Electronic Supplementary Material (ESI) for Chemical Communications.

Bicyclic (amino)(borata)carbene derived from diazadiborinine

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Table of Contents

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

2. Crystal structural parameters

3. Theoretical calculations

4. References

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. ^{1}H, ^{11}B, ^{13}C NMR spectra were obtained with a Bruker AVIII 400MHz BBFO 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.

Synthesis of 2

A deuterated benzene (0.6 mL) solution of 1,4,2,5-diazadiborinine **1**[S1] (20 mg, 0.06 mmol) was added phenyl isocyanide (12.2 mg, 0.12 mmol) in a Young NMR tube. The reaction was monitored by NMR. After 10 minutes at room temperature, all volatiles were removed under vacuum, and recrystallization from a benzene solution afforded colorless single crystals of **2**, which were collected and dried under vacuum (15 mg, 47%).

M. p.(219 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (dd, *J* = 7.9, 1.4 Hz, 2H, Ar-*H*), 8.01 (dd, *J* = 6.5, 3.0 Hz, 2H, Ar-*H*), 7.59 – 7.49 (m, 3H, Ar-*H*), 7.33 (m, 4H, Ar-*H*), 7.24 – 7.21 (m, 1H, Ar-*H*), 7.10 (dd, *J* = 8.4, 7.3 Hz, 2H), 6.99 (d, *J* = 1.6 Hz, 1H, C*H*), 6.85 – 6.79 (m, 2H, Ar-*H*), 6.68 – 6.59 (m, 3H, Ar-*H*), 6.56 (d, *J* = 1.6 Hz, 1H, C*H*), 6.41 (d, *J* = 1.6 Hz, 1H, C*H*), 6.36 (d, *J* = 1.6 Hz, 1H, C*H*), 5.47 (s, 1H, N*H*), 3.47 (s, 3H, N-CH_3), 3.01 (s, 3H, N-CH_3); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 148.7 (Ar-*C*), 141.2 (Ar-*C*), 136.1 (Ar-*C*H), 135.8 (Ar-*C*H), 129.2 (Ar-*C*), 128.8 (Ar-*C*H), 128.0 (Ar-*C*H), 127.9 (Ar-*C*H), 127.8 (Ar-*C*H), 127.0 (Ar-*C*H), 121.9 (Ar-*C*H), 121.6 (Ar-*C*), 121.4 (Ar-*C*H), 120.0 (Ar-*C*H), 119.9 (Ar-*C*H), 119.3 (*C*H), 118.6 (*C*H), 116.9 (*C*H), 116.6 (*C*H), 114.1 (Ar-*C*H), 113.9 (Ar-*C*H), 36.6 (*C*H_3), 35.5 (*C*H_3); $^{11}B\{H\}$ NMR (128 MHz, $CDCl_3$): δ = – 3.0 (br), – 6.8 (br). HRMS (ESI): *m/z* calcd for $C_{34}H_{31}B_2N_6$: 545.2796 $[(M+H)]^+$; found: 545.2787.

Synthesis of 3

Deuterated benzene (0.5 mL) was added to the mixture of 1,4,2,5-diazadiborinine **1** (20 mg, 0.06 mmol) and 2,6-dimethylphenyl isocyanide (15.5 mg, 0.12 mmol) in a Young NMR tube. The reaction was monitored by NMR. After 10 minutes at room temperature, recrystallization from a benzene solution afforded yellow single crystals of **3**, which were collected and dried under vacuum (18 mg, 51%).

M. p.(198 °C).^{1}H NMR (400 MHz, C_6D_6): δ = 8.18 – 8.12 (m, 2H, Ar-*H*), 7.37 (t, *J* = 7.3 Hz, 2H, Ar-*H*), 7.30 – 7.24 (m, 3H, Ar-*H*), 7.16 (m, 3H, Ar-*H*), 7.06 (s, 3H, Ar-*H*), 6.89 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 6.81 (m, 3H, C*H*, Ar-*H*), 5.73 (d, *J* = 1.5 Hz, 1H, C*H*), 5.67 (d, *J* = 1.6 Hz, 1H, C*H*), 2.54 (s, 3H, N-CH_3), 2.44 (s, 3H, N-CH_3), 2.09 (s, 6H, CH_3), 1.92 (s, 3H, CH_3), 1.84 (s, 3H, CH_3); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ = 207.1 (C*C*N), 148.9 (Ar-*C*), 144.2 (Ar-*C*), 139.6 (Ar-*C*), 138.6 (Ar-*C*), 135.5 (Ar-*C*H), 134.2 (Ar-*C*H), 131.0 (Ar-*C*), 128.5 (Ar-*C*H), 128.22 (Ar-*C*H), 128.20 (Ar-*C*H), 128.16 (Ar-*C*H), 128.1 (Ar-*C*H), 127.3 (Ar-*C*H), 127.0 (Ar-*C*H), 125.0 (Ar-*C*H), 123.8 (Ar-*C*H), 120.8 (*C*H), 120.6 (*C*H), 119.8 (*C*H), 119.3 (*C*H), 34.9 (N-*C*H_3), 34.6 (N-*C*H_3), 19.6 (*C*H_3), 19.2 (*C*H_3), 18.1 (*C*H_3); ^{11}B{H} NMR (128 MHz, C_6D_6): δ = – 4.2 (br), – 6.9 (br); HRMS (ESI): *m/z* calcd for $C_{38}H_{39}B_2N_6$: 601.3422 [(*M+H*)]$^{+}$; found: 601.3414.

Synthesis of 4

A THF (1 mL) solution of 1,4,2,5-diazadiborinine **1** (30 mg, 0.089 mmol) was added *p*-methyl phenyl(phenyl isocyanide)gold(I)[S2] (34.7 mg, 0.089 mmol) at room temperature. The orange color of **1** fades within 5 minutes. Recrystallization from a THF solution afforded colorless crystals of **4**, which were collected and dried under vacuum (39 mg, 60%).

M. p.:128 °C (dec.). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 9.04 (d, *J* = 6.8 Hz, 2H, Ar-*H*), 7.55 (t, *J* = 7.5 Hz, 2H, Ar-*H*), 7.47 – 7.37 (m, 2H, Ar-*H*), 7.34 (t, *J* = 7.4 Hz, 1H, Ar-*H*), 7.30 – 7.16 (m, 7H, Ar-*H*), 7.10 (d, *J* = 1.6 Hz, 1H, C*H*), 7.02 (d, *J* = 7.7 Hz, 2H, Ar-*H*), 6.96 (d, *J* = 7.4 Hz, 1H, Ar-*H*), 6.90 (d, *J* = 1.6 Hz, 1H, C*H*), 6.85 (d, *J* = 7.3 Hz, 2H, Ar-*H*), 6.65 (d, *J* = 1.6 Hz, 1H, C*H*), 6.64 (d, *J* = 1.6 Hz, 1H, C*H*), 3.21 (s, 3H, N-CH_3), 3.06 (s, 3H, N-CH_3), 2.21 (s, 3H, CH_3); ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): δ = 170.6 (Ar-*C*), 154.6 (Ar-*C*), 141.1 (Ar-*C*H), 137.5 (Ar-*C*H), 135.1 (Ar-*C*H), 133.1 (Ar-*C*), 129.0 (Ar-*C*H), 128.4 (Ar-*C*H), 128.21 (Ar-*C*H), 128.20 (Ar-*C*H),127.62 (Ar-*C*H), 127.57 (Ar-*C*H), 127.5 (Ar-*C*H),

126.6 (Ar-*C*H), 126.4 (Ar-*C*H), 125.9 (Ar-*C*H), 122.4 (*C*H), 122.0 (*C*H), 121.7 (*C*H), 121.2 (*C*H), 36.16 (N-*C*H_3), 35.6 (N-*C*H_3), 21.3 (N-*C*H_3); $^{11}B\{H\}$ NMR (128 MHz, CD_2Cl_2): δ = – 3.1 (br), – 5.8 (br). HRMS (ESI): *m/z* calcd for $C_{27}H_{25}AuB_2N_5$: 638.1962[(*M*-C_7H_7)]$^+$; found: 638.1968.

Synthesis of 5

A dichloromethane (0.6 mL) solution of **4** (25 mg, 0.034mmol) was added HCl (ether solution, 2M, 18μL) at room temperature. After 5 minutes at room temperature, all volatiles were removed under vacuum to afford **5** as a grey solid (15 mg, 65%).

M. p.: 151 °C (dec). ^1H NMR (400 MHz, CD_2Cl_2): δ = 8.74 (d, *J* = 7.1 Hz, 2H, Ar-*H*), 7.54 (t, *J* = 7.4 Hz, 2H, Ar-*H*), 7.43 (dd, *J* = 14.8, 7.5 Hz, 2H, Ar-*H*), 7.36 (t, *J* = 7.4 Hz, 1H, Ar-*H*), 7.28-7.22 (m, 4H, Ar-*H*), 7.17 (d, *J* = 1.4 Hz, 1H, C*H*), 7.13-7.08 (m, 3H, Ar-*H*), 6.85-6.82 (m, 2H, Ar-*H* ×1, C*H* ×1), 6.72 (s, 1H, C*H*), 6.66 (s, 1H, C*H*), 3.24 (s, 3H, N-CH_3), 3.03 (s, 3H, N-CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ = 155.0 (Ar-*C*), 136.6 (Ar-*C*H), 134.9 (Ar-*C*H), 129.5 (Ar-*C*H), 128.8 (Ar-*C*H), 128.4 (Ar-*C*H), 128.3 (Ar-*C*H), 127.9 (Ar-*C*H), 127.8 (Ar-*C*H), 127.3 (Ar-*C*H), 125.9 (Ar-*C*H), 125. (Ar-*C*H), 122.6 (*C*H), 122.4(*C*H), 122.0 (*C*H), 121.6 (*C*H), 36.4 (N-*C*H_3), 35.6 (N-*C*H_3); $^{11}B\{^1H\}$ NMR (128 MHz, CD_2Cl_2): δ = –2.7 (br), –6.2 (br). HRMS (ESI): *m/z* calcd for $C_{27}H_{25}AuB_2N_5$: 638.1962[(*M*-*Cl*)]$^+$; found: 638.1964.

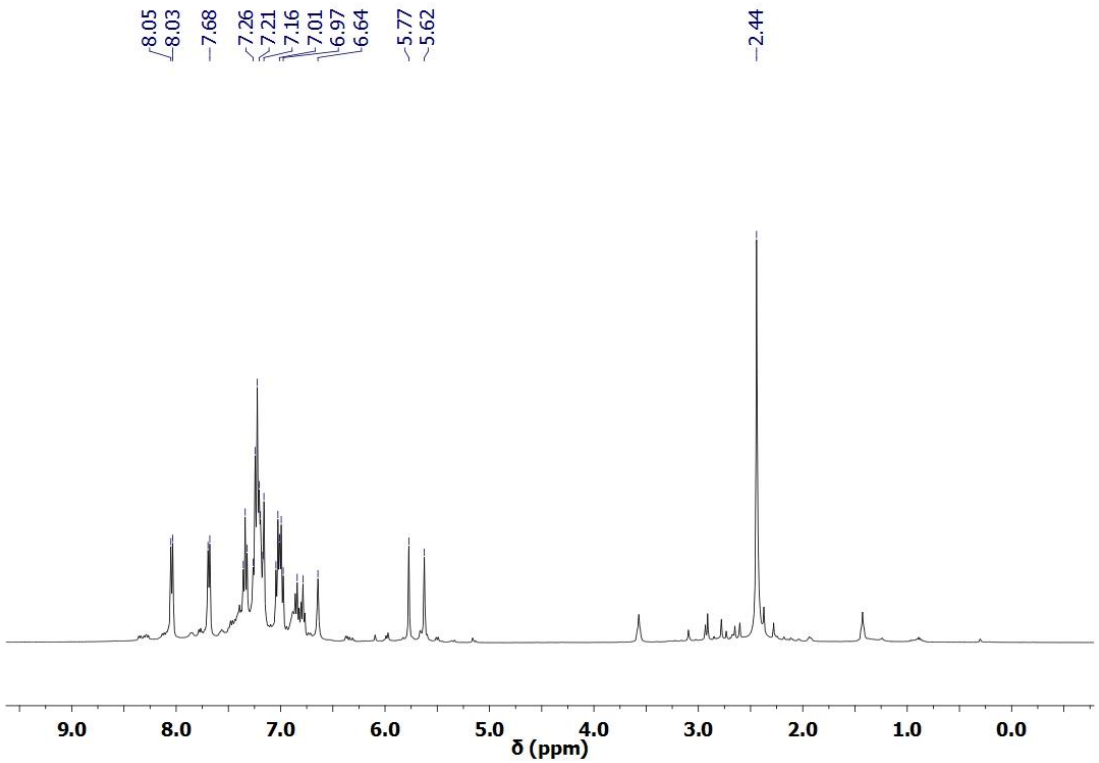


Figure S1 Crude ^{1}H NMR spectrum (C_6D_6) of the reaction of **1** with two equivalents of phenyl isonitrile, indicating the formation of initial product.

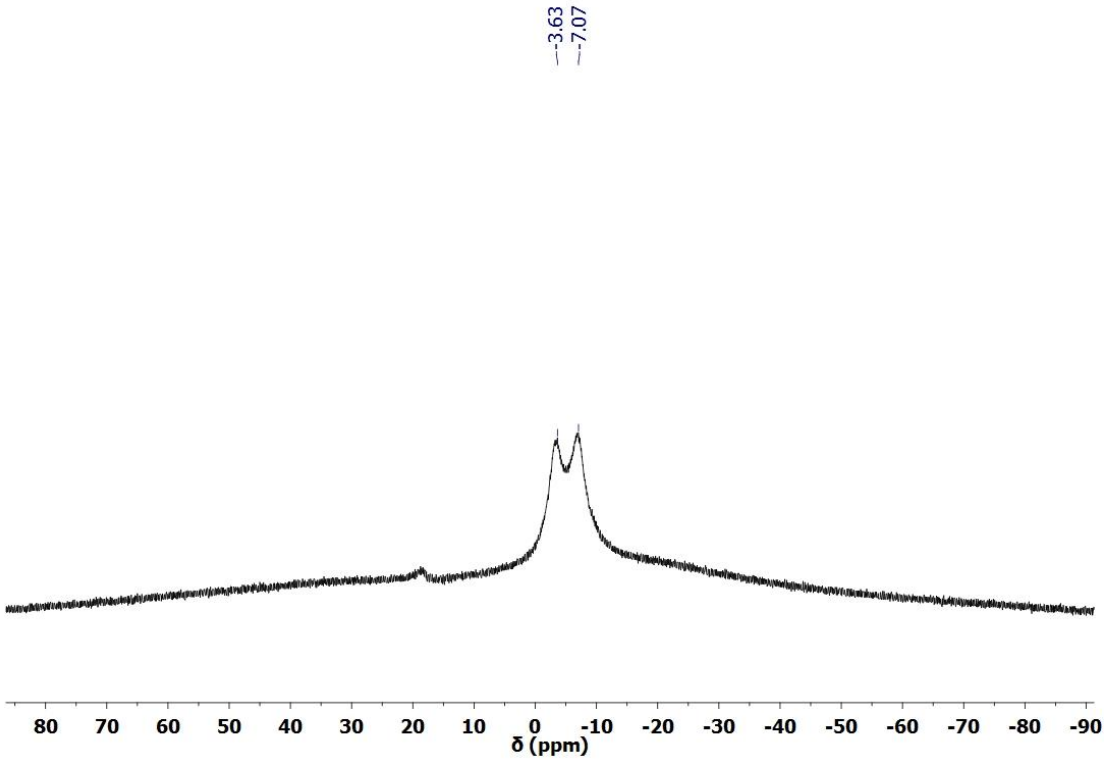


Figure S2 Crude ^{11}B NMR spectrum (C_6D_6) of the reaction of **1** with two equivalents of phenyl isonitrile, indicating the formation of initial product

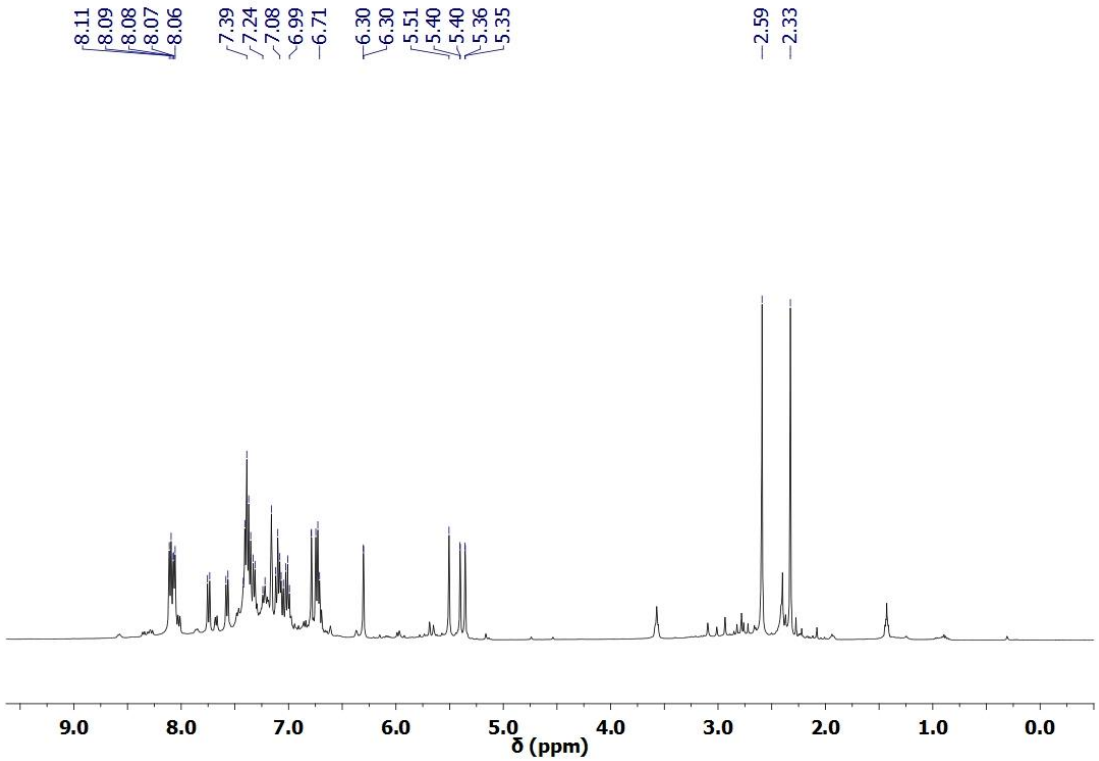


Figure S3 Crude ^{1}H NMR spectrum (C_6D_6) of the reaction mixture of **1** and two equivalents of phenyl isonitrile, after 48 hours at room temperature.

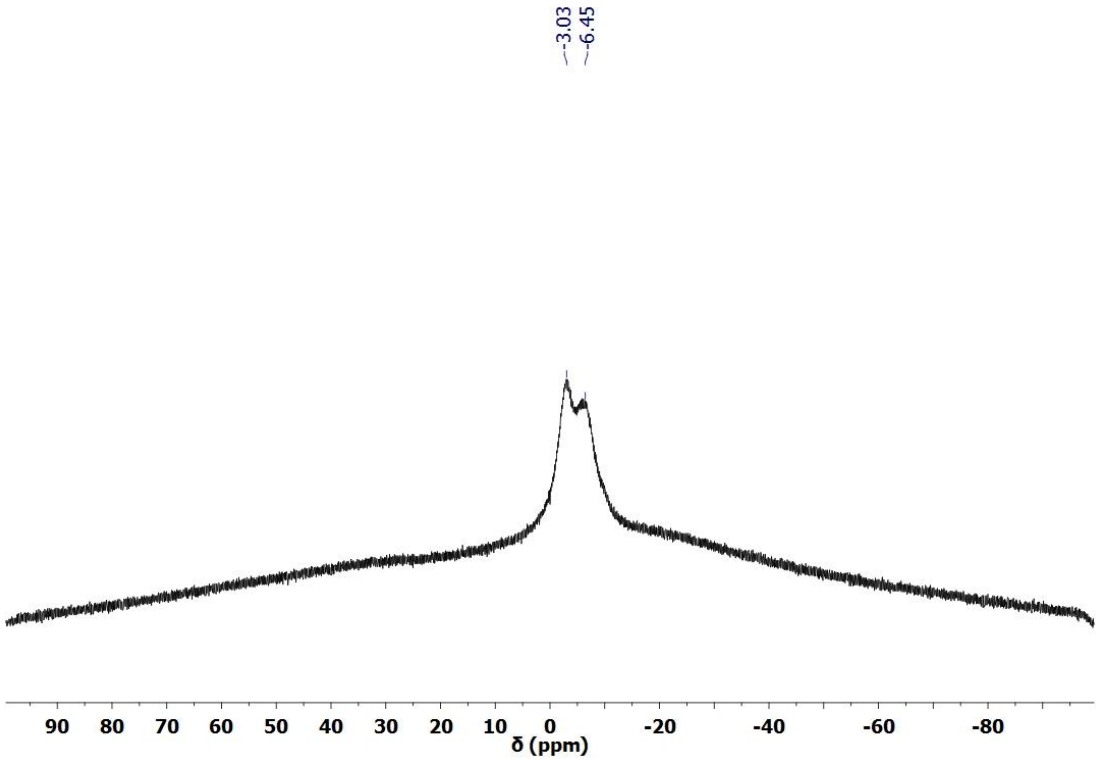


Figure S4 Crude ^{11}B NMR spectrum (C_6D_6) of the reaction mixture of **1** and two equivalents phenyl isonitrile, after 48 hours at room temperature.

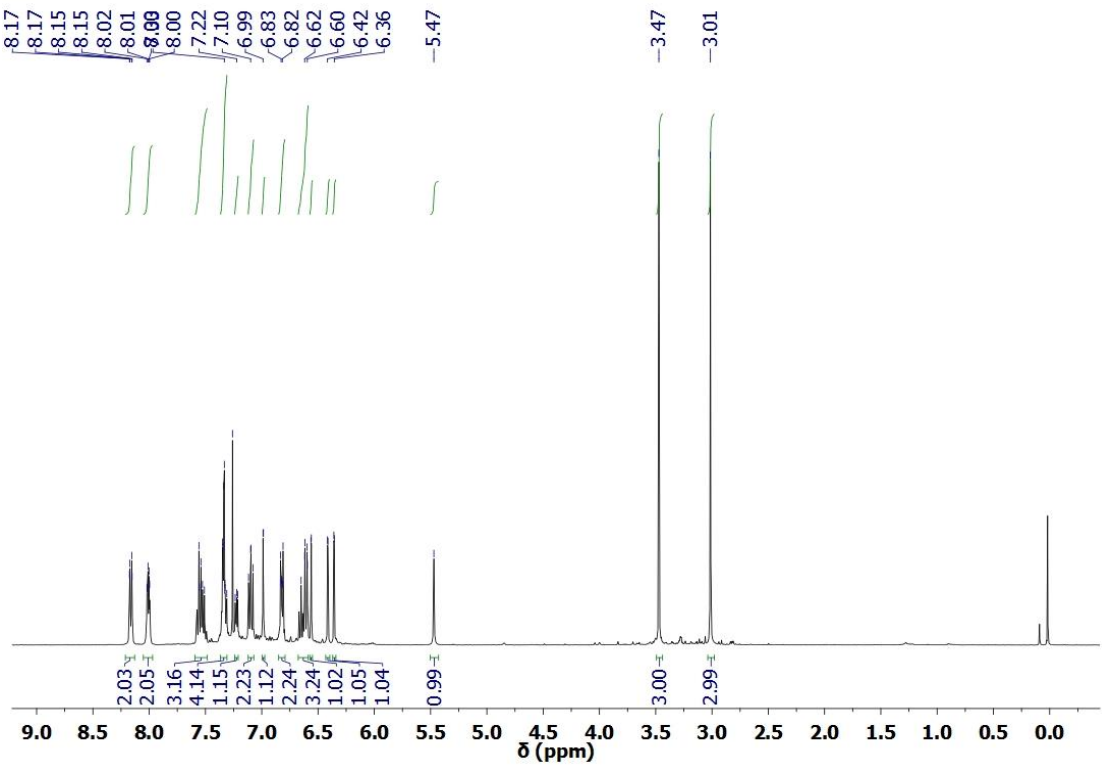


Figure S5 ^{1}H NMR spectrum ($CDCl_3$) of **2**.

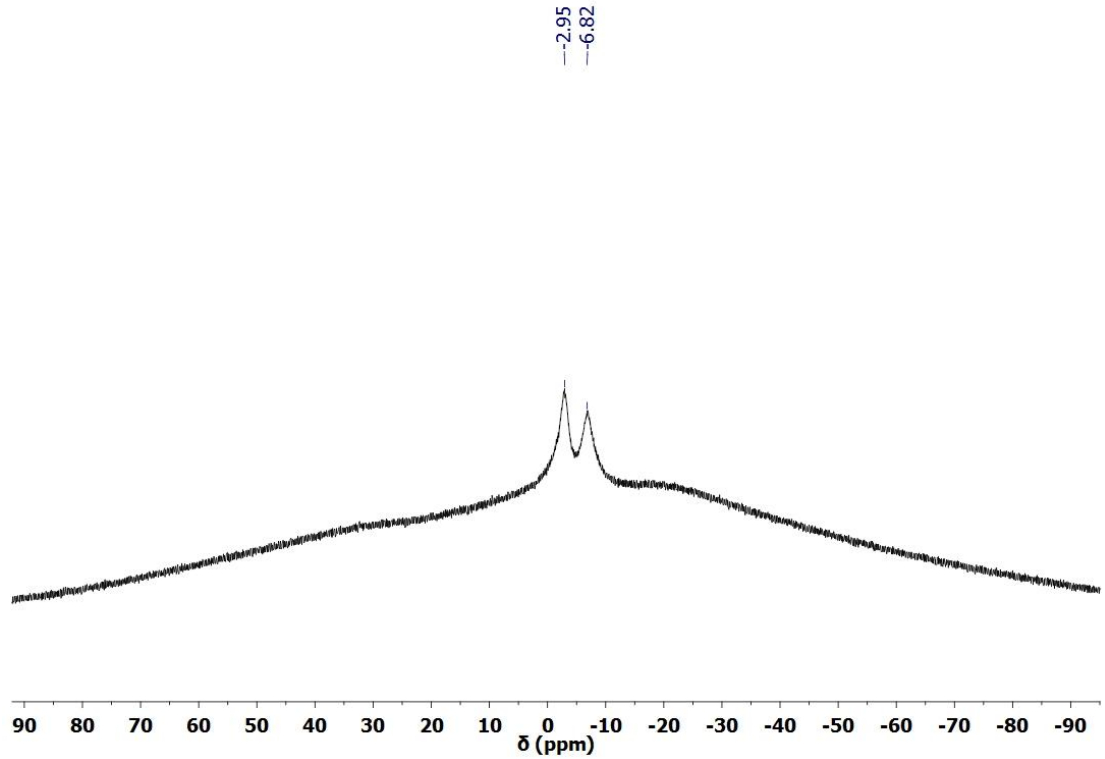


Figure S6 $^{11}B\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **2**.

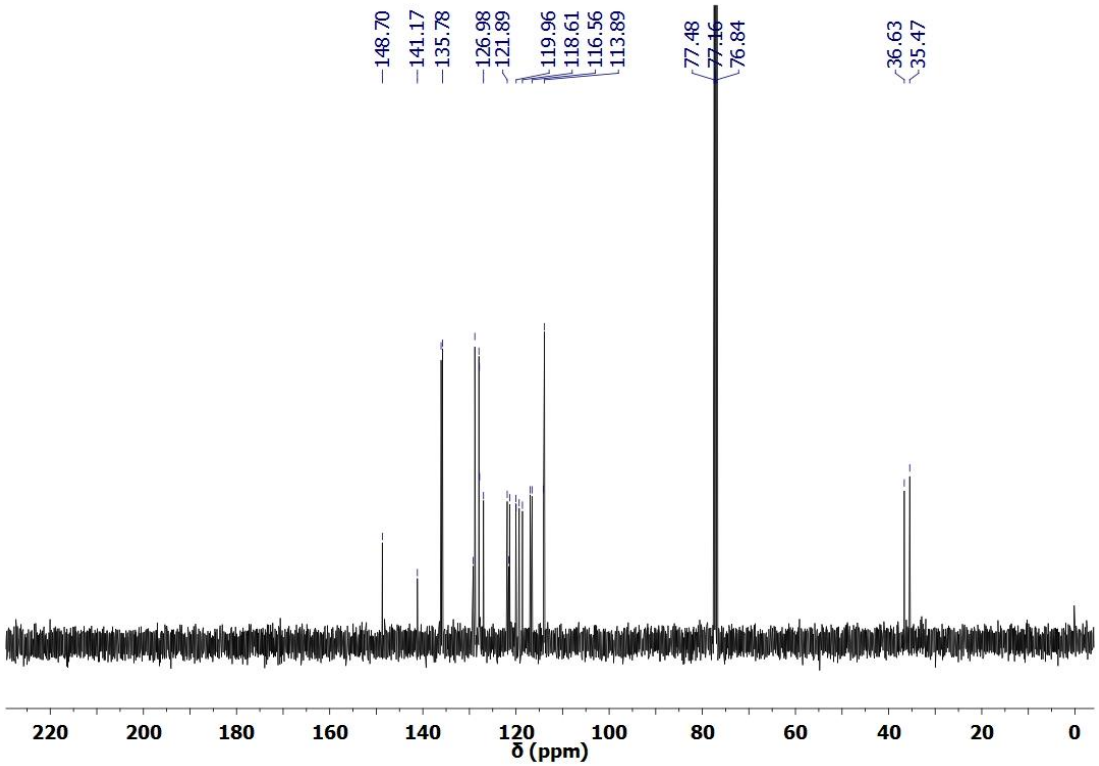


Figure S7 $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **2**.

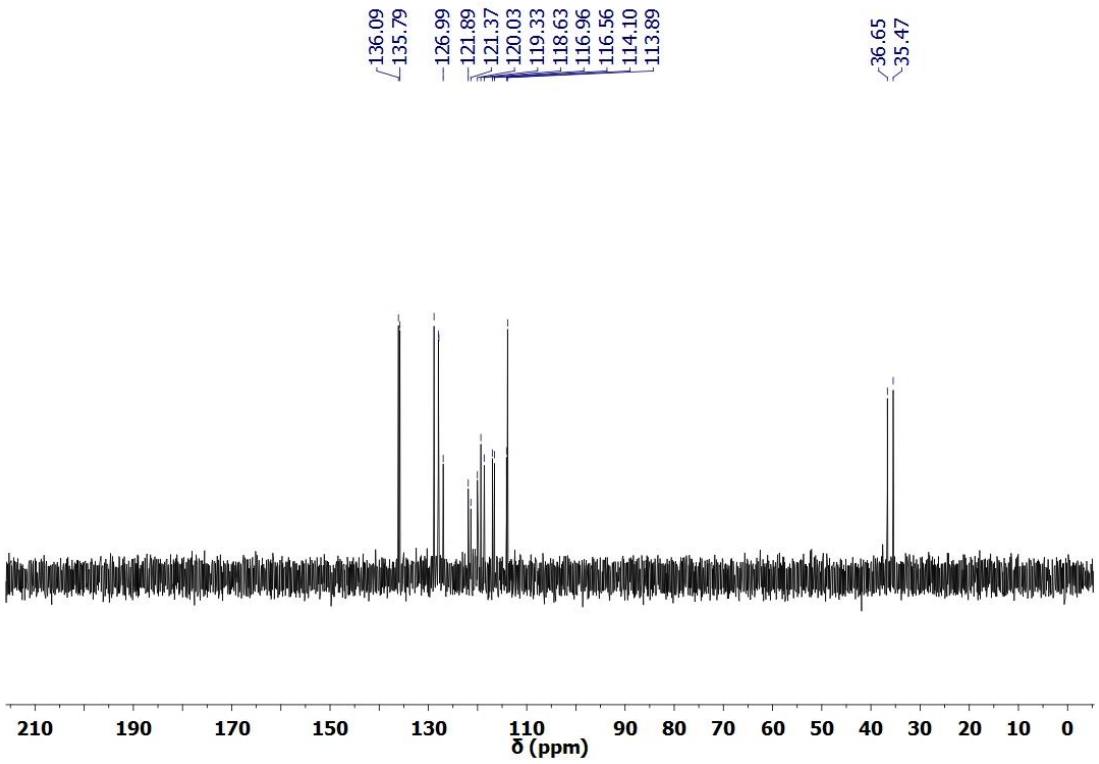


Figure S8 ^{13}C DEPT 135 NMR spectrum ($CDCl_3$) of **2**.

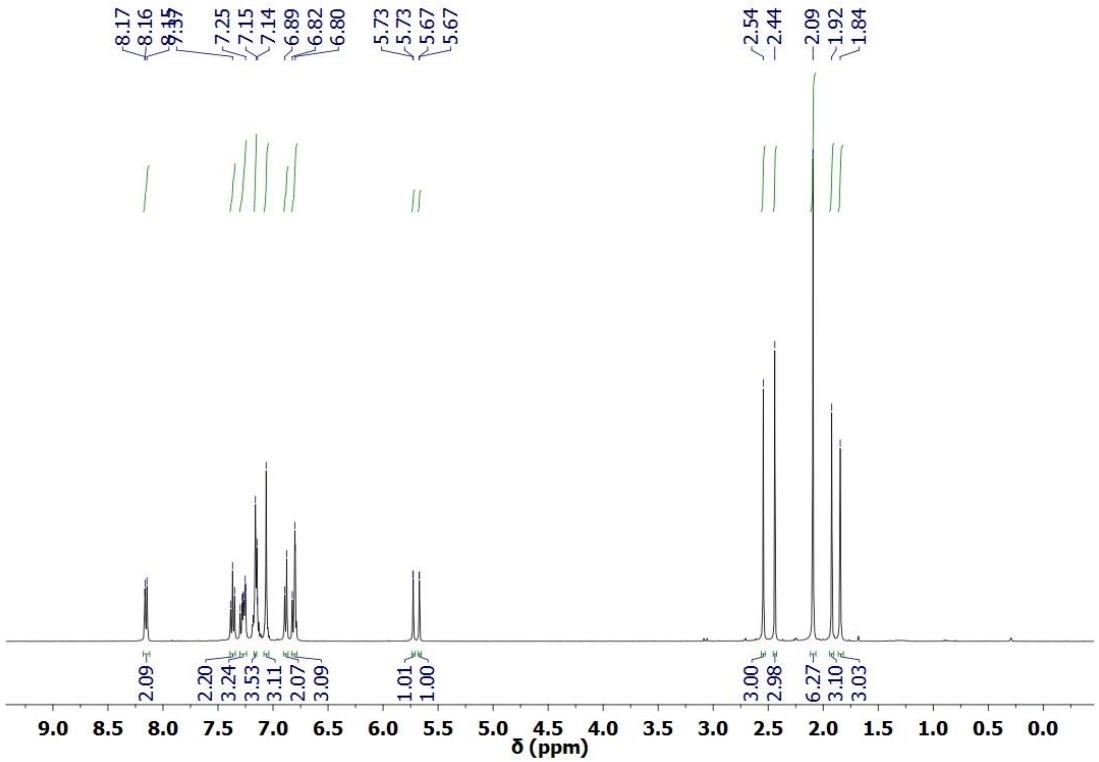


Figure S9 ^{1}H NMR spectrum (C_6D_6) of **3**.

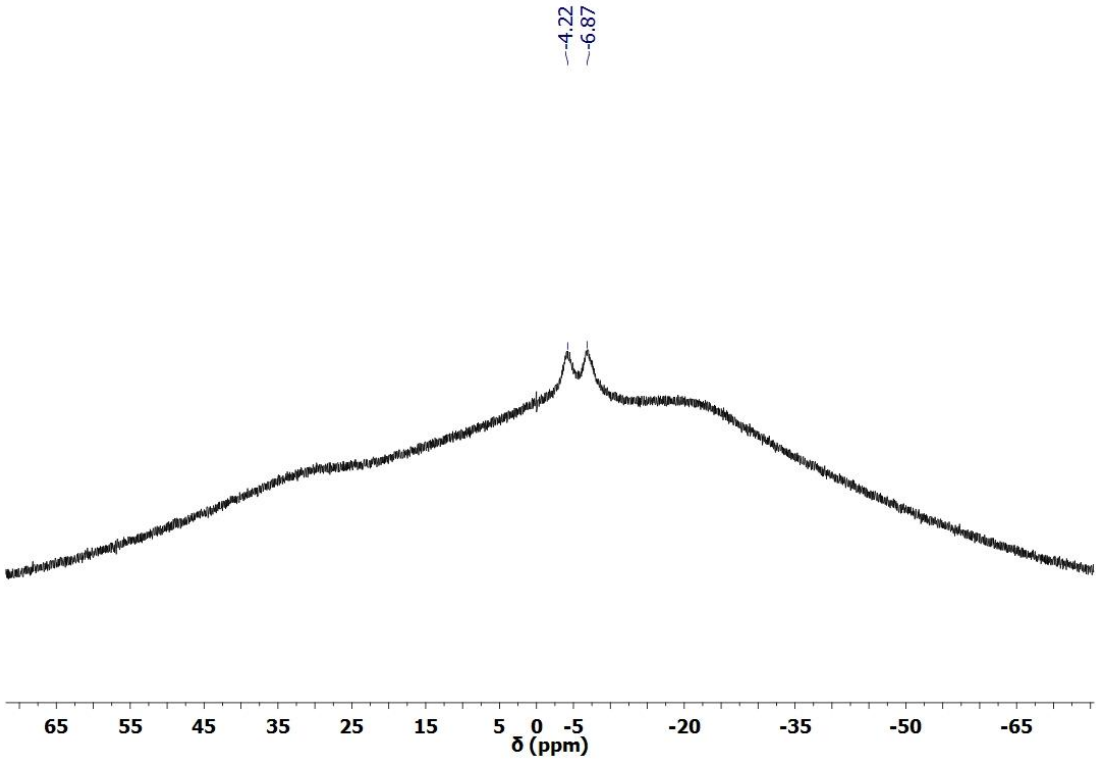


Figure S10 $^{11}B\{^{1}H\}$ NMR spectrum (C_6D_6) of **3**.

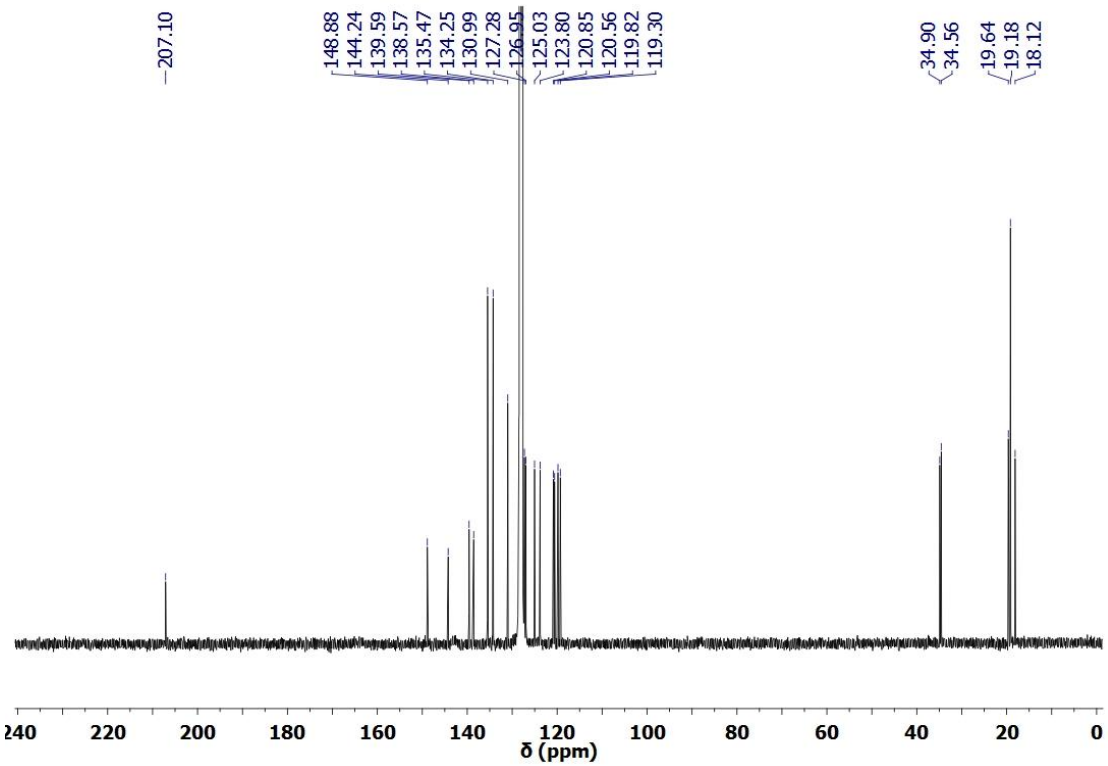


Figure S11 $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6) of **3**.

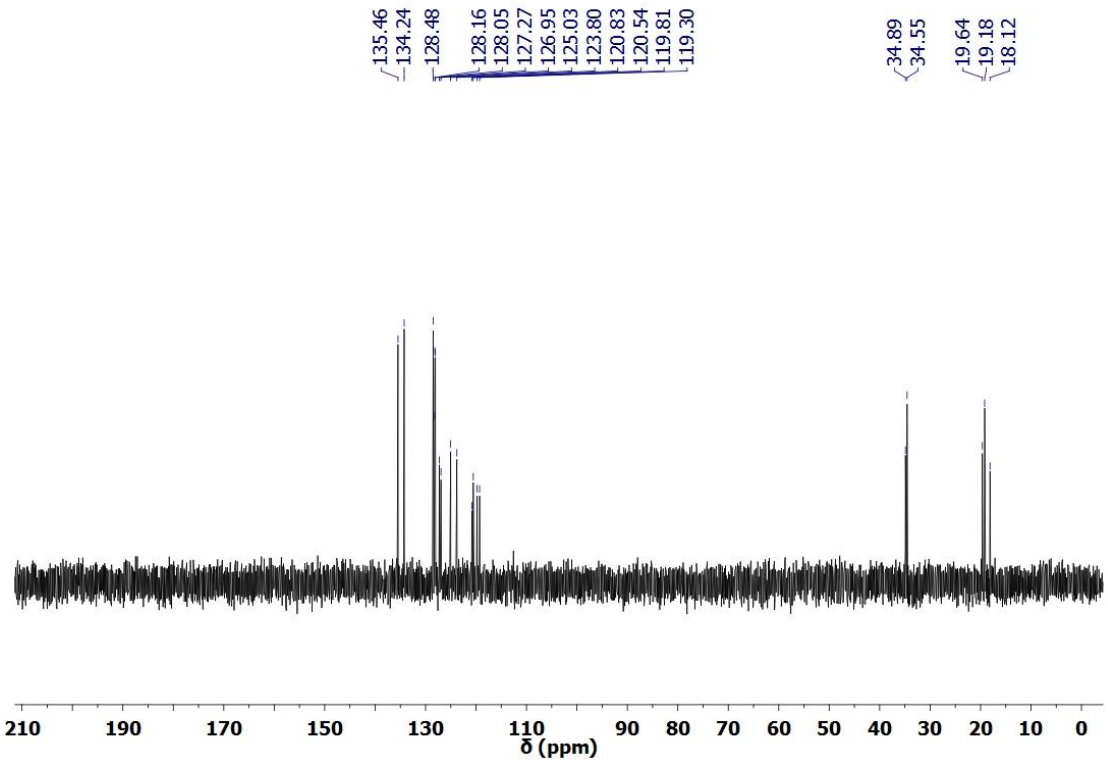


Figure S12 ^{13}C DEPT 135 NMR spectrum (C_6D_6) of **3**.

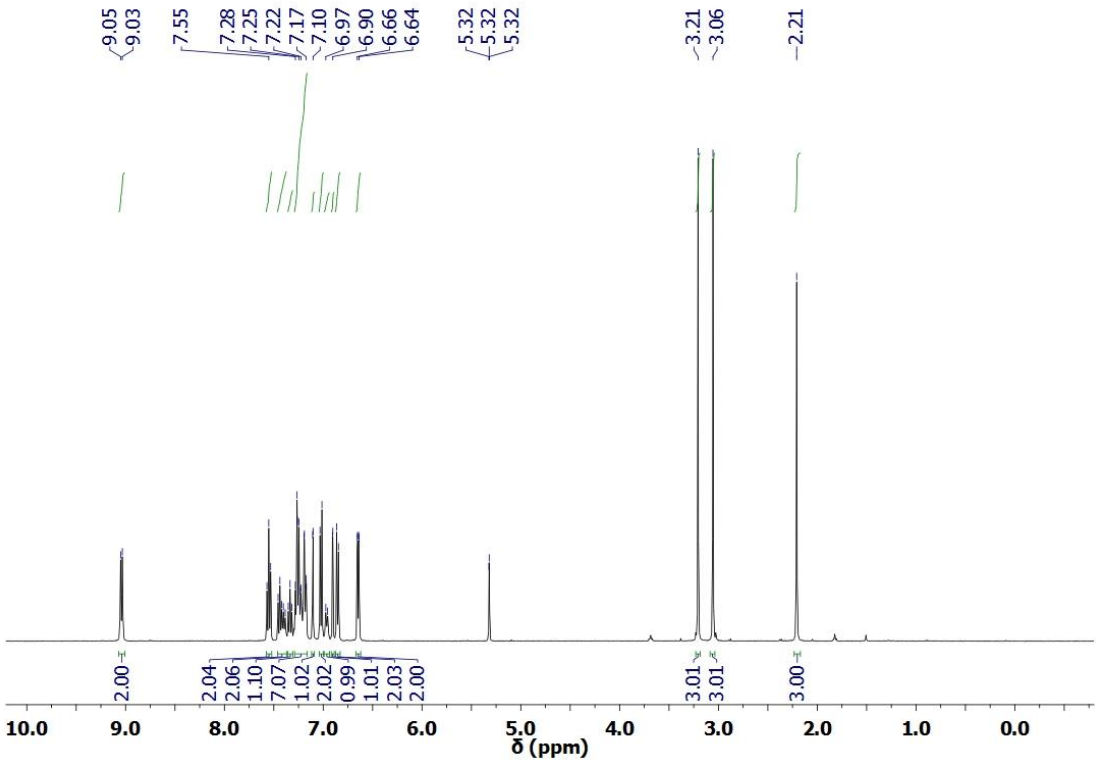


Figure S13 ^{1}H NMR spectrum (CD_2Cl_2) of **4**.

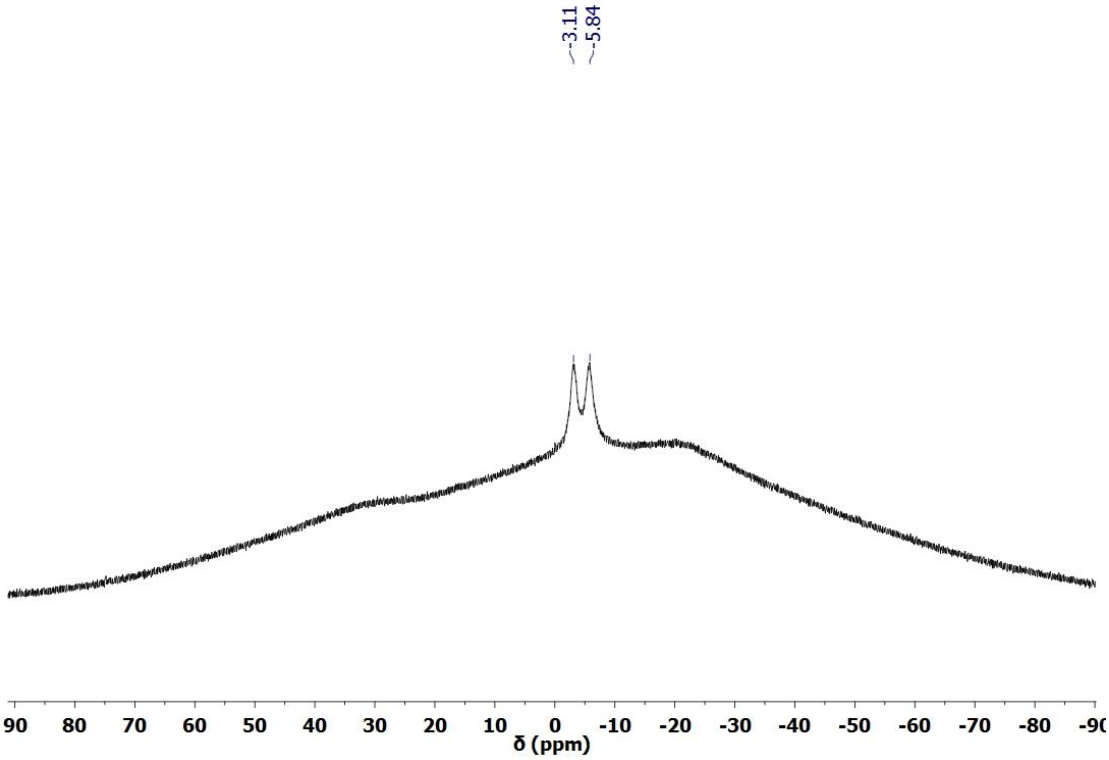


Figure S14 $^{11}B\{^{1}H\}$ NMR spectrum (CD_2Cl_2) of **4**.

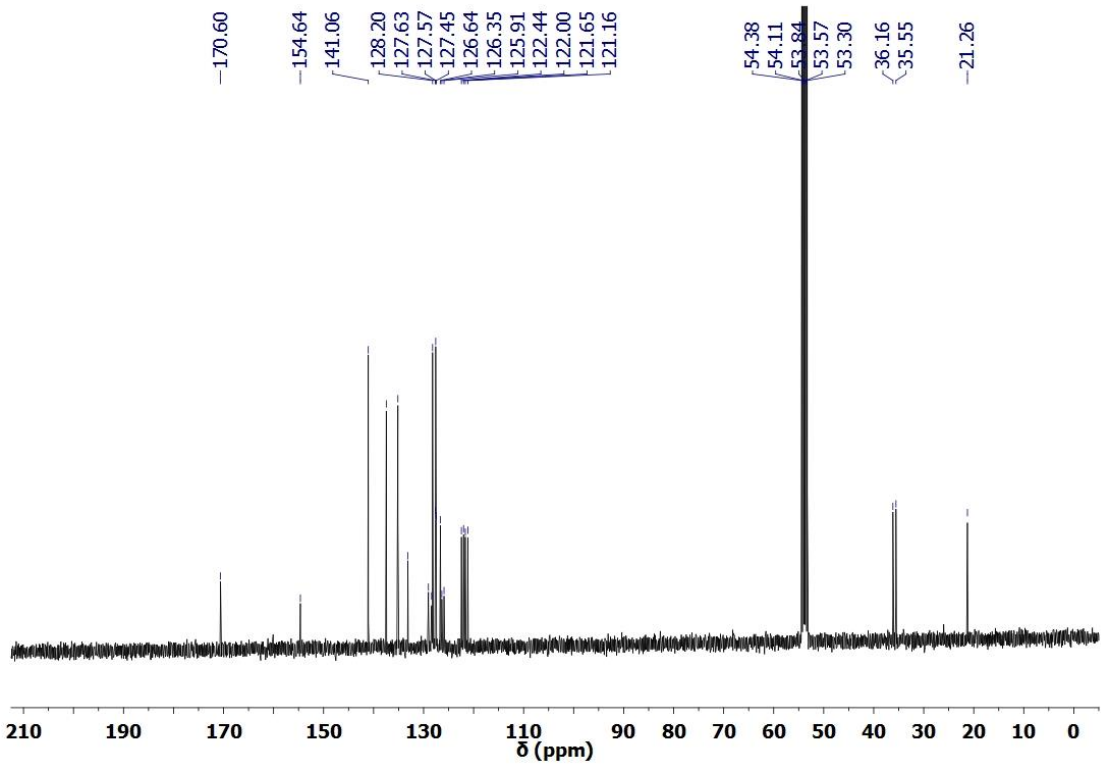


Figure S15 $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2) of **4**.

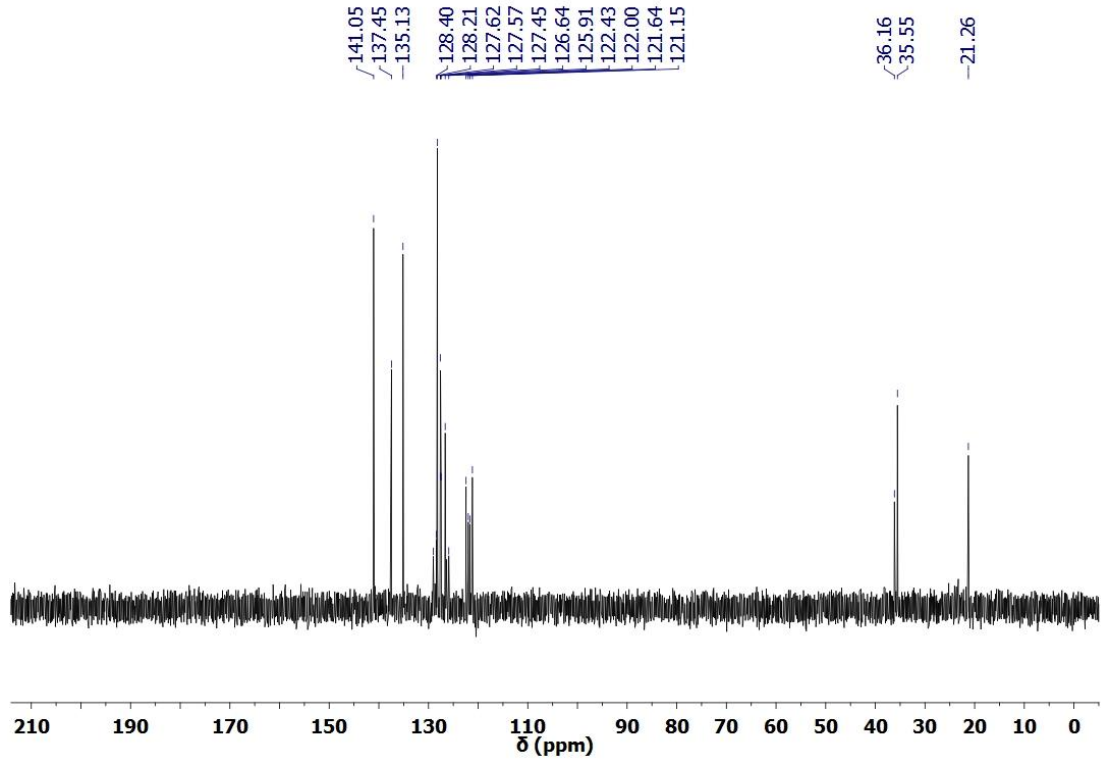


Figure S16 ^{13}C DEPT 135 NMR spectrum (CD_2Cl_2) of **4**.

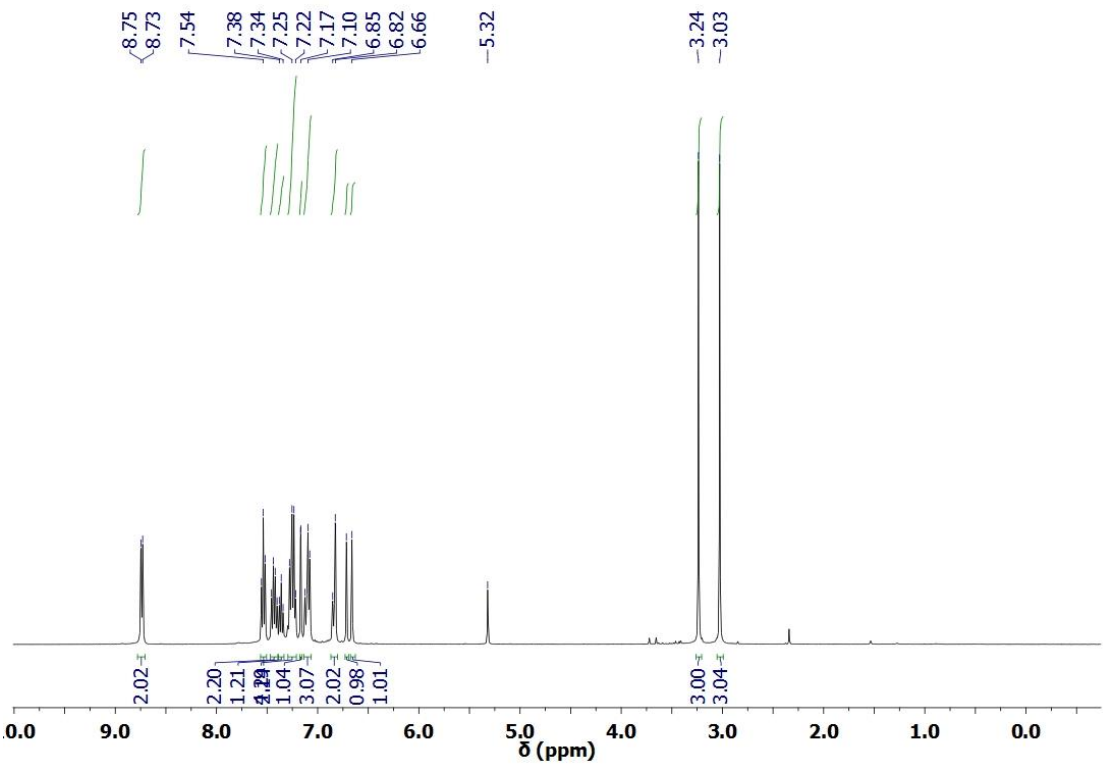


Figure S17 ^{1}H NMR spectrum (CD_2Cl_2) of **5**.

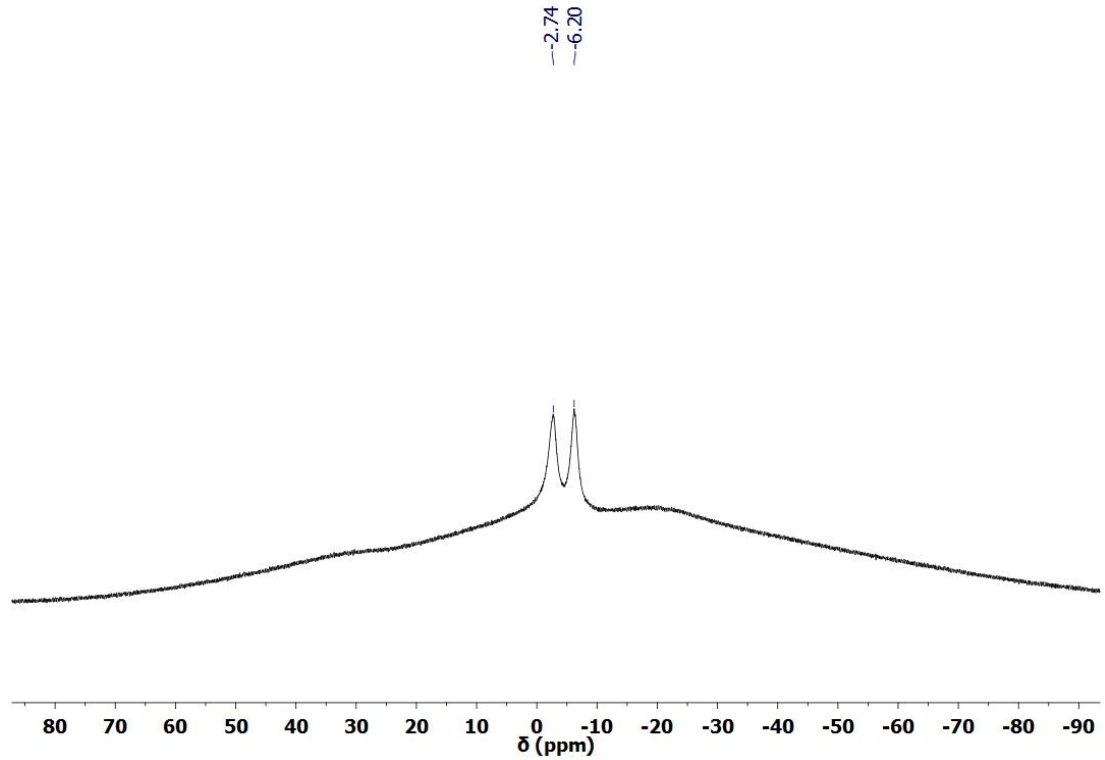


Figure S18 $^{11}B\{^{1}H\}$ NMR spectrum (CD_2Cl_2) of **5**.

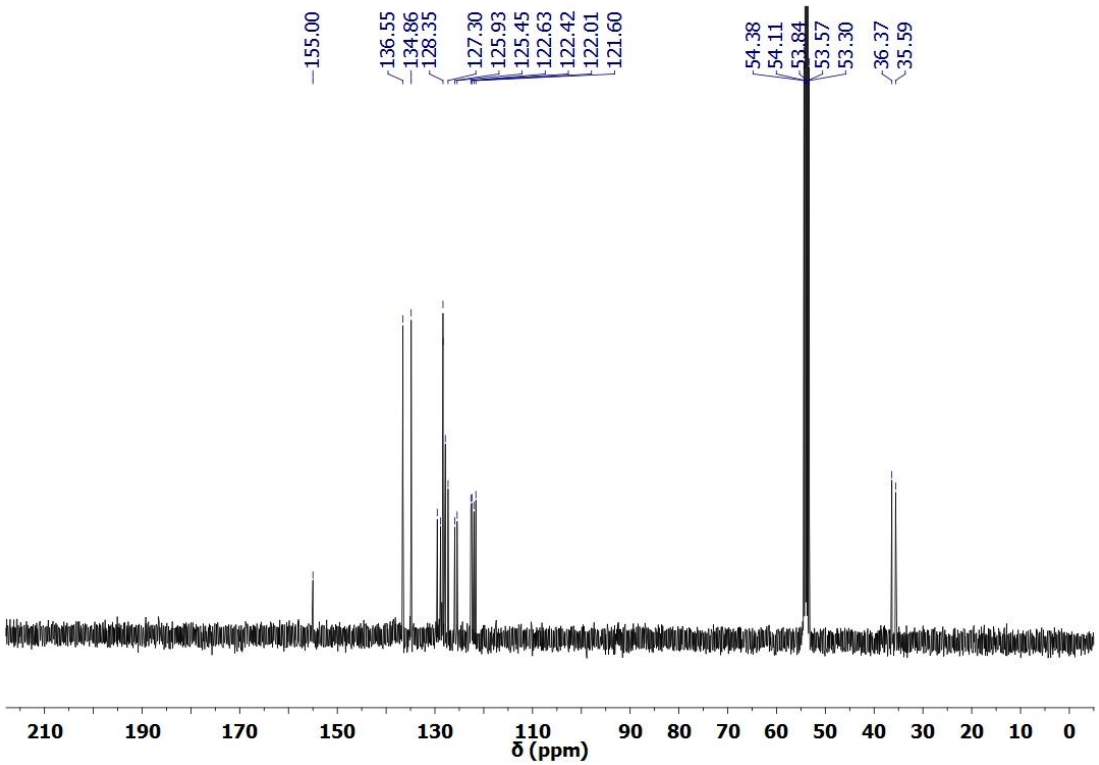


Figure S19 $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2) of **5**.

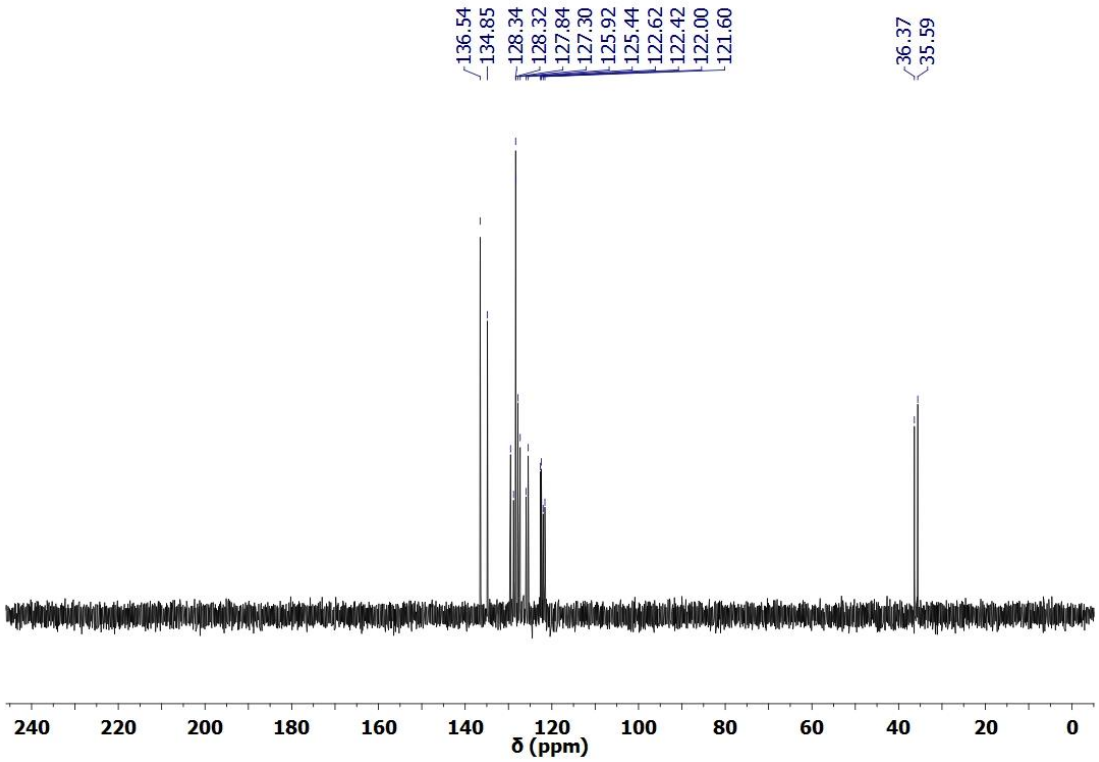
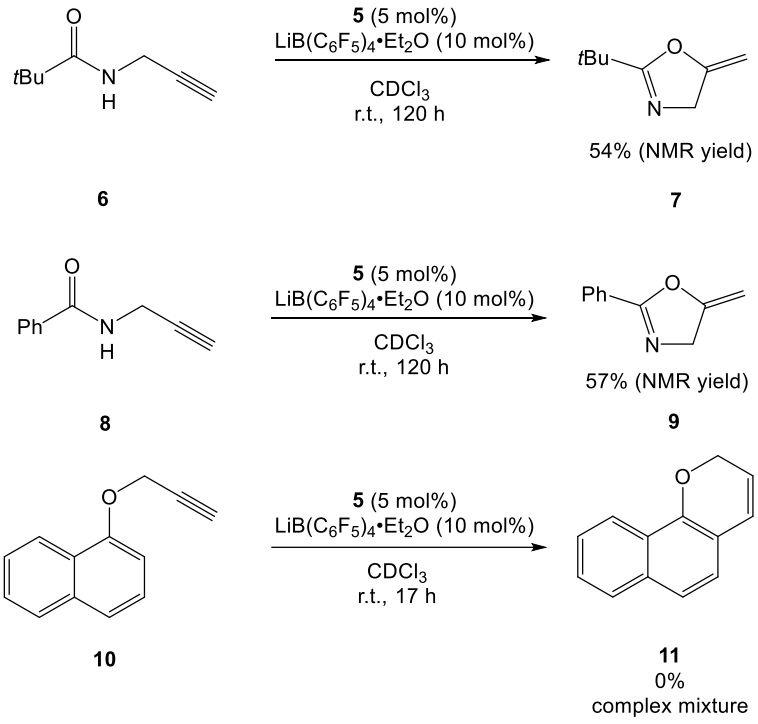


Figure S20 ^{13}C DEPT 135 NMR spectrum (CD_2Cl_2) of **5**.

Preliminary catalytic study of 5

With B,N-carbene gold (I) complex **5** in hand, a catalytic activity of **5** on alkylidene oxazoles synthesis was briefly investigated.

The catalytic reaction was carried out in a J-Young NMR tube at room temperature and monitored by NMR spectroscopy. Substrates **6** and **8** were slowly converted to the corresponding alkylidene oxazoles **7** and **9**, respectively. Meanwhile, when 1-naphthalenyl propargyl ether **10** was employed, the desired product **11** was not detected and a complex mixture was obtained.



Reaction conditions: **6** (0.1 mmol), **8** (0.087 mmol), **10** (0.1 mmol); $CDCl_3$ (0.25 mL). Yields were determined by ^1H NMR spectroscopy using 1,3,5-trimethoxy benzene as an internal standard.

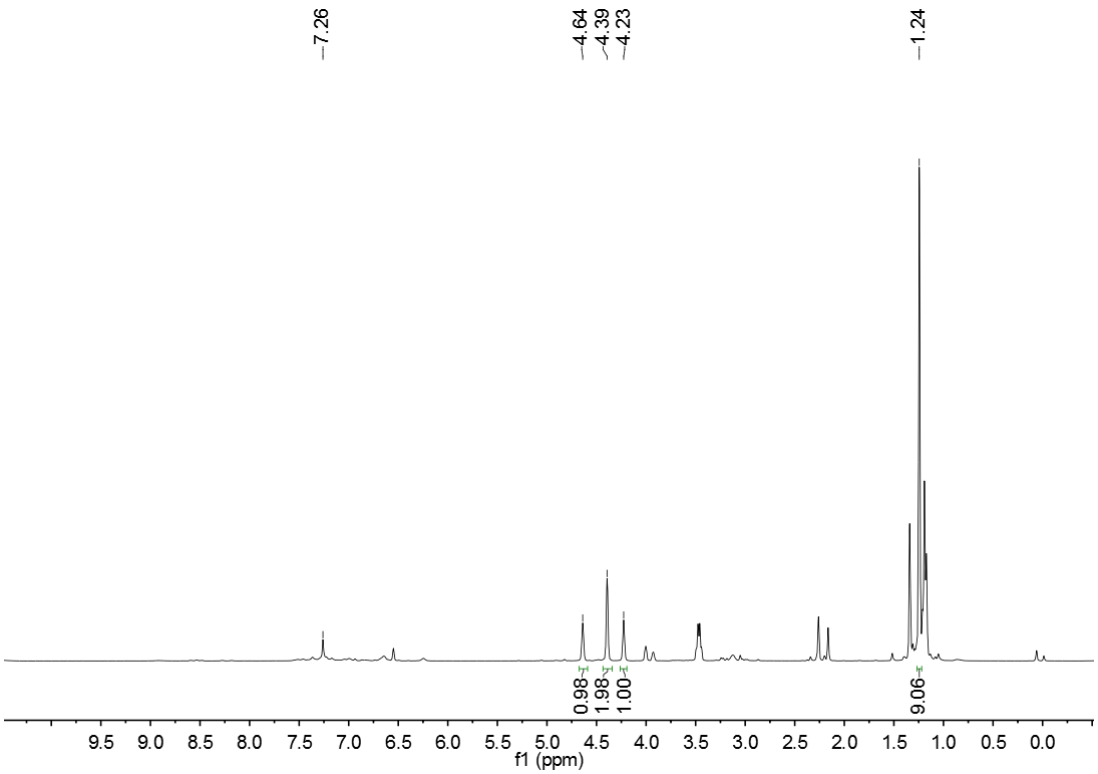


Figure S21 ^{1}H NMR spectrum ($CDCl_3$) of the reaction mixture of **6**, **5** (5 mol%) and $LiB(B_6F_5)_4{\cdot}Et_2O$ (10 mol%) after 120 h at room temperature.

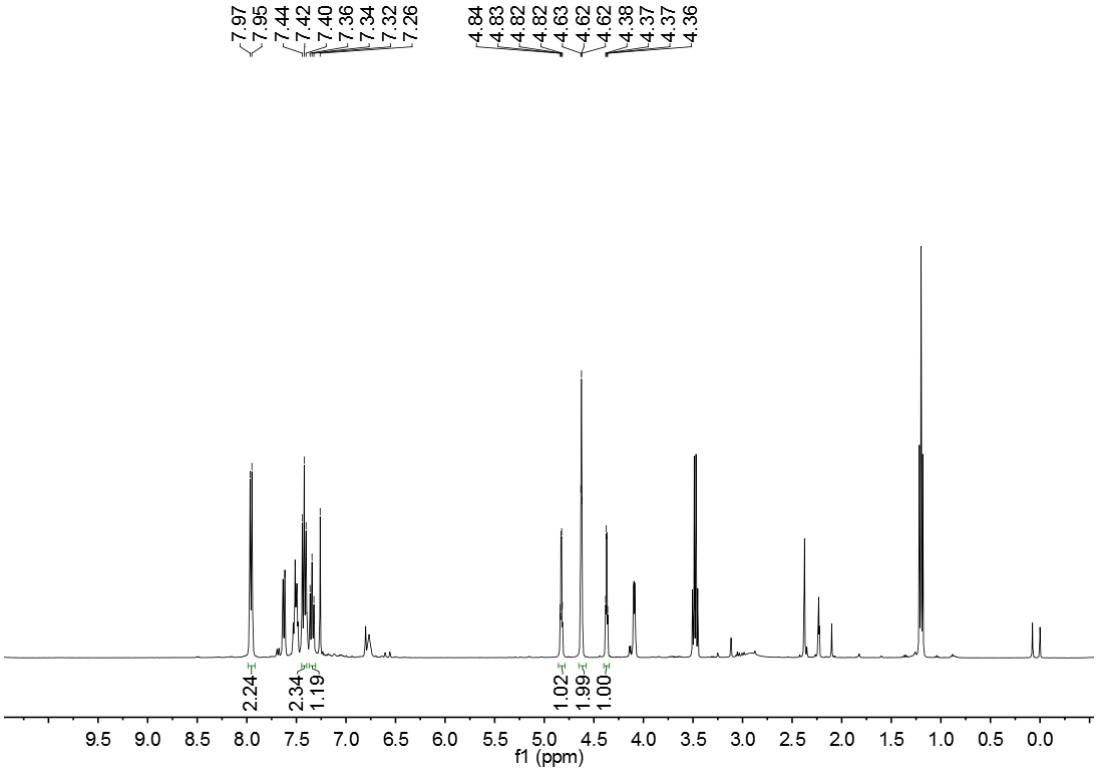


Figure S22 ^{1}H NMR spectrum ($CDCl_3$) of the reaction mixture of **8**, **5** (5 mol%) and $LiB(B_6F_5)_4{\cdot}Et_2O$ (10 mol%) after 120 h at room temperature.

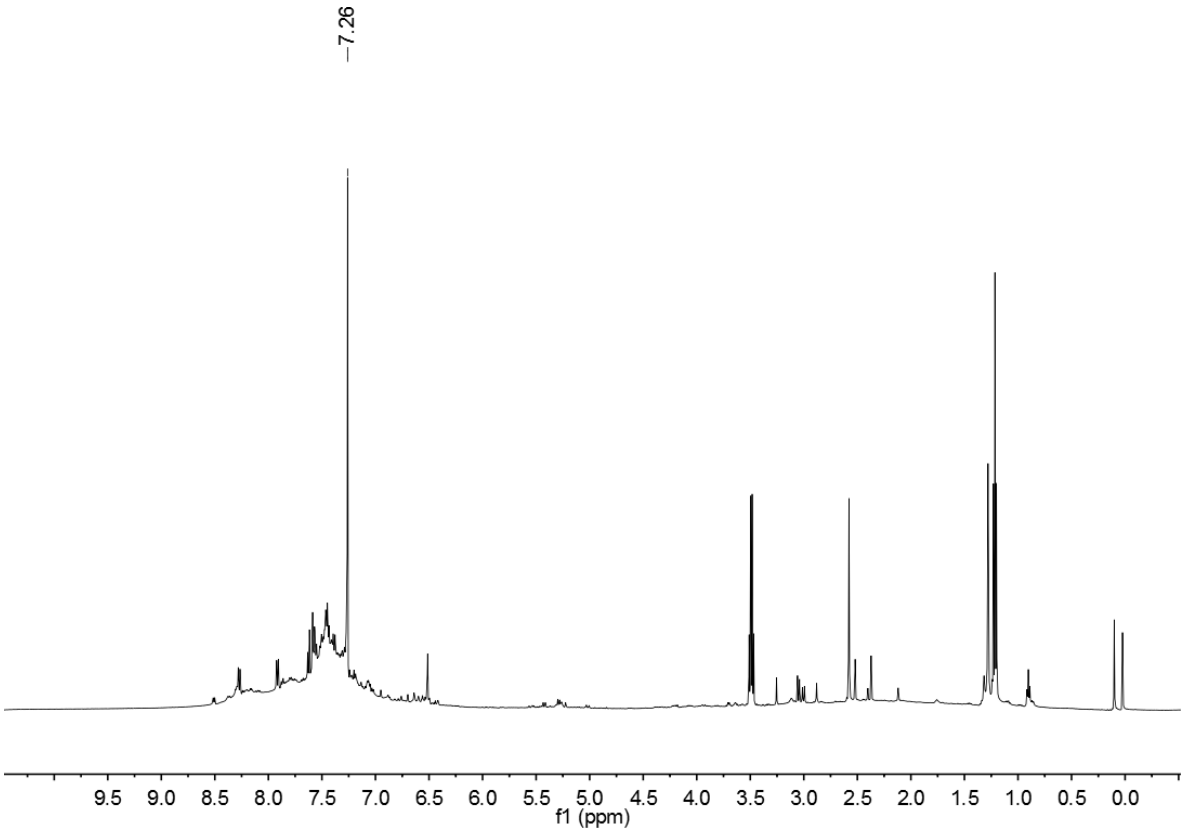


Figure S23 ^{1}H NMR spectrum ($CDCl_3$) of the reaction mixture of **10**, **5** (5 mol%) and $LiB(B_6F_5)_4 \cdot Et_2O$ (10 mol%) after 17 h at room temperature.

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 103(2) K, 100(2) K, 133(2) K and 103(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.[S3,S4] 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: 1948002-1948005 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**.

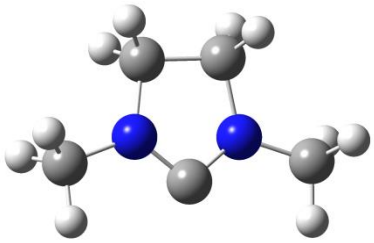
Compounds	**2·C_6H_6**	**3**	**4**	**5·C_6D_6**
Formula	$C_{40}H_{36}B_2N_6$	$C_{38}H_{38}B_2N_6$	$C_{34}H_{32}AuB_2N_5$	$C_{33}H_{25}AuB_2ClD_6N_5$
Fw	622.37	600.36	729.23	757.70
Cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$
Size (mm^3)	0.260 x 0.320 x 0.360	0.040 x 0.120 x 0.240	0.040 x 0.060 x 0.200	0.140 x 0.200 x 0.340
T, K	103(2)	100(2)	133(2)	103(2)
a, Å	11.2990(18)	8.9487(3)	12.1073(2)	13.2614(6)
b, Å	11.6148(18)	20.3068(7)	11.2713(2)	11.0676(5)
c, Å	25.321(4)	17.8492(8)	21.9583(4)	21.3350(9)
α, deg	90	90	90	90
β, deg	102.163(4)	97.5939(14)	98.2737(8)	100.4820(15)
γ, deg	90	90	90	90
V, $Å^3$	3248.4(9)	3215.1(2)	2965.35(9)	3079.1(2)
Z	4	4	4	4

d_{calcd} g·cm^{-3}	1.273	1.240	1.633	1.634
???mm^{-1}	0.076	0.074	9.567	4.896
Refl collected	26885	7156	30853	44118
T_{max}/T_{min}	0.9810 /0.9730	0.9970 /0.9830	0.7010/0.2510	0.5470/0.2870
N_{measd}	7780	7156	5210	5464
[R_{int}]	0.0581	0.0661	0.0525	0.0821
R [I>2sigma(I)]	0.0709	0.0545	0.0308	0.0313
R_w[I>2sigma(I)]	0.1362	0.1350	0.0865	0.0663
GOF	1.130	1.097	1.095	1.046
Largest diff. peak/hole[e·Å^{-3}]	0.298/-0.257	0.333/-0.302	0.782 / -1.743	2.008 /-0.773

3. Theoretical calculations

Gaussian 09[S5] was used for all density functional theory (DFT) calculations including geometry optimization, frequency calculation. Optimization, frequency for **A-E** were performed at the M052X/6-311G(d,p) level of theory.

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

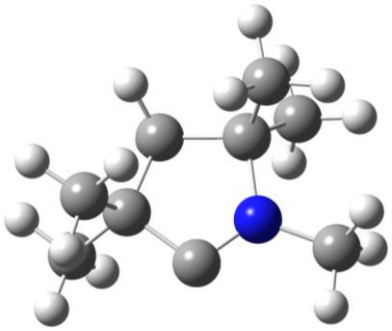


Zero-point correction=	0.151321 (Hartree/Particle)
Thermal correction to Energy=	0.159025
Thermal correction to Enthalpy=	0.159969
Thermal correction to Gibbs Free Energy=	0.119457
Sum of electronic and zero-point Energies=	-305.878353
Sum of electronic and thermal Energies=	-305.870649
Sum of electronic and thermal Enthalpies=	-305.869705
Sum of electronic and thermal Free Energies=	-305.910217

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

C	-0.75981469	1.22540993	-0.08476640
C	0.75988596	1.22536701	0.08476284
N	1.06587846	-0.19936281	-0.09101960
C	-0.00002946	-1.01173968	-0.00004439
N	-1.06588832	-0.19931369	0.09087959
C	-2.42924585	-0.65963019	0.00555834
C	2.42920984	-0.65965441	-0.00547778
H	-1.06240867	1.55569849	-1.08343058
H	-1.27451722	1.83779897	0.65498062
H	1.06240466	1.55546270	1.08352247
H	1.27469056	1.83783520	-0.65484057
H	-2.42123091	-1.73876955	0.12500894
H	-2.87233282	-0.40808376	-0.96321237
H	-3.03859254	-0.21040561	0.79257186
H	2.42107917	-1.73896155	-0.12341472
H	2.87251434	-0.40676706	0.96284859
H	3.03842757	-0.21158837	-0.79324979

3.2 optimized structure of B (atom, x-, y-, z-positions in Å)



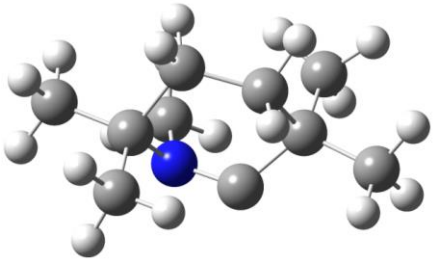
Zero-point correction=	0.247610 (Hartree/Particle)
Thermal correction to Energy=	0.259039
Thermal correction to Enthalpy=	0.259983
Thermal correction to Gibbs Free Energy=	0.212052
Sum of electronic and zero-point Energies=	-407.687434
Sum of electronic and thermal Energies=	-407.676006
Sum of electronic and thermal Enthalpies=	-407.675061
Sum of electronic and thermal Free Energies=	-407.722992

Supplementary Table 3. Calculated geometries of **B** (atom, x-, y-, z-positions in Å)

C	-0.44887285	1.10611696	-0.43867757
C	0.94661270	0.56489631	-0.09750801
N	0.64705034	-0.89468979	0.06723508
C	-0.59776453	-1.28294560	0.10773634
C	-1.43345785	-0.02271596	-0.04788478
C	-2.50309711	-0.24512754	-1.11681423
C	-2.11687375	0.23745039	1.30087047
C	1.75326818	-1.83263451	0.21013222
C	1.49663529	1.13809498	1.20953668
C	1.94784231	0.78825536	-1.22753358
H	-0.51348431	1.29913587	-1.51111392
H	-0.65297064	2.04301387	0.08107058
H	-3.15471723	-1.06858448	-0.82622337
H	-2.04631940	-0.49636157	-2.07515647
H	-3.10587052	0.65702826	-1.24560755
H	-2.72591383	-0.62210158	1.57942177
H	-2.75870717	1.11827692	1.23042902
H	-1.38853555	0.40409905	2.09504015
H	1.31740244	-2.80792193	0.39526620
H	2.39350501	-1.54815681	1.04529829
H	2.35036110	-1.86144870	-0.70111661

H	2.45081920	0.68138398	1.47371484
H	0.79602774	0.98010747	2.02800543
H	1.66119035	2.21010332	1.09455786
H	2.94280889	0.42797702	-0.96326544
H	2.02337297	1.85613046	-1.43546002
H	1.61592424	0.28180503	-2.13465153

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



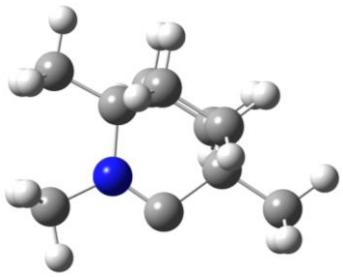
Zero-point correction=	0.275817 (Hartree/Particle)
Thermal correction to Energy=	0.287813
Thermal correction to Enthalpy=	0.288757
Thermal correction to Gibbs Free Energy=	0.240142
Sum of electronic and zero-point Energies=	-446.893379
Sum of electronic and thermal Energies=	-446.881383
Sum of electronic and thermal Enthalpies=	-446.880439
Sum of electronic and thermal Free Energies=	-446.929054

Supplementary Table 4. Calculated geometries of **C** (atom, x-, y-, z-positions in Å)

C	-1.49299127	-0.26444928	0.01061821
N	-0.58955683	0.57490763	-0.83789227
C	0.50060595	-0.22542318	-1.04856296
C	1.64357978	-0.06934332	-0.11820947
C	0.81873110	-0.97416386	0.95200496
C	-0.62375447	-0.53887624	1.27886138
C	-0.51586958	1.99416003	-0.45201316
C	-1.88892645	-1.55941627	-0.69902113
C	-2.76968000	0.48777734	0.37573021
C	2.14764186	1.21078208	0.57180509
C	2.84979636	-0.88910656	-0.56838918
H	1.43083113	-0.91433943	1.85639497
H	0.83752697	-2.00546779	0.60725002
H	-1.09838878	-1.30922482	1.89102327
H	-0.59891281	0.36904335	1.88639920
H	0.36734195	2.42825578	-0.91069506
H	-0.49205760	2.18544906	0.62237446
H	-1.38840730	2.49591786	-0.86843570
H	-2.61487139	-2.09097951	-0.08150887

H	-1.03436739	-2.19638149	-0.89553945
H	-2.35208992	-1.31366504	-1.65439210
H	-3.39248536	-0.15763851	0.99559639
H	-3.32712077	0.73839184	-0.52763559
H	-2.57526558	1.40029454	0.93597658
H	2.98336169	0.94620309	1.22293940
H	1.39663556	1.69946430	1.18343445
H	2.52109295	1.92595675	-0.16164186
H	3.45899674	-1.18577356	0.28883571
H	3.47610941	-0.29669508	-1.23777633
H	2.51416861	-1.77480915	-1.10429735

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



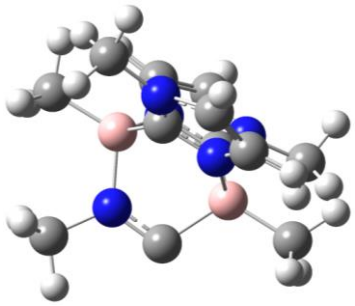
Zero-point correction=	0.256651 (Hartree/Particle)
Thermal correction to Energy=	0.267449
Thermal correction to Enthalpy=	0.268393
Thermal correction to Gibbs Free Energy=	0.221451
Sum of electronic and zero-point Energies=	-445.792494
Sum of electronic and thermal Energies=	-445.781695
Sum of electronic and thermal Enthalpies=	-445.780751
Sum of electronic and thermal Free Energies=	-445.827693

Supplementary Table 5. Calculated geometries of **D** (atom, x-, y-, z-positions in Å)

C	-1.03498295	-0.48848271	0.00000176
N	-0.71752828	0.96790056	0.00001860
C	0.52803221	1.37693550	-0.00010919
C	1.44906693	0.17447619	-0.00010312
C	1.12867634	-0.66656109	1.25458942
C	-0.35502157	-1.07485865	1.24617535
C	-0.35497968	-1.07507929	-1.24599267
C	1.12869976	-0.66656164	-1.25459642
C	-2.52381494	-0.79313981	-0.00001606
C	2.90768829	0.60719969	0.00005954

C	-1.79732455	1.95190945	-0.00005335
H	1.36214741	-0.07335605	2.13933187
H	1.78373198	-1.54039836	1.26861766
H	-0.47517013	-2.15958163	1.22272748
H	-0.87092100	-0.70627024	2.13395905
H	-0.87092209	-0.70693704	-2.13393966
H	-0.47494777	-2.15982679	-1.22214334
H	1.78386414	-1.54032430	-1.26891254
H	1.36184524	-0.07334720	-2.13943536
H	-2.64953935	-1.87664983	-0.00022344
H	-3.01976382	-0.40039940	-0.88713126
H	-3.01977313	-0.40076088	0.88723468
H	3.11882849	1.21412948	-0.88066936
H	3.57453455	-0.25877507	0.00041290
H	3.11835376	1.21468078	0.88050300
H	-1.31461231	2.92284444	-0.00003389
H	-2.42063998	1.84736674	0.88785519
H	-2.42055712	1.84727564	-0.88801477

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



Zero-point correction=	0.319056 (Hartree/Particle)
Thermal correction to Energy=	0.337389
Thermal correction to Enthalpy=	0.338333
Thermal correction to Gibbs Free Energy=	0.274520
Sum of electronic and zero-point Energies=	-792.007695
Sum of electronic and thermal Energies=	-791.989363
Sum of electronic and thermal Enthalpies=	-791.988419
Sum of electronic and thermal Free Energies=	-792.052232

Supplementary Table 6. Calculated geometries of **E** (atom, x-, y-, z-positions in Å)

B	0.70203689	1.11598976	0.80373808
B	-0.62611214	-1.17214710	0.08341252
C	1.34918802	2.51966356	1.23081429
C	1.48453649	0.10945761	-0.19157906
C	1.62014852	-1.81586759	-1.28494468

H	1.28500463	-2.75836521	-1.67713434
C	2.83388465	-1.21476693	-1.37338789
H	3.74396526	-1.51936497	-1.85628249
C	3.81573991	0.93553039	-0.52523051
H	3.40175000	1.86317416	-0.14815860
H	4.28964637	1.11209222	-1.48871161
H	4.55127812	0.55378031	0.18095865
C	-1.36470173	0.21705948	-0.30555288
C	-1.43704988	2.42213094	-0.24143187
H	-1.08742536	3.41770041	-0.04015061
C	-2.60495969	1.99519006	-0.79202295
H	-3.45959570	2.53462153	-1.15652931
C	-3.61167052	-0.24987829	-1.29080547
H	-4.10225682	0.21443330	-2.14302527
H	-4.33820809	-0.41164857	-0.49573860
H	-3.19002954	-1.20131428	-1.59422183
C	0.31786471	0.10591758	2.06743548
C	-0.86003671	-1.91372311	2.59594694
C	-1.29068157	-2.57244468	-0.32842252
N	0.80589444	-0.98963443	-0.55198203
N	2.73156302	-0.01808640	-0.68713618
N	-0.68468479	1.31159488	0.04166436
N	-2.53908154	0.61616896	-0.83311203
N	-0.33823677	-0.93309670	1.64220424
H	-0.57629104	-1.58026194	3.58965245
H	-1.94821317	-1.97705327	2.52139595
H	-0.44376312	-2.90348283	2.39948611
H	-2.28340527	-2.70812169	0.10442504
H	-1.38834451	-2.67630043	-1.41320236
H	-0.68051604	-3.40995970	0.01720006
H	2.26531738	2.35815467	1.80272018
H	1.57403641	3.20078791	0.40345342
H	0.66567324	3.03367676	1.91172829

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S2 T. Seki, Y. Takamatsu and H. Ito, *J. Am. Chem. Soc.*, 2016, **138**, 6252−6260.

S3 G. M. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3-8.

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