Electronic Supporting Information

Transient Hydroboration and hydroalumination of activated azo-species: Avenues to NBO and NAlO-heterobicycles

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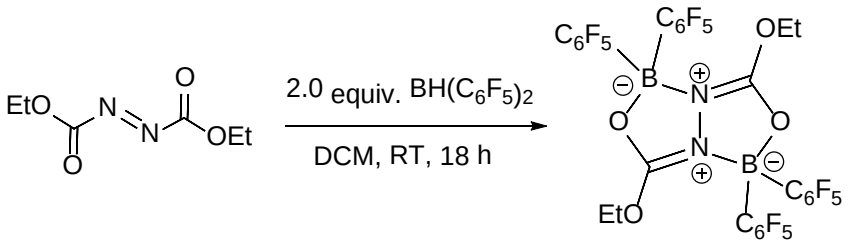
Experimental

General information for synthesis

Experiments were carried under inert conditions using standard Schlenk techniques or a glove box as appropriate. Dichloromethane (DCM, CH_2Cl_2) and *n*-hexanes (C_6H_{14}) were dispensed from an MBRAUN Solvent Purification System, deoxygenated by bubbling Ar for 20 min, and stored over 3 Å molecular sieves prior to use. Chloroform-d ($CDCl_3$) and benzene-d_6 (C_6D_6) solvents were used as received without any purification and those were stored over 4 Å molecular sieves prior to use. Vials and stir bar for reactions were oven-dried overnight before experiments. ^{1}H (500 or 400 MHz), ^{19}F (471 or 377 MHz), and $^{13}C\{^{1}H\}$ (126 or 101 MHz) NMR spectra were run at 298 K on Bruker 500 or 400 spectrometers. The chemical shifts (δ, ppm) for ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra are given relative to solvent signals whereas an external reference standards used for ^{19}F ($CFCl_3$) and ^{11}B ($BF_3.OEt_2$) NMR spectra. These NMR data are written as: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz) and integration. The single-crystal *X*-ray data were collected either on a Bruker D8 QUEST diffractometer using Cu (60W, Diamond, ⌈K⟨ = 12.894 mm^{-1}) micro-focus *X*-ray sources at 150 K or on a Bruker Kappa Apex II diffractometer which was equipped with rotation anode using graphite-monochromated MoKα radiation (λ = 0.71073 Å). The structure was solved and refined using Full-matrix least-squares based on F^2 with a suite of programs SHELXS and SHELXL[1] compiled in OLEX2.[2] High-resolution mass spectra (HRMS) were obtained on an AccuTOF Plus 4G (DART) at AIMS Mass Spectrometry Laboratory whilst elemental (CHN) alaysis was carried out at ANALEST Facility, University of Toronto. The reagents $HB(C_6F_5)_2$[3] and nacnacAlH_2[4] were prepared by following literature method or a slight variations thereof. All other reagents were purchased commercially and used as received.

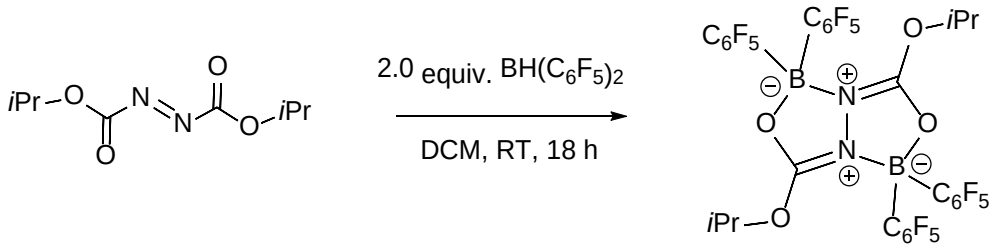
Synthetic procedures and characterization data

Synthesis 1



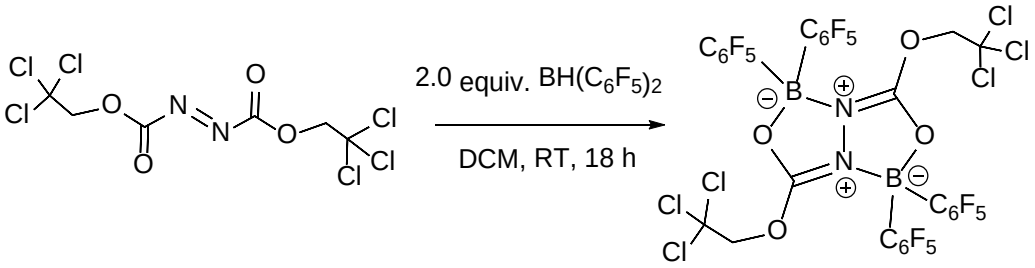
Into a 4 mL open top PTFE vial equipped with a stir bar, $BH(C_6F_5)_2$ (69.2 mg, 0.20 mmol, 2.0 equiv.) was taken in DCM (0.5 mL). A solution of diethyl azodicarboxylate (17.4 mg, 0.10 mmol, 1.0 equiv.) in DCM (0.5 mL) was transferred to the vial. At addition a strong bubble observed whilst reaction changes to colorless in few min. The reaction mixture was allowed to stir at RT for 18 h. After removal of all volatiles, the residue was washed with *n*-hexane (3 x 1 mL) and to that followed by drying afforded compound **1** (73 mg, 84%). *X*-ray quality crystals were grown with a mixture of solvent of DCM:*n*-hexane (1:5) and stored at -30 °C for three days. **1**: $C_{30}H_{10}B_2F_{20}N_2O_4$ requires: C 41.7, H 1.17, N 3.24. Found: C 41.7, H 1.14, N 3.16%. ^{1}H NMR (500 MHz, CD_2Cl_2): δ_H 4.53 (q, *J* = 7.8 Hz, 4 H, -OC*H*$_2$), 1.35 (t, *J* = 7.2 Hz, 3 H, -OCH$_2$C*H*$_3$), ^{19}F NMR (471 MHz, CD_2Cl_2): δ_F -136.6 (m, 8 F, *o*-C$_6$*F*$_5$ of -B(C$_6$*F*$_5$)$_2$), -155.0 (m, 4 F, *p*-C$_6$*F*$_5$ of -B(C$_6$*F*$_5$)$_2$), -163.6 (m, 8 F, *m*-C$_6$*F*$_5$ of -B(C$_6$*F*$_5$)$_2$); ^{11}B NMR (161 MHz, CD_2Cl_2): δ_B 4.3 (br s, 2 B, -*B*(C$_6$F$_5$)$_2$); ^{13}C NMR (126 MHz, CD_2Cl_2): δ_C 160.3 (s, N=*C*(OEt)O-), 149.6 (br s, -*C*$_6$F$_5$), 147.7 (br s, -*C*$_6$F$_5$), 142.8 (br s, -*C*$_6$F$_5$), 140.8 (br s, -*C*$_6$F$_5$), 138.9 (br s, -*C*$_6$F$_5$), 136.9 (br s, -*C*$_6$F$_5$), 71.7 (s, *C*H$_2$ of OEt), 14.5 (s, *C*H$_3$ of OEt); HRMS (DART) m/z: 865.0575 for [M$^+$+1] (calcd.: 865.0580).

Synthesis 2



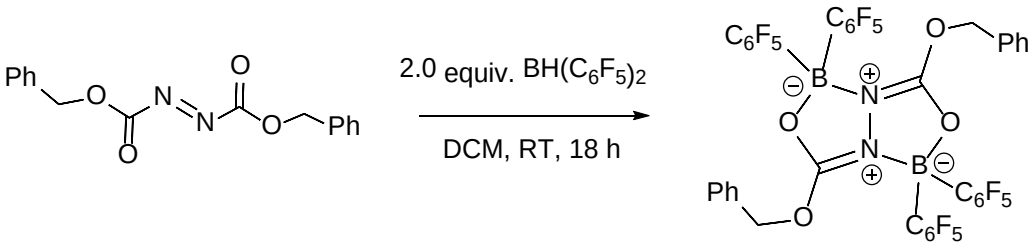
2 (70 mg, 79%) was prepared by following the protocol for **1**. *X*-ray quality crystals were grown with a mixture of solvent of DCM:*n*-hexane (1:5) and stored at -30 °C for three days. **2**: $C_{32}H_{14}B_2F_{20}N_2O_4$ requires: C 43.1, H 1.58, N 3.14. Found: C 43.0, H 1.57, N 3.09%. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 5.15 (m, 2 H, C*H* of OC*H*$(CH_3)_2$), 1.27 (d, *J* = 6.3 Hz, 12 H, C*H*$_3$ of -OCH(*CH*$_3)_2$), ^{19}F NMR (377 MHz, $CDCl_3$): δ_F -136.3 (m, 8 F, *o*-C_6F_5 of -B($C_6F_5)_2$), -154.3 (m, 4 F, *p*-C_6F_5 of -B($C_6F_5)_2$), -162.9 (m, 8 F, *m*-C_6F_5 of -B($C_6F_5)_2$); ^{11}B NMR (128 MHz, $CDCl_3$): δ_B 4.0 (br s, 2 B, -*B*($C_6F_5)_2$); ^{13}C NMR (101 MHz, $CDCl_3$): δ_C 159.3 (s, N=*C*(OCH(*C*$H_3)_2$)O-), 149.0 (br s, -*C*$_6F_5$), 146.7 (br s, -*C*$_6F_5$), 142.2 (br s, -*C*$_6F_5$), 139.8 (br s, -*C*$_6F_5$), 138.5 (br s, -*C*$_6F_5$), 135.9 (br s, -*C*$_6F_5$), 81.1 (s, O*C*H$(CH_3)_2$), 21.5 (s, OCH(*C*$H_3)_2$); HRMS (DART) m/z: 892.0811 for [M^+] (calcd.: 892.0815).

Synthesis 3



3 (87 mg, 81%) was prepared by following the protocol for **1**. *X*-ray quality crystals were grown with a mixture of solvent of DCM:*n*-hexane (1:5) and stored at -30 °C for three days. **3**: $C_{30}H_4B_2Cl_6F_{20}N_2O_4$ requires: C 33.7, H 0.38, N 2.62. Found: C 33.5, H 0.32, N 2.51%. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.24 (s, 4 H, -OC*H*$_2$CCl_3), ^{19}F NMR (377 MHz, $CDCl_3$): δ_F -135.8 (m, 8 F, *o*-C_6F_5 of -B($C_6F_5)_2$), -153.0 (m, 4 F, *p*-C_6F_5 of -B($C_6F_5)_2$), -162.4 (m, 8 F, *m*-C_6F_5 of -B($C_6F_5)_2$); ^{11}B NMR (128 MHz, $CDCl_3$): δ_B 5.4 (br s, 2 B, -*B*($C_6F_5)_2$); ^{13}C NMR (101 MHz, $CDCl_3$): δ_C 158.9 (s, N=*C*(OCH_2CCl_3)O-), 149.2 (br s, -*C*$_6F_5$), 146.6 (br s, -*C*$_6F_5$), 142.8 (br s, -*C*$_6F_5$), 140.0 (br s, -*C*$_6F_5$), 138.3 (br s, -*C*$_6F_5$), 136.0 (br s, -*C*$_6F_5$), 91.5 (s, *C*H_2CCl_3), 79.9 (s, CH_2*C*Cl_3); MS (DART) m/z: 1069.8 for [M^+] (calcd.: 1069.8).

Synthesis 4



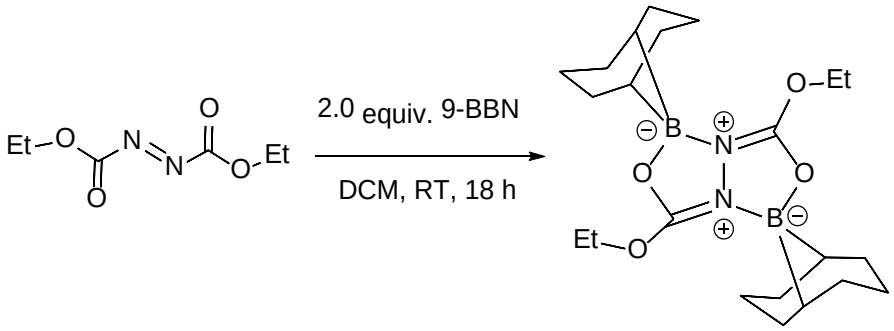
4 (77 mg, 78%) was prepared by following the protocol for **1**. *X*-ray quality crystals were grown with a mixture of solvent of DCM:*n*-hexane (1:5) and stored at -30 °C for three days. **4**: $C_{40}H_{14}B_2F_{20}N_2O_4$ requires: C 48.6, H 1.43, N 2.83. Found: C 46.8, H 1.40, N 2.61%. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.41 (tt, *J* = 7.6, 1.4 Hz, 2 H, Ar-*H*), 7.37 - 7.30 (m, 4 H, Ar-*H*), 7.20 - 7.13 (m, 4 H, Ar-*H*); 5.42 (s, 4 H, OCH_2); ^{19}F NMR (377 MHz, $CDCl_3$): δ_F -136.1 (m, 8 F, *o*-C$_6F_5$ of -B(C$_6F_5$)$_2$), -153.7 (m, 4 F, *p*-C$_6F_5$ of -B(C$_6F_5$)$_2$), -162.5 (m, 8 F, *m*-C$_6F_5$ of -B(C$_6F_5$)$_2$); ^{11}B NMR (128 MHz, $CDCl_3$): δ_B 4.4 (br s, 2 B, -*B*(C$_6F_5$)$_2$); ^{13}C NMR (101 MHz, $CDCl_3$): δ_C 160.0 (s, N=*C*(OCH$_2$Ph)O-), 149.1 (br s, -*C*$_6F_5$), 146.7 (br s, -*C*$_6F_5$), 142.5 (br s, -*C*$_6F_5$), 140.0 (br s, -*C*$_6F_5$), 138.4 (br s, -*C*$_6F_5$), 136.0 (br s, -*C*$_6F_5$), 131.6 (s, -*C*$_6H_5$),130.1 (s, -*C*$_6H_5$), 129.0 (s, -*C*$_6H_5$), 128.7 (s, -*C*$_6H_5$), 75.9 (s, -O*C*H$_2$); HRMS (DART) m/z: 988.0809 for [M$^+$] (calcd.: 988.0815).

Synthesis 5

5 (85 mg, 90%) was prepared by following the protocol for **1**. **5**: $C_{36}H_{20}B_2F_{20}N_2O_2$ requires: C 45.9, H 2.14, N 5.95. Found: C 45.7, H 2.03, N 5.79%. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 3.35 (t, *J* = 5.3 Hz, 8 H, N-CH_2), 1.64 - 1.45 (m, 4 H, CH_2), 1.36 - 1.16 (m, 8 H, CH_2); ^{19}F NMR (377 MHz, $CDCl_3$): δ_F -136.1 (m, 8 F, *o*-C$_6F_5$ of -B(C$_6F_5$)$_2$), -154.8 (m, 4 F, *p*-C$_6F_5$ of -B(C$_6F_5$)$_2$), -162.7 (m, 8 F, *m*-C$_6F_5$ of -B(C$_6F_5$)$_2$); ^{11}B NMR (128 MHz, $CDCl_3$): δ_B 1.9 (br s, 2 B, -*B*(C$_6F_5$)$_2$); ^{13}C NMR (101 MHz, $CDCl_3$): δ_C 153.2 (s, N=*C*(O)-), 149.4 (br s, -*C*$_6F_5$), 146.9 (br s, -*C*$_6F_5$),

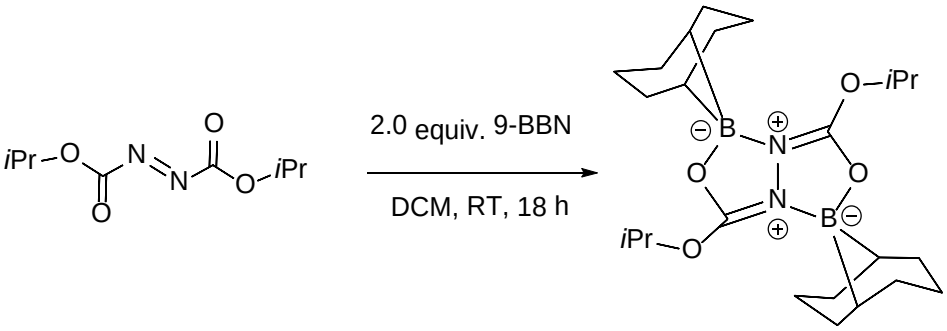
145.1 (br s, -C_6F_5), 142.3 (br s, -C_6F_5), 138.7 (br s, -C_6F_5), 136.2 (br s, -C_6F_5), 47.2 (s, -NCH_2), 25.1 (s, -CH_2), 23.3 (s, -CH_2); HRMS (DART) m/z: 943.1527 (M^++1) (calcd.: 942.1526).

Synthesis 6



6 (27 mg, 65%) was prepared by following the protocol for **1**. *X*-ray quality crystals were grown with a mixture of solvent of DCM:*n*-hexane (1:5) and stored at -30 °C for three days. **6**: $C_{22}H_{38}B_2N_2O_4$ requires: C 63.5, H 9.20, N 6.73. Found: C 63.4, H 9.35, N 6.63%. δ_H ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 4.41 (q, *J* = 7.70 Hz, 4 H, -OC*H*$_2$CH$_3$), 2.04 - 0.58 (m, 28 H, 9-BBN C*H* & C*H*$_2$), 1.38 (t, *J* = 7.43 Hz, 6 H, -OCH$_2$C*H*$_3$); ^{11}B NMR (128 MHz, $CDCl_3$): δ_B 13.2 (br s, 2 B); ^{13}C NMR (101 MHz, $CDCl_3$): δ_C 158.1 (s, N=*C*(OCH$_2$CH$_3$)O-), 66.7 (s, *C*H$_2$ of OEt), 32.2 (s, *C*H$_2$, 9-BBN), 30.6 (s, *C*H$_2$, 9-BBN), 26.4 (s, *C*H, 9-BBN), 24.4 (s, *C*H$_2$, 9-BBN), 24.1 (s, *C*H$_2$, 9-BBN), 14.0 (s, *C*H$_3$ of OEt); HRMS (DART) m/z: 417.3102 for [M^++1] (calcd.: 417.3091).

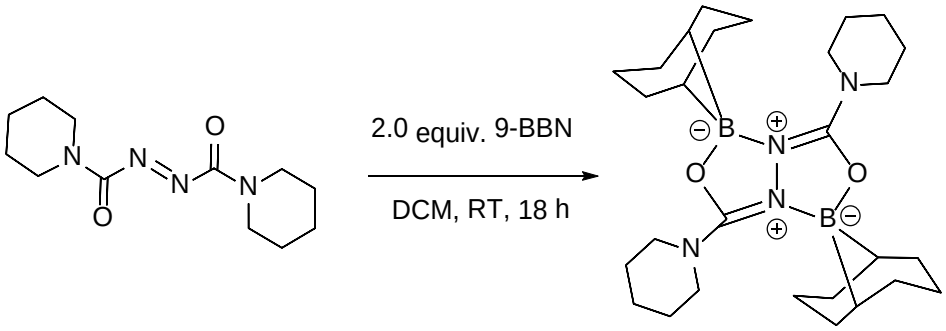
Synthesis 7



7 (27 mg, 61%) was prepared by following the protocol for **1**. *X*-ray quality crystals were grown with a mixture of solvent of DCM:*n*-hexane (1:5) and stored at -30 °C for three days. **7**: $C_{24}H_{42}B_2N_2O_4$ requires: C 64.9, H 9.53, N 6.31. Found: C 63.3, H 9.46, N 5.88%. δ_H ^{1}H NMR

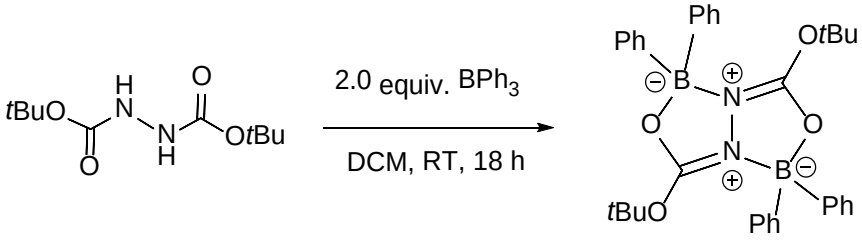
(400 MHz, $CDCl_3$): δ_H 5.01 (m, 2 H, -OC*H*(CH_3)$_2$), 2.04 - 0.66 (m, 28 H, 9-BBN C*H* & CH_2), 1.36 (q, *J* = 7.01 Hz, 12 H, -OCH(CH_3)$_2$); ^{11}B NMR (128 MHz, $CDCl_3$): δ_B 12.7 (br s, 2 B, 9-BBN); ^{3}C NMR (101 MHz, $CDCl_3$): δ_C 157.7 (s, N=*C*(O*i*Pr)O-), 75.7 (s, -O*C*H(CH_3)$_2$), 32.3 (s, *C*H_2, 9-BBN), 30.7 (s, *C*H_2, 9-BBN), 26.4 (s, *C*H, 9-BBN), 24.5 (s, *C*H_2, 9-BBN), 24.1 (s, *C*H_2, 9-BBN), 21.7 (s, OCH(*C*H_3)$_2$); HRMS (DART) m/z: 444.3410 for [M^++1] (calcd.: 444.3404).

Synthesis 8



8 (39 mg, 79%) was prepared by following the protocol for **1**. **8**: $C_{28}H_{48}B_2N_4O_2$ requires: C 68.0, H 9.79, N 11.33. Found: C 67.7, H 9.80, N 11.02%. δ_H ^{1}H NMR (400 MHz, CH_2Cl_2): δ_H 2.82 (s, 8 H, -NCH_2), 1.47 - 1.14 (m, 12 H, -CH_2), 1.13 - 0.95 (m, 20 H, -CH_2), 0.93 - 0.77 (m, 4 H, -C*H*), 0.30 (s, 4 H, -CH_2); ^{11}B NMR (128 MHz, CH_2Cl_2): δ_B 9.5 (br s, 2 B); ^{13}C NMR (101 MHz, CH_2Cl_2): δ_C 161.3 (s, N=*C*(O)-), 49.9 (s, -N*C*H_2), 33.1 (s, -*C*H_2), 30.2 (s, -*C*H_2), 25.7 (-*C*H_2), 24.2 (-*C*H_2), 22.7 (-*C*H_2); HRMS (DART) m/z: 495.4030 for [M^++1] (calcd.: 494.4036).

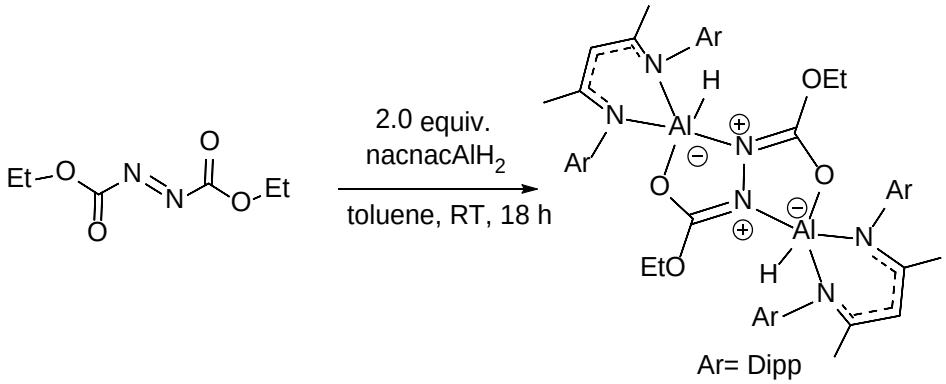
Synthesis 9



9 (41 mg, 73%) was prepared by following the protocol for **1**. **8**: δ_H ^{1}H NMR (500 MHz, CD_2Cl_2): δ_H 7.44 - 7.37 (m, 8 H, Ph*H*), 7.33 - 7.23 (m, 12 H, Ph*H*), 1.41 (s, 18 H, -*t*Bu*H*); ^{11}B NMR (128 MHz, CD_2Cl_2): δ_B 9.7 (br s, 2 B); ^{13}C NMR (126 MHz, CD_2Cl_2): δ_C 160.3 (s,

N=*C*(O)-), 132.6 (s, Ph*C*), 127.8 (Ph*C*), 127.5 (Ph*C*), 90.3 (-O*C*(CH_3)$_3$), 28.6 (-OC(*C*H_3)$_3$), MS (ESI) m/z: 561.2680 for [M^++1] (calcd.: 561.2960 for $C_{34}H_{39}B_2N_2O_4$).

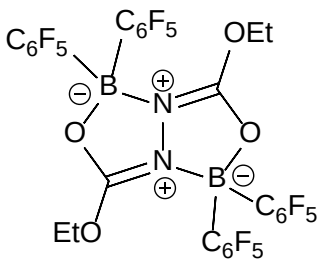
Synthesis 10



10 (87 mg, 89%) was prepared by following the protocol for **1** except the reaction was carried out in toluene. *X*-ray quality crystals were grown with a mixture of solvent of toluene:*n*-hexane (1:5) and stored at -30 °C for three days. **10**: δ_H ^{1}H NMR (500 MHz, C_6D_6): δ_H 12.5 (s, 2 H, Al-*H*), 7.28 - 7.13 (m, 12 H, Ar-*H*), 4.89 (s, 4 H, OCH_2), 3.91 (br m, 2 H, C*H*), 3.32 (m, 8 H, C*H*), 1.7 (s, 12 H, CH_3), 1.22 (d, *J* = 6.5 Hz, 24 H, CH_3), 1.16 (d, *J* = 6.9 Hz, 24 H, CH_3), 0.89 (t, *J* = 7.4 Hz, CH_3); ^{13}C NMR (101 MHz, C_6D_6): δ_C 161.9 (s, N=*C*(O)-), 156.0 (N=C-CH_3), 143.1 (s, Ar*C*), 141.6 (s, Ar*C*), 126.2 (s, Ar*C*), 124.0 (s, Ar*C*), 94.6 (*C*H), 73.5 (s, -O*C*H_2), 61.7 (s, *C*H), 29.0 (s, *C*HMe_2), 24.8 (s, CH*Me*$_2$), 23.8 (s, CH*Me*$_2$), 21.1 (s, Me), 14.7 (s, -OCH$_2$*C*H_3).

NMR spectra of all the compounds

Compound 1



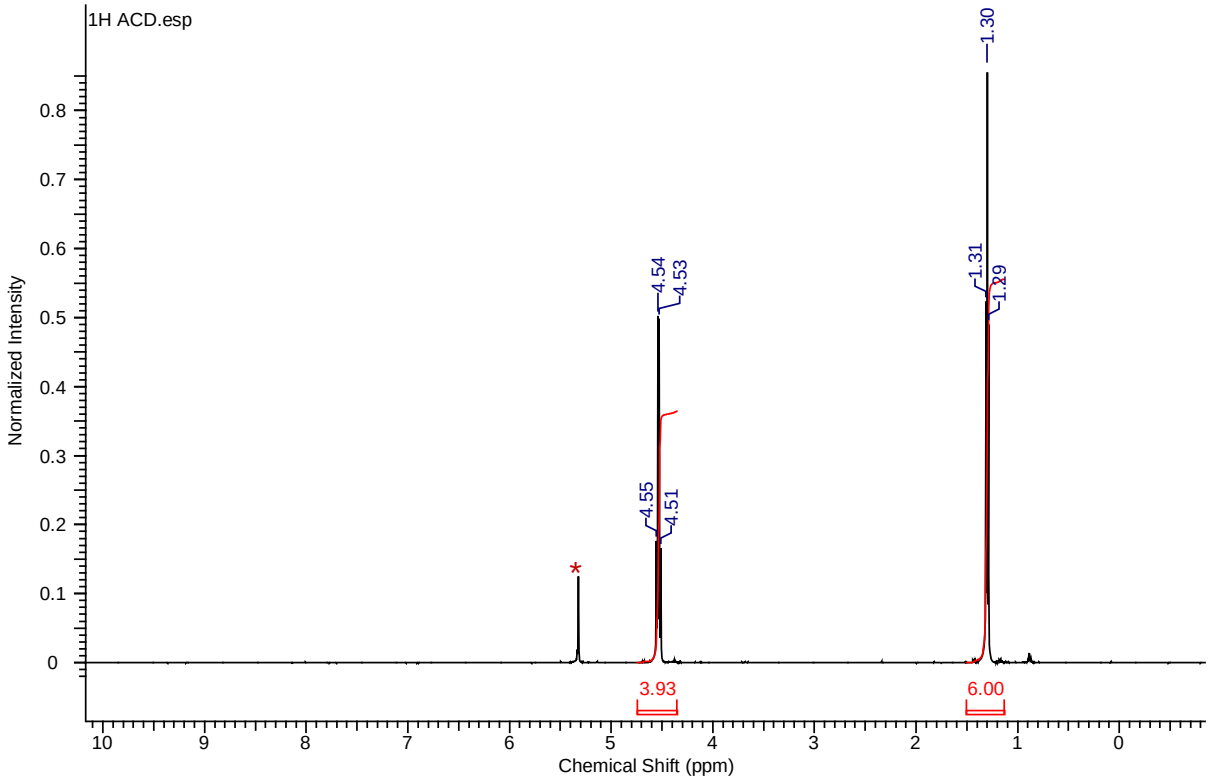


Figure S1. ^{1}H NMR (500 MHz) spectrum of the compound **1** in CD_2Cl_2 (*= CD_2Cl_2).

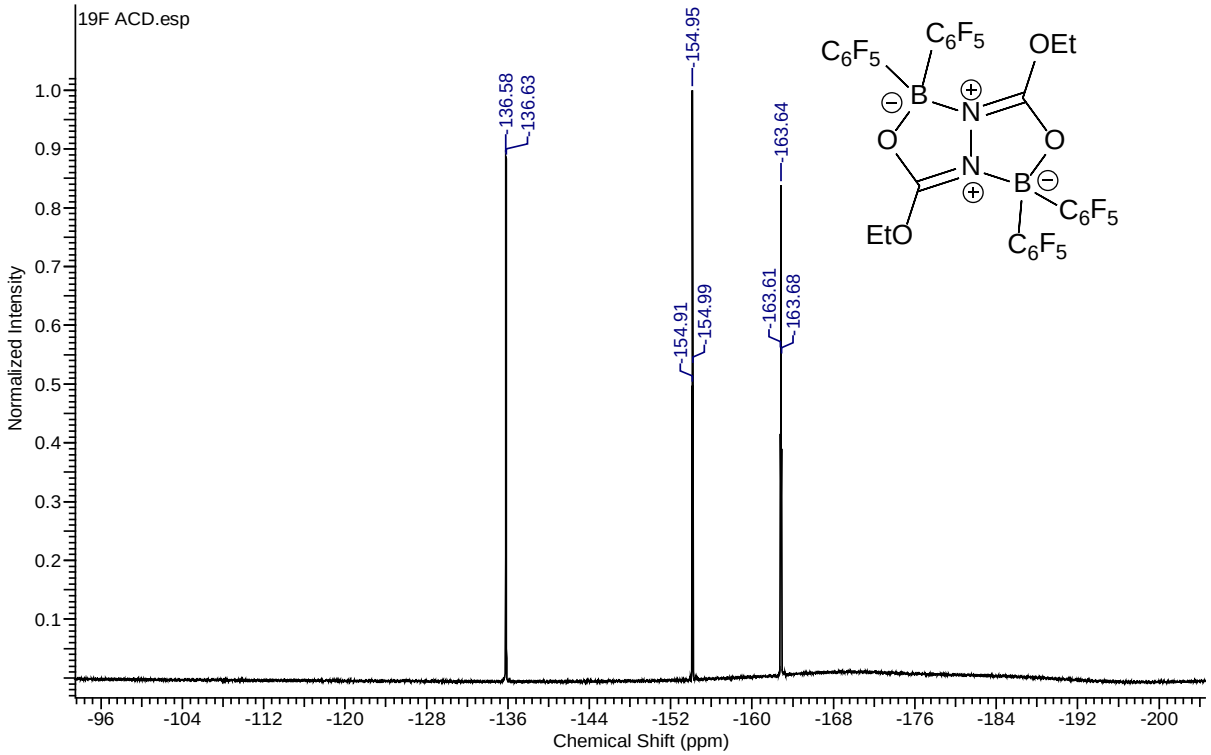


Figure S2. ^{19}F NMR (471 MHz) spectrum of the compound **1** in CD_2Cl_2.

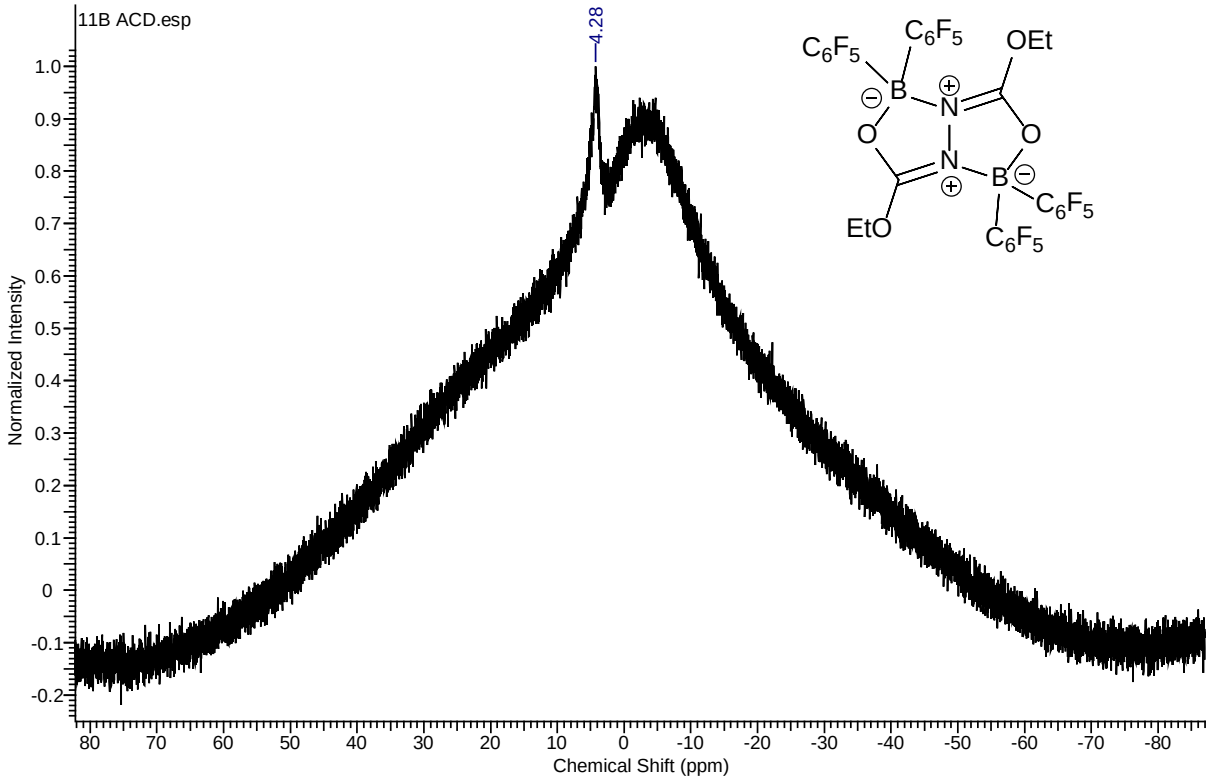


Figure S3. ^{11}B NMR (161 MHz) spectrum of the compound **1** in CD_2Cl_2.

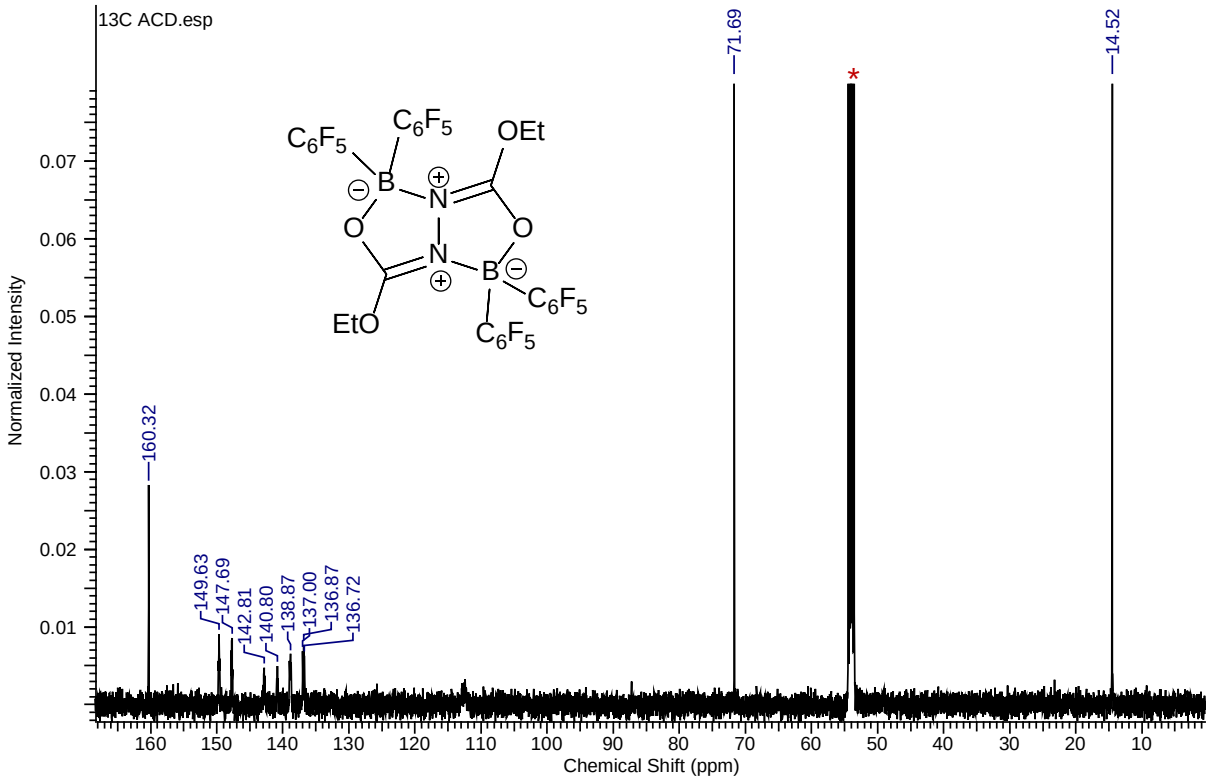


Figure S4. ^{13}C NMR (126 MHz) spectrum of the compound **1** in CD_2Cl_2 (*= CD_2Cl_2).

Compound 2

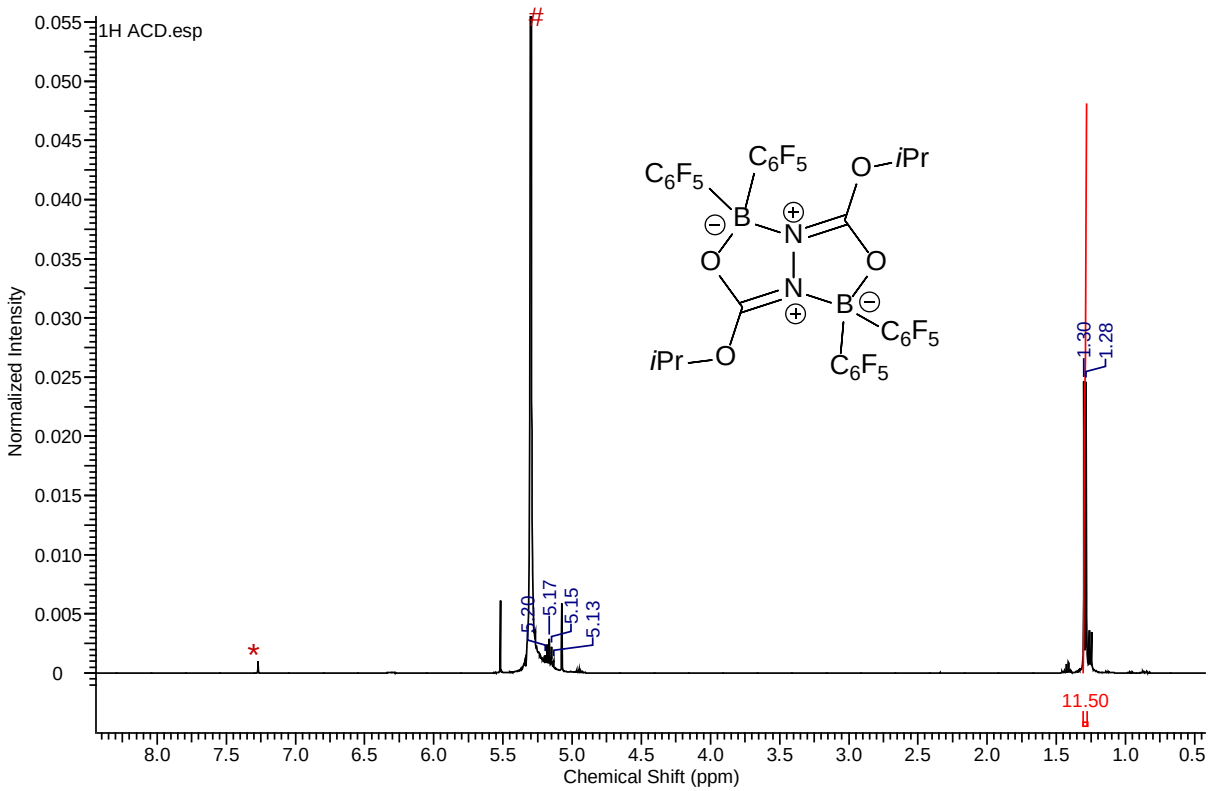


Figure S5. 1H NMR (400 MHz) spectrum of the compound **2** in $CDCl_3/CH_2Cl_2$ (1:5) (*= $CDCl_3$; #= CH_2Cl_2).

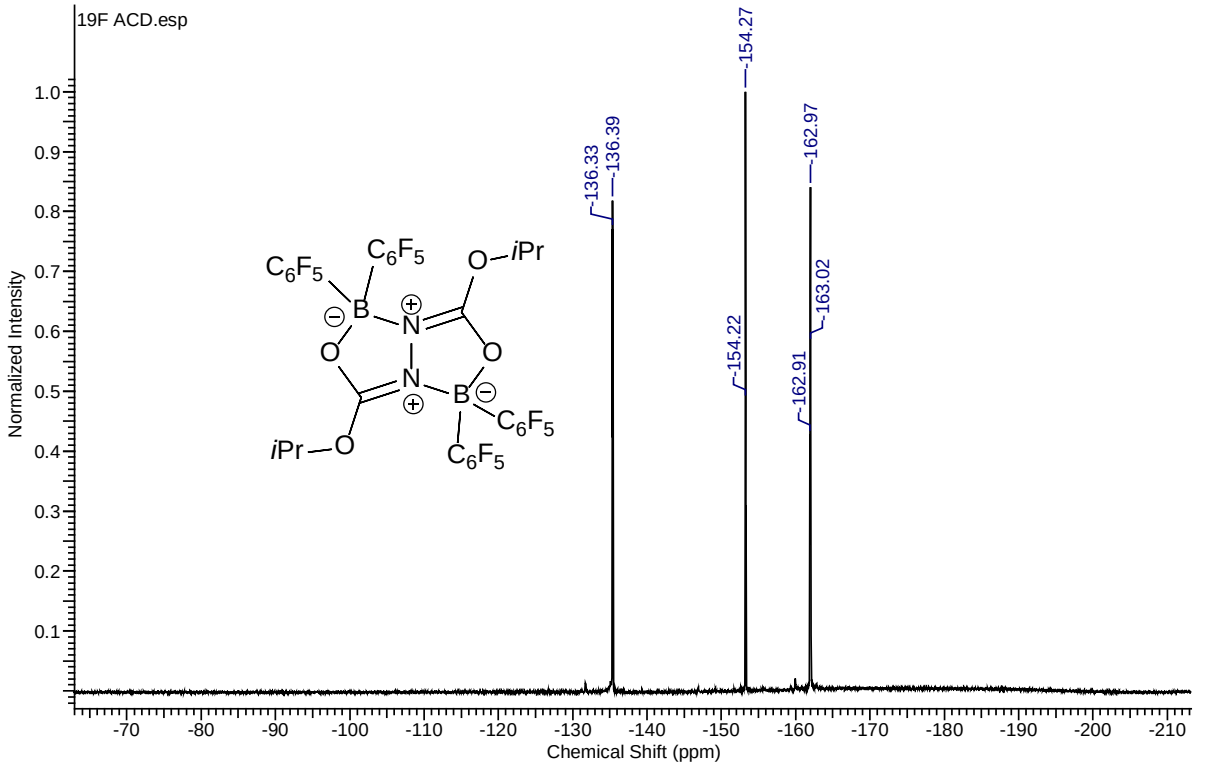


Figure S6. ^{19}F NMR (377 MHz) spectrum of the compound **2** in $CDCl_3/CH_2Cl_2$ (1:5).

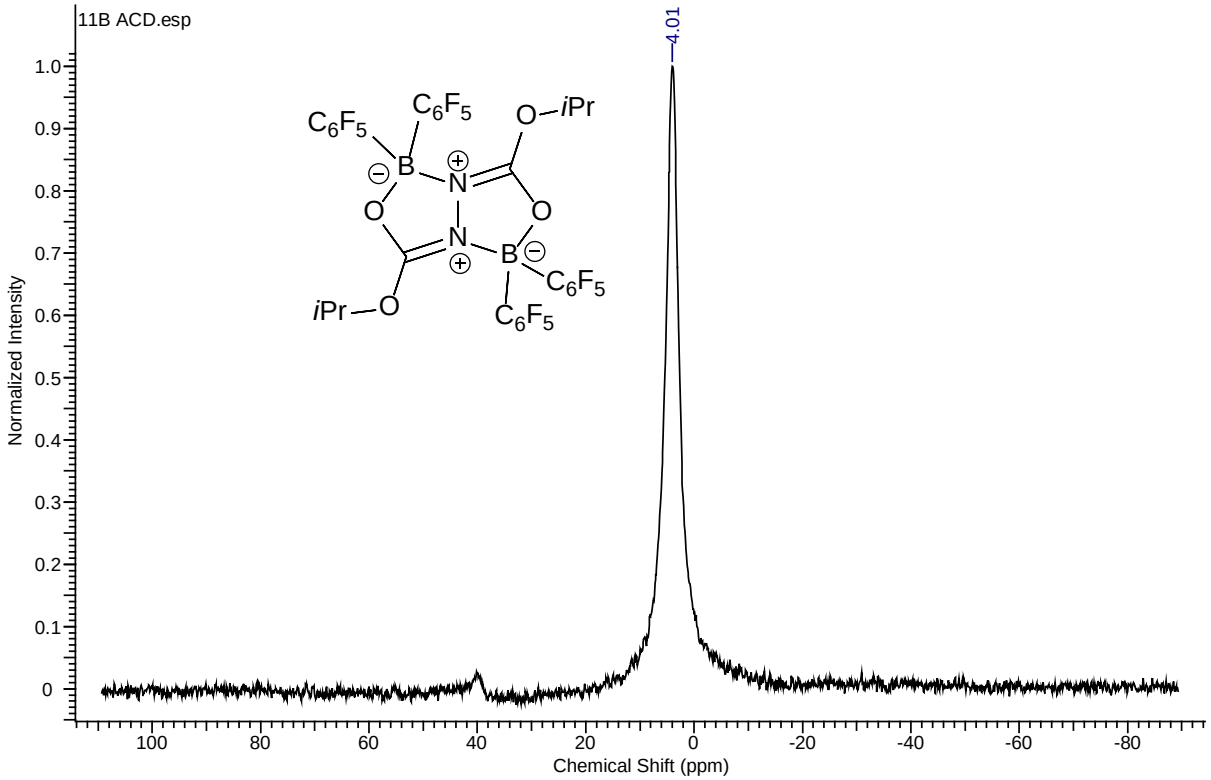


Figure S7. ^{11}B NMR (128 MHz) spectrum of the compound **2** in $CDCl_3/CH_2Cl_2$ (1:5).

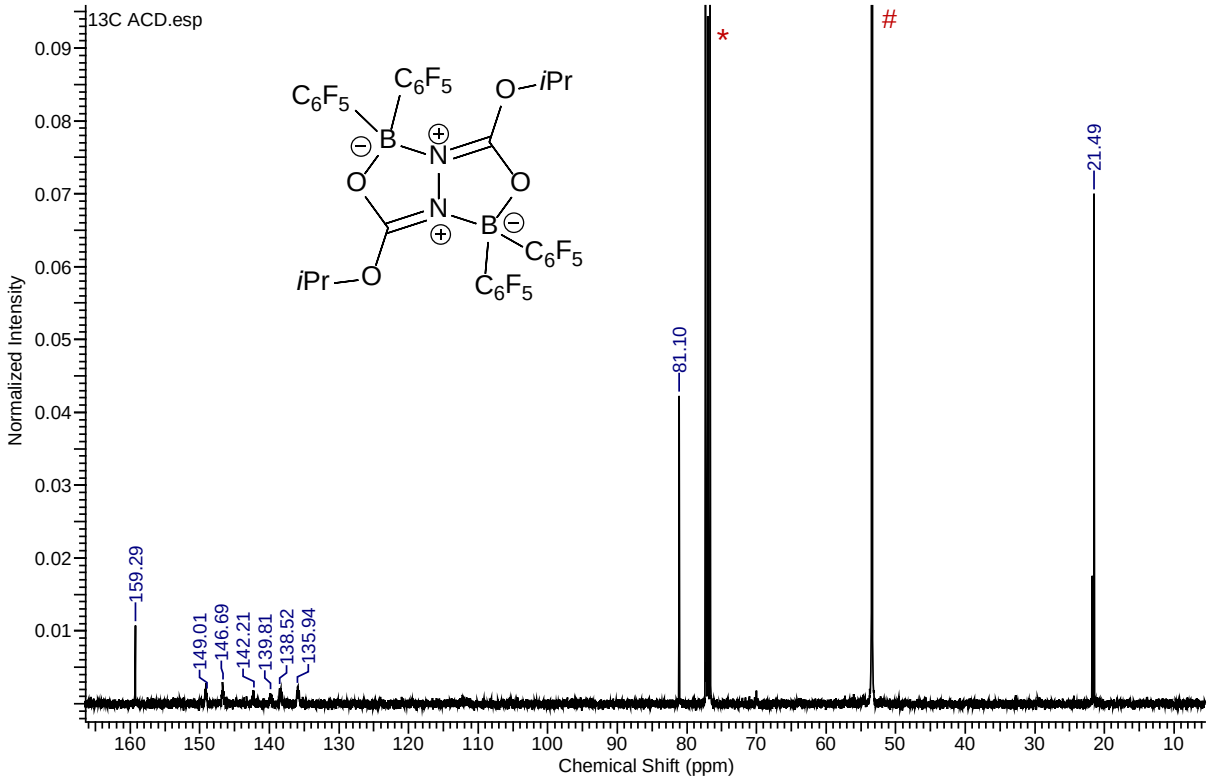


Figure S8. ^{13}C NMR (101 MHz) spectrum of the compound **2** in $CDCl_3/CH_2Cl_2$ (1:5) (*= $CDCl_3$; #= CH_2Cl_2).

Compound 3

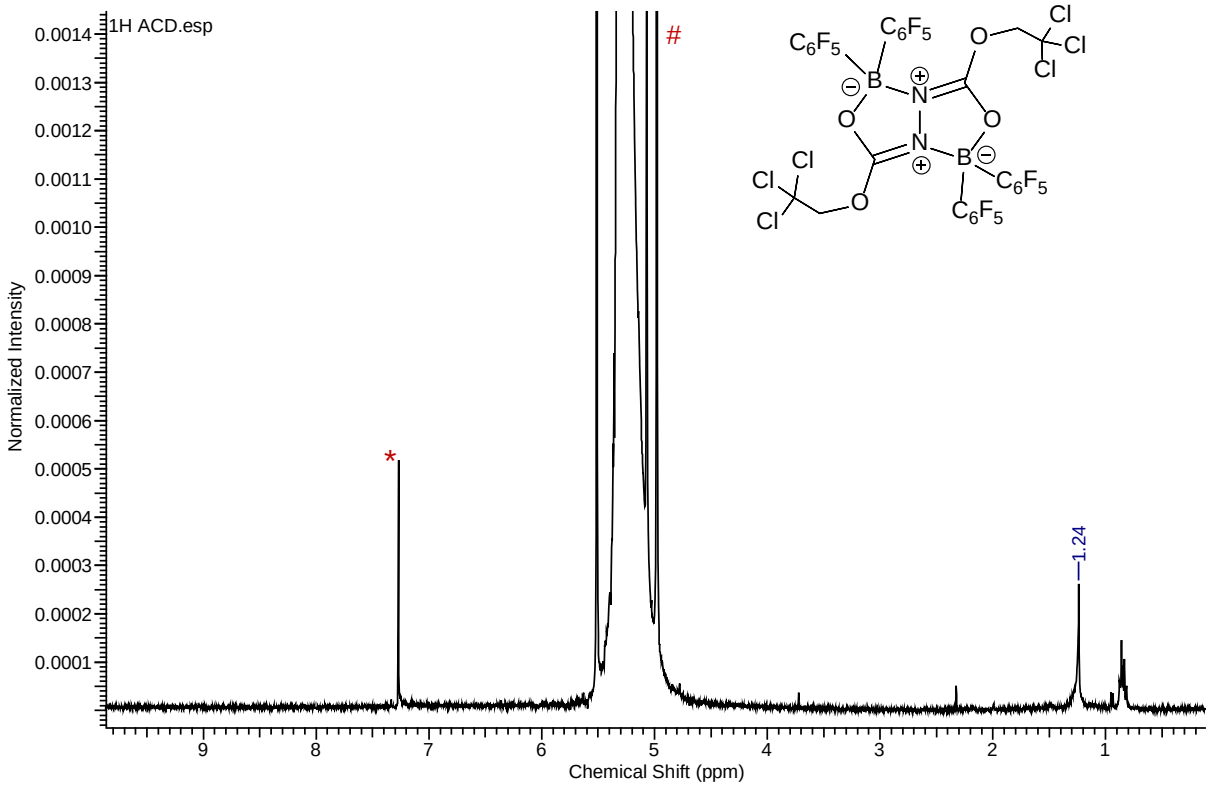


Figure S9. ^{1}H NMR (400 MHz) spectrum of the compound **3** in $CDCl_3/CH_2Cl_2$ (1:5) (*= $CDCl_3$; #= CH_2Cl_2).

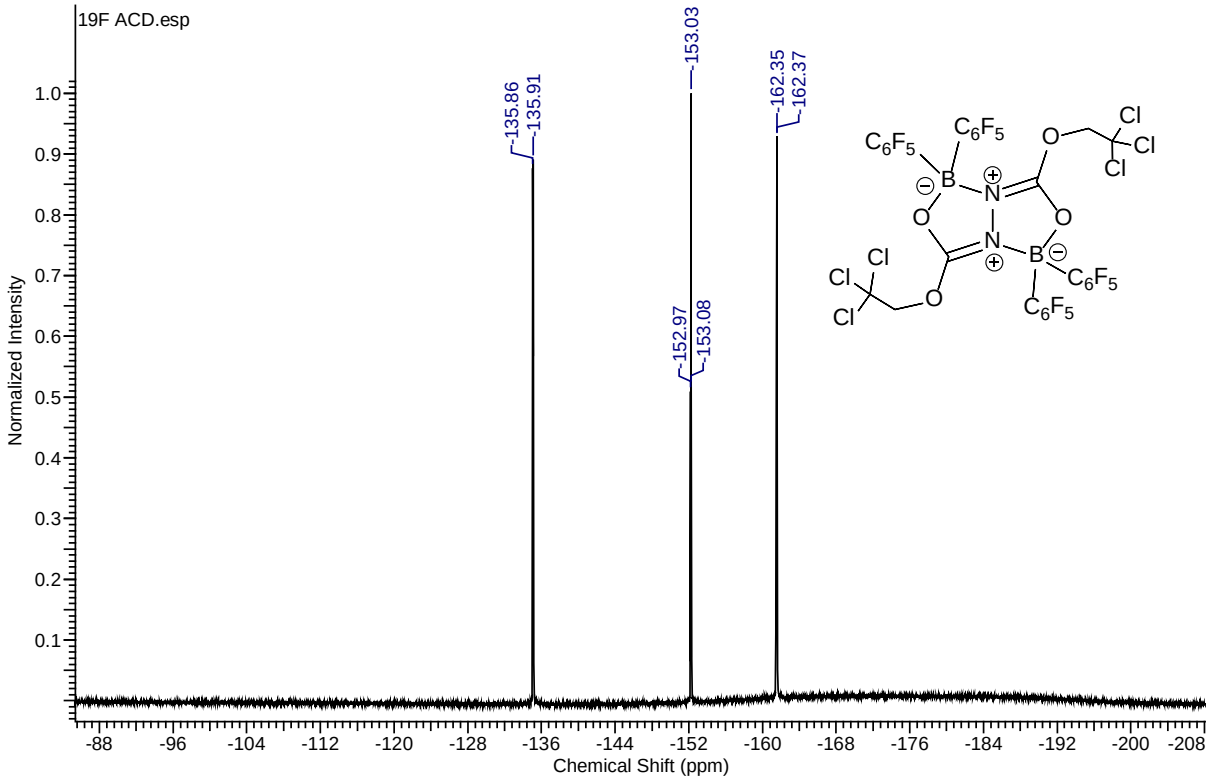


Figure S10. ^{19}F NMR (377 MHz) spectrum of the compound **3** in $CDCl_3/CH_2Cl_2$ (1:5)..

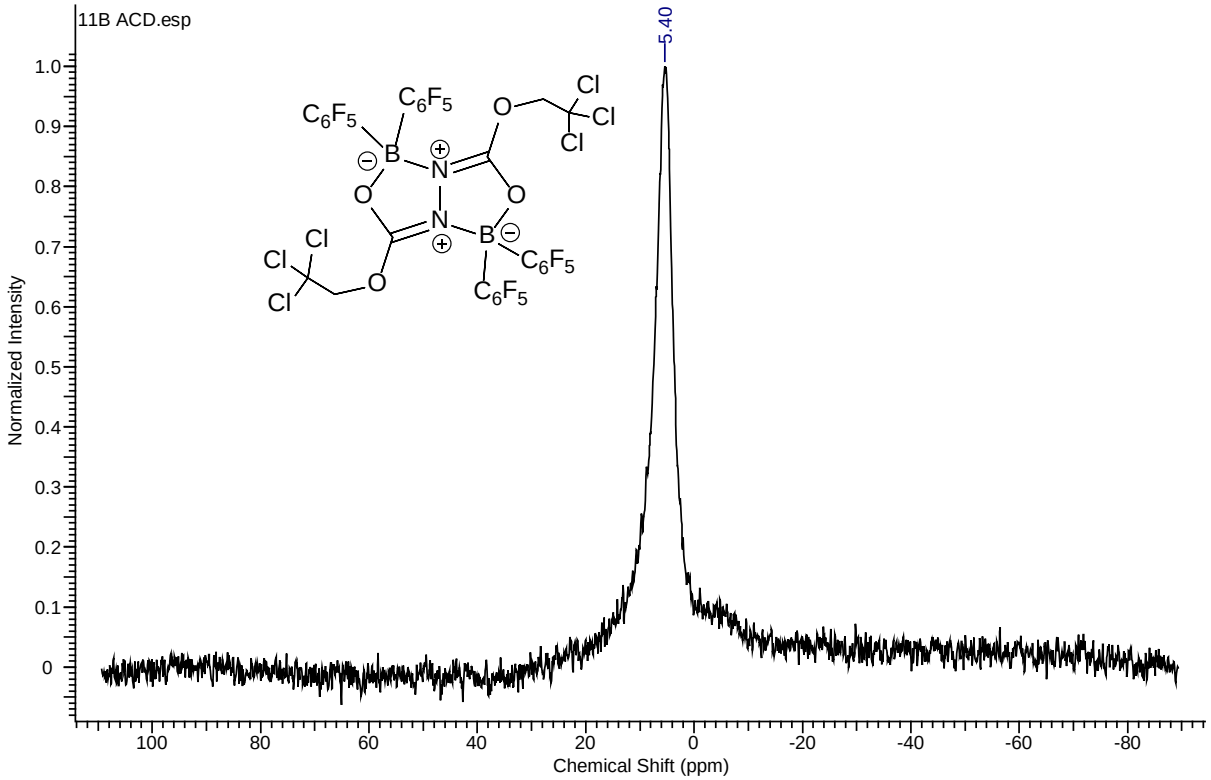


Figure S11. ^{11}B NMR (128 MHz) spectrum of the compound **3** in $CDCl_3/CH_2Cl_2$ (1:5).

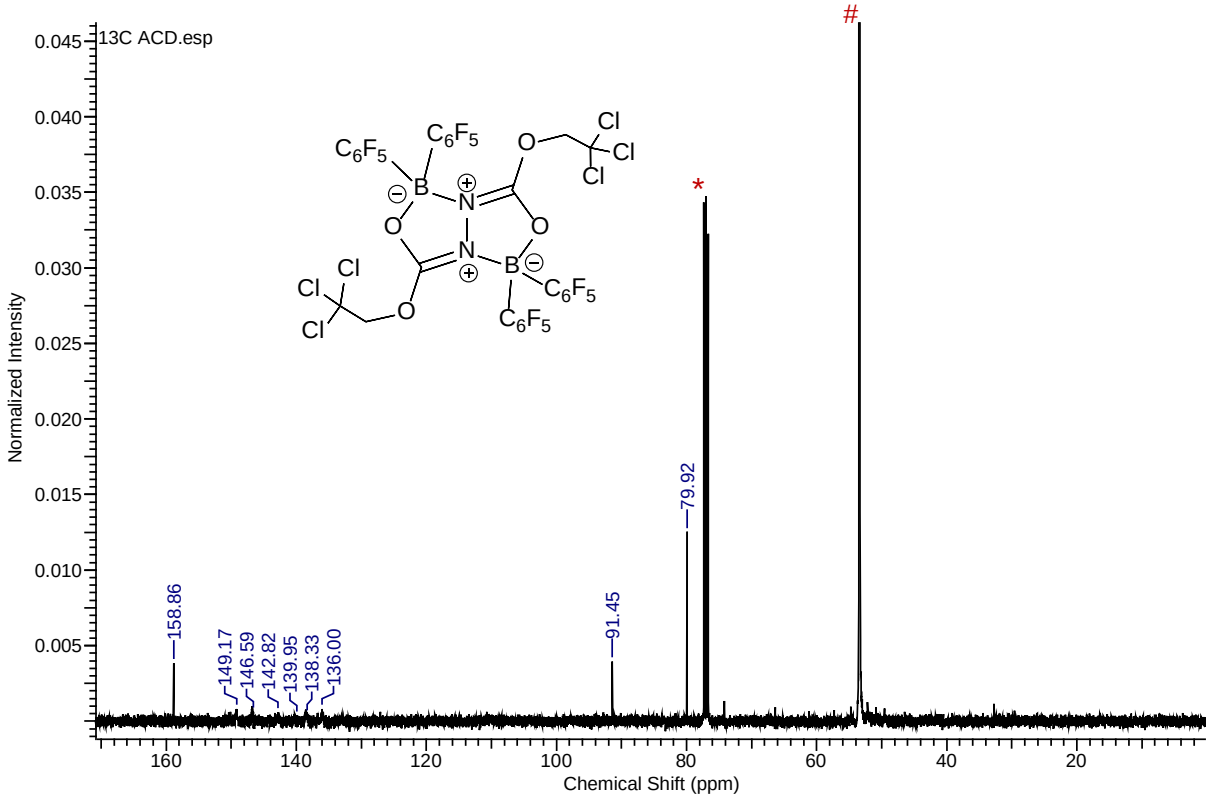


Figure S12. ^{13}C NMR (101 MHz) spectrum of the compound **3** in $CDCl_3/CH_2Cl_2$ (1:5) (*= $CDCl_3$; #= CH_2Cl_2).

Compound 4

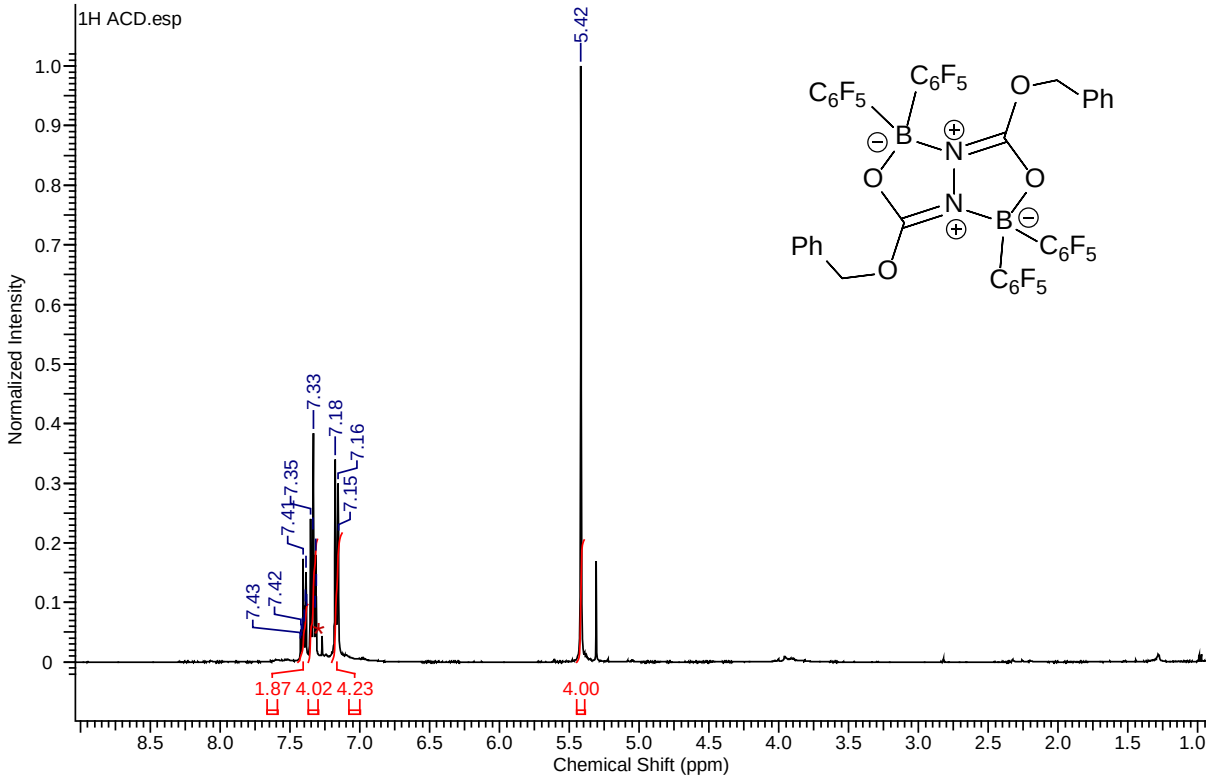


Figure S13. ^{1}H NMR (400 MHz) spectrum of the compound **4** in $CDCl_3$ (*= $CDCl_3$).

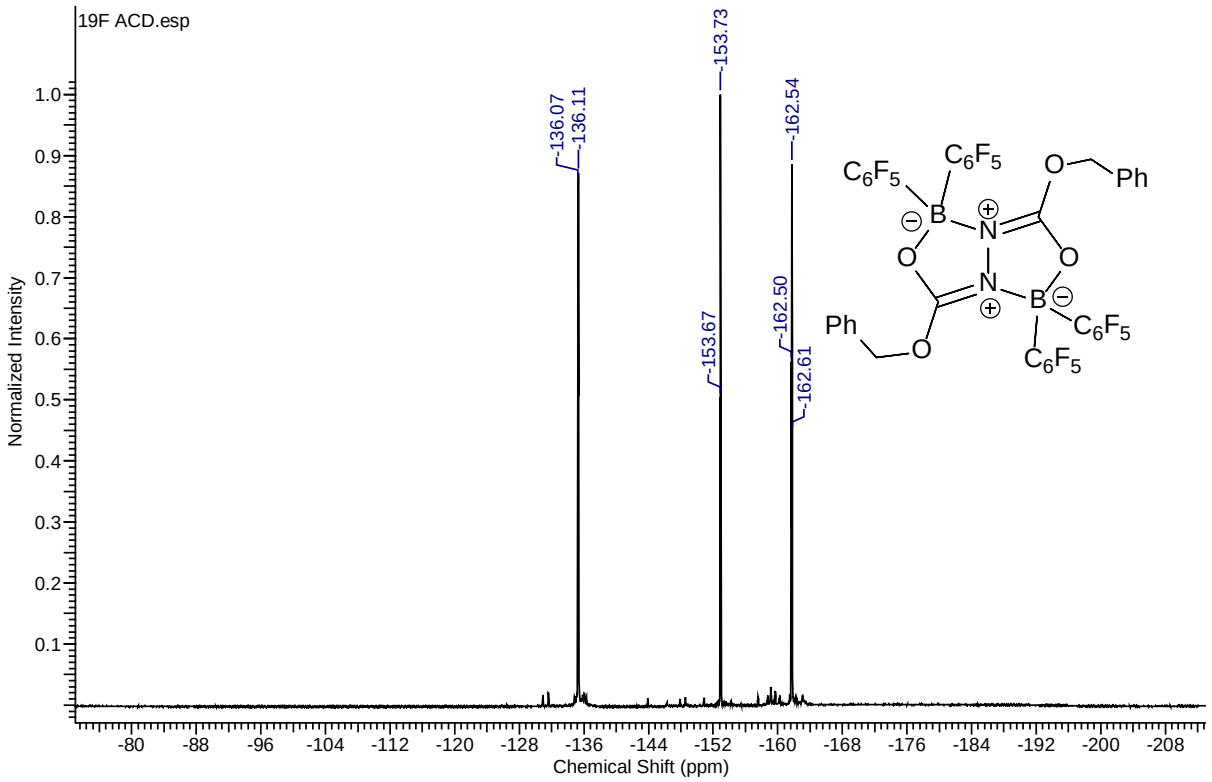


Figure S14. ^{19}F NMR (377 MHz) spectrum of the compound **4** in $CDCl_3$.

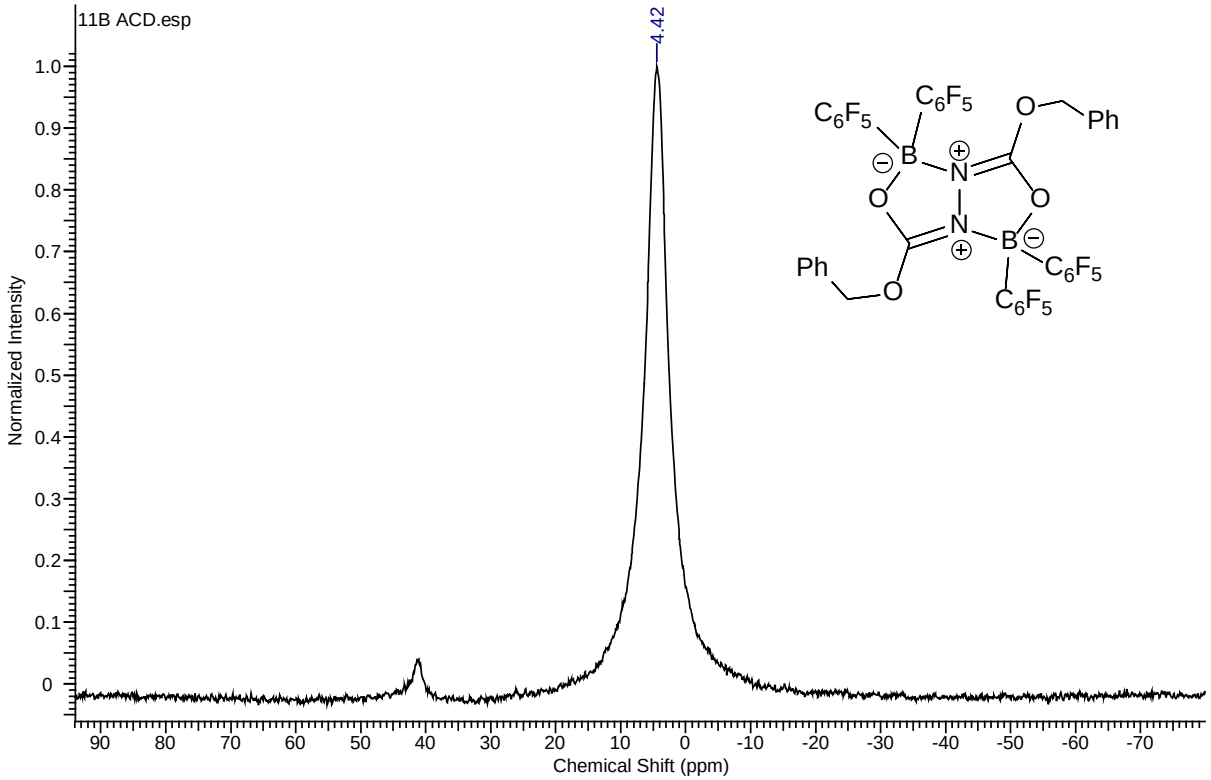


Figure S15. ^{11}B NMR (128 MHz) spectrum of the compound **4** in $CDCl_3$.

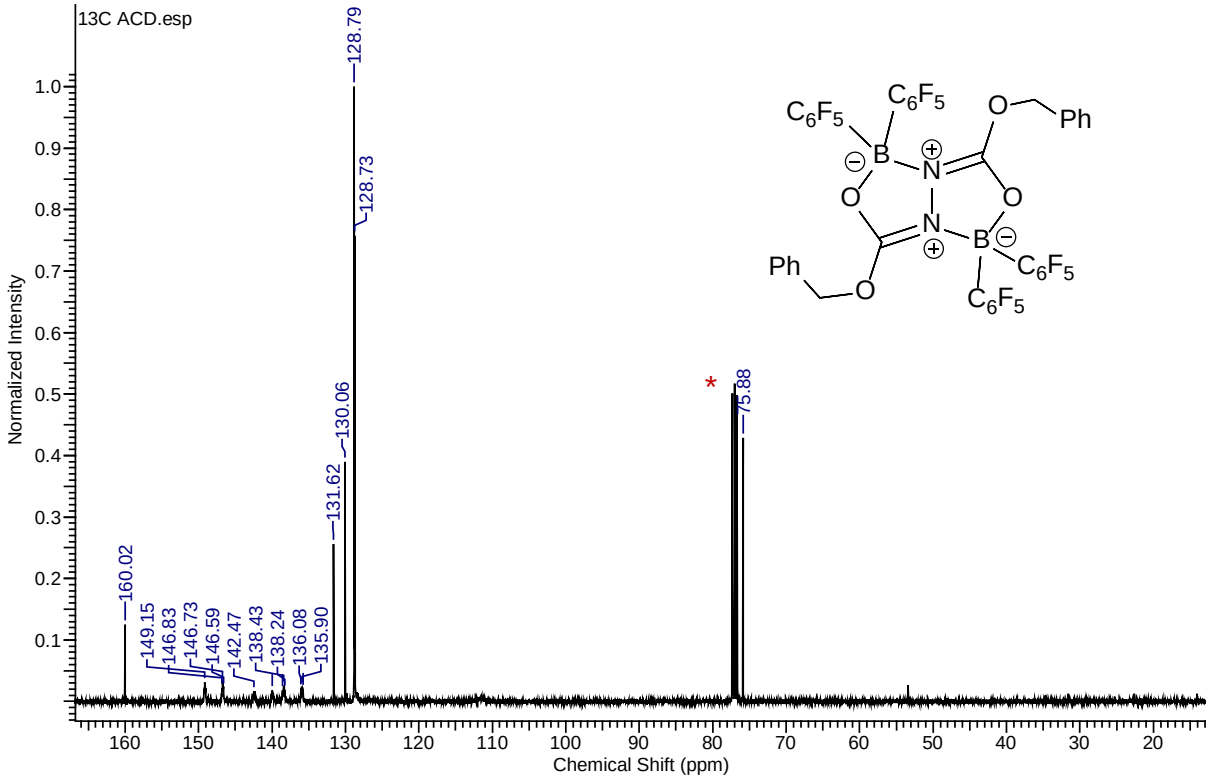


Figure S16. ^{13}C NMR (126 MHz) spectrum of the compound **4** in CDC_{l3} (*= $CDCl_3$).

Compound 5

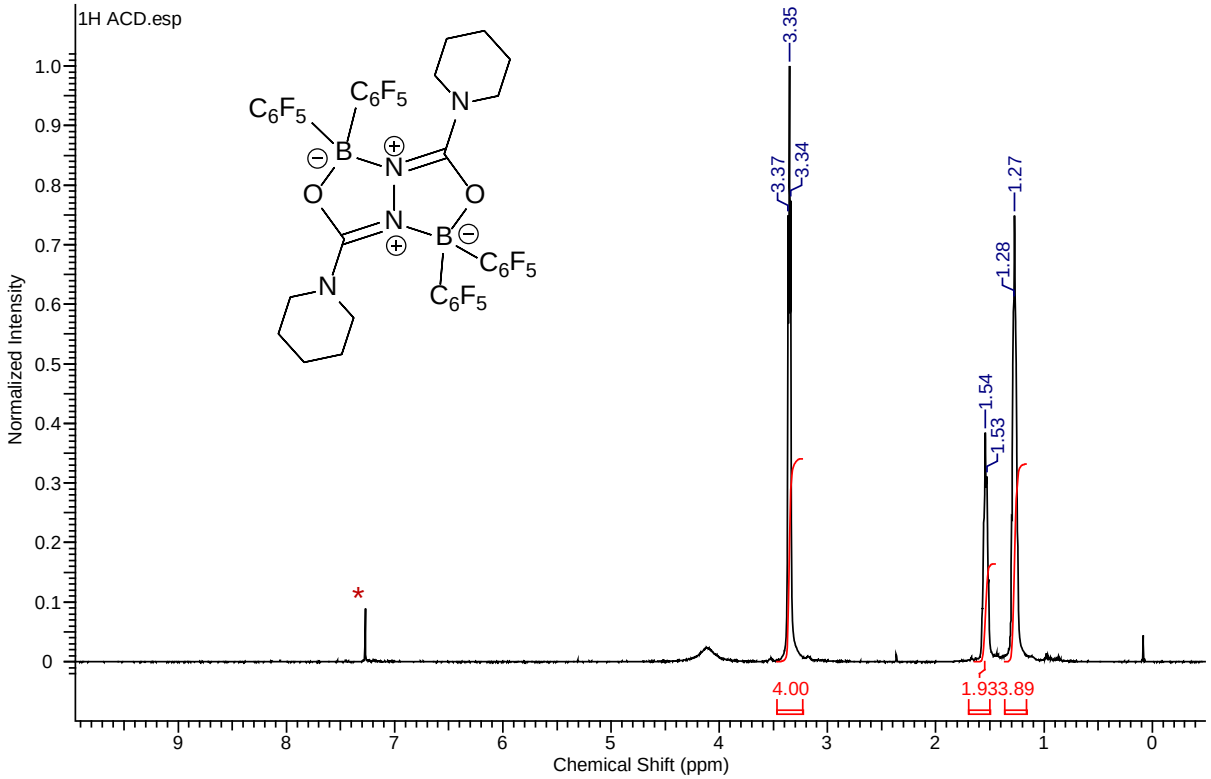


Figure S17. ^{1}H NMR (400 MHz) spectrum of the compound **5** in $CDCl_3$ (*= $CDCl_3$).

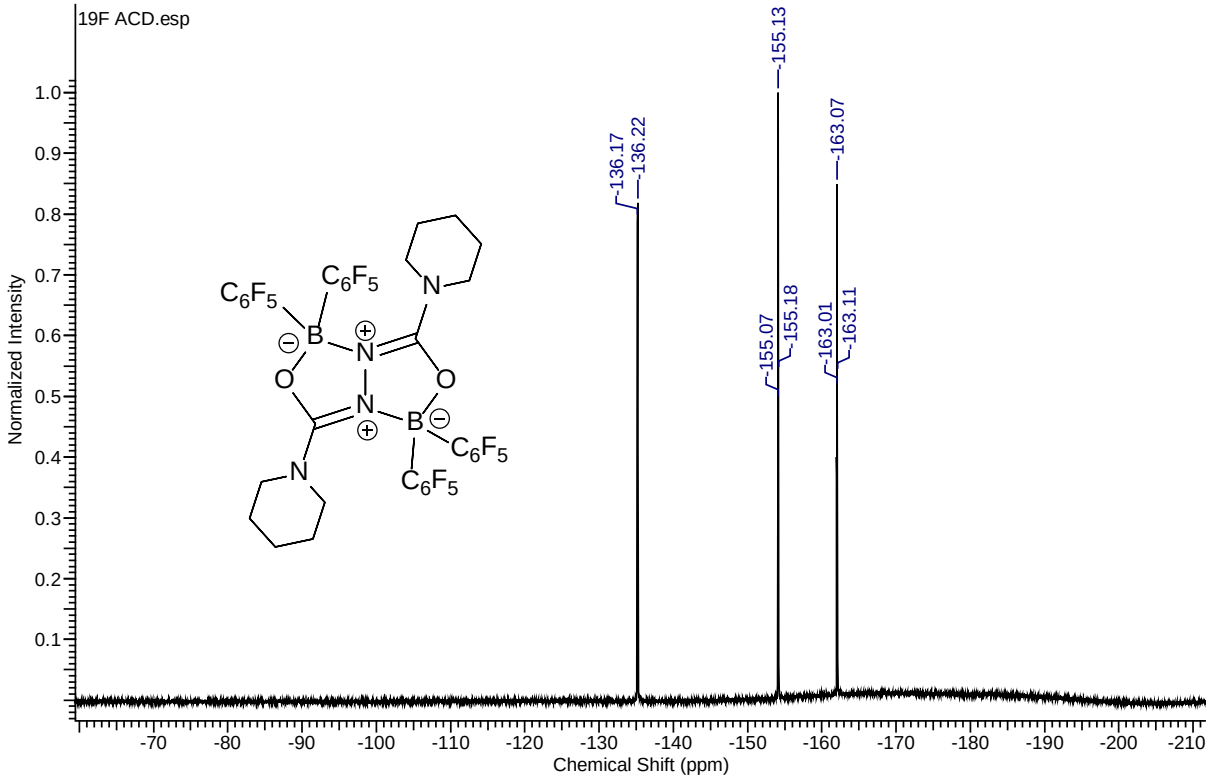


Figure S18. ^{19}F NMR (377 MHz) spectrum of the compound 5 in $CDCl_3$.

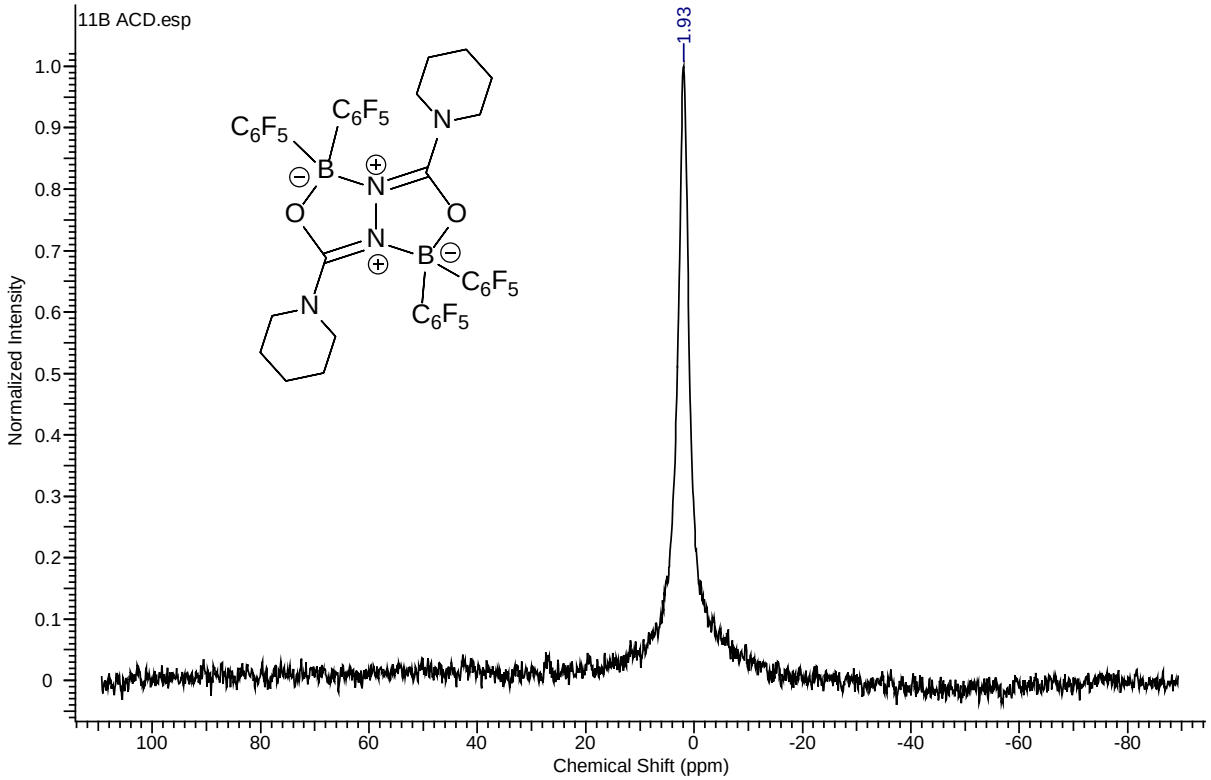


Figure S19. ^{11}B NMR (128 MHz) spectrum of the compound **5** in $CDCl_3$.

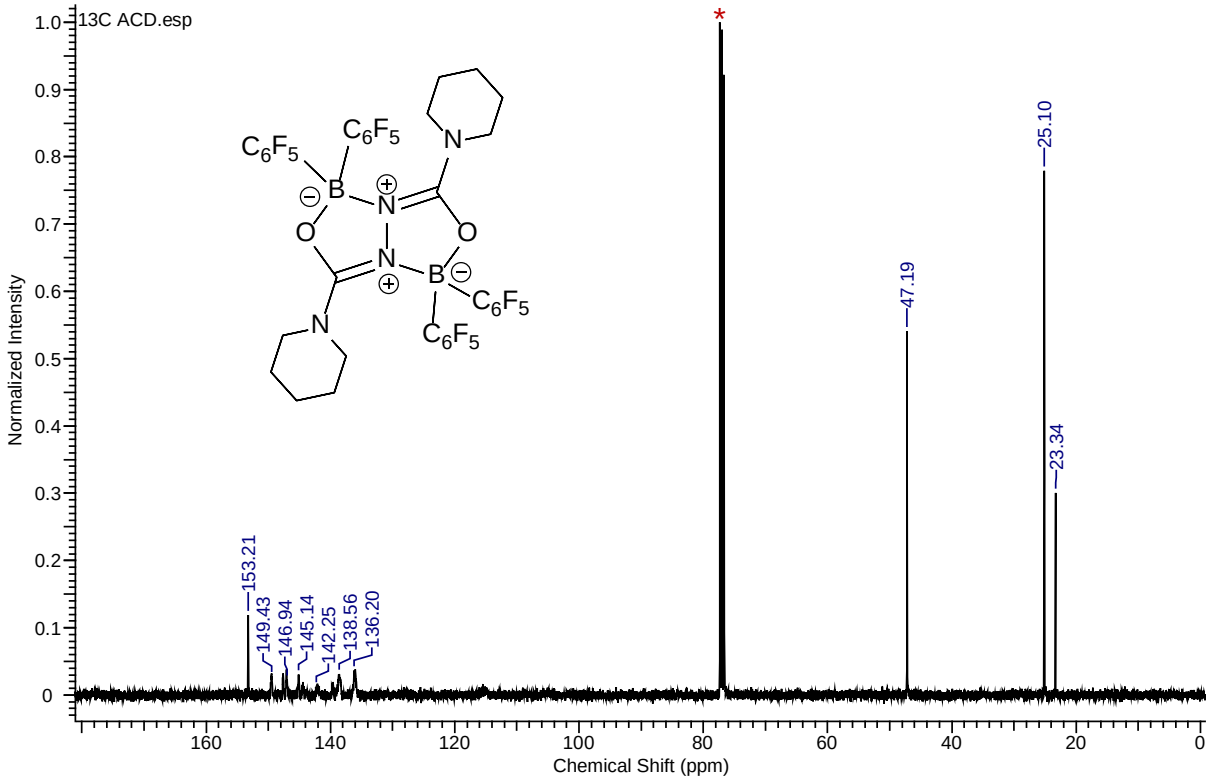


Figure S20. ^{13}C NMR (126 MHz) spectrum of the compound **5** in CDC_{l3} (*= $CDCl_3$).

Compound 6

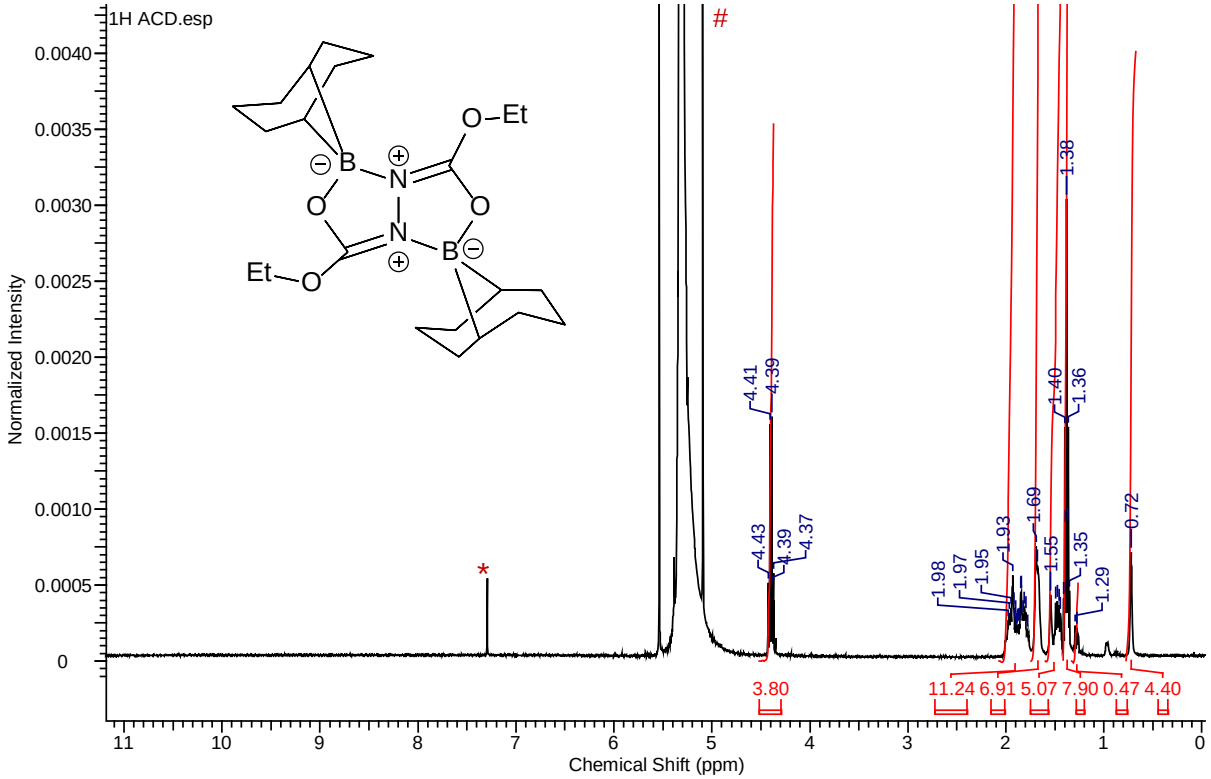


Figure S21. ^{1}H NMR (500 MHz) spectrum of the compound **6** in $CDCl_3/CH_2Cl_2$ (1:5) (*= $CDCl_3$; #= CH_2Cl_2).

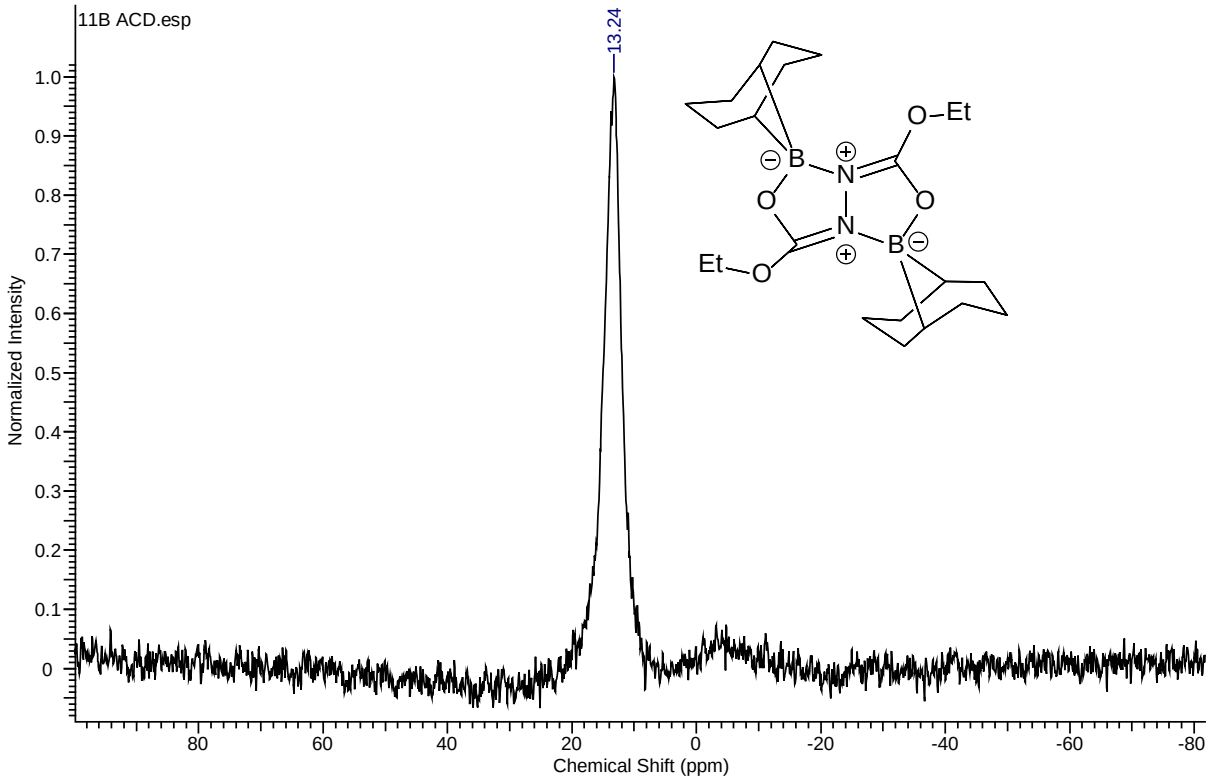


Figure S22. ^{11}B NMR (161 MHz) spectrum of the compound **6** in $CDCl_3/CH_2Cl_2$ (1:5).

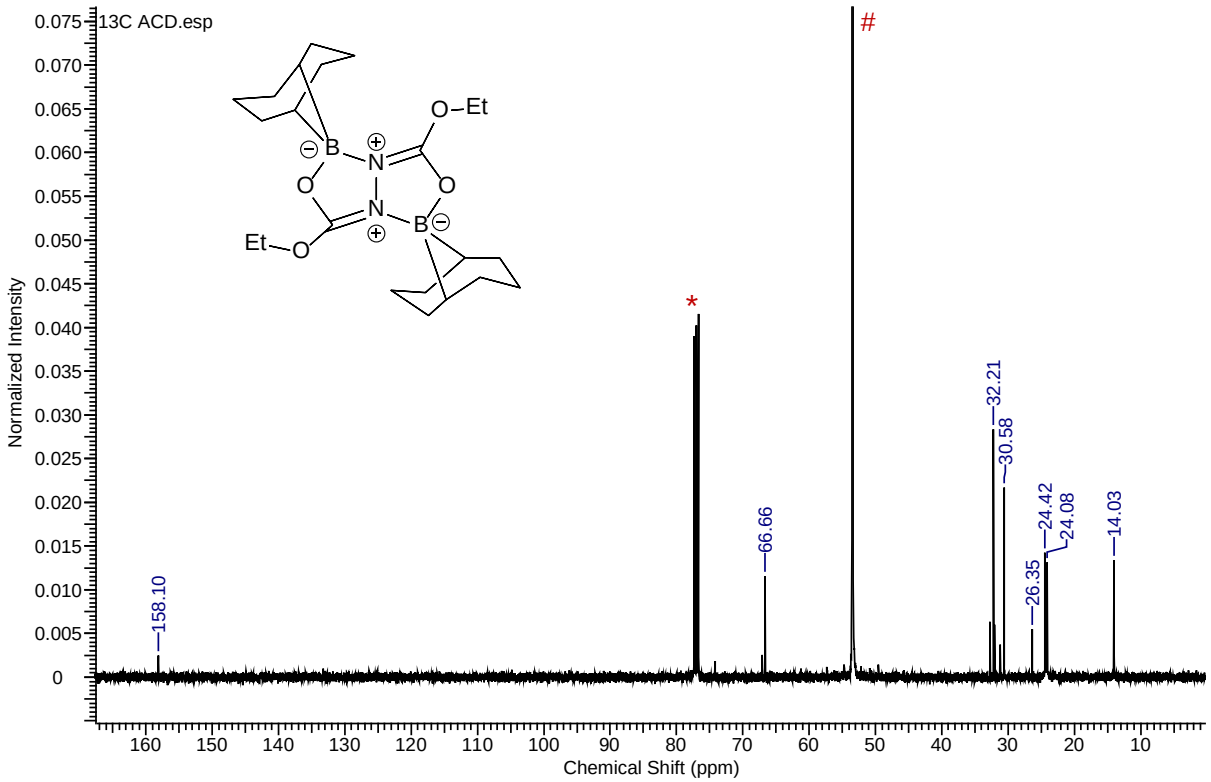


Figure S23. ^{13}C NMR (101 MHz) spectrum of the compound **6** in $CDCl_3/CH_2Cl_2$ (1:5) (*= $CDCl_3$; #= CH_2Cl_2).

Compound 7

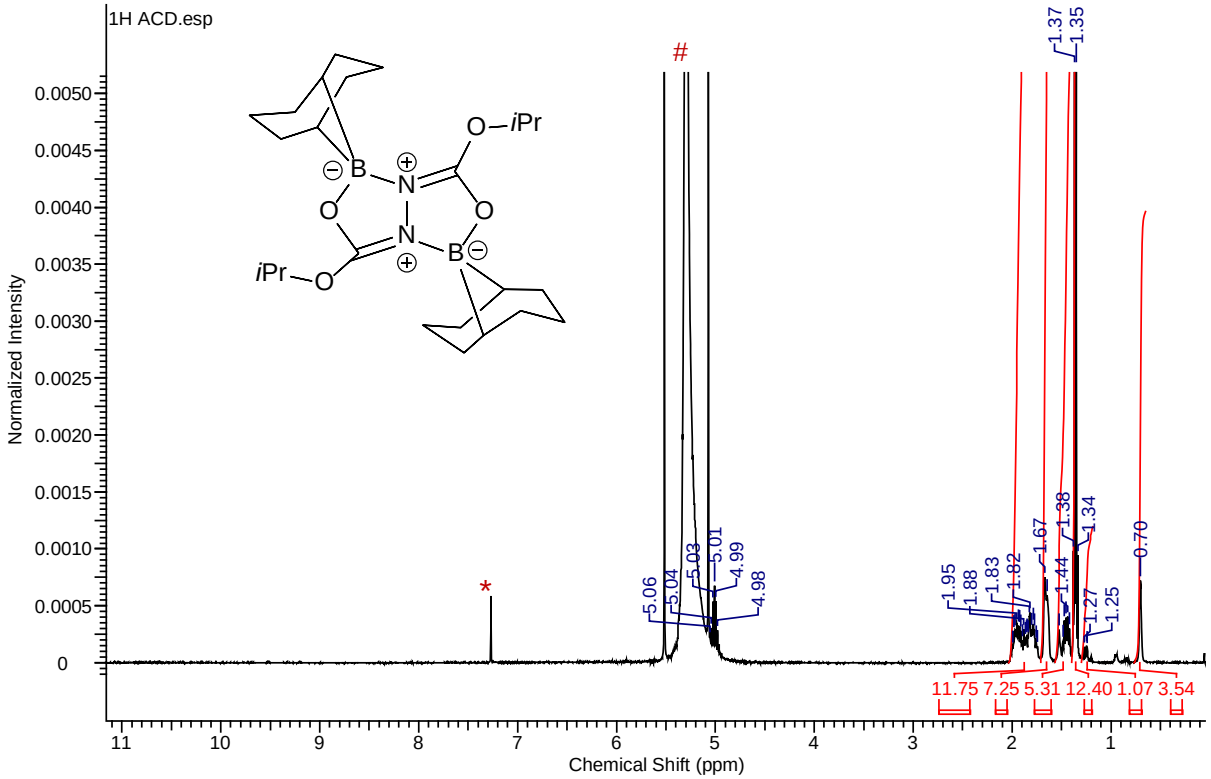


Figure S24. ^{1}H NMR (400 MHz) spectrum of the compound **7** in $CDCl_3/CH_2Cl_2$ (1:5) (*= $CDCl_3$; #= CH_2Cl_2).

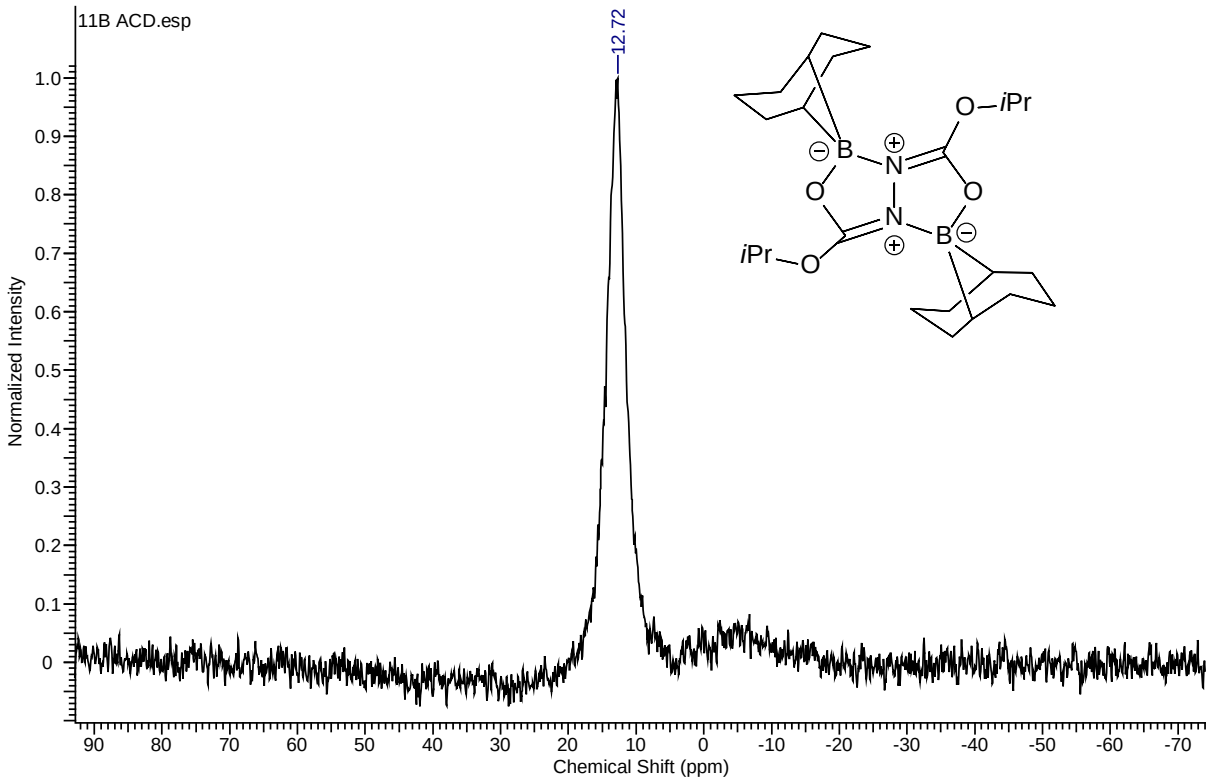


Figure S25. ^{11}B NMR (128 MHz) spectrum of the compound **7** in $CDCl_3/CH_2Cl_2$ (1:5) .

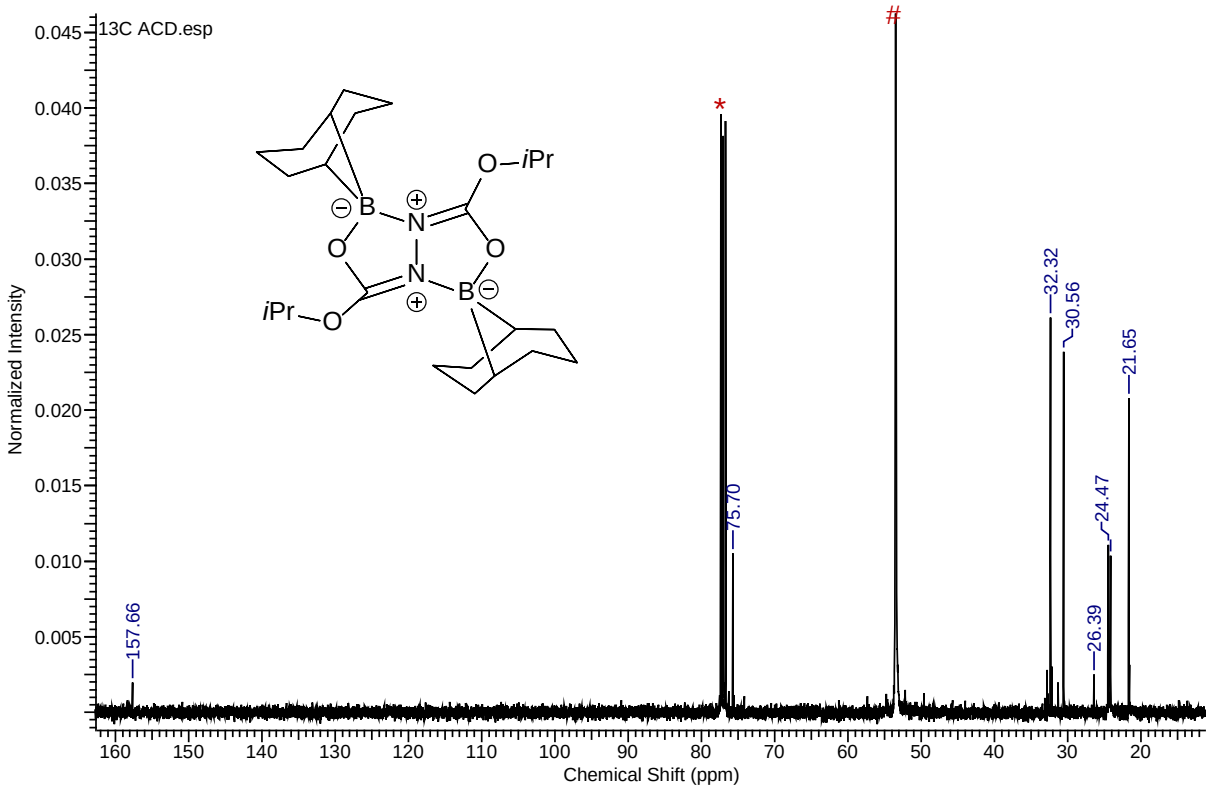


Figure S26. ^{13}C NMR (101 MHz) spectrum of the compound **7** in $CDCl_3$ (*= $CDCl_3$; #= CH_2Cl_2).

Compound 8

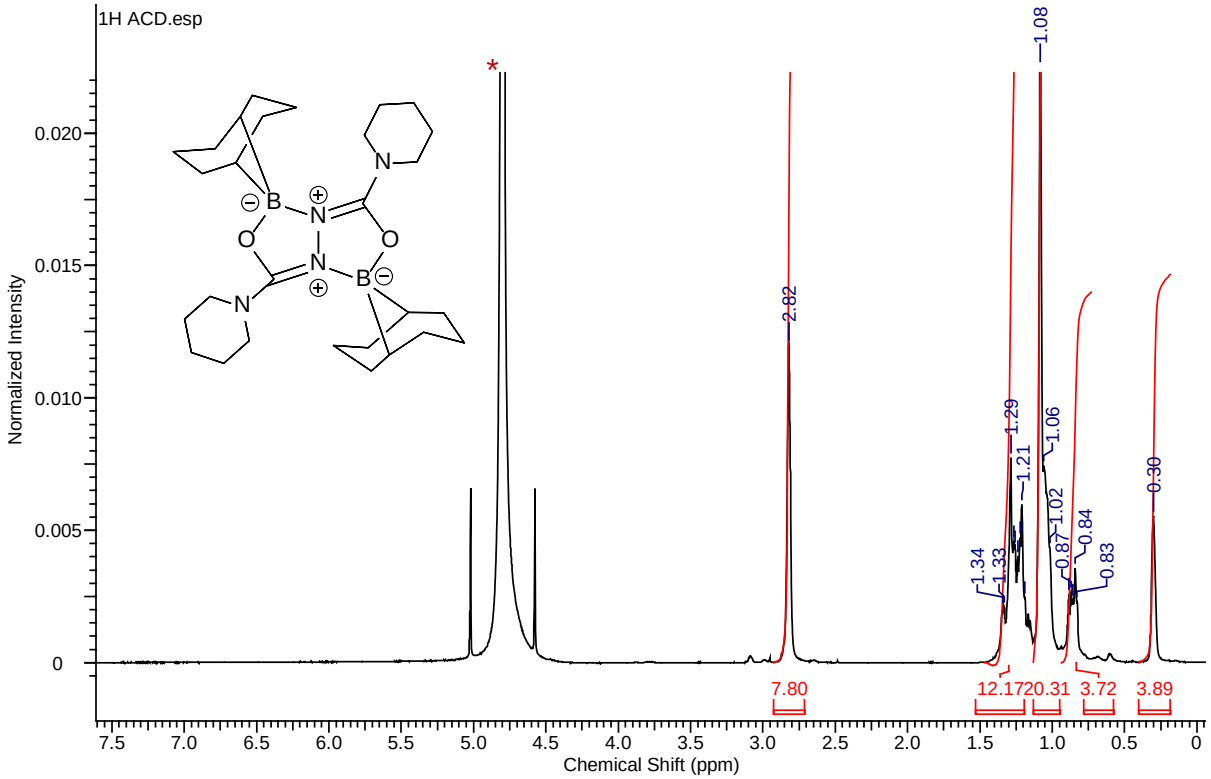


Figure S27. ^{1}H NMR (400 MHz) spectrum of the compound **8** in CH_2Cl_2 (*= CH_2Cl_2).

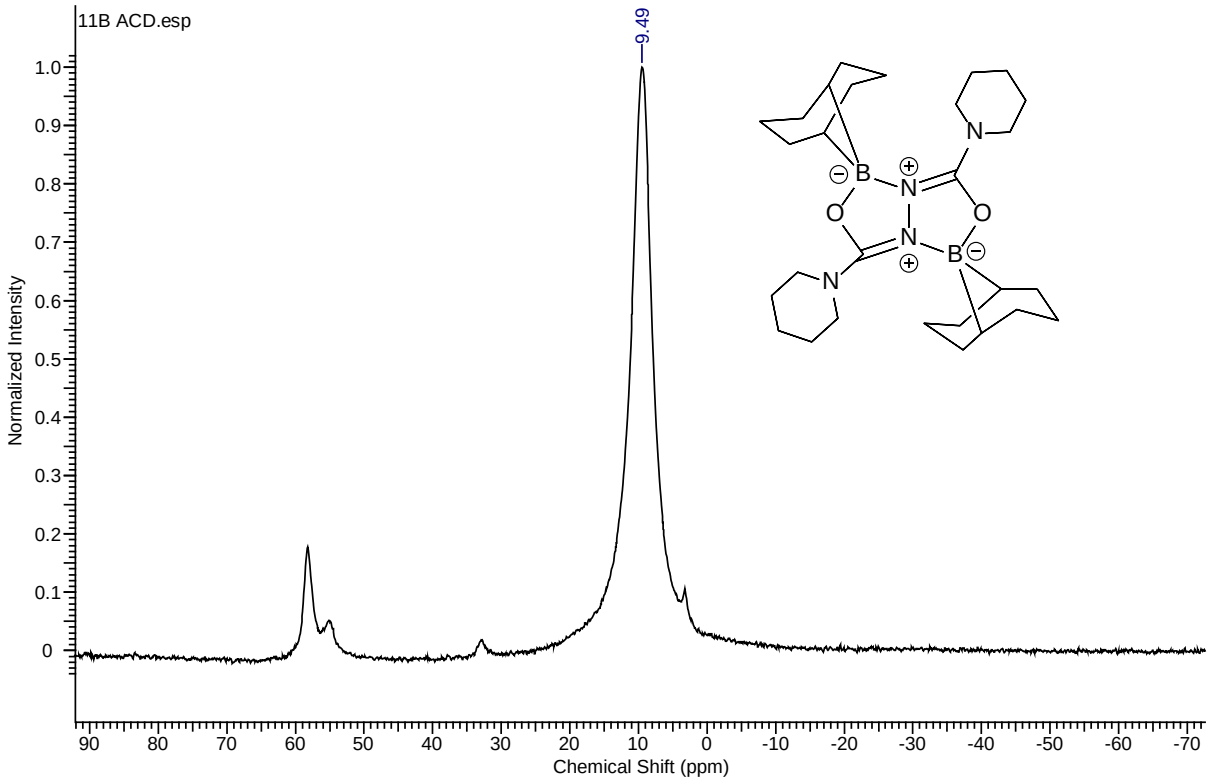


Figure S28. ^{11}B NMR (128 MHz) spectrum of the compound **8** in CH_2Cl_2.

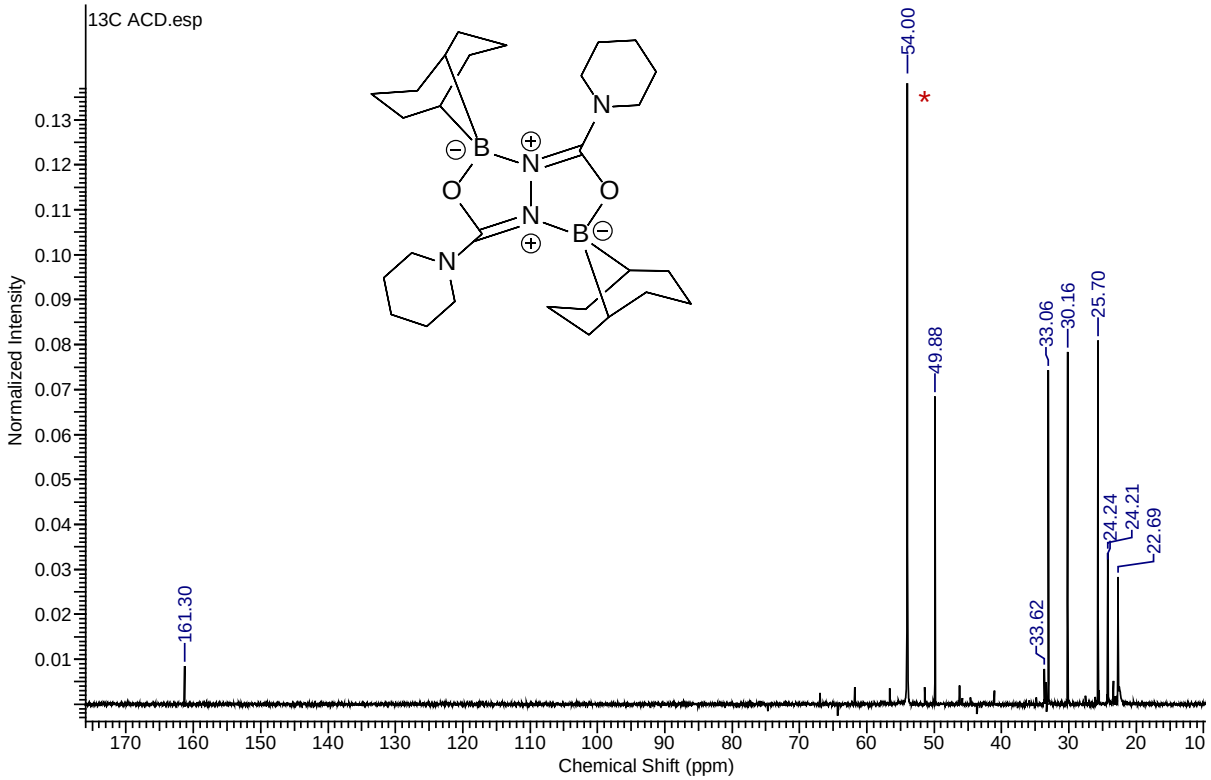


Figure S29. ^{13}C NMR (101 MHz) spectrum of the compound **8** in CH_2Cl_2 (*= CH_2Cl_2).

Compound 9

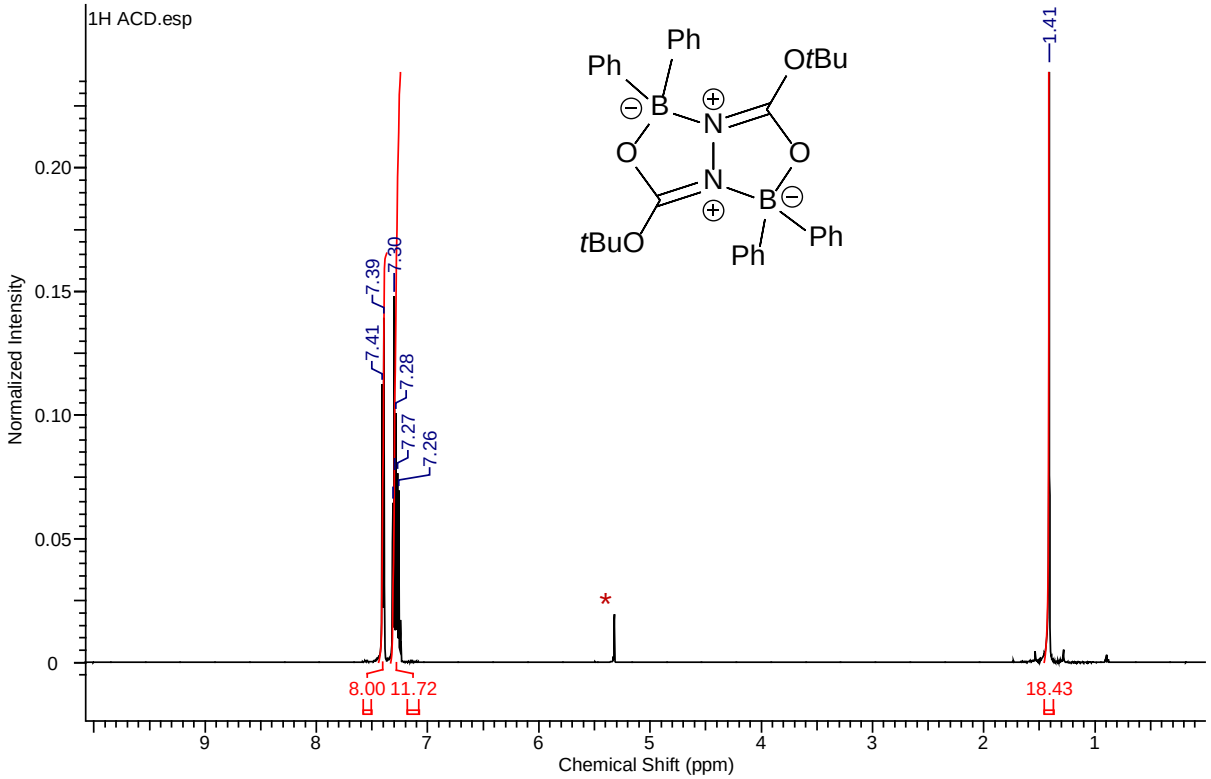


Figure S30. ^{1}H NMR (500 MHz) spectrum of the compound **9** in CD_2Cl_2 (*= CD_2Cl_2).

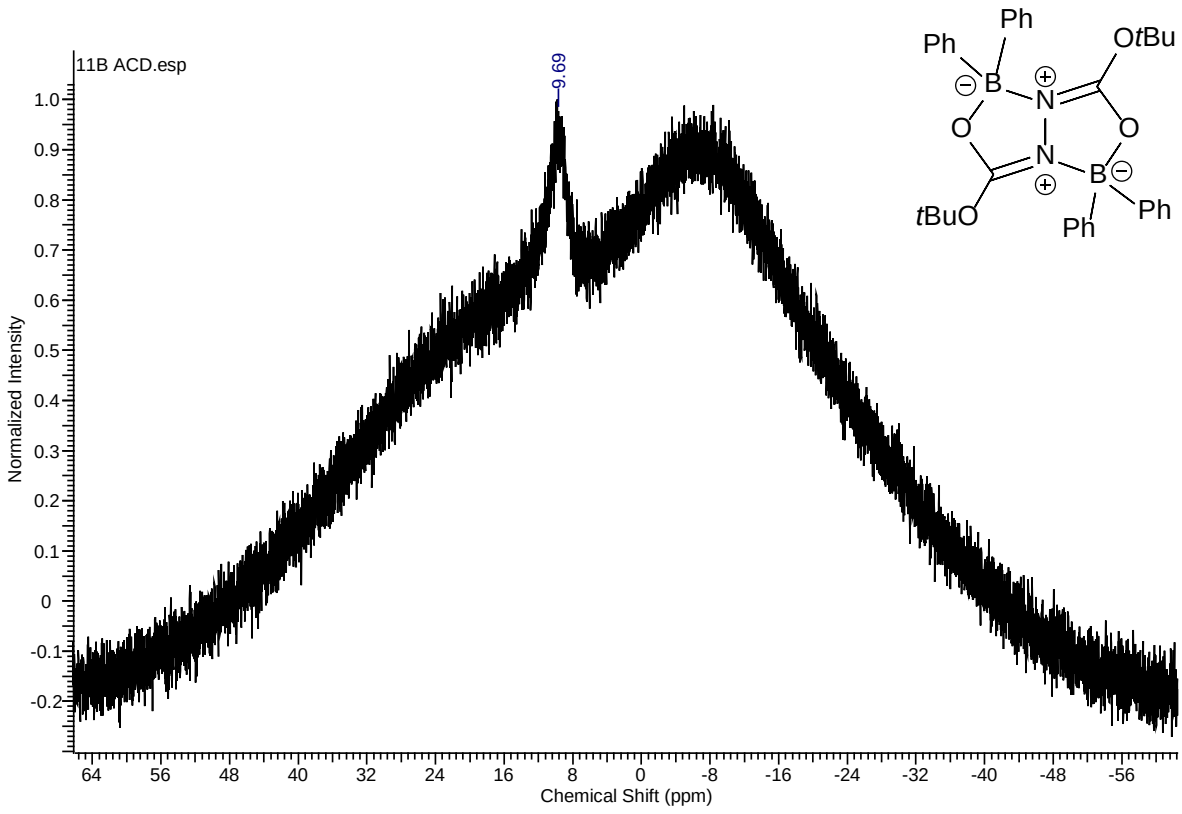


Figure S31. ^{11}B NMR (128 MHz) spectrum of the compound **9** in CD_2Cl_2 (*= CD_2Cl_2).

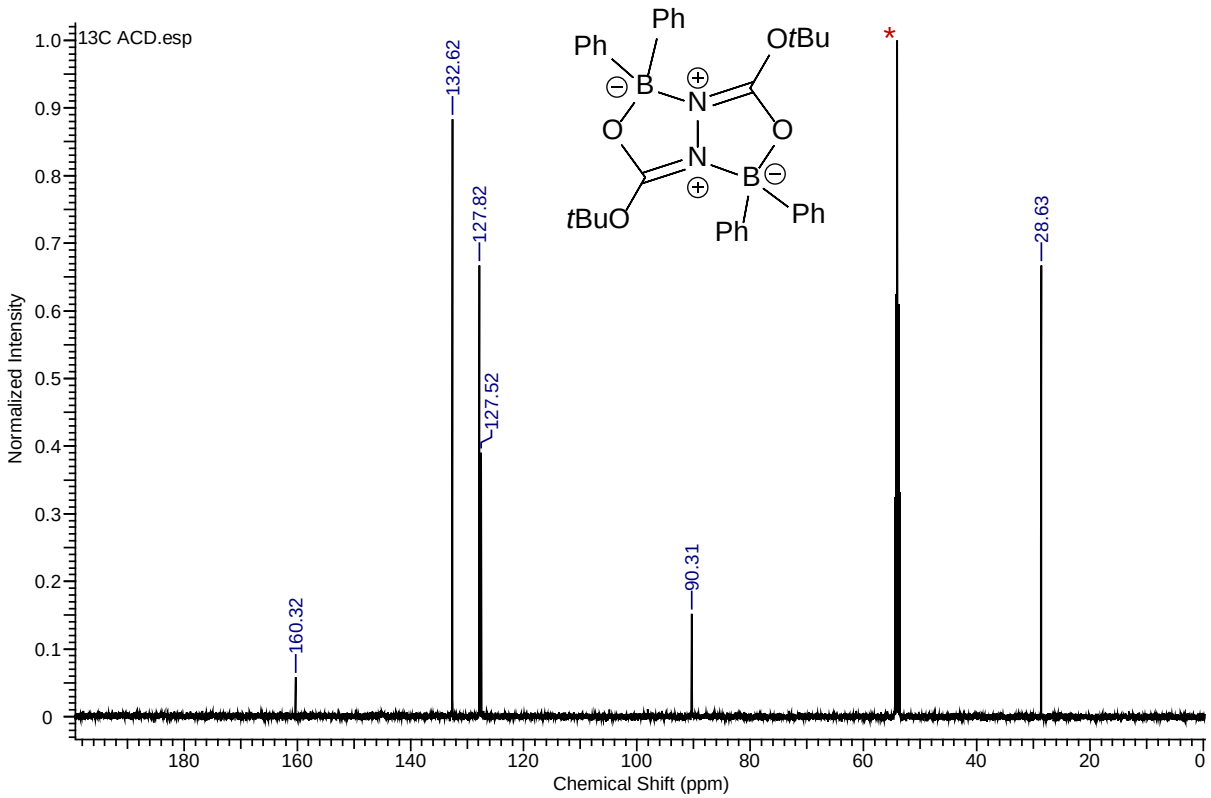
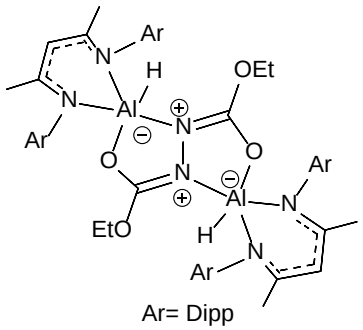


Figure S32. ^{13}C NMR (126 MHz) spectrum of the compound **9** in CD_2Cl_2 (*= CD_2Cl_2).

Compound 10



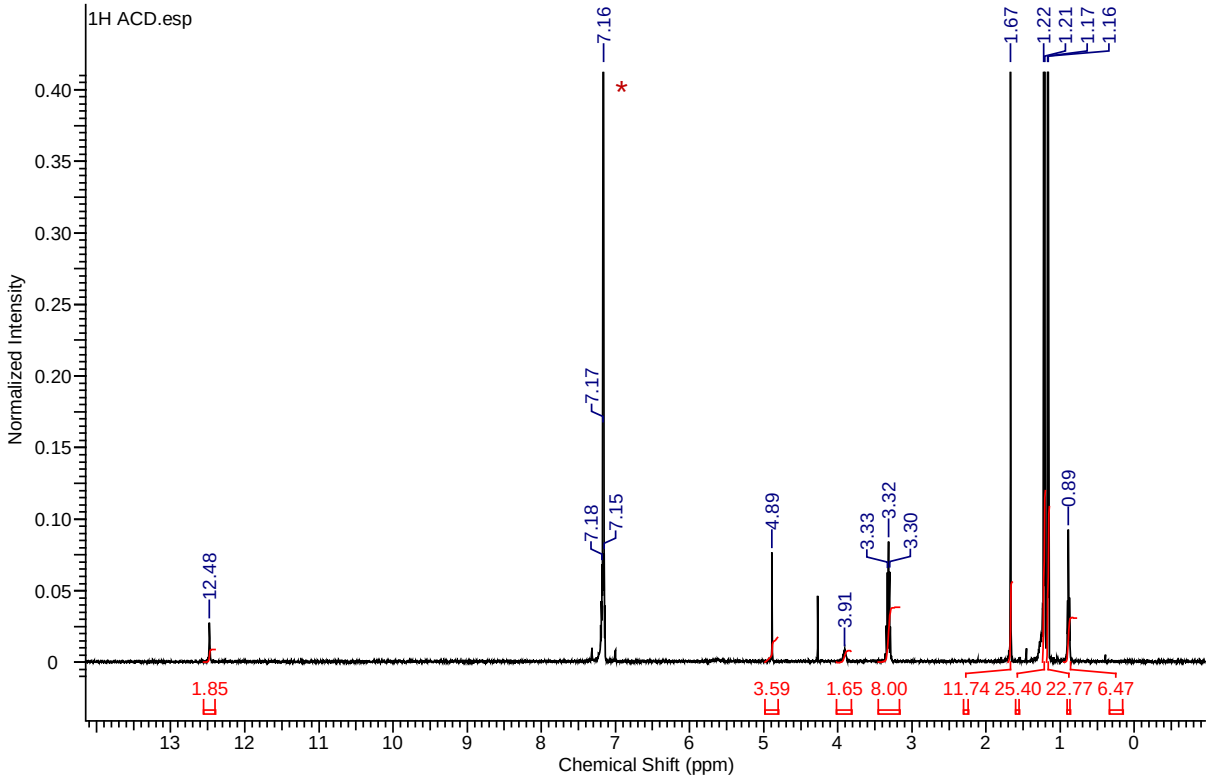
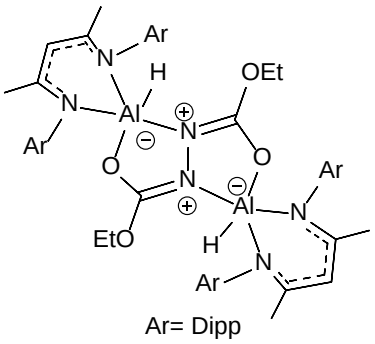


Figure S33. ^{1}H NMR (500 MHz) spectrum of the compound **10** in C_6D_6 (*= C_6D_6).



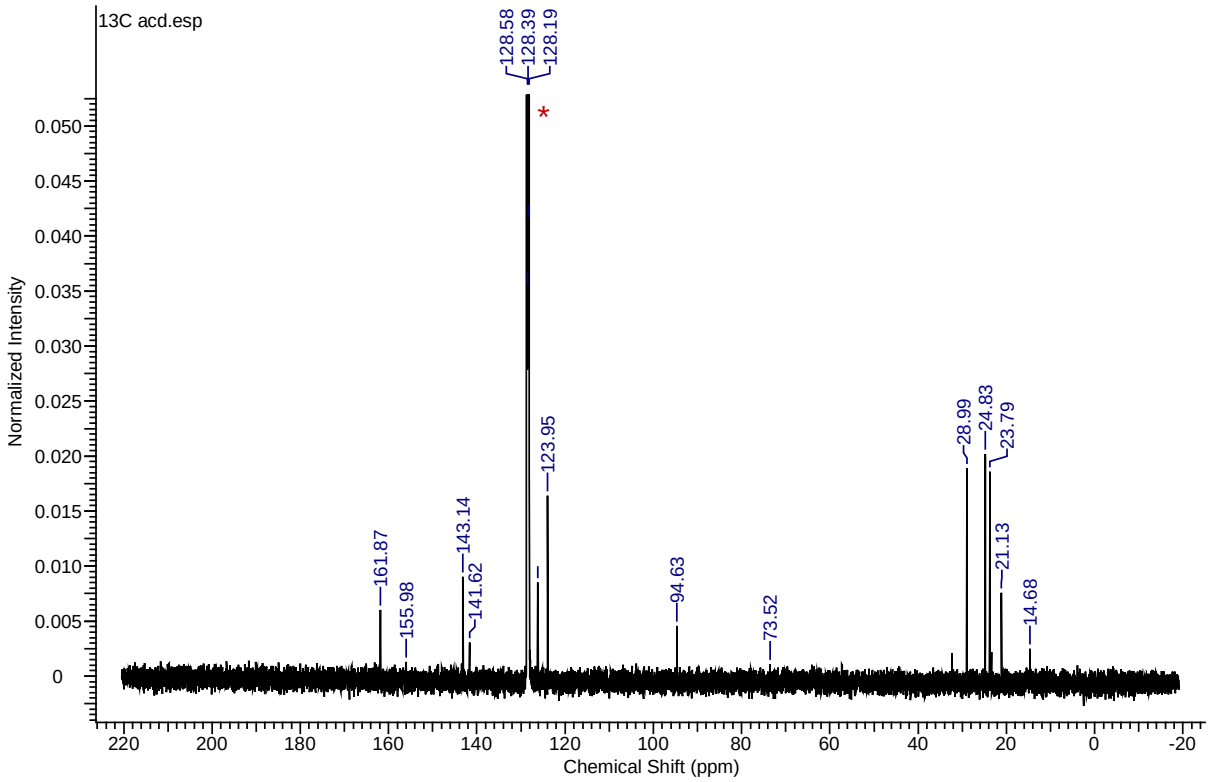
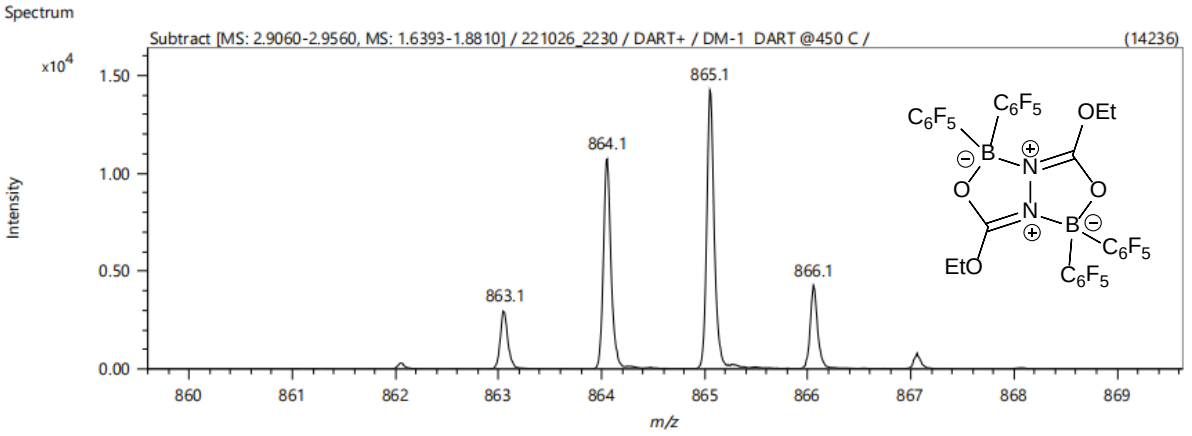


Figure S34. ^{13}C NMR (126 MHz) spectrum of the compound **10** in C_6D_6 (*= C_6H_6).

HRMS spectra of all the compounds

Compound 1



Elemental Composition

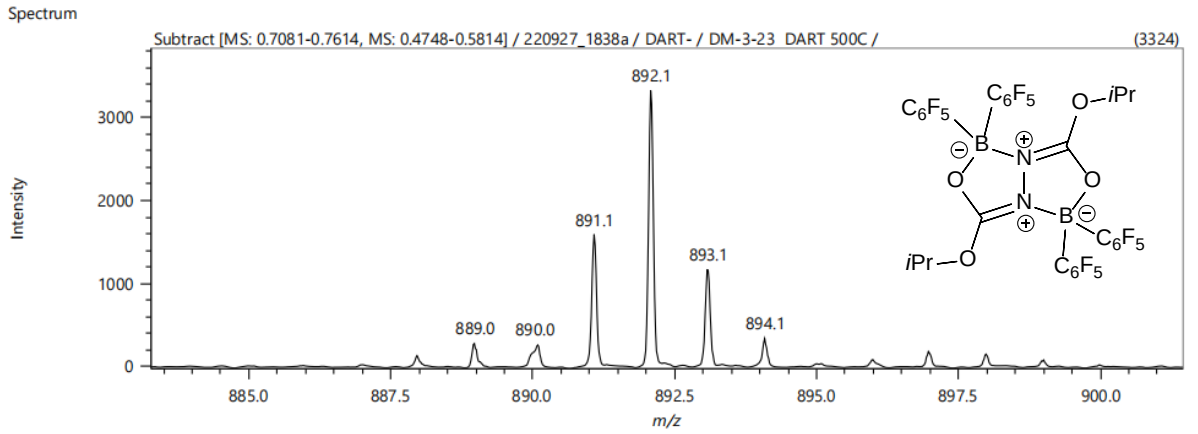
Parameters		Elements Set 1:						
Tolerance:	±10.00 mDa	Symbol	C	H	O	N	B	F
Electron:	Odd/Even	Min	0	0	0	0	2	20
Charge:	+1	Max	100	100	20	10	2	20
DBE:	-1.5 - 100.0							

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
865.05748	14235.88	C15 H17 B2 N3 O14 F20	865.05718	0.30	0.35	0.0
		C14 H11 B2 N10 O9 F20	865.05717	0.31	0.35	5.5
		C30 H11 B2 N2 O4 F20	865.05801	-0.53	-0.61	17.5
		C28 H9 B2 N5 O3 F20	865.05667	0.81	0.94	18.0
		C16 H13 B2 N7 O10 F20	865.05852	-1.04	-1.20	5.0
		C17 H19 B2 O15 F20	865.05852	-1.04	-1.20	-0.5

Figure S35. HRMS (DART) spectrum of the compound **1**.

Compound 2



Elemental Composition

Parameters		Elements Set 1:						
Tolerance:	±10.00 mDa	Symbol	C	H	O	N	B	F
Electron:	Odd/Even	Min	0	0	0	0	2	20
Charge:	+1	Max	100	100	20	10	2	20
DBE:	-1.5 - 100.0							

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
892.08106	3324.28	C17 H20 B2 N3 O14 F20	892.08065	0.41	0.46	0.5
		C16 H14 B2 N10 O9 F20	892.08065	0.41	0.46	6.0
		C32 H14 B2 N2 O4 F20	892.08148	-0.42	-0.47	18.0
		C30 H12 B2 N5 O3 F20	892.08014	0.92	1.03	18.5
		C18 H16 B2 N7 O10 F20	892.08199	-0.93	-1.04	5.5
		C19 H22 B2 O15 F20	892.08200	-0.94	-1.05	0.0

Figure S36. HRMS (DART) spectrum of the compound **2**.

Compound 3

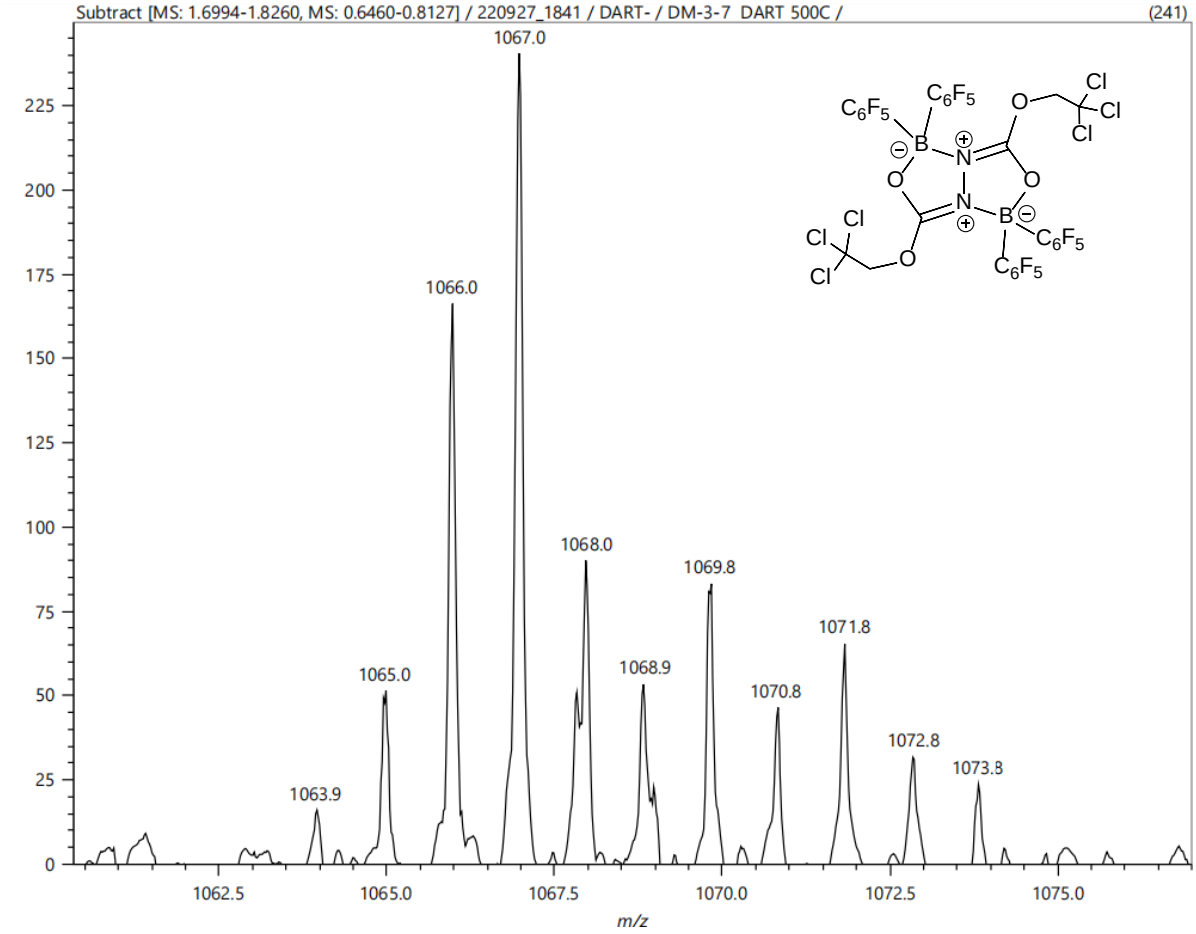
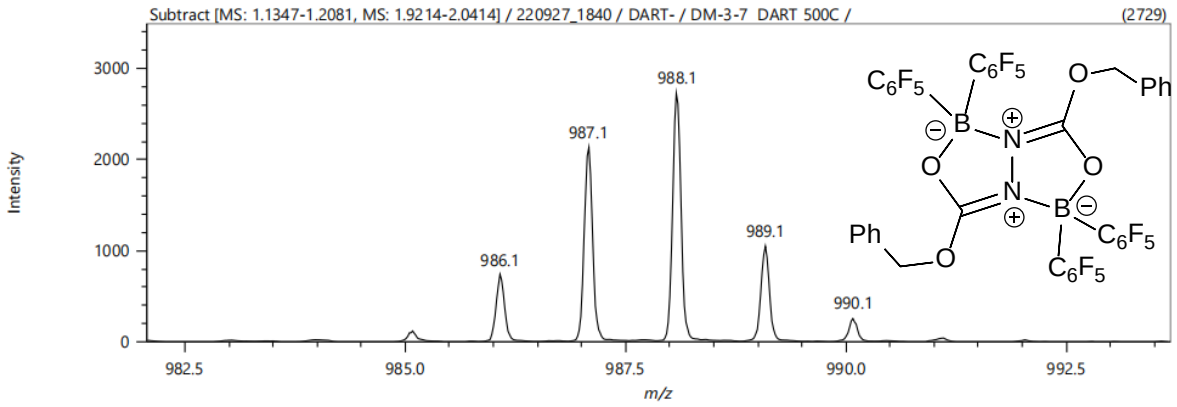


Figure S37. MS (DART) spectrum of the compound **3**.

Compound 4

Spectrum



Elemental Composition

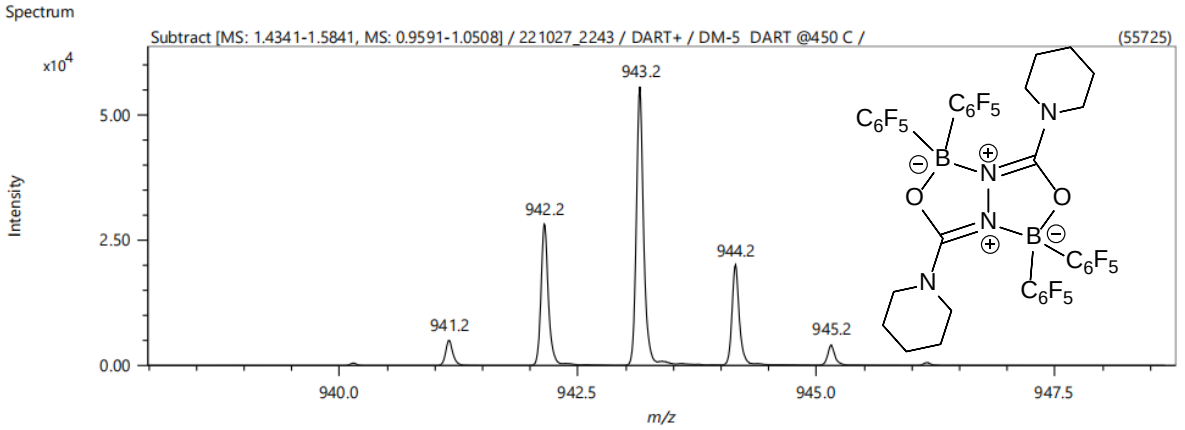
Parameters		Elements Set 1:						
Tolerance:	± 10.00 mDa	Symbol	C	H	O	N	B	F
Electron:	Odd/Even	Min	0	0	0	0	2	20
Charge:	+1	Max	100	100	20	10	2	20
DBE:	-1.5 - 100.0							

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
988.08088	2729.29	C25 H20 B2 N3 O14 F20	988.08065	0.23	0.23	8.5
		C24 H14 B2 N10 O9 F20	988.08065	0.23	0.24	14.0
		C40 H14 B2 N2 O4 F20	988.08148	-0.60	-0.61	26.0
		C38 H12 B2 N5 O3 F20	988.08014	0.74	0.75	26.5
		C26 H16 B2 N7 O10 F20	988.08199	-1.11	-1.12	13.5
		C27 H22 B2 O15 F20	988.08200	-1.12	-1.13	8.0

Figure S38. HRMS (DART) spectrum of the compound **4**.

Compound 5



Elemental Composition

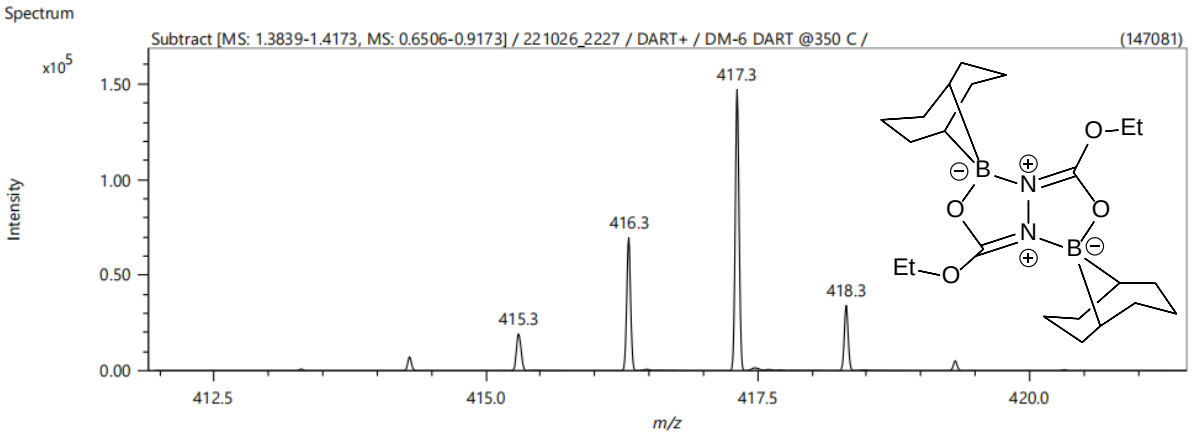
Parameters		Elements Set 1:						
Tolerance:	±10.00 mDa	Symbol	C	H	O	N	B	F
Electron:	Odd/Even	Min	0	0	0	0	2	20
Charge:	+1	Max	100	100	20	10	2	20
DBE:	-1.5 - 100.0							

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
943.15274	55725.12	C36 H21 B2 N4 O2 F20	943.15258	0.16	0.17	19.5
		C22 H23 B2 N9 O8 F20	943.15309	-0.34	-0.36	7.0
		C23 H29 B2 N2 O13 F20	943.15309	-0.35	-0.37	1.5
		C21 H27 B2 N5 O12 F20	943.15175	0.99	1.05	2.0
		C38 H23 B2 N O3 F20	943.15392	-1.18	-1.25	19.0
		C35 H25 B2 O6 F20	943.15124	1.50	1.59	14.5

Figure S39. HRMS (DART) spectrum of the compound **5**.

Compound 6



Elemental Composition

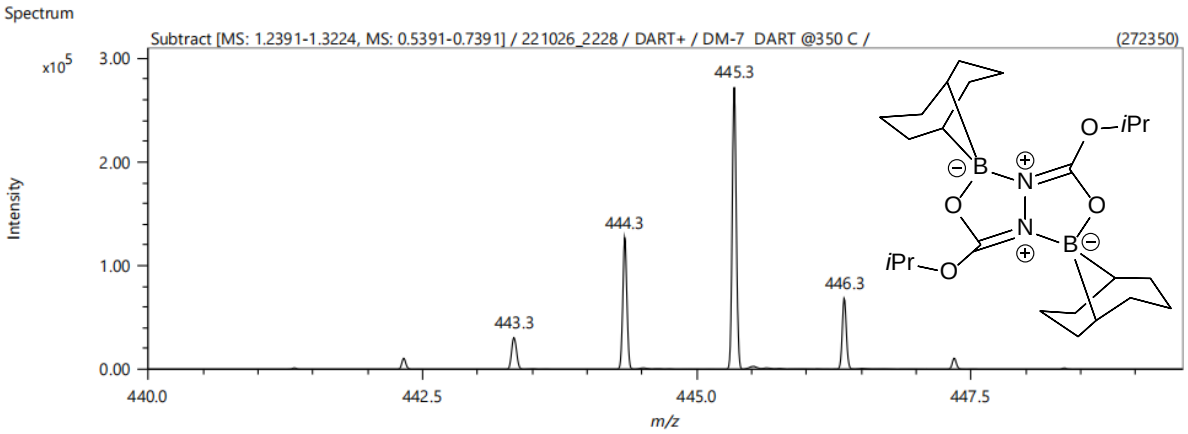
Parameters		Elements Set 1:					
Tolerance:	±10.00 mDa	Symbol	C	H	O	N	B
Electron:	Odd/Even	Min	0	0	0	0	2
Charge:	+1	Max	100	100	20	10	2
DBE:	-1.5 - 100.0						

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
417.31019	147081.16	C23 H35 B2 N6	417.31038	-0.19	-0.46	10.5
		C22 H39 B2 N2 O4	417.30905	1.15	2.75	5.5
		C25 H37 B2 N3 O	417.31173	-1.53	-3.67	10.0
		C20 H37 B2 N5 O3	417.30770	2.49	5.97	6.0
		C27 H39 B2 O2	417.31307	-2.88	-6.89	9.5
		C19 H41 B2 N O7	417.30637	3.83	9.17	1.0

Figure S40. HRMS (DART) spectrum of the compound **6**.

Compound 7



Elemental Composition

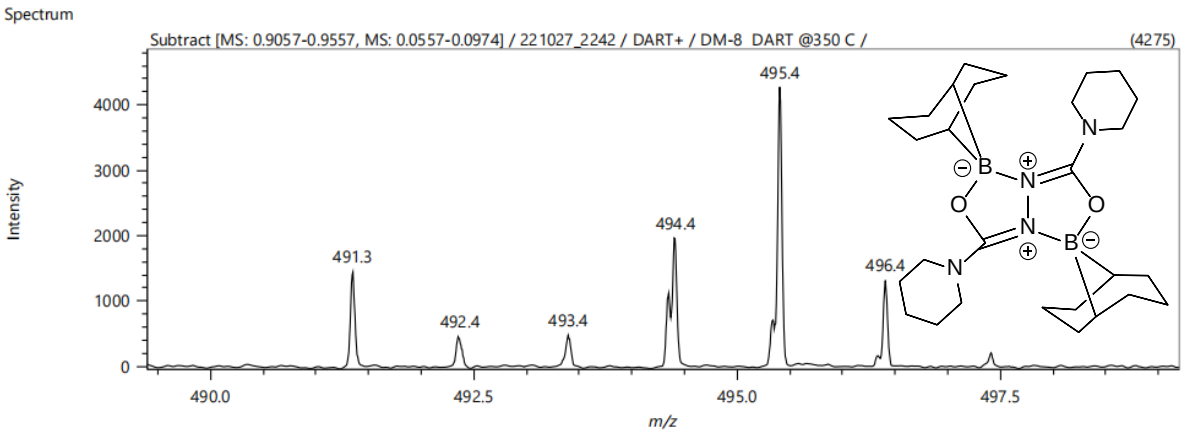
Parameters		Elements Set 1:					
Tolerance:	±10.00 mDa	Symbol	C	H	O	N	B
Electron:	Odd/Even	Min	0	0	0	0	2
Charge:	+1	Max	100	100	20	10	2
DBE:	-1.5 - 100.0						

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
445.34101	272349.94	C24 H43 B2 N2 O4	445.34035	0.66	1.49	5.5
		C25 H39 B2 N6	445.34168	-0.68	-1.52	10.5
		C22 H41 B2 N5 O3	445.33900	2.00	4.50	6.0
		C27 H41 B2 N3 O	445.34303	-2.02	-4.53	10.0
		C21 H45 B2 N O7	445.33767	3.34	7.50	1.0
		C20 H39 B2 N8 O2	445.33766	3.35	7.52	6.5

Figure S41. HRMS (DART) spectrum of the compound **7**.

Compound 8



Elemental Composition

Parameters		Elements Set 1:					
Tolerance:	±10.00 mDa	Symbol	C	H	O	N	B
Electron:	Odd/Even	Min	0	0	0	0	2
Charge:	+1	Max	100	100	20	10	2
DBE:	-1.5 - 100.0						

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
495.40302	4275.38	C28 H49 B2 N4 O2	495.40361	-0.59	-1.20	7.5
		C27 H53 B2 O6	495.40228	0.74	1.50	2.5
		C26 H47 B2 N7 O	495.40227	0.75	1.51	8.0
		C30 H51 B2 N O3	495.40496	-1.94	-3.91	7.0
		C25 H51 B2 N3 O5	495.40093	2.09	4.21	3.0
		C24 H45 B2 N10	495.40093	2.09	4.22	8.5

Figure S42. HRMS (DART) spectrum of the compound **8**.

Compound 9

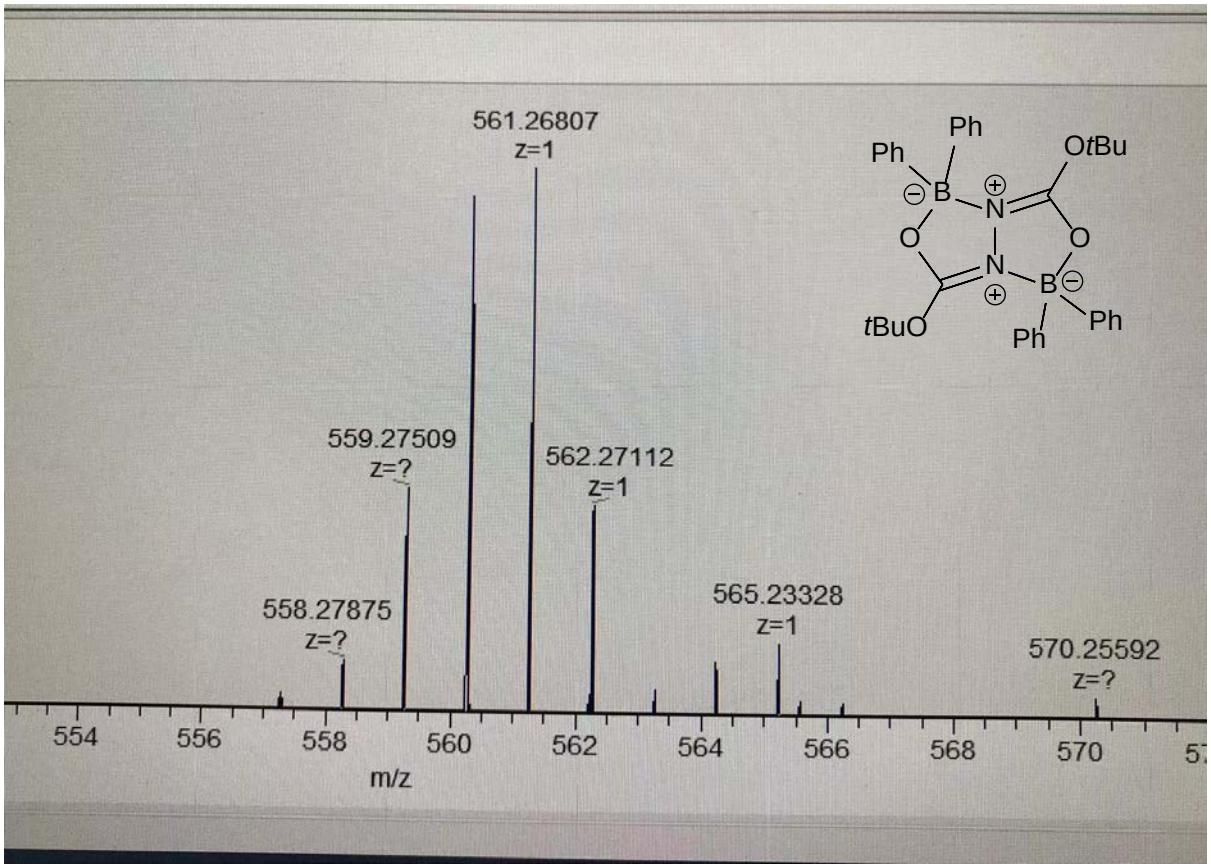


Figure S43. HRMS (ESI) spectrum of the compound **9**.

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