Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supporting Information

Kinetic stabilization allows structural analysis of a benzoborirene

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1. Experimental Methods

General Procedures. All experiments were performed under anhydrous conditions using argon as protective gas. All NMR spectra were referenced to residual solvent signals (1H, 13C) and externally (11B: BF3•OEt2). If not stated otherwise NMR measurements were performed at 298 K. All commercially available compounds were purchased and used without further purification. Dry solvents were either purchased or taken from a *MBraun* solvent purification system MB-SPS-800. NMR spectra were recorded on Bruker Avance III HDX600, Bruker Avance III HDX400 and on Bruker Avance III 400 spectrometers. For HR-APCI-TOF-MS measurements a Bruker maXis 4G Spectrometer (sample application: DIP) was used.
[2-(Dichloroboryl)phenyl]trimethylsilane, 2-Bromophenyldichloroborane and $Et_2OLiC_6H_3$-2,6-$Trip_2$ (Trip= 2,4,6-i-$Pr_3C_6H_2$-) were synthesized as described in the literature.[1, 2]

Synthesis.

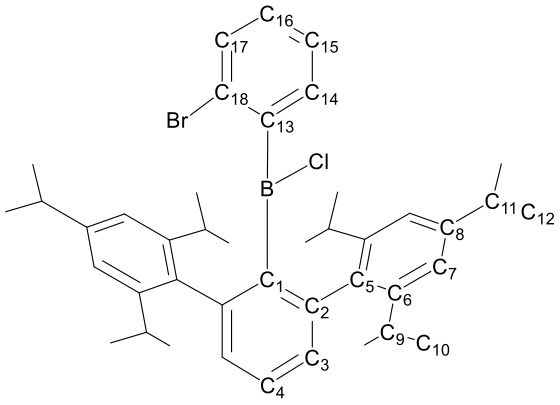
Compound **3**. A vigorously stirred solution of 630mg (1.12 mmol) $Et_2OLiC_6H_3$-2,6-$Trip_2$ in 18 mL hexane was cooled to -78 °C. Then 266 mg (1.12 mmol) 2-Bromophenyldichloroborane solved in 2 mL hexane were added dropwise and the reaction mixture was slowly heated to rt over 16h. The reaction mixture was filtered and the solvent removed under reduced pressure. Solving in 3 mL pentane and storing at -30 °C overnight yields colourless crystals suitable for x-ray crystallography. Yield: 411mg (0.60 mmol, 53.6 %).
^{1}H (400 MHz, C_6D_6): δ = 1.12 (d, $^3J_{H,H}$ = 6.79 Hz, 12H, **10**), 1.18 (d, $^3J_{H,H}$ = 6.79 Hz, 12H, **10**), 1.26 (d, $^3J_{H,H}$ = 6.90 Hz, 12H, **12**), 2.83 (sept, $^3J_{H,H}$ = 6.90 Hz, 2H, **11**), 3.00 (sept, $^3J_{H,H}$ = 6.79 Hz, 4H, **9**), 6.54 (dt, $^3J_{H,H}$ = 7.66 Hz, $^4J_{H,H}$ = 1.71 Hz, 1H, **16**), 6.83 (dt, $^3J_{H,H}$ = 7.48 Hz, $^4J_{H,H}$ = 0.95 Hz, 1H, **15**), 7.10-7.14 (m, 1H, **14**), 7.12 (s, 4H, **7**), 7.20-7.25 (m, 1H, **4**), 7.26-7.30 (m, 2H, **3**), 7.31 (dd, $^3J_{H,H}$ = 7.48 Hz, $^4J_{H,H}$ = 1.71 Hz, 1H, **17**) ppm;
^{13}C{^{1}H } NMR (100 MHz, C_6D_6): δ = 22.6 (**10**), 24.4 (**12**), 26.7 (**10**), 31.5 (**9**), 34.9 (**11**), 121.0 (**7**), 126.0 (**15**), 128.7 (**4**), 129.0 (**18**), 130.0 (**3**), 132.0 (**16**), 134.0 (**14**), 135.1 (**17**), 136.8 (**5**), 144.4 (**2**), 147.3 (**6**), 149.2 (**8**) ppm;
^{11}B{^{1}H } NMR (128 MHz): δ = 65.2 ppm;
HRMS(APCI): APCI T_{heater} = 300 °C, m/z calcd. for $C_{42}H_{53}BBrCl$ 682.31139 Da, found 682.31100 Da [M]•+.

Compound **4**. 0,821 mmol (1,9 M in pentane, 0,432 mL) tert-Buthyllithium diluted in 10 mL toluene was added dropwise to a vigorously stirred solution of 468mg (0,684 mmol) **1** solved in 80 mL toluene at -78 °C. The reaction mixture was slowly heated to rt over night. The solvent was removed from the blue reaction mixture unter reduced pressure. The remaining solid was solved in 5 mL pentane upon which the reaction mixture turns yellow, filtered and stored at -30 °C over night, affording colourless crystalss suitable for x-ray cristallography. Yield: 147 mg (0.258 mmol, 37.7 %).
^{1}H (400 MHz, C_6D_{12}): δ = 0.76 (d, $^3J_{H,H}$ = 6.84 Hz, 12H, **10**), 1.08 (d, $^3J_{H,H}$ = 6.84 Hz, 12H, **10**), 1.32 (d, $^3J_{H,H}$ = 6.90 Hz, 12H, **12**), 2.70 (sept, $^3J_{H,H}$ = 6.84 Hz, 4H, **9**), 3.00 (sept, $^3J_{H,H}$ = 6.90 Hz, 2H, **11**), 6.83-6.87 (m, 2H, **14**), 7.02 (s, 4H, **7**), 7.17-7.21 (m, 2H, **15**), 7.25 (d, $^3J_{H,H}$ = 7.55 Hz, 2H, **3**), 7.52 (t, $^3J_{H,H}$ = 7.55 Hz, 1H, **4**) ppm;
^{13}C{^{1}H } (150 MHz, CD_2Cl_2, 235 K): δ = 23.2 (**10**), 24.2 (**12**), 24.4 (**10**), 30.7 (**9**), 34.6 (**11**), 120.2 (**7**), 123.3 (**14**), 127.7 (**3**), 130.7 (**1**), 131.5 (**4**), 136.0 (**15**), 138.0 (**5**), 146.1 (**6**), 147.7 (**8**), 150.2 (**2**), 153.8 (**13**) ppm;
^{11}B{^{1}H } (128 MHz): δ = 34.4
HRMS(APCI): APCI T_{heater} = 400 °C, m/z calcd. for $C_{42}H_{53}B$ 568.42420 Da, found 568.42496 Da [M]•+.

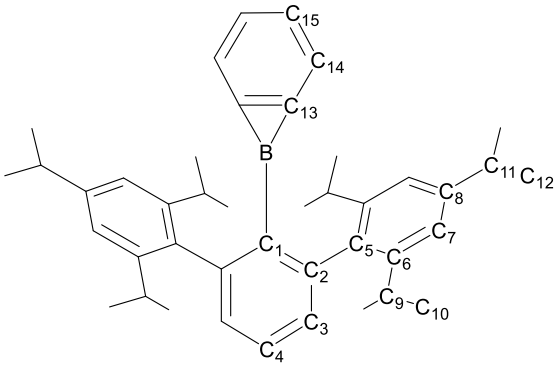
Compound **5**. A vigorously stirred solution of 630mg (1.12 mmol) $Et_2OLiC_6H_3$-2,6-$Trip_2$ in 18 mL hexane was cooled to -78 °C. Then 249 mg (1.12 mmol) [2-(Dichloroboryl)phenyl]trimethylsilane solved in 2 mL hexane were added dropwise and the reaction mixture was slowly heated to rt over 16h. The reaction mixture was filtered and the solvent removed under reduced pressure. Solving in 3 mL pentane and storing at -30 °C overnight yields colourless crystals suitable for x-ray crystallography. Yield: 366mg (0.54 mmol, 48.2 %).
^{1}H (600 MHz, CD_2Cl_2): δ = 0.1 (s, 9H, **19**), 0.43-0.59 (br, 6H, **10**), 0.78-0.93 (br, 6H, **10**), 1.04-1.17 (br, 6H, **10**), 1.21 (d, $^3J_{H,H}$ = 6.96 Hz, 12H, **10**), 1.25-1.40 (br, 6H, **10**), 2.76-2.87 (m, 6H, **9+11**), 6.77-7.04 (m, 4H, **7**), 7.17 (d, $^3J_{H,H}$ = 7.65 Hz, 2H, **3**), 7.19 (dt, $^3J_{H,H}$ = 7.48 Hz, $^4J_{H,H}$ = 1.23 Hz, 1H, **15**), 6.83 (dt, $^3J_{H,H}$ = 7.47 Hz, $^4J_{H,H}$ = 1.26 Hz, 1H, **16**), 7.31 (t, $^3J_{H,H}$ = 7.63 Hz, 1H, **4**), 7.52-7.60 (m, 2*H*, **14+17**) ppm;
^{13}C{^{1}H } (150 MHz, CD_2Cl_2): δ = 22.0 (**10**), 22.6 (**10**), 24.2 (**12**), 25.9 (**10**), 26.8 (**10**), 31.2 (**9**), 31.7 (**9**), 34.6 (**11**), 121.0 (**7**), 127.5 (**4**), 128.4 (**15**), 130.2 (**3**), 131.5 (**16**), 136.4 (**14**), 136.9 (**6**), 139.7 (**17**), 141.7 (**1**), 143.0 (**2**), 146.1 (**13**), 148.6 (**5**) , 148.9 (**8**) , 149.4 (**18**) ppm;
^{11}B{^{1}H } (128 MHz): δ = 64.0 ppm.

Compound **6**. To 20 mg (0,035 mmol) **5** solved in 0,5 mL C_6D_{12} was added 1,42 µL (0.035 mmol) methanol. The solvent was removed under reduced pressure and the remaining solid solved in pentane and stored at -30 °C to yield colourless crystalls suitable for x-ray crystallography. Yield: quantitative
^{1}H (400 MHz, C_6D_{12}): δ = 0.99 (d, $^3J_{H,H}$ = 6.50 Hz, 12H, **10**), 1.00 (d, $^3J_{H,H}$ = 6.58 Hz, 12H, **10**), 1.25 (d, $^3J_{H,H}$ = 6.78 Hz, 12H, **12**), 2.78 (sept, $^3J_{H,H}$ = 6.82 Hz, 4H, **9**), 2.84 (sept, $^3J_{H,H}$ = 6.88 Hz, 2H, **11**), 3.02 (s, 3H, **19**), 6.32-6.37 (m, 2H, **15**), 6.82-6.88 (m, 2H, **14**), 6.91 (s, 4H, **7**), 6.91-6.96 (m, 1H, **16**), 7.08 (d, $^3J_{H,H}$ = 7.55 Hz, 2H, **4**), 7.23-7.29 (m, 1H, **4**) ppm;
^{13}C{^{1}H } (100 MHz, C_6D_{12}): δ = 22.6 (**10**), 24.6 (**12**), 26.7 (**10**), 31.4 (**9**), 35.4 (**11**), 54.7 (**19**), 120.4 (**7**), 127.2 (**4**), 127.5 (**14**), 128.3 (**16**), 129.1 (**3**), 131.2 (**15**), 138.6 (**5**), 139.2 (**13**), 143.0 (**1**), 144.1 (**2**), 147.7 (**6**), 148.3 (**8**) ppm;
^{11}B{^{1}H } (128 MHz): δ = 50.5 ppm;
HRMS(APCI): APCI T_{heater} = 350 °C, m/z calcd. for $C_{43}H_{57}BO$ 600.45044 Da, found 600.44970 Da [M]•+.

Compound **7**. To 40 mg (0,035 mmol) **5** solved in 0,5 mL C_6D_6 was added 3,7 µL (0.046 mmol) methanol in C_6D_6. The compound was not isolated.
^{1}H (400 MHz, C_6D_6): δ = 1.05 (d, $^3J_{H,H}$ = 6.86 Hz, 12H, **10**), 1.19 (d, $^3J_{H,H}$ = 6.78 Hz, 12H, **10**), 1.35 (d, $^3J_{H,H}$ = 6.93 Hz, 12H, **12**), 2.92 (sept, $^3J_{H,H}$ = 6.82 Hz, 2H, **11**), 3.05 (sept, $^3J_{H,H}$ = 6.80 Hz, 4H, **9**), 6.37 (br, 2.6H, **17** and pyridine), 6.66 (br, 1.3H, **18** and pyridine), 7.07-7.11 (m, 2H, **15**), 7.12 (s, 4H, **7**), 7.20-7.24 (m, 2H, **14**), 7.26-7.33 (m, 3H, **3 + 4**), 8.22 (br, 2.6H, **16** and pyridine) ppm;
^{13}C{^{1}H } (100 MHz, C_6D_6): δ = 23.3 (**10**), 24.7 (**12**), 26.1 (**10**), 31.1 (**9**), 35.0 (**11**), 120.3 (**7**), 122.8 (**15**), 123.9 (**17** and pyridine), 126.8 (**4**), 129.4 (**14**), 130.2 (**3**), 136.7 (**18** and pyridine), 140.7 (**5**), 146.7 (**6**), 147.5 (**8**), 148.2 (**16** and pyridine), 151.2 (**13**) ppm;
^{11}B{^{1}H } (128 MHz): δ = -5.1 ppm.



3



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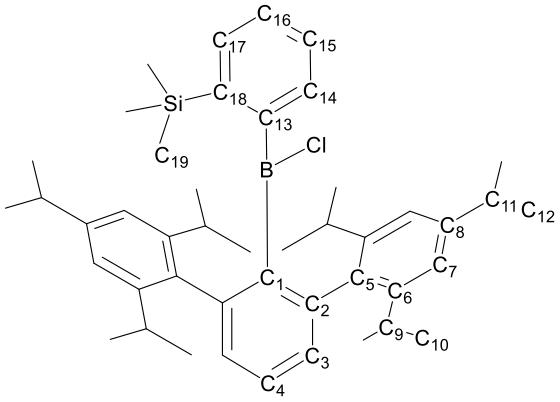

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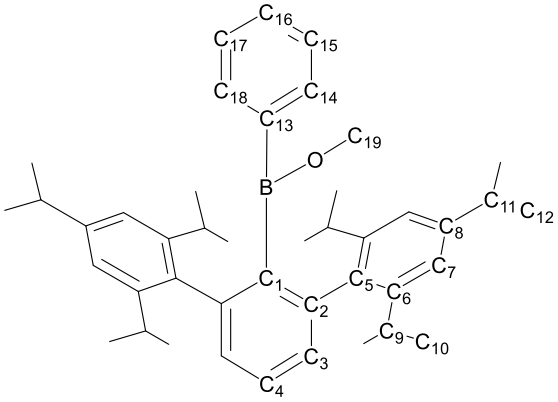

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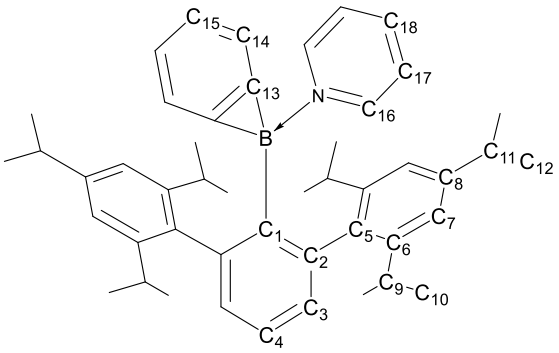

7

Scheme S1: NMR Nomenclature of compounds **3**, **4**, **5**, **6**, and **7**.

2. NMR-Spectra

Solvent signals are denoted by an asterisk (*)

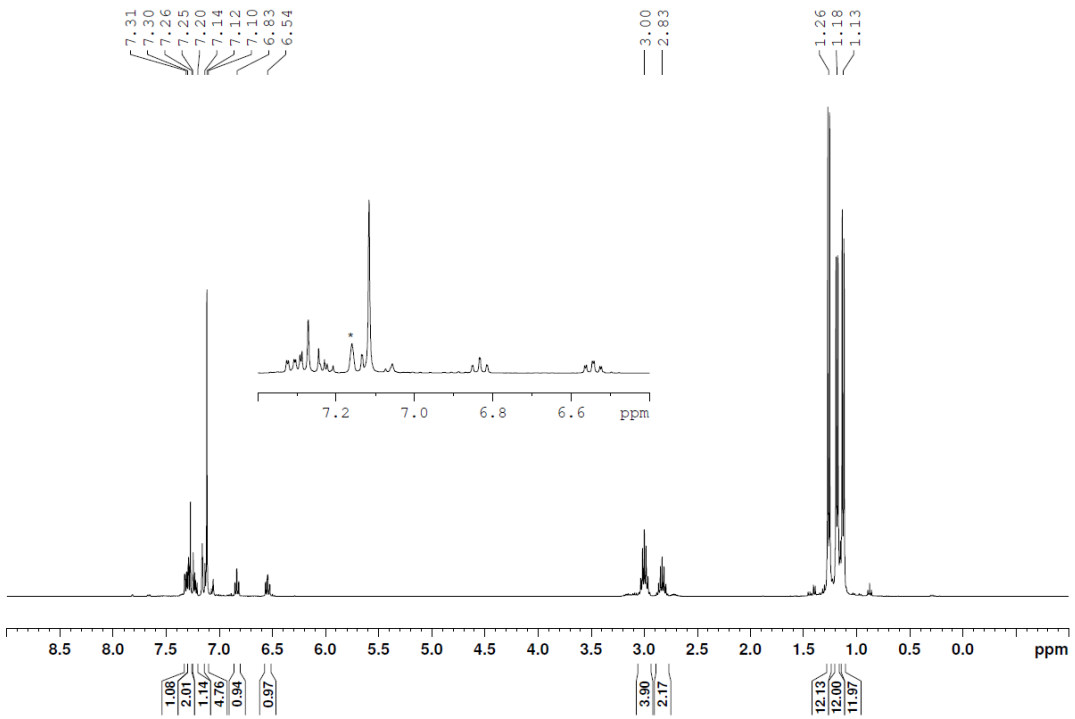

Figure S1. ^{1}H NMR Spectrum of compound **3** in C_6D_6

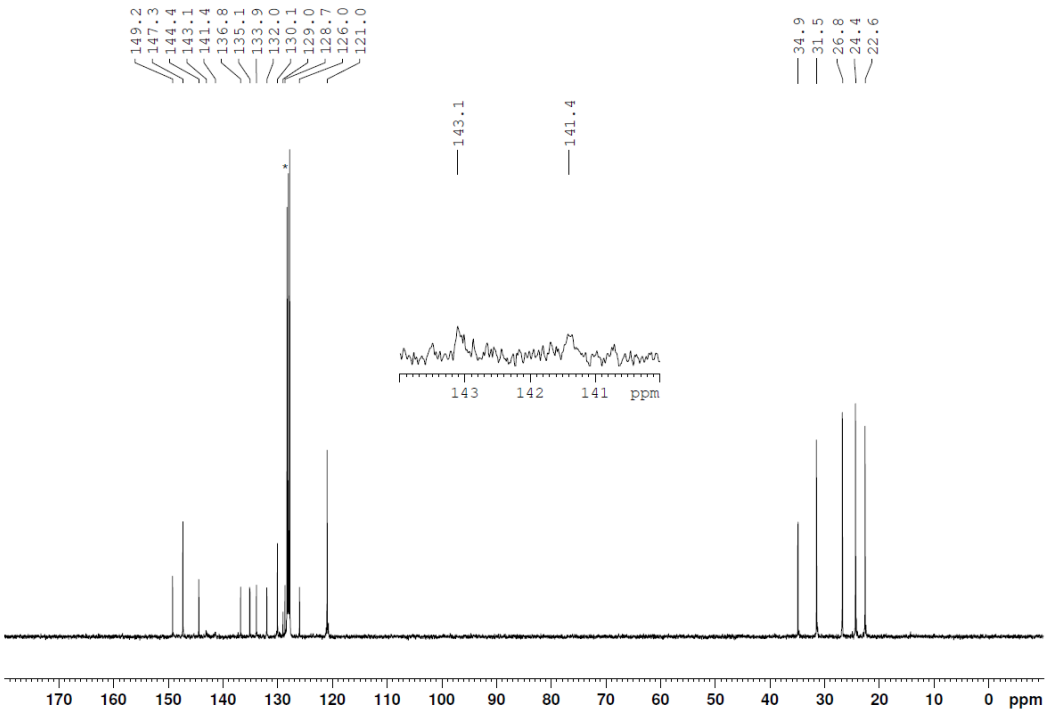

Figure S2. ^{13}C{H} NMR Spectrum of compound **3** in C_6D_6

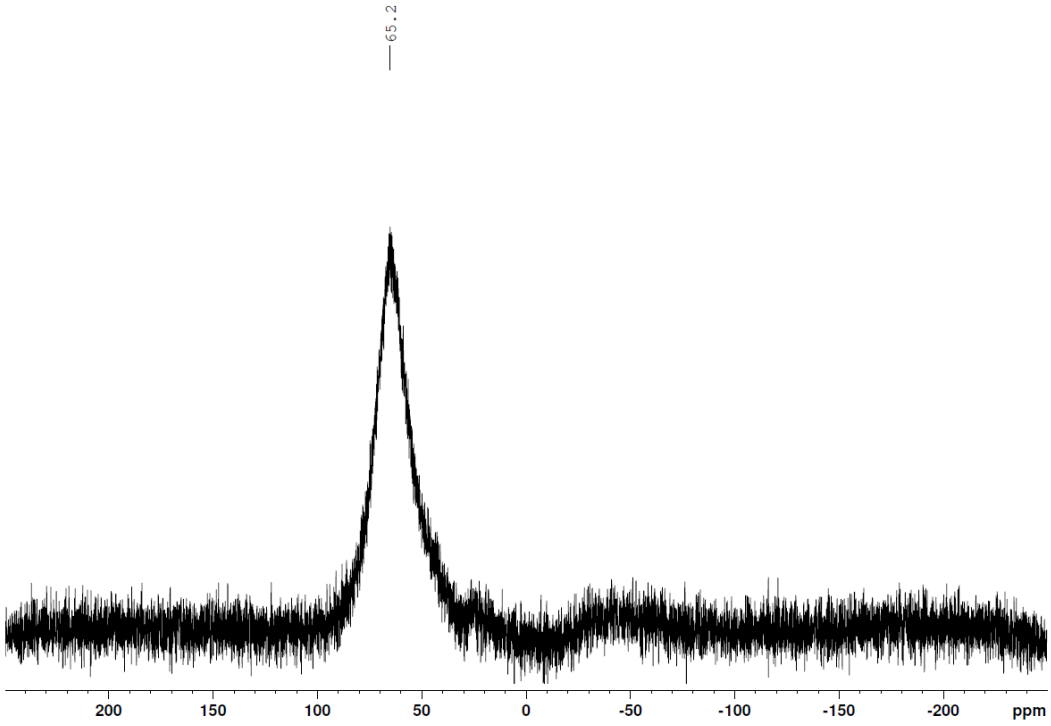

Figure S3. $^{11}B\{H\}$ NMR Spectrum of compound **3** in C_6D_6

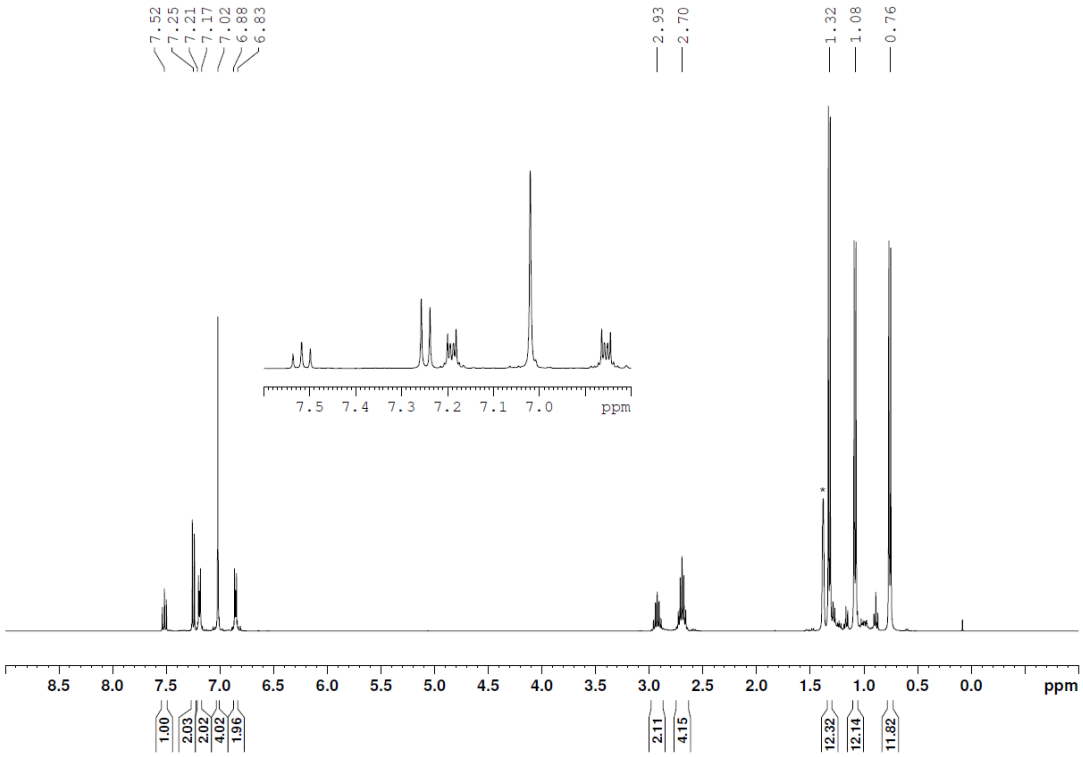

Figure S4. ^{1}H NMR Spectrum of compound **4** in C_6D_{12}

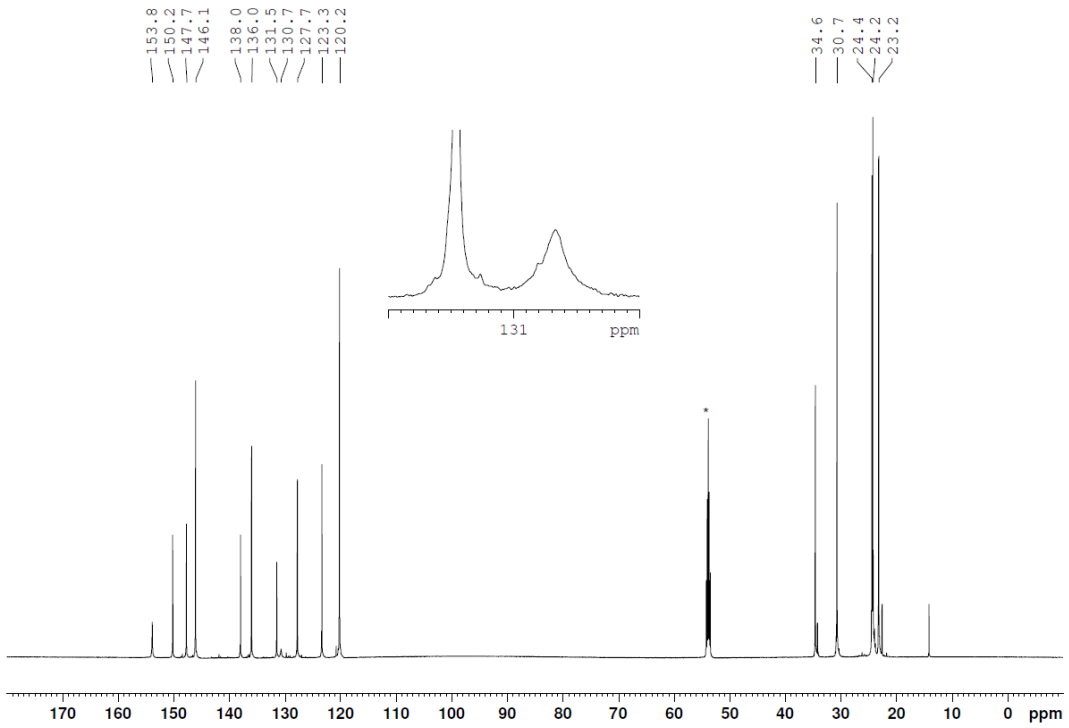

Figure S5. $^{13}C\{H\}$ NMR Spectrum of compound **4** in CD_2Cl_2 at 235 K

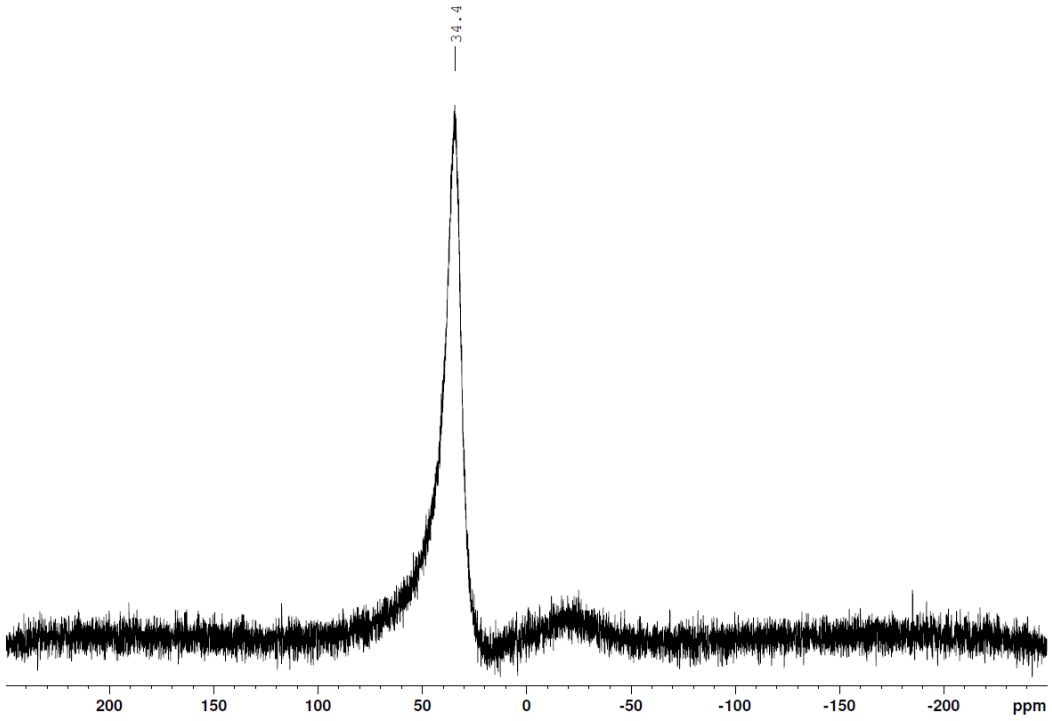

Figure S6. $^{11}B\{H\}$ NMR Spectrum of compound **4** in C_6D_{12}

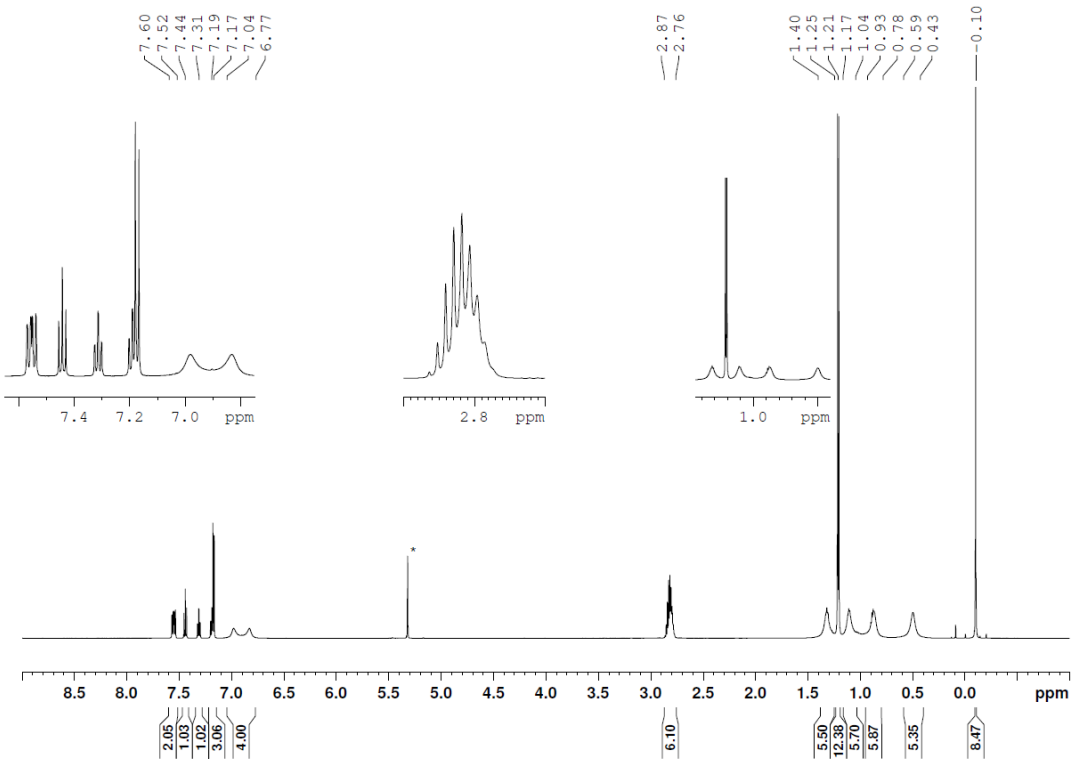

Figure S7. ^{1}H NMR Spectrum of compound **5** in CD_2Cl_2

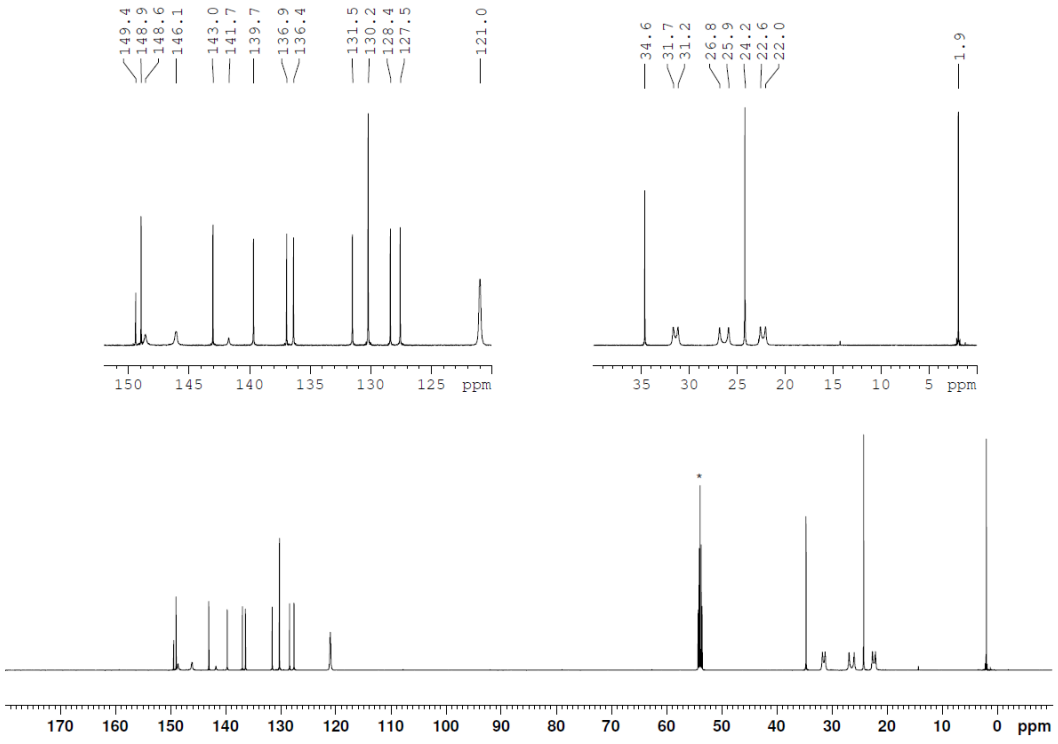

Figure S8. ^{13}C{H} NMR Spectrum of compound **5** in CD_2Cl_2

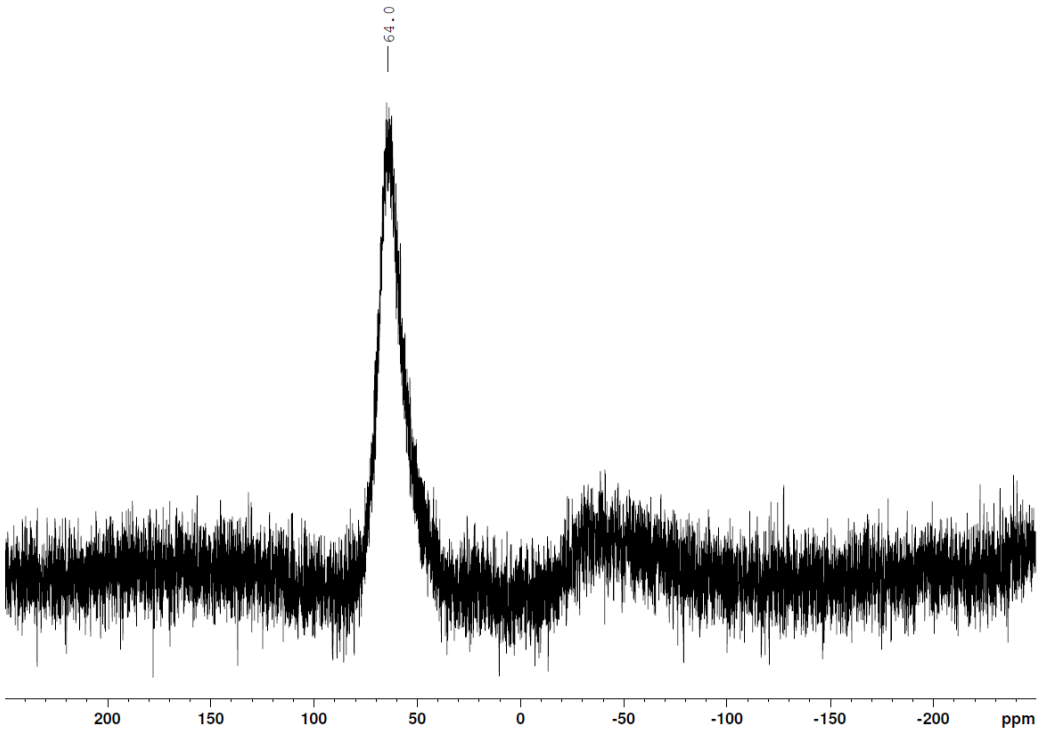

Figure S9. $^{11}B\{H\}$ NMR Spectrum of compound **5** in CD_2Cl_2

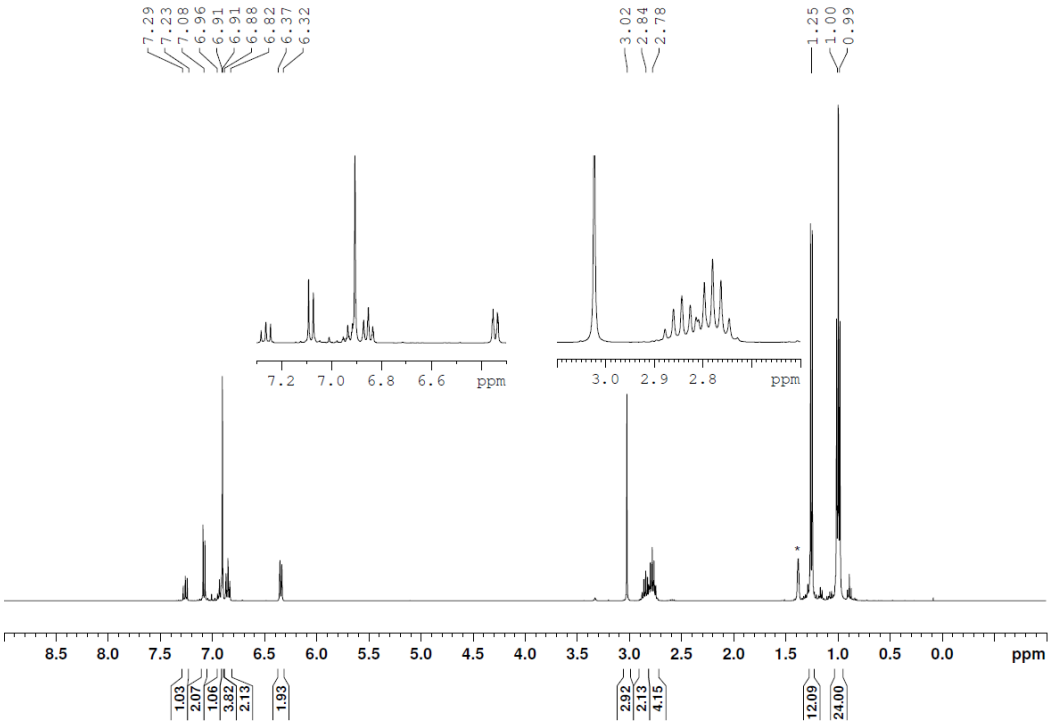

Figure S10. ^{1}H NMR Spectrum of compound **6** in C_6D_{12}

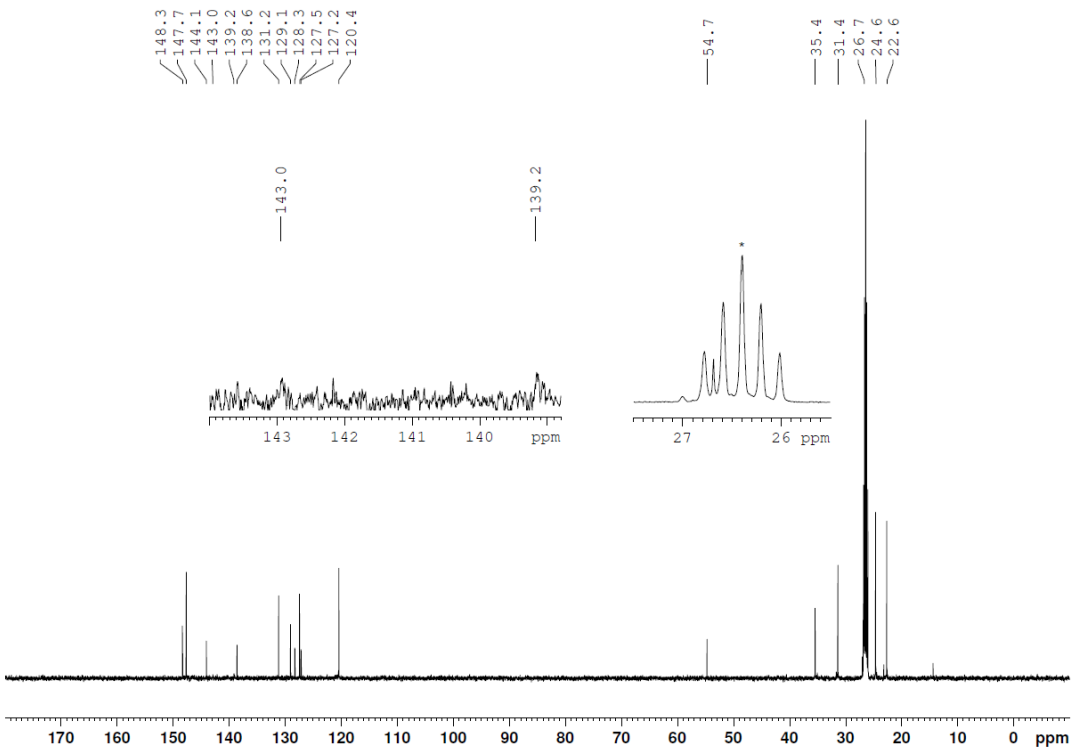

Figure S11. $^{13}C\{H\}$ NMR Spectrum of compound **6** in C_6D_{12}

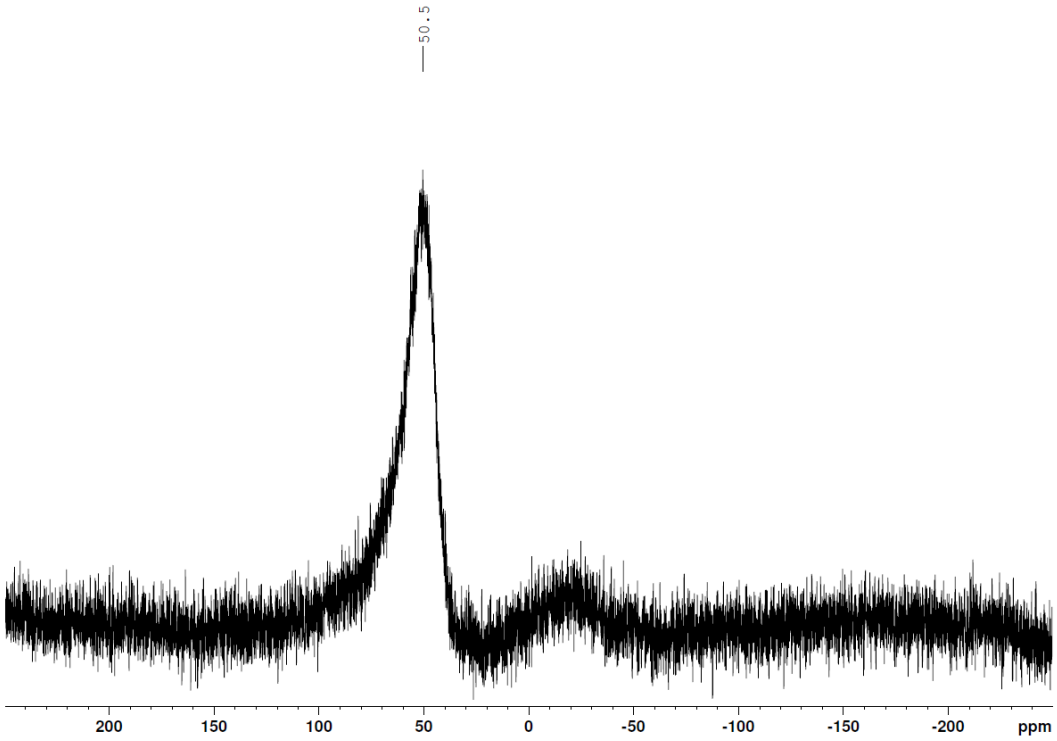

Figure S12. $^{11}B\{H\}$ NMR Spectrum of compound **6** in C_6D_{12}

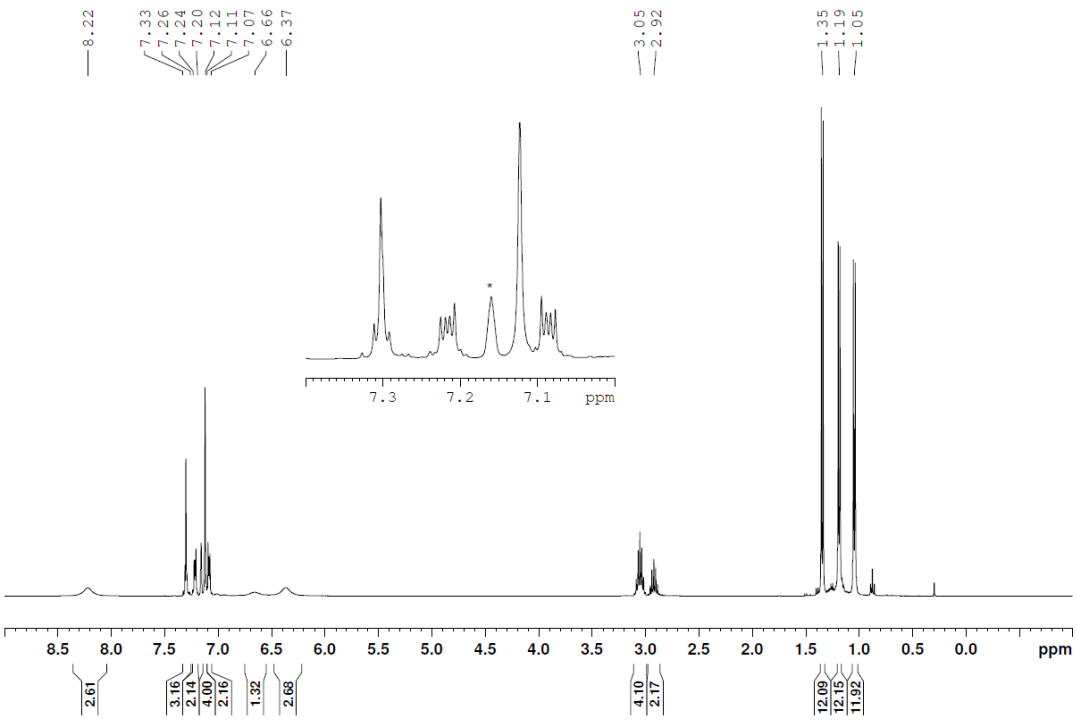

Figure S13. ^{1}H NMR Spectrum of compound **7** in C_6D_6

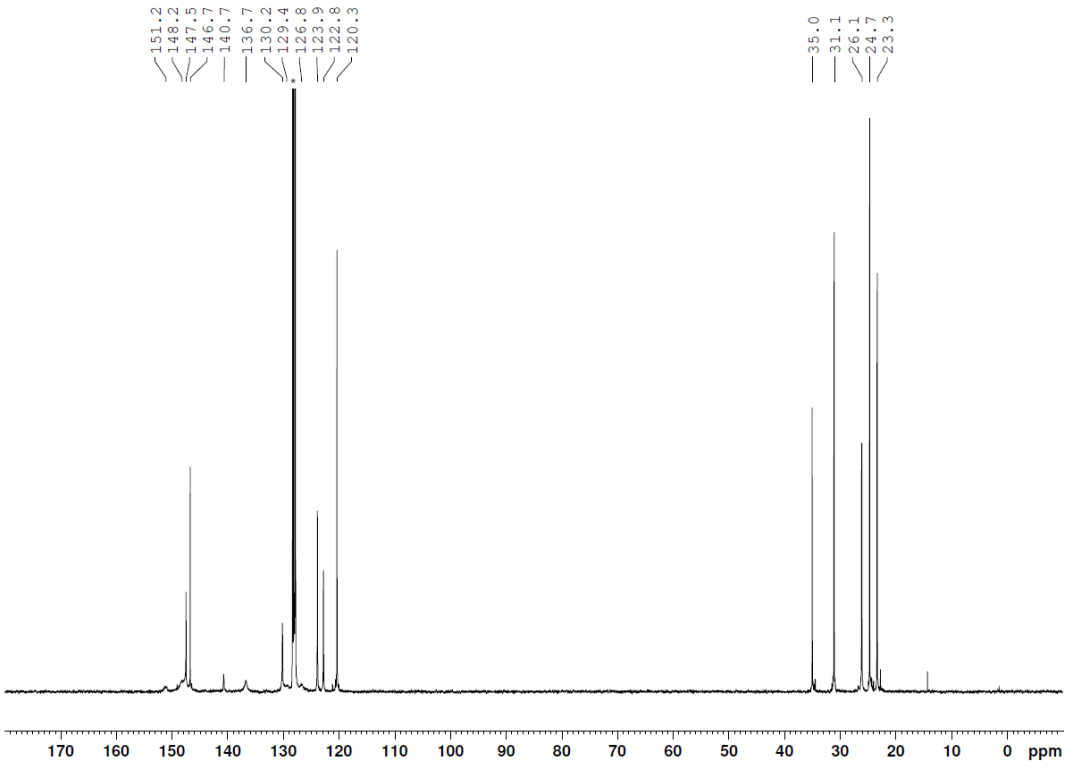

Figure S14. ^{13}C NMR Spectrum of compound **7** in C_6D_6

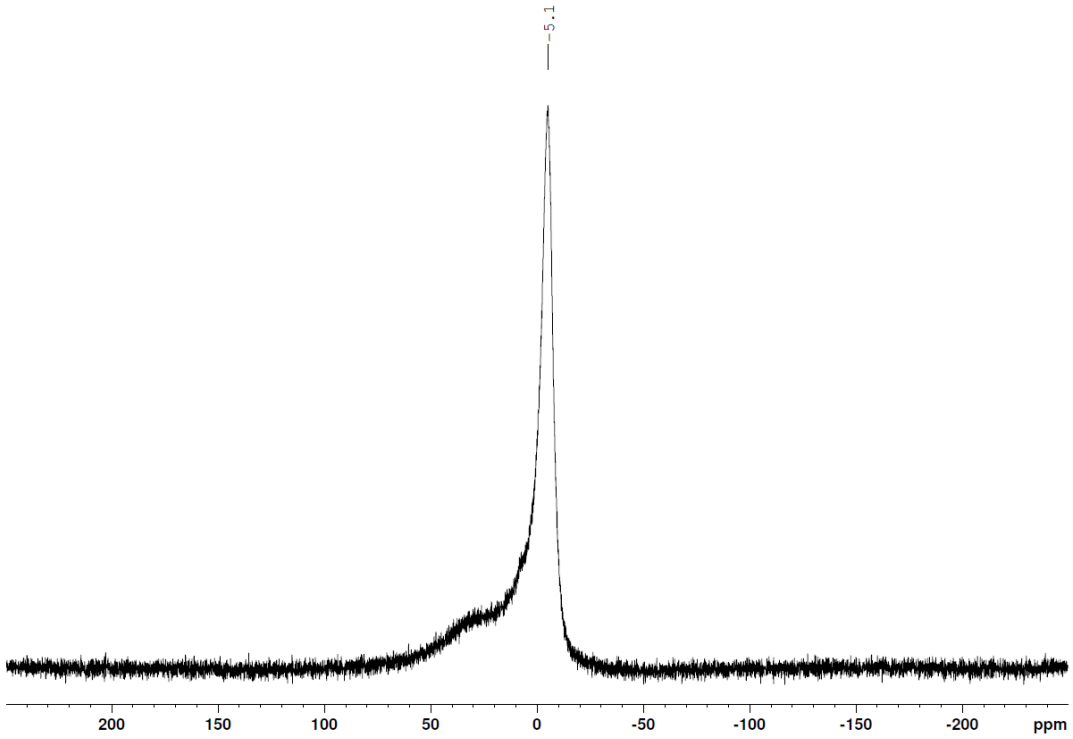

Figure S15. ^{11}B NMR Spectrum of compound **7** in C_6D_6

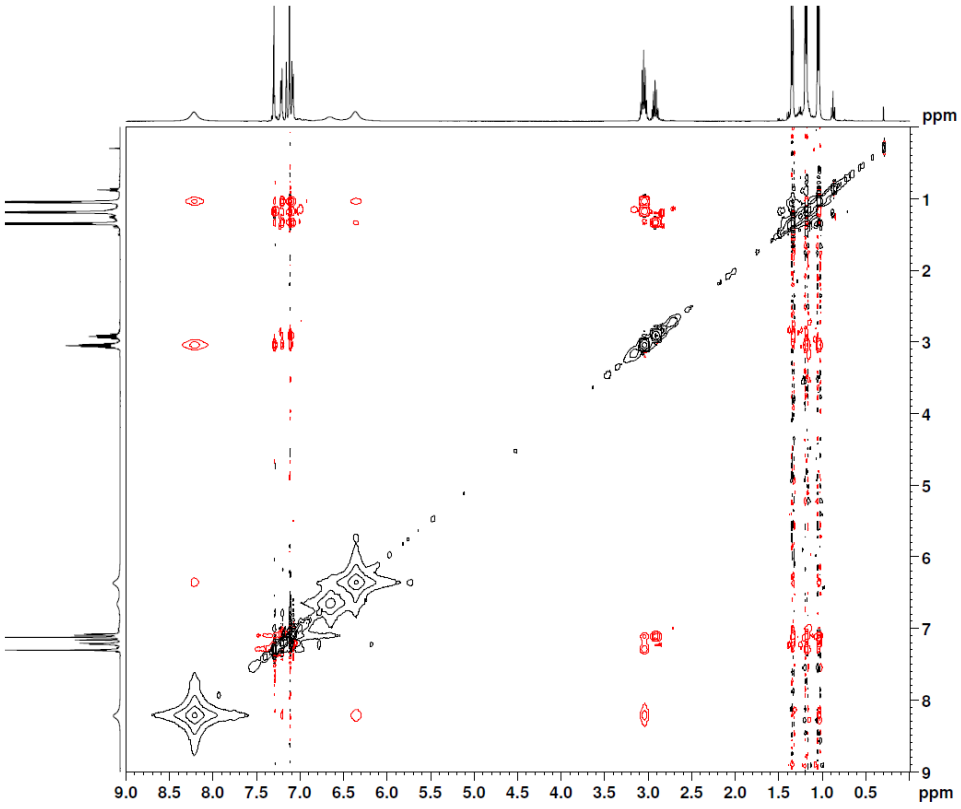

Figure S16. NOESY NMR Spectrum of compound **7** in C_6D_6

3. X-Ray Crystallography

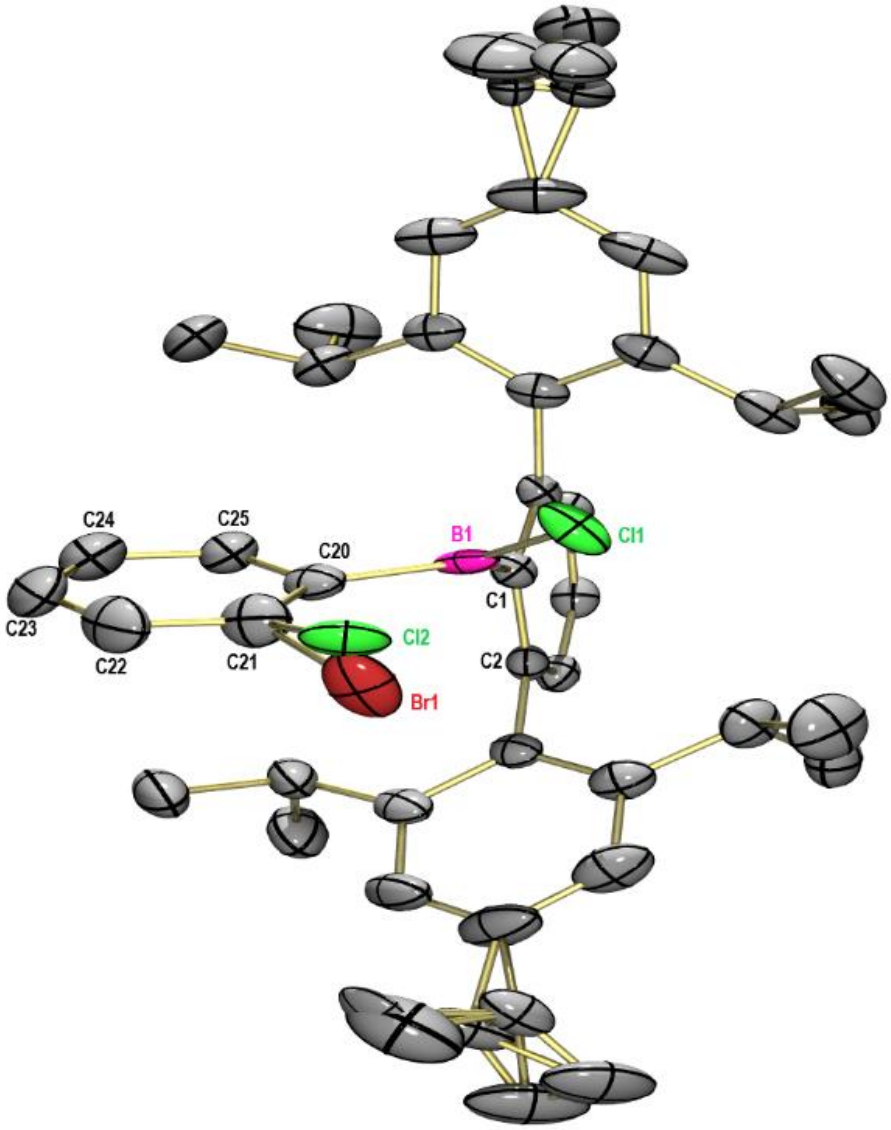

Figure S17. Nomenclature and Molecular structure of **3** in the solid state. Thermal ellipsoids are shown at the 50 % probability level. Hydrogen atoms have been omitted for clarity. Selected distances [pm] and angles [°] for 5: C1-B1 1.600, B1-Cl1 1.698, B1-C20 1.595, C20-C25 1.386, C20-C21 1.394, C21-C22 1.404, C22-C23 1.368, C23-C24 1.357, C24-C25 1.407, C21-Cl2 1.806, C21-Br1 1.908, C1-B1-Cl1 120.69, C1-B1-C20 117,86, Cl1-B1-C20 121.43, C20-C21-Cl2 123.93, C20-C21-Br1 121.56, Cl1-C21-C22 111.72, Br1-C21-C22 116.06, Cl1-B1-C20-C21 -31.59, Cl1-B1-C1-C2 106.17.

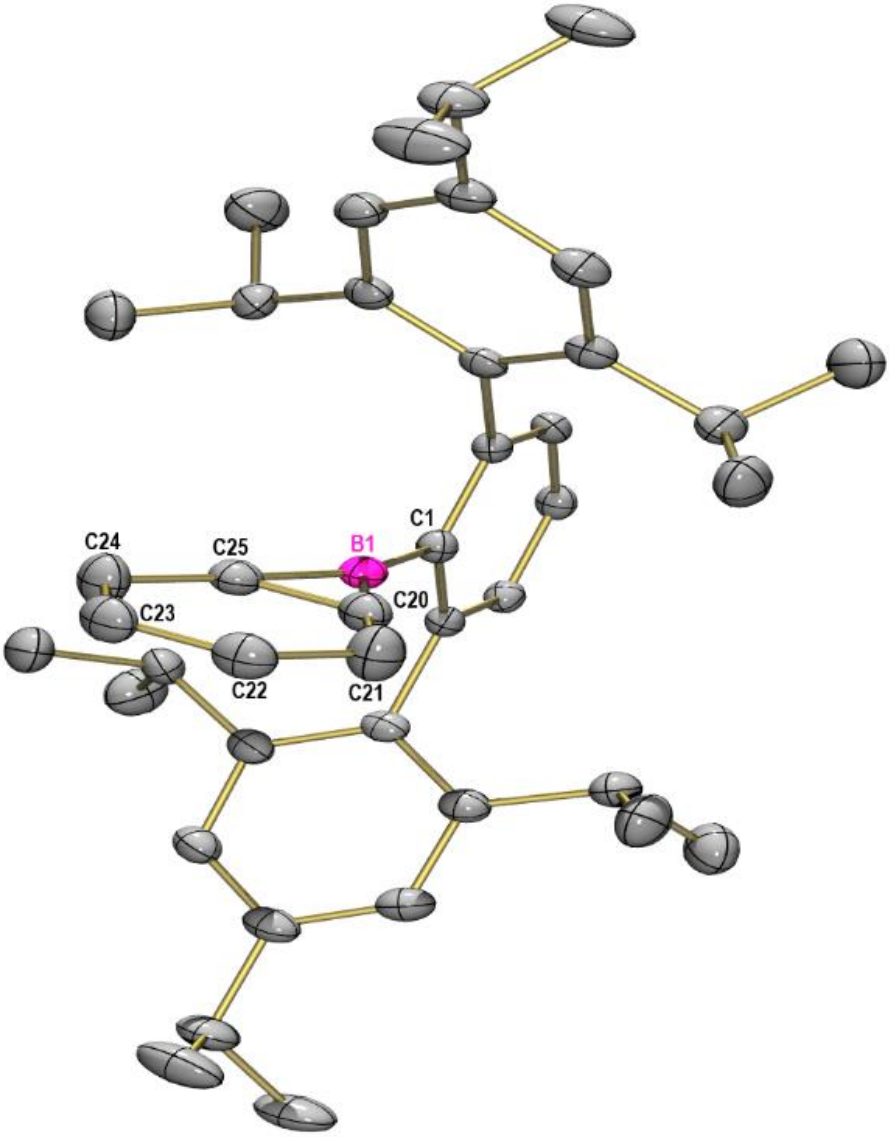

Figure S18. Nomenclature and Molecular structure of **4** in the solid state. Thermal ellipsoids are shown at the 50 % probability level. Hydrogen atoms have been omitted for clarity. Selected distances [pm] and angles [°] for 5: B1-C20 146.3, B1-C25 146.2, C20-C25 138.0, C20-C21 140.6, C21-C22 136.8, C22-C23 140.8, C23-C24 137.0, C24-C25 140.8, B1-C1 157.2, C20-B1-C25 56.49, B1-C20-C25 61.36, C20-C25-B1 62.15.

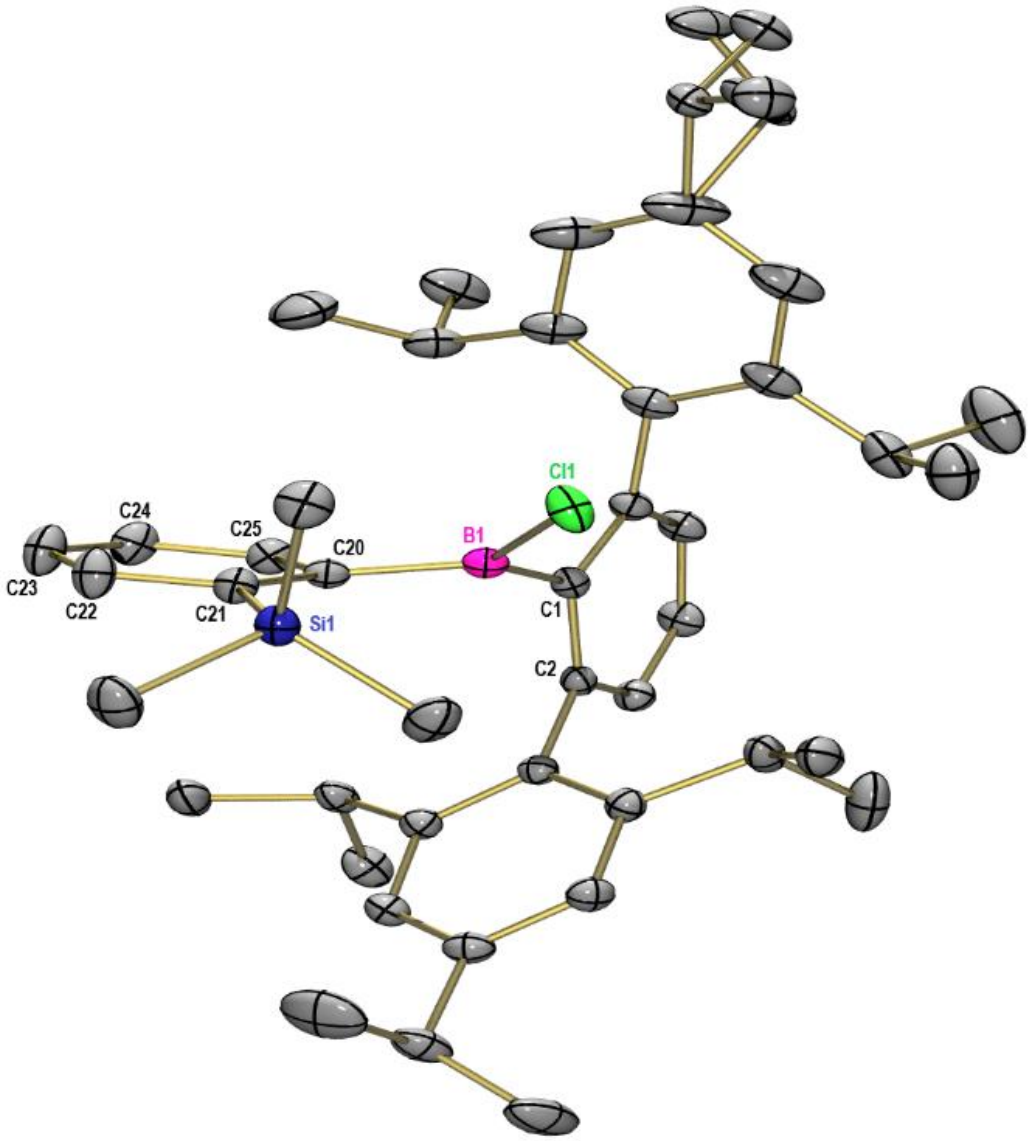

Figure S19. Nomenclature and Molecular structure of **5** in the solid state. Thermal ellipsoids are shown at the 50 % probability level. Hydrogen atoms have been omitted for clarity. Selected distances [pm] and angles [°] for 5: C1-B1 1.577, B1-Cl1 1.764, B1-C20 1.559, C20-C25 1.406, C20-C21 1.429, C21-C22 1.399, C22-C23 1.395, C23-C24 1.377, C24-C25 1.388, C21-Si1 1.901, C1-B1-Cl1 118.48, C1-B1-C20 122.26, Cl1-B1-C20 118.74, C20-C21-Si1 129.20, Si1-C21-C22 113.68, Cl1-B1-C20-C21 -27.11, Cl1-B1-C1-C2 120.11.

Table S1. Crystallographic Information for **2**, **5** and **6**			
	3	**4**	**5**
Empirical formula	$C_{42}H_{53.194}BBr_{0.741}Cl_{1.065}O_{0.194}$	$C_{42}H_{53}B$	$C_{45}H_{62}BClSi$
Formula weight	669.06	568.65	677.29
Temperature [K]	100.0(1)	99.99(11) K	100(2) K
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	P 1 2_1/c 1	Pnma	P 2_1/c
Unit cell dimensions	a = 12.6646(1) Å	a = 16.6182(1) Å	a = 12.5107(5) Å
	b = 18.2257(1) Å	b = 25.1186(2) Å	b = 18.5950(8) Å
	c = 16.7666(1) Å	c = 8.47933(6) Å	c = 18.2194(7) Å
	α = 90°	α = 90°	α = 90°
	β = 105.860(1)°	β = 90°	β = 105.6620(10)°.
	γ = 90°	γ = 90°	γ = 90°
Volume [$Å^3$]	3722.76(5)	3539.49(5)	4081.1(3)
Z	4	4	4
Density (calculated) [Mg/m^3]	1.194	1.067	1.102
Crystal size [mm^3]	0.201 x 0.18 x 0.11	0.123 x 0.106 x 0.065	0.311 x 0.134 x 0.101
Crystal Colour	colourless	colourless	colourless
Theta range for data collection	3.660 to 58.932°	3.519 to 63.683°	1.596 to 28.314°
Index ranges	$-14 \leq h \leq 14$, $-20 \leq k \leq 20$, $-18 \leq l \leq 18$	$-19 \leq h \leq 19$, $-29 \leq k \leq 29$, $-9 \leq l \leq 9$	-16<=h<=16, -24<=k<=24, -24<=l<=24
Reflections collected	91312	80754	80271
Independent reflections	5346 [R(int) = 0.0630]	2989 [R(int) = 0.0625]	10161 [R(int) = 0.0666]
Goodness-of-fit on F2	1.093	1.024	1.029
Final R indices [I>2sigma(I)]	R1 = 0.0622, wR2 = 0.1350	R1 = 0.0439, wR2 = 0.1118	R1 = 0.0495, wR2 = 0.1121
R indices (all data)	R1 = 0.0629, wR2 = 0.1353	R1 = 0.0506, wR2 = 0.1167	R1 = 0.0714, wR2 = 0.1270
CCDC number	2062895	2081435	2121518

Experimental Data

Crystals suitable for X-Ray crystallography were grown by standard techniques from pentane -30 °C. Single crystals were selected, coated with Parabar 10312 (previously known as Paratone N, Hampton Research) and fixed on a microloop.
Compound **2**: Data were collected on a Bruker APEX DUO instrument equipped with an IμS microfocus sealed tube and QUAZAR optics for MoKα radiation (λ = 0.71073 Å). The Data collection strategy was determined using COSMO[3] employing ω-scans. Raw data were processed using APEX[4] and SAINT[5, 6], corrections for absorption effects were applied using SADABS[7]. The structure was solved by direct methods[8] and refined against all data by full-matrix least-squares methods on F2 using SHELXTL[8, 9] and Shelxle.[10]
Compounds **5** and **6**: Data were collected on a Rigaku XtaLab Synergy-S diffractometer with Mo-K_α radiation (λ = 0.71073 Å) and a mirror monochromator. Corrections for absorption effects were applied with CrysAlisPro 1.171.41.65a (Rigaku Oxford Diffraction, 2020). The structure was solved by direct methods (SHELXS)[11], and full-matrix least-squares structure refinements were performed with SHELXL-2014[9] implemented in Olex2 1.3-ac4.

4. Computational Details

All computationas were conducted with the Gaussian 16 program.[12] The geometries were fully optimized using the M06-2X functional in conjunction with the 6-311+G** basis set.[13] Subsequently, the stationary points were confirmed to correspond to minima by analytic computation of the Hessian matrix that showed no negative eigenvalue. The harmonic vibrational frequencies obtained were used without scaling for computation of zero-point vibrational energies, enthalpies and free energies at T = 298.15 K.

The natural bond orbital (NBO) analysis[14, 15] was performed for molecule **4** at the M06-2X/6-311+G** level of theory using the NBO 6.0 program.[16, 17].

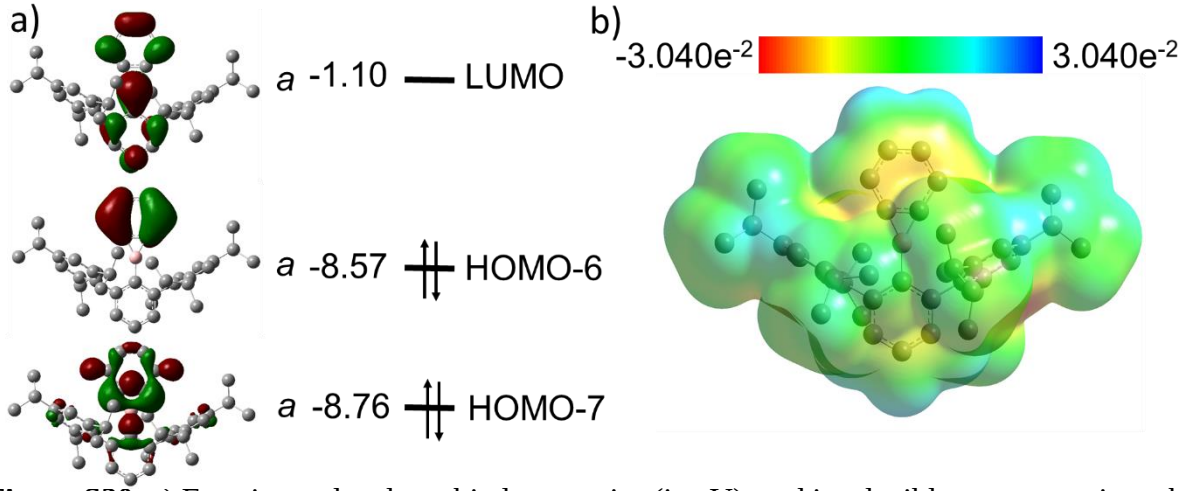

Figure S20. a) Frontier molecular orbitals, energies (in eV), and irreducible representations; b) electrostatic potential as computed at the M06-2X/6-311+G** level of theory. Hydrogen atoms have been omitted for clarity.

5. Cartesian Coordiantes

Computed at the M06-2X/6-311+G** level of theory and given in Å.

Benzoborirene

Atomic Number	Coordinates		
5	0.000000	0.000000	2.232621
6	-0.000000	0.696857	0.928470
6	-0.000000	1.443036	-0.266169
6	-0.000000	-1.443036	-0.266169
6	-0.000000	0.712714	-1.431096
6	-0.000000	-0.712714	-1.431096
6	-0.000000	-0.696857	0.928470
1	-0.000000	1.223479	-2.387934
1	-0.000000	-1.223479	-2.387934
1	0.000000	0.000000	3.409598
1	-0.000000	2.526899	-0.285647
1	-0.000000	-2.526899	-0.285647

Compound **4**

Atomic Number	Coordinates		
5	0.042502	-0.624951	0.165598
6	0.696251	-1.950948	0.073868
6	-0.667344	-1.907382	0.368114
6	-1.431655	-3.072652	0.551342
6	-0.748595	-4.261842	0.422011
6	0.644260	-4.307045	0.125486
6	1.393764	-3.165015	-0.052431
1	-2.492978	-3.049011	0.775557
1	-1.274505	-5.202573	0.545955
1	1.115939	-5.280200	0.039285
1	2.454008	-3.212689	-0.276959
6	0.051237	3.669266	-0.418572
6	1.255785	2.996319	-0.252572
6	1.270804	1.619705	-0.038320
6	0.051955	0.911282	0.037701
6	-1.170987	1.605412	-0.103971
6	-1.153883	2.977065	-0.353585
1	0.049473	4.738370	-0.599340
1	2.193811	3.539207	-0.283518
1	-2.093241	3.502179	-0.488705
6	-4.935304	-0.534458	-0.240458
6	-4.127926	-0.399472	-1.358988
6	-2.915137	0.291678	-1.316531
6	-2.489278	0.876895	-0.110694
6	-3.301018	0.763572	1.039886
6	-4.499870	0.056620	0.943544
1	-4.450406	-0.844413	-2.296025
1	-5.113577	-0.033980	1.835350
6	5.014251	-0.525514	0.328171
6	4.329272	-0.080868	1.446761
6	3.125493	0.628992	1.365908
6	2.586409	0.908269	0.096176
6	3.284903	0.496632	-1.063286
6	4.472988	-0.217987	-0.916478

1	4.737768	-0.293976	2.431617
1	4.993571	-0.538115	-1.815100
6	2.509825	0.972697	2.724832
1	3.372597	1.091407	3.389165
6	1.713648	-0.226057	3.261272
1	1.323212	-0.011080	4.260142
1	0.868971	-0.464179	2.614084
1	2.343159	-1.117100	3.316113
6	1.714977	2.275863	2.857279
1	1.565833	2.483915	3.920469
1	2.254682	3.118330	2.419518
1	0.731462	2.227731	2.391073
6	-2.956728	1.305339	2.424687
1	-3.844803	1.107926	3.032675
6	-1.797292	0.535977	3.061832
1	-1.654488	0.849678	4.100182
1	-1.973650	-0.542357	3.041390
1	-0.872690	0.736460	2.523619
6	-2.711352	2.817765	2.505318
1	-2.777673	3.138178	3.548566
1	-1.720732	3.089326	2.140574
1	-3.456153	3.374259	1.931301
6	-6.240713	-1.302585	-0.300888
1	-6.378370	-1.623530	-1.338819
6	-6.184856	-2.557116	0.578358
1	-7.114022	-3.127137	0.498236
1	-5.356184	-3.204692	0.283839
1	-6.045464	-2.285956	1.628531
6	-7.434445	-0.422197	0.084035
1	-8.370761	-0.974783	-0.027356
1	-7.359331	-0.098655	1.125630
1	-7.481771	0.470582	-0.542586
6	-2.110610	0.395057	-2.602416
1	-1.166318	0.884671	-2.375453
6	-2.838884	1.268092	-3.631568
1	-2.234473	1.375406	-4.536277
1	-3.797065	0.823395	-3.914631
1	-3.036061	2.264147	-3.228177
6	-1.781464	-0.983349	-3.187832
1	-1.129432	-0.875210	-4.058684
1	-1.273951	-1.613549	-2.453111
1	-2.685659	-1.505630	-3.511773
6	2.899278	0.812228	-2.510119
1	3.444508	0.073400	-3.105468
6	1.426737	0.667674	-2.904224
1	1.355592	0.600810	-3.993839
1	0.981658	-0.235325	-2.479167
1	0.838404	1.530342	-2.589034
6	3.430560	2.190490	-2.930433
1	3.286690	2.338044	-4.004431
1	2.894890	2.986612	-2.409625
1	4.495081	2.287828	-2.706769
6	6.300416	-1.317045	0.455146
1	6.539416	-1.376216	1.522174
6	7.467651	-0.621107	-0.252891
1	8.397206	-1.173446	-0.093996
1	7.292456	-0.566248	-1.330656
1	7.601433	0.396808	0.118483
6	6.120511	-2.746156	-0.069598
1	7.039595	-3.323731	0.058298
1	5.314059	-3.258434	0.459495

1	5.873960	-2.736632	-1.135057

Compound **4**, broken bond, triplet

Atomic Number	Coordinates		
5	0.043636	0.317192	0.028045
6	1.129389	2.580472	-0.085515
6	-0.019443	1.794418	0.013238
6	-1.249073	2.514804	0.091026
6	-1.249862	3.898433	0.063110
6	-0.058706	4.626546	-0.038286
6	1.164197	3.949683	-0.116324
1	-2.184454	1.967126	0.166586
1	-2.195610	4.425452	0.118909
1	-0.080050	5.709590	-0.058677
1	2.097666	4.494130	-0.200574
6	0.075915	-3.915868	-0.509390
6	1.280446	-3.211963	-0.514937
6	1.297268	-1.833848	-0.359833
6	0.065011	-1.145537	-0.222711
6	-1.165701	-1.854427	-0.246320
6	-1.137167	-3.235582	-0.364614
1	0.079190	-4.993503	-0.618761
1	2.216822	-3.741929	-0.650202
1	-2.071820	-3.786610	-0.354711
6	-4.645609	0.616251	0.493459
6	-3.868285	0.115219	1.528341
6	-2.765879	-0.707607	1.294985
6	-2.424888	-1.058934	-0.030402
6	-3.230131	-0.593847	-1.096183
6	-4.314787	0.236567	-0.804194
1	-4.124469	0.380101	2.549927
1	-4.912196	0.603190	-1.632327
6	4.654532	0.869035	-0.031614
6	4.062250	0.617143	-1.255981
6	3.016933	-0.301152	-1.419314
6	2.544949	-1.000925	-0.290067
6	3.189879	-0.814602	0.962084
6	4.215211	0.122344	1.059179
1	4.412520	1.158957	-2.131158
1	4.687047	0.270114	2.026252
6	2.507892	-0.405691	-2.859671
1	3.414026	-0.298783	-3.466622
6	1.613720	0.795860	-3.200487
1	1.291936	0.747775	-4.244743
1	0.724512	0.815228	-2.570338
1	2.145579	1.737025	-3.043264
6	1.872974	-1.723777	-3.308665
1	1.788795	-1.714090	-4.398813
1	2.488904	-2.579584	-3.023949
1	0.875231	-1.881117	-2.901365
6	-3.000554	-0.892170	-2.574345
1	-3.849875	-0.432547	-3.088522
6	-1.736039	-0.216535	-3.106999
1	-1.679222	-0.313791	-4.194970
1	-1.715271	0.846675	-2.850833
1	-0.849227	-0.684203	-2.683211
6	-3.024761	-2.380090	-2.947393

1	-3.156104	-2.479980	-4.028062
1	-2.091750	-2.876729	-2.681348
1	-3.849887	-2.901036	-2.455802
6	-5.754689	1.607217	0.784196
1	-6.057356	1.454289	1.825642
6	-5.204957	3.035517	0.656383
1	-5.975094	3.772991	0.896993
1	-4.355512	3.188840	1.326732
1	-4.864852	3.216137	-0.368174
6	-6.989614	1.421431	-0.099190
1	-7.794435	2.078805	0.237504
1	-6.776086	1.676331	-1.140277
1	-7.349791	0.391161	-0.067646
6	-2.006215	-1.244858	2.496153
1	-1.087263	-1.703018	2.137424
6	-2.824795	-2.342534	3.187955
1	-2.267674	-2.758688	4.031415
1	-3.769676	-1.942208	3.566572
1	-3.055625	-3.153526	2.493252
6	-1.617955	-0.142786	3.487540
1	-0.970278	-0.553838	4.266008
1	-1.081216	0.667303	2.985927
1	-2.494164	0.284148	3.982104
6	2.925326	-1.626293	2.231112
1	3.446069	-1.077013	3.021160
6	1.473180	-1.757122	2.696982
1	1.462122	-2.084256	3.740874
1	0.950817	-0.800346	2.635365
1	0.922189	-2.496330	2.113686
6	3.592941	-3.006206	2.146557
1	3.540345	-3.508129	3.116596
1	3.085776	-3.638709	1.416248
1	4.642721	-2.919070	1.858346
6	5.735721	1.918546	0.119895
1	5.915461	2.343245	-0.873317
6	7.051057	1.314733	0.622932
1	7.829148	2.080394	0.674969
1	6.928069	0.895357	1.625057
1	7.394793	0.515596	-0.036839
6	5.264668	3.048424	1.042610
1	6.011574	3.844799	1.092185
1	4.322007	3.471888	0.689672
1	5.101354	2.674698	2.057068

Benzyne

Atomic Number	Coordinates		
6	-0.000000	1.458762	-0.132584
6	-0.000000	0.619629	-1.230439
6	-0.000000	0.702118	1.051810
1	-0.000000	1.224859	2.002072
6	-0.000000	-0.619629	-1.230439
6	-0.000000	-0.702118	1.051810
1	-0.000000	-1.224859	2.002072
6	-0.000000	-1.458762	-0.132584
1	0.000000	-2.540098	-0.134791
1	0.000000	2.540098	-0.134791

$Trip_2C_6H_3B$

Atomic Number	Coordinates		
6	-0.007005	-1.066159	-3.090930
6	-1.217263	-0.848918	-2.443680
6	-1.233674	-0.383000	-1.129280
6	-0.018090	-0.212906	-0.445259
6	1.207970	-0.468419	-1.094014
6	1.202916	-0.856698	-2.428589
1	-0.002165	-1.396915	-4.123557
1	-2.156456	-1.008940	-2.962386
1	2.144694	-1.010209	-2.943679
6	-5.001089	0.312886	0.851514
6	-4.398084	-0.936962	0.860550
6	-3.178004	-1.171219	0.224816
6	-2.538215	-0.111501	-0.441120
6	-3.124157	1.171821	-0.461103
6	-4.346734	1.347155	0.185584
1	-4.889263	-1.753002	1.382657
1	-4.796994	2.336037	0.171154
6	4.933112	0.067491	1.012687
6	4.374983	-1.196716	0.864083
6	3.169413	-1.416564	0.193900
6	2.497905	-0.303849	-0.348448
6	3.033723	0.990277	-0.195416
6	4.243864	1.149269	0.475627
1	4.893370	-2.050398	1.292444
1	4.655466	2.148183	0.585050
6	-2.568237	-2.562364	0.307980
1	-1.646075	-2.570251	-0.274163
6	-2.501977	2.428004	-1.069948
1	-3.340324	3.121407	-1.190278
6	-6.325388	0.548848	1.550034
1	-6.633936	-0.406201	1.987823
6	6.242047	0.261678	1.751628
1	6.584279	-0.728432	2.070188
6	2.349520	2.228927	-0.756193
1	1.384789	1.935921	-1.175107
6	2.713159	-2.871921	0.098283
1	3.252898	-3.381432	0.902479
6	-6.180489	1.566267	2.687329
1	-7.127307	1.683480	3.220402
1	-5.416283	1.252100	3.400802
1	-5.892567	2.545752	2.295928
6	-7.410204	0.988465	0.560723
1	-8.371016	1.099309	1.069497
1	-7.156752	1.952066	0.110541
1	-7.526224	0.260859	-0.245035
6	-1.521451	3.082810	-0.088360
1	-1.195762	4.054719	-0.470497
1	-1.974398	3.226339	0.894564
1	-0.630981	2.463060	0.041795
6	-1.854250	2.297484	-2.453826
1	-1.740986	3.295995	-2.884305
1	-0.860660	1.848278	-2.404450
1	-2.465824	1.701987	-3.135121
6	-2.197854	-2.906793	1.755721
1	-1.690567	-3.874311	1.798698
1	-1.536365	-2.147793	2.182141
1	-3.090853	-2.963791	2.384448
6	-3.495084	-3.623996	-0.294144

1	-3.011998	-4.604082	-0.271986
1	-4.429698	-3.700064	0.267490
1	-3.743896	-3.385533	-1.330853
6	1.224819	-3.149825	0.343937
1	1.093901	-4.213156	0.562604
1	0.841121	-2.580389	1.195011
1	0.615198	-2.918119	-0.531337
6	3.171329	-3.520093	-1.215980
1	2.979663	-4.596293	-1.191327
1	2.625857	-3.104097	-2.065224
1	4.239336	-3.363184	-1.381499
6	2.078580	3.264159	0.341745
1	1.510409	4.105275	-0.063503
1	1.507588	2.824662	1.164043
1	3.011360	3.658687	0.752967
6	3.174054	2.835907	-1.897690
1	2.661081	3.703933	-2.319677
1	4.154230	3.162707	-1.539718
1	3.333244	2.106725	-2.695545
6	7.315488	0.862817	0.837653
1	8.267501	0.947035	1.367609
1	7.466536	0.246620	-0.050951
1	7.026560	1.864448	0.507687
6	6.049315	1.122683	3.005024
1	6.986914	1.208379	3.559924
1	5.725630	2.131584	2.734967
1	5.292502	0.693497	3.664335
5	-0.023297	0.132657	1.070783

6. References

1. D. Kaufmann, *Chem. Ber.*, 1987, **120**, 901-905.
2. B. Schiemenz and P. P. Power, *Organometallics*, 1996, **15**, 958-964.
3. COSMO (1.61), Bruker AXS INC., Madison, WI, 2012.
4. APEX3 (2017.3-0), Bruker AXS INC., Madison, WI, 2017.
5. SAINT (8.34A), Bruker AXS INC., Madison, WI, 2013.
6. SAINT (8.37A), Bruker AXS INC., Madison, WI, 2015.
7. L. Krause, R. Herbst-Irmer, G. M. Sheldrick and D. Stalke, *J. Appl. Crystallogr.*, 2015, **48**, 3-10.
8. G. M. Sheldrick, *Acta Cryst. A*, 2008, **64**, 112-122.
9. G. M. Sheldrick, *Acta Crystallogr., Sect. C Structural Chemistry*, 2015, **71**, 3-8.
10. C. B. Hübschle, G. M. Sheldrick and B. Dittrich, *J. Appl. Crystallogr.*, 2011, **44**, 1281-1284.
11. G. Sheldrick, Shelxs University of Göttingen, Germany, 1997.
12. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian 16 (Rev. C.01), Wallingford, CT, 2016.

13. Y. Zhao and D. Truhlar, *Theoretical Chemistry Accounts*, 2008, **120**, 215-241.
14. E. D. Glendening, C. R. Landis and F. Weinhold, *WIREs Computational Molecular Science*, 2012, **2**, 1-42.
15. F. Weinhold, *J. Comput. Chem.*, 2012, **33**, 2363-2379.
16. E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis and F. Weinhold, NBO 6.0, Theoretical Chemistry Institute, University of Wisconsin-Madison, Madison, WI, 2013.
17. E. D. Glendening, C. R. Landis and F. Weinhold, *J. Comput. Chem.*, 2013, **34**, 1429-1437.