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Supporting Information for:

Multiple Metal-Bound Insertion Products from the Ir-Catalysed Dehydropolymerisation of $H_3B{\cdot}NH_3$ as Probed by Computation and Experiment

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Contents

(1) Computational Details

Calculations were run with Gaussian 03 Revision D.01[1] with PCM solvent corrections run with Gaussian 09, Revision A.02.[2] Geometry optimisations were performed using the BP86 functional[3] with Ir and P centres described with the Stuttgart RECPs and associated basis sets[4] (with added d-orbital polarisation on P (z = 0.387)[5] and 6-31G** basis sets for all other atoms.[6] All stationary points were fully characterized via analytical frequency calculations as either minima (all positive eigenvalues) or transition states (one negative eigenvalue) and IRC calculations and subsequent geometry optimizations were used to confirm the minima linked by each transition state. Frequency calculations also provided a free energy in the gas-phase, computed at 298.15 K and 1 atm. Energies reported in the text are based on the gas-phase free energies and incorporate a correction for dispersion effects using Grimme's D3 parameter set[7] (i.e. BP86-D3) as well as solvation (PCM approach) in C_6H_5F, this being emplyed in the absence of parameters for 1,2-$C_6H_4F_2$.

(2) Model 1. Dehydrogenation of 6a' in the absence of added $H_3B{\cdot}NH_3$

Figure S1. Computed reaction profile for amineborane dehydrogenation in **6a'** in the absence of added $H_3B{\bullet}NH_3$

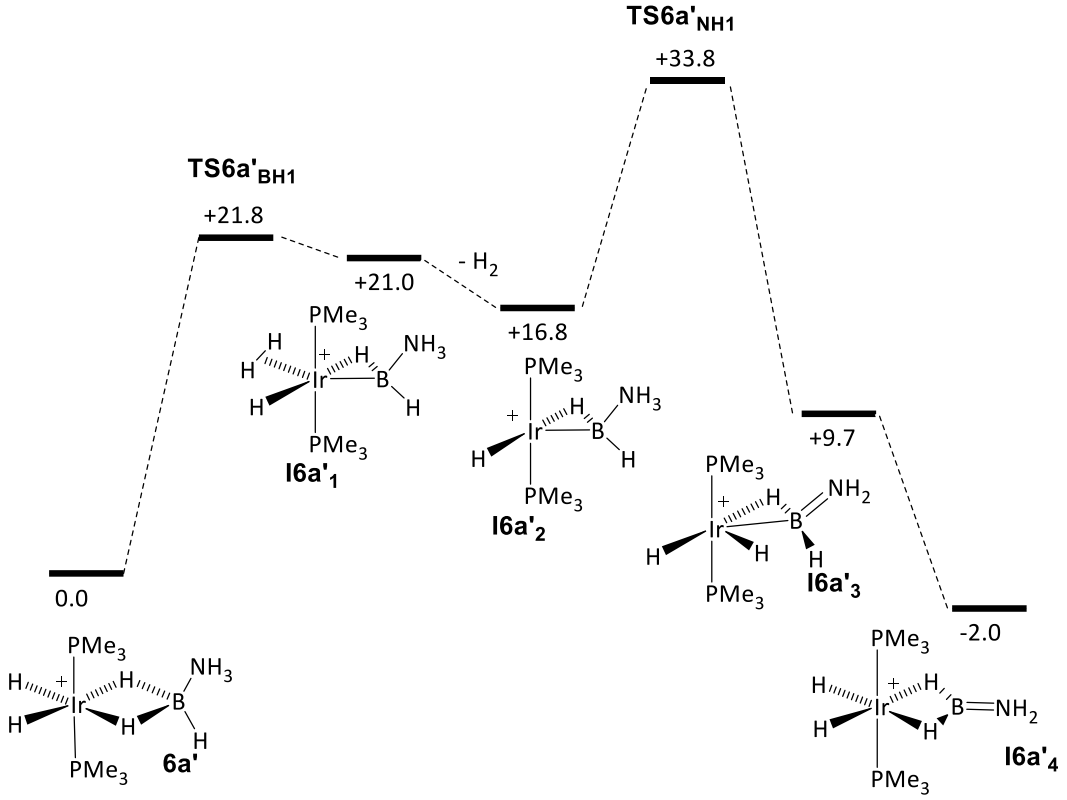
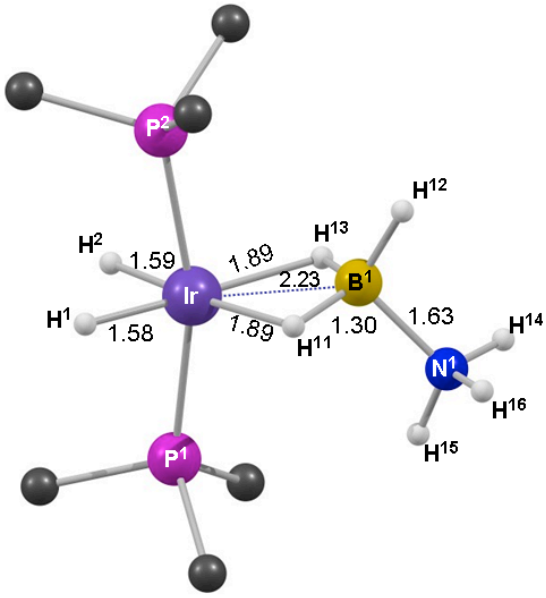
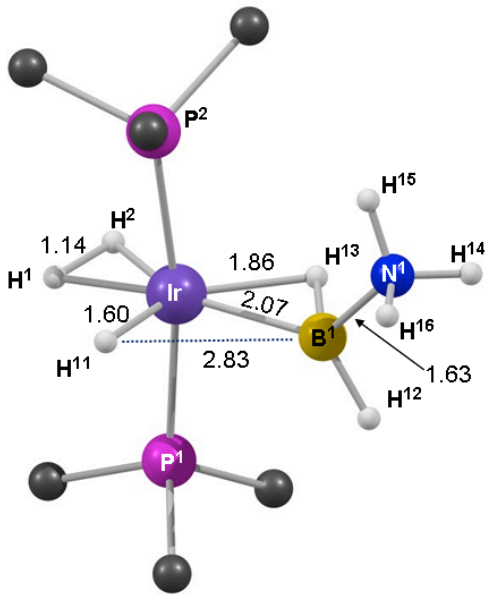


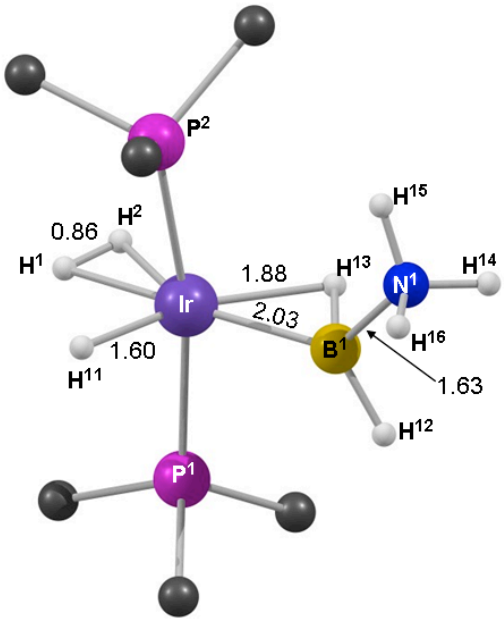
Figure S2. Computed Geometries



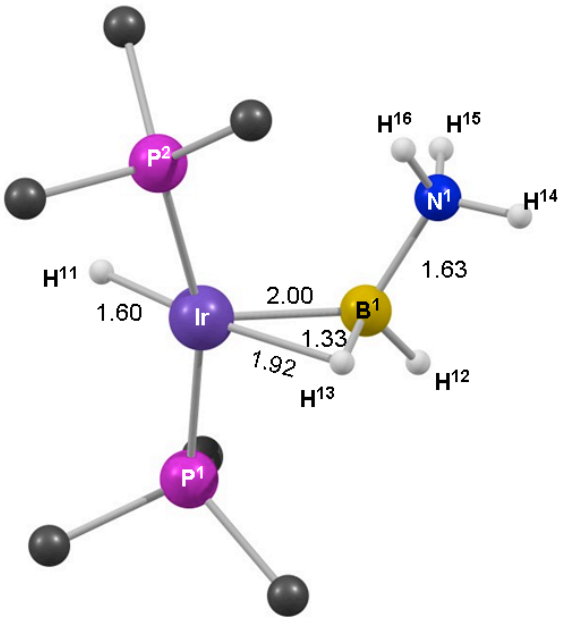
6a'
(+0.0 kcal/mol)



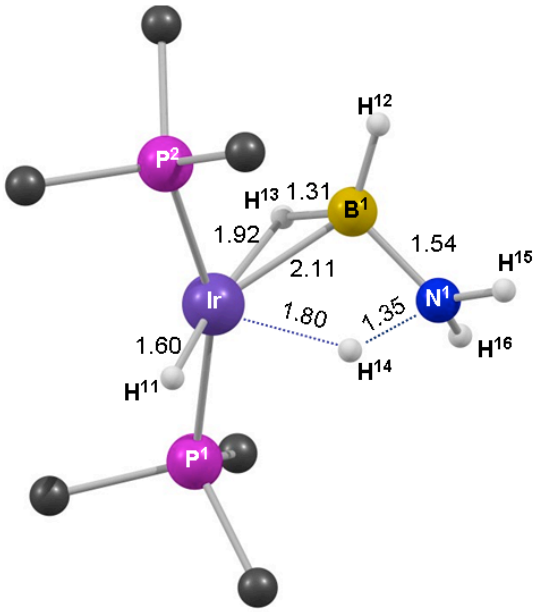
TS6a'$_{BH1}$
(+21.8 kcal/mol)



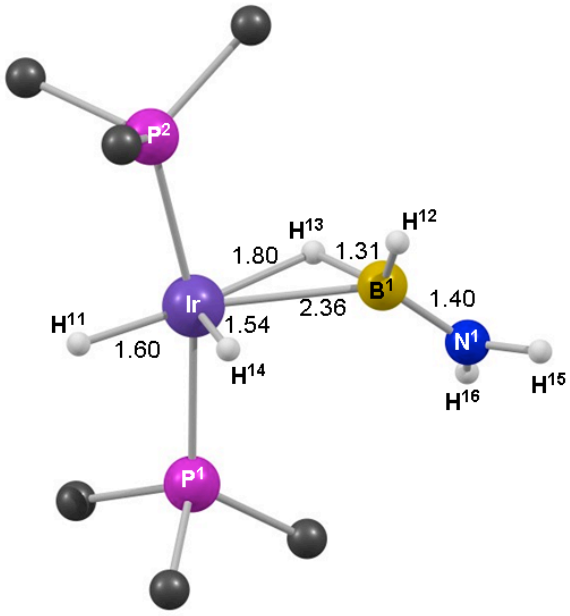
I6a'$_1$
(+21.0 kcal/mol)



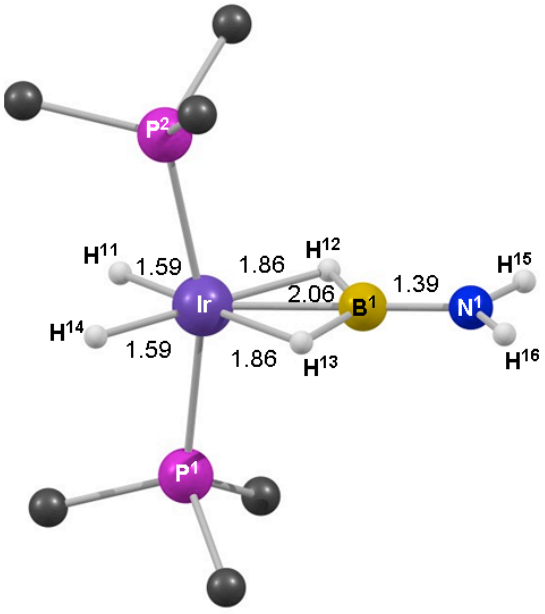
I6a'$_2$
(+16.8 kcal/mol)



TS6a'$_{NH1}$
(+33.8 kcal/mol)

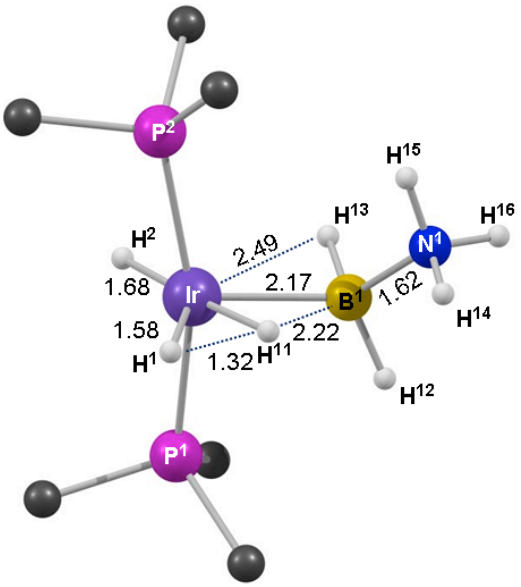


I6a'$_3$
(+9.7 kcal/mol)



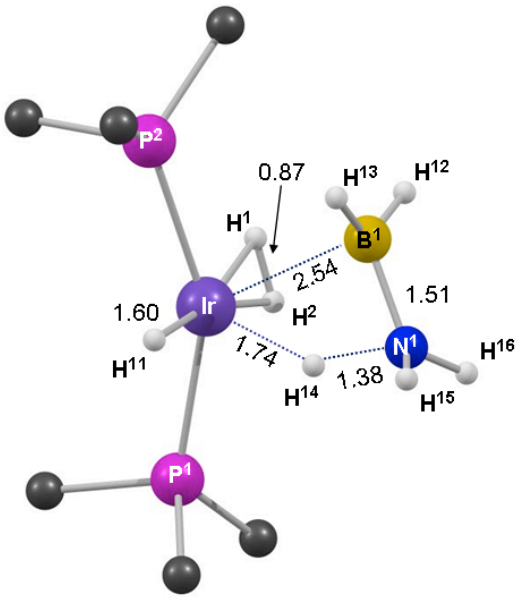
I6a'$_4$
(-2.0 kcal/mol)

Figure S3. Alternative Transition States
(a) Alternative B-H activation transition state

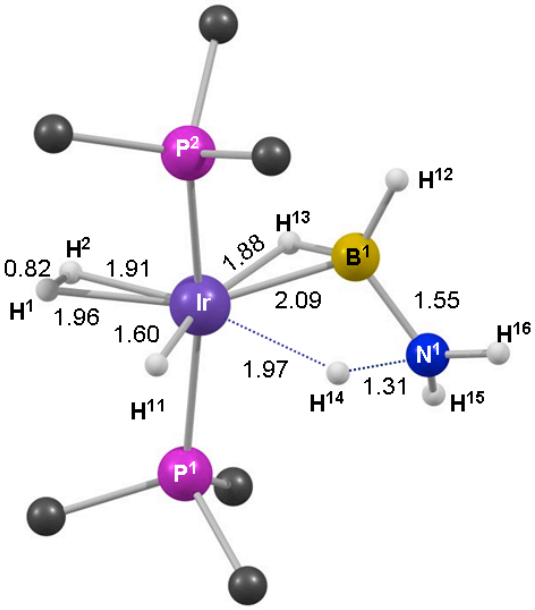


TS6a'$_{BH1}$ (alt)
(+24.4 kcal/mol)

(b) NH activation without prior H_2 loss



TS6a'$_{NH1}$ (H_2 1)
(+36.3 kcal/mol)



TS6a'$_{NH1}$ (H_2 2)
(+43.6 kcal/mol)

H_2

```
H   0.00000  0.00000  0.37525
H   0.00000  0.00000 -0.37525

SCF (BS1) =     -1.17646513415
H 0K=           -1.166541
H 298K=         -1.164180
G 298K=         -1.178048
SCF (C6H5F) =   -1.17656538794
BP86-D3 =       -1.17646516415
Lowest Frequency = 4356.2794cm-1
```

H_3BNH_3

```
B  -0.93462  0.00015 -0.00016
N   0.72902  0.00001  0.00002
H  -1.24462 -1.00219 -0.62233
H  -1.24469 -0.03902  1.17903
H  -1.24593  1.03967 -0.55563
H   1.10226 -0.84367  0.45096
H   1.10140  0.81290  0.50512
H   1.10153  0.03153 -0.95647

SCF (BS1) =     -83.2100017753
H 0K=           -83.141716
H 298K=         -83.137848
G 298K=         -83.165228
SCF (C6H5F) =   -83.2237006753
BP86-D3 =       -83.2124917353
Lowest Frequency = 266.3637cm-1
```

$H_2B{=}NH_2$

```
B  -0.78403  0.00006 -0.00006
N   0.61464 -0.00007 -0.00017
H  -1.36525 -1.05670  0.00014
H  -1.36439  1.05686  0.00036
H   1.17356  0.85017  0.00036
H   1.17379 -0.85014  0.00063

SCF (BS1) =     -82.0327609808
H 0K=           -81.985966
H 298K=         -81.982688
G 298K=         -82.008409
SCF (C6H5F) =   -82.0357047946
BP86-D3 =       -82.0338633008
Lowest Frequency = 577.9850cm-1
```

(a) Model 1. Dehydrogenation in $[Ir(PMe_3)_2(H)_2(\eta^2\text{-}H_3BNH_3)]^+$ (6a′) without added H_3BNH_3.

6a'

```
Ir -0.04545 -0.07043 -0.00012
H   0.98884  3.82238  0.82704
P  -2.39882 -0.27477  0.00003
P   2.27051 -0.50858  0.00004
B  -0.20748  2.15024  0.00010
N   1.03402  3.20950 -0.00002
C  -3.26740  0.47103  1.46362
C  -2.97872 -2.03666 -0.00045
C   3.25729  0.09417  1.46442
C   2.64473 -2.32737 -0.00301
C  -3.26779  0.47191 -1.46288
C   3.25936  0.09925 -1.46090
H   0.98847  3.82255 -0.82692
H  -0.09151 -1.31473 -0.98086
H  -0.09138 -1.31473  0.98065
H  -0.08311  1.46437 -1.10276
H  -0.08277  1.46415  1.10279
H  -1.21441  2.81696  0.00030
H   1.95609  2.75164 -0.00030
H  -3.06684  1.55294  1.49362
H  -2.87758  0.01249  2.38546
H  -4.35448  0.30118  1.40007
H  -2.58710 -2.54574  0.89326
H  -2.58737 -2.54516 -0.89461
H  -4.07958 -2.08341 -0.00030
H   2.79437 -0.29061  2.38626
H   3.25111  1.19549  1.51239
H   4.30198 -0.25261  1.40628
H   2.19443 -2.78383 -0.89745
H   2.19277 -2.78713  0.88890
H   3.73210 -2.50536 -0.00233
H  -2.87826  0.01388 -2.38510
H  -3.06720  1.55384 -1.49232
H  -4.35485  0.30206 -1.39912
H   3.25441  1.20078 -1.50444
H   2.79715 -0.28137 -2.38482
H   4.30369 -0.24867 -1.40299

SCF (BS1) =     -441.491395970
H 0K=           -441.179582
H 298K=         -441.158149
G 298K=         -441.230236
SCF (C6H5F) =   -441.548123416
BP86-D3 =       -441.537085440
Lowest Frequency = 14.9862cm-1
```

TS6a′BH1

```
C  -3.17354  0.25354  1.55769
P  -2.30324 -0.39548  0.04160
Ir  0.04991 -0.13502 -0.07309
P   2.41961 -0.19044  0.05064
C   3.10668 -1.91531  0.05222
C  -3.31108  0.30193 -1.36694
C  -2.82551 -2.17895  0.03824
B   0.22525  1.92679 -0.09872
N  -0.98675  3.00174  0.07756
H  -0.89219  3.81007 -0.55740
H  -0.94890  3.37752  1.03668
C   3.31827  0.62910 -1.35299
C   3.16043  0.56929  1.57220
H   0.12852 -1.81355  0.03149
H  -4.24700  0.00513  1.53337
H  -2.71026 -0.20120  2.44681
H  -3.06373  1.34670  1.64132
H  -3.92189 -2.26769  0.10377
H  -2.47163 -2.65592 -0.88850
H  -2.36246 -2.68873  0.89695
H  -4.37830  0.05399 -1.24688
```

H -3.21058 1.39832 -1.43161
H -2.93919 -0.12538 -2.31111
H   0.07266 -1.50160 -1.06502
H -1.92366 2.59789 -0.05644
H   0.06728 1.27716 -1.28467
H   0.03629 -0.38853 1.50891
H   1.22966 2.60198 -0.04784
H   4.25854 0.47907 1.55855
H   2.87687 1.63115 1.62028
H   2.75804 0.05537 2.45864
H   4.40831 0.54266 -1.21610
H   3.02691 0.14419 -2.29747
H   3.03780 1.69218 -1.39798
H   4.20628 -1.89428 0.12033
H   2.69659 -2.46735 0.91178
H   2.80677 -2.42721 -0.87505

SCF (BS1) =   -441.451559536
H 0K=   -441.145361
H 298K=   -441.123998
G 298K=   -441.194705
SCF (C6H5F) =   -441.507819543
BP86-D3 =   -441.498524916
Lowest Frequency = -701.5678cm-1

I6a'1

C -3.06646 0.19316 1.66849
P -2.29567 -0.37647 0.06939
Ir 0.05252 -0.13395 -0.12102
P   2.41339 -0.17331 0.07917
C   3.12004 -1.89172 0.02263
C -3.40802 0.37824 -1.23085
C -2.82465 -2.15971 0.00807
B   0.21929 1.88472 -0.10492
N -1.00381 2.95219 0.06894
H -0.87970 3.77966 -0.53504
H -1.00790 3.29565 1.04046
C   3.38309 0.72535 -1.22611
C   3.06597 0.50496 1.67777
H   0.13709 -1.96373 -0.50798
H -4.13756 -0.06395 1.70323
H -2.54110 -0.29695 2.50236
H -2.95757 1.28228 1.79270
H -3.91380 -2.25086 0.14843
H -2.54526 -2.59008 -0.96604
H -2.30408 -2.71493 0.80331
H -4.45985 0.10001 -1.05381
H -3.34123 1.47952 -1.24261
H -3.09428 0.01323 -2.22117
H   0.06539 -1.55659 -1.25913
H -1.93353 2.55520 -0.12402
H   0.10452 1.30257 -1.33009
H   0.05960 -0.88955 1.29092
H   1.21726 2.56284 0.01530
H   4.16398 0.42209 1.71817
H   2.77083 1.56096 1.76734
H   2.62030 -0.05812 2.51199
H   4.46412 0.64699 -1.02726
H   3.15780 0.28380 -2.20921
H   3.08869 1.78542 -1.23763
H   4.21364 -1.86497 0.15535
H   2.66935 -2.49633 0.82462
H   2.88408 -2.35432 -0.94833

SCF (BS1) =   -441.454713184
H 0K=   -441.146887
H 298K=   -441.125193
G 298K=   -441.196334
SCF (C6H5F) =   -441.510670465
BP86-D3 =   -441.501691044
Lowest Frequency = 30.5395cm-1

I6a'2

C -3.21951 0.25463 1.58391
P -2.37578 -0.26348 0.01257
C -2.84506 -2.05444 -0.17404
C -3.35899 0.58056 -1.31963
Ir -0.04541 -0.02072 -0.02361
P   2.27262 -0.44506 0.01039
C   2.50545 -2.20919 -0.54903
B -0.26725 1.96002 -0.16029
N   0.97003 2.97479 0.13329
H   0.95244 3.26190 1.12299
C   3.45911 0.46836 -1.11189
C   3.15504 -0.41556 1.65089
H   1.88511 2.54045 -0.05379
H -0.07026 -0.92557 1.29091
H -0.10779 1.38003 -1.33962
H -1.27673 2.60588 0.01362
H   0.89829 3.83734 -0.43011
H -3.06656 1.33402 1.73620
H -2.76964 -0.28803 2.42918
H -4.29944 0.04029 1.53723
H -2.40512 -2.63494 0.65116
H -2.45640 -2.43985 -1.12947
H -3.94136 -2.16725 -0.15719
H   2.59909 -1.04730 2.36021
H   3.18029 0.61008 2.05154
H   4.18664 -0.79048 1.55059
H   2.13383 -2.32151 -1.57915
H   1.93403 -2.87906 0.11179
H   3.57190 -2.48586 -0.51255
H -3.01109 0.22740 -2.30260
H -3.20141 1.66813 -1.25773
H -4.43317 0.36078 -1.20923
H   3.62426 1.50225 -0.76089
H   3.04705 0.49987 -2.13226
H   4.44002 -0.03470 -1.12985

SCF (BS1) =   -440.269999941
H 0K=   -439.977673
H 298K=   -439.956453
G 298K=   -440.027937
SCF (C6H5F) =   -440.328144524
BP86-D3 =   -440.311614561
Lowest Frequency = 23.5160cm-1

TS6a'NH1

C -3.28658 0.41034 1.40122
P -2.32288 -0.37278 0.02255
C -2.60640 -2.19496 0.25604

```
C  -3.30350  0.01667 -1.50694
Ir -0.00180  0.05185 -0.02033
P   2.32490 -0.39354  0.00060
C   2.58087 -2.21804 -0.25198
B  -0.56617  2.00796 -0.55773
N   0.39242  2.82201  0.32305
H  -0.00399  3.55530  0.92239
C   3.35181  0.37856 -1.34495
C   3.27187 -0.02879  1.55681
H   0.50852  1.56561  0.80879
H  -0.03231 -0.78565  1.33743
H  -0.00349  1.28200 -1.48894
H  -1.64972  2.48055 -0.77678
H   1.29415  3.11513 -0.06506
H  -3.28032  1.50385  1.27525
H  -2.81279  0.15794  2.36201
H  -4.32758  0.04894  1.39527
H  -2.17704 -2.50905  1.21912
H  -2.11006 -2.75231 -0.55347
H  -3.68585 -2.41753  0.24042
H   2.78088 -0.53678  2.40071
H   3.26971  1.05500  1.75130
H   4.31307 -0.37879  1.46876
H   2.12833 -2.52525 -1.20722
H   2.09779 -2.77119  0.56753
H   3.65839 -2.45011 -0.26737
H  -2.87257 -0.52980 -2.36011
H  -3.26068  1.09529 -1.71791
H  -4.35407 -0.28761 -1.37244
H   3.37153  1.47298 -1.22333
H   2.90626  0.14000 -2.32285
H   4.38550 -0.00246 -1.30916

SCF (BS1) =     -440.242859578
H 0K=           -439.956904
H 298K=         -439.936262
G 298K=         -440.006385
SCF (C6H5F) =   -440.295696468
BP86-D3 =       -440.284331978
Lowest Frequency = -1129.7469cm-1
```

I6a'3

```
C  -3.11070 -0.58086  1.68705
P  -2.41842 -0.21993  0.00429
C  -3.03685 -1.62147 -1.05091
C  -3.40195  1.24146 -0.58457
Ir -0.04959 -0.06728 -0.05000
P   2.28312 -0.47660  0.01895
C   2.70460 -1.93457 -1.05955
B   0.04605  2.28091  0.13232
N   1.08648  3.19548 -0.06328
H   1.14592  4.06026  0.47289
C   3.51865  0.80549 -0.52161
C   2.89619 -0.97029  1.69992
H  -0.04936  0.26794  1.45478
H  -0.08198 -1.54858  0.56017
H  -0.10002  1.50515 -0.91668
H  -0.82869  2.55908  0.90831
H   1.79741  3.12107 -0.78796
H  -2.87183  0.25296  2.36517
H  -2.64940 -1.50016  2.07844
H  -4.20406 -0.70742  1.63525
H  -2.59144 -2.56545 -0.70174
H  -2.74566 -1.45600 -2.10024
H  -4.13531 -1.68920 -0.99003
H   2.30199 -1.82159  2.06474
H   2.77022 -0.12642  2.39582
H   3.96043 -1.25230  1.65626
H   2.45657 -1.70868 -2.10885
H   2.12008 -2.80891 -0.73569
H   3.78024 -2.16455 -0.98738
H  -3.13774  1.46390 -1.63023
H  -3.16028  2.11787  0.03603
H  -4.48204  1.03319 -0.51830
H   3.44523  1.68334  0.13775
H   3.31210  1.10590 -1.56138
H   4.54027  0.39575 -0.46623

SCF (BS1) =     -440.279880026
H 0K=           -439.990238
H 298K=         -439.968934
G 298K=         -440.041357
SCF (C6H5F) =   -440.335608218
BP86-D3 =       -440.321888156
Lowest Frequency = 12.4998cm-1
```

I6a'4

```
C  -3.25442  0.30904  1.46568
P  -2.34858 -0.38242  0.00000
C  -3.25447  0.30918 -1.46558
Ir -0.00009 -0.02958 -0.00001
B   0.00054  2.02830 -0.00000
N   0.00099  3.41578  0.00000
P   2.34849 -0.38275  0.00000
C   3.25443  0.30882 -1.46555
C  -2.80413 -2.17890 -0.00008
C   3.25433  0.30850  1.46576
C   2.80384 -2.17928 -0.00018
H   0.00118  3.97354  0.85252
H   0.00117  3.97354 -0.85251
H  -0.00050 -1.24936 -1.02262
H  -0.00049 -1.24938  1.02258
H   0.00067  1.41457 -1.16577
H   0.00067  1.41457  1.16577
H  -3.14582  1.40461  1.48138
H  -2.81773 -0.10349  2.38817
H  -4.32434  0.04907  1.41806
H  -2.37975 -2.65992  0.89415
H  -2.37979 -2.65984 -0.89437
H  -3.89943 -2.29840 -0.00006
H   2.81753 -0.10405  2.38819
H   3.14588  1.40409  1.48157
H   4.32422  0.04841  1.41819
H   2.37945 -2.66010 -0.89451
H   2.37938 -2.66031  0.89400
H   3.89912 -2.29891 -0.00015
H  -2.81781 -0.10326 -2.38813
H  -3.14587  1.40475 -1.48118
H  -4.32439  0.04921 -1.41794
H   3.14598  1.40441 -1.48113
H   2.81768 -0.10353 -2.38810
H   4.32432  0.04872 -1.41796
```

SCF (BS1) = -440.305871714
H 0K= -440.016583
H 298K= -439.995779
G 298K= -440.067512
SCF (C6H5F) = -440.355551209
BP86-D3 = -440.346327234
Lowest Frequency = 15.0554cm-1

(b) Alternative Transition States

TS6a'BH1(alt)

C	3.45315	0.38107	-1.20452
P	2.31964	-0.42943	0.03510
C	3.12813	-0.06241	1.66913
C	2.67658	-2.23814	-0.21731
Ir	-0.02836	-0.05566	-0.07163
P	-2.36587	-0.31623	0.01999
C	-3.16201	0.13195	1.63358
B	-0.34707	2.00987	0.51374
N	0.65337	3.10685	-0.14309
H	0.41580	3.27098	-1.13294
H	0.57062	4.00973	0.35018
C	-3.37055	0.58717	-1.25438
C	-2.84079	-2.09543	-0.22911
H	1.64014	2.81696	-0.11002
H	0.04735	0.95323	-1.40402
H	4.48198	-0.00203	-1.10562
H	3.08353	0.17633	-2.22125
H	3.47373	1.47292	-1.05291
H	3.75878	-2.43182	-0.13767
H	2.13884	-2.81858	0.54736
H	2.32256	-2.54849	-1.21243
H	4.19375	-0.34310	1.65133
H	3.03823	1.00984	1.90415
H	2.60585	-0.63164	2.45291
H	-0.08258	-0.97712	1.33463
H	0.03914	1.74647	1.64411
H	-0.12048	-0.34078	-1.62779
H	-1.45879	2.46345	0.35852
H	-4.44307	0.36378	-1.13592
H	-3.20978	1.67018	-1.14297
H	-3.04195	0.27853	-2.25900
H	-4.24731	-0.05395	1.59290
H	-2.70884	-0.47575	2.43134
H	-2.97794	1.19518	1.84880
H	-3.93637	-2.20869	-0.18534
H	-2.47785	-2.44141	-1.20914
H	-2.37398	-2.70569	0.55864

SCF (BS1) = -441.447233222
H 0K= -441.140941
H 298K= -441.118976
G 298K= -441.191421
SCF (C6H5F) = -441.503252271
BP86-D3 = -441.493567512
Lowest Frequency = -605.6336cm-1

TS6a'NH1 (H_2 1)

C	-3.00165	-0.21981	1.79044
P	-2.28671	-0.45659	0.09741
C	-2.45618	-2.28701	-0.19922
Ir	0.02225	0.06689	-0.16043
P	2.31513	-0.41670	0.07984
C	2.52066	-2.26392	0.10051
C	-3.54504	0.28785	-1.04391
C	3.12670	0.13884	1.65321
C	3.49313	0.14446	-1.24341
B	-0.98151	2.40142	-0.10111
N	0.35338	2.98102	0.30089
H	0.88546	3.53321	-0.37712
H	-0.39812	0.16760	-1.89574
H	-2.38983	-0.77411	2.51786
H	-4.03969	-0.58813	1.81902
H	-2.98430	0.84904	2.04976
H	-3.50492	-2.59435	-0.05373
H	-1.81509	-2.83579	0.50706
H	-2.14701	-2.52915	-1.22755
H	0.66765	1.63659	0.20505
H	0.45012	0.35442	-1.87066
H	0.00586	-0.08098	1.43703
H	-1.27629	2.52347	-1.25953
H	-1.79891	2.33981	0.77760
H	0.48762	3.31104	1.26062
H	-3.55719	1.38029	-0.91633
H	-4.54481	-0.12040	-0.82468
H	-3.27456	0.05417	-2.08546
H	2.14823	-2.68866	-0.84406
H	1.94260	-2.68549	0.93649
H	3.58571	-2.52192	0.22244
H	2.54580	-0.23602	2.50924
H	3.14421	1.23903	1.69180
H	4.15942	-0.24122	1.70928
H	3.50238	1.24456	-1.28880
H	3.16114	-0.24713	-2.21767
H	4.51294	-0.21741	-1.03417

SCF (BS1) = -441.428566307
H 0K= -441.126559
H 298K= -441.104617
G 298K= -441.177032
SCF (C6H5F) = -441.479983556
BP86-D3 = -441.474865277
Lowest Frequency = -698.2132cm-1

TS6a'NH1 (H_2 2)

C	-3.12035	0.69854	1.52208
P	-2.39836	-0.22204	0.08319
C	-2.97713	-1.96613	0.36032
C	-3.40083	0.33150	-1.37897
Ir	-0.02896	-0.08714	-0.11117
P	2.34296	-0.33315	0.06524
C	2.85504	-2.12013	0.03937
B	-0.39692	1.94397	-0.42956
N	0.73695	2.78740	0.21604
H	0.47475	3.63790	0.72455
C	3.38655	0.40984	-1.28657
C	3.12543	0.29321	1.63075
H	0.61999	1.58458	0.71570
H	-0.04361	-0.79413	1.32574
H	-0.04632	1.20252	-1.48529

```
H  -1.46532  2.49495 -0.48036
H   1.62134  2.90305 -0.28519
H  -2.92496  1.77474  1.40398
H  -2.63966  0.34808  2.44819
H  -4.20729  0.52809  1.58111
H  -2.49265 -2.37220  1.26135
H  -2.70417 -2.58964 -0.50529
H  -4.07114 -1.98923  0.49038
H   2.64821 -0.20514  2.48843
H   2.96737  1.37849  1.72599
H   4.20676  0.08178  1.63555
H   2.56297 -2.57504 -0.91971
H   2.34813 -2.65448  0.85743
H   3.94614 -2.20755  0.16564
H  -3.13243 -0.28302 -2.25229
H  -3.18072  1.38527 -1.60525
H  -4.47686  0.21923 -1.16946
H   3.28318  1.50633 -1.29807
H   3.04889  0.01982 -2.25914
H   4.44903  0.15679 -1.13827
H  -0.15218 -1.99692 -0.53460
H   0.03477 -1.62905 -1.24411

SCF (BS1) =     -441.416668576
H 0K=           -441.116014
H 298K=         -441.094423
G 298K=         -441.164933
SCF (C6H5F) =   -441.467624757
BP86-D3 =       -441.463943766
Lowest Frequency = -1400.9997cm-1
```

(3) Model 2. Dehydrogenation of 6a' in the presence of one additional $H_3B{\cdot}NH_3$ molecule

Figure S4. Computed reaction profile for amineborane dehydrogenation in **6a'** in the presence of added $H_3B{\bullet}NH_3$

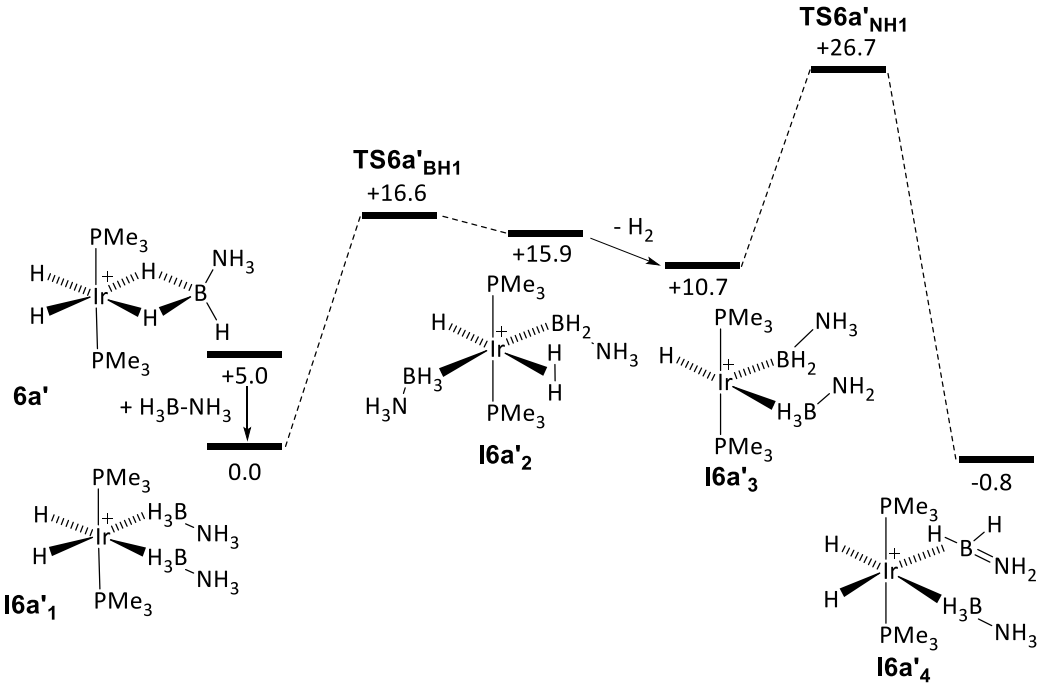
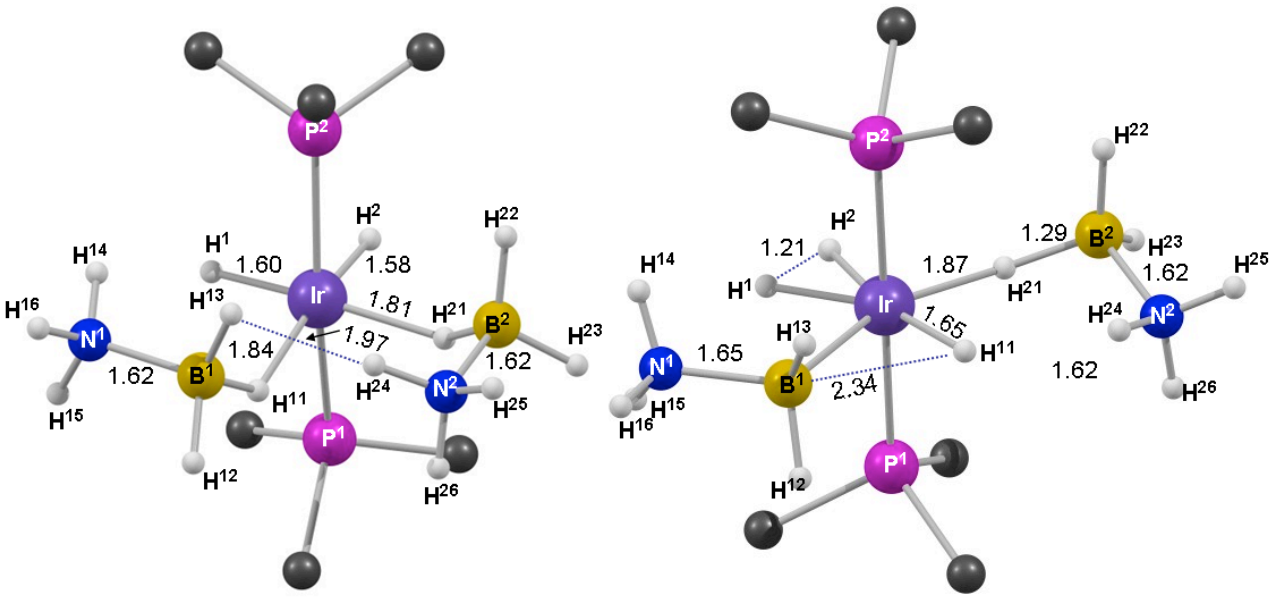
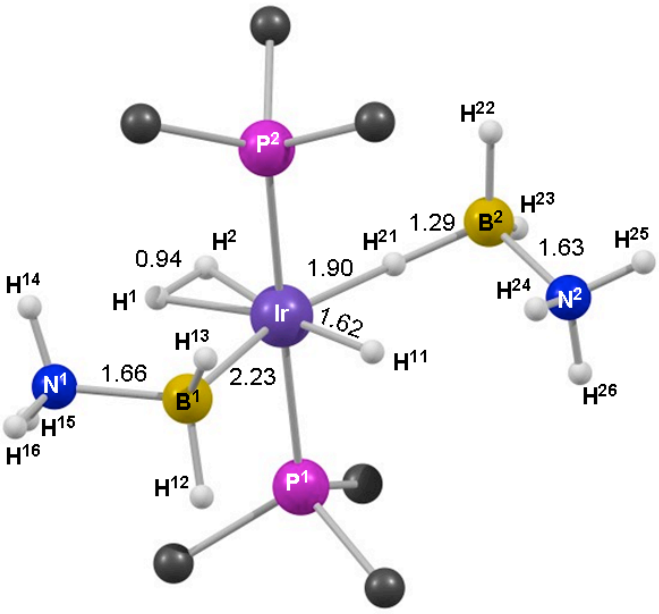
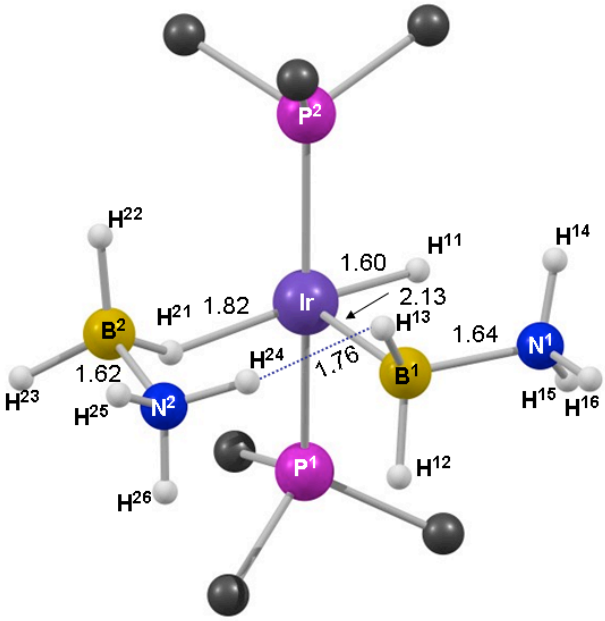


Figure S5. Computed Geometries

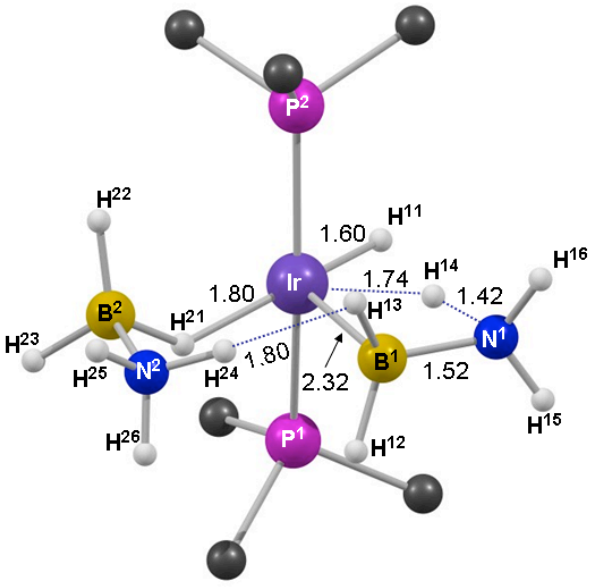




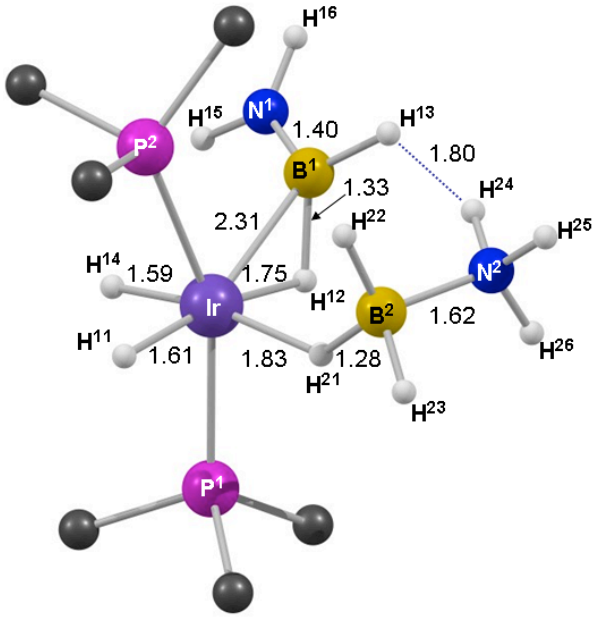
I6a'$_2$
(+15.9 kcal/mol)



I6a'$_3$
(+10.7 kcal/mol)

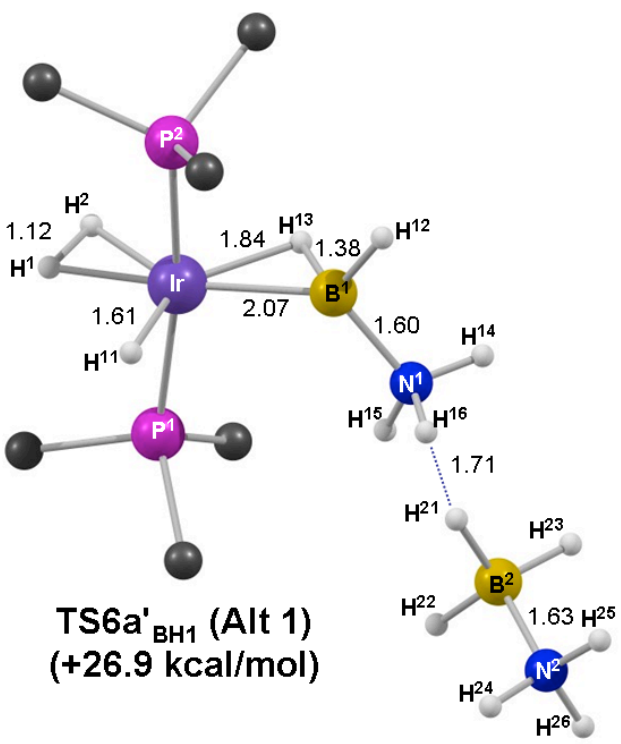


TS6a'$_{NH1}$
(+26.7 kcal/mol)

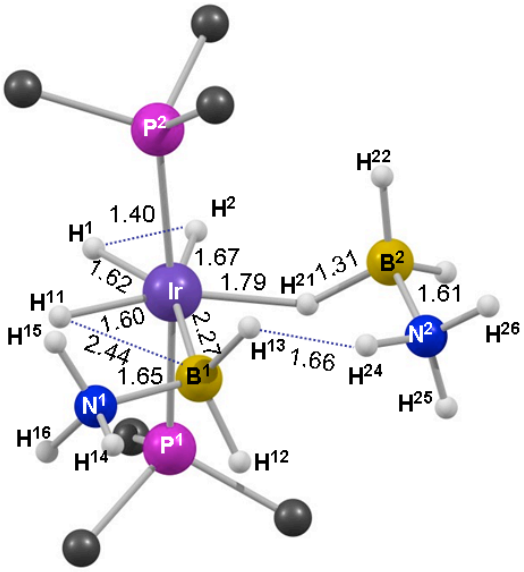


I6a'$_4$
(-0.8 kcal/mol)

Figure S6. Alternative Transition States
(a) Alternative B-H activation transition states

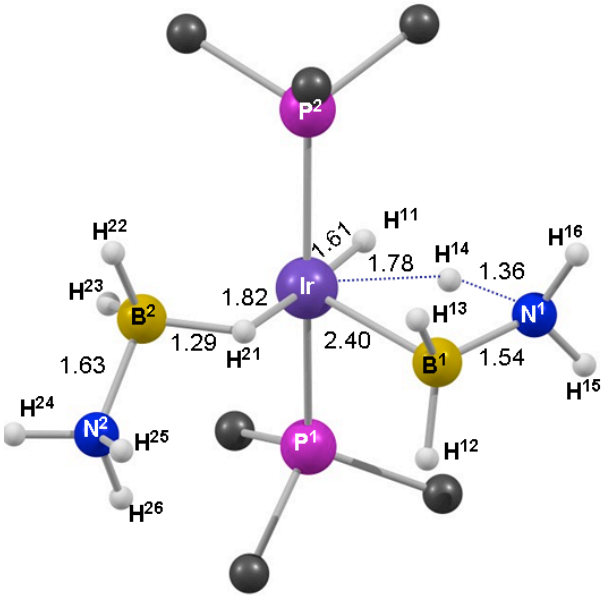


TS6a'$_{BH1}$ (Alt 1)
(+26.9 kcal/mol)

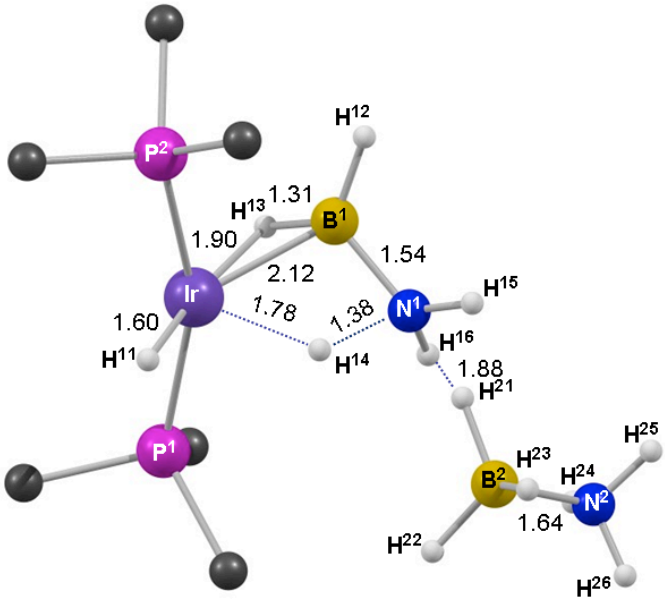


TS6a'$_{BH1}$ (Alt 2)
(+19.3 kcal/mol)

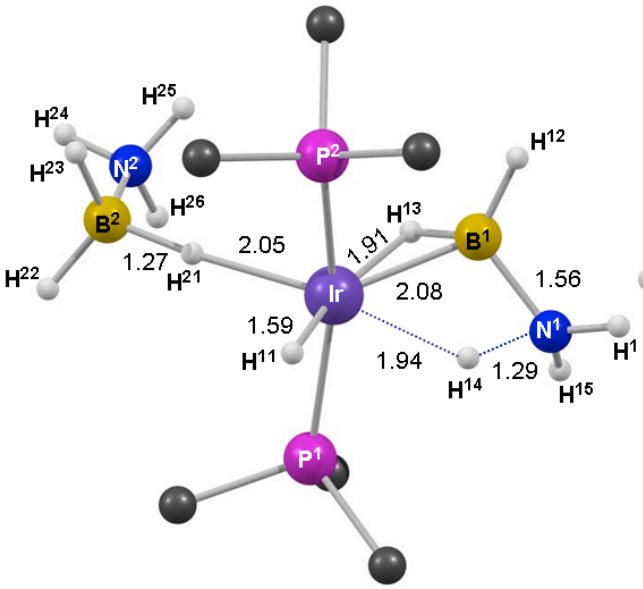
(b) Alternative N-H activation transition states



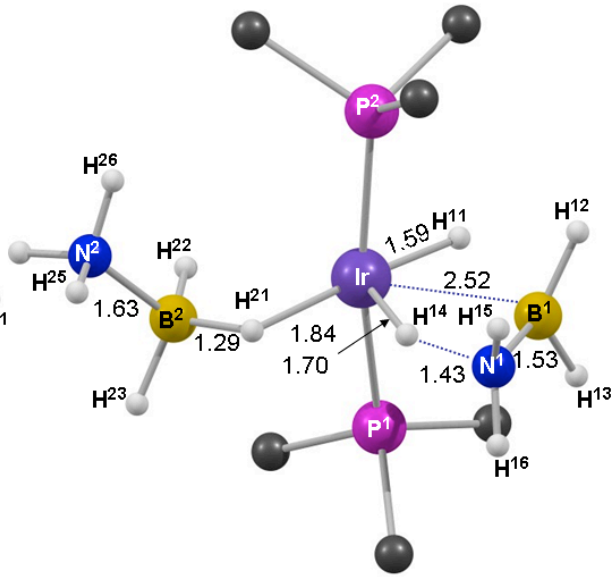
TS6a'$_{NH1}$ (Alt 1)
(+26.9 kcal/mol)



TS6a'$_{NH1}$ (Alt 2)
(+39.6 kcal/mol)



TS6a'$_{NH1}$ (Alt 3)
(+36.6 kcal/mol)



TS6a'$_{NH1}$ (Alt 4)
(+30.5 kcal/mol)

(a) Model 2. Dehydrogenation in $[Ir(PMe_3)_2(H)_2(\eta^2\text{-}H_3BNH_3)]^+$ (6a′) with added H_3BNH_3.

I6a′

C	-2.68228	-1.79199	-1.43856
P	-2.24185	-0.64469	-0.04308
C	-3.52913	0.69470	-0.22063
Ir	0.08102	-0.18206	0.01931
P	2.42322	-0.41110	0.00118
C	3.07604	-1.64899	1.22368
C	-2.86745	-1.58558	1.44108
B	-0.35461	2.28975	1.35503
N	-0.53427	1.68268	2.84167
C	3.08558	-1.03431	-1.61956
C	3.47857	1.09121	0.32522
H	0.37230	1.56801	3.31323
H	-1.11898	2.28522	3.43709
H	-0.95806	0.74528	2.78651
H	0.11124	-0.88894	1.45315
H	-3.76205	-2.01287	-1.43658
H	-2.40088	-1.32073	-2.39204
H	-2.11296	-2.72697	-1.32460
H	-4.53703	0.24911	-0.23796
H	-3.45982	1.40663	0.61560
H	-3.35929	1.23363	-1.16509
H	-3.90714	-1.91775	1.28782
H	-2.22052	-2.46046	1.60614
H	-2.83129	-0.94882	2.34028
H	0.40196	1.49227	0.70738
H	-1.45392	2.50332	0.88845
H	0.13003	-1.65206	-0.56931
H	0.33850	3.28468	1.42921
H	4.16466	-1.77851	1.11159
H	2.84949	-1.30984	2.24623
H	2.56926	-2.61152	1.05614
H	4.54892	0.82865	0.30775
H	3.28380	1.85017	-0.44859
H	3.22607	1.51993	1.30736
H	4.18119	-1.14691	-1.58106
H	2.62214	-2.00752	-1.84244
H	2.81269	-0.33004	-2.42046
H	0.32046	0.42445	-1.66864
B	-0.38505	1.18315	-2.43829
N	-0.34710	2.70135	-1.87487
H	0.29011	1.13932	-3.44436
H	-1.53816	0.86669	-2.59621
H	-0.80707	3.33558	-2.54219
H	-0.82660	2.78534	-0.96257
H	0.61146	3.04701	-1.73922

SCF (BS1) = -524.722381046
H 0K= -524.340099
H 298K= -524.313489
G 298K= -524.399371
SCF (C6H5F) = -524.780217151
BP86-D3 = -524.787277216
Lowest Frequency = 1.3146cm-1

TS6a′ BH1

C	-3.14092	0.78673	-1.59754
P	-2.36817	-0.02585	-0.11530
C	-3.16606	0.82283	1.33139
Ir	0.00173	-0.04716	-0.12507
P	2.36512	-0.07851	-0.14066
C	3.15114	-1.70661	-0.58719
C	-3.21144	-1.68889	-0.10707
B	0.03454	-1.82211	1.25766
N	-0.11097	-3.26644	0.46586
C	3.13639	1.08241	-1.37339
C	3.21914	0.34097	1.45722
H	0.64523	-3.42346	-0.21356
H	-0.08045	-4.04030	1.14577
H	-1.00059	-3.34241	-0.04521
H	-0.01930	-1.28254	-1.19200
H	-4.24000	0.78674	-1.51584
H	-2.77359	1.82062	-1.67351
H	-2.84063	0.23863	-2.50435
H	-4.26437	0.75127	1.27788
H	-2.80600	0.35170	2.25894
H	-2.87336	1.88390	1.32267
H	-4.30675	-1.56815	-0.10664
H	-2.92415	-2.25089	-1.01148
H	-2.91361	-2.23912	0.79929
H	0.00581	0.50708	1.42908
H	-0.91461	-1.80831	2.01983
H	-0.00498	-0.22788	-1.78440
H	1.10247	-1.91698	1.83761
H	4.24800	-1.61191	-0.63386
H	2.89262	-2.44934	0.18380
H	2.77763	-2.03646	-1.56973
H	4.31055	0.21688	1.36972
H	3.00023	1.38479	1.73193
H	2.82776	-0.31939	2.24590
H	4.23634	1.05704	-1.31019
H	2.81965	0.78776	-2.38608
H	2.77608	2.10691	-1.19301
H	0.12579	1.74370	-0.64219
B	-0.23279	2.95377	-0.35635
N	0.26507	3.25426	1.15862
H	0.39651	3.64404	-1.12519
H	-1.43308	3.08650	-0.38173
H	-0.13333	4.13636	1.50735
H	-0.02749	2.48104	1.77771
H	1.28719	3.33075	1.23310

SCF (BS1) = -524.692456215
H 0K= -524.314743
H 298K= -524.288823
G 298K= -524.368639
SCF (C6H5F) = -524.751552594
BP86-D3 = -524.760435835
Lowest Frequency = -434.6284cm-1

I6a′2

C	-3.18963	0.79174	-1.51497
P	-2.36698	-0.01010	-0.05154
C	-3.08475	0.89001	1.40672
Ir	0.00286	-0.05281	-0.13259
P	2.36374	-0.09749	-0.07614
C	3.16958	-1.68967	-0.61113

C	-3.25877	-1.64738	0.02396
B	0.03614	-1.89537	1.11524
N	-0.18903	-3.28600	0.24442
C	3.19959	1.14070	-1.18976
C	3.14785	0.20671	1.58197
H	0.53488	-3.42381	-0.47317
H	-0.15821	-4.10236	0.87278
H	-1.10011	-3.30172	-0.23283
H	-0.02252	-1.15742	-1.45124
H	-4.28394	0.81549	-1.38569
H	-2.80522	1.81617	-1.62647
H	-2.94360	0.22175	-2.42504
H	-4.18574	0.84646	1.39775
H	-2.70120	0.43101	2.33090
H	-2.76672	1.94300	1.36082
H	-4.34636	-1.48900	0.10372
H	-3.06226	-2.21690	-0.90031
H	-2.91194	-2.21044	0.90418
H	0.01328	0.49555	1.39007
H	-0.87710	-1.90317	1.92265
H	-0.00598	-0.31067	-1.85411
H	1.11858	-2.07152	1.65192
H	4.26743	-1.59621	-0.59272
H	2.86813	-2.49073	0.08100
H	2.84922	-1.93712	-1.63591
H	4.24279	0.09587	1.52864
H	2.90585	1.22484	1.92522
H	2.73176	-0.51381	2.30211
H	4.29472	1.10800	-1.07004
H	2.93956	0.91329	-2.23554
H	2.83139	2.15437	-0.96909
H	0.10942	1.73753	-0.74791
B	-0.20096	2.96382	-0.51614
N	0.31506	3.31182	0.98676
H	0.43966	3.62136	-1.30494
H	-1.39774	3.13742	-0.53212
H	-0.01435	4.24232	1.27682
H	-0.03610	2.61085	1.65602
H	1.33992	3.31410	1.06283

SCF (BS1) = -524.693583291
H 0K= -524.314431
H 298K= -524.288053
G 298K= -524.369369
SCF (C6H5F) = -524.753054586
BP86-D3 = -524.761558941
Lowest Frequency = 26.2335cm-1

I6a'3

C	2.85399	-0.14354	-2.08457
P	2.31249	-0.36824	-0.31484
Ir	-0.02970	-0.15386	-0.14982
P	-2.36094	-0.28441	-0.31858
C	-2.86949	-0.86793	-2.01384
C	3.46645	0.75940	0.61931
C	3.00365	-2.05277	0.09438
B	-0.10396	0.33015	1.92367
N	0.07535	-1.00978	2.85749
C	-3.24049	-1.47462	0.81245
C	-3.35006	1.27867	-0.10047
B	0.38537	2.64504	-0.70274
N	0.14486	3.26442	0.76977
H	3.94053	-0.30090	-2.18331
H	2.32499	-0.86787	-2.72394
H	2.59689	0.87557	-2.41099
H	4.51519	0.49736	0.40567
H	3.27944	1.79853	0.31074
H	3.28006	0.66958	1.70091
H	4.07371	-2.11541	-0.16228
H	2.89004	-2.25918	1.17138
H	2.44455	-2.81657	-0.46727
H	-0.05967	-1.71530	0.19949
H	-0.27786	1.54356	-0.75492
H	-1.18524	0.80407	2.25595
H	0.85073	1.04879	2.24220
H	-0.67462	-1.68475	2.65767
H	0.96128	-1.49052	2.65336
H	0.05160	-0.79007	3.86483
H	-4.31836	-1.51237	0.58616
H	-2.80784	-2.47945	0.68721
H	-3.11255	-1.14435	1.85607
H	-4.42470	1.09667	-0.26305
H	-3.20074	1.65579	0.92385
H	-2.99472	2.03087	-0.82222
H	-3.96706	-0.93393	-2.09185
H	-2.49456	-0.16116	-2.77065
H	-2.42930	-1.85870	-2.20565
H	-0.22294	3.31272	-1.51154
H	1.57269	2.57227	-0.90395
H	0.65114	4.15283	0.87836
H	-0.84847	3.45286	0.95419
H	0.46678	2.60235	1.50220

SCF (BS1) = -523.514516737
H 0K= -523.150638
H 298K= -523.124961
G 298K= -523.205984
SCF (C6H5F) = -523.572983037
BP86-D3 = -523.576948067
Lowest Frequency = 24.9935cm-1

TS6a'NH1

C	2.79970	-0.67034	-2.03103
P	2.30189	-0.49741	-0.24558
Ir	-0.03848	-0.19117	-0.06983
P	-2.38550	-0.32918	-0.26543
C	-2.85583	-1.09649	-1.89505
C	3.50276	0.76845	0.40819
C	2.94116	-2.07295	0.51355
B	-0.02121	0.94569	1.95107
N	-0.02549	-0.28550	2.85155
C	-3.27795	-1.39178	0.97373
C	-3.36492	1.25249	-0.24584
B	0.40079	2.43594	-1.13965
N	0.40719	3.48265	0.09062
H	3.88014	-0.87215	-2.11456
H	2.23815	-1.50161	-2.48491
H	2.55514	0.25914	-2.56716
H	4.53817	0.44577	0.21320
H	3.32347	1.73181	-0.09170
H	3.35900	0.89309	1.49258
H	4.01629	-2.20179	0.30909

```
H   2.78244 -2.05258  1.60323
H   2.38313 -2.92503  0.09620
H  -0.08184 -1.78062  0.13522
H  -0.33598  1.46472 -0.71117
H  -1.04735  1.59319  1.96668
H   1.04024  1.54976  1.95770
H  -0.05754 -0.83540  1.54761
H   0.82294 -0.54051  3.36292
H  -0.86318 -0.50664  3.39530
H  -4.34624 -1.47750  0.71730
H  -2.82232 -2.39377  0.98651
H  -3.18844 -0.94502  1.97636
H  -4.43871  1.05264 -0.39152
H  -3.21704  1.75848  0.72120
H  -3.00326  1.90691 -1.05444
H  -3.95178 -1.16603 -1.99086
H  -2.45651 -0.48150 -2.71650
H  -2.41698 -2.10379 -1.96294
H  -0.29897  2.86849 -2.02822
H   1.53739  2.19365 -1.45574
H   1.01785  4.28465 -0.11317
H  -0.53000  3.85425  0.29198
H   0.74009  3.02169  0.95854

SCF (BS1) =     -523.486915103
H 0K=           -523.130501
H 298K=         -523.105084
G 298K=         -523.185687
SCF (C6H5F) =   -523.541195700
BP86-D3 =       -523.548307743
Lowest Frequency = -864.4863cm-1
```

I6a'4

```
C   2.46422 -0.69139 -2.30420
P   2.17064 -0.56795 -0.47465
Ir -0.11658 -0.11630  0.02555
P  -2.46895 -0.34562 -0.12067
C  -3.19552  0.31152 -1.69681
C   3.54838  0.56112  0.06984
C   2.72030 -2.21960  0.16931
B   0.85900  0.68317  1.95925
N   1.22672 -0.13884  3.03734
C  -3.04103 -2.10913 -0.07287
C  -3.48278  0.47315  1.20676
B   0.31936  2.45557 -1.21912
N   0.37710  3.51755  0.00492
H   3.52475 -0.90974 -2.50968
H   1.83308 -1.49389 -2.71460
H   2.18168  0.26071 -2.77786
H   4.50773  0.18007 -0.31596
H   3.37327  1.57080 -0.33077
H   3.59129  0.60624  1.16773
H   3.75093 -2.43933 -0.15275
H   2.67278 -2.20922  1.26886
H   2.03920 -2.99643 -0.20941
H  -0.20226 -0.82959 -1.41323
H  -0.41201  1.48543 -0.79984
H  -0.41745  0.58924  1.60230
H   1.40069  1.77063  1.91423
H  -0.13089 -1.57125  0.66004
H   1.93124  0.12068  3.72534
H   0.79531 -1.04466  3.21386
H  -4.13475 -2.16756 -0.19403
H  -2.54745 -2.66592 -0.88367
H  -2.75087 -2.55848  0.88907
H  -4.55674  0.27939  1.05195
H  -3.17965  0.08179  2.19029
H  -3.30531  1.55971  1.18748
H  -4.28901  0.17529 -1.70856
H  -2.95249  1.38043 -1.79560
H  -2.74642 -0.22506 -2.54639
H  -0.37111  2.92029 -2.09874
H   1.45208  2.19954 -1.54409
H   0.92934  4.34274 -0.26420
H  -0.55407  3.85379  0.28224
H   0.81809  3.09415  0.83969

SCF (BS1) =     -523.537573569
H 0K=           -523.176522
H 298K=         -523.151121
G 298K=         -523.231575
SCF (C6H5F) =   -523.590555405
BP86-D3 =       -523.598174769
Lowest Frequency = 14.4854cm-1
```

(b) Alternative Transition States

TS6a'BH1 (Alt 1)

```
Ir -0.67562  0.33577  0.04981
P  -2.42056 -1.24948 -0.16679
P   0.97486  2.02423 -0.09031
B   0.42736 -1.17517  0.94562
N   1.98645 -1.14424  1.31544
C  -2.04586 -2.71234 -1.24575
C  -3.96477 -0.54642 -0.92346
C   2.46537  1.68770 -1.15592
C   0.32049  3.59841 -0.83355
C  -3.03173 -2.00488  1.41701
C   1.71510  2.64671  1.50776
B   4.63764 -2.05400  0.00717
N   5.83918 -2.83343 -0.77274
H  -1.80619  1.55066  0.37880
H  -1.70645  1.42156 -0.73668
H  -0.24447 -0.25983  1.73264
H  -0.34607  0.06335 -1.49901
H   0.07379 -2.31727  1.14871
H   2.18906 -1.59343  2.22140
H   2.40268 -0.20436  1.33860
H   2.54578 -1.68545  0.61301
H  -1.18008 -3.24970 -0.83092
H  -1.78727 -2.35174 -2.25318
H  -2.91251 -3.39046 -1.30470
H  -3.72779 -0.14632 -1.92121
H  -4.33607  0.27492 -0.29142
H  -4.74329 -1.32120 -1.01321
H   2.11255  1.43805 -2.16860
H   3.04212  0.82896 -0.77638
H   3.12156  2.57230 -1.20168
H  -0.50366  3.97622 -0.20927
H  -0.07004  3.38176 -1.83962
H   1.11256  4.36166 -0.90115
H  -3.40050 -1.20363  2.07585
H  -2.19983 -2.52172  1.91863
```

```
H  -3.84445 -2.72213  1.21817
H   2.26482  1.85044  2.03621
H   0.89867  2.98562  2.16419
H   2.40711  3.48374  1.31924
H   3.59306 -2.51221 -0.45926
H   4.76607 -0.86624 -0.24073
H   4.76784 -2.30801  1.19209
H   5.80019 -3.84875 -0.61493
H   5.80418 -2.67842 -1.78855
H   6.75877 -2.50979 -0.44556

SCF (BS1) =     -524.689234769
H 0K=           -524.313096
H 298K=         -524.286449
G 298K=         -524.371152
SCF (C6H5F) =   -524.742636502
BP86-D3 =       -524.743946859
Lowest Frequency = -687.4789cm-1
```

TS6a'BH1 (Alt 2)

```
C  -3.10116 -0.55523 -1.83617
P  -2.34956 -0.43751 -0.14067
Ir  0.01843 -0.27300 -0.15373
P   2.37736 -0.38449 -0.19995
C   3.05339 -1.62188 -1.40997
C  -2.96800 -1.99329  0.67550
C  -3.38630  0.87709  0.67403
B   0.13774  1.09529  1.65895
N   0.04026  0.34995  3.12286
C   3.25828  1.18463 -0.66949
C   3.22144 -0.86342  1.38861
N  -0.09097  3.40727 -0.33864
B  -0.41546  2.28692 -1.44358
H   0.80581 -0.32525  3.24530
H   0.09189  1.02110  3.90286
H  -0.83464 -0.17910  3.22597
H   0.03208 -1.27390  1.09920
H  -4.19714 -0.65619 -1.77713
H  -2.84114  0.34808 -2.40817
H  -2.67591 -1.43096 -2.35033
H  -4.45473  0.62090  0.58979
H  -3.11491  0.97219  1.73611
H  -3.20300  1.84136  0.17755
H  -4.06233 -2.08048  0.57946
H  -2.48778 -2.86196  0.19961
H  -2.69780 -1.99033  1.74324
H   0.27587  1.23988 -1.06940
H  -0.81303  1.88309  1.69607
H   0.00420 -1.77705 -0.76753
H   1.19675  1.71442  1.72045
H   4.31167 -0.94036  1.24789
H   3.01714 -0.09363  2.14968
H   2.83225 -1.83677  1.72660
H   4.34778  1.02574 -0.71332
H   2.89731  1.51884 -1.65457
H   3.03520  1.95456  0.08570
H   4.15533 -1.63318 -1.39702
H   2.67164 -2.62208 -1.15243
H   2.69747 -1.36239 -2.41895
H  -0.02930 -0.77439 -1.74454
H   0.15704  2.54557 -2.47694
H  -1.60849  2.14721 -1.52350
H  -0.65338  4.25186 -0.50310
H  -0.31087  3.03519  0.61304
H   0.89674  3.69036 -0.33688

SCF (BS1) =     -524.692535095
H 0K=           -524.313849
H 298K=         -524.288346
G 298K=         -524.367523
SCF (C6H5F) =   -524.748815965
BP86-D3 =       -524.760160965
Lowest Frequency = -508.4459cm-1
```

TS6a'NH1 (Alt 1)

```
C   2.98573  0.96591 -1.73783
P   2.39610 -0.06586 -0.30594
C   3.39735  0.57067  1.12590
C   3.16187 -1.72520 -0.65482
Ir  0.04125 -0.05925 -0.11319
B   0.17960  2.40285  0.32540
H   1.24725  2.93351  0.53467
B  -0.13368 -0.82090  2.15465
N   0.14716 -2.29361  1.82021
P  -2.28240 -0.29740 -0.39265
C  -2.98808 -1.95826  0.06589
C  -3.47282  0.85994  0.47111
C  -2.79010 -0.11512 -2.17490
H   4.08367  0.92057 -1.82397
H   2.52933  0.59101 -2.66696
H   2.67011  2.00871 -1.58301
H   4.47510  0.51621  0.90276
H   3.11369  1.61550  1.32284
H   3.17459 -0.02653  2.02344
H   4.25093 -1.63167 -0.79418
H   2.96510 -2.41191  0.18295
H   2.70822 -2.14548 -1.56538
H   0.06518 -1.30341 -1.13194
H   0.14887  1.33470  1.04927
H  -1.27725 -0.58055  2.47132
H   0.77089 -0.25662  2.72107
H   0.20528 -1.67965  0.60262
H   1.03557 -2.70322  2.11968
H  -0.61228 -2.97586  1.88785
H  -4.05108 -2.02380 -0.21683
H  -2.42300 -2.74564 -0.45629
H  -2.89847 -2.10193  1.15412
H  -4.51593  0.52905  0.33846
H  -3.24395  0.88715  1.54875
H  -3.38655  1.86783  0.02920
H  -3.87885 -0.24019 -2.29273
H  -2.49247  0.88000 -2.54081
H  -2.26539 -0.87521 -2.77365
H  -0.12384  2.31946 -0.85290
N  -0.94238  3.32047  1.07698
H  -0.97098  4.26042  0.65843
H  -1.88996  2.92220  1.01739
H  -0.72230  3.44105  2.07525

SCF (BS1) =     -523.486713642
H 0K=           -523.129677
```

H 298K= -523.104369
G 298K= -523.183784
SCF (C6H5F) = -523.542429649
BP86-D3 = -523.548315512
Lowest Frequency = -985.1565cm-1

TS6a'NH1 (Alt 2)

Ir	-0.50560	0.15837	0.01483
P	-2.72443	-0.63659	0.00870
P	1.29056	1.69797	0.00038
B	0.00971	-1.84729	0.46749
N	1.17962	-2.04622	-0.47651
C	-3.19940	-1.78507	-1.37111
C	-3.90660	0.78639	-0.17935
C	2.38014	1.75878	-1.50171
C	0.60476	3.42331	0.12221
C	-3.34087	-1.49034	1.54146
C	2.48608	1.59712	1.41846
N	5.87732	-2.33270	0.19208
B	4.50177	-1.51009	-0.14343
H	0.61927	-0.86308	-0.90532
H	-1.00168	0.94525	-1.28438
H	0.16745	-0.95034	1.40973
H	-0.70027	-2.79134	0.70025
H	1.15694	-2.84968	-1.11377
H	2.15063	-1.85038	-0.17431
H	-2.63405	-2.72437	-1.27175
H	-2.94490	-1.31532	-2.33340
H	-4.27915	-2.00333	-1.33915
H	-3.71759	1.28839	-1.14001
H	-3.74326	1.50890	0.63524
H	-4.94858	0.42843	-0.14474
H	1.75140	1.85353	-2.40000
H	2.96642	0.82854	-1.56373
H	3.07085	2.61545	-1.43978
H	-0.00449	3.51474	1.03454
H	-0.03113	3.62528	-0.75278
H	1.42746	4.15620	0.15854
H	-3.22968	-0.80997	2.39999
H	-2.74712	-2.39710	1.72910
H	-4.40230	-1.76424	1.42816
H	3.05682	0.65831	1.34244
H	1.92630	1.60912	2.36631
H	3.18487	2.44947	1.39199
H	6.30644	-2.01388	1.07023
H	6.57370	-2.19928	-0.55252
H	5.71560	-3.34411	0.27993
H	3.74720	-1.72580	0.80286
H	4.81459	-0.33641	-0.22084
H	4.08684	-1.95961	-1.20032

SCF (BS1) = -523.476576787
H 0K= -523.120627
H 298K= -523.094578
G 298K= -523.178518
SCF (C6H5F) = -523.528332097
BP86-D3 = -523.527187967
Lowest Frequency = -1109.6944cm-1

TS6a'NH1 (Alt 3)

C	3.06568	-1.89003	0.70964
P	2.33057	-0.22284	0.34454
Ir	0.00149	-0.19672	-0.02178
B	0.44005	-1.50577	-1.57507
N	-0.63148	-2.63665	-1.48157
C	2.80462	0.77285	1.83689
C	3.42957	0.45758	-0.99370
P	-2.34126	-0.04521	0.35451
C	-3.17415	-1.56250	1.04170
C	-2.73603	1.23756	1.63865
C	-3.45207	0.42498	-1.06905
H	-0.30817	-3.60865	-1.55165
H	-0.61546	-2.01003	-0.35811
H	0.02328	-0.42700	1.55587
H	-0.00685	-0.31114	-1.92804
H	1.50555	-1.84405	-2.02697
H	-1.51975	-2.50908	-1.97606
H	2.96687	-2.54105	-0.17183
H	2.51864	-2.34170	1.55137
H	4.13119	-1.79138	0.97320
H	2.31815	0.33982	2.72406
H	2.45132	1.80633	1.70564
H	3.89838	0.76231	1.97254
H	-2.64239	-1.87250	1.95428
H	-3.12863	-2.38775	0.31436
H	-4.22857	-1.35148	1.28317
H	-2.31047	2.20475	1.33199
H	-2.26662	0.94048	2.58894
H	-3.82598	1.32466	1.77627
H	3.20287	1.52709	-1.12422
H	3.23907	-0.07470	-1.93808
H	4.49114	0.34699	-0.71897
H	-3.37026	-0.31997	-1.87625
H	-3.13922	1.40269	-1.46673
H	-4.50298	0.48837	-0.74221
B	0.29070	3.10378	0.12573
H	0.11962	1.84717	0.10593
N	0.14483	3.59849	-1.42900
H	-0.59011	3.65029	0.75519
H	1.42013	3.38233	0.47014
H	0.30163	4.61362	-1.49050
H	0.82832	3.14488	-2.04859
H	-0.78826	3.41153	-1.81693

SCF (BS1) = -523.470031754
H 0K= -523.114909
H 298K= -523.089033
G 298K= -523.171674
SCF (C6H5F) = -523.526256458
BP86-D3 = -523.527789694
Lowest Frequency = -1325.7527cm-1

TS6a'NH1 (Alt 4)

C	-3.05502	-1.34423	-1.42305
P	-2.40320	-0.02495	-0.28891
Ir	-0.03763	0.00897	-0.08586
P	2.28692	-0.28450	-0.36417
C	3.26698	-1.09181	1.00278
C	-3.37954	-0.27528	1.27604
C	-3.16594	1.51001	-1.01660
B	-0.20396	2.40332	0.55527

```
N   1.04257  3.34501  1.02879
H   0.90573  4.30017  0.66987
B  -0.15189 -2.35136  0.77770
N  -0.03075 -1.90841  2.23522
H  -0.84905 -1.94912  2.84528
C   3.33400  1.23369 -0.70482
C   2.69353 -1.35066 -1.83195
H  -2.65247 -1.17188 -2.43323
H  -4.15601 -1.31352 -1.45702
H  -2.72034 -2.33143 -1.07281
H  -4.25353  1.37414 -1.13184
H  -2.71639  1.70226 -2.00319
H  -2.96605  2.37212 -0.36436
H   0.00713 -0.71724  1.45052
H  -0.01721  1.30869  1.21943
H  -0.11039 -1.16224 -1.16519
H  -1.24750 -2.73764  0.46378
H   0.82266 -2.89960  0.32795
H   0.83536 -2.07740  2.74979
H  -3.13273 -1.26011  1.70164
H  -4.46123 -0.23816  1.06826
H  -3.11846  0.51184  2.00012
H   2.28842 -0.88070 -2.74142
H   2.20828 -2.32935 -1.69754
H   3.78231 -1.48493 -1.93720
H   2.86691 -2.10257  1.17533
H   3.17834 -0.50057  1.92807
H   4.32982 -1.17234  0.72268
H   3.49839  1.79431  0.23262
H   2.83765  1.87451 -1.45065
H   4.32622  0.94501 -1.08899
H  -1.20310  2.91345  1.00745
H  -0.16913  2.34923 -0.66606
H   1.11118  3.41725  2.05320
H   1.94945  3.01063  0.67395

SCF (BS1) =     -523.480846819
H 0K=           -523.123372
H 298K=         -523.098353
G 298K=         -523.177082
SCF (C6H5F) =   -523.537191258
BP86-D3 =       -523.542745819
Lowest Frequency = -554.0387cm-1
```

(4) Model 2. Second Dehydrogenation of $H_3B{\cdot}NH_3$ at 6a'

Figure S7. Computed reaction profile for dehydrogenation of a second $H_3B{\bullet}NH_3$ molecule at **6a'**.

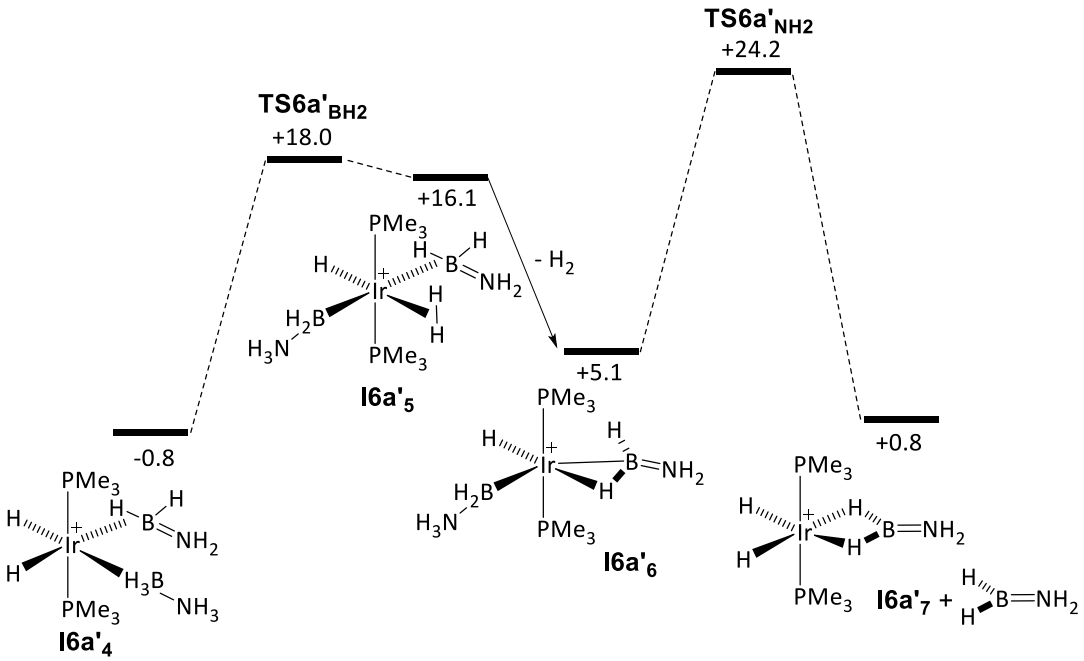
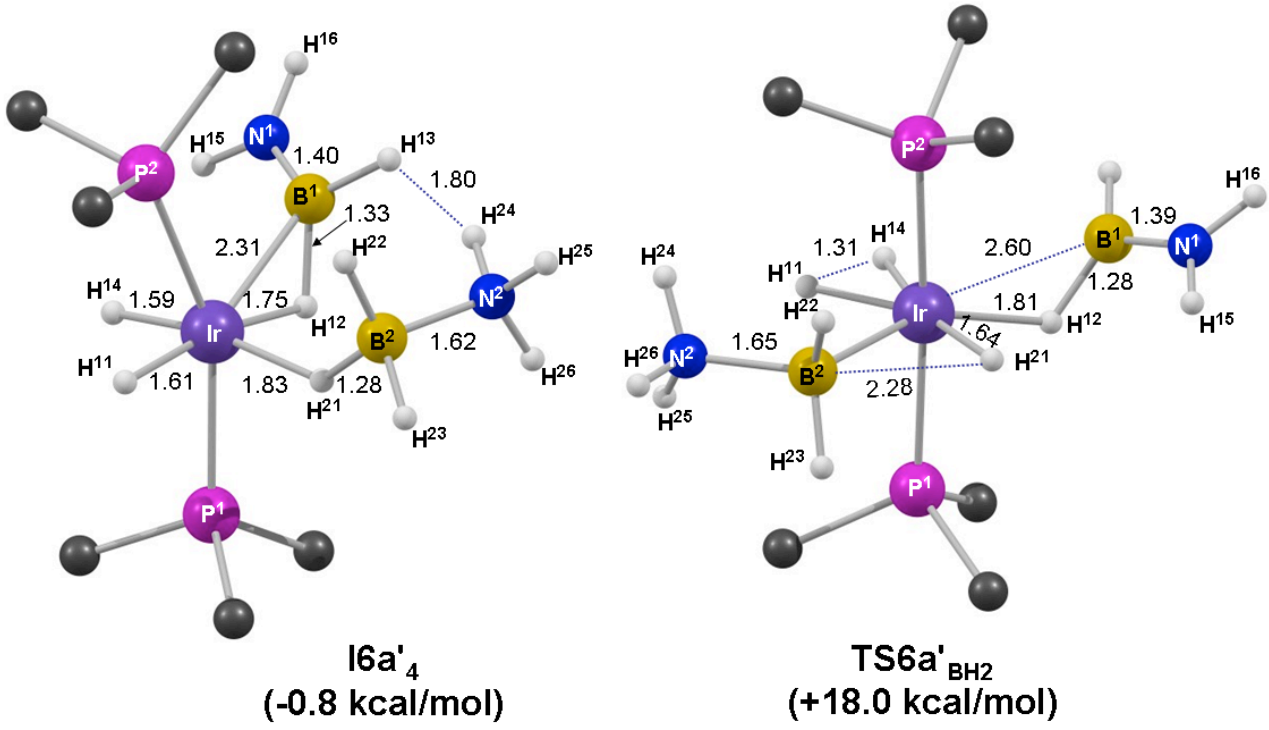
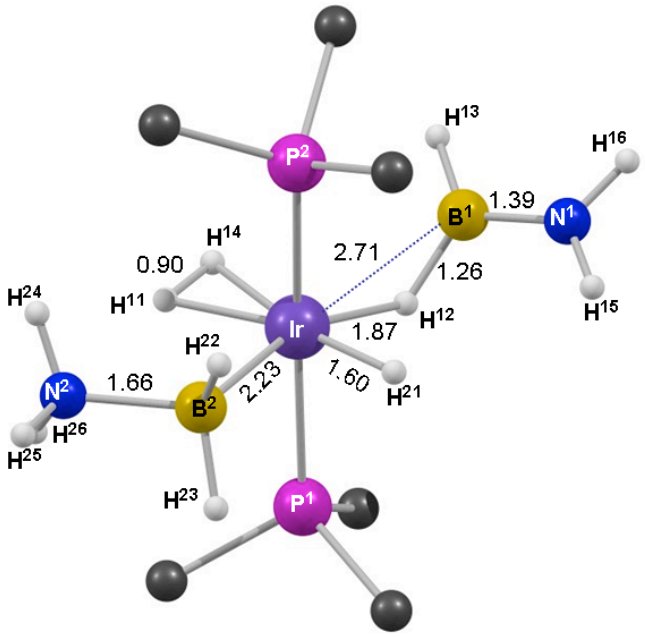
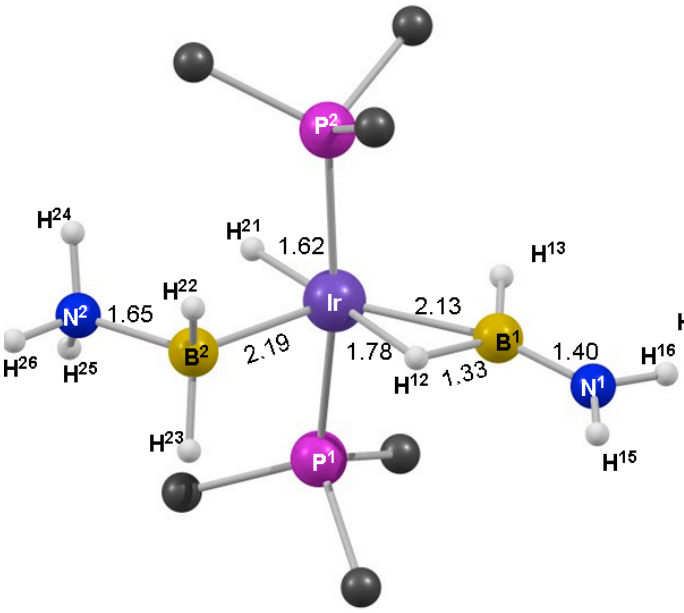


Figure S8. Computed Geometries

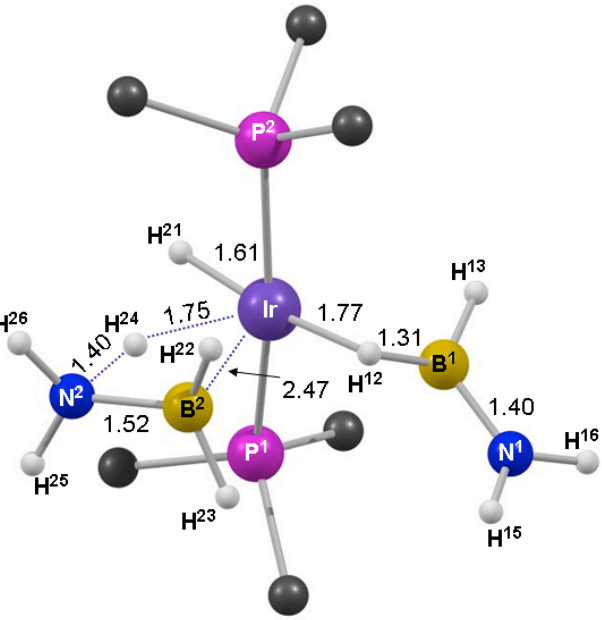




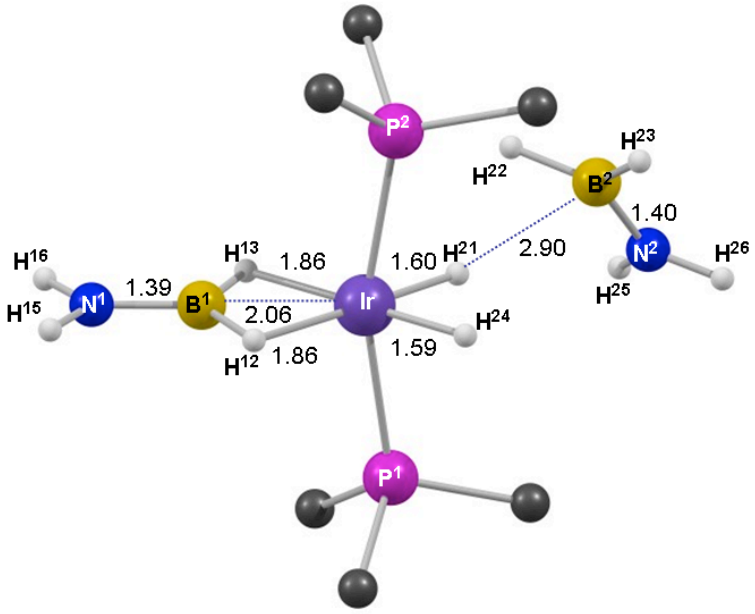
I6a'$_5$
(+16.1 kcal/mol)



I6a'$_6$
(+5.1 kcal/mol)

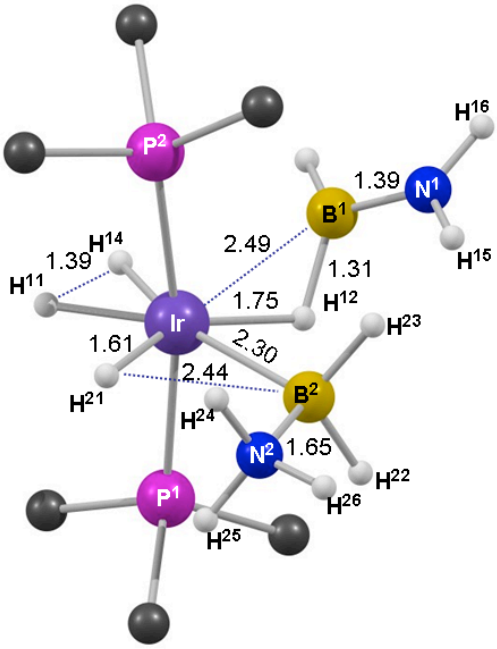


TS6a'$_{NH2}$
(+24.2 kcal/mol)

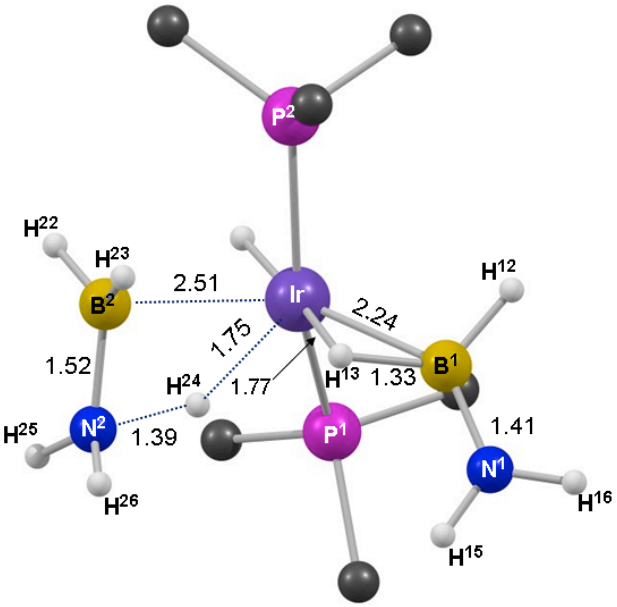


I6a'$_7$ + $H_2B{=}NH_2$
(+0.8 kcal/mol)

Figure S9. Alternative B-H and N-H activation transition states



TS6a'$_{BH2}$ (Alt)
(+20.8 kcal/mol)



TS6a'$_{NH2}$ (Alt)
(+26.1 kcal/mol)

(a) Dehydrogenation of a second $H_3N{\bullet}BH_3$ molecule

TS6a′ BH2

```
C   3.34801 -0.73792 -1.25883
P   2.30590  0.24075 -0.06492
C   2.88482  1.97141 -0.44910
C   3.09010 -0.09670  1.58108
Ir -0.05783 -0.07070 -0.13999
B  -0.20352  1.83204  1.08844
N  -0.32092  3.18768  0.14820
P  -2.43191 -0.16776 -0.02693
C  -3.12296 -0.58410  1.64256
C  -3.35500  1.37825 -0.49801
C  -3.19200 -1.44016 -1.15032
B   0.70830 -2.54692 -0.34553
N   1.08895 -3.17305  0.83969
H  -1.14533  3.17105 -0.46672
H  -0.40329  4.02005  0.75036
H   0.50287  3.32414 -0.45294
H  -0.13892  1.06591 -1.29424
H   4.40510 -0.43907 -1.17003
H   3.25780 -1.81338 -1.05036
H   2.99730 -0.55117 -2.28574
H   4.16739  0.13311  1.55896
H   2.58781  0.51967  2.34173
H   2.94414 -1.15931  1.82629
H   3.98587  2.01288 -0.43847
H   2.53124  2.26593 -1.45080
H   2.50237  2.66110  0.31857
H  -0.01524 -0.40321  1.47001
H   0.78644  2.02712  1.76643
H  -0.05135 -0.13640 -1.80668
H  -1.22383  1.85159  1.75067
H  -4.44154  1.19642 -0.47580
H  -3.11977  2.17304  0.22690
H  -3.06661  1.68655 -1.51581
H  -4.22468 -0.57803  1.62621
H  -2.76594 -1.58321  1.93617
H  -2.75255  0.15258  2.37116
H  -4.29034 -1.43807 -1.05975
H  -2.90725 -1.22321 -2.19151
H  -2.80783 -2.43719 -0.88373
H  -0.36543 -1.84912 -0.28625
H   1.12335 -2.90121 -1.40956
H   1.72838 -3.96655  0.86416
H   0.72519 -2.90579  1.75343

SCF (BS1) =     -523.501459454
H 0K=           -523.143998
H 298K=         -523.119096
G 298K=         -523.196610
SCF (C6H5F) =   -523.555335060
BP86-D3 =       -523.566250594
Lowest Frequency = -439.0954cm-1
```

I6a′5

```
C  -3.41596  0.88673 -0.97664
P  -2.30669 -0.21691  0.03786
C  -2.98554 -1.89073 -0.43444
C  -2.95043  0.01683  1.76198
Ir  0.05347  0.04406 -0.14183
B   0.18884 -1.92903  0.87786
N   0.23373 -3.20692 -0.17791
P   2.42002  0.14388  0.04804
C   3.05085  0.35943  1.77896
C   3.37722 -1.32840 -0.57397
C   3.22236  1.54564 -0.87918
B  -0.63137  2.62727 -0.61234
N  -0.91885  3.36742  0.53266
H   1.03841 -3.16259 -0.81713
H   0.30960 -4.09055  0.34732
H  -0.61402 -3.26867 -0.75779
H   0.17235 -0.88951 -1.62226
H  -4.47040  0.60842 -0.81647
H  -3.27085  1.93625 -0.68389
H  -3.16927  0.78364 -2.04485
H  -4.03304 -0.18222  1.80933
H  -2.41149 -0.66667  2.43489
H  -2.75319  1.05406  2.07280
H  -4.08271 -1.89636 -0.33204
H  -2.73162 -2.11323 -1.48414
H  -2.56755 -2.65543  0.23729
H   0.01600  0.44134  1.41038
H  -0.77657 -2.16658  1.58211
H   0.00125 -0.06014 -1.91324
H   1.23004 -2.04261  1.50251
H   4.46022 -1.15498 -0.46791
H   3.10272 -2.21267  0.02151
H   3.14723 -1.49877 -1.63819
H   4.15245  0.35528  1.79848
H   2.68019  1.31683  2.17619
H   2.66035 -0.45865  2.40235
H   4.31643  1.52741 -0.74752
H   2.98190  1.46341 -1.95076
H   2.82796  2.50306 -0.50473
H   0.35226  1.83977 -0.55083
H  -1.12194  2.89172 -1.67248
H  -1.54085  4.17479  0.52727
H  -0.50528  3.17497  1.44344

SCF (BS1) =     -523.504890643
H 0K=           -523.145855
H 298K=         -523.120324
G 298K=         -523.200235
SCF (C6H5F) =   -523.558866888
BP86-D3 =       -523.568901753
Lowest Frequency = 22.7428cm-1
```

I6a′6

```
C  -3.06703  0.72116  1.68844
P  -2.33020 -0.15312  0.22087
C  -2.99217 -1.88250  0.41464
Ir  0.01848  0.07869  0.08166
B   0.05832 -1.54227 -1.38393
N   0.12003 -3.03644 -0.68758
C  -3.30950  0.49099 -1.22050
P   2.38181  0.00793  0.19270
C   3.28226  0.72596 -1.26518
C   3.07335  0.93729  1.64809
C   3.17370 -1.66738  0.37155
```

B	-0.17805	2.14901	-0.36065
N	-0.47379	3.37798	-0.95131
H	-4.15843	0.57361	1.72874
H	-2.60795	0.33013	2.60964
H	-2.84601	1.79742	1.61820
H	-4.38708	0.30560	-1.08431
H	-3.13396	1.57368	-1.31690
H	-2.95886	-0.00974	-2.13628
H	-4.08544	-1.86136	0.55049
H	-2.76803	-2.45886	-0.49700
H	-2.53313	-2.35682	1.29682
H	0.04379	-1.04713	1.24019
H	0.03463	1.21709	-1.29118
H	1.07207	-1.47541	-2.06161
H	-0.96898	-1.54846	-2.04384
H	-0.69396	-3.21145	-0.08413
H	0.14138	-3.77166	-1.40940
H	0.95608	-3.14900	-0.09966
H	4.26484	-1.56570	0.48651
H	2.76842	-2.17489	1.26158
H	2.97526	-2.25925	-0.53626
H	4.37321	0.62152	-1.15046
H	2.95247	0.20238	-2.17590
H	3.02584	1.79302	-1.35678
H	4.17370	0.87745	1.66676
H	2.76547	1.99240	1.58318
H	2.66516	0.51064	2.57735
H	-0.00957	2.08392	0.87422
H	-0.57393	4.23629	-0.41217
H	-0.57264	3.51600	-1.95591

SCF (BS1) = -522.334839165
H 0K= -521.992683
H 298K= -521.968315
G 298K= -522.045954
SCF (C6H5F) = -522.388235806
BP86-D3 = -522.393175355
Lowest Frequency = 23.6077cm-1

TS6a'NH2

C	2.92430	0.84921	-1.77743
P	2.27196	-0.25088	-0.42700
C	2.75621	-1.94640	-1.02157
Ir	-0.06730	0.02077	-0.09816
B	-0.18678	-1.05453	2.12703
N	-0.07350	-2.46226	1.56214
C	3.44859	0.04565	0.98114
P	-2.42748	0.06910	-0.29947
C	-3.34827	1.16342	0.88626
C	-2.96109	0.68064	-1.97128
C	-3.29679	-1.56567	-0.13782
B	0.46944	2.11833	0.55336
N	1.24369	2.86701	1.44584
H	3.98964	0.63913	-1.96570
H	2.34711	0.67316	-2.69815
H	2.80480	1.90264	-1.48223
H	4.48488	-0.15581	0.66562
H	3.35942	1.09265	1.30673
H	3.18678	-0.61045	1.82543
H	3.83860	-1.99118	-1.22268
H	2.50244	-2.70018	-0.26049
H	2.19891	-2.17712	-1.94206
H	-0.15855	-1.02504	-1.32480
H	-0.20438	1.20882	1.21247
H	-1.28269	-0.73635	2.51454
H	0.80789	-0.63516	2.66217
H	-0.01388	-1.65016	0.42851
H	0.78418	-2.99751	1.71671
H	-0.89542	-3.07095	1.55113
H	-4.37314	-1.45043	-0.34382
H	-2.86313	-2.28410	-0.85016
H	-3.17158	-1.94376	0.88885
H	-4.43429	1.10955	0.70743
H	-3.12901	0.84532	1.91724
H	-3.00922	2.20303	0.75543
H	-4.06068	0.70272	-2.04359
H	-2.56470	1.69511	-2.13193
H	-2.55279	0.01606	-2.74784
H	0.16350	2.57000	-0.52774
H	1.58278	3.80202	1.22497
H	1.43504	2.58237	2.40540

SCF (BS1) = -522.299965260
H 0K= -521.964832
H 298K= -521.940215
G 298K= -522.018404
SCF (C6H5F) = -522.350699050
BP86-D3 = -522.358035070
Lowest Frequency = -852.3473cm-1

I6a'7

C	-3.00018	-1.72865	-1.35603
P	-2.29600	-0.37187	-0.30217
C	-2.94238	1.18241	-1.07755
Ir	0.06733	-0.37714	-0.10514
B	-0.10900	3.97145	0.89255
N	-1.32035	4.66754	0.91451
C	-3.24080	-0.49994	1.29196
P	2.35414	0.23765	-0.27380
C	3.06349	0.93403	1.29249
C	3.53564	-1.11168	-0.75686
C	2.65044	1.56500	-1.53093
B	0.29224	-2.08409	1.02519
N	0.44828	-3.23137	1.79113
H	-4.09362	-1.62383	-1.44602
H	-2.54316	-1.68170	-2.35638
H	-2.76234	-2.70458	-0.90513
H	-4.32493	-0.42227	1.10940
H	-3.02091	-1.46641	1.77163
H	-2.92269	0.31066	1.96547
H	-4.04129	1.14920	-1.15193
H	-2.63353	2.04494	-0.46669
H	-2.50660	1.28948	-2.08257
H	0.00459	0.07975	-1.62814
H	0.14546	-0.94131	1.66210
H	0.53799	3.96656	-0.12682
H	0.25051	3.38995	1.88716
H	-0.11961	1.19127	0.08277
H	-1.89357	4.76346	1.75067
H	-1.65799	5.22345	0.13092
H	3.71645	1.84299	-1.55224
H	2.34318	1.20028	-2.52286

```
H   2.04163  2.44393 -1.26902
H   4.10567  1.25650  1.13586
H   2.45280  1.79492  1.60549
H   3.03178  0.16877  2.08347
H   4.55867 -0.71360 -0.85484
H   3.52448 -1.90157  0.01028
H   3.21857 -1.54477 -1.71812
H   0.29897 -2.21553 -0.28269
H   0.56760 -4.15883  1.38715
H   0.45622 -3.22545  2.80972

SCF (BS1) =     -522.343190762
H 0K=           -522.006284
H 298K=         -521.980113
G 298K=         -522.067949
SCF (C6H5F) =   -522.392215005
BP86-D3 =       -522.390773092
Lowest Frequency = 10.8341cm-1
```

(b) Alternative Transition States

TS6a′ BH2 (Alt)

```
P  -2.44682 -0.18080 -0.24011
B   0.70197 -1.74117  1.56825
N   1.32327 -1.26511  2.71925
B  -0.17572  1.43496  1.47420
N  -0.19960  3.00041  0.95960
P   2.28240  0.04426 -0.52371
C  -3.29554  1.47092 -0.33218
Ir -0.07386 -0.15284 -0.18936
C  -3.25041 -0.98712  1.22568
C  -3.15405 -1.09467 -1.69284
C   3.16208 -1.55843 -0.86040
C   2.67219  1.02939 -2.05406
C   3.36042  0.84544  0.76096
H  -0.37262 -1.04039  1.28987
H   0.82778 -2.87243  1.20448
H   1.90973 -1.84848  3.31432
H   1.17713 -0.31097  3.05672
H  -1.20509  1.32497  2.12224
H   0.80813  1.39462  2.19896
H  -0.25978  3.64255  1.76309
H  -1.00531  3.19411  0.35099
H   0.64135  3.25482  0.42688
H  -2.93697  2.01831 -1.21822
H  -3.07013  2.03799  0.58457
H  -4.38724  1.34139 -0.40721
H  -0.05957 -1.64278 -0.94530
H  -0.12308 -0.53453 -1.77388
H  -0.12577  1.25829 -0.96132
H  -4.34822 -0.94610  1.14001
H  -2.92992 -0.46439  2.14007
H  -2.92815 -2.03868  1.27934
H  -2.81089 -0.61654 -2.62344
H  -4.25563 -1.09251 -1.66173
H  -2.78567 -2.13183 -1.67535
H   2.66789 -2.06311 -1.70480
H   3.09789 -2.21221  0.02230
H   4.22107 -1.37655 -1.10538
H   2.30373  2.06051 -1.93916
H   2.16170  0.57221 -2.91525
H   3.75852  1.04846 -2.23776
H   3.29818  0.26846  1.69471
H   3.01476  1.87031  0.96152
H   4.40434  0.87222  0.40939

SCF (BS1) =     -523.497227650
H 0K=           -523.139716
H 298K=         -523.114761
G 298K=         -523.192970
SCF (C6H5F) =   -523.550484413
BP86-D3 =       -523.561828380
Lowest Frequency = -581.4474cm-1
```

TS6a′ NH2 (Alt)

```
C   3.31908  1.30715 -1.02744
P   2.39564 -0.15184 -0.35705
C   2.62970 -1.45342 -1.66566
Ir  0.04746  0.05916  0.01233
B   0.86641  2.11202  1.20483
N  -0.48896  2.36580  1.83454
C   3.44438 -0.74923  1.05301
P  -2.23465  0.05536 -0.58729
C  -2.53214 -1.26411 -1.86254
C  -2.81924  1.60633 -1.42637
C  -3.56353 -0.25389  0.67511
B  -0.27088 -1.85535  1.13107
N  -1.14940 -2.39837  2.08581
H   2.80868  1.66991 -1.93233
H   4.35239  1.01446 -1.27346
H   3.33132  2.11330 -0.27988
H   3.70368 -1.59476 -1.87015
H   2.11967 -1.13879 -2.58878
H   2.19409 -2.40396 -1.32201
H  -0.71306  1.24119  1.05376
H   0.23316 -0.71091  1.59239
H   0.06910  0.92117 -1.35561
H   1.70520  1.67030  1.94681
H   1.12728  2.81775  0.26919
H  -0.62700  2.17156  2.82969
H  -1.03582  3.17175  1.52078
H   3.41005 -0.01223  1.86956
H   4.48801 -0.88635  0.72692
H   3.04574 -1.70817  1.41874
H  -2.31680 -2.25121 -1.42625
H  -1.86002 -1.09847 -2.71802
H  -3.57936 -1.23261 -2.20525
H  -2.17066  1.81458 -2.29009
H  -2.75479  2.45447 -0.72739
H  -3.86329  1.49335 -1.76031
H  -3.55355  0.55163  1.42630
H  -3.36839 -1.21429  1.17449
H  -4.55249 -0.28200  0.18993
H   0.26195 -2.62169  0.35830
H  -1.35871 -3.39480  2.12389
H  -1.54456 -1.87595  2.86580

SCF (BS1) =     -522.297121512
H 0K=           -521.962229
H 298K=         -521.937536
G 298K=         -522.016054
SCF (C6H5F) =   -522.348013831
```

BP86-D3 = -522.354376312
Lowest Frequency = -760.8415cm-1

(5) Model 2. Oligomerisation to form 6b'

Figure S10. Computed reaction profile for oligomerisation and formation of **6b'**.

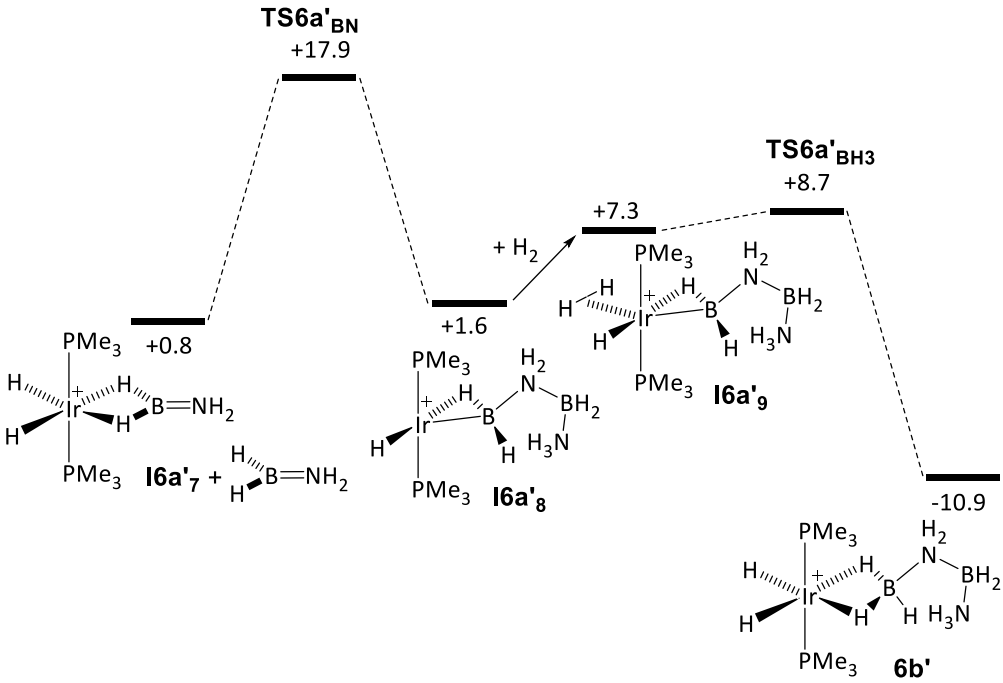
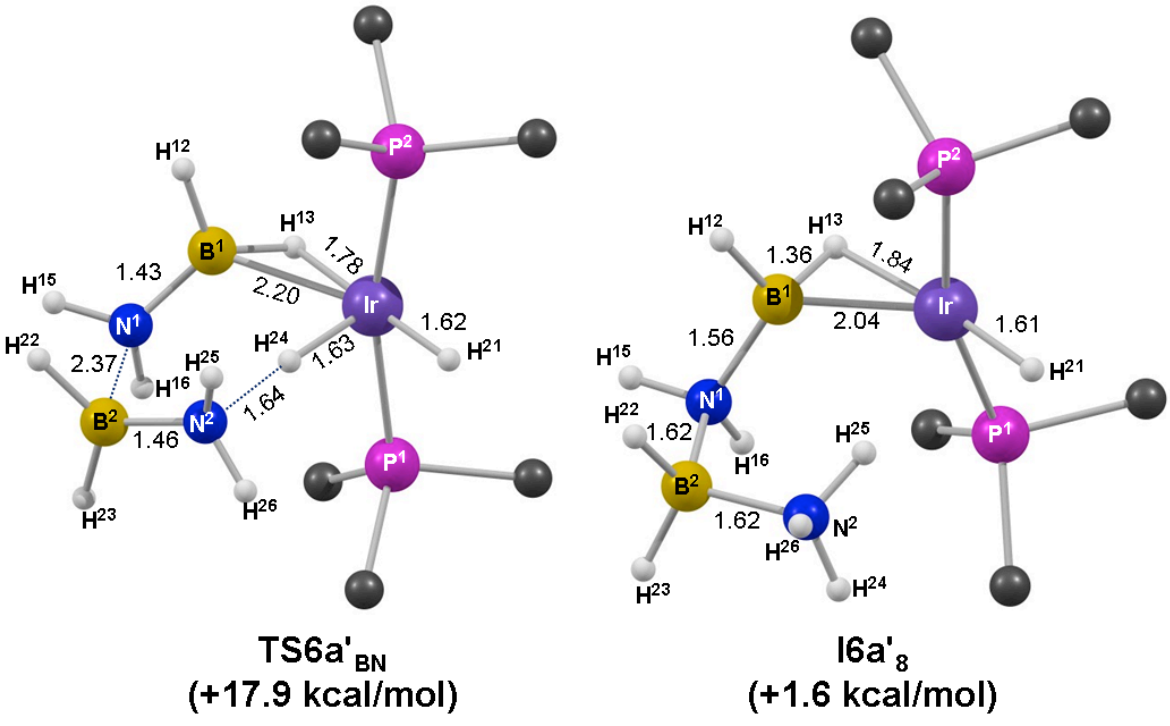
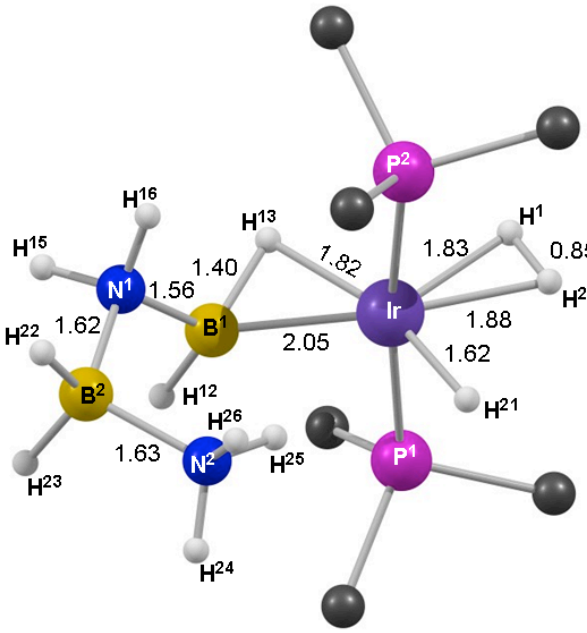
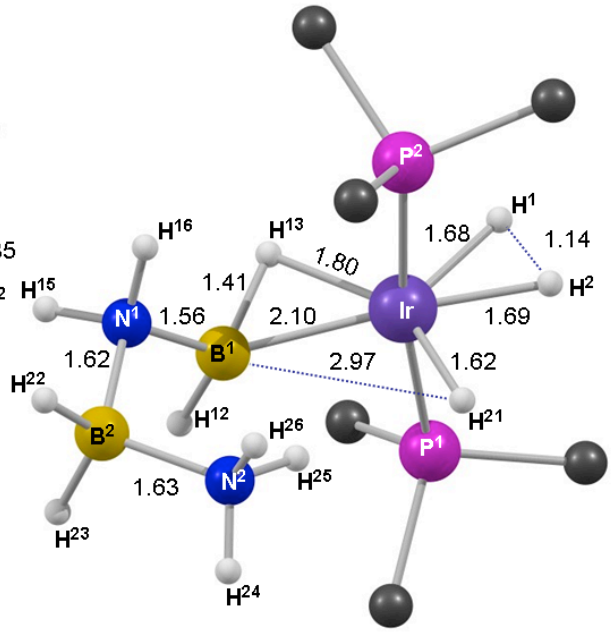


Figure S11. Computed geometries

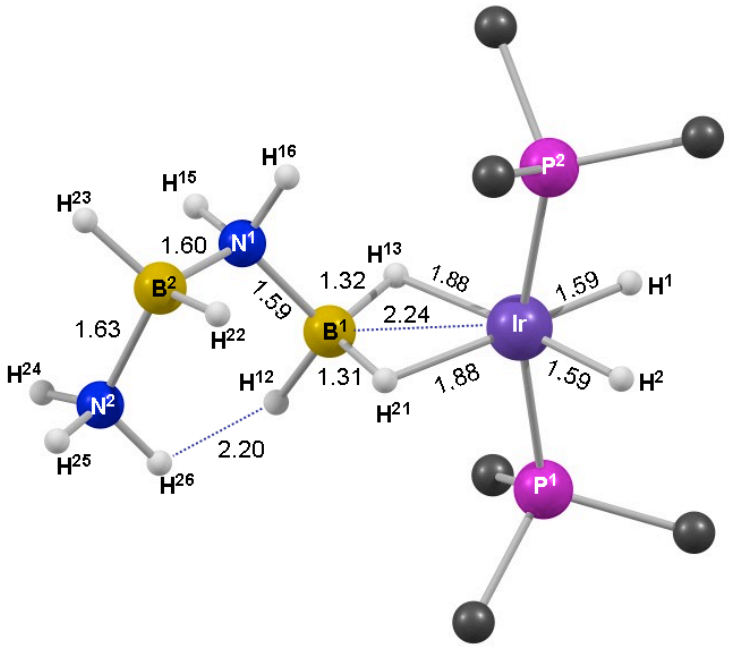




I6a'$_9$
(+7.3 kcal/mol)



TS6a'$_{BH3}$
(+8.7 kcal/mol)

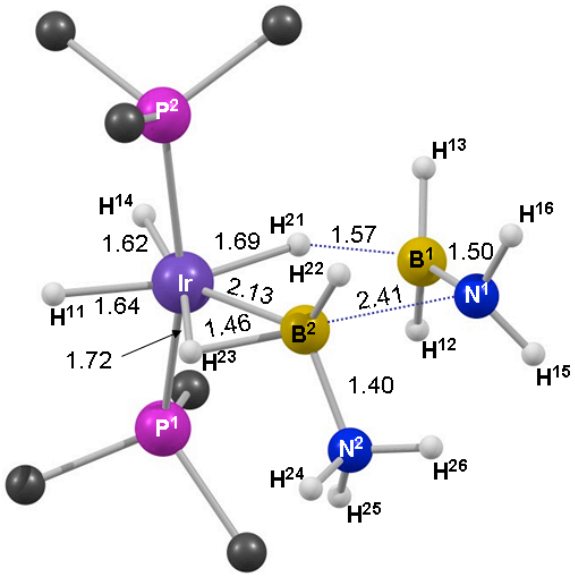


6b'
(-10.9 kcal/mol)

Figure S12. Alternative B-N Bond Coupling Processes

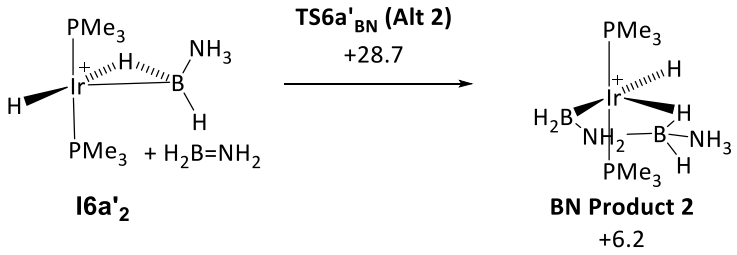
(a) Direct reaction of $H_2B{=}NH_2$ with **6a'**

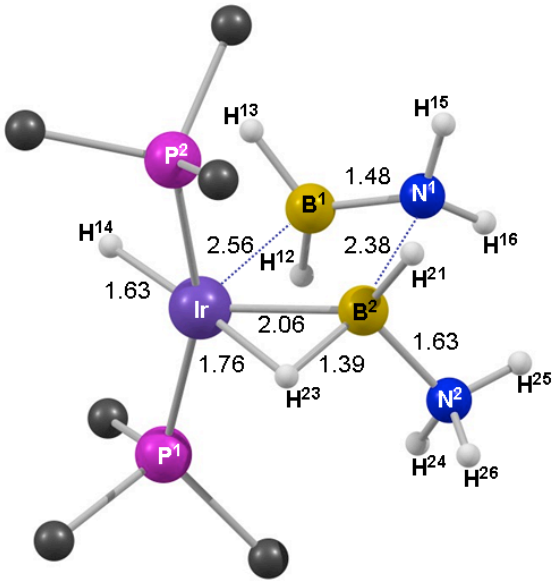
6a' **6b'**



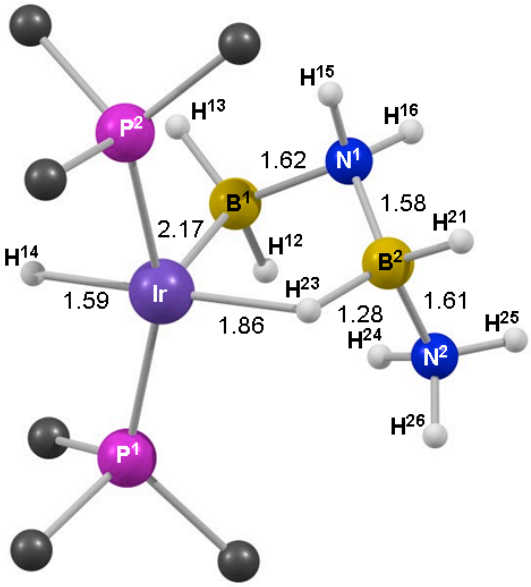
TS6a'$_{BN}$ (Alt 1)
(+27.5 kcal/mol)

(b) Direct reaction of $H_2B{=}NH_2$ with **I6a'$_2$**





TS6a'$_{BN}$ (Alt 2)
(+28.7 kcal/mol)

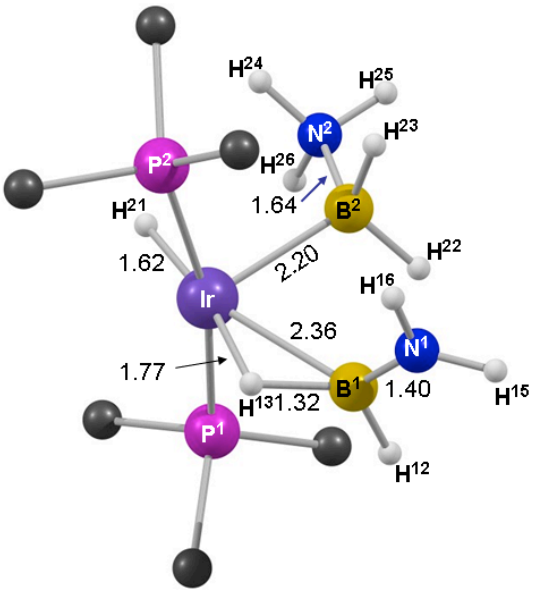


BN Product 2
(+6.2 kcal/mol)

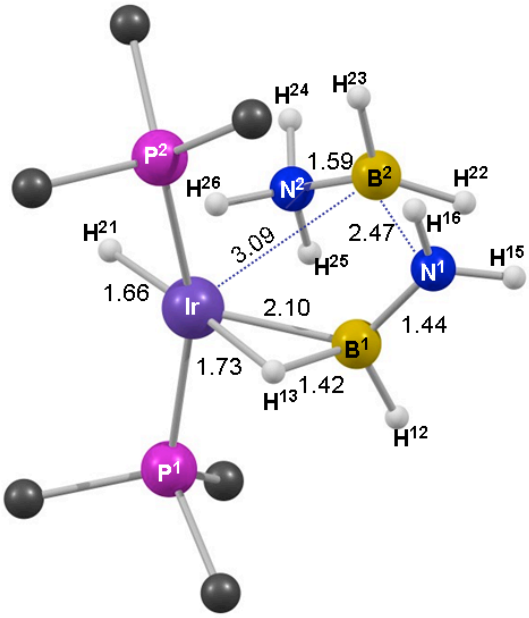
(c) B-N Coupling from an isomer of **I6a'$_6$**

I6a'$_6$ (Isomer 2)
+6.0

I6a'$_8$

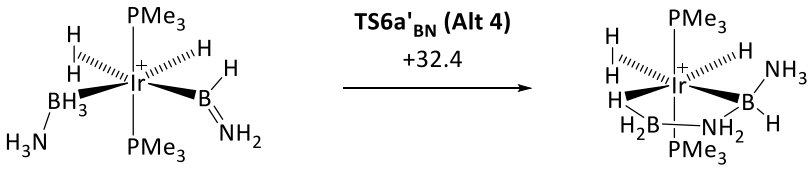


I6a'$_6$ (Isomer 2)
(+6.0 kcal/mol)



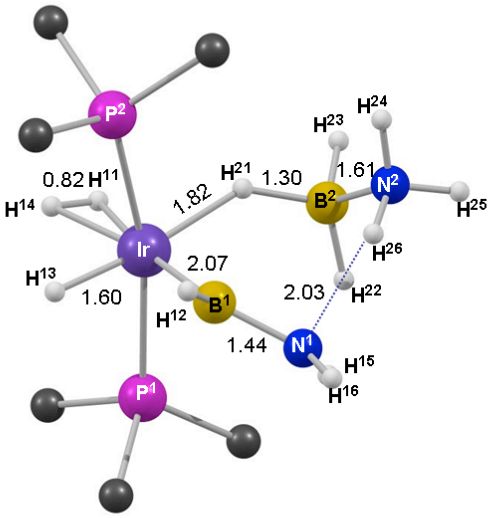
TS6a'$_{BN}$ (Alt 3)
(+30.6 kcal/mol)

(d) B-N Coupling from **I6a'$_9$**. **I6a'$_9$** is related to **I6a'$_4$** via B-H activation of the aminoborane ligand. B-N coupling proceeds via initial proton transfer of H^{26} from N^2 to N^1 with cleavage of the B^2-H^{21} bond to give a {$H_2B{=}NH_2$} moiety which then undergoes B^1-N^2 bond formation with reformation of the B^2-H^{21} bond.

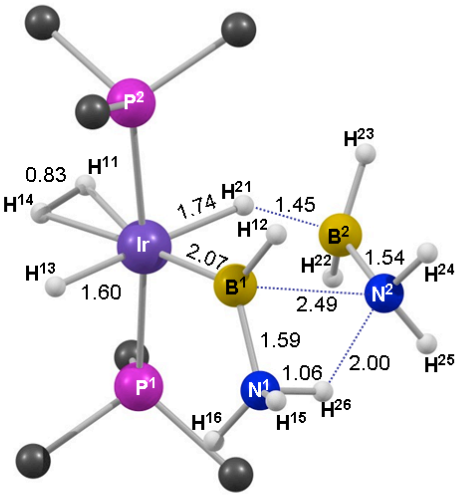


I6a'$_9$
+4.5

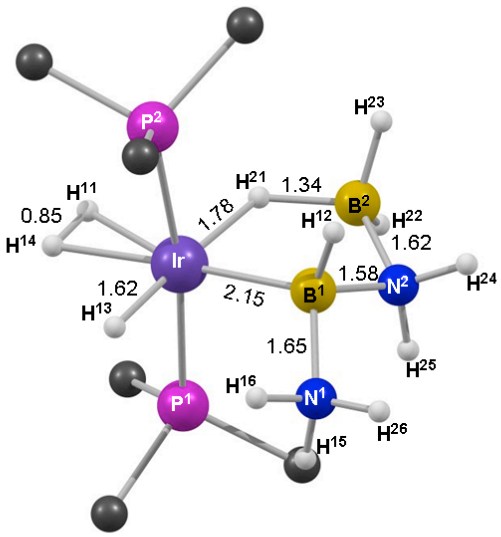
BN Product 3
+2.7



I6a'$_9$
(+4.5 kcal/mol)

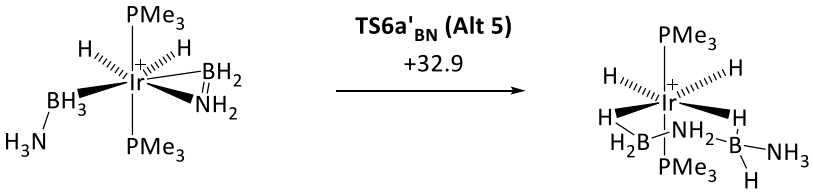


TS6a'$_{BN}$ (Alt 4)
(+32.4 kcal/mol)



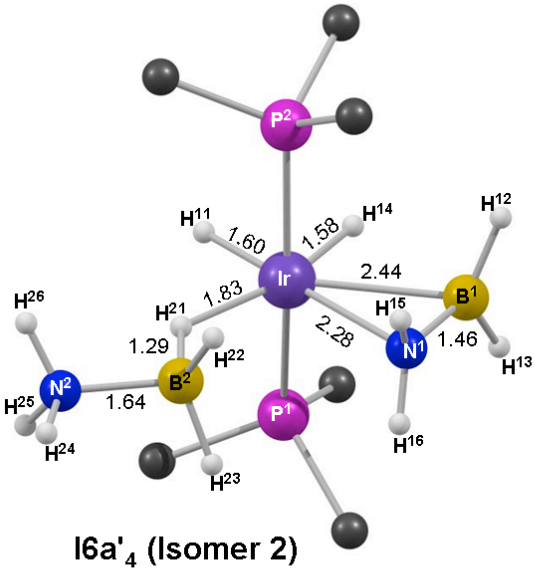
BN Product 3
(+2.7 kcal/mol)

(e) B-N Coupling from an isomer of **I6a'$_4$** with $H_2B{=}NH_2$ initially h^2-bound. B-N bond formation is coupled with formation of a {H_2B-NH_3} moiety (produced via B^2-H^{21} bond cleavage of the H_3B-NH_3 ligand) which attacks a {H_3BNH_2} moiety formed via B^1-H^{14} reductive coupling.

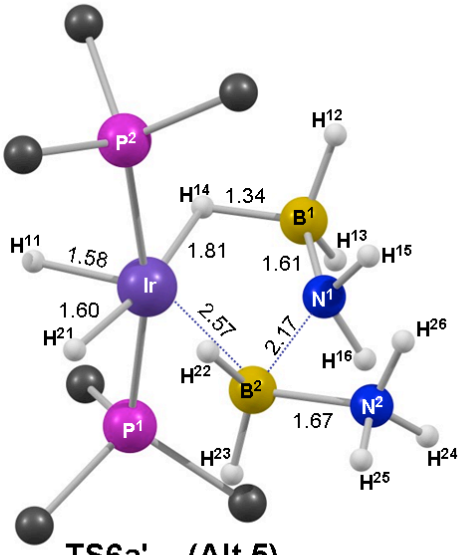


I6a'$_4$ (Isomer 2)
-3.5

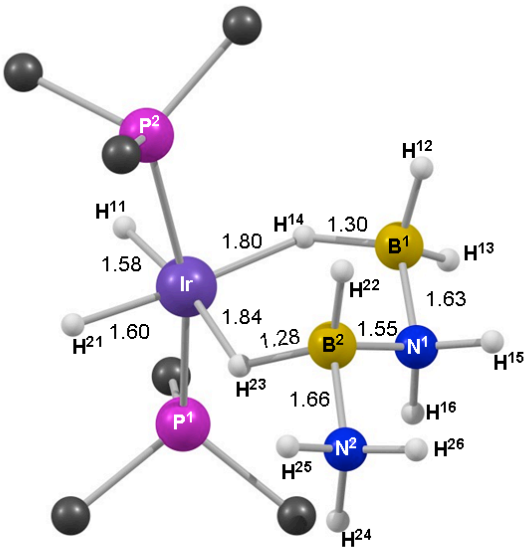
BN Product 4
-7.1



I6a'$_4$ (Isomer 2)
(-3.5 kcal/mol)

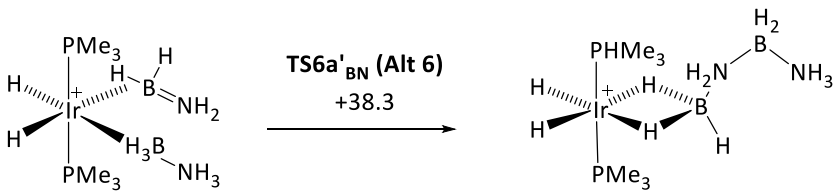


TS6a'$_{BN}$ (Alt 5)
(+32.9 kcal/mol)

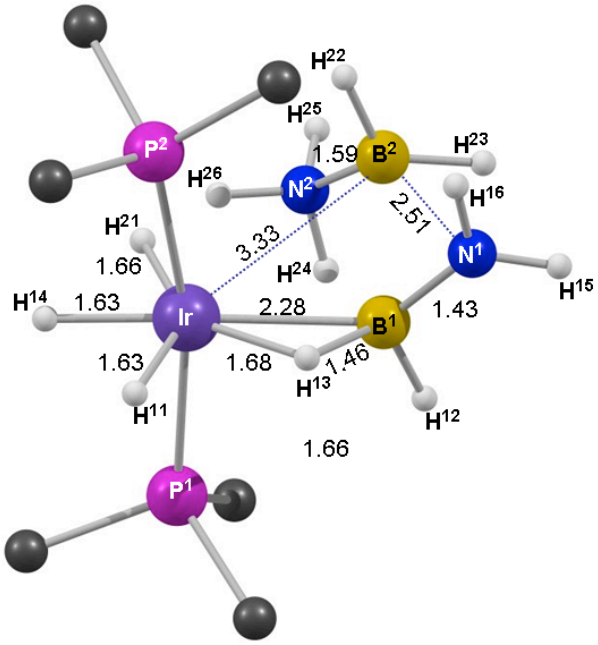


BN Product 4
(-7.1 kcal/mol)

(f) B^2-H^{21} cleavage yields a {H_2BNH_3} moiety that attacks the {$H_2B{=}NH_2$} ligand.



I6a'$_4$ **6b'**



TS6a'$_{BN}$ (Alt 6)
(+38.3 kcal/mol)

TS6a'BN

P	-2.43601	-0.37744	-0.06371
P	2.25045	-0.73703	-0.05771
C	-3.01754	-1.87694	-0.99575
C	-3.27501	1.03199	-0.93596
C	3.34213	-0.40286	1.41530
C	2.49006	-2.56441	-0.32880
C	-3.34364	-0.50510	1.55356
C	3.19270	0.03192	-1.46379
Ir	-0.07476	-0.30067	0.07491
B	-0.28361	1.42919	1.41967
N	0.76471	2.40247	1.50183
B	0.83058	3.46576	-0.62061
N	0.35737	2.48084	-1.59325
H	-2.63183	-1.83652	-2.02557
H	-4.11873	-1.91923	-1.01208
H	-2.62910	-2.78574	-0.50977
H	-4.36618	0.87956	-0.95325
H	-2.90279	1.08935	-1.97072
H	-3.04811	1.97259	-0.41095
H	4.34180	-0.84056	1.26002
H	2.88811	-0.84243	2.31673
H	3.46024	0.68157	1.56862
H	2.05613	-3.12481	0.51428
H	3.56345	-2.80347	-0.40468
H	1.97984	-2.86523	-1.25642
H	-3.00173	-1.40382	2.09043
H	-4.42964	-0.57702	1.38082
H	-3.12827	0.37996	2.17049
H	4.22780	-0.34523	-1.48976
H	3.21397	1.12611	-1.33760
H	2.69092	-0.21704	-2.41158
H	0.01641	0.16718	1.79390
H	-0.13006	-0.80007	-1.46067
H	0.09798	1.08993	-0.76572
H	-1.39073	1.83681	1.66630
H	0.58400	3.30889	1.93538
H	1.74797	2.14042	1.55515
H	0.04920	4.28723	-0.22622
H	2.02034	3.59025	-0.49108
H	1.01828	2.11198	-2.27916
H	-0.56148	2.62254	-2.01674

SCF (BS1) = -522.309460092
H 0K= -521.971673
H 298K= -521.947750
G 298K= -522.025302
SCF (C6H5F) = -522.363706936
BP86-D3 = -522.367207962
Lowest Frequency = -254.3888cm-1

I6a'8

P	-2.43684	-0.36467	-0.05323
P	2.19215	-0.83916	-0.02099
C	-2.97593	-1.98734	-0.78529
C	-3.31370	0.89956	-1.09660
C	3.20905	-0.69417	1.53602
C	2.25208	-2.67096	-0.36652
C	-3.34464	-0.30299	1.56676
C	3.34348	-0.15518	-1.32216
Ir	-0.10068	-0.25702	0.04168
B	-0.27394	1.45078	1.13978
N	0.88619	2.49359	1.14178
B	0.80403	3.51166	-0.12152
N	0.74832	2.60052	-1.46032
H	-2.58865	-2.07088	-1.81197
H	-4.07593	-2.05636	-0.79834
H	-2.56946	-2.81476	-0.18306
H	-4.39951	0.71145	-1.10500
H	-2.92707	0.84996	-2.12631
H	-3.12223	1.90282	-0.68561
H	4.18279	-1.19660	1.41592
H	2.65716	-1.15740	2.36825
H	3.39137	0.36458	1.78297
H	1.68927	-3.20978	0.41134
H	3.29561	-3.02621	-0.37135
H	1.79115	-2.87393	-1.34520
H	-2.98700	-1.12220	2.20939
H	-4.42991	-0.40847	1.40738
H	-3.13980	0.65538	2.06701
H	4.30199	-0.69953	-1.31670
H	3.55071	0.90970	-1.12618
H	2.87454	-0.26033	-2.31291
H	-0.05753	0.28748	1.80219
H	-0.15388	-0.56249	-1.54306
H	0.35294	1.63489	-1.22894
H	-1.31157	2.00679	1.41783
H	0.80158	3.11260	1.96290
H	1.81418	2.05396	1.20693
H	-0.23939	4.11557	-0.03628
H	1.79957	4.19862	-0.14830
H	1.66633	2.45915	-1.89953
H	0.14182	3.03966	-2.16404

SCF (BS1) = -522.342361541
H 0K= -521.998241
H 298K= -521.974548
G 298K= -522.051553
SCF (C6H5F) = -522.398238956
BP86-D3 = -522.398191071
Lowest Frequency = 21.7446cm-1

I6a'9

C	3.14503	1.22072	-1.06860
P	2.49952	-0.19934	-0.06012
C	3.31745	-1.67360	-0.84318
C	3.38676	-0.03066	1.56252
Ir	0.14330	-0.40817	0.06151
P	-2.19988	-0.80029	-0.05615
C	-2.59423	-2.45681	-0.80785
B	0.15685	1.41039	1.01482
N	-1.06771	2.37313	1.16831
B	-1.11297	3.49146	-0.00967
N	-0.78474	2.72831	-1.40971
C	-3.10940	-0.88480	1.57010
C	-3.29174	0.32487	-1.07375
H	0.31209	-2.19085	0.45922
H	0.36834	-2.21931	-0.39128
H	0.07947	0.23500	1.76488
H	0.16274	-0.50011	-1.55429
H	1.15514	2.04576	1.27907

H	-0.98676	2.92682	2.03354
H	-1.96511	1.87573	1.23173
H	2.79262	2.16564	-0.62795
H	2.76495	1.13193	-2.09830
H	4.24678	1.21549	-1.08519
H	2.91360	-1.81798	-1.85703
H	3.10429	-2.57258	-0.24414
H	4.40816	-1.52725	-0.89965
H	-2.92111	0.33846	-2.11137
H	-3.29252	1.35081	-0.67046
H	-4.32952	-0.04622	-1.07384
H	-2.13600	-3.25131	-0.19895
H	-2.17318	-2.50267	-1.82396
H	-3.68358	-2.61657	-0.85248
H	3.17473	-0.91709	2.18006
H	3.02006	0.86366	2.08806
H	4.47369	0.05523	1.40295
H	-3.06260	0.08149	2.09771
H	-2.62366	-1.64064	2.20645
H	-4.16632	-1.15724	1.41737
H	-0.22526	4.28365	0.19950
H	-2.22555	3.96477	-0.07117
H	-1.61594	2.58187	-1.99470
H	-0.11236	3.26997	-1.96574
H	-0.36101	1.77937	-1.20349

SCF (BS1) = -523.524009519
H 0K= -523.164245
H 298K= -523.140006
G 298K= -523.216534
SCF (C6H5F) = -523.577809602
BP86-D3 = -523.586040059
Lowest Frequency = 38.1283cm-1

TS6a'BH3

C	3.18241	1.22891	-1.03107
P	2.51056	-0.20035	-0.05458
C	3.33987	-1.66958	-0.82996
C	3.34970	-0.05003	1.59441
Ir	0.14916	-0.40715	0.03368
P	-2.17823	-0.87684	-0.03934
C	-2.54166	-2.52643	-0.81520
B	0.14398	1.47061	0.97036
N	-1.08244	2.42008	1.17125
B	-1.13167	3.58863	0.04613
N	-0.95085	2.87197	-1.40256
C	-3.01389	-1.01909	1.61977
C	-3.34154	0.23612	-0.98958
H	0.33866	-2.03399	0.42795
H	0.36889	-1.91273	-0.70419
H	0.06671	0.26846	1.69598
H	0.10125	-0.09286	-1.55531
H	1.13824	2.09858	1.26103
H	-0.99862	2.94292	2.05571
H	-1.97964	1.92003	1.21930
H	2.81482	2.16934	-0.59356
H	2.82978	1.14854	-2.07115
H	4.28426	1.22526	-1.01766
H	2.96326	-1.79930	-1.85614
H	3.09888	-2.57179	-0.24702
H	4.43274	-1.53065	-0.85372
H	-3.00123	0.29681	-2.03583
H	-3.36788	1.24772	-0.55221
H	-4.36550	-0.17142	-0.97307
H	-2.02199	-3.31208	-0.24580
H	-2.16137	-2.53074	-1.84823
H	-3.62463	-2.72990	-0.81835
H	3.10862	-0.93748	2.19955
H	2.97754	0.84601	2.11341
H	4.44178	0.02464	1.46755
H	-2.97391	-0.05865	2.15837
H	-2.47473	-1.76782	2.22032
H	-4.06668	-1.32512	1.50763
H	-0.17729	4.30846	0.22018
H	-2.20948	4.13743	0.07896
H	-1.84236	2.66838	-1.87118
H	-0.40909	3.47932	-2.02969
H	-0.43887	1.96073	-1.29099

SCF (BS1) = -523.521043424
H 0K= -523.162705
H 298K= -523.138802
G 298K= -523.214828
SCF (C6H5F) = -523.575368913
BP86-D3 = -523.582046904
Lowest Frequency = -706.5666cm-1

6b'

C	3.14306	1.20491	-1.24745
P	2.53077	-0.06250	-0.03011
C	3.29562	0.47658	1.57669
Ir	0.20518	-0.42229	0.02428
B	-0.24047	1.71248	0.54310
N	-1.67756	2.34688	0.80228
P	-1.94763	-1.37096	-0.06866
C	-3.00743	-1.29073	1.46649
C	3.50044	-1.57979	-0.47950
C	-3.07846	-0.74064	-1.40852
C	-1.90381	-3.19716	-0.40499
H	0.59733	-1.80591	0.69546
H	0.46654	-1.37612	-1.21918
H	-0.03756	0.77708	1.44562
H	-0.22169	1.26575	-0.69158
H	0.59983	2.58525	0.68175
H	-1.70186	2.73997	1.75489
H	-2.37971	1.59430	0.81681
B	-2.22641	3.40815	-0.25821
H	2.71435	2.18636	-0.99240
H	2.80968	0.92286	-2.25807
H	4.24304	1.27153	-1.22802
H	3.18708	-1.92425	-1.47674
H	3.28108	-2.37428	0.24981
H	4.58184	-1.36810	-0.48290
H	-2.58335	-0.88859	-2.38084
H	-3.26213	0.33798	-1.28102
H	-4.03986	-1.27982	-1.40070
H	-1.34524	-3.69737	0.40066
H	-1.37752	-3.37190	-1.35550
H	-2.92333	-3.61122	-0.46290
H	3.07382	-0.27719	2.34783
H	2.85226	1.43578	1.88559
H	4.38735	0.59002	1.47656

```
H  -3.26765 -0.24854  1.71403
H  -2.44155 -1.71321  2.31115
H  -3.94080 -1.86063  1.32806
N  -1.06337  4.52149 -0.49586
H  -3.19644  3.98891  0.17364
H  -2.38804  2.85004 -1.32067
H  -1.34705  5.12348 -1.28055
H  -0.90192  5.13771  0.31306
H  -0.15967  4.08770 -0.73722

SCF (BS1) =     -523.557879927
H 0K=           -523.194177
H 298K=         -523.169687
G 298K=         -523.249353
SCF (C6H5F) =   -523.614064916
BP86-D3 =       -523.613567747
Lowest Frequency = 18.8782cm-1
```

Alternative BN Coupling Processes

(a) Direct reaction of H2B=NH2 with 6a′

TS6a′ BN (Alt 1)

```
C  -2.80555 -2.24989 -0.82839
P  -2.26132 -0.72832  0.08628
Ir  0.06484 -0.27876 -0.09040
P   2.41988 -0.46251  0.02318
C   3.29106  0.76002  1.11484
C  -3.53210  0.53191 -0.46761
C  -2.79806 -1.05474  1.83271
N  -0.07890  3.28167  0.84430
B  -0.34782  2.17852  1.81630
C   2.98050 -2.10586  0.67248
C   3.30293 -0.31369 -1.60402
B   0.21506  1.67502 -0.93218
H   1.24601  2.25566 -1.14364
H   0.11150  0.41747 -1.66328
N  -0.98629  2.48182 -1.64258
H  -2.20353 -3.10092 -0.47534
H  -2.61606 -2.11633 -1.90464
H  -3.87506 -2.45543 -0.65911
H   0.01123  0.76986  1.23139
H   0.10834 -1.27288  1.19177
H   0.16138 -1.67780 -0.94110
H  -4.55215  0.16938 -0.25828
H  -3.45730  0.70047 -1.55587
H  -3.38885  1.47241  0.09193
H  -2.22928 -1.91423  2.21845
H  -3.87729 -1.27249  1.87974
H  -2.56476 -0.17427  2.45059
H   2.86624  0.70355  2.12859
H   3.13374  1.77623  0.72197
H   4.37187  0.54835  1.15239
H   2.56667 -2.90174  0.03511
H   2.59484 -2.23797  1.69473
H   4.08071 -2.16684  0.67972
H   3.10448  0.67722 -2.04085
H   2.92181 -1.08696 -2.28857
H   4.38936 -0.44161 -1.47136
H   0.47609  1.93024  2.66453
H  -1.51702  1.97026  2.04519
H  -0.80951  3.99880  0.84991
H   0.82535  3.74638  0.95121
H  -0.95914  2.34021 -2.66514
H  -1.91120  2.16566 -1.31315
H  -0.89203  3.48571 -1.44027

SCF (BS1) =     -523.482561319
H 0K=           -523.125978
H 298K=         -523.101421
G 298K=         -523.179619
SCF (C6H5F) =   -523.540136229
BP86-D3 =       -523.545534809
Lowest Frequency = -318.8736cm-1
```

(b) Direct reaction of $H_2B=NH_2$ with I6a′$_2$

TS6a′ BN (Alt 2)

```
C  -2.66803 -2.22015 -0.83299
P  -2.29070 -0.63115  0.06684
C  -2.96599 -0.95042  1.76791
Ir  0.03175 -0.18946 -0.07455
B   0.29724  1.67794 -0.91459
N  -0.91850  2.65031 -1.38388
C  -3.57934  0.52742 -0.64635
P   2.36030 -0.51757 -0.03283
C   3.24702 -0.31135 -1.65603
C   3.38572  0.49390  1.14248
C   2.76881 -2.26780  0.44574
N   0.31075  2.89590  1.13339
B  -0.11750  1.61837  1.73860
H   1.32603  2.22387 -1.22888
H   0.05452  0.53483 -1.67564
H  -2.03988 -3.02435 -0.41944
H  -2.43274 -2.10599 -1.90223
H  -3.72965 -2.49261 -0.71421
H   0.07079 -1.00204  1.33338
H  -4.58750  0.09015 -0.55554
H  -3.37929  0.70899 -1.71538
H  -3.57905  1.47809 -0.08451
H  -2.39600 -1.77770  2.21732
H  -4.03494 -1.21463  1.72501
H  -2.82558 -0.05482  2.39150
H   2.97149  0.40114  2.15753
H   3.35209  1.55135  0.83730
H   4.43274  0.15045  1.13329
H   2.25518 -2.96257 -0.23680
H   2.41175 -2.45172  1.47026
H   3.85593 -2.44190  0.39279
H   3.13498  0.72571 -2.00764
H   2.79796 -0.98732 -2.40021
H   4.31835 -0.54648 -1.54965
H   0.67474  1.03261  2.42875
H  -1.30721  1.55272  1.95056
H  -0.31778  3.69670  1.22624
H   1.27986  3.19287  1.25724
H  -0.99447  2.65577 -2.41273
H  -1.82532  2.33555 -1.00735
H  -0.74941  3.61606 -1.07189

SCF (BS1) =     -522.288209588
H 0K=           -521.947296
H 298K=         -521.923070
G 298K=         -522.002720
SCF (C6H5F) =   -522.345979130
BP86-D3 =       -522.347806308
Lowest Frequency = -241.3794cm-1
```

BN Product 2

```
C  -2.54598 -2.26156 -0.95490
P  -2.24666 -0.70170  0.02165
C  -2.87433 -1.12713  1.71851
Ir  0.02933 -0.16764 -0.06672
B   0.13686  2.44490 -0.74532
N  -1.38175  2.97744 -0.65703
C  -3.62210  0.39822 -0.62397
P   2.35887 -0.49105 -0.05876
C   2.77421 -1.87686 -1.23544
C   3.58021  0.82792 -0.58233
C   3.06427 -1.07248  1.55907
N   0.68004  2.50684  0.73545
B  -0.07394  1.30778  1.51621
H   0.75096  3.11331 -1.54538
H   0.08571  1.26503 -1.24839
H  -1.88454 -3.05459 -0.57425
H  -2.31387 -2.08694 -2.01716
H  -3.59557 -2.58462 -0.85987
H   0.06500 -1.45403  0.86867
H  -4.58543 -0.13622 -0.58254
H  -3.42526  0.67488 -1.67308
H  -3.71716  1.30448 -0.00358
H  -2.25148 -1.93508  2.13097
H  -3.92747 -1.44934  1.68318
H  -2.77495 -0.24610  2.37081
H   3.65231  1.62073  0.18146
H   3.26312  1.27468 -1.53743
H   4.58507  0.39072 -0.70308
H   2.54421 -1.99498  1.85872
H   2.87926 -0.30927  2.33089
H   4.14601 -1.26508  1.47550
H   2.52031 -1.57837 -2.26447
H   2.18534 -2.76744 -0.96751
H   3.84801 -2.12020 -1.18160
H   0.49950  0.96993  2.52984
H  -1.23863  1.68976  1.70475
H   0.58327  3.43658  1.17811
H   1.69026  2.32060  0.71789
H  -1.93755  2.66700 -1.46350
H  -1.79664  2.56855  0.20600
H  -1.45180  4.00380 -0.60959

SCF (BS1) =     -522.330233654
H 0K=           -521.985138
H 298K=         -521.961670
G 298K=         -522.037557
SCF (C6H5F) =   -522.389493877
BP86-D3 =       -522.389289084
Lowest Frequency = 19.6113cm-1
```

(c) B-N Coupling from an isomer of I6a′6

I6a′6 (Isomer 2)

```
C   3.11762 -1.51832  0.85372
P   2.31702 -0.33651 -0.34122
C   2.74380 -1.07079 -2.00073
Ir -0.01402 -0.06797 -0.16825
P  -2.37347 -0.22065 -0.31832
C  -3.43724  0.31825  1.11203
C   3.44657  1.14135 -0.23854
C  -3.07461  0.74680 -1.74731
C  -2.98404 -1.94460 -0.66944
B  -0.31537  2.25786  0.07189
N   0.65460  3.20296  0.42402
H   0.41772  4.04540  0.94506
B   0.12916  0.32401  1.98949
N  -0.10205 -1.07568  2.82200
H  -0.03530 -0.89719  3.83552
H   0.07401  1.51437 -0.94800
H  -1.46886  2.53798  0.25785
H   1.65258  3.09742  0.25888
H   1.25910  0.67799  2.27217
H  -0.76301  1.06302  2.35616
H   0.59934 -1.78638  2.57544
H  -1.02438 -1.48973  2.63532
H   2.62433 -2.49994  0.77579
H   3.00777 -1.12419  1.87668
H   4.19084 -1.63474  0.63278
H  -0.04217 -1.62286  0.27146
H   4.49780  0.84263 -0.38157
H   3.33903  1.60567  0.75479
H   3.17466  1.86573 -1.02310
H   2.21883 -2.03103 -2.12136
H   3.83034 -1.23627 -2.08507
H   2.41896 -0.38679 -2.80034
H  -2.58528  0.42435 -2.67986
H  -2.87753  1.81855 -1.59517
H  -4.16080  0.58127 -1.83330
H  -2.72954 -2.60756  0.17190
H  -2.48431 -2.32789 -1.57268
H  -4.07488 -1.95249 -0.82574
H  -3.17203  1.34705  1.39707
H  -3.26823 -0.34046  1.97836
H  -4.50185  0.27089  0.83198

SCF (BS1) =     -522.321548909
H 0K=           -521.978911
H 298K=         -521.954078
G 298K=         -522.032680
SCF (C6H5F) =   -522.377378977
BP86-D3 =       -522.381203549
Lowest Frequency = 25.6089cm-1
```

TS6a′ BN (Alt 3)

```
C  -3.19610 -0.23881 -1.63568
P  -2.25641 -0.64057 -0.07772
C  -2.40726 -2.49790  0.01038
Ir  0.04729 -0.17057  0.03298
P   2.38103 -0.44240  0.01341
C   3.44633  0.82742 -0.84513
C  -3.44813 -0.08824  1.24904
C   3.19667 -0.59572  1.67706
C   2.86047 -2.02541 -0.83872
B   0.23275  1.39568  1.41909
N  -0.86337  2.24526  1.80231
H  -0.71384  3.16006  2.22824
B  -0.68037  2.75984 -0.60731
N   0.13412  2.28085 -1.88370
H  -0.25978  2.70834 -2.73957
H   0.03975  0.02835  1.75594
H   1.32405  1.86868  1.65364
H  -1.83541  1.94147  1.82325
H  -1.84873  2.53079 -0.70439
H  -0.23272  3.77465 -0.16251
H   0.07511  1.22600 -1.92362
H   1.13138  2.52730 -1.83481
H  -2.65684 -0.66592 -2.49527
H  -3.26228  0.85339 -1.76011
H  -4.21481 -0.65783 -1.59777
H   0.07351 -0.45918 -1.60023
H  -4.40425 -0.62898  1.15565
H  -3.65575  0.98959  1.14449
H  -3.01765 -0.28892  2.24257
H  -1.81526 -2.95070 -0.79982
H  -3.46147 -2.80393 -0.09311
H  -2.01600 -2.85175  0.97640
H   2.73412 -1.43227  2.22327
H   3.03717  0.33018  2.25017
H   4.27758 -0.78090  1.56938
H   2.52711 -1.99010 -1.88697
H   2.36048 -2.87017 -0.33973
H   3.95164 -2.17595 -0.79934
H   3.30071  1.80964 -0.36702
H   3.17018  0.88264 -1.91077
H   4.51217  0.55546 -0.77387

SCF (BS1) =     -522.282810061
H 0K=           -521.942777
H 298K=         -521.918643
G 298K=         -521.995866
SCF (C6H5F) =   -522.337008351
BP86-D3 =       -522.341720541
Lowest Frequency = -248.1738cm-1
```

(d) B-N Coupling from I6a'9

I6a'9

C	3.49324	0.87646	-0.65853
P	2.36679	-0.46701	-0.03224
C	3.02278	-0.79859	1.67494
Ir	-0.00496	-0.27236	-0.12946
P	-2.35363	-0.54351	0.05909
C	-3.41034	0.98807	0.16969
C	2.96425	-1.94595	-0.99224
C	-3.13545	-1.46127	-1.35827
C	-2.87793	-1.52178	1.54516
B	0.11370	2.28817	-1.56776
N	-0.67466	3.31376	-0.60322
B	-0.06030	0.85489	1.60520
H	-0.77805	0.57674	2.54502
H	-0.33678	1.11068	-1.27160
H	1.29526	2.45197	-1.39471
H	-1.69647	3.25824	-0.69742
H	-0.40159	4.28156	-0.81953
N	0.64903	2.09019	1.78325
H	-0.27520	2.41534	-2.70618
H	3.36209	1.80024	-0.07455
H	3.25868	1.09546	-1.71060
H	4.54167	0.54733	-0.57150
H	0.10737	-1.05302	-1.87509
H	-0.09532	-1.68490	-1.38799
H	0.07247	-1.51179	0.87163
H	4.04813	-2.08653	-0.85171
H	2.75444	-1.79924	-2.06336
H	2.43206	-2.84449	-0.64390
H	2.79830	0.05849	2.32786
H	4.11142	-0.96628	1.64817
H	2.52080	-1.68937	2.08236
H	-2.68054	-2.46099	-1.43816
H	-2.95469	-0.91348	-2.29633
H	-4.22073	-1.57084	-1.20123
H	-2.50625	-1.02504	2.45401
H	-2.42980	-2.52538	1.48458
H	-3.97531	-1.60912	1.58957
H	-3.32135	1.55682	-0.77036
H	-3.08018	1.60467	1.02058
H	-4.46910	0.71922	0.31570
H	0.66516	2.56249	2.68911
H	1.43472	2.35762	1.18741
H	-0.42320	3.10860	0.39174

SCF (BS1) = -523.524900441
H 0K= -523.166276
H 298K= -523.140958
G 298K= -523.220002
SCF (C6H5F) = -523.578115459
BP86-D3 = -523.588482301
Lowest Frequency = 24.5134cm-1

TS6a'BN (Alt 4)

C	3.47476	0.77518	0.10117
P	2.26387	-0.64266	-0.00435
C	2.89745	-1.81164	1.29705
Ir	-0.10898	-0.30446	0.02061
P	-2.47580	-0.27472	0.00038
C	-3.26639	1.05088	-1.02855
C	2.79850	-1.44844	-1.59395
C	-3.21062	-1.84087	-0.68079
C	-3.29836	-0.11213	1.65688
B	0.50972	1.88894	-1.88979
N	0.71652	2.97272	-0.81761
B	-0.22673	1.47965	0.93277
H	-1.18323	2.21870	0.96481
H	-0.07284	0.63251	-1.44767
H	1.54234	1.47370	-2.37126
H	-0.01350	3.69051	-0.86854
H	1.59865	3.46271	-1.00834
N	0.88812	2.12384	1.86654
H	-0.41848	2.06500	-2.65078
H	3.49911	1.21512	1.11119
H	3.19260	1.54192	-0.63504
H	4.48806	0.40812	-0.12851
H	-0.23154	-1.70481	-1.22500
H	-0.13362	-2.10717	-0.50010
H	-0.17563	-1.08786	1.45808
H	3.88680	-1.62139	-1.59618
H	2.52466	-0.78987	-2.43258
H	2.27987	-2.41259	-1.71070
H	2.71812	-1.38880	2.29803
H	3.97435	-2.00588	1.16594
H	2.34141	-2.75905	1.22525
H	-2.86925	-2.69777	-0.07964
H	-2.88284	-1.97803	-1.72303
H	-4.31105	-1.79170	-0.65218
H	-3.00592	0.84193	2.12159
H	-2.96620	-0.93919	2.30263
H	-4.39464	-0.14084	1.54984
H	-2.89341	0.97394	-2.06109
H	-2.98998	2.03885	-0.63061
H	-4.36326	0.94668	-1.01684
H	0.53599	2.71012	2.63585
H	1.60513	1.47665	2.21445
H	1.26899	2.73604	1.09498

SCF (BS1) = -523.474136632
H 0K= -523.118946
H 298K= -523.094275
G 298K= -523.171446
SCF (C6H5F) = -523.530206410
BP86-D3 = -523.538999832
Lowest Frequency = -332.6736cm-1

BN Product 3

C	3.45179	0.88098	-0.41762
P	2.30565	-0.52049	0.06025
C	3.00524	-1.05777	1.70108
Ir	-0.06223	-0.28568	-0.02105
P	-2.42370	-0.33224	0.05247
C	-3.34940	0.64377	-1.22564
C	2.90842	-1.85503	-1.09040
C	-3.11066	-2.04871	-0.16308
C	-3.19477	0.20845	1.65516
B	0.17231	1.47949	-2.09986
N	0.51108	2.49101	-0.88637

```
B  -0.20953  1.82526  0.35289
H  -1.32827  2.30284  0.43760
H  -0.00234  0.20482 -1.73596
H   1.11264  1.37545 -2.85879
H   0.19213  3.43971 -1.12584
H   1.53280  2.53627 -0.79187
N   0.49924  2.31355  1.76417
H  -0.88607  1.77466 -2.59843
H   3.37145  1.72618  0.28746
H   3.20398  1.22036 -1.43687
H   4.49852  0.53580 -0.40720
H  -0.10043 -1.94368 -0.85811
H  -0.09133 -2.13496 -0.03155
H  -0.11902 -0.61425  1.56151
H   4.00405 -1.95970 -1.03455
H   2.61423 -1.59973 -2.12033
H   2.43831 -2.81185 -0.81526
H   2.83772 -0.27823  2.46132
H   4.08529 -1.26353  1.62559
H   2.47819 -1.96767  2.02667
H  -2.70265 -2.70771  0.61908
H  -2.81538 -2.43949 -1.14931
H  -4.21035 -2.03830 -0.09303
H  -2.94088  1.26221  1.84551
H  -2.80120 -0.41613  2.47176
H  -4.29091  0.10615  1.60978
H  -3.05022  0.30207 -2.22784
H  -3.09788  1.71019 -1.13124
H  -4.43484  0.50675 -1.09359
H   0.01364  1.79752  2.51114
H   1.49250  2.05599  1.84436
H   0.40900  3.32113  1.97146

SCF (BS1) =     -523.524244658
H 0K=           -523.163613
H 298K=         -523.139337
G 298K=         -523.216260
SCF (C6H5F) =   -523.582408679
BP86-D3 =       -523.589532158
Lowest Frequency = 9.0994cm-1
```

(e) B-N Coupling from an isomer of I6a′$_4$

I6a′4 (Isomer 2)

```
C  -3.11733  1.00572 -1.37745
P  -2.35104 -0.29898 -0.29402
Ir  0.00023 -0.17037 -0.09287
P   2.35158 -0.29750 -0.29397
C   2.94111 -1.88329 -1.05590
C  -3.36372 -0.17666  1.26505
C  -2.93929 -1.88436 -1.05781
N   0.00034 -0.37095  2.17853
B   0.00105 -1.77159  1.75006
C   3.11679  1.00656 -1.37892
C   3.36412 -0.17252  1.26500
B  -0.00263  2.48609  0.86354
H  -1.02981  2.46173  1.50283
H   1.02255  2.46446  1.50616
N  -0.00317  3.89438  0.02709
H  -2.63558  0.98158 -2.36688
H  -2.95552  1.99489 -0.92092
H  -4.20040  0.83702 -1.49148
H   0.00054 -1.69030 -0.53187
H   0.00018 -0.03215 -1.68205
H   0.00063  1.65938 -0.12505
H  -4.43745 -0.27606  1.03757
H  -3.18971  0.80005  1.74451
H  -3.07234 -0.98386  1.95577
H  -2.47905 -1.99440 -2.05162
H  -4.03694 -1.89360 -1.15344
H  -2.61593 -2.72507 -0.42517
H   2.48106 -1.99478 -2.04964
H   2.61831 -2.72353 -0.42235
H   4.03877 -1.89180 -1.15141
H   2.95414  1.99617 -0.92363
H   2.63505  0.98087 -2.36831
H   4.20000  0.83861 -1.49275
H   3.07354 -0.97928  1.95657
H   3.18913  0.80451  1.74344
H   4.43796 -0.27112  1.03765
H   1.05003 -2.36109  1.75550
H  -1.04737 -2.36205  1.75551
H  -0.84022  0.06345  2.56256
H   0.84040  0.06451  2.56248
H  -0.00539  4.68485  0.68681
H   0.82604  4.00293 -0.57201
H  -0.83064  4.00060 -0.57484

SCF (BS1) =     -523.538398570
H 0K=           -523.176155
H 298K=         -523.150762
G 298K=         -523.230801
SCF (C6H5F) =   -523.594694425
BP86-D3 =       -523.600861630
Lowest Frequency = 23.4553cm-1
```

TS6a′BN (Alt 5)

```
C  -3.04411 -0.74438 -1.83929
P  -2.36238 -0.47537 -0.13444
Ir -0.01211 -0.26415 -0.03413
P   2.32721 -0.56126 -0.11940
C   2.91227 -1.98860  0.91382
C  -3.39483  0.93093  0.52379
C  -2.99333 -1.92767  0.83492
N  -0.00791  1.69761  1.16592
B  -0.02434  0.53459  2.28049
C   3.00197 -0.92588 -1.80941
C   3.40864  0.83767  0.47569
B   0.02668  2.13099 -0.95621
H   0.99611  1.91712 -1.63259
H  -1.09251  2.11850 -1.39206
N   0.26042  3.73281 -0.53320
H  -2.56809 -1.63753 -2.27222
H  -2.79521  0.12273 -2.47031
H  -4.13689 -0.88351 -1.81330
H  -0.02622 -0.68503  1.72632
H  -0.03877 -1.77981 -0.46509
H  -0.01423 -0.24047 -1.62988
H  -4.46743  0.68792  0.45404
H  -3.20205  1.84276 -0.06402
H  -3.13969  1.10461  1.58189
H  -2.52579 -2.84633  0.44886
H  -4.08935 -2.01052  0.75588
H  -2.70513 -1.80381  1.89020
H   2.41357 -2.90722  0.56875
H   2.62889 -1.80868  1.96234
H   4.00478 -2.11189  0.83915
H   2.77896 -0.08106 -2.47932
H   2.49976 -1.82274 -2.20326
H   4.09011 -1.09633 -1.77578
H   3.15794  1.07049  1.52327
H   3.24694  1.72526 -0.15747
H   4.47323  0.55796  0.42115
H   1.00367  0.56700  2.92148
H  -1.05998  0.57362  2.90783
H  -0.85527  2.25984  1.28779
H   0.81887  2.26941  1.35575
H   0.18801  4.23316 -1.43317
H  -0.44109  4.16094  0.09071
H   1.19419  3.95911 -0.15873

SCF (BS1) =     -523.474464088
H 0K=           -523.113016
H 298K=         -523.088740
G 298K=         -523.166246
SCF (C6H5F) =   -523.536452170
BP86-D3 =       -523.537730188
Lowest Frequency = -309.4435cm-1
```

BN Product 4

```
C  -2.92346 -1.35186 -1.71870
P  -2.28155 -0.70260 -0.09877
Ir  0.03629 -0.28522 -0.03312
P   2.37896 -0.52754 -0.04422
C   3.30976 -0.03438  1.48569
C  -3.49965  0.66587  0.29118
C  -2.80511 -2.00815  1.11639
N  -0.58105  2.56137  1.04756
B  -0.09814  1.44883  2.14011
C   2.89303 -2.29509 -0.29475
C   3.29619  0.35306 -1.40538
```

```
B   0.23991  2.38326 -0.25696
H   1.40896  2.61925 -0.09236
H  -0.04665  1.32402 -0.91290
N  -0.25324  3.47532 -1.40779
H  -2.35020 -2.25318 -1.98422
H  -2.76613 -0.59924 -2.50690
H  -3.99515 -1.60048 -1.65250
H  -0.11225  0.22724  1.68998
H   0.07741 -1.76863  0.50434
H   0.11958 -0.97433 -1.47359
H  -4.53672  0.29468  0.24174
H  -3.39542  1.48884 -0.43618
H  -3.31464  1.03779  1.31287
H  -2.26363 -2.93962  0.89171
H  -3.89078 -2.18962  1.06113
H  -2.53320 -1.68270  2.13233
H   2.90822 -0.59508  2.34361
H   3.16164  1.03856  1.67776
H   4.38469 -0.24975  1.37195
H   2.45658 -2.66730 -1.23400
H   2.50515 -2.90299  0.53687
H   3.99087 -2.38225 -0.33340
H   3.17147  1.44048 -1.28812
H   2.88027  0.04357 -2.37673
H   4.37030  0.10823 -1.37263
H   1.02150  1.72954  2.49305
H  -0.92977  1.38772  3.02180
H  -1.59262  2.43729  0.90708
H  -0.45205  3.47894  1.49788
H   0.30000  3.31900 -2.26284
H  -1.24431  3.39911 -1.67997
H  -0.08195  4.45125 -1.12322

SCF (BS1) =     -523.540363015
H 0K=           -523.176625
H 298K=         -523.152155
G 298K=         -523.231036
SCF (C6H5F) =   -523.604236642
BP86-D3 =       -523.600729015
Lowest Frequency = 11.5057cm-1
```

(f) B^2-H^{21} cleavage yields a $\{H_2BNH_3\}$ moiety

TS6a′ BN (Alt 6)

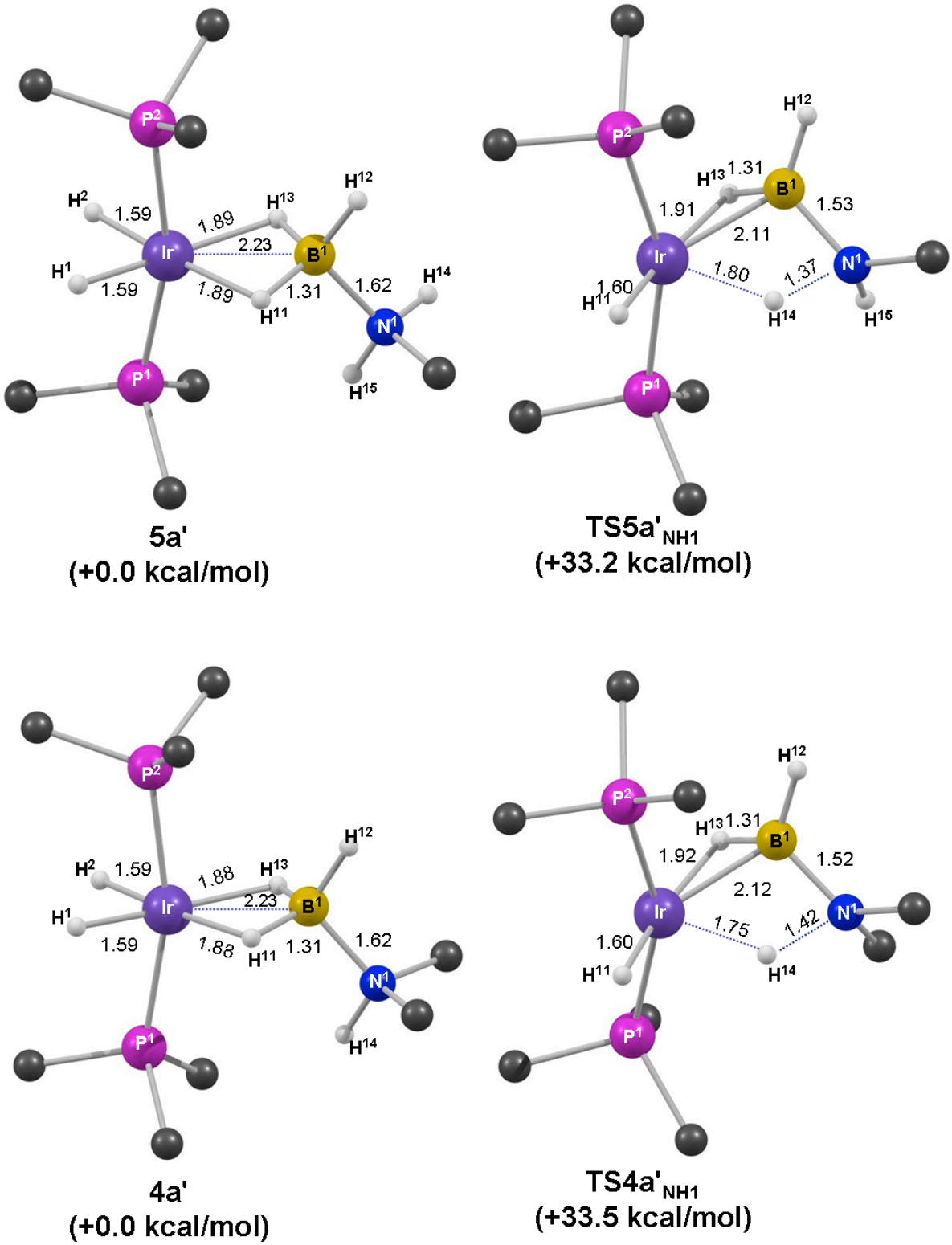
C	-3.06337	-0.32985	-1.77531
P	-2.31881	-0.61746	-0.09682
C	-2.82464	-2.36211	0.29081
Ir	0.02467	-0.30146	0.01770
P	2.38521	-0.50188	0.01934
C	3.40322	0.86115	-0.74667
C	-3.43788	0.37290	1.01782
C	3.13561	-0.66688	1.70966
C	2.99336	-2.00986	-0.87466
B	0.25408	1.61710	1.21972
N	-0.72784	2.39389	1.91396
H	-0.49041	3.22643	2.45398
B	-0.57856	2.93330	-0.53464
N	0.40683	2.70922	-1.76179
H	0.24078	3.42624	-2.48912
H	-0.02314	0.23764	1.61223
H	1.37749	2.03727	1.40346
H	-1.72789	2.19658	1.89956
H	-1.69907	2.58506	-0.76192
H	-0.32759	3.98809	-0.02695
H	0.26839	1.74193	-2.12300
H	1.39481	2.77596	-1.48127
H	-2.53526	-0.95776	-2.50908
H	-2.93474	0.72737	-2.05421
H	-4.13639	-0.58120	-1.77892
H	-0.01104	0.23651	-1.54765
H	-4.48135	0.03404	0.91110
H	-3.38902	1.43830	0.74042
H	-3.12699	0.23979	2.06624
H	-2.29186	-3.04517	-0.38810
H	-3.91257	-2.49411	0.17385
H	-2.53059	-2.59993	1.32467
H	2.68285	-1.53500	2.21273
H	2.91155	0.23707	2.29665
H	4.22710	-0.80409	1.64475
H	2.67888	-1.95854	-1.92836
H	2.53552	-2.89985	-0.41695
H	4.09117	-2.08641	-0.81733
H	3.19915	1.80757	-0.21967
H	3.14818	0.95218	-1.81510
H	4.47974	0.64061	-0.66146
H	0.06177	-1.54924	-1.02436
H	0.05677	-1.68089	0.88284

SCF (BS1) = -523.469159653
H 0K= -523.112392
H 298K= -523.087803
G 298K= -523.165044
SCF (C6H5F) = -523.522614156
BP86-D3 = -523.533541863
Lowest Frequency = -248.3193 cm-1

(6) Reactions of $H_3B{\bullet}NMeH_2$ and $H_3B{\bullet}NMe_2H$

Model 1. Dehydrogenation of 5a' and 4a' in the absence of added amineborane

Figure S13. Computed Structures.



5a'

C	3.23458	0.82203	-1.37727
P	2.47449	-0.20763	-0.02977
C	3.29671	0.40889	1.51846
Ir	0.11435	-0.24603	0.01687
B	0.05073	1.96141	0.33086
N	-1.27985	2.87176	0.49075
P	-2.14510	-0.91235	-0.02286
C	-3.15498	-0.61645	1.51822
C	3.22825	-1.88329	-0.28514
C	-3.22292	-0.21602	-1.37757
C	-2.33794	-2.74263	-0.27110
C	-1.39730	3.97008	-0.53017
H	-1.26822	3.29239	1.43220
H	0.30521	-1.60382	0.81317
H	0.26210	-1.33113	-1.13024
H	0.02233	1.11022	1.32439
H	-0.02740	1.42130	-0.85756
H	0.99464	2.71180	0.41837
H	-2.12102	2.27751	0.45628
H	2.92440	1.87071	-1.25193
H	2.87514	0.46003	-2.35288
H	4.33434	0.75815	-1.34417
H	2.86981	-2.29834	-1.23934
H	2.90914	-2.55021	0.53012
H	4.32802	-1.81720	-0.30015
H	-2.74899	-0.42426	-2.34927
H	-3.32293	0.87666	-1.27168
H	-4.22773	-0.66868	-1.35531
H	-1.82470	-3.27058	0.54683
H	-1.86266	-3.02647	-1.22225
H	-3.40212	-3.02784	-0.28749
H	2.97532	-0.21284	2.36828
H	2.98884	1.44923	1.70424
H	4.39367	0.36216	1.42304
H	-3.26094	0.46341	1.71321
H	-2.63417	-1.06951	2.37591
H	-4.15974	-1.05974	1.42332
H	-2.30018	4.57128	-0.34925
H	-0.50133	4.60158	-0.46052
H	-1.43961	3.51351	-1.52878

SCF (BS1) = -480.799385121
H 0K= -480.459875
H 298K= -480.437086
G 298K= -480.512952
SCF (C6H5F) = -480.852872823
BP86-D3 = -480.849452051
Lowest Frequency = 13.6111cm-1

TS5a'NH1

C	3.29183	0.38936	-1.30561
P	2.31296	-0.56834	-0.05298
Ir	-0.00261	-0.12953	0.04972
B	0.56297	1.72267	0.88249
N	-0.39676	2.67324	0.16818
C	2.58113	-2.34215	-0.54002
C	3.29484	-0.40808	1.51667
P	-2.32920	-0.55693	-0.03801
C	-3.27013	0.03042	-1.52878
C	-2.59773	-2.39715	-0.04963
C	-3.36235	0.01860	1.39900
C	0.08151	3.91442	-0.48437
H	-0.49744	1.49988	-0.52316
H	0.01877	-0.76302	-1.41696
H	0.00918	0.84649	1.68619
H	1.65235	2.15177	1.16011
H	-1.31721	2.78537	0.60694
H	3.29989	1.45347	-1.02423
H	2.81721	0.28335	-2.29290
H	4.32797	0.01678	-1.35040
H	2.14868	-2.51400	-1.53702
H	2.07917	-3.00265	0.18391
H	3.65848	-2.57479	-0.55694
H	-2.77926	-0.35591	-2.43490
H	-3.26031	1.13080	-1.56780
H	-4.31379	-0.32167	-1.49380
H	-2.15241	-2.84026	0.85425
H	-2.11208	-2.83048	-0.93691
H	-3.67658	-2.62250	-0.07339
H	2.85499	-1.06333	2.28442
H	3.26294	0.63090	1.87639
H	4.34244	-0.70245	1.34265
H	-3.38149	1.11937	1.43386
H	-2.92195	-0.35662	2.33547
H	-4.39631	-0.35173	1.30492
H	-0.68055	4.30078	-1.17751
H	0.31309	4.68419	0.27087
H	0.99676	3.69048	-1.05106

SCF (BS1) = -479.550395161
H 0K= -479.237045
H 298K= -479.214729
G 298K= -479.289013
SCF (C6H5F) = -479.601159452
BP86-D3 = -479.596003951
Lowest Frequency = -1125.3735cm-1

4a'

C	-3.21408	0.95348	1.46282
P	-2.55489	0.01558	0.00002
C	-3.21418	0.95378	-1.46255
Ir	-0.22602	-0.36494	-0.00006
B	0.17249	1.83166	0.00001
N	1.62280	2.54533	-0.00001
P	1.91123	-1.35441	0.00001
C	3.01953	-1.00713	-1.46081
C	-3.55347	-1.54776	-0.00011
C	3.01848	-1.00826	1.46187
C	1.83414	-3.20992	-0.00082
C	1.82881	3.36981	1.23922
C	1.82871	3.36991	-1.23919
H	-0.57558	-1.56055	-0.98285
H	-0.57554	-1.56062	0.98267
H	0.11556	1.12282	-1.10124
H	0.11563	1.12274	1.10122
H	-0.65297	2.71636	0.00007
H	2.33530	1.79982	-0.00008
H	-2.74918	1.95081	1.49373
H	-2.95215	0.41164	2.38470
H	-4.30907	1.06040	1.39790

H -3.29940 -2.13767 0.89360
H -3.29945 -2.13749 -0.89395
H -4.63181 -1.32138 -0.00005
H   2.47941 -1.27171 2.38502
H   3.27649 0.06251 1.50853
H   3.94934 -1.59549 1.40072
H   1.28559 -3.54454 -0.89428
H   1.28487 -3.54530 0.89191
H   2.84599 -3.64618 -0.00060
H -2.95231 0.41211 -2.38455
H -2.74926 1.95111 -1.49329
H -4.30915 1.06069 -1.39753
H   3.27777 0.06365 -1.50639
H   2.48108 -1.26972 -2.38456
H   3.95026 -1.59452 -1.39950
H   2.82438 3.83936 1.22242
H   1.05024 4.14538 1.26952
H   1.72917 2.72222 2.12174
H   2.82427 3.83949 -1.22242
H   1.72903 2.72239 -2.12176
H   1.05012 4.14546 -1.26939

SCF (BS1) =   -520.107608730
H 0K=   -519.740959
H 298K=   -519.716873
G 298K=   -519.795237
SCF (C6H5F) =   -520.158127506
BP86-D3 =   -520.163523800
Lowest Frequency = 19.3142cm-1

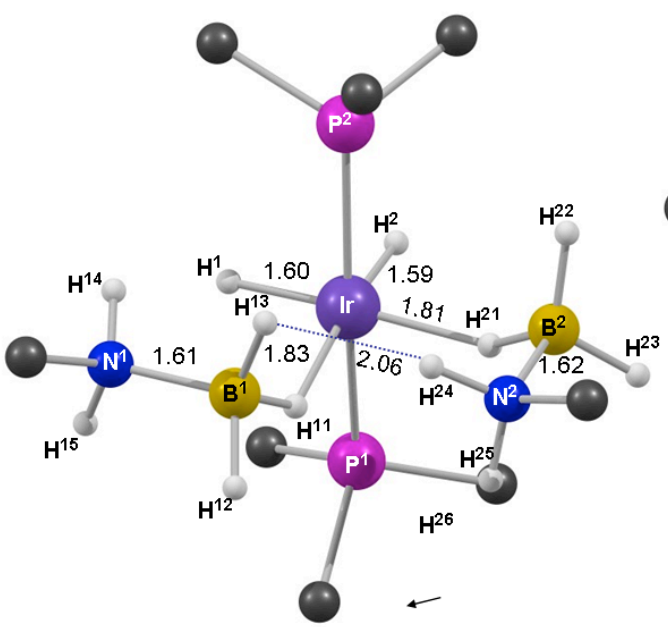
TS4a'NH1

C   3.36756 0.48672 -1.22888
P   2.39951 -0.51204 0.00011
Ir 0.05718 -0.22395 0.03543
B   0.52017 1.70217 0.78730
N -0.43349 2.58849 -0.00620
C   2.78993 -2.27125 -0.45802
C   3.31290 -0.28066 1.60186
P -2.20974 -0.90337 -0.06701
C -3.27548 -0.24393 -1.43888
C -2.25508 -2.74461 -0.33070
C -3.24677 -0.68150 1.46227
C   0.18227 3.62296 -0.86750
H -0.53167 1.30096 -0.60202
H   0.15574 -0.91927 -1.39697
H -0.03712 0.85554 1.61673
H   1.59300 2.16409 1.08281
C -1.71535 3.02260 0.58966
H   3.31562 1.55141 -0.95451
H   2.93096 0.35061 -2.22997
H   4.42169 0.16551 -1.23815
H   2.40818 -2.47630 -1.46933
H   2.29875 -2.95409 0.25238
H   3.87886 -2.44043 -0.43043
H -2.77209 -0.42466 -2.40080
H -3.41588 0.84052 -1.31195
H -4.25982 -0.73946 -1.43727
H -1.70729 -3.24677 0.48145
H -1.77408 -2.98803 -1.28974
H -3.29881 -3.09942 -0.33892
H   2.89327 -0.96371 2.35655
H   3.19655 0.75435 1.95541
H   4.38365 -0.50220 1.46479
H -3.41256 0.38845 1.65998
H -2.71898 -1.12129 2.32244
H -4.22300 -1.17821 1.33777
H -2.41795 3.33447 -0.20057
H -2.15230 2.19693 1.16900
H -1.54872 3.87774 1.26969
H -0.53385 3.94323 -1.64156
H   0.47587 4.50135 -0.26503
H   1.07612 3.21172 -1.35830

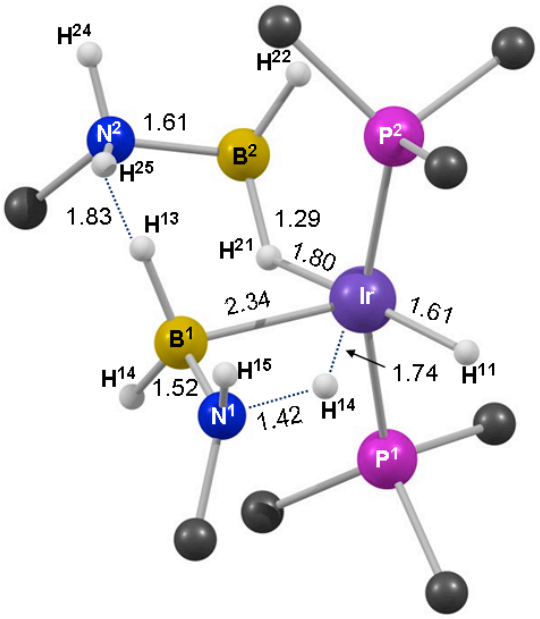
SCF (BS1) =   -518.855329210
H 0K=   -518.514847
H 298K=   -518.491161
G 298K=   -518.568081
SCF (C6H5F) =   -518.904345460
BP86-D3 =   -518.908313170
Lowest Frequency = -973.7727cm-1

(7) Model 2. Dehydrogenation of 5a' and 4a' in the presence of added amine-borane

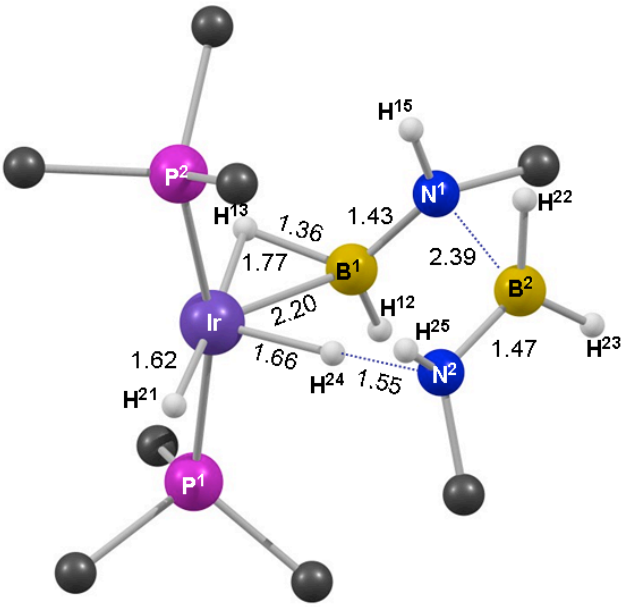
Figure S14. Computed Structures.



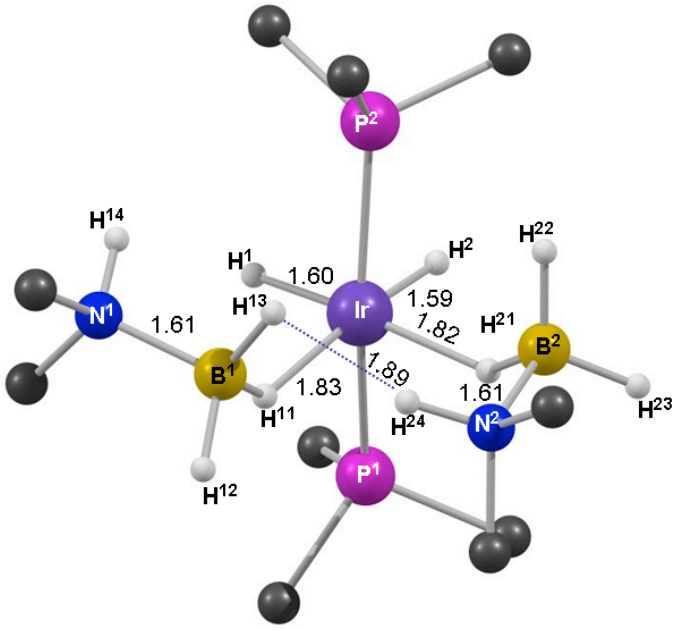
I5a'$_1$
(+0.0 kcal/mol)



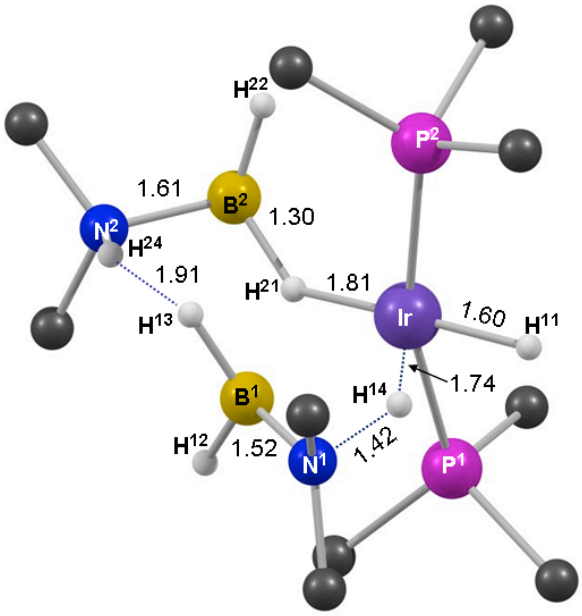
TS5a'$_{NH1}$
(+25.2 kcal/mol)



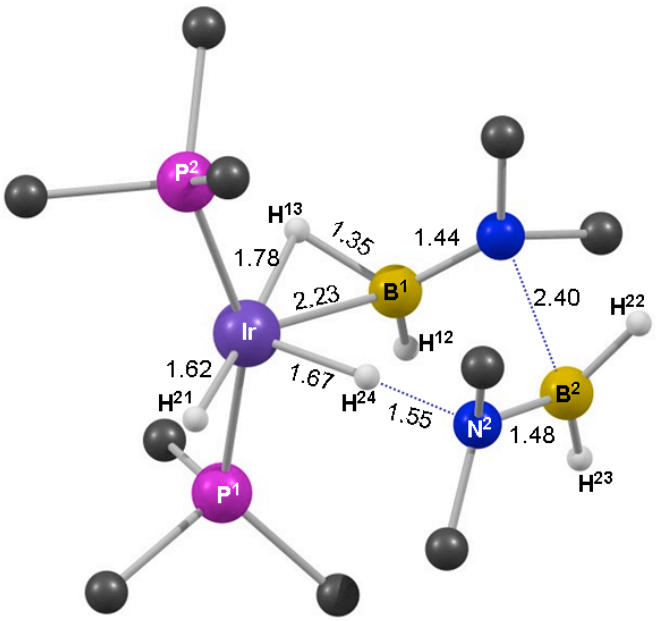
TS5a'$_{BN}$
(+19.9 kcal/mol)



I4a'$_1$
(+0.0 kcal/mol)



TS4a'$_{NH1}$
(+26.2 kcal/mol)



TS4a'$_{BN}$
(+26.5 kcal/mol)

I5a'

C	-2.17425	0.97706	-2.72369
P	-1.98226	-0.11035	-1.22771
C	-2.51874	-1.77212	-1.88233
C	-3.45333	0.39126	-0.19538
Ir	0.22938	-0.06660	-0.38725
P	2.57469	-0.09098	-0.21160
C	3.35418	-0.27452	1.47260
C	3.38935	-1.44382	-1.19109
C	3.38479	1.44609	-0.87191
B	-0.64126	-0.89315	2.20451
N	-0.67414	-2.47290	1.90606
B	-0.36649	2.63483	0.34251
N	-0.64055	2.38736	1.91125
H	0.28739	-2.83765	1.94949
C	-1.54950	-3.26293	2.83168
H	-0.95981	-2.60332	0.92367
H	0.33021	-1.61568	-0.77277
H	-3.20509	0.93331	-3.11121
H	-1.92465	2.01186	-2.44519
H	-1.47140	0.64137	-3.50127
H	-4.37936	0.30023	-0.78616
H	-3.52653	-0.24425	0.69988
H	-3.32890	1.43954	0.11599
H	-3.48745	-1.69741	-2.40281
H	-1.75262	-2.14397	-2.57946
H	-2.61868	-2.49208	-1.05368
H	0.22199	-0.36484	1.42103
H	-1.77205	-0.45667	2.13837
H	0.54427	0.20666	-1.91684
H	-0.12057	-0.71857	3.29033
H	4.48722	-1.36491	-1.13711
H	3.07028	-2.42230	-0.80039
H	3.06355	-1.36580	-2.23947
H	4.45383	-0.27281	1.39710
H	3.03647	0.55778	2.11973
H	3.02623	-1.21924	1.93343
H	4.48213	1.37774	-0.79629
H	3.09448	1.57523	-1.92582
H	3.02700	2.32027	-0.30654
H	0.41119	1.70996	-0.11715
H	0.37336	3.59153	0.23529
H	-1.42669	2.75737	-0.22332
C	-1.34440	3.53449	2.57173
H	-1.18397	1.51706	2.03677
H	0.25026	2.21432	2.39641
H	-1.51232	3.32707	3.63918
H	-0.72812	4.43615	2.45203
H	-2.30482	3.69181	2.06204
H	-1.51462	-4.33429	2.58406
H	-1.19979	-3.10169	3.86076
H	-2.57823	-2.88813	2.74208

SCF (BS1) = -603.337114800
H 0K= -602.899248
H 298K= -602.870036
G 298K= -602.960672
SCF (C6H5F) = -603.389328937
BP86-D3 = -603.410482640
Lowest Frequency = 15.2276cm-1

TS5a'NH

C	2.91181	-0.85860	-2.05892
P	2.35792	-0.62320	-0.29704
C	2.96648	-2.17581	0.53378
Ir	0.01758	-0.29258	-0.23940
B	-0.03155	0.58495	1.92664
N	-0.12590	-0.74459	2.65952
C	3.56126	0.65023	0.34296
P	-2.29754	-0.39185	-0.67188
C	-3.38614	1.00346	-0.09646
C	-2.59215	-0.41288	-2.51057
C	-3.19856	-1.91117	-0.09027
B	0.49655	2.34654	-1.02759
N	0.81666	3.29134	0.24082
H	3.99398	-1.06357	-2.10366
H	2.36107	-1.70303	-2.50126
H	2.68476	0.05260	-2.63340
H	4.59634	0.29210	0.22252
H	3.43722	1.58291	-0.22753
H	3.36772	0.84350	1.40980
H	4.04059	-2.33047	0.34203
H	2.80672	-2.10595	1.62148
H	2.39623	-3.03555	0.15034
H	-0.01441	-1.89729	-0.27932
H	-0.30414	1.45462	-0.53778
H	-1.03678	1.25741	1.98949
H	1.04985	1.14415	2.03861
H	-0.15376	-1.10797	1.28324
H	0.75162	-1.10850	3.04354
C	-1.29206	-1.12893	3.47566
H	-4.24550	-1.90163	-0.43414
H	-2.68842	-2.80184	-0.48812
H	-3.17874	-1.95913	1.00927
H	-4.43127	0.83581	-0.40302
H	-3.33371	1.08688	0.99991
H	-3.02265	1.94292	-0.54130
H	-3.67093	-0.46956	-2.73071
H	-2.17466	0.50341	-2.95588
H	-2.08340	-1.28392	-2.95160
H	-0.25864	2.92694	-1.77815
H	1.53088	1.99573	-1.54042
H	1.63535	3.87356	0.01752
C	-0.30629	4.17888	0.68724
H	1.09082	2.68092	1.03343
H	-0.00066	4.78617	1.55260
H	-0.59327	4.82766	-0.15127
H	-1.15646	3.54124	0.96459
H	-1.33161	-2.22090	3.61648
H	-1.26101	-0.64250	4.46662
H	-2.20917	-0.79790	2.96546

SCF (BS1) = -602.097977294
H 0K= -601.686013
H 298K= -601.657766
G 298K= -601.744987
SCF (C6H5F) = -602.148572643
BP86-D3 = -602.170261784
Lowest Frequency = -834.9461cm-1

TS5a'BN

C	3.13014	-2.00060	0.82235
P	2.45828	-0.53690	-0.10621
Ir	0.09272	-0.49370	-0.08292
B	0.20485	1.31574	-1.32361
N	-0.87785	2.25589	-1.36929
C	3.42994	0.88927	0.58240
C	3.16791	-0.75246	-1.81219
P	-2.19377	-1.08428	0.05886
C	-3.15024	-0.60609	1.58213
C	-3.36519	-0.62851	-1.31784
C	-2.28921	-2.94536	0.06990
B	-1.09286	3.01743	0.89031
N	-0.55454	2.01376	1.81498
H	2.86212	-1.90866	1.88574
H	4.22585	-2.05754	0.71818
H	2.68012	-2.92443	0.42652
H	4.50884	0.70588	0.45310
H	3.20674	1.00280	1.65346
H	3.15029	1.81263	0.05323
H	-4.32215	-1.16345	-1.20302
H	-2.91465	-0.89252	-2.28698
H	-3.57122	0.45382	-1.30002
H	-1.84247	-3.34397	-0.85450
H	-3.33880	-3.27614	0.13467
H	-1.72762	-3.33376	0.93313
H	2.74675	-1.66101	-2.27042
H	4.26528	-0.84418	-1.76715
H	2.89750	0.11550	-2.43245
H	-4.13927	-1.09231	1.58726
H	-3.29619	0.48612	1.59944
H	-2.58805	-0.91792	2.47597
H	-0.07593	0.05622	-1.75745
H	0.22710	-1.08992	1.41810
H	-0.15565	0.83905	0.88203
H	1.29116	1.76465	-1.59942
C	-0.80249	3.56630	-2.04775
H	-1.82864	1.88089	-1.36088
H	-0.40078	3.96322	0.63504
H	-2.27944	3.00246	0.68643
H	-1.25838	1.48553	2.33921
C	0.63556	2.29337	2.65033
H	1.08268	1.35181	3.00842
H	1.37307	2.84153	2.04721
H	0.36956	2.91418	3.52212
H	-1.46700	4.29633	-1.55892
H	0.23007	3.93974	-1.99269
H	-1.08928	3.47688	-3.10982

SCF (BS1) = -600.914403794
H 0K= -600.521913
H 298K= -600.495080
G 298K= -600.578769
SCF (C6H5F) = -600.964885180
BP86-D3 = -600.983342354
Lowest Frequency = -302.1793cm-1

I4a'

C	-1.95282	-0.04279	-3.18917
P	-1.91474	-0.56996	-1.40558
C	-2.49955	-2.33692	-1.51971
C	-3.42384	0.28956	-0.71821
Ir	0.23265	-0.35623	-0.44249
P	2.54415	-0.58466	-0.08324
C	3.22702	-0.42351	1.64499
C	3.19556	-2.24294	-0.61291
C	3.60009	0.59479	-1.06011
B	-0.85151	0.32780	2.09064
N	-1.51106	-1.03310	2.64743
B	-0.08207	2.45026	-0.99897
N	-0.18455	3.15541	0.44869
C	-0.50707	-1.95004	3.27841
C	-2.64707	-0.75003	3.58421
H	-1.88541	-1.52506	1.82232
H	0.14874	-1.92182	-0.14922
H	-2.95666	-0.19188	-3.61920
H	-1.67115	1.01826	-3.25800
H	-1.21800	-0.64063	-3.74954
H	-4.30428	0.06923	-1.34366
H	-3.62168	-0.04450	0.31204
H	-3.24663	1.37523	-0.70716
H	-3.43937	-2.40791	-2.09115
H	-1.71936	-2.93430	-2.01546
H	-2.65883	-2.75070	-0.51095
H	0.12972	-0.02048	1.35087
H	-1.73091	0.99945	1.59072
H	0.64205	-0.75992	-1.92180
H	-0.28560	0.87942	3.01750
H	4.28827	-2.29893	-0.48096
H	2.70976	-3.03146	-0.01811
H	2.94153	-2.40114	-1.67201
H	4.32119	-0.55679	1.64733
H	2.98122	0.56771	2.05625
H	2.76943	-1.18979	2.28976
H	4.67139	0.38757	-0.90498
H	3.35320	0.48771	-2.12748
H	3.37677	1.62954	-0.75903
H	0.62063	1.37570	-0.85892
H	0.65173	3.11743	-1.70015
H	-1.20269	2.32300	-1.43164
C	-0.99084	4.41538	0.36060
H	-0.69339	2.49461	1.06356
C	1.14547	3.42073	1.07689
H	-1.07093	4.88987	1.35154
H	-0.49168	5.09867	-0.34208
H	-1.98995	4.17323	-0.02605
H	-3.10382	-1.69012	3.93127
H	-2.25160	-0.18851	4.44301
H	-3.39401	-0.13308	3.06585
H	1.02046	3.88388	2.06856
H	1.68093	2.46681	1.17711
H	1.71280	4.09366	0.41729
H	-0.99648	-2.87262	3.62845
H	0.25984	-2.18961	2.52900
H	-0.04721	-1.42470	4.12784

TS4a'NH1

SCF (BS1) = -681.948913250
H 0K= -681.456799
H 298K= -681.424939
G 298K= -681.520849
SCF (C6H5F) = -681.997444739
BP86-D3 = -682.036303100
Lowest Frequency = 21.7188cm-1

C	2.53299	-0.83393	-2.51984
P	2.05923	-1.09117	-0.73613
C	2.31760	-2.92504	-0.53106
Ir	-0.14947	-0.32938	-0.39025
B	0.02291	0.17306	1.88987
N	-0.30870	-1.21209	2.43288
C	3.51731	-0.37805	0.18248
P	-2.44569	0.11262	-0.69716
C	-3.27514	1.50560	0.22053
C	-2.73919	0.57772	-2.47762
C	-3.61729	-1.31235	-0.45303
B	0.89333	2.31360	-0.72231
N	1.21273	3.03396	0.68457
H	3.54019	-1.23807	-2.71394
H	1.80415	-1.34995	-3.16396
H	2.51424	0.24155	-2.75158
H	4.45045	-0.86760	-0.13989
H	3.58101	0.69912	-0.03183
H	3.38679	-0.51963	1.26639
H	3.33672	-3.21337	-0.83580
H	2.15798	-3.21536	0.51843
H	1.58347	-3.45806	-1.15460
H	-0.53535	-1.85997	-0.66581
H	-0.05652	1.48022	-0.42854
H	-0.83795	1.00342	2.07796
H	1.19091	0.49397	2.03290
H	-0.37726	-1.33007	1.01857
C	0.75670	-2.04889	3.01404
C	-1.62057	-1.44594	3.06481
H	-4.64153	-1.03230	-0.74803
H	-3.27637	-2.16043	-1.06649
H	-3.61617	-1.62350	0.60268
H	-4.33811	1.57787	-0.06125
H	-3.19473	1.34234	1.30620
H	-2.76963	2.44992	-0.03471
H	-3.80986	0.76932	-2.65801
H	-2.15832	1.48158	-2.71812
H	-2.40145	-0.24287	-3.12926
H	0.31367	3.09503	-1.44755
H	1.91605	1.86859	-1.18065
C	2.45888	3.86299	0.60014
C	0.06762	3.85362	1.19627
H	1.37074	2.27389	1.37186
H	0.31803	4.29263	2.17503
H	-0.14003	4.65103	0.46832
H	-0.81220	3.20437	1.29701
H	2.65651	4.35533	1.56541
H	3.30396	3.21783	0.32499
H	2.31889	4.62268	-0.18283
H	-1.88940	-2.51502	3.01786
H	-1.59942	-1.13597	4.12603
H	-2.38958	-0.85401	2.54822
H	0.48462	-3.11698	2.96307
H	1.69569	-1.88608	2.46606
H	0.92343	-1.78112	4.07399

SCF (BS1) = -680.709757771
H 0K= -680.243378
H 298K= -680.212446
G 298K= -680.304685
SCF (C6H5F) = -680.756709535
BP86-D3 = -680.794965831
Lowest Frequency = -845.3636cm-1

TS4a'BN

C	2.79771	-2.36379	1.07989
P	2.34152	-0.99300	-0.09083
Ir	0.02165	-0.56838	-0.08607
B	0.55541	1.13101	-1.42017
N	-0.14443	2.39160	-1.46436
C	3.66668	0.27309	0.23881
C	2.82770	-1.67922	-1.75263
P	-2.28982	-1.12566	-0.01631
C	-3.40310	-0.59103	1.37516
C	-3.34505	-0.85822	-1.52911
C	-2.31924	-2.98544	0.14503
B	0.48168	3.10462	0.74240
N	0.09476	2.08767	1.74022
H	2.63392	-2.02605	2.11450
H	3.85281	-2.65356	0.94734
H	2.15245	-3.23541	0.89096
H	4.64928	-0.14717	-0.03030
H	3.67301	0.52948	1.30862
H	3.48086	1.18085	-0.35271
H	-4.30986	-1.37997	-1.42018
H	-2.81455	-1.25215	-2.40989
H	-3.53219	0.21483	-1.68278
H	-1.76136	-3.44166	-0.68785
H	-3.35917	-3.35102	0.12232
H	-1.84570	-3.27802	1.09406
H	2.17461	-2.52952	-2.00443
H	3.87569	-2.02062	-1.73635
H	2.70710	-0.89868	-2.51899
H	-4.37024	-1.11516	1.30580
H	-3.57772	0.49410	1.32548
H	-2.92367	-0.83363	2.33559
H	-0.15325	0.03400	-1.75098
H	0.06933	-1.17457	1.41126
H	0.01415	0.81850	0.85308
H	1.69501	1.19190	-1.80911
C	0.46192	3.52607	-2.19582
C	-1.61267	2.49761	-1.43023
H	1.65005	3.19086	0.47659
H	-0.29807	3.98571	0.50214
C	-1.23454	2.21838	2.38165
C	1.11896	1.66652	2.72828
H	0.20202	4.47947	-1.70558
H	1.55476	3.41833	-2.21388
H	0.08747	3.55225	-3.23566
H	-1.91836	3.47208	-1.01393
H	-2.03238	2.41270	-2.45069
H	-2.02440	1.69655	-0.80095
H	0.87769	0.66515	3.12309
H	2.10468	1.64451	2.24669
H	1.15473	2.38205	3.56908

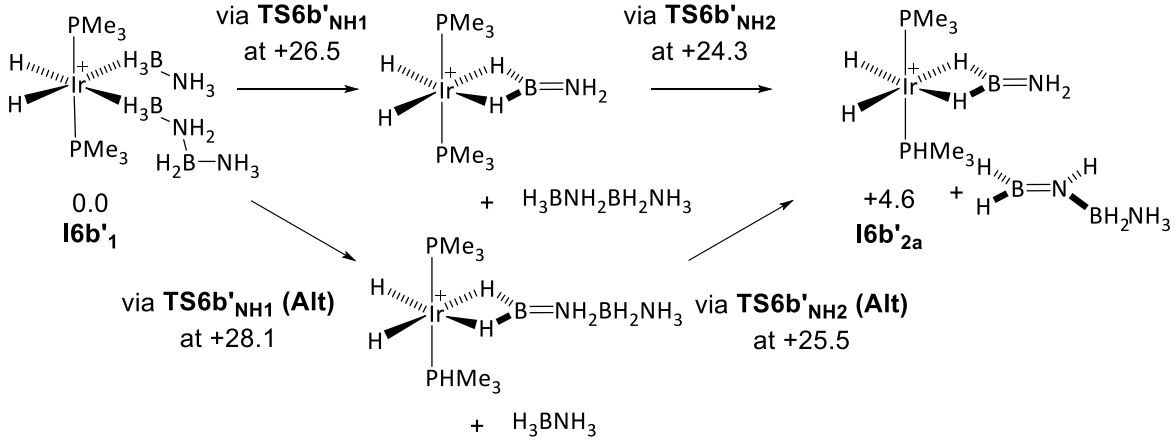
```
H  -1.53047  1.25953  2.83750
H  -1.20698  2.98842  3.17348
H  -1.98202  2.51396  1.63266

SCF (BS1) =     -679.513312349
H 0K=           -679.066491
H 298K=         -679.036970
G 298K=         -679.125706
SCF (C6H5F) =   -679.561016625
BP86-D3 =       -679.598114999
Lowest   Frequency   =   -306.3638cm-1
```

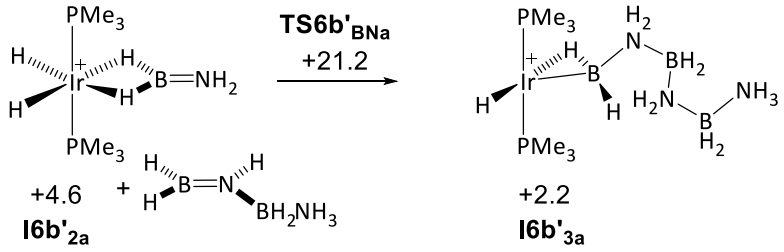
(8) Second Oligomerisation Step

Figure S15. Second Oligomerisation Step for H_3NBH_3

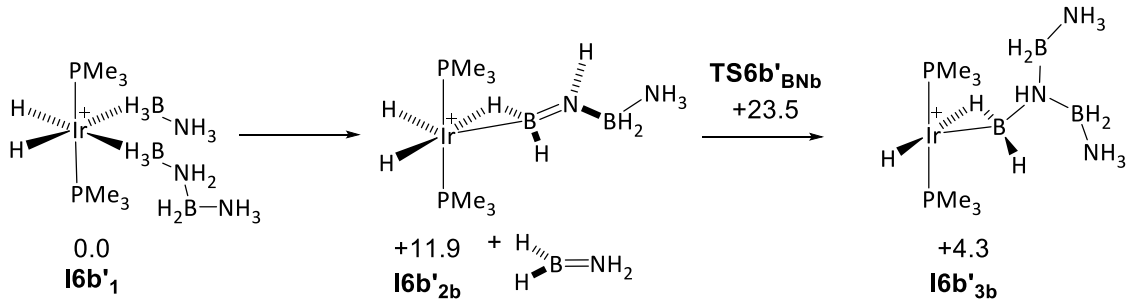
(a) Dehydrogenation



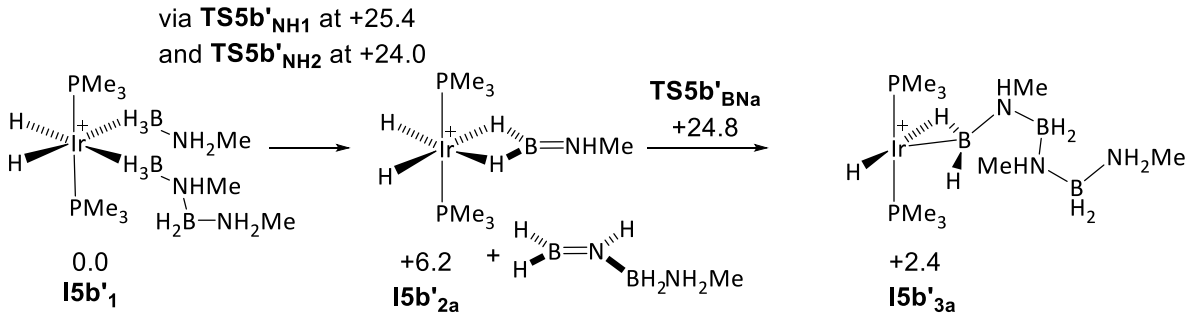
(a) B-N Coupling to give a straight chain oligomer

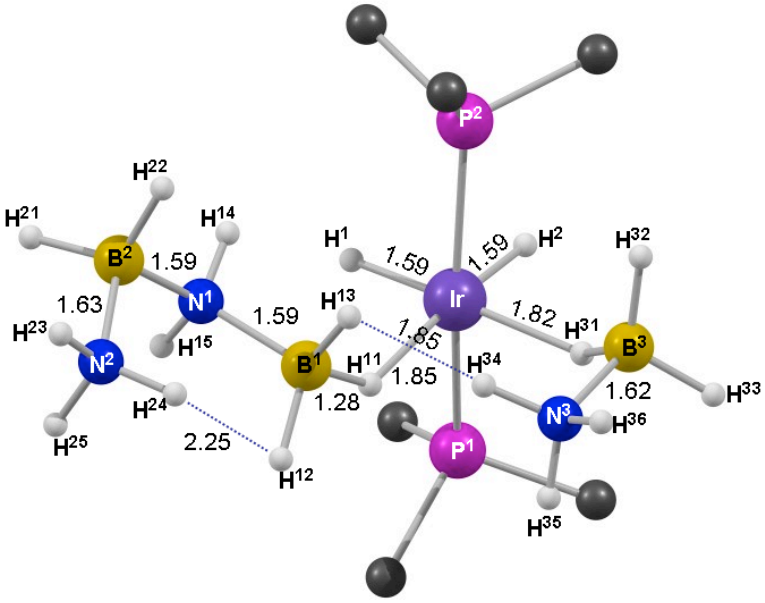


(b) B-N Coupling to give a branched chain oligomer

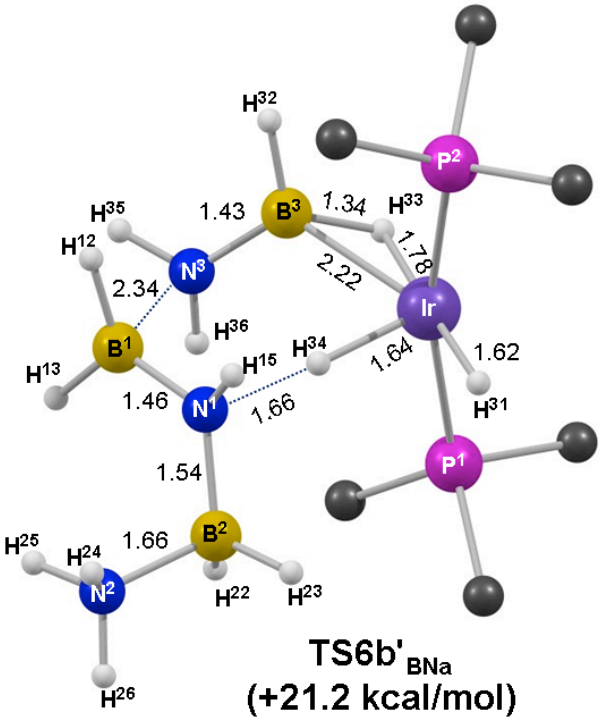


(c) for $H_3B{\bullet}NMeH_2$

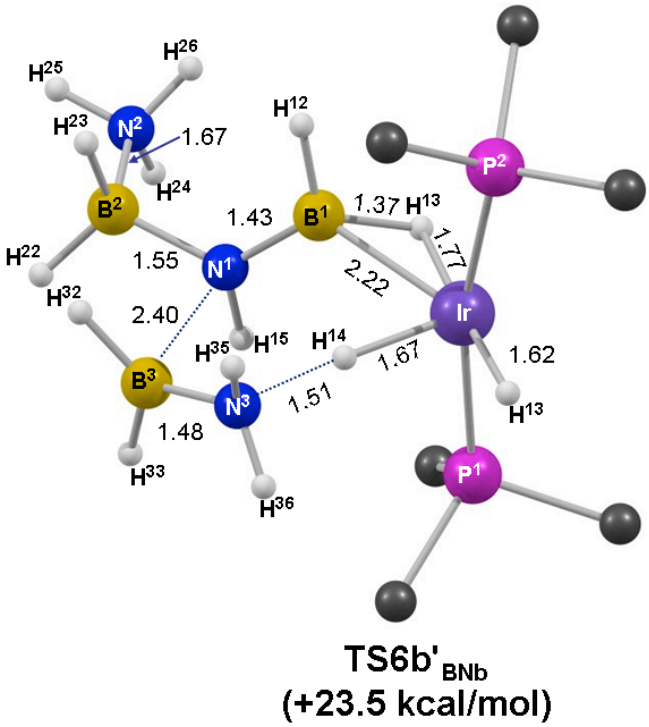




I6b'$_1$
(0.0 kcal/mol)



TS6b'$_{BNa}$
(+21.2 kcal/mol)



TS6b'$_{BNb}$
(+23.5 kcal/mol)

2nd Oligomerisation Step
(a) To give straight chain oligomer

I6b'1

C	0.60704	-3.66297	0.02638
P	1.22669	-1.94895	-0.34365
C	1.86296	-2.13804	-2.08558
C	2.80850	-1.87327	0.64212
Ir	-0.46550	-0.31172	-0.12148
P	-2.45979	0.90939	-0.33898
C	-2.47031	2.71142	0.14150
C	-3.11704	0.95077	-2.07679
C	-3.89106	0.21702	0.62604
B	1.48416	1.70639	0.58527
N	2.16380	1.89910	-0.83963
B	-0.50562	-1.07028	2.62452
N	0.20985	0.25057	3.22965
H	1.59924	2.55064	-1.40163
B	3.70281	2.29203	-0.85955
H	2.07468	1.00597	-1.34334
H	-0.19551	0.06252	-1.64875
H	1.40920	-4.40606	-0.11208
H	0.24170	-3.69766	1.06334
H	-0.22974	-3.89131	-0.65121
H	3.44889	-2.73664	0.39801
H	3.35046	-0.94168	0.41722
H	2.56483	-1.89635	1.71522
H	2.53658	-3.00674	-2.16612
H	1.00583	-2.26991	-2.76321
H	2.41230	-1.23324	-2.39162
H	0.28706	1.26747	0.45713
H	2.19898	1.01192	1.29235
H	-1.35239	-1.50017	-0.68175
H	1.26967	2.80206	1.09203
H	-4.08397	1.47757	-2.12272
H	-2.38804	1.45637	-2.72838
H	-3.24121	-0.08345	-2.43221
H	-3.46103	3.16043	-0.03701
H	-2.21525	2.81163	1.20803
H	-1.71473	3.25086	-0.45031
H	-4.80823	0.80232	0.45022
H	-4.05439	-0.82662	0.31633
H	-3.64841	0.22206	1.69983
H	-1.09401	-0.76097	1.52186
H	-1.46763	-1.32844	3.31667
H	0.32041	-1.94861	2.57070
H	0.59049	0.04958	4.16396
H	0.98293	0.56942	2.61734
H	-0.44267	1.03836	3.32740
H	4.04007	2.73614	-1.93469
N	3.90498	3.47849	0.24024
H	4.35711	1.35139	-0.46336
H	4.91120	3.62976	0.38785
H	3.49931	4.38104	-0.04243
H	3.47850	3.21924	1.14342

SCF (BS1) = -606.785731100
H 0K= -606.351556
H 298K= -606.322004
G 298K= -606.413848
SCF (C6H5F) = -606.843604635
BP86-D3 = -606.859954010
Lowest Frequency = 6.5242cm-1

TS6b'NH1

C	-1.27212	2.56172	-2.12300
P	-1.05505	2.11957	-0.32644
C	-2.81555	1.94480	0.26233
C	-0.55102	3.73999	0.44011
Ir	0.48528	0.35449	-0.10389
P	2.24257	-1.20018	-0.32678
C	3.89632	-0.71862	0.37771
B	-0.00236	-0.00861	2.16236
N	1.11210	0.88700	2.69937
H	1.93417	0.45960	3.13267
C	1.97836	-2.91648	0.33874
C	2.63101	-1.49782	-2.12373
B	-1.69481	-1.54100	-0.52468
N	-2.49452	-1.77425	0.82571
H	-1.95911	3.41619	-2.23784
H	-0.29179	2.81982	-2.55218
H	-1.67469	1.69077	-2.66310
H	-3.38866	2.86312	0.05593
H	-3.28307	1.10031	-0.26726
H	-2.82105	1.75109	1.34654
H	-1.26207	4.53993	0.17738
H	-0.52217	3.63528	1.53613
H	0.45494	4.00919	0.08372
H	1.58231	1.50459	-0.33550
H	-0.51546	-1.12430	-0.20227
H	0.18466	-1.19858	2.31067
H	-1.11830	0.43598	2.32603
H	1.25617	1.02286	1.30850
H	0.87021	1.76812	3.15945
H	4.66380	-1.46790	0.12482
H	4.18983	0.26119	-0.02920
H	3.82500	-0.63811	1.47360
H	2.84953	-3.55861	0.13121
H	1.80985	-2.86439	1.42564
H	1.08169	-3.34625	-0.13416
H	3.45768	-2.21940	-2.22967
H	1.73513	-1.89191	-2.62796
H	2.91302	-0.54499	-2.59756
H	-1.38799	-2.61411	-1.02136
H	-2.30410	-0.81049	-1.27984
B	-3.56573	-2.95788	0.81490
H	-1.82170	-2.00494	1.57115
H	-2.91486	-0.89092	1.14154
H	-4.47362	-2.74235	1.58721
N	-4.20483	-3.02646	-0.68362
H	-2.99146	-4.01206	0.97306
H	-4.77729	-3.87694	-0.75975
H	-4.80543	-2.22803	-0.92788
H	-3.45139	-3.07829	-1.38834

SCF (BS1) = -605.548703428
H 0K= -605.140633
H 298K= -605.111901
G 298K= -605.201350
SCF (C6H5F) = -605.602818178
BP86-D3 = -605.619107298
Lowest Frequency = -856.8134cm-1

TS6b'NH2

C	-1.86407	-2.96090	-1.00431
P	-1.89322	-1.15261	-0.56173
C	-3.23740	-1.05040	0.71829
C	-2.67591	-0.38468	-2.06167
Ir	0.28132	-0.33544	-0.08272
B	0.26171	-1.81316	1.60480
N	-0.48258	-2.23270	2.71721
B	-0.23549	1.79815	1.19614
N	-0.73832	2.51660	-0.02453
P	2.54899	0.32342	-0.22819
C	2.88773	1.97391	-1.01590
C	3.52340	0.39935	1.35349
C	3.52846	-0.85665	-1.27984
H	-2.86636	-3.29587	-1.31768
H	-1.15068	-3.12040	-1.82743
H	-1.53608	-3.54836	-0.13349
H	-4.17667	-1.46921	0.32203
H	-2.92857	-1.61696	1.60921
H	-3.38943	0.00523	0.98939
H	-3.65142	-0.85396	-2.26887
H	-2.81566	0.69317	-1.89066
H	-2.00598	-0.52708	-2.92321
H	0.31005	-0.11490	-1.68361
H	0.44849	-0.51114	1.67259
H	0.86251	2.08666	1.60896
H	-1.09319	1.42661	1.96321
H	-0.46023	1.21640	-0.44246
B	-2.19761	2.94052	-0.28679
H	-0.02746	3.04880	-0.53766
H	3.97226	2.13329	-1.12935
H	2.40650	2.01067	-2.00526
H	2.47637	2.77114	-0.37705
H	4.56489	0.70469	1.16233
H	3.04723	1.11903	2.03710
H	3.51618	-0.59559	1.82567
H	4.58529	-0.54805	-1.33375
H	3.46425	-1.86692	-0.84690
H	3.09715	-0.88082	-2.29213
H	0.97699	-2.60358	1.02899
H	-0.46299	-3.19213	3.05835
H	-1.00823	-1.59927	3.31712
H	-2.36440	3.40270	-1.39744
H	-2.98064	2.06208	0.02148
N	-2.55952	4.17633	0.76195
H	-3.54460	4.45110	0.64714
H	-2.42867	3.88834	1.74181
H	-1.98805	5.01788	0.60640

SCF (BS1) = -604.359455762
H 0K= -603.972457
H 298K= -603.944596
G 298K= -604.029934
SCF (C6H5F) = -604.411652801
BP86-D3 = -604.428215182
Lowest Frequency = -850.9861cm-1

TS6b'NH1(Alt)

C	-1.74923	-3.15410	-0.78513
P	-1.92122	-1.33675	-0.41551
Ir	0.18671	-0.30795	-0.16801
P	2.34791	0.54218	-0.51345
C	3.28916	-0.46967	-1.76304
C	-3.09298	-1.30540	1.02775
C	-2.95539	-0.72509	-1.83199
B	0.63227	-1.85655	1.76180
N	1.72727	-1.58056	2.94415
B	-0.34112	1.68324	1.13691
N	-0.98446	2.43863	-0.00849
C	2.45233	2.25968	-1.22838
C	3.58785	0.65998	0.88648
H	-0.24617	-2.52495	2.26187
H	-2.74004	-3.61564	-0.92921
H	-1.15009	-3.28199	-1.69998
H	-1.22935	-3.64586	0.05087
H	-4.01727	-1.85791	0.79265
H	-2.59943	-1.76212	1.89901
H	-3.33574	-0.25723	1.25903
H	-3.88930	-1.30520	-1.91058
H	-3.19271	0.33766	-1.67412
H	-2.37759	-0.82790	-2.76335
H	0.07997	0.00648	-1.74171
H	0.13440	-0.67709	1.60798
H	0.74759	2.06968	1.51254
H	-1.12519	1.27738	1.97064
H	-0.65608	1.20820	-0.52577
B	-2.48276	2.77619	-0.11584
H	-0.35623	3.06573	-0.52127
H	3.49254	2.51639	-1.48660
H	1.82822	2.30865	-2.13396
H	2.07901	2.98321	-0.48647
H	4.50237	1.18681	0.56791
H	3.13856	1.21005	1.72946
H	3.88302	-0.35703	1.19833
H	4.29875	-0.05998	-1.93071
H	3.36750	-1.50863	-1.40638
H	2.72956	-0.47128	-2.71083
H	1.20994	-2.39601	0.83534
H	2.14382	-2.46718	3.25931
H	2.49275	-0.96581	2.63424
H	1.29241	-1.13992	3.76600
H	-2.76603	3.37753	-1.13237
H	-3.18177	1.80451	0.10906
N	-2.84984	3.81127	1.13235
H	-3.86043	4.00287	1.14972
H	-2.59212	3.38965	2.03589
H	-2.36519	4.71582	1.06011

SCF (BS1) = -605.543653380
H 0K= -605.134834
H 298K= -605.106262
G 298K= -605.193160
SCF (C6H5F) = -605.601019399
BP86-D3 = -605.616098100
Lowest Frequency = -969.1545cm-1

TS6b'NH2(Alt)

C	2.41065	-1.39958	-1.90843
P	1.39463	-1.74944	-0.39136

Ir	-0.40235	-0.21290	-0.11589
P	-2.38771	1.05418	-0.28965
C	-2.75714	1.52825	-2.04927
C	2.67316	-1.94433	0.94441
C	0.82743	-3.49982	-0.67678
B	1.29347	1.30993	-0.01742
N	2.49101	1.57568	0.64788
B	-0.75114	-0.57955	2.26419
N	-1.43893	-1.92978	2.07877
H	-0.94670	-2.78308	2.35351
C	-3.94979	0.21135	0.26351
C	-2.43852	2.67533	0.61855
H	3.16473	-2.18980	-2.05530
H	1.74730	-1.35687	-2.78606
H	2.91271	-0.42670	-1.79260
H	3.37647	-2.75081	0.68164
H	3.22486	-0.99870	1.04988
H	2.18127	-2.18036	1.90051
H	1.68870	-4.16379	-0.85436
H	0.26802	-3.86221	0.19954
H	0.15793	-3.52076	-1.55004
H	-1.19337	-1.26465	-1.05339
H	0.29882	1.12449	0.82488
H	-1.48171	0.32429	2.59123
H	0.37615	-0.63578	2.69052
H	-1.14911	-1.52389	0.77126
H	-2.44438	-2.01120	2.24732
H	-4.82630	0.84695	0.05843
H	-4.05741	-0.74487	-0.27102
H	-3.89364	0.02135	1.34671
H	-3.40758	3.17987	0.47436
H	-2.27436	2.49077	1.69147
H	-1.63065	3.32191	0.24155
H	-3.68256	2.12416	-2.10804
H	-1.91704	2.11539	-2.45138
H	-2.86675	0.61464	-2.65326
H	1.10553	1.63365	-1.17281
B	3.81031	2.05351	0.02836
H	2.53068	1.29490	1.63232
H	4.78030	1.50895	0.52446
H	3.77737	2.02642	-1.18694
N	4.01663	3.66483	0.39626
H	4.88958	4.00238	-0.03089
H	3.24723	4.24125	0.02974
H	4.08222	3.84226	1.40765

SCF (BS1) = -604.357556377
H 0K= -603.970677
H 298K= -603.942791
G 298K= -604.029138
SCF (C6H5F) = -604.410979480
BP86-D3 = -604.424033177
Lowest Frequency = -847.9072cm-1

I6b′2a + $H_2B{=}NH_2BH_2NH_3$

C	1.54389	-2.70799	-1.73170
P	1.96631	-1.71152	-0.22817
Ir	0.74327	0.31539	-0.09676
B	1.72593	1.17613	1.49438
N	2.38892	1.74764	2.57362
C	1.65237	-2.87778	1.18020
C	3.81677	-1.55739	-0.29761
P	-0.87409	2.00453	-0.49177
C	-2.04840	1.55620	-1.85104
C	-1.98822	2.39126	0.93966
C	-0.18557	3.65214	-1.00442
B	-2.36176	-2.47299	0.04113
N	-3.52083	-1.78812	-0.35119
H	0.46502	-2.92700	-1.71561
H	2.11564	-3.64991	-1.74309
H	1.77717	-2.12160	-2.63336
H	2.18555	-3.82958	1.02344
H	0.56905	-3.06374	1.24544
H	1.99237	-2.41763	2.12100
H	-2.71404	3.17229	0.66009
H	-1.38639	2.73899	1.79366
H	-2.52973	1.47447	1.22341
H	0.43759	4.05849	-0.19257
H	-0.99998	4.36004	-1.22897
H	0.44219	3.51928	-1.89896
H	4.09538	-0.92429	-1.15417
H	4.28561	-2.54883	-0.40726
H	4.18012	-1.08274	0.62719
H	-2.78036	2.36426	-2.00984
H	-2.57216	0.63115	-1.56319
H	-1.48158	1.37870	-2.77755
H	0.69301	0.40497	1.75717
H	0.80297	0.25894	-1.68622
H	-0.48696	-0.65244	-0.37883
H	2.17449	1.44726	0.29086
H	3.19590	2.36016	2.47003
H	2.11187	1.59617	3.54185
H	-1.76534	-3.16355	-0.75798
H	-1.98067	-2.38168	1.18755
B	-4.41554	-0.87917	0.48322
H	-3.79765	-1.90648	-1.32978
H	-4.99239	-0.02471	-0.17033
N	-5.65409	-1.82359	1.09844
H	-3.85716	-0.45777	1.48289
H	-6.27424	-1.26583	1.69998
H	-6.23317	-2.24294	0.35882
H	-5.27338	-2.59449	1.66358

SCF (BS1) = -604.396992750
H 0K= -604.008030
H 298K= -603.979054
G 298K= -604.072446
SCF (C6H5F) = -604.448715381
BP86-D3 = -604.455199850
Lowest Frequency = 9.6825cm-1

TS6b′BNa

C	-3.25770	-0.16105	-1.96476
P	-2.54856	0.35837	-0.32595
Ir	-0.37816	-0.51329	0.00907
B	-0.47682	0.46639	1.99451
N	0.71217	1.04727	2.54030

C	-2.75966	2.20543	-0.33960
C	-3.83624	-0.22748	0.88260
P	1.65139	-1.73280	-0.11806
C	2.58614	-1.59574	-1.71340
C	2.96154	-1.46864	1.17771
C	1.29308	-3.55746	0.01762
B	1.10469	2.88514	1.14608
N	1.13009	2.40184	-0.22676
H	-2.62988	0.24110	-2.77414
H	-4.29108	0.20580	-2.07595
H	-3.25349	-1.26016	-2.03283
H	-3.82128	2.47141	-0.46859
H	-2.18117	2.62577	-1.17736
H	-2.38596	2.62606	0.60605
H	3.79877	-2.16966	1.02653
H	2.53270	-1.63527	2.17875
H	3.33943	-0.43713	1.09358
H	0.84409	-3.77556	0.99902
H	2.22117	-4.14127	-0.09800
H	0.58341	-3.85266	-0.77120
H	-3.87804	-1.32784	0.85923
H	-4.82614	0.17818	0.61779
H	-3.56644	0.09561	1.89881
H	3.48088	-2.23915	-1.69945
H	2.87606	-0.54505	-1.86281
H	1.92315	-1.90018	-2.53776
H	-0.47093	-0.85863	1.75318
H	-0.25404	-0.31654	-1.58581
H	0.43266	0.90452	-0.11504
H	-1.51014	0.94259	2.39261
H	0.65619	1.68011	3.33880
H	1.63015	0.61485	2.44520
H	0.13458	3.47627	1.55067
H	2.16473	2.99772	1.72289
B	2.43038	2.14537	-1.00983
H	0.33231	2.69884	-0.79592
H	2.23814	1.80570	-2.16229
N	3.25695	3.58515	-1.11265
H	3.19831	1.42326	-0.39401
H	4.16384	3.44814	-1.57863
H	2.74467	4.30464	-1.64057
H	3.44092	3.96335	-0.17235

SCF (BS1) = -604.364758270
H 0K= -603.975056
H 298K= -603.948102
G 298K= -604.031608
SCF (C6H5F) = -604.419075162
BP86-D3 = -604.434641770
SCF (BS2) = -1274.34593640
Lowest Frequency = -259.0297cm-1

I6b'3a

C	3.67852	0.16728	-1.42165
P	2.57699	-0.77610	-0.25509
Ir	0.55726	0.34981	0.04057
B	0.11716	-0.99843	1.49681
N	-1.36400	-1.34158	1.85962
C	2.51228	-2.47663	-1.00559
C	3.65354	-1.00448	1.24376
P	-1.11904	2.02550	-0.01221
C	-2.18789	2.20045	-1.52456
C	-2.33782	2.24084	1.38623
C	-0.20356	3.65309	0.01477
B	-1.92782	-2.54250	0.93705
N	-2.00826	-1.98245	-0.55979
H	3.18281	0.25066	-2.40060
H	4.64706	-0.34580	-1.53904
H	3.85135	1.17950	-1.02406
H	3.52723	-2.88254	-1.14610
H	2.00208	-2.41899	-1.97952
H	1.94118	-3.14111	-0.33906
H	-2.85632	3.21014	1.30100
H	-1.80498	2.20041	2.34924
H	-3.09544	1.44078	1.34460
H	0.35705	3.74478	0.95732
H	-0.91172	4.49314	-0.07873
H	0.50806	3.68772	-0.82503
H	3.87410	-0.01722	1.67817
H	4.59674	-1.50624	0.97350
H	3.11806	-1.60846	1.99148
H	-2.79931	3.11597	-1.46712
H	-2.84393	1.32253	-1.61998
H	-1.53404	2.24898	-2.40894
H	0.57337	0.22711	1.87562
H	0.45746	0.29768	-1.56889
H	-1.26770	-1.23615	-0.64942
H	0.82156	-1.91756	1.85042
H	-1.41252	-1.69053	2.82856
H	-1.98603	-0.52224	1.80770
H	-1.15905	-3.47565	1.00927
H	-3.04549	-2.83822	1.35184
B	-3.38993	-1.36651	-1.01863
H	-1.68813	-2.71211	-1.21057
H	-3.39029	-1.04555	-2.18796
N	-4.50468	-2.53597	-0.82563
H	-3.70882	-0.47889	-0.24832
H	-5.45107	-2.14124	-0.89642
H	-4.44089	-3.29653	-1.51609
H	-4.38970	-2.94654	0.11953

SCF (BS1) = -604.404678332
H 0K= -604.008034
H 298K= -603.981565
G 298K= -604.064473
SCF (C6H5F) = -604.459721082
BP86-D3 = -604.471250742
Lowest Frequency = 29.2928cm-1

(b) To give branched chain oligomer

I6b′2b + $H_2B{=}NH_2$

C	-0.08232	3.48677	1.57563
P	-0.79244	2.34730	0.29137
Ir	0.59920	0.47258	-0.14753
B	-1.44186	-0.26559	-1.27366
N	-2.14182	-1.33197	-0.70481
C	-2.51798	2.05247	0.91181
C	-1.01561	3.45715	-1.18625
P	2.34869	-1.10978	-0.24100
C	3.03821	-1.58118	1.41511
C	1.99993	-2.74636	-1.05062
C	3.82407	-0.46500	-1.17569
B	-0.88096	-3.14925	2.26840
N	-2.02190	-2.51050	2.75297
H	0.02457	2.93784	2.52374
H	-0.73791	4.35980	1.72618
H	0.91404	3.82403	1.25181
H	-3.02681	3.01566	1.07887
H	-2.46047	1.49931	1.86197
H	-3.08555	1.44994	0.18755
H	2.90145	-3.38044	-1.05061
H	1.67005	-2.57816	-2.08765
H	1.19704	-3.25689	-0.49615
H	3.53947	-0.24777	-2.21732
H	4.63638	-1.21027	-1.17167
H	4.17813	0.46337	-0.70175
H	-0.02968	3.78811	-1.54951
H	-1.61258	4.34208	-0.91143
H	-1.52720	2.90351	-1.98775
H	3.88237	-2.27995	1.29935
H	2.24608	-2.05884	2.01237
H	3.37547	-0.67239	1.93588
H	-0.16763	-0.46837	-1.47086
H	1.52909	1.18708	0.94086
H	0.02637	-0.26307	1.07928
H	-2.00418	0.56270	-1.94323
B	-3.65819	-1.49916	-0.60418
H	-1.58340	-2.00032	-0.16277
H	-0.83220	-3.43653	1.09065
H	0.03340	-3.40171	3.01029
H	-2.14520	-2.26859	3.73465
H	-2.82966	-2.28436	2.17020
N	-4.13927	-2.60142	-1.75597
H	-4.00985	-2.00758	0.45217
H	-4.26572	-0.48516	-0.88790
H	-5.16077	-2.71991	-1.72336
H	-3.89275	-2.28037	-2.70202
H	-3.71604	-3.53013	-1.62521

SCF (BS1) = -604.377110341
H 0K= -603.987629
H 298K= -603.958004
G 298K= -604.051407
SCF (C6H5F) = -604.434164351
BP86-D3 = -604.436488301
Lowest Frequency = 13.7981cm-1

TS6b′BNb

C	3.80707	-1.05723	0.01673
P	2.55664	0.31513	-0.08959
Ir	0.34524	-0.49859	-0.13426
B	-0.33747	1.59048	-0.44941
N	-1.63468	2.03606	-0.05186
C	3.02300	1.42996	1.32351
C	3.10895	1.26461	-1.59125
P	-1.60464	-1.82915	-0.19498
C	-2.47487	-2.16873	1.41457
C	-3.00893	-1.36446	-1.33104
C	-1.16096	-3.53582	-0.79745
B	-1.63436	1.75363	2.33723
N	-0.61397	0.72874	2.63785
H	3.64986	-1.61647	0.95133
H	4.83256	-0.65415	-0.00863
H	3.66752	-1.74615	-0.83107
H	4.07587	1.74413	1.23893
H	2.88571	0.88669	2.27162
H	2.37439	2.31939	1.31312
H	-3.77054	-2.16094	-1.35534
H	-2.61492	-1.20535	-2.34680
H	-3.48512	-0.43352	-0.98477
H	-0.72410	-3.46978	-1.80631
H	-2.05549	-4.17904	-0.83260
H	-0.41588	-3.97634	-0.11778
H	2.99785	0.62682	-2.48213
H	4.16305	1.57041	-1.49201
H	2.47690	2.15715	-1.71058
H	-3.29912	-2.88573	1.26937
H	-2.88462	-1.22811	1.81641
H	-1.75181	-2.58956	2.13068
H	-0.26427	0.59819	-1.38410
H	0.89421	-1.57870	0.94358
H	-0.11084	0.17941	1.31961
H	0.51689	2.44401	-0.52379
B	-2.09098	3.51189	0.02018
H	-2.39116	1.34797	-0.11090
H	-1.33952	2.90087	2.49596
H	-2.77181	1.37012	2.25674
H	-0.93243	-0.15104	3.05051
H	0.24534	1.04363	3.09442
N	-2.39799	4.04302	-1.53730
H	-3.15414	3.64836	0.59003
H	-1.20284	4.24719	0.39758
H	-2.68569	5.02993	-1.49389
H	-1.56185	3.99109	-2.13448
H	-3.15219	3.52643	-2.00917

SCF (BS1) = -604.359828211
H 0K= -603.970824
H 298K= -603.943670
G 298K= -604.027842
SCF (C6H5F) = -604.416919237
BP86-D3 = -604.427060831
Lowest Frequency = -281.5940cm-1

I6b′3b

C	3.53227	-1.61436	-0.18243
P	2.56272	-0.02988	-0.07279
Ir	0.27276	-0.47216	-0.05785
B	-0.08098	1.54475	-0.22617

N	-1.37746	2.16915	0.28444
C	3.27752	0.81314	1.42244
C	3.23686	0.96862	-1.49014
P	-1.80936	-1.58343	-0.17161
C	-2.86438	-1.84123	1.34807
C	-3.07208	-1.04450	-1.43660
C	-1.45149	-3.33748	-0.69642
B	-1.18493	2.51127	1.85051
N	-0.93858	1.09954	2.63509
H	3.30388	-2.23959	0.69387
H	4.61392	-1.40472	-0.21572
H	3.24067	-2.16039	-1.09310
H	4.36966	0.92434	1.32509
H	3.05007	0.21188	2.31632
H	2.81595	1.80683	1.53053
H	-3.90586	-1.76321	-1.49452
H	-2.58196	-0.97464	-2.42009
H	-3.47878	-0.05541	-1.16941
H	-0.91354	-3.32986	-1.65694
H	-2.38910	-3.90635	-0.80814
H	-0.81668	-3.82099	0.06162
H	2.97701	0.46921	-2.43628
H	4.33214	1.06282	-1.41375
H	2.78413	1.97141	-1.47668
H	-3.67234	-2.56254	1.14276
H	-3.32384	-0.88809	1.65736
H	-2.23510	-2.22623	2.16543
H	-0.14848	0.73625	-1.34998
H	0.62661	-1.43740	1.19432
H	-0.38802	0.43863	2.01154
H	0.79398	2.38211	-0.32590
B	-1.81822	3.54805	-0.38613
H	-2.16012	1.50565	0.19727
H	-0.17501	3.16276	1.99301
H	-2.19010	3.01507	2.29976
H	-1.80395	0.62017	2.91262
H	-0.39978	1.27085	3.49301
N	-1.50001	3.49636	-2.00570
H	-3.01740	3.69463	-0.29164
H	-1.14548	4.46398	0.02364
H	-1.77817	4.40479	-2.40046
H	-0.49560	3.37315	-2.19647
H	-2.01047	2.77018	-2.52605

SCF (BS1) = -604.393428036
H 0K= -603.998126
H 298K= -603.971049
G 298K= -604.055403
SCF (C6H5F) = -604.453743847
BP86-D3 = -604.460495996
Lowest Frequency = 23.1782cm-1

TS5b'NH1

C	-0.37826	2.72957	-2.33893
P	0.10150	2.37306	-0.57514
Ir	0.64047	0.09646	-0.28932
B	1.41228	0.54014	1.94077
N	2.87057	0.78014	1.53883
C	3.97058	-0.07565	2.01878
C	-1.29135	3.17642	0.37486
C	1.49045	3.57989	-0.27979
P	1.33001	-2.13737	-0.54610
C	0.37263	-2.99833	-1.89286
C	3.09133	-2.40183	-1.08466
C	1.14257	-3.29459	0.89918
B	-1.69595	-0.70192	0.35000
N	-2.73976	0.07932	1.27292
B	-4.19006	0.21558	0.62167
N	-4.58652	-1.20949	-0.03651
C	-2.74200	-0.43599	2.68086
H	-0.60702	3.79876	-2.47890
H	0.45078	2.43880	-3.00193
H	-1.26290	2.12831	-2.60041
H	-1.33535	4.25732	0.16281
H	-2.25151	2.72753	0.07032
H	-1.12839	3.03560	1.45585
H	1.19816	4.59588	-0.59106
H	1.73336	3.59722	0.79473
H	2.37555	3.26311	-0.85264
H	1.75739	0.46544	-1.39102
H	-0.55666	-0.48771	0.93666
H	1.24015	-0.49373	2.54268
H	0.79266	1.52970	2.26507
H	2.25380	0.44498	0.35197
H	3.15174	1.76265	1.46437
H	3.29512	-3.47206	-1.25124
H	3.26411	-1.84352	-2.01758
H	3.77858	-2.01727	-0.31600
H	1.47238	-4.31261	0.63570
H	1.73571	-2.92173	1.74812
H	0.08349	-3.31271	1.19852
H	0.72171	-4.03615	-2.02111
H	-0.69491	-2.99695	-1.62548
H	0.50286	-2.44783	-2.83737
H	-1.87556	-1.90292	0.49073
H	-1.79519	-0.34308	-0.81798
H	-2.41032	1.05261	1.32312
H	-3.42136	0.16489	3.30391
H	-3.08421	-1.48247	2.68158
H	-1.72236	-0.40890	3.09654
H	4.87221	0.05433	1.39844
H	4.22452	0.15364	3.06882
H	3.65018	-1.12774	1.97422
H	-5.02690	0.47190	1.46262
H	-4.13480	1.01127	-0.29572
C	-5.88981	-1.16035	-0.77459
H	-3.82497	-1.49484	-0.67338
H	-4.63534	-1.94506	0.68277
H	-6.13096	-2.14351	-1.20480
H	-6.67582	-0.85141	-0.07198
H	-5.80724	-0.40801	-1.57047

SCF (BS1) = -723.465996210
H 0K= -722.974356
H 298K= -722.941800
G 298K= -723.039051
SCF (C6H5F) = -723.514657914
BP86-D3 = -723.553436130
Lowest Frequency = -961.4963cm-1

TS5b'NH2

C	-1.08395	3.36763	-1.08999
P	0.20844	2.02958	-1.13880
Ir	-0.62827	0.03299	-0.19350
P	-2.20824	-1.68169	0.22566
C	-3.86849	-0.87741	0.48207
C	1.71920	2.86160	-0.44539
C	0.61269	1.91515	-2.94970
B	-0.72097	1.14166	1.78279
N	0.12269	1.96050	2.55331
B	0.96488	-1.99189	-0.01604
N	2.08245	-1.26611	-0.70063
B	3.25284	-0.65966	0.11853
N	4.13466	-1.90715	0.73000
C	-2.53995	-2.87702	-1.15496
C	-2.02575	-2.76743	1.72195
H	-0.71930	4.27137	-1.60549
H	-1.99792	3.00599	-1.58533
H	-1.31991	3.60922	-0.04279
H	1.96079	3.76282	-1.03210
H	1.52557	3.14487	0.59925
H	2.56685	2.15942	-0.47513
H	0.91038	2.90073	-3.34304
H	1.43660	1.20056	-3.09675
H	-0.27141	1.54807	-3.49193
H	-1.04052	-0.21685	-1.73692
H	-0.07451	0.03370	1.48305
H	0.39052	-2.83374	-0.66053
H	1.04276	-2.08432	1.18650
H	1.01343	-0.36708	-0.61758
C	2.31266	-1.56548	-2.13255
H	-3.36233	-3.55807	-0.88264
H	-2.81105	-2.30836	-2.05722
H	-1.63120	-3.46100	-1.36203
H	-2.88730	-3.44809	1.81611
H	-1.09937	-3.35413	1.63218
H	-1.95798	-2.13297	2.61937
H	-4.64445	-1.64471	0.63886
H	-3.82203	-0.21482	1.35963
H	-4.12232	-0.27603	-0.40412
H	-1.91768	1.28004	1.91032
C	-0.28713	3.02187	3.47707
H	1.12942	1.78495	2.54546
H	4.02171	-0.01923	-0.57674
H	2.84498	-0.06086	1.09863
C	5.28745	-1.46948	1.57958
H	3.50076	-2.50229	1.28472
H	4.48643	-2.50156	-0.03395
H	0.17535	3.98925	3.21128
H	-1.38074	3.13279	3.43502
H	-0.00241	2.78095	4.51641
H	2.93444	-0.78108	-2.59291
H	2.83555	-2.53235	-2.25513
H	1.35258	-1.63855	-2.66893
H	5.83978	-2.33553	1.97355
H	5.95144	-0.84534	0.96596
H	4.89410	-0.86409	2.40757

SCF (BS1) = -722.273510071
H 0K= -721.804100
H 298K= -721.771719
G 298K= -721.868653
SCF (C6H5F) = -722.320668676
BP86-D3 = -722.356903831
Lowest Frequency = -679.4555cm-1

I5b'2a

C	-1.00038	3.27739	-1.34080
P	-1.74115	2.16816	-0.05486
C	-3.56958	2.46297	-0.21154
Ir	-1.01565	-0.07936	-0.24664
P	0.18989	-2.02007	-0.87472
C	-0.82368	-3.36570	-1.65910
C	-1.27859	2.98044	1.54783
B	-2.26801	-0.92203	1.17033
N	-3.10710	-1.47177	2.12898
C	1.51554	-1.66785	-2.11900
C	1.10151	-2.86944	0.49995
B	2.55280	1.85674	0.60725
N	3.59916	1.19931	-0.05660
B	4.25181	-0.08967	0.45710
N	5.65568	0.33853	1.23441
H	0.09545	3.24141	-1.24204
H	-1.35263	4.31287	-1.20676
H	-1.28350	2.91513	-2.34069
H	-1.57303	4.04256	1.54590
H	-0.18859	2.89595	1.67829
H	-1.77967	2.46221	2.38017
H	1.64718	-3.74666	0.11557
H	0.38756	-3.19135	1.27391
H	1.81793	-2.15579	0.93770
H	-1.57009	-3.73089	-0.93662
H	-0.18079	-4.20329	-1.97537
H	-1.35065	-2.95675	-2.53491
H	-3.91843	2.06657	-1.17763
H	-3.79697	3.53992	-0.15395
H	-4.09614	1.93534	0.59890
H	2.03603	-2.59730	-2.40057
H	2.23370	-0.96340	-1.67141
H	1.06450	-1.20795	-3.01125
H	-1.10136	-0.47248	1.57111
H	-0.96596	0.24057	-1.80431
H	0.41705	0.60476	-0.33987
H	-2.69062	-0.89409	-0.07096
C	-4.44527	-2.04390	1.92045
H	-2.78949	-1.50303	3.09942
H	2.08558	2.87487	0.13649
H	2.14078	1.41700	1.65611
C	4.13426	1.73479	-1.32012
H	4.61896	-0.83217	-0.44416
H	3.59336	-0.64481	1.32106
C	6.42123	-0.81596	1.79359
H	6.25944	0.86810	0.58986
H	5.40811	0.99503	1.98852
H	4.05241	0.98852	-2.13140
H	3.59743	2.64960	-1.61700
H	5.20903	1.99522	-1.23833

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H    7.33373 -0.48105  2.30986
H    5.76747 -1.35386  2.49408
H    6.68186 -1.48934  0.96538
H   -5.20174 -1.49948  2.51033
H   -4.71215 -1.97022  0.85585
H   -4.46893 -3.10651  2.21539

SCF (BS1) =      -722.310301369
H 0K=            -721.838716
H 298K=          -721.805416
G 298K=          -721.909741
SCF (C6H5F) =    -722.357907488
BP86-D3 =        -722.380417259
Lowest Frequency = 8.5328cm-1
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TS6b′BNa

```
C    3.15348 -0.77042 -2.34437
P    2.57283 -0.96395 -0.58821
C    4.07028 -0.47371  0.40573
Ir   0.75956  0.46089 -0.08197
P   -0.65743  2.35638  0.00783
C    0.42780  3.87098  0.11601
C    2.52856 -2.81250 -0.37680
B    0.70368 -0.58009  1.86654
N   -0.53502 -0.74204  2.56936
C   -1.71113  2.71220 -1.47662
C   -1.81661  2.59173  1.44650
B   -1.78199 -2.12532  1.08236
N   -1.70520 -1.64429 -0.29665
B   -2.87191 -0.76887 -0.83187
N   -4.23991 -1.69010 -0.81901
H    2.36793 -1.13229 -3.02505
H    4.08342 -1.33702 -2.51475
H    3.33041  0.29589 -2.55357
H    3.53678 -3.22819 -0.53577
H    1.83941 -3.24813 -1.11498
H    2.18221 -3.06425  0.63609
H   -2.30670  3.57759  1.38935
H   -1.24852  2.52826  2.38827
H   -2.58665  1.80486  1.41895
H    1.02147  3.83777  1.04262
H   -0.18780  4.78574  0.10863
H    1.11395  3.89442 -0.74517
H    4.27084  0.59964  0.26176
H    4.95360 -1.05258  0.08993
H    3.87279 -0.65745  1.47287
H   -2.25549  3.66236 -1.35099
H   -2.41808  1.88211 -1.61728
H   -1.05799  2.77324 -2.36074
H    1.11086  0.69231  1.63667
H    0.44624  0.38679 -1.66510
H   -0.53090 -0.60152 -0.17036
H    1.56610 -1.37161  2.16433
C   -0.68401 -1.55391  3.79115
H   -1.22984  0.00471  2.50070
H   -1.16056 -3.10637  1.40326
H   -2.71520 -1.75017  1.75816
C   -1.10056 -2.55064 -1.30595
H   -2.71594 -0.43796 -1.99371
H   -3.12940  0.15384 -0.07740
C   -5.45741 -0.97404 -1.31381
H   -4.09948 -2.54154 -1.38147
H   -4.39492 -2.01238  0.14860
H   -0.64038 -1.96503 -2.11848
H   -0.34531 -3.19862 -0.83727
H   -1.86296 -3.21259 -1.75980
H   -6.34460 -1.62319 -1.26930
H   -5.61124 -0.08377 -0.68868
H   -5.27471 -0.65555 -2.34929
H   -1.67649 -2.03228  3.82534
H    0.08503 -2.33952  3.79341
H   -0.55539 -0.93402  4.69558

SCF (BS1) =      -722.270781026
H 0K=            -721.799354
H 298K=          -721.767976
G 298K=          -721.861683
SCF (C6H5F) =    -722.320120332
BP86-D3 =        -722.357600466
Lowest Frequency = -307.7676cm-1
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I5b′3a

```
C    3.98278 -0.44109 -1.48196
P    2.70837 -1.15180 -0.32613
C    3.71212 -1.60569  1.17239
Ir   0.96719  0.36327 -0.01426
P   -0.27706  2.37865 -0.02807
C    1.00913  3.73345 -0.07069
C    2.31284 -2.80070 -1.09134
B    0.24200 -0.89830  1.40737
N   -1.27050 -0.92733  1.79414
C   -1.34344  2.81183 -1.48961
C   -1.33024  2.88996  1.42579
B   -2.02763 -1.98653  0.84745
N   -2.07064 -1.37333 -0.63184
B   -3.27262 -0.36903 -0.86792
N   -4.65002 -1.19734 -0.68589
H    3.51770 -0.25177 -2.46120
H    4.82863 -1.13780 -1.60145
H    4.35425  0.51250 -1.07557
H    3.22878 -3.39698 -1.23385
H    1.82717 -2.63598 -2.06557
H    1.62113 -3.34522 -0.43015
H   -1.61156  3.95296  1.34533
H   -0.76652  2.73271  2.35846
H   -2.25231  2.28633  1.44579
H    1.62247  3.68896  0.84191
H    0.52239  4.72041 -0.14180
H    1.66327  3.59148 -0.94518
H    4.12312 -0.68672  1.61801
H    4.53725 -2.28337  0.89954
H    3.06253 -2.09760  1.91180
H   -1.70405  3.85097 -1.41463
H   -2.20006  2.12391 -1.54149
H   -0.74240  2.69540 -2.40462
H    0.94929  0.20135  1.81137
H    0.86635  0.37351 -1.62619
H   -1.19504 -0.79531 -0.71972
H    0.74669 -1.94712  1.74326
C   -1.46247 -1.29380  3.23892
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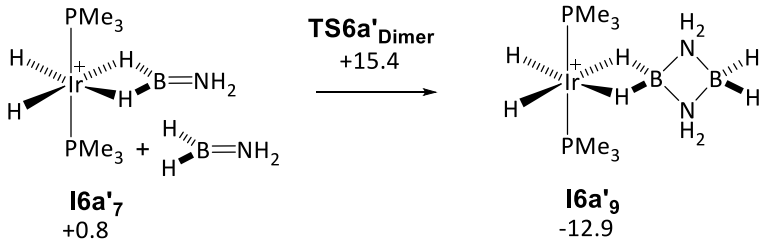
H  -1.69233  0.00156  1.64135
H  -1.41061 -3.03062  0.86697
H  -3.16929 -2.13630  1.28163
C  -1.96583 -2.43757 -1.67915
H  -3.26841  0.08479 -1.99591
H  -3.27020  0.48076  0.00907
C  -5.87397 -0.33524 -0.65184
H  -4.75594 -1.89344 -1.43739
H  -4.55859 -1.73425  0.19730
H  -2.06636 -1.99470 -2.68293
H  -0.99944 -2.95487 -1.59230
H  -2.75540 -3.19210 -1.52828
H  -6.77936 -0.95049 -0.54456
H  -5.78722  0.35759  0.19585
H  -5.92089  0.24355 -1.58472
H  -2.53575 -1.28459  3.48258
H  -1.06664 -2.30729  3.39455
H  -0.92212 -0.58863  3.88951

SCF (BS1) =     -722.317731424
H 0K=           -721.838920
H 298K=         -721.808047
G 298K=         -721.900881
SCF (C6H5F) =   -722.366763339
BP86-D3 =       -722.401371494
Lowest Frequency = 27.8380cm-1
```

(9) Dimerisation Processes

(a) On-metal



(b) Off-metal

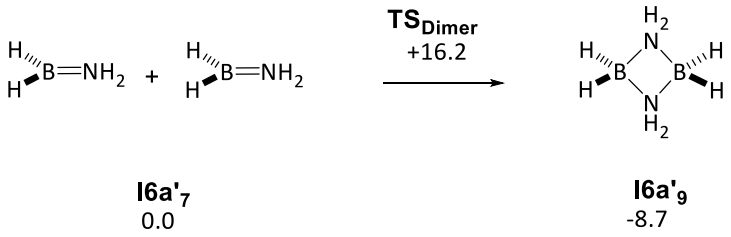
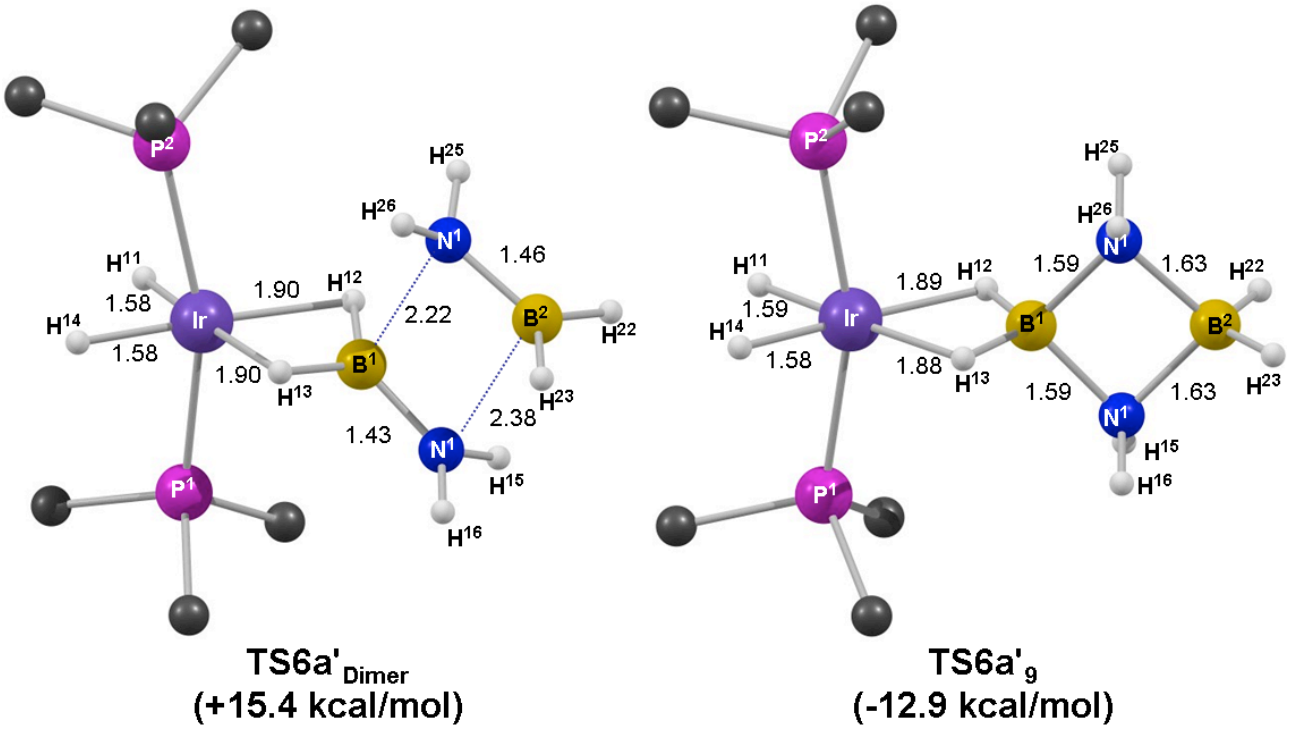
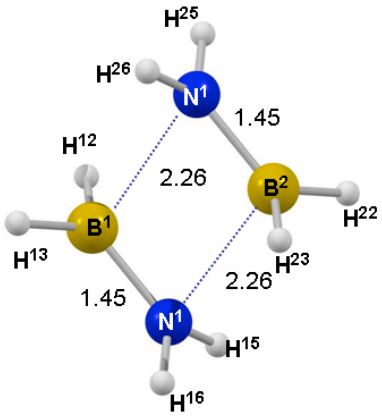
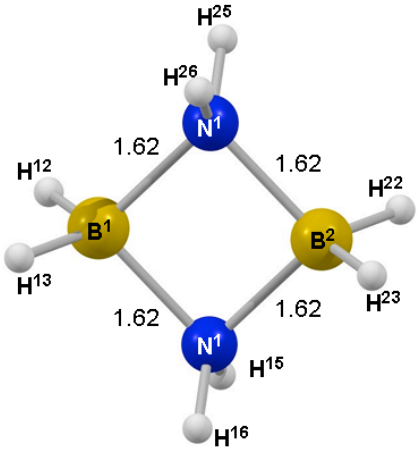


Figure S16. Computed Structures





TS_{Dimer}
(+16.2 kcal/mol)



Dimer
(-8.7 kcal/mol)

TS6a'Dimer

Ir	0.03852	-0.30798	-0.00023
P	-2.27266	-0.83078	0.00015
P	2.39333	-0.55390	0.00003
B	0.22915	1.82789	-0.00021
C	-3.26752	-0.26253	-1.46631
C	-3.26524	-0.26618	1.46955
C	-2.56146	-2.66459	-0.00200
C	3.29305	0.15014	-1.46444
C	3.29246	0.14959	1.46514
C	2.90353	-2.33771	-0.00018
N	1.18858	2.89466	0.00029
B	-0.81115	4.18326	0.00102
N	-1.65735	2.99696	-0.00107
H	0.11318	-1.52461	-1.01202
H	0.11307	-1.52460	1.01160
H	-0.03630	1.22924	1.11842
H	-0.03617	1.22931	-1.11891
H	-2.79409	-0.63886	-2.38618
H	-3.29181	0.83688	-1.51082
H	-4.30076	-0.64116	-1.40443
H	-3.28888	0.83313	1.51719
H	-2.79067	-0.64529	2.38769
H	-4.29875	-0.64412	1.40809
H	-2.09299	-3.10566	0.89081
H	-2.09467	-3.10330	-0.89685
H	-3.64067	-2.88676	-0.00129
H	3.15502	1.24149	-1.48453
H	2.87470	-0.28036	-2.38720
H	4.36897	-0.08106	-1.40620
H	2.87355	-0.28102	2.38759
H	3.15470	1.24097	1.48544
H	4.36836	-0.08184	1.40738
H	2.49394	-2.83167	-0.89431
H	2.49370	-2.83197	0.89367
H	4.00185	-2.42552	-0.00006
H	1.58538	3.28434	0.85177
H	1.58470	3.28574	-0.85093
H	-0.55699	4.69871	1.05491
H	-0.55608	4.70161	-1.05123
H	-2.17756	2.76187	-0.84653
H	-2.17867	2.75961	0.84307

SCF (BS1) = -522.319245191
H 0K= -521.981199
H 298K= -521.956947
G 298K= -522.035206
SCF (C6H5F) = -522.370290136
BP86-D3 = -522.374287651
SCF (BS2) = -1192.28225383
Lowest Frequency = -349.3471cm-1

I6a'9

Ir	0.00000	-0.32411	-0.00982
P	-2.33400	-0.68695	0.00593
P	2.33400	-0.68695	0.00593
B	0.00000	1.89268	-0.05278
C	-3.32241	0.03171	-1.39895
C	-3.24864	-0.12023	1.52500
C	-2.76089	-2.49116	-0.07876
C	3.32241	0.03171	-1.39895
C	3.24864	-0.12023	1.52500
C	2.76089	-2.49116	-0.07876
N	1.15341	2.98402	-0.05182
B	0.00000	4.12606	0.13148
N	-1.15341	2.98402	-0.05182
H	0.00000	-1.57682	-0.97912
H	0.00000	-1.54573	1.00277
H	0.00000	1.22375	1.06829
H	0.00000	1.17125	-1.14540
H	-2.89352	-0.31267	-2.35258
H	-3.27892	1.13150	-1.37068
H	-4.37628	-0.28468	-1.33603
H	-3.18574	0.97469	1.62368
H	-2.78354	-0.57614	2.41252
H	-4.30952	-0.41476	1.47450
H	-2.30023	-3.01025	0.77530
H	-2.35231	-2.91498	-1.00866
H	-3.85303	-2.63499	-0.05495
H	3.27892	1.13150	-1.37068
H	2.89352	-0.31267	-2.35258
H	4.37628	-0.28468	-1.33603
H	2.78354	-0.57614	2.41252
H	3.18574	0.97469	1.62368
H	4.30952	-0.41476	1.47450
H	2.35231	-2.91498	-1.00866
H	2.30023	-3.01025	0.77530
H	3.85303	-2.63499	-0.05495
H	1.82707	2.92595	0.71768
H	1.68246	3.06578	-0.92632
H	0.00000	4.55543	1.25846
H	0.00000	4.92399	-0.77167
H	-1.68246	3.06578	-0.92632
H	-1.82707	2.92595	0.71768

SCF (BS1) = -522.365595407
H 0K= -522.022483
H 298K= -521.999302
G 298K= -522.076703
SCF (C6H5F) = -522.420885270
BP86-D3 = -522.419949497
SCF (BS2) = -1192.32527160
Lowest Frequency = 14.9876cm-1

TSDimer

B	-0.74774	-0.97640	0.00001
N	-1.41363	0.31081	-0.00005
H	-0.65195	-1.56087	-1.05001
H	-0.65200	-1.56080	1.05008
H	-1.78208	0.73308	0.84795
H	-1.78204	0.73302	-0.84809

```
N   1.41411 -0.31038  0.00004
B   0.74838  0.97687 -0.00000
H   1.77833 -0.73586  0.84823
H   1.77837 -0.73589 -0.84811
H   0.65241  1.56101  1.05012
H   0.65247  1.56097 -1.05016

SCF (BS1) =     -164.055418034
H 0K=           -163.958897
H 298K=         -163.953066
G 298K=         -163.986754
SCF (C6H5F) =   -164.059490598
BP86-D3 =       -164.063715554
Lowest Frequency = -344.8887cm-1
```

Aminoborane Dimer

```
B  -0.00000 -1.12283  0.00013
N   1.16294 -0.00000 -0.00012
H   0.00009 -1.77158  1.02588
H  -0.00008 -1.77178 -1.02549
H   1.76395 -0.00010 -0.82728
H   1.76400  0.00012  0.82700
N  -1.16293  0.00001 -0.00005
B  -0.00003  1.12285  0.00008
H  -1.76357 -0.00024 -0.82748
H  -1.76427  0.00006  0.82685
H  -0.00014  1.77203 -1.02536
H   0.00011  1.77131  1.02597

SCF (BS1) =     -164.099179913
H 0K=           -163.997958
H 298K=         -163.993066
G 298K=         -164.025025
SCF (C6H5F) =   -164.105596608
BP86-D3 =       -164.106525853
Lowest  Frequency  =  86.9801cm-1
```

(10) Model 2. Oligomerisation vs. Dimerisation in the presence of 2 extra H_3BNH_3 molecules

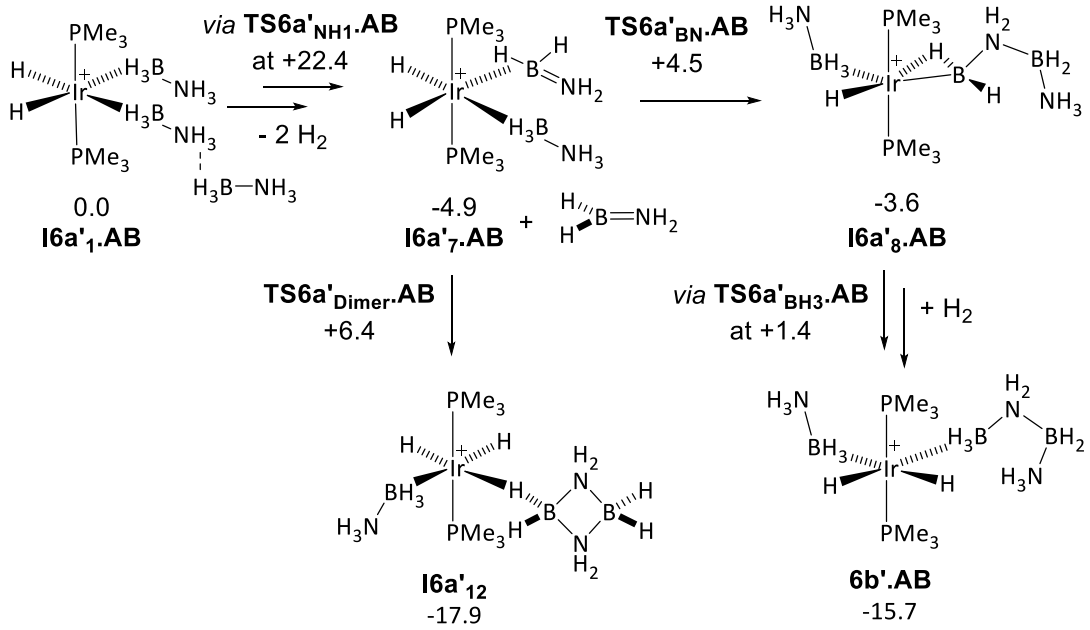
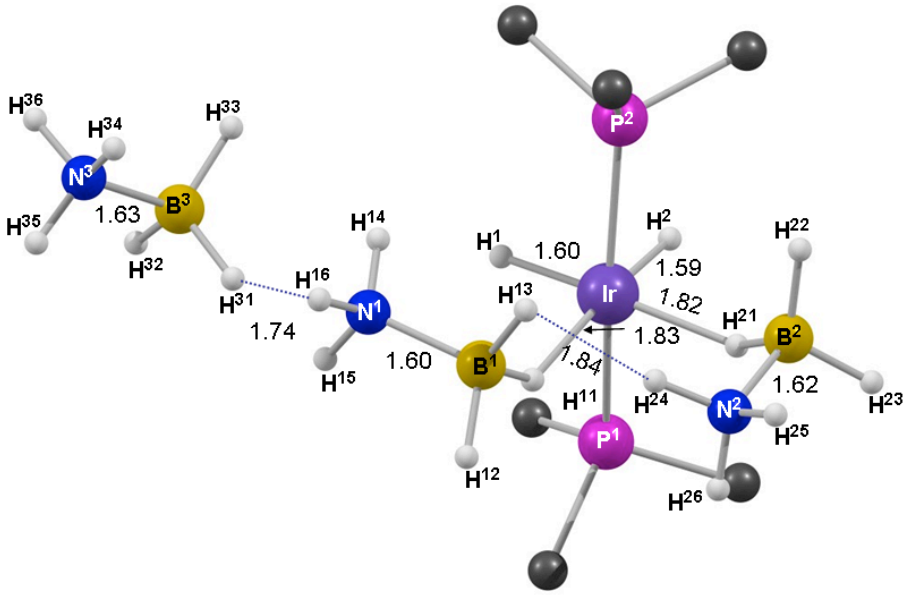
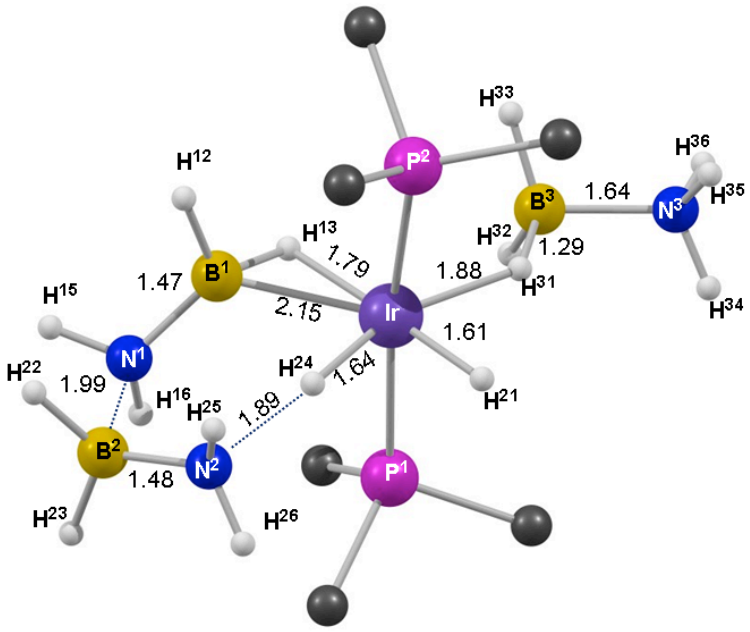


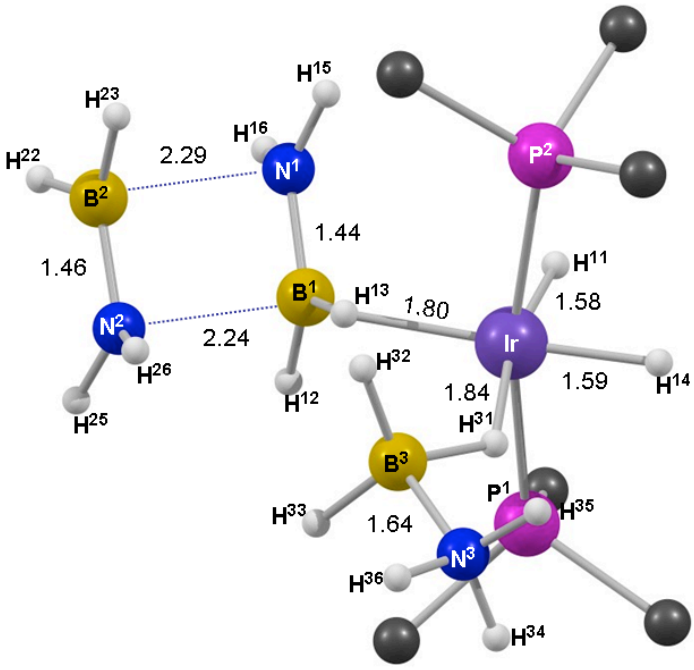
Figure S17. Computed Structures



I6a'$_1$.AB
(+0.0 kcal/mol)



TS6a'$_{BN}$.AB
(+4.5 kcal/mol)



TS6a'$_{Dimer}$.AB
(+6.4 kcal/mol)

I6a'1.AB

C	0.47078	3.64383	-0.60293
P	-0.58335	2.11568	-0.48632
C	-1.49626	2.15342	-2.11142
C	-1.90818	2.64632	0.71557
Ir	0.70229	0.16047	-0.16605
P	2.29364	-1.54979	-0.40608
C	2.05371	-3.14571	0.52836
C	2.50367	-2.13388	-2.15805
C	4.02008	-1.04949	0.07141
B	-1.40772	-1.10604	1.33138
N	-2.41052	-1.48854	0.14606
B	1.45715	1.34568	2.31611
N	0.62429	0.37841	3.31059
H	-2.15327	-2.37703	-0.30177
H	-3.40078	-1.58804	0.46102
H	-2.39884	-0.77848	-0.59737
H	0.04867	-0.39204	-1.51280
H	-0.15124	4.53585	-0.78273
H	1.03239	3.76414	0.33528
H	1.18655	3.51858	-1.42957
H	-2.36680	3.59143	0.38168
H	-2.68521	1.87101	0.79361
H	-1.45391	2.79453	1.70688
H	-1.95886	3.13925	-2.28203
H	-0.78442	1.93295	-2.92132
H	-2.28341	1.38259	-2.12219
H	-0.22776	-1.04995	0.84080
H	-1.80363	-0.09394	1.87689
H	1.69920	0.96176	-1.10611
H	-1.30967	-2.05135	2.09042
H	3.30768	-2.88394	-2.23292
H	1.55655	-2.56997	-2.51100
H	2.74442	-1.26726	-2.79236
H	2.86350	-3.85887	0.30326
H	2.04244	-2.94274	1.61055
H	1.08730	-3.59285	0.24876
H	4.73254	-1.87393	-0.09417
H	4.31576	-0.17858	-0.53345
H	4.03599	-0.75254	1.13138
H	1.72869	0.70310	1.23250
H	2.57472	1.48191	2.76814
H	0.83961	2.37581	2.19502
H	0.50732	0.82976	4.22755
H	-0.31555	0.16392	2.92896
H	1.09397	-0.52128	3.47176
H	-5.06444	-1.79934	0.92856
B	-5.51186	-1.60842	-0.20264
H	-5.11011	-2.43316	-1.00556
N	-7.12405	-1.83439	-0.07161
H	-5.34827	-0.45867	-0.57445
H	-7.58838	-1.69438	-0.97813
H	-7.35161	-2.78590	0.24417
H	-7.55035	-1.17820	0.59506

SCF (BS1) = -607.957092751
H 0K= -607.504875
H 298K= -607.472810
G 298K= -607.572486
SCF (C6H5F) = -608.013667874
BP86-D3 = -608.028277061
Lowest Frequency = 6.8822cm-1

TS6a'NH1.AB

C	3.16537	1.36010	-0.76888
P	2.29117	-0.27031	-0.52699
C	3.39857	-1.10333	0.72080
C	2.72295	-1.16996	-2.09912
Ir	-0.04746	-0.12244	-0.17378
B	-0.12301	-1.98148	1.18089
N	-0.14029	-3.14223	0.13975
P	-2.40957	-0.06539	-0.33638
C	-3.29246	-1.70507	-0.34416
C	-3.32996	0.88587	0.97136
C	-2.99946	0.69898	-1.92355
B	-0.28360	2.96841	-0.91032
N	0.56867	3.69144	0.27049
B	0.52602	1.11052	2.35663
N	0.33605	0.00973	3.50822
H	4.20980	1.20497	-1.08474
H	2.63097	1.94016	-1.53754
H	3.16389	1.90723	0.18801
H	4.44462	-1.08075	0.37503
H	3.32214	-0.57784	1.68487
H	3.08491	-2.14787	0.86532
H	3.81385	-1.20974	-2.24970
H	2.32204	-2.19455	-2.05605
H	2.25186	-0.64976	-2.94733
H	-0.14367	-0.60650	-1.68720
H	-0.27288	0.74044	1.42625
H	0.02995	1.73337	-0.87778
H	-1.14503	-1.90115	1.84042
H	0.91348	-1.98146	1.83896
H	-0.09700	-1.90024	-0.47181
H	0.68662	-3.73600	0.05122
H	-0.99594	-3.69080	0.03431
H	-4.37662	-1.55454	-0.47080
H	-2.91531	-2.31289	-1.18171
H	-3.10729	-2.23158	0.60449
H	-4.41245	0.89348	0.76475
H	-3.15264	0.41861	1.95283
H	-2.95237	1.91955	0.98744
H	-4.10077	0.72319	-1.95768
H	-2.59992	1.72073	-1.99977
H	-2.61790	0.10446	-2.76802
H	0.08247	3.41835	-1.97478
H	-1.45580	3.13763	-0.64738
H	0.30057	4.68145	0.34535
H	0.40570	3.24775	1.19104
H	1.58079	3.66224	0.09372
H	0.01367	2.15864	2.72079
H	1.70197	1.21045	2.09786

```
H   0.98191  0.15769  4.29401
H  -0.61835 -0.00714  3.88933
H   0.51511 -0.93350  3.09420

SCF (BS1) =     -606.717619180
H 0K=           -606.290436
H 298K=         -606.260894
G 298K=         -606.348525
SCF (C6H5F) =   -606.772832989
BP86-D3 =       -606.800147690
Lowest Frequency = -1038.5676cm-1
```

I6a'7.AB

```
C   3.38963 -2.05018 -0.53540
P   1.53943 -2.07549 -0.33592
Ir  0.53144  0.06139 -0.19829
B  -1.45172 -0.91457  0.53017
N  -2.67529 -0.27747  0.78768
C   0.97220 -3.06396 -1.80088
C   1.29405 -3.23544  1.09547
P  -0.38047  2.22147 -0.49499
C  -1.83987  2.29800 -1.64091
C  -0.95540  3.14533  1.01840
C   0.80266  3.43551 -1.26314
B  -6.18474 -1.10140  0.57920
N  -7.50439 -1.54430  0.55512
H   3.65289 -1.42950 -1.40529
H   3.78388 -3.06969 -0.67570
H   3.84117 -1.61603  0.37051
H   1.47619 -4.04322 -1.83686
H   1.18990 -2.49949 -2.72050
H  -0.11620 -3.21224 -1.72799
H  -1.28792  4.16235  0.75372
H  -0.12744  3.20085  1.74175
H  -1.78893  2.61212  1.50072
H   1.68043  3.55824 -0.60978
H   0.32138  4.41572 -1.41232
H   1.14125  3.03785 -2.23182
H   1.68352 -2.76478  2.01117
H   1.81461 -4.19034  0.91739
H   0.21760 -3.42300  1.22544
H  -2.22033  3.32833 -1.72970
H  -2.62993  1.63458 -1.25799
H  -1.52806  1.93272 -2.63162
H  -0.45456 -0.37541  1.22267
H   1.52838  0.47115 -1.39193
H  -0.35583 -0.37856 -1.43410
B   2.07181  0.66944  2.13052
H   1.81852  0.79736  0.87051
H  -1.48770 -2.08356  0.24714
H  -3.57294 -0.75365  0.67842
H  -2.76914  0.66236  1.16592
H  -5.29836 -1.92054  0.48270
H  -5.95835  0.07897  0.69522
H  -8.30412 -0.91930  0.63242
H  -7.76541 -2.52367  0.46143
H   1.35741  1.38494  2.79155
H   2.19017 -0.46822  2.51572
N   3.57209  1.33334  2.15993
H   3.93068  1.31399  3.12472
H   4.24689  0.82343  1.57448
H   3.58147  2.31530  1.85435

SCF (BS1) =     -605.574950846
H 0K=           -605.166945
H 298K=         -605.135539
G 298K=         -605.235171
SCF (C6H5F) =   -605.628503658
BP86-D3 =       -605.637775346
Lowest Frequency = 9.8571cm-1
```

TS6a'BN.AB

```
C   3.40171  0.51676 -1.23752
P   2.36285 -0.58194 -0.15327
Ir  0.09507  0.09285 -0.01591
B  -0.16919 -1.52652  1.37199
N  -1.45081 -2.21898  1.57591
C   2.64120 -2.26479 -0.88367
C   3.31959 -0.61346  1.43860
P  -2.14692  0.85355 -0.20512
C  -3.34154 -0.24694 -1.10663
C  -3.02898  1.26475  1.38349
C  -2.29355  2.45187 -1.14802
B  -1.77625 -3.51243  0.09425
N  -1.17661 -2.98470 -1.15137
H   2.94731  0.57835 -2.23787
H   4.42877  0.12601 -1.32009
H   3.43929  1.52362 -0.79310
H   3.71706 -2.49812 -0.92861
H   2.21574 -2.28756 -1.89876
H   2.12922 -3.01488 -0.26213
H  -4.03306  1.67178  1.18145
H  -2.43121  2.00688  1.93498
H  -3.12911  0.36786  2.01466
H  -1.75258  3.23519 -0.59502
H  -3.34954  2.74866 -1.25353
H  -1.84397  2.32716 -2.14491
H   3.28579  0.38906  1.89238
H   4.36641 -0.90681  1.25851
H   2.85183 -1.32996  2.12996
H  -4.34263  0.21265 -1.13572
H  -3.40111 -1.23036 -0.61423
H  -2.97642 -0.39100 -2.13544
H  -0.07220 -0.20820  1.74035
H   0.21566  0.34410 -1.60641
H  -0.40916 -1.33984 -0.63517
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H 0.68009 4.36294 -0.60310

SCF (BS1) = -605.553837538
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H 298K= -605.116575
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SCF (BS2) = -1275.53875293
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I6a'8.AB

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N -1.79800 -2.24066 1.21541
C 2.53261 -2.40222 -0.98911
C 3.13988 -1.09180 1.54925
P -2.02188 1.06773 -0.08490
C -3.43248 0.24255 -1.00017
C -2.80807 1.51228 1.54815
C -1.99299 2.72082 -0.94502
B -2.15993 -3.26893 0.00906
N -1.56931 -2.62603 -1.35966
H 3.11835 0.54671 -1.96619
H 4.49258 -0.13414 -1.02347
H 3.56918 1.26399 -0.37684
H 3.59347 -2.70089 -0.98795
H 2.18987 -2.28132 -2.02883
H 1.93477 -3.18404 -0.49664
H -3.74898 2.06786 1.40318
H -2.09422 2.13036 2.11450
H -3.01489 0.60547 2.13923
H -1.33182 3.38843 -0.37246
H -3.00350 3.15749 -0.99548
H -1.59440 2.58976 -1.96283
H 3.16566 -0.14295 2.10708
H 4.16598 -1.46583 1.40168
H 2.55930 -1.82656 2.12692
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H -0.11964 -0.50339 1.78754
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SCF (BS1) = -605.572290251
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BP86-D3 = -605.647397651
Lowest Frequency = 27.7128cm-1

TS6a'BH3.AB

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P -1.39387 -1.89683 -0.23348
C -0.90099 -3.46724 -1.10330
C 1.36136 3.16977 -0.68484
C 2.75468 1.78428 1.44905
B -1.27678 1.20482 0.58756
N -2.09904 2.02314 -0.53931
B -3.47780 2.67860 -0.06902
N -3.28670 3.12382 1.48232
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C -2.97532 -1.44656 -1.10561
B 2.56514 -2.11674 0.40623
N 2.08813 -2.41191 1.92989
H -2.35340 1.38751 -1.30594
H -1.48613 2.72348 -0.97663
H -0.33074 0.43196 -1.55323
H 4.08848 2.00179 -1.27572
H 3.83001 0.22621 -1.11202
H 2.96218 1.13883 -2.38137
H 3.47595 2.61444 1.37799
H 1.98073 2.02341 2.19446
H 3.28470 0.86992 1.75679
H 2.20120 3.88263 -0.65640
H 0.96031 3.13372 -1.71058
H 0.57789 3.50580 0.01153
H 0.35734 -0.31460 1.44672
H -0.73497 2.04806 1.29551
H 0.50125 -0.43047 -1.84422
H -2.11510 0.57143 1.22571
H -3.67142 -2.30097 -1.11206
H -3.45263 -0.60078 -0.58601

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H  -2.84766 -3.20293  1.29442
H  -1.19646 -2.99555  1.96060
H  -2.34274 -1.62274  2.00158
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6b′.AB

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Ir -0.08063 -0.34605 -0.20768
P   2.18721 -0.96802 -0.37232
C   3.32766 -0.58119  1.05092
B  -0.20842  2.02411  1.41370
N   0.96768  3.10913  1.47481
B   1.83965  3.38274  0.16352
N   0.87798  3.17633 -1.11827
C   2.40095 -2.80392 -0.57211
C   3.11563 -0.28016 -1.82917
B  -0.85356 -1.89684  2.05926
N  -0.57545 -0.86560  3.27489
H  -2.79915 -1.95852 -2.01271
H  -4.33449 -1.44046 -1.22756
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H  -2.31715  0.83955 -2.81299
H  -2.51438  2.15252 -1.60603
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H   2.94593 -1.06127  1.96580
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H   1.89071 -3.12471 -1.49317
H  -3.48216 -0.19468  1.67530
H  -4.53979  0.65268  0.50021
H  -3.13664  1.51067  1.23017
H   4.12171 -0.72457 -1.89880
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H   2.55155 -0.49877 -2.74872
H  -0.62721  1.81292  2.54854
H   0.38694  0.94447  1.03202
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BP86-D3 =       -606.866539708
Lowest Frequency = 26.6210cm-1
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TS6a′Dimer2

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P   2.23482 -0.74124 -0.49150
C   2.74436 -2.45850  0.01568
C  -3.04717  0.67932 -1.97868
B  -0.13245  2.23956 -0.09627
N   0.21358  3.25233  1.87471
B   1.21329  3.97995  1.10195
N   0.83101  2.95026 -0.90268
C   2.86561 -0.63453 -2.23687
C   3.42899  0.31672  0.47026
B   0.04653 -0.81481  2.51572
N  -0.27730 -2.20577  3.32688
H  -2.83870 -2.39135 -1.47748
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SCF (BS1) =     -605.553657903
H 0K=           -605.144482
H 298K=         -605.114830
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BP86-D3 =       -605.624929373
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6b′Dimer

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P   2.19770 -0.82983 -0.46710
C   2.52296 -2.19947 -1.68057
C  -2.96622  0.29241 -2.13778
B  -0.10765  2.57887 -0.14102
N   0.15578  2.89797  1.38984
B   1.49997  3.68384  0.92641
N   1.07159  3.53467 -0.63652
C   3.24375  0.56054 -1.13097
C   3.18803 -1.37372  1.02122
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H  -2.53706  1.27763 -2.37679
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H   3.60358 -2.38468 -1.79119
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H   2.81407  0.89937 -2.08723
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H  -0.30247 -1.93763 -0.16261
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H  -0.36687 -2.36200  3.77251
H  -0.18345 -2.63146  2.13480
H   1.08140 -2.03824  3.02967
H  -0.55478  3.49730  1.82157
H   0.29374  2.08902  2.00397
H   1.53920  4.83017  1.30158
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SCF (BS1) =     -605.599190261
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G 298K=         -605.243265
SCF (C6H5F) =   -605.655004928
BP86-D3 =       -605.672393531
Lowest Frequency =  25.1061cm-1
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(11) General experimental procedures

All manipulations, unless otherwise stated, were performed under an argon atmosphere using standard Schlenk and glove-box techniques. Glassware was oven dried at 130 °C overnight and flamed under vacuum prior to use. Pentane, THF and MeCN were dried using a Grubbs type solvent purification system (MBraun SPS-800) and degassed by successive freeze-pump-thaw cycles.[8] C_6H_5F and 1,2-$F_2C_6H_4$ were dried over CaH_2, vacuum distilled and stored over 3 Å molecular sieves. $H_3B{\cdot}NH_3$ was purchased from Aldrich and sublimed prior to use. $Na[BAr^F{}_4]$,[9] $Na[BAr^{Cl}{}_4]$,[10] $H_3B{\cdot}NH_2BH_2{\cdot}NH_3$,[11] $H_3B{\cdot}NH_2BH_2NH_2BH_2{\cdot}NH_3$,[12] $[IrHPCy_2(\eta^2\text{-}C_6H_9)PCy_2(\eta^3\text{-}C_6H_8)][BAr^F{}_4]$[13] and $[IrHPCy_2(\eta^2\text{-}C_6H_9)PCy_2(\eta^3\text{-}C_6H_8)][BAr^{Cl}{}_4]$[14] were prepared by literature methods. NMR spectra were recorded on a Bruker AVIII-500 spectrometer at room temperature, unless otherwise stated. In C_6H_5F and 1,2-$F_2C_6H_4$, ^{1}H NMR spectra were referenced to the centre of the downfield solvent multiplet, δ = 7.11 and 7.07 respectively. ^{31}P and ^{11}B NMR spectra were referenced against 85% H_3PO_4 (external) and $BF_3{\cdot}OEt_2$ (external) respectively. The spectrometer was pre-locked and pre-shimmed to the solvent mixture of 0.3 ml of 1,2-$F_2C_6H_4$ and 0.1 ml of C_6D_6. Chemical shifts (δ) are quoted in ppm and coupling constants (*J*) in Hz. ESI-MS were recorded on a Bruker micrOTOF instrument interfaced with a glove-box.[15] Microanalysis was performed by Elemental Microanalysis Ltd. IR spectrum was recorded on a Bruker Tensor 27 FTIR spectrometer equipped with an attenuated total reflectance attachment with internal calibration. For hydrogenation reactions a high pressure NMR tube equipped with a J. Young's valve and the dissolved compound of interest was cooled to 77 K. The tube was evacuated and H_2 admitted (1 atm). The tube was sealed and warmed to 298 K, resulting in a pressure of ~ 4 atm (298/77 ~ 4).

(12) Synthesis of new complexes

$[Ir(H)_2(PCy_3)_2(H_3B{\cdot}NH_3)][BAr^F{}_4]$ (6a)

In a high pressure NMR tube equipped with a J. Young's valve $[IrHPCy_2(\eta^2\text{-}C_6H_9)PCy_2(\eta^3\text{-}C_6H_8)][BAr^F{}_4]$ (23 mg, 0.014 mmol) in C_6H_5F was hydrogenated at 4 atm at 298 K. The tube was occasionally shaken over a period of 20 min to produce a colourless solution $[Ir(H)_2(PCy_3)_2(H_2)_2][BAr^F{}_4]$ (**1**). The solution of **1** was rapidly transferred under argon to another high pressure NMR tube containing ammonia-borane (0.5 mg, 0.016 mmol) and an immediate change from colourless to purple was observed. A gentle inversion of NMR tube for another 50 min made the solution again colourless. It was then degassed through one freeze-pump-thaw cycle and gently inverted for 10 more minutes. Analysis by NMR spectroscopy at this point showed the formation of $[Ir(H)_2(PCy_3)_2(H_3B{\cdot}NH_3)][BAr^F{}_4]$ (**6a**) in more than 95% yield. Attempt to isolate crystals of **6a** by layering with pentane or hexane was not successful and resulted in the yellow oil and some unidentified white suspension.

^{1}H NMR (500 MHz, C_6H_5F): δ 8.35 (s, 8H, $[BAr^F{}_4]^-$), 7.66 (s, 4H, $[BAr^F{}_4]^-$), 3.63 (s, 3H, NH_3), 1.93-1.21 (m, 66H, Cy), -5.96 (br, 2H, σ-bound BH_2), -20.28 (t, $^2J_{HP}$ = 15, 2H, IrH_2), The remaining BH signal is not observed, presumably as too broad or obscured by solvent peak (In case of $[Ir(H)_2(PCy_3)_2(H_3B{\cdot}NH_2Me)][BAr^F{}_4]$ unbound B-H signal comes at 6.09 in C_6H_5F at 250K).[14]

^{31}P{^{1}H} NMR (202 MHz, C_6H_5F): δ 38.18 (br, 1P), 33.43 (br, 1P).

^{31}P{^{1}H} NMR (202 MHz, C_6H_5F, 250 K): δ 38.59 (d, $^2J_{PP}$ = 273, 1P), 32.17 (d, $^2J_{PP}$ = 273, 1P).

^{11}B NMR (160 MHz, C_6H_5F): δ 10.51 (br, bound BH_3), -5.90 (s, $[BAr^F{}_4]^-$).

ESI-MS (C_6H_5F, 60 °C) positive ion: m/z 786.5012 $[M]^+$ (calc. 786.5021).

$[Ir(H)_2(PCy_3)_2(H_3B{\cdot}NH_3)][BAr^{Cl}{}_4]$ (6a[$BAr^{Cl}{}_4$])

In a Young's flask $[IrHPCy_2(\eta^2\text{-}C_6H_9)PCy_2(\eta^3\text{-}C_6H_8)][BAr^{Cl}{}_4]$ (30 mg, 0.022 mmol) in C_6H_5F was hydrogenated as described in the general procedures. It was stirred for 20 min to produce a colourless solution of $[Ir(H)_2(PCy_3)_2(H_2)_2][BAr^{Cl}{}_4]$ **2**. The solution, then, was rapidly transferred under argon to another Young's flask containing $H_3B{\cdot}NH_3$ (0.8 mg, 0.026 mmol). Stirring for another 50 min was followed by degassing by a freeze-pump-thaw cycle. Stirring the solution for 30 more minutes resulted in a white precipitate. The solvent was removed by cannula filtration and the white precipitate was dried to obtain the white solid of **$[Ir(H)_2(PCy_3)_2(H_3B{\cdot}NH_3)][BAr^{Cl}{}_4]$ (6a[$BAr^{Cl}{}_4$])** in 48 % yield. Crystals suitable for X-ray diffraction were obtained by recrystallisation from 1,2-$F_2C_6H_4$/pentane at 5 °C.

^{1}H NMR (500 MHz, 1,2-$F_2C_6H_4$): δ 7.37 (s, 8H, $[BAr^{Cl}{}_4]^-$), 4.22 (s, 3H, NH_3), 1.9-1.1 (m, 66H, Cy), -5.91 (br, 2H, σ-bound BH_2), -20.33 (br, t, $^2J_{HP}$ = 15, 2H, IrH_2). The remaining BH signal is not observed, presumably as too broad or obscured by solvent peak. Other $[BAr^{Cl}{}_4]^-$ peak is also obscured by the solvent.

^{1}H NMR (500 MHz, CD_2Cl_2, 250 K): δ 7.22 (br, m, 2H, $[BAr^{Cl}{}_4]^-$), 7.16 (br, m, 2H, $[BAr^{Cl}{}_4]^-$), 7.10 (s, 6H, $[BAr^{Cl}{}_4]^-$), 7.06 (s, 2H, $[BAr^{Cl}{}_4]^-$), 6.13 (br, 1H, BH not σ-bound), 3.95 (s, 3H, NH_3), 1.96-1.26 (m, 66H, Cy), -6.14 (br, 2H, σ-bound BH_2), -20.32 (br, t, $^2J_{HP}$ = 15, 2H, IrH_2).

^{31}P{^{1}H} NMR (202 MHz, 1,2-$F_2C_6H_4$): δ 38.06 (br, 1P), 32.88 (br, 1P).

^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2): δ 38.06 (br, 1P), 33.26 (br, 1P).

^{31}P{^{1}H} NMR (202 MHz, 1,2-$F_2C_6H_4$, 250K): δ 38.5 (d, $^2J_{PP}$ = 273, 1P), 31.95 (d, $^2J_{PP}$ = 273, 1P).

^{11}B NMR (160 MHz, 1,2-$F_2C_6H_4$): δ 10.76 (br, bound BH_3), -6.63 (s, $[BAr^{Cl}{}_4]^-$).

^{11}B NMR (160 MHz, CD_2Cl_2): δ 10.25 (br, bound BH_3), -6.96 (s, $[BAr^{Cl}{}_4]^-$).

Elemental Microanalysis: Calc. $[C_{60}H_{86}B_2Cl_8IrNP_2 + C_6H_4F_2]$ (1494.83 $gmol^{-1}$): C, 53.03; H, 6.07; N, 0.94. Found: C, 53.22; H, 5.84; N, 1.22.

$[Ir(H)_2(PCy_3)_2(H_3B{\cdot}NH_2BH_2{\cdot}NH_3)][BAr^F{}_4]$ (6b)

In a high pressure NMR tube equipped with a J. Young's valve $[IrHPCy_2(\eta^2\text{-}C_6H_9)PCy_2(\eta^3\text{-}C_6H_8)][BAr^F{}_4]$ (32 mg, 0.02 mmol) in C_6H_5F was hydrogenated as described in the general procedures. The tube was occasionally shaken over a period of 20 min to produce a colourless solution $[Ir(H)_2(PCy_3)_2(H_2)_2][BAr^F{}_4]$ (**1**). The solution of **1** was rapidly transferred under argon to another high pressure NMR tube containing $H_3B{\cdot}NH_2BH_2{\cdot}NH_3$ (1.3 mg, 0.02 mmol). The NMR tube was sonicated for 5 minutes and then gently inverted for 2 hours. ESI-MS and NMR spectra showed the formation of $[Ir(H)_2(PCy_3)_2(H_3B{\cdot}NH_2BH_2{\cdot}NH_3)][BAr^F{}_4]$ (**6b**) in more than 95% yield as measured by ^{1}H NMR spectroscopy.

^{1}H NMR (500 MHz, C_6H_5F): δ 8.35 (s, 8H, $[BAr^F{}_4]^-$), 7.66 (s, 4H, $[BAr^F{}_4]^-$), 3.35 (s, 3H, NH_3), 2.74 (s, 2H, NH_2), 2.35 (br, 2H, BH_2), 1.98-1.22 (m, 66H, Cy), -6.32 (br, 2H, σ-bound BH_2), -19.87 (apparent triplet, $^2J_{HP}$ = 15, 2H, IrH_2). The remaining BH signal is not observed, presumably as too broad or obscured by solvent peak.

^{1}H{^{11}B} NMR (500 MHz, CD_2Cl_2): δ 7.78 (s, 8H, $[BAr^F{}_4]^-$), 7.62 (s, 4H, $[BAr^F{}_4]^-$), 6.23 (br, 1H, not σ-bound), 4.01 (s, 3H, NH_3), 3.00 (s, 2H, NH_2), 2.32 (br, 2H, BH_2), 1.98-1.30 (m, 66H, Cy), -6.33 (br, 2H, σ-bound BH_2), -20.09 (t, $^2J_{HP}$ = 15, 2H, IrH_2).

$^{31}P\{^{1}H\}$ NMR (202 MHz, C_6H_5F): δ 37.38 (d, $^{2}J_{PP}$ = 284, 1P), 32.18 (d, $^{2}J_{PP}$ = 284, 1P).

^{11}B NMR (160 MHz, C_6H_5F): δ 13.76 (br, bound BH_3), -6.11 (s, $[BAr^{F}_4]^-$), -11.47 (br, BH_2).

ESI-MS (C_6H_5F, 60 °C) positive ion: m/z 815.5471 $[M]^+$ (calc. 815.5464).

$[Ir(H)_2(PCy_3)_2(H_3B{\cdot}NH_2BH_2{\cdot}NH_3)][BAr^{Cl}_4]$ (6b$[BAr^{Cl}_4]$)

In a high pressure NMR tube equipped with a J. Young's valve $[IrHPCy_2(\eta^2\text{-}C_6H_9)PCy_2(\eta^3\text{-}C_6H_8)][BAr^{Cl}_4]$ (25 mg, 0.019 mmol) in 1,2-$F_2C_6H_4$ was hydrogenated as described in the general procedures. The tube was occasionally shaken over a period of 20 min to produce a colourless solution $[Ir(H)_2(PCy_3)_2(H_2)_2][BAr^{Cl}_4]$ **2**, which was rapidly transferred under argon to another high pressure NMR tube containing containing $H_3B{\cdot}NH_2BH_2{\cdot}NH_3$ (1.4 mg, 0.02 mmol). The NMR tube was sonicated for 15 minutes and then gently inverted for 4 hours. ESI-MS and NMR spectra at this stage showed the formation of $[Ir(H)_2(PCy_3)_2(H_3B{\cdot}NH_2BH_2{\cdot}NH_3)][BAr^{Cl}_4]$ (**6b$[BAr^{Cl}_4]$**), in more than 95% yield as measured by ^{1}H NMR spectroscopy. Solid or crystalline (**6b$[BAr^{Cl}_4]$**) could not be obtained through recrystallisation from 1,2-$F_2C_6H_4$/pentane at -30 °C.

$^{1}H\{^{11}B\}$ NMR (500 MHz, 1,2-$F_2C_6H_4$): δ 7.37 (s, 8H, $[BAr^{Cl}_4]^-$), 3.86 (s, 3H, NH_3), 3.03 (s, 2H, NH_2), 2.41 (s, 2H, BH_2), 1.94-1.20 (m, 66H, Cy), -6.36 (br, 2H, σ-bound BH_2), -19.87 (br, 2H, IrH_2). The remaining BH signal is not observed, presumably as too broad or obscured by solvent peak. Other $[BAr^{Cl}_4]^-$ peak is also obscured by the solvent.

$^{31}P\{^{1}H\}$ NMR (202 MHz, 1,2-$F_2C_6H_4$): δ 37.6 (d, $^{2}J_{PP}$ = 284, 1P), 32.2 (d, $^{2}J_{PP}$ = 284, 1P).

^{11}B NMR (160 MHz, 1,2-$F_2C_6H_4$): δ 13.94 (br, bound BH_3), -6.66 (s, $[BAr^{Cl}_4]^-$), -10.90 (br, BH_2).

$[Ir(H)_2(PCy_3)_2(H_3B{\cdot}NH_2BH_2NH_2BH_2{\cdot}NH_3)][BAr^{F}_4]$ (6c)

In a high pressure NMR tube equipped with a J. Young's valve $[IrHPCy_2(\eta^2\text{-}C_6H_9)PCy_2(\eta^3\text{-}C_6H_8)][BAr^{F}_4]$ (32 mg, 0.02 mmol) in C_6H_5F was hydrogenated as described in the general procedures. The tube was occasionally shaken over a period of 20 min to produce a colourless solution $[Ir(H)_2(PCy_3)_2(H_2)_2][BAr^{F}_4]$ (**1**). The solution of **1** was rapidly transferred under argon to another high pressure NMR tube containing $H_3B{\cdot}NH_2BH_2NH_2BH_2{\cdot}NH_3$ (1.8 mg, 0.02 mmol). The NMR tube was sonicated for 15 minutes and then gently inverted for 20 hours. ESI-MS and NMR spectra showed the formation of $[Ir(H)_2(PCy_3)_2(H_3B{\cdot}NH_2BH_2NH_2BH_2{\cdot}NH_3)][BAr^{F}_4]$ (**6c**) in more than 95% yield (by NMR spectroscopy). Solid or crystalline (**6c**) could not be obtained through recrystallization.

$^{1}H\{^{11}B\}$ NMR (500 MHz, C_6H_5F): δ 8.35 (s, 8H, $[BAr^{F}_4]^-$), 7.66 (s, 4H, $[BAr^{F}_4]^-$), 3.04 (br, 3H, NH_3), 2.79 (br, 2H, NH_2), 2.37 (br, 2H, NH_2), 2.27 (br, 2H, BH_2), 2.02-1.25 (m, 66H, Cy), -6.48 (br, 2H, σ-bound BH_2), -19.61(apparent triplet, $^{2}J_{HP}$ = 15, 2H, IrH_2). The remaining BH signals are not observed, presumably the terminal unbound B-H signal is obscured by solvent and the remaining BH_2 signal by cyclohexyl peaks.

$^{1}H\{^{11}B\}$ NMR (500 MHz, CD_2Cl_2): δ 7.78 (s, 8H, $[BAr^{F}_4]^-$), 7.62 (s, 4H, $[BAr^{F}_4]^-$), 6.39 (br, 1H, terminal B-H not σ-bound), 3.94 (br, 3H, NH_3), 2.92 (br, 2H, NH_2), 2.72 (br, 2H, NH_2), 2.32 (br, 2H, BH_2), 1.96-1.30 (m, 66H, Cy), -6.58 (br, 2H, σ-bound BH_2), -19.84 (t, $^{2}J_{HP}$ = 15, 2H, IrH_2). The remaining BH signals are not observed, presumably as too broad or obscured by cyclohexyl peaks.

$^{31}P\{^{1}H\}$ NMR (202 MHz, C_6H_5F): δ 37.12 (d, $^{2}J_{PP}$ = 284, 1P), 32.19 (d, $^{2}J_{PP}$ = 284, 1P).

^{11}B NMR (160 MHz, C_6H_5F): δ 15.6 (br, bound BH_3), -6.10 (s, $[BAr^F{}_4]^-$), -11.7 (br, BH_2 and BH_3).

ESI-MS (C_6H_5F, 60 °C) positive ion: m/z 844.5880 $[M]^+$ (calc. 844.5905).

$[Ir(H)_2(PCy_3)_2(H_3B{\cdot}NH_2BH_2NH_2BH_2{\cdot}NH_3)][BAr^{Cl}{}_4]$ (6c[$BAr^{Cl}{}_4$])

In a high pressure NMR tube equipped with a J. Young's valve $[IrHPCy_2(\eta^2\text{-}C_6H_9)PCy_2(\eta^3\text{-}C_6H_8)][BAr^{Cl}{}_4]$ (25 mg, 0.019 mmol) in 1,2-$F_2C_6H_4$ was hydrogenated as described in the general procedures. The tube was occasionally shaken over a period of 20 min to produce a colourless solution $[Ir(H)_2(PCy_3)_2(H_2)_2][BAr^{Cl}{}_4]$ **2** which was rapidly transferred under argon to a Schlenk tube containing $H_3B{\cdot}NH_2BH_2NH_2BH_2{\cdot}NH_3$ (1.7 mg, 0.019 mmol). The resulting mixture was stirred at room temperature for 3.5 hours under an argon atmosphere. The solution was then filtered to another Schlenk. Excess pentane was added to it while stirring which resulted in white emulsion. Sonication for 15 minutes gave yellow oil and similar white emulsion. This white emulsion was cannula transferred to another Schlenk and dried in vacuum resulting in white solid. Crystals suitable for X-ray diffraction were obtained by recrystallisation from 1,2-$F_2C_6H_4$/pentane at -30 °C in 48% yield.

^{1}H NMR (500 MHz, 1,2-$F_2C_6H_4$): δ 7.37 (s, 8H, $[BAr^{Cl}{}_4]^-$), 3.64 (br, 3H, NH_3), 2.97 (br, 2H, NH_2), 2.65 (br, 2H, NH_2), 2.35 (br, 2H, BH_2), 1.95-1.16 (m, 66H, Cy), -6.58 (br, 2H, σ-bound BH_2), -19.62 (br, 2H, IrH_2), The remaining BH signals are not observed, presumably the terminal B-H (not σ-bound) signal is obscured by solvent and the remaining BH_2 signal by cyclohexyl peaks. Other $[BAr^{Cl}{}_4]^-$ peak is also obscured by the solvent.

^{31}P{^{1}H} NMR (202 MHz, 1,2-$F_2C_6H_4$): δ 37.1 (d, $^2J_{PP}$ = 286, 1P), 32.1 (d, $^2J_{PP}$ = 286, 1P).

^{11}B NMR (160 MHz, 1,2-$F_2C_6H_4$): δ 15.83 (br, bound BH_3), -6.71 (s, $[BAr^{Cl}{}_4]^-$), -11.67 (br, BH_2 and BH_3).

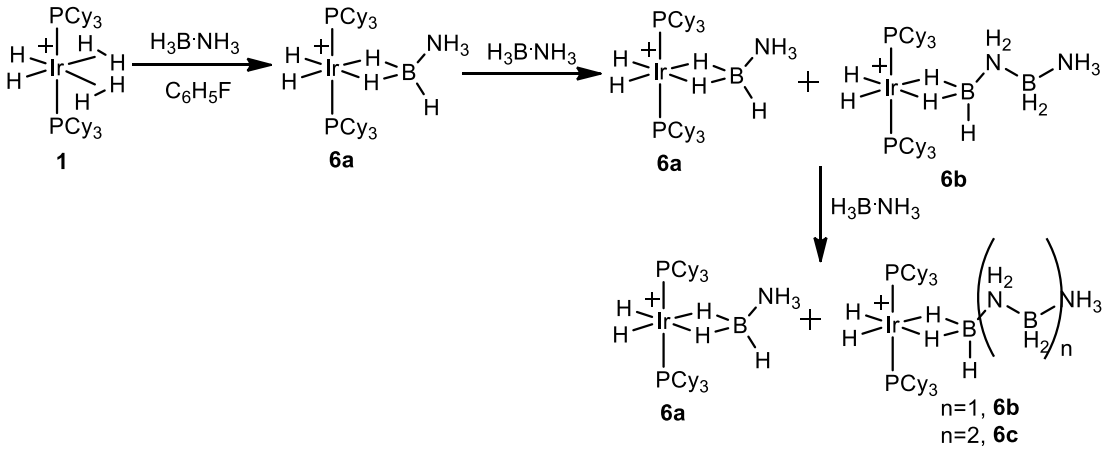
Elemental Microanalysis: Calc. $[C_{60}H_{94}B_4Cl_8IrN_3P_2]$ (1435.44 $gmol^{-1}$): C, 50.10; H, 6.59; N, 2.92. Found: C, 50.81; H, 6.28; N, 2.90.

(13) General method for the dehydropolymerisation of $H_3B{\cdot}NH_3$

In a high pressure NMR tube equipped with a J. Young's valve $[IrHPCy_2(\eta^2\text{-}C_6H_9)PCy_2(\eta^3\text{-}C_6H_8)][BAr^F{}_4]$ (23 mg, 0.014 mmol) in C_6H_5F was hydrogenated at 4 atm. It was occasionally shaken over a period of 20 min to produce the colourless solution $[Ir(H)_2(PCy_3)_2(H_2)_2][BAr^F{}_4]$ (**1**). The solution of **1** was rapidly transferred under argon to another high pressure NMR tube containing $H_3B{\cdot}NH_3$ (1-10 equivalents) and gently inverted for 50 min. It was then degassed through freeze-pump-thaw cycle and the reaction progress was monitored by ESI-MS and NMR spectroscopy. All the time scales for the dehydrocoupling of $H_3B{\cdot}NH_3$ mentioned in this paper are subsequent to degassing step.

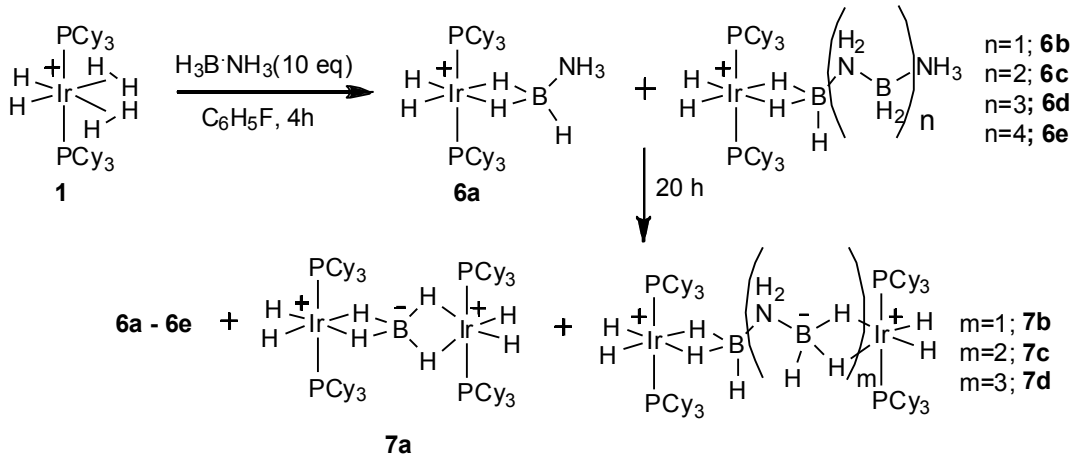
(14) Sequential addition of $H_3B{\cdot}NH_3$ to $[Ir(H)_2(PCy_3)_2(H_2)_2][BAr^F{}_4]$ (1)

Addition of 1.1 eq of $H_3B{\cdot}NH_3$ to **1** as described in the general method (Section 13) resulted in the formation of sigma complex **6a**. No dehydrogenation was observed when the reaction mixture was kept at room temperature for another 4 h. An additional 1.1 equivalent of $H_3B{\cdot}NH_3$ was added to this reaction mixture. ESI-MS and ^{1}H NMR spectra after 4 h showed the presence of mixture of complexes **6a** and **6b** which remained unchanged for next 50 h. $H_3B{\cdot}NH_3$ (1.1 equivalents) was added to this solution. ESI-MS and ^{1}H NMR spectra after 4 h indicated the presence of mixture of complexes containing **6a**, **6b** and **6c** (Figures S28 and S43).



Scheme S1: Sequential addition of 1.1 equivalent of $H_3B{\cdot}NH_3$ to **1** resulting in the formation of **6a**, then to **6a** resulting in the mixture of **6a** and **6b** and then to the mixture of **6a** and **6b** ($[BAr^F{}_4]^-$ anion not shown).

(15) Addition of 10 equivalents of $H_3B{\cdot}NH_3$ to $[Ir(H)_2(PCy_3)_2(H_2)_2][BAr^F{}_4]$ (1)



Scheme S2: Addition of 10 equivalents of $H_3B{\cdot}NH_3$ to $[Ir(H)_2(PCy_3)_2(H_2)_2][BAr^F{}_4]$ **(1)** ($[BAr^F{}_4]^-$ anion not shown).

As per the general method described above (Section 13) 10 equivalents of $H_3B{\cdot}NH_3$ was added to **1**. An ESI-MS spectrum (Figure S18) after 4 h showed the presence of mixture of the metal bound species **6a**-**6e**. The formation of bound polymeric fragments was also observed by NMR spectroscopy. The ^1H NMR spectrum (Figure S40) showed peaks at δ -20.29, -19.87 and -19.60 corresponding to the IrH_2 protons of **6a**, **6b** and **6c** respectively in a 1:10:10 ratio respectively. The ^{11}B NMR spectrum (Figure S42) also showed the peaks at δ 14.23 corresponding to Ir···H_3B protons and at δ -11.79 corresponding to unbound BH_2 and BH_3 protons along with the formation of borazine in ~ 10% yield. The ^{31}P NMR spectrum (Figure S41) was consistent with two sets of overlapping AB doublets at δ 37.2 and 32.2 [$^2J_{PP}$ ~ 280 Hz]. Sigma-complexes **6a** - **6e** slowly decomposed to give dimeric species **7a** – **7d** as the ESI-MS after 24 h showed mixture of species containing **6a** - **6e** and **7a** – **7d** (Figure S19). During the course of dehydrocoupling an insoluble white solid was obtained whose FTIR spectrum (Figure S46) matches with the polyaminoborane.[16] The ^1H, $^{31}P\{^1H\}$ and ^{11}B NMR spectra of this mixture match well with independently synthesised complexes **6a**, **6b** and **6c** (Figure S43 to S45).

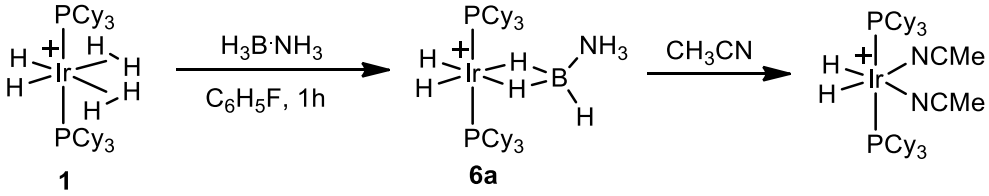
(16) Synthesis of $[Ir(H)_2(PCy_3)_2BH_4Ir(H)_2(PCy_3)_2][BAr^F{}_4]$ (7a)

As per the general method of dehydropolymerisation (Section 13) 3 equivalents of $H_3B{\cdot}NH_3$ was added to the complex **1**. After 1 hour of degassing (Section 13), the fluorobenzene solution was cannula filtered, layered with pentane and kept for 7 days at 5 °C which resulted in yellow-brownish oil at the bottom with some white suspension and crystals of **7a.**

ESI-MS (C_6H_5F, 60 °C) positive ion: m/z 1525.9290 $[M]^+$ (calc. 1525.9256).

(17) Addition of acetonitrile to 6a

10 equivalents of acetonitrile were added to **6a** in C_6H_5F solution which resulted in the displacement of $H_3B{\cdot}NH_3$ [δ (^{11}B) 21.7 ppm, q, J_{HB} = 97 Hz)][17] and the formation of the known complex $[Ir(H)_2(PCy_3)_2(NCMe)_2][BAr^F{}_4]$[18] (Scheme S3).



Scheme S3: Displacement of bound $H_3B{\cdot}NH_3$ by acetonitrile ($[BAr^F{}_4]^-$ anion not shown).

(18) Addition of $[Ir(H)_2(PCy_3)_2(H_2)_2][BAr^F{}_4]$ (1) to 10 equivalents of $H_3B{\cdot}NMe_3$

As per the general method (Section 13) $[Ir(H)_2(PCy_3)_2(H_2)_2][BAr^F{}_4]$ (**1**) in C_6H_5F was added to 10 equivalents of $H_3B{\cdot}NMe_3$. ESI-MS after 4 h showed the formation of previously reported $[Ir(H)_2(PCy_3)_2(H_3B{\cdot}NMe_3)][BAr^F{}_4]$ (**3a**) (Figure S20).[18b]

(19) Addition of $[Ir(H)_2(PCy_3)_2(H_2)_2][BAr^F{}_4]$ (1) to $H_3B{\cdot}NMe_2H$

As per the general method (Section 13) $[Ir(H)_2(PCy_3)_2(H_2)_2][BAr^F{}_4]$ (**1**) in C_6H_5F was added to 3 equivalents of $H_3B{\cdot}NMe_2H$. An ESI-MS spectrum (Figure S21) after 4 days showed complete dehydrogenation of $[Ir(H)_2(PCy_3)_2(H_3B{\cdot}NMe_2H)][BAr^F{}_4]$ (**4a**) and formation of bound amino–borane complex $[Ir(H)_2(PCy_3)_2(H_2B{\cdot}NMe_2)][BAr^F{}_4]$ (**4a***).[18b] However, when 10 equivalents of $H_3B{\cdot}NMe_2H$ are used, the ESI-MS spectrum (Figure S22) after 10 days showed the mixture of the sigma-complex $[Ir(H)_2(PCy_3)_2(H_3B{\cdot}NMe_2H)][BAr^F{}_4]$ (**4a**) and the bound amino–borane $[Ir(H)_2(PCy_3)_2(H_2B{\cdot}NMe_2)][BAr^F{}_4]$ (**4a***). In addition to these species there were some unidentified decomposition products.

(20) Addition of $[Ir(H)_2(PCy_3)_2(H_2)_2][BAr^F{}_4]$ (1) to 10 equivalents of $H_3B{\cdot}NMeH_2$

As per the general method (Section 13) $[Ir(H)_2(PCy_3)_2(H_2)_2][BAr^F{}_4]$ (**1**) in C_6H_5F was added to the 10 equivalents of $H_3B{\cdot}NMeH_2$. An ESI-MS spectrum (Figure S23) after 4h showed the formation of sigma-complex $[Ir(H)_2(PCy_3)_2(H_3B{\cdot}NMeH_2)][BAr^F{}_4]$ (**5a**) and the bound oligomer $[Ir(H)_2(PCy_3)_2(H_3B{\cdot}NMeHBH_2{\cdot}NMeH_2)][BAr^F{}_4]$ (**5b**).[14]

(21) Observation of bound copolymers of $H_3B{\cdot}NH_3$ and $H_3B{\cdot}NMeH_2$

As per the general method of dehydropolymerization (Section 13) a C_6H_5F solution of $[Ir(H)_2(PCy_3)_2(H_2)_2][BAr^F{}_4]$ (**1**) was added to a mixture of $H_3B{\cdot}NH_3$ (5 equivalents) and $H_3B{\cdot}NMeH_2$ (5 equivalents). An ESI-MS spectrum after 4 h showed the presence of metal bound co-oligomers $[Ir(PCy_3)_2(H)_2\{H(H_2BNH_2)_x(H_2BNMeH)_yH][BAr^F{}_4]$ (x = 0, 1 and y = 1, 2; x = 1 and y = 0; x = 2 and y = 1) (Figure S24).

(22) Addition of $H_3B{\cdot}NH_3$ to 6c

1.3 equivalents of $H_3B{\cdot}NH_3$ (0.8 mg, 0.026 mmol) was added to a C_6H_5F solution of $[Ir(H)_2(PCy_3)_2(H_3B{\cdot}NH_2BH_2NH_2BH_2{\cdot}NH_3)][BAr^F{}_4]$ (**6c**). An ESI-MS spectrum after 4 h showed the presence of mixture of species containing **6a**-**6e** which remained unchanged for next 20 h (Figure S25).

(23) Addition of $H_3B{\cdot}NMeH_2$ to 6c

1 equivalent of monomethyl amine-borane (0.9 mg, 0.02 mmol) was added to the C_6H_5F solution of $[Ir(H)_2(PCy_3)_2(H_3B{\cdot}NH_2BH_2NH_2BH_2{\cdot}NH_3)][BAr^F{}_4]$ (**6c**). ESI-MS after 4 h showed the presence of metal bound co-oligomers $[Ir(PCy_3)_2(H)_2\{H(H_2BNH_2)_x(H_2BNMeH)_yH][BAr^F{}_4]$ (x = 0, 1 and y = 1, 2; x = 1,2 and y = 0; x = 2 and y = 1) (Figure S26).

(24) Addition of $H_3B{\cdot}NH_2BH_2{\cdot}NH_3$ to 6a

2 equivalent of $H_3B{\cdot}NH_2BH_2{\cdot}NH_3$ (1.7 mg, 0.028 mmol) was added to the C_6H_5F solution of $[Ir(H)_2(PCy_3)_2(H_3B{\cdot}NH_3)]$ $[BAr^F{}_4]$ (**6a**). ESI-MS after 4 h showed the presence of **6b-6e** with **6b** being the major species (Figure S27).

(25) Selected ESI-MS and NMR spectra

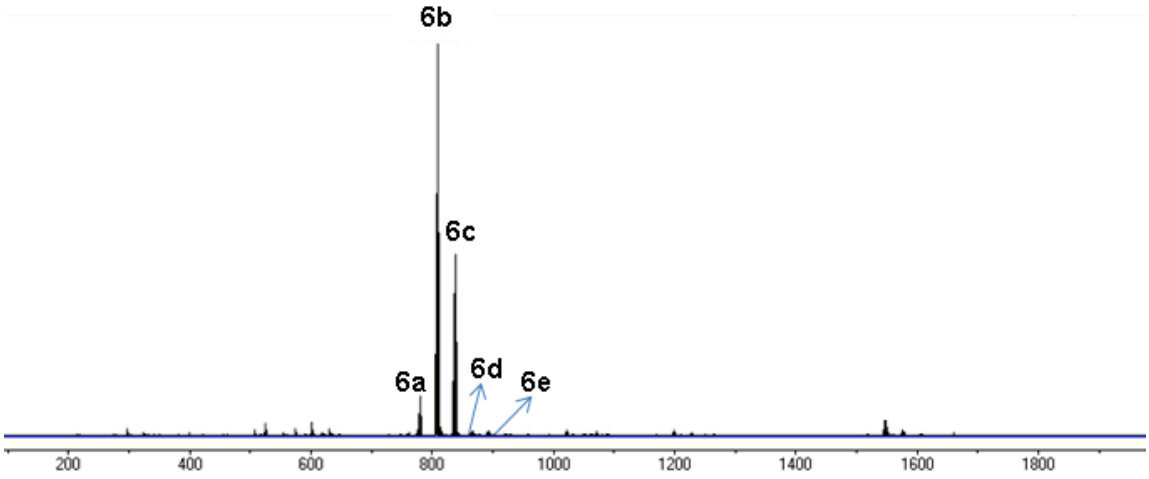


Figure S18: ESI-MS after 4 h of adding 10 equivalents of $H_3B{\cdot}NH_3$ to **1**.

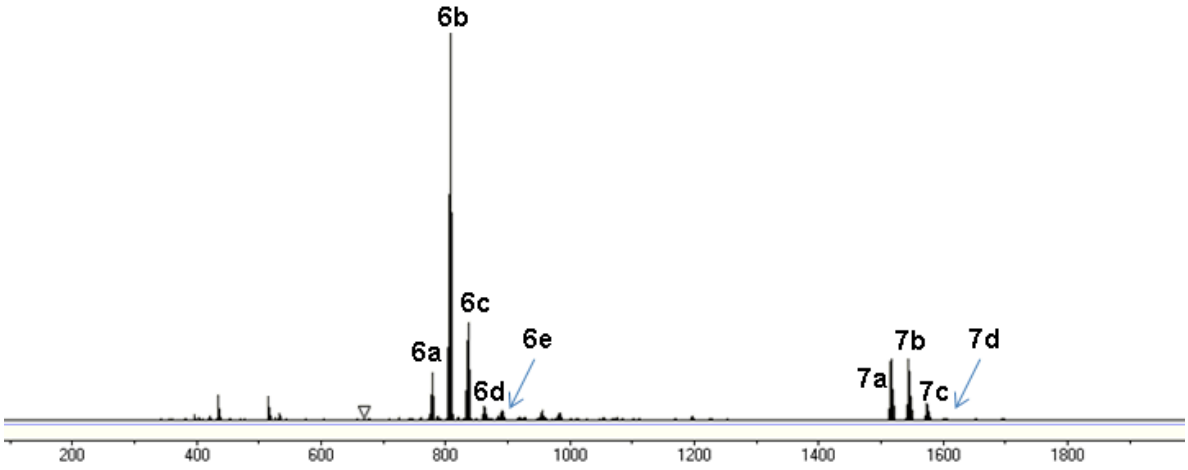


Figure S19: ESI-MS after 24 h of adding 10 equivalents of $H_3B{\cdot}NH_3$ to **1** (see Scheme S2).

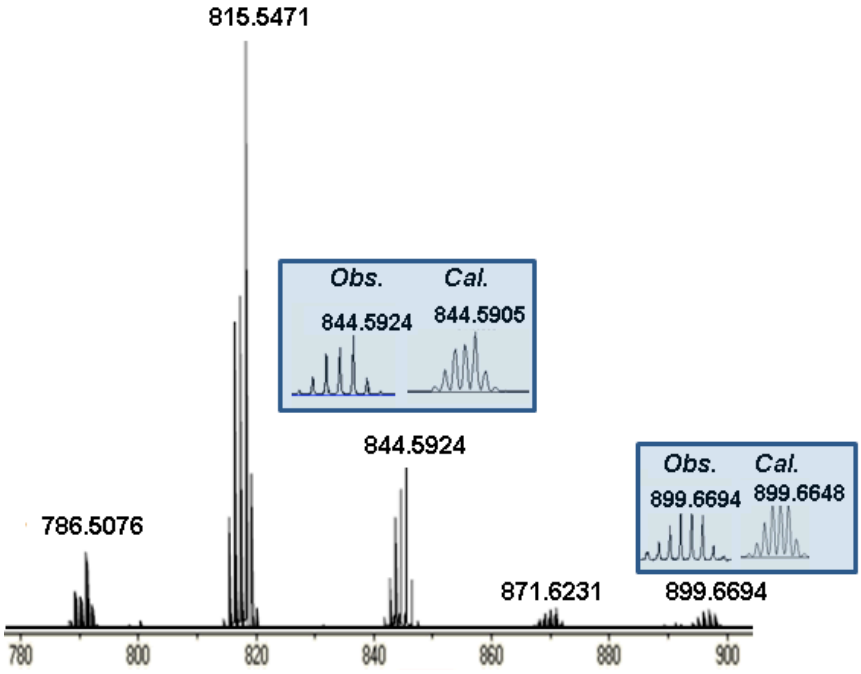


Figure S19(a): Expansion of Figure S19 in the region m/z = 780 to 900.

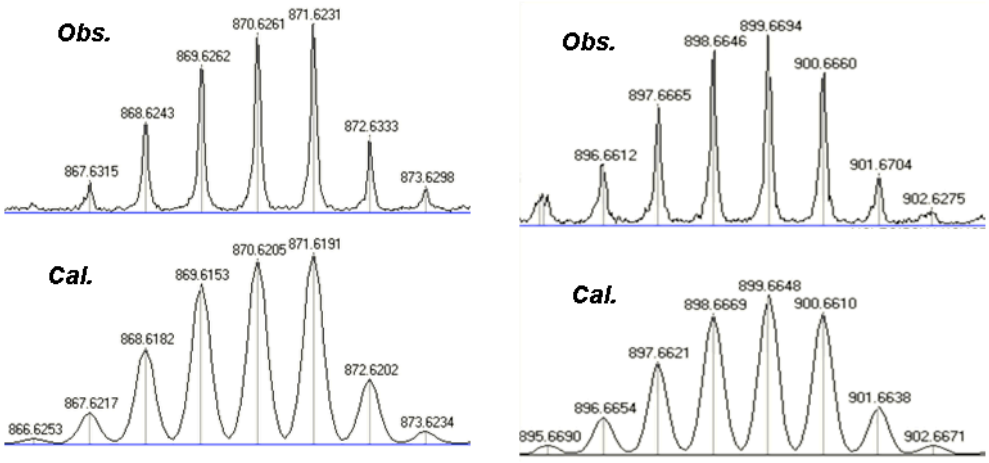


Figure S19(b): Observed and calculated isotopomers $(M\text{-}H_2)^+$ for **6d** and **6e**. Left: $[Ir(H)_2(PCy_3)_2(H_3B{\cdot}NH_2BH_2NH_2BH_2NH_2BHNH_2]^+$, right: $[Ir(H)_2(PCy_3)_2(H_3B{\cdot}NH_2BH_2NH_2BH_2NH_2BH_2NH_2BHNH_2]^+$.

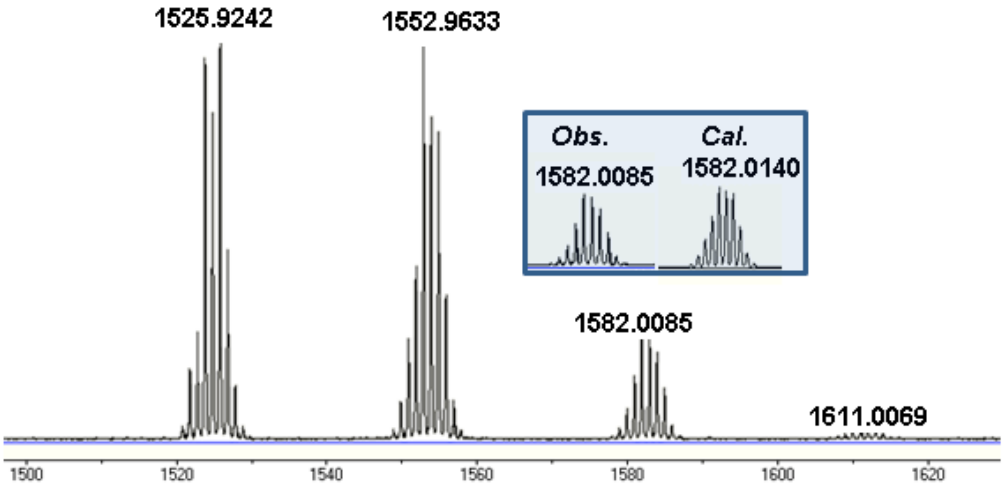


Figure S19(c): Expansion of Figure S19 in the region m/z = 1500 to 1620.

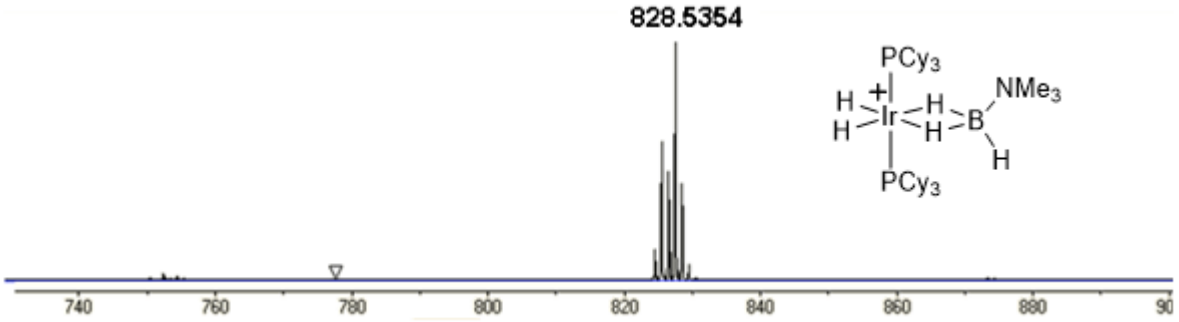


Figure S20: ESI-MS after 4 h of adding 10 equivalents of $H_3B{\cdot}NMe_3$ to **1**.

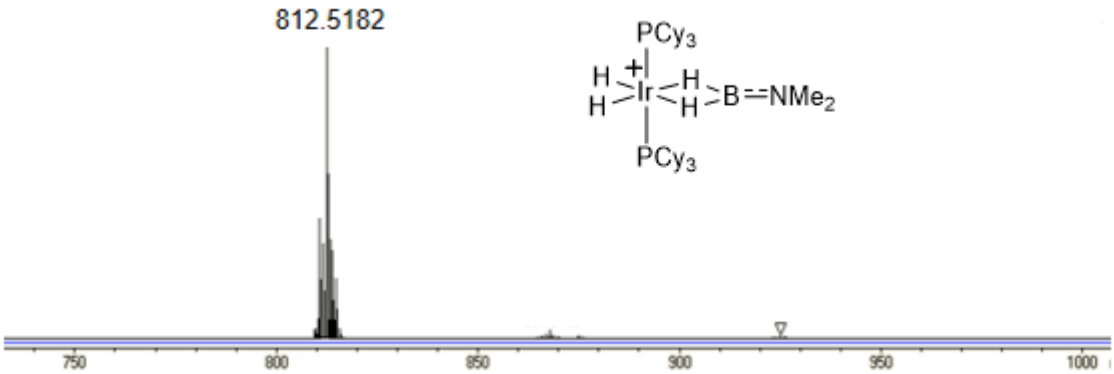


Figure S21: ESI-MS after 4 days of adding 3 equivalents of $H_3B{\cdot}NMe_2H$ to **1**.

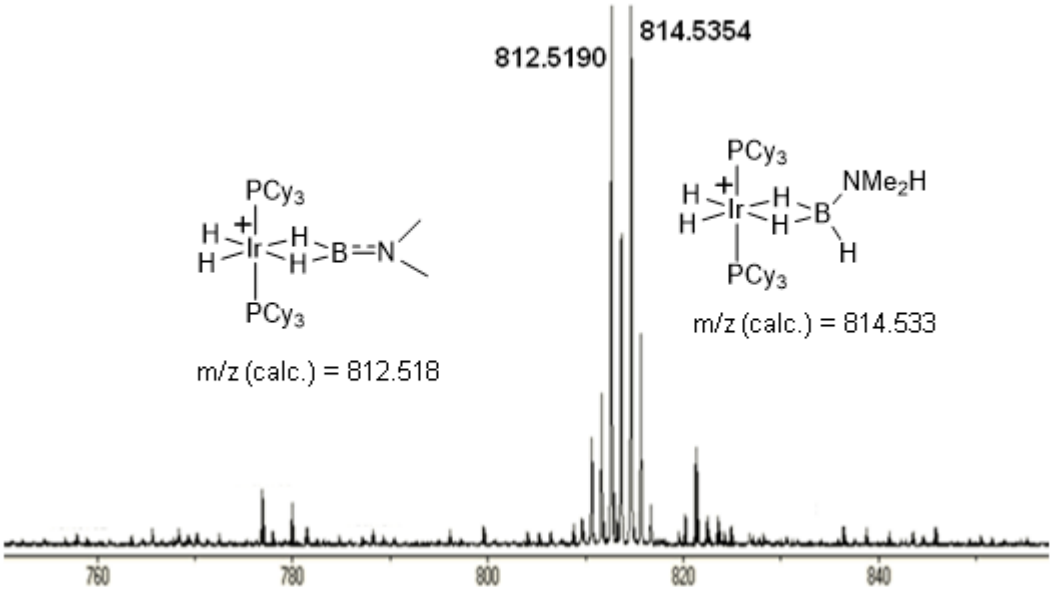


Figure S22: ESI-MS after 10 days of adding 10 equivalents of $H_3B{\cdot}NMe_2H$ to **1**.

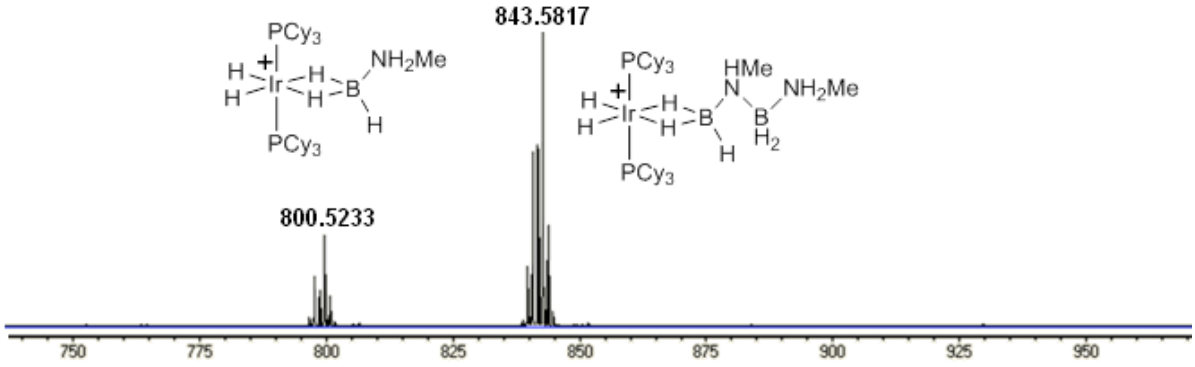


Figure S23: ESI-MS after 4 h of adding 10 equivalents of $H_3B{\cdot}NMeH_2$ to **1**.

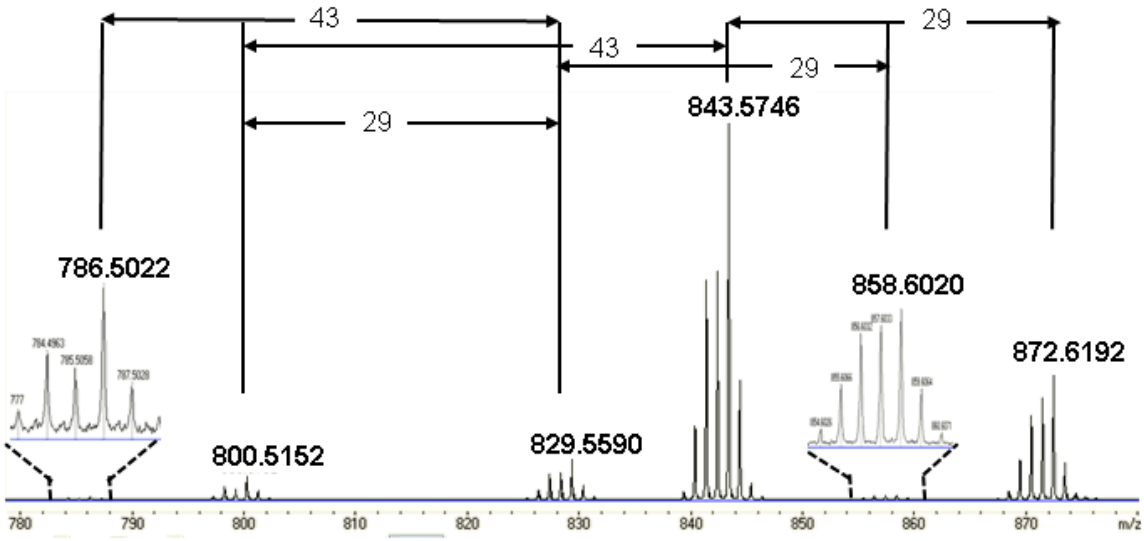


Figure S24: Observing bound copolymers of $H_3B{\cdot}NH_3$ and $H_3B{\cdot}NMeH_2$ (29 = molar mass of H_2BNH_2 and 43 = molar mass of H_2BNHMe).

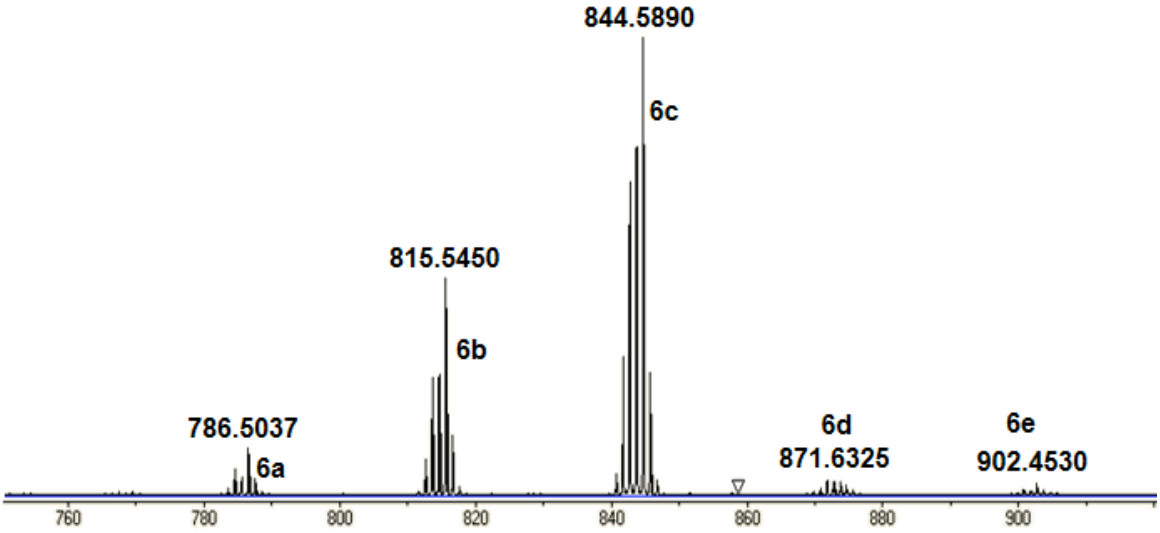


Figure S25: ESI-MS after 4 h of addition of $H_3B{\cdot}NH_3$ to $[Ir(H)_2(PCy_3)_2(H_3B{\cdot}NH_2BH_2NH_2BH_2{\cdot}NH_3)][BAr^F{}_4]$ (**6c**).

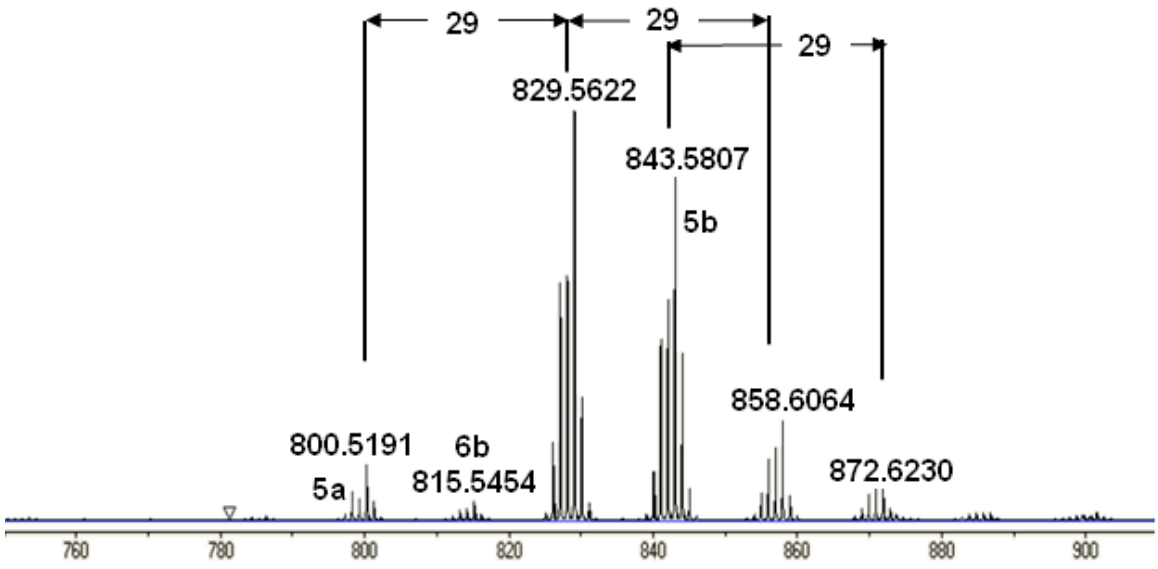


Figure S26: ESI-MS after 4 h of addition of $H_3B{\cdot}NMeH_2$ to $[Ir(H)_2(PCy_3)_2(H_3B{\cdot}NH_2BH_2NH_2BH_2{\cdot}NH_3)][BAr^F{}_4]$ (**6c**) (29 = molar mass of H_2BNH_2).

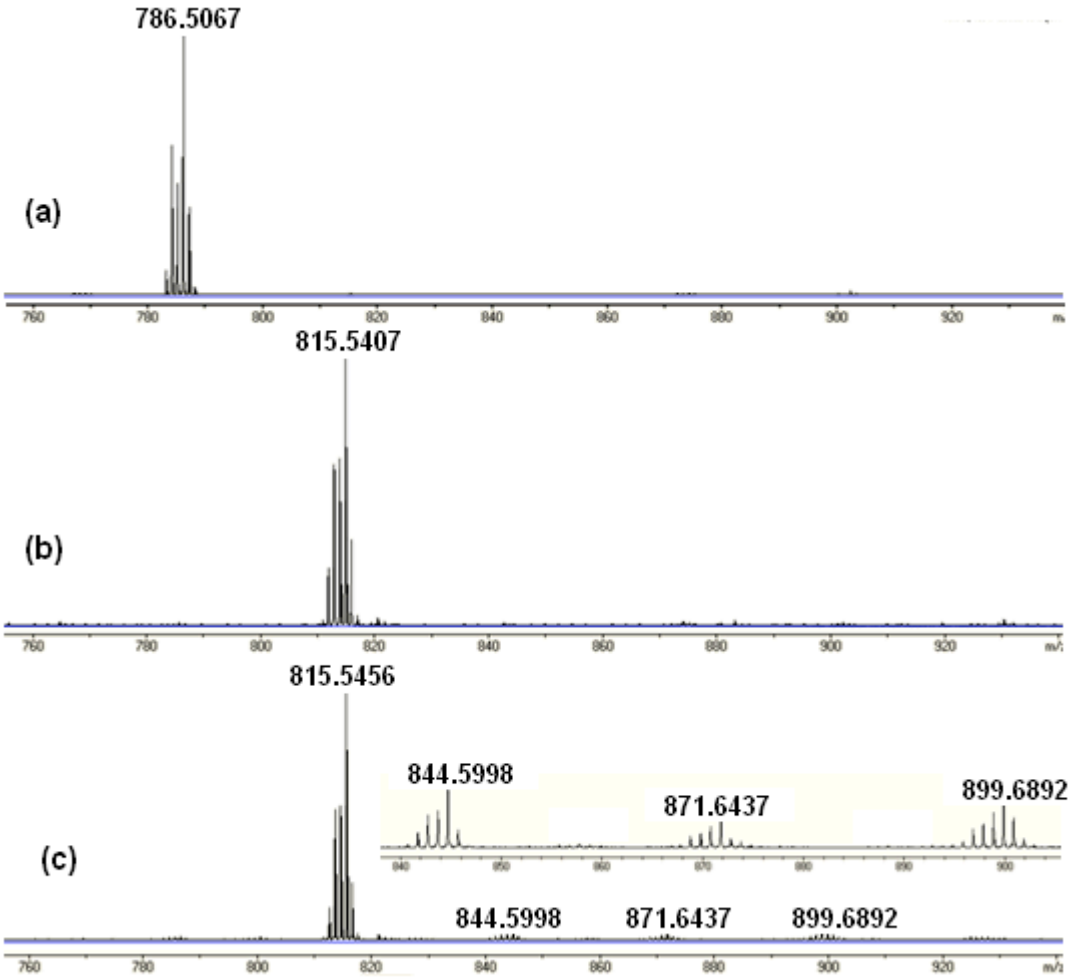


Figure S27: (**a**) ESI-MS for **6a** (b) ESI-MS for **6b** (**c**) ESI-MS after 4 h of addition of 2 equivalents of $H_3B{\cdot}NH_2BH_2{\cdot}NH_3$ to $[Ir(H)_2(PCy_3)_2(H_3B{\cdot}NH_3)][BAr^F{}_4]$ (**6a**).

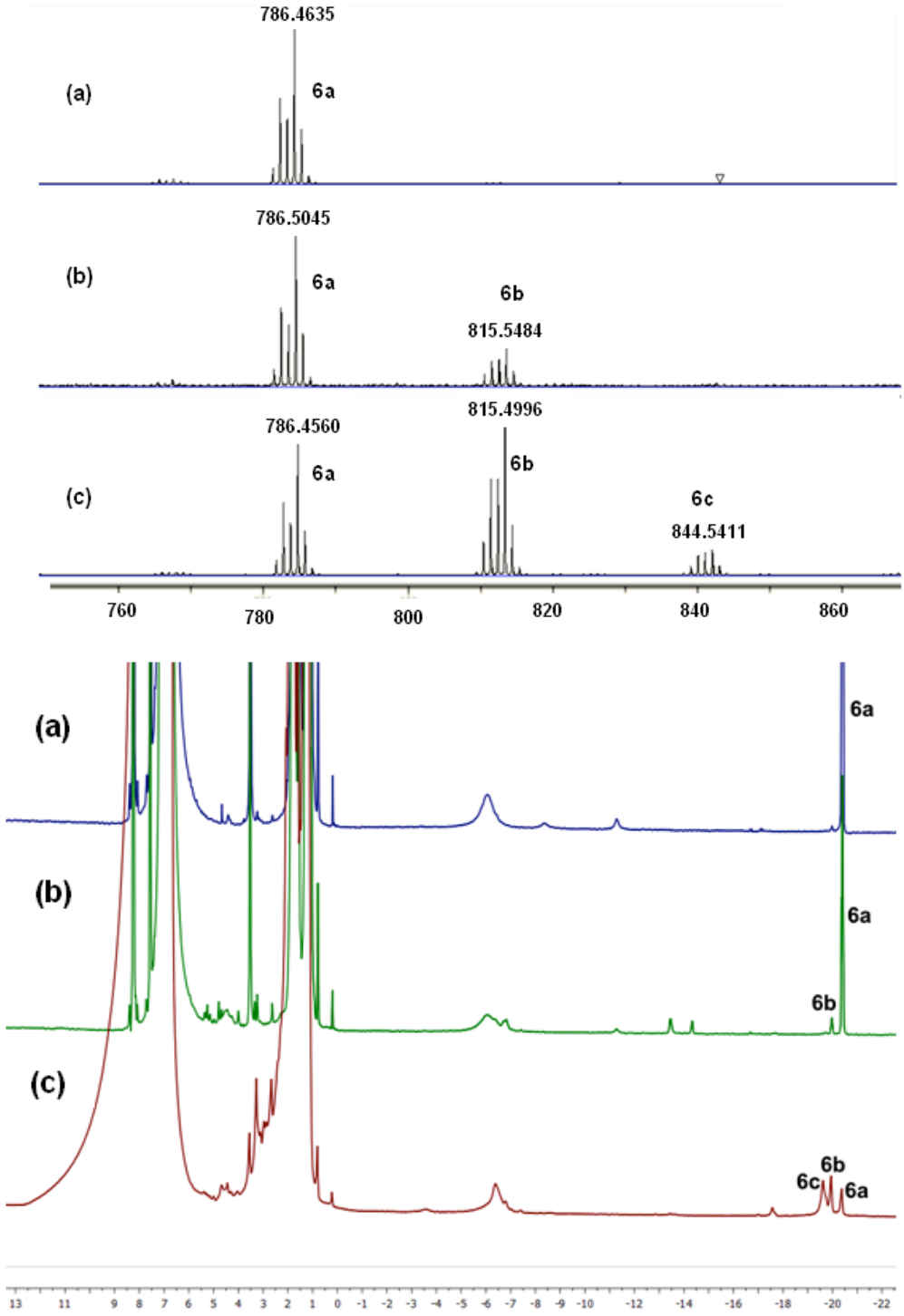


Figure S28: ESI-MS and ^{1}H NMR spectra for the sequential addition of $H_3B{\cdot}NH_3$. (**a**) After 4 h of the addition of 1.1 equivalent of $H_3B{\cdot}NH_3$ to the complex $[Ir(H)_2(PCy_3)_2(H_2)_2][BAr^F{}_4]$ (**1**) resulting in the formation of **6a**. (**b**) After 4 h of the addition of 1.1 additional equivalent of $H_3B{\cdot}NH_3$ to **6a** (total 2.2 equivalents to **1**) resulting in the formation of mixture of **6a** and **6b.** (**c**) After 4 h of the addition of 1.1 additional equivalent of $H_3B{\cdot}NH_3$ to the mixture of **6a** and **6b** (total 3.3 equivalents to **1**) resulting in the formation of mixture of **6a, 6b** and **6c.**

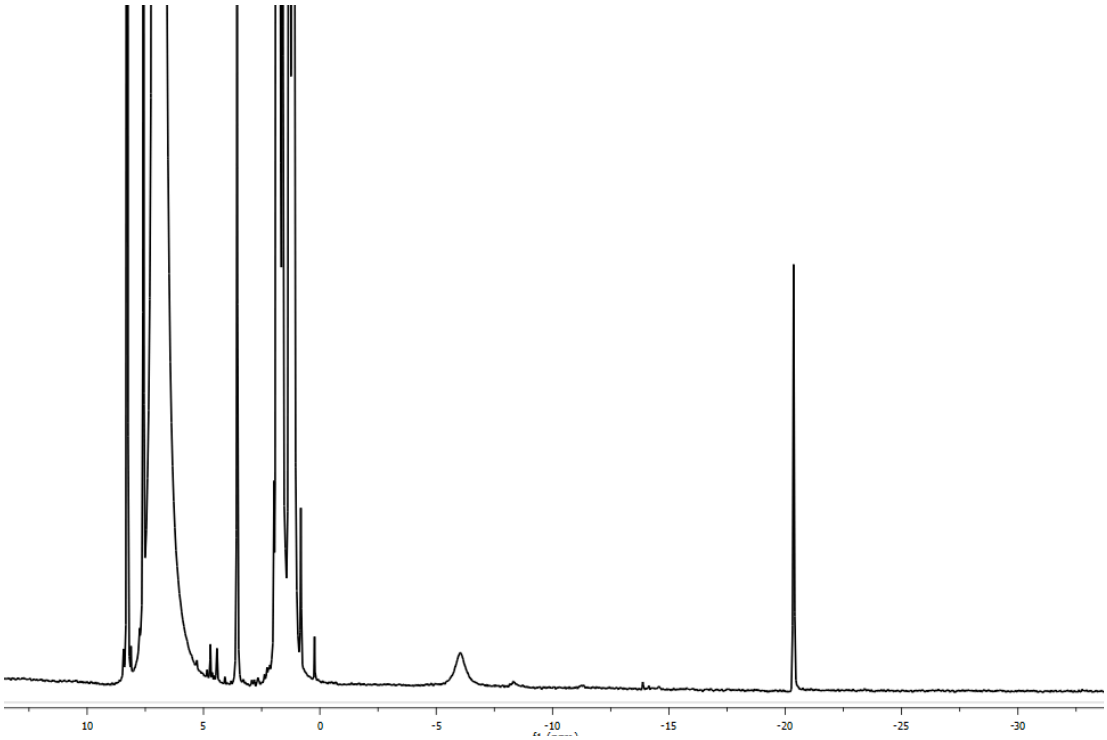


Figure S29: ^{1}H NMR (500 MHz, C_6H_5F) spectrum of **6a**.

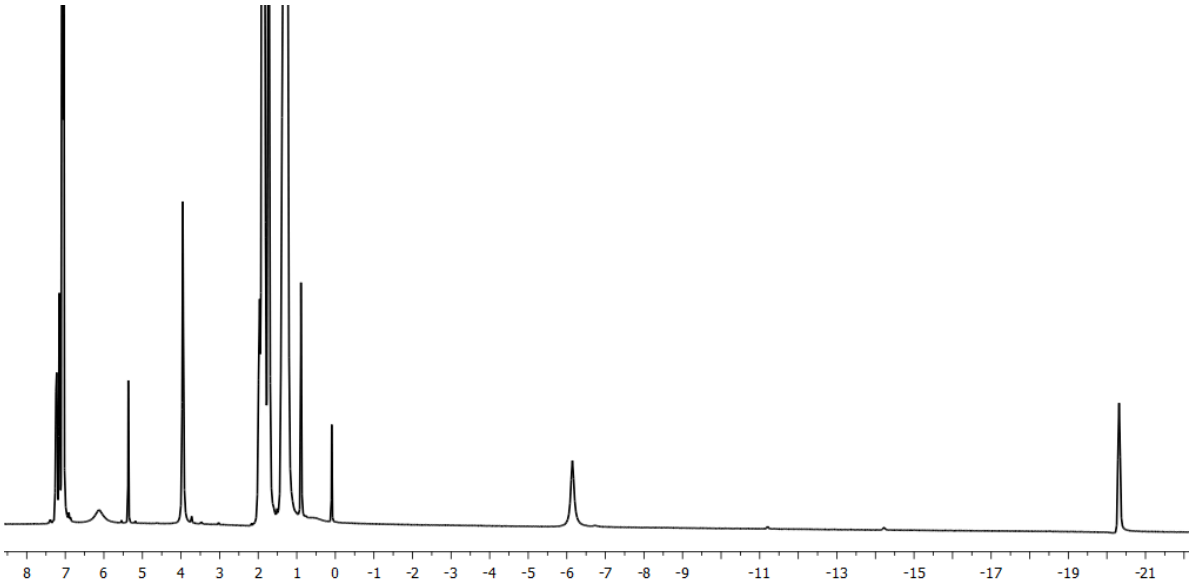


Figure S30: ^{1}H NMR (500 MHz, CD_2Cl_2, 250 K) spectrum of (**6a[BAr$^{Cl}_4$]**), terminal B-H (not σ-bound) signal at δ 6.13 is observed.

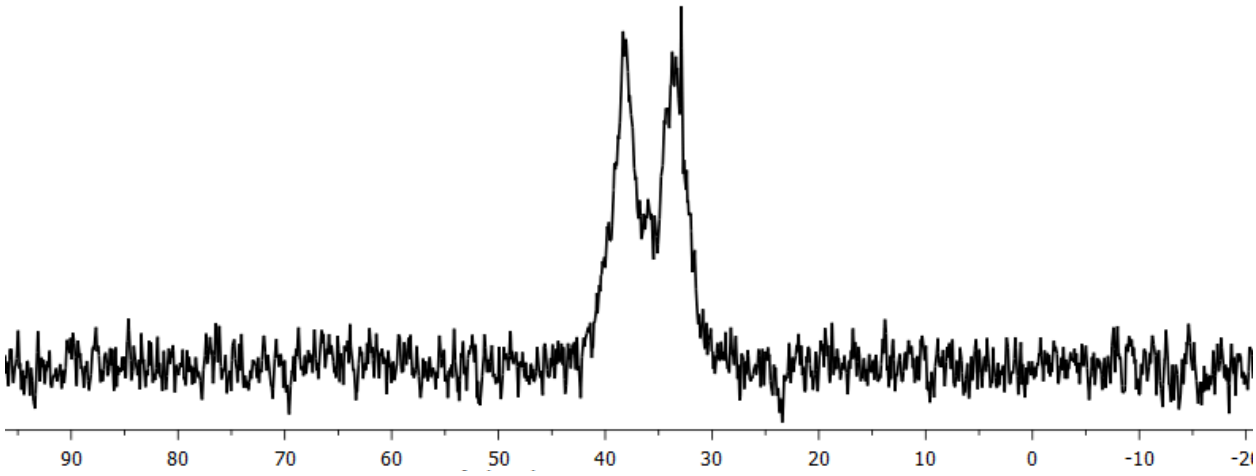
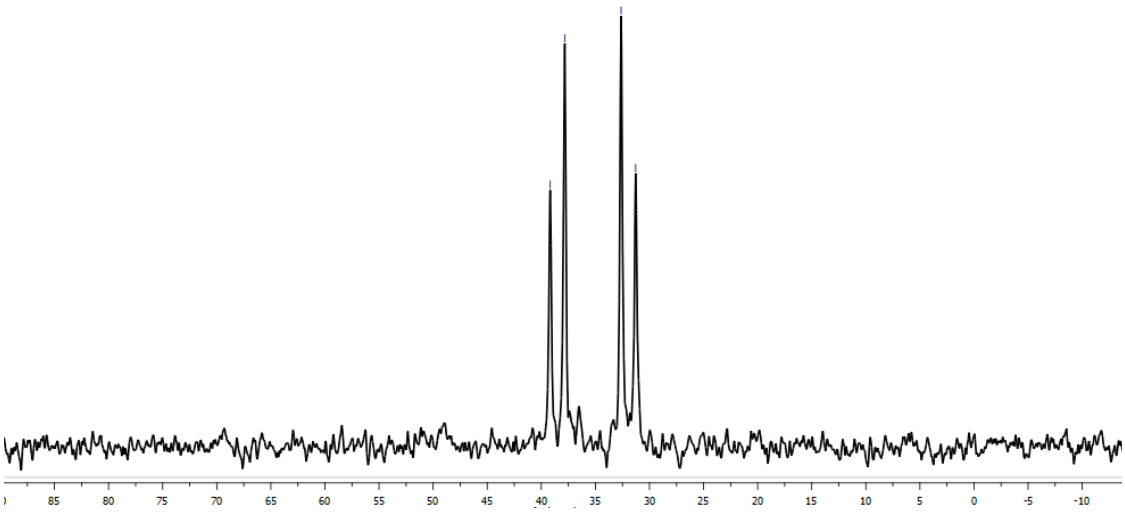


Figure S31: $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2) spectrum of (**6a[BAr$^{Cl}_4$]**) at 298 K.



`**Figure S32**: $^{31}P\{^{1}H\}$ NMR (202 MHz, C_6H_5F) spectrum of (**6a[BAr$^{Cl}_4$]**) at 250 K.

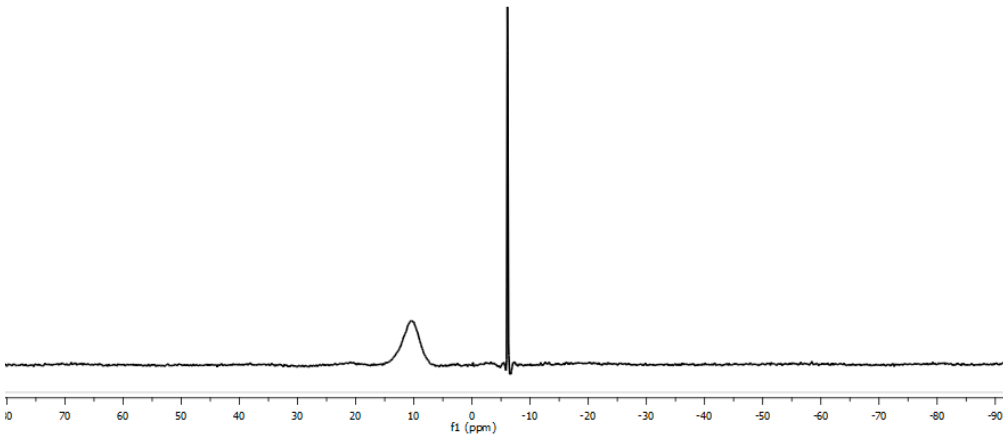


Figure S33: ^{11}B NMR (160 MHz, C_6H_5F) spectrum of **6a**.

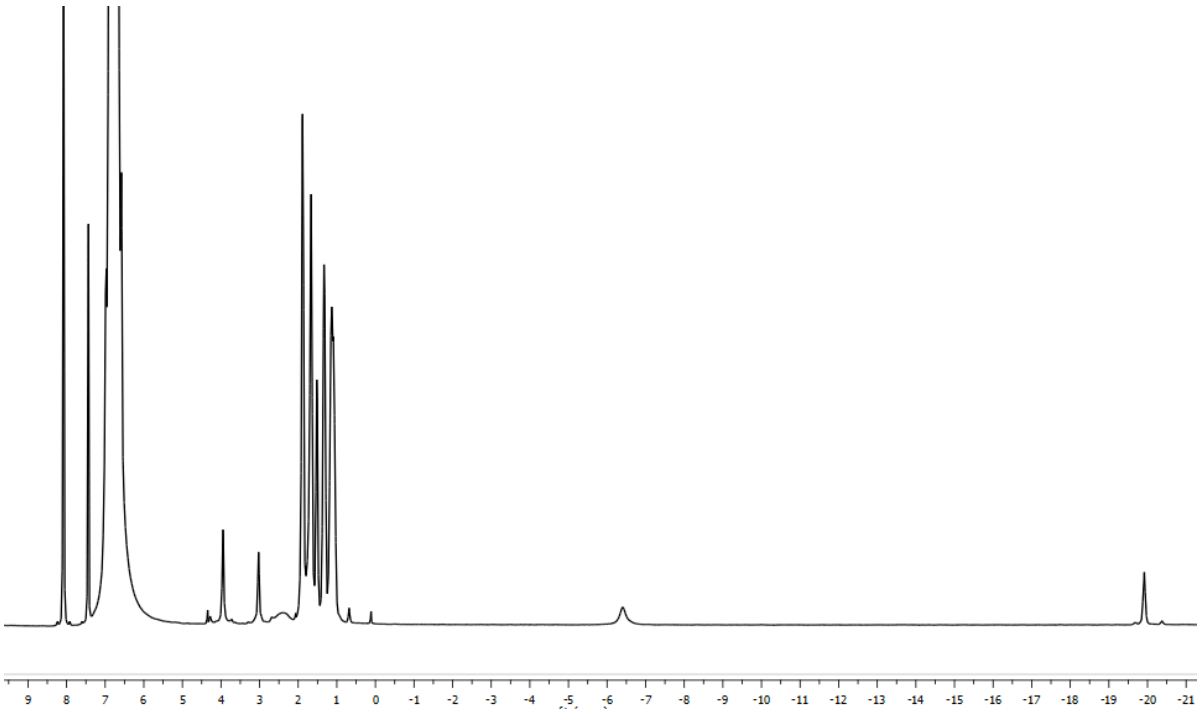


Figure S34: ^{1}H NMR (500 MHz, C_6H_5F) spectrum of **6b**.

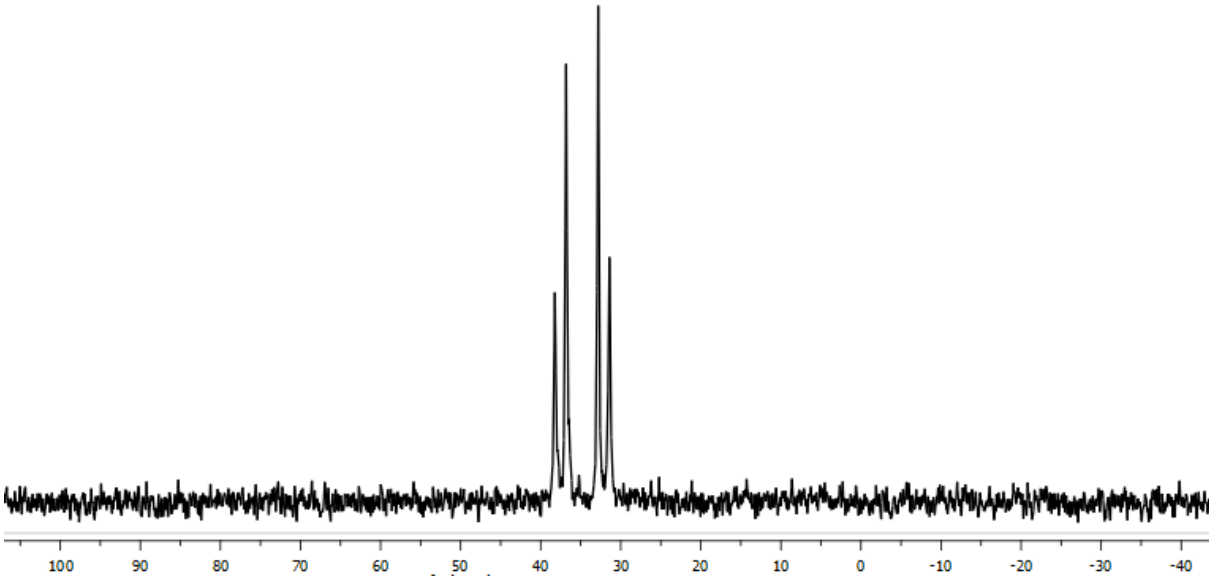


Figure S35: $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2) spectrum of **6b**.

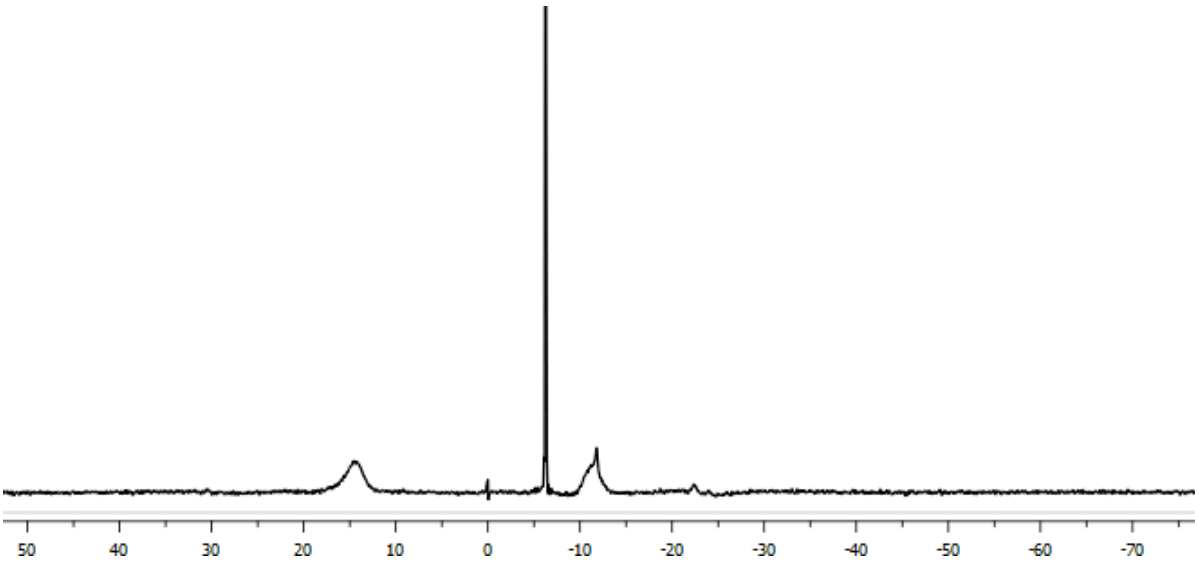


Figure S36: ^{11}B NMR (160 MHz, C_6H_5F) spectrum of **6b**.

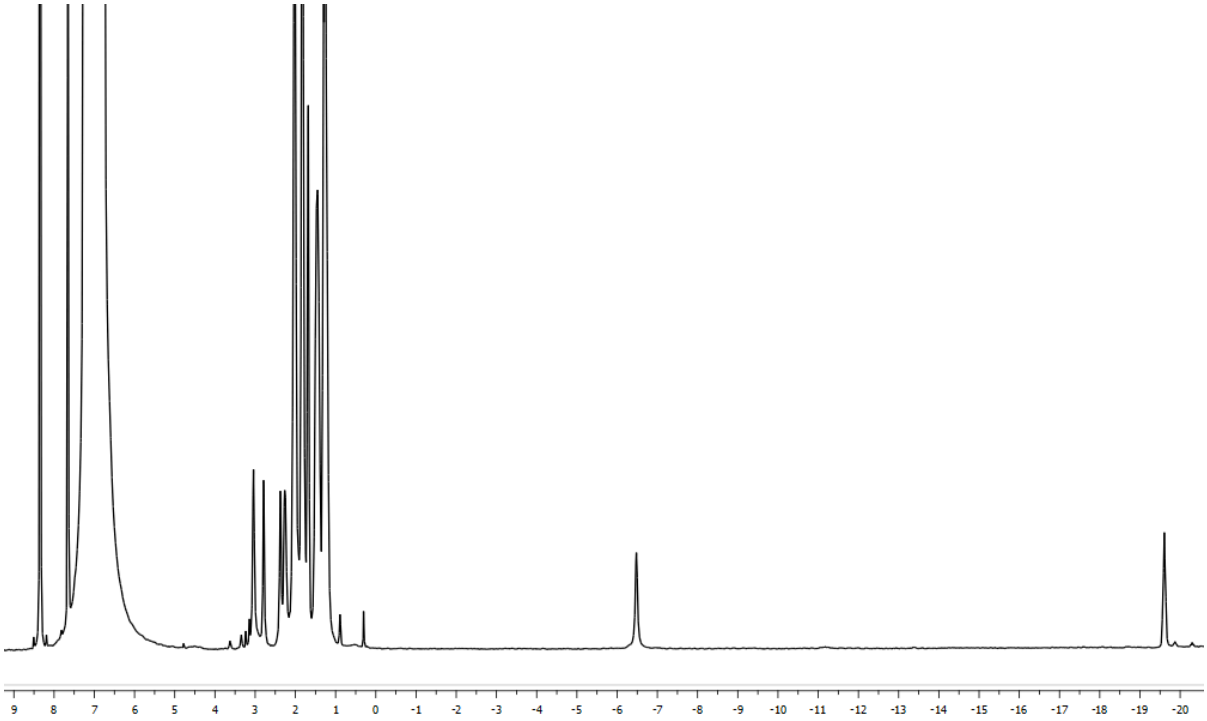


Figure S37: $^{1}H\{^{11}B\}$ NMR (500 MHz, C_6H_5F) spectrum of **6c**.

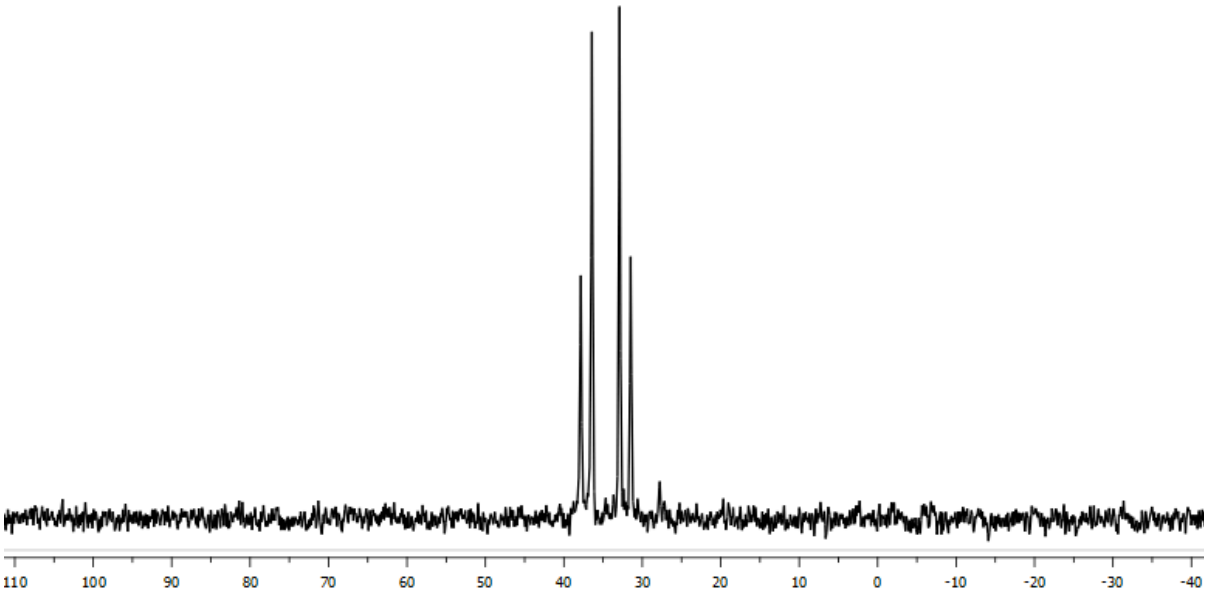


Figure S38: $^{31}P\{^{1}H\}$ NMR (202 MHz, C_6H_5F) spectrum of **6c**.

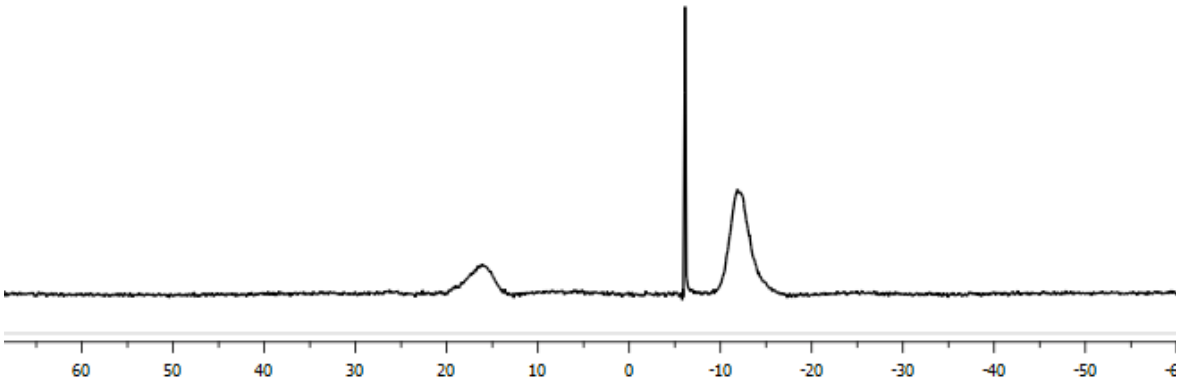


Figure S39: ^{11}B NMR (160 MHz, C_6H_5F) spectrum of **6c**.

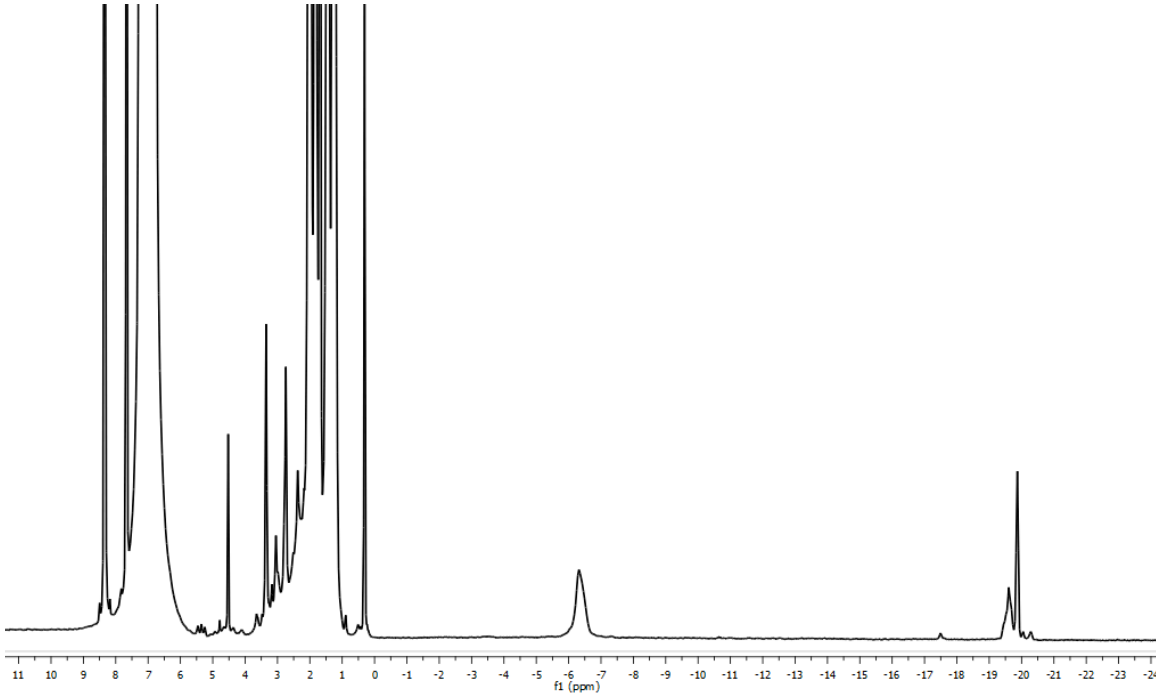


Figure S40: ^{1}H NMR (500 MHz, C_6H_5F) spectrum after 4 hours of reaction of 10 equivalents of $H_3B{\cdot}NH_3$ with **1**.

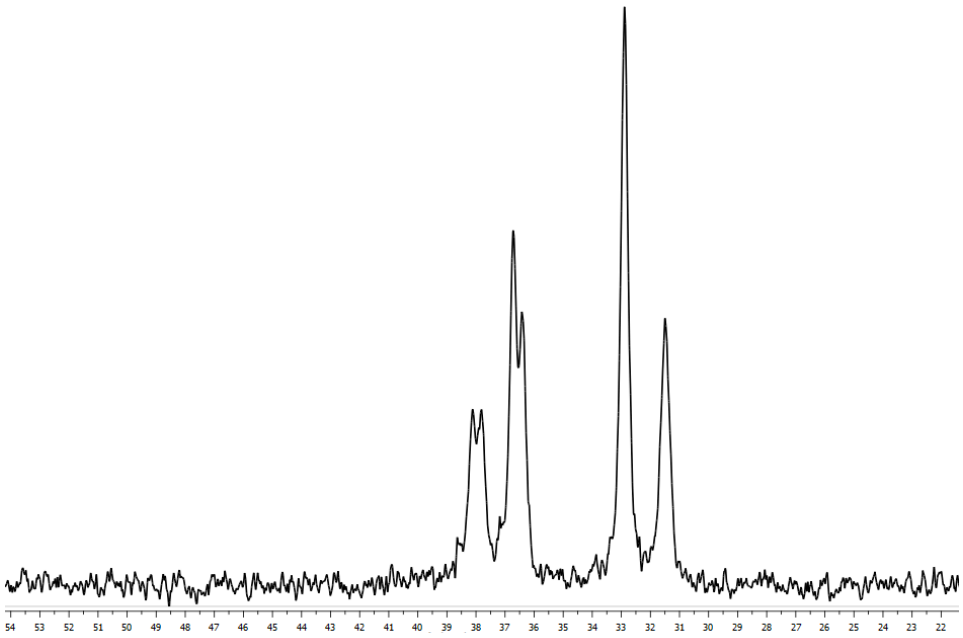


Figure S41: $^{31}P\{^{1}H\}$ NMR (202 MHz, C_6H_5F) spectrum after 4 hours of reaction of 10 equivalents of $H_3B{\cdot}NH_3$ with **1**.

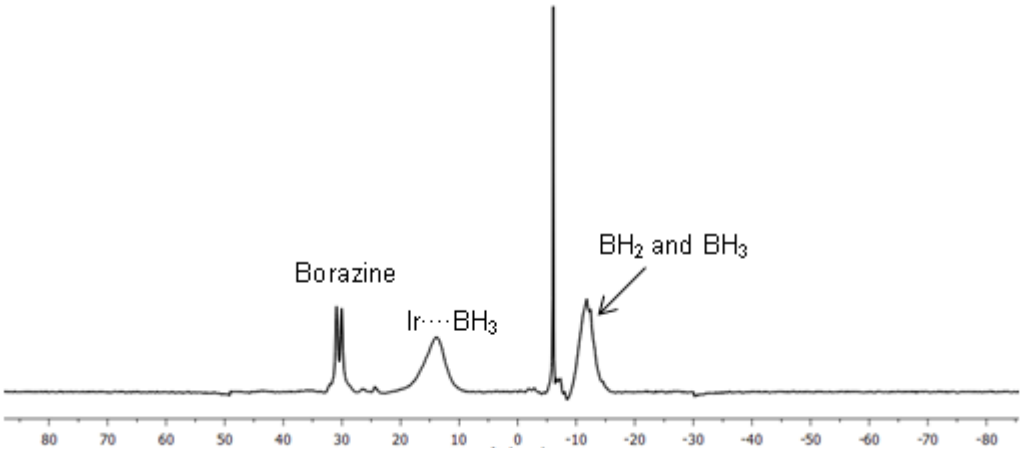


Figure S42: ^{11}B NMR (160 MHz, C_6H_5F) spectrum after 4 hours of reaction of 10 equivalents of $H_3B{\cdot}NH_3$ with **1**.

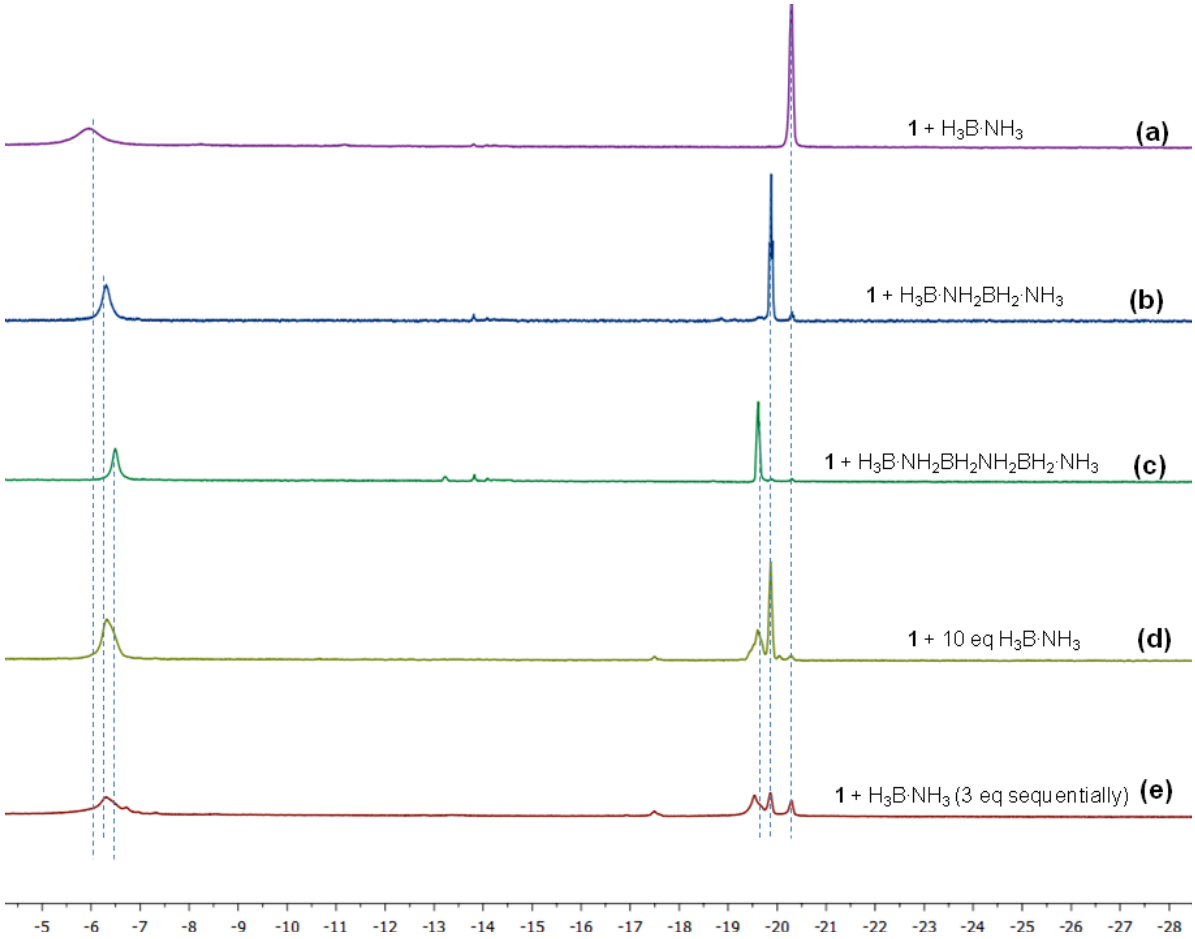


Figure S43: Stacked ^{1}H NMR (500 MHz, C_6H_5F) spectra in the region δ = -4 to -28. (a): **6a**, (b): **6b**, (c): **6c**, (d): after 4 hours of reaction of 10 equivalents of $H_3B{\cdot}NH_3$ with **1, (e)**: sequential addition of 3 equivalents of $H_3B{\cdot}NH_3$ to **1** (Figure S28 (c)).

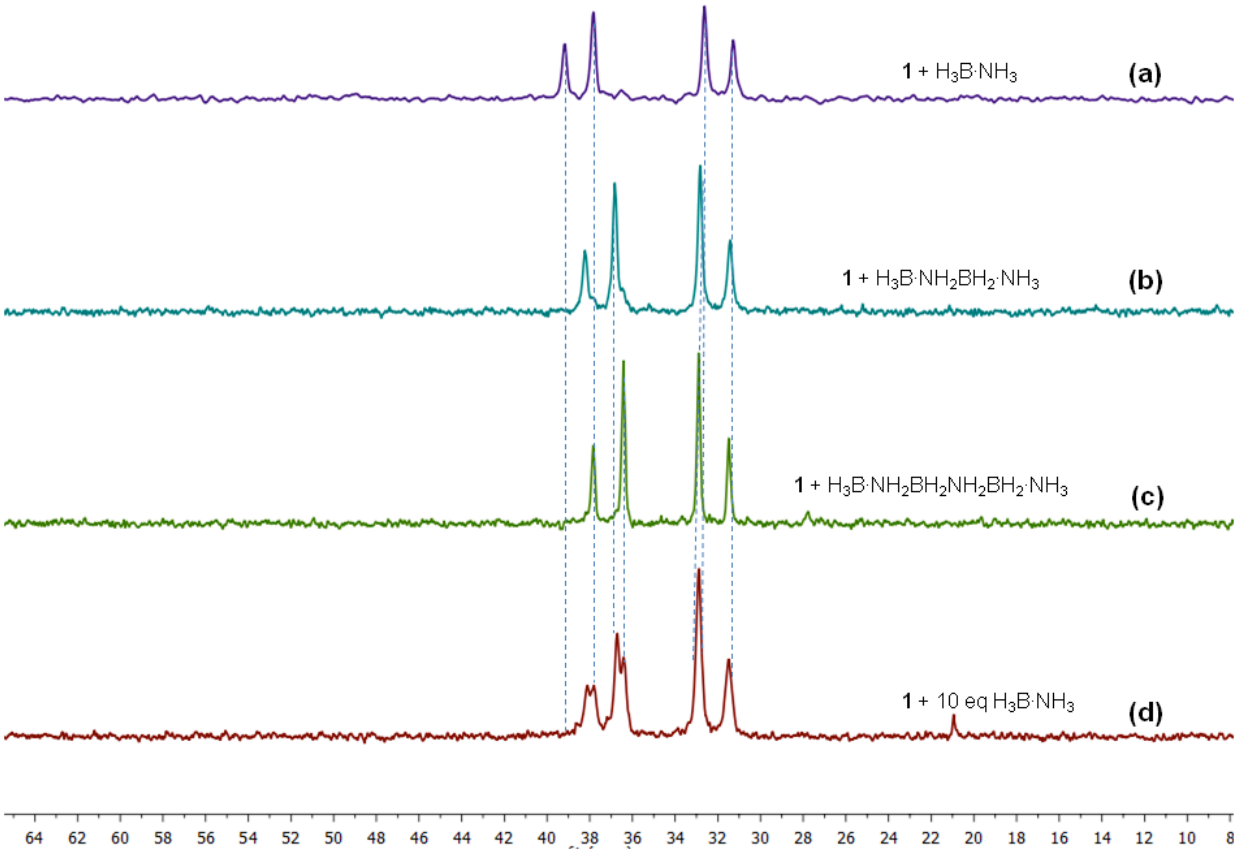


Figure S44: Stacked $^{31}P\{^{1}H\}$ NMR (202 MHz, C_6H_5F) spectra. (a): **6a[BAr$^{Cl}_4$]** at 250 K, (b): **6b**, (c): **6c**, (d): after 4 hours of reaction of 10 equivalents of $H_3B{\cdot}NH_3$ with **1**.

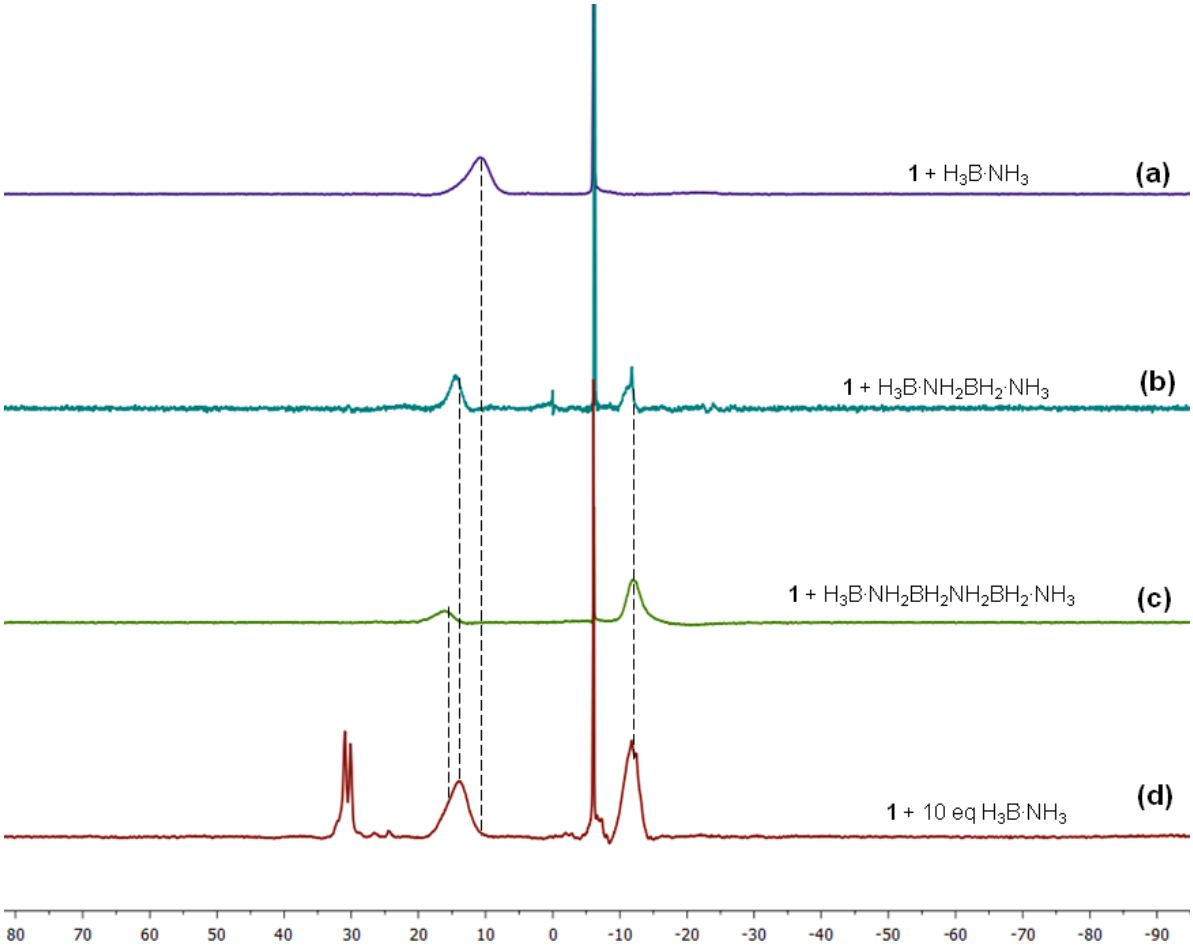


Figure S45: Stacked ^{11}B NMR (160 MHz, C_6H_5F) spectra. (a): **6a**, (b): **6b**, (c): **6c**, (d): after 4 hours of reaction of 10 equivalents of $H_3B{\cdot}NH_3$ with **1**.

(26) IR spectrum

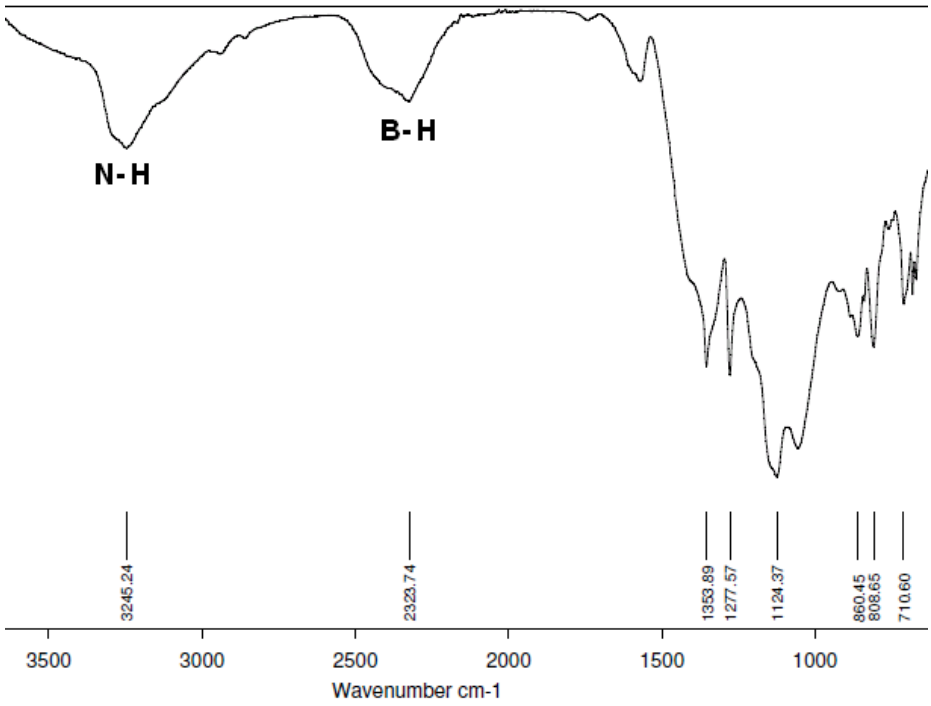


Figure S46: FTIR spectrum of insoluble white sold obtained at the end of dehydrocoupling of $H_3B{\cdot}NH_3$ (10 mol% condition).

(27) Crystallography

Relevant details about the structure refinements are given in Table 1. Data were collected on an Enraf Nonius Kappa CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) and a low temperature device; [19] data were collected using COLLECT, reduction and cell refinement was performed using DENZO/SCALEPACK.[20] The structures were solved by direct methods using SUPERFLIP (**6a[BAr$^{Cl}_4$]**)[21], SIR 92 (**6c[BAr$^{Cl}_4$]**) or by using SHELXS-97 (**7a**)[22] and refined full-matrix least squares on F^2 using SHELXL-97 (**7a**)[22] or by CRYSTALS.[23] All non-hydrogen atoms were refined anisotropically.

Compound 6a[BAr$^{Cl}_4$]

The Fourier difference map indicated the presence of two areas of diffuse electron density believed to be disordered difluorobenzene solvent. The SQUEEZE algorithm was used, leaving a void from which the electron density was removed.[24] Of the remaining two molecules of difluorobenzene, one showed disorder of the fluorine atoms. The two fluorine atoms were modelled over three sites and their geometries restrained. A planarity restraint was applied. The molecule has occupancy of 0.634.

The hydrides H(3), H(4) and H(5) of **6a[BAr$^{Cl}_4$]** were located on the Fourier map and were refined before adding RIDE restraints connecting them to B(1). Remaining two hydrides of **6a[BAr$^{Cl}_4$]** H(1) and H(2) were placed in calculated positions geometrically trans to the appropriate B-H atom, and set at a sensible bond length of 1.55 Å.

Compound 7a

One of the CF_3 groups of the [BAr^F_4] anion was modelled as being disordered over two sites and the occupancy freely refined to give a 53:47 ratio. The C-F distances of this disordered group were fixed to 1.32 Å using the DFIX command and the F atoms described by the EADP command. A solvent fluorobenzene molecule was found to be disordered over 2 sites and modelled as 50:50 occupancy. The fluorine atoms were described by the EADP command. Squeeze was employed to remove a molecule of highly disordered solvent which was found to be a half occupancy pentane molecule (one of the crystallisation solvents). This solvent of crystallisation has been included in the molecular formula for completeness.

The hydride ligands H1 and H2 and hydrogen atoms of borohydydride units (H1A and H1B) were located in the difference map and restrained in position using the DFIX (Ir-Hydride distances fixed to 1.70 Å, B-H distances fixed to 1.15 Å, Ir-HB distances fixed to 1.40 Å) and DANG (hydrogen atoms in the borohydride molecule fixed to1.88 Å apart) commands.

Compound 6c[BAr^{Cl}_4]

All H atoms were found on the Fourier map, except those on the disordered pentane molecules, for which hydrogen atoms were added in calculated positions.

Table 1: Crystallographic data for **6a[BAr$^{Cl}_4$]**, **7a** and **6c[BAr$^{Cl}_4$]**

	6a[BAr$^{Cl}_4$]	**7a**	**6c[BAr$^{Cl}_4$]**
CCDC number	971346	971347	988696
Formula	$IrP_2C_{69.80}H_{92.54}B_2Cl_8F_{3.27}N$	$Ir_2P_4C_{112.5}H_{163}B_2F_{25}$	$Ir_1P_2N_3C_{70}H_{118}B_4Cl_8$
M	1567.19	2484.26	1582.76
Crystal System	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_1/c$	$P2_122_1$	*P*-1
T [K]	150(2)	150(2)	150(2)
a [Å]	13.2199 (1)	16.435 (3)	12.7377(1)
b [Å]	34.9437 (2)	17.300 (4)	12.8491(1)
c [Å]	18.4595 (1)	20.951 (4)	25.1406(2)
α [deg]	90	90	99.5231(4)
β [deg]	105.9144 (2)	90	98.2550(3)
γ [deg]	90	90	95.4001(3)
V [Å^3]	8200.57 (9)	5957 (2)	3986.57(5)
Z	4	2	2
Density [g cm^{-3}]	1.269	1.385	1.318
μ [mm^{-1}]	1.97	2.37	2.022
θ range [deg]	5.097 ≤ θ ≤ 27.469	5.10 ≤ θ ≤ 27.49	5.11 ≤ θ ≤ 27.515
Reflns collected	118540	13594	58065
R_{int}	0.041	0.048	0.030
Completeness	99.00%	99.10%	98.6%
Data/restr/param	18580/1027/820	13594/13/654	18071/140/1075
R_1 [I > 2σ(I)]	0.0553	0.034	0.0353
wR_2 [all data]	0.1376	0.0927	0.0763
GoF	1.0845	0.935	1.0098
Largest diff. pk and hole [eÅ^{-3}]	1.82, -1.21	1.14, −1.69	1.12, -1.01

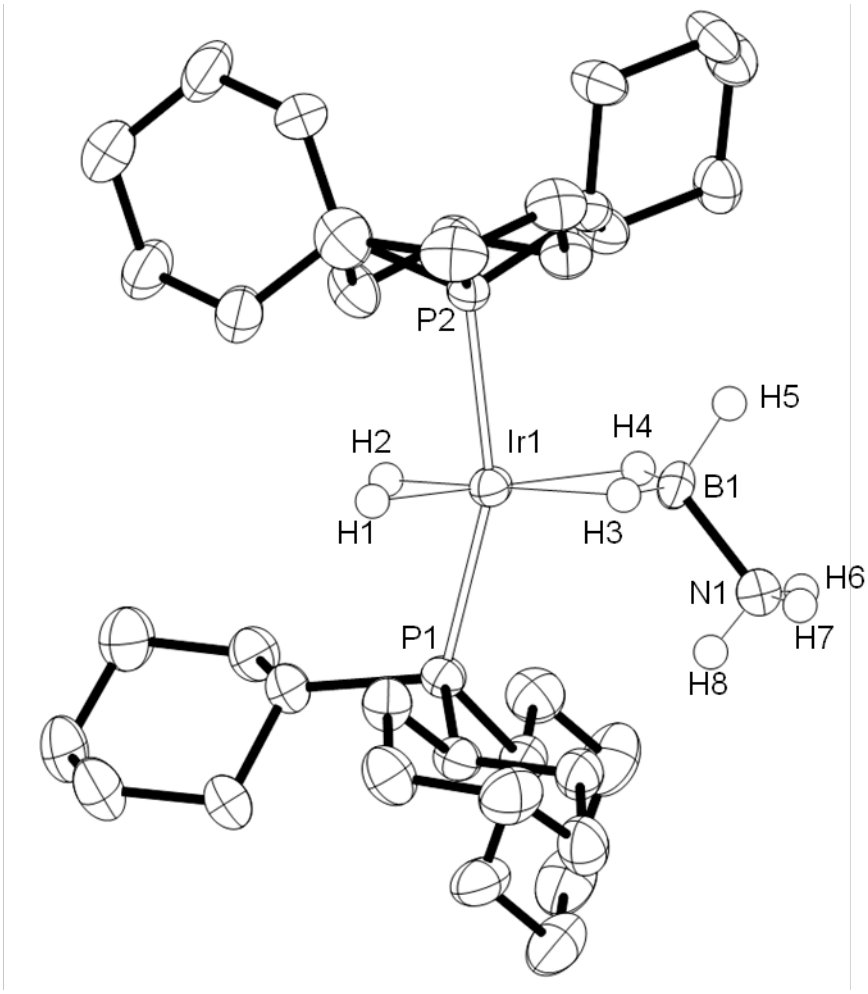


Figure S47: Structure of the cationic portion of (**6a[BAr$^{Cl}_4$]**) with thermal ellipsoids at the 50% probability level. The minor disordered component is not shown. Selected bond lengths (Å): Ir1-B1, 2.209(5); Ir1-P1, 2.3206(12); Ir1-P2, 2.3319(12); B1-N1, 1.595(7). Selected bond angles (deg): P1-Ir1-P2, 159.52(4).

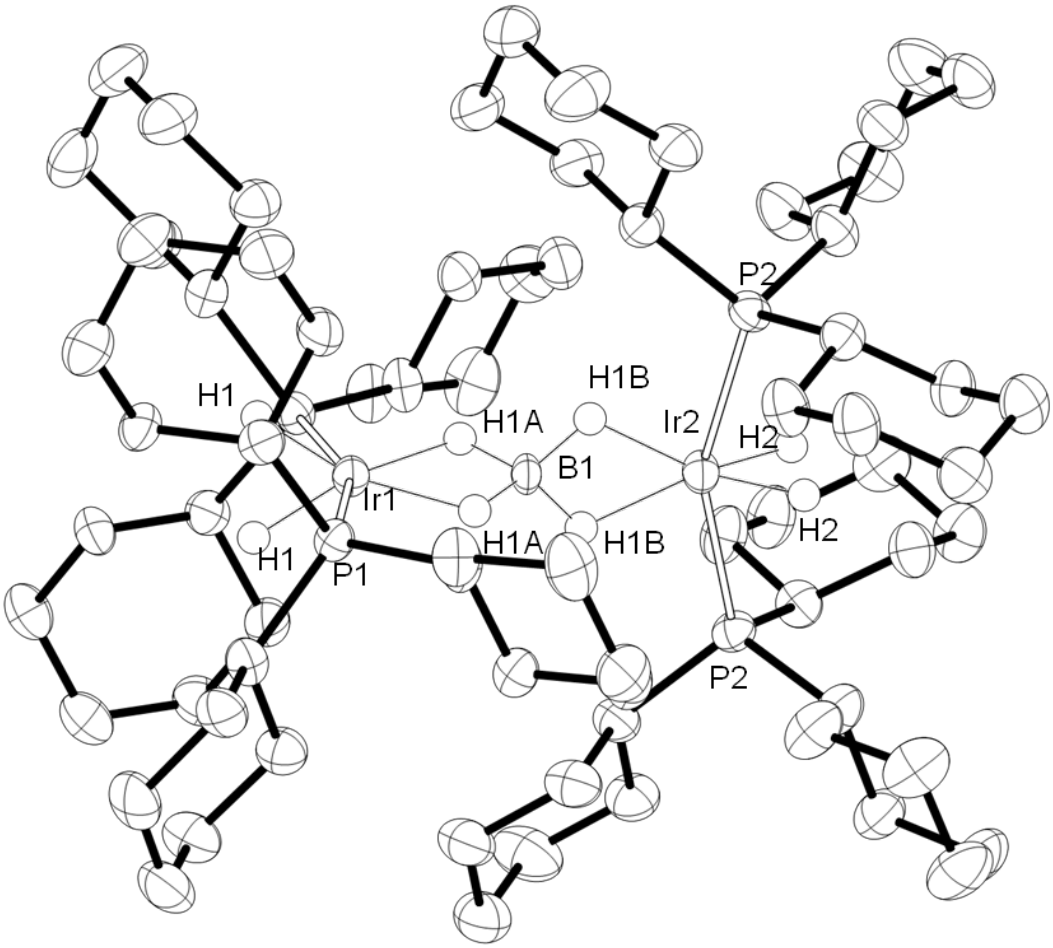


Figure S48: Structure of the cationic portion of **7a** with thermal ellipsoids at the 50% probability level. The minor disordered component is not shown. Selected bond lengths (Å): Ir1-B1, 2.170(5); Ir2-B1, 2.159(5); Ir1-P1, 2.3357(11); Ir2-P2, 2.3327(11). Selected bond angles (deg): P1-Ir1-P1, 157.98(5); P2-Ir2-P2, 154.77(6).

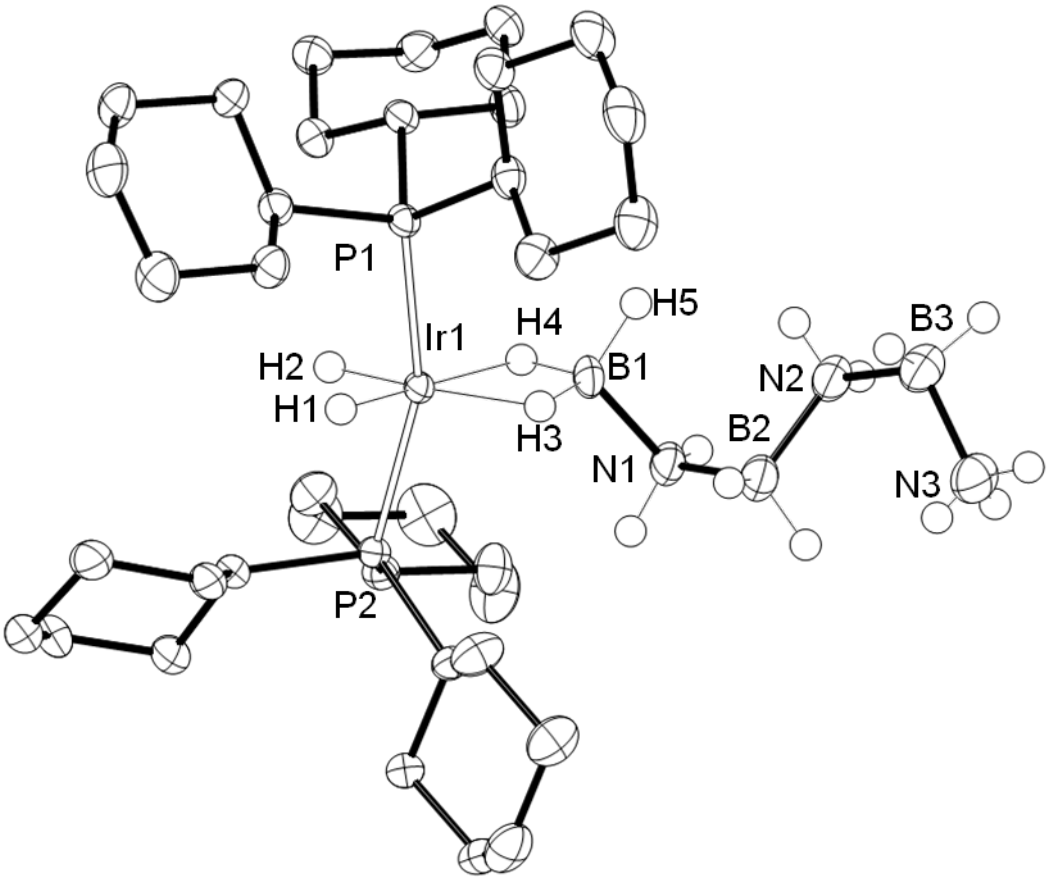


Figure S49: Structure of the cationic portion of (**6c[BAr$^{Cl}_4$]**) with thermal ellipsoids at the 50% probability level. The minor disordered component is not shown. Selected bond lengths (Å): Ir1-B1, 2.198(3); Ir1-P1, 2.3182(8); Ir1-P2, 2.3188(7). Selected bond angles (deg): P1-Ir1-P2, 160.64(3).

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