

Electronic Supporting Information

Accessing unusual heterocycles: Ring expansion of benzoborirene by formal cycloaddition reactions

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1. Experimental Methods

General Procedures. All experiments were performed under anhydrous conditions using argon as protective gas. The NMR spectra were recorded with either a *Bruker Avance III HD 300 NanoBay* NMR spectrometer (5 mm BBFO probe head) operating at 96.29 (^{11}B), and 121.49 (^{31}P), a *Bruker Avance III HD 400* NMR spectrometer (5 mm BBFO probe head) operating at 400.11 (^1H), 100.62 (^{13}C), 128.39 (^{11}B) and 161.97 MHz (^{31}P), a *Bruker Avance III HDX* NMR spectrometer (5 mm BBO probe head (^1H coil tunable for ^{19}F)) operating at 400.11 (^1H), 100.62 (^{13}C), 128.39 (^{11}B) and 161.97 MHz (^{31}P), a *Bruker Avance III HDX 600* spectrometer (5 mm triple resonance probe head) operating at 600.13 (^1H), 150.90 MHz (^{13}C) and 242.94 (^{31}P) and a *Bruker Avance III HDX 700* NMR (5 mm TXI probe head) operating at 700.29 (^1H) and 176.09 MHz (^{13}C). The chemical shifts are reported as δ in ppm relative to the following external standards: tetramethylsilane (^1H , ^{13}C), boron trifluoride etherate (^{11}B), 85 % phosphorous acid (^{31}P).¹ The chemical shifts were referenced using the chemical shift of the solvent 2H resonance frequency as followed: $\Xi = 32.08397\%$ for ^{11}B , $\Xi = 25.145020\%$ for ^{13}C , and $\Xi = 40.480742$ for ^{31}P .¹ The multiplicity of the signals is abbreviated as s = singlet, d = doublet, t = triplet, q = quartet, sept = septet and m = multiplet or br. = broad/unresolved. The proton and carbon signals were assigned via detailed analysis of ^1H , $^{13}\text{C}\{^1\text{H}\}$ (-UDEFT), ^1H - ^1H -COSY, ^1H - ^1H -NOESY, ^1H - ^{13}C -HSQC and ^1H - ^{13}C -HMBC NMR spectra. Selected 1D- and 2D-NMR spectra of the compounds can be found below. 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. For HR-APCI-TOF-MS measurements a *Bruker* maXis 4G spectrometer (sample application: DIP) was used, for HR-LIFDI-Orbitrap-MS a *Thermo Fisher Scientific* Exactive Plus Orbitrap mass spectrometer equipped with a *Linden CMS* LIFDI source was used. Benzoborirene **1** was synthesized as described in the literature.²

Synthesis.

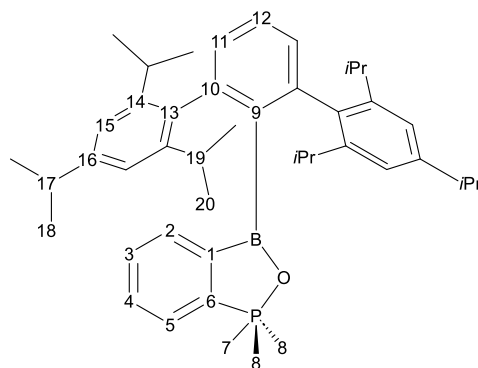
Compound **2**. To 197.6 mg (0.3475 mmol) **1** solved in 8 mL toluene was added 32.0 mg (0.3475 mmol) trimethylphosphine oxide. The solvent was removed under reduced pressure and the remaining solid solved in pentane and stored at $-30\text{ }^\circ\text{C}$ to yield colourless crystals suitable for x-ray crystallography. Yield: 212.1 mg (0.321 mmol, 92 %) ^1H (600.13 MHz, *tol-d*₈, 235 K): $\delta = 0.53$ (d, 3H, 7, $^2J_{\text{PH}} = 4.71$ Hz), 0.78 (d, 6H, 20.2, $^3J_{\text{HH}} = 6.13$ Hz), 0.95 (d, 6H, 8, $^2J_{\text{PH}} = 13.90$ Hz), 1.17 (m, 12H, 18), 1.20 (d, 6H, 20.1, $^3J_{\text{HH}} = 6.37$ Hz), 1.24 (d, 6H, 20.2, $^3J_{\text{HH}} = 5.44$ Hz), 1.60 (d, 6H, 20.1, $^3J_{\text{HH}} = 6.14$ Hz), 2.70 (sept, 2H, 17, $^3J_{\text{HH}} = 6.79$ Hz), 3.25 (sept, 2H, 19.2, $^3J_{\text{HH}} = 6.37$ Hz), 3.33 (sept, 2H, 19.1, $^3J_{\text{HH}} = 6.37$ Hz), 6.90 (s, 2H, 15), 6.99-7.05 (m, 1H, 4), 7.16 (s, 2H, 15), 7.18-7.23 (m, 1H, 5), 7.28-7.32 (m, 2H, 11), 7.32-7.37 (m, 2H, 3, 12), 7.69 (d, 1H, 2, $^3J_{\text{HH}} = 7.02$ Hz) ppm;

$^{13}\text{C}\{^1\text{H}\}$ (150.90 MHz, *tol-d*₈, 235 K): $\delta = 21.3$ (d, 8, $^1J_{\text{CP}} = 108.0$ Hz), 22.8 (20.1), 23.1 (20.2), 24.3 (18), 24.7 (18), 25.8 (20.1), 27.1 (20.2), 27.3 (d, 7, $^1J_{\text{CP}} = 17.8$ Hz), 30.7 (19.1), 31.1 (19.2), 34.8 (17), 120.3 (15), 126.4 (11), 128.5 (12), 129.1 (4), 131.9 (3), 132.4 (d, 5, $^2J_{\text{CP}} = 18.9$ Hz), 133.9 (d, 2, $^3J_{\text{CP}} = 18.1$ Hz), 138.8 (13), 140.3 (d, 6, $^1J_{\text{CP}} = 132.1$ Hz), 142.8 (10), 143.2 (9), 145.6 (14.2), 145.8 (d, 1, $^2J_{\text{CP}} = 31.2$ Hz), 147.4 (16), 145.6 (14.1) ppm;

$^{11}\text{B}\{^1\text{H}\}$ (128.39 MHz, *tol-d*₈): $\delta = 41.2$ ppm;

$^{31}\text{P}\{^1\text{H}\}$ (242.94 MHz, *tol-d*₈, 235 K): $\delta = -68.2$ ppm;

HR-APCI-TOF-MS: APCI $T_{\text{heater}} = 350\text{ }^\circ\text{C}$, calc. for $\text{C}_{45}\text{H}_{62}\text{BOP} + \text{H}$ 661.47118 Da, found 661.47129 Da $[\text{M}+\text{H}]^{\bullet+}$.



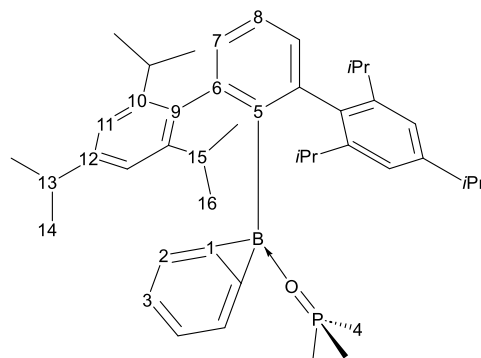
If the reaction is performed at -60 °C coordination complex **1**•OPMe₃ can be observed.

¹H (400.11 MHz, tol-d₈, 218 K): δ = 0.07-0.17 (m, 3H, **4**), 1.11 (d, 6H, **20.2**, ³J_{HH} = 6.61 Hz), 1.24-1.38 (m, 18H, **16.1+16.2**), 1.41 (d, 6H, **14.1**, ³J_{HH} = 6.42 Hz), 1.45 (d, 6H, **14.2**, ³J_{HH} = 6.80 Hz), 2.92-3.01 (m, 2H, **13.1+13.2**), 3.06 (sept, 2H, **15.2**, ³J_{HH} = 6.58 Hz), 3.42 (m, 2H, **15.1**), 6.98-7.03 (m, 1H, **3.2**), 7.18-7.22 (m, 1H, **2.2**), 7.24-7.28 (s, 2H, **11.1**), 7.28-7.30 (m, 1H, **2.1**), 7.30-7.31 (m, 1H, **3.1**), 7.31-7.33 (s, 2H, **11.2**), 7.33-7.43 (m, 3H, **7+8**) ppm;

¹³C{¹H} (100.62 MHz, tol-d₈, 218 K): δ = 13.2 (d, **4**, ¹J_{CP} = 70.92 Hz), 23.4 (**16.1**), 24.2 (**16.2**), 24.9 (**16.2**), 25.0 (**14**), 26.2 (**16.1**), 30.9 (**15.1**), 31.4 (**15.2**), 35.3 (**13**), 120.2 (**11.1**), 120.6 (**11.2**), 122.5 (**2.1**), 123.8 (**2**), 127.6 (**3.1**), 128.2 (**7**), 129.3 (**8**), 136.6 (**3**), 138.7 (**9.2**), 142.9 (**9.1**), 145.1 (**6**), 146.0 (**12.1**), 146.4 (**10.2**), 146.9 (**10.1**), 148.0 (**12.2**), 151.2 (**5**), 154.6 (**1.2**), 154.9 (**1.1**) ppm;

¹¹B{¹H} (128.39 MHz, tol-d₈, 218 K): δ = -5.31 ppm;

³¹P{¹H} (161.97 MHz, tol-d₈, 218 K): δ = 63.0 ppm



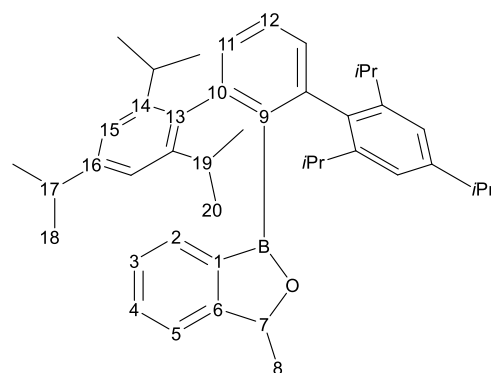
Compound **3**. To a vigorously stirred solution of 225.3 mg (0.396 mmol) **1** in 10 mL benzene was added 22.3 μL (0.396 mmol) acetaldehyde. After ten days the solvent was removed under reduced pressure and the remaining solid purified by column chromatography (silica, toluene : n-hexane 10 : 90). The purified product was solved in toluene, which was then carefully removed under reduced pressure to yield colourless crystals suitable for x-ray crystallography. Yield: 131.5 mg (0.215 mmol, 54 %).

¹H (700.29 MHz, C₆D₆): δ = 0.70 (d, ³J_{H,H} = 6.66 Hz, 3H, **8**), 1.09-1.14 (m, 24H, **18+20**), 1.28 (d, ³J_{H,H} = 6.85 Hz, 6H, **20**), 1.43 (d, ³J_{H,H} = 6.85 Hz, 6H, **20**), 2.70 (sept, ³J_{H,H} = 6.92 Hz, 2H, **17**), 3.23 (sept, ³J_{H,H} = 6.85 Hz, 2H, **19**), 3.26 (sept, ³J_{H,H} = 6.85 Hz, 2H, **19**), 4.82 (q, ³J_{H,H} = 6.66 Hz, 1H, **7**), 6.59 (d, ³J_{H,H} = 7.56 Hz, 1H, **2**), 6.94 (dt, ⁴J_{H,H} = 0.93 Hz, ³J_{H,H} = 7.43 Hz, 1H, **3**), 6.97 (d, ⁴J_{H,H} = 1.62 Hz, 2H, **15**), 7.04 (t, ³J_{H,H} = 7.36 Hz, 1H, **4**), 7.11 (d, ⁴J_{H,H} = 1.62 Hz, 2H, **15**), 7.32-7.36 (m, 3H, **11+12**), 7.53 (d, ³J_{H,H} = 7.36 Hz, 1H, **5**) ppm;

¹³C{¹H} (176.09 MHz, C₆D₆): δ = 21.9 (**8**), 22.7 (**20**), 23.2 (**20**), 24.2 (**18**), 24.4 (**18**), 26.3 (**20**), 26.6 (**20**), 30.9 (**19**), 31.2 (**19**), 34.7 (**17**), 82.6 (**7**), 120.4 (**2+15**), 120.6 (**15**), 126.4 (**4**), 127.8 (**12**), 128.8 (**11**), 130.6 (**3**), 132.6 (**5**), 137.1 (**1**), 138.2 (**13**), 139.2 (**5**), 144.1 (**10**), 147.0 (**14**), 147.5 (**14**), 148.3 (**16**), 158.8 (**6**) ppm;

¹¹B{¹H} (96.29 MHz, C₆D₆): δ = 50.8 ppm;

HR-APCI-TOF-MS: APCI T_{heater} = 300 °C, m/z calcd. for C₄₂H₅₃B 612.45045 Da, found 612.44948 Da [M]^{•+}.



Compound **4**. To 225.0 mg (0.398 mmol) **1** solved in 5 mL toluene were added 90.0 μ L (0.795 mmol) *tert*-butyl isonitrile. Volatiles were removed under reduced pressure and the remaining solid was solved in pentane. Storage at -30 °C yields the product as a red solid. Evaporation of toluene from a concentrated solution yields red crystals suitable for x-ray crystallography. Yield: 192.3 mg (0.339 mmol, 68 %)

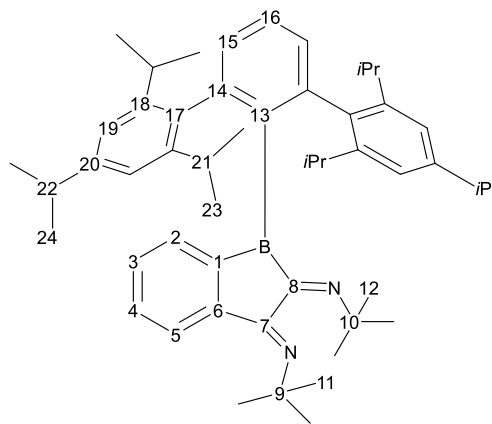
^1H (700.29 MHz, C_6D_{12} , 343 K): δ = 0.88 (br, 12H, **23.1**), 0.98 (d, 12H, **23.2**, $^3J_{\text{HH}}$ = 6.66 Hz), 1.04 (s, 9H, **12**), 1.10 (s, 9H, **11**), 1.18 (d, 12H, **24**, $^3J_{\text{HH}}$ = 6.88 Hz), 2.75 (sept, 2H, **22**, $^3J_{\text{HH}}$ = 6.93 Hz), 2.96 (sept, 4H, **21**, $^3J_{\text{HH}}$ = 6.74 Hz), 6.82 (s, 4H, **19**), 7.07 (d, 2H, **15**, $^3J_{\text{HH}}$ = 7.61 Hz), 7.08-7.13 (m, 1H, **4**), 7.24 (t, 1H, **3**, $^3J_{\text{HH}}$ = 7.51 Hz), 7.30 (t, 1H, **16**, $^3J_{\text{HH}}$ = 7.59 Hz), 7.39 (d, 1H, **5**, $^3J_{\text{HH}}$ = 7.75 Hz), 7.44 (d, 1H, **2**, $^3J_{\text{HH}}$ = 7.40 Hz) ppm;

$^{13}\text{C}\{^1\text{H}\}$ (176.09 MHz, C_6D_{12} , 343 K): δ = 23.0 (**23.1**), 23.8 (**24**), 25.7 (**23.2**), 26.3 (**23.2**), 30.6 (**11**), 30.7 (**21**), 31.2 (**12**), 34.5 (**22**), 56.3 (**9**), 60.2 (**10**), 120.8 (**19**), 126.0 (**5**), 126.6 (**16**), 128.6 (**4**), 129.5 (**15**), 132.6 (**3**), 133.9 (**2**), 138.1 (**17**), 142.0 (**14**), 142.6 (**13**), 147.1 (**18**), 147.8 (**20**), 148.2 (**1**), 148.3 (**6**), 166.7 (**7**), 185.8 (**8**) ppm;

$^{11}\text{B}\{^1\text{H}\}$: no signal detectable, ^{11}B NMR spectra in the solid state were measured instead (see S13),

^{11}B MAS NMR: δ_{iso} = 66.0 ppm

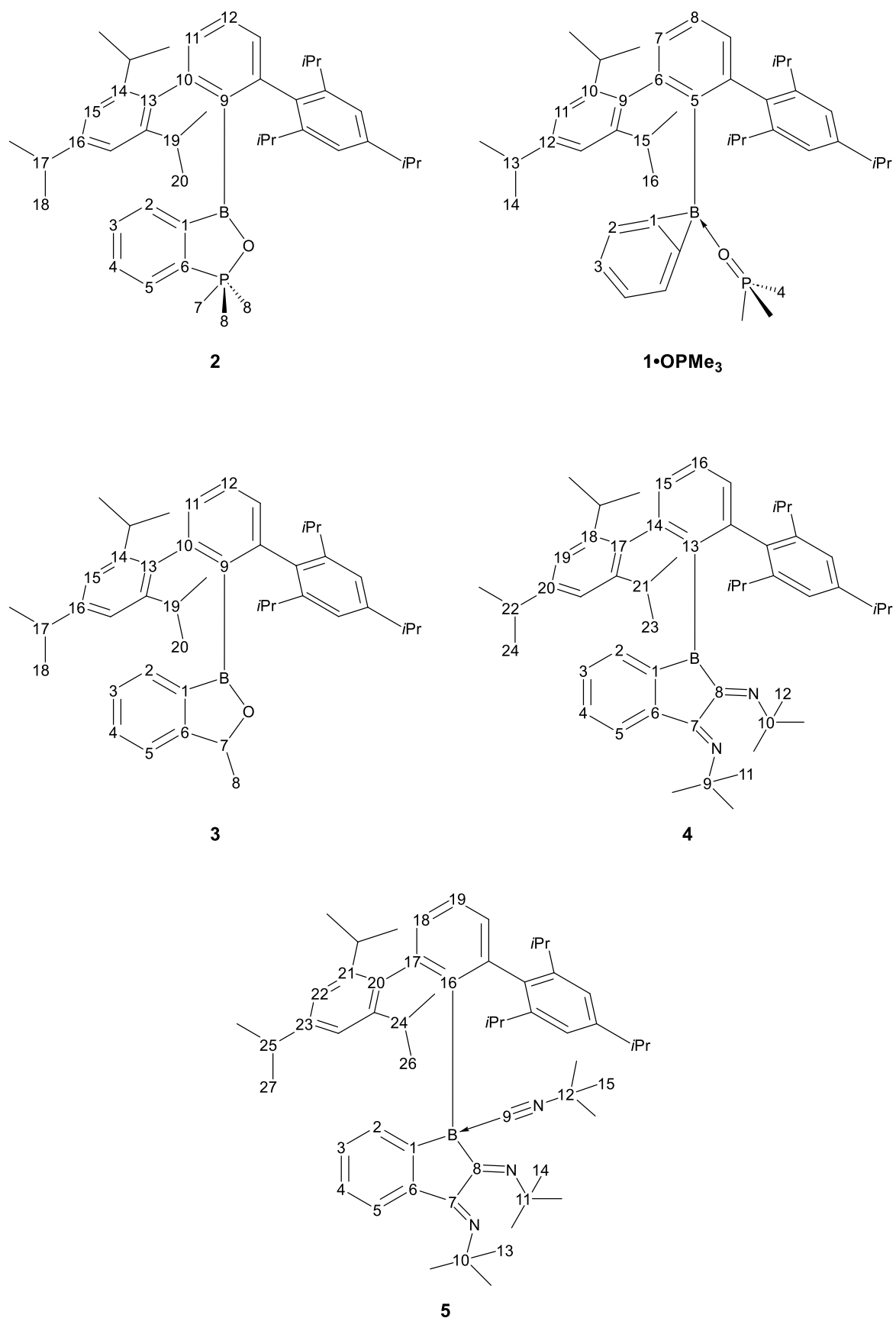
HR-LIFDI-Orbitrap-MS: calc. for $\text{C}_{52}\text{H}_{71}\text{BN}_2$ 734.57135 Da, found 734.57013 Da [M] $^{+}$.



Compound **5**. To 98.0 mg (0.133 mmol) **4** solved in toluene was added 15 μ L (0.133 mmol) *tert*-butyl isonitrile. Volatiles were removed under reduced pressure. The remaining yellow foam could not be purified further. Identified signals:

^1H (400 MHz, tol-d_8 , 318 K): δ = 0.52(s, 9H, **13**, **14** or **15**), 1.34(s, 9H, **13**, **14** or **15**), 1.64 ppm (s, 9H, **13**, **14** or **15**), 2.70-3.40 (multiple septets, 6H, **24+25**), 6.81-6.85 (m, 2H, **22**), 6.90-6.95 (m, 1H, **3** or **4**), 7.45 (d, 1H, **2** or **5**, $^3J_{\text{HH}}$ = 7.25 Hz), 7.57 (d, 1H, **2** or **5**, $^3J_{\text{HH}}$ = 7.81 Hz),

$^{11}\text{B}\{^1\text{H}\}$ (128 MHz, tol-d_8): δ = -12.6 ppm.



Scheme S1. NMR Nomenclature of compounds **2**, **3**, **4**, **5** and coordination complex **1•OPMe₃**.

2. NMR-Spectra

Solvent signals are denoted by an asterisk (*)

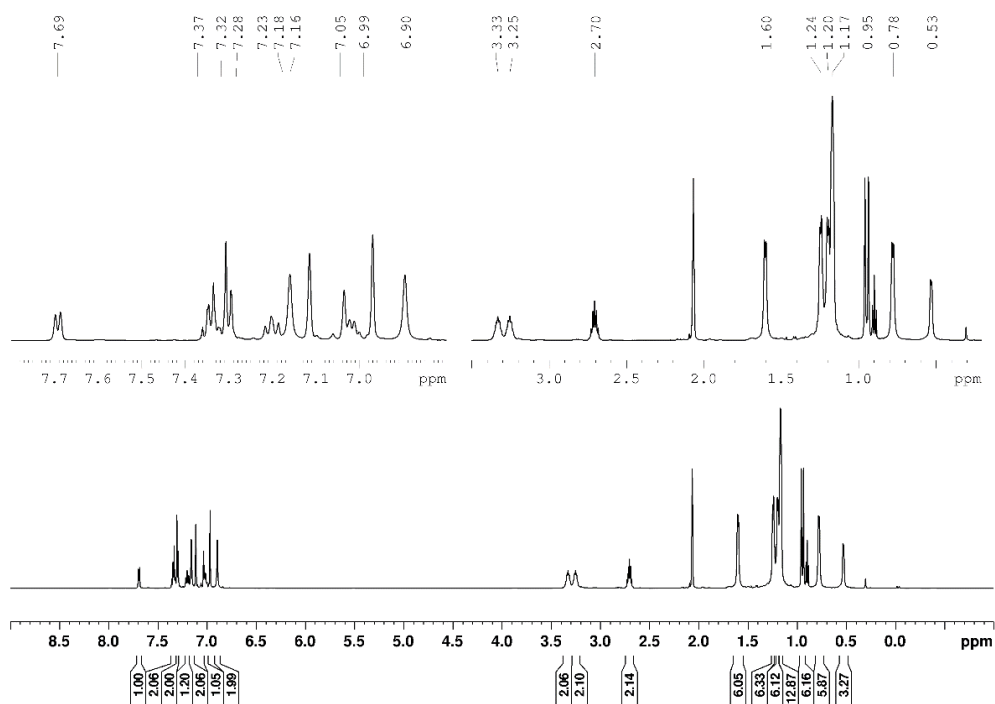


Figure S1. ¹H NMR spectrum of compound **2** in tol-d₈ at 235 K

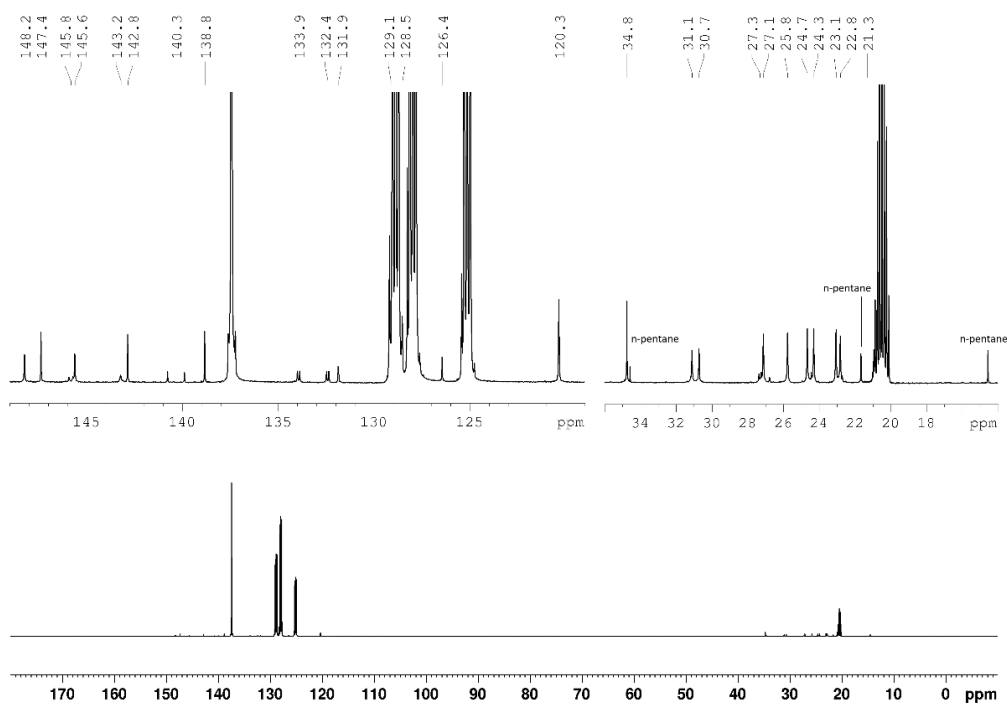


Figure S2. ¹³C{¹H} NMR spectrum of compound **2** in tol-d₈ at 235 K

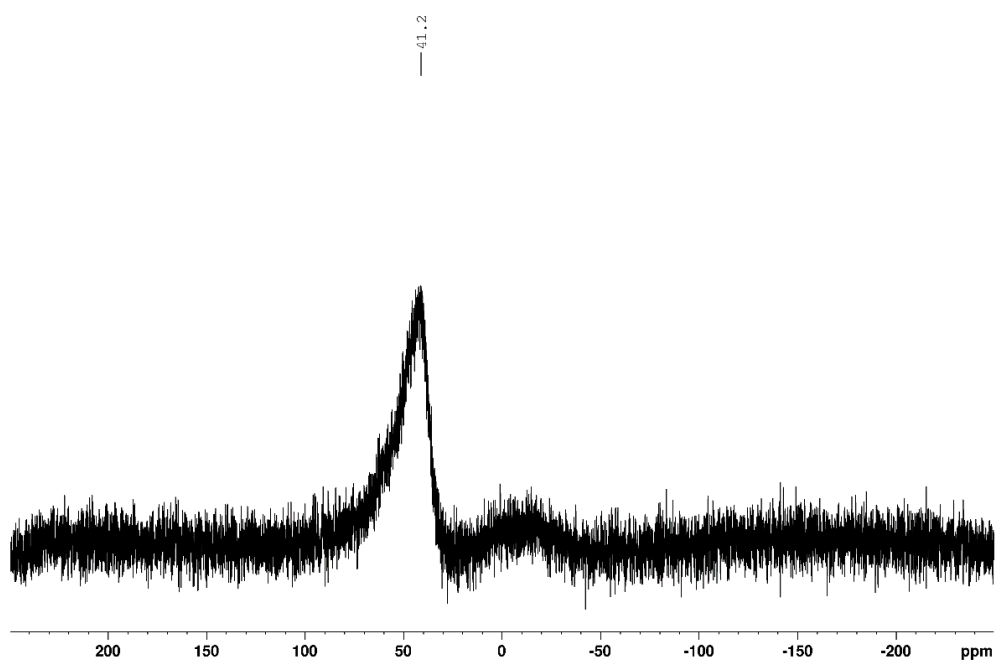


Figure S3. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of compound **2** in tol-d_8

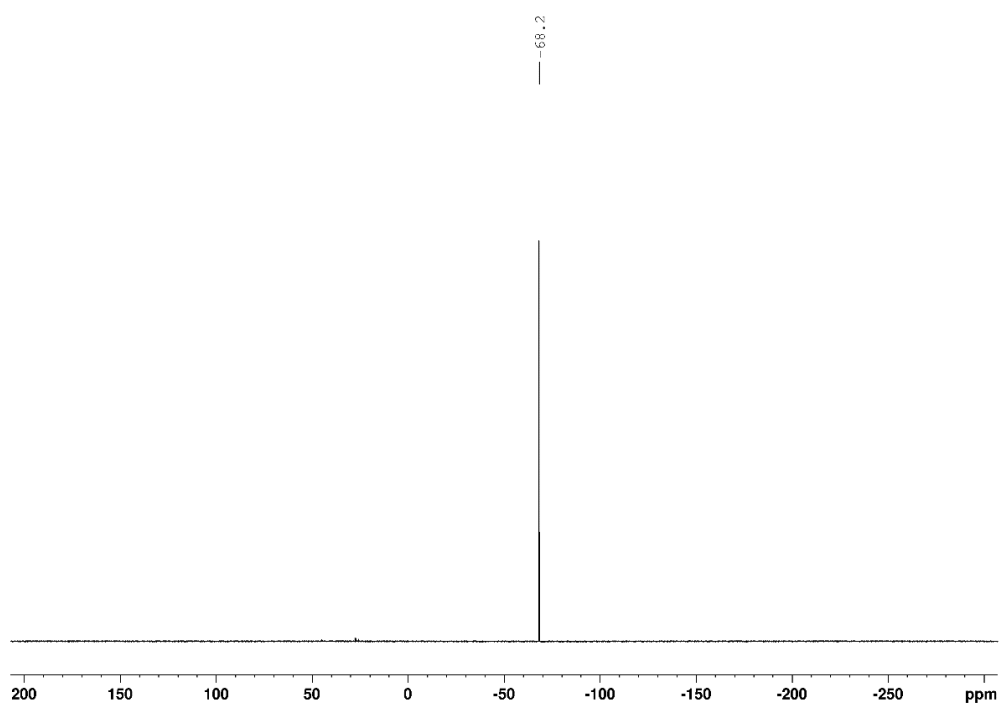


Figure S4. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of compound **2** in tol-d_8 at 235 K

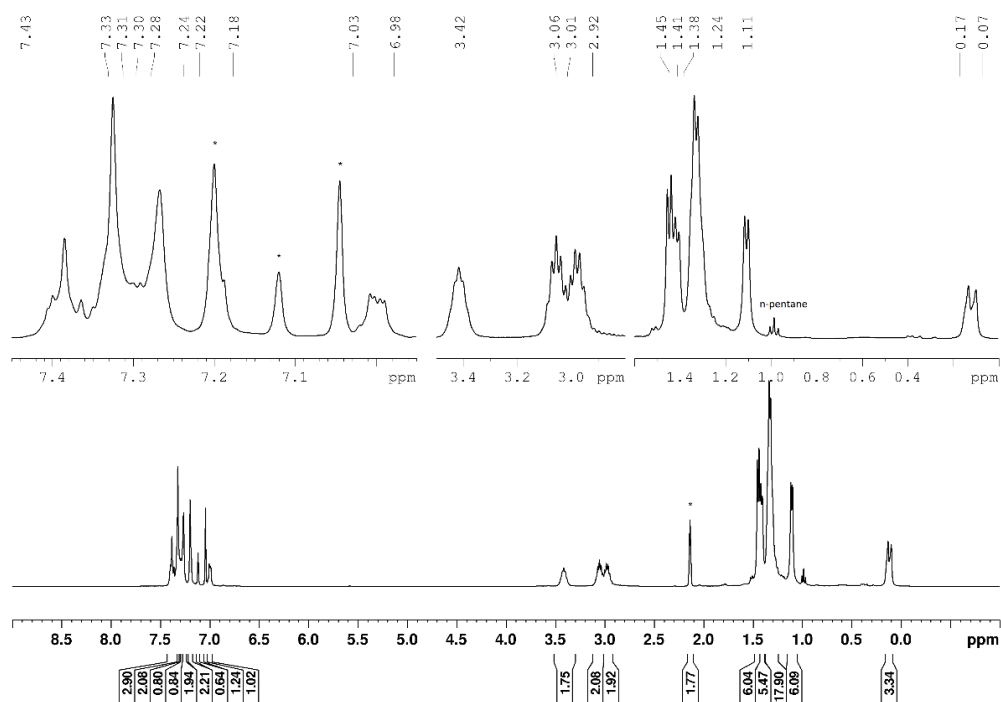


Figure S5. ^1H NMR Spectrum of coordination complex $\mathbf{1}\cdot\text{OPMe}_3$ in tol-d_8 at 213 K

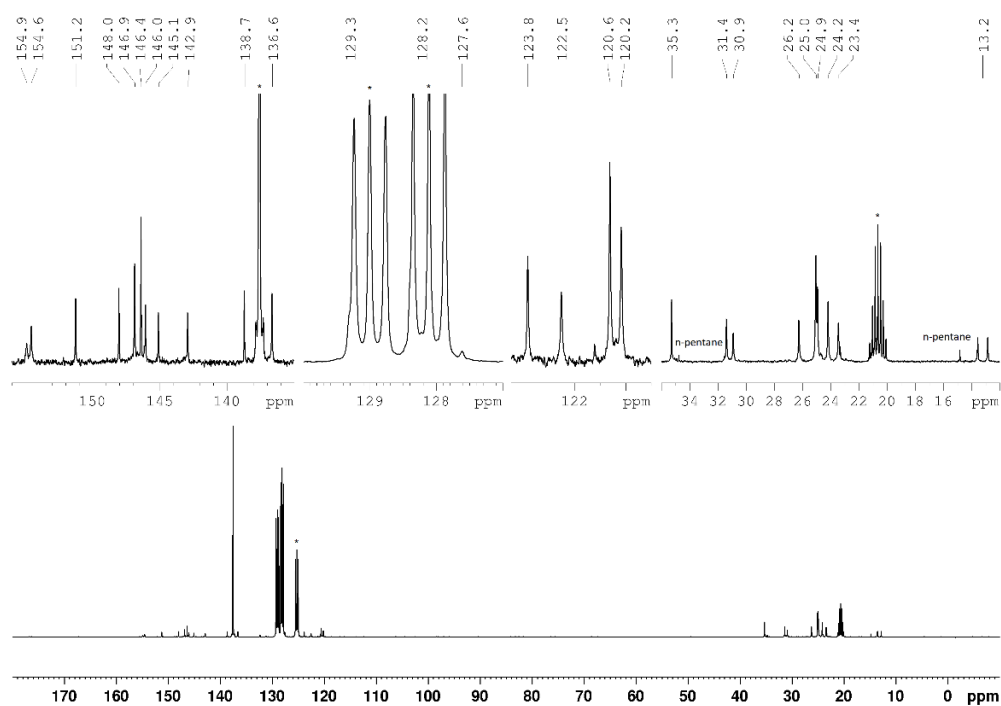


Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of coordination complex $\mathbf{1}\cdot\text{OPMe}_3$ in tol-d_8 at 213 K

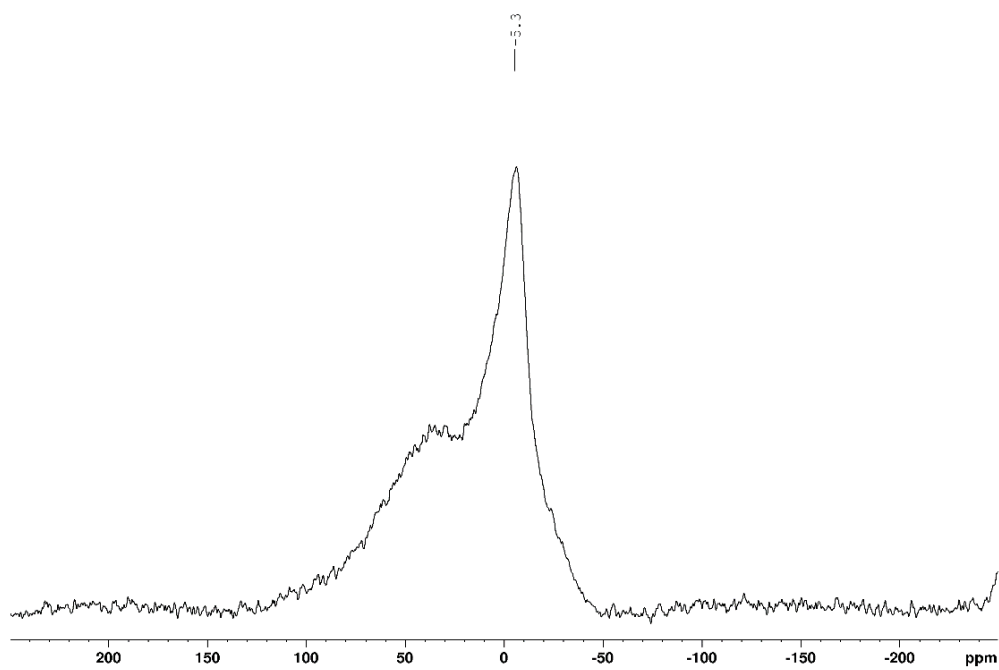


Figure S7. $^{11}\text{B}\{^1\text{H}\}$ NMR Spectrum of coordination complex **1•OPMe₃** in tol-d_8 at 213 K

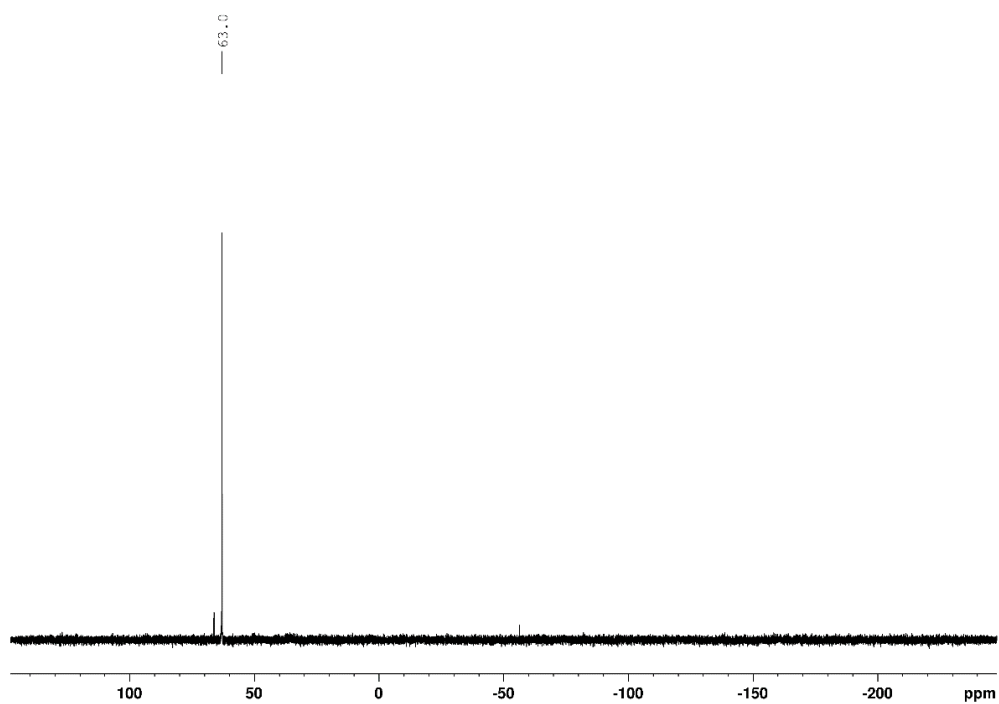


Figure S8. $^{31}\text{P}\{^1\text{H}\}$ NMR Spectrum of coordination complex **1•OPMe₃** in tol-d_8 at 213 K

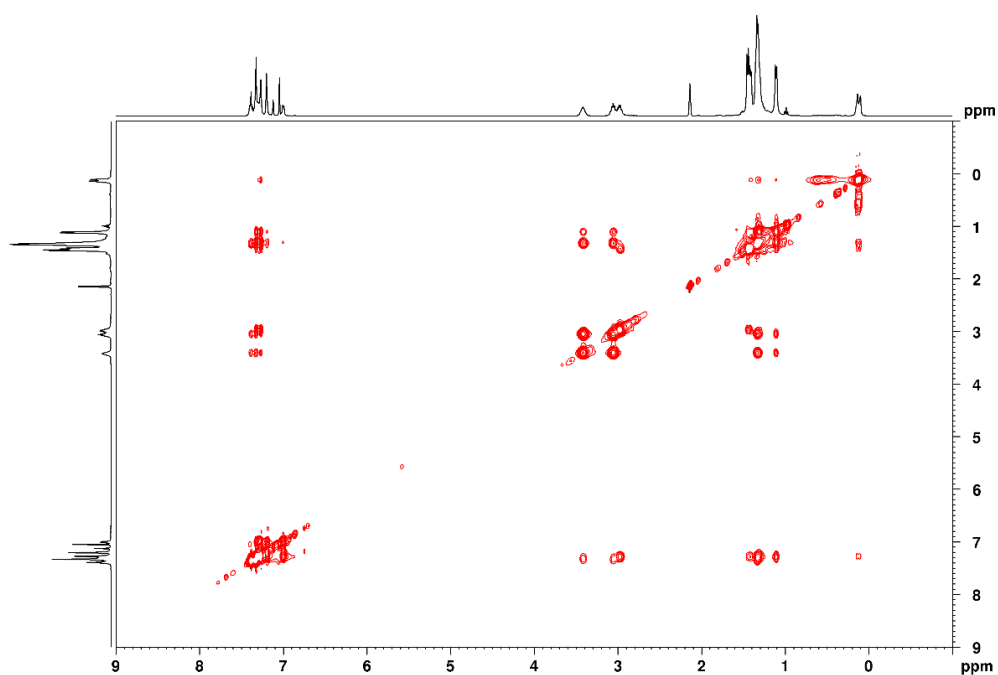


Figure S9. NOESY NMR Spectrum of coordination complex **1•OPMe₃** in tol-d₈ at 213 K

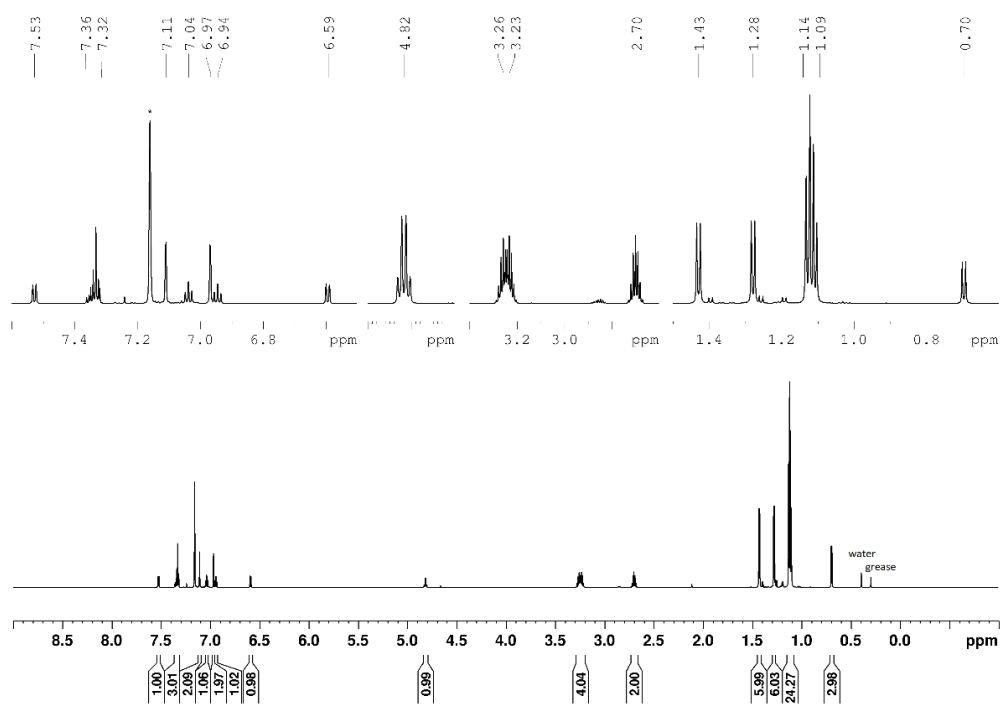


Figure S10. ¹H NMR Spectrum of compound **3** in C₆D₆

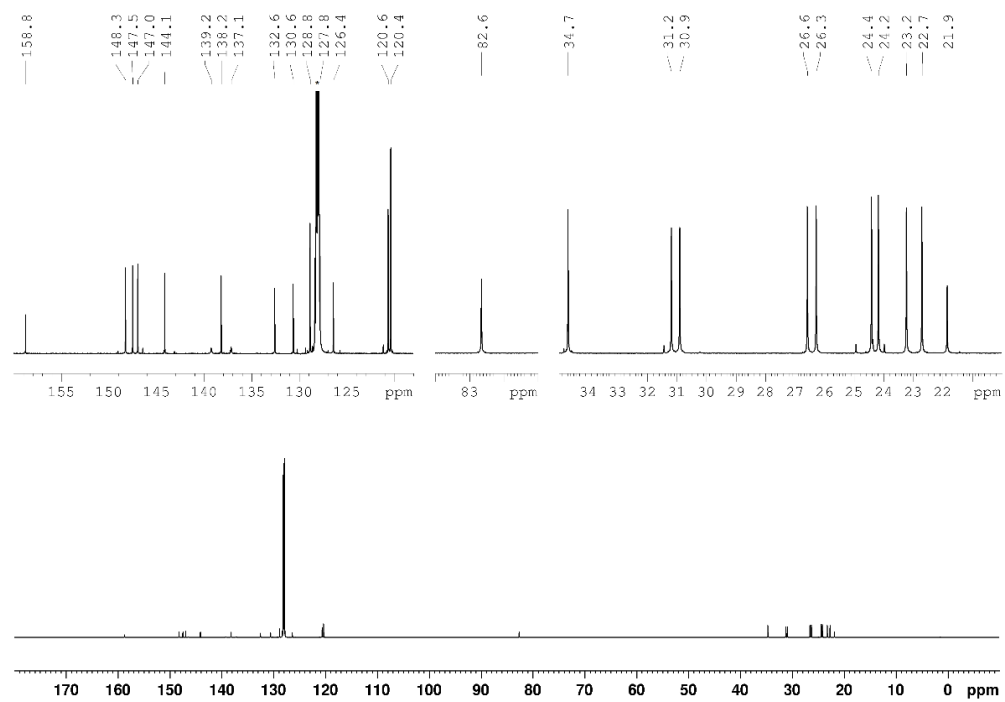


Figure S11. $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of compound **3** in C_6D_6

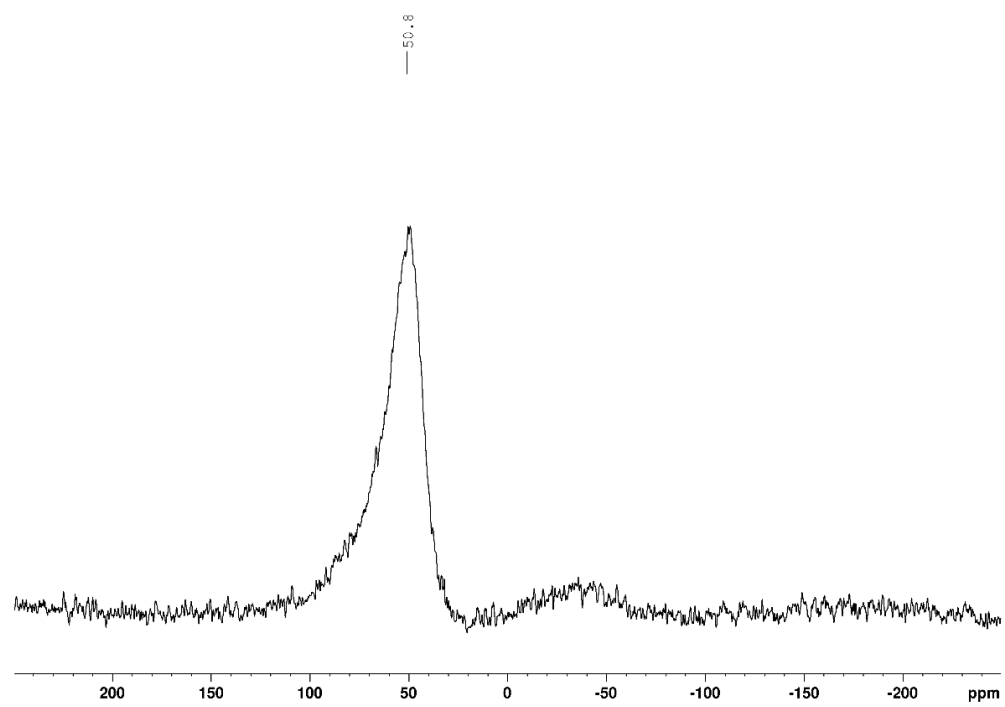


Figure S12. $^{11}\text{B}\{^1\text{H}\}$ NMR Spectrum of compound **3** in C_6D_6

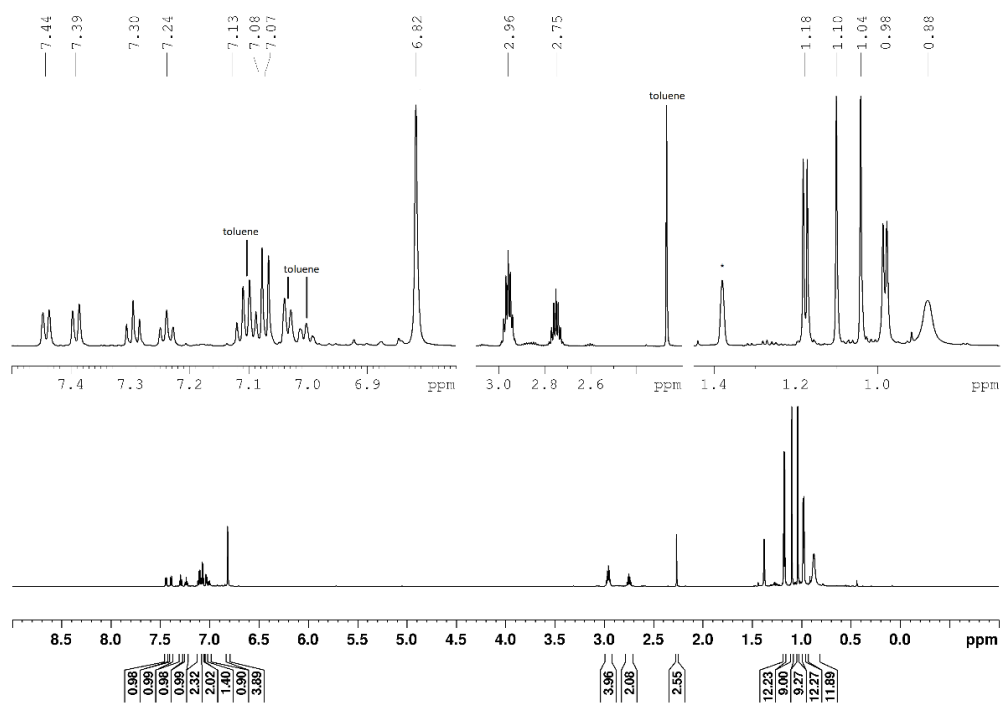


Figure S13. ^1H NMR Spectrum of compound **4** in C_6D_{12} at 343 K.

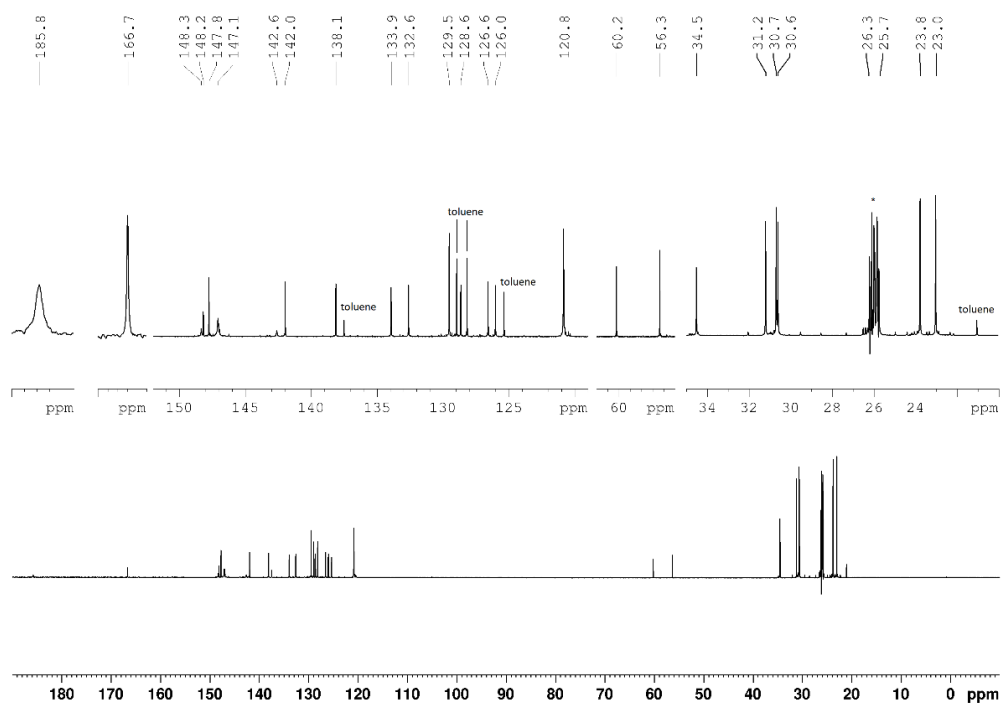


Figure S14. $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of compound **4** in C_6D_{12} at 343 K.

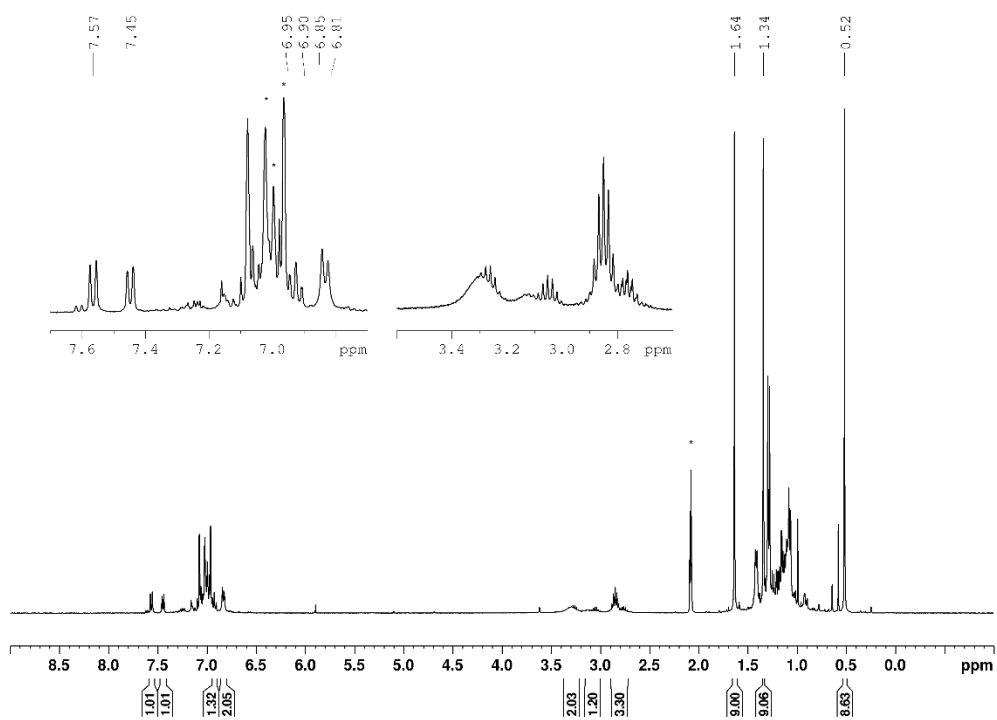


Figure S15. ^1H NMR Spectrum of the reaction mixture of compound **5** in at 45 °C.

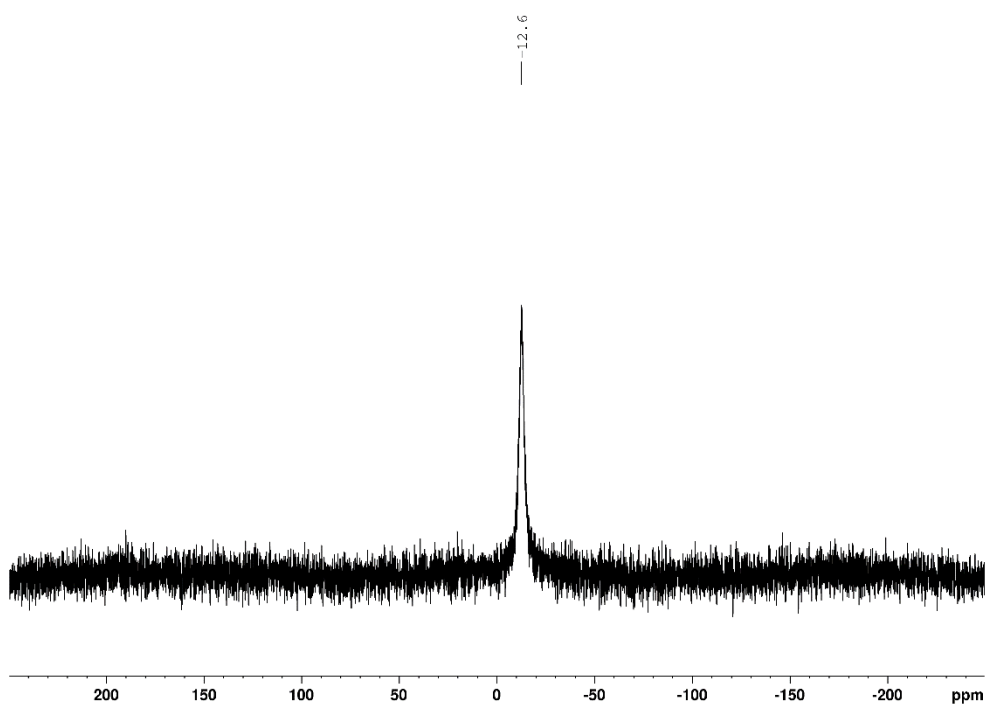


Figure S16. $^{11}\text{B}\{^1\text{H}\}$ NMR Spectrum of the reaction mixture of compound **5** in tol-d_8 .

3. Solid state ^{11}B -NMR

A powdered sample of compound **4** was packed in a 4 mm o.d. zirconia rotor under the inert atmosphere of a glove box. Solid-state NMR spectra were obtained on a Bruker Avance III HD 300 wide-bore NMR spectrometer ($B_0 = 7.05\text{ T}$) operating at 300.13 (^1H) and 96.29 (^{11}B) MHz. Spectra of the ^{11}B central transition were acquired under high-power proton decoupling and employing a background suppression sequence³ after a 1 μs pulse (30° tip angle) to eliminate the strong ^{11}B background signal of the boron nitride ceramics in the probe head. Referencing against $\Xi = 32.083974\%$ (^{11}B)¹ was achieved by the substitution method: an external sample of CHCl_3 in acetone in a zirconia rotor was spun at 1.5 kHz and the external magnetic field was adjusted such that the ^1H chemical shift of CHCl_3 matched a predetermined chemical shift wrt. external 1% TMS in CHCl_3 . Simulation of spectra was achieved using the sola module of Bruker TopSpin 4.1.4.⁴

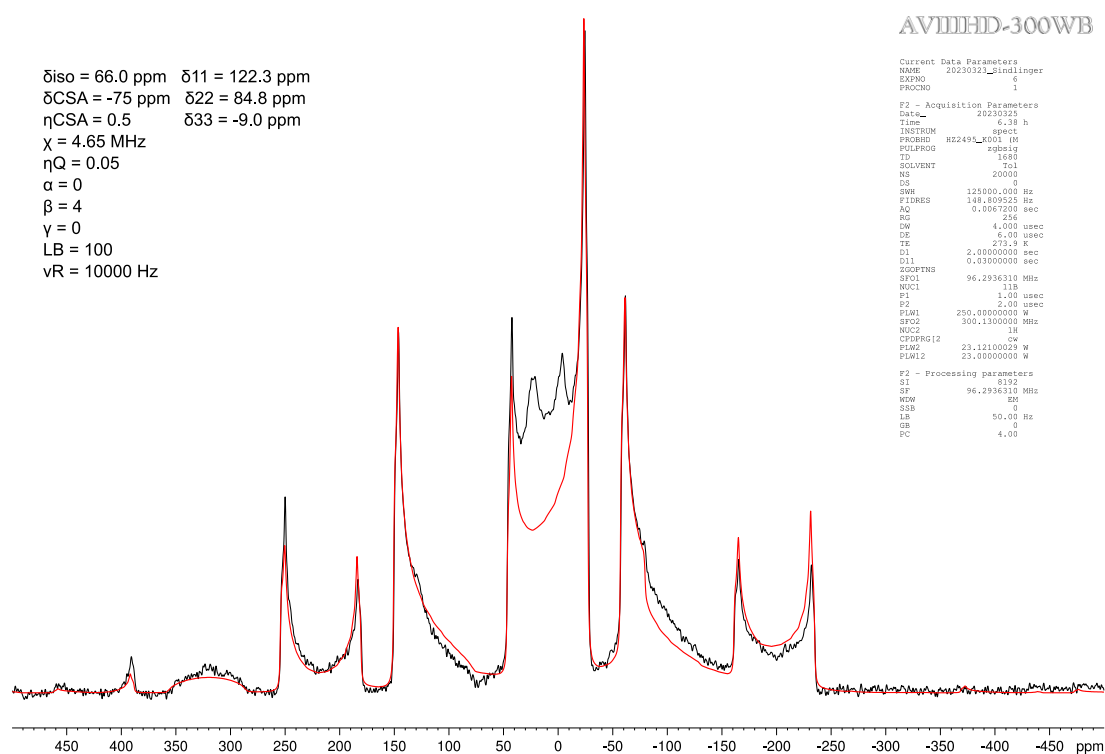


Figure S17. Experimental (black) and calculated (red) 96.29 MHz ^{11}B MAS NMR spectra of compound **4** obtained at a spinning rate of 10 kHz. The theoretical spectrum has been calculated with the parameters given on the left side of the figure. The two features at 22.7 and -2.1 ppm are attributed to an impurity ($\leq 8\%$).

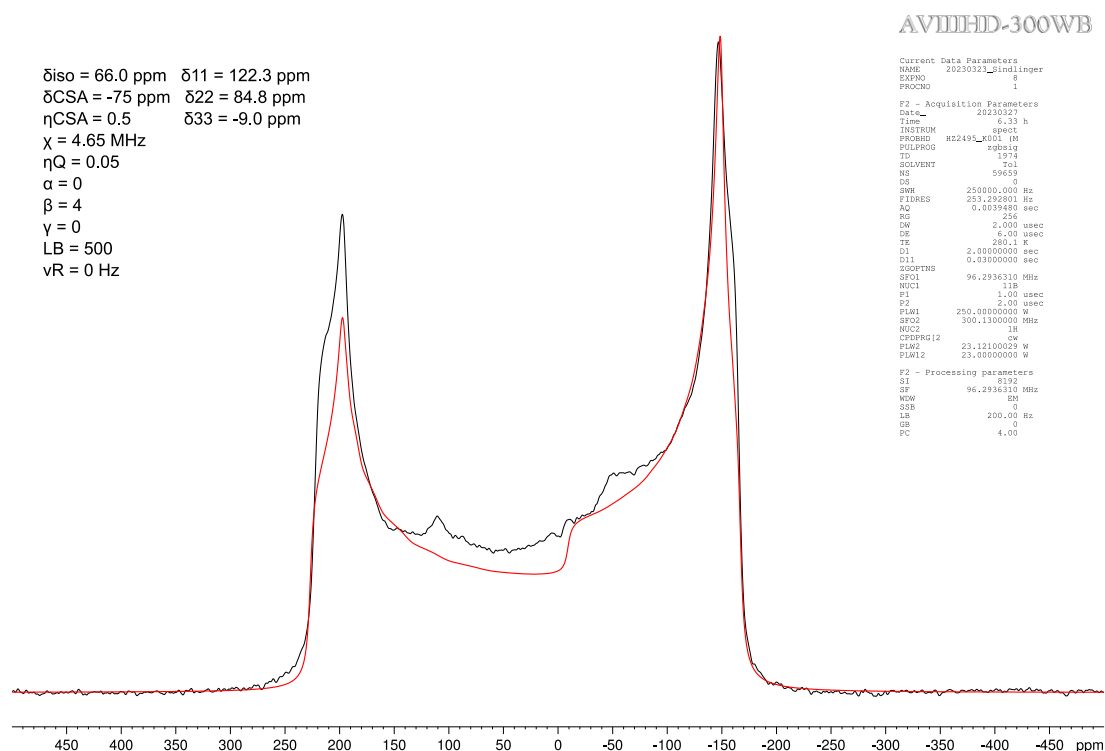


Figure S18. Experimental (black) and calculated (red) 96.29 MHz ^{11}B MAS NMR spectra of a static sample of compound **4**. The theoretical spectrum has been calculated with the parameters given on the left side of the figure. The two features at 110.7 and -50.1 ppm are attributed to an impurity ($\leq 8\%$).

The parameters employed for the simulation of the ^{11}B NMR spectra of compound **4** indicate that the direction of highest magnetic shielding and the greatest component of the electric field gradient are almost coincident ($\beta = 4^\circ$), as expected for an almost trigonal planar boron atom (359.99°). The nuclear quadrupolar coupling constant, $\chi = 4.65 \text{ MHz}$, is similar to the value reported for trimesitylborane, 4.75 MHz .⁵

4. Mass Spectra

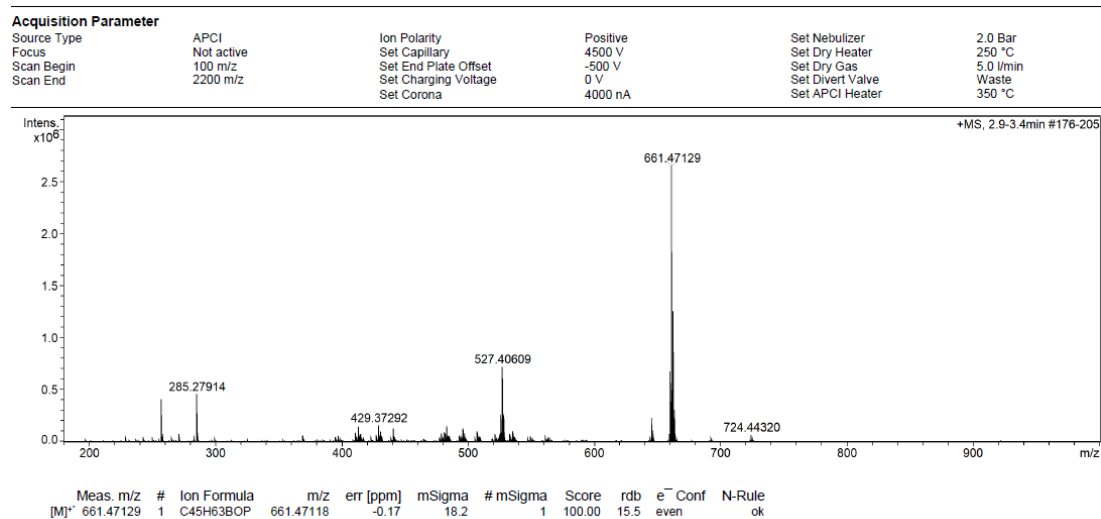


Figure S19. Mass spectrum of compound 2.

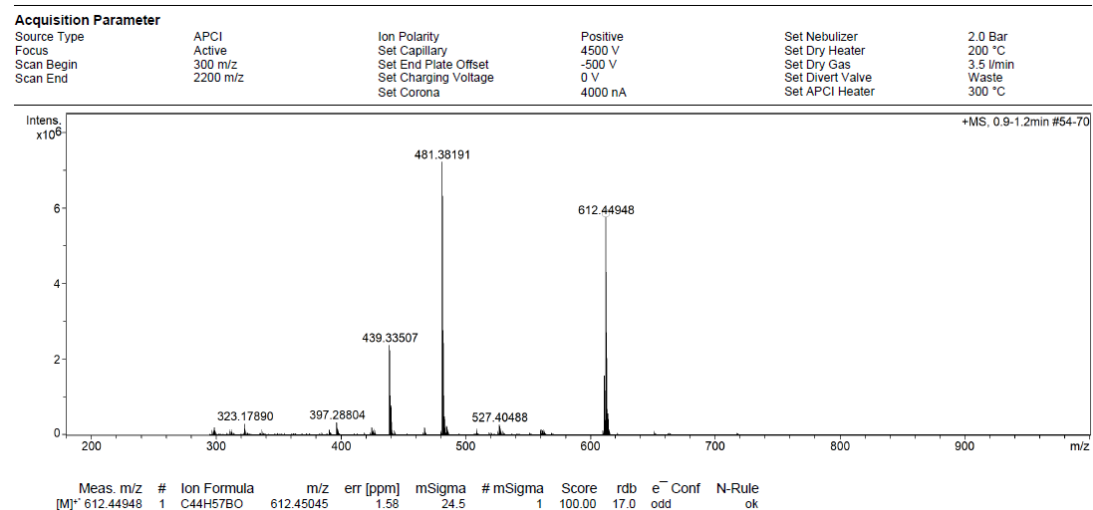


Figure S20. Mass spectrum of compound 3.

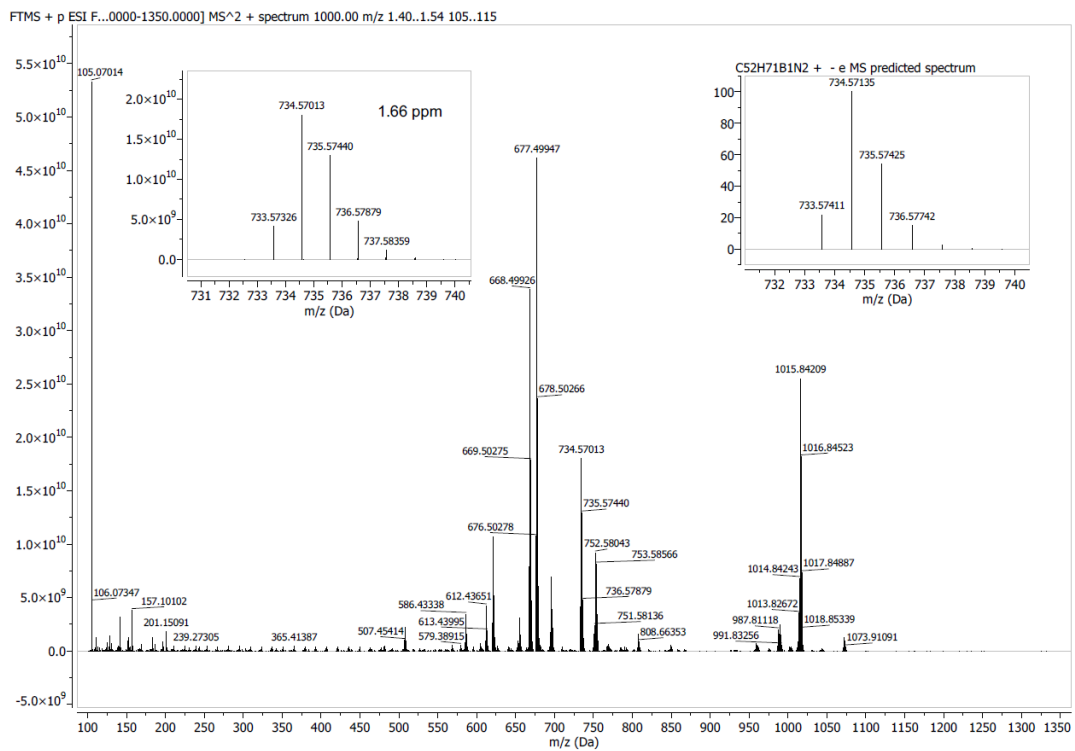


Figure S21. Mass spectrum of compound 4.

5. X-Ray Crystallography

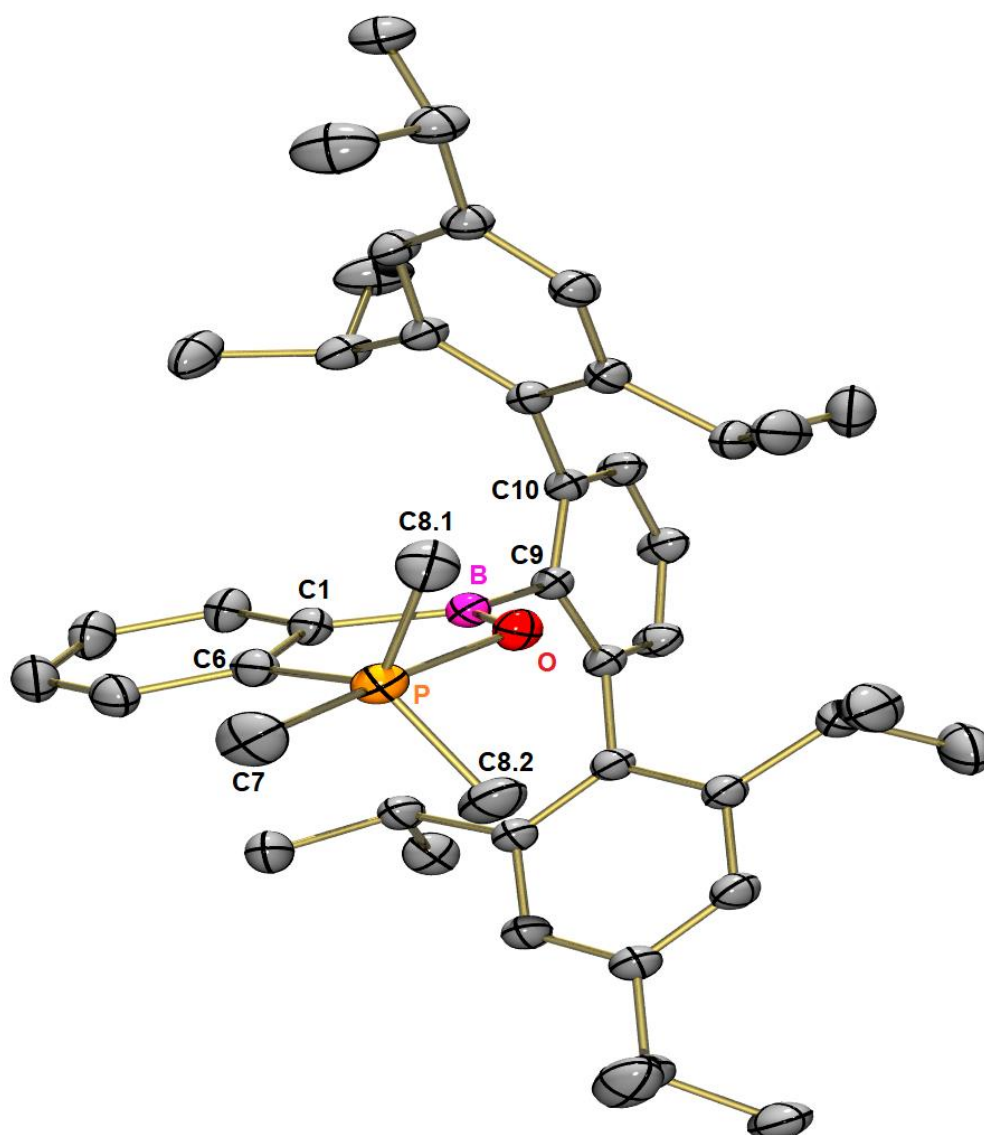


Figure S22. Molecular structure of **2** in the solid state. Thermal ellipsoids are shown at the 50 % probability level. Hydrogen atoms have been omitted for clarity. Selected distances [pm] and angles [°]: P-O 194.0, B-O 132.1, B-O-P 114.5, C1-B-O 112.3, O-P-C6 86.7, O-P-C7 175.2, O-P-C8.1 83.7, O-P-C8.2 83.3, C6-P-C8.1 118.6, C6-P-C8.2 118.1, C8.1-P-C8.2 120.6, C1-B-C10-C11 85.5.

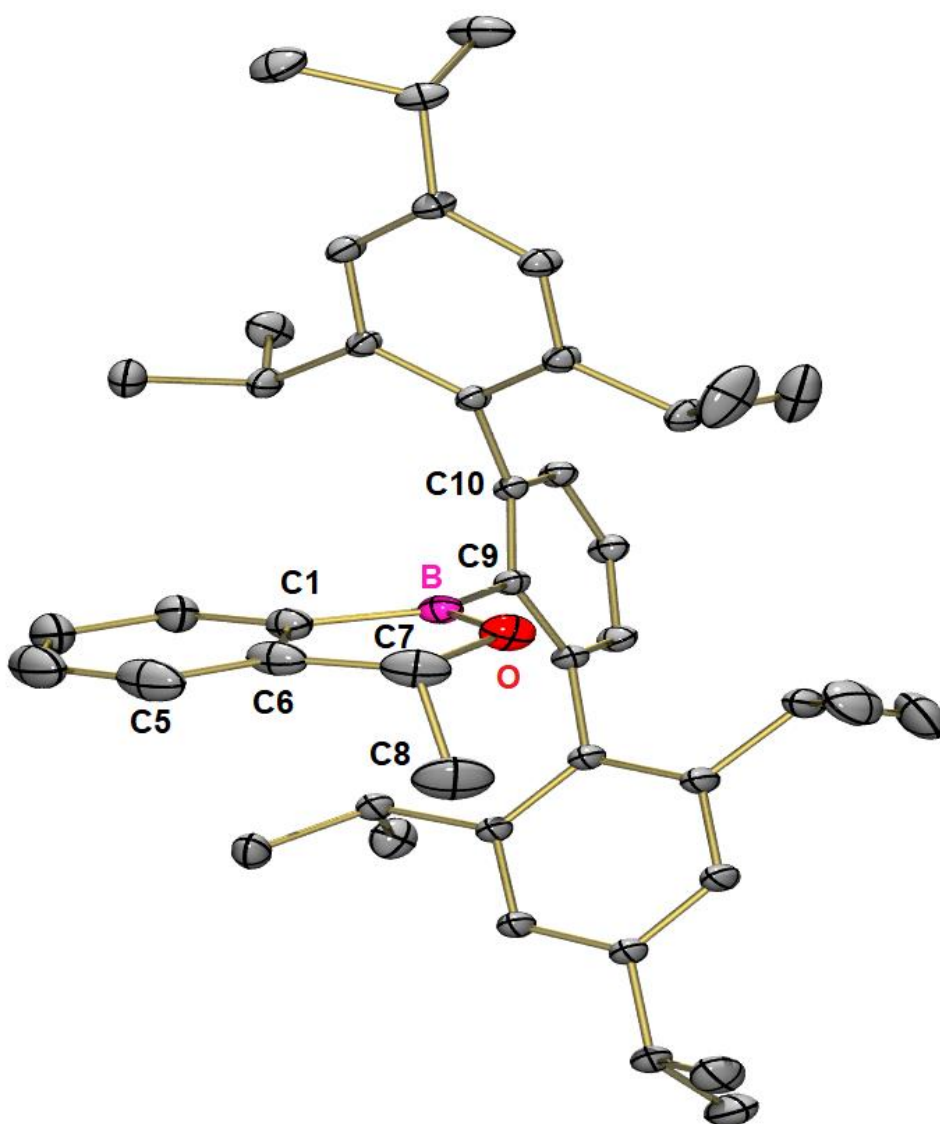


Figure S23. Nomenclature and Molecular structure of **3** in the solid state. Thermal ellipsoids are shown at the 50 % probability level. Hydrogen atoms have been omitted for clarity. Selected distances [pm] and angles [°]: C1-B 155.5, B-C9 157.5, B-O 136.4, C1-C6 140.0, C6-C7 150.6, C7-C8 152.3, C7-O 145.0, C1-B-O 108.2, C1-B-C9 128.6, C9-B-O 123.0, C6-C1-B 105.1, B-O-C7 111.4, O-C7-C6 105.1, O-C7-C8 108.9, C6-C7-C8 113.2, C1-C6-C7 110.2, C1-B-C9-C10 75.8, C5-C6-C7-C8 63.4, C1-C6-C7-C8 -115.7.

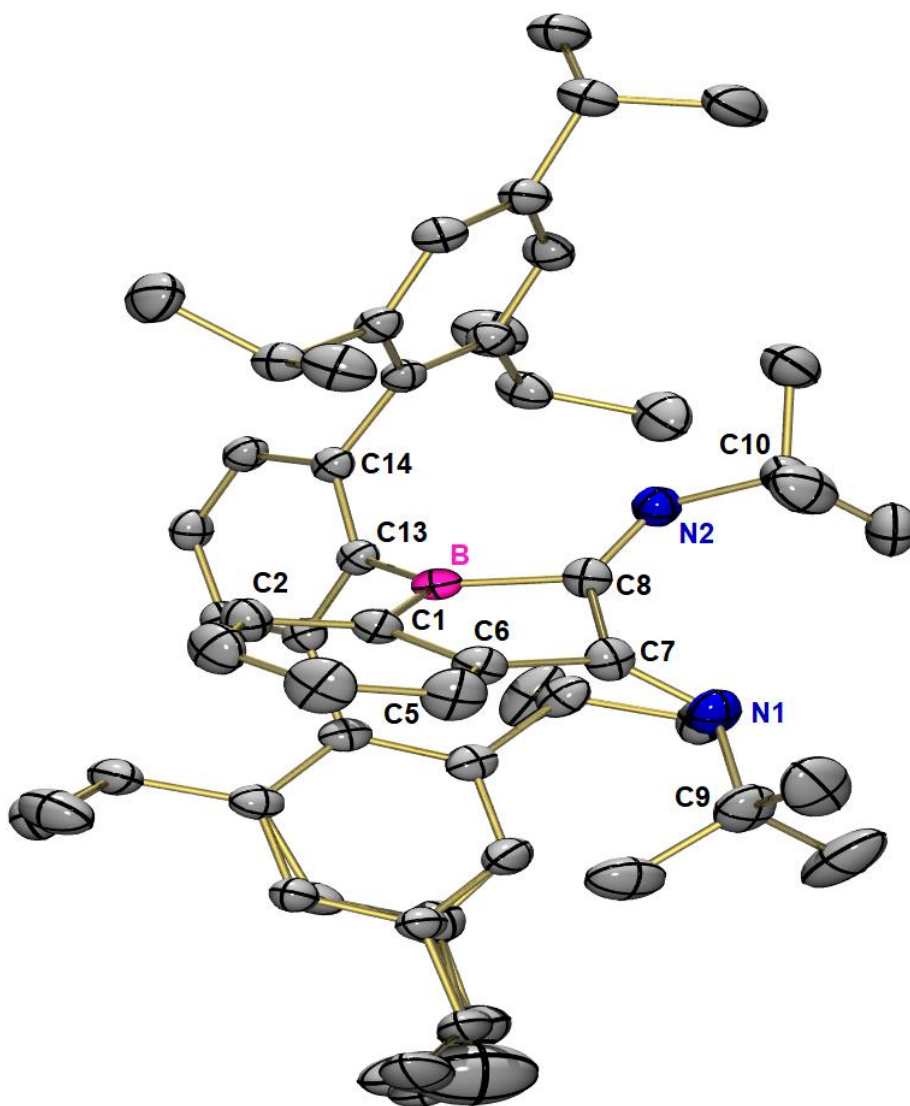


Figure S24. Molecular structure of **4** in the solid state. Thermal ellipsoids are shown at the 50 % probability level. Hydrogen atoms and a co-crystallized toluene molecule have been omitted for clarity. Selected distances [pm] and angles [°]: B-C1 155.7, B-C8 158.1, C6-C7 150.0, C7-C8 152.6, N1-C7 127.3, N1-C9 148.1, N2-C8 127.9, N2-C10 147.9, C1-B-C8 101.5, B-C8-C7 104.4, C8-C7-C6 104.5, C7-N1-C9 127.2, C8-N2-C10 125.0, C6-C1-B-C8 -15.2, C1-C6-C7-C8 22.6, C1-B-C13-C14 107.5, C1-C6-C7-N1 -145.2, N1-C7-C8-N2 -53.0.

Table S1 Crystallographic Information for **2**, **3** and **4**

	2	3	4
Empirical formula	C ₄₅ H ₆₂ BOP	C ₄₄ H ₅₇ BO	C ₅₉ H ₇₉ BN ₂
Formula weight	660.791	612.767	827.05
Temperature [K]	150.00(10)	149.99(11)	149.99(10)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P 2 ₁ /c	P 2 ₁ /n	P 2 ₁ /c
Unit cell dimensions	a = 9.3698(1) Å b = 42.8233(3) Å c = 10.2352(1) Å	a = 13.0778(1) Å b = 16.2591(1) Å c = 18.6511(2) Å	a = 21.8427(2) Å b = 10.73860(10) Å c = 22.3596(2) Å
	$\alpha = 90^\circ$ $\beta = 103.371(1)^\circ$ $\gamma = 90^\circ$	$\alpha = 90^\circ$ $\beta = 109.678(1)^\circ$ $\gamma = 90^\circ$	$\alpha = 90^\circ$ $\beta = 99.8700(10)^\circ$ $\gamma = 90^\circ$
Volume [Å ³]	3995.51(7)	3734.24(6)	5167.04(8)
Z	4	4	4
Density (calculated) [Mg/m ³]	1.099	1.090	1.063
Crystal size [mm ³]	0.14×0.10×0.06	0.21×0.10×0.09	0.24×0.20×0.12
Crystal Colour	colourless	colourless	colourless
Theta range for data collection	4.13° to 79.91°	3.62° to 79.97°	4.014° to 68.243°
Index ranges	-11 ≤ h ≤ 11, -54 ≤ k ≤ 54, -13 ≤ l ≤ 12	-16 ≤ h ≤ 14, -20 ≤ k ≤ 20, -23 ≤ l ≤ 23	-26 ≤ h ≤ 26, -12 ≤ k ≤ 12, -26 ≤ l ≤ 26
Reflections collected	172476	178302	211996
Independent reflections	8631 [R(int) = 0.0399]	8080 [R(int) = 0.0229]	9448 [R(int) = 0.0563]
Goodness-of-fit on F ²	10.989	10.997	1.014
Final R indices [I > 2σ(I)]	R1 = 0.0230, wR2 = 0.0545	R1 = 0.0158, wR2 = 0.0343	R1 = 0.0498, wR2 = 0.1368
R indices (all data)	R1 = 0.0257, wR2 = 0.0557	R1 = 0.0173, wR2 = 0.0349	R1 = 0.0513, wR2 = 0.1381
CCDC number	2172288	2252479	2220111

Experimental Data

Crystals suitable for X-Ray crystallography were grown as described in the synthesis. Single crystals were selected, coated with Parabar 10312 (previously known as Paratone N, Hampton Research) and fixed on a microloop.

Data were collected on a Rigaku XtaLAP Synergy-S single-crystal diffractometer, equipped with a HyPix-6000HE detector and monochromatic Cu-K_α radiation. Corrections for absorption effects were applied with CrysAlisPro 1.171.41.65a (Rigaku Oxford Diffraction, 2020). The structure was solved by direct methods (SHELXS)⁶, and full-matrix least-squares structure refinements were performed with SHELXL-2014⁷ implemented in Olex2 1.3-ac4.⁸

6. Reference experiments for the Me₃PO ³¹P-NMR chemical shift

To place the relative Lewis acidity of the boron centre of **1**, one equivalent of Me₃PO each has been added to various Lewis acids dissolved in tol-d₈ and ³¹P-NMR chemical shifts were recorded at 213 K. The unmarked signal at ~16 ppm in figures S26-S28 is due to a slight impurity in the Me₃PO that is significantly more pronounced at 213 K (compare Figures S25 and S26, the measurements are from the same sample).

Table S2. ³¹P-NMR chemical shifts of various Lewis acids with 1 eq. Me₃PO at 213 K.

Lewis acid	chemical shift
none	33.0 ppm
B(NMe ₂) ₃	31.8 ppm
B(OMe) ₃	34.2 ppm
B(OCH ₂ CF ₃) ₃	62.9 ppm
B(C ₆ F ₅) ₃	65.8 ppm
1	63.0 ppm

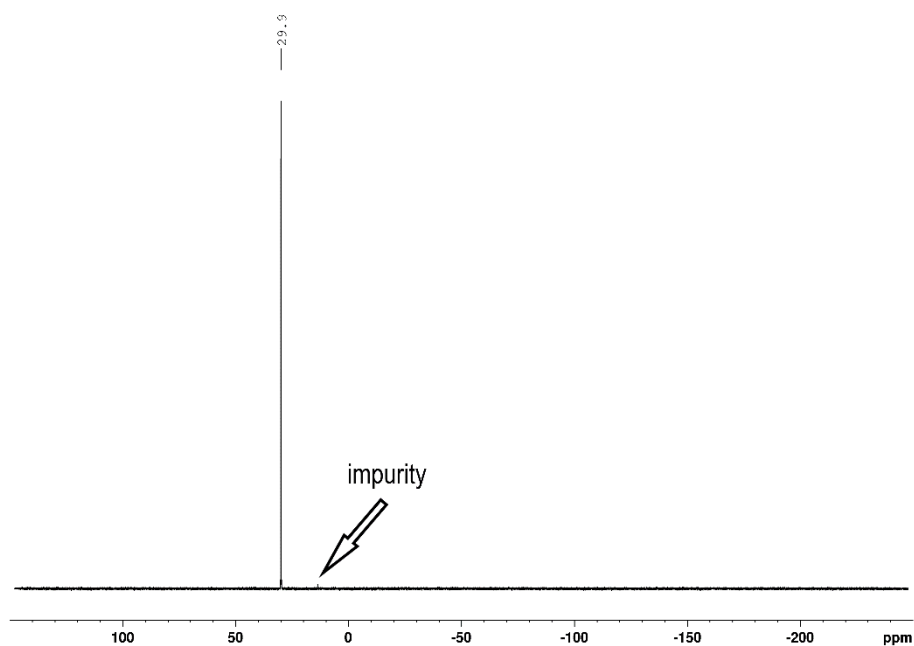


Figure S25. ³¹P{¹H} NMR Spectrum of Me₃PO in tol-d₈ at 298 K

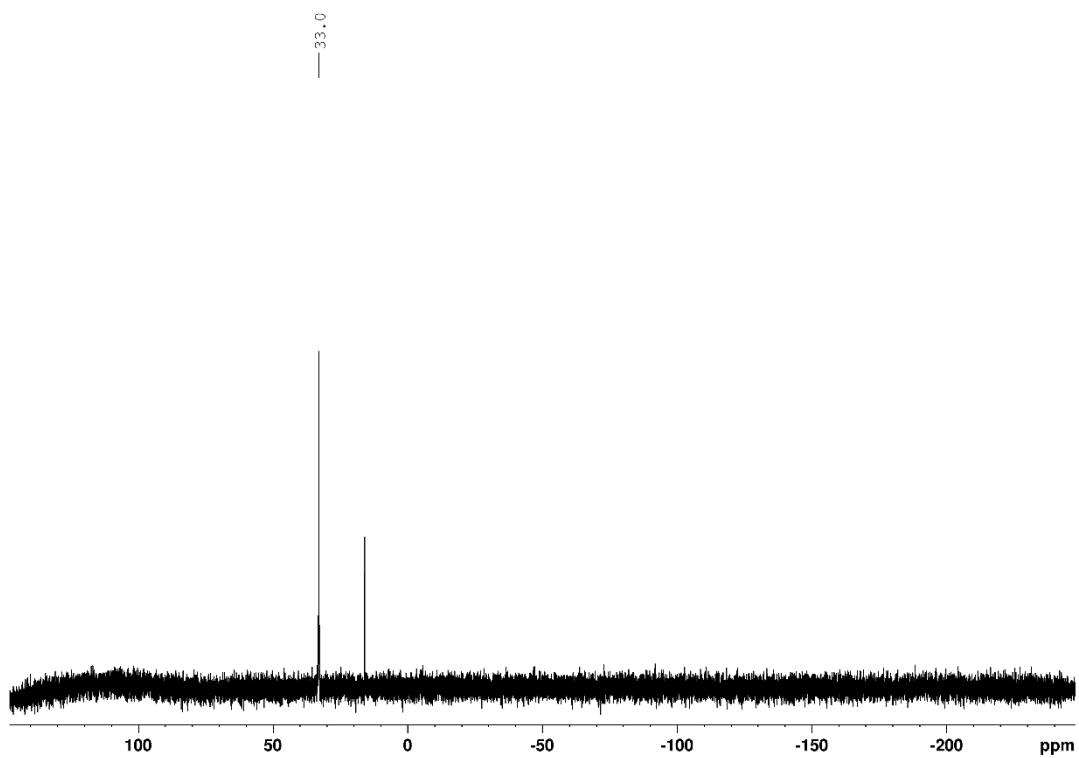


Figure S26. $^{31}\text{P}\{^1\text{H}\}$ NMR Spectrum of Me_3PO in tol-d_8 (same sample as fig. 25) at 213 K

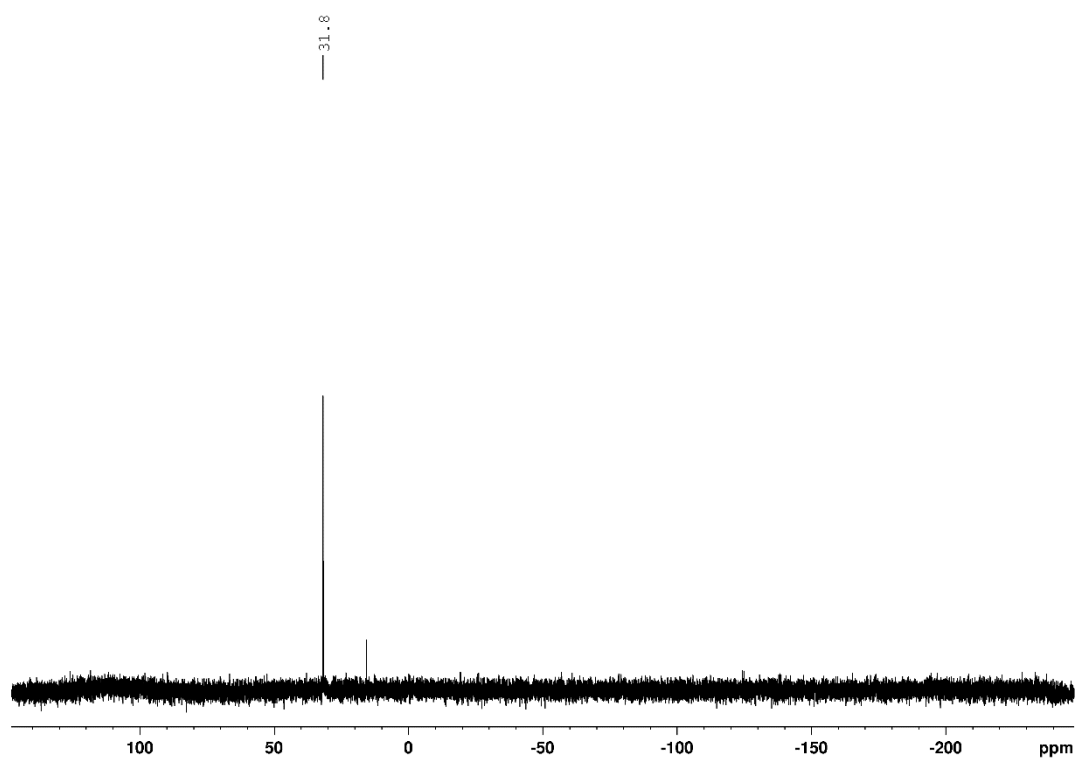


Figure S27. $^{31}\text{P}\{^1\text{H}\}$ NMR Spectrum of $\text{B}(\text{NMe}_2)_3$ with 1 eq of Me_3PO in tol-d_8 at 213 K

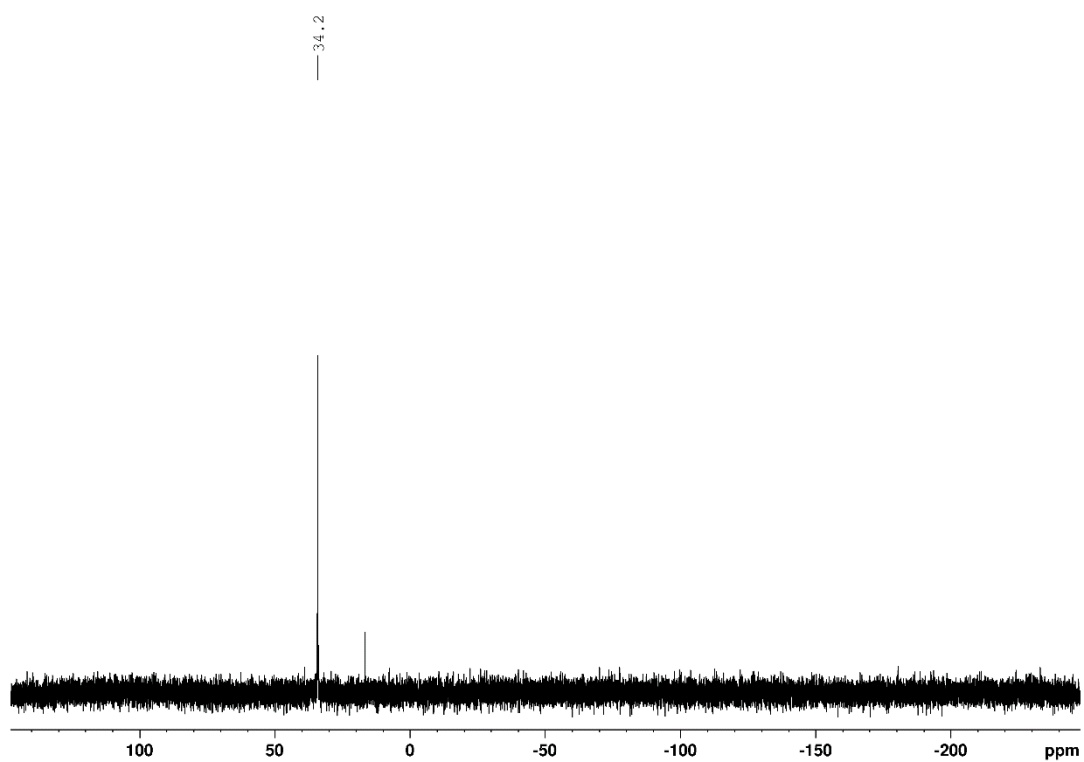


Figure S28. $^{31}\text{P}\{^1\text{H}\}$ NMR Spectrum of $\text{B}(\text{OMe})_3$ 1 eq of Me_3PO in tol-d_8 at 213 K

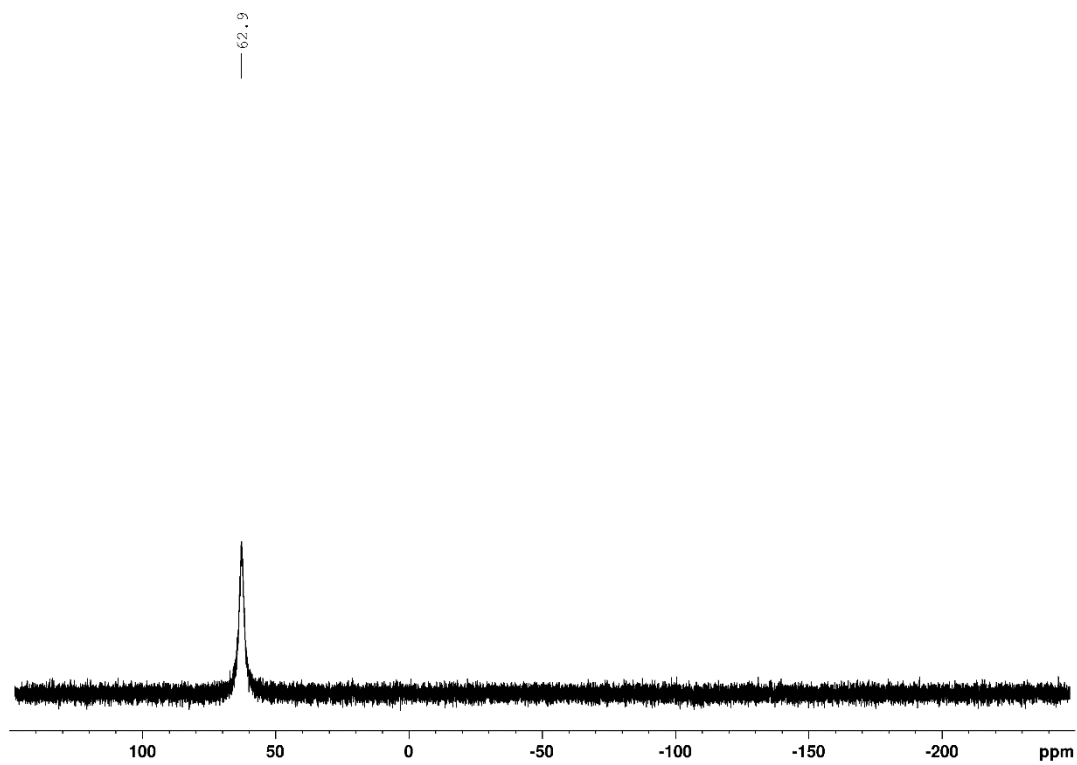


Figure S29. $^{31}\text{P}\{^1\text{H}\}$ NMR Spectrum of $\text{B}(\text{OCH}_2\text{CF}_3)_3$ 1 eq of Me_3PO in tol-d_8 at 213 K

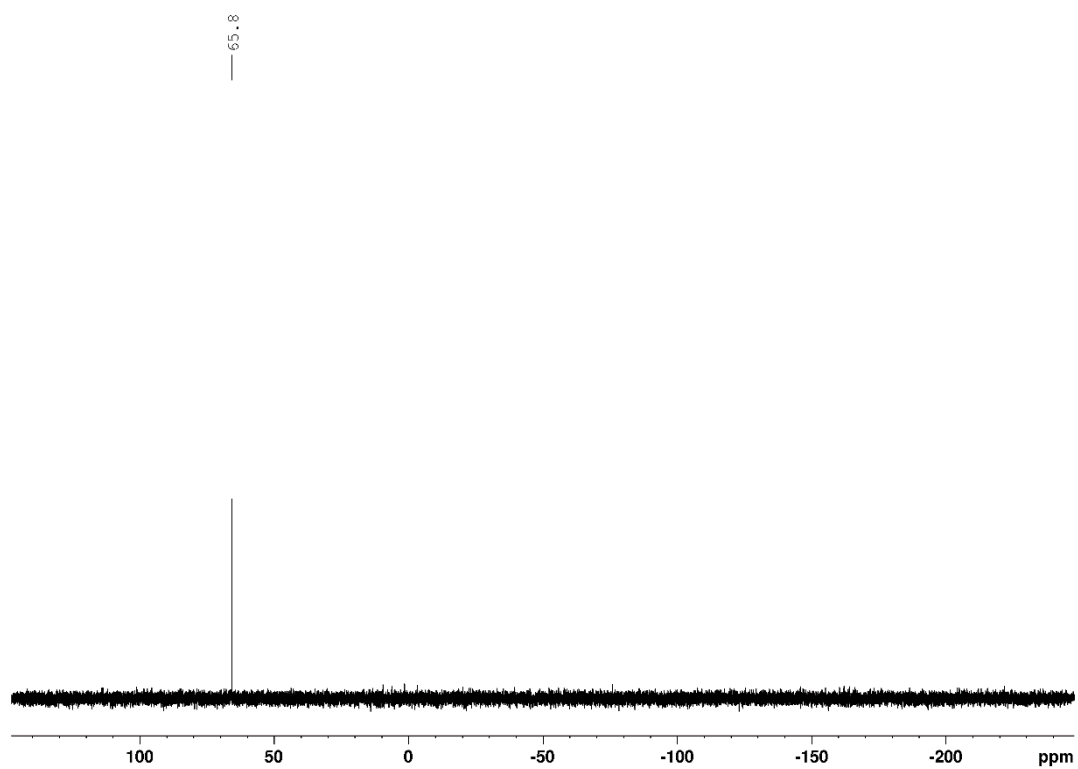


Figure S30. $^{31}\text{P}\{^1\text{H}\}$ NMR Spectrum of $\text{B}(\text{C}_6\text{F}_5)_3$ 1 eq of Me_3PO in tol-d_8 at 213 K

7. Computational Details

All computations of the stationary points on the potential energy surface were conducted with the Gaussian 16 program.⁹ If not stated otherwise, the geometries were fully optimized using the M06-2X functional¹⁰ in conjunction with the 6-311+G** basis set.¹¹⁻¹⁹ 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^{20, 21} was performed for molecule **3** at the M06-2X/6-311+G** level of theory using the NBO 6.0 program.^{22, 23}

All relaxed force constants were computed with the range-separated version of Becke's 97 functional including dispersion correction (ω B97XD) and a def2-tzvp basis, in order to get a more balanced description of subtle electron correlation effects. Following the geometry optimization, all calculations of the Cartesian force constants with Gaussian, the relaxed internal force constants were computed using the freely available COMPLIANCE 3.0.2 code.²⁴

In order to allow a unique transformation into the internal coordinate system, this code applies a modified Moore–Penrose algorithm developed at the TU Braunschweig.²⁵ This implementation avoids the annoying dependence of the calculated force constants on the coordinate system using a (pseudo) inversion of the Hesse matrix. Furthermore, our algorithm completely bypasses the construction and the nontrivial inversion of the complete B matrix (Wilson). Thus, provided that a Cartesian Hessian matrix is available as input, all internal force constants for arbitrary atom–atom pairs, as well as their couplings, can be selected and calculated within seconds using a graphical interface.

Once the Cartesian Hessian is read in, the Moore–Penrose inverse of the Cartesian Hessian is calculated by performing a singular value decomposition. Upon defining the internal coordinates of interest by simple mouse clicks, the user has access to the compliance matrix or a corresponding submatrix, respectively. The coordinates may be defined in arbitrary redundant or non-redundant sets of internal coordinates. The transformation is valid at any, even non-stationary, point on the potential energy surface and the following analysis is based on the full information contained in the quantum-chemical Hessian matrix, without any approximation or truncation concerning the force field.

The idea and theory of “relaxed” force constants is nearly as old as the theory of molecular vibrations itself. They can be viewed as coefficients if we expand the molecular potential energy into the forces. That means, in contrast to the real-space (rigid) force constants, which are defined as the coefficients of a Taylor series in terms of displacements, the compliance force constant measures the displacement of a specific coordinate due to a unit force on it, while all other coordinates are allowed to relax.

This relaxation is missing if one uses traditional (rigid) force constants, and exactly those induced forces depend on the definition of all other coordinates in the case of traditional force constants. Just like the compliance diagonal terms, the compliance *coupling* terms are unique as well and can therefore be used as precise descriptors for any type of electronic coupling.²⁶

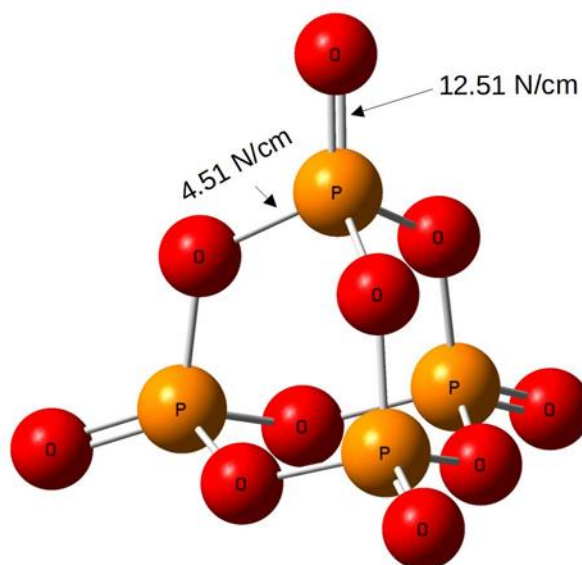


Figure S31. Computed relaxed force constants for P_4O_{10} in the gas phase as reference at the wB97xd/def2-tzvp level of theory.

Table S3. The relative energies for the cycloaddition of trimethylphosphine oxide into the C-B bond of the parent benzoborirene (BBI) as computed at the M06-2X/6-311+G** level of theory. (Energies in kcal/mol).

	BBI + Me ₃ PO	M-1	TS-1	M-2
relative Δ el	0.0	-19.6	-6.7	-39.5
relative Δ el + ZPE	0.0	-18.0	-5.1	-36.9
relative Δ E	0.0	-17.6	-5.2	-36.8
relative Δ H	0.0	-18.2	-5.8	-37.4
relative Δ G	0.0	-5.8	7.8	-24.2

Table S4. The relative energies for the cycloaddition of acetaldehyde oxide into the C-B bond of the parent benzoborirene (BBI) as computed at the M06-2X/6-311+G** level of theory. (Energies in kcal/mol).

	BBI + CH ₃ CHO	M-3	TS-2	M-4
relative Δ el	0.0	-5.3	7.0	-89.7
relative Δ el + ZPE	0.0	-4.2	8.4	-84.6
relative Δ E	0.0	-2.8	8.8	-84.9
relative Δ H	0.0	-3.4	8.2	-85.5
relative Δ G	0.0	4.7	19.5	-72.1

Table S5. The relative energies for the cycloadditions of methyl isonitrile (MeNC) into the C-B bond of the parent benzoborirene (BBI), model compound M-6 and model compound M-8 as computed at the M06-2X/6-311+G** level of theory. (Energies in kcal/mol).

	BBI + MeNC	TS-3	M-5	TS-4	M-6
relative Δ el	0.0	0.3	-14.8	-5.6	-29.5
relative Δ el + ZPE	0.0	1.0	-12.8	-4.0	-26.8
relative Δ E	0.0	1.6	-12.5	-4.2	-27.0
relative Δ H	0.0	1.0	-13.1	-4.8	-27.6
relative Δ G	0.0	9.5	-3.0	7.4	-15.5

	M-6 + MeNC	TS-5	M-7	TS-6	M-8
relative Δ el	-29.5	-36.2	-58.0	-44.8	-74.8
relative Δ el + ZPE	-26.8	-32.7	-52.9	-40.1	-68.3
relative Δ E	-27.0	-32.4	-52.8	-40.5	-69.1
relative Δ H	-27.6	-33.5	-54.0	-41.7	-70.3
relative Δ G	-15.5	-10.9	-30.9	-16.5	-44.0

	M-8 + MeNC	TS-7	M-9	TS-8	M-10
relative Δ el	-74.8	-81.4	-101.0	-80.8	-98.3
relative Δ el + ZPE	-68.3	-74.2	-92.3	-72.7	-88.8
relative Δ E	-69.1	-74.4	-92.8	-73.6	-89.8
relative Δ H	-70.3	-76.2	-94.5	-75.4	-91.5
relative Δ G	-44.0	-39.2	-57.5	-36.2	-52.1

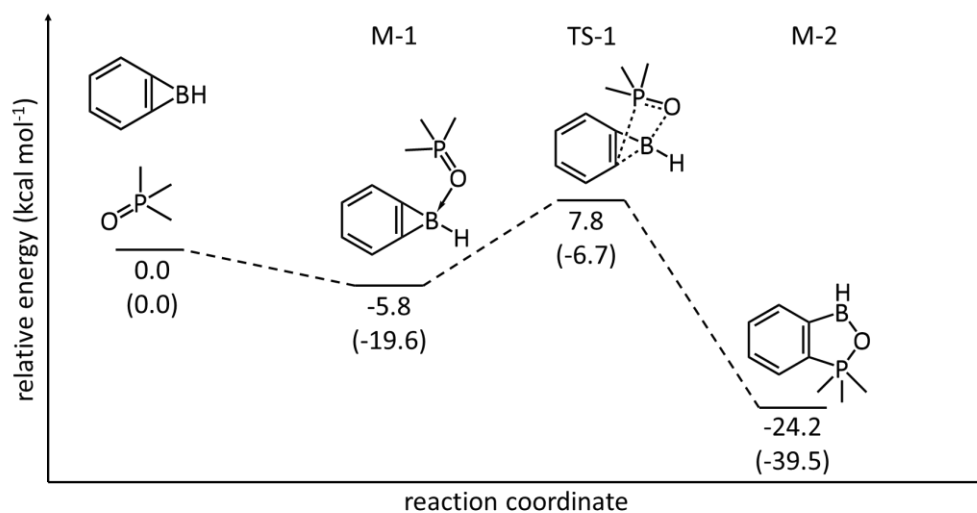


Figure S32. Energy profile calculated for the cycloaddition of parent benzoborirene (BBI) and trimethylphosphine oxide. The relative free energies (calculated at 298 K) and electronic energies (in parentheses) are given in kcal/mol.

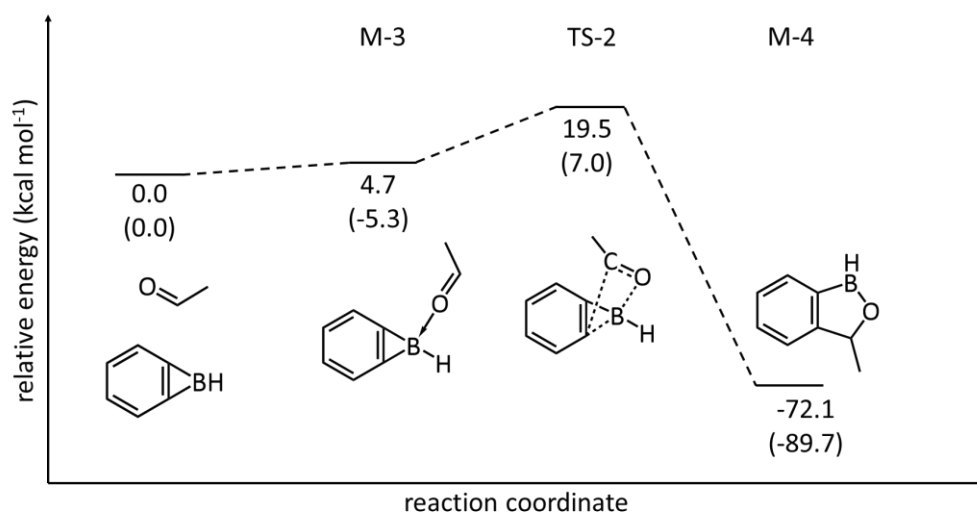


Figure S33. Energy profile calculated for the cycloaddition of parent benzoborirene (BBI) and acetaldehyde. The relative free energies (calculated at 298 K) and electronic energies (in parentheses) are given in kcal/mol.

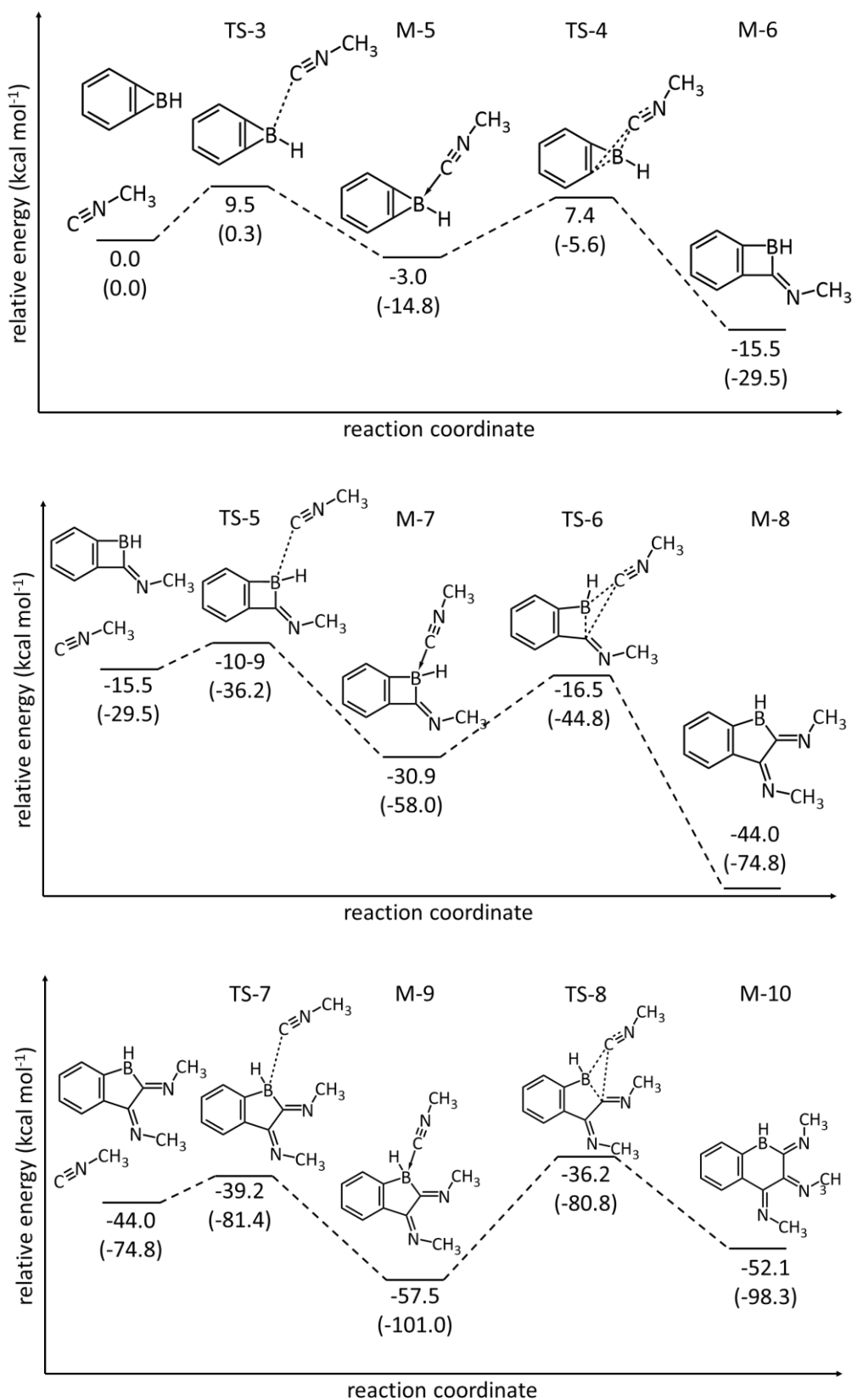


Figure S34. Energy profiles calculated for the cycloaddition of parent benzoborirene (BBI) with the first (top), second (middle) and third (bottom) equivalent of methyl isonitrile. The relative free energies (calculated at 298 K) and electronic energies (in parentheses) are given in kcal/mol.

8. Cartesian Coordinates

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

Trimethylphosphine oxide

Atomic Number	Coordinates		
15	-0.000009	0.000057	0.182962
8	0.000027	0.000362	1.674342
6	-1.566091	0.556993	-0.553213
1	-1.527530	0.543546	-1.644065
1	-2.368485	-0.097054	-0.208802
1	-1.775619	1.570603	-0.208351
6	1.265546	1.077529	-0.553343
1	2.248171	0.751050	-0.209723
1	1.233611	1.052052	-1.644187
1	1.101386	2.099189	-0.207660
6	0.300539	-1.634915	-0.552855
1	0.291093	-1.595334	-1.643710
1	1.268915	-2.002064	-0.209814
1	-0.471589	-2.323379	-0.206387

Model compound M-1

Atomic Number	Coordinates		
5	-0.196332	-0.870873	-1.600319
6	-1.155958	0.249376	-1.036942
6	-1.366075	-1.043899	-0.575849
6	-2.337258	-1.331538	0.376095
6	-3.099930	-0.264713	0.854895
6	-2.889895	1.042391	0.392229
6	-1.910049	1.319433	-0.563618
1	-2.512355	-2.333930	0.757958
1	-3.872603	-0.441374	1.596155
1	-3.506280	1.845137	0.783800
1	-1.767866	2.344535	-0.901104
8	1.256060	-0.895460	-1.002740

6	3.387140	-0.491887	0.566449
1	4.009629	-0.435866	-0.326948
1	3.802230	0.148393	1.346319
1	3.362835	-1.525169	0.914241
1	-0.134492	-1.282267	-2.716199
15	1.713791	0.023422	0.145294
6	0.727419	-0.083965	1.652182
1	1.274089	0.392928	2.469220
1	-0.239904	0.401824	1.510188
1	0.557035	-1.136207	1.884552
6	1.787264	1.754557	-0.349711
1	0.782691	2.083846	-0.613948
1	2.179396	2.362722	0.467641
1	2.435971	1.843611	-1.222157

Transition state T-1

Atomic Number	Coordinates		
5	-0.109951	1.573551	0.744782
6	-0.740953	-0.106607	0.383971
6	-1.349640	1.092837	0.002678
6	-2.698445	1.176778	-0.337809
6	-3.443887	0.006491	-0.335488
6	-2.865613	-1.206231	0.069032
6	-1.531701	-1.264528	0.449340
1	-3.162345	2.122217	-0.598536
1	-4.489801	0.026535	-0.621341
1	-3.474217	-2.104155	0.085919
1	-1.116860	-2.226456	0.748939
8	1.225407	1.490098	0.146278
6	3.317346	0.222341	-0.516028
1	3.830313	0.720528	0.308210
1	3.815869	-0.725900	-0.729246
1	3.381995	0.864345	-1.396116
1	-0.139226	2.112297	1.809334
15	1.546699	-0.054292	-0.072786
6	1.017964	-0.929091	-1.589568
1	1.890392	-1.215305	-2.178707
1	0.416472	-1.800390	-1.338524
1	0.391995	-0.244522	-2.163394
6	1.761246	-1.100099	1.398591
1	0.969834	-1.841477	1.473581
1	2.741801	-1.578583	1.387697
1	1.691899	-0.434641	2.261523

Model compound M-2

Atomic Number	Coordinates		
5	-0.148275	2.140537	-0.000074
6	-0.602966	-0.207620	0.000089
6	-1.238096	1.031600	0.000060
6	-2.632311	1.121549	-0.000039

6	-3.394069	-0.039857	-0.000095
6	-2.759841	-1.283658	-0.000009
6	-1.370127	-1.372538	0.000115
1	-3.116869	2.092946	-0.000005
1	-4.476530	0.012629	-0.000227
1	-3.356575	-2.189272	-0.000038
1	-0.907949	-2.356579	0.000263
8	1.103773	1.621799	-0.000136
6	3.165200	0.338627	-0.000192
1	3.403681	0.935473	0.881837
1	3.780476	-0.564293	-0.000227
1	3.403551	0.935442	-0.882277
1	-0.305828	3.320804	-0.000142
15	1.336042	-0.123105	-0.000003
6	1.461832	-1.140171	-1.537571
1	2.455610	-1.574606	-1.639341
1	0.694674	-1.909691	-1.585488
1	1.298322	-0.450417	-2.371070
6	1.461920	-1.139614	1.537848
1	0.694759	-1.909138	1.585980
1	2.455680	-1.574037	1.639832
1	1.298309	-0.449667	2.371173

Acetaldehyde

Atomic Number	Coordinates		
6	-0.240119	0.411616	0.000009
1	-0.349883	1.514165	-0.000017
8	-1.215790	-0.287894	-0.000004
6	1.166539	-0.134546	-0.000011
1	1.912702	0.658812	-0.000802
1	1.302756	-0.765458	0.880807
1	1.302231	-0.766788	-0.879949

Model compound M-3

Atomic Number	Coordinates		
5	0.160373	-2.060281	-0.000879
6	0.874973	-0.956085	0.694702
6	0.874546	-0.955301	-0.695757
6	1.482446	0.071471	-1.439995
6	2.078513	1.078007	-0.710562
6	2.078803	1.077239	0.711300
6	1.483112	0.069849	1.439866
1	1.492937	0.089487	-2.524372
1	2.565569	1.900514	-1.223382
1	2.566070	1.899188	1.224799
1	1.494160	0.086577	2.524254
8	-2.221859	-0.909127	0.000250
6	-3.269359	1.239898	0.000292
1	-4.211919	0.695700	0.000353
1	-3.204387	1.886895	0.879240
1	-3.204373	1.886798	-0.878705
1	-0.385047	-3.100268	-0.001420
6	-2.109567	0.288372	0.000348
1	-1.100806	0.748826	0.000458

Transition state T-2

Atomic Number	Coordinates		
5	-0.755246	1.176425	-0.809578
6	0.193443	-0.105644	-0.689699
6	0.580840	1.049033	-0.065457
6	1.812259	1.179572	0.569259
6	2.630452	0.054063	0.552363
6	2.234220	-1.133541	-0.086697
6	1.003840	-1.237841	-0.730457
1	2.137567	2.093171	1.054891
1	3.600682	0.087346	1.035953
1	2.909873	-1.982160	-0.078326
1	0.723351	-2.162461	-1.226760
8	-2.060518	1.054234	0.233997
6	-2.456349	-1.237555	0.807612
1	-2.201841	-0.927642	1.818440
1	-3.478620	-1.625269	0.761329
1	-1.786955	-2.036300	0.475474
1	-1.134093	1.752667	-1.775498
6	-2.323284	-0.105609	-0.139478
1	-2.562115	-0.290201	-1.194260

Model compound M-4

Atomic Number	Coordinates		
5	-0.964646	1.812923	-0.002856
6	-0.078912	-0.344906	-0.224374
6	0.342149	0.966720	0.021316
6	1.698726	1.226716	0.221884
6	2.608937	0.177460	0.173889
6	2.170941	-1.126689	-0.071794
6	0.821768	-1.402254	-0.272756
1	2.043249	2.237096	0.413811
1	3.664982	0.365385	0.327537
1	2.893365	-1.934149	-0.105692
1	0.491910	-2.418088	-0.463455
8	-2.009248	0.973757	-0.243564
6	-2.289265	-1.264696	0.620651
1	-2.033839	-0.940614	1.631419
1	-3.369287	-1.195227	0.486498
1	-1.984577	-2.306344	0.499995
1	-1.150385	2.974682	0.146882
6	-1.576635	-0.389092	-0.395887
1	-1.844453	-0.696971	-1.411778

Methyl isonitrile

Atomic Number	Coordinates		
6	-1.109176	-0.000249	-0.000131
7	0.313484	0.000865	0.000445

6	1.479608	-0.000504	-0.000263
1	-1.471485	-1.024990	0.071715
1	-1.473152	0.574054	0.850929
1	-1.472346	0.449401	-0.923398

Transition state **T-3**

Atomic Number	Coordinates		
5	0.020946	1.867830	-0.010958
6	0.856008	0.825927	-0.698505
6	1.623152	-0.085796	-1.436792
6	1.628216	-0.065531	1.436601
6	2.397544	-0.964586	-0.703890
6	2.400043	-0.954586	0.713447
6	0.858448	0.835692	0.688232
1	3.024246	-1.687349	-1.215539
1	3.028520	-1.670117	1.233021
1	-0.400519	2.965268	-0.017986
1	1.626005	-0.117125	-2.521215
1	1.634833	-0.081595	2.521340
6	-3.762095	-1.154534	0.005994
7	-2.882739	-0.035657	0.001861
6	-2.149281	0.865939	-0.001614
1	-3.642480	-1.701466	0.940074
1	-4.790028	-0.807001	-0.086280
1	-3.518351	-1.805310	-0.832494

Model compound **M-5**

Atomic Number	Coordinates		
5	-0.510538	0.002561	1.366569
6	0.664888	0.683010	0.553759
6	1.676089	1.431067	-0.028393
6	1.675162	-1.431376	-0.024307
6	2.699900	0.699044	-0.637386
6	2.699414	-0.701773	-0.635452
6	0.664429	-0.680982	0.555655
1	3.518767	1.222081	-1.119837
1	3.517887	-1.226716	-1.116501
1	-0.685005	0.004240	2.548697
1	1.699923	2.515913	-0.028308
1	1.698172	-2.516238	-0.021295
6	-3.985140	-0.001784	-0.894882
7	-2.824160	0.000190	-0.073122
6	-1.861635	0.001791	0.563931
1	-4.016347	0.922816	-1.469535
1	-3.941743	-0.855813	-1.569304
1	-4.868491	-0.074404	-0.262456

Transition state **T-4**

Atomic Number	Coordinates		
5	0.502029	1.639586	0.660934
6	-0.109727	0.038478	0.492204
6	-0.695631	-1.205930	0.689515
6	-2.050317	0.983732	-0.561221
6	-1.973444	-1.353202	0.148321
6	-2.635498	-0.279067	-0.463301
6	-0.749079	1.095328	-0.093145
1	-2.472912	-2.313729	0.209521
1	-3.638625	-0.434430	-0.844532
1	0.567237	2.286962	1.652363
1	-0.208854	-2.027435	1.202427
1	-2.601123	1.818426	-0.978925
6	2.930414	-1.088426	-0.428728
7	2.632233	0.323686	-0.350198
6	1.677578	0.896641	0.093351
1	3.768958	-1.308009	0.232384
1	2.057130	-1.680235	-0.140038
1	3.226641	-1.330604	-1.448471

Model compound **M-6**

Atomic Number	Coordinates		
5	0.471063	2.039752	0.000032
6	0.066309	-0.052451	0.000009
6	-0.451198	-1.349269	0.000035
6	-2.155317	0.954818	-0.000031
6	-1.837404	-1.460731	0.000017
6	-2.675803	-0.332775	-0.000016
6	-0.765572	1.090114	-0.000018
1	-2.291930	-2.445300	0.000032
1	-3.749397	-0.481978	-0.000026
1	0.663911	3.207326	0.000111
1	0.176772	-2.231412	0.000051
1	-2.815034	1.814964	-0.000056
6	2.890357	-1.020775	-0.000026
7	2.591236	0.406032	-0.000011
6	1.363759	0.718863	0.000012
1	2.471110	-1.510659	0.886996
1	2.470964	-1.510686	-0.886968
1	3.968852	-1.170004	-0.000114

Transition state **T-5**

Atomic Number	Coordinates		
5	0.272259	-0.973367	1.195212
6	-2.002689	1.170306	-0.407144
6	-2.345420	-1.590333	0.277004
6	-3.191930	0.496253	-0.656442
6	-3.360489	-0.859737	-0.326392
6	-1.143540	-0.931479	0.538260
1	-4.016673	1.024585	-1.121730
1	-4.309633	-1.334563	-0.547362
1	-1.892103	2.215390	-0.668479
1	-2.492887	-2.633727	0.530331
6	-0.978878	0.424723	0.183935

6	0.440818	0.529842	0.668638
7	1.339055	1.424914	0.612102
6	0.960008	2.676665	-0.035136
1	1.831494	3.324532	-0.123859
1	0.549468	2.501614	-1.036828
1	0.201981	3.204643	0.554748
1	0.850265	-1.679781	1.946428
6	3.942901	-0.346855	-0.345753
7	2.884346	-1.272784	-0.575516
6	1.971477	-1.981132	-0.713425
1	4.339693	-0.010249	-1.302821
1	3.529213	0.496217	0.210480
1	4.730538	-0.836264	0.225660

Model compound **M-7**

Atomic Number	Coordinates		
5	0.749719	-0.212038	1.234552
6	-2.297808	0.421001	-0.542798
6	-1.310145	-2.074681	0.416859
6	-3.024652	-0.756372	-0.711103
6	-2.538322	-1.980669	-0.241642
6	-0.575197	-0.909695	0.593954
1	-3.985808	-0.727298	-1.211851
1	-3.136442	-2.873257	-0.390627
1	-2.685566	1.365384	-0.905722
1	-0.962401	-3.036651	0.778524
6	-1.070164	0.315062	0.111736
6	0.097878	1.141989	0.549797
7	0.444828	2.349658	0.396501
6	-0.501852	3.210241	-0.309001
1	-0.719028	2.825782	-1.312948
1	-1.449552	3.284884	0.236380
1	-0.083547	4.211757	-0.405852
1	0.967753	-0.244889	2.413665
6	4.215369	-0.885216	-0.934681
7	3.034842	-0.718112	-0.158153
6	2.075146	-0.546288	0.457368
1	5.033513	-1.181308	-0.280095
1	4.041130	-1.656473	-1.683230
1	4.452136	0.059211	-1.422379

Transition state **T-6**

Atomic Number	Coordinates		
5	0.275534	-1.363658	1.237725
6	-1.515504	1.141107	-0.739581
6	-2.405987	-1.291689	0.427263
6	-2.828468	0.711565	-0.894944
6	-3.266877	-0.482129	-0.310111
6	-1.080850	-0.892302	0.568920
1	-3.526623	1.310728	-1.467335

1	-4.299704	-0.783266	-0.444489
1	-1.175740	2.065611	-1.191101
1	-2.767290	-2.217363	0.859944
6	-0.668746	0.331841	0.018296
6	0.728348	0.396397	0.481418
7	1.594105	1.263391	0.747741
6	1.260093	2.670293	0.538915
1	1.631813	2.988501	-0.439655
1	0.184387	2.865210	0.590813
1	1.773596	3.264633	1.294163
1	0.499491	-1.527823	2.391009
6	3.175877	-0.711168	-1.226617
7	2.312153	-1.618013	-0.499030
6	1.388686	-1.401885	0.253721
1	4.153969	-0.713443	-0.743757
1	3.296391	-1.092871	-2.239722
1	2.788806	0.308552	-1.243156

Model compound **M-8**

Atomic Number	Coordinates		
5	-0.165539	-2.024502	-0.280693
6	1.642175	1.214602	0.252503
6	2.438074	-1.450091	-0.135167
6	2.988116	0.856093	0.282437
6	3.391846	-0.462776	0.079432
6	1.082487	-1.118109	-0.158122
1	3.734254	1.619764	0.470218
1	4.445895	-0.712724	0.102929
1	1.373430	2.244304	0.434526
1	2.741603	-2.482063	-0.274427
6	0.681595	0.229598	0.016116
6	-0.814851	0.361848	-0.052160
7	-1.561907	1.379915	-0.189413
6	-1.009405	2.716546	-0.309150
1	-0.677594	3.087921	0.666387
1	-0.165634	2.761385	-1.005625
1	-1.792962	3.383416	-0.666633
1	-0.211135	-3.193099	-0.464585
6	-3.657465	-0.513513	0.364813
7	-2.579364	-1.447307	0.086184
6	-1.377051	-1.051087	-0.073745
1	-3.911550	0.037427	-0.545210
1	-4.526531	-1.083292	0.691564
1	-3.386313	0.232531	1.115202

Transition state **T-7**

Atomic Number	Coordinates		
5	-0.197891	-1.848886	-0.595478
6	-2.151730	1.315839	-0.049431
6	-2.775770	-1.421366	0.016344
6	-3.457205	0.887779	0.176528
6	-3.769540	-0.470550	0.222370
6	-1.464434	-1.016851	-0.228162
1	-4.241878	1.622582	0.315434

1	-4.791825	-0.779588	0.406588
1	-1.942800	2.375556	-0.102076
1	-3.019254	-2.477968	0.035946
6	-1.151424	0.361799	-0.238825
6	0.306172	0.572842	-0.509038
7	1.083089	1.533055	-0.203287
6	0.580550	2.696903	0.507497
1	0.140708	3.414611	-0.192766
1	-0.169842	2.443914	1.263976
1	1.420423	3.194556	0.993800
1	-0.091351	-3.020142	-0.707236
6	2.673980	0.135921	-2.278270
7	1.859325	-0.961622	-1.780084
6	0.843182	-0.745448	-1.045633
1	3.485813	0.325821	-1.569294
1	3.124324	-0.178761	-3.220200
1	2.127465	1.071354	-2.411646
6	0.999645	-1.701223	1.743179
7	1.878587	-0.966086	1.942223
6	2.956060	-0.041362	2.053344
1	2.918434	0.624935	1.189358
1	2.847630	0.532846	2.972808
1	3.897673	-0.588428	2.071305

Model compound M-9

Atomic Number	Coordinates		
5	0.819817	-0.724066	-1.085651
6	-2.654780	0.027431	0.302015
6	-1.410936	-2.241587	-0.754153
6	-3.372229	-1.151322	0.134123
6	-2.750121	-2.287959	-0.378895
6	-0.675929	-1.068168	-0.602721
1	-4.423264	-1.181976	0.396587
1	-3.319548	-3.202036	-0.505417
1	-3.166220	0.904445	0.672635
1	-0.944490	-3.119434	-1.190314
6	-1.298950	0.065109	-0.044650
6	-0.355324	1.221667	0.038807
7	-0.380893	2.273946	0.756059
6	-1.465657	2.520081	1.687806
1	-2.334563	2.938662	1.168309
1	-1.784322	1.617598	2.220946
1	-1.133955	3.260962	2.415442
1	1.121566	-1.062985	-2.199844
6	1.737620	3.089617	-0.997382
7	1.793721	1.648564	-1.202914
6	0.874086	0.878311	-0.791316
1	2.041684	3.334262	0.024024
1	2.434239	3.557811	-1.693691
1	0.736265	3.503687	-1.136449

6	1.898630	-1.355746	-0.127536
7	2.720956	-1.758020	0.573298
6	3.756014	-2.214255	1.436686
1	4.461278	-2.810948	0.860423
1	4.263382	-1.351116	1.864906
1	3.317837	-2.819108	2.228893

Transition state **T-8**

Atomic Number	Coordinates		
5	-0.014722	-1.943109	0.379316
6	2.267778	1.135286	-0.092676
6	2.576086	-1.623234	0.192742
6	3.537179	0.573106	-0.077598
6	3.690847	-0.805725	0.051900
6	1.288930	-1.082370	0.169298
1	4.409086	1.211460	-0.154241
1	4.684403	-1.238633	0.065063
1	2.165412	2.209871	-0.151390
1	2.707560	-2.691174	0.328398
6	1.141275	0.311929	0.005979
6	-0.266364	0.778886	0.072182
7	-0.855603	1.825380	-0.344363
6	-0.139457	2.848124	-1.085002
1	0.321311	3.564014	-0.396068
1	0.638610	2.438642	-1.737017
1	-0.859221	3.398212	-1.690587
1	-0.143723	-2.720509	1.266125
6	-2.347439	0.914995	2.232857
7	-2.045097	-0.308310	1.502026
6	-1.148698	-0.314690	0.622472
1	-3.264327	1.338414	1.814518
1	-2.549632	0.644026	3.269148
1	-1.561364	1.669992	2.177778
6	-1.164190	-1.629359	-0.509027
7	-2.004075	-1.656424	-1.408189
6	-3.097417	-0.714924	-1.582027
1	-3.123523	-0.415835	-2.630071
1	-4.028708	-1.240818	-1.364031
1	-3.020039	0.171207	-0.947119

Model compound **M-10**

Atomic Number	Coordinates		
5	-0.079570	-2.074721	-0.278249
6	2.337666	0.867593	0.295796
6	2.459370	-1.903562	0.097449
6	3.540927	0.201557	0.508304
6	3.610082	-1.183834	0.394412
6	1.227298	-1.262940	-0.089184
1	4.428616	0.768870	0.763155
1	4.552664	-1.695073	0.548959
1	2.295535	1.945174	0.398003
1	2.501752	-2.985025	0.023663
6	1.185292	0.148350	-0.018702

6	-0.122367	0.843397	-0.238905
7	-0.349948	1.913255	-0.883876
6	0.692135	2.625855	-1.600202
1	1.021578	3.482689	-1.004168
1	1.563610	2.016840	-1.856770
1	0.251072	3.026871	-2.513292
1	-0.067011	-3.248466	-0.453342
6	-2.056827	1.946718	1.639084
7	-2.194834	0.600192	1.112109
6	-1.338531	0.125856	0.308861
1	-2.687210	2.617916	1.050112
1	-2.430900	1.949481	2.663278
1	-1.035706	2.336488	1.616239
6	-1.437070	-1.300125	-0.169795
7	-2.508560	-1.909273	-0.517059
6	-3.797032	-1.241362	-0.515485
1	-4.426583	-1.722226	-1.264408
1	-4.260524	-1.389424	0.464072
1	-3.741296	-0.164749	-0.692264

Compound 3

Atomic Number	Coordinates		
6	0.182445	2.754198	0.236144
6	-0.252171	1.536363	0.769584
6	-0.832838	1.513480	2.034264
6	-0.986234	2.687370	2.763625
6	-0.536605	3.893412	2.233247
6	0.050866	3.934000	0.970666
5	0.028307	0.324106	-0.208671
6	-0.222542	-3.873449	1.074245
6	-1.381150	-3.196516	0.718928
6	-1.333857	-1.856697	0.321755
6	-0.096203	-1.197733	0.231677
6	1.079875	-1.906443	0.549946
6	1.004995	-3.223598	0.999060
8	0.471086	0.734171	-1.382023
15	0.916378	2.677310	-1.455727
6	-4.974291	0.219561	-0.732453
6	-4.057714	-0.164084	-1.706577
6	-2.882763	-0.846653	-1.391562
6	-2.606973	-1.145160	-0.039277
6	-3.534327	-0.782563	0.958511
6	-4.697953	-0.106901	0.590389
6	4.983728	-0.063090	0.262712
6	4.163233	0.149609	1.363430
6	2.896312	-0.429845	1.463237
6	2.428706	-1.256338	0.421669
6	3.242822	-1.483216	-0.708215
6	4.500060	-0.876502	-0.757576
6	-3.335362	-1.129588	2.428184
6	-1.963237	-1.334954	-2.501770
6	2.095228	-0.232161	2.741356
6	2.899717	-2.387142	-1.892858
6	6.338275	0.610972	0.163130
6	-6.236866	0.972177	-1.104095

6	1.387519	4.486605	-1.633688
6	-2.085926	-0.550623	-3.808436
6	-2.205856	-2.826831	-2.773865
6	-6.256923	2.368808	-0.472592
6	-7.494832	0.185108	-0.720893
6	1.477164	-2.282989	-2.452424
6	3.266998	-3.849928	-1.604617
6	2.217051	1.179373	3.323030
6	2.517019	-1.279297	3.782019
6	6.286102	1.776300	-0.832622
6	7.455279	-0.369215	-0.206367
6	-0.226386	2.638888	-2.886316
6	2.616704	2.018473	-1.633168
1	-1.157886	0.564848	2.449325
1	-1.444104	2.666074	3.746729
1	-0.641676	4.809528	2.802716
1	0.392437	4.885026	0.585569
1	-0.273754	-4.906067	1.399873
1	-2.336169	-3.709418	0.738362
1	1.916543	-3.743256	1.274727
1	-4.274742	0.073858	-2.742344
1	-5.406116	0.177657	1.362502
1	4.526294	0.779284	2.169332
1	5.116878	-1.050426	-1.635124
1	-2.279014	-1.365854	2.581714
1	-0.937624	-1.216038	-2.157273
1	1.043203	-0.405562	2.509791
1	3.566775	-2.052220	-2.694412
1	6.565747	1.022942	1.152086
1	-6.232842	1.093101	-2.192522
1	2.109315	4.798786	-0.875373
1	0.518261	5.146965	-1.597593
1	-2.028663	0.525699	-3.639949
1	-1.269386	-0.834343	-4.477372
1	-3.023919	-0.768879	-4.327481
1	-2.039268	-3.430786	-1.880691
1	-3.234861	-2.986365	-3.110199
1	-1.529080	-3.182923	-3.555781
1	-5.369599	2.939504	-0.754028
1	-7.143433	2.923585	-0.790626
1	-6.277564	2.298271	0.618424
1	-7.491196	-0.807253	-1.176145
1	-7.556569	0.057420	0.363298
1	-8.394106	0.713905	-1.047006
1	1.155697	-1.240729	-2.509513
1	1.458956	-2.716672	-3.456961
1	0.755388	-2.833508	-1.844476
1	4.292249	-3.936795	-1.237438
1	2.594099	-4.277550	-0.859301
1	3.174637	-4.444944	-2.517470
1	2.021732	1.943890	2.566038
1	1.489640	1.310671	4.127918
1	3.208343	1.355532	3.748987
1	2.358425	-2.292045	3.405869
1	3.577952	-1.167135	4.023973
1	1.940434	-1.159441	4.703275
1	5.537113	2.512185	-0.531663
1	7.256269	2.275856	-0.898492
1	6.020294	1.413031	-1.830018
1	7.480687	-1.215385	0.483033
1	7.317835	-0.761118	-1.217382

1	8.426099	0.131496	-0.176390
1	-0.253888	3.595956	-3.404339
1	-1.215261	2.385140	-2.501501
1	3.325091	2.812575	-1.863787
1	2.621334	1.248634	-2.403293
6	-4.153541	-2.373080	2.807009
1	-3.873047	-3.241978	2.211693
1	-4.009677	-2.618557	3.862750
1	-5.218228	-2.183427	2.642760
6	-3.715942	0.022338	3.370791
1	-4.801267	0.116718	3.459777
1	-3.327501	-0.172301	4.373967
1	-3.326125	0.979958	3.022685
1	2.885356	1.532285	-0.692032
1	0.082983	1.837135	-3.555070
1	1.856988	4.605264	-2.614098

Compound 4

Atomic Number	Coordinates		
6	1.315621	1.231966	7.569191
6	-1.367365	0.453811	7.719790
6	0.674150	0.690172	6.462501
6	-0.665167	0.308366	6.531737
1	1.226392	0.556563	5.539225
1	-1.151743	-0.118662	5.662423
1	2.356357	1.505480	7.486632
1	-2.392852	0.115488	7.775914
6	-0.741949	0.989487	8.851175
6	0.612642	1.399057	8.762845
6	1.121344	1.897873	10.088455
6	0.109127	1.385023	11.115463
5	-1.251438	1.221183	10.309523
7	0.230032	0.998336	12.319280
7	2.032377	2.691853	10.464396
6	2.981990	3.479614	9.670846
6	1.469736	0.906614	13.111627
6	-2.693695	1.377597	10.912419
6	-3.015624	2.581874	11.574668
6	-3.683152	0.378037	10.823447
6	-4.289864	2.769553	12.109412
6	-4.886158	0.525051	11.516413
6	-5.205169	1.725434	12.135724
1	-4.541090	3.730007	12.544085
1	-5.591073	-0.297959	11.516546
1	-6.166589	1.852680	12.620308
6	-2.020193	3.696412	11.657168
6	-1.457979	4.078210	12.888548
6	-1.656286	4.380759	10.470931
6	-0.517932	5.116818	12.894977
6	-0.728966	5.415222	10.542863
6	-0.143954	5.801227	11.747482
1	-0.071742	5.388349	13.846811
1	-0.464807	5.958843	9.640559
6	-3.531743	-0.821151	9.944430
6	-2.589819	-1.826908	10.240036

6	-4.346699	-0.934944	8.795734
6	-2.495294	-2.939273	9.406030
6	-4.207980	-2.075122	7.998095
6	-3.299343	-3.087288	8.281334
1	-1.773593	-3.713831	9.644581
1	-4.824026	-2.163412	7.106774
6	-1.790161	3.515690	14.275932
1	-0.862558	3.646536	14.842156
6	-2.162260	2.033349	14.414900
1	-3.216312	1.849085	14.208163
1	-1.564414	1.403794	13.754924
1	-1.976341	1.729159	15.449687
6	-2.833159	4.399893	14.979153
1	-2.945558	4.086418	16.020692
1	-2.540471	5.452132	14.963850
1	-3.809525	4.311124	14.498875
6	0.799456	6.990254	11.773663
1	1.396786	6.948084	10.854884
6	1.755095	6.993995	12.967408
1	2.509134	7.774280	12.841863
1	1.219047	7.205423	13.896694
1	2.266093	6.035176	13.082057
6	-0.008924	8.295719	11.738829
1	0.656702	9.162689	11.718058
1	-0.658431	8.336348	10.862120
1	-0.640114	8.368028	12.628984
6	-2.367952	4.108768	9.149457
1	-2.668822	3.063252	9.126440
6	-3.656075	4.941681	9.081818
1	-4.313166	4.716457	9.925042
1	-3.419225	6.009507	9.107606
1	-4.199603	4.729319	8.156728
6	-1.506659	4.348445	7.908000
1	-0.552795	3.819999	7.973962
1	-2.034641	3.981468	7.023783
1	-1.304066	5.411051	7.747450
6	-5.349255	0.101708	8.265262
1	-5.415919	-0.132371	7.197572
6	-4.941218	1.580602	8.326832
1	-4.999316	2.002416	9.331307
1	-3.928018	1.734220	7.947322
1	-5.621724	2.153679	7.690346
6	-6.769854	-0.093407	8.817790
1	-7.482957	0.462801	8.203224
1	-7.056151	-1.147469	8.805079
1	-6.856016	0.278252	9.838853
6	-3.169752	-4.297183	7.377929
1	-3.913732	-4.188649	6.581702
6	-1.782750	-4.354128	6.727609
1	-1.005727	-4.478970	7.486672
1	-1.715826	-5.197062	6.035130
1	-1.568466	-3.434526	6.178876
6	-3.470367	-5.596635	8.132730
1	-4.461442	-5.566027	8.589678
1	-3.426807	-6.453016	7.455201
1	-2.738093	-5.761450	8.927718
6	-1.702036	-1.774842	11.474798
1	-1.711961	-0.766053	11.890726
6	-2.255434	-2.706274	12.561309
1	-3.277424	-2.427607	12.828676
1	-2.265589	-3.743252	12.212502

1	-1.636413	-2.650544	13.460652
6	-0.243666	-2.118273	11.152961
1	-0.123500	-3.172364	10.889720
1	0.134102	-1.513829	10.322971
1	0.381181	-1.921972	12.025744
6	1.130209	-0.020999	14.287748
1	0.918393	-1.034038	13.937030
1	1.967610	-0.069089	14.988465
1	0.248574	0.347462	14.815080
6	2.669316	0.317209	12.355826
1	2.354808	-0.535083	11.746300
1	3.146374	1.051177	11.711778
1	3.406000	-0.040502	13.080015
6	1.789266	2.301597	13.669897
1	1.957778	3.008324	12.858052
1	0.957910	2.653615	14.284358
1	2.682044	2.241556	14.299831
6	3.514733	4.535632	10.649876
1	3.965604	4.048510	11.517506
1	4.261151	5.175239	10.171288
1	2.687408	5.154720	11.000585
6	4.162947	2.591470	9.252425
1	4.889125	3.184523	8.690480
1	4.661375	2.197058	10.140787
1	3.861114	1.741415	8.642388
6	2.342089	4.225804	8.493446
1	1.501286	4.819878	8.861449
1	3.077211	4.907373	8.057360
1	1.975427	3.576625	7.701846

9. References

1. R. K. Harris, E. D. Becker, S. M. Cabral de Menezes, R. Goodfellow and P. Granger, NMR nomenclature. Nuclear spin properties and conventions for chemical shifts (IUPAC Recommendations 2001), 2001, **73**, 1795-1818.
2. M. Sindlinger, M. Ströbele, C. Maichle-Mössmer and H. F. Bettinger, Kinetic stabilization allows structural analysis of a benzoborirene, *Chem. Commun.*, 2022, 2818-2821.
3. D. G. Cory and W. M. Ritchey, Suppression of signals from the probe in bloch decay spectra, *Journal of Magnetic Resonance (1969)*, 1988, **80**, 128-132.
4. *Journal*, 2022.
5. D. L. Bryce, R. E. Wasylshen and M. Gee, Characterization of Tricoordinate Boron Chemical Shift Tensors: Definitive High-Field Solid-State NMR Evidence for Anisotropic Boron Shielding, *J. Phys. Chem. A*, 2001, **105**, 3633-3640.
6. G. Sheldrick, *Journal*, 1997.
7. G. M. Sheldrick, Crystal structure refinement with SHELXL, *Acta Crystallographica Section C Structural Chemistry*, 2015, **71**, 3-8.
8. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program, *J. Appl. Crystallogr.*, 2009, **42**, 339-341.
9. 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, *Journal*, 2016.
10. Y. Zhao and D. Truhlar, The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals, *Theoretical Chemistry Accounts*, 2008, **120**, 215-241.
 11. J.-P. Blaudeau, M. P. McGrath, L. A. Curtiss and L. Radom, Extension of Gaussian-2 (G2) theory to molecules containing third-row atoms K and Ca, *Chem. Phys.*, 1997, **107**, 5016-5021.
 12. L. A. Curtiss, M. P. McGrath, J. P. Blaudeau, N. E. Davis, R. C. Binning and L. Radom, Extension of Gaussian-2 theory to molecules containing third-row atoms Ga–Kr, *Chem. Phys.*, 1995, **103**, 6104-6113.
 13. P. J. Hay, Gaussian basis sets for molecular calculations. The representation of 3d orbitals in transition-metal atoms, *Chem. Phys.*, 1977, **66**, 4377-4384.
 14. R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions, *Chem. Phys.*, 1980, **72**, 650-654.
 15. M. P. McGrath and L. Radom, Extension of Gaussian-1 (G1) theory to bromine-containing molecules, *Chem. Phys.*, 1991, **94**, 511-516.
 16. A. D. McLean and G. S. Chandler, Contracted Gaussian basis sets for molecular calculations. I. Second row atoms, Z=11–18, *Chem. Phys.*, 1980, **72**, 5639-5648.
 17. K. Raghavachari and G. W. Trucks, Highly correlated systems. Excitation energies of first row transition metals Sc–Cu, *Chem. Phys.*, 1989, **91**, 1062-1065.
 18. A. J. H. Wachters, Gaussian Basis Set for Molecular Wavefunctions Containing Third-Row Atoms, *Chem. Phys.*, 1970, **52**, 1033-1036.
 19. R. C. Binning and L. A. Curtiss, Compact contracted basis sets for third-row atoms: Ga-Kr, *J. Comput. Chem.*, 1990, **11**, 1206-1216.
 20. E. D. Glendening, C. R. Landis and F. Weinhold, Natural bond orbital methods, *WIREs Computational Molecular Science*, 2012, **2**, 1-42.
 21. F. Weinhold, Natural bond orbital analysis: A critical overview of relationships to alternative bonding perspectives, *J. Comput. Chem.*, 2012, **33**, 2363-2379.
 22. E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis and F. Weinhold, *Journal*, 2013, Software.
 23. E. D. Glendening, C. R. Landis and F. Weinhold, NBO 6.0: Natural bond orbital analysis program, *J. Comput. Chem.*, 2013, **34**, 1429-1437.
 24. Compliance 3.0.2., <http://www.oc.tu-bs.de/Grunenberg/compliance.html>, (accessed 23.06., 2023).
 25. K. Brandhorst, Braunschweig, 2009.
 26. J. Grunenberg, III-defined concepts in chemistry: rigid force constants vs. compliance constants as bond strength descriptors for the triple bond in diboryne, *Chem. Sci.*, 2015, **6**, 4086-4088.