Electronic Supplementary Material (ESI) for Chemical Science.

Boron-based stepwise dioxygen activation by 1,4,2,5-diazadiborinine

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1. Synthesis of compounds 2, 3, 4, 5 and their spectral data

General considerations: All reactions were performed under an atmosphere of argon or nitrogen by using standard schlenk or dry box techniques; solvents were dried over Na metal, K metal or CaH_2. Reagents were of analytical grade, obtained from commercial suppliers and used without further purification. ^1H, ^{11}B, ^{13}C NMR spectra were obtained with a Bruker AVIII 400MHz BBFO1 spectrometer at 298 K unless otherwise stated. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad signal. Coupling constants *J* are given in Hz. Electrospray ionization (ESI) mass 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. Fourier transform infrared (FT-IR) spectrum was recorded on a Bruker ALPHA-Transmittance FT-IR Spectrometer. Raman spectrum was performed using x-y hyperspectral imaging mode of the Raman touch microspectrometer (Nanophoton Inc., Osaka, Japan) with an excitation wavelength of 532 nm and 100s collection time.

Synthesis of 2

A benzene (5.0 ml) solution of 1,4,2,5-diazadiborinine[S1] (172 mg, 0.51 mmol) was degassed using a freeze-pump-thaw method, and then O_2 (1 bar) was introduced into the schlenk tube. After stirring for 5 minutes at room temperature, all the volatiles were removed under vacuum to afford **2** as a white solid (158 mg, 84 %).

M.p.: 195 °C. ^1H NMR (400MHz, $CDCl_3$): δ = 7.78 (d, 4H, *J* = 7.3 Hz, Ar-*H*), 7.44 (t, 4H, *J* = 7.3Hz, Ar-*H*), 7.37 (dd, 2H, *J* = 5.0, 3.7 Hz, Ar-*H*), 6.98 (d, 2H, *J* = 1.0 Hz, C*H*), 6.61 (d, 2H, *J* = 1.0 Hz, C*H*), 3.24 (s, 6H, N-C*H*$_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 132.7 (Ar-*C*H), 128.0 (Ar-*C*H), 127.4 (Ar-*C*H), 120.3 (*C*H), 120.1 (*C*H), 35.1 (N-*C*H$_3$); $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ = –0.4 (s). HRMS (ESI): m/z calcd for $C_{20}H_{21}B_2N_4O_2$: 371.1851 $[(M+H)]^+$; found: 371.1854.

Synthesis of 3

A benzene (5.0 ml) solution of 1,4,2,5-diazadiborinine (150 mg, 0.44 mmol) was added TEMPO (139 mg, 0.88 mmol). After stirring for 5 minutes at room temperature, all the volatiles were removed under vacuum to afford **3** as a white solid (231mg, 80%).

M.p.: 237 °C. ^{1}H NMR (400MHz, $CDCl_3$): δ = 7.78-7.66 (m, 4H, Ar-*H*), 7.23 (t, 4H, *J* = 7.3Hz, Ar-*H*), 7.18-7.12 (m, 4H, 2Ar-*H* and 2C*H*), 6.63 (d, 2H, *J* = 1.6 Hz, C*H*), 3.69 (s, 6H, N-CH_3), 1.56-1.44 (m, 2H, CH_2), 1.39-1.21 (m, 10H, CH_2), 1.19 (s, 6H, CH_3), 1.10 (s, 6H, CH_3), 0.48 (s, 6H, CH_3), 0.26 (s, 6H, CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 133.9 (Ar-CH), 126.8 (Ar-*C*H), 125.5 (Ar-*C*H), 119.7 (*C*H), 59.7 (*C*^{tert}), 59.5 (*C*^{tert}), 41.0 (*C*H_2), 40.5(*C*H_2), 36.7 (N-*C*H_3), 33.0 (*C*H_3), 32.2 (*C*H_3), 21.2 (*C*H_3), 21.1 (*C*H_3), 17.6 (*C*H_2); ^{11}B{^{1}H} NMR ($CDCl_3$): δ = –0.3 (s). HRMS (ESI): m/z calcd for $C_{38}H_{57}B_2N_6O_2$: 651.4729 [(M+H)]$^+$; found: 651.4733.

Synthesis of 4

A toluene (5.0 ml) solution of 1,4,2,5-diazadiborinine (135 mg, 0.40mmol) was added compound **2** (148 mg, 0.40 mmol). The mixture was heated at 80 °C for 10 hours. After filtration, the all volatiles were removed under vacuum to afford **4** as a light yellow powder (43 mg, 15%).

M.p.: 319 °C(dec). ^{1}H NMR (400MHz, CD_2Cl_2): δ = 8.75 (d, 4H, *J* = 6.8Hz, Ar-*H*), 7.49 (t, 4H, *J* = 6.7Hz, Ar-*H*), 7.17 (tt, 4H, *J* = 7.3Hz, 1.4Hz, Ar-H), 7.07 (t, 4H, *J* = 6.7Hz, Ar-*H*), 6.66 (d, 4H, *J* = 6.7Hz, Ar-*H*), 6.41 (d, 4H, *J* = 1.6 Hz, C*H*), 6.15 (d, 4H, *J* = 1.6 Hz, C*H*), 3.03 (s, 12H, N-CH_3); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 133.2 (Ar-*C*H), 132.6 (Ar-*C*H), 127.4 (Ar-*C*H), 125.8 (Ar-*C*H), 121.2 (*C*H), 121.0 (*C*H), 34.7 (N-*C*H_3); ^{11}B{^{1}H} NMR (CD_2Cl_2): δ = –2.4 (s). HRMS (ESI): m/z calcd for $C_{40}H_{41}B_4N_8O_2$: 709.3725 [(M+H)]$^+$; found: 709.3730.

Synthesis of 5

A dichloromethane (5.0 ml) solution of **2** (150 mg, 0.41mmol) was added pinacolborane (156 mg, 1.22 mmol). The mixture was stirred at room temperature for 10 hours. After removing solvent under vacuum, the residue was washed with hexane, then the all volatiles were removed under vacuum to afford **5** as white power (104mg, 41%).

M.p.: 246 °C. ^{1}H NMR (400MHz, CD_2Cl_2): δ = 7.53 (d, 4H, *J* = 7.4Hz, Ar-*H*), 7.19 (t, 4H, *J* = 7.0Hz, Ar-*H*), 7.15-7.11 (m, 2H, Ar-*H*), 6.86 (s, 2H, C*H*), 6.71 (s, 2H, C*H*), 3.40 (s, 6H, N-CH_3), 1.11 (OC(CH_3)$_2$, 24H); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 132.5 (Ar-*C*H), 127.4 (Ar-*C*H), 126.3 (Ar-*C*H), 121.8 (*C*H), 121.7 (*C*H), 81.3 (O*C*(CH_3)$_2$,) 35.1 (N-*C*H_3), 24.9 (OC(*C*H_3)$_2$), 24.7 (OC(*C*H_3)$_2$); ^{11}B{^{1}H} NMR (CD_2Cl_2): δ = 21.2 (br), –2.5 (s). HRMS (ESI): m/z calcd for $C_{32}H_{45}B_4N_4O_6$: 625.3711 [(M+H)]$^+$; found: 625.3716.

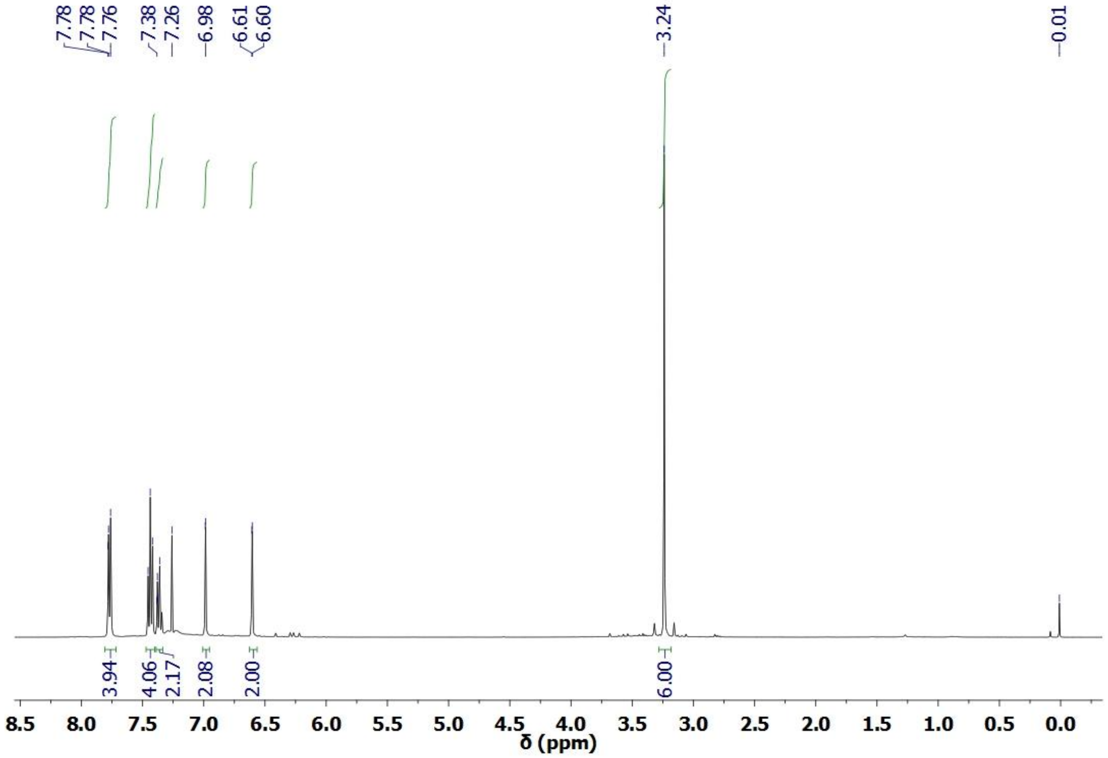


Figure S1 ^{1}H NMR spectrum (CDCl$_3$) of **2**.

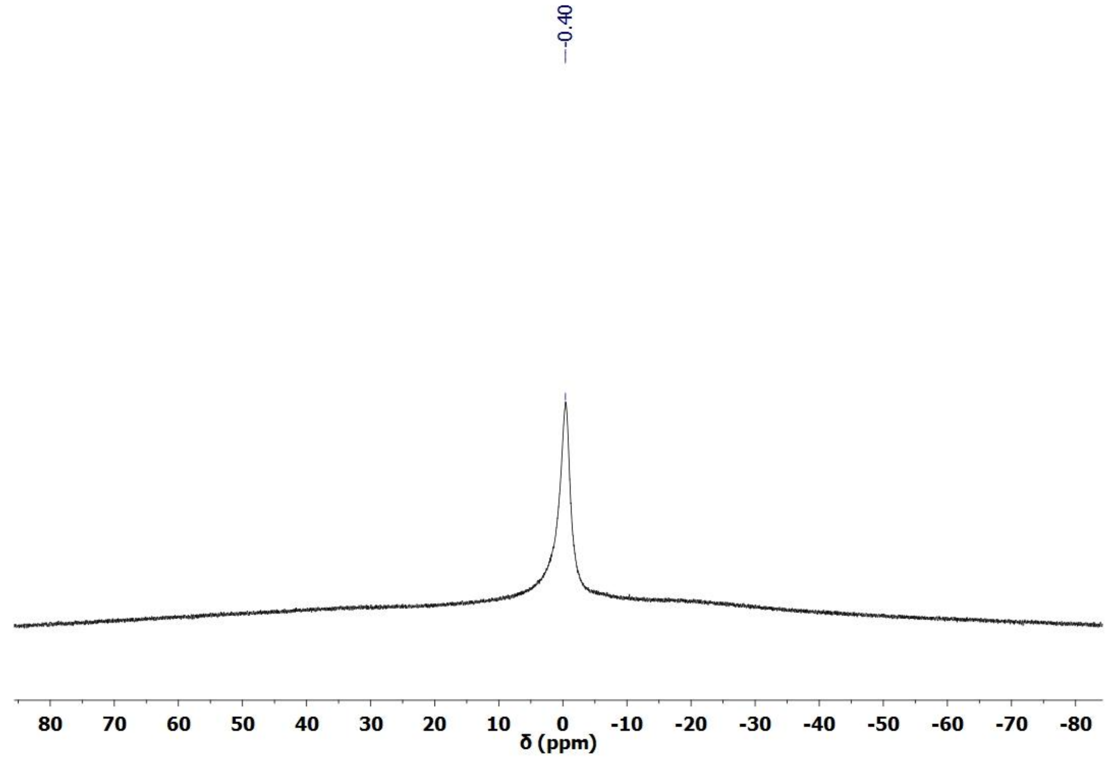


Figure S2 ^{11}B{^{1}H} NMR spectrum (CDCl$_3$) of **2**.

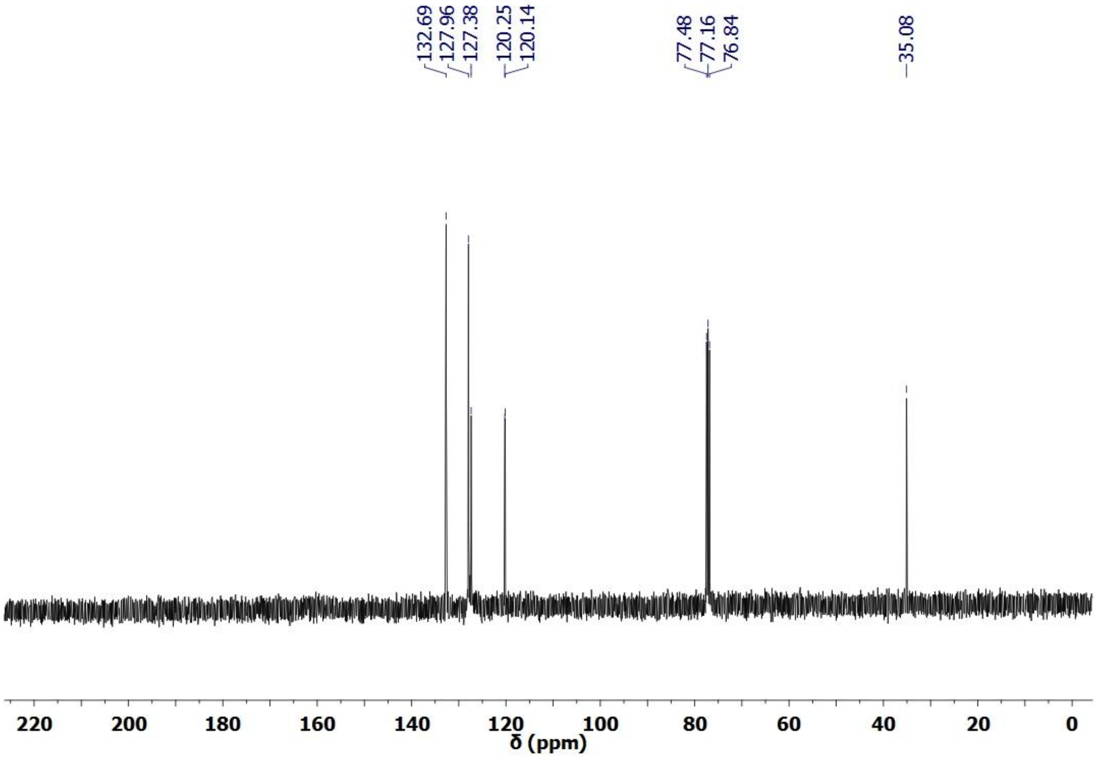


Figure S3 $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$) of **2**.

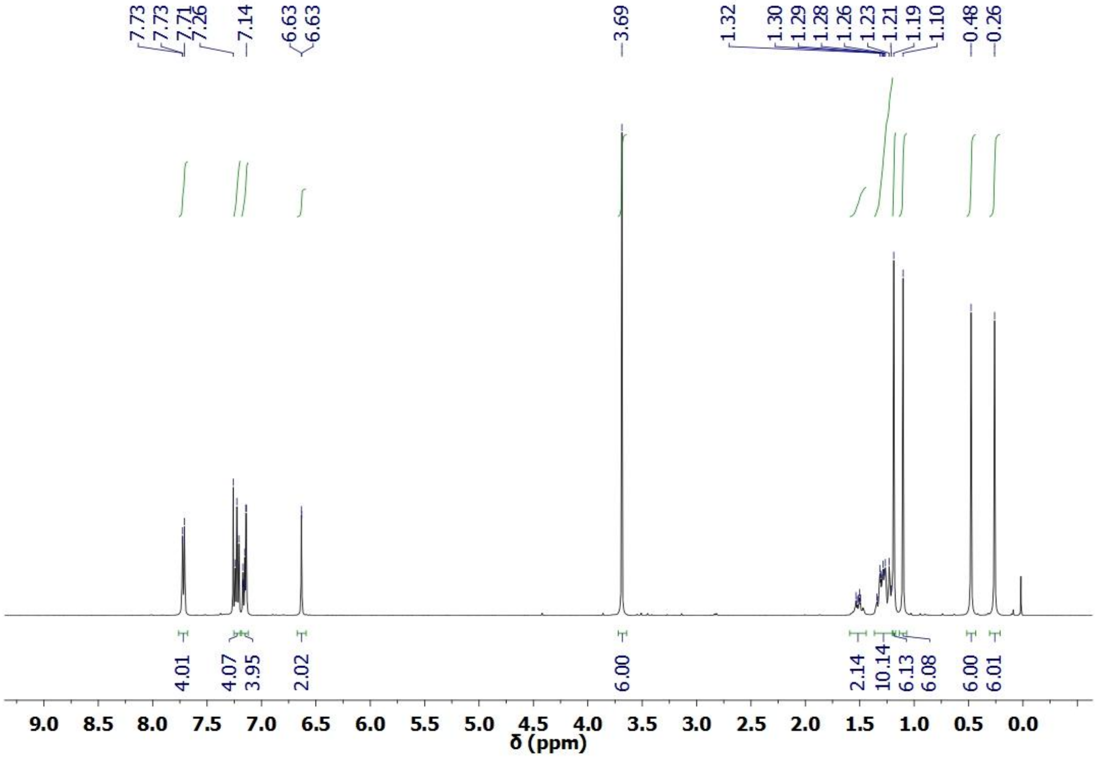


Figure S4 ^1H NMR spectrum ($CDCl_3$) of **3**.

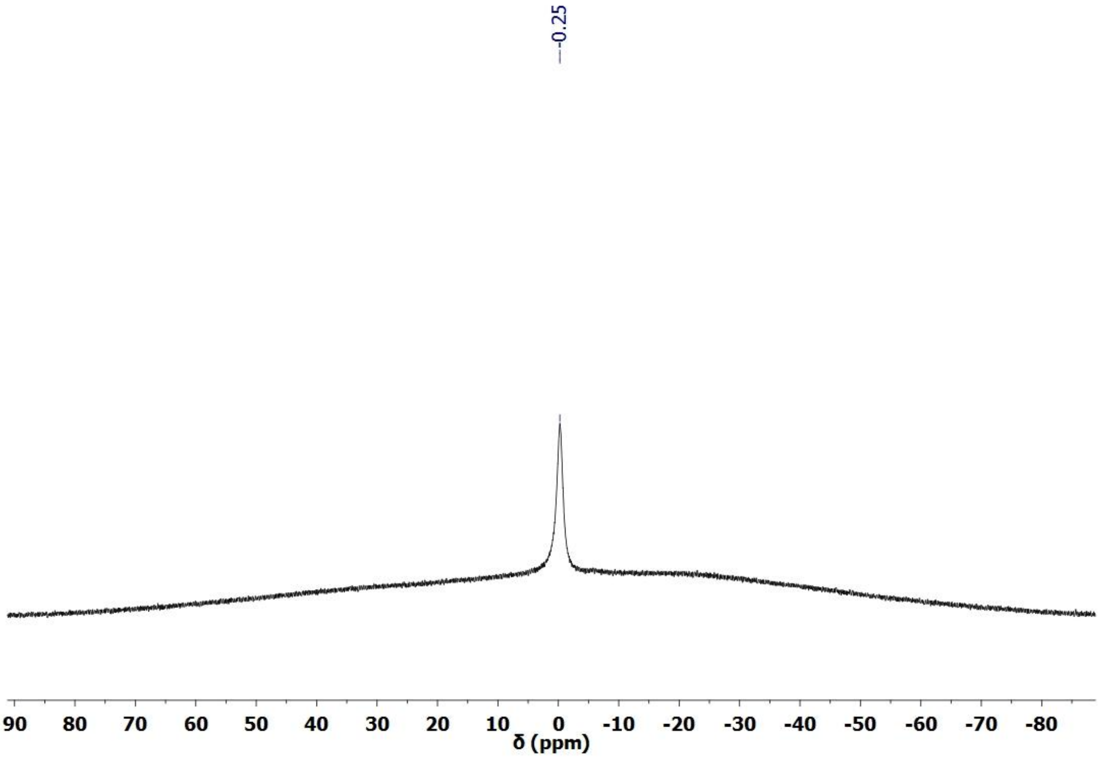


Figure S5 $^{11}B\{^1H\}$ NMR spectrum ($CDCl_3$) of **3**.

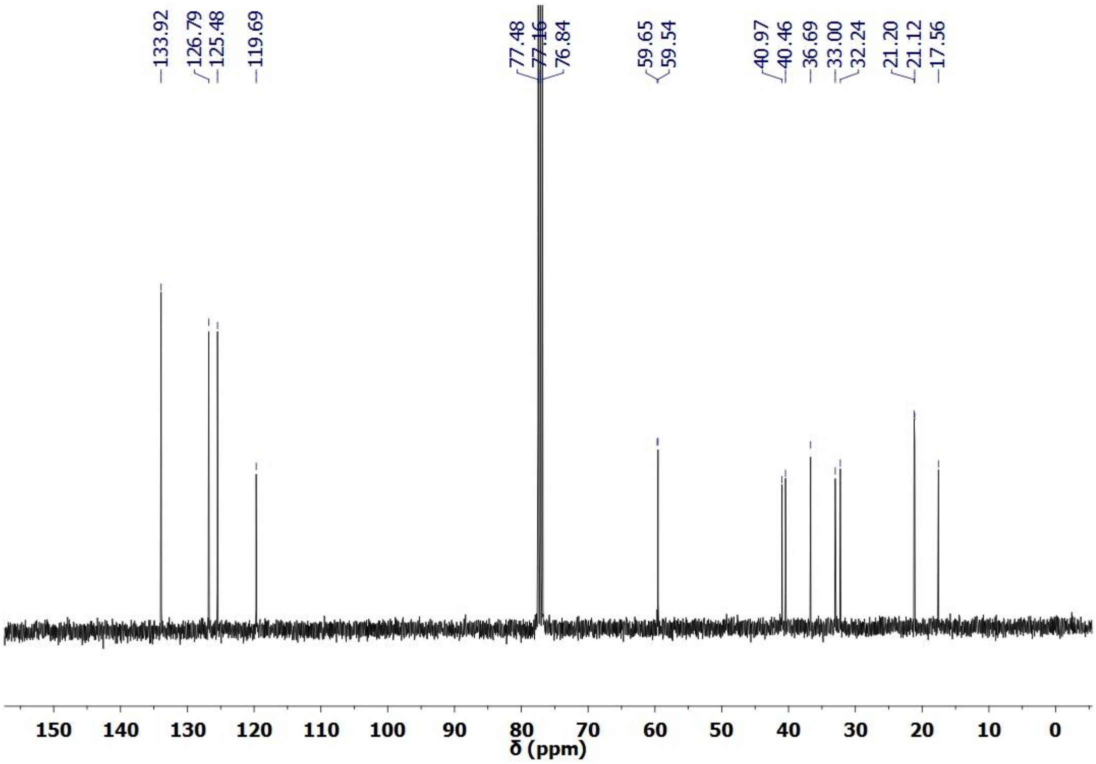


Figure S6 $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$) of **3**.

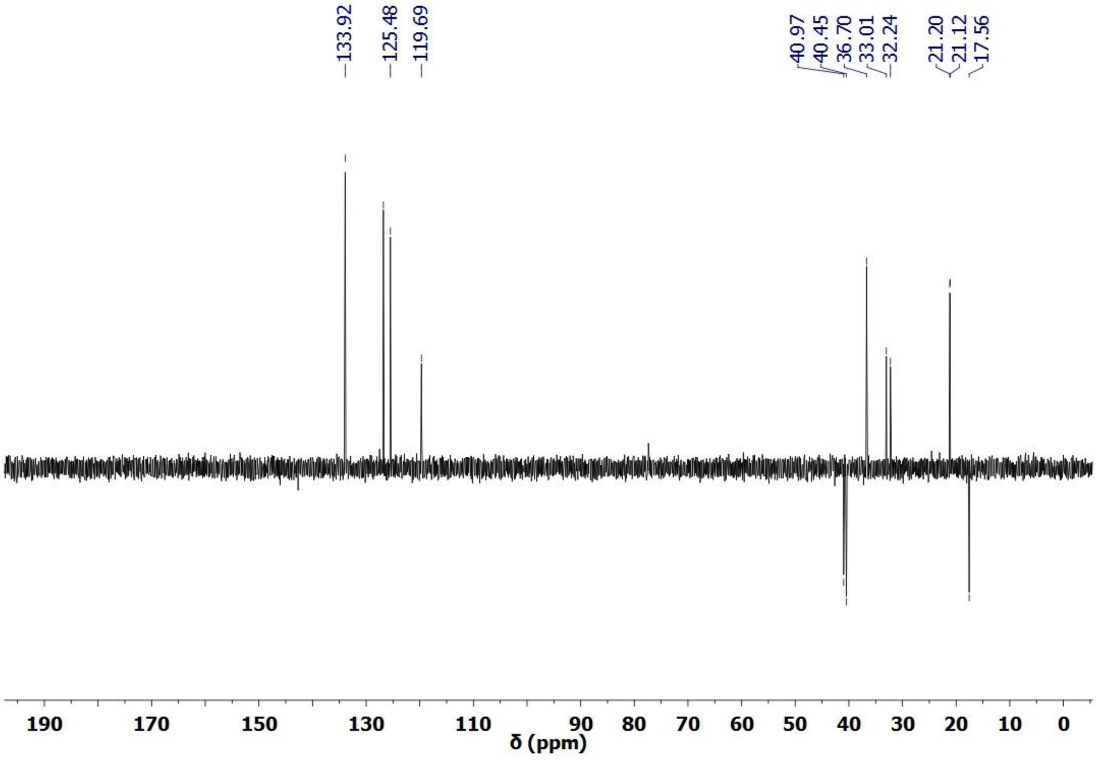


Figure S7 ^{13}C NMR (DEPT 135) spectrum (CDCl$_3$) of **3**.

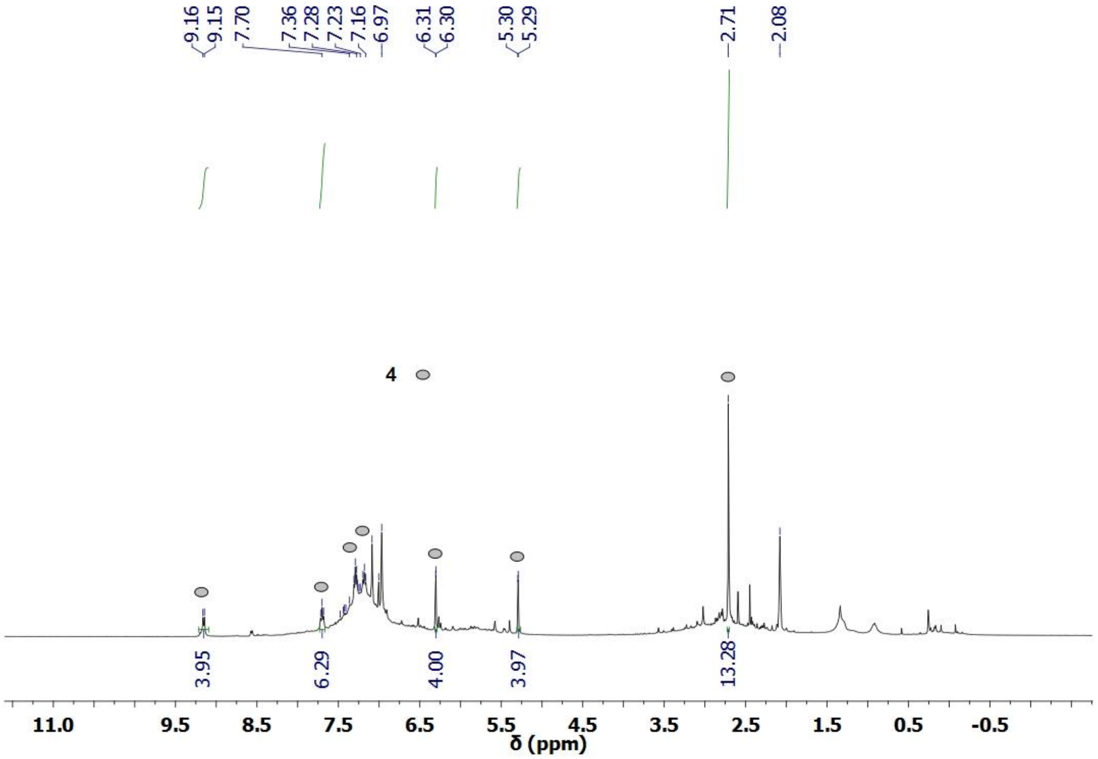


Figure S8 Crude ^{1}H NMR spectrum (D-toluene) of the reaction of **2** with **1**.

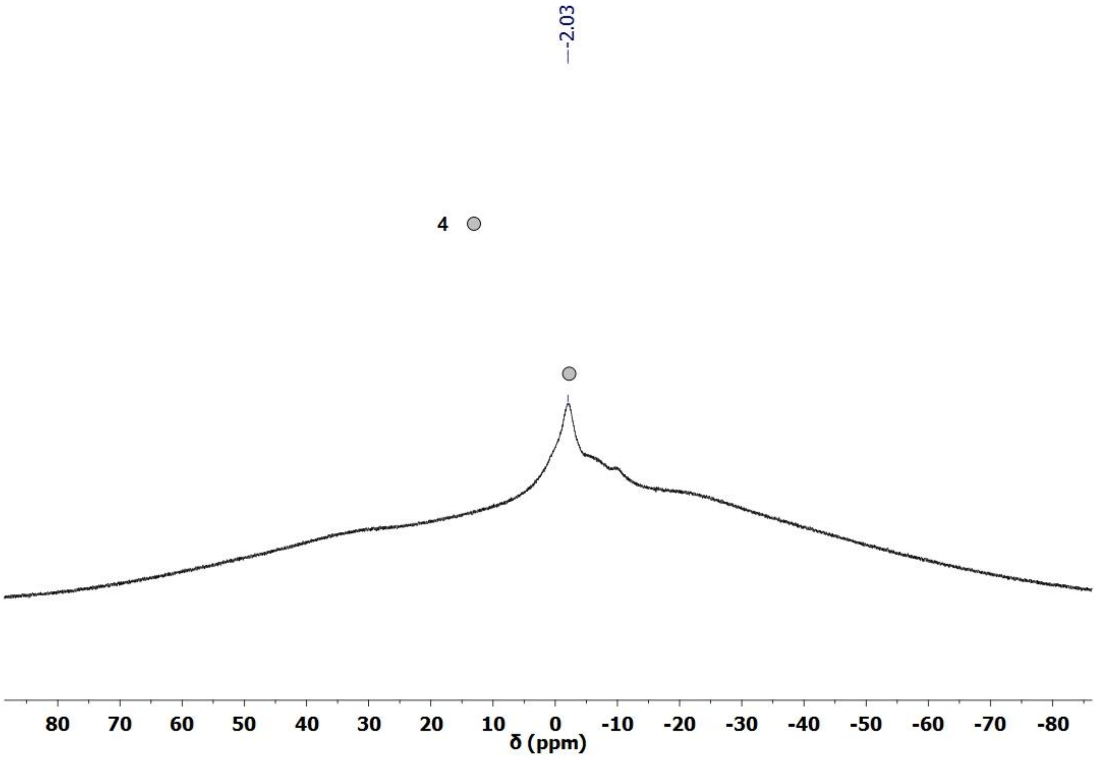


Figure S9 Crude ^{11}B NMR spectrum (D-toluene) of the reaction of **2** with **1**.

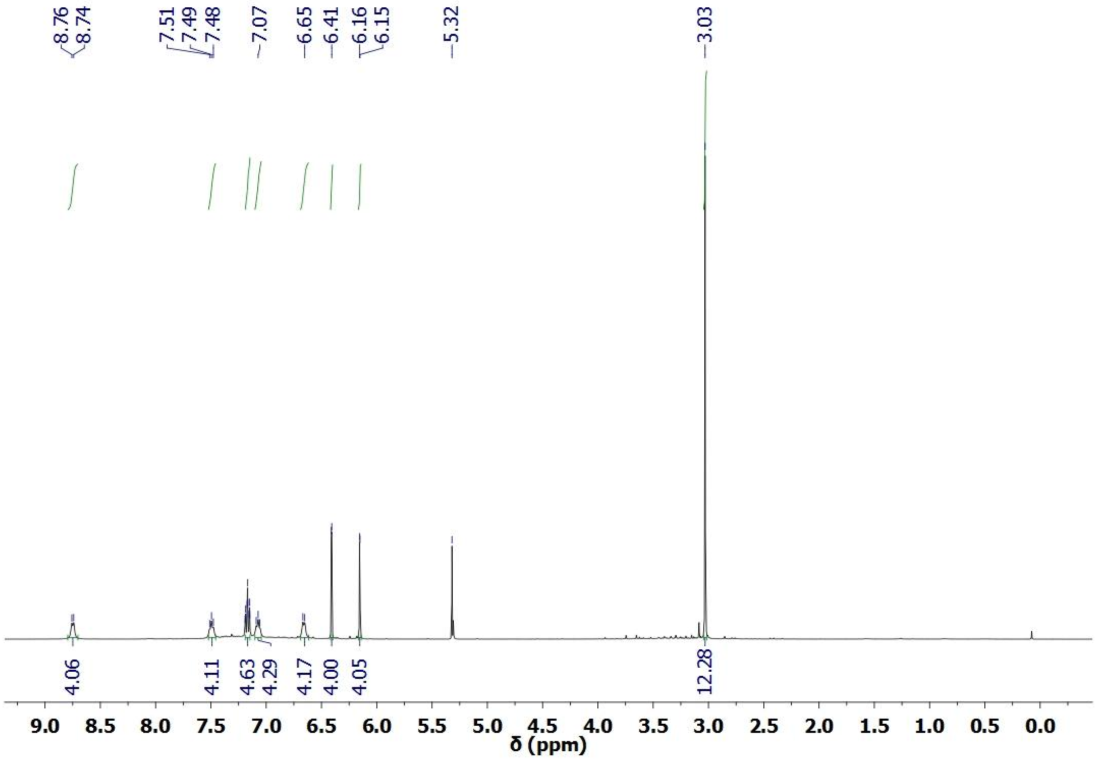


Figure S10 ^1H NMR spectrum (CD_2Cl_2) of **4**.

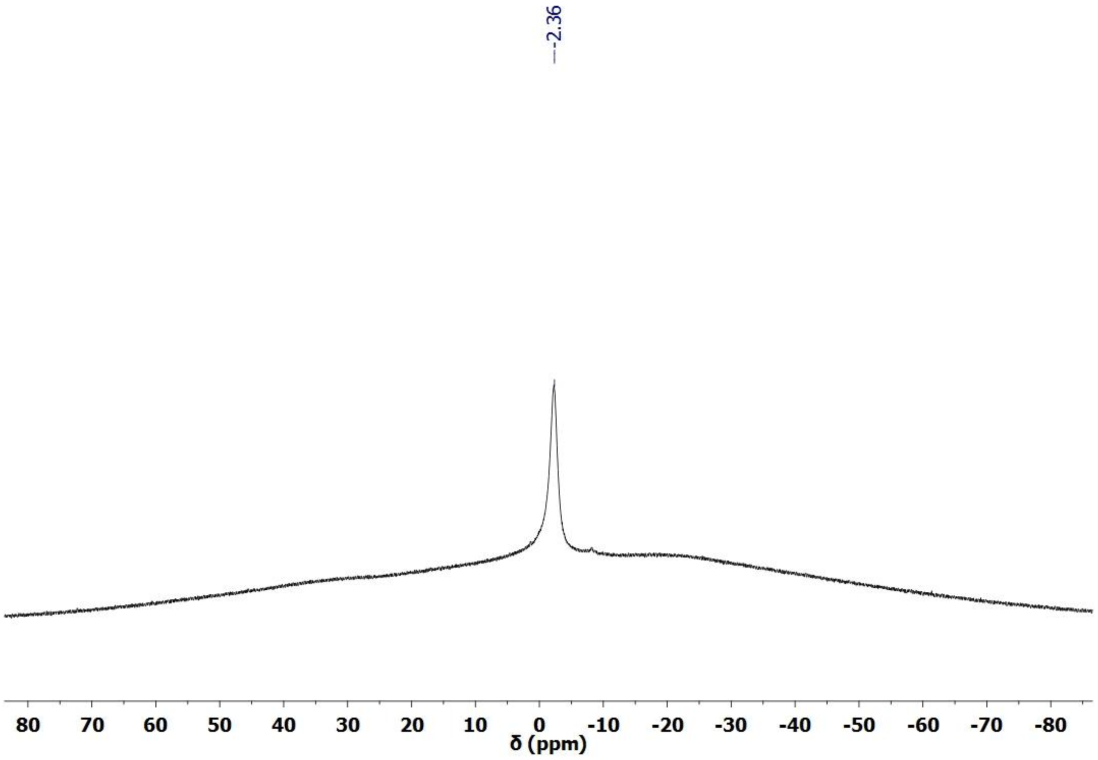


Figure S11 $^{11}B\{^1H\}$ NMR spectrum (CD_2Cl_2) of **4**.

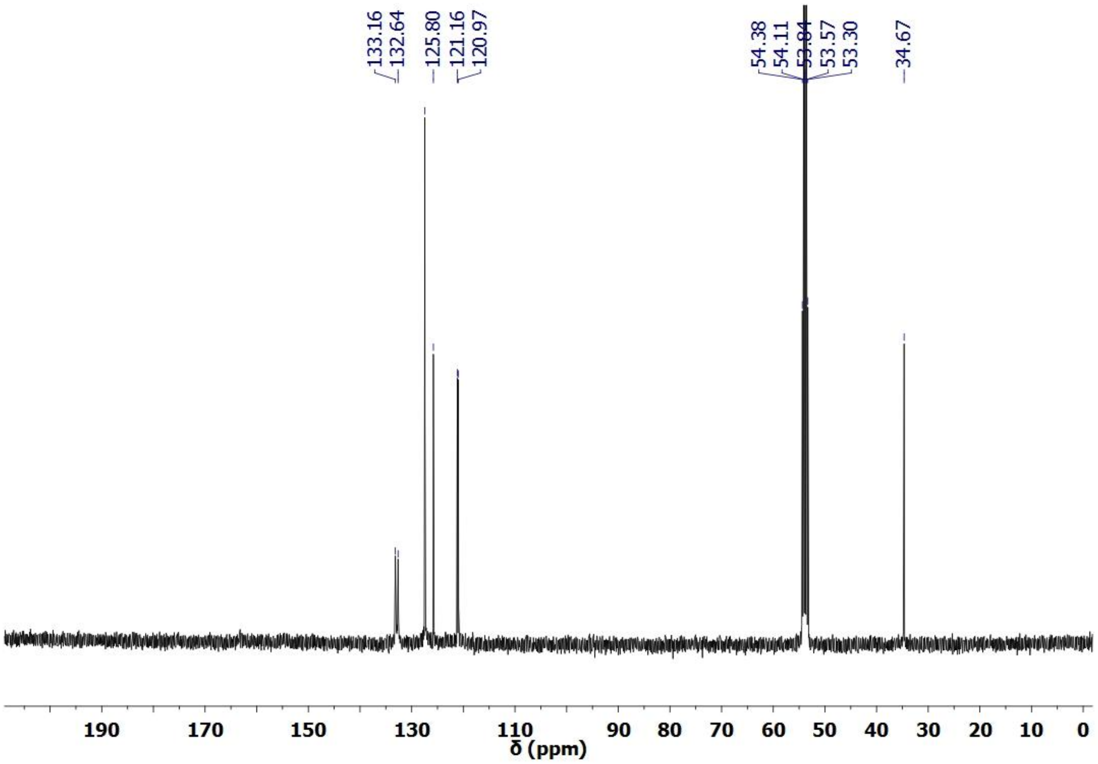


Figure S12 $^{13}C\{^1H\}$ NMR spectrum (CD_2Cl_2) of **4**.

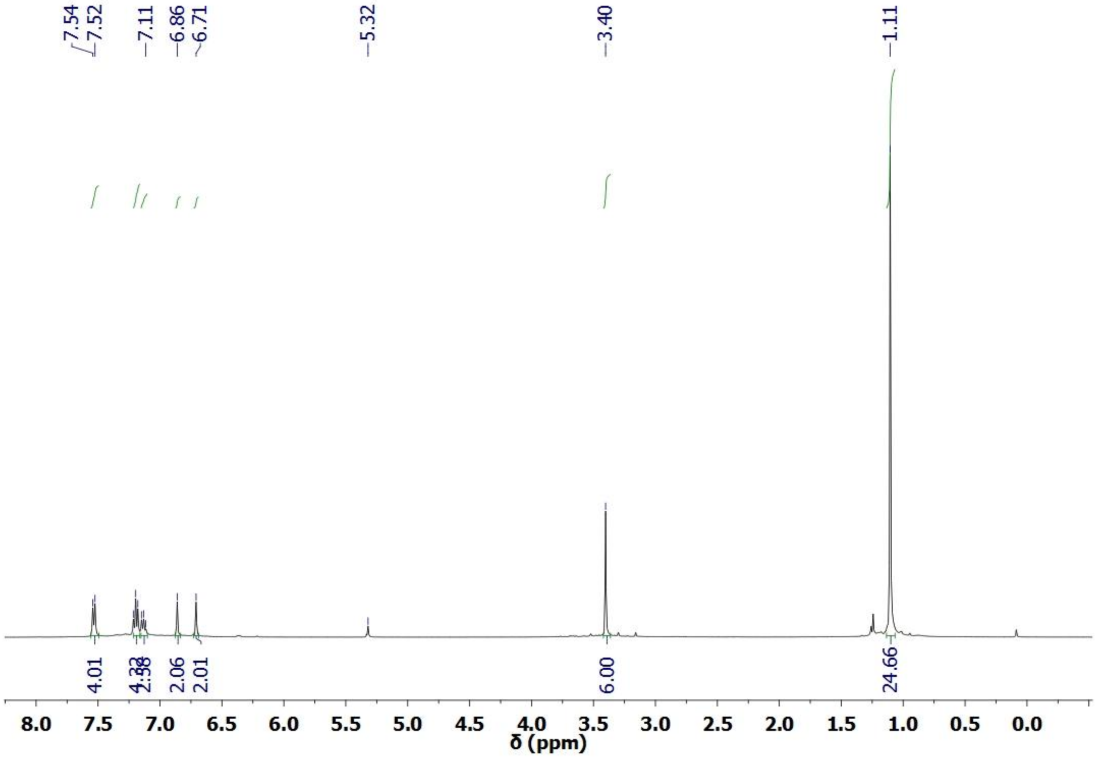


Figure S13 ^{1}H NMR spectrum (CD_2Cl_2) of **5**.

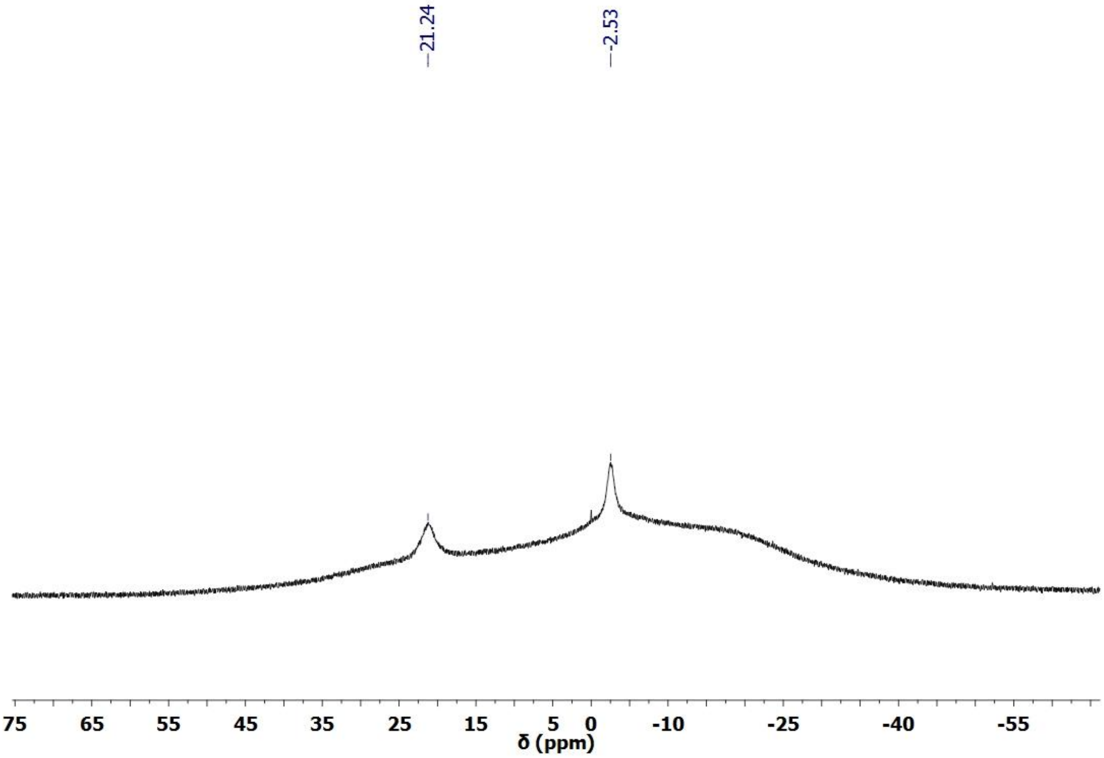


Figure S14 $^{11}B\{^1H\}$ NMR spectrum (CD_2Cl_2) of **5**.

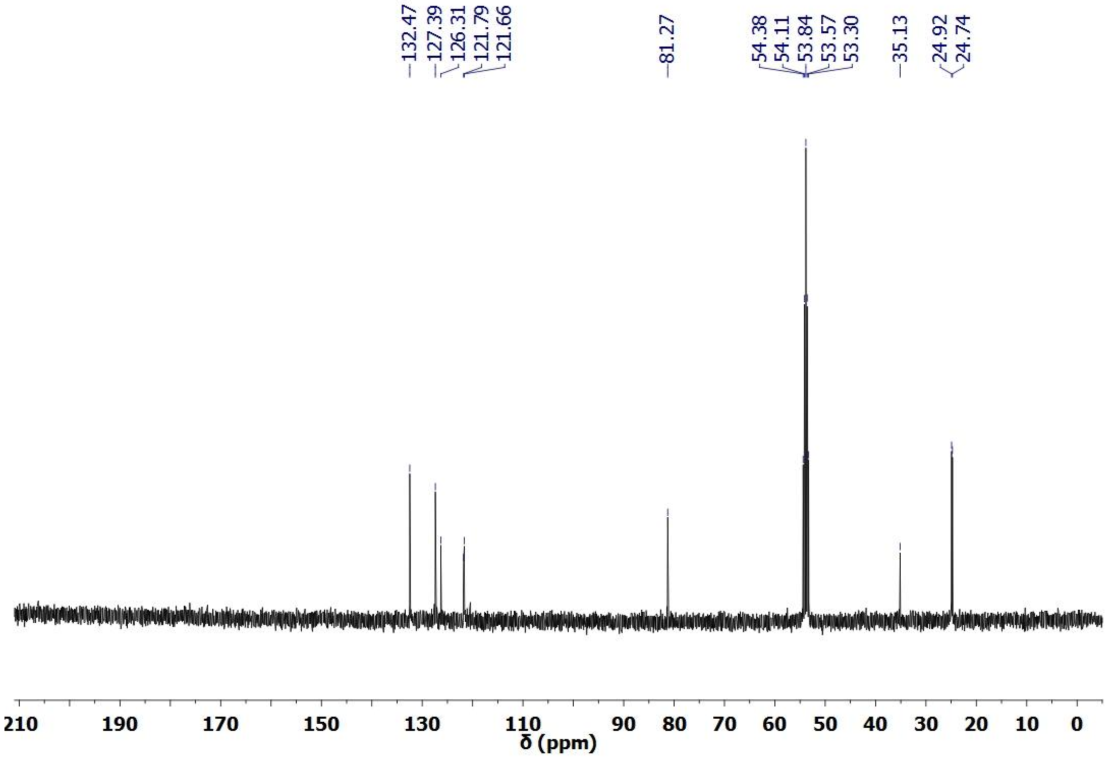
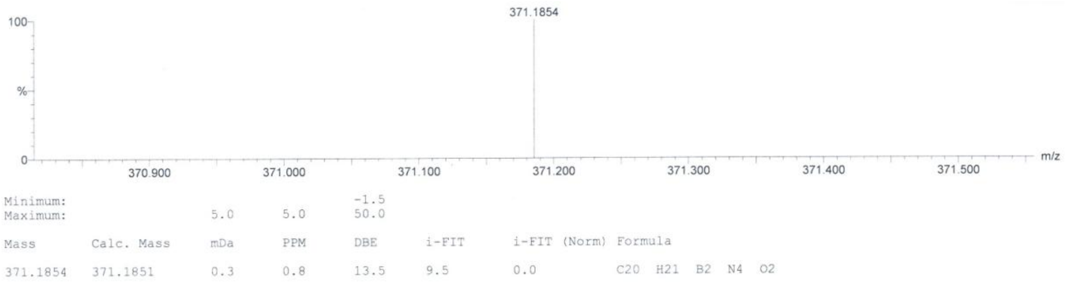


Figure S15 $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2) of **5**.



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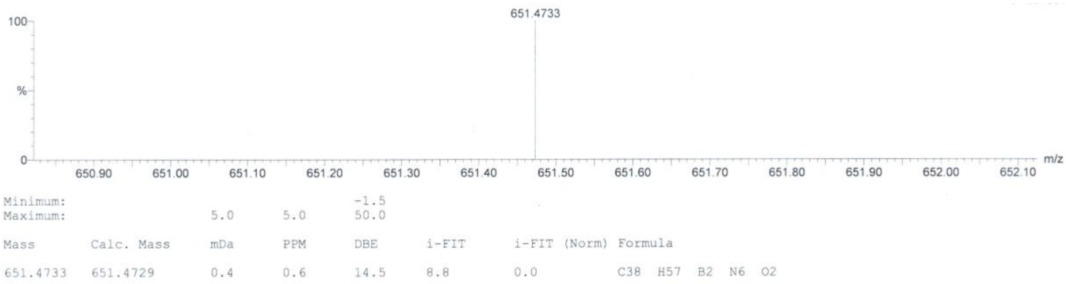
Minimum:                          -1.5
Maximum:              5.0    5.0    50.0

Mass      Calc. Mass   mDa    PPM    DBE     i-FIT      i-FIT (Norm) Formula

371.1854  371.1851     0.3    0.8    13.5    9.5        0.0          C20  H21  B2  N4  O2
```

Figure S16 HRMS spectrum of **2**.

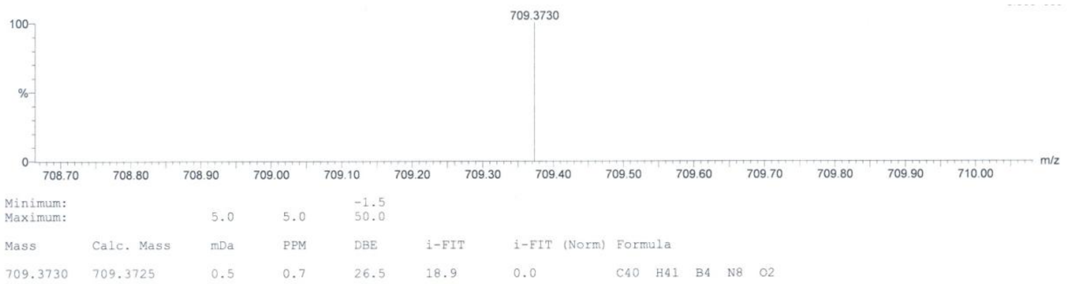


```
Minimum:                          -1.5
Maximum:              5.0    5.0    50.0

Mass      Calc. Mass   mDa    PPM    DBE     i-FIT      i-FIT (Norm) Formula

651.4733  651.4729     0.4    0.6    14.5    8.8        0.0          C38  H57  B2  N6  O2
```

Figure S17 HRMS spectrum of **3**.



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Minimum:                          -1.5
Maximum:              5.0    5.0    50.0

Mass      Calc. Mass   mDa    PPM    DBE     i-FIT      i-FIT (Norm) Formula

709.3730  709.3725     0.5    0.7    26.5    18.9       0.0          C40  H41  B4  N8  O2
```
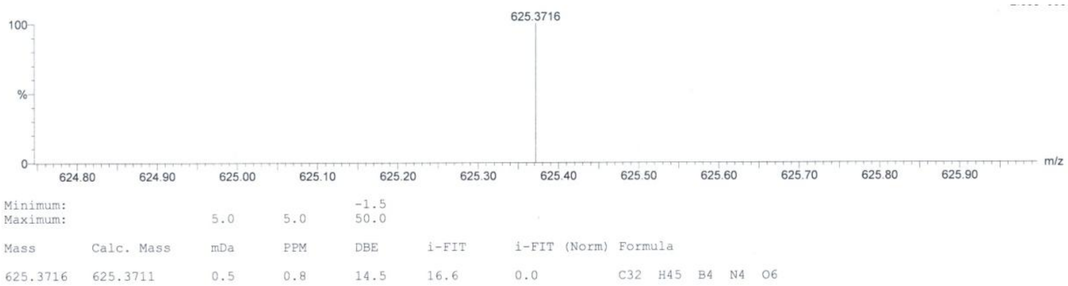

Figure S18 HRMS spectrum of **4**.



```
Minimum:                          -1.5
Maximum:              5.0    5.0    50.0

Mass      Calc. Mass   mDa    PPM    DBE     i-FIT      i-FIT (Norm) Formula

625.3716  625.3711     0.5    0.8    14.5    16.6       0.0          C32  H45  B4  N4  O6
```

Figure S19 HRMS spectrum of **5**.

2. Crystal structural parameters

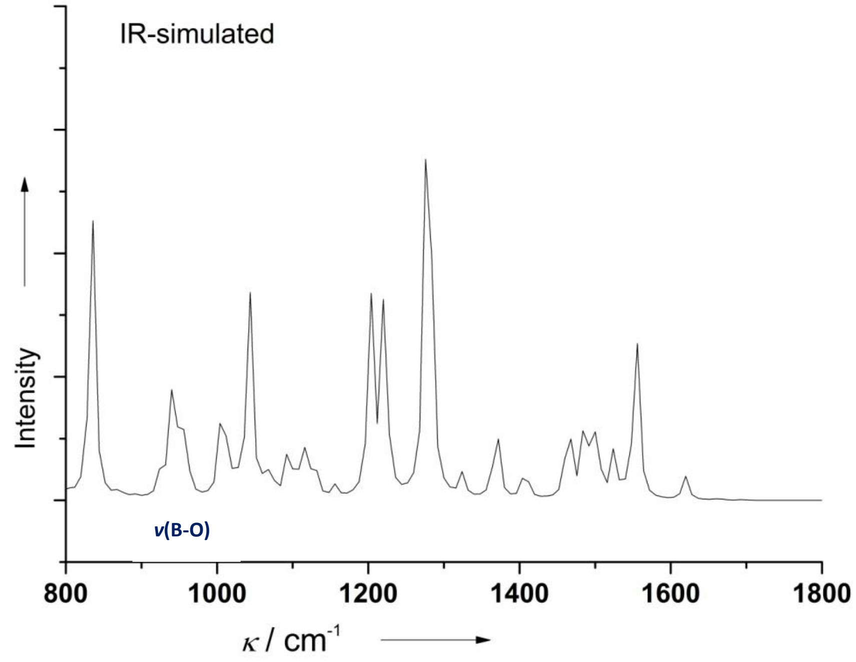
Crystallographic Methods: X-ray data collection and structural refinement. Intensity data for compounds **2**, **3**, **4** and **5** were collected using a Bruker APEX II diffractometer. The crystals of **2**, **3**, **4** and **5** were measured at 100(2) K, 103(2) K, 133(2) K and 153(2) K respectively. The structure was solved by direct phase determination (SHELXS-2014) and refined for all data by full-matrix least squares methods on F^2.[S2,S3] 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: 1873774-1873777 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.

Supplementary Table 1. Crystal data and structure refinement of **2-5**.

Compounds	**2·3CHCl$_3$**	**3**	**4·C$_2$H$_4$Cl$_2$**	**5**
Formula	$C_{23}H_{23}B_2Cl_9N_4O_2$	$C_{38}H_{56}B_2N_6O_2$	$C_{42}H_{44}B_4Cl_2N_8O_2$	$C_{16}H_{22}B_2N_2O_3$
Fw	728.12	650.50	806.99	311.97
Cryst syst	orthorhombic	monoclinic	triclinic	monoclinic
Space group	P n a 21	P 1 21/c 1	P -1	P 1 21/n 1
Size (mm^3)	0.140 x 0.220 x 0.300	0.020 x 0.040 x 0.320	0.100 x 0.120 x 0.140	0.020 x 0.040 x 0.380
T, K	100(2)	103(2)	133(2)	153(2)
a, Å	15.8691(3)	8.1816(5)	11.1827(2)	7.0474(3)
b, Å	12.5093(3)	26.3954(16)	13.5841(2)	10.6520(4)
c, Å	15.8466(4)	17.1380(11)	13.7474(2)	22.2574(9)
α, deg	90	90	83.0226(11)	90
β, deg	90	99.443(4)	81.9334(10)	90.2535(8)
γ, deg	90	90	86.2235(11)	90
V, Å^3	3145.73(12)	3650.9(4)	2049.82(6)	1670.82(12)
Z	4	4	2	4
d_{calcd} g·cm^{-3}	1.537	1.183	1.307	1.240 g

μ, mm^{-1}	0.831	0.568	1.799	0.669
Refl collected	30057	24967	26046	13205
T_{max}/T_{min}	0.8920/0.7890	0.9890/0.8390	0.8410/0.7870	0.9870 /0.7850
N_{measd}	9277	6292	7187	2937
[R_{int}]	0.0912	0.0946	0.0630	0.0723
R [I>2sigma(I)]	0.0556	0.0810	0.0713	0.0537
R_w[I>2sigma(I)]	0.0842	0.2053	0.1888	0.1327
GOF	1.037	1.086	1.049	1.073
Largest diff. peak/hole[e·Å^{-3}]	0.431/-0.469	0.375/-0.346	1.492/-1.001	0.314/ -0.278

3. IR and Raman spectra of 2.



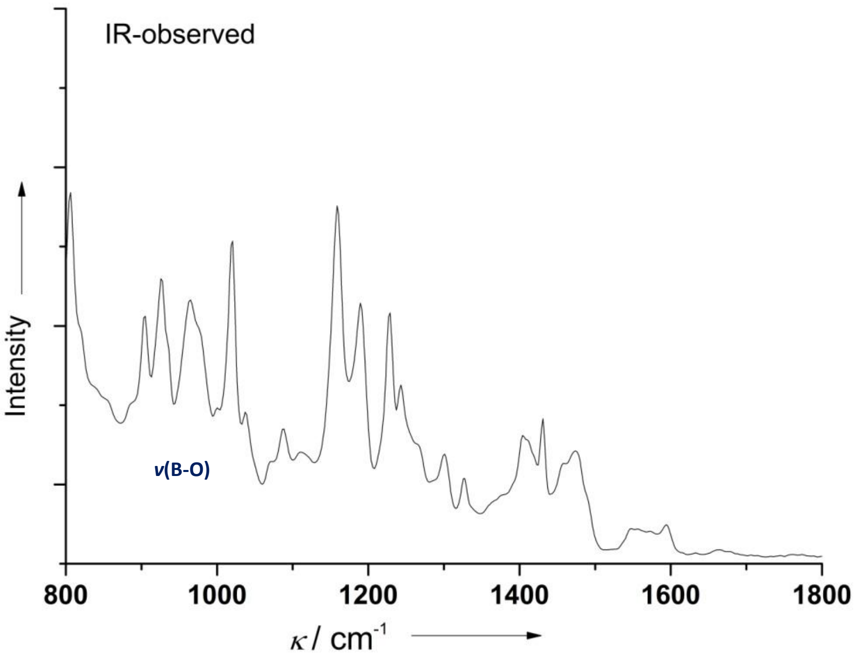
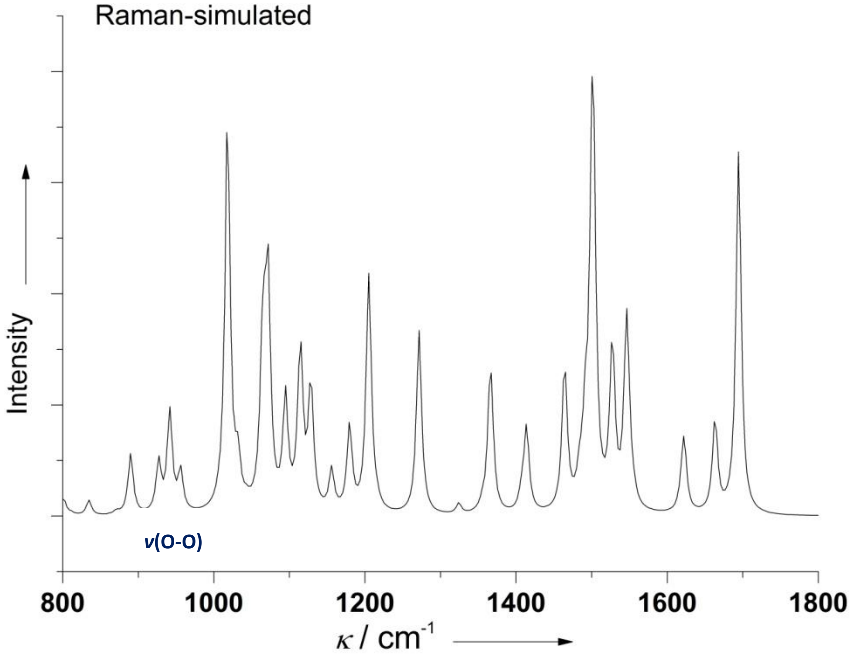


Figure S20 Solid-state IR spectra (top: simulated; bottom: observed) of **2**.



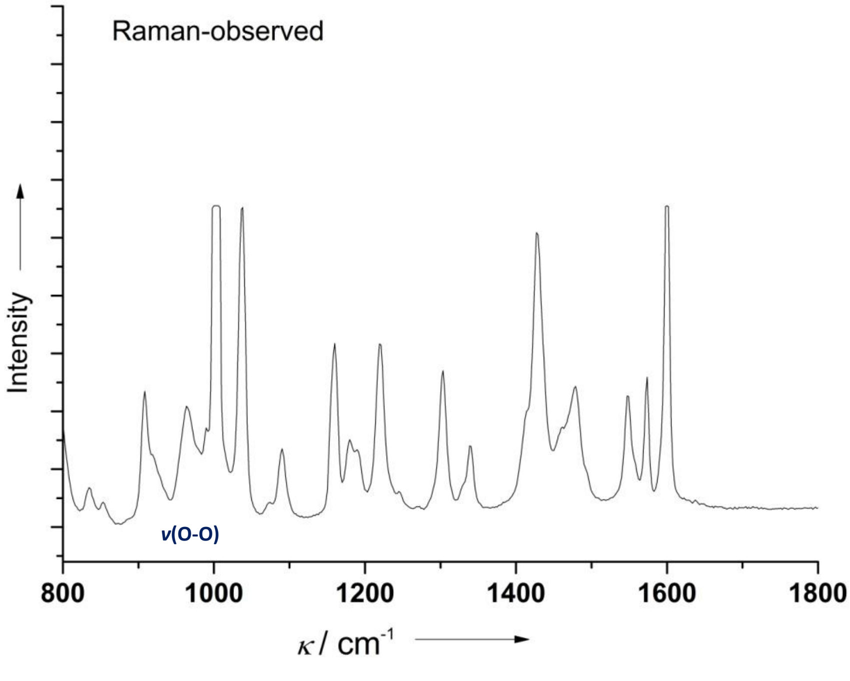
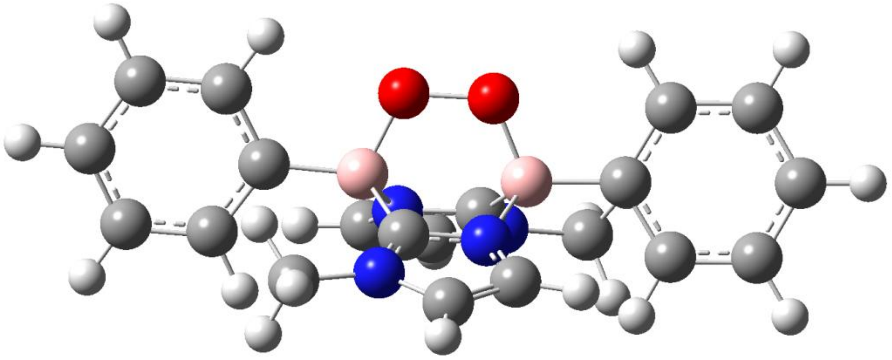


Figure S21 Simulated Raman spectrum (top, at the M062X/6-31G(d,p) level of DFT) and the observed Raman spectrum (bottom, on a quartz plate upon excitation at 532 nm) .

4. Theoretical calculation

Gaussian 09[S4] was used for all density functional theory (DFT) calculations including geometry optimization, frequency calculation. Optimization, frequency, Raman calculations for **2** were performed at the M062X/6-31G(d,p) level of theory.

Optimized structure of 2 (atom, x-, y-, z-positions in Å)



Zero-point correction= 0.385520 (Hartree/Particle)
Thermal correction to Energy= 0.408741
Thermal correction to Enthalpy= 0.409685
Thermal correction to Gibbs Free Energy= 0.331923
Sum of electronic and zero-point Energies= -1192.576495
Sum of electronic and thermal Energies= -1192.553274
Sum of electronic and thermal Enthalpies= -1192.552330
Sum of electronic and thermal Free Energies= -1192.630092

Supplementary Table 2. Calculated geometries of dication part of **2** (atom, x-, y-, z-positions in Å)

B	1.31648871	-0.10198618	0.34659022
C	0.72987628	1.22978535	-0.40495644
C	-0.99058701	2.53561181	-0.89207330
H	-2.02782543	2.82027261	-0.97333126
C	0.14558598	3.23600906	-1.16213354
H	0.29673612	4.23181156	-1.54661869
C	2.61476843	2.77151596	-0.95745174
H	3.02889016	2.41710727	-1.90388415
H	3.17045023	2.32047482	-0.13602910
H	2.69889942	3.85740240	-0.90506413
C	2.90044594	-0.26400439	0.42048166
C	3.66337092	-0.47390600	-0.73727492
H	3.16007097	-0.54792685	-1.70193507
C	5.05116681	-0.58080709	-0.68541610
H	5.62041400	-0.74563645	-1.59577814
C	5.70735258	-0.47418038	0.53917231
H	6.78912973	-0.55501380	0.58666681
C	4.96861616	-0.26453587	1.70108252
H	5.47629337	-0.18225611	2.65775240
C	3.57998776	-0.16242916	1.63968727
H	3.00176187	-0.00222455	2.54542234
N	-0.60562557	1.29955092	-0.43780082

N	1.20826301	2.40987653	-0.84234965
O	0.71715500	-0.09149527	1.67931975
N	0.60562091	-1.29957527	-0.43781100
B	-1.31649397	0.10195772	0.34659275
O	-0.71715719	0.09145667	1.67932118
C	-0.72988275	-1.22981610	-0.40496257
C	0.99058679	-2.53563483	-0.89208208
C	-2.90044883	0.26400148	0.42048863
N	-1.20826373	-2.40990362	-0.84237613
H	2.02782608	-2.82029366	-0.97333521
C	-0.14558267	-3.23603964	-1.16213650
C	-3.66336044	0.47402590	-0.73725533
C	-3.57999953	0.16235433	1.63968320
C	-2.61476253	-2.77154882	-0.95752911
H	-0.29672858	-4.23184633	-1.54661288
H	-3.16005170	0.54811336	-1.70190523
C	-5.05115303	0.58096282	-0.68539505
C	-4.96862533	0.26449662	1.70107897
H	-3.00178289	0.00206130	2.54540817

5. References

S1 B. Wang, Y. Li, R. Ganguly, H. Hirao and R. Kinjo, *Nat. Commun.*,2016, **7**, 11871.

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