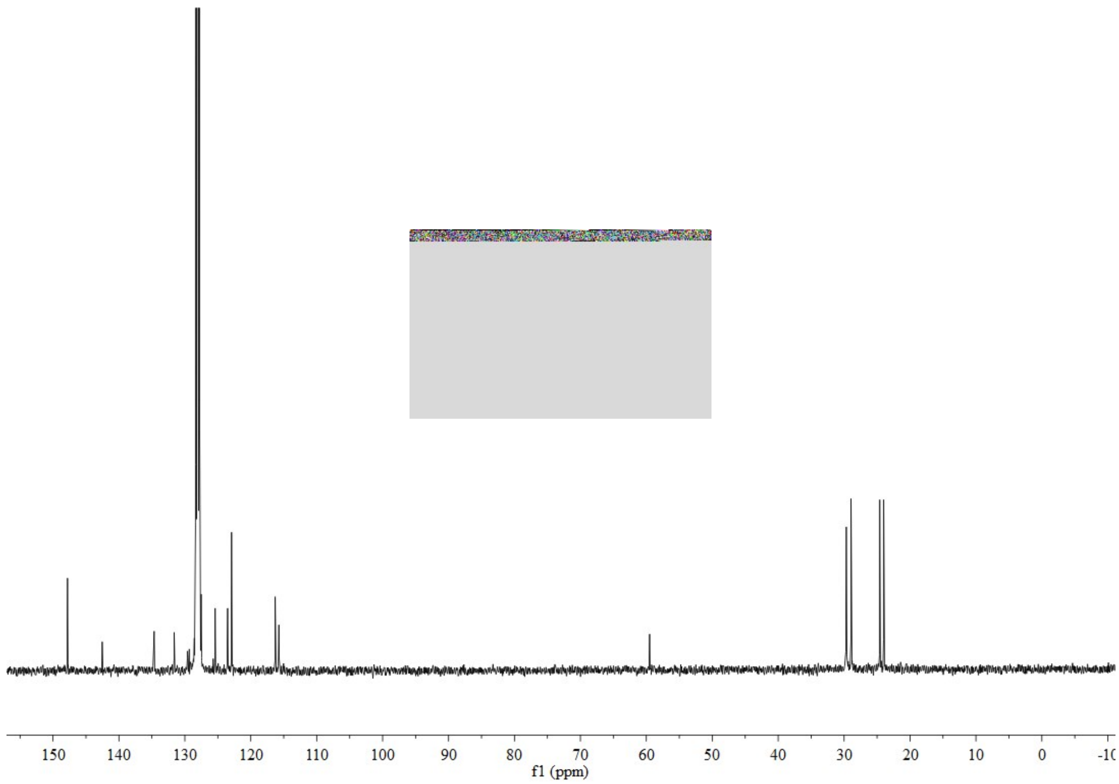


Figure S5 ^{13}C-NMR (100 MHz) spectrum of **3** in C_6D_6.

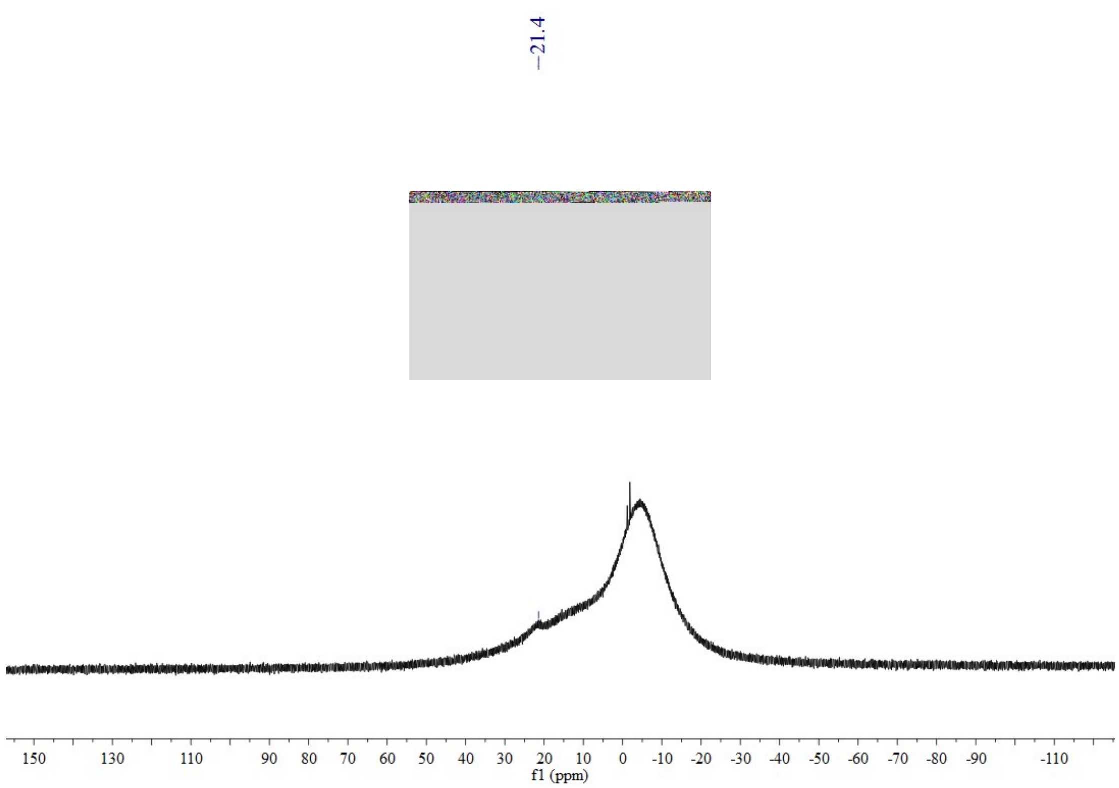


Figure S6 ^{11}B-NMR (128.3 MHz) spectrum of **3** in C_6D_6.

Compound **4**

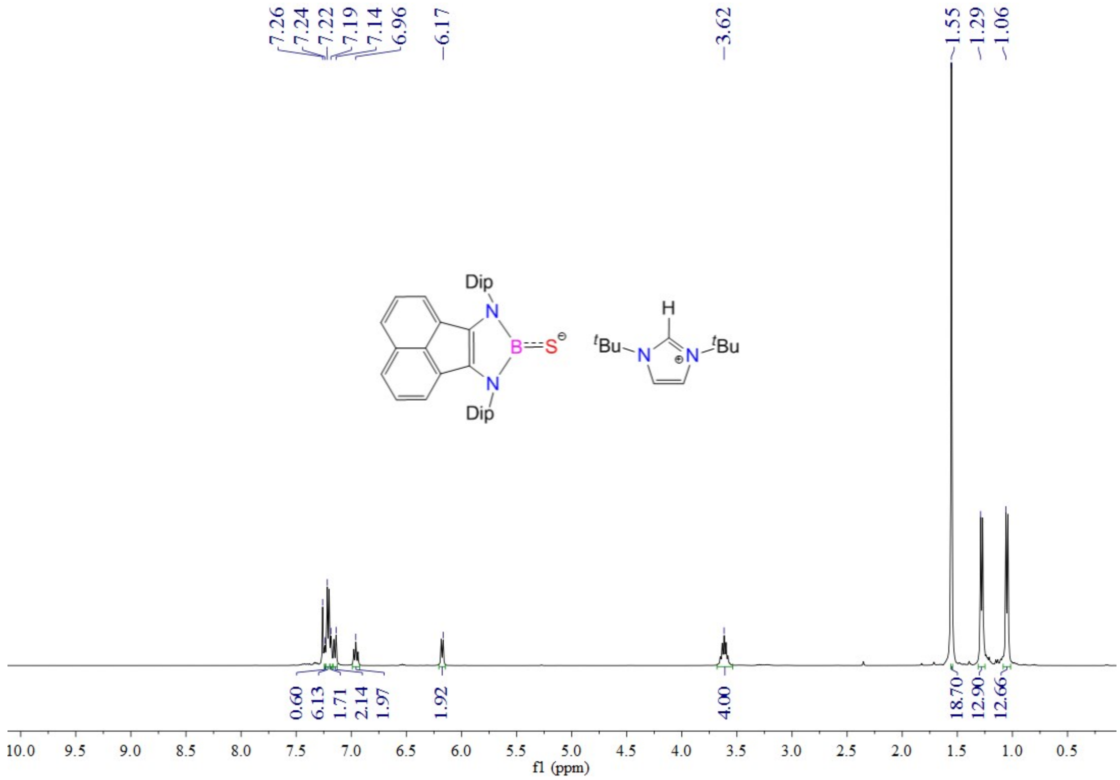


Figure S7 ^{1}H-NMR (400 MHz) spectrum of **4** in $CDCl_3$.

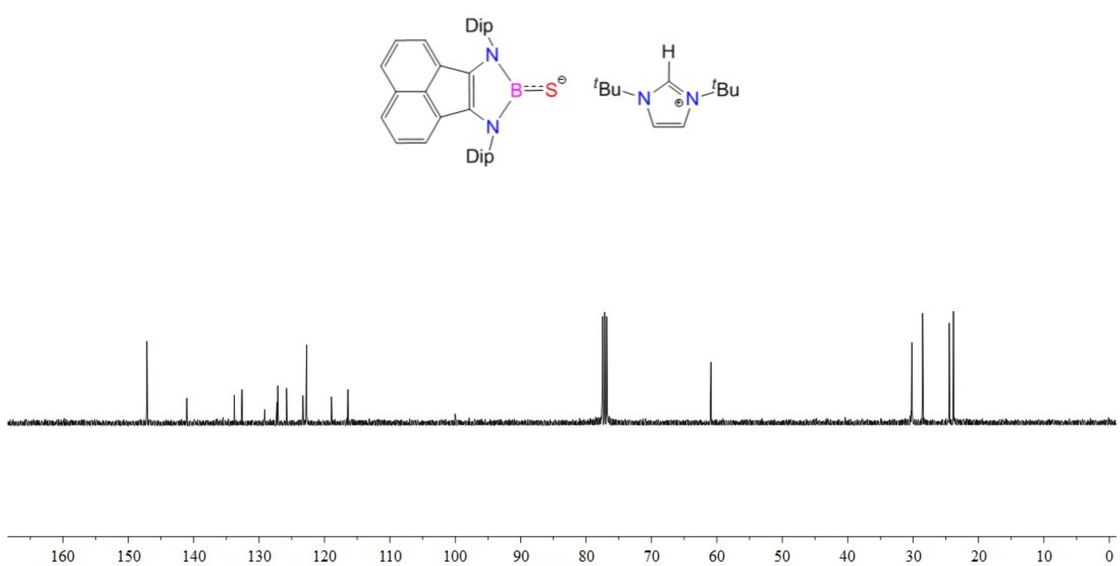


Figure S8 ^{13}C-NMR (100 MHz) spectrum of **4** in $CDCl_3$.

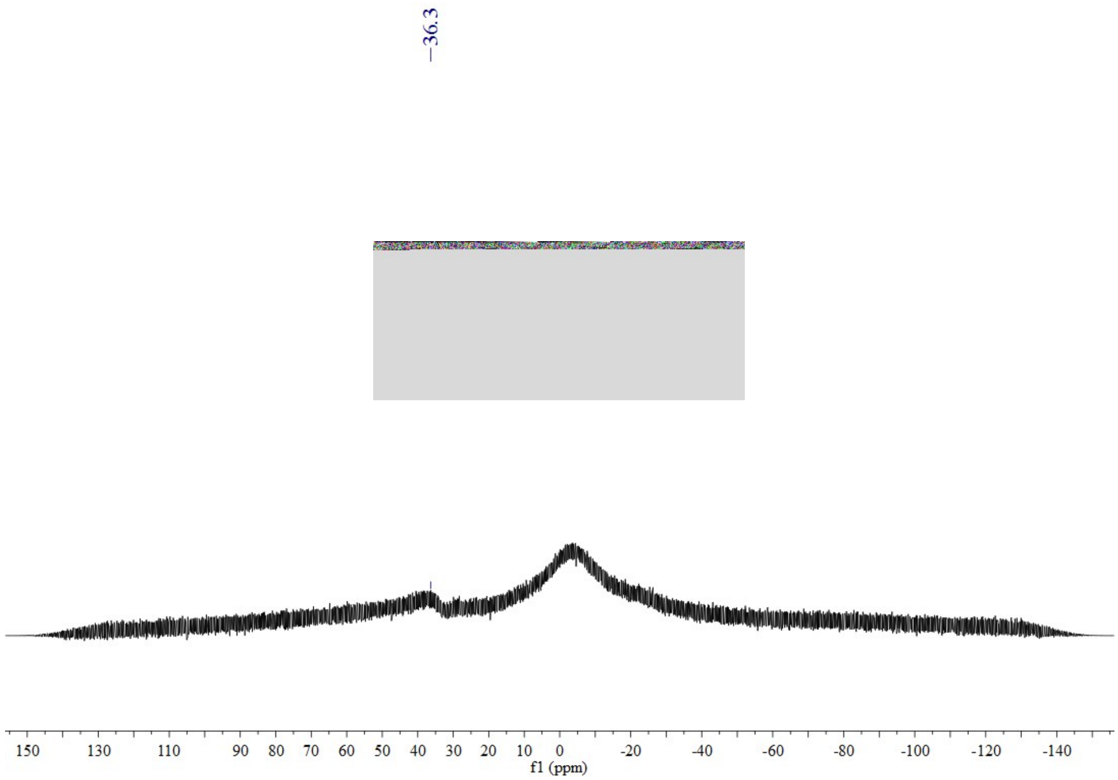


Figure S9 ^{11}B-NMR (128.3 MHz) spectrum of **4** in $CDCl_3$.

F. UV-Vis and IR spectra of 3 and 4

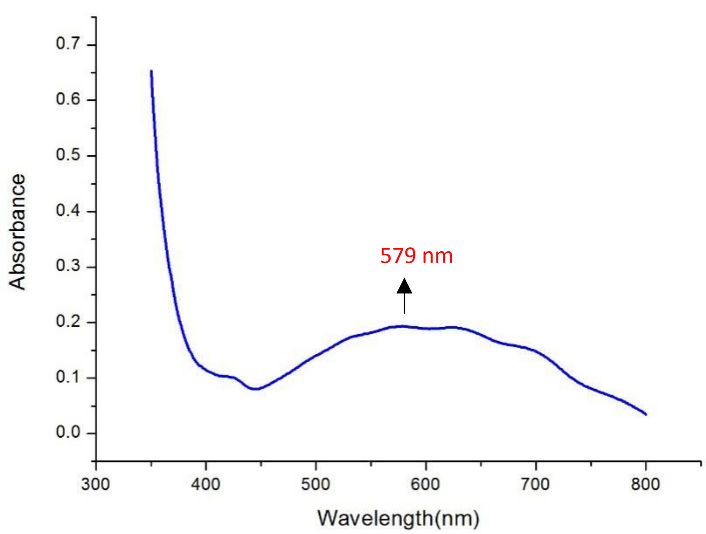


Figure S10 UV-Vis spectrum of **3** in toluene (1.81×10^{-4} mol/L).

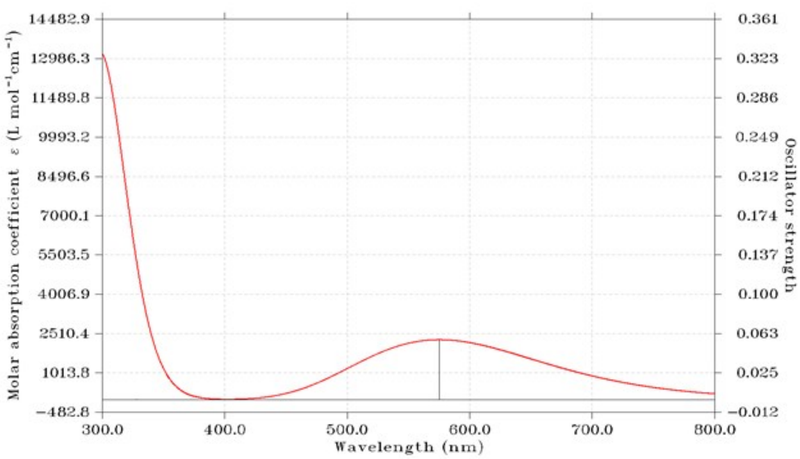


Figure S11 Calculated UV-Vis spectrum of **3**

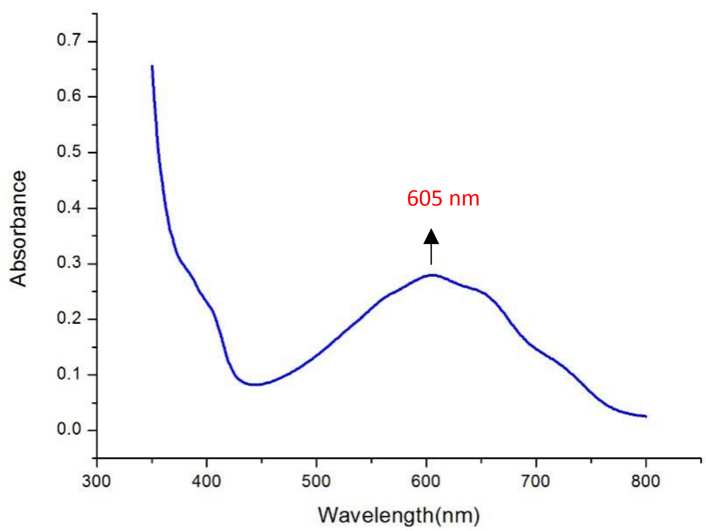


Figure S12 UV-Vis spectrum of **4** in toluene (1.77×10^{-4} mol/L).

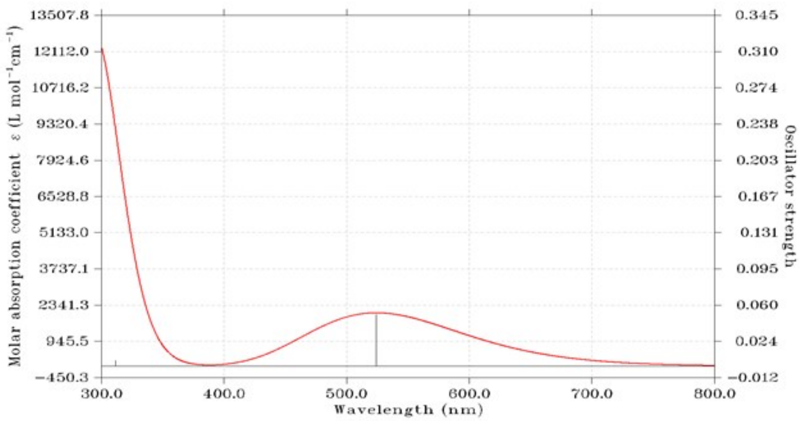


Figure S13 Calculated UV-Vis spectrum of **4**

Compounds	peaks/nm		energy/eV	orbit
	experiment	theory		
3	579	575.07	2.1560	HOMO→LUMO 95.4%
4	605	524.09	2.3657	HOMO→LUMO 90.5%

Table S4. Part of UV-Vis data in **3** and **4**

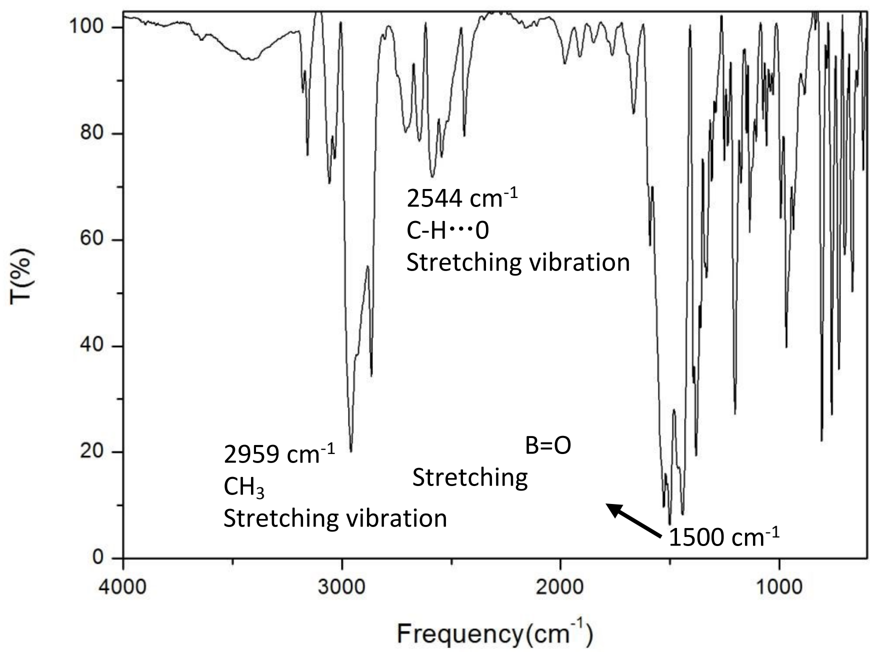


Figure S14 IR spectrum for **3.**

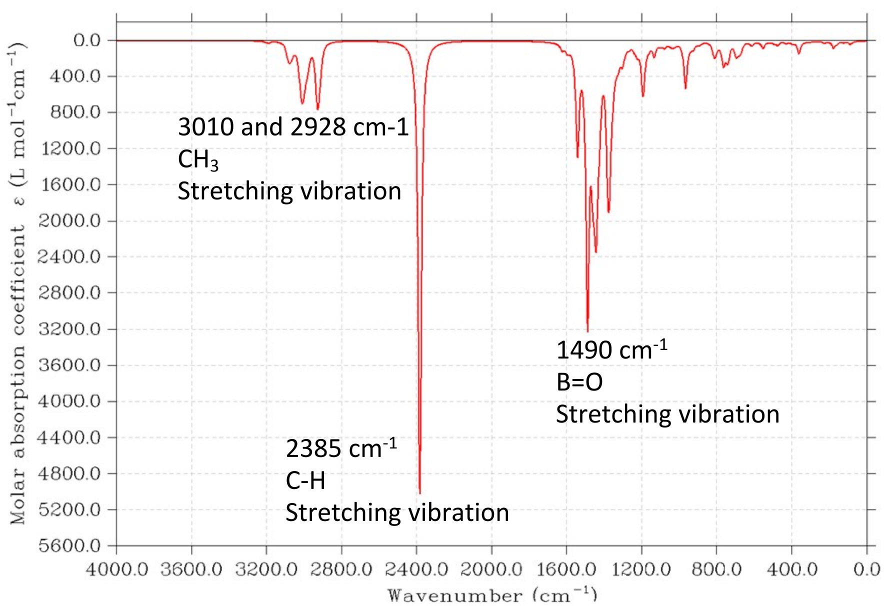


Figure S15 Calculated IR spectrum for **3**.

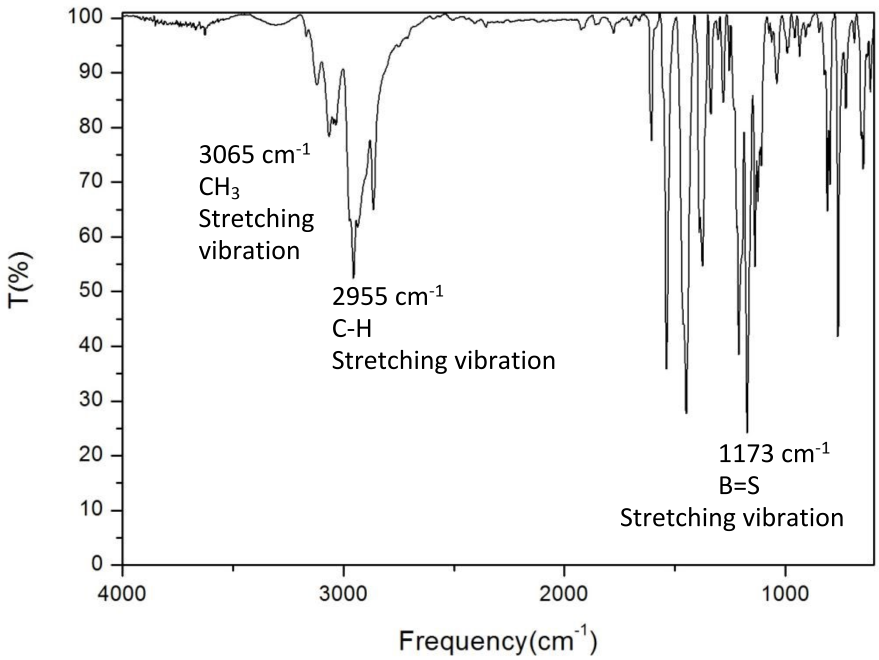


Figure S16 IR spectrum for **4.**

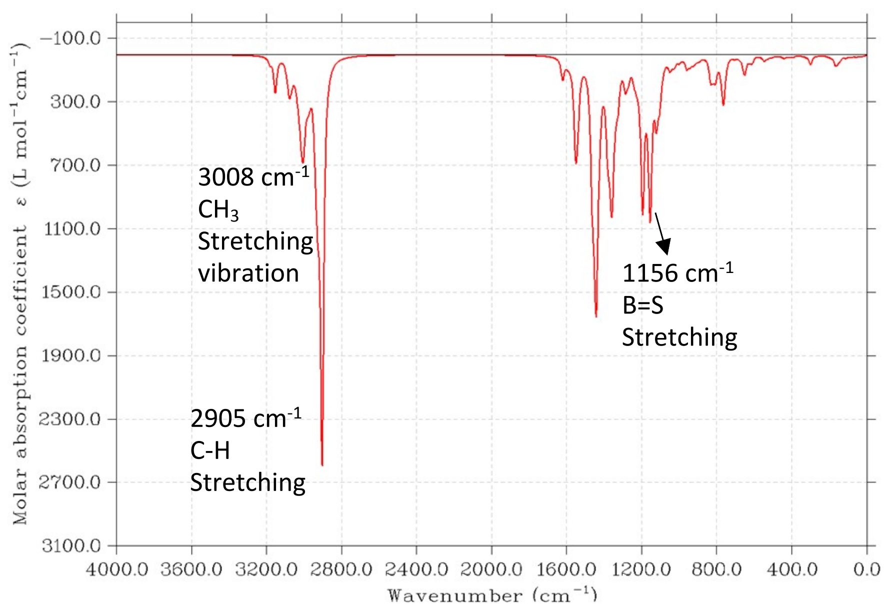


Figure S17 Calculated IR spectrum for **4**.

Table S5. Part of IR data in **3** and **4**

group	experiment	theory

B=O	1500.584	1489.830
B=S	1172.693	1156.385
C-H(compound **3**)	2544.049	2384.795
C-H(compound **4**)	2954.877	2904.968
CH_3(compound **3**)	2958.734	2927.643 and 3010.337
CH_3(compound **4**)	3064.817	3007.669

G. Computational details

The geometries of **3** and **4** were optimized by hybrid functional M06-2x[6] with the def2-TZVP (default2 split valence triple-zeta size polarization) basis set[7]. Table S6-S7 list the key geometries of **3** and **4**, and the optimized structures are excellent agreement with single-crystal XRD results of **3** and **4**.

Table S6. Key geometries in internal coordinates (R is bond length in Å, θ is bond and ϕ is dihedral angle in degrees °) of **3** and **4**

Bond parameters	3		4	
	experiment	theory	experiment	theory
$R_{\text{B1-O1/S1}}$	1.293(3)	1.303	1.7682(17)	1.764
$R_{\text{B1-N1}}$	1.505(3)	1.485	1.477(2)	1.472
$R_{\text{B1-N2}}$	1.499(3)	1.495	1.477(2)	1.484
$R_{\text{N1-C1}}$	1.378(3)	1.385	1.3860(19)	1.375
$R_{\text{N2-C2}}$	1.386(2)	1.382	1.3965(18)	1.391
$R_{\text{C1-C2}}$	1.367(3)	1.365	1.359(2)	1.360
$\theta_{\text{N1–B1–O1}}$	129.22(19)	128.51	128.55(12)	126.3
$\theta_{\text{N1–B1–N2}}$	101.72(16)	102.9	103.03(12)	103.1

$\theta_{N2-B1-O1}$	129.07(18)	128.6	128.42(12)	130.6
$\phi_{C2N2B-O/S}$	179.3	179.5	179.7	178.9

Table S7. Part of NPA charges in **3** and **4**

Atom	3	4
B	1.143	0.690
O/S	-1.131	-0.735
C_2N_2B-ring	0.003	-0.451

H. References

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