Electronic Supporting Information

Thermal dehydrochlorination in the 4-fluoroaniline–trichloroborane system: Identification of reactive intermediates involved in the formation of *B*,*B*',*B*''-trichloro-*N*,*N*',*N*''-tri((4-fluoro)phenyl)borazine

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Contents

I. Concentration dependence measured in experiment 1.

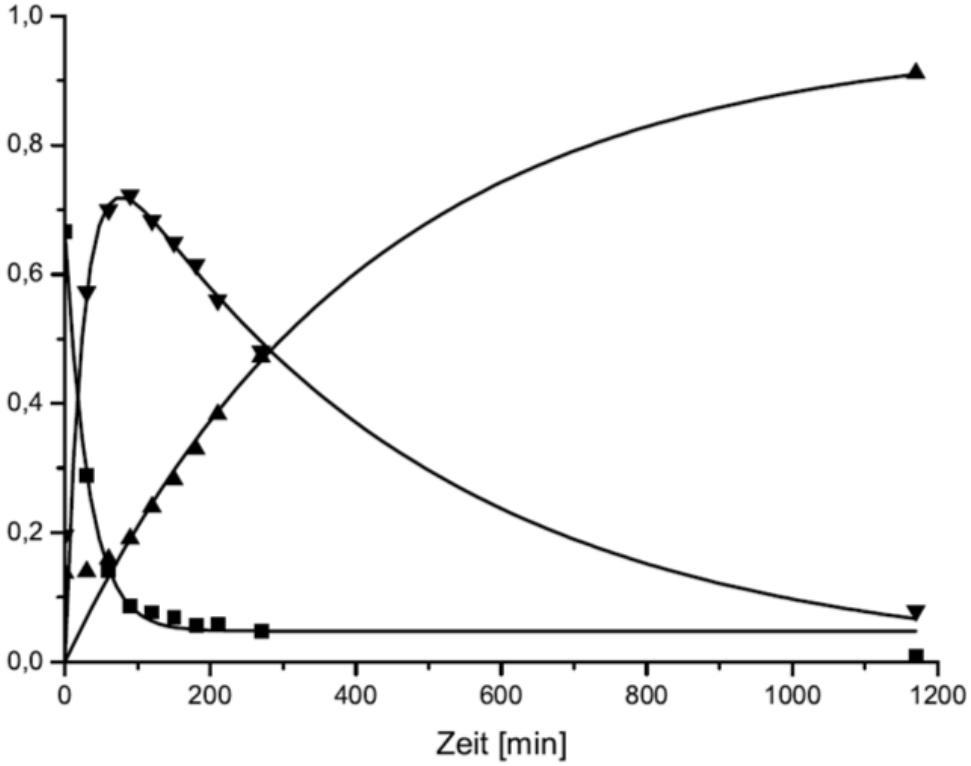


Figure S1. Data obtained by ^{19}F NMR (experiment 1) in rel. intensities using signals at -112.0 ppm (**1a**, square), -117.2 ppm (**2a**, triangle up) and -115.5 (**3a**, triangle down).

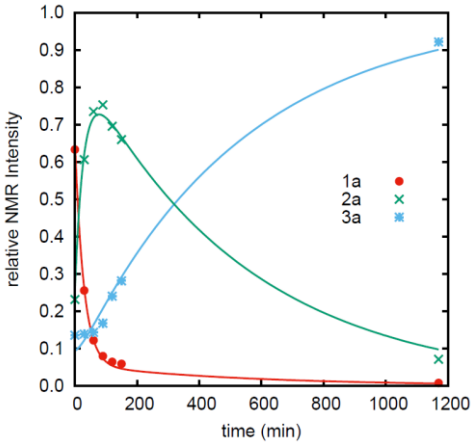


Figure S2. Data obtained by $^{11}B\{^{1}H\}$ NMR (experiment 1) in relative intensities using the signals at 6.6 ppm (**1a**, red), 32 ppm (small $h_{1/2}$; **2a**, green) and 32.0 pmm (large $h_{1/2}$; **3a**, blue).

II. Spectra

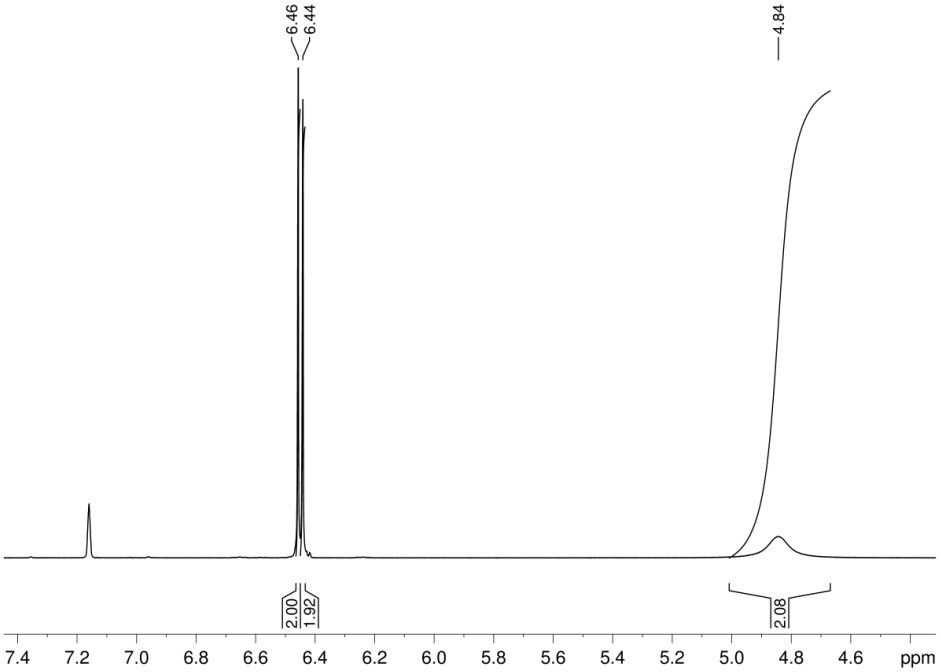


Figure S3. ^{1}H NMR (400 MHz, C_6D_6) of **1a**

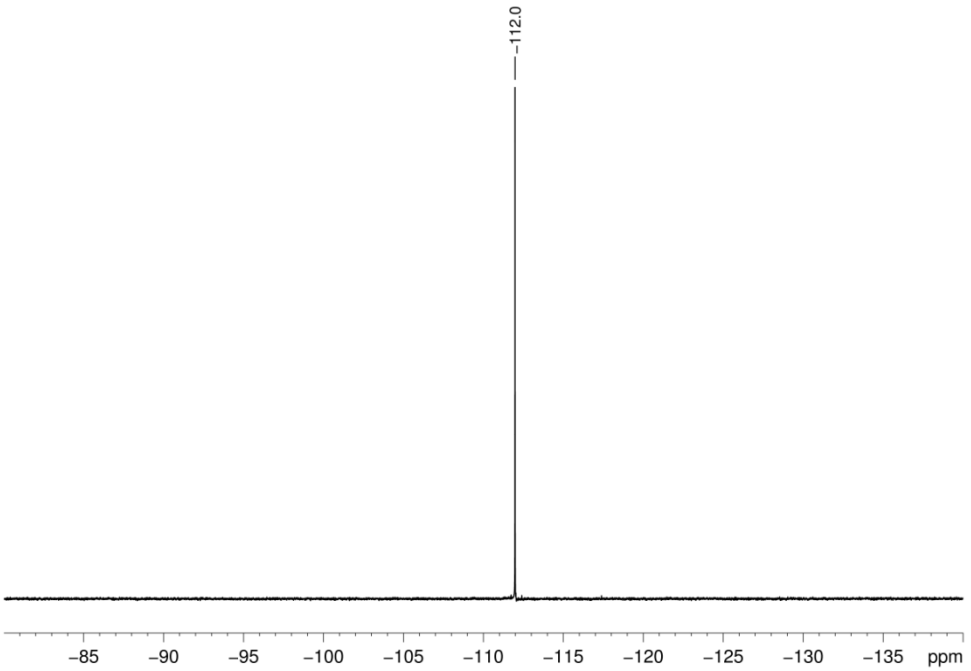


Figure S4. $^{19}F\{^{1}H\}$ (376 MHz, C_6D_6) of **1a**

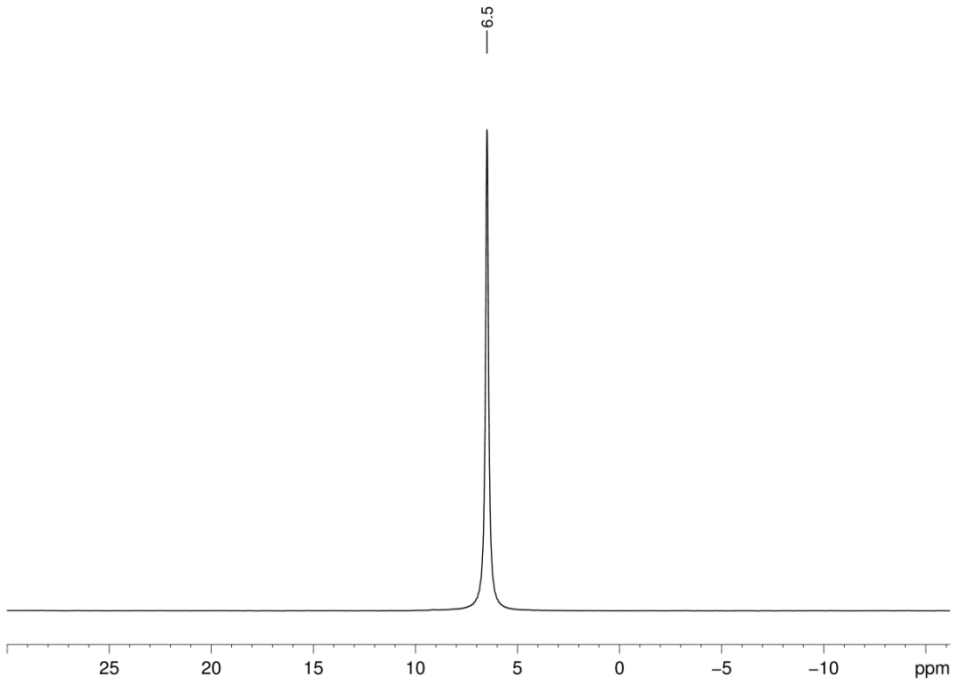


Figure S5. $^{11}B\{^{1}H\}$ (80 MHz, zgbsig, C_6D_6) of **1a** (with background suppression sequence)

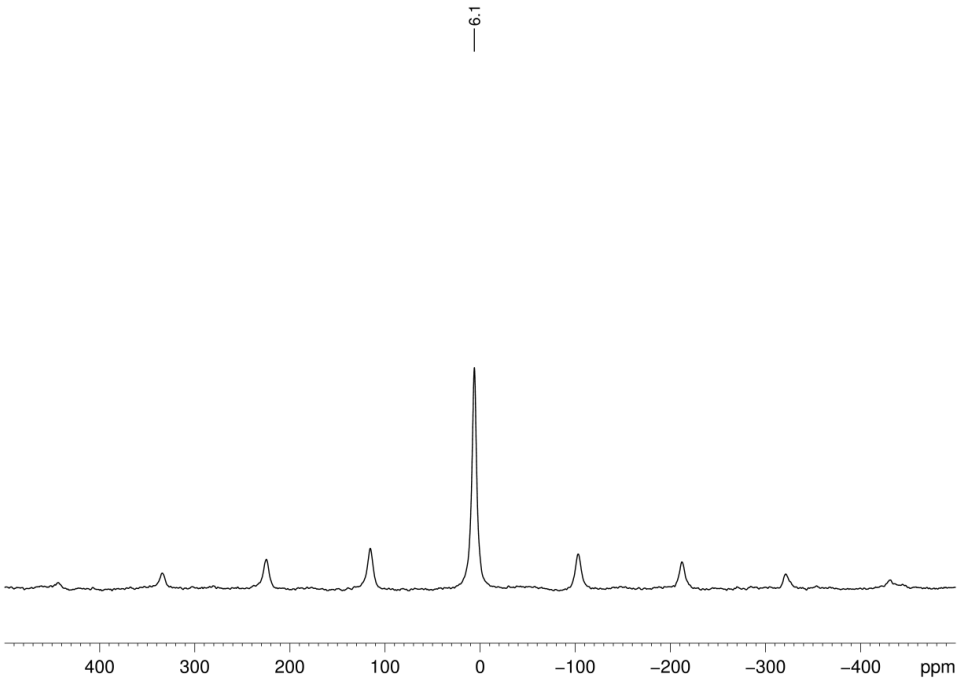


Figure S6. ^{11}B (64 MHz, MAS, Rf 10 kHz) of **1a**

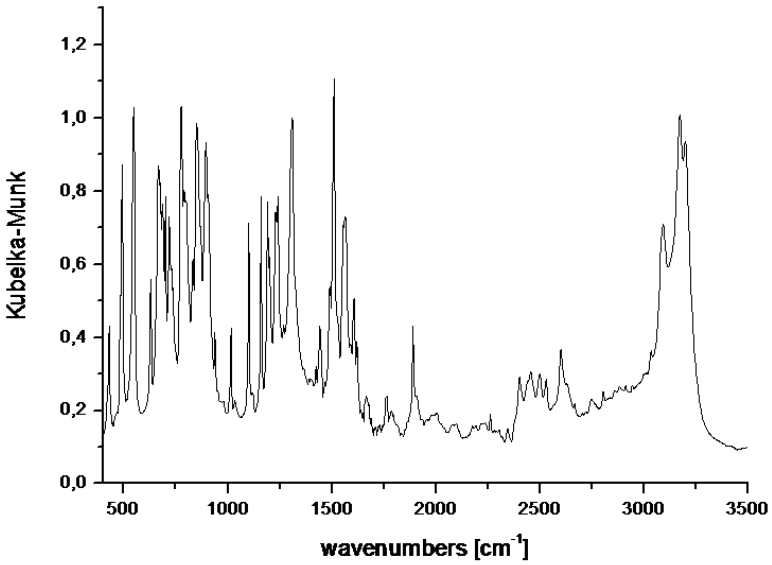


Figure S7. DRIFT-IR (KBr) of **1a**

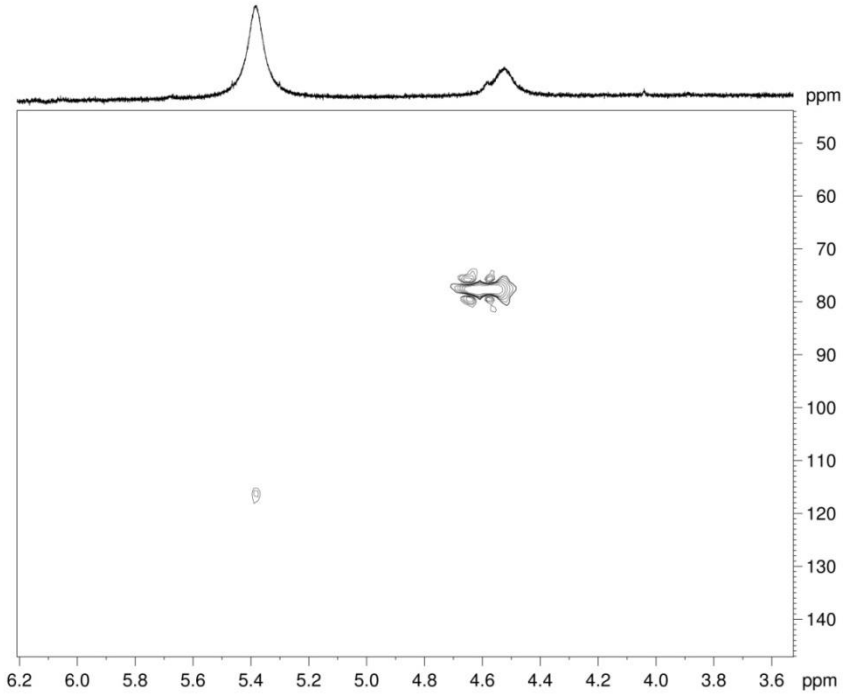


Figure S8. ^{15}N-^{1}H-HSQC (189 MHz, C_6D_6) of **2a**

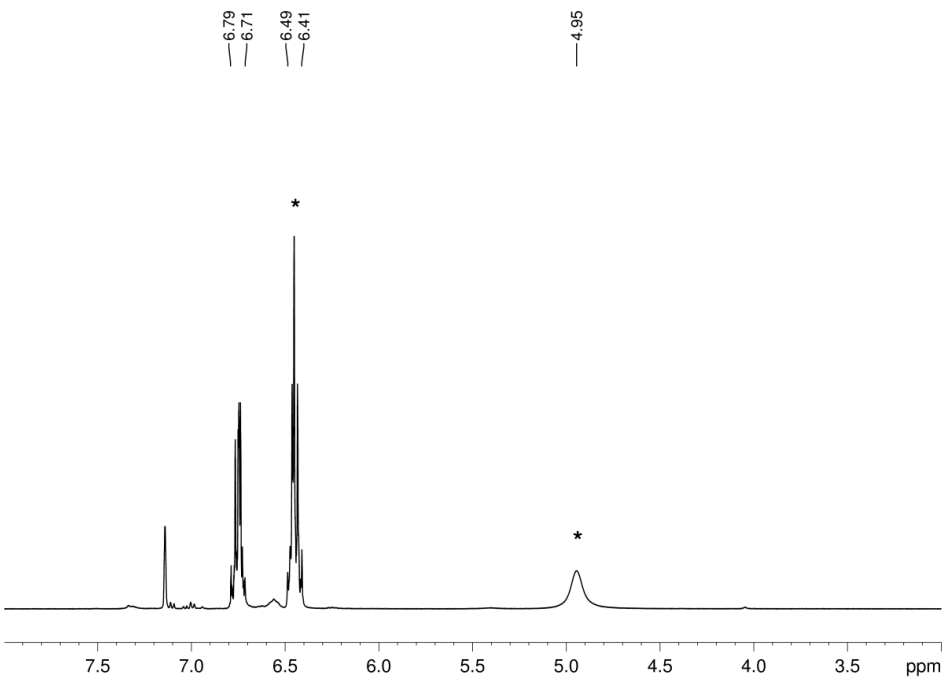


Figure S9. ^{1}H NMR (400 MHz, C_6D_6) of **3a** (after 19h at 100 °C without gentle argon passing over the reaction mixture, undecomposed **1a** is marked with *)

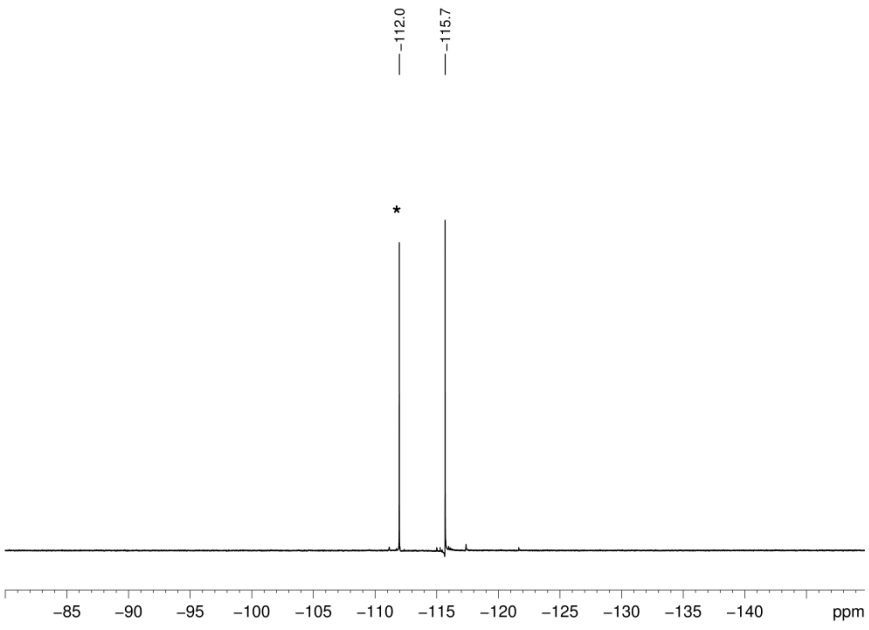


Figure S10. $^{19}F\{^{1}H\}$ NMR (376 MHz, C_6D_6) of **3a** (after 19h at 100 °C without gentle argon passing over the reaction mixture, undecomposed **1a** is marked with *)

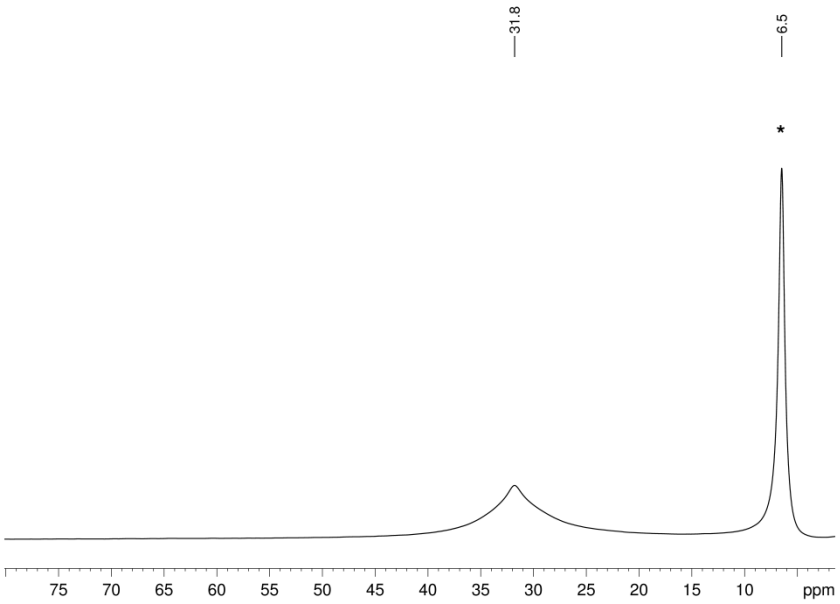


Figure S11. $^{11}B\{^{1}H\}$ (80 MHz, zgbsig, C_6D_6) of **3a** (after 19h at 100 °C without gentle argon passing over the reaction mixture, undecomposed **1a** is marked with *)

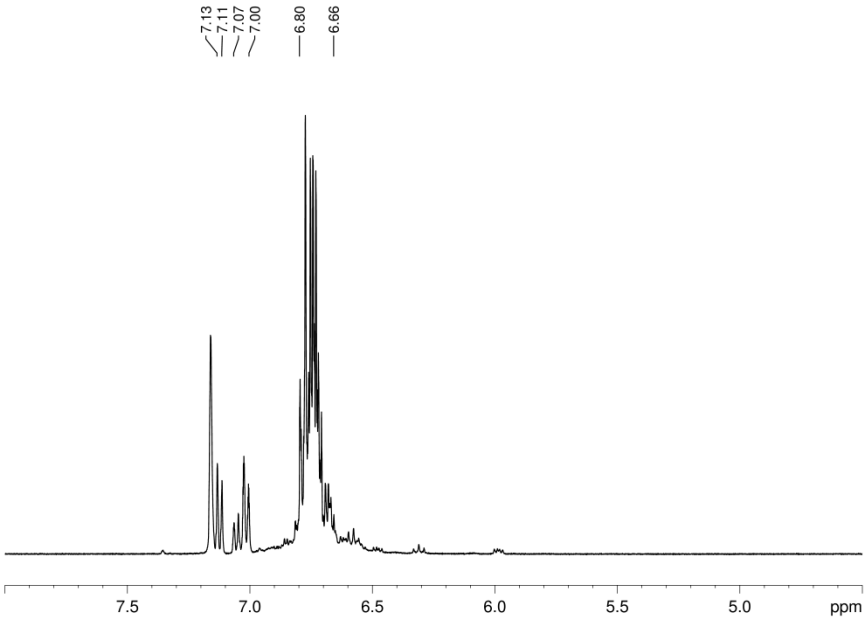


Figure S12. ^{1}H NMR (400 MHz, C_6D_6) of **3a** (after 19h at 100 °C with gentle argon passing over the reaction mixture)

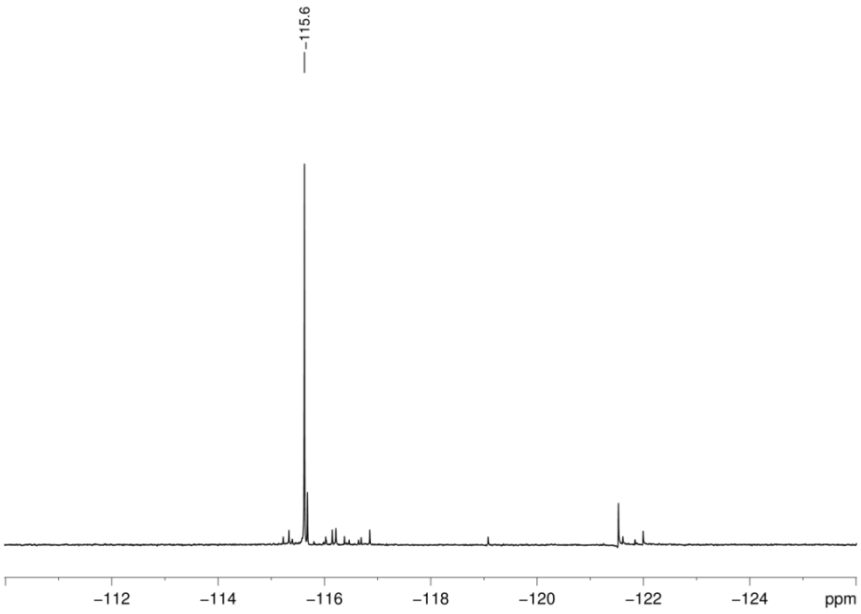


Figure S13. $^{19}F\{^{1}H\}$ (376 MHz, C_6D_6) of **3a** (after 19h at 100 °C with gentle argon passing over the reaction mixture)

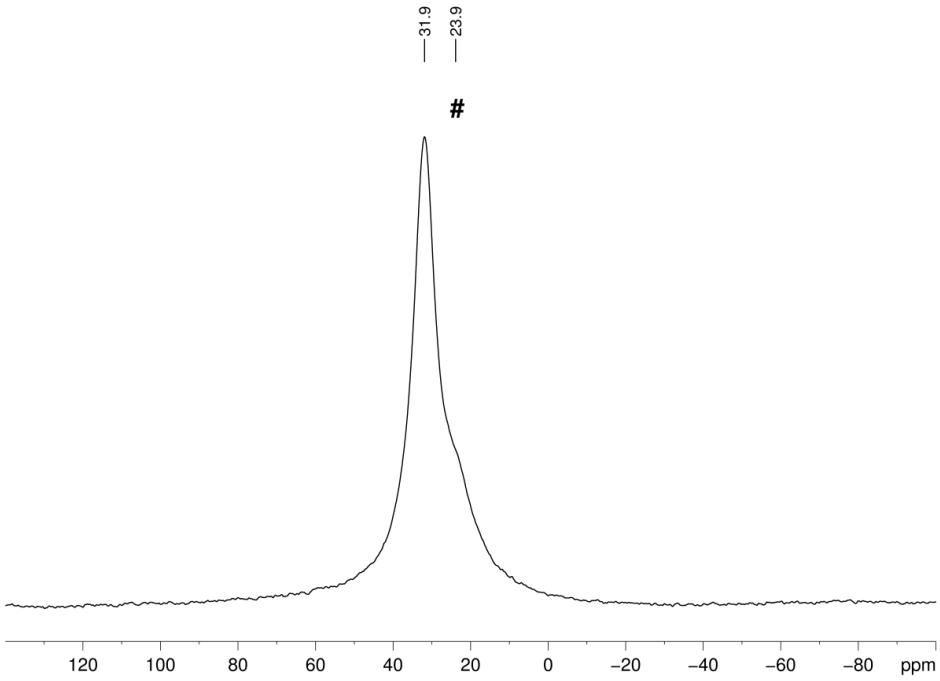


Figure S14. $^{11}B\{^{1}H\}$ (80 MHz, zgbsig, C_6D_6) of **3a** (with background suppression sequence; after 19h at 100 °C with gentle argon passing over the reaction mixture; partly decomposed **3a** is marked with #)

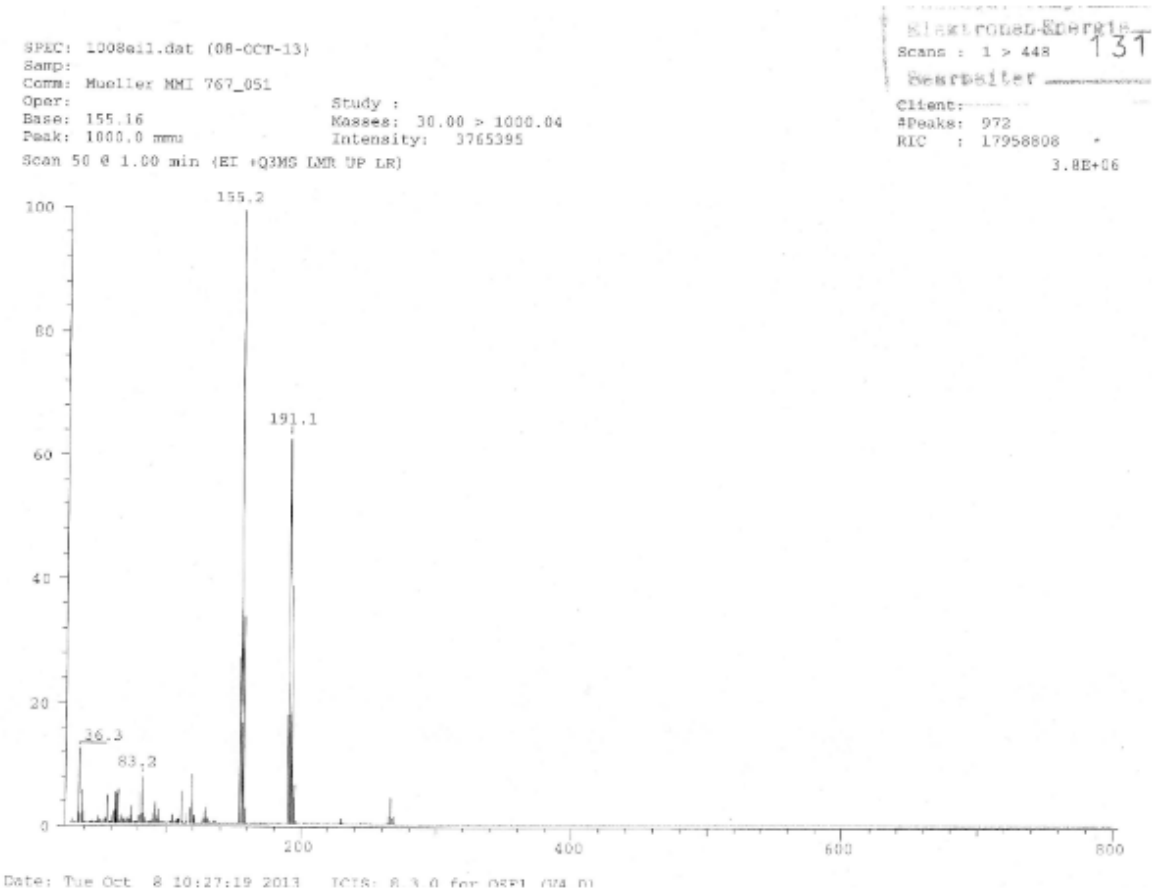


Figure S15. EI-MS (quadrupole, 70 eV) of **3a** (low evaporation temperature)

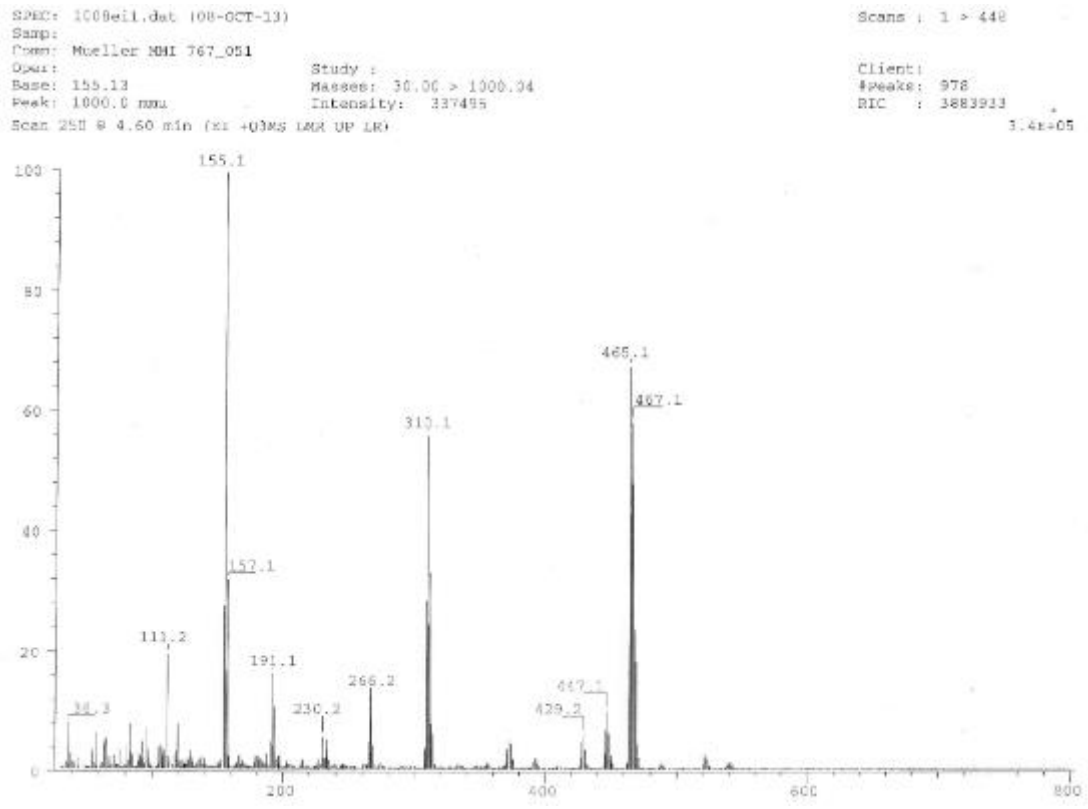
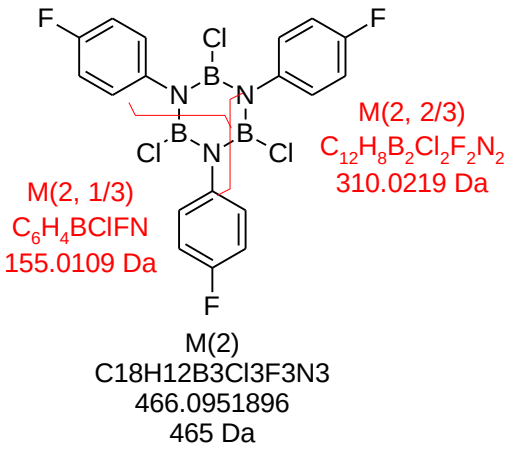


Figure S16. EI-MS (quadrupole, 70 eV) of **3a** (high evaporation temperature)



M(2)
C18H12B3Cl3F3N3
466.0951896
465 Da

Figure S17. Species appearing in the EI-MS spectra of **3a**

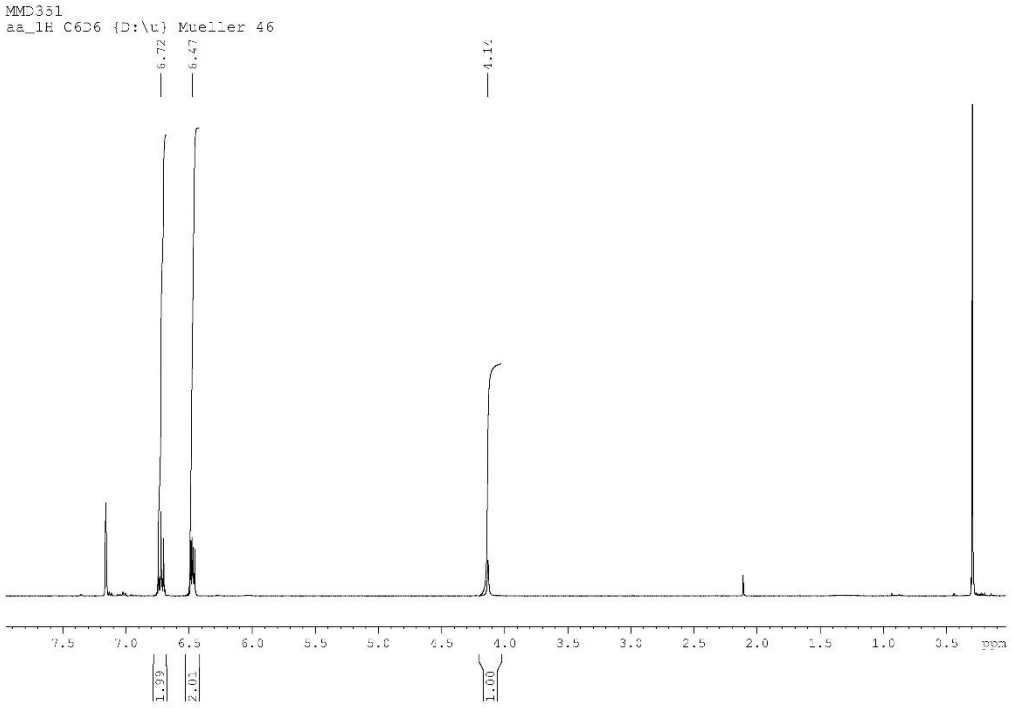


Figure S18. ^{1}H NMR (400 MHz, C_6D_6) of **4a**

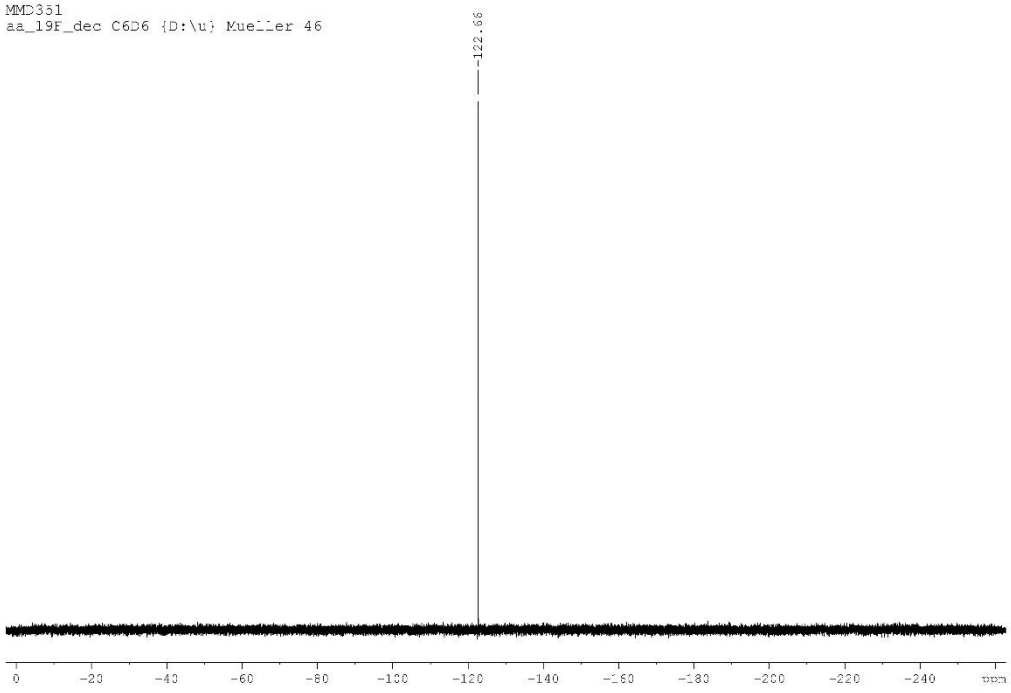


Figure S19. $^{19}F\{^{1}H\}$ NMR (376 MHz, C_6D_6) of **4a**

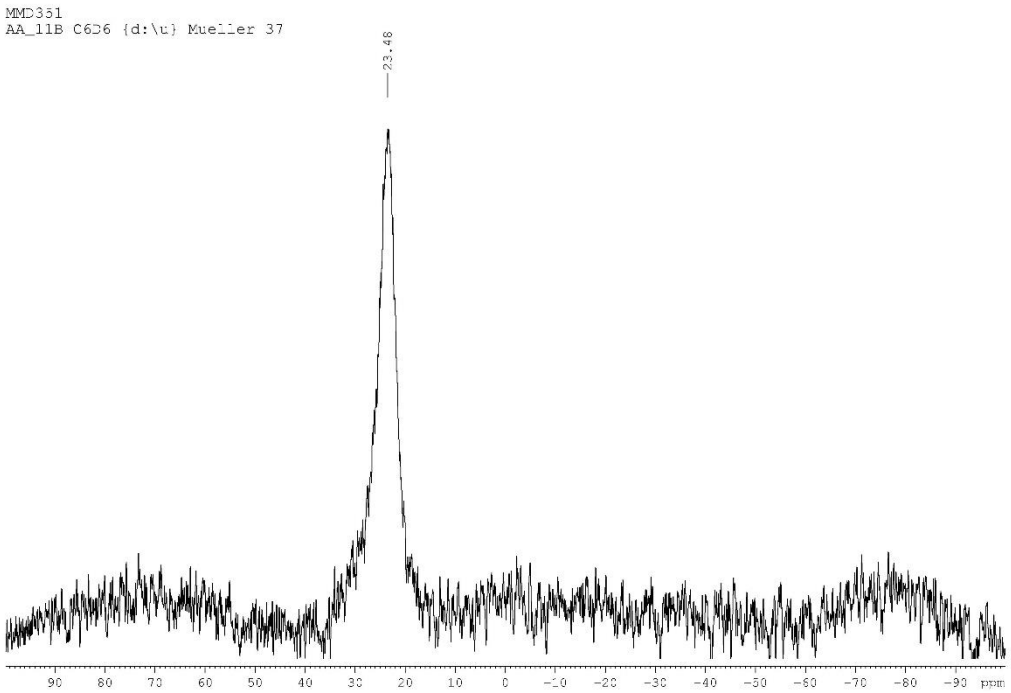


Figure S20. $^{11}B\{^{1}H\}$ NMR (80 MHz, C_6D_6) of **4a**

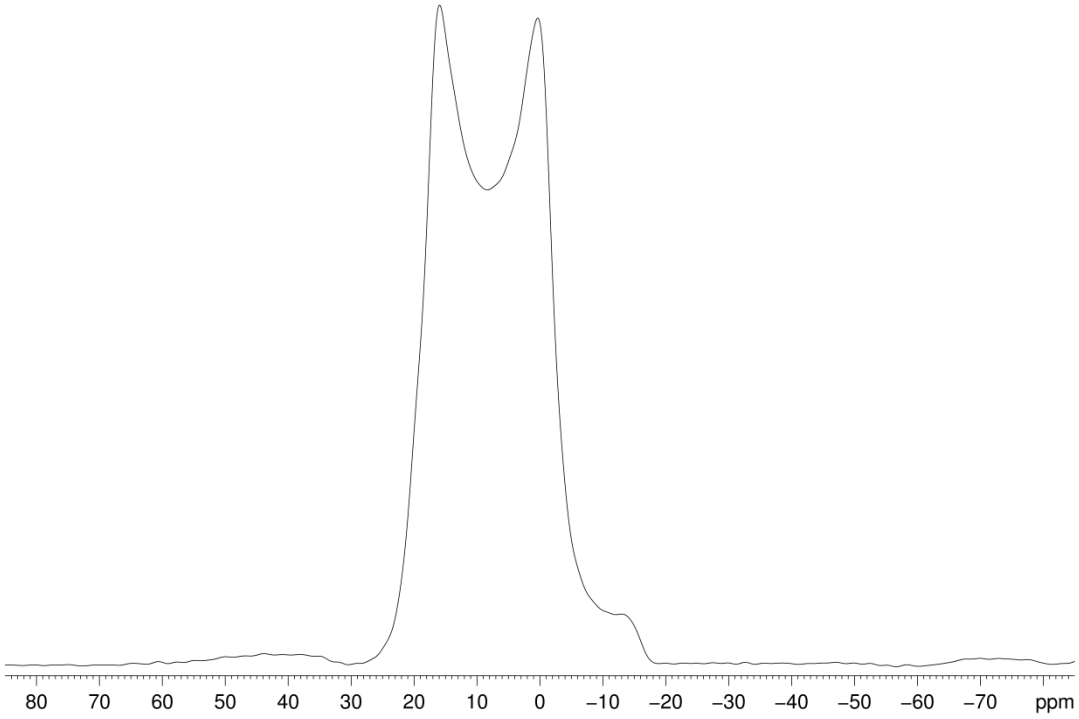


Figure S21. ^{11}B (64 MHz, MAS, Rf 10 kHz) of **4a**.

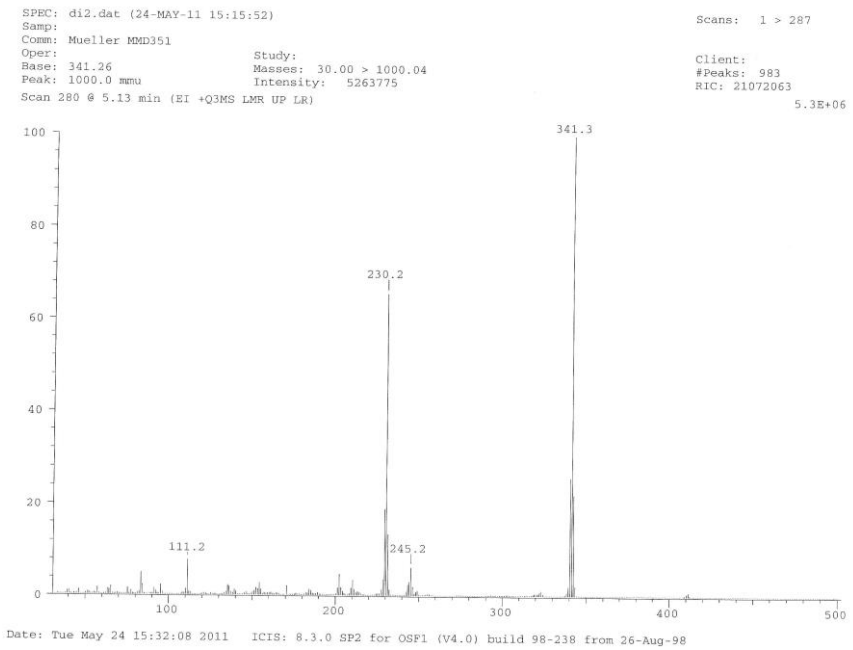


Figure S22. EI-MS (quadrupole, 70 eV) of **4a**

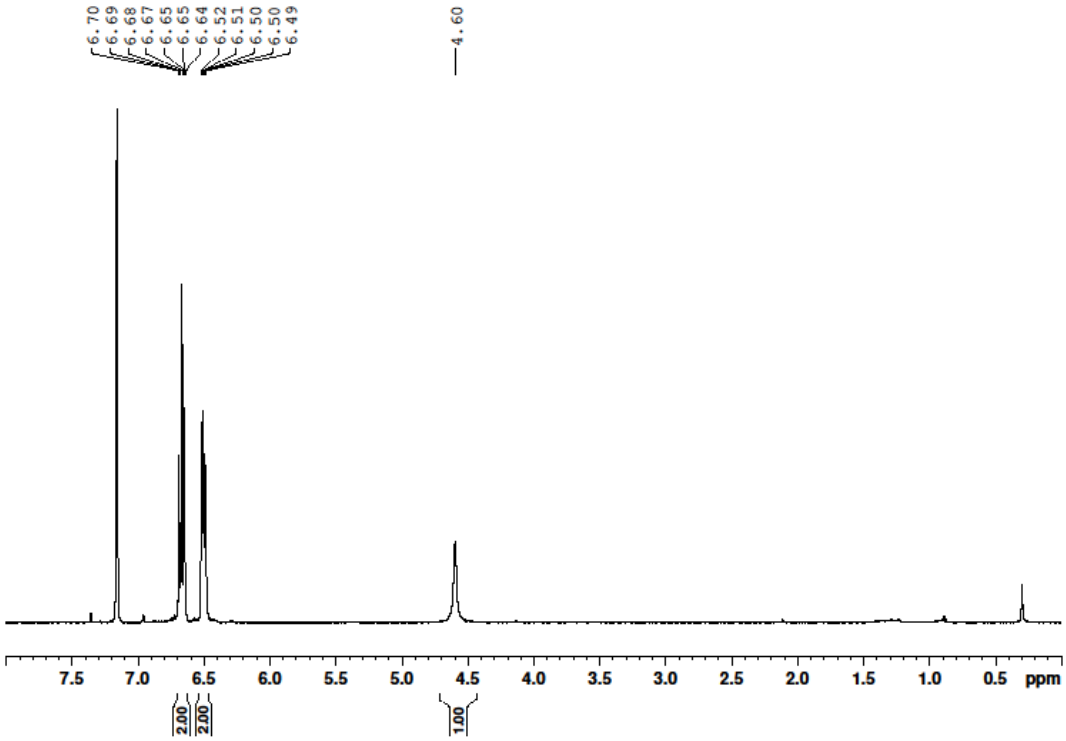


Figure S24. ^{1}H NMR (400 MHz, C_6D_6) of **5a**

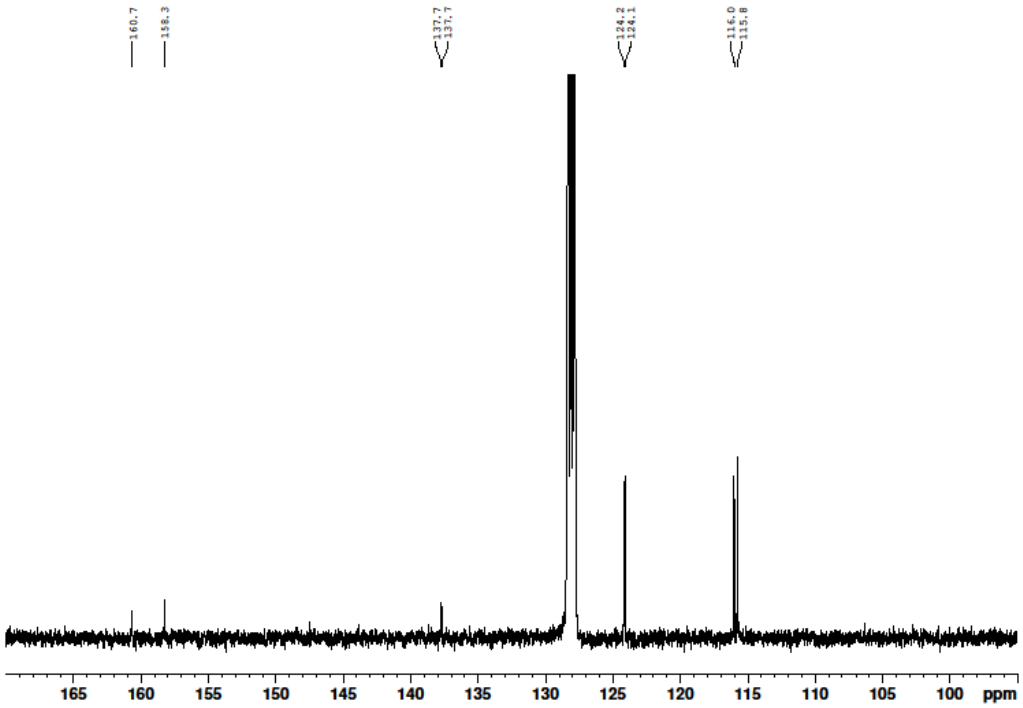


Figure S25. ^{13}C NMR (100 MHz, C_6D_6) of **5a**

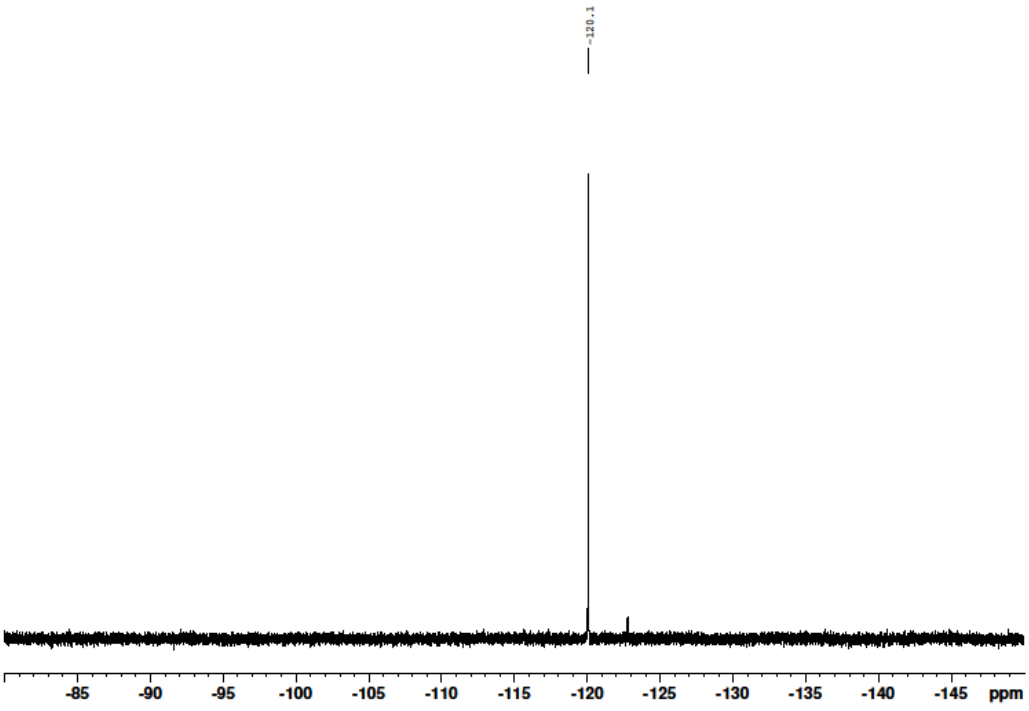


Figure S26. ^{19}F NMR (376 MHz, C_6D_6) of **5a**

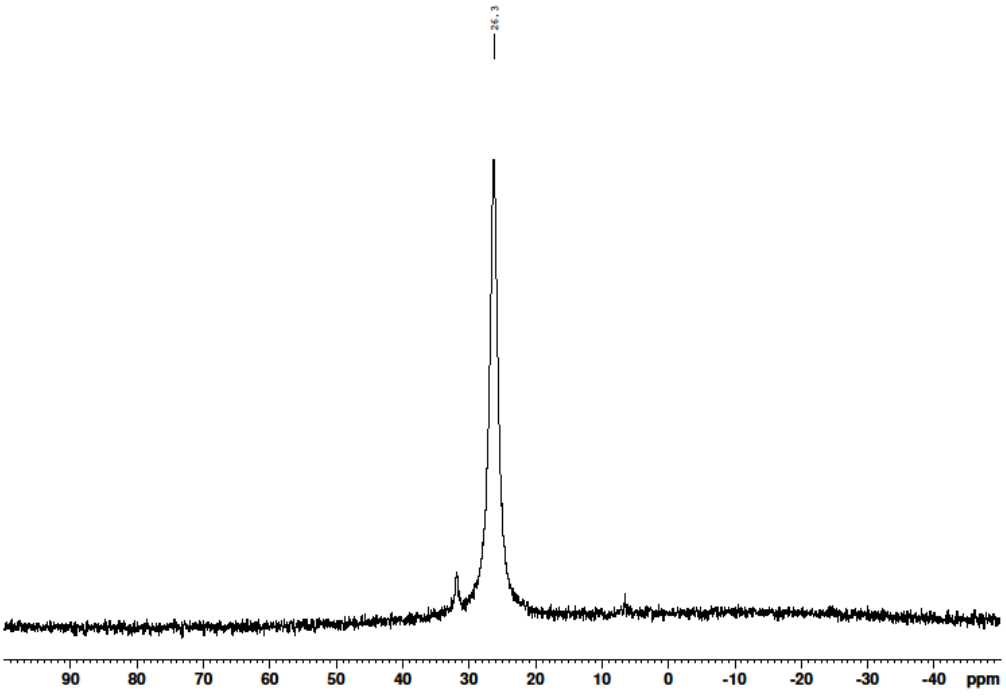
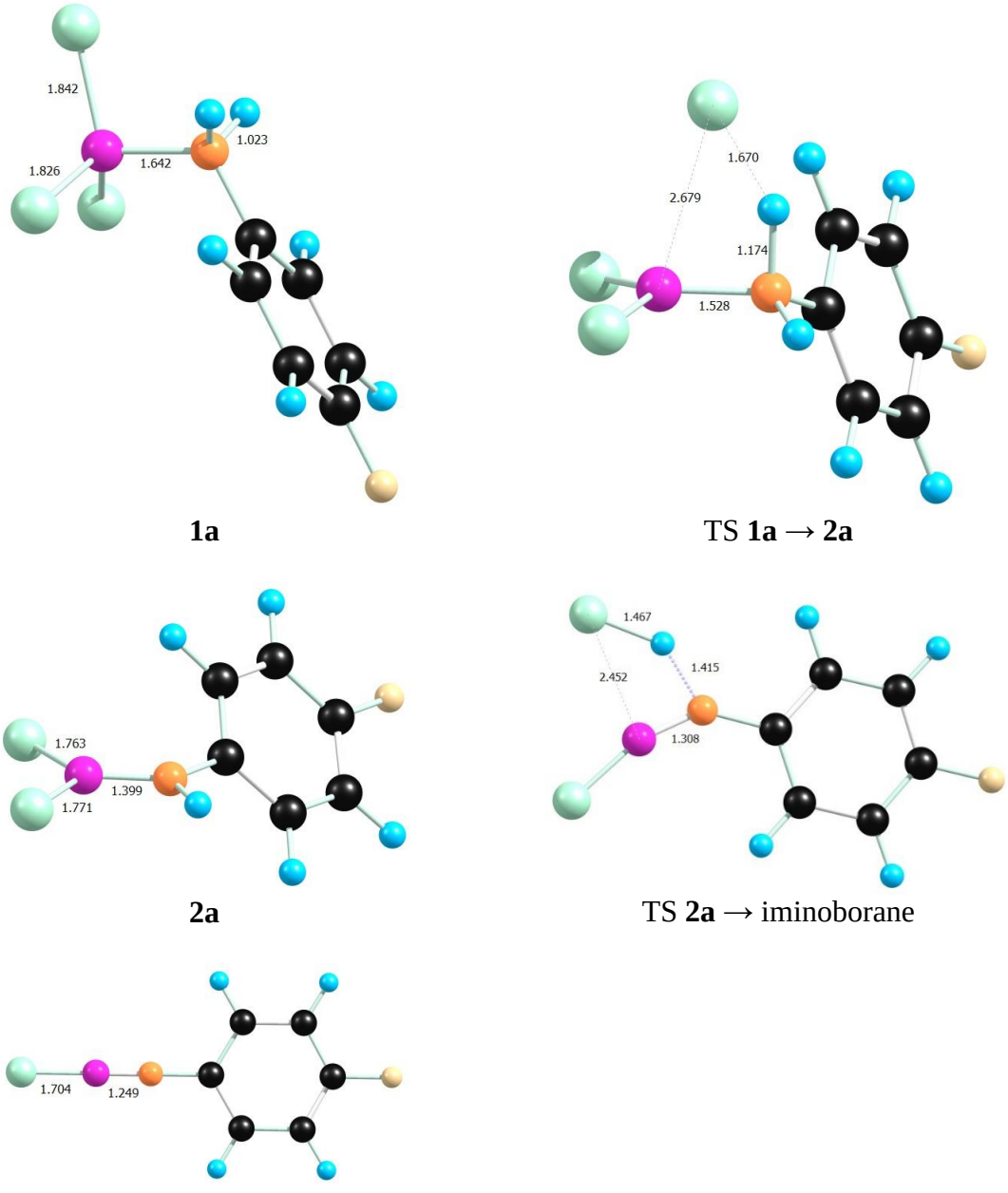


Figure S27. ^{11}B NMR (80 MHz, C_6D_6) of **5a**

III. Computational Supplementary Information

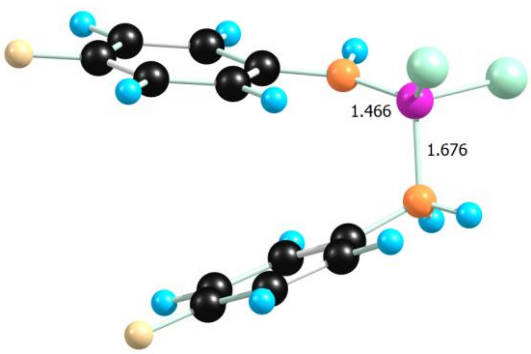


1a TS **1a** → **2a**

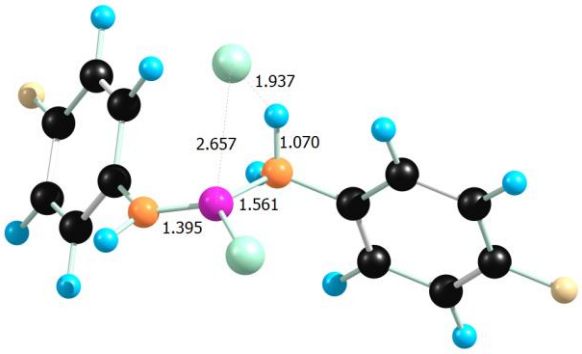
2a TS **2a** → iminoborane

iminoborane

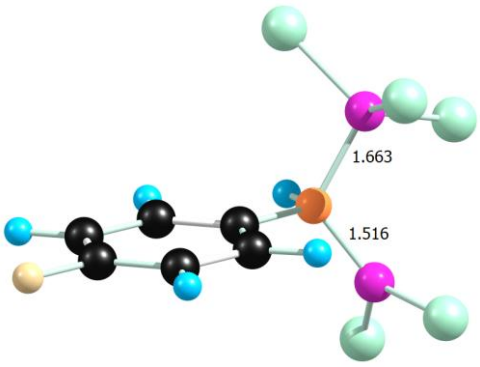
Figure S28. Structures computed at the SCS-MP2/cc-pVTZ level of theory for the 1:1 adduct **1a** between 4-fluoroaniline and borontrichloride.



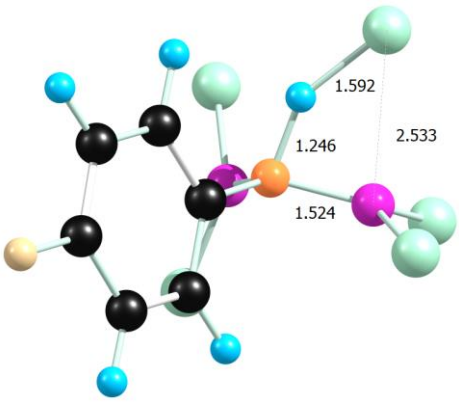
2aA



TS for HCl loss from **2aA**



2aB



TS for HCl loss from **2aB**

Figure S29. Structures computed at the M062X/6-311+G** level of theory for the adducts of **2a** with 4-fluoroaniline (**2aA**) and with trichloroborane (**2aB**) and the transition states for HCl elimination from **2aA** and **2aB**.

Cartesian Coordinates optimized at the SCS-MP2(fc)/cc-pVTZ level of theory

Unit is Angstrom

```
   18
4-fluoroaniline-BCl3 adduct, ArNH2BCl3, 1a
 B     2.613924    -0.419278     0.000000
Cl     4.187735     0.538619     0.000000
Cl     2.374386    -1.385835     1.529987
Cl     2.374386    -1.385835    -1.529987
 C    -2.560408    -0.376220     0.000000
 C    -1.920626    -0.192017    -1.212807
 C    -0.586107     0.190027    -1.210170
 C     0.066552     0.378383     0.000000
 C    -0.586107     0.190027     1.210170
 C    -1.920626    -0.192017     1.212807
 F    -3.848396    -0.740542     0.000000
 H    -2.462505    -0.350634    -2.135748
 H    -0.056152     0.324451    -2.145441
 H    -0.056152     0.324451     2.145441
 H    -2.462505    -0.350634     2.135748
 N     1.475489     0.763767     0.000000
 H     1.681834     1.341995    -0.817803
 H     1.681834     1.341995     0.817803

   18
TS for HCl loss from 1a
 C    -0.443262     1.071634     0.293063
 C    -1.799160     1.126090     0.604732
 C    -2.605063     0.036728     0.300310
 C    -2.104126    -1.107783    -0.304393
 C    -0.745229    -1.161979    -0.608085
 C     0.070265    -0.074376    -0.310033
 F    -3.912885     0.092260     0.597910
 N     1.486408    -0.126220    -0.630370
 B     2.516588    -0.467974     0.445606
Cl     2.053658    -0.413060     2.116445
Cl     3.951391    -1.290265    -0.110042
Cl     3.027424     2.091244    -0.161078
 H    -2.764792    -1.932957    -0.525531
 H    -0.329994    -2.047559    -1.071792
 H     0.211132     1.904305     0.511600
 H    -2.231366     1.998488     1.072282
 H     1.663456    -0.644083    -1.487004
 H     1.955554     0.945507    -0.733619

   16
4-fluoroanilinodichloroborane, ArNHBCl2, 2a
 C     1.002740    -0.292721    -0.428054
 C     0.929070    -1.674268    -0.592168
 C    -0.149762    -2.359038    -0.051779
 C    -1.157289    -1.706998     0.644566
 C    -1.083358    -0.323486     0.787156
 C    -0.008308     0.389872     0.251054
 N     0.051812     1.800195     0.436766
 B     0.283746     2.814522    -0.498450
Cl     0.573166     2.481528    -2.204884
Cl     0.259384     4.495040     0.060607
 F    -0.218061    -3.694511    -0.201414
 H    -1.981866    -2.272538     1.053223
 H    -1.869217     0.206643     1.309059
 H     1.848895     0.251720    -0.819577
 H     1.700659    -2.218213    -1.117211
 H    -0.181609     2.102253     1.371106

   16
TS for HCl loss from 2a
 N    -1.207937    -0.158561     1.174047
 B    -1.877200    -1.078499     1.819957
Cl    -2.457735    -2.573485     2.376317
Cl    -3.046735     0.745850     2.967549
 C    -0.209443    -0.004745     0.203755
 H    -1.995083     0.728906     1.944537
 C     0.178848     1.285027    -0.169798
 C     1.168513     1.475247    -1.131478
 C     1.760617     0.362497    -1.710581
 C     1.394938    -0.930434    -1.358939
```

C	0.405312	-1.110369	-0.397286
H	-0.297460	2.136730	0.295914
H	1.479262	2.465598	-1.430592
F	2.717148	0.539029	-2.640113
H	1.879078	-1.772286	-1.832206
H	0.107876	-2.110505	-0.111083

16
B-chloro-N-(4-fluoroanilino)iminoborane

N	0.000000	0.000000	2.077280
B	0.000000	0.000000	3.326189
Cl	0.000000	0.000000	5.030350
C	0.000000	0.000000	-2.072621
C	1.213204	0.000000	-1.398774
C	1.208899	0.000000	-0.006423
C	0.000000	0.000000	0.700558
C	-1.208899	0.000000	-0.006423
C	-1.213204	0.000000	-1.398774
F	0.000000	0.000000	-3.419524
H	2.137405	0.000000	-1.958203
H	2.140177	0.000000	0.542330
H	-2.140177	0.000000	0.542330
H	-2.137405	0.000000	-1.958203

40
Tri(4-fluoroanilino)borane, **4a**

C	2.387630	0.921486	0.041695
C	3.206652	1.726208	0.845609
H	2.750447	2.421273	1.539161
C	4.595015	1.643023	0.770598
H	5.228459	2.264915	1.386555
C	5.164867	0.729124	-0.103681
C	4.385348	-0.082083	-0.914391
H	4.859820	-0.769410	-1.600041
C	2.996722	0.026674	-0.849751
H	2.382296	-0.571264	-1.507698
C	-1.991845	1.607005	0.041695
C	-3.098266	1.913938	0.845609
H	-3.472108	1.171320	1.539161
C	-3.720407	3.157888	0.770598
H	-4.575704	3.395521	1.386555
C	-3.213874	4.108344	-0.103681
C	-2.121588	3.838864	-0.914391
H	-1.763581	4.593432	-1.600041
C	-1.521461	2.581900	-0.849751
H	-0.696419	2.348761	-1.507698
C	-0.395785	-2.528491	0.041695
C	-0.108386	-3.640146	0.845609
H	0.721661	-3.592593	1.539161
C	-0.874607	-4.800911	0.770598
H	-0.652756	-5.660436	1.386555
C	-1.950994	-4.837468	-0.103681
C	-2.263760	-3.756781	-0.914391
H	-3.096238	-3.824022	-1.600041
C	-1.475260	-2.608574	-0.849751
H	-1.685877	-1.777497	-1.507698
H	0.678932	1.955562	0.416660
H	-2.033033	-0.389809	0.416660
H	1.354101	-1.565754	0.416660
N	0.987982	1.044794	0.114291
N	-1.398809	0.333221	0.114291
N	0.410827	-1.378014	0.114291
F	6.507776	0.633082	-0.172096
F	-3.802153	5.319358	-0.172096
F	-2.705623	-5.952440	-0.172096
B	0.000000	0.000000	0.099271

28
Chloro-di(4-fluoroanilino)borane, **5a**

H	-1.945297	-3.282666	1.488153
H	0.466326	-2.724501	1.805515
H	0.443935	-0.560107	-1.889671
H	-1.984594	-1.058244	-2.162654
H	2.553725	-2.017861	0.487531
H	2.553353	2.018130	-0.487187
H	0.443648	0.560844	1.890258
H	-1.984911	1.058927	2.163028

H	-1.945907	3.281339	-1.489006
H	0.465825	2.723442	-1.805983
B	2.610148	0.000192	0.000381
C	-0.064133	2.370714	-0.930376
C	0.609399	1.590273	0.013458
C	-0.081715	1.137676	1.142021
C	-1.436442	1.416018	1.303378
C	-2.082030	2.182218	0.342785
C	-1.413588	2.679592	-0.766567
C	0.609746	-1.590304	-0.013299
C	-0.081389	-1.137302	-1.141685
C	-1.436081	-1.415729	-1.303196
C	-2.081581	-2.182492	-0.342994
C	-1.413075	-2.680386	0.766087
C	-0.063679	-2.371360	0.930103
N	1.971881	1.255135	-0.179124
N	1.972131	-1.254924	0.179557
F	-3.390567	2.460712	0.497673
F	-3.390109	-2.460976	-0.497975
Cl	4.404432	0.000454	0.000930

Cartesian Coordinates optimized at the M062X/6-311+G** level of theory

30
2aA

6	-0.095142000	1.564763000	-0.160725000
6	-0.774850000	0.864853000	0.844061000
6	-2.127040000	1.088635000	1.076956000
6	-2.804268000	2.020576000	0.315011000
6	-2.162570000	2.744728000	-0.672035000
6	-0.814213000	2.510982000	-0.904546000
9	-4.117985000	2.231285000	0.538900000
7	1.250102000	1.346581000	-0.485722000
5	2.255782000	0.407024000	0.019400000
7	2.043149000	-1.109076000	-0.663424000
17	3.939996000	0.861651000	-0.637562000
17	2.320773000	0.059672000	1.843208000
1	-2.715133000	3.476662000	-1.247636000
1	-0.306176000	3.068613000	-1.684768000
1	-0.254281000	0.138170000	1.450309000
1	-2.655344000	0.544294000	1.850248000
1	1.626895000	2.060112000	-1.092101000
6	0.704451000	-1.668672000	-0.562014000
1	2.733946000	-1.728758000	-0.237388000
1	2.308010000	-0.999545000	-1.643183000
6	-0.245474000	-1.311519000	-1.509554000
6	-1.553908000	-1.749445000	-1.366471000
6	-1.871734000	-2.534712000	-0.271355000
6	-0.932865000	-2.908337000	0.674181000
6	0.375705000	-2.466793000	0.524680000
1	0.024713000	-0.658408000	-2.331718000
1	-2.326175000	-1.474255000	-2.072692000
9	-3.135910000	-2.950654000	-0.121807000
1	-1.230816000	-3.525738000	1.511558000
1	1.126093000	-2.717329000	1.265450000

30
TS for HCl loss from 2aA

6	-2.382279000	0.243091000	0.677637000
6	-3.133769000	-0.610682000	1.487573000
6	-4.192129000	-1.333011000	0.954608000
6	-4.469173000	-1.203301000	-0.396234000
6	-3.740902000	-0.366834000	-1.221212000
6	-2.696960000	0.374244000	-0.675493000
9	-5.483884000	-1.911096000	-0.916668000
7	-1.299619000	0.972685000	1.247871000
5	0.001812000	1.084164000	0.757434000
7	0.433337000	0.063143000	-0.342087000

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17      -0.034876000      2.609696000     -1.418257000
17       1.256895000      1.881552000      1.699071000
1       -4.006828000     -0.280119000     -2.267070000
1       -2.145065000      1.085867000     -1.282492000
1       -2.883273000     -0.706498000      2.537936000
1       -4.793869000     -1.995672000      1.563527000
1       -1.534204000      1.525446000      2.061525000
6        1.795197000     -0.458918000     -0.308805000
1        0.303957000      0.717967000     -1.177916000
1       -0.252948000     -0.692092000     -0.408129000
6        2.051184000     -1.669256000      0.316229000
6        3.352322000     -2.155717000      0.352659000
6        4.353916000     -1.404493000     -0.236005000
6        4.108824000     -0.190733000     -0.855998000
6        2.807461000      0.290719000     -0.893473000
1        1.246627000     -2.231428000      0.777788000
1        3.595040000     -3.097024000      0.827742000
9        5.609222000     -1.871423000     -0.203909000
1        4.928276000      0.359759000     -1.299498000
1        2.572700000      1.242986000     -1.358613000


20
2aB
6        1.589185000      0.291679000      1.006753000
6        2.970185000      0.285226000      1.152762000
6        3.763597000      0.113645000      0.032752000
6        3.231760000     -0.052440000     -1.233750000
6        1.851898000     -0.040636000     -1.376191000
6        1.041226000      0.133230000     -0.260640000
7       -0.417783000      0.127412000     -0.469513000
5       -1.096799000      1.430460000     -0.096025000
17      -1.327242000      1.900057000      1.547991000
17      -1.501870000      2.505513000     -1.403281000
9        5.093768000      0.106431000      0.178919000
1        3.889820000     -0.192834000     -2.080963000
1        1.410029000     -0.184124000     -2.356464000
1        0.954734000      0.400142000      1.874017000
1        3.432686000      0.403306000      2.123989000
1       -0.546319000      0.048028000     -1.482869000
5       -1.254855000     -1.225829000      0.015268000
17      -0.973051000     -1.585112000      1.770146000
17      -3.002981000     -0.722695000     -0.341820000
17      -0.664810000     -2.552566000     -1.098196000


20
TS for HCl loss from 2aB
6       -1.715471000      0.093643000     -1.095126000
6       -3.101879000      0.089003000     -1.087593000
6       -3.759262000      0.045144000      0.131687000
6       -3.087473000      0.006851000      1.339274000
6       -1.697620000      0.011643000      1.325019000
6       -1.023263000      0.053601000      0.111005000
7        0.438925000      0.070870000      0.135916000
5        1.014680000      1.442670000      0.044857000
17       0.732687000      2.416856000     -1.371390000
17       1.910067000      2.077325000      1.386994000
9       -5.098135000      0.038852000      0.137509000
1       -3.646520000     -0.031691000      2.264937000
1       -1.139566000     -0.032807000      2.253744000
1       -1.173519000      0.124400000     -2.032475000
1       -3.675904000      0.115193000     -2.004620000
1        0.817240000     -0.477516000      1.189415000
5        1.227365000     -1.052323000     -0.527671000
17       0.390663000     -2.426244000     -1.198941000
17       2.851359000     -0.633008000     -1.057266000
17       1.569847000     -1.687540000      1.899925000


16
2a
6        0.961994000      0.637665000      0.776690000
6        2.315163000      0.932622000      0.671054000
6        3.141282000      0.044230000      0.006915000
6        2.663484000     -1.124618000     -0.557284000
6        1.305837000     -1.400971000     -0.461801000
6        0.450698000     -0.522990000      0.201050000
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7       -0.933784000     -0.843013000      0.303500000
5       -2.042551000     -0.051706000      0.010232000
17      -1.899676000      1.604433000     -0.576468000
17      -3.659643000     -0.745096000      0.212874000
9        4.451575000      0.323638000     -0.090595000
1        3.345707000     -1.792316000     -1.067357000
1        0.902960000     -2.300208000     -0.913589000
1        0.301308000      1.306872000      1.312370000
1        2.734339000      1.830888000      1.105730000
1       -1.121580000     -1.802720000      0.563913000


14
4-fluoroanilinie
6        1.375284000      0.000007000     -0.007680000
6        0.662529000      1.202625000     -0.007127000
6       -0.726478000      1.206549000     -0.000807000
6       -1.400619000      0.000015000      0.002655000
6       -0.726470000     -1.206548000     -0.000793000
6        0.662504000     -1.202632000     -0.007285000
1        1.201569000      2.143535000     -0.017161000
1       -1.287922000      2.132356000      0.001080000
9       -2.749742000      0.000001000      0.010325000
1       -1.287934000     -2.132343000      0.001064000
1        1.201589000     -2.143510000     -0.017642000
7        2.773476000     -0.000158000     -0.072908000
1        3.212779000      0.834171000      0.286683000
1        3.212765000     -0.833220000      0.289632000

4
trichloroborane
5        0.000000000      0.000000000      0.000000000
17       0.000000000      1.742600000      0.000000000
17       1.509136000     -0.871300000      0.000000000
17      -1.509136000     -0.871300000      0.000000000
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