Effect of strain and π-acidity on the catalytic efficiency of carbones in carbodiimide hydroboration

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Fig. S52 Steepest descent path from **TS 6–7** toward structures **6** and **7**. Distances on 3D geometries reported in Ångströms.

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Hydroboration of carbodiimide 4 catalyzed by cyclic carbodiphosphorane 1

Carbodiimide activation pathway

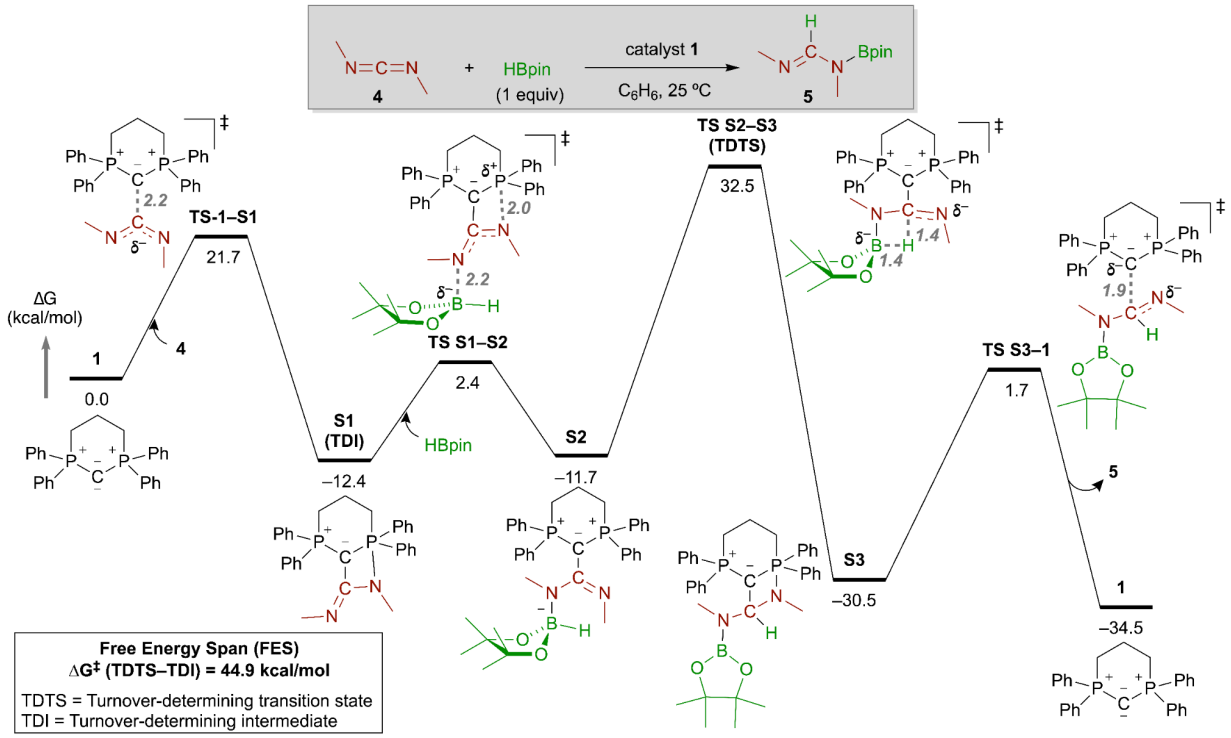

Fig. S1 Computed carbodiimide activation pathway for the hydroboration of carbodiimide **4** by carbodiphosphorane **1**. Geometries and energies at 25 ºC calculated at the ωB97XD/def2-TZVPP/PCM(Benzene)//ωB97XD/6-31G(d,p) level.

We investigated an alternative mechanism for the hydroboration of carbodiimide **4**, catalyzed by carbodiphosphorane **1** (**Fig. S1**). In this mechanism, the initial step involves the nucleophilic addition of **1** to **4**, resulting in the formation of the carbone-amidinate species **S1** through a transition state characterized by C-C bond formation (**TS 1–S1**). This process has a barrier of 21.7 kcal/mol, which is 6.2 kcal/mol higher than the highest energy transition state (**TS 6–7**, $\Delta G^{\ddagger}$ = 15.5 kcal/mol) for the preferred borane activation mechanism, as illustrated in **Fig. 2** of the manuscript. Consequently, the energetic barrier for the formation of carbone-amidinate precludes this pathway from being energetically favored in the hydroboration of carbodiimide by carbodiphosphorane 1.

Once formed, adduct **S1** can bind to HBpin via N-B bond formation (**TS S1–S2**) to create intermediate **S2**. An intramolecular hydride transfer from the bound borane to the central carbon of the amidine fragment occurs through the highest energy transition state in this pathway (**TS S2–S3**, $\Delta G^{\ddagger}$ = 32.5 kcal/mol), leading to the formation of intermediate **S3**, which features a phosphoramide bond with one of the flanking phosphine ligands on the carbodiphosphorane. In the final step, dissociation occurs to yield the *N*-boryl formamidine product **5** and release carbodiphosphorane **1** through a concerted breaking of C-C and P-N bonds (**TS S3–1**).

The computed free energy span for the carbodiimide activation pathway, from the turnover-determining intermediate **S1** to the turnover-determining transition state **TS S2–S3**, is 44.9 kcal/mol. This is 24.6 kcal/mol greater than that of the borane activation pathway reported in **Fig. 2** of the manuscript, rendering it energetically unlikely under the reaction conditions. In summary, we conclude that the borane activation pathway is the most probable mechanism for the hydroboration of carbodiimide **4** catalyzed by carbodiphosphorane **1**.

Hydroboration of carbodiimide 4 catalyzed by acyclic carbodiphosphorane 2

Complete borane activation pathway

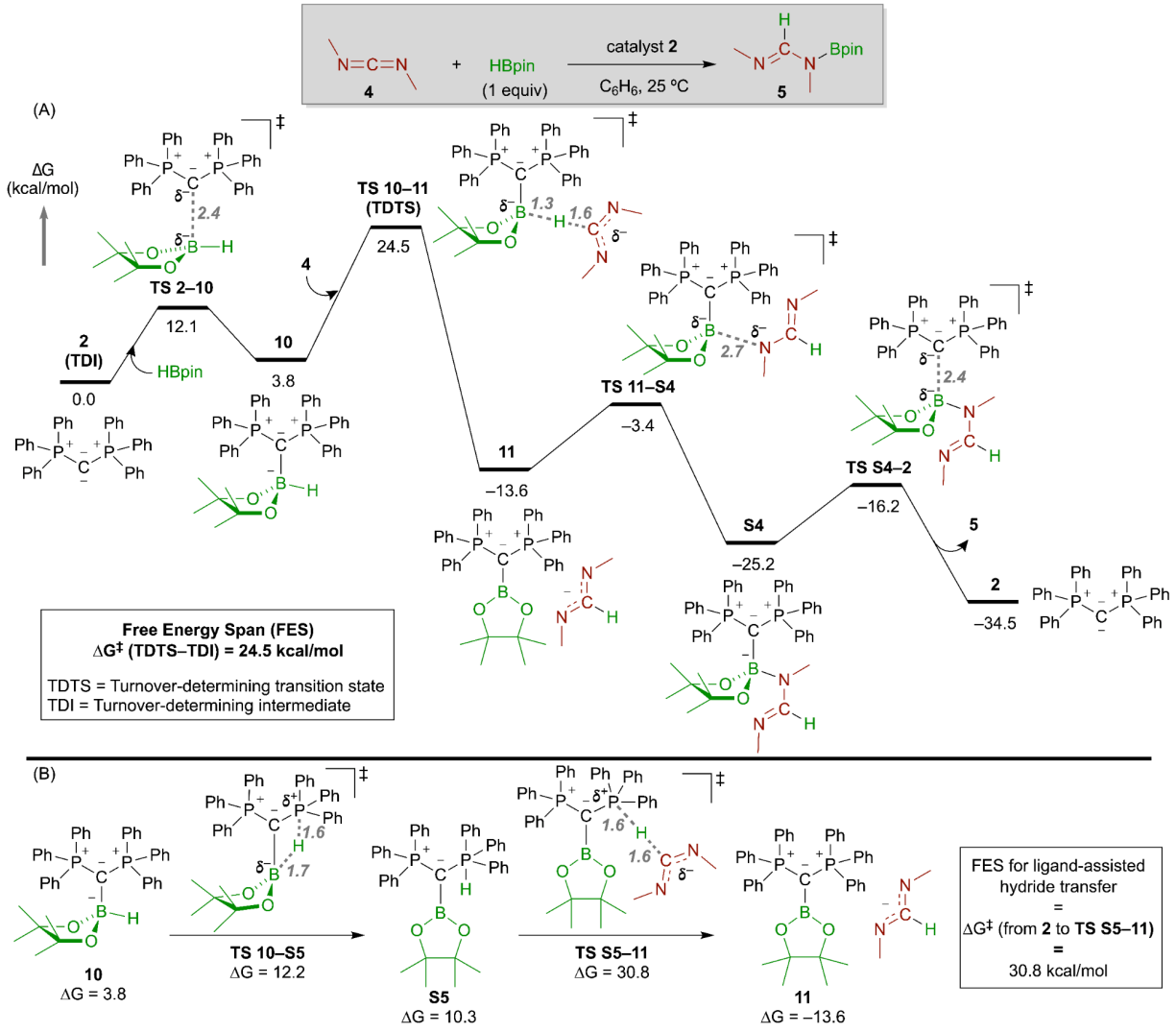

Fig. S2 Computed likely pathway for the hydroboration of carbodiimide **4** by carbodiphosphorane **2**. Geometries and energies at 25 ºC calculated at the ωB97XD/def2-TZVPP/PCM(Benzene)//ωB97XD/6-31G(d,p) level.

We calculated the likely pathway for the hydroboration of carbodiimide **4**, catalyzed by acyclic carbodiphosphorane **2** (**Fig. S2**). In **Fig. 3** of the manuscript, we detailed the pathway leading to the formation of ion pair **11**, which consists of a carbone-Bpin cation and an amide anion. This step represents the kinetically irreversible part of the reaction mechanism. The coupling of these ions through B-N bond formation (**TS 11–S4**) is facile, with a free energy barrier ($\Delta G^{\ddagger}$) of 10.2 kcal/mol, resulting in the carbone-*N*-boryl formamidine complex **S4**. The subsequent release of *N*-boryl formamidine **5** regenerates carbodiphosphorane **2**, allowing for another cycle to occur.

We also explored the possibility of the PPh_3 ligand participating in the hydroboration mechanism (**Fig. S2B**). Similar to our discussion of this process involving carbodiphosphorane **1** in **Fig. 2C** of the

manuscript, intramolecular hydride transfer occurs from the bound borane in intermediate **10** to the phosphine. This transfer goes through transition state **TS 10–S5**, resulting in the formation of intermediate **S5**. From this point, the phosphine can act as a hydride donor, transferring the hydride to carbodiimide **4** through transition state **TS 5–11** to create ion pair **11**. The free energy span for this phosphine-assisted hydride transfer process is 30.8 kcal/mol. In contrast, the free energy span for the direct hydride transfer process is 24.5 kcal/mol. Thus, phosphine-assisted hydride transfer is energetically unfavorable by 6.5 kcal/mol and is considered an unlikely pathway when using acyclic carbodiphosphorane **2**.

Comparison of the preferred borane activation pathway with the carbodiimide activation pathway

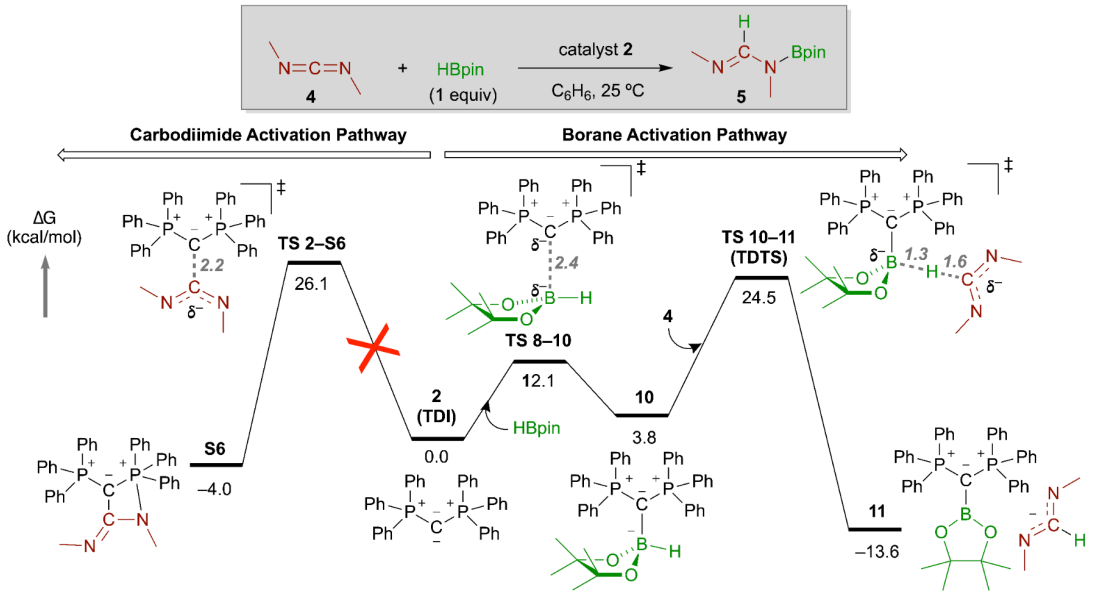

Fig. S3 Comparison of the first elementary step in the carbodiimide activation pathway with the free energy span of the borane activation step in the hydroboration of carbodiimide **4** by carbodiphosphorane **2**. Geometries and energies at 25 ºC calculated at the ωB97XD/def2-TZVPP/PCM(Benzene)//ωB97XD/6-31G(d,p) level.

We investigated whether the carbodiimide activation pathway is preferred for the hydroboration of carbodiimide **4** by carbodiphosphorane **2** (**Fig. S3**). The first elementary step for this pathway is the nucleophilic addition of **2** to **4** through **TS 2–S6** to form the carbone-amidinate species **S6**. This step has a free energy activation barrier of 26.1 kcal/mol, which is 1.6 kcal/mol higher in energy than the highest energy transition state for the borane activation pathway (**TS 10–11**). This energy difference confirms that the borane activation pathway is energetically preferred, as is the case for carbodiimide hydroboration by cyclic carbodiphosphorane **1** discussed in this manuscript.

Hydroboration of carbodiimide 4 catalyzed by carbodicarbene 3

Comparison of the preferred borane activation pathway with the carbodiimide activation pathway

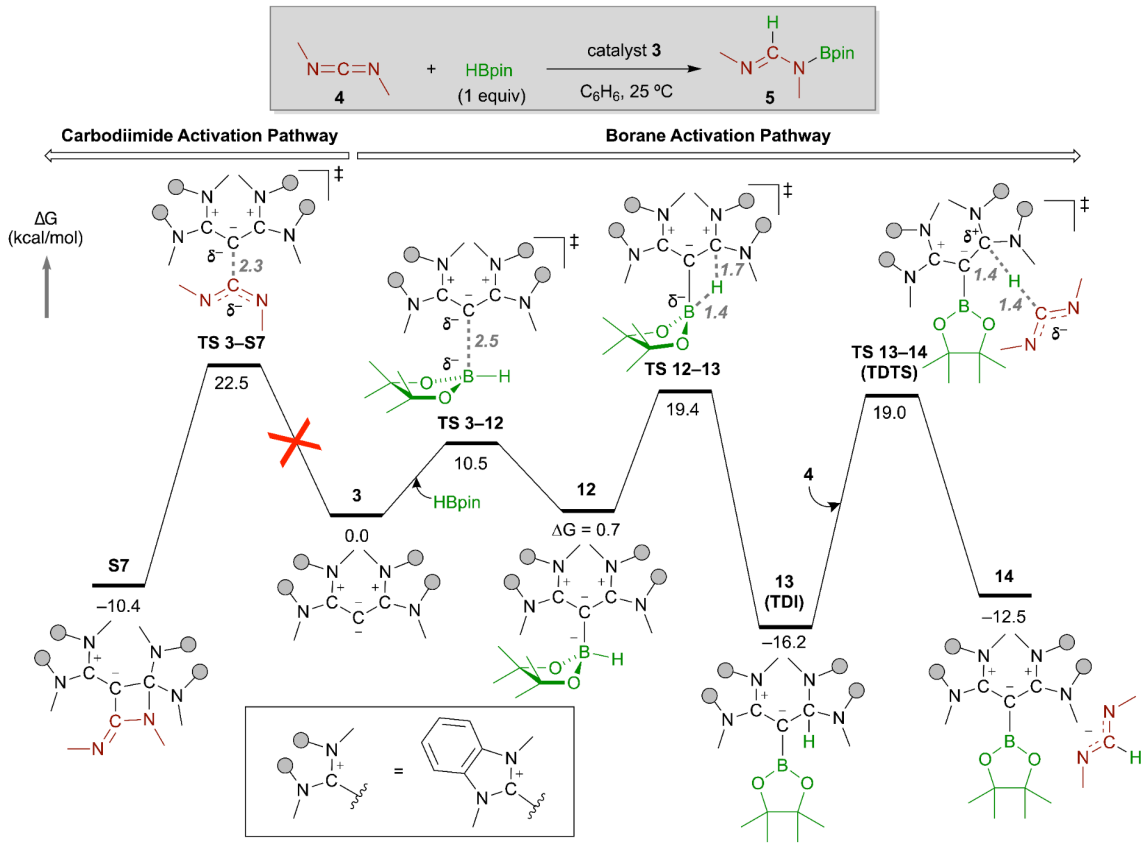

Fig. S4 Comparison of the first elementary step in the carbodiimide activation pathway with the free energy span of the borane activation step in the hydroboration of carbodiimide **4** by carbodicarbene **3**. Geometries and energies at 25 ºC calculated at the ωB97XD/def2-TZVPP/PCM(Benzene)//ωB97XD/6-31G(d,p) level.

We investigated whether the carbodiimide activation pathway is preferred for the hydroboration of carbodiimide **4** by carbodicarbene **3** (**Fig. S4**). The first elementary step for this pathway is the nucleophilic addition of **3** to **4** through **TS 3–S7** to form the carbone-amidinate species **S7**. This step has a free energy activation barrier of 22.5 kcal/mol, which is 3.5 kcal/mol higher in energy than the highest energy transition state for the borane activation pathway (**TS 13–14**). This energy difference confirms that the borane activation pathway is energetically preferred, as is the case for carbodiimide hydroboration by cyclic and acyclic carbodiphosphoranes **1** and **2** discussed in this manuscript.

Geometries, thermochemistry, and vibrational frequencies computed at the ωB97XD/6-31G(d,p) level

1

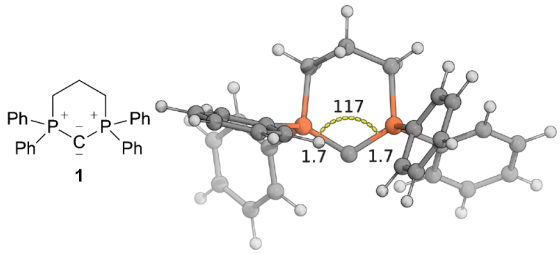

Fig. S5 Three dimensional picture of structure **1** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

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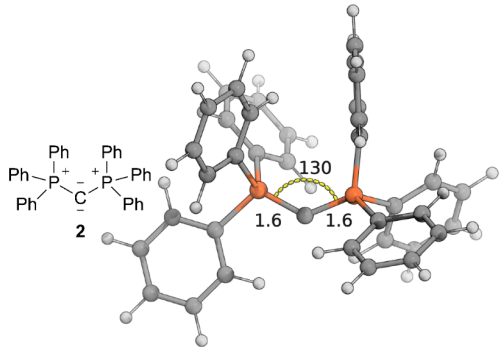

Fig. S6 Three dimensional picture of structure **2** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

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Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -2110.17386055 | Predicted change in Energy=-4.008766D-09
Zero-point correction (ZPE) = -2109.61140255 0.562458
Internal Energy (U) = -2109.57828755 0.595573
Enthalpy (H) = -2109.57734355 0.596517
Gibbs Free Energy (G) = -2109.67959055 0.49427

Frequencies
14.6214 19.3195 24.2455
31.8978 34.8058 43.5569
46.6703 54.4868 58.4732
63.4274 69.3198 73.2263
77.6749 91.5633 98.1114
101.3619 113.1558 163.9938
181.8293 191.1779 206.1303
228.2377 237.0041 241.4687
248.0648 248.8031 258.7988
265.6655 283.4435 286.4148
318.5507 379.7196 405.7235
410.0379 412.8085 415.2240
418.5010 420.6722 426.0120
452.8794 454.4449 460.4014
473.2636 511.8594 521.6517
534.2216 538.5482 543.8360
557.0458 635.0675 635.7779
636.7058 636.8981 637.1343
637.9230 680.1824 703.6768
716.2238 717.0796 720.7388
722.9066 723.5099 725.4665
728.3492 730.1273 732.1798

734.0673 766.0669 770.3988
770.8900 771.6410 779.2878
780.2254 809.0825 879.5533
881.3961 883.7915 887.0858
888.5643 891.3186 956.5549
957.1376 957.8602 962.8716
964.0107 968.0267 1006.3473
1007.5395 1008.4693 1011.9163
1013.6276 1014.9719 1021.8656
1022.5834 1022.6693 1023.9873
1024.3065 1024.5267 1025.5388
1028.5545 1030.6317 1032.9283
1033.2755 1040.1261 1064.4752
1064.5621 1065.7524 1066.1184
1066.6130 1067.6891 1111.9913
1114.0355 1117.8200 1121.0221
1122.6786 1125.2494 1133.9259
1139.4430 1140.2359 1143.2987
1145.2968 1146.1959 1193.5175
1194.8269 1195.2078 1195.8253
1196.1781 1196.7241 1215.1083
1216.3561 1218.7482 1221.9150
1227.1140 1231.9321 1311.9893
1329.1743 1330.2778 1337.7514
1338.9043 1340.1999 1341.7407
1362.5178 1363.9726 1367.1931
1368.8434 1371.2822 1375.3784
1487.6628 1488.3920 1492.7895
1493.3850 1493.8509 1494.2493
1536.6182 1537.8375 1539.7698
1540.4662 1541.7771 1543.8656
1660.9028 1661.7441 1664.4780
1664.5931 1666.4865 1667.3889
1681.7550 1682.0258 1682.8676
1683.8370 1684.2459 1684.4982
3200.4165 3201.2146 3202.1879
3203.3523 3203.4401 3204.3534
3205.5029 3207.1548 3208.0407
3210.2622 3212.0479 3213.1917
3214.6410 3215.0167 3215.3198
3216.7990 3221.1552 3221.8991
3222.2189 3223.2286 3224.0231
3224.5861 3228.7509 3229.6125
3232.3485 3232.6587 3232.8050
3233.5626 3234.5833 3235.6326

3

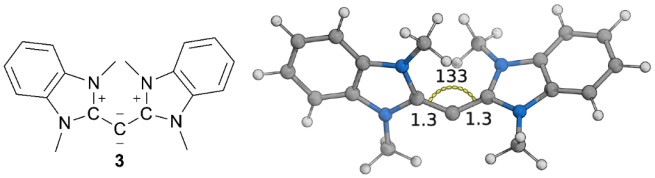

Fig. S7 Three dimensional picture of structure **3** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman

---

Full point group C1 NOp 1
Stoichiometry C19H20N4 Framework group C1[X(C19H20N4)]

Num atoms: 43
Charge = 0 Multiplicity = 1

SCF = -954.755082721 | Predicted change in Energy=-1.503783D-09

Optimization completed.

Maximum Force	0.000004	0.000450	YES
RMS Force	0.000000	0.000300	YES
Maximum Displacement	0.001395	0.001800	YES
RMS Displacement	0.000238	0.001200	YES

Atom Type	Coordinates (in Angstroms) X	Y	Z
C	0.102422	-0.859071	-0.298019
C	1.323689	-1.362619	-0.044001
C	0.731874	-3.159292	1.592601
H	0.363956	-4.055998	1.081419
H	1.199235	-3.456952	2.534655
H	-0.119809	-2.509608	1.808831
C	2.628566	0.289448	-1.377801
H	3.345389	1.022615	-0.994654
H	2.938057	-0.019738	-2.382703
H	1.634690	0.739704	-1.429841
C	3.059394	-2.538046	0.874599
C	3.599559	-1.531065	0.056020
C	4.967588	-1.382306	-0.093157
C	5.795835	-2.267063	0.607574
C	5.261920	-3.262898	1.419462

C 3.877321 -3.416783 1.562676
H 5.382495 -0.608835 -0.730526
H 6.872338 -2.174159 0.510107
H 5.926230 -3.938800 1.947465
H 3.464793 -4.203561 2.185274
C -1.102115 -1.428176 -0.484558
C -2.798695 -2.762705 -1.245324
C -3.371456 -1.678467 -0.558135
C -4.743729 -1.554802 -0.426003
C -5.542735 -2.545621 -1.008825
C -4.976578 -3.618161 -1.690763
C -3.587593 -3.745648 -1.816370
H -5.183695 -0.720913 0.110377
H -6.621789 -2.474755 -0.921591
H -5.618550 -4.375152 -2.128684
H -3.149615 -4.590953 -2.336428
C -2.460240 0.336477 0.634608
H -3.198835 0.993259 0.164198
H -2.761800 0.146019 1.670945
H -1.480959 0.820412 0.627824
N 2.537691 -0.831880 -0.482112
N 1.680119 -2.424160 0.798200
N -2.332857 -0.884763 -0.113885
N -1.423775 -2.597343 -1.186553
C -0.451663 -3.396322 -1.884614
H -0.057345 -4.210393 -1.266103
H -0.907652 -3.823574 -2.781291
H 0.380025 -2.752753 -2.181795

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -954.755082721 | Predicted change in Energy=-1.503783D-09
Zero-point correction (ZPE) = -954.395021721 0.360061
Internal Energy (U) = -954.373900721 0.381182
Enthalpy (H) = -954.372956721 0.382126
Gibbs Free Energy (G) = -954.446365721 0.308717

Frequencies
21.4571 26.3235 45.4638
78.3034 79.5747 99.0473
106.6994 114.5497 116.0096
118.0215 126.0556 126.5726
163.6811 205.8243 252.3868
257.8359 258.3048 271.2503

294.2036 306.5710 316.1368
326.8795 357.5197 443.9857
448.3700 480.5565 534.1259
567.7670 575.9669 576.3172
586.8301 586.9457 607.8024
649.8245 657.1044 673.7147
685.7399 719.6904 752.3912
752.4591 757.3131 757.3879
767.8512 852.3517 857.5369
862.1767 862.2714 898.4157
920.8890 920.9911 978.1369
978.1580 1003.9336 1057.8942
1059.0612 1060.1178 1065.3686
1114.0007 1118.9845 1155.6155
1155.8165 1160.8062 1162.5888
1164.7068 1164.7086 1174.7640
1176.0213 1196.5269 1196.9733
1265.7057 1279.1120 1280.8755
1314.3417 1366.7727 1367.9189
1396.6419 1396.6978 1435.0471
1447.0550 1452.8037 1452.8733
1470.9682 1471.7619 1472.9527
1478.1392 1502.0549 1509.9661
1510.0379 1513.2215 1520.3705
1521.6589 1524.3268 1529.8052
1541.3181 1541.3493 1573.4758
1580.3847 1606.0582 1697.6372
1697.7963 1702.3073 1702.7869
1817.2829 3044.4465 3045.0239
3050.5279 3052.2744 3117.3015
3117.3189 3125.2436 3127.0416
3160.3451 3160.6576 3162.4884
3162.7203 3212.1481 3212.1537
3222.5417 3222.5580 3231.4375
3231.4516 3239.8788 3239.9685

Pinacolborane (HBpin)

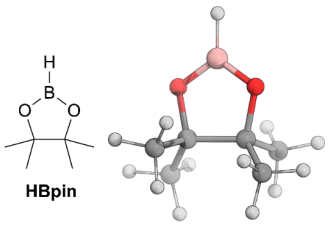

Fig. S8 Three dimensional picture of HBpin reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman

---
Full point group C1 NOp 1
Stoichiometry C6H13BO2 Framework group C1[X(C6H13BO2)]

Num atoms: 22
Charge = 0 Multiplicity = 1

SCF = -411.766637846 | Predicted change in Energy=-6.355293D-09

Optimization completed.
Maximum Force 0.000008 0.000450 YES
RMS Force 0.000003 0.000300 YES
Maximum Displacement 0.000656 0.001800 YES
RMS Displacement 0.000124 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

C -0.294668 1.887688 3.459973
O 0.827205 0.975816 3.463642
B 1.960508 1.736353 3.433427
O 1.732198 3.070367 3.612278
C 0.347144 3.214353 4.000934
H 3.045775 1.279247 3.266767
C -0.769654 1.995306 2.010055
H -1.011044 0.994991 1.642915
H -1.662419 2.621149 1.926549
H 0.010798 2.412706 1.367978
C -1.401033 1.310512 4.331212
H -1.779809 0.389329 3.881538
H -1.041038 1.074870 5.333684

H -2.232385 2.017834 4.412951
C -0.206930 4.490882 3.384738
H 0.302123 5.357144 3.814506
H -0.058444 4.512499 2.304202
H -1.277079 4.584381 3.594946
C 0.326619 3.315461 5.526975
H 0.961413 4.150135 5.833665
H -0.684957 3.491514 5.902986
H 0.717475 2.404862 5.989179

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -411.766637846 | Predicted change in Energy=-6.355293D-09
Zero-point correction (ZPE) = -411.57378584599996 0.192852
Internal Energy (U) = -411.564505846 0.202132
Enthalpy (H) = -411.56356184599997 0.203076
Gibbs Free Energy (G) = -411.606599846 0.160038

Frequencies
101.8252 238.4397 249.5038
284.6417 297.3340 299.1576
311.5659 323.0596 368.6740
376.6391 403.6377 454.0196
518.6306 532.1828 589.8767
677.7657 755.0992 831.5993
893.8621 908.5312 948.1924
954.4059 974.6052 995.9380
1023.6350 1031.9201 1070.6067
1160.4084 1206.3661 1208.2842
1220.2706 1262.9627 1289.0308
1322.8158 1400.9435 1424.1667
1424.6990 1434.5881 1444.2606
1489.0638 1498.8800 1501.4272
1505.3002 1522.6024 1525.4429
1528.4862 1547.7251 2708.1670
3069.7111 3071.0146 3074.6574
3077.3271 3153.6868 3154.2384
3158.3068 3158.6432 3165.1948
3165.2104 3181.3369 3181.5621

4

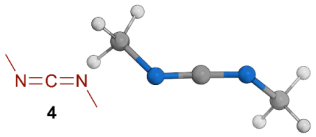

Fig. S9 Three dimensional picture of structure **4** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman

---
Full point group C1 NOp 1
Stoichiometry C3H6N2 Framework group C1[X(C3H6N2)]

Num atoms: 11
Charge = 0 Multiplicity = 1

SCF = -227.321463249 | Predicted change in Energy=-5.296428D-09

Optimization completed.
Maximum Force 0.000027 0.000450 YES
RMS Force 0.000008 0.000300 YES
Maximum Displacement 0.000635 0.001800 YES
RMS Displacement 0.000262 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

C 1.241346 1.121171 -0.066079
H 0.968913 2.127225 0.263512
H 1.798591 0.627942 0.737654
H 1.894969 1.223726 -0.936483
N 0.037777 0.409976 -0.454109
C -0.357308 -0.645135 0.019681
N -0.903077 -1.628020 0.499121
C -0.728465 -2.999568 0.059510
H -1.702055 -3.408842 -0.222603
H -0.045868 -3.100741 -0.791160
H -0.346322 -3.597933 0.890954

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -227.321463249 | Predicted change in Energy=-5.296428D-09
Zero-point correction (ZPE) = -227.230299249 0.091164
Internal Energy (U) = -227.223704249 0.097759

Enthalpy (H) = -227.222760249 0.098703
Gibbs Free Energy (G) = -227.26070324900002 0.06076

Frequencies
73.1451 79.2961 139.7771
203.2135 255.3465 620.8463
624.1252 855.4967 1057.3751
1137.4570 1148.3404 1158.4900
1167.4650 1466.5032 1474.8378
1502.3036 1510.1273 1511.8095
1523.3051 1546.5285 2296.3721
3049.1807 3052.2627 3135.4491
3135.6157 3145.7000 3145.8317

5

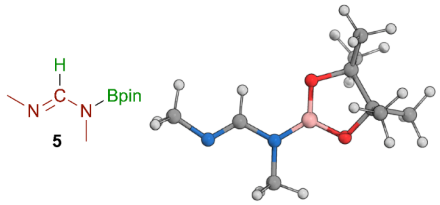

Fig. S10 Three dimensional picture of structure **5** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman

---
Full point group C1 NOp 1
Stoichiometry C9H19BN2O2 Framework group C1[X(C9H19BN2O2)]

Num atoms: 33
Charge = 0 Multiplicity = 1

SCF = -639.178412566 | Predicted change in Energy=-6.155395D-08

Optimization completed.
Maximum Force 0.000051 0.000450 YES
RMS Force 0.000011 0.000300 YES
Maximum Displacement 0.000864 0.001800 YES
RMS Displacement 0.000214 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

N 1.397130 1.285484 -0.353645
C 0.798253 0.293565 0.402660
N 0.919532 0.240939 1.665391
H 0.221914 -0.425153 -0.192584
B 1.236830 1.322818 -1.767548
C 1.277489 2.111809 -3.880009
C 0.738516 0.637606 -3.858168
C 2.189422 2.279647 0.357003
H 1.572990 2.798819 1.095981
H 3.011442 1.798644 0.894236
H 2.586509 2.994441 -0.363152
O 0.437245 0.443676 -2.461378
O 1.868648 2.241249 -2.571220
C 0.161407 3.153304 -3.975278

H -0.290931 3.167114 -4.970695
H -0.623114 2.959908 -3.238352
H 0.582843 4.140666 -3.771973
C 2.343693 2.385032 -4.930517
H 2.657708 3.430309 -4.873415
H 3.223578 1.758052 -4.779411
H 1.948189 2.201923 -5.934564
C -0.527641 0.409521 -4.670285
H -0.827802 -0.638920 -4.598172
H -1.352047 1.024179 -4.306056
H -0.353148 0.642585 -5.725402
C 1.803425 -0.392918 -4.237223
H 1.429351 -1.390819 -3.996106
H 2.034242 -0.357761 -5.305452
H 2.727560 -0.231023 -3.675348
C 0.246844 -0.845686 2.341434
H -0.309342 -1.519138 1.668722
H 0.978192 -1.444915 2.894714
H -0.457026 -0.442457 3.077612

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -639.178412566 | Predicted change in Energy=-6.155395D-08
Zero-point correction (ZPE) = -638.888125566 0.290287
Internal Energy (U) = -638.872357566 0.306055
Enthalpy (H) = -638.871413566 0.306999
Gibbs Free Energy (G) = -638.929909566 0.248503

Frequencies
41.6140 71.9009 92.7853
118.3488 133.4991 158.0947
186.5445 216.4805 222.0439
229.6699 243.8348 278.2830
287.1938 315.9268 322.3684
325.6634 338.5464 374.0747
380.0973 407.7708 423.4417
440.1315 473.2004 532.6155
544.5887 593.5614 667.0916
682.9006 733.1413 870.4944
884.4741 914.8167 948.7022
951.4665 990.7575 997.5151
1013.8217 1022.0122 1031.1320
1061.0739 1107.3627 1148.8029
1164.1336 1166.2401 1168.6302

1204.8828 1210.8917 1216.9924
1267.4044 1286.3998 1321.2531
1336.3252 1400.2342 1423.1715
1423.7548 1432.1857 1434.6095
1443.1632 1466.8591 1476.6811
1489.5302 1497.9869 1499.7817
1500.2812 1503.2202 1504.9522
1505.3491 1521.1616 1524.3591
1524.6563 1525.7809 1542.7552
1569.9172 1791.8721 2991.4194
3069.0842 3070.5267 3072.9319
3074.0702 3076.5785 3089.0240
3094.6270 3114.5472 3142.1958
3153.3563 3153.6876 3156.7828
3158.4312 3164.3073 3164.7453
3178.5940 3179.3417 3193.7511

TS 1–6

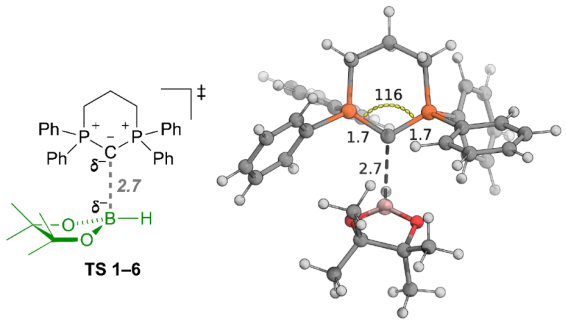

Fig. S11 Three dimensional picture of structure **TS 1–6** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman

---

Full point group C1 NOp 1
Stoichiometry C34H39BO2P2 Framework group C1[X(C34H39BO2P2)]

Num atoms: 78
Charge = 0 Multiplicity = 1

SCF = -2176.70627974 | Predicted change in Energy=-6.979680D-10

Optimization completed.
Maximum Force 0.000003 0.000450 YES
RMS Force 0.000000 0.000300 YES
Maximum Displacement 0.000367 0.001800 YES
RMS Displacement 0.000079 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

P 1.416617 -0.797755 -0.990013
C 1.273062 -1.835009 -2.516810
C -0.042826 -2.631525 -2.566226
C -1.290806 -1.729537 -2.576998
P -1.403630 -0.800357 -0.981298
H 2.142157 -2.492429 -2.618740
H 1.312341 -1.129685 -3.354383
H -0.102478 -3.315749 -1.710070
H -0.046563 -3.256963 -3.465242
H -1.218851 -1.013157 -3.402046
H -2.196348 -2.325688 -2.724006

C	-3.005971	-4.203069	1.723667
C	-3.836026	-3.666101	0.740565
C	-3.381759	-2.622577	-0.056913
C	-2.095210	-2.103185	0.122423
C	-1.273117	-2.642758	1.111093
C	-1.726231	-3.691349	1.908053
H	-3.361488	-5.018057	2.346650
H	-4.837485	-4.060329	0.598631
H	-4.036945	-2.200076	-0.814754
H	-0.280215	-2.229746	1.257893
H	-1.076858	-4.102349	2.674429
C	-4.706461	2.402872	-1.316593
C	-4.514656	1.713935	-0.122484
C	-3.555442	0.710191	-0.041379
C	-2.779115	0.385170	-1.156478
C	-2.969448	1.088779	-2.347652
C	-3.931567	2.089631	-2.430270
H	-5.454413	3.187178	-1.378669
H	-5.105547	1.963611	0.752843
H	-3.391495	0.198372	0.900039
H	-2.354667	0.872500	-3.216060
H	-4.072431	2.628671	-3.361731
C	4.622842	2.270129	-2.263117
C	3.268058	2.585140	-2.325482
C	2.318873	1.654947	-1.914542
C	2.717647	0.405758	-1.438265
C	4.077343	0.093344	-1.380198
C	5.026703	1.023895	-1.791405
H	5.364925	2.997225	-2.578084
H	2.950629	3.558626	-2.685969
H	1.257701	1.887066	-1.940394
H	4.396831	-0.872062	-0.998161
H	6.082694	0.778666	-1.736955
C	3.246335	-3.378274	2.383044
C	2.901558	-3.991801	1.183901
C	2.399790	-3.230659	0.130476
C	2.238097	-1.850574	0.268491
C	2.584180	-1.239497	1.481182
C	3.087590	-2.001245	2.528391
H	3.635155	-3.971406	3.204950
H	3.019957	-5.064340	1.065425
H	2.127280	-3.729938	-0.794098
H	2.436024	-0.170200	1.610536
H	3.349862	-1.518247	3.464231
C	0.006471	-0.073918	-0.498898
B	-0.186050	0.901176	2.001445
O	-1.280346	1.726524	1.888379
C	-0.801995	3.037486	1.536473

C 0.688640 3.002178 2.046238
O 1.003587 1.599595 2.039774
H -0.280141 -0.227160 2.363043
C -0.921925 3.193910 0.020053
H -0.379513 2.389666 -0.482975
H -0.549362 4.168693 -0.309531
H -1.974485 3.113598 -0.264005
C -1.687867 4.067172 2.228292
H -2.702779 3.989858 1.828772
H -1.734165 3.905461 3.306604
H -1.322527 5.081884 2.038748
C 1.684683 3.730155 1.154361
H 2.689752 3.637187 1.575055
H 1.700302 3.302877 0.151636
H 1.438934 4.795118 1.086033
C 0.840897 3.475358 3.494296
H 1.856691 3.253817 3.831906
H 0.670035 4.551742 3.589786
H 0.143966 2.949333 4.152356

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -2176.70627974 | Predicted change in Energy=-6.979680D-10
Zero-point correction (ZPE) = -2176.04824874 0.658031
Internal Energy (U) = -2176.01231974 0.69396
Enthalpy (H) = -2176.01137574 0.694904
Gibbs Free Energy (G) = -2176.11638874 0.589891

Frequencies
-32.4223 21.7286 22.8150
31.0019 40.4590 42.1488
45.0261 54.9886 57.3056
61.6772 69.0850 70.1875
80.7681 86.4815 94.7467
96.8479 110.7141 138.6022
142.7166 185.7893 192.3255
213.3311 219.0989 233.4155
245.3130 250.3146 257.5404
263.0199 269.3551 273.1311
276.4821 301.2667 307.0787
318.3332 324.5001 337.0755
344.1085 356.3809 357.0468
375.1516 383.8579 407.0472
409.1665 411.0931 419.0096

420.2956 420.7542 425.0477
463.7465 469.6357 480.4733
497.6773 501.3146 510.6071
525.3032 529.8333 533.2036
567.7516 592.4416 635.2013
635.5152 636.5034 637.1747
651.0884 678.1642 686.8426
712.6420 716.5286 718.8655
724.9262 727.5300 728.3424
730.9832 737.0003 753.0341
767.8169 773.2096 773.9750
778.2482 806.0295 816.6088
840.4333 860.3310 870.7862
884.5847 887.2335 889.1405
897.2583 906.6968 943.2660
943.3843 946.7951 951.0891
959.5591 962.0046 964.0277
976.4921 992.2363 994.6370
997.8459 1010.3501 1011.2893
1013.1390 1018.1913 1022.2938
1023.1342 1023.8697 1025.0951
1026.2959 1028.7678 1029.7700
1034.9860 1041.3959 1058.7553
1064.7793 1066.0583 1067.3452
1067.8431 1068.7139 1102.1052
1117.0034 1120.7361 1126.1329
1129.5036 1138.9289 1147.2508
1150.0448 1156.4156 1162.0727
1175.2126 1187.1546 1195.5764
1195.6439 1197.4304 1198.0875
1202.0580 1212.0193 1214.0575
1220.2007 1223.3468 1230.1599
1237.8250 1263.1978 1263.3400
1284.8333 1304.5367 1316.6494
1332.8226 1334.4186 1339.2216
1341.0526 1343.5925 1363.4773
1367.0135 1368.5095 1372.9377
1380.8051 1388.0571 1418.4028
1419.8564 1430.3088 1439.9155
1463.8087 1486.8970 1487.0461
1489.7408 1490.8385 1493.6725
1494.0385 1498.5263 1500.4507
1504.8971 1516.7133 1522.3083
1524.1841 1530.2606 1540.8399
1541.1954 1545.7555 1548.2728
1548.9401 1663.2172 1664.3921
1666.7924 1667.3951 1683.5539
1684.1970 1684.6394 1686.5260

2708.7768 3057.6106 3063.7244
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3077.6560 3081.2001 3107.3727
3136.4553 3144.2947 3144.4543
3146.9324 3154.4752 3156.6268
3157.7444 3167.5415 3172.9136
3192.5798 3196.9224 3203.1452
3203.6568 3204.6372 3208.4033
3209.1766 3209.9772 3213.0470
3216.8153 3217.1609 3220.1305
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3230.5000 3232.4503 3233.0183
3234.1682 3239.4743 3245.2681

6

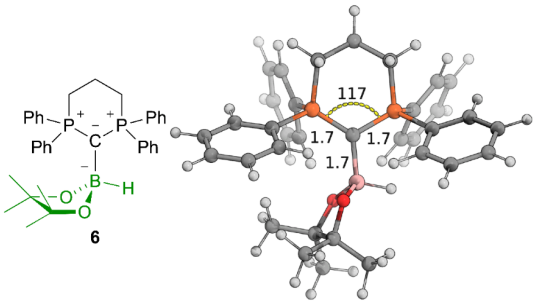

Fig. S12 Three dimensional picture of structure **6** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman

---
Full point group C1 NOp 1
Stoichiometry C34H39BO2P2 Framework group C1[X(C34H39BO2P2)]

Num atoms: 78
Charge = 0 Multiplicity = 1

SCF = -2176.73043812 | Predicted change in Energy=-1.901628D-08

Optimization completed.
Maximum Force 0.000014 0.000450 YES
RMS Force 0.000003 0.000300 YES
Maximum Displacement 0.001480 0.001800 YES
RMS Displacement 0.000245 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

P -6.907076 4.453911 -2.887892
C -6.368216 5.970236 -2.006072
C -6.439261 5.818717 -0.481697
C -7.882849 5.653285 0.005020
P -8.707035 4.145352 -0.641980
H -7.044652 6.762075 -2.344462
H -5.365559 6.250718 -2.337833
H -6.007145 6.708381 -0.012330
H -5.832391 4.964479 -0.157608
H -7.931957 5.653498 1.096913
H -8.497297 6.492090 -0.338744
C -13.107047 5.071089 0.343456
C -12.230250 4.720213 1.365710

C	-10.909908	4.401293	1.067244
C	-10.461046	4.438998	-0.254803
C	-11.343864	4.782450	-1.282033
C	-12.663700	5.095849	-0.975885
H	-14.139483	5.314093	0.574778
H	-12.574847	4.685163	2.394195
H	-10.239423	4.103972	1.867878
H	-11.010709	4.757096	-2.315691
H	-13.351224	5.347964	-1.776683
C	-7.160059	0.607020	1.906274
C	-7.483893	0.444355	0.562614
C	-7.959382	1.518400	-0.181336
C	-8.123788	2.770429	0.421859
C	-7.793302	2.927171	1.772092
C	-7.313738	1.850573	2.511233
H	-6.783043	-0.232837	2.481418
H	-7.361560	-0.522316	0.085272
H	-8.201482	1.387447	-1.231745
H	-7.898437	3.890288	2.262863
H	-7.056432	1.985786	3.556903
C	-3.447801	1.405843	-2.470401
C	-4.726378	1.002208	-2.844811
C	-5.752659	1.932091	-2.969957
C	-5.499166	3.287525	-2.727100
C	-4.211434	3.688694	-2.355383
C	-3.191119	2.750773	-2.225369
H	-2.652142	0.674397	-2.368005
H	-4.931097	-0.046096	-3.038237
H	-6.757596	1.621355	-3.259803
H	-3.984687	4.731803	-2.160966
H	-2.197356	3.073423	-1.931416
C	-7.074986	5.752443	-7.291185
C	-5.881768	5.259969	-6.768797
C	-5.822750	4.847819	-5.442453
C	-6.961230	4.928465	-4.636506
C	-8.159584	5.418510	-5.161026
C	-8.209324	5.831120	-6.488470
H	-7.122653	6.064593	-8.329829
H	-5.000129	5.185680	-7.397013
H	-4.898003	4.442495	-5.043344
H	-9.057428	5.396547	-4.553482
H	-9.145546	6.192958	-6.900992
C	-8.413206	3.926163	-2.301182
B	-9.403111	2.814826	-3.025562
O	-8.687854	1.694140	-3.689783
C	-9.260137	1.446776	-4.960814
C	-10.537173	2.379466	-4.988296
O	-10.184423	3.428498	-4.113358

H -10.127946 2.364204 -2.121140
C -8.225030 1.820178 -6.030459
H -7.998222 2.886927 -6.003322
H -8.560788 1.558904 -7.039693
H -7.298322 1.273650 -5.827471
C -9.576368 -0.045023 -5.085234
H -8.644392 -0.619064 -5.066232
H -10.198070 -0.386035 -4.255398
H -10.091543 -0.267706 -6.026595
C -10.849923 2.968030 -6.362603
H -11.738075 3.603737 -6.292404
H -10.022711 3.579839 -6.727900
H -11.053427 2.179049 -7.094979
C -11.796398 1.680104 -4.449471
H -12.586072 2.429926 -4.343434
H -12.153052 0.893778 -5.122410
H -11.614670 1.246686 -3.463544

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -2176.73043812 | Predicted change in Energy=-1.901628D-08
Zero-point correction (ZPE) = -2176.07086712 0.659571
Internal Energy (U) = -2176.0350641200002 0.695374
Enthalpy (H) = -2176.0341201200004 0.696318
Gibbs Free Energy (G) = -2176.13843312 0.592005

Frequencies
15.7187 26.1060 32.6312
37.6438 40.5011 47.5705
49.4583 62.7102 66.3587
68.9857 80.0593 90.9624
98.3959 110.0869 121.8893
132.5508 148.6245 158.5617
176.0354 184.6473 206.4838
220.2676 234.0340 238.8065
249.0649 254.2662 259.3151
264.0901 268.7681 270.7894
290.3224 297.6174 311.7399
321.8771 323.6460 359.4008
370.9405 378.4785 382.8850
402.8332 409.5798 411.3017
413.3798 416.9427 419.2963
423.4383 439.5604 450.0523
470.2650 477.1726 493.9535
496.9123 509.8296 520.1744
529.9209 533.2229 576.7635
584.5254 633.4953 633.8539

635.4461 636.6361 649.1647
672.0599 677.6596 703.9290
710.7341 714.3995 719.2477
725.8910 729.1805 732.2523
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769.2014 774.9197 780.3619
781.2400 814.6560 869.9078
875.4978 879.3886 882.3682
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1002.1006 1006.7063 1009.2860
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1146.0432 1150.9369 1153.5461
1155.2497 1188.5127 1193.2172
1198.6738 1198.8033 1199.6892
1199.9517 1219.5495 1224.9096
1230.8914 1232.2901 1236.6998
1242.9077 1263.6027 1266.7909
1273.6591 1283.3659 1307.0022
1319.8272 1335.6458 1339.4659
1342.0810 1343.2070 1348.5980
1374.9627 1376.6994 1379.6040
1390.2168 1390.6356 1410.0113
1411.4163 1422.2489 1431.9062
1465.4761 1485.5642 1487.5037
1490.3024 1491.3593 1493.5277
1494.4132 1498.5490 1501.2290
1501.7084 1519.7281 1521.2936
1523.6374 1526.6810 1544.3157
1544.7123 1546.8284 1548.1886
1551.4910 1661.8465 1662.9433
1665.6422 1666.9836 1682.7818
1683.7049 1684.2098 1684.6091
2272.0607 3056.5505 3059.9856
3062.4420 3066.1022 3067.4748
3089.3217 3093.4828 3118.9468
3128.3900 3134.3555 3135.9786
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3151.8147 3164.6015 3170.1086
3170.4492 3196.1230 3203.1194
3205.6585 3206.0687 3207.4755
3212.5796 3215.1119 3216.1979
3216.6832 3221.0649 3223.2033
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TS 6–7

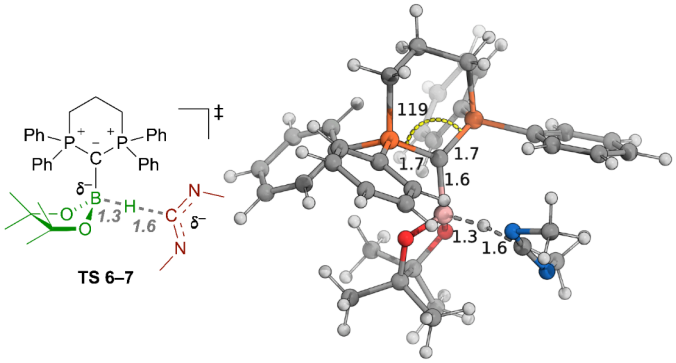

Fig. S13 Three dimensional picture of structure **TS 6–7** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250,ts,calcfc,noeigentest) freq=noraman

---
Full point group C1 NOp 1
Stoichiometry C37H45BN2O2P2 Framework group C1[X(C37H45BN2O2P2)]

Num atoms: 89
Charge = 0 Multiplicity = 1

SCF = -2404.05105682 | Predicted change in Energy=-3.781023D-09

Optimization completed.
Maximum Force 0.000012 0.000450 YES
RMS Force 0.000001 0.000300 YES
Maximum Displacement 0.000966 0.001800 YES
RMS Displacement 0.000162 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

P 1.577948 -0.177339 -1.119952
C 1.829631 0.520606 -2.813785
C 0.978071 1.733982 -3.194942
C -0.519784 1.449567 -3.056834
P -1.000988 1.217926 -1.305581
H 1.609354 -0.304504 -3.498781
H 2.895180 0.745633 -2.916660
H 1.199661 1.995971 -4.234607
H 1.244839 2.610272 -2.593747
H -1.116629 2.259768 -3.482322

H -0.793677 0.531156 -3.586473
C -5.403250 -0.064498 -1.595594
C -4.376382 -0.943952 -1.928713
C -3.051425 -0.544387 -1.807001
C -2.750797 0.741141 -1.348897
C -3.780561 1.616668 -0.999479
C -5.105610 1.211905 -1.126775
H -6.437548 -0.380820 -1.685395
H -4.603360 -1.949963 -2.264879
H -2.248464 -1.248141 -2.006529
H -3.552261 2.605780 -0.617216
H -5.904810 1.890802 -0.848076
C -0.646337 5.468000 0.474817
C -0.210178 4.355044 1.185809
C -0.348287 3.079551 0.646055
C -0.926554 2.912391 -0.613724
C -1.375709 4.034970 -1.320830
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H -0.533841 6.462389 0.895460
H 0.239445 4.473190 2.166683
H -0.037613 2.199993 1.201552
H -1.848236 3.926394 -2.292906
H -1.582947 6.172407 -1.332898
C 4.703710 1.880646 1.585701
C 4.672804 0.491505 1.519370
C 3.758272 -0.151451 0.690046
C 2.872376 0.595361 -0.086067
C 2.900845 1.991359 -0.006306
C 3.813836 2.631979 0.821968
H 5.412176 2.377993 2.240341
H 5.350766 -0.098367 2.127756
H 3.712109 -1.234368 0.669726
H 2.183069 2.586463 -0.563011
H 3.820411 3.715469 0.881013
C 2.807376 -4.535332 -1.915799
C 3.730539 -3.508045 -2.104027
C 3.366275 -2.194773 -1.833352
C 2.076962 -1.905681 -1.369550
C 1.151302 -2.931517 -1.188179
C 1.525532 -4.244285 -1.462028
H 3.092356 -5.562180 -2.123997
H 4.732145 -3.729439 -2.458620
H 4.093770 -1.398871 -1.972455
H 0.141424 -2.736317 -0.832337
H 0.799917 -5.036537 -1.308842
C -0.012962 0.060376 -0.554749
B -0.365752 -0.592062 0.901952
O -0.705839 0.311977 1.994174

C 0.057836 -0.032798 3.143825
C 0.636894 -1.452167 2.789751
O 0.732273 -1.401993 1.373058
C 1.156421 1.023995 3.319818
H 1.825044 1.041372 2.455532
H 1.753922 0.851110 4.220530
H 0.687052 2.009065 3.413355
C -0.855502 -0.017508 4.367423
H -1.220581 0.999448 4.540095
H -0.318411 -0.344741 5.264594
H -1.720678 -0.665857 4.219691
C 2.021215 -1.732060 3.366786
H 2.355652 -2.720814 3.038852
H 2.753748 -0.995250 3.035697
H 1.992283 -1.728260 4.461660
C -0.302253 -2.598665 3.184919
H 0.049377 -3.512463 2.698250
H -1.328590 -2.425657 2.856950
H -0.304489 -2.758023 4.268074
H -1.443288 -1.337145 0.672594
C -2.458387 -2.502130 0.524353
N -1.936290 -3.226887 -0.366494
N -3.361356 -2.312127 1.368838
C -3.806609 -1.001044 1.773173
H -4.557000 -0.599391 1.079821
H -4.266071 -1.062358 2.764388
H -2.966786 -0.294747 1.817665
C -2.826787 -4.149424 -1.051158
H -3.888521 -3.951439 -0.847107
H -2.659553 -4.096989 -2.134632
H -2.617703 -5.181357 -0.741927

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -2404.05105682 | Predicted change in Energy=-3.781023D-09
Zero-point correction (ZPE) = -2403.30071682 0.75034
Internal Energy (U) = -2403.25816182 0.792895
Enthalpy (H) = -2403.2572178200003 0.793839
Gibbs Free Energy (G) = -2403.3748878200004 0.676169

Frequencies
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73.8074 79.9576 87.3702
96.8806 100.3536 107.5682

110.4519 114.8543 134.7542
144.2844 155.0872 160.9785
166.1357 172.0338 178.2758
189.2438 203.9430 209.9516
216.0416 228.2459 230.9675
238.4259 247.0093 253.3971
262.8466 268.2606 268.6115
275.3414 297.0359 305.0142
317.0435 324.6999 331.1417
353.4934 358.3133 372.8103
376.4657 394.3096 398.2398
409.4913 413.5805 413.7393
421.0237 422.1522 427.4710
432.5388 442.8440 448.2552
481.1979 490.1263 501.0452
503.6188 514.0330 519.6859
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635.7686 636.4940 637.1726
661.2188 677.9784 699.5856
713.7274 714.6556 716.4501
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843.8286 875.2666 876.6677
881.1391 884.9133 887.0125
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959.3658 966.6856 968.5543
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1007.1857 1008.8568 1011.9442
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1021.3033 1022.1116 1022.3490
1023.7934 1027.6437 1032.7100
1032.9751 1033.1894 1042.7448
1055.5547 1059.4725 1065.7246
1066.6613 1068.0017 1068.5599
1071.5157 1082.6499 1111.6201
1120.3834 1122.8830 1124.0481
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1151.2549 1152.8018 1154.3219
1167.8373 1172.7036 1195.0629
1196.3180 1197.2334 1198.4734
1198.6855 1199.6760 1211.4687
1222.8720 1226.3947 1230.6220
1233.8808 1238.0512 1248.6893

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1312.4856	1324.8165	1337.5425
1339.0376	1341.1424	1342.9373
1345.0520	1350.0322	1371.5697
1376.0767	1376.8950	1382.4873
1389.9252	1408.2672	1419.2872
1426.0967	1437.6408	1453.8109
1468.2000	1476.4105	1483.2765
1488.5912	1489.5239	1490.9794
1494.0331	1494.5851	1498.1483
1502.5123	1505.1954	1507.2683
1515.2567	1517.8364	1519.9856
1523.9917	1526.1801	1528.9349
1530.6255	1541.6537	1544.3140
1546.2702	1547.1002	1551.1273
1662.8892	1664.9855	1666.1521
1667.5942	1681.9433	1683.4028
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3083.2846	3086.0583	3094.2182
3099.4707	3120.5098	3120.5911
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3170.5692	3172.0918	3180.2202
3184.5337	3186.5681	3195.6872
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3219.3239	3222.2828	3224.3586
3225.6669	3225.9264	3229.8114
3233.5920	3234.4971	3235.3119
3235.6870	3240.7434	3247.8666

7

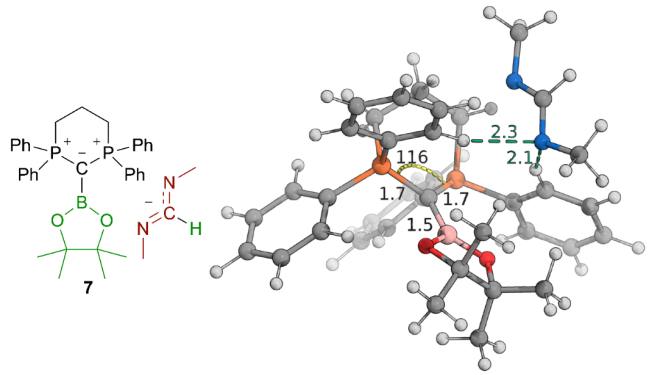

Fig. S14 Three dimensional picture of structure **7** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman

---
Full point group C1 NOp 1
Stoichiometry C37H45BN2O2P2 Framework group C1[X(C37H45BN2O2P2)]

Num atoms: 89
Charge = 0 Multiplicity = 1

SCF = -2404.11144041 | Predicted change in Energy=-3.476490D-09

Optimization completed.
Maximum Force 0.000013 0.000450 YES
RMS Force 0.000002 0.000300 YES
Maximum Displacement 0.001475 0.001800 YES
RMS Displacement 0.000271 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

P 1.328561 -1.246013 -0.542761
C 1.937846 -0.821084 -2.213399
C 0.848213 -0.073421 -2.997279
C 0.494503 1.336928 -2.486368
P 0.887654 1.649603 -0.735682
H 2.200201 -1.759609 -2.710546
H 2.847220 -0.216668 -2.126900
H -0.085262 -0.647350 -2.980281
H 1.162247 -0.003850 -4.041890

H 0.951147 2.127754 -3.087694
H -0.609155 1.401151 -2.542206
C -1.977048 4.926050 0.683695
C -2.460501 3.708740 0.211106
C -1.583954 2.719631 -0.216162
C -0.207901 2.966978 -0.172133
C 0.283783 4.181067 0.310810
C -0.606050 5.161514 0.737218
H -2.669380 5.693324 1.017234
H -3.526843 3.510651 0.178699
H -1.997313 1.754519 -0.523709
H 1.351913 4.364324 0.363305
H -0.226761 6.106035 1.113695
C 5.241470 3.196116 -0.623241
C 4.333356 3.763686 -1.515367
C 3.019139 3.313645 -1.550351
C 2.599598 2.294476 -0.687635
C 3.511974 1.738605 0.210708
C 4.830229 2.185565 0.239213
H 6.268970 3.545013 -0.601694
H 4.650777 4.555648 -2.185780
H 2.317256 3.768176 -2.243793
H 3.181919 0.950695 0.881295
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C 4.779181 -3.135568 1.861664
C 3.467574 -3.207104 2.325133
C 2.430662 -2.656240 1.582294
C 2.703696 -2.026545 0.361369
C 4.021293 -1.954498 -0.098058
C 5.055152 -2.508766 0.651201
H 5.585923 -3.568125 2.444828
H 3.250057 -3.693108 3.270585
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H 4.255202 -1.468586 -1.039139
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C -1.924614 -4.397857 -1.229158
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C 0.060985 -2.515472 -0.757904
C -1.266099 -2.104410 -0.879527
C -2.256187 -3.053224 -1.115849
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H -0.337619 -5.858105 -1.194484
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H -3.281596 -2.709058 -1.201091
C 0.737559 0.200782 0.191968
B -0.056296 0.096383 1.486592

O -0.711804 1.128607 2.102659
C -1.358138 0.615804 3.278341
C -1.364029 -0.936625 3.025130
O -0.227254 -1.106437 2.150996
C -0.500871 1.033589 4.473246
H 0.498321 0.592880 4.411397
H -0.957435 0.737448 5.422064
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C -2.740783 1.248327 3.360066
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C -1.150432 -1.787378 4.268748
H -1.157651 -2.845300 3.992368
H -0.197342 -1.565189 4.752625
H -1.957134 -1.620833 4.989465
C -2.591301 -1.415596 2.251718
H -2.439591 -2.459915 1.965080
H -3.496410 -1.351868 2.863183
H -2.736502 -0.834977 1.333704
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C -3.442850 0.270864 -2.031303
N -2.354055 0.296354 -2.769975
N -3.457838 0.236549 -0.712410
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H -4.927286 -0.504205 0.612077
H -4.879011 1.249290 0.487823
C -2.555706 0.249738 -4.195151
H -3.607206 0.396294 -4.504502
H -1.965107 1.027999 -4.706143
H -2.231742 -0.711319 -4.631058

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -2404.11144041 | Predicted change in Energy=-3.476490D-09
Zero-point correction (ZPE) = -2403.35837941 0.753061
Internal Energy (U) = -2403.3147544099998 0.796686
Enthalpy (H) = -2403.31380941 0.797631
Gibbs Free Energy (G) = -2403.43706941 0.674371

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127.5897 132.9927 144.8128
155.2010 158.5004 181.4157
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221.8983 230.9600 236.0317
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284.9273 291.2738 305.8629
308.1375 319.0110 323.7983
330.8365 354.3266 361.7876
376.4202 394.3884 404.4159
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417.0758 419.7930 423.1048
453.7326 467.9313 475.1670
489.9714 493.3464 500.7259
521.2449 527.3231 530.1636
534.9317 542.5201 585.7574
594.0550 600.9858 631.8967
633.2881 635.6495 635.9046
662.5144 680.7718 695.4574
707.9794 713.8328 714.7278
715.8388 721.3571 734.3038
743.8408 745.1184 753.7175
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779.9905 797.6915 827.6339
858.7731 879.0610 883.0492
885.4723 888.2303 888.5768
899.9679 952.3841 952.8355
956.8419 957.6785 964.9467
966.7691 969.2660 987.0952
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1017.7256 1020.3936 1022.5787
1023.5427 1024.0534 1027.5733
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1065.4247 1066.5507 1068.1473
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1127.0307 1127.7223 1129.5021
1139.5383 1146.0329 1147.2937
1151.4053 1152.6182 1153.9529
1164.9409 1165.6015 1175.0228
1181.7839 1194.2289 1197.2310

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1316.3948	1326.8272	1335.8652
1336.7291	1343.6644	1344.1921
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1372.6206	1377.9779	1381.1999
1383.9214	1399.9634	1413.1610
1420.5435	1427.1836	1435.2937
1448.8539	1452.1526	1458.6479
1464.8833	1474.8001	1482.4705
1488.7608	1489.8316	1489.8889
1493.5704	1494.3158	1495.0281
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1509.2574	1524.9954	1527.5425
1527.8162	1530.9490	1533.8286
1534.4924	1537.0126	1541.9888
1545.4172	1546.7792	1556.4411
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1665.8916	1678.5033	1679.7763
1683.6592	1685.5005	1702.2754
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2947.2440	2986.4881	2992.6664
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3065.8462	3069.2500	3071.7399
3078.6334	3083.1394	3102.8782
3125.3990	3141.1746	3141.9309
3146.2913	3147.4458	3149.0707
3152.9244	3155.3056	3160.4136
3169.9938	3179.1312	3199.4827
3203.8316	3205.4659	3207.6504
3210.3183	3212.9459	3213.9392
3219.3209	3220.9602	3223.0762
3227.6976	3229.4767	3229.8617
3231.1451	3235.8118	3237.7019
3237.9987	3238.5909	3241.7775

TS 7–8

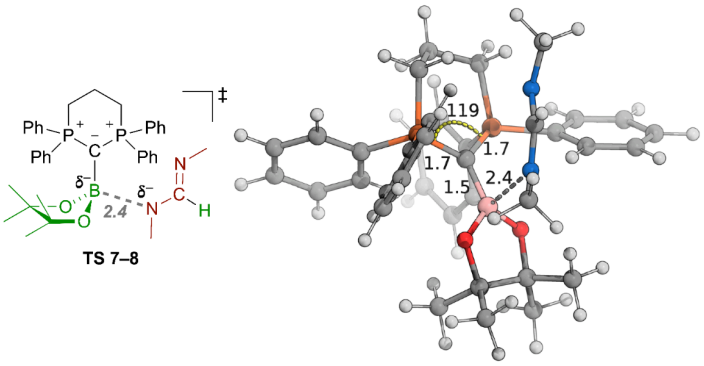

Fig. S15 Three dimensional picture of structure **TS 7–8** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250,ts,calcfc,noeigentest) freq=noraman

---

Full point group C1 NOp 1
Stoichiometry C37H45BN2O2P2 Framework group C1[X(C37H45BN2O2P2)]

Num atoms: 89
Charge = 0 Multiplicity = 1

SCF = -2404.10785304 | Predicted change in Energy=-2.543225D-08

Optimization completed.
Maximum Force 0.000026 0.000450 YES
RMS Force 0.000004 0.000300 YES
Maximum Displacement 0.001622 0.001800 YES
RMS Displacement 0.000336 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

P -1.384145 -0.138112 -1.287264
C -0.929915 -0.554807 -3.003127
C 0.325038 0.157015 -3.524124
C 1.577070 -0.242190 -2.734486
P 1.511635 0.347120 -1.009032
H -1.795711 -0.375529 -3.646993
H -0.752121 -1.633240 -2.944182
H 0.201996 1.247107 -3.510230

H 0.471761 -0.127369 -4.570812
H 1.634716 -1.332146 -2.676710
H 2.482952 0.153357 -3.202111
C 2.250794 4.891760 -1.397349
C 1.066734 4.416152 -0.845642
C 0.861711 3.045023 -0.712899
C 1.839342 2.145888 -1.135995
C 3.033159 2.629769 -1.682794
C 3.237010 3.997361 -1.813375
H 2.411879 5.960222 -1.501281
H 0.297376 5.107458 -0.517490
H -0.056093 2.661053 -0.279163
H 3.812517 1.937253 -1.990461
H 4.165280 4.368462 -2.235754
C 5.196751 -1.292775 1.201969
C 4.648316 -0.066229 1.565273
C 3.539889 0.427692 0.889360
C 2.971596 -0.307088 -0.154538
C 3.522344 -1.538539 -0.513805
C 4.633154 -2.027340 0.163652
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H 5.079997 0.505368 2.380240
H 3.105969 1.376435 1.183364
H 3.064843 -2.138249 -1.291554
H 5.048734 -2.990085 -0.114167
C -4.648457 -3.200386 -0.256893
C -3.382182 -3.344136 0.302516
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C -2.653065 -1.342946 -0.807927
C -3.927595 -1.190290 -1.363225
C -4.923381 -2.121858 -1.092527
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H -3.168540 -4.181249 0.959274
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H -4.152828 -0.337908 -1.998592
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C -2.424940 2.227880 -2.494853
C -3.009999 3.491865 -2.431770
H -3.924743 4.971103 -1.169294
H -3.718993 3.591838 0.885780
H -2.655550 1.352944 0.776462
H -2.068836 1.860941 -3.452123
H -3.101563 4.087905 -3.334106
C 0.002818 0.014430 -0.290086

B -0.106795 -0.245426 1.223346
O -1.380337 -0.267132 1.799410
C -1.239245 -0.186143 3.218002
C 0.182749 0.473082 3.374331
O 0.854030 0.109116 2.165805
C -2.386716 0.655007 3.769414
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C -1.341409 -1.607799 3.770670
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H -1.243328 -1.632095 4.860085
H -0.585856 -2.248659 3.317753
C 0.132433 2.004646 3.394413
H 1.153955 2.387878 3.322084
H -0.428982 2.384284 2.535021
H -0.319932 2.393100 4.311676
C 0.988505 -0.042174 4.559107
H 1.968944 0.442307 4.573628
H 0.480341 0.181480 5.503014
H 1.144314 -1.119345 4.486316
H 1.687237 -4.011725 -0.029694
C 0.937520 -3.184721 -0.083530
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N 0.720190 -2.523800 1.042004
C 1.641286 -2.850396 2.106547
H 2.353229 -3.648473 1.834238
H 2.234123 -1.970362 2.392855
H 1.124955 -3.192963 3.017338
C 0.686392 -3.951058 -2.266468
H -0.176466 -4.599563 -2.489242
H 0.956658 -3.473775 -3.225655
H 1.525760 -4.623927 -2.001430

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -2404.10785304 | Predicted change in Energy=-2.543225D-08
Zero-point correction (ZPE) = -2403.35358504 0.754268
Internal Energy (U) = -2403.31148804 0.796365
Enthalpy (H) = -2403.31054404 0.797309
Gibbs Free Energy (G) = -2403.42735304 0.6805

Frequencies
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103.2876 108.2357 112.4907
129.9955 138.5002 148.8436
153.1826 156.8770 164.1436
175.9231 191.8239 195.3562
213.7338 218.2318 221.7252
226.2947 237.2244 242.7105
244.4393 256.4063 268.6980
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3238.4977 3244.3483 3250.9709

8

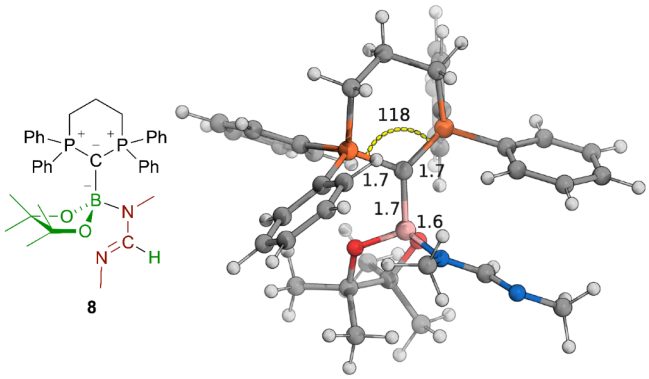

Fig. S16 Three dimensional picture of structure **8** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman

---

Full point group C1 NOp 1
Stoichiometry C37H45BN2O2P2 Framework group C1[X(C37H45BN2O2P2)]

Num atoms: 89
Charge = 0 Multiplicity = 1

SCF = -2404.14413436 | Predicted change in Energy=-1.080333D-08

Optimization completed.
Maximum Force 0.000032 0.000450 YES
RMS Force 0.000003 0.000300 YES
Maximum Displacement 0.001215 0.001800 YES
RMS Displacement 0.000205 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

P 1.211131 0.337442 -1.394330
C 0.903676 0.768045 -3.159313
C -0.406116 1.525954 -3.388893
C -1.622563 0.682116 -2.989895
P -1.696430 0.380133 -1.184706
H 0.896855 -0.160920 -3.736899
H 1.758642 1.356619 -3.504177
H -0.481313 1.790059 -4.448692
H -0.396112 2.469041 -2.829324

H -2.561602 1.135112 -3.317060
H -1.572922 -0.307591 -3.455872
C -5.012343 -2.755107 -0.678917
C -3.730418 -3.128665 -1.069897
C -2.740760 -2.164549 -1.208866
C -3.028568 -0.823865 -0.948559
C -4.315610 -0.449930 -0.553548
C -5.305109 -1.417957 -0.422206
H -5.781689 -3.510824 -0.555808
H -3.482179 -4.172661 -1.222784
H -1.727122 -2.454329 -1.466113
H -4.540703 0.588773 -0.334698
H -6.302069 -1.129066 -0.105751
C -3.177377 4.332560 0.731038
C -2.739503 3.268782 1.515781
C -2.315946 2.084688 0.923781
C -2.327495 1.952045 -0.470792
C -2.775701 3.021533 -1.252385
C -3.195455 4.206456 -0.653571
H -3.502565 5.257709 1.196559
H -2.720021 3.360072 2.597370
H -1.939110 1.264709 1.533622
H -2.801594 2.952900 -2.334434
H -3.535278 5.030266 -1.273043
C 2.881455 4.316845 0.233211
C 3.596561 3.641279 -0.754191
C 3.129724 2.426175 -1.242625
C 1.948263 1.875448 -0.737447
C 1.239092 2.554304 0.250951
C 1.702164 3.774256 0.733490
H 3.247039 5.266257 0.611499
H 4.518632 4.061652 -1.142659
H 3.697423 1.900198 -2.006058
H 0.334280 2.105643 0.646851
H 1.141242 4.293563 1.504072
C 4.512746 -2.868861 -1.652801
C 3.356567 -2.981251 -2.418294
C 2.377100 -1.997553 -2.341797
C 2.548767 -0.893174 -1.505324
C 3.703630 -0.793667 -0.728637
C 4.683111 -1.775904 -0.807198
H 5.275380 -3.639283 -1.705509
H 3.208824 -3.840919 -3.063411
H 1.457015 -2.120114 -2.905733
H 3.818753 0.034824 -0.039961
H 5.574786 -1.695403 -0.194085
C -0.202934 -0.198564 -0.609324
B 0.042243 -0.875990 0.903464

O -0.647906 -0.179228 1.993764
C 0.206206 -0.091957 3.123901
C 1.631791 -0.583548 2.592651
O 1.465249 -0.669752 1.192750
C 0.188495 1.367326 3.596551
H -0.842621 1.646509 3.836981
H 0.794913 1.512788 4.495821
H 0.550341 2.046737 2.823436
C -0.363126 -0.957248 4.254229
H 0.263647 -0.908731 5.151141
H -1.360279 -0.589928 4.515561
H -0.460811 -2.000639 3.952683
C 2.774105 0.398135 2.865411
H 3.699352 -0.010231 2.446588
H 2.592632 1.367262 2.396303
H 2.930748 0.546960 3.938748
C 2.049114 -1.964195 3.122316
H 2.972852 -2.258073 2.614807
H 2.236609 -1.952624 4.201002
H 1.293406 -2.718543 2.899969
N -0.335506 -2.380039 0.929972
C 0.481637 -3.328807 0.210511
H 0.485510 -4.291003 0.730419
H 0.108750 -3.519949 -0.809809
H 1.499318 -2.940640 0.140300
C -1.475481 -2.849267 1.488552
N -1.870565 -4.072619 1.420606
H -2.045573 -2.073833 2.016332
C -3.098989 -4.370032 2.115917
H -3.847474 -4.778164 1.421201
H -2.935287 -5.137808 2.884117
H -3.559951 -3.496370 2.611668

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -2404.14413436 | Predicted change in Energy=-1.080333D-08
Zero-point correction (ZPE) = -2403.38729936 0.756835
Internal Energy (U) = -2403.34542336 0.798711
Enthalpy (H) = -2403.34447936 0.799655
Gibbs Free Energy (G) = -2403.46131436 0.68282

Frequencies
14.7667 19.4622 23.0968
35.9309 42.2582 48.2713

54.9164 55.3934 57.5912
63.9658 74.0278 79.1615
89.2631 94.6646 101.0348
110.4462 119.4389 122.1693
140.2732 145.5218 159.7807
164.1769 174.1657 189.8269
198.1243 205.2180 222.4022
224.2690 229.6952 234.9262
240.0158 245.2825 260.7967
265.2422 271.3363 275.7697
283.8846 294.5432 296.5837
307.0424 310.5428 316.2148
331.1875 344.0595 358.5350
363.1560 375.1235 398.2663
401.7117 409.1927 413.2553
415.1449 417.6719 424.1192
431.8865 434.0585 446.0358
461.7674 470.0237 481.1402
485.7570 488.7759 494.0671
504.3731 518.3057 526.6003
529.9692 548.5713 578.6937
606.0998 635.0729 635.8241
636.5363 637.2369 659.5543
677.5170 699.9316 709.2821
713.4289 714.9874 719.7536
723.3220 728.7957 736.5792
738.5603 744.1261 766.1240
771.8687 773.4797 777.9805
788.6703 818.8443 859.1442
874.1300 874.7956 878.6353
887.3697 889.5124 897.8653
918.3046 931.3860 938.5764
951.4574 953.3923 960.1345
964.5515 964.5617 969.4094
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1003.8274 1011.9961 1014.7182
1016.2524 1017.4343 1020.0988
1021.1774 1022.5479 1024.0434
1024.6599 1027.0951 1028.4141
1029.2583 1045.9881 1049.2656
1054.2601 1057.0249 1067.0442
1067.3549 1068.0689 1070.1431
1071.7918 1077.6710 1106.1703
1117.2400 1125.7315 1126.2208
1131.1101 1133.4466 1136.3142
1147.2951 1148.9648 1152.1292
1153.1413 1157.1396 1161.8542
1163.3684 1185.3190 1195.7311

1197.4952	1199.4447	1200.0414
1200.7057	1213.0785	1219.6804
1225.3316	1229.3074	1233.5106
1247.5087	1260.6499	1262.1553
1271.9600	1275.8973	1290.4425
1324.6117	1338.5235	1339.7137
1343.1339	1346.7519	1352.7963
1371.4073	1374.7549	1375.9058
1391.4765	1394.3756	1396.2847
1410.8914	1416.5962	1423.7697
1433.5850	1437.7731	1461.2447
1466.4687	1471.3711	1485.0398
1486.7200	1491.1964	1491.7156
1493.7702	1494.9220	1496.6204
1497.1740	1503.7208	1505.9937
1507.4993	1516.3920	1519.4892
1520.4999	1526.7967	1528.5074
1530.2196	1541.2901	1544.2631
1547.1824	1554.6243	1555.1146
1662.3054	1666.1178	1666.5355
1669.4553	1684.8471	1684.9016
1685.8169	1687.0406	1742.3572
2959.2031	2984.8504	3040.6597
3059.9704	3062.7874	3065.4223
3065.6842	3068.9737	3070.3964
3076.5557	3090.5882	3094.7672
3104.3158	3119.2335	3132.3235
3136.8467	3140.4994	3145.1844
3149.2032	3153.6253	3163.6259
3171.3406	3172.9187	3180.1735
3183.7099	3189.6823	3200.1131
3206.0764	3207.3945	3211.3085
3211.5019	3214.2393	3218.2230
3223.3579	3223.5741	3225.9418
3227.9632	3228.9025	3233.9024
3235.3943	3236.7125	3238.1150
3243.4315	3247.5656	3253.1147

TS 8–1

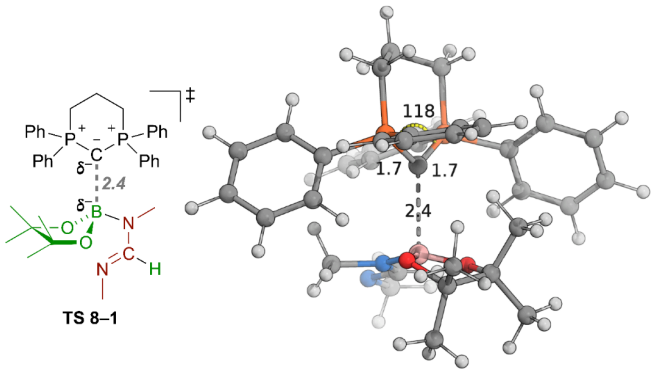

Fig. S17 Three dimensional picture of structure **TS 8–1** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250,ts,calcfc,noeigentest) freq=noraman

---
Full point group C1 NOp 1
Stoichiometry C37H45BN2O2P2 Framework group C1[X(C37H45BN2O2P2)]

Num atoms: 89
Charge = 0 Multiplicity = 1

SCF = -2404.11936675 | Predicted change in Energy=-2.719210D-10

Optimization completed.
Maximum Force 0.000001 0.000450 YES
RMS Force 0.000000 0.000300 YES
Maximum Displacement 0.000194 0.001800 YES
RMS Displacement 0.000035 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

P 1.233858 0.200822 -1.521441
C 1.030740 -0.190025 -3.316046
C 0.308006 -1.537297 -3.468465
C -1.156351 -1.449424 -3.019757
P -1.361452 -0.962236 -1.235626
H 2.018750 -0.215345 -3.784237
H 0.444801 0.593564 -3.807601
H 0.844780 -2.306547 -2.899531
H 0.338390 -1.845866 -4.518659

H -1.669046 -0.680121 -3.606822
H -1.689836 -2.386680 -3.202888
C -2.304656 -4.822018 1.129709
C -2.769989 -3.592526 1.586036
C -2.516573 -2.433102 0.861109
C -1.813124 -2.496012 -0.345805
C -1.340749 -3.733681 -0.791969
C -1.581586 -4.890187 -0.057462
H -2.496047 -5.723965 1.702329
H -3.316163 -3.530690 2.521979
H -2.820308 -1.469029 1.255693
H -0.766081 -3.804125 -1.710975
H -1.204706 -5.843784 -0.413098
C -5.209953 1.597583 -1.640902
C -3.950624 2.111036 -1.942465
C -2.824397 1.311659 -1.793641
C -2.934615 -0.007627 -1.343824
C -4.203708 -0.522945 -1.075684
C -5.333908 0.279783 -1.214845
H -6.091687 2.222442 -1.742128
H -3.845066 3.136826 -2.281022
H -1.838579 1.716734 -2.007135
H -4.318205 -1.550689 -0.749354
H -6.313543 -0.128746 -0.987808
C 2.393815 4.648672 -1.076243
C 2.886569 3.697505 -0.187200
C 2.581176 2.353028 -0.364463
C 1.779212 1.943140 -1.432488
C 1.283009 2.905294 -2.315028
C 1.592158 4.250494 -2.142393
H 2.631338 5.698635 -0.937231
H 3.504492 4.002006 0.651193
H 2.962043 1.618162 0.336237
H 0.639505 2.615691 -3.140339
H 1.203175 4.987767 -2.837437
C 4.955708 -2.389956 -0.648192
C 3.701344 -2.761185 -0.178918
C 2.599845 -1.946088 -0.424224
C 2.748287 -0.755892 -1.130041
C 4.014055 -0.384255 -1.597830
C 5.112997 -1.198976 -1.357804
H 5.817380 -3.020959 -0.452882
H 3.578167 -3.666511 0.405139
H 1.616203 -2.206866 -0.045010
H 4.142346 0.549249 -2.139700
H 6.094285 -0.904503 -1.716567
C -0.078652 -0.146565 -0.561101
B -0.001970 0.308892 1.839501

O -1.383083 0.260811 2.047769
C -1.780060 1.556343 2.514702
C -0.631552 2.499033 1.988171
O 0.486471 1.609804 1.899021
C -3.165019 1.871287 1.964689
H -3.890622 1.159800 2.370123
H -3.478824 2.878820 2.257424
H -3.187943 1.796746 0.876914
C -1.830072 1.476672 4.043979
H -2.520366 0.678604 4.330135
H -0.845848 1.232736 4.453306
H -2.176765 2.412564 4.492198
C -0.903906 3.067505 0.598039
H -0.023829 3.621617 0.262202
H -1.076451 2.250283 -0.100862
H -1.763653 3.744528 0.597840
C -0.259513 3.632536 2.938310
H 0.556752 4.213029 2.499397
H -1.110729 4.303593 3.094442
H 0.074965 3.255679 3.906238
N 0.864518 -0.777814 2.275418
C 0.339753 -2.099916 2.551904
H -0.705359 -2.010639 2.846800
H 0.393579 -2.759876 1.676014
H 0.920763 -2.558302 3.354426
C 2.208148 -0.573474 2.435781
N 3.030335 -1.486717 2.780104
H 2.509966 0.465523 2.253357
C 4.410577 -1.085527 2.910012
H 4.776486 -1.301678 3.921015
H 5.032108 -1.659873 2.211852
H 4.587890 -0.014446 2.708095

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -2404.11936675 | Predicted change in Energy=-2.719210D-10
Zero-point correction (ZPE) = -2403.36376475 0.755602
Internal Energy (U) = -2403.32176075 0.797606
Enthalpy (H) = -2403.32081675 0.79855
Gibbs Free Energy (G) = -2403.4372767500004 0.68209

Frequencies
-111.7954 17.9957 20.3822
32.1949 38.2875 43.4982

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79.7988 86.7771 94.8388
96.0170 105.0874 109.2919
122.8283 125.3331 145.0752
148.9749 161.6991 184.1585
193.0304 196.9479 203.2101
221.4848 230.4517 231.6123
240.0248 241.1447 249.3552
251.5669 258.0167 266.6634
267.1673 276.9408 279.2600
292.8744 299.3338 311.6843
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636.0734 636.9536 637.4417
650.9360 682.7886 686.2562
713.3637 716.2452 719.8740
720.8156 727.6296 728.1642
731.6383 734.5597 737.8681
766.9916 772.7063 773.0192
775.3529 810.1666 825.5389
858.4242 872.0946 874.5357
880.6573 885.5423 886.7096
894.6683 920.9240 940.6925
942.9916 948.2737 951.4748
955.6212 963.7897 967.7996
992.0441 996.9824 998.1650
1003.2938 1005.5476 1013.5167
1014.2971 1017.9188 1020.9501
1023.2952 1023.9997 1024.8471
1025.3681 1026.7556 1029.1972
1031.1872 1033.2798 1037.8873
1058.8993 1064.5477 1065.1008
1066.7294 1068.7000 1070.4637
1105.3204 1108.1381 1118.7669
1120.2635 1125.7733 1128.7305
1137.5249 1143.0796 1149.0332
1151.9020 1154.2742 1160.6282
1164.8502 1167.0852 1178.6887
1192.8502 1195.9614 1196.3824

1197.7392	1199.2324	1201.5009
1215.8925	1218.7991	1220.5393
1223.9537	1228.7460	1236.9978
1264.9565	1267.0697	1283.9838
1308.5165	1309.2311	1313.2114
1332.0643	1333.5507	1338.0152
1341.2503	1342.8800	1365.9116
1368.2918	1370.3128	1377.9679
1379.9400	1389.6965	1417.1193
1417.7469	1418.0937	1428.9536
1438.0376	1449.1998	1464.4707
1467.7343	1476.9202	1484.1735
1485.2762	1488.6137	1490.1095
1494.1997	1494.6553	1496.9545
1498.1693	1498.2768	1504.3734
1513.0574	1514.3149	1518.9669
1522.3401	1523.3380	1527.1743
1535.4332	1538.9745	1540.2106
1544.0630	1546.9771	1548.5927
1663.0932	1663.8738	1665.9174
1666.9025	1684.2751	1684.6938
1685.7013	1686.3270	1773.0679
2970.4840	3046.2404	3062.5621
3064.2850	3066.3323	3069.1978
3071.4778	3076.4698	3082.6969
3085.2890	3087.2608	3098.0101
3112.1949	3136.0897	3140.4020
3143.8048	3144.2939	3147.3353
3154.1442	3156.6618	3158.4459
3174.3568	3189.5068	3193.3980
3197.6677	3199.4732	3204.9381
3205.6046	3208.9384	3209.8022
3211.4486	3212.8400	3214.2478
3220.3697	3222.5578	3223.5538
3224.0002	3227.4504	3231.4951
3232.7031	3233.8696	3238.7578
3240.5745	3241.5287	3241.6133

TS 6–9

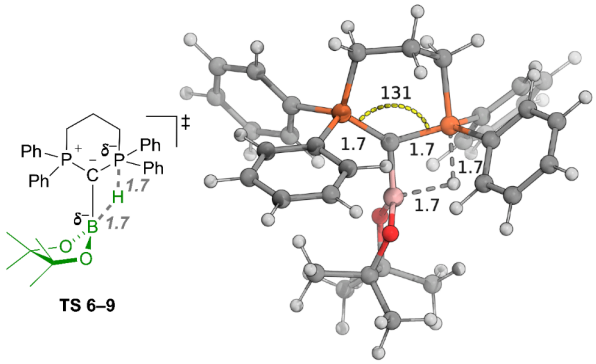

Fig. S18 Three dimensional picture of structure **TS 6–9** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250,ts,calcfc,noeigentest) freq=noraman

---
Full point group C1 NOp 1
Stoichiometry C34H39BO2P2 Framework group C1[X(C34H39BO2P2)]

Num atoms: 78
Charge = 0 Multiplicity = 1

SCF = -2176.70512860 | Predicted change in Energy=-1.052817D-08

Optimization completed on the basis of negligible forces.
Maximum Force 0.000004 0.000450 YES
RMS Force 0.000001 0.000300 YES
Maximum Displacement 0.009938 0.001800 NO
RMS Displacement 0.002147 0.001200 NO

Atom Coordinates (in Angstroms)
Type X Y Z

B -0.016325 -0.072568 1.185176
C -0.453078 -0.628084 3.363273
C -1.013800 0.802288 3.063394
O -0.289104 -1.157672 2.043321
O -0.370708 1.128477 1.830547
C -1.398380 -1.533122 4.140993
H -0.928648 -2.507567 4.301011
H -1.630337 -1.101642 5.120213
H -2.332371 -1.690752 3.597844

C 0.924383 -0.597083 4.030185
H 1.344461 -1.606395 4.016710
H 1.607786 0.056442 3.481265
H 0.863637 -0.259851 5.069198
C -2.521618 0.804638 2.788006
H -2.795293 1.767968 2.348795
H -2.785823 0.023950 2.067905
H -3.106633 0.653577 3.700453
C -0.666624 1.856377 4.105531
H -1.095670 2.818532 3.812049
H -1.074480 1.585291 5.084960
H 0.414041 1.979579 4.196823
C 3.827196 4.018480 -0.499150
C 2.769619 3.706516 0.351195
C 2.185685 2.445376 0.312534
C 2.627401 1.479695 -0.599478
C 3.682884 1.808461 -1.454034
C 4.287879 3.062131 -1.395973
H 4.291004 4.999301 -0.460224
H 2.403414 4.444583 1.058456
H 1.379360 2.204749 0.999514
H 4.055859 1.091150 -2.175901
H 5.117242 3.289083 -2.058817
C 4.447505 -3.833176 0.273018
C 4.875549 -2.890066 -0.654609
C 4.076361 -1.787518 -0.947471
C 2.854753 -1.604521 -0.298114
C 2.438876 -2.547345 0.645897
C 3.225133 -3.660921 0.918392
H 5.065582 -4.697538 0.495780
H 5.830980 -3.011491 -1.155808
H 4.424663 -1.067662 -1.680750
H 1.499956 -2.397456 1.171776
H 2.886487 -4.392865 1.645425
H 1.686474 -0.007911 1.010781
C 0.046920 -0.237067 -0.362326
P 1.752166 -0.161529 -0.637356
C 1.758154 -0.380581 -2.535236
C 0.764110 0.537306 -3.259180
C -0.675362 0.013826 -3.172946
P -1.252011 -0.117041 -1.437990
H 1.501696 -1.430326 -2.727373
H 2.755030 -0.240613 -2.959053
H 0.819116 1.555732 -2.853783
H 1.021816 0.616802 -4.321296
H -1.372372 0.658385 -3.717137
H -0.732352 -0.987877 -3.611926
C -4.212523 -3.647184 -1.240166

C -3.335750 -3.395379 -0.189182
C -2.436344 -2.335468 -0.261922
C -2.423252 -1.514541 -1.392623
C -3.302992 -1.772602 -2.448995
C -4.194536 -2.837174 -2.373056
H -4.907697 -4.478709 -1.180755
H -3.343957 -4.031224 0.690243
H -1.737976 -2.149549 0.551217
H -3.297451 -1.142335 -3.334627
H -4.872230 -3.035777 -3.197131
C -3.699078 3.670428 -0.441226
C -2.307964 3.671062 -0.378057
C -1.596681 2.516592 -0.680655
C -2.273212 1.355077 -1.065343
C -3.668608 1.358145 -1.124808
C -4.378189 2.513698 -0.812013
H -4.254680 4.569405 -0.192960
H -1.774798 4.566713 -0.076562
H -0.515805 2.499469 -0.586306
H -4.207319 0.455740 -1.394375
H -5.462758 2.506319 -0.849917

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -2176.70512860 | Predicted change in Energy=-1.052817D-08
Zero-point correction (ZPE) = -2176.0485206000003 0.656608
Internal Energy (U) = -2176.0127266 0.692402
Enthalpy (H) = -2176.0117816 0.693347
Gibbs Free Energy (G) = -2176.1181316 0.586997

Frequencies
-397.8598 6.6209 18.7995
22.7097 35.2052 41.0295
44.1329 46.2581 49.1744
56.3563 72.1752 73.7542
74.4017 94.5562 112.3717
128.7114 141.8728 154.9093
166.3655 170.3224 177.2983
214.7715 215.8233 232.6191
235.8321 241.9325 244.0065
247.9808 257.7012 265.9273
277.0473 287.8891 308.2421
311.6257 315.6681 331.1375
347.7795 360.6900 376.2240

384.1875 399.9303 405.2556
409.0917 412.7263 415.2275
418.6207 422.1597 449.1418
463.6521 470.3892 484.2506
500.3536 511.7083 519.0311
531.6265 537.4219 554.3121
585.6645 592.7281 632.2842
634.6988 636.2190 636.9976
644.8365 680.7071 697.8664
701.0256 716.0530 719.0811
723.6120 724.4975 727.0722
733.8740 739.1503 765.9684
768.8002 771.7684 777.9700
784.1446 801.2497 861.2120
874.8821 880.8117 882.7232
885.7152 890.7029 892.3284
935.4569 940.3096 947.1720
948.4273 950.8955 958.3554
965.5964 969.1411 988.7016
997.2480 1002.7833 1006.6143
1008.1525 1012.6434 1015.7128
1021.0150 1021.7308 1022.0996
1023.1543 1024.5580 1028.5063
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1042.4630 1066.6892 1067.8099
1068.5208 1068.8039 1075.0281
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1123.9580 1127.4015 1128.8795
1130.6026 1134.4349 1141.6870
1144.3480 1153.8199 1157.0146
1176.2530 1194.7475 1197.8443
1198.4268 1198.7026 1199.2135
1203.8204 1226.6452 1230.7267
1232.7624 1235.3734 1240.1903
1254.4793 1270.2083 1274.5800
1282.4821 1300.5144 1310.9405
1333.6980 1338.0050 1340.0930
1341.7957 1342.2840 1345.8697
1373.6079 1375.7528 1378.9906
1381.3836 1383.5783 1418.5376
1420.5088 1429.8561 1438.7012
1467.5826 1470.2993 1485.8280
1489.3266 1489.9503 1491.6369
1494.2358 1495.8880 1497.1093
1500.3815 1502.2178 1515.8090
1518.5963 1521.8298 1526.0411
1541.2877 1544.0425 1545.9831
1547.4898 1549.1437 1663.5594

1664.3378	1665.8023	1667.1374
1682.5130	1683.9571	1684.0980
1684.4712	3056.6876	3060.4735
3065.3975	3067.7764	3070.2479
3070.4400	3080.8110	3101.7449
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3145.7854	3147.2395	3153.7156
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3172.6549	3197.7608	3200.4321
3200.8266	3201.9255	3207.9372
3209.5834	3211.5883	3212.6529
3217.8820	3218.5407	3220.4033
3223.6747	3225.1745	3226.7281
3228.7279	3232.4908	3233.7091
3234.7281	3238.3668	3242.8274

9

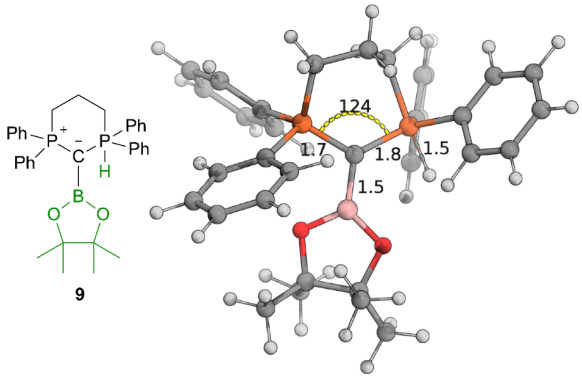

Fig. S19 Three dimensional picture of structure **9** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman

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Full point group C1 NOp 1
Stoichiometry C34H39BO2P2 Framework group C1[X(C34H39BO2P2)]

Num atoms: 78
Charge = 0 Multiplicity = 1

SCF = -2176.71438546 | Predicted change in Energy=-1.031246D-08

Optimization completed.
Maximum Force 0.000011 0.000450 YES
RMS Force 0.000002 0.000300 YES
Maximum Displacement 0.001367 0.001800 YES
RMS Displacement 0.000315 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

B	-0.096653	1.262007	0.657881
C	-0.055463	3.307762	1.645121
C	-1.210729	2.452797	2.265950
O	0.744493	2.314788	0.984462
O	-1.303891	1.365637	1.341462
C	0.809661	4.048917	2.654061
H	1.586213	4.611626	2.129682
H	0.207234	4.754852	3.235085
H	1.300457	3.356956	3.340395

C	-0.553523	4.272108	0.564477
H	0.310257	4.672779	0.027920
H	-1.193826	3.753907	-0.156169
H	-1.115449	5.106867	0.993562
C	-0.848091	1.855311	3.627322
H	-1.596965	1.104038	3.891079
H	0.127421	1.361880	3.588301
H	-0.825111	2.616310	4.412770
C	-2.563711	3.149128	2.334606
H	-3.298323	2.478085	2.788096
H	-2.506005	4.056872	2.944131
H	-2.922029	3.409980	1.336891
C	4.224485	1.598157	-4.115106
C	3.319735	2.304336	-3.324146
C	2.640981	1.656717	-2.299103
C	2.817953	0.287926	-2.074610
C	3.724473	-0.409256	-2.872950
C	4.436563	0.244836	-3.877485
H	4.768767	2.104519	-4.906496
H	3.155842	3.363593	-3.499046
H	1.970385	2.211421	-1.645653
H	3.900878	-1.467651	-2.708243
H	5.155243	-0.307009	-4.476082
C	3.722964	-2.906114	2.848730
C	3.720020	-3.469826	1.577564
C	3.178516	-2.770221	0.500864
C	2.658674	-1.484890	0.670141
C	2.695783	-0.921205	1.950085
C	3.202934	-1.627378	3.034613
H	4.133949	-3.457034	3.689298
H	4.134512	-4.461264	1.421233
H	3.171558	-3.241270	-0.475063
H	2.321374	0.091737	2.085327
H	3.205804	-1.175881	4.022317
H	2.311705	0.722567	0.107552
C	0.160739	0.126478	-0.323017
P	1.834790	-0.431653	-0.649037
C	1.305841	-1.983035	-1.716050
C	0.364128	-1.597561	-2.859199
C	-1.094645	-1.576174	-2.395930
P	-1.256519	-0.739991	-0.765027
H	0.829055	-2.733365	-1.069296
H	2.191118	-2.470758	-2.130780
H	0.635675	-0.610380	-3.251779
H	0.444760	-2.294157	-3.701354
H	-1.742140	-1.055803	-3.107272
H	-1.475708	-2.596000	-2.283549
C	-2.436346	-4.047324	2.229545

C -3.169292 -3.907219 1.052134
C -2.835481 -2.911137 0.142317
C -1.771522 -2.042515 0.409413
C -1.043251 -2.186630 1.590027
C -1.374192 -3.189899 2.496107
H -2.693334 -4.830300 2.936044
H -3.996734 -4.577286 0.841936
H -3.410859 -2.807234 -0.774335
H -0.209241 -1.518822 1.782746
H -0.795057 -3.302443 3.406691
C -4.701713 2.287825 -1.246826
C -3.524202 2.407859 -1.981955
C -2.514253 1.465105 -1.833124
C -2.675079 0.394638 -0.948179
C -3.852708 0.279635 -0.213190
C -4.863846 1.223647 -0.365781
H -5.489428 3.026138 -1.358526
H -3.389818 3.239443 -2.666173
H -1.580924 1.576338 -2.378842
H -3.972378 -0.527968 0.500448
H -5.775500 1.133128 0.215990

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -2176.71438546 | Predicted change in Energy=-1.031246D-08
Zero-point correction (ZPE) = -2176.05602446 0.658361
Internal Energy (U) = -2176.0193814599997 0.695004
Enthalpy (H) = -2176.01843746 0.695948
Gibbs Free Energy (G) = -2176.13052046 0.583865

Frequencies
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38.1246 41.0231 42.4935
48.2969 57.9523 67.7162
79.4768 91.7854 110.3741
119.4665 140.4489 149.3236
175.5492 188.2605 202.5661
208.4246 209.0695 225.9920
228.4993 236.7600 243.6032
248.1162 264.1201 283.4482
290.0681 298.1734 311.9709
315.9881 321.8855 331.6271
356.1852 368.8916 377.4495

390.1701 397.3613 409.1056
411.1680 415.3267 416.5785
421.6434 444.9120 461.0629
465.2484 479.9774 495.1549
504.8516 508.4970 522.2027
526.5124 533.8949 574.8144
589.7921 594.4400 634.5886
636.0225 636.8624 639.2565
677.5825 682.4217 691.9515
701.8630 713.3434 717.5709
717.9294 720.2249 721.3962
730.8434 731.2502 761.5195
764.9602 769.9805 772.4695
784.3531 805.8531 854.7634
876.8422 877.9914 879.9238
884.3297 884.9039 898.4970
945.3111 945.7307 947.2765
948.8394 951.5709 953.0495
962.4600 974.0837 985.8549
990.0095 999.5941 1001.8382
1004.1977 1009.1848 1017.4231
1019.0317 1020.2618 1021.4208
1022.0287 1023.1402 1024.0016
1024.5342 1026.6011 1029.8076
1043.6667 1056.1232 1064.2317
1064.5431 1066.3166 1066.7171
1089.4238 1113.1662 1117.8042
1119.3551 1122.0456 1123.2360
1126.9340 1134.4424 1143.5838
1148.8681 1157.6350 1181.2578
1193.8230 1194.7555 1197.1995
1197.8024 1202.0382 1213.4830
1219.3436 1221.8767 1225.4513
1226.7852 1235.8512 1254.1732
1266.1751 1266.7794 1282.9088
1288.0897 1312.0087 1322.4287
1329.8112 1336.6654 1340.1546
1340.9308 1356.2420 1365.6105
1367.0169 1370.2874 1371.7434
1385.5329 1393.8976 1419.1373
1420.9581 1430.2419 1439.8485
1478.3133 1487.7298 1489.0617
1491.1675 1491.3548 1495.3837
1496.7998 1498.0137 1503.0041
1510.5283 1518.9362 1519.0046
1521.5838 1523.9246 1537.2652
1539.5335 1540.8347 1541.9982
1543.2455 1664.3087 1664.9365

1665.1850	1667.7838	1679.8313
1680.8007	1683.1012	1685.2062
2119.5669	3052.4805	3060.6580
3062.0029	3064.6974	3067.9962
3071.0913	3087.7878	3103.7883
3140.8027	3146.0317	3148.3807
3149.3291	3149.8678	3153.4364
3157.5651	3158.6836	3169.7888
3175.2147	3186.1306	3188.3547
3197.5007	3200.1305	3201.9201
3202.4594	3209.6505	3210.8548
3211.5375	3212.2299	3219.3253
3221.8647	3222.6770	3226.2094
3228.9621	3229.5801	3231.9262
3237.6941	3239.7492	3243.3392

TS 9–7

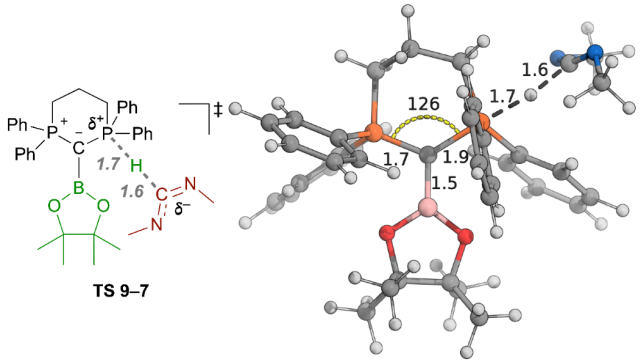

Fig. S20 Three dimensional picture of structure **TS 9–7** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250,ts,calcfc,noeigentest) freq=noraman

---
Full point group C1 NOp 1
Stoichiometry C37H45BN2O2P2 Framework group C1[X(C37H45BN2O2P2)]

Num atoms: 89
Charge = 0 Multiplicity = 1

SCF = -2404.02489384 | Predicted change in Energy=-3.998236D-09

Optimization completed.
Maximum Force 0.000004 0.000450 YES
RMS Force 0.000001 0.000300 YES
Maximum Displacement 0.001672 0.001800 YES
RMS Displacement 0.000291 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

C 0.201541 -0.093875 -0.437804
B 0.822450 0.893540 0.529287
C 1.141302 2.693774 1.889000
C 2.398855 1.765506 1.932647
O 0.156448 1.828570 1.309019
O 2.193837 0.939662 0.779986
C 1.307383 3.882089 0.939266
H 0.324927 4.329647 0.768771
H 1.978872 4.640879 1.351888

H 1.698557 3.553949 -0.028180
C 0.638890 3.166494 3.245201
H -0.251079 3.786248 3.107995
H 0.370523 2.324320 3.886123
H 1.400807 3.765811 3.753844
C 3.734290 2.481330 1.793488
H 4.548572 1.752633 1.833573
H 3.800963 3.008529 0.840479
H 3.876511 3.199229 2.607705
C 2.409743 0.839248 3.151753
H 3.165708 0.064819 2.997535
H 1.440833 0.344500 3.273348
H 2.645559 1.380628 4.072605
P -1.628964 -0.375884 -0.474623
C -1.952604 -2.545080 3.609680
C -1.665774 -1.183340 3.567421
C -1.592919 -0.513603 2.349604
C -1.820962 -1.202490 1.153501
C -2.137282 -2.562949 1.204139
C -2.191240 -3.231240 2.422946
H -1.999290 -3.065747 4.560883
H -1.492962 -0.634793 4.488635
H -1.338049 0.540177 2.325332
H -2.349574 -3.112040 0.292723
H -2.425367 -4.290959 2.442691
C -2.694411 4.138860 -0.599626
C -3.346876 3.282830 0.285041
C -3.044471 1.927199 0.290754
C -2.052636 1.425444 -0.548346
C -1.393940 2.283245 -1.423268
C -1.728622 3.633183 -1.464407
H -2.944670 5.195138 -0.619481
H -4.103747 3.669740 0.960072
H -3.585638 1.252222 0.948187
H -0.603116 1.895361 -2.056035
H -1.224873 4.292610 -2.164583
H -3.304582 -0.477470 -0.572580
C -4.559679 -0.210236 -1.455200
N -5.535387 -0.718207 -0.844946
N -4.100187 0.342595 -2.487196
C -5.574203 -0.830480 0.588728
H -6.236009 -1.651905 0.878783
H -5.961475 0.085171 1.057442
H -4.575226 -1.022498 1.010914
C -4.877747 1.396423 -3.111554
H -4.895788 1.248373 -4.197077
H -5.914916 1.432794 -2.751882
H -4.409375 2.370999 -2.919683

H -2.718065 -2.114605 -1.700411
C -1.775303 -1.594515 -1.877032
H -1.962149 -0.971194 -2.757506
C -0.669647 -2.622399 -2.118971
H -1.019602 -3.299193 -2.905966
H -0.518966 -3.243316 -1.226618
C 0.665421 -2.017844 -2.545110
H 1.374550 -2.788807 -2.859762
H 0.527038 -1.327030 -3.382506
P 1.376827 -1.095794 -1.148294
C 4.889482 1.303338 -2.935262
C 3.599847 1.432755 -3.443863
C 2.561181 0.688327 -2.897397
C 2.804488 -0.197717 -1.844476
C 4.095798 -0.312898 -1.330429
C 5.134286 0.433388 -1.877219
H 5.701048 1.886626 -3.358570
H 3.401392 2.117771 -4.261707
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H 4.286167 -0.966977 -0.486997
H 6.135353 0.341745 -1.468313
C 2.943587 -4.447146 1.620568
C 2.013419 -3.520064 2.078258
C 1.574064 -2.501166 1.238125
C 2.060973 -2.406637 -0.065727
C 2.993463 -3.344740 -0.522384
C 3.435389 -4.358763 0.319087
H 3.286004 -5.242788 2.274758
H 1.619266 -3.588009 3.086882
H 0.839658 -1.781730 1.586272
H 3.387079 -3.277990 -1.533526
H 4.161014 -5.081752 -0.039526

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -2404.02489384 | Predicted change in Energy=-3.998236D-09
Zero-point correction (ZPE) = -2403.27688584 0.748008
Internal Energy (U) = -2403.23313384 0.79176
Enthalpy (H) = -2403.23218984 0.792704
Gibbs Free Energy (G) = -2403.35723384 0.66766

Frequencies
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30.5073 37.9866 42.8434
48.4116 49.3875 51.6890
59.4119 63.9140 77.3729
83.6316 89.8659 99.6443
103.3298 105.6376 114.1273
129.3126 136.3951 139.5682
156.9285 159.7926 176.9575
181.9010 193.8486 206.4915
213.1813 221.3281 225.7850
230.0579 231.6207 239.6515
243.9084 251.6548 260.5764
269.8781 282.7731 296.0318
302.1987 304.9004 319.5318
335.3262 346.8197 352.3194
361.2921 379.4501 384.3196
391.7665 399.0831 409.8663
410.2900 419.5606 420.6794
424.6267 448.0770 452.3248
485.0707 489.3291 498.3886
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536.2693 538.9905 568.5993
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636.9661 638.2861 638.5259
653.4076 681.1168 684.9920
702.0705 713.9921 714.6723
718.8086 720.9082 725.1632
727.9353 734.9130 746.0141
756.9318 767.0056 767.7982
773.6981 784.4936 796.2183
815.1855 870.4316 871.0763
875.2615 878.4499 887.7355
888.0419 898.9141 943.9244
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951.2174 951.8546 965.7983
968.4460 989.8731 994.5388
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1026.7147 1027.3603 1032.4357
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1125.7770 1129.8096 1135.8650
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1150.7497 1156.7745 1159.0995
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1283.8804	1288.5831	1311.1610
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1372.2939	1377.8920	1387.3346
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1431.1343	1440.2715	1449.9545
1455.6186	1465.4196	1473.7170
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1497.5964	1499.8850	1502.3701
1507.5401	1510.9113	1515.5533
1520.5576	1521.4184	1522.1605
1523.5317	1532.6581	1538.7344
1541.8772	1542.9029	1544.6626
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3211.3681	3211.7890	3212.8731
3217.6857	3223.0815	3223.4470
3224.8371	3228.5375	3230.6785
3234.1820	3234.4315	3237.2191
3237.9743	3242.6041	3243.0302

TS 2–10

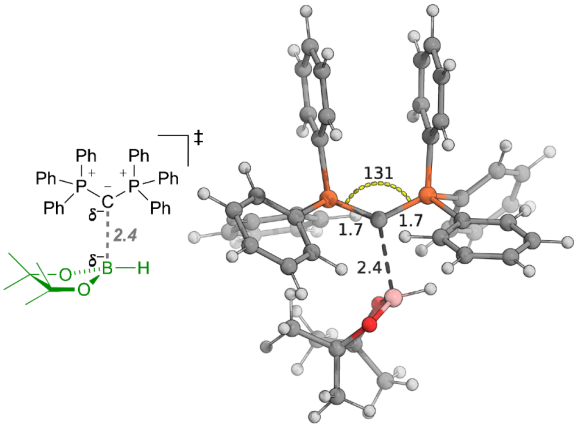

Fig. S21 Three dimensional picture of structure **TS 2–10** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250,ts,calcfc,noeigentest) freq=noraman

---
Full point group C1 NOp 1
Stoichiometry C43H43BO2P2 Framework group C1[X(C43H43BO2P2)]

Num atoms: 91
Charge = 0 Multiplicity = 1

SCF = -2521.95553854 | Predicted change in Energy=-1.915682D-09

Optimization completed.
Maximum Force 0.000006 0.000450 YES
RMS Force 0.000001 0.000300 YES
Maximum Displacement 0.000997 0.001800 YES
RMS Displacement 0.000217 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

P -0.216464 -1.389836 0.050168
P 1.335391 1.194968 -0.093597
C 1.648126 3.726313 -3.956814
C 1.040045 2.474209 -3.958485
C 0.936859 1.750004 -2.776168
C 1.449018 2.264875 -1.583519
C 2.052796 3.523427 -1.587090
C 2.150268 4.250551 -2.769475

H	1.723011	4.296711	-4.877462
H	0.635263	2.065061	-4.878715
H	0.443929	0.783102	-2.758249
H	2.434379	3.950322	-0.666013
H	2.613662	5.232089	-2.760589
C	1.513538	4.128940	3.494379
C	2.672213	3.855523	2.771809
C	2.629093	2.974337	1.697131
C	1.426088	2.358714	1.329081
C	0.270212	2.632556	2.062914
C	0.317174	3.515504	3.138697
H	1.546714	4.815079	4.335145
H	3.612052	4.322901	3.048658
H	3.542544	2.752912	1.152864
H	-0.669602	2.160324	1.795971
H	-0.589833	3.722458	3.697947
C	-3.035095	-2.307762	3.603074
C	-2.208463	-1.188141	3.602165
C	-1.406769	-0.915481	2.498865
C	-1.401603	-1.776480	1.399365
C	-2.235433	-2.897149	1.404716
C	-3.055178	-3.155991	2.498793
H	-3.671962	-2.513900	4.457665
H	-2.203042	-0.512911	4.451789
H	-0.786558	-0.025834	2.469560
H	-2.262608	-3.560993	0.546852
H	-3.709443	-4.021975	2.488825
C	-1.802355	-3.411822	-3.803937
C	-1.852536	-2.030131	-3.648489
C	-1.385972	-1.438897	-2.477802
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C	-0.811467	-3.616635	-1.616028
C	-1.282396	-4.205758	-2.784607
H	-2.164107	-3.871286	-4.718680
H	-2.260627	-1.406002	-4.437436
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H	-1.233745	-5.283644	-2.903102
C	-0.021596	0.241899	-0.139106
B	-1.900852	1.760849	-0.423801
O	-2.537193	1.670637	0.819039
C	-3.942255	1.553921	0.582174
C	-4.008262	0.947134	-0.869264
O	-2.759824	1.359768	-1.444006
H	-1.072659	2.587957	-0.654624
C	-4.565137	0.679753	1.662992
H	-4.105301	-0.308018	1.700000
H	-5.640704	0.564049	1.491952

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H -4.080466 3.622935 -0.087323
H -5.610850 2.976018 0.546018
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H -5.094496 1.041516 -2.725375
H -6.109569 1.294169 -1.295179
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C 3.478080 -4.004747 1.043890
C 3.268731 -3.534308 -0.250630
C 2.149005 -2.766334 -0.538357
C 1.223156 -2.457591 0.464397
C 1.444320 -2.924912 1.760712
C 2.567592 -3.696658 2.048033
H 4.352747 -4.607441 1.268017
H 3.983537 -3.759222 -1.035301
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H 0.735193 -2.694372 2.549242
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C 3.780493 0.263102 -1.166646
C 5.012677 -0.381822 -1.094290
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H 5.008864 -1.187526 2.202316
H 2.833199 -0.034982 2.080227
H 3.440850 0.669987 -2.113702
H 5.624330 -0.474261 -1.986310

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -2521.95553854 | Predicted change in Energy=-1.915682D-09
Zero-point correction (ZPE) = -2521.19837454 0.757164
Internal Energy (U) = -2521.15558254 0.799956
Enthalpy (H) = -2521.1546385399997 0.8009
Gibbs Free Energy (G) = -2521.2750565399997 0.680482

Frequencies

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522.7493 530.3089 532.8830
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704.9490 713.8888 716.4724
717.9328 718.5229 725.3203
727.9367 729.3558 730.3349
732.4369 733.0629 741.3311
757.0766 766.6610 772.7282
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3203.7137 3204.4079 3204.6962
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10

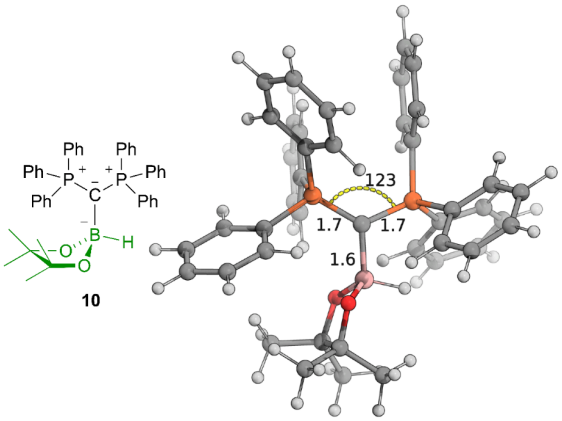

Fig. S22 Three dimensional picture of structure **10** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman

---
Full point group C1 NOp 1
Stoichiometry C43H43BO2P2 Framework group C1[X(C43H43BO2P2)]

Num atoms: 91
Charge = 0 Multiplicity = 1

SCF = -2521.97306083 | Predicted change in Energy=-2.145332D-08

Optimization completed.
Maximum Force 0.000055 0.000450 YES
RMS Force 0.000006 0.000300 YES
Maximum Displacement 0.001132 0.001800 YES
RMS Displacement 0.000266 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

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P 2.405217 1.280845 -1.384813
C 2.705298 -1.738265 -4.870249
C 2.964891 -2.170385 -3.571830
C 2.910889 -1.270354 -2.514042
C 2.625978 0.078233 -2.749840
C 2.329508 0.495231 -4.047434
C 2.373585 -0.408092 -5.104431

H 2.743613 -2.443471 -5.694497
H 3.197879 -3.212881 -3.380600
H 3.075432 -1.625723 -1.501597
H 2.053615 1.532178 -4.217372
H 2.143431 -0.071272 -6.110234
C 5.613058 0.783350 1.888659
C 5.770539 0.070481 0.705546
C 4.804453 0.152204 -0.294771
C 3.673844 0.947675 -0.110377
C 3.526325 1.681739 1.076062
C 4.490960 1.590506 2.070936
H 6.368502 0.719611 2.665648
H 6.650866 -0.545703 0.551832
H 4.958680 -0.377877 -1.227811
H 2.664058 2.339497 1.190784
H 4.372052 2.159706 2.987200
C 2.206022 5.900315 -6.441946
C 3.566010 5.669767 -6.254938
C 4.007001 5.013040 -5.111739
C 3.091843 4.581236 -4.144860
C 1.724748 4.801006 -4.344311
C 1.291434 5.463174 -5.489175
H 1.860533 6.414118 -7.333667
H 4.284356 5.995591 -7.000369
H 5.067354 4.811302 -4.994534
H 1.001635 4.461818 -3.607187
H 0.229855 5.636249 -5.632904
C 5.917336 6.669138 0.102937
C 4.902131 5.874556 0.624822
C 4.182181 5.016449 -0.201089
C 4.481568 4.949179 -1.563087
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C 6.213923 6.609143 -1.256041
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H 3.363151 4.432966 0.207347
H 5.747915 5.711698 -3.139677
H 7.000944 7.229687 -1.672439
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B 1.293376 3.985136 -1.174825
O 1.233134 3.820225 0.297128
C -0.039483 4.250870 0.742629
C -0.855828 4.535995 -0.602053
O -0.110251 3.863060 -1.595902
H 1.736928 5.109494 -1.476775
C -0.633693 3.121430 1.590144
H 0.060718 2.894200 2.405645
H -0.765305 2.212241 1.002851

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H 0.685289 6.272413 1.102616
H -0.821838 5.890653 1.966758
C -2.278862 3.977789 -0.594914
H -2.741608 4.164720 -1.568885
H -2.287268 2.902011 -0.416331
H -2.891415 4.464442 0.171871
C -0.933596 6.029645 -0.965950
H -1.415674 6.117495 -1.944409
H -1.521357 6.602397 -0.241687
H 0.059960 6.474373 -1.044289
C 7.072307 0.872154 -3.803395
C 6.062864 1.143997 -4.722707
C 5.040252 2.024987 -4.392856
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C 6.031968 2.365228 -2.222469
C 7.057212 1.486602 -2.555529
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H 6.022835 2.831903 -1.242789
H 7.839623 1.279842 -1.832699
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C 0.803616 -0.135541 0.440034
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C -0.337968 0.929175 -1.405832
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H -2.504223 -0.894711 0.468708
H -0.420075 -1.323734 1.744369
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Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -2521.97306083 | Predicted change in Energy=-2.145332D-08
Zero-point correction (ZPE) = -2521.21475683 0.758304
Internal Energy (U) = -2521.1719348300003 0.801126
Enthalpy (H) = -2521.17099083 0.80207
Gibbs Free Energy (G) = -2521.2913698300003 0.681691

Frequencies

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280.0696 285.0616 286.4739
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636.1281 637.1909 637.3685
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1493.0739	1493.8220	1494.6206
1495.0564	1496.1642	1499.3349
1503.4201	1518.7492	1523.4057
1524.2777	1542.2105	1543.8814
1545.5350	1546.4381	1548.0314
1548.7672	1550.0492	1661.5147
1662.3749	1665.7659	1666.3177
1666.6085	1667.7209	1682.7125
1683.6045	1684.0496	1684.8102
1685.3295	1686.7895	2252.9136
3055.9411	3061.4042	3062.8162
3068.2299	3128.0854	3134.6322
3135.9126	3143.5315	3162.5908
3163.9086	3175.0074	3180.4883
3196.1736	3204.4098	3205.9163
3206.0951	3206.9916	3209.0516
3209.1643	3210.1993	3212.5904
3215.6127	3218.1851	3218.2684
3219.7121	3220.9307	3221.1564
3225.8505	3226.9265	3227.4612
3228.8610	3229.9146	3231.5602
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TS 10–11

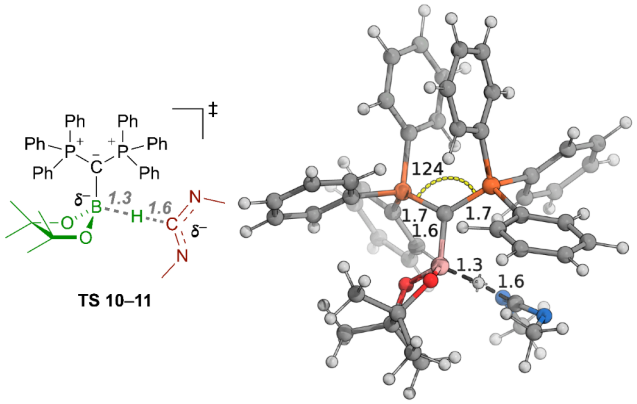

Fig. S23 Three dimensional picture of structure **TS 10–11** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250,ts,calcfc,noeigentest) freq=noraman

---
Full point group C1 NOp 1
Stoichiometry C46H49BN2O2P2 Framework group C1[X(C46H49BN2O2P2)]

Num atoms: 102
Charge = 0 Multiplicity = 1

SCF = -2749.29394802 | Predicted change in Energy=-1.121009D-08

Optimization completed.
Maximum Force 0.000031 0.000450 YES
RMS Force 0.000003 0.000300 YES
Maximum Displacement 0.000826 0.001800 YES
RMS Displacement 0.000179 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

P -0.930938 -1.365160 -0.400980
P -0.429269 1.549540 0.212566
C 0.958001 4.565200 -2.991967
C 0.294400 3.392866 -3.343649
C -0.089663 2.492391 -2.357703
C 0.149544 2.774344 -1.009492
C 0.823743 3.944605 -0.662805
C 1.231499 4.832857 -1.654149

H 1.275829 5.261644 -3.761221
H 0.100226 3.166912 -4.387003
H -0.564234 1.554909 -2.629876
H 1.053664 4.151791 0.376177
H 1.770184 5.733476 -1.378154
C -5.032339 1.971778 0.465413
C -4.369236 2.461481 -0.654198
C -2.986990 2.339815 -0.760835
C -2.255589 1.724526 0.255454
C -2.928721 1.241342 1.384463
C -4.309065 1.358576 1.485109
H -6.110237 2.071331 0.546451
H -4.926765 2.940059 -1.452546
H -2.485358 2.731483 -1.637932
H -2.371208 0.779252 2.192764
H -4.816949 0.978126 2.365364
C 1.183384 -4.771895 -2.684955
C 1.275975 -3.457387 -3.131482
C 0.673929 -2.431279 -2.414942
C -0.039654 -2.715103 -1.245039
C -0.092555 -4.030401 -0.778071
C 0.512163 -5.053631 -1.500421
H 1.656666 -5.572102 -3.245440
H 1.836533 -3.222642 -4.030224
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B 1.738409 -0.199258 -0.202593
O 2.368882 0.933300 0.429303
C 3.703628 0.997133 -0.043530
C 3.577281 0.450286 -1.517939
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C 4.183882 2.441786 0.064378
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H 5.191821 2.552523 -0.349432
H 4.212353 2.734186 1.118225

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H 2.958637 -2.713519 -0.696495
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H -5.763274 -0.667914 -1.474552
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C 0.796511 1.517156 2.756468
C -0.015889 2.217503 1.866404
C -0.599780 3.428455 2.261810
C -0.354350 3.945803 3.526990
H 0.645265 3.642914 5.408515
H 1.650986 1.478521 4.719498
H 1.261510 0.576059 2.473798
H -1.256921 3.966235 1.583467
H -0.805614 4.887579 3.822486

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -2749.29394802 | Predicted change in Energy=-1.121009D-08
Zero-point correction (ZPE) = -2748.44503102 0.848917
Internal Energy (U) = -2748.3954590199996 0.898489
Enthalpy (H) = -2748.3945150199997 0.899433
Gibbs Free Energy (G) = -2748.52728802 0.76666

Frequencies
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80.3181 82.6136 90.5821
92.9907 96.9405 99.5521
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773.1353 777.5356 777.8538

784.3120 838.0337 862.4819
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1374.1213 1376.1820 1378.7439
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1473.6923 1486.8561 1488.6558
1488.8458 1491.0667 1491.3651
1494.5175 1495.6219 1496.1756
1498.0485 1501.7305 1508.7885
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1541.9024 1543.5766 1544.6816
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1547.9620 1663.3303 1664.1734
1664.3391 1665.1728 1667.3490
1668.4319 1682.3350 1682.9278
1684.1135 1684.6068 1685.1588
1685.8968 1766.6850 2014.5752

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3142.5285	3153.7879	3173.7704
3174.6630	3185.3752	3196.1462
3201.6292	3206.8217	3208.3530
3209.3205	3209.3415	3209.5172
3209.7727	3209.7955	3214.6731
3219.8482	3220.6659	3221.3600
3222.8689	3224.1006	3227.1394
3229.0555	3229.4081	3232.2668
3232.3930	3233.7913	3235.7976
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11

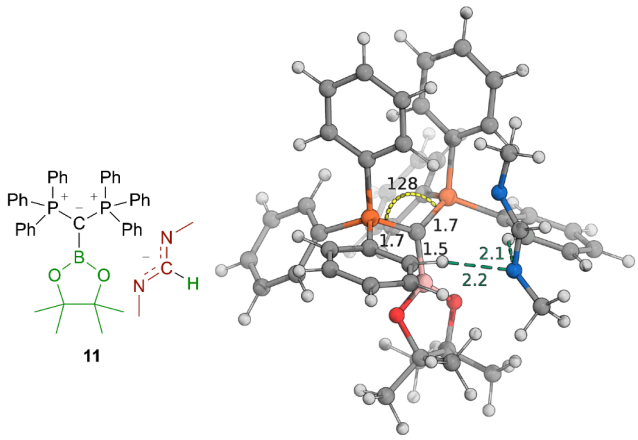

Fig. S24 Three dimensional picture of structure **11** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

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Full point group C1 NOp 1
Stoichiometry C46H49BN2O2P2 Framework group C1[X(C46H49BN2O2P2)]

Num atoms: 102
Charge = 0 Multiplicity = 1

SCF = -2749.35599006 | Predicted change in Energy=-6.498092D-09

Optimization completed.
Maximum Force 0.000238 0.000450 YES
RMS Force 0.000038 0.000300 YES
Maximum Displacement 0.000179 0.001800 YES
RMS Displacement 0.000036 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

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P -1.718596 0.511362 0.814746
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C -4.821430 2.693893 -0.678611
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C -2.696675 1.849218 0.085434
C -2.038636 2.911259 -0.527977
C -2.782571 3.870173 -1.208737

H -4.742770 4.522502 -1.809088
H -5.901160 2.604619 -0.742831
H -4.598201 0.875586 0.439027
H -0.954698 3.023951 -0.515690
H -2.247802 4.684030 -1.687751
C -2.052459 -2.532211 -2.594775
C -1.352002 -1.337935 -2.747809
C -1.234306 -0.448613 -1.687613
C -1.816451 -0.776630 -0.456264
C -2.540285 -1.960033 -0.305779
C -2.650540 -2.840630 -1.377967
H -2.139766 -3.220422 -3.429983
H -0.887364 -1.089857 -3.695982
H -0.684286 0.492429 -1.816164
H -3.030453 -2.196467 0.631984
H -3.211605 -3.762276 -1.261117
C 2.097450 -2.331333 5.001551
C 1.150619 -1.312972 4.979831
C 0.927499 -0.593368 3.810297
C 1.646628 -0.889387 2.651665
C 2.597184 -1.917325 2.679614
C 2.821188 -2.632988 3.849922
H 2.270996 -2.893745 5.913539
H 0.578599 -1.077043 5.871167
H 0.178874 0.190755 3.791562
H 3.155611 -2.166503 1.782360
H 3.558143 -3.429360 3.861459
C 1.688068 -2.891536 -2.326809
C 2.119979 -1.579587 -2.487424
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C 1.124332 -3.298651 -1.120671
H 1.779649 -3.597248 -3.146515
H 2.544006 -1.256066 -3.431961
H 2.270610 0.373793 -1.602126
H 0.594404 -2.726073 0.875086
H 0.766422 -4.315316 -0.998185
C -0.118628 1.011608 1.247763
B -0.081631 2.264728 2.121985
O 1.054847 2.763516 2.714247
C 0.662154 3.859720 3.557474
C -0.726934 4.262753 2.954057
O -1.204602 2.998313 2.448586
C 0.561113 3.309062 4.980798
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H 1.511721 2.837877 5.243458

C 1.734112 4.935306 3.467946
H 2.664011 4.564372 3.906977
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H 1.932729 5.198168 2.427907
C -1.733562 4.794908 3.962171
H -2.669338 5.034759 3.450645
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H -0.266674 6.197679 2.057963
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H 0.896575 3.984049 -3.440663
C 0.701320 3.443005 -2.482946
N 0.547539 2.134069 -2.543094
N 0.651248 4.163756 -1.380910
C 0.901028 5.573006 -1.527887
H 1.792659 5.895213 -0.962077
H 1.059851 5.891625 -2.575678
H 0.065771 6.176570 -1.135516
C 0.540707 1.585819 -3.875636
H 0.917918 2.279521 -4.650005
H -0.471794 1.284172 -4.200782
H 1.160322 0.676636 -3.938229
C 4.902552 2.954732 0.560456
C 5.056609 1.841756 1.384624
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C 2.767462 1.222397 0.963938
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C 3.679326 3.201977 -0.053737
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H 6.005761 1.652390 1.875868
H 4.116143 0.122014 2.250429
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H 3.530843 4.066998 -0.691778
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C -2.185188 -1.298328 2.879682
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C -3.417848 0.769518 3.043028
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H -3.927945 -1.168297 5.786346
H -2.374787 -2.649443 4.534911
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Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -2749.35599006 | Predicted change in Energy=-6.498092D-09
Zero-point correction (ZPE) = -2748.50374706 0.852243
Internal Energy (U) = -2748.45357106 0.902419
Enthalpy (H) = -2748.45262706 0.903363
Gibbs Free Energy (G) = -2748.58843106 0.767559

Frequencies

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67.7532	73.4493	76.0944
78.3278	79.5469	83.3673
89.9055	96.6409	105.3374
106.0339	108.2639	117.8872
127.0156	128.9436	136.4871
142.6920	151.0395	168.8489
173.8765	197.3315	204.1518
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229.6567	238.3045	239.2098
242.3616	245.2590	253.5408
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1497.1240 1497.2857 1501.3164
1506.0132 1520.7979 1525.6112
1528.4282 1532.0597 1535.1986
1539.0155 1539.5328 1540.4695
1543.3190 1545.5455 1546.3392
1557.9710 1662.4902 1662.7284
1664.1438 1665.7123 1666.5626
1667.0638 1676.6896 1679.3101
1682.4980 1683.2087 1684.5038
1685.8034 1699.0272 2835.4670

2933.6224	2939.5856	2979.2138
2987.5326	3004.6237	3019.9892
3056.0309	3056.9751	3063.2213
3069.9782	3071.8948	3146.5422
3147.8599	3149.7255	3151.4049
3157.5328	3159.6670	3167.4760
3169.2056	3178.8830	3190.8576
3202.2320	3205.6410	3206.2217
3207.1375	3208.6793	3210.5746
3211.3944	3213.7006	3215.9141
3219.1263	3220.8831	3222.6713
3225.1940	3225.4966	3226.2534
3227.4855	3233.2372	3234.3048
3235.2269	3235.2670	3235.9824
3236.1225	3239.2281	3239.5210
3240.6208	3242.8524	3252.9582

TS 3–12

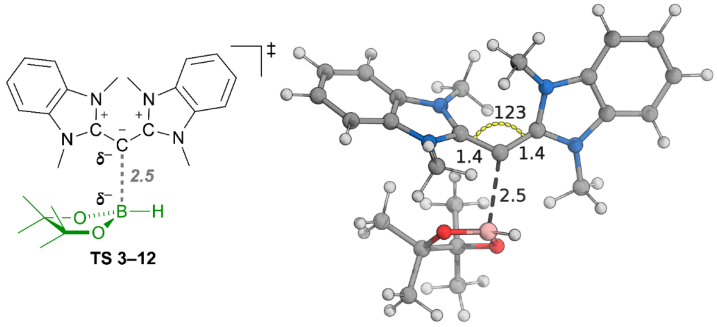

Fig. S25 Three dimensional picture of structure **TS 3–12** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250,ts,calcfc,noeigentest) freq=noraman

---
Full point group C1 NOp 1
Stoichiometry C25H33BN4O2 Framework group C1[X(C25H33BN4O2)]

Num atoms: 65
Charge = 0 Multiplicity = 1

SCF = -1366.54141850 | Predicted change in Energy=-3.721858D-09

Optimization completed.
Maximum Force 0.000016 0.000450 YES
RMS Force 0.000002 0.000300 YES
Maximum Displacement 0.001313 0.001800 YES
RMS Displacement 0.000295 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

C 0.410018 -0.829373 0.335265
C -0.215804 -1.361038 -2.036266
H -0.985530 -2.137938 -2.099030
H -0.707310 -0.387797 -1.990043
H 0.412283 -1.402391 -2.929625
C 1.524311 -0.911776 2.568759
H 2.423502 -0.321699 2.751290
H 0.655911 -0.303454 2.822756
H 1.530425 -1.823465 3.175735
C 1.723474 -2.330545 -0.770136

C 2.241505 -2.157694 0.521204
C 3.378398 -2.831096 0.938572
C 3.986908 -3.692194 0.022675
C 3.469657 -3.866985 -1.260720
C 2.322265 -3.187964 -1.678724
H 3.780750 -2.690011 1.935624
H 4.879044 -4.234391 0.317350
H 3.963769 -4.544222 -1.949053
H 1.916443 -3.332438 -2.674113
C -1.821384 0.062482 0.335508
C -4.017833 0.580911 0.006665
C -3.935274 -0.810002 0.167589
C -5.065783 -1.606443 0.110111
C -6.295793 -0.973189 -0.103713
C -6.377072 0.407249 -0.260641
C -5.232693 1.210334 -0.207220
H -5.006978 -2.684366 0.217477
H -7.198216 -1.573410 -0.151183
H -7.343153 0.872259 -0.426286
H -5.295643 2.287012 -0.320955
C -2.105898 -2.375696 0.852756
H -2.946661 -2.959911 1.231855
H -1.591264 -2.959389 0.081853
H -1.405703 -2.196858 1.674166
N 1.420786 -1.257955 1.171208
N 0.606748 -1.514038 -0.862037
N -2.594241 -1.112796 0.358721
N -2.734751 1.084574 0.098470
C -2.403181 2.477225 -0.076363
H -2.935150 2.871866 -0.948344
H -2.685105 3.062976 0.805068
H -1.330428 2.579992 -0.231977
C -0.491351 0.175204 0.584905
B 0.808639 2.156406 1.233700
C 1.824434 2.850987 -0.699022
C 2.878850 2.148410 0.239512
H 0.120996 2.274349 2.200034
O 0.709274 3.056258 0.176423
O 2.073571 1.584007 1.278839
C 1.358493 1.968670 -1.859023
H 0.514562 2.456831 -2.354955
H 2.153136 1.817565 -2.595548
H 1.021385 1.000386 -1.491688
C 2.261919 4.206812 -1.243502
H 1.465938 4.622374 -1.867327
H 2.464270 4.916148 -0.439791
H 3.160840 4.106124 -1.860345
C 3.675048 1.030833 -0.425879

H 4.334057 0.562648 0.310545
H 3.023228 0.254150 -0.828877
H 4.295243 1.423416 -1.238305
C 3.836013 3.132976 0.916731
H 4.420435 2.593671 1.666730
H 4.526713 3.590551 0.202487
H 3.281478 3.923946 1.428232

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -1366.54141850 | Predicted change in Energy=-3.721858D-09
Zero-point correction (ZPE) = -1365.9856305 0.555788
Internal Energy (U) = -1365.9554954999999 0.585923
Enthalpy (H) = -1365.9545515 0.586867
Gibbs Free Energy (G) = -1366.0452615 0.496157

Frequencies
-107.6953 19.8831 27.5707
35.8290 40.7044 56.1490
78.2914 90.7510 103.7700
108.8595 121.9928 126.7634
132.8843 146.9108 162.6002
165.2609 167.8184 190.9565
208.5381 219.7206 225.5160
244.1372 259.8582 263.6354
273.4880 290.9113 293.3385
297.8049 309.9021 312.2130
322.1111 326.0612 327.8638
333.6914 335.9245 348.5823
368.5281 383.0408 401.2903
413.1165 445.5299 452.0569
468.7560 491.9349 525.9587
534.6224 540.7719 569.2374
578.0513 578.1729 587.4251
588.8993 592.3936 607.6848
650.3718 658.2794 676.3193
684.9248 696.9724 739.0964
751.3249 753.2493 757.1567
757.8685 762.8970 769.1415
846.3169 852.6633 855.0174
861.8751 867.8018 871.6562
899.2766 922.2854 932.4854
935.1352 942.3786 946.4118
969.4833 979.1957 986.2504

995.9810 1002.7006 1021.7023
1030.5483 1055.5491 1057.9400
1059.4894 1061.5925 1066.5991
1118.8169 1125.7117 1148.7570
1154.9282 1158.8428 1160.0554
1160.8549 1164.5155 1169.4410
1170.6872 1174.6096 1179.9158
1195.8026 1196.7709 1200.2333
1214.4064 1260.6792 1268.2774
1276.9492 1283.1484 1284.7861
1314.8067 1317.9418 1325.4491
1365.1942 1370.9773 1393.7233
1402.1035 1416.7218 1420.0577
1429.6236 1435.0152 1439.6749
1450.8627 1453.2744 1457.9662
1473.3318 1480.6232 1483.4302
1484.5199 1487.1009 1496.1397
1499.9774 1501.5604 1505.6517
1510.1684 1513.5667 1516.7598
1520.5404 1522.4444 1523.3814
1524.9309 1527.0661 1532.1166
1532.4142 1541.5582 1544.0735
1548.0812 1570.9121 1575.4967
1589.2536 1694.8956 1698.8583
1700.2192 1704.5374 1709.7635
2669.1918 3053.3231 3056.1848
3058.0431 3062.0536 3065.6820
3069.3052 3070.8375 3077.5489
3120.9702 3126.7636 3135.2660
3144.3751 3146.2605 3151.8314
3155.9220 3158.9039 3159.2099
3162.5993 3177.1627 3177.7723
3178.4228 3192.8707 3206.4054
3211.5547 3214.2270 3214.5610
3221.8902 3225.1628 3231.5477
3234.5809 3239.9446 3241.7862

12

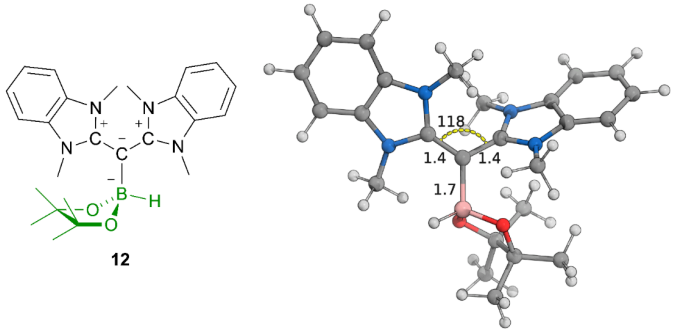

Fig. S26 Three dimensional picture of structure **12** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman

---
Full point group C1 NOp 1
Stoichiometry C25H33BN4O2 Framework group C1[X(C25H33BN4O2)]

Num atoms: 65
Charge = 0 Multiplicity = 1

SCF = -1366.55837276 | Predicted change in Energy=-1.837394D-08

Optimization completed.
Maximum Force 0.000027 0.000450 YES
RMS Force 0.000004 0.000300 YES
Maximum Displacement 0.001541 0.001800 YES
RMS Displacement 0.000223 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

C 4.293645 -0.476931 2.649706
C 5.773727 -0.548931 0.637897
H 6.195653 0.390633 0.285672
H 6.445093 -1.389646 0.435613
H 4.819536 -0.691809 0.133100
C 3.458264 -0.427616 4.992022
H 3.912942 -0.021730 5.896933
H 2.743717 0.295456 4.592731
H 2.938831 -1.361641 5.226296
C 6.503250 -0.631531 3.030897

C	5.851051	-0.733984	4.263940
C	6.559260	-0.899044	5.446558
C	7.947391	-0.954004	5.352746
C	8.599317	-0.854009	4.118746
C	7.887244	-0.689779	2.934132
H	6.056444	-0.984371	6.403431
H	8.534273	-1.077659	6.256358
H	9.682257	-0.901692	4.083979
H	8.389856	-0.601545	1.977666
C	1.990359	-1.040266	2.363294
C	-0.099442	-1.877151	2.630636
C	0.801816	-2.897661	2.946847
C	0.367046	-4.151492	3.343951
C	-1.012444	-4.363492	3.406795
C	-1.912413	-3.347327	3.089916
C	-1.469063	-2.083426	2.694653
H	1.064926	-4.939451	3.605973
H	-1.385705	-5.335419	3.710922
H	-2.978385	-3.539410	3.148280
H	-2.170623	-1.298172	2.437215
C	3.256614	-3.197502	2.651575
H	2.948243	-4.227056	2.459922
H	3.850605	-2.849931	1.802283
H	3.880773	-3.174494	3.550724
N	4.492984	-0.629929	3.999376
N	5.523304	-0.488148	2.064337
N	2.077360	-2.372220	2.776817
N	0.640421	-0.752556	2.300984
C	0.024041	0.556996	2.157586
H	-0.317413	0.717220	1.132956
H	-0.830024	0.604083	2.839849
H	0.737271	1.339843	2.417003
C	3.054670	-0.227088	2.023786
B	2.900096	1.260413	1.248833
C	4.331515	3.088692	1.056520
C	3.530572	3.239260	2.395327
H	2.053801	1.144722	0.364118
O	4.217398	1.710821	0.782424
O	2.492507	2.298419	2.242356
C	5.812729	3.446595	1.158428
H	6.286926	3.335608	0.177927
H	5.951121	4.483104	1.484840
H	6.328535	2.787000	1.861116
C	3.689193	3.880731	-0.091429
H	4.156657	3.571228	-1.030479
H	2.620909	3.659222	-0.157055
H	3.821885	4.961452	0.024193
C	4.381506	2.869386	3.621931

H 3.716700 2.741815 4.482135
H 4.921415 1.933521 3.459394
H 5.114688 3.644923 3.867349
C 2.921557 4.622754 2.618059
H 2.401091 4.647317 3.580708
H 3.693358 5.400783 2.629219
H 2.195571 4.857920 1.837883

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -1366.55837276 | Predicted change in Energy=-1.837394D-08
Zero-point correction (ZPE) = -1366.00107576 0.557297
Internal Energy (U) = -1365.9711587600002 0.587214
Enthalpy (H) = -1365.9702137600002 0.588159
Gibbs Free Energy (G) = -1366.0599237600002 0.498449

Frequencies
25.4618 31.0815 35.7725
38.9295 54.0740 68.2102
96.2609 106.2605 131.9802
135.7651 138.2318 149.1560
153.2398 169.8681 179.8661
187.2581 189.0815 202.7677
215.5373 233.5377 240.7793
252.3594 256.2083 273.1070
290.8303 296.0188 301.8764
311.9823 316.8665 321.5736
330.0009 333.0216 341.1393
355.8507 369.3864 372.7591
378.8076 401.6577 415.7238
444.5015 451.0746 468.3236
505.5119 522.4692 535.0450
547.1668 575.0386 579.6226
582.1422 587.4972 589.1020
590.5685 608.6491 647.6663
657.9164 675.3423 679.3921
696.8151 718.0864 735.3999
757.9714 761.9207 763.0142
766.1516 785.1862 820.0259
849.5649 855.2747 865.4660
867.3825 872.5666 889.6802
918.8719 931.7417 933.6151
942.9486 947.1517 967.4080
986.9889 996.9256 999.5768

1010.1071	1018.4922	1021.4660
1024.7062	1054.4851	1057.6980
1060.3678	1062.6904	1075.5990
1109.1470	1124.1924	1135.3420
1144.0033	1155.9703	1161.0963
1162.0957	1165.8238	1170.5561
1173.1953	1175.4062	1185.6327
1191.4787	1198.1007	1200.5458
1224.1806	1241.3066	1265.4875
1277.2166	1277.9140	1287.6293
1293.4159	1316.0244	1327.4011
1366.8427	1374.3342	1391.7507
1399.3060	1407.9648	1410.2802
1421.1716	1427.7377	1429.3553
1439.5960	1451.4281	1458.8720
1471.4621	1479.7765	1488.3830
1489.3041	1493.1471	1495.9036
1499.0470	1500.7132	1502.0449
1503.6036	1514.2598	1517.2906
1517.7887	1519.6178	1520.6717
1524.8849	1527.2126	1531.5768
1535.8736	1543.2456	1543.9962
1548.7751	1563.2595	1570.2958
1579.7613	1618.2871	1698.5323
1701.9416	1703.6269	1708.5312
2382.0596	3056.5055	3057.2409
3060.5552	3061.2270	3062.7312
3064.4694	3067.6439	3070.9117
3131.1717	3133.6696	3137.6067
3139.2542	3144.2571	3150.9907
3153.4108	3153.6880	3160.6582
3166.7672	3167.0849	3171.1586
3179.9470	3181.4210	3183.0556
3211.9496	3214.7251	3219.4930
3225.3880	3230.5956	3235.4441
3239.9775	3243.9719	3246.6978

TS 12–13

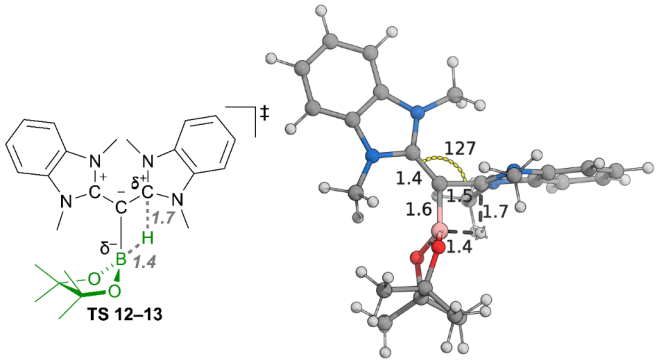

Fig. S27 Three dimensional picture of structure **TS 12–13** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250,ts,calcfc,noeigentest) freq=noraman

---
Full point group C1 NOp 1
Stoichiometry C25H33BN4O2 Framework group C1[X(C25H33BN4O2)]

Num atoms: 65
Charge = 0 Multiplicity = 1

SCF = -1366.52322672 | Predicted change in Energy=-1.292020D-08

Optimization completed.
Maximum Force 0.000008 0.000450 YES
RMS Force 0.000002 0.000300 YES
Maximum Displacement 0.001746 0.001800 YES
RMS Displacement 0.000393 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

C -5.121365 0.381752 0.033899
C -4.539517 -2.395231 0.095913
C -5.857846 -1.931636 0.156123
C -6.142036 -0.569577 0.124557
H -5.349807 1.441578 0.015962
H -4.323347 -3.457416 0.132837
H -6.667999 -2.648719 0.233478
H -7.172670 -0.234973 0.175455
C -3.816451 -0.078490 -0.026886
C -3.531077 -1.452261 -0.001899

N	-2.150017	-1.583291	-0.091768
C	-1.560747	-0.324223	-0.132424
N	-2.604193	0.583132	-0.113136
C	-0.245681	0.030947	-0.182907
C	-1.449647	-2.844466	-0.128060
C	-2.391586	2.009938	-0.190649
C	0.905044	-0.857965	-0.109526
H	1.800915	0.543811	-0.023782
C	1.052547	-1.065564	2.348725
B	0.639447	1.344079	-0.084643
O	0.806351	2.240707	-1.194253
C	1.225384	3.505578	-0.693744
C	1.419542	3.265673	0.861173
O	0.600135	2.132462	1.117016
C	2.499540	3.932173	-1.422942
C	0.114472	4.513322	-1.010779
C	2.865834	2.920451	1.245901
C	0.941600	4.416613	1.742659
H	2.889001	4.876852	-1.027934
H	3.276473	3.170062	-1.337576
H	2.280630	4.072161	-2.485532
H	-0.093843	4.475233	-2.083703
H	-0.807283	4.268138	-0.478726
H	0.401143	5.536946	-0.749524
H	2.881142	2.625442	2.299329
H	3.246921	2.081891	0.658483
H	3.538552	3.773577	1.116821
H	1.102470	4.160658	2.793743
H	1.496401	5.335762	1.526745
H	-0.123687	4.610247	1.604468
C	1.476155	-0.879902	-2.505049
C	2.384131	-2.364976	0.671619
C	2.510959	-2.314463	-0.722438
C	3.501099	-3.025121	-1.381691
C	4.364638	-3.796114	-0.602069
C	4.237332	-3.846634	0.786604
C	3.241274	-3.127357	1.448589
H	3.609449	-2.977585	-2.459557
H	5.154400	-4.359891	-1.086840
H	4.929441	-4.449024	1.365094
H	3.149575	-3.156269	2.528739
H	-0.624224	-2.796315	-0.840280
H	-1.049650	-3.121435	0.852906
H	-2.141223	-3.619307	-0.462613
H	-1.808808	2.354294	0.668803
H	-1.828309	2.251854	-1.096226
H	-3.357791	2.513651	-0.214238
H	0.973199	-1.904916	3.043069

H 1.857570 -0.391802 2.662640
H 0.120096 -0.502386 2.338621
H 2.223418 -0.080313 -2.565544
H 1.669809 -1.640776 -3.263128
H 0.492481 -0.438591 -2.665017
N 1.303162 -1.558996 1.012743
N 1.495679 -1.487417 -1.192982

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -1366.52322672 | Predicted change in Energy=-1.292020D-08
Zero-point correction (ZPE) = -1365.9693477199999 0.553879
Internal Energy (U) = -1365.93888372 0.584343
Enthalpy (H) = -1365.9379397199998 0.585287
Gibbs Free Energy (G) = -1366.03018972 0.493037

Frequencies
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63.7860 82.7596 89.4835
97.2622 105.1993 113.6832
126.0917 133.5573 141.6217
146.3070 154.1296 176.6857
186.8911 196.8706 199.3624
207.9540 247.4140 260.7966
272.6184 278.6589 293.9043
298.3386 307.2764 308.8428
312.6828 319.9083 330.4978
344.9732 350.7739 362.9717
370.2291 393.8365 416.7998
422.6756 441.6369 454.5023
458.4716 524.4296 527.5111
536.9588 552.7901 575.8630
577.6384 584.1971 585.3869
594.3351 598.0818 611.6332
637.6110 656.4524 668.0014
704.3809 709.1094 725.4601
749.0897 755.4117 764.6030
765.9035 778.5675 836.9072
841.0485 858.1340 860.8765
873.0140 889.9131 896.9519
921.2649 936.9615 940.5487
940.7288 954.3726 974.0279
978.9974 991.9385 992.9078

1018.4872	1021.6366	1032.7820
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1124.1792	1138.2517	1146.0136
1155.1029	1160.6274	1166.1581
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1179.6831	1185.5236	1191.8567
1193.0061	1198.7393	1199.9898
1225.4032	1226.6236	1265.2347
1276.4424	1281.1578	1284.8750
1292.5527	1311.3273	1345.0580
1364.0092	1374.4002	1392.2889
1394.7723	1412.1673	1413.0501
1425.0720	1430.4043	1435.4175
1449.1139	1454.1579	1468.2390
1473.2532	1481.1354	1486.1142
1488.8111	1491.1625	1498.6559
1500.2078	1501.1961	1502.5863
1503.3970	1505.5155	1511.2434
1515.3989	1518.0588	1522.8713
1524.7151	1525.8726	1530.9401
1532.9404	1536.8778	1543.0121
1548.9621	1550.7009	1562.5169
1581.8853	1597.4723	1698.0643
1699.3583	1702.7300	1708.5044
1717.8025	3060.6040	3062.3569
3062.6448	3065.0106	3066.2972
3066.6004	3068.6317	3071.0609
3138.4487	3142.7929	3146.4001
3146.8459	3147.7297	3149.9349
3150.8008	3153.0894	3159.6375
3163.8243	3168.1968	3172.7397
3180.6042	3187.8812	3194.4979
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3224.0482	3227.3231	3232.9595
3236.4798	3241.2103	3243.4371

13

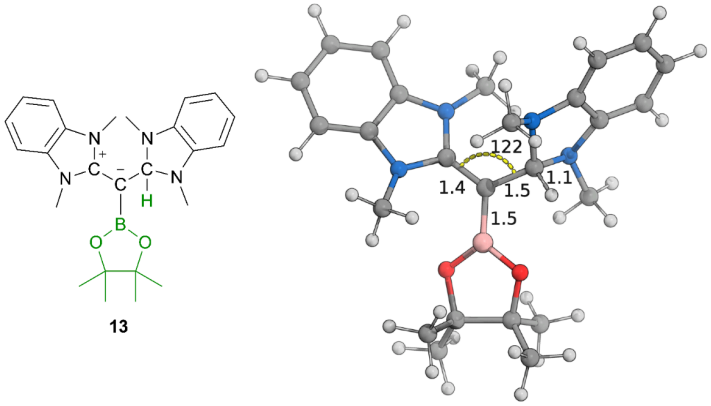

Fig. S28 Three dimensional picture of structure **13** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman

---
Full point group C1 NOp 1
Stoichiometry C25H33BN4O2 Framework group C1[X(C25H33BN4O2)]

Num atoms: 65
Charge = 0 Multiplicity = 1

SCF = -1366.59119012 | Predicted change in Energy=-1.115416D-07

Optimization completed.
Maximum Force 0.000062 0.000450 YES
RMS Force 0.000009 0.000300 YES
Maximum Displacement 0.001721 0.001800 YES
RMS Displacement 0.000389 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

C -3.537688 3.812740 4.564569
C -5.486069 5.650149 3.608455
C -5.854716 4.515777 4.333020
C -4.898031 3.615699 4.804816
H -2.794943 3.108626 4.922467
H -6.229242 6.356920 3.256159
H -6.904911 4.335113 4.535743
H -5.215560 2.744934 5.368395
C -3.176828 4.939216 3.840692

C -4.133459 5.840549 3.370388
N -3.448242 6.829305 2.680531
C -2.084040 6.588011 2.735891
N -1.935935 5.421204 3.455727
C -1.112534 7.377352 2.118807
C -4.104242 7.720915 1.750998
C -0.706453 4.874283 3.994293
C 0.162108 6.783654 1.567894
H 0.469562 7.433129 0.719883
C 1.934250 7.914196 2.895764
B -1.255135 8.880268 1.973666
O -2.181940 9.694772 2.615273
C -2.049228 11.015547 2.068208
C -0.566373 11.015133 1.565808
O -0.367892 9.639054 1.217887
C -3.057507 11.150436 0.923587
C -2.358764 12.033604 3.156835
C -0.302442 11.878023 0.339500
C 0.432128 11.360100 2.673591
H -3.042683 12.154299 0.490138
H -2.849532 10.426675 0.130116
H -4.063411 10.960234 1.307405
H -2.173466 13.051101 2.797833
H -3.411299 11.959782 3.443205
H -1.754118 11.859500 4.048027
H 0.754518 11.816469 0.067632
H -0.890589 11.543671 -0.516582
H -0.541648 12.926461 0.544888
H 1.440451 11.122104 2.325406
H 0.395922 12.421609 2.934710
H 0.234891 10.773567 3.575522
C -0.760925 5.198484 -0.095100
C 2.105003 5.623601 2.009294
C 1.310966 4.832047 1.160529
C 1.819822 3.690897 0.570588
C 3.150400 3.336707 0.847393
C 3.933378 4.116464 1.684145
C 3.416517 5.280030 2.276845
H 1.214992 3.088422 -0.099183
H 3.569075 2.447089 0.388163
H 4.963314 3.835120 1.878411
H 4.039069 5.896225 2.917179
H -3.435540 7.889152 0.903197
H -5.021702 7.243460 1.397582
H -4.326911 8.684676 2.208872
H 0.080914 5.624305 3.927485
H -0.875627 4.604695 5.040954
H -0.391062 3.993339 3.431040

H 2.720151 7.710890 3.627138
H 2.365902 8.473279 2.050696
H 1.180772 8.542580 3.374758
H -0.947639 4.132092 -0.244821
H -1.724145 5.696476 0.036265
H -0.276673 5.602781 -0.999193
N 1.319154 6.675784 2.486926
N 0.034281 5.396720 1.092591

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -1366.59119012 | Predicted change in Energy=-1.115416D-07
Zero-point correction (ZPE) = -1366.03141812 0.559772
Internal Energy (U) = -1366.00169112 0.589499
Enthalpy (H) = -1366.00074712 0.590443
Gibbs Free Energy (G) = -1366.0897411199999 0.501449

Frequencies
30.8812 32.9068 38.2859
46.7953 59.9368 70.3791
105.1500 114.2724 121.9465
126.0738 134.3849 144.6472
153.4225 164.1581 175.7069
193.4253 202.2020 210.8646
220.2707 231.5149 246.5170
247.9069 254.3149 274.6156
291.4887 295.2860 299.2184
315.4226 316.2305 327.0020
335.0278 342.7246 346.8596
350.8412 363.3822 373.8848
383.5624 396.6073 409.6049
450.2051 462.5964 470.8802
502.1929 533.0876 541.6827
557.3014 570.2243 582.4393
583.7969 589.2147 590.7145
594.5256 605.1655 622.3384
634.8249 666.9434 685.0977
724.2067 734.9706 757.0594
758.7029 760.8639 764.4001
767.2244 809.2377 832.8343
851.3850 862.9414 869.1413
874.3721 886.7385 903.3315
914.9476 937.3947 947.2504
949.0776 971.4195 972.2680

987.7796	988.3839	996.5882
1013.2548	1020.7672	1030.2765
1049.1255	1060.6843	1063.7677
1075.1534	1102.4531	1133.8406
1152.0828	1155.0782	1159.4009
1161.7967	1162.9022	1164.4777
1168.1169	1174.6948	1179.7732
1189.8530	1195.8998	1201.4253
1202.6037	1216.3047	1240.0690
1266.9885	1277.6008	1282.7924
1289.0801	1302.5618	1309.4816
1321.2185	1332.7208	1343.9857
1352.7010	1369.0926	1398.8917
1407.4353	1410.6968	1419.2044
1419.8595	1431.0395	1431.8000
1440.2202	1442.7225	1450.8708
1466.3806	1471.5322	1475.9308
1484.6700	1490.1866	1493.5525
1497.9095	1500.8524	1503.2496
1508.1357	1509.9523	1511.4880
1516.0416	1518.5578	1519.5297
1521.6861	1523.3451	1525.3815
1528.2220	1531.0632	1532.9525
1544.1036	1546.3013	1570.5990
1571.8041	1612.2024	1696.1648
1697.8275	1704.4338	1705.0929
2892.8695	2993.9686	3006.8049
3066.3347	3067.1598	3067.3426
3071.2365	3072.4531	3073.7364
3115.5533	3122.2320	3148.9266
3150.1917	3153.5785	3153.5964
3154.8805	3157.0860	3158.8163
3160.8158	3162.6932	3167.2576
3175.7509	3177.5528	3182.9544
3186.1064	3205.7440	3215.3585
3216.3703	3225.1787	3226.8920
3234.6184	3236.6823	3243.3417

TS 13–14

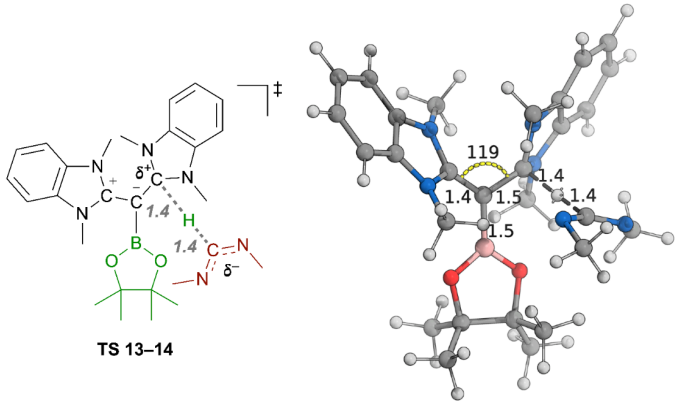

Fig. S29 Three dimensional picture of structure **TS 13–14** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250,ts,calcfc,noeigentest) freq=noraman

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Full point group C1 NOp 1
Stoichiometry C28H39BN6O2 Framework group C1[X(C28H39BN6O2)]

Num atoms: 76
Charge = 0 Multiplicity = 1

SCF = -1593.88415775 | Predicted change in Energy=-5.152996D-10

Optimization completed.
Maximum Force 0.000006 0.000450 YES
RMS Force 0.000000 0.000300 YES
Maximum Displacement 0.000441 0.001800 YES
RMS Displacement 0.000056 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

C 0.319800 1.113859 -0.148740
C -0.040661 3.344246 0.177614
C 0.898481 3.207246 -0.856887
C 1.547075 4.308157 -1.389247
C 1.214189 5.568034 -0.875482
C 0.273399 5.704710 0.139330
C -0.372364 4.587975 0.684992
H 2.290439 4.201544 -2.171710
H 1.708370 6.448511 -1.272131

H	0.039457	6.691422	0.524779
H	-1.101210	4.695091	1.480933
C	1.843692	1.310686	-2.164152
H	1.443106	0.355971	-2.506126
H	1.885251	2.000931	-3.010693
H	2.854335	1.143541	-1.775035
N	0.962660	1.861109	-1.170139
N	-0.497036	2.076657	0.501879
C	-1.213839	1.805473	1.731756
H	-0.869709	2.484981	2.517827
H	-0.981861	0.791866	2.061713
H	-2.293161	1.931643	1.590454
C	-0.188615	-0.252109	-0.382100
B	0.814059	-1.387321	-0.504528
C	1.730327	-3.399760	-1.046252
C	2.831045	-2.436803	-0.483343
O	0.513566	-2.728735	-0.673168
O	2.178930	-1.161885	-0.568541
C	1.730057	-4.793674	-0.435474
H	0.930258	-5.392158	-0.880115
H	2.681688	-5.299123	-0.628164
H	1.568326	-4.753837	0.642965
C	1.741401	-3.491391	-2.573307
H	0.832318	-4.000044	-2.903605
H	1.755677	-2.495006	-3.024447
H	2.606556	-4.052069	-2.938408
C	3.149119	-2.685392	0.990818
H	3.723092	-1.836760	1.372835
H	2.231874	-2.750706	1.580831
H	3.731257	-3.601163	1.129340
C	4.115498	-2.382999	-1.298013
H	4.815271	-1.685915	-0.829166
H	4.591347	-3.368107	-1.336615
H	3.928469	-2.043178	-2.318362
H	1.275252	0.833679	0.766549
C	1.883994	0.468900	1.923873
N	2.997148	1.059849	2.073929
N	1.059729	-0.313032	2.505816
C	1.574930	-1.030298	3.660050
H	2.649922	-1.243807	3.582347
H	1.426244	-0.446470	4.578793
H	1.035908	-1.977520	3.781193
C	3.769319	1.533859	0.954350
H	4.717674	1.939080	1.317399
H	3.991594	0.741003	0.225280
H	3.254737	2.350152	0.419800
C	-1.565417	-0.478050	-0.283773
N	-2.570273	0.308222	-0.796541

C -3.547611 -1.410415 0.247073
C -3.802312 -0.238998 -0.472649
C -5.096243 0.176116 -0.752256
C -6.136328 -0.625638 -0.285280
C -5.883370 -1.794177 0.438187
C -4.581594 -2.208676 0.714389
H -5.291889 1.088759 -1.304316
H -7.161475 -0.333833 -0.486103
H -6.715778 -2.393692 0.790372
H -4.385755 -3.121165 1.266168
C -1.509315 -2.360613 1.356387
C -2.388366 1.387426 -1.743385
H -1.178357 -3.300730 0.915301
H -0.641334 -1.811690 1.739534
H -2.213700 -2.545557 2.170723
H -1.389333 1.308679 -2.173619
H -3.134495 1.292485 -2.536776
H -2.482750 2.362612 -1.260179
N -2.169570 -1.521638 0.368649

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -1593.88415775 | Predicted change in Energy=-5.152996D-10
Zero-point correction (ZPE) = -1593.23575575 0.648402
Internal Energy (U) = -1593.19903175 0.685126
Enthalpy (H) = -1593.19808675 0.686071
Gibbs Free Energy (G) = -1593.30198875 0.582169

Frequencies
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97.3685 103.4751 116.9510
122.2138 124.5260 132.2908
136.6777 141.4819 145.6238
158.2523 166.7464 168.7173
171.5547 185.1475 188.7997
201.1415 203.3760 208.6495
215.8931 228.2156 233.9458
238.6910 250.8943 262.3459
282.3910 283.6413 297.5598
303.2306 307.4983 308.9417
320.6781 322.5601 332.5887
343.8358 345.3371 352.6339

360.5696 369.5369 386.6815
395.7425 406.8019 422.3765
449.5312 455.7783 467.2186
512.4613 533.8938 548.9708
557.9209 577.3366 580.1075
584.8219 590.9160 594.1231
600.0072 617.6363 623.4110
644.7182 652.6727 665.5267
687.2580 721.6337 756.6555
758.3757 759.1135 763.2614
766.3432 775.4679 785.3596
836.6734 848.4819 850.1240
863.6525 873.0074 887.3856
906.1394 916.9034 923.3913
944.4944 949.7841 951.5772
979.3141 982.0572 992.5954
993.8834 1012.8287 1023.8688
1028.9068 1040.6846 1050.3412
1058.4356 1059.3079 1064.4798
1078.8797 1107.6076 1119.6891
1134.8775 1142.0836 1148.0969
1154.3239 1155.5884 1159.2831
1161.1382 1162.6925 1166.8445
1167.7798 1174.2465 1176.4166
1181.3556 1188.6590 1196.4632
1199.0964 1205.3607 1214.3330
1233.4377 1266.9712 1271.7171
1279.7397 1286.4328 1292.1943
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1360.4887 1371.2152 1378.0931
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1420.9685 1423.3311 1427.7692
1431.1933 1437.8473 1440.6833
1442.2939 1454.0983 1457.8455
1463.0446 1469.2940 1478.1820
1482.4952 1486.4846 1487.9481
1494.7796 1497.6036 1498.2090
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1513.6925 1514.7589 1518.0571
1521.6311 1522.3073 1523.5443
1524.6519 1526.9791 1532.1806
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1549.4474 1563.8238 1568.4702
1574.5440 1623.7193 1699.6715
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3046.5521 3047.8148 3049.6351

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3070.7095	3072.3337	3073.8851
3074.1388	3093.9317	3123.2219
3123.9653	3137.0611	3145.7893
3148.1665	3149.7578	3153.4586
3155.4304	3158.1227	3160.8906
3167.4889	3171.1089	3176.3637
3177.0948	3179.7577	3183.1224
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3238.9535	3240.9138	3245.3290

14

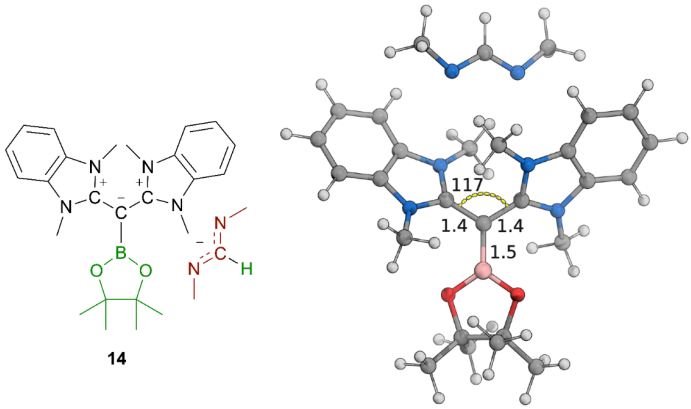

Fig. S30 Three dimensional picture of structure **14** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman

---
Full point group C1 NOp 1
Stoichiometry C28H39BN6O2 Framework group C1[X(C28H39BN6O2)]

Num atoms: 76
Charge = 0 Multiplicity = 1

SCF = -1593.93341546 | Predicted change in Energy=-3.198276D-08

Optimization completed.
Maximum Force 0.000065 0.000450 YES
RMS Force 0.000008 0.000300 YES
Maximum Displacement 0.001416 0.001800 YES
RMS Displacement 0.000325 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

C -1.309502 -0.110279 0.004173
C -3.139088 -1.333984 -0.422112
C -2.418135 -1.958845 0.593386
C -2.842582 -3.153885 1.159894
C -4.034678 -3.682827 0.685409
C -4.769956 -3.047169 -0.326476
C -4.333501 -1.861126 -0.902166
H -2.230598 -3.673347 1.885763
H -4.395477 -4.620815 1.093057

H -5.693852 -3.496522 -0.674488
H -4.900144 -1.370808 -1.685952
C -0.383612 -1.378311 1.952517
H 0.480113 -2.000341 1.643522
H -0.058645 -0.402024 2.320484
H -0.924910 -1.887722 2.751239
N -1.317315 -1.159116 0.856481
N -2.416577 -0.204045 -0.786532
C -2.681125 0.580368 -1.973738
H -3.140072 -0.068417 -2.722322
H -1.732383 0.956561 -2.361608
H -3.329212 1.428985 -1.751517
C -0.318558 0.916683 -0.056237
B -0.696919 2.372491 -0.267241
C -0.530272 4.552081 -0.891501
C -1.926911 4.284084 -0.235929
O 0.216490 3.385020 -0.504084
O -1.996870 2.847177 -0.245970
C 0.190408 5.791423 -0.381022
H 1.153363 5.892708 -0.888224
H -0.398091 6.691500 -0.584583
H 0.375967 5.731609 0.692840
C -0.581733 4.563136 -2.420478
H 0.439259 4.533172 -2.808102
H -1.114538 3.686992 -2.801775
H -1.072925 5.462550 -2.801900
C -1.992924 4.725050 1.227541
H -2.899731 4.315660 1.678844
H -1.134267 4.347393 1.790553
H -2.018544 5.814248 1.320747
C -3.114636 4.841736 -1.006826
H -4.041544 4.601767 -0.479521
H -3.043062 5.930593 -1.091505
H -3.174299 4.417113 -2.010481
H 1.324515 -5.404259 0.862225
C 1.045738 -4.332762 0.705968
N 1.842526 -3.410974 1.208700
N -0.057288 -4.076878 0.031404
C -0.702486 -5.209954 -0.576873
H -0.329236 -6.185672 -0.210433
H -1.788570 -5.194196 -0.397381
H -0.579783 -5.224019 -1.674200
C 2.906049 -3.887755 2.052383
H 3.072625 -4.980201 1.985809
H 3.861686 -3.401832 1.802124
H 2.727146 -3.666517 3.119382
C 1.043998 0.514022 0.090933
N 1.610968 -0.587334 -0.449591

C 3.201215 0.476855 0.700533
C 2.938731 -0.661078 -0.059521
C 3.920473 -1.609805 -0.315027
C 5.184204 -1.356999 0.199850
C 5.454348 -0.204168 0.952566
C 4.465723 0.733742 1.220120
H 3.682892 -2.530268 -0.832284
H 5.976434 -2.078596 0.032993
H 6.453940 -0.046463 1.343153
H 4.673487 1.623613 1.803883
C 1.778043 2.273964 1.713911
C 0.973805 -1.509279 -1.379701
H 1.955641 3.234886 1.229516
H 0.740536 2.238881 2.052182
H 2.437959 2.149378 2.574677
H 0.246870 -0.945927 -1.969853
H 1.746133 -1.888831 -2.050490
H 0.494781 -2.360927 -0.856780
N 2.003486 1.174839 0.799661

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -1593.93341546 | Predicted change in Energy=-3.198276D-08
Zero-point correction (ZPE) = -1593.2800864600001 0.653329
Internal Energy (U) = -1593.24347246 0.689943
Enthalpy (H) = -1593.2425284600001 0.690887
Gibbs Free Energy (G) = -1593.3474894600001 0.585926

Frequencies
15.3123 24.6303 26.8090
41.1478 42.8457 52.3119
54.3464 70.5159 81.8582
104.0489 113.0595 113.9490
117.1994 129.4198 140.4114
149.6054 154.3710 157.4445
162.9833 184.3973 195.6911
203.4300 208.7490 225.9690
232.6013 238.7739 240.8218
243.2705 251.4664 256.1388
267.4051 278.2498 292.5448
301.4972 303.5308 305.5430
317.3390 320.5464 321.6854
333.0419 334.3910 338.2023
347.7689 349.2329 354.1277

364.5574 366.2428 378.4558
406.5915 419.5765 445.9822
450.1150 462.1802 512.1188
528.6071 531.0548 551.7007
559.7772 581.0843 581.3223
590.0405 590.0511 592.8587
604.5137 617.0062 620.3412
644.3505 664.4434 673.8166
685.3501 709.0450 738.3784
755.9547 758.9475 763.8903
764.8204 782.0640 787.0054
848.1935 853.2920 858.7073
860.3903 862.1073 884.3833
904.8584 944.8050 945.2784
948.1450 950.4455 985.8020
989.8964 993.8357 994.0295
1020.8880 1024.2596 1028.9952
1031.9402 1052.8313 1058.5361
1058.6672 1062.9194 1073.5857
1081.6621 1084.7317 1143.6179
1149.7866 1153.5550 1156.0501
1159.3106 1164.9732 1166.0059
1167.1962 1169.9646 1170.9390
1177.9756 1178.7936 1180.0544
1180.3360 1184.4283 1202.7987
1203.8665 1204.2281 1212.0335
1265.8902 1271.4890 1285.5020
1299.2618 1302.5928 1320.7382
1322.3291 1349.7247 1380.2849
1382.6430 1394.9096 1412.7504
1413.4459 1419.5525 1421.7956
1422.8932 1423.5400 1428.2449
1432.7984 1442.1348 1458.4935
1459.2692 1472.3593 1473.8489
1483.9219 1489.9147 1491.3586
1497.0910 1497.7961 1497.9640
1498.0019 1499.7768 1504.3517
1508.5550 1510.6281 1512.4730
1519.4911 1521.2292 1524.2695
1526.3873 1526.8110 1527.8067
1532.2281 1536.1643 1536.4822
1541.4247 1543.1098 1546.8976
1553.2328 1556.6605 1558.9677
1561.9377 1563.8959 1588.4575
1601.2200 1695.4599 1700.5452
1700.7022 1711.4987 1712.0016
2827.9258 2870.7007 2880.3980
2932.9100 2941.0565 2982.1146

2983.0021	3032.1286	3033.4768
3068.2015	3069.1456	3073.3642
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3117.0346	3117.6714	3152.6322
3153.1809	3154.7622	3155.2437
3165.6770	3165.7007	3172.6730
3173.1264	3173.6504	3173.8854
3174.2621	3174.3047	3181.3809
3181.4627	3217.9337	3217.9383
3230.6775	3230.6861	3240.8926
3240.9515	3266.0690	3266.1173

TS 14–15

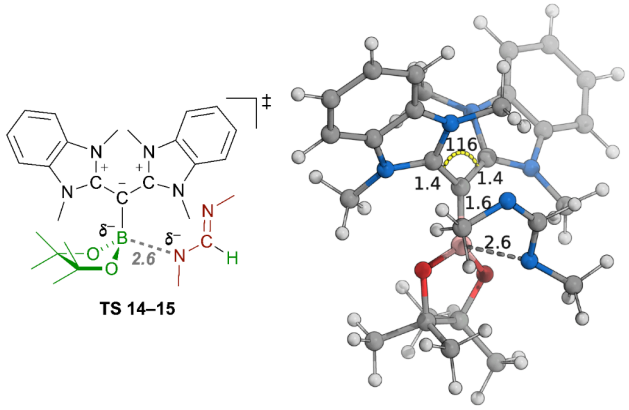

Fig. S31 Three dimensional picture of structure **TS 14–15** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250,ts,calcfc,noeigentest) freq=noraman

---
Full point group C1 NOp 1
Stoichiometry C28H39BN6O2 Framework group C1[X(C28H39BN6O2)]

Num atoms: 76
Charge = 0 Multiplicity = 1

SCF = -1593.92073359 | Predicted change in Energy=-3.220036D-09

Optimization completed.
Maximum Force 0.000002 0.000450 YES
RMS Force 0.000000 0.000300 YES
Maximum Displacement 0.000887 0.001800 YES
RMS Displacement 0.000138 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

C 0.749445 -1.052181 -0.315710
C 2.588588 -2.246090 -0.786224
C 1.930816 -2.859202 0.278413
C 2.444924 -3.991362 0.897696
C 3.639549 -4.493657 0.395535
C 4.292830 -3.886019 -0.685277
C 3.780326 -2.746583 -1.294830
H 1.946301 -4.449236 1.743777
H 4.080539 -5.370752 0.856333

H 5.225097 -4.306331 -1.046382
H 4.296234 -2.262491 -2.116229
C -0.012008 -2.317278 1.725443
H -0.490738 -3.299409 1.681161
H 0.654655 -2.187177 2.584014
H -0.768168 -1.539605 1.786422
N 0.788062 -2.117121 0.528313
N 1.819048 -1.152303 -1.150407
C 2.044364 -0.395368 -2.366144
H 1.132356 0.144346 -2.614639
H 2.298101 -1.097235 -3.165640
H 2.840423 0.334121 -2.223156
C -0.233534 -0.011411 -0.300126
B 0.243472 1.484281 -0.274422
C 0.067520 3.655366 -0.953918
C 1.585944 3.223854 -0.902895
O -0.619903 2.563197 -0.322266
O 1.495024 1.799625 -0.768035
C -0.495233 3.739754 -2.375961
H -0.061202 4.569274 -2.941379
H -0.314808 2.809773 -2.923215
H -1.576644 3.888338 -2.316978
C -0.241358 4.940659 -0.198989
H 0.275755 5.789609 -0.658020
H -1.316862 5.137151 -0.233135
H 0.063358 4.867401 0.845180
C 2.362023 3.525927 -2.182528
H 3.387243 3.160641 -2.075790
H 1.917685 3.045793 -3.057213
H 2.407568 4.604796 -2.362114
C 2.357205 3.758971 0.302984
H 3.369632 3.345758 0.273615
H 2.431016 4.850499 0.281466
H 1.893216 3.406296 1.227667
C -1.569493 -0.428040 -0.243345
N -2.076117 -1.565317 -0.845454
C -3.786708 -0.524161 0.144947
C -3.443006 -1.649857 -0.606040
C -4.391658 -2.591982 -0.975159
C -5.706178 -2.363895 -0.570111
C -6.049221 -1.238867 0.183806
C -5.091894 -0.296635 0.555294
H -4.127615 -3.475587 -1.545692
H -6.475053 -3.078487 -0.842848
H -7.080438 -1.094273 0.486849
H -5.355545 0.579850 1.136123
C -2.499083 1.230766 1.377010
C -1.379020 -2.380108 -1.815254

H -1.461244 1.254009 1.711570
H -2.755630 2.207179 0.967139
H -3.154068 0.979250 2.214830
H -0.684918 -1.751088 -2.377034
H -0.820460 -3.193541 -1.343060
H -2.108207 -2.799357 -2.510336
N -2.620570 0.192681 0.369049
N 0.698934 1.805725 2.234995
C -0.142218 2.760443 2.915254
H -0.781673 3.298216 2.200315
H -0.808771 2.308915 3.679268
H 0.443754 3.529630 3.446323
C 0.898788 0.662386 2.897572
N 1.841988 -0.226606 2.738509
H 0.159124 0.397841 3.685374
C 2.934573 0.188488 1.879441
H 2.665044 0.319515 0.821703
H 3.345694 1.164930 2.183733
H 3.738838 -0.556921 1.929443

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -1593.92073359 | Predicted change in Energy=-3.220036D-09
Zero-point correction (ZPE) = -1593.26653059 0.654203
Internal Energy (U) = -1593.23110159 0.689632
Enthalpy (H) = -1593.23015659 0.690577
Gibbs Free Energy (G) = -1593.33049159 0.590242

Frequencies
-103.8506 23.8553 31.7627
34.7889 46.7069 57.0997
69.7764 76.0859 90.7513
111.0663 112.5872 122.0969
129.5484 140.1861 143.4632
147.8643 157.9369 161.3062
162.9676 186.8912 200.1591
206.3247 214.4227 224.2158
227.6172 241.4523 242.7126
250.2133 254.1210 256.1208
268.6320 276.0650 281.4493
287.1167 300.4380 309.6941
315.0493 320.7287 329.7761
331.6784 334.8856 343.0801
350.0134 351.6131 370.8070

375.7153 385.6151 401.2204
416.4486 424.5071 446.5172
456.6009 476.3347 509.0459
519.6045 530.8070 554.6765
561.0237 577.9009 581.6148
584.0813 589.2890 592.0380
596.4575 612.2105 620.3212
656.8438 664.2679 683.1300
709.6098 732.1193 736.7042
760.9234 764.4611 766.7643
768.6223 780.9417 785.4776
841.6036 854.1609 866.9026
872.1174 874.8264 891.4078
908.0627 944.5727 945.2685
952.8836 953.8718 986.3106
990.8507 995.3177 998.0819
1000.9956 1012.8651 1024.5567
1027.0773 1034.8634 1045.2371
1057.6392 1059.3905 1061.5924
1075.0625 1081.7218 1130.8044
1135.8701 1141.1590 1145.8009
1150.5700 1157.2833 1157.6406
1162.6991 1166.6311 1172.3132
1174.0500 1177.9691 1178.9341
1182.9775 1185.0553 1199.5136
1200.3336 1201.2281 1213.1104
1260.0092 1261.5705 1283.8427
1293.1275 1299.3647 1309.9424
1319.3584 1344.3041 1356.9269
1370.8674 1377.3396 1384.0576
1400.9356 1412.2697 1417.9203
1419.7096 1421.4425 1428.8040
1431.5932 1431.9794 1438.4712
1441.5248 1450.8854 1463.1179
1465.1967 1468.0623 1484.7917
1486.0425 1489.8690 1496.5135
1498.4867 1500.7738 1502.1266
1502.5912 1503.6412 1508.0905
1510.8983 1516.4027 1516.8562
1519.0834 1521.4797 1523.7034
1525.3496 1526.1445 1530.7287
1533.2198 1539.7158 1546.1054
1551.2188 1552.1695 1554.8845
1558.1621 1565.8470 1574.6751
1609.8223 1684.7586 1703.0481
1705.0877 1707.0684 1711.7717
2889.1179 2912.2587 2985.2967
2993.1629 3053.1163 3057.6396

3058.1385	3060.0944	3064.2217
3068.2300	3071.3676	3071.7082
3074.6901	3080.6017	3084.7591
3141.6422	3144.4411	3148.4994
3151.3059	3152.9319	3154.3628
3158.4545	3162.5660	3166.2625
3173.4567	3176.5728	3182.8268
3190.1975	3192.3503	3210.4282
3219.4964	3221.3442	3224.6769
3229.7744	3233.3021	3239.1745
3244.0816	3246.7948	3250.6332

15

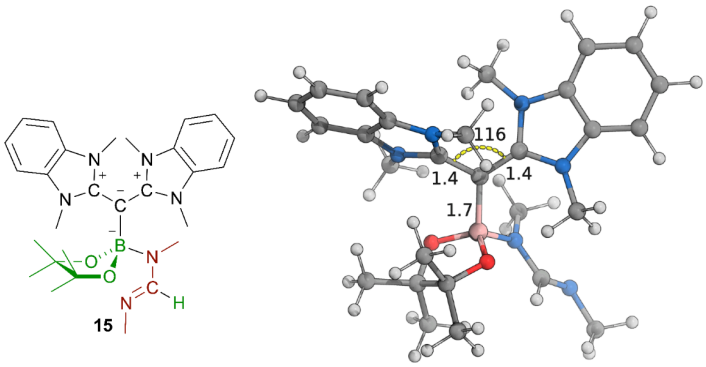

Fig. S32 Three dimensional picture of structure **15** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman

---
Full point group C1 NOp 1
Stoichiometry C28H39BN6O2 Framework group C1[X(C28H39BN6O2)]

Num atoms: 76
Charge = 0 Multiplicity = 1

SCF = -1593.97124327 | Predicted change in Energy=-5.990825D-09

Optimization completed.
Maximum Force 0.000009 0.000450 YES
RMS Force 0.000001 0.000300 YES
Maximum Displacement 0.000510 0.001800 YES
RMS Displacement 0.000128 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

C -5.051380 -8.375462 -2.108598
C -5.001028 -10.232292 -0.835998
C -6.256340 -9.641132 -0.669977
C -7.216878 -10.200069 0.161667
C -6.873729 -11.373740 0.828655
C -5.618277 -11.966843 0.660223
C -4.657766 -11.404915 -0.176655
H -8.194725 -9.748456 0.286485
H -7.597171 -11.836914 1.490646

H -5.386124 -12.881964 1.193908
H -3.680938 -11.857788 -0.302826
C -7.263738 -7.459213 -1.402172
H -7.996591 -7.564167 -2.207812
H -7.770036 -7.508845 -0.436851
H -6.763102 -6.493167 -1.494866
N -6.258834 -8.498665 -1.457690
N -4.294420 -9.447411 -1.731594
C -3.061552 -9.883711 -2.357602
H -2.854983 -9.239656 -3.208860
H -3.186829 -10.921852 -2.682982
H -2.226286 -9.790523 -1.665419
C -4.678362 -7.287132 -2.922766
B -3.283118 -6.427315 -2.519395
C -3.103447 -5.617564 -0.304827
C -1.960120 -6.654666 -0.586177
O -3.574626 -5.311301 -1.600108
O -2.422274 -7.323357 -1.738783
C -2.637234 -4.328340 0.367337
H -3.492510 -3.665620 0.530848
H -2.175106 -4.533947 1.339067
H -1.915842 -3.799521 -0.258307
C -4.255948 -6.217634 0.516175
H -5.109101 -5.533843 0.467723
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C -0.614278 -5.986114 -0.899756
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H -0.721555 -5.217826 -1.668173
H -0.160072 -5.535834 -0.010966
C -1.759409 -7.682669 0.527368
H -0.930684 -8.348947 0.266974
H -1.513540 -7.198232 1.478569
H -2.655187 -8.293387 0.666778
H -2.299360 -4.026322 -2.975476
C -2.131239 -4.619305 -3.883768
N -2.661110 -5.866572 -3.812704
N -1.521622 -4.155928 -4.915647
C -1.046918 -2.796586 -4.809843
H 0.042730 -2.759321 -4.938676
H -1.475849 -2.175661 -5.607633
H -1.283291 -2.309355 -3.846040
C -2.430023 -6.706775 -4.966612
H -2.748800 -6.203985 -5.887386
H -1.365755 -6.945670 -5.087994
H -2.993687 -7.636428 -4.854830
C -5.616651 -6.879615 -3.869133
N -5.816886 -5.628380 -4.401626

C -7.227682 -7.005476 -5.473373
C -6.778963 -5.685824 -5.398119
C -7.303486 -4.695940 -6.215703
C -8.297355 -5.073062 -7.118766
C -8.745467 -6.392759 -7.194319
C -8.218937 -7.384293 -6.365370
H -6.946694 -3.673739 -6.163122
H -8.727119 -4.324841 -7.775896
H -9.519206 -6.655151 -7.907642
H -8.580275 -8.405608 -6.417130
C -6.411480 -9.169445 -4.542984
C -5.342500 -4.357754 -3.879291
H -7.004147 -9.628221 -3.745340
H -6.765819 -9.537057 -5.507545
H -5.365994 -9.463406 -4.420775
H -4.579980 -3.934493 -4.536725
H -6.196825 -3.676050 -3.817690
H -4.914430 -4.501480 -2.887482
N -6.500808 -7.726373 -4.532969

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -1593.97124327 | Predicted change in Energy=-5.990825D-09
Zero-point correction (ZPE) = -1593.3164952700001 0.654748
Internal Energy (U) = -1593.28041527 0.690828
Enthalpy (H) = -1593.27947027 0.691773
Gibbs Free Energy (G) = -1593.38288127 0.588362

Frequencies
9.3526 28.6492 33.6659
36.8524 43.3386 54.1790
67.3465 80.2773 84.2607
99.9283 127.8257 135.4475
140.2233 145.0738 153.2847
162.2328 168.5919 171.5217
174.3992 185.6360 190.6327
201.0340 203.6801 217.5310
222.4838 233.5231 243.3365
252.1607 257.7116 264.6979
273.2213 283.6243 294.4650
297.6397 300.2304 308.9856
318.4652 320.8354 324.7987
333.6602 338.8751 345.7334
349.4140 356.4469 368.3829

377.7984 391.9293 421.1137
431.8932 449.7911 452.1147
466.6261 472.4896 497.2168
533.7493 540.0425 552.5265
556.4902 580.5034 581.0008
589.2649 590.2110 595.2130
606.0205 609.7429 655.7752
664.0957 679.7334 701.4460
712.6682 739.2374 757.6104
760.0693 762.4691 764.7925
766.7145 784.5194 812.6926
852.0931 861.8988 870.4576
871.7672 872.9183 899.6732
918.6659 938.2152 940.1673
940.6323 946.9000 972.3783
986.3631 991.8375 997.0964
1011.1833 1012.9810 1022.8484
1027.1413 1036.2338 1051.5850
1057.1416 1057.6470 1059.3292
1061.3705 1071.8259 1078.4267
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1197.3510 1199.1632 1215.1627
1236.2413 1266.7488 1270.8132
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1292.9156 1316.0520 1327.8765
1368.3406 1372.9080 1390.0721
1396.3718 1405.9466 1408.0590
1412.8681 1423.9674 1426.2297
1427.8957 1433.4022 1435.1778
1451.5182 1459.5687 1460.8197
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1488.3606 1488.9858 1497.3070
1497.6008 1498.2935 1499.7580
1501.9332 1502.9309 1503.2934
1505.6902 1509.5996 1511.9110
1515.5073 1519.6453 1521.1557
1522.8010 1524.6235 1525.7030
1526.2818 1529.5125 1530.1009
1545.5343 1546.0403 1548.3517
1564.0095 1567.8290 1576.6656
1598.7073 1699.8189 1703.8117
1704.9842 1707.9002 1750.8446
2957.9613 3034.0922 3053.9176
3056.1396 3059.9975 3061.1869

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3082.3347	3090.5865	3132.3808
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3144.2698	3147.8829	3150.4107
3153.0213	3154.4554	3168.4103
3171.6252	3172.7573	3174.0520
3180.7054	3183.7050	3184.2692
3217.6800	3219.1148	3225.8657
3228.2242	3229.6866	3238.3414
3239.0499	3245.7869	3246.5292

TS 15–3

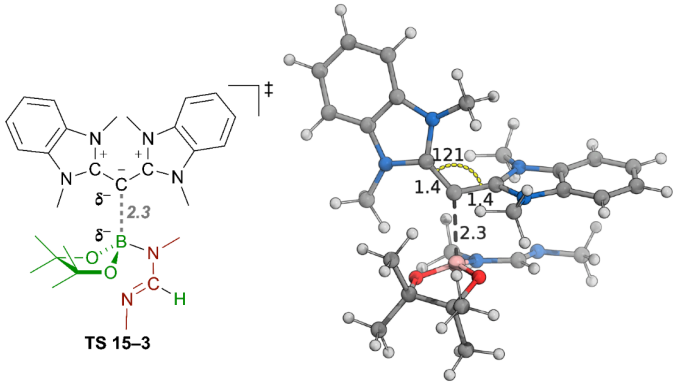

Fig. S33 Three dimensional picture of structure **TS 15–3** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250,ts,calcfc,noeigentest) freq=noraman

---
Full point group C1 NOp 1
Stoichiometry C28H39BN6O2 Framework group C1[X(C28H39BN6O2)]

Num atoms: 76
Charge = 0 Multiplicity = 1

SCF = -1593.95613680 | Predicted change in Energy=-8.869247D-09

Optimization completed.
Maximum Force 0.000022 0.000450 YES
RMS Force 0.000002 0.000300 YES
Maximum Displacement 0.001695 0.001800 YES
RMS Displacement 0.000211 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

C 1.857030 -0.304004 0.160867
C 3.841924 -1.425456 0.447771
C 4.096475 -0.261137 -0.288481
C 5.369240 0.040628 -0.742335
C 6.398739 -0.852274 -0.424080
C 6.148485 -2.003805 0.315673
C 4.857248 -2.312922 0.759938
H 5.562342 0.935375 -1.323834
H 7.406842 -0.641901 -0.765265

H 6.963137 -2.682184 0.545994
H 4.664693 -3.224427 1.315658
C 2.752149 1.549854 -1.306441
H 1.768862 1.994714 -1.172442
H 3.509418 2.299883 -1.055286
H 2.885061 1.256962 -2.355382
N 2.896667 0.411686 -0.433134
N 2.481601 -1.438839 0.717316
C 1.860206 -2.317399 1.675394
H 2.635309 -2.769758 2.297291
H 1.277141 -3.113322 1.200104
H 1.193863 -1.738584 2.321704
C 0.542692 0.034342 0.262307
B -0.837396 1.712632 -0.598158
C -0.166674 3.673627 0.359148
C -1.603573 3.289431 0.853003
O -0.022513 2.836162 -0.792498
O -1.699661 1.905915 0.492266
C 0.930926 3.316649 1.365547
H 1.905795 3.468031 0.893554
H 0.882618 3.951872 2.254857
H 0.863765 2.265010 1.654181
C -0.016755 5.124955 -0.079147
H 1.009245 5.304206 -0.411956
H -0.687391 5.362531 -0.906364
H -0.227196 5.804123 0.753544
C -1.816892 3.444921 2.352543
H -1.693833 4.491664 2.648578
H -2.832887 3.137156 2.617023
H -1.113083 2.840017 2.926003
C -2.707526 4.030568 0.092122
H -3.668967 3.571678 0.337123
H -2.749940 5.090121 0.360968
H -2.557597 3.945390 -0.987416
C -0.424191 -0.941447 0.467452
N -0.695350 -2.033883 -0.334347
C -2.330252 -1.936700 1.186649
C -1.869723 -2.645110 0.072968
C -2.559171 -3.739186 -0.425433
C -3.735503 -4.103253 0.229620
C -4.194109 -3.397574 1.344533
C -3.495685 -2.298383 1.845020
H -2.206891 -4.279407 -1.296968
H -4.305833 -4.949809 -0.137188
H -5.112888 -3.707452 1.830756
H -3.853082 -1.745176 2.706493
C -1.428687 -0.073418 2.582964
C -0.041285 -2.348411 -1.584759

H -1.409094 -0.694310 3.485505
H -0.538459 0.552236 2.538920
H -2.308578 0.570987 2.586241
H -0.733977 -2.151790 -2.411417
H 0.835572 -1.712641 -1.689554
H 0.276408 -3.394803 -1.587305
N -1.425636 -0.915087 1.411470
N -1.293669 0.989122 -1.785960
C -0.465466 0.963301 -2.976107
H 0.303432 0.182216 -2.920384
H -1.089971 0.761635 -3.847797
H 0.031195 1.929358 -3.084444
H -2.984858 0.314862 -0.819686
C -2.397213 0.184080 -1.737748
N -2.723973 -0.635344 -2.664152
C -3.972749 -1.342359 -2.477387
H -4.403459 -1.230267 -1.468137
H -4.716824 -0.996198 -3.205660
H -3.827632 -2.413571 -2.653552

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -1593.95613680 | Predicted change in Energy=-8.869247D-09
Zero-point correction (ZPE) = -1593.3025208 0.653616
Internal Energy (U) = -1593.2664138 0.689723
Enthalpy (H) = -1593.2654698 0.690667
Gibbs Free Energy (G) = -1593.3677258 0.588411

Frequencies
-175.7678 18.2744 28.6684
43.9090 48.2368 54.4407
67.1155 80.3446 86.0121
92.8541 105.6711 112.1916
115.8356 122.6859 127.8397
138.4365 155.2183 161.4820
169.9579 174.6973 188.1347
198.5854 201.9845 215.0097
218.5748 224.9615 230.5172
233.3906 240.3449 254.4093
260.4236 264.7361 278.7342
288.8085 296.8534 303.6632
309.2781 312.6781 316.9923
319.9472 328.0981 336.0473
342.0170 342.1764 356.4678

363.5831 385.2539 395.8009
413.9427 433.9241 437.6835
447.1997 455.8672 482.7625
497.8768 534.0842 538.5056
544.7990 561.6389 577.9343
580.5452 587.4704 591.1676
594.6228 599.8244 607.9198
648.6864 661.3794 684.1236
687.0488 707.1951 737.7893
753.4428 756.8744 760.7412
763.3427 770.0467 772.6969
852.7165 854.2064 861.7635
861.8354 871.6118 889.6481
914.5062 920.9143 922.5695
939.8622 946.2092 949.2809
978.2863 990.4065 993.5790
1001.0859 1002.5384 1022.0041
1029.8311 1047.1614 1051.7276
1055.2401 1057.2362 1060.6301
1067.6780 1100.9164 1120.6010
1127.1374 1146.7950 1151.0422
1154.2197 1159.9585 1163.3426
1163.5116 1164.4636 1166.5862
1170.1189 1171.5946 1175.2191
1179.1680 1185.9926 1195.1218
1197.3136 1201.0758 1223.3236
1265.5920 1268.4904 1275.3670
1280.4932 1287.6885 1291.3432
1319.4913 1323.6313 1363.6923
1372.7781 1376.5308 1392.6955
1404.0902 1407.0544 1418.3212
1419.8555 1428.1384 1430.3806
1438.9405 1447.3675 1449.2840
1451.3355 1453.9327 1463.2690
1466.7615 1475.6285 1476.9078
1486.6805 1489.1269 1490.4438
1494.8834 1496.0674 1498.3579
1499.9844 1504.0801 1505.3264
1509.9313 1513.0373 1513.8066
1519.1366 1519.7246 1522.1397
1523.7731 1526.3647 1533.1771
1534.5690 1537.1444 1542.4146
1544.5051 1545.4278 1547.2332
1565.2064 1569.9470 1583.0842
1672.7631 1700.6179 1702.4471
1703.0006 1708.0176 1761.6549
2986.0714 3039.7513 3047.1222
3050.6738 3057.0711 3060.4118

3066.0500	3067.1160	3069.6703
3072.4136	3074.7435	3084.0633
3106.5928	3109.3027	3129.1927
3131.5921	3135.4004	3143.4877
3145.6629	3152.4573	3155.6525
3157.8740	3160.2530	3162.1204
3169.3878	3175.4167	3179.5667
3180.2314	3205.6013	3207.0146
3211.9064	3215.1715	3215.7904
3223.0536	3227.2588	3232.4911
3236.9636	3240.5339	3243.3502

TS 12–14

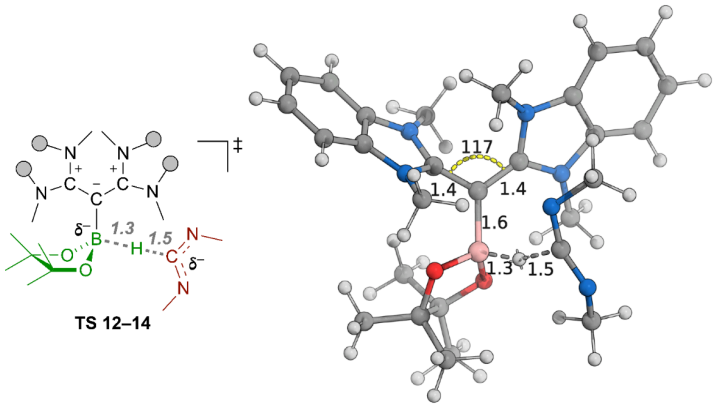

Fig. S34 Three dimensional picture of structure **TS 12–14** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250,ts,calcfc,noeigentest) freq=noraman

---
Full point group C1 NOp 1
Stoichiometry C28H39BN6O2 Framework group C1[X(C28H39BN6O2)]

Num atoms: 76
Charge = 0 Multiplicity = 1

SCF = -1593.87596798 | Predicted change in Energy=-3.154163D-09

Optimization completed on the basis of negligible forces.
Maximum Force 0.000004 0.000450 YES
RMS Force 0.000001 0.000300 YES
Maximum Displacement 0.003000 0.001800 NO
RMS Displacement 0.000288 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

C 1.285665 -0.460505 -0.425615
C 2.332147 1.505828 -1.640105
H 1.306755 1.803971 -1.853770
H 2.897871 1.414193 -2.572651
H 2.792402 2.275790 -1.014345
C 1.174313 -2.486346 1.032322
H 0.741941 -1.798968 1.765162
H 0.412739 -3.176852 0.659175
H 1.956797 -3.065486 1.524333

C 3.501889 -0.535059 -0.864784
C 3.146808 -1.758233 -0.294076
C 4.087262 -2.752689 -0.079780
C 5.405813 -2.481012 -0.451166
C 5.758309 -1.259185 -1.023696
C 4.807251 -0.261110 -1.241345
H 3.816222 -3.708934 0.354340
H 6.166958 -3.237012 -0.291384
H 6.790669 -1.077102 -1.302211
H 5.081645 0.694349 -1.673787
C -1.011504 -1.011910 -0.063474
C -2.752558 -2.192331 0.715125
C -2.369823 -2.757530 -0.505449
C -3.025361 -3.862511 -1.033220
C -4.087163 -4.379643 -0.297009
C -4.470608 -3.814873 0.925193
C -3.809797 -2.710027 1.452676
H -2.723222 -4.307855 -1.974579
H -4.626374 -5.239932 -0.678292
H -5.301505 -4.246556 1.472454
H -4.109105 -2.266871 2.395561
C -0.652797 -2.152601 -2.248865
H 0.212721 -2.818062 -2.178986
H -1.369574 -2.552685 -2.967981
H -0.316957 -1.166505 -2.575816
N 1.780020 -1.702189 -0.030031
N 2.349087 0.227777 -0.958806
N -1.302484 -2.001623 -0.966383
N -1.890158 -1.138642 0.966155
C -1.767788 -0.480861 2.259111
H -1.887776 -1.240854 3.036752
H -0.772704 -0.032219 2.333854
H -2.514836 0.304249 2.357138
C -0.016815 -0.020177 -0.238987
B -0.460434 1.538527 -0.011403
C -1.747379 2.823281 -1.467777
C -2.436038 2.759919 -0.067204
H 0.464499 1.947366 0.859497
O -0.417004 2.437361 -1.161308
O -1.790807 1.646748 0.527036
C -1.727372 4.205919 -2.108121
H -1.235149 4.157425 -3.083992
H -2.744599 4.583377 -2.258296
H -1.177191 4.914979 -1.486837
C -2.333982 1.800123 -2.451269
H -1.668253 1.726332 -3.316153
H -2.403223 0.811670 -1.986966
H -3.328810 2.089533 -2.804234

C -2.155689 4.002601 0.785094
H -2.471269 3.799204 1.811853
H -2.699288 4.880579 0.422142
H -1.087173 4.230648 0.802946
C -3.936425 2.487758 -0.107981
H -4.148069 1.517725 -0.562583
H -4.462137 3.265146 -0.672574
H -4.338392 2.479225 0.909619
C 1.514580 1.885019 1.947011
N 1.539392 0.677371 2.319568
N 1.920412 3.061273 2.106702
C 2.782302 0.203716 2.907313
H 2.652875 0.028142 3.982868
H 3.077883 -0.751272 2.453507
H 3.610822 0.912675 2.780810
C 1.884001 4.054097 1.066568
H 1.645584 5.033890 1.493086
H 2.861581 4.147635 0.572167
H 1.139161 3.809939 0.293571

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -1593.87596798 | Predicted change in Energy=-3.154163D-09
Zero-point correction (ZPE) = -1593.22733898 0.648629
Internal Energy (U) = -1593.1907269800001 0.685241
Enthalpy (H) = -1593.18978298 0.686185
Gibbs Free Energy (G) = -1593.29464198 0.581326

Frequencies
-417.5872 20.2418 24.7241
31.3731 38.2777 45.8718
48.2423 58.1711 68.1938
79.3171 81.6033 103.6039
125.6355 126.7649 133.3070
141.2498 141.8202 150.7600
159.7347 161.9555 169.8037
181.5743 188.5261 195.9346
207.8418 214.1849 227.2757
229.2183 234.7101 239.1273
248.2268 262.9970 274.9286
289.6883 297.7521 302.7430
305.2139 319.6713 326.7660
328.8092 331.6390 333.6598
345.6862 352.4430 365.2500

371.9734 377.4552 393.2067
404.6570 422.0627 430.5502
448.5739 453.9726 472.0931
510.8339 533.2542 544.4675
555.5192 579.0818 580.4853
589.6886 591.2701 594.4308
596.4635 612.7937 619.9577
656.4724 662.7451 685.3384
695.3534 709.0482 741.2341
753.8887 761.2408 763.7858
764.1378 768.4022 792.3332
819.8959 849.6628 861.1429
866.8798 869.7453 873.8427
889.5358 900.5016 935.8319
937.0717 942.1851 949.6531
958.0518 978.5724 989.3292
998.3140 1008.6563 1014.3268
1022.2351 1029.1808 1038.5023
1048.6373 1057.0168 1061.0598
1061.9772 1064.1666 1082.3856
1117.7307 1127.4190 1132.1098
1136.6892 1151.4092 1153.8812
1158.0563 1160.8578 1163.1301
1170.2349 1171.8140 1173.2002
1176.0254 1179.3986 1186.2665
1194.9941 1196.9976 1199.0167
1199.5059 1227.1761 1247.7094
1271.3649 1274.2834 1280.5221
1290.5349 1294.9200 1324.1537
1326.5286 1367.4474 1369.6326
1374.6577 1389.3140 1408.4497
1411.7475 1415.2573 1425.0916
1426.6727 1433.3344 1434.6402
1452.3970 1455.1458 1460.5344
1474.3467 1479.9174 1482.3068
1489.1351 1494.3439 1496.5747
1499.6676 1500.5104 1503.6928
1505.2233 1511.4573 1512.9684
1515.6739 1519.2636 1519.4526
1520.3330 1522.1279 1523.0988
1524.6620 1528.1127 1529.9887
1533.6721 1534.4514 1537.7271
1539.6979 1545.7930 1553.1681
1561.1760 1570.0641 1579.8825
1609.6140 1697.9252 1703.9760
1705.4069 1708.6995 1790.8160
1997.2542 3000.8927 3014.6998
3058.7258 3059.0958 3059.2343

3062.0896	3063.9251	3064.6510
3067.6425	3069.3768	3071.1932
3084.6198	3094.4501	3107.0908
3138.1236	3138.6508	3139.1189
3146.4728	3147.2256	3149.6024
3151.4574	3152.5690	3155.6082
3164.8413	3168.1652	3171.4793
3177.0527	3179.6857	3194.4763
3207.7369	3216.6309	3219.4298
3227.2081	3230.3900	3237.2149
3239.9378	3245.2120	3247.0076

TS 1–S1

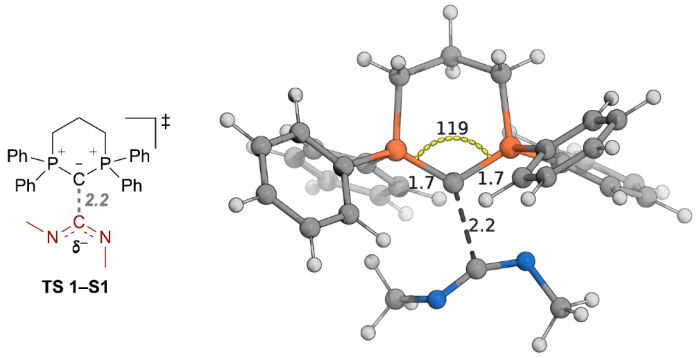

Fig. S35 Three dimensional picture of structure **TS 1–S1** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250,ts,calcfc,noeigentest) freq=noraman

---
Full point group C1 NOp 1
Stoichiometry C31H32N2P2 Framework group C1[X(C31H32N2P2)]

Num atoms: 67
Charge = 0 Multiplicity = 1

SCF = -1992.23857227 | Predicted change in Energy=-1.024853D-08

Optimization completed.
Maximum Force 0.000013 0.000450 YES
RMS Force 0.000002 0.000300 YES
Maximum Displacement 0.001565 0.001800 YES
RMS Displacement 0.000401 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

P -1.558047 0.179387 -0.552885
C -1.532439 0.436624 -2.380622
C -0.368892 -0.334692 -3.012062
C 0.991755 0.213843 -2.568191
P 1.317782 0.126913 -0.735976
H -1.426540 1.510302 -2.571249
H -2.487029 0.109286 -2.803807
H -0.437905 -0.259289 -4.102371
H -0.460335 -1.400033 -2.770286
H 1.804549 -0.308564 -3.081631
H 1.061655 1.270790 -2.846395

C 3.957544 3.893199 -0.331183
C 4.356279 2.870176 -1.186843
C 3.587403 1.714924 -1.292311
C 2.420383 1.574267 -0.537170
C 2.023084 2.604480 0.313387
C 2.790050 3.759666 0.416190
H 4.556498 4.794854 -0.248012
H 5.264636 2.970811 -1.772563
H 3.906607 0.918381 -1.959658
H 1.112350 2.479943 0.890899
H 2.477809 4.556256 1.084066
C 3.919153 -3.694176 -0.411868
C 4.432357 -2.485937 0.051678
C 3.673413 -1.323102 -0.032377
C 2.392445 -1.354862 -0.584986
C 1.881771 -2.573184 -1.040451
C 2.639538 -3.736777 -0.956848
H 4.512018 -4.600771 -0.342086
H 5.425088 -2.448398 0.489318
H 4.066818 -0.389809 0.354523
H 0.875269 -2.622033 -1.446892
H 2.228370 -4.675970 -1.313438
C -3.816130 -3.854502 -0.227026
C -4.518637 -2.721475 -0.630462
C -3.872045 -1.492630 -0.711341
C -2.516152 -1.387145 -0.392013
C -1.821655 -2.524613 0.021715
C -2.467683 -3.754330 0.101947
H -4.323108 -4.812173 -0.161909
H -5.573422 -2.793832 -0.876212
H -4.436143 -0.613498 -1.008169
H -0.776297 -2.418446 0.301189
H -1.919168 -4.631939 0.429449
C -4.275240 3.538277 1.085050
C -4.547047 2.996956 -0.168176
C -3.742743 1.981233 -0.674634
C -2.660674 1.497712 0.068478
C -2.381391 2.058507 1.318077
C -3.192815 3.069347 1.823754
H -4.902747 4.330614 1.481119
H -5.381848 3.368240 -0.754194
H -3.958913 1.580689 -1.661176
H -1.527852 1.701841 1.890013
H -2.972364 3.494511 2.797621
C -0.072121 0.113077 0.198603
C 0.604911 -0.041529 2.307306
N 1.837231 -0.011879 2.076245
N -0.345222 0.005869 3.116785

C -1.507114 -0.835794 3.042976
H -2.125763 -0.672512 3.929246
H -2.119731 -0.595210 2.163054
H -1.265576 -1.905444 2.982264
C 2.729871 -0.387029 3.160484
H 3.373523 0.463300 3.414242
H 2.199033 -0.701535 4.067631
H 3.381155 -1.205522 2.830426

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -1992.23857227 | Predicted change in Energy=-1.024853D-08
Zero-point correction (ZPE) = -1991.68277627 0.555796
Internal Energy (U) = -1991.65000127 0.588571
Enthalpy (H) = -1991.64905627 0.589516
Gibbs Free Energy (G) = -1991.7491822700001 0.48939

Frequencies
-268.6235 10.9968 19.8947
29.5651 41.2842 44.6488
53.8372 57.6899 62.3921
68.3863 77.6389 81.9967
89.3217 96.7953 107.8041
118.2788 131.0777 142.5633
153.7023 155.3126 176.6372
187.8914 194.5361 207.2266
218.8546 228.4040 241.4892
252.0546 259.2312 264.6617
266.9466 290.2933 309.0738
318.4370 362.8296 377.1499
410.2229 411.2305 416.5148
420.9559 422.2489 427.5964
463.7999 477.8986 501.1421
509.8004 516.4655 525.0619
560.2705 572.9829 634.5940
635.2465 636.4576 638.4823
652.3399 656.0393 688.7579
710.8439 715.7996 718.7566
720.8518 725.6838 729.3563
730.2104 734.8067 768.6147
768.9620 773.8971 780.7542
816.1213 821.9700 869.5662
875.2695 878.7822 885.6426
890.6460 906.0039 945.9147
950.0157 953.3339 961.8436
967.5943 999.0277 999.7535
1001.9077 1012.7310 1015.0633

1019.6309	1021.2596	1022.0259
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1071.2589	1075.7898	1112.7745
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1489.6430	1490.4008	1493.2884
1494.6471	1497.8092	1510.1933
1513.0048	1517.7898	1521.2681
1538.1084	1541.3180	1542.6596
1544.6454	1663.0774	1664.5820
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3202.4050	3203.3901	3205.2689
3207.6420	3208.4082	3210.5813
3213.8368	3216.7879	3218.0679
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3234.4371	3235.4905	3242.1516

S1

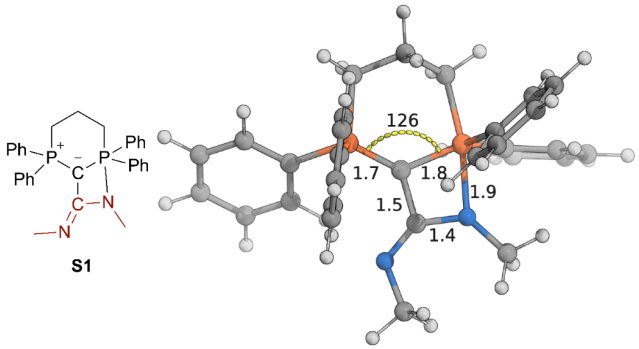

Fig. S36 Three dimensional picture of structure **S1** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman

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Full point group C1 NOp 1
Stoichiometry C31H32N2P2 Framework group C1[X(C31H32N2P2)]

Num atoms: 67
Charge = 0 Multiplicity = 1

SCF = -1992.30224325 | Predicted change in Energy=-1.112594D-08

Optimization completed.
Maximum Force 0.000015 0.000450 YES
RMS Force 0.000002 0.000300 YES
Maximum Displacement 0.001724 0.001800 YES
RMS Displacement 0.000309 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

P -1.358575 0.758154 -0.034286
C -1.457993 -0.130822 -1.724724
C -0.330267 -1.133523 -1.985383
C 1.023041 -0.450343 -2.235032
P 1.618493 0.519929 -0.811730
H -1.446978 0.642103 -2.503508
H -2.423434 -0.638055 -1.815198
H -0.560167 -1.740454 -2.868675
H -0.254296 -1.832306 -1.142806

H 1.798709 -1.170949 -2.513079
H 0.937893 0.261854 -3.062188
C 4.974335 3.211440 -2.419672
C 5.049177 1.830909 -2.595710
C 4.042998 1.015901 -2.092770
C 2.953033 1.583385 -1.425370
C 2.881950 2.964297 -1.239771
C 3.899438 3.773425 -1.738221
H 5.762919 3.848407 -2.808200
H 5.892711 1.391634 -3.118268
H 4.113317 -0.062411 -2.212301
H 2.059350 3.381545 -0.667208
H 3.853004 4.846877 -1.586659
C 3.457507 -2.280562 2.354144
C 3.514889 -0.895691 2.497518
C 3.004665 -0.065801 1.506623
C 2.425588 -0.624844 0.358842
C 2.370826 -2.013406 0.219362
C 2.887636 -2.838028 1.214613
H 3.856443 -2.924555 3.131629
H 3.956229 -0.458572 3.387368
H 3.009546 1.015044 1.628343
H 1.917329 -2.466714 -0.655975
H 2.839030 -3.915963 1.099162
C -2.183892 -3.142672 2.348341
C -3.114274 -2.712658 1.408413
C -2.898921 -1.530994 0.702861
C -1.771603 -0.744956 0.955361
C -0.851192 -1.179504 1.914870
C -1.046922 -2.376443 2.593443
H -2.343766 -4.071104 2.887804
H -4.005587 -3.301004 1.213490
H -3.624512 -1.223521 -0.044405
H 0.021260 -0.570968 2.127507
H -0.309951 -2.706163 3.318989
C -4.893931 3.611322 -0.936379
C -3.650390 3.792967 -1.536576
C -2.608416 2.913826 -1.264703
C -2.795526 1.843678 -0.385508
C -4.040231 1.674150 0.223022
C -5.084990 2.551930 -0.055905
H -5.708275 4.296335 -1.150341
H -3.490683 4.623285 -2.217531
H -1.633531 3.063388 -1.721210
H -4.198665 0.862350 0.926187
H -6.049003 2.408164 0.422338
C 0.290738 1.370666 -0.157531
C 0.299529 2.082473 1.135336

N 1.310652 2.745643 1.595093
N -0.958149 1.766702 1.572277
C -1.776802 2.421233 2.559245
H -2.645879 1.785273 2.759109
H -1.256299 2.560870 3.510834
H -2.154812 3.398605 2.224435
C 1.226797 3.332877 2.916866
H 2.177261 3.826906 3.144028
H 0.439651 4.094868 3.015011
H 1.055668 2.584373 3.706657

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -1992.30224325 | Predicted change in Energy=-1.112594D-08
Zero-point correction (ZPE) = -1991.74286725 0.559376
Internal Energy (U) = -1991.71084625 0.591397
Enthalpy (H) = -1991.70990225 0.592341
Gibbs Free Energy (G) = -1991.8079962499999 0.494247

Frequencies
16.1812 25.6275 30.2440
34.1745 41.0107 47.1164
53.6132 55.1059 64.0294
74.6956 75.6207 88.6987
96.6629 111.7241 137.5172
141.9270 159.2781 185.2052
188.7078 207.3678 222.9182
227.0143 244.4195 248.8897
251.1302 263.3469 267.9729
279.1396 283.1023 300.4203
308.3986 329.2726 360.5657
377.6065 393.6002 408.1892
410.8140 412.1825 415.4856
421.0642 447.8273 478.1714
502.9113 505.2904 510.6572
524.3575 533.9641 552.5902
581.2295 621.3520 634.1688
635.0533 637.5776 640.5536
700.7462 702.9553 710.4190
719.1759 722.0180 727.4182
732.7773 738.7725 747.1199
749.8164 770.7563 772.7625
774.6500 779.6749 811.2529
819.4239 869.8781 873.9132
877.7144 883.5536 887.3342

904.6256 939.4518 950.0372
951.3490 957.8770 959.6417
997.3408 998.6066 1001.8310
1006.3042 1009.0413 1015.6009
1018.7387 1020.7173 1021.3607
1023.8255 1024.0313 1026.4348
1029.1591 1032.9112 1066.9177
1067.5648 1067.9779 1068.4685
1077.9314 1112.5736 1118.6126
1120.9940 1121.8370 1126.2339
1128.6086 1132.0812 1136.9967
1141.7225 1151.4312 1153.5188
1156.2309 1166.9080 1191.2051
1195.5050 1196.2974 1199.3322
1199.8726 1220.4612 1223.8216
1228.1492 1233.9576 1236.6887
1271.8531 1302.6360 1314.1765
1330.5894 1336.8863 1337.6822
1344.6303 1347.8328 1366.7352
1372.3012 1381.9105 1382.0425
1396.3003 1406.6523 1452.5729
1467.8988 1472.1405 1484.5112
1488.4856 1492.1229 1492.7827
1494.7409 1501.8489 1514.6172
1517.2023 1525.8723 1537.3614
1540.7355 1543.1180 1546.9862
1547.5629 1661.9957 1662.1681
1664.4256 1666.8744 1683.1731
1684.6092 1684.8456 1685.6115
1727.1946 2988.7307 3011.3127
3049.4022 3057.6792 3066.8823
3084.2959 3095.2548 3099.1481
3103.9217 3130.2843 3132.3333
3141.0385 3195.6133 3196.8020
3200.6435 3202.1009 3206.7973
3209.1947 3210.6934 3210.8305
3215.7077 3219.9102 3220.1488
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3237.1618 3237.5293 3239.5319

TS S1–S2

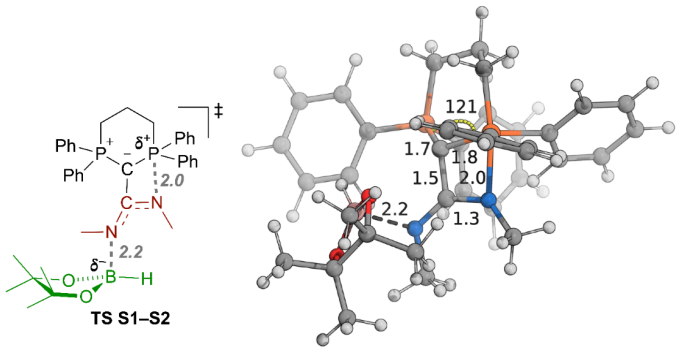

Fig. S37 Three dimensional picture of structure **TS S1–S2** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250,ts,calcfc,noeigentest) freq=noraman

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Full point group C1 NOp 1
Stoichiometry C37H45BN2O2P2 Framework group C1[X(C37H45BN2O2P2)]

Num atoms: 89
Charge = 0 Multiplicity = 1

SCF = -2404.08078437 | Predicted change in Energy=-4.239514D-08

Optimization completed.
Maximum Force 0.000049 0.000450 YES
RMS Force 0.000006 0.000300 YES
Maximum Displacement 0.001537 0.001800 YES
RMS Displacement 0.000279 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

P 1.407756 1.349744 -1.080753
C 2.101250 0.767172 -2.661245
C 2.502141 -0.714721 -2.656868
C 1.318105 -1.646218 -2.390423
P 0.678442 -1.566461 -0.602838
H 2.948407 1.406015 -2.928133
H 1.317541 0.935745 -3.407295
H 3.290200 -0.891456 -1.914392
H 2.945002 -0.935399 -3.634523

H 0.483251 -1.382668 -3.050162
H 1.597559 -2.672765 -2.642461
C 4.505163 -3.532775 1.163538
C 4.045281 -2.313055 1.651281
C 2.869480 -1.760299 1.155954
C 2.153414 -2.398304 0.139400
C 2.629722 -3.619017 -0.350018
C 3.787315 -4.191050 0.169952
H 5.416074 -3.971490 1.558796
H 4.596458 -1.787556 2.424747
H 2.495325 -0.828522 1.562835
H 2.088841 -4.143507 -1.131897
H 4.130838 -5.148704 -0.208537
C -2.898253 -4.401083 -1.327677
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C -1.791733 -2.278996 -1.650356
C -0.719549 -2.714196 -0.867267
C -0.757252 -3.987708 -0.296477
C -1.844069 -4.827171 -0.526061
H -3.743054 -5.057515 -1.511128
H -3.694177 -2.781377 -2.501890
H -1.804174 -1.262795 -2.031535
H 0.059033 -4.327397 0.333695
H -1.864441 -5.815269 -0.076992
C 0.028046 5.704833 -1.669200
C -0.303514 5.013996 -0.507404
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H -0.280633 6.737844 -1.795003
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H -0.220457 3.130099 0.538939
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C 4.822833 1.660294 2.021234
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C -0.296911 0.131351 0.819375

N 0.007559 -1.125328 1.202458
N -0.939789 1.140934 1.353972
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H -1.862120 2.027456 2.973975
B -2.633650 1.618590 0.053352
C -4.681249 1.369612 1.051338
C -4.270598 0.030070 0.327179
H -1.971906 2.301863 -0.661784
O -3.481468 2.143421 1.033488
O -3.152166 0.429941 -0.465163
C -5.137238 1.192694 2.495759
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H -6.028606 0.558765 2.550102
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H -3.381634 -1.888916 0.692143
H -3.050580 -0.710559 1.963511
C -5.344855 -0.535253 -0.598882
H -4.987900 -1.470519 -1.037043
H -6.263819 -0.751197 -0.043619
H -5.578033 0.155555 -1.410739
C -0.453831 -1.916450 2.313187
H 0.236695 -2.759614 2.431543
H -0.446926 -1.358918 3.253837
H -1.458772 -2.328743 2.158021

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -2404.08078437 | Predicted change in Energy=-4.239514D-08
Zero-point correction (ZPE) = -2403.32584637 0.754938
Internal Energy (U) = -2403.28443637 0.796348
Enthalpy (H) = -2403.2834923699997 0.797292
Gibbs Free Energy (G) = -2403.39848637 0.682298

Frequencies
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29.7041 36.9300 43.5288

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65.9482 70.0816 77.5184
78.1460 90.2338 93.7801
101.3922 109.0418 112.6505
125.8545 137.9206 144.4189
158.9381 177.5303 183.8406
188.4852 202.8680 210.4557
222.2651 231.1197 237.4836
245.6632 251.8364 256.8355
259.4483 268.7455 278.8623
284.5045 295.4110 297.9357
304.4839 310.1523 314.7683
316.0672 331.3918 336.5106
354.7316 362.0550 372.3872
384.6972 398.7497 403.4550
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417.0705 419.7311 423.1795
447.1882 465.2061 474.1043
500.5881 511.5757 518.4509
524.3778 527.8771 533.7264
541.9324 565.7281 589.2529
591.5825 625.3366 635.5001
636.9667 637.2250 641.2672
677.3241 701.5765 701.9907
716.1806 718.6220 725.4321
726.2299 733.6872 738.0819
749.5565 751.3241 759.3332
769.8882 775.5165 777.4037
779.5919 816.2454 825.7420
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880.6287 886.2427 888.8679
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953.3194 954.0382 962.4005
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1023.6854 1024.5772 1025.1032
1027.3075 1028.7843 1030.4547
1054.7469 1067.0792 1067.9789
1068.3597 1069.8838 1071.8028
1082.3345 1117.3635 1121.0812
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1153.0548 1155.1514 1155.7185
1167.5518 1193.6309 1196.2532

1197.2249	1197.6097	1199.9364
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1278.6301	1287.9617	1308.6070
1313.3060	1317.3577	1333.2594
1333.9345	1339.3228	1341.6020
1350.9628	1371.2828	1373.8013
1377.2906	1395.2185	1397.0141
1415.0030	1417.0774	1425.1887
1431.3509	1436.5076	1449.7754
1474.8214	1478.9707	1484.6924
1488.7331	1490.7454	1492.9257
1494.8915	1495.5500	1495.7107
1498.3472	1500.3886	1505.1113
1506.7792	1518.4034	1519.1375
1521.1339	1523.9013	1528.7426
1535.6643	1543.0482	1543.7126
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1665.1771	1682.1951	1683.8999
1684.3835	1686.6527	1687.4675
2698.3315	3004.6051	3037.0883
3060.2476	3063.2186	3064.3943
3068.5238	3071.0759	3077.9306
3078.4124	3083.9344	3101.2476
3107.3349	3133.8503	3142.6463
3143.9123	3144.5235	3144.7141
3150.1602	3153.5460	3156.5180
3158.8511	3171.5546	3176.8283
3189.2950	3204.8677	3205.6708
3208.4984	3210.2843	3210.8781
3213.8657	3215.2746	3216.5209
3221.7519	3222.8445	3223.0648
3224.0565	3230.5190	3231.3472
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3238.1097	3238.8669	3259.4934

S2

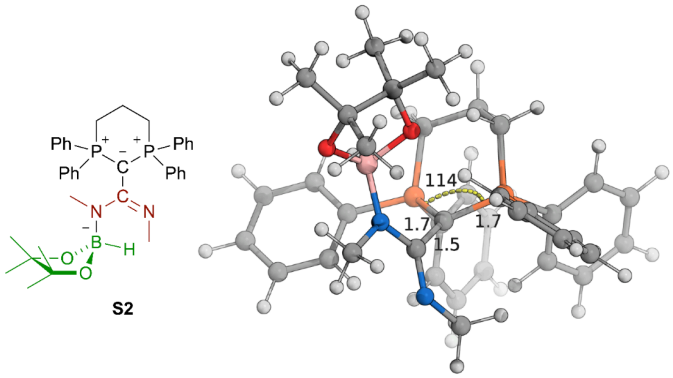

Fig. S38 Three dimensional picture of structure **S2** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman

---
Full point group C1 NOp 1
Stoichiometry C37H45BN2O2P2 Framework group C1[X(C37H45BN2O2P2)]

Num atoms: 89
Charge = 0 Multiplicity = 1

SCF = -2404.10299238 | Predicted change in Energy=-9.319585D-09

Optimization completed.
Maximum Force 0.000015 0.000450 YES
RMS Force 0.000002 0.000300 YES
Maximum Displacement 0.001328 0.001800 YES
RMS Displacement 0.000254 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

P -2.157852 0.418766 -0.417032
C -3.221903 -1.042931 -0.676291
C -2.549502 -2.086626 -1.583534
C -1.235517 -2.679874 -1.026051
P 0.047215 -1.430196 -0.632803
H -4.197210 -0.753514 -1.075811
H -3.341433 -1.447908 0.336689
H -2.392930 -1.660607 -2.580991
H -3.246639 -2.920714 -1.711036

H -1.430968 -3.156341 -0.060567
H -0.842123 -3.431067 -1.717360
C 1.895769 0.062123 -4.607905
C 0.835863 -0.834266 -4.658318
C 0.283111 -1.330864 -3.479741
C 0.776437 -0.921789 -2.241321
C 1.856708 -0.032420 -2.201143
C 2.413417 0.455417 -3.374498
H 2.325189 0.449149 -5.526404
H 0.433694 -1.151006 -5.614962
H -0.538694 -2.034620 -3.544357
H 2.258457 0.284673 -1.243088
H 3.251386 1.143286 -3.328100
C 3.691106 -3.359529 1.383870
C 3.381704 -2.029009 1.644973
C 2.267134 -1.437045 1.061136
C 1.454009 -2.191428 0.211707
C 1.772638 -3.523105 -0.062405
C 2.887207 -4.105629 0.526825
H 4.557400 -3.817458 1.850210
H 4.001800 -1.445556 2.317120
H 2.027945 -0.403461 1.291346
H 1.147504 -4.117735 -0.720893
H 3.123194 -5.144512 0.321713
C -4.205836 3.360635 2.441480
C -3.909395 2.066233 2.859508
C -3.295525 1.170989 1.992409
C -2.979799 1.583070 0.693175
C -3.275623 2.881865 0.270494
C -3.889839 3.767945 1.148691
H -4.680688 4.056579 3.126029
H -4.147350 1.748504 3.869683
H -3.050995 0.158394 2.309749
H -3.022960 3.205240 -0.733889
H -4.116134 4.777856 0.823010
C -1.857959 2.398610 -4.585724
C -0.783140 2.448909 -3.704256
C -0.886361 1.865270 -2.446759
C -2.061374 1.218792 -2.061158
C -3.142469 1.181576 -2.949107
C -3.040431 1.769641 -4.204760
H -1.776642 2.849357 -5.569718
H 0.143508 2.931556 -3.995895
H -0.048823 1.889486 -1.761595
H -4.071004 0.695789 -2.667606
H -3.883572 1.733196 -4.886827
C -0.641432 -0.103200 0.222392
C -0.218428 0.317975 1.617389

N 0.323267 1.469518 1.873746
N -0.413095 -0.570724 2.627220
C 0.130596 -0.149876 3.906634
H 1.182767 0.143553 3.800939
H -0.394415 0.732828 4.294660
H 0.036599 -0.977313 4.606671
B -1.126144 -1.964876 2.527573
C -3.324137 -2.693304 2.954374
C -2.504651 -2.695156 4.284676
H -0.544484 -2.677658 1.711098
O -2.573856 -1.802882 2.152806
O -1.173794 -2.643725 3.822981
C -4.754954 -2.176348 3.077561
H -5.252588 -2.212647 2.102381
H -5.335289 -2.790583 3.774401
H -4.777335 -1.141832 3.427144
C -3.333077 -4.073477 2.279880
H -3.721601 -3.964668 1.260857
H -2.316786 -4.472385 2.223310
H -3.966320 -4.792105 2.809861
C -2.806941 -1.453555 5.139785
H -2.071796 -1.396184 5.947155
H -2.717075 -0.540348 4.543939
H -3.806264 -1.491456 5.586735
C -2.685496 -3.950039 5.135273
H -2.093921 -3.862078 6.051136
H -3.734778 -4.091105 5.418931
H -2.340723 -4.836420 4.599271
C 0.596858 2.395226 0.810161
H -0.310307 2.878649 0.410244
H 1.232907 3.199698 1.194850
H 1.123587 1.943797 -0.047946

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -2404.10299238 | Predicted change in Energy=-9.319585D-09
Zero-point correction (ZPE) = -2403.3473053800003 0.755687
Internal Energy (U) = -2403.3058493800004 0.797143
Enthalpy (H) = -2403.30490538 0.798087
Gibbs Free Energy (G) = -2403.41940238 0.68359

Frequencies
20.4781 30.9397 36.2196
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54.6891 57.2496 64.0693
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89.0015 97.3350 102.9202
106.6611 126.8186 134.5373
146.6105 167.5912 178.6340
187.8022 195.9936 199.5745
211.2435 220.7322 221.8069
229.1097 232.2303 233.9512
240.0032 243.5707 254.3164
256.6359 264.2552 265.7306
278.3233 283.4503 292.5139
306.8520 317.6968 328.9139
335.0375 346.5341 351.6510
370.2668 376.4804 380.2916
399.0297 409.8726 412.1644
413.7627 415.7502 416.5244
420.2813 422.5666 445.1302
455.0755 471.6280 484.7725
491.7169 508.4493 509.2193
520.8191 532.8923 536.5798
572.7266 583.7583 592.7024
634.2446 635.1976 635.5280
636.4733 668.9005 681.5926
689.3265 702.8645 714.6884
716.3832 717.0887 719.6053
724.9268 733.0050 738.3293
739.2741 745.2809 748.0632
767.4471 774.1955 776.7025
778.7007 836.9469 854.7965
865.6812 875.9447 876.4415
878.5300 883.9246 886.1344
891.7058 916.6103 935.0430
937.1471 941.2052 953.8018
958.7775 959.6425 973.2959
976.2506 1002.8049 1006.2293
1008.0475 1011.6909 1015.3303
1018.3973 1018.6328 1020.8751
1022.2663 1023.3601 1023.8707
1025.0200 1026.4127 1031.2654
1032.8900 1041.1290 1051.8589
1063.5223 1066.8674 1068.7066
1069.8006 1070.5619 1072.1788
1076.4289 1118.9457 1122.3737
1125.0665 1128.5432 1129.0697
1130.4462 1134.1743 1141.3851
1142.1688 1147.0158 1151.4294
1153.3977 1158.4232 1159.5876
1167.0148 1190.0928 1199.5418

1199.6356	1200.6302	1201.5528
1203.7164	1206.1436	1228.7820
1232.2451	1233.9131	1239.4887
1241.2721	1246.4375	1266.4225
1272.7076	1282.8752	1284.5270
1321.1811	1328.4151	1339.6692
1340.1504	1343.4224	1346.5272
1366.4021	1372.0538	1375.6980
1386.3248	1391.3673	1406.0889
1407.7476	1409.0468	1415.0566
1421.8504	1429.9348	1453.6431
1466.3909	1470.0293	1483.8797
1489.6882	1493.0310	1493.3186
1494.7855	1496.2344	1497.7342
1498.0222	1498.9687	1500.7635
1505.3887	1516.8862	1517.2905
1518.9003	1520.3777	1521.2488
1528.8708	1538.6672	1544.5076
1546.5031	1551.0137	1551.4987
1661.4517	1665.3547	1666.0462
1666.6358	1669.0692	1684.8599
1685.1921	1685.4365	1686.5756
2404.9483	2971.0726	3022.9141
3030.1847	3048.7496	3050.5915
3057.4632	3058.4594	3062.8099
3073.6724	3077.4877	3088.3533
3094.7404	3119.8691	3126.1615
3133.1252	3136.0998	3144.4847
3145.0980	3155.3853	3155.9533
3158.2731	3162.0494	3168.0934
3168.7540	3198.0678	3209.2890
3209.6907	3211.0388	3211.1873
3217.2236	3217.8066	3220.5259
3222.6062	3223.7045	3226.1774
3228.8536	3232.6684	3232.7263
3235.3509	3237.7418	3239.1806
3240.5008	3245.8243	3267.4108

TS S2–S3

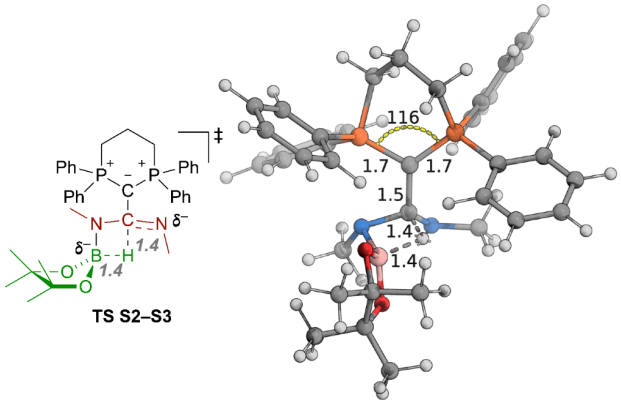

Fig. S39 Three dimensional picture of structure **TS S2–S3** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250,ts,calcfc,noeigentest) freq=noraman

---
Full point group C1 NOp 1
Stoichiometry C37H45BN2O2P2 Framework group C1[X(C37H45BN2O2P2)]

Num atoms: 89
Charge = 0 Multiplicity = 1

SCF = -2404.02674692 | Predicted change in Energy=-4.264565D-09

Optimization completed.
Maximum Force 0.000011 0.000450 YES
RMS Force 0.000001 0.000300 YES
Maximum Displacement 0.000777 0.001800 YES
RMS Displacement 0.000171 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

P -0.820242 -1.402681 0.639891
C -2.445438 -1.335669 1.522047
C -2.538846 -0.291491 2.644927
C -1.932339 1.090132 2.317361
P -1.653356 1.392086 0.531138
H -2.650261 -2.330478 1.926580
H -3.207914 -1.142195 0.761196
H -2.039320 -0.681244 3.536274
H -3.595633 -0.171601 2.899515

H -2.534972 1.902648 2.732851
H -0.931646 1.186007 2.749669
C 0.309257 5.536767 0.416251
C -1.050189 5.423575 0.136700
C -1.660212 4.174798 0.146075
C -0.906536 3.036895 0.440280
C 0.459791 3.148138 0.713598
C 1.061879 4.401758 0.701441
H 0.785062 6.512153 0.401610
H -1.634435 6.306822 -0.099264
H -2.714049 4.085824 -0.097476
H 1.050587 2.255592 0.901133
H 2.124893 4.485711 0.900553
C -5.826510 1.341226 -1.427566
C -4.724626 0.778922 -2.067649
C -3.468312 0.825842 -1.472739
C -3.314361 1.446911 -0.227350
C -4.422289 2.008615 0.413411
C -5.676204 1.957013 -0.188068
H -6.805458 1.298755 -1.894394
H -4.840644 0.303508 -3.036138
H -2.597625 0.388226 -1.966163
H -4.315194 2.489556 1.381832
H -6.534450 2.393642 0.312276
C -1.552186 -4.858309 -2.314089
C -0.492617 -4.941967 -1.414893
C -0.255670 -3.909701 -0.515624
C -1.091392 -2.792067 -0.499063
C -2.146847 -2.705881 -1.408602
C -2.374639 -3.736365 -2.314009
H -1.727821 -5.660691 -3.023388
H 0.164407 -5.805450 -1.425813
H 0.599364 -3.956422 0.149537
H -2.779135 -1.824361 -1.430687
H -3.189720 -3.656464 -3.025637
C 1.753435 -2.706840 4.232422
C 0.732652 -3.536484 3.771434
C -0.011556 -3.166495 2.658323
C 0.265540 -1.965104 1.992461
C 1.279253 -1.135141 2.462329
C 2.024559 -1.511570 3.576701
H 2.336963 -2.997598 5.100404
H 0.517533 -4.471979 4.277770
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H 1.521821 -0.226798 1.924076
H 2.827305 -0.868100 3.922224
C -0.602439 0.169968 -0.041956
C 0.236441 0.162547 -1.337547

N -0.206316 0.477031 -2.543884
N 1.121998 -1.002367 -1.180792
C 1.306071 -1.808300 -2.386219
H 2.006015 -2.615165 -2.144807
H 0.358565 -2.250050 -2.702441
H 1.704349 -1.227324 -3.221533
B 2.213553 0.003037 -0.923009
C 4.459366 0.310539 -1.302670
C 4.103040 0.739710 0.160267
O 3.188016 0.259016 -1.929798
O 2.851074 0.094558 0.359896
C 5.068012 -1.096627 -1.358185
H 5.077295 -1.428138 -2.399689
H 6.093071 -1.120978 -0.974045
H 4.458480 -1.800080 -0.783539
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H 5.556143 0.905092 -3.057553
H 4.861373 2.261461 -2.165870
H 6.306769 1.431476 -1.539719
C 5.075152 0.253401 1.229026
H 4.756279 0.614613 2.212155
H 5.105423 -0.836943 1.263505
H 6.086024 0.630640 1.041234
C 3.906726 2.254495 0.287159
H 3.477126 2.469544 1.271593
H 4.852387 2.798267 0.201247
H 3.218538 2.617921 -0.481358
H 1.259530 1.079473 -0.980529
C -0.555050 1.848574 -2.730546
H -1.389082 2.248637 -2.110197
H 0.303795 2.517401 -2.508800
H -0.849994 2.023765 -3.771848

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -2404.02674692 | Predicted change in Energy=-4.264565D-09
Zero-point correction (ZPE) = -2403.2744269199998 0.75232
Internal Energy (U) = -2403.2330979199996 0.793649
Enthalpy (H) = -2403.23215292 0.794594
Gibbs Free Energy (G) = -2403.34727992 0.679467

Frequencies
-721.5777 19.3743 25.0927
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78.8174 82.8371 93.6958
95.6738 105.5515 111.1693
128.8388 135.5499 154.3511
174.2384 175.1880 182.4033
200.2104 210.2254 215.1229
225.1924 229.5263 232.7428
242.6499 244.2817 256.5980
258.7733 263.5009 272.3943
276.1374 281.8906 288.1704
302.6303 305.7116 322.1708
327.6683 334.9777 337.1549
349.1135 355.5484 375.0637
379.2351 395.7121 405.4052
409.8051 418.9199 422.1048
426.4435 430.5649 443.4946
470.0813 475.9059 485.9454
498.2039 500.1744 505.0883
518.7111 525.8877 533.8780
561.5738 576.2680 589.5464
602.2782 633.3096 635.0280
635.4420 638.0666 662.9528
677.8832 687.9216 710.5030
711.4964 716.1470 718.0696
724.6716 733.7385 740.5309
744.6789 754.1350 762.5287
771.9683 773.8417 775.4636
779.8340 782.8507 845.6864
872.4351 873.2476 881.0185
884.5271 888.7073 898.7735
908.7210 926.9730 942.7794
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999.4478 1005.9938 1013.1638
1018.4882 1019.4308 1020.4179
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1025.2813 1027.1996 1031.7030
1034.8324 1037.2465 1066.7664
1067.9985 1068.7426 1069.6830
1088.5806 1097.1267 1105.2735
1106.3194 1119.3450 1124.5895
1125.7625 1128.1329 1128.9231
1131.6032 1139.8788 1147.5505
1150.3002 1153.1473 1155.0141
1163.2914 1177.6296 1180.7401
1184.0313 1194.8062 1198.0671
1198.4239 1199.2501 1200.6986

1201.0185	1215.4418	1227.3948
1229.7814	1231.4002	1232.2062
1239.3870	1256.3973	1272.5487
1277.8367	1278.8472	1286.8240
1295.0567	1302.1571	1327.0072
1338.5397	1340.4133	1342.3871
1345.9729	1354.4534	1373.0890
1375.0590	1376.7642	1383.4711
1386.8324	1413.0434	1414.1043
1425.1975	1433.6634	1454.8822
1466.5095	1472.5234	1479.6297
1489.2907	1490.5816	1491.4917
1494.6407	1495.7291	1496.4917
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1521.2342	1522.4952	1525.5101
1530.1684	1538.4395	1542.5761
1542.8987	1544.9747	1546.3201
1548.1520	1663.0674	1665.1675
1666.2104	1668.5849	1682.4065
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1699.8838	2875.1266	2903.9915
3055.4047	3059.9083	3061.0649
3062.4031	3065.6617	3079.9331
3085.1434	3093.4714	3097.2187
3132.7443	3133.2652	3137.4760
3139.2968	3142.3764	3143.2204
3147.8986	3149.6526	3155.5503
3155.6718	3157.6157	3163.5533
3170.2614	3173.0591	3202.6043
3204.4687	3210.3610	3210.9989
3211.1847	3214.7968	3215.1434
3220.2038	3223.4065	3223.5617
3227.3674	3228.5668	3233.4382
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3240.5966	3243.6413	3252.6192

S3

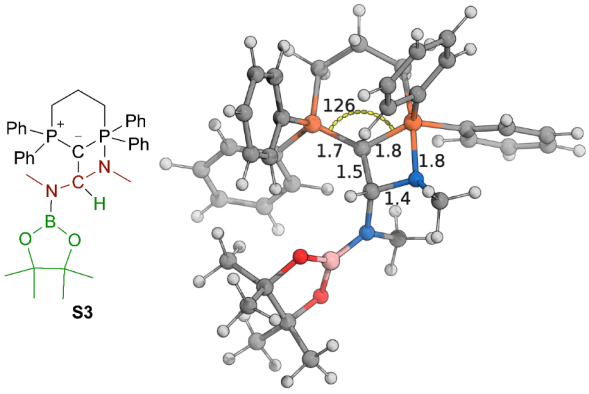

Fig. S40 Three dimensional picture of structure **S3** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman

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Full point group C1 NOp 1
Stoichiometry C37H45BN2O2P2 Framework group C1[X(C37H45BN2O2P2)]

Num atoms: 89
Charge = 0 Multiplicity = 1

SCF = -2404.13515975 | Predicted change in Energy=-2.353137D-08

Optimization completed.
Maximum Force 0.000047 0.000450 YES
RMS Force 0.000006 0.000300 YES
Maximum Displacement 0.001345 0.001800 YES
RMS Displacement 0.000265 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

P -2.134626 0.316330 0.052623
C -3.097198 -1.173444 -0.355216
C -2.563357 -1.894463 -1.602727
C -1.135064 -2.411171 -1.416048
P 0.248278 -1.061842 -1.367371
H -4.150139 -0.890003 -0.454002
H -3.021788 -1.827766 0.519408
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H -3.245000 -2.725431 -1.820604

H -1.080325 -2.983280 -0.480970
H -0.903016 -3.123452 -2.214661
C -0.485559 0.194868 -5.787104
C -0.567488 1.117612 -4.747943
C -0.296814 0.722612 -3.442625
C 0.032846 -0.603831 -3.145641
C 0.099944 -1.522793 -4.196580
C -0.143561 -1.124746 -5.508611
H -0.687494 0.502082 -6.808617
H -0.841424 2.148534 -4.949663
H -0.355836 1.452013 -2.640818
H 0.348422 -2.560712 -3.995577
H -0.074138 -1.850998 -6.312800
C 3.575311 -4.235359 -0.656844
C 2.610524 -3.979569 0.314742
C 1.605023 -3.050925 0.073234
C 1.549648 -2.353788 -1.137323
C 2.527005 -2.609703 -2.102190
C 3.529364 -3.548016 -1.864537
H 4.358523 -4.963676 -0.471272
H 2.641561 -4.505932 1.264085
H 0.862221 -2.850283 0.841105
H 2.513599 -2.074611 -3.046929
H 4.278410 -3.737653 -2.627620
C -3.240268 1.403024 4.391503
C -4.099579 1.770104 3.357167
C -3.766664 1.476971 2.039589
C -2.576824 0.801760 1.753328
C -1.718111 0.437220 2.791434
C -2.047840 0.742871 4.108618
H -3.497848 1.641742 5.418613
H -5.024221 2.293512 3.577666
H -4.425493 1.784699 1.232426
H -0.790636 -0.071767 2.550530
H -1.367567 0.473272 4.909501
C -3.437202 3.804555 -2.683911
C -2.571509 4.016034 -1.613442
C -2.240184 2.968010 -0.762797
C -2.773399 1.690033 -0.977474
C -3.641121 1.485675 -2.053154
C -3.972592 2.539287 -2.900420
H -3.692056 4.623621 -3.349002
H -2.144625 4.999058 -1.441112
H -1.545635 3.146054 0.054085
H -4.058875 0.503923 -2.249114
H -4.646237 2.366772 -3.733513
C -0.486778 -0.026579 -0.124681
C 0.625869 1.011293 -0.107546

H 0.339026 1.991094 -0.525787
N 1.478469 0.251579 -0.974245
N 1.205274 1.310525 1.208409
B 0.915453 2.505829 1.876086
C 1.032718 4.161533 3.423037
C -0.035828 4.527178 2.330158
O 1.247743 2.762758 3.196444
O 0.253909 3.582189 1.288584
C -1.470849 4.278931 2.795644
H -2.150244 4.380477 1.944954
H -1.582547 3.269987 3.197150
H -1.775321 4.997613 3.561997
C 0.089779 5.933373 1.759159
H -0.690524 6.095455 1.009973
H -0.035949 6.683245 2.546748
H 1.057284 6.085669 1.278589
C 0.562231 4.354523 4.858451
H 1.364558 4.078135 5.547600
H 0.297700 5.400574 5.043841
H -0.303988 3.727051 5.076125
C 2.371870 4.870175 3.205893
H 3.116807 4.423141 3.868731
H 2.717968 4.745736 2.175951
H 2.306544 5.939505 3.426702
C 1.905782 0.221979 1.860898
H 1.244691 -0.642704 2.010811
H 2.743073 -0.122220 1.247512
H 2.273583 0.558521 2.831284
C 2.565431 0.864805 -1.676735
H 3.171825 1.467517 -0.986904
H 3.219783 0.090981 -2.094301
H 2.248755 1.519943 -2.509448

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -2404.13515975 | Predicted change in Energy=-2.353137D-08
Zero-point correction (ZPE) = -2403.3771877500003 0.757972
Internal Energy (U) = -2403.33552375 0.799636
Enthalpy (H) = -2403.33457975 0.80058
Gibbs Free Energy (G) = -2403.45023175 0.684928

Frequencies
23.0834 27.1441 28.6653
40.6185 47.8372 50.5452

53.5940 60.0544 63.9081
68.2638 72.1808 76.7840
85.5165 93.7355 99.4887
106.3927 111.6355 123.2032
136.7334 144.5710 154.1701
160.0259 161.7549 188.4540
194.3189 202.5401 210.9964
222.1733 228.8932 238.3875
241.9802 254.0361 257.8405
260.2825 268.6451 275.2406
279.8839 290.2697 295.3927
302.5658 310.3171 326.3332
333.4235 338.1876 352.2125
365.5472 381.2159 386.5385
393.8848 398.8771 413.7556
414.1019 415.5623 421.2351
425.5775 446.1415 458.4142
465.5194 485.0249 496.7839
503.1310 519.6942 524.4359
531.8933 540.2003 558.0059
568.1401 580.2599 594.2717
630.2467 635.1084 635.8120
640.4088 643.0071 660.6558
682.8783 688.1843 702.5727
715.7557 717.7224 723.0423
730.4262 730.7946 732.1913
738.4449 748.3165 770.1183
772.4590 772.9780 779.9478
801.1513 815.8833 855.4425
868.4874 878.7586 882.7138
886.4407 890.8549 891.5481
910.2150 935.7944 945.2230
948.6869 949.6974 954.8509
962.3039 965.2456 977.7025
984.3258 994.4280 995.9802
1001.6298 1006.6024 1009.2156
1015.7537 1016.2867 1020.2486
1022.5512 1022.8394 1023.7670
1024.0247 1024.9225 1025.6628
1027.1412 1046.6666 1048.1022
1065.0067 1066.9672 1067.1889
1068.4658 1076.2792 1087.0749
1117.4220 1119.5597 1120.8623
1127.7758 1130.6051 1141.1062
1144.4939 1147.5748 1150.6178
1151.2455 1161.8805 1165.0435
1171.3809 1187.5855 1187.7914
1195.5222 1195.7537 1196.8604

1198.9545	1204.4153	1218.4553
1219.8202	1225.6378	1230.9061
1231.1873	1238.9266	1250.3474
1267.0362	1271.9919	1285.7045
1307.0301	1318.0176	1321.1045
1328.5565	1334.7484	1335.9650
1340.8995	1344.0858	1347.2487
1352.0559	1368.1709	1369.5069
1375.5189	1382.9097	1389.9739
1421.1633	1421.8032	1431.2274
1432.6511	1440.9089	1461.8131
1468.3675	1476.7936	1485.6944
1487.7297	1489.5121	1489.9917
1491.5961	1492.8900	1493.3855
1498.5445	1500.5690	1503.4865
1504.8924	1515.5193	1519.9550
1521.7782	1522.6577	1525.3040
1529.4992	1539.4298	1542.7819
1543.8030	1545.0091	1549.3256
1596.1886	1661.1249	1662.5733
1663.3161	1665.0673	1682.0436
1683.7367	1684.2650	1684.7116
2951.8972	2989.4014	3036.8539
3049.0106	3052.1715	3063.4627
3066.3356	3068.7639	3070.6100
3075.9633	3081.7553	3099.6981
3106.9139	3114.9940	3123.5573
3138.5520	3144.6008	3148.7680
3154.0942	3156.2693	3160.6636
3172.2146	3172.9059	3177.8976
3184.3475	3193.8493	3200.4885
3201.9964	3206.1522	3206.7548
3209.2512	3211.6332	3213.7081
3214.1469	3217.8243	3220.6148
3220.7725	3226.5495	3227.4056
3229.5529	3229.8646	3234.4871
3235.0020	3237.8423	3244.3804

TS S3–1

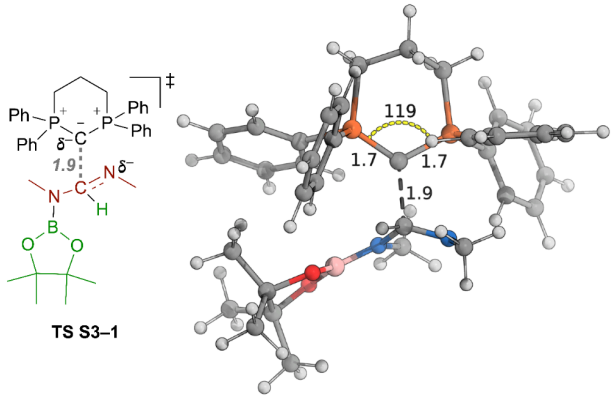

Fig. S41 Three dimensional picture of structure **TS S3–1** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250,ts,calcfc,noeigentest) freq=noraman

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Full point group C1 NOp 1
Stoichiometry C37H45BN2O2P2 Framework group C1[X(C37H45BN2O2P2)]

Num atoms: 89
Charge = 0 Multiplicity = 1

SCF = -2404.08050910 | Predicted change in Energy=-1.331989D-08

Optimization completed.
Maximum Force 0.000024 0.000450 YES
RMS Force 0.000002 0.000300 YES
Maximum Displacement 0.001129 0.001800 YES
RMS Displacement 0.000225 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

P -2.445196 0.270807 -0.659043
C -3.002404 -0.475594 -2.253232
C -2.438811 -1.877693 -2.496883
C -0.927712 -1.833545 -2.744561
P 0.003165 -1.177235 -1.295003
H -2.682040 0.178603 -3.069973
H -4.096345 -0.492681 -2.244027
H -2.931502 -2.309292 -3.374281
H -2.680950 -2.528462 -1.648588

H -0.526437 -2.814117 -3.017418
H -0.706531 -1.157010 -3.576760
C 3.892473 0.236710 -3.322189
C 2.986689 1.161806 -2.811885
C 1.827134 0.723780 -2.177426
C 1.585252 -0.641458 -2.031260
C 2.504677 -1.568742 -2.531451
C 3.650291 -1.129794 -3.184767
H 4.794971 0.578318 -3.819545
H 3.183066 2.225255 -2.895680
H 1.108493 1.429451 -1.774178
H 2.330897 -2.633307 -2.399215
H 4.361864 -1.850859 -3.573884
C 1.072317 -4.795113 1.390672
C 0.096922 -4.939953 0.409429
C -0.206679 -3.875686 -0.435202
C 0.464581 -2.655473 -0.309519
C 1.442435 -2.518000 0.682009
C 1.741841 -3.581964 1.525061
H 1.306608 -5.624175 2.050851
H -0.430575 -5.882048 0.298594
H -0.976855 -4.010756 -1.188006
H 1.962665 -1.574035 0.815446
H 2.497210 -3.455383 2.294175
C -5.201472 -2.051824 2.226451
C -5.633694 -0.832406 1.711150
C -4.806982 -0.095784 0.869106
C -3.534645 -0.571538 0.544124
C -3.103652 -1.790071 1.071833
C -3.935056 -2.529994 1.905100
H -5.848116 -2.622498 2.885613
H -6.616054 -0.449953 1.969719
H -5.147491 0.857676 0.477746
H -2.097053 -2.138494 0.859274
H -3.583745 -3.470667 2.316979
C -4.109869 4.592334 -0.800653
C -3.526310 4.093336 0.360378
C -3.015067 2.800896 0.398482
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C -3.676856 2.493595 -1.904614
C -4.183306 3.789806 -1.933777
H -4.505365 5.603321 -0.824224
H -3.461400 4.715836 1.247446
H -2.505796 2.393971 1.280814
H -3.761866 1.892595 -2.802190
H -4.637563 4.167730 -2.844303
C -0.783823 0.025161 -0.419388
C -0.159004 0.653053 1.270178

H 0.360185 -0.253030 1.606629
N -1.178984 1.088252 2.014851
N 0.828835 1.623838 0.855382
B 2.200722 1.402329 1.017506
C 4.405700 1.901210 1.218991
C 4.183612 0.364882 1.472374
O 3.174939 2.301585 0.607446
O 2.758031 0.276712 1.617682
C 4.586869 -0.496990 0.276829
H 4.258517 -1.526675 0.443330
H 4.116666 -0.135508 -0.638600
H 5.671472 -0.505080 0.134959
C 4.831867 -0.172340 2.741850
H 4.620590 -1.241300 2.836295
H 5.918413 -0.042862 2.706104
H 4.445645 0.327904 3.631007
C 5.548736 2.227943 0.266667
H 5.627306 3.311989 0.148533
H 6.501300 1.857220 0.658837
H 5.376461 1.789745 -0.718219
C 4.552553 2.703533 2.514502
H 4.508078 3.768611 2.273855
H 3.736591 2.480539 3.207632
H 5.503683 2.498931 3.014629
C 0.329163 2.904613 0.405896
H -0.303693 3.353074 1.177499
H 1.167448 3.567454 0.186492
H -0.279929 2.783661 -0.499844
C -1.583595 0.200799 3.075725
H -1.235776 -0.842569 2.949269
H -1.204484 0.533451 4.058640
H -2.678975 0.149806 3.167979

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -2404.08050910 | Predicted change in Energy=-1.331989D-08
Zero-point correction (ZPE) = -2403.3245601000003 0.755949
Internal Energy (U) = -2403.2830291 0.79748
Enthalpy (H) = -2403.2820851 0.798424
Gibbs Free Energy (G) = -2403.3973381 0.683171

Frequencies
-375.9093 22.7409 27.7454
31.2305 42.1474 44.9511

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63.8608 71.1344 78.4542
82.0365 85.7777 91.3803
96.0869 101.7274 109.5822
120.2733 124.8404 137.3012
151.0370 156.7897 185.6201
199.3754 205.7151 217.5254
220.4832 224.9434 240.0566
242.1572 246.2832 252.1195
263.7806 268.3666 271.8281
274.9474 279.6273 287.7541
290.1547 309.4936 323.6435
325.2150 337.7787 342.2064
350.0272 358.5256 377.8922
389.2752 399.1892 412.2601
414.5274 416.6996 421.7407
422.0895 432.2414 436.7795
456.0109 462.6006 473.0789
482.1546 496.9435 502.3102
508.6482 525.0744 526.3252
534.8032 546.8951 577.0067
594.1802 635.0613 636.6788
637.3613 637.5095 647.9388
661.2087 682.5241 695.8670
712.7606 715.8770 717.6950
722.7673 726.0010 727.6221
730.6269 732.2661 736.5259
768.5013 773.1419 776.2009
779.0834 808.2806 826.5920
863.4623 879.7334 880.6969
882.7538 888.8324 892.6446
893.5331 917.0231 945.7432
948.4213 950.3236 958.1544
958.5925 963.1135 968.0143
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1005.7191 1007.3477 1013.6210
1015.7470 1018.5296 1020.7461
1021.0766 1022.4698 1024.8677
1025.3747 1027.5466 1029.2218
1047.6613 1050.4751 1064.6868
1067.4929 1068.2829 1069.3389
1072.1920 1079.1871 1115.2123
1118.3496 1122.0372 1124.5368
1127.1114 1132.9053 1138.2512
1140.6168 1146.2602 1146.4514
1148.8644 1154.4016 1160.0917
1164.7723 1167.7094 1182.0144
1196.4374 1197.5378 1197.6659

1199.1285	1203.8187	1206.0914
1219.0784	1220.2554	1226.7552
1230.0435	1232.4665	1242.1758
1261.2064	1266.1838	1278.7557
1286.4069	1316.0903	1317.5616
1333.9757	1335.1033	1340.5365
1342.0281	1345.3900	1350.0967
1368.2114	1374.0618	1375.1961
1381.1285	1388.6347	1394.6636
1420.9174	1422.3522	1431.7433
1434.2824	1441.7817	1460.9985
1473.6160	1488.7159	1489.4022
1489.5389	1491.3881	1493.1243
1493.3736	1495.6635	1496.4173
1497.3276	1499.6153	1507.4787
1516.3402	1519.4221	1519.5336
1522.9703	1526.6910	1530.6916
1539.9459	1544.1135	1544.5818
1546.3581	1546.8331	1557.1636
1591.9140	1658.4830	1662.3539
1664.6904	1666.3390	1682.2014
1683.7678	1684.4782	1684.7620
2932.4934	2976.8450	3038.7061
3039.4131	3043.2953	3059.5772
3066.0469	3068.6972	3070.5084
3071.0924	3077.3844	3082.6619
3085.1928	3115.0881	3118.7615
3143.0831	3144.9558	3146.7174
3148.2566	3153.5699	3156.6327
3160.4039	3170.4720	3170.8002
3178.8796	3194.6091	3202.7949
3203.7402	3205.5919	3206.2060
3212.9554	3214.1654	3214.5469
3216.4308	3221.6045	3221.9273
3226.5982	3226.7966	3227.4282
3228.5533	3234.1296	3235.0280
3235.4137	3243.2225	3243.3797

TS 11–S4

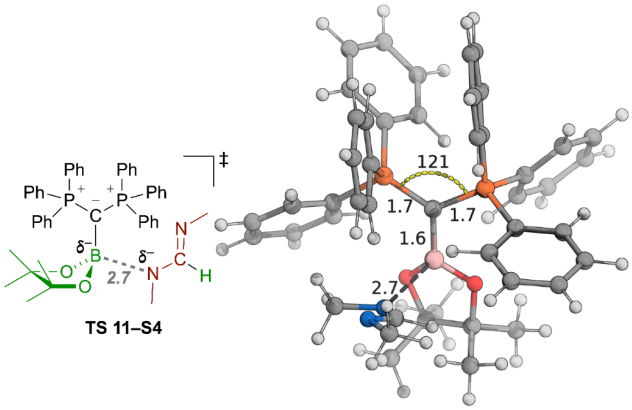

Fig. S42 Three dimensional picture of structure **TS 11–S4** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250,ts,calcfc,noeigentest) freq=noraman

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Full point group C1 NOp 1
Stoichiometry C46H49BN2O2P2 Framework group C1[X(C46H49BN2O2P2)]

Num atoms: 102
Charge = 0 Multiplicity = 1

SCF = -2749.33874133 | Predicted change in Energy=-1.208554D-08

Optimization completed.
Maximum Force 0.000018 0.000450 YES
RMS Force 0.000002 0.000300 YES
Maximum Displacement 0.001489 0.001800 YES
RMS Displacement 0.000283 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

P -0.063417 1.703061 0.167714
P -1.274126 -0.982266 -0.428832
C -4.636257 0.276231 -3.338001
C -4.864045 -0.742509 -2.415234
C -3.865797 -1.110626 -1.521616
C -2.637825 -0.439983 -1.522014
C -2.403375 0.551256 -2.474499
C -3.400335 0.912513 -3.376056
H -5.416133 0.558570 -4.037925

H -5.817034 -1.261080 -2.400381
H -4.038518 -1.934155 -0.835936
H -1.436198 1.041015 -2.510463
H -3.205593 1.688616 -4.109128
C -0.592972 -5.098403 -2.349260
C -1.133041 -5.018696 -1.071757
C -1.304531 -3.779538 -0.462895
C -0.930608 -2.617169 -1.136509
C -0.416137 -2.697307 -2.433711
C -0.238407 -3.936141 -3.031138
H -0.448441 -6.066889 -2.817492
H -1.407316 -5.920603 -0.535383
H -1.704813 -3.728065 0.542916
H -0.124454 -1.797175 -2.960278
H 0.181030 -3.995200 -4.029967
C 2.885402 2.802160 3.513154
C 2.350311 1.520722 3.425249
C 1.495990 1.193470 2.379212
C 1.160597 2.157071 1.428650
C 1.705415 3.439336 1.508801
C 2.569182 3.757234 2.551069
H 3.559953 3.053409 4.325490
H 2.610049 0.760142 4.153885
H 1.118399 0.181494 2.281339
H 1.477809 4.186008 0.756468
H 2.999773 4.751800 2.606831
C 0.407956 4.796407 -3.230407
C -0.223012 5.171320 -2.047443
C -0.382447 4.247199 -1.020027
C 0.089668 2.939456 -1.170722
C 0.716976 2.568531 -2.362335
C 0.875544 3.494794 -3.387024
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H -0.595187 6.183063 -1.924257
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H 1.070342 1.550410 -2.486665
H 1.365493 3.197265 -4.308425
C 0.087172 0.079751 -0.412715
B 1.544699 -0.335388 -0.782200
O 2.552184 0.564281 -0.511303
C 3.768056 0.112542 -1.122570
C 3.289880 -1.084865 -2.060392
O 1.896744 -1.242086 -1.749894
C 4.361817 1.308373 -1.866179
H 3.668813 1.717491 -2.605164
H 5.294403 1.038132 -2.370509
H 4.580492 2.097855 -1.142395
C 4.708764 -0.309241 0.003793

H 4.878979 0.553362 0.654726
H 5.674833 -0.643811 -0.387012
H 4.245077 -1.104398 0.590381
C 3.354018 -0.771500 -3.556854
H 2.916216 -1.607236 -4.109721
H 2.784410 0.128797 -3.804865
H 4.384320 -0.636406 -3.898300
C 3.984829 -2.413342 -1.781767
H 3.544209 -3.184901 -2.419879
H 5.055438 -2.352984 -2.002141
H 3.834090 -2.699805 -0.740451
H 2.979417 -1.063046 2.581997
C 2.433232 -2.003950 2.369403
N 2.091927 -2.776301 3.370179
N 2.197524 -2.194440 1.071277
C 1.729555 -3.531340 0.771444
H 0.768110 -3.793821 1.248295
H 1.608719 -3.640862 -0.312713
H 2.433917 -4.300434 1.129377
C 2.529553 -2.342619 4.670357
H 3.157996 -3.101960 5.160307
H 3.126041 -1.406313 4.661097
H 1.679257 -2.170777 5.353261
C -4.145172 2.483708 2.190715
C -3.035712 2.136486 2.954728
C -1.806322 1.920719 2.344719
C -1.674699 2.053511 0.958925
C -2.790579 2.418177 0.198754
C -4.021015 2.624919 0.811923
H -5.105487 2.647441 2.669332
H -3.125362 2.019267 4.029120
H -0.954122 1.636227 2.950956
H -2.705369 2.544595 -0.873790
H -4.879662 2.900837 0.208831
C -2.569633 -1.744918 3.906762
C -3.534729 -1.272770 3.019980
C -3.209483 -1.032033 1.688081
C -1.905519 -1.261073 1.250260
C -0.929249 -1.712423 2.147549
C -1.264491 -1.965537 3.471239
H -2.836486 -1.937005 4.941592
H -4.545285 -1.079639 3.365962
H -3.959141 -0.625440 1.018270
H 0.098467 -1.856845 1.814932
H -0.485589 -2.342420 4.126278

Statistical Thermodynamic Analysis

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -2749.33874133 | Predicted change in Energy=-1.208554D-08
Zero-point correction (ZPE) = -2748.48527633 0.853465
Internal Energy (U) = -2748.4363253300003 0.902416
Enthalpy (H) = -2748.4353813300004 0.90336
Gibbs Free Energy (G) = -2748.56765733 0.771084

Frequencies
-62.4596 17.9255 28.3561
32.1331 34.5139 40.0268
44.5331 46.5201 48.9073
49.7635 54.2888 59.6340
59.8476 64.4942 72.7406
75.7623 82.7009 87.0716
89.8253 94.7163 102.1369
104.9855 112.2045 115.2759
120.6010 138.4100 140.4533
154.1160 173.9030 183.5028
199.1308 205.4042 208.2672
210.1148 222.3697 229.4238
231.5078 234.3331 244.7046
247.2385 253.9345 261.9091
266.4377 267.6122 275.7186
282.0470 287.1026 293.1214
303.8145 318.3822 327.9301
331.7724 345.7640 364.5119
367.9117 386.7999 410.6927
412.8387 416.2328 417.8997
418.9016 423.2531 426.8331
430.0824 438.1584 442.4916
446.3885 460.8609 472.4527
476.2374 495.6114 509.0439
511.7348 521.9455 526.4945
526.9788 533.3431 537.0746
551.2763 582.5085 590.5126
606.4750 632.1328 634.6053
635.4287 635.8052 637.3784
639.1160 673.4167 705.2657
707.8474 709.8017 714.6079
716.6983 720.4255 722.9310
729.9093 732.5698 737.4569
740.8726 741.6212 745.2911
767.8902 771.0418 773.3412
778.4143 779.4257 783.3690
793.9900 863.9782 878.3197

879.6559 884.2317 888.0692
888.5674 899.8291 910.7539
941.4588 949.4432 950.4431
955.9373 963.4519 965.7868
967.4348 975.0005 983.5345
990.6502 995.4058 1004.2045
1008.2787 1008.9387 1010.9530
1015.5499 1019.5996 1020.2624
1022.5883 1023.2211 1023.9803
1024.0786 1025.9232 1026.9255
1027.4827 1029.8111 1030.3462
1031.9547 1032.2496 1032.6924
1041.5178 1049.2042 1057.8724
1067.0131 1067.4227 1068.0212
1069.2881 1070.2028 1080.9122
1087.8270 1104.4263 1122.9333
1125.4240 1127.7613 1129.8723
1132.3592 1133.2827 1136.3558
1142.7158 1143.1740 1145.0879
1145.7057 1147.1132 1149.6086
1150.7418 1152.7269 1174.8259
1188.1512 1191.6032 1198.0265
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1200.5037 1200.8408 1207.6264
1224.9860 1228.6710 1230.7965
1231.1620 1236.0443 1237.5351
1252.7749 1282.4992 1297.8694
1332.4781 1334.2398 1335.8134
1342.5954 1342.8870 1344.6242
1347.7096 1367.6163 1371.1657
1372.2140 1373.5619 1376.5254
1379.4891 1380.2664 1397.9999
1410.6557 1418.3987 1419.4625
1425.4860 1438.9693 1450.5580
1465.8992 1482.3860 1484.6134
1489.9198 1491.3133 1491.7184
1494.4529 1494.6080 1494.9899
1496.3400 1497.4520 1501.0089
1503.0850 1517.2725 1521.7812
1526.4823 1527.6616 1534.5885
1539.2600 1542.0408 1542.8615
1543.7964 1544.7628 1547.5652
1574.7777 1658.1203 1662.3232
1664.9436 1665.9992 1667.7019
1668.4535 1674.3662 1681.8735
1683.5724 1684.0478 1684.4180
1684.7129 1686.6297 2906.4221
2948.4765 2961.3592 2981.3253

3002.2292	3025.7162	3058.5992
3064.0870	3066.3153	3072.6461
3099.0790	3140.5515	3145.5547
3147.5361	3153.6423	3158.3341
3162.1049	3166.7140	3173.6504
3189.9250	3207.4115	3210.6623
3211.0655	3211.6862	3211.7801
3213.0785	3218.0260	3218.2000
3223.2108	3225.0716	3225.9238
3226.6421	3226.6765	3227.0657
3234.1077	3235.0867	3235.1938
3236.5573	3237.0006	3238.9201
3240.9880	3243.5228	3243.6167
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3249.7364	3253.4680	3254.2529

S4

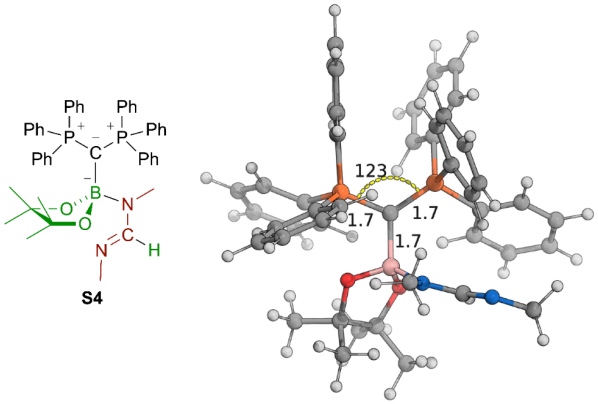

Fig. S43 Three dimensional picture of structure **S4** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman

---
Full point group C1 NOp 1
Stoichiometry C46H49BN2O2P2 Framework group C1[X(C46H49BN2O2P2)]

Num atoms: 102
Charge = 0 Multiplicity = 1

SCF = -2749.38677487 | Predicted change in Energy=-2.984587D-09

Optimization completed.
Maximum Force 0.000047 0.000450 YES
RMS Force 0.000009 0.000300 YES
Maximum Displacement 0.001399 0.001800 YES
RMS Displacement 0.000282 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

P -1.107652 0.690559 -4.071362
P 0.958164 -1.173682 -2.948423
C 1.288063 -5.063549 -0.506338
C 2.376245 -4.199154 -0.565977
C 2.275903 -2.998129 -1.259464
C 1.077197 -2.648864 -1.884896
C -0.008035 -3.527597 -1.841662
C 0.099731 -4.726498 -1.147310
H 1.366048 -5.997509 0.041185

H 3.305455 -4.454326 -0.067354
H 3.132394 -2.334702 -1.301264
H -0.954454 -3.242924 -2.286211
H -0.755498 -5.392485 -1.098011
C 1.969790 -3.376156 -6.886662
C 2.994915 -2.742183 -6.193094
C 2.721409 -2.044951 -5.019528
C 1.410863 -1.945683 -4.550754
C 0.390848 -2.612601 -5.235875
C 0.667603 -3.323675 -6.396057
H 2.187092 -3.923182 -7.798608
H 4.015290 -2.796525 -6.558415
H 3.536986 -1.585317 -4.472872
H -0.626939 -2.553486 -4.861340
H -0.135283 -3.832590 -6.919809
C 1.811822 1.345949 -7.626726
C 1.820894 2.237515 -6.559933
C 0.941394 2.066069 -5.494474
C 0.038148 0.999658 -5.482335
C 0.006888 0.139064 -6.585782
C 0.895855 0.297974 -7.640264
H 2.505233 1.475074 -8.451717
H 2.514715 3.072047 -6.550242
H 0.968287 2.771362 -4.673301
H -0.714705 -0.667750 -6.620330
H 0.869843 -0.398651 -8.471414
C -4.780241 -0.786639 -6.429128
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C -3.150344 0.936948 -6.004610
C -2.612474 0.173658 -4.963850
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C -4.233277 -1.556017 -5.407332
H -5.625056 -1.160422 -6.999028
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B -1.605031 -0.518602 -1.561376
O -2.349859 -1.780327 -1.467714
C -3.628883 -1.510244 -0.915157
C -3.834485 0.063221 -1.135876
O -2.645762 0.483838 -1.778732
C -4.646884 -2.384565 -1.654167
H -4.353739 -3.433121 -1.545323
H -5.652802 -2.267139 -1.238655
H -4.689248 -2.153220 -2.718616
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H -3.411933 -3.006204 0.615245
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C -5.005929 0.431086 -2.051589
H -5.966820 0.138930 -1.615888
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H -4.912655 -0.026991 -3.036951
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H 0.499170 1.444799 -0.187107
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N 0.610651 -0.996121 1.431660
H -0.684531 -2.197542 0.312111
C 1.025009 -2.164452 2.174481
H 0.808251 -2.042953 3.244204
H 0.546242 -3.101176 1.839565
H 2.110933 -2.306137 2.087668
C -1.617237 4.903376 -2.256881
C -2.669104 4.353242 -2.984889
C -2.547093 3.087028 -3.545270
C -1.368609 2.360816 -3.380001
C -0.325442 2.905191 -2.628493
C -0.445246 4.176234 -2.077317
H -1.718065 5.890523 -1.817171
H -3.594591 4.906918 -3.106494
H -3.386251 2.651825 -4.075744
H 0.570481 2.319323 -2.439198
H 0.369701 4.584148 -1.488335
C 4.099791 1.946546 -1.646894
C 3.888474 1.709531 -3.001924
C 3.004986 0.714179 -3.406167
C 2.324301 -0.058148 -2.458499
C 2.533183 0.191116 -1.095560
C 3.420948 1.186194 -0.699055
H 4.787108 2.725168 -1.331090
H 4.407485 2.300572 -3.750075
H 2.837674 0.557043 -4.465250
H 1.993200 -0.359799 -0.326209
H 3.564495 1.369277 0.360712

Statistical Thermodynamic Analysis

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -2749.38677487 | Predicted change in Energy=-2.984587D-09
Zero-point correction (ZPE) = -2748.53003787 0.856737
Internal Energy (U) = -2748.48149687 0.905278
Enthalpy (H) = -2748.48055287 0.906222
Gibbs Free Energy (G) = -2748.61111987 0.775655

Frequencies
12.0197 16.1443 35.8911
40.7177 45.6021 48.5172
50.3400 53.6499 56.4352
60.4434 64.2636 67.5486
73.0683 75.1377 79.0849
84.5045 89.6761 102.0564
107.1445 113.5130 120.8182
127.4019 131.9596 138.8031
148.5197 155.0129 168.7912
170.1910 200.9739 204.3437
216.9380 219.5037 222.5832
228.2877 231.9397 239.8820
242.2043 245.5383 256.7037
258.9723 263.2784 266.3527
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289.7486 292.0170 301.6983
302.8056 321.8326 329.4666
347.7841 371.5385 388.0317
398.9800 408.2970 412.5155
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425.5253 430.9093 436.0173
439.6043 442.0505 446.0979
455.5465 463.1885 485.1115
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520.4049 523.5343 526.7479
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557.2601 587.2228 606.8900
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636.3473 637.8031 638.9204
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709.3420 715.3163 718.1261
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729.7660 733.6998 736.3543
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855.8334 877.3284 878.0071

884.2146 888.2554 894.5284
898.2381 905.4563 912.7531
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967.3245 973.0842 979.3210
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1138.4038 1140.9108 1141.5981
1146.9306 1147.6507 1151.1064
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1197.9157 1198.2278 1198.3491
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1375.4210 1378.6408 1381.0012
1384.8629 1392.9305 1398.0130
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1435.9326 1438.5176 1466.5411
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1489.9334 1491.0117 1494.5036
1495.0659 1496.5337 1497.2123
1499.9358 1501.2652 1505.0629
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1525.7665 1530.2491 1534.2948
1543.7896 1546.0043 1546.6610
1546.8613 1547.7267 1553.5567
1559.7087 1660.5643 1663.8025
1665.7752 1666.3143 1668.4904
1669.2250 1681.8903 1684.4009
1684.6544 1685.2315 1686.6682
1686.7281 1734.3035 2972.6778
3044.2296 3052.4434 3061.5554

3065.9858	3067.2619	3069.6884
3072.9198	3104.2041	3110.9940
3134.0375	3138.9179	3142.2628
3147.1164	3172.7937	3178.7349
3181.0070	3183.6540	3192.7802
3194.1762	3197.4341	3203.0931
3206.8003	3208.3977	3208.4871
3209.2249	3210.1588	3210.5492
3213.6015	3217.2602	3221.9440
3222.2557	3222.3649	3222.7940
3224.2884	3225.4033	3232.2674
3233.7212	3233.7678	3234.0632
3234.7793	3234.8829	3243.6135
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3251.7611	3252.5079	3259.1134

TS S4–2

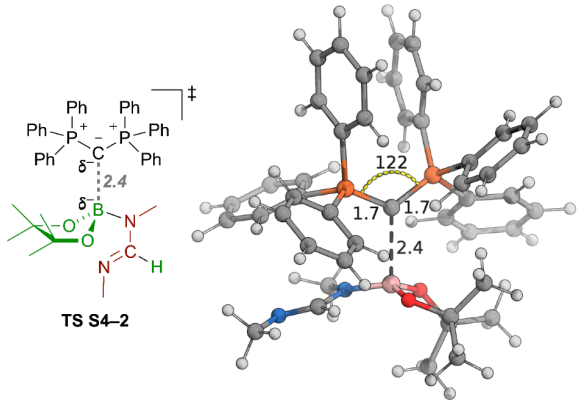

Fig. S44 Three dimensional picture of structure **TS S4–2** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250,ts,calcfc,noeigentest) freq=noraman

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Full point group C1 NOp 1
Stoichiometry C46H49BN2O2P2 Framework group C1[X(C46H49BN2O2P2)]

Num atoms: 102
Charge = 0 Multiplicity = 1

SCF = -2749.36735980 | Predicted change in Energy=-3.778500D-09

Optimization completed.
Maximum Force 0.000008 0.000450 YES
RMS Force 0.000001 0.000300 YES
Maximum Displacement 0.000688 0.001800 YES
RMS Displacement 0.000168 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

P -1.287919 1.149898 -0.093593
P -0.125936 -1.540308 0.048812
C 1.139510 -3.724073 -3.827899
C 0.224858 -2.672410 -3.846284
C -0.117789 -2.033517 -2.662487
C 0.424329 -2.453669 -1.442219
C 1.341368 -3.502810 -1.433362
C 1.701801 -4.129397 -2.623830

H 1.423388 -4.214474 -4.753735
H -0.207488 -2.340448 -4.784994
H -0.805287 -1.192589 -2.677282
H 1.813674 -3.812050 -0.509439
H 2.441096 -4.922926 -2.605401
C 2.073733 -3.403181 3.672191
C 2.187148 -2.043259 3.409883
C 1.540571 -1.483307 2.309478
C 0.780661 -2.284733 1.461035
C 0.649394 -3.650333 1.744374
C 1.299369 -4.207763 2.837594
H 2.580455 -3.838643 4.527870
H 2.786017 -1.409309 4.056248
H 1.656566 -0.426416 2.090914
H 0.026280 -4.278544 1.114038
H 1.196073 -5.268279 3.043964
C -2.723974 2.305830 4.167385
C -1.572517 1.551458 3.968796
C -1.165516 1.231612 2.676966
C -1.899120 1.660311 1.571562
C -3.062251 2.411325 1.781742
C -3.469922 2.734304 3.071385
H -3.045131 2.556331 5.173607
H -0.989016 1.209984 4.817954
H -0.269535 0.642580 2.505629
H -3.666157 2.727963 0.936336
H -4.374704 3.314807 3.221355
C -0.504111 4.969430 -2.582625
C -0.037233 3.725641 -2.997220
C -0.234764 2.606382 -2.199194
C -0.925099 2.708397 -0.988290
C -1.371293 3.963377 -0.568857
C -1.158894 5.088635 -1.361428
H -0.343390 5.846360 -3.201957
H 0.502542 3.628449 -3.933519
H 0.172574 1.645528 -2.492839
H -1.870270 4.078648 0.386077
H -1.504740 6.058835 -1.019402
C 0.036363 0.126665 -0.109893
B 2.321077 0.817614 -0.256077
O 2.714394 1.073517 1.067905
C 2.848379 2.490518 1.222726
C 2.998158 2.975095 -0.260582
O 2.224023 2.011944 -0.979159
C 1.591269 3.034896 1.897423
H 1.425527 2.496661 2.834384
H 1.689528 4.100419 2.125715
H 0.714385 2.895404 1.264695

C 4.061989 2.760680 2.104949
H 3.867310 2.400135 3.119153
H 4.948828 2.248603 1.728242
H 4.269962 3.834310 2.160177
C 2.453321 4.370300 -0.528730
H 2.593671 4.624268 -1.582544
H 1.387164 4.433552 -0.309686
H 2.986289 5.111645 0.076338
C 4.440511 2.872848 -0.772368
H 4.434902 3.027717 -1.854336
H 5.091120 3.625345 -0.316748
H 4.857911 1.880932 -0.576707
N 2.855832 -0.373888 -0.922992
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H 2.855496 -1.486019 -2.695663
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H 3.652089 0.094930 -2.819692
C 3.619349 -1.288903 -0.251209
N 4.206180 -2.276865 -0.809986
H 3.677481 -1.095695 0.825175
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H 4.873191 -2.879599 1.138889
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C -5.071582 -0.353612 -0.901829
C -3.959658 0.141712 -0.228160
C -2.842234 0.593850 -0.932889
C -2.867673 0.538600 -2.331170
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H -5.948688 -0.801807 -2.814864
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H -3.961270 0.149143 0.855000
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C -2.545867 -2.938992 -0.560562
C -1.797057 -2.244934 0.389364
C -2.327249 -2.065066 1.673145
C -3.582763 -2.562861 1.995956
H -5.305222 -3.646526 1.291261
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H -1.751179 -1.535757 2.426311
H -3.979146 -2.416875 2.995813

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -2749.36735980 | Predicted change in Energy=-3.778500D-09
Zero-point correction (ZPE) = -2748.5123198 0.85504
Internal Energy (U) = -2748.4637018 0.903658
Enthalpy (H) = -2748.4627568 0.904603
Gibbs Free Energy (G) = -2748.5924618 0.774898

Frequencies
-149.2025 19.8375 25.2501
34.2201 40.1313 48.2828
49.0137 55.3842 58.2230
59.5958 65.7005 68.9669
71.8447 76.7259 82.0371
83.8985 86.9407 91.2913
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128.7101 137.6992 152.4698
159.0009 167.6289 204.8955
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259.9255 262.4384 269.0010
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283.1492 286.1458 300.9807
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415.2175 418.7723 425.2003
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717.7443 721.4958 724.6481
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766.4869 768.5920 772.1072
773.9123 778.4841 779.2906

805.3354 859.1570 872.1355
875.7592 880.3260 880.4865
889.5513 895.0443 896.2122
919.8325 944.1223 947.2067
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1001.1530 1006.4817 1009.1240
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1019.5308 1019.8968 1020.3966
1020.6884 1022.7490 1023.4890
1023.7728 1024.4810 1025.9165
1026.1486 1028.3425 1028.9794
1042.4692 1049.2938 1057.7788
1065.2681 1067.6909 1067.9408
1068.6459 1069.1751 1070.0386
1100.3469 1116.8042 1123.0642
1124.2614 1127.5301 1128.9820
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1138.9197 1141.0138 1144.4854
1144.9371 1147.3002 1149.1597
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1195.8271 1196.6171 1196.7841
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1335.7967 1339.5434 1342.1052
1346.4664 1365.3566 1368.5733
1370.1000 1373.9464 1376.5813
1376.9986 1378.1345 1400.9343
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1438.9668 1445.6670 1466.1185
1474.0934 1488.1095 1488.6897
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1491.5174 1494.6387 1495.0423
1498.0378 1499.1798 1501.9061
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1523.4577 1526.8881 1538.5782
1540.8276 1542.9085 1544.3476
1544.9327 1545.3533 1545.8939
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1667.8116 1682.7315 1683.9455
1683.9478 1684.6792 1685.0419
1685.9341 1766.1772 2974.1464

3053.9424 3060.7537 3064.6453
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3154.6564 3157.5025 3175.4558
3192.4514 3195.5699 3196.5617
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3205.7236 3206.7374 3207.0227
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3216.0643 3217.5373 3218.9962
3220.9721 3221.9921 3222.6180
3225.9677 3228.1427 3229.3867
3229.6698 3230.6235 3231.9692
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3245.8073 3255.6145 3258.0006

TS 10–S5

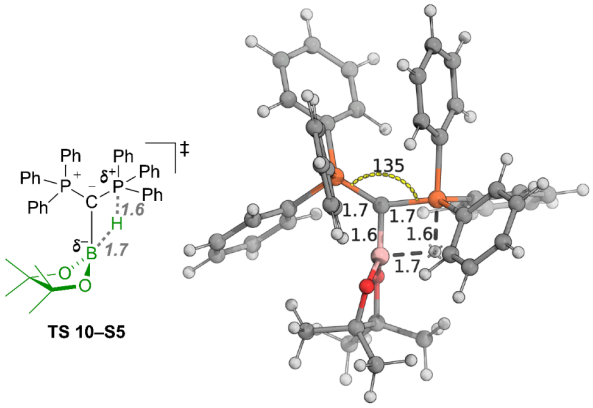

Fig. S45 Three dimensional picture of structure **TS 10–S5** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250,ts,calcfc,noeigentest) freq=noraman

---
Full point group C1 NOp 1
Stoichiometry C43H43BO2P2 Framework group C1[X(C43H43BO2P2)]

Num atoms: 91
Charge = 0 Multiplicity = 1

SCF = -2521.95525130 | Predicted change in Energy=-1.401391D-09

Optimization completed on the basis of negligible forces.
Maximum Force 0.000004 0.000450 YES
RMS Force 0.000000 0.000300 YES
Maximum Displacement 0.001904 0.001800 NO
RMS Displacement 0.000313 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

C 0.185118 0.155711 -0.309332
B 1.149390 1.383354 -0.199914
C 2.926101 2.593877 0.654710
C 2.575130 3.056410 -0.809962
O 1.842157 1.718289 0.982420
O 1.776509 1.976348 -1.298836
C 2.973500 3.722922 1.678390
H 3.210174 3.313073 2.664517
H 3.747347 4.452998 1.419295

H 2.014234 4.239378 1.746330
C 4.208464 1.764713 0.738791
H 4.275445 1.321919 1.736361
H 4.197151 0.951724 0.011080
H 5.100000 2.376644 0.570963
C 1.712665 4.321530 -0.854780
H 1.362224 4.466288 -1.879957
H 0.830530 4.218422 -0.217198
H 2.274307 5.208777 -0.547618
C 3.782922 3.216411 -1.725185
H 3.449538 3.531739 -2.717641
H 4.469147 3.976675 -1.337996
H 4.323991 2.273947 -1.831097
P -1.334795 0.985410 -0.089223
C -2.815932 2.650967 4.003990
C -1.471075 2.720617 3.650289
C -1.043263 2.231642 2.420658
C -1.950265 1.633592 1.541595
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H -3.151262 3.046368 4.958036
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H -4.779371 2.012432 3.395344
C -2.991780 3.269275 -3.768706
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C -3.263144 2.539141 -1.484965
C -2.035072 1.878799 -1.540171
C -1.282786 1.928353 -2.716088
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H -3.364229 3.808171 -4.634456
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H -4.661180 -3.792247 -0.224189
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H -2.012011 -1.144233 1.852071
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H -4.697713 -2.226198 -2.150226
H -0.318016 2.234330 -0.029833

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C 0.144675 -2.612199 4.376195
C 0.710536 -1.392909 4.010516
C 0.903538 -1.087584 2.668816
C 0.541349 -2.012846 1.680809
C -0.029707 -3.230781 2.050997
C -0.226563 -3.527647 3.396671
H -0.017988 -2.843012 5.424273
H 0.986178 -0.669225 4.770480
H 1.313863 -0.122261 2.378790
H -0.363599 -3.932273 1.295059
H -0.683079 -4.471497 3.677218
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C 0.144984 -2.737045 -1.160355
C -0.690977 -2.395987 -2.220330
C -1.104690 -3.369573 -3.124889
H -0.988848 -5.439590 -3.693283
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H 1.319382 -4.313914 -0.262123
H -1.010065 -1.366927 -2.334582
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C 5.250721 -1.507117 -0.997906
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C 3.458537 -1.953156 0.553416
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C 2.980723 -0.955217 -1.594620
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H 6.307208 -1.531508 -1.245427
H 5.526128 -2.380288 0.948831
H 3.123273 -2.323103 1.516604
H 2.269271 -0.528259 -2.292920
H 4.670209 -0.611565 -2.869589

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -2521.95525130 | Predicted change in Energy=-1.401391D-09
Zero-point correction (ZPE) = -2521.1990223 0.756229
Internal Energy (U) = -2521.1563902999997 0.798861
Enthalpy (H) = -2521.1554453 0.799806
Gibbs Free Energy (G) = -2521.2759483 0.679303

Frequencies

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177.0360 197.8400 206.7755
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235.0149 247.1255 249.8090
255.0877 259.5684 262.9126
263.8161 271.3444 281.4000
284.5644 308.4644 309.3925
319.7166 335.8260 367.5829
382.1066 390.7180 403.7022
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530.7198 534.3212 536.9007
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636.5377 637.2681 638.5110
639.1207 677.3184 691.1832
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717.6470 719.6793 724.4904
726.4707 731.7686 734.1988
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770.3675 773.0764 775.4791
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1122.9254	1124.7922	1124.8453
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1135.9350	1143.7777	1146.0500
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1193.6742	1195.4317	1197.1546
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1227.2956	1228.3473	1235.3479
1236.5396	1238.6477	1254.0094
1258.2628	1272.2762	1284.4962
1303.1010	1326.1037	1330.5810
1335.7678	1336.6889	1339.8678
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1372.7413	1373.6488	1378.3326
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1419.7441	1429.4989	1439.3991
1485.1739	1487.3076	1489.5107
1490.5736	1491.3528	1493.3157
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1503.1470	1522.3883	1524.9493
1527.0728	1540.9268	1543.2132
1543.9676	1544.2512	1545.5698
1547.1089	1549.5239	1559.7950
1660.6232	1663.0304	1663.9401
1665.9780	1666.3722	1667.7760
1681.3133	1682.2196	1683.1881
1683.8203	1684.1562	1685.9868
3064.7755	3066.6888	3069.4609
3074.2979	3142.7161	3146.9834
3152.0140	3156.8101	3159.2990
3168.4149	3170.8701	3189.9052
3192.6154	3194.6168	3200.9854
3201.4281	3202.3338	3205.3162
3209.4836	3209.8042	3211.1192
3211.4098	3213.5843	3213.8733
3219.8330	3220.8279	3221.7062
3221.8149	3222.2608	3225.9831
3227.5223	3227.8362	3228.6099
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S5

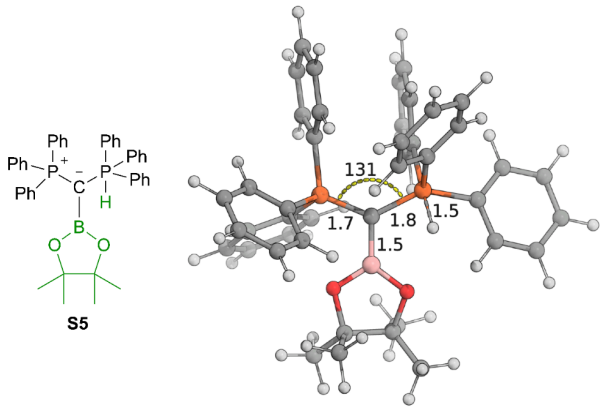

Fig. S46 Three dimensional picture of structure **S5** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman

---
Full point group C1 NOp 1
Stoichiometry C43H43BO2P2 Framework group C1[X(C43H43BO2P2)]

Num atoms: 91
Charge = 0 Multiplicity = 1

SCF = -2521.96013303 | Predicted change in Energy=-3.319222D-09

Optimization completed.
Maximum Force 0.000008 0.000450 YES
RMS Force 0.000001 0.000300 YES
Maximum Displacement 0.001100 0.001800 YES
RMS Displacement 0.000181 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

C 0.026810 0.550224 0.150685
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C 2.129970 3.593338 -0.412035
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O 1.945312 2.187344 -0.221915
O -0.149407 3.088463 -0.375662
C 2.408094 4.204719 0.962961
H 3.257187 3.683100 1.412774
H 2.648692 5.269589 0.893806

H 1.544055 4.084245 1.623212
C 3.318469 3.804153 -1.340103
H 4.236019 3.484128 -0.839102
H 3.212949 3.213852 -2.252094
H 3.423008 4.860838 -1.607043
C 0.304939 5.435887 -0.652189
H -0.669734 5.639161 -1.103995
H 0.212235 5.569258 0.426882
H 1.020512 6.168844 -1.038661
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H -0.398470 3.880420 -2.811632
H 1.239132 4.521902 -3.071527
H 0.994291 2.786923 -2.774553
P -1.770603 0.393505 0.376544
C -3.188905 -1.490446 4.381268
C -1.917504 -0.933158 4.260937
C -1.510038 -0.387058 3.049278
C -2.350754 -0.413160 1.933714
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H -1.246008 -0.914887 5.114161
H -0.528361 0.071839 2.963938
H -4.305759 -0.962365 1.219966
H -5.045492 -1.904191 3.376558
C -5.348227 2.571335 -1.749800
C -4.316818 3.280702 -1.143190
C -3.263564 2.600913 -0.538220
C -3.200141 1.205743 -0.562172
C -4.235219 0.504631 -1.191615
C -5.309600 1.180112 -1.762482
H -6.178870 3.098466 -2.209829
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C -2.437231 -3.482728 -1.382443
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C -1.906290 -1.180751 -0.786792
C -1.587661 -0.966616 -2.135479
C -1.674464 -1.975586 -3.086017
H -2.181390 -4.041958 -3.445994
H -2.766363 -4.470013 -1.070948
H -2.581006 -2.689716 0.595647
H -1.289893 0.032452 -2.450404
H -1.421255 -1.769732 -4.122584
H -1.694518 1.653699 1.123126

P 1.274028 -0.626139 0.249040
C 4.193774 -0.142886 -3.305594
C 4.712904 -0.328452 -2.028519
C 3.860163 -0.496358 -0.941650
C 2.478342 -0.477375 -1.126322
C 1.961116 -0.284034 -2.410202
C 2.814456 -0.124801 -3.495594
H 4.861842 -0.008033 -4.150399
H 5.787016 -0.333101 -1.872995
H 4.279179 -0.612889 0.051202
H 0.886392 -0.249754 -2.551059
H 2.400980 0.022630 -4.488199
C 3.796544 -0.213194 4.112737
C 3.909824 -1.360299 3.331115
C 3.149931 -1.491421 2.174205
C 2.275047 -0.471686 1.783194
C 2.163109 0.670507 2.575061
C 2.920182 0.799069 3.735298
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H 4.583679 -2.157983 3.626607
H 3.229402 -2.397102 1.579980
H 1.471169 1.452515 2.283309
H 2.821350 1.691424 4.344938
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C 0.654181 -4.563402 -0.729628
C 0.980065 -3.213504 -0.810100
C 0.800678 -2.385626 0.297633
C 0.297284 -2.922756 1.487185
C -0.032004 -4.269152 1.560700
H -0.104608 -6.146348 0.511059
H 0.788401 -5.198263 -1.598983
H 1.364215 -2.809229 -1.739513
H 0.154609 -2.289668 2.356119
H -0.430586 -4.673483 2.485322

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -2521.96013303 | Predicted change in Energy=-3.319222D-09
Zero-point correction (ZPE) = -2521.20234203 0.757791
Internal Energy (U) = -2521.1591210300003 0.801012
Enthalpy (H) = -2521.1581770300004 0.801956
Gibbs Free Energy (G) = -2521.28021703 0.679916

Frequencies

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105.3266 112.0794 123.7768
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220.7254 222.8755 227.1188
231.2604 235.3181 239.1331
244.5809 259.1740 262.6700
264.5720 284.7911 287.3792
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331.1538 337.7434 363.6813
379.0296 392.6185 401.9564
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422.1170 423.7044 429.2781
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536.7753 539.1735 541.7034
544.1944 583.5019 596.0792
635.2026 635.4670 636.6352
637.1421 638.0761 639.8734
671.9910 678.5880 682.1218
695.8765 706.4988 712.5667
714.2811 718.2714 720.7134
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888.0881 897.0277 947.3810
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1022.6389 1023.5222 1024.0227
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1069.2267 1107.6826 1111.1993

1115.5896 1120.8137 1122.8943
1127.9352 1129.7059 1130.2198
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1197.6687 1198.3815 1199.1357
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1225.0690 1230.9154 1231.7581
1233.2955 1233.6537 1267.7355
1271.3955 1283.0613 1311.3766
1322.2939 1329.2474 1335.9454
1337.6689 1338.0486 1345.1986
1361.5772 1367.7832 1369.2108
1372.3732 1374.0929 1375.8271
1376.2398 1387.2901 1419.2903
1420.9171 1430.8409 1439.8079
1483.2463 1489.0885 1490.3389
1491.0354 1492.2050 1493.0009
1496.1890 1497.3681 1501.1858
1503.1810 1521.5062 1523.2900
1524.4226 1538.6648 1541.9475
1542.3974 1542.6758 1543.3733
1544.5787 1545.9232 1658.4235
1663.9275 1665.1172 1666.1511
1666.1613 1668.2821 1677.0098
1679.3890 1683.0866 1683.9111
1684.4224 1686.7653 2046.2174
3063.3677 3064.4727 3069.2656
3071.6324 3147.6919 3148.4940
3149.8818 3151.8392 3158.1171
3161.5609 3173.4254 3174.1031
3175.3936 3195.0126 3198.3648
3199.1137 3204.2270 3206.7908
3207.8809 3208.7458 3209.3526
3210.0731 3215.0292 3215.5353
3219.4991 3221.0808 3222.5719
3222.7058 3223.6082 3224.9953
3231.0553 3231.1611 3231.3431
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3244.7698 3245.0957 3245.3965

TS S5–11

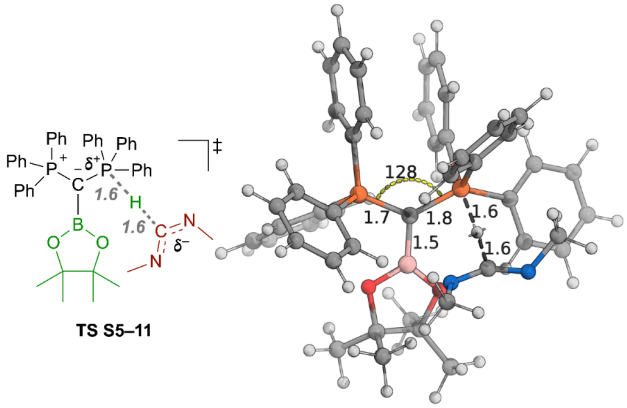

Fig. S47 Three dimensional picture of structure **TS S5–11** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250,ts,calcfc,noeigentest) freq=noraman

---
Full point group C1 NOp 1
Stoichiometry C46H49BN2O2P2 Framework group C1[X(C46H49BN2O2P2)]

Num atoms: 102
Charge = 0 Multiplicity = 1

SCF = -2749.28367893 | Predicted change in Energy=-9.118048D-09

Optimization completed.
Maximum Force 0.000018 0.000450 YES
RMS Force 0.000001 0.000300 YES
Maximum Displacement 0.001777 0.001800 YES
RMS Displacement 0.000226 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

C 0.207196 -0.210957 0.191006
B 0.906137 -1.559974 0.342789
C 1.445179 -3.587883 1.222374
C 2.630082 -3.061993 0.338261
O 0.362277 -2.726143 0.841554
O 2.271853 -1.687986 0.145874
C 1.676097 -3.367583 2.719632
H 0.738518 -3.554845 3.249365
H 2.442275 -4.040554 3.115545

H 1.980213 -2.335400 2.919093
C 1.035482 -5.028501 0.953044
H 0.213180 -5.306566 1.618167
H 0.695234 -5.151796 -0.076093
H 1.870843 -5.711409 1.138738
C 3.999027 -3.108714 1.004553
H 4.753451 -2.727472 0.311168
H 4.024641 -2.486878 1.901757
H 4.267674 -4.135822 1.272071
C 2.679161 -3.712248 -1.044379
H 1.693549 -3.665438 -1.514649
H 3.012401 -4.752919 -0.990351
H 3.383230 -3.152591 -1.666953
P -1.570634 -0.095971 0.175577
C -1.960849 3.513704 3.219819
C -1.382856 2.295745 3.574833
C -1.281421 1.279319 2.634872
C -1.735125 1.442483 1.318876
C -2.309952 2.667767 0.983703
C -2.423966 3.693407 1.923320
H -2.048599 4.312573 3.949867
H -1.024850 2.135949 4.587825
H -0.865893 0.318668 2.931767
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C -1.641841 0.634081 -2.522775
C -2.375305 0.592221 -1.333602
C -3.717862 0.972149 -1.353364
C -4.312473 1.402732 -2.536760
H -4.034805 1.797462 -4.633902
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C -4.617549 -2.634080 2.646456
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C -2.599103 -2.480517 1.331203
C -2.736408 -1.092347 1.250889
C -3.828462 -0.486879 1.884742
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H -5.347974 -3.232455 3.182538
H -3.390298 -4.316736 2.102803
H -1.768721 -2.964775 0.834990
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N -2.546233 -3.109529 -1.990894
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C 2.177270 0.994890 -1.706906
C 2.947204 2.074587 -2.156224
C 3.580457 2.015472 -3.392066
H 3.930766 0.839122 -5.159132
H 2.543605 -1.065612 -4.375159
H 1.412195 -0.962485 -2.178940
H 3.044792 2.968165 -1.546353
H 4.175427 2.856231 -3.734059
C -0.057342 5.439500 -0.023210
C -0.287831 4.637474 -1.137789
C 0.124763 3.311831 -1.137528
C 0.762047 2.773237 -0.014549
C 0.988877 3.579980 1.100438
C 0.578829 4.908974 1.093291
H -0.375005 6.477454 -0.025498
H -0.786536 5.043585 -2.011672
H -0.051935 2.696968 -2.013355
H 1.479271 3.175050 1.978226
H 0.753339 5.526905 1.967663
C 4.669891 0.675141 3.131905
C 5.030594 0.927693 1.812235
C 4.053647 1.064797 0.830957
C 2.705143 0.947918 1.165383
C 2.347364 0.688490 2.490915
C 3.324432 0.559195 3.471080
H 5.435065 0.562845 3.893435
H 6.078149 1.006687 1.540063
H 4.350646 1.230498 -0.198108
H 1.299921 0.570259 2.745182
H 3.034349 0.356256 4.497014

Statistical Thermodynamic Analysis

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -2749.28367893 | Predicted change in Energy=-9.118048D-09
Zero-point correction (ZPE) = -2748.43523193 0.848447
Internal Energy (U) = -2748.38533693 0.898342
Enthalpy (H) = -2748.3843919299998 0.899287
Gibbs Free Energy (G) = -2748.51846593 0.765213

Frequencies
-769.1810 16.5636 22.9469
30.5980 36.6427 43.6304
46.2075 48.9747 53.3134
54.1841 63.0979 64.7364
66.8938 72.2382 76.4689
84.2178 84.8368 86.2821
93.1903 96.8117 100.0174
103.3098 108.3107 112.1488
114.5335 130.0178 132.8343
137.7956 143.0847 154.9422
175.1955 181.0079 190.1746
204.2308 207.6195 213.7659
217.1344 227.7835 229.8616
236.7648 243.1855 244.7950
249.2098 254.9778 261.2044
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348.6850 369.2009 380.9123
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425.4251 430.3404 431.7166
438.8502 451.6044 462.0634
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512.6268 521.5631 530.9079
538.2574 542.3051 547.2807
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642.9387 658.3094 682.1258
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720.8535 727.8413 729.0763
732.6297 736.4606 737.1485
763.1158 769.8804 771.9322
774.3391 777.1491 779.2046
783.6506 826.2722 869.1551

875.7782 878.2794 879.8166
886.3297 888.4534 898.2000
900.9228 945.0604 948.8785
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1196.7141 1197.6905 1198.5680
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1340.1805 1347.3497 1353.0557
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1375.8226 1376.7037 1383.3803
1392.2097 1419.5716 1421.0324
1430.6644 1439.8949 1453.3272
1472.4893 1485.8399 1487.5744
1488.3624 1491.0575 1491.4576
1493.3158 1496.4147 1497.7265
1498.1727 1500.2912 1502.2674
1509.3553 1516.2629 1520.1278
1520.3315 1523.4496 1528.7000
1538.3125 1540.5842 1541.9357
1545.3049 1545.8415 1547.7472
1548.0739 1551.2629 1660.5255
1663.1414 1664.1250 1665.1086
1666.6457 1668.3148 1679.7535
1680.3123 1682.2790 1683.7067
1684.7862 1686.3855 1997.1329
3009.9217 3033.3352 3063.6066

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3203.1879	3205.3208	3206.7688
3208.8780	3210.0267	3210.2618
3214.0107	3214.3319	3215.1581
3220.5114	3222.3841	3224.0049
3224.7373	3225.1265	3227.2557
3230.4735	3231.4351	3233.0395
3233.8368	3236.3784	3238.2513
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TS 2–S6

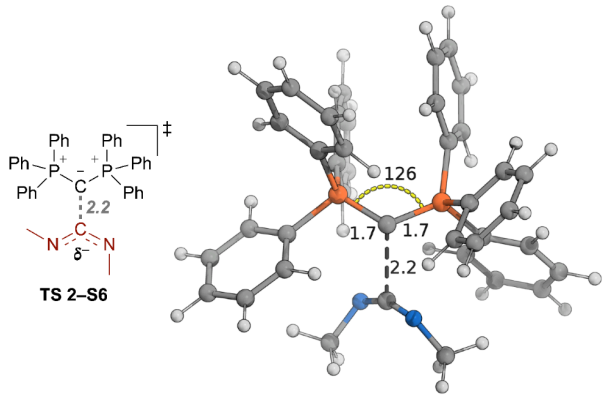

Fig. S48 Three dimensional picture of structure **TS 2–S6** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250,ts,calcfc,noeigentest) freq=noraman

---
Full point group C1 NOp 1
Stoichiometry C40H36N2P2 Framework group C1[X(C40H36N2P2)]

Num atoms: 80
Charge = 0 Multiplicity = 1

SCF = -2337.48845673 | Predicted change in Energy=-1.205986D-10

Optimization completed.
Maximum Force 0.000001 0.000450 YES
RMS Force 0.000000 0.000300 YES
Maximum Displacement 0.000509 0.001800 YES
RMS Displacement 0.000061 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

P -1.467063 0.246440 -0.101896
P 1.481440 -0.004047 -0.137304
C 4.640876 -3.042942 -1.587348
C 4.836047 -2.393086 -0.373974
C 3.881199 -1.495064 0.099775
C 2.724350 -1.249781 -0.637563
C 2.532512 -1.904073 -1.857295
C 3.485489 -2.797537 -2.327952
C 2.955501 3.632115 -2.599668

C 1.718852 3.050548 -2.859852
C 1.284685 1.967922 -2.099641
C 2.079341 1.465188 -1.070011
C 3.333707 2.035678 -0.832951
C 3.765635 3.119837 -1.588164
C -4.374161 -2.507709 2.216329
C -4.884877 -1.635503 1.260208
C -4.028135 -0.801437 0.546544
C -2.653377 -0.838061 0.784205
C -2.145374 -1.718316 1.743886
C -3.003118 -2.547342 2.457474
C -0.804797 3.925897 2.626720
C -0.623681 4.031824 1.250235
C -0.879321 2.940475 0.428109
C -1.324715 1.729675 0.971678
C -1.503033 1.633071 2.353765
C -1.243382 2.725319 3.175082
C -0.050233 -0.541551 -0.481782
C -3.803856 1.491910 -3.884039
C -2.951434 0.390410 -3.884797
C -2.250581 0.045497 -2.733697
C -2.407968 0.805081 -1.569889
C -3.274367 1.901550 -1.567958
C -3.966724 2.246315 -2.725349
C 1.971812 0.749003 4.386842
C 2.113360 1.824430 3.517948
C 2.036972 1.627692 2.141027
C 1.818377 0.349835 1.628203
C 1.655101 -0.730172 2.507790
C 1.740729 -0.529200 3.879332
H 5.384208 -3.743499 -1.955002
H 5.730625 -2.585138 0.210111
H 4.036338 -0.998632 1.052663
H 1.615809 -1.728943 -2.413202
H 3.324353 -3.309186 -3.271484
H 3.294760 4.477358 -3.190379
H 1.091537 3.434577 -3.658103
H 0.327749 1.495431 -2.305703
H 3.976521 1.631116 -0.056099
H 4.737367 3.562021 -1.392258
H -5.042916 -3.161171 2.768046
H -5.951795 -1.607320 1.062508
H -4.433463 -0.133577 -0.206504
H -1.071869 -1.777208 1.897492
H -2.597686 -3.234344 3.193449
H -0.602122 4.776834 3.269576
H -0.280430 4.964306 0.813478
H -0.728327 3.032616 -0.642361

H -1.837889 0.700104 2.794097
H -1.378137 2.632694 4.247812
H -4.343870 1.762058 -4.786401
H -2.831632 -0.203339 -4.785561
H -1.592632 -0.821043 -2.708293
H -3.405060 2.491377 -0.665463
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H 2.270046 2.825082 3.908114
H 2.119539 2.479252 1.474267
H 1.441034 -1.717077 2.098322
H 1.619582 -1.369637 4.555779
C -0.324591 -2.742154 -0.536401
N -1.239369 -2.872677 -1.380562
N 0.500009 -3.149708 0.315619
C 1.186338 -4.406012 0.051012
C -2.249168 -3.887725 -1.107111
H 2.268420 -4.231926 0.021319
H 0.984807 -5.113836 0.863062
H 0.887358 -4.874056 -0.896435
H -2.355472 -4.544372 -1.977087
H -2.018936 -4.505876 -0.228850
H -3.217527 -3.402283 -0.934931

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -2337.48845673 | Predicted change in Energy=-1.205986D-10
Zero-point correction (ZPE) = -2336.83429773 0.654159
Internal Energy (U) = -2336.79432673 0.69413
Enthalpy (H) = -2336.79338273 0.695074
Gibbs Free Energy (G) = -2336.90904173 0.579415

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68.3224 70.2952 74.5822
78.7670 90.8701 93.8172
101.6828 108.4714 111.2901
120.8510 131.5819 134.2413
149.6594 168.7539 180.7681
193.9963 200.0355 221.4846
229.3723 238.7182 243.5423

252.3831 253.8501 257.0243
263.3192 266.1054 272.5218
277.1164 283.0659 323.4254
374.8404 404.6337 409.0721
412.3280 414.2957 418.6204
420.2953 426.3821 447.2227
459.5919 472.2161 484.6564
503.7688 521.1255 533.2356
537.9517 544.5513 564.5239
592.8184 635.1216 635.3246
635.7133 636.4397 637.4759
638.4158 686.5624 697.5554
705.1131 710.6183 717.1640
718.8218 721.1953 725.0297
727.8448 729.9924 733.5673
734.9863 736.7178 768.1483
768.3942 772.6142 774.5355
779.0350 779.6718 814.8078
871.3963 878.4109 883.7481
887.3988 889.1309 895.6514
903.6873 947.5218 953.9669
958.9084 964.3306 965.5423
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1226.8184 1227.9644 1230.4428
1257.8072 1331.1443 1332.6313
1337.5741 1339.5553 1341.0330
1341.3135 1364.3842 1367.4750
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1684.3576	1684.8815	2017.1745
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3098.9922	3106.7808	3113.9165
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3203.8735	3204.5453	3204.7643
3205.7390	3205.8894	3206.1184
3212.4448	3212.7823	3212.8713
3215.7538	3217.3678	3218.3536
3219.3905	3222.2302	3222.6073
3222.8135	3226.7735	3226.9603
3228.1161	3230.6472	3231.4021
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S6

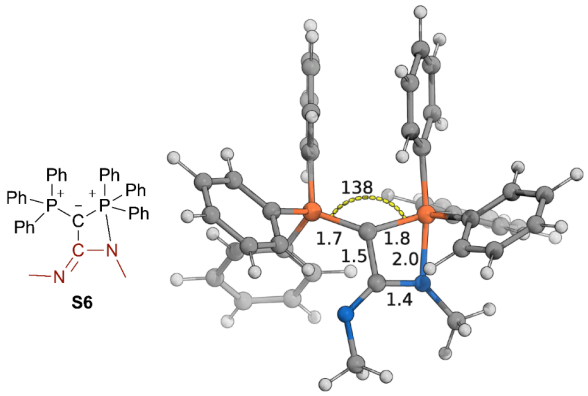

Fig. S49 Three dimensional picture of structure **S6** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman

---
Full point group C1 NOp 1
Stoichiometry C40H36N2P2 Framework group C1[X(C40H36N2P2)]

Num atoms: 80
Charge = 0 Multiplicity = 1

SCF = -2337.54531177 | Predicted change in Energy=-3.295223D-10

Optimization completed.
Maximum Force 0.000003 0.000450 YES
RMS Force 0.000000 0.000300 YES
Maximum Displacement 0.000243 0.001800 YES
RMS Displacement 0.000052 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

P -1.598020 0.698500 -1.019079
P 1.396992 -0.194153 -0.140589
C 1.608662 -4.682418 1.018635
C 2.676786 -3.845728 1.323557
C 2.644692 -2.501474 0.960586
C 1.540478 -1.977207 0.285272
C 0.475941 -2.827636 -0.024812
C 0.506214 -4.168336 0.341275
C 2.417787 -0.344521 -4.749961

C 2.191749 -1.540819 -4.081974
C 1.852211 -1.540030 -2.728105
C 1.717880 -0.346482 -2.017186
C 1.936521 0.851286 -2.715378
C 2.285839 0.858942 -4.059071
C -1.423937 -1.847497 -4.856933
C -1.943122 -2.385867 -3.684576
C -2.015684 -1.608294 -2.534180
C -1.553050 -0.289793 -2.546426
C -1.042011 0.247880 -3.730008
C -0.978618 -0.529364 -4.879101
C -4.994649 -1.314132 1.365930
C -3.663785 -1.627766 1.630239
C -2.644303 -0.989678 0.933877
C -2.954763 -0.034506 -0.038107
C -4.288330 0.284088 -0.294868
C -5.305521 -0.356751 0.405608
C -0.132235 0.683427 -0.133239
C -0.169136 0.927002 1.322574
N -1.036527 1.692094 1.897962
N 0.882124 0.145327 1.715324
C 1.612636 0.206262 2.954777
C -1.096906 1.743269 3.344040
C -2.179451 2.355747 -1.508456
C -2.988372 2.566102 -2.630236
C -1.823266 3.434150 -0.692688
C -3.426712 3.848957 -2.942080
C -2.268186 4.712808 -1.011234
C -3.063305 4.922833 -2.134482
C 2.981361 0.721577 0.113686
C 2.962590 1.991512 0.693423
C 4.198605 0.193126 -0.322214
C 4.141864 2.713424 0.845960
C 5.382190 0.900774 -0.139277
C 5.355838 2.164405 0.443218
H 1.635674 -5.729292 1.303820
H 3.542067 -4.237610 1.849202
H 3.485988 -1.863065 1.209431
H -0.378458 -2.439263 -0.569839
H -0.331156 -4.813129 0.092417
H 2.696897 -0.346592 -5.799491
H 2.285920 -2.485213 -4.609993
H 1.700970 -2.491664 -2.230232
H 1.845746 1.796712 -2.185630
H 2.461962 1.802591 -4.567443
H -1.367250 -2.454300 -5.754980
H -2.300799 -3.410035 -3.664314
H -2.444369 -2.026080 -1.628881

H -0.683182 1.270144 -3.752954
H -0.563538 -0.107054 -5.787425
H -5.789067 -1.811047 1.913891
H -3.415883 -2.363974 2.387902
H -1.606380 -1.218898 1.155410
H -4.537614 1.040012 -1.032623
H -6.340973 -0.102330 0.203743
H 2.128590 1.164656 3.117146
H 0.972657 0.009850 3.820518
H 2.380577 -0.574425 2.936787
H -1.322494 0.762386 3.790006
H -0.176870 2.113370 3.819533
H -1.904490 2.421113 3.638142
H -3.269749 1.733671 -3.267873
H -1.994221 5.548517 -0.375453
H -1.240108 3.246279 0.206448
H -3.403872 5.924038 -2.379866
H -4.048951 4.008386 -3.816846
H 2.018615 2.419480 1.017278
H 6.323011 0.470876 -0.468501
H 4.220817 -0.768498 -0.826898
H 6.277178 2.723195 0.574509
H 4.111684 3.705152 1.286376

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -2337.54531177 | Predicted change in Energy=-3.295223D-10
Zero-point correction (ZPE) = -2336.88698277 0.658329
Internal Energy (U) = -2336.8481167699997 0.697195
Enthalpy (H) = -2336.84717277 0.698139
Gibbs Free Energy (G) = -2336.95933277 0.585979

Frequencies
13.4041 25.2976 37.9528
41.0472 43.9102 45.9151
52.0715 58.8199 62.0641
66.0978 67.2023 69.9819
74.8161 77.5262 89.0776
95.6791 103.7904 120.9926
128.7221 134.5599 155.0851
163.1413 173.1503 195.3551
200.6989 213.5733 221.8677
233.6056 238.6463 243.0674
246.2479 250.4823 261.9208

264.9917 270.0276 281.4671
284.5959 291.7008 301.1190
318.8937 375.6329 391.8241
410.3501 412.4377 412.8366
417.3511 423.6097 428.6530
430.0267 451.1380 466.1785
486.1116 495.8164 514.0015
526.6378 529.8892 538.5365
544.1504 563.0910 614.6084
634.1056 635.7260 636.2491
637.2070 638.6164 640.5054
692.2637 706.1512 712.7660
715.1615 717.9313 721.6038
723.1636 725.4424 728.9283
731.5509 735.1657 739.4949
754.2195 769.8157 770.2790
773.1396 775.4700 779.1499
781.4371 809.7344 875.3867
879.0516 881.3369 881.6130
886.3142 886.9000 893.6333
944.8675 947.0353 958.6062
960.4605 964.5236 968.3814
998.0104 1000.5003 1005.6893
1008.0036 1009.2307 1010.3622
1014.0063 1018.9382 1020.9362
1021.6952 1021.9828 1022.7855
1022.9877 1024.7082 1025.3223
1026.0773 1028.4521 1034.5565
1037.4177 1065.6124 1066.7136
1068.0920 1068.5659 1068.9635
1069.6633 1117.5440 1119.7426
1120.8452 1122.4713 1124.6448
1125.3310 1126.7418 1127.6107
1129.1420 1138.6154 1140.9165
1141.7820 1149.2967 1152.4113
1153.4787 1170.0706 1195.1257
1196.1361 1196.7376 1197.4840
1199.0615 1199.9929 1223.1303
1225.5215 1227.2182 1230.5492
1232.0265 1235.4433 1236.8295
1287.5193 1330.2850 1331.6643
1336.5388 1338.4386 1341.3689
1346.0998 1368.5036 1370.8145
1374.0677 1375.6460 1377.1895
1382.9843 1400.1674 1452.9888
1475.8524 1486.7791 1489.7057
1490.7347 1493.4333 1493.5913
1496.5562 1502.6320 1509.8069

1524.1837	1531.9099	1541.4071
1543.4848	1543.6223	1544.8701
1545.3788	1546.4831	1661.2865
1662.5115	1662.5822	1665.8954
1666.6547	1667.7892	1681.5633
1682.7555	1683.8764	1684.0890
1685.2154	1686.7598	1730.5145
2992.4978	3009.2359	3052.4497
3094.7322	3104.5307	3129.2326
3190.9244	3195.5496	3199.7744
3203.2705	3203.9673	3207.4865
3208.0718	3210.0778	3210.6233
3211.6842	3212.7774	3216.3830
3217.2260	3218.5917	3222.1993
3222.8161	3223.4091	3224.4948
3226.6987	3226.7969	3230.2406
3230.9123	3231.9004	3234.3160
3234.8301	3235.5681	3237.2754
3237.5495	3238.1420	3250.6116

TS 3–S7

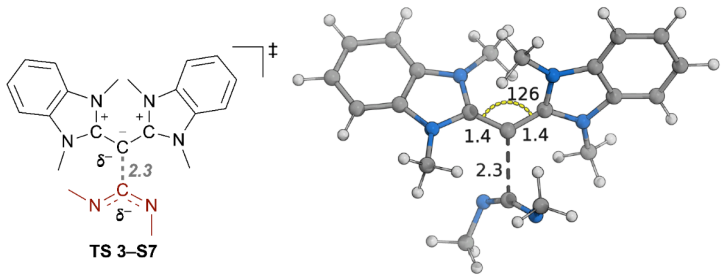

Fig. S50 Three dimensional picture of structure **TS 3–S7** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250,ts,calcfc,noeigentest) freq=noraman

---
Full point group C1 NOp 1
Stoichiometry C22H26N6 Framework group C1[X(C22H26N6)]

Num atoms: 54
Charge = 0 Multiplicity = 1

SCF = -1182.07507931 | Predicted change in Energy=-1.454224D-09

Optimization completed.
Maximum Force 0.000004 0.000450 YES
RMS Force 0.000000 0.000300 YES
Maximum Displacement 0.000530 0.001800 YES
RMS Displacement 0.000130 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

C -1.252572 -0.005783 0.010473
C -2.311012 1.545243 -1.648071
H -2.661016 2.496823 -1.242341
H -1.275216 1.670505 -1.966497
H -2.923455 1.248905 -2.504901
C -0.897253 -1.841156 1.655729
H -1.551751 -2.343735 2.369893
H -0.239999 -2.581445 1.187754
H -0.273242 -1.116052 2.186709

C -3.473416 -0.271813 -0.370362
C -3.060892 -1.311934 0.475523
C -3.954177 -2.270988 0.924754
C -5.283739 -2.158360 0.510409
C -5.693491 -1.124825 -0.330739
C -4.790820 -0.161313 -0.786293
H -3.637259 -3.085320 1.567372
H -6.006970 -2.892745 0.848410
H -6.732286 -1.064272 -0.637133
H -5.110146 0.648226 -1.433267
C 1.173215 -0.079896 0.071674
C 3.393992 -0.493769 0.317564
C 2.870548 -1.477517 -0.534616
C 3.676473 -2.472772 -1.061546
C 5.032500 -2.454913 -0.721248
C 5.551804 -1.476658 0.123874
C 4.736430 -0.475732 0.659203
H 3.275101 -3.244122 -1.709998
H 5.688358 -3.220280 -1.122193
H 6.607958 -1.488166 0.371197
H 5.141701 0.291579 1.309701
C 0.638754 -1.809486 -1.644813
H 0.061146 -1.017945 -2.130821
H 1.239832 -2.321766 -2.397991
H -0.059665 -2.525594 -1.198899
N -1.700376 -1.137707 0.686813
N -2.358013 0.497780 -0.650145
N 1.513644 -1.214967 -0.664623
N 2.346177 0.329606 0.682895
C 2.443241 1.408461 1.633442
H 1.437339 1.654202 1.974447
H 3.045985 1.089759 2.489686
H 2.888239 2.298268 1.179709
C -0.018627 0.574846 0.092221
C 0.163481 2.814903 -0.132126
N 1.103968 2.881017 -0.953327
C 1.793128 4.160290 -1.061275
H 2.861736 4.027540 -0.852557
H 1.711482 4.532960 -2.088287
H 1.395699 4.928829 -0.384784
N -0.784756 3.316397 0.507854
C -1.178865 2.929587 1.833840
H -1.177128 1.834215 1.937301
H -0.506670 3.338377 2.602114
H -2.184652 3.303681 2.042741

Statistical Thermodynamic Analysis

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -1182.07507931 | Predicted change in Energy=-1.454224D-09
Zero-point correction (ZPE) = -1181.6211223100001 0.453957
Internal Energy (U) = -1181.5941103100001 0.480969
Enthalpy (H) = -1181.59316631 0.481913
Gibbs Free Energy (G) = -1181.67894731 0.396132

Frequencies
-248.8000 18.8434 30.2336
33.4262 38.0905 68.8817
76.4971 82.6079 103.4230
117.3412 128.5681 136.3556
141.2837 146.2310 149.8889
170.7098 174.5790 178.0196
181.9365 193.1423 198.9726
208.2028 229.5984 263.5381
273.9681 282.2045 283.6991
296.1423 319.3147 325.6253
331.7048 336.3042 373.4859
389.9286 440.6573 449.8738
475.4444 538.0301 563.6070
577.3396 577.9635 587.6565
587.8184 609.4966 610.9324
641.0733 658.1721 663.4932
690.7763 704.9111 753.1234
755.0586 756.4833 759.4366
763.8254 771.8844 851.3383
859.7257 863.5310 866.2187
881.7166 919.4210 926.7326
931.7496 981.8806 985.4884
1013.2591 1059.0157 1060.7121
1061.1816 1064.1294 1069.1873
1115.7319 1124.2637 1131.8158
1139.3304 1144.4178 1157.4586
1159.8702 1160.9936 1162.7955
1167.8134 1169.9407 1171.1211
1177.6140 1179.3397 1197.3459
1197.9248 1267.9053 1283.1336
1286.3179 1320.5698 1368.4940
1371.6344 1397.2106 1398.1942
1406.0573 1439.3880 1445.0560
1447.2117 1453.6973 1458.3096
1465.3341 1474.1935 1477.4060
1485.1255 1489.2552 1501.3380
1505.4083 1509.0736 1509.8611

1514.9347	1517.4917	1518.5497
1521.2748	1526.0819	1526.8784
1528.8042	1534.2873	1543.4131
1544.6512	1570.1402	1574.4668
1593.1859	1696.0427	1698.0946
1702.6012	1703.8613	1718.0876
2053.7266	3001.1651	3017.8251
3058.2910	3059.4343	3059.9235
3062.8963	3067.2561	3093.7482
3106.4559	3124.5489	3131.5583
3132.2383	3139.5392	3154.3127
3169.8415	3170.4298	3181.0622
3186.2923	3213.0042	3215.0405
3223.2618	3225.5692	3232.3016
3234.9238	3240.5192	3242.8647

S7

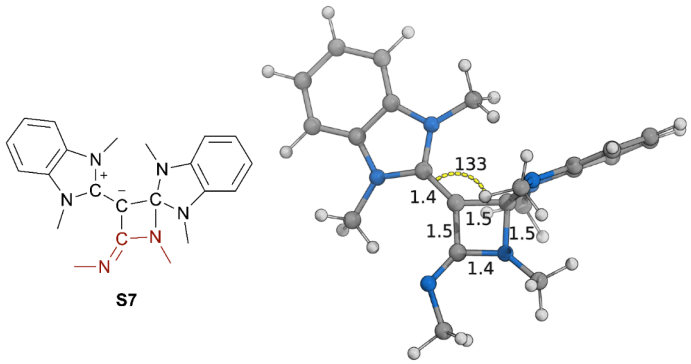

Fig. S51 Three dimensional picture of structure **S7** reported in this manuscript. Distances reported in Ångströms; angles in degrees.

ωB97XD/6-31G(d,p) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman

---
Full point group C1 NOp 1
Stoichiometry C22H26N6 Framework group C1[X(C22H26N6)]

Num atoms: 54
Charge = 0 Multiplicity = 1

SCF = -1182.14190399 | Predicted change in Energy=-1.059770D-08

Optimization completed.
Maximum Force 0.000019 0.000450 YES
RMS Force 0.000003 0.000300 YES
Maximum Displacement 0.001619 0.001800 YES
RMS Displacement 0.000276 0.001200 YES

Atom Coordinates (in Angstroms)
Type X Y Z

C 0.355898 -0.711202 0.486589
C 2.684054 0.284267 0.639736
H 3.680612 -0.154803 0.522145
H 2.397902 0.741671 -0.310059
H 2.741496 1.066109 1.409927
C -1.599929 -2.147764 1.064929
H -1.807766 -3.216860 1.165612
H -2.109540 -1.606545 1.873211
H -2.004043 -1.808018 0.109107

C 1.829854 -1.586116 2.053023
C 0.632054 -2.321376 2.129254
C 0.436254 -3.255480 3.126327
C 1.475588 -3.461301 4.050678
C 2.657888 -2.742540 3.968324
C 2.851781 -1.782022 2.960315
H -0.492435 -3.811482 3.200566
H 1.341414 -4.190309 4.843041
H 3.445126 -2.912713 4.695381
H 3.770062 -1.206583 2.905000
C 0.136229 -1.128405 -2.119464
C -0.152706 -1.866247 -4.240767
C 0.552237 -2.847930 -3.540729
C 0.932085 -4.033903 -4.147392
C 0.585321 -4.206967 -5.490426
C -0.120484 -3.228196 -6.187308
C -0.505384 -2.035232 -5.569272
H 1.466914 -4.805147 -3.604507
H 0.866696 -5.125377 -5.994383
H -0.381735 -3.394237 -7.226894
H -1.061252 -1.275895 -6.107619
C 1.559526 -3.056219 -1.274371
H 2.033142 -2.331788 -0.614228
H 0.969951 -3.747273 -0.667411
H 2.338444 -3.607218 -1.806641
N -0.174921 -1.932127 1.064842
N 1.730763 -0.744082 0.956365
N 0.741250 -2.368889 -2.252385
N -0.383480 -0.818706 -3.362122
C -1.183709 0.330588 -3.735527
H -0.801740 0.733297 -4.678553
H -2.228275 0.031496 -3.876725
H -1.128639 1.102611 -2.962293
C 0.078572 -0.379634 -0.967478
C -0.522445 0.884550 -0.532769
N -0.974533 1.919182 -1.125261
C -1.576358 2.970973 -0.326473
H -2.148910 3.630562 -0.984270
H -2.265831 2.585389 0.437866
H -0.829213 3.594534 0.182609
N -0.408747 0.525011 0.825460
C -0.097690 1.370781 1.958937
H -0.992467 1.875649 2.331038
H 0.285720 0.733444 2.759969
H 0.661399 2.130868 1.731979

Statistical Thermodynamic Analysis

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF = -1182.14190399 | Predicted change in Energy=-1.059770D-08
Zero-point correction (ZPE) = -1181.68414399 0.45776
Internal Energy (U) = -1181.65803799 0.483866
Enthalpy (H) = -1181.65709399 0.48481
Gibbs Free Energy (G) = -1181.74022999 0.401674

Frequencies
24.8718 29.8912 35.4613
40.3805 62.6226 96.0983
102.4242 108.4840 113.6213
129.2230 130.9860 136.5968
167.5353 172.3724 175.3822
194.0167 204.4574 216.6697
241.5827 242.7023 255.5633
257.4352 273.7845 281.1537
294.2789 296.4620 319.5850
321.6092 342.5652 365.9634
375.4325 390.1497 431.5986
449.0900 456.0196 497.6213
550.0703 557.3097 572.8403
579.8706 587.7142 589.5956
612.8076 646.1282 647.8092
669.4998 692.7204 732.1647
754.3211 755.5055 755.8294
761.4592 786.1513 803.2509
822.3721 858.7026 862.4007
866.5369 866.7163 910.1480
915.3588 930.2448 932.0513
971.1731 985.7500 991.9640
1044.1517 1057.8938 1058.9145
1061.4518 1103.2229 1114.1020
1122.8244 1135.9494 1144.2849
1150.1702 1153.0037 1158.4636
1160.0762 1162.9278 1164.5852
1171.2334 1174.1145 1188.8181
1195.4488 1197.9987 1208.8179
1220.4901 1258.6850 1268.5335
1294.7825 1333.2287 1352.0006
1358.8728 1369.4203 1371.6343
1393.3160 1402.7106 1418.1467
1447.6674 1456.4545 1460.9944
1469.3400 1469.8341 1478.0668
1479.5237 1493.5365 1500.2208
1507.3785 1507.5785 1510.1931

1514.3708	1517.6472	1522.2090
1527.3414	1527.9716	1529.6630
1532.1154	1533.1136	1542.0757
1549.6130	1554.2922	1574.7329
1583.8937	1694.5981	1699.8811
1700.4744	1703.1585	1708.7461
1802.8143	3011.9068	3022.6555
3027.2085	3034.7500	3035.8635
3076.5936	3080.0959	3097.0978
3116.5271	3118.7630	3122.7925
3124.3244	3132.1810	3157.2389
3157.7452	3158.9051	3163.9929
3203.7471	3208.5021	3216.2574
3219.3162	3227.9447	3227.9778
3236.9554	3237.7263	3244.2031

Single point energies computed at the ωB97XD/def2-TZVPP/PCM(Benzene) Level

Table S1. Calculated single point energies (at the ωB97XD/def2-TZVPP/PCM(Benzene) Level) for each structure reported in this manuscript. Energies are reported in Hartrees unit.

Structure Number	Single Point Energy (Hartrees)
1	-1765.33892
2	-2110.70232
3	-955.06974
pinacolborane (HBpin)	-411.90986
4	-227.40620
5	-639.39873
TS 1–6	-2177.26396
6	-2177.28428
TS 6–7	-2404.68159
7	-2404.74110
TS 7–8	-2404.73536
8	-2404.77198
8–1	-2404.75025
TS 6–9	-2177.25876
9	-2177.26897
TS 9–7	-2404.65902
TS 2–10	-2522.61896
10	-2522.63367
TS 10–11	-2750.03100
11	-2750.09276
TS 3–12	-1366.99040
12	-1367.00830
TS 12–13	-1366.97301
13	-1367.03825
TS 13–14	-1594.40821
14	-1594.46221
TS 14–15	-1594.44893

Structure Number	Single Point Energy (Hartrees)
15	-1594.49614
TS 15–3	-1594.47815
TS 12–14	-2404.67002
TS 1–S1	-1992.73434
S1	-1992.79422
TS S1–S2	-2404.70862
S2	-2404.73194
TS S2–S3	-2404.65782
S3	-2404.76364
TS S3–1	-2404.71057
11–S04	-2750.07993
S4	-2750.11924
TS S4–2	-2750.10421
TS 10–S5	-2522.61785
S5	-2522.62151
TS S5–11	-2750.01964
TS 2–S6	-2338.09146
S6	-2338.14599
TS 3–S7	-1182.46673
S7	-1182.52478

Intrinsic reaction coordinate (IRC) analysis for the turnover-determining transition states

Protocol

To confirm that the computed transition state structures connect to minima along the reaction coordinate for carbone-catalyzed hydroboration, intrinsic reaction coordinate (IRC) analysis was performed.

The following parameters were used for each calculation:

Level of theory: ωB97XD/6-31G(d,p)
Self-consistent field parameters: scf=(direct,tight,maxcycle=300,xqc)
IRC parameters: irc=(maxpoints=160,calcfc,vtight,lqa)
Stepsize: 10 x 0.01 Bohr (default)

Where plotting the IRC graph, the energies on the y-axis are single point energies at the ωB97XD/6-31G(d,p) level of theory. They are reported in kcal/mol units relative to the lowest energy structure on the IRC. On the x-axis, the "reactant" side of the reaction path is always positioned on the left, and the "product" side on the right.

Plots

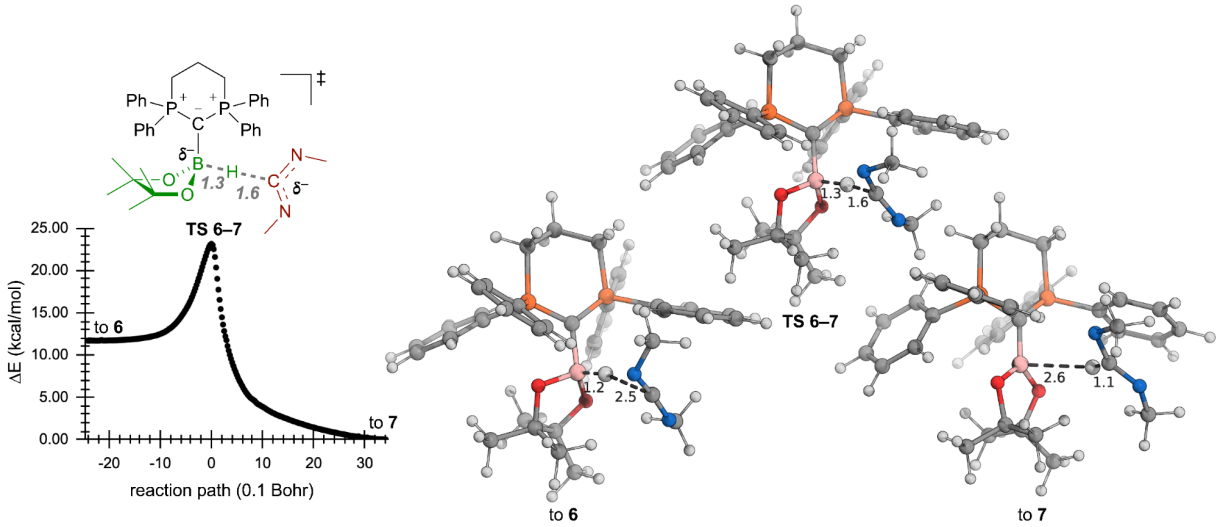

Fig. S52 Steepest descent path from **TS 6–7** toward structures **6** and **7**. Distances on 3D geometries reported in Ångströms.

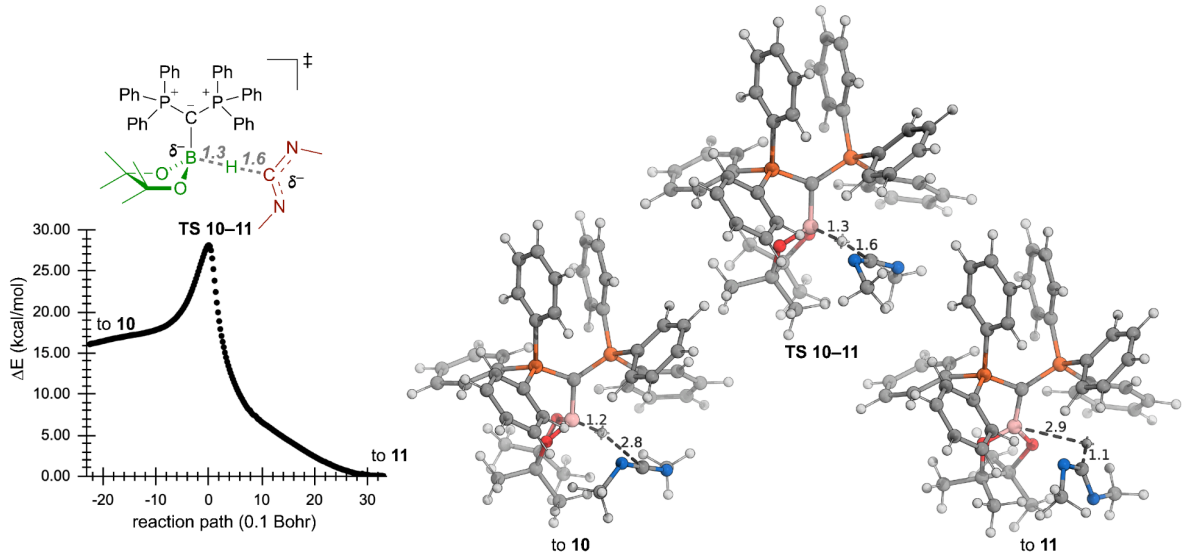

Fig. S53 Steepest descent path from **TS 10–11** toward structures **10** and **11**. Distances on 3D geometries reported in Ångströms.

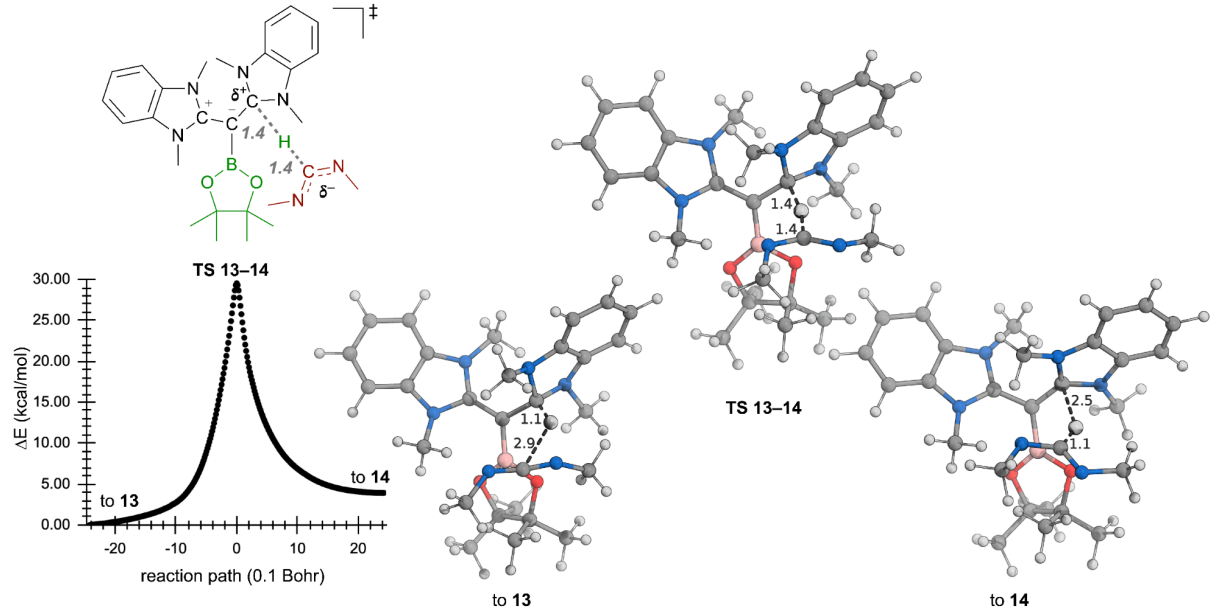

Fig. S54 Steepest descent path from **TS 13–14** toward structures **13** and **14**. Distances on 3D geometries reported in Ångströms.

References

1 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian 16 Rev. C.01 2016.